

## CHAPTER 1

## ALLYLBORATION OF CARBONYL COMPOUNDS

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## ALLYLBORATION OF CARBONYL COMPOUNDS

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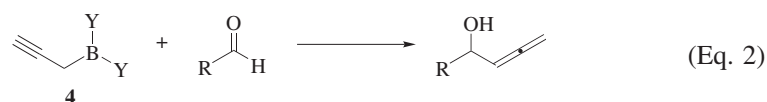
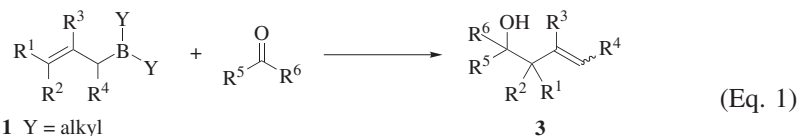
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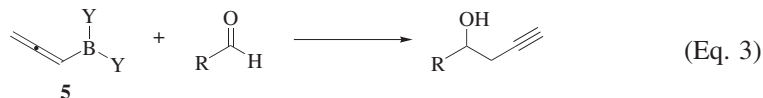
## INTRODUCTION

Allylic boron compounds have gained a prominent position as a useful class of synthetic reagents in the past 25 years. Their general structures, **1** and **2**, and their utility in carbonyl additions are shown in Eq. 1. The main use of these reagents is in the stereoselective synthesis of homoallylic alcohols **3** by an allyl-transfer reaction to carbonyl compounds. In this process, a new carbon-carbon bond is formed, and up to two new stereogenic centers are created. Moreover, the residual allylic unit can be manipulated through a number of different transformations such as oxidative cleavage, olefin metathesis, and many others. Although less prevalent, the propargyl and allenyl reagents typified by **4** and **5** have also been described (Eqs. 2 and 3). Most examples of allylic boron reagents used in carbonyl additions belong to one of two main classes, boranes (structure **1**, Y = alkyl) and boronate derivatives (structure **2**, Y = OR or NR<sub>2</sub> for bis(sulfonamide) derivatives). This chapter focuses on describing and comparing both classes, and when needed, they will be discussed separately. A chart of ligand structures with the acronyms used in this text can be found preceding the Tables.



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Allylic boron reagents react with several classes of carbonyl compounds and their derivatives, including imines. Their most common use, however, is in nucleophilic additions to aldehydes to produce homoallylic secondary alcohols (i.e., the process of Eq. 1 where  $\text{R}^5 = \text{H}$ ). This reaction process was discovered by Mikhailov and Bubnov in 1964, who observed the formation of a homoallylic alcohol product from the reaction of triallylborane with aldehydes.<sup>1</sup> The first example of allylboration using an allylic boronate was disclosed by Gaudemar and coworkers in 1966.<sup>2</sup> The true beginnings of this chemistry in terms of practical synthetic applications can be traced back to the late 1970's, with Hoffmann's crucial realization of the regio- and diastereospecific nature of the additions of both crotylboronate isomers to aldehydes (see "Mechanism and Stereochemistry").<sup>3</sup> In the following two decades, the work of Hoffmann, Brown, Roush, and Corey was determinant in maturing carbonyl allylboration chemistry into one of the primary methodological tools in stereoselective synthesis. In particular, numerous syntheses of polyacetate and polypropionate natural products feature stereoselective allylboration as key steps (see "Applications to the Synthesis of Natural Products"). The discovery of the Lewis acid catalyzed manifold by Hall and Miyaura recently opened new doors for further development of this important reaction.

In addition to the predominant allyl and crotyl reagents, a large number of allylic borane **1** and boronate derivatives **2** (Eq. 1) with various substituents ( $\text{R}^1\text{--}\text{R}^4$ ) have been reported. Interested readers can refer to the comprehensive Tabular Survey at the end of this monograph, which covers the literature up to the end of 2005. Several reviews on allylic boron compounds and other allylmatal reagents and their additions to carbonyl compounds and imines have been written prior to this one,<sup>4-14</sup> and these sources may be consulted if a more in-depth historical perspective is desired.

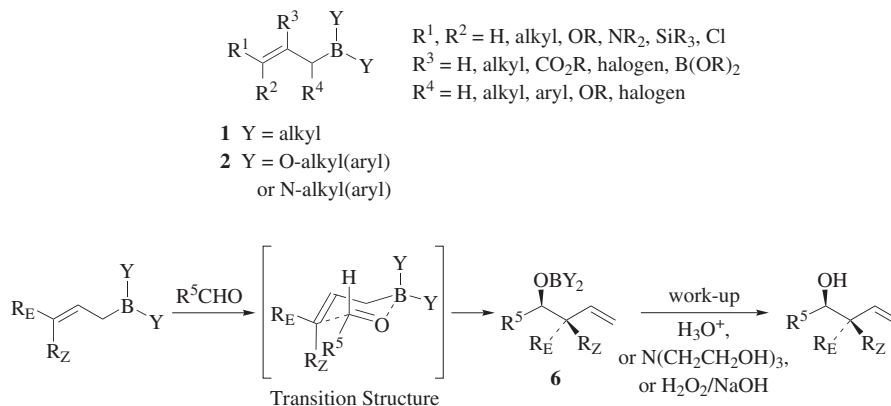
## MECHANISM AND STEREOCHEMISTRY

## Thermal Uncatalyzed Reactions

Mechanistically, allylic boron reagents belong to the Type I class of carbonyl allylation reagents.<sup>15</sup> Type I reactions proceed through a rigid, chairlike transition structure which requires a synclinal orientation of reacting  $\pi$  systems. Although catalytic variants for additions of allylic boronates have been reported recently, the reaction between most allylic boron reagents and aldehydes is spontaneous, irreversible, and requires no external activator. The uncatalyzed reactions of these Type I reagents proceed by way of a six-membered, chairlike transition structure that features a dative bond between the boron and the carbonyl oxygen of the aldehyde (Scheme 1).<sup>16-20</sup> Competitive kinetics in the addition of

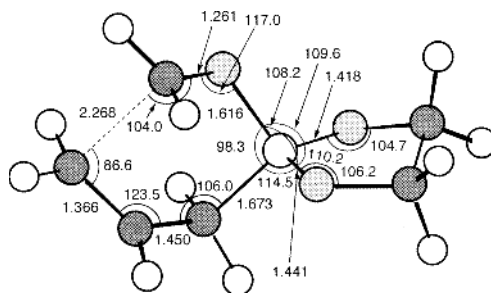
## ALLYLBORATION OF CARBONYL COMPOUNDS

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**Scheme 1.** Overall aldehyde allylboration process.

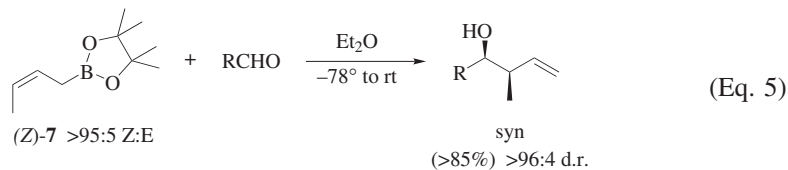
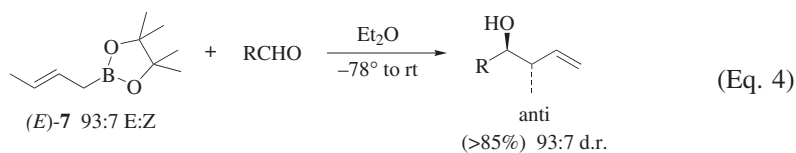
an allylboronate to benzaldehyde and deuterobenzaldehyde in different solvents revealed a negative secondary deuterium kinetic isotope effect, which rules out a single-electron transfer mechanism.<sup>20</sup> Theoretical studies using *ab initio* MO and DFT methods strongly suggest that the strength of the dative bond between the boron and the aldehyde carbonyl oxygen in the transition structure is the dominant factor in determining the rate of the reaction.<sup>19,20</sup> Indeed, whereas the B–O bond is short ( $\sim 1.6$  Å) and very advanced in the transition state, the incipient C–C bond between the carbonyl carbon and the allylic unit has merely initiated ( $\sim 2.4$  Å) (Fig. 1). A weakly bound B–O coordinated complex was detected as an early intermediate in the calculated reaction pathway.<sup>19</sup> Not surprisingly, allylboration reactions tend to proceed faster in non-coordinating solvents, and the most electrophilic boron reagents react faster.<sup>21</sup>



**Figure 1.** Calculated transition structure for the allylboration reaction between *B*-allyl-1,3,2-dioxaborolane ( $\text{CH}_2=\text{CHCH}_2\text{B}[\text{OCH}_2]_2$ ) and formaldehyde at the MP2/6-31G\*\* level of theory. Indicated bond distances are in angstrom. Reprinted with permission from *J. Org. Chem.* **1998**, *63*, 8331.<sup>19</sup> Copyright 1998 American Chemical Society.

The immediate products of additions between carbonyl substrates and allylic boranes **1** or boronate derivatives **2** are borinate or borate esters, respectively. To cleave the covalent B–O bond in these intermediates (structure **6**, Scheme 1) and to obtain the desired free alcohol, a hydrolytic or oxidative work-up is required. This issue is discussed in detail in the section “Work-Up Conditions”. In the interest of simplifying chemical equations, specific work-up conditions are not included in most of the examples highlighted in this chapter.

One of the main reasons for the popularity of allylic boron reagents in stereocontrolled synthesis is that their additions to aldehydes are reliably highly stereoselective and the outcome is predictable. The diastereospecificity of the reaction was first recognized by Hoffmann and Zeiss using both *E*- and *Z*-crotylboronates **7** (Eqs. 4 and 5).<sup>3,22</sup> For both crotylboranes and crotylboronates, the additions generally proceed with near-perfect reflection of the olefin geometry of the reagent into the configuration of the product. Specifically, the *E*-crotylboron reagents (Scheme 1,  $R_E = \text{Me}$ ,  $R_Z = \text{H}$ ) lead to anti-propanoate products and the *Z*-crotyl reagents (Scheme 1,  $R_E = \text{H}$ ,  $R_Z = \text{Me}$ ) lead to syn-products. In both instances, of the two possible chairlike transition structures the favored one places the aldehyde substituent ( $R^5$ ) in a pseudo-equatorial orientation. This model, which has been reproduced computationally for both crotylborane<sup>17</sup> and crotylboronate<sup>18</sup> derivatives, accounts for the high diastereospecificity of most allylboration. Even highly functionalized reagents and most intramolecular additions follow the same trend.

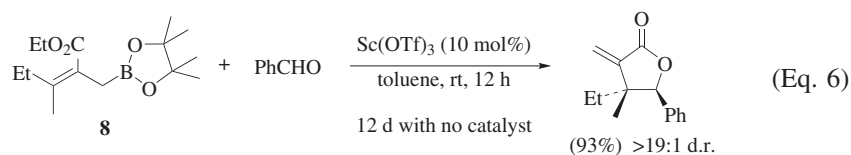


It is well accepted that the high diastereospecificity of aldehyde allylboration reactions is a consequence of the compact cyclic transition structure. Theoretical calculations have shown that the chairlike transition structure shown in Scheme 1 and Fig. 1 is the lowest in energy relative to other possibilities such as the twist-boat conformation.<sup>16</sup> With boronate reagents, it has also been suggested that a weak hydrogen bond between the axial boronate oxygen and the hydrogen of the polarized formyl unit contributes to the preference for the transition structure with the aldehyde substituent in the pseudo-equatorial position.<sup>23</sup>

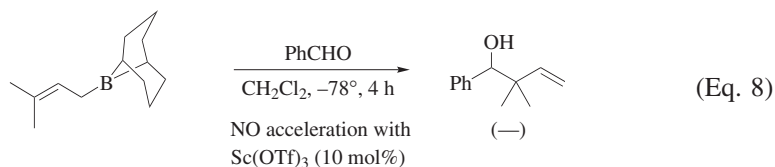
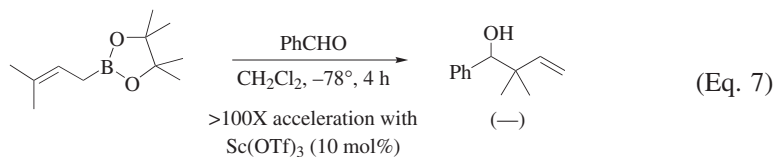
### Lewis Acid Catalyzed Reactions

As described above, allylic boron reagents are self-activating, Type I reagents where the allylation is effected by coordination of the aldehyde carbonyl oxygen

to the boron atom within a cyclic six-membered transition structure. Because of this self-activation mechanism, there would appear to be no advantage to using an external promoter such as a Lewis or Brønsted acid. Furthermore, one could expect an added Lewis acid to compete with the boron atom for the basic aldehyde oxygen, potentially leading to a switch from the highly diastereospecific Type I mechanism to a less selective, open-chain Type II mechanism.<sup>15</sup> Recent publications, however, show that the additions of allylic boronates can be efficiently and beneficially catalyzed by several Lewis acids.<sup>24–28</sup> Allylic boranes are not subject to this catalytic effect.<sup>29</sup> For additions of allylic boronates, the rate enhancements observed in the presence of these catalysts are quite dramatic.<sup>24,29</sup> For example, the addition of 2-ethoxycarbonyl allylboronate **8** to benzaldehyde to give an exo-methylene butyrolactone requires almost two weeks at room temperature, but only 12 hours in the presence of a catalytic amount of Sc(OTf)<sub>3</sub> (Eq. 6).<sup>24</sup> Note that in this example the resulting homoallylic alcohol intermediate cyclizes in situ with the carboxy ester group to form a lactone product.



It is noteworthy that the stereospecificity observed in the thermal reaction is fully preserved under this new catalytic manifold. Furthermore, the presence of a 2-alkoxycarbonyl substituent on the allylic boronate is not necessary for the metal-promoted activation to occur (Eq. 7).<sup>24,25</sup> According to mechanistic studies, a chairlike bimolecular transition structure similar to the thermal additions can be proposed for these catalyzed allylborations.<sup>29</sup> Control experiments have confirmed the inefficiency of Lewis acids with dialkylallylboranes (Eq. 8). Hence, the catalytic effect is thought to derive from an increase in the electrophilicity of the boron atom through binding of the metal ion to one of the boronate oxygens [transition structure (T.S.) **9**], as opposed to coordination of the carbonyl oxygen (T.S. **10**).<sup>29</sup>

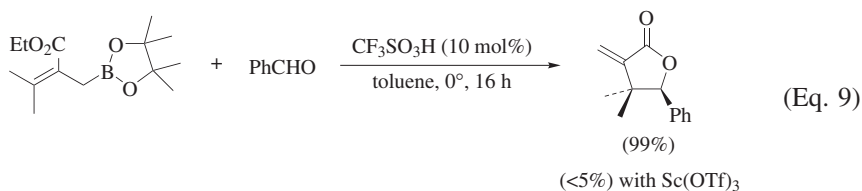




Coordination of the Lewis acid to the boronate oxygens is thought to decrease the overlap between the oxygen lone electron pairs and the vacant p-orbital of the boron atom. Consequently, the boron center is rendered more electron-deficient, and compensates by strengthening the key boron–carbonyl oxygen interaction and concomitantly lowering the activation energy of the reaction. This idea is consistent with theoretical calculations of the non-catalyzed allylboration<sup>19</sup> and from an experimental study consisting of a quantitative survey of steric and electronic effects in the reactions of different allylboronates.<sup>21</sup> The latter results led to the conclusion that the rate of a given allylboration can “be rationalized in terms of the relative availability of lone pairs of electrons on the oxygen atoms attached to the boron”.

#### Brønsted Acid Catalyzed Reactions

In line with the effect of Lewis acids, the huge rate acceleration in the additions of allylic boronates to aldehydes by strong protic acids such as triflic acid was recently reported.<sup>30</sup> In the example of Eq. 9, the reaction yield is almost quantitative after 16 hours at 0° under conditions where the use of Sc(OTf)<sub>3</sub> gives less than 5% of the product. Interestingly, additions with geometrically defined allylic boronates are not always stereospecific. Although definitive mechanistic studies have not yet appeared, it can be presumed that the origin of the acceleration could be similar to that of Lewis acid catalysis, with activation by protonation of a boronate oxygen in the cyclic chairlike transition structure.



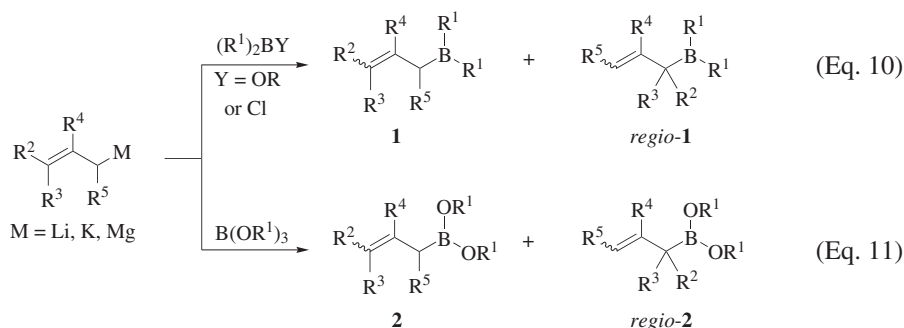
#### SCOPE AND LIMITATIONS

##### Preparation of Allylic Boron Reagents

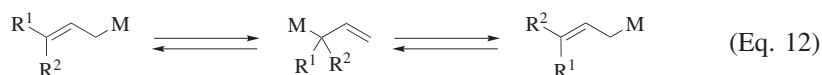
Unlike aldehydes and ketones, allylic boron compounds are not ubiquitous, commercial organic substrates. There are several methods for the preparation of allylic boronates, however, and many of these have been developed in the past decade. This topic has been reviewed recently<sup>14</sup> so only the most common methods are emphasized in this section. As a result of the lesser stability of allylic boranes, methods to access these reagents are more limited and it is generally easier to prepare allylic boronates with a wide range of functional groups.



**From Hard Allylic Organometallics.** The most common preparation of allylic boranes and boronates is the addition of a reactive allylic metal species to a borinic or boric ester, respectively (Eqs. 10 and 11). Preparations from allyllithium,<sup>31–34</sup> allylmagnesium,<sup>32,35</sup> and allylpotassium<sup>22,31,36–40</sup> reagents are all well known. These methods are popular because the required allylic anions are quite easy to prepare, and because they generally lead to high yields of products.



One potential drawback to this approach is that the allylic metal precursor may not be configurationally stable and may be subject to facile metallotropic rearrangement leading to either constitutional or geometrical isomers (Eq. 12).<sup>41–43</sup> This is in fact a major problem even with 3-substituted allylic boranes, whose geometrical integrity can be compromised according to Eq. 12 even at temperatures well below 0° (see section “Stability and Handling”). Because of their potential configurational instability, and also because of their high sensitivity to air, allylic boranes are not isolated from the process depicted in Eq. 10, but rather are used in situ for their addition to carbonyl substrates. In contrast, allylic boronates are much more stable and can be isolated and purified prior to subsequent carbonyl allylation reactions.



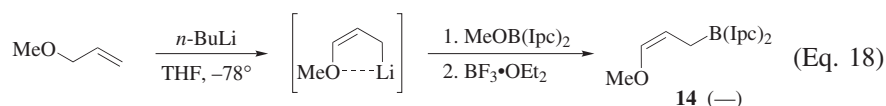
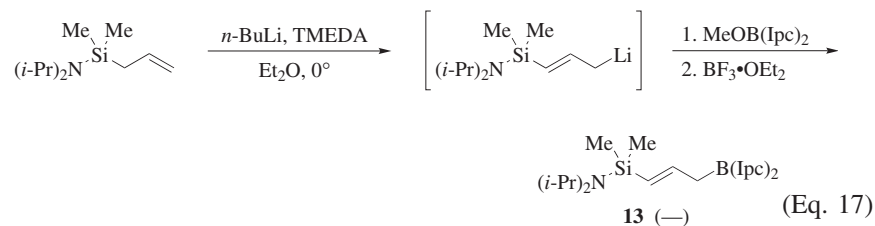
Another potential problem with the preparations from allylic organometallics is that they often involve highly reactive reagents that can lead to incompatibilities with many functional groups. While these impediments constitute no real problem for simple allyl- or crotylboron reagents, they can lead to poor regio- and stereoselectivities in more substituted examples. Significantly, as shown with the diisopropyl tartrate (DIPT) derivatives (*E*)-**11** and (*Z*)-**11** of Eqs. 13 and 14,<sup>37</sup> the use of Schlosser’s “superbase” conditions<sup>43</sup> to prepare the configurationally stable crotylpotassium anions allows the preparation of both *E*- and *Z*-crotylboronates with very high selectivity from the respective (*E*)- and (*Z*)-2-butene. Likewise, the bis(isopinocampheyl)crotylboranes [bis(Ipc)crotylboranes] **12** are prepared by anion trapping with the requisite borinic ester [MeOB(Ipc)<sub>2</sub>] at –78° (Eqs. 15 and 16).<sup>44</sup> Because of the strong Lewis acidity of the resulting dialkylborane, however, the addition of BF<sub>3</sub> is required in order to remove the methoxide anion



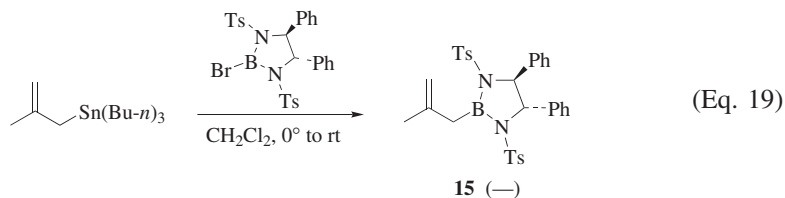
## ALLYLBORATION OF CARBONYL COMPOUNDS

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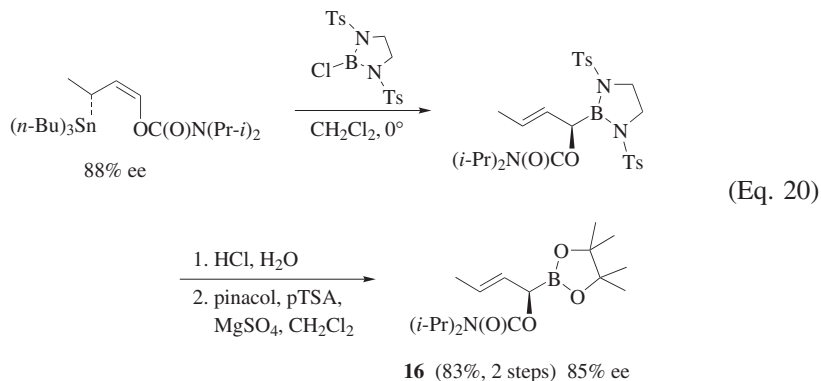
its preparation (Eq. 18).<sup>33,46</sup> Like most allylic dialkylboranes, reagents **13** and **14** are not isolated and rather are allowed to react in situ with carbonyl substrates (see section “Stability and Handling”).



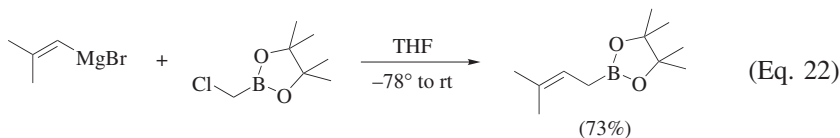
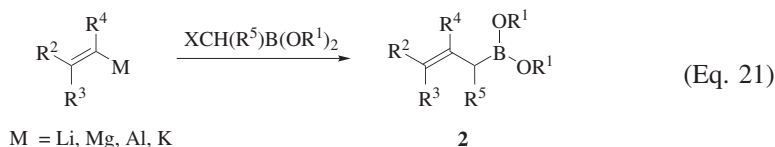
If the presence of sensitive functional groups poses problems of chemoselectivity in the use of hard allylic metal reagents, allylboronate derivatives also can be accessed by a milder transmetalation of allylic tin species with boron halides.<sup>49</sup> This approach has been used by Corey in the synthesis of chiral bis(sulfonamido)boron reagents such as the methallyl reagent **15** (Eq. 19) (see section “Chiral Boronate Derivatives”).<sup>50</sup>



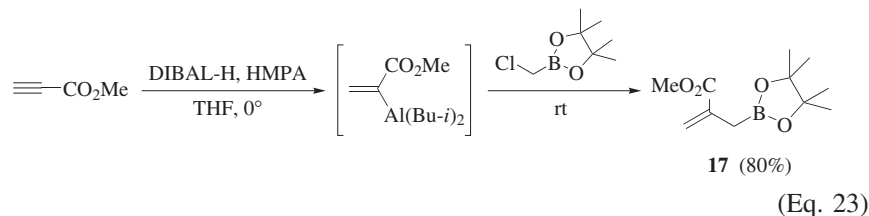
Recently, the enantiomerically enriched  $\alpha$ -carbamoyloxycrotylboronate **16** has been synthesized using a similar anti- $S_E'$  reaction with in situ generated 2-chloro-1,3-bis(toluenesulfonyl)-1,3,2-diazaborolidine (Eq. 20). Following a ligand-exchange with pinacol, the resulting chiral  $\alpha$ -substituted boronate **16** is isolated in a good overall yield with minimal erosion of enantiomeric purity.<sup>51</sup>



**From Alkenylmetal Precursors.** The reaction of an alkenylmetal with a halomethyl boronic ester also leads to allylic boronates (Eq. 21).<sup>52</sup> This strategy takes advantage of the configurational stability of vinylic carbanions and circumvents the rearrangements that can plague allylic metal intermediates. For example, an alkenylmagnesium reagent reacts readily with pinacol chloromethylboronate to give the corresponding isoprenylboronate in good yield (Eq. 22).<sup>53</sup>

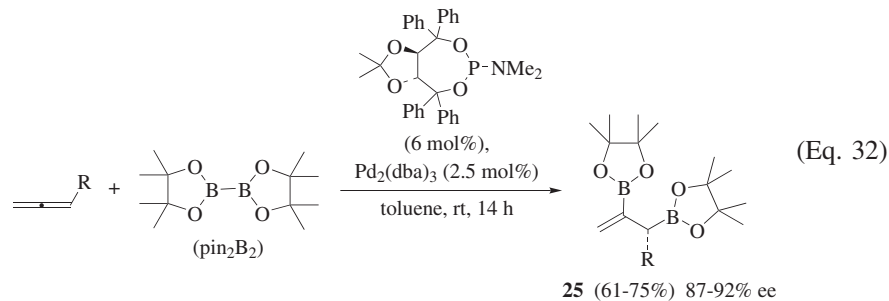
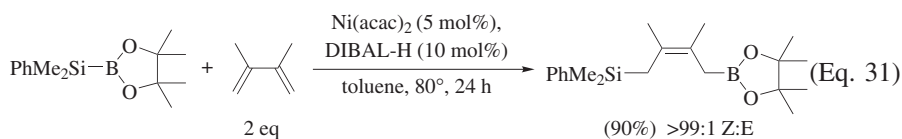
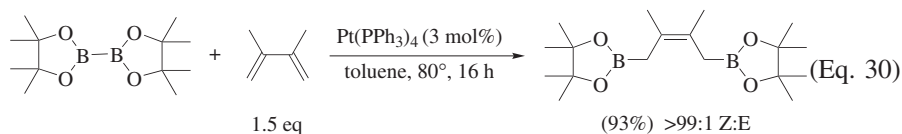
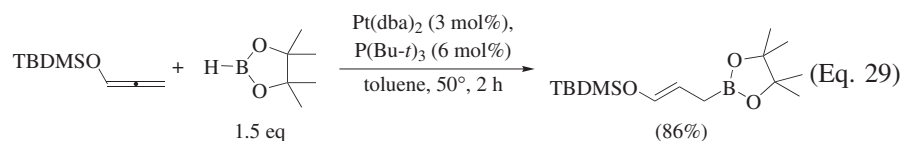
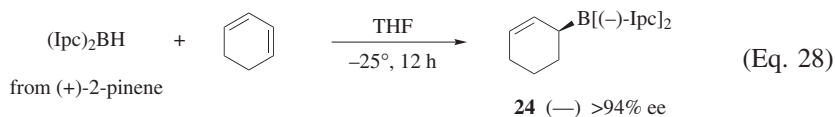


Alkenylmetal reagents are generally more configurationally stable than allylic metal species and so alkylations with these anions are usually more stereoselective than with allylic anions. The low reactivity of many alkenylmetal species, however, can sometimes bring about poor yields in the alkylation step. While the reactions of alkenyllithium<sup>54–56</sup> and alkenylmagnesium<sup>53</sup> reagents with halomethylboronates are well established, the high reactivity of these organometallics limits the type of functional groups that may be present. In this regard, less reactive alkenylaluminum<sup>57,58</sup> (Eq. 23) and alkenylcopper<sup>26,59,60</sup> reagents (Eq. 24) have been used to produce more sensitive, functionalized allylic boronates such as 2-ethoxycarbonyl derivatives of types **17** and **19** from the corresponding alkyne precursors. In the generic example in Eq. 24, the *cis*-carbocupration of alkynoic esters provides a weakly nucleophilic and configurationally unstable 1-alkoxycarbonylalkenylcopper intermediate **18**, and the presence of hexamethylphosphoric triamide (HMPA) as an additive was found to be crucial to avoid erosion of the *E/Z* stereoselectivity in the alkylation step with the iodomethylboronate electrophile.<sup>26,59,60</sup> Under these conditions, a variety of unsymmetrically substituted 3,3-dialkylated allylboronates **19** have been prepared in over 20:1 selectivity, and these reagents have been subsequently employed in the stereoselective preparation of quaternary carbon centers by reaction with aldehydes.

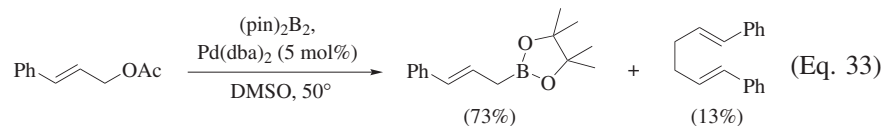




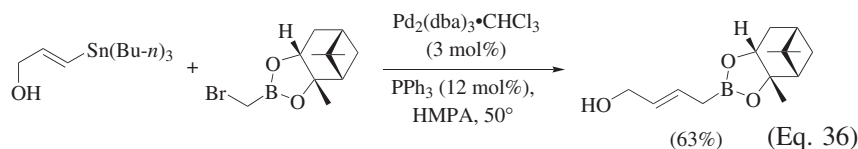
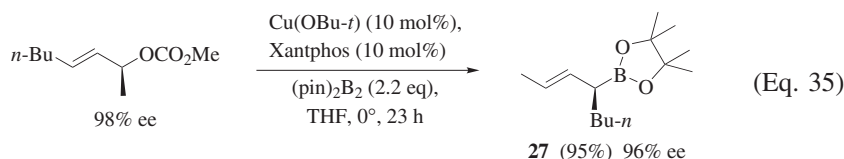
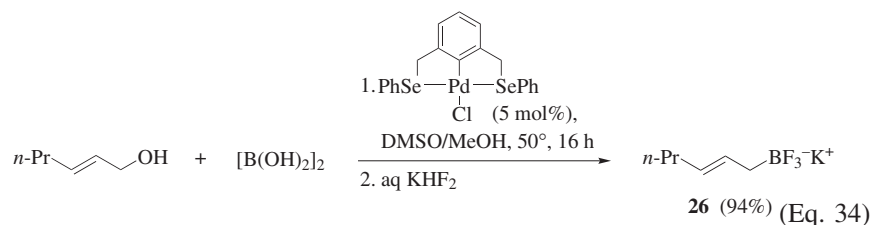
**From Other Organic Fragments.** Other direct methods to access allylic boron reagents, including chiral ones such as 2-cyclohexenylborane **24**, are based on the hydroboration of 1,3-dienes<sup>69</sup> (Eq. 28) and allenes<sup>70</sup> (Eq. 29). Allylic boronates can also be accessed by the transition-metal-catalyzed diboration<sup>71</sup> (Eq. 30) and silaboration<sup>72</sup> (Eq. 31) of dienes and allenes. With allenes as substrates, the use of a chiral phosphoramidite ligand leads to high enantioselectivities in the preparation of chiral 2-borylated  $\alpha$ -substituted reagents of type **25** (Eq. 32).<sup>73</sup>



Allylic boronates with a wide variety of functional groups can also be obtained by the treatment of allylic acetates with pinacolatodiboron [(pin)<sub>2</sub>B<sub>2</sub>], although side products of oxidative homodimerization can be observed in some instances (Eq. 33).<sup>74</sup>

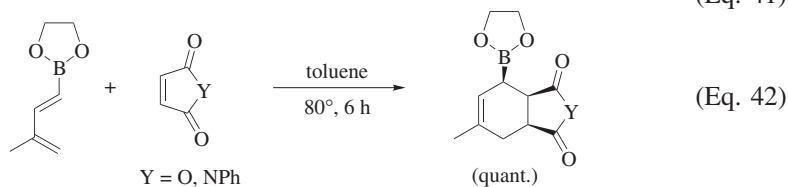
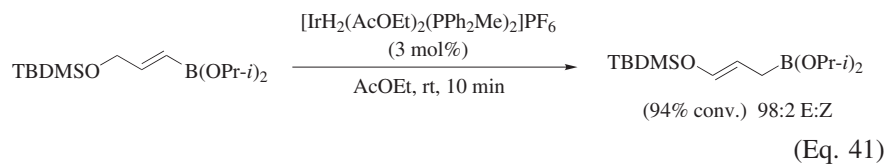
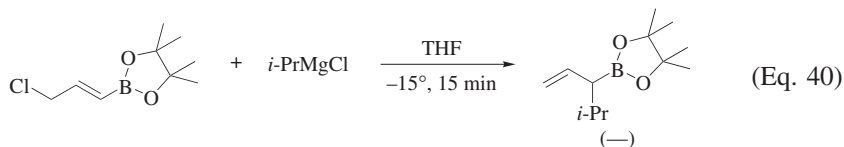
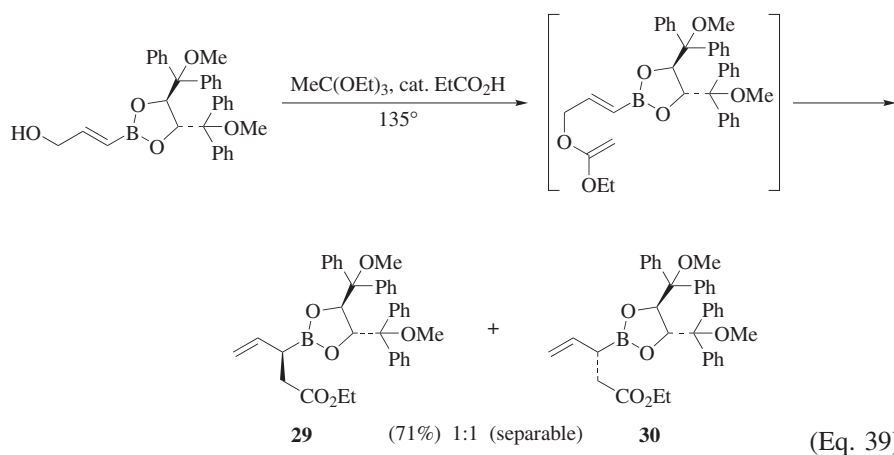
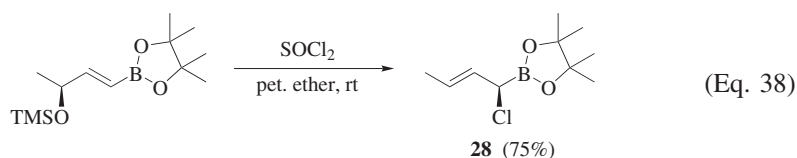
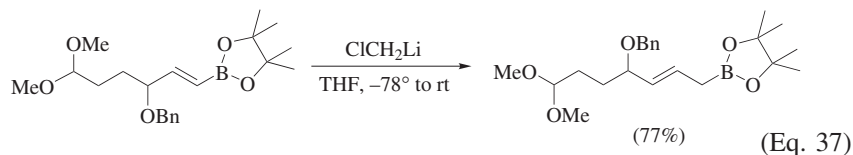


Very recently, it was shown that allylic trifluoroborates such as **26** can be prepared stereospecifically from allylic alcohols using a palladium complex made from a pincer ligand (Eq. 34).<sup>75</sup> A copper-catalyzed, site selective and stereospecific substitution of allylic carbonates with (pin)<sub>2</sub>B<sub>2</sub> has been optimized to afford several examples of  $\alpha$ -substituted allylic boronates.<sup>76</sup> When using the E-isomer of an enantiomerically pure secondary allylic carbonate, the resulting chiral  $\alpha$ -substituted allylic boronate **27** is obtained with minimal erosion of enantiomeric purity (Eq. 35). The corresponding Z-configured allylic carbonate affords the other enantiomer, and this stereochemical outcome has been explained with a mechanism involving anti attack of the borylcopper reagent in a conformation minimizing allylic 1,3-strain. Allylic halides are also suitable substrates with pinacolborane as the borylating agent under platinum catalysis.<sup>77</sup> As shown in a palladium-catalyzed Stille cross-coupling reaction with soft alkenylmetal electrophiles (Eq. 36),<sup>78</sup> transition-metal-catalyzed processes can even tolerate unprotected acidic functionalities. Related Negishi-type coupling strategies have also been employed.<sup>79,80</sup>



**From Boron-Containing Fragments.** A number of indirect methods to synthesize more highly functionalized allylic boronates are based on the isomerization or derivatization of organoboron substrates. Selected examples include the homologation of alkenylboronates with chloromethyl lithium<sup>56,81</sup> (Eq. 37),<sup>82</sup> and the allylic rearrangement of 3-siloxyalkenylboronates to give chiral  $\alpha$ -chloro derivatives such as **28** (Eq. 38).<sup>83</sup> A variant of Eq. 37 using lithiated allyl chloride has also been described.<sup>84</sup> The Johnson orthoester Claisen rearrangement of a chiral 3-hydroxypropenylboronic ester leads to an epimeric, separable mixture of  $\alpha$ -substituted allylic boronates **29** and **30** (Eq. 39).<sup>85,86</sup> A related intermolecular method based on the S<sub>N</sub>2' addition of Grignard reagents has been reported (Eq. 40).<sup>87</sup> These reagents are not isolated, rather, they

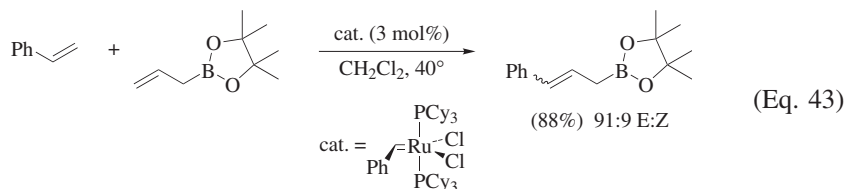
are immediately combined with aldehydes. Other methods of preparation of allylic boronates involving boronic ester fragments include the isomerization of alkenylboronates (Eq. 41),<sup>88</sup> cycloadditions of dienylboronates (Eq. 42),<sup>89</sup> and olefin cross-metathesis (Eq. 43).<sup>90</sup>



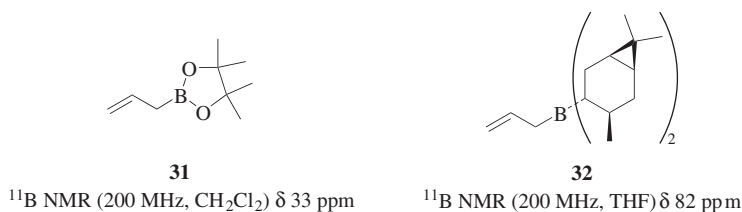


## ALLYLBORATION OF CARBONYL COMPOUNDS

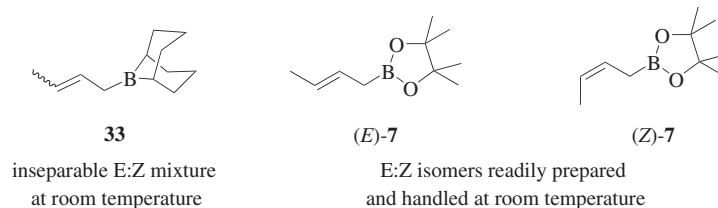
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**Stability and Handling of Allylic Boron Reagents**

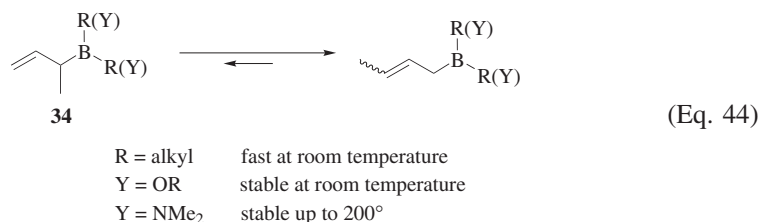
Allylic boronates are more stable to atmospheric oxidation and are thus much easier to handle than the corresponding allylic boranes. The stability of the boronate reagents arises from the partial donation of the lone pairs of electrons on the oxygen atoms into the empty p-orbital of boron. This mesomeric effect is responsible for the upfield shift of the boron atom in  $^{11}\text{B}$  NMR compared to that of allylic boranes (compare allylboronate **31** and allylborane **32**).<sup>21</sup>



As a consequence of their superior stability, many types of allylic boronates can be isolated and purified. It should be noted that most pinacol allylic boronic esters and other bulky esters are stable to hydrolysis and can be conveniently purified by chromatography on silica gel. A potential pitfall of all allylic boron compounds is their stereochemical integrity, and substituted allylic boranes are known to undergo reversible borotropic rearrangements at temperatures above  $-45^\circ$  (see Eq. 12,  $\text{M} = \text{BR}_2$ ).<sup>22,91,92</sup> For this reason, allylic boranes are normally not handled under atmospheric conditions, and are rather prepared and employed in situ at low temperatures. These borotropic rearrangements are the bane of stereoselective syntheses since they can scramble the double bond geometry of the reagent. Thus, a major advantage in using allylic boronates compared to boranes is that they are much less prone to such rearrangement. For example, whereas *B*-crotyl-9-borabicyclo[3.3.1]nonane (*B*-crotyl-9-BBN) (**33**) exists as an equilibrating mixture of *E*- and *Z*-isomers at room temperature,<sup>92</sup> the two isomers of pinacol crotylboronate (**7**) are sufficiently stable to be independently prepared, isolated, and employed at that temperature (Fig. 2).<sup>22,54</sup> The allylic borotropic rearrangement has been studied in detail with a few distinct reagents, including the  $\alpha$ -methyl allylic reagents of generic structure **34** (Eq. 44). The dialkylboranes are fluxional at room temperature and exist almost exclusively as the thermodynamically favored crotylborane with a more highly substituted double bond.<sup>91–93</sup>



**Figure 2.** Comparison of the stereochemical stability of crotylboranes vs crotylboronates.



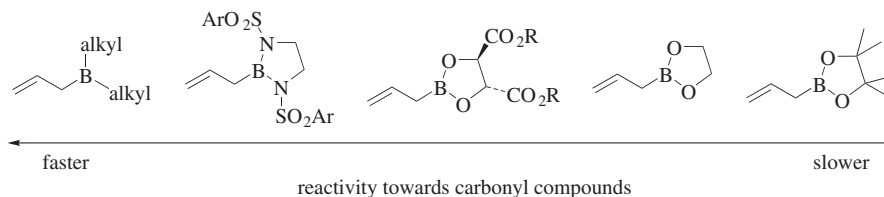
The speed of the rearrangement depends on the Lewis acidity of the boron atom.<sup>94</sup> Electron-donating substituents that reduce the acidity of boron slow down the process. Thus, whereas a monoamino derivative slowly isomerizes at 150°,<sup>95</sup> the corresponding diamino derivative is stable up to a temperature of 200°.<sup>96</sup> The corresponding boronic esters are less stabilized towards the borotropic rearrangement, but they are stable enough to be conveniently handled at room temperature. The presence of Lewis acids, however, can promote or accelerate the rearrangement.<sup>49</sup> These allylic borotropic rearrangements obey first-order kinetics and the absence of crossover products in control experiments demonstrates their intramolecular nature.<sup>92</sup> In the case of the *B*-allyl 9-BBN reagent, the coalescence temperature is 10°, which corresponds to a rate of exchange of 330 sec<sup>-1</sup> ( $\Delta G^\ddagger$  13.3 kcal/mol).<sup>92</sup> Unsurprisingly, bases such as pyridine completely stop the rearrangement.<sup>92,94</sup> Activation parameters of several allylic dialkylboranes have been determined by dynamic NMR spectroscopy.<sup>91</sup>

### Reactivity of Allylic Boron Reagents

The boron–oxygen mesomeric effect described in the previous section explains the lower reactivity of allylic boronates towards carbonyl compounds compared to that of allylic boranes. The use of Lewis acids, however, allows boronate derivatives, including hindered ones, to react at temperatures comparable to the analogous boranes. As described above (see section “Mechanism and Stereochemistry”), the most reactive allylic boronates are those with the most electrophilic boron centers.<sup>19,21</sup> The nucleophilicity of the  $\gamma$ -position of an allylic boron reagent (the position that forms the new C–C bond with the aldehyde) is also important to the reactivity of the reagent. For example, allylic boronates with

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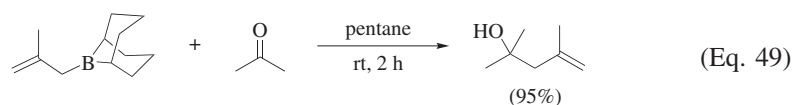
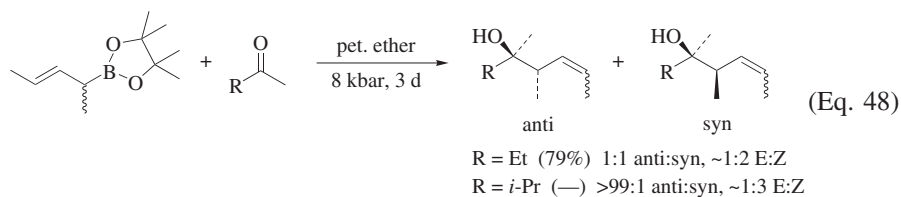
**Figure 3.** Scale of reactivity for selected allylboron derivatives toward carbonyl compounds.

substituents that reduce electron density at this position, such as 2-ethoxycarbonyl groups,<sup>58,59</sup> are correspondingly less reactive than similar allylboronates that lack these groups. Between the crotylboronate isomers, the *E*-isomer reacts noticeably faster than the *Z* counterpart.<sup>22,34</sup> The electronic and steric effects of different allylic borane and boronate derivatives has been studied by qualitative kinetic analysis.<sup>21</sup> The resulting scale of reactivity depicted in Fig. 3 emphasizes the importance of both effects in the reactivity of these boron-based reagents. In general, acyclic boronates react faster than cyclic ones. Moreover, the reaction is quite sensitive to electronic effects. For example, *N,N,N',N'*-tartramide derivatives react at a much slower rate than the corresponding esters.

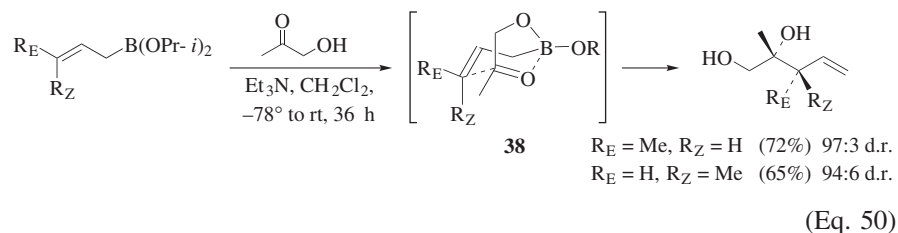
Allylic dihaloboranes have been isolated and characterized.<sup>97</sup> The highly electrophilic difluoroallylborane is predicted to be extremely reactive in carbonyl allylation.<sup>19</sup> Allylic difluoroboranes are postulated intermediates in the Lewis acid promoted additions of allylic trifluoroborate salts.<sup>98,99</sup> These reagents combine stability and reactivity as desirable attributes in a single class of allylic boron reagents. They are prepared by reaction of the corresponding allylic boronic acids with aqueous  $\text{KHF}_2$ , and they can be purified by recrystallization and stored as air- and water-stable solids for extended periods of time at room temperature. For example, the crotyl trifluoroborates (*E*)- and (*Z*)-**35** do not interconvert. Allylic trifluoroborate salts are inert to carbonyl compounds until activated by an external Lewis acid, at which point they become efficient allylating agents that produce homoallylic alcohols in high yields. Instead of aldehyde coordination, this new method of activation is thought to involve a mechanism whereby the electrophilic additive (usually  $\text{BF}_3 \cdot \text{OEt}_2$ ) strips off a fluoride anion from the trifluoroborate salt. The expected product of this equilibration is a highly electrophilic tricoordinate allylic difluoroborane, which is thought to react with aldehydes through the usual Type I mechanism. Consistent with this hypothesis, the crotyl reagents (*E*)- and (*Z*)-**35** provide, in over 90% yield, the respective anti and syn addition products expected from a cyclic, chairlike transition structure (Eq. 45). Although the reaction is usually carried out using two equivalents of  $\text{BF}_3 \cdot \text{OEt}_2$  at  $-78^\circ$ , it can also be performed with as low as 5 mol% of the same additive, albeit at room temperature. A phase-transfer procedure has also been developed.<sup>100</sup>



of additions of allylic boron reagents involve aldehydes as substrates, additions to ketones are also possible. Additions to simple ketones are much slower than similar reactions with aldehydes, and forcing conditions may be required. The stereoselectivity observed in these additions is variable depending on the difference in size between the two substituents on the ketone. As exemplified in Eq. 48, ketones react slowly with allylic boronates, under high pressure, to yield tertiary homoallylic alcohols as products.<sup>102</sup> Additions of allylic boranes are also much slower with ketones. For example, additions of methallyl-BBN are performed at room temperature, compared to  $-78^\circ$  for aldehydes (Eq. 49), and they were found to be highly sensitive to the steric bulk of the ketone.<sup>103</sup> Because of the high temperature required, these additions are accompanied by reversible allylic rearrangement in reactions of 3-monosubstituted allylic boranes, which renders them impractical.

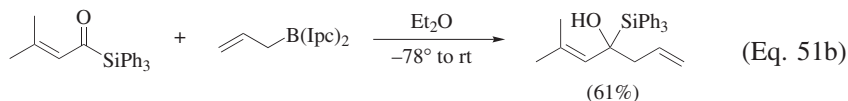
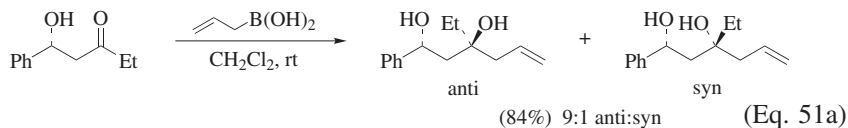


The additions of allylic boronates to ketones are greatly enhanced if an appropriate chelating group is present on the ketone (such as an  $\alpha$ - or  $\beta$ -hydroxy or carboxylic acid group).<sup>104–109</sup> For example, both (*E*)- and (*Z*)-diisopropyl crotylboronate exchange 2-propanol and add to  $\alpha$ -hydroxyacetone within reasonable time frames to give the expected products in high diastereoselectivity (Eq. 50).<sup>109</sup> In the proposed transition structure **38**, the ketone residue bearing the  $\alpha$ -hydroxy group occupies an axial position due to the formation of a cyclic boronate complex.

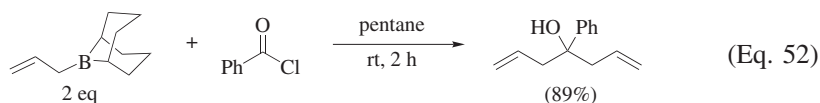


Moderate levels of diastereomeric differentiation are observed in the additions of achiral allylboronates to  $\beta$ -hydroxy ketones, as exemplified in Eq. 51a.<sup>110</sup> The major product is tentatively assigned as the anti diastereomer. Few reports describe the use of carbonyl substrates other than aldehydes and ketones, and these reactions have not led to applications. For instance, low reactivity leading

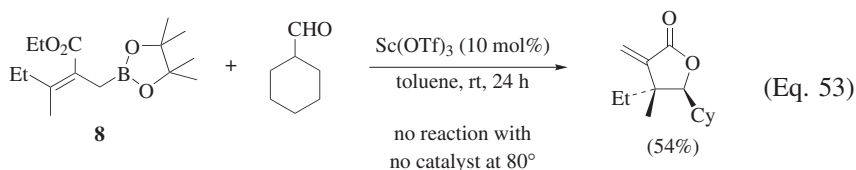
to modest yields and stereoselectivity are observed in the additions of allylic boranes to acylsilanes (Eq. 51b).<sup>111</sup>



Acid chlorides (which react vigorously), esters, and *N,N*-dimethylamides react with two equivalents of the reagent to give diallyl tertiary alcohols after work-up (Eq. 52).<sup>103</sup>

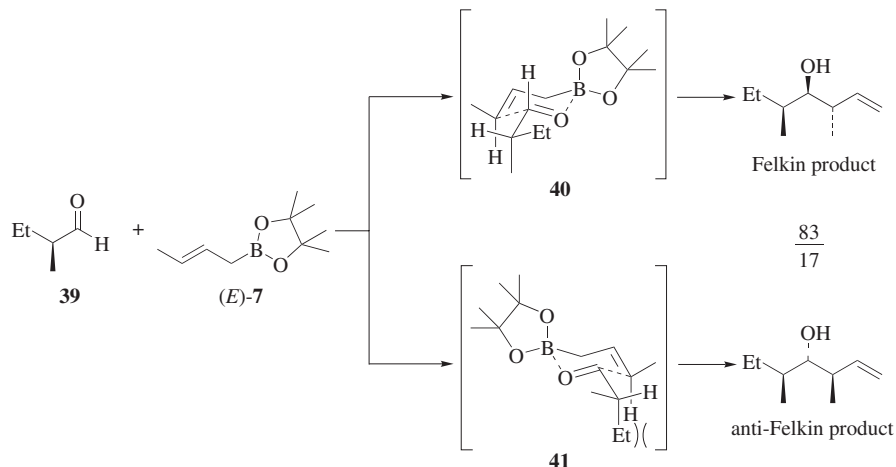


The Lewis acid catalyzed reactions expand the scope of aldehyde substrates with certain boronate reagents. For example, whereas cyclohexanecarboxaldehyde is unreactive under thermal (uncatalyzed) conditions, it does react with allylic boronate **8** under Sc(OTf)<sub>3</sub> catalysis at room temperature (Eq. 53, see also Eq. 6).<sup>26</sup>



### Diastereoselective Additions to Chiral $\alpha$ -Substituted Carbonyl Substrates

The presence of a stereogenic center on the aldehyde can strongly influence the diastereoselectivity in allylboration reactions, especially if this center is in the  $\alpha$ -position. Predictive rules for nucleophilic addition on such  $\alpha$ -substituted carbonyl substrates such as the Felkin model are not always suitable for closed transition structures.<sup>112</sup> For  $\alpha$ -substituted aldehydes devoid of a polar substituent, Roush has established that the minimization of “gauche-gauche” (“syn-pentane”) interactions can overrule the influence of stereoelectronic effects.<sup>113</sup> This model is valid for any 3-monosubstituted allylic boron reagent. For example, although crotylboronate (*E*)-**7** adds to aldehyde **39** to afford as the major product the diastereomer predicted by the Felkin model (Scheme 2),<sup>114,115</sup> it is proposed that the dominant factor is rather the minimization of syn-pentane interactions between the  $\gamma$ -substituents of the allyl unit and the  $\alpha$ -carbon of the aldehyde. With this

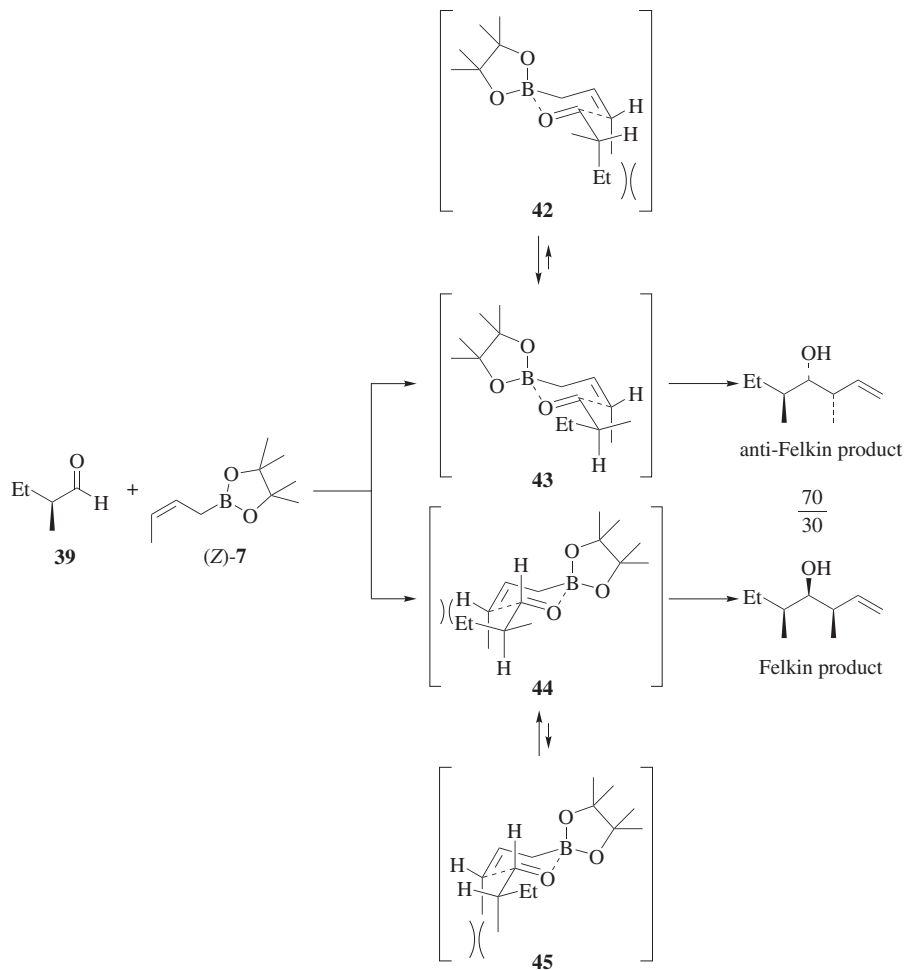


**Scheme 2.** Stereoinduction model for additions of (*E*)-**7** to  $\alpha$ -chiral aldehyde **39**.

model, **40** is the favored transition structure leading to the Felkin product because the two smallest substituents on the  $\alpha$ -carbon (H, Me) are aligned respectively with a methyl and a hydrogen of the *E*-crotyl unit. This arrangement leaves the largest group (Et) of the aldehyde “outside” the chair, away from the reactive centers and almost orthogonal with the plane of the carbonyl unit. This conformer, which in this instance also happens to be the reactive one predicted by the Felkin model, best minimizes the so-called gauche-gauche (syn-pentane) interactions. In the alternative transition structure **41** that leads to the minor diastereomer, the ethyl group induces slightly more important gauche-gauche interactions compared to those found in **40** (Et–H for **41** vs. Me–H for **40**). Other transition structures with the smallest group (H) outside the chair are less favorable and are not considered in this analysis. These transition structures feature Me–Me or Et–Me “syn-pentane” interactions, and thus are significantly higher in energy.

The value of this model is more apparent in rationalizing the results of crotylboronate (*Z*)-**7** for which the possible transition structures, **42–45**, are shown in Scheme 3.<sup>113</sup> In these examples, the major diastereomer is the anti-Felkin product.<sup>115</sup> The Felkin transition structure **45** shows a severe Me–Me syn-pentane interaction. Structure **43**, analogous to **40** in Scheme 2, best minimizes these interactions by aligning the smallest groups together. With respect to the minor diastereomer, structure **44** is preferable over **45**, but not quite as effective as **43** in minimizing the overall effect of syn-pentane interactions because it places the methyl group outside the chair instead of the larger ethyl group.

The stereoinductive effect of the  $\alpha$ -substituent is often more powerful when this substituent is a polar group such as an alkoxy or amino group. In this instance as well, minimization of syn-pentane interactions with 3-monosubstituted reagents is important, and the selectivity can be amplified if it acts in concert with other effects. Known models include the stereoelectronic preference



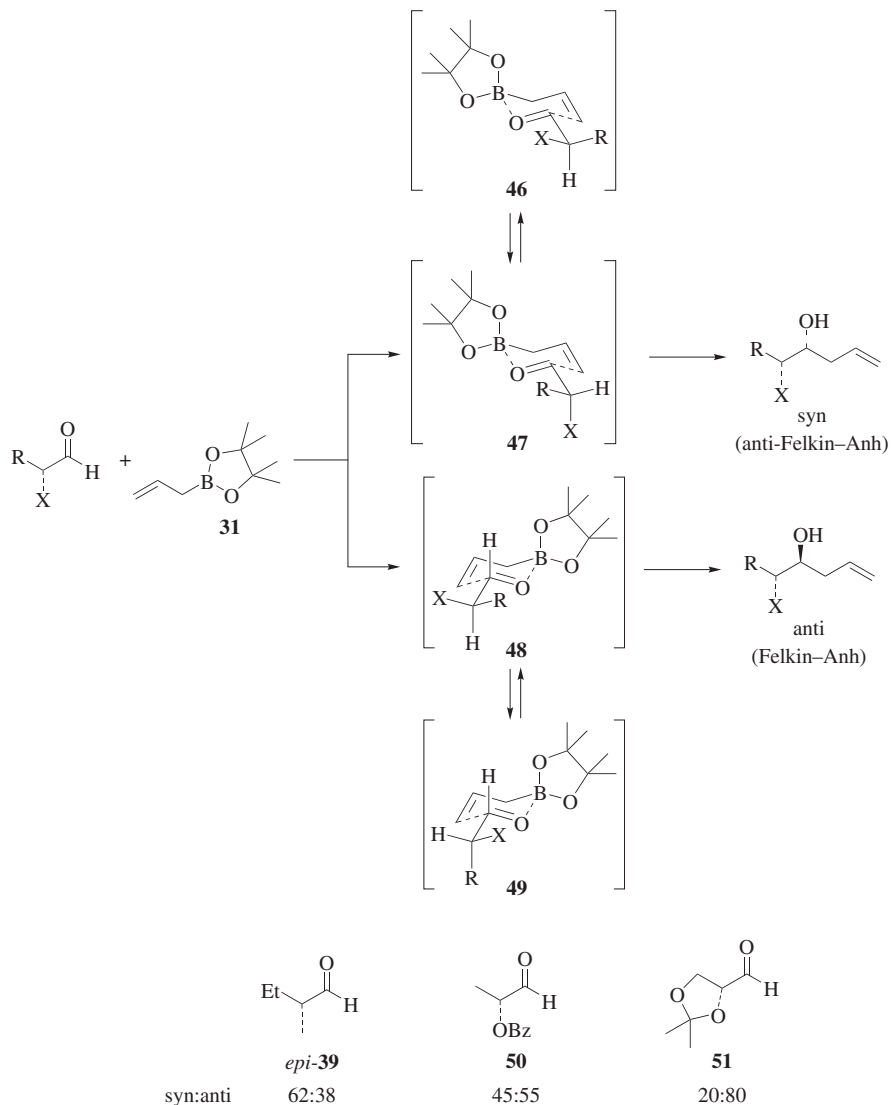
**Scheme 3.** Stereoinduction model for additions of (Z)-7 to  $\alpha$ -chiral aldehyde **39**.

for the orthogonal polar group dictated by the Felkin–Anh model,<sup>116</sup> and the minimization of dipoles (i.e., the Cornforth model<sup>117</sup>). With such aldehydes as glyceraldehyde acetals (e.g., **51** in Scheme 4), Z-crotylboron reagents tend to be more selective than the E-isomers.<sup>118</sup> In the absence of any  $\gamma$ -substituents, or with 3,3-disubstituted reagents, syn-pentane interactions are not expected to play a key role. As shown in Scheme 4, the generic addition of pinacol allylboronate (**31**) to aldehydes substituted with a polar substituent can proceed through four reasonable transition structures **46–49** (high-energy rotamers with the small group, the hydrogen atom, in the “outside” position are not considered).<sup>115,118</sup> Comparison of the selectivity among aldehydes **39**, **50**, and **51** shows an increase in the anti product with a polar aldehyde substituent. By presenting the polar group almost



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**Scheme 4.** Stereinduction model for additions of allylboronate **31** to aldehydes with a polar  $\alpha$ -substituent.

perpendicular to the plane of the aldehyde carbonyl group, structures **46** and **49** are stereoelectronically favorable and probably comparable in energy even if structure **49** is formally the reactive conformer according to the Felkin-Anh interpretation. The results of reactions of allylboronate **31** and the corresponding crotyl reagents suggest that with aldehyde **51**, the Cornforth-like conformer **48** (minimizing dipole repulsion between the  $\alpha$ -alkoxy substituent and the carbonyl)

is particularly important in explaining the increase of the anti stereoisomer. A computational study supports the importance of the Cornforth model in these allylboration reactions.<sup>119</sup> Moreover, this conformer (**48**) also favorably places the large methylene(oxy) substituent of aldehyde **51** on the “outside” on the chairlike transition structure.

To improve the levels of selectivity in additions to chiral aldehydes, it is possible to resort to the tactic of double diastereoselection with the use of chiral allylic boranes and boronates (see section “Double Diastereoselection”). Bis(isopinocampheyl) allylic boranes and the tartrate allylic boronates (see following section), in particular, are very useful in the synthesis of polypropionate natural products by reaction with  $\alpha$ -methyl and  $\alpha$ -alkoxy functionalized aldehydes.

### Enantioselective Allylations and Crotylations with Chiral Auxiliary Reagents

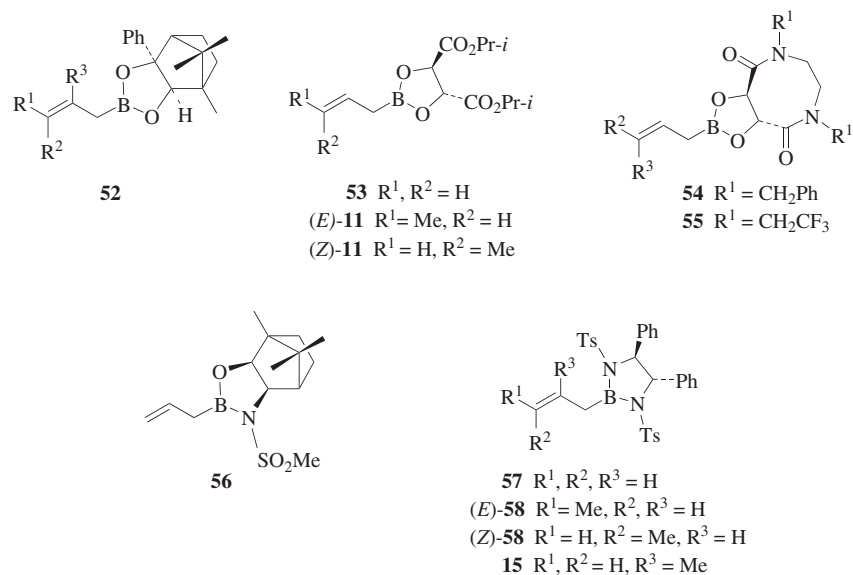
The most common application of the allylboration reaction is in the allylation and crotylation of aldehydes. Many strategies have been devised for controlling the absolute stereoselectivity.<sup>10,11</sup> These strategies involve two general classes of chiral reagents: (1) allylic boronates or boranes containing a stereogenic  $\alpha$ -carbon on the allylic unit; (2) allylic boronates fitted with a chiral auxiliary that creates the cyclic boronate, or that is attached to the non-allylic substituents in boranes. The use of chiral auxiliary-based reagents is more popular because it is generally easier to manipulate the non-allylic substituents than it is to make an enantiomerically pure allylic boronate with a stereogenic  $\alpha$ -carbon on the allylic unit. Several examples of both classes of reagents have been reported and reviewed recently, both for boronate derivatives and boranes.<sup>10,11</sup>

**Chiral Boronate Derivatives.** A large number of chiral auxiliary reagents based on allylic boronates has been reported.<sup>10,11</sup> This section provides a brief overview of the historically important ones, but it focuses mainly on the most popular systems and the emerging ones (Fig. 4).

The first examples of chiral allylic boronates<sup>120</sup> were prepared from rigid camphor-derived 1,2-diols, providing allylation reagents of generic structure **52**.<sup>114,120–122</sup> Although they did not provide very high levels of stereoinduction in their reactions with aldehydes, these reagents inspired more work by several other groups, and these efforts led to significantly improved systems. For example, the class of tartrate-derived allenyl-, allyl- **53**, and crotylboronates **11** has evolved into one of the most recognizable class of reagents in organic synthesis.<sup>37,123,124</sup> These reagents are very reactive, allowing additions to aldehydes to proceed readily at  $-78^\circ$ . Their reactivity comes at a price, however, as they are hydrolytically unstable and must be employed in conjunction with molecular sieves to rigorously eliminate adventitious traces of water.<sup>125</sup> Nonetheless, when appropriately stored at  $-20^\circ$ , the crotylboronates **11** can be kept for months without appreciable deterioration. As expected, reagents (*E*)-**11** and (*Z*)-**11** give the respective anti- and syn-propionate units in a diastereospecific manner and with very high diastereoselectivity (Eqs. 54 and 55).<sup>37</sup> The enantioselectivity tends to be higher

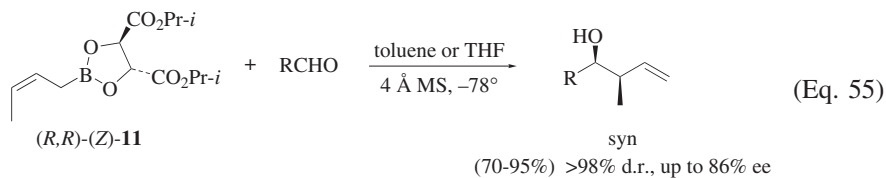
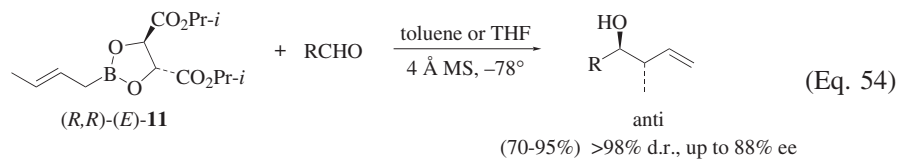
## ALLYLBORATION OF CARBONYL COMPOUNDS

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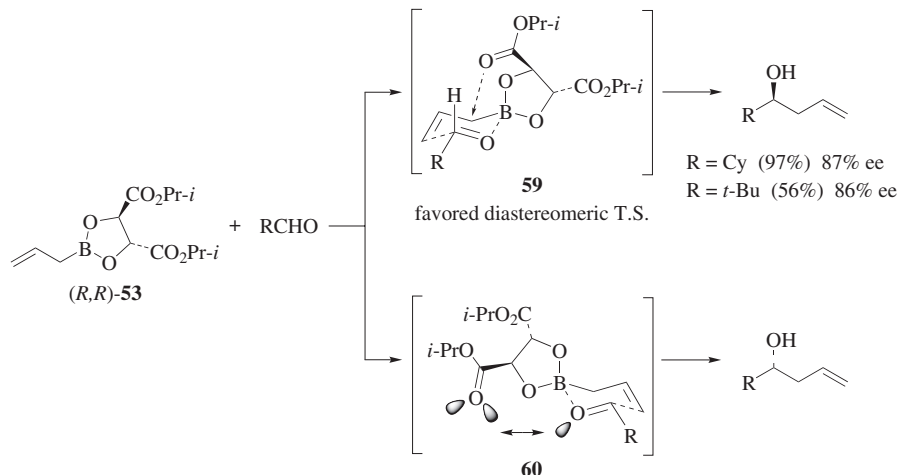


**Figure 4.** Common allylic boronate derivatives used as chiral auxiliary reagents in enantioselective carbonyl additions. (Only one stereoisomer is shown for simplicity.)

with (*E*)-11, but values are typically less than 85% ee for most aldehydes. In this regard, toluene is the best solvent for aliphatic aldehydes whereas THF is optimal for aromatic ones.<sup>125</sup> Although simple stereoselection with these reagents does not provide practical levels of enantioselectivity, their use in double diastereoselection with  $\alpha$ -substituted aldehydes<sup>126</sup> has been amply demonstrated in the context of numerous total syntheses of complex natural products.<sup>11</sup>



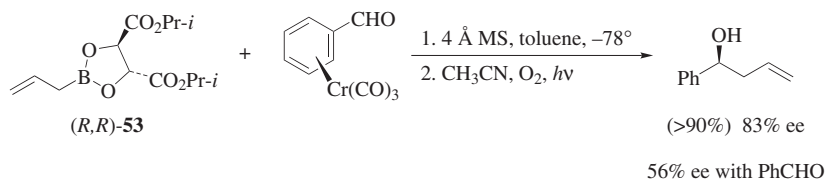
Originally, it was proposed that lone pair repulsions between one of the tartrate ester carbonyl oxygens and the aldehyde oxygen in transition structure **60** were responsible for the preference for transition structure **59** and the consequent enantiofacial selectivity (Scheme 5). Recent theoretical calculations,



**Scheme 5.** Model for absolute stereoinduction in additions of tartrate allylic boronate **53** to aldehydes.

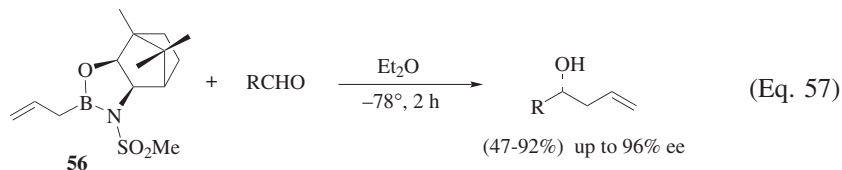
however, point to an attractive  $n_{\text{O}}-\pi^*_{\text{C}=\text{O}}$  interaction between the basic oxygen atom of one of the two ester groups and the boron-activated aldehyde carbonyl as the main factor favoring transition structure **59** in these stereoselective allylations.<sup>127</sup>

Significantly higher levels of enantioselectivity can be obtained with aromatic and unsaturated aldehydes by making use of the corresponding metal carbonyl complexes (Eq. 56).<sup>128,129</sup> The selectivity is higher in toluene as solvent, and the resulting product can be easily decomplexed oxidatively to afford enantioenriched material. Likewise, dicobalt hexacarbonyl complexes of propargylic aldehydes provide much improved selectivities.<sup>128,130</sup>



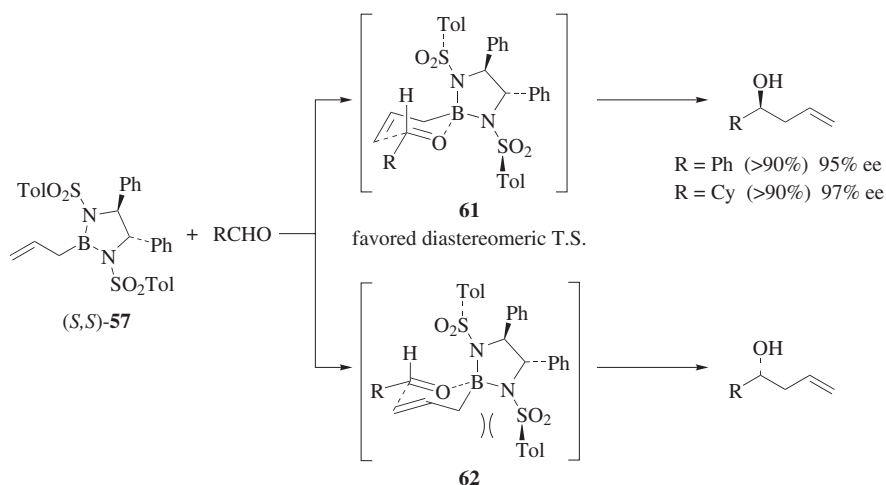
(Eq. 56)

Cyclic derivatives **54** and **55** lead to higher levels of enantioselectivity with several types of aldehydes but their preparation requires more effort than the simpler parent reagents **53** and **11** (Fig. 4).<sup>131,132</sup> The mixed O/N boronate derivative **56** provides high enantioselectivities with aliphatic aldehydes (Eq. 57).<sup>133</sup> Its preparation, however, is also tedious and requires five steps from enantiomerically pure camphorquinone.



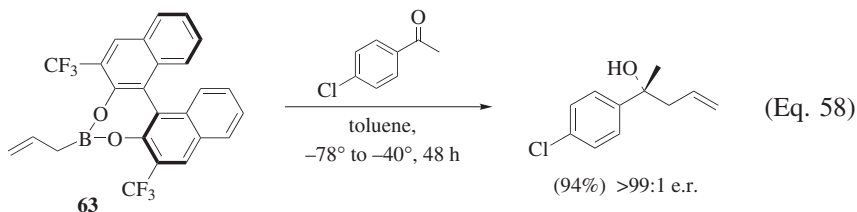
The bis(sulfonamide)-derived reagents (e.g., **57**, **58**, and **15** in Fig. 4) are based on a 1,2-diamino-1,2-diphenylethane auxiliary.<sup>50</sup> These hydrolytically unstable boronate derivatives are typically prepared by Sn-to-B exchange of allylic tin precursors (e.g., Eq. 19). When employed at  $-78^\circ$  in toluene or methylene chloride, unsubstituted allyl and methallyl reagents **57** and **15** provide very high enantioselectivities ( $>95\%$  ee).<sup>50</sup> The 2-bromoallyl reagent is also quite efficient but the crotylation reagents **58** provide slightly lower enantioselectivities (90–95% ee). It is thought that in the favored transition state **61** involving a tetracoordinate boron atom, the tolylsulfonyl groups orient away from the phenyl substituents of the chiral auxiliary (Scheme 6). It was proposed that the high enantioselectivity can be rationalized by the presence of a steric interaction between the methylene group of the allyl unit and the sulfonyl substituent on the pseudo-equatorial nitrogen atom in the disfavored transition state **62**.<sup>50</sup> Several 2-substituted derivatives of these bis(sulfonamide) allylation reagents have been employed in the total synthesis of complex natural products (see section “Applications to the Synthesis of Natural Products”).

There are only a few examples where chiral allylic boronates react successfully with ketones, and the enantioselectivities are modest.<sup>134</sup> A recent report, however,

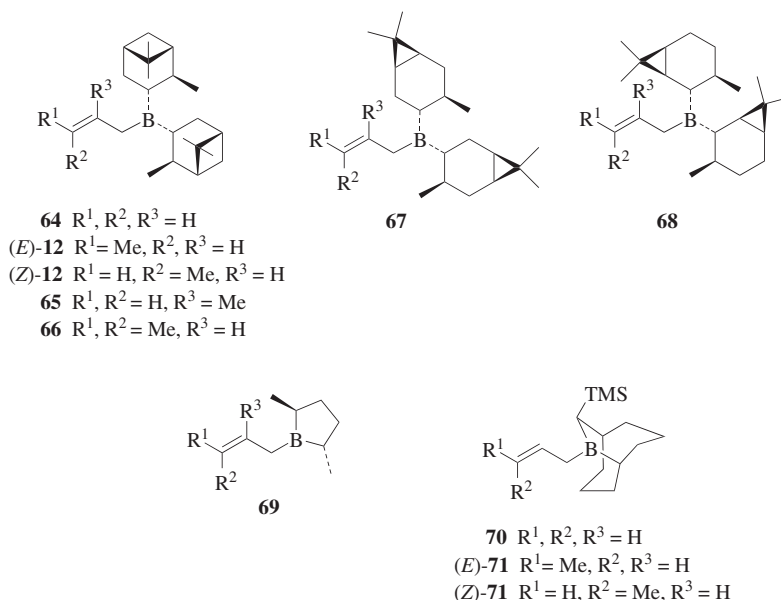


**Scheme 6.** Model for absolute stereoinduction in additions of bis(sulfonamide) reagent **57** to aldehydes.

describes the use of very reactive binaphthol-derived allylboronates. In particular, high levels of enantioselection ( $>96\%$  ee) are obtained in the reaction of the 3,3'-(CF<sub>3</sub>)<sub>2</sub>-BINOL reagent **63** with several aromatic ketones, as exemplified with 4-chloroacetophenone (Eq. 58).<sup>135</sup>



**Chiral Dialkylboranes.** Several allylic boranes have been developed as chiral auxiliary reagents (Fig. 5). The introduction of terpene-based reagents such as **12** and **64–68** has been pioneered by H.C. Brown, and the most popular class remains the bis(isopinocampheyl) derivatives (structures **12**, **64–66**).<sup>136</sup> A wide variety of substituted analogs have been reported,<sup>9,12</sup> including the popular crotylboranes **12**,<sup>44,137</sup> but also a number of other reagents bearing heteroatom-substituents. All are made from the inexpensive precursor  $\alpha$ -pinene, readily available in both enantiomeric forms.

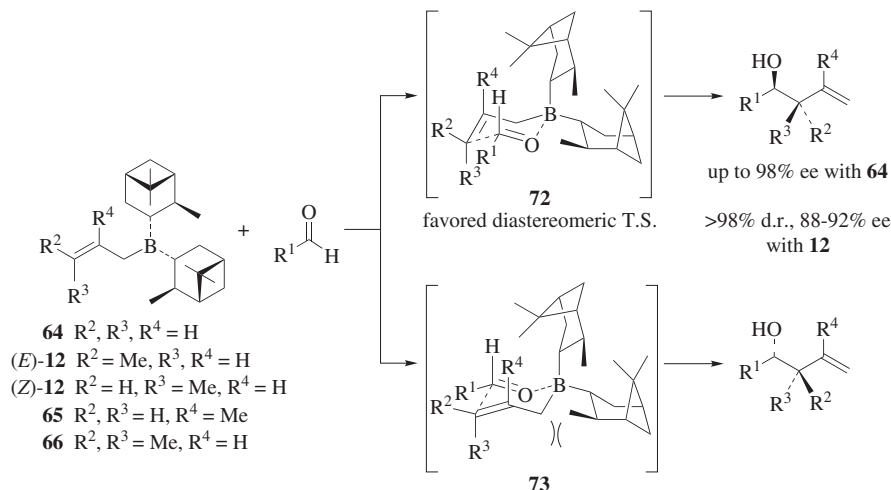


**Figure 5.** Chiral allylic boranes used as chiral auxiliary reagents in enantioselective additions to carbonyl compounds. (Only one isomer is shown for simplicity. For reagents **12** and **64–66**, (–)-Ipc is shown.)

Most of the bis(isopinocampheyl) reagents, which are prepared from hard allylic organometallic precursors (e.g., Eqs. 15 and 16), are very reactive and add rapidly to aldehydes at  $-78^{\circ}$ . Like other boranes, they are oxidatively unstable in ambient atmosphere and must be reacted with aldehydes in situ. Moreover, because of the borotropic rearrangement discussed above, the crotylboranes must be preserved and used at a low temperature to avoid geometrical isomerization with consequent formation of mixtures of diastereomeric products (see section on “Stability and Handling”). Not surprisingly, the 3,3-disubstituted reagent **66**, which provides quaternary carbon centers in the products, reacts more slowly and necessitates a higher reaction temperature.<sup>138</sup> The alcohol products from these additions are most often isolated through a basic hydrolytic oxidative work-up of the borinate intermediate (see Eq. 46). The unsubstituted reagent **64**, allyl(Ipc)<sub>2</sub>borane, is very enantioselective.<sup>136</sup> It provides enantioselectivities over 95% for a wide range of aldehyde substrates. The removal of residual Mg<sup>2+</sup> salts from the preparation of **64** leads to a dramatic increase of the reagent’s reactivity, allowing reactions to be carried out at  $-100^{\circ}$  with improved enantioselectivities (up to 98% ee).<sup>139</sup> Simple allylation reactions have been performed successfully in good to high yields with a wide variety of aliphatic, aromatic and heteroaromatic aldehydes (see section “Applications to the Synthesis of Natural Products”). Crotylations of aldehydes with reagents **12** are less selective, providing enantioselectivities in the range of 88–92% ee at  $-78^{\circ}$ .<sup>137</sup> The bis(isopinocampheyl)boranes behave poorly with ketones as substrates. For example, the simple allylation of acetophenone with reagent **64** gives the addition product with only 5% ee.<sup>140</sup>

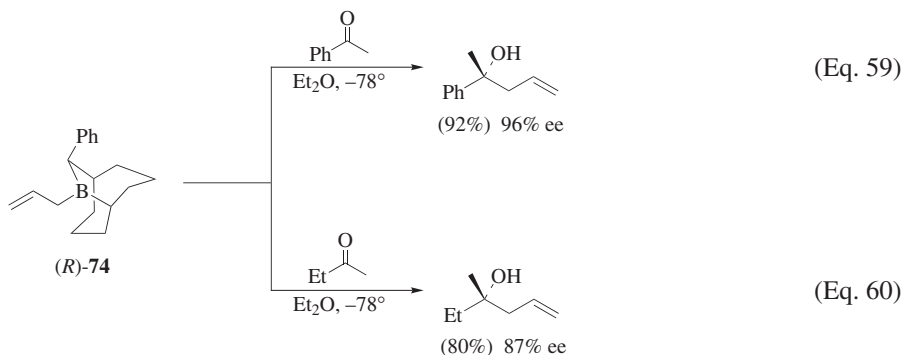
The enantioselectivity of these reagents is explained by comparison of transition structures **72** and **73** shown in Scheme 7. The disfavored transition structure **73** leading to the minor enantiomer displays a steric interaction between the methylene of the allylic unit and the methyl group of one of the pinane units. Unlike the tartrate boronates described above, the directing effect of the bis(isopinocampheyl) allylic boranes is extremely powerful, giving rise to high reagent control in double diastereoselective additions (see section on “Double Diastereoselection”).

Other chiral dialkylallylboranes have been reported, including the borolanes **69** (Fig. 5).<sup>141,142</sup> Although the high reactivity and outstanding enantioselectivity of these borolanes make them very attractive reagents, they are notorious for their tedious preparation and have thus remained rather under-utilized. Recently, the 10-TMS-9-borabicyclo[3.3.2]decane allylborane and crotylboranes (**70**) and (**71**) were shown to provide remarkable stereoselectivities (>98% d.r., 94–99% ee) and good to high yields for a wide range of aldehydes.<sup>143</sup> These reagents require reaction times of just a few hours at  $-78^{\circ}$ , and are said to be robust and recyclable. They can be prepared using allylic carbanions in three simple steps that includes, however, a resolution of the borinic ester precursor as a stable and crystalline pseudoephedrine complex. The corresponding allenylborane has been reported.<sup>144</sup> Reagent **74**, the 10-phenyl analog of reagent **70**, is particularly effective in allylations of ketones.<sup>145</sup> As exemplified in the reaction between (*R*)-**74** and acetophenone, enantioselectivities are excellent for aromatic ketones



**Scheme 7.** Model for absolute stereoselection in additions of (-)-bis(isopinocampheyl) allylic boranes to aldehydes.

(Eq. 59), and even surprisingly high for aliphatic ketones such as 2-butanone, a substrate that offers very little steric discrimination (Eq. 60). Reagent **74** is less effective than **70** in allylations of aldehydes (e.g., 90% ee vs. >98% ee for **70** in the allylation of benzaldehyde). The superior reactivity and selectivity of **74** with ketones is ascribed in part to the lesser steric bulk of the phenyl substituent compared to the trimethylsilyl unit of reagent **70**. The smaller phenyl substituent of **74** would provide a better fit for ketones in the chiral “pocket” of the reagent.



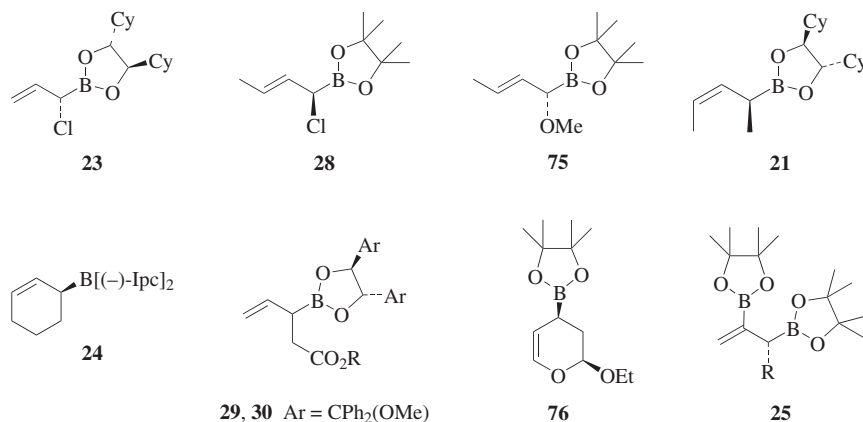
### Enantioselective Allylations and Crotylations with Chiral $\alpha$ -Substituted Reagents

One major advantage of chiral auxiliary reagents over chiral  $\alpha$ -substituted reagents is the fact that the chiral diol or diamine unit is not modified in the bond-making process and is thus potentially recyclable. The preparation of enantiomerically pure  $\alpha$ -substituted reagents requires a stereoinductive transformation



such as the Matteson asymmetric homologation (see Eqs. 26 and 27), and their addition to aldehydes leads to destruction of the stereogenic  $\alpha$ -center. Despite these disadvantages, many such reagents have found extensive use in the total synthesis of complex natural products.<sup>11</sup> Examples of chiral  $\alpha$ -substituted allylic boronates are shown in Fig. 6.<sup>4,5</sup> The possibility for allylic rearrangement precludes the use of chiral  $\alpha$ -substituted allylic boranes except in special instances such as the cyclohexenyl derivative **24**, which can be prepared by the asymmetric hydroboration of cyclohexadiene (Eq. 28). Enantiomerically enriched reagent **24** (94% ee) adds to aldehydes at  $-78^\circ$  to give the corresponding homoallylic alcohols with high enantioselectivities (94% ee).<sup>70</sup>

From the useful  $\alpha$ -chloro allylic boronates **23** and **28**,<sup>65-67,83,146</sup> a number of other  $\alpha$ -substituted reagents can be obtained by nucleophilic substitution of the chloride substituent (Fig. 6). For example, the  $\alpha$ -methoxy reagent **75**<sup>68,147</sup> and  $\alpha$ -methyl substituted reagent **21**<sup>63-65</sup> provide excellent enantiofacial discrimination with levels of enantiocontrol over 95% ee. These reagents provide interesting insight into the important steric and electronic factors involved in the allylboration transition structure. For all of these  $\alpha$ -substituted reagents, two competing chairlike transition structure models can be proposed where the  $\alpha$  substituent is positioned either in a pseudo-equatorial or in a pseudo-axial orientation.<sup>146</sup> These two competing structures lead to opposite configurations for the resulting homoallylic alcohols, and their relative energy difference depends on the nature of the substituent on the  $\alpha$ -carbon, on the nature of the diol boronate auxiliary, and also on the presence of  $\gamma$ -substituents on the allylic boronate. For example, in reactions with  $\alpha$ -chloro reagent **23**, the chloroalkenyl homoallylic alcohol product (*Z*)-**78** is largely predominant (>99:1) over the *E*-configured product **80**, and it is obtained in a very high level of enantioselectivity (Scheme 8).<sup>65,66</sup> This very high enantioselectivity of the product reflects the high enantiopurity of reagent **23**. The predominance of stereoisomer **78** and its *Z*-olefin geometry can be explained in

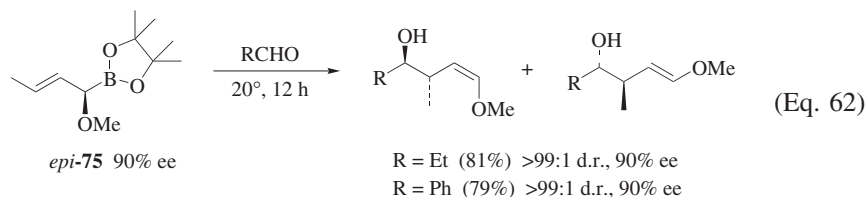


**Figure 6.** Chiral  $\alpha$ -substituted allylic boron reagents.



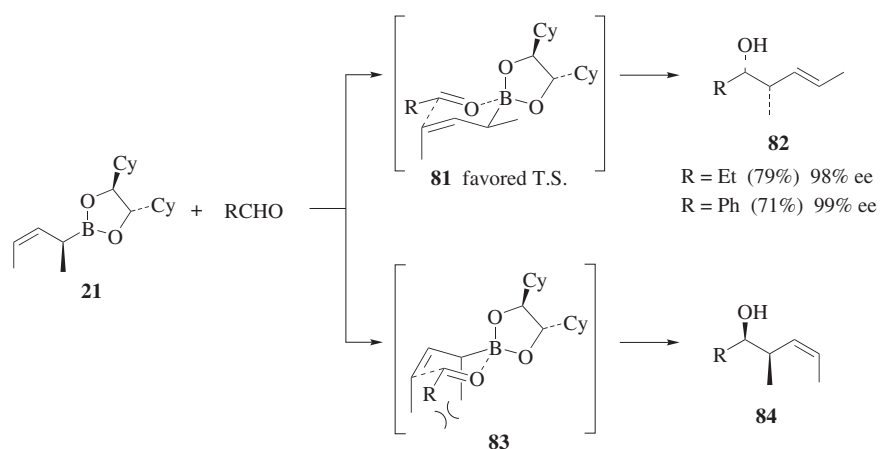
## ALLYLBORATION OF CARBONYL COMPOUNDS

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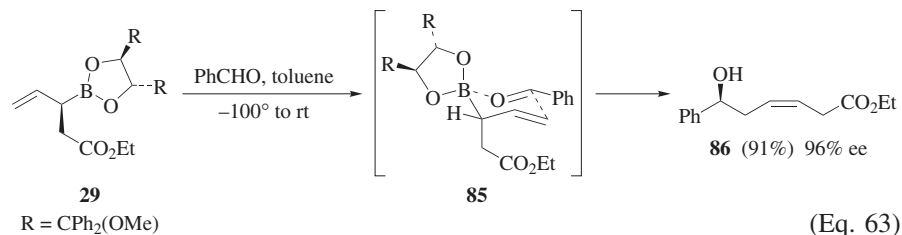


The  $\alpha$ -methyl *Z*-crotylboronate derivative **21** can be obtained in high enantiomeric purity, and its additions to aldehydes are highly diastereoselective and occur with almost perfect enantiofacial selectivity (Scheme 9).<sup>63,64</sup> In this instance, the unfavored transition structure **83** (leading to *Z*-product **84**) with the pseudo-axial  $\alpha$ -methyl group develops a strong pseudo-1,3-diaxial interaction between the two methyl substituents of the reagent. The favored transition structure **81** is devoid of such an interaction, and provides the *E*-configured synpropionate adducts **82** with very high stereoselectivity. Reagents **21**, **28**, and **75** (Fig. 6) have also been used extensively in double diastereoselective synthesis with chiral aldehydes, and they generally lead to high levels of reagent control (see section “Double Diastereoselection”).<sup>63,64,67,68,83,149</sup>

The enantiomerically pure  $\alpha$ -substituted reagents of type **29/30** (Fig. 6, Eq. 39) react with benzaldehyde to give the expected homoallylic alcohol products such as **86** with high enantioselectivity (Eq. 63).<sup>85,86</sup> By analogy with the above-described reagents, the addition is presumed to occur through transition structure **85** with the pseudo-axial  $\alpha$ -alkyl substituent. The competing transition structure with the pseudo-equatorial substituent would experience severe non-bonding interactions between this group and the bulky boronic ester moiety.

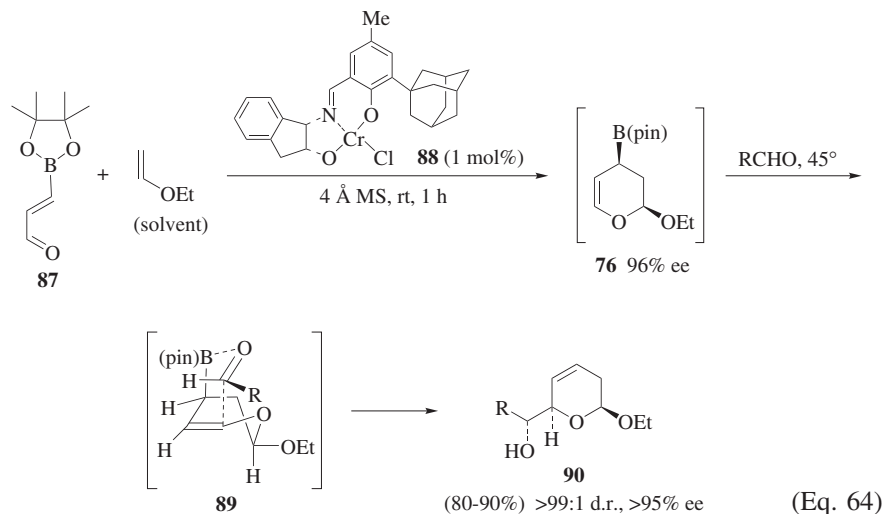


**Scheme 9.** Stereoinduction model for the additions of chiral  $\alpha$ -methyl crotylboronate **21**.



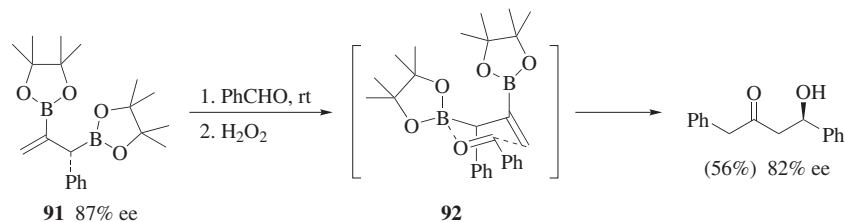
Recently, the first examples of catalytic enantioselective preparations of chiral  $\alpha$ -substituted allylic boronates have appeared. Cyclic dihydropyranylboronate **76** (Fig. 6) is prepared in very high enantiomeric purity by an inverse electron-demand hetero-Diels–Alder reaction between 3-boronoacrolein pinacolate (**87**) and ethyl vinyl ether catalyzed by chiral Cr(III) complex **88** (Eq. 64). The resulting boronate **76** adds stereoselectively to aldehydes to give 2-hydroxyalkyl dihydropyran products **90** in a “one-pot” process.<sup>150–152</sup> The diastereoselectivity of the addition is explained by invoking transition structure **89**. Key to this process is the fact that the possible “self-allylboration” between **76** and **87** does not take place at room temperature. Several applications of this three-component reaction to the synthesis of complex natural products have been described (see section on “Applications to the Synthesis of Natural Products”).

The catalytic asymmetric diboration of allenes provides  $\alpha$ -substituted 2-boronyl allylic boronates of type **25** (see Eq. 32). One of them, **91**, adds to benzaldehyde, albeit with a slight erosion of stereoselectivity (Eq. 65).<sup>73</sup> The major  $\beta$ -hydroxy ketone stereoisomer, isolated after an oxidative work-up, originates from the putative chairlike transition structure **92**.



## ALLYLBORATION OF CARBONYL COMPOUNDS

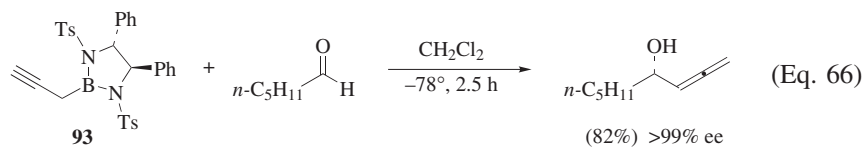
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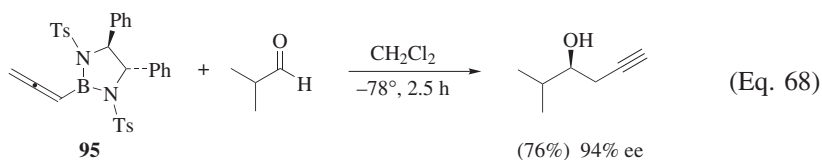
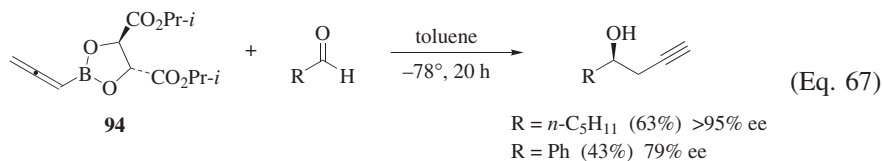
(Eq. 65)

**Enantioselective Additions with Chiral Propargyl Reagents**

As demonstrated by the example in Eq. 66, propargylboron reagent **93** affords allenic alcohols in very high enantioselectivities.<sup>153</sup> Although this reagent has not been widely employed, the selectivity it provides with all classes of aldehydes is truly remarkable (>99% ee for model aliphatic, unsaturated, and aromatic aldehydes).

**Enantioselective Additions with Chiral Allenyl Reagents**

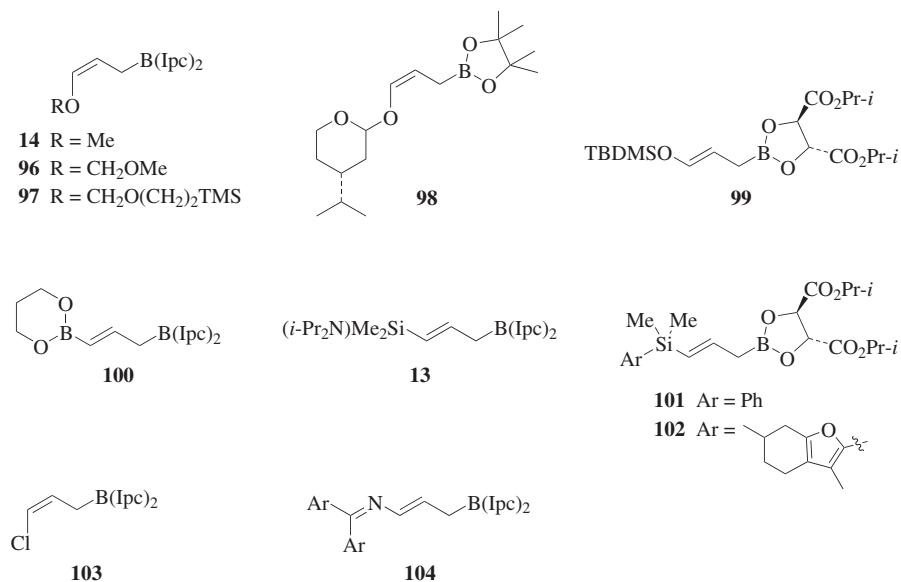
Although they were among the first examples to illustrate the use of tartrate boronate auxiliaries, allenylboronate reagents are seldom employed. The tartrate-derived reagent **94** provides homopropargylic alcohols in high enantioselectivity from aliphatic aldehydes (Eq. 67).<sup>123</sup> This reagent provides optimal selectivity when substituted with the bulkier diisopropyl tartrate ester, and even in this situation aromatic aldehydes react sluggishly and with low stereoselectivity. The efficacy and scope of bis(sulfonamide) allenylboron reagent **95** has been investigated in detail.<sup>153</sup> As exemplified in Eq. 68, this reagent adds to most types of aldehydes with high enantioselectivities. A recently described chiral dialkylallenylborane provides comparable selectivities.<sup>144</sup>



### Enantioselective Additions with Chiral 3-Heterosubstituted Reagents

A large number of chiral 3-substituted allylic borane and boronate reagents have been described (Fig. 7). To be effective, these reagents must be prepared in geometrically pure form. Like the corresponding crotyl reagents, additions to aldehydes are diastereospecific as the anti/syn configuration of the resulting homoallylic alcohol products is dependent upon the geometry of the original allyl unit.

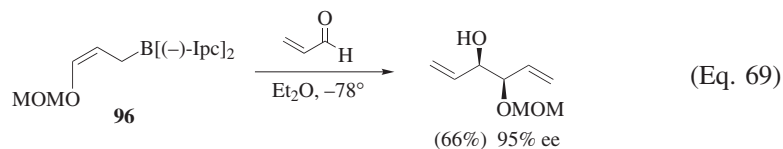
**Preparation of 1,2-Diols.** The most direct method of preparation of 1,2 diols from allylic boron reagents involves the use of 3-alkoxy-substituted reagents. Although these reagents are prepared easily from the corresponding lithiated 3-alkoxypropene, only the *Z*-isomers are prepared directly in this fashion as a result of the preference for a *cis*-configuration in the lithium-chelated allylic carbanion (see Eq. 18, section "Preparation of Allylic Boron Reagents"). The resulting *Z*-configured reagents provide the syn-1,2-diol products in excellent diastereoselectivity in agreement with the usual cyclic chairlike transition structure. These reagents are very effective in double diastereoselection with  $\alpha$ -substituted aldehydes.<sup>11</sup> Several chiral analogues such as **14**, **96**, **97**,<sup>48,154</sup> and **98**,<sup>155</sup> are sufficiently effective for use in absolute stereocontrol (Fig. 7). In particular, the bis(isopinocampheyl)-derived 3-alkoxyallylboranes such as **96** react highly enantioselectively with a wide range of aldehyde substrates, including the notoriously troublesome acrolein (Eq. 69).<sup>156</sup>



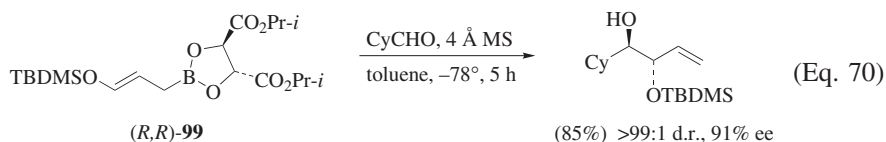
**Figure 7.** Chiral 3-substituted allylic boron reagents.

## ALLYLBORATION OF CARBONYL COMPOUNDS

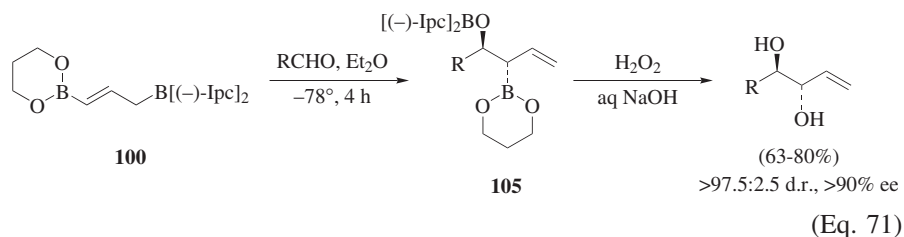
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To access anti-1,2-diols, indirect methods are required for the preparation of geometrically pure, chiral E-3-alkoxy reagents. To this end, the isomerization of alkenylboronic esters described above (Eq. 41), provides a reliable route to tartrate-derived E-3-siloxy allylboronate **99** (Fig. 7). The latter shows variable enantioselectivities in additions to aldehydes, with cyclohexanecarboxaldehyde affording the highest selectivity (Eq. 70).<sup>88</sup>



Alternatively, masked hydroxy groups may be used as the  $\gamma$ -substituent. For example, following allylation with the E-3-boronyl reagent **100** (Fig. 7), the second hydroxy group is generated upon an oxidative work-up that transforms the alkylboronate unit of intermediate **105** with full retention of configuration (Eq. 71).<sup>157</sup> Likewise, provided it can be protodesilylated in the presence of an allylsilane moiety, a suitable silyl substituent can be subjected to stereospecific Tamao–Fleming oxidative conditions to afford the desired anti 1,2-diol. The requisite E-3-silyl-substituted reagents are conveniently prepared by trapping of the corresponding allylic carbanions<sup>154</sup> with a borate ester (Eq. 17).<sup>38–40,45,46</sup> Both borane and boronate reagents, exemplified by the respective pinene- and tartrate-derived reagents **13**<sup>45</sup> and **102**<sup>158</sup> (Fig. 7, Eqs. 72 and 73), afford diol products in moderate yields but with high enantioselectivities after a stereospecific Tamao–Fleming protodesilylation/oxidation of the  $\beta$ -hydroxy silyl intermediates (e.g., **106**). As with other substituted reagents, however, only the bis(isopinocampheyl) allylic boranes **100** and **13** lead to practical levels of enantioselectivity suitable for absolute stereocontrol. Reagent **100**, in particular, has found useful application in the synthesis of complex natural products (see section on “Applications to the Synthesis of Natural Products”).

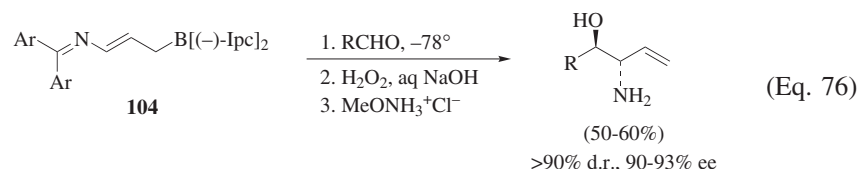
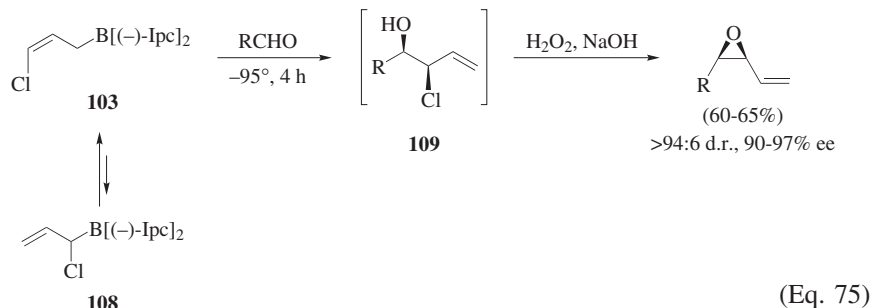




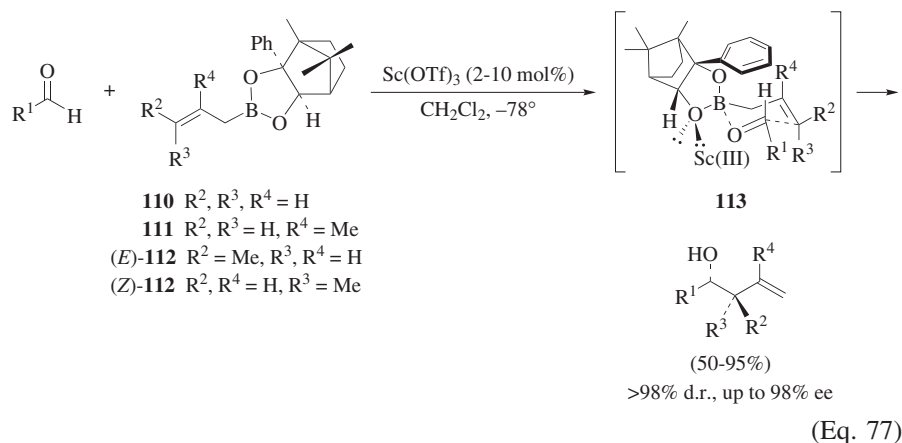


## ALLYLBORATION OF CARBONYL COMPOUNDS

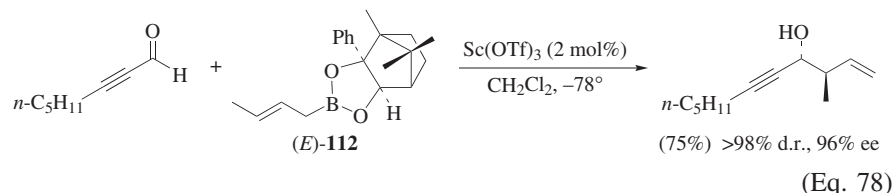
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**Lewis and Brønsted Acid Catalyzed Enantioselective Additions**

The recent advent of the Lewis acid catalyzed allylboration reactions opened new doors for enantioselective allylborations and motivated the reexamination of a number of chiral auxiliary systems. In this perspective, reagents **110–112**<sup>121</sup> are extremely enantioselective at  $-78^\circ$  in the presence of  $\text{Sc}(\text{OTf})_3$  as catalyst (Eq. 77).<sup>27,28</sup> These hydrolytically stable reagents can be conveniently purified by silica gel chromatography. Consistently high levels of absolute stereoselection ( $>95\%$  ee) are observed with a broad range of aldehydes for the unsubstituted allyl reagent **110** as well as the methallyl reagent **111**, and both crotyl reagents (*E*)- and (*Z*)-**112**. Although this method requires a stoichiometric amount of the chiral diol auxiliary, this diol is readily recovered after the hydrolytic work-up. Aromatic aldehydes and, unless they are very hindered, aliphatic aldehydes (including functionalized ones) react efficiently to give good to high yields of products. Although  $\alpha,\beta$ -unsaturated aldehydes react poorly, acetylenic aldehydes are very competent substrates even with the crotyl reagents **112** (Eq. 78).<sup>28</sup>

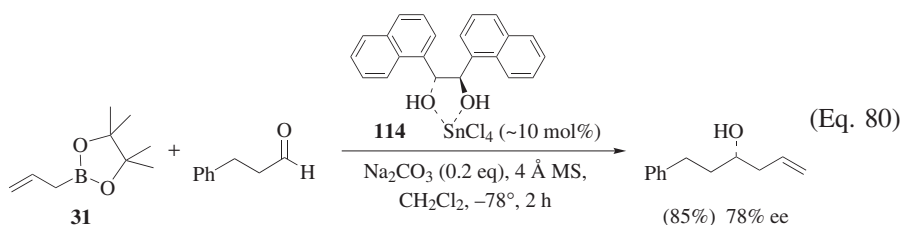
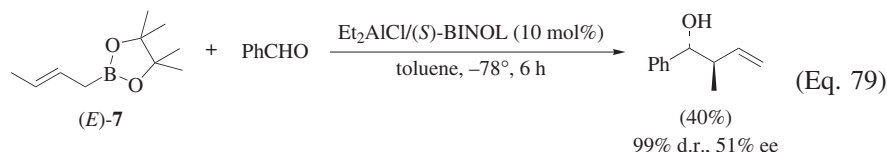


**110**  $\text{R}^2, \text{R}^3, \text{R}^4 = \text{H}$   
**111**  $\text{R}^2, \text{R}^3 = \text{H}, \text{R}^4 = \text{Me}$   
*(E)*-**112**  $\text{R}^2 = \text{Me}, \text{R}^3, \text{R}^4 = \text{H}$   
*(Z)*-**112**  $\text{R}^2, \text{R}^4 = \text{H}, \text{R}^3 = \text{Me}$



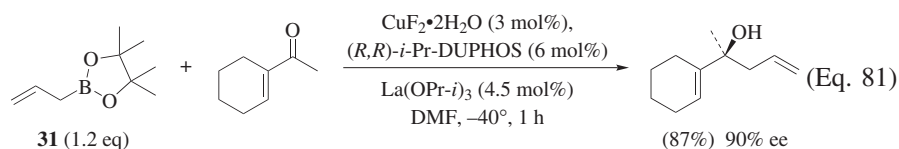
On the basis of mechanistic studies,<sup>29</sup> a closed bimolecular transition structure **113** involving activation of the boronate unit via coordination of the scandium to one of the dioxaborolane oxygen atoms has been proposed (Eq. 77). A possible interpretation to explain the enantioselectivity of this allylation system originates from the accepted stereoreinduction model for the non-catalyzed reaction arising from a  $\pi_{\text{phenyl}}-\pi^*_{\text{C=O}}$  attraction.<sup>121,161</sup> It has been proposed that the Sc(III) ion coordinates to the least hindered lone pair (syn to H) of the pseudo-equatorial oxygen, thereby suppressing  $n_{\text{O}}-p_{\text{B}}$  conjugation and maximizing boron-carbonyl bonding.<sup>29</sup>

The real promise of this catalytic reaction is the eventual development of an efficient enantioselective allylboration catalyzed by chiral Lewis acids. A stereoselective reaction using a substoichiometric amount of a chiral director has been reported, but only modest levels of stereo-induction were achieved with an aluminum–BINOL catalyst system (Eq. 79).<sup>25</sup> Recently, a chiral Brønsted acid catalyzed system has been devised based on a diol–tin(IV) complex (Eq. 80).<sup>162</sup> In this approach, aliphatic aldehydes provide enantioselectivities (up to 80% ee) higher than those of aromatic aldehydes when using the optimal complex **114**.<sup>163</sup> Although the levels of absolute stereoselectivity of this method remain too low for practical uses, promising applications are possible in double diastereoselection (see section on “Double Diastereoselection”).



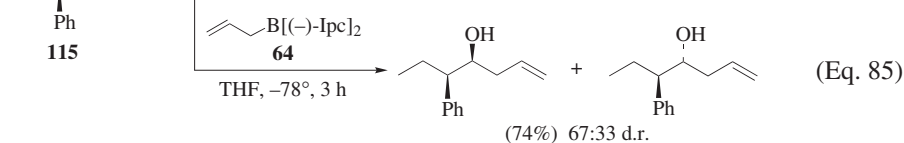
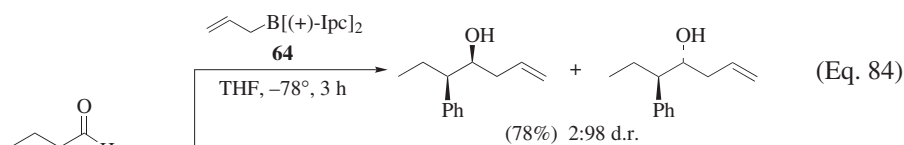
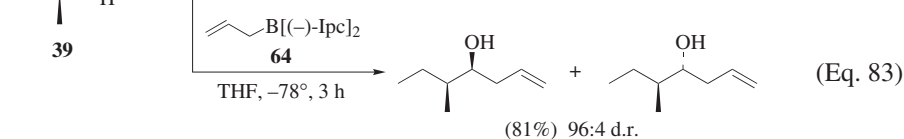
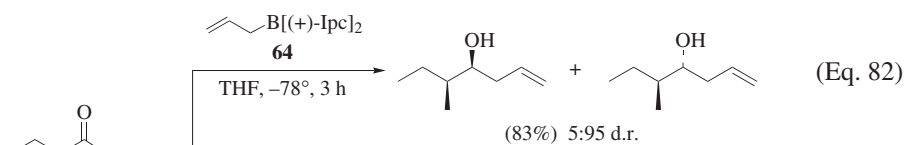
A copper-catalyzed reaction using a chiral diphosphine ligand, DuPHOS, with an added lanthanide salt, provides good levels of enantioselectivity (67–91% ee) in additions of the simple allylboronate **31** to both aromatic and aliphatic ketones that present a large difference of steric bulk on the two sides of the carbonyl group.<sup>164</sup> One such example is shown in Eq. 81. On the basis of <sup>11</sup>B NMR experiments and on the lack of diastereoselectivity in crotylation reactions, the

mechanism of this allylation is believed to involve transmetalation of the boron to an allylcopper species.

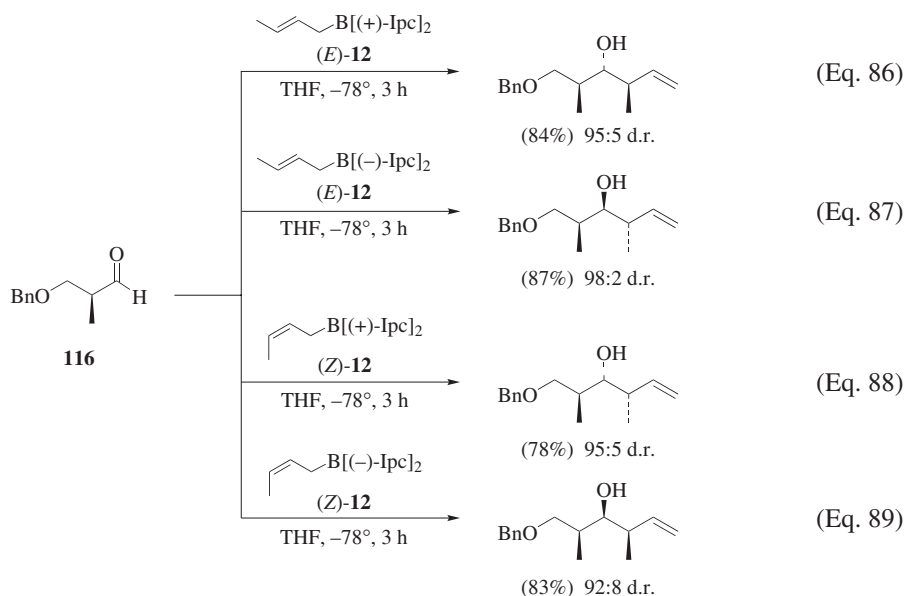


### Double Diastereoselection with Chiral Carbonyl Substrates

Double diastereoselective additions between chiral allylic boron reagents and enantiopure chiral carbonyl compounds can be highly advantageous because the resulting diastereomers are separable (in theory, though not always in practice).<sup>165</sup> The most desirable situation is where there is very high reagent control to override the intrinsic effect of the stereogenic center of the aldehyde or ketone on the diastereofacial selectivity. The success of this approach depends heavily on the structure of the particular chiral aldehyde used and the nature of its substituents, including protecting groups. Fortunately, the directing effect of the bis(isopinocampheyl) allylic boranes is extremely powerful, giving rise to high reagent control in double diastereoselective additions. As demonstrated with the simple allylations of chiral,  $\alpha$ -substituted aldehydes **39** and **115**, reagent-controlled additions are very effective (Eqs. 82–85).<sup>166</sup> Both examples involving aldehyde **39** (Eqs. 82 and 83) are very favorable in comparison to the modest selectivity of the achiral pinacol allylboronates (compare to Scheme 2). Reagent control is observed even in mismatched situations such as the difficult case of  $\alpha$ -phenyl aldehyde **115** (Eq. 85).<sup>166,167</sup>



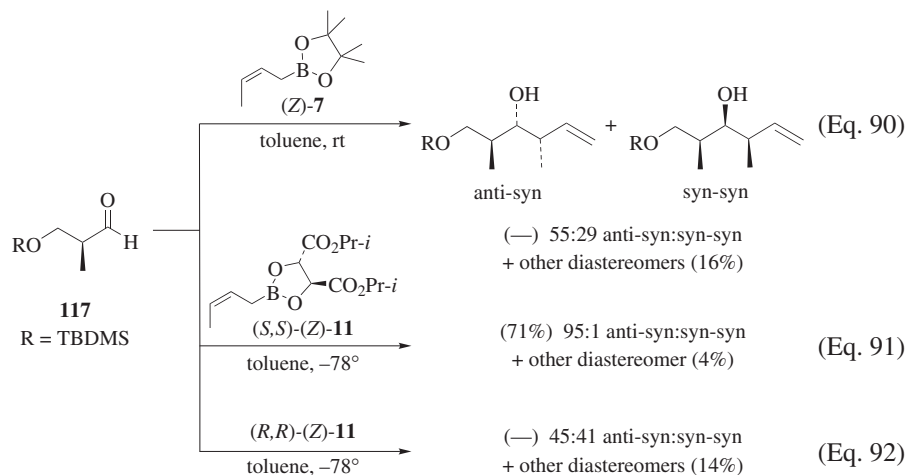
By using a judicious combination of the appropriate double bond geometry and pinene enantiomer, the corresponding crotylboranes present a very nice solution to the problem of full stereocontrol of acyclic dipropionate units when combined with chiral  $\alpha$ -methyl  $\beta$ -alkoxy aldehydes such as **116** (Eqs. 86–89).<sup>167</sup> In this situation as well, reagent-controlled additions are very selective even in mismatched cases, affording stereotriads in high yields and >90% d.r. Simple  $\alpha$ -alkoxy aldehydes provide comparable levels of selectivities but exceptions have been reported with stereogenic  $\beta$ -alkoxy centers and more complex aldehydes.<sup>168</sup>



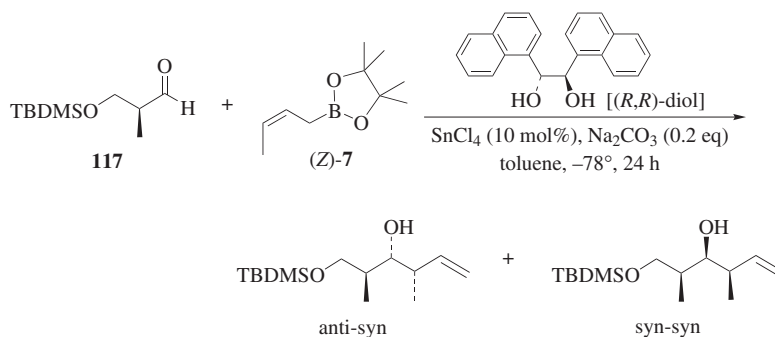
In comparison, additions of chiral allylic boronates such as tartrate-based reagents tend to be less selective in double diastereoselective additions to  $\alpha$ -methyl aldehydes, especially in mismatched cases (Eqs. 90–92).<sup>169</sup> Nonetheless, these reagents are advantageous as they can increase, even in the mismatched manifold, the intrinsic levels of selectivities dictated by the chiral aldehyde substrate, and the resulting diastereomeric products are usually separable by chromatography. When used with  $\alpha$ -alkoxy aldehydes such as glyceraldehyde acetone (**51**, Scheme 4), tartrate-based reagents are highly effective.<sup>126,170</sup> Several applications of double diastereoselective additions of tartrate-based allylic boronate reagents have been described in the course of the synthesis of complex natural products (see section on “Applications to the Synthesis of Natural Products”).

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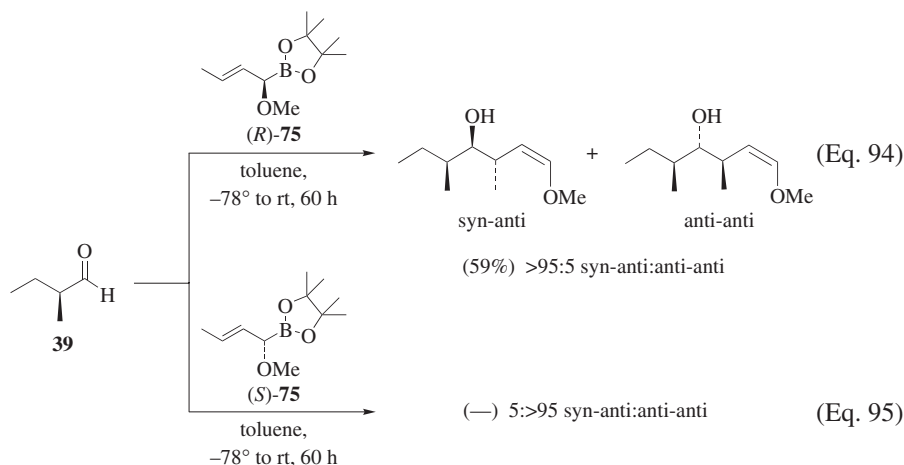
The use of chiral Brønsted acids is illustrated in Eq. 93 as a method for catalyst-controlled double diastereoselective additions of pinacol allylic boronates.<sup>163</sup> Aside from circumventing the need for a chiral boronate, these additions can lead to very good amplification of facial stereoselectivity. For example, compared to both non-catalyzed (room temperature, Eq. 90) and  $\text{SnCl}_4$ -catalyzed variants, the use of the “matched” diol- $\text{SnCl}_4$  enantiomer at a low temperature leads to a significant improvement in the proportion of the desired anti-syn diastereomer in the crotylation of aldehyde **117** with pinacol reagent **(Z)-7** (Eq. 93). Moreover, unlike reagent **(Z)-11** (Eq. 91) none of the other diastereomers arising from *Z*- to *E*-isomerization is observed.



Conditions	anti-syn:syn-syn	
$\text{SnCl}_4$ alone	(81%)	66:34
$\text{SnCl}_4$ , <b>(R,R)</b> -diol (11 mol%)	(77%)	95:5
$\text{SnCl}_4$ , <b>(S,S)</b> -diol (11 mol%)	(50%)	68:32

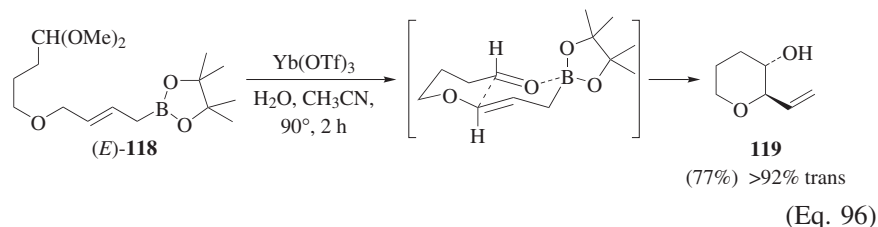
(Eq. 93)

The chiral  $\alpha$ -substituted reagents **21**, **23**, **28**, and **75** (Fig. 6) are very powerful controllers of double diastereoselective additions and perform admirably well even in mismatched situations.<sup>63–66,68,83,147,149</sup> Reagent **75** tends to be more selective than the  $\alpha$ -chloro analog **28**, and the high stereocontrol displayed by reagent **75** in the examples of Eqs. 94 and 95 can be explained using a transition structure model similar to that of Scheme 8.<sup>68,147</sup> Remarkably, even the mismatched pair (Eq. 95) affords outstanding selectivity. Several other examples have been described, including applications to the synthesis of complex polypropionate natural products (see section on “Applications to the Synthesis of Natural Products”: Scheme 19).



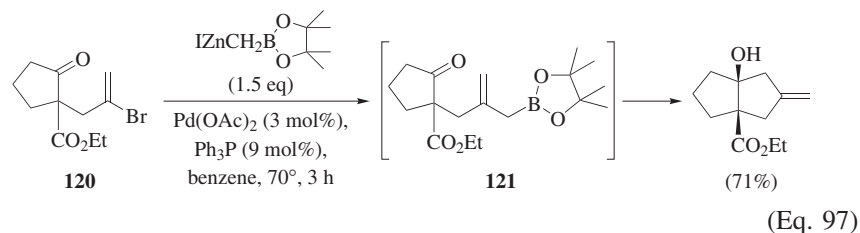
### Intramolecular Reactions

Intramolecular additions generally follow the same trends of stereoselectivity as observed in the bimolecular reactions.<sup>80,82,171,172</sup> For example, allylic boronates (*E*)- and (*Z*)-**118** provide the respective *trans*- and *cis*-fused products of intramolecular allylation.<sup>173</sup> As shown with allylboronate (*E*)-**118**, a  $\text{Yb}(\text{OTf})_3$ -catalyzed hydrolysis of the acetal triggers the intramolecular allylboration and leads to isolation of the *trans*-fused product **119** in agreement with the usual cyclic transition structure (Eq. 96).



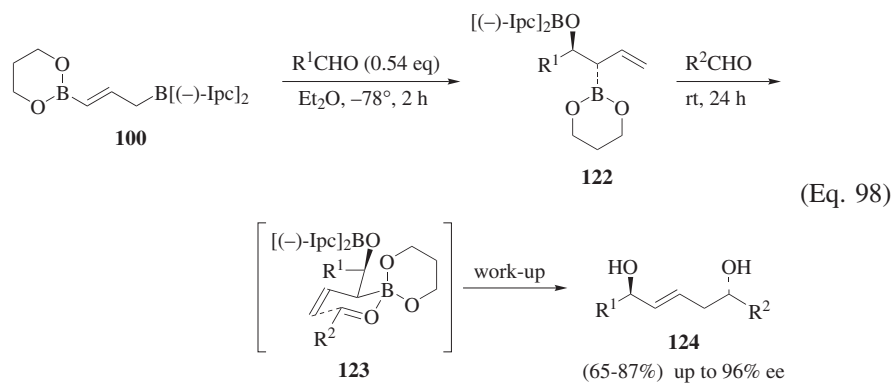
Intramolecular allylations can also provide five-membered rings with ease, and the entropic benefits facilitate additions to ketone substrates. For example, the allylic boronate **121**, formed by a Negishi-type coupling between alkenyl

bromide **120** and a methylzinc dialkoxyboron reagent, cyclizes in situ into a cyclopentanone to provide a [3.3.0] bicyclic alcohol product (Eq. 97).<sup>174</sup> This example constitutes a formal 5-exo-trig cyclization, and seven-membered ring systems can also be elaborated using a similar approach.<sup>79,80,174</sup>



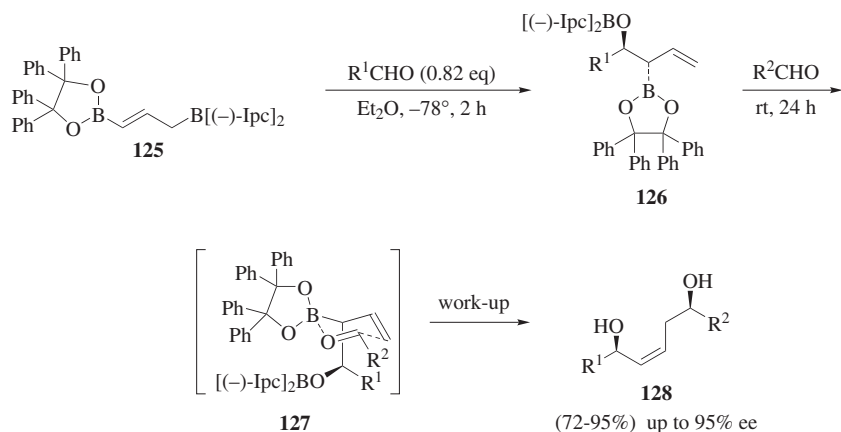
### Reagents for Multiple Additions

A tandem double-allylation strategy, based on the E-3-boronallylborane reagent **100**,<sup>157</sup> has been optimized for the synthesis of 1,5-diol products from two different aldehyde substrates.<sup>175</sup> Specifically, reagent **100** undergoes allylation with a limiting amount of an aldehyde, R<sup>1</sup>CHO, and the resulting  $\alpha$ -substituted allylboronate **122** can then add to a second added aldehyde (R<sup>2</sup>CHO) (Eq. 98). The first allylation with the bis(isopinocampheyl)allylic borane unit is highly enantioselective and the resulting configuration of **122** controls the fate of the second allylation. Thus, from intermediate **122**, transition structure **123** featuring a pseudo-equatorial  $\alpha$ -substituent explains the stereocontrolled formation of 1,5-diol **124**. The lower reactivity of **122** compared to **100**, as well as a tight control of reagent stoichiometry, helps to minimize the formation of the double allylation product of the first aldehyde (R<sup>1</sup>CHO).

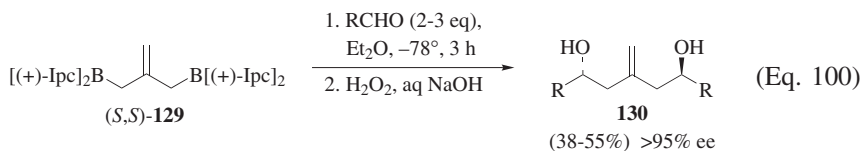


With the analogous reagent **125**, however, the corresponding allylboronate intermediate **126** is thought to favor a transition structure **127** where the  $\alpha$ -substituent is positioned in a pseudo-axial orientation in order to escape non-bonding interactions with the bulky tetraphenyl dioxaborolane (Eq. 99). This way, a Z-configured allylic alcohol unit of opposite configuration is obtained in diol product **128**. This type of steric control with chiral  $\alpha$ -substituted allylboronates

had been demonstrated before (see section on  $\alpha$ -substituted reagents). The usefulness of this powerful tandem allylation/allylation strategy is demonstrated by the preparation of several examples of both types of 1,5-diols **124** and **128**, and by a number of successful applications to the synthesis of complex natural products (see section on “Applications to the Synthesis of Natural Products”).



A double Brown-type allylation reagent, **129**, gives  $C_2$ -symmetric 3-methylenepentane-1,5-diols **130** in modest yields but high enantioselectivities with both aliphatic and aromatic aldehydes (Eq. 100).<sup>176</sup> This reagent can be prepared by double deprotonation of 2-methylpropene followed by condensation with either antipodes of  $(\text{Ipc})_2\text{BCl}$ . For example,  $(S,S)$ -**129** originates from  $[(+)\text{-Ipc}]_2\text{BCl}$ . Double allylboration of an excess of aldehyde with  $(S,S)$ -**129** affords  $C_2$ -symmetric diol product **130** accompanied with approximately 5–15% proportion of “monoallylboration” alcohol after the oxidative work-up.



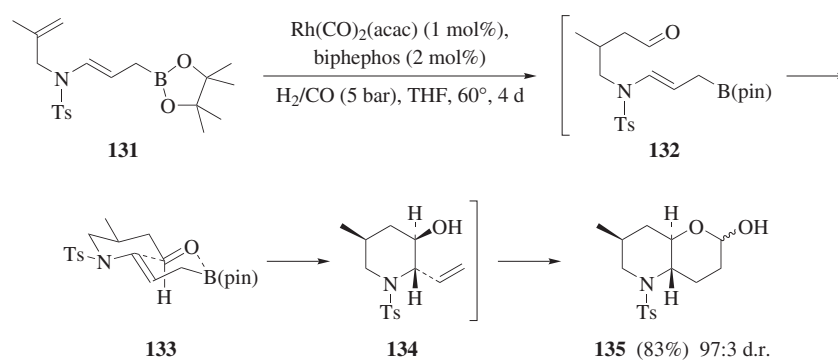
### Tandem Reactions

Many of the recent advances in synthetic applications of allylic boron reagents have focused on the use of these reagents as key components of tandem reactions and “one-pot” sequential processes, including multicomponent reactions. The following examples briefly illustrate the range of possibilities. Most cases involve masked allylboration as substrates, and the tandem process is usually terminated by the allylboration step.

**Intramolecular Allylboration.** In one rare but impressive example involving a masked aldehyde, a domino hydroformylation/allylboration/hydroformylation reaction cascade has been designed to generate bicyclic annulated

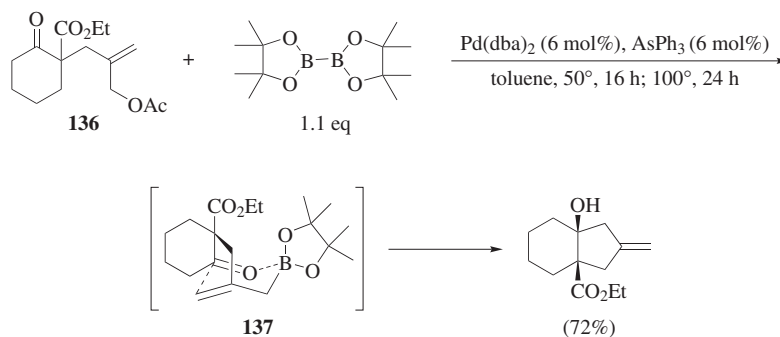


tetrahydropyrans<sup>177</sup> and nitrogen heterocycles.<sup>178,179</sup> For example, treatment of allylboronate **131** under hydroformylation conditions first leads to aldehyde intermediate **132** (Eq. 101). With a poised allylic boronate, formation of **132** triggers the key intramolecular allylation to give intermediate **134**.<sup>179</sup> This intermediate then undergoes a second hydroformylation, followed by a final cyclization to give the bicyclic lactol product **135** in 83% yield as a 1 : 1 mixture of anomers. The final products are obtained in this one-pot process with a very high diastereoselectivity (97 : 3 ratio) as a result of simple diastereocontrol in the allylboration step involving the putative transition structure **133**. Similar approaches are employed to access pyran derivatives.<sup>177</sup>



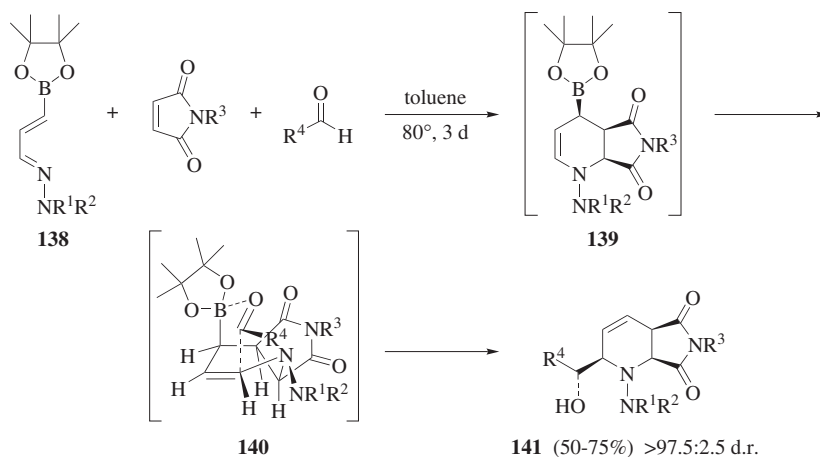
(Eq. 101)

A masked allylic boron unit can be revealed through a transition-metal-catalyzed borylation reaction. For example, a one-pot borylation/allylation tandem process based on the borylation of various ketone-containing allylic acetates has been developed.<sup>180</sup> The intramolecular allylboration step is very slow in DMSO, which is the usual solvent for these borylations of allylic acetates (see Eq. 33). The use of a non-coordinating solvent like toluene is more suitable for the overall process provided that an arsine or phosphine ligand is added to stabilize the active Pd(0) species during the borylation reaction. With cyclic ketones such as **136**, the intramolecular allylation provides cis-fused bicyclic products in agreement with the involvement of the usual chairlike transition structure, **137** (Eq. 102).

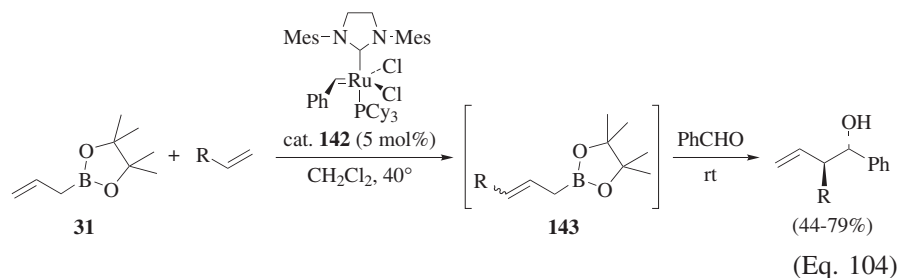


(Eq. 102)

**Intermolecular Allylboration.** A tandem aza[4+2] cycloaddition/allylboration three-component reaction<sup>181,182</sup> has been designed based on the precedented carbocyclic [4+2] cycloaddition/allylboration<sup>89</sup> and a subsequent one-pot variant.<sup>183</sup> Thus, the thermal reaction between hydrazonobutadienes **138**, *N*-substituted maleimides, and aldehydes provides polysubstituted  $\alpha$ -hydroxy-alkylpiperidines **141** via the cyclic allylboronate intermediate **139** and the proposed chairlike transition structure **140** (Eq. 103).<sup>181</sup> Monoactivated dienophiles like acrylates fail to react with heterodienes **138** but the scope of aldehydes is very broad; both aliphatic and aromatic aldehydes are suitable, including electron-rich ones.<sup>182</sup> An inverse electron-demand variant to access the corresponding dihydropyran derivatives via the intermediacy of enantiomerically enriched pyranlyl allylic boronate **76** has been subsequently developed (see Eq. 64).<sup>150–152</sup>




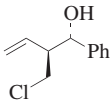
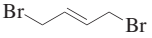
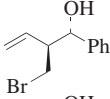

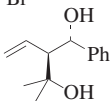

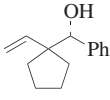

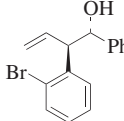
As described above in Eq. 43, simple allylboronates can be transformed into more elaborated ones using olefin cross-metathesis.<sup>184</sup> Treatment of pinacol allylboronate **31** with a variety of olefin partners in the presence of Grubbs' second-generation catalyst **142** smoothly leads to formation of 3-substituted allylboronates **143** as cross-metathesis products (Eq. 104). Unfortunately, these new allylic boronates are formed as mixtures of geometrical isomers with modest *E/Z* selectivity. They are not isolated but rather are treated directly with benzaldehyde to give the corresponding homoallylic alcohol products in good yields (Table A).



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Table A. Functionalized homoallylic alcohols from olefin cross metathesis and subsequent allylboration reactions with benzaldehyde

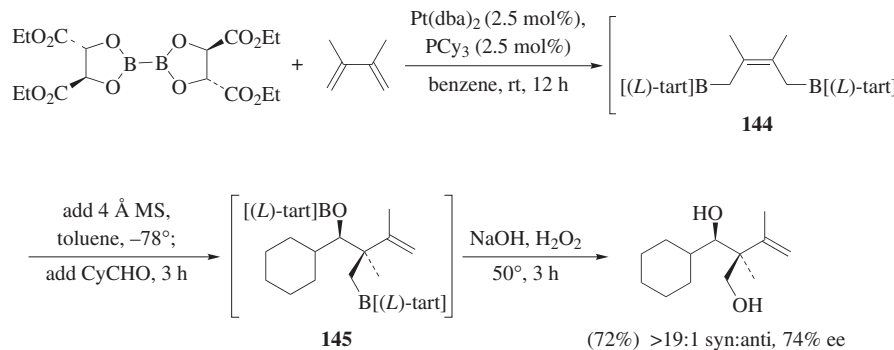
Entry	Cross Partner	Product	Yield	d.r.
1			(73%)	3.8:1
2			(78%)	4.9:1
3			(58%)	>20:1
4			(66%)	—
5			(60%)	>20:1

The main advantage of this one-pot sequence is that it is exceptionally tolerant of sensitive functional groups. Entry 3 (Table A) shows an example with an unprotected alcohol, and entries 1, 2, and 5 all show examples with halogenated groups that are delivered directly from an allylboronate intermediate. These groups, which would not survive the strongly basic conditions or the active metals used in many other preparative methods, are carried through this procedure without incident. Entry 4 is also noteworthy because it shows that quaternary carbon centers can be made with this tandem process. A serious limitation of this approach, however, is that the diastereoselectivity seen in the formation of allylation products is quite variable as a consequence of the low geometric (*E/Z*) selectivity in the cross-metathesis. Olefin partners with large allylic substituents (entries 3–5) react to give exclusively the anti product shown in Table A. Unfortunately, olefins with smaller substituents (entries 1 and 2) show a much lower preference. Furthermore, both *E*- and *Z*-olefins afford the same stereoisomer (compare entries 1 and 2).

A mild one-pot procedure based on a platinum-catalyzed diborylation of 1,3-butadienes (see Eq. 30) gives doubly allylic boronate **144**, which adds to an aldehyde to form a quaternary carbon center in the intermediate **145** (Eq. 105).<sup>185</sup> The use of a tartrate auxiliary in this process leads to good levels of enantioselectivity in the final diol product, which is obtained after oxidation of the primary alkylboronate intermediate. Although examples of aliphatic, aromatic, and unsaturated aldehydes have been described, enantioselectivities vary widely (33 to 74% ee), and are good only for aliphatic aldehydes. An intramolecular variant of this interesting tandem reaction is also known.<sup>186</sup>

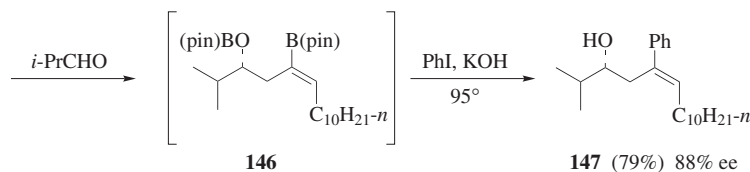
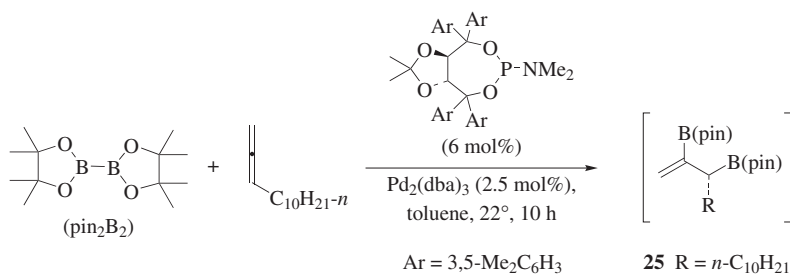
52

## ALLYLBORATION OF CARBONYL COMPOUNDS



(Eq. 105)

The diboration of allenes can also be employed in a similar tandem process. By taking advantage of an improved, more enantioselective variant for the preparation of allylboronates of type **25** (Eq. 32), a one-pot sequence involving allene diboration, aldehyde allylation, and Suzuki cross-coupling has been developed (Eq. 106). It is noteworthy that no change of solvent, nor any addition of palladium catalyst is needed in the last stage involving the cross-coupling of alkenylboronate intermediate **146** to give final product **147**.<sup>187</sup>



(Eq. 106)

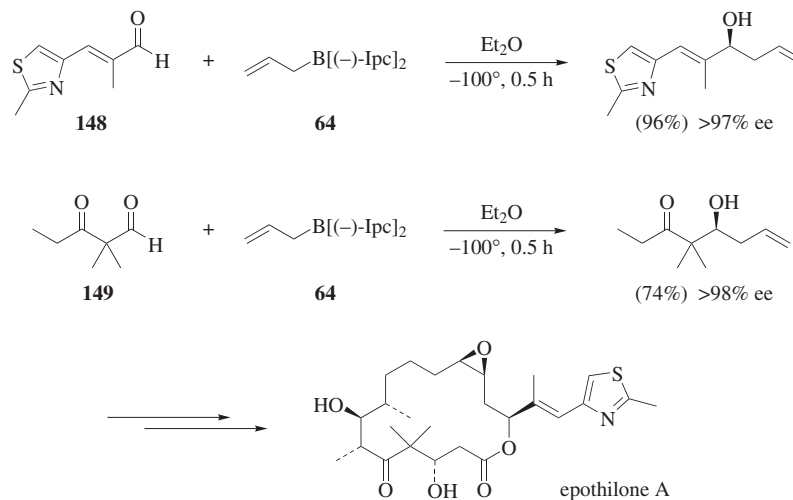
## APPLICATIONS TO THE SYNTHESIS OF NATURAL PRODUCTS

## Enantioselective Additions

The bis(isopinocampheyl)borane reagents described in the sections on enantioselective additions have found extensive use in the total synthesis of complex, bioactive natural products. A synthesis of the potent anticancer agent epothilone

## ALLYLBORATION OF CARBONYL COMPOUNDS

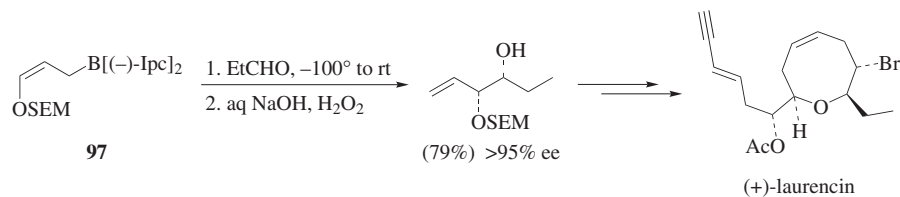
53

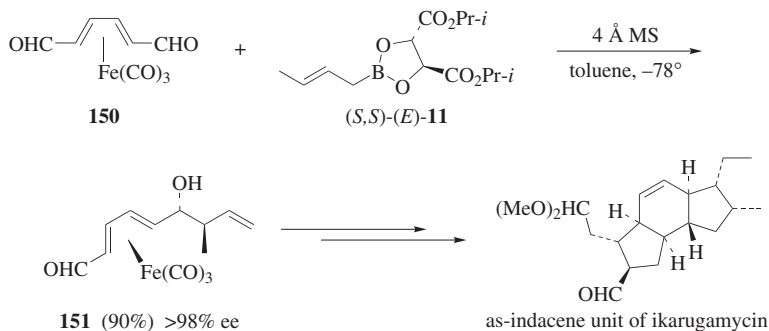


exemplifies particularly well the suitability of the Brown allylation with highly functionalized and hindered aldehydes (Scheme 10). Thus, using the salt-free, low-temperature conditions, reagent **64** is added to unsaturated heterocyclic aldehyde **148** to afford the desired secondary homoallylic alcohol in very high yield and excellent enantioselectivity. The synthesis also featured another Brown allylation on the hindered  $\alpha$ -dimethylated  $\beta$ -keto aldehyde **149**, thus providing two of the key fragments necessary to assemble the structure of the anticancer agents epothilones.<sup>188</sup>

The applicability of the bis(isopinocampheyl) reagents is not limited to simple allylations and crotylations. For example, reagent **97** affords syn vicinal diols in very high enantioselectivity (Scheme 11).<sup>189</sup> Compared with reagents **14** and **96** (Fig. 7), reagent **97** possesses the added advantage of yielding the alcohol product with an easily removable (2-trimethylsilyloxy)methyl (SEM) protecting group. In this example, the resulting monoprotected diol has been subsequently converted into the eight-membered ring ether laurencin.

With only a small number of substrate types are the tartrate-based allylic boronate reagents enantioselective enough for applications in the control of





Scheme 12

absolute stereochemistry. One such example involves iron dienyl complexes such as the dialdehyde **150**, which reacts with crotylboronate reagent (*E*)-**11** to give the anti-propionate product in the form of complex **151** in over 98% ee (Scheme 12). After a few transformations and decomplexation, the resulting diene is further elaborated into a triene precursor that undergoes an intramolecular Diels–Alder reaction leading to the tricyclic core of ikarugamycin.<sup>190</sup>

The Corey allylation system based on a chiral bis(sulfonamide) auxiliary was put to use with success in a number of synthetic efforts, including the total synthesis of the anticancer agent leucascandrolide (Scheme 13).<sup>191</sup> Chiral reagent **152** is added to an achiral aldehyde, 3-(*p*-methoxybenzyloxy)propanal, affording intermediate **153** in high stereoselectivity. The latter is transformed into a pyranaldehyde, which is subjected to a second allylation (this time, a doubly diastereoselective addition) en route to the completion of leucascandrolide.

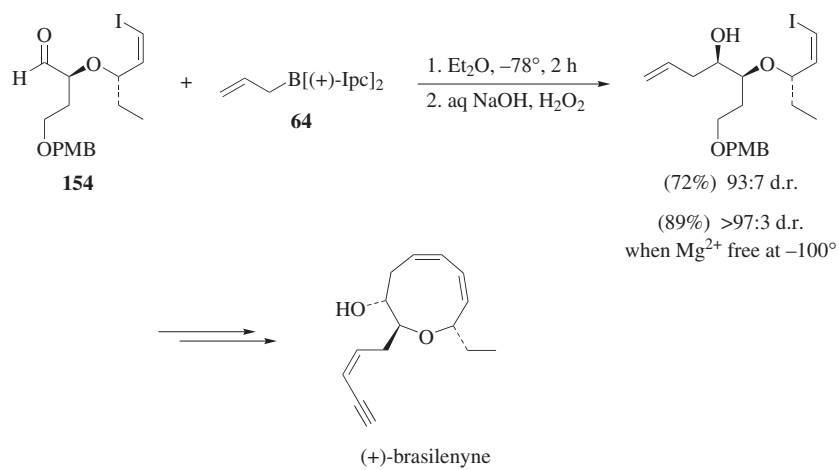
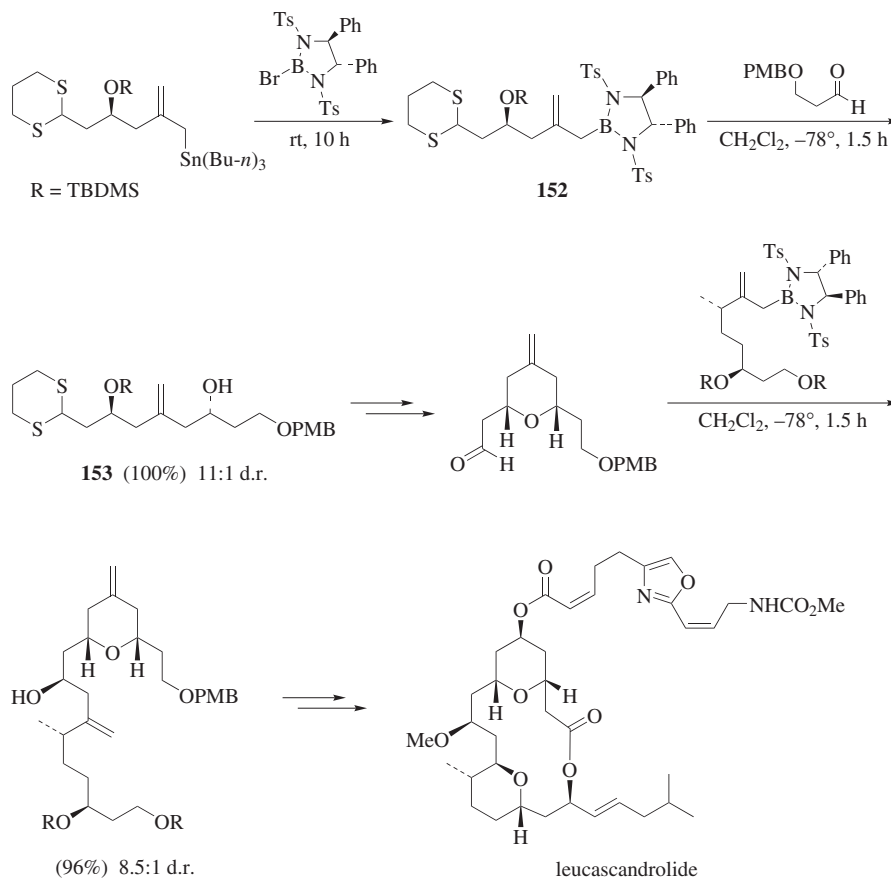
### Double Diastereoselection

The powerful directing effect of bis(isopinocampheyl) allylic boranes has been put to great use in the context of several applications of double diastereoselective allylations in the total synthesis of natural products. As discussed in a previous section, the Brown allylation can be exploited to overcome the stereodirecting effect of chiral  $\alpha$ -stereogenic aldehydes, including  $\alpha$ -alkoxy substituted ones. Thus, the simple allylation of aldehyde **154** provides as major product the desired diastereomer needed towards a total synthesis of brasilenyne (Scheme 14).<sup>192</sup> The yield and stereoselectivity is even increased to over 97:3 under the low-temperature, magnesium-free conditions described before.<sup>139</sup>

A synthesis of the naturally occurring phosphatase inhibitor calyculin C showcased several other interesting examples of doubly diastereoselective additions involving the Brown reagents.<sup>168</sup> The addition of tetrasubstituted reagent **155** to 2,3-*O*-isopropylidene-D-glyceraldehyde (**51**) provides intermediate **156** in very high selectivity despite a substrate-reagent mismatch, which is overruled by the borane reagent (Scheme 15). The latter is transformed in several steps into aldehyde **157**, and a crotylboration of this  $\beta$ -alkoxy aldehyde provided a very high diastereoselectivity for the desired anti-propanoate unit. With the subsequent aldehyde intermediate **158**, a third example involves a difficult mismatched case that

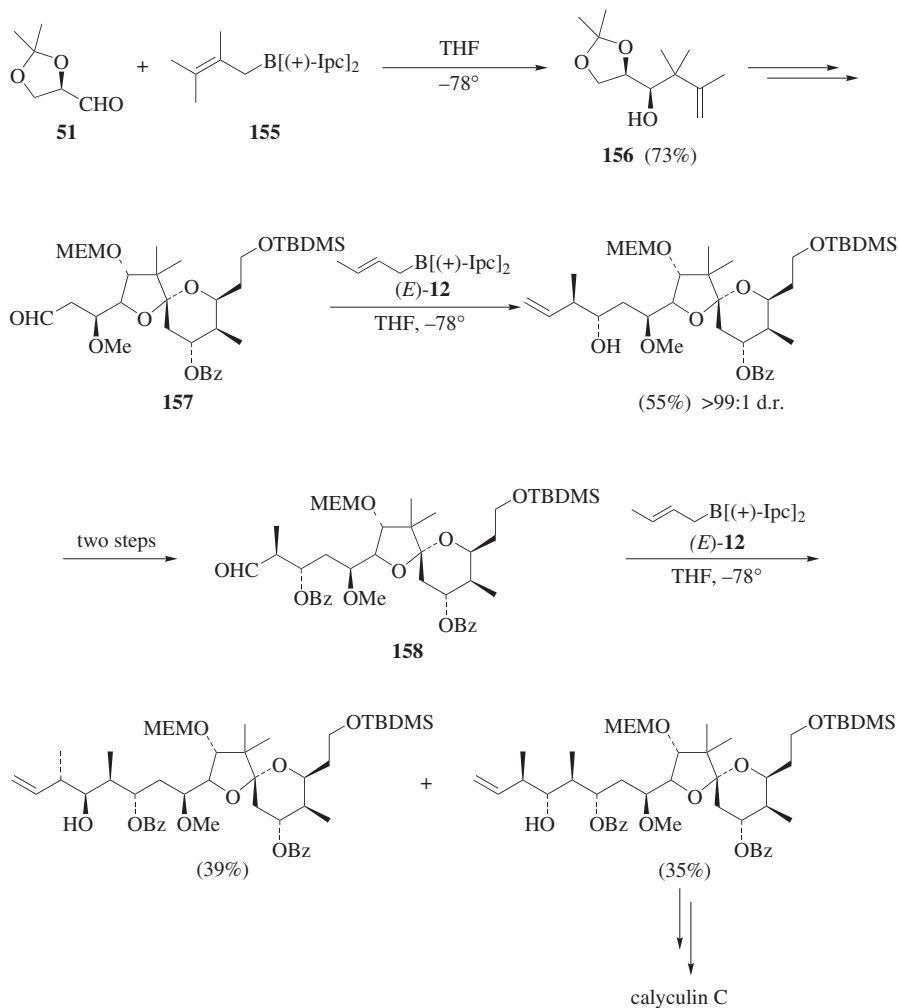
## ALLYLBORATION OF CARBONYL COMPOUNDS

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## ALLYLBORATION OF CARBONYL COMPOUNDS



Scheme 15

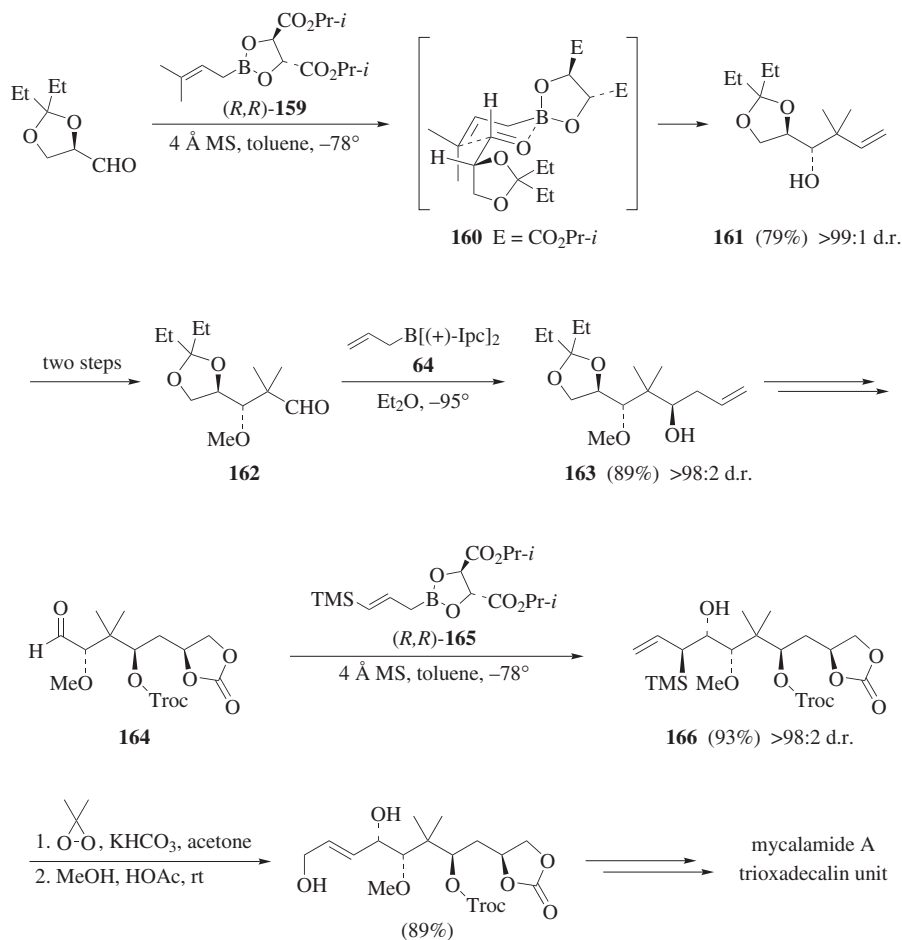
provides an unusually low level of diastereoselectivity (almost 1 : 1), indicating that high selectivity is never guaranteed even with the bis(isopinocampheyl) allylic boranes. In this example of an  $\alpha$ -methyl- $\beta$ -alkoxy aldehyde, reagent control by crotylborane (*E*-**12**) is overruled by the substrate and it was found that the nature of the protecting group on the  $\beta$ -hydroxy substituent is crucial, with the most favorable group a benzoyl. The minor diastereomer of this mismatched double diastereoselective addition possesses the requisite configuration for completing the synthesis of calyculin C.

Several allylic boron reagents have been recently employed in a series of doubly diastereoselective additions toward a synthesis of mycalamide.<sup>193,194</sup> Thus,



## ALLYLBORATION OF CARBONYL COMPOUNDS

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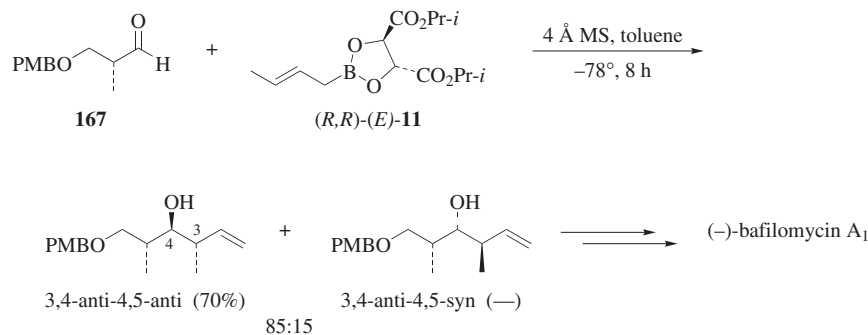
Scheme 16

the addition of tartrate-derived reagent **159** to 2,3-*O*-isopropylidene-D-glyceraldehyde provides diastereomer **161** with very high selectivity (Scheme 16). This result contrasts with the formation of **156** using a bis(isocampheyl)-borane reagent (Scheme 15). As described in a previous section, double diastereoselective additions of allylic boron reagents to the glyceraldehyde acetals usually proceed with high selectivity in both matched and mismatched cases due to the lack of a strong bias among the four main rotamers in the transition structures minimizing syn-pentane interactions (see Scheme 4). Unlike the additions of crotyl reagents (see Schemes 2 and 3), transition structures from additions of 3,3-disubstituted reagents cannot escape from syn-pentane interactions and all four of the structures of Scheme 4 display one such interaction between a methyl group and the dioxolane ring. Thus, as substrate control is somewhat mitigated in these instances,

reagent control is more effective, which explains the formation of epimeric alcohols with a judicious choice of the right enantiomer of reagents **155** or **159**. In the formation of product **161** from reagent (*R,R*)-**159**, the stereoselectivity of this matched manifold can be explained by a Felkin–Anh transition structure **160**. Such double diastereoselective additions between tartrate-derived reagents and glyceraldehyde ketals usually proceed with very high stereoselectivity.<sup>170</sup> The intermediate **161** is transformed into the hindered  $\alpha$ -dimethylated aldehyde **162**, which undergoes another doubly diastereoselective addition with Brown’s reagent **64** that results in stereomerically pure product **163**. The corresponding tartrate-derived reagent [(*S,S*)-**53**, Fig. 4] gives a much lower selectivity with the same aldehyde. Further transformations of the intermediate **163** leads to  $\alpha$ -methoxy aldehyde **164**, whose reaction with *E*-3-trimethylsilyl tartrate reagent **165** (similar to reagent **101**, Fig. 7) occurred with high selectivity in the matched manifold to give product **166**. The stereoselectivity of this addition can be explained by minimization of syn-pentane interactions just as observed with an *E*-crotyl reagent (see structure **40** in Scheme 2). As with reagent **101** (see Eq. 74), the allylsilane unit of **166** is oxidized with rearrangement to give an advanced intermediate towards mycalamide A.

As demonstrated in the course of a total synthesis of the macrolide bafilomycin,<sup>195</sup> double diastereoselective additions can be useful even in the mismatched manifold. For example, the crotylation of chiral  $\alpha$ -substituted aldehyde **167** with (*E*)-**11** affords an 85:15 ratio of diastereomers favoring the desired anti-anti product (Scheme 17). Without a chiral tartrate reagent, the undesired anti-syn diastereomer would be intrinsically favored from aldehyde **167**. The use of the appropriate tartrate reagent, the (*R,R*) unit in this instance, overturns this preference to afford an acceptable ratio of the two separable diastereomers.

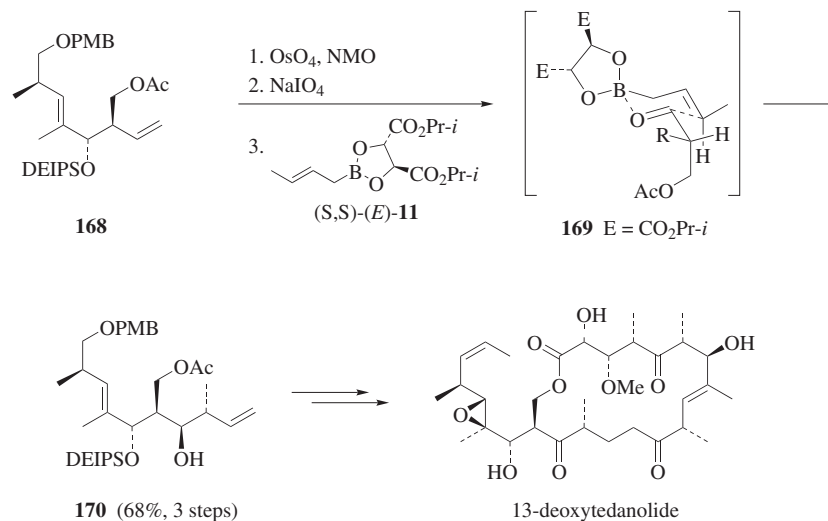
Although the class of bis(isopinocampheyl)allylboranes often leads to better levels of double diastereoselectivity, the basic oxidative work-up required in these allylations is not compatible with all substrates. This is true for the crotylation of the aldehyde derived from the terminal alkene of **168** (Scheme 18),



Scheme 17

## ALLYLBORATION OF CARBONYL COMPOUNDS

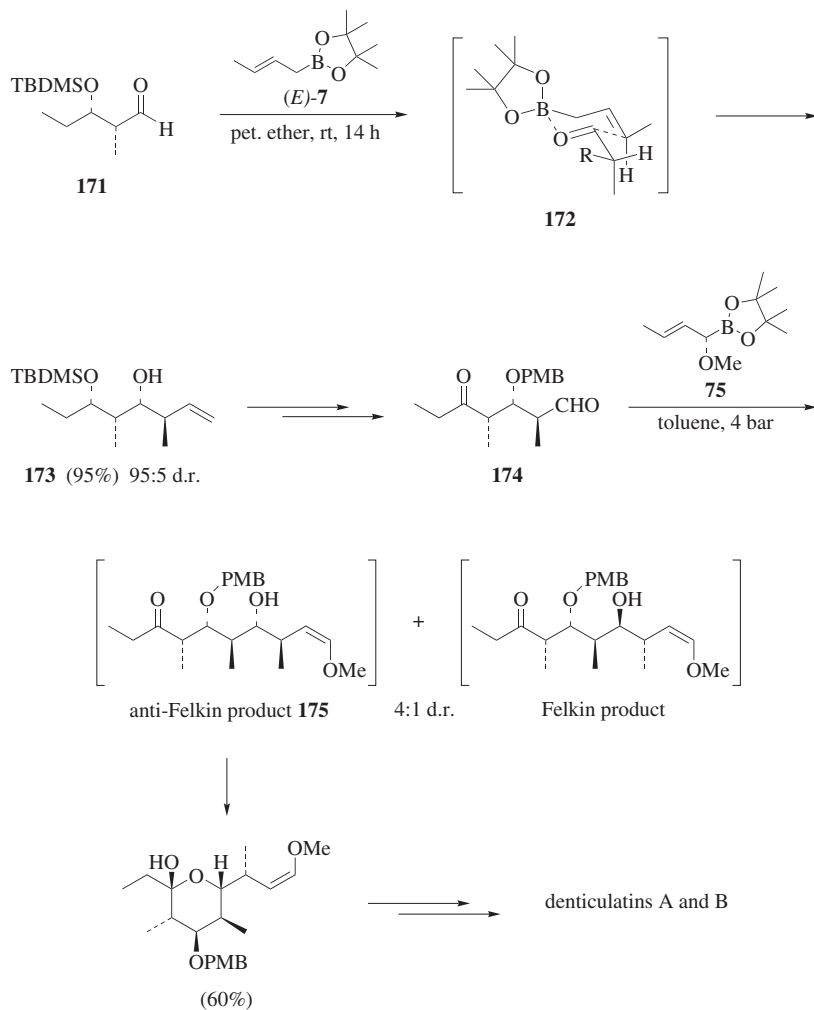
59



Scheme 18

which requires the use of boronate (*E*)-**11** because of the milder hydrolytic workup associated with this class of reagents.<sup>196</sup> This matched case of double diastereoselection is very efficient, giving intermediate **170** as the exclusive diastereomer, which was further elaborated to reach the targeted natural product, 13-deoxytedanolide. The high stereoselectivity in favor of the Felkin product **170** can be explained through chairlike transition structure **169** using the same stereoselection model described in Scheme 2, with the largest chain (R) occupying the “outside” position.

As demonstrated in a total synthesis of the denticulatins A and B, the class of chiral  $\alpha$ -substituted allylic boronates is very effective in double diastereoselection (Scheme 19).<sup>197</sup> From aldehyde **171**, a simple *E*-crotylation provides the Felkin product **173**. The high stereoselectivity of this crotylation can be explained by invoking transition structure **172** using the same model described in Scheme 2, which minimizes syn-pentane interactions with the largest of the three  $\alpha$ -substituents positioned at the outside. Intermediate **173** is then transformed into aldehyde **174**, which is subjected to another *E*-crotylation, however this time with  $\alpha$ -methoxy reagent **75**. The use of reagent **75** is necessary to optimize the diastereomeric ratio in favor of the desired anti-Felkin stereoisomer **175**, which results from a mismatched situation. Thus, the 4:1 diastereoselectivity of this reagent-controlled addition is remarkable as additions to  $\alpha$ -methyl  $\beta$ -branched aldehydes like **171** and **174** intrinsically favor the Felkin product (e.g., **173** from **171**). Here, the stereocontrolling effect of reagent **75** is powerful enough to reverse this trend and to favor diastereomer **175**. The latter cyclizes spontaneously into a hemiketal intermediate en route to the synthesis of the denticulatins A and B.



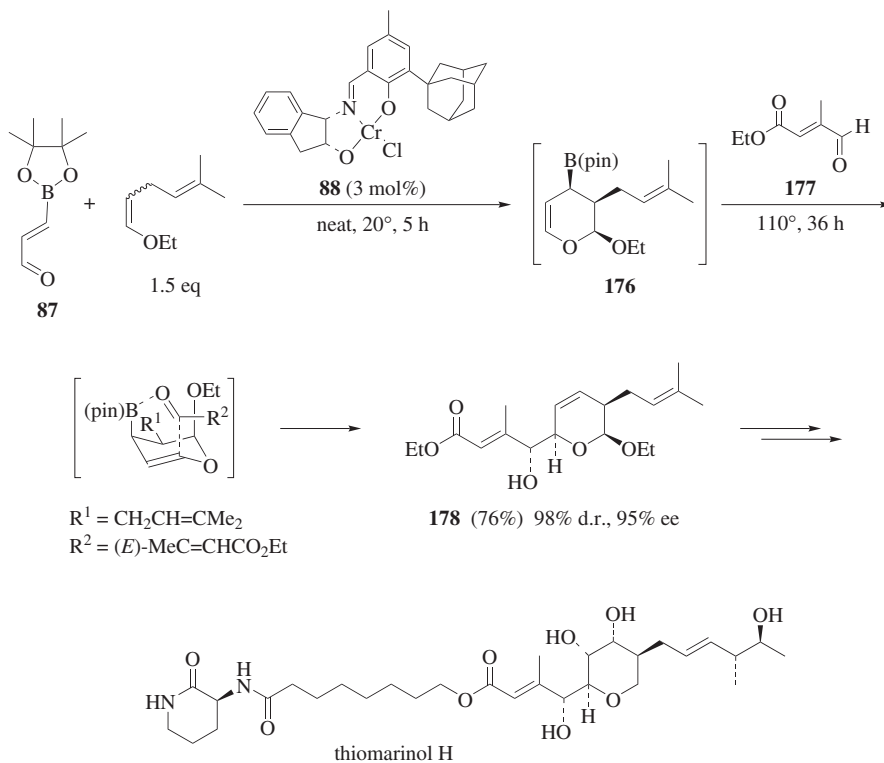
Scheme 19

### Tandem Reactions

Allylic boronates are very suitable for the design of tandem reactions that can be applied in natural product synthesis. Using the strategy illustrated in Eq. 64, an inverse electron-demand hetero-Diels–Alder reaction between **87** and a 2-substituted enol ether, catalyzed by chiral Cr(III) complex **88**, leads in high enantioselectivity to cyclic dihydropyran boronate **176** (Scheme 20).<sup>198</sup> The latter adds stereoselectively, in a one-pot sequential process, to unsaturated aldehyde **177** to give 2-hydroxyalkyl dihydropyran product **178**. Interestingly, the large, chiral catalyst **88** promotes the cycloaddition of the requisite *Z*-enol ether faster than that of the corresponding *E*-isomer. The remarkable selectivity of this tandem

## ALLYLBORATION OF CARBONYL COMPOUNDS

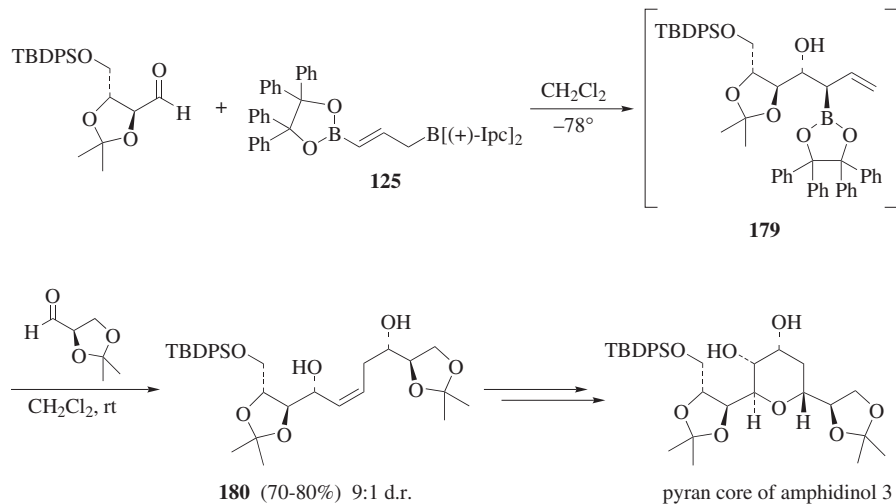
61



Scheme 20

reaction allowed an expedient enantioselective synthesis of a potent antibiotic of the thiomarinol family. A related aza[4+2] cycloaddition/allylboration has been applied to the enantioselective synthesis of palustrine alkaloids.<sup>199,200</sup>

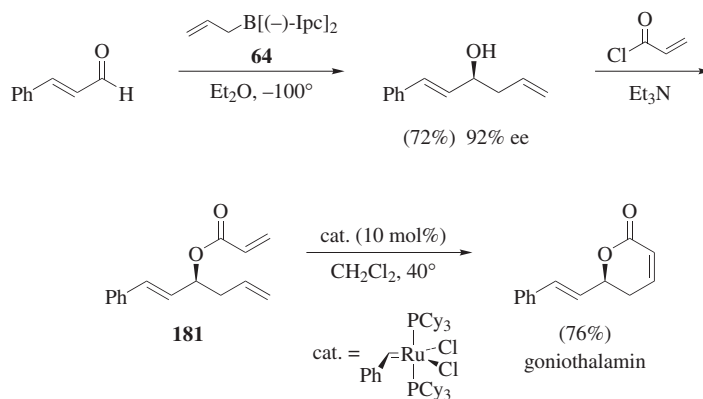
The double allylation reagent **125** described in a previous section (see Eq. 99) has been put to use with remarkable efficiency in the context of natural product synthesis. In the construction of the pyran-containing C43-C67 fragment of the complex marine natural product amphidinol 3, a one-pot double allylation with two different acetonide-protected chiral  $\alpha$ -substituted aldehydes is performed (Scheme 21).<sup>201</sup> The first allylation involved a stereochemically mismatched case of double diastereoselection, which is resolved by the strong directing power of the bis(isopinocampheyl)boryl unit and the optimal choice of protecting group. The desired intermediate **179** then reacts with the second aldehyde to give product **180** in high yield and with good overall stereoselectivity (9:1 d.r.). Functional group manipulations and a subsequent cyclization afford the pyran core of amphidinol 3. Reagent **125** is also used in the construction of the C1-C25 fragment of the same natural product.<sup>202</sup> The related reagent **100** (see Eq. 98) has been put to use toward the synthesis of peloruside.<sup>203</sup>



Scheme 21

### Transformations of Residual Groups

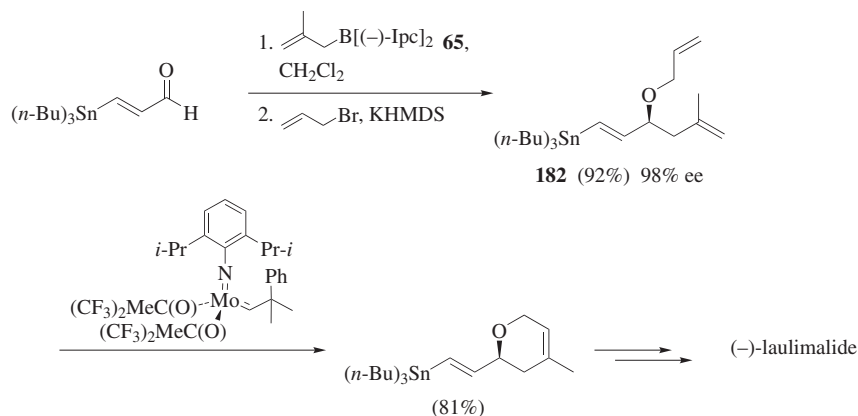
The residual alkenyl unit obtained in the products of addition of allylic boron reagents offers myriad possibilities for further derivatization in the synthesis of natural products. For instance, earlier sections (see sections on Preparation of 1,2-Diols, and 1,4-Diols) describe oxidative processes involving allylic silane units originating from additions of 3-silyl-substituted reagents. With the recent advent of alkene metathesis reactions, the possibilities of manipulations of the residual alkenyl unit have grown further. One attractive application in the synthesis of  $\gamma$ -lactones is exemplified in a synthesis of goniotalamin.<sup>204</sup> Thus, a simple allylation of cinnamaldehyde followed by acryloylation provide intermediate **181** (Scheme 22). The latter then undergoes a ring-closing metathesis using Grubbs' first-generation ruthenium catalyst to afford the desired natural product.



Scheme 22

## ALLYLBORATION OF CARBONYL COMPOUNDS

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Scheme 23

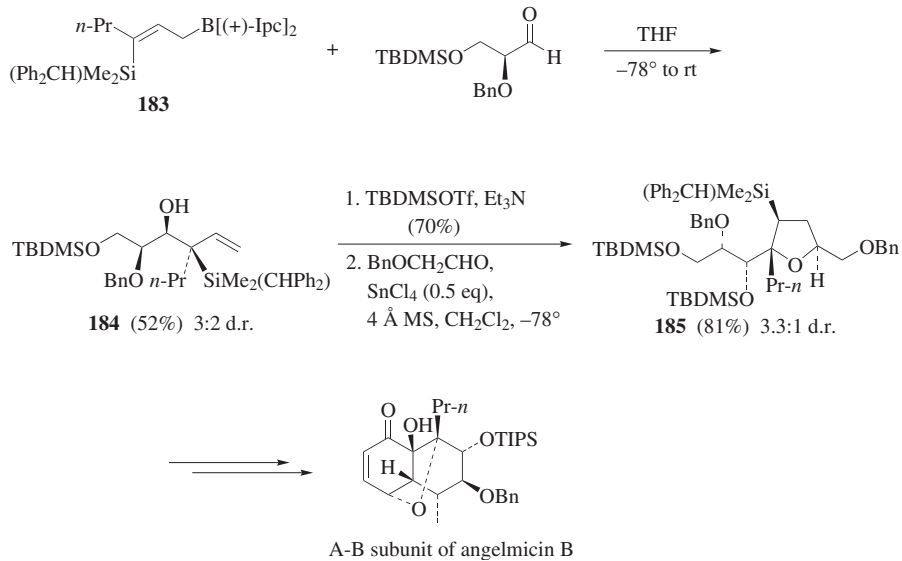
A similar strategy has been employed in the synthesis of a dihydropyran required to achieve the synthesis of (–)-lulimalide (Scheme 23).<sup>205</sup> Thus, allylation of the secondary alcohol resulting from a methallylation of 3-tri-*n*-butylstannylacrolein provided unsymmetrical ether **182**, which is closed to a pyran with a ring-closing metathesis using Schrock's molybdenum catalyst.

The class of 3-silyl-substituted reagents provides, upon addition with aldehydes, allylic silanes that offer many options for further derivatization. Oxidative processes are described in previous sections (see the sections on Preparation of 1,2-Diols and 1,4-Diols). If the appropriate silicon substituents are chosen, formal [3+2] cycloadditions with aldehydes can be promoted under Lewis acid catalysis. For example, the mismatched addition of the *Z*-3-propyl-3-benzhydryldimethyl allylsilane **183** to an  $\alpha$ -benzyloxy aldehyde proceeds with low diastereofacial selectivity in favor of product **184**; however, after protection of the secondary alcohol, an efficient [3+2] annulation provides the polysubstituted furan **185** in good yield and acceptable stereoselectivity (Scheme 24).<sup>206</sup> The latter is brought forward to a tricyclic unit found in the antitumor natural product angelmicin B.

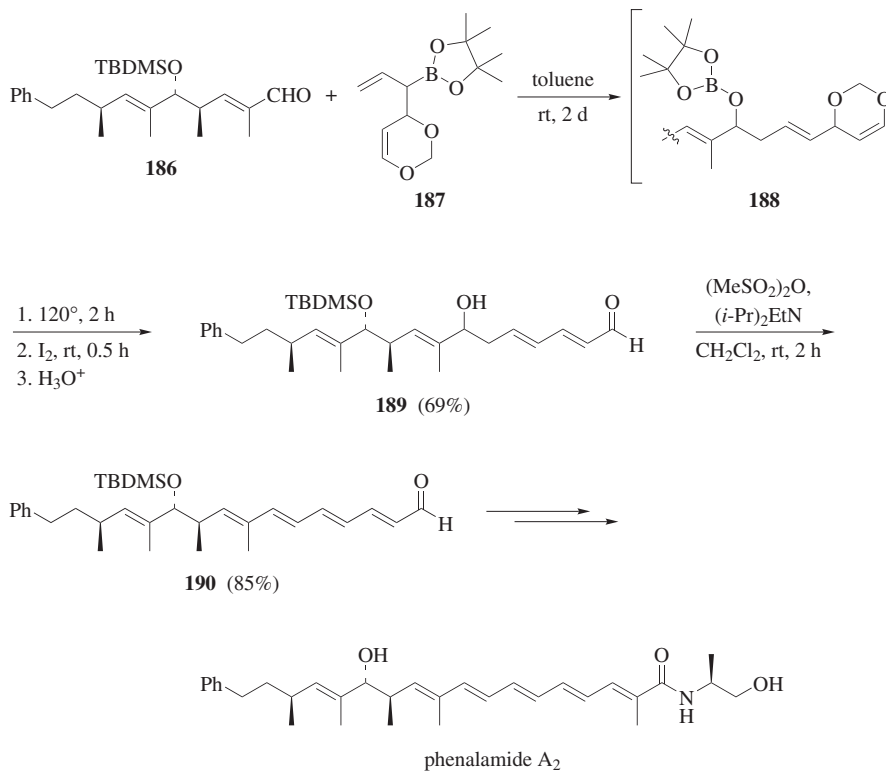
A special  $\alpha$ -substituted allylic boronate, reagent **187**, has been developed as part of a tandem method for synthesizing trienes through an extended homologation of aldehydes.<sup>207</sup> This process, a one-pot aldehyde allylation/dioxene thermolysis, has been applied to a total synthesis of phenalamide A<sub>2</sub> (Scheme 25).<sup>208</sup> Thus, reagent **187** is added to unsaturated aldehyde **186** to give dioxene intermediate **188**. Upon warming to 120°, **188** undergoes a formal retro[4+2] cycloaddition to give the desired dienal as a mixture of geometrical isomers. The addition of iodine promotes a complete *Z*- to *E*- isomerization to give the *E,E*-dienal intermediate **189**. A dehydration of the latter then provides the tetraenal **190**, an advanced intermediate subsequently transformed into phenalamide A<sub>2</sub>.

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## ALLYLBORATION OF CARBONYL COMPOUNDS



Scheme 24



Scheme 25



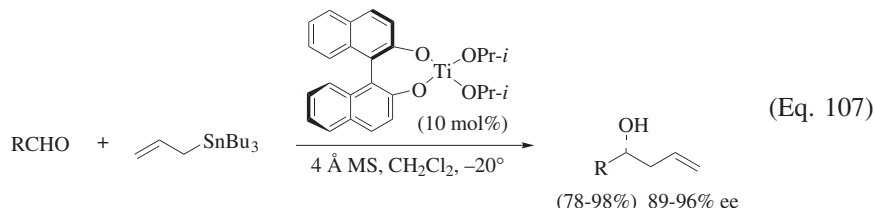
### COMPARISON WITH OTHER METHODS

Despite the extensive efforts by numerous research groups over the course of more than two decades, there is still no carbonyl allylation methodology that possesses all of the following attributes: mildness and chemoselectivity, substrate generality (for both allylmetal reagent and aldehyde substrate), high levels of diastereo- and enantioselectivity, and high practicality (ease of use, low cost, non-toxicity, and low environmental impact). Very importantly, the ideal enantioselective allylation methodology would circumvent the use of a chiral auxiliary through a simple and efficient chiral catalyst.<sup>209</sup> While several systems based on allylic boron reagents do possess many of the above attributes, several other allylation systems based on other metals (mainly tin, titanium, and silicon) demonstrate very interesting properties. It is noteworthy that a wide body of aldol-based reaction methods have been developed to afford chiral secondary alcohols, propionate units, and other useful intermediates closely related to those afforded by allylation processes. These methods are not described in this section but the interested reader will find several excellent reviews and monographs on the topic of aldol reactions.<sup>210–212</sup> This section focuses on presenting a brief comparison of allylic boron reagents with other enantioselective allylation reagents.

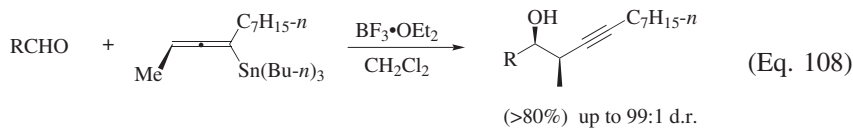
#### Methods Employing Allylic Tin Reagents

Allylic trialkyltin reagents can react at high temperatures with aldehydes<sup>213</sup> but because of the low acidity of the trialkyltin center, they are always employed as Type II allylation reagents that normally require activation of the carbonyl substrate with an external Lewis acid.<sup>15</sup> This behavior contrasts the cyclic, organized transition structure of allylboration reactions. Consequently, additions of allylic tin reagents proceed through open transition structures that tend to demonstrate lower levels of diastereoselectivity (with 3-substituted reagents) compared with the corresponding boron reagents. Allylic trialkyltin reagents are highly nucleophilic in comparison to the corresponding trialkylsilanes. Their reactivity has contributed largely to their popularity. One major drawback of organotin-based reagents, however, is their high toxicity. Moreover, crotylation reagents are rather difficult to synthesize in geometrically pure form, albeit, this point is rather inconsequential because of the stereoconvergent (Type II) behavior of 3-substituted tin-based reagents. Catalytic enantioselective methods that make use of achiral reagents constitute the most attractive carbonyl allylation processes. In this respect, the Keck allylation remains the most efficient and most popular system based on achiral allylic tin reagents (Eq. 107).<sup>214,215</sup> This system has been employed mainly for simple allylations and methallylations of aldehydes. It makes use of a chiral BINOL-based titanium Lewis acid, which provides enantiomeric excesses as high as 94–96% for several types of aldehydes, both aliphatic and aromatic. The catalyst can be employed in a loading as low as 1 mol% when *i*-PrSSiMe<sub>3</sub> is added.<sup>216</sup> Efficient variants of these systems have been described for the allylation of ketones.<sup>217</sup> A BINAP–AgOTf complex catalyzes the simple allylation of aldehydes with enantiomeric excesses as high as

96% for benzaldehyde.<sup>218</sup> Methallylations and crotylations of aldehydes under this catalytic system provide good enantioselectivities.<sup>219</sup>

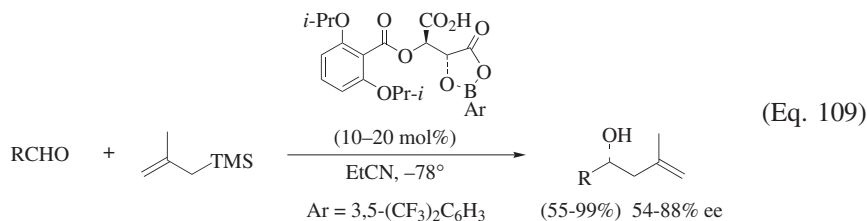


Additions of enantiomerically enriched allenyltin reagents provide homopropargylic alcohol products with high levels of stereoselectivity (Eq. 108).<sup>220</sup> These reagents also function through Lewis acid catalysis. Although their preparation requires several steps through the intermediacy of enantiomerically pure propargylic alcohols, allenyltin reagents are effective with a wide range of aldehydes, including double diastereoselective additions with chiral  $\alpha$ -substituted aldehydes.<sup>220</sup>



### Methods Employing Allylic Silicon Reagents

Allylic trialkylsilicon reagents are less nucleophilic than the corresponding tin reagents. However, they are cheap and safer in terms of toxicity. One of the early successes in the area of catalytic enantioselective carbonyl allylation chemistry makes use of chiral acyloxy borane (CAB) catalysts and methallyltrimethylsilane (Eq. 109).<sup>221,222</sup> This system works for aromatic, unsaturated, and aliphatic aldehydes but it gives the highest enantioselectivities in the reactions of 3-alkyl substituted reagents and aromatic aldehydes. Aliphatic aldehydes give noticeably lower selectivities, which probably accounts for the low level of adoption of this allylation method.

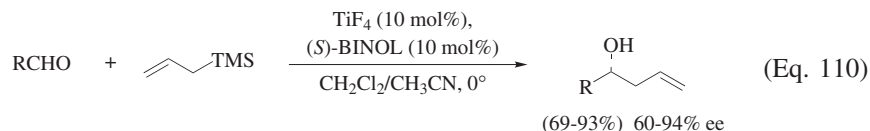


A method using dual activation has been developed in which a Lewis acid activates the aldehyde with concomitant nucleophilic activation of the allylic silicon reagent with fluoride anion. Thus, by using a BINOL-based titanium

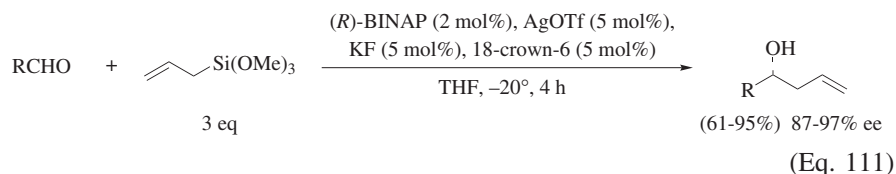
## ALLYLBORATION OF CARBONYL COMPOUNDS

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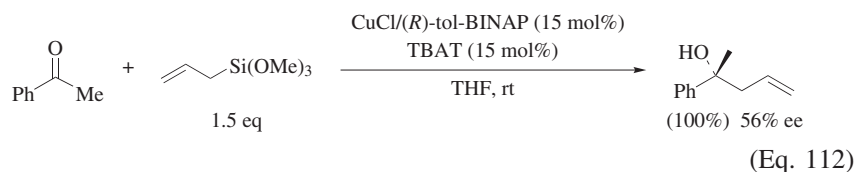
tetrafluoride complex, both aromatic and aliphatic aldehydes can be reacted with allyltrimethylsilane with enantioselectivities up to 94% (Eq. 110).<sup>223</sup> Aromatic aldehydes provide lower selectivity but this method is particularly efficient with hindered  $\alpha,\alpha$ -dialkylated aldehydes such as pivalaldehyde.<sup>224</sup>



Allylic trialkoxysilanes are effective nucleophiles under the bifunctional Ag(I)-fluoride catalytic system when using a combination of KF and 18-crown-6 as catalytic source of soluble fluoride anion (Eq. 111).<sup>225</sup> Although this method requires the use of three molar equivalents of allyltrimethoxysilane, only 5 mol% of AgOTf with 2 mol% of BINAP are sufficient to afford enantiomeric excesses in the range of 93–97% for aromatic aldehydes. Aliphatic aldehydes display lower selectivities, and require a higher loading of the catalyst. The corresponding crotylation reactions are stereoconvergent, as both (*E*)- and (*Z*)-crotyltrimethoxysilane provide the anti-propanoate product in 95% ee.<sup>225</sup>

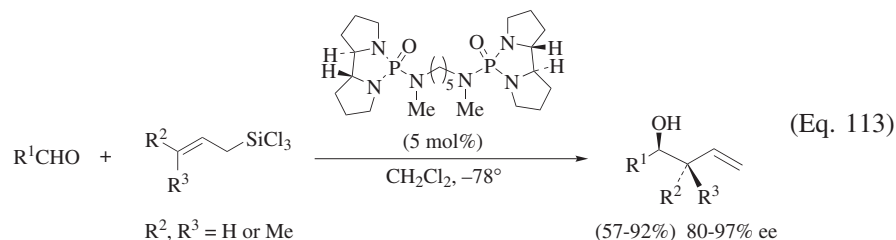


A similar Cu(I)-catalyzed reaction has been reported, and one example represents a modestly enantioselective addition to a ketone (Eq. 112).<sup>226</sup>

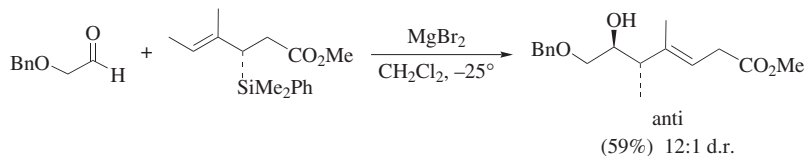


Another approach toward activating allylic silanes exploits the ability of some basic solvents and additives to accelerate the additions of allylic halosilanes. In the latest advance, treatment of an allylic trichlorosilane with a dimeric chiral phosphoramidate catalyst generates a highly reactive silane species which then allylates aldehydes to give homoallylic alcohols in high stereoselectivity (Eq. 113).<sup>227</sup> Aromatic and unsaturated aldehydes react smoothly with the simple allyl reagent and both crotylsilanes to give homoallylic alcohols in good yields and high diastereo- and enantioselectivities.<sup>228</sup> The mechanism of these allylations has been studied in detail. The high diastereoselectivity and the dependence of product stereochemistry on the geometry of  $\gamma$ -substituted silanes indicate that these allyltrichlorosilanes react like allylic boron reagents through the Type I

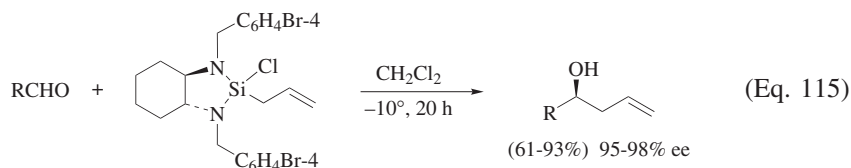
pathway. A significant limitation to this approach is that it is not applicable to aliphatic aldehydes.



Non-racemic  $\alpha$ -substituted allylic silanes, in particular crotylsilanes, are very attractive reagents despite their rather tedious preparation. They were found to provide very high transfer of chirality in their additions to achiral aldehydes under Lewis acid catalysis (Eq. 114).<sup>229</sup> These reagents have been tested several times in the context of natural product synthesis. Their diastereoselectivity (syn/anti) depends on several factors, including the nature of the aldehyde substrate, the reagent, and the nature of the Lewis acid employed. For example, the syn product can be obtained predominantly in the reaction of Eq. 114 by switching to the use of a monodentate Lewis acid such as  $\text{BF}_3$ .

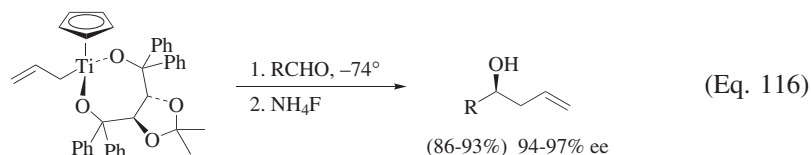


Another approach for the activation of allylic silanes takes advantage of the fact that constraining silicon in a small ring increases its Lewis acidity. By reacting allyltrichlorosilane with 1,2-diols, diamines, or amino alcohols, allylchlorosilanes are generated in which the silicon is part of a strained heterocyclic 5-membered ring. The most interesting aspect of this recent work comes from allylsilanes bearing chiral 1,2-amino alcohols and 1,2-diamines as substituents. The optimal reagents are derived from  $C_2$ -symmetrical cyclohexanediamines, and are exceptionally selective for a broad range of aldehydes, including unsaturated and aromatic ones (Eq. 115).<sup>230</sup> These novel reagents are stable and easy to handle, and possess a long shelf-life. Interestingly, the corresponding crotylsilanes are also efficient reagents, and behave as Type I reagents by providing stereospecific crotylations of aldehydes.<sup>231</sup>

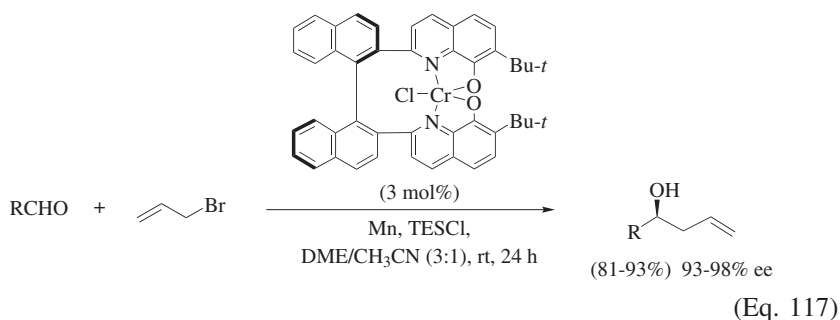


### Methods Employing Other Metals

Several other metals have been examined in allyl transfer reactions to carbonyl compounds. Only modest success has been obtained except for a class of cyclopentadienyl titanium reagents based on a tartrate-derived auxiliary (Eq. 116).<sup>232</sup> These reagents display a very high level of enantioselectivity in the simple allylation of several types of aldehydes, including hindered ones like pivalaldehyde (63% yield, 97% ee). A number of 3-substituted derivatives have been examined, including the E-crotyl reagent, which provides the anti propanoate products in excellent yields and over 98% ee for model aromatic and aliphatic aldehydes. These reagents are remarkably effective in double diastereoselective additions. Their inherent disadvantages are their preparation and their stoichiometric mode of stereochemical induction.



Allylic chromium species can also add to aldehydes. In this regard, an efficient catalytic enantioselective variant using allylic halides as substrates and manganese as co-oxidant has been described recently (Eq. 117).<sup>233</sup> This method provides high enantiomeric excesses in the simple allylation of a wide range of aliphatic, aromatic, and heteroaromatic aldehydes. Crotylation examples are also very enantioselective, albeit with modest anti/syn diastereoselectivity.

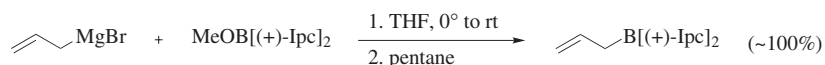


### EXPERIMENTAL CONDITIONS

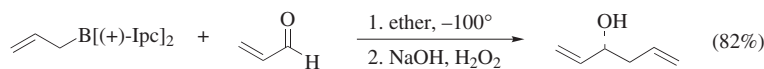
Additions of allylic boron reagents are typically performed under experimentally simple conditions, and under a wide range of temperatures that is dictated by the reactivity of the particular reagent employed. Work-up conditions are discussed in a previous section. For the reaction itself, uncatalyzed additions can be performed in a wide variety of aprotic solvents. Non-coordinating solvents usually lead to shorter reaction times,<sup>21</sup> but the identification of an optimal solvent in stereoselective additions is rather unpredictable and may require coordinating

solvents for higher selectivity. The use of molecular sieves is strongly recommended when using water-sensitive allylic boronates. Lewis or Brønsted acid catalyzed additions are also better performed with non-coordinating solvents, typically toluene or methylene chloride. The literature describes only a few examples of allylations with a polymer-supported reagent,<sup>234</sup> and with supported aldehydes.<sup>235,236</sup>

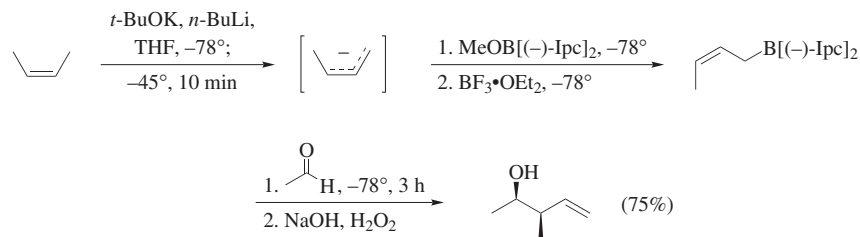
#### EXPERIMENTAL PROCEDURES



**(+)-*B*-Allyl bis(Isopinocampheyl)borane [General Procedure for Preparation of the Reagent Free of MgBr(OMe)].**<sup>139</sup> Allylmagnesium bromide in ether (48 mL, 1.0 M, 48 mmol) was added dropwise to a well-stirred solution of (+)-*B*-methoxy bis(isopinocampheyl)borane (15.8 g, 50 mmol) in THF (50 mL) at 0°. After completion of addition, the reaction mixture was vigorously stirred for 1 hour at room temperature, and the solvents were removed under vacuum (14 mm Hg, 2 hours). The residue was extracted with pentane (2 × 100 mL) under nitrogen, and stirring was discontinued to permit the MgBr(OMe) salt to settle. The clear supernatant pentane extract (free from the magnesium salts) was transferred to another flask using a double-ended needle through a Kramer filter. Evaporation of pentane (14 mm Hg, 1 hour; 2 mm Hg, 1 hour) afforded the pure title product in nearly quantitative yield.

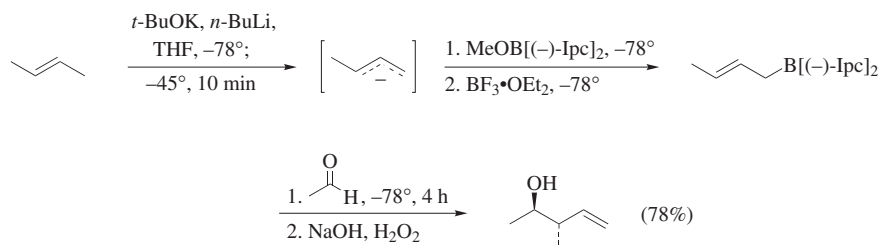


**(*R*)-1,5-Hexadien-3-ol [Typical Procedure for the Simple Allylation of a Representative Aldehyde with the AllylB(Ipc)<sub>2</sub> Reagent].**<sup>139</sup> Anhydrous ether (100 mL) was added to allylB[(+)-Ipc]<sub>2</sub>, and the resulting solution was cooled to -100°. A solution of acrolein (2.8 g, 50 mmol) in Et<sub>2</sub>O (50 mL), maintained at -78°, was slowly added along the side of the flask, kept at -100°. The reaction mixture was stirred for 0.5 hour at -100°, and MeOH (1 mL) was added. The reaction mixture was then brought to room temperature (1 hour) and treated with 3 N NaOH (20 mL) and 30% H<sub>2</sub>O<sub>2</sub> (40 mL). Heating the reaction mixture at reflux for 3 hours ensured the completion of the oxidation. The organic layer was separated, washed with water (30 mL) and brine (30 mL), dried over anhydrous MgSO<sub>4</sub>, and filtered and concentrated under reduced pressure. Distillation afforded 4.17 g of the title product (82% yield), bp 54° at 20 mm Hg; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 5.85 (m, 2H), 5.20 (m, 4H), 4.19 (m, 1H), 2.33 (m, 2H), 1.72 (br, 1H); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>) δ 139.3, 133.4, 117.9, 115.2, 72.1, 41.0. GC analysis of its Mosher ester on a capillary Supelcowax column (15 m × 0.25 cm) showed the enantiomeric excess to be 96%.



**(2R,3R)-3-Methyl-4-penten-2-ol [Preparation of (-)-(Z)-Crotyl Bis(isopinocampheyl)borane and a Representative Reaction with Acetaldehyde].<sup>137</sup>**

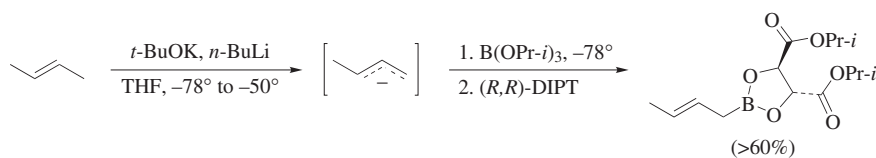
To a stirred mixture of *t*-BuOK (2.8 g, 25 mmol, dried at 80°/0.5 mm Hg for 8 hours), *cis*-2-butene (4.5 mL, 50 mmol), and THF (7 mL) at -78° was added *n*-BuLi (2.3 M in THF, 25 mmol). After complete addition of *n*-BuLi, the mixture was stirred at -45° for 10 minutes. The resulting solution was cooled to -78°, and methoxydiisopinocampheylborane in ether [1 M, 30 mmol, derived from (+)- $\alpha$ -pinene] was added dropwise. After the reaction mixture was stirred at -78° for 30 minutes, BF<sub>3</sub>·OEt<sub>2</sub> (4 mL, 33.5 mmol) was added dropwise. Acetaldehyde (2 mL, 35 mmol) was then added dropwise at -78°. The reaction solution was stirred at -78° for 3 hours and treated with 3 N NaOH (18.3 mL, 55 mmol) and 30% H<sub>2</sub>O<sub>2</sub> (7.5 mL). The resulting mixture was heated at reflux for 1 hour. The organic layer was separated, washed with water (30 mL) and brine (30 mL), dried over anhydrous MgSO<sub>4</sub>, and filtered and concentrated under reduced pressure to afford the title product (75% yield, 90% ee,  $\geq$ 99% d.r.), bp 78°/85 mm Hg; [ $\alpha$ ]<sub>D</sub><sup>23</sup> +19.40° (neat); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  6.00–5.68 (m, 1H), 5.21–4.91 (m, 2H), 3.70 (p, *J* = 6 Hz, 1H), 2.25 (sextet, *J* = 7 Hz, 1H), 2.07 (s, br, 1H), 1.16 (d, *J* = 6 Hz, 3H), 1.04 (d, *J* = 7 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, Me<sub>4</sub>Si)  $\delta$  140.62, 115.06, 70.78, 44.87, 19.96, 14.85.



**(2R,3S)-3-Methyl-4-penten-2-ol [Preparation of (-)-(E)-Crotyl Bis(isopinocampheyl)borane and a Representative Reaction with Acetaldehyde].<sup>137</sup>**

To a stirred mixture of *t*-BuOK (2.8 g, 25 mmol, dried at 80°/0.5 mm for 8 h), *trans*-2-butene (4.5 mL, 50 mmol), and THF (7 mL) at -78°, was added *n*-BuLi (2.3 M in THF, 25 mmol). The mixture was stirred at -45° for 10 minutes. The resulting solution was recooled to -78°, and a solution of methoxydiisopinocampheylborane (1.0 M in ether, 30 mmol, derived from (+)- $\alpha$ -pinene) was added. After the reaction mixture was stirred at -78° for 30 minutes, BF<sub>3</sub>·OEt<sub>2</sub> (4 mL,

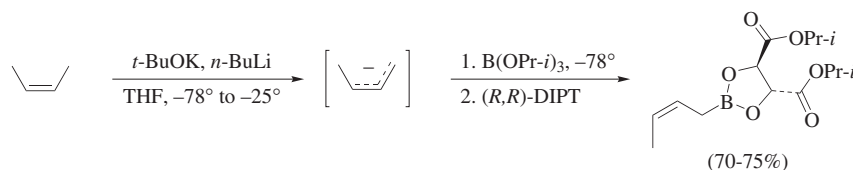
33.5 mmol) was added dropwise. Acetaldehyde (35 mmol) was added dropwise at  $-78^{\circ}$ . The reaction mixture was stirred at  $-78^{\circ}$  for 4 hours and treated with 18.3 mL (55 mmol) of 3 N NaOH and 30%  $\text{H}_2\text{O}_2$  (7.5 mL). After the mixture was heated at reflux for 1 hour, the organic layer was separated, washed with water (30 mL) and brine (30 mL), dried over anhydrous  $\text{MgSO}_4$ , and filtered and concentrated under reduced pressure to afford the title product (78% yield, 90% ee,  $\geq 99\%$  d.r.); bp  $78^{\circ}/85$  mm Hg;  $[\alpha]_D^{23} +9.141^{\circ}$  (neat);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  6.00–5.55 (m, 1 H), 5.30–4.95 (m, 2H), 3.4 (p,  $J = 7$  Hz, 1H), 2.15 (sextet,  $J = 7$  Hz, 1H), 1.70 (s, 1 H), 1.20 (d,  $J = 7$  Hz, 3H), 1.05 (d,  $J = 7$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ )  $\delta$  140.73, 115.76, 70.72, 45.64, 19.94, 15.72.



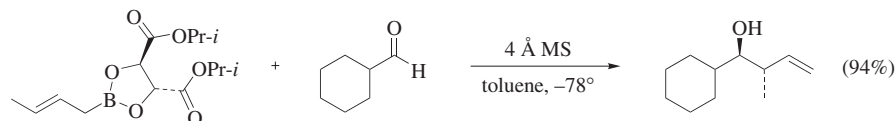
**(*R,R*)-[(*E*)-2-Butenyl]diisopropyl Tartrate Boronate [Preparation of the (*E*)-Crotyl Diisopropyl Tartrate Boronate Reagent].<sup>37</sup>** An oven-dried 1-L three-neck round-bottom flask equipped with a magnetic stir bar and a  $-100^{\circ}$  thermometer was charged with anhydrous THF (472 mL) and *t*-BuOK (48.0 g, 425 mmol). This mixture was flushed with Ar and cooled to  $-78^{\circ}$ . *trans*-2-Butene (42.0 mL, 450 mmol), condensed from a gas lecture bottle into a rubber-stoppered 250-mL graduated cylinder immersed in a  $-78^{\circ}$  dry ice–acetone bath, was added via cannula. *n*-BuLi (2.5 M in hexane, 170 mL, 425 mmol) was then added dropwise via cannula at a rate such that the internal temperature did not rise above  $-65^{\circ}$ . After completion of the addition (roughly 2 hours on this scale), the cooling bath was removed and the reaction mixture was allowed to warm until the internal temperature reached  $-50^{\circ}$ . The solution was maintained at  $-50^{\circ}$  for exactly 15 minutes and then was immediately cooled to  $-78^{\circ}$ . Triisopropylborate (80.0 g, 98.2 mL, 425 mmol) was added dropwise via cannula to the (*E*)-crotylpotassium solution at a rate such that the internal temperature did not rise above  $-65^{\circ}$ . On this scale the addition time was approximately 2 hours. After the addition was complete, the reaction mixture was maintained at  $-78^{\circ}$  for 10 minutes and then rapidly poured into a 2-L separatory funnel containing 800 mL of 1 N HCl saturated with NaCl. The aqueous layer was adjusted to pH 1 by using aqueous 1 N HCl, and a solution of (*R,R*)-diisopropyl tartrate (100 g, 425 mmol) in 150 mL of  $\text{Et}_2\text{O}$  was added. The phases were separated, and the aqueous layer was extracted with additional  $\text{Et}_2\text{O}$  ( $4 \times 200$  mL). The combined extracts were dried with anhydrous  $\text{MgSO}_4$  for at least 2 hours at room temperature and then vacuum filtered through a fritted glass funnel under a  $\text{N}_2$  blanket into an oven-dried round-bottom flask. The filtrate was



concentrated under reduced pressure to afford a colorless thick liquid, which was then pumped to constant weight (125 g) at 0.5–1.0 mm Hg. It was necessary for the neat reagent to be stirred to remove residual volatile materials, especially THF. Analysis of the crude product by capillary GC [50 m  $\times$  0.25 mm fused quartz SE-54 column (0.2  $\mu$ m polydiphenylvinyl-dimethylsiloxane), 170° isotherm;  $t_r$  of the E-isomer, 10.9 min vs.  $t_r$  of the Z-isomer, 11.3 min;  $t_r$  of butylboronate, 10.5 min] indicated that the isomeric purity of this batch of reagent was 99%; 12% of tartrate butylboronate was also present, reflecting incomplete metalation of (*E*)-2-butene in this experiment. The reagent is moisture sensitive, and it is better handled as a stable solution in toluene or THF. The (*S,S*)-reagent derived from (*S,S*)-DIPT had  $[\alpha]_D^{23} +36.5^\circ$  (neat);  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  5.63–5.53 (m, 1H), 5.48–5.37 (m, 1H), 5.00–4.83 (m, 2H), 4.89 (s, 2H), 1.86 (br d,  $J = 6.4$  Hz, 2H), 1.53 (br d,  $J = 6.3$  Hz, 3H), 0.90 (d,  $J = 6.3$  Hz, 12H);  $^{13}\text{C NMR}$  (75.4 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  169.0, 126.1, 125.3, 78.4, 69.6, 21.6, 18.1;  $^{11}\text{B NMR}$  (115.8 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  34.4; CIMS ( $\text{NH}_3$ ) ( $m/z$ ):  $[\text{M} + 1]^+$  299; HRMS ( $m/z$ ): calcd for  $\text{C}_{14}\text{H}_{23}^{10}\text{BO}_6$ , 297.1617; found, 297.1618; HRMS ( $m/z$ ): calcd for  $\text{C}_{14}\text{H}_{23}^{11}\text{BO}_6$ , 298.1581; found, 298.1683.

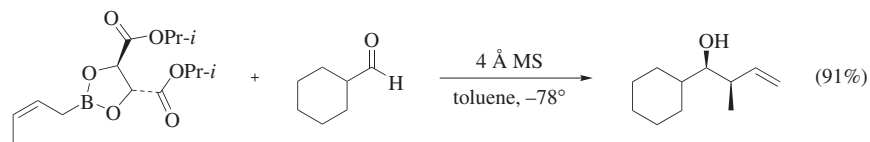


**(*R,R*)-[(*Z*)-2-Butenyl]diisopropyl Tartrate Boronate [Preparation of the (*Z*)-Crotlyl Diisopropyl Tartrate Boronate Reagent].<sup>37</sup>** The preparation of *Z*-crotlylboronate from (*Z*)-2-butene is analogous to that described for the corresponding *E*-reagent with the following modification: on completion of the *n*-BuLi addition, the reaction mixture was warmed to  $-20^\circ$  to  $-25^\circ$  for 30–45 minutes before being cooled to  $-78^\circ$ . This ensured near quantitative formation of the (*Z*)-crotlylpotassium. Temperature control is less critical here since the (*Z*)-crotlylpotassium species is highly favored at equilibrium (99 : 1). The remainder of this preparation was the same as that described above for the synthesis of the *E*-crotlylboronate reagent. On a 100-mmol scale, the yield of *Z*-crotlylboronate was 70–75% (1–2% of butylboronate) and the isomeric purity was >98% (generally >99%). The (*R,R*)-(*Z*)-reagent prepared from (*R,R*)-DIPT had  $[\alpha]_D^{23} -80.2^\circ$  ( $c$  2.42,  $\text{CHCl}_3$ ); IR (thin film) 3500 (br), 3220 (m), 2980 (s), 1745 (s), 1375 (s), 1220 (s), 1100 (s)  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  5.76–5.67 (m, 1H), 5.55–5.48 (m, 1H), 5.05–4.99 (m, 2H), 4.92 (s, 2H), 1.91 (d,  $J = 7.8$  Hz, 2H), 1.56 (d,  $J = 6.6$  Hz, 3H), 0.94 (d,  $J = 6.3$  Hz, 12H);  $^{13}\text{C NMR}$  (75.4 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  169.0, 124.6, 124.4, 78.4, 69.6, 21.3, 12.7;  $^{11}\text{B NMR}$  (115.8 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  34.8; CIMS ( $\text{NH}_3$ ) ( $m/z$ ):  $[\text{M}^+]$  298; HRMS ( $m/z$ ): calcd for  $\text{C}_{14}\text{H}_{23}^{11}\text{BO}_6$ , 298.1581; found, 298.1624.



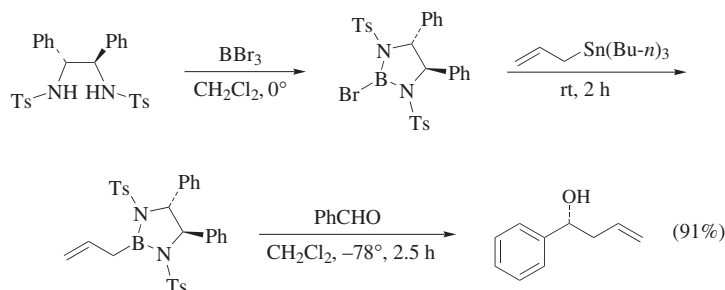
**(1*S*,2*R*)-1-Cyclohexyl-2-methyl-3-buten-1-ol [Representative Procedure for Additions of (*E*)-Crotyl Diisopropyl Tartrate Boronate to Aldehydes].<sup>37</sup>**

A solution of (*R,R*)-isopropyl tartrate (*E*)-crotylboronate (3.19 g, 10.7 mmol, crude reagent, 99.3% isomeric purity) in 32 mL of dry toluene under N<sub>2</sub> was treated with powdered 4 Å molecular sieves (600 mg) and cooled to -78°. A solution of freshly distilled cyclohexanecarboxaldehyde (1.00 g, 8.92 mmol) in 10 mL of toluene was added dropwise over 30 minutes. The reaction mixture was stirred at -78° for 3 hours and then was treated with 10 mL of 2 N NaOH to hydrolyze the DIPT borate. The two-phase mixture was warmed to 0° and stirred for 20 minutes before being filtered through a pad of Celite. The aqueous layer was extracted with Et<sub>2</sub>O (4 × 10 mL), and the combined organic extracts were dried over anhydrous K<sub>2</sub>CO<sub>3</sub> and filtered. Flash chromatographic purification on silica gel (60 × 150 mm column, 6:1 hexane/ether) provided 1.41 g of the title product (94% yield) in >99% d.r. (capillary GC analysis: Carbowax 20 column; 70° for 4 minutes then 10°/min to a final temperature of 150°) and 86% ee as determined by chiral capillary GC analysis of the methyl ether. The product had [α]<sub>D</sub><sup>25</sup> -15.8° (*c* 1.02, CHCl<sub>3</sub>, data obtained on a sample with >99% d.r. and 86% ee); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 5.80 (ddd, *J* = 18.0, 10.9, 7.2 Hz, 1H), 5.15–5.10 (m, 2H), 3.11 (dd, *J* = 5.1, 5.1 Hz, 1H), 2.39 (m, 1H), 1.85–1.60 (m, 5H), 1.48–1.35 (m, 2H), 1.28–1.06 (m, 5H), 1.04 (d, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>) δ 140.4, 116.0, 78.8, 40.5, 40.3, 30.0, 27.0, 26.5, 26.4, 26.1, 17.0; Anal. Calcd for C<sub>11</sub>H<sub>20</sub>O: C, 78.52; H, 11.98. Found: C, 78.22; H, 12.20.



**(1*R*,2*R*)-1-Cyclohexyl-2-methyl-3-buten-1-ol [Representative Procedure for Additions of (*Z*)-Crotyl Diisopropyl Tartrate Boronate to Aldehydes].<sup>37</sup>**

The title product was prepared by the procedure described above using (*R,R*)-isopropyl tartrate (*Z*)-crotylboronate (91% yield); [α]<sub>D</sub><sup>25</sup> +28.0° (*c* 0.61, CHCl<sub>3</sub>, data obtained on a sample with >99% d.r.); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.80 (ddd, *J* = 17.3, 10.0, 7.0 Hz, 1H), 5.08 (d, *J* = 17.3 Hz, 1H), 5.06 (d, *J* = 10.0 Hz, 1H), 3.18 (ddd, *J* = 5.0, 5.0, 4.3 Hz, 1H), 2.38 (m, 1H), 1.91 (d, *J* = 13.0 Hz, 1H), 1.73 (m, 2H), 1.64 (m, 1H), 1.58 (m, 1H), 1.41 (m, 1H), 1.35 (d, *J* = 4.3 Hz, 1H), 1.30–1.00 (m, 5H), 0.97 (d, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>) δ 142.0, 114.4, 78.6, 40.2, 39.8, 29.6, 27.8, 26.4, 26.2, 25.9, 13.1; MS (*m/z*): [M<sup>+</sup> - crotyl] 113. Anal. Calcd for C<sub>11</sub>H<sub>20</sub>O: C, 78.51; H, 11.98. Found: C, 78.33; H, 12.03.

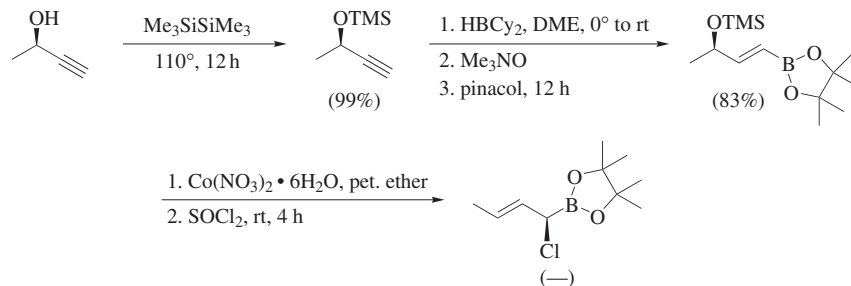


**(*R*)-(+)-1-Phenyl-3-buten-1-ol [Preparation of (*1R,2R*)-*N,N'*-Bis-(*p*-Toluenesulfonamide)-1,2-diamino-1,2-diphenylethane Allyldiazaborolidine and a Representative Reaction with Benzaldehyde].<sup>50</sup> (+)-(1*R*,2*R*)-**

*N,N'*-Bis(*p*-toluenesulfonamide)-1,2-diamino-1,2-diphenylethane (0.75 g, 1.44 mmol) was placed in a dry 25-mL round-bottom flask equipped with a magnetic stir bar and sealed with a septum. The flask was evacuated and flushed with argon three times. Freshly distilled CH<sub>2</sub>Cl<sub>2</sub> (12 mL) was added and the resulting solution was cooled to 0°, at which point BBr<sub>3</sub> (1 M in CH<sub>2</sub>Cl<sub>2</sub>, 1.4 mL, 1.4 mmol) was added. The resulting solution was stirred at 0° for 10 minutes and then warmed to room temperature and stirred for 40 minutes. The solution was concentrated under vacuum (2 mm Hg) and rigorously protected from moisture. Freshly distilled CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added and removed under vacuum to give the bromoborane intermediate; <sup>11</sup>B NMR (96 MHz, CDCl<sub>3</sub>) δ 25.7; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.32–7.28 (m, 6H), 7.26–7.22 (m, 4H), 7.20–7.09 (m, 4H), 7.02–6.98 (m, 4H), 5.11 (s, 2H), 2.33 (s, 6H). Freshly distilled CH<sub>2</sub>Cl<sub>2</sub> was added and the homogeneous solution was cooled to 0° and allyltri-*n*-butyltin (435 μL, 464 mg, 1.4 mmol) was added dropwise. The reaction mixture was stirred at 0° for 10 minutes, followed by 2 hours at room temperature. A purified aliquot displayed the following spectroscopic data: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.52–6.92 (m, 18H), 6.21–6.09 (m, 1H), 5.34–5.11 (m, 2H), 4.78 (s, 2H), 2.77 (dd, *J* = 8.9, 1.9 Hz, 2H), 2.32 (s, 3H).

The resulting solution was cooled to –78° and a solution of benzaldehyde (1.28 mL, 133.6 mg, 1.26 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) was added dropwise. The reaction mixture was stirred at –78° for 2.5 hours, and aqueous buffer (pH 7.5) was added. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (5 mL), the combined organic phases were washed with brine, and the solvent was evaporated. The residue was taken up in Et<sub>2</sub>O/hexane (2 : 1, 10 mL), and the resulting solution was cooled to 0° for 20 minutes to complete precipitation of the solid. After removal of the (*R,R*)-bis(sulfonamide) (0.694 g, 92%) by filtration through a sintered glass funnel, the filtrate was vigorously stirred with aqueous KF (50%, 15 mL) at room temperature for 40 minutes. The organic layer was separated and dried with anhydrous MgSO<sub>4</sub>, filtered, and the solvent was removed under reduced pressure. The product was purified by silica gel chromatography (hexane/Et<sub>2</sub>O, 5 : 1) to afford 170 mg (1.12 mmol) of the title product (91% yield) as a colorless liquid; [α]<sub>D</sub> +44.78° (c 1.26, benzene); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.41–7.28

(m, 5H), 5.92–5.73 (m, 1H), 5.22–5.13 (m, 2H), 4.80–4.61 (m, 1H), 2.51–2.30 (m, 2H), 2.05 (d,  $J = 3.0$  Hz, 1H).

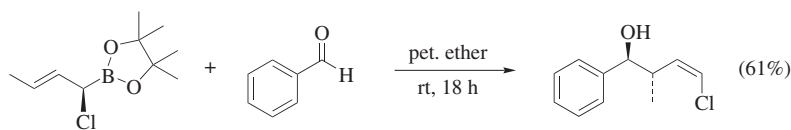


**(1R)-2-[1-Chloro-2-(*E*)-butenyl]pinacol Boronate [Preparation of a Chiral  $\alpha$ -Chloro Allylic Boronate].<sup>83,237</sup>**

(*R*)-3-Hydroxy-1-butyne (16.58 g, 236.5 mmol) and hexamethyldisilazane (19.09 g, 118 mmol) were heated to 110° for 12 hours. The mixture was then filtered through a short pad of silica gel to give 33.30 g (99%) of 3-trimethylsiloxy-1-butyne as an almost colorless liquid. Under an atmosphere of N<sub>2</sub>, borane dimethylsulfide complex (8.4 mL, 84 mmol) was dissolved in DME (120 mL). The solution was cooled to 0° and cyclohexene (13.80 g, 168 mmol) was added. The mixture was stirred at 0° for 15 minutes and then warmed to room temperature and stirred for another 1 hour. The solution was cooled to 0° and 3-trimethylsiloxy-1-butyne (15.0 g, 84 mmol) was added. The reaction mixture was warmed to room temperature to dissolve the dicyclohexylborane, and stirred for an additional 1 hour. Anhydrous trimethylamine oxide (12.65 g, 84 mmol) was added in small portions to maintain the solution at reflux. The mixture was cooled to room temperature and stirred for an additional 1 hour. Pinacol (10.0 g, 84 mmol) was added and the mixture was stirred for 12 hours. The solution was filtered and the solvent was removed under reduced pressure. The resulting liquid was distilled (0.3 Torr) to give 18.60 g of pinacol (*R*)-(*E*)-2-(3-trimethylsiloxy-1-butene)boronate (83% yield), bp 68°/0.1 Torr; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.58 (dd,  $J = 17.9, 4.3$  Hz, 1H), 5.58 (dd,  $J = 17.9, 1.7$  Hz, 2H), 4.30 (ddq,  $J = 6.5, 4.3, 1.7$  Hz, 1H), 1.25 (s, 12H), 1.20 (d,  $J = 6.5$  Hz, 3H), 0.09 (s, 9H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  156.5, 83.0, 69.6, 24.7, 23.5, 0.0. Anal. Calcd for C<sub>13</sub>H<sub>27</sub>BO<sub>3</sub>Si: C, 57.78; H, 10.07. Found: C, 57.71; H, 10.16.

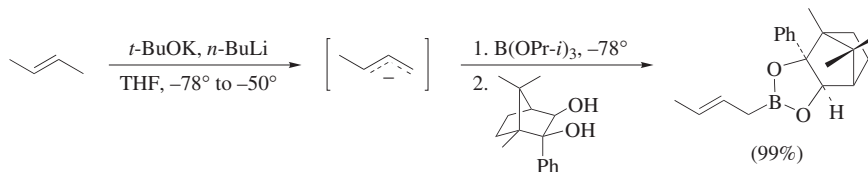
The excess of trimethylamine was removed by washing the pinacol (*R*)-(*E*)-2-(3-trimethylsiloxy-1-butene)boronate (5.0 g) in petroleum ether (50 mL) using 5% aqueous AcOH (10 mL), 4% aqueous NaHCO<sub>3</sub> (10 mL), and saturated aqueous Na<sub>2</sub>SO<sub>4</sub> solution. The aqueous phases were back extracted each time with petroleum ether (10 mL). The combined organic layers were dried over anhydrous MgSO<sub>4</sub>, filtered, and the solvent was removed under reduced pressure to afford pure pinacol (*E*)-2-(3-trimethylsiloxy-1-butene)boronate (4.84 g). Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (20 mg, 0.069 mmol) was added to a stirred solution of pinacol (*R*)-(*E*)-2-(3-trimethylsiloxy-1-butene)boronate (5.70 g, 21.1 mmol) in petroleum ether (130 mL). Freshly distilled SOCl<sub>2</sub> (2.75 g, 23.1 mmol) was added, and

slow evolution of SO<sub>2</sub> was observed. After 4 hours, when no more bubbling was observed, the mixture was filtered, and the solvent was removed under reduced pressure to afford 4.39 g of the crude title product (96% yield), which was distilled, bp 30°/0.1 Torr; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.78 (ddq, *J* = 15.1, 6.4, 0.8 Hz, 1H), 5.65 (ddq, *J* = 15.1, 9.2, 1.5 Hz, 1H), 3.94 (d, *J* = 9.2 Hz, 1H), 1.71 (ddd, *J* = 6.4, 1.5, 0.8 Hz, 3H), 1.28 (s, 12H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 129.0, 128.1, 84.4, 24.4, 17.7. Anal. Calcd for C<sub>10</sub>H<sub>18</sub>BClO<sub>2</sub>: C, 55.47; H, 8.38. Found: C, 55.50; H, 8.64.



**(1*S*,2*S*)-(Z)-4-Chloro-2-methyl-1-phenylbut-3-en-1-ol [Representative Addition of Pinacol (1*R*)-2-[1-Chloro-2-(*E*)-butenyl]boronate to Aldehydes].<sup>67</sup>**

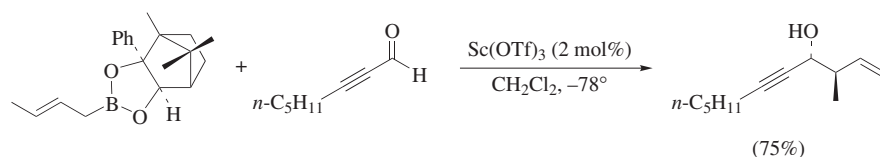
To a solution of crude pinacol (1*R*)-2-[1-chloro-2-(*E*)-butenyl]boronate (1.80 g, 8.3 mmol) in petroleum ether (15 mL) was added benzaldehyde (0.59 g, 5.5 mmol) at 0°. After 18 hours at room temperature, the mixture was evaporated, the residue was dissolved in Et<sub>2</sub>O, and triethanolamine (1.24 g, 1.10 mL, 8.3 mmol) was added under vigorous stirring. After 4 hours, the mixture was filtered and the solvent was removed by evaporation. The crude product was purified by flash column chromatography (7:3 petroleum ether/ether) to afford 0.66 g of the title product (61% yield); [α]<sub>D</sub><sup>20</sup> +44.5° (*c* 10, CDCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.34 (m, 5H), 6.13 (dd, *J* = 0.9, 7.2 Hz, 1H), 5.75 (dd, *J* = 7.2, 9.4 Hz, 1H), 4.50 (d, *J* = 7.3 Hz, 1H), 3.14 (dddq, *J* = 0.9, 6.9, 7.3, 9.4 Hz, 1H), 2.02 (br s, 1H), 0.90 (d, *J* = 6.9 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 142.3, 133.6, 128.2, 127.7, 126.6, 119.2, 77.8, 39.8, 16.0. Anal. Calcd for C<sub>11</sub>H<sub>13</sub>ClO: C, 67.18; H, 6.66. Found: C, 67.27; H, 6.74.



**(1*R*,2*S*,3*R*,4*S*)-2,3-*O*-[(*E*)-2-Butenylboryl]-2-phenyl-1,7,7-trimethylboranediol [Preparation of the (*E*)-Crotyl Camphordiols Boronate Reagent].<sup>28</sup>**

A 200-mL three-neck round-bottom flask equipped with a magnetic stir bar and a thermometer was charged with 110 mL of THF and *t*-BuOK (4.65 g, 41.5 mmol). The mixture was flushed with Ar and cooled to -78°. *trans*-2-Butene (2.46 g, 43.9 mmol), condensed into a rubber-stoppered 10-mL round-bottom flask kept at -78°, was added via cannula. *n*-BuLi (1.43 M in hexane, 29 mL, 41.5 mmol) was added dropwise over 1 hour with a syringe pump, so that the internal temperature did not rise at all. After completion of the addition, the reaction mixture

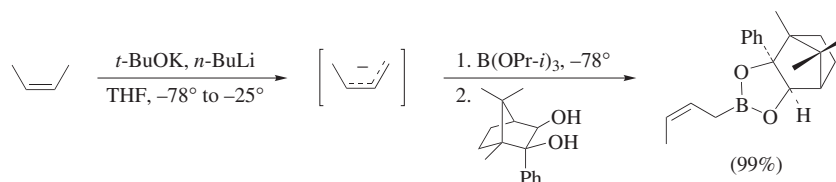
was allowed to warm until the internal temperature reached  $-52^{\circ}$ . The solution was maintained at  $-52^{\circ}$  for 15 minutes, and then cooled back to  $-78^{\circ}$ . Triisopropyl borate (10.53 mL, 45.6 mmol) was added dropwise over 30 minutes through a syringe pump. The reaction mixture was maintained at  $-78^{\circ}$  for 2 hours, and was sealed under Ar and stored in a freezer for a few weeks without any noticeable change of its quality. The stored solution (10 mL) was reacted with 15 mL of aqueous 1 N HCl, and extracted with ether three times. The combined organic layers were mixed with (1*R*,2*S*,3*R*,4*S*)-2-phenyl-1,7,7-trimethylbornanediol (220 mg, 0.89 mmol), stirred at ambient temperature for 45 minutes, and then concentrated under reduced pressure. Flash chromatography (5% EtOAc/hexanes, SiO<sub>2</sub> pre-treated with 5% Et<sub>3</sub>N/hexanes) yielded 277 mg of the title product as a colorless oil (99% yield);  $[\alpha]_D^{25} +10.5^{\circ}$  (*c* 1.84, CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.42–7.41 (m, 2H), 7.34–7.24 (m, 3H), 5.43–5.30 (m, 2H), 4.71 (s, 1H), 2.13 (d, *J* = 5.5 Hz, 1H), 1.84–1.78 (m, 1H), 1.61–1.52 (m, 5H), 1.20–1.13 (m, 5H), 1.04–0.94 (m, 1H), 0.93 (s, 3H), 0.92 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  141.8, 127.4, 127.2, 126.7, 125.7, 125.2, 95.6, 88.5, 52.0, 50.2, 48.8, 29.6, 24.8, 23.6, 20.7, 18.0, 9.3; <sup>11</sup>B NMR (64 MHz, CDCl<sub>3</sub>)  $\delta$  34.2; HRMS-EI (*m/z*): calcd for C<sub>20</sub>H<sub>27</sub>O<sub>2</sub>B, 310.21042; found, 310.20994. Anal. Calcd for C<sub>20</sub>H<sub>27</sub>O<sub>2</sub>B: C, 77.43; H, 8.77. Found: C, 77.24; H, 8.86.



**(3*R*,4*R*)-3-Methyl-1-undecen-5-yn-4-ol [Representative Procedure for Scandium-Catalyzed *E*-Crotylation of Aldehydes].**<sup>28</sup> Scandium trifluoromethanesulfonate (238 mg, 0.48 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (5 mL) were introduced in a 50-mL round-bottom flask, and the mixture was cooled to  $-78^{\circ}$ . 2-Octynal (1.03 mL, 7.25 mmol) was added, followed by a solution of (1*R*,2*S*,3*R*,4*S*)-2,3-*O*-[(*E*)-2-butenylboryl]-2-phenyl-1,7,7-trimethylbornanediol (1.50 g, 4.83 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (7 mL) dropwise over 30 minutes. The resulting mixture was stirred at  $-78^{\circ}$  for 24 hours, then DIBAL-H (1.0 M in toluene, 14.5 mL, 14.5 mmol) was added. The mixture was stirred at  $-78^{\circ}$  for 1 hour, then carefully poured into a 250-mL separatory funnel containing aqueous 1 N NaOH (50 mL). After the resulting layers were separated, the aqueous layer was extracted with EtOAc (3  $\times$  25 mL). The combined organic layers were dried over anhydrous MgSO<sub>4</sub>, filtered, and the solvent was removed under reduced pressure. Flash chromatography (5% EtOAc/hexanes) afforded 594 mg of the title product as a colorless oil (75% yield);  $[\alpha]_D^{25} +16.55^{\circ}$  (*c* 2.00, CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  5.82 (ddd, *J* = 17.7, 10.4, 7.6 Hz, 1H), 5.17–5.12 (m, 2H), 4.19 (ddd, *J* = 6.2, 3.8, 1.9 Hz, 1H), 2.44–2.40 (m, 1H), 2.21 (ddd, *J* = 9.0, 7.1, 1.9 Hz, 2H), 1.82 (br s, 1H), 1.54–1.48 (m, 2H), 1.40–1.29 (m, 4H), 1.12 (d, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  139.6, 116.4,

86.6, 79.5, 66.4, 44.7, 31.0, 28.3, 22.1, 18.6, 15.2, 13.9; HRMS-ES ( $m/z$ ): calcd for  $C_{12}H_{20}ONa$ , 203.14064; found, 203.14084.  $^{19}F$  NMR analysis of the Mosher ester derivative indicated 97% ee: (376 MHz,  $CDCl_3$ )  $\delta$  - 71.88 (major), -72.14 (minor).

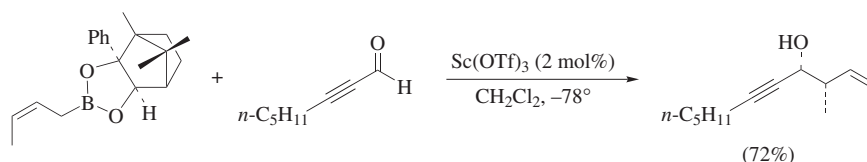
The fractions containing the diol auxiliary and those containing borate derivatives were concentrated, and treated with a solution of THF (2 mL), 1 N NaOH (1 mL), and  $H_2O_2$  (1 mL of a 30% aqueous solution) for 16 hours. The resulting mixture was diluted with water (5 mL) and extracted with EtOAc ( $3 \times 10$  mL). The combined organic layers were dried over anhydrous  $MgSO_4$ , filtered, and concentrated. Flash chromatography (5% EtOAc/hexanes) afforded 891 mg of recovered (1*R*,2*S*,3*R*,4*S*)-2-phenyl-1,7,7-trimethylbornanediol (75% yield).



**(1*R*,2*S*,3*R*,4*S*)-2,3-*O*-[(*Z*)-2-Butenylboryl]-2-phenyl-1,7,7-trimethylbornanediol [Preparation of the (*Z*)-Crotlyl Camphordiols Boronate Reagent].<sup>28</sup>**

A 300-mL three-neck round-bottom flask equipped with a magnetic stir bar and a thermometer was charged with 110 mL of THF and *t*-BuOK (2.86 g, 25.5 mmol). After the mixture was flushed with Ar and cooled to  $-78^\circ$ , *cis*-2-butene (1.50 g, 26.8 mmol), condensed into a rubber-stoppered 10-mL round-bottom flask kept at  $-78^\circ$ , was added via cannula. *n*-BuLi (1.43 M in hexane, 17.9 mL, 25.5 mmol) was added dropwise over 1 hour such that the internal temperature did not rise above  $-70^\circ$ . After completion of the addition, the cooling bath was removed and the reaction mixture was allowed to warm up until the internal temperature reached  $-25^\circ$ . The solution was maintained at  $-25^\circ$  for 30 minutes, and then cooled back to  $-78^\circ$ . Triisopropyl borate (6.48 mL, 28.1 mmol) was added dropwise over 30 minutes. The reaction mixture was maintained at  $-78^\circ$  for 2 hours, and was then rapidly poured into a 500-mL separatory funnel containing 200 mL of aqueous 1 N HCl. The layers were separated, and the aqueous layer was extracted with  $Et_2O$  ( $2 \times 100$  mL). The combined organic layers were dried over anhydrous  $MgSO_4$ , filtered, and concentrated on the rotary evaporator to a volume of about 60 mL. The resulting solution was approximately 0.4 M in (*Z*)-2-butenylboronic acid, and could be kept at  $4^\circ$  for a few weeks without any noticeable change in its concentration or its reactivity with diols. To this solution (3.00 mL, 1.20 mmol) was added (1*R*,2*S*,3*R*,4*S*)-2-phenyl-1,7,7-trimethylbornanediol (246 mg, 1.00 mmol). The resulting mixture was stirred at ambient temperature for 30 minutes, and concentrated under reduced pressure. Flash chromatography (10% EtOAc/hexanes,  $SiO_2$  pre-treated with 5%  $Et_3N$ /hexanes) yielded 307 mg of the title product as a colorless oil (99% yield);  $[\alpha]_D^{25} +12.8^\circ$  ( $c$  1.73,  $CHCl_3$ );  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$  7.44–7.38 (m,

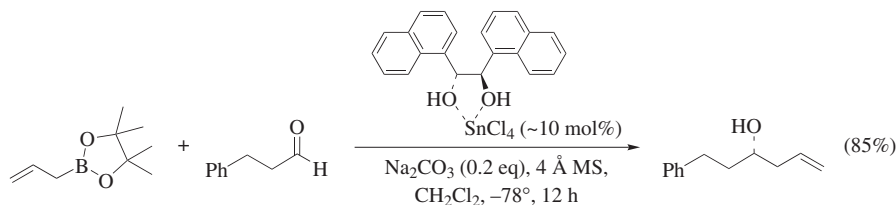
2H), 7.35–7.22 (m, 3H), 5.52–5.34 (m, 2H), 4.70 (s, 1H), 2.13 (d,  $J = 5.2$  Hz, 1H), 1.87–1.74 (m, 1H), 1.66–1.61 (m, 2H), 1.54–1.50 (m, 3H), 1.21 (s, 3H), 1.21–1.10 (m, 2H), 1.07–0.96 (m, 1H), 0.94 (s, 3H), 0.91 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  141.8, 127.4, 127.2, 126.7, 124.9, 123.5, 95.7, 88.6, 52.0, 50.2, 48.9, 29.6, 24.7, 23.6, 20.7, 12.5, 9.3;  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  34.1; HRMS-EI ( $m/z$ ): calcd for  $\text{C}_{20}\text{H}_{27}\text{O}_2\text{B}$ , 310.21042; found, 310.21036. Anal. Calcd for  $\text{C}_{20}\text{H}_{27}\text{O}_2\text{B}$ : C, 77.43; H, 8.77. Found: C, 77.41; H, 8.77.



**(3S,4R)-3-Methyl-1-undecen-5-yn-4-ol [Representative Procedure for Scandium-Catalyzed Z-Crotylation of Aldehydes].<sup>28</sup>**

The title compound was prepared in 72% yield by using a procedure analogous to that used to prepare (3*R*,4*R*)-3-methyl-1-undecen-5-yn-4-ol;  $[\alpha]_{\text{D}}^{25} +22.7^\circ$  ( $c$  1.27,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  5.94–5.80 (m, 1H), 5.20–5.17 (m, 1H), 5.15–5.12 (m, 1H), 4.26 (ddd,  $J = 4.8, 2.0, 2.0$  Hz, 1H), 2.50–2.38 (m, 1H), 2.22 (ddd,  $J = 6.9, 6.9, 2.0$  Hz, 2H), 1.72 (br s, 1H), 1.57–1.46 (m, 2H), 1.44–1.26 (m, 4H), 1.11 (d,  $J = 6.9$  Hz, 3H), 0.91 (t,  $J = 6.9$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  139.2, 116.8, 86.7, 79.2, 66.3, 44.5, 31.0, 28.4, 22.1, 18.6, 15.6, 13.9; HRMS-EI ( $m/z$ ): calcd for  $\text{C}_{12}\text{H}_{20}\text{O}$ , 180.15141; found, 180.15092.  $^{19}\text{F}$  NMR analysis of the Mosher ester derivative indicated an optical purity of 95% ee: (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -71.90 (major), -72.19 (minor).

The fractions containing the diol auxiliary and the ones containing diol-borate derivatives were concentrated, and treated with a solution of THF (2 mL), 1 N NaOH (1 mL), and  $\text{H}_2\text{O}_2$  (1 mL of a 30% aqueous solution) for 16 hours. The resulting mixture was diluted with water (5 mL) and extracted with EtOAc ( $3 \times 10$  mL). The combined organic layers were dried over anhydrous  $\text{MgSO}_4$ , filtered, and concentrated. Flash chromatography (5% EtOAc/hexanes) afforded 891 mg of recovered (1*R*,2*S*,3*R*,4*S*)-2-phenyl-1,7,7-trimethylbornanediol (75% yield).

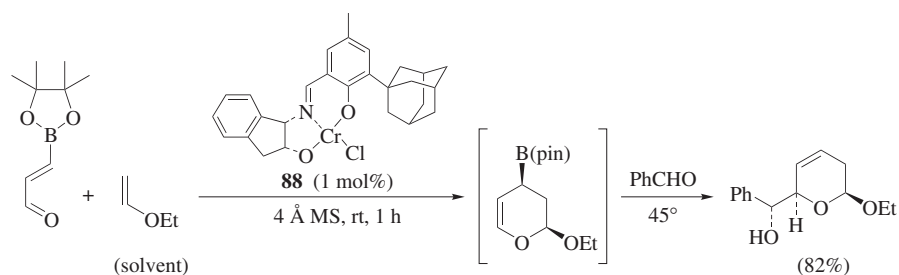


**(3S)-1-Phenylhex-5-en-3-ol [Representative Allylation Catalyzed by a Chiral Diol-SnCl<sub>4</sub> Complex].<sup>163</sup>**

Into a flame-dried 25-mL round-bottom flask equipped with a rice needle stir bar were successively added (*R,R*)-1,2-dinaphthylethanediol (8.65 mg, 0.025 mmol, 0.11 eq), anhydrous  $\text{Na}_2\text{CO}_3$  (5.6 mg,



0.05 mmol, 0.05 eq), activated 4 Å molecular sieves (50 mg), and freshly distilled toluene (0.5 mL). To the stirred mixture under argon at room temperature was added 25  $\mu$ L (0.025 mmol, 0.10 eq) of a 1.0 M solution of SnCl<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub>; in order to obtain reproducible results, it is necessary to use a gas tight 25  $\mu$ L syringe, and that all of the SnCl<sub>4</sub> drops into the diol solution without touching the side walls. The resulting mixture was stirred for 5 minutes, cooled to  $-78^\circ$ , and maintained at this temperature for 15 minutes, after which allyl boronic pinacol ester (46.2 mg, 1.1 eq) dissolved in 0.5 mL of toluene was added via syringe and this mixture was maintained at  $-78^\circ$  for 15 minutes. Freshly distilled hydrocinnamaldehyde (32.6  $\mu$ L, 0.25 mmol, 1.0 eq) was added and the reaction mixture was stirred at  $-78^\circ$  for 12 hours. DIBAL-H in toluene (0.5 mL, 0.50 mmol, 2.0 eq) was added to reduce any remaining aldehyde. After 30 minutes, 2 mL of aqueous 1 N HCl was added, after which the reaction mixture was brought to room temperature and stirred for 1 hour. The dark brown biphasic mixture was extracted with Et<sub>2</sub>O (2  $\times$  25 mL) to give a clear ethereal solution, which was washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. Purification of the residue by flash chromatography (5% EtOAc/hexanes) afforded 37.4 mg of the title product (85% yield, 78% ee); HPLC (chiracel-OD, 5% *i*-PrOH/hexane, 0.5 mL/min, 254 nm)  $t_r$  (major, 89%) = 26.19 min,  $t_r$  (minor, 11%) = 37.62 min;  $[\alpha]_D^{25} -4.54^\circ$  (*c* 0.41, CHCl<sub>3</sub>); IR (thin film) 3370, 1640 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.32–7.28 (m, 2H), 7.23–7.18 (m, 3H), 5.90–5.78 (m, 1H), 5.18 (m, 1H), 5.14 (m, 1H), 3.72–3.65 (m, 1H), 2.87–2.79 (m, 1H), 2.74–2.67 (m, 1H), 2.37–2.32 (m, 1H), 2.24–2.16 (m, 1H), 1.86–1.75 (m, 2H), 1.68–1.66 (s, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  142.05, 134.6, 128.43, 128.38, 125.8, 118.3, 69.9, 42.1, 38.5, 32.05; HRMS-EI (*m/z*): calcd for C<sub>12</sub>H<sub>16</sub>O, 176.12011; found, 176.12011. Anal. Calcd for C<sub>12</sub>H<sub>16</sub>O: C, 81.77; H, 9.15. Found: C, 81.80; H, 9.14.



**(R)-[(2R,6S)-6-Ethoxy-5,6-dihydro-2H-pyran-2-yl]phenylmethanol [Representative Example of a Tandem Catalytic Enantioselective [4+2] Cycloaddition/Allylboration].<sup>150</sup>** A mixture of 3-boronoacrolein pinacol ester (364 mg, 2.00 mmol) and ethyl vinyl ether (1.90 mL, 20.0 mmol) was placed in an oven-dried 10-mL round-bottom flask with a stir bar. To this solution was added the Jacobsen tridentate chromium(III) catalyst **88** (9.60 mg, 0.020 mmol) and powdered BaO (400 mg). After the mixture had been stirred for 1 hour at room

temperature, benzaldehyde (424 mg, 4.00 mmol) was added. The reaction mixture was stirred at 40–45° for 24 hours, and diluted with EtOAc and filtered through Celite. The EtOAc solution was stirred for 30 minutes with an aqueous saturated solution of NaHCO<sub>3</sub>. The organic layer was separated and the aqueous layer was extracted with EtOAc (2 × 20 mL). The combined organic layers were washed with an aqueous saturated solution of NaCl (20 mL), dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated to afford the crude product. Purification by flash column chromatography (deactivated silica gel, 9:1 hexanes/Et<sub>2</sub>O) afforded 384 mg of the pure title product as a clear oil (82% yield, 96% ee); HPLC (chiralpak AD-RH, 50% *i*-PrOH/H<sub>2</sub>O, 0.300 mL/min, 210.8 nm) *t*<sub>r</sub> (major) = 8.60 min, *t*<sub>r</sub> (minor) = 10.64 min; [α]<sup>23</sup><sub>D</sub> +24.9° (*c* 1.0, CHCl<sub>3</sub>); IR (CH<sub>2</sub>Cl<sub>2</sub>, cast) 3451, 3035, 2877, 1640, 1257 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.40–7.26 (m, 5H), 5.79–5.75 (m, 1H), 5.40–5.36 (m, 1H), 4.78 (dd, *J* = 5.9, 5.9 Hz, 1H), 4.56 (dd, *J* = 7.4, 1.5 Hz, 1H), 4.32–4.28 (m, 1H), 3.96 (dq, *J* = 9.7, 7.1 Hz, 1H), 3.58 (dq, *J* = 9.7, 7.1 Hz, 1H), 3.11 (br s, 1H), 2.12–2.10 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 139.8, 128.3, 128.0, 127.2, 125.4, 124.8, 98.5, 78.7, 76.8, 64.5, 31.1, 15.3; HRMS-ESI (*m/z*): [M + Na]<sup>+</sup> calcd for C<sub>14</sub>H<sub>18</sub>O<sub>3</sub>Na, 257.1154; found, 257.1152.

#### TABULAR SURVEY

Within each table, entries are organized in the order of increasing number of carbons in the carbonyl substrate, not including protecting groups. This system was adopted so as to have similar substrates grouped together. The tables cover entries from the literature up until December 31, 2005. See pages 573–580 for supplemental references for Tables 1–9 and for recent information about experimental methods, reviews, and mechanisms. In each table, for the same aldehyde, allyl transfer reagents are grouped by the type of boron reagent involved; boranes are followed by boronates, and then the others such as borinates and borate salts. In all tables, entries with the same experimental conditions but differing only in the results (yield and selectivities) are listed under a single entry. In these instances, the results noted correspond to the best reported example. Table 1A contains entries of simple allyl (C<sub>3</sub>H<sub>5</sub>) transfer to non-aromatic carbonyl substrates. Table 1B contains entries for aromatic and heteroaromatic substrates. Tables 2 and 3 cover entries of *Z*-crotylation and *E*-crotylation respectively (cis and trans C<sub>4</sub>H<sub>7</sub>). In the instances where a mixture of *E/Z* crotyl reagents is used, these entries are found in Table 2. It should be noted that readers interested specifically in the propionate products of crotylation reactions should also consult Table 4, which contains several entries of α-substituted crotylation reagents. Table 4 includes all entries with reagents having a substituent in the α position of the allylic group. Table 5 lists entries involving allyl transfer where the β position is substituted with a variety of functional groups. Table 6 reports entries where the γ position of the reagent is functionalized with a carbon or heteroatom-containing group. Table 7 presents examples of allenyl and propargyl group transfer. Table 8 consists of entries of cyclic allylic boron reagents, where the allylic unit is part

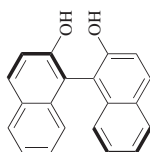
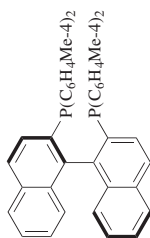
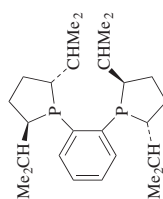
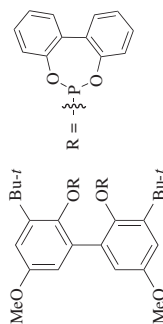
of a ring. Table 9 contains entries of intramolecular allylboration reactions. For multiple substitution patterns, the entries are ordered by least to most substituted; entries with the same number of substitutions are prioritized by  $\alpha > \gamma > \beta$ . The authors would like to mention that some entries employing the Ipc reagents are inconsistent with respect to the nomenclature used for the absolute configuration of the reagent. These inconsistencies originate from the source references.

The following abbreviations were used in the text and the Tables:

Ac	acetyl
acac	acetylacetone
Adm	adamantyl
AIBN	2,2'-azo(bis)isobutyronitrile
Ald	aldehyde
All	allyl
B <sub>2</sub> (cat) <sub>2</sub>	bis(catecholato)diboron
BBN	9-borabicyclo[3.3.1]nonanyl
BEC	2-bromoethyloxycarbonyl
bmim	butylmethylimidazolium
Bn	benzyl
Boc	<i>tert</i> -butoxycarbonyl
BPS	<i>tert</i> -butyldiphenylsilyl
Bu	butyl
Bz	benzoyl
Cbz	carbobenzyloxy
Conc.	concentration
Cy	cyclohexyl
dba	dibenzylideneacetone
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DEIPS	diethylisopropylsilyl
DIPT	diisopropyl tartrate
DMB	3,4-dimethoxybenzyl
DMF	dimethylformamide
DMPM	3,4-dimethoxybenzyl
DMSO	dimethyl sulfoxide
dppe	diphenylphosphinoethane
dppf	diphenylphosphinoferrrocene
d.r.	diastereomeric ratio
ee	enantiomeric excess
emim	ethylmethylimidazolium
equiv or eq.	equivalent
e.r.	enantiomeric ratio
Et	ethyl
HQ	hydroquinone
8-HQ	8-hydroquinoline



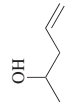

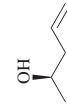



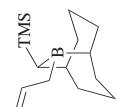

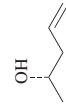


Icr	isocaranyl
IL	ionic liquid
Ipc	isopinocampheyl
Ket	ketone
L.A.	Lewis acid
LDA	lithium diisopropylamide
MEM	2-methoxyethoxymethyl
Mes	mesityl
min	minute
MOM	methoxymethyl
MS	molecular sieves
Nph	naphthyl
Ph	phenyl
Phth	phthalyl
Piv	pivaloyl
PMB	<i>p</i> -methoxybenzyl
PMP	<i>p</i> -methoxyphenyl
Pr	propyl
PTC	phase-transfer catalyst
pTSA	<i>p</i> -toluenesulfonic acid
pyr	pyridine
rt	room temperature
SEM	2-(trimethylsilyl)ethoxymethyl
siamyl	<i>sec</i> -isoamyl
TBAT	tetrabutylammonium triphenylsilyldifluorosilicate
TBDMS	<i>tert</i> -butyldimethylsilyl
TBDPS	<i>tert</i> -butyldiphenylsilyl
TEAN	tetraethylammonium nitrate
TES	triethylsilyl
Thex	thexyl (2,3-dimethyl-2-butyl)
Tf	trifluoromethanesulfonyl
TFA	trifluoroacetic acid
TfOH	trifluoromethanesulfonic acid
THF	tetrahydrofuran
THP	tetrahydropyranyl
TIPS	triisopropylsilyl
TMP	2,2,6,6-tetramethylpiperidine
TMS	trimethylsilyl
TMSE	2-(trimethylsilyl)ethyl
Tol	<i>p</i> -tolyl
Ts	<i>p</i> -toluenesulfonyl
TPS	triphenylsilyl
Tr	trityl

CHART 1. ACRONYMS FOR LIGANDS USED IN TABLES

*(R)*-BINOL*(R)*-Tol-BINAP*(R,R)*-*t*Pr-DUPHOS

BIPHEPHOS

TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS  
A. NON-AROMATIC CARBONYL SUBSTRATES

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
$\text{C}_2$ 		Neat, 0-10°	 (88)	238
		Ether, -78° to rt	 (72), 7  I	239, 136a
		THF, -78°, 3 h	I (-), 92	136, 239, 240
	"	Ether, -78° to rt	I (74), 93	240, 136a
	"	Ether, -100° <sup>a</sup>	I (-), >99	139, 241
		Ether, -78° to rt	I (72), 99	239, 136a
	"	THF, -78°, 3 h	I (-), 98	240
	"	Ether, -100° <sup>a</sup>	I (-), >99	139
		Ether, 3 h	Temp I rt (-), 94 0° (-), 93 -25° (-), 98 -78° (71), 96	143
		Pentane, ether, -100°	 (70), 94  I	204
		THF, -78°, 3 h	I (-), 98	240
	"	Ether, -100° <sup>a</sup>	I (-), >99	139, 242











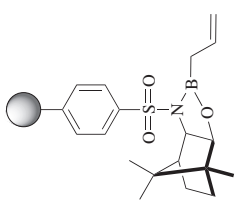
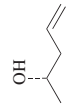


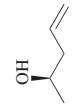


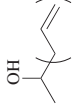


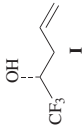


	Ether, -78° to rt	<b>I</b> (65), 11	239, 136a
	Ether, -78° to rt	<b>I</b> (72), 93	239, 136a
	Ether, -78° to rt	<b>I</b> (67), 34	239, 136a
	Hexane, -40°	 (86), 86	122, 243
..	Hexane, -40°, 1 h; rt, 12 h	<b>I</b> (92), 65	244
	Hexane, -40°	<b>I</b> (82), 33	122
	Hexane, -40°	 (92), 38	122
	Ether, -78° to rt, 2 h	<b>I</b> (47), 96	133

TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBOXYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
$C_2$ 		Ether, $-78^\circ$ , 7 h	 (51), 92	245, 246
	$B[(-)-Ipc]_2$ 	Pentane, ether, $-100^\circ$	 (71), 94	247
	BBN 	Pentane, rt, 2 h	 R Cl (95) OAc (95) OEt (90) NMe <sub>2</sub> (50-57) OBBN (84)	103
	$B[(+)-Ipc]_2$ 	Pentane, ether, $-100^\circ$	 I (50), 99	248, 249
	$B(2-dIcp)_2$ 	Pentane, ether, $-100^\circ$	<b>I</b> (—), >99	248



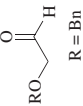

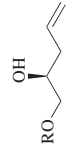

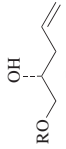

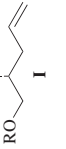

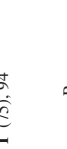
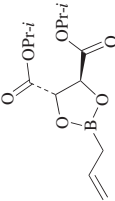
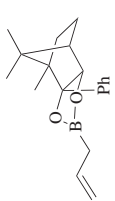
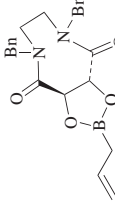
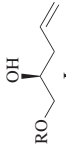
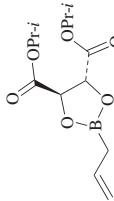
 R = Bn		—	 <b>I</b> (74), 92	250								
		Pentane, ether, $-100^\circ$ , 1 h	 <b>I</b> (95), 71	251								
		Ether, $-78^\circ$ to rt, 12 h	 <b>I</b>	252								
R = PMB		Ether, $-78^\circ$ , 4 h	 <b>I</b> (75), 94	253								
R = Bn, TBDPS		4 Å MS, toluene, $-78^\circ$	<table border="0"> <tr> <td>R</td> <td></td> </tr> <tr> <td>Bn</td> <td>(42-70), 59</td> </tr> <tr> <td>TBDPS</td> <td>(42-70), 56</td> </tr> </table>	R		Bn	(42-70), 59	TBDPS	(42-70), 56	170		
R												
Bn	(42-70), 59											
TBDPS	(42-70), 56											
R = Bn, TBDMS, TBDPS		Sc(OTf) <sub>3</sub> (10 mol%), CH <sub>2</sub> Cl <sub>2</sub> , $-78^\circ$ , 12 h	<table border="0"> <tr> <td>R</td> <td></td> </tr> <tr> <td>Bn</td> <td>(62), 77</td> </tr> <tr> <td>TBDMS</td> <td>(76), 90</td> </tr> <tr> <td>TBDPS</td> <td>(61), 90</td> </tr> </table>	R		Bn	(62), 77	TBDMS	(76), 90	TBDPS	(61), 90	27, 28
R												
Bn	(62), 77											
TBDMS	(76), 90											
TBDPS	(61), 90											
R = Bn		4 Å MS, toluene, $-78^\circ$ , 46 h	 <b>I</b>	131								
R = TBDMS		4 Å MS, toluene, $-78^\circ$	<b>I</b> (42-70), 59	170								

TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBOXYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		THF, -100°, 4 h		(80), >98, 97:3 d.r. 254, 255
		THF, -100°, 4 h		(82), >98, 97:3 d.r. 254
		Neat, 0°		238
		Neat, 0°	<b>I</b> (88)	238
		Neat, 0°	<b>I</b> (70)	238
		Neat, 0-20°	<b>I</b> (80)	238
		Ether, -110° to 20°, 15 min		(50), 89 256
		Ether, -110° to 20°, 15 min		(50), 92 256
		Ether, -100°, 1 h		(82), 94 257

C <sub>3</sub>						240
		B(-)-Ipc <sub>2</sub>	THF, -78°, 3 h		I (-), 96	139
		"	Ether, -100° <sup>a</sup>		I (79), 86	239, 136a
		B(4-d-1cr) <sub>2</sub>	Ether, -78° to rt		I (-), 93	240
		"	THF, -78°, 3 h		I (-), 98	139
		"	Ether, -100° <sup>a</sup>			
		B(2-d-1cr) <sub>2</sub>	THF, -78°, 3 h		I (-), 95	240
		"	Ether, -100° <sup>a</sup>		I (-), >99	139
			Ether, -78°, 3 h		I (71), >99	143
			Hexane, -40°		I (86), 50	122
		B(+)-Ipc <sub>2</sub>	Ether, -90°		I (49), 95	258
		B(-)-Ipc <sub>2</sub>	Ether, -78°		I (49), 90	259

TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBOXYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Ether, -100°, 1 h	(48), 98	261
		-70° to 130°	(71)	262, 1
		Neat, 0-10°	<b>I</b> (92)	238
		Neat, 0-10°	<b>I</b> (90)	238
		Ether, -100°, 3 h	(80), 96	141
		THF, -78° to rt Ether, -78°, 3 h	<b>I</b> (71), 86 <b>I</b> (-), 86	136, 136a 240
		Ether, -78° to rt THF, -78°, 3 h	<b>I</b> (76), 91 <b>I</b> (-), 91	239, 136a 240
		THF, -78°, 3 h	(-), 94	240

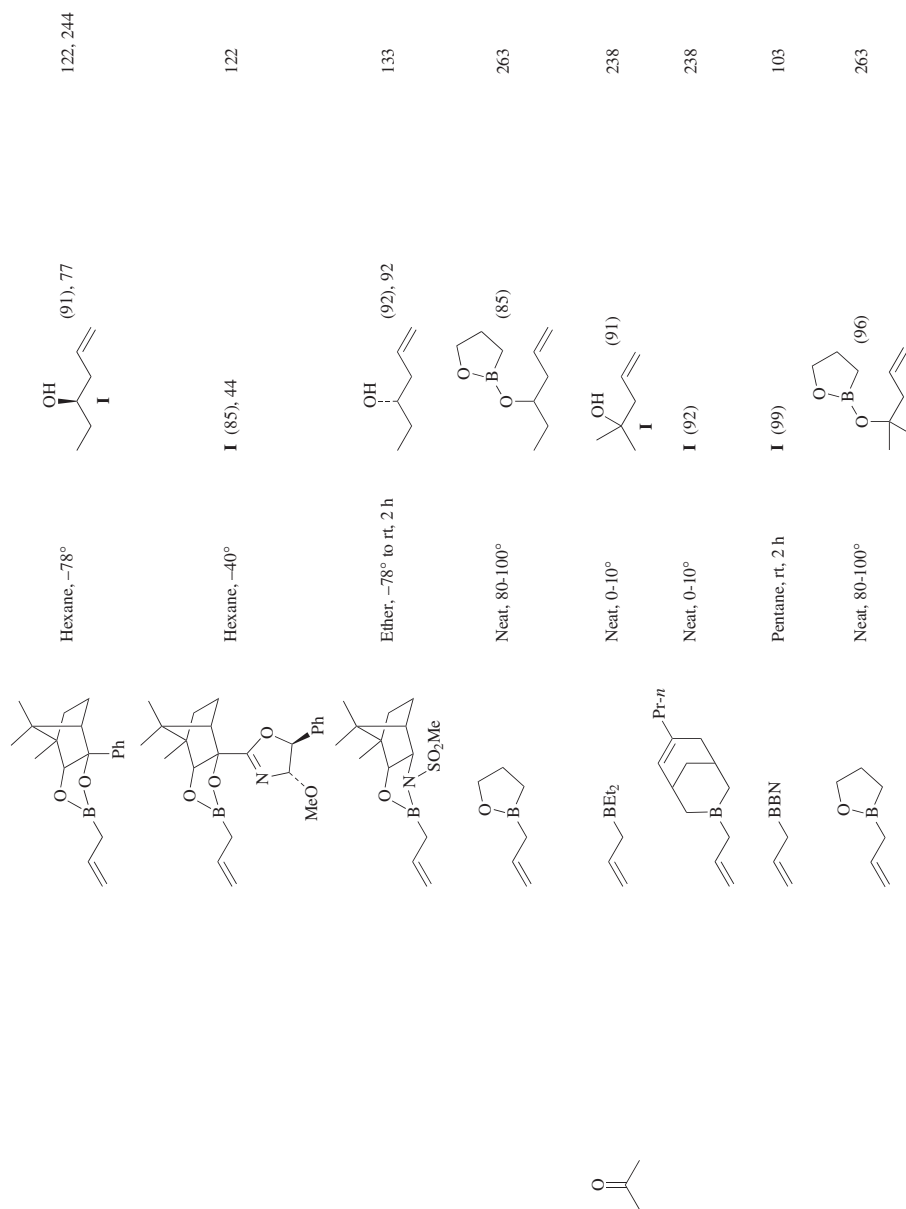

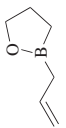
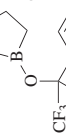


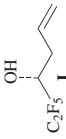



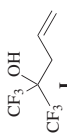
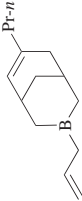
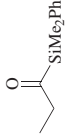




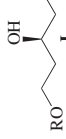

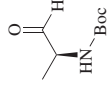

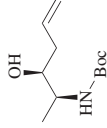
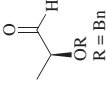

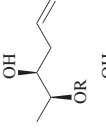

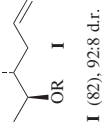

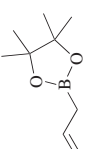
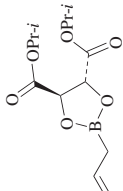
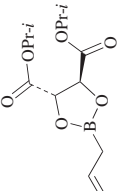
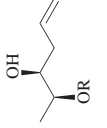
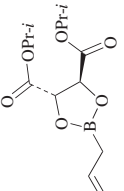
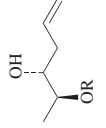


TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBONYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
$C_3$ 		Neat, 80-100°		263
	$B[(+)-\text{Ipc}]_2$ 	Pentane, ether, -100°	 (65), >99	248
	$B(2\text{-}d\text{-Icr})_2$ 	Pentane, ether, -100°	$I(-)$ , >99	248
	$BEt_2$ 	Neat, 0-10°	 (78)	238
		Neat, 0-10°	$I(83)$	238
	$B[(+)\text{-Ipc}]_2$ 	Ether, -78° to rt, 3 h	 (66), 6	111
		Ether, -100°, 3 h	 (92), 84	141
$R = \text{Bn}$	$B[(+)\text{-Ipc}]_2$ 	Ether, -78°, 4 h	$I(90)$ , 85	264
$R = \text{TBDMS}$	"	Ether, -100° to -78°	$I(82)$ , 85	265

R = TBDPS		THF, -78° Ether, -78°	<b>I</b> (99), 88 <b>I</b> (97), 91	266 267
R = PMB		Ether, -78° to rt, 4 h	<b>I</b> (90), 85	253, 268
R = Bn		Ether, -78° to rt, 3 h	<b>I</b> (83), 94	269, 270
R = TBDPS		THF, -78°, 3 h		264
R = Bn	"	Toluene, -78°	<b>I</b> (98), 84	271
R = Bn		Ether, THF	<b>I</b> (87), >95	272
R = PMB		Ether, -78°	<b>I</b> (96)	273
R = Bn, TBDPS		4 Å MS, toluene, -78°	$\frac{\text{R}}{\text{Bn}}$ <b>I</b> (90), 66 TBDPS (91), 63	170
R = TBDMS		4 Å MS, toluene, -78°		170
R = TBDPS		Sc(OTf) <sub>3</sub> (10 mol%), CH <sub>2</sub> Cl <sub>2</sub> , -78°, 12 h		27, 28

TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBOXYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		—	 (75), 97:3 d.r.	274
		Ether, -78°, 3 h	 (80), 94:6 d.r.	167, 166
		Ether, -78°, 3 h	 (75), 96:4 d.r.	167, 166
R = TBDMS		Ether, -78°, 3 h	<b>I</b> (82), 92:8 d.r.	167, 166
R = Bn		—	<b>I</b> (—), 55:45 d.r.	118
		THF, -78° to rt, 12 h	<b>I</b> (97), 65:35 d.r.	275
		4 Å MS, toluene, -78°, 4 h	 (—), 72:28 d.r.	170
		4 Å MS, toluene, -78°, 4 h	 (16), 84:16 d.r.	170



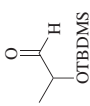

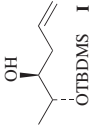
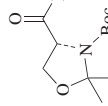

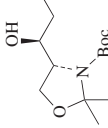
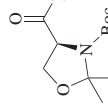
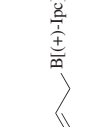
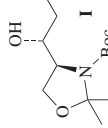

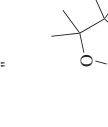
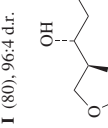

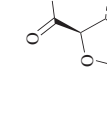
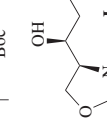

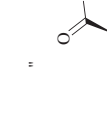
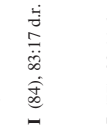









		$\text{BF}_3 \cdot \text{OEt}_2$ (0.05 mol%), $\text{CH}_2\text{Cl}_2$ , rt, 3-6 h		99
		<i>n</i> -Bu <sub>4</sub> Ni (10 mol%), $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ , rt, 30 min		276
		Ether		281
		Ether		277, 278
		—		279, 280
		$\text{CH}_2\text{Cl}_2$ , rt		277
		4 Å MS, -78°		277
		Toluene, -78°, 3 h		282
		Toluene		278

TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBOXYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		4 Å MS, -78°	 Solvent: toluene (→) 85:15 d.r., THF (→) 87:13, Et <sub>2</sub> O (84) 90:10	277
	"	Toluene, -78°, 3 h	<b>I</b> (78), 82:18 d.r.	282
		Ether	<b>I</b> (84), 90:12 d.r.	278
		THF, -78° to rt	 (75)	283, 284
		Toluene, -78°, 3 h	 (89)	282
		Toluene, -78°, 3 h	 (84)	282
		Ether, -78°, 3.5 h	 TBDDPSO (68), 12:1 d.r.	285

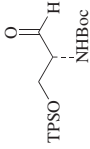

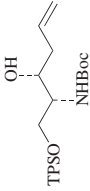






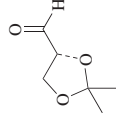

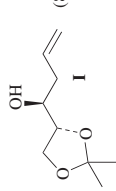
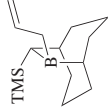
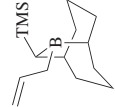
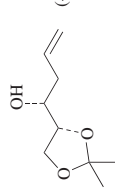
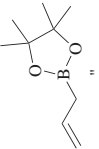
		Ether, -78°, 3.5 h		(-), 12:1 d.r.	286
		Et3N, CH2Cl2, -10° to rt, 13 h		(86)	105
		Et3N, CH2Cl2, -10° to rt, 15 h		(84)	109
		Ether, -100°, 6 h		(88), 97:3 d.r.	287
		Ether, -78°	<b>I</b> (-), 95:5 d.r.		143
		Ether, -78°		(-), >99:1 d.r.	143
		Petroleum ether, -78° to rt, 13 h	<b>I</b> (60), 78:22 d.r.		288
		CH2Cl2, -78°, 24-48 h	<b>I</b> (75), 80:20 d.r.		124
		Toluene, -78°, 24-48 h	<b>I</b> (-), 71:29 d.r.		124

TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (*Continued*)  
 A. NON-AROMATIC CARBOXYL SUBSTRATES (*Continued*)

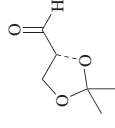
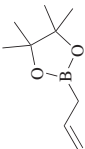
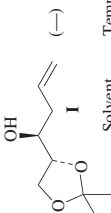
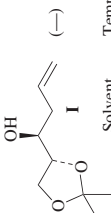
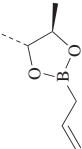
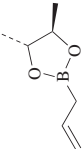


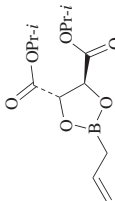
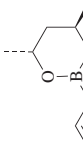
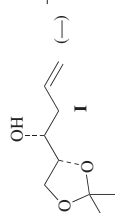
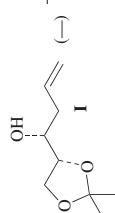
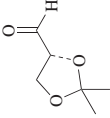
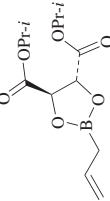
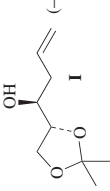
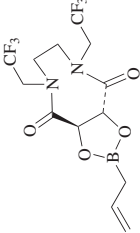
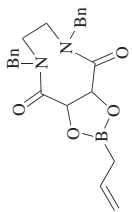
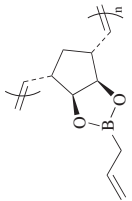
Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.			
		See table	 	118			
					Solvent	d.r.	
					CH <sub>2</sub> Cl <sub>2</sub>	-78°	80:20
					CH <sub>2</sub> Cl <sub>2</sub>	rt	77:23
					toluene	-78°	71:29
					toluene	rt	73:27
					hexane	-78°	75:25
					hexane	rt	79:21
					ether	rt	77:23
					THF	rt	71:29
DMF	0° to rt	58:42					
		CH <sub>2</sub> Cl <sub>2</sub> , -78°, 24-48 h		124			
					Toluene, -78°, 24-48 h		124
		CH <sub>2</sub> Cl <sub>2</sub> , -78°, 24-48 h		124			
					4 Å MS, toluene		d.r. rt 64:36 0° 70:30 -23° 77:23 -78° 93:7



TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBONYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		4 Å MS, -78°	 d.r. 98:2 Solvent: toluene CH <sub>2</sub> Cl <sub>2</sub> 96:4	125, 170
C <sub>3</sub>	"	4 Å MS, toluene	Temp d.r. rt 93:7 0° 94:6 -23° 96:4 -78° 98:2	125
		4 Å MS, toluene, -78°, 8 h	<b>I</b> (73), >99:1 d.r.	132
		4 Å MS, toluene, -78°, 43 h	Reagent % Conv. d.r. R,R <b>I</b> 81 99.7:0.3 S,S 84 2:98	131
		CH <sub>2</sub> Cl <sub>2</sub> , H <sub>2</sub> O, rt, 5 h	<b>I</b> (81), 67:33 d.r.	234

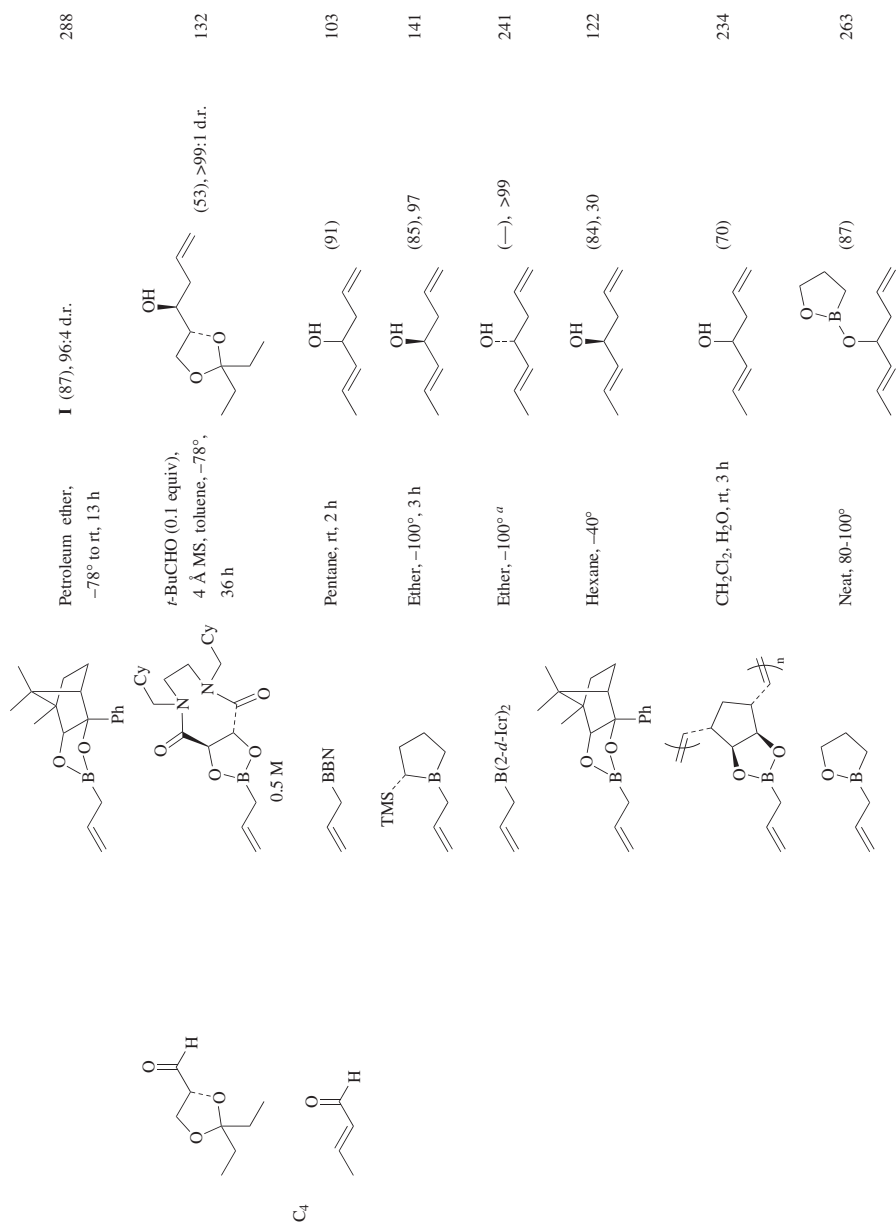





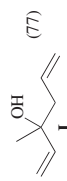

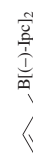
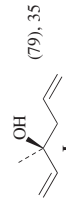
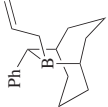


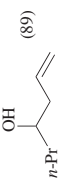

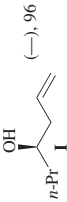
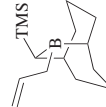


TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBONYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		THF, -78° to rt	 (76), 79	136a
		Neat, 0-10°	 (77)	238
		Pentane, rt, 2 h	<b>I</b> (94)	103
		THF, -78° to rt	 (79), 35	136a
		Ether, -78°	<b>I</b> (77), 81	145
		Neat, 0-10°	 (89)	238
		Ether, -100° <sup>a</sup>	 (-), 96	139, 289
	"	Ether, -78° to rt	<b>I</b> (72), 87	136, 136a 240
	"	THF, -78° to rt	<b>I</b> (88), 83	166
		Ether, -78°, 3 h	<b>I</b> (79), >99	143








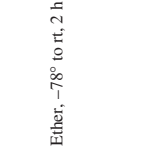

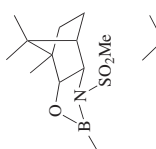
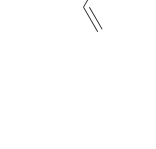

	Ether, $-100^{\circ}$ <sup>a</sup>	<b>I</b> (—), 98	139
"	Ether, $-78^{\circ}$ to rt	<b>I</b> (73), 89	239, 166, 240
"	THF, $-78^{\circ}$ , 3 h	<b>I</b> (—), 88	240
	Ether, $-100^{\circ}$ <sup>a</sup>		139, 241, 242
"	THF, $-78^{\circ}$ , 3 h	<b>I</b> (—), 94	240
	—		2
	Toluene, $-78^{\circ}$ , 18 h		290
	Ether, $-78^{\circ}$ to rt, 2 h	<b>I</b> (78), 96	133
	Hexane, $-40^{\circ}$		122
"	Hexane, $-40^{\circ}$ , 1 h; rt, 12 h	<b>I</b> (93), 72	244

TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBONYL SUBSTRATES (Continued)


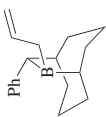

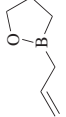
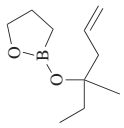

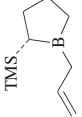
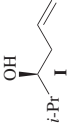
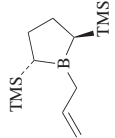
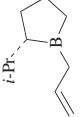
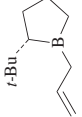

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C <sub>4</sub> 		Ether, -78°	 (80), 87	145
		Neat, 80-100°	 (86)	263
		Ether, -100°, 3 h	 (85), 96	141
		Ether, -100°, 3 h	<b>I</b> (82), 71	141
		Ether, -100°, 3 h	<b>I</b> (87), 24	141
		Ether, -100°, 3 h	<b>I</b> (95), 72	141
		Ether, -78° to rt	<b>I</b> (86), 90	136, 136a
	"	Ether, -78°, 3 h	<b>I</b> (-), 88	240
	"	Ether, -100° <sup>a</sup>	<b>I</b> (-), 96	139



TABLE 1. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBONYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Et3N, CH2Cl2, -10° to rt, 13 h		105
	Neat, 0-10°		238	
	Ether, -100°, 0.5 h		291	
	Ether, -100° to -78°, 3 h		(68), 91	
	THF, reflux, 2 h		293, 294	
	4 Å MS, toluene, -78°		R TBDMS (-), 77 TBDPS (-), 74 Bn (-), 78	
	4 Å MS, toluene, -78°		I (-), 82	

R = TBDMS, TBDPS, Bn

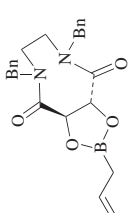
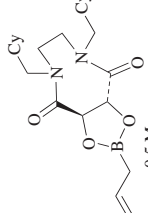
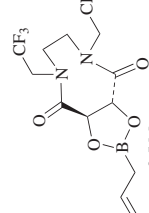
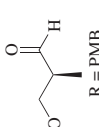

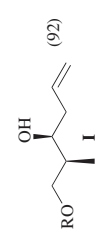


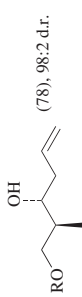


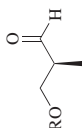
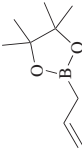
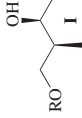
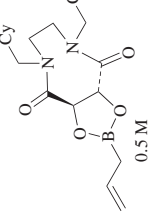
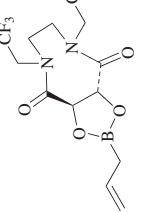
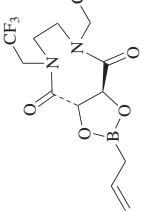
		4 Å MS, toluene, -78°, 37 h	<b>I</b> (58), 94	131
		<i>t</i> -BuCHO (0.1 equiv), 4 Å MS, toluene, -78°, 36 h	<b>I</b> (72), 94	132
		<i>t</i> -BuCHO (0.1 equiv), 4 Å MS, THF, -78°, 5 h	<b>I</b> (80), 95	132
		Ether, -110°, 3 h <sup>a</sup>		295
	"	Ether, -100°	<b>I</b> (70)	296
R = Bn		Ether, -78°, 3 h	<b>I</b> (80), 96:4 d.r.	167
		Ether, -78°, 3 h		167
R = TBDPDS		—		280

TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBOXYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
 R = TBDMS, TBDPS, Bn		Toluene, rt	 OH RO I R TBDMS TBDPS Bn d.r. 52:48 54:46 54:46	169
		4 Å MS, toluene, -78°	R TBDMS (71) TBDPS (-) Bn (-) d.r. 89:11 79:21 83:17	169, 297, 170
R = TBDPS	 0.5 M	4 Å MS, THF, -78°, 36 h	I (71), 95.5 d.r.	132
R = TBDPS, TBDMS	 CF <sub>3</sub>	4 Å MS, THF, -78°	R TBDPS TBDMS Time 8 h (82) 9 h (72) d.r. 92:8 95:5	132
R = TBDMS	 CF <sub>3</sub>	4 Å MS, THF, -78°, 9 h	OH RO I (76), 94:6 d.r.	132

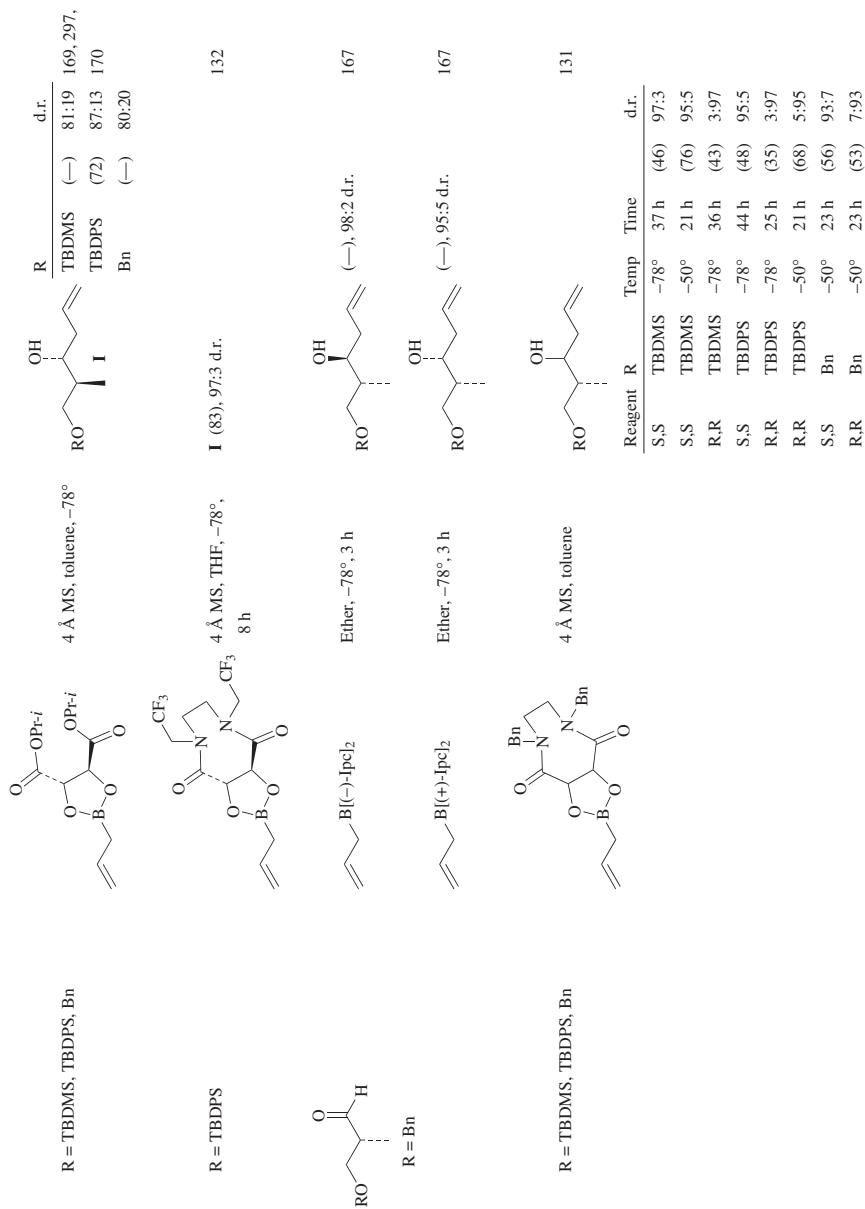
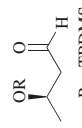

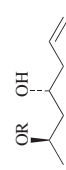

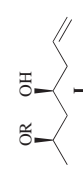

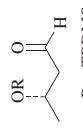

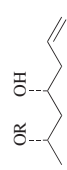


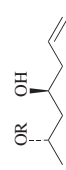
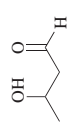
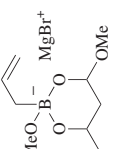
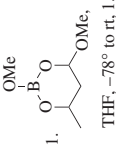
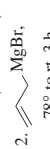
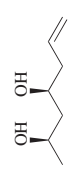
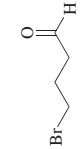
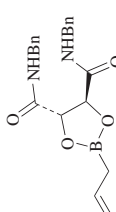
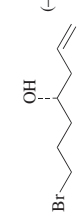


TABLE 1. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBOXYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
$C_4$  R = TBDMS		Ether, $-78^\circ$ , 1 h		298
R = Bn		Ether, $-78^\circ$ to $0^\circ$ , 3 h		253
R = TBDMS		Ether, $-78^\circ$ , 1 h	<b>I</b> (67)	298
 R = TBDMS		Ether, $-78^\circ$ , 1 h		298
 R = TBDMS		Ether, $-78^\circ$ , 1 h		298
	 1.  THF, $-78^\circ$ to rt, 1.5 h 2.  $-78^\circ$ to rt, 3 h			299
	 Toluene, $-78^\circ$ , 18 h			290



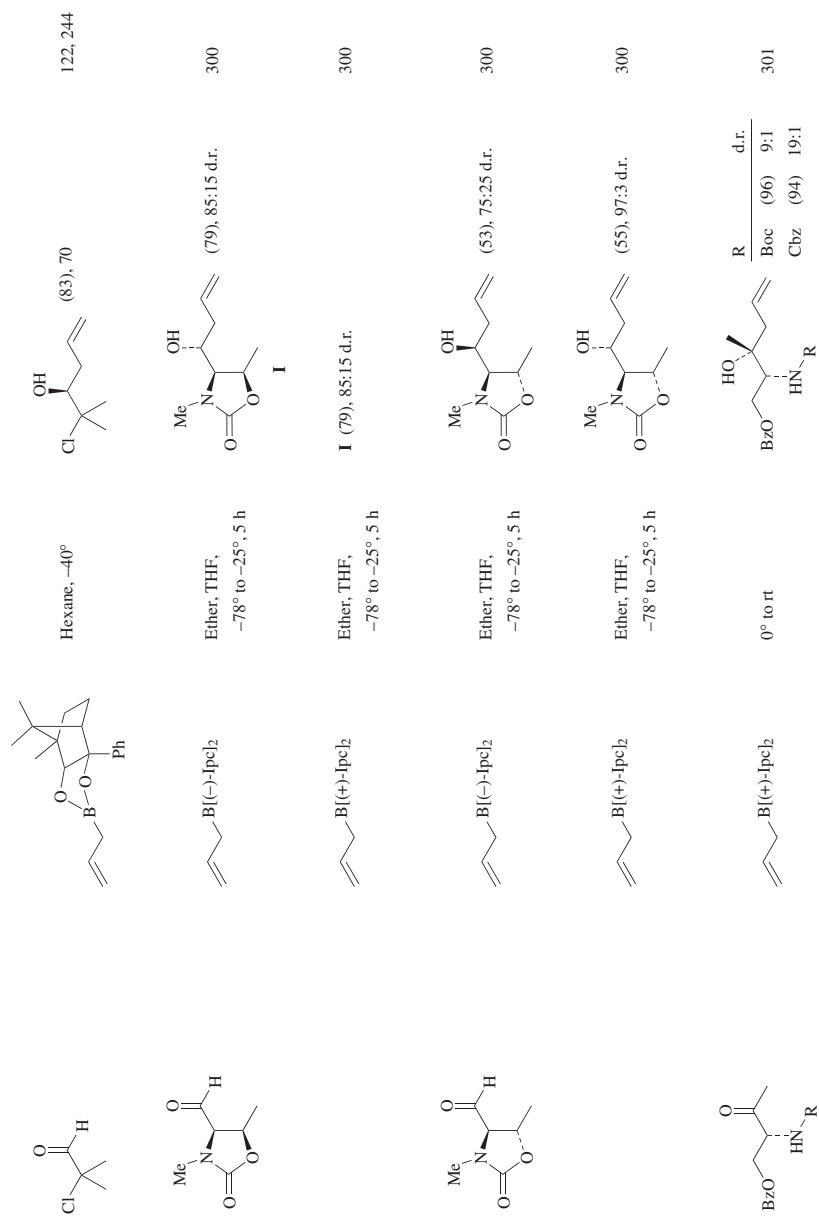
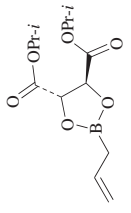
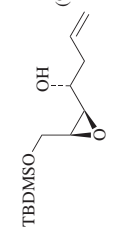
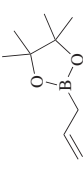
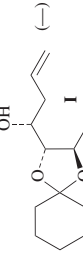
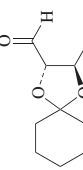
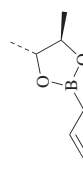
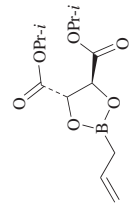
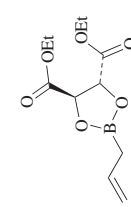
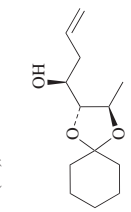


TABLE 1. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBONYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		4 Å MS, toluene, -78°	 (95), >96, 96:4 d.r.	302
		4 Å MS, toluene, -78°	 (86), >97, 74:26 d.r.	302
		4 Å MS, toluene, -78°	 (83), 96:4 d.r.	170
		4 Å MS, toluene, -78°	 (79), 84:16 d.r.	170
		4 Å MS, toluene, -78°	 (-), 75:25 d.r.	302
		4 Å MS, toluene, -78°	 (82), >97, 70:30 d.r.	302

C<sub>4</sub>

	4 Å MS, toluene, -78°		(96), >98, 99:1 d.r.	302
	See table		(-)	118
				
"	CH <sub>2</sub> Cl <sub>2</sub> , -78°, 24-48 h		<b>I</b> (85), 90:10 d.r.	124
"	Toluene, -78°, 24-48 h		<b>I</b> (-), 90:10 d.r.	124
	CH <sub>2</sub> Cl <sub>2</sub> , -78°, 24-48 h		<b>I</b> (-), 86:14 d.r.	124
	4 Å MS, toluene, -78°		<b>I</b> (-), >300:1 d.r.	170
"	CH <sub>2</sub> Cl <sub>2</sub> , -78°, 24-48 h		<b>I</b> (94), 98:2 d.r.	124
	Toluene, -78°, 24-48 h		(65), 68:32 d.r.	124

Solvent	Temp	d.r.
CH <sub>2</sub> Cl <sub>2</sub>	-78°	90:10
CH <sub>2</sub> Cl <sub>2</sub>	rt	87:13
toluene	-78°	90:10
toluene	rt	87:13
<i>n</i> -BuLi, THF	-78° to rt	79:21

TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBONYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		CH <sub>2</sub> Cl <sub>2</sub> , -78°, 24-48 h	 (-), 71:29 d.r.	124
	"	Toluene, -78°, 24-48 h	<b>I</b> (-), 64:36 d.r.	124
	"	4 Å MS, toluene, -78°	<b>I</b> (63), 73:27 d.r.	170
		Toluene, -78°, 24-48 h	<b>I</b> (-), 60:40 d.r.	124
		4 Å MS, CH <sub>2</sub> Cl <sub>2</sub> , -78° to rt, 24 h	 (93), >99:1 d.r.	303, 304
		Ether, -78° to rt	 (72), 6:1 d.r.	305
		-70°	 (60-65), 9:1 d.r.	306
		Ether, -75°, 2 h	 (40), 9:1 d.r.	309
		Ether, -75°, 2 h	<b>I</b> (52), 93:7 d.r.	309

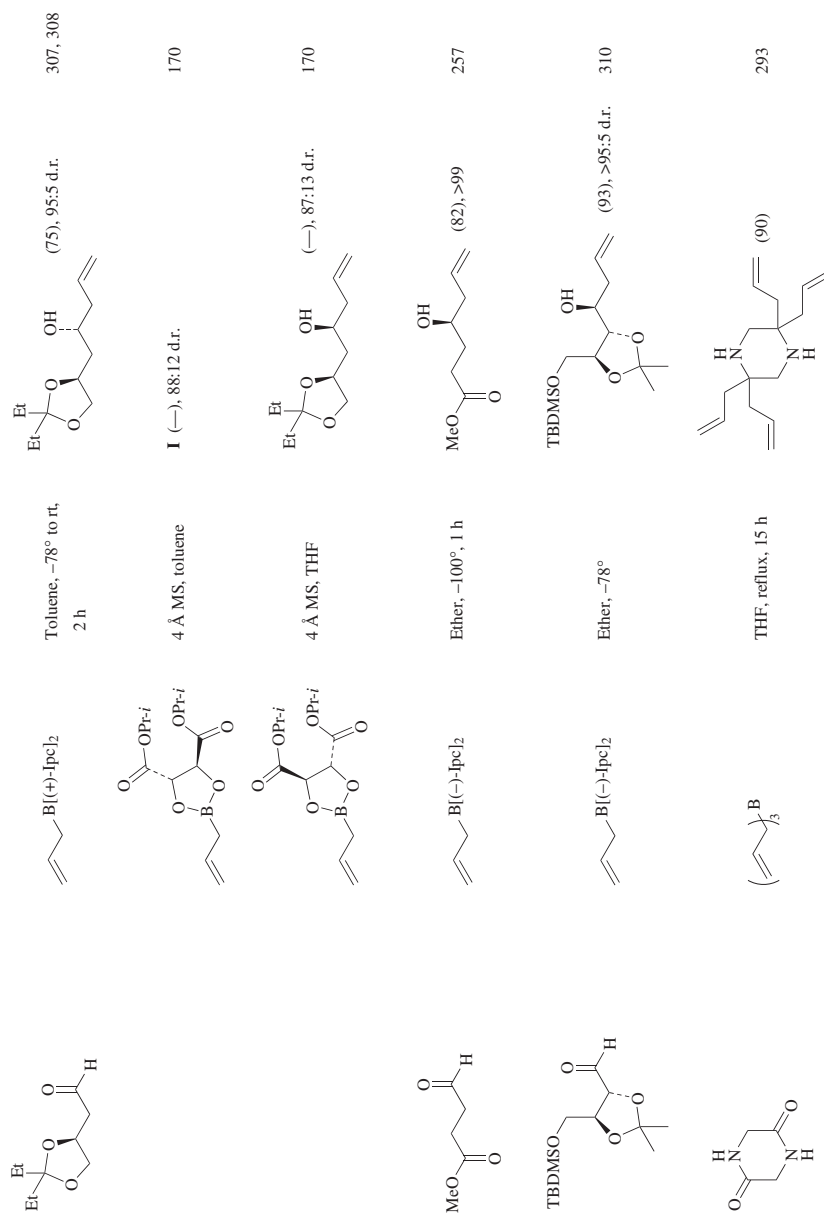
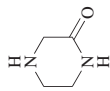

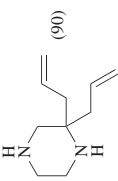
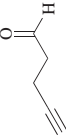

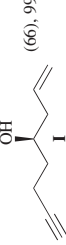





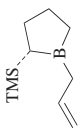
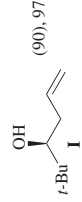


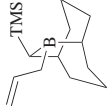


TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBONYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C <sub>4</sub> 		THF, reflux, 15 h	 (90)	294
C <sub>5</sub> 		Ether, -100° <sup>a</sup>	 (66), 99	311
	"	Ether, -78°	<b>I</b> (66), 95	312
		Pentane, rt, 2 h	 (97)	103
		Ether, -100°, 3 h	 (90), 97	141
		THF, -78°, 3 h	<b>I</b> (-), 83	240
	"	THF, -78° to rt	<b>I</b> (88), 83	136, 136a
	"	Ether, -100° <sup>a</sup>	<b>I</b> (-), >99	139
	"	—	<b>I</b> (60), 99	313
		THF, -78°, 3 h	<b>I</b> (-), 99	240
	"	Ether, -100° <sup>a</sup>	<b>I</b> (-), >99	139
		Ether, -78°, 3 h	<b>I</b> (79), >98	143




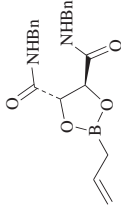
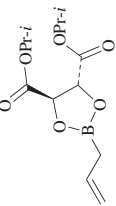
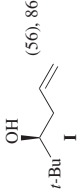
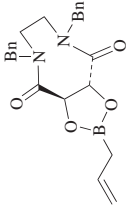
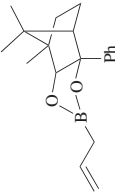
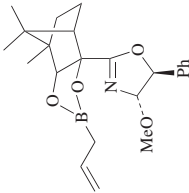

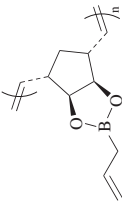
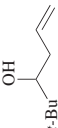
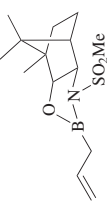
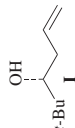
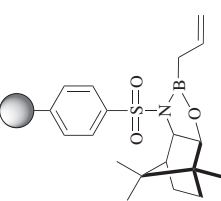

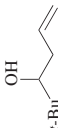

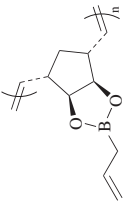
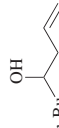

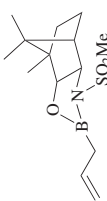
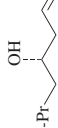
	Ether, -100° <sup>a</sup>		241
	THF, -78° to rt	<b>I</b> (80), 88	239, 136a
"	THF, -78°, 3 h	<b>I</b> (-), 88	240
"	Ether, -100° <sup>a</sup>	<b>I</b> (-), >99	139
	Toluene, -78°, 18 h	<b>I</b> (-), 98	290
	4 Å MS, toluene, -78°		131, 170
	4 Å MS, toluene, -78°, 67 h	<b>I</b> (-), 96	131
	Hexane, -40°	<b>I</b> (85), 45	122, 244
	Hexane, -40°	<b>I</b> (87), 48	122

TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBOXYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		CH <sub>2</sub> Cl <sub>2</sub> , H <sub>2</sub> O, rt, 4 h	 (49)	234
		Ether, -78° to rt, 2 h	 (80), 88	133
		Ether, -78°, 7h	<b>I</b> (84), 84	245, 246
		<i>n</i> -Bu <sub>4</sub> Ni (10 mol%), CH <sub>2</sub> Cl <sub>2</sub> , H <sub>2</sub> O, rt, 15 min	 (95)	100
		CH <sub>2</sub> Cl <sub>2</sub> , H <sub>2</sub> O, rt, 3 h	 (82)	234
		Ether, -78° to rt, 2 h	 (69), 90	133



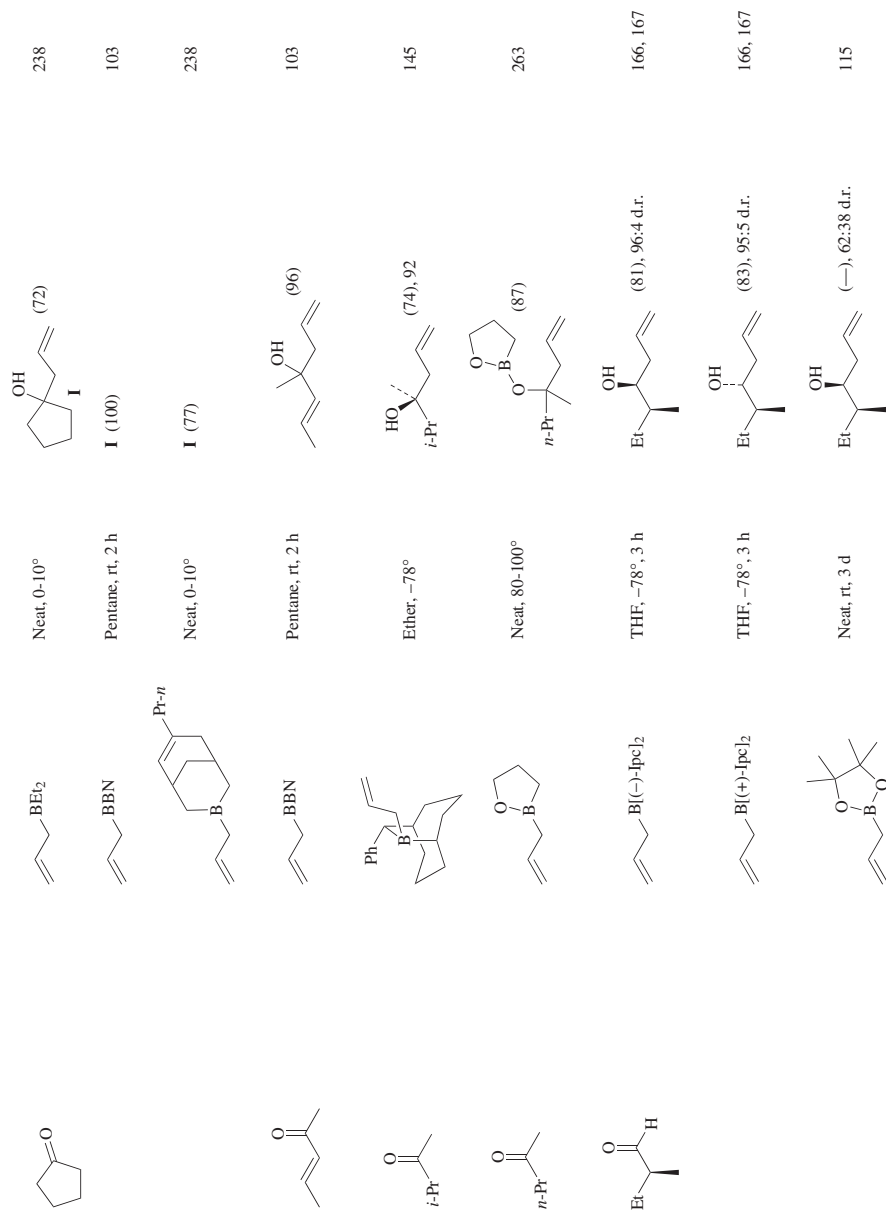
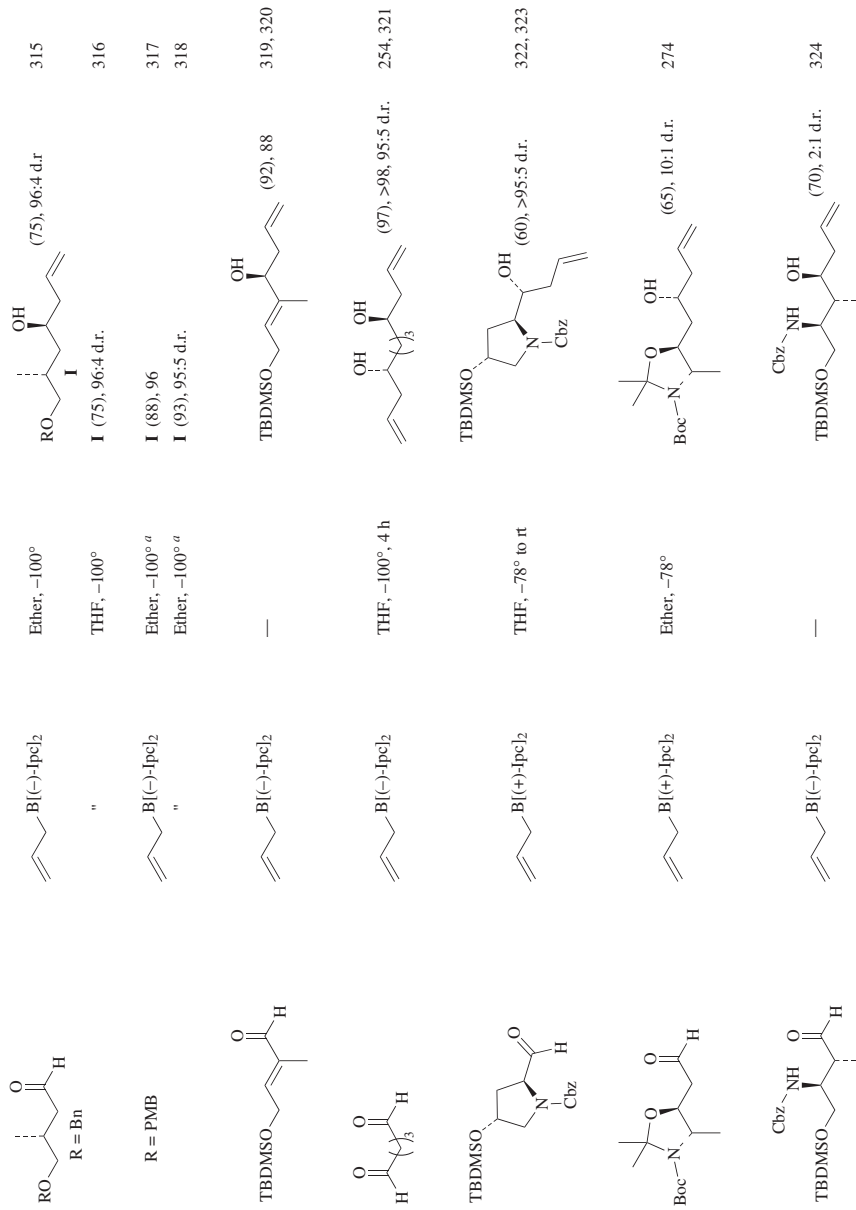


TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBOXYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Ether, -78° to rt, 3 h	 R TMS (72), 89 TES (32), 59 TPS (61), 92 SiMe <sub>2</sub> Ph (53), 81 SiMe <sub>2</sub> Bn (44), 79	111
		THF, reflux, 2 h		293, 294
		Ether, -78°		314
		Ether, -78°		314
		Neat, rt, 3 d		115
		Neat, rt, 3 d		115



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319, 320

254, 321

322, 323

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TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBOXYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Ether, -78° to rt, 2 h	 (92), 83	270
		Ether, -78°, 4 h	 (75), 96:4 d.r.	264
		Ether, -78° to rt, 16 h	 (44)	325
		Ether, -78° to rt	 (94)	326
		Ether, -78°	 (66), 91, 5,8,5 d.r.	327
		Ether, -78°	 (74)	328, 329
		Toluene, -78°	 (74), 80, 5,5:1 d.r.	330

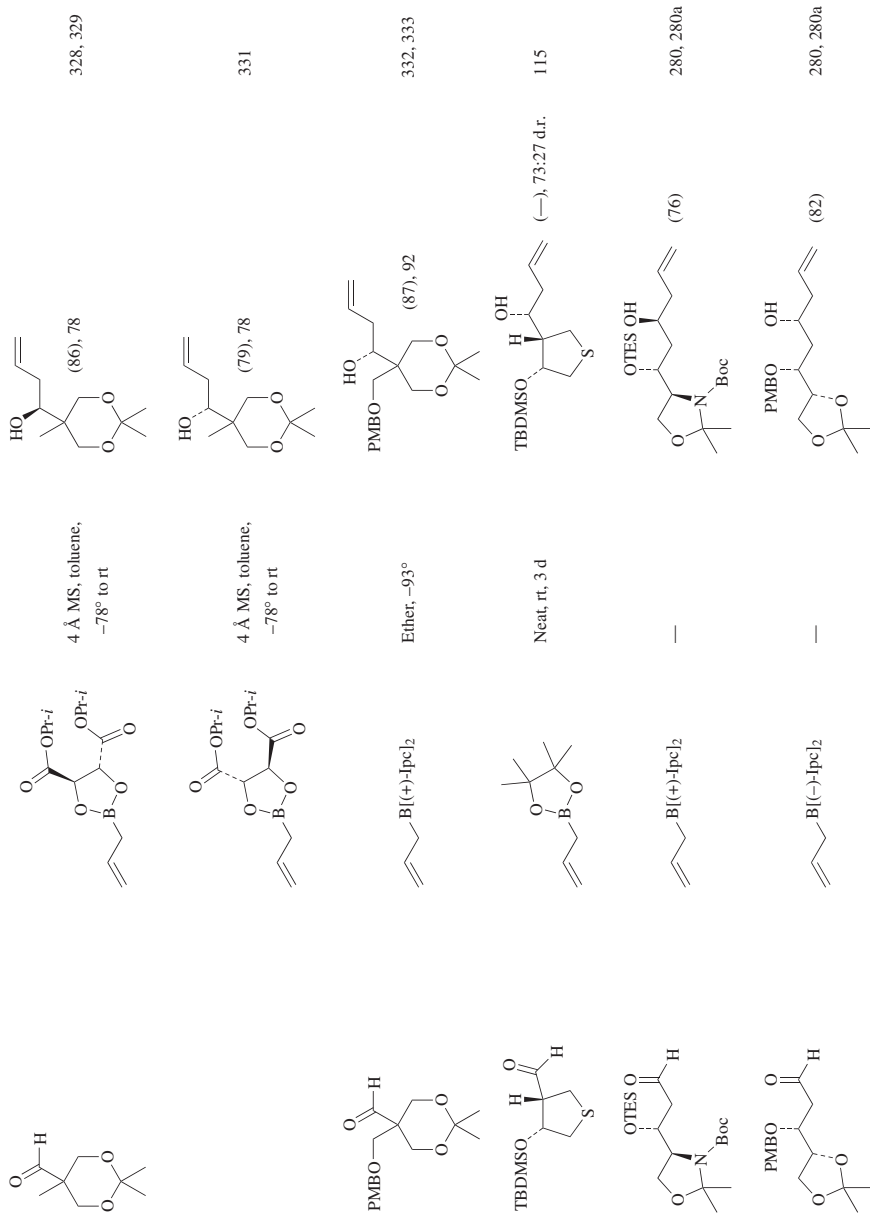


TABLE 1. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBONYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Ether, -78°		335
		Ether, -78°		336
		Ether, -78°		335
		Ether, -78°		337
		Ether, -78°		338
		Ether, -100°, 1 h		257

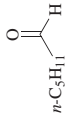

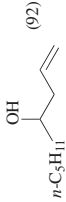

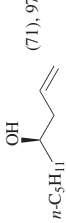

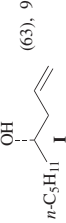
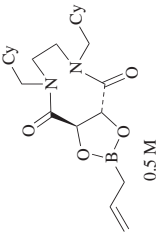
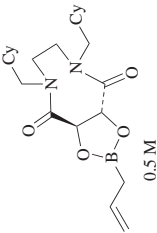
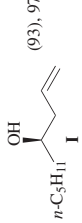
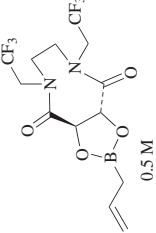
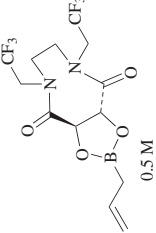
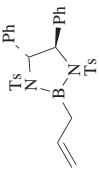
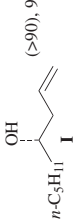


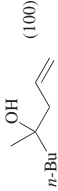
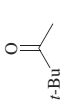
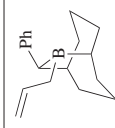

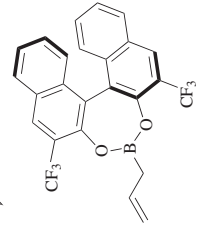
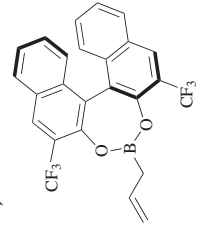

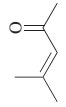

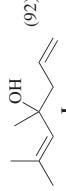

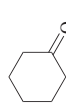

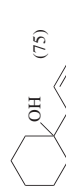

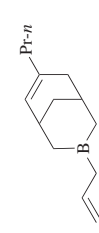
C <sub>6</sub>			Pentane, rt, 2 h		103
			Pentane, ether, -100°		204
			—		250
		"	—	<b>I</b> (91), 88	339
			<i>t</i> -BuCHO (0.1 equiv), 4 Å MS, toluene, -78°, 7 h		132
			<i>t</i> -BuCHO (0.1 equiv), 4 Å MS, THF, -78°, 5 h	<b>I</b> (95), 95	132
			CH <sub>2</sub> Cl <sub>2</sub> , -78°, 2 h		50
		"	Toluene, -78°, 2 h	<b>I</b> (>90), 95	50
			Pentane, rt, 2 h		103

TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBOXYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Ether, -78°		145
		THE, -78° to -40°, 48 h	<b>I</b> (75), 90	135
		( <i>R,R</i> )- <i>t</i> -Pr-DuPHOS, CuF, L <sub>2</sub> (OPr- <i>i</i> )- <sub>3</sub> , DMF, -40°, 1 h		164
		Neat, 0-10°		238
		Pentane, rt, 2 h	<b>I</b> (94)	103
		Neat, 0-10°		238
		Pentane, rt, 2 h	<b>I</b> (100)	103
		Neat, 0-10°	<b>I</b> (88)	238



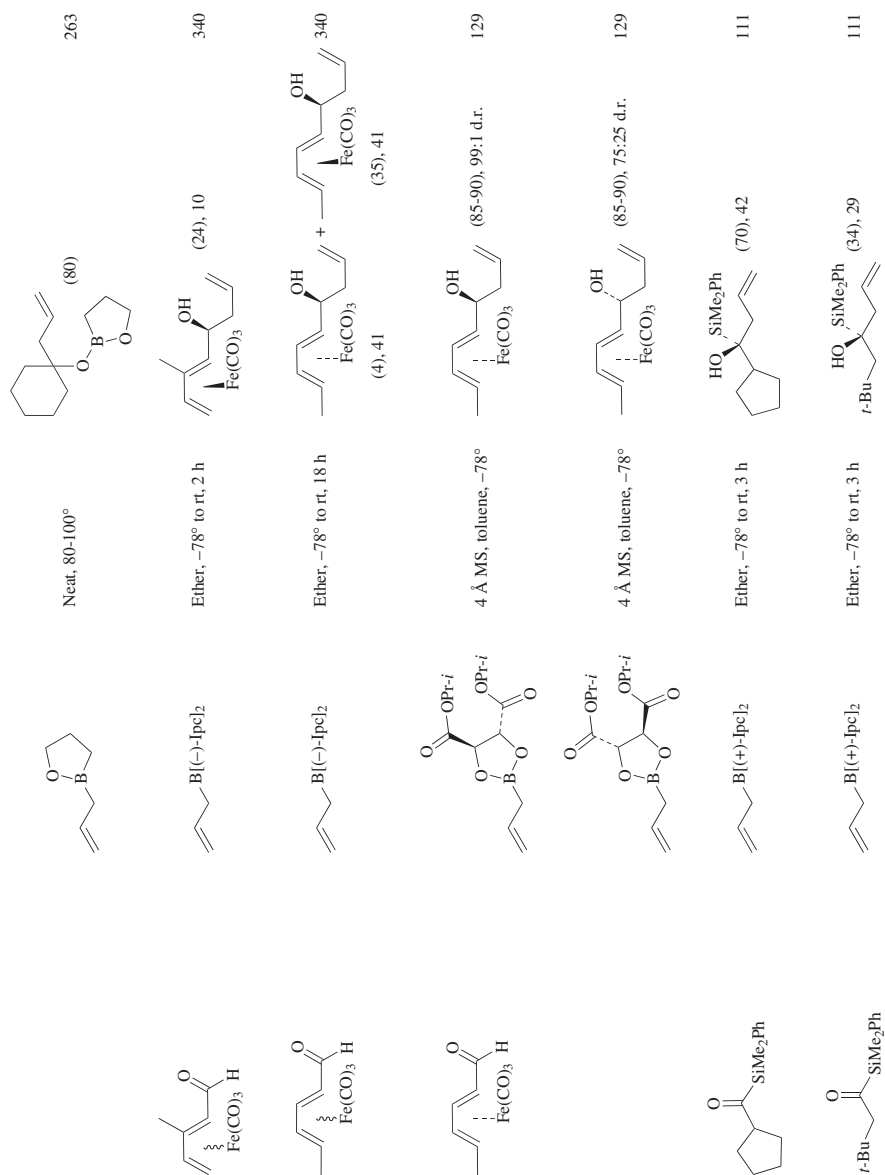
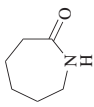

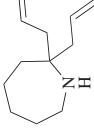
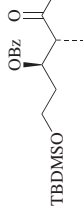
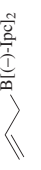
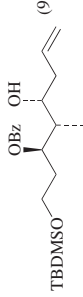
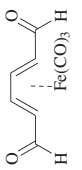
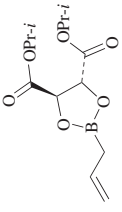
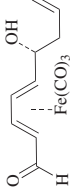

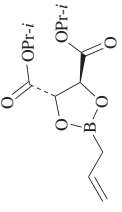
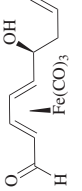
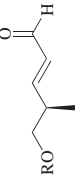

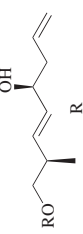
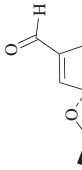
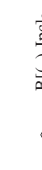
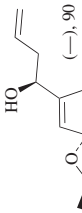
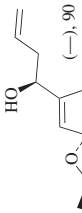
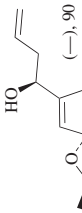


TABLE 1. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBONYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		THF, reflux, 2 h	 (50)	293, 294
		—	 (93)	341
		4 Å MS, toluene, -78°	 (82), 45:1 d.r.	129
		4 Å MS, toluene, -78°	 (83), >98, >50:1 d.r.	342
		Either, -100° to -78°, 3 h	 (88), d.r.	292
		—	 (89), >99:1	343
			 (83), 88	65:35
			 (90), (-)	

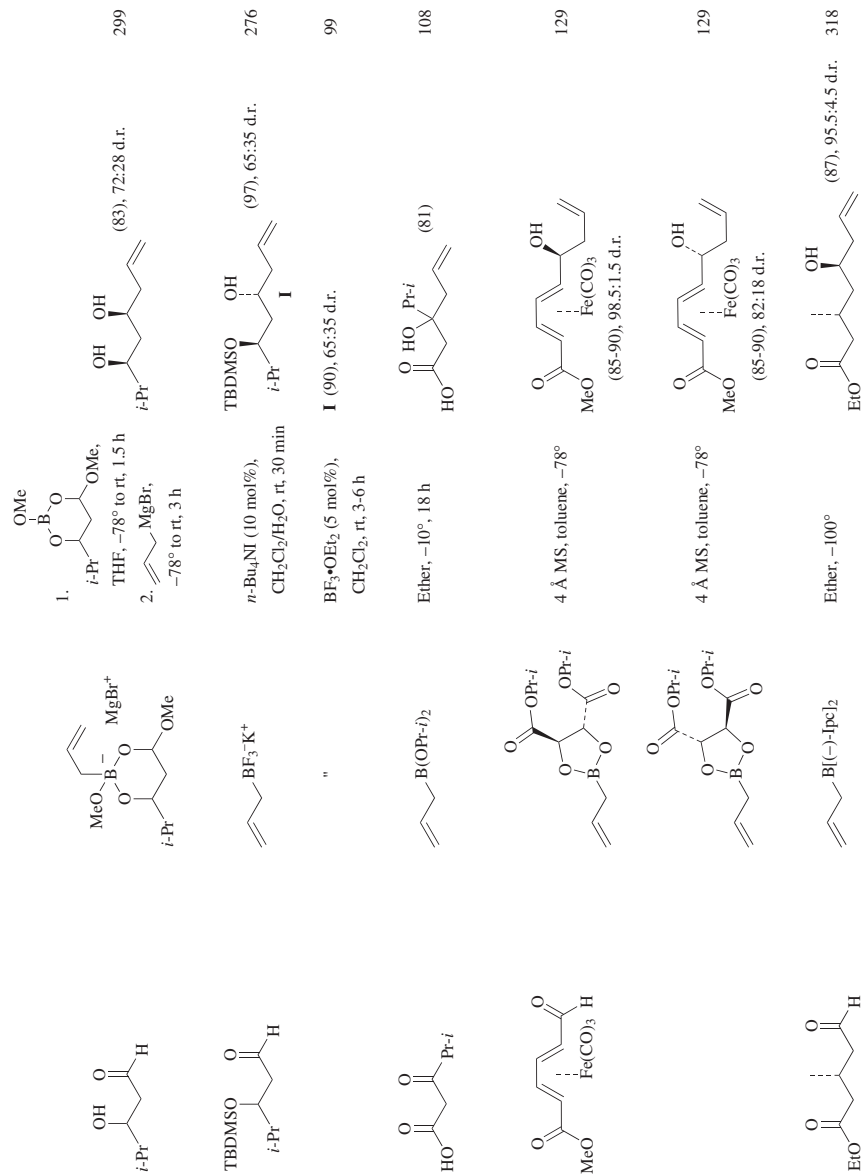


TABLE 1. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBOXYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Ether, -78° to 0°, 18 h		253
		Ether, -78° to rt, 2 h		344, 340, 345
		Ether, -78° to rt, 2 h		344, 340, 345
		—		346
	"	Ether, -78° to rt, 14 h	<b>I</b> (88)	347
		Ether, -100°, 1 h		257
		Et3N, CH2Cl2, -10° to rt, 13 h		105

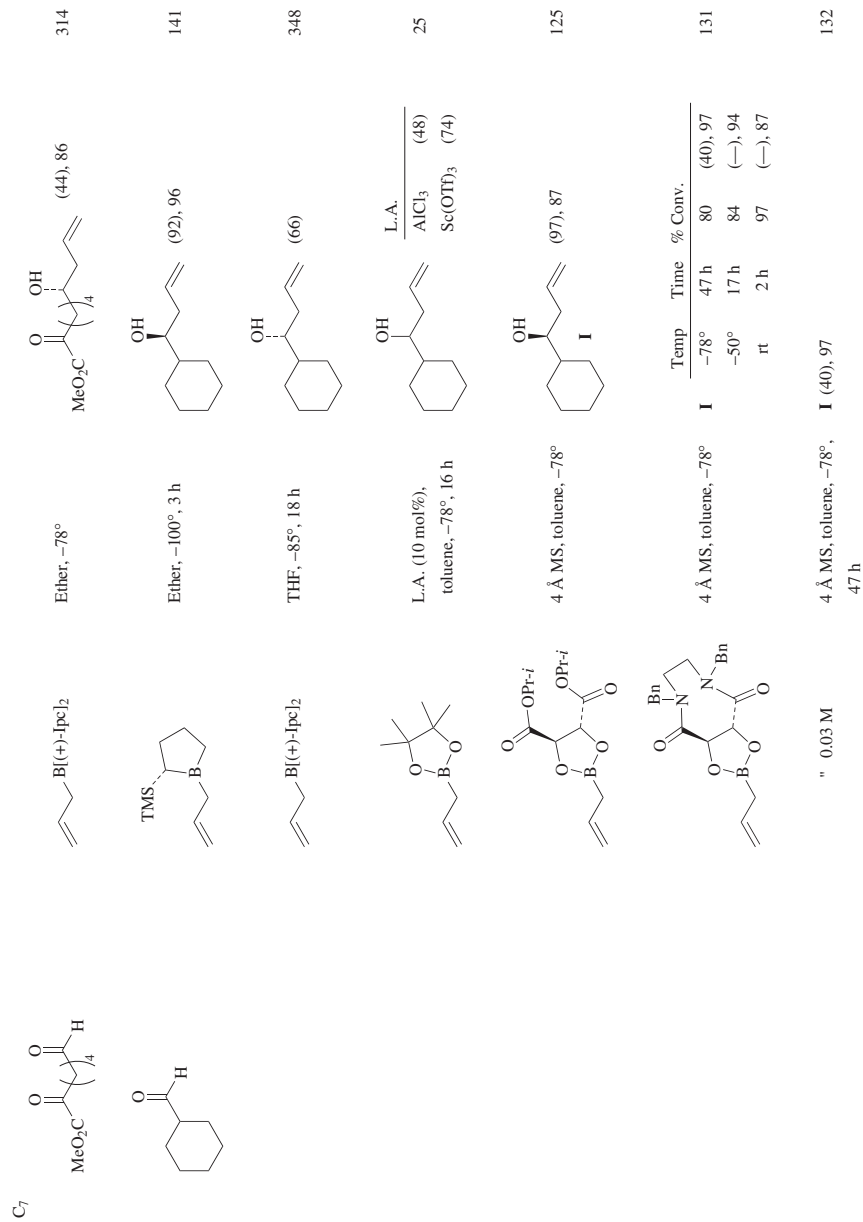

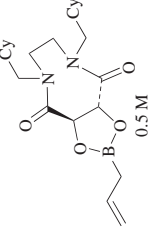
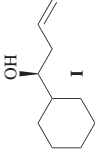
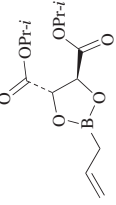
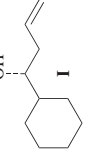
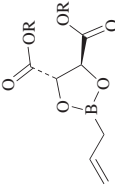


TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBOXYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
	 0.5 M	4 Å MS, toluene, -78°	 I	Time 5 h (—), 62 3 h (—), 91 132
	" 0.5 M	MeCHO (0.1 equiv), 4 Å MS, toluene, -78°, 5 h	I (—), 90	132
	" x M	<i>t</i> -BuCHO (0.1 equiv), 4 Å MS, -78°	I	x Solvent Time 0.5 toluene 7 h (82), 95 0.1 toluene 1 h (71), 94 0.5 THF 5 h (91), 94 132
		4 Å MS, -78°	 I	Solvent toluene (—), 87 ether (—), 82 THF (—), 78 CH <sub>2</sub> Cl <sub>2</sub> (—), 59 131, 125
	"	Toluene	I	Temp -78° (—), 87 -50° (—), 82 0° (—), 57 rt (—), 50 131
		4 Å MS, toluene, -78°	I	R Pr- <i>i</i> (—), 86 Et (—), 86 Me (—), 84 C <sub>10</sub> H <sub>19</sub> - <i>c</i> (—), 86 CH(Pr- <i>i</i> ) <sub>2</sub> (—), 86 125

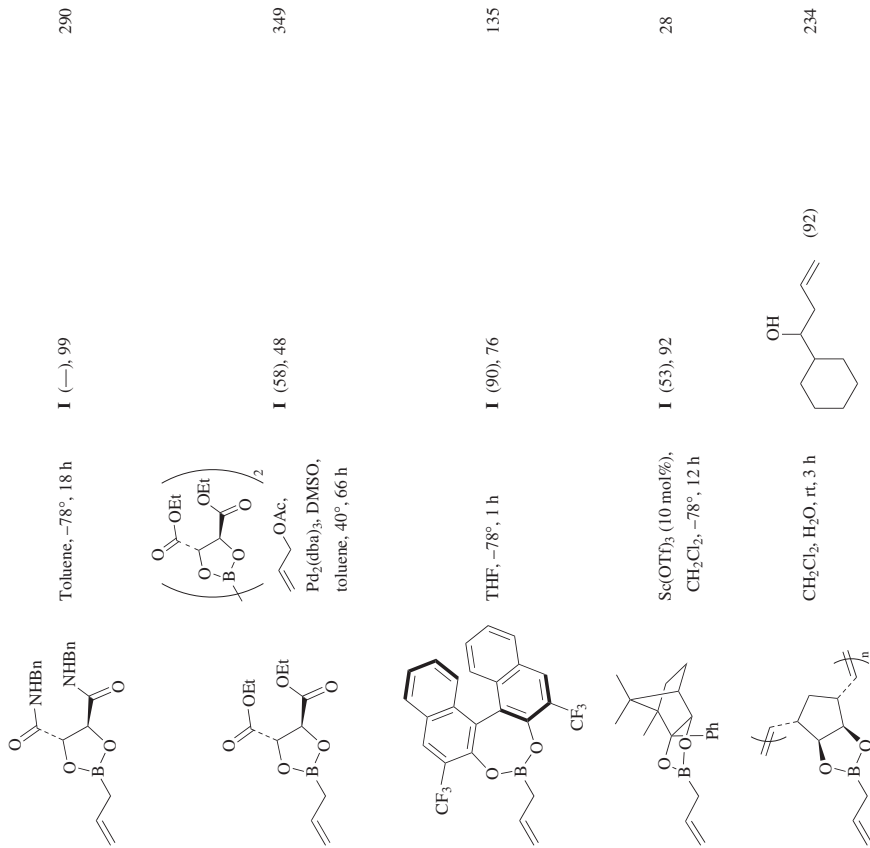
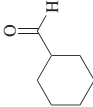
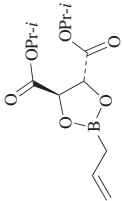
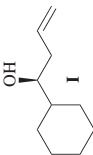
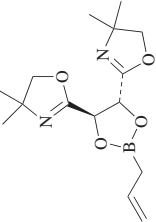
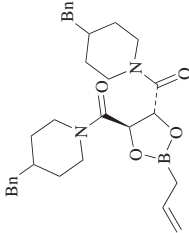
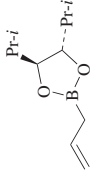


TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBOXYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.																				
 0.05 M	 -78°		 <b>I</b> <table border="1"> <thead> <tr> <th>Solvent</th> <th>Time</th> <th>% Conv.</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>toluene</td> <td>0.25 h</td> <td>95</td> <td>87</td> </tr> <tr> <td>THF</td> <td>1.5 h</td> <td>70</td> <td>78</td> </tr> <tr> <td>CH<sub>2</sub>Cl<sub>2</sub></td> <td>—</td> <td>—</td> <td>59</td> </tr> </tbody> </table>	Solvent	Time	% Conv.	% ee	toluene	0.25 h	95	87	THF	1.5 h	70	78	CH <sub>2</sub> Cl <sub>2</sub>	—	—	59	350				
Solvent	Time	% Conv.	% ee																					
toluene	0.25 h	95	87																					
THF	1.5 h	70	78																					
CH <sub>2</sub> Cl <sub>2</sub>	—	—	59																					
x M	 -78°		<table border="1"> <thead> <tr> <th>x</th> <th>Solvent</th> <th>Time</th> <th>% Conv.</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>0.08</td> <td>toluene</td> <td>16 h</td> <td>27</td> <td>21</td> </tr> <tr> <td>0.08</td> <td>ether</td> <td>20 h</td> <td>14</td> <td>32</td> </tr> <tr> <td>0.1</td> <td>CH<sub>2</sub>Cl<sub>2</sub></td> <td>18 h</td> <td>80</td> <td>53</td> </tr> </tbody> </table>	x	Solvent	Time	% Conv.	% ee	0.08	toluene	16 h	27	21	0.08	ether	20 h	14	32	0.1	CH <sub>2</sub> Cl <sub>2</sub>	18 h	80	53	350
x	Solvent	Time	% Conv.	% ee																				
0.08	toluene	16 h	27	21																				
0.08	ether	20 h	14	32																				
0.1	CH <sub>2</sub> Cl <sub>2</sub>	18 h	80	53																				
0.05 M	 -78°		<table border="1"> <thead> <tr> <th>Solvent</th> <th>Time</th> <th>% Conv.</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>toluene</td> <td>16 h</td> <td>24</td> <td>27</td> </tr> <tr> <td>THF</td> <td>16 h</td> <td>8</td> <td>30</td> </tr> <tr> <td>CH<sub>2</sub>Cl<sub>2</sub></td> <td>18 h</td> <td>40</td> <td>46</td> </tr> </tbody> </table>	Solvent	Time	% Conv.	% ee	toluene	16 h	24	27	THF	16 h	8	30	CH <sub>2</sub> Cl <sub>2</sub>	18 h	40	46	350				
Solvent	Time	% Conv.	% ee																					
toluene	16 h	24	27																					
THF	16 h	8	30																					
CH <sub>2</sub> Cl <sub>2</sub>	18 h	40	46																					
x M	 -25°, 40h		<table border="1"> <thead> <tr> <th>x</th> <th>Solvent</th> <th>% Conv.</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>0.06</td> <td>toluene</td> <td>18</td> <td>37</td> </tr> <tr> <td>0.07</td> <td>THF</td> <td>10</td> <td>29</td> </tr> <tr> <td>0.07</td> <td>CHCl<sub>3</sub></td> <td>30</td> <td>56</td> </tr> </tbody> </table>	x	Solvent	% Conv.	% ee	0.06	toluene	18	37	0.07	THF	10	29	0.07	CHCl <sub>3</sub>	30	56	350				
x	Solvent	% Conv.	% ee																					
0.06	toluene	18	37																					
0.07	THF	10	29																					
0.07	CHCl <sub>3</sub>	30	56																					



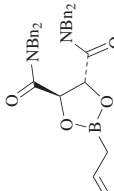
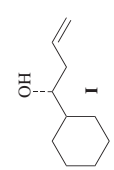
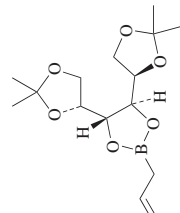
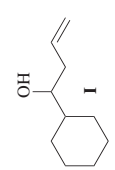
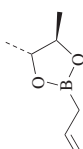
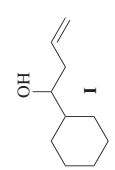
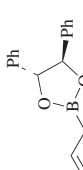
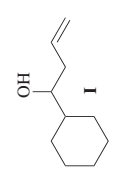
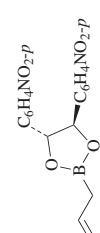
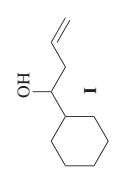
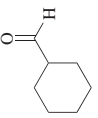
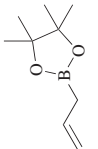
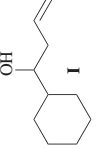
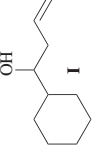
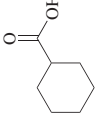
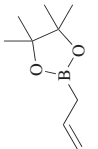
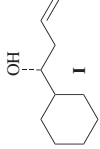
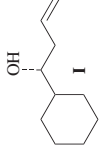
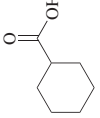
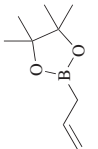
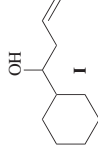
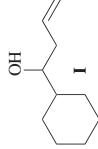
0.06 M		-78°, 16 h		Solvent	% Conv.	% ee			
				toluene	50	15			
				CH <sub>2</sub> Cl <sub>2</sub>	67	6			
0.08 M		See table		Solvent	Temp	Time	% Conv.	% ee	
				I	toluene	-25°	40 h	75	25
					THF	-25°	40 h	91	23
					CH <sub>2</sub> Cl <sub>2</sub>	-25°	40 h	94	27
					CH <sub>2</sub> Cl <sub>2</sub>	-78°	15 h	21	30
x M		See table		Solvent	Temp	Time	% Conv.	% ee	
				I	toluene	-25°	20 h	46	1
					CH <sub>2</sub> Cl <sub>2</sub>	-25°	20 h	46	4
					CH <sub>2</sub> Cl <sub>2</sub>	-78°	15 h	2	13
					CHCl <sub>3</sub>	-25°	19 h	80	7
x M		See table		Solvent	Temp	Time	% Conv.	% ee	
				I	toluene	-78°	5 h	21	11
					CH <sub>2</sub> Cl <sub>2</sub>	-78°	16 h	64	6
					CHCl <sub>3</sub>	-58°	21 h	85	13
0.05 M		-78°		Solvent	Temp	Time	% Conv.	% ee	
				I	toluene	15 h	82	11	
					CH <sub>2</sub> Cl <sub>2</sub>	18 h	95	6	

TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBOXYL SUBSTRATES (Continued)

Carboxyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
 0.1 M		Toluene	 <b>I</b>	Temp. Time % Conv. -78° 72 h 4 -25° 20 h 46 350
		Toluene	 <b>I</b>	Temp. Time % Conv. -78° 15 h 15 -25° 20 h 73 350
		-78°, 2 h	 <b>I</b>	Solvent CH <sub>2</sub> Cl <sub>2</sub> (>90), 93 toluene (>90), 97 50
		—	 <b>I</b> (84), 92	351
		<i>n</i> -Bu <sub>4</sub> Ni (10 mol%), CH <sub>2</sub> Cl <sub>2</sub> , H <sub>2</sub> O, rt, 15 min	 <b>I</b> (97)	100
		<i>n</i> -Bu <sub>3</sub> P, PhSeCl, AIBN, <i>n</i> -Bu <sub>3</sub> SnH, THF, reflux	 <b>I</b> (56)	352

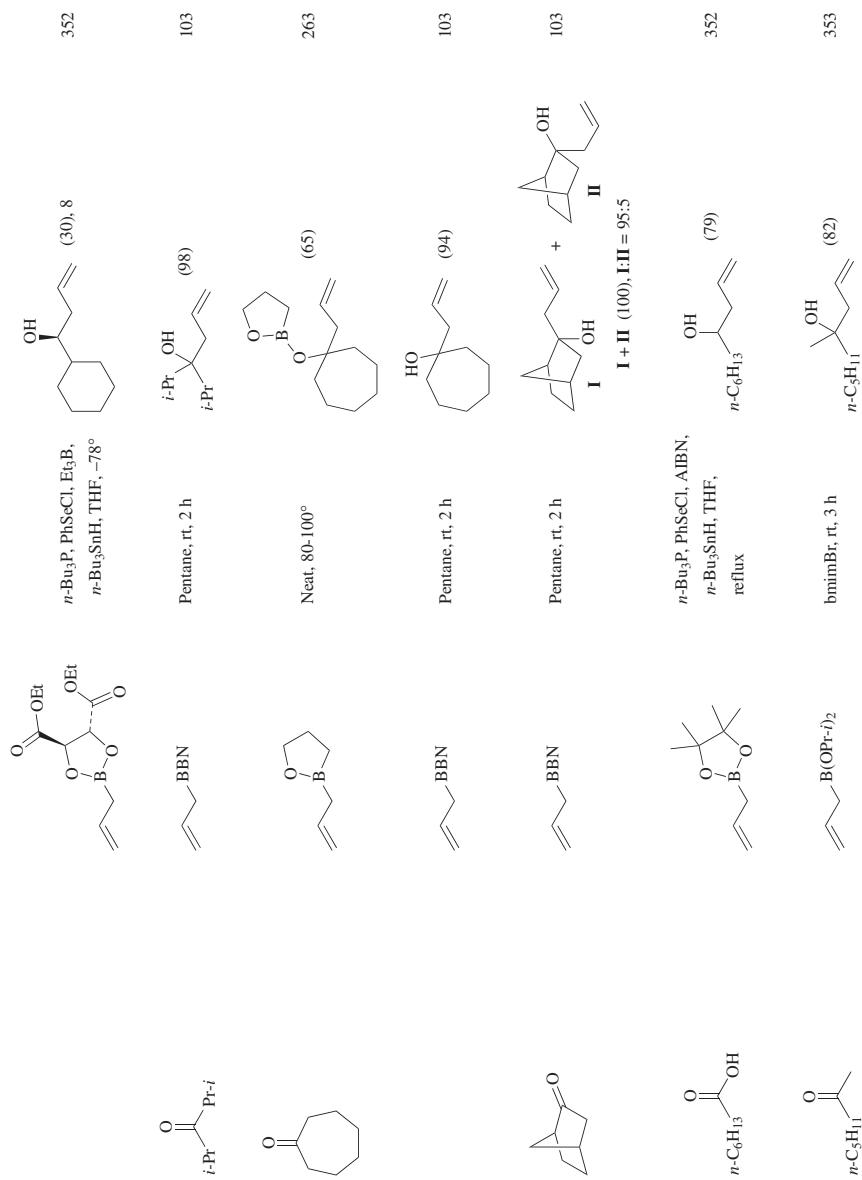
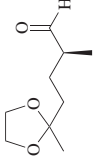
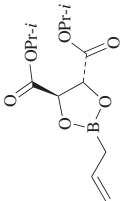
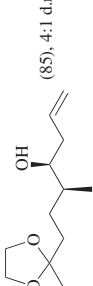
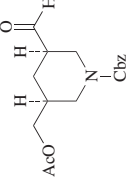
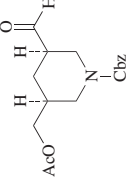
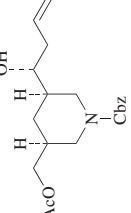
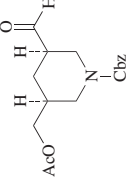
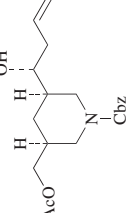
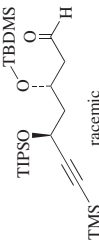
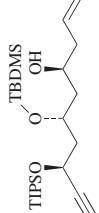
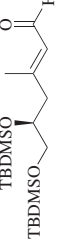
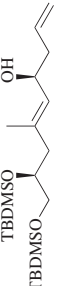

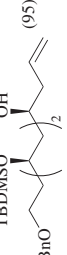


TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBONYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Ether, -100°, 2 h	 (95), 10:1 d.r.	354, 355, 356
		4 Å MS, toluene, -78°	 (98), 9:1 d.r.	357
	"	CH <sub>2</sub> Cl <sub>2</sub> , -78°	<b>I</b> (73), 2:1 d.r.	357
		CH <sub>2</sub> Cl <sub>2</sub> , -78°	 (77), 2:1 d.r.	357
		4 Å MS, toluene, -78°	 (76), 1:1 d.r.	357
		CH <sub>2</sub> Cl <sub>2</sub> , rt	 (84), 68:32 d.r.	110
		CH <sub>2</sub> Cl <sub>2</sub> , rt	 (86), 70:30 d.r.	110
		Ether, -100°	 (60), 80	358



TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBOXYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		4 Å MS, toluene, -78°	 (85), 4:1 d.r.	364
	Bi(-)-Ipc <sub>2</sub>	—	<b>I</b> (48), 8.6:1 d.r.	364
	Bi(-)-Ipc <sub>2</sub>	Ether, -78°	 (76), 10:1 d.r.	365
	Bi(+)-Ipc <sub>2</sub>	Ether, -78°	 (65), 10:1 d.r.	365
	Bi(+)-Ipc <sub>2</sub>	1. Allylation 2. K <sub>2</sub> CO <sub>3</sub> , MeOH	 (78), >95, 42:36 d.r.	366
	Bi(-)-Ipc <sub>2</sub>	Ether, -78°, 1 h	 (88), 95:5 d.r.	367
	Bi(-)-Ipc <sub>2</sub>	Ether, -78° to rt, 2 h	 (95)	270

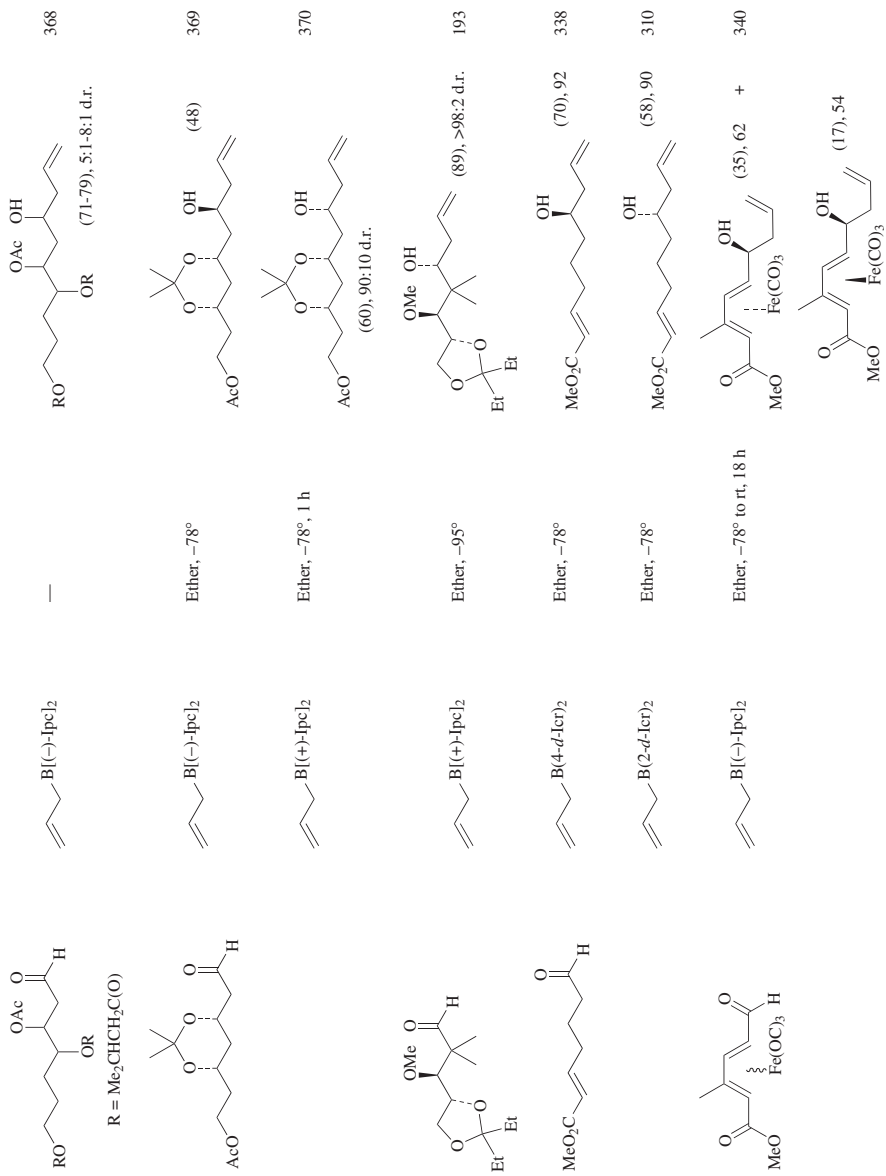


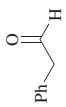

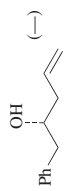
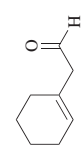

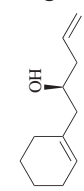
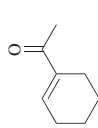
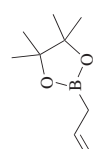
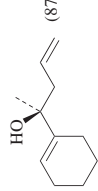
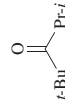

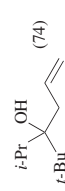
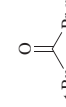

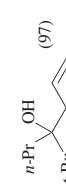
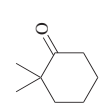
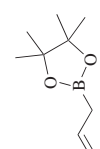
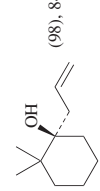
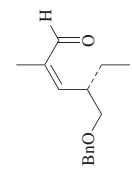

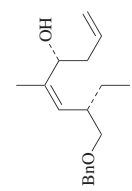
TABLE 1. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBOXYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		$\text{Et}_3\text{N}$ , $\text{CH}_2\text{Cl}_2$ , -10° to rt, 13 h		105
		Ether, -78°, 1 h		371
		Ether, -78°, 1 h		372, 373
		Ether, -78°, 1 h		372, 373
		$\text{CH}_2\text{Cl}_2$ , -78°		364
		Ether, -100°		374





TABLE 1. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBONYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		CH <sub>2</sub> Cl <sub>2</sub> , -78°	 (-)	381
		Sc(OTf) <sub>3</sub> , THF, -78, 6 h	 (92), 96	101
		( <i>R,R</i> )- <i>i</i> -Pr-DuPHOS, La(O <i>i</i> Pr) <sub>3</sub> , CuF, DMF, -40°, 1 h	 (87), 90	164
		Pentane, rt, 7 d	 (74)	103
		Pentane, rt, 2 h	 (97)	103
		( <i>R,R</i> )- <i>i</i> -Pr-DuPHOS, La(O <i>i</i> Pr) <sub>3</sub> , CuF, DMF, -40°, 1 h	 (98), 84	164
		Ether, -80°, 3 h	 (65), 93; 7 d.r.	382

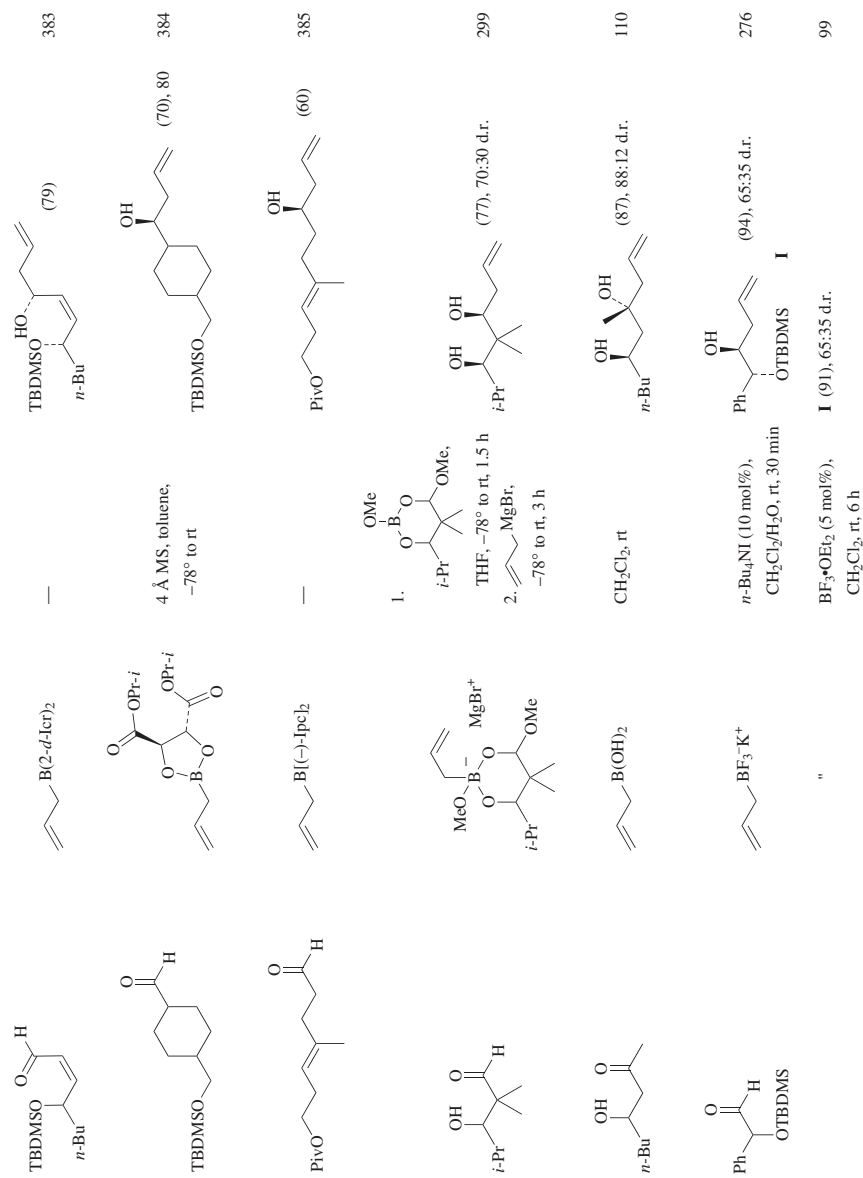
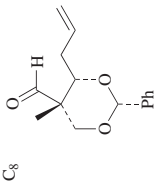
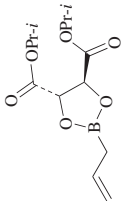
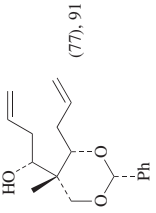
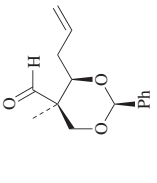
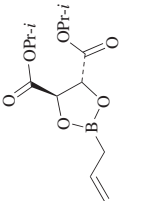
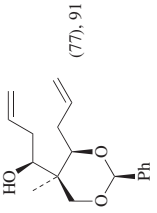
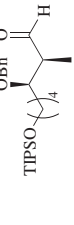
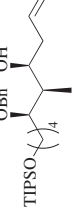
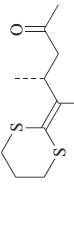
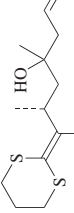
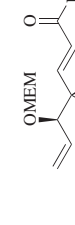
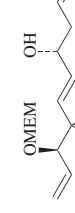
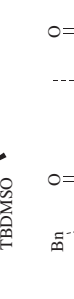



TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBOXYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		4 Å MS, toluene, -78° to rt	 (77), 91	328, 329
		4 Å MS, toluene, -78° to rt	 (77), 91	331
	Bi(-)-Ipc <sub>2</sub>	Toluene, -78°	 (64), >90, 14:1 d.r.	330
	Bi(-)-Ipc <sub>2</sub>	Ether	 (56), 3:1 d.r.	386, 387
	Bi(+)-Ipc <sub>2</sub>	—	 (65), 87	388
	Bi(4- <i>d</i> -Icp) <sub>2</sub>	Ether, -78°, 1 h <sup>a</sup>	 (52)	389, 390

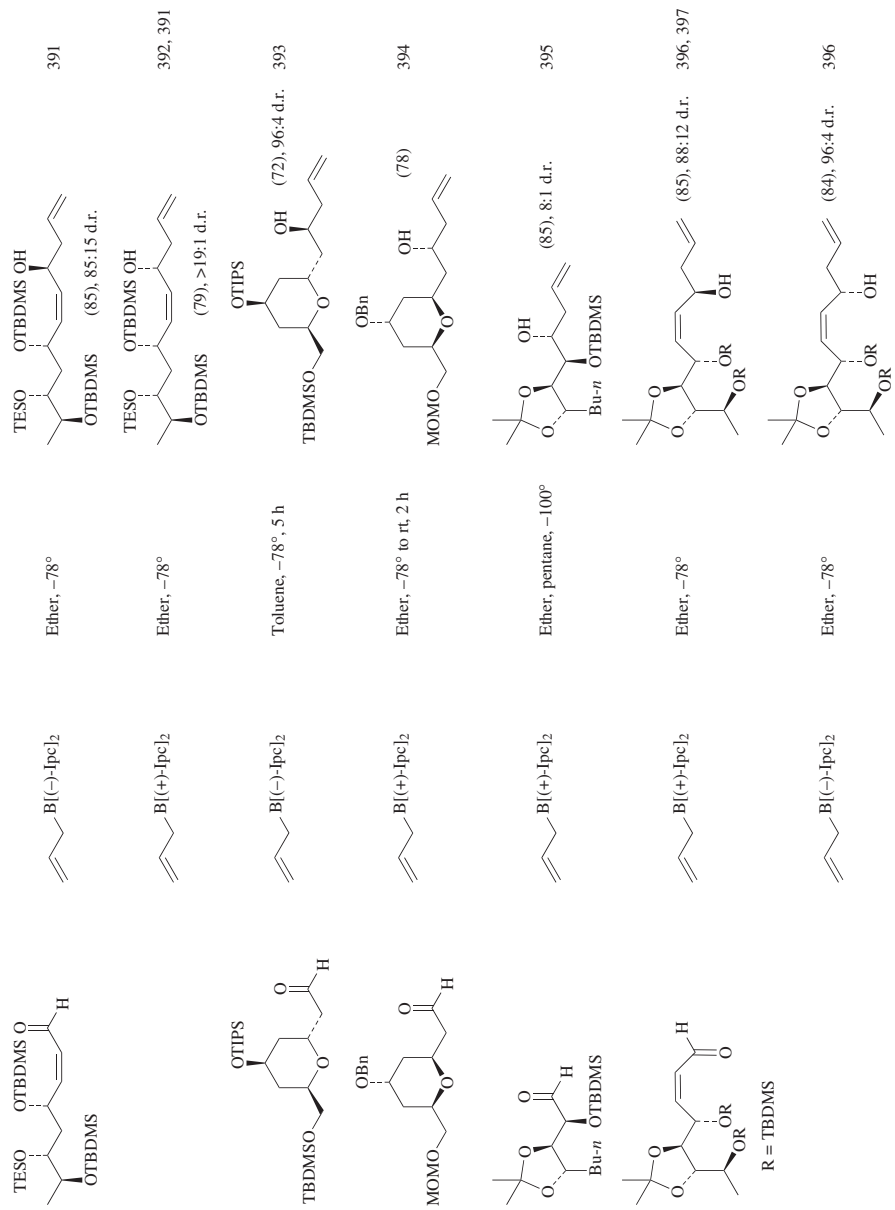


TABLE 1. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBOXYL SUBSTRATES (Continued)

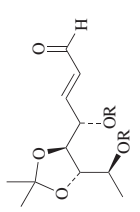

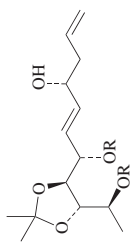

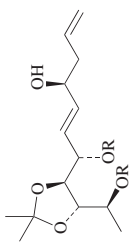
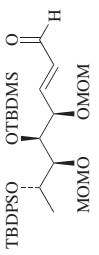

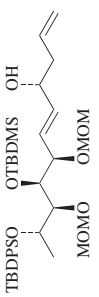
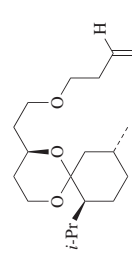

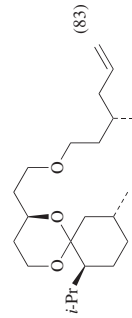
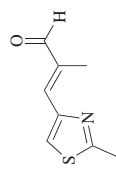

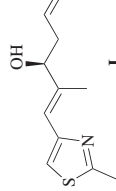
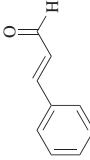

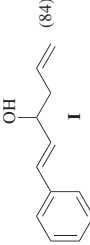
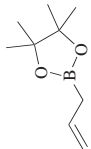
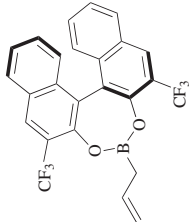
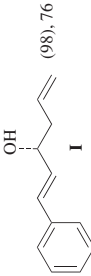
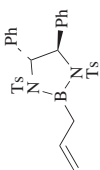

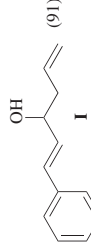
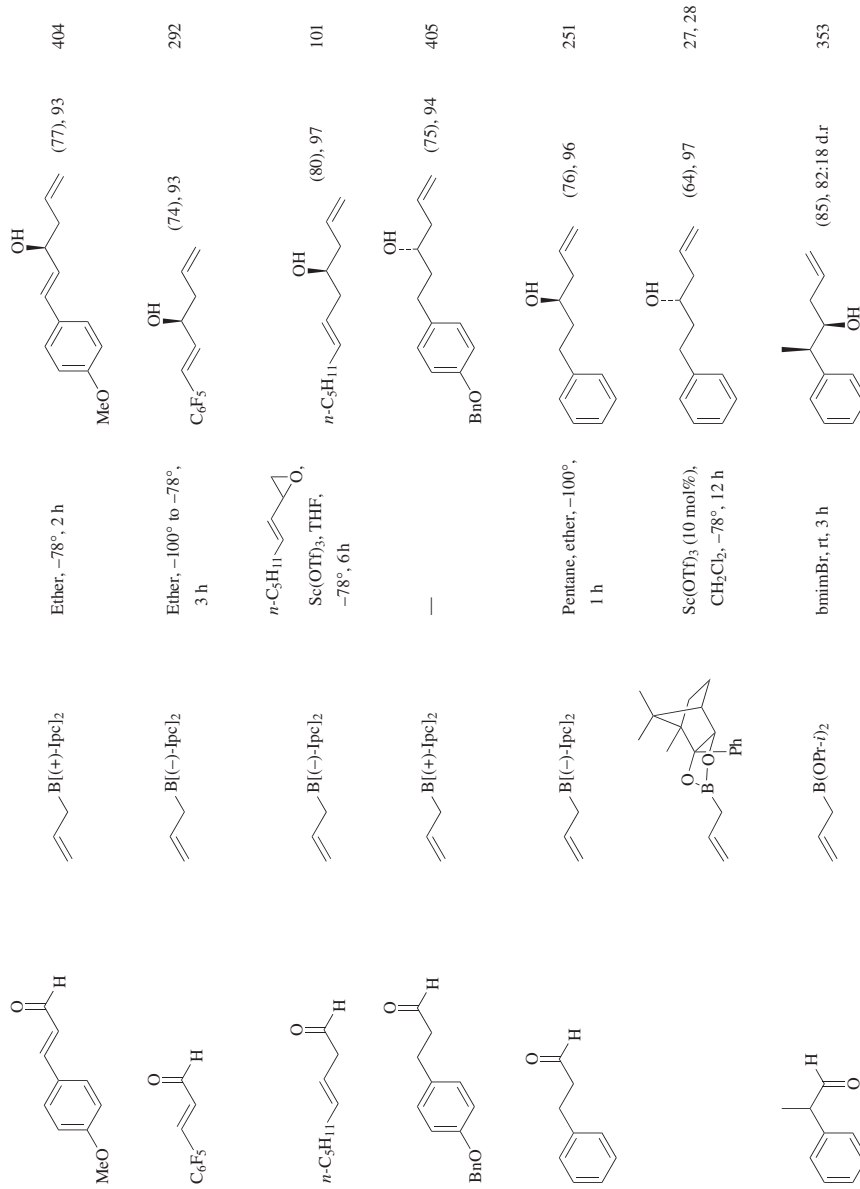
Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
 C <sub>8</sub> R = TBDMS		Ether, -78°	 (80), 96:4 d.r.	396
		Ether, -78°	 (88), >19:1 d.r.	396
		Ether, -78°, 3 h	 (74), 88:12 d.r.	398
		CH <sub>2</sub> Cl <sub>2</sub> , -78° to rt	 (83)	399
		Ether, -100°, 0.5 h	 (89-96), >97 <b>I</b>	188, 400



TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBONYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		bmmBr, rt, 3 h	 (84)	353
		L.A. (10 mol%), toluene, -78°, 24 h	L.A. I $\xrightarrow{\text{AlCl}_3}$ (69) Sc(OTf) <sub>3</sub> (74)	25
		THF, -78°, 1 h	 (98), 76	135
		-78°, 2 h	Solvent I toluene (>90), 97 CH <sub>2</sub> Cl <sub>2</sub> (>90), 98	50
		BF <sub>3</sub> ·OEt <sub>2</sub> (5 mol%), CH <sub>2</sub> Cl <sub>2</sub> , rt, 3-6 h	 (91)	99
	"	<i>n</i> -Bu <sub>4</sub> Ni (10 mol%), CH <sub>2</sub> Cl <sub>2</sub> , H <sub>2</sub> O, rt, 15 min	I (95)	100





Ether,  $-78^{\circ}$ , 2 h

Ether,  $-100^{\circ}$  to  $-78^{\circ}$ ,  
3 h

*n*-C<sub>3</sub>H<sub>11</sub>  
Sc(OTf)<sub>3</sub>, THF,  
 $-78^{\circ}$ , 6 h

Pentane, ether,  $-100^{\circ}$ ,  
1 h

Sc(OTf)<sub>3</sub> (10 mol%),  
CH<sub>2</sub>Cl<sub>2</sub>,  $-78^{\circ}$ , 12 h

bmimBr, rt, 3 h

TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBOXYL SUBSTRATES (Continued)

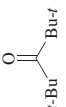


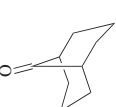

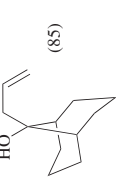
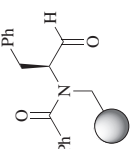
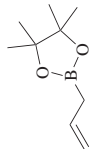
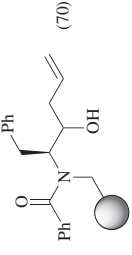
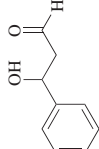

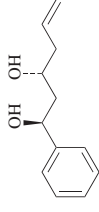
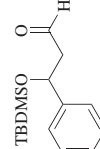

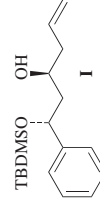
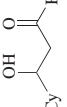
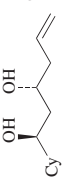
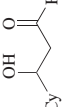

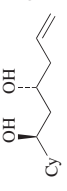
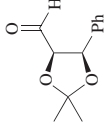

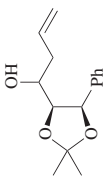
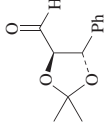
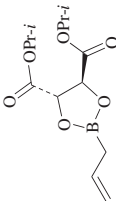
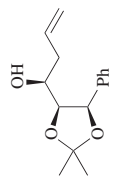
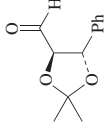

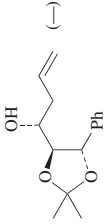
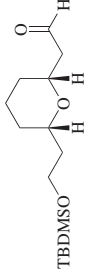

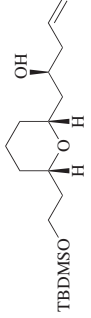
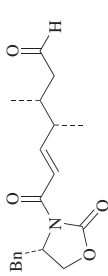

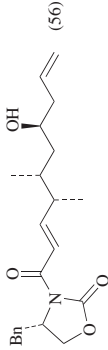


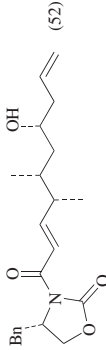
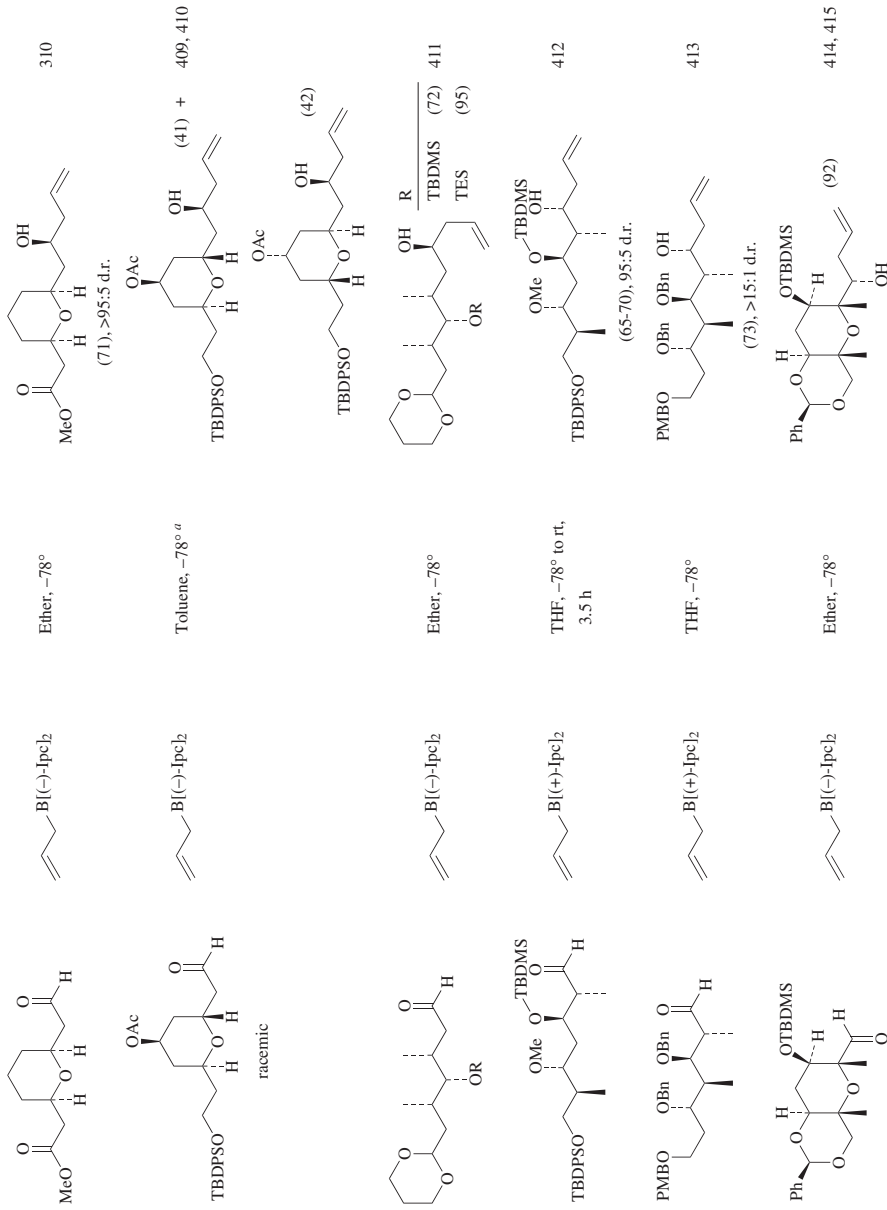
Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Octane, 125°, 5 d	 (25)	103
		Pentane, rt, 2 h	 (85)	103
		CH <sub>2</sub> Cl <sub>2</sub> , rt, 16 h	 (70)	235
		CH <sub>2</sub> Cl <sub>2</sub> , rt	 (85), 72:28 d.r.	110
		<i>n</i> -Bu <sub>4</sub> Ni (1 mol%), CH <sub>2</sub> Cl <sub>2</sub> , H <sub>2</sub> O, rt, 30 min	 I (94), 65:35 d.r.	276
	"	BF <sub>3</sub> ·OEt <sub>2</sub> (5 mol%), CH <sub>2</sub> Cl <sub>2</sub> , rt, 3-6 h	 I (86), 70:30 d.r.	347
		CH <sub>2</sub> Cl <sub>2</sub> , rt	 (85), 67:33 d.r.	110



TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBOXYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Ether, 18°	 (50), 1:1 d.r.	408
		Ether, -78°	 (89), 11:1 d.r.	408
		Ether, pentane, -100°	 (71), (-)	407
		Ether, -78°	 (71), >95:5 d.r.	310
		Ether, -78°, 1 h <sup>a</sup>	 (56)	389, 373, 390
		Ether, -78°, 1 h <sup>a</sup>	 (52)	389



Ether, -78°

Toluene, -78°<sup>a</sup>

Ether, -78°

THF, -78° to rt,  
3.5 h

THF, -78°

Ether, -78°

TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBONYL SUBSTRATES (Continued)

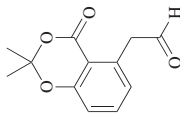

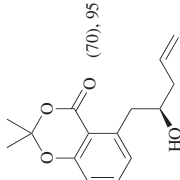
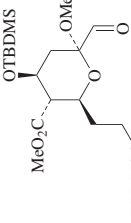
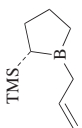
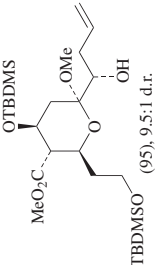
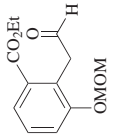

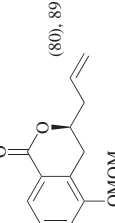
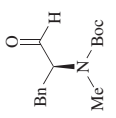

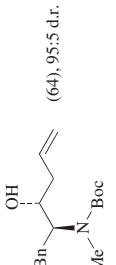
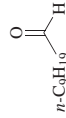

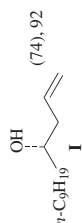
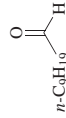

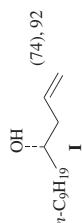



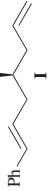

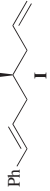


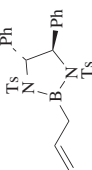

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Ether, $-100^{\circ}$ , 2 h	 (70), 95	416, 417
		Ether, $-100^{\circ}$ , 3 h	 (95), 9.5:1 d.r.	418
		Ether, $-78^{\circ}$	 (80), 89	419
		THF, $-78^{\circ}$ to rt, 3, 5 h	 (64), 95:5 d.r.	420, 421, 422
		Pentane, ether, $-100^{\circ}$	 (74), 92	204
		Ether, $-50^{\circ}$ , 17 h	 (22), 76	423



TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBOXYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
 C <sub>10</sub>		 Sc(OTf) <sub>3</sub> , THF, 6 h	 I (94), >98 (96), 97	101
		 Sc(OTf) <sub>3</sub> , THF, -78°, 6 h	 I (100), 95 (100), 89 (100), 86	101
	"	 L.A., THF, -78°, 6 h	L.A. Sm(OTf) <sub>3</sub> (28), 96 SnCl <sub>4</sub> (18), 83 Ag(OTf) (33), 94 Y(OTf) <sub>3</sub> (65), 94 Sc(OTf) <sub>3</sub> (92), 96 BF <sub>3</sub> •OEt <sub>2</sub> (59), 96	101
		 L.A., THF, -78°, 6 h	L.A. none (40), 27 BF <sub>3</sub> •OEt <sub>2</sub> (70), 47	101
		 BF <sub>3</sub> •OEt <sub>2</sub> , THF, -78°, 6 h	I (33), 37	101



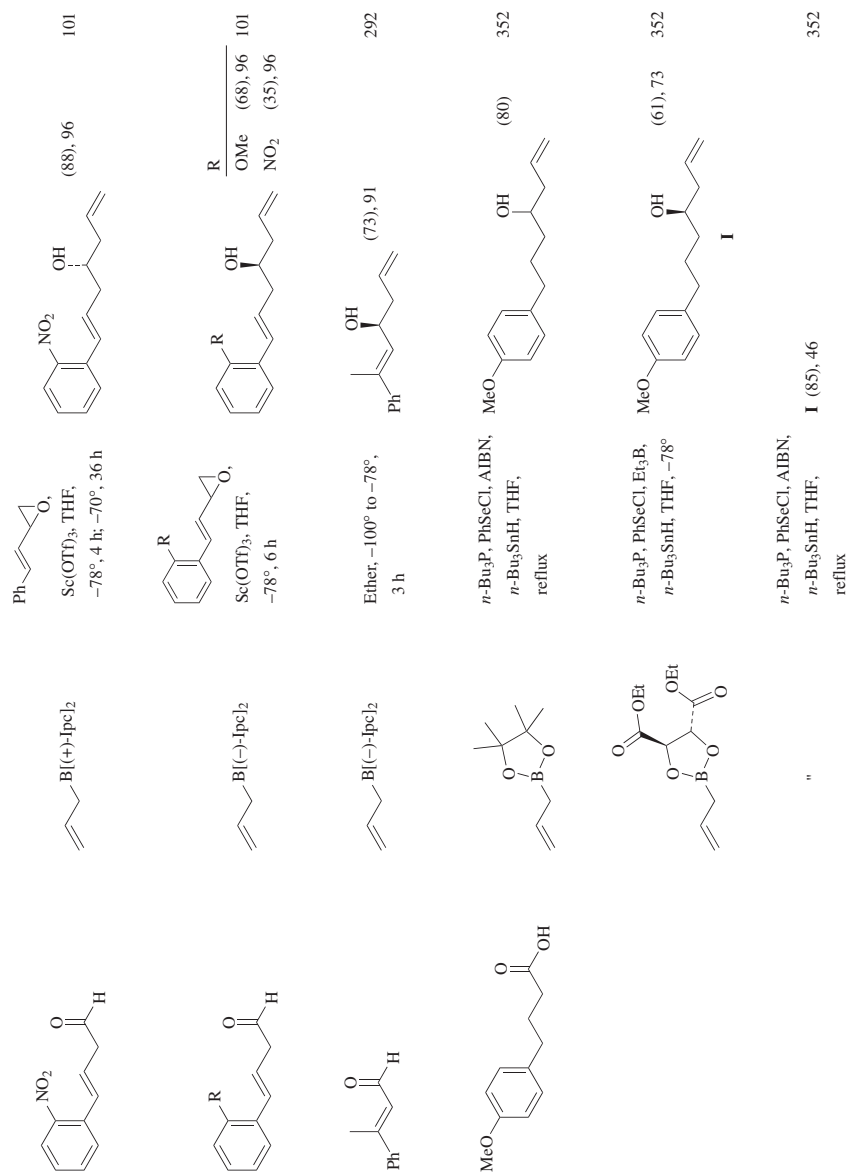
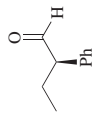

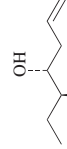
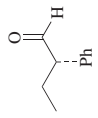

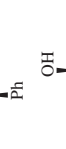
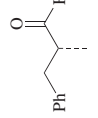

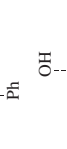
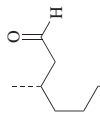

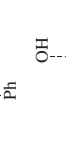
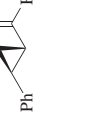

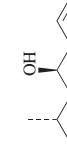




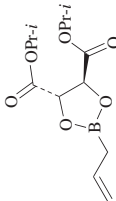



TABLE 1. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBONYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Ether, -78°	 (72), 67:33 d.r.	166, 167
		Ether, -78°	 (72), 98:2 d.r.	166, 167
		Ether, -78°	 (74), 97:3 d.r.	166, 167
		Ether, -78°	 (74), 74:26 d.r.	166, 167
		Ether, -78°, 4 h	 (63), 98:5:1.5 d.r.	425
		—	 (—)	426
		Toluene, -78°	 (94), 81:19 d.r.	427

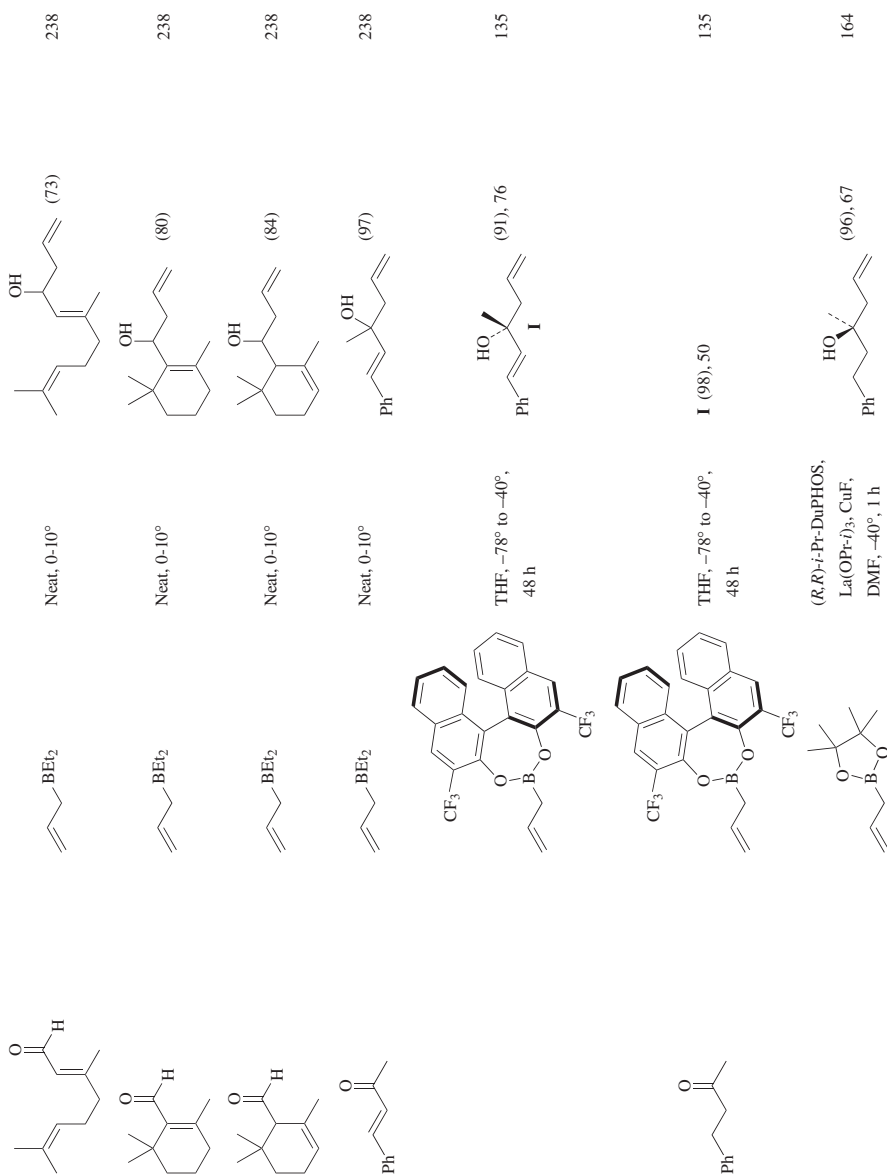
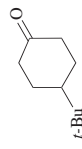

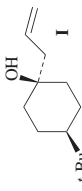
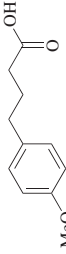
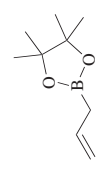

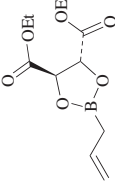
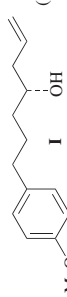
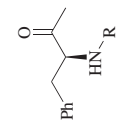

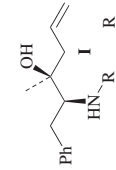


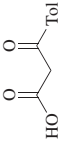

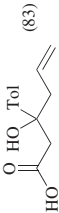
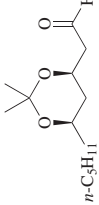

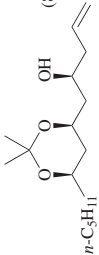
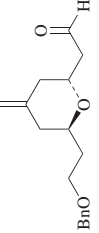

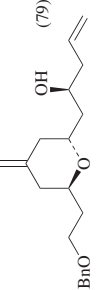
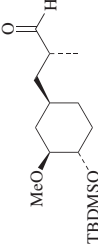
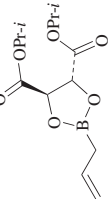
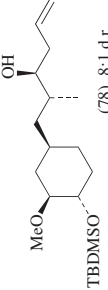
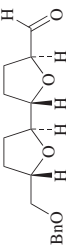

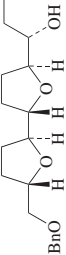
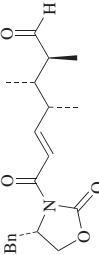

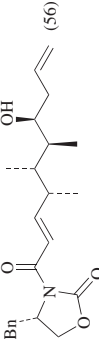
TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBOXYL SUBSTRATES (Continued)

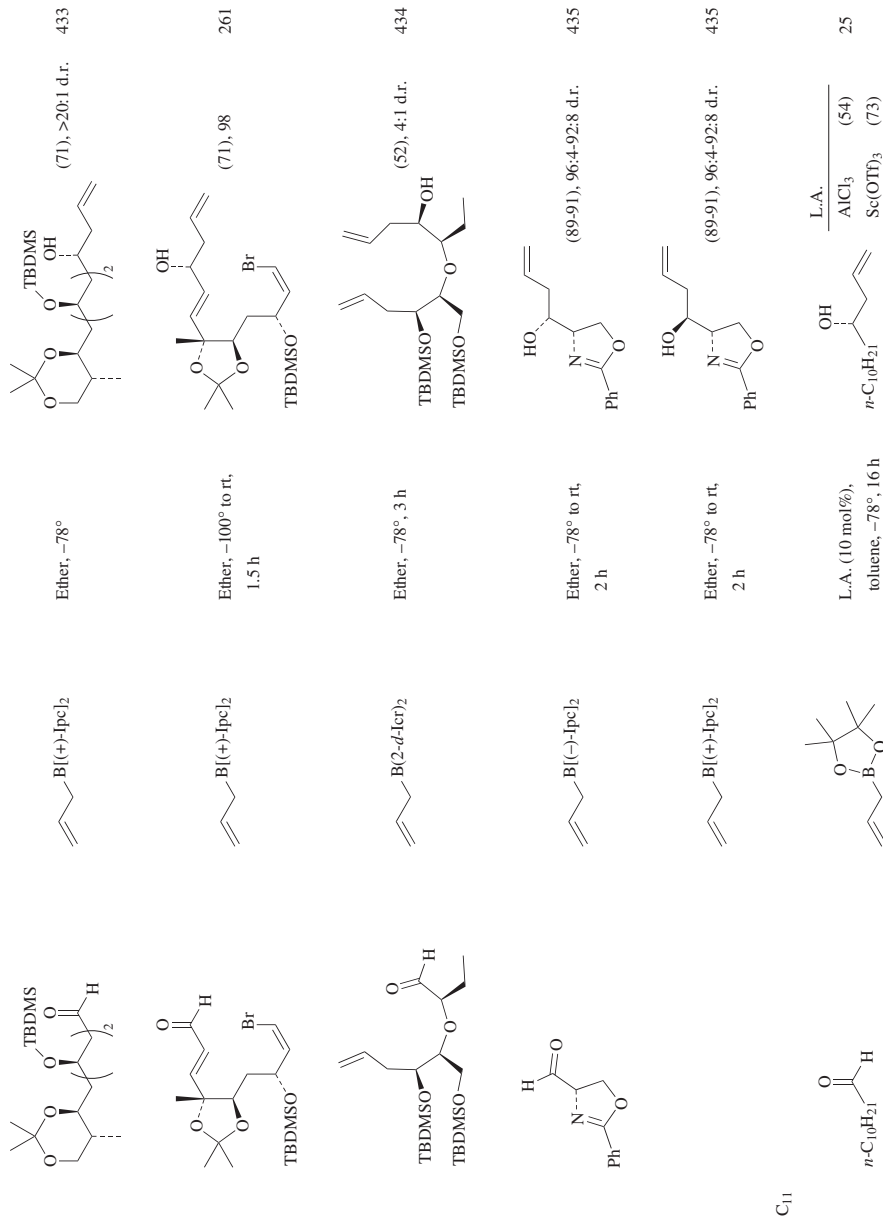
Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Pentane, rt, 2 h	 I + II (100), I:II = 55:45	103
		<i>n</i> -Bu <sub>3</sub> P, PhSeCl, AIBN, <i>n</i> -Bu <sub>3</sub> SnH, THF, reflux	 (80)	352
		<i>n</i> -Bu <sub>3</sub> P, PhSeCl, AIBN, <i>n</i> -Bu <sub>3</sub> SnH, THF, reflux	 I (85), 46	352
	"	<i>n</i> -Bu <sub>3</sub> P, PhSeCl, Et <sub>3</sub> B, <i>n</i> -Bu <sub>3</sub> SnH, THF, -78°	I (61), 73	352
		CH <sub>2</sub> Cl <sub>2</sub> , rt	 I	107
			d.r.	
			Boc (80)	80:20
			Ts (94)	79:21
			Ac (80)	80:20
			Bn (80)	85:15
			<i>p</i> -Tol (85)	85:15
			4-( <i>t</i> -Bu)Bn (90)	99:1
			DMPM (90)	88:12

R = Boc, Ts, Ac, Bn, *p*-Tol,  
4-(*t*-Bu)Bn, DMPM



TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBOXYL SUBSTRATES (Continued)

Carboxyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Ether, -10°, 18 h	 (83)	108
		Ether, -78° to rt	 (82), >10:1 d.r.	428
		Ether, -78°	 (79)	429
		Toluene, -78°	 (78), 8:1 d.r.	430
		THF, -78°	 (73), 85:15 d.r.	431, 432
		Ether, -78°, 1 h <sup>a</sup>	 (56)	390



C11

TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBOXYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
$n\text{-C}_{10}\text{H}_{21}\text{CHO}$		4 Å MS, toluene, $-78^\circ$	 (86), 86	125
	$\text{B}((-)\text{-ipcl})_2$	$\text{Sc}(\text{OTf})_3$ , THF, $-78^\circ$ , 6 h	 (83), 96	101
	$\text{B}((-)\text{-ipcl})_2$	$\text{Sc}(\text{OTf})_3$ , THF, $-78^\circ$ , 6 h	 (92), >95, 1:1 d.r.	101
$1\text{-AdmCO}_2\text{H}$		$n\text{-Bu}_3\text{P}$ , $\text{PhSeCl}$ , AIBN, $n\text{-Bu}_3\text{SnH}$ , THF, reflux	 (54)	352
	$\text{B}((-)\text{-ipcl})_2$	—	 (82), 9:1 d.r.	436





TABLE 1. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBOXYL SUBSTRATES (Continued)

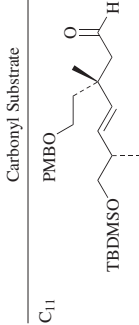

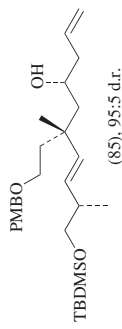
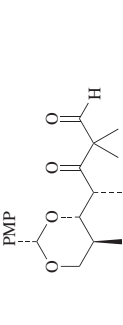

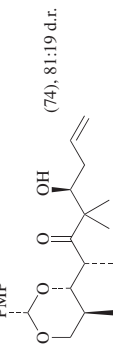
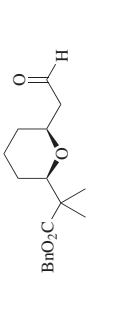

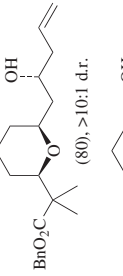
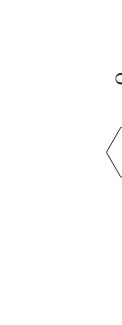

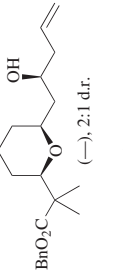
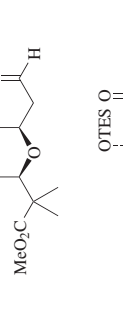

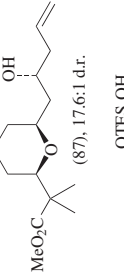
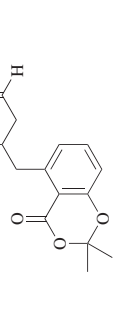

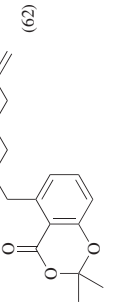
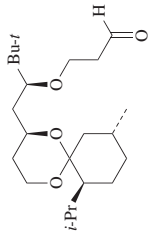

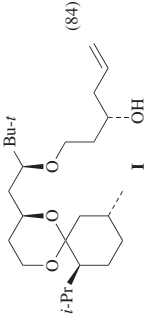
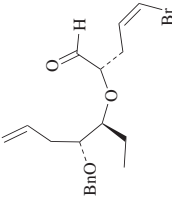
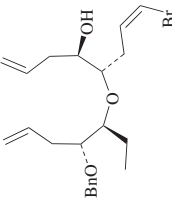
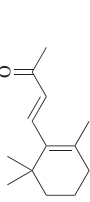

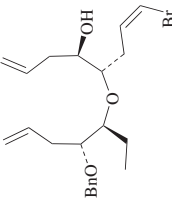
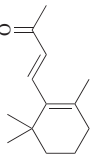

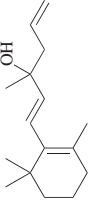
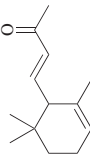

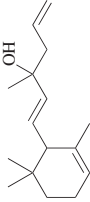



Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
 C11		Ether, -78°	 (85), 95:5 d.r.	442
		Ether, -78°, 1 h	 (74), 81:19 d.r.	443
		Ether, -100°	 (80), >10:1 d.r.	444
		Ether, -78°	 (-), 2:1 d.r.	444
		THF, -78° to rt, 2 h	 (87), 17.6:1 d.r.	445
		Ether, -100°, 2 h	 (62)	416, 417



TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBONYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
 C <sub>12</sub>		CH <sub>2</sub> Cl <sub>2</sub> , -78° to rt	 (84)	399
 I (67)	"	Ether, -78°	 I (67)	326
 C <sub>13</sub>		Ether, -78°	 (92), >98:2 d.r.	450
 C <sub>13</sub>		Neat, 0-10°	 (90)	238
 C <sub>13</sub>		Neat, 0-10°	 (86)	238
 C <sub>13</sub>		Ether, -78°, 4 h	 (48)	451

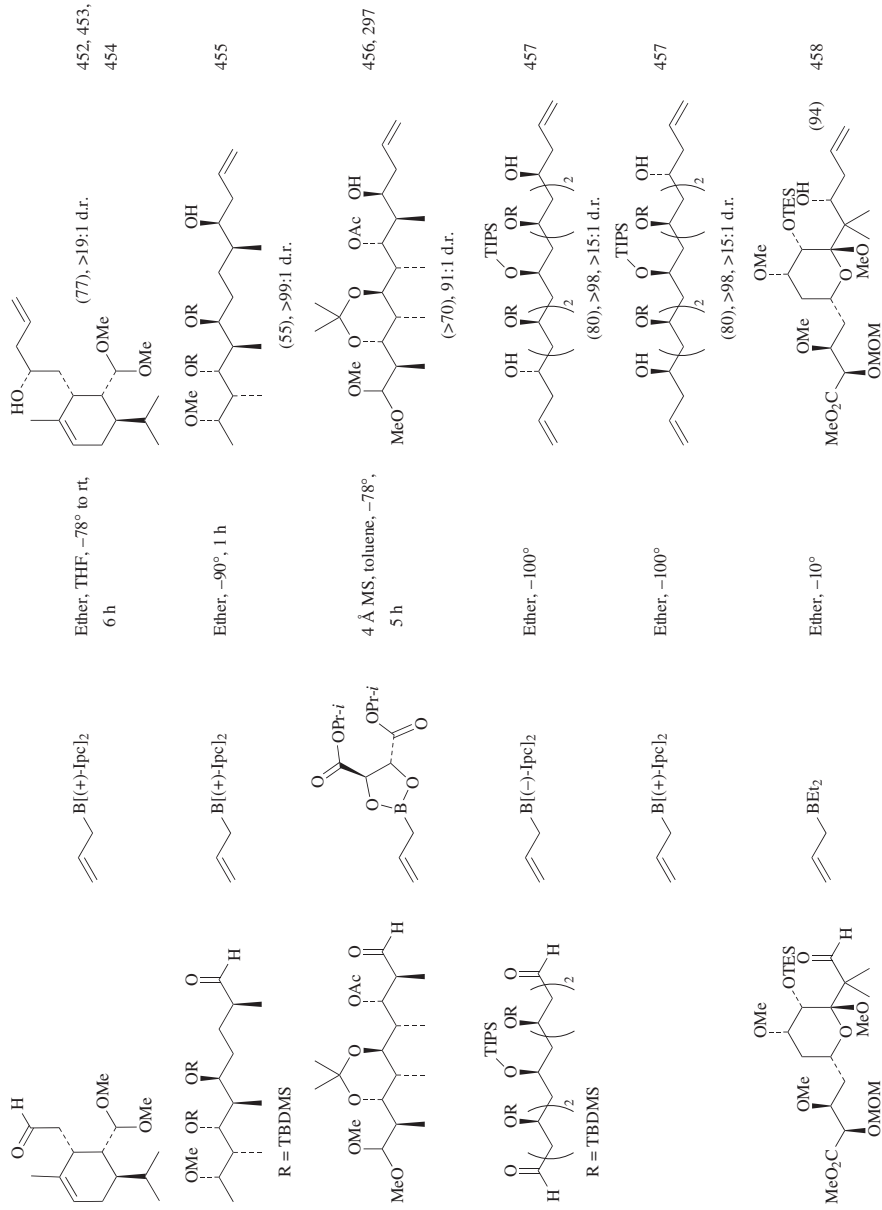
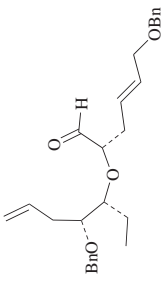

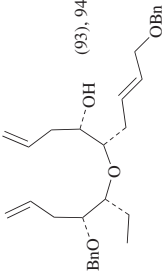
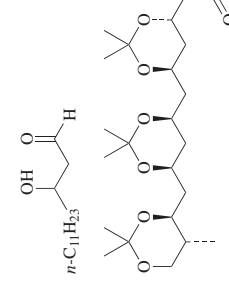

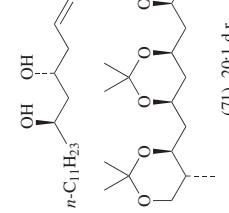
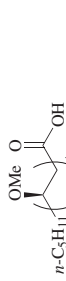

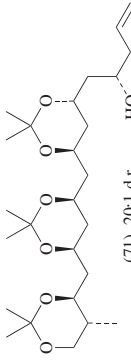
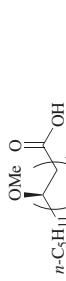
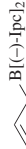
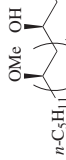
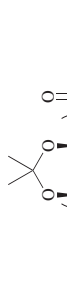
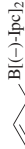
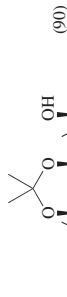
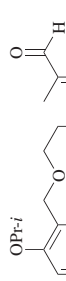
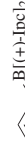
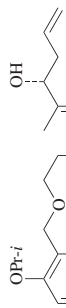


TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBOXYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
 C <sub>13</sub>		Ether, -78°, 2 h	 (93), 94:6 d.r.	434
 C <sub>14</sub>		CH <sub>2</sub> Cl <sub>2</sub> , rt	 (88), 65:35 d.r.	110
 C <sub>13</sub>		Ether, -78°	 (71), 20:1 d.r.	433
 C <sub>13</sub>		Toluene, -78°	 (99), 5:1 d.r.	459
 C <sub>13</sub>		Ether, -78° to rt	 (90)	428
 C <sub>13</sub>		Ether, -78°, 1.5 h	 (60), 71	460

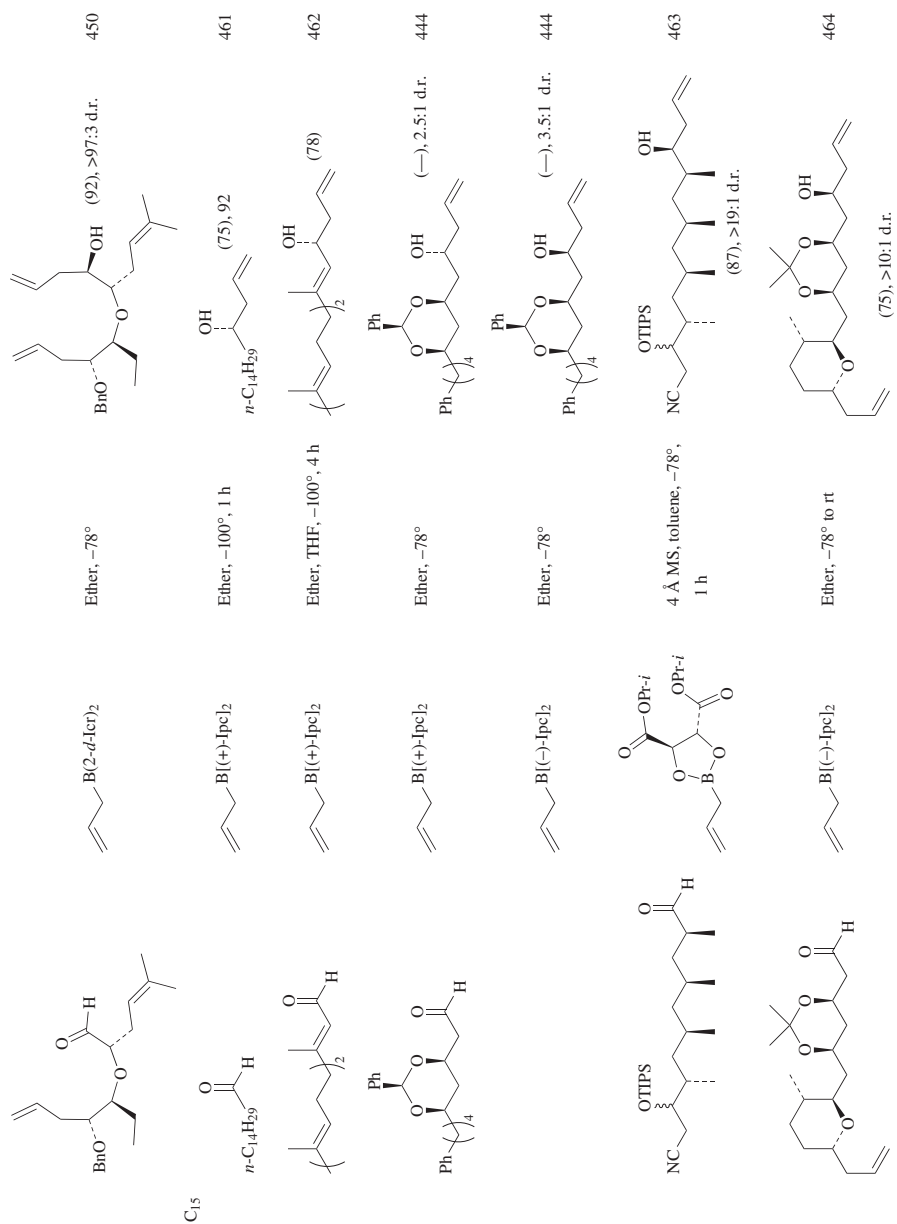


TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBONYL SUBSTRATES (Continued)

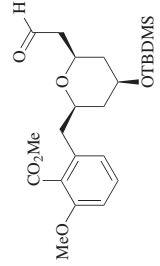

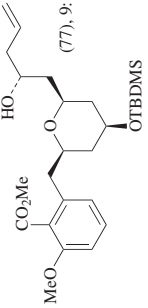
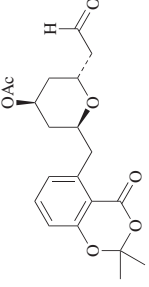

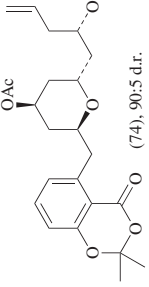
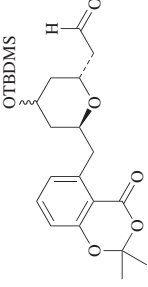

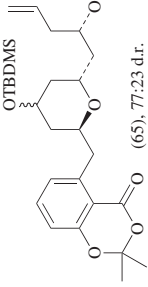
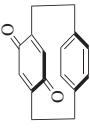

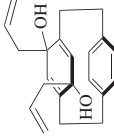
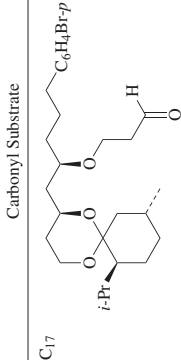

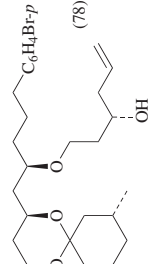
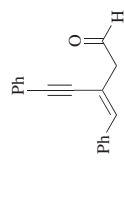

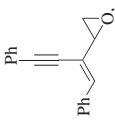
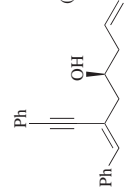
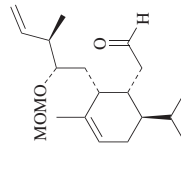

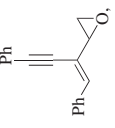
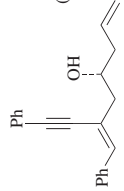
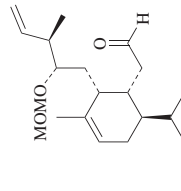

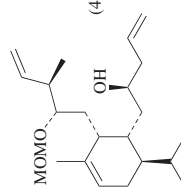
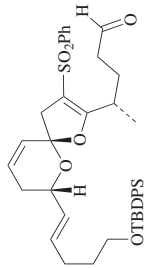
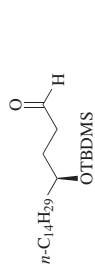
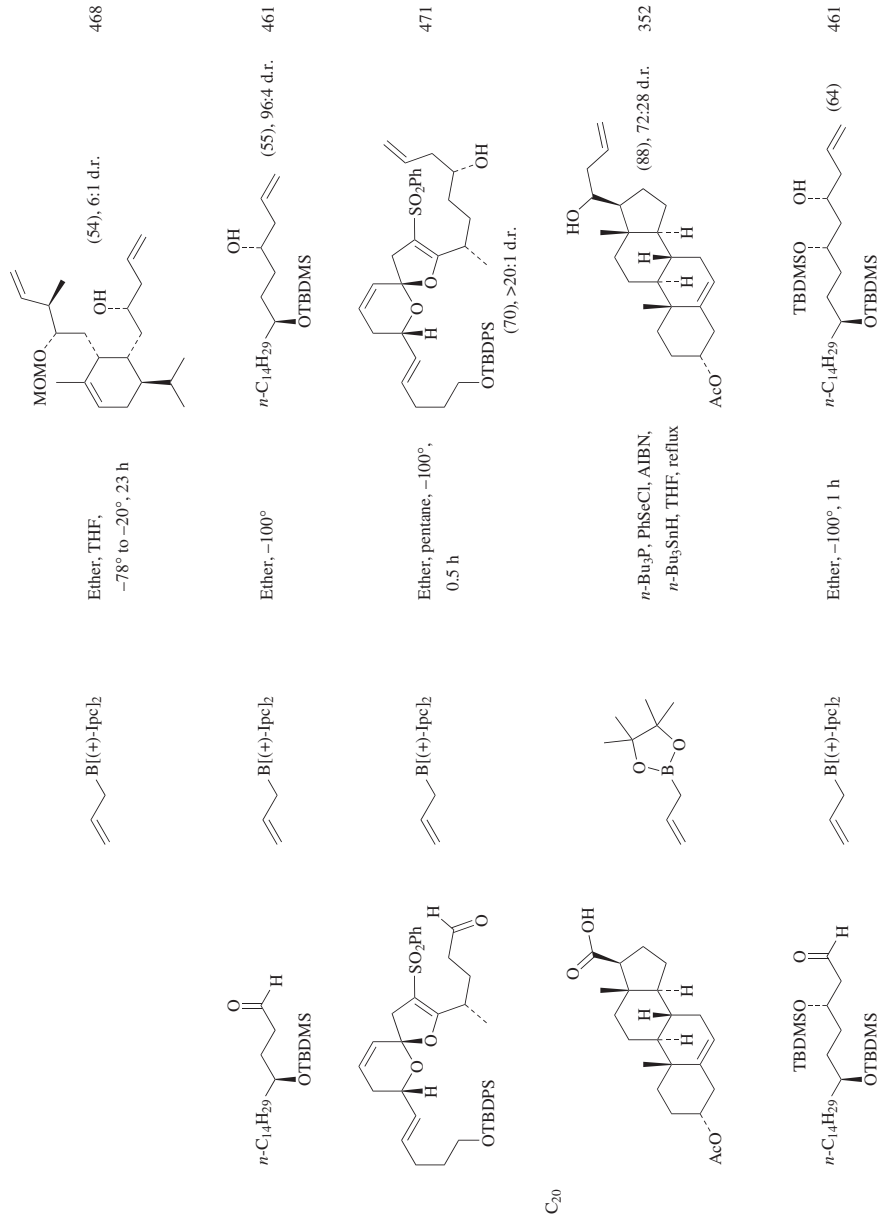
Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
 C <sub>15</sub>		Ether, -78°, 3 h	 (77), 9:1 d.r.	465
		Ether, -100°, 2 h	 (74), 90:5 d.r.	416, 417
		Ether, -78°	 (65), 77:23 d.r.	466
 C <sub>16</sub>		Toluene, 20°, 0.5 h	 (98)	467





TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBOXYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
 C17	 Bi((-)-Ipc) <sub>2</sub>	Ether, -78°	 (78)	326
 C18	 Bi((-)-Ipc) <sub>2</sub>	 Sc(OTf) <sub>3</sub> , THF, -78°, 6 h	 (23), 93	101
	 Bi(+)-Ipc) <sub>2</sub>	 Sc(OTf) <sub>3</sub> , THF, -78°, 4 h; -70°, 36 h	 (76), 93	101
	 Bi((-)-Ipc) <sub>2</sub>	Ether, THF, -78° to -20°, 23 h	 (48), 3:1 d.r.	468



C<sub>20</sub>

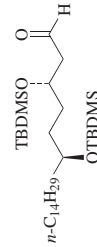
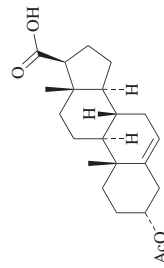
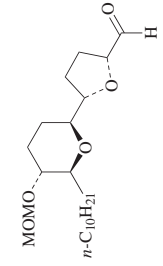
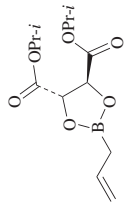
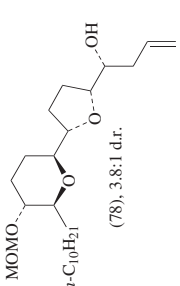
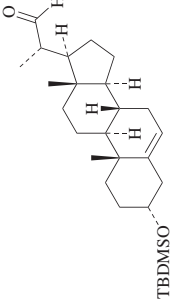
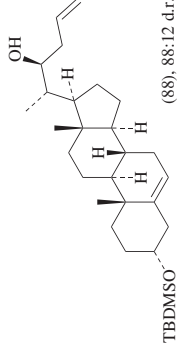
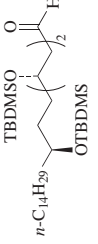
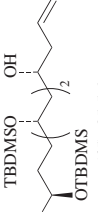

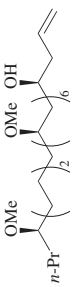
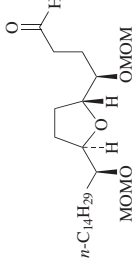
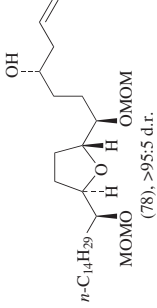


TABLE 1. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBOXYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
 MOMO <i>n</i> -C <sub>10</sub> H <sub>21</sub>	 OPr- <i>i</i>	4 Å MS, toluene, -78°, 3 h	 (78), 3.8:1 d.r.	472
 TBDMMSO	BBN	—	 (88), 88:12 d.r.	473
 TBDMMSO <i>n</i> -C <sub>14</sub> H <sub>29</sub>	B[(+)- <i>i</i> pcl] <sub>2</sub>	Ether, -100°, 1 h	 (65), 95:5 d.r.	461
 MOMe <i>n</i> -Pr	B[(-)- <i>i</i> pcl] <sub>2</sub>	Toluene, -78°	 (83), 88:12 d.r.	474
 MOMO <i>n</i> -C <sub>14</sub> H <sub>29</sub>	B[(-)- <i>i</i> pcl] <sub>2</sub>	Ether, -100°	 (78), >95:5 d.r.	475

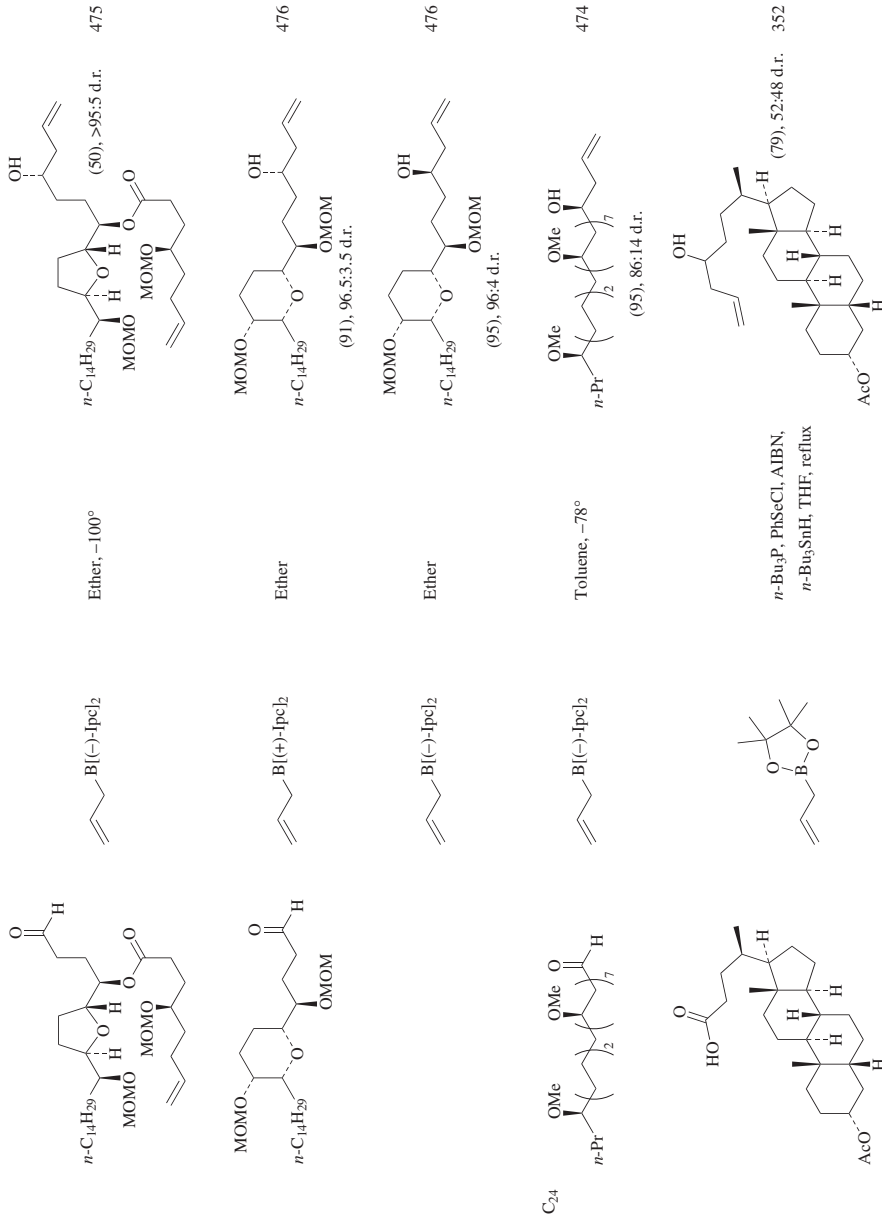
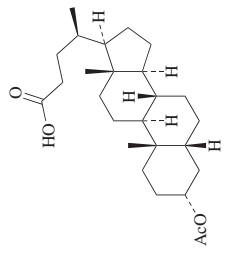
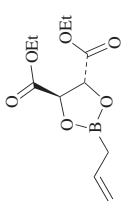
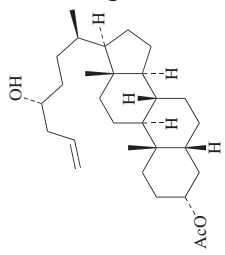
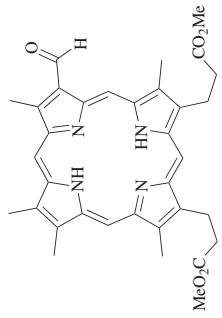

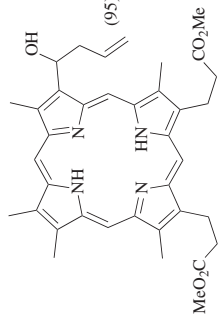
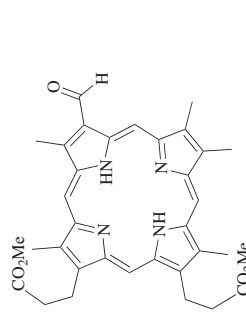

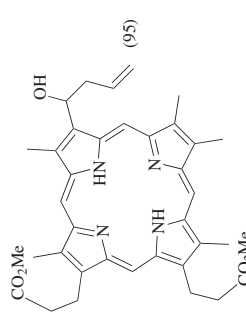
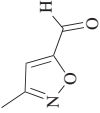

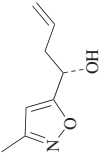
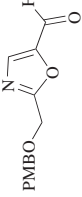
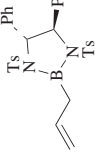
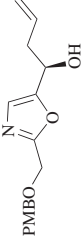
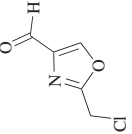

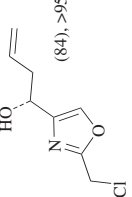
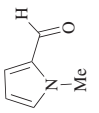

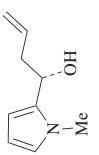
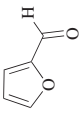

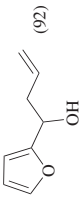


TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 A. NON-AROMATIC CARBOXYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
 $C_{24}$		$n\text{-Bu}_3\text{P}$ , $\text{PhSeCl}$ , $\text{Et}_3\text{B}$ , $n\text{-Bu}_3\text{SnH}$ , THF, $-78^\circ$	 (60), 85:15 d.r.	352
 $C_{32}$		$\text{CH}_2\text{Cl}_2$ , ether, $0^\circ$ , 0.33 h	 (95)	477
		$\text{CH}_2\text{Cl}_2$ , ether, $0^\circ$ , 0.33 h	 (95)	477

<sup>a</sup>The reaction mixture was free of  $\text{Mg}^{2+}$  ions.

TABLE 1. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 B. AROMATIC AND HETEROAROMATIC CARBONYL SUBSTRATES

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Ether, -100° to rt, 18 h	 (44), 92	378
		CH <sub>2</sub> Cl <sub>2</sub> , -78°	 (-), >95	280
		Ether, -100°	 (84), >95	374
		Ether, -100°, 1 h	 (78), >99	478
		Neat, 0-10°	 (92)	238

C<sub>5</sub>

TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 B. AROMATIC AND HETEROAROMATIC CARBONYL SUBSTRATES (Continued)

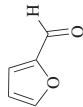
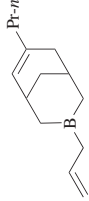
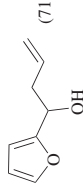

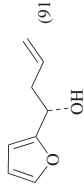
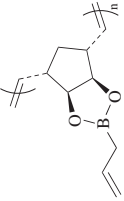
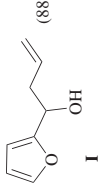


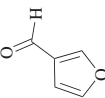

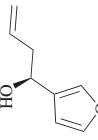

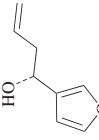


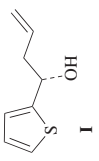
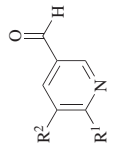

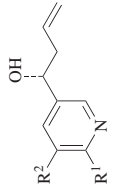
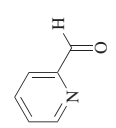

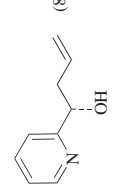
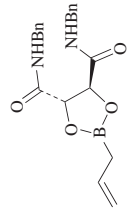
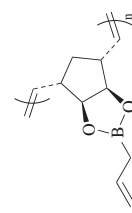
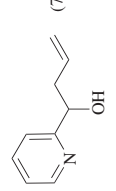
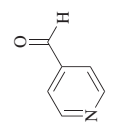

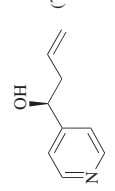
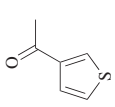
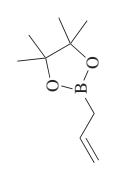
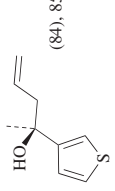
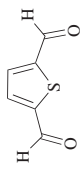

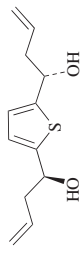
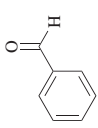

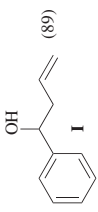
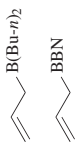
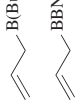
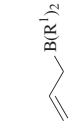
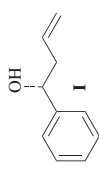
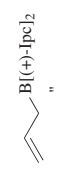
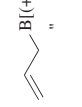
Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Neat, 0-10°	 (71)	238
		Ether, -100°, 1 h	 (91), >99	478
		CH <sub>2</sub> Cl <sub>2</sub> , H <sub>2</sub> O, rt, 6 h	 (88)	234
		<i>n</i> -Bu <sub>4</sub> Ni (10 mol%), CH <sub>2</sub> Cl <sub>2</sub> , H <sub>2</sub> O, rt, 15 min	 (95)	100
		Ether, -100°, 1 h	 (80), >91	478
		Ether, -100°, 1 h	 (88), >99	478
		Ether, -100°, 1 h	 (80), 90	478





TABLE 1. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 B. AROMATIC AND HETEROAROMATIC CARBOXYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.																												
		Ether, -100°, 1 h		<table border="1"> <thead> <tr> <th>R<sup>1</sup></th> <th>R<sup>2</sup></th> <th>Yield (%)</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>(94), 94</td> <td>479</td> </tr> <tr> <td>H</td> <td>Br</td> <td>(75), 66</td> <td></td> </tr> <tr> <td>Cl</td> <td>H</td> <td>(74), 85.5</td> <td></td> </tr> <tr> <td>Cl</td> <td>Cl</td> <td>(73), 90</td> <td></td> </tr> <tr> <td>H</td> <td>MeO</td> <td>(75), 91.5</td> <td></td> </tr> <tr> <td>MeO</td> <td>H</td> <td>(78), 88</td> <td></td> </tr> </tbody> </table>	R <sup>1</sup>	R <sup>2</sup>	Yield (%)	% ee	H	H	(94), 94	479	H	Br	(75), 66		Cl	H	(74), 85.5		Cl	Cl	(73), 90		H	MeO	(75), 91.5		MeO	H	(78), 88	
R <sup>1</sup>	R <sup>2</sup>	Yield (%)	% ee																													
H	H	(94), 94	479																													
H	Br	(75), 66																														
Cl	H	(74), 85.5																														
Cl	Cl	(73), 90																														
H	MeO	(75), 91.5																														
MeO	H	(78), 88																														
		Ether, -100°, 1 h		(85), >99 478																												
		Toluene, -78°, 18 h	<b>I</b> (92), 94	290																												
		CH <sub>2</sub> Cl <sub>2</sub> , H <sub>2</sub> O, rt, 3 h		(79) 234																												
		Ether, -100°, 1 h		(78), >99 478																												

		<p>(<i>R,R</i>)-<i>t</i>-Pr-DuPHOS, CuF, La(OPr-<i>i</i>)<sub>3</sub>, DMF, -40°, 1 h</p>	 (84), 85	164
		THF, -100°, 4 h	 (93), >98, 98;2 d.r.	482
		-70° to 130°	 I (95)	262, 1
		Neat, 0-10°	I (96)	238
		Pentane, rt, 2 h		103
		$\text{CH}_2=\text{CH}-\text{OR}^2$ , BR <sup>1</sup> <sub>3</sub> , Pd(PPh <sub>3</sub> ) <sub>4</sub> , THF	 I	483
		—		250
		Ether, -100°, 1 h		479, 484

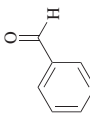

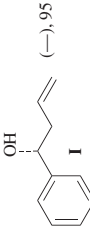

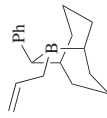

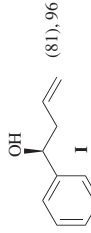

R <sup>1</sup>	R <sup>2</sup>	Temp	Time
Et	COPh	rt	4 h (68)
Bu	COPh	rt; 40°	16 h; 4 h (74)
Et	Ph	rt	6 h (59)
Et	Bn	rt; 50°	4.5 h; 17 h (47)

I (76), 98

I (83), 95

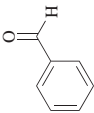
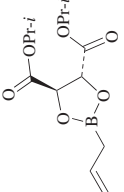
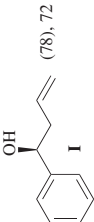
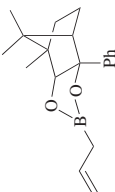
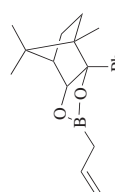
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TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 B. AROMATIC AND HETEROAROMATIC CARBOXYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		THF, -78°, 3 h	 I (-), 95	240
	"	Ether, -100° <sup>a</sup>	I (-), >99	139, 241
		Ether, -78°, 3 h	I (80), >98	143
	"	Ether, 3 h	I (-)	143
			Temp % ee rt 90 0° 93 -25° 94	
		Ether, -78°	I (82), 90	145
		Ether, -78° to rt	 I (81), 96	136, 136a
	"	Ether, -78°, 3 h	I (-), 94	240
	"	Ether, -100° <sup>a</sup>	I (-), 96	139, 289
		THF, -78°, 3 h	I (-), 87	240
	"	Ether, -100° <sup>a</sup>	I (-), 98	139

	Ionic liquid, rt, 3 h		Ionic liquid bmimBr (87) bmimBF <sub>4</sub> (89) emimBr (88) TEAN (85)	353
	L.A. (10 mol%), toluene, -78°, 16 h		L.A. AlCl <sub>3</sub> (88) Sc(OTf) <sub>3</sub> (80)	25
	CH <sub>2</sub> Cl <sub>2</sub> , -78°, 24 h			424
	Toluene, -78°, 24 h			424
	4 Å MS, CH <sub>2</sub> Cl <sub>2</sub> , -78°, 12 h			485
	4 Å MS, CH <sub>2</sub> Cl <sub>2</sub> , -78°, 12 h			485
	See table		Solvent    Temp    Time I    toluene    0°    14 h    (77.7), 34 toluene    -20°    14 h    (80.5), 46 ether        -78°    18 h    (87), 83 toluene    -78°    14 h    (87.8), 90	290

TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 B. AROMATIC AND HETEROAROMATIC CARBONYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		4 Å MS, THF, -78°	 (78), 72	125
	"	Cr(CO) <sub>3</sub> , 4 Å MS, toluene, -78°	<b>I</b> (90), 83	128
	"	4 Å MS, toluene, -78°	<b>I</b> (-), 60	131
	"	Sc(OTf) <sub>3</sub> (10 mol%), CH <sub>2</sub> Cl <sub>2</sub> , -78°, 2 h	<b>I</b> (100), 7	27, 28
		Hexane, -40°	<b>I</b> (90), 36	122
		L.A. (10 mol%)	L.A. Solvent Temp Time % Conv. % ee	
			<b>I</b> none CH <sub>2</sub> Cl <sub>2</sub> rt 72 h 50 11	27, 28
			AlCl <sub>3</sub> CH <sub>2</sub> Cl <sub>2</sub> -78° 2 h 14 63	
			TiCl <sub>4</sub> CH <sub>2</sub> Cl <sub>2</sub> -78° 2 h 22 78	
			TiOH CH <sub>2</sub> Cl <sub>2</sub> -78° 2 h 72 84	
			Cu(OTf) <sub>2</sub> CH <sub>2</sub> Cl <sub>2</sub> -40° 2 h 4 52	
			Yb(OTf) <sub>3</sub> CH <sub>2</sub> Cl <sub>2</sub> -40° 2 h 4 38	
			Sc(OTf) <sub>3</sub> CH <sub>2</sub> Cl <sub>2</sub> -78° 2 h 90 92	
			Sc(OTf) <sub>3</sub> toluene -78° 2 h 30 46	
			Sc(OTf) <sub>3</sub> hexane -78° 2 h 20 8	

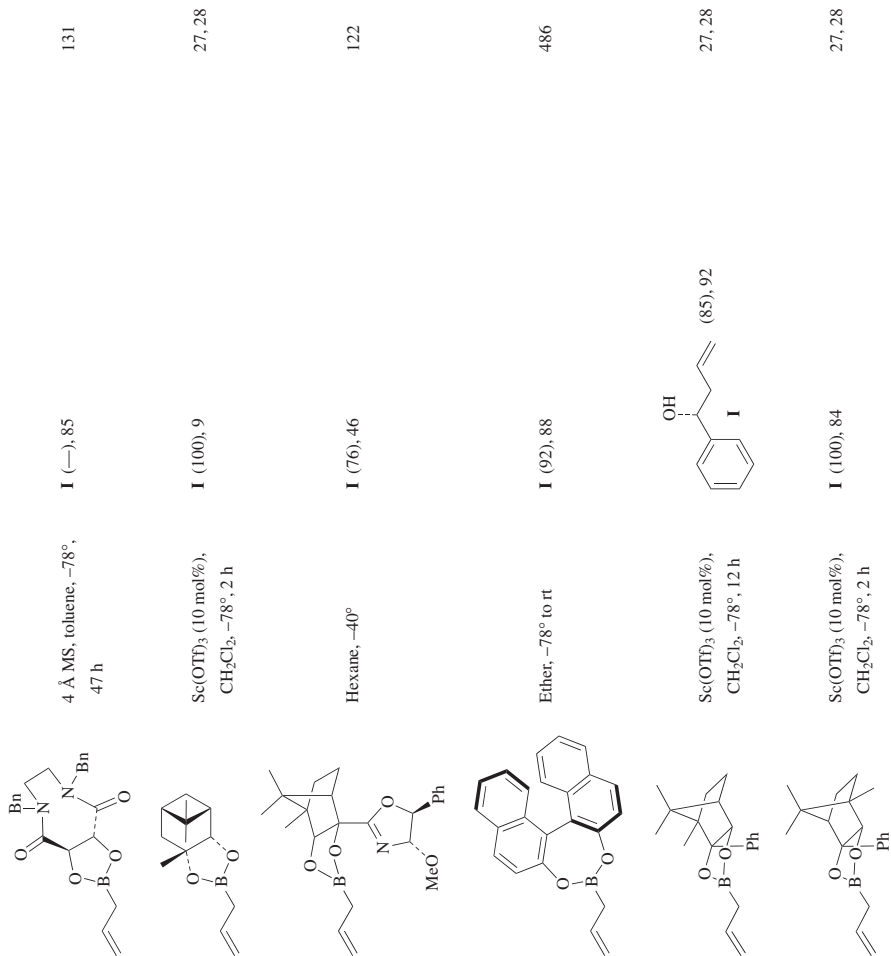
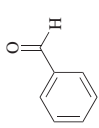
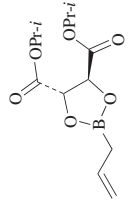
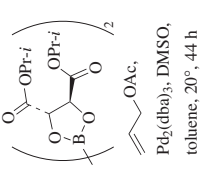
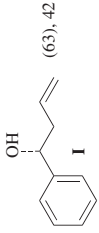
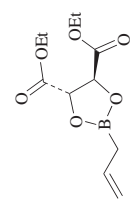
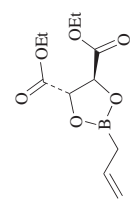
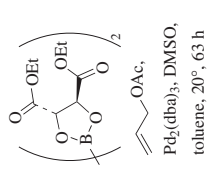

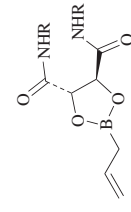
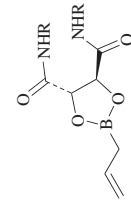


TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 B. AROMATIC AND HETEROAROMATIC CARBONYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
			 (63), 42	349
"	"	4 Å MS, -78°	Solvent % ee toluene 60 ether 59	125
			 (83), 45	349
		See table	R Solvent Temp Time Ph ether rt 18 h (62.5), 6.4 Bn THF -40° 16 h (79.6), 61 Bn toluene -60° 16 h (83.5), 85 Ph THF -78° 14 h (76.2), 72 Ph toluene -78° 18 h (82.3), 80	290



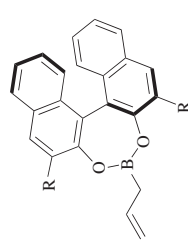
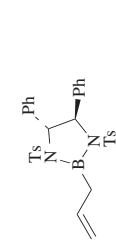
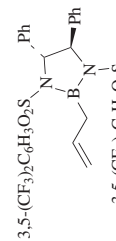
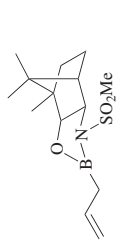
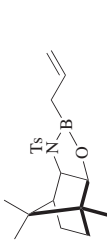
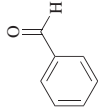
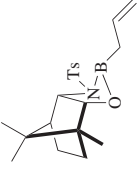
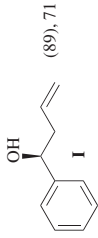
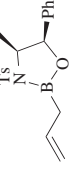
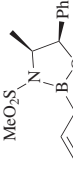
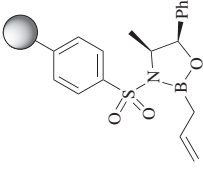
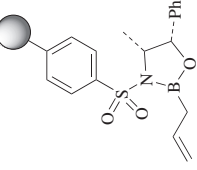
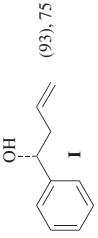
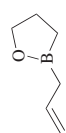
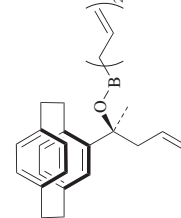
	THF, -78°, 1 h	<b>I</b>	R	(50), 42 (91), 74 (91), 86 (90), 46 (89), 62 (94), 60 (92), 66 (92), 80 (90), 50 (90), 96	135
	CH <sub>2</sub> Cl <sub>2</sub> , -78°, 2 h	<b>I</b>	(>90), 94	50	
"	Toluene, -78°, 2 h	<b>I</b>	(>90), 95	50	
	Toluene, -78°, 2 h	<b>I</b>	(92), 96	351	
	Ether, -78° to rt, 2 h	<b>I</b>	(91), 88	133	
	-78°	<b>I</b>	Solvent THF ether	245, 246 (88), 74 (90), 81	

TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 B. AROMATIC AND HETEROAROMATIC CARBONYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Ether, -78°, 7 h	 (89), 71	245, 246
		Ether, -78°, 7 h	<b>I</b> (93), 75	245, 246
		Ether, -78°	<b>I</b> (90), 66	246
		Ether, -78°, 7 h	<b>I</b> (93), 75	245, 246
		Ether, -78°, 7 h	 (93), 75	245, 246

	Solvent	Temp	
	I THF	-40°	(91), 65
	THF	-78°	(94), 78
	THF	-100°	(96), 88
	toluene	-78°	(91), 72
	ether	-78°	(93), 85
			(92), 74
			245, 246
			(81)
			263
			(-), 18
			487
	X		
	I Cl	-40° to rt	(57)
	Br		(53)
	X		
	I Cl	-40° to rt	(67)
	Br		(38)

See table

Ether, -78°, 7 h

Neat, 80-100°

THF, -70°, 17 h

CH<sub>2</sub>Cl<sub>2</sub>, -40° to rtCH<sub>2</sub>Cl<sub>2</sub>, -40° to rt

TABLE 1. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 B. AROMATIC AND HETEROAROMATIC CARBONYL SUBSTRATES (Continued)

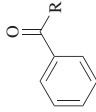

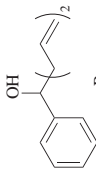
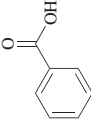
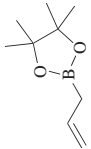
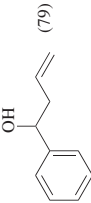
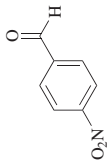
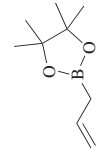
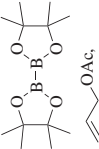
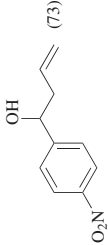
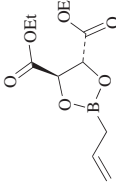
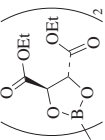
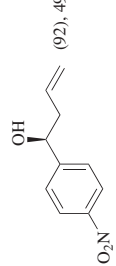
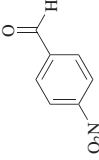

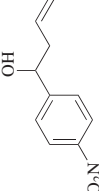
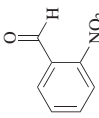

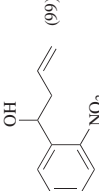
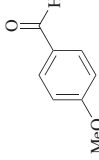

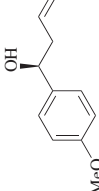
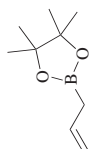
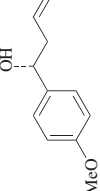

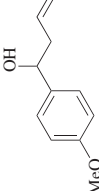
Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.																				
		See table		103																				
			<table border="1"> <thead> <tr> <th>R</th> <th>Solvent</th> <th>Temp</th> <th>Time</th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>pentane</td> <td>rt</td> <td>2 h (89)</td> </tr> <tr> <td>OC(O)Ph</td> <td>pentane</td> <td>rt</td> <td>2 h (82)</td> </tr> <tr> <td>OEt</td> <td>hexane</td> <td>68°</td> <td>50 h (59)</td> </tr> <tr> <td>NMe<sub>2</sub></td> <td>pentane</td> <td>rt</td> <td>3 h (91)</td> </tr> </tbody> </table>	R	Solvent	Temp	Time	Cl	pentane	rt	2 h (89)	OC(O)Ph	pentane	rt	2 h (82)	OEt	hexane	68°	50 h (59)	NMe <sub>2</sub>	pentane	rt	3 h (91)	
R	Solvent	Temp	Time																					
Cl	pentane	rt	2 h (89)																					
OC(O)Ph	pentane	rt	2 h (82)																					
OEt	hexane	68°	50 h (59)																					
NMe <sub>2</sub>	pentane	rt	3 h (91)																					
		<i>n</i> -Bu <sub>3</sub> P, PhSeCl, AIBN, <i>n</i> -Bu <sub>3</sub> SnH, THF, reflux		352																				
		 Pd <sub>2</sub> (dba) <sub>3</sub> , DMSO, toluene, 20°, 21 h		349																				
		 Pd <sub>2</sub> (dba) <sub>3</sub> , DMSO, toluene, 20°, 22 h		349																				



TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 B. AROMATIC AND HETEROAROMATIC CARBONYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		L.A., CH <sub>2</sub> Cl <sub>2</sub> , -78°, 15 min	 L.A. B(OMe) <sub>3</sub> (0) AlCl <sub>3</sub> (16) Ti(OPr- <i>i</i> ) <sub>4</sub> (20) TMSCl (28) SnCl <sub>4</sub> (41) BF <sub>3</sub> •OEt <sub>2</sub> (93)	99
		<i>n</i> -Bu <sub>4</sub> Ni (10 mol%), CH <sub>2</sub> Cl <sub>2</sub> , H <sub>2</sub> O, rt, 15 min		100
		THF, -78° to rt, 2 h	 (72), 89	488
		L.A. (10 mol %), toluene, -78°, 36 h	 L.A. AlCl <sub>3</sub> (82) Sc(OTf) <sub>3</sub> (84)	25
		<i>n</i> -Bu <sub>4</sub> Ni (10 mol%), CH <sub>2</sub> Cl <sub>2</sub> /H <sub>2</sub> O, rt, 15 min	 (98)	100

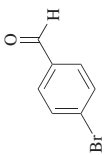

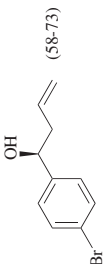
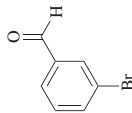

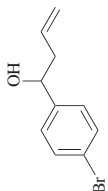
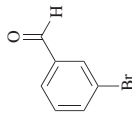

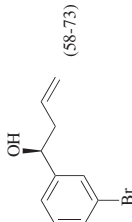
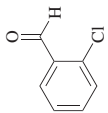

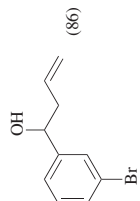
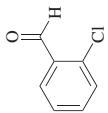

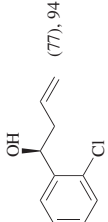
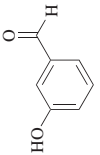

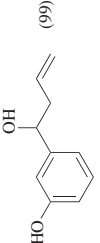
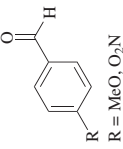
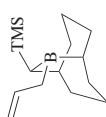
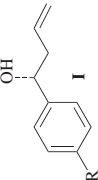
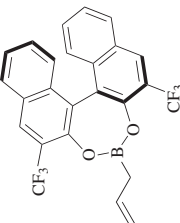
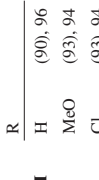
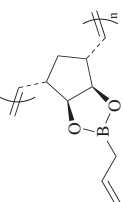
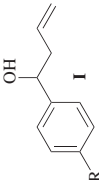

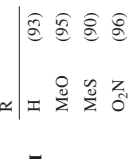
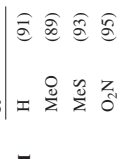
		Ether, -78° to rt, 3 h		489
		PTC (10 mol%), CH <sub>2</sub> Cl <sub>2</sub> /H <sub>2</sub> O, rt, 15 min		100
		Ether, -78° to rt, 3 h		489
		bmimBr, rt, 3 h		353
		THF, -78° to rt, 2 h		488
		<i>n</i> -Bu <sub>4</sub> Ni (10 mol%), CH <sub>2</sub> Cl <sub>2</sub> /H <sub>2</sub> O, rt, 15 min		100

TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 B. AROMATIC AND HETEROAROMATIC CARBONYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
 R = MeO, O <sub>2</sub> N		Ether, -78°, 3 h	 R MeO (90), 96 O <sub>2</sub> N (87), 97	143
R = H, MeO, Cl, O <sub>2</sub> N		THF, -78°, 1 h	 R H (90), 96 MeO (93), 94 Cl (93), 94 O <sub>2</sub> N (96), 92	135
		CH <sub>2</sub> Cl <sub>2</sub> , H <sub>2</sub> O, rt	 R H (87) MeO (93) Cl (85) O <sub>2</sub> N (90)	234
R = H, MeO, MeS, O <sub>2</sub> N		BF <sub>3</sub> ·OEt <sub>2</sub> (2 equiv), CH <sub>2</sub> Cl <sub>2</sub> , -78°, 15 min	 R H (93) MeO (95) MeS (90) O <sub>2</sub> N (96)	98, 99
	"	BF <sub>3</sub> ·OEt <sub>2</sub> (5 mol%), CH <sub>2</sub> Cl <sub>2</sub> , rt, 3-6 h	 R H (91) MeO (89) MeS (93) O <sub>2</sub> N (95)	99



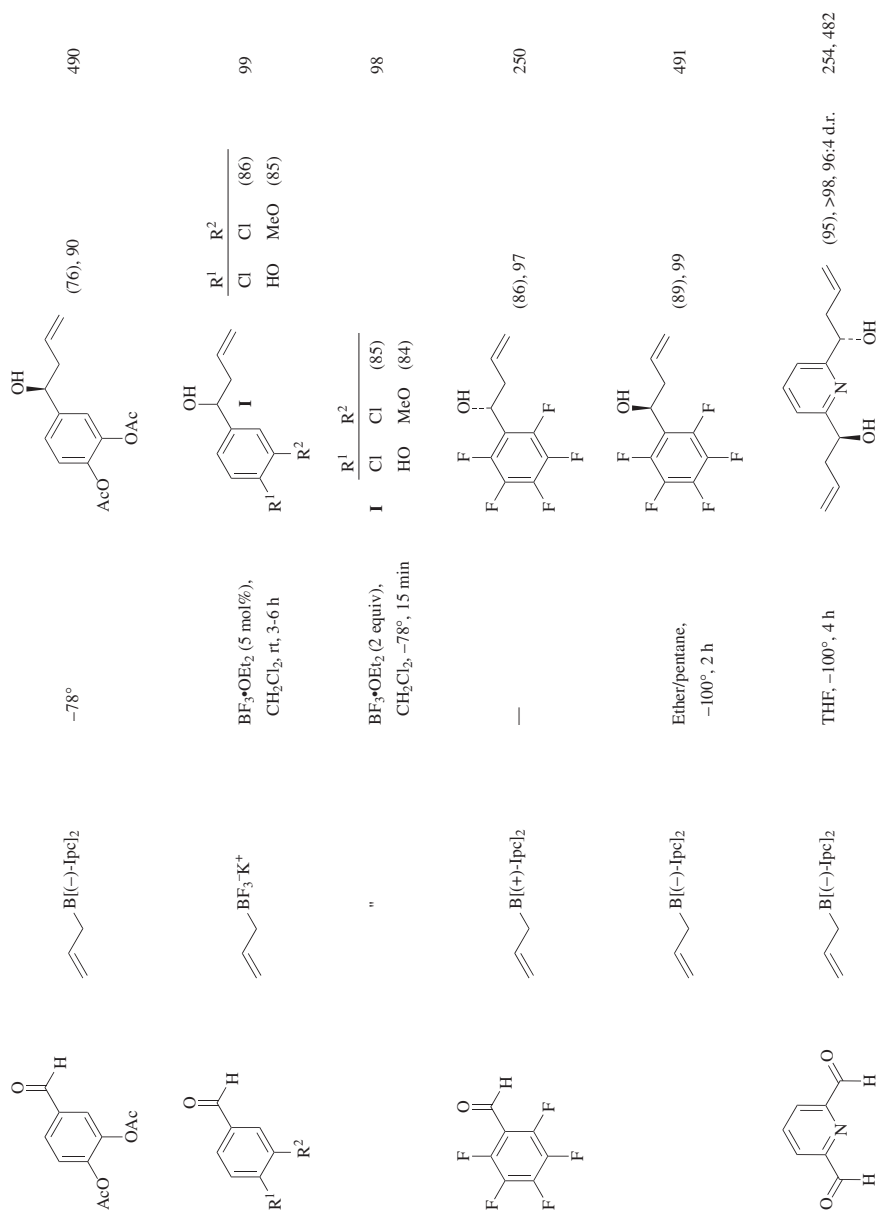
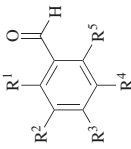

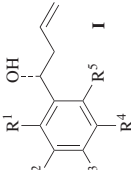
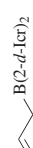
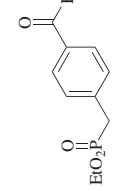

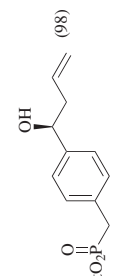


TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 B. AROMATIC AND HETEROAROMATIC CARBONYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.																																																								
 C <sub>7</sub>	 B[(+)-Ipc] <sub>2</sub>	Pentane, ether, -100°	 I	248																																																								
			<table border="1"> <thead> <tr> <th>R<sup>1</sup></th> <th>R<sup>2</sup></th> <th>R<sup>3</sup></th> <th>R<sup>4</sup></th> <th>R<sup>5</sup></th> <th>Yield (%)</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>F</td> <td>F</td> <td>F</td> <td>F</td> <td>F</td> <td>(86), 99.8</td> <td></td> </tr> <tr> <td>F</td> <td>H</td> <td>H</td> <td>H</td> <td>F</td> <td>(88), 99.6</td> <td></td> </tr> <tr> <td>H</td> <td>F</td> <td>H</td> <td>F</td> <td>H</td> <td>(90), 95.2</td> <td></td> </tr> <tr> <td>F</td> <td>H</td> <td>F</td> <td>H</td> <td>H</td> <td>(86), 95.3</td> <td></td> </tr> <tr> <td>F</td> <td>H</td> <td>H</td> <td>H</td> <td>H</td> <td>(80), 98.1</td> <td></td> </tr> <tr> <td>H</td> <td>F</td> <td>H</td> <td>H</td> <td>H</td> <td>(85), 95.0</td> <td></td> </tr> <tr> <td>H</td> <td>H</td> <td>F</td> <td>H</td> <td>H</td> <td>(90), 98.0</td> <td></td> </tr> </tbody> </table>	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>	Yield (%)	% ee	F	F	F	F	F	(86), 99.8		F	H	H	H	F	(88), 99.6		H	F	H	F	H	(90), 95.2		F	H	F	H	H	(86), 95.3		F	H	H	H	H	(80), 98.1		H	F	H	H	H	(85), 95.0		H	H	F	H	H	(90), 98.0		
R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>	Yield (%)	% ee																																																						
F	F	F	F	F	(86), 99.8																																																							
F	H	H	H	F	(88), 99.6																																																							
H	F	H	F	H	(90), 95.2																																																							
F	H	F	H	H	(86), 95.3																																																							
F	H	H	H	H	(80), 98.1																																																							
H	F	H	H	H	(85), 95.0																																																							
H	H	F	H	H	(90), 98.0																																																							
	 B(2- <i>i</i> Pr) <sub>2</sub>	Pentane, ether, -100°	<table border="1"> <thead> <tr> <th>R<sup>1</sup></th> <th>R<sup>2</sup></th> <th>R<sup>3</sup></th> <th>R<sup>4</sup></th> <th>R<sup>5</sup></th> <th>Yield (%)</th> <th>% ee</th> </tr> </thead> <tbody> <tr> <td>F</td> <td>F</td> <td>F</td> <td>F</td> <td>F</td> <td>96</td> <td>96</td> </tr> <tr> <td>F</td> <td>H</td> <td>H</td> <td>H</td> <td>F</td> <td>97</td> <td>97</td> </tr> <tr> <td>H</td> <td>F</td> <td>H</td> <td>F</td> <td>H</td> <td>98</td> <td>98</td> </tr> <tr> <td>F</td> <td>H</td> <td>F</td> <td>H</td> <td>H</td> <td>96</td> <td>96</td> </tr> <tr> <td>F</td> <td>H</td> <td>H</td> <td>H</td> <td>H</td> <td>96</td> <td>96</td> </tr> <tr> <td>H</td> <td>F</td> <td>H</td> <td>H</td> <td>H</td> <td>97</td> <td>97</td> </tr> <tr> <td>H</td> <td>H</td> <td>F</td> <td>H</td> <td>H</td> <td>98</td> <td>98</td> </tr> </tbody> </table>	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>	Yield (%)	% ee	F	F	F	F	F	96	96	F	H	H	H	F	97	97	H	F	H	F	H	98	98	F	H	F	H	H	96	96	F	H	H	H	H	96	96	H	F	H	H	H	97	97	H	H	F	H	H	98	98	248, 249
R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>	Yield (%)	% ee																																																						
F	F	F	F	F	96	96																																																						
F	H	H	H	F	97	97																																																						
H	F	H	F	H	98	98																																																						
F	H	F	H	H	96	96																																																						
F	H	H	H	H	96	96																																																						
H	F	H	H	H	97	97																																																						
H	H	F	H	H	98	98																																																						
 C <sub>8</sub>	 B[(-)-Ipc] <sub>2</sub>	-78°	 (98)	492																																																								

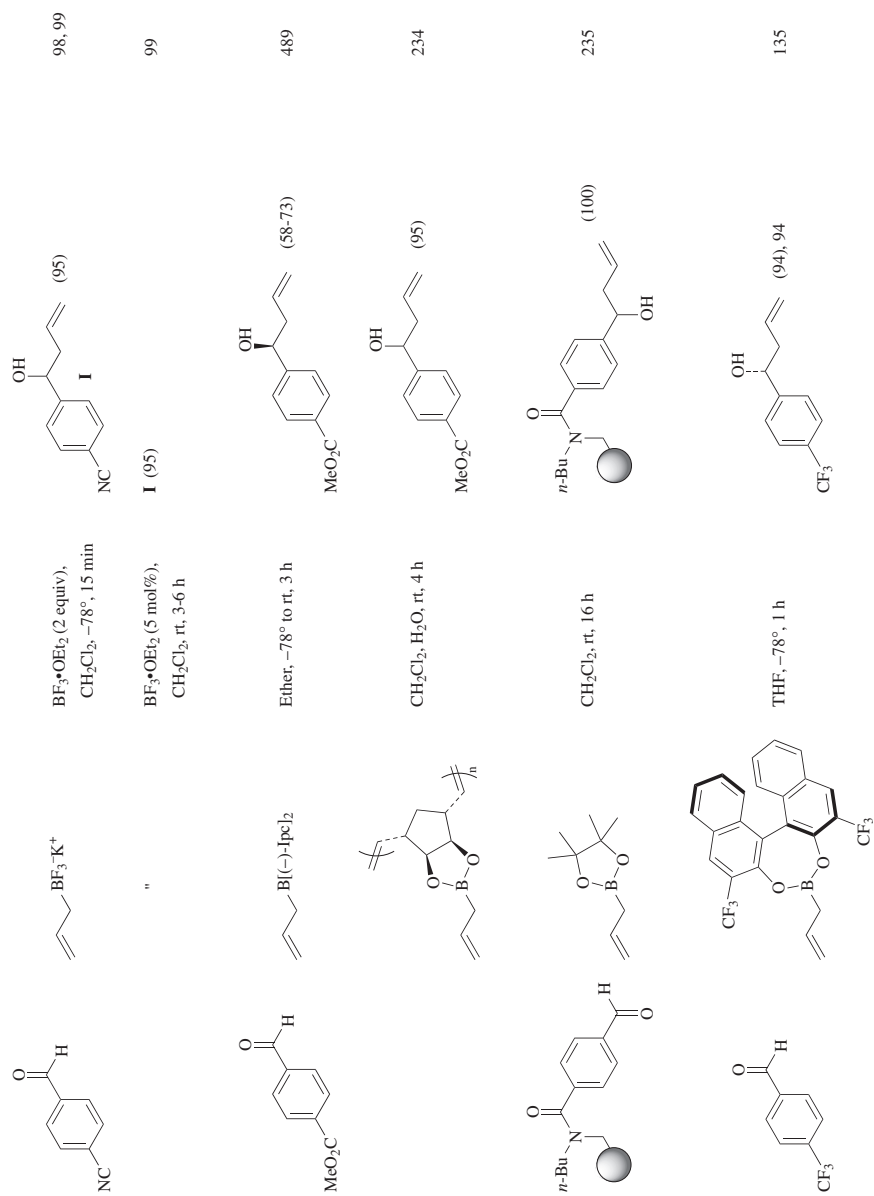


TABLE 1. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 B. AROMATIC AND HETEROAROMATIC CARBONYL SUBSTRATES (Continued)

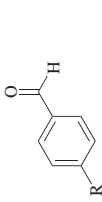
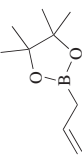
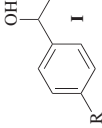

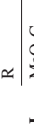
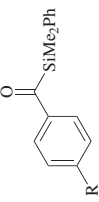

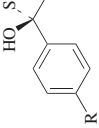
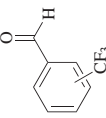

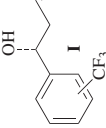


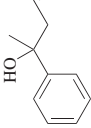


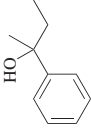
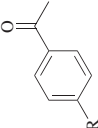
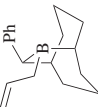
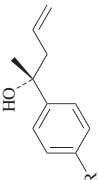
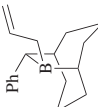
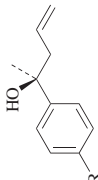
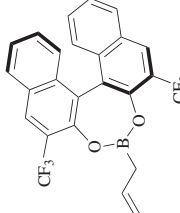
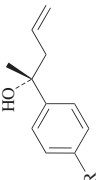
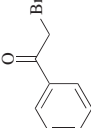
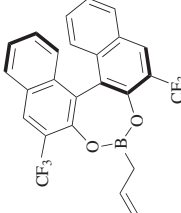
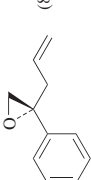
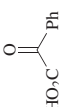

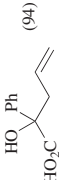
Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
 R = CF <sub>3</sub> , Me		L.A. (10 mol%), toluene, -78°	 I R    L.A.    Time CF <sub>3</sub> AlCl <sub>3</sub> 16 h    (80) CF <sub>3</sub> Sc(OTf) <sub>3</sub> 16 h    (69) Me    AlCl <sub>3</sub> 24 h    (47) Me    Sc(OTf) <sub>3</sub> 24 h    (62)	25
R = MeO <sub>2</sub> C, NC		<i>n</i> -Bu <sub>4</sub> Ni (10 mol%), CH <sub>2</sub> Cl <sub>2</sub> /H <sub>2</sub> O, rt, 15 min	 I R    MeO <sub>2</sub> C    (97) NC        (98)	100
 R = SiMe <sub>2</sub> Ph		Ether, -78° to rt, 3 h	 I R    HO, SiMe <sub>2</sub> Ph CF <sub>3</sub> (81), 36 Me        (65), 26	111
		Pentane, ether, -100°	 I Isomer ortho    (96), 96.8 meta    (80), 99.9 para    (81), 95.2	248
		Pentane, ether, -100°	 I (-) Isomer    % ee ortho    96 meta    97 para    97	248
		Pentane, rt, 2 h	 I (100)	103



TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 B. AROMATIC AND HETEROAROMATIC CARBONYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
 R = H, O <sub>2</sub> N		Ether, -78°	 R H (92), 96 O <sub>2</sub> N (90), >98	145
R = MeO, Br		Ether, -78°	 R MeO (89), 94 Br (96), 98	145
R = MeO, Cl		THF, -78° to -40°, 48 h	 R MeO (95), 98 Cl (94), >98	135
		THF, -78° to -40°, 48 h	 (87), 92	135
		Et <sub>3</sub> N, CH <sub>2</sub> Cl <sub>2</sub> , -10° to rt, 13 h	 (94)	105

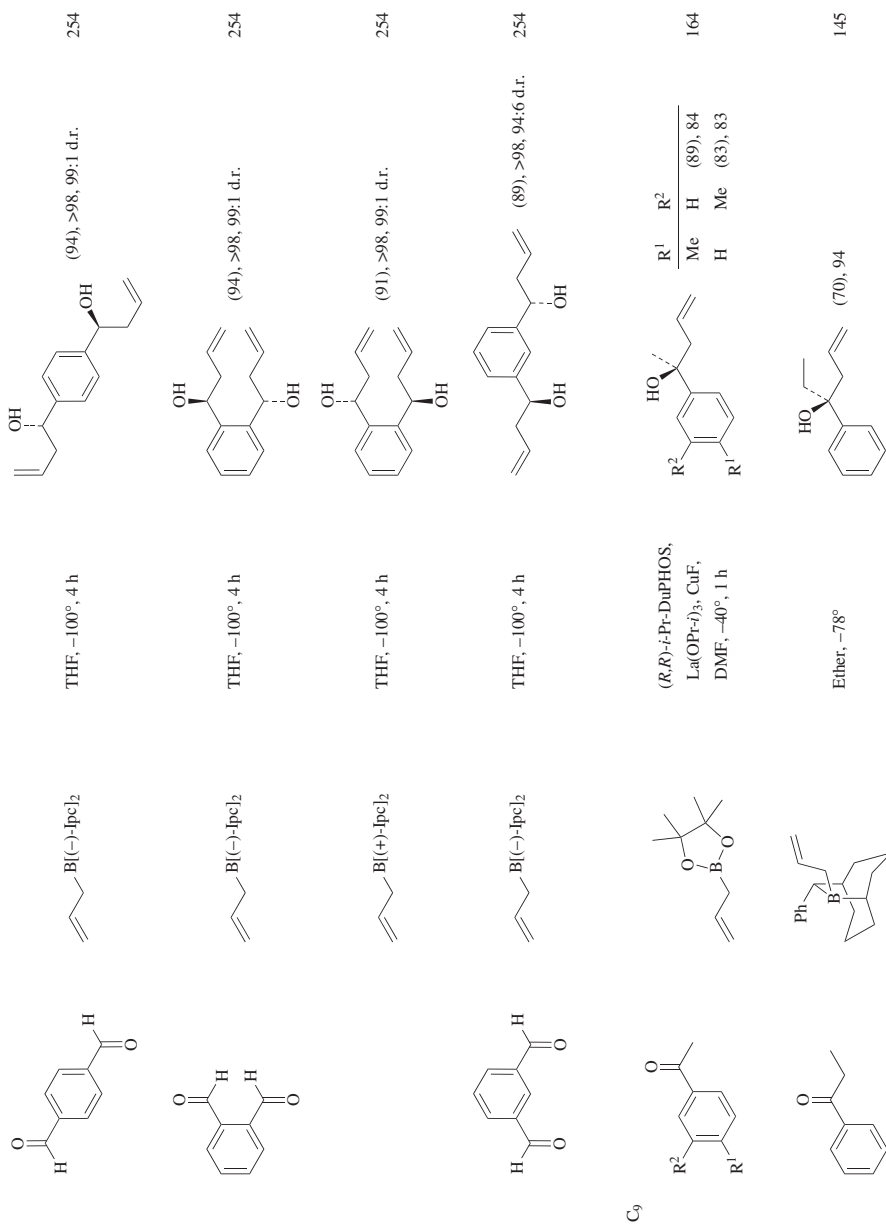
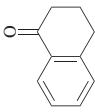
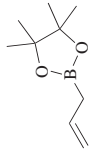
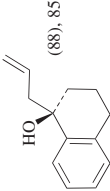
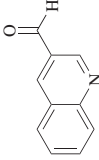

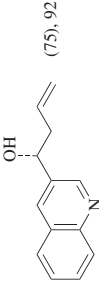
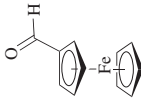

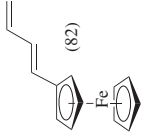
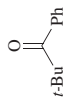

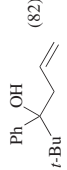
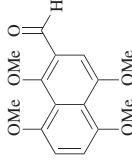

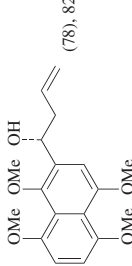


TABLE 1. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 B. AROMATIC AND HETEROAROMATIC CARBONYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		( <i>R,R</i> )- <i>t</i> -Pr-DuPHOS, LiAl(OPr- <i>t</i> ) <sub>3</sub> , CuI, DMF, -40°, 1 h	 (88), 85	164
		Ether, -100°, 1 h	 (75), 92	479
		bmmBr, rt, 3 h	 (82)	353
		Pentane, rt, 4 h	 (82)	103
		Ether, -78°, 30 min	 (78), 82	493



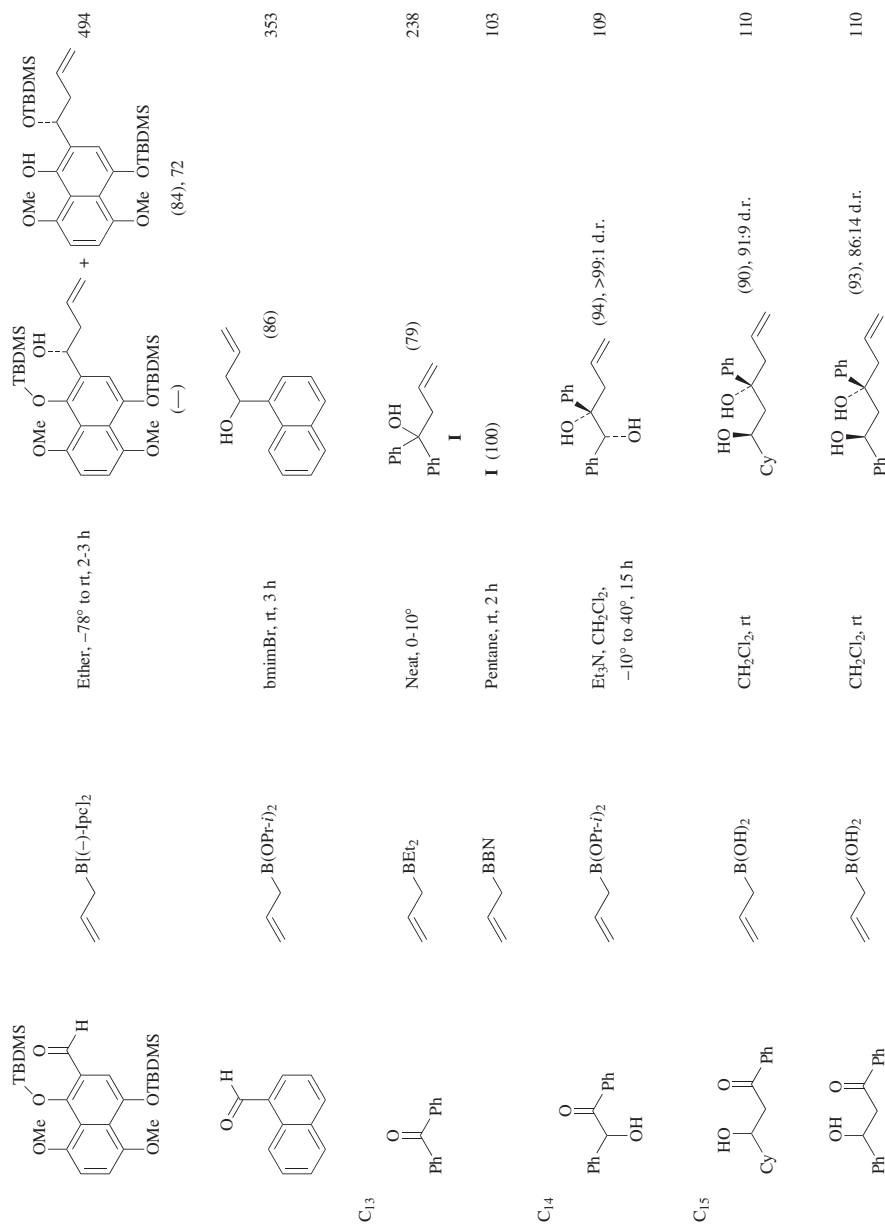
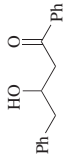

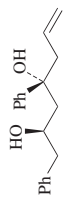
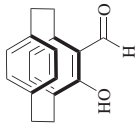

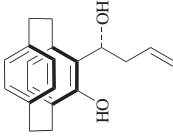
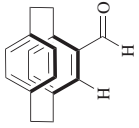

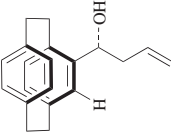
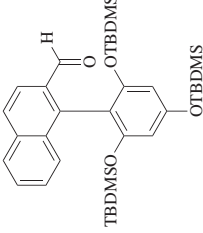

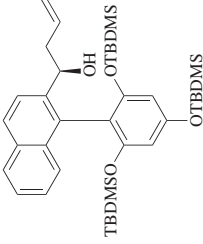
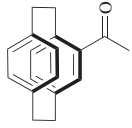

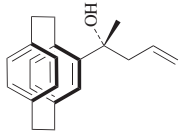
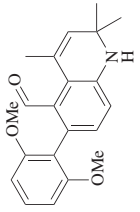

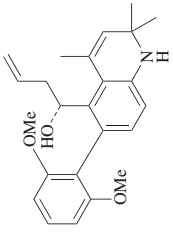
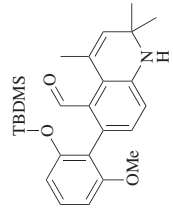

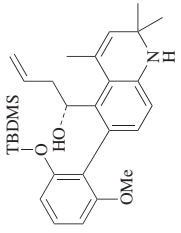
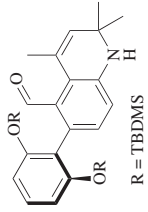

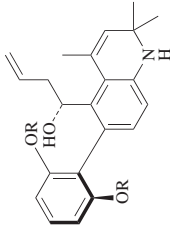


TABLE I. ADDITION OF UNSUBSTITUTED ALLYL REAGENTS (Continued)  
 B. AROMATIC AND HETEROAROMATIC CARBONYL SUBSTRATES (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.															
		CH <sub>2</sub> Cl <sub>2</sub> , rt	 (93), 92:8 d.r.	110															
		CH <sub>2</sub> Cl <sub>2</sub> , -78° to rt, 0.5 h	 <table border="1" data-bbox="625 640 722 840"> <tr> <td>AlI<sub>3</sub>B/Ald</td> <td>d.r.</td> </tr> <tr> <td>1:1</td> <td>(85) &gt;99:1</td> </tr> <tr> <td>2:1</td> <td>(87) &gt;99:1</td> </tr> </table> 487, 464	AlI <sub>3</sub> B/Ald	d.r.	1:1	(85) >99:1	2:1	(87) >99:1	487, 464									
AlI <sub>3</sub> B/Ald	d.r.																		
1:1	(85) >99:1																		
2:1	(87) >99:1																		
		CH <sub>2</sub> Cl <sub>2</sub> , -78° to rt, 0.5 h	 <table border="1" data-bbox="852 567 998 840"> <tr> <td>AlI<sub>3</sub>B/Ald</td> <td>Conc.</td> <td>d.r.</td> </tr> <tr> <td>1:1</td> <td>0.08 M</td> <td>(98) 1:1</td> </tr> <tr> <td>1:2</td> <td>0.08 M</td> <td>(93) 1.5:1</td> </tr> <tr> <td>1:3</td> <td>0.08 M</td> <td>(85) 1.8:1</td> </tr> <tr> <td>1:3</td> <td>0.01 M</td> <td>(60) 7:1</td> </tr> </table> 487, 464	AlI <sub>3</sub> B/Ald	Conc.	d.r.	1:1	0.08 M	(98) 1:1	1:2	0.08 M	(93) 1.5:1	1:3	0.08 M	(85) 1.8:1	1:3	0.01 M	(60) 7:1	487, 464
AlI <sub>3</sub> B/Ald	Conc.	d.r.																	
1:1	0.08 M	(98) 1:1																	
1:2	0.08 M	(93) 1.5:1																	
1:3	0.08 M	(85) 1.8:1																	
1:3	0.01 M	(60) 7:1																	
		THF	 (95), 86	495															

C <sub>18</sub>			CH <sub>2</sub> Cl <sub>2</sub> , 40°, 5 h		Al <sub>3</sub> B/Ket			d.r.
					1:2	Conc.	(75)	
					0.08 M	(93)	>99:1	487, 464
					0.08 M	(90)	>99:1	
					0.04 M	(95)	>99:1	
					0.04 M	(95)	>99:1	
C <sub>19</sub>			THF		(95), 69			496
			THF		(95), 90-95, 1:1 d.r.			495, 496
			THF		(95), 90			495, 496

<sup>a</sup> The reaction mixture was free of Mg<sup>2+</sup> ions.

TABLE 2. ADDITION OF Z-CROTYL REAGENTS



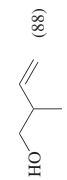

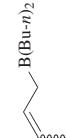
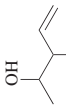

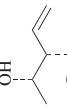

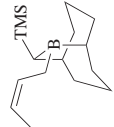

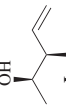

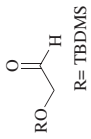
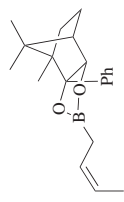
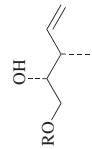


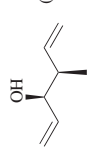

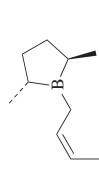
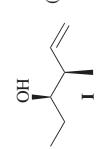



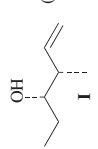

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C <sub>1</sub> 		Pentane, rt, 2 h	 (88)	103
C <sub>2</sub> 		Neat, 0-5°	 (92)	238
		THF, -78°, 3 h	 (72), 96, >99:1 d.r. <b>I</b>	137
	"	Ether, -78°, 3 h	<b>I</b> (72), 92, >99:1 d.r.	497
		Ether, -78°, 3 h	<b>I</b> (75), 94, >99:1 d.r.	497
		Ether, -78°, 3 h	<b>I</b> (68), 95, >98:2 d.r.	143
		Ether, -78°, 3 h	 (75), 90, >99:1 <b>I</b>	497
	"	THF, -78°, 3 h	<b>I</b> (75), 95, >99:1 d.r.	137
		Ether, -78°, 3 h	<b>I</b> (-), 94, >99:1 d.r.	497



TABLE 2. ADDITION OF Z-CROTYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C <sub>2</sub>  R = TBDMS		Sc(OTf) <sub>3</sub> (10 mol%), CH <sub>2</sub> Cl <sub>2</sub> , -78°, 24 h	 (57), 96, >49:1 d.r.	27, 28
C <sub>3</sub> 	B(-)-Ipc]2 	THF, -78°, 3 h	 (63), 90, >99:1 d.r.	137
C <sub>3</sub> 		THF, -78°, 4 h	 (73), 86, 93:7 d.r.	142
	B(-)-Ipc]2 	THF, -78°, 3 h	<b>I</b> (70), 90, 99:1 d.r.	137, 497
	"	THF, ether, -78°, 3 h	<b>I</b> (70), 95-96, 98.5:1.5 d.r.	506
	B(4- <i>d</i> -Ict)2 	THF, -78°, 3 h	<b>I</b> (75), 94, >99:1 d.r.	137, 497
	B(+)-Ipc]2 	THF, ether, -78°, 3 h	 (70), 95-96, 98.5:1.5 d.r.	506
	"	THF, -78°, 3 h	<b>I</b> (78), 92, 99:1 d.r.	137, 497
	B(2- <i>d</i> -Ict)2 	Ether, -78°, 3 h	<b>I</b> (78), 96, >99:1 d.r.	497

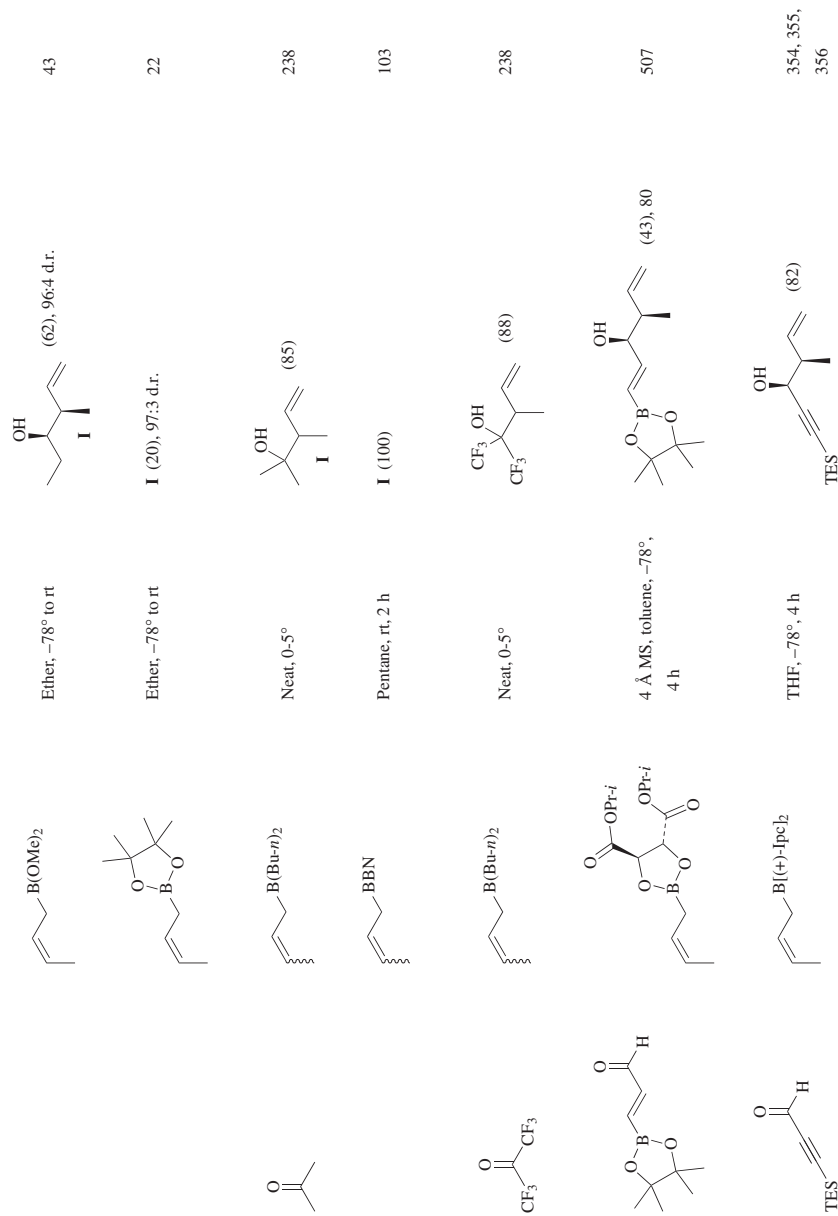
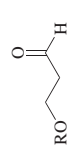









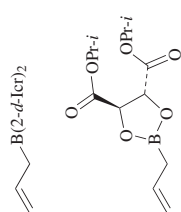
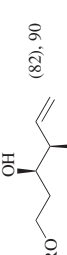
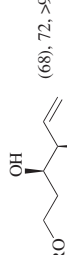


TABLE 2. ADDITION OF Z-CROTYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C <sub>3</sub>  R = TBDPS R = 3,4-DMB R = TBDMS R = PMB R = Bn TBDPSO-CH2-CH2-CHO	         	THF, -78° THF, ether, -78° THF, -78°, 5 h THF, -78° THF, -78° THF, -78° BF <sub>3</sub> •Et <sub>2</sub> O, THF, -78°, 3 h — THF, -78°, 3 h THF, -78° 4 Å MS, toluene, -78°, 4 h	 (82), 90 I (72), >97.5:2.5 d.r. I (82) I (72), 97, >95:5 d.r. I (78), 90 TBBDPSO-CH2-CH(OH)-CH2-CH=CH2 (81) I (—) I (82), >98, >99:1 d.r. I (62)  (68), 72, >98:2 d.r.	508, 509, 510 511 512, 513, 501 514 515 533 517 501 518 519, 37



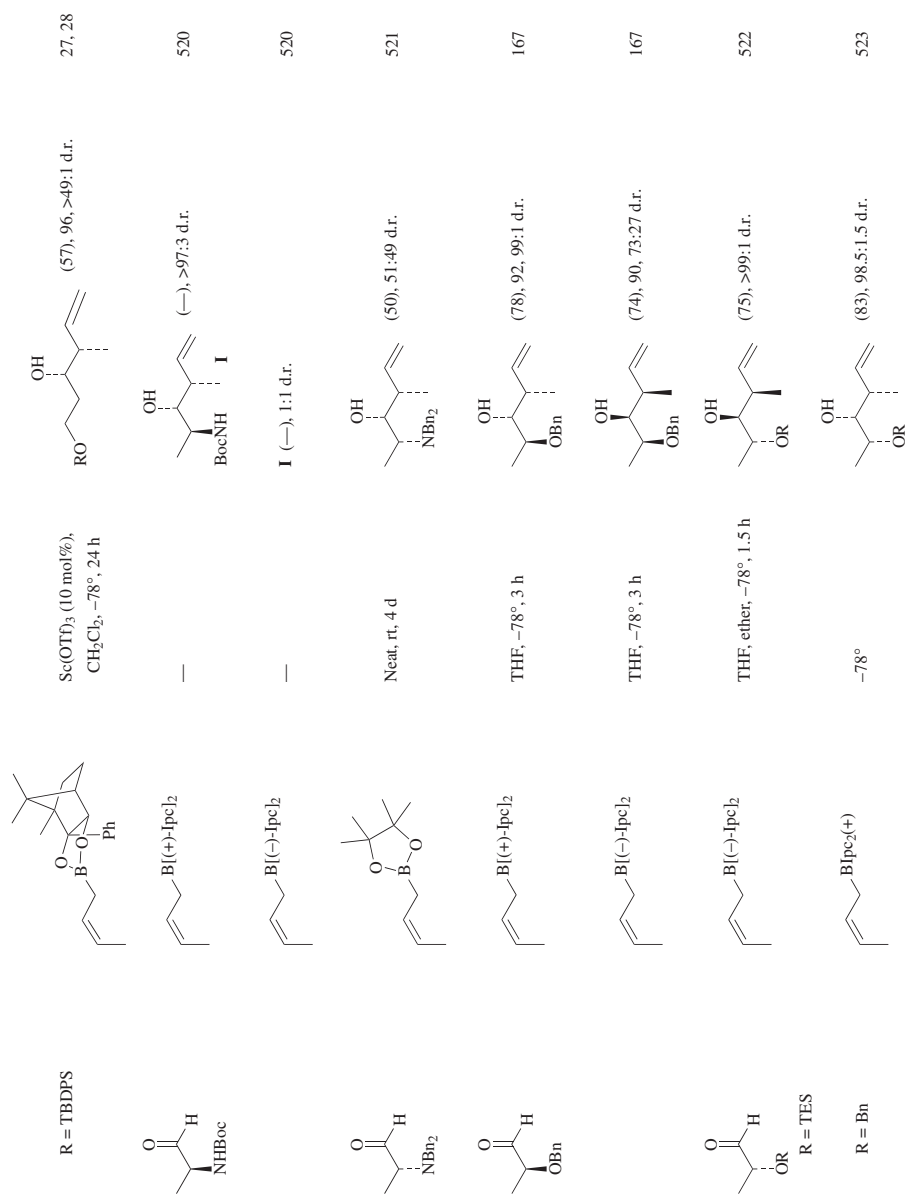


TABLE 2. ADDITION OF Z-CROTYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C <sub>3</sub>  R = Bn R = TBDFPS	 	Neat, rt, 4 d  4 Å MS, toluene, -78°, 1.5 h	 (98), 88:12 d.r.	521  524
 TBDMSO		BF <sub>3</sub> ·OEt <sub>2</sub> (5 mol%), CH <sub>2</sub> Cl <sub>2</sub> , rt, 6 h  <i>n</i> -Bu <sub>4</sub> Ni (10 mol%), CH <sub>2</sub> Cl <sub>2</sub> , H <sub>2</sub> O, rt, 30 min	 (73), 95:5 d.r.	99  276
 Boc		THF, rt, 72 h	 (46), 75:25 d.r.	525
 Boc		THF, -78°, 4 h	 (65), 5.3:1 d.r., 97:3 syn:anti	142
 Boc		THF, -78°, 4 h	 (66), 57:1 d.r., 93:7 syn:anti	142

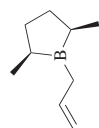
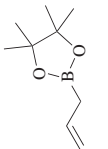
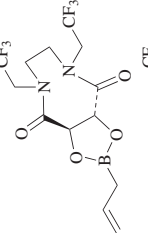
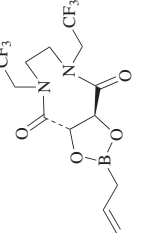
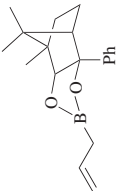
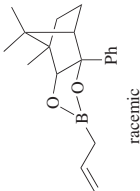


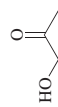
	THF, -78°, 4 h	<b>I</b> (57), 4.2:1 d.r., 96:4 syn:anti	142
	CH <sub>2</sub> Cl <sub>2</sub> , -78° to rt, 24-48 h	<b>I</b> (75-85), 96:4 d.r., 94:6 syn:anti	118
	4 Å MS, toluene, -78° to rt, 10 h	<b>I</b> (95), >99:1 d.r.	132
	4 Å MS, toluene, -78°, 12 h	<b>I</b> (58), 61:39 d.r.	132
	Petroleum ether, -78° to rt, 18 h	<b>I</b> (86), >99:1 d.r.	288
	Petroleum ether, -78° to rt, 18 h	<b>I</b> (←), 97:3 d.r.	288
	Et <sub>3</sub> N, CH <sub>2</sub> Cl <sub>2</sub> , -10° to rt, 36 h	 (65), 94:6 d.r.	106
			

TABLE 2. ADDITION OF Z-CROTYL REAGENTS (Continued)





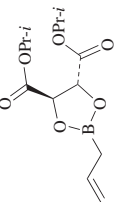
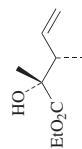

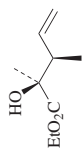


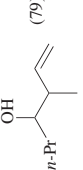
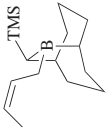
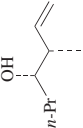

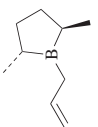
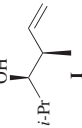
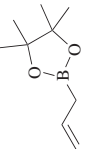
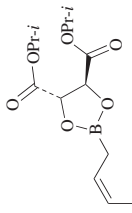
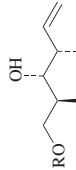
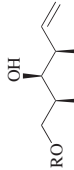
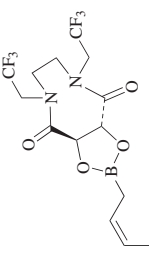

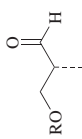

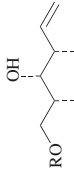

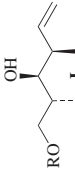
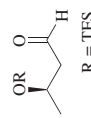
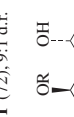

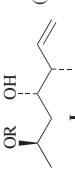
Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C <sub>3</sub> 		Et <sub>3</sub> N, CH <sub>2</sub> Cl <sub>2</sub> , -10° to rt	 (96), 99:1 d.r.	106
		4 Å MS, toluene, -78° to rt, 6 h	 (87), 9, 5, 4:1 d.r.	134
		BF <sub>3</sub> ·OEt <sub>2</sub> , CH <sub>2</sub> Cl <sub>2</sub> , -78°, 2 h	 (90), >98:2 d.r.	98
C <sub>4</sub> 		Either, rt	 (79)	31
		Either, -78°, 3 h	 (91), 94, >98:2 d.r.	143
		THF, -78°, 4 h	 (70), 93, 96:4 d.r.	142
		Either, -78°	<b>I</b> (51), 94:6 d.r.	22



TABLE 2. ADDITION OF Z-CROTYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.		
C <sub>4</sub> 	R = TBDMS, TBDPS, Bn	4 Å MS, toluene, -78°		R TBDMS (71) 99:1 96:4 TBDPS (—) 97:3 89:11 Bn (—) 91:9 97:3	169, 297	
				R TBDMS 53:47 86:14 TBDPS 73:27 88:12 Bn 53:47 90:10	169	
R = TBDPS, TBDMS		4 Å MS, toluene, -78°		R TBDPS 12 h (90) 88:12 95:5 TBDMS 10 h (82) 63:37 99:1	132	
	R = Bn	THF, -78°, 3 h			(—), 99:1 d.r.	167
					(—), 94:6 d.r.	167
	R = TES	THF, -90°, 16 h	"		I (72), 9:1 d.r.	269
					(41), 3:1 d.r.	522

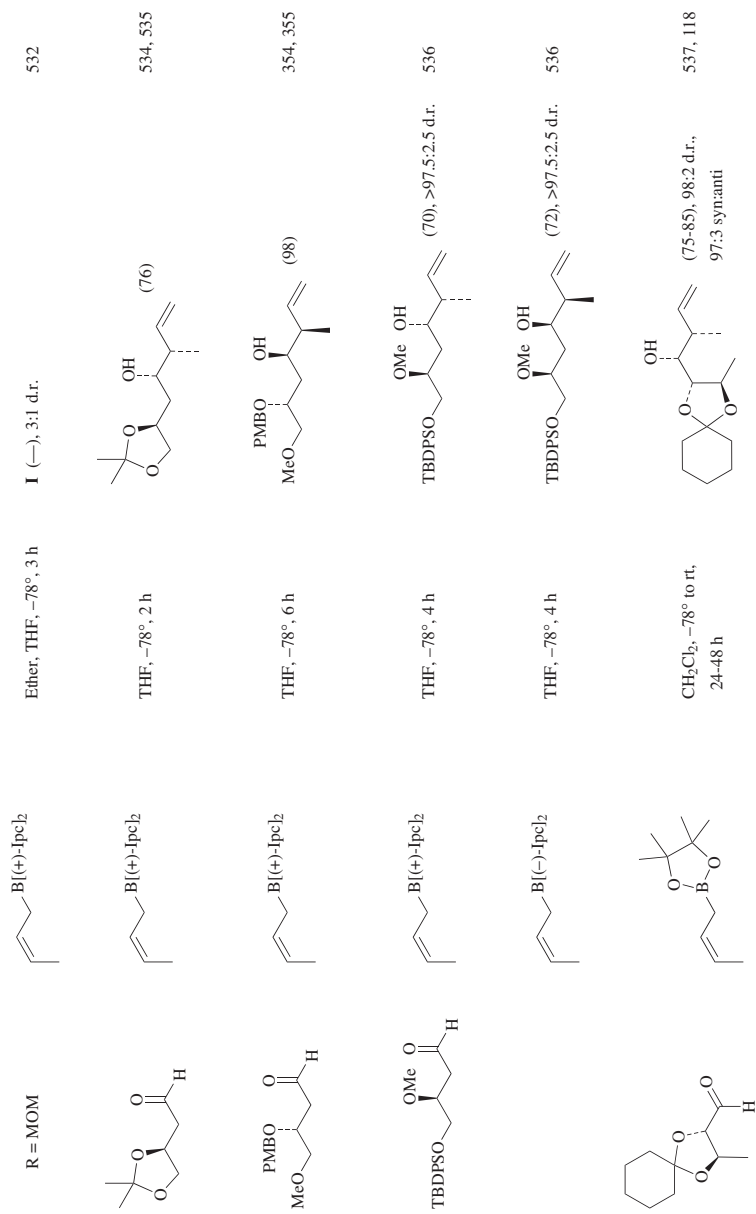


TABLE 2. ADDITION OF Z-CROTYL REAGENTS (Continued)

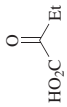

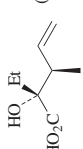
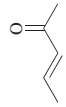

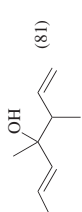
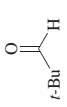
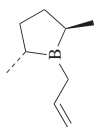

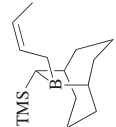
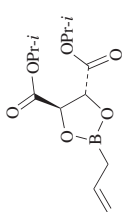

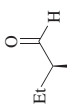

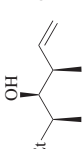
Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C <sub>4</sub> 		Et <sub>3</sub> N, CH <sub>2</sub> Cl <sub>2</sub> , -10° to rt	 (92), 99:1 d.r.	106
C <sub>5</sub> 		Neat, 0-5°	 (81)	238
		THF, -78°, 4 h	 (75), 97, 95:5 d.r.	142
		Ether, -78°, 3 h	<b>I</b> (92), 94, >98:2 d.r.	143
		4 Å MS, toluene, -78°, 7 d	<b>I</b> (66), 70, 99:1 d.r.	519, 37
		<i>n</i> -Bu <sub>4</sub> NI (10 mol%), CH <sub>2</sub> Cl <sub>2</sub> , H <sub>2</sub> O, rt, 15 min	<b>I</b> (96), >98:2 d.r.	100
		Ether, -78°, 3 h	 (73), 82:18 d.r.	538, 167





TABLE 2. ADDITION OF Z-CROTYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		—	 I (50), >95:5 d.r.	278, 525
		—	I (50), 80:20 d.r.	278, 525
		THF, rt, 72 h	I (70), 93:7 d.r., 89:11 syn:anti	525, 541
		—	I (72), 87:13 d.r.	278, 525
		—	I (68), 96:4 d.r.	278, 525
		THF	 R H rt 24 h (78) 72:28 d.r. Me 0° 96 h (85) 86:14	525

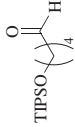

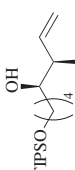
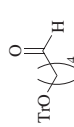

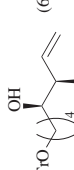
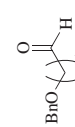

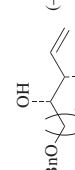
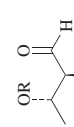
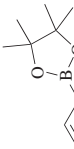
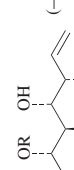
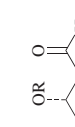
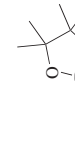
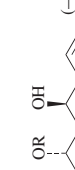
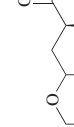

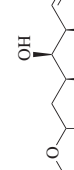
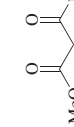

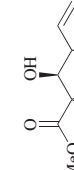
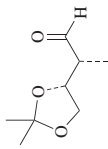

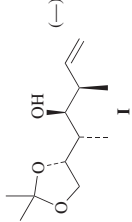

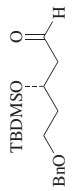

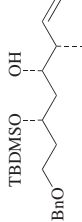

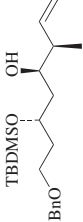
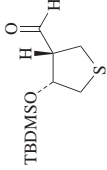
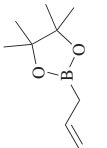
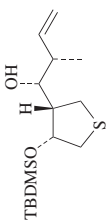
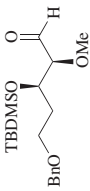
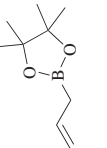
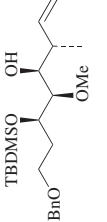
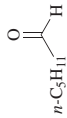

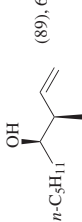
		THF, -78°		(65), 90, >20:1 d.r.	330
		THF, -78°		(68), 90	542
		THF, -78°		(-), 93	543
		Neat, rt, 3 d		(-)	115, 113
		Neat, rt, 3 d		(-)	115
		THF, -78°		(72)	411
		THF, -78°, 7 h		(39), 85, >99:1 d.r.	544

TABLE 2. ADDITION OF Z-CROTYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		THF/ether, -78°	 I (-), 97, 15:1 d.r.	522, 532
		THF/ether, -78°	I (-), 1:1 d.r.	522
		—	 (49-82)	341
		—	 (49-82)	341
		Neat, rt, 3 d	 (-), 68:32 d.r.	115
		—	 (-), >99:1 d.r. <sup>a</sup>	545
		Pentane, rt, 2 h	 (89), 60:40 d.r.	103

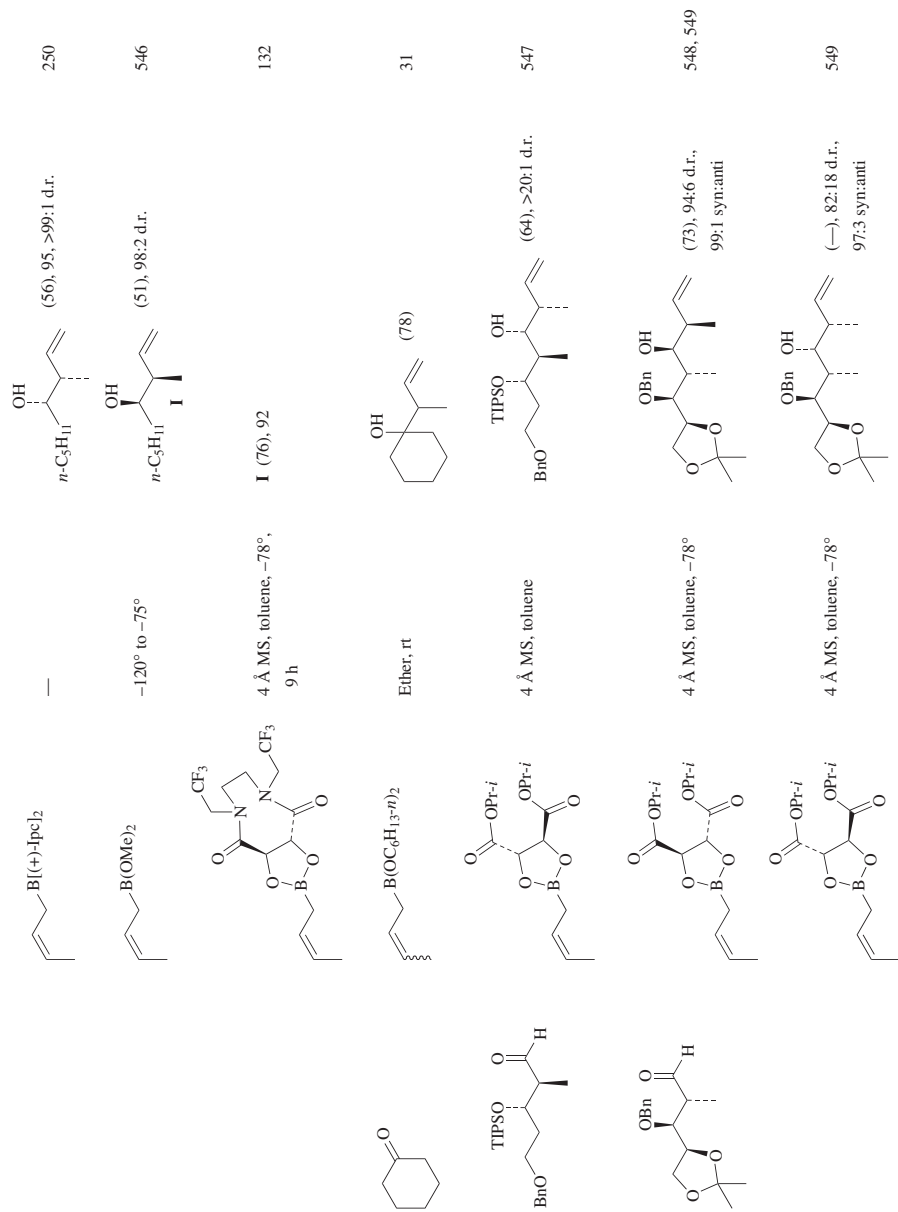
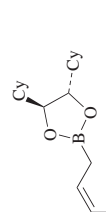
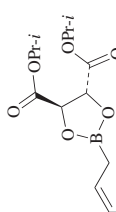
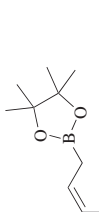
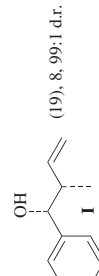
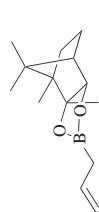

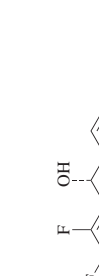
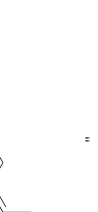

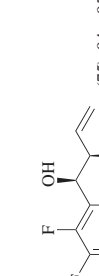


TABLE 2. ADDITION OF Z-CROTYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Pentane, rt, 2 h	 (87)	103
		—	 (60), 96, >99:1 d.r.	250
		THF, -78°, 3 h	 (72), 88, 99:1 d.r.	137
		Ether, -78°, 3 h	<b>I</b> (72), 98, >98:2 d.r.	143
		Ether, -78°	<b>I</b> (40), 96:4 d.r.	43
		Ether, -78°	<b>I</b> (22), 96:4 d.r.	22
	"	—	<b>I</b> (97), 20:1 d.r.	52
	"	L.A. (10 mol%), toluene, -78°, 4 h	L.A. d.r. <b>I</b> AlCl <sub>3</sub> (87) 99:1 Sc(OTf) <sub>3</sub> (89) 99:1	25
		 Pd(PPh <sub>3</sub> ) <sub>4</sub>	<b>I</b> (81)	550

	Petroleum ether, rt, 12 h	<b>I</b> (62)	64
	4 Å MS, THF, -78°, 6 h	<b>I</b> (90), 55, 98; 2 d.r.	37
	Et <sub>2</sub> AlCl/(S)-BINOL (10 mol%), toluene, -78°, 6 h	 (19), 8, 99:1 d.r.	25
	Sc(OTf) <sub>3</sub> (10 mol%), CH <sub>2</sub> Cl <sub>2</sub> , -78°, 24 h	<b>I</b> (53), 59, >49:1 d.r.	27, 28
	—	 (77), 97, >99:1 d.r.	250
	Pentane/ether (1:1), -100°	<b>I</b> (75), 94, >19:1 d.r.	249
	THF, -78°, 3 h	 (75), 94, >95:5 d.r.	491

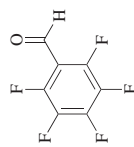


TABLE 2. ADDITION OF Z-CROTYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		CH <sub>2</sub> Cl <sub>2</sub> , -78° to rt	 R Me (100) TBDMS (99)	551
		BF <sub>3</sub> ·OEt <sub>2</sub> (2 equiv), CH <sub>2</sub> Cl <sub>2</sub> , -78°, 15 min	 R H (91) >98:2 MeO (91) 96:4 O <sub>2</sub> N (95) >98:2	98, 99
R = H, MeO, O <sub>2</sub> N	"	BF <sub>3</sub> ·OEt <sub>2</sub> (5 mol%), CH <sub>2</sub> Cl <sub>2</sub> , rt, 3-6 h	 R H (92) >98:2 MeO (93) 96:4 O <sub>2</sub> N (94) >98:2	99
R = H, MeO		<i>n</i> -Bu <sub>4</sub> NI (10 mol%), CH <sub>2</sub> Cl <sub>2</sub> , H <sub>2</sub> O, rt, 15 min	 R H (96) >98:2 MeO (98) >98:2	100
		4 Å MS, toluene, -78°, 6 h	 (90), 83, 98:2 d.r.	519, 37
		4 Å MS, toluene, -78°, 9 h	 I (80), 92	132



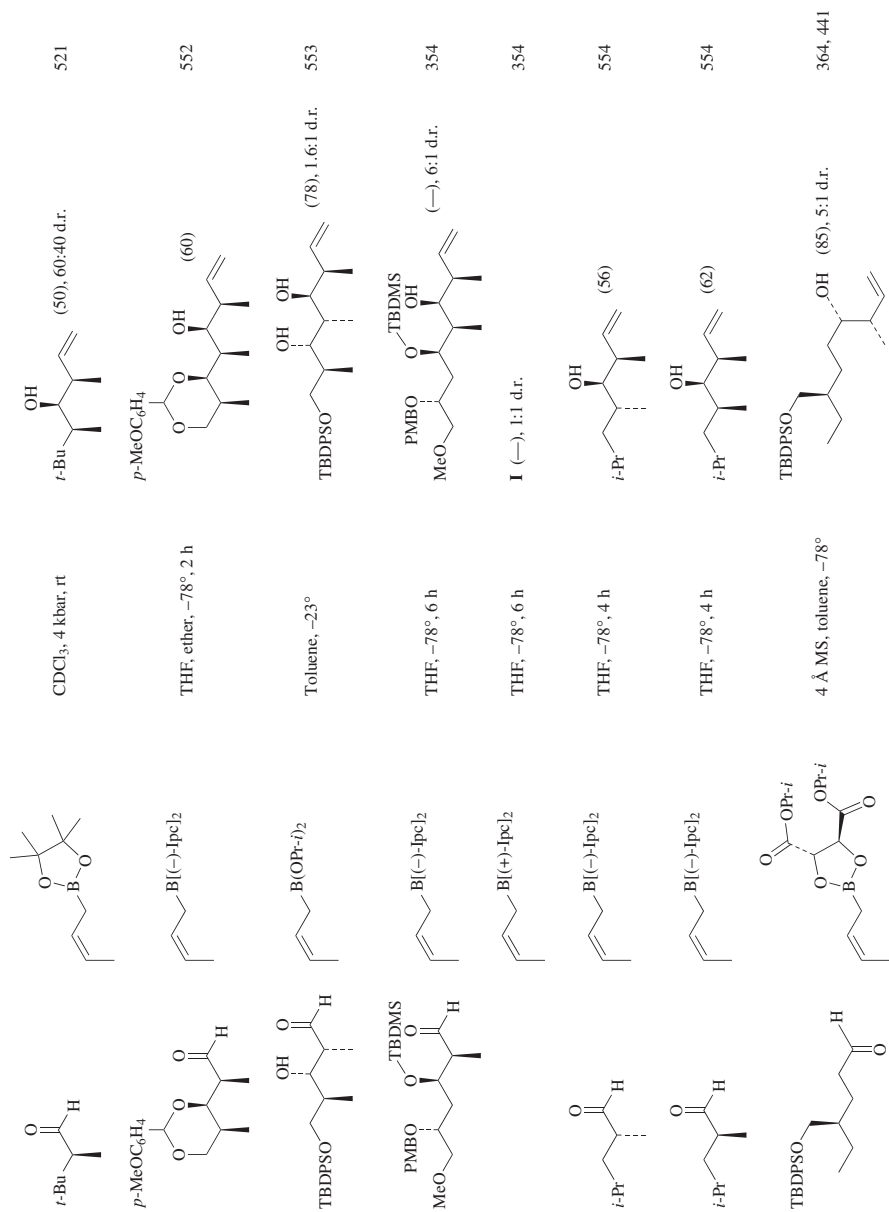


TABLE 2. ADDITION OF Z-CROTYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		4 Å MS, toluene, -78°, 6 h		555
		THF, -78° to rt		420
	"	BF <sub>3</sub> •OEt <sub>2</sub> , THF, -78° to rt	<b>I</b> (72), 95:5 d.r.	422
	"	BF <sub>3</sub> •OEt <sub>2</sub>	<b>I</b> (90)	421
	"	THF, -78° to rt, 3.5 h	<b>I</b> (90), 95:5 d.r.	420
		BF <sub>3</sub> •OEt <sub>2</sub> (2 equiv), CH <sub>2</sub> Cl <sub>2</sub> , -78°, 15 min	<b>I</b> (74), >98:2 d.r.	98, 99
	"	BF <sub>3</sub> •OEt <sub>2</sub> (5 mol%), CH <sub>2</sub> Cl <sub>2</sub> , rt, 3-6 h	<b>I</b> (76), >98:2 d.r.	99
	"	<i>n</i> -Bu <sub>4</sub> NI (10 mol%), CH <sub>2</sub> Cl <sub>2</sub> , H <sub>2</sub> O, rt, 15 min	<b>I</b> (94), >98:2 d.r.	100
		THF, -78°, 18 h		556
	"	THF, -78° to rt, 2 h	<b>I</b> (80)	557
	"	—	<b>I</b> (85-90), >95	558

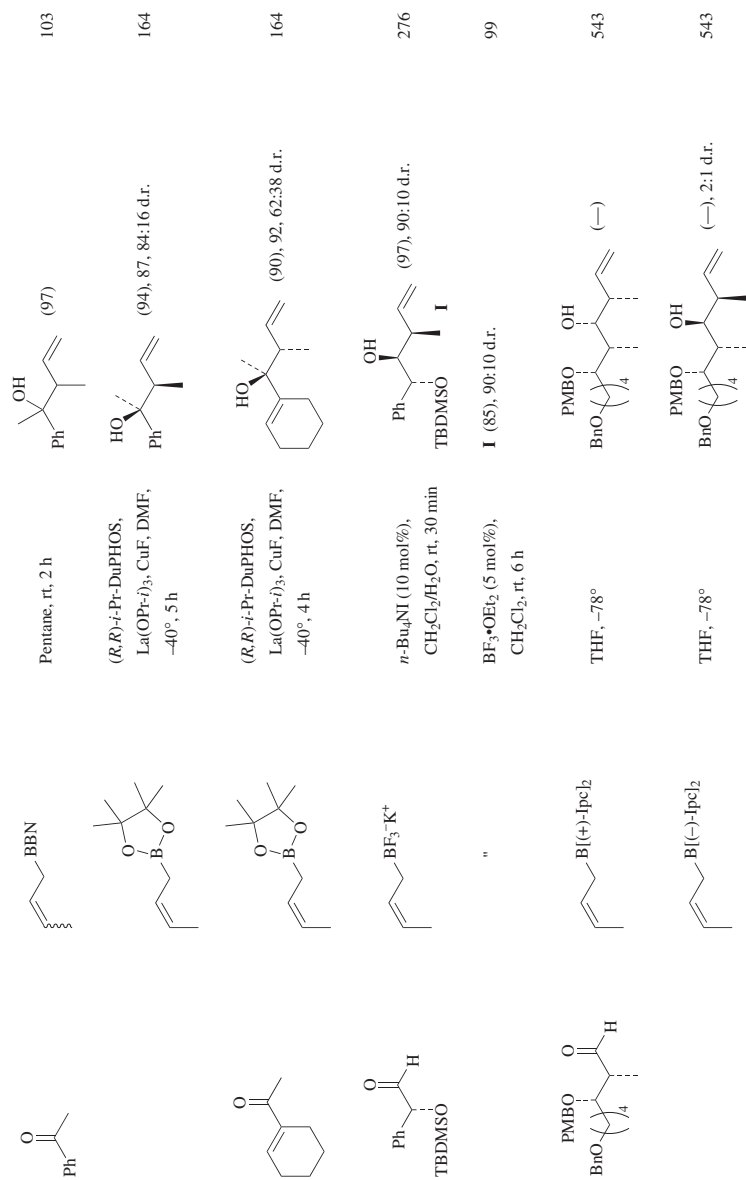


TABLE 2. ADDITION OF Z-CROTYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		THF, -78°		543
		THF, -78°		543
		4 Å MS, toluene, -78°		559
		4 Å MS, toluene, -78°		559
		Et3N, CH2Cl2, -10° to rt		106
		Sc(OTf)3 (10 mol%), CH2Cl2, -78°, 24 h		28
		n-Bu4NI (10 mol%), CH2Cl2, H2O, rt, 1.5 min		100

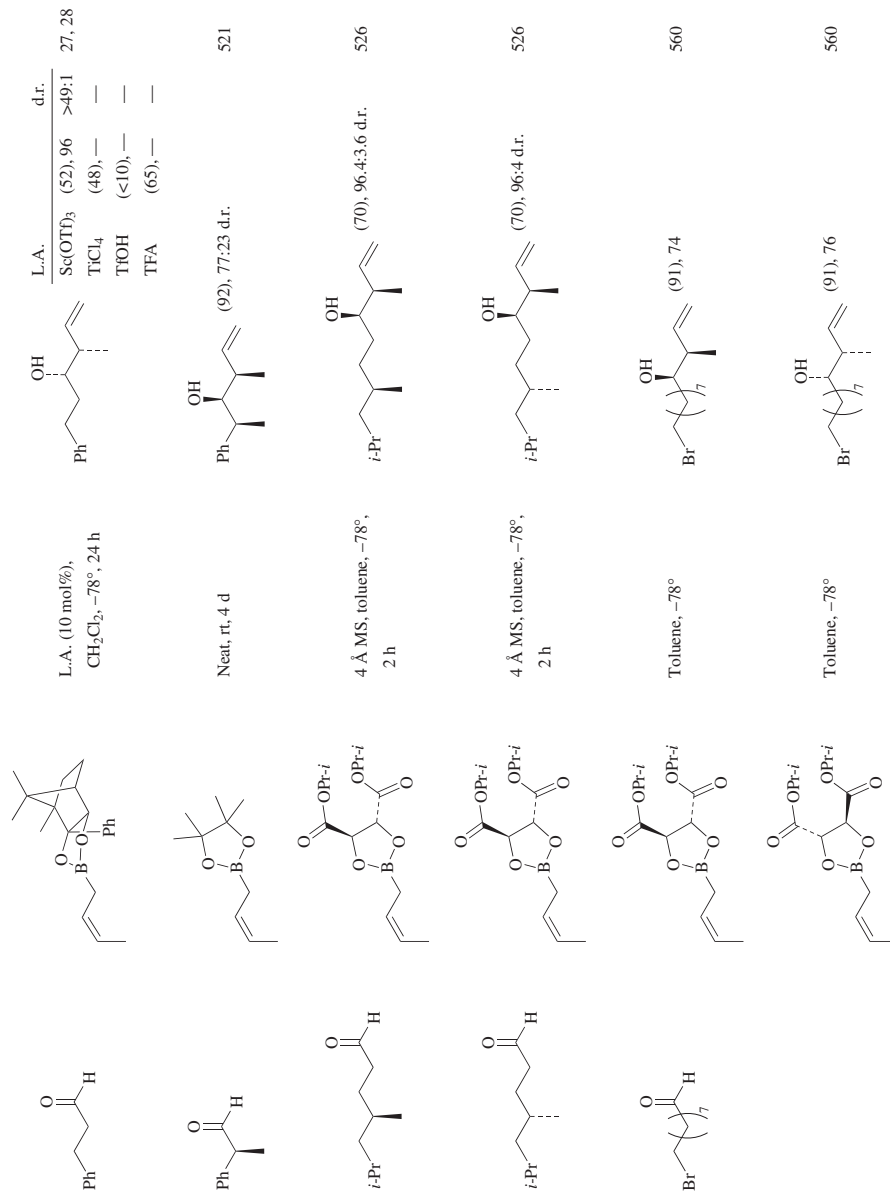


TABLE 2. ADDITION OF Z-CROTYL REAGENTS (Continued)

	Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C <sub>9</sub>			BF <sub>3</sub> ·OEt <sub>2</sub> (5 mol%), CH <sub>2</sub> Cl <sub>2</sub> , rt, 3–6 h	TBDMSO Ph (84), 75:25 d.r.	99
		"	<i>n</i> -Bu <sub>4</sub> Ni (10 mol%), CH <sub>2</sub> Cl <sub>2</sub> , H <sub>2</sub> O, rt, 30 min	TBDMSO Ph (96), 75:25 d.r.	276
C <sub>10</sub>			4 Å MS, toluene, -78°	<i>n</i> -C <sub>6</sub> H <sub>13</sub> (55-70), 61	130
		"	Cr(CO) <sub>3</sub> , 4 Å MS, toluene	<i>n</i> -C <sub>6</sub> H <sub>13</sub> Temp -78° (55-70), 83 -90° (55-70), 88	130
			Cr(CO) <sub>3</sub> , 4 Å MS, toluene, -78°	<i>n</i> -C <sub>7</sub> H <sub>15</sub> (85-95), 86, 97:3 d.r.	128
			4 Å MS, toluene, -78°, 6 h	<i>n</i> -C <sub>7</sub> H <sub>15</sub> (83), 62, 97:3 d.r.	519, 37

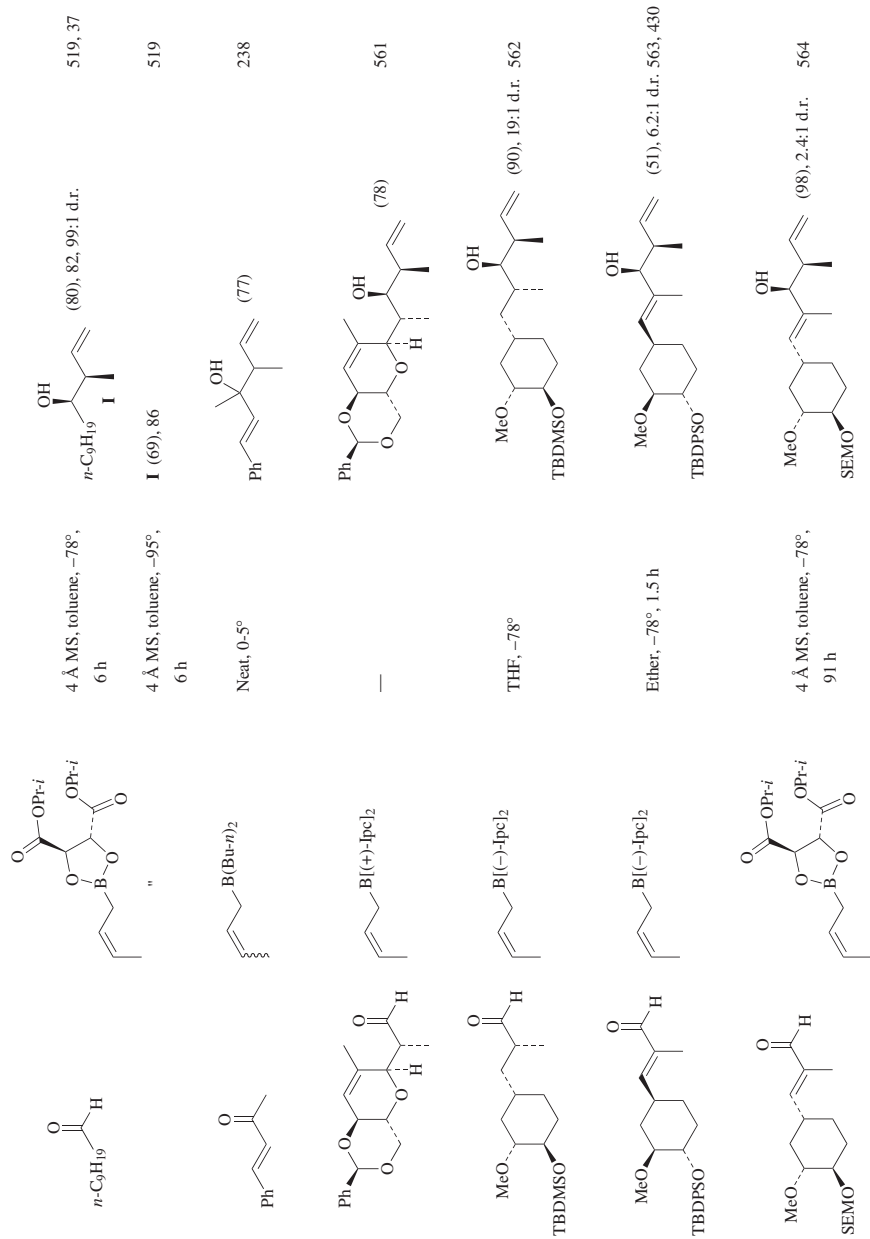
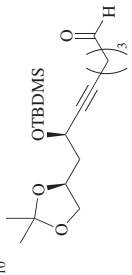

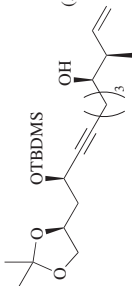
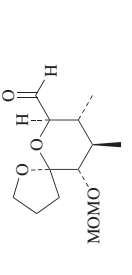
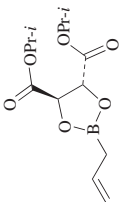
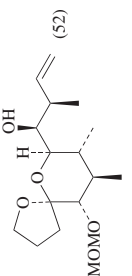
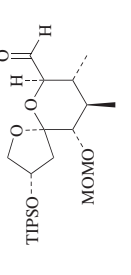
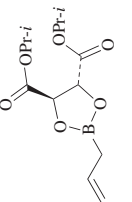
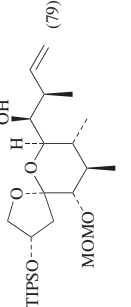
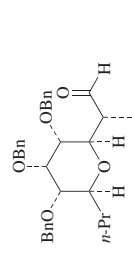
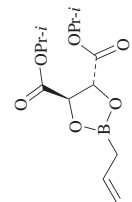
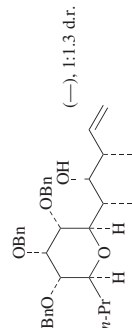

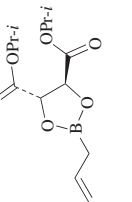



TABLE 2. ADDITION OF Z-CROTYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		THF, -78°	 (59), >95	565
		Toluene, -80° to -70°	 (52)	566
		4 Å MS, toluene, -78°	 (79)	566, 567, 568, 569, 570
		4 Å MS, toluene, -78°	 I (-), 1:1.3 d.r.	559
		4 Å MS, toluene, -78°	 I (-), 1:1 d.r.	559



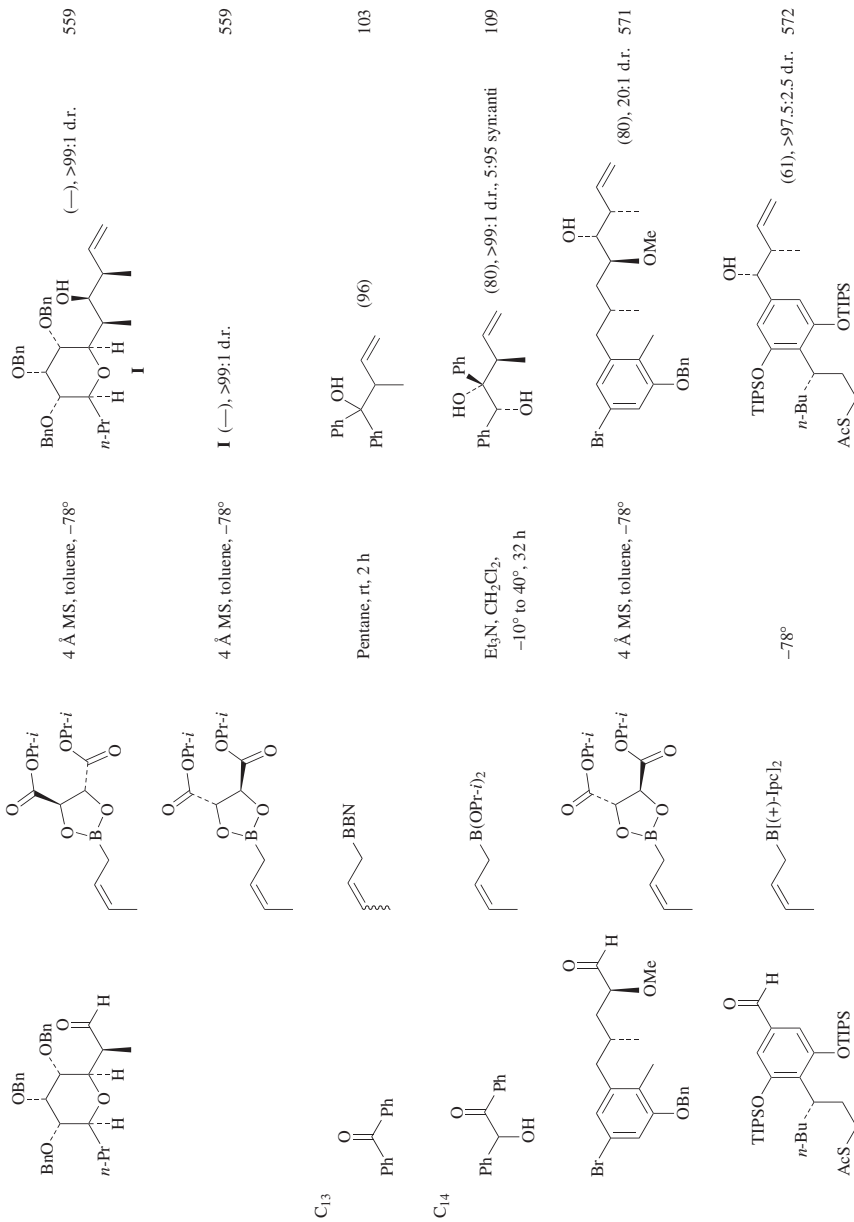
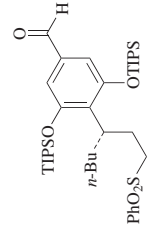

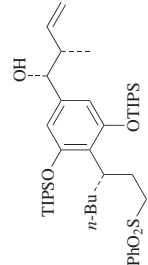
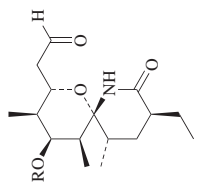

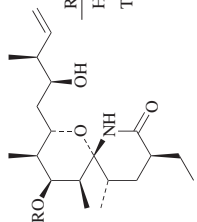
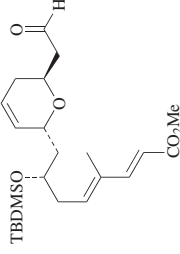
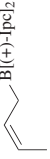
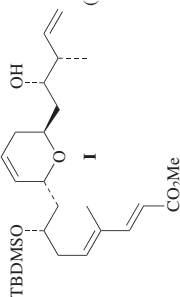


TABLE 2. ADDITION OF Z-CROTYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
 C <sub>14</sub>		-78°	 (65), 11:1 d.r.	572
 C <sub>16</sub>		THF, -78°, 2 h; rt	 R H TES	573, 574 (67), 7:1 d.r. (67), 3:1 d.r.
		4 Å MS, toluene, -90° to rt, 18 h	 I	(80), 67:33 d.r. 575, 576
		THF, -78°, 2 h	I (60), >95:5 d.r.	575, 576

<sup>a</sup> The reference reports uncertainty over the stereochemical assignment of the product.

TABLE 3. ADDITION OF E-CROTYL REAGENTS








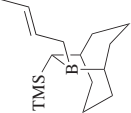
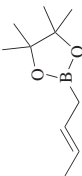


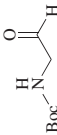

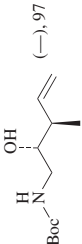
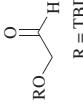

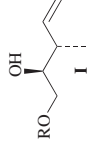
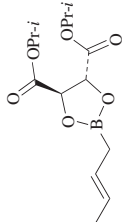
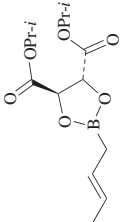
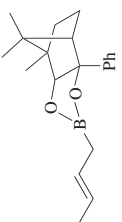
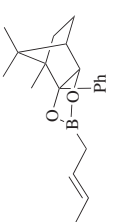
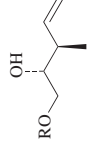
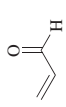
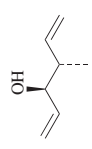
Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		THF, -78°, 3 h	 (76), 96, 99:1 d.r.	44, 497
		Ether, -78°, 3 h	<b>I</b> (75), 96, >99:1 d.r.	497
		THF, -78°, 3 h	 (78), 95, 99:1 d.r.	44, 497
		Ether, -78°, 3 h	<b>I</b> (-), 94, >99:1 d.r.	497
		Ether, -78°, 3 h	<b>I</b> (73), 97, >98:2 d.r.	143
		Ether, -78° to rt	<b>I</b> (40), 93:7 d.r.	22
		 Li <sup>+</sup> B(Bu- <i>n</i> ) <sub>3</sub> , ether, -70°	<b>I</b> (-), 80:20-92.5:7.5 d.r.	577
		—	 (—), 97	517

TABLE 3. ADDITION OF E-CROTYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C <sub>2</sub>  R = TBDDPS		THF, ether, -78°	 I (79)	(61), 92, >99:1 d.r. 578, 579, 580
R = PMB		4 Å MS, toluene, -78°	I (79)	559
R = TIPS		Toluene, -78°	I (80), 92, 20:1 d.r.	330
R = Bn		Ether, rt	I (86), 52, >95:5 d.r.	581
R = TBDDMS		Sc(OTf) <sub>3</sub> (10 mol%), CH <sub>2</sub> Cl <sub>2</sub> , -78°, 24 h	 I (74)	(74), 95, >49:1 d.r. 27, 28
C <sub>3</sub> 	B[(-)-Ipc]2	THF, -78°, 3 h	 I (65)	(65), 90, 99:1 d.r. 137



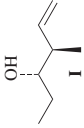

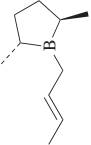
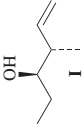



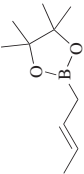
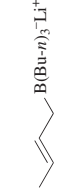

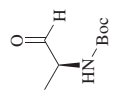

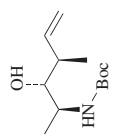

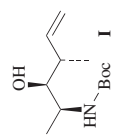

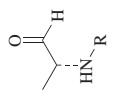

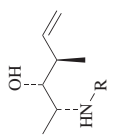
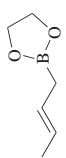
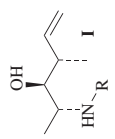
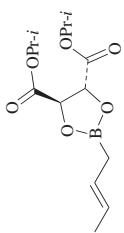
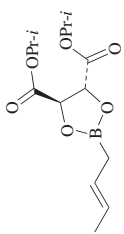
		Ether, -78°, 3 h		(76), 98, >99:1 d.r.	497
		THF, -78°, 3 h	<b>I</b> (78), 92, 99:1 d.r.		137, 497
	"	THF, ether, -78°, 3 h	<b>I</b> (70), 95-96, 98:2 d.r.		506
		THF, -78°, 4 h		(81), 96, 93:7 d.r.	142
		Ether, -78°, 3 h	<b>I</b> (70), 90, 99:1 d.r.		137, 497
	"	THF/ether, -78°, 3 h	<b>I</b> (70), 95-96, 98:2 d.r.		506
		THF, -78°, 3 h	<b>I</b> (75), 94, >99:1 d.r.		137
	"	Ether, -78°, 3 h	<b>I</b> (-), 94, >99:1 d.r.		497
		Ether, -78° to rt	<b>I</b> (61), 97:3 d.r.		43
		Ether, -78°	<b>I</b> (62), 97:3 d.r.		22
		 B(Bu- <i>n</i> ) <sub>3</sub> Li <sup>+</sup> , ether, -70°	<b>I</b> (-), 80:20:92.5:7.5 d.r.		577

TABLE 3. ADDITION OF E-CROTYL REAGENTS (Continued)

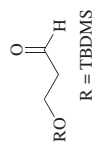

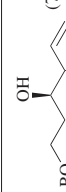

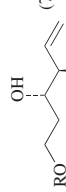
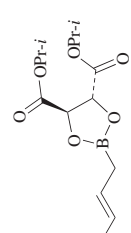
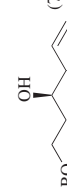
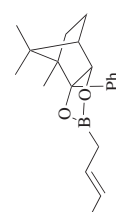
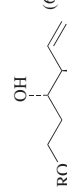
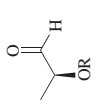
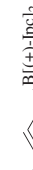

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
 C <sub>3</sub>		—	 (–), >97:3 d.r.	520
		—	 (–), >97:3 d.r.	520, 582
	"	–78°, 4 h	 <b>I</b> (81)	583
 R = Boc		4 Å MS, toluene, –78°, 15 h	 (85), >95:5 d.r.	278
		4 Å MS, toluene, –78°, 15 h	 (53), 75:25	278
R = Ac		4 Å MS, toluene, acetone, –78°	<b>I</b> (67), 87:13 d.r.	584, 278
R = Boc		4 Å MS, toluene, –78°, 15 h	<b>I</b> (68), 75:25 d.r.	278

	4 Å MS, toluene, -78°, 15 h		(68), >95:5 d.r.	278
	4 Å MS, toluene, acetone, -78°		(94), >95:5 d.r.	278
	Neat, rt, 4 d		(92), 9:1 d.r.	521
	THF, -78° to -30°		(55)	406
"	-78° to rt		<b>I</b> (71), >85, >50:1 d.r.	585
"	2 h		<b>I</b> (48)	586
"	-78°		<b>I</b> (67), >99, >99:1 d.r.	587
"	—		(70)	341
	THF, -78°		(62), 92	413, 339
"	Ether, THF, -78°, 3 h		<b>I</b> (76), 91	588, 589

R = TBDMMS

R = PMB

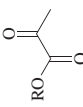

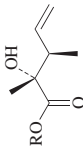
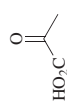

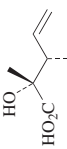
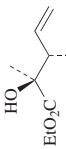
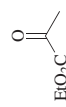
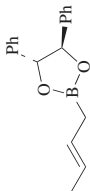

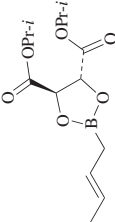
TABLE 3. ADDITION OF E-CROTYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
 R = TBDMS	 B[(-)-IpcCl <sub>2</sub> ]	THF, -78°	 I (72), 95, 20:1 d.r.	590, 591
	"	THF, -78°	I (81), 95, 20:1 d.r.	592, 593
	"	THF, -78°, 2 h	I (68)	594
	 B[(+)-IpcCl <sub>2</sub> ]	THF, -78° to rt, 4 h	 I (70), >95, >20:1 d.r.	595
	 B[(+)-IpcCl <sub>2</sub> ]	4 Å MS, toluene, -78°, 4 h	 I (71), 85, >98:2 d.r.	519, 37
R = TBDPS	 B[(+)-IpcCl <sub>2</sub> ]	Sc(OTf) <sub>3</sub> (10 mol%), CH <sub>2</sub> Cl <sub>2</sub> , -78°, 24 h	 I (63), 94, >49:1 d.r.	27, 28
 R = Bn	 B[(+)-IpcCl <sub>2</sub> ]	THF, -78°, 3 h	 I (85), 97:3 d.r.	167, 538



			THF, -78°, 3 h		(80), 95:5 d.r.	167, 538
R = PMB			Ether, -78°	<b>I</b> (64)		597
R = Bn			Neat, rt, 4 d	<b>I</b> (46)	77:23 d.r.	521
			BF <sub>3</sub> ·OEt <sub>2</sub> (5 mol%), CH <sub>2</sub> Cl <sub>2</sub> , rt, 6 h		(72), 75:25 d.r.	99
			<i>n</i> -Bu <sub>4</sub> Ni (10 mol%), CH <sub>2</sub> Cl <sub>2</sub> , H <sub>2</sub> O, rt, 30 min	<b>I</b> (95)	75:25 d.r.	276
			Et <sub>3</sub> N, CH <sub>2</sub> Cl <sub>2</sub> , -10° to rt, 1.5 h		(72), 97:3 d.r.	109
			THF, -78°		(66), 90	266
			THF, -78°		(67)	573

TABLE 3. ADDITION OF E-CROTYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.	
 $\text{C}_3$		Ether, $-76^\circ$ to $0^\circ$ , 30 min		598	
			R	d.r.	
			Me	(96)	73:27
			<i>t</i> -BuCH <sub>2</sub>	(90)	85:15
			PhCH <sub>2</sub>	(94)	80:20
			Ph	(89)	80:20
			2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	(79)	75:25
			3,5-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	(88)	65:35
			2,3,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	(80)	70:30
			2,6-( <i>t</i> -Bu) <sub>2</sub> -3-MeC <sub>6</sub> H <sub>2</sub>	(90)	100:0
		Et <sub>3</sub> N, CH <sub>2</sub> Cl <sub>2</sub> , $-10^\circ$ to rt		(95), 99:1 d.r. 106	
				(86), 6, 53:47 d.r. 134	
		4 Å MS, toluene, $-78^\circ$ to rt, 6 h	Solvent	d.r.	
			I	toluene (84), 73 THF (82), 53 ether (80), 62 CH <sub>2</sub> Cl <sub>2</sub> (83), 33	7:1 3:2:1 5:1 2:1
			I (92), $>98.2$ d.r.	98	
		BF <sub>3</sub> ·OEt, CH <sub>2</sub> Cl <sub>2</sub> , $-78^\circ$ , 2 h	Solvent	d.r.	
			I	toluene (84), 73 THF (82), 53 ether (80), 62 CH <sub>2</sub> Cl <sub>2</sub> (83), 33	7:1 3:2:1 5:1 2:1

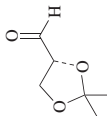
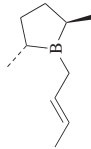
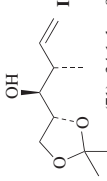
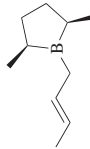

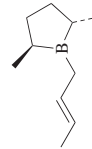
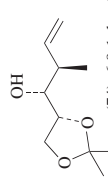
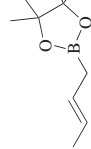
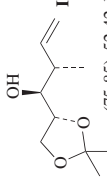
		THF, -78°, 4 h		142															
		THF, -78°, 4 h	<b>I</b> (62), 2:1 d.r., 89:11 anti:syn (71), 34:1 d.r., 99:1 anti:syn	142															
		—	<b>I</b> (72), >20:1 d.r.	599															
		THF, -78°, 4 h		142															
		CH <sub>2</sub> Cl <sub>2</sub> , -78° to rt, 24-48 h		537, 118															
	"	CH <sub>2</sub> Cl <sub>2</sub> , 24 h	<table border="1" data-bbox="1023 588 1153 903"> <thead> <tr> <th>Temp</th> <th>d.r.</th> <th>Anti:Syn</th> </tr> </thead> <tbody> <tr> <td><b>I</b> (-)</td> <td>-78° to rt</td> <td>52:42 94:6</td> </tr> <tr> <td></td> <td>rt</td> <td>51:44 95:5</td> </tr> <tr> <td></td> <td>-20°</td> <td>51:46 97:3</td> </tr> <tr> <td></td> <td>-78°</td> <td>53:47 &gt;99:1</td> </tr> </tbody> </table>	Temp	d.r.	Anti:Syn	<b>I</b> (-)	-78° to rt	52:42 94:6		rt	51:44 95:5		-20°	51:46 97:3		-78°	53:47 >99:1	118
Temp	d.r.	Anti:Syn																	
<b>I</b> (-)	-78° to rt	52:42 94:6																	
	rt	51:44 95:5																	
	-20°	51:46 97:3																	
	-78°	53:47 >99:1																	

TABLE 3. ADDITION OF E-CROTYL REAGENTS (Continued)

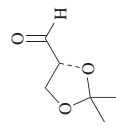
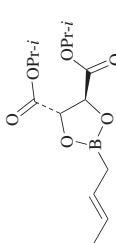
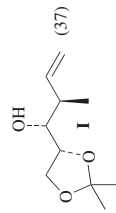
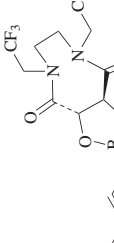
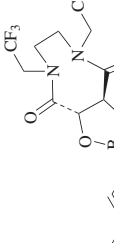
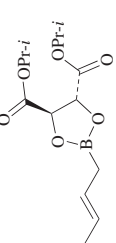
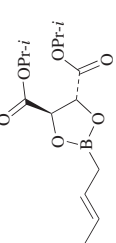
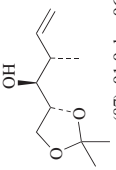
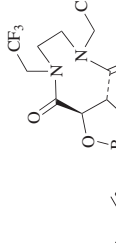
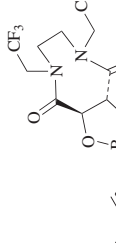
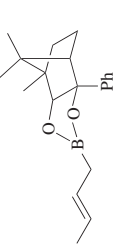
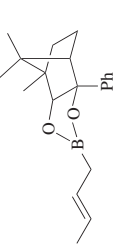
Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		—	 (37)	600
"	"	4 Å MS, toluene, -78°	<b>I</b> (85), 98:2 d.r., 98:2 anti:syn	601, 602, 170
"	"	4 Å MS, toluene, -78° to rt, 18 h	<b>I</b> (65)	603
		4 Å MS, toluene, -78°, 7 h	<b>I</b> (84), >99:1 d.r.	132
		4 Å MS, toluene, -78°	 (87), 91:9 d.r., 96:4 anti:syn	126, 548, 602, 170
		4 Å MS, toluene, -78°, 9 h	<b>I</b> (77), 95:5 d.r.	132
		Petroleum ether, -78° to rt, 18 h	<b>I</b> (-), 72:28 d.r.	288



TABLE 3. ADDITION OF E-CROTYL REAGENTS (Continued)


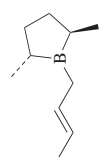
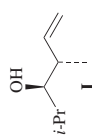

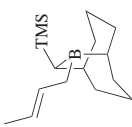
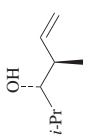
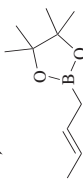
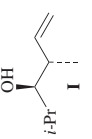


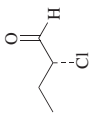
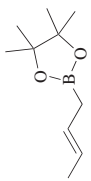
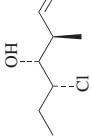

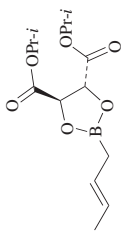
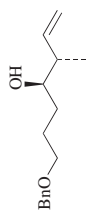
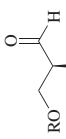
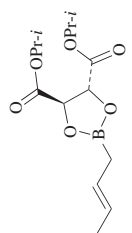
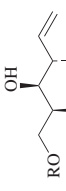
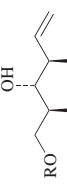
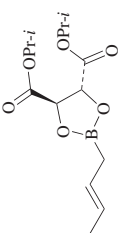
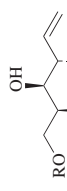
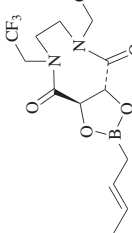

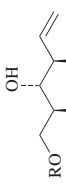
Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		THF, -78°, 4 h	 (76), 97, 96:4 d.r.	142
		Ether, -78°, 3 h	<b>I</b> (80), 88:12 d.r.	305, 607, 608
		Ether, -78°, 3 h	 (94), 96, >98:2 d.r.	143
		Ether, -78°	 (59), 96:4 d.r.	22
		 B(Bu- <i>n</i> ) <sub>3</sub> , ether, -70°	<b>I</b> (-), 80:20:92.5:7.5 d.r.	577
		Neat, rt, 4 d	 (71), 53:47 d.r.	521
		4 Å MS, toluene, -78°	 (87), 80	609



TABLE 3. ADDITION OF E-CROTYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.	
C <sub>4</sub>  R = TBDMS, TBDPS, Bn		4 Å MS, toluene, -78°	 R	d.r. Anti:Syn TBDMS (80) 97:3 >99:1 TBDPS (-) 82:16 98:2 Bn (-) 93:5 98:2	297, 456, 169, 612, 613, 614
			 R	d.r. Anti:Syn TBDMS (-) 81:16 97:3 TBDPS (85) 88:11 99:1 Bn (-) 85:14 99:1	297, 169, 615
R = TBDPS, TBDMS		4 Å MS, toluene, -78°, 18 h	 R	d.r. TBDPS (77), 60 — TBDMS (81), — >97:3 d.r.	596
R = TBDPS, TBDMS		4 Å MS, toluene, -55° to 0°	 I	R Time d.r. TBDPS 12 h (87) 95:5 TBDMS 10 h (85) >97:3	132
			 R	R Time d.r. TBDPS 12 h (80) 96:4 TBDMS 10 h (78) 90:10	132



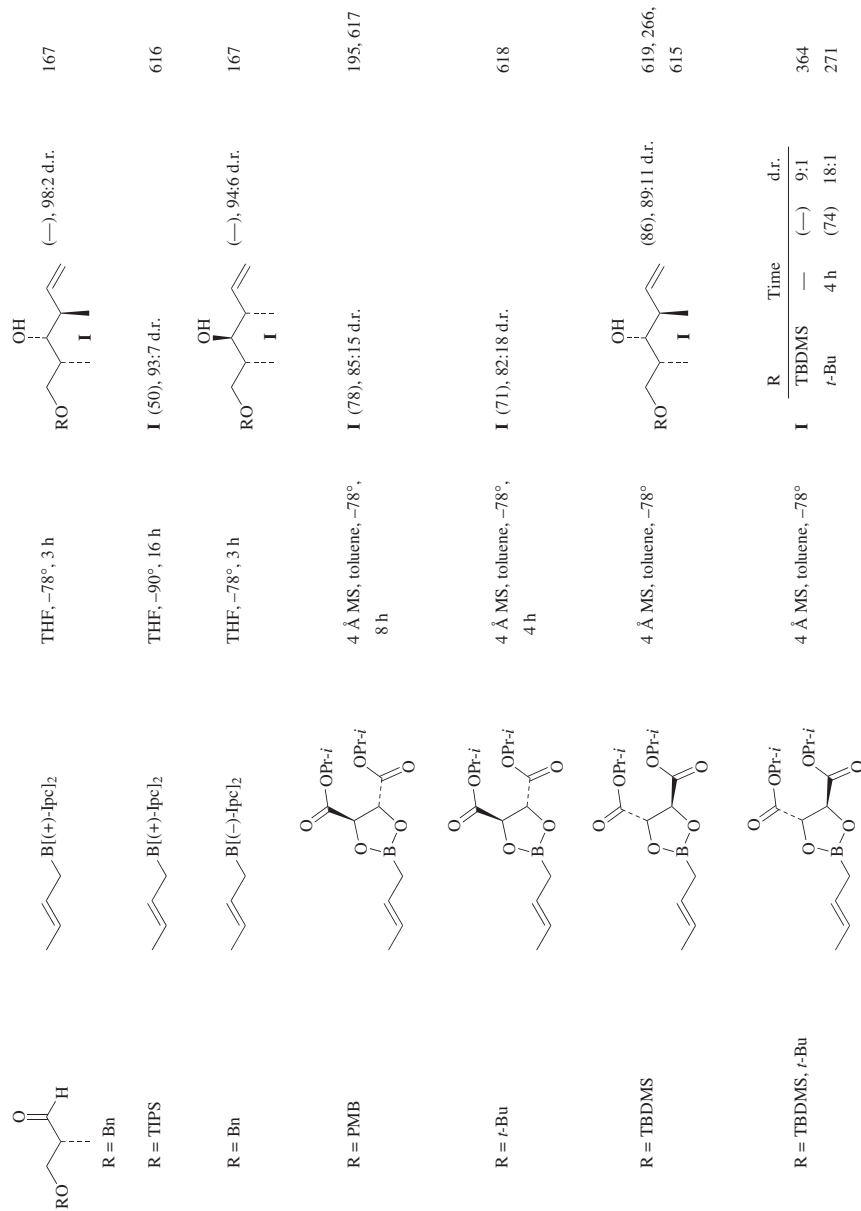
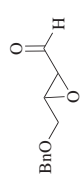
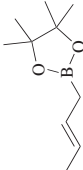
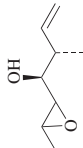
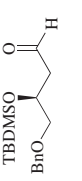
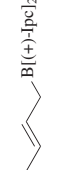
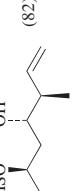
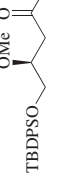
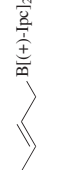
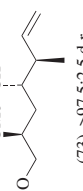

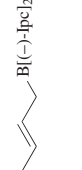
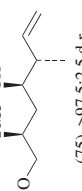
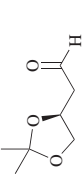
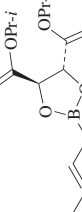
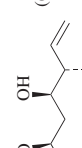
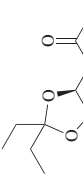
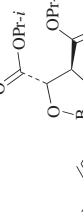
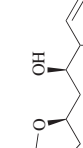
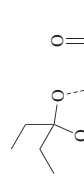
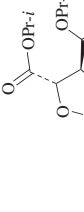
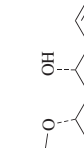


TABLE 3. ADDITION OF E-CROTYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		—	 (95), 9:1 d.r.	52
		THF, -78°, 3 h	 (82)	250
		THF, -78°, 4 h	 (73), >97.5:2.5 d.r.	536
		THF, -78°, 4 h	 (75), >97.5:2.5 d.r.	536
		4 Å MS, toluene, -78°	 (63), 87:13 d.r.	620
		4 Å MS, toluene, -78°, 1 h	 (88), 95:5 d.r.	621
		Toluene, -78°	 (88), 95:5 d.r.	622

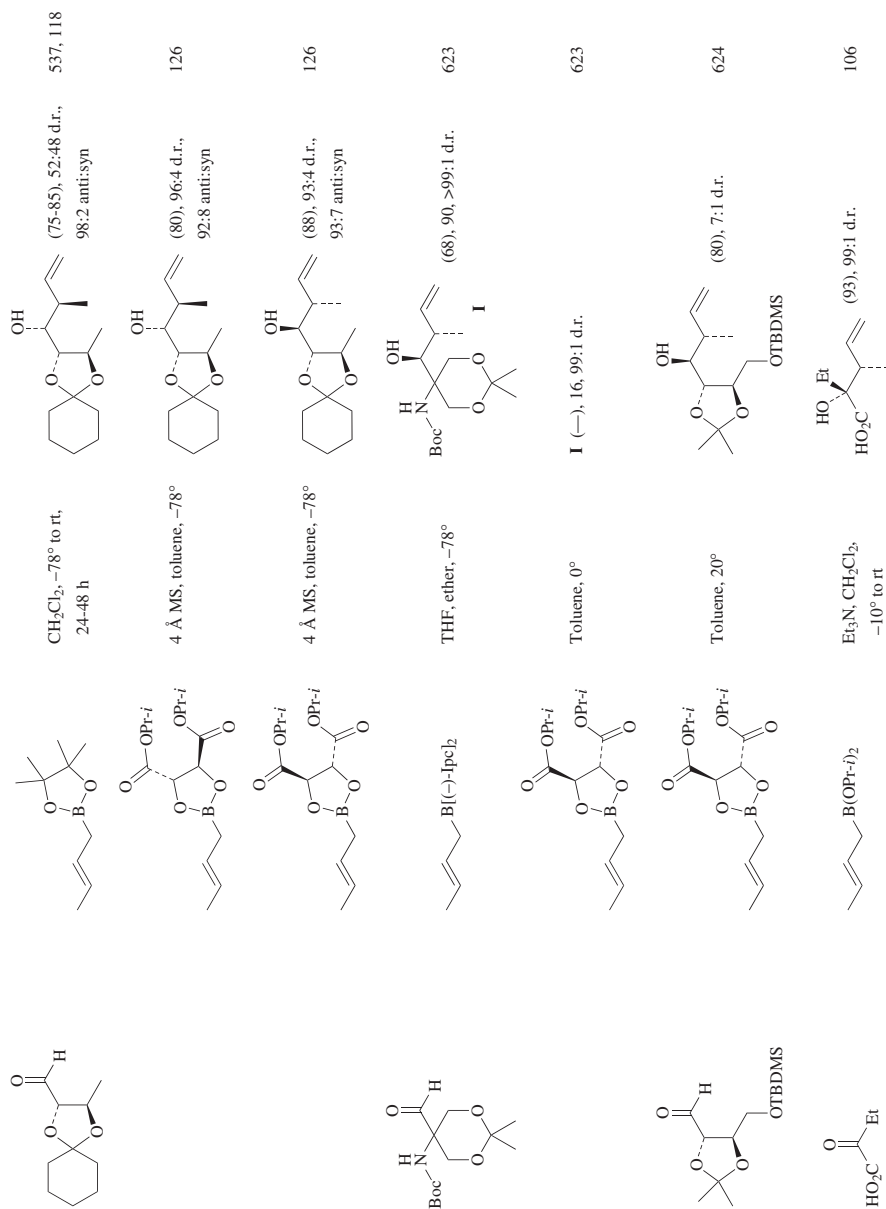

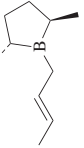
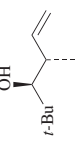
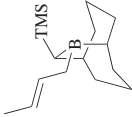
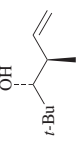
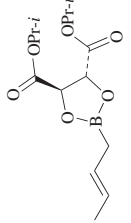
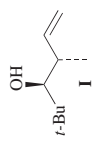




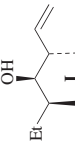
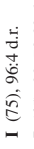
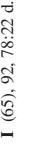

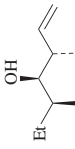

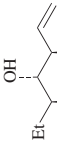

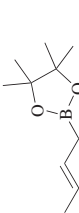
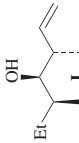


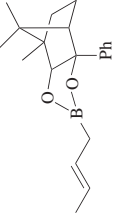
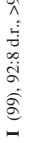
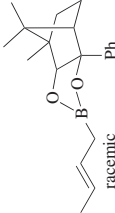
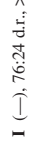

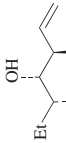
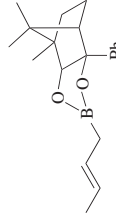
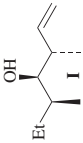
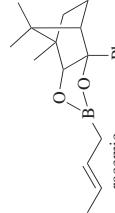
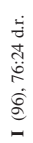


TABLE 3. ADDITION OF E-CROTYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		THF, -78°, 4 h	 (72), 95, 96:4 d.r.	142
		Ether, -78°, 3 h	 (69), 99, >98:2 d.r.	143
		4 Å MS, toluene, -78°, 6 d	 (41), 73, 95:5 d.r.	519, 37
		<i>n</i> -Bu <sub>4</sub> Ni (10 mol%), CH <sub>2</sub> Cl <sub>2</sub> , H <sub>2</sub> O, rt, 15 min	 I (95), >98:2 d.r.	100
		THF, -78°, 3 h	 (75), 96:4 d.r.	167
	"	Ether, -78°	 I (75), 96:4 d.r.	538
	"	Ether, -78°, 3 h	 I (65), 92, 78:22 d.r., 85:15 antisyn	607
		Ether, -70°, 3 h	 (65), >90, >3:1 d.r.	306

	THF, $-78^{\circ}$ , 3 h		(70), 91:9 d.r.	167
"	Ether, $-78^{\circ}$		I (70), 91:9 d.r.	538
	Neat, rt, 4 d		(46), 77:23 d.r.	539, 115, 113
	Petroleum ether, $-78^{\circ}$ to rt		I (95), 76:24 d.r., >99:1 anti:syn	114
	Petroleum ether, $-78^{\circ}$ to rt		I (99), 92:8 d.r., >99:1 anti:syn	114, 540
	Petroleum ether, $-78^{\circ}$ to rt		I (-), 76:24 d.r., >99:1 anti:syn	540
	Ether, $-78^{\circ}$ , 3 h		(65), 54, 78:22 d.r.	607
	Petroleum ether, $-78^{\circ}$ to rt		(98), 75:25 d.r., >99:1 anti:syn	114, 540
	Petroleum ether, $-78^{\circ}$ to rt		I (96), 76:24 d.r.	114

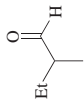


TABLE 3. ADDITION OF E-CROTYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		THF, rt, 60 h	 (81), 95:5 d.r., 74:26 anti:syn	525
		THF, -78°	 (-), 75	543
		—	 TBDMMSO OH (49-82)	341
		—	 TBDMMSO OH (49-82)	341
		Neat, rt, 3 d	 OR OH (-)	R TBDMMS MOM 98:2 89:11 d.r.
		Neat, rt, 3 d	 OR OH (-)	R TBDMMS MOM 98:2 94:6 d.r.
		4 Å MS, toluene, -78°	 OR OH (85), >98:2 d.r.	625, 626

R = DMPM

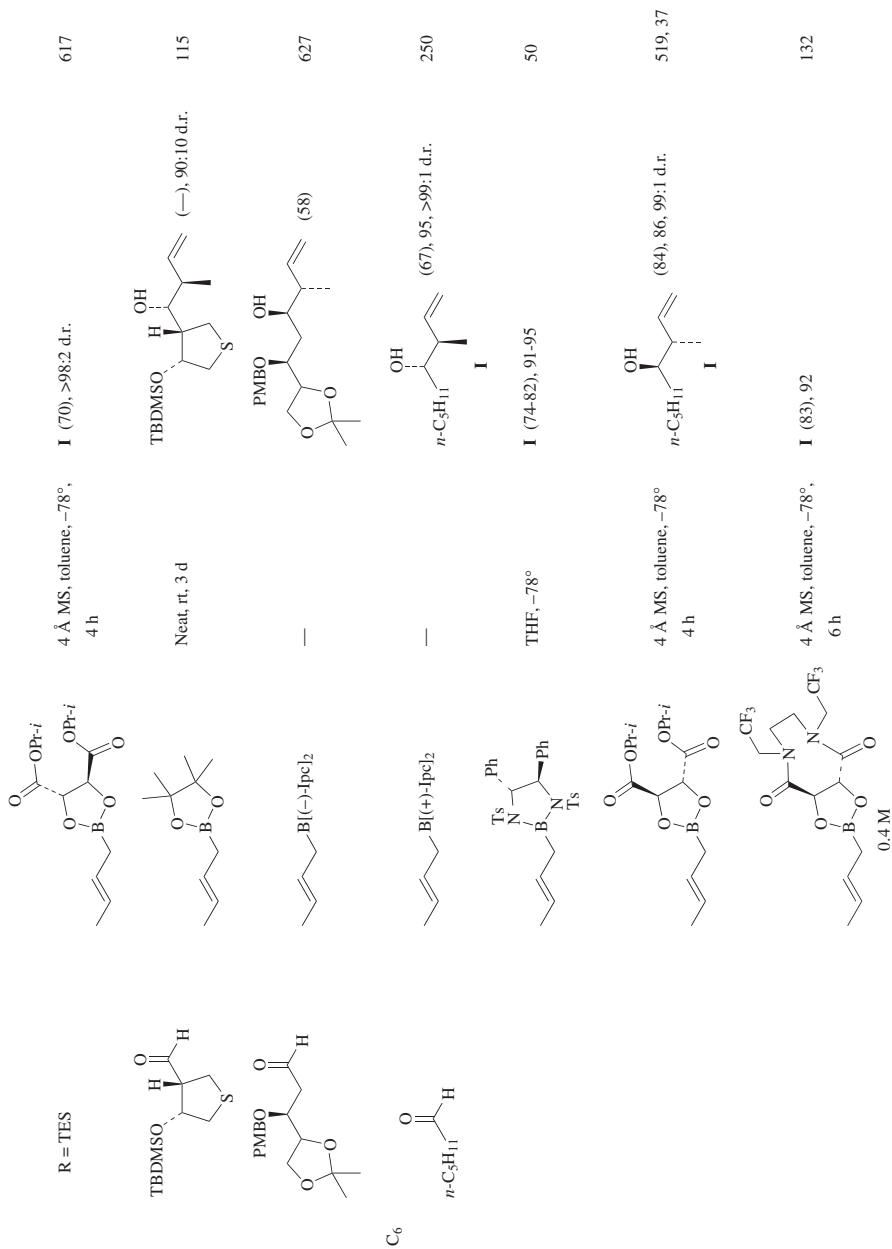


TABLE 3. ADDITION OF E-CROTYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yields( %), % ee	Refs.
		4 Å MS, toluene, -78°	 (90), >98, >50:1 d.r.	342, 190
		Petroleum ether, 0° to rt, 14 h	TBDMSO  (99), 95:5 d.r., >99:1 anti:syn	149, 628, 197
		4 Å MS, toluene, -78°	TBDPSO  (87), 94:6 d.r.	629, 630
		4 Å MS, toluene, -78°	 (76), 80:20 d.r.	584, 278

C<sub>6</sub>



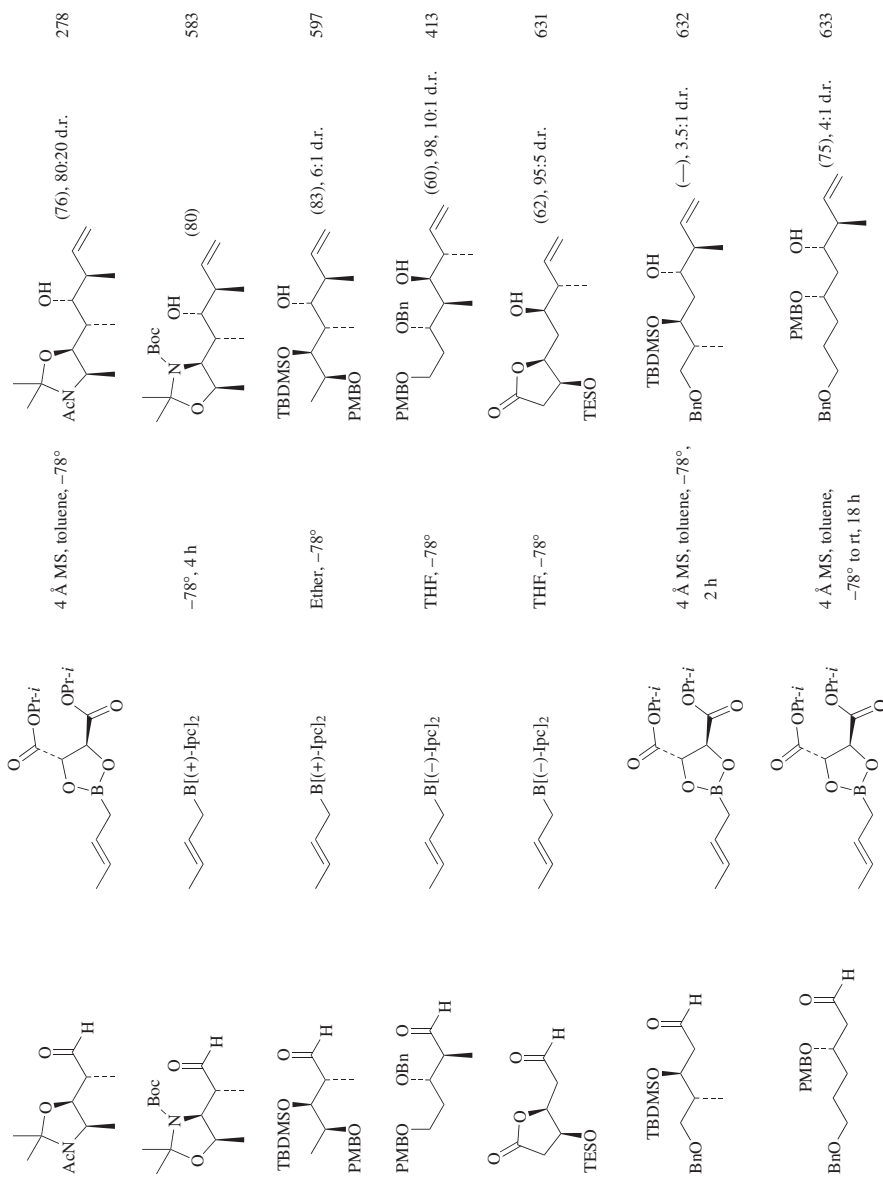
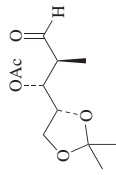
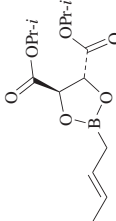
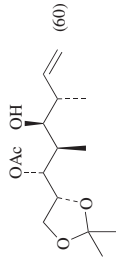
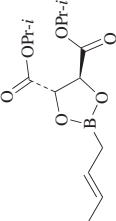
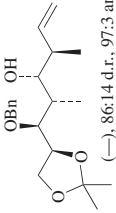


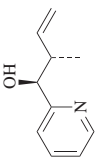


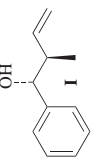



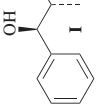


TABLE 3. ADDITION OF E-CROTYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
 $C_6$		4 Å MS, toluene, -78° to rt, 18 h	 (60)	603
		4 Å MS, toluene, -78°	 (-), 86:14 d.r., 97:3 anti:syn	549
 $C_7$		THF, ether, -78°, 3 h	 (31), 83, >96:4 d.r.	634
		 $BEt_3$ , Pd(PPh <sub>3</sub> ) <sub>4</sub> , THF, rt, 24 h	 (64), 2.6:1 d.r.	483
	"	 $BEt_3$ , Pd(PPh <sub>3</sub> ) <sub>4</sub> , THF, rt, 24 h; 40°, 2 h	<b>I</b> (60), 2.2:1 d.r.	483
		—	<b>I</b> (59), 96, >99:1 d.r.	250
	THF, -78°, 3 h	 (79), 88, 99:1 d.r.	137	

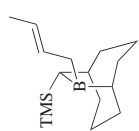


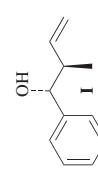
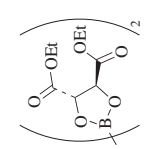
	Ether, -78°, 3 h	<b>I</b> (82), 97, >98:2 d.r.	143
	Ether, -75°	<b>I</b> (50), 99:1 d.r.	43
	Ether, -78°	<b>I</b> (80), 94:6 d.r.	22
"	—	<b>I</b> (97), 10:1 d.r.	52
"	L.A. (10 mol%), toluene, -78°, 4 h	$\frac{\text{L.A.}}{\text{AlCl}_3}$ (92) >99:1 $\frac{\text{d.r.}}{\text{Sc(OTf)}_3}$ (94) >99:1	25
"	AlCl <sub>3</sub> /(S)-BINOL (10 mol%), toluene, -78°, 4 h		25
"	Et <sub>2</sub> AlCl/(S)-BINOL (10 mol%), toluene, -78°, 6 h	<b>I</b> (40), 51, 99:1	25
	$\left( \begin{array}{c} \text{O} \\ \parallel \\ \text{O} \end{array} \right)_2$ Pd <sub>2</sub> (dba) <sub>3</sub> , DMSO, toluene, 20°, 21 h	<b>I</b> (76), 33	349

TABLE 3. ADDITION OF E-CROTYL REAGENTS (Continued)

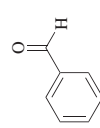
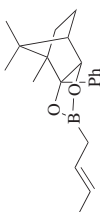
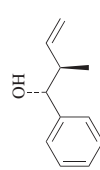
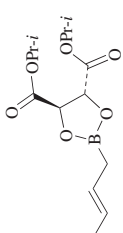
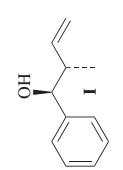
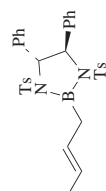
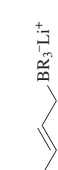

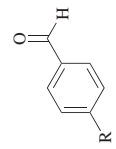
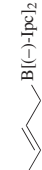
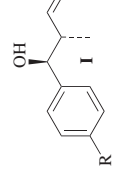

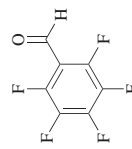

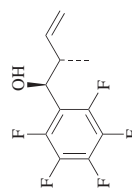
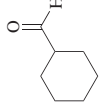

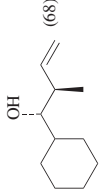
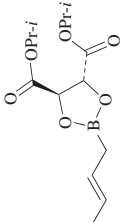
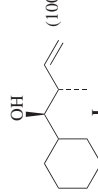
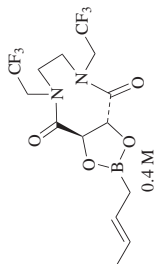
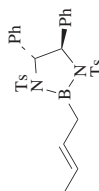
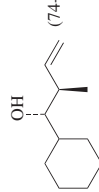
Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.								
		$\text{Sc}(\text{OTf})_3$ (10 mol%), $\text{CH}_2\text{Cl}_2$ , $-78^\circ$ , 24 h	 (60), 97, >49:1 d.r.	27, 28								
		4 Å MS, THF, $-78^\circ$ , 3 h	 (91), 67, >99:1 d.r.	519, 37								
	"	$\text{Co}(\text{CO})_3$ , 4 Å MS, toluene, $-78^\circ$	<b>I</b> (90), 92, 98:2 d.r.	128								
		$\text{CH}_2\text{Cl}_2$ , $-78^\circ$	<b>I</b> (74-82), 91-95	50								
		 $\text{Li}^+$ $\text{BR}_3$ , ether, $-70^\circ$	<table border="1" data-bbox="893 630 974 903"> <tr><td>R</td><td>d.r.</td></tr> <tr><td>Et</td><td>(-)</td></tr> <tr><td><i>n</i>-Bu</td><td>(-)</td></tr> </table> 90:10-91.5:8.5 90:10-91.5:8.5	R	d.r.	Et	(-)	<i>n</i> -Bu	(-)	577		
R	d.r.											
Et	(-)											
<i>n</i> -Bu	(-)											
		THF, ether, $-78^\circ$ , 4.5 h	 (82), >99:1 d.r.	635								
R = H, MeO, $\text{O}_2\text{N}$		$\text{BF}_3 \cdot \text{OEt}_2$ (2 equiv), $\text{CH}_2\text{Cl}_2$ , $-78^\circ$ , 15 min	<table border="1" data-bbox="1169 693 1266 903"> <tr><td>R</td><td>d.r.</td></tr> <tr><td>H</td><td>(94)</td></tr> <tr><td>MeO</td><td>(91)</td></tr> <tr><td><math>\text{O}_2\text{N}</math></td><td>(96)</td></tr> </table> >98:2 >97:3 >98:2	R	d.r.	H	(94)	MeO	(91)	$\text{O}_2\text{N}$	(96)	98, 99
R	d.r.											
H	(94)											
MeO	(91)											
$\text{O}_2\text{N}$	(96)											



TABLE 3. ADDITION OF E-CROTYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		THF, -78°, 3 h	 (72), 92, >95:5 d.r.	491
		THF, -85°, 18 h	 (68)	348
		4 Å MS, toluene, -95°, 3 h	 (100), 91, >99:1 d.r.	519, 37
	"	4 Å MS, toluene, rt, 1 h	<b>I</b> (96), 46, >99:1 d.r.	37
	"	4 Å MS, toluene, -78°, 3 h	Solvent toluene (85), 87 ether (87), 77 THF (88), 70 CH <sub>2</sub> Cl <sub>2</sub> (87), 62	d.r. 96:4 >99:1 >99:1 >99:1
		4 Å MS, toluene, -78°, 6 h	<b>I</b> (85), 94	132
		THF, -78°	 (74-82), 91-95	50

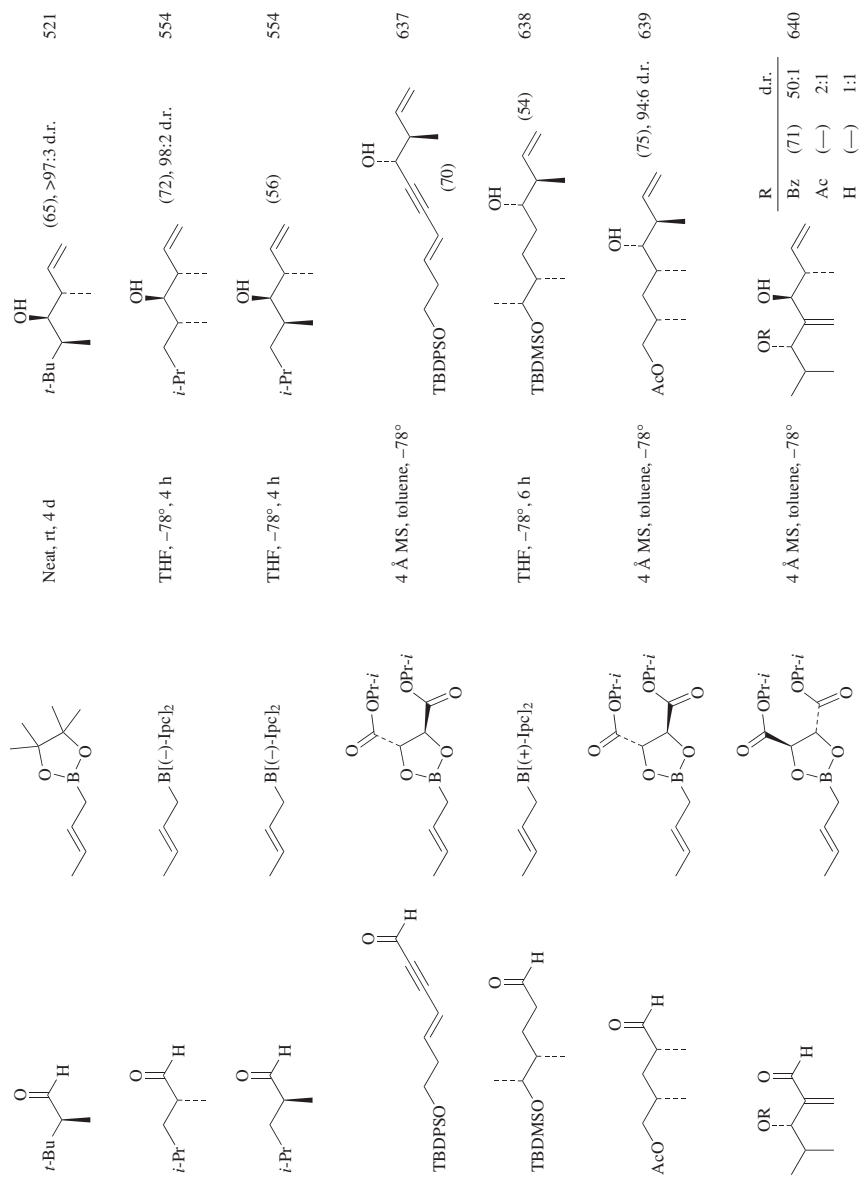
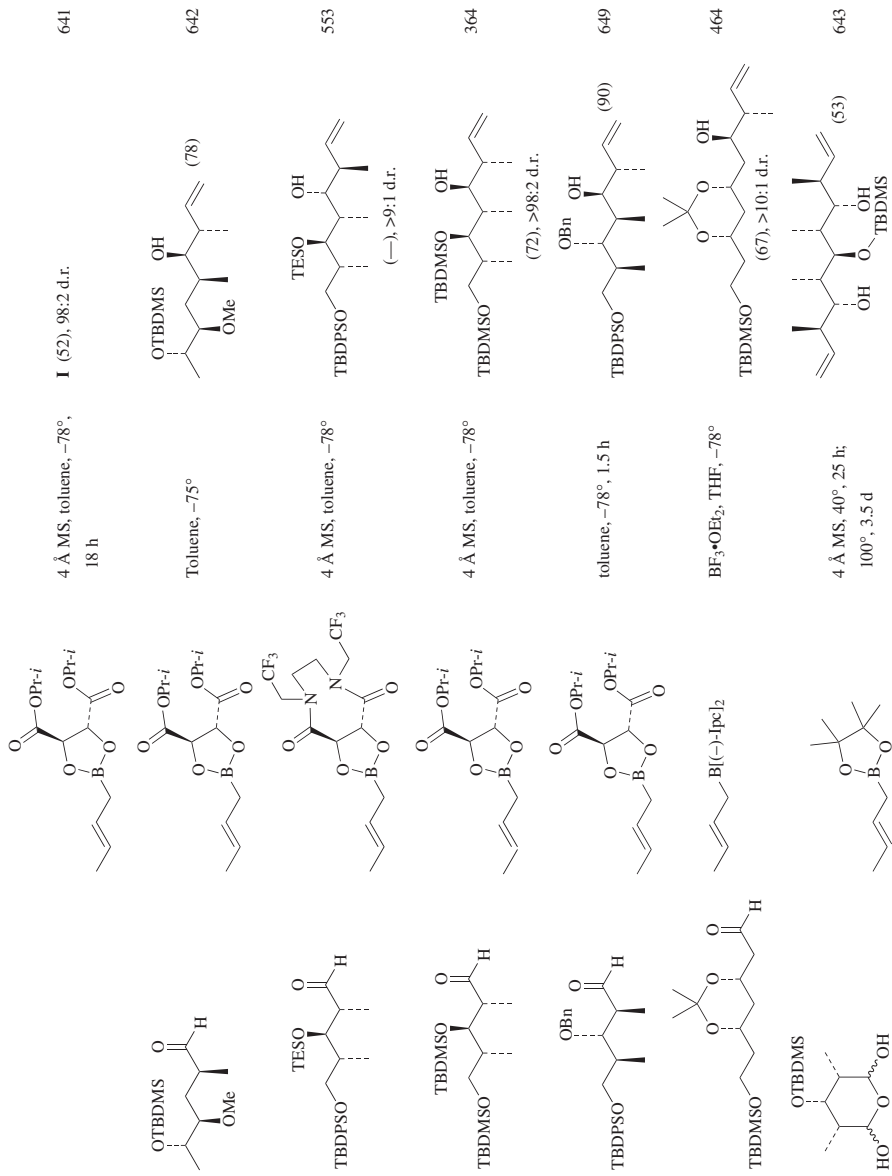


TABLE 3. ADDITION OF E-CROTYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		BF <sub>3</sub> •OEt <sub>2</sub> , THF, -78°, 12 h		641
		BF <sub>3</sub> •OEt <sub>2</sub> , THF, -78°, 12 h	<b>I (75)</b> , 98:2 d.r.	641
		4 Å MS, toluene, -78°, 18 h	<b>I (70)</b> , 98:2 d.r.	641
		4 Å MS, toluene, -78°, 18 h		641
		BF <sub>3</sub> •OEt <sub>2</sub> , THF, -78°, 12 h		641
		BF <sub>3</sub> •OEt <sub>2</sub> , THF, -78°, 12 h	<b>I (72)</b> , 98:2 d.r.	641
		4 Å MS, toluene, -78°, 18 h	<b>I (78)</b> , 98:2 d.r.	641







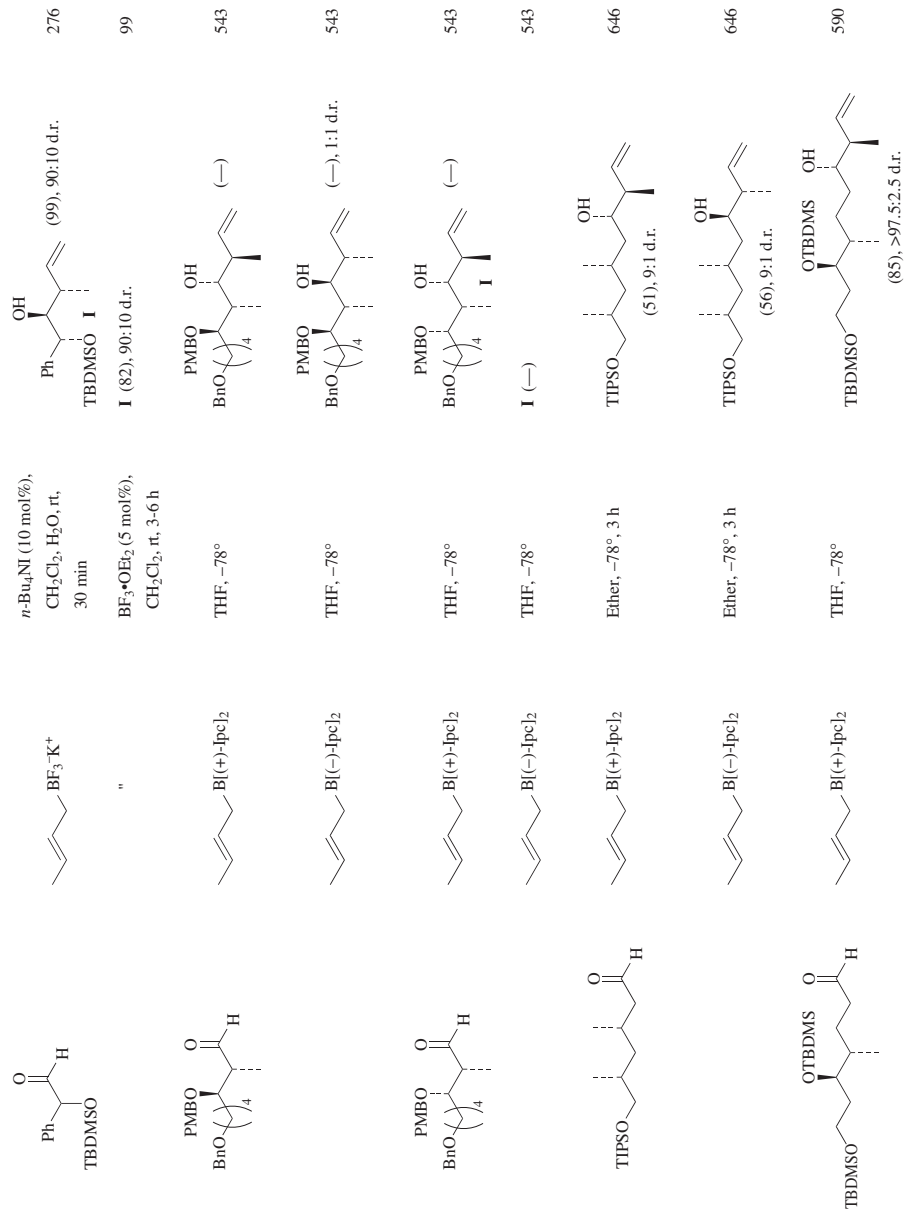


TABLE 3. ADDITION OF E-CROTYL REAGENTS (Continued)

$C_8$	Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
			4 Å MS, toluene, -78°	TBDMMSO OH TBDMMSO (78), >99:1 d.r.	619
			4 Å MS, toluene, -78°	TBDMPSO OH OBn OH (-), 2.5:1	647
			4 Å MS, toluene, -78° to rt, 15 h	OTES OH BnO (93), >99:1 d.r.	648
			Et3N, CH2Cl2, -10° to rt	HO Ph HO2C (96), 99:1 d.r.	106
			4 Å MS, toluene, -78°	PMBO OH OBn OH OBn OBn (-), 9:1 d.r.	559

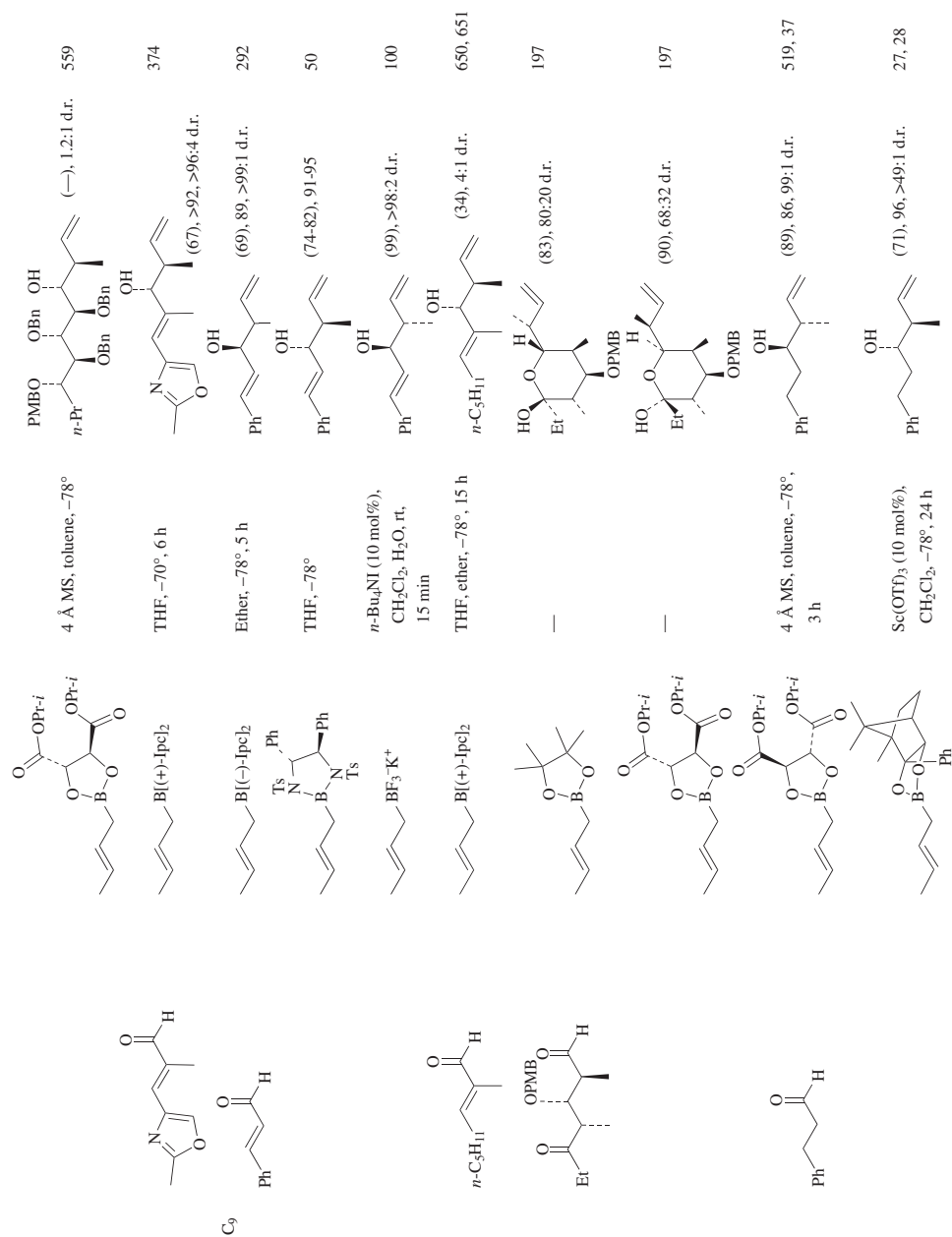


TABLE 3. ADDITION OF E-CROTYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yields (%), % ee	Refs.
		Neat, rt, 4 d	 (53), 75:25 d.r.	521
		4 Å MS, toluene, -78°, 2 h	 (70), 97:3 d.r.	526
		4 Å MS, toluene, -78°, 2 h	 (70), 95.5:4.5 d.r.	526
		BF <sub>3</sub> ·OEt <sub>2</sub> (5 mol%), CH <sub>2</sub> Cl <sub>2</sub> , rt, 3-6 h	 (87), 75:25 d.r.	99
	"	<i>n</i> -Bu <sub>4</sub> Ni (0.1 eq), CH <sub>2</sub> Cl <sub>2</sub> /H <sub>2</sub> O, rt, 30 min	 (96), 75:25 d.r.	276
		Cr(CO) <sub>3</sub> , 4 Å MS, toluene, -78°	 (85-95), 96, 97:3	128
		4 Å MS, toluene, -78°	 (55-70), 69	130

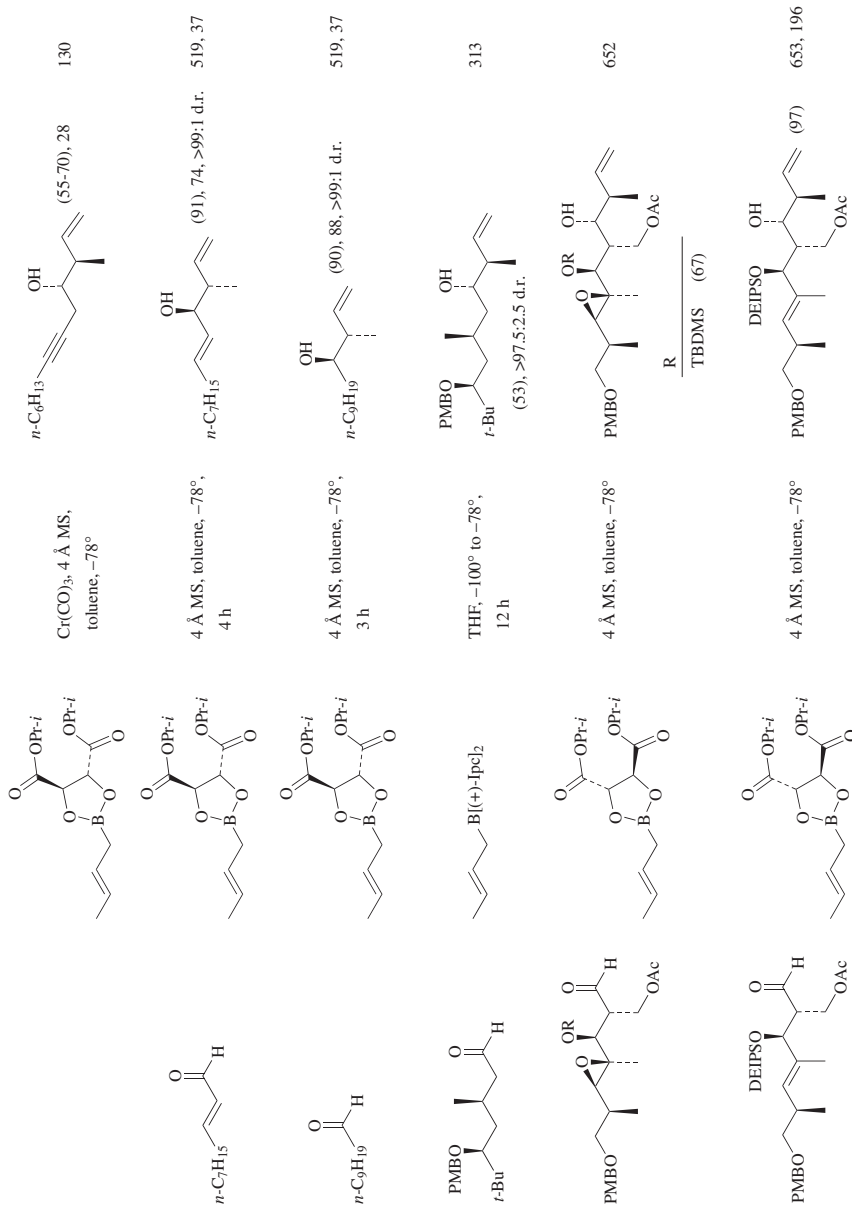
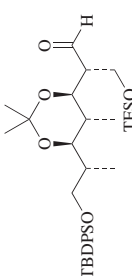
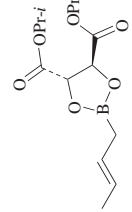
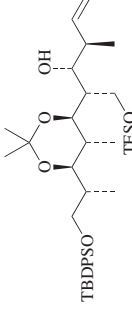
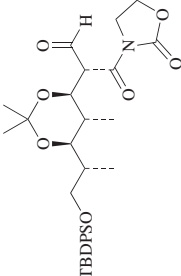
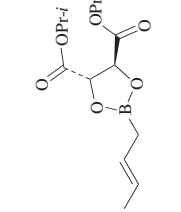
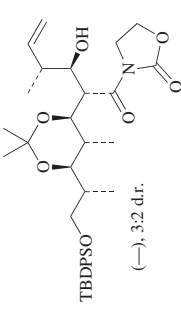
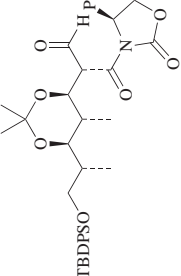
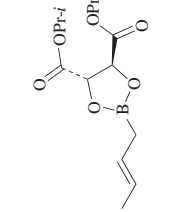
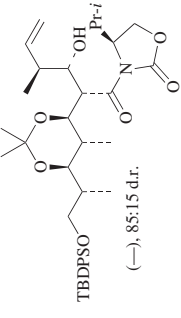
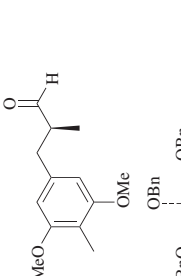
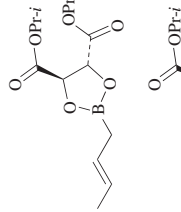
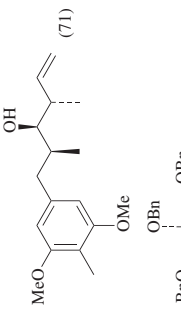
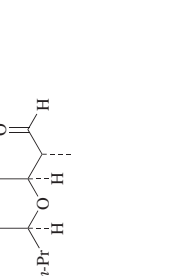
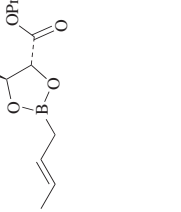
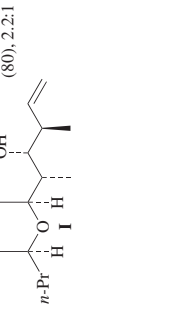


TABLE 3. ADDITION OF E-CROTYL REAGENTS (Continued)

	Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C <sub>10</sub>			4 Å MS, toluene, -78°	 (90), >99:1 d.r.	654
			4 Å MS, toluene, -78°	 (-), 3:2 d.r.	654
			4 Å MS, toluene, -78°	 (-), 85:15 d.r.	654
C <sub>11</sub>			4 Å MS, toluene, -78°	 (71)	655
			4 Å MS, toluene, -78°	 (80), 2.2:1 d.r.	559



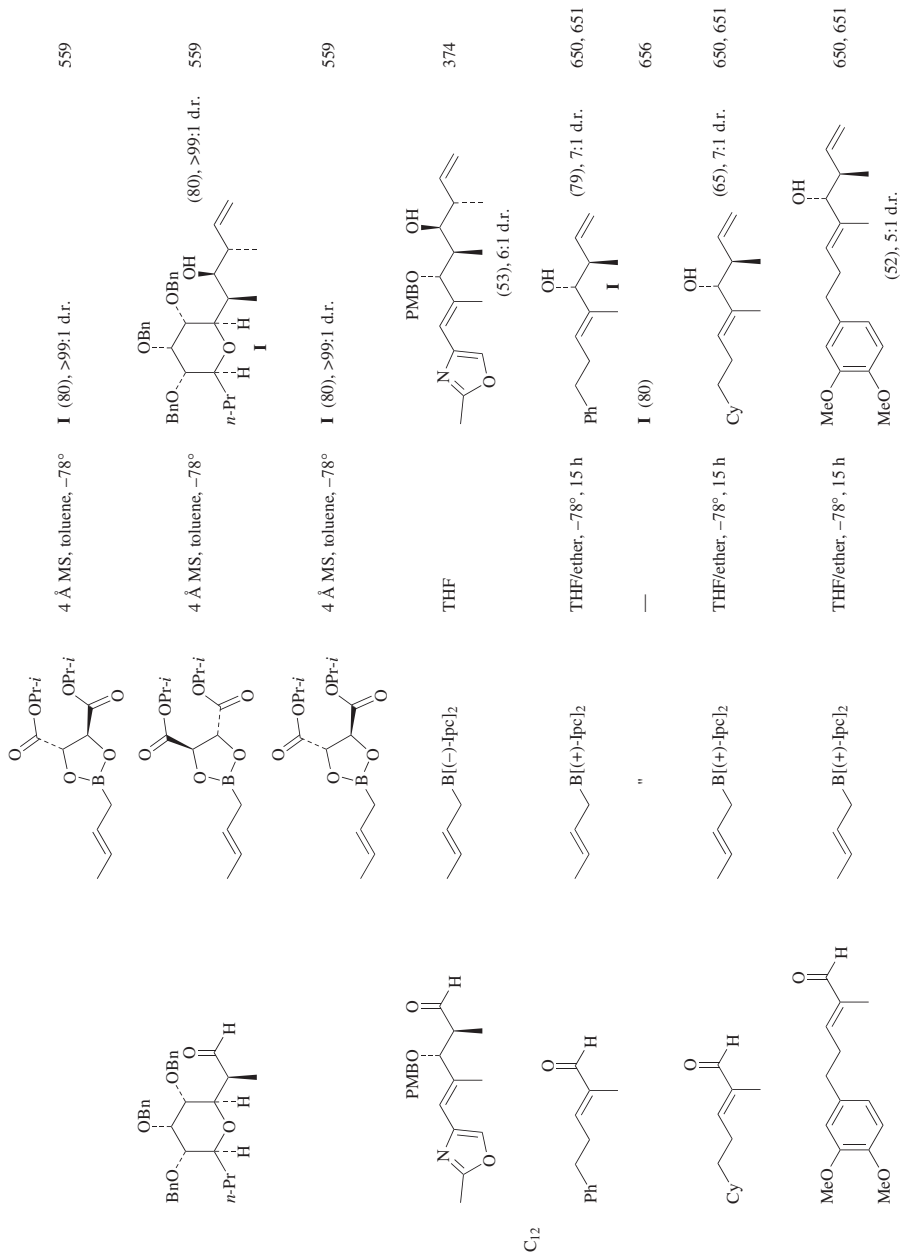


TABLE 3. ADDITION OF E-CROTYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Toluene, -78°		334
	Bi(-)-IpcI <sub>2</sub>	—		561
		4 Å MS, toluene, -78°		654
	Bi(+)-IpcI <sub>2</sub>	THF, -78° to rt, 1 h		445
		—		657, 658

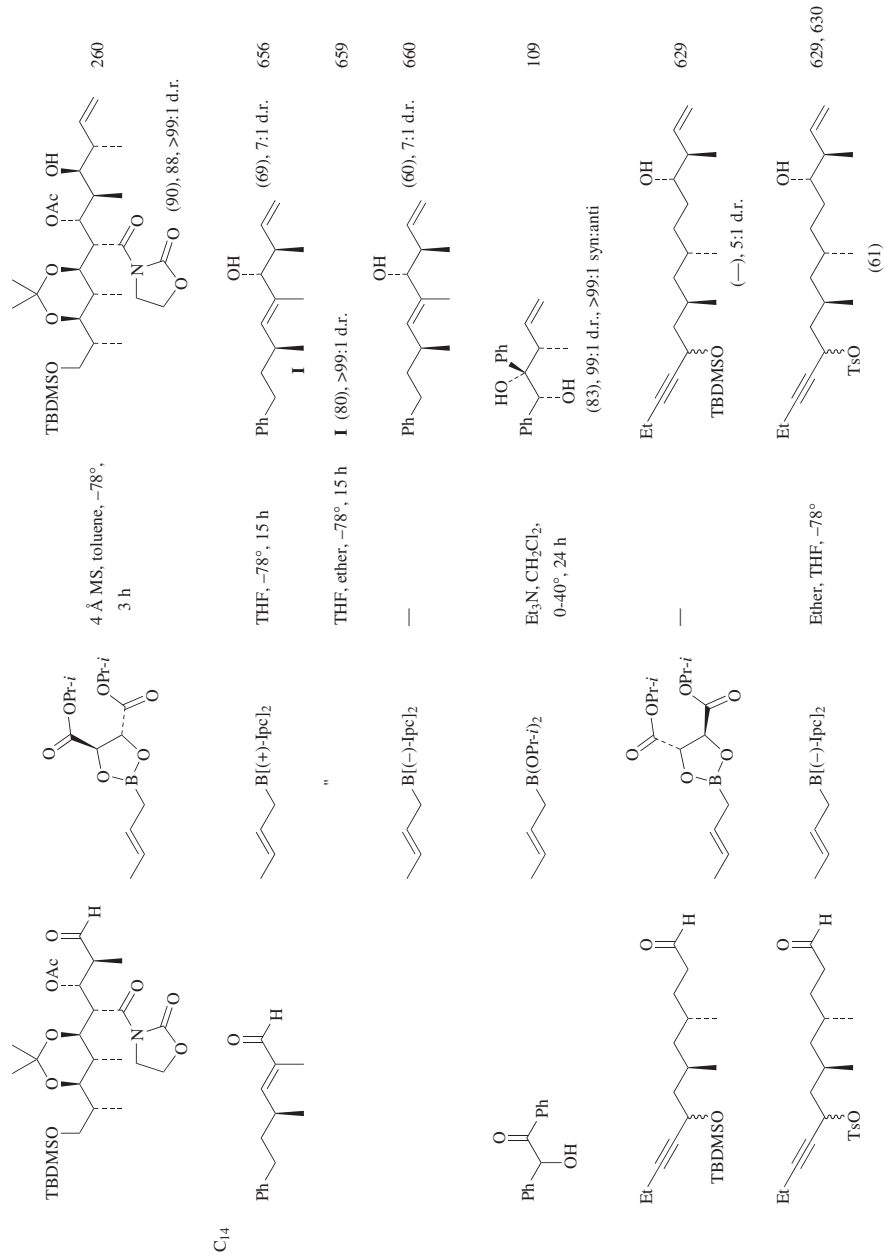
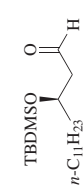

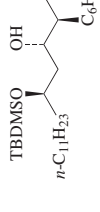
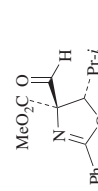

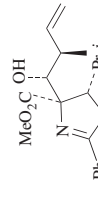

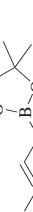


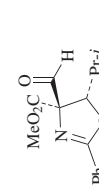

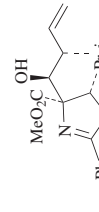
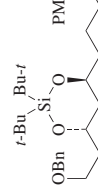

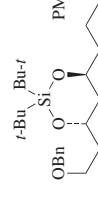


TABLE 3. ADDITION OF E-CROTYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
 TBDMMSO <i>n</i> -C <sub>11</sub> H <sub>23</sub>	 <i>n</i> -C <sub>8</sub> H <sub>13</sub> CH=CHCH <sub>2</sub> BF <sub>3</sub> ·K <sup>+</sup>	<i>n</i> -Bu <sub>4</sub> Ni (10 mol%), CH <sub>2</sub> Cl <sub>2</sub> , H <sub>2</sub> O, rt, 30 min	 (68), 75:25 d.r. C <sub>6</sub> H <sub>13</sub> <sup><i>n</i></sup>	276
 MeO <sub>2</sub> C Ph Pr- <i>i</i>	 BI(+)-IpcI <sub>2</sub>	—	 (—), 4:1 d.r. I	661
 MeO <sub>2</sub> C Ph Pr- <i>i</i>	 BI(+)-IpcI <sub>2</sub>	—	I (—), 2:1 d.r.	661
 MeO <sub>2</sub> C Ph Pr- <i>i</i>	 BI(+)-IpcI <sub>2</sub>	—	I (—), 3:1 d.r.	661
 MeO <sub>2</sub> C Ph Pr- <i>i</i>	 BI(+)-IpcI <sub>2</sub>	THF, -78°, 18 h	 (70), 4:1 d.r.	661, 662
 MeO <sub>2</sub> C Ph Pr- <i>i</i>	 BI(+)-IpcI <sub>2</sub>	—	 (65), 1.5:1 d.r.	334

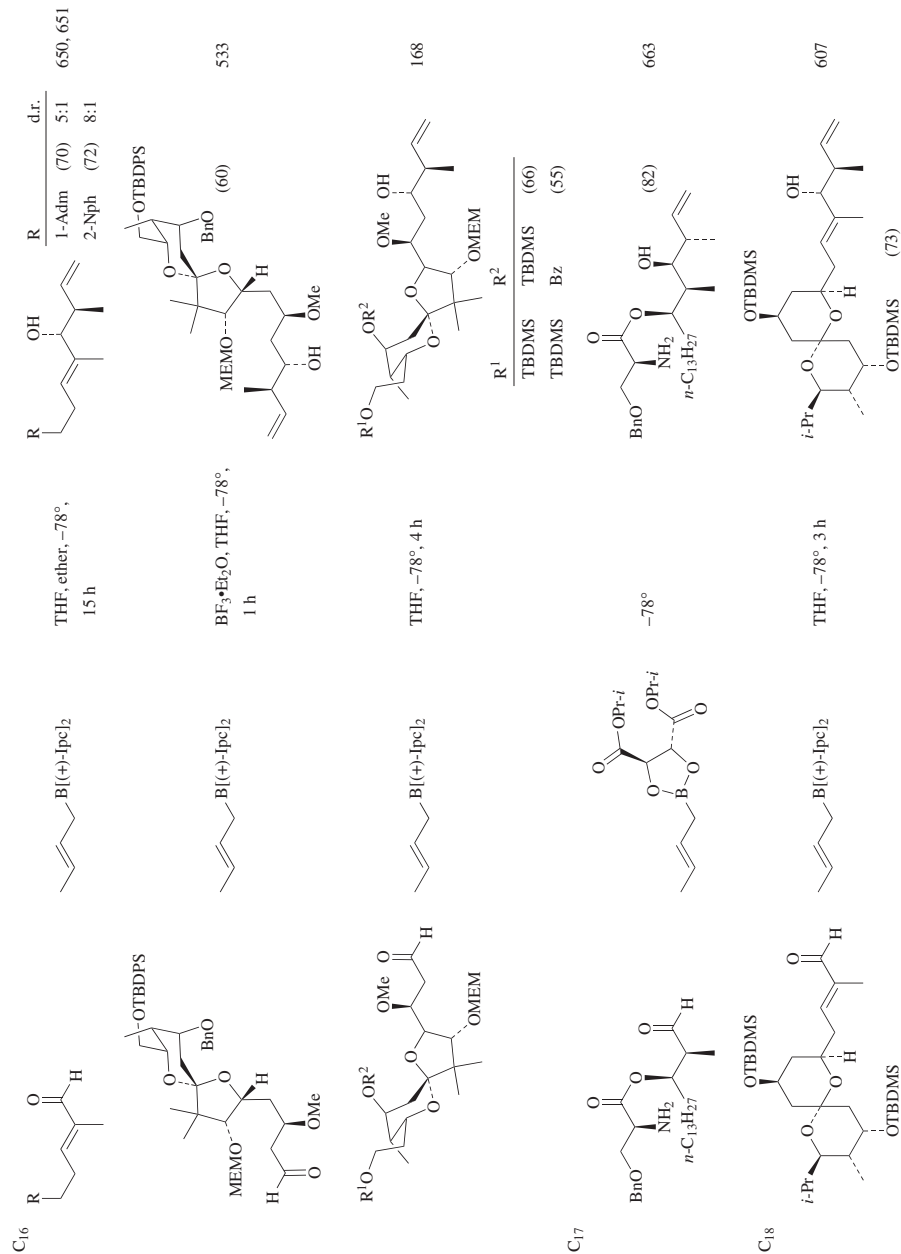
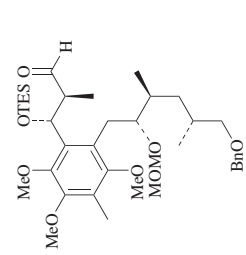

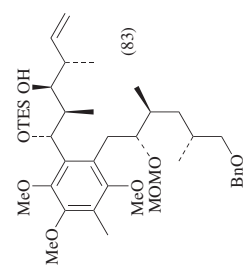
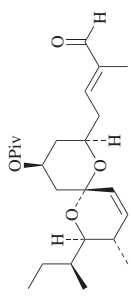
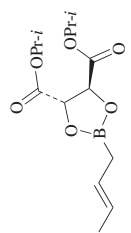
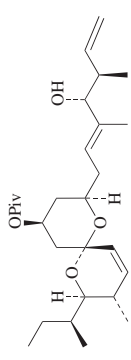
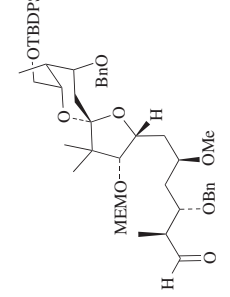

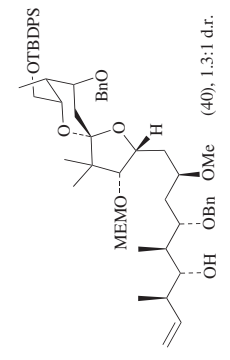
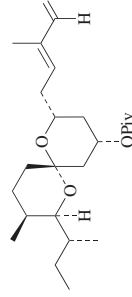
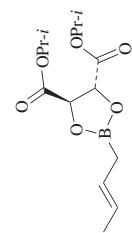
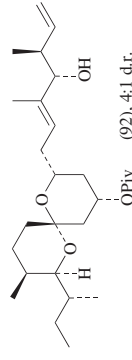
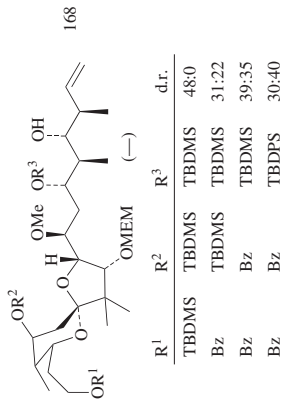
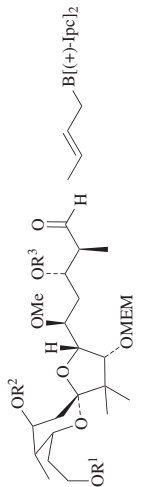


TABLE 3. ADDITION OF E-CROTYL REAGENTS (Continued)

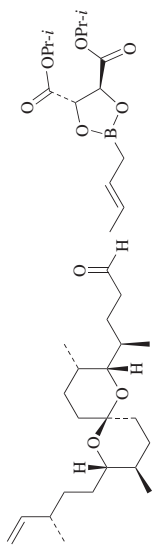
Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		-78°	 361	
		4 Å MS, toluene, -78°, 1.5 h	 664	
		BF <sub>3</sub> •Et <sub>2</sub> O, THF, -78°, 1 h	 533	
		4 Å MS, toluene, -78°	 665	



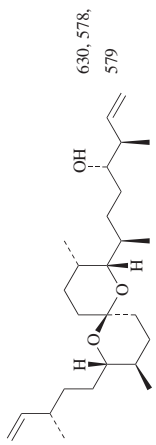
THF, -78°, 4 h



C<sub>22</sub>

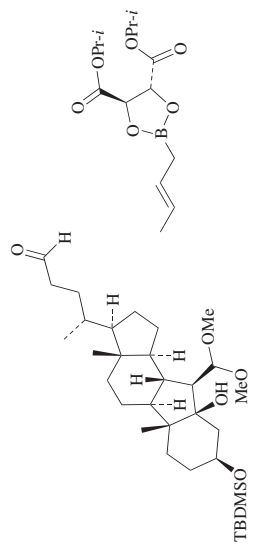


4 Å MS, toluene, -78°

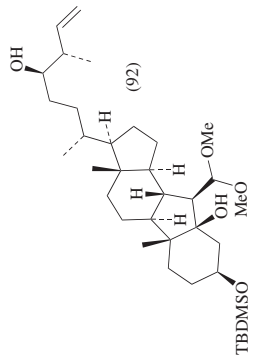


630, 578, 579

C<sub>24</sub>


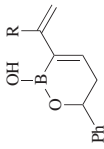


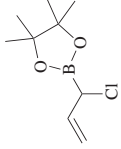
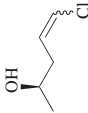
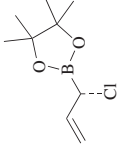
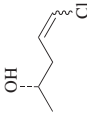
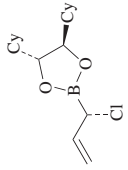
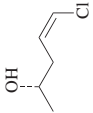
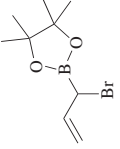
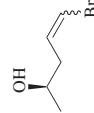
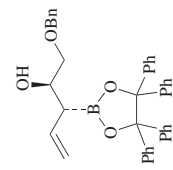
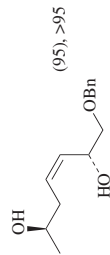


4 Å MS, toluene, -78°



666, 667

TABLE 4. ADDITION OF  $\alpha$ -SUBSTITUTED REAGENTS

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yields( %), % ee	Refs.
C <sub>1</sub> 		Toluene, 80°	 R i-Pr (79) 4:1 n-Pr (78) 6:1	236
C <sub>2</sub> 		Neat, 0°, 15 h		146, 668
		Neat, 0°, 15 h		66, 669
		THF, -78° to rt, 18 h		65
		Neat, 0°, 15 h		146, 668
		-78°, 2 h; rt, 24 h		670



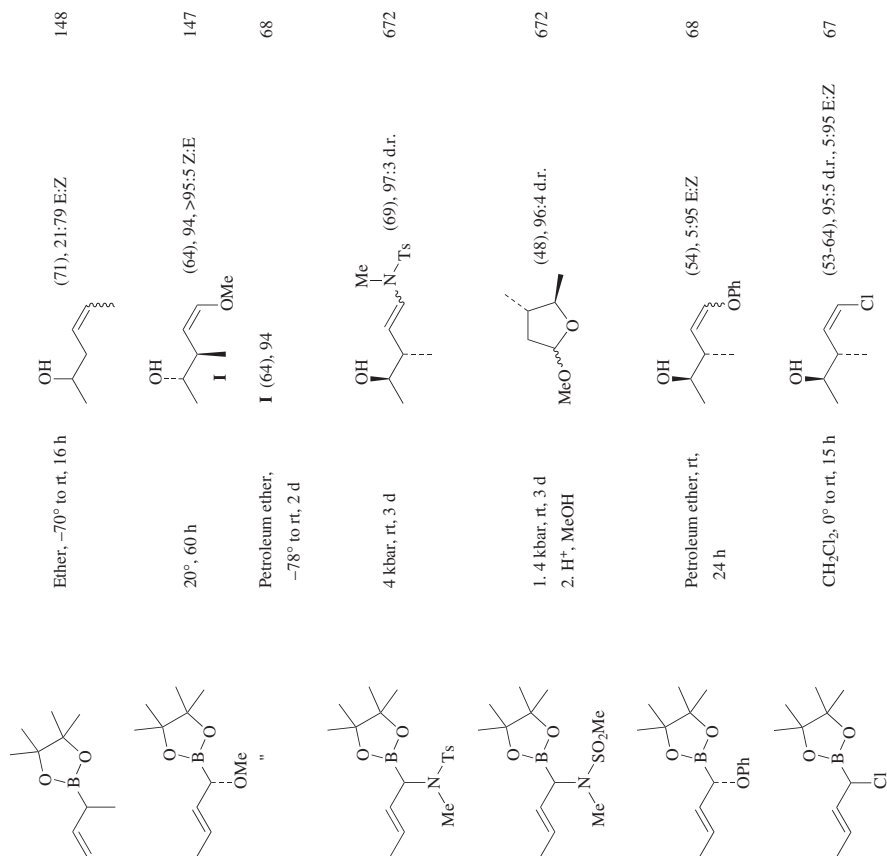

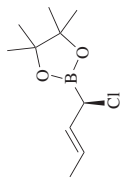
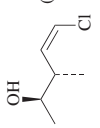
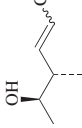
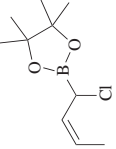
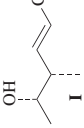
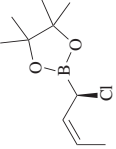
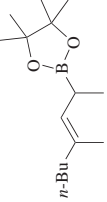
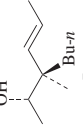
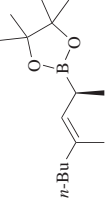
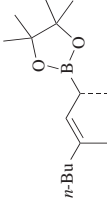
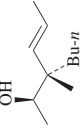


TABLE 4. ADDITION OF  $\alpha$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C <sub>2</sub> 		Petroleum ether, rt, 18 h	 (53-64), 95, 95:5 d.r.	67
	"	Petroleum ether, rt, 12 h	 (53-60), 92, 95:5 d.r.	83
		CH <sub>2</sub> Cl <sub>2</sub> , 0° to rt, 15 h	 (70), 97:3 d.r., 85:12 E:Z	67
		CH <sub>2</sub> Cl <sub>2</sub> , 0° to rt, 15 h	<b>I</b> (70), 73, 97:3 d.r.	67
		Neat, rt, 5-8 d	 (79), 96:4 d.r.	673
		Neat, rt, 5-8 d	<b>I</b> (75), 97:3 d.r.	673
		Neat, rt, 5-8 d	 (70), 87, 97:3 d.r.	673

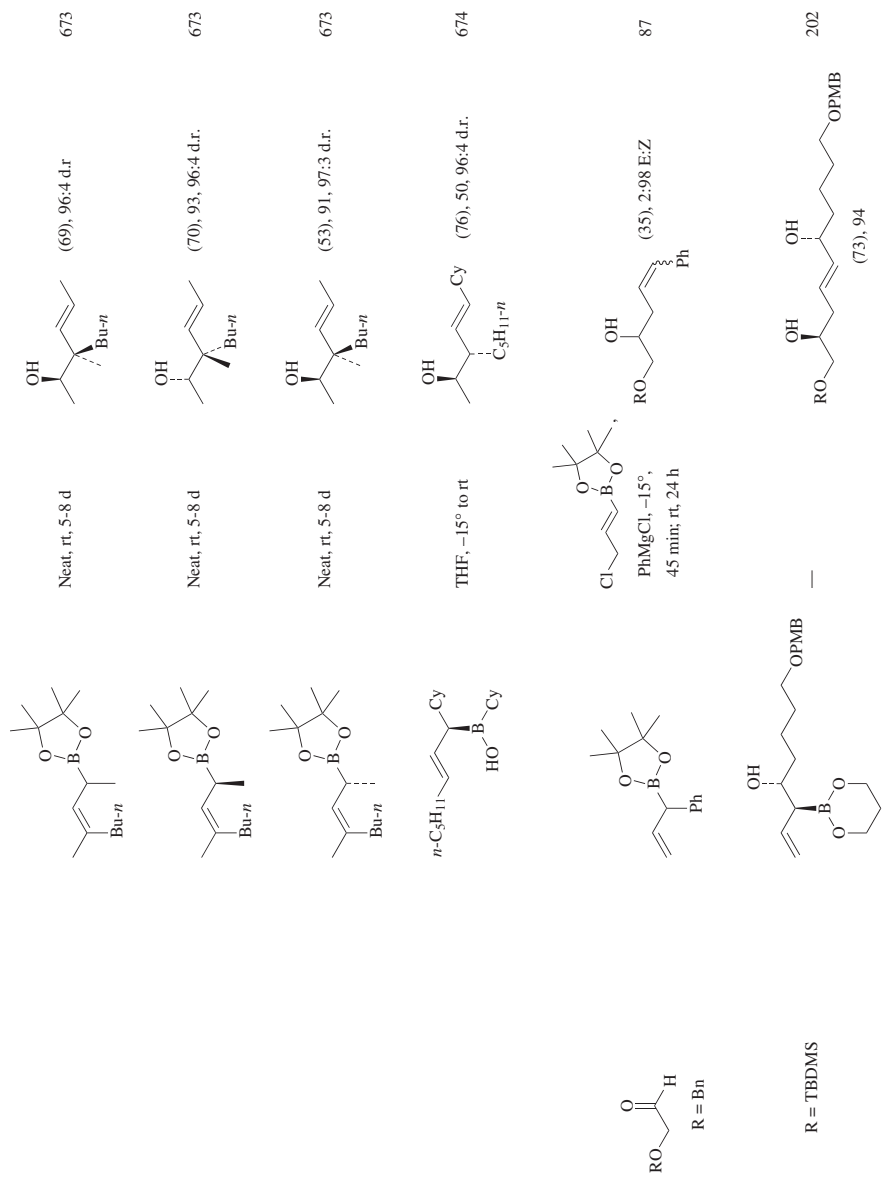

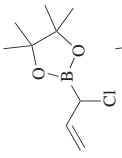
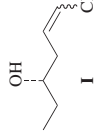
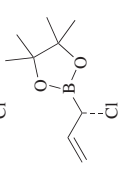

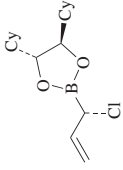
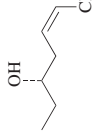
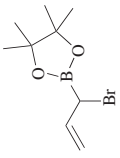
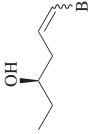
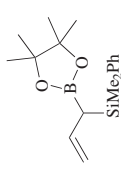
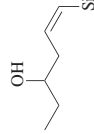
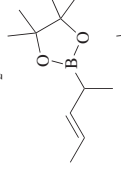
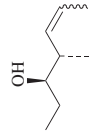
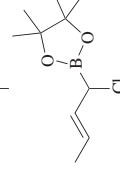
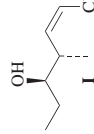


TABLE 4. ADDITION OF  $\alpha$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
 C <sub>3</sub>		Neat, 0°, 15 h	 I (86), 6:94 E:Z	146, 668
		Neat, 0°, 15 h	 I (→), 89, 4:96 E:Z	66, 669
		THF, -78° to rt, 18 h	 I (81), >99, >81:1 Z:E	65
		Neat, 0°, 15 h	 I (82), 6:94 E:Z	146, 668
		THF, 100°, 24 h	 I (74), 15:85 E:Z	675
		Petroleum ether, -78° to rt	 I (81), 35:65 E:Z	676
		CH <sub>2</sub> Cl <sub>2</sub> , 0° to rt, 15 h	 I (47-65), 95:5 d.r., 5:95 E:Z	67

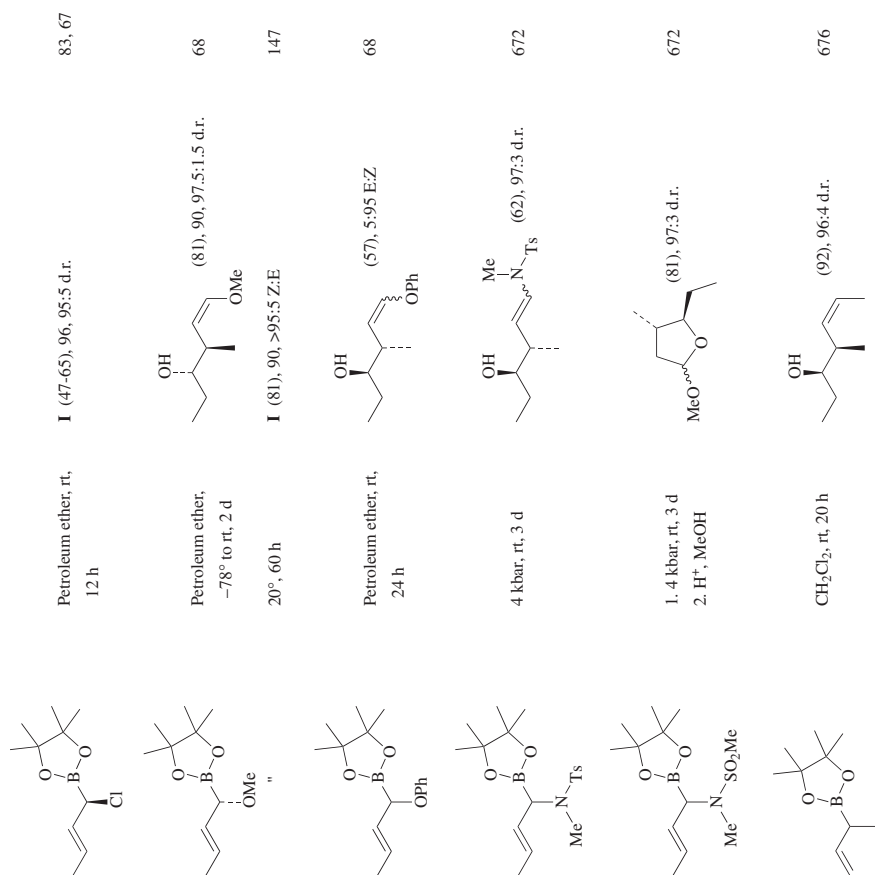

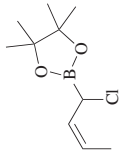
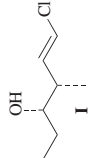
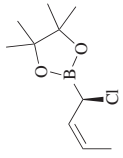
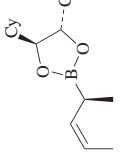
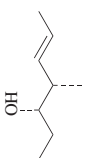
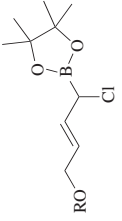
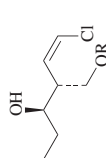
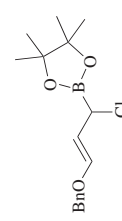
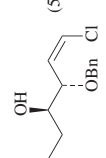
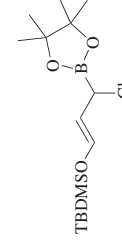
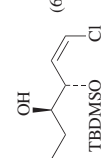
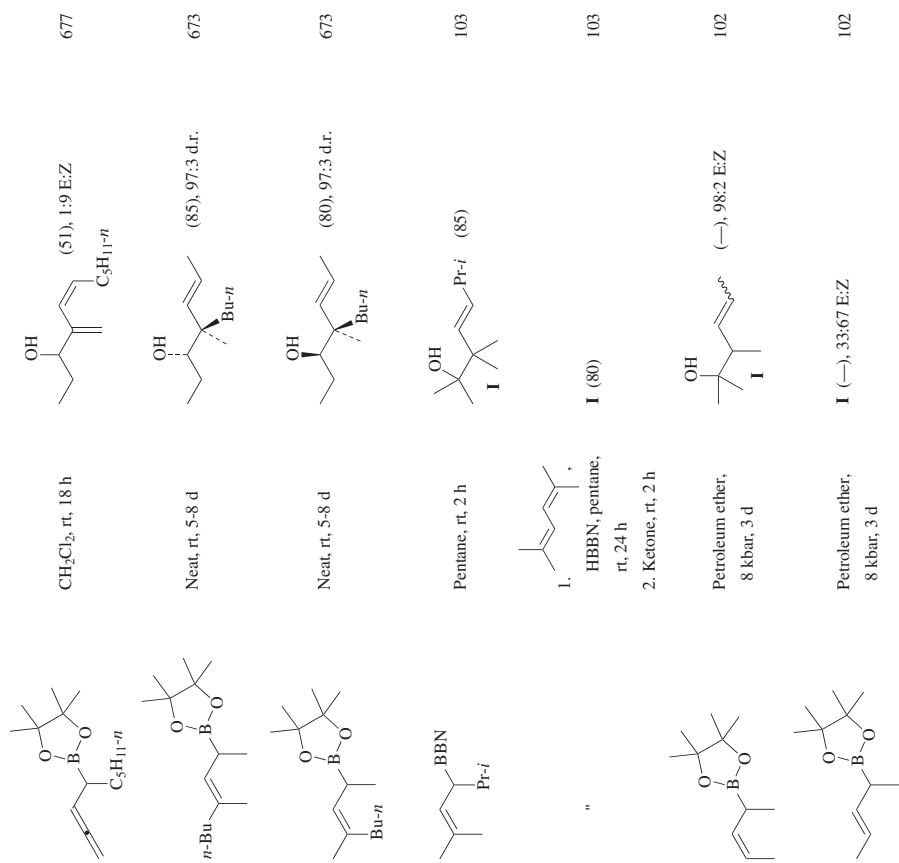


TABLE 4. ADDITION OF  $\alpha$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yields(%) , % ee	Refs.
C <sub>3</sub> 		CH <sub>2</sub> Cl <sub>2</sub> , 0° to rt, 15 h	 I (81), 97:3 d.r., 91:6 E/Z	67
		CH <sub>2</sub> Cl <sub>2</sub> , 0° to rt, 15 h	I (81), 85, 97:3 d.r.	67
		Petroleum ether	 (85), 99	628, 197
		Neat, rt, 10 h	 R Bn (55) TBDMS (62)	67
		Neat, rt, 10 h	 (55)	67
		Neat, rt, 10 h	 TBDMSO (62)	67



CH<sub>2</sub>Cl<sub>2</sub>, rt, 18 h

Neat, rt, 5-8 d

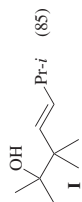
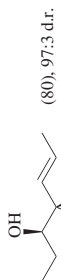
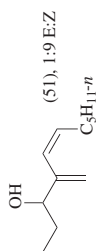
Neat, rt, 5-8 d

Pentane, rt, 2 h

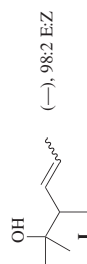
1. HIBBN, pentane, rt, 24 h  
2. Ketone, rt, 2 h

Petroleum ether, 8 kbar, 3 d

Petroleum ether, 8 kbar, 3 d



**I** (80)



**I** (-), 33:67 E:Z

677

673

673

103

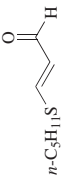
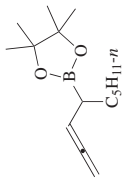
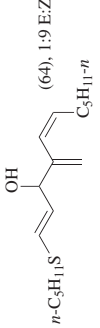
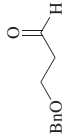
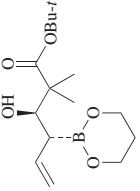
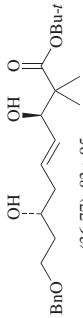

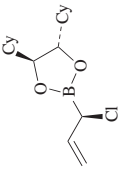
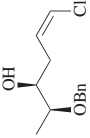

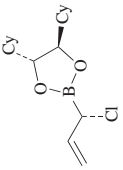
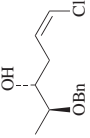
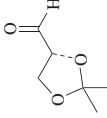
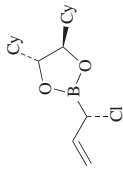
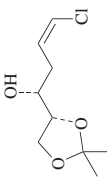
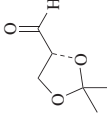
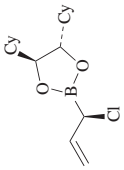
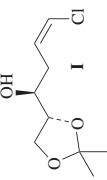
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TABLE 4. ADDITION OF  $\alpha$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		CH <sub>2</sub> Cl <sub>2</sub> , rt, 18 h	 (64), 1:9 E:Z C <sub>5</sub> H <sub>11-n</sub>	677
		-78° to rt	 (36-77), 83->95	203
		(MeO) <sub>2</sub> CH <sub>2</sub> , -30° to rt, 18 h	 (73), 92:8 d.r.	65
		(MeO) <sub>2</sub> CH <sub>2</sub> , -30° to rt, 18 h	 (74), 97:3 d.r.	65
		(MeO) <sub>2</sub> CH <sub>2</sub> , -30° to rt, 18 h	 (67), 92:8 d.r.	65
		(MeO) <sub>2</sub> CH <sub>2</sub> , -30° to rt, 18 h	 (72), 96:4 d.r.	65



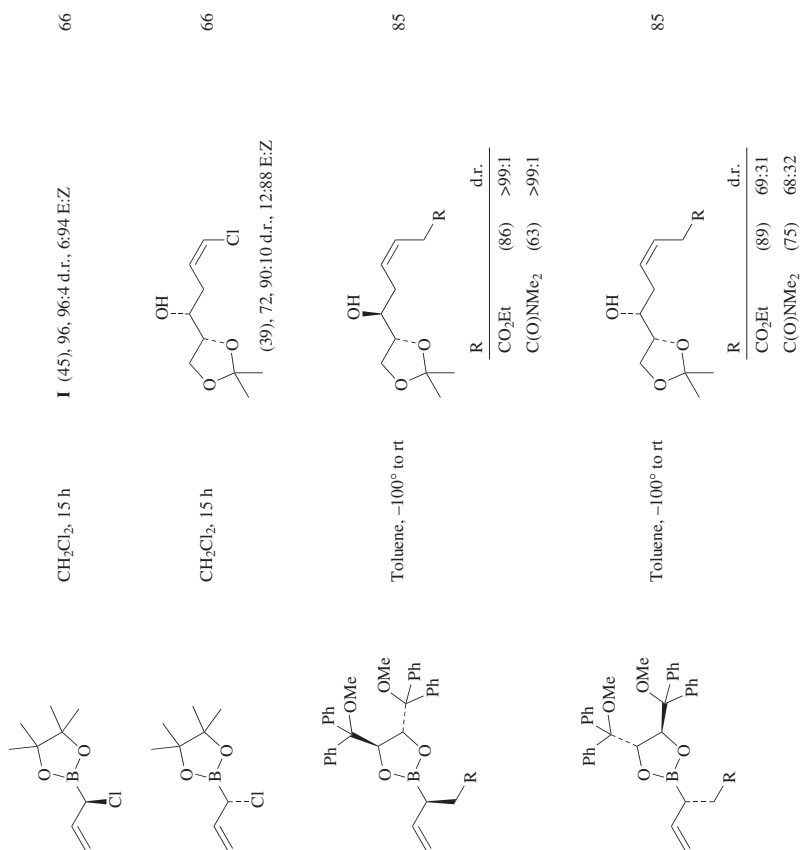
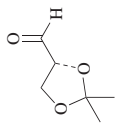
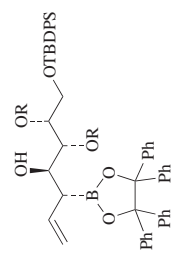
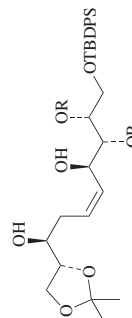
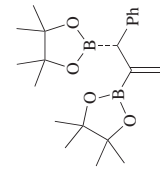
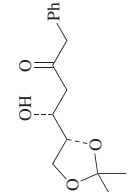
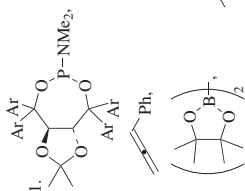
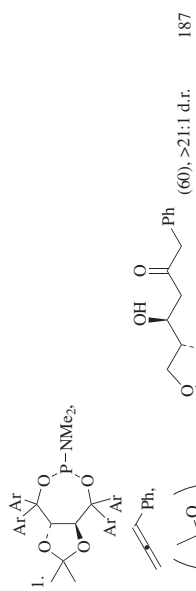


TABLE 4. ADDITION OF  $\alpha$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		$\text{CH}_2\text{Cl}_2$ , rt	 201	
		$\text{R}$	$\frac{\text{PMB (57)}}{t\text{-Bu (70-90)}}$	d.r. 4:1 9:1
			 (73), 21:1 d.r.	187
				
				1. $\text{Pd}_2(\text{dba})_3$ , 22°, 10 h 2. Aldehyde, 22°, 14 h 3. $\text{NaOH}$ , $\text{H}_2\text{O}_2$ Ar = 3,5-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>



$\text{Pd}_2(\text{dba})_3$ , 22°, 10 h  
 2. Aldehyde, 22°, 14 h  
 3. NaOH,  $\text{H}_2\text{O}_2$   
 Ar = 3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>

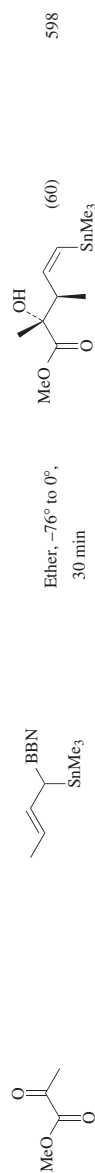
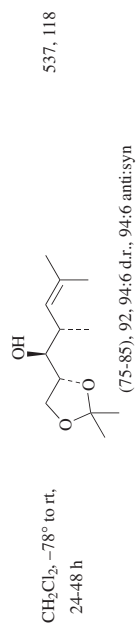
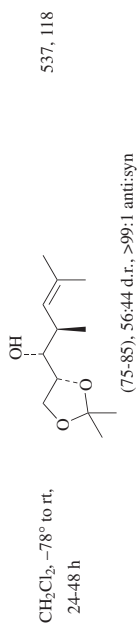
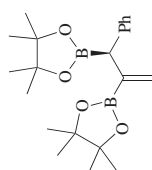


TABLE 4. ADDITION OF  $\alpha$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.														
		Ether, $-76^{\circ}$ to $0^{\circ}$ , 30 min	 +  <b>I + II (65),</b> <b>I:II = 63:37</b>	598														
		Petroleum ether, rt, 5 d		678, 679														
		$\text{CH}_2\text{Cl}_2$ , rt, 18 h		677														
			<table border="1"> <thead> <tr> <th>R</th> <th>E:Z</th> </tr> </thead> <tbody> <tr> <td><math>n\text{-C}_3\text{H}_7</math></td> <td>(82) 1:9</td> </tr> <tr> <td></td> <td>(80) 9:91</td> </tr> <tr> <td></td> <td>(75) 11:89</td> </tr> <tr> <td></td> <td>(79) 12:88</td> </tr> <tr> <td><math>t\text{-Bu}</math></td> <td>(62) 12:88</td> </tr> <tr> <td></td> <td>(83) 1:9</td> </tr> </tbody> </table>	R	E:Z	$n\text{-C}_3\text{H}_7$	(82) 1:9		(80) 9:91		(75) 11:89		(79) 12:88	$t\text{-Bu}$	(62) 12:88		(83) 1:9	
R	E:Z																	
$n\text{-C}_3\text{H}_7$	(82) 1:9																	
	(80) 9:91																	
	(75) 11:89																	
	(79) 12:88																	
$t\text{-Bu}$	(62) 12:88																	
	(83) 1:9																	

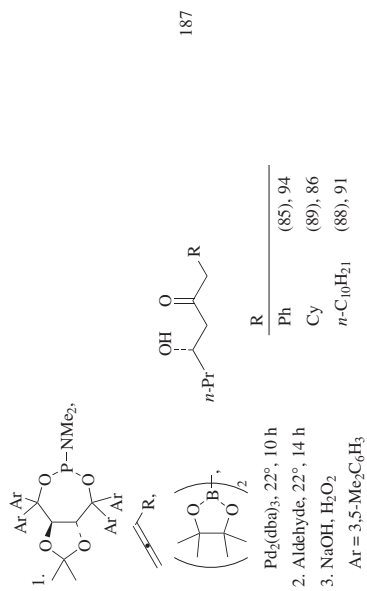
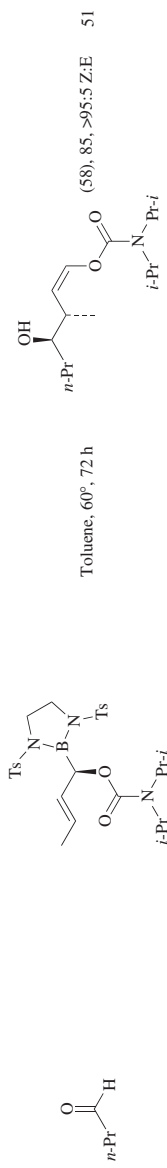


TABLE 4. ADDITION OF  $\alpha$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		1. Cy <sub>2</sub> BH 2. Aldehyde, <i>n</i> -Bu <sub>4</sub> NBr, 0°	 (46), 16:84 E:Z	680
		Neat, 0°, 15 h	 (83), 4:96 E:Z	146, 668, 669
		Neat, 0°, 15 h	 (-), 92, 5:95 E:Z	66
		Neat, 0°, 15 h	 R	146
			R	E:Z
			Ph	(68) 34:66
			CH <sub>3</sub> OMe	(78) 61:39
			OCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> - <i>p</i>	(74) 82:18

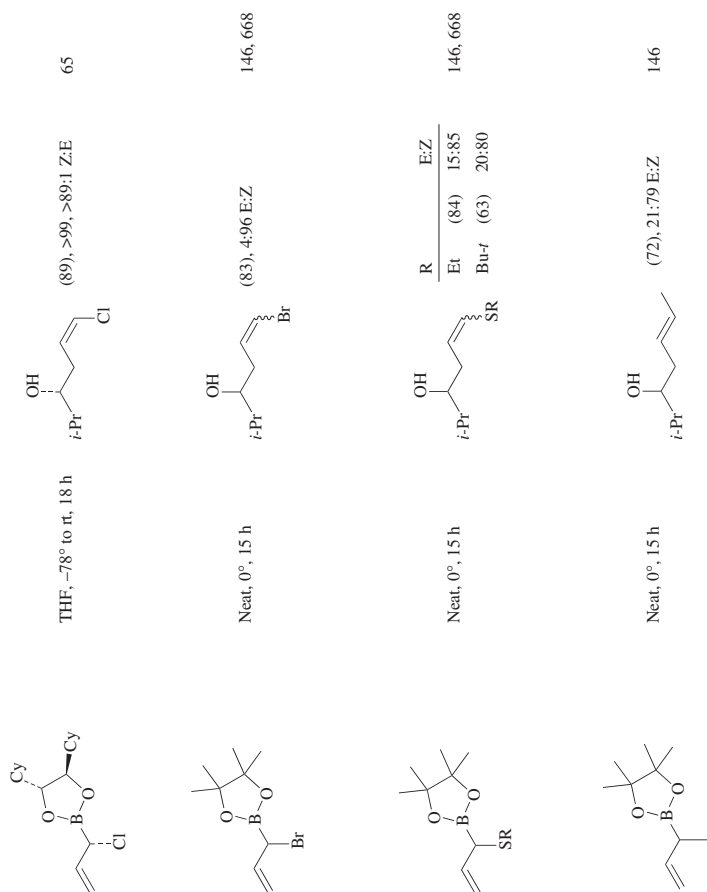
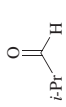
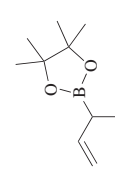
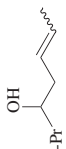
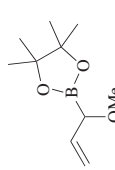
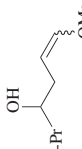
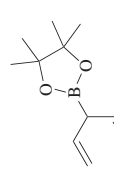

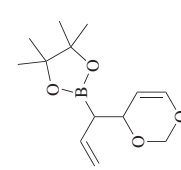
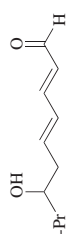


TABLE 4. ADDITION OF  $\alpha$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Ether, $-70^{\circ}$ to rt, 16 h	 (72), 21:79 E:Z	148
		Neat, $0^{\circ}$ , 15 h	 (55), >95:5 Z:E	146, 668
		Neat, $0^{\circ}$ , 15 h	 (94), 60:40 E:Z	146
		1. Toluene, rt, 2 d 2. $I_2$ , $110^{\circ}$	 (90-94)	207, 208

C<sub>4</sub>



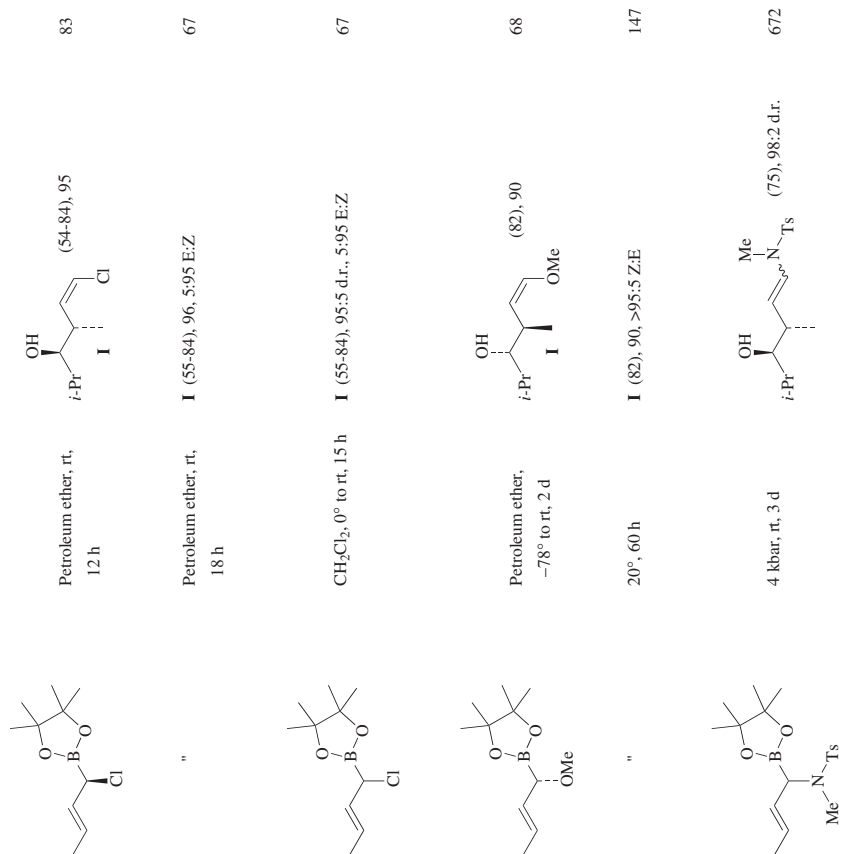


TABLE 4. ADDITION OF  $\alpha$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
$i$ -Pr-CHO		1. 4 kbar, rt, 3 d 2. H <sup>+</sup> , MeOH		672
		Toluene, 60°, 72 h		51
		CH <sub>2</sub> Cl <sub>2</sub> , 0° to rt, 15 h		67
		CH <sub>2</sub> Cl <sub>2</sub> , 0° to rt, 15 h	<b>I</b> (58), 97:3 d.r., 91:6 E:Z	67
		Petroleum ether, rt, 3 d		681
		Neat, rt, 10 h		67

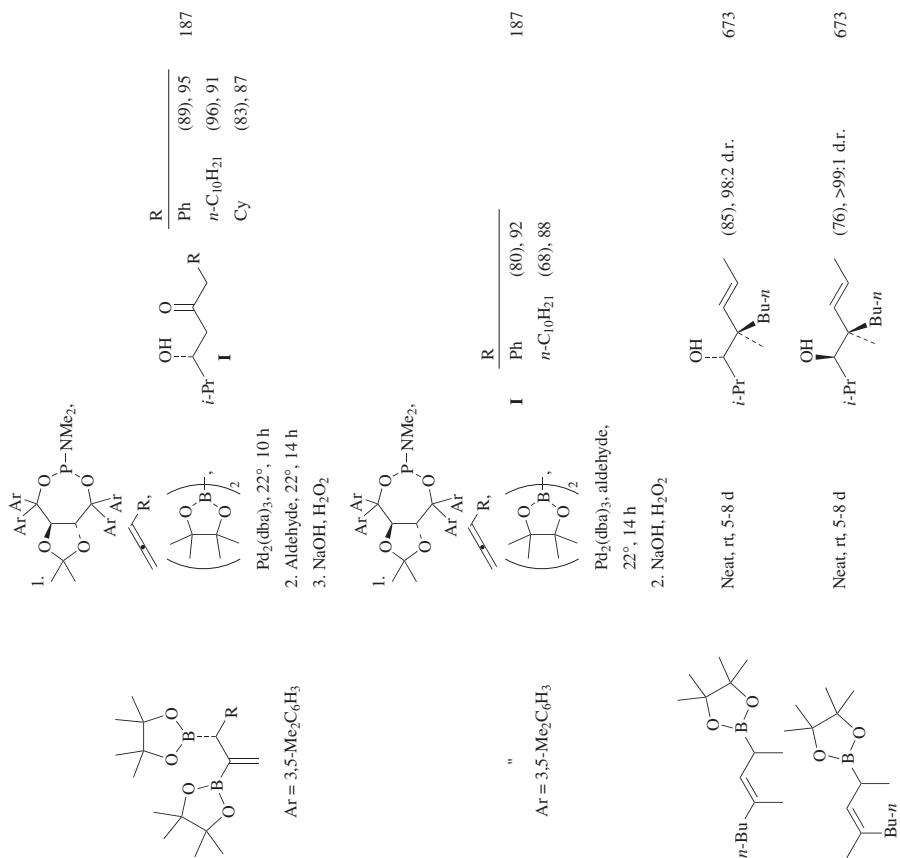


TABLE 4. ADDITION OF  $\alpha$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yields(%) , % ee	Refs.
		THF, -15° to 15°	 (62), 85, 96:4 d.r.	674
		Petroleum ether, 8 kbar, 3 d	 (-), 1:1 d.r., 98:2 E:Z	102
		Petroleum ether, 8 kbar, 3 d	 (-), 72:28 d.r., 29:71 E:Z	102
		Pyr, ether, -78°, 30 min	 (40)	682
		Toluene, 60°, 48 h	 (60), 85, >95:5 Z:E	51
		CH2Cl2, rt, 20 h	 (90), 90:10 d.r.	676

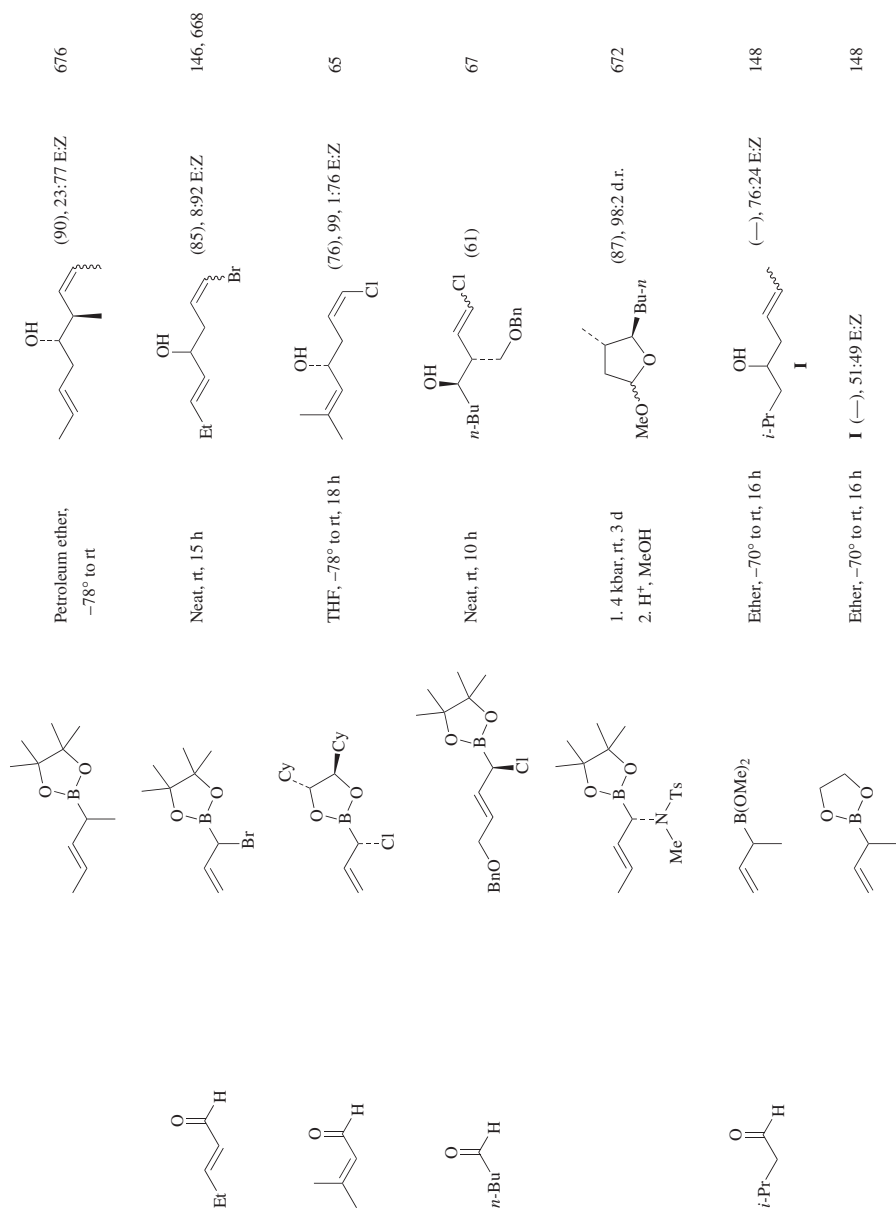
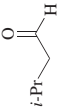
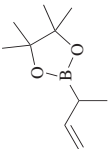
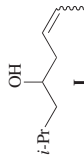
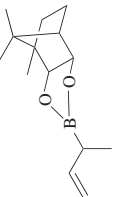
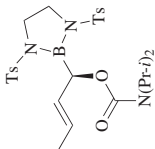
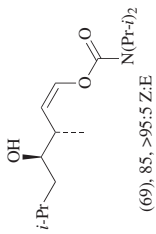

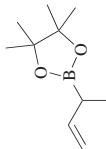

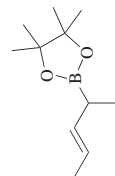
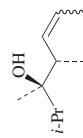
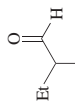
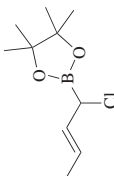
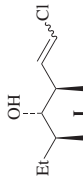


TABLE 4. ADDITION OF  $\alpha$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Ether, $-70^\circ$ to rt, 16 h	 (75), 31:69 E:Z	148
		Ether, $-70^\circ$ to rt, 16 h	<b>I</b> (—), 41:59 E:Z	148
		Toluene, $60^\circ$ , 72 h	 (69), 85, >95:5 Z:E	51
		Petroleum ether, 8 kbar, 3 d	 (—), 49:51 d.r., 98:2 E:Z	102
		Petroleum ether, 8 kbar, 3 d	 (—), >99:1 d.r., 25:75 E:Z	102
		Petroleum ether, $0^\circ$ to rt, 12 h	 (—), 80:20 d.r.	149

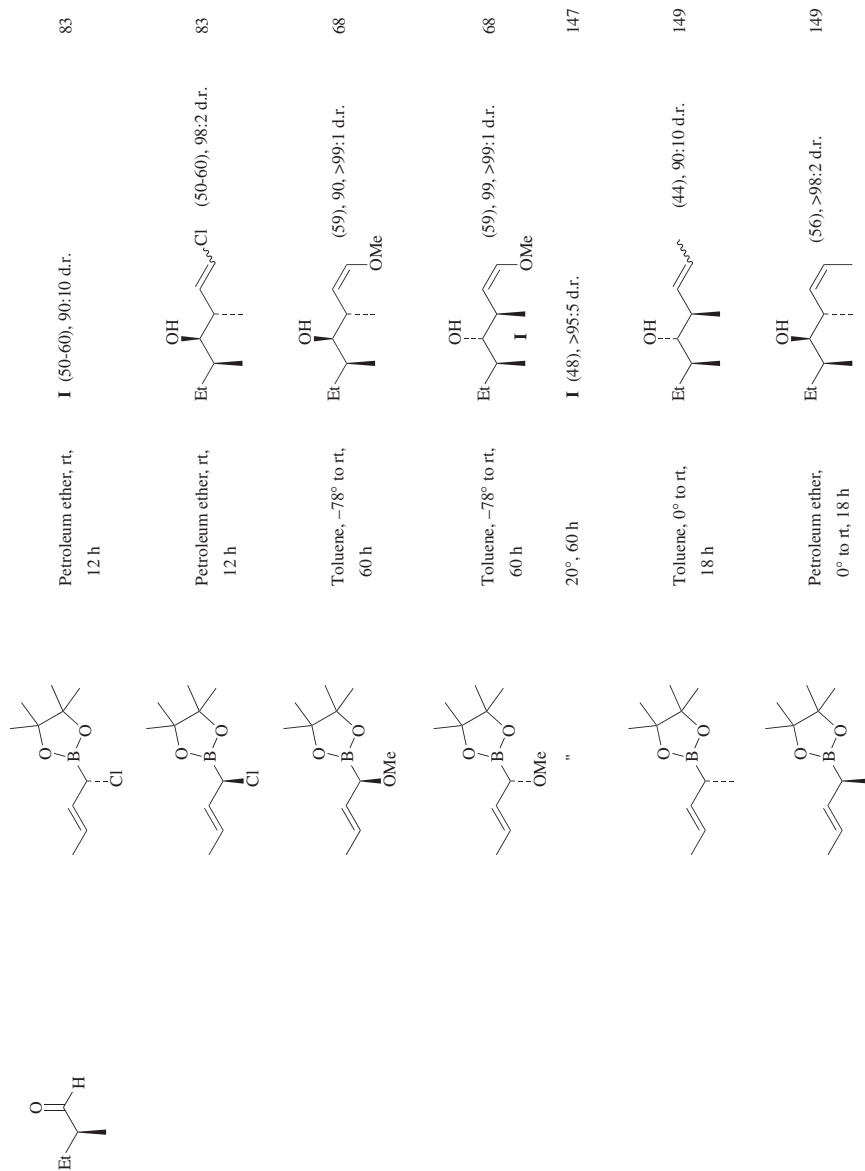


TABLE 4. ADDITION OF  $\alpha$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		—	 I (92), >99:1 d.r., >95:5 Z:E (93), >98:2 d.r., >95:5 Z:E	683
		—	I (92), >99:1 d.r., >95:5 Z:E	683
		Petroleum ether, rt, 3 d	 I (81), 99	681
		—	 I  II  III  IV	684
			Work-Up	
	R <sup>1</sup>	R <sup>2</sup>	I + II + III + IV	E:III:IV
	Me	BBN	NaOH (77)	94:1:4:1
	Me	BBN	H <sub>2</sub> SO <sub>4</sub> (80)	1:90:3:6
	Me	BCy <sub>2</sub>	NaOH (78)	0:0:98:2
	Me	BCy <sub>2</sub>	H <sub>2</sub> SO <sub>4</sub> (70)	0:0:8:92
	<i>n</i> -Bu	BBN	NaOH (68)	97:1:2:0
	<i>n</i> -Bu	BBN	H <sub>2</sub> SO <sub>4</sub> (65)	1:93:2:4
	<i>n</i> -Bu	BCy <sub>2</sub>	NaOH (77)	0:0:97:3
	<i>n</i> -Bu	BCy <sub>2</sub>	H <sub>2</sub> SO <sub>4</sub> (73)	0:0:9:91



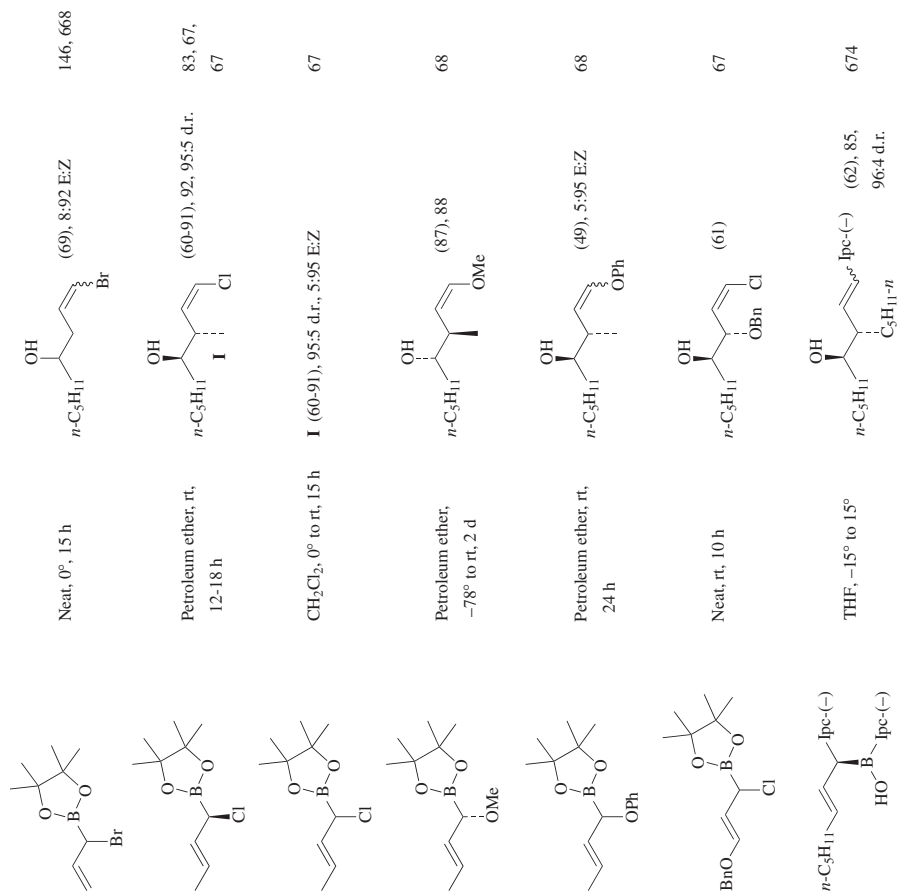

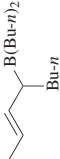
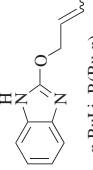
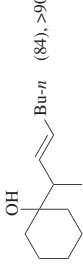

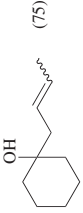



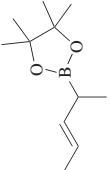
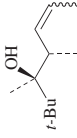

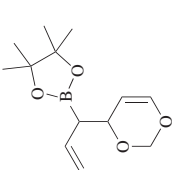
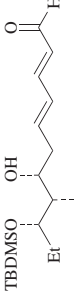

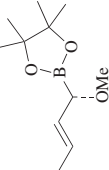
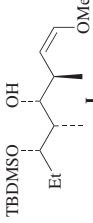


TABLE 4. ADDITION OF  $\alpha$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		 <i>n</i> -BuLi, B(Bu- <i>n</i> ) <sub>3</sub> , THF, -100°	 (84), >90:10 E:Z	685
		Ether, rt	 (75)	31
		Ether, rt	 (80)	31
		Petroleum ether, 8 kbar, 3 d	 (-), >99:1 d.r., 25:75 E:Z	102
		1. Toluene, rt, 2 d 2. I <sub>2</sub> , 110°	 (93), 6:1 d.r.	207
		4 kbar, 60°, 12 h	 (66), 88:12 d.r.	147
	"	Toluene, rt	<b>I</b> (66), >99:1 d.r.	68

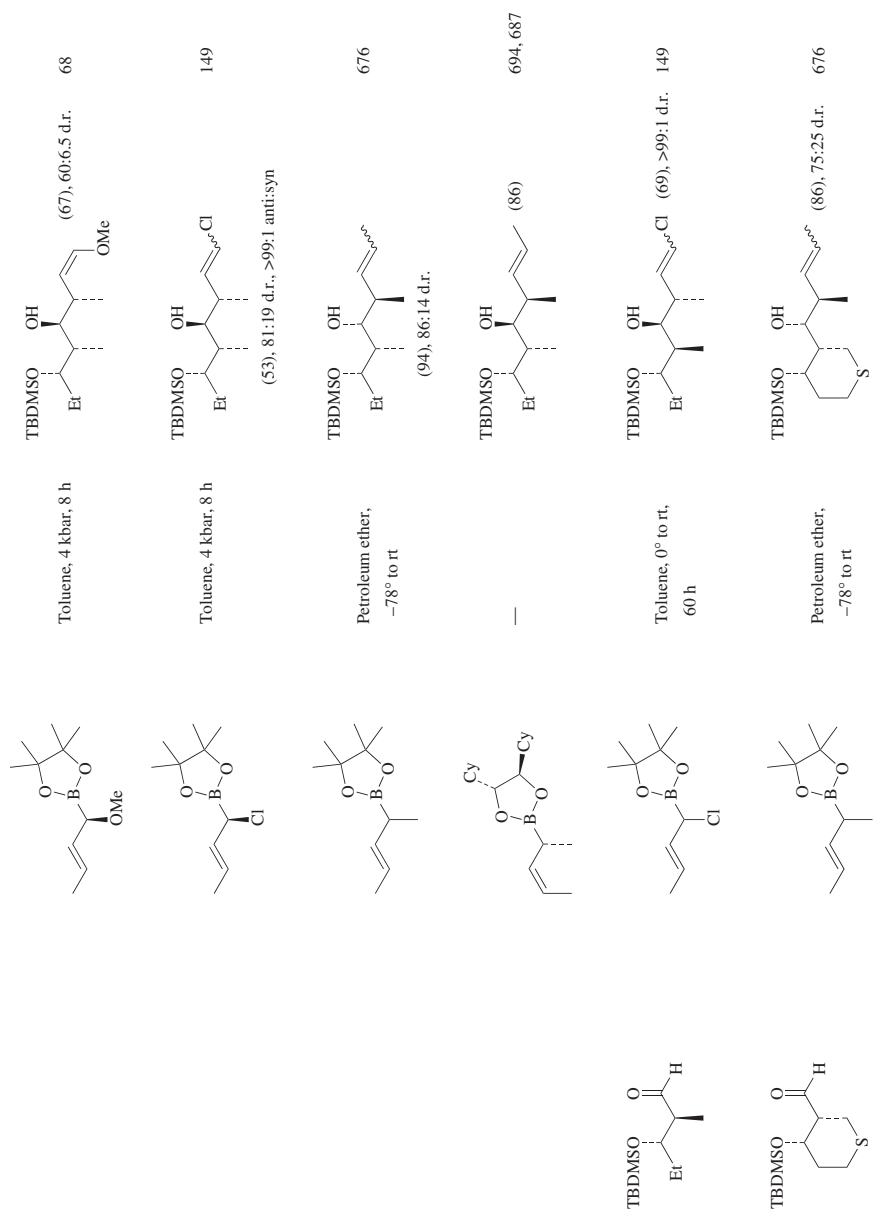
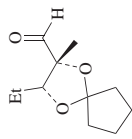
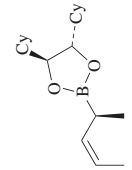
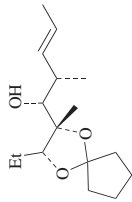

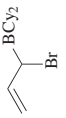

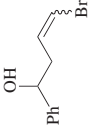
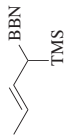
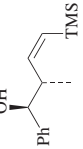
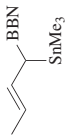
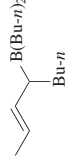
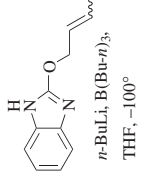
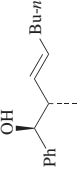


TABLE 4. ADDITION OF  $\alpha$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.																				
		Benzene, 80°, 3 d	 (81), >96:4 d.r.	688, 681																				
		1.  Cy <sub>2</sub> BH 2. Aldehyde, <i>n</i> -Bu <sub>4</sub> NBr, 0°	 (56), 15:85 E:Z	680																				
		Base, ether, -78°, 30 min		682																				
		Base, ether, -78°, 30 min	<table border="1"> <thead> <tr> <th>Base</th> <th>Equiv</th> <th>d.r.</th> <th>Z:E</th> </tr> </thead> <tbody> <tr> <td>pyr</td> <td>1</td> <td>(75)</td> <td>88:5</td> </tr> <tr> <td>pyr</td> <td>2</td> <td>(90)</td> <td>&gt;92:1</td> </tr> <tr> <td><i>n</i>-BuLi</td> <td>1</td> <td>(50)</td> <td>&gt;98:2</td> </tr> <tr> <td><i>s</i>-BuLi</td> <td>1</td> <td>(56)</td> <td>&gt;98:2</td> </tr> </tbody> </table>	Base	Equiv	d.r.	Z:E	pyr	1	(75)	88:5	pyr	2	(90)	>92:1	<i>n</i> -BuLi	1	(50)	>98:2	<i>s</i> -BuLi	1	(56)	>98:2	682
Base	Equiv	d.r.	Z:E																					
pyr	1	(75)	88:5																					
pyr	2	(90)	>92:1																					
<i>n</i> -BuLi	1	(50)	>98:2																					
<i>s</i> -BuLi	1	(56)	>98:2																					
		 <i>n</i> -BuLi, B(Bu- <i>n</i> ) <sub>3</sub> , THF, -100°	 (84), >95:5 d.r., >90:10 E:Z	685																				

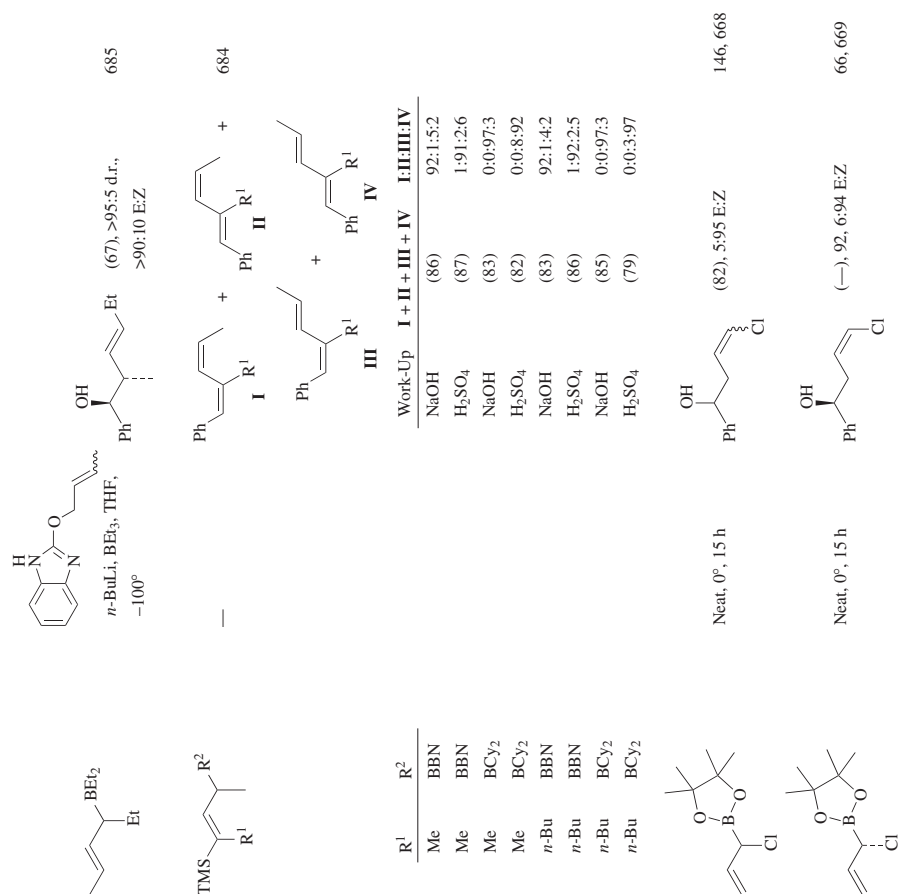


TABLE 4. ADDITION OF  $\alpha$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		THF, -78° to rt, 18 h	 (79), >99, >79:1 Z:E	65
		Ether, rt, 24 h	 >14:1 d.r.	R Pr-i CH <sub>2</sub> CH <sub>2</sub> Ph (88), 92 (92), 94 175
		Ether, rt, 24 h	 >20:1 d.r.	R Ph Cy (65), 95 (83), 92 CH <sub>2</sub> CH <sub>2</sub> Ph (83), 92 175
		Neat, rt, 15 h	 (80), 3:97 E:Z	146, 668
		Neat, 0°, 15 h	 (89), 12:88 E:Z	146

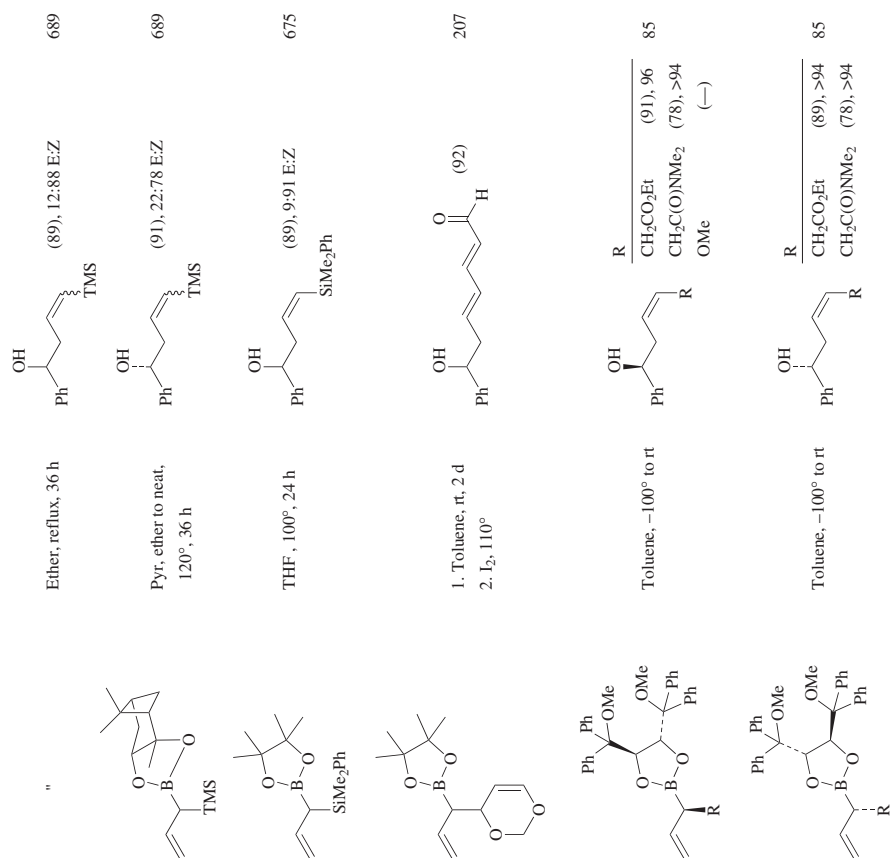

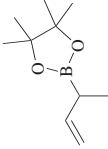
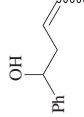
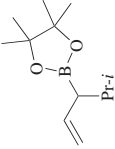
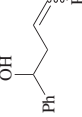
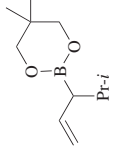
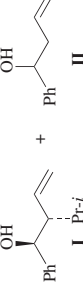
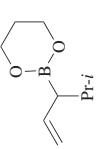
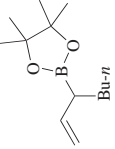
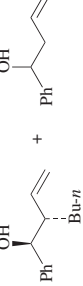


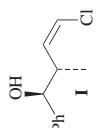
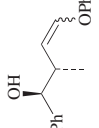
TABLE 4. ADDITION OF  $\alpha$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Ether, $-70^{\circ}$ to rt, 16 h	 (73), 23:77 E:Z	148
		1. $i$ -PrMgCl, THF, $-15^{\circ}$ , 45 min 2. Aldehyde, rt, 24 h	 (55), 30:70 E:Z	87
		1. $i$ -PrMgCl, THF, $-15^{\circ}$ , 15 min 2. Aldehyde, rt, 24 h	 (52), 30:70 E:Z	87
		1. $i$ -PrMgCl, THF, $-78^{\circ}$ to rt 2. Aldehyde, 24 h	<b>I</b> (13), >99:1 d.r. + <b>II</b> (32), 30:70 E:Z	87
		1. $n$ -BuMgCl, THF, $-15^{\circ}$ , 45 min 2. Aldehyde, rt, 24 h	 (59), 20:80 E:Z	87



R	Catalyst	Additive	Temp	Time	E:Z
Et	—	4 Å MS	0°	15 h	(75) 2:1
Et	Sc(OTf) <sub>3</sub>	4 Å MS	-78°	40 h	(63) 1:1.3
Et	TfOH	4 Å MS	-78°	40 h	(99) 1:1.7
Br	—	4 Å MS	0°	15 h	(75) 13:1
Br	Sc(OTf) <sub>3</sub>	4 Å MS	-78°	40 h	(50) 10:1
Br	TfOH	4 Å MS	-78°	40 h	(24) 9:1
TMS	—	—	0°	15 h	(46) 1:6.7
TMS	Sc(OTf) <sub>3</sub>	—	-78°	40 h	(40) 4:1
TMS	TfOH	—	-78°	40 h	(43) 3:1
SiMe <sub>2</sub> Ph	—	—	0°	15 h	(22) 1:6.2
SiMe <sub>2</sub> Ph	Sc(OTf) <sub>3</sub>	—	-78°	40 h	(11) 4:1
SiMe <sub>2</sub> Ph	TfOH	—	-78°	40 h	(26) 4:1

Petroleum ether, rt, 12-18 h		(53-73), 96-98, 95:5 d.r.	83, 67
CH <sub>2</sub> Cl <sub>2</sub> , 0° to rt, 15 h	<b>I</b>	(53-73), 95:5 d.r., 5:95 E:Z	67
Petroleum ether, rt, 24 h		(63), 5:95 E:Z	68

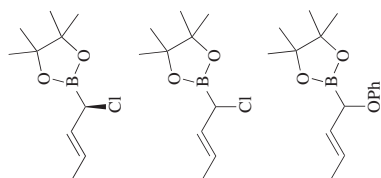
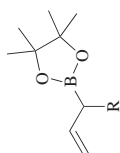

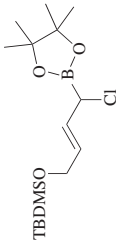
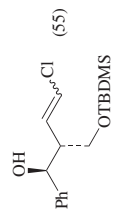
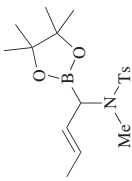
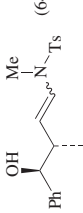
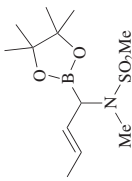
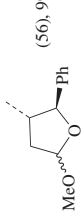
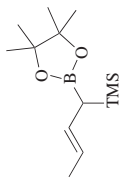

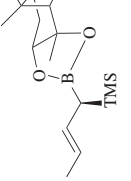
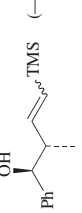
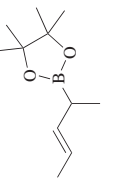
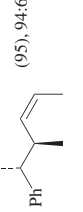


TABLE 4. ADDITION OF  $\alpha$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Neat, rt, 10 h	 (55)	67
		4 kbar, rt, 3 d	 (64), 99:1 d.r.	672
		1. 4 kbar, rt, 3 d 2. H <sup>+</sup> , MeOH	 (56), 99:1 d.r.	672
		Ether to neat, 125°, 16 h	 (–), 90:10 E:Z	689
		Pyr, ether to neat, 120°, 36 h	 (–), 96:4 E:Z	689
		CH <sub>2</sub> Cl <sub>2</sub> , rt, 20 h	 (95), 94:6 d.r.	676

C<sub>7</sub>

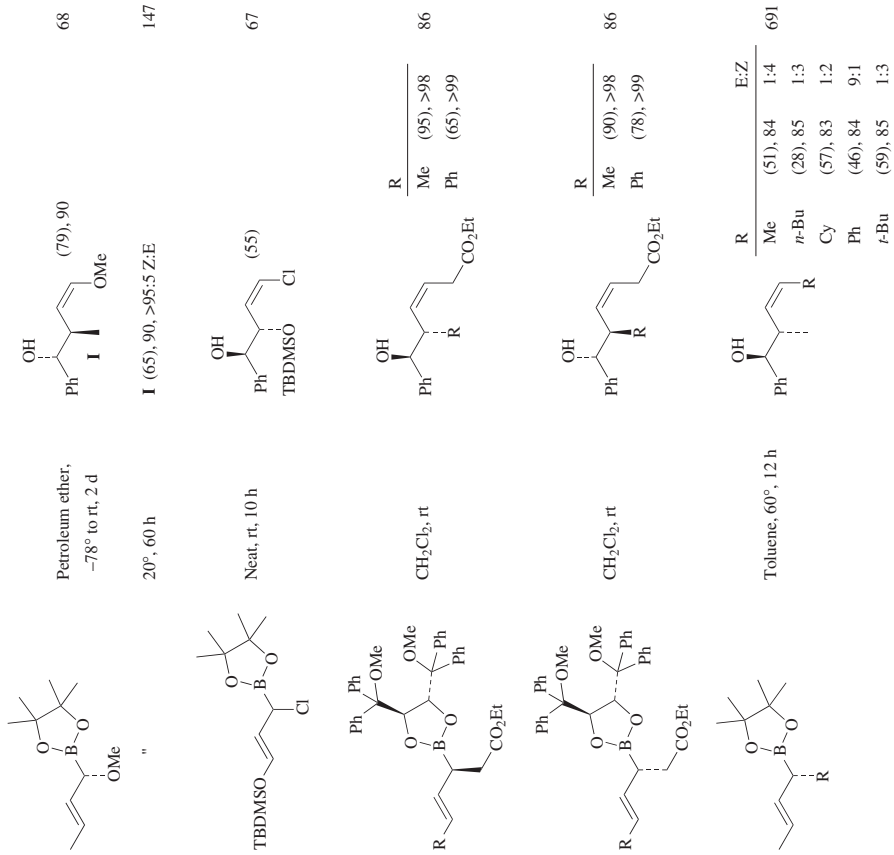

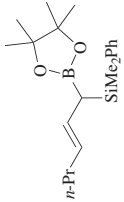
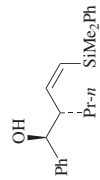
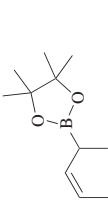
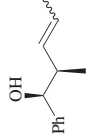
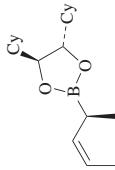
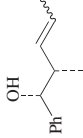
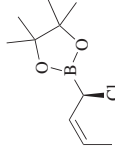
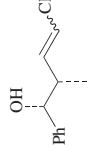
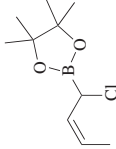
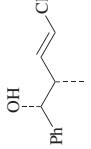
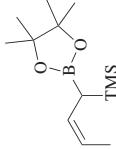
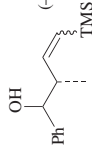


TABLE 4. ADDITION OF  $\alpha$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		—	 (89), 9:91 E:Z	675
		Petroleum ether, -78° to rt	 (95), 94:6 d.r.	676
		Petroleum ether, 12 h	 (71), 99	64, 63
		CH <sub>2</sub> Cl <sub>2</sub> , 0° to rt, 15 h	 (56), 97, 96:4 d.r.	67
		CH <sub>2</sub> Cl <sub>2</sub> , 0° to rt, 15 h	 (56), 96:4 d.r., 93:3 E:Z	67
		Ether to neat, 125°, 16 h	 (—), 13:87 E:Z	689

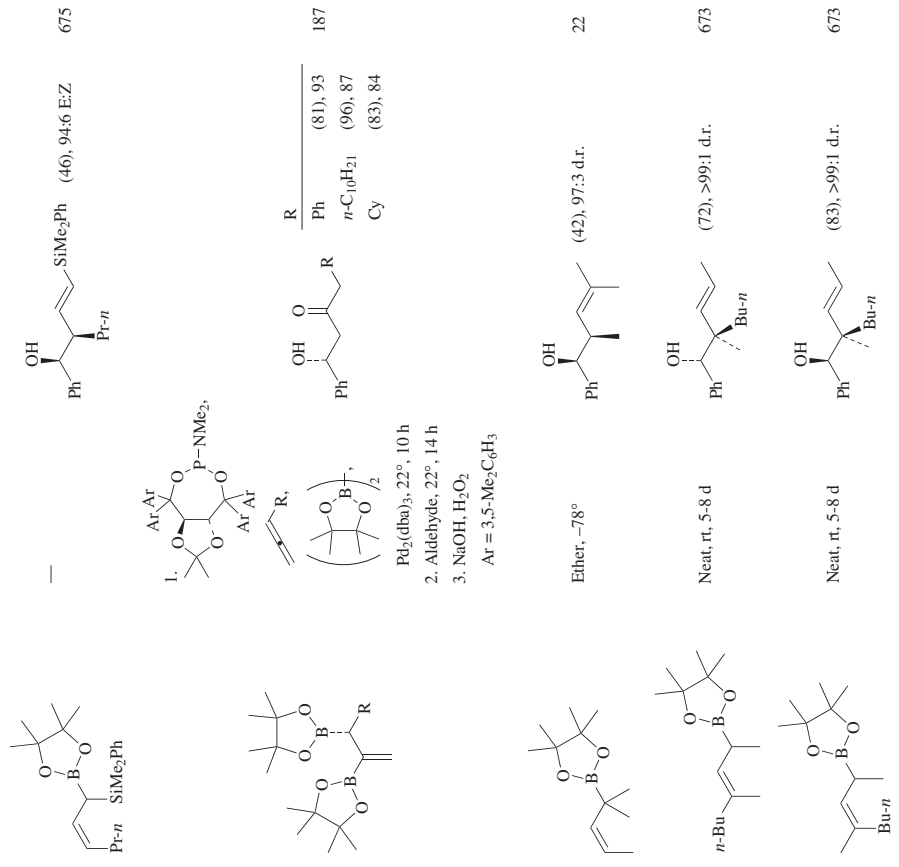

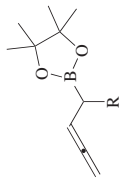
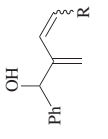
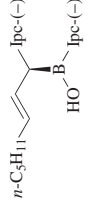
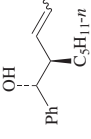
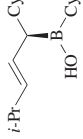
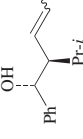
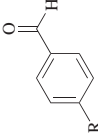
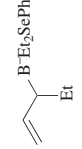
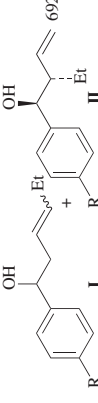


TABLE 4. ADDITION OF  $\alpha$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.																
		$\text{CH}_2\text{Cl}_2$ , rt, 18 h		E:Z (86) 6:94 677 (82) 5:95 (72) 6:94 (77) 5:95 (65) 5:95 (88) 4:96																
		THF, $-15^\circ$ to $5^\circ$		(72), 79, 98:2 d.r. 674																
		THF, $-15^\circ$ to $5^\circ$		(70), 60, 99:1 d.r. 674																
		1. PhSeCH=CH <sub>2</sub> , LDA, THF, $-78^\circ$ , 30 min 2. Et <sub>3</sub> B, $-78^\circ$ to $0^\circ$ , 1 h		692																
			<table border="1"> <thead> <tr> <th>R</th> <th>I + II</th> <th>I:II</th> <th>E:Z</th> </tr> </thead> <tbody> <tr> <td>H (88)</td> <td>94:6</td> <td>86:14</td> <td></td> </tr> <tr> <td>MeO (80)</td> <td>71:29</td> <td>—</td> <td></td> </tr> <tr> <td>O<sub>2</sub>N (65)</td> <td>77:23</td> <td>—</td> <td></td> </tr> </tbody> </table>	R	I + II	I:II	E:Z	H (88)	94:6	86:14		MeO (80)	71:29	—		O <sub>2</sub> N (65)	77:23	—		
R	I + II	I:II	E:Z																	
H (88)	94:6	86:14																		
MeO (80)	71:29	—																		
O <sub>2</sub> N (65)	77:23	—																		

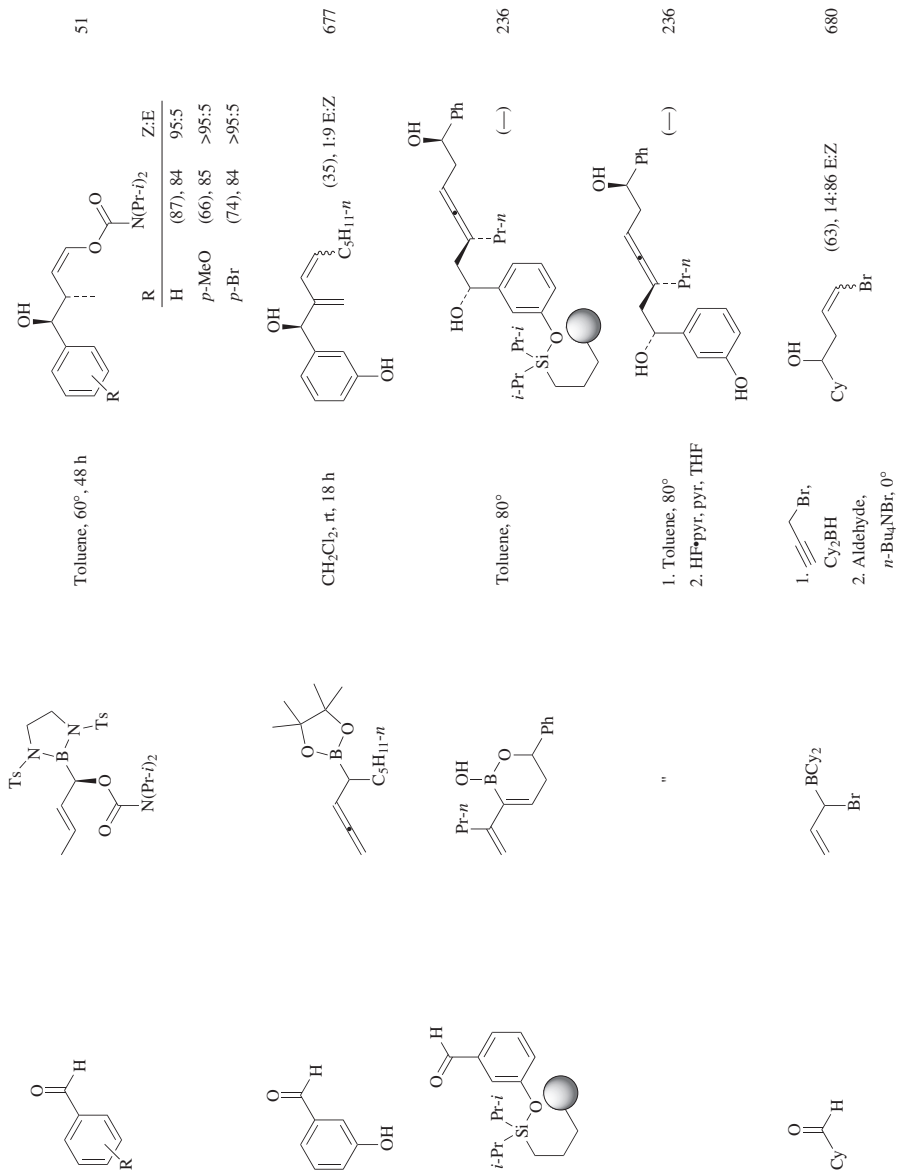

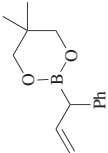
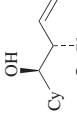
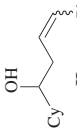
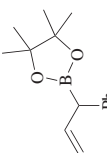


TABLE 4. ADDITION OF  $\alpha$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yields (%), % ee	Refs.															
 C <sub>7</sub>		1. Cl-CH <sub>2</sub> -CH=CH <sub>2</sub> , THF, -78° to rt 2. Aldehyde, 24 h	 <b>I</b> (9), >99:1 d.r.  <b>II</b> (39), 2:98 E:Z	87															
		1. Cl-CH <sub>2</sub> -CH=CH <sub>2</sub> , THF, -15°, time 1 2. Aldehyde, rt, 24 h	<table border="1"> <thead> <tr> <th>Time</th> <th><b>I</b></th> <th>d.r.</th> <th><b>II</b></th> <th>E:Z</th> </tr> </thead> <tbody> <tr> <td>15 min</td> <td>(17)</td> <td>98:2</td> <td>(41)</td> <td>2:98</td> </tr> <tr> <td>30 min</td> <td>(34)</td> <td>&gt;99:1</td> <td>(15)</td> <td>98:2</td> </tr> </tbody> </table>	Time	<b>I</b>	d.r.	<b>II</b>	E:Z	15 min	(17)	98:2	(41)	2:98	30 min	(34)	>99:1	(15)	98:2	87
		Time	<b>I</b>	d.r.	<b>II</b>	E:Z													
		15 min	(17)	98:2	(41)	2:98													
30 min	(34)	>99:1	(15)	98:2															
1. Cl-CH <sub>2</sub> -CH=CH <sub>2</sub> , THF, -78° to rt 2. Aldehyde, 24 h	<b>I</b> (8), >99:1 d.r. + <b>II</b> (32), 98:2 E:Z	87																	
1. Cl-CH <sub>2</sub> -CH=CH <sub>2</sub> , THF, -15°, 45 min 2. Aldehyde, rt, 24 h	<b>I</b> (21), >99:1 d.r. + <b>II</b> (21), 2:98 E:Z	87																	
		1. Cl-CH <sub>2</sub> -CH=CH <sub>2</sub> , THF, -15°, 30 min 2. Aldehyde, rt, 24 h	<b>II</b> (60), 2:98 E:Z	87															



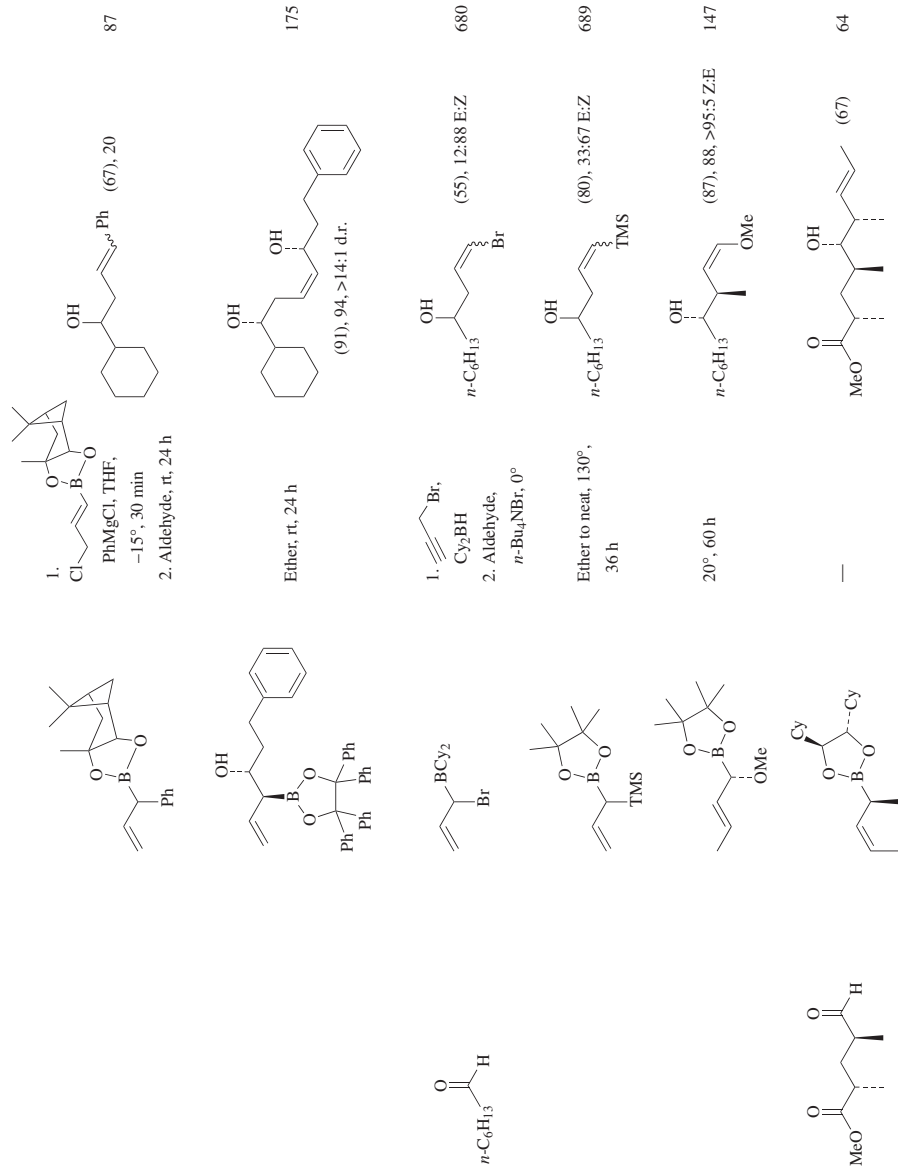


TABLE 4. ADDITION OF  $\alpha$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		rt, 7 d	 (80), 97.5:2.5 d.r.	693
		1. PhSe-CH=CH <sub>2</sub> , LDA, THF, -78°, 30 min 2. Et <sub>3</sub> B, -78° to 0°, 1 h	 I + II (90), EII > 99:1	692
		CH <sub>2</sub> Cl <sub>2</sub> , rt, 18 h	 (87), 5:95 E:Z	677
		Toluene, 60°, 48 h	 (69), 85, >95:5 Z:E	51
		 <i>n</i> -BuLi, B(Bu- <i>n</i> ) <sub>3</sub> , THF, -100°	 (75), >95:5 d.r., >90:10 E:Z	685

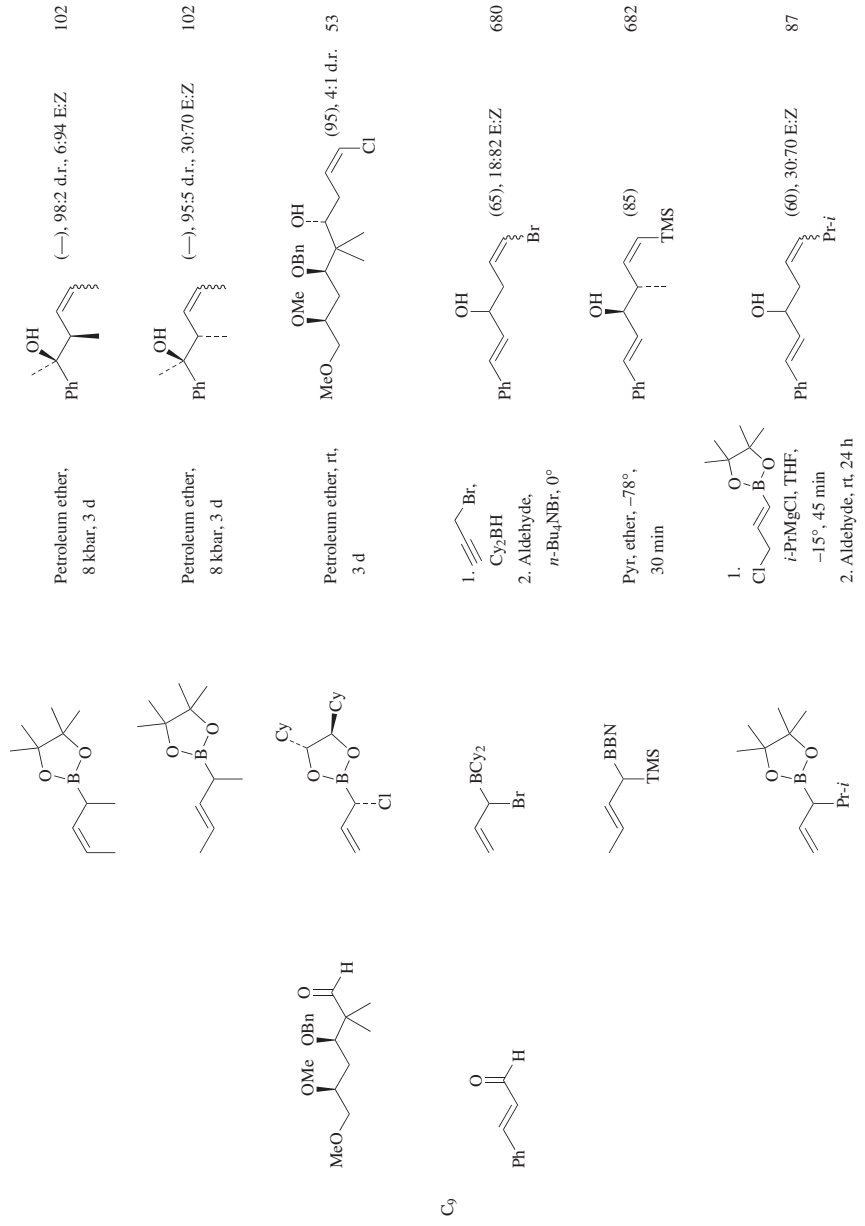


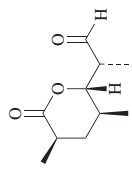
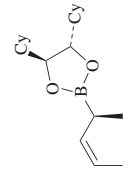
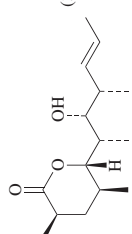
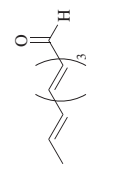
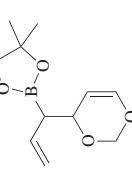
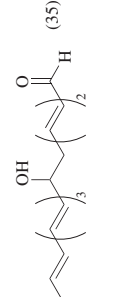
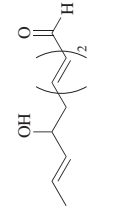
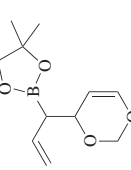
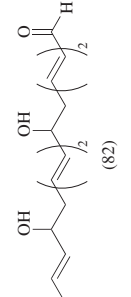
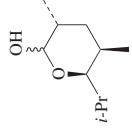
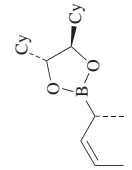
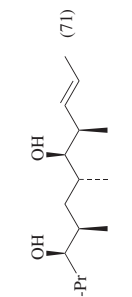
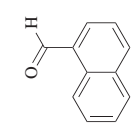
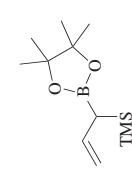
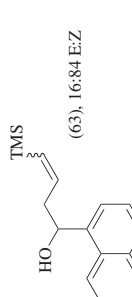
TABLE 4. ADDITION OF  $\alpha$ -SUBSTITUTED REAGENTS (Continued)

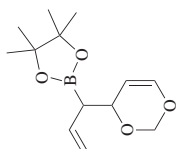
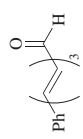
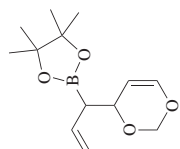
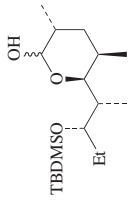
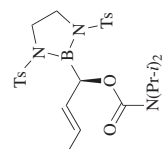
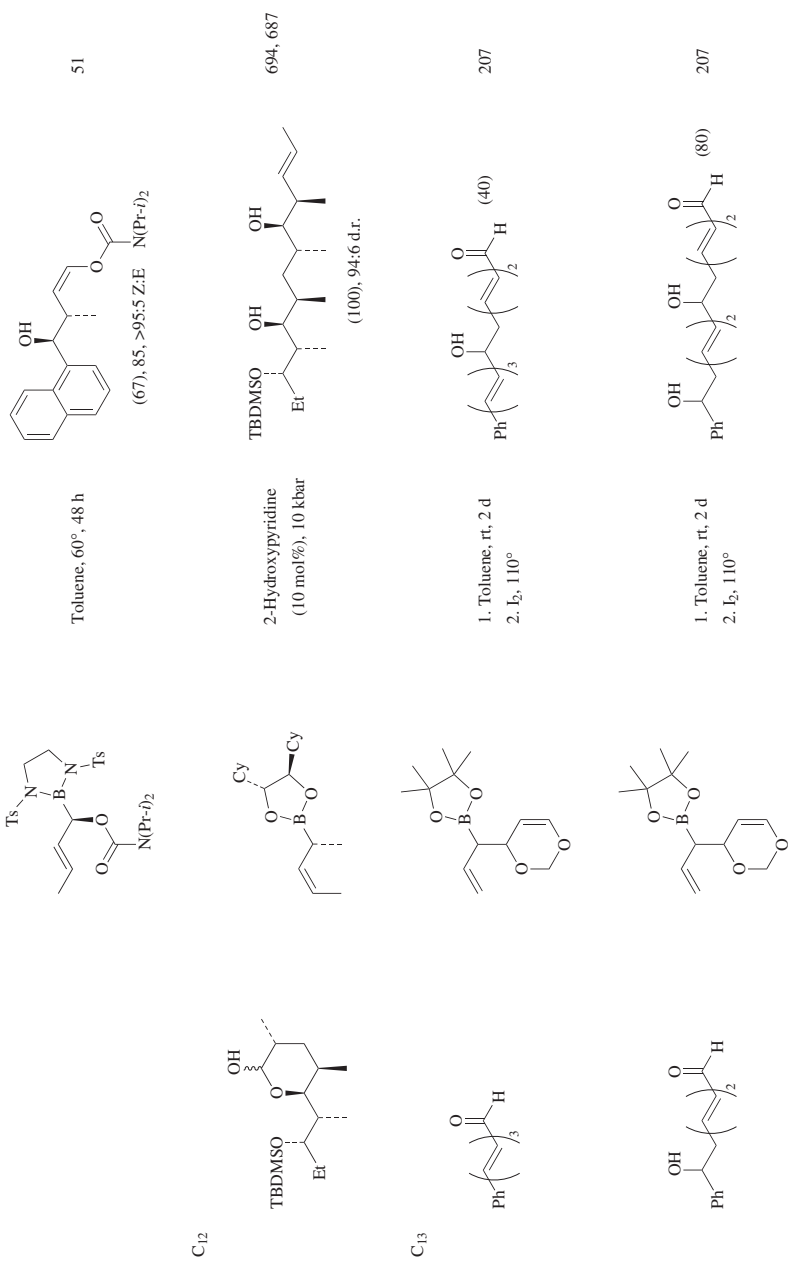
Carbonyl Substrate	Alylborane Reagent	Conditions	Product(s) and Yields( %), % ee	Refs.
		CH <sub>2</sub> Cl <sub>2</sub> , rt, 18 h	 (77), 91:9 Z:E	677
		 <i>n</i> -BuLi, BEt <sub>3</sub> , THF, -100°	 (52), 97:3 d.r., >90:10 E:Z	685
		Ether, rt, 24 h	 R Ph (95), 95 >14:1 <i>i</i> -Pr (95), 95 >14:1 d.r.	175
		Ether, rt, 24 h	 R Ph (87), 91 >20:1 <i>i</i> -Pr (69), 92 50:1 d.r.	175
		CH <sub>2</sub> Cl <sub>2</sub> , rt, 18 h	 (75), 5:95 E:Z	677

C<sub>9</sub>



TABLE 4. ADDITION OF  $\alpha$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yields (%), % ee	Refs.
		4 kbar, 12 h	 (35), 63:27 dr.	693
		1. Toluene, rt, 2 d 2. I <sub>2</sub> , 110°	 (35)	207
		1. Toluene, rt, 2 d 2. I <sub>2</sub> , 110°	 (82)	207
		2-Hydroxypyridine (10 mol%), 10 kbar	 (71)	694, 687
		Ether, reflux, 16 h	 (63), 16:84 E:Z	689



C<sub>12</sub>

C<sub>13</sub>

TABLE 4. ADDITION OF  $\alpha$ -SUBSTITUTED REAGENTS (Continued)

	Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yields(%) <sup>a</sup> , % ee	Refs.
C <sub>13</sub>	 $R = $		$CH_2Cl_2, -78^\circ$ to rt, 48 h	 (55)	202
C <sub>14</sub>			Petroleum ether, rt, 4 d	 (53)	695, 208
C <sub>15</sub>			Petroleum ether, 10 kbar, 3 d	 (79), >95:5 d.r.	688, 696
C <sub>18</sub>			Petroleum ether, 10 kbar, 3 d	 (70), 89:11 d.r.	688, 696



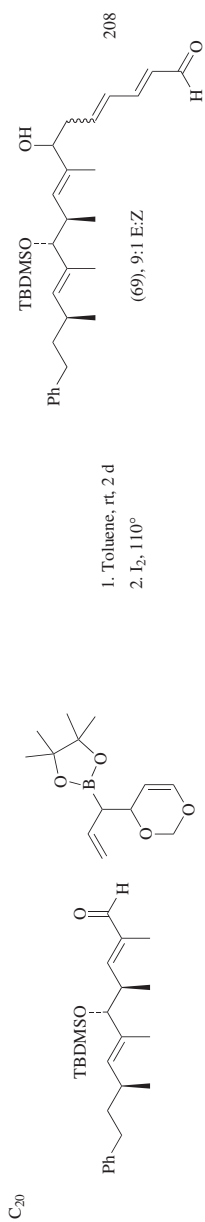











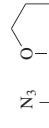

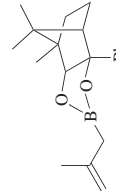



TABLE 5. ADDITION OF  $\beta$ -SUBSTITUTED REAGENTS

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
$C_2$ 		Neat, 0-20°	 (92)	238
		Neat, 0-20°	<b>I</b> (93)	238
		Ether, -78° to rt	 (56), 90	697, 136a
		-70° to rt	 (84)	698
		THF, ether, -78°, 1 h	<b>I</b> (65)	699
		THF, ether, -78°, 1 h	 (65), 90	699, 700
		Ether, 0°, 1 h	 (75)	701
		Hexane, -40°	 (82), 74	122, 244

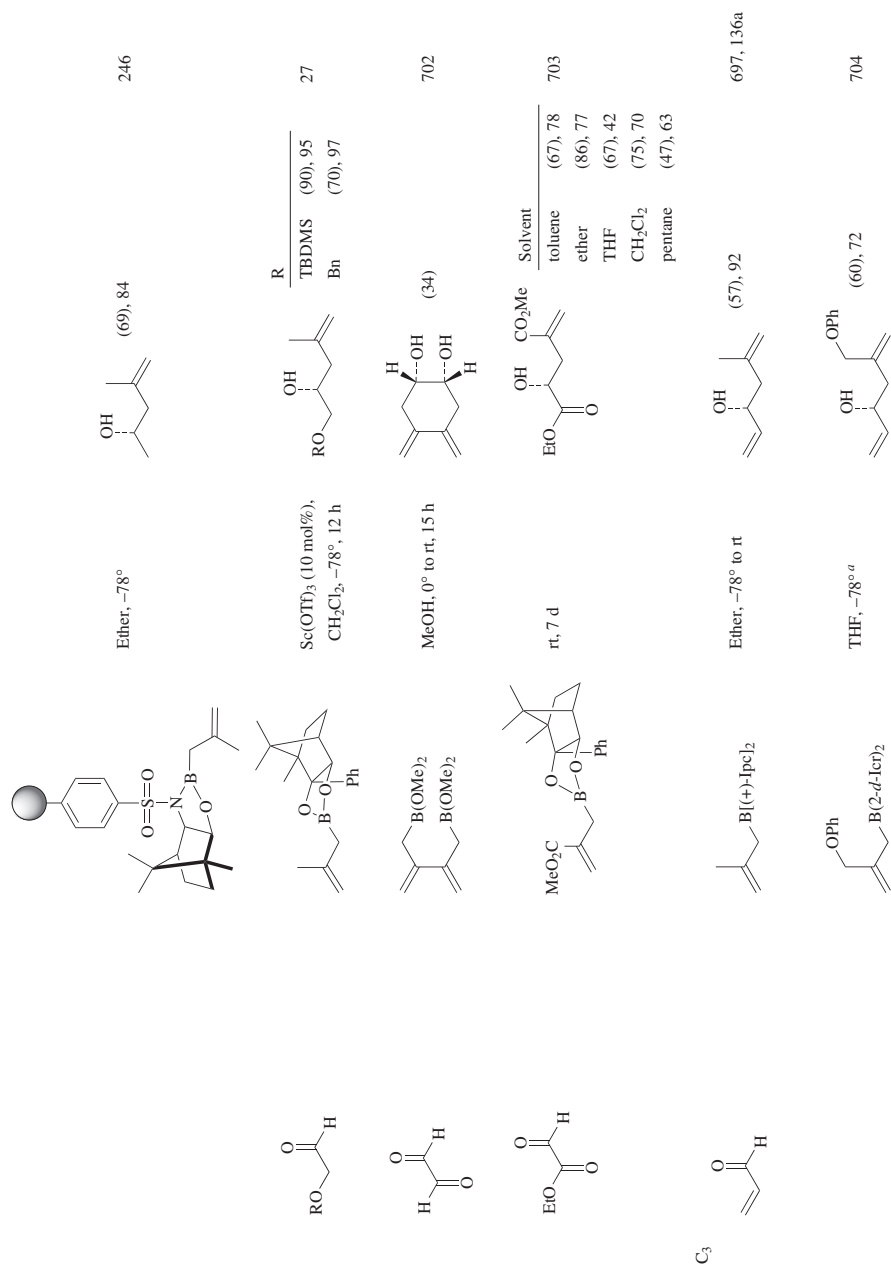
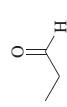
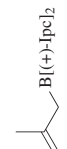
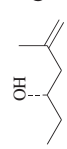

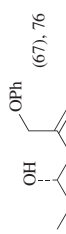
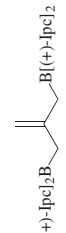
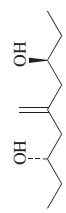
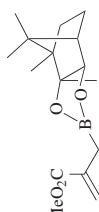
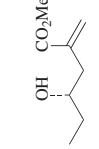
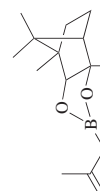
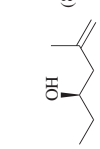


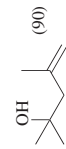
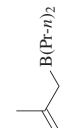



TABLE 5. ADDITION OF  $\beta$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Ether, $-78^{\circ}$ to rt	 (54), 90	697, 136a
		THF, $-78^{\circ a}$	 (67), 76	704
		Ether, $-78^{\circ a}$	 (45), $>95$ , 93;7 d.r.	176, 705
		rt, 7 d	 Solvent: toluene (99), 78; ether (95), 70; pentane (100), 68; neat (99), 67	703
		Hexane, $-40^{\circ}$	 (85), 70	122, 244
		Neat, 0- $20^{\circ}$	 (90)	238
		Neat, 0- $20^{\circ}$	 (94)	238

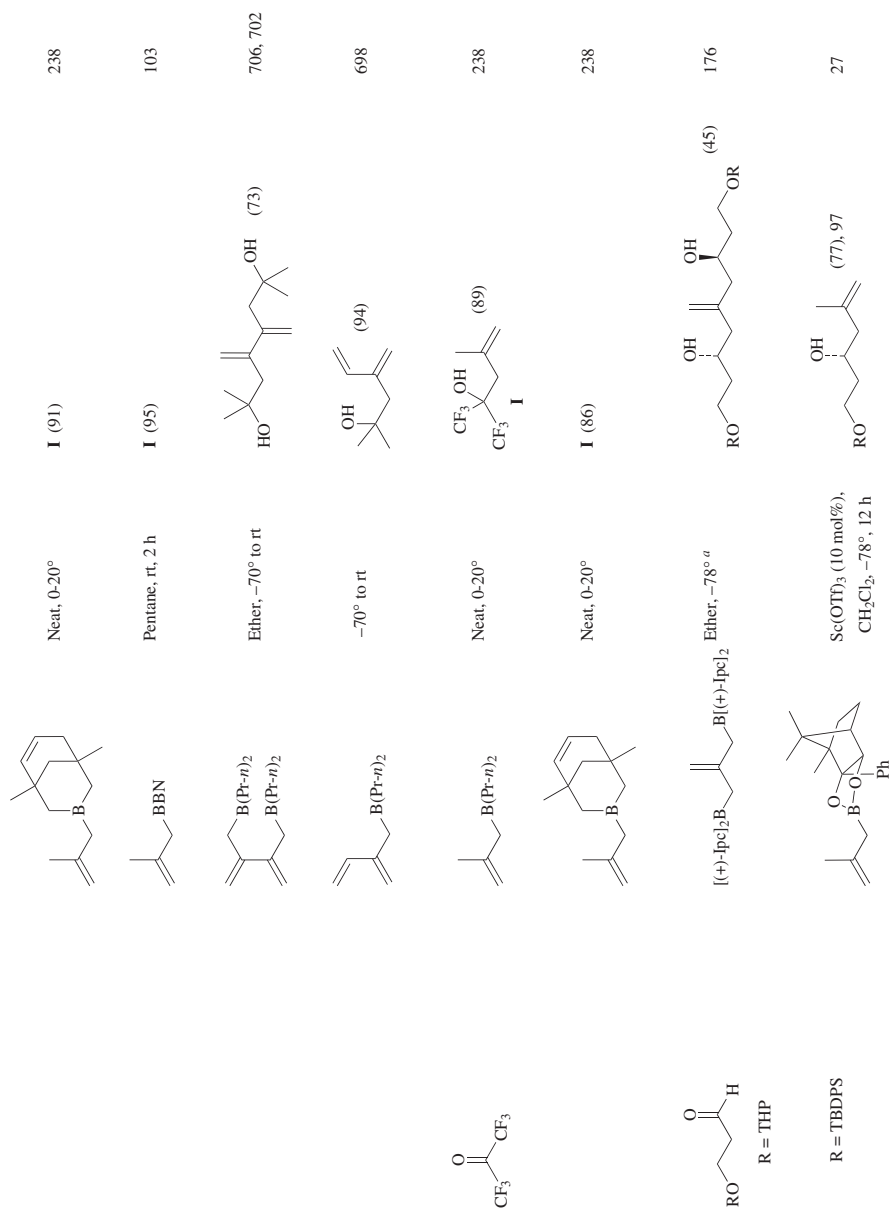
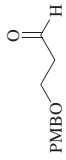
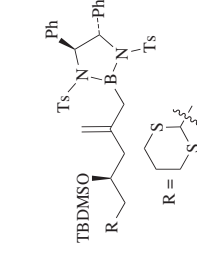
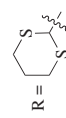
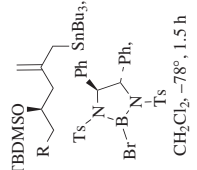
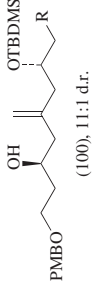
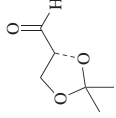

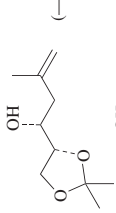


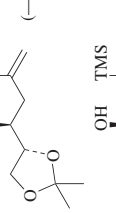

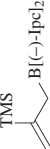
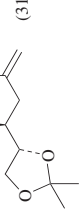


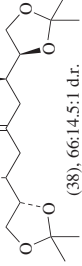

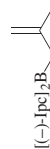
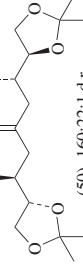


TABLE 5. ADDITION OF  $\beta$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
 PMBO	 R = 	 $\text{CH}_2\text{Cl}_2$ , $-78^\circ$ , 1.5 h	 (100), 11:1 d.r.	191
		Ether, $-78^\circ$	 (—)	571
		Ether, $-78^\circ$	 (—), 97:3 d.r.	571
		THF, $-78^\circ$ , 3 h	 (31), 85:15 d.r.	707
		Ether, $-78^\circ$ <sup>a</sup>	 (38), 66:14.5:1 d.r.	176, 705
		Ether, $-78^\circ$ <sup>a</sup>	 (50), 160:22:1 d.r.	176, 705

C<sub>3</sub>



TABLE 5. ADDITION OF  $\beta$ -SUBSTITUTED REAGENTS (Continued)




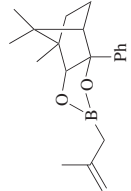
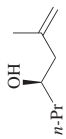

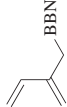
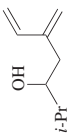
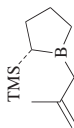
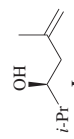
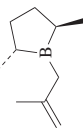

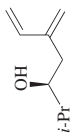

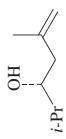

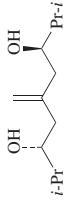
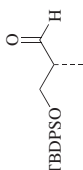
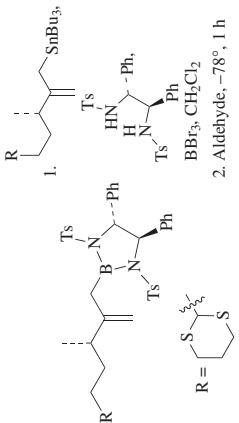
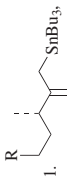
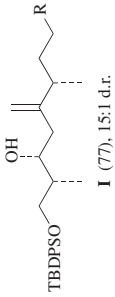
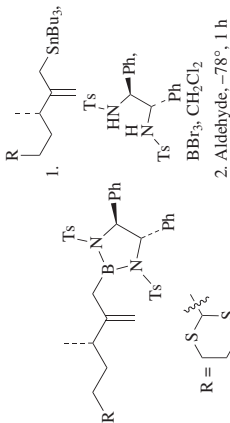
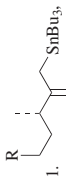

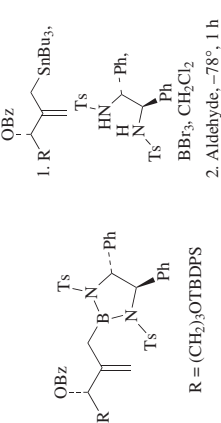
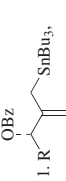
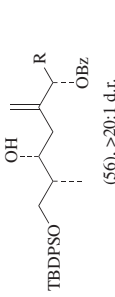
Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
$C_4$ 		Ether, $-78^\circ a$	 (78), 74	704
		Hexane, $-40^\circ$	 (84), 65	122, 244
$i$ -Pr-CHO 		THF, hexane, $-78^\circ$ , 1 h	 (65)	699
		Ether, $-100^\circ$ , 3 h	 I (78), 81	141
		Ether, $-100^\circ$ , 3 h	I (80), 27	141
		THF, hexane, $-78^\circ$ , 1 h	 (65), 92	699
		Ether, $-78^\circ$ to rt	 (57), 96	697, 136a
		Ether, $-78^\circ a$	 (41), >95, 93:7 d.r.	176, 705





TABLE 5. ADDITION OF  $\beta$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
	 1.  2. Aldehyde, $-78^{\circ}$ , 1 h	 <b>I (77)</b> , 15:1 d.r.	708	
	 1.  2. Aldehyde, $-78^{\circ}$ , 1 h	 <b>I (80)</b> , 4:1 d.r.	708	
	 1.  2. Aldehyde, $-78^{\circ}$ , 1 h	 <b>(56)</b> , >20:1 d.r.	708	

C<sub>4</sub>

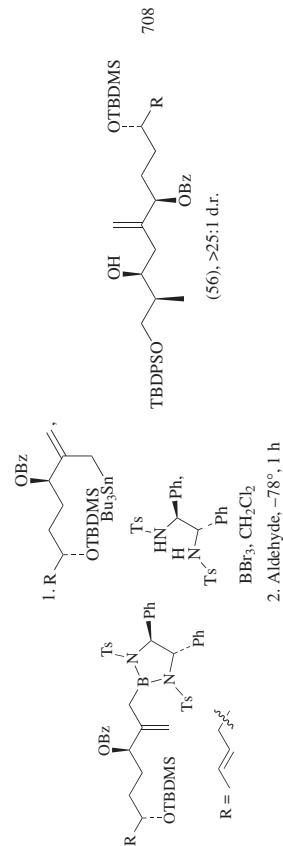
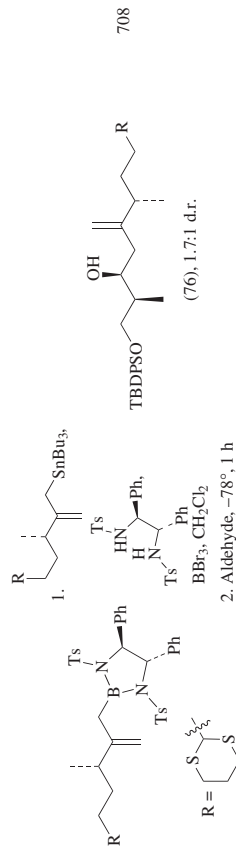
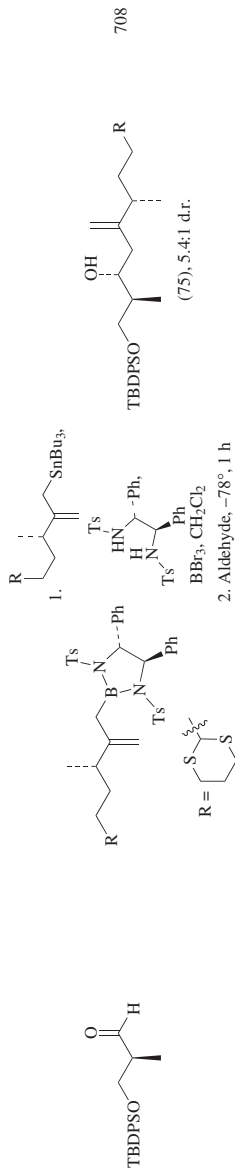


TABLE 5. ADDITION OF  $\beta$ -SUBSTITUTED REAGENTS (Continued)

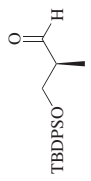
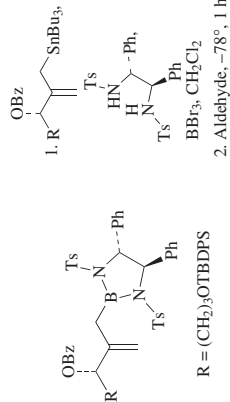
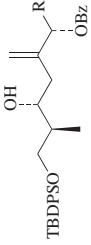
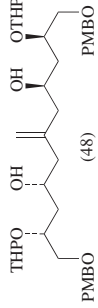

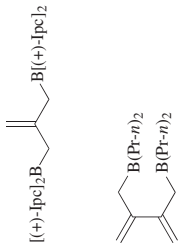
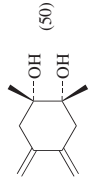
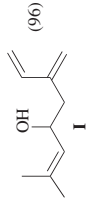

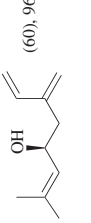
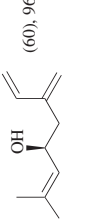

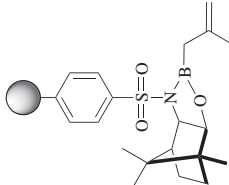
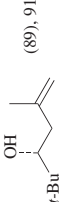
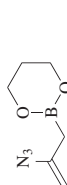
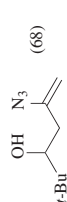
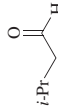

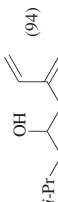


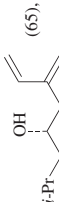

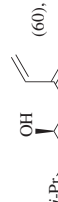
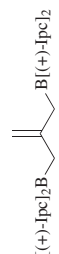
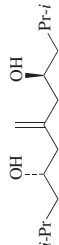
Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
	 R = (CH <sub>2</sub> ) <sub>3</sub> OTBDPS	1. R, OBz, SnBu <sub>3</sub> , Ts 2. Aldehyde, -78°, 1 h	 (83), >20:1 d.r.	708
			 (48)	176
	 (+)-Ipc <sub>12</sub> B	Ether, -78° <sup>a</sup>	 (50)	702
			 (96)	698
			 (60)	699
			 (60), 96	699, 700
			 (60), 96	699, 700



TABLE 5. ADDITION OF  $\beta$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Ether, $-78^\circ$	 (89), 91	246
		Ether, $0^\circ$ , 1 h	 (68)	701
		$-70^\circ$ to $0^\circ$	 (94)	698
		THF, ether, $-78^\circ$ , 1 h	<b>I</b> (65)	699
		THF, ether, $-78^\circ$ , 1 h	 (65), 96	699, 700
		THF, ether, $-78^\circ$ , 1 h	 (60), 94	699, 700
		Ether, $-78^\circ$ <sup>a</sup>	 (53), >95, 93;7 d.r.	176, 705

C<sub>5</sub>

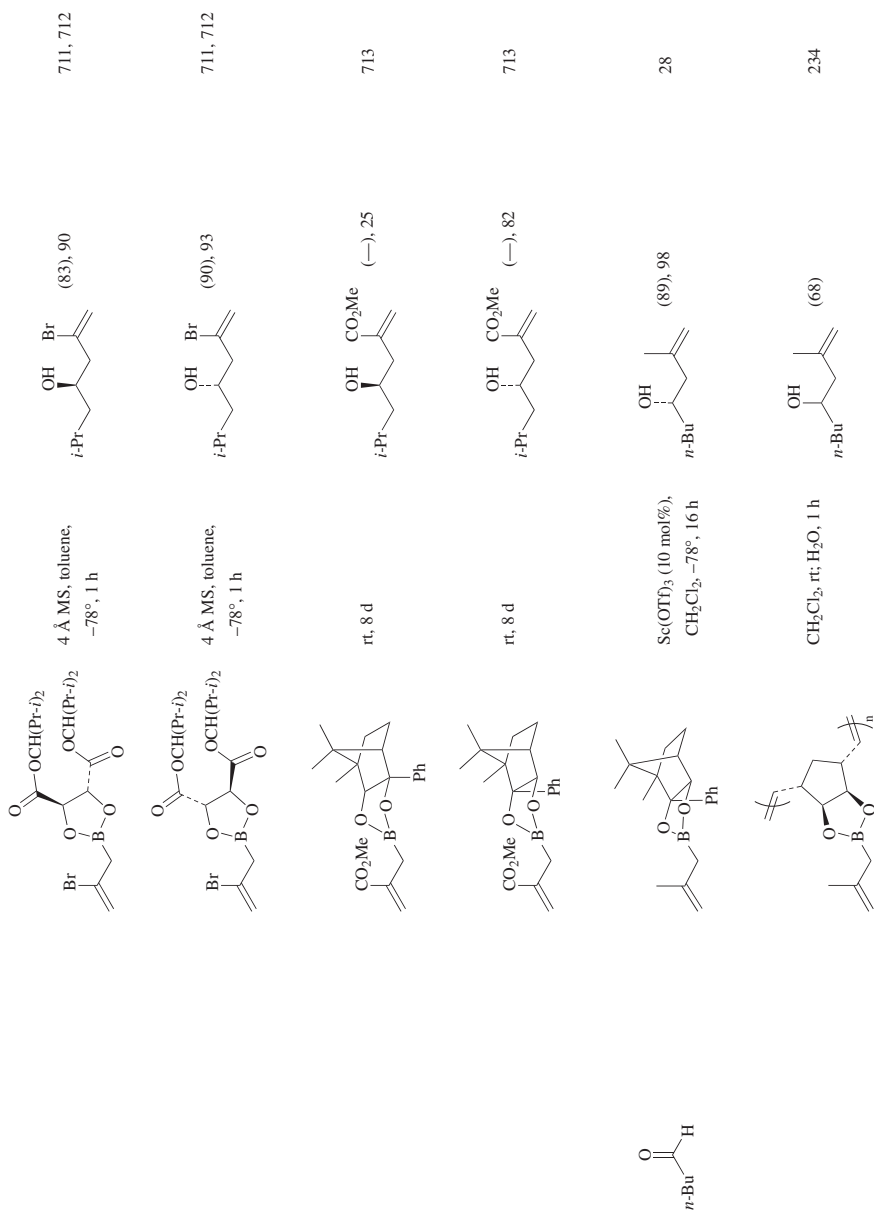


TABLE 5. ADDITION OF  $\beta$ -SUBSTITUTED REAGENTS (Continued)


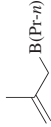
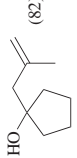
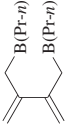
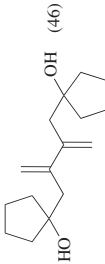
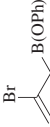
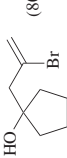
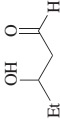

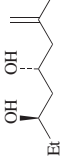
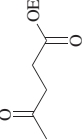
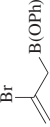
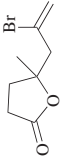

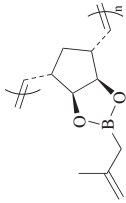
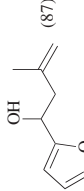
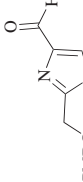
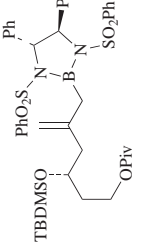
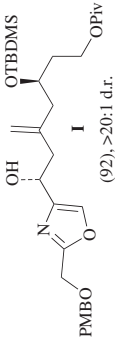
Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C <sub>5</sub> 		Neat, 0-20°	 (82)	238
		Ether, -70° to rt	 (46)	706, 702
		THF, 0° to rt, 18 h	 (80)	709
		—	 (64), 54:46 d.r.	714
		THF, 0° to rt, 18 h	 (80)	709
		CH <sub>2</sub> Cl <sub>2</sub> , rt; H <sub>2</sub> O, 2 h	 (87)	234
		CH <sub>2</sub> Cl <sub>2</sub> , rt; -78°, 2-3 h	 (92), >20:1 d.r.	710, 715



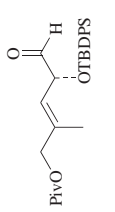
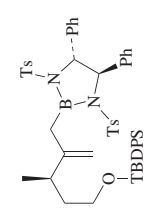
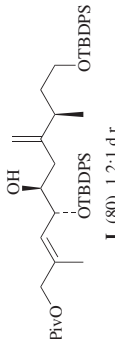
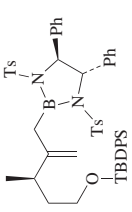

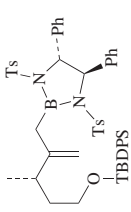
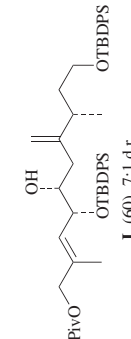


TABLE 5. ADDITION OF  $\beta$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
$n\text{-C}_5\text{H}_{11}\text{CHO}$		THF, 0° to rt, 18 h	(87)	709
		$\text{CH}_2\text{Cl}_2$ , -78°, 2.5 h	(71), 94	50
		4 Å MS, toluene, -78°, 1 h	<b>I</b> (86), 88	712
		4 Å MS, toluene, -78°, 1 h	(78), 92	712
		$\text{CH}_2\text{Cl}_2$ , -78°, 2.5 h	(77), 99	50
		$\text{CH}_2\text{Cl}_2$ , -78°, 2.5 h	(79), 88	50



TABLE 5. ADDITION OF  $\beta$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		1. $\text{SnBu}_3$ ,  2. Aldehyde, $-78^\circ$ , 1 h	<b>I</b> (80), 1.2:1 d.r. 708	
		1. $\text{SnBu}_3$ ,  2. Aldehyde, $-78^\circ$ , 1 h	<b>I</b> (70), 4:1 d.r. 708	
		1. $\text{SnBu}_3$ ,  2. Aldehyde, $-78^\circ$ , 1 h	<b>I</b> (60), 7:1 d.r. 708	

C<sub>6</sub>

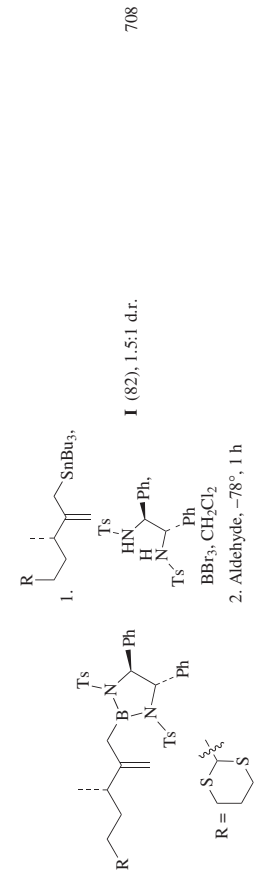
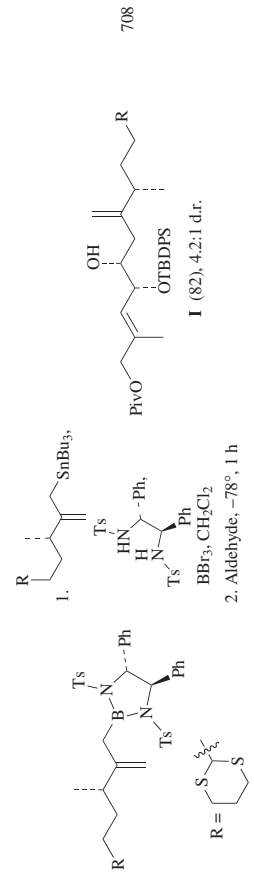
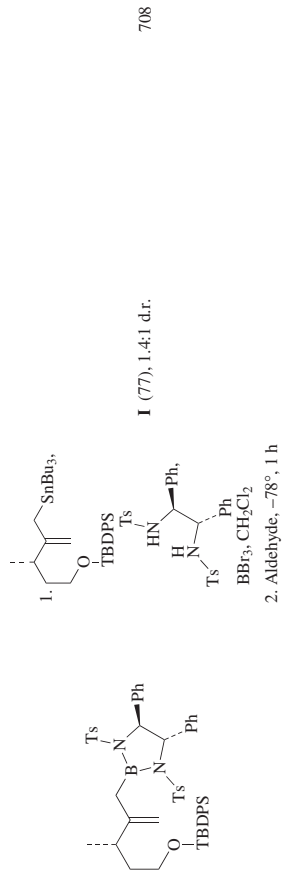
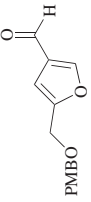
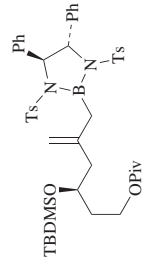
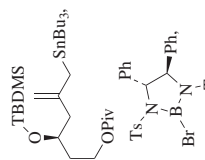
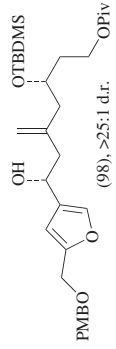
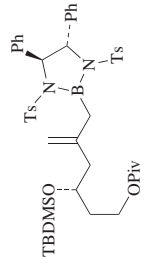
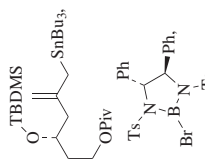
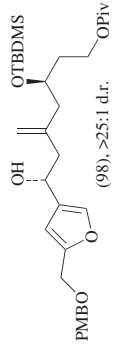
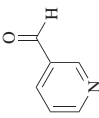
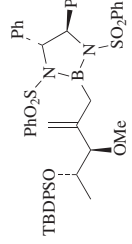
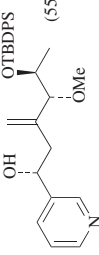
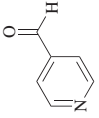
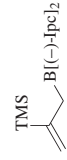
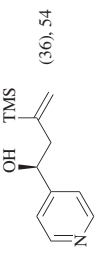


TABLE 5. ADDITION OF  $\beta$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		 CH <sub>2</sub> Cl <sub>2</sub> , -78°	 (98), >25:1 d.r.	716
		 CH <sub>2</sub> Cl <sub>2</sub> , -78°	 (98), >25:1 d.r.	716
		CH <sub>2</sub> Cl <sub>2</sub> , -78°, 2-3 h	 (55), >20:1 d.r.	710
		THF, -78°, 3 h	 (36), 54	707

C<sub>6</sub>

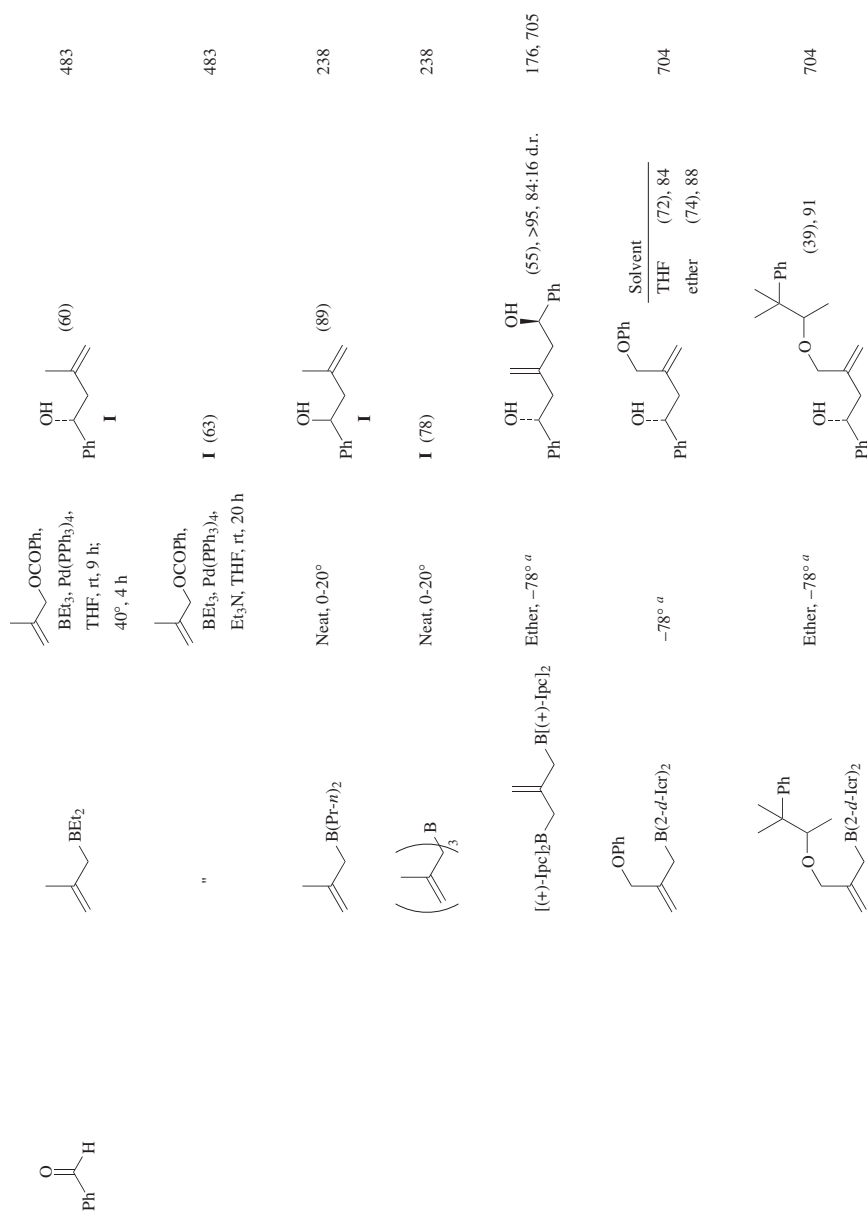

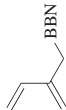
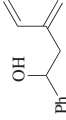

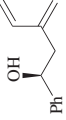

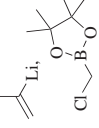
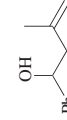
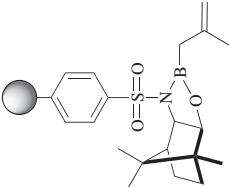
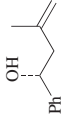
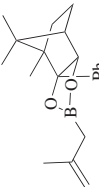
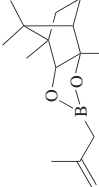
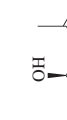


TABLE 5. ADDITION OF  $\beta$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Alylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		THF, ether, $-78^{\circ}$ , 1 h	 (60)	699
		THF, ether, $-78^{\circ}$ , 1 h	 (60), 93	699
			 (80)	52
		Ether, $-78^{\circ}$	 <b>I</b> (92), 89	246
		Sc(OTf) <sub>3</sub> (10 mol%), CH <sub>2</sub> Cl <sub>2</sub> , $-78^{\circ}$ , 12 h	<b>I</b> (64), 98	27
		Hexane, $-40^{\circ}$	 (83), 40	122



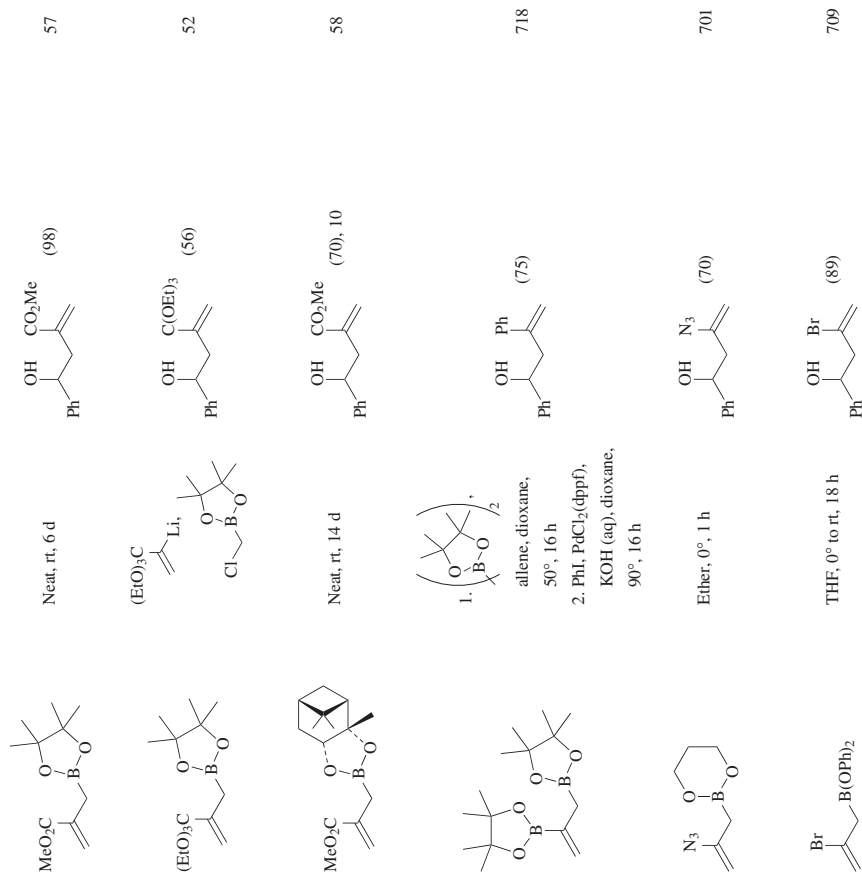

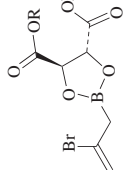
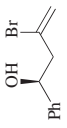
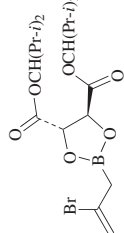
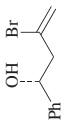
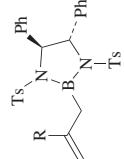
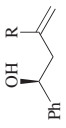
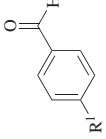
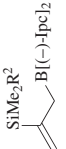
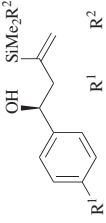
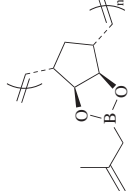
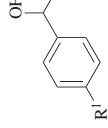


TABLE 5. ADDITION OF  $\beta$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yields(%) <sup>a</sup> , % ee	Refs.
		4 Å MS, toluene, -78°, 1 h	 R Et (92), 47 Pr- <i>i</i> (97), 47 CH(Pr- <i>i</i> ) <sub>2</sub> (98), 84	712
		4 Å MS, toluene, -78°, 1 h	 (98), 84	712
		CH <sub>2</sub> Cl <sub>2</sub> , -78°, 2.5 h	 R Br (73), 79 Cl (79), 84	50
 R <sup>1</sup> = H, O <sub>2</sub> N		THF, -78°, 3 h	 R <sup>1</sup> R <sup>2</sup> H Me (46), 75 H Ph (63), 22 O <sub>2</sub> N Me (72), 33	707
R <sup>1</sup> = H, MeO, O <sub>2</sub> N		CH <sub>2</sub> Cl <sub>2</sub> , H <sub>2</sub> O, rt	 R <sup>1</sup> Time H 2 h (87) MeO 5 h (95) O <sub>2</sub> N 3 h (96)	234

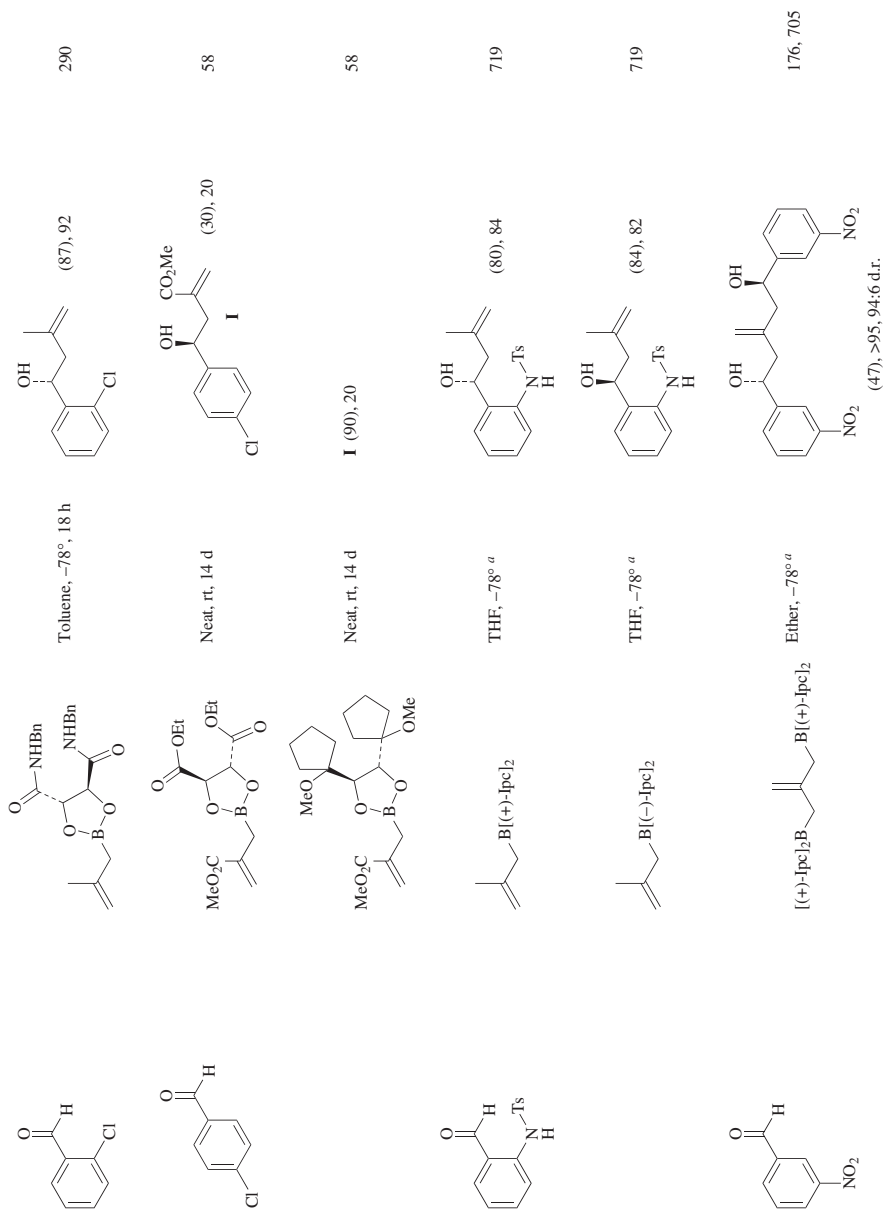
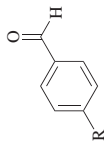
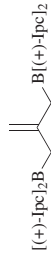
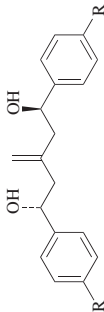
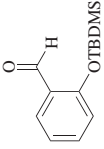

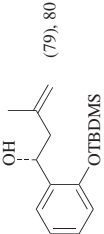
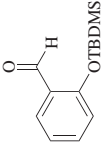

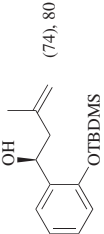
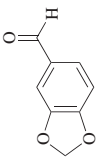
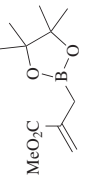
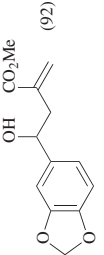
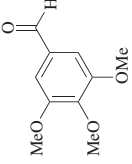
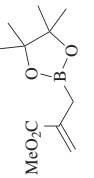
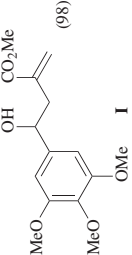
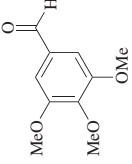
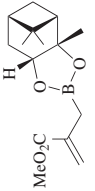


TABLE 5. ADDITION OF  $\beta$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yields( %), % ee	Refs.
		Ether, $-78^{\circ}$ <sup>a</sup>	 $\text{O}_2\text{N}$ (51), >95 $\text{MeO}$ (55), >95 d.r.	176, 705
		THF, $-78^{\circ}$ <sup>a</sup>	 (79), 80	719
		THF, $-78^{\circ}$ <sup>a</sup>	 (74), 80	719
		Neat, rt, 14 d	 (92)	57
		Neat, rt, 14 d	 (98) <b>I</b>	57
		Neat, rt, 14 d	<b>I</b> (95), 6	58

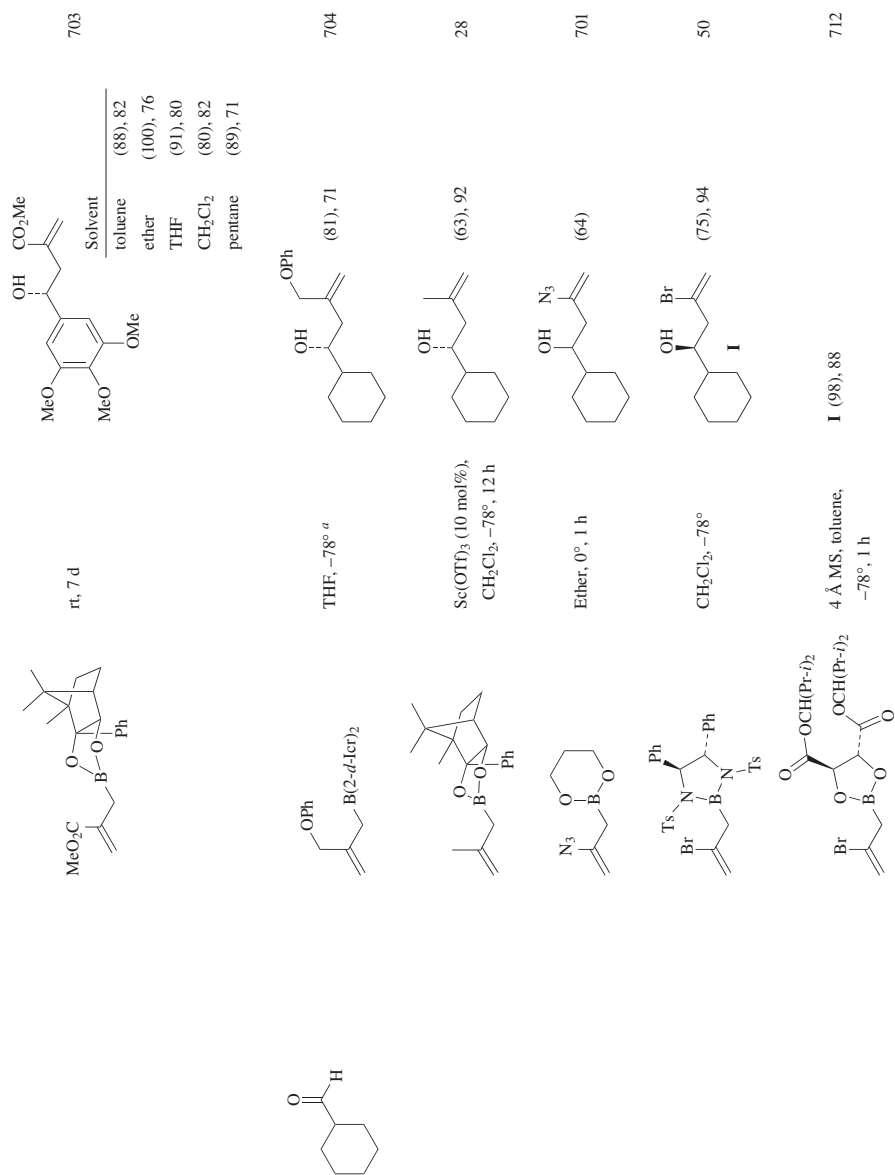
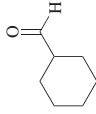
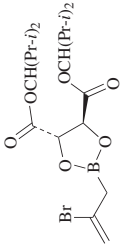
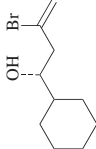
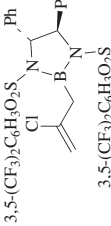
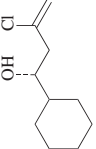
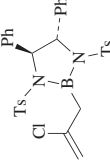
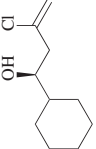
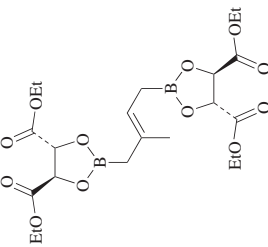
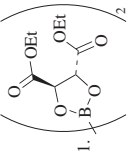
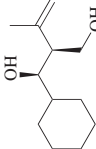


TABLE 5. ADDITION OF  $\beta$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		4 Å MS, toluene, -78°, 1 h	 (95), 85	712
	3,5-(CF <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> O <sub>2</sub> S 	—	 (76), 88	351
		CH <sub>2</sub> Cl <sub>2</sub> , -78°	 (81), 99	50
		1.  / 2 (Ph <sub>3</sub> P) <sub>2</sub> Pt(CH <sub>2</sub> CH <sub>2</sub> ) (5 mol%), THF, 80°, 14 h 2. H <sub>2</sub> O <sub>2</sub>	 (75)	186

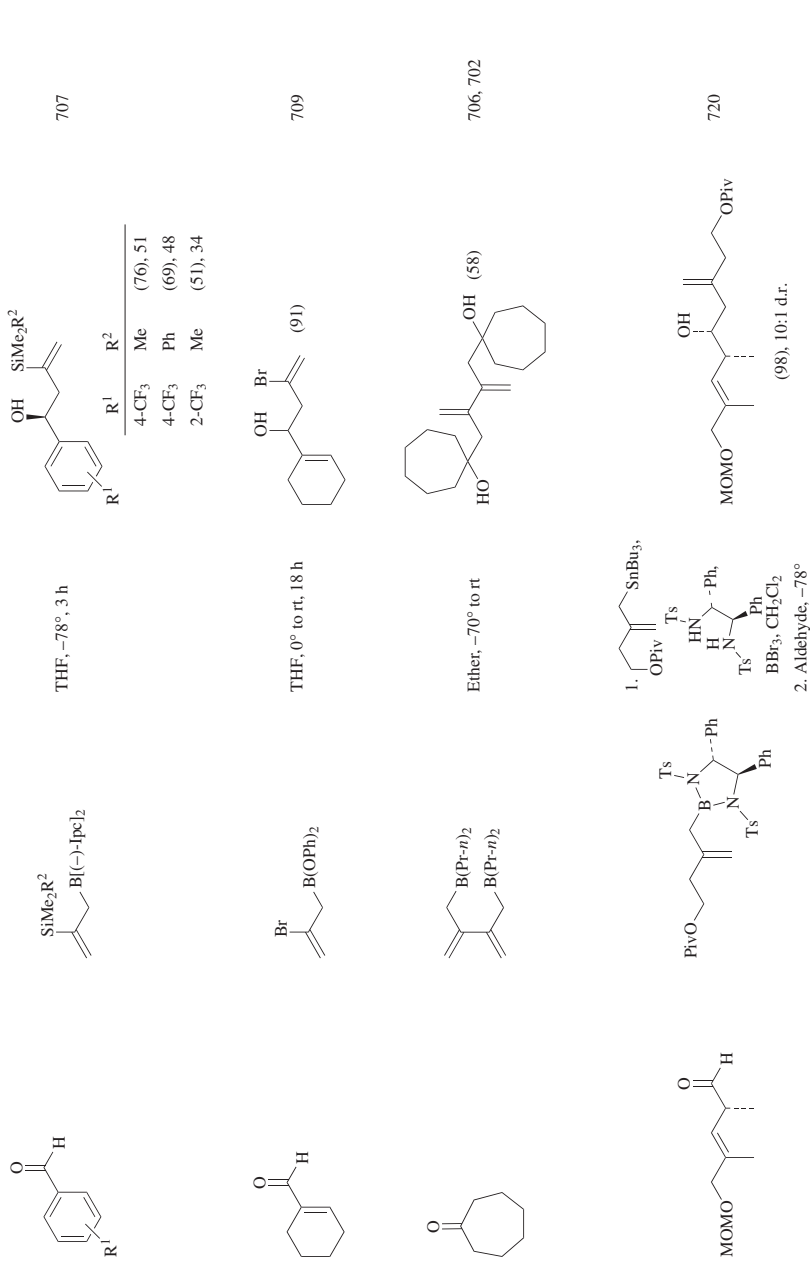
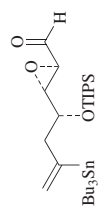
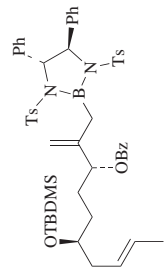
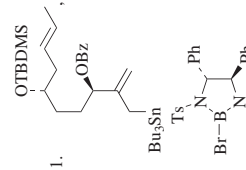
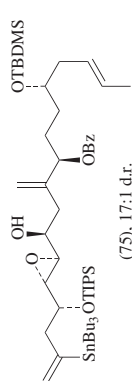
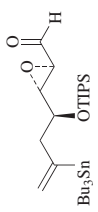
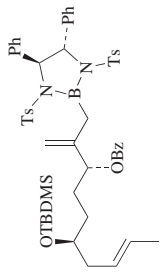
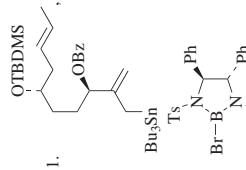
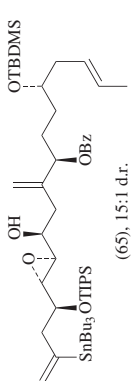


TABLE 5. ADDITION OF  $\beta$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		1.  2. Aldehyde, $-78^\circ$ , 3 h	 (75), 17:1 d.r.	710
		1.  2. Aldehyde, $-78^\circ$ , 3 h	 (65), 15:1 d.r.	708

C7







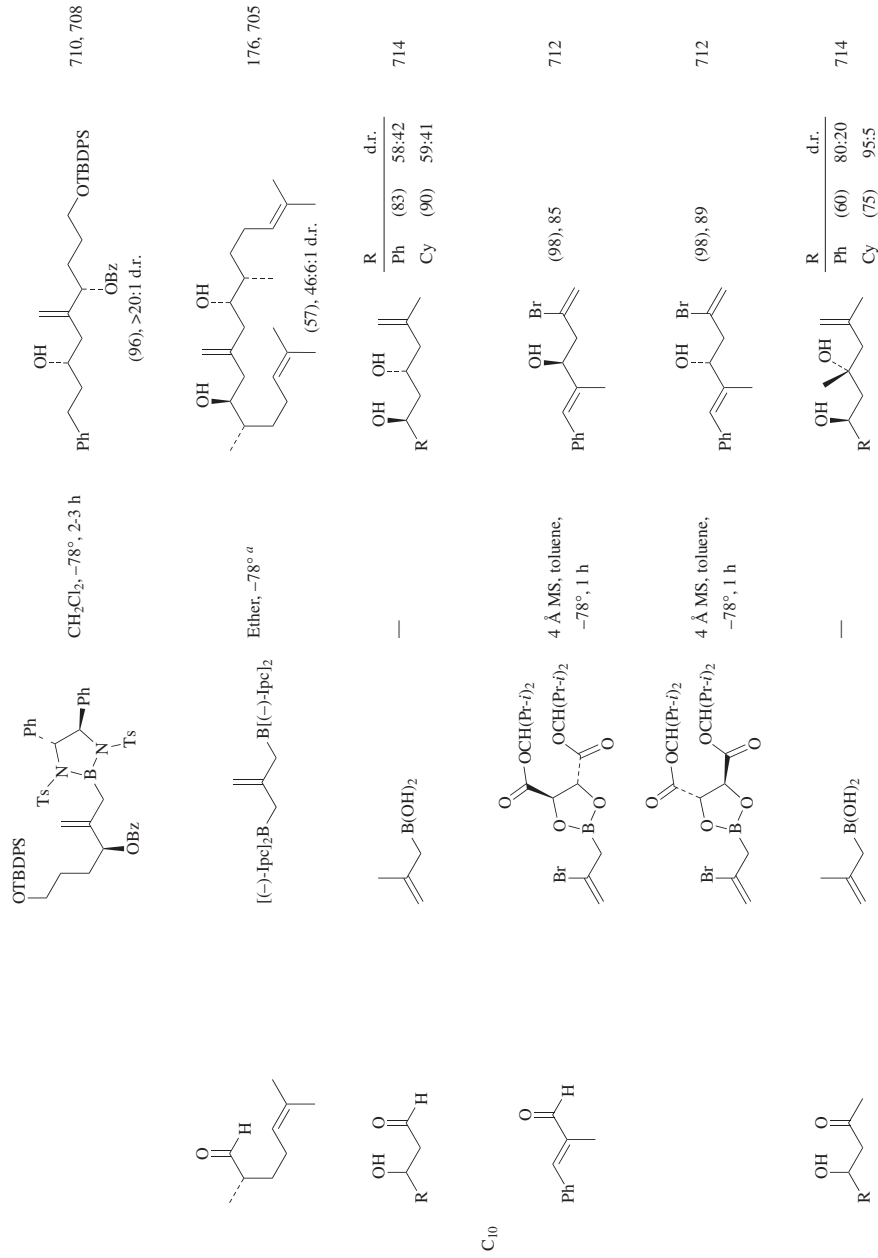
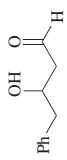

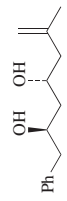
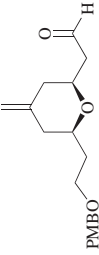
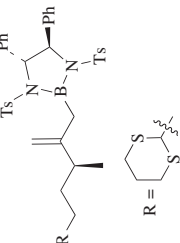

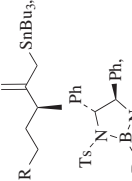
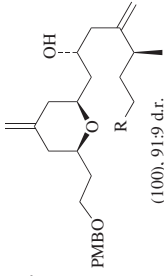

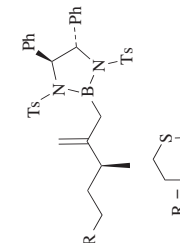

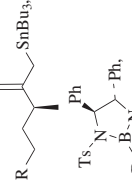
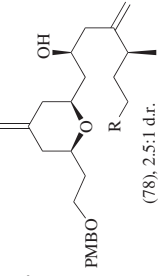

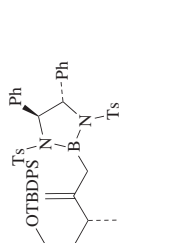
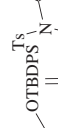
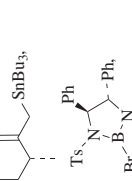
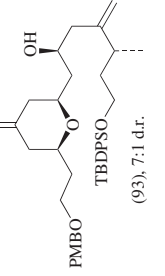


TABLE 5. ADDITION OF  $\beta$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		—	 (81), 55:45 d.r.	714
	 R = 	 CH <sub>2</sub> Cl <sub>2</sub> , -78°, 2 h	 (100), 91:9 d.r.	723, 708
	 R = 	 CH <sub>2</sub> Cl <sub>2</sub> , -78°, 2 h	 (78), 2.5:1 d.r.	708
	 R = 	 CH <sub>2</sub> Cl <sub>2</sub> , -78°, 2 h	 (93), 7:1 d.r.	708

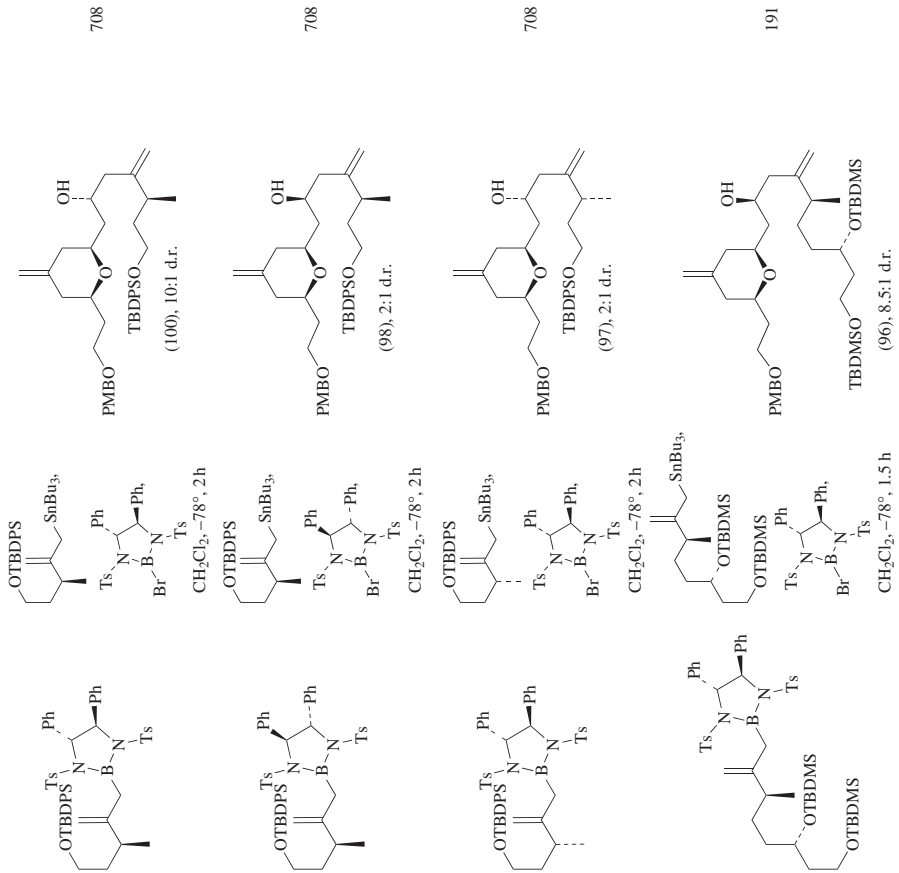


TABLE 5. ADDITION OF  $\beta$ -SUBSTITUTED REAGENTS (Continued)

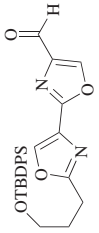
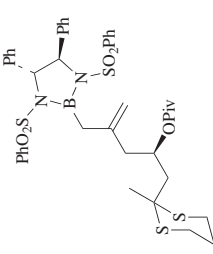
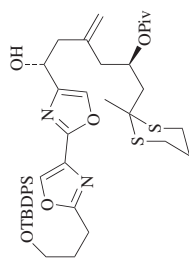
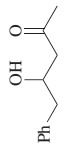

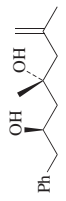
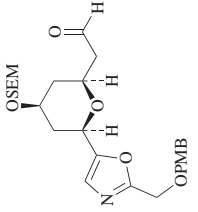
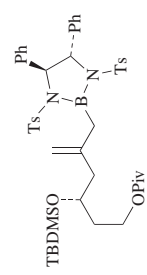
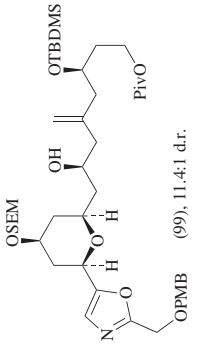

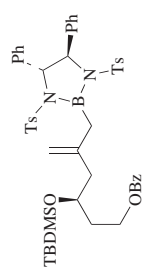
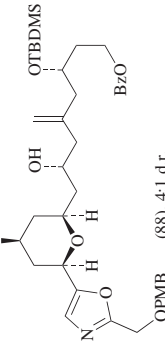
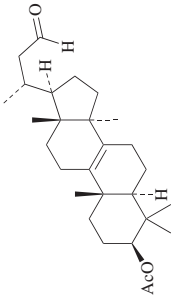
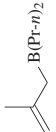
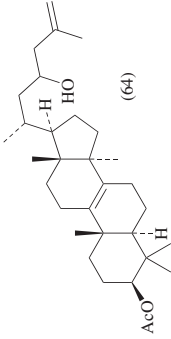
Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		$\text{CH}_2\text{Cl}_2, -78^\circ$	 (95), 10.5:1 d.r.	724
		—	 (60), 80:20 d.r.	714
		$\text{CH}_2\text{Cl}_2, -78^\circ, 2-3 \text{ h}$	 (99), 11:4:1 d.r.	710
		$\text{CH}_2\text{Cl}_2, -78^\circ, 2-3 \text{ h}$	 (88), 4:1 d.r.	710



TABLE 5. ADDITION OF  $\beta$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		THF, $-70^{\circ}$ to $0^{\circ}$ , 30 min	 (64) 728	

<sup>a</sup> The reaction mixture was free of  $Mg^{2+}$  ions.



TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS


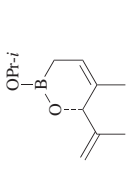
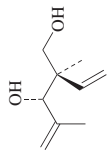

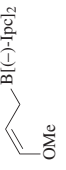
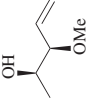

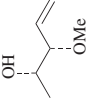
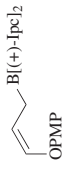
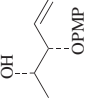
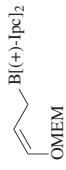
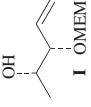


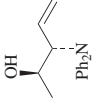
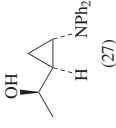


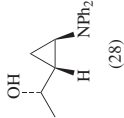
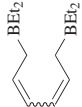
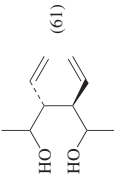

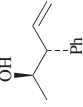
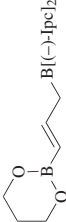
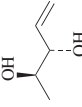

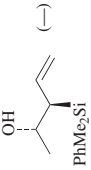

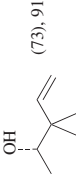
Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C <sub>1</sub> 		Toluene, 80°, 12 h	 (68), >98, >20:1 d.r.	729
C <sub>2</sub> 		THF, -78°, 3 h	 (57), 90, >99:1 d.r.	48
		THF, -78°, 3 h	 (59), 92, >99:1 d.r.	48, 503
		THF, -100°, 10 h	 (-), 95, >99:1 d.r.	407
		THF, -78°, 10 h	 (-), 93, >99:1 d.r.	388
	"	THF, -78°, 3 h	 I (75), >95	505
		THF, -78° to 0°, 3 h	 (40), >95, >95:5 d.r. +  (27)	730, 731

TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		THF, $-78^\circ$ to $0^\circ$ , 3 h	 (28) (41), >95, >95.5 d.r.	730, 731
		$-70^\circ$ to $0^\circ$	 (61)	732
		THF, $-78^\circ$ to rt, 4 h	 R Cy (82), — (-)lpc (75), 84	d.r. >99:1 >99:1
		1. Ether, $-78^\circ$ to $0^\circ$ , 4 h 2. $\text{H}_2\text{O}_2$ , NaOH	 (75), 92, >97:3 d.r.	157
		B[(+)-lpc] <sub>2</sub> THF, $-78^\circ$ , 4 h	 (—)	734
		THF, $-78^\circ$ , 12 h	 (73), 91	138, 136a

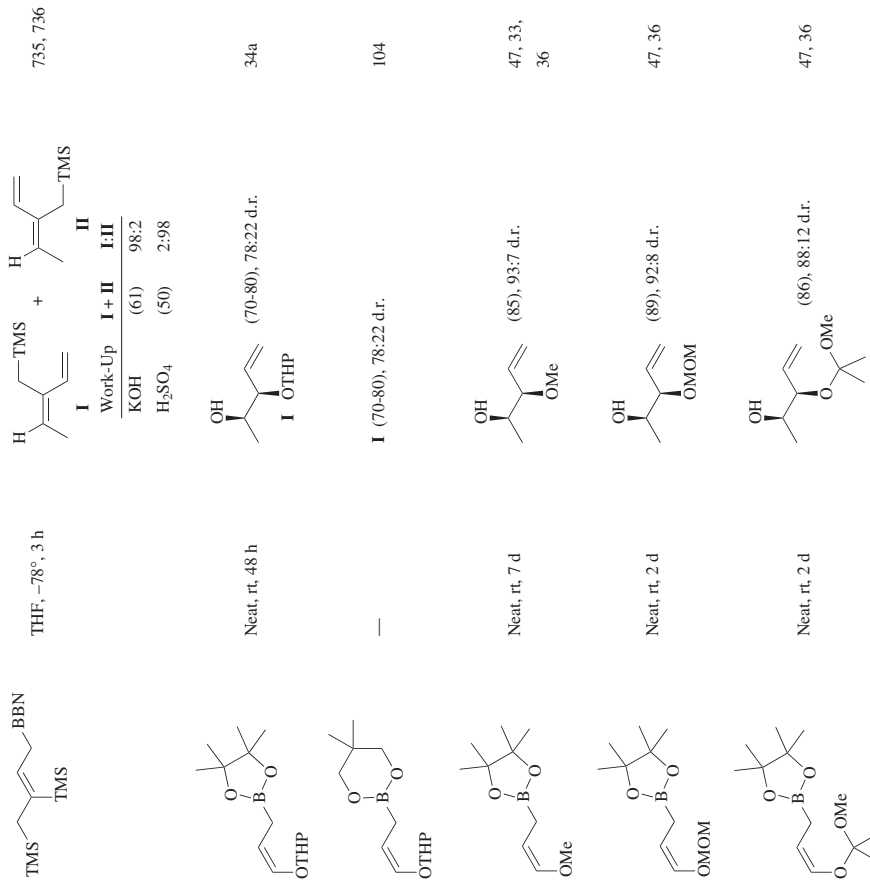

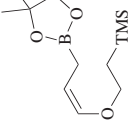
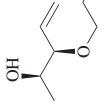
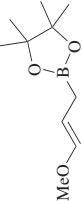
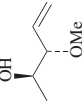
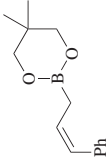
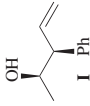
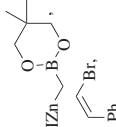

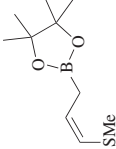
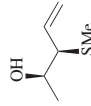
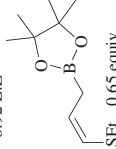
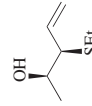


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C <sub>2</sub> 		Neat, rt, 2 d	 (91), 93:7 d.r.	47
		Petroleum ether, rt, 36 h	 (76), 95:5 d.r.	47, 36
		THF, rt, 16 h	 (57), >99:1 d.r.	79
	"	 IZn, rt, >99:1 d.r. Cl <sub>2</sub> Pd(PPh <sub>3</sub> ) <sub>2</sub> , THF, 50°, 3 h; rt, 16 h	 (57), >99:1 d.r.	79
		—	 (86), 92:8 d.r.	737
		—	 (80), 9:1 d.r.	737

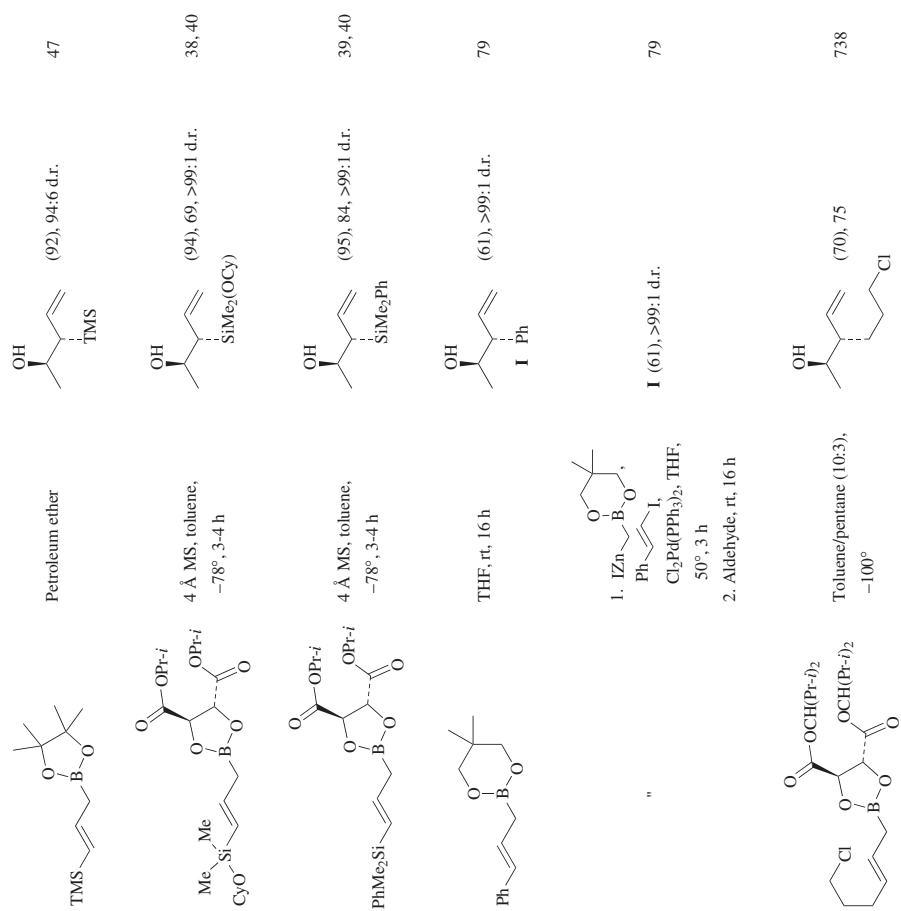

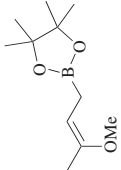
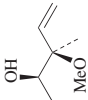
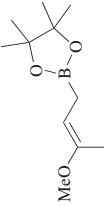
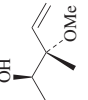
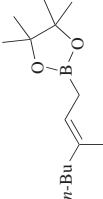
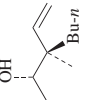
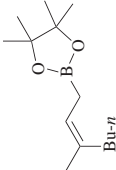
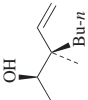
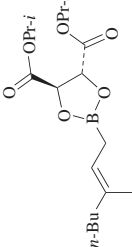
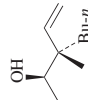
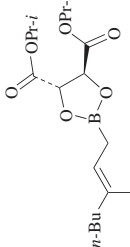
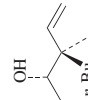


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C <sub>2</sub> 		Petroleum ether, 20°, 3 d	 (50), 70:30 d.r.	739
		Petroleum ether, 20°, 6 d	 (61), 95:5 d.r.	739
		Neat, rt, 5-8 d	 (83), 95:5 d.r.	55
		Neat, rt, 5-8 d	 (83), 88:12 d.r.	55
		4 Å MS, toluene, -78°, 5 h	 (88), 72, 96:4 d.r.	740
		4 Å MS, toluene, -78°, 5 h	 (86), 67, 96:4 d.r.	740

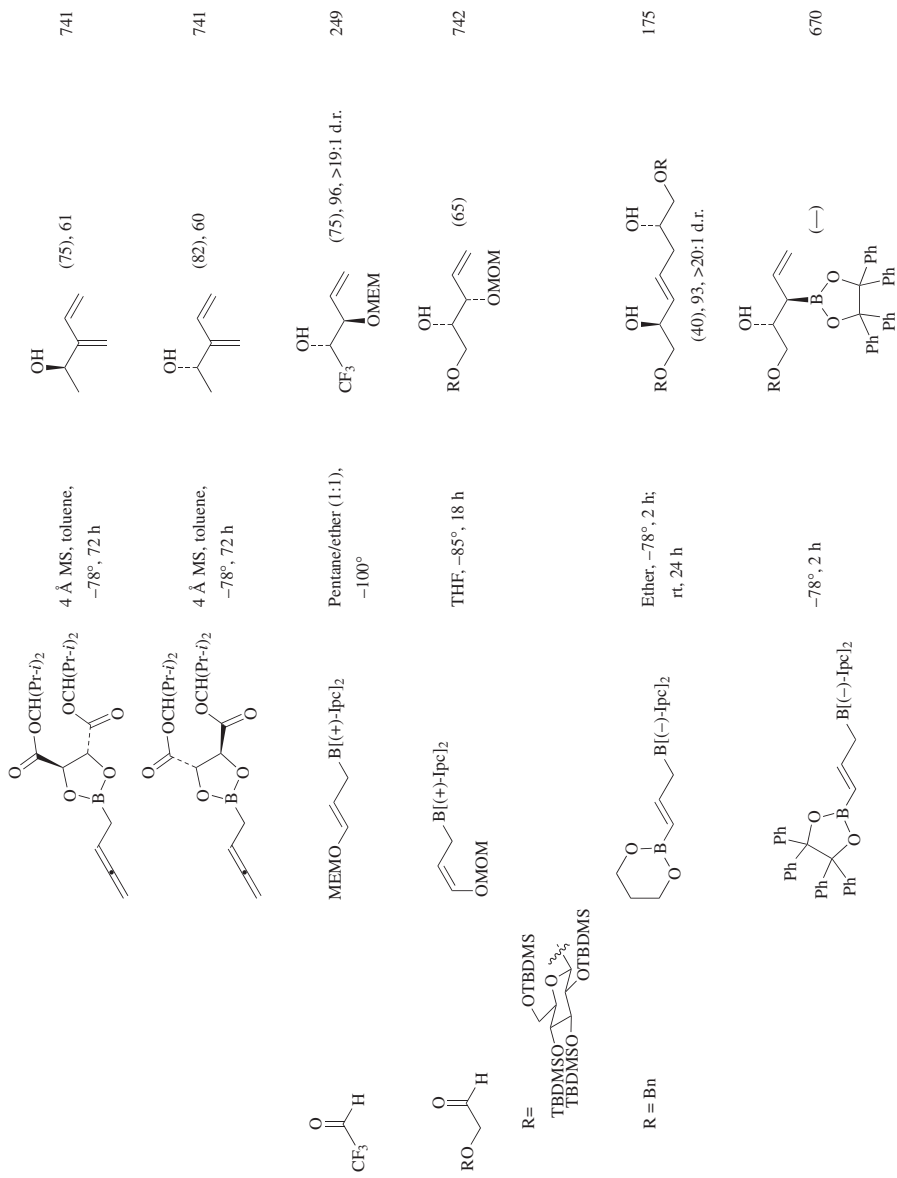
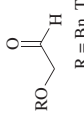

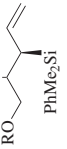
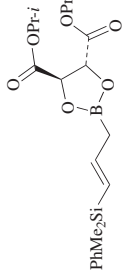
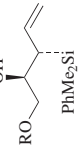

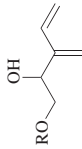
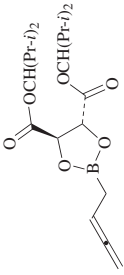
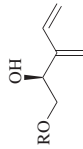
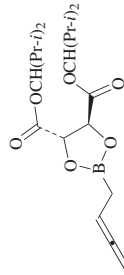
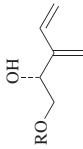
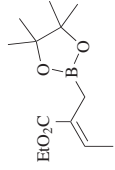
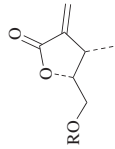
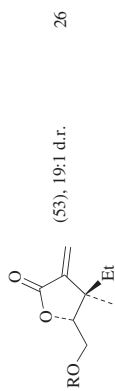


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

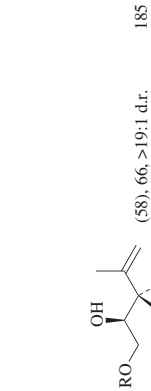
Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
$C_2$  R = Bn, TBDPS		THF, $-78^\circ$ , 4 h	 (85), 88	734
R = Bn		4 Å MS, toluene, $-78^\circ$	 (99)	743
		$CH_2Cl_2$ , rt, 3 d	 (59)	741, 744
		4 Å MS, toluene, $-78^\circ$ , 72 h	 (36), 50	741
		4 Å MS, toluene, $-78^\circ$ , 72 h	 (29), 48	741
		$SeI(OTf)_3$ , toluene, rt, 24 h	 (33), >20:1 d.r.	26





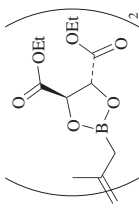
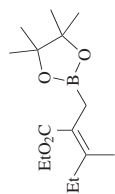
26

Sc(OTf)<sub>3</sub>, toluene,  
rt, 24 h

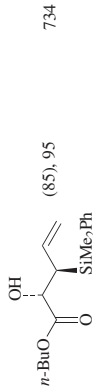


185

1. ,  
Pt(dba)<sub>2</sub>, PCy<sub>3</sub>,  
benzene, rt  
2. Aldehyde, -78°, 3 h  
3. NaOH, H<sub>2</sub>O<sub>2</sub>

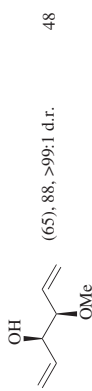


R = PMB



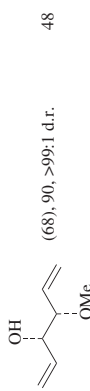
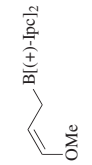
734

THF, -78°, 4 h



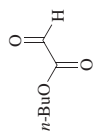
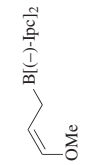
48

THF, -78°, 3 h



48


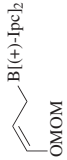
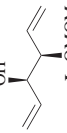

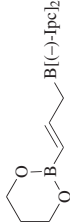
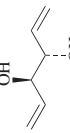

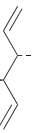

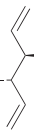

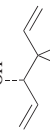

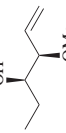

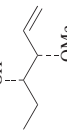
THF, -78°, 3 h



C<sub>3</sub>



TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
 $C_3$		THF, $-78^\circ$ , 3 h	 (62), 90, >99:1 d.r.	48, 156
	"	—	 I (66), >95	745
		1. Ether, $-78^\circ$ to $0^\circ$ , 4 h 2. $H_2O_2$ , NaOH	 (63), >97:3 d.r.	157
		THF, $-78^\circ$ to $0^\circ$ , 3 h	 (45), >95, >95:5 d.r.	730, 731
		THF, $-78^\circ$ to $0^\circ$ , 3 h	 (47), >95, >95:5 d.r.	730, 731
		THF, $-78^\circ$ , 12 h	 (70), 95	138, 136a
		THF, $-78^\circ$ , 3 h	 (65), 88, >99:1 d.r.	48
		THF, $-78^\circ$ , 3 h	 (68), 90, >99:1 d.r.	48

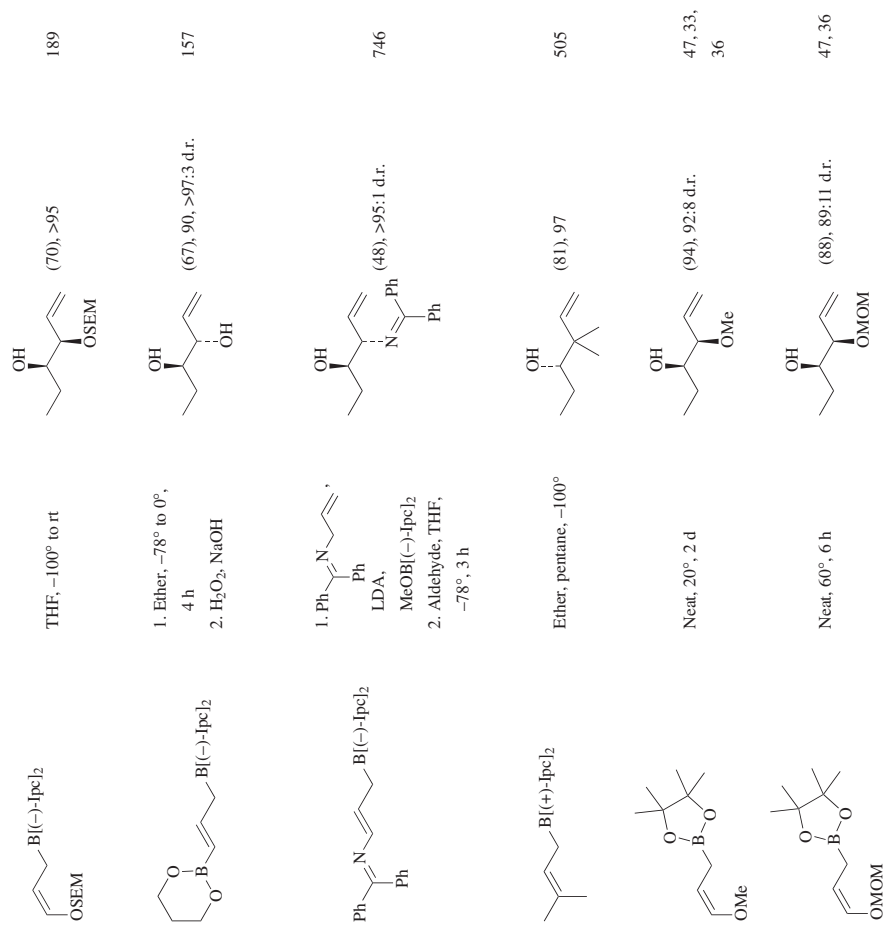

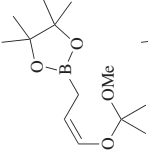
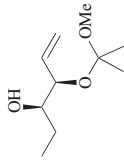
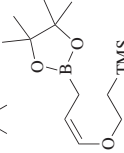
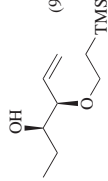
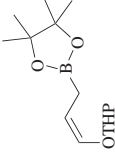
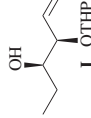
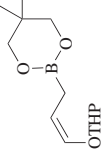

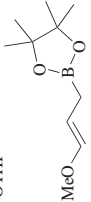
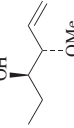
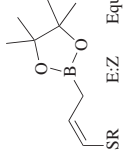
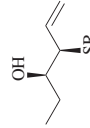


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C <sub>3</sub> 		Neat, rt	 (88), 80:20 d.r.	47, 36
		Neat, 20°, 4 d	 (94), 93:7 d.r.	47
		Neat, rt, 48 h	 I OTHP (70-80), >80:20 d.r.	34a
		—	 I (70-80), 80:20 d.r.	104
		Petroleum ether, rt, 36 h	 (68), 95:5 d.r.	47, 33
		—	 SR R	737
		E:Z Equiv		d.r.
	8:92 1.0		Me (91) 91:9	
	44:56 1.0		Et (90) 56:44	
	73:27 1.0		Et (94) 27:73	
	44:56 0.4		Et (95) 91:9	

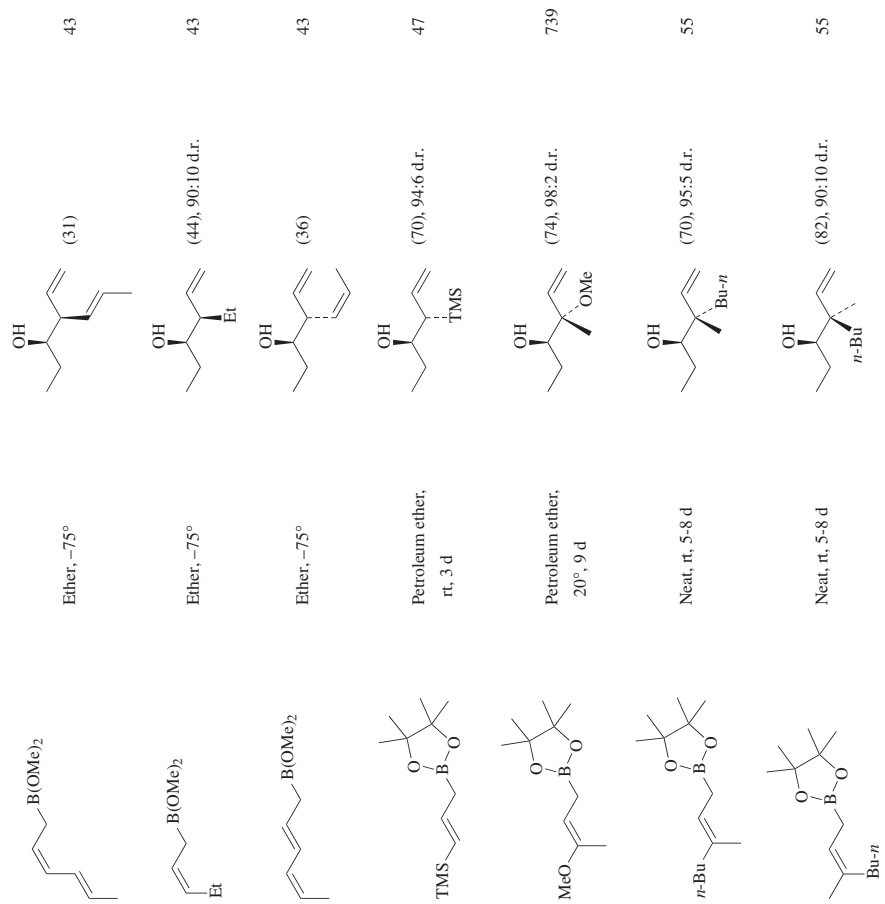


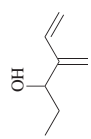

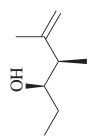

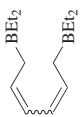
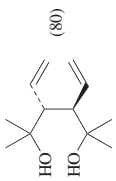
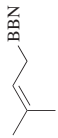
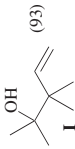
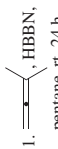


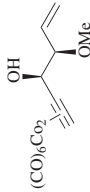

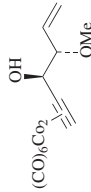


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

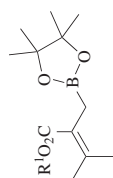
Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee		Refs.
			Product	Solvent Time Yield (%) ee	
		rt		toluene 3 h (84) neat 1 h (82)	744
		Ether, -75°		(34), 98:2 d.r.	43
		-70° to 0°		(80)	732
		Pentane, rt, 2 h		(93)	103
	"	1.  , pentane, rt, 24 h 2. Ketone, rt, 2 h	<b>I</b> (80)		103
		THF, -78° to rt, 15 h		(76), >96, 94:6 d.r.	747
		THF, -78° to rt, 15 h		(20), >95, >97.5:2.5 d.r.	747

				46
R = Ac				(59)
R = PMB				748
R = PMB				(80), 90
R = TBDMS				631
R = TBDMS				(85), >95, >95.5 d.r.
R = Bn, PMB				734
R = Bn, PMB				R (74), 90 PMB (72), 95
R = TBDMS				749
R = TBDMS				(-), 99
R = PMB				749
R = PMB				(49), 95
R = PMB				505
R = PMB				I (82), 95
R = Bn				545
R = Bn				(46), 88

TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		—	 (71), 13:1 d.r.	52
		4 Å MS, toluene, -78°, 5 h	 (56), 85, 97:3 d.r.	740
		4 Å MS, toluene, -78°, 5 h	 (57), 82, 97:3 d.r.	740
		4 Å MS, toluene, -78°, 5 h	 (56), 73, 97:3 d.r.	740
		4 Å MS, toluene, -78°, 5 h	 (46), 80, 97:3 d.r.	740
		Neat, rt, >12 d	 I	59





R<sup>1</sup> = (-)-8-phenylmenthyl

59

I (80), 82

1. Neat, rt, 14 d  
2. pTSA

59, 26

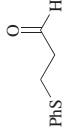
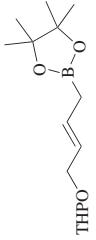
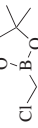
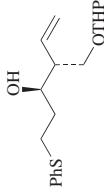

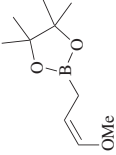
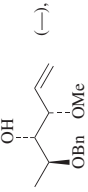
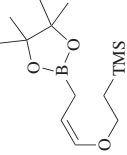
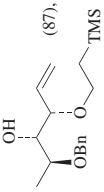
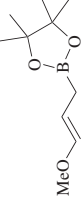
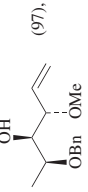
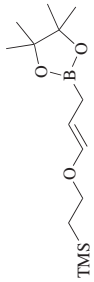
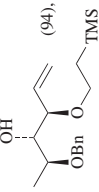
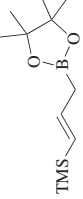
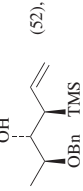
I

rt

Solvent	Time	R <sup>1</sup>	R <sup>2</sup>
neat	>12 d	Et	—
neat	8 d		—
neat	14 d		—
toluene	26 d		—
neat	8 d		H
toluene	36 d	"	Ph
toluene	14 d	"	2-Nph
CH <sub>2</sub> Cl <sub>2</sub>	14 d	"	2-Nph
toluene	14 d	"	4-MeOC <sub>6</sub> H <sub>4</sub>
toluene	14 d	"	4-PhC <sub>6</sub> H <sub>4</sub>
toluene	14 d	"	3,5-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>

"  
R<sup>1</sup> = see table

TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		THPO-CH=CH-Li, 	 (50), 13:1 d.r.	52
		—	 (—), 88:12 d.r.	275, 750
		Petroleum ether, 22°, 7 d	 (87), 92, 82:18 d.r.	275
		Petroleum ether, 22°, 7 d	 (97), 92, 57:43 d.r.	275
		Petroleum ether, 22°, 4 d	 (94), 92, 60:40 d.r.	275
		Neat, rt, 4 d	 (52), 58:42 d.r.	521

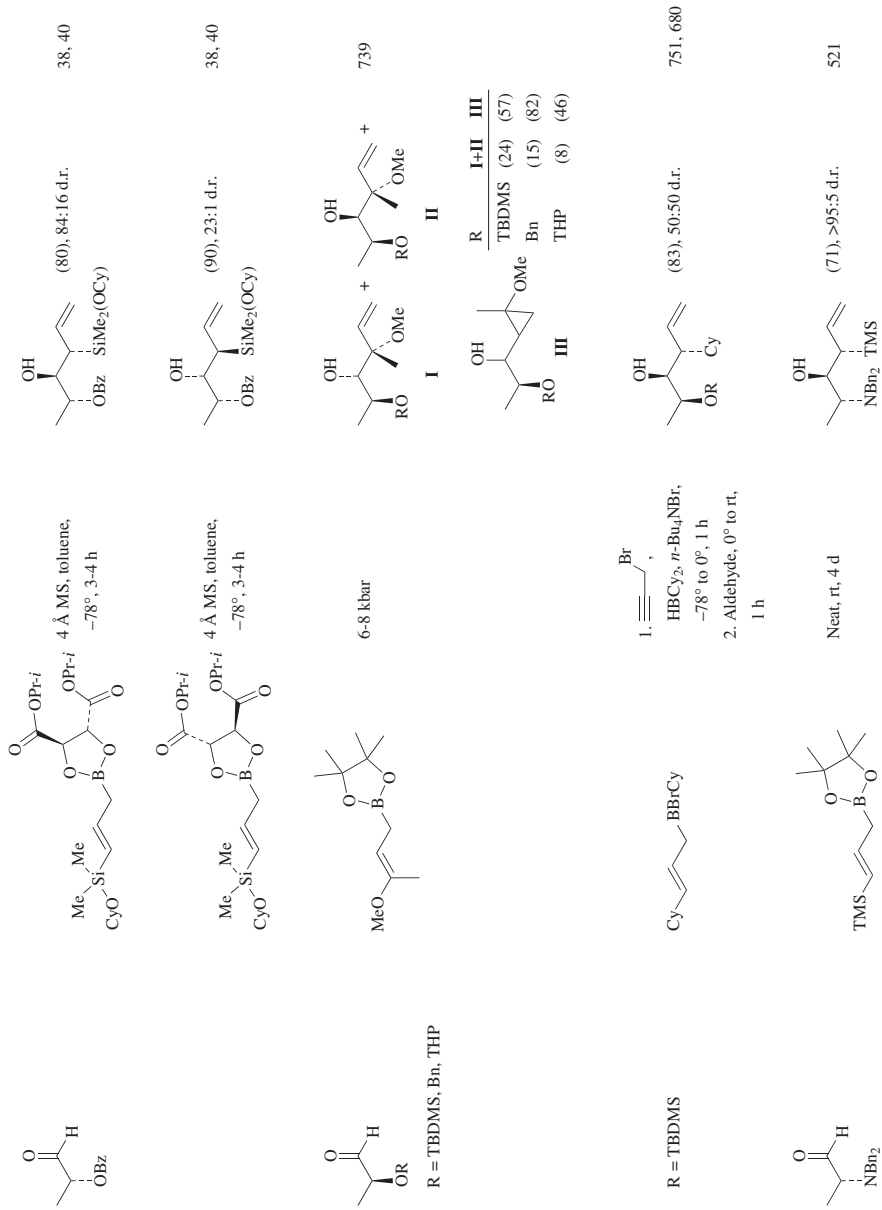


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

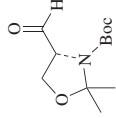

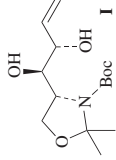
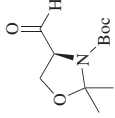

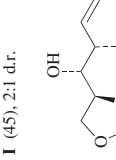
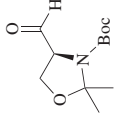
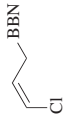
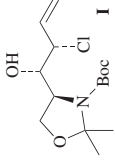
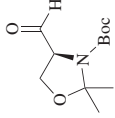

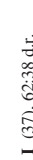
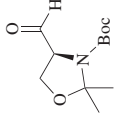


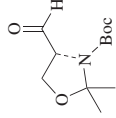

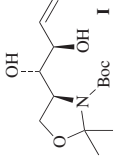
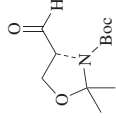

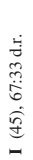
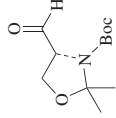
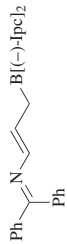
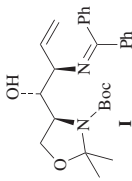
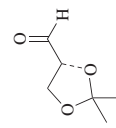

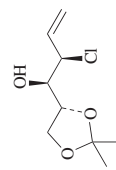

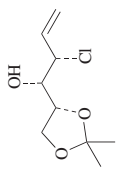
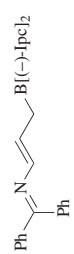
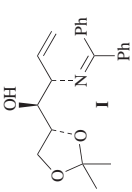
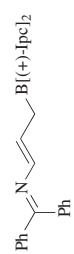
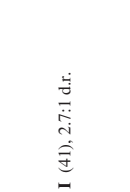
Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		1. Ether, $-78^{\circ}$ , 3.5 h 2. KF, H <sub>2</sub> O <sub>2</sub>	 (57), >95:5 d.r.	752
		1. Ether, $-78^{\circ}$ , 3.5 h 2. KF, H <sub>2</sub> O <sub>2</sub>	 I (45), 2:1 d.r.	752, 45, 511
		Ether, THF, $-95^{\circ}$ , 6 h	 (68), 95:5 d.r.	753, 754
		Ether, THF, $-95^{\circ}$ , 6 h	 I (37), 62:38 d.r.	753
		Ether, THF, $-95^{\circ}$ , 6 h	 I (72), >97:3 d.r.	753, 754
		1. KHCO <sub>3</sub> 2. KF, H <sub>2</sub> O <sub>2</sub>	 (57), >98:2 d.r.	278
		1. KHCO <sub>3</sub> 2. KF, H <sub>2</sub> O <sub>2</sub>	 I (45), 67:33 d.r.	278
		THF, $-78^{\circ}$	 (58), 1.2:1 d.r.	160



TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Ether, $-95^\circ$ , 4 h	 (65), 99.5:0.5 d.r.	756
		Ether, $-95^\circ$ , 4 h	 (68), 61:39 d.r.	756
		1. Ph-CH=CH-CH=CH-N(Ph)-CH=CH-CH=CH- LDA, MeOB[(-)-Ipc] <sub>2</sub> , 2. Aldehyde, THF, $-78^\circ$ , 3 h	 (43), >95:5 d.r.	746
	"	THF, $-78^\circ$	<b>I</b> (43), >95:5 d.r.	160
		1. Ph-CH=CH-CH=CH-N(Ph)-CH=CH-CH=CH- LDA, MeOB[(+)-Ipc] <sub>2</sub> , 2. Aldehyde, THF, $-78^\circ$ , 3 h	 <b>I</b> (41), 2.7:1 d.r.	746
	"	THF, $-78^\circ$	<b>I</b> (41), 2.7:1 d.r.	160

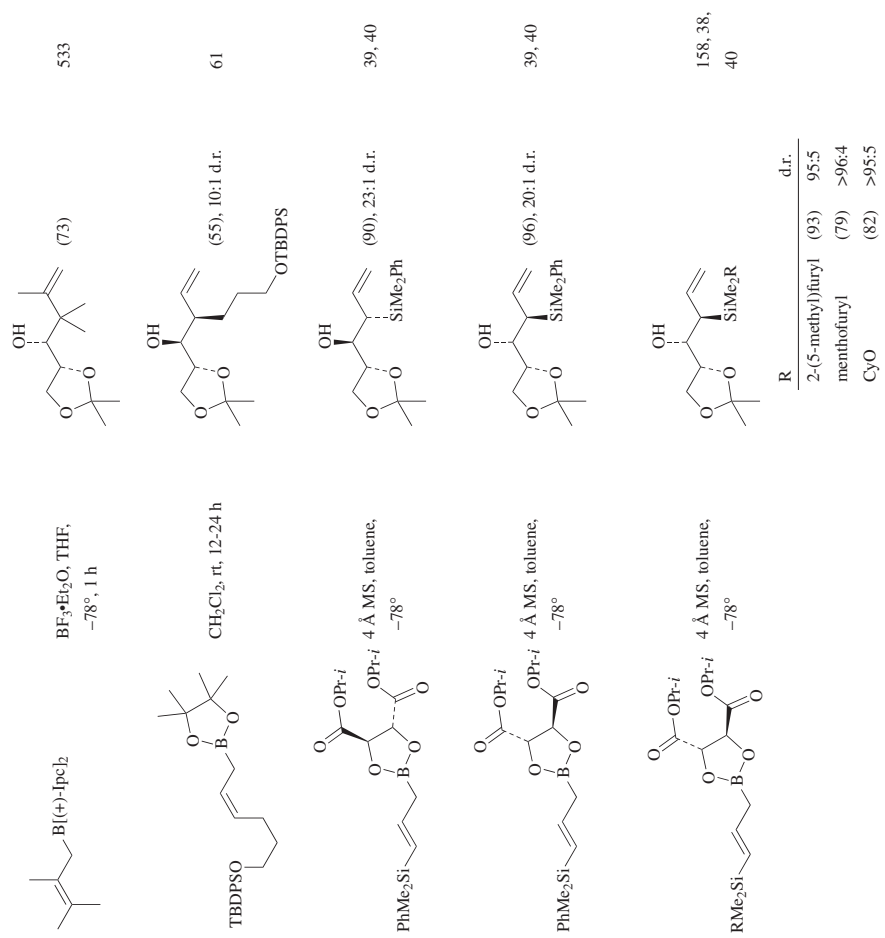
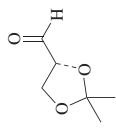
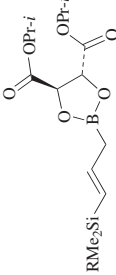
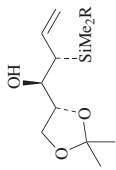
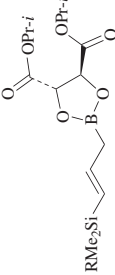
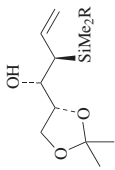
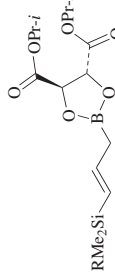
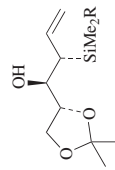

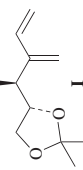


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		4 Å MS, toluene, -78°		158, 38, 40
			R	
			2-(5-methyl)furyl	d.r. 94:6
			menthothuryl	(85) 92:8
			CyO	(88) 85:15
		4 Å MS, toluene, -78°		757
				(79), >96:4 d.r.
		4 Å MS, toluene, -78°		757
				(85), 92:8 d.r.
		CH2Cl2, 12 h		Temp d.r. rt (93) 87:13 0° (-) 92:8
			<b>I</b>	
	"	Toluene, rt, 3 h	<b>I</b> (90), 89:11 d.r.	741



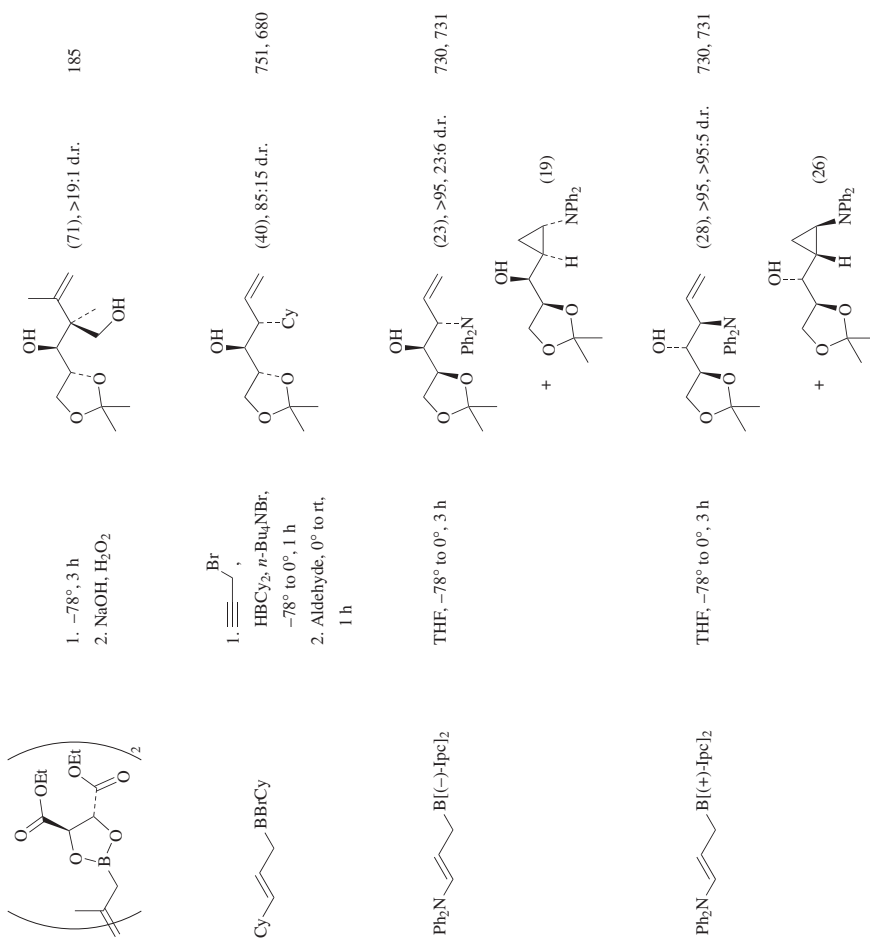


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		1. $-78^{\circ}$ , 3 h 2. NaOH, H <sub>2</sub> O <sub>2</sub>	(66), 1:1 d.r.	185
		4 Å MS, toluene, $-78^{\circ}$	(79), >99:1 d.r.	194, 758
		Petroleum ether, 6 kbar, $45^{\circ}$ , 80 h	(85), 14:1 d.r.	104
		THF, $-78^{\circ}$	(65-68), 82	759
		THF, $-78^{\circ}$	(85), 96	138, 140
		THF, $-78^{\circ}$	(83), 96	138, 140

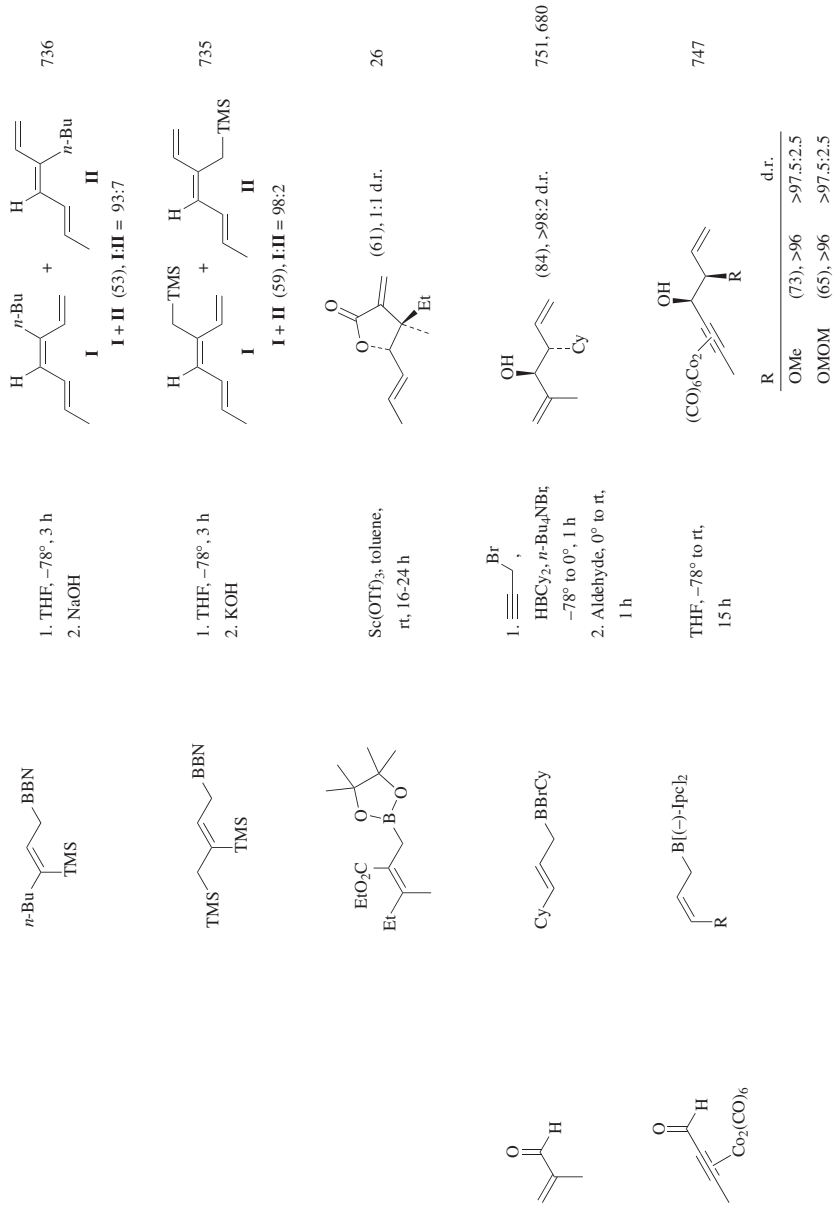


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		THF, $-78^\circ$ to rt, 15 h		747
			(44), >95, >97.5:2.5 d.r.	
		THF, $-78^\circ$		760
		Neat, $60^\circ$		238
		Ether, $-78^\circ$ , 12 h		138, 136a
		Neat, rt, 48 h		34a
		Neat, rt, 48 h	(70-80), >80:20 d.r.	
		Toluene/pentane (10:3), $-100^\circ$		738
		Toluene/pentane (10:3), $-100^\circ$		738

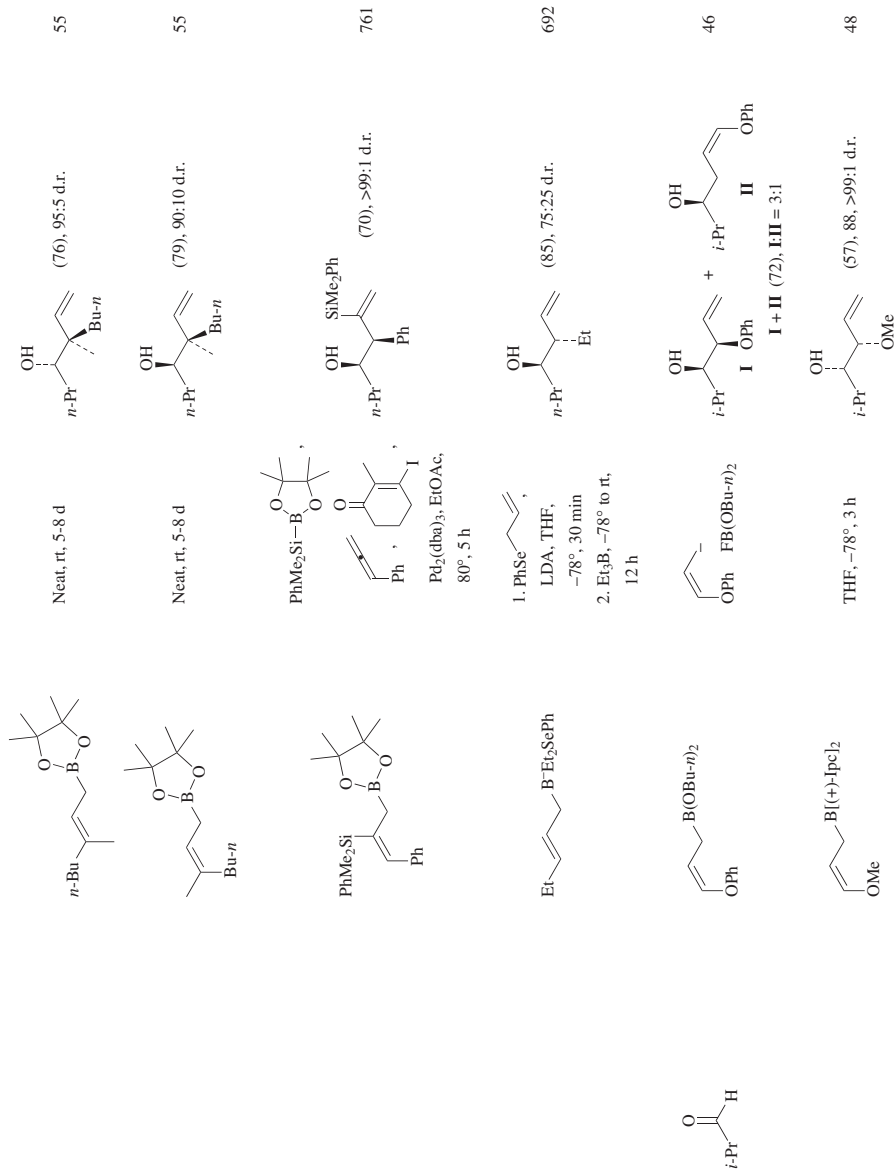


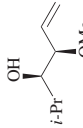


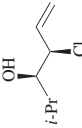
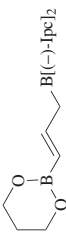
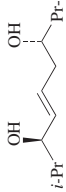
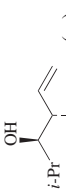

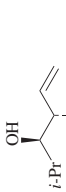

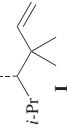


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
$C_4$ 		THF, $-78^\circ$ , 3 h	 (62), 88, >99:1 d.r.	48
		1.  MeOB[(-)-Ipc]2, LDA, ether, $-78^\circ$ 2. $BF_3 \cdot OEt_2$ 3. Aldehyde	 (77)	159, 762
		Ether, $-78^\circ$ , 2 h; rt, 24 h	 (34), 84, >20:1 d.r.	175
	"	Ether, $-78^\circ$ , 2 h	 (73)	175
		Ether, $-78^\circ$ , 2 h	 (85), 95	175
		Ether, pentane, $-100^\circ$ $-78^\circ$ , 12 h	 (89)	505
	"	$-78^\circ$ , 12 h	<b>I</b> (73), 89	138, 136a

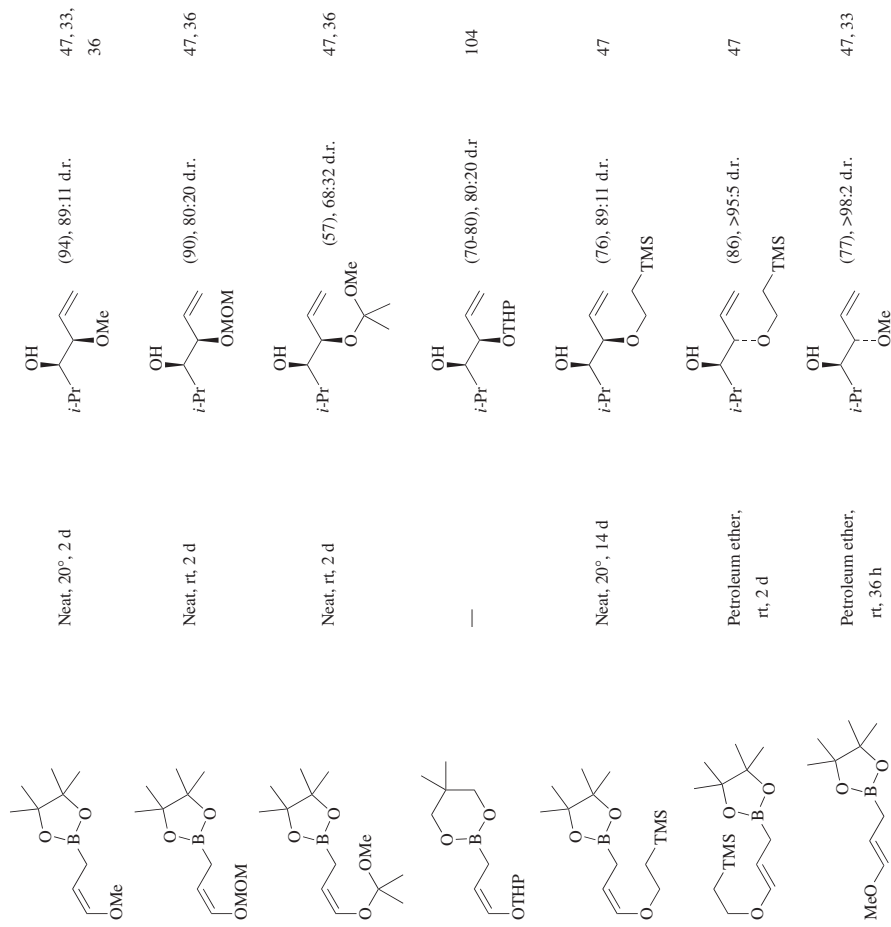
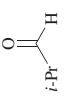
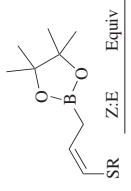
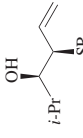
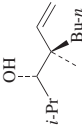
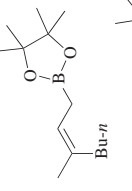

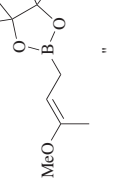
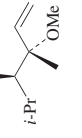
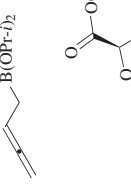
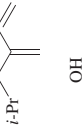
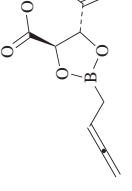
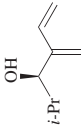


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C <sub>4</sub> 	 SR      Z:E      Equiv >95:5      1.0 56:44      0.4	—	 737	737
		Neat, 4 kbar, rt	 55	55
	 SR      Z:E      Equiv >95:5      1.0 56:44      0.4	Neat, 4 kbar, rt	 55	55
	 SR      Z:E      Equiv >95:5      1.0 56:44      0.4	Petroleum ether, 20°, >20 d	 739	739
	"	Petroleum ether, 8 kbar, 46°, 5 h	<b>I</b> (70), 97:3 d.r. 739	739
	 SR      Z:E      Equiv >95:5      1.0 56:44      0.4	Toluene, rt, 8 h	 80	741, 744
	 SR      Z:E      Equiv >95:5      1.0 56:44      0.4	4 Å MS, toluene, -78°, 72 h	 741	741



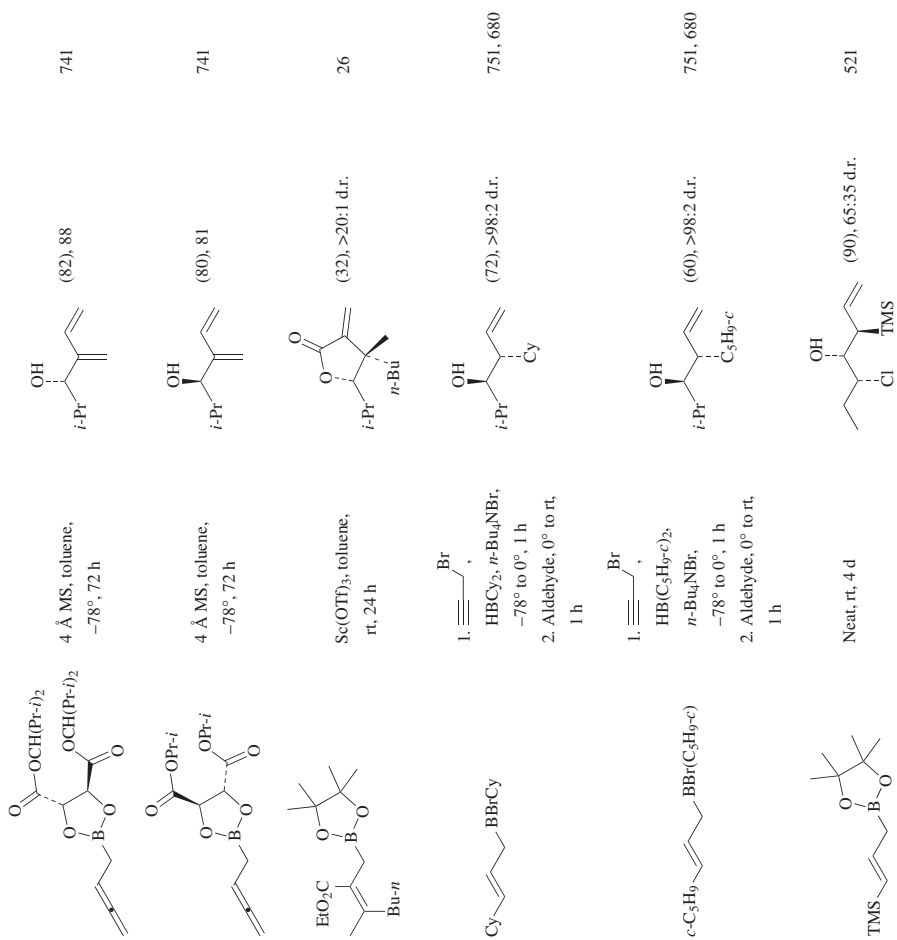


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		THF, -78°, 3 h	 I + II (68), I:II = 55:45	735, 736
		—		388
		Ether, -95°, 4 h		651
		Ether, -95°, 4 h		651
		THF, rt		602
		4 Å MS, toluene, -78°		158, 38, 40
			R	d.r.
			2-(5-methyl)furyl	(67) >96:4
			menthothuryl	(82) 94:6
			CyO	(76) >95:5



TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Ether, -95°, 4 h	 (56), 95:5 d.r.	651
R = TBDMS R = PMB		Ether, pentane, -100°	 (90), 96:4 d.r.	505
R = TBDPS		4 Å MS, toluene, -78°	 I (91), >20:1 d.r.	743
R = TBDMS		4 Å MS, toluene, -78°	 (92), 1.5:1 d.r.	39, 40
		Ether, -95°, 4 h	 (68), 93:7 d.r.	765
		1. -78° to rt, 1.5 h 2. L.A., -78° to rt, 3 h	 L.A., Solvent FeCl3 THF (61) 87:13 Ti(OPr-i)4 ether (84) 72:28 ZnCl4 THF (72) 77:23	299

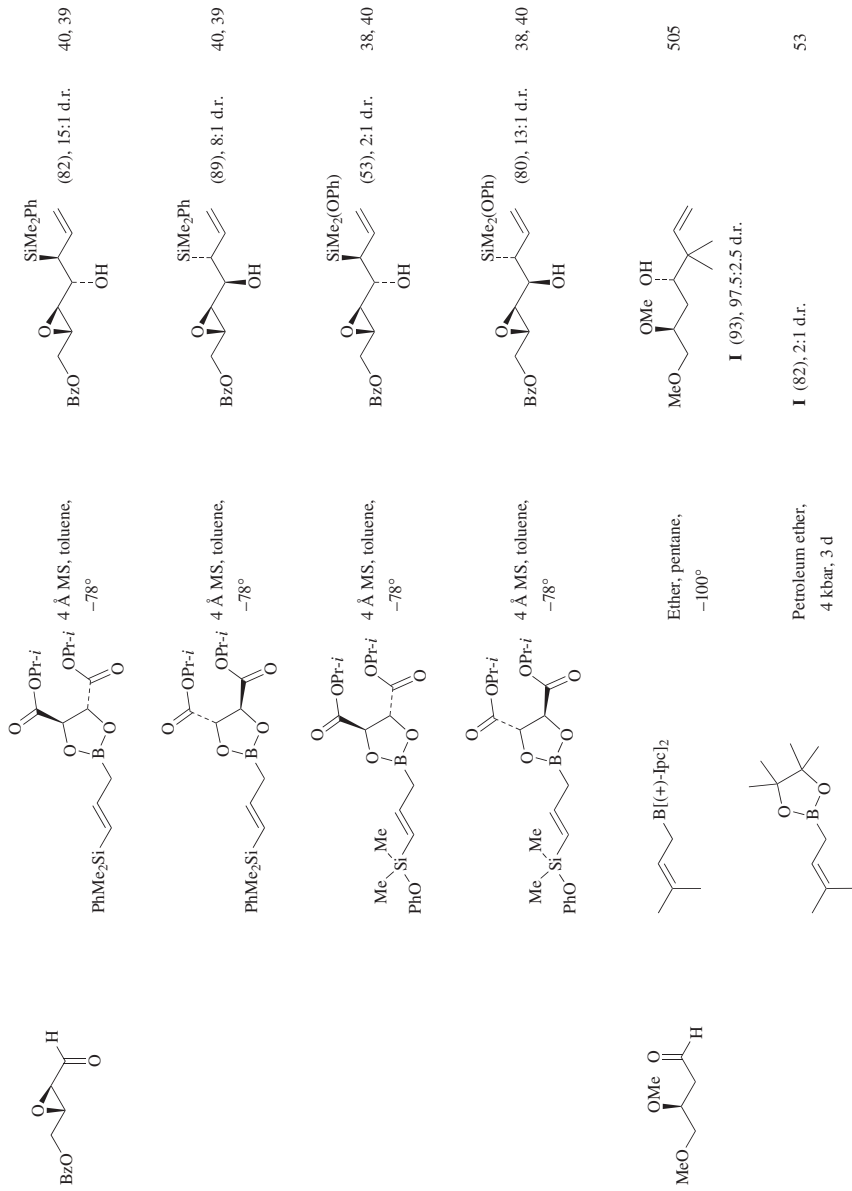
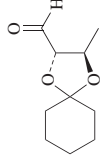

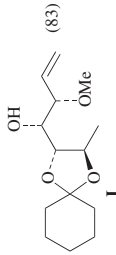
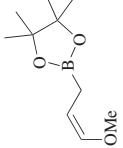
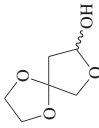
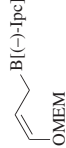
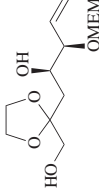
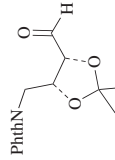

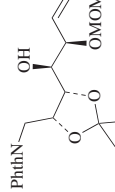
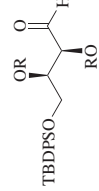
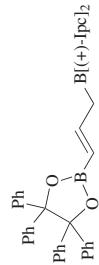
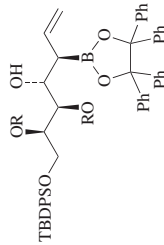


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		THF, -78°	 (83)	766, 767
		CH <sub>2</sub> Cl <sub>2</sub> , -78° to rt, 24-48 h	<b>I</b> (70-75), 95:5 d.r.	118, 767, 768
		THF, -95°, 3 h; rt	 (87), 95, >99:1 d.r.	769, 770
		THF, -78°	 (60), >96.5:3.5 d.r.	771
		CH <sub>2</sub> Cl <sub>2</sub> , -78°		201
			R PMB (-) t-Bu (-)	

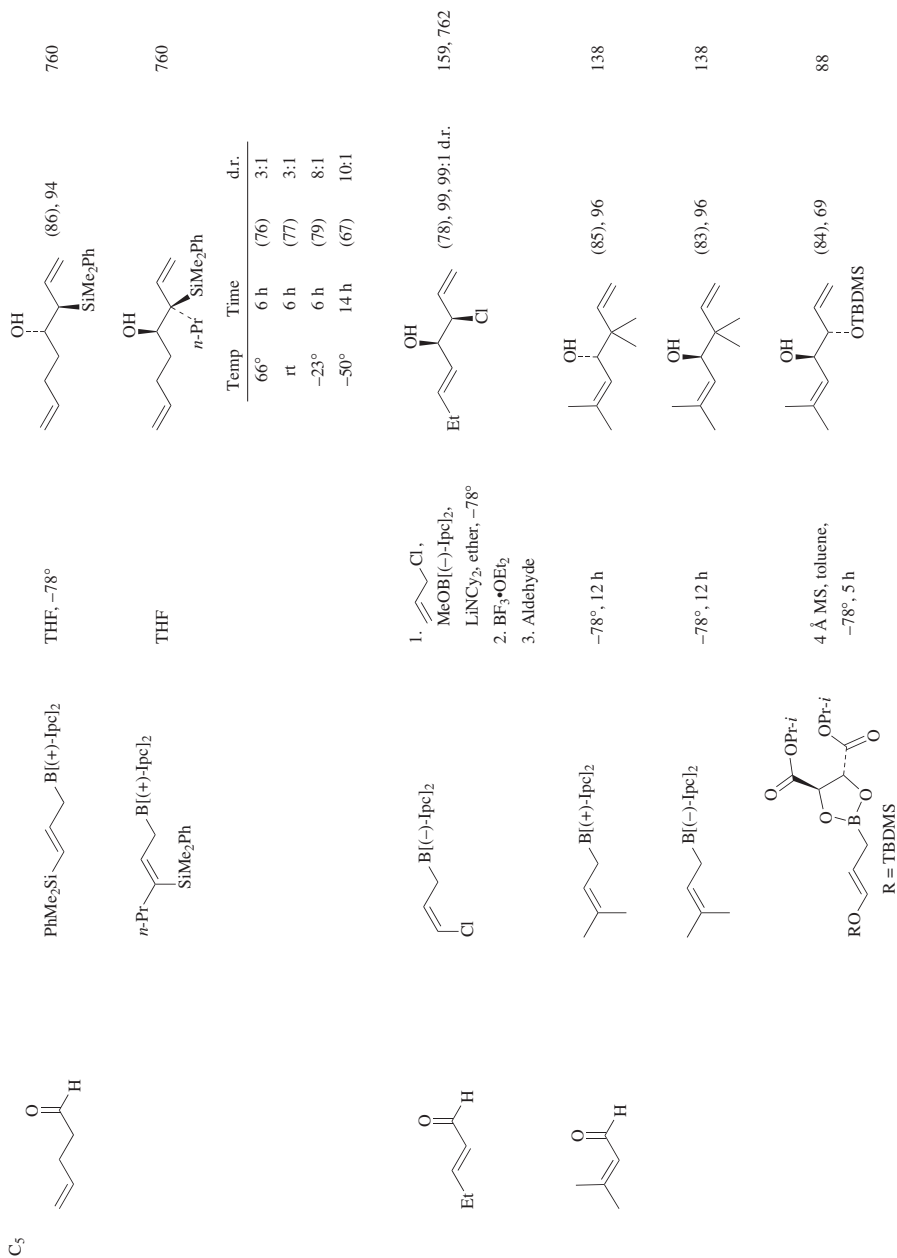
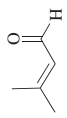
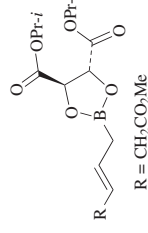
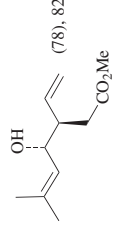

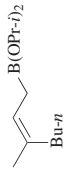
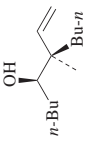
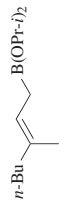
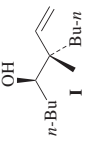
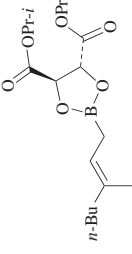
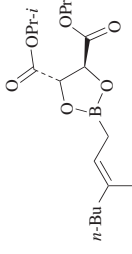
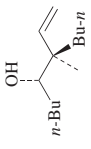
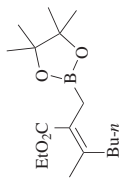
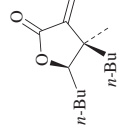


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C <sub>5</sub> 	 R = CH <sub>2</sub> CO <sub>2</sub> Me	-78°, 5 h	 (78), 82	90
		THF, -78° to rt, 18 h	 (81), 89:11 d.r.	772
		THF, -78° to rt, 18 h	 (89), 95:5 d.r.	772
		4 Å MS, toluene, -78°, 5 h	<b>I</b> (83), 73, 97:3 d.r.	740
		4 Å MS, toluene, -78°, 5 h	 (77), 71, 96:4 d.r.	740
		Sc(OTf) <sub>3</sub> , toluene, rt, 6-24 h	 (62), 19:1 d.r.	24, 26



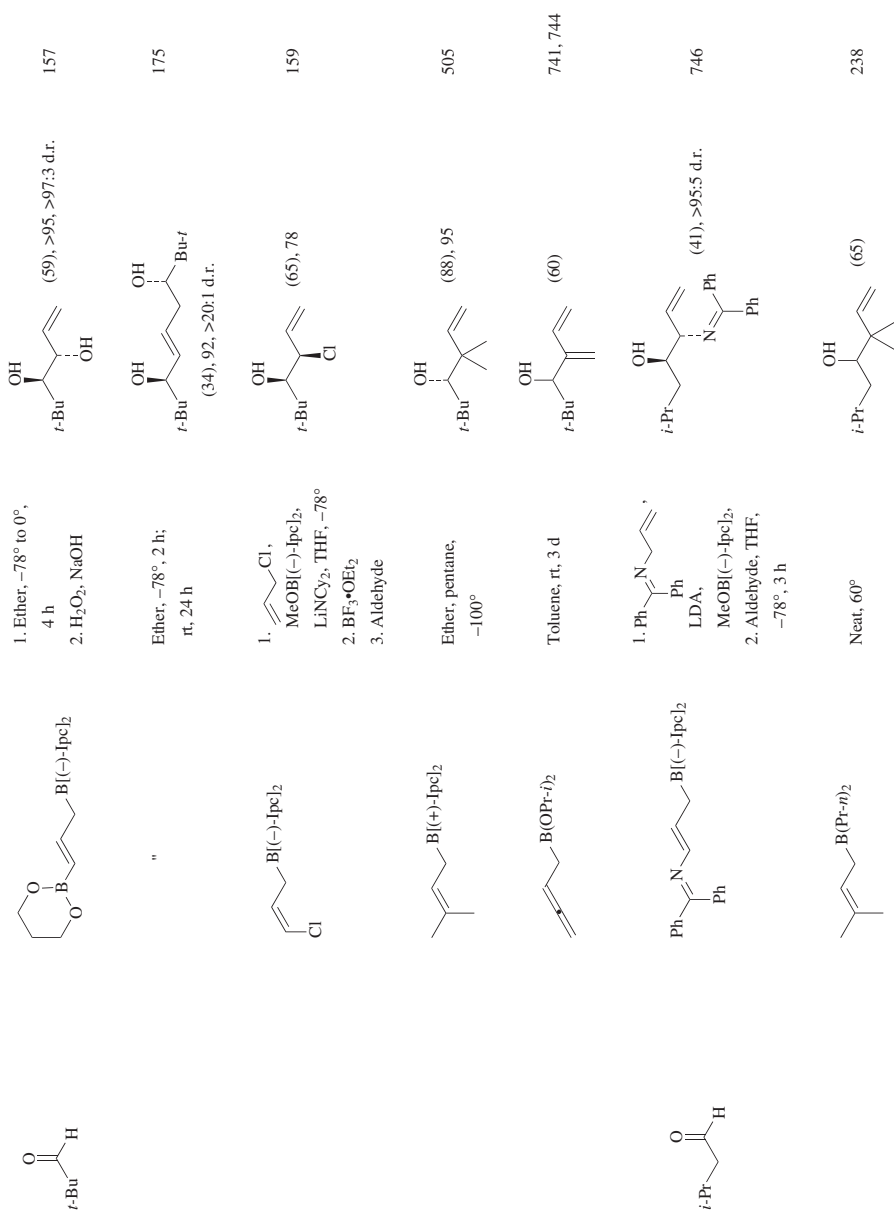
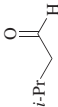
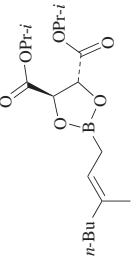
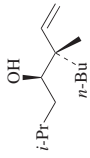
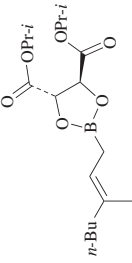
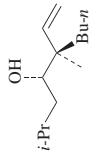
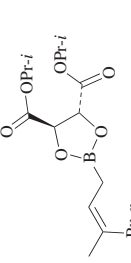
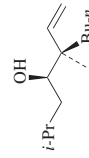
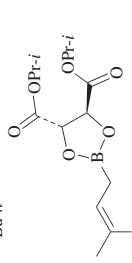
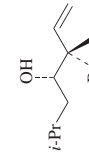
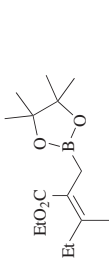
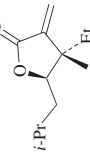
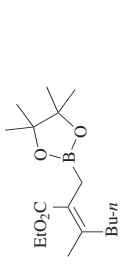
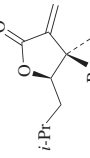


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		4 Å MS, toluene, -78°, 5 h	 (93), 84, 96:4 d.r.	740
		4 Å MS, toluene, -78°, 5 h	 (85), 72, 96:4 d.r.	740
		4 Å MS, toluene, -78°, 5 h	 (72), 63, 96:4 d.r.	740
		4 Å MS, toluene, -78°, 5 h	 (76), 66, 96:4 d.r.	740
		Sc(OTf) <sub>3</sub> , toluene, rt, 24 h	 (46), >20:1 d.r.	26
		Sc(OTf) <sub>3</sub> , toluene, rt, 6-24 h	 (53), 19:1 d.r.	24, 26

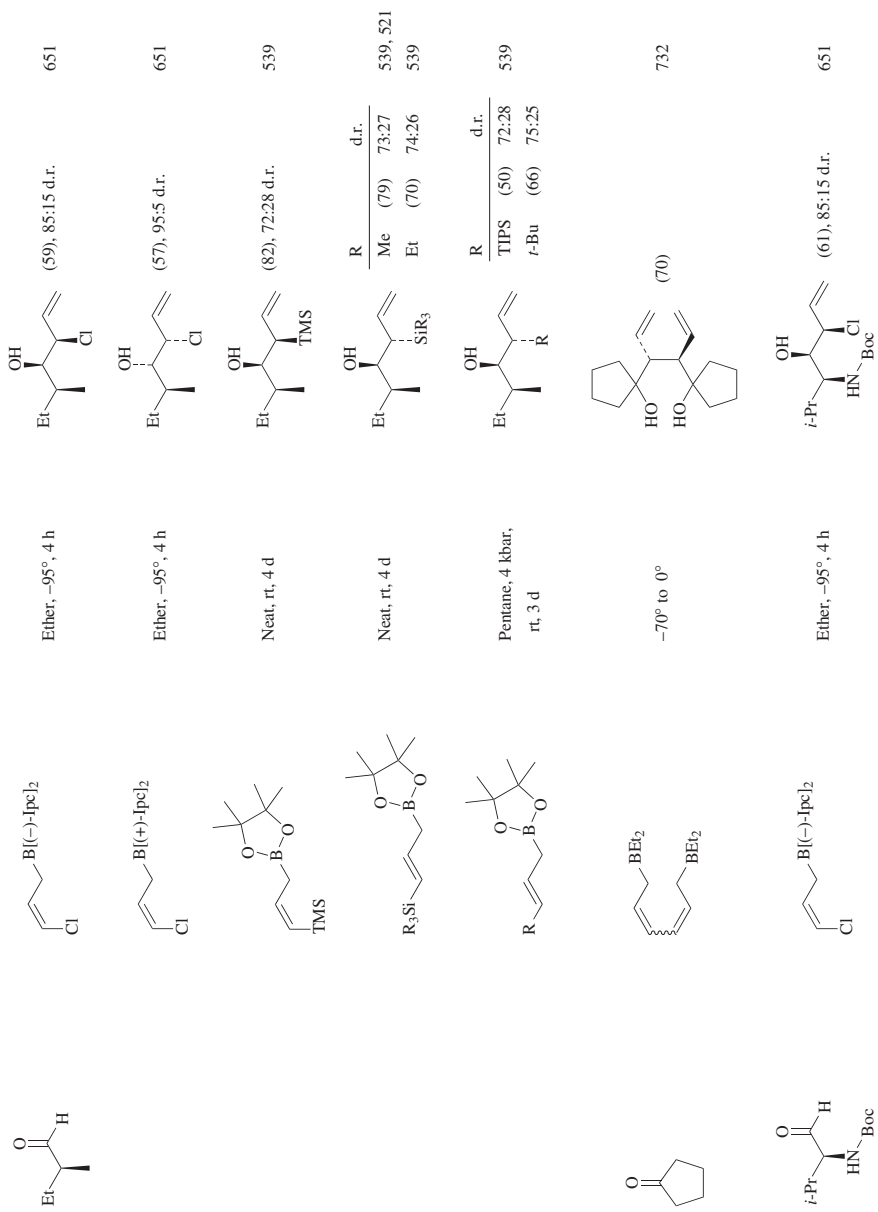
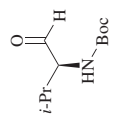

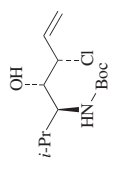

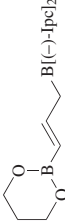
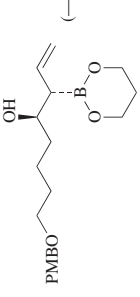
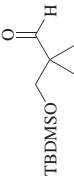
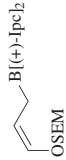
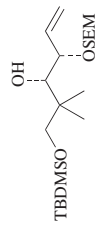
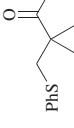
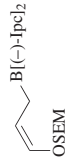
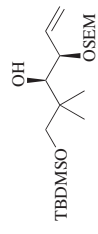
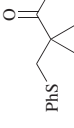
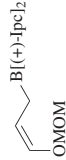
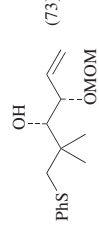
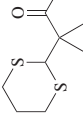

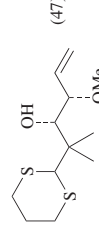


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
 $C_5$		Ether, $-95^\circ$ , 4 h	 (60), 99:1 d.r.	651
		—	 (—)	202
		THF, ether, $-78^\circ$	 (60), >95, >97.5:2.5 d.r.	511
		THF, ether, $-78^\circ$	 (49), >95, >19:1 d.r.	513
		THF, $-78^\circ$ to rt, 3 h	 (73)	773
		THF, $-78^\circ$	 (47)	515

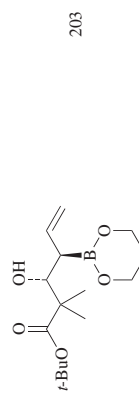
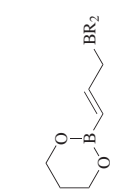
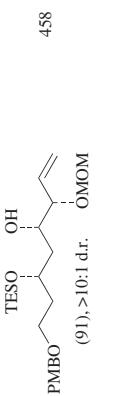
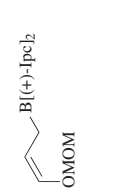
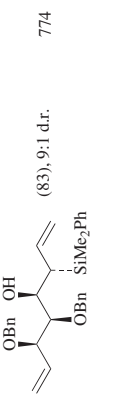
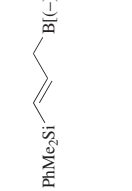
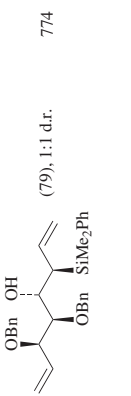
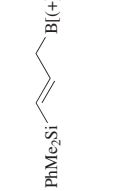
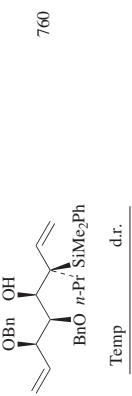
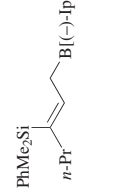
	-78°		203																				
<table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="text-align: left;">R</th> <th style="text-align: left;">Solvent</th> <th style="text-align: left;">Yield</th> <th style="text-align: left;">ee</th> </tr> </thead> <tbody> <tr> <td>(+)-Ipc</td> <td>ether</td> <td>77</td> <td>85</td> </tr> <tr> <td>(+)-Ipc</td> <td>CH<sub>2</sub>Cl<sub>2</sub></td> <td>74</td> <td>85</td> </tr> <tr> <td>(+)-Ipc</td> <td>toluene</td> <td>69</td> <td>83</td> </tr> <tr> <td>2-d-Icr</td> <td>ether</td> <td>36</td> <td>&gt;95</td> </tr> </tbody> </table>				R	Solvent	Yield	ee	(+)-Ipc	ether	77	85	(+)-Ipc	CH <sub>2</sub> Cl <sub>2</sub>	74	85	(+)-Ipc	toluene	69	83	2-d-Icr	ether	36	>95
R	Solvent	Yield	ee																				
(+)-Ipc	ether	77	85																				
(+)-Ipc	CH <sub>2</sub> Cl <sub>2</sub>	74	85																				
(+)-Ipc	toluene	69	83																				
2-d-Icr	ether	36	>95																				
	THF, -95° to rt, 3 h		458																				
	—		774																				
	—		774																				
	THF		760																				
<table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="text-align: left;">Temp</th> <th style="text-align: left;">d.r.</th> </tr> </thead> <tbody> <tr> <td>-30°</td> <td>(90)</td> </tr> <tr> <td>-78°</td> <td>(79)</td> </tr> </tbody> </table>				Temp	d.r.	-30°	(90)	-78°	(79)														
Temp	d.r.																						
-30°	(90)																						
-78°	(79)																						

TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

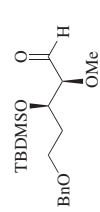
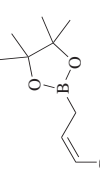
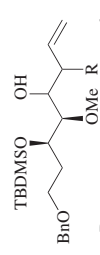
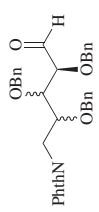
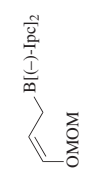
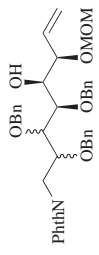
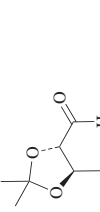
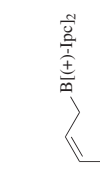
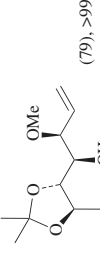
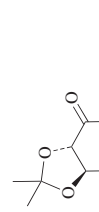
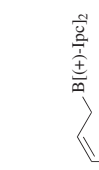
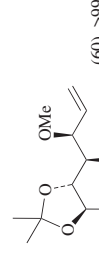
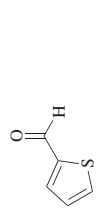
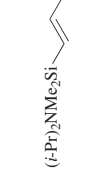
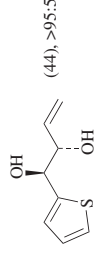
Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		—	 (85) 19:4 d.r. Synr:Anti 2:21 (86) 8:20 21:6	545
		THF, $-78^\circ$ to $-23^\circ$ , 12.5 h	 (73)	775
		$-78^\circ$	 (79), >99:1 d.r.	776
		$-78^\circ$	 (60), >99:1 d.r.	776
		1. Ether, $-78^\circ$ , 3 h 2. KF, H <sub>2</sub> O <sub>2</sub>	 (44), >95:5 d.r.	45



TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
$n$ -C <sub>5</sub> H <sub>11</sub> CHO		—	 (59), 97, >99:1 d.r.	250
		THF, -78° to 0°, 3 h	 (43), >95, >95:5 d.r.	730, 731
		THF, -78° to 0°, 3 h	 (40), >95, >95:5 d.r.	730, 731
		THF	 777	



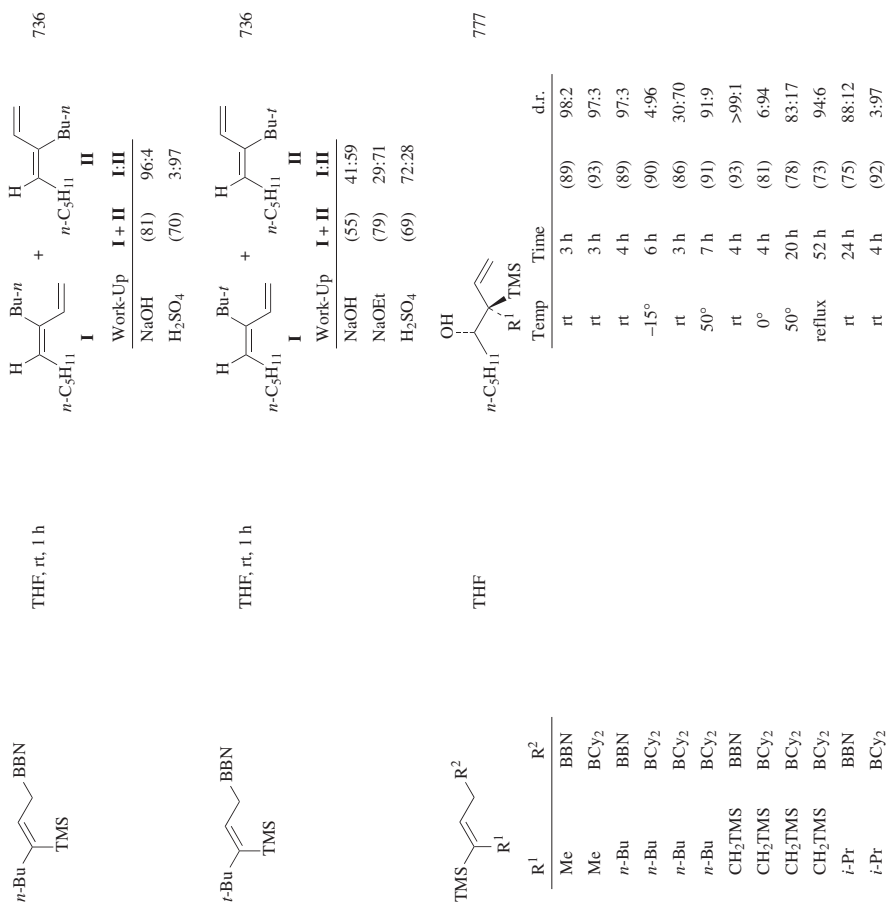
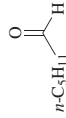
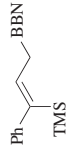
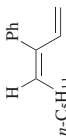
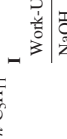
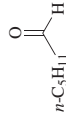
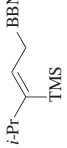
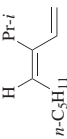
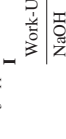
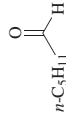
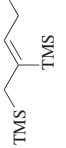
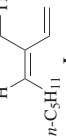
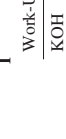
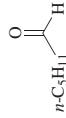
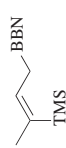
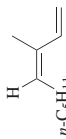
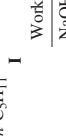


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.		
$C_6$ 		THF, rt, 1 h	 I +  II	736		
			Work-Up		I + II	I:II
			NaOH		(67)	96:4
			NaOEt		(80)	95:5
		H <sub>2</sub> SO <sub>4</sub>	(84)	5:95		
		THF, rt, 1 h	 I +  II	736		
			Work-Up		I + II	I:II
			NaOH		(77)	88:12
			NaOEt		(82)	88:12
		H <sub>2</sub> SO <sub>4</sub>	(65)	11:89		
		THF, rt, 1 h	 I +  II	735, 736		
			Work-Up		I + II	I:II
			KOH		(82)	97:3
			NaOEt		(85)	97:3
		H <sub>2</sub> SO <sub>4</sub>	(87)	0.5:99.5		
		THF, rt, 1 h	 I +  II	736		
			Work-Up		I + II	I:II
			NaOH		(73)	95:5
			NaOEt		(72)	98:2
		H <sub>2</sub> SO <sub>4</sub>	(65)	3:97		

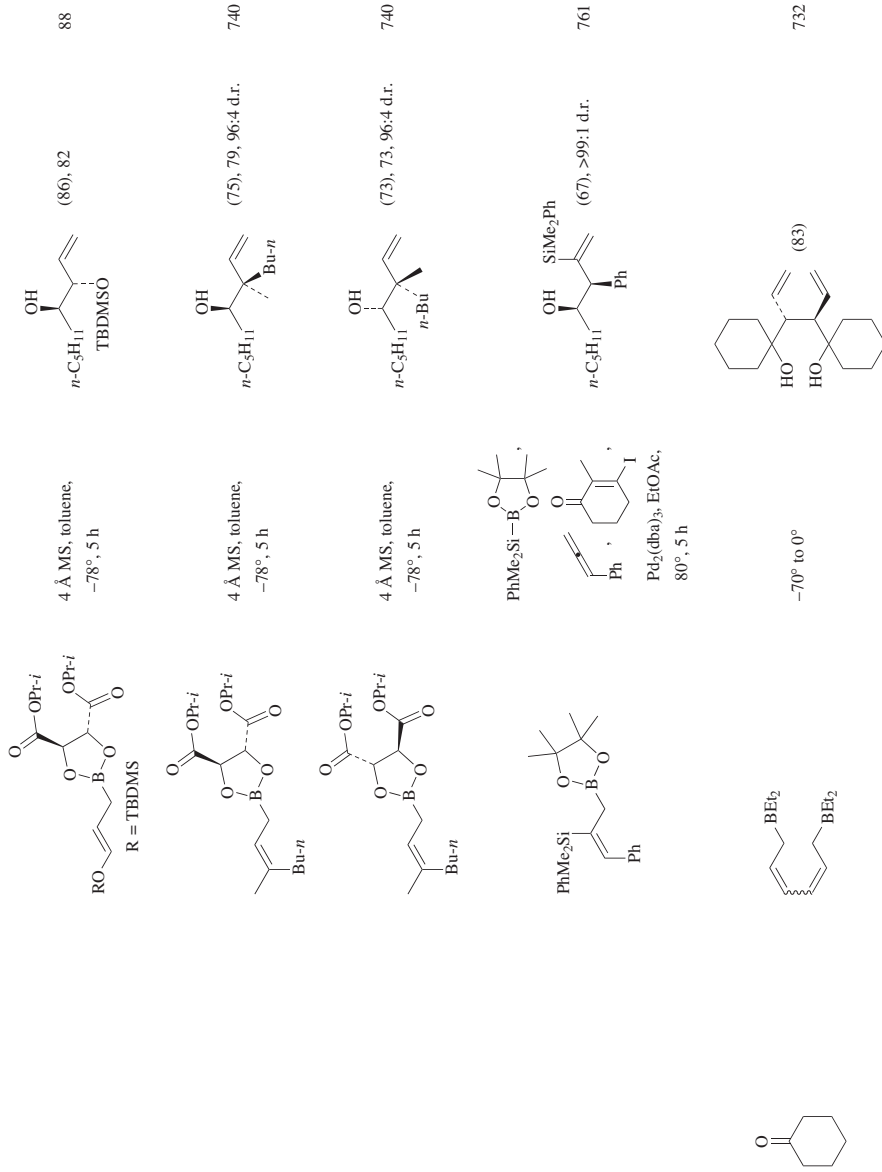


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)



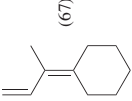
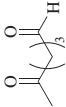
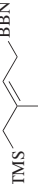
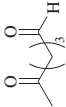
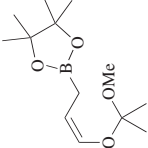
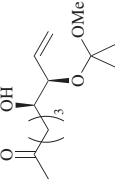



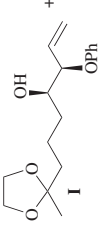
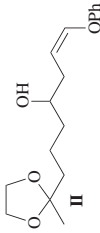
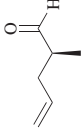
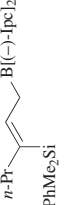


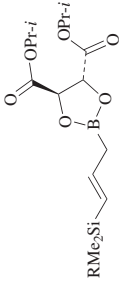
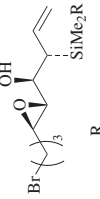
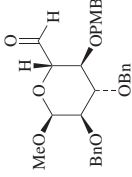
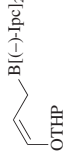
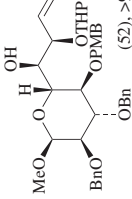
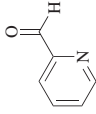

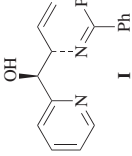
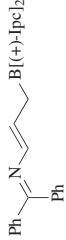
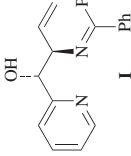
Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		1. THF, rt, 1 h 2. NaOH	 (67)	736
		THF, rt, 1 h	Work-Up KOH (58) H <sub>2</sub> SO <sub>4</sub> (61)	735, 736
		Neat, 10 d	 (77), 94:6 d.r.	47, 36
			 I +  II I + II (50), EII = 1.85:1	46
		THF, -50°	 (73), 83:10 d.r.	760



TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		4 Å MS, toluene, -78°	 R 2-(5-methyl)furyl (68) 90:10 menthothuryl (82) 96:4 d.r.	158
		THF, -78° to rt, 3 h		778
		1. Ph-CH=CH-CH <sub>2</sub> -N(Ph)-CH=CH <sub>2</sub> , LDA, MeOB[(-)-]ipc]2 2. Aldehyde, THF, -78°, 3 h	 I (49), 91, >95:5 d.r.	746
		THF, -78°	I (49), 91, >95:5 d.r.	160
		1. Ph-CH=CH-CH <sub>2</sub> -N(Ph)-CH=CH <sub>2</sub> , LDA, MeOB[(+)-]ipc]2 2. Aldehyde, THF, -78°, 3 h	 I (51), 90, >95:5 d.r.	746
		THF, -78°	I (51), 90, >95:5 d.r.	160

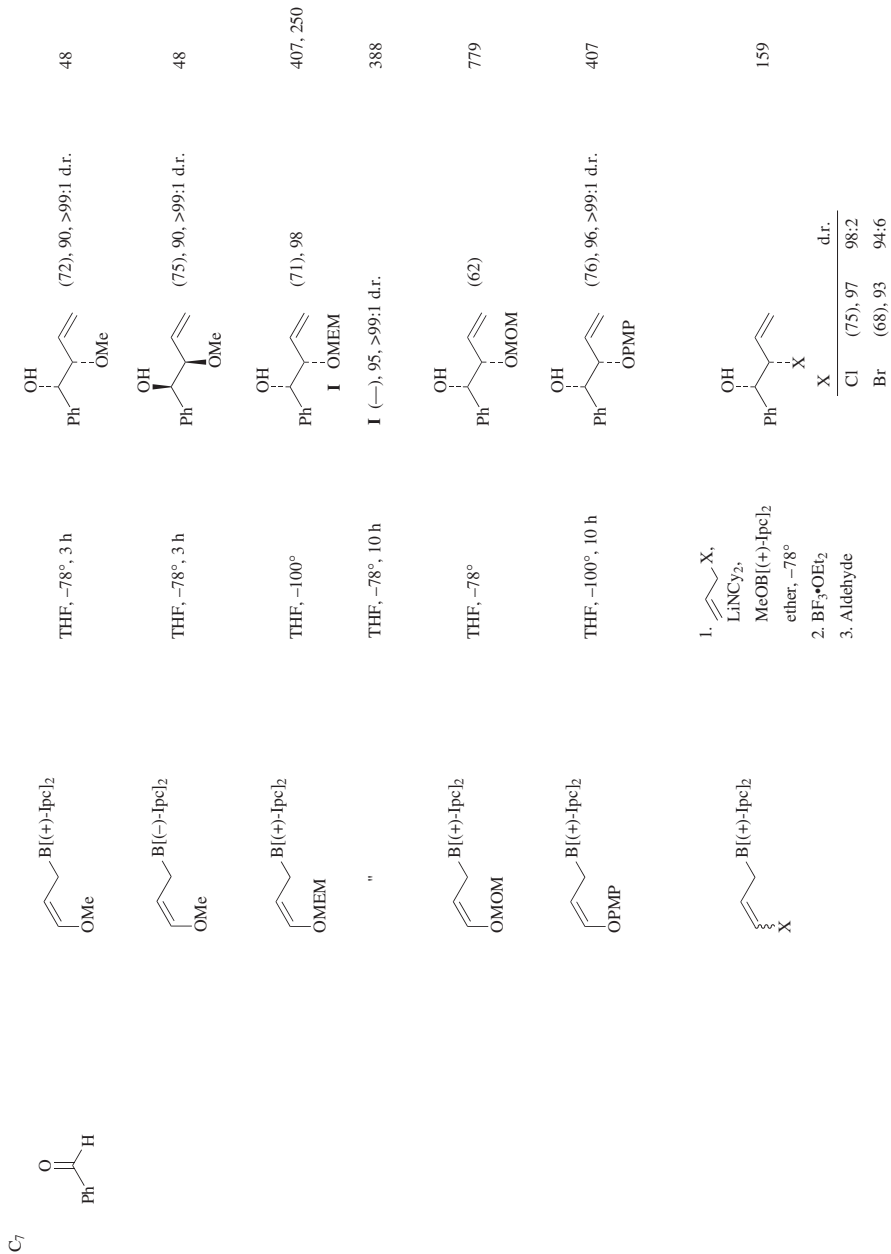



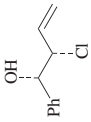


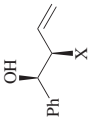

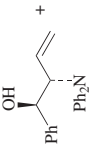

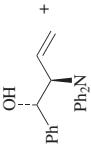


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		1.  LDA, MeOB[(-)-Ipc]2, ether, -78° 2. BF <sub>3</sub> ·OEt <sub>2</sub> (x equiv) 3. Aldehyde	 x 2.5 (-), 84 1.33 (-), 95	159
		1.  MeOB[(-)-Ipc]2, LiNCy <sub>2</sub> , -78° 2. BF <sub>3</sub> ·OEt <sub>2</sub> 3. Aldehyde	 X Solvent d.r. Cl ether (78), 98 98:2 Cl THF (77), 76 99:1 Br ether (77), 95 96:4	159
		THF, -78° to 0°, 3 h	 (48), >95, >95:5 d.r. (15)	730, 731
		THF, -78° to 0°, 3 h	 (47), >95, >95:5 (12)	730



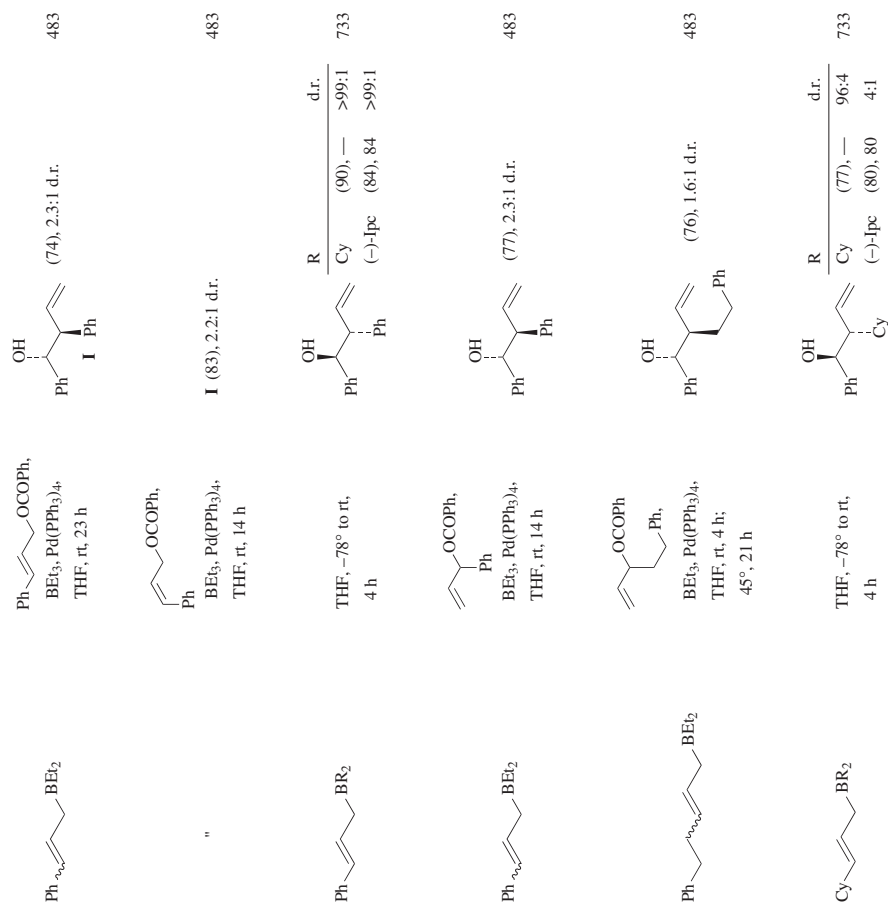


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)



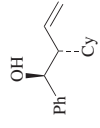

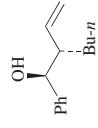

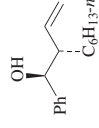
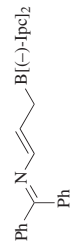
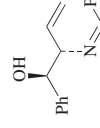
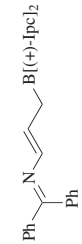
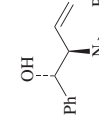
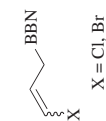
Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
$C_7$ 		$CCl_4, 0^\circ$	 (-), 96:4 d.r.	733
		THF, $-78^\circ$ to rt, 4 h	 R Cy (81), — (-)-Ipc (78), 78	d.r. 87:13 88:12 733
		THF, $-78^\circ$ to rt, 4 h	 R Cy (82), — (-)-Ipc (81), 74	d.r. 88:12 9:1 733
		THF, $-78^\circ$	 (53), 93, >95:5 d.r.	160
		1. Ph-CH=CH-CH2-N(Ph)Ph, LDA, MeOB[(+)-Ipc]2 2. Aldehyde, THF, $-78^\circ$ , 3 h	 I (52), 90, >95:5 d.r.	746
	"	THF, $-78^\circ$	I (52), 90, >95:5 d.r.	160



TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Ether, -78°, 2 h		175
"	"	Ether, -78°, 2 h; rt, 24 h		175
"		1. Ether, -78° to 0°, 4 h 2. H <sub>2</sub> O <sub>2</sub> , NaOH		157
"	"	Ether, -78°, 2 h; rt, 24 h		175
"		1. MeOB[(-)-Ipc] <sub>2</sub> , LiNCy <sub>2</sub> , ether 2. BF <sub>3</sub> ·OEt <sub>2</sub> (x equiv) 3. Aldehyde		159, 762

x	Temp	X	(I+II):III	II:I	II % ee
2.63	-78°	Cl	98:2	91:9	78
2.63	-78°	Br	96:4	9:1	74
2.63	-95°	Cl	99:1	99:1	88
2.65	-95°	Br	98:2	94:6	86
2.65	-95°	Cl	>99:1	99:1	87
1.33	-95°	Cl	>99:1	99:1	98
1.66	-95°	Cl	>99:1	99:1	97
2.63	-95° to -78°	Cl	>99:1	99:1	86
1.33	-95° to -78°	Cl	>99:1	99:1	85



1.  $\text{MeOBBN}$ ,  
LDA, THF
2.  $\text{BF}_3 \cdot \text{OEt}_2$
3. Aldehyde

**I + II + III**

159

X	Temp	I + II + III	II:(I+II)
Cl	-78°	(79)	85:15
Br	-78°	(76)	88:12
Cl	-95°	(77)	91:9

1.  $\text{MeOBBN}$ ,  
LiNCy<sub>2</sub>, THF
2.  $\text{BF}_3 \cdot \text{OEt}_2$  (x equiv)
3. Aldehyde



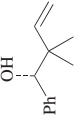
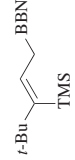
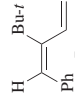

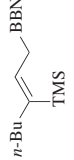
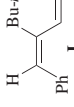

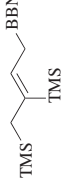
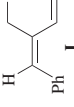

"  
X = Cl

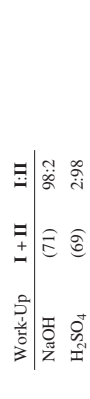
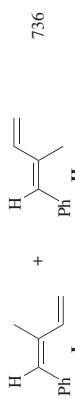
**I + II + III, II:I = 99:1**

159

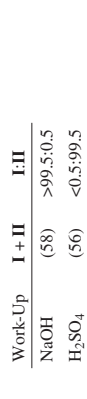
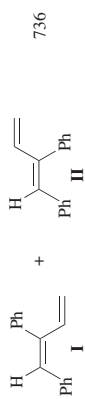
x	Temp	(I+II):III
2.63	-95°	95:5
1.33	-95° to -78°	99:1
1.33	-95° to -62°	99:1
1.33	-95° to -41°	>99:1
1.33	-95°	>99:1
1.5	-95°	96:4

TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

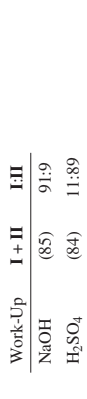
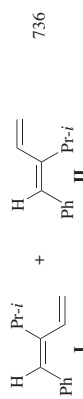
Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Ether, pentane, -100°	 (92), 95	505
		THF, rt, 1 h	 I +  II Work-Up I + II I:II NaOH (70) 41:59 NaOEt (83) 29:71 H <sub>2</sub> SO <sub>4</sub> (68) 62:38	736
		THF, rt, 1 h	 I +  II Work-Up I + II I:II NaOH (81) 98:2 H <sub>2</sub> SO <sub>4</sub> (75) 2:98	736
		THF, rt, 1 h	 I +  II Work-Up I + II I:II KOH (88) 98:2 H <sub>2</sub> SO <sub>4</sub> (83) 2:98	735, 736



736



736


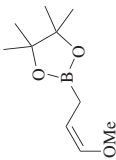
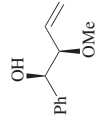
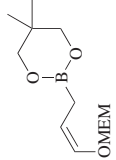
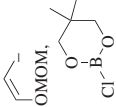
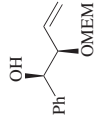
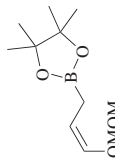
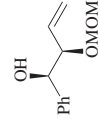
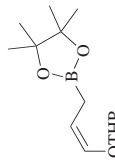
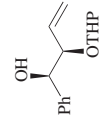
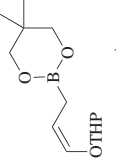
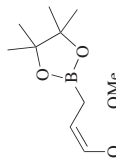
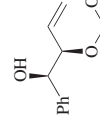


736



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TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
$C_7$ 		Neat, 20°, 2 d	 (86), >95:5 d.r.	47, 33, 36
		 OMOM, Cl <sup>-</sup>	 (59)	46
		Neat, 60°, 4 h	 (82), >95:5 d.r.	47, 36
		Neat, rt, 48 h	 I (70-80), 93:7 d.r.	34
		—	I (70-80), 93:7 d.r.	104
		Neat, rt	 (93), 94:6 d.r.	47, 36



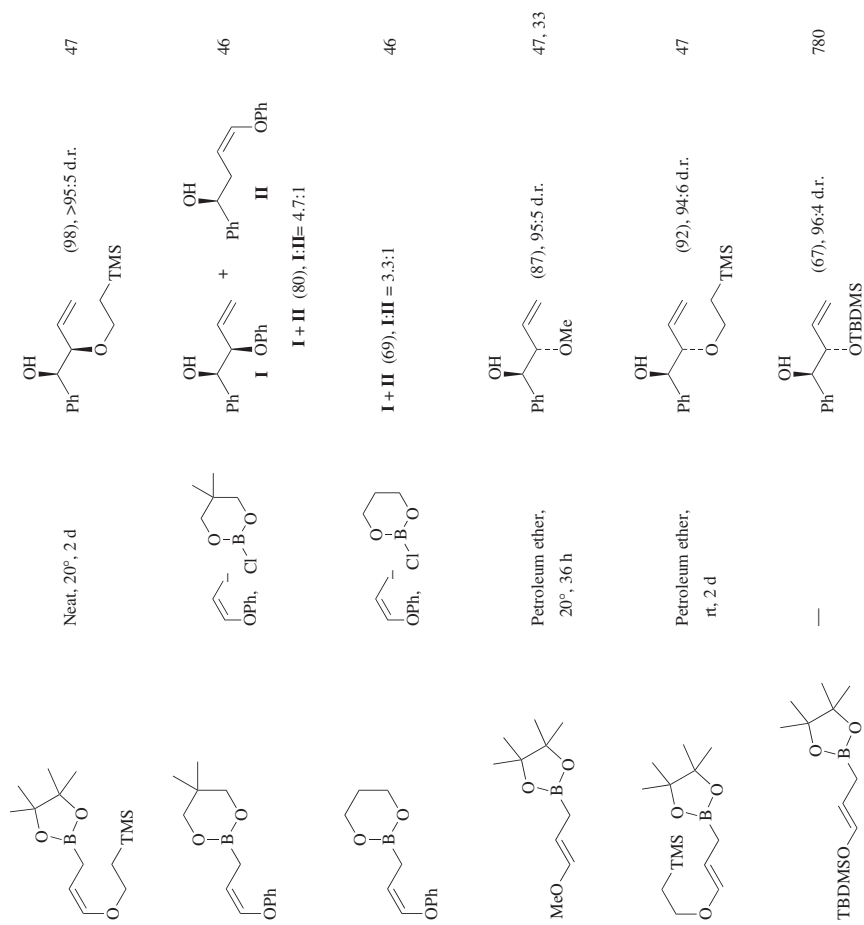

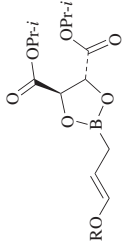
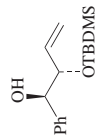
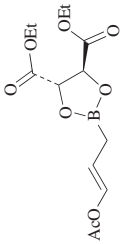
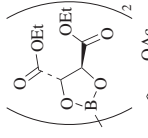
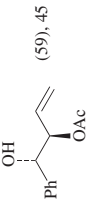
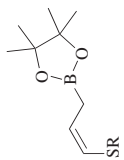
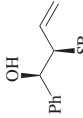
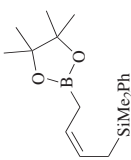
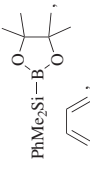
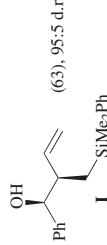


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
	 R = TBDMS	4 Å MS, toluene, -78°, 5 h	 (82), 67	88
		 Pd <sub>2</sub> (dba) <sub>3</sub> , DMSO, toluene, 20°, 21 h	 (59), 45	349
		—		737
		 Pr(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> , octane, 50°	 (63), 95:5 d.r.	781
	"	CH <sub>2</sub> Cl <sub>2</sub> , rt	<b>I</b> (85)	72

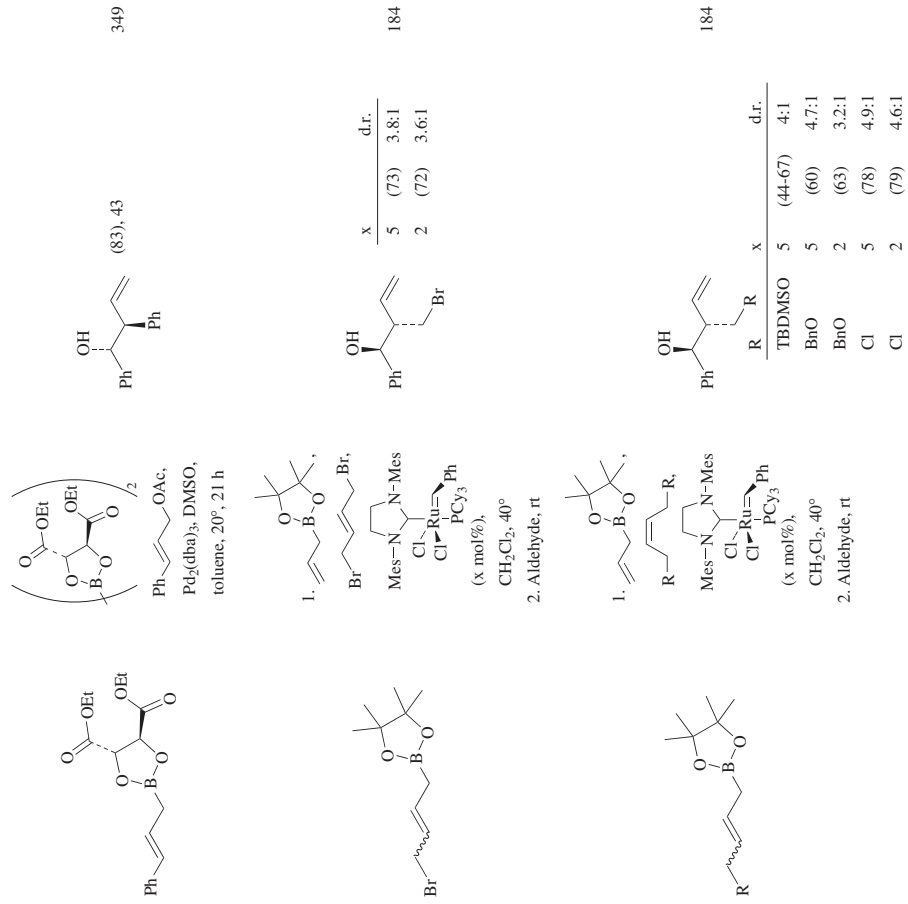

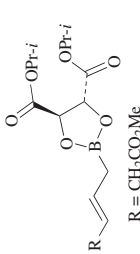
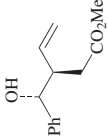
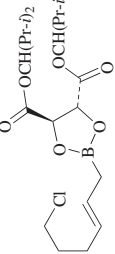
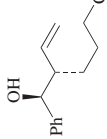
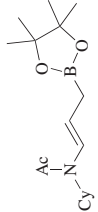
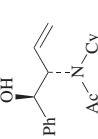
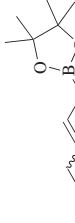
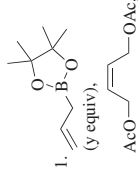
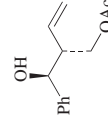


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
$C_7$ 	 R = $CH_2CO_2Me$	$-78^\circ$ , 5 h	 (30), 49	90
		Toluene/pentane (10:3), $-100^\circ$	 (80), 83	738
		Neat, $60^\circ$ , 5 h	 (52)	178
x equiv		1.  (y equiv), AcO-CH=CH-CH2-OAc, Cl $^+$ -Ru-PCy $_3$ , Cl $^-$ -PCy $_3$ , Mes-N-N-Mes Cl $^-$ -N-Mes Cl $^-$ -N-Mes PCy $_3$ , Ph, PCy $_3$ , CH $_2$ Cl $_2$ , $40^\circ$ 2. Aldehyde, rt	 x y Cat. d.r. 1.5 3 A (32) 1.8:1 1.5 3 B (75) 4.5:1 1.5 3 B (75) 4.5:1 1.5 0.5 B (57) 4.7:1 0.75 3 B (75) 4.5:1	184

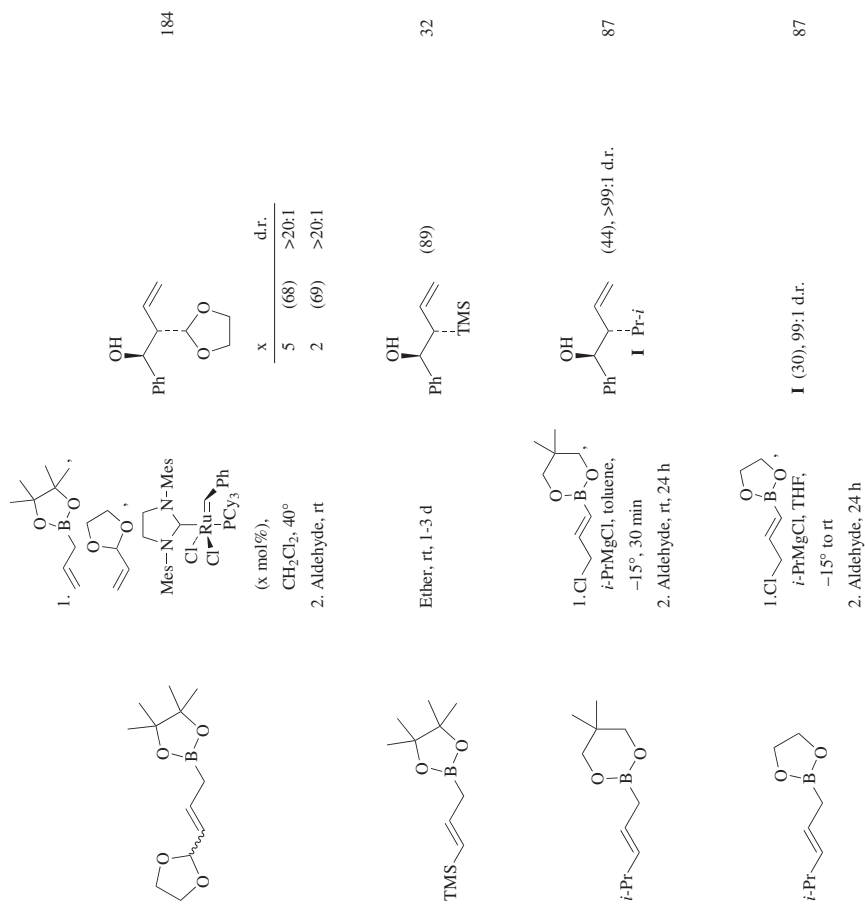
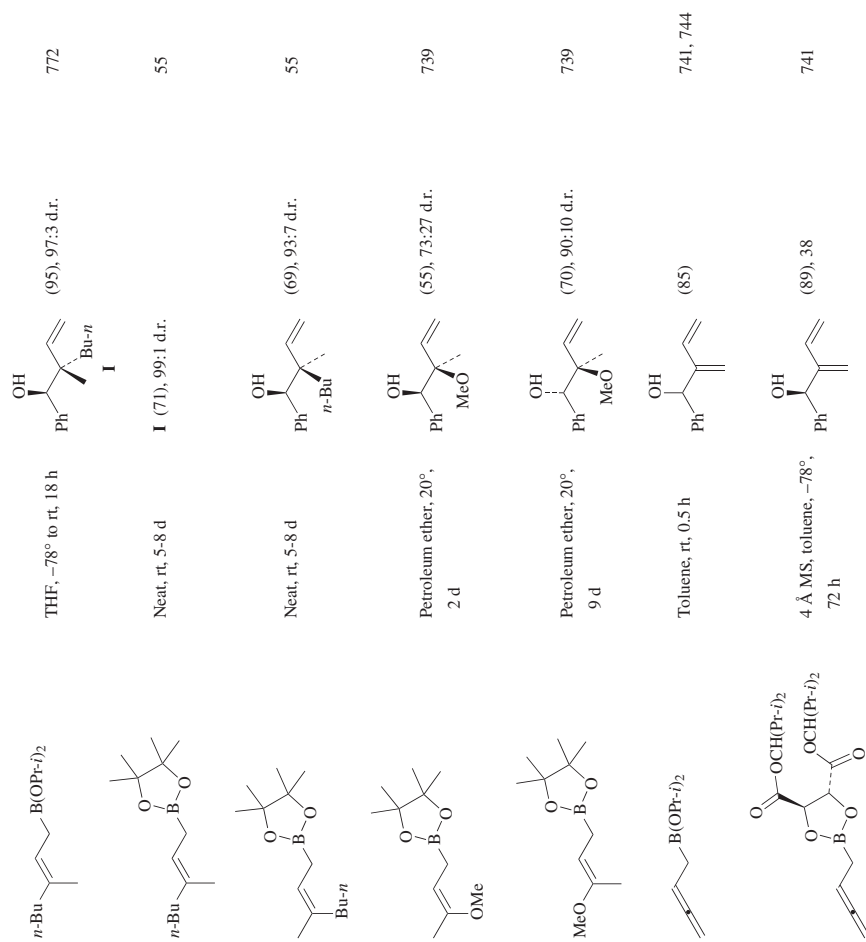


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.																																	
		1.		184																																	
		$R^2$ (x equiv), Mes-N-N-Mes Cl Cl Ph PCy <sub>3</sub> Ru Cl Cl ( $\gamma$ mol%), CH <sub>2</sub> Cl <sub>2</sub> , -40° 2. Aldehyde, rt	<table border="1"> <thead> <tr> <th>R<sup>2</sup></th> <th>x</th> <th>y</th> </tr> </thead> <tbody> <tr> <td><i>t</i>-Bu</td> <td>5</td> <td>5</td> </tr> <tr> <td>Me<sub>2</sub>COH</td> <td>20</td> <td>5</td> </tr> <tr> <td>Me<sub>2</sub>COH</td> <td>20</td> <td>2</td> </tr> <tr> <td>-(CH<sub>2</sub>)<sub>4</sub>-</td> <td>3</td> <td>5</td> </tr> <tr> <td>-(CH<sub>2</sub>)<sub>4</sub>-</td> <td>10</td> <td>5</td> </tr> <tr> <td>-(CH<sub>2</sub>)<sub>5</sub>-</td> <td>10</td> <td>5</td> </tr> <tr> <td>Ph</td> <td>20</td> <td>5</td> </tr> <tr> <td>2-BrC<sub>6</sub>H<sub>4</sub></td> <td>20</td> <td>5</td> </tr> <tr> <td>2-BrC<sub>6</sub>H<sub>4</sub></td> <td>5</td> <td>5</td> </tr> <tr> <td>2-BrC<sub>6</sub>H<sub>4</sub></td> <td>10</td> <td>5</td> </tr> </tbody> </table>	R <sup>2</sup>	x	y	<i>t</i> -Bu	5	5	Me <sub>2</sub> COH	20	5	Me <sub>2</sub> COH	20	2	-(CH <sub>2</sub> ) <sub>4</sub> -	3	5	-(CH <sub>2</sub> ) <sub>4</sub> -	10	5	-(CH <sub>2</sub> ) <sub>5</sub> -	10	5	Ph	20	5	2-BrC <sub>6</sub> H <sub>4</sub>	20	5	2-BrC <sub>6</sub> H <sub>4</sub>	5	5	2-BrC <sub>6</sub> H <sub>4</sub>	10	5	(35) (51) (17) (49) (58) (34) (66) (45) (25) (60)
R <sup>2</sup>	x	y																																			
<i>t</i> -Bu	5	5																																			
Me <sub>2</sub> COH	20	5																																			
Me <sub>2</sub> COH	20	2																																			
-(CH <sub>2</sub> ) <sub>4</sub> -	3	5																																			
-(CH <sub>2</sub> ) <sub>4</sub> -	10	5																																			
-(CH <sub>2</sub> ) <sub>5</sub> -	10	5																																			
Ph	20	5																																			
2-BrC <sub>6</sub> H <sub>4</sub>	20	5																																			
2-BrC <sub>6</sub> H <sub>4</sub>	5	5																																			
2-BrC <sub>6</sub> H <sub>4</sub>	10	5																																			
		4 Å MS, toluene, -78°, 5 h		740																																	
		4 Å MS, toluene, -78°, 5 h		740																																	
		THF, -78° to rt, 18 h		772																																	

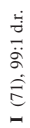
C<sub>7</sub>



772

(95), 97:3 d.r.

55



55

(69), 93:7 d.r.

739



(55), 73:27 d.r.

739



(70), 90:10 d.r.

741, 744

(85)


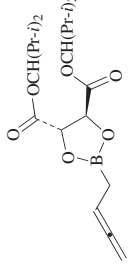
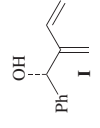
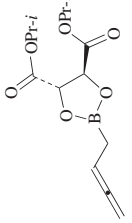
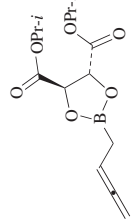
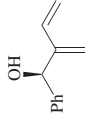
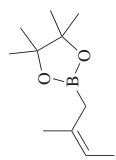
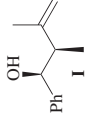
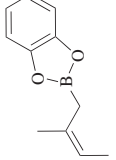
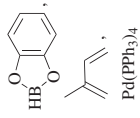
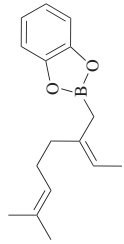
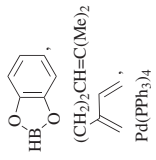
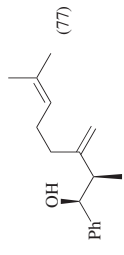


741

(89), 38



TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		4 Å MS, toluene, -78°, 72 h	 (86), 37	741
		4 Å MS, toluene, -78°, 72 h	<b>I</b> (90), 49	741
		4 Å MS, toluene, -78°, 72 h	 (95), 43	741
		—	 (80), 9:1 d.r.	52
			<b>I</b> (89)	550
			 (77)	550





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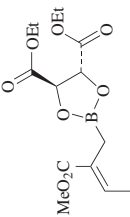
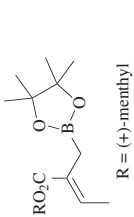
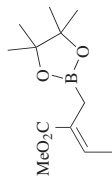
See table

Solvent	Temp	Time	d.r.
THF	rt	7 d	(64) 84:16
THF	70°	4 d	(83) 85:15
toluene	100°	1 d	(87) 87:13

782

THF, rt, 5 d

**I** (50), 25, 87:13 d.r.



782

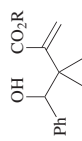
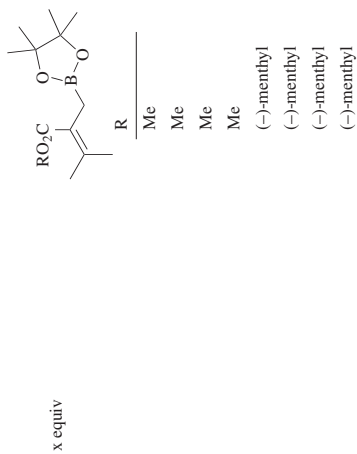
See table

Solvent	Temp	Time	d.r.
DMF	rt	2 d	(80), 26 94:6
DMF	0°	3 d	(52), 27 95:5
DMF/THF	-25°	6 d	(76), 25 96:4
DMF/THF	-78°	6 d	(40), 20 94:6
DMF/THF	-25°	7 d	(56), 21 98:2
THF	0°	2 d	(75), 22 98:2
THF <sup>b</sup>	0°	2 d	(69), 19 98:2
CH <sub>2</sub> Cl <sub>2</sub>	0°	2 d	(64), 16 98:2
4 Å MS, CH <sub>2</sub> Cl <sub>2</sub>	0°	2 d	(67), 22 98:2
toluene	0°	2 d	(74), 25 98:2
4 Å MS, toluene	0°	2 d	(76), 12 98:2

TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.	
		See table		782	
			Solvent	d.r.	
			THF	rt	7 d (75), 10 79:21
			toluene	100°	3 d (80), 8 83:17
			<b>I</b> (60), >20:1 d.r.		59, 26
		Toluene, 80°, 16-120 h		550	
		1. Neat, rt, 14 d 2. pTSA		(55), >95	
		L.A., rt, 6-24 h		L.A.	
			Solvent		
			Sc(OTf) <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub> (72)	
			Sc(OTf) <sub>3</sub>	toluene (93)	
			Cu(OTf) <sub>2</sub>	toluene (67)	
			Yb(OTf) <sub>3</sub>	toluene (91)	

Toluene, rt, >12 d **I** (89), >20:1 d.r. 59, 26



Catalyst, toluene

30

x	Catalyst	Temp	Time
0.9	none	rt	24 h (<5)
0.9	CF <sub>3</sub> CO <sub>2</sub> H	rt	24 h (77)
0.9	Tf <sub>2</sub> NH	rt	24 h (99)
0.9	TfOH	rt	24 h (99)
0.9	TfOH	0°	16 h (78)
0.9	Sc(OTf) <sub>3</sub>	0°	16 h (<5)
1.5	TfOH	0°	16 h (96)
2.0	TfOH	0°	16 h (99)

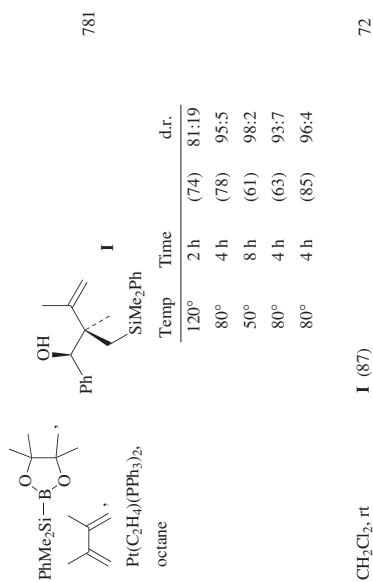
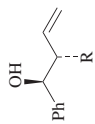
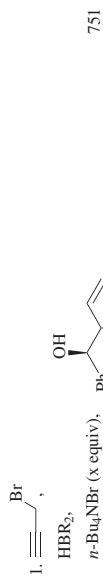
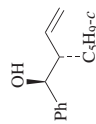
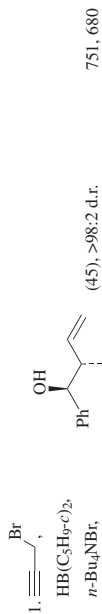


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		1. 2. $\text{Pt}(\text{dba})_2$ , $\text{PCy}_3$ , benzene, rt 3. Aldehyde, $-78^\circ$ , 3 h 3. $\text{NaOH}$ , $\text{H}_2\text{O}_2$	(65), 33, >19:1 d.r.	185
		$\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ , octane, $80^\circ$	(60), 99:1 d.r.	781
		1. $\text{HBCy}_2$ , $n\text{-Bu}_4\text{NBr}$ , $-78^\circ$ to $0^\circ$ , 1 h 2. Aldehyde, $0^\circ$ to rt, 1 h	(68), >98:2 d.r.	680
		1. $\text{HB}(\text{Thex})_2$ , $n\text{-Bu}_4\text{NBr}$ , $-78^\circ$ to $0^\circ$ , 1 h 2. Aldehyde, $0^\circ$ to rt, 1 h	(40), >98:2 d.r.	680



x	Time 1	Time 2	R
none	0.5 h	2 h	Cy (22)
none	2 h	2 h	Cy (63)
none	12 h	2 h	Cy (73)
0.1	1 h	2 h	Cy (85)
none	1 h	3 h	siamyl (1)
none	12 h	3 h	siamyl (26)
0.1	12 h	3 h	siamyl (46)

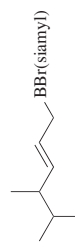
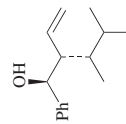
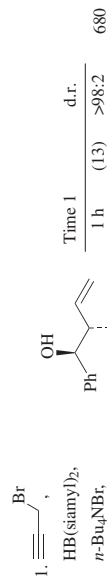

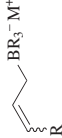

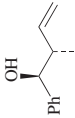
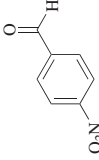

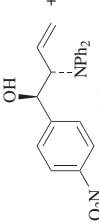
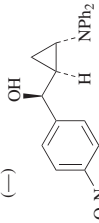
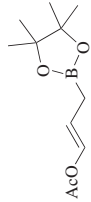

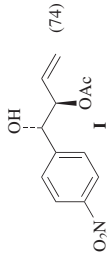


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.																												
		 BR <sub>3</sub> , -70°, 1 h		783																												
			<table border="1"> <thead> <tr> <th>R</th> <th>M</th> <th>Solvent</th> <th>d.r.</th> </tr> </thead> <tbody> <tr> <td>Et</td> <td>Li</td> <td>ether</td> <td>(90) 82:18</td> </tr> <tr> <td>Et</td> <td>MgBr</td> <td>ether</td> <td>(95) 50:50</td> </tr> <tr> <td>Et</td> <td>Li</td> <td>THF</td> <td>(91) 83:17</td> </tr> <tr> <td>Et</td> <td>Li</td> <td>ether, HMPA</td> <td>(83) 83:17</td> </tr> <tr> <td><i>n</i>-Bu</td> <td>Li</td> <td>ether</td> <td>(89) 83:17</td> </tr> <tr> <td><i>s</i>-Bu</td> <td>Li</td> <td>ether</td> <td>(85) 61:39</td> </tr> </tbody> </table>	R	M	Solvent	d.r.	Et	Li	ether	(90) 82:18	Et	MgBr	ether	(95) 50:50	Et	Li	THF	(91) 83:17	Et	Li	ether, HMPA	(83) 83:17	<i>n</i> -Bu	Li	ether	(89) 83:17	<i>s</i> -Bu	Li	ether	(85) 61:39	
R	M	Solvent	d.r.																													
Et	Li	ether	(90) 82:18																													
Et	MgBr	ether	(95) 50:50																													
Et	Li	THF	(91) 83:17																													
Et	Li	ether, HMPA	(83) 83:17																													
<i>n</i> -Bu	Li	ether	(89) 83:17																													
<i>s</i> -Bu	Li	ether	(85) 61:39																													
		THF, -78° to 0°, 3 h		730																												
			 (-), >95, >95:5 d.r.																													
		 Pd <sub>2</sub> (dba) <sub>3</sub> , DMSO, toluene, 20°, 91 h		349																												

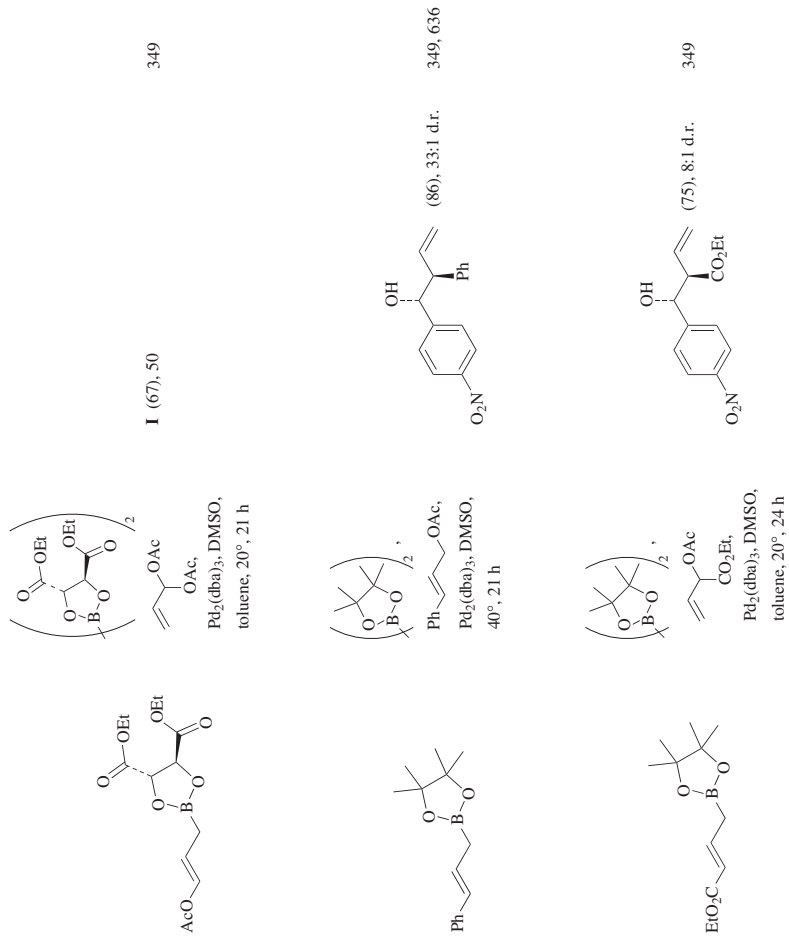
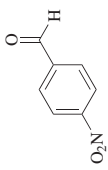
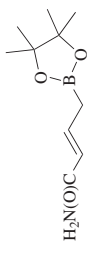
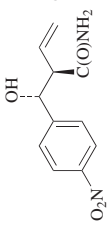
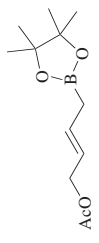
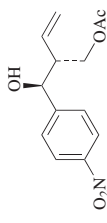
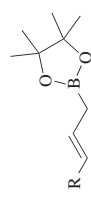
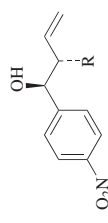
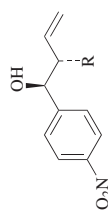


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

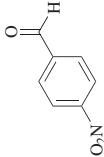
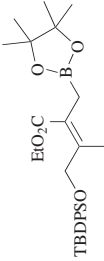
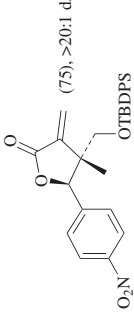
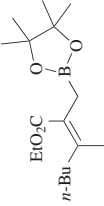
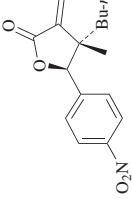
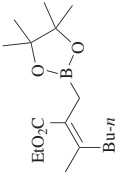
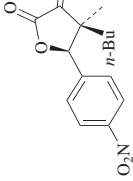
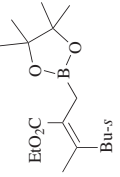
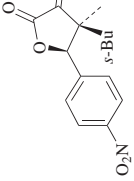
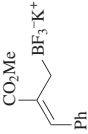
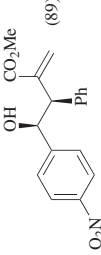
Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.																				
		$(\text{C}(\text{O})(\text{NH}_2)_2)$ , $\text{Pd}_2(\text{dba})_3$ , DMSO, toluene, 20°, 21 h	 (61), 8:1 d.r.	349																				
		$(\text{C}(\text{O})(\text{NH}_2)_2)$ , $\text{Pd}_2(\text{dba})_3$		636																				
		$(\text{C}(\text{O})(\text{NH}_2)_2)$ , $\text{Pd}_2(\text{dba})_3$ , DMSO	 R	349																				
			 R	636																				
			<table border="1"> <thead> <tr> <th>R</th> <th>Time</th> <th>Temp</th> <th>d.r.</th> </tr> </thead> <tbody> <tr> <td><math>\text{C}_6\text{H}_4\text{OMe-}p</math></td> <td>21 h</td> <td>40°</td> <td>(83) 10:1</td> </tr> <tr> <td><math>\text{CO}_2\text{Et}</math></td> <td>21 h</td> <td>40°</td> <td>(75) 8:1</td> </tr> <tr> <td><math>\text{C}(\text{O})(\text{NH}_2)</math></td> <td>21 h</td> <td>20°</td> <td>(61) 8:1</td> </tr> <tr> <td>OAc</td> <td>91 h</td> <td>20°</td> <td>(74) &gt;99:1</td> </tr> </tbody> </table>	R	Time	Temp	d.r.	$\text{C}_6\text{H}_4\text{OMe-}p$	21 h	40°	(83) 10:1	$\text{CO}_2\text{Et}$	21 h	40°	(75) 8:1	$\text{C}(\text{O})(\text{NH}_2)$	21 h	20°	(61) 8:1	OAc	91 h	20°	(74) >99:1	
R	Time	Temp	d.r.																					
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OAc	91 h	20°	(74) >99:1																					

C<sub>7</sub>

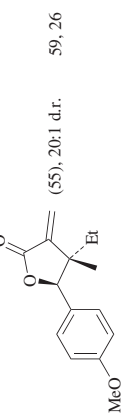




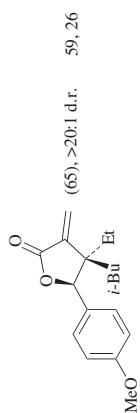
TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Toluene, 80°, 16–120 h	 (75), >20:1 d.r.	59, 26
		Toluene, 80°, 16–120 h	 (76), >20:1 d.r.	59, 26
		CH <sub>2</sub> Cl <sub>2</sub> , 40°, 48 h	 (67), >20:1 d.r.	59, 26
		Toluene, rt, 12 d	 (26), 15:1 d.r.	59
		<i>n</i> -Bu <sub>4</sub> Ni (0.1 equiv), CH <sub>2</sub> Cl <sub>2</sub> /H <sub>2</sub> O (1:1), rt, 5 h	 (89)	784

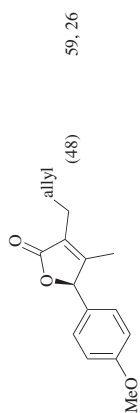
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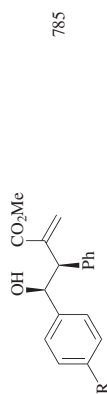
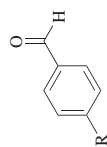
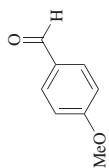
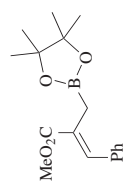
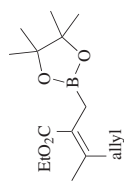
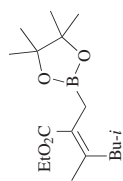
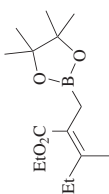
Toluene, 110°, 16-24 h



Toluene, 110°, 16-24 h



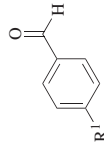
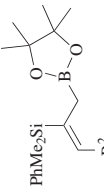
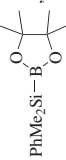
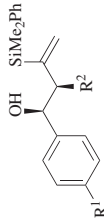
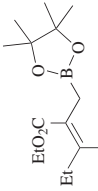
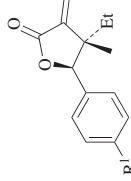
Toluene, 110°, 16-24 h

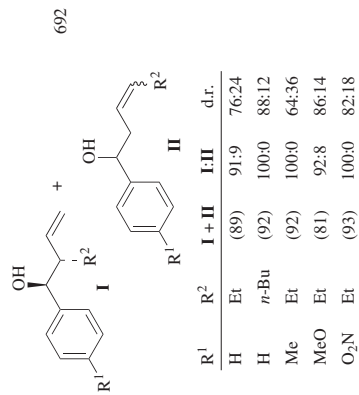
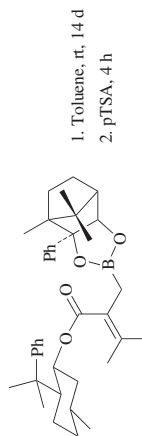
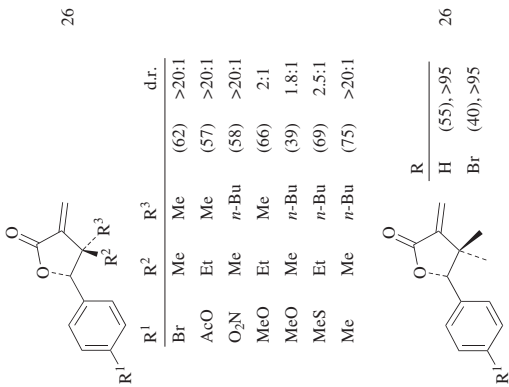


Catalyst, toluene

R	Catalyst	Temp	Time
O <sub>2</sub> N	none	rt	192 h (74)
O <sub>2</sub> N	Sc(OTf) <sub>3</sub>	rt	62 h (48)
O <sub>2</sub> N	BF <sub>3</sub> ·OEt <sub>2</sub>	rt	48 h (81)
O <sub>2</sub> N	BF <sub>3</sub>	rt	24 h (83)
H	BF <sub>3</sub>	rt	48 h (67)
MeO	none	90°	48 h (62)
Cl	BF <sub>3</sub>	rt	24 h (78)

TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.																														
		 Pd <sub>2</sub> (dba) <sub>3</sub> , EtOAc, 80°, 5 h		761																														
			<table border="1"> <thead> <tr> <th>R<sup>1</sup></th> <th>R<sup>2</sup></th> <th>d.r.</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Ph</td> <td>(96) &gt;99:1</td> </tr> <tr> <td>MeO</td> <td>Ph</td> <td>(55) &gt;99:1</td> </tr> <tr> <td>Cl</td> <td>Ph</td> <td>(92) &gt;99:1</td> </tr> <tr> <td>H</td> <td>4-MeC(O)C<sub>6</sub>H<sub>4</sub></td> <td>(86) &gt;99:1</td> </tr> <tr> <td>H</td> <td>4-MeOC<sub>6</sub>H<sub>4</sub></td> <td>(87) &gt;99:1</td> </tr> <tr> <td>H</td> <td>4-EtO<sub>2</sub>CC<sub>6</sub>H<sub>4</sub></td> <td>(70) &gt;99:1</td> </tr> <tr> <td>H</td> <td><i>n</i>-Bu</td> <td>(92) 95:5</td> </tr> <tr> <td>H</td> <td>Cy</td> <td>(75) 97:3</td> </tr> <tr> <td>H</td> <td><i>c</i>-Pr</td> <td>(85) 97:3</td> </tr> </tbody> </table>	R <sup>1</sup>	R <sup>2</sup>	d.r.	H	Ph	(96) >99:1	MeO	Ph	(55) >99:1	Cl	Ph	(92) >99:1	H	4-MeC(O)C <sub>6</sub> H <sub>4</sub>	(86) >99:1	H	4-MeOC <sub>6</sub> H <sub>4</sub>	(87) >99:1	H	4-EtO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub>	(70) >99:1	H	<i>n</i> -Bu	(92) 95:5	H	Cy	(75) 97:3	H	<i>c</i> -Pr	(85) 97:3	
R <sup>1</sup>	R <sup>2</sup>	d.r.																																
H	Ph	(96) >99:1																																
MeO	Ph	(55) >99:1																																
Cl	Ph	(92) >99:1																																
H	4-MeC(O)C <sub>6</sub> H <sub>4</sub>	(86) >99:1																																
H	4-MeOC <sub>6</sub> H <sub>4</sub>	(87) >99:1																																
H	4-EtO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub>	(70) >99:1																																
H	<i>n</i> -Bu	(92) 95:5																																
H	Cy	(75) 97:3																																
H	<i>c</i> -Pr	(85) 97:3																																
		Toluene, 80°, 16–120 h		59, 26																														
			<table border="1"> <thead> <tr> <th>R<sup>1</sup></th> <th>d.r.</th> </tr> </thead> <tbody> <tr> <td>MeO (70)</td> <td>19:1</td> </tr> <tr> <td>O<sub>2</sub>N (81)</td> <td>&gt;20:1</td> </tr> </tbody> </table>	R <sup>1</sup>	d.r.	MeO (70)	19:1	O <sub>2</sub> N (81)	>20:1																									
R <sup>1</sup>	d.r.																																	
MeO (70)	19:1																																	
O <sub>2</sub> N (81)	>20:1																																	



1. PhSe-CH=CH<sub>2</sub>,  
 LDA, THF, -78°,  
 30 min  
 2. BR<sup>2</sup>, -78° to rt,  
 12 h



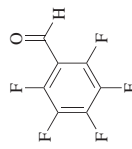
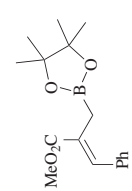
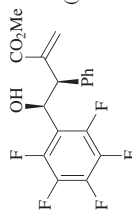
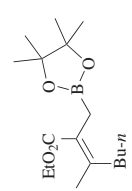
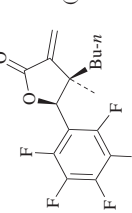



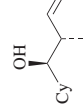
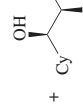
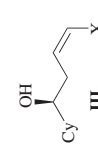


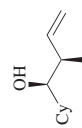
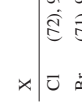
TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		$\text{PhMe}_2\text{Si-B}(\text{Ph})_2$ $\text{Pt}(\text{C}_3\text{H}_5)(\text{PPh}_3)_2$ , octane, 120°	 R H (79) 99:1 4-MeO (77) 99:1 2-MeO (83) 99:1	781
		$\text{Sc}(\text{OTf})_3$ , toluene, rt, 6-24 h	 (55), 19:1 d.r.	24, 26
		Ether, -78° <sup>a</sup>	 (97), 90, 4:3 d.r.	786, 787
		1. Toluene, 110°, 2 d 2. pTSA, rt, 6 h	 (74)	30

C<sub>7</sub>



TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.									
 $C_7$		$BF_3$ , toluene, rt, 24 h	 (87)	785									
		$Sc(OTf)_3$ , toluene, rt, 6-24 h	 (53), 19:1 d.r.	24, 26									
		1.  , $MeOBBN$ 2. LDA, $BF_3 \cdot OEt_2$ , THF 3. Aldehyde	 I  II  III <table border="1" data-bbox="990 630 1088 882"> <thead> <tr> <th>X</th> <th>Temp</th> <th>II:(I+III)</th> </tr> </thead> <tbody> <tr> <td>Br</td> <td>-78°</td> <td>89:11</td> </tr> <tr> <td>Cl</td> <td>-95°</td> <td>95:5</td> </tr> </tbody> </table>	X	Temp	II:(I+III)	Br	-78°	89:11	Cl	-95°	95:5	159
X	Temp	II:(I+III)											
Br	-78°	89:11											
Cl	-95°	95:5											
		1.  , $MeOB[(-)-ipc]_2$ , $LiNCy_2$ , ether, -78° 2. $BF_3 \cdot OEt_2$ 3. Aldehyde	 (72), 95  (71), 94 <table border="1" data-bbox="1120 588 1201 630"> <thead> <tr> <th>X</th> <th>d.r.</th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>98:2</td> </tr> <tr> <td>Br</td> <td>94:6</td> </tr> </tbody> </table>	X	d.r.	Cl	98:2	Br	94:6	159, 762			
X	d.r.												
Cl	98:2												
Br	94:6												



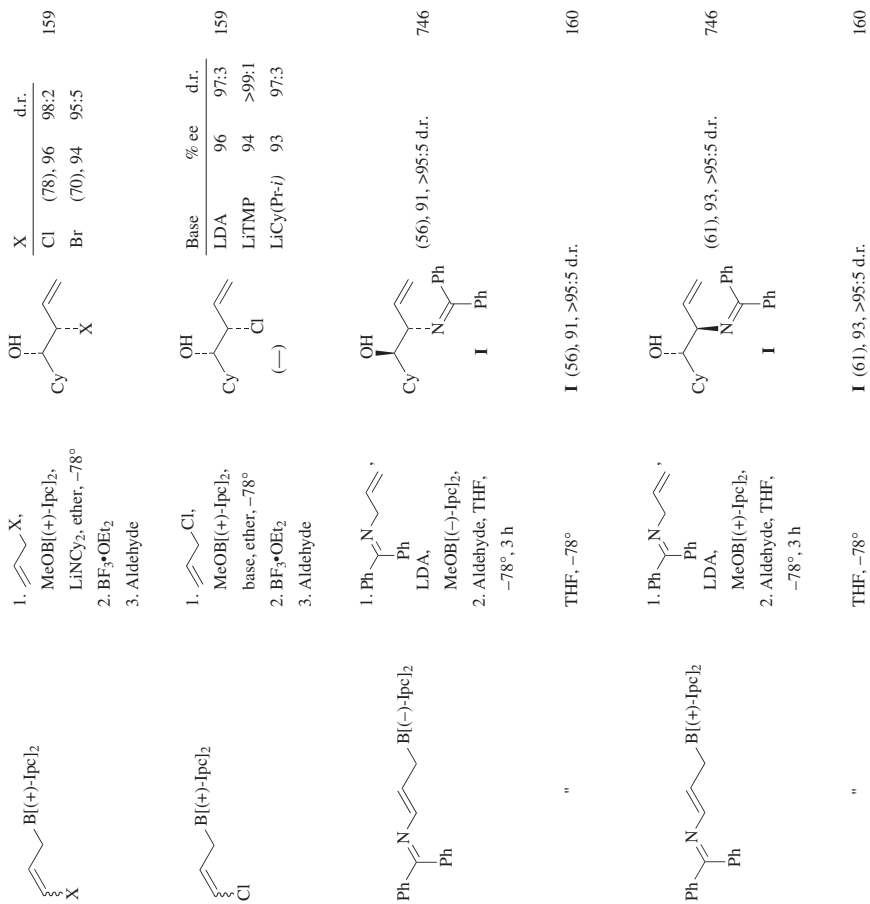


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		1. Ether, -78°, 3.5 h 2. KF, H <sub>2</sub> O <sub>2</sub>	 I (63), >95:5 d.r.	752
	"	1. Ether, -78° 2. KF, H <sub>2</sub> O <sub>2</sub>		45
		THF, -78°, 4 h	 (85), 91	734
		Ether, -78°, 2 h	 (-)	175
		Ether, -78°, 2 h	 (-)	175
	"	1. Ether, -78° to 0°, 4 h 2. H <sub>2</sub> O <sub>2</sub> , NaOH	 (70), 94, >97:3 d.r.	157

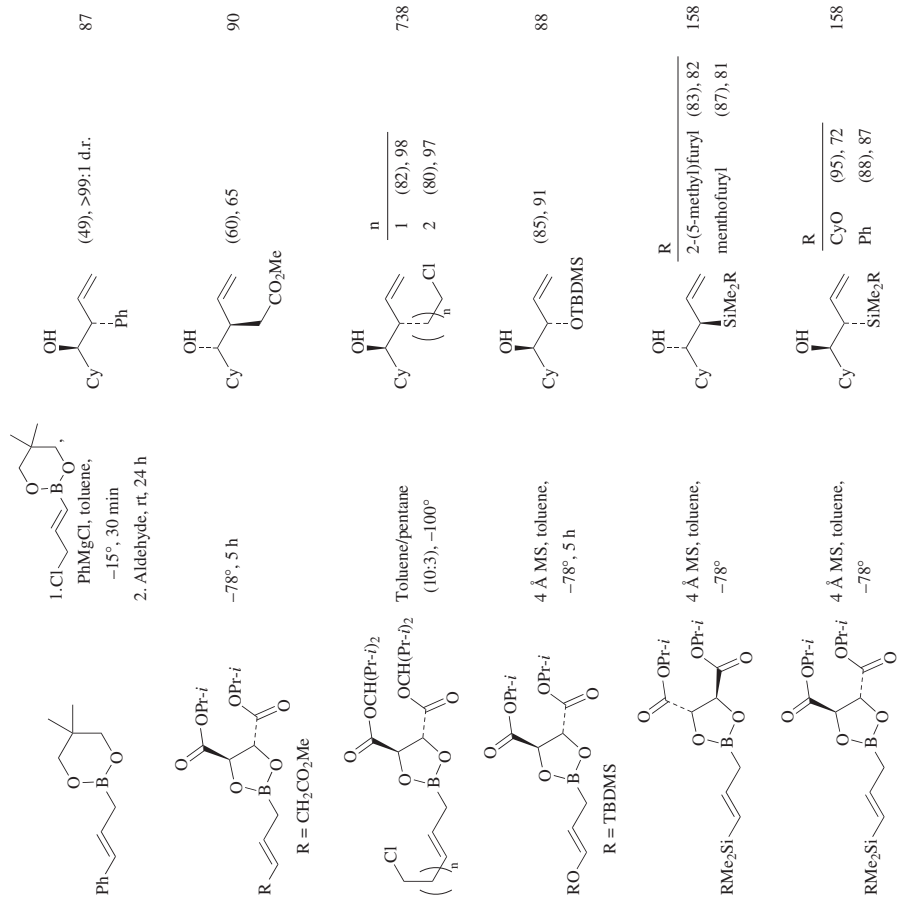

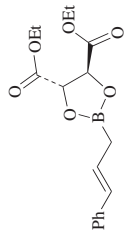
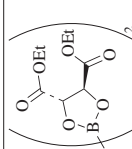
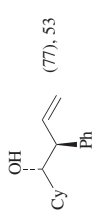
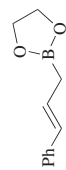
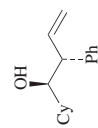

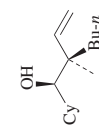

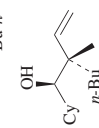

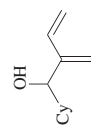
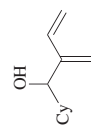
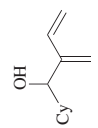
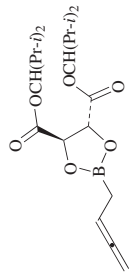
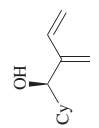


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		 Ph-CH=CH-OAc, Pd <sub>2</sub> (dba) <sub>3</sub> , DMSO, toluene, 20°, 69 h	 (77), 53	349
		1. Cl-CH=CH-B(OAc) <sub>2</sub> , PhMgCl, THF, -15°, 24 h 2. Aldehyde, rt, 24 h	 (36), 96:4 d.r.	87
		THF, -78° to rt, 18 h	 (82), 89:11 d.r.	772
		THF, -78° to rt, 18 h	 (84), 95:5 d.r.	772
		rt	 (91), 91%  (90), 91%  (94), 89%	744, 741
		4 Å MS, toluene, -78°, 72 h	 (94), 89%	741

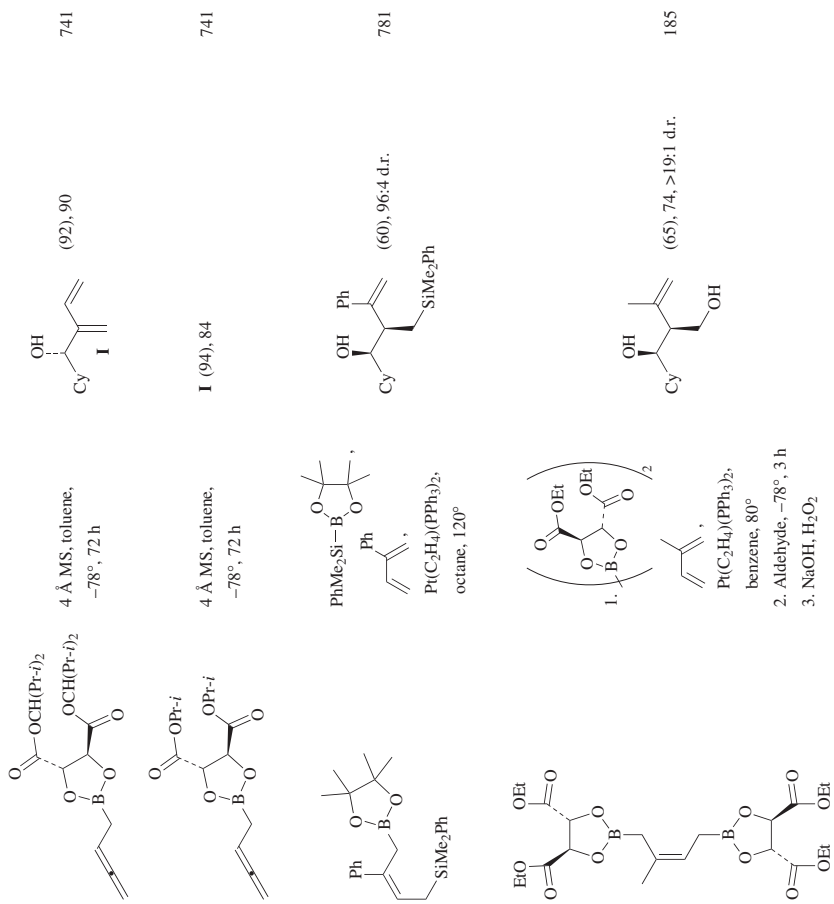


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
$C_7$ 		Sc(OTf) <sub>3</sub> , toluene, rt, 24 h	 (32), >20:1 d.r.	26
		Cu(OTf) <sub>2</sub> , toluene, 60°, 16 h	 (54), 19:1 d.r.	24, 26
		1. Pt(dba) <sub>2</sub> , PCy <sub>3</sub> , benzene, rt 2. Aldehyde, -78°, 3 h 3. NaOH, H <sub>2</sub> O <sub>2</sub>	 (72), 74: >19:1 d.r.	185
		1. Pt(dba) <sub>2</sub> , PCy <sub>3</sub> , benzene, rt 2. Aldehyde, -78°, 3 h 3. NaOH, H <sub>2</sub> O <sub>2</sub>	 R Me (21), 72 Et (68), 74 Pr- <i>i</i> (38), 58 CH(Fr- <i>t</i> ) <sub>2</sub> (17), 60	185

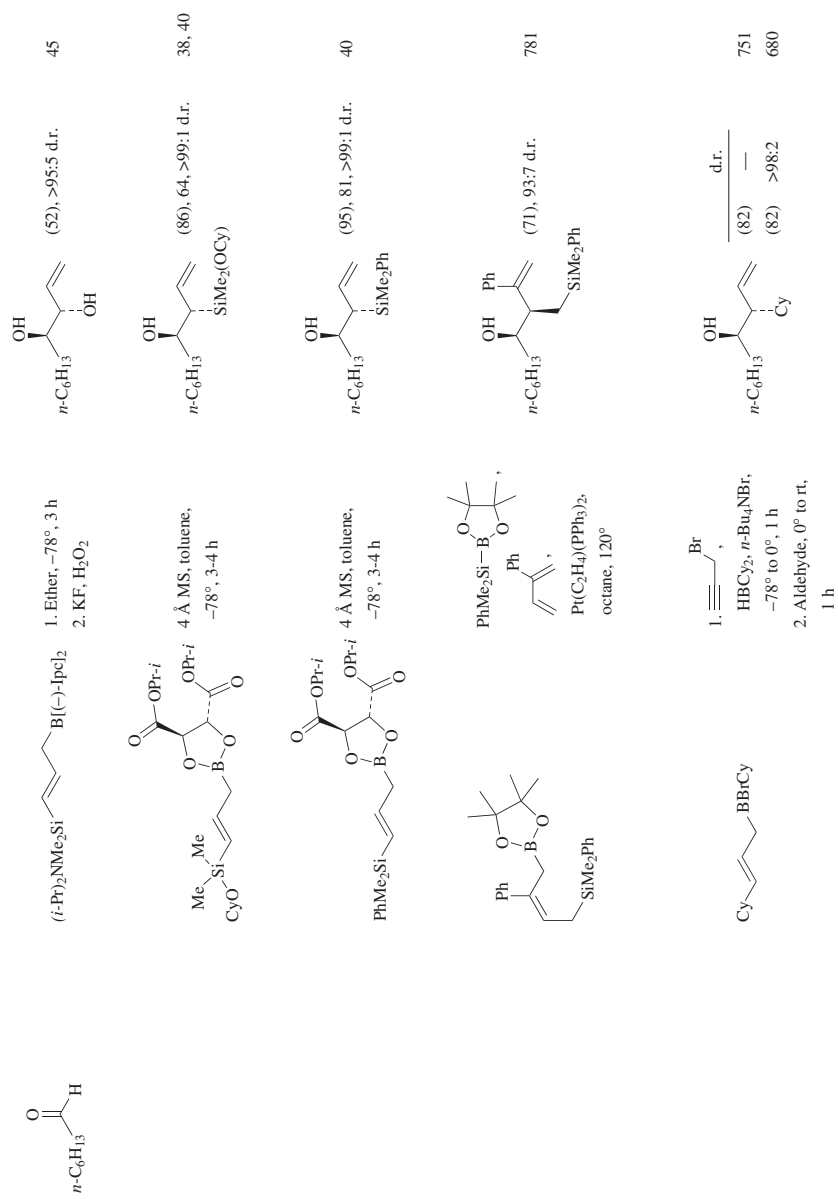


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		FB(OBu- <i>n</i> ) <sub>2</sub>	 I + II (73), I:II = 37.3:1	46
		Neat, rt, 4 d	(48), 89:11 d.r.	521
		THF, -78°, 4 h	 (77), >90, 9:1 d.r.	734, 788
		THF, -78°	 (75)	335
	  	PhMe <sub>2</sub> Si-B(OBu- <i>n</i> ) <sub>2</sub> , Pt(C <sub>2</sub> H <sub>4</sub> )(PPh <sub>3</sub> ) <sub>2</sub> , octane, 120°	 (80), 99:1 d.r.	781



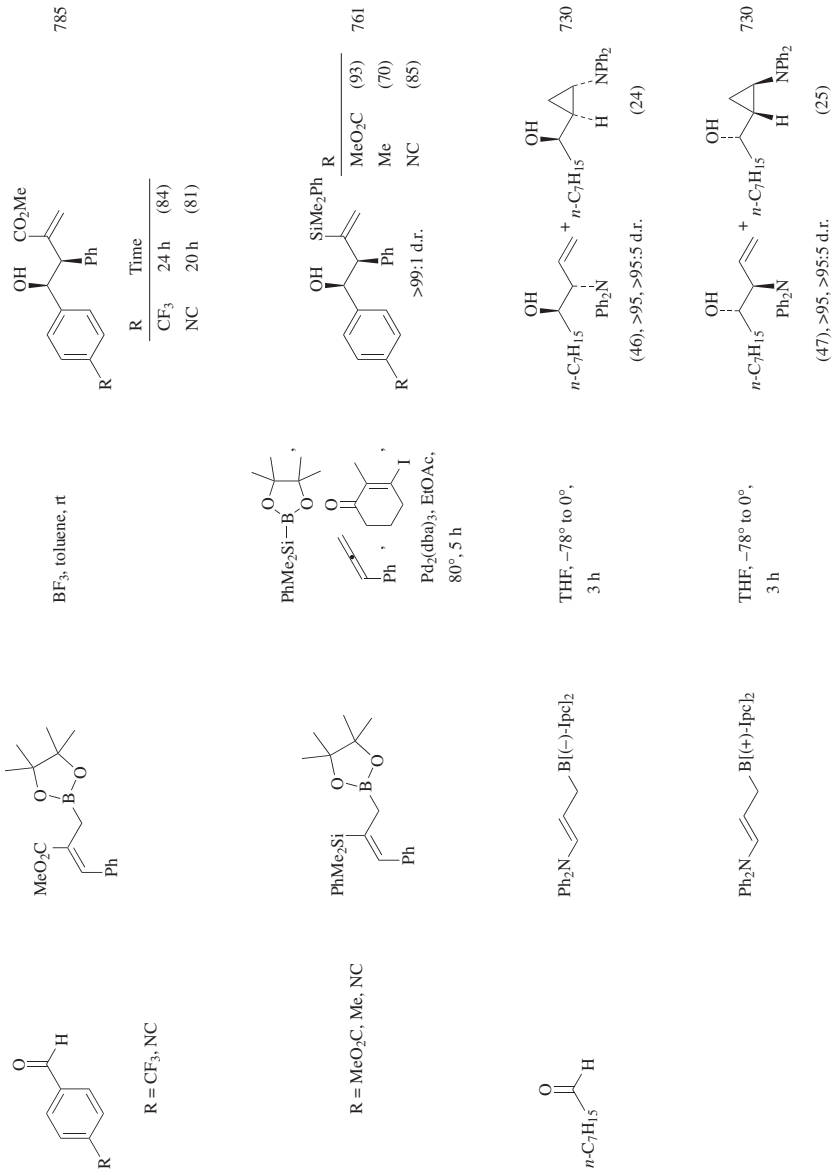


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
$n\text{-C}_7\text{H}_{15}\text{CHO}$		Ether, rt, 1-3 d	 (79)	32
		1. benzene, rt		
		2. Aldehyde, $-78^\circ$ , 3 h 3. NaOH, H <sub>2</sub> O <sub>2</sub>	 (68), 70, >19:1 d.r.	185
		Ether, $-95^\circ$ to $0^\circ$ , 6 h	 (57), 97:3 d.r.	789
		1. Ether, $-95^\circ$ to rt, 6 h 2. 8-HQ 3. DBU	 (-), 90	790
		1. Ether, $-95^\circ$ to rt, 6 h 2. 8-HQ 3. DBU	 (-), 88	790

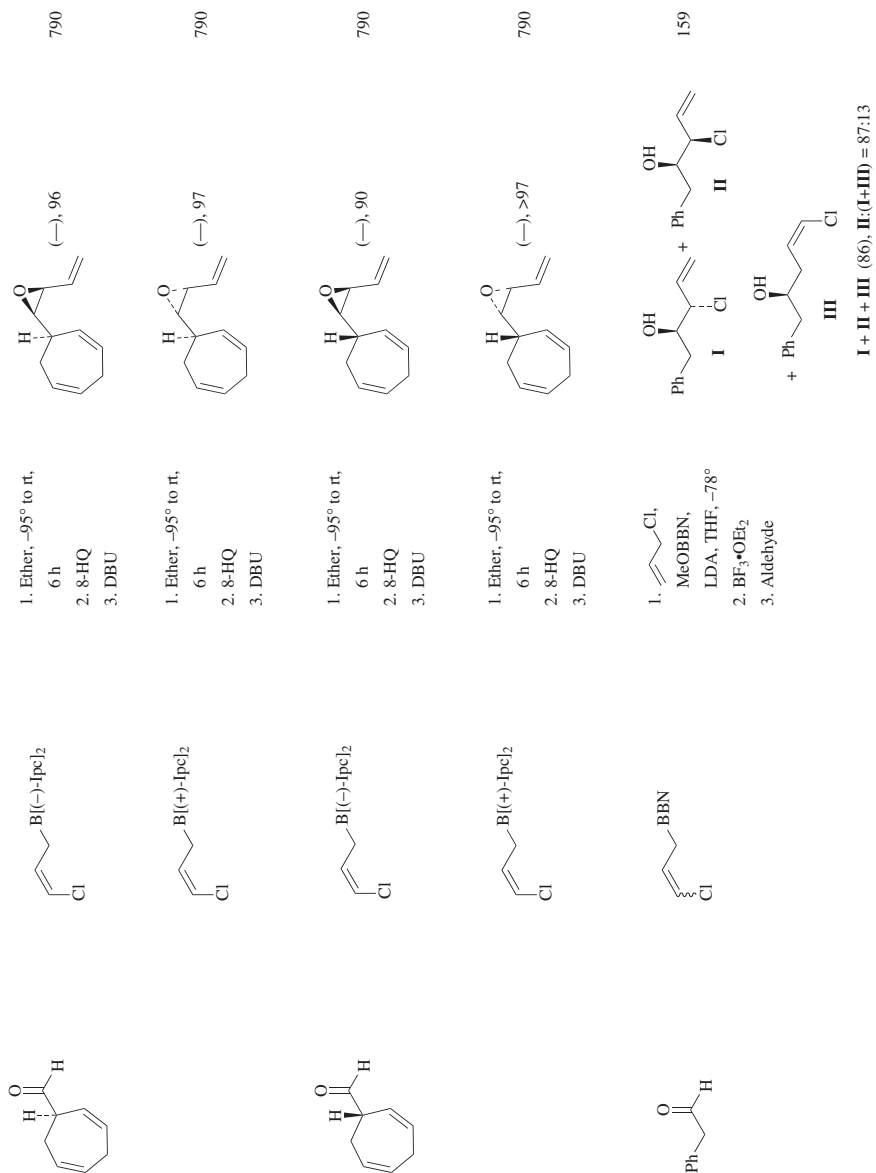


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

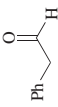


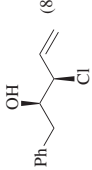
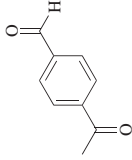
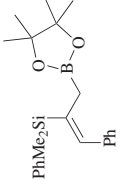
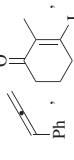
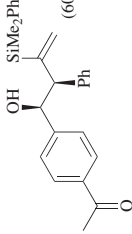
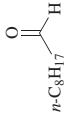


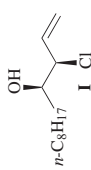


Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C <sub>8</sub> 		1.  MeOB[(-)-Ipc] <sub>2</sub> LiNCy <sub>2</sub> , ether, -78° 2. BF <sub>3</sub> ·OEt <sub>2</sub> 3. Aldehyde	 (85), 90, 99:1 d.r.	159, 762
C <sub>9</sub> 		PhMe <sub>2</sub> Si-B(OtBu) <sub>2</sub>  Pd <sub>2</sub> (dba) <sub>3</sub> , EtOAc, 80°, 5 h	 (60), >99:1 d.r.	761
		1.  MeOB[(-)-Ipc] <sub>2</sub> LiNCy <sub>2</sub> , ether, -78° 2. BF <sub>3</sub> ·OEt <sub>2</sub> 3. Aldehyde	 (70), 98, 99:1 d.r.	159, 762
		1.  MeOB[(-)-Ipc] <sub>2</sub> LDA, ether, -78° 2. BF <sub>3</sub> ·OEt <sub>2</sub> (x equiv) 3. Aldehyde	x I 2.5 (-), 93 1.33 (-), 92	159



TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		THF, -78° to rt, 1.5 h	 (50), >95, >97.5:2.5 d.r.	747
		Ether, -78°, 5 h	 (76), 94, >99:1 d.r.	292
		1. MeOB[(-)-Ipc]2, LiNCy2, ether, -78° 2. BF3·OEt2 3. Aldehyde	 (85), 98, 98:2 d.r.	159
		Ether, pentane, -100°	 (90), 87	505
		 OTHP, Cl- -100°	 I + II I + II (76), EII = 5.9:1	46
		THPO-CH2-CH=CH-B[Li, Cl-] -100°	 II (62), 13:1 d.r.	52

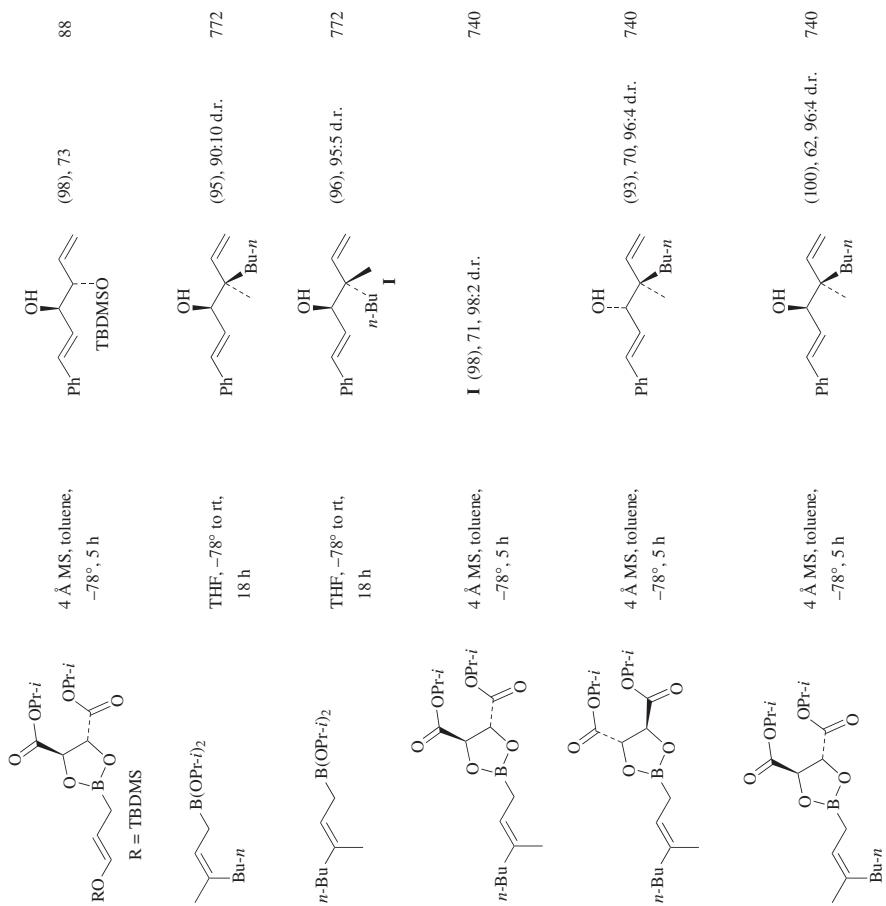
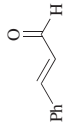
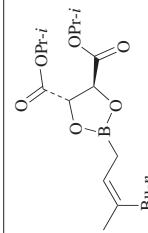
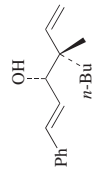


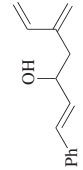
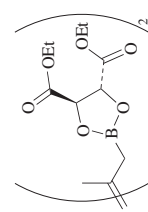
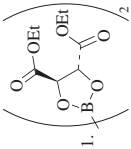
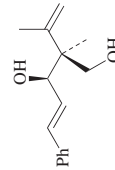
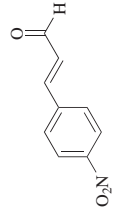
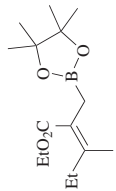
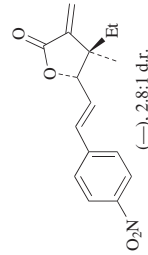


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		4 Å MS, toluene, -78°, 5 h	 (100), 68, 96:4 d.r.	740
		CH <sub>2</sub> Cl <sub>2</sub> , rt, 5 h	 (95)	744
		1. Pt(dba) <sub>2</sub> , PCy <sub>3</sub> , benzene, rt 2. Aldehyde, -78°, 3 h 3. NaOH, H <sub>2</sub> O <sub>2</sub>	 (59), 40, >19:1 d.r.	185
		Se(OTf) <sub>3</sub> , toluene, rt, 16-24 h	 (-), 2.8:1 d.r.	26



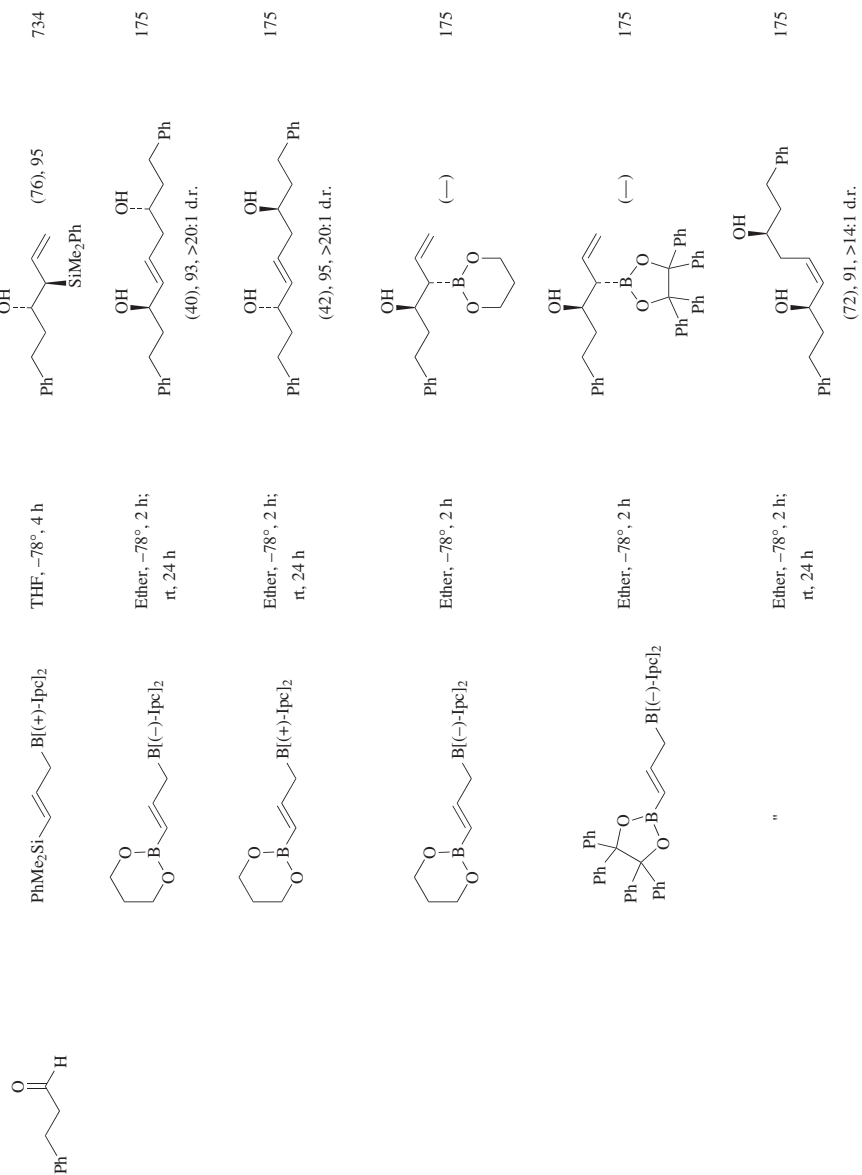
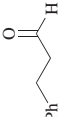
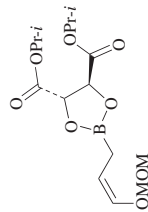
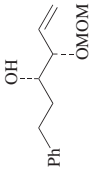
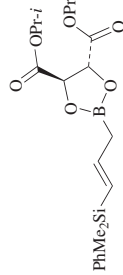
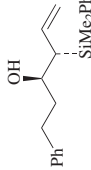
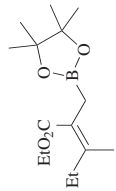
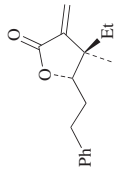
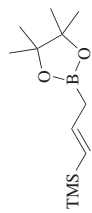
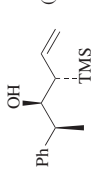


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		4 Å MS, toluene, -78° to 0°, 1 h	 (70), 90	792
		4 Å MS, toluene, -78°	 (75), 75	743
		L.A., rt, 24 h		26, 24
		Neat, rt, 4 d	 (—), 90:10 d.r.	521

L.A.	Solvent
Sc(OTf) <sub>3</sub>	toluene (64)
Cu(OTf) <sub>2</sub>	toluene (63)
Yb(OTf) <sub>3</sub>	toluene (66)
Sc(OTf) <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub> (62)
Cu(OTf) <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub> (52)
Yb(OTf) <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub> (38)

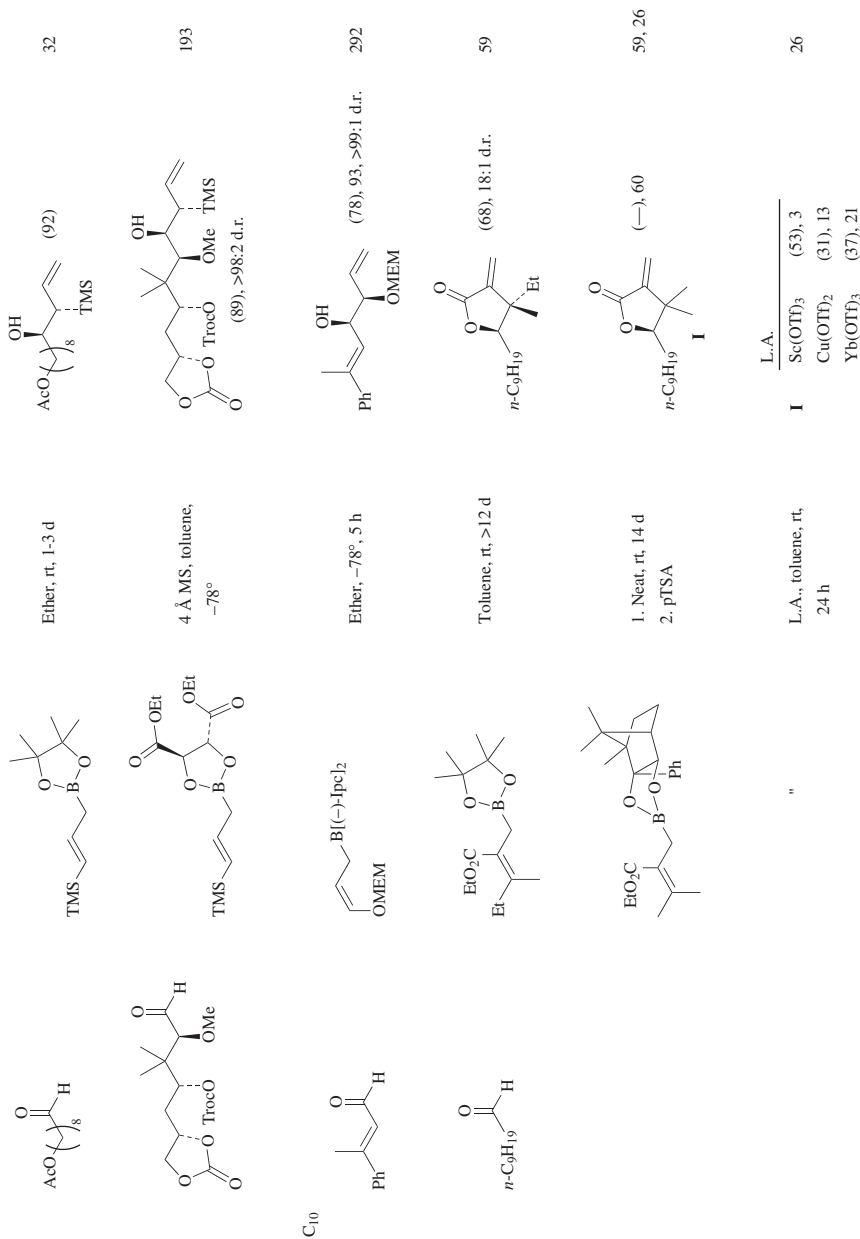
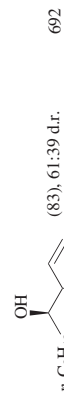


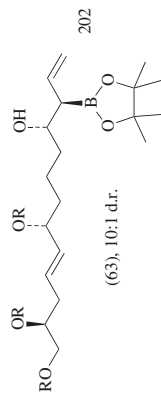
TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
$n\text{-C}_9\text{H}_{19}\text{CHO}$		Toluene	 R Temp Time Me 60-80° 16-120 h (40) Et 110° 16-24 h (68)	26
		L.A., toluene, rt, 24 h	L.A. Sc(OTf) <sub>3</sub> (29), -10 Cu(OTf) <sub>2</sub> (93), 71 Yb(OTf) <sub>3</sub> (30), 31	26
		1. Neat, rt, 14 d 2. pTSA	(-), 10	59, 26
		1. Neat, rt, 14 d 2. pTSA	(75), 98	59, 26
		1. Toluene, rt, 14 d 2. pTSA, 3 h	(-), 82	26



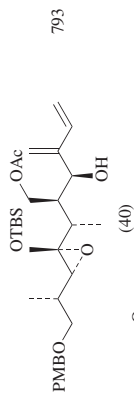
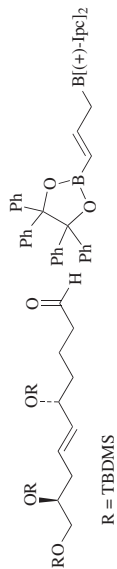
692

1. PhSe-CH=CH<sub>2</sub>,  
 LDA, THF, -78°,  
 30 min  
 2. Et<sub>3</sub>B, -78° to rt,  
 12 h



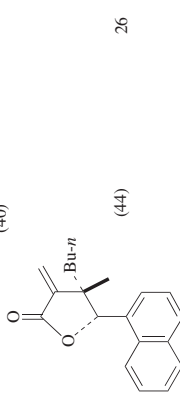
202

CH<sub>2</sub>Cl<sub>2</sub>, MeOH,  
 -78° to rt



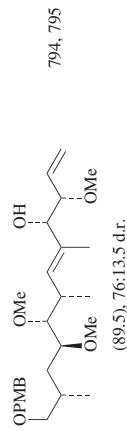
793

TMSCl



26

Sc(OTf)<sub>3</sub>, toluene,  
 rt, 24 h



794, 795

THF, -78° to -20°,  
 2 h

TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
$n\text{-C}_{12}\text{H}_{25}\text{CHO}$		Ether, $-90^\circ$	 (81), 95, >98:2 d.r.	796
		$\text{Sc}(\text{OTf})_3$ (10 mol%), rt, 3 d	 (12)	797
	"	$90^\circ$ , 3 d	 I (19)	797
	"	$\text{BF}_3 \cdot \text{SiO}_2$ , rt, 3 d	 I (15)	797
		Ether, THF, $-78^\circ$ to $-20^\circ$ , 23 h	 (96), >97:5:2.5 d.r.	468
		$\text{OPr-i}$ $\text{OPr-i}$ 4 Å MS, toluene, $-78^\circ$	 (80)	788

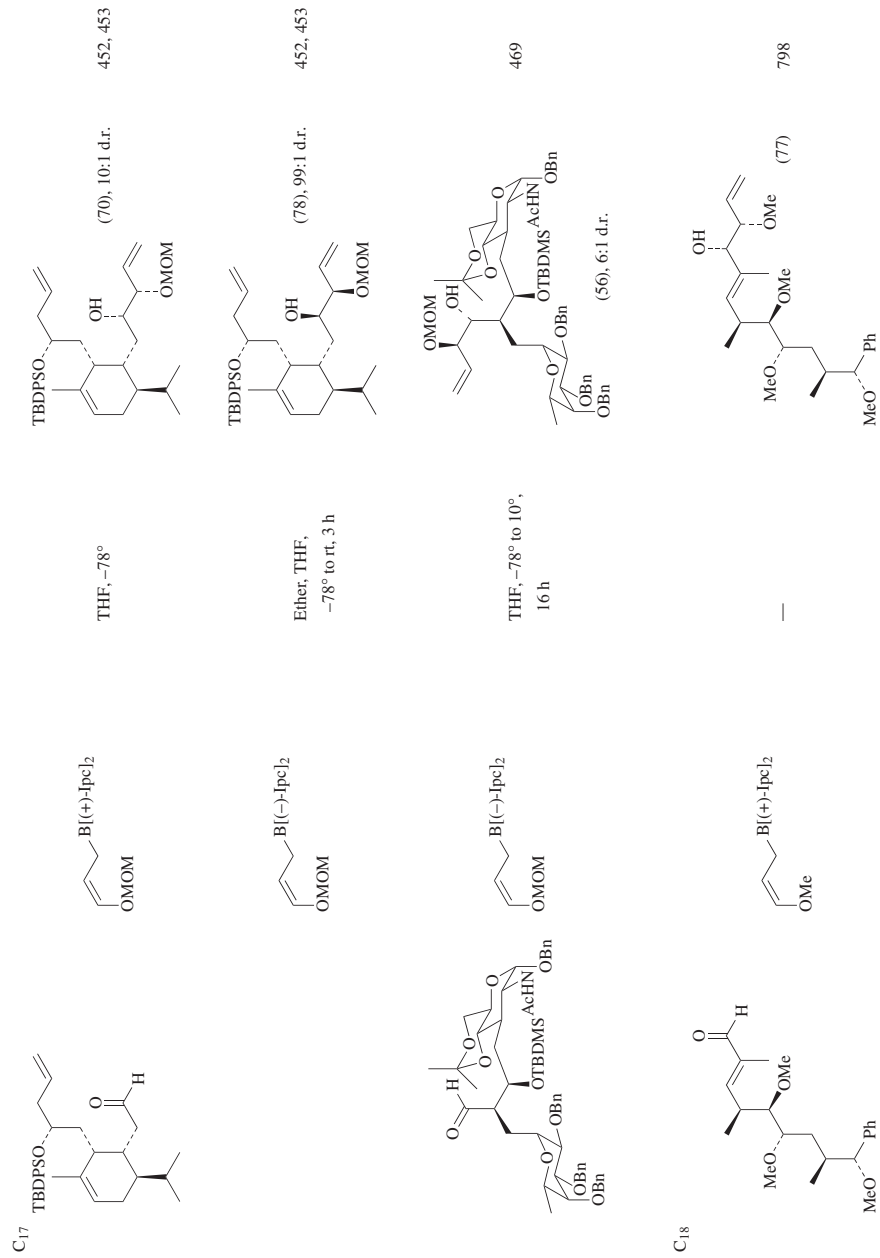


TABLE 6. ADDITION OF  $\gamma$ -SUBSTITUTED REAGENTS (Continued)

	Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C <sub>20</sub>	 $R^1 = \text{TIPS}, R^2 = \text{MOM}$		1. Toluene, 0°, 1 h 2. KH, THF, 0°, 10 min	 (80), >20:1 Z:E	799
	 $R^1 = \text{TIPS}, R^2 = \text{MOM}$		1. Toluene, 0°, 1 h 2. KH, THF, 0°, 10 min	 (70), >20:1 Z:E	800
C <sub>25</sub>	 $R^1 = \text{TIPS}, R^2 = \text{MOM}$		1. CH <sub>2</sub> Cl <sub>2</sub> , rt, 1 h 2. KOBu- <i>t</i> , THF, rt, 1 h	 (83), 15:1 Z:E	801

<sup>a</sup> The reaction mixture was free of Mg<sup>2+</sup> ions.<sup>b</sup> The starting material was prepared using different conditions.



TABLE 7. ADDITION OF ALLENYL AND PROPARGYL REAGENTS


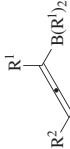
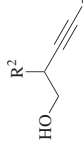
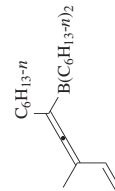
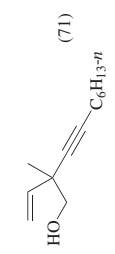
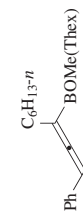
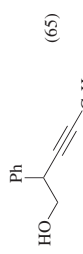


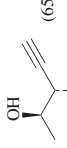
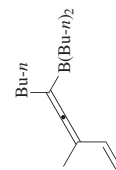
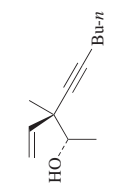
Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.	
C <sub>1</sub> 		1. <i>n</i> -BuLi, THF 2. BR <sub>1</sub> <sup>3</sup> , -78° 3. BCl <sub>3</sub> , -78° to rt		R <sup>1</sup> R <sup>2</sup> <i>n</i> -Bu Me (45) Ph (68) <i>n</i> -C <sub>6</sub> H <sub>13</sub> Ph (84) <i>n</i> -Bu Ph (89)	802
		1. <i>n</i> -BuLi, THF 2. B(C <sub>6</sub> H <sub>13-n</sub> ) <sub>3</sub> , -78° 3. BCl <sub>3</sub> , -78° to rt		(71)	802
		1. <i>n</i> -BuLi, THF 2. ( <i>n</i> -C <sub>6</sub> H <sub>13</sub> )BOMe(Thex), -78° 3. BCl <sub>3</sub> , -78° to rt		(65)	802
C <sub>2</sub> 		Ether, 0°		(65)	803
		1. <i>n</i> -BuLi, THF 2. B(Bu- <i>n</i> ) <sub>3</sub> , -78° 3. BCl <sub>3</sub> , -78° to rt		(60), 56:44 d.r.	802

TABLE 7. ADDITION OF ALLENYL AND PROPARGYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C <sub>2</sub> 		Ether, -100°, 2 h	 R Me (68), 89 <i>n</i> -Pr (74), 87	804
		Ether, -100°, 3 h		805
		THF, -78°, 3 h		806
		Ether, 0°		803
C <sub>3</sub> 		Ether, -78°, 3 h		144
		1. Li-CH=CH-Cl, B(C <sub>5</sub> H <sub>9</sub> -c) <sub>3</sub> , THF, -90° 2. Aldehyde, -78° to rt, 1.5 h		807
		1. Li-CH=CH-Cl, B(C <sub>5</sub> H <sub>9</sub> -c) <sub>3</sub> , THF, -90° to rt 2. Aldehyde, -78° to rt, 1.5 h		807

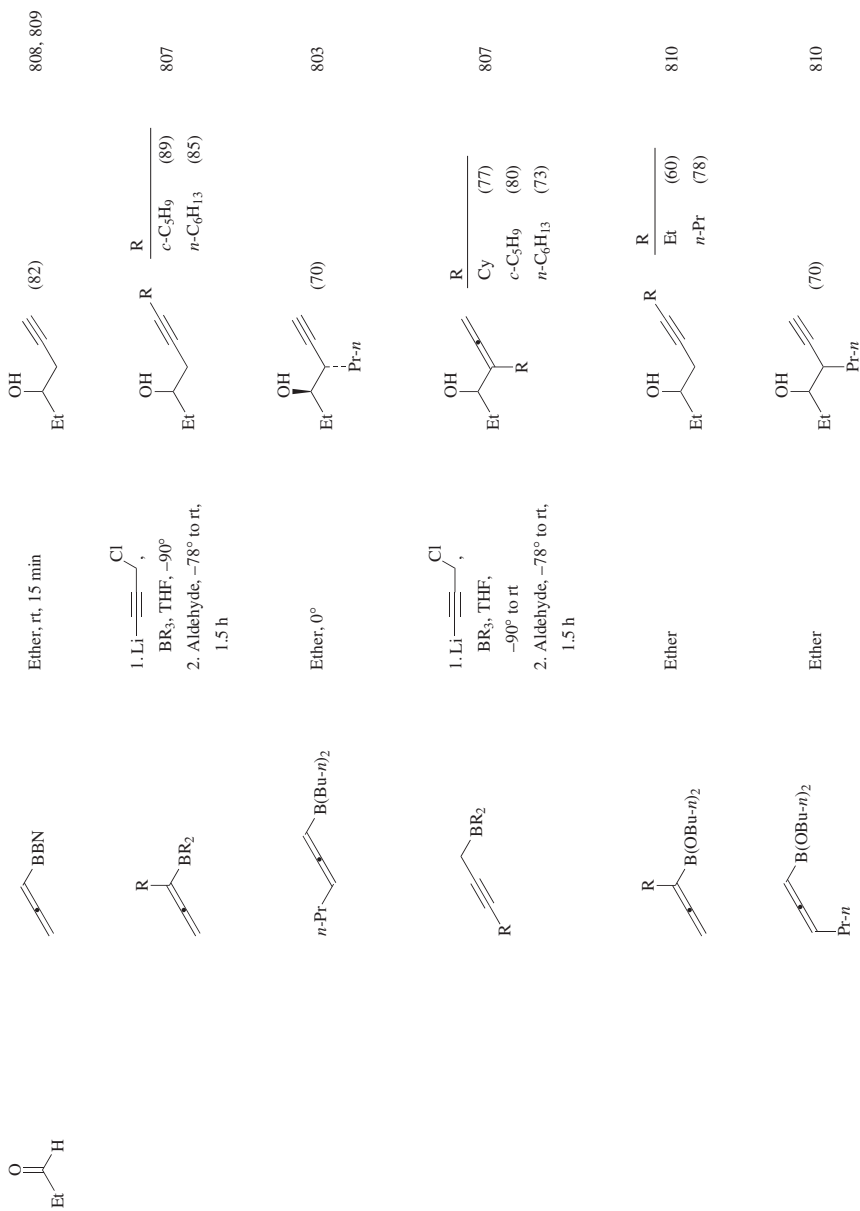

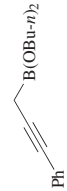
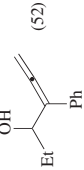
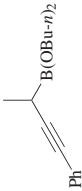
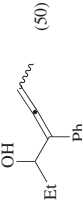
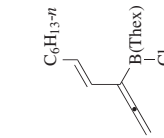


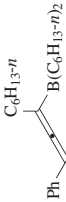
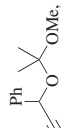
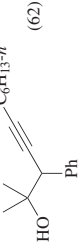

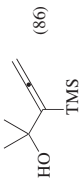


TABLE 7. ADDITION OF ALLENYL AND PROPARGYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Ether	 (52)	810
		Ether	 (50)	810
		1. Li-C≡C-CH <sub>2</sub> -Cl, C <sub>6</sub> H <sub>13-n</sub> (Thex)B Cl, THF, -90° 2. Aldehyde, -78° to rt, 1.5 h	 (76)	807
		1.  <i>n</i> -BuLi, THF 2. B(C <sub>6</sub> H <sub>13-n</sub> ) <sub>3</sub> , -78° 3. BCl <sub>3</sub> , -78° to rt	 (62)	802
		THF, rt, 1.5 h	 (86)	811

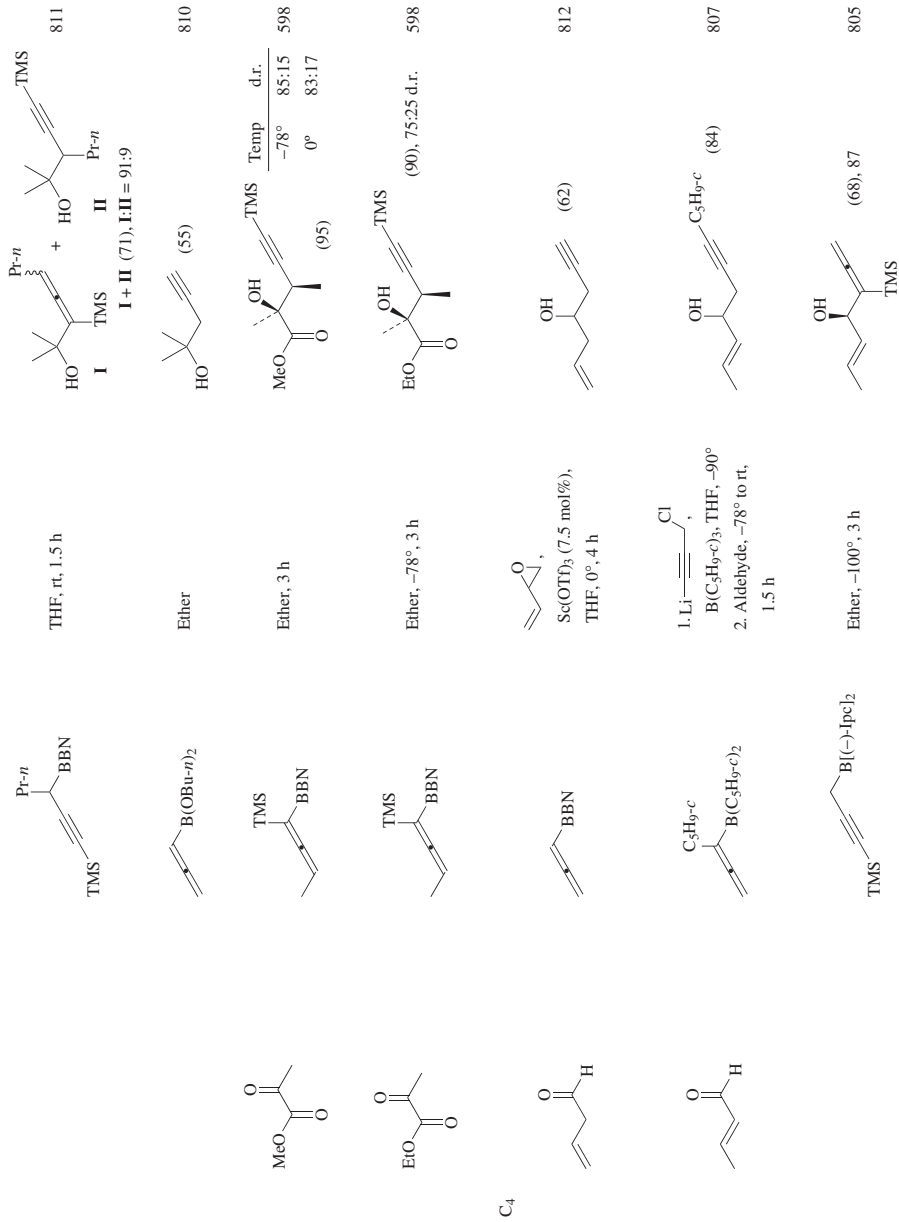


TABLE 7. ADDITION OF ALLENYL AND PROPARGYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		1. $\text{Li}-\text{C}\equiv\text{C}-\text{Cl}$ $\text{B}(\text{C}_5\text{H}_9\text{-}c)_3$ , THF, $-90^\circ$ to rt 2. Aldehyde, $-78^\circ$ to rt, 1.5 h		807
		THF, rt, 1.5 h		811
		THF, $-78^\circ$ , 3 h		806
		Ether		810
		$\text{CH}_2\text{Cl}_2$ , $-78^\circ$ , 2.5 h		153
		Ether, $-78^\circ$ , 3 h		144

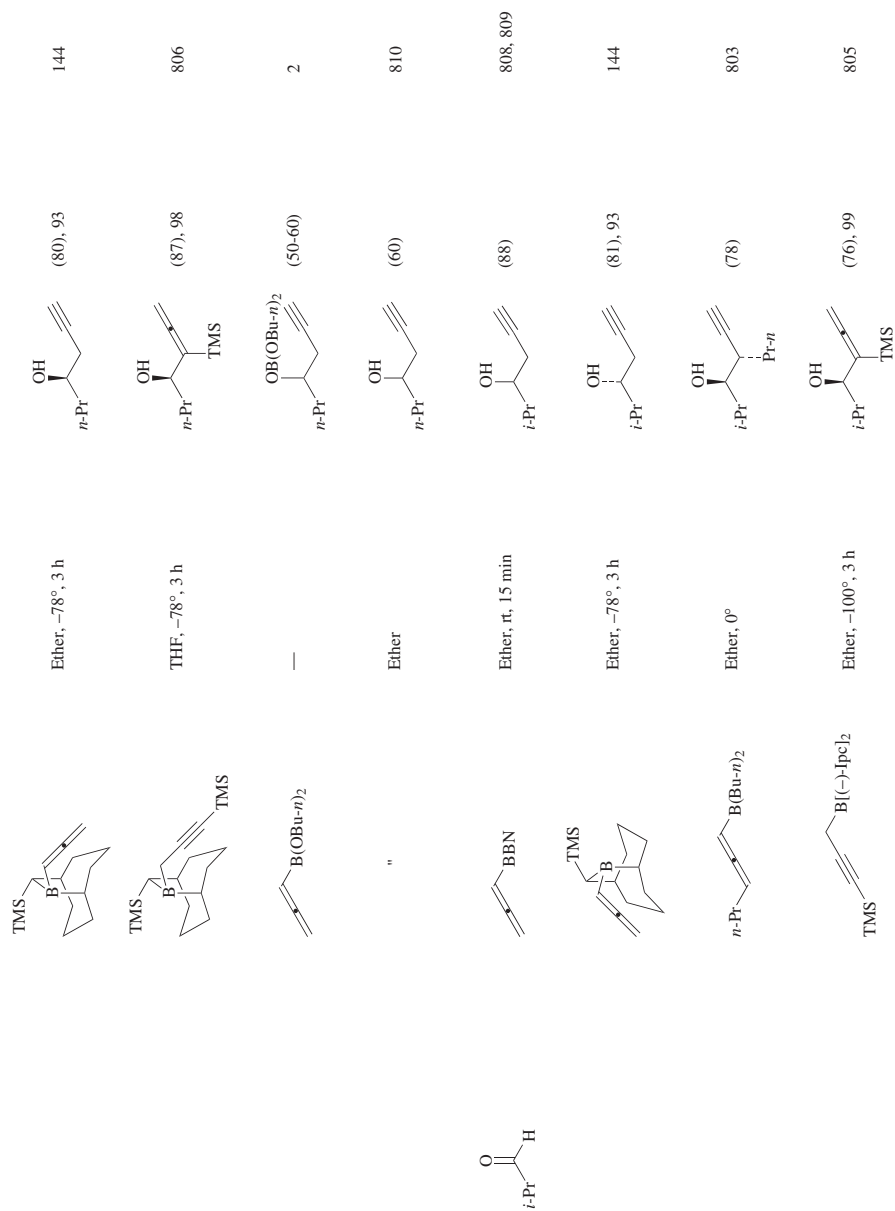


TABLE 7. ADDITION OF ALLENYL AND PROPARGYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
$C_4$ 		Ether, $-100^\circ$ , 2 h	 R Me (72), 96 <i>n</i> -Pr (80), 96 Ph (70), 96	804
		1. Li- $B(C_5H_9-c)_3$ , THF, $-90^\circ$ to rt 2. Aldehyde, $-78^\circ$ to rt, 1.5 h	 (78)	807
		THF, rt, 1.5 h	 (82)	811
		THF, $-78^\circ$ , 3 h	 (77), 97	806
		THF, rt, 1.5 h	 I TMS I + II (74), E:II = 88:12 II	811
		$CH_2Cl_2$ , $-78^\circ$ , 2.5 h	 (76), 94	153



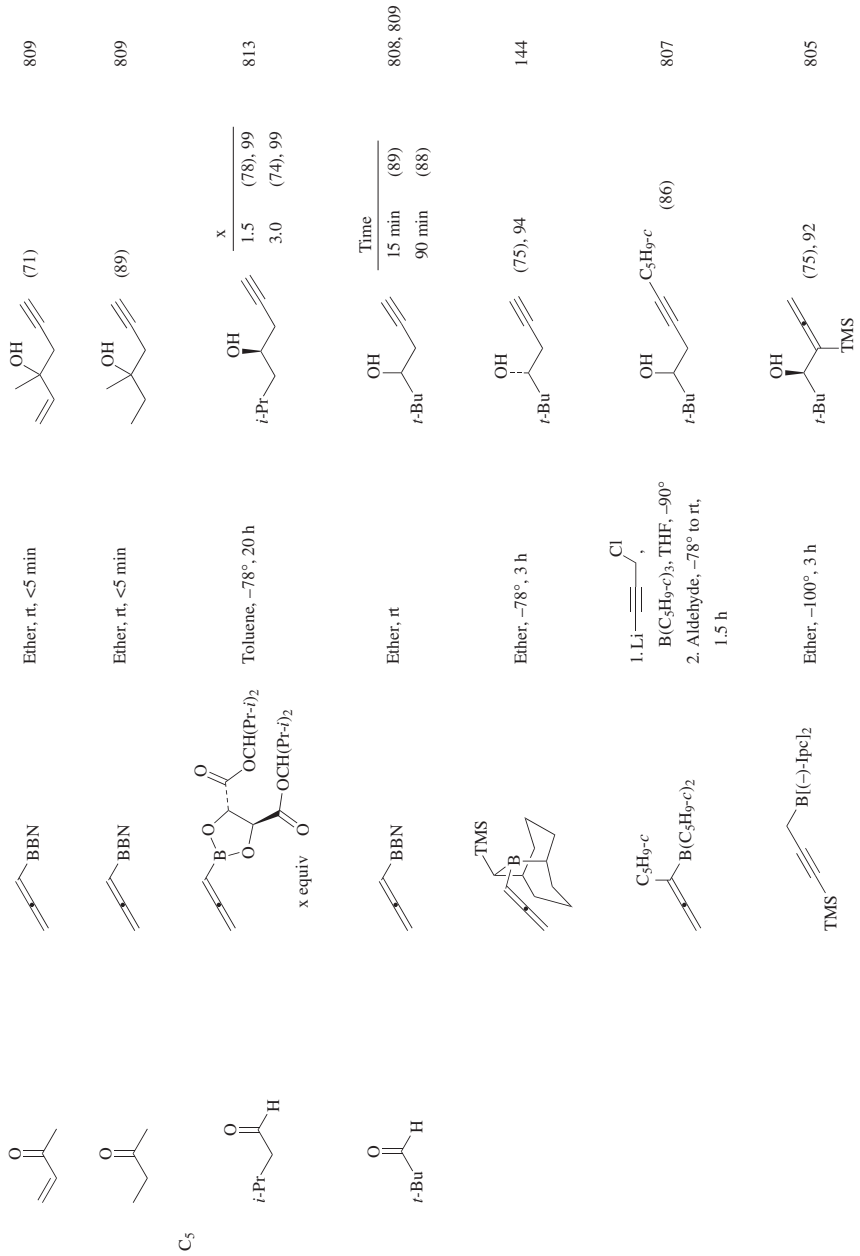


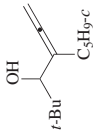

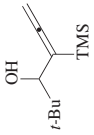
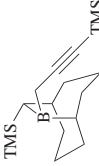
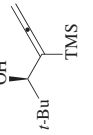

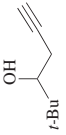
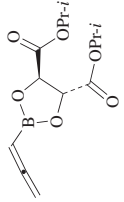
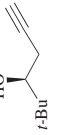
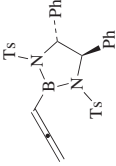
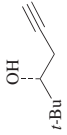


TABLE 7. ADDITION OF ALLENYL AND PROPARGYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
 $t\text{-BuCHO}$	 $c\text{-C}_5\text{H}_9\text{B}(\text{C}_5\text{H}_9\text{-}c)_2$	1. $\text{Li-C}\equiv\text{C-CH}_2\text{Cl}$ , $\text{B}(\text{C}_5\text{H}_9\text{-}c)_3$ , THF, $-90^\circ$ to rt 2. Aldehyde, $-78^\circ$ to rt, 1.5 h	 (79)	807
	 BBN	THF, rt, 1.5 h	 (85)	811
	 TMS	THF, $-78^\circ$ , 3 h	 (80), 98	806
	 $\text{B}(\text{OBu-}n)_2$	Ether, $40^\circ$ , 48 h	 (50)	814
	 OPri- <i>i</i>	Toluene, $-78^\circ$	 (47), 93	123
	 Ts, Ph	$\text{CH}_2\text{Cl}_2$ , $-78^\circ$ , 2.5 h	 (74), 98	153

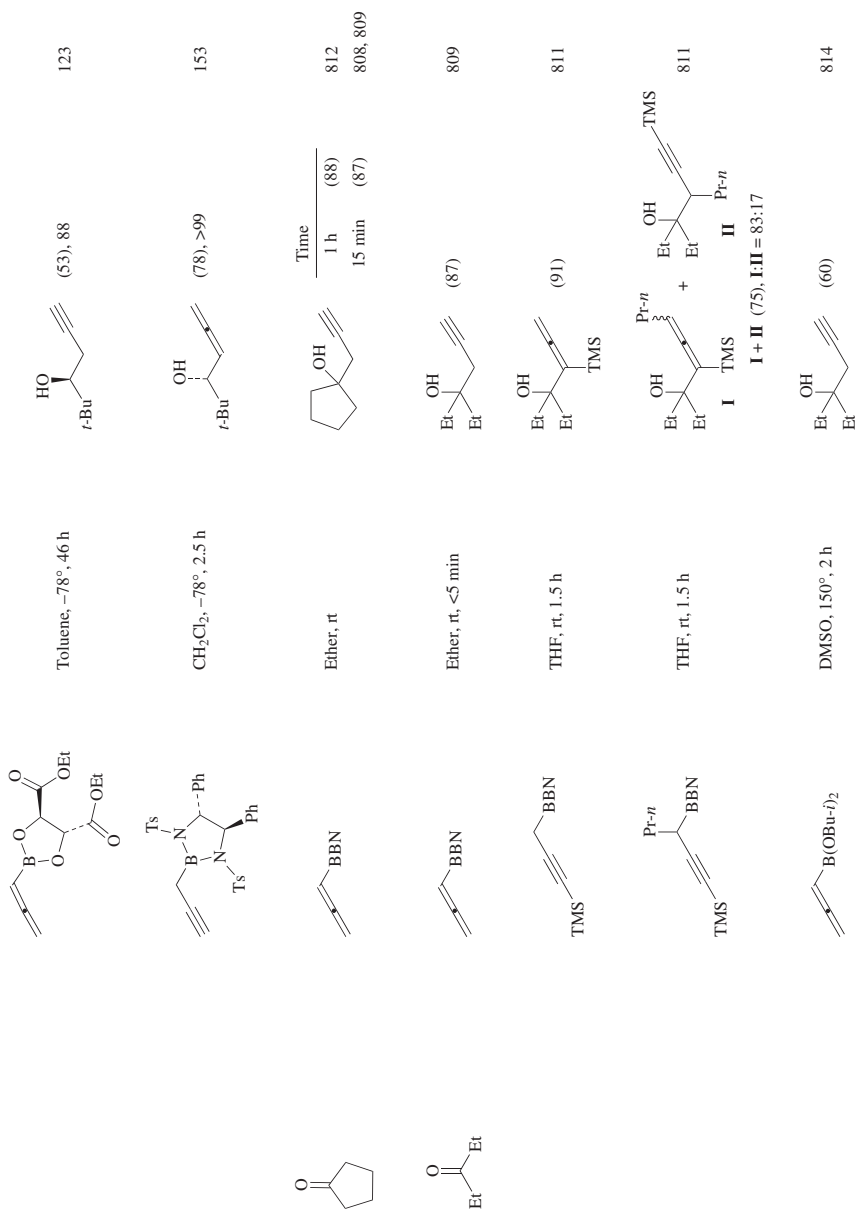
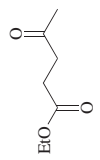

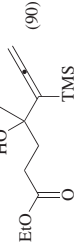

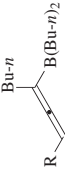

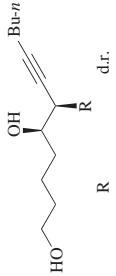
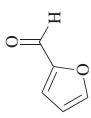

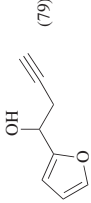
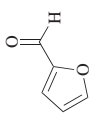
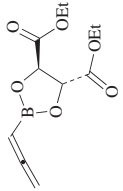
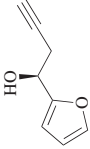
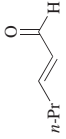
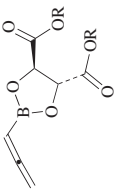

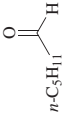

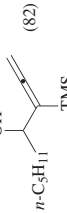


TABLE 7. ADDITION OF ALLENYL AND PROPARGYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		THF, rt, 2 h	 (90)	815
		1.  , <i>n</i> -BuLi, THF 2. B(Bu- <i>n</i> ) <sub>3</sub> , -78° 3. BCl <sub>3</sub> , -78° to rt	 (802)	802
		Ether, rt, 15 min	 (79)	808, 809
		Toluene, -78°, 46 h	 (50), 70	123
		Toluene, -78° to rt	 (39), —	123
		THF, rt, 1.5 h	 (82)	811

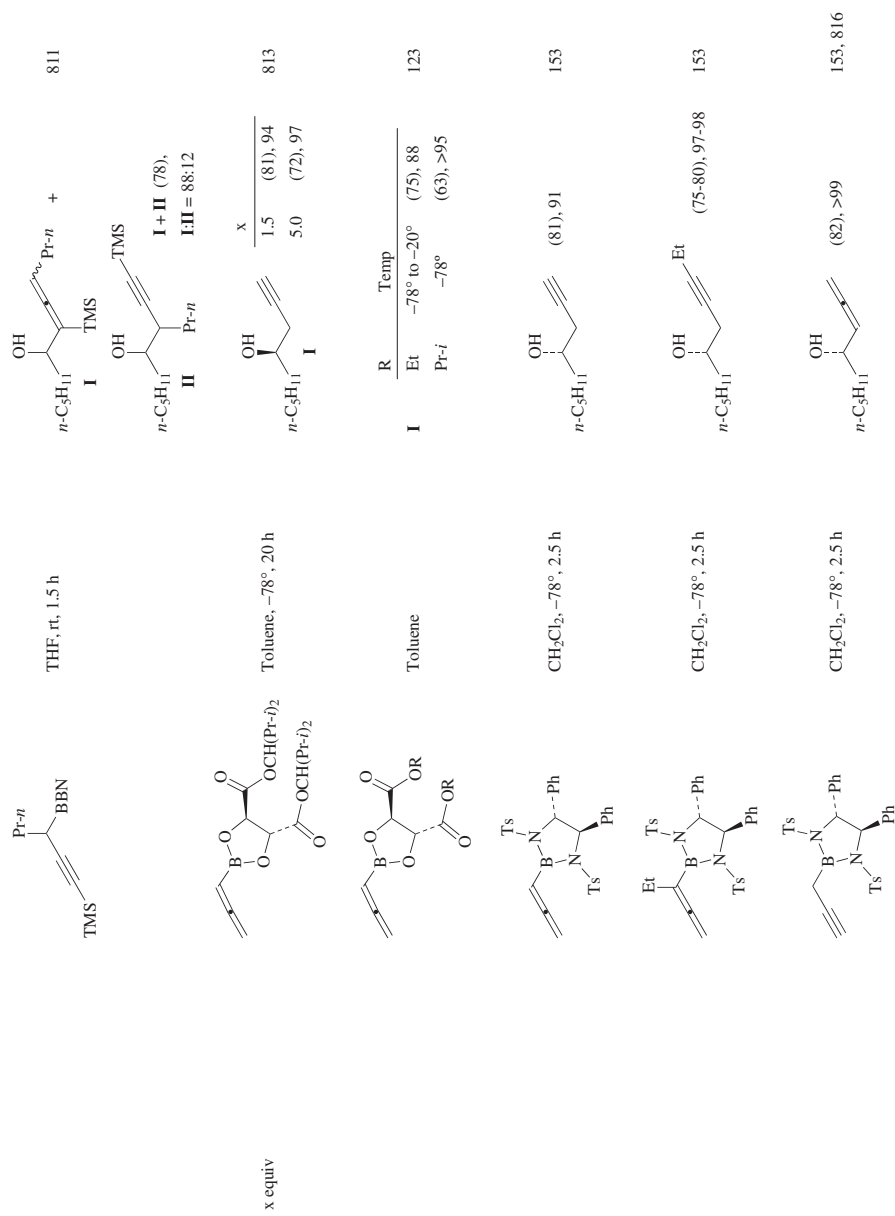


TABLE 7. ADDITION OF ALLENYL AND PROPARGYL REAGENTS (Continued)



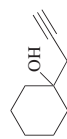

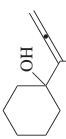
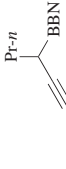
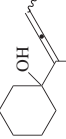
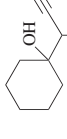
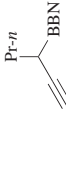
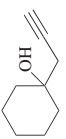



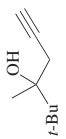

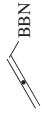
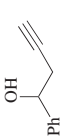

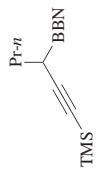
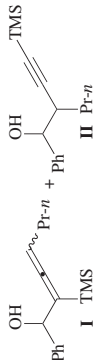


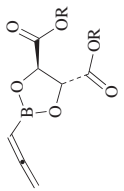
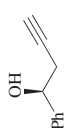
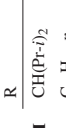
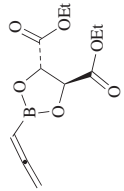
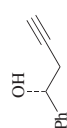
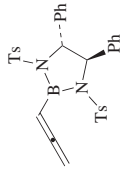

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Ether, rt, 1 h	 <b>I</b> (88) (94)	812
	"	Ether, rt, 15 min	808, 809	
		THF, rt, 1.5 h	 (91)	811
		THF, rt, 1.5 h	 <b>I</b> +  <b>II</b> (76), <b>III</b> = 91:9	811
		THF, rt, 1.5 h	 (68)	814
		Ether, 40°, 12 h		
		Ether, rt, 1 h	 (88)	812
		Ether, rt, 15 min	 (82)	808, 809



TABLE 7. ADDITION OF ALLENYL AND PROPARGYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.									
		THF, rt, 1.5 h	 I + II (72), I:II = 87:13	811									
		Ether, 40°, 3 h		814									
	 R = Et, Pr-i	Toluene	 I	123									
			<table border="1"> <thead> <tr> <th>R</th> <th>Temp</th> <th>Time</th> </tr> </thead> <tbody> <tr> <td>Et</td> <td>-78° to -20°</td> <td>21 h</td> </tr> <tr> <td>Pr-i</td> <td>-78°</td> <td>44 h</td> </tr> </tbody> </table>	R	Temp	Time	Et	-78° to -20°	21 h	Pr-i	-78°	44 h	(52), 60 (43), 79
R	Temp	Time											
Et	-78° to -20°	21 h											
Pr-i	-78°	44 h											
	" R = CH(Pr-i)2, C10H21-n	Toluene, -78°, 20 h	 I	813									
		Toluene, -78°, 44 h	 I	123									
		CH2Cl2, -78°, 2.5 h	 I (76), 96	153									



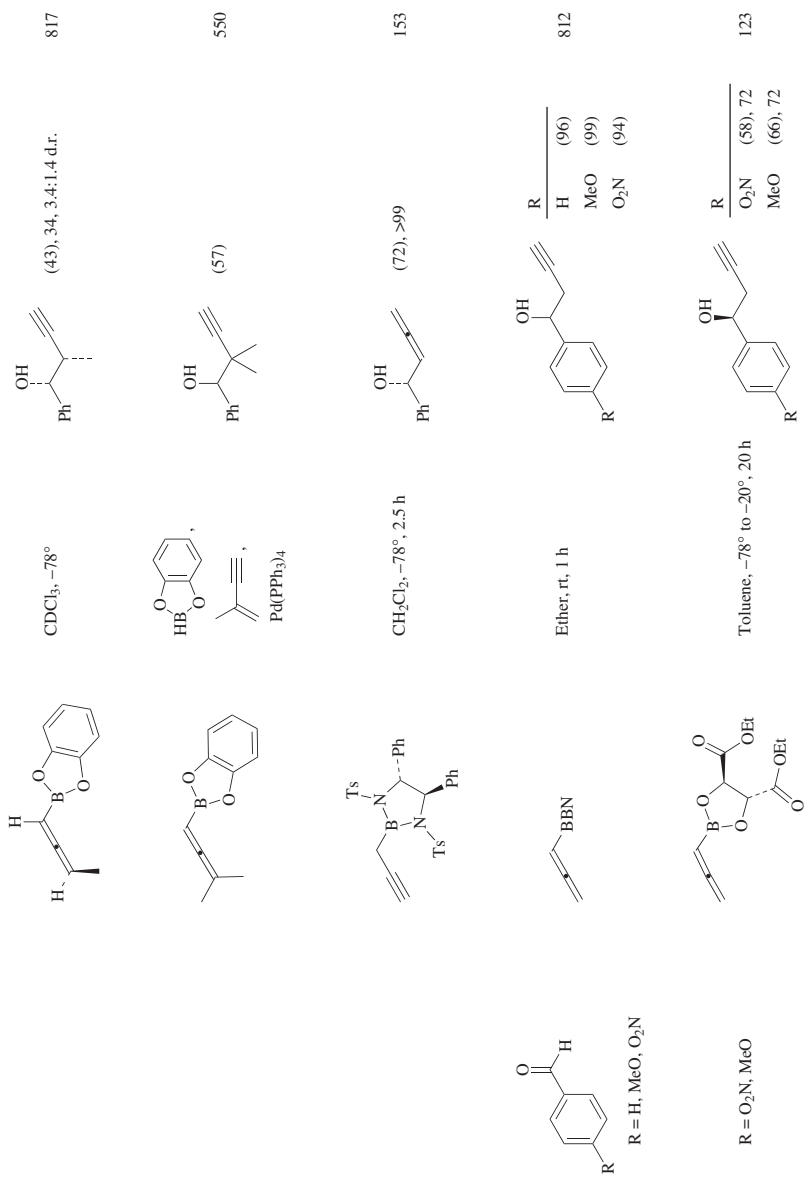



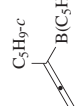




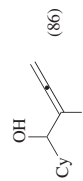
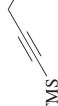
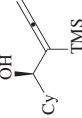
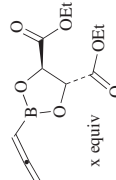
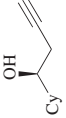
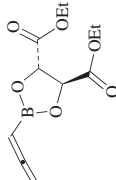
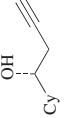


TABLE 7. ADDITION OF ALLENYL AND PROPARGYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Ether, rt, 1 h		812
		1. Li-  , B(C <sub>5</sub> H <sub>9-c</sub> ) <sub>3</sub> , THF, -90° 2. Aldehyde, -78° to rt, 1.5 h		807
		1. Li-  , B(C <sub>5</sub> H <sub>9-c</sub> ) <sub>3</sub> , THF, -90° to rt 2. Aldehyde, -78° to rt, 1.5 h		807
		Ether, -100°, 3 h		805
		Toluene, -78° to rt, 20 h		123
		Toluene, -78°, 44 h		123

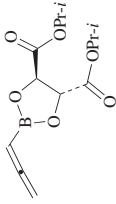
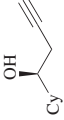
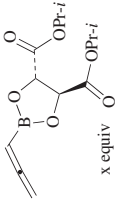
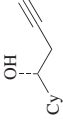
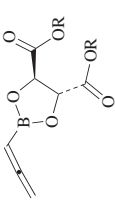
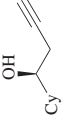
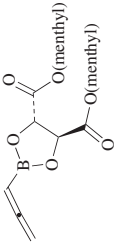
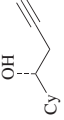
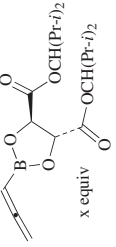
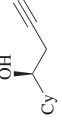
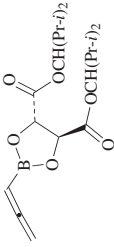
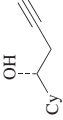

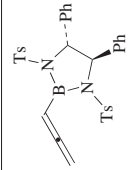
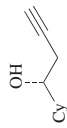
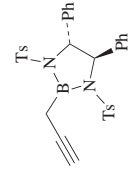
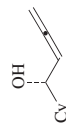
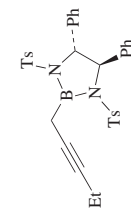
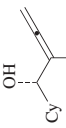





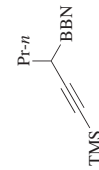
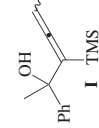
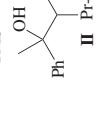
	Toluene, -78°, 24 h		(42), 90	123
	Toluene, -78°, 22 h		x 1.0 (70), 91 1.5 (81), 95	123
	Toluene, -78°, 20 h		R Et (81), 91 <i>i</i> -Pr (88), 92 <i>c</i> -C <sub>3</sub> H <sub>9</sub> (42), 91 menthyl (37), 93 <i>c</i> -C <sub>10</sub> H <sub>19</sub> (85), 98	813
	Toluene, -78°, 20 h		(69), 92	813
	Toluene, -78°, 20 h		x 1.0 (88), 98 3.0 (89), 99	813
	Toluene, -78°, 20 h		(82), 99	813

TABLE 7. ADDITION OF ALLENYL AND PROPARGYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
 C <sub>7</sub>		CH <sub>2</sub> Cl <sub>2</sub> , -78°, 2.5 h	 (82), 92	153
		CH <sub>2</sub> Cl <sub>2</sub> , -78°, 2.5 h	 (78), >99	153
		CH <sub>2</sub> Cl <sub>2</sub> , -78°, 2.5 h	 (78), 95	153
 C <sub>8</sub>		Eiher, rt	 (86)	808, 809
		THF, rt, 1.5 h	 (93)	811
		THF, rt, 1.5 h	 I TMS  II Pr- <i>n</i> I + II (88), I:II = 54:46	811

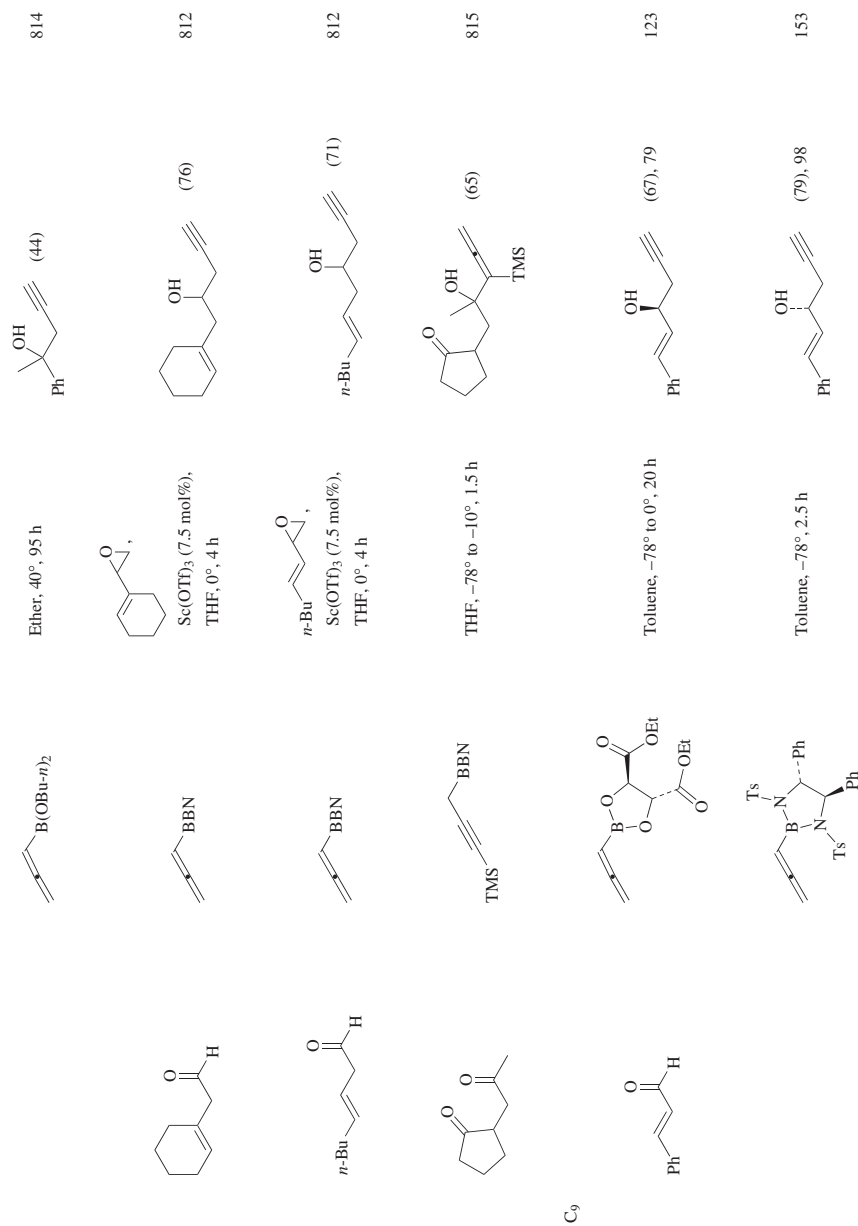
C<sub>9</sub>

TABLE 7. ADDITION OF ALLENYL AND PROPARGYL REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.	
C <sub>9</sub>		Toluene, -78°, 2.5 h		(74), >99	153
		THF, -78° to -15°, 1.5 h		(86)	815
		THF, rt, 2 h		(82)	815
		Ether, rt, 1 h		(99)	812
C <sub>10</sub>		, Se(OTf) <sub>3</sub> (7.5 mol%), THF, 0°, 4 h		R H (73) OMe (77) NO <sub>2</sub> (98)	812
		BF <sub>3</sub> ·OEt <sub>2</sub> (15 mol%), THF, 20°, 4 h		R H (73) NO <sub>2</sub> (22)	812

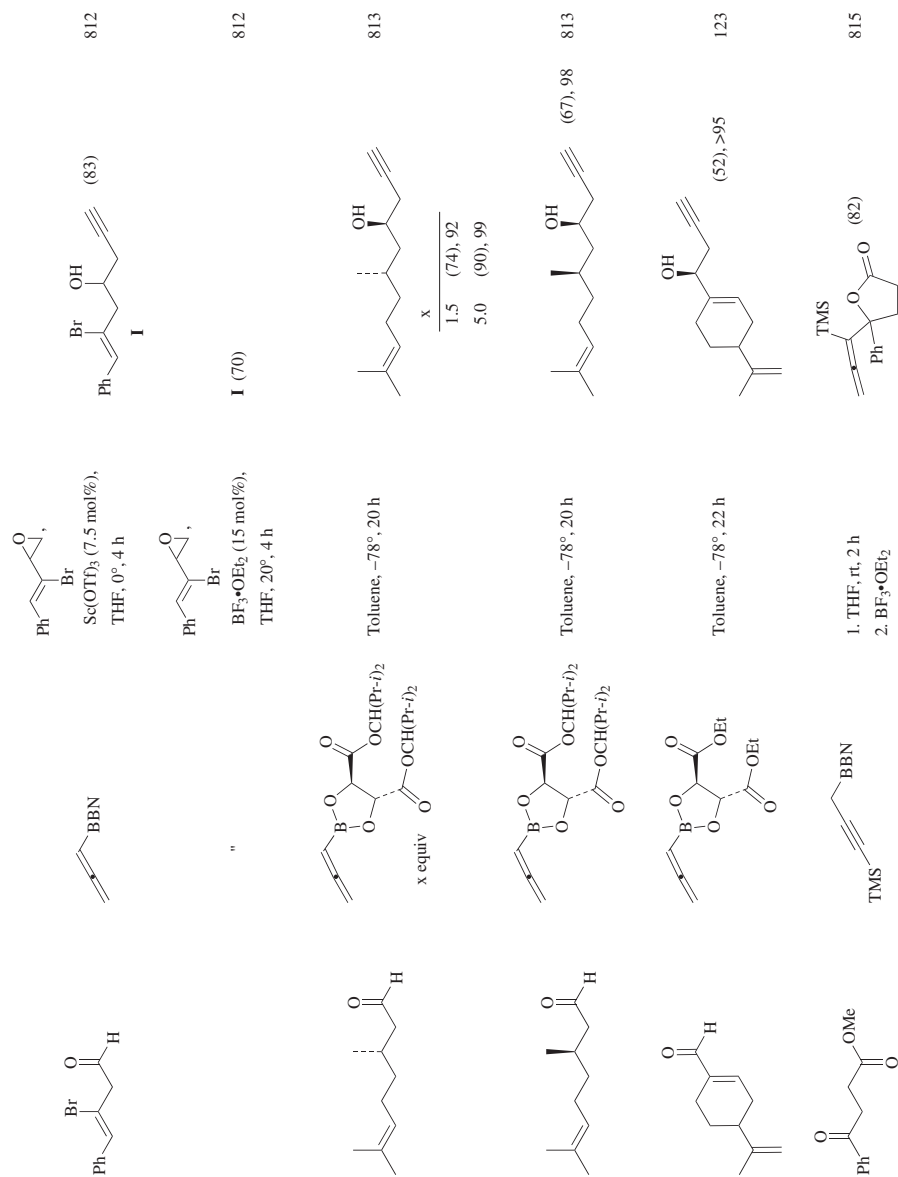


TABLE 7. ADDITION OF ALLENYL AND PROPARGYL REAGENTS (Continued)

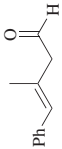

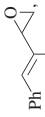
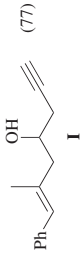
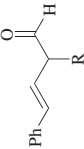


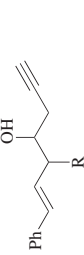


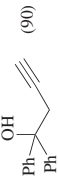
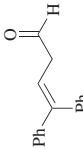

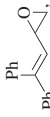
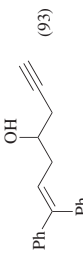
Carbonyl Substrate	Allenyl/Propargyl Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		 , Sc(OTf) <sub>3</sub> (7.5 mol%), THF, 0°, 4 h	 (77)	812
	"	BF <sub>3</sub> •OEt <sub>2</sub> (15 mol%), THF, 20°, 4 h	<b>I</b> (78)	812
		 , Sc(OTf) <sub>3</sub> (7.5 mol%), THF, 0°, 4 h		812
		Ether, rt, <5 min	 (90)	809
		 , Sc(OTf) <sub>3</sub> (7.5 mol%), THF, 0°, 4 h	 (93)	812



TABLE 8. ADDITION OF CYCLIC REAGENTS


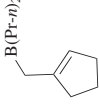
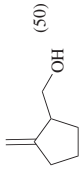
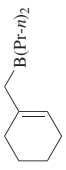
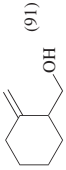
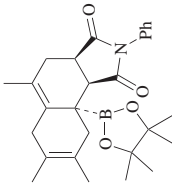
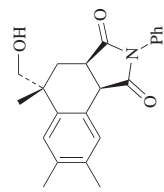

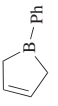
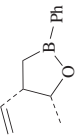
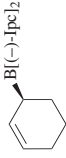
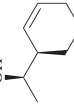
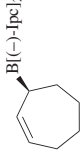
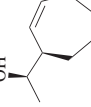
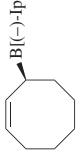
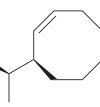

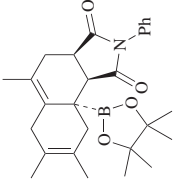
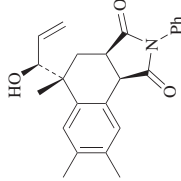

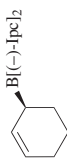
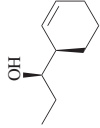
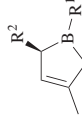
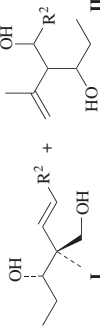
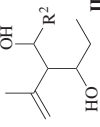
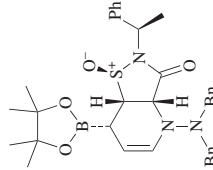
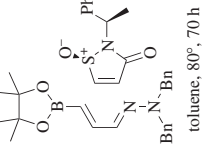
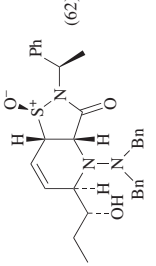
Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C <sub>1</sub> 		-60° to 0°	 (50)	545
		-60° to 0°	 (91)	545
		1. 100° 2. DDQ	 (29), >95:5 d.r.	818
C <sub>2</sub> 		Ether, -78° to rt	 (94), >97.5:2.5 d.r.	819
		THF, -78° to rt	 (66), 94, >99:1 d.r.	69, 820
		THF, -78°	 (36), 93, >99:1 d.r.	820
		THF, -78°	 (24), 95, >99:1 d.r.	820

TABLE 8. ADDITION OF CYCLIC REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		-70° to 0°	 I + II (65-80), I:II = 53:47 	545
		-60° to 0°	(70)	545
		-60° to 0°	(74)	545
		Ether, -78° to rt	 (94), >97.5:2.5 d.r.	819
		Ether, -78° to rt	 (95), >97.5:2.5 d.r.	819
		THF, -78°, 4 h	 (81), >98, 98:2 d.r.	255



TABLE 8. ADDITION OF CYCLIC REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.																				
		1. 40° 2. DDQ	 (71), >95:5 d.r.	818																				
		THF, -78° to rt	 (65), 93, >99:1 d.r.	820																				
		—	 I	601																				
			 II																					
			<table border="1"> <thead> <tr> <th>R<sup>1</sup></th> <th>R<sup>2</sup></th> <th>I + II</th> <th>II/I</th> </tr> </thead> <tbody> <tr> <td>Thex</td> <td>Cy</td> <td>(70)</td> <td>98:2</td> </tr> <tr> <td>Thex</td> <td>Cy</td> <td>(85)</td> <td>97:3</td> </tr> <tr> <td>Thex</td> <td><i>n</i>-C<sub>6</sub>H<sub>13</sub></td> <td>(72)</td> <td>54:46</td> </tr> <tr> <td>Cy</td> <td>Cy</td> <td>(89)</td> <td>54:46</td> </tr> </tbody> </table>	R <sup>1</sup>	R <sup>2</sup>	I + II	II/I	Thex	Cy	(70)	98:2	Thex	Cy	(85)	97:3	Thex	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	(72)	54:46	Cy	Cy	(89)	54:46	
R <sup>1</sup>	R <sup>2</sup>	I + II	II/I																					
Thex	Cy	(70)	98:2																					
Thex	Cy	(85)	97:3																					
Thex	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	(72)	54:46																					
Cy	Cy	(89)	54:46																					
		 toluene, 80°, 70 h	 (62)	199																				

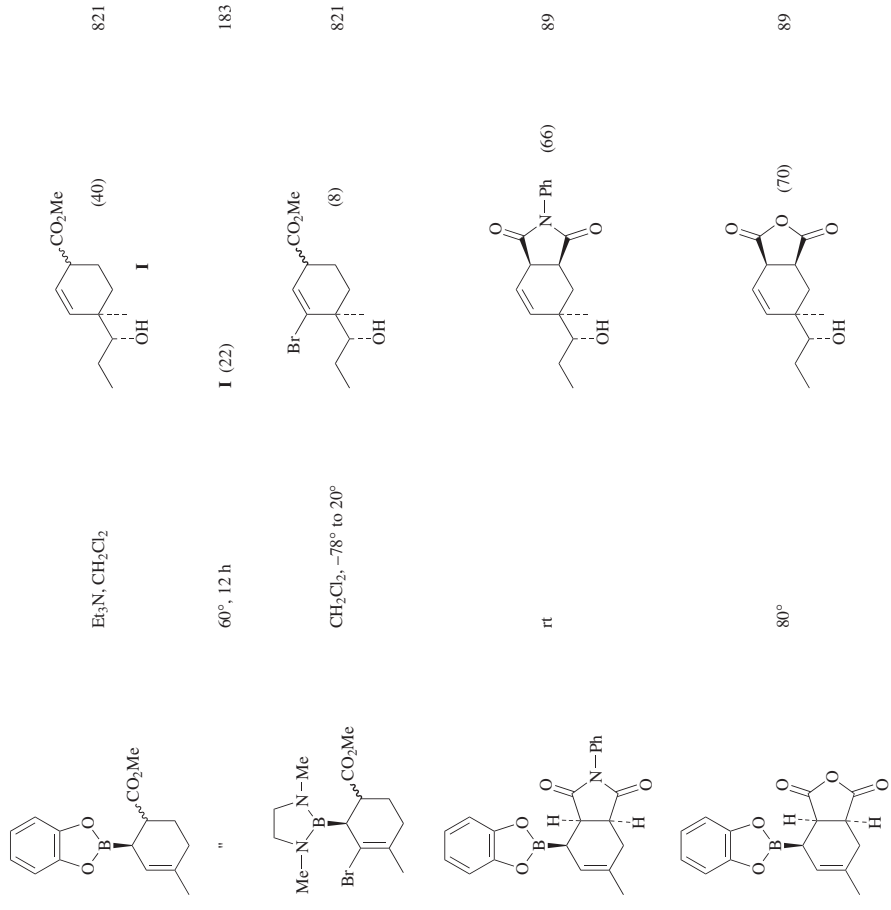


TABLE 8. ADDITION OF CYCLIC REAGENTS (Continued)


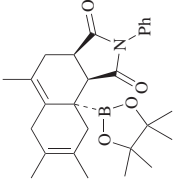
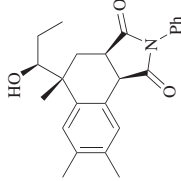


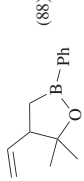
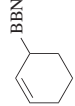
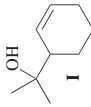



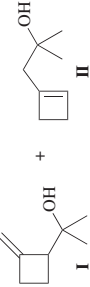

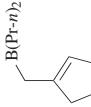
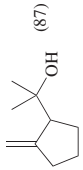
Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		1. -40° 2. DDQ	 (61), >95:5 d.r.	818
		Ether, -78° to rt	 (88)	819
		Pentane, rt, 2 h	 (86)	103
	"	1.  , HBEN, pentane, rt, 24 h 2. Ketone, rt, 2 h	 (68)	103
		-70° to 0°	 (87) +  (86) I + II (65-80), I:II = >100:1	545
		-60° to 0°	 (87)	545



TABLE 8. ADDITION OF CYCLIC REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.												
$C_4$ 		—		601												
			<table border="1"> <thead> <tr> <th>R<sup>1</sup></th> <th>R<sup>2</sup></th> <th>I + II</th> <th>I:II</th> </tr> </thead> <tbody> <tr> <td>Thex</td> <td>Cy</td> <td>(85)</td> <td>97:3</td> </tr> <tr> <td>Thex</td> <td>C<sub>5</sub>H<sub>9</sub>-c</td> <td>(81)</td> <td>53:47</td> </tr> </tbody> </table>	R <sup>1</sup>	R <sup>2</sup>	I + II	I:II	Thex	Cy	(85)	97:3	Thex	C <sub>5</sub> H <sub>9</sub> -c	(81)	53:47	
R <sup>1</sup>	R <sup>2</sup>	I + II	I:II													
Thex	Cy	(85)	97:3													
Thex	C <sub>5</sub> H <sub>9</sub> -c	(81)	53:47													
		rt		89												
		80°		89												
		Benzene, 20°, 4 h		822												



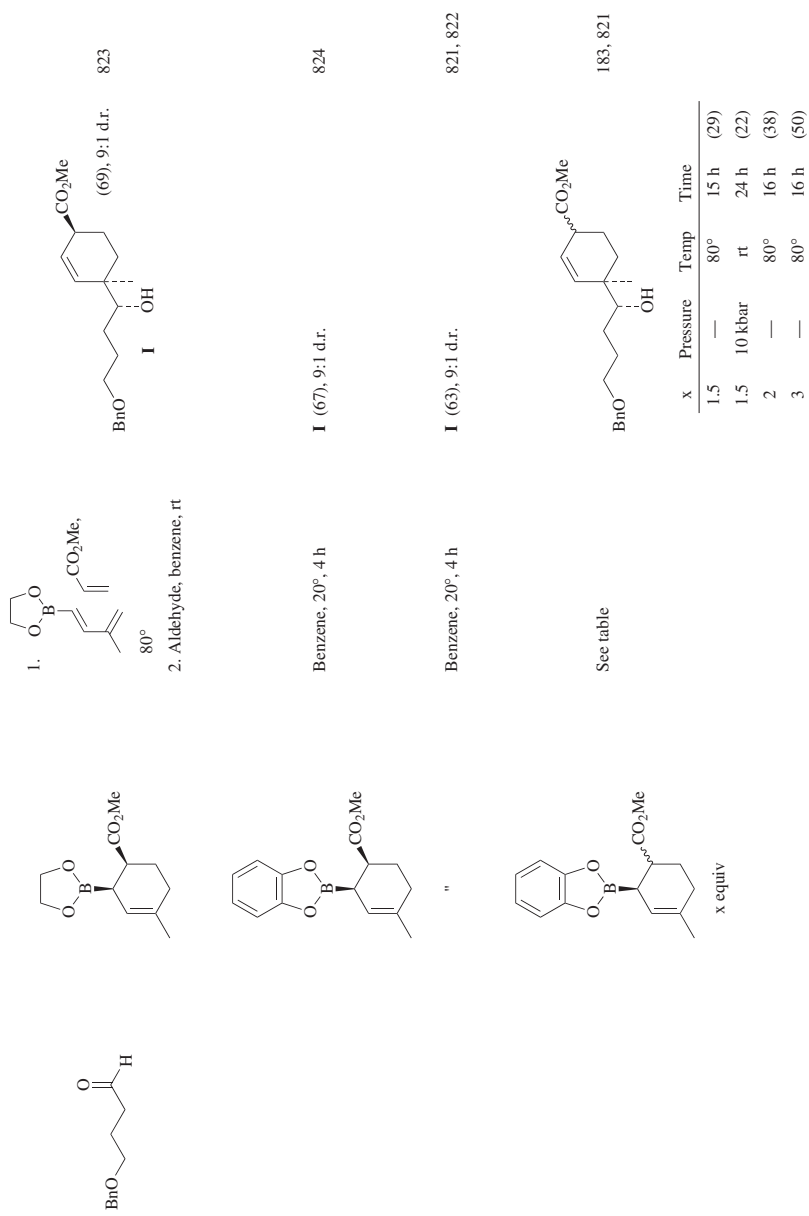

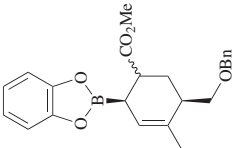
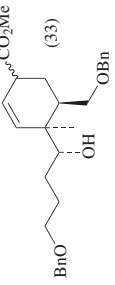
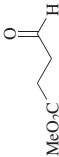
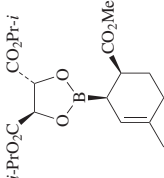
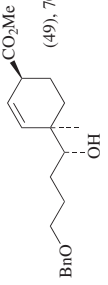
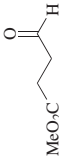
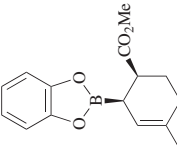
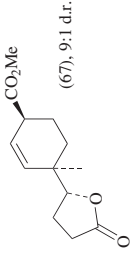


TABLE 8. ADDITION OF CYCLIC REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		80°, 15.5 h	 (33)	183, 821
		1. <i>i</i> -PrO <sub>2</sub> C, CO <sub>2</sub> Pr- <i>i</i> , O, O, CO <sub>2</sub> Me, 80° 2. Aldehyde, benzene, rt	 (49), 70	823
		Benzene, 20°, 4 h	 (67), 9:1 d.r.	822

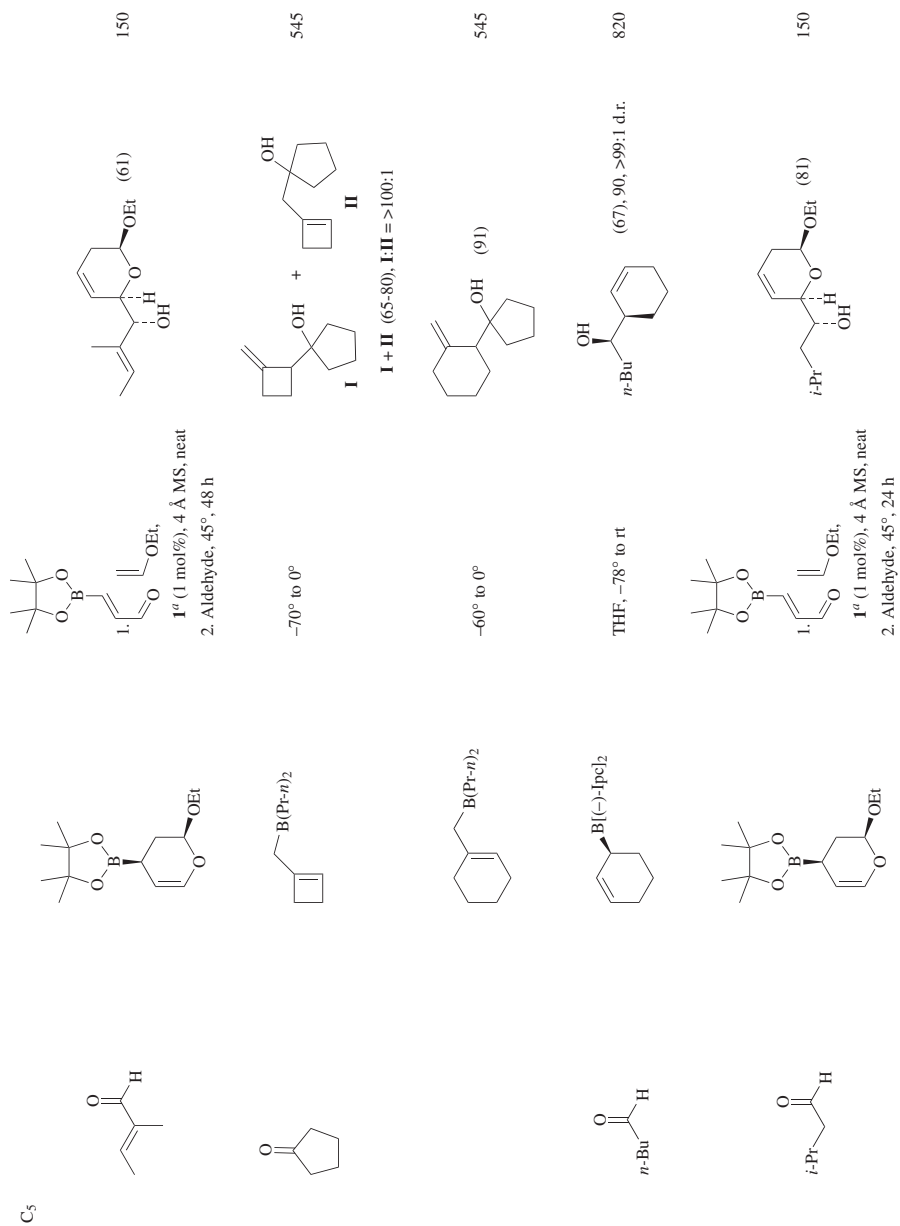
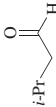
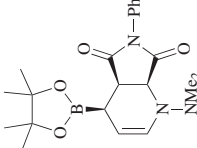
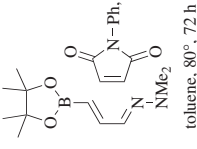
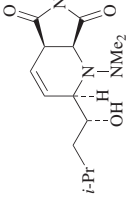
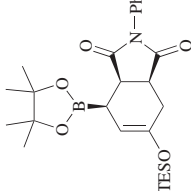
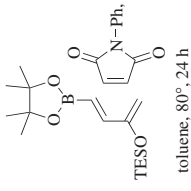
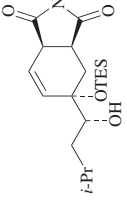


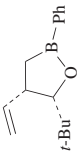
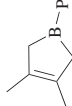
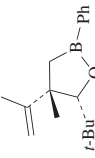


TABLE 8. ADDITION OF CYCLIC REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		 toluene, 80°, 72 h	 (50)	181
		 toluene, 80°, 24 h	 (88)	825
		Ether, -78° to rt	 (95), >97:5:2.5 d.r.	819
		Ether, -78° to rt	 (94), >97:5:2.5 d.r.	819

C<sub>5</sub>

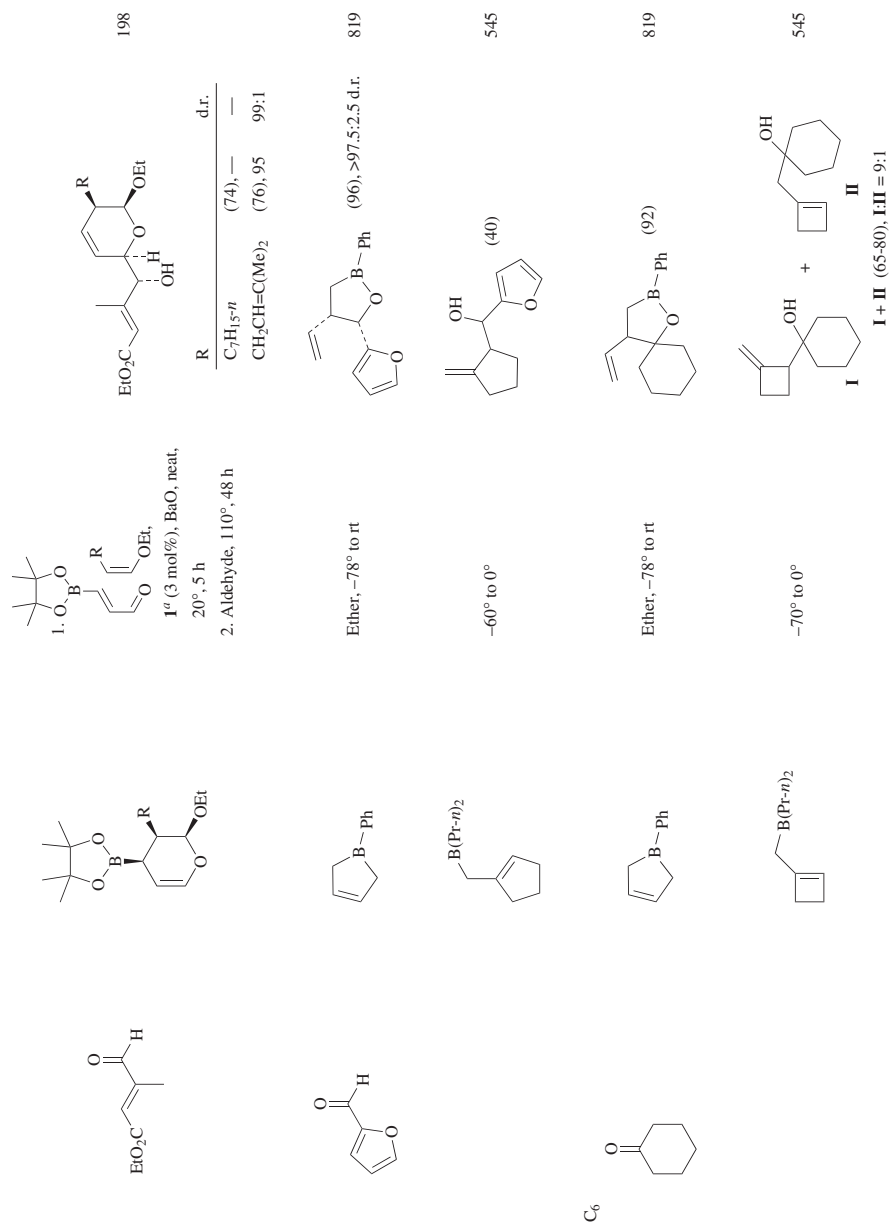

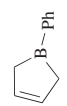
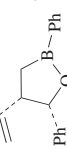

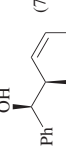
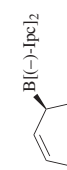
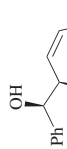

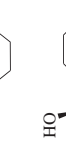
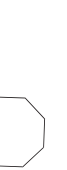
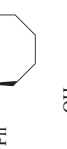
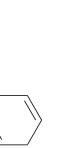
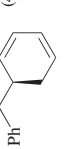
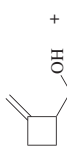

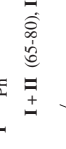


TABLE 8. ADDITION OF CYCLIC REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		Ether, -78° to rt	 (97), >97.5:2.5 d.r.	819
		THF, -78° to rt	 (71), 94, >99:1 d.r.	820
		THF, -78°	 (38), 95, >99:1 d.r.	820
		THF, -78°	 (28), 93, >99:1 d.r.	820
		THF, -78°	 (40), 79, 24:1 d.r.	826
		-70° to 0°	 <b>I</b> +  <b>II</b> (65-80), <b>I:II</b> = 3:2	545
		Ether, -78° to rt	 (94), >97.5:2.5 d.r.	819

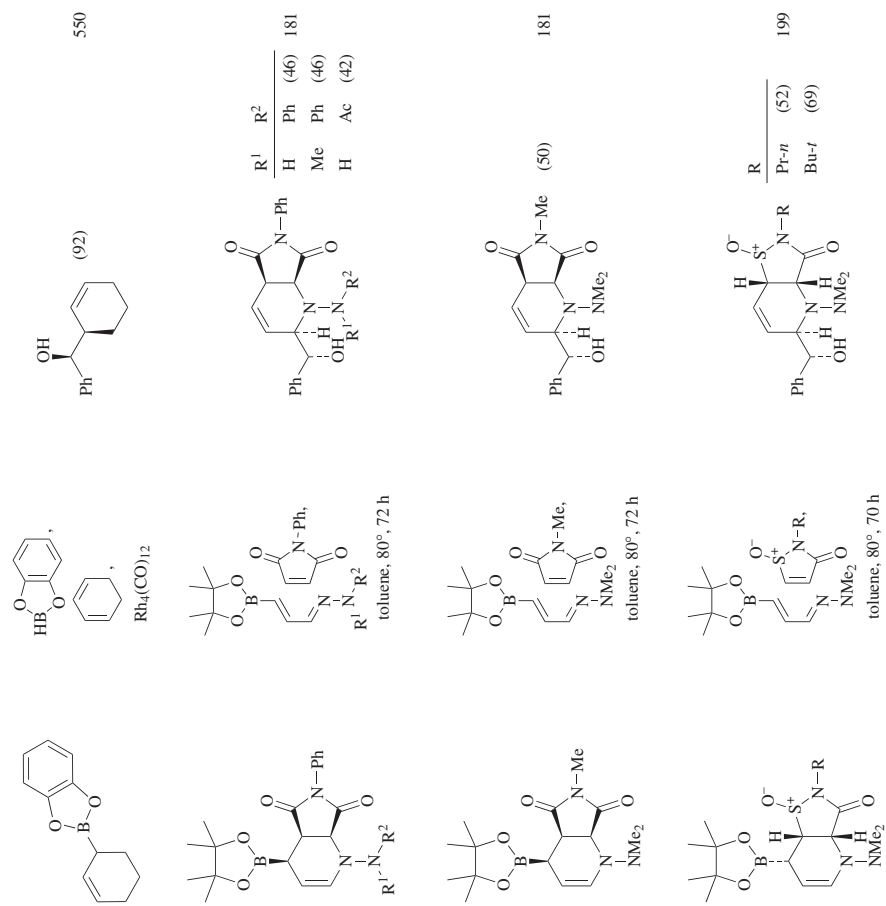

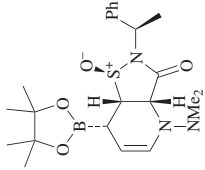
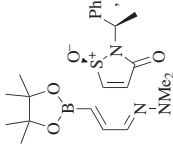
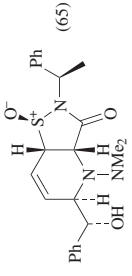
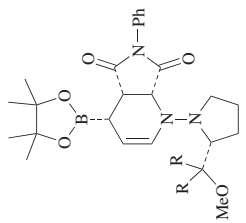
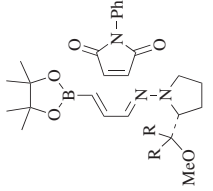
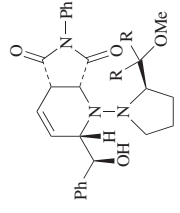
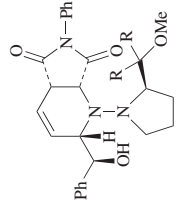
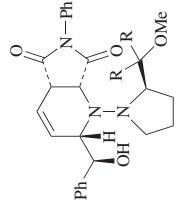
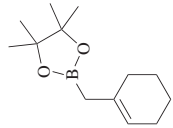
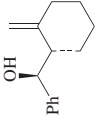


TABLE 8. ADDITION OF CYCLIC REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		 toluene, 80°, 70 h	 (65) 199	
		 toluene, 80°, 72 h	   R d.r. H (55) 9:1 Me (55) >97.5:2.5	182 181, 182
		—	 (90), >100:1	52

C<sub>7</sub>



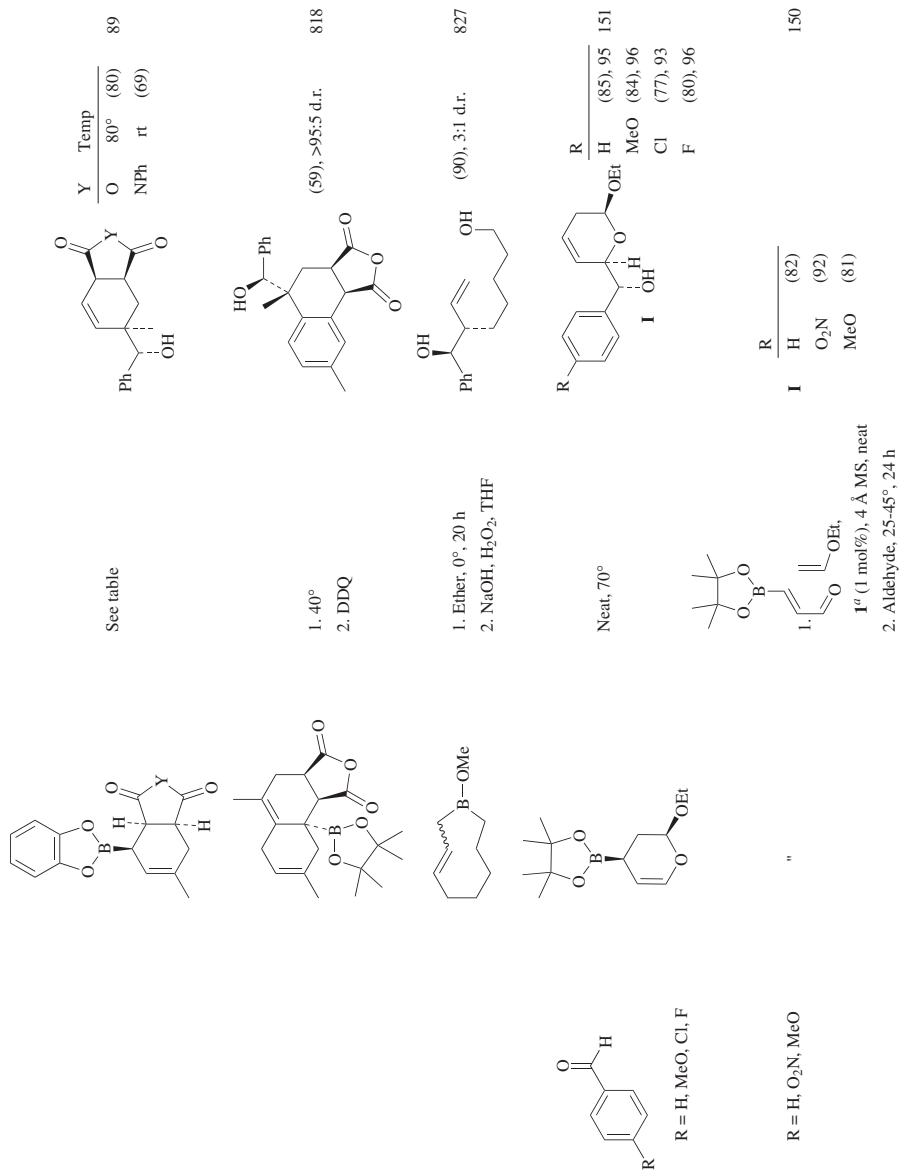
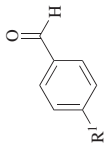
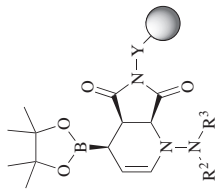
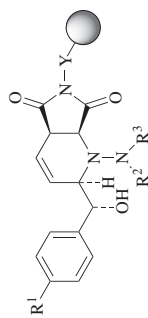
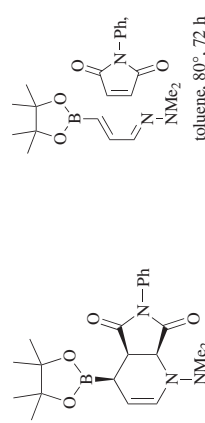
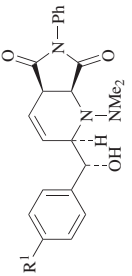


TABLE 8. ADDITION OF CYCLIC REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.												
 <p>R<sup>1</sup> = H, Br</p>	 <p>R<sup>2</sup>, R<sup>3</sup></p> <p>Y = C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>p</p>	toluene, 80°, 72 h	 <p>182</p> <table border="1"> <thead> <tr> <th>R<sup>1</sup></th> <th>R<sup>2</sup></th> <th>R<sup>3</sup></th> </tr> </thead> <tbody> <tr> <td>H</td> <td>Me</td> <td>Me</td> </tr> <tr> <td>Br</td> <td>Me</td> <td>Me</td> </tr> <tr> <td>H</td> <td>Me</td> <td>H</td> </tr> </tbody> </table>	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	H	Me	Me	Br	Me	Me	H	Me	H	(62) (54) (60)
R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>														
H	Me	Me														
Br	Me	Me														
H	Me	H														
<p>R<sup>1</sup> = H, O<sub>2</sub>N, MeO</p>	 <p>NMe<sub>2</sub></p>	toluene, 80°, 72 h	 <p>181</p> <table border="1"> <thead> <tr> <th>R<sup>1</sup></th> </tr> </thead> <tbody> <tr> <td>H</td> </tr> <tr> <td>O<sub>2</sub>N</td> </tr> <tr> <td>MeO</td> </tr> </tbody> </table>	R <sup>1</sup>	H	O <sub>2</sub> N	MeO	(47) (48) (52)								
R <sup>1</sup>																
H																
O <sub>2</sub> N																
MeO																

C<sub>7</sub>

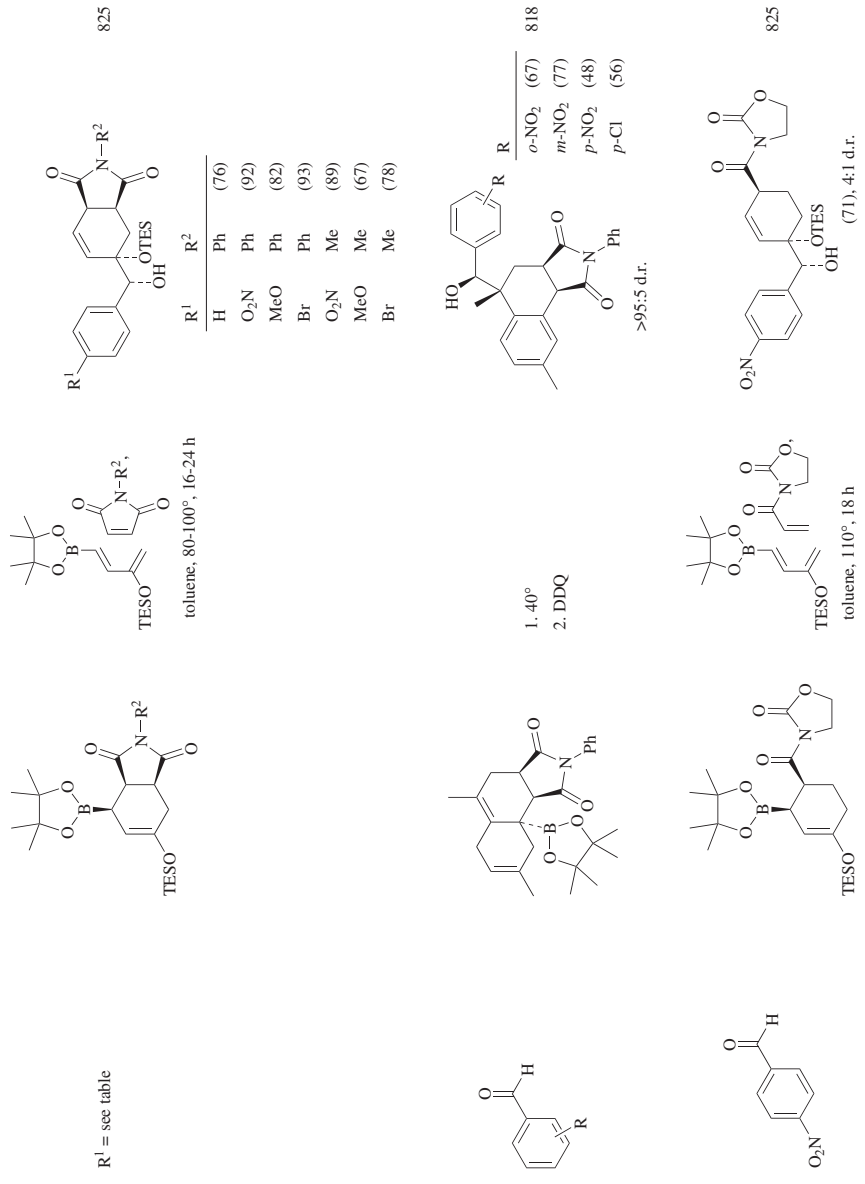
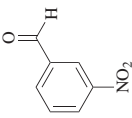
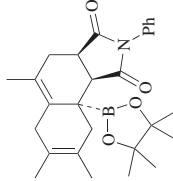
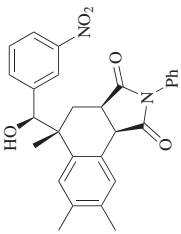
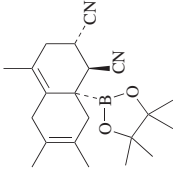
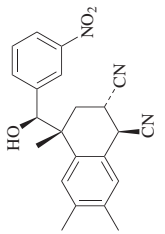
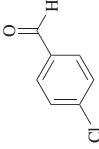
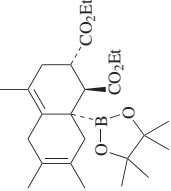
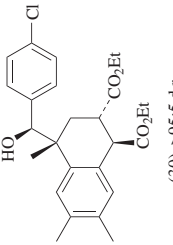


TABLE 8. ADDITION OF CYCLIC REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
		1. 40° 2. DDQ	 (83), >95:5 d.r.	818
		1. 40° 2. DDQ	 (52), >95:5 d.r.	818
		1. 40° 2. DDQ	 (30), >95:5 d.r.	818

C7

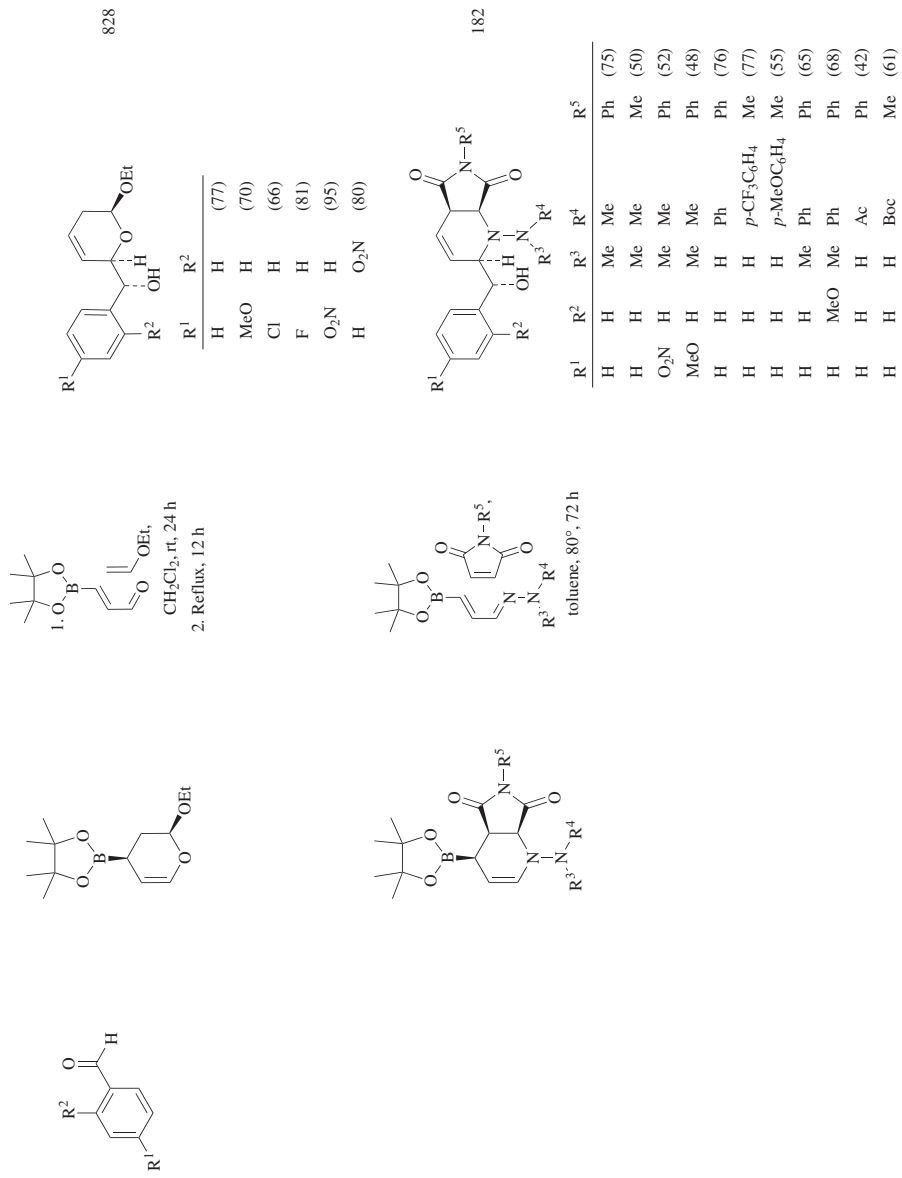

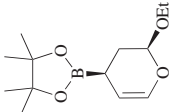

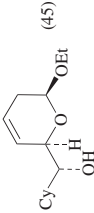
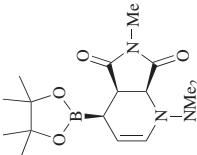
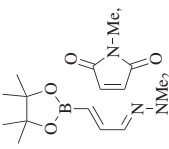
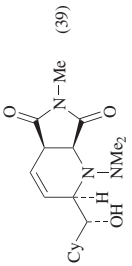
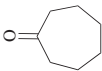

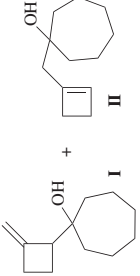
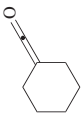

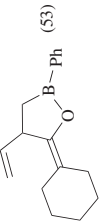


TABLE 8. ADDITION OF CYCLIC REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
C <sub>7</sub> 		1.  CH <sub>2</sub> Cl <sub>2</sub> , rt, 24 h 2. Reflux, 12 h	 (45)	828
		 toluene, 80°, 72 h	 (39)	182
		-70° to 0°	 I + II (65-80), <b>III</b> = 98:2	545
		Ether, -78° to rt	 (53)	819

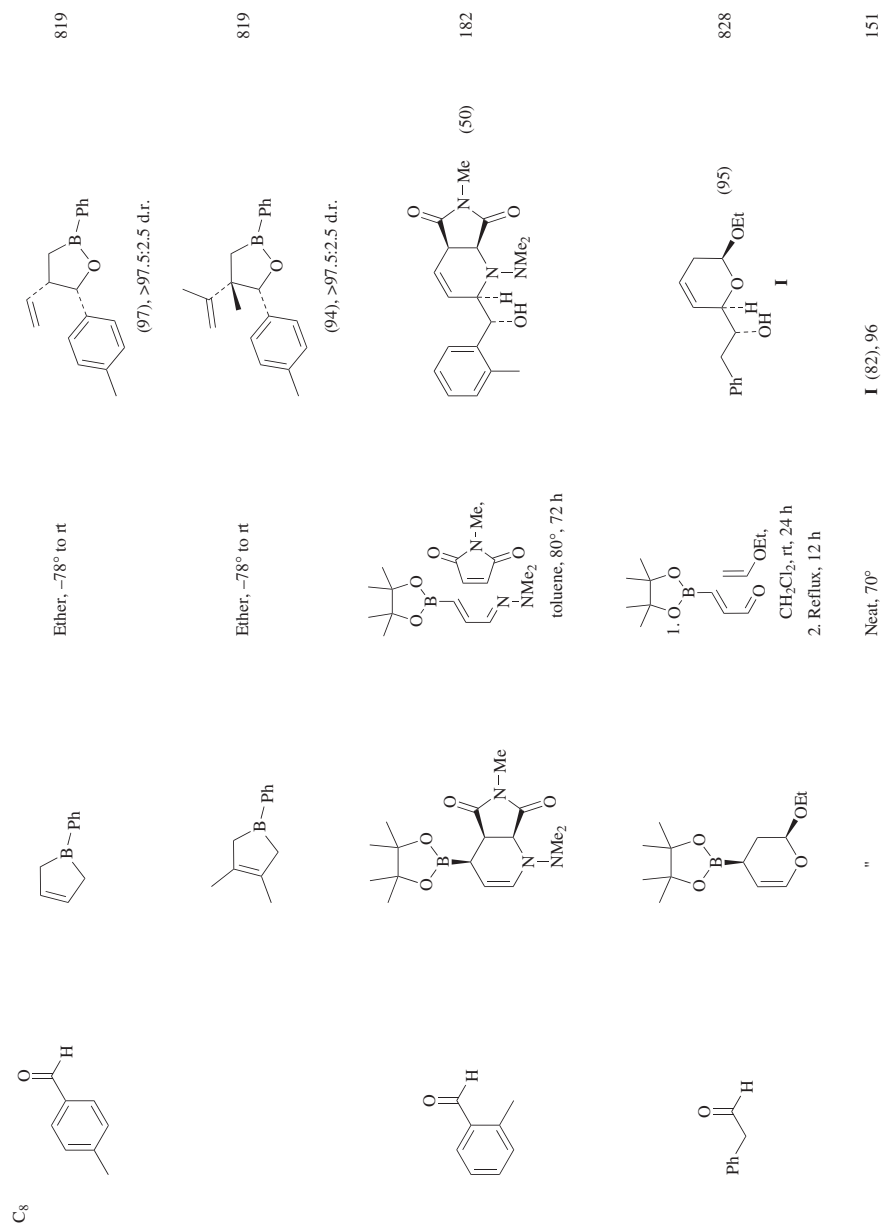
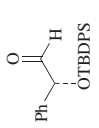
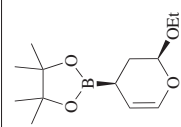
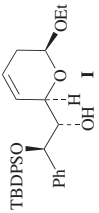
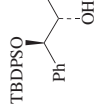
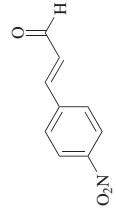
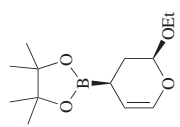
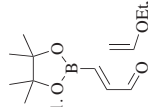
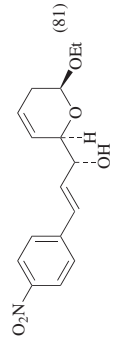
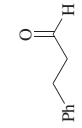
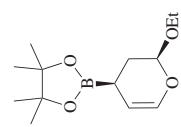
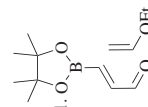
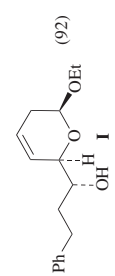



TABLE 8. ADDITION OF CYCLIC REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.												
		Neat, 70°	 (82), 96  I	151												
	"	70°	<table border="1"> <thead> <tr> <th>Solvent</th> <th>Time</th> <th>Yield (%)</th> <th>ee (%)</th> </tr> </thead> <tbody> <tr> <td>toluene</td> <td>48 h</td> <td>(78)</td> <td></td> </tr> <tr> <td>neat</td> <td>10 h</td> <td>(65)</td> <td></td> </tr> </tbody> </table>	Solvent	Time	Yield (%)	ee (%)	toluene	48 h	(78)		neat	10 h	(65)		829
Solvent	Time	Yield (%)	ee (%)													
toluene	48 h	(78)														
neat	10 h	(65)														
		1.  I' (1 mol%), 4 Å MS, neat 2. Aldehyde, 40°, 24 h	 (81)	150												
		1.  I' (1 mol%), 4 Å MS, neat 2. Reflux, 12 h	 (92)	828												
	"	Neat, 70°	 I (87), 96	151												



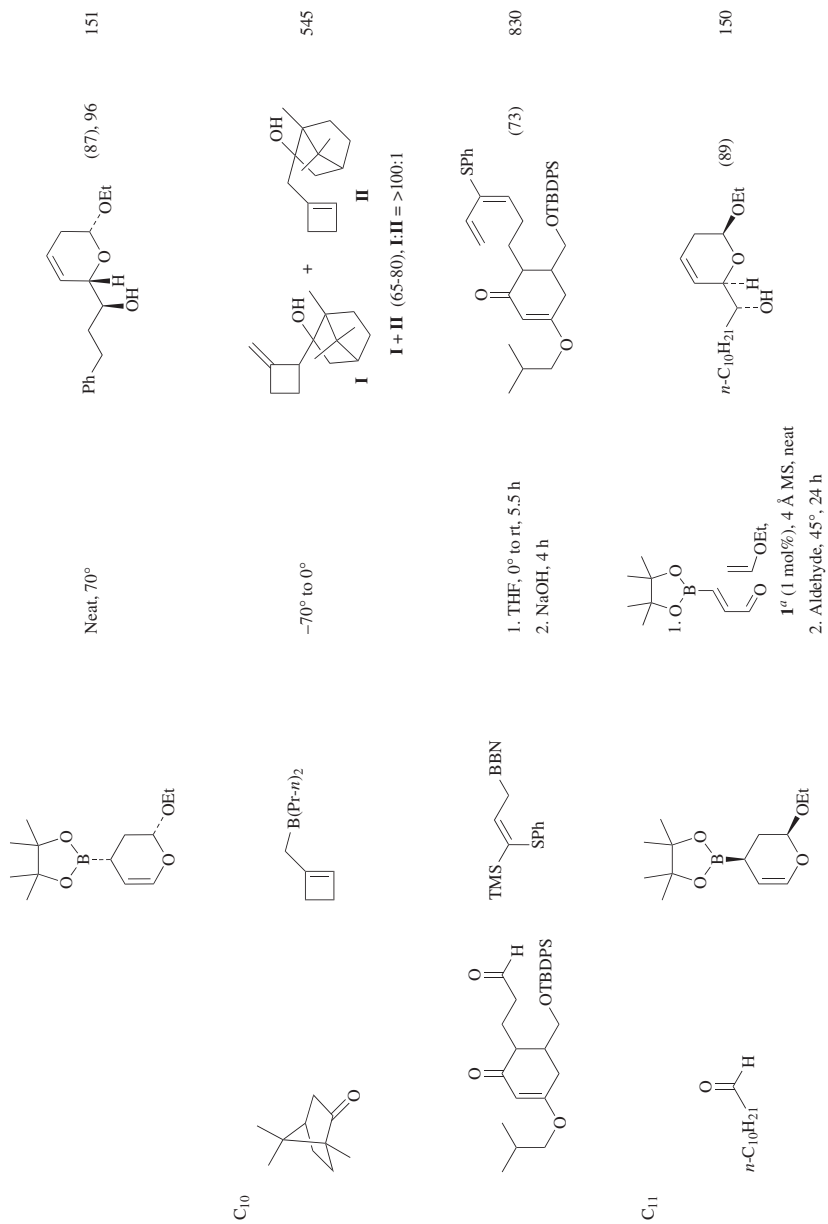
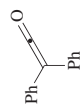
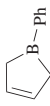
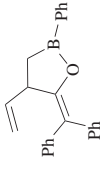
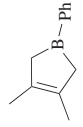
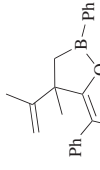


TABLE 8. ADDITION OF CYCLIC REAGENTS (Continued)

Carbonyl Substrate	Allylborane Reagent	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
 $\text{Ph}-\text{CH}=\text{CH}-\text{C}(=\text{O})-\text{Ph}$		Ether, $-78^\circ$ to rt	 (90)	819
		Ether, $-78^\circ$ to rt	 (94)	819

<sup>a</sup>The structure for catalyst **1** appears on the third page of Table 8.

TABLE 9. INTRAMOLECULAR ADDITIONS

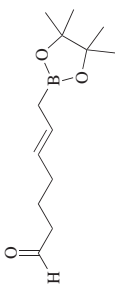
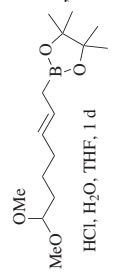
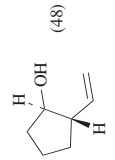
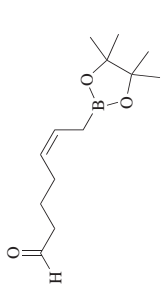
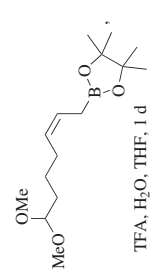
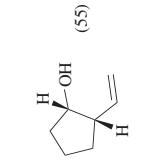
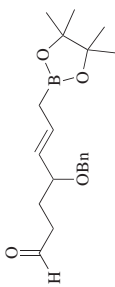
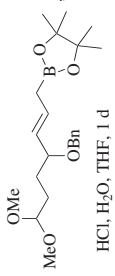
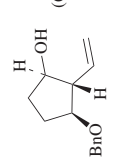
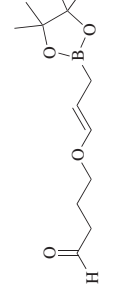
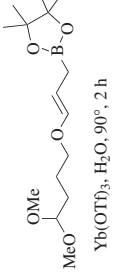
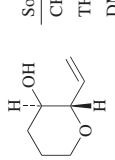
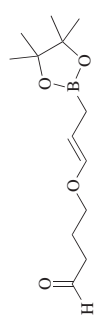
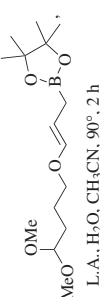
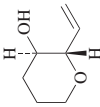

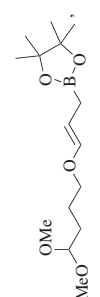

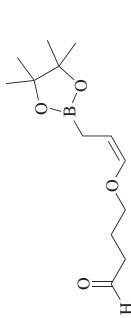
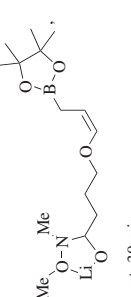
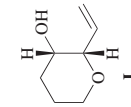

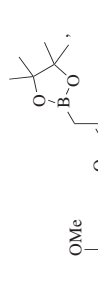

Carbonyl Substrate	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
	 HCl, H <sub>2</sub> O, THF, 1 d	 (48)	82
	 TFA, H <sub>2</sub> O, THF, 1 d	 (55)	82
	 HCl, H <sub>2</sub> O, THF, 1 d	 (66), 53:47 d.r.	82
	 Yb(OTf) <sub>3</sub> , H <sub>2</sub> O, 90°, 2 h	 (58) Solvent CH <sub>2</sub> Cl <sub>2</sub> (58) THF (28) DMF (18)	173

TABLE 9. INTRAMOLECULAR ADDITIONS (Continued)

Carbonyl Substrate	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
	 L.A., H <sub>2</sub> O, CH <sub>3</sub> CN, 90°, 2 h	 L.A. d.r. (56) — CuOTf (44) — AgOTf (42) — Sm(OTf) <sub>3</sub> (55) — Er(OTf) <sub>3</sub> (58) — Yb(OTf) <sub>3</sub> (77) >96:4	173
	 Yb(OTf) <sub>3</sub> , H <sub>2</sub> O, CH <sub>3</sub> CN, rt, 12 h	 <b>I (66)</b>	177
	 rt, 30 min	 Conditions pH 7 buffer, THF (60) H <sub>2</sub> O (pH 7) (70-74)	831 832
	 Yb(OTf) <sub>3</sub> , H <sub>2</sub> O, CH <sub>3</sub> CN, 90°, 2 h	 <b>I (61)</b> , >93.5:6.5 d.r.	173

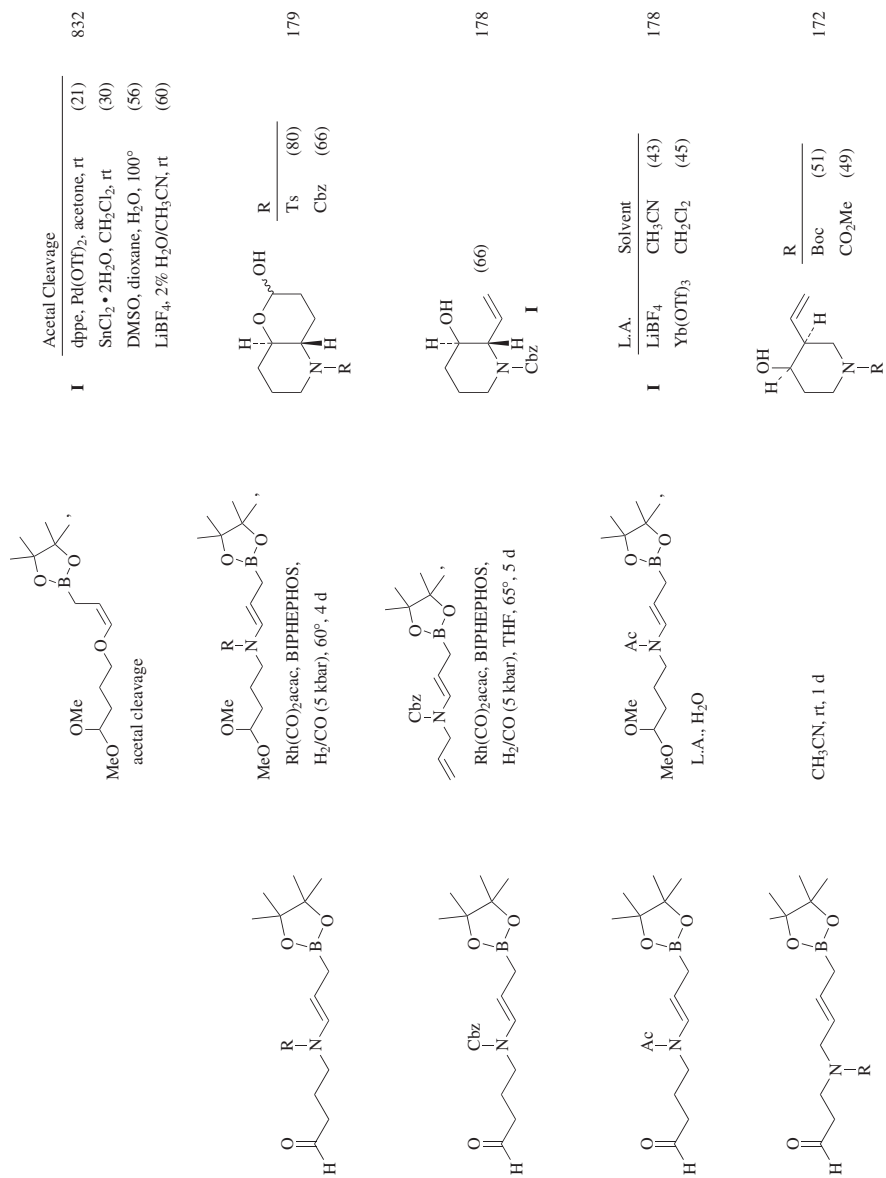


TABLE 9. INTRAMOLECULAR ADDITIONS (Continued)

Carbonyl Substrate	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
	CH <sub>3</sub> CN, rt, 1 d	(70), 94:6 d.r.	172
	CH <sub>3</sub> CN, rt, 1 d	(72)	172
	MeO HCl, H <sub>2</sub> O, THF, 1 d	(17), 20:80 E:Z	82
	acetal cleavage	Acetal Cleavage dippe, Pt(OTf) <sub>2</sub> , acetone (17) TFA, H <sub>2</sub> O, CHCl <sub>3</sub> , 0° (55)	80
	acetal cleavage	Acetal Cleavage TFA, H <sub>2</sub> O, CHCl <sub>3</sub> , 0° (51) SnCl <sub>2</sub> • 2H <sub>2</sub> O, CH <sub>2</sub> Cl <sub>2</sub> (51) TMSOTf, acetone (9) LiBF <sub>4</sub> , H <sub>2</sub> O, CH <sub>3</sub> CN (74)	80

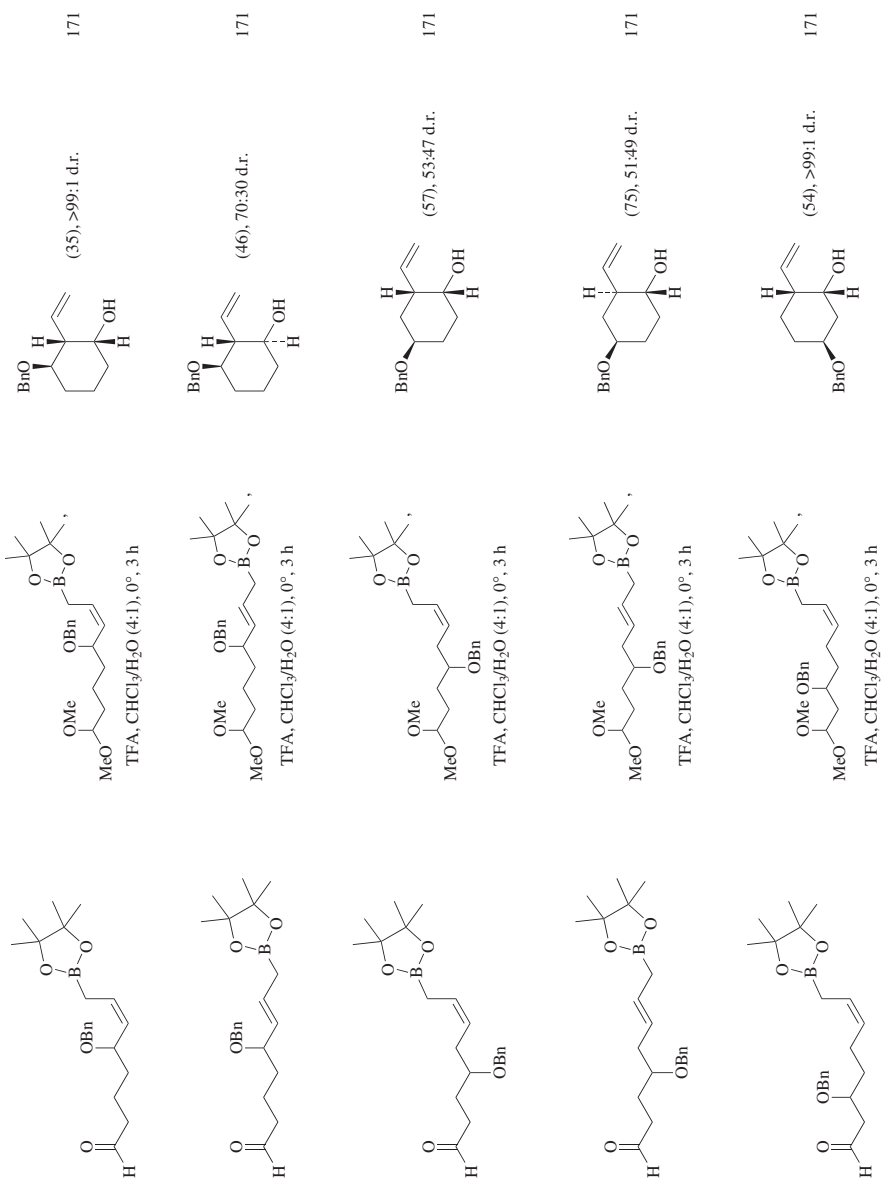
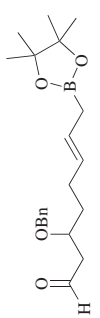
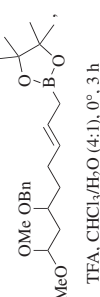
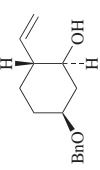
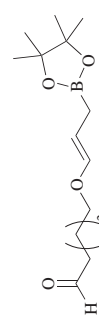
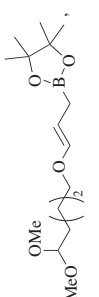
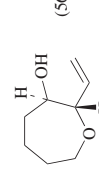
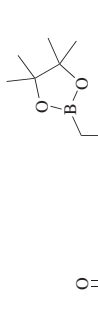
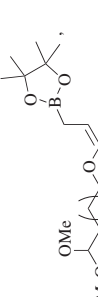
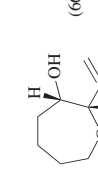
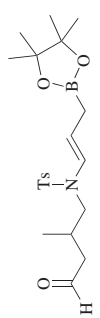

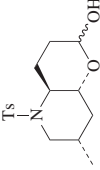
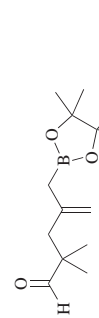

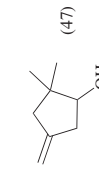


TABLE 9. INTRAMOLECULAR ADDITIONS (Continued)

Carbonyl Substrate	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
	 TFA, CHCl <sub>3</sub> /H <sub>2</sub> O (4:1), 0°, 3 h	 (58), 51:49 d.r.	171
	 Yb(OTf) <sub>3</sub> , H <sub>2</sub> O, CH <sub>3</sub> CN, 90°, 2 h	 (50), >98.5:1.5 d.r.	173
	 Yb(OTf) <sub>3</sub> , H <sub>2</sub> O, CH <sub>3</sub> CN, 90°, 2 h	 (66), >90.5:9.5 d.r.	173
	 Rh(CO) <sub>2</sub> acetac, BIPHEPHOS, H <sub>2</sub> , CO, 5 kbar, 60°, 4 d	 (83), 97:3 d.r.	179
	 Pd(OAc) <sub>2</sub> , PPh <sub>3</sub> (3 equiv) <sup>a</sup>	 (47)	174



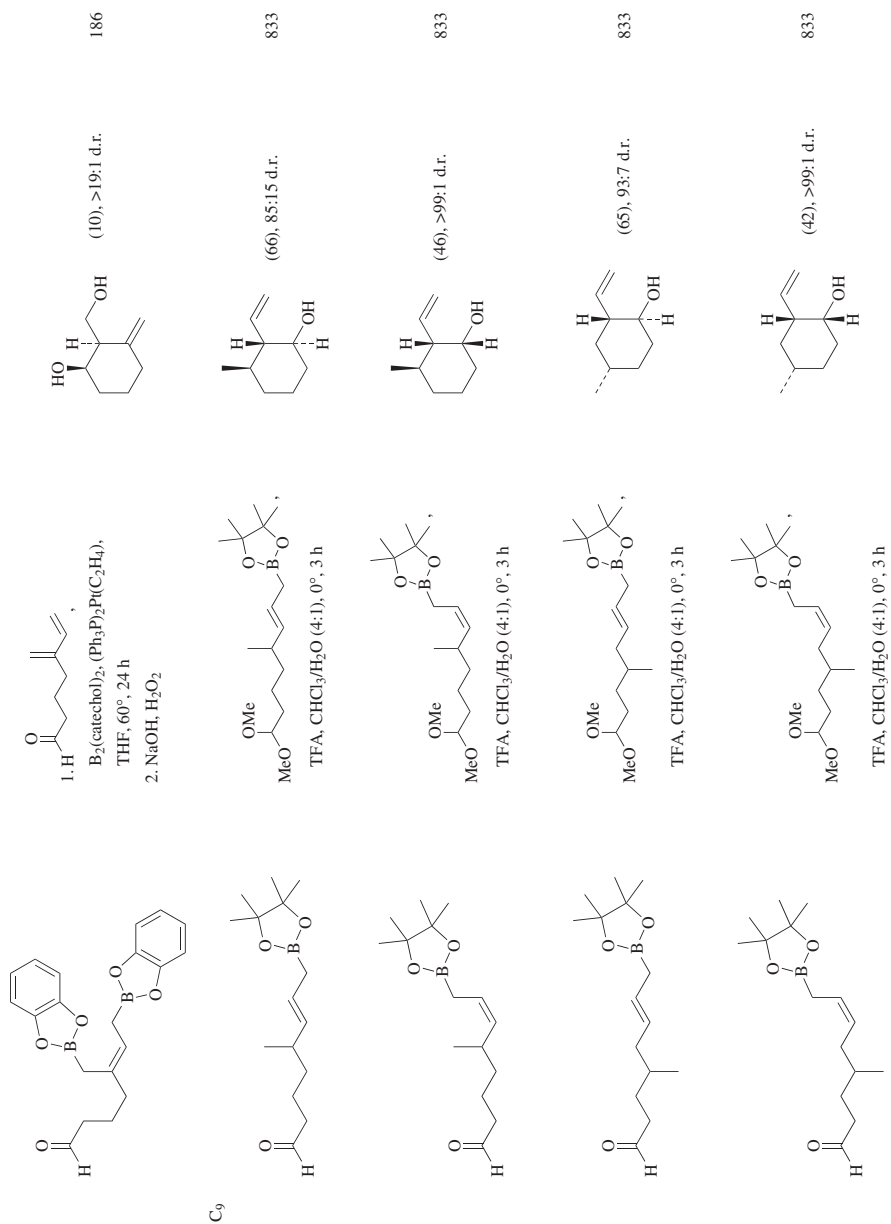
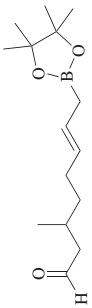

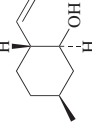
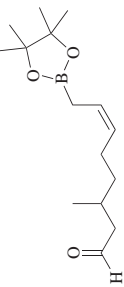

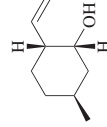
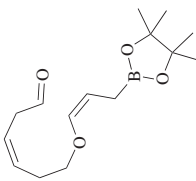
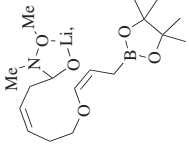
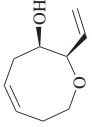
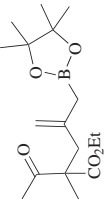
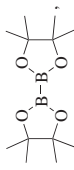
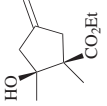
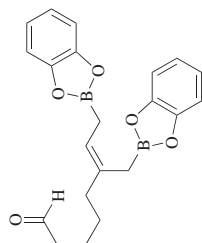
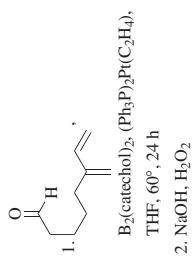
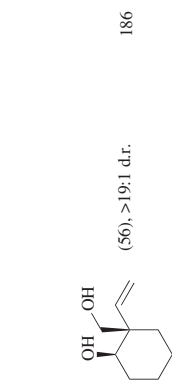


TABLE 9. INTRAMOLECULAR ADDITIONS (Continued)

Carbonyl Substrate	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
	 TFA, CHCl <sub>3</sub> /H <sub>2</sub> O (4:1), 0°, 3 h	 (44), 95:5 d.r.	833
	 TFA, CHCl <sub>3</sub> /H <sub>2</sub> O (4:1), 0°, 3 h	 (47), >99:1 d.r.	833
	 pH 7 buffer, THF, rt, 30 min	 (35)	834
	 Pd(dba) <sub>2</sub> , AsPh <sub>3</sub> (2 equiv) <sup>6</sup> , toluene, 100°	 (62)	180



C<sub>10</sub>

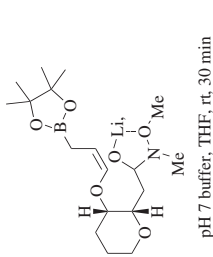
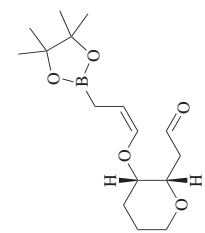
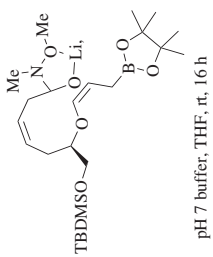
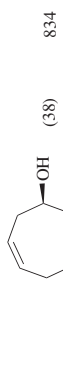
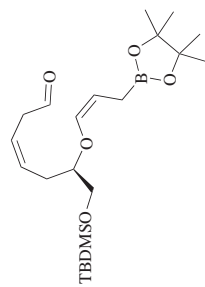
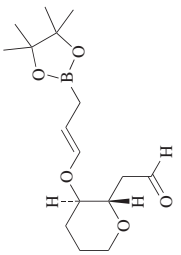
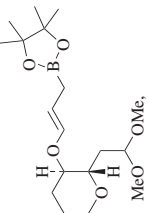
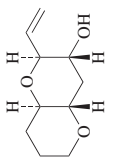
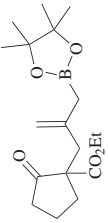
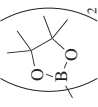
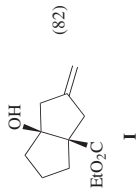
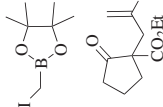
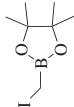
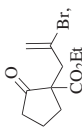


TABLE 9. INTRAMOLECULAR ADDITIONS (Continued)

Carbonyl Substrate	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
 $C_{10}$	 MeCO <sub>2</sub> OMe, LiBF <sub>4</sub> , H <sub>2</sub> O, CH <sub>3</sub> CN, rt, 1 d	 (76)	177
	 Pd(dba) <sub>2</sub> , AsPh <sub>3</sub> (2 equiv) <sup>a</sup> , toluene, 100°	 (82)	180
	 Pd(OAc) <sub>2</sub> , PPh <sub>3</sub> (3 equiv) <sup>a</sup>	 (71)	174

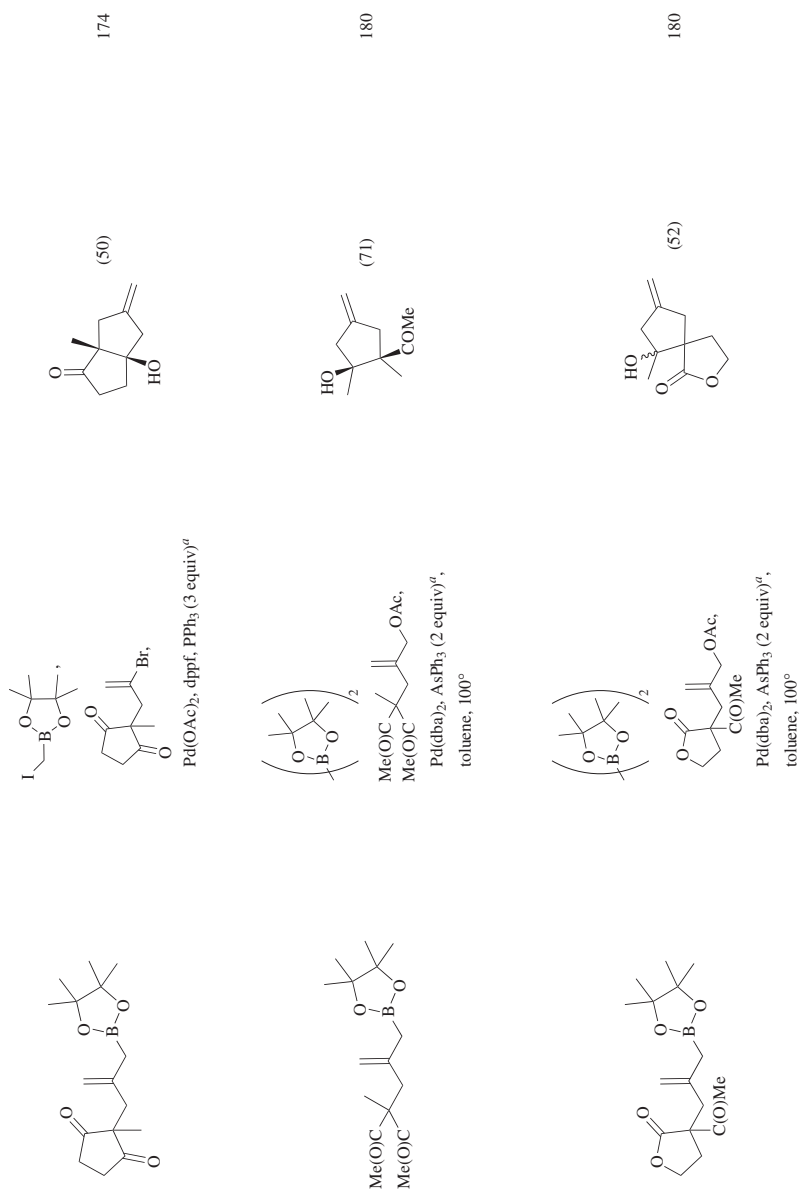
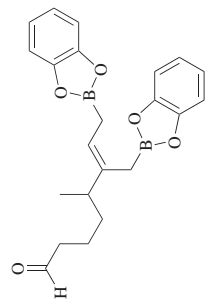
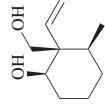
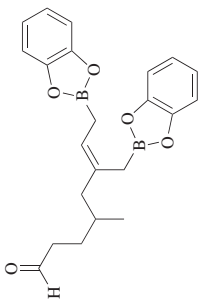
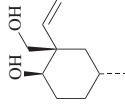
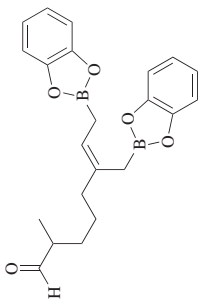
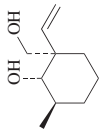


TABLE 9. INTRAMOLECULAR ADDITIONS (Continued)

Carbonyl Substrate	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
	1. $\text{H}_2$ , $\text{B}_2(\text{catechol})_2$ , $(\text{Ph}_3\text{P})_2\text{Pt}(\text{C}_2\text{H}_4)$ , THF, $60^\circ$ , 24 h 2. NaOH, $\text{H}_2\text{O}_2$	 (44), >19:1 d.r.	186
	1. $\text{H}_2$ , $\text{B}_2(\text{catechol})_2$ , $(\text{Ph}_3\text{P})_2\text{Pt}(\text{C}_2\text{H}_4)$ , THF, $60^\circ$ , 24 h 2. NaOH, $\text{H}_2\text{O}_2$	 (57), >19:1 d.r.	186
	1. $\text{H}_2$ , $\text{B}_2(\text{catechol})_2$ , $(\text{Ph}_3\text{P})_2\text{Pt}(\text{C}_2\text{H}_4)$ , THF, $60^\circ$ , 24 h 2. NaOH, $\text{H}_2\text{O}_2$	 (64), >19:1 dr	186

C<sub>10</sub>

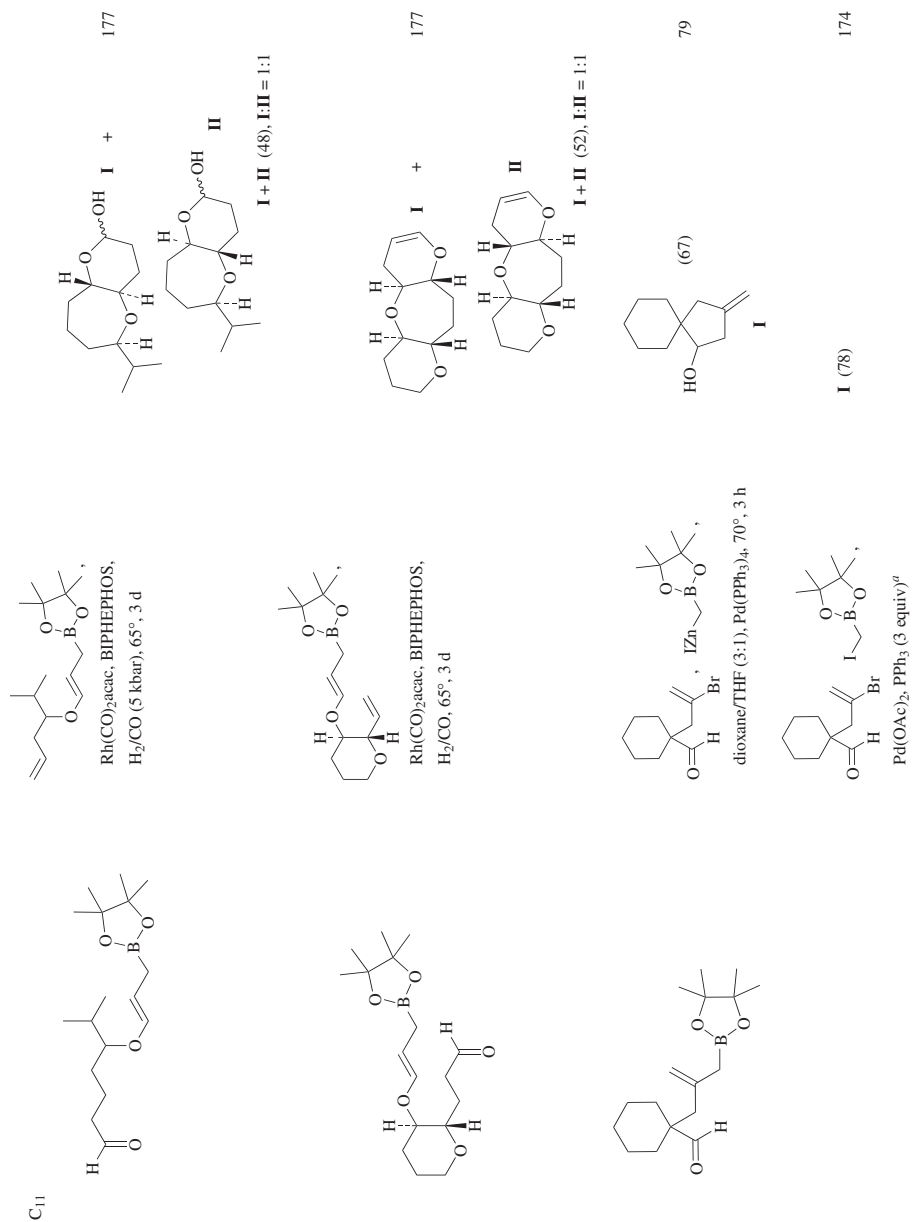
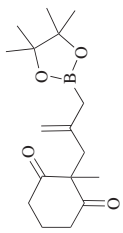
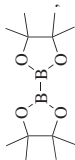
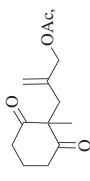
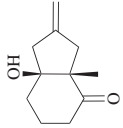
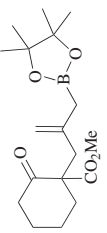
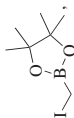
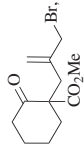
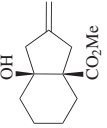
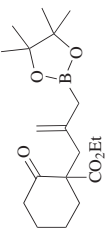
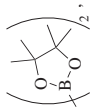
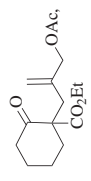
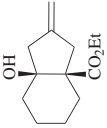


TABLE 9. INTRAMOLECULAR ADDITIONS (Continued)

Carbonyl Substrate	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
	 ,  Pd(dba) <sub>2</sub> , AsPh <sub>3</sub> (2 equiv) <sup>a</sup> , toluene, 100°	 (77)	180
	 ,  Pd(OAc) <sub>2</sub> , PPh <sub>3</sub> (3 equiv) <sup>a</sup>	 (71)	174
	 ,  Pd(dba) <sub>2</sub> , AsPh <sub>3</sub> (2 equiv) <sup>a</sup> , toluene, 100°	 (72)	180

C<sub>11</sub>



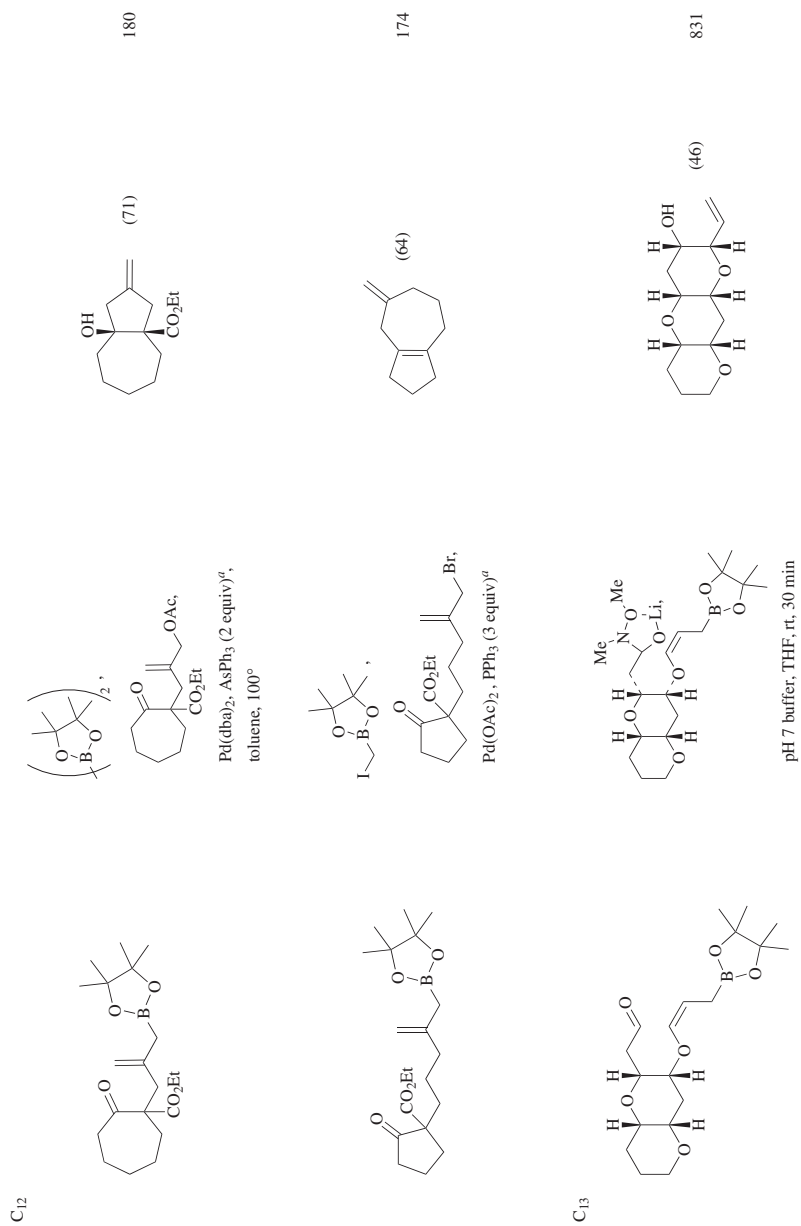
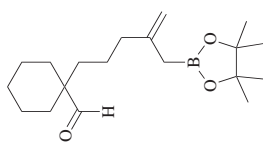
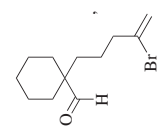
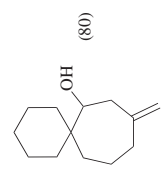


TABLE 9. INTRAMOLECULAR ADDITIONS (Continued)

Carbonyl Substrate	Conditions	Product(s) and Yield(s) (%), % ee	Refs.
	 Pd(OAc) <sub>2</sub> , PPh <sub>3</sub> (3 equiv) <sup>a</sup>	 (80)	174

<sup>a</sup> Equivalents are relative to catalyst.

## REFERENCES

- <sup>1</sup> Mikhailov, B. M.; Bubnov, Y. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1964**, 1874.
- <sup>2</sup> Favre, E.; Gaudemar, M. C. R. *Hebd. Seances Acad. Sci. Ser. C* **1966**, 263, 1543.
- <sup>3</sup> Hoffmann, R. W.; Zeiss, H.-J. *Angew. Chem., Int. Ed. Engl.* **1979**, 18, 306.
- <sup>4</sup> Hoffmann, R. W. *Pure Appl. Chem.* **1988**, 60, 123.
- <sup>5</sup> Hoffmann, R. W.; Niel, G.; Schlapbach, A. *Pure Appl. Chem.* **1990**, 62, 1993.
- <sup>6</sup> Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, 93, 2207.
- <sup>7</sup> Hoffmann, R. W. In *Stereoselective Organic Synthesis*; Trost, B. M., Ed.; Blackwell Scientific Publications: Cambridge, U.K., 1994, pp 259–274.
- <sup>8</sup> Roush, W. R. In *Methoden der Organischen Chemie (Houben-Weyl)*; Georg Thieme: Stuttgart, 1995; Vol. E21b, pp 1410–1486.
- <sup>9</sup> Brown, H. C.; Ramachandran, P. V. *J. Organomet. Chem.* **1995**, 500, 1.
- <sup>10</sup> Denmark, S. E.; Almstead, N. G. In *Modern Carbonyl Chemistry*; Otera, J., Ed.; Wiley-VCH: Weinheim, 2000, pp 299–402.
- <sup>11</sup> Chemler, S. R.; Roush, W. R. In *Modern Carbonyl Chemistry*; Otera, J., Ed.; Wiley-VCH: Weinheim, 2000, pp 403–490.
- <sup>12</sup> Ramachandran, P. V. *Aldrichim. Acta* **2002**, 35, 23.
- <sup>13</sup> Kennedy, J. W. J.; Hall, D. G. *Angew. Chem., Int. Ed.* **2003**, 42, 4732.
- <sup>14</sup> Kennedy, J. W. J.; Hall, D. G. In *Boronic Acids*; Hall, D. G., Ed.; Wiley-VCH: Weinheim, 2005, pp 241–277.
- <sup>15</sup> Denmark, S. E.; Weber, E. J. *Helv. Chim. Acta* **1983**, 66, 1655.
- <sup>16</sup> Li, Y.; Houk, K. N. *J. Am. Chem. Soc.* **1989**, 111, 1236.
- <sup>17</sup> Gennari, C.; Fioravanzo, E.; Bernardi, A.; Vulpetti, A. *Tetrahedron* **1994**, 50, 8815.
- <sup>18</sup> Vulpetti, A.; Gardner, M.; Gennari, C.; Bernardi, A.; Goodman, J. M.; Paterson, I. *J. Org. Chem.* **1993**, 58, 1711.
- <sup>19</sup> Omoto, K.; Fujimoto, H. *J. Org. Chem.* **1998**, 63, 8331.
- <sup>20</sup> Gajewski, J. J.; Bician, W.; Brichford, N. L.; Henderson, J. L. *J. Org. Chem.* **2002**, 67, 4236.
- <sup>21</sup> Brown, H. C.; Racherla, U. S.; Pellechia, P. J. *J. Org. Chem.* **1990**, 55, 1868.
- <sup>22</sup> Hoffmann, R. W.; Zeiss, H.-J. *J. Org. Chem.* **1981**, 46, 1309.
- <sup>23</sup> Corey, E. J.; Rohde, J. J. *Tetrahedron Lett.* **1997**, 38, 37.
- <sup>24</sup> Kennedy, J. W. J.; Hall, D. G. *J. Am. Chem. Soc.* **2002**, 124, 11586.
- <sup>25</sup> Ishiyama, T.; Ahiko, T.-a.; Miyaura, N. *J. Am. Chem. Soc.* **2002**, 124, 12414.
- <sup>26</sup> Kennedy, J. W. J.; Hall, D. G. *J. Org. Chem.* **2004**, 69, 4412.
- <sup>27</sup> Lachance, H.; Lu, X. S.; Gravel, M.; Hall, D. G. *J. Am. Chem. Soc.* **2003**, 125, 10160.
- <sup>28</sup> Gravel, M.; Lachance, H.; Lu, X. S.; Hall, D. G. *Synthesis* **2004**, 1290.
- <sup>29</sup> Rauniyar, V.; Hall, D. G. *J. Am. Chem. Soc.* **2004**, 126, 4518.
- <sup>30</sup> Yu, S.-H.; Ferguson, M. J.; McDonald, R.; Hall, D. G. *J. Am. Chem. Soc.* **2005**, 127, 12808.
- <sup>31</sup> Blais, J.; L'Honoré, A.; Soulié, J.; Cadiot, P. *J. Organomet. Chem.* **1974**, 78, 323.
- <sup>32</sup> Tsai, D. J. S.; Matteson, D. S. *Tetrahedron Lett.* **1981**, 22, 2751.
- <sup>33</sup> Hoffmann, R. W.; Kemper, B. *Tetrahedron Lett.* **1981**, 22, 5263.
- <sup>34</sup> Hoffmann, R. W.; Kemper, B. *Tetrahedron* **1984**, 40, 2219.
- <sup>34a</sup> Hoffmann, R. W.; Kemper, B.; Metternich, R.; Lehmeier, T. *Liebigs Ann. Chem.* **1985**, 2246.
- <sup>35</sup> Stürmer, R. *Angew. Chem., Int. Ed. Engl.* **1990**, 29, 59.
- <sup>36</sup> Hoffmann, R. W.; Kemper, B. *Tetrahedron Lett.* **1982**, 23, 845.
- <sup>37</sup> Roush, W. R.; Ando, K.; Powers, D. B.; Palkowitz, A. D.; Halterman, R. L. *J. Am. Chem. Soc.* **1990**, 112, 6339.
- <sup>38</sup> Roush, W. R.; Grover, P. T.; Lin, X. F. *Tetrahedron Lett.* **1990**, 31, 7563.
- <sup>39</sup> Roush, W. R.; Grover, P. T. *Tetrahedron Lett.* **1990**, 31, 7567.
- <sup>40</sup> Roush, W. R.; Grover, P. T. *Tetrahedron* **1992**, 48, 1981.
- <sup>41</sup> Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1982**, 21, 555.
- <sup>42</sup> Schlosser, M.; Rauchsvalbe, G. *J. Am. Chem. Soc.* **1978**, 100, 3258.
- <sup>43</sup> Fujita, K.; Schlosser, M. *Helv. Chim. Acta* **1982**, 65, 1258.
- <sup>44</sup> Brown, H. C.; Bhat, K. S. *J. Am. Chem. Soc.* **1986**, 108, 293.
- <sup>45</sup> Barrett, A. G. M.; Malecha, J. W. *J. Org. Chem.* **1991**, 56, 5243.

- <sup>46</sup> Wuts, P. G. M.; Bigelow, S. S. *J. Org. Chem.* **1982**, *47*, 2498.
- <sup>47</sup> Hoffmann, R. W.; Kemper, B.; Metternich, R.; Lehmeier, T. *Liebigs Ann. Chem.* **1985**, 2246.
- <sup>48</sup> Brown, H. C.; Jadhav, P. K.; Bhat, K. S. *J. Am. Chem. Soc.* **1988**, *110*, 1535.
- <sup>49</sup> Hoffmann, R. W.; Feussner, G.; Zeiss, H.-J.; Schulz, S. *J. Organomet. Chem.* **1980**, *187*, 321.
- <sup>50</sup> Corey, E. J.; Yu, C.-M.; Kim, S. S. *J. Am. Chem. Soc.* **1989**, *111*, 5495.
- <sup>51</sup> Beckmann, E.; Hoppe, D. *Synthesis* **2005**, 217.
- <sup>52</sup> Wuts, P. G. M.; Thompson, P. A.; Callen, G. R. *J. Org. Chem.* **1983**, *48*, 5398.
- <sup>53</sup> Hoffmann, R. W.; Schlapbach, A. *Tetrahedron* **1992**, *48*, 1959.
- <sup>54</sup> Brown, H. C.; De Lue, N. R.; Yamamoto, Y.; Maruyama, K.; Kasahara, T.; Murahashi, S.-i.; Sonoda, A. *J. Org. Chem.* **1977**, *42*, 4088.
- <sup>55</sup> Hoffmann, R. W.; Schlapbach, A. *Liebigs Ann. Chem.* **1990**, 1243.
- <sup>56</sup> Matteson, D. S.; Majumdar, D. *J. Am. Chem. Soc.* **1980**, *102*, 7588.
- <sup>57</sup> Nyzam, V.; Belaud, C.; Villiéras, J. *Tetrahedron Lett.* **1993**, *34*, 6899.
- <sup>58</sup> Nyzam, V.; Belaud, C.; Zammattio, F.; Villiéras, J. *Bull. Soc. Chim. Fr.* **1997**, *134*, 583.
- <sup>59</sup> Kennedy, J. W. J.; Hall, D. G. *J. Am. Chem. Soc.* **2002**, *124*, 898.
- <sup>60</sup> Zhu, N.; Hall, D. G. *J. Org. Chem.* **2003**, *68*, 6066.
- <sup>61</sup> Roush, W. R.; Peseckis, S. M.; Walts, A. E. *J. Org. Chem.* **1984**, *49*, 3429.
- <sup>62</sup> Matteson, D. S. *Tetrahedron* **1998**, *54*, 10555.
- <sup>63</sup> Ditrich, K.; Bube, T.; Stürmer, R.; Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1028.
- <sup>64</sup> Hoffmann, R. W.; Ditrich, K.; Köster, G.; Stürmer, R. *Chem. Ber.* **1989**, *122*, 1783.
- <sup>65</sup> Stürmer, R.; Hoffmann, R. W. *Synlett* **1990**, 759.
- <sup>66</sup> Hoffmann, R. W.; Landmann, B. *Chem. Ber.* **1986**, *119*, 2013.
- <sup>67</sup> Hoffmann, R. W.; Dresely, S.; Lanz, J. W. *Chem. Ber.* **1988**, *121*, 1501.
- <sup>68</sup> Hoffmann, R. W.; Dresely, S. *Chem. Ber.* **1989**, *122*, 903.
- <sup>69</sup> Brown, H. C.; Jadhav, P. K.; Bhat, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 2564.
- <sup>70</sup> Yamamoto, Y.; Fujikawa, R.; Yamada, A.; Miyaura, N. *Chem. Lett.* **1999**, 1069.
- <sup>71</sup> Ishiyama, T.; Yamamoto, M.; Miyaura, N. *Chem. Commun.* **1996**, 2073.
- <sup>72</sup> Suginome, M.; Matsuda, T.; Yoshimoto, T.; Ito, Y. *Org. Lett.* **1999**, *1*, 1567.
- <sup>73</sup> Pelz, N. F.; Woodward, A. R.; Burks, H. E.; Sieber, J. D.; Morken, J. P. *J. Am. Chem. Soc.* **2004**, *126*, 16328.
- <sup>74</sup> Ishiyama, T.; Ahiko, T.-A.; Miyaura, N. *Tetrahedron Lett.* **1996**, *37*, 6889.
- <sup>75</sup> Olsson, V. J.; Sebelius, S.; Selander, N.; Szabó, K. J. *J. Am. Chem. Soc.* **2006**, *128*, 4588.
- <sup>76</sup> Ito, H.; Kawakami, C.; Sawamura, M. *J. Am. Chem. Soc.* **2005**, *127*, 16034.
- <sup>77</sup> Murata, M.; Watanabe, S.; Masuda, Y. *Tetrahedron Lett.* **2000**, *41*, 5877.
- <sup>78</sup> Falck, J. R.; Bondlela, M.; Ye, J.; Cho, S.-D. *Tetrahedron Lett.* **1999**, *40*, 5647.
- <sup>79</sup> Watanabe, T.; Miyaura, N.; Suzuki, A. *J. Organomet. Chem.* **1993**, *444*, C1.
- <sup>80</sup> Hoffmann, R. W.; Sander, T.; Hense, A. *Liebigs Ann. Chem.* **1993**, 771.
- <sup>81</sup> Sadhu, K. M.; Matteson, D. S. *Organometallics* **1985**, *4*, 1687.
- <sup>82</sup> Hoffmann, R. W.; Niel, G. *Liebigs Ann. Chem.* **1991**, 1195.
- <sup>83</sup> Hoffmann, R. W.; Dresely, S. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 189.
- <sup>84</sup> Brown, H. C.; Rangaishenvi, M. V.; Jayaraman, S. *Organometallics* **1992**, *11*, 1948.
- <sup>85</sup> Pietruszka, J.; Schöne, N. *Angew. Chem., Int. Ed.* **2003**, *42*, 5638.
- <sup>86</sup> Pietruszka, J.; Schöne, N. *Eur. J. Org. Chem.* **2004**, 5011.
- <sup>87</sup> Lombardo, M.; Morganti, S.; Tozzi, M.; Trombini, C. *Eur. J. Org. Chem.* **2002**, 2823.
- <sup>88</sup> Yamamoto, Y.; Miyairi, T.; Ohmura, T.; Miyaura, N. *J. Org. Chem.* **1999**, *64*, 296.
- <sup>89</sup> Vaultier, M.; Truchet, F.; Carboni, B.; Hoffmann, R. W.; Denne, I. *Tetrahedron Lett.* **1987**, *28*, 4169.
- <sup>90</sup> Yamamoto, Y.; Takahashi, M.; Miyaura, N. *Synlett* **2002**, 128.
- <sup>91</sup> Bubnov, Y. N.; Gurskii, M. E.; Gridnev, I. D.; Ignatenko, A. V.; Ustynyuk, Y. A.; Mstislavsky, V. I. *J. Organomet. Chem.* **1992**, *424*, 127.
- <sup>92</sup> Kramer, G. W.; Brown, H. C. *J. Organomet. Chem.* **1977**, *132*, 9.
- <sup>93</sup> Zweifel, G.; Horng, A. *Synthesis* **1973**, 67, 672.
- <sup>94</sup> Jutzi, P.; Seufert, A. *Chem. Ber.* **1979**, *112*, 2481.

- <sup>95</sup> Hancock, K. G.; Kramer, J. D. *J. Am. Chem. Soc.* **1973**, *95*, 6463.
- <sup>96</sup> Hancock, K. G.; Kramer, J. D. *J. Organomet. Chem.* **1974**, *64*, C29.
- <sup>97</sup> Le Serre, S.; Guillemin, J. C. *Organometallics* **1997**, *16*, 5844.
- <sup>98</sup> Batey, R. A.; Thadani, A. N.; Smil, D. V. *Tetrahedron Lett.* **1999**, *40*, 4289.
- <sup>99</sup> Batey, R. A.; Thadani, A. N.; Smil, D. V.; Lough, A. J. *Synthesis* **2000**, 990.
- <sup>100</sup> Thadani, A. N.; Batey, R. A. *Org. Lett.* **2002**, *4*, 3827.
- <sup>101</sup> Lautens, M.; Maddess, M. L.; Sauer, E. L. O.; Ouellet, S. G. *Org. Lett.* **2002**, *4*, 83.
- <sup>102</sup> Hoffmann, R. W.; Sander, T. *Chem. Ber.* **1990**, *123*, 145.
- <sup>103</sup> Kramer, G. W.; Brown, H. C. *J. Org. Chem.* **1977**, *42*, 2292.
- <sup>104</sup> Metternich, R.; Hoffmann, R. W. *Tetrahedron Lett.* **1984**, *25*, 4095.
- <sup>105</sup> Wang, Z.; Meng, X.-J.; Kabalka, G. W. *Tetrahedron Lett.* **1991**, *32*, 4619.
- <sup>106</sup> Wang, Z.; Meng, X.-J.; Kabalka, G. W. *Tetrahedron Lett.* **1991**, *32*, 5677.
- <sup>107</sup> Pace, R. D.; Kabalka, G. W. *J. Org. Chem.* **1995**, *60*, 4838.
- <sup>108</sup> Kabalka, G. W.; Yang, K.; Wang, Z. *Synth. Commun.* **2001**, *31*, 511.
- <sup>109</sup> Wang, Z.; Meng, X. J.; Kabalka, G. W. *Tetrahedron Lett.* **1991**, *32*, 1945.
- <sup>110</sup> Kabalka, G. W.; Narayana, C.; Reddy, N. K. *Tetrahedron Lett.* **1996**, *37*, 2181.
- <sup>111</sup> Buynak, J. D.; Geng, B.; Uang, S.; Strickland, J. B. *Tetrahedron Lett.* **1994**, *35*, 985.
- <sup>112</sup> Cherest, M.; Felkin, H.; Prudent, N. *Tetrahedron Lett.* **1968**, *9*, 2199.
- <sup>113</sup> Roush, W. R. *J. Org. Chem.* **1991**, *56*, 4151.
- <sup>114</sup> Hoffmann, R. W.; Zeiss, H.-J.; Ladner, W.; Tabche, S. *Chem. Ber.* **1982**, *115*, 2357.
- <sup>115</sup> Hoffmann, R. W.; Weidmann, U. *Chem. Ber.* **1985**, *118*, 3966.
- <sup>116</sup> Anh, N. T.; Eisenstein, O. *Nouv. J. Chim.* **1977**, *1*, 61.
- <sup>117</sup> Cornforth, J. W.; Cornforth, R. H.; Mathew, K. K. *J. Chem. Soc.* **1959**, 112.
- <sup>118</sup> Roush, W. R.; Adam, M. A.; Walts, A. E.; Harris, D. J. *J. Am. Chem. Soc.* **1986**, *108*, 3422.
- <sup>119</sup> Gung, B. W.; Xue, X. W. *Tetrahedron: Asymmetry* **2001**, *12*, 2955.
- <sup>120</sup> Hoffmann, R. W.; Herold, T. *Angew. Chem., Int. Ed. Engl.* **1978**, *18*, 768.
- <sup>121</sup> Herold, T.; Schrott, U.; Hoffmann, R. W.; Schnelle, G.; Ladner, W.; Steinbach, K. *Chem. Ber.* **1981**, *114*, 359.
- <sup>122</sup> Hoffmann, R. W.; Herold, T. *Chem. Ber.* **1981**, *114*, 375.
- <sup>123</sup> Haruta, R.; Ishiguro, M.; Ikeda, N.; Yamamoto, H. *J. Am. Chem. Soc.* **1982**, *104*, 7667.
- <sup>124</sup> Roush, W. R.; Walts, A. E.; Hoong, L. K. *J. Am. Chem. Soc.* **1985**, *107*, 8186.
- <sup>125</sup> Roush, W. R.; Hoong, L. K.; Palmer, M. A. J.; Park, J. C. *J. Org. Chem.* **1990**, *55*, 4109.
- <sup>126</sup> Roush, W. R.; Halterman, R. L. *J. Am. Chem. Soc.* **1986**, *108*, 294.
- <sup>127</sup> Gung, B. W.; Xue, X. W.; Roush, W. R. *J. Am. Chem. Soc.* **2002**, *124*, 10692.
- <sup>128</sup> Roush, W. R.; Park, J. C. *J. Org. Chem.* **1990**, *55*, 1143.
- <sup>129</sup> Roush, W. R.; Park, J. C. *Tetrahedron Lett.* **1990**, *31*, 4707.
- <sup>130</sup> Roush, W. R.; Park, J. C. *Tetrahedron Lett.* **1991**, *32*, 6285.
- <sup>131</sup> Roush, W. R.; Banfi, L. *J. Am. Chem. Soc.* **1988**, *110*, 3979.
- <sup>132</sup> Roush, W. R.; Grover, P. T. *J. Org. Chem.* **1995**, *60*, 3806.
- <sup>133</sup> Reetz, M. T.; Zierke, T. *Chem. Ind. (London)* **1988**, 663.
- <sup>134</sup> Chen, Y.; Eltepu, L.; Wentworth, J. P. *Tetrahedron Lett.* **2004**, *45*, 8285.
- <sup>135</sup> Wu, T. R.; Shen, L.; Chong, J. M. *Org. Lett.* **2004**, *6*, 2701.
- <sup>136</sup> Brown, H. C.; Jadhav, P. K. *J. Am. Chem. Soc.* **1983**, *105*, 2092.
- <sup>136a</sup> Jadhav, P. K.; Bhat, K. S.; Perumal, P. T.; Brown, H. C. *J. Org. Chem.* **1986**, *51*, 432.
- <sup>137</sup> Brown, H. C.; Bhat, K. S. *J. Am. Chem. Soc.* **1986**, *108*, 5919.
- <sup>138</sup> Brown, H. C.; Jadhav, P. K. *Tetrahedron Lett.* **1984**, *25*, 1215.
- <sup>139</sup> Racherla, U. S.; Brown, H. C. *J. Org. Chem.* **1991**, *56*, 401.
- <sup>140</sup> Jadhav, P. K.; Bhat, K. S.; Perumal, P. T.; Brown, H. C. *J. Org. Chem.* **1986**, *51*, 432.
- <sup>141</sup> Short, R. P.; Masamune, S. *J. Am. Chem. Soc.* **1989**, *111*, 1892.
- <sup>142</sup> Garcia, J.; Kim, B. M.; Masamune, S. *J. Org. Chem.* **1987**, *52*, 4831.
- <sup>143</sup> Burgos, C. H.; Canales, E.; Matos, K.; Soderquist, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 8044.
- <sup>144</sup> Lai, C.; Soderquist, J. A. *Org. Lett.* **2005**, *7*, 799.
- <sup>145</sup> Canales, E.; Prasad, K. G.; Soderquist, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 11572.
- <sup>146</sup> Hoffmann, R. W.; Landmann, B. *Chem. Ber.* **1986**, *119*, 1039.

- <sup>147</sup> Hoffmann, R. W.; Dresely, S. *Tetrahedron Lett.* **1987**, 28, 5303.
- <sup>148</sup> Hoffmann, R. W.; Weidmann, U. *J. Organomet. Chem.* **1980**, 195, 137.
- <sup>149</sup> Hoffmann, R. W.; Dresely, S.; Hildebrandt, B. *Chem. Ber.* **1988**, 121, 2225.
- <sup>150</sup> Gao, X.; Hall, D. G. *J. Am. Chem. Soc.* **2003**, 125, 9308.
- <sup>151</sup> Deligny, M.; Carreaux, F.; Toupet, L.; Carboni, B. *Adv. Synth. Catal.* **2003**, 345, 1215.
- <sup>152</sup> Gao, X.; Hall, D. G.; Deligny, M.; Favre, A.; Carreaux, F.; Carboni, C. *Chem.—Eur. J.* **2006**, 13, 3132.
- <sup>153</sup> Corey, E. J.; Yu, C.-M.; Lee, D.-H. *J. Am. Chem. Soc.* **1990**, 112, 878.
- <sup>154</sup> Tamao, K.; Nakajo, E.; Ito, Y. *J. Org. Chem.* **1987**, 52, 957.
- <sup>155</sup> Wuts, P. G. M.; Bigelow, S. S. *J. Chem. Soc., Chem. Commun.* **1984**, 736.
- <sup>156</sup> Coleman, R. S.; Kong, J.-S. *J. Am. Chem. Soc.* **1998**, 120, 3538.
- <sup>157</sup> Brown, H. C.; Narla, G. *J. Org. Chem.* **1995**, 60, 4686.
- <sup>158</sup> Hunt, J. A.; Roush, W. R. *J. Org. Chem.* **1997**, 62, 1112.
- <sup>159</sup> Hu, S.; Jayaraman, S.; Oehlschlager, A. C. *J. Org. Chem.* **1996**, 61, 7513.
- <sup>160</sup> Barrett, A. G. M.; Seefeld, M. A.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1994**, 1053.
- <sup>161</sup> Chataigner, I.; Zammattio, F.; Lebreton, J.; Villiéras, J. *Synlett* **1998**, 275.
- <sup>162</sup> Ishihara, K.; Kaneeda, M.; Yamamoto, H. *J. Am. Chem. Soc.* **1994**, 116, 11179.
- <sup>163</sup> Rauniyar, V.; Hall, D. G. *Angew. Chem., Int. Ed.* **2006**, 45, 2426.
- <sup>164</sup> Wada, R.; Oisaki, K.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2004**, 126, 8910.
- <sup>165</sup> Masamune, S.; Choy, W.; Petersen, J. S.; Sita, L. R. *Angew. Chem., Int. Ed. Engl.* **1985**, 24, 1.
- <sup>166</sup> Brown, H. C.; Bhat, K. S.; Randad, R. S. *J. Org. Chem.* **1987**, 52, 319.
- <sup>167</sup> Brown, H. C.; Bhat, K. S.; Randad, R. S. *J. Org. Chem.* **1989**, 54, 1570.
- <sup>168</sup> Ogawa, A. K.; Armstrong, R. W. *J. Am. Chem. Soc.* **1998**, 120, 12435.
- <sup>169</sup> Roush, W. R.; Palkowitz, A. D.; Palmer, M. A. *J. Org. Chem.* **1987**, 52, 316.
- <sup>170</sup> Roush, W. R.; Hoong, L. K.; Palmer, M. A. J.; Straub, J. A.; Palkowitz, A. D. *J. Org. Chem.* **1990**, 55, 4117.
- <sup>171</sup> Sander, T.; Hoffmann, R. W. *Liebigs Ann. Chem.* **1993**, 1193.
- <sup>172</sup> Hoffmann, R. W.; Hense, A. *Liebigs Ann.* **1996**, 1283.
- <sup>173</sup> Yamamoto, Y.; Kurihara, K.; Yamada, A.; Takahashi, M.; Takahashi, Y.; Miyaura, N. *Tetrahedron* **2003**, 59, 537.
- <sup>174</sup> Watanabe, T.; Sakai, M.; Miyaura, N.; Suzuki, A. *J. Chem. Soc., Chem. Commun.* **1994**, 467.
- <sup>175</sup> Flamme, E. M.; Roush, W. R. *J. Am. Chem. Soc.* **2002**, 124, 13644.
- <sup>176</sup> Barrett, A. G. M.; Braddock, D. C.; de Koning, P. D.; White, A. J. P.; Williams, D. J. *J. Org. Chem.* **2000**, 65, 375.
- <sup>177</sup> Hoffmann, R. W.; Krüger, J.; Brückner, D. *New J. Chem.* **2001**, 25, 102.
- <sup>178</sup> Hoffmann, R. W.; Brückner, D.; Gerusz, V. *J. Heterocycles* **2000**, 52, 121.
- <sup>179</sup> Hoffmann, R. W.; Brückner, D. *New J. Chem.* **2001**, 25, 369.
- <sup>180</sup> Ahiko, T.-a.; Ishiyama, T.; Miyaura, N. *Chem. Lett.* **1997**, 811.
- <sup>181</sup> Tailor, J.; Hall, D. G. *Org. Lett.* **2000**, 2, 3715.
- <sup>182</sup> Touré, B. B.; Hoveyda, H. R.; Tailor, J.; Ulaczyk-Lesanko, A.; Hall, D. G. *Chem. Eur. J.* **2003**, 9, 466.
- <sup>183</sup> Six, Y.; Lallemand, J.-Y. *Tetrahedron Lett.* **1999**, 40, 1295.
- <sup>184</sup> Goldberg, S. D.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2002**, 41, 807.
- <sup>185</sup> Morgan, J. B.; Morken, J. P. *Org. Lett.* **2003**, 5, 2573.
- <sup>186</sup> Ballard, C. E.; Morken, J. P. *Synthesis* **2004**, 1321.
- <sup>187</sup> Woodward, A. R.; Burks, H. E.; Chan, L. M.; Morken, J. P. *Org. Lett.* **2005**, 7, 5505.
- <sup>188</sup> Nicolaou, K. C.; Ninkovic, S.; Sarabia, F.; Vourloumis, D.; He, Y.; Vallberg, H.; Finlay, M. R. V.; Yang, Z. *J. Am. Chem. Soc.* **1997**, 119, 7974.
- <sup>189</sup> Bratz, M.; Bullock, W. H.; Overman, L. E.; Takemoto, T. *J. Am. Chem. Soc.* **1995**, 117, 5958.
- <sup>190</sup> Roush, W. R.; Wada, C. K. *J. Am. Chem. Soc.* **1994**, 116, 2151.
- <sup>191</sup> Williams, D. R.; Plummer, S. V.; Patnaik, S. *Angew. Chem., Int. Ed.* **2003**, 42, 3934.
- <sup>192</sup> Denmark, S. E.; Yang, S.-M. *J. Am. Chem. Soc.* **2002**, 124, 15196.
- <sup>193</sup> Marron, T. G.; Roush, W. R. *Tetrahedron Lett.* **1995**, 36, 1581.
- <sup>194</sup> Roush, W. R.; Marron, T. G. *Tetrahedron Lett.* **1993**, 34, 5421.

- <sup>195</sup> Scheidt, K. A.; Tasaka, A.; Bannister, T. D.; Wendt, M. D.; Roush, W. R. *Angew. Chem., Int. Ed.* **1999**, *38*, 1652.
- <sup>196</sup> Smith, A. B., III; Adams, C. M.; Barbosa, S. A. L.; Degnan, A. P. *J. Am. Chem. Soc.* **2003**, *125*, 350.
- <sup>197</sup> Andersen, M. W.; Hildebrandt, B.; Dahmann, G.; Hoffmann, R. W. *Chem. Ber.* **1991**, *124*, 2127.
- <sup>198</sup> Gao, X.; Hall, D. G. *J. Am. Chem. Soc.* **2005**, *127*, 1628.
- <sup>199</sup> Touré, B. B.; Hall, D. G. *Angew. Chem., Int. Ed.* **2004**, *43*, 2001.
- <sup>200</sup> Touré, B. B.; Hall, D. G. *J. Org. Chem.* **2005**, *69*, 8429.
- <sup>201</sup> Hicks, J. D.; Flamme, E. M.; Roush, W. R. *Org. Lett.* **2005**, *7*, 5509.
- <sup>202</sup> Flamme, E. M.; Roush, W. R. *Org. Lett.* **2005**, *7*, 1411.
- <sup>203</sup> Owen, R. M.; Roush, W. R. *Org. Lett.* **2005**, *7*, 3941.
- <sup>204</sup> Ramachandran, P. V.; Reddy, M. V. R.; Brown, H. C. *Tetrahedron Lett.* **2000**, *41*, 583.
- <sup>205</sup> Nelson, S. G.; Cheung, W. S.; Kassick, A. J.; Hilfiker, M. A. *J. Am. Chem. Soc.* **2002**, *124*, 13654.
- <sup>206</sup> Lambert, W. T.; Roush, W. R. *Org. Lett.* **2005**, *7*, 5501.
- <sup>207</sup> Hoffmann, R. W.; Schäfer, F.; Haeblerlin, E.; Rohde, T.; Körber, K. *Synthesis* **2000**, 2060.
- <sup>208</sup> Hoffmann, R. W.; Rohde, T.; Haeblerlin, E.; Schäfer, F. *Org. Lett.* **1999**, *1*, 1713.
- <sup>209</sup> Denmark, S. E.; Fu, J. *Chem. Rev.* **2003**, *103*, 2763.
- <sup>210</sup> *Modern Aldol Reactions*; Mahrwald, R., Ed.; Wiley-VCH: Weinheim, 2004.
- <sup>211</sup> Cowden, C. J.; Paterson, I. *Org. React.* **1997**, *51*, 1.
- <sup>212</sup> Mukaiyama, T.; Kobayashi, S. *Org. React.* **1994**, *46*, 1.
- <sup>213</sup> König, K.; Neuman, W. P. *Tetrahedron Lett.* **1967**, 493.
- <sup>214</sup> Keck, G. E.; Tarbet, K. H.; Geraci, L. S. *J. Am. Chem. Soc.* **1993**, *115*, 8467.
- <sup>215</sup> Costa, A. L.; Piazza, M. G.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A. *J. Am. Chem. Soc.* **1993**, *115*, 7001.
- <sup>216</sup> Faller, J. W.; Sams, D. W. T.; Liu, X. *J. Am. Chem. Soc.* **1996**, *118*, 1217.
- <sup>217</sup> Kim, J. G.; Waltz, K. M.; Garcia, I. F.; Kwiatkowski, D.; Walsh, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 12580.
- <sup>218</sup> Yanagisawa, A.; Nakashima, H.; Ishiba, A.; Yamamoto, H. *J. Am. Chem. Soc.* **1996**, *118*, 4723.
- <sup>219</sup> Yanagisawa, A.; Nakashima, H.; Ishiba, A.; Yamamoto, H. *Synlett* **1997**, 88.
- <sup>220</sup> Marshall, J. A. *Chem. Rev.* **1996**, *96*, 31.
- <sup>221</sup> Furuta, K.; Mouri, M.; Yamamoto, H. *Synlett* **1991**, 561.
- <sup>222</sup> Ishihara, K.; Mouri, M.; Gao, Q.; Maruyama, T.; Furuta, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1993**, *115*, 11490.
- <sup>223</sup> Gauthier, D. R.; Carreira, E. M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2363.
- <sup>224</sup> Bode, J. W.; Gauthier, D. R.; Carreira, E. M. *Chem. Commun.* **2001**, 2560.
- <sup>225</sup> Wadamoto, M.; Ozasa, N.; Yanagisawa, A.; Yamamoto, H. *J. Org. Chem.* **2003**, *68*, 5593.
- <sup>226</sup> Yamasaki, S.; Fujii, K.; Wada, R.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2002**, *124*, 6536.
- <sup>227</sup> Denmark, S. E.; Fu, J. *J. Am. Chem. Soc.* **2001**, *123*, 9488.
- <sup>228</sup> Denmark, S. E.; Fu, J. *Chem. Commun.* **2003**, 167.
- <sup>229</sup> Masse, C. E.; Panek, J. S. *Chem. Rev.* **1995**, *95*, 1293.
- <sup>230</sup> Kubota, K.; Leighton, J. L. *Angew. Chem., Int. Ed.* **2003**, *42*, 946.
- <sup>231</sup> Hackman, B. M.; Lombardi, P. J.; Leighton, J. L. *Org. Lett.* **2004**, *6*, 4375.
- <sup>232</sup> Duthaler, R. O.; Hafner, A. *Chem. Rev.* **1992**, *92*, 807.
- <sup>233</sup> Xia, G.; Yamamoto, H. *J. Am. Chem. Soc.* **2006**, *128*, 2554.
- <sup>234</sup> Arnould, T.; Barrett, A. G. M.; Seifried, R. *Tetrahedron Lett.* **2001**, *42*, 7899.
- <sup>235</sup> Cavallaro, C. L.; Herpin, T.; McGuinness, B. F.; Shimshock, Y. C.; Dolle, R. E. *Tetrahedron Lett.* **1999**, *40*, 2711.
- <sup>236</sup> Micalizio, G. C.; Schreiber, S. L. *Angew. Chem., Int. Ed.* **2002**, *41*, 3272.
- <sup>237</sup> Hoffmann, R. W.; Dresely, S. *Synthesis* **1988**, 103.
- <sup>238</sup> Mikhailov, B. M.; Bubnov, Y. N.; Tsyban, A. V.; Grigoryan, M. S. *J. Organomet. Chem.* **1978**, *154*, 131.
- <sup>239</sup> Brown, H. C.; Jadhav, P. K. *J. Org. Chem.* **1984**, *49*, 4089.

- <sup>240</sup> Brown, H. C.; Randad, R. S.; Bhat, K. S.; Zaidlewicz, M.; Racherla, U. S. *J. Am. Chem. Soc.* **1990**, *112*, 2389.
- <sup>241</sup> Brown, H. C.; Kulkarni, S. V.; Racherla, U. S. *J. Org. Chem.* **1994**, *59*, 365.
- <sup>242</sup> Brown, H. C.; Kulkarni, S. V.; Racherla, U. S.; Dhokte, U. P. *J. Org. Chem.* **1998**, *63*, 7030.
- <sup>243</sup> Redlich, H.; Schneider, B.; Hoffmann, R. W.; Geueke, K. J. *Liebigs Ann. Chem.* **1983**, 393.
- <sup>244</sup> Herold, T.; Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 768.
- <sup>245</sup> Itsuno, S.; Watanabe, K.; El-Shehawy, A. A. *Adv. Synth. Catal.* **2001**, *343*, 89.
- <sup>246</sup> Itsuno, S.; El-Shehawy, A. A.; Sarhan, A. A. *React. Funct. Polym.* **1998**, *37*, 283.
- <sup>247</sup> Reddy, M. V. R.; Yucel, A. J.; Ramachandran, P. V. *J. Org. Chem.* **2001**, *66*, 2512.
- <sup>248</sup> Kumar, D. J. S.; Madhavan, S.; Ramachandran, P. V.; Brown, H. C. *Tetrahedron: Asymmetry* **2000**, *11*, 4629.
- <sup>249</sup> Ramachandran, P. V.; Padiya, K. J.; Rauniyar, V.; Reddy, M. V. R.; Brown, H. C. *Tetrahedron Lett.* **2004**, *45*, 1015.
- <sup>250</sup> Ramachandran, P. V.; Prabhudas, B.; Chandra, J. S.; Reddy, M. V. R. *J. Org. Chem.* **2004**, *69*, 6294.
- <sup>251</sup> Reddy, M. V. R.; Brown, H. C.; Ramachandran, P. V. *J. Organomet. Chem.* **2001**, *624*, 239.
- <sup>252</sup> Bonini, C.; Chiummiento, L.; Pullez, M.; Solladie, G.; Colobert, F. *J. Org. Chem.* **2004**, *69*, 5015.
- <sup>253</sup> Paterson, I.; Coster, M. J.; Chen, D. Y. M.; Gibson, K. R.; Wallace, D. J. *Org. Biomol. Chem.* **2005**, *3*, 2410.
- <sup>254</sup> Ramachandran, P. V.; Chen, G. M.; Brown, H. C. *Tetrahedron Lett.* **1997**, *38*, 2417.
- <sup>255</sup> Chen, G. M.; Ramachandran, P. V. *Tetrahedron: Asymmetry* **1997**, *8*, 3935.
- <sup>256</sup> Bubnov, Y. N.; Lavrinovich, L. I.; Zykov, A. Y.; Ignatenko, A. V. *Mendeleev Commun.* **1992**, 86.
- <sup>257</sup> Ramachandran, P. V.; Krzeminski, M. P.; Reddy, M. V. R.; Brown, H. C. *Tetrahedron: Asymmetry* **1999**, *10*, 11.
- <sup>258</sup> Trost, B. M.; Frederiksen, M. U.; Papillon, J. P. N.; Harrington, P. E.; Shin, S.; Shireman, B. T. *J. Am. Chem. Soc.* **2005**, *127*, 3666.
- <sup>259</sup> Smith, A. B., III; Ott, G. R. *J. Am. Chem. Soc.* **1996**, *118*, 13095.
- <sup>260</sup> Roush, W. R.; Palkowitz, A. D. *J. Org. Chem.* **1989**, *54*, 3009.
- <sup>261</sup> Reddy, Y. K.; Falck, J. R. *Org. Lett.* **2002**, *4*, 969.
- <sup>262</sup> Mikhailov, B. M.; Bubnov, Y. N. *Russ. Chem. Bull.* **1964**, *13*, 1774.
- <sup>263</sup> Zhou, W.; Liang, S.; Yu, S.; Luo, W. *J. Organomet. Chem.* **1993**, *452*, 13.
- <sup>264</sup> Paterson, I.; Wallace, D. J.; Gibson, K. R. *Tetrahedron Lett.* **1997**, *38*, 8911.
- <sup>265</sup> White, J. B.; Blakemore, P. R.; Browder, C. C.; Hong, J.; Lincoln, C. M.; Nagornyy, P. A.; Robarge, L. A.; Wardrop, D. J. *J. Am. Chem. Soc.* **2001**, *123*, 8593.
- <sup>266</sup> Dineen, T. A.; Roush, W. R. *Org. Lett.* **2004**, *6*, 2043.
- <sup>267</sup> Smith, A. B., III; Safonov, I. G.; Corbett, R. M. *J. Am. Chem. Soc.* **2002**, *124*, 11102.
- <sup>268</sup> Smith, A. B., III; Minbiole, K. P.; Verhoest, P. R.; Schelhaas, M. *J. Am. Chem. Soc.* **2001**, *123*, 10942.
- <sup>269</sup> Diez-Martin, D.; Kotecha, N. R.; Ley, S. V.; Mantegani, S.; Menendez, J. C.; Organ, H. M.; White, A. D.; Bank, B. J. *Tetrahedron* **1992**, *48*, 7899.
- <sup>270</sup> Nicolaou, K. C.; Ahn, K. H. *Tetrahedron Lett.* **1989**, *30*, 1217.
- <sup>271</sup> Smith, A. B., III; Lin, Q. L.; Nakayama, K.; Boldi, A. M.; Brook, C. S.; McBriar, M. D.; Moser, W. H.; Sobukawa, M.; Zhuang, L. *Tetrahedron Lett.* **1997**, *38*, 8675.
- <sup>272</sup> Crimmins, M. T.; Washburn, D. G. *Tetrahedron Lett.* **1998**, *39*, 7487.
- <sup>273</sup> Wu, Y. S.; Esser, L.; De Brabander, J. K. *Angew. Chem., Int. Ed.* **2000**, *39*, 4308.
- <sup>274</sup> Shi, Y.; Peng, L. F.; Kishi, Y. *J. Org. Chem.* **1997**, *62*, 5666.
- <sup>275</sup> Hoffmann, R. W.; Metternich, R.; Lanz, J. W. *Liebigs Ann. Chem.* **1987**, 881.
- <sup>276</sup> Thadani, A. N.; Batey, R. A. *Tetrahedron Lett.* **2003**, *44*, 8051.
- <sup>277</sup> Roush, W. R.; Hunt, J. A. *J. Org. Chem.* **1995**, *60*, 798.
- <sup>278</sup> Yakelis, N. A.; Roush, W. R. *J. Org. Chem.* **2003**, *68*, 3838.
- <sup>279</sup> Pattenden, G.; Plowright, A. T. *Tetrahedron Lett.* **2000**, *41*, 983.



- 280 Pattenden, G.; Gonzalez, M. A.; Little, P. B.; Millan, D. S.; Plowright, A. T.; Tornos, J. A.; Ye, T. *Org. Biomol. Chem.* **2003**, *1*, 4173.
- 280a Pattenden, G.; Plowright, A. T.; Tornos, J. A.; Ye, T. *Tetrahedron Lett.* **1998**, *39*, 6099.
- 281 Deng, L.; Scharer, O. D.; Verdine, G. L. *J. Am. Chem. Soc.* **1997**, *119*, 7865.
- 282 Jingsons, A.; Marinozzi, M.; Pellicciari, R. *Tetrahedron* **2005**, *61*, 373.
- 283 Nicolaou, K. C.; Groneberg, R. D.; Stylianides, N. A.; Miyazaki, T. *J. Chem. Soc., Chem. Commun.* **1990**, 1275.
- 284 Groneberg, R. D.; Miyazaki, T.; Stylianides, N. A.; Schulze, T. J.; Stahl, W.; Schreiner, E. P.; Suzuki, T.; Iwabuchi, Y.; Smith, A. L.; Nicolaou, K. C. *J. Am. Chem. Soc.* **1993**, *115*, 7593.
- 285 Nicolaou, K. C.; Koide, K.; Bunnage, N. E. *Chem. Eur. J.* **1995**, *1*, 454.
- 286 Nicolaou, K. C.; Bunnage, M. E.; Koide, K. *J. Am. Chem. Soc.* **1994**, *116*, 8402.
- 287 Nicolaou, K. C.; Pihko, P. M.; Diedrichs, N.; Zou, N.; Bernal, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 1262.
- 288 Hoffmann, R. W.; Endesfelder, A.; Zeiss, H. J. *Carbohydr. Res.* **1983**, *123*, 320.
- 289 Barrett, A. G. M.; Beall, J. C.; Gibson, V. C.; Gilles, M. R.; Walker, G. L. *P. Chem. Commun.* **1996**, 2229.
- 290 Chen, W.; Liu, Y.; Chen, Z. *Eur. J. Org. Chem.* **2005**, *8*, 1665.
- 291 Nicolaou, K. C.; King, N. P.; Finlay, M. R. V.; He, Y.; Roschangar, F.; Vourloumis, D.; Vallberg, H.; Sarabia, F.; Ninkovic, S.; Hepworth, D. *Bioorg. Med. Chem.* **1999**, *7*, 665.
- 292 Ramachandran, P. V.; Burghardt, T. E.; Reddy, M. V. R. *J. Org. Chem.* **2005**, *70*, 2329.
- 293 Nieczypor, P.; Mol, J. C.; Bepalova, N. B.; Bubnov, Y. N. *Eur. J. Org. Chem.* **2004**, 812.
- 294 Bubnov, Y. N.; Pastukhov, F. V.; Yampolsky, I. V.; Ignatenko, A. V. *Eur. J. Org. Chem.* **2000**, 1503.
- 295 Nicolaou, K. C.; Patron, A. P.; Ajito, K.; Richter, P. K.; Khatuya, H.; Bertinato, P.; Miller, R. A.; Tomaszewski, M. J. *Chem. Eur. J.* **1996**, *2*, 847.
- 296 Aissa, C.; Riveiros, R.; Ragot, J.; Fürstner, A. *J. Am. Chem. Soc.* **2003**, *125*, 15512.
- 297 Roush, W. R.; Palkowitz, A. D.; Ando, K. *J. Am. Chem. Soc.* **1990**, *112*, 6348.
- 298 Judd, T. C.; Bischoff, A.; Kishi, Y.; Adusumilli, S.; Small, P. L. *C. Org. Lett.* **2004**, *6*, 4901.
- 299 Hoffmann, R. W.; Froech, S. *Tetrahedron Lett.* **1985**, *26*, 1643.
- 300 Matsushima, Y.; Nakayama, T.; Tohyama, S.; Eguchi, T.; Kakinuma, K. *J. Chem. Soc., Perkin Trans. 1* **2001**, 569.
- 301 Chen, Z.; Ye, T. *Synlett* **2005**, 2781.
- 302 Roush, W. R.; Straub, J. A.; Vannieuwenhze, M. S. *J. Org. Chem.* **1991**, *56*, 1636.
- 303 Roush, W. R.; Straub, J. A. *Tetrahedron Lett.* **1986**, *27*, 3349.
- 304 Roush, W. R.; Lin, X. F.; Straub, J. A. *J. Org. Chem.* **1991**, *56*, 1649.
- 305 Steel, P. G.; Thomas, E. J. *J. Chem. Soc., Perkin Trans. 1* **1997**, 371.
- 306 Merifield, E.; Steel, P. G.; Thomas, E. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1826.
- 307 Smith, A. B., III; Chen, S. S. Y.; Nelson, F. C.; Reichert, J. M.; Salvatore, B. A. *J. Am. Chem. Soc.* **1995**, *117*, 12013.
- 308 Smith, A. B., III; Chen, S. S. Y.; Nelson, F. C.; Reichert, J. M.; Salvatore, B. A. *J. Am. Chem. Soc.* **1997**, *119*, 10935.
- 309 Barth, M.; Bellamy, F. D.; Renaut, P.; Samreth, S.; Schubert, F. *Tetrahedron* **1990**, *46*, 6731.
- 310 Paterson, I.; Anderson, E. A.; Dalby, S. M.; Loiseleur, O. *Org. Lett.* **2005**, *7*, 4125.
- 311 White, J. D.; Kim, T. S.; Nambu, M. *J. Am. Chem. Soc.* **1995**, *117*, 5612.
- 312 Nagle, D. G.; Gerald, R. S.; Yoo, H. D.; Gerwick, W. H.; Kim, T. S.; Nambu, M.; White, J. D. *Tetrahedron Lett.* **1995**, *36*, 1189.
- 313 Xu, Z.; Chen, Z.; Ye, T. *Tetrahedron: Asymmetry* **2004**, *15*, 355.
- 314 Ramachandran, P. V.; Krezminski, M. P.; Reddy, M. V. R.; Brown, H. C. *Tetrahedron: Asymmetry* **1999**, *10*, 11.
- 315 Ghosh, A. K.; Wang, Y. *Tetrahedron Lett.* **2000**, *41*, 2319.
- 316 Naito, H.; Kawahara, E.; Maruta, K.; Maeda, M.; Sasaki, S. *J. Org. Chem.* **1995**, *60*, 4419.
- 317 Mulzer, J.; Hanbauer, M. *Tetrahedron Lett.* **2000**, *41*, 33.
- 318 Ahmed, A.; Hoegenauer, E. K.; Enev, V. A. S.; Hanbauer, M.; Kaehlig, H.; Ohler, E.; Mulzer, J. *J. Org. Chem.* **2003**, *68*, 3026.

- 319 Provencal, D. P.; Gardelli, C.; Lafontaine, J. A.; Leahy, J. W. *Tetrahedron Lett.* **1995**, *36*, 6033.
- 320 Lafontaine, J. A.; Provencal, D. P.; Gardelli, C.; Leahy, J. W. *J. Org. Chem.* **2003**, *68*, 4215.
- 321 Takahata, H.; Ouchi, H.; Ichinose, M.; Nemoto, H. *Org. Lett.* **2002**, *4*, 3459.
- 322 Dinh, T. Q.; Du, X.; Smith, C. D.; Armstrong, R. W. *J. Org. Chem.* **1997**, *62*, 6773.
- 323 Dinh, T. Q.; Smith, C. D.; Armstrong, R. W. *J. Org. Chem.* **1997**, *62*, 790.
- 324 McAlpine, I. J.; Armstrong, R. W. *Tetrahedron Lett.* **2000**, *41*, 1849.
- 325 Rychnovsky, S. D.; Griesgraber, G.; Schlegel, R. *J. Am. Chem. Soc.* **1995**, *117*, 197.
- 326 Wender, P. A.; Clarke, M. O.; Horan, J. C. *Org. Lett.* **2005**, *7*, 1995.
- 327 Wender, P. A.; Koehler, M. F. T.; Sendzik, M. *Org. Lett.* **2003**, *5*, 4549.
- 328 Kang, S. H.; Kang, S. Y.; Kim, C. M.; Choi, H. W.; Jun, H. S.; Lee, B. M.; Park, C. M.; Jeong, J. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 4779.
- 329 Kang, S. H.; Kang, S. Y.; Choi, H. W.; Kim, C. M.; Jun, H. S.; Youn, J. H. *Synthesis* **2004**, 1102.
- 330 Hayward, M. M.; Roth, R. M.; Duffy, K. J.; Dalko, P. I.; Stevens, K. L.; Guo, J.; Kishi, Y. *Angew. Chem., Int. Ed.* **1998**, *37*, 192.
- 331 Kang, S. H.; Choi, H. W.; Kim, C. M.; Jun, H. S.; Kang, S. Y.; Jeong, J. W.; Youn, J. H. *Tetrahedron Lett.* **2003**, *44*, 6817.
- 332 Murai, A. *J. Toxicol.: Toxin Rev.* **2003**, *22*, 617.
- 333 Ishihara, J.; Yamamoto, Y.; Kanoh, N.; Murai, A. *Tetrahedron Lett.* **1999**, *40*, 4387.
- 334 Grieco, P. A.; Speake, J. D.; Yeo, S. K.; Miyashita, M. *Tetrahedron Lett.* **1998**, *39*, 1125.
- 335 Liu, B.; Zhou, W. S. *Org. Lett.* **2004**, *6*, 71.
- 336 Ghosh, A. K.; Kim, J. H. *Tetrahedron Lett.* **2003**, *44*, 3967.
- 337 Jirousek, M. R.; Cheung, A. W. H.; Babine, R. E.; Sass, P. M.; Schow, S. R.; Wick, M. M. *Tetrahedron Lett.* **1993**, *34*, 3671.
- 338 Bhattacharjee, A.; Soltani, O.; De Brabander, J. K. *Org. Lett.* **2002**, *4*, 481.
- 339 Barry, C. S.; Bushby, N.; Harding, J. R.; Hughes, R. A.; Parker, G. D.; Roe, R.; Willis, C. L. *Chem. Commun.* **2005**, 3727.
- 340 Prahlad, V.; El-Ahl, A. A. S.; Donaldson, W. A. *Tetrahedron: Asymmetry* **2000**, *11*, 3091.
- 341 White, J. D.; Hong, J.; Robarge, L. A. *Tetrahedron Lett.* **1999**, *40*, 1463.
- 342 Roush, W. R.; Wada, C. K. *Tetrahedron Lett.* **1994**, *35*, 7347.
- 343 Truesdale, L. K.; Swanson, D.; Sun, R. C. *Tetrahedron Lett.* **1985**, *26*, 5009.
- 344 Barmann, H.; Prahlad, V.; Tao, C.; Yun, Y. K.; Wang, Z.; Donaldson, W. A. *Tetrahedron* **2000**, *56*, 2283.
- 345 Prahlad, V.; Donaldson, W. A. *Tetrahedron Lett.* **1996**, *37*, 9169.
- 346 Rychnovsky, S. D.; Rodriguez, C. *J. Org. Chem.* **1992**, *57*, 4793.
- 347 Rychnovsky, S. D.; Hoye, R. C. *J. Am. Chem. Soc.* **1994**, *116*, 1753.
- 348 Ahmed, M.; Barrett, A. G. M.; Beall, J. C.; Braddock, D. C.; Flack, K.; Gibson, V. C.; Procopiou, P. A.; Salter, M. M. *Tetrahedron* **1999**, *55*, 3219.
- 349 Sebelius, S.; Szabó, K. J. *Eur. J. Org. Chem.* **2005**, 2539.
- 350 Roush, W. R.; Banfi, L.; Park, J. C.; Hoong, L. K. *Tetrahedron Lett.* **1989**, *30*, 6457.
- 351 Corey, E. J.; Kim, S. S. *Tetrahedron Lett.* **1990**, *31*, 3715.
- 352 Ollivier, C.; Panchoaud, P.; Renaud, P. *Synthesis* **2001**, 1573.
- 353 Kabalka, G. W.; Venkataiah, B.; Das, B. C. *Green Chem.* **2002**, *4*, 472.
- 354 Nicolaou, K. C.; Fylaktakidou, K. C.; Monenschein, H.; Li, Y. W.; Weyershausen, B.; Mitchell, H. J.; Wei, H. X.; Guntupalli, P.; Hepworth, D.; Sugita, K. *J. Am. Chem. Soc.* **2003**, *125*, 15433.
- 355 Nicolaou, K. C.; Li, Y.; Fylaktakidou, K. C.; Mitchell, H. J.; Wei, H. X.; Weyershausen, B. *Angew. Chem., Int. Ed.* **2001**, *40*, 3849.
- 356 Nicolaou, K. C.; Li, Y. W.; Weyershausen, B.; Wei, H. X. *Chem. Commun.* **2000**, 307.
- 357 Smith, A. B., III; Barbosa, J.; Wong, W.; Wood, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 8316.
- 358 Hoemann, M. Z.; Agrios, K. A.; Aube, J. *Tetrahedron* **1997**, *53*, 11087.
- 359 Vong, B. G.; Kim, S. H.; Abraham, S.; Theodorakis, E. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 3947.
- 360 Williams, D. R.; Ihle, D. C.; Plummer, S. V. *Org. Lett.* **2001**, *3*, 1383.
- 361 White, J. D.; Smits, H. *Org. Lett.* **2005**, *7*, 235.

- <sup>362</sup> Nadolski, G. T.; Davidson, B. S. *Tetrahedron Lett.* **2001**, *42*, 797.
- <sup>363</sup> Ito, H.; Imai, N.; Tanikawa, S.; Kobayashi, S. *Tetrahedron Lett.* **1996**, *37*, 1795.
- <sup>364</sup> Fujiwara, K.; Goto, A.; Sato, D.; Ohtaniuchi, Y.; Tanaka, H.; Murai, A.; Kawai, H.; Suzuki, T. *Tetrahedron Lett.* **2004**, *45*, 7011.
- <sup>365</sup> Danieli, B.; Lesma, G.; Passarella, D.; Sacchetti, A.; Silvani, A.; Viridis, A. *Org. Lett.* **2004**, *6*, 493.
- <sup>366</sup> Hilli, F.; White, J. M.; Rizzacasa, M. A. *Org. Lett.* **2004**, *6*, 1289.
- <sup>367</sup> Ding, F.; Jennings, M. P. *Org. Lett.* **2005**, *7*, 2321.
- <sup>368</sup> Fan, X.; Flentke, G. R.; Rich, D. H. *J. Am. Chem. Soc.* **1998**, *120*, 8893.
- <sup>369</sup> Bonini, C.; Racioppi, R.; Viggiani, L. *Tetrahedron: Asymmetry* **1993**, *4*, 793.
- <sup>370</sup> Bonini, C.; Giugliano, A.; Racioppi, R.; Righi, G. *Tetrahedron Lett.* **1996**, *37*, 2487.
- <sup>371</sup> Schneider, C.; Rehfeuter, M. *Tetrahedron Lett.* **1998**, *39*, 9.
- <sup>372</sup> Schneider, C.; Rehfeuter, M. *Chem. Eur. J.* **1999**, *5*, 2850.
- <sup>373</sup> Schneider, C. *Synlett* **2001**, 1079.
- <sup>374</sup> White, J. D.; Kranemann, C. L.; Kuntiyong, P. *Org. Lett.* **2001**, *3*, 4003.
- <sup>375</sup> Le Flohic, A.; Meyer, C.; Cossy, J. *Org. Lett.* **2005**, *7*, 339.
- <sup>376</sup> Yang, H. W.; Romo, D. *J. Org. Chem.* **1997**, *62*, 4.
- <sup>377</sup> Yang, H. W.; Zhao, C. X.; Romo, D. *Tetrahedron* **1997**, *53*, 16471.
- <sup>378</sup> Salmon, A.; Carboni, B. *J. Organomet. Chem.* **1998**, *567*, 31.
- <sup>379</sup> Ramachandran, P. V.; Reddy, M. V. R.; Brown, H. C. *J. Indian Chem. Soc.* **1999**, *76*, 739.
- <sup>380</sup> Pitts, M. R.; Mulzer, J. *Tetrahedron Lett.* **2002**, *43*, 8471.
- <sup>381</sup> Kumar, V. S.; Wan, S.; Aubele, D. L.; Floreancig, P. E. *Tetrahedron: Asymmetry* **2005**, *16*, 3570.
- <sup>382</sup> Ghosh, A. K.; Kim, J. H. *Tetrahedron Lett.* **2003**, *44*, 7659.
- <sup>383</sup> Reddy, M. V. R.; Rearick, J. P.; Hoch, N.; Ramachandran, P. V. *Org. Lett.* **2001**, *3*, 19.
- <sup>384</sup> Gingras, K.; Avedissian, H.; Thouin, E.; Boulanger, V.; Essagian, C.; McKerracher, L.; Lubell, W. D. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 4931.
- <sup>385</sup> Nagasawa, K. *J. Synth. Org. Chem. Jpn.* **2000**, *58*, 877.
- <sup>386</sup> Liu, B.; Duan, S.; Sutterer, A. C.; Moeller, K. D. *J. Am. Chem. Soc.* **2002**, *124*, 10101.
- <sup>387</sup> Liu, B.; Moeller, K. D. *Tetrahedron Lett.* **2001**, *42*, 7163.
- <sup>388</sup> Ramachandran, P. V.; Liu, H.; Reddy, M. V. R.; Brown, H. C. *Org. Lett.* **2003**, *5*, 3755.
- <sup>389</sup> Schneider, C.; Schuffenhauer, A. *Eur. J. Org. Chem.* **2000**, 73.
- <sup>390</sup> Schneider, C. *Synlett* **1997**, 815.
- <sup>391</sup> Garcia-Fortanet, J.; Murga, J.; Carda, M.; Marco, J. A. *Tetrahedron* **2004**, *60*, 12261.
- <sup>392</sup> Murga, J.; Garcia-Fortanet, J.; Carda, M.; Marco, J. A. *Tetrahedron Lett.* **2003**, *44*, 1737.
- <sup>393</sup> Wolbers, P.; Hoffmann, H. M. R. *Tetrahedron* **1999**, *55*, 1905.
- <sup>394</sup> Yadav, J. S.; Prakash, S. J.; Gangadhar, Y. *Tetrahedron: Asymmetry* **2005**, *16*, 2722.
- <sup>395</sup> Trost, B. M.; Yeh, V. S. C. *Org. Lett.* **2002**, *4*, 3513.
- <sup>396</sup> Falomir, E.; Murga, J.; Ruiz, P.; Carda, M.; Marco, J. A. *J. Org. Chem.* **2003**, *68*, 5672.
- <sup>397</sup> Falomir, E.; Murga, J.; Carda, M.; Marco, J. A. *Tetrahedron Lett.* **2003**, *44*, 539.
- <sup>398</sup> Diaz-Oltra, S.; Murga, J.; Falomir, E.; Carda, M.; Marco, J. A. *Tetrahedron* **2004**, *60*, 2979.
- <sup>399</sup> Wender, P. A.; De Brabander, J.; Harran, P. G.; Hinkle, K. W.; Lippa, B.; Pettit, G. R. *Tetrahedron Lett.* **1998**, *39*, 8625.
- <sup>400</sup> Fürstner, A.; Mathes, C.; Lehmann, C. W. *Chem. Eur. J.* **2001**, *7*, 5299.
- <sup>401</sup> Taylor, R. E.; Chen, Y. *Org. Lett.* **2001**, *3*, 2221.
- <sup>402</sup> Meng, D. F.; Bertinato, P.; Balog, A.; Su, D. S.; Kamenecka, T.; Sorensen, E. J.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1997**, *119*, 10073.
- <sup>403</sup> Denmark, S. E.; Yang, S. M. *J. Am. Chem. Soc.* **2004**, *126*, 12432.
- <sup>404</sup> Ritter, T.; Kvaerno, L.; Werder, M.; Hauser, H.; Carreira, E. M. *Org. Biomol. Chem.* **2005**, *3*, 3514.
- <sup>405</sup> Jennings, M. P.; Clemens, R. T. *Tetrahedron Lett.* **2005**, *46*, 2021.
- <sup>406</sup> Dreher, S. D.; Leighton, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 341.
- <sup>407</sup> Ramachandran, P. V.; Chandra, J. S.; Reddy, M. V. R. *J. Org. Chem.* **2002**, *67*, 7547.

- 408 Banwell, M. G.; Coster, M. J.; Edwards, A. J.; Karunaratne, O. P.; Smith, J. A.; Welling, L. L.; Willis, A. C. *Aust. J. Chem.* **2003**, *56*, 585.
- 409 Greer, P. B.; Donaldson, W. A. *Tetrahedron* **2002**, *58*, 6009.
- 410 Greer, P. B.; Donaldson, W. A. *Tetrahedron Lett.* **2000**, *41*, 3801.
- 411 Kadota, I.; Oguro, N.; Yamamoto, Y. *Tetrahedron Lett.* **2001**, *42*, 3645.
- 412 Chattopadhyay, S. K.; Pattenden, G. *Tetrahedron Lett.* **1995**, *36*, 5271.
- 413 Tan, C. H.; Kobayashi, Y.; Kishi, Y. *Angew. Chem., Int. Ed.* **2000**, *39*, 4282.
- 414 Kadota, I.; Park, C. H.; Sato, K.; Yamamoto, Y. *Tetrahedron Lett.* **2001**, *42*, 6195.
- 415 Kadota, I.; Kadowaki, C.; Park, C. H.; Takamura, H.; Sato, K.; Chan, P. W. H.; Thorand, S.; Yamamoto, Y. *Tetrahedron* **2002**, *58*, 1799.
- 416 Nicolaou, K. C.; Kim, D. W.; Baati, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 3701.
- 417 Nicolaou, K. C.; Kim, D. W.; Baati, R.; O'Brate, A.; Giannakakou, P. *Chem. Eur. J.* **2003**, *9*, 6177.
- 418 Duplantier, A. J.; Masamune, S. *J. Am. Chem. Soc.* **1990**, *112*, 7079.
- 419 Sun, L. Q.; Takaki, K.; Chen, J.; Bertenshaw, S.; Iben, L.; Mahle, C. D.; Ryan, E.; Wu, D. D.; Gao, Q.; Xu, C. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 1345.
- 420 Dinh, T. Q.; Du, X.; Armstrong, R. W. *J. Org. Chem.* **1996**, *61*, 6606.
- 421 Nishiyama, S. *J. Synth. Org. Chem. Jpn.* **2001**, *59*, 938.
- 422 Dinh, T. Q.; Armstrong, R. W. *J. Org. Chem.* **1995**, *60*, 8118.
- 423 Fuhrhop, J. H.; Bedurke, T.; Hahn, A.; Grund, S.; Gatzmann, J.; Riederer, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 350.
- 424 Hooper, F.; Montforts, F. P. *Tetrahedron: Asymmetry* **1993**, *4*, 1439.
- 425 Paterson, I.; Fessner, K.; Finlay, M. R. V. *Tetrahedron Lett.* **1997**, *38*, 4301.
- 426 Crimmins, M. T.; Stanton, M. G.; Allwein, S. P. *J. Am. Chem. Soc.* **2002**, *124*, 5958.
- 427 Pietruszka, J.; Wilhelm, T. *Synlett* **2003**, 1698.
- 428 Sarraf, S. T.; Leighton, J. L. *Org. Lett.* **2000**, *2*, 3205.
- 429 Vitale, J. P.; Wolckenhauer, S. A.; Do, N. M.; Rychnovsky, S. D. *Org. Lett.* **2005**, *7*, 3255.
- 430 Goulet, M. T.; Boger, J. *Tetrahedron Lett.* **1990**, *31*, 4845.
- 431 Koert, U.; Stein, M.; Harms, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1180.
- 432 Koert, U.; Stein, M.; Wagner, H. *Chem. Eur. J.* **1997**, *3*, 1170.
- 433 Schreiber, S. L.; Goulet, M. T. *J. Am. Chem. Soc.* **1987**, *109*, 8120.
- 434 Crimmins, M. T.; Emmitte, K. A.; Choy, A. L. *Tetrahedron* **2002**, *58*, 1817.
- 435 Mascavage, L. M.; Lu, Q.; Vey, J.; Dalton, D. R.; Carroll, P. J. *J. Org. Chem.* **2001**, *66*, 3621.
- 436 Andrus, M. B.; Hicken, E. J.; Meredith, E. L.; Sommons, B. L.; Cannon, J. F. *Org. Lett.* **2003**, *5*, 3859.
- 437 Muir, J. C.; Pattenden, G.; Ye, T. *J. Chem. Soc., Perkin Trans. 1* **2002**, 2243.
- 438 Muir, J. C.; Pattenden, G.; Ye, T. *Tetrahedron Lett.* **1998**, *39*, 2861.
- 439 Wipf, P.; Xu, W. *J. Org. Chem.* **1996**, *61*, 6556.
- 440 Rychnovsky, S. D.; Khire, U. R.; Yang, G. *J. Am. Chem. Soc.* **1997**, *119*, 2058.
- 441 White, J. D.; Ohba, Y.; Porter, W. J.; Wang, S. *Tetrahedron Lett.* **1997**, *38*, 3167.
- 442 Williams, D. R.; Brugel, T. A. *Org. Lett.* **2000**, *2*, 1023.
- 443 Mulzer, J.; Mantoulidis, A. *Tetrahedron Lett.* **1996**, *31*, 9179.
- 444 Bolshakov, S.; Leighton, J. L. *Org. Lett.* **2005**, *7*, 3809.
- 445 Kang, E. J.; Cho, E. J.; Ji, M. K.; Lee, Y. E.; Shin, D. M.; Choi, S. Y.; Chung, Y. K.; Kim, J. S.; Kim, H. J.; Lee, S. G.; Lah, M. S.; Lee, E. *J. Org. Chem.* **2005**, *70*, 6321.
- 446 Ruiz, P.; Murga, J.; Carda, M.; Marco, J. A. *J. Org. Chem.* **2005**, *70*, 713.
- 447 Hanessian, S.; Tehim, A.; Chen, P. *J. Org. Chem.* **1993**, *58*, 7768.
- 448 Jadhav, P. K. *Tetrahedron Lett.* **1989**, *30*, 4763.
- 449 Dirat, O.; Kouklovsky, C.; Langlois, Y.; Lesot, P.; Courtieu, J. *Tetrahedron: Asymmetry* **1999**, *10*, 3197.
- 450 Crimmins, M. T.; Powell, M. T. *J. Am. Chem. Soc.* **2003**, *125*, 7592.
- 451 Wipf, P.; Reeves, J. T.; Balachandran, R.; Day, B. W. *J. Med. Chem.* **2002**, *45*, 1901.
- 452 Beumer, R.; Bayon, P.; Bugada, P.; Ducki, S.; Mongelli, N.; Sirtori, F. R.; Telsler, J.; Gennari, C. *Tetrahedron* **2003**, *59*, 8803.

- 453 Beumer, R.; Bayon, P.; Bugada, P.; Ducki, S.; Mongelli, N.; Sirtori, F. R.; Telser, J.; Gennari, C. *Tetrahedron Lett.* **2003**, *44*, 681.
- 454 Telser, J.; Beumer, R.; Bell, A. A.; Ceccarelli, S. M.; Monti, D.; Gennari, C. *Tetrahedron Lett.* **2001**, *42*, 9187.
- 455 Murga, J.; Garcia-Fortanet, J.; Carda, M.; Marco, J. A. *Tetrahedron Lett.* **2004**, *45*, 7499.
- 456 Roush, W. R.; Palkowitz, A. D. *J. Am. Chem. Soc.* **1987**, *109*, 953.
- 457 Wang, Z.; Deschenes, D. *J. Am. Chem. Soc.* **1992**, *114*, 1090.
- 458 Liao, X. B.; Wu, Y. S.; De Brabander, J. K. *Angew. Chem., Int. Ed.* **2003**, *42*, 1648.
- 459 Nakata, T.; Suenaga, T.; Nakashima, K.; Oishi, T. *Tetrahedron Lett.* **1989**, *30*, 6529.
- 460 Lemarchand, A.; Bach, T. *Synthesis* **2005**, 1977.
- 461 Murga, J.; Garcia-Fortanet, J.; Carda, M.; Marco, J. A. *Tetrahedron Lett.* **2003**, *44*, 7909.
- 462 Du, Y.; Wiemer, D. F. *J. Org. Chem.* **2002**, *67*, 5701.
- 463 Vong, B. G.; Abraham, S.; Xiang, A. X.; Theodorakis, E. A. *Org. Lett.* **2003**, *5*, 1617.
- 464 Hornberg, K. R.; Hamblett, C. L.; Leighton, J. L. *J. Am. Chem. Soc.* **2000**, *122*, 12894.
- 465 Lewis, A.; Stefanuti, I.; Swain, S. A.; Smith, S. A.; Taylor, R. J. K. *Org. Biomol. Chem.* **2003**, *1*, 104.
- 466 Bhattacharjee, A.; De Brabander, J. K. *Tetrahedron Lett.* **2000**, *41*, 8069.
- 467 Vorontsova, N. V.; Rozenberg, V. I.; Vorontsov, E. V.; Antonov, D. Y.; Starikova, Z. A.; Bubnov, Y. N. *Russ. Chem. Bull., Int. Ed.* **2002**, *51*, 1483.
- 468 Castoldi, D.; Caggiano, L.; Bayon, P.; Costa, A. M.; Cappella, P.; Sharon, O.; Gennari, C. *Tetrahedron* **2005**, *61*, 2123.
- 469 Sutherlin, D. P.; Armstrong, R. W. *J. Org. Chem.* **1997**, *62*, 5267.
- 470 Sutherlin, D. P.; Armstrong, R. W. *J. Am. Chem. Soc.* **1996**, *118*, 9802.
- 471 Carter, R. G.; Bourland, T. C.; Zhou, X. T.; Gronemeyer, M. A. *Tetrahedron* **2003**, *59*, 8963.
- 472 Hwang, C. H.; Keum, G.; Sohn, K. I.; Lee, D. H.; Lee, E. *Tetrahedron Lett.* **2005**, *46*, 6621.
- 473 Yamamoto, Y.; Nishii, S.; Yamada, J. I. *J. Am. Chem. Soc.* **1986**, *108*, 7116.
- 474 Mori, Y.; Kohchi, Y.; Noguchi, H.; Suzuki, M.; Carmeli, S.; Moore, R. E.; Patterson, G. M. L. *Tetrahedron* **1991**, *47*, 4889.
- 475 Hanessian, S.; Giroux, S.; Buffat, M. *Org. Lett.* **2005**, *7*, 3989.
- 476 Takahashi, S.; Ogawa, N.; Koshino, H.; Nakata, T. *Org. Lett.* **2005**, *7*, 2783.
- 477 Hopner, F.; Montforts, F. P. *Liebigs Ann. Chem.* **1995**, 1033.
- 478 Racherla, U. S.; Liao, Y.; Brown, H. C. *J. Org. Chem.* **1992**, *57*, 6614.
- 479 Felpin, F. X.; Bertrand, M. J.; Lebreton, J. *Tetrahedron* **2002**, *58*, 7381.
- 480 Felpin, F. X.; Girard, S.; Vo-Thanh, G.; Robins, R. J.; Villieras, J.; Lebreton, J. *J. Org. Chem.* **2001**, *66*, 6305.
- 481 Felpin, F. X.; Vo-Thanh, G.; Robins, R. J.; Villieras, J.; Lebreton, J. *Synlett* **2000**, 1646.
- 482 Chen, G. M.; Brown, H. C.; Ramachandran, P. V. *J. Org. Chem.* **1999**, *64*, 721.
- 483 Kimura, M.; Kiyama, I.; Tomizawa, Y.; Horino, Y.; Tanaka, S.; Tamaru, Y. *Tetrahedron Lett.* **1999**, *40*, 6795.
- 484 Felpin, F. X.; Lebreton, J. *J. Org. Chem.* **2002**, *67*, 9192.
- 485 Mears, R. J.; DeSilva, H.; Whiting, A. *Tetrahedron* **1997**, *53*, 17395.
- 486 Thormeier, S.; Carboni, B.; Kaufmann, D. E. *J. Organomet. Chem.* **2002**, *657*, 136.
- 487 Vorontsova, N. V.; Rozenberg, V. I.; Vorontsov, E. V.; Tok, O. L.; Bubnov, Y. N. *Russ. Chem. Bull.* **2000**, *49*, 912.
- 488 Crosby, S. R.; Harding, J. R.; King, C. D.; Parker, G. D.; Willis, C. L. *Org. Lett.* **2002**, *4*, 577.
- 489 Koide, K.; Finkelstein, J. M.; Ball, Z.; Verdine, G. L. *J. Am. Chem. Soc.* **2001**, *123*, 398.
- 490 Crosby, S. R.; Harding, J. R.; King, C. D.; Parker, G. D.; Willis, C. L. *Org. Lett.* **2002**, *4*, 3407.
- 491 Ramachandran, P. V.; Padiya, K. J.; Rauniyar, V.; Reddy, M. V. R.; Brown, H. C. *J. Fluorine Chem.* **2004**, *125*, 615.
- 492 Wang, X. Z.; Burke, J., T. R. *Synlett* **2004**, 469.
- 493 Couladouros, E. A.; Plyta, Z. F.; Strongilos, A. T.; Papageorgiou, V. P. *Tetrahedron Lett.* **1997**, *38*, 7263.
- 494 Couladouros, E. A.; Strongilos, A. T.; Papageorgiou, V. P.; Plyta, Z. F. *Chem. Eur. J.* **2002**, *8*, 1795.

- <sup>495</sup> Ku, Y. Y.; Grieme, T.; Rajee, P.; Sharma, P.; King, S. A.; Morton, H. E. *J. Am. Chem. Soc.* **2002**, *124*, 4282.
- <sup>496</sup> Ku, Y. Y.; Grieme, T. *Curr. Opin. Drug Discov. Devel.* **2002**, *5*, 852.
- <sup>497</sup> Brown, H. C.; Randad, R. S. *Tetrahedron* **1990**, *46*, 4457.
- <sup>498</sup> Hoffmann, R. W.; Ladner, W. *Tetrahedron Lett.* **1979**, 4653.
- <sup>499</sup> Hoffmann, R. W.; Ladner, W.; Steinbach, K.; Massa, W.; Schmidt, R.; Snatzke, G. *Chem. Ber.* **1981**, *114*, 2786.
- <sup>500</sup> Richter, P. K.; Tomaszewski, M. J.; Miller, R. A.; Patron, A. P.; Nicolaou, K. C. *J. Chem. Soc., Chem. Commun.* **1994**, 1151.
- <sup>501</sup> N'Zoutani, M. A.; Pancrazi, A.; Ardisson, J. *Synlett* **2001**, 769.
- <sup>502</sup> Ireland, R. E.; Highsmith, T. K.; Gegnas, L. D.; Gleason, J. L. *J. Org. Chem.* **1992**, *57*, 5071.
- <sup>503</sup> Ramachandran, P. V.; Prabhudas, B.; Pratihar, D.; Chandra, J. S.; Reddy, M. V. R. *Tetrahedron Lett.* **2003**, *44*, 3745.
- <sup>504</sup> La Cruz, T. E.; Rychnovsky, S. D. *Org. Lett.* **2005**, *7*, 1873.
- <sup>505</sup> Ramachandran, P. V.; Chandra, J. S.; Prabhudas, B.; Pratihar, D.; Reddy, M. V. R. *Org. Biomol. Chem.* **2005**, *3*, 3812.
- <sup>506</sup> Bates, R. B.; Gangwar, S. *Tetrahedron: Asymmetry* **1993**, *4*, 69.
- <sup>507</sup> Wu, B.; Liu, Q.; Sulikowski, G. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 6673.
- <sup>508</sup> Brimble, M. A.; Furkert, D. P. *Org. Biomol. Chem.* **2004**, *2*, 3573.
- <sup>509</sup> Brimble, M. A.; Fares, F. A.; Turner, P. *Aust. J. Chem.* **2000**, *53*, 845.
- <sup>510</sup> Boeckman, R. K.; Charette, A. B.; Asberom, T.; Johnston, B. H. *J. Am. Chem. Soc.* **1987**, *109*, 7553.
- <sup>511</sup> Anderson, O. P.; Barrett, A. G. M.; Edmunds, J. J.; Hachiya, S. I.; Hendrix, J. A.; Horita, K.; Malecha, J. W.; Parkinson, C. J.; VanSickle, A. *Can. J. Chem.* **2001**, *79*, 1562.
- <sup>512</sup> Berque, I.; Le Menez, P.; Razon, P.; Mahuteau, J.; Ferezou, J. P.; Pancrazi, A.; Ardisson, J.; Brion, J. D. *J. Org. Chem.* **1999**, *64*, 373.
- <sup>513</sup> Barrett, A. G. M.; Edmunds, J. J.; Hendrix, J. A.; Horita, K.; Parkinson, C. J. *J. Chem. Soc., Chem. Commun.* **1992**, 1238.
- <sup>514</sup> Meilert, K.; Brimble, M. A. *Org. Lett.* **2005**, *7*, 3497.
- <sup>515</sup> Smith, A. B., III; Friestad, G. K.; Barbosa, J.; Bertounesque, E.; Hull, K. G.; Iwashima, M.; Qiu, Y. P.; Salvatore, B. A.; Spoor, P. G.; Duan, J. J. W. *J. Am. Chem. Soc.* **1999**, *121*, 10468.
- <sup>516</sup> Vidya, R.; Eggen, M.; Georg, G. I.; Himes, R. H. *Bioorg. Med. Chem. Lett.* **2003**, *13*, 757.
- <sup>517</sup> Statsuk, A. V.; Liu, D.; Kozmin, S. A. *J. Am. Chem. Soc.* **2004**, *126*, 9546.
- <sup>518</sup> Schinzer, D.; Schulz, C.; Krug, O. *Synlett* **2004**, 2689.
- <sup>519</sup> Roush, W. R.; Ando, K.; Powers, D. B.; Halterman, R. L.; Palkowitz, A. D. *Tetrahedron Lett.* **1988**, *29*, 5579.
- <sup>520</sup> Giordano, A.; Spinella, A.; Sodano, G. *Tetrahedron: Asymmetry* **1999**, *10*, 1851.
- <sup>521</sup> Brinkmann, H.; Hoffmann, R. W. *Chem. Ber.* **1990**, *123*, 2395.
- <sup>522</sup> Nakata, M.; Ishiyama, T.; Akamatsu, S.; Hirose, Y.; Maruoka, H.; Suzuki, R.; Tatsuta, K. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 967.
- <sup>523</sup> Ireland, R. E.; Wipf, P.; Roper, T. D. *J. Org. Chem.* **1990**, *55*, 2284.
- <sup>524</sup> Roush, W. R.; Koyama, K.; Curtin, M. L.; Moriarty, K. J. *J. Am. Chem. Soc.* **1996**, *118*, 7502.
- <sup>525</sup> Niel, G.; Roux, F.; Maisonnasse, Y.; Maugras, I.; Poncet, J.; Jouin, P. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1275.
- <sup>526</sup> Guo-qiang, L.; Wei-chu, X. *Tetrahedron Lett.* **1993**, *34*, 5931.
- <sup>527</sup> Boons, G. J.; Brown, D. S.; Clase, J. A.; Lennon, I. C.; Ley, S. V. *Tetrahedron Lett.* **1994**, *35*, 319.
- <sup>528</sup> Boons, G. J.; Clase, J. A.; Lennon, I. C.; Ley, S. V.; Staunton, J. *Tetrahedron* **1995**, *51*, 5417.
- <sup>529</sup> Zampella, A.; Sorgente, M.; D'Auria, M. V. *Tetrahedron: Asymmetry* **2002**, *13*, 681.
- <sup>530</sup> Ley, S. V.; Brown, D. S.; Clase, J. A.; Fairbanks, A. J.; Lennon, I. C.; Osborn, H. M. I.; Stokes, E. S. E.; Wadsworth, D. J. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2259.
- <sup>531</sup> Francavilla, C.; Chen, W.; Kinder, J., F. R. *Org. Lett.* **2003**, *5*, 1233.
- <sup>532</sup> Nakata, M.; Ishiyama, T.; Hirose, Y.; Maruoka, H.; Tatsuta, K. *Tetrahedron Lett.* **1993**, *34*, 8439.

- 533 Scarlato, G. R.; DeMattei, J. A.; Chong, L. S.; Ogawa, A. K.; Lin, M. R.; Armstrong, R. W. *J. Org. Chem.* **1996**, *61*, 6139.
- 534 Czuba, I. R.; Zammit, S.; Rizzacasa, M. A. *Org. Biomol. Chem.* **2003**, *1*, 2044.
- 535 Czuba, I. R.; Rizzacasa, M. A. *Chem. Commun.* **1999**, 1419.
- 536 Zampella, A.; Bassarello, C.; Bifulco, G.; Gomez-Paloma, L.; D'Auria, M. V. *Eur. J. Org. Chem.* **2002**, 785.
- 537 Roush, W. R.; Adam, M. A.; Harris, D. J. *J. Org. Chem.* **1985**, *50*, 2000.
- 538 Brown, H. C.; Bhat, K. S.; Randad, R. S. *J. Org. Chem.* **1987**, *52*, 3701.
- 539 Hoffmann, R. W.; Brinkmann, H.; Frenking, G. *Chem. Ber.* **1990**, *123*, 2387.
- 540 Hoffmann, R. W.; Zeiss, H. J. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 218.
- 541 Roux, F.; Maugras, I.; Poncet, J.; Niel, G.; Jouin, P. *Tetrahedron* **1994**, *50*, 5345.
- 542 Terauchi, T.; Morita, M.; Kimijima, K.; Nakamura, Y.; Hayashi, G.; Tanaka, T.; Kanoh, N.; Nakata, M. *Tetrahedron Lett.* **2001**, *42*, 5505.
- 543 Kobayashi, Y.; Lee, J.; Tezuka, K.; Kishi, Y. *Org. Lett.* **1999**, *1*, 2177.
- 544 Monica, C. D.; Maulucci, N.; De Riccardis, F.; Izzo, I. *Tetrahedron: Asymmetry* **2003**, *14*, 3371.
- 545 Wuts, P. G.; Bigelow, S. S. *J. Org. Chem.* **1988**, *53*, 5023.
- 546 Moret, E.; Schlosser, M. *Tetrahedron Lett.* **1984**, *25*, 4491.
- 547 Lipomi, D. J.; Langille, N. F.; Panek, J. S. *Org. Lett.* **2004**, *6*, 3533.
- 548 Roush, W. R.; Brown, B. B.; Drozda, S. E. *Tetrahedron Lett.* **1988**, *29*, 3541.
- 549 Roush, W. R.; Brown, B. B. *J. Am. Chem. Soc.* **1993**, *115*, 2268.
- 550 Satoh, M.; Nomoto, Y.; Miyaura, N.; Suzuki, A. *Tetrahedron Lett.* **1989**, *30*, 3789.
- 551 Wang, X.; Porco, J., J. A. *Angew. Chem., Int. Ed.* **2005**, *44*, 3067.
- 552 Nakata, M.; Ishiyama, T.; Akamatsu, S.; Suzuki, R.; Tatsuta, K. *Synlett* **1994**, 601.
- 553 Chemler, S. R.; Roush, W. R. *J. Org. Chem.* **2003**, *68*, 1319.
- 554 Turk, J. A.; Visbal, G. S.; Lipton, M. A. *J. Org. Chem.* **2003**, *68*, 7841.
- 555 Burke, S. D.; Hong, J.; Lennox, J. R.; Mongin, A. P. *J. Org. Chem.* **1998**, *63*, 6952.
- 556 Cundy, D. J.; Donohue, A. C.; McCarthy, T. D. *J. Chem. Soc., Perkin Trans. 1* **1999**, 559.
- 557 Bauer, S. M.; Armstrong, R. W. *J. Am. Chem. Soc.* **1999**, *121*, 6355.
- 558 Cundy, D. J.; Donohue, A. C.; McCarthy, T. D. *Tetrahedron Lett.* **1998**, *39*, 5125.
- 559 Zheng, W. J.; DeMattei, J. A.; Wu, J. P.; Duan, J. J. W.; Cook, L. R.; Oinuma, H.; Kishi, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7946.
- 560 Knapp, S.; Dong, Y. *Tetrahedron Lett.* **1997**, *38*, 3813.
- 561 Ireland, R. E.; Armstrong, J. D.; Lebreton, J.; Meissner, R. S.; Rizzacasa, M. A. *J. Am. Chem. Soc.* **1993**, *115*, 7152.
- 562 Andrus, M. B.; Schreiber, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 10420.
- 563 Ireland, R. E.; Gleason, J. L.; Gegnas, L. D.; Highsmith, T. K. *J. Org. Chem.* **1996**, *61*, 6856.
- 564 White, J. D.; Toske, S. G.; Yakura, T. *Synlett* **1994**, 591.
- 565 Hermitage, S. A.; Roberts, S. M.; Watson, D. J. *Tetrahedron Lett.* **1998**, *39*, 3567.
- 566 Inoue, M.; Yamashita, S.; Tatami, A.; Miyazaki, K.; Hiram, M. *J. Org. Chem.* **2004**, *69*, 2797.
- 567 Uehara, H.; Oishi, T.; Inoue, M.; Shoji, M.; Nagumo, Y.; Kosaka, M.; Le Brazidec, J. Y.; Hiram, M. *Tetrahedron* **2002**, *58*, 6493.
- 568 Oishi, T.; Nagumo, Y.; Shoji, M.; Le Brazidec, J. Y.; Uehara, H.; Hiram, M. *Chem. Commun.* **1999**.
- 569 Tatami, A.; Inoue, M.; Uehara, H.; Hiram, M. *Tetrahedron Lett.* **2003**, *44*, 5229.
- 570 Inoue, M.; Hiram, M. *Synlett* **2004**, 577.
- 571 Jiang, X.; García-Fortanet, J. G.; De Brabander, J. K. *J. Am. Chem. Soc.* **2005**, *127*, 11254.
- 572 Smith, A. B., III; Adams, C. M.; Kozmin, S. A.; Paone, D. V. *J. Am. Chem. Soc.* **2001**, *123*, 5925.
- 573 Nicolaou, K. C.; Murphy, F.; Barluenga, S.; Ohshima, T.; Wei, H.; Xu, J.; Gray, D. L. F.; Baudoin, O. *J. Am. Chem. Soc.* **2000**, *122*, 3830.
- 574 Nicolaou, K. C.; Xu, J. Y.; Murphy, F.; Barluenga, S.; Baudoin, O.; Wei, H. X.; Gray, D. L. F.; Ohshima, T. *Angew. Chem., Int. Ed.* **1999**, *38*, 2447.
- 575 Paterson, I.; Cumming, J. G.; Smith, J. D.; Ward, R. A.; Yeung, K. S. *Tetrahedron Lett.* **1994**, *35*, 3405.

- 576 Paterson, I.; Ward, R. A.; Smith, J. D.; Cumming, J. G.; Yeung, K. S. *Tetrahedron* **1995**, *51*, 9437.
- 577 Yamamoto, Y.; Yatagai, H.; Maruyama, K. *J. Am. Chem. Soc.* **1981**, *103*, 1969.
- 578 Oikawa, M.; Ueno, T.; Oikawa, H.; Ichihara, A. *J. Org. Chem.* **1995**, *60*, 5048.
- 579 Oikawa, M.; Ueno, T.; Oikawa, H.; Ichihara, A. *J. Synth. Org. Chem. Jpn.* **1995**, *53*, 1123.
- 580 Oikawa, M.; Oikawa, H.; Ichihara, A. *Tetrahedron Lett.* **1993**, *34*, 4797.
- 581 Hoffmann, R. W.; Helbig, W. *Chem. Ber.* **1981**, *114*, 2802.
- 582 Giordano, A.; Della Monica, C.; Landi, F.; Spinella, A.; Sodano, G. *Tetrahedron Lett.* **2000**, *41*, 3979.
- 583 Zampella, A.; D'Auria, M. V. *Tetrahedron: Asymmetry* **2001**, *12*, 1543.
- 584 Roush, W. R.; Hertel, L.; Schnaderbeck, M. J.; Yakelis, N. A. *Tetrahedron Lett.* **2002**, *43*, 4885.
- 585 White, J. D.; Hong, J.; Robarge, L. A. *Tetrahedron Lett.* **1998**, *39*, 8779.
- 586 Feutrill, J. T.; Holloway, G. A.; Hilli, F.; Hugel, H. M.; Rizzacasa, M. A. *Tetrahedron Lett.* **2000**, *41*, 8569.
- 587 Dhokte, U. P.; Khau, V. V.; Hutchison, D. R.; Martinelli, M. J. *Tetrahedron Lett.* **1998**, *39*, 8771.
- 588 Eggen, M.; Mossman, C. J.; Buck, S. B.; Nair, S. K.; Bhat, L.; Ali, S. M.; Reiff, E. A.; Boge, T. C.; Georg, G. I. *J. Org. Chem.* **2000**, *65*, 7792.
- 589 Eggen, M. J.; Georg, G. I. *Bioorg. Med. Chem. Lett.* **1998**, *8*, 3177.
- 590 Andrus, M. B.; Argade, A. B. *Tetrahedron Lett.* **1996**, *37*, 5049.
- 591 McRae, K. J.; Rizzacasa, M. A. *J. Org. Chem.* **1997**, *62*, 1196.
- 592 Paterson, I.; Ashton, K.; Britton, R.; Knust, H. *Org. Lett.* **2003**, *5*, 1963.
- 593 Paterson, I.; Britton, R.; Delgado, O.; Meyer, A.; Poullennec, K. G. *Angew. Chem., Int. Ed.* **2004**, *43*, 4629.
- 594 Cuzzupe, A. N.; Hutton, C. A.; Lilly, M. J.; Mann, R. K.; McRae, K. J.; Zammit, S. C.; Rizzacasa, M. A. *J. Org. Chem.* **2001**, *66*, 2382.
- 595 Nicolaou, K. C.; Bertinato, P.; Piscopio, A. D.; Chakraborty, T. K.; Minowa, N. *J. Chem. Soc., Chem. Commun.* **1993**, 619.
- 596 Cossy, J.; Bauer, D.; Bellosta, V. *Tetrahedron* **2002**, *58*, 5909.
- 597 Yu, W. S.; Zhang, Y.; Jin, Z. D. *Org. Lett.* **2001**, *3*, 1447.
- 598 Yamamoto, Y.; Maruyama, K.; Komatsu, T.; Ito, W. *J. Org. Chem.* **1986**, *51*, 886.
- 599 White, J. D.; Wang, G. Q.; Quaranta, L. *Org. Lett.* **2003**, *5*, 4109.
- 600 Hermitage, S. A.; Murphy, A.; Nielsen, P.; Roberts, S. M. *Tetrahedron* **1998**, *54*, 13185.
- 601 Zweifel, G.; Shoup, T. M. *J. Am. Chem. Soc.* **1988**, *110*, 5578.
- 602 Coe, J. W.; Roush, W. R. *J. Org. Chem.* **1989**, *54*, 915.
- 603 Liu, B.; Zhou, W. *Tetrahedron Lett.* **2003**, *44*, 4933.
- 604 Jyojima, T.; Katohno, M.; Miyamoto, N.; Nakata, M.; Matsumura, S.; Toshima, K. *Tetrahedron Lett.* **1998**, *39*, 6003.
- 605 Merifield, E.; Thomas, E. J. *J. Chem. Soc., Perkin Trans. 1* **1999**, 3269.
- 606 Merifield, E.; Thomas, E. J. *J. Chem. Soc., Chem. Commun.* **1990**, 464.
- 607 Menager, E.; Merifield, E.; Smallridge, M.; Thomas, E. J. *Tetrahedron* **1997**, *53*, 9377.
- 608 Khandekar, G.; Robinson, G. C.; Stacey, N. A.; Steel, P. G.; Thomas, E. J.; Vather, S. J. *J. Chem. Soc., Chem. Commun.* **1987**, 877.
- 609 Kang, S. H.; Jeong, J. W. *Tetrahedron Lett.* **2002**, *43*, 3613.
- 610 Paterson, I.; Yeung, K. S.; Watson, C.; Ward, R. A.; Wallace, P. A. *Tetrahedron* **1998**, *54*, 11935.
- 611 Zampella, A.; D'Auria, M. V. *Tetrahedron: Asymmetry* **2002**, *13*, 1237.
- 612 Cossy, J.; Bauer, D.; Bellosta, V. *Synlett* **2002**, 715.
- 613 Toshima, H.; Ichihara, A. *Biosci. Biotechnol. Biochem.* **1998**, *62*, 599.
- 614 Minguez, J. M.; Kim, S. Y.; Giuliano, K. A.; Balachandran, R.; Madiraju, C.; Day, B. W.; Curran, D. P. *Bioorg. Med. Chem.* **2003**, *11*, 3335.
- 615 Archibald, S. C.; Barden, D. J.; Bazin, J. F. Y.; Fleming, I.; Foster, C. F.; Mandal, A. K.; Parker, D.; Takaki, K.; Ware, A. C.; Williams, A. R. B.; Zwicky, A. B. *Org. Biomol. Chem.* **2004**, *2*, 1051.
- 616 Stenkamp, D.; Hoffmann, R. W.; Göttlich, R. *Eur. J. Org. Chem.* **1999**, 2929.



- <sup>617</sup> Scheidt, K. A.; Bannister, T. D.; Tasaka, A.; Wendt, M. D.; Savall, B. M.; Fegley, G. J.; Roush, W. R. *J. Am. Chem. Soc.* **2002**, *124*, 6981.
- <sup>618</sup> Spino, C.; Allan, M. *Can. J. Chem.* **2004**, *82*, 177.
- <sup>619</sup> White, J. D.; Tiller, T.; Ohba, Y.; Porter, W. J.; Jackson, R. W.; Wang, S.; Hanselmann, R. *Chem. Commun.* **1998**, 79.
- <sup>620</sup> Williams, D. R.; Rojas, C. M.; Bogen, S. L. *J. Org. Chem.* **1999**, *64*, 736.
- <sup>621</sup> Smith, A. B., III; Zheng, J. *Tetrahedron* **2002**, *58*, 6455.
- <sup>622</sup> Smith, A. B., III; Zheng, J. *Synlett* **2001**, 1019.
- <sup>623</sup> Ooi, H.; Ishibashi, N.; Iwabuchi, Y.; Ishihara, J.; Hatakeyama, S. *J. Org. Chem.* **2004**, *69*, 7765.
- <sup>624</sup> Kang, S. H.; Kim, C. M. *Synlett* **1996**, 515.
- <sup>625</sup> Roush, W. R.; Bannister, T. D. *Tetrahedron Lett.* **1992**, *33*, 3587.
- <sup>626</sup> Roush, W. R.; Bannister, T. D.; Wendt, M. D.; Jablonowski, J. A.; Scheidt, K. A. *J. Org. Chem.* **2002**, *67*, 4275.
- <sup>627</sup> Kende, A. S.; Koch, K.; Dorey, G.; Kaldor, I.; Liu, K. *J. Am. Chem. Soc.* **1993**, *115*, 9842.
- <sup>628</sup> Andersen, M. W.; Hildebrandt, B.; Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 97.
- <sup>629</sup> Oikawa, H.; Yoneta, Y.; Ueno, T.; Oikawa, M.; Wakayama, T.; Ichihara, A. *Tetrahedron Lett.* **1997**, *38*, 7897.
- <sup>630</sup> Oikawa, H. *Curr. Med. Chem.* **2002**, *9*, 2033.
- <sup>631</sup> Paterson, I.; Anderson, E. A.; Dalby, S. M.; Loiseleur, O. *Org. Lett.* **2005**, *7*, 4121.
- <sup>632</sup> Fisher, M. J.; Myers, C. D.; Joglar, J.; Chen, S. H.; Danishefsky, S. J. *J. Org. Chem.* **1991**, *56*, 5826.
- <sup>633</sup> Labrecque, D.; Charron, S.; Rej, R.; Blais, C.; Lamothe, S. *Tetrahedron Lett.* **2001**, *42*, 2645.
- <sup>634</sup> Barrett, A. G. M.; Lebold, S. A. *J. Org. Chem.* **1991**, *56*, 4875.
- <sup>635</sup> Barrett, A. G. M.; Lebold, S. A. *J. Org. Chem.* **1990**, *55*, 5818.
- <sup>636</sup> Sebelius, S.; Wallner, O. A.; Szabó, K. *J. Org. Lett.* **2003**, *5*, 3065.
- <sup>637</sup> Dineen, T. A.; Roush, W. R. *Org. Lett.* **2003**, *5*, 4725.
- <sup>638</sup> Maurer, K. W.; Armstrong, R. W. *J. Org. Chem.* **1996**, *61*, 3106.
- <sup>639</sup> Lin, G. Q.; Xu, W. C. *Tetrahedron* **1996**, *52*, 5907.
- <sup>640</sup> Kang, S. H.; Jun, H. S.; Youn, J. H. *Synlett* **1998**, 1045.
- <sup>641</sup> Zampella, A.; Sepe, V.; D'Orsi, R.; D'Auria, M. V. *Lett. Org. Chem.* **2004**, 308.
- <sup>642</sup> Hori, K.; Kazuno, H.; Nomura, K.; Yoshii, E. *Tetrahedron Lett.* **1993**, *34*, 2183.
- <sup>643</sup> Harada, T.; Kagamihara, Y.; Tanaka, S.; Sakamoto, K.; Oku, A. *J. Org. Chem.* **1992**, *57*, 1637.
- <sup>644</sup> White, J. D.; Johnston, A. T. *J. Org. Chem.* **1994**, *59*, 3347.
- <sup>645</sup> White, J. D.; Johnston, A. T. *J. Org. Chem.* **1990**, *55*, 5938.
- <sup>646</sup> Hoffmann, R. W.; Göttlich, R.; Schopfer, U. *Eur. J. Org. Chem.* **2001**, 1865.
- <sup>647</sup> Chen, S. H.; Horvath, R. F.; Joglar, J.; Fisher, M. J.; Danishefsky, S. J. *J. Org. Chem.* **1991**, *56*, 5834.
- <sup>648</sup> May, S. A.; Grieco, P. A. *Chem. Commun.* **1998**, 1597.
- <sup>649</sup> Tatsuta, K.; Ishiyama, T.; Tajima, S.; Koguchi, Y.; Gunji, H. *Tetrahedron Lett.* **1990**, *31*, 709.
- <sup>650</sup> Andrus, M. B.; Turner, T. M.; Sauna, Z. E.; Ambudkar, S. V. *J. Org. Chem.* **2000**, *65*, 4973.
- <sup>651</sup> Hu, H. S.; Jayaraman, S.; Oehlschage, A. C. *J. Org. Chem.* **1998**, *63*, 8843.
- <sup>652</sup> Roush, W. R.; Lane, G. C. *Org. Lett.* **1999**, *1*, 95.
- <sup>653</sup> Smith, A. B., III; Adams, C. M.; Barbosa, S. A. L.; Degnan, A. P. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 12042.
- <sup>654</sup> Roush, W. R.; Coffey, D. S.; Madar, D.; Palkowitz, A. D. *J. Braz. Chem. Soc.* **1996**, *7*, 327.
- <sup>655</sup> Sengoku, T.; Arimoto, H.; Uemura, D. *Chem. Commun.* **2004**, 1220.
- <sup>656</sup> Andrus, M. B.; Lepore, S. D.; Turner, T. M. *J. Am. Chem. Soc.* **1997**, *119*, 12159.
- <sup>657</sup> Akita, H.; Yamada, H.; Matsukura, H.; Nakata, T.; Oishi, T. *Tetrahedron Lett.* **1990**, *31*, 1735.
- <sup>658</sup> Oishi, T.; Akita, H. *J. Synth. Org. Chem. Jpn.* **1991**, *49*, 657.
- <sup>659</sup> Zeng, X.; Zeng, F.; Negishi, E. *Org. Lett.* **2004**, *6*, 3245.
- <sup>660</sup> Andrus, M. B.; Lepore, S. D. *J. Am. Chem. Soc.* **1997**, *119*, 2327.
- <sup>661</sup> Nagamitsu, T.; Sunazuka, T.; Tanaka, H.; Omura, S.; Sprengeler, P. A.; Smith, A. B., III *J. Am. Chem. Soc.* **1996**, *118*, 3584.

- <sup>662</sup> Sunazuka, T.; Nagamitsu, T.; Matsuzaki, K.; Tanaka, H.; Omura, S.; Smith, A. B., III *J. Am. Chem. Soc.* **1993**, *115*, 5302.
- <sup>663</sup> Kohyama, N.; Yamamoto, Y. *Synlett* **2001**, 694.
- <sup>664</sup> Danishefsky, S. J.; Armistead, D. M.; Wincott, F. E.; Selnick, H. G.; Hungate, R. *J. Am. Chem. Soc.* **1989**, *111*, 2967.
- <sup>665</sup> Danishefsky, S. J.; Armistead, D. M.; Wincott, F. E.; Selnick, H. G.; Hungate, R. *J. Am. Chem. Soc.* **1987**, *109*, 8117.
- <sup>666</sup> Liu, B.; Zhou, W. S. *Tetrahedron* **2003**, *59*, 3379.
- <sup>667</sup> Liu, B.; Zhou, W. *Tetrahedron Lett.* **2002**, *43*, 4187.
- <sup>668</sup> Hoffmann, R. W.; Landmann, B. *Tetrahedron Lett.* **1983**, *24*, 3209.
- <sup>669</sup> Hoffmann, R. W.; Landmann, B. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 437.
- <sup>670</sup> Mandal, A. K.; Schneekloth, J., J. S.; Crews, C. M. *Org. Lett.* **2005**, *7*, 3645.
- <sup>671</sup> Yang, Z.; He, Y.; Vourloumis, D.; Vallberg, H.; Nicolaou, K. C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 166.
- <sup>672</sup> Schlapbach, A.; Hoffmann, R. W. *Eur. J. Org. Chem.* **2001**, 323.
- <sup>673</sup> Hoffmann, R. W.; Schlapbach, A. *Liebigs Ann. Chem.* **1991**, 1203.
- <sup>674</sup> Midland, M. M.; Preston, S. B. *J. Am. Chem. Soc.* **1982**, *104*, 2330.
- <sup>675</sup> Shimizu, M.; Kitagawa, H.; Kurahashi, T.; Hiyama, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 4283.
- <sup>676</sup> Andersen, M. W.; Hildebrandt, B.; Koster, G.; Hoffmann, R. W. *Chem. Ber.* **1989**, *122*, 1777.
- <sup>677</sup> Zheng, B.; Srebnik, M. *J. Org. Chem.* **1995**, *60*, 486.
- <sup>678</sup> Hoffmann, R. W.; Dahmann, G.; Andersen, M. W. *Synthesis* **1994**, 629.
- <sup>679</sup> Hoffmann, R. W.; Dahmann, G. *Tetrahedron Lett.* **1993**, *34*, 1115.
- <sup>680</sup> Lombardo, M.; Morganti, S.; Trombini, C. *J. Org. Chem.* **2000**, *65*, 8767.
- <sup>681</sup> Hoffmann, R. W.; Stürmer, R. *Chem. Ber.* **1994**, *127*, 2511.
- <sup>682</sup> Yamamoto, Y.; Yatagai, H.; Maruyama, K. *J. Am. Chem. Soc.* **1981**, *103*, 3229.
- <sup>683</sup> Andemichael, Y. W.; Wang, K. K. *J. Org. Chem.* **1992**, *57*, 796.
- <sup>684</sup> Wang, K. K.; Gu, G.; Liu, C. *J. Am. Chem. Soc.* **1990**, *112*, 4424.
- <sup>685</sup> Yamaguchi, M.; Mukaiyama, T. *Chem. Lett.* **1980**, 993.
- <sup>686</sup> Patron, A. P.; Richter, P. K.; Tomaszewski, M. J.; Miller, R. A.; Nicolaou, K. C. *J. Chem. Soc., Chem. Commun.* **1994**, 1147.
- <sup>687</sup> Hoffmann, R. W.; Rolle, U.; Göttlich, R. *Liebigs Ann. Chem.* **1996**, 1717.
- <sup>688</sup> Stürmer, R.; Ritter, K.; Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 101.
- <sup>689</sup> Tsai, D. J. S.; Matteson, D. S. *Organometallics* **1983**, *2*, 236.
- <sup>690</sup> Carosi, L.; Lachance, H.; Hall, D. G. *Tetrahedron Lett.* **2005**, *46*, 8981.
- <sup>691</sup> Beckmann, E.; Desai, V.; Hoppe, D. *Synlett* **2004**, 2275.
- <sup>692</sup> Yamamoto, Y.; Saito, Y.; Maruyama, K. *J. Org. Chem.* **1983**, *48*, 5408.
- <sup>693</sup> Hoffmann, R. W.; Ladner, W.; Ditrich, K. *Liebigs Ann. Chem.* **1989**, 883.
- <sup>694</sup> Hoffmann, R. W.; Rolle, U. *Tetrahedron Lett.* **1994**, *35*, 4751.
- <sup>695</sup> Hoffmann, R. W.; Haeberlin, E.; Rohde, T. *Synthesis* **2002**, 207.
- <sup>696</sup> Stürmer, R.; Hoffmann, R. W. *Chem. Ber.* **1994**, *127*, 2519.
- <sup>697</sup> Brown, H. C.; Jadhav, P. K.; Perumal, P. T. *Tetrahedron Lett.* **1984**, *25*, 5111.
- <sup>698</sup> Bubnov, Y. N.; Etinger, M. Y. *Tetrahedron Lett.* **1985**, *26*, 2797.
- <sup>699</sup> Brown, H. C.; Randad, R. S. *Tetrahedron* **1990**, *46*, 4463.
- <sup>700</sup> Brown, H. C.; Randad, R. S. *Tetrahedron Lett.* **1990**, *31*, 455.
- <sup>701</sup> Salunkhe, A. M.; Ramachandran, P. V.; Brown, H. C. *Tetrahedron Lett.* **1999**, *40*, 1433.
- <sup>702</sup> Gurskii, M. E.; Golovin, S. B.; Ignatenko, A. V.; Bubnov, Y. N. *Russ. Chem. Bull.* **1993**, *42*, 139.
- <sup>703</sup> Chataigner, I.; Lebreton, J.; Zammattio, F.; Villieras, J. *Tetrahedron Lett.* **1997**, *38*, 3719.
- <sup>704</sup> van der Heide, T. A. J.; van der Baan, J. L.; Bijpost, E. A.; de Kanter, F. J. J.; Bickelhaupt, F.; Klumpp, G. W. *Tetrahedron Lett.* **1993**, *34*, 4655.
- <sup>705</sup> Barrett, A. G. M.; Braddock, D. C.; de Koning, P. D. *Chem. Commun.* **1999**, 459.
- <sup>706</sup> Gurskii, M. E.; Golovin, S. B.; Bubnov, Y. N. *Russ. Chem. Bull.* **1990**, *39*, 433.
- <sup>707</sup> Barrett, A. G. M.; Wan, P. W. H. *J. Org. Chem.* **1996**, *61*, 8667.
- <sup>708</sup> Williams, D. R.; Meyer, K. G.; Shamim, K.; Patnaik, S. *Can. J. Chem.* **2004**, *82*, 120.

- 709 Hara, S.; Suzuki, A. *Tetrahedron Lett.* **1991**, 32, 6749.
- 710 Williams, D. R.; Brooks, D. A.; Meyer, K. G.; Clark, M. P. *Tetrahedron Lett.* **1998**, 39, 7251.
- 711 Yamamoto, Y.; Hara, S.; Suzuki, A. *Synth. Commun.* **1997**, 27, 1029.
- 712 Hara, S.; Yamamoto, Y.; Fujita, A.; Suzuki, A. *Synlett* **1994**, 639.
- 713 Draillard, K.; Lebreton, J.; Villieras, J. *Tetrahedron: Asymmetry* **1999**, 10, 4281.
- 714 Brzezinski, L. J.; Leahy, J. W. *Tetrahedron Lett.* **1998**, 39, 2039.
- 715 Williams, D. R.; Clark, M. P.; Berliner, M. A. *Tetrahedron Lett.* **1999**, 40, 2287.
- 716 Williams, D. R.; Kiryanov, A. A.; Emde, U.; Clark, M. P.; Berliner, M. A.; Reeves, J. T. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, 101, 12058.
- 717 Williams, D. R.; Kiryanov, A. A.; Emde, U.; Clark, M. P.; Berliner, M. A.; Reeves, J. T. *Angew. Chem., Int. Ed.* **2003**, 42, 1258.
- 718 Ishiyama, T.; Kitano, T.; Miyaura, N. *Tetrahedron Lett.* **1998**, 39, 2357.
- 719 Goujon, J. Y.; Zammattio, F.; Chretien, J. M.; Beaudet, I. *Tetrahedron* **2004**, 60, 4037.
- 720 Williams, D. R.; Clark, M. P.; Emde, U.; Berliner, M. A. *Org. Lett.* **2000**, 2, 3023.
- 721 Williams, D. R.; Meyer, K. G. *J. Am. Chem. Soc.* **2001**, 123, 765.
- 722 Zhai, H. B.; Luo, S. J.; Ye, C. F.; Ma, Y. X. *J. Org. Chem.* **2003**, 68, 8268.
- 723 Williams, D. R.; Patnaik, S.; Plummer, S. V. *Org. Lett.* **2003**, 5, 5035.
- 724 Williams, D. R.; Brooks, D. A.; Berliner, M. A. *J. Am. Chem. Soc.* **1999**, 121, 4924.
- 725 Corey, E. J.; Huang, H. C. *Tetrahedron Lett.* **1989**, 30, 5235.
- 726 Kim, S.; Sutton, S. C.; Guo, C.; LaCour, T. G.; Fuchs, P. L. *J. Am. Chem. Soc.* **1999**, 121, 2056.
- 727 Kim, S. K.; Sutton, S. C.; Fuchs, P. L. *Tetrahedron Lett.* **1995**, 36, 2427.
- 728 Thaper, R. K.; Zykov, A. Y.; Bubnov, Y. N.; Reshetova, I. G.; Kamernitsky, A. V. *Synth. Commun.* **1993**, 23, 939.
- 729 Jernelius, J. A.; Schrock, R. R.; Hoveyda, A. H. *Tetrahedron* **2004**, 60, 7345.
- 730 Barrett, A. G. M.; Seefeld, M. A. *Tetrahedron* **1993**, 49, 7857.
- 731 Barrett, A. G. M.; Seefeld, M. A. *J. Chem. Soc., Chem. Commun.* **1993**, 339.
- 732 Gurskii, M. E.; Geiderickh, A. V.; Ignatenko, A. V.; Bubnov, Y. N. *Russ. Chem. Bull.* **1993**, 42, 144.
- 733 Narla, G.; Brown, H. C. *Tetrahedron Lett.* **1997**, 38, 219.
- 734 Roush, W. R.; Pinchuk, A. N.; Micalizio, G. C. *Tetrahedron Lett.* **2000**, 41, 9413.
- 735 Wang, K. K.; Liu, C. *J. Org. Chem.* **1986**, 51, 4733.
- 736 Wang, K. K.; Liu, C.; Gu, Y. G.; Burnett, F. N.; Sattsangi, P. D. *J. Org. Chem.* **1991**, 56, 1914.
- 737 Hoffmann, R. W.; Kemper, B. *Tetrahedron Lett.* **1980**, 21, 4883.
- 738 Brown, H. C.; Phadke, A. S. *Synlett* **1993**, 927.
- 739 Hoffmann, R. W.; Metternich, R. *Liebigs Ann. Chem.* **1985**, 2390.
- 740 Yamamoto, Y.; Hara, S.; Suzuki, A. *Synlett* **1996**, 883.
- 741 Soundararajan, R.; Li, G. S.; Brown, H. C. *J. Org. Chem.* **1996**, 61, 100.
- 742 Barrett, A. G. M.; Beall, J. C.; Braddock, D. C.; Flack, K.; Gibson, V. C.; Salter, M. M. *J. Org. Chem.* **2000**, 65, 6508.
- 743 Micalizio, G. C.; Roush, W. R. *Org. Lett.* **2000**, 2, 461.
- 744 Soundararajan, R.; Li, G.; Brown, H. C. *Tetrahedron Lett.* **1995**, 36, 2441.
- 745 Coleman, R. S. *Synlett* **1998**, 1031.
- 746 Barrett, A. G. M.; Seefeld, M. A.; White, A. J. P.; Williams, D. J. *J. Org. Chem.* **1996**, 61, 2677.
- 747 Ganesh, P.; Nicholas, K. M. *J. Org. Chem.* **1997**, 62, 1737.
- 748 Wang, X.; Porco, J. A. *J. Am. Chem. Soc.* **2003**, 125, 6040.
- 749 Schinzer, D.; Limberg, A.; Bohm, O. M. *Chem. Eur. J.* **1996**, 2, 1477.
- 750 Wuts, P. G. M.; Bigelow, S. S. *J. Org. Chem.* **1983**, 48, 3489.
- 751 Gaddoni, L.; Lombardo, M.; Trombini, C. *Tetrahedron Lett.* **1998**, 39, 7571.
- 752 Barrett, A. G. M.; Malecha, J. W. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1901.
- 753 Hertweck, C.; Boland, W. *J. Org. Chem.* **1999**, 64, 4426.
- 754 Hertweck, C.; Goerls, H.; Boland, W. *Chem. Commun.* **1998**, 1955.
- 755 Roush, W. R.; Michaelides, M. R. *Tetrahedron Lett.* **1986**, 27, 3353.
- 756 Hu, S. J.; Jayaraman, S.; Oehlschlager, A. C. *J. Org. Chem.* **1998**, 63, 8843.
- 757 Hunt, J. A.; Roush, W. R. *Tetrahedron Lett.* **1995**, 36, 501.

- <sup>758</sup> Roush, W. R.; Grover, P. T.; Marron, T. G. In *Current Topics in the Chemistry of Boron*, Proceedings of the Eighth International Meeting, Knoxville, Tennessee, 1993; Kabalka, G. W., Ed.; Royal Society of Chemistry: Cambridge, U.K., 1994.
- <sup>759</sup> Roush, W. R.; Follows, B. C. *Tetrahedron Lett.* **1994**, *35*, 4935.
- <sup>760</sup> Heo, J. N.; Micalizio, G. C.; Roush, W. R. *Org. Lett.* **2003**, *5*, 1693.
- <sup>761</sup> Chang, K. J.; Rayabarapu, D. K.; Yang, F. Y.; Cheng, C. H. *J. Am. Chem. Soc.* **2005**, *127*, 126.
- <sup>762</sup> Jayaraman, S.; Hu, S.; Oehlschlager, A. C. *Tetrahedron Lett.* **1995**, *36*, 4765.
- <sup>763</sup> Micalizio, G. C.; Pinchuk, A. N.; Roush, W. R. *J. Org. Chem.* **2000**, *65*, 8730.
- <sup>764</sup> Barrett, A. G. M.; Bennett, A. J.; Menzer, S.; Smith, M. L.; White, A. J. P.; Williams, D. J. *J. Org. Chem.* **1999**, *64*, 162.
- <sup>765</sup> Barluenga, S.; Lopez, P.; Moulin, E.; Winssinger, N. *Angew. Chem., Int. Ed.* **2004**, *43*, 3467.
- <sup>766</sup> Roush, W. R.; Michaelides, M. R.; Tai, D. F.; Chong, W. K. M. *J. Am. Chem. Soc.* **1987**, *109*, 7575.
- <sup>767</sup> Roush, W. R.; Michaelides, M. R.; Tai, D. F.; Lesur, B. M.; Chong, W. K. M.; Harris, D. J. *J. Am. Chem. Soc.* **1989**, *111*, 2984.
- <sup>768</sup> Roush, W. R.; Harris, D. J.; Lesur, B. M. *Tetrahedron Lett.* **1983**, *24*, 2227.
- <sup>769</sup> Smith, A. L.; Pitsinos, E. N.; Hwang, C. K.; Mizuno, Y.; Saimoto, H.; Scarlato, G. R.; Suzuki, T.; Nicolaou, K. C. *J. Am. Chem. Soc.* **1993**, *115*, 7612.
- <sup>770</sup> Smith, A. L.; Hwang, C. K.; Pitsinos, E.; Scarlato, G. R.; Nicolaou, K. C. *J. Am. Chem. Soc.* **1992**, *114*, 3134.
- <sup>771</sup> Burgess, K.; Henderson, I. *Tetrahedron Lett.* **1990**, *31*, 6949.
- <sup>772</sup> Sato, M.; Yamamoto, Y.; Hara, S.; Suzuki, A. *Tetrahedron Lett.* **1993**, *34*, 7071.
- <sup>773</sup> Duan, J. J. W.; Smith, A. B., III *J. Org. Chem.* **1993**, *58*, 3703.
- <sup>774</sup> Heo, J. N.; Holson, E. B.; Roush, W. R. *Org. Lett.* **2003**, *5*, 1697.
- <sup>775</sup> Burgess, K.; Chaplin, D. A.; Henderson, I.; Pan, Y. T.; Elbein, A. D. *J. Org. Chem.* **1992**, *57*, 1103.
- <sup>776</sup> Jadhav, P. K.; Woemer, F. J. *Tetrahedron Lett.* **1994**, *35*, 8973.
- <sup>777</sup> Gu, Y. G.; Wang, K. K. *Tetrahedron Lett.* **1991**, *32*, 3029.
- <sup>778</sup> Sutherland, D. P.; Armstrong, R. W. *Tetrahedron Lett.* **1993**, *34*, 4897.
- <sup>779</sup> Kim, J. D.; Kim, I. S.; Hua, J. C.; Zee, O. P.; Jung, Y. H. *Tetrahedron Lett.* **2005**, *46*, 1079.
- <sup>780</sup> Moriya, T.; Suzuki, A.; Miyaura, N. *Tetrahedron Lett.* **1995**, *36*, 1887.
- <sup>781</sup> Suginome, M.; Nakamura, H.; Matsuda, T.; Ito, Y. *J. Am. Chem. Soc.* **1998**, *120*, 4248.
- <sup>782</sup> Ramachandran, P. V.; Pratihari, D.; Biswas, D.; Srivastava, A.; Reddy, M. V. R. *Org. Lett.* **2004**, *6*, 481.
- <sup>783</sup> Yamamoto, Y.; Yatagai, H.; Maruyama, K. *J. Chem. Soc., Chem. Commun.* **1980**, 1072.
- <sup>784</sup> Kabalka, G. W.; Venkataiah, B.; Dong, G. *J. Org. Chem.* **2004**, *69*, 5807.
- <sup>785</sup> Kabalka, G. W.; Venkataiah, B.; Dong, G. *Tetrahedron Lett.* **2005**, *46*, 4209.
- <sup>786</sup> Coleman, R. S.; Gurralla, S. R.; Mitra, S.; Rao, A. *J. Org. Chem.* **2005**, *70*, 8932.
- <sup>787</sup> Coleman, R. S.; Gurralla, S. R. *Org. Lett.* **2005**, *7*, 1849.
- <sup>788</sup> Micalizio, G. C.; Roush, W. R. *Org. Lett.* **2001**, *3*, 1949.
- <sup>789</sup> Hertweck, C.; Boland, W. *Tetrahedron* **1997**, *53*, 14651.
- <sup>790</sup> Hertweck, C.; Boland, W. *J. Org. Chem.* **2000**, *65*, 2458.
- <sup>791</sup> Suginome, M.; Yamamoto, Y.; Fujii, K.; Ito, Y. *J. Am. Chem. Soc.* **1995**, *117*, 9608.
- <sup>792</sup> Jadhav, P. K.; Man, H. W. *Tetrahedron Lett.* **1996**, *37*, 1153.
- <sup>793</sup> Taylor, R. E.; Hearn, B. R.; Ciavari, J. P. *Org. Lett.* **2002**, *4*, 2953.
- <sup>794</sup> Nakata, M.; Osumi, T.; Ueno, A.; Kimura, T.; Tamai, T.; Tatsuta, K. *Tetrahedron Lett.* **1991**, *32*, 6015.
- <sup>795</sup> Nakata, M.; Osumi, T.; Ueno, A.; Kimura, T.; Tamai, T.; Tatsuta, K. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2974.
- <sup>796</sup> Zhang, Q.; Lu, H.; Richard, C.; Curran, D. P. *J. Am. Chem. Soc.* **2004**, *126*, 36.
- <sup>797</sup> Kabalka, G. W.; Venkataiah, B. *Tetrahedron Lett.* **2005**, *46*, 7325.
- <sup>798</sup> Carter, K. D.; Panek, J. S. *Org. Lett.* **2004**, *6*, 55.
- <sup>799</sup> Harried, S. S.; Lee, C. P.; Yang, G.; Lee, T. I. H.; Myles, D. C. *J. Org. Chem.* **2003**, *68*, 6646.
- <sup>800</sup> Harried, S. S.; Yang, G.; Strawn, M. A.; Myles, D. C. *J. Org. Chem.* **1997**, *62*, 6098.

- 801 Zakarian, A.; Batch, A.; Holton, R. A. *J. Am. Chem. Soc.* **2003**, *125*, 7822.  
802 Carrié, D.; Carboni, B.; Vaultier, M. *Tetrahedron Lett.* **1995**, *36*, 8209.  
803 Favre, E.; Gaudemar, M. *J. Organomet. Chem.* **1975**, *92*, 17.  
804 Kulkarni, S. V.; Brown, H. C. *Tetrahedron Lett.* **1996**, *37*, 4125.  
805 Brown, H. C.; Khire, U. R.; Narla, G. *J. Org. Chem.* **1995**, *60*, 8130.  
806 Hernandez, E.; Soderquist, J. A. *Org. Lett.* **2005**, *7*, 5397.  
807 Zweifel, G.; Backlund, S. J.; Leung, T. *J. Am. Chem. Soc.* **1978**, *100*, 5561.  
808 Brown, H. C.; Khire, U. R.; Racherla, U. S. *Tetrahedron Lett.* **1993**, *34*, 15.  
809 Brown, H. C.; Khire, U. R.; Narla, G.; Racherla, U. S. *J. Org. Chem.* **1995**, *60*, 544.  
810 Favre, E.; Gaudemar, M. *J. Organomet. Chem.* **1974**, *76*, 297.  
811 Wang, K. K.; Nikam, S. S.; Ho, C. D. *J. Org. Chem.* **1983**, *48*, 5376.  
812 Maddess, M. L.; Lautens, M. *Org. Lett.* **2005**, *7*, 3557.  
813 Ikeda, N.; Arai, I.; Yamamoto, H. *J. Am. Chem. Soc.* **1986**, *108*, 483.  
814 Favre, E.; Gaudemar, M. *J. Organomet. Chem.* **1974**, *76*, 305.  
815 Wang, K. K.; Liu, C. *J. Org. Chem.* **1985**, *50*, 2578.  
816 Corey, E. J.; Jones, G. B. *Tetrahedron Lett.* **1991**, *32*, 5713.  
817 Matsumoto, Y.; Naito, M.; Uozumi, Y.; Hayashi, T. *J. Chem. Soc., Chem. Commun.* **1993**, 1468.  
818 Hilt, G.; Luers, S.; Smolko, K. I. *Org. Lett.* **2005**, *7*, 251.  
819 Herberich, G. E.; Englert, U.; Wang, S. *Chem. Ber.* **1993**, *126*, 297.  
820 Brown, H. C.; Bhat, K. S.; Jadhav, P. K. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2633.  
821 Lallemand, J. Y.; Six, Y.; Ricard, L. *Eur. J. Org. Chem.* **2002**, 503.  
822 Renard, J. Y.; Lallemand, J. Y. *Bull. Soc. Chim. Fr.* **1996**, *133*, 143.  
823 Renard, P. Y.; Lallemand, J. Y. *Tetrahedron: Asymmetry* **1996**, *7*, 2523.  
824 Ohanessian, G.; Six, Y.; Lallemand, J. Y. *Bull. Soc. Chim. Fr.* **1996**, *133*, 1143.  
825 Gao, X.; Hall, D. G. *Tetrahedron Lett.* **2003**, *44*, 2231.  
826 Schleth, F.; Vogler, T.; Harms, K.; Studer, A. *Chem. Eur. J.* **2004**, *10*, 4171.  
827 Brown, H. C.; Jayaraman, S. *Tetrahedron Lett.* **1993**, *34*, 3997.  
828 Deligny, M.; Carreaux, F.; Carboni, B.; Toupet, L.; Dujardin, G. *Chem. Commun.* **2003**, 276.  
829 Deligny, M.; Carreaux, F.; Carboni, B. *Synlett* **2005**, 1462.  
830 Grieco, P. A.; Dai, Y. J. *J. Am. Chem. Soc.* **1998**, *120*, 5128.  
831 Hoffmann, R. W.; Munster, I. *Tetrahedron Lett.* **1995**, *36*, 1431.  
832 Hoffmann, R. W.; Munster, I. *Liebigs Ann. Rec.* **1997**, 1143.  
833 Hoffmann, R. W.; Sander, T. *Liebigs Ann. Chem.* **1993**, 1185.  
834 Kruger, J.; Hoffmann, R. W. *J. Am. Chem. Soc.* **1997**, *119*, 7499.

**Supplemental References for Table 1A.**

- 835 Allais, F.; Ducrot, P-H. *Synthesis* **2010**, *10*, 1649.  
836 Álvarez-Bercedo, P.; Falomir, E.; Murga, J.; Carda, M.; Marco, J. A. *Eur. J. Org. Chem.* **2008**, 4015.  
837 Barker, T. J.; Jarvo, E. R. *Org. Lett.* **2009**, *11*, 1047.  
838 Barnett, D. S.; Moquist, P. N.; Schaus, S. E. *Angew. Chem., Int. Ed.* **2009**, *48*, 8679.  
839 Boshra, R.; Doshi, A.; Jäkle, F. *Angew. Chem., Int. Ed.* **2008**, *47*, 1134.  
840 Brimble, M. A.; Bachu, P.; Sperry, J. *Synthesis* **2007**, *18*, 2887.  
841 Burgos, C. H.; Canales, E.; Matos, K.; Soderquist, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 8044.  
842 Canales, E.; Prasad, K. G.; Soderquist, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 11572.  
843 Cardona, W.; Quiñones, W.; Robledo, S.; Vélez, I. D.; Murga, J.; García-Fortanet, J.; Carda, M.; Cardona, D.; Echeverri, F. *Tetrahedron* **2006**, *62*, 4086.  
844 Castoldi, D.; Caggiano, L.; Bayón, P.; Costa, A. M.; Cappella, P.; Sharon, O.; Gennari, C. *Tetrahedron* **2005**, *61*, 2123.  
845 Chen, W.; Liu, Y.; Chen, Z. *Eur. J. Org. Chem.* **2005**, 1665.  
846 Chen, Z.; Sinha, S. C. *Tetrahedron* **2008**, *64*, 1603.  
847 Chen, Z.; Ye, T. *Synlett* **2005**, *18*, 2781.  
848 Ding, F.; Jennings, M. P. *Org. Lett.* **2005**, *7*, 2321.

- <sup>849</sup> Fandrick, K. R.; Fandrick, D. R.; Gao, J. J.; Reeves, J. T.; Tan, Z.; Li, W.; Song, J. J.; Lu, B.; Yee, N. K.; Senanayake, C. H. *Org. Lett.* **2010**, *12*, 3748.
- <sup>850</sup> García-Fortanet, J.; Murga, J.; Carda, M.; Marco, J. A. *Arkivoc* **2005**, *ix*, 175.
- <sup>851</sup> García-Fortanet, J.; Murga, J.; Carda, M.; Marco, J. A. *Tetrahedron* **2004**, *60*, 12261.
- <sup>852</sup> Hiebel, M.-A.; Pelotier, B.; Pia, O. *Tetrahedron Lett.* **2010**, *51*, 5091.
- <sup>853</sup> Jain, P.; Antilla, J. C. *J. Am. Chem. Soc.* **2010**, *132*, 11884.
- <sup>854</sup> Jennings, M. P.; Clemens, R. T. *Tetrahedron Lett.* **2005**, *46*, 2021.
- <sup>855</sup> Jirgensons, A.; Marinozzi, M.; Pellicciari, R. *Tetrahedron* **2005**, *61*, 373.
- <sup>856</sup> Kawai, N.; Hande, S. M.; Uenishi, J. *Tetrahedron* **2007**, *63*, 9049.
- <sup>857</sup> Liu, S.; Fan, Y.; Peng, X.; Wang, W.; Hua, W.; Akber, H.; Liao, L. *Tetrahedron Lett.* **2006**, *47*, 7681.
- <sup>858</sup> Lou, S.; Moquist, P. N.; Schaus, S. E. *J. Am. Chem. Soc.* **2006**, *128*, 12660.
- <sup>859</sup> Mamane, V.; García, A. B.; Umarye, J. D.; Lessmann, T.; Sommer, S.; Waldmann, H. *Tetrahedron* **2007**, *63*, 5754.
- <sup>860</sup> Martínez-Solorio, D.; Jennings, M. P. *J. Org. Chem.* **2007**, *72*, 6621.
- <sup>861</sup> Matsuoka, H.; Kondo, K. *Tetrahedron Lett.* **2009**, *50*, 2320.
- <sup>862</sup> Mitton-Fry, J. J.; Cullen, A. J.; Sammakia, T. *Angew. Chem., Int. Ed.* **2007**, *46*, 1066.
- <sup>863</sup> Nowrouzi, F.; Thadani, A. N.; Batey, R. A. *Org. Lett.* **2009**, *11*, 2631.
- <sup>864</sup> Nowrouzi, F.; Janetzko, J.; Batey, R. A. *Org. Lett.* **2010**, *12*, 5490.
- <sup>865</sup> Paterson, I.; Anderson, E. A.; Dalby, S. M.; Loiseleur, O. *Org. Lett.* **2005**, *7*, 4125.
- <sup>866</sup> Pattenden, G.; Ashweek, N. J.; Baker-Glenn, C. A. G.; Kempson, J.; Walker, G. M.; Yee, J. G. K. *Org. Biomol. Chem.* **2008**, *6*, 1478.
- <sup>867</sup> Peña-López, M.; Martínez, M. M.; Sarandeses, L. A.; Sestelo, J. P. *Org. Lett.* **2010**, *12*, 852.
- <sup>868</sup> Ramachandran, P. V.; Burghardt, T. E.; Reddy, M. V. R. *J. Org. Chem.* **2005**, *70*, 2329.
- <sup>869</sup> Rauniyar, V.; Hall, D. G. *Angew. Chem., Int. Ed.* **2006**, *45*, 2426.
- <sup>870</sup> Rauniyar, V.; Hall, D. G. *J. Org. Chem.* **2009**, *74*, 4236.
- <sup>871</sup> Rauniyar, V.; Hall, D. G. *Synthesis* **2007**, *21*, 3421.
- <sup>872</sup> Rauniyar, V.; Zhai, H.; Hall, D. G. *J. Am. Chem. Soc.* **2008**, *130*, 8481.
- <sup>873</sup> Reilly, M. K.; Rychnovsky, S. D. *Org. Lett.* **2010**, *12*, 4892.
- <sup>874</sup> Ruiz, P.; Murga, J.; Carda, M.; Marco, J. A. *J. Org. Chem.* **2005**, *70*, 713.
- <sup>875</sup> Schneider, U.; Dao, H. T.; Kobayashi, S. *Org. Lett.* **2010**, *12*, 2488.
- <sup>876</sup> Schneider, U.; Kobayashi, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 5909.
- <sup>877</sup> Sebelius, S.; Szabó, K. J. *Eur. J. Org. Chem.* **2005**, 2539.
- <sup>878</sup> Shi, S.-L.; Xu, L.-W.; Oisaki, K.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2010**, *132*, 6638.
- <sup>879</sup> Shimizu, M.; Kawanishi, M.; Mizota, I.; Hachiya, I. *Org. Lett.* **2010**, *12*, 3571.
- <sup>880</sup> Sieber, J. D.; Morken, J. P. *J. Am. Chem. Soc.* **2008**, *130*, 4978.
- <sup>881</sup> Singh, A. J.; Xu, C.-X.; Xu, X.; West, L. M.; Wilmes, A.; Chan, A.; Hamel, E.; Miller, J. H.; Northcote, P. T.; Ghosh, A. K. *J. Org. Chem.* **2010**, *75*, 2.
- <sup>882</sup> Soto-Cairolí, B.; Soderquist, J. A. *Org. Lett.* **2009**, *11*, 401.
- <sup>883</sup> Sugiura, M.; Mori, C.; Hirano, K.; Kobayashi, S. *Can. J. Chem.* **2005**, *83*, 937.
- <sup>884</sup> Takahata, H.; Saito, Y.; Ichinose, M. *Org. Biomol. Chem.* **2006**, *4*, 1587.
- <sup>885</sup> Umarye, J. D.; Leßmann, T.; García, A. B.; Mamane, V.; Sommer, S.; Waldmann, H. *Chem. Eur. J.* **2007**, *13*, 3305.
- <sup>886</sup> Yadav, J. S.; Prakash, S. J.; Gangadhar, Y. *Tetrahedron: Asymmetry* **2005**, *16*, 2722.
- <sup>887</sup> Yamaguchi, M.; Morita, N.; Schneider, U.; Kobayashi, S. *Adv. Synth. Catal.* **2010**, *352*, 1461.
- <sup>888</sup> Yin, X.; Zhao, G.; Schneller, S. W. *Tetrahedron Lett.* **2007**, 4809.
- <sup>889</sup> Zhang, P.; Morken, J. P. *J. Am. Chem. Soc.* **2009**, *131*, 12550.
- <sup>890</sup> Zhang, X.; Da, S.; Zhang, C.; Xie, Z.; Li, Y. *Tetrahedron Lett.* **2006**, *47*, 507.

## Supplemental References for Table 1B.

- <sup>837</sup> Barker, T. J. Jarvo, E. R. *Org. Lett.* **2009**, *11*, 1047.
- <sup>838</sup> Barnett, D. S.; Moquist, P. N.; Schaus, S. E. *Angew. Chem., Int. Ed.* **2009**, *48*, 8679.
- <sup>839</sup> Boshra, R.; Doshi, A.; Jäkle, F. *Angew. Chem., Int. Ed.* **2008**, *47*, 1134.

- 841 Burgos, C. H.; Canales, E.; Matos, K.; Soderquist, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 8044.  
 842 Canales, E.; Prasad, G.; Soderquist, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 11572.  
 845 Chen, W.; Liu, Y.; Chen, Z. *Eur. J. Org. Chem.* **2005**, 1665.  
 849 Fandrick, K. R.; Fandrick, D. R.; Gao, J. J.; Reeves, J. T.; Tan, Z.; Li, W.; Song, J. J.; Lu, B.; Yee, N. K.; Senanayake, C. H. *Org. Lett.* **2010**, *12*, 3748.  
 891 Friberg, A.; Sarvary, I.; Wendt, O. F.; Frejd, T. *Tetrahedron: Asymmetry* **2008**, *19*, 1765.  
 853 Jain, P.; Antilla, J. C. *J. Am. Chem. Soc.* **2010**, *132*, 11884.  
 858 Lou, S.; Moquist, P. N.; Schaus, S. E. *J. Am. Chem. Soc.* **2006**, *128*, 12660.  
 892 Lou, S.; Moquist, P. N.; Schaus, S. E. *J. Am. Chem. Soc.* **2007**, *129*, 15398.  
 859 Mamane, V.; García, A. B.; Umarye, J. D.; Lessmann, T.; Sommer, S.; Waldmann, H. *Tetrahedron* **2007**, *63*, 5754.  
 861 Matsuoka, H.; Kondo, K. *Tetrahedron Lett.* **2009**, *50*, 2320.  
 893 Melancon, B. J.; Perl, N. R.; Taylor, R. E. *Org. Lett.* **2007**, *9*, 1425.  
 863 Nowrouzi, F.; Thadani, A. N.; Batey, R. A. *Org. Lett.* **2009**, *11*, 2631.  
 869 Rauniyar, V.; Hall, D. G. *Angew. Chem., Int. Ed.* **2006**, *45*, 2426.  
 843 Rauniyar, V.; Hall, D. G. *Synthesis* **2007**, *21*, 3421.  
 844 Rauniyar, V.; Zhai, H.; Hall, D. G. *J. Am. Chem. Soc.* **2008**, *130*, 8481.  
 845 Reilly, M. K.; Rychnovsky, S. D. *Org. Lett.* **2010**, *12*, 4892.  
 894 Schneider, U.; Chen, I-H.; Kobayashi, S. *Org. Lett.* **2008**, *10*, 737.  
 876 Schneider, U.; Kobayashi, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 5909.  
 895 Schneider, U.; Ueno, M.; Kobayashi, S. *J. Am. Chem. Soc.* **2008**, *130*, 13824.  
 875 Schneider, U.; Dao, H. T.; Kobayashi, S. *Org. Lett.* **2010**, *12*, 2488.  
 877 Sebelius, S.; Szabó, K. J. *Eur. J. Org. Chem.* **2005**, 2539.  
 896 Selander, N.; Sebelius, S.; Estay, C.; Szabó, K. J. *Eur. J. Org. Chem.* **2006**, 4085.  
 878 Shi, S-L.; Xu, L-W.; Oisaki, K.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2010**, *132*, 6638.  
 897 Vorontsova, N. V.; Zhuravsky, R. P.; Sergeeva, E. V.; Vorontsov, E. V.; Starikova, Z. A.; Rozenberg, V. I. *Russ. Chem. Bull., Int. Ed.* **2007**, *56*, 2225.  
 887 Yamaguchi, M.; Morita, N.; Schneider, U.; Kobayashi, S. *Adv. Synth. Catal.* **2010**, *352*, 1461.

#### Supplemental References for Table 2.

- 838 Barnett, D. S.; Moquist, P. N.; Schaus, S. E. *Angew. Chem., Int. Ed.* **2009**, *48*, 8679.  
 841 Burgos, C. H.; Canales, E.; Matos, K.; Soderquist, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 8044.  
 898 Domon, D.; Fujiwara, K.; Ohtaniuchi, Y.; Takezawa, A.; Takeda, S.; Kawasaki, H.; Murai, A.; Kawai, H.; Suzuki, T. *Tetrahedron Lett.* **2005**, *46*, 8279.  
 899 Horneff, T.; Herdtweck, E.; Randoll, S.; Bach, T. *Bioorg. Med. Chem.* **2006**, *14*, 6223.  
 853 Jain, P.; Antilla, J. C. *J. Am. Chem. Soc.* **2010**, *132*, 11884.  
 858 Lou, S.; Moquist, P. N.; Schaus, S. E. *J. Am. Chem. Soc.* **2006**, *128*, 12660.  
 859 Mamane, V.; García, A. B.; Umarye, J. D.; Lessmann, T.; Sommer, S.; Waldmann, H. *Tetrahedron* **2007**, *63*, 5754.  
 863 Nowrouzi, F.; Thadani, A. N.; Batey, R. A. *Org. Lett.* **2009**, *11*, 2631.  
 900 Ramachandran, P. V.; Chandra, J. S.; Prabhudas, B.; Pratihar, D.; Reddy, M. V. R. *Org. Biomol. Chem.* **2005**, *3*, 3812.  
 901 Ramachandran, P. V.; Pratihar, D.; Biswas, D. *Chem. Commun.* **2005**, 1988.  
 902 Ramachandran, P. V.; Srivastava, A.; Hazra, D. *Org. Lett.* **2007**, *9*, 157.  
 869 Rauniyar, V.; Hall, D. G. *Angew. Chem., Int. Ed.* **2006**, *45*, 2426.  
 871 Rauniyar, V.; Hall, D. G. *Synthesis* **2007**, *21*, 3421.  
 872 Rauniyar, V.; Zhai, H.; Hall, D. G. *J. Am. Chem. Soc.* **2008**, *130*, 8481.  
 873 Reilly, M. K.; Rychnovsky, S. D. *Org. Lett.* **2010**, *12*, 4892.  
 875 Schneider, U.; Dao, H. T.; Kobayashi, S. *Org. Lett.* **2010**, *12*, 2488.  
 878 Shi, S-L.; Xu, L-W.; Oisaki, K.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2010**, *132*, 6638.  
 879 Shimizu, M.; Kawanishi, M.; Mizota, I.; Hachiya, I. *Org. Lett.* **2010**, *12*, 3571.  
 903 Va, P.; Roush, W. R. *Tetrahedron* **2007**, *63*, 5768.

## Supplemental References for Table 3.

- 838 Barnett, D. S.; Moquist, P. N.; Schaus, S. E. *Angew. Chem., Int. Ed.* **2009**, *48*, 8679.
- 841 Burgos, C. H.; Canales, E.; Matos, K.; Soderquist, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 8044.
- 904 Chakraborty, T. K.; Chattopadhyay, A. K. *J. Org. Chem.* **2008**, *73*, 3578.
- 849 Fandrick, K. R.; Fandrick, D. R.; Gao, J. J.; Reeves, J. T.; Tan, Z.; Li, W.; Song, J. J.; Lu, B.; Yee, N. K.; Senanayake, C. H. *Org. Lett.* **2010**, *12*, 3748.
- 905 Gao, X.; Hall, D. G. *J. Am. Chem. Soc.* **2005**, *127*, 1628.
- 906 Ghosh, A. K.; Yuan, H. *Org. Lett.* **2010**, *12*, 3120.
- 907 Hirose, T.; Sunazuka, T.; Yamamoto, D.; Mouri, M.; Hagiwara, Y.; Matsumaru, T.; Kaji, E.; Omura, S. *Tetrahedron Lett.* **2007**, *48*, 413.
- 853 Jain, P.; Antilla, J. C. *J. Am. Chem. Soc.* **2010**, *132*, 11884.
- 908 Hua, Z.; Jin, Z. *Tetrahedron Lett.* **2007**, *48*, 7695.
- 909 Keck, G. E.; Giles, R. L.; Cee, V. J.; Wager, C. A.; Yu, T.; Kraft, M. B. *J. Org. Chem.* **2008**, *73*, 9675.
- 858 Lou, S.; Moquist, P. N.; Schaus, S. E. *J. Am. Chem. Soc.* **2006**, *128*, 12660.
- 910 Magnin-Lachaux, M.; Tan, Z.; Liang, B.; Negishi, E.-i. *Org. Lett.* **2004**, *6*, 1425.
- 859 Mamane, V.; García, A. B.; Umarye, J. D.; Lessmann, T.; Sommer, S.; Waldmann, H. *Tetrahedron* **2007**, *63*, 5754.
- 911 Morita, A.; Kuwahara, S. *Tetrahedron Lett.* **2007**, *48*, 3163.
- 863 Nowrouzi, F.; Thadani, A. N.; Batey, R. A. *Org. Lett.* **2009**, *11*, 2631.
- 912 Penner, M.; Rauniyar, V.; Kaspar, L. T.; Hall, D. G. *J. Am. Chem. Soc.* **2009**, *131*, 14216.
- 868 Ramachandran, P. V.; Burghardt, T. E.; Reddy, M. V. R. *J. Org. Chem.* **2005**, *70*, 2329.
- 902 Ramachandran, P. V.; Srivastava, A.; Hazra, D. *Org. Lett.* **2007**, *9*, 157.
- 901 Ramachandran, P. V.; Pratihari, D.; Biswas, D. *Chem. Commun.* **2005**, 1988.
- 869 Rauniyar, V.; Hall, D. G. *Angew. Chem., Int. Ed.* **2006**, *45*, 2426.
- 870 Rauniyar, V.; Hall, D. G. *J. Org. Chem.* **2009**, *74*, 4236.
- 871 Rauniyar, V.; Hall, D. G. *Synthesis* **2007**, *21*, 3421.
- 872 Rauniyar, V.; Zhai, H.; Hall, D. G. *J. Am. Chem. Soc.* **2008**, *130*, 8481.
- 873 Reilly, M. K.; Rychnovsky, S. D. *Org. Lett.* **2010**, *12*, 4892.
- 875 Schneider, U.; Dao, H. T.; Kobayashi, S. *Org. Lett.* **2010**, *12*, 2488.
- 877 Sebelius, S.; Szabó, K. J. *Eur. J. Org. Chem.* **2005**, 2539.
- 878 Shi, S.-L.; Xu, L.-W.; Oisaki, K.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2010**, *132*, 6638.
- 879 Shimizu, M.; Kawanishi, M.; Mizota, I.; Hachiya, I. *Org. Lett.* **2010**, *12*, 3571.
- 913 Suenaga, K.; Kimura, T.; Kuroda, T.; Matsui, K.; Miya, S.; Kuribayashi, S.; Sakakura, A.; Kigoshi, H. *Tetrahedron* **2006**, *62*, 8278.
- 885 Umarye, J. D.; Leßmann, T.; García, A. B.; Mamane, V.; Sommer, S.; Waldmann, H. *Chem. Eur. J.* **2007**, *13*, 3305.
- 914 Vogt, M.; Ceylan, S.; Kirschning, A. *Tetrahedron* **2010**, *66*, 6450.
- 915 Zampella, A.; Sepe, V.; D'Orsi, R.; D'Auria, M. V. *Lett. Org. Chem.* **2004**, *1*, 308.

## Supplemental References for Table 4.

- 916 Althaus, J.; Mahmood, A.; Suárez, J. R.; Thomas, S. P.; Aggarwal, V. K. *J. Am. Chem. Soc.* **2010**, *132*, 4025.
- 917 Beckmann, E.; Hoppe, D. *Synthesis* **2005**, *2*, 217.
- 918 Berrée, F.; Gernigon, N.; Hercouet, A.; Lin, C. H.; Carboni, B. *Eur. J. Org. Chem.* **2009**, 329.
- 919 Bishop, M.; Doum, V.; Nordschild (née Rieche), A. C. M.; Pietruszka, J.; Sandkuhl, D. *Synthesis* **2010**, *3*, 527.
- 920 Burks, H. E.; Kilman, L. T.; Morken, J. P. *J. Am. Chem. Soc.* **2009**, *131*, 9134.
- 921 Carosi, L.; Hall, D. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 5913.
- 922 Carosi, L.; Hall, D. G. *Can. J. Chem.* **2009**, *87*, 650.
- 923 Carosi, L.; Lachance, H.; Hall, D. G. *Tetrahedron Lett.* **2005**, *46*, 8981.
- 924 Chen, M.; Ess, D. H.; Roush, W. R. *J. Am. Chem. Soc.* **2010**, *132*, 7881.
- 925 Chen, M.; Roush, W. R. *Org. Lett.* **2010**, *12*, 2706.



- <sup>926</sup> (a) Cho, H. Y.; Morken, J. P. *J. Am. Chem. Soc.* **2008**, *130*, 16140. (b) Cho, H. Y.; Morken, J. P. *J. Am. Chem. Soc.* **2010**, *132*, 7576.
- <sup>927</sup> Cmrecki, V.; Eichenauer, N. C.; Frey, W.; Pietruszka, J. *Tetrahedron* **2010**, *66*, 6550.
- <sup>928</sup> Fang, G. Y.; Aggarwal, V. K. *Angew. Chem., Int. Ed.* **2007**, *46*, 359.
- <sup>849</sup> Fandrick, K. R.; Fandrick, D. R.; Gao, J. J.; Reeves, J. T.; Tan, Z.; Li, W.; Song, J. J.; Lu, B.; Yee, N. K.; Senanayake, C. H. *Org. Lett.* **2010**, *12*, 3748.
- <sup>929</sup> Fernández, E.; Pietruszka, J. *Synlett* **2009**, *9*, 1474.
- <sup>930</sup> Fernández, E.; Pietruszka, J.; Frey, W. *J. Org. Chem.* **2010**, *75*, 5580.
- <sup>931</sup> Flamme, E. M.; Roush, W. R. *Org. Lett.* **2005**, *7*, 1411.
- <sup>932</sup> González, J. R.; González, A. Z.; Soderquist, J. A. *J. Am. Chem. Soc.* **2009**, *131*, 9924.
- <sup>933</sup> Hicks, J. D.; Flamme, E. M.; Roush, W. R. *Org. Lett.* **2005**, *7*, 5509.
- <sup>934</sup> Ito, H.; Ito, S.; Sasaki, Y.; Matsuura, K.; Sawamura, M. *J. Am. Chem. Soc.* **2007**, *129*, 14856.
- <sup>935</sup> Ito, H.; Okura, T.; Matsuura, K.; Sawamura, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 560.
- <sup>936</sup> Kister, J.; DeBaillie, A. C.; Lira, R.; Roush, W. R. *J. Am. Chem. Soc.* **2009**, *131*, 14174.
- <sup>937</sup> Kobayashi, S.; Endo, T.; Schneider, U.; Ueno M. *Chem. Commun.* **2010**, *46*, 1260.
- <sup>938</sup> Kobayashi, S.; Konishi, H.; Schneider, U. *Chem. Comm.* **2008**, 2313.
- <sup>939</sup> Li, F.; Roush, W. R. *Org. Lett.* **2009**, *11*, 2932.
- <sup>940</sup> Lira, R.; Roush, W. R. *Org. Lett.* **2007**, *9*, 533.
- <sup>941</sup> Owen, R. M.; Roush, W. R. *Org. Lett.* **2005**, *7*, 3941.
- <sup>942</sup> Pardo-Rodríguez, V.; Marco-Martínez, J.; Buñuel, E.; Cárdenas, D. J. *Org. Lett.* **2009**, *11*, 4548.
- <sup>943</sup> Peng, F.; Hall, D. G. *J. Am. Chem. Soc.* **2007**, *129*, 3070.
- <sup>944</sup> Peng, F.; Hall, D. G. *Tetrahedron Lett.* **2007**, *48*, 3305.
- <sup>945</sup> Pietruszka, J.; Rieche, A. C. M.; Schöne, N. *Synlett* **2007**, 2525.
- <sup>946</sup> Pietruszka, J.; Schöne, N. *Eur. J. Org. Chem.* **2004**, 5011.
- <sup>947</sup> Pietruszka, J.; Schöne, N. *Synthesis* **2006**, *1*, 24.
- <sup>948</sup> Pietruszka, J.; Schöne, N.; Frey, W.; Grundl, L. *Chem. Eur. J.* **2008**, *14*, 5178.
- <sup>949</sup> Possémé, F.; Deligny, M.; Carreaux, F.; Carboni, B. *J. Org. Chem.* **2007**, *72*, 984.
- <sup>950</sup> Ramachandran, P. V.; Chatterjee, A. *Org. Lett.* **2008**, *10*, 1195.
- <sup>901</sup> Ramachandran, P. V.; Pratihari, D.; Biswas, D. *Chem. Commun.* **2005**, 1988.
- <sup>951</sup> Ramachandran, P. V.; Pratihari, D.; Nair, H. N. G.; Walters, M.; Smith, S.; Yip-Schneider, M. T.; Wu, H.; Schmidt, C. M. *Bioorg. Med. Chem. Lett.* **2010**, *20*, 6620.
- <sup>952</sup> Robinson, A.; Aggarwal, V. K. *Angew. Chem., Int. Ed.* **2010**, *49*, 6673.
- <sup>953</sup> Ros, A.; Bermejo, A.; Aggarwal, V. K. *Chem. Eur. J.* **2010**, *16*, 9741.
- <sup>875</sup> Schneider, U.; Dao, H. T.; Kobayashi, S. *Org. Lett.* **2010**, *12*, 2488.
- <sup>954</sup> Sivasubramaniam, U.; Hall, D. G. *Heterocycles* **2010**, *80*, 1449.
- <sup>955</sup> Tang, S.; Xie, X.; Wang, X.; He, L.; Xu, K.; She, X. *J. Org. Chem.* **2010**, *75*, 8234.
- <sup>956</sup> Winbush, S. M.; Roush, W. R. *Org. Lett.* **2010**, *12*, 4344.
- <sup>957</sup> Woodward, A. R.; Burks, H. E.; Chan, L. M.; Morken, J. P. *Org. Lett.* **2005**, *7*, 5505.
- <sup>887</sup> Yamaguchi, M.; Morita, N.; Schneider, U.; Kobayashi, S. *Adv. Synth. Catal.* **2010**, *352*, 1461.
- <sup>958</sup> Yamamoto, A.; Ikeda, Y.; Suginome, M. *Tetrahedron Lett.* **2009**, *50*, 3168.

#### Supplemental References for Table 5.

- <sup>959</sup> Arndt, M.; Reinhold, A.; Hilt, G. *J. Org. Chem.* **2010**, *75*, 5203.
- <sup>960</sup> Chataigner, I.; Zammattio, F.; Lebreton, J.; Villiéras, J. *Tetrahedron* **2008**, *64*, 2441.
- <sup>845</sup> Chen, W.; Liu, Y.; Chen, Z. *Eur. J. Org. Chem.* **2005**, 1665.
- <sup>961</sup> Elford, T. G.; Ulaczyk-Lesanko, A.; De Pascale, G.; Wright, G. D.; Hall, D. G. *J. Comb. Chem.* **2009**, *11*, 155.
- <sup>849</sup> Fandrick, K. R.; Fandrick, D. R.; Gao, J. J.; Reeves, J. T.; Tan, Z.; Li, W.; Song, J. J.; Lu, B.; Yee, N. K.; Senanayake, C. H. *Org. Lett.* **2010**, *12*, 3748.
- <sup>962</sup> Faveau, C.; Mondon, M.; Gesson, J-P.; Mahnke, T.; Gebhardt, S.; Koert, U. *Tetrahedron Lett.* **2006**, *47*, 8305.
- <sup>963</sup> Lachance, H.; Marion, O.; Hall, D. G. *Tetrahedron Lett.* **2008**, *49*, 6061.
- <sup>964</sup> Ohmura, T.; Taniguchi, H.; Kondo, Y.; Suginome, M. *J. Am. Chem. Soc.* **2007**, *129*, 3518.

- <sup>951</sup> Ramachandran, P. V.; Pratihari, D.; Nair, H. N. G.; Walters, M.; Smith, S.; Yip-Schneider, M. T.; Wu, H.; Schmidt, C. M. *Bioorg. Med. Chem. Lett.* **2010**, *20*, 6620.
- <sup>870</sup> Rauniyar, V.; Hall, D. G. *J. Org. Chem.* **2009**, *74*, 4236.
- <sup>871</sup> Rauniyar, V.; Hall, D. G. *Synthesis* **2007**, *21*, 3421.
- <sup>872</sup> Rauniyar, V.; Zhai, H.; Hall, D. G. *J. Am. Chem. Soc.* **2008**, *130*, 8481.
- <sup>965</sup> Román, J. G.; Soderquist, J. A. *J. Org. Chem.* **2007**, *72*, 9772.
- <sup>966</sup> Sánchez, C.; Ariza, X.; Cornella, J.; Farràs, J.; Garcia, J.; Ortiz, J. *Chem. Eur. J.* **2010**, *16*, 11535.
- <sup>967</sup> Selander, N.; Kipke, A.; Sebelius, S.; Szabó, K. J. *J. Am. Chem. Soc.* **2007**, *129*, 13723.
- <sup>955</sup> Tang, S.; Xie, X.; Wang, X.; He, L.; Xu, K.; She, X. *J. Org. Chem.* **2010**, *75*, 8234.

#### Supplemental References for Table 6.

- <sup>844</sup> Castoldi, D.; Caggiano, L.; Bayón, P.; Costa, A. M.; Cappella, P.; Sharon, O.; Gennari, C. *Tetrahedron* **2005**, *61*, 2123.
- <sup>968</sup> Chang, K.-J.; Rayabarapu, D. K.; Yang, F.-Y.; Cheng, C.-H. *J. Am. Chem. Soc.* **2005**, *127*, 126.
- <sup>960</sup> Chataigner, I.; Zammattio, F.; Lebreton, J.; Villiéras, J. *Tetrahedron* **2008**, *64*, 2441.
- <sup>969</sup> Chen, M.; Handa, M.; Roush, W. R. *J. Am. Chem. Soc.* **2009**, *131*, 14602.
- <sup>970</sup> Crotti, S.; Bertolini, F.; Macchia, F.; Pineschi, M. *Org. Lett.* **2009**, *11*, 3762.
- <sup>971</sup> Elford, T. G.; Arimura, Y.; Yu, S. H.; Hall, D. G. *J. Org. Chem.* **2007**, *72*, 1276.
- <sup>961</sup> Elford, T. G.; Ulaczyk-Lesanko, A.; De Pascale, G.; Wright, G. D.; Hall, D. G. *J. Comb. Chem.* **2009**, *11*, 155.
- <sup>972</sup> Ely, R. J.; Morken, J. P. *J. Am. Chem. Soc.* **2010**, *132*, 2534.
- <sup>973</sup> Ess, D. H.; Kister, J.; Chen, M.; Roush, W. R. *Org. Lett.* **2009**, *11*, 5538.
- <sup>931</sup> Flamme, E. M.; Roush, W. R. *Org. Lett.* **2005**, *7*, 1411.
- <sup>974</sup> Fürstner, A.; Bonnekessel, M.; Blank, J. T.; Radkowski, K.; Seidel, G.; Lacombe, F.; Gabor, B.; Mynott, R. *Chem. Eur. J.* **2007**, *13*, 8762.
- <sup>975</sup> González, A. Z.; Román, J. G.; Alicea, E.; Canales, E.; Soderquist, J. A. *J. Am. Chem. Soc.* **2009**, *131*, 1269.
- <sup>933</sup> Hicks, J. D.; Flamme, E. M.; Roush, W. R. *Org. Lett.* **2005**, *7*, 5509.
- <sup>976</sup> Hoffmann, R. W.; Menzel, K.; Harms, K. *Eur. J. Org. Chem.* **2002**, 2603.
- <sup>977</sup> Kabalka, G. W.; Venkataiah, B. *Tetrahedron Lett.* **2005**, *46*, 7325.
- <sup>978</sup> Kabalka, G. W.; Venkataiah, B.; Dong, G. *Tetrahedron Lett.* **2005**, *46*, 4209.
- <sup>936</sup> Kister, J.; DeBaillie, A. C.; Lira, R.; Roush, W. R. *J. Am. Chem. Soc.* **2009**, *131*, 14174.
- <sup>939</sup> Li, F.; Roush, W. R. *Org. Lett.* **2009**, *11*, 2932.
- <sup>979</sup> Lira, R.; Roush, W. R. *Org. Lett.* **2007**, *9*, 4315.
- <sup>940</sup> Lira, R.; Roush, W. R. *Org. Lett.* **2007**, *9*, 533.
- <sup>980</sup> Mitra, S.; Gurrula, S. R.; Coleman, R. S. *J. Org. Chem.* **2007**, *72*, 8724.
- <sup>941</sup> Owen, R. M.; Roush, W. R. *Org. Lett.* **2005**, *7*, 3941.
- <sup>981</sup> Purser, S.; Wilson, C.; Moore, P. R.; Gouverneur, V. *Synlett* **2007**, *7*, 1166.
- <sup>868</sup> Ramachandran, P. V.; Burghardt, T. E.; Reddy, M. V. R. *J. Org. Chem.* **2005**, *70*, 2329.
- <sup>900</sup> Ramachandran, P. V.; Chandra, J. S.; Prabhudas, B.; Pratihari, D.; Reddy, M. V. R. *Org. Biomol. Chem.* **2005**, *3*, 3812.
- <sup>982</sup> Ramachandran, P. V.; Chatterjee, A. *J. Fluorine Chem.* **2009**, *130*, 144.
- <sup>983</sup> Ramachandran, P. V.; Pratihari, D. *Org. Lett.* **2007**, *9*, 2087.
- <sup>984</sup> Ramachandran, P. V.; Pratihari, D.; Biswas, D. *Org. Lett.* **2006**, *8*, 3877.
- <sup>951</sup> Ramachandran, P. V.; Pratihari, D.; Nair, H. N. G.; Walters, M.; Smith, S.; Yip-Schneider, M. T.; Wu, H.; Schmidt, C. M. *Bioorg. Med. Chem. Lett.* **2010**, *20*, 6620.
- <sup>877</sup> Sebelius, S.; Szabó, K. J. *Eur. J. Org. Chem.* **2005**, 2539.
- <sup>967</sup> Selander, N.; Kipke, A.; Sebelius, S.; Szabó, K. J. *J. Am. Chem. Soc.* **2007**, *129*, 13723.
- <sup>896</sup> Selander, N.; Sebelius, S.; Estay, C.; Szabó, K. J. *Eur. J. Org. Chem.* **2006**, 4085.
- <sup>985</sup> Selander, N.; Szabó, K. J. *Adv. Synth. Catal.* **2008**, *350*, 2045.
- <sup>986</sup> Selander, N.; Szabó, K. J. *Chem. Commun.* **2008**, 3420.
- <sup>987</sup> Selander, N.; Szabó, K. J. *J. Org. Chem.* **2009**, *74*, 5695.
- <sup>879</sup> Shimizu, M.; Kawanishi, M.; Mizota, I.; Hachiya, I. *Org. Lett.* **2010**, *12*, 3571.

- <sup>988</sup> Sumida, Y.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.* **2006**, *128*, 15960.  
<sup>989</sup> Sumida, Y.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2008**, *10*, 4677.  
<sup>903</sup> Va, P.; Roush, W. R. *Tetrahedron* **2007**, *63*, 5768.  
<sup>914</sup> Vogt, M.; Ceylan, S.; Kirschning, A. *Tetrahedron* **2010**, *66*, 6450.  
<sup>990</sup> Wu, J. Y.; Moreau, B.; Ritter, T. *J. Am. Chem. Soc.* **2009**, *131*, 12915.  
<sup>991</sup> Yu, S. H.; Ferguson, M. J.; McDonald, R.; Hall, D. G. *J. Am. Chem. Soc.* **2005**, *127*, 12808.

**Supplemental References for Table 7.**

- <sup>992</sup> Canales, E.; Gonzalez, A. Z.; Soderquist, J. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 397.  
<sup>993</sup> Fandrick, D. R.; Fandrick, K. R.; Reeves, J. T.; Tan, Z.; Johnson, C. S.; Lee, H.; Song, J. J.; Yee, N. K.; Senanayake, C. H. *Org. Lett.* **2010**, *12*, 88.  
<sup>994</sup> Fandrick, D. R.; Reeves, J. T.; Tan, Z.; Lee, H.; Song, J. J.; Yee, N. K.; Senanayake, C. H. *Org. Lett.* **2009**, *11*, 5458.  
<sup>995</sup> Hernandez, E.; Burgos, C. H.; Alicea, E.; Soderquist, J. A. *Org. Lett.* **2006**, *8*, 4089.  
<sup>996</sup> Ito, H.; Sasaki, Y.; Sawamura, M. *J. Am. Chem. Soc.* **2008**, *130*, 15774.  
<sup>997</sup> Lai, C.; Soderquist, J. A. *Org. Lett.* **2005**, *7*, 799.  
<sup>998</sup> Maddess, M. L.; Lautens, M. *Org. Lett.* **2005**, *7*, 3557.  
<sup>875</sup> Schneider, U.; Dao, H. T.; Kobayashi, S. *Org. Lett.* **2010**, *12*, 2488.  
<sup>878</sup> Shi, S-L.; Xu, L-W.; Oisaki, K.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2010**, *132*, 6638.

**Supplemental References for Table 8.**

- <sup>999</sup> Bouziane, A.; Régnier, T.; Carreaux, F.; Carboni, B.; Bruneau, C.; Renaud, J-L. *Synlett* **2010**, *2*, 207.  
<sup>1000</sup> Carreaux, F.; Favre, A.; Carboni, B.; Rouaud, I.; Boustie, J. *Tetrahedron Lett.* **2006**, *47*, 4545.  
<sup>970</sup> Crotti, S.; Bertolini, F.; Macchia, F.; Pineschi, M. *Org. Lett.* **2009**, *11*, 3762.  
<sup>1001</sup> Deligny, M.; Carreaux, F.; Carboni, B. *Synlett* **2005**, *9*, 1462.  
<sup>1002</sup> Favre, A.; Carreaux, F.; Deligny, M.; Carboni, B. *Eur. J. Org. Chem.* **2008**, 4900.  
<sup>905</sup> Gao, X.; Hall, D. G. *J. Am. Chem. Soc.* **2005**, *127*, 1628.  
<sup>1003</sup> Gao, X.; Hall, D. G.; Deligny, M.; Favre, A.; Carreaux, F.; Carboni, B. *Chem. Eur. J.* **2006**, *12*, 3132.  
<sup>1004</sup> Gerdin, M.; Penhoat, M.; Zalubovskis, R.; Pétermann, C.; Moberg, C. *J. Organomet. Chem.* **2008**, *693*, 3519.  
<sup>1005</sup> Hercouet, A.; Berrée, F.; Lin, C. H.; Toupet, L.; Carboni, B. *Org. Lett.* **2007**, *9*, 1717.  
<sup>1006</sup> Hilt, G.; Hess, W.; Harms, K. *Org. Lett.* **2006**, *8*, 3287.  
<sup>1007</sup> Hilt, G.; Lüers, S.; Smolko, K. I. *Org. Lett.* **2005**, *7*, 251.  
<sup>1008</sup> Ito, H.; Kunii, S.; Sawamura, M. *Nature Chem.* **2010**, *2*, 972.  
<sup>935</sup> Ito, H.; Okura, T.; Matsuura, K.; Sawamura, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 560.  
<sup>963</sup> Lachance, H.; Marion, O.; Hall, D. G. *Tetrahedron Lett.* **2008**, *49*, 6061.  
<sup>1009</sup> Lessard, S.; Peng, F. *J. Am. Chem. Soc.* **2009**, *131*, 9612.  
<sup>1010</sup> Marion, O.; Gao, X.; Marcus, S.; Hall, D. G. *Bioorg. Med. Chem.* **2009**, *17*, 1006.  
<sup>1011</sup> Nakagawa, D.; Middyashita, M.; Tanino, K. *Tetrahedron Lett.* **2010**, *51*, 2771.  
<sup>1012</sup> Olsson, V. J.; Szabó, K. J. *Angew. Chem., Int. Ed.* **2007**, *46*, 6891.  
<sup>1013</sup> Olsson, V. J.; Szabó, K. J. *J. Org. Chem.* **2009**, *74*, 7715.  
<sup>967</sup> Selander, N.; Kipke, A.; Sebelius, S.; Szabó, K. J. *J. Am. Chem. Soc.* **2007**, *129*, 13723.  
<sup>896</sup> Selander, N.; Sebelius, S.; Estay, C.; Szabó, K. J. *Eur. J. Org. Chem.* **2006**, 4085.  
<sup>986</sup> Selander, N.; Szabó, K. J. *Chem. Commun.* **2008**, 3420.  
<sup>1014</sup> Ulaczyk-Lesanko, A.; Pelletier, E.; Lee, M.; Prinz, H.; Waldmann, H.; Hall, D. G. *J. Comb. Chem.* **2007**, *9*, 695.

**Supplemental References for Table 9.**

- <sup>1015</sup> Bandur, N. G.; Brükner, D.; Hoffmann, R. W.; Koert, U. *Org. Lett.* **2006**, *8*, 3829.

**Selected Supplemental References on New Preparative Methods for Allylic Boronates**

- <sup>920</sup> Burks, H. E.; Kilman, L. T.; Morken, J. P. *J. Am. Chem. Soc.* **2009**, *131*, 9134.  
<sup>921</sup> Carosi, L.; Hall, D. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 5913.  
<sup>1016</sup> Dutheil, G.; Selander, N.; Szabó, K. J.; Aggarwal, V. K. *Synthesis* **2008**, 2293.  
<sup>972</sup> Ely, R. J.; Morken, J. P. *J. Am. Chem. Soc.* **2010**, *132*, 2534.  
<sup>929</sup> Fernández, E.; Pietruszka, J. *Synlett* **2009**, 9, 1474.  
<sup>1017</sup> Guzman-Martinez, A.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2010**, *132*, 10634.  
<sup>934</sup> Ito, H.; Ito, S.; Sasaki, Y.; Matsuura, K.; Sawamura, M. *J. Am. Chem. Soc.* **2007**, *129*, 14856.  
<sup>1018</sup> Ito, H.; Kawakami, C.; Sawamura, M. *J. Am. Chem. Soc.* **2005**, *127*, 16034.  
<sup>1009</sup> Lessard, S.; Peng, F. *J. Am. Chem. Soc.* **2009**, *131*, 9612.  
<sup>1019</sup> Sasaki, Y.; Zhong, C.; Sawamura, M.; Ito, H. *J. Am. Chem. Soc.* **2010**, *132*, 1226.  
<sup>1020</sup> Sumida, Y.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2008**, *10*, 4677.  
<sup>990</sup> Wu, J. Y.; Moreau, B.; Ritter, T. *J. Am. Chem. Soc.* **2009**, *131*, 12915.

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- <sup>1021</sup> Hall, D. G. *Synlett* **2007**, 1644.  
<sup>1022</sup> Hall, D. G. *Pure Appl. Chem.* **2008**, *80*, 913.

**Selected References on the Mechanism of Catalytic Allylborations**

- <sup>1023</sup> Sakata, K.; Fujimoto, H. *J. Am. Chem. Soc.* **2008**, *130*, 12519.