CHAPTER 1

ADDITIONS OF ALLYL, ALLENYL, AND PROPARGYLSTANNANES TO ALDEHYDES AND IMINES

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CONTENTS

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INTRODUCTION

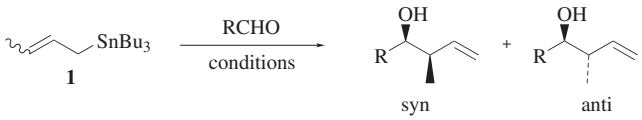
Natural products that contain contiguous stereocenters such as those having polyacetate and polypropionate structures are of considerable interest. Current technology for constructing these chiral molecules consists of strategies broadly defined as "acyclic stereocontrol." The most efficient tools in acyclic stereocontrol include modern aldol reactions[1–3] and the reactions of carbonyl compounds with allylmetal reagents.[4–9] In order to achieve highly efficient syntheses of natural products rich with stereochemistry, highly stereoselective transformations are required. One solution to this challenge has been the use of allylstannane reagents. Reasons that allylstannane reagents have attracted widespread interest include, but are not limited to, their ease of handling, their relative stability, and their selective reactivity. The addition of allylstannanes to aldehydes combines the process of C–C bond formation with the stereoselective production of one or two new stereocenters. The configuration of these new stereocenters is predictable on the basis of reaction conditions. Oxygen substitution at either the α- or γ-position of allylstannanes also contributes to the versatility of these reagents. Recently developed chiral allenylstannane reagents and the use of $InCl_3$ as a transmetalation agent have greatly enhanced the practical utilities of these reagents. Previous reviews concerning allylstannane chemistry are available,[5–9] and this review is limited mainly to carbonyl and imine addition reactions, most of which create one or two new stereocenters.

Only a few examples of addition to ketones by allylstannane reagents have been reported. These are listed in the Tables, but are not discussed in the text.

MECHANISM AND STEREOCHEMISTRY

Three types of conditions have been developed for the addition of allylstannanes to aldehydes. These include thermal additions, additions in the presence of a Lewis acid, and additions involving prior transmetalation. The study of thermal reactions

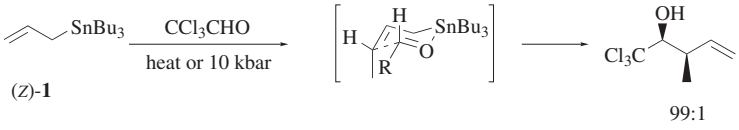
of allylstannanes began 30 years ago,[10] and Lewis acid promoted reactions became more dominant in the field about 20 years ago.[11] However, transmetalation of allylstannanes prior to their reaction with aldehydes has become the new focal point of research in recent years.[12,13] The configuration of the products will vary depending on the reaction conditions



When 2-butenyl(tributyl)stannane (**1**) is added to an aldehyde, two new stereocenters are generated simultaneously. There are two fundamental control elements for this reaction that determine the stereochemical outcome: reagent control and substrate control. Only simple diastereoselectivity needs to be considered with achiral aldehydes, and the products are commonly denoted as syn and anti isomers. However with chiral aldehydes there are two stereochemical relationships that result in the products. Furthermore, with enantiopure aldehydes, the absolute configuration needs to be considered. In reactions under substrate control, a chiral aldehyde and an achiral stannane are employed, and the diastereoselectivity is usually based on the Felkin-Anh transition state model.[14–16] In this review, the Evans model for 1,3-asymmetric induction is also introduced to explain the observed stereochemistry with β-branched aldehydes.[17]

Thermal Additions

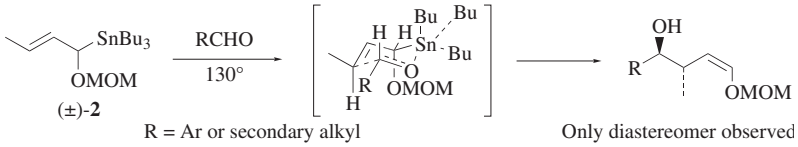
Reactions in the absence of a Lewis acid usually require high temperature, high pressure, or an extremely reactive aldehyde. Under these conditions, the tin atom of the stannane reagent serves as an electrophilic center associating with the carbonyl oxygen of the aldehyde. The thermal reactions are consistent with the involvement of a cyclic, six-membered, chair-like transition structure. Thus, (*Z*)- and (*E*)-2-butenyl(tributyl)stannanes react with aldehydes with good stereoselectivity to give the syn and anti homoallylic alcohols, respectively. The reaction of (*Z*)-**1** with trichloroacetaldehyde is illustrative (Eq. 1).[10] The same stereoselectivity is observed for reactions performed at room temperature but under high pressure.[18]



(Eq. 1)

A cyclic transition structure is also believed to be involved in the thermal reactions of α-alkoxy-2-butenylstannane **2** with aldehydes.[19,20] Excellent diastereoselectivity is observed when **2** is heated with aromatic and secondary aliphatic aldehydes at 130° to give the 1,2-anti Z alkenes (Eq. 2). The configuration of the products is consistent with the participation of a six-membered, cyclic transition structure, in which the alkoxy group α to tin is in an axial position. It has been suggested that the preference of the alkoxy group for the axial position may be due to a combination of steric and electronic effects.[21] Despite the excellent diastereoselectivity observed in

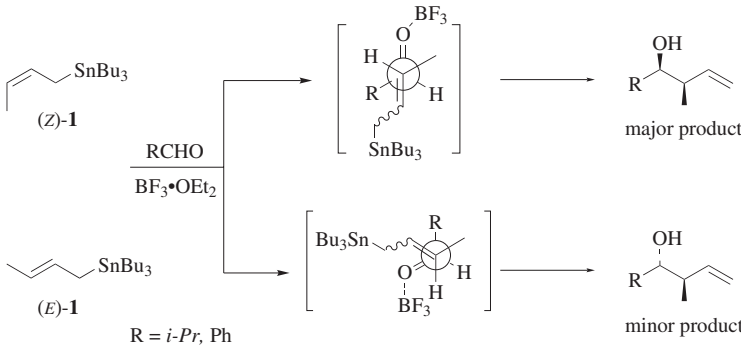
these thermal reactions, the high temperature required for the addition often leads to low chemical yields. As a result, thermal reactions of allylstannanes have not found widespread applications.



(Eq. 2)

Lewis Acid Promoted Additions

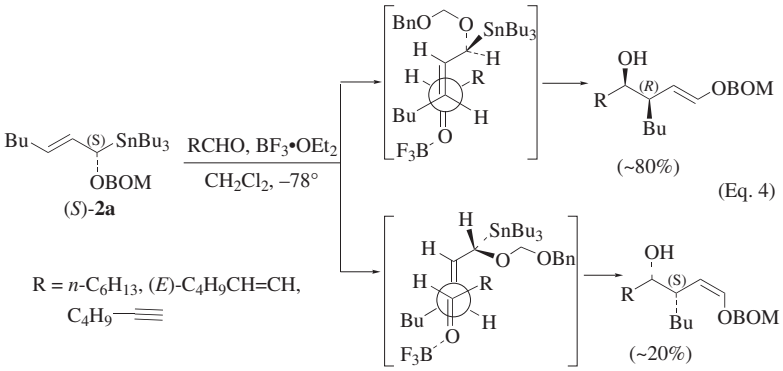
Yamamoto first reported the Lewis acid promoted addition of crotyl tributylstannanes (*E*)- and (*Z*)-**1** to aldehydes in 1980.[5,11] The $BF_3{\cdot}OEt_2$ promoted additions of **1** to benzaldehyde afford >90% of the syn homoallylic alcohol regardless of the geometry of the 2-butenyl unit. More recent studies have shown that aromatic aldehydes are less sensitive to the geometry of the 2-butenyl unit while aliphatic aldehydes, such as cyclohexanecarboxaldehyde, give variable syn/anti ratios of addition products proportional to the starting material geometry.[22] In any case, the syn isomer is always the predominant product (Eq. 3).



(Eq. 3)

An acyclic transition structure was proposed, in which the boron trifluoride is coordinated to the carbonyl oxygen to activate the carbonyl group. Therefore, association of the tin center with the carbonyl oxygen is precluded, unlike as in thermal additions. Since there is no participation of a six-membered, cyclic transition structure, the geometry of the 2-butenyl unit is not of primary importance in the outcome of the product configuration. Among the possible acyclic transition structures, one antiperiplanar arrangement is suggested to lead to the syn homoallylic alcohol.[23] Steric effects are proposed to account for the preference for the syn isomer. The arrangement leading to the syn isomer has the aldehyde alkyl group anti to the methyl group of the 2-butenyl unit in the transition structure (Eq. 3), while the other arrangement, which leads to the anti isomer, has the aldehyde R group gauche to the methyl group. Torsional strain between these two alkyl groups is believed to play a significant role in determining the stereochemical outcome of the reactions. More recent studies, however, suggest that a syn synclinal arrangement is more likely to be the preferred transition state structure on the basis of both steric and secondary orbital interactions.[22]

The reactions of enantioenriched α-alkoxy-2-butenyl(tributyl)stannane **2a** with aldehydes are believed to proceed by a similar mechanism (Eq. 4).[24] Lewis acid promoted additions afford mainly syn products. A molar equivalent of Lewis acid is generally required. There is a strong correlation between the stannane configuration at the allylic center and the configuration of the products. These results are consistent with the acyclic transition structure proposed for 2-butenyltrialkylstannane **1**. The major adducts are believed to be produced by way of the antiperiplanar orientation of the C=C double bond and the aldehyde C=O to minimize steric interactions between the butyl group of the stannane and the aldehyde R group. The energy difference between the two antiperiplanar transition structures has been attributed to the steric environment of the alkoxy group.



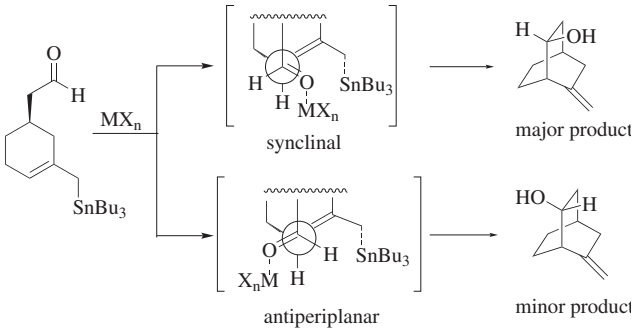
(Eq. 4)

A necessary feature of this acyclic transition structure is the anti relationship between the Bu_3Sn moiety and the forming C–C bond.[6] It is this feature that accounts for the stereoselectivity observed in these additions.

Advantages of these Lewis acid promoted reactions include mild conditions and high chemical yields, while disadvantages include the low diastereoselectivity of the reagents and the difficulty in the preparations of the chiral α-(alkoxy)allylstannanes.

Antiperiplanar vs. Synclinal Arrangement

A model system designed to evaluate the relative importance of the synclinal vs. antiperiplanar arrangements in the Lewis acid promoted additions of allylstannanes to aldehydes has been reported (Eqs. 5 and 6).[25,26]



(Eq. 5)

(Eq. 6)

The stereoselectivity observed for this model system suggests a preference for the synclinal orientation of double bonds. The preference for the synclinal arrangement is explained in terms of stereoelectronic effects such as secondary orbital overlap and/or minimization of charge separation in the transition structures (Figure 1).

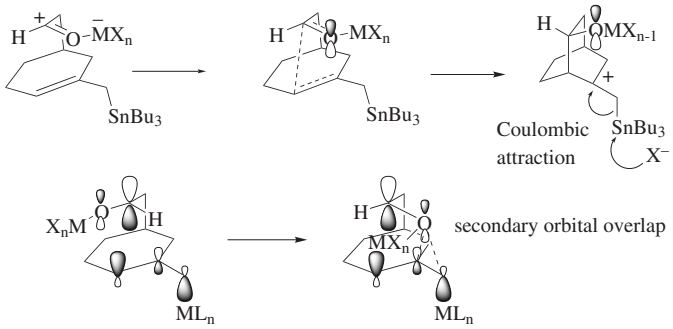
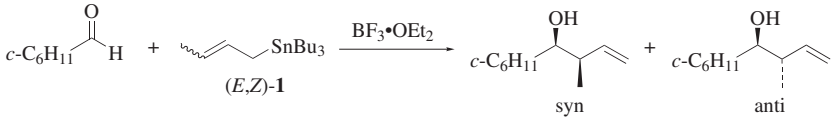


Figure 1. Coulombic attraction and interaction between the HOMO of the allyl metal and LUMO of the aldehyde.

The HOMO of the allylstannane moiety and the LUMO of the aldehyde may participate in secondary orbital overlap in the synclinal transition structure. The preference for the synclinal arrangement is also explained by the minimal charge separation in this rotamer, compared to the antiperiplanar arrangement. Under otherwise identical conditions, the synclinal transition structure appears to be more favorable than the antiperiplanar arrangement. However, the steric repulsion suggested in intermolecular reactions is absent in the model system since there is a carbon tether connecting the aldehyde function and the allylstannane moiety.

The relative importance of the synclinal vs. antiperiplanar arrangements is also a consideration in $BF_3{\cdot}OEt_2$ promoted intermolecular additions of 2-butenylstannane **1** to aldehydes (Eq. 7).[22,27] Stannane (*E*)-**1** is more selective for the formation of the syn homoallylic alcohols than (*Z*)-**1** in the case of cyclohexanecarboxaldehyde.



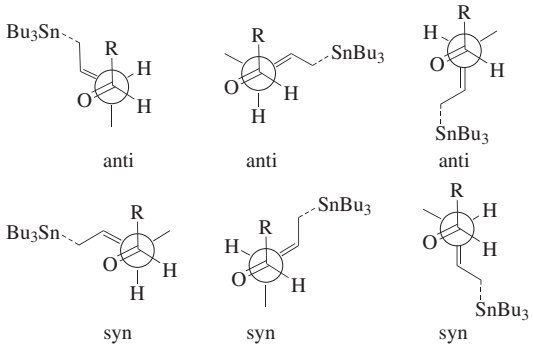
E:Z
90:10
74:26
12:88

syn:anti	
94:6	(88%)
86:14	(80%)
58:42	(82%)

(Eq. 7)

There are six possible staggered conformations leading to the products of these addition reactions. They are labeled "anti" and "syn" for whether they lead to anti or syn diastereomers. The energy differences among these staggered rotamers are small. The diastereoselectivity observed in the reactions of 2-butenyl(trialkyl)stannanes with aldehydes is dependent on the aldehyde structure, stannane configuration, and Lewis acid employed.[22] The higher selectivity observed for (*E*)-2-butenyl(tributyl)stannane is attributed to the synclinal arrangement (first rotamer leading to syn isomer). A

similar conclusion is reached for intramolecular cyclizations in which the synclinal arrangement may be favored due to secondary molecular orbital overlap.[27]

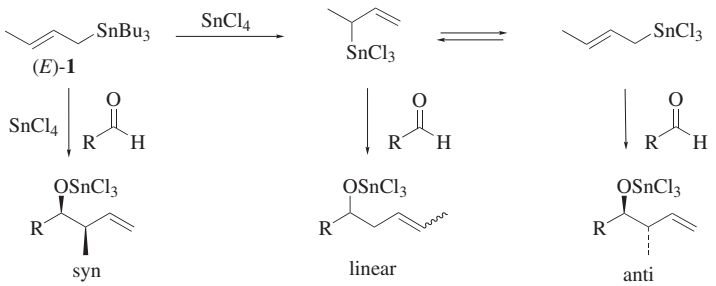


In summary, these studies conclude that there are small energy differences among the rotamers considered. The relative stabilities of the different rotamers may change as structures of the aldehydes or the stannanes change. The configuration of the products is not directly related to antiperiplanar or synclinal arrangement in the transition states in intermolecular reactions. Continuing studies in this area are important to broaden understanding of the mechanism of stereocontrol in these reactions.

Transmetalation Followed by Addition

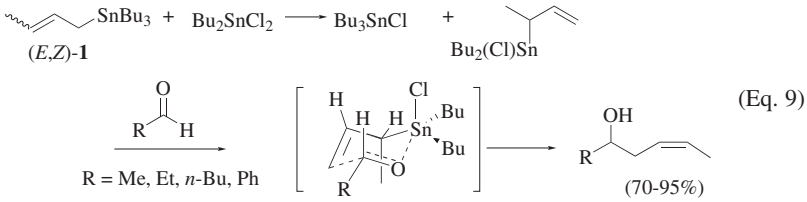
Certain Lewis acids, such as $TiCl_4$, $SnCl_4$, and $InCl_3$, react with allylstannanes in a transmetalation process.[28] The new in situ generated allylic halometal species is usually more reactive than the parent allylstannane and can react with aldehydes at low temperatures. The allylmetal reagents may undergo 1,3-migration of the metal; the rate of migration is often competitive with the addition reaction to aldehydes. This phenomenon can lead to multiple reaction pathways and complex reaction mixtures.[29,30]

Different results may be obtained depending on the order of reagent addition, because the Lewis acid sometimes reacts with the stannane by transmetalation, producing a nucleophile that competes with the stannane itself for the aldehyde. When 2-butenyl(tributyl)stannane (**1**) is treated with $SnCl_4$, the species from transmetalation reacts with the aldehyde affording mainly syn and anti homoallylic alcohols.[28] This observation is consistent with participation of an S_E' reaction between the 2-butenylstannane and $SnCl_4$, generating 3-buten-2-yltin trichloride, which isomerizes to the more stable 2-butenyltin trichloride (Eq. 8).

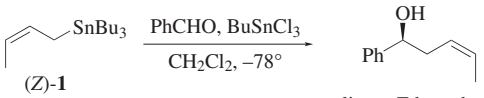


(Eq. 8)

Upon addition of an aldehyde to a mixture of 2-butenyl(tributyl)stannane and $SnCl_4$, the syn homoallylic alcohols are produced by the usual pathway via an acyclic transition structure with $SnCl_4$ acting as the Lewis acid. The anti homoallylic alcohols are produced by way of a six-membered, cyclic transition structure with 2-butenyltin trichloride as the actual reagent. In addition, dibutyltin dichloride and butyltin trichloride also undergo S_E' transmetalation reactions with 2-butenyl(tributyl)stannane (Eqs. 9 and 10).[31–36]



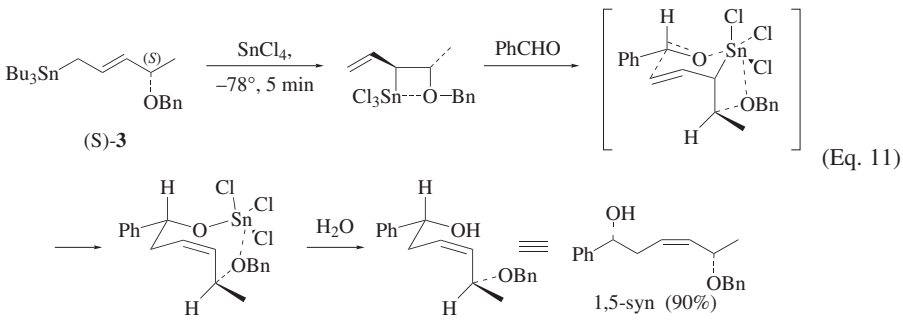
(Eq. 9)



(Eq. 10)

Depending on the character of the Lewis acid, different products can be produced through three distinct reaction pathways (Eq. 8). Adding the reagents to a mixture of the aldehyde and the Lewis acid minimizes transmetalation. Despite potential complications associated with transmetalation, more recent trends have been to employ transmetalation for control of product configuration (see below).

When chiral stannane reagent S-**3** is treated with $SnCl_4$ at $-78°$, the intermediate reacts with aldehydes to give a syn-1,5-enediol (Eq. 11).[12,37] This reaction is selective for both aromatic and aliphatic aldehydes. Other products, including the 1,5-anti diastereomers, account for less than 7% of the product mixture. These reactions proceed with effective 1,5-asymmetric induction.



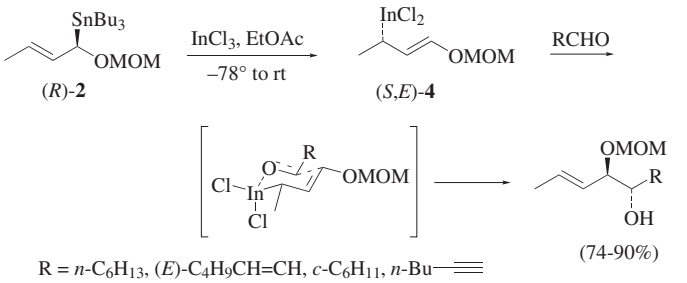
(Eq. 11)

The formation of the 1,5-syn product in these reactions is consistent with a mechanism that involves initial transmetalation of the stannane to give the allylic tin trichloride. It is believed that this trichlorostannane is stabilized by coordination of the oxygen of the benzyloxy group to the electron-deficient tin atom (Eq. 11). The coordination complex is formed stereoselectively so that the methyl and vinyl groups

are trans-disposed about the four-membered ring. The allylic tin trichloride then reacts with the aldehyde, which is added 5 minutes after the allylstannane and $SnCl_4$ are mixed. A six-membered, chair-like, cyclic transition structure controls the facial selectivity of the reaction and establishes the Z geometry of the double bond in the product.

The mild Lewis acid $InCl_3$ undergoes transmetalation with α-alkoxy-2-butenylstannanes in various donor solvents such as ethyl acetate or acetonitrile (Eq. 12).[38] The anti : syn ratio approaches 98 : 2 when the reaction is performed at low temperature. These allylic indium intermediates react with aldehydes to yield anti 1,2-diol monoethers directly. Anti 1,2-diols with greater than 95% ee are obtained from an α-MOM allylic stannane of equal enantiomeric purity. A simplified pathway is presented to explain the stereospecificity (Eq. 12). The chiral stannane (*R*)-**2** experiences anti S_E2' attack on the $InCl_3$ to afford mainly the S,E γ-alkoxy crotyl indium species **4**. Subsequent addition to the aldehyde takes place through a chair-like, cyclic transition structure affording the anti product. However, the $InCl_3$ promoted reactions of 2-butenylstannanes proceed with 2-butenylindium dichloride as the actual addition reagent.[38]

Studies in allylstannane chemistry have evolved from an emphasis on thermal reactions,[10] through Lewis acid promoted reactions,[11] to a current focus on transmetalation prior to addition to aldehydes. Current research seeks to further promote that stereochemical outcomes can be better controlled through transmetalation prior to additions.[13]

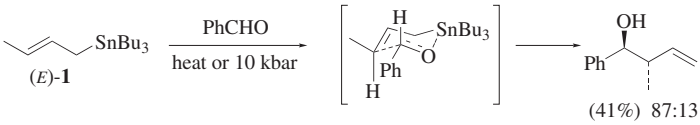


(Eq. 12)

SCOPE AND LIMITATIONS

Reactions of Simple Allyl- and 2-Butenylstannane Reagents

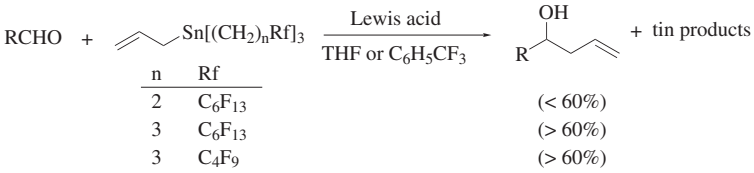
Thermal Reactions. Thermal additions of E 2-butenylstannanes to aldehydes proceed with good to excellent stereoselectivity to give anti homoallylic alcohols (Eq. 13). However, because of the high temperatures or pressure required, their use in synthesis is limited to simple aldehydes.[39]



(Eq. 13)

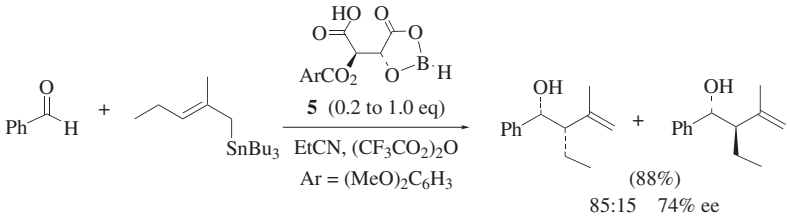
Lewis Acid Promoted Reactions. *Reactions with Achiral Aldehydes*. Lewis acid promoted reactions between allylstannanes and aldehydes typically proceed at −78° and have become practical methods in organic synthesis. Reactions between 2-butenyl(tributyl)stannane (**1**) and aldehydes in the presence of boron trifluoride give syn homoallylic alcohols as the major products with stereoselectivities in the range 90:10 to 98:2 irrespective of the stannane geometry (see Eq. 3).[5,11] When other Lewis acids are examined, mixtures of isomers are observed (see "Transmetalation Followed by Addition" in this section).[28] The geometry of the 2-butenylstannane has a small influence on the configuration of the products.[22]

Recently, a new class of tris-(perfluoroalkylpropyl)allylstannane reagents has been reported (Eq. 14).[40–42] The reagents were developed to facilitate the separation of toxic tin byproducts in organic synthesis. The tris-(alkylpropyl)allylstannane is better than the corresponding tris-(perfluoroalkylpropyl)allylstannane because of its solubility in organic solvents. This new class of "fluorous" reagents is suitable for Lewis acid promoted additions to aldehydes and enables simple workup procedures.[40]



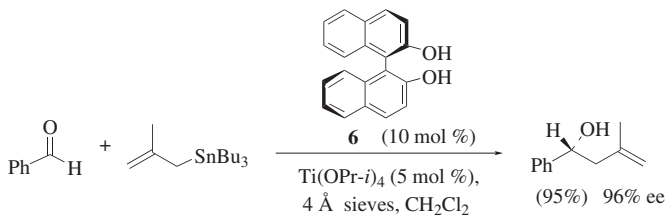
(Eq. 14)

The tartrate derived chiral (acyloxy)borane catalyst (CAB, **5**) promotes catalytic enantioselective reactions of allylic stannanes with aldehydes (Eq. 15).[43] Both aliphatic and aromatic aldehydes can be employed with substituted allylstannanes to produce homoallylic alcohols in good yield and moderate to high regio- and enantioselectivities.



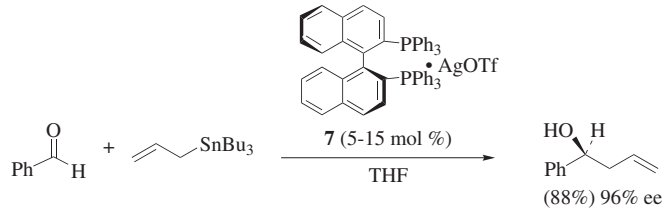
(Eq.15)

A number of binaphthol (**6**) derived chiral Lewis acids have also been applied to the addition of allylstannanes to aldehydes.[44–49] Initial studies used BINOL and either $Ti(OPr\text{-}i)_4$ or $TiCl_2(OPr\text{-}i)_2$ as the Lewis acid promoter. Good yields of homoallylic alcohols with high enantiomeric enrichment are obtained with as little as 10 mol % of the catalyst (Eq. 16).[44] The reaction rate is accelerated when *i*-$PrSSiMe_3$ is added, allowing as little as 2% of the catalyst to be used.[49] The effect of *i*-$PrSSiMe_3$ is presumably due to the formation of $Bu_3SnSPr\text{-}i$ and Me_3SiOR, which results in regeneration of the catalyst.



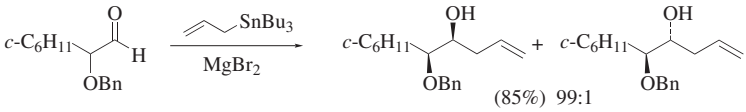
(Eq. 16)

The chiral Lewis acid complex *S*-BINAP · AgOTf (**7**) catalyzes reactions of allylstannanes with aldehydes (Eq. 17).[50,51] The optimal catalyst is generated from a combination of BINAP and AgOTf. This catalyst is more efficient with aromatic aldehydes than with aliphatic aldehydes as measured in both chemical yield and enantioselectivity. It is believed that the BINAP · Ag(I) complex acts as a chiral Lewis acid catalyst rather than as a transmetalation reagent.



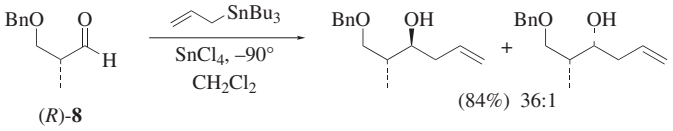
(Eq. 17)

Reactions with Chiral Aldehydes. The Lewis acid promoted additions of allyltributylstannane to chiral α-alkoxy aldehydes give varying degrees of diastereofacial selectivity depending on the Lewis acid and the aldehyde appendages (Eq. 18).[52] The addition of allyltributylstannane to an α-benzyloxy aldehyde is highly syn-selective when $MgBr_2$ is used as the promoter[53,54] under Cram chelation control.[14,55] When $BF_3 \cdot OEt_2$ is the promoter, the addition to α-*tert*-butyldimethylsilyloxy (TBDMSO) aldehydes proceeds via the Felkin-Anh model[16,56] of facial selection to give the anti products. Boron trifluoride has only one coordination site, and therefore cannot form a chelate. The TBDMS protecting group is also known to disfavor chelate formation.[57]



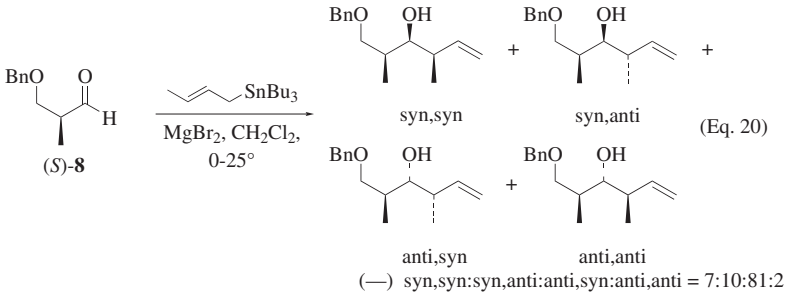
(Eq. 18)

Highly anti selective additions can be realized with α-methyl-β-benzyloxy aldehyde **8** and allyltributylstannane using $SnCl_4$ as the Lewis acid.[58–60] The reaction must be carried out at low temperatures (−90 to −100°) in order to achieve high diastereofacial selectivity. At low temperatures, the six-membered chelate formed between the aldehyde and $SnCl_4$ should be more stable, producing the Cram chelation product (Eq. 19). Competitive transmetalation apparently does not occur at −90°, resulting in an acyclic transition state for the addition reaction. Thus the tin(IV) chloride serves only as Lewis acid with the aldehyde.



(Eq. 19)

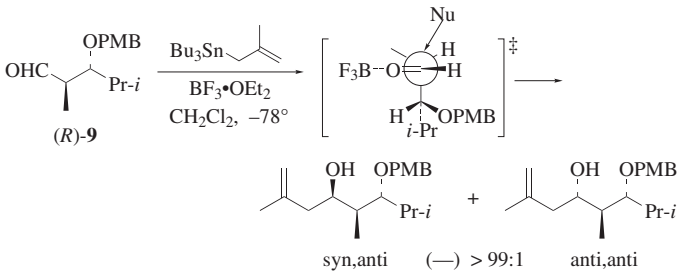
Diminished stereocontrol is observed in the Lewis acid promoted reactions of aldehyde **8** with 2-butenylstannane **1** (Eq. 20).[58] The chelation-controlled reaction catalyzed by $MgBr_2$ is relatively more selective. The observed stereoselectivity is consistent with the Cram chelation-control model.



(Eq. 20)

(Eq. 20)

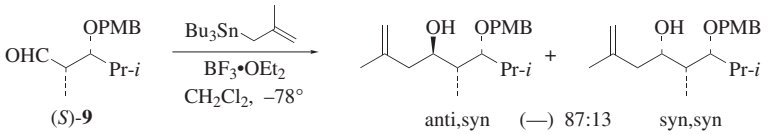
Reactions between a chiral aldehyde and an achiral nucleophile proceed under substrate control. Although aldehyde **8,** with one α-stereocenter, shows only a modest diastereofacial bias, chiral aldehyde (*R*)-**9** with a second stereocenter at the β-carbon shows excellent stereoselectivity under similar reaction conditions (Eq. 21).[17]



(Eq. 21)

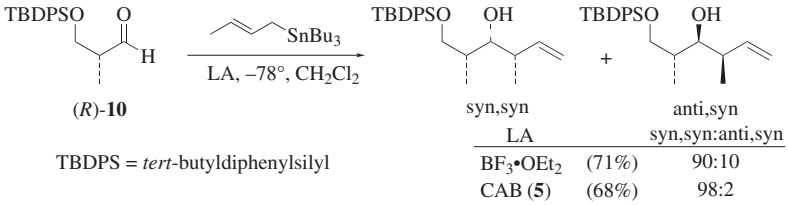
Aldehydes with two stereocenters and allyl- and methallyltributylstannanes react in the presence of boron trifluoride to give homoallylic alcohols with >99 : 1 stereoselectivity. The product configuration is consistent with the nucleophilic attack following the Felkin-Anh model.[17,61] This is an example of merged 1,2- and 1,3-asymmetric induction, with the stereogenic centers operating in a cooperative fashion to direct the facial selection.[11] Although there are relatively few examples to demonstrate the generality of this trend, all reported results follow the selection rules. The enhanced selectivity is explained as shown in Eq. 21. The relative orientation of the BF_3-complexed carbonyl and the α-chiral center follow the Felkin-Anh model, resulting in a 1,2-syn, 1,3-anti stereochemical relationship.

Under the same conditions the 2,3-syn aldehyde diastereomer **(*S*)-9** produces the anti, syn isomer with reduced selectivity (Eq. 22). This finding is consistent with a mismatch in 1,2- and 1,3-asymmetric induction with a higher level of control of facial selectivity by the β-stereocenter. When a bulky Lewis acid (Ph_3CClO_4) is employed, the process reverts to 1,2-stereocontrol and the syn, syn product is predominant. This reversal in aldehyde facial induction indicates that the α-stereocenter becomes the dominant control element as the steric demands of the Lewis acid increase.[17]

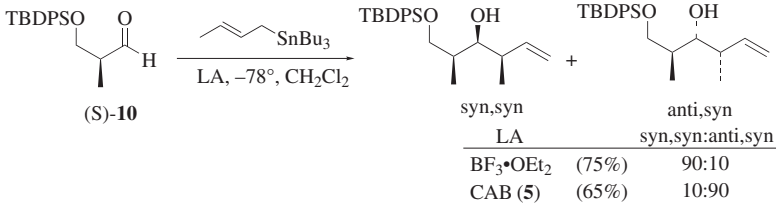


(Eq. 22)

Reactions of the α-methyl-β-silyloxy aldehyde **10** with 2-butenyl(tributyl)stannane (**1**) have been studied with one equivalent of either $BF_3{\cdot}OEt_2$ or the chiral catalyst CAB (**5**) (Eqs. 23 & 24).[62] This study provides an example of a reaction with both a chiral aldehyde and a chiral promoter. A matched/mismatched pairing of the aldehyde and CAB promoter is observed. It was previously shown that CAB promotes the addition of allylic stannanes to achiral aldehydes in up to 90% ee. The dipropionate adduct with syn, syn configuration is obtained with 98 : 2 diastereoselectivity when CAB is used as the promoter with the aldehyde (*R*)-**10** (Eq. 23). The $BF_3{\cdot}OEt_2$ promoted reactions give 90 : 10 diastereofacial selectivity in favor of the syn, syn isomer with either aldehyde (Eqs. 23 and 24).



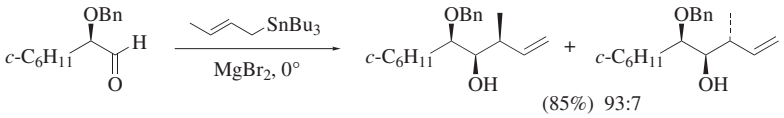
(Eq. 23)



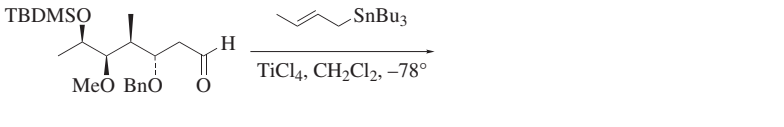
(Eq. 24)

The reaction promoted by CAB with the aldehyde (*S*)-**10** affords 90 : 10 diastereoselectivity in favor of the anti, syn product (Eq. 24). The chiral Lewis acid CAB overrides the diastereofacial bias of aldehyde (*S*)-**10** in this case. Similar to a previous example involving aldehyde **8** (Eqs. 19 and 20), the α-methyl-β-alkoxy aldehyde **10** has a relatively weak diastereofacial bias.

$MgBr_2$ promoted additions of 2-butenyl(tributyl)stannane (**1**) to α-alkoxy chiral aldehydes gives a mixture of isomers in the range of 93 : 7 in favor of the syn, syn diastereomer (Eq. 25).[22,63] The starting stannane **1**, enriched in the E isomer, gives slightly higher selectivity than the stannane **1** mixture that is enriched in the Z isomer. The addition of **1** to the β-alkoxy aldehyde shown in Eq. 26 preferentially gives the 1,3-anti diol when either $TiCl_4$ or $BF_3 \cdot OEt_2$ is used as the promoter.[64] Both the Cram chelation model and the Evans dipolar model predict the anti product.



(85%) 93:7 (Eq. 25)



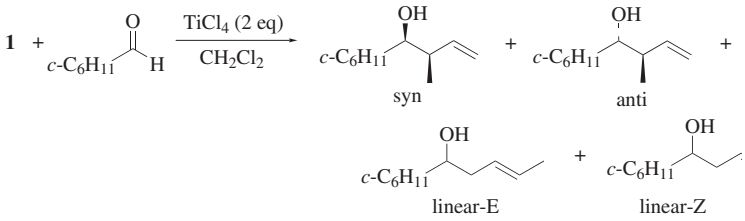
(65%) 12:1 (Eq. 26)

TBDMS = *tert*-butyldimethylsilyl

In Lewis acid mediated additions, allylstannanes attach to aldehydes through an open transition state. Therefore, 1,2-syn configuration is obtained in the major product when 2-butenylstannane is used. As described in this section, the configuration of the substrate controls the stereochemistry of the product in a predictable course, i.e., 1,2-syn and 1,3-anti product configurations are favored. The diastereoselectivity varies depending on the substrates and reaction conditions. The ready availability of various allylstannanes from their corresponding 2-alkenyl halides and the predictability of the stereochemical outcome have made allylstannane reagents a popular choice for many synthetic chemists.

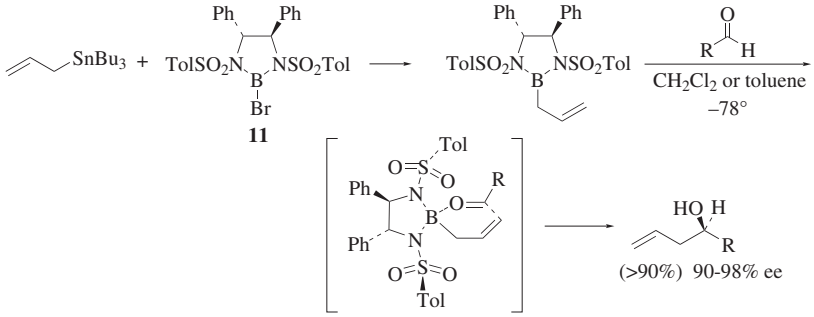
Transmetalation Followed by Addition. Certain Lewis acids (either achiral or chiral) react with allylstannanes to give new allylmetal species, which afford homoallylic alcohols in a stereocontrolled fashion when reacted with aldehydes. The desired outcome can be obtained by choosing an appropriate Lewis acid.

Reactions Promoted by $TiCl_4$. Transmetalation occurs when $TiCl_4$ is used as the Lewis acid. A crossover in syn/anti preference is observed when the order of addition of the reactants is reversed. Addition of the 2-butenylstannane **1** to a 1 : 1 mixture of the aldehyde and $TiCl_4$ affords the syn adduct as the major product (Eq. 27). However, when the aldehyde is added to premixed stannane and excess $TiCl_4$ the anti isomer is predominant. It is proposed that a transient allyltitanium species is generated, which adds to the aldehyde through a cyclic transition structure.[28] When the Lewis acids employed are $SnCl_4$, $BuSnCl_3$, or Bu_2SnCl_2, transmetalation also occurs prior to aldehyde addition (Eqs. 10 & 11). The major product is usually the linear Z alkene.[31–36]



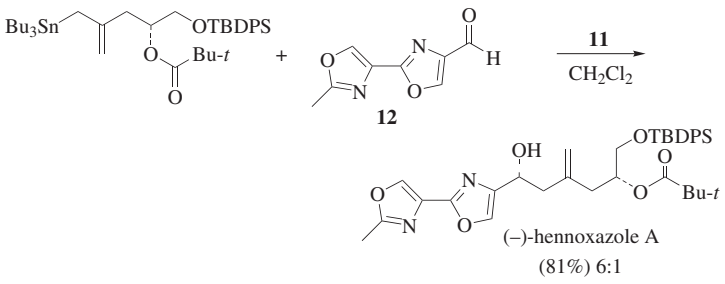
(Eq. 27)

Reactions Promoted by a Chiral Borane. The (*R*,*R*)- and (*S*,*S*)-1,2-diamino-1,2-diphenylethane derived bromoborane **11** promotes enantioselective reactions of allylic stannanes with aldehydes (Eq. 28).[65] Both aliphatic and aromatic aldehydes can be employed with the allylstannane to produce homoallylic alcohols in high yield and high enantioselectivity. A chiral allylic borane species is believed to be the intermediate.



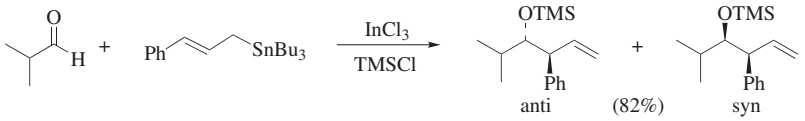
(Eq. 28)

A number of applications of this methodology using more complex allylstannanes are reported.[66,67] An example is shown for the preparation of the marine alkaloid (−)-hennoxazole A (Eq. 29).[67] The formation of the key intermediate homoallylic alcohol is achieved by transmetalation of the allylic stannane with bromoborane (*R*,*R*)-**11** to yield an allylic borane for addition to aldehyde **12**. Stereocontrol is principally induced from the sulfonamide in this case.



(Eq. 29)

Reactions Promoted by $InCl_3$. Cinnamyl tributyltin adds to isobutyraldehyde in the presence of $InCl_3$.[68] In this case, $InCl_3$ serves as the catalyst and TMSCl is used as the catalyst-liberating reagent (Eq. 30). The diastereoselectivity of the addition is solvent dependent ranging from 88 : 12 anti : syn in acetonitrile at 25°, to 12 : 88 anti : syn in methylene chloride at −30°. The former addition proceeds by transmetalation to the cinnamyl dichloroindium species, which adds to the aldehyde by way of a cyclic transition state. In the latter addition, $InCl_3$ serves as a Lewis acid and the reaction proceeds by the usual acyclic transition state to give predominantly the syn adduct.

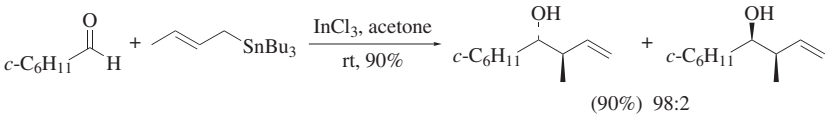


(Eq. 30)

TMS = trimethylsilyl

	anti:syn
CH_3CN, 25°	88:12
CH_2Cl_2, –30°	12:88

$InCl_3$ is found to undergo transmetalation with 2-butenylstannane **1** in acetone and acetonitrile and the resulting intermediates afford anti adducts with aldehydes (Eq. 31).[38] These findings allow direct access to anti homoallylic alcohols and expand the scope of the reactions of 2-butenyl(tributyl)stannane.

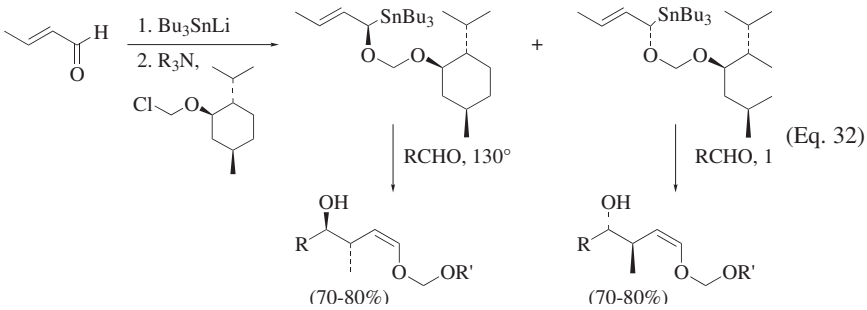


(Eq.31)

The reactive nature of allylstannanes makes it possible to transfer the allyl group to a different metal center (Ti, B, and In) before the addition to a carbonyl group occurs. This new allylmetal species can react with different stereochemical outcomes. Thus transmetalation provides a means to expand the scope of allylstannane chemistry. More work is needed in this area to explore the scope and limitations of transmetalation.

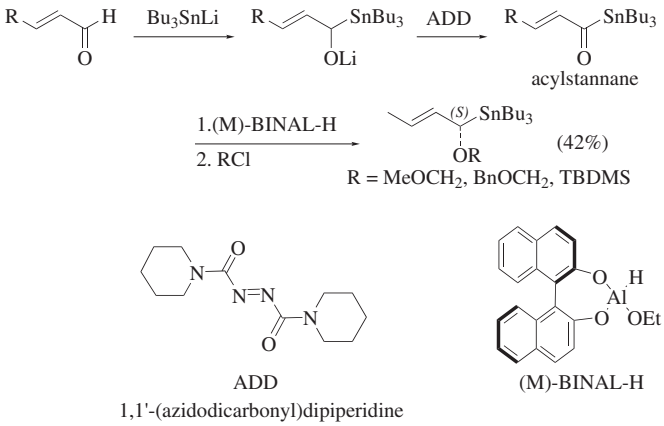
Reactions of α-(Alkoxy)allylstannane Reagents

Preparation of α-(Alkoxy)allylstannane Reagents. Racemic α-(alkoxy)allylstannane reagents are prepared by the addition of (tri-*n*-butylstannyl)lithium to (*E*)-2-butenal followed by protection of the hydroxy group with methyl chloromethyl ether (MOMCl) or benzyl chloromethyl ether (BOMCl).[69,70] Enantiomerically pure α-(alkoxy)allylstannane reagents were initially prepared by replacing the MOM ether protecting group with (−)-(menthyloxy)methyl ether followed by chromatographic separation of the resulting diastereomers (Eq. 32).[71]



(Eq. 32)

A more general, but also more technically demanding, approach to enantioenriched α-(alkoxy)allylstannanes involves asymmetric reduction of the stannyl ketone, which is obtained by oxidation of the α-hydroxystannane (Eq. 33).[24,72] Reduction of the acylstannane with BINAL-H reagents[73] or with the Chirald® reagent produces enantioenriched α-hydroxystannanes. ("Chirald reagent" is a complex formed from $LiAlH_4$ and Darvon alcohol. Darvon alcohol is available from Aldrich Chemical Company as "Chirald®" [(*2S,3R*)-(+)-4-dimethylamino-1,2-diphenyl-3-methyl-2-butanol].) The BINAL-H reduction affords materials of 95% ee or better. The Chirald reagent is less selective yielding alcohols of 70% ee. These hydroxystannanes are unstable and should be converted into stable alkoxymethyl or silyl ethers immediately after they are generated.

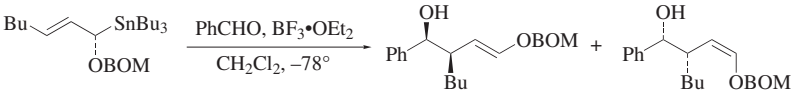


(Eq. 33)

Thermal Reactions. Thermal additions of α-(alkoxy)allylstannanes to aromatic and secondary alkyl aldehydes proceed efficiently to give the 1,2-anti Z alkenes with excellent stereoselectivity (see Eq. 2).[19,20] However, because of the high temperatures required for these reactions, thermal additions have not found widespread use in synthesis.

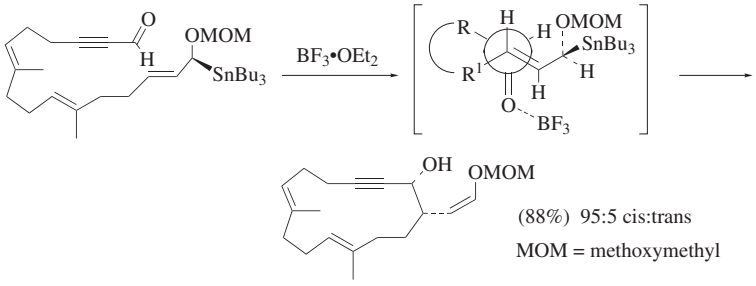
Lewis Acid Promoted Reactions. *Reactions with Achiral Aldehydes.* Boron trifluoride promoted reactions between enantioenriched α-(alkoxy)allylstannanes

and aldehydes proceed at −78° through an allylic inversion process (S_E').[24] In contrast to thermal reactions, $BF_3 \cdot OEt_2$ promoted reactions afford mainly syn products with syn : anti ratios in the range of 90 : 10 (Eq. 34). Stereoinduction from the stannane reagents to the homoallylic alcohols is high with the major product containing an E enol ether and the minor isomer a Z enol ether. These two diastereomeric products have opposite configurations at the two stereocenters.



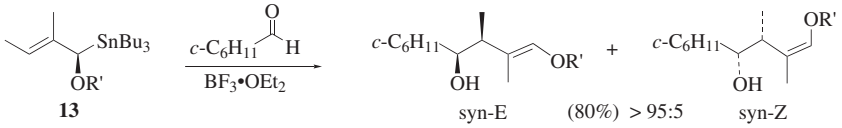
BOM = benzyloxymethyl (80%) 90:10 (Eq. 34)

Although the intermolecular reactions of α-(alkoxy)allylstannanes and aldehydes produce mainly the diastereomer with an E enol ether, the corresponding intramolecular reactions afford mainly the Z enol ether.[74] The enantioenriched S α-alkoxy allylic stannanyl ynal depicted in Eq. 35 is treated with $BF_3 \cdot OEt_2$ at −78° giving the 14-membered cembranolide precursor in 88% yield with only minor amounts of other diastereomers.[74] The preference for the Z enol ether isomer is explained by assuming a synclinal transition structure. Since the aldehyde and stannane are connected by a carbon tether in the intramolecular reaction, the antiperiplanar arrangement of C=O and C=C is disfavored. The usually unfavorable steric interactions between R^1 and R are overcome in the intramolecular reactions. The alternate synclinal transition state, which would produce an E enol ether, appears to be disfavored possibly due to the "outside" alkoxy arrangement.[75,76]



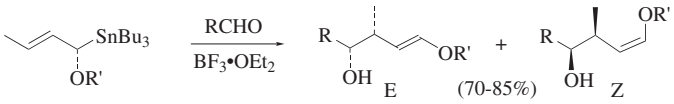
(88%) 95:5 cis:trans
MOM = methoxymethyl (Eq. 35)

The addition of β-methyl-α-(alkoxy)allylstannane **13** to aldehydes in the presence of $BF_3 \cdot OEt_2$ has also been studied.[77] Of the four possible diastereomeric products, a uniformly high yield of syn-E-isomer is obtained (Eq. 36). The stannane **13** fails to react with benzaldehyde under the same conditions.



(80%) > 95:5 (Eq. 36)

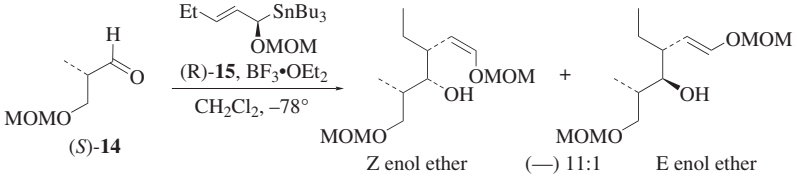
Fair to good syn E selectivities are observed for the reactions of α-(alkoxy)-2-butenylstannanes with aliphatic aldehydes, while excellent syn Z selectivities are observed with aromatic aldehydes (Eq. 37).[78,79] The difference between aromatic and aliphatic aldehydes is explained on the basis of steric and electronic effects as well as the importance of the Lewis acid-aldehyde complexes.[79–81]



R'	R	E:Z
CH_2OBn	*c*-C_6H_{11}	80:20
CH_2OBn	Ph	< 5:95
(8-phenylmenthyl)oxymethyl	*c*-C_6H_{11}	82:18
(8-phenylmenthyl)oxymethyl	Ph	< 5:95

(Eq. 37)

Reactions with Chiral Aldehydes. Double stereodifferentiation is observed when α-(alkoxy)allylstannanes are treated with α-substituted aldehydes in the presence of boron trifluoride.[82] The reaction of aldehyde (*S*)-**14** with stannane (*R*)-**15** proceeds at $-78°$ to give an 11:1 mixture of Z and E enol ethers in 85% yield (Eq. 38). The configuration of the major isomer is consistent with the Felkin-Anh model of facial selection with respect to the aldehyde. The syn relationship between the two new stereocenters is consistent with the open transition structure arrangement discussed earlier. The E enol ether is presumed to arise from a small amount of S stannane present in the starting material. Addition of (*S*)-**15** to (*S*)-**14** proceeds slowly and produces a mixture of five products of which the E enol ether is the major one. Thus the S aldehyde and the R stannane represent a matched pair whereas the S aldehyde and the S stannane are mismatched.

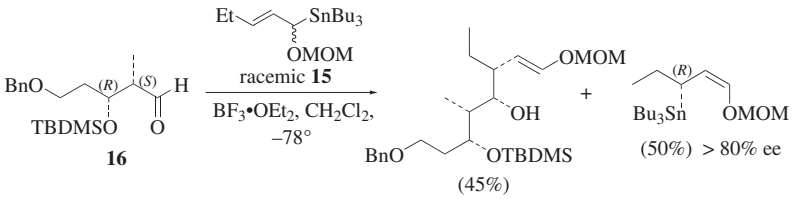


(Eq. 38)

In contrast to the above example, products with E enol ethers are predominant in reactions between achiral aldehydes and α-(alkoxy)allylstannanes. Therefore, this example shows that small changes in aldehyde structure can lead to significant changes in product stereostructure. Since all reported cases of electrophilic additions to chiral allylic stannanes proceed by an exclusive anti S_E' pathway, the product configurational change corresponds to variations in the transition structure arrangement. This result is consistent with an earlier conclusion that the various staggered rotamers of the transition structures differ only slightly in energy.[22]

When an aldehyde with both an α- and a β-chiral center is allowed to react with racemic α-(alkoxy)allylstannane **15**, a mixture of products is isolated (Eq. 39). The addition product is the E enol ether (45%). The configuration of this adduct con-

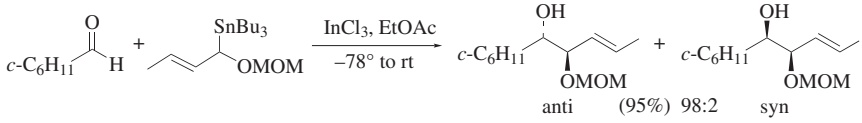
forms to the usual pattern of facial selection, i.e., Felkin-Anh control with respect to the aldehyde and syn selectivity with respect to the newly formed two stereocenters. Other products include the recovered aldehyde **16** (40%) and the optically active γ-alkoxy allylic stannane (50%). A kinetic resolution occurs in which only (*S*)-**15** reacts with aldehyde **16**. The γ-alkoxy allylic stannane is produced via a stereospecific 1,3-migration of tributyltin, which is discussed in the next section. The α-S-β-R aldehyde **16** reacts with the reagent S stannane but not the R stannane. Since the α-S aldehyde **14** and the R stannane are a matched pair in asymmetric induction, this result suggests that the β stereocenter plays a role in determining the outcome of the reaction. However, it is not a deciding role as in those reactions that employ achiral allylstannanes.[17] The E enol ether double bond of the adduct is more in line with additions involving achiral aldehydes.



(Eq. 39)

Racemic α-(alkoxy)allylstannanes are easily prepared by addition of Bu_3SnLi to an α,β-unsaturated aldehyde followed by protection of the resulting hydroxy group. However, the preparation of enantiomerically pure α-(alkoxy)allylstannanes requires a laborious procedure. The diastereofacial selectivity in a reagent-controlled reaction is moderate. Chiral allylboranes and boronates may be a better choice if a reagent-controlled asymmetric induction is required.

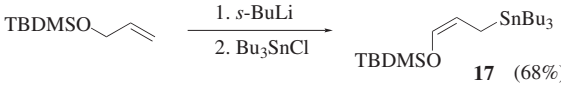
Transmetalation Followed by Addition. *Reactions Promoted by $InCl_3$.* $InCl_3$ is found to effect a stereospecific anti S_E2' transmetalation of alkoxy stannanes to give a transient allylindium reagent, which adds stereoselectively to aldehydes yielding anti adducts.[83] Ethyl acetate is found to be a superior solvent for this reaction. While 2-butenyl(tributyl)stannane (**1**) reacts with aldehydes under these conditions through a more stable 2-butenylindium species, the α-alkoxy stannanes react through 3-butenyl-2-yl indium species. Apparently the alkoxy group slows the rate of 1,3-migration of the indium. The chirality of the alkoxy stannanes is effectively transferred to the products. These findings allow direct access to monoprotected 1,2-anti diols (Eq. 40) and expand the scope of the reactions of α-alkoxy-2-butenyl(tributyl)stannanes. The utility of this reaction is demonstrated in the stereoselective synthesis of four of the eight possible isomers of hexose precursors.[83] In each case, reagent control is a dominant factor in determining product stereochemistry.



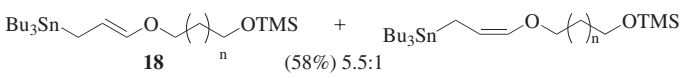
(Eq. 40)

Reactions of Achiral γ-(Alkoxy)- and γ-(Silyloxy)Allylstannane Reagents

Preparation of γ-(Alkoxy)- and γ-(Silyloxy)Allylstannane Reagents. Simple Z γ-alkoxy and γ-silyloxyallylstannane reagents **17** are prepared by lithiation of the allylic ether and subsequent addition of Bu_3SnCl (Eq. 41).[84] Preparation of the corresponding E isomers **18** is more difficult, but can be effected through addition of Bu_3SnH to an allenyl ether in the presence of a palladium catalyst (Eq. 42).[85]



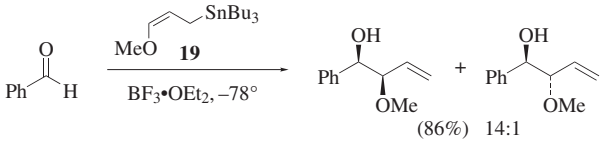
17 (68%) (Eq. 41)



18 (58%) 5.5:1 (Eq. 42)

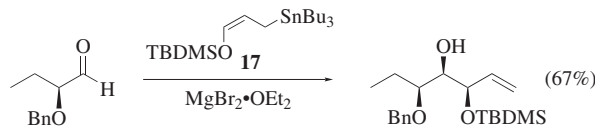
TBAF = tetrabutylammonium fluoride
HMDS = hexamethyldisilazane

Lewis Acid Promoted Reactions. *Reactions with Achiral Aldehydes*. While the addition of 2-butenylstannanes to aldehydes produces homoallylic alcohols, which are useful in the preparation of polypropionates (polyketides), the addition of γ-(alkoxy)allylstannanes to aldehydes gives monoprotected 1,2-diols, as illustrated by the addition of γ-(methoxy)allylstannane **19** to benzaldehyde (Eq. 43).[86] The diols are useful intermediates for the preparation of carbohydrates and other polyhydroxy natural products. The reactions of (γ-methoxy)allylstannanes with both aromatic and aliphatic aldehydes have been reported.[86] By analogy to simple 2-butenylstannanes, mainly syn adducts are isolated with all aldehydes in the presence of $BF_3{\cdot}OEt_2$ at −78°.

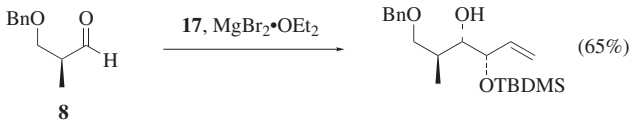


(86%) 14:1 (Eq. 43)

Reactions with Chiral Aldehydes. The reactions of γ-(silyloxy)allylstannane **17** with both α-alkoxy and α-methyl aldehydes in the presence of $MgBr_2$ have been studied (Eqs. 44 and 45).[84] With α-substituted aldehydes, the products are the syn, syn adduct for the α-alkoxy aldehyde and the syn, anti isomer for the α-methyl aldehyde **8**. In both cases the observed products arise by attack of the allylic stannane on a $MgBr_2$-chelated aldehyde.

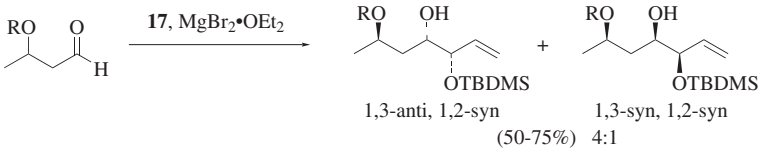


(Eq. 44)



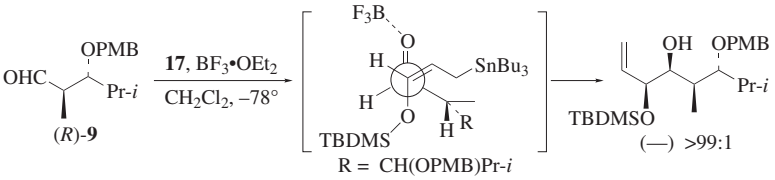
(Eq. 45)

Diminished selectivity is observed for β-alkoxy aldehydes (Eq. 46). The major isomer arises from 1,3-anti asymmetric induction, which is consistent with both a chelation-controlled model and Evans' dipolar model.[17] The 1,2-syn diol relationship in the products is consistent with the acyclic transition structure described earlier.



(Eq. 46)

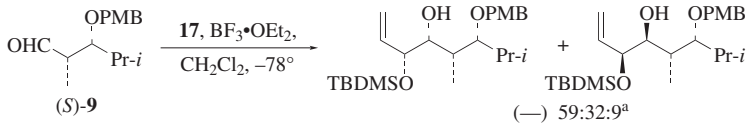
The reactions of γ-(silyloxy)allylstannane **17** with aldehydes possessing both an α and a β stereocenter with the use of $BF_3{\cdot}OEt_2$ as the promoter have been reported. With anti β-branched aldehyde (*R*)-**9**, merged 1,2- and 1,3-asymmetric induction is observed (Eq. 47), similar to the reaction observed for simple allylstannanes (vide infra).[17] Namely, 1,2-asymmetric induction follows the Felkin-Anh model and 1,3-asymmetric induction follows the dipolar model. The major syn, syn, anti product is favored by >99 : 1.



(Eq. 47)

With syn β-branched aldehyde (*S*)-**9** under the same conditions, the reaction gives a mixture of three isomers (ratio = 59 : 32 : 9) with the major product being the all syn isomer (Eq. 48). In this case the two stereocenters of the aldehyde are biased in opposite directions for attack on the carbonyl group. In contrast to reactions involving simple allylstannanes, the α-stereo center of aldehyde substrates is more important in determining the outcome of the facial attack (Felkin-Anh control), even with

a small Lewis acid for reactions of γ-oxygenated stannanes. This change in π-facial selection from simple allylstannanes to (γ-silyloxy)allylstannanes is attributed to the steric bulk of the TBDMSO group of stannane **17**. Thus, either an increase in the size of the Lewis acid or an increase in the size of the nucleophile can enhance the facial selectivity controlled by the aldehyde α-stereo center.

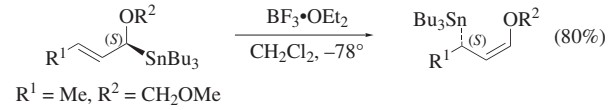


(Eq. 48)

[a] The third unpictured product is the Felkin-Anh 3,4-*anti* diastereomer.

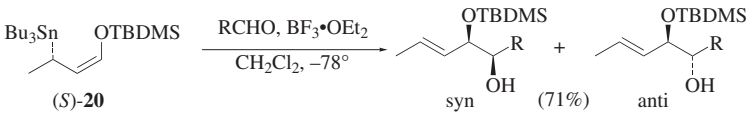
Reactions of Chiral γ-(Alkoxy) and γ-(Silyloxy)Allylstannane Reagents

Preparation of Enantioenriched γ-(Alkoxy) and γ-(Silyloxy)Allylstannane Reagents. In the absence of a reactive aldehyde, α-(alkoxy)allylstannanes are isomerized by BF_3·OEt_2 to Z γ-(alkoxy)allylic stannanes (Eq. 49).[87] This isomerization proceeds by an intermolecular pathway with allylic and configurational inversion.[72] This discovery opened an efficient entry to enantiomerically enriched γ-(alkoxy)- and γ-(silyloxy)allylstannane reagents.



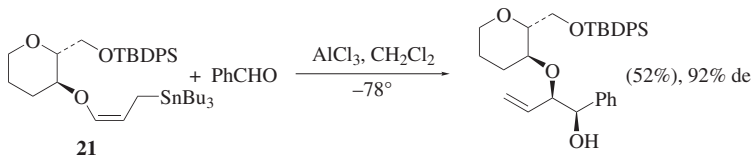
(Eq. 49)

Lewis Acid Promoted Reactions. *Reactions with Achiral Aldehydes*. When the γ-(alkoxy)allylstannane **20** is reacted with aldehydes in the presence of a Lewis acid, mainly syn monoprotected 1,2-diols are isolated (Eq. 50).[6] These reactions proceed stereospecifically by an anti S_E2' pathway, similar to the pathway described for simple allylstannanes. The enantiomeric purity of the product is equal to that of the starting stannane. This method has been applied in natural product total synthesis as discussed in the section entitled Applications in Synthesis.



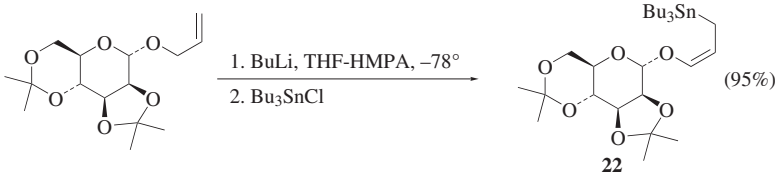
(Eq. 50)

The reaction of the chiral γ-(alkoxy)allylstannane **21** with aldehydes in the presence of a Lewis acid entails a synthesis of syn 1,2-diol derivatives (Eq. 51).[88] Both aromatic and aliphatic aldehydes afford syn adducts with diastereoselectivities greater than 97 : 3 in reactions promoted by BF_3·OEt_2, $AlCl_3$, or $AlCl_3$ · OEt_2. The use of $TiCl_4$ and $SnCl_4$ gives unsatisfactory results. The diastereoselectivity is highest when $AlCl_3$ or $AlCl_3$ · OEt_2 is used, whereas BF_3·OEt_2 leads to slightly decreased selectivity.



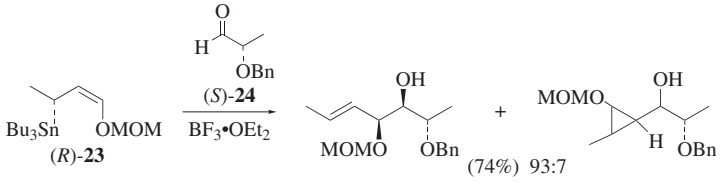
21 (Eq. 51)

The mannose-derived γ-(alkoxy)allylstannane **22** is prepared from allyl 2,3:5,6-di-*O*-isopropylidene-α-D-mannopyranoside by metalation with *n*-BuLi in THF-HMPA at −78° followed by treatment of the allyl anion with Bu_3SnCl (Eq. 52).[89] This γ-(alkoxy)allylstannane is reported to give modest diastereoselectivity (ratio = 7:1) when reacted with α-(benzyloxy)acetaldehyde in the presence of $BF_3{\cdot}OEt_2$, and high selectivity with chiral aldehydes.[89] The configuration of the major product deriving from the $BF_3{\cdot}OEt_2$ catalyzed reaction is suggested to result from an acyclic transition structure pathway.

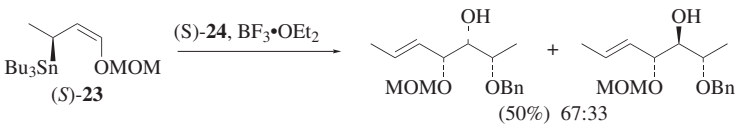


22 (Eq. 52)

Reactions with Chiral Aldehydes. Reactions of γ-(alkoxy)- and γ-(silyloxy)allystannane reagents and (*S*)-2-(benzyloxy)propanal (**24**) with Lewis acids $BF_3{\cdot}OEt_2$ and $MgBr_2$ as the promoters have been studied (Eqs. 53–56).[90,91] In the $BF_3{\cdot}OEt_2$ promoted reaction, the R stannane and the S aldehyde exhibit matching pair characteristics (Eq. 53). Addition of the (MOM)oxystannane (*R*)-**23** to propanal **24** in the presence of $BF_3{\cdot}OEt_2$ gives a 93:7 mixture of E syn, anti alcohol and cyclopropyl adduct in 74% yield. On the other hand, the stannane (*S*)-**23** affords a 67:33 mixture of E syn, syn and E anti, anti diastereomers upon addition of the S aldehyde (Eq. 54). The matched pair reaction is proposed to be consistent with an anti S_E' pathway. The E geometry of the product indicates a preferred E arrangement of the incipient double bond in the transition state. With these two constraints, the transition structure is suggested to have the C=O and the C=C assume an antiperiplanar relationship. The diastereofacial selection with respect to (*S*)-2-(benzyloxy)-propanal (**24**) is consistent with the Felkin-Anh model. The $BF_3{\cdot}OEt_2$ promoted addition of γ-(silyloxy) and γ-(alkoxy)allylstannanes (e.g. **23**) to aldehyde **24** is proposed to be under reagent control.

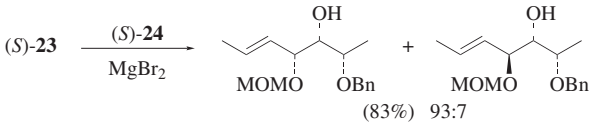


(*R*)-**23** (Eq. 53)

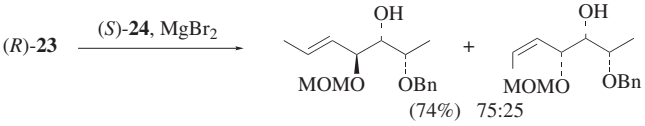


(Eq. 54)

Addition of the γ-(alkoxy)allylstannanes **23** to aldehyde **24** in the presence of $MgBr_2$ proceeds slowly to give a reversed matched/mismatched pair (Eqs. 55 and 56). A 93 : 7 mixture of E syn, syn and E anti, syn alcohols is obtained in the reaction of the S stannane and (*S*)-**24**. The corresponding R stannane gives a 75 : 25 mixture of E anti, syn and Z syn, syn alcohols. The major product of Eq. 55 arises from chelation control while the major isomer of Eq. 56 is consistent with Felkin-Anh selection.

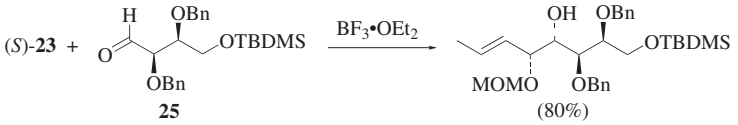


(Eq. 55)



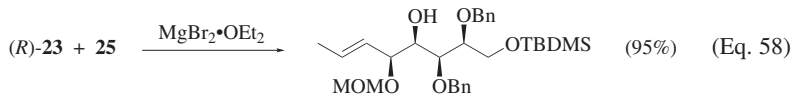
(Eq. 56)

When the S stannane **23** reacts with the tartrate-derived aldehyde **25** in the presence of $BF_3{\cdot}OEt_2$, the only detectable product is the syn, anti, syn alcohol (Eq. 57). The aldehyde **25** has an α-R chiral center. All three stereogenic centers in the starting materials favor the same stereochemical path in this reaction. However, examination of a model transition structure indicates a mutual exclusion of Felkin-Anh and Evans' dipolar models for this reaction. A combination of Cornforth model for 1,2-asymmetric induction and Evans' model for 1,3-asymmetric induction appears to be more reasonable.[92] Further studies are needed to clarify the true transition structure.

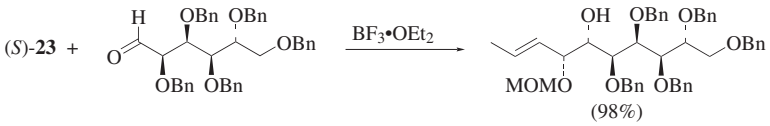


(Eq. 57)

Several other matched pairings were also examined. The tartrate-derived aldehyde **25** affords the syn, syn, syn alcohol as the only detectable product upon $MgBr_2$ promoted reaction with the stannane (*R*)-**23** (Eq. 58). This reaction proceeds by chelation control and matched pairing of stannane and aldehyde. Addition of stannane (*S*)-**23** to pentabenzylglucose yields a single alcohol in the presence of $BF_3{\cdot}OEt_2$ (Eq. 59). This reaction follows Felkin-Anh selection with regard to aldehyde facial differentiation. The S stannane reagent greatly enhances the stereoselectivity by matched double asymmetric induction.

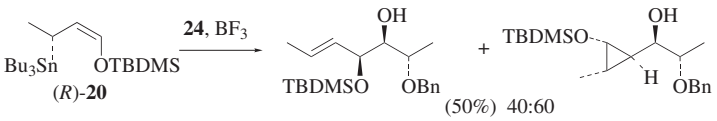


(Eq. 58)



(Eq. 59)

Protecting groups appear to play a significant role in the outcome of these reactions. Up to 60% of the total adduct is the cyclopropylcarbinol when the γ oxygen of the stannane reagent is protected as a TBDMS ether (Eq. 60).[91] A 40:60 mixture of the E syn, anti adduct and the cyclopropylcarbinol is isolated when the protected stannane (*R*)-**20** is reacted with (*S*)-2-(benzyloxy)propanal (**24**) in the presence of $BF_3{\cdot}OEt_2$. The cyclopropylcarbinol is suggested to arise by the initial attack of the enol ether double bond on the aldehyde-$BF_3{\cdot}OEt_2$ complex followed by 1,3-nucleophilic ring closure of the intermediate carbocation (Figure 2).



(Eq. 60)

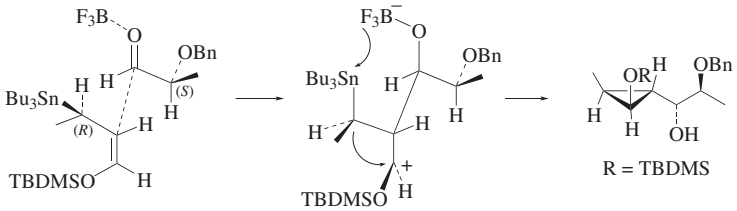
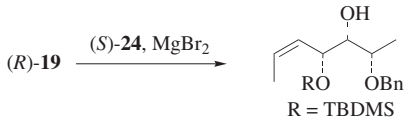
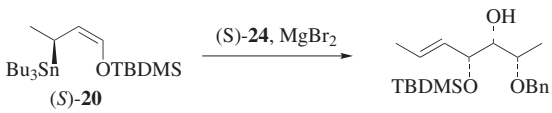


Figure 2. Reaction pathways leading to cyclopropane from stannane (*R*)-**20.**

When stannanes **20** react with aldehyde (*S*)-**24** in the presence of $MgBr_2$, only one product is isolated for each reaction. Stannane (*R*)-**20** gives the Z syn, syn adduct (Eq. 61) while stannane (*S*)-**20** produces the E syn, syn adduct (Eq. 62). The $MgBr_2$ promoted addition of γ-(silyloxy)allylstannanes **20** to (*S*)-**24** is proposed to proceed under substrate control. The Cram chelation control products are produced regardless of the stannane configuration. The S stannane is matched to the S aldehyde.

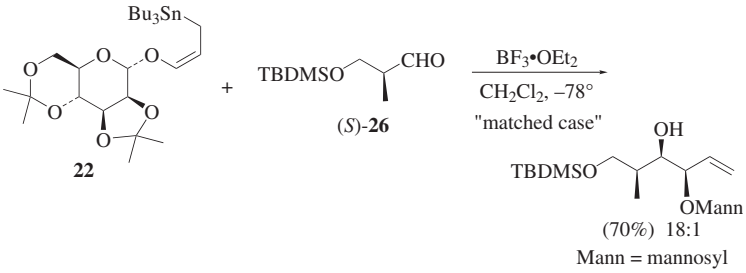


(Eq. 61)

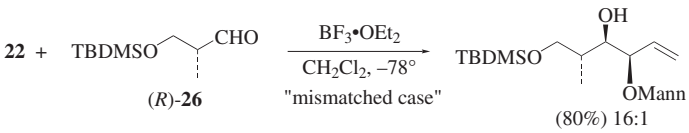


(*S*)-**20** (Eq. 62)

High diastereoselectivity is observed when the carbohydrate-derived γ-(alkoxy)allylstannane **22** is reacted with the β-alkoxy-α-methylpropionaldehyde **26**.[89] Double asymmetric reactions of **22** with both enantiomers of chiral aldehyde **26** were examined (Eqs. 63 and 64). In the presence of $BF_3{\cdot}OEt_2$, the facial selectivity of stannane **22** is sufficient to completely overcome the intrinsic diastereofacial bias of (*R*)-**26** in the mismatched pair giving a 16 : 1 mixture in favor of the anti, syn isomer (Eq. 64).[89] The matched pair gives an 18 : 1 mixture in favor of the syn, syn isomer (Eq. 63). The chiral stannane is able to dominate the outcome of the reaction since the intrinsic diastereofacial selectivity of the aldehyde is not overwhelmingly high.

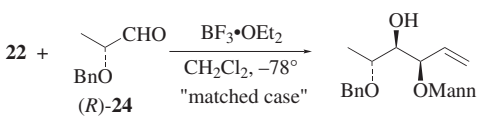


(Eq. 63)



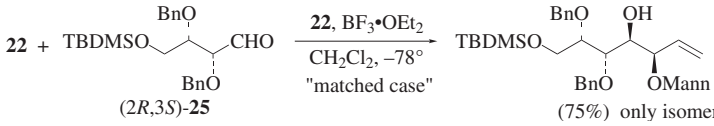
(Eq. 64)

Double asymmetric reactions of stannane **22** with aldehydes (*R*)- and (*S*)-**24** were also examined. The $BF_3{\cdot}OEt_2$ promoted matched reaction of stannane **22** with aldehyde (*R*)-**24** gives the anti, syn product as the only diastereomer (Eq. 65).[89] The mismatched pair involving stannane **22** and aldehyde (*S*)-**24** gives the all syn diastereomer as the major component of a 5 : 1 mixture. Selectivity in the mismatched pair is increased to 7 : 1 by using a TBDMS-protected lactaldehyde analog of (*S*)-**24** as the substrate. The major product of the mismatched pair is assumed to arise via a synclinal transition structure, in which aldehyde **24** adopts an anti-Felkin-Anh conformation. This example shows the high enantioselectivity of the chiral stannane reagent **22**, which overcomes the usual π facial preference of the α-alkoxy aldehyde to react by way of the Felkin-Anh transition structure.



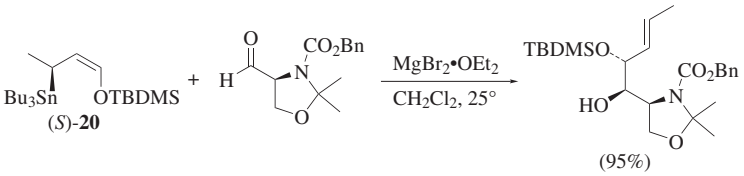
(Eq. 65)

Double asymmetric reactions of stannane **22** were further examined with the tartrate-derived aldehydes (2*R*,3*S*)- and (2*S*,3*R*)-**25** (Eq. 66).[89] The $BF_3{\cdot}OEt_2$-promoted matched reaction of stannane **22** with aldehyde (*2R,3S*)-**25** gives the syn, anti, syn product as the only diastereomer. This result is similar to the reaction with stannane **23** in that no other isomer is identified in this asymmetric reaction. The mismatched pair involving stannane **22** and aldehyde (2*S*,3*R*)-**25** gives the all syn diastereomer as the major component of a 2:1 mixture. The diminished selectivity with aldehyde (2*S*,3*R*)-**25** is attributed to its increased intrinsic diastereofacial preference. This increased preference may arise from a combination of a merged 1,2- and 1,3-π facial bias.[17] The stannane reagent is required to overcome both of these preferences in order to produce the all syn isomer.



(Eq. 66)

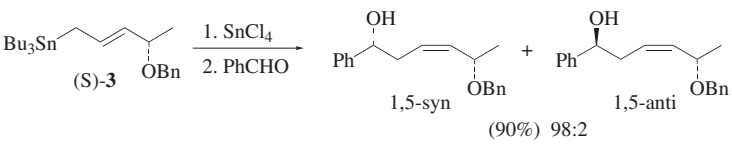
The reaction between γ-silyoxy-α-methylallylstannane (*S*)-**20** and a serine-derived aldehyde in the presence of $MgBr_2$ has been studied (Eq. 67).[93] The aldehyde was mixed with $MgBr_2$ at $-20°$ followed by slow addition of stannane **20**. Upon warming to 25°, stannane addition to the aldehyde occurs to afford the monoprotected diol in near quantitative yield with >10:1 selectivity for the syn diastereomer. Adding 2.3 equivalents of the racemic stannane to the aldehyde effects a useful level of kinetic resolution (>10:1 S/R), thus avoiding the need to prepare the enantiomerically pure γ-(alkoxy)stannane. Both reagents **20** and **22** are useful in the preparation of enantiomerically enriched monoprotected 1,2-diols. However the relatively lengthy preparation of these reagents may hinder widespread applications.



(Eq. 67)

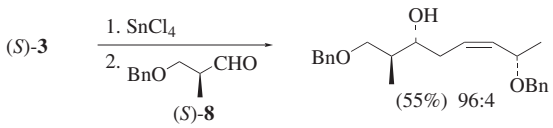
Reactions of 4-Alkoxy-2-pentenylstannane Reagents

Transmetalation Followed by Addition. *Reactions with Achiral Aldehydes*. The reactions of 4-(alkoxy)pentenylstannanes, such as (*S*)-**3**, with various aldehydes to introduce a new stereocenter at a remote position have been extensively studied.[21] The stannane reagents undergo transmetalation with $SnCl_4$ prior to addition to aldehydes.[12] With both aromatic and aliphatic achiral aldehydes, the major product is the Z alkene with a 1,5-syn relationship for the two stereocenters. The diastereoselectivity for the reactions with achiral aldehydes is in the range 92:8 to 98:2 (Eq. 68).

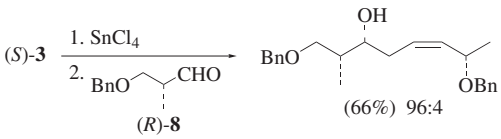


(Eq. 68)

Reactions with Chiral Aldehydes. Double asymmetric synthesis using stannane **3** with chiral aldehydes has been studied to evaluate the synthetic utility of the reagent. Under standard conditions, stannane (*S*)-**3** completely overcomes the π-facial bias of aldehyde **8** (Eq. 69). The reaction of stannane (*S*)-**3** with aldehyde (*S*)-**8** gives the anti product as the major component while the same reaction with (*R*)-**8** gives the syn product as the major component of a 96:4 mixture (Eq. 70).



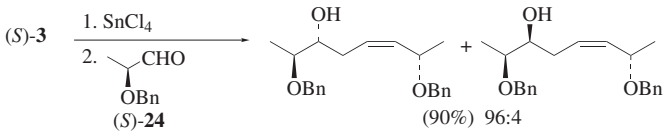
(Eq. 69)



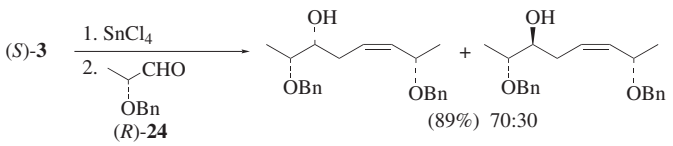
(Eq. 70)

Chelation control does not seem to be in effect in these reactions. The results support the intermediacy of an internally coordinated trichlorostannane (see Eq. 11). Coordination of the aldehyde oxygen to the internally coordinated tin atom saturates the six coordination sites of the tin atom.

Matching and mismatching characteristics are observed for the reactions of stannane (*S*)-**3** and chiral aldehyde **24**.[12] The matched pair appears to be (*S*)-**3** and (*S*)-**24**, which react to produce the anti product as the major component of a 96:4 mixture (Eq. 71). The reaction between stannane (*S*)-**3** and aldehyde (*R*)-**24** gives the syn product as the major component of a 70:30 mixture (Eq. 72). In both reactions, the minor diastereomer has the 1,5-anti relationship, which is suggested to arise from equilibration of the trichlorostannane intermediate. The formation of the 1,5-syn product in these reactions implies initial transmetalation of the stannane to the allylic tin trichloride, which is stabilized by coordination of the benzyloxy group to the electron-deficient tin atom (Eq. 11). The coordination complex is formed stereoselectively so that the methyl and vinyl groups are trans-disposed about the four-membered ring. The allylic tin trichloride then reacts with the aldehyde, which is added 5 minutes after the allylstannane and $SnCl_4$ are mixed. A six-membered, chair-like, cyclic transition structure controls the facial selectivity of the reaction. However the intermediate allylic tin trichloride may racemize through 1,3-tin migration when its addition to the aldehyde is relatively slow. This is suggested to account for the formation of the minor diastereomer.



(Eq. 71)

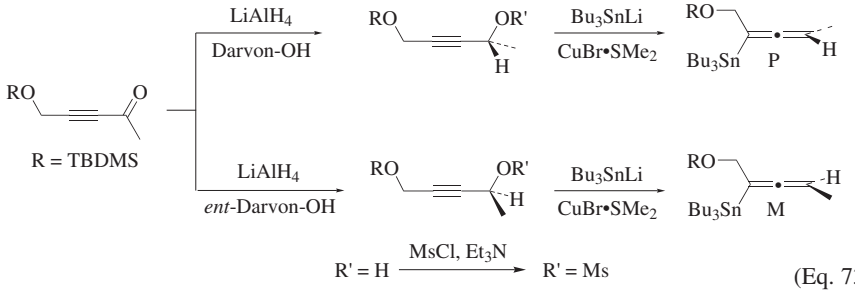


(Eq. 72)

Application of a δ-(alkoxy)allylstannane has been found in the total synthesis of (±)-patulolide C. If a 1,5-syn diol structure unit is the desired target one should consider using this reagent.

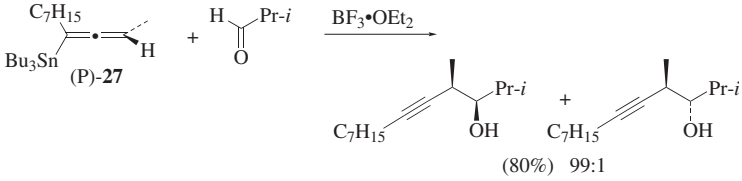
Reactions of Allenylstannane Reagents

Preparation of Allenylstannane Reagents. When propargylic mesylates are treated with Bu_3SnLi in the presence of an equimolar amount of $CuBr_2 \cdot SMe_2$, an S_N2' reaction occurs to afford allenylstannanes.[94,95] Enantioenriched mesylates are obtained by asymmetric reduction of propargylic ketones with Chirald reagent. The stereochemical nomenclature of chiral allenes cited in this review follows the recommendations of Prelog and Helmchen (Eq. 73).[96]



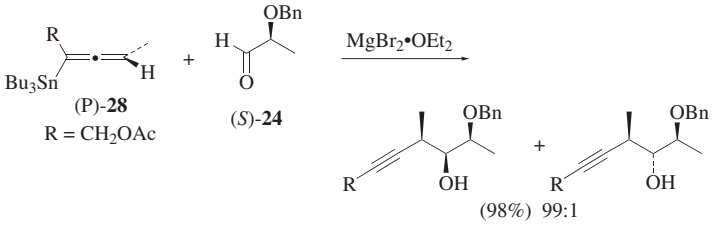
(Eq. 73)

Lewis Acid Promoted Reactions. *Reactions with Achiral Aldehydes*. The reactions of allenylstannanes, e.g., **27**, with α-branched aldehydes in the presence of equimolar $BF_3 \cdot OEt_2$ afford mainly syn adducts (Eq. 74). With straight-chain aldehydes a mixture of both anti and syn isomers is produced with the anti isomer slightly in excess.[94,97]

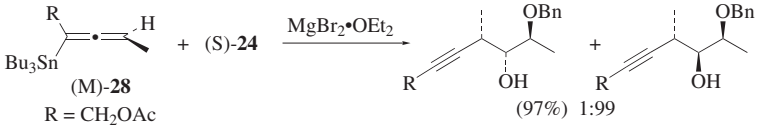


(Eq. 74)

Reactions with Chiral Aldehydes. Chiral allenylstannane (P)-**28** adds to (*S*)-α-benzyloxy propanal (**24**) to afford the syn, syn adduct exclusively in the presence of $MgBr_2 \cdot OEt_2$ (Eq. 75). The same reaction pair is less selective when $BF_3 \cdot OEt_2$ is used as the promoter. However, the enantiomeric allenylstannane (M)-**28** adds to (*S*)-**24** to afford predominantly the anti, syn adduct in the presence of $MgBr_2 \cdot OEt_2$ (Eq. 76) and the syn, syn adduct in the presence of $BF_3 \cdot OEt_2$.[94]



(Eq. 75)

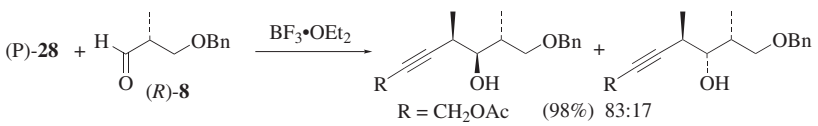


(Eq. 76)

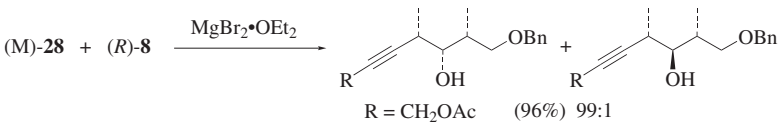
In $BF_3 \cdot OEt_2$ promoted additions, the major product comes from attack by the allenylstannane on the *si*-face of the S aldehyde (anti-Felkin-Anh approach), a mismatched pairing. The favored reaction pairing is accounted for by a transition structure in which the S aldehyde is juxtaposed to follow either the Cornforth dipolar model or the Felkin-Anh model.

The $MgBr_2 \cdot OEt_2$ promoted reactions are proposed to proceed through chelated transition structures. The intrinsic bias of the chiral aldehyde is enhanced by this chelation. The vinyl hydrogen of the stannane preferentially assumes a position over the most congested region of the chelate to minimize steric repulsion. As in allylstannane additions, the Bu_3Sn grouping is oriented anti to the forming C–C bond. In order to satisfy these stereoelectronic constraints, the M stannane reagents must assume orientations that lead to anti adducts. Anti adducts are rarely formed in Lewis acid promoted additions of related allylstannanes to aldehydes.

The reactions of P and M allenylstannanes with chiral aldehyde (*R*)-**8** were studied using either $BF_3 \cdot OEt_2$ or $MgBr_2 \cdot OEt_2$ (Eqs. 77 and 78).[94] In the $BF_3 \cdot OEt_2$ promoted additions, stannane (P)-**28** and aldehyde (*R*)-**8** are a mismatched pair, whereas stannane (M)-**28** and aldehyde (*R*)-**8** are stereochemically matched. In the mismatched case, the syn, anti product is favored in the ratio of 84 : 16 while in the matched case the ratio is >99 : 1 in favor of the syn, syn isomer. In the $MgBr_2 \cdot OEt_2$ promoted reactions, stannane (P)-**28** adds to aldehyde (*R*)-**8** favoring the syn, anti isomer by >99 : 1 whereas stannane (M)-**28** affords the syn, syn diastereomer. The absence of the anti, syn-isomer in the addition products suggests the absence of chelation control in contrast to the reactions of α-(benzyloxy)propanal. Comparison of the results in Eqs. 75 and 76 vs. Eqs. 77 and 78 implies that a five-membered chelate is more stable than a six-membered chelate when $MgBr_2$ is used as the Lewis acid.



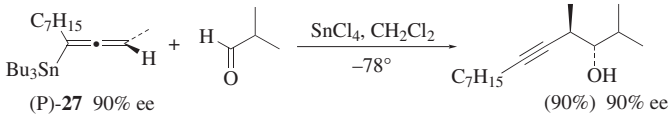
(Eq. 77)



(Eq. 78)

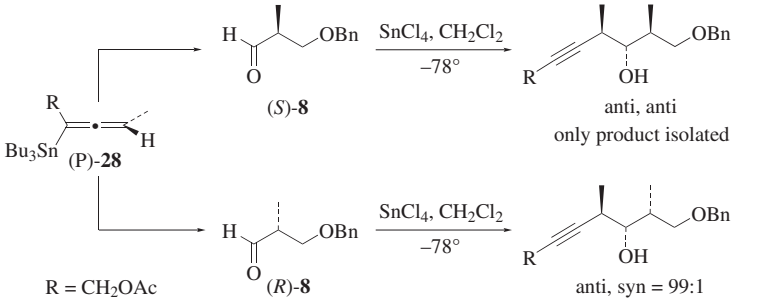
Most allenylmetal reagents are known to be in equilibrium with their propargylic isomers. These chiral allenylstannane reagents represent the first examples of practical applications of allenylmetals in diastereoselective reactions.

Transmetalation Followed by Addition. *Reactions Promoted by $SnCl_4$.* To obtain the anti, syn- and the anti, anti-stereotriads commonly found in natural products, the reactions of allenylstannanes and aldehydes with $SnCl_4$ as the Lewis acid were examined.[98–100] The anti isomer is obtained when the allenylstannane (P)-**27** is mixed with $SnCl_4$ at $-78°$ in CH_2Cl_2 prior to addition of the aldehyde (Eq. 79). The reaction proceeds in 90% yield with perfect enantioselectivity.



(Eq. 79)

All four triads are synthesized from allenylstannane (P)-**28** and (*S*)- and (*R*)-2-methyl-3-(benzyloxy)propanal (**8**).[100] The syn, syn and syn, anti diastereomers are obtained through the use of $BF_3{\cdot}OEt_2$ and $MgBr_2 \cdot OEt_2$. As described earlier, these two isomers arise through acyclic transition structures in which the aldehyde orientation follows the Felkin-Anh and chelation models, respectively. The anti, anti and anti, syn diastereomers are obtained through the use of $SnCl_4$ with (P)-**28** and (*S*)-**8** (Eq. 80).

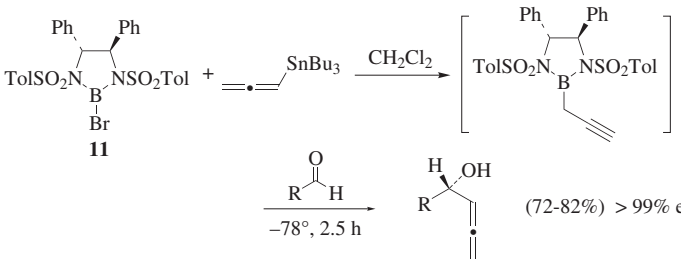


(Eq. 80)

Transmetalation occurs before the addition to aldehydes when $SnCl_4$ is used as the promoter. A six-membered, cyclic transition structure is proposed, in which the aldehyde is chelated by $SnCl_4$. The anti, syn diastereomer is also obtained through a six-membered, cyclic transition state in which the aldehyde is not chelated, i.e., attack under Felkin-Anh control. Apparently the interplay between the chiral aldehyde and the allenylstannane is important. Steric effects in the transition states determine whether the aldehyde is chelated. Thus all four triads can be obtained with high diastereofacial selectivity from allenylstannane **28**.

There are other allylmetal reagents such as allylboranes and allylboronates that have proven to be valuable synthetic tools for the preparation of the four stereotriads commonly found in natural products. These newly developed allenylstannane reagents should find their use in total synthesis and should be complementary to existing reagents.

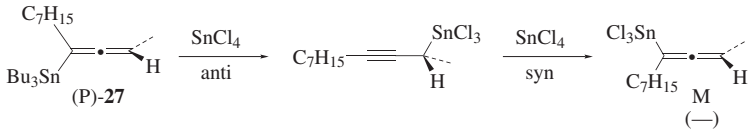
Reactions Promoted by a Chiral Borane. The R,R and S,S isomers of the 1,2-diamino-1,2-diphenylethane derived bromoborane **11** also promote enantioselective reactions of allenylstannanes with aldehydes (Eq. 81).[101] Both aliphatic and aromatic aldehydes can be employed with the allenylstannane to produce allenylic alcohols in good yield and excellent enantioselectivity. A propargylborane intermediate is involved in this reaction. The extraordinary enantioselectivity is rationalized with a cyclic transition state, in which the aldehyde oxygen is associated with the electrophilic boron atom and the chiral controller effectively blocks one π-face of the aldehyde. Under these conditions, the allenylstannane is effectively transmetallated into the propargylic borane intermediate, and the product is the allenyl alcohol.



(Eq. 81)

Reactions of Propargylstannane Reagents

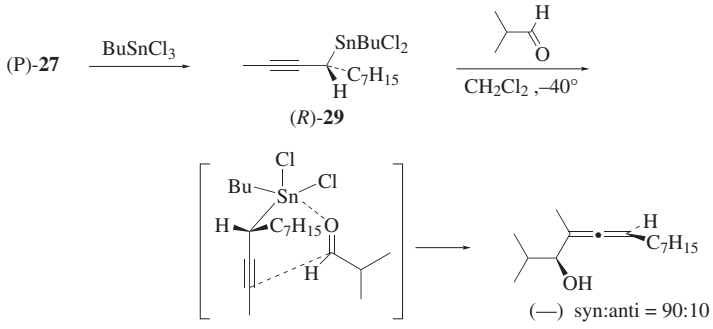
Preparation of Propargylstannane Reagents. The addition of $SnCl_4$ to allenylstannanes leads to the transient formation of a propargylic chlorostannane by a presumed anti S_E' transmetalation (Eq. 82).[98] The resulting propargylstannanes isomerize to the more stable allenylstannanes. The overall process proceeds with inversion of allene configuration.



(Eq. 82)

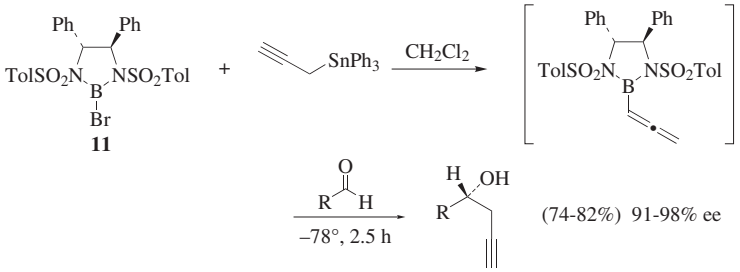
Reactions Promoted by $BuSnCl_3$. Replacing $SnCl_4$ with $BuSnCl_3$ decreases the rate of both transmetalation and isomerization (Eq. 83).[99] With allenylstannane (P)-**27**, the transformation to propargylic chlorostannane can be monitored by ^1H NMR spectroscopy. Conversion into propargylic chlorostannane (*R*)-**29** at $-40°$ is instantaneous, but subsequent isomerization to the allenylstannane requires several hours at room temperature. Thus the product is the allenyl alcohol if an aldehyde is added before the isomerization occurs. The reactions of propargylstannane **29** with

α-branched aldehydes yield allenylcarbinols in a ratio of 90:10 in favor of the syn isomer (Eq. 83). The terms "syn" and "anti" refer to the relationship between the δ allenic and the α-carbinyl hydrogens of the allenylcarbinols.[99] The preferential formation of the syn adduct is explained by a cyclic transition structure as shown in Eq. 83.



(Eq. 83)

Reactions Promoted by a Chiral Borane. Bromoborane **11** also promotes enantioselective reactions of propargylic stannanes with aldehydes (Eq. 84).[101] Both aliphatic and aromatic aldehydes can be employed to produce homopropargylic alcohols in good yield and high enantioselectivity. The reaction is arranged under the heading of propargylic stannanes because propargylic triphenylstannane is used as the reagent. The actual reactive intermediate is an allenylborane species. This procedure produces homopropargyl alcohols in 74–82% yield and 91–98% ee using the chiral controller **11**. Chiral Lewis acid **11** is complementary to chiral allenylstannane reagents **27** in that the products are homopropargyl alcohols without methyl substitution at the propargylic carbon. Therefore each reagent is rather specific for the preparation of a unique type of homopropargylic alcohol.



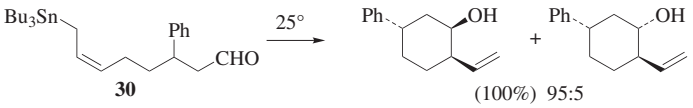
(Eq. 84)

Intramolecular Reactions of Allyl- and Allenylstannanes

One of the advantages of the stannane reagents is their relative stability toward mild electrophiles such as aldehydes.[22,25] α-(Alkoxy)allylstannanes are stable to normal workup procedures and to chromatographic separation. They are not reactive toward the aldehyde function until a Lewis acid is added or the mixture is heated to

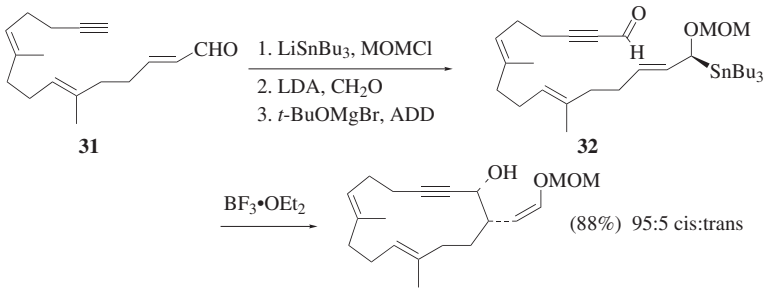
about 130°. Because of this stability, it is possible to prepare compounds containing both the allylstannane moiety and the aldehyde function. Intramolecular additions usually are carried out in dilute solutions to avoid intermolecular reactions.

Reactions Forming Carbocycles. *Thermal Reactions*. The cyclization of allylstannanes (*Z*)- and (*E*)-**30** to produce six-membered rings has been examined (Eq. 85).[27] Formation of these rings can be achieved under either thermal or Lewis acidic conditions. As illustrated below, the Z stannane preferentially forms the 1,2-syn adduct under both thermal and $BF_3{\cdot}OEt_2$ conditions. However the E stannane affords the 1,2-anti adduct as the major isomer when treated with $BF_3{\cdot}OEt_2$. Under thermal conditions the 1,2-syn adduct is still the major product. Thermal reactions of allylstannyl aldehydes appear to afford only six-membered rings.



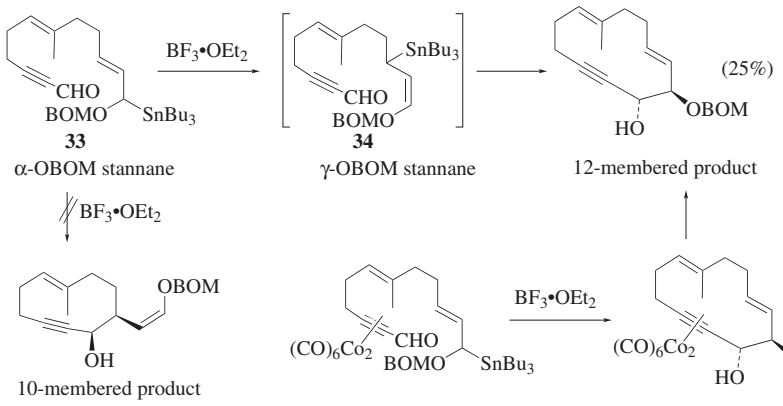
30 (100%) 95:5 (Eq. 85)

Lewis Acid Promoted Reactions. An intramolecular α-(alkoxy)allylstannane-aldehyde addition yielding a 14-membered carbocycle is illustrated in Eq. 86.[102] The three steps leading to the cyclization precursor **32** from the aldehyde **31** are mild, which allows the synthesis to proceed in high yield. Although heating the aldehyde gives no identifiable product, treatment of **32** with $BF_3{\cdot}OEt_2$ at $-78°$ in CH_2Cl_2 at high dilution affords the 14-membered carbocycle in 88% yield with the cis isomer as the major component of a 95:5 mixture. An enantioselective version of this macrocyclization was later reported.[103] The macrocycle was converted into a naturally occurring cembrane lactone.



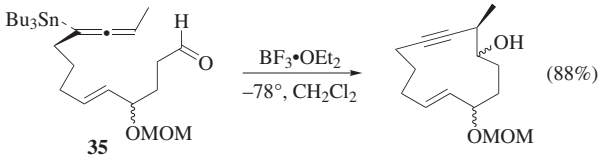
31 **32** (88%) 95:5 cis:trans (Eq. 86)

The success of the macrocyclization depends on the structure of the precursor and the size of the ring. From an attempt to prepare a 10-membered carbocycle by this strategy, an unexpected 12-membered ring was isolated (Eq. 87). A 1,3-migration of the tributyltin group occurs from the initial α-(alkoxy)allylstannane **33** to produce a γ-(alkoxy)allylstannane **34**, which undergoes subsequent addition to the aldehyde to afford the 12-membered cycle.[87,104] The yield of the 12-membered ring is improved by changing the geometry of the acetylene moiety using a cobalt complex.

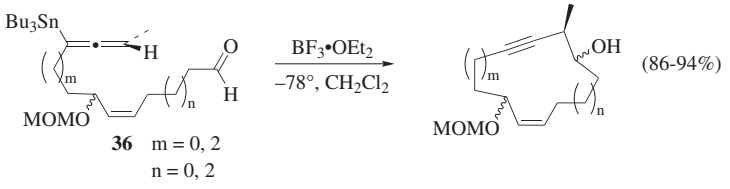


(Eq. 87)

The cyclizations of allenylstannane aldehydes **35** and **36** have also been studied (Eqs. 88 and 89).[105] Stannanes **35** and **36** cyclize smoothly in the presence of $BF_3 \cdot OEt_2$ to afford 12- and 14-membered carbocycles in high yield. In each case, a nearly 1 : 1 mixture of syn and anti adducts is obtained.



(Eq. 88)

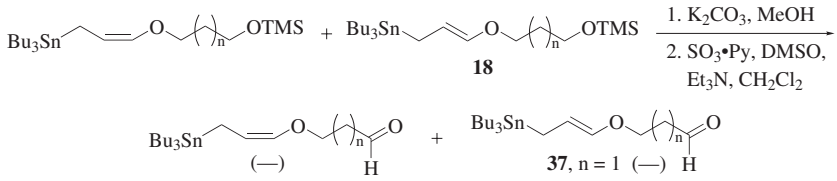


(Eq. 89)

The requirement for the union of the allyl- or allenylstannane moiety with the aldehyde carbonyl carbon depends on the proper alignment of the two sp^2 carbons. The connecting chain has a direct influence on the alignment of the reacting carbons. It has been observed that the intramolecular reaction works well for one substrate but not another due to a change in chain length and/or functional groups on the chain. Therefore the intramolecular allylstannane addition to aldehydes is not a general method for the formation of macrocycles.

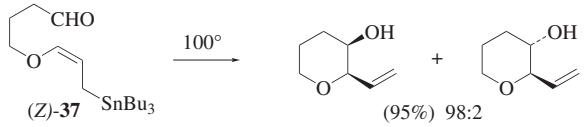
Reactions Forming Cyclic Ethers. The cyclization of α-(alkoxy)allylstannanyl aldehydes has been studied.[74,94] The cyclization precursors are prepared from the corresponding TMS ethers (Eq. 90). The γ-(alkoxy)allylstannane function is

stable under the conditions of TMS ether removal and oxidation of the resulting alcohol to the aldehyde.



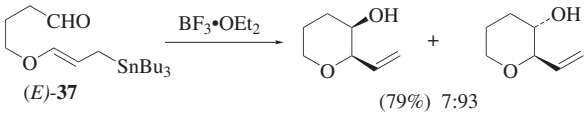
(Eq. 90)

The thermal and Lewis acid promoted cyclizations of allylstannane aldehydes (*Z*)- and (*E*)-**37** has been studied (Eq. 91).[85] The formation of five- and six-membered rings can be achieved through either thermal or Lewis acid promoted intramolecuar additions. The formation of a seven-membered ring can only be achieved in high yield through Lewis acid and protic acid promoted reactions. In general, under thermal conditions the Z stannane favors formation of the cis adducts and the E stannane favors formation of the trans isomer.



(Eq. 91)

This trend is consistent with the cyclic transition structure proposed for additions of allylstannanes to aldehydes under thermal conditions. However, the anti products are preferentially produced in the Lewis acid promoted reactions from both Z and E stannanes (Eq. 92). This relationship is explained through a transition structure where both the aldehyde-Lewis acid complex moiety and the allylstannane portion of the substrate assume pseudo-equatorial positions.



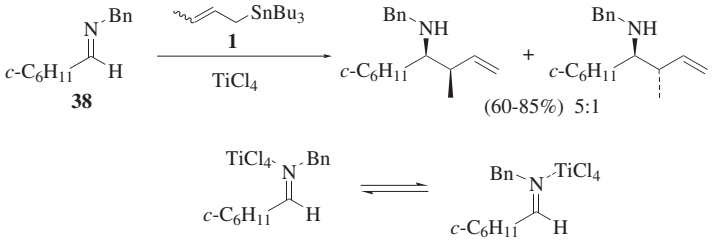
(Eq. 92)

Intramolecular addition of allylstannanes to aldehydes is an efficient method for sythesizing 5–7 membered cyclic ethers. The most desirable characteristic of the reaction is the simultaneous production of both the 2-vinyl and 3-hydroxy substituents on the resulting cyclic ether, allowing for an iteration of the same reaction to produce a polycyclic ether.

Reactions of Simple Allyl and 2-Butenylstannane Reagents with Imines

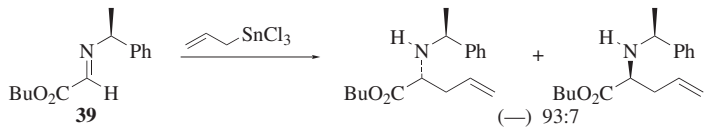
Reactions Promoted by Lewis Acids. The addition of allylstannanes to imines can be promoted by Lewis acids.[106,107] Imines are less reactive than aldehydes under

the same conditions. The syn isomer is obtained as the major component of a ca. 5 : 1 mixture when 2-butenylstannane **1** reacts with imine **38** (Eq. 93). If $TiCl_4$ is used as the Lewis acid, the ratio of products depends on the time of pre-mixing the imine and the Lewis acid.[106] The longer the pre-mix time, the higher the syn : anti ratio observed. This effect may have its origin in the configuration of the aldimine-$TiCl_4$ complex. Similar results are obtained in the BF_3 promoted addition of crotyltributylstannane to imines.[107] An antiperiplanar transition structure similar to that suggested for the reactions with aldehydes also accounts for the stereochemical course of the imine reactions. However, unlike aldehydes, no reaction occurs when imines and the stannane reagents are heated under high pressure.



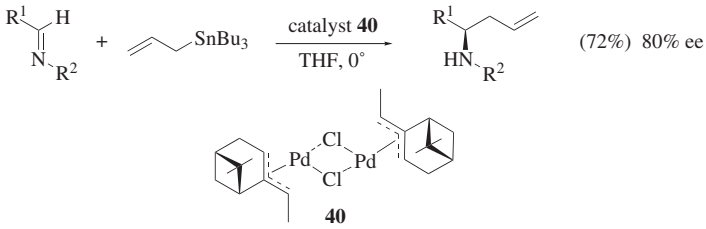
(Eq. 93)

Additions to more reactive imines using allyltrichlorostannane are reported.[21] A useful level of stereoselectivity is observed when imine **39** (prepared from butyl glyoxalate and (*S*)-α-methylbenzylamine) is subjected to the reaction (Eq. 94). The products are the amino esters in a ratio of 93 : 7. This stereoselectivity is complementary to the reaction with allyl-9-BBN, which gives the opposite selectivity in a ratio of 10 : 90.[108]



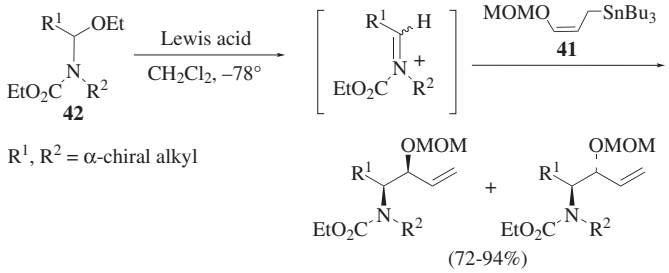
(Eq. 94)

Reactions Promoted by a Palladium Catalyst. Imines undergo the allylation reaction in the presence of palladium catalysts to afford homoallylamines in high yields.[109,110] Allylation of imines occurs preferentially in the presence of aldehydes. Mechanistic studies reveal that a bis-π-allylpalladium complex is a reactive intermediate for this allylation reaction. Although ordinary π-allylpalladium complexes, such as π-allyl-PdX (X = OAc or halides), act as electrophiles, the bis-π-allylpalladium complex reacts with imines as a nucleophile. The lone pair of electrons on the nitrogen atom of imines associates with the palladium atom more strongly than those of the aldehyde oxygen atom, which explains why imines are more reactive under these conditions.[109,110] By proper choice of the allyl ligands, one of the allyl groups is selectively transferred to the imine. A chiral allyl group serves as a nontransferable ligand. The chiral π-allylpalladium complex **40** induces asymmetric allylations of imines by the allylstannane with up to 80% ee (Eq. 95).[111]



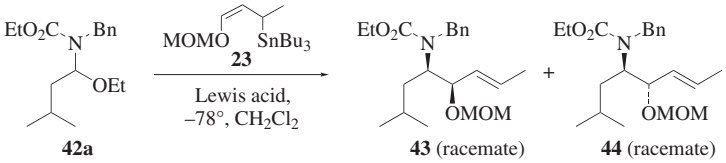
(Eq. 95)

Reactions of γ-(Alkoxy)allylstannanes with Iminium Ions. The addition of γ-MOM allylic stannane **41** to several *N*-acyliminium intermediates is described (Eq. 96).[112] The acyliminium ions are generated from the corresponding α-ethoxy carbamates **42** in the presence of a Lewis acid. High yields of the amino alcohol derivatives are obtained from the reactions of γ-MOM allylic stannane **41** and the acyliminium ions. The Lewis acids $TiCl_4$ and $BF_3{\cdot}OEt_2$ are effective. Formation of the acyliminium ion under these conditions is confirmed by low temperature NMR spectroscopy.[112]



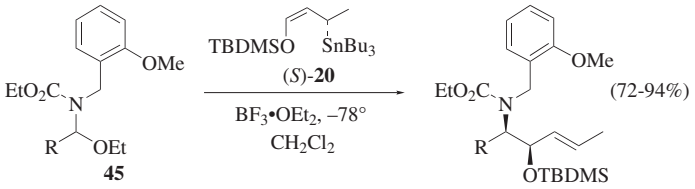
(Eq. 96)

Addition of the chiral γ-(alkoxy)allylstannanes **20** and **23** to iminium ions is also reported (Eq. 97).[113] Addition of the racemic γ-oxygenated allylic stannanes (*Z*)-**23** to the *N*-acyliminium precursor **42a**, derived from isovaleraldehyde, proceeds in high yield to afford a mixture of syn and anti isomers **43** and **44**.



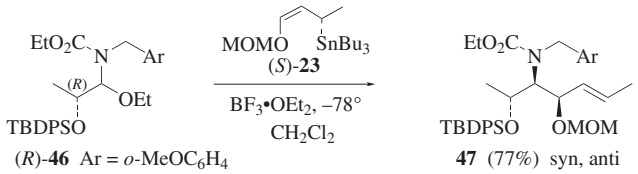
(Eq. 97)

The reaction between the *o*-methoxybenzyl derivative **45** and the enantioenriched γ-(silyloxy)allylic stannane (*S*)-**20** has also been examined (Eq. 98). The syn adduct predominates over the anti adduct by >95:5.

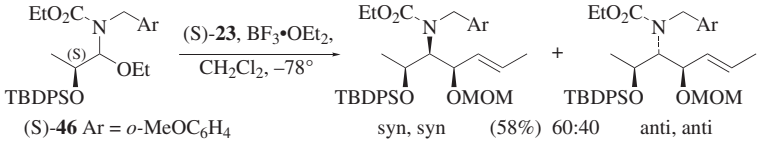


(Eq. 98)

The matched/mismatched characteristics of the addition process have been examined with the allylic stannane (*S*)-**23** and the *N*-(*o*-methoxybenzyl)carbamates **46** derived from (*R*)- and (*S*)-lactic aldehyde (Eqs. 99 and 100). Similar to analogous additions to aldehydes, the R/S combination is the matched pairing and affords the syn, anti adduct **47** as the exclusive product (Eq. 99). The S/S combination leads to a 60:40 mixture of the syn, syn and anti, syn adducts (Eq. 100).



(Eq. 99)



(Eq. 100)

The observed diastereoselectivity is consistent with a preferred antiperiplanar acyclic transition structure. The reason for the unprecedented enhanced diastereoselectivity of the *o*-methoxybenzyl derivatives is unclear.

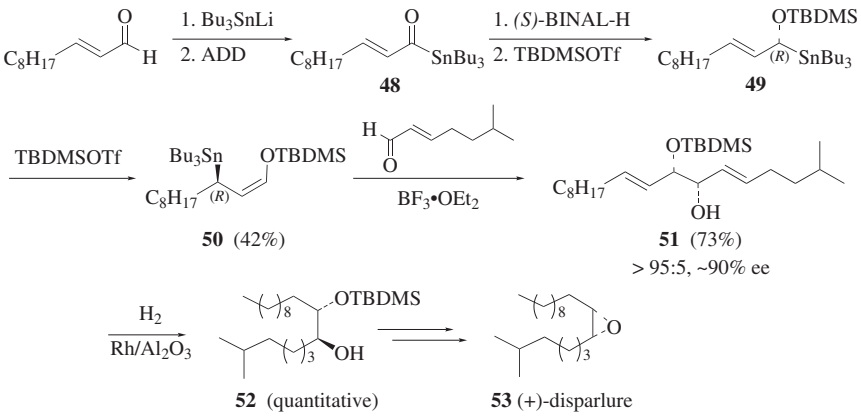
APPLICATIONS TO SYNTHESIS

A few representative examples of applications of stannane chemistry in natural product syntheses are presented here to show the diversity of this useful reaction. No effort was made to provide an exhaustive coverage of all published applications. The following total syntheses were chosen because of the relative importance of the stannane reagents in the overall processes.

(+)-Disparlure

The sex attractant of the female gypsy moth, (+)-disparlure (**53**), has been the object of numerous synthetic investigations. The earliest approaches employ chiral pool starting materials with diol functionality of appropriate chirality. More recently, the Sharpless asymmetric epoxidation and dihydroxylation have been employed to introduce the requisite epoxide stereocenters. The use of γ-(alkoxy)allylstannane

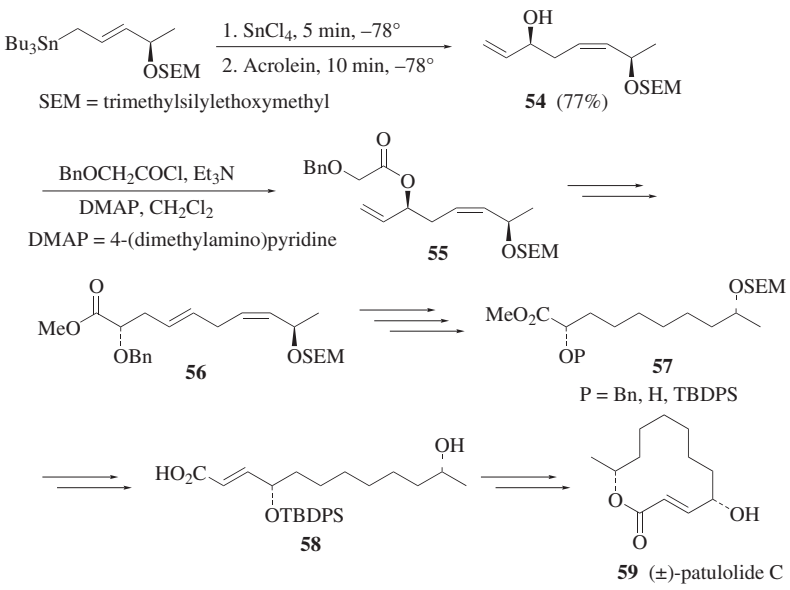
chemistry combines chain elongation and introduction of the chiral diol centers in a single step (Scheme 1).[114] The α-(silyloxy)stannane reagent provides the desired configuration at the two centers. Thus, addition of Bu_3SnLi to (*E*)-2-undecenal followed by in situ oxidation affords the acylstannane **48**. Reduction with (*S*)-BINAL-H and in situ treatment with TBSOTf yields the R γ-(silyloxy)stannane **50** via the α-isomer **49** in 42% overall yield. Stannane **50** is readily purified by column chromatography on silica gel. Addition of **50** to 6-methyl-2-heptenal in the presence of $BF_3{\cdot}OEt_2$ affords the syn adduct **51** in 73% yield and >90% ee. Less than 5% of the anti diastereomer is formed in the addition. Hydrogenation of **51** over Rh/Al_2O_3 affords the tetrahydro adduct **52** quantitatively. The tosylate derivative of **52** upon treatment with TBAF in THF smoothly cyclizes to (+)-disparlure (**53**) in high yield.



Scheme 1

(±)-Patulolide C

A combination of δ-(alkoxy)allylstannane chemistry and a sigmatropic rearrangement can be used to stereoselectively prepare compounds with distant stereogenic centers (Scheme 2).[115] As one stereogenic center is used to influence the introduction of the second, this approach can be used to synthesize racemic compounds diastereoselectively, as well as for the synthesis of enantiomerically enriched compounds. In the total synthesis of (±)-patulolide C (**59**), the relative configuration of 1,8-stereogenic centers is controlled by the tin(IV) chloride promoted reaction of acrolein with (4-hydroxy-pent-2-enyl)tributylstannane (trimethylsilyl)ethoxymethyl ether, which proceeds with >97:3 1,5-asymmetric induction in favor of the desired syn isomer **54**. An Ireland-Claisen rearrangement is carried out with the ester **55**, which goes through a Z silylketene acetal intermediate and rearranges through a chair-like transition structure giving the 2,9-anti configuration in ester **56**. Diimide reduction of **56** followed by protecting group transformation affords the saturated ester **57**, which is then elaborated into hydroxy acid **58**. Acid **58** is then cyclized to (±)-patulolide C (**59**).

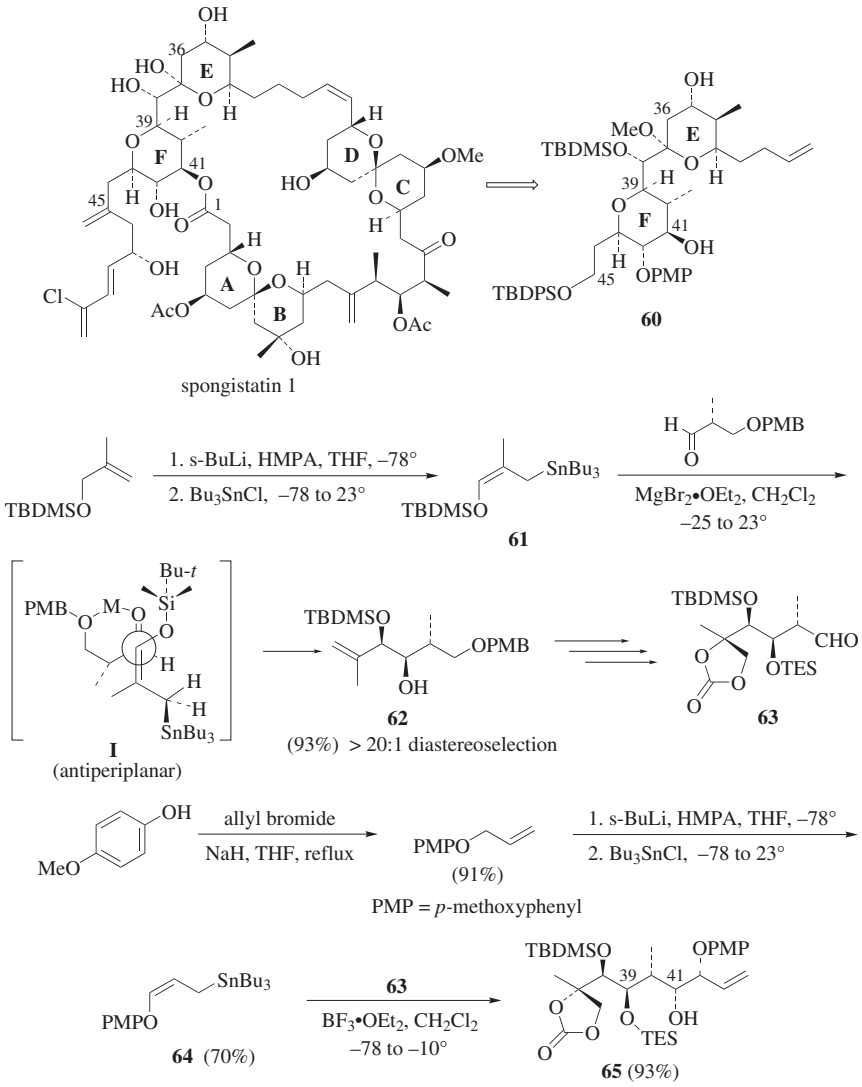


Scheme 2

Spongistatin 1

The efficiency and convenience of the applications of achiral γ-(alkoxy)allylstannanes are demonstrated in the diastereoselective synthesis of the C(29)-C(45) subunit **60** of spongistatin 1 (Scheme 3).[116] Spongistatin 1, one of the most active members of the spongipyran family, is a complex macrocyclic structure with six highly oxygenated heterocycles. The synthesis proceeds in 19 steps from chiral aldehyde **8**, and features highly diastereoselective α-alkoxyallylation reactions using the γ-alkoxy substituted allylstannanes **61** and **64**. Metallation of *tert*-butyldimethylsilyl methallyl ether followed by addition of Bu_3SnCl affords the β-methyl-γ-(alkoxy)allylstannane **61** (64%). Chelation controlled addition of **61** to aldehyde (*R*)-**8** ($MgBr_2 \cdot Et_2O$, CH_2Cl_2, –25 to 23°) provides the anticipated homoallylic alcohol **62** in 93% yield with greater than 20 : 1 stereoselectivity.

It is suggested that the antiperiplanar transition structure **I** is preferred in this case compared to synclinal transition structures because it can better accommodate the large *tert*-butyl substituent of γ-(alkoxy)allylstannane **61**. The homoallylic alcohol **62** is transformed into aldehyde **63** using standard protocols. γ-(Alkoxy)allylstannane **64**, needed for homologation of **63**, is generated by alkylation of *p*-methoxyphenol with allyl bromide followed by metalation with *s*-BuLi and addition of Bu_3SnCl. The treatment of aldehyde **63** with allylstannane reagent **64** and $BF_3 \cdot Et_2O$ in CH_2Cl_2 at $-78°$ gives the desired alcohol **63** in 93% yield with $>20:1$ diastereoselectivity. The configuration of product **65** is consistent with 1,2- and 1,3-merged asymmetric induction. With these efficient steps, the **E**-**F** bis-pyran portion of spongistatin 1 was prepared successfully.

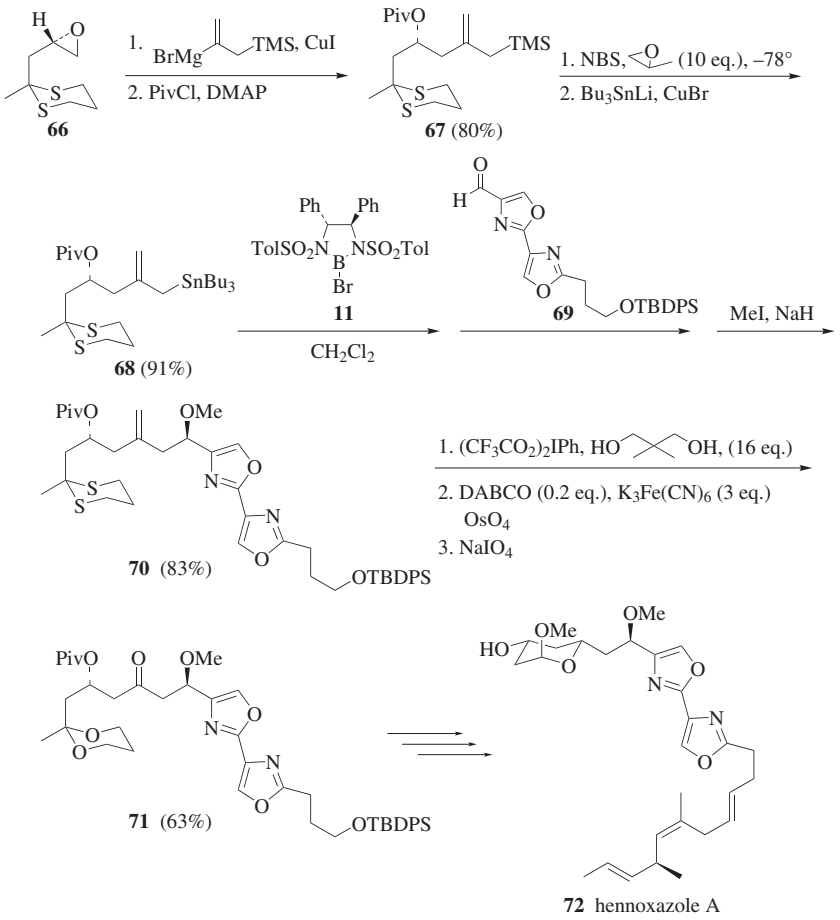


Scheme 3

Hennoxazole A

Efficient application of a highly functionalized allylstannane using chiral controller **11** is demonstrated in the total synthesis of hennoxazole A (**72**).[117] Compound **72** is isolated from the sponge *polyfibrospongia* and displays potency against herpes simplex virus type 1. The application of the mild asymmetric allylation strategy developed on the basis of stannane chemistry is employed to construct the C1-C17 portion of the target compound (Scheme 4). Stannane **68** is prepared via copper-catalyzed Grignard addition starting from 2-bromo-3-trimethylsilylpropene and epoxide **66**. The superior reactivity of allylstannane **68** is required as the silane **67** fails to

undergo transmetalation with the bromoborane **11**. Formation of the protected homoallylic alcohol (*R*)-**70** by transmetalation of optically pure stannane **68** with bromoborane (*R*,*R*)-**11** yields an intermediate borane for condensation with aldehyde **69**. Stereocontrol (10.5 : 1 d.s.) is induced from the 1,2-diphenylethane sulfonamide auxiliary. The final target is obtained in six more steps consisting of mostly functional group transformations, including oxidation of intermediate product **70** to ketone **71**.

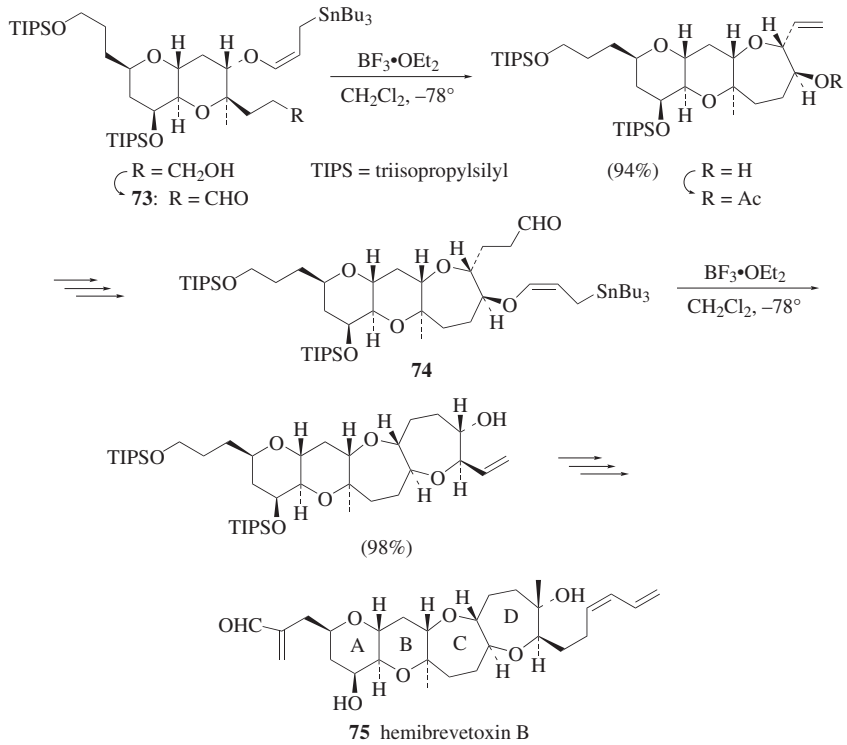


Scheme 4

Hemibrevetoxin B

The most extensive application of allylstannane chemistry in an intramolecular setting is shown in the total synthesis of hemibrevetoxin B (**75**). The efficiency of the intramolecular reaction of a γ-alkoxystannane with aldehydes as a tool for the synthesis of a polycyclic ether was documented in this synthesis.[118] The total synthesis is accomplished with high stereoselectivity in 56 steps and 0.75% overall yield from mannose. The efficiency of the synthesis exceeds other synthetic routes by

factors of 15–20. Two key transformations in the synthesis, shown in Scheme 5, involve intramolecular additions of allylstannanes to aldehydes (**73** and **74**) in the presence of $BF_3{\cdot}OEt_{22}$. As discussed earlier, both the aldehyde-Lewis acid complex and the allylstannane portion of the substrate assume pseudoequatorial positions in the cyclization process affording the trans isomer stereoselectively.



75 hemibrevetoxin B

Scheme 5

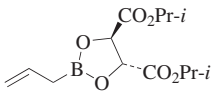
COMPARISON WITH OTHER METHODS

The versatility of stannane reagents is illustrated in this chapter. The fact that an oxygen atom can be incorporated at various positions in allylstannane reagents improves their utility in natural product synthesis. The ready exchange of stannane with other metals before addition to an electrophilic carbon further increases the applications of stannane reagents. As a group, stannane reagents provide versatile tools for the synthetic chemist. For certain transformations, however, other reagents may have superior or complementary properties. For example, in the presence of a Lewis acid, 2-butenylstannanes form 1,2-syn adducts in addition reactions with aldehydes. In a substrate-controlled reaction, three contiguous stereocenters can be produced with 2-butenylstannane reagents. The triads with 1,2-syn, 2,3-syn or 1,2-syn, 2,3-anti configuration can be obtained depending on the choice of chelating or non-chelating Lewis acid. To obtain 1,2-anti configuration from stannane reagents, transmetalation with a chelating Lewis acid, such as $SnCl_4$, $TiCl_4$, or $InCl_3$, is required before the

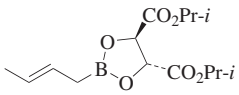
addition reaction takes place. In this regard, other allylmetal reagents, such as allylboranes, are complementary for the synthesis of 1,2-anti adducts. The reagent-controlled addition of an allyl or a crotyl group to an aldehyde by a tartrate-derived boronate reagent or a diisopinocampheylborane in particular has attracted widespread applications. Many other allylic metal reagents have been developed. A brief discussion of allylsilane, allylzinc, allyllithium, allylchromium, and allyltitanium reagents follows the discussion of allylboron species.

Tartrate Derived Allylboronate Reagents

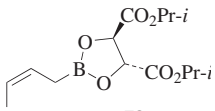
Tartrate derived chiral allyl- and crotylboronate reagents have been developed.[9,119] These reagents have been used in the synthesis of complex natural products.[114–121] In comparison to chiral (alkoxy)allylstannanes, chiral boronates are more convenient to prepare from commercially available materials. Allylboronate **76** is prepared from the reaction of allylmagnesium bromide with trimethylborate followed by esterification with diisopropyl tartrate (DIPT) in the presence of $MgSO_4$.[120] In analogous fashion, the E and Z crotylboronates **77** and **78** are prepared in high isomeric purity (>98%) from (*E*)- and (*Z*)-2-butene by way of the (*E*)- and (*Z*)-crotylpotassiums.[121]



(*R*,*R*)-**76**

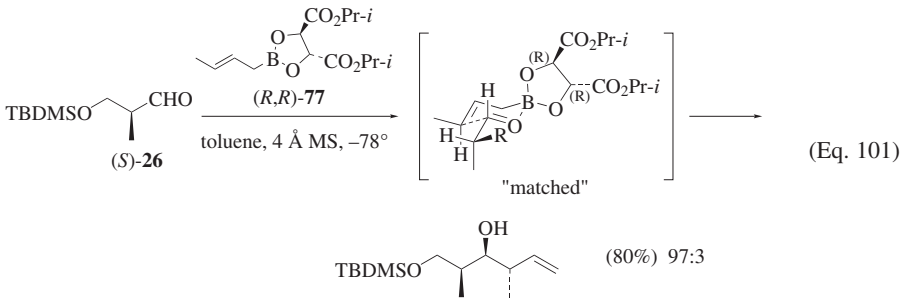


(*R*,*R*)-**77**

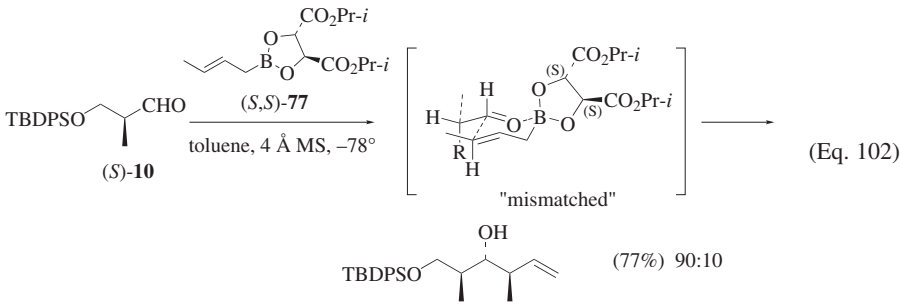


(*R*,*R*)-**78**

In Lewis acid mediated additions, allylstannanes add to aldehydes through an open transition state. In contrast, allylboronate reagents add to aldehydes through a cyclic six-membered, chair-like transition state. These reagents give high levels of asymmetric induction (83–98% ee) with metal carbonyl complexed unsaturated aldehydes.[122–124] The complementary properties to allylstannanes are shown in the following equations. Crotylboronate reagent (*R*,*R*)-**77** adds to aldehydes yielding 1,2-anti products in high stereoselectivity. The tartrate-derived crotylboronate reagents are most useful in the context of double asymmetric reactions with chiral aldehydes.[125,126] Equations 101–102 demonstrate the utility of (*E*)-**77** and (*Z*)-**78** in the synthesis of dipropionate adducts. The TBDMS-protected S α-methyl-β-alkoxy aldehyde **26** reacts with the crotylboronate (*R,R*)-(*E*)-**77** to give the syn, anti dipropionate as the major adduct with high diastereoselectivity (97:3). The stereochemical outcome of this reaction is rationalized by the matched transition structure, where C–C bond formation occurs by addition of the crotylboronate anti to the TBDMSOCH$_2$-substituent of the Felkin-Anh rotamer of the aldehyde. Both the crotylboronate reagent and the α-chiral aldehyde prefer this pathway. The anti, anti-dipropionate is obtained with useful selectively (90:10) from the reaction of the aldehyde (*S*)-**10** with (*S*,*S*)-(*E*)-**77**. The stereochemical outcome of this mismatched double asymmetric reaction is depicted in the transition structure where C–C bond formation occurs with the crotylboronate adding to the anti-Felkin-Anh rotamer of aldehyde (*S*)-**10**. The reagent is dominant in the stereochemical outcome.



(Eq. 101)

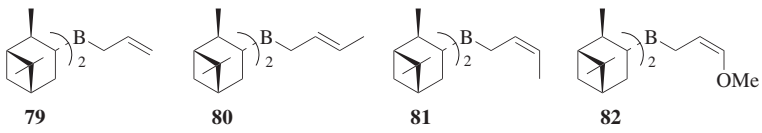


(Eq. 102)

Although these anti triads can also be prepared using allylstannane chemistry, a more elaborate procedure needs to be followed. On the other hand, allylstannanes are excellent reagents for preparing syn triads.

Diisopinocampheyl-, Allyl-, and Crotylborane Reagents

A family of highly enantioselective chiral allylborane reagents derived from naturally occurring pinene has been developed.[127,128] A list of literature references that documents the use of these pinene-derived reagents in natural product synthesis from 1985–1993 appears in a review.[127,128] These allylborane reagents add to aldehydes through a six-membered, cyclic transition state. While allylstannanes are relatively insensitive to moisture and air, these borane reagents must be used under an inert atmosphere (nitrogen or argon).



79 **80** **81** **82**

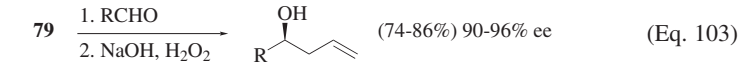
(–)-Ipc$_2$BOMe, derived from (+)-pinene

Reagents **79**–**82** are synthesized starting from commercially available β-methoxydiisopinocampheylborane, (−)-Ipc_2BOMe, or (+)-Ipc_2BOMe. The $(Ipc)_2BAll$ reagent **79** is prepared by reaction of (−)-Ipc_2BOMe with allylmagnesium bromide followed by removal of the Mg^{2+} salts by filtration.[129,130] Removal of the Mg^{2+} salts dramatically increases the reactivity of **79** with aldehydes, making it possible to perform these reactions at −100° with substantially improved enantioselectivity compared to reactions performed at −78°.

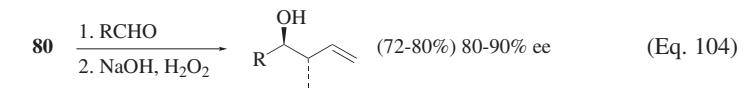
Reagents **80** and **81** are prepared from *trans*- and *cis*-2-butene,[131] respectively, through a modification of the deprotonation conditions developed by Schlosser.[132] Addition of (−)-Ipc_2BOMe to the E and Z crotylpotassium reagents, respectively, generates the corresponding allylborate complexes, which upon treatment with $BF_3{\cdot}OEt_2$ give the crotylboranes **80** and **81**.

Reagent **82** is prepared from allyl methyl ether via deprotonation with *sec*-butyllithium and subsequent treatment with (−)-Ipc_2BOMe and then $BF_3{\cdot}OEt_2$.[133] For best results, these reagents should be prepared just prior to use because **80**, **81**, and **82** are configurationally unstable at temperatures above –78°.

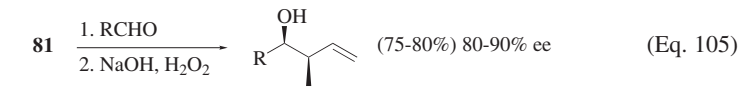
These reagents react in a highly diastereo- and enantioselective manner with achiral aldehydes (Eqs 103–106).[129–131,134] The double asymmetric reactions of reagents **79**–**81** with chiral aldehydes generally result in selective formation of the product predicted from reagent control of asymmetric induction. Results of the reactions of aldehyde **8** and reagents **79–81** are summarized in Eqs. 107–109.[135–137] Compared to allylstannane reagents, these borane reagents are more sensitive to air and moisture and must be freshly prepared before each reaction.



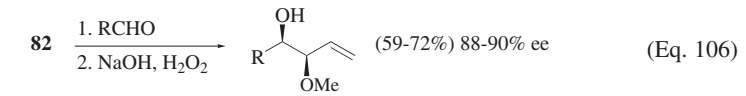
(Eq. 103)



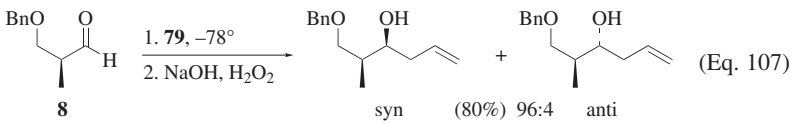
(Eq. 104)



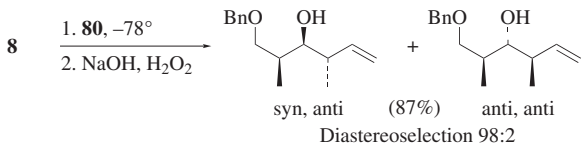
(Eq. 105)



(Eq. 106)



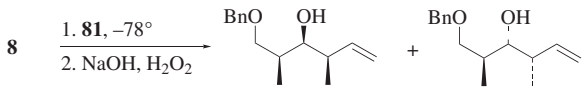
(Eq. 107)



syn, anti (87%) anti, anti

Diastereoselection 98:2

(Eq. 108)



syn, syn (83%) anti, syn

Diastereoselection 92:8

(Eq. 109)

Allyllithium Reagents

The reactions of allylic lithium reagents with ketones or aldehydes have been used extensively to prepare homoallylic alcohols.[138] The corresponding 2-butenyllithium reagents are configurationally unstable, existing as a mixture of rapidly equilibrating E and Z isomers.[139] The utility of the 2-butenyllithium reagents increases when a heteroatom or heterocycle-stabilized allylic anion is employed. The control of α- vs. γ-substitution in allyl anions depends upon a number of conditions, including the nature of the stabilizing group, charge delocalization, steric effects, solvation, and the counterion. The heteroatom or heterocycle-stabilized reagents show their greatest utility after transmetalation to another metal, such as tin.[140] The advantages of the allylic lithium reagents include their easy availability and their disadvantages are their strong basicity and their lack of stereocontrol in reactions with aldehydes.

Allylsilanes

The reaction of allylsilanes with various electrophiles is one of the most studied methods of carbon-carbon bond formation.[141–144] One of the advantages of allylic silicon reagents when compared to other reagents is their stability. Allylsilanes are insensitive to water and have low toxicity. They are readily handled and can be stored for long periods of time without special precautions; they are considerably less reactive than allylstannanes. For example, transmetalation to an allylborane from an allylsilane failed while a corresponding allylstannane succeeded.[117] If the electrophile is not reactive, transmetalation is required to convert the stable allylsilane into a more reactive allylic metal reagent, such as an allylstannane.[117]

One of the more important developments in allylation reactions is the catalytic enantioselective variant. Examples of catalytic enantioselective allylation of aldehydes using allylsilanes have been reported.[145] The chiral (acyloxy)borane (CAB) catalyst is used to produce the desired homoallylic alcohols in moderate to good yields when substituted allylsilanes are employed. The reaction gives best results when β-alkyl substituted allylsilanes are used in conjunction with aromatic aldehydes. Aliphatic aldehydes afford the homoallylic alcohols in 20–36% yield, although with a good enantioselectivity (85–90%). A BINOL-titanium complex is also employed as a catalyst in the addition of allylsilanes to aldehydes.[146] This catalyst affords ho-

moallylic alcohols in moderate diastereo- and enantioselectivity with 2-butenylsilane and methyl glyoxylate.

Allylchromium Reagents

The chromium(II) mediated reaction of 2-butenyl bromide with aldehydes affords the anti homoallylic alcohol in high diastereoselectivity regardless of the geometry of the starting allylic bromide.[147,148] The allylchromium reagents are complementary to allylstannane reagents in that they generate 1,2-anti stereochemistry. Chromium mediated reactions of allylic phosphates with aldehydes have also been developed.[149] The reactions of γ-disubstituted and β,γ-disubstituted allylic phosphates with aldehydes mediated by chromium proceed with good to excellent diastereoselectivity. The geometry of the starting allylic phosphate reagent determines the stereochemical outcome of the reaction. An efficient catalytic enantioselective employment of allylchromium reagents has yet to be developed.[150,151] Compared to allylstannanes, allylchromium reagents have rather limited applications in synthesis.

Allylzinc Reagents

The allylation of aldehydes with allylic zinc reagents proceeds in moderate to high yield and high regioselectivity to afford homoallylic alcohols.[152] However, the 2-butenylzinc reagents are configurationally unstable, providing a mixture of syn and anti homoallylic alcohols upon reaction with aldehydes.

The addition of allylzinc reagents to electrophiles is known to be a reversible process. An application of masked allylic zinc reagents for highly diastereoselective allylation takes advantage of this reversible process.[153,154] Upon formation of a zinc alkoxide, a sterically hindered tertiary homoallylic alcohol undergoes fragmentation to generate an allylic zinc reagent that subsequently undergoes reaction with an electrophile. High yields and diastereoselectivities have been reported for the generation of 1,2-anti homoallylic alcohols in this manner.

Although simple dialkylzinc reagents give excellent enantioselectivity in the addition to aldehydes in the presence of an amino alcohol,[155] allylations of aldehydes are better conducted with allylstannane reagents.

Allylindium Reagents

The addition of 2-butenylindium reagents to aldehydes has been shown to give homoallylic alcohols in high yields albeit low selectivity. Allylindium reagents can be prepared by reductive metalation of allylic halides or phosphates with indium metal, or by transmetalation of allylstannanes with indium trichloride.[83,156] Indium reagents are inert to water and are used in aqueous solutions. For the allylic indium reagents generated by reductive metalation, the formation of allylindium(I), rather than allylindium(III), is proposed.[157] The allylindium reagents generated from transmetalation with allylstannanes derive from an S_E' attack by $InCl_3$ on the allylstannane.[83] Allylindium reagents alone are incomparable to allylstannane reagents in terms of stereoselectivity and versatility. Reactions performed in water produce homoallylic alcohols in high yield albeit low stereoselectivity.[158] However, through transmetalation with the chiral α-(alkoxy)allylstannane, the transient allylindium reagents react with aldehydes with excellent diastereoselectivity.[83]

EXPERIMENTAL CONDITIONS

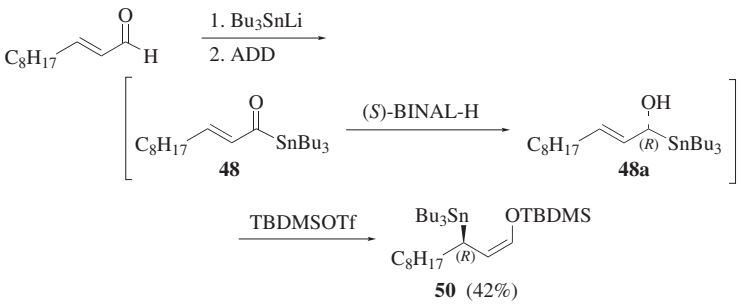
The intermolecular addition of α-(alkoxy)allylstannanes to aldehydes without a catalyst or promoter requires heating the mixture at 100–130°. In the presence of one equivalent of a Lewis acid, such as $BF_3{\cdot}OEt_2$, the addition proceeds at −78°. In certain cases where a chelation-controlled addition is required, $SnCl_4$ is used as the desired Lewis acid and the temperature should be controlled at around −90°. In general, anhydrous conditions and an inert atmosphere are required for these reactions. However, the whole operation is relatively simple and does not require extreme measures in drying the reagents or apparatus. Allyltributylstannane is commercially available. Other simple alkyl-substituted allylstannanes can be prepared by known procedures using the corresponding allylic halide and tributyltin chloride.

Caution! Volatile organotin compounds, such as trimethylallylstannane, are highly toxic. Tributylallylstannane is not volatile and therefore less hazardous. All reactions involving the use of organotin reagents should be conducted in a well-ventilated fume hood.

The preparation of the optically enriched α-(alkoxy)allylstannanes requires the preparation of a chiral reducing reagent and an acylstannane. The chiral reducing reagent BINAL-H gives the highest enantioselectivity. The protocol for preparing this reagent is well documented (see "Experimental Procedures"). The BINAL-H must be freshly prepared just before the acylstannane is ready for reduction due to the lability of the acylstannane. The resulting α-(hydroxy)stannane is also labile and needs to be protected as its MOM, BOM, or TBDMS ether immediately after isolation. Therefore, planning ahead is key to the success of the preparation of the enantiomerically enriched α-(alkoxy)allylstannanes, which can be stored in a refrigerator for weeks. Additions of α-(alkoxy)allylstannanes to aldehydes usually proceed at –78° with a full equivalent of $BF_3{\cdot}OEt_2$.

The reaction conditions for the addition of allenylstannanes to aldehydes are similar to those described for allylstannanes. When $MgBr_2 \cdot OEt_2$ is used as the Lewis acid promoter, the reactions are usually conducted at 0° due to the weaker acidity of $MgBr_2$.

EXPERIMENTAL PROCEDURES



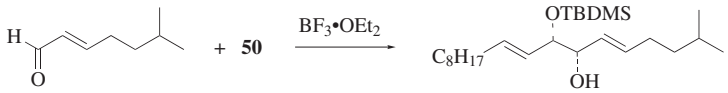
(*Z*)-(*R*)-1-(*tert*-Butyldimethylsilyloxy)-3-tri-*n*-butylstannyl-1-undecene (50) [Preparation of a Chiral γ-(Silyloxy)allylstannane from an α,β-Unsaturated Aldehyde].[114] Diisopropylamine (1.67 mL, 11.9 mmol) in 75 mL of anhydrous THF was cooled to 0° and *n*-BuLi was added (2.5 M solution in hexane, 4.72 mL, 11.8 mmol), followed after 15 minutes by tributyltin hydride (3.17 mL, 11.8 mmol). The resulting yellow solution was stirred for 20 minutes. The solution was cooled to −78° and 2-undecenal (1.81 g, 10.8 mmol) was added, followed after 30 minutes by 1,1′-(azodicarbonyl)dipiperidine (ADD, 4.15 g, 16.5 mmol), and the resulting dark red reaction mixture was warmed to 0° and stirred for 1 hour. The reaction was then quenched with dilute aqueous NH_4Cl solution and the mixture was extracted with Et_2O. The organic extracts were combined, dried over $MgSO_4$, and the solvent was removed under reduced pressure. Hexane was added to the orange residue and the solution was concentrated under reduced pressure to remove any traces of THF. Precipitating residual ADD with hexane purified the acyl stannane **48**. The solid was removed by vacuum filtration and the filtrate concentrated to provide the acyl stannane.

Because of the lability of the acyl stannane it is important to have a freshly prepared solution of BINAL-H at −78° ready for the subsequent reduction. This is best achieved by starting the following procedure for BINAL-H just prior to the acyl stannane sequence.

$LiAlH_4$ powder (1.02 g, 27.0 mmol) was suspended in 50 mL of THF. Over a period of 15 minutes, a solution of EtOH (1.24 g, 27.0 mmol) in 5 mL of THF was added with vigorous evolution of hydrogen gas after which (*S*)-1,1′-bi-2-naphthol (7.73 g, 27.0 mmol) in 50 mL of THF was added by cannula over 1 hour. The resulting milky solution was refluxed for 1 hour and put aside to cool to room temperature. The solution was then cooled to −78° and a solution of acyl stannane **48** in 45 mL of THF was added by cannula over 1 hour. After stirring for 16 hours at −78° the solution was quenched at −78° with dilute aqueous NH_4Cl (100 mL) over 0.5 hour. The solution was left to come to room temperature and then diluted with water and ether. The layers were separated and the aqueous phase was diluted with 1 M HCl and extracted with ether. The organic extracts were combined, dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure. The residual hydroxy stannane **48a** (yellow oil) and binaphthol (white powder) were triturated twice with hexane. The binaphthol was recovered by filtration and the hexane extracts were concentrated under reduced pressure to afford crude hydroxy stannane.

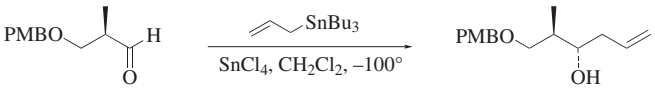
The hydroxy stannane was dissolved in CH_2Cl_2 and cooled to 0°. Diisopropylethylamine (2.5 mL, 27.0 mmol) was added followed by *t*-butyldimethylsilyl triflate (TBSOTf, 4.96 mL, 21.6 mmol). The reaction mixture was stirred overnight to ensure complete isomerization. The reaction was then quenched with saturated $NaHCO_3$ and the aqueous layer was extracted three times with CH_2Cl_2. The combined organic extracts were dried over sodium sulfate and the solvent was removed under reduced pressure. The material was purified by column chromatography on silica gel with hexane as eluent affording 2.6 g (42%) of stannane **50**: $[\alpha]_D^{26}$ 117° (*c* 1.6, $CHCl_3$); IR (film) 3563, 3450 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.99 (dd, J = 4.8, 1.0 Hz, 1H), 4.24 (ddd, J = 11.1, 5.7, 1.0 Hz, 1H), 2.55 (dq, J = 11.0,

6.4 Hz, 1H), 1.64–1.39 (m, 6H), 1.40–1.12 (m, 18H), 1.02–0.69 (m, 20H), 0.92 (s, 9H), 0.02 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.0, 115.1, 33.4, 32.0, 30.6, 29.7, 29.5, 29.4, 27.7, 25.8, 23.0, 22.8, 18.4, 14.2, 13.8, −2.8, −5.0, −5.3.



51 (73%) > 95:5, 95% ee

(*E,E*)-(7*S*,8*S*)-8-(*tert*-Butyldimethylsilyloxy)-2-methyloctadeca-5,9-dien-7-ol (51) [Reaction of a Chiral γ-(Silyloxy)allylstannane with an α,β-Unsaturated Aldehyde].[114] A solution of stannane **50** (552 mg, 0.97 mmol) and 6-methyl-2-heptenal (67 mg, 0.54 mmol) in CH_2Cl_2 was cooled to –78°, $BF_3{\cdot}OEt_2$ (96 μL, 0.94 mmol) was added, and the mixture was stirred for 1.5 hours. TLC analysis indicated that the aldehyde had not been consumed so additional $BF_3{\cdot}OEt_2$ (100 μL, 0.98 mmol) was added. After 1 hour, the reaction was quenched with saturated $NaHCO_3$ solution and the aqueous layer was extracted three times with CH_2Cl_2. The combined organic extracts were dried over sodium sulfate and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel with 2.5% EtOAc in hexane as eluent to afford 213 mg (73%) of adduct **51**: IR (film) 3563, 3450 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.64 (m, 2H), 5.35 (m, 2H), 3.84 (m, 2H), 2.04 (m, 4H), 1.56 (m, 1H), 1.46–1.08 (m, 16H), 1.03–0.73 (m, 9H), 0.90 (s, 9H), 0.07 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 133.8, 133.7, 129.6, 128.4, 77.9, 76.0, 38.3, 32.2, 31.9, 30.3, 29.5, 29.3, 29.2, 29.1, 27.4, 25.9, 22.7, 22.6, 22.5, 18.2, 14.1, −3.8, −4.7; Anal. Calcd for $C_{25}H_{50}O_2Si$: C, 73.10; H, 12.27. Found: C, 73.00; H, 12.24.

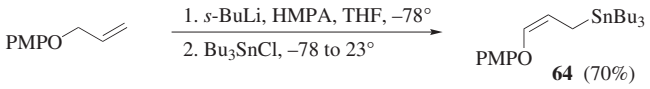


83 (76%)

(2*R*,3*S*)-1-(4-Methoxybenzyloxy)-2-methylhex-5-en-3-ol (83) [Reaction of an Allylstannane with an α-Chiral β-Alkoxyaldehyde].[60] To a cooled (–100°) solution of tri-*n*-butylallylstannane (1.95 g, 5.89 mmol) in dry CH_2Cl_2 (12.0 mL) was added dropwise a solution of tin tetrachloride in CH_2Cl_2 (5.89 mL, 1.0 M, 5.89 mmol) at −100°. After addition was complete, the solution was stirred for 15 minutes, and a solution of (*R*)-3-(4-methoxybenzyloxy)-2-methylpropanal (754 mg, 3.93 mmol) in CH_2Cl_2 (3.6 mL) was added dropwise via cannula. The mixture was stirred at –100° for 1 hour, quenched with saturated aqueous $NaHCO_3$ solution, and brought gradually to room temperature. The aqueous layer was extracted with Et_2O, and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was purified by flash chromatography (silica gel, elution with 20% Et_2O in hexanes) to give 0.747 g (2.99 mmol, 76%) of **83** and its 3-R stereoisomer (20:1) as a colorless oil: R_f 0.32 (50% Et_2O in hexanes, PMA);

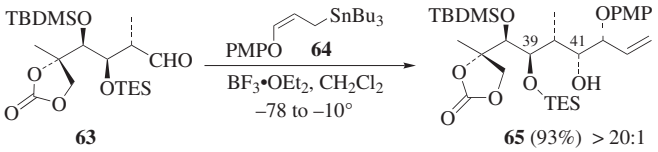
$[\alpha]_D^{22}$ −6.46° (c 1.30, $CHCl_3$); IR (film) 3463 (br), 2959, 1612, 1513, 1248, 1089, 1036, 820 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.25 (AA′ of AA′BB′, 2H), 6.87 (BB′ of AA′BB′, 2H), 5.88 (m, 1H), 5.10 (m, 2H), 4.45 (s, 2H), 3.80 (s, 3H), 3.57 (m, 2H), 3.44 (dd, J = 7.1, 9.2 Hz, 1H), 3.30 (s, 1H), 2.32 (m, 1H), 2.18 (m, 1H), 1.86 (m, 1H), 0.90 (d, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.2, 135.2, 129.9, 129.2, 117.1, 113.8, 75.0, 74.4, 73.0, 55.2, 39.3, 37.79, 13.78; HRMS (CI, m/z): [M^+] calcd for $C_{15}H_{22}O_3$, 250.1569; found 250.1565.

^1H NMR analysis of the *S*-Mosher ester indicated an ee of ~90%



64 (70%)

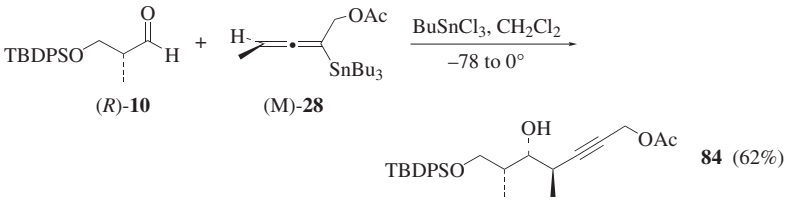
(*Z*)-γ-(4-Methoxyphenoxy)allyltributylstannane (64) [Preparation of an Achiral γ-(Alkoxy)allylstannane].[159] To a solution of 4-methoxyphenyl allyl ether (14.8g, 90 mmol) in 150 mL of THF at −78°, was added 75 mL of *s*-BuLi (1.27 M in cyclohexane, 95 mmol), followed immediately by the addition of HMPA (15 mL). The solution was stirred at −78° for 15 minutes, then Bu_3SnCl (26 mL, 96 mmol) was added via syringe, and the −78° bath was removed. The solution was stirred for 2 hours at ambient temperature, then quenched with NH_4Cl (saturated), diluted with hexanes and EtOAc, washed with $NaHCO_3$ (saturated), and then washed with H_2O. The organic phase was dried over $MgSO_4$ and concentrated to afford a crude oil, which was purified by distillation at reduced pressure (ca 0.3 mm Hg; bp 195 to 205°), providing 28.7 g (70%) of title compound **64**. The distilled product was used as is for the next reaction, however, a small portion was purified by HPLC (21-mm column, 8 ml/min, 100% hexanes, 15 minutes; then 20% EtOAc/hexanes, 10 minutes) to afford a sample for analytical characterization: IR (thin film) 3043, 2956, 2925, 2871, 2853, 1652, 1591, 1505, 1465, 1442, 1418, 1373, 1340, 1292, 1241, 1225, 1180, 1153, 1102, 1052 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.94–6.90 (m, 2H), 6.86–6.83 (m, 2H), 6.19–6.14 (m, 1H), 4.99–4.94 (m, 1H), 3.78 (s, 3H), 1.87–1.72 (m, 2H), 1.58–1.45 (m, 6H), 1.35–1.26 (m, 6H), 0.91–0.87 (m, 15H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.7, 152.0, 137.4, 116.9, 114.5, 111.4, 55.7, 29.1, 27.4, 13.7, 9.4, 6.0; HRMS (CI, NH_3) *m/z*: [$M–C_4H_9$]$^+$ calcd for $C_{18}H_{29}O_2SiSn$, 397.1190; found, 397.1184. The configuration of stannane **64** was confirmed by the observation of ^1H nOe's between the two olefinic protons.



63 **65** (93%) > 20:1

4-[(1*S*,2*R*,3*R*,4*R*,5*R*)-1-(*tert*-Butyldimethylsilyloxy)-4-hydroxy-5-(4-methoxyphenoxy)-3-methyl-2-triethylsilanyloxyhept-6-enyl]-4-methyl-1,3-dioxolan-2-one (65) [Reaction of an Achiral γ-(Alkoxy)allylstannane with a Chiral

Aldehyde].[159] To a −78° solution of crude 2,3-anti aldehyde **63** (8.62 mmol) and γ-(alkoxy)allylstannane **64** (5.5 g, 12.1 mmol) in 25 mL of CH_2Cl_2 was added $BF_3{\cdot}OEt_2$ (2.2 mL, 17.4 mmol). The reaction mixture was stirred at −78° for 16 hours, then warmed slowly to –20° and quenched by the addition of 10 mL $NaHCO_3$ (saturated). The cold bath was removed and the solution was brought to room temperature. The solution was diluted with EtOAc and washed with $NaHCO_3$ (saturated) followed by brine. The organic layer was dried over $MgSO_4$, filtered and concentrated to provide title compound **65** as a crude oil (>20:1 ds by ^{1}H NMR analysis) which was purified by flash column chromatography [160 g SiO_2, 18:1 hexanes/EtOAc (1 L); 9:1 hexanes/EtOAc (1 L); 5:1 hexanes/EtOAc (1 L)] providing 4.92 g of analytically pure **65** (93% over 2 steps): $[\alpha]_D^{24}$ +16.3° (*c* 1.0, CH_2Cl_2); IR (thin film) 3586, 2955, 2881, 1808, 1644, 1614, 1593, 1505, 1471, 1417, 1392, 1365, 1225, 1101, 1006 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.89–6.86 (m, 2H), 6.82–6.79 (m, 2H), 5.68 (ddd, *J* = 17.6, 10.4, 7.4 Hz, 1H), 5.33–5.28 (m, 1H), 4.70 (d, *J* = 7.8 Hz, 1H), 4.37 (dd, *J* = 8.2, 8.2 Hz, 1H), 4.05 (d, *J* = 2.7 Hz, 1H), 3.99 (d, *J* = 8.5 Hz, 1H), 3.95 (d, *J* = 7.8 Hz, 1H), 3.84 (dd, *J* = 9.5, 2.7 Hz, 1H), 3.76 (s, 3H), 2.57 (s, 1H), 1.6–1.5 (m, 1H), 1.52 (s, 3H), 1.06 (d, *J* = 6.6 Hz, 3H), 1.01 (t, *J* = 7.9 Hz, 9H), 0.90 (s, 9H), 0.75–0.66 (m, 6H), 0.15 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 154.2, 151.8, 134.4, 120.2, 118.4, 114.5, 86.9, 84.0, 77.2, 75.1, 71.7, 70.4, 55.6, 36.1, 25.8, 23.8, 18.1, 10.2, 7.1, 5.3, −4.1, −4.8; HRMS (CI, NH_3) *m/z*: $[M + NH_4]^+$ calcd for $C_{31}H_{58}Si_2NO_8$, 628.3701; observed, 628.3699.



(2*R*,3*R*,4*R*)-(+)-1-(tert-Butyldiphenylsilyloxy)-2,4-dimethyl-7-acetoxy-5-heptyn-3-ol (84). [Standard Procedure with Butyltin Trichloride]. To a solution of allenic stannane (M)-**28** (0.133 g, 0.320 mmol) in CH_2Cl_2 (0.7 mL) at −78° was added $BuSnCl_3$ (0.056 mL, 0.335 mmol). The dry ice bath was removed, and after 5 hours, aldehyde (*R*)-**10** (95.0 mg, 0.291 mmol) was added in CH_2Cl_2 (0.2 mL). After 18 hours, the reaction was quenched with 10% HCl solution (0.5 mL) and the solution was extracted with Et_2O. The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. Triethylamine (0.5 mL) was added, and the mixture was vigorously stirred at 0° for 15 minutes. The resulting white slurry was filtered through a pad of Celite with Et_2O, and the filtrate was concentrated to give the crude alcohol as a yellow oil. The residue was chromatographed on silica gel (first with 25% Et_2O in hexanes, and then with 25% EtOAc in hexanes) yielding 68.9 mg (62%) of alcohol **84** as a clear oil. $[\alpha]_D$ +3.6° (c 6.27, $CHCl_3$).

TABULAR SURVEY

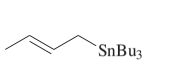
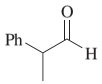
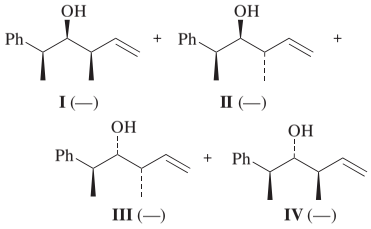
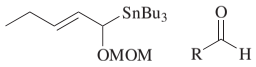
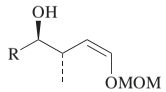
An effort has been made to tabulate all examples of additions to aldehydes, ketones, and imines using allylstannane reagents reported from the mid-1980s to the end of 2000. In general, the reactions are arranged in order of increasing carbon count of the allylstannane reagent, excluding functional groups such as esters, ethers, amines, etc. The reactions using simple allylstannanes that are promoted by a Lewis acid are listed in Table 1. The reactions promoted by heat are listed in Table 2. The catalytic enantioselective reactions are listed in Table 3. The reactions promoted by a chiral borane are listed in Table 4. The reactions using α-(alkoxy)allylstannanes that are promoted by a Lewis acid are listed in Table 5. The reactions using achiral γ-(alkoxy)allylstannanes that are promoted by a Lewis acid are listed in Table 6. The reactions using chiral γ-(alkoxy)allylstannanes that are promoted by a Lewis acid are listed in Table 7. The reactions using allenylstannanes are listed in Table 8. The reactions using propargylstannanes are listed in Table 9. Intramolecular additions of allylstannane-aldehydes are listed in Table 10. Table 11 contains reactions using the allylstannanes that are not easily classified under the above definitions.

Isolated yields of the combined allylation products are included in parentheses and a dash, (−), indicates that no yield was reported. Where an enantiomeric excess is reported, it relates to the major product of a reaction.

The following abbreviations have been used in the tables:

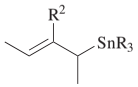
BINOL	binaphthol
Bn	benzyl
Boc	*tert*-butoxycarbonyl
BOM	benzyloxymethyl
Bz	benzoyl
Cbz	benzyloxycarbonyl
FSPE	Fluorous Solid Phase Extraction
LDA	lithium diisopropylamide
MEM	methoxyethoxymethyl
MOM	methoxymethyl
PMB	*p*-methoxybenzyl
PMP	*p*-methoxyphenyl
TBDMS	*tert*-butyldimethylsilyl
TBDPS	*tert*-butyldiphenylsilyl
TBS	*tert*-butyldimethylsilyl
TES	triethylsilyl
TFA	trifluoroacetic acid
THP	2-tetrahydropyranyl
TIPS	triisopropylsilyl
TMS	trimethylsilyl
Ts	*p*-toluenesulfonyl

TABLE 1. THERMALLY PROMOTED ADDITION OF ALLYLIC TRIBUTYLSTANNANES TO ALDEHYDES

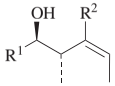
Allylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 		Lewis acid or pressure	 **I** (—) **II** (—) **III** (—) **IV** (—)	160
			I:II:III:IV	
		BF_3	86:0:14:0	
		10 kbar	18:52:14:16	
C_5 		140°		161

R	Time	
Ph	11 h	(70)
PhCH=CH	11.5 h	(60)
p-ClC_6H_4	36 h	(76)
Et	40 h	(33)
C_6H_{13}	36 h	(47)
i-Pr	40 h	(72)
t-Bu	40 h	(5)

$C_{5\text{-}6}$



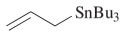
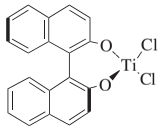
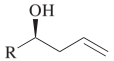
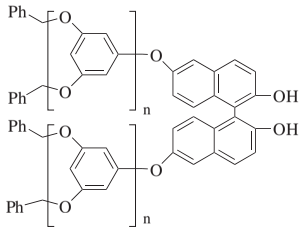
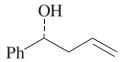
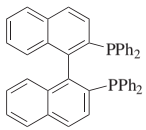
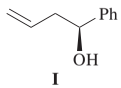
Heat, 18 h



39

R	R^1	R^2	Temp	
Bu	Ph	H	150°	(72)
Bu	*p*-$O_2NC_6H_4$	H	80°	(87)
Bu	*p*-ClC_6H_4	H	110°	(70)
Bu	*p*-C_6H_{11}	H	150°	(62)
Bu	*i*-Pr	H	150°	(55)
Ph	Ph	H	150°	(74)
Ph	*p*-$O_2NC_6H_4$	H	80°	(80)
Bu	Ph	Me	150°	(89)
Bu	*p*-$O_2NC_6H_4$	Me	80°	(69)
Bu	*i*-Pr	Me	150°	(50)

TABLE 2A. LEWIS ACID PROMOTED ADDITION OF ALLYLIC TRIBUTYLSTANNANES TO ACHIRAL ALDEHYDES

Allylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
		BINOL-Ti(IV) 4 Å MS, CH_2Cl_2 	 R = C_3H_{11} 98 (75) C_7H_{13} 97 (83) *c*-C_6H_{11} 93 (75) (*E*)-PhCH=CH 89 (85) Ph 82 (96)	47
			 n: % ee 1 92 (18) 2 89 (36) 3 88 (36)	162
		 (*S*)-BINAP (*S*)-BINAP•$AgOCOCF_3$ (*S*)-BINAP•$AgClO_4$ (*S*)-BINAP•$AgNO_3$ (*S*)-BINAP•AgOTf	 **I** **I** % ee S (47) 40 S (1) 26 S (26) 53 S (88) 96 S	50

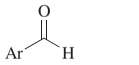
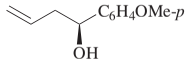
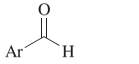
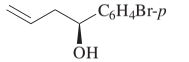
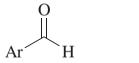
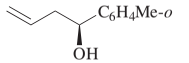
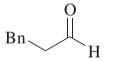
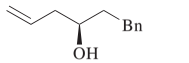
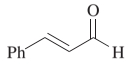
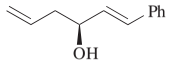
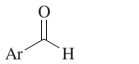
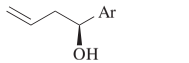
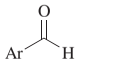
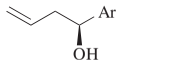
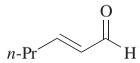
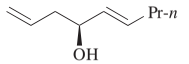
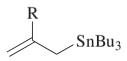
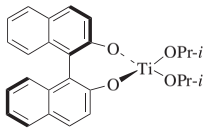
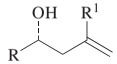
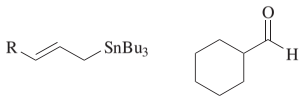
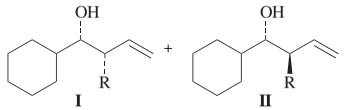
 Ar = C_6H_4OMe-*p*	(*S*)-BINAP•AgOTf		(59) % ee = 97	50
 Ar = C_6H_4Br-*p*	(*S*)-BINAP•AgOTf		(95) % ee = 96	50
 Ar = C_6H_4Me-*o*	(*S*)-BINAP•AgOTf		(85) % ee = 97	50
	(*S*)-BINAP•AgOTf		(47) % ee = 88	50
	(*S*)-BINAP•AgOTf		(83) % ee = 88 (*S*)	50
 Ar = 1-naphthyl	(*S*)-BINAP•AgOTf		(89) % ee = 97	50
 Ar = 2-furanyl	(*S*)-BINAP•AgOTf		(94) % ee = 93	50
	(*S*)-BINAP•AgOTf		(72) % ee = 93	50

TABLE 2A. LEWIS ACID PROMOTED ADDITION OF ALLYLIC TRIBUTYLSTANNANES TO ACHIRAL ALDEHYDES (*Continued*)

Allylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{3\text{-}4}$ 		 4 Å MS, CH_2Cl_2, –20°, 12-70 h		163

R	R^1		% ee
H	*c*-C_6H_{11}	(66)	94
H	Ph	(88)	95
H	$PhCH_2CH_2$	(93)	96
H	$C_6H_5CH{=}CH$	(42)	89
Me	*c*-C_6H_{11}	(50)	84
Me	Ph	(75)	91
Me	$PhCH_2CH_2$	(97)	98
Me	$C_6H_5CH{=}CH$	(68)	87





62

I **II**

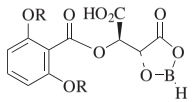
R	**I+II**	% ee	**I:II**
Me	(18)	95	65:35
Me	(71)	93	93:7
H	(53)	87	—
H	(42)	55	—

BINOL-Ti(IV)

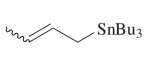
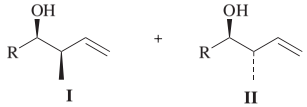
CAB

BINOL-Ti(IV)

CAB



CAB

C_4   $BF_3{\bullet}OEt_2$, CH_2Cl_2, –78°  11

E:*Z*
100:0
90:10
60:40
0:100
100:0
100:0
100:0
100:0
100:0
100:0
100:0

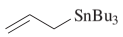
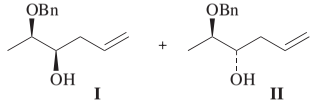
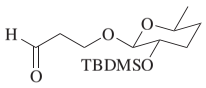
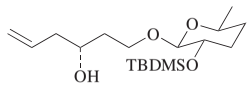
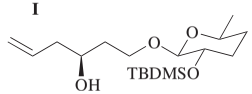
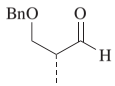
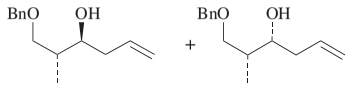
R	**I+II**	**I**:**II**
Ph	(90)	98:2
Ph	(90)	98:2
Ph	(90)	96:4
Ph	(90)	99:1
Ph	(90)	95:5
Me	(82)	91:9
Et	(87)	91:9
i-Pr	(89)	95:5
i-Pr	(90)	91:9
i-Bu	(90)	90:10
n-pent-3-yl	(92)	98:2

 $BF_3{\bullet}OEt_2$, CH_2Cl_2, –78° 22

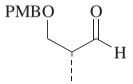
E:*Z*
90:10
74:26
12:88
90:10
74:26
12:88
90:10
74:26
12:88

R	**I+II**	**I**:**II**
c-C_6H_{11}	(88)	94:6
c-C_6H_{11}	(80)	86:14
c-C_6H_{11}	(82)	58:42
Ph	(85)	98:2
Ph	(86)	95:5
Ph	(80)	81:19
PhCH=CH	(85)	98:2
PhCH=CH	(70)	92:8
PhCH=CH	(70)	82:18

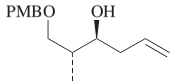
TABLE 2B. LEWIS ACID PROMOTED ADDITION OF ALLYLIC TRIBUTYLSTANNANES TO CHIRAL ALDEHYDES

Allylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3 		1. Aldehyde, Lewis acid, –78° 2. Allylstannane, –78°	 **I** + **II**	164
			I+II (76); **I**:**II** = 100:0	
			$TiCl_4$	
			$TiCl_4$•$AsPh_3$ (70); 100:0	
			$TiCl_4$•$SbPh_3$ (76); 95:5	
			$TiCl_4$•PPh_3 (70); 52:48	
		1. Aldehyde, allylstannane, –78° 2. Lewis acid, –78°		164
			I+II (76); **I**:**II** = 52:48	
			$TiCl_4$	
			$TiCl_4$•$AsPh_3$ (70); 94:6	
			$TiCl_4$•$SbPh_3$ (73); 82:18	
		$MgBr_2$•OEt_2, CH_2Cl_2, –78 to –30°	 **I** +  **II** **I+II** (96); **I**:**II** = 88:12	165
		Lewis acid	 **I** + **II**	

		I+II	I:II	
	BF_3•OEt_2, –78°	(—)	52:48	58
	ZnI_2, 0°	(—)	64:36	58
	$MgBr_2$, –22°	(—)	72:28	58
	MgI_2, –22°	(—)	70:30	58
	$TiCl_4$, –78°	(—)	82:18	58
	$TiCl_4$, –78°, inverse addition	(—)	53:47	58
	$SnCl_4$, –78°	(90)	90:10	58
	$SnCl_4$, –78°, inverse addition	(88)	98:2	58
	$SnCl_4$, CH_2Cl_2, –78°	(91)	97:3	166
	$SnCl_4$, CH_2Cl_2, –90°	(84)	97:3	59

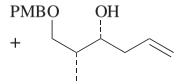


$SnCl_4$, CH_2Cl_2, –100°



I

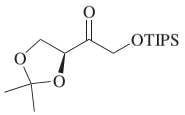
+



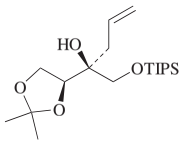
II

60

I+II (76); **I:II** = 95:5

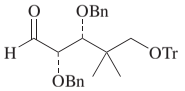


$MgBr_2$, CH_2Cl_2, –40°

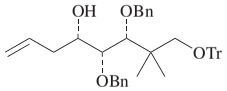


(85)

167

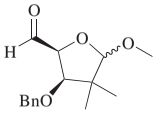


$MgBr_2$•OEt_2, CH_2Cl_2

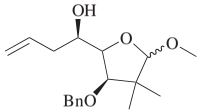


(92)

54



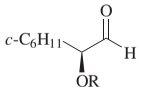
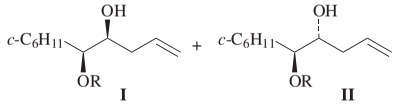
$MgBr_2$•OEt_2, CH_2Cl_2



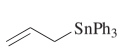
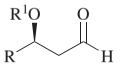
(95)

54

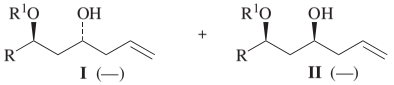
TABLE 2B. LEWIS ACID PROMOTED ADDITION OF ALLYLIC TRIBUTYLSTANNANES TO CHIRAL ALDEHYDES *(Continued)*

Allylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3 		Lewis acid, CH_2Cl_2	 **I** + **II**	168

	R	**I**:**II**	
BF_3•OEt_2	Bn	39:61	(—)
$MgBr_2$	Bn	100:0	(85)
ZnI_2	Bn	97:3	(92)
$TiCl_4$	Bn	100:0	(75)
BF_3•OEt_2	TBDMS	5:95	(83)

Lewis acid


I (—) + **II** (—)

169

	R	R^1	**I**:**II**
$TiCl_4$	Me	Bn	97:3
$TiCl_4$	n-C_6H_{13}	Bn	99:1
$TiCl_4$	n-C_6H_{13}	Me	79:21
$TiCl_4$	n-C_6H_{13}	Et	98:2
$TiCl_4$	n-C_6H_{13}	TBDMS	48:52
$MgBr_2$	Me	Bn	89:11
$MgBr_2$	n-C_6H_{13}	Bn	91:9
$MgBr_2$	n-C_6H_{13}	Me	57:43
$MgBr_2$	n-C_6H_{13}	Et	90:10
$MgBr_2$	n-C_6H_{13}	TBDMS	63:37
$SnCl_4$	Me	Bn	77:23
$SnCl_4$	n-C_6H_{13}	Bn	77:23
$SnCl_4$	n-C_6H_{13}	Me	23:77
$SnCl_4$	n-C_6H_{13}	Et	75:25
$SnCl_4$	n-C_6H_{13}	TBDMS	63:37

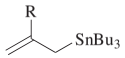
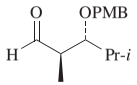
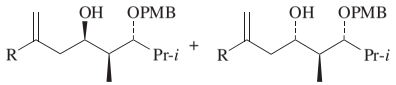
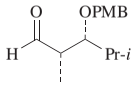
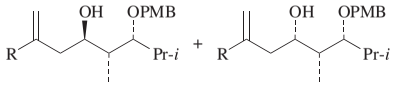
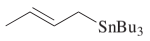
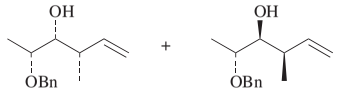
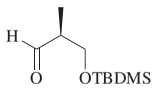
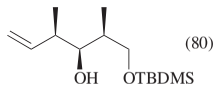
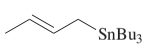
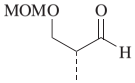
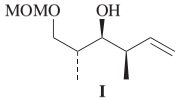
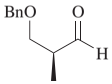
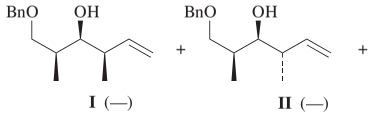
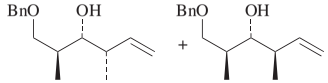
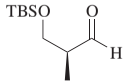
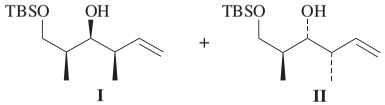
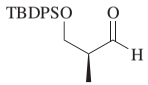
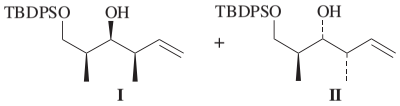
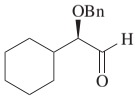
		BF_3•OEt_2	Me	Bn	80:20
		BF_3•OEt_2	n-C_6H_{13}	Bn	83:17
		BF_3•OEt_2	n-C_6H_{13}	Me	78:22
		BF_3•OEt_2	n-C_6H_{13}	Et	80:20
		BF_3•OEt_2	n-C_6H_{13}	TBDMS	77:23
$C_{3\text{-}4}$	 	Lewis acid	 **I** (—) **II** (—)		17
			R	**I**:**II**	
		BF_3•OEt_2, –78°	H	>99:1	
		BF_3•OEt_2, –78°	Me	>99:1	
		Ph_3CClO_4, CH_2Cl_2	H	>99:1	
		Lewis acid	 **I** (—) **II** (—)		17
			R	**I**:**II**	
		BF_3•OEt_2, –78°	H	87:13	
		BF_3•OEt_2, –78°	Me	80:20	
		Ph_3CClO_4, CH_2Cl_2	H	62:38	
C_4	 	$MgBr_2$, CH_2Cl_2	 **I** **II** **I**+**II** (75); **I**:**II** = 12:1		64
		BF_3•OEt_2, CH_2Cl_2, –78°, 0.5 h	 (80)		170

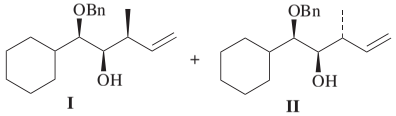
TABLE 2B. LEWIS ACID PROMOTED ADDITION OF ALLYLIC TRIBUTYLSTANNANES TO CHIRAL ALDEHYDES *(Continued)*

Allylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
		$MgBr_2 \cdot OEt_2$, CH_2Cl_2, –23°	 **I**	**I+II** (88); **I**:**II** = 87.5:12.5	171, 172
		Lewis acid, CH_2Cl_2	 **I** (—) **II** (—)	58
			 **III** (—) **IV** (—)	
			I:**II**:**III**:**IV**	
		$SnCl_4$	42:0:58:0	
		ZnI_2	48:7:40:5	
		$TiCl_4$	41:0:59:0	
		$MgBr_2$	7:10:81:2	
		$BF_3 \cdot OEt_2$, –78°	 **I** **II**	**I+II** (92); **I**:**II** = 95:5	58
				I+II (81); **I**:**II** = 18:1	173
		Lewis acid, CH_2Cl_2	 **I** **II**	58

	I+II	I:II
$ZnBr_2$, –78 to 0°	(—)	67:27:others
$ZnBr_2$, 0 to 23°	(—)	50:19:others
$BF_3{\bullet}OEt_2$, –78°	(90)	90:10
$BF_3{\bullet}OEt_2$ (2.1 eq), –78°	(87)	88:12
$TiCl_4$, –78°	(—)	67:33
Et_2AlCl, –78°	(—)	83:17
$ZrCl_4$, –78°	(—)	78:2:others



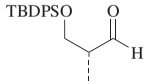
$MgBr_2$



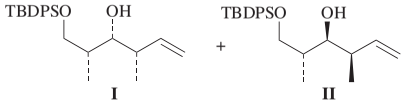
I **II**

63

I+II (85); **I**:**II** = 93:7



Lewis acid

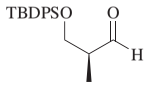


I **II**

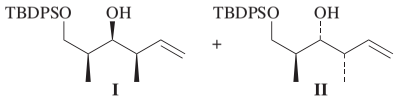
62

$BF_3{\bullet}OEt_2$ **I+II** (71); **I**:**II** = 90:10

CAB **I+II** (68); **I**:**II** = 98:2



Lewis acid



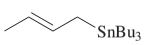
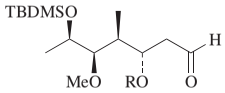
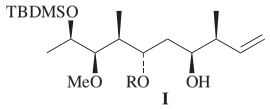
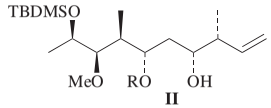
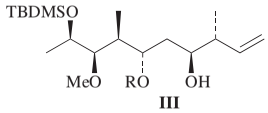
I **II**

62

$BF_3{\bullet}OEt_2$ **I+II** (75); **I**:**II** = 90:10

CAB **I+II** (65); **I**:**II** = 10:90

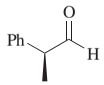
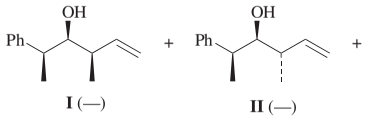
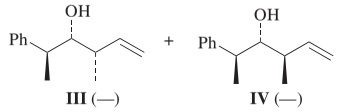
TABLE 2B. LEWIS ACID PROMOTED ADDITION OF ALLYLIC TRIBUTYLSTANNANES TO CHIRAL ALDEHYDES *(Continued)*

Allylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 		Lewis acid, CH_2Cl_2	 +  + 	64

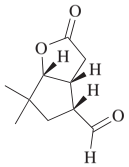
R	I+II+III	I:II:III
PMB	(64)	71.5:21.5:7
Bn	(65)	86:7:7

BF_3•OEt_2

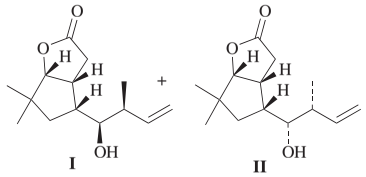
$TiCl_4$

		Lewis acid or pressure	 + 	160

	I:II:III:IV
BF_3	86:0:14:0
10 kbar	18:52:14:16



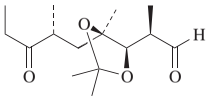
$BF_3{\bullet}Et_2O$, CH_2Cl_2, –78°



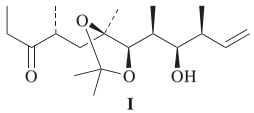
I **II**

I+II (74); **I**:**II** = 89:11

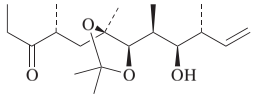
174



$BF_3{\bullet}OEt_2$, –90°

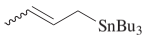


I

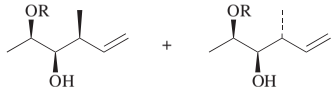


II **I+II** (82); **I**:**II** = 80:20

175



$MgBr_2$, CH_2Cl_2



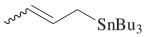
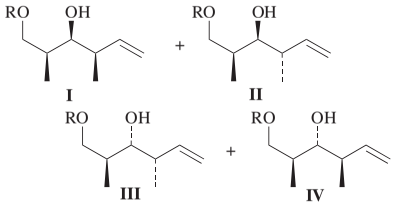
I **II**

22

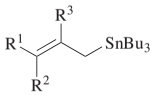
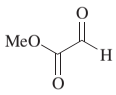
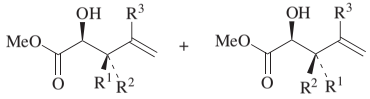
E:*Z*
90:10
76:24
12:88
90:10
90:10
76:24
12:88

R	**I+II**	**I**:**II**
BOM	(88)	91:9
BOM	(85)	88:12
BOM	(80)	85:15
Bn	(84)	92.5:7.5
Bn	(89)	93:7
Bn	(79)	91.2:8.8
Bn	(82)	78.6:21.4

TABLE 2B. LEWIS ACID PROMOTED ADDITION OF ALLYLIC TRIBUTYLSTANNANES TO CHIRAL ALDEHYDES *(Continued)*

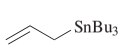
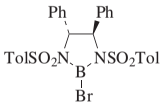
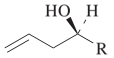
Allylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 		Lewis acid		22

E:*Z*		R	I+II+III+IV	I:II:III:IV
90:10	$TiCl_4$	Bn	(82)	0:0:41:59
76:24	$TiCl_4$	Bn	(76)	0:0:57:43
12:88	$TiCl_4$	Bn	(80)	0:0:80:20
93:7	BF_3	TBDMS	(86)	99:1:0:0
55:45	BF_3	TBDMS	(83)	95:5:0:0
8:92	BF_3	TBDMS	(88)	75:25:0:0
93:7	$MgBr_2$	Bn	(—)	9:5:73:13
55:45	$MgBr_2$	Bn	(—)	6:5:75:14
8:92	$MgBr_2$	Bn	(—)	5:0:87:8

$C_{4\text{-}6}$ 		BINOL-Ti(IV), 4 Å MS, CH_2Cl_2		146

R^1	R^2	R^3	I+II	% ee I	% ee II	I:II
Me	H	H	(53)	84	16	75:25
H	Me	H	(38)	34	38	56:44
Me	H	Me	(80)	2	2	53:47

TABLE 3. ADDITION OF ALLYLIC TRIBUTYLSTANNANES VIA TRANSMETALATION

Allylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
		 **11**		65

Solvent	R		% ee
CH_2Cl_2	*n*-C_5H_{11}	(>90)	90 S
Toluene	*n*-C_5H_{11}	(>90)	95 S
CH_2Cl_2	*c*-C_6H_{11}	(>90)	93 R
Toluene	*c*-C_6H_{11}	(>90)	97 R
CH_2Cl_2	Ph	(>90)	94 R
Toluene	Ph	(>90)	95 R
CH_2Cl_2	(*E*)-C_6H_5CH=CH	(>90)	98 R
Toluene	(*E*)-C_6H_5CH=CH	(>90)	97 R

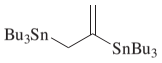
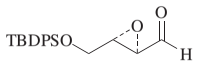
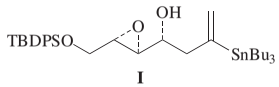
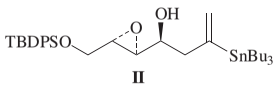
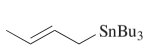
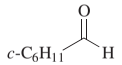
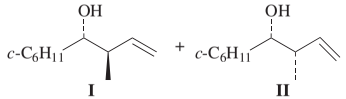
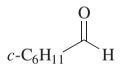
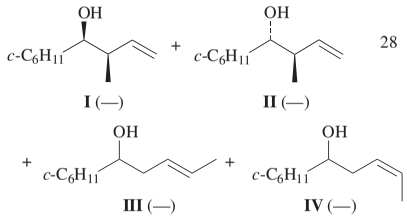
		(*R*,*R*)-**11**	 **I** +  **II** **I**+**II** (85); **I**:**II** = 3.2:1	66

TABLE 3. ADDITION OF ALLYLIC TRIBUTYLSTANNANES VIA TRANSMETALATION *(Continued)*

Allylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 		$InCl_3$	 **I** + **II**	13

Solvent	Temp.	Time		**I**:**II**
EtOH (aq)	rt	24 h	(67)	81:19
THF	rt	24 h	(78)	86:14
DMF	rt	24 h	(33)	84:16
MeCN	rt	0.5 h	(88)	87:13
MeCN	–40°	18 h	(90)	94:6
Acetone	rt	0.25 h	(96)	87:13
Acetone	–78° to rt	5 h	(90)	98:2

		Lewis acid, CH_2Cl_2	 **I** (—) + **II** (—) + **III** (—) + **IV** (—)	28

	I:**II**:**III**:**IV**
BF_3•OEt_2	96:4:0:0
$MgBr_2$	52:36:0:12
$SnCl_4$	23:26:15:36
$TiCl_4$	90:7:1:2
$TiCl_4$ (2 eq)	4:91:5:0

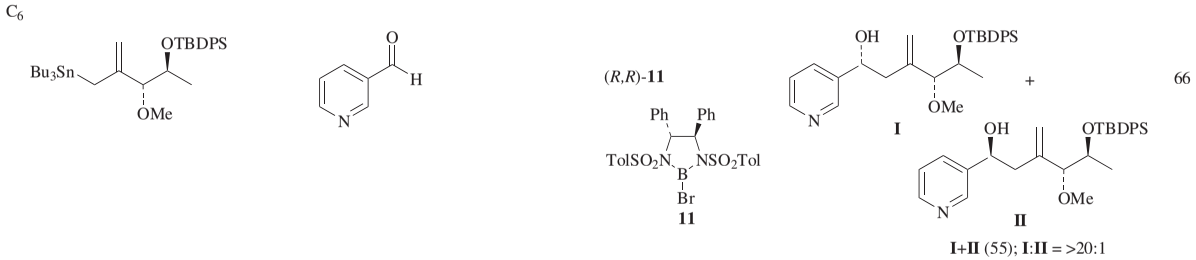


TABLE 3. ADDITION OF ALLYLIC TRIBUTYLSTANNANES VIA TRANSMETALATION *(Continued)*

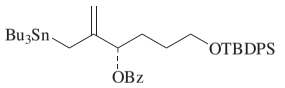
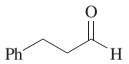
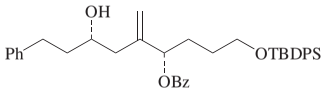
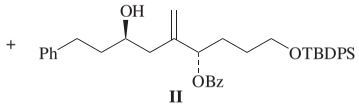
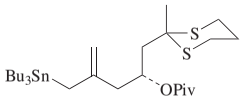
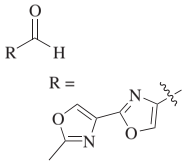
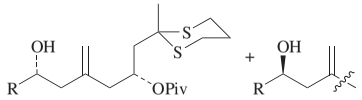
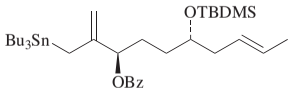
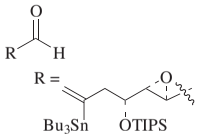
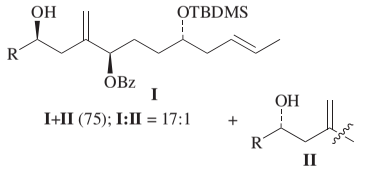
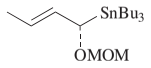
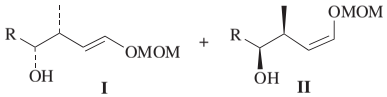
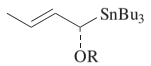
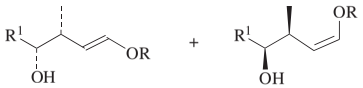
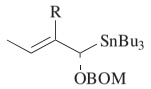
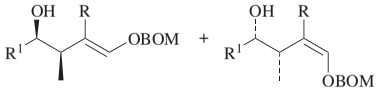
Allylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 			 **I** +  **II**	66
		(*R*,*R*)-**11**	**I**+**II** (96); **I**:**II** > 20:1	
		(*S*,*S*)-**11**	**I**+**II** (94); **I**:**II** = 1:1	
C_8 		(*R*,*R*)-**11**	 **I** **II** **I**+**II** (95); **I**:**II** = 10.5:1	66
C_{11} 		(*S*,*S*)-**11**	 **I** **I**+**II** (75); **I**:**II** = 17:1 **II**	66

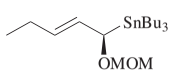
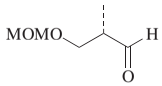
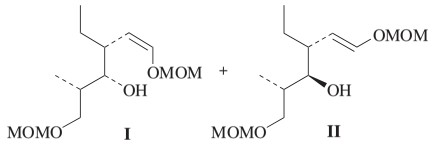
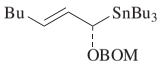
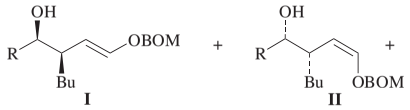
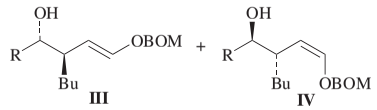
TABLE 4. LEWIS ACID PROMOTED ADDITION OF α-(ALKOXY)ALLYLSTANNANES TO ALDEHYDES

Allylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 	 R = TBDMSO(CH$_2$)$_3$—≡	BF_3•OEt_2, CH_2Cl_2, –78°	 **I** **II** **I**+**II** (—); **I**:**II** = 2.5:1	70
 R = (8-phenylmenthyl)-oxymethyl		BF_3•OEt_2, CH_2Cl_2, –78°	 **I** **II**	78
$C_{4\text{-}5}$ 		BF_3•OEt_2, CH_2Cl_2, –78°	 **I** **II**	77

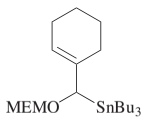
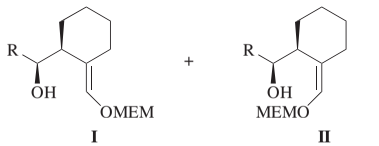
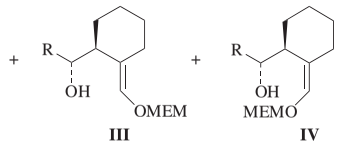
R^1		**I**:**II**
c-C_6H_{11}	(—)	82:12
Ph	(—)	< 5:95

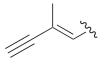
R	R^1		**I**:**II**
H	*n*-C_6H_{13}	(76)	55:45
Me	*n*-C_6H_{13}	(80)	> 95:5
Me	(*E*)-C_4H_9CH=CH	(72)	> 95:5
H	*c*-C_6H_{11}	(45)	80:20
Me	*c*-C_6H_{11}	(51)	> 95:5
H	Ph	(68)	< 1:> 99

TABLE 4. LEWIS ACID PROMOTED ADDITION OF α-(ALKOXY)ALLYLSTANNANES TO ALDEHYDES *(Continued)*

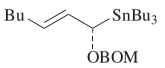
Allylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 		$BF_3{\bullet}OEt_2$, CH_2Cl_2, –78°	 **I**:**II** = 92:8 (—)	82
C_7 		$BF_3{\bullet}OEt_2$, CH_2Cl_2, –78°	 	24

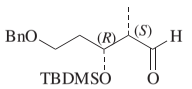
R	**I**:**II**:**III**:**IV**	
C_6H_{13}	70:27:0:3	(80)
(*E*)-$C_4H_9CH{=}CH$	80:17:1:2	(72)
$C_4H_9C{\equiv}CH$	51:25:7:17	(88)

		Lewis acid, CH_2Cl_2, –78°, 2 to 5 h	 	176

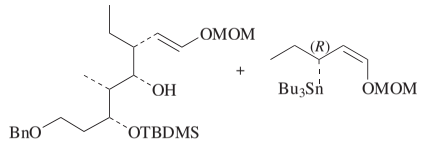
R		I+II+III+IV	I:II:III:IV
i-Pr	$BF_3{\bullet}OEt_2$	(13)	—
i-Pr	$EtAlCl_2$	(69)	73:2:23:2
	$BF_3{\bullet}OEt_2$	(80)	85:9:3:3
	$BF_3{\bullet}OEt_2$	(63)	90:0:10:0
	$BF_3{\bullet}OEt_2$	(69)	100:0:0:0
c-C_6H_{11}	$BF_3{\bullet}OEt_2$	(0)	—
c-C_6H_{11}	$EtAlCl_2$	(61)	82:3:12:3
Ph	$BF_3{\bullet}OEt_2$	(84)	83:0:6:11
Ph	$EtAlCl_2$	(95)	63:16:7:14
$BnOCH_2$	$BF_3{\bullet}OEt_2$	(46)	72:14:12:2
$BnOCH_2CH_2$	$BF_3{\bullet}OEt_2$	(70)	80:6:8:6

C_7





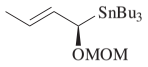
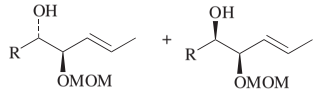
$BF_3{\bullet}OEt_2$, CH_2Cl_2, –78°



82

(45) % ee > 80

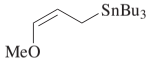
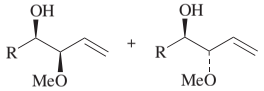
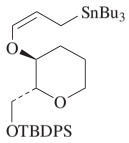
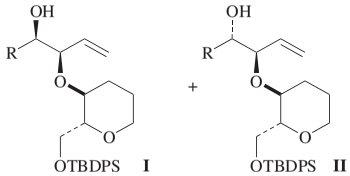
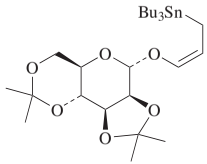
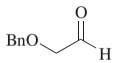
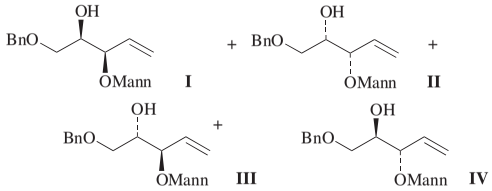
TABLE 5. ADDITION OF α-(ALKOXY)ALLYLSTANNANES TO ALDEHYDES VIA TRANSMETALATION

Allylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 		$InCl_3$, acetone	 **I** **II**	13
		$InCl_3$, EtOAc	**I + II**	83

R	I+II	I:II	% ee I
c-C_6H_{11}	(88)	98:2	> 95
(*E*)-BuCH=CH	(76)	84:16	(—)
c-C_6H_{11}—≡	(88)	96:4	(—)
(*E*)-BuCH=CH	(87)	83:17	> 95

R	I+II	I:II
n-C_6H_{13}	(99)	95:5
c-C_6H_{11}	(95)	98:2
(*E*)-BuCH=CH	(85)	90:10
n-C_6H_{13}—≡	(85)	90:10

TABLE 6A. LEWIS ACID PROMOTED ADDITION OF γ-(ALKOXY)ALLYLSTANNANES TO ACHIRAL ALDEHYDES

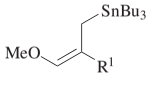
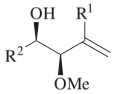
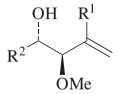
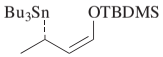
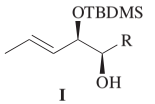
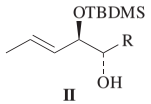
Allylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3 		$BF_3{\bullet}OEt_2$, –78°	 **I** + **II**	86
		Lewis acid, CH_2Cl_2, –78°	 **I** + **II**	88
		Lewis acid, CH_2Cl_2	 **I** + **II** + **III** + **IV**	89

R	I+II	I:II
i-Pr	(60)	96:4
c-C_6H_{11}	(44)	83:17
Ph	(86)	91:9

	R	I+II	I:II
$BF_3{\bullet}OEt_2$	Ph	(82)	97:3
$AlCl_3{\bullet}OEt_2$	Ph	(68)	97:3
$TiCl_4$	Ph	(48)	73:27
$AlCl_3{\bullet}OEt_2$	Bu	(21)	96:4
$AlCl_3{\bullet}OEt_2$	C_7H_{15}	(26)	93:7
$BF_3{\bullet}OEt_2$	C_7H_{15}	(17)	100:0

	I+II+III+IV	I:II:(III+IV)
$BF_3{\bullet}OEt_2$, –78°	(30)	73.5:10.5:16
$MgBr_2{\bullet}OEt_2$, –23°	(56)	54.5:45.5:0
ZnI_2, 0°	(43)	37:55.5:7.5

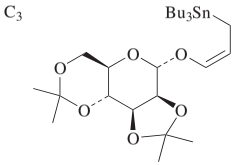
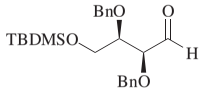
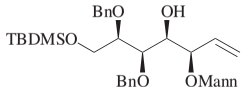
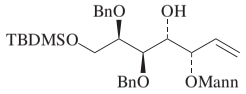
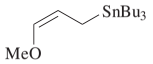
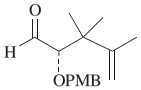
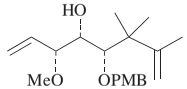
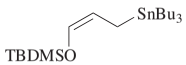
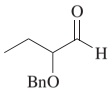
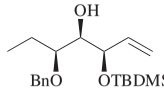
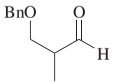
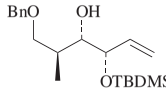
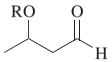
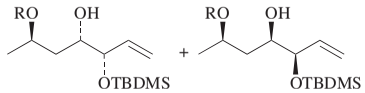
TABLE 6A. LEWIS ACID PROMOTED ADDITION OF γ-(ALKOXY)ALLYLSTANNANES TO ACHIRAL ALDEHYDES *(Continued)*

Allylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{3\text{-}7}$ 		$BF_3{\bullet}OEt_2$, CH_2Cl_2	 +  **I** **II**	177
C_4 		$BF_3{\bullet}OEt_2$, CH_2Cl_2, –78°	 +  **I** **II**	178

R^1	R^2	**I+II**	**I:II**
H	Ph	(86)	91:9
t-Bu	Ph	(77)	5:95
t-Bu	*n*-C_7H_{13}	(59)	10:90
t-Bu	*c*-C_6H_{11}	(61)	4:96
t-Bu	PhCH=CH	(63)	50:50

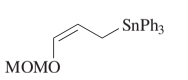
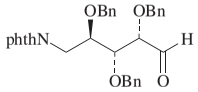
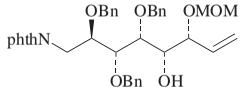
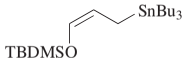
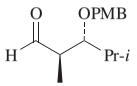
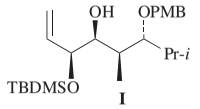
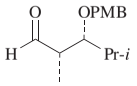
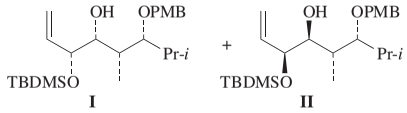
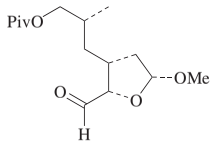
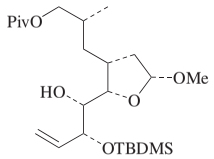
R	**I+II**	**I:II**
n-C_6H_{13}	(86)	97:3
(*E*)-*n*-BuCH=CH	(81)	> 99:1
n-Bu—≡	(84)	93:7

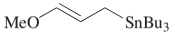
TABLE 6B. LEWIS ACID PROMOTED ADDITION OF γ-(ALKOXY)ALLYLSTANNANES TO CHIRAL ALDEHYDES

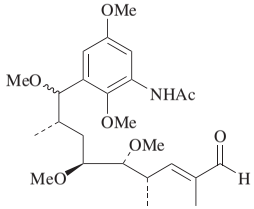
Allylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
		$BF_3{\bullet}OEt_2$, CH_2Cl_2, –78°	 +  **I** **II** **I+II** (69); **I**:**II** = 67:33	89
		$MgBr_2{\bullet}OEt_2$, CH_2Cl_2, –40°	 (71)	179
		$MgBr_2{\bullet}OEt_2$	 (67)	84
		$MgBr_2{\bullet}OEt_2$	 (65)	84
		$MgBr_2{\bullet}OEt_2$	 **I** **II**	84

R	I+II	I:II
BOMO	(75)	80:20
Bn	(50)	80:20

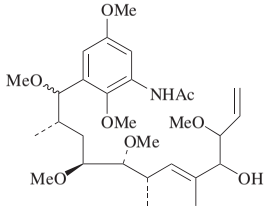
TABLE 6B. LEWIS ACID PROMOTED ADDITION OF γ-(ALKOXY)ALLYLSTANNANES TO CHIRAL ALDEHYDES *(Continued)*

Allylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3 		$MgBr_2 \cdot OEt_2$, CH_2Cl_2, –78 to 0°	 (87)	180
		$BF_3 \cdot OEt_2$, CH_2Cl_2, –78°	 (—) > 99:1	17
		$BF_3 \cdot OEt_2$, CH_2Cl_2, –78°	 **I+II+III** (—); **I**:**II**:**III** = 59:32:9	17
		$MgBr_2 \cdot OEt_2$, CH_2Cl_2, –5°	 (70) > 99:1	181



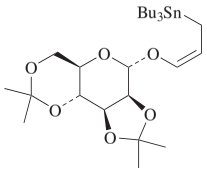


$BF_3{\bullet}OEt_2$, CH_2Cl_2, –78 to –20°, 10 h

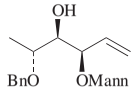


(70)

182



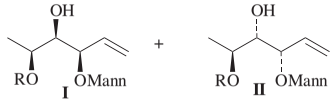
$BF_3{\bullet}OEt_2$, CH_2Cl_2, –78°



(52)

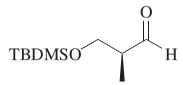
89

$BF_3{\bullet}OEt_2$, CH_2Cl_2, –78°

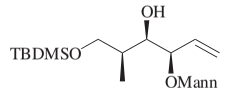


89

R	I+II	I:II
Bn	(61)	83:17
TBDMS	(41)	87.5:12.5

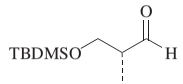


$BF_3{\bullet}OEt_2$, CH_2Cl_2, –78°

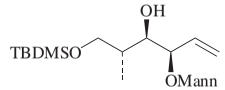


(70) 20:1

89



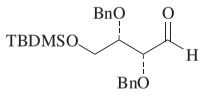
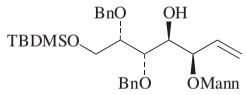
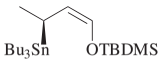
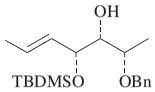
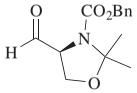
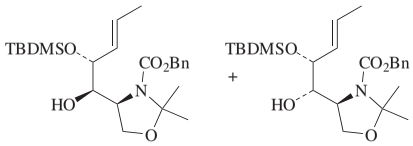
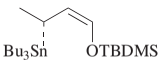
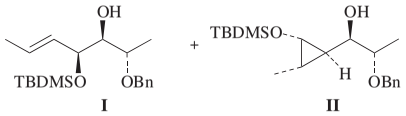
$BF_3{\bullet}OEt_2$, CH_2Cl_2, –78°



(80) > 30:1

89

TABLE 6B. LEWIS ACID PROMOTED ADDITION OF γ-(ALKOXY)ALLYLSTANNANES TO CHIRAL ALDEHYDES *(Continued)*

Allylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3		BF_3•OEt_2, CH_2Cl_2, –78°	 (75)	89
C_4 		$MgBr_2$	 (71)	91
		$MgBr_2$, CH_2Cl_2, –25°	 **I=II** (95); **I:II** = 91:9	93
		BF_3	 **I+II** (50); **I:II** = 40:60	91

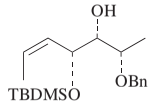
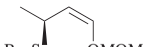
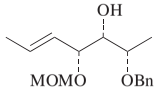
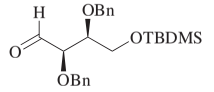
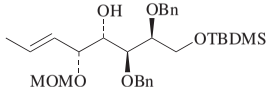
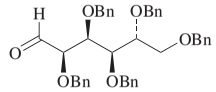
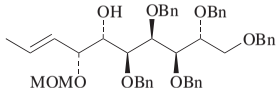
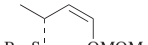
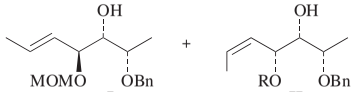
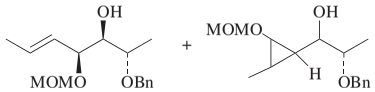
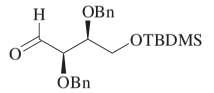
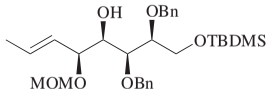
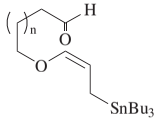
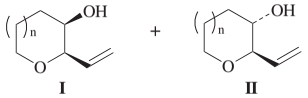
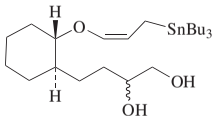
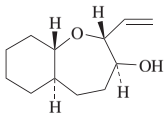
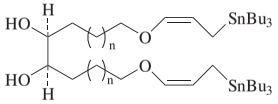
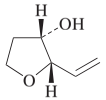
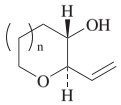
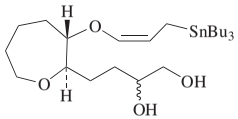
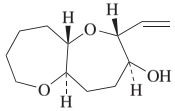
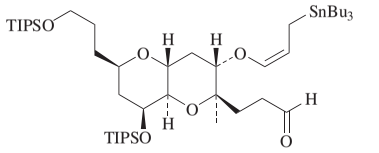
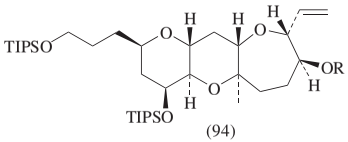
		$MgBr_2$		(66)	91
		$MgBr_2$		(83)	91
		$BF_3{\bullet}OEt_2$		(80)	91
		$BF_3{\bullet}OEt_2$		(98)	91
		$MgBr_2$	 **I** **II** **I+II** (74); **I**:**II** = 75:25		91
		$BF_3{\bullet}OEt_2$, CH_2Cl_2, −78°	 **I** **II** **I+II** (74); **I**:**II** = 93:7		183
		$MgBr_2$		(95)	91

TABLE 7. INTRAMOLECULAR ADDITIONS OF ALLYLSTANNANYL ALDEHYDES

Allylstannyl Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3 	Lewis acid or heat	 **I** + **II**	85
		n = 0: **I+II** (95), **I:II** 10:90	
	$BF_3•OEt_2$, 100°	n = 0: (95), 98:2	
		n = 1: (80), 32:68	
	$BF_3•OEt_2$, 100°	n = 1: (78), 98:2	
		n = 2: (45), 2:98	
	$BF_3•OEt_2$, 100°	n = 2: (trace), —	
	1. *n*-Bu_4NIO_4, CH_2Cl_2, 0 to 25°, 3 h 2. $BF_3•OEt_2$, −78°	 (65)	184
 n = 0	1. *n*-Bu_4NIO_4, CH_2Cl_2, 0 to 25°, 3 h 2. $BF_3•OEt_2$, −78°	 (58)	184
	1. *n*-Bu_4NIO_4, CH_2Cl_2, 0 to 25°, 3 h 2. $BF_3•OEt_2$, −78°	 n = 1: (63); n = 2: (71); n = 3: (12)	184
	1. *n*-Bu_4NIO_4, CH_2Cl_2, 0 to 25°, 3 h 2. $BF_3•OEt_2$, −78°	 (98)	184

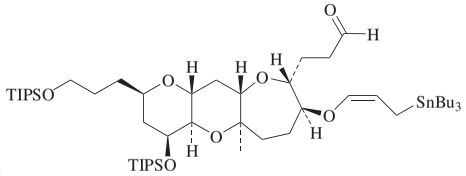


$BF_3{\bullet}OEt_2$, CH_2Cl_2, –78°

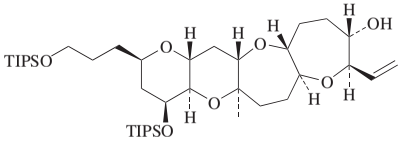


(94)

118



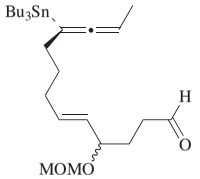
$BF_3{\bullet}OEt_2$, CH_2Cl_2, –78°



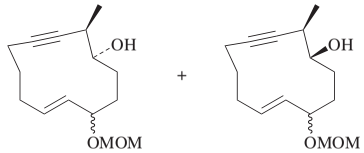
(98)

118

C_{13}



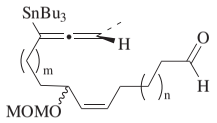
$BF_3{\bullet}OEt_2$, CH_2Cl_2, –78°



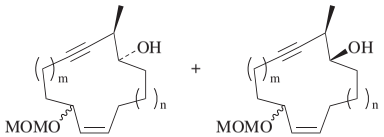
I (88) **I**:**II** = 50:50 **II**

105

$C_{13\text{-}15}$



$BF_3{\bullet}OEt_2$, CH_2Cl_2, –78°



I **II**

105

m	n	**I+II**	**I**:**II**
1	1	(86)	50:50
2	1	(94)	50:50
2	2	(94)	50:50

TABLE 7. INTRAMOLECULAR ADDITIONS OF ALLYLSTANNANYL ALDEHYDES *(Continued)*

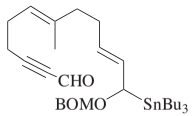
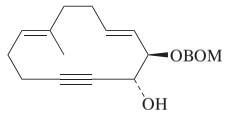
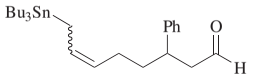
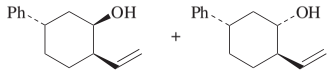
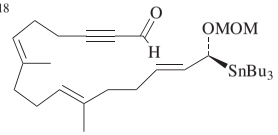
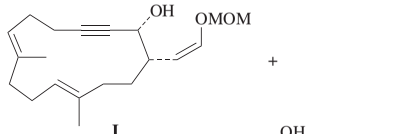
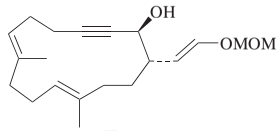
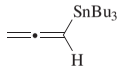
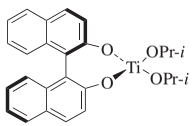
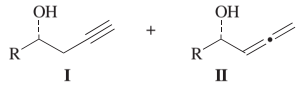
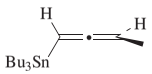
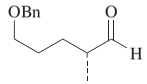
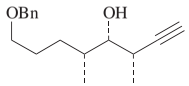
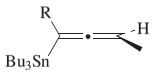
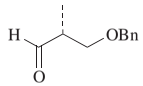
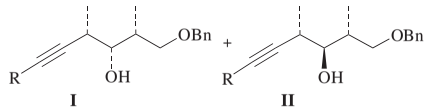
Allylstannyl Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 	$BF_3{\bullet}OEt_2$, CH_2Cl_2, –78°	 (70)	103
	Lewis acid or heat	 **I** **II**	27
		SM / **I+II**+others / **I**:**II**:others	
	$BF_3{\bullet}OEt_2$, 25°	Z / (—) / 85:15:—	
		Z / (100) / 95:5:0	
	$BF_3{\bullet}OEt_2$, 110°	E / (—) / 24:60:12	
		E / (50) / 80:9:11	
C_{18} 	$BF_3{\bullet}OEt_2$, CH_2Cl_2, –78°	 **I**  **II** I+II (**88**); **I**:**II** = 95:5 (88)	102

TABLE 8. LEWIS ACID PROMOTED ADDITION OF ALLENYLSTANNANES TO ALDEHYDES

Allenylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3 		Additive, 	 (—)	185

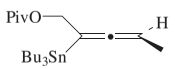
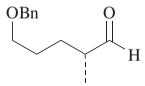
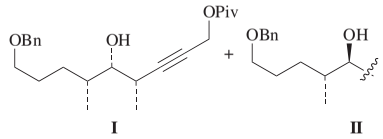
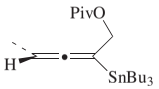
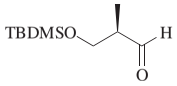
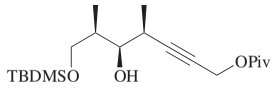
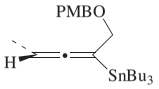
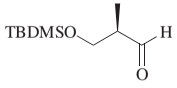
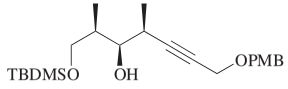
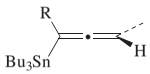
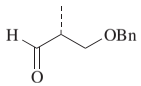
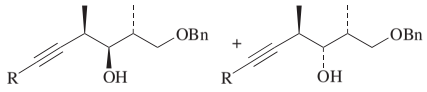
Additive	R	I+II	I:II	% ee
50 mol % None	c-C_6H_{11}	(64)	80:20	89
10 mol % i-PrSBEt$_2$	c-C_6H_{11}	(73)	> 98:2	91
50 mol % None	Ph	(48)	93:7	> 99
10 mol % i-PrSBEt$_2$	Ph	(52)	> 98:2	92
50 mol % None	$PhCH_2CH_2$	(76)	96:4	95
10 mol % i-PrSBEt$_2$	$PhCH_2CH_2$	(86)	> 98:2	94

C_4

		BF_3•OEt_2	 (88)	186
		Lewis acid		187

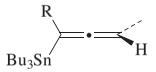
	R	I+II	I:II
BF_3•OEt_2	Et	(92)	99:1
BF_3•OEt_2	CH_2OAc	(96)	99:1
$MgBr_2$•OEt_2	Et	(95)	50:50
$MgBr_2$•OEt_2	CH_2OAc	(96)	99:1

TABLE 8. LEWIS ACID PROMOTED ADDITION OF ALLENYLSTANNANES TO ALDEHYDES *(Continued)*

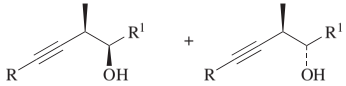
Allenylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
		$BF_3{\bullet}OEt_2$, CH_2Cl_2	 **I** + **II** **I+II** (92); **I**:**II** = 94:6	186
		$BF_3{\bullet}OEt_2$	 (71)	188
		$BF_3{\bullet}OEt_3$	 (75)	188
$C_{5\text{-}6}$				
		Lewis acid	 **I** + **II**	187

	R	I+II	I:II
$BF_3{\bullet}OEt_2$	Et	(88)	84:16
$BF_3{\bullet}OEt_2$	CH_2OAc	(98)	83:17
$MgBr_2{\bullet}OEt_2$	Et	(93)	99:1
$MgBr_2{\bullet}OEt_2$	CH_2OAc	(95)	99:1

$C_{5\text{-}11}$



$BF_3{\bullet}OEt_2$, CH_2Cl_2, –78°

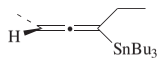


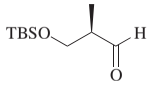
I **II**

187

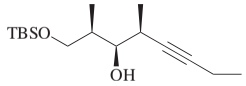
R	R^1	**I+II**	**I:II**	% ee
n-C_7H_{15}	*n*-C_6H_{13}	(83)	39:61	92
n-C_7H_{15}	*i*-Pr	(95)	99:1	—
CH_2OPiv	*c*-$C_6H_{11}CH{=}C(CH_3)$	(58)	81:19	98

C_6





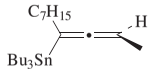
$BF_3{\bullet}OEt_3$



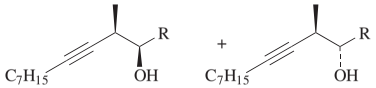
(75)

188

C_{11}



Lewis acid, CH_2Cl_2



I **II**

94

	R	**I+II**	**I:II**	% ee
$BF_3{\bullet}OEt_2$	*n*-C_6H_{13}	(83)	37:63	—
$MgBr_2$	*n*-C_6H_{13}	(56)	69:31	92
$BF_3{\bullet}OEt_2$	*i*-Pr	(80)	99:1	—
$MgBr_2$	*i*-Pr	(48)	88:12	—
$BF_3{\bullet}OEt_2$	*t*-Bu	(92)	99:1	98

TABLE 9. ADDITION OF ALLENYLSTANNANES TO ALDEHYDES VIA TRANSMETALATION

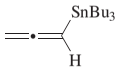
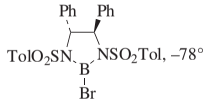
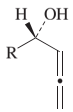
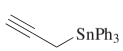
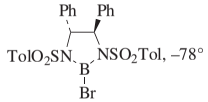
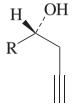
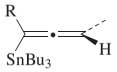
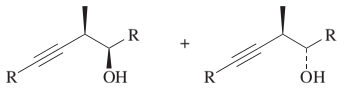
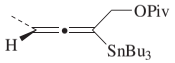
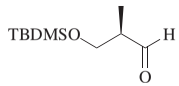
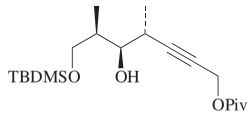
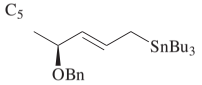
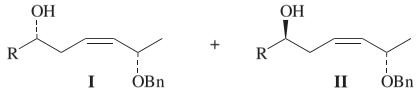
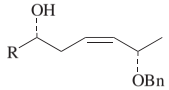
Allenylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3 			 R: *i*-Pr (74) > 99 S; *t*-Bu (78) > 99 S; *n*-C_5H_{11} (82) > 99 S; *c*-C_6H_{11} (78) > 99 S; Ph (72) > 99 R; PhCH=CH (74) > 99 S	101
			 R: *i*-Pr (76) 94 R; *t*-Bu (74) 98 R; *n*-C_5H_{11} (81) 91 S; *c*-C_6H_{11} (82) 92 R; Ph (76) 96 R; PhCH=CH (79) 98 R	101
$C_{5\text{-}11}$ 		$SnCl_4$, CH_2Cl_2, –78°	 **I** + **II**; R, R^1, **I+II**, **I:II**: *n*-C_7H_{15}, *i*-Pr, (90), 1:99; CH_2OAc, TBDPSO$(CH_2)_2$, (81), 1:99	187
C_5 		$InBr_3$, EtOAc	 (78)	189

TABLE 10. ADDITIONS OF 4-(ALKOXY)-2-PENTENYLSTANNANES TO ALDEHYDES VIA TRANSMETALATION

Pentenylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
	RCHO	$SnCl_4$	 **I** + **II**	12

R	I+II	I:II
CO_2Me	(68)	98:2
n-Pr	(84)	95:5
i-Pr	(84)	93:7
2-furyl	(72)	95:5
c-C_6H_{11}	(78)	92:8
Ph	(90)	98:2
p-ClC_6H_4	(77)	94:6
p-$O_2NC_6H_4$	(77)	95:5
p-$MeOC_6H_4$	(77)	97:3
PhCH=CH	(64)	95:5
2-naphthyl	(72)	95:5

	RCHO	$SnCl_4$, 5min, –78°		37

R	
CO_2Me	(57)
n-Pr	(84)
i-Pr	(78)
$CH_3CH=CH$	(70)
2-furyl	(72)
c-C_6H_{11}	(71)
Ph	(90)
p-ClC_6H_4	(77)
p-$O_2NC_6H_4$	(77)
p-$MeOC_6H_4$	(77)

TABLE 10. ADDITIONS OF 4-ALKOXY-2-PENTENYLSTANNANES TO ALDEHYDES VIA TRANSMETALATION *(Continued)*

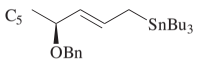
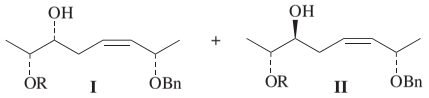
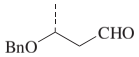
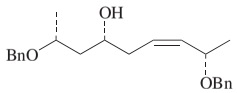
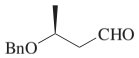
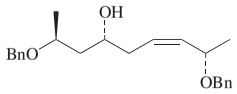
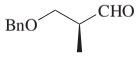
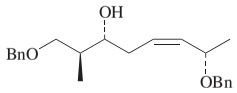
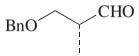
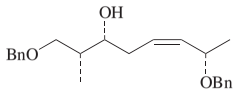
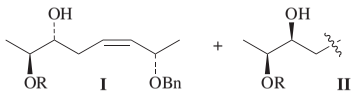
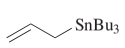
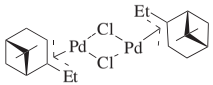
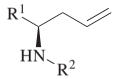
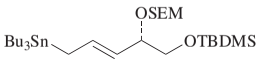
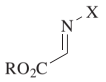
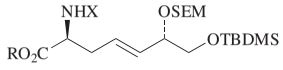
Pentenylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
		$SnCl_4$		12
			R / I+II / I:II Bn (89) 70:30 $SiMe_2Bu$-*t* (65) 70:30 MOM (68) 65:35	
		$SnCl_4$	 (76) 1,5-syn: 1,5-anti = 96:4	12
		$SnCl_4$	 (85) 1,5-syn: 1,5-anti = 96:4	12
		$SnCl_4$	 (53) 1,5-syn: 1,5-anti = 96:4	12
		$SnCl_4$	 (66) 1,5-syn: 1,5-anti = 96:4	12
		$SnCl_4$		12
			R / I+II / I:II Bn (90) 96:4 $SiMe_2Bu$-*t* (72) 96:4 MOM (72) 96:4	

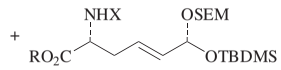
TABLE 11. ADDITION OF ALLYLSTANNANES TO IMINES

Allylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3 		 (3 %)		111

R^1	R^2		% ee
c-C_6H_{11}	Bn	(44)	40
Ph	Bn	(62)	81
Ph	*p*-$MeOC_6H_4CH_2$	(72)	80
Ph	Ph	(82)	61
Ph	Pr	(30)	70
p-$MeOC_6H_4$	Bn	(48)	78
PhCH=CH	Bn	(68)	61
2-naphthyl	Bn	(69)	79

C_5   $SnCl_4$ 

I

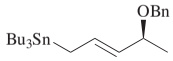
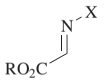
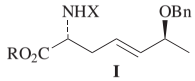
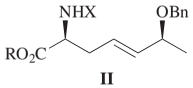


II

190

X	R	**I+II**	**I:II**
$SC_6H_4NO_2^{-4}$	Me	(81)	96:4
$CHPh_2$	Me	(71)	100:0
(*S*)-CHMePh	Bu	(68)	96:4
(*R*)-CHMePh	Bu	(72)	99:1

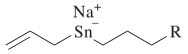
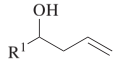
TABLE 11. ADDITION OF ALLYLSTANNANES TO IMINES *(Continued)*

Allylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 		$SnCl_4$	 + 	190

I **II**

X	R	I+II	I:II
$SC_6H_4NO_2$-*o*	Me	(87)	89:11
OBn	Me	(76)	90:10
CMe_2Ph	Bu	(75)	90:10
$CHPh_2$	Bu	(79)	90:10

TABLE 12A. LEWIS ACID PROMOTED ADDITION OF OTHER ALLYLSTANNANES TO ALDEHYDES AND KETONES

Allylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
		1. $SnCl_4$/THF, –78° to 25° 2. FSPE		40

R	R^1	
n-C_4H_9	Ph	(68)
n-C_6F_{13}	Ph	(82)
n-C_4H_9	p-$MeOC_6H_4$	(65)
n-C_6F_{13}	p-$MeOC_6H_4$	(—)
n-C_4H_9	o-$O_2NC_6H_4$	(74)
n-C_6F_{13}	o-$O_2NC_6H_4$	(81)
n-C_4H_9	1-naphthyl	(68)
n-C_6F_{13}	1-naphthyl	(81)

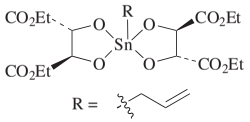
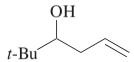
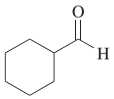
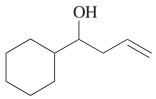
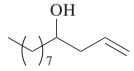
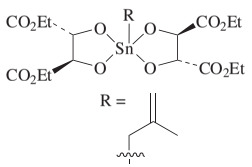
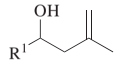
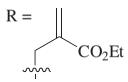
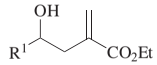
$C_{3\text{-}5}$				
		$SnCl_2$, (+)-diethyl tartrate, 18 h	 (64) % ee = 36	191
		$SnCl_2$, (+)-diethyl tartrate, 18 h	 (53) % ee = 65	191
		$SnCl_2$, (+)-diethyl tartrate, 22 h	 (78) % ee = 54	191

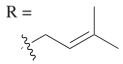
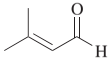
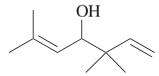
TABLE 12A. LEWIS ACID PROMOTED ADDITION OF OTHER ALLYLSTANNANES TO ALDEHYDES AND KETONES *(Continued)*

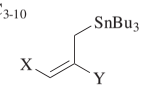
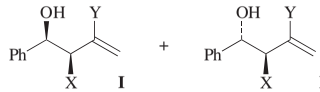
Allylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{3\text{-}5}$ 		$SnCl_2$, (+)-diethyl tartrate, 19 h		191

R^1	Time		% ee
Ph	19 h	(65)	46
c-C_6H_{11}	18 h	(68)	51

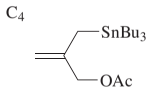
Allylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
R = 		$SnCl_2$, (+)-diethyl tartrate, 16 h		191

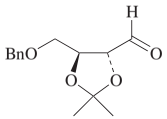
R^1	Time		% ee
Ph	16 h	(76)	58
n-C_8H_{17}	18 h	(68)	16

Allylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
R = 		$SnCl_2$, (+)-diethyl tartrate, 16 h	 (72) % ee = 25	191

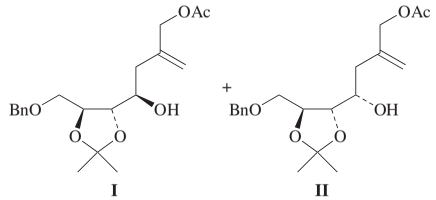
Allylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_{3\text{-}10}$ 		$BF_3{\bullet}OEt_2$, CH_2Cl_2	 **I** + **II**	177

X	Y	I:II	I+II
Et	H	78:22	(59)
Et	Me	91:9	(80)
Et	*i*-Pr	84:16	(92)
Et	*t*-Bu	13:87	(72)
Et	*t*-$BuCH_2$	91:9	(83)
Et	TMS	33:67	(79)
Et	$SiEt_3$	30:70	(61)
OMe	H	91:9	(86)
OMe	*t*-Bu	5:95	(77)



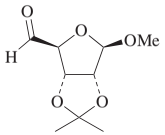


$BF_3{\bullet}OEt_2$, CH_2Cl_2, –78°

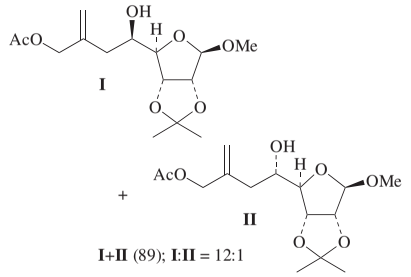


I+II (65); **I**:**II** = 91:9

192

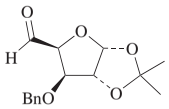


$BF_3{\bullet}OEt_2$, CH_2Cl_2, –78°

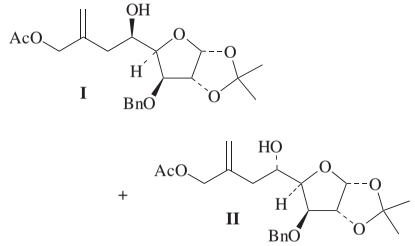


I+II (89); **I**:**II** = 12:1

192



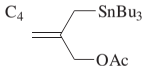
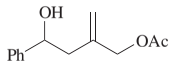
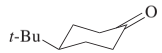
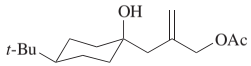
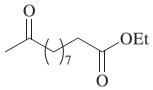
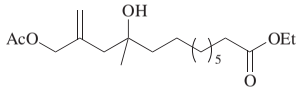
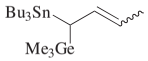
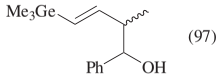
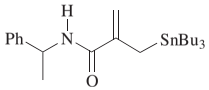
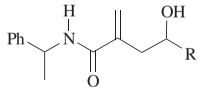
$BF_3{\bullet}OEt_2$, CH_2Cl_2, –78°



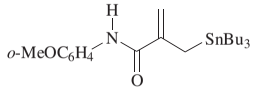
I+II (76); **I**:**II** > 95:5

192

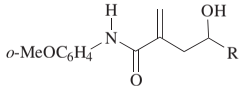
TABLE 12A. LEWIS ACID PROMOTED ADDITION OF OTHER ALLYLSTANNANES TO ALDEHYDES AND KETONES *(Continued)*

Allylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
		$BF_3{\bullet}OEt_2$, CH_2Cl_2, –78°	 (92)	192
		$BF_3{\bullet}OEt_2$, CH_2Cl_2, –78°	 (76)	192
		$BF_3{\bullet}OEt_2$, CH_2Cl_2, –78°	 (74)	192
		$BF_3{\bullet}OEt_2$, CH_2Cl_2, –78°	 (97)	193
		Lewis acid		194

	R	
$BF_3{\bullet}OEt_2$	*i*-$PrCH_2$	(80)
$TiCl_4$	*n*-C_5H_{11}	(83)
$TiCl_4$	*n*-C_6H_{13}	(71)
$BF_3{\bullet}OEt_2$	*c*-C_6H_{11}	(83)
$TiCl_4$	*c*-C_6H_{11}	(83)
$BF_3{\bullet}OEt_2$	Ph	(80)
$TiCl_4$	Ph	(81)
$TiCl_4$	*p*-ClC_6H_4	(85)
$TiCl_4$	*m*-BrC_6H_4	(84)



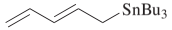
BF_3•OEt_2

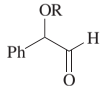


194

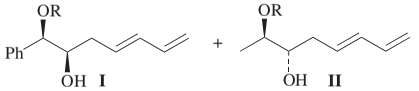
R	
i-Pr	(82)
i-Bu	(88)
n-C_5H_{11}	(100)
c-C_6H_{11}	(86)
n-C_6H_{13}	(90)
Ph	(91)
n-C_8H_{17}	(89)

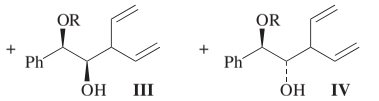
C_5





Lewis acid, solvent

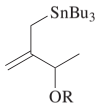




195

	R	I+II+III+IV	III+IV:I+II	I+III:II+IV
$MgBr_2$•OEt_2, CH_2Cl_2	Bn	(70)	12:88	> 99:1
$MgBr_2$•OEt_2, CH_2Cl_2	MOM	(93)	6:94	97:3
BF_3•OEt_2, CH_2Cl_2	TBS	(80)	< 1:99	20:80
$ZnCl_2$, Et_2O	Bn	(80)	77:23	> 99:1
$SnCl_4$, CH_2Cl_2	Bn	(72)	> 99:1	> 99:1
$InCl_3$, CH_3CN	Bn	(76)	> 99:1	> 99:1
$SnCl_4$, CH_2Cl_2	MOM	(62)	> 99:1	> 99:1
$ZnCl_2$, Et_2O	TBS	(77)	86:14	75:25
$InCl_3$, CH_2Cl_2	TBS	(78)	> 99:1	78:22
$InCl_3$, CH_3CN	TBS	(73)	> 99:1	43:57
$InCl_3$, EtOH	TBS	(70)	> 99:1	25:75

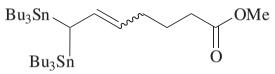
TABLE 12A. LEWIS ACID PROMOTED ADDITION OF OTHER ALLYLSTANNANES TO ALDEHYDES AND KETONES *(Continued)*

Allylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 	 Ar = *p*-$O_2NC_6H_4$	Lewis acid, CH_2Cl_2, –78°		196

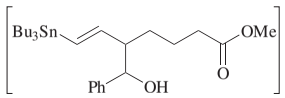
R	I+II	I:II
H	(84)	98:2
Me	(100)	62:38
Me	(99)	38:62
Me	(100)	93:7
MOM	(100)	100:0
Ac	(100)	66:34
Ac	(98)	22:78

Lewis acid
BF_3•OEt_2
i-$PrOTiCl_3$
$SnCl_4$
$SnCl_4$
$SnCl_4$
$SnCl_4$
$TiCl_4$•OEt_2

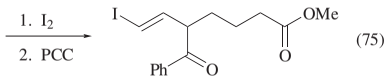
C_6



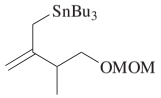
BF_3•OEt_2, CH_2Cl_2, –78°



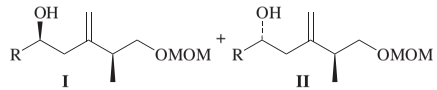
193



(75)

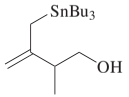


$SnCl_4$

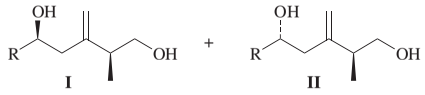


196

R	I+II	I:II
Et_2CH	(62)	89:11
Ph	(84)	93:7
p-MeC_6H_4	(75)	90:10
n-C_7H_{15}	(64)	86:14



$SnCl_4$

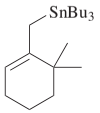


I **II**

196

R	I+II	I:II
Et_2CH	(53)	96:4
Ph	(57)	90:10
p-MeC_6H_4	(42)	85:15
n-C_7H_{15}	(46)	89:11

C_9

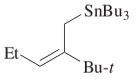


$BF_3{\bullet}OEt_2$, CH_2Cl_2

I **II**

177

R	I+II	I:II
Ph	(68)	90:10
n-C_7H_{13}	(49)	89:11



$BF_3{\bullet}OEt_2$, CH_2Cl_2

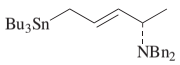
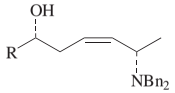
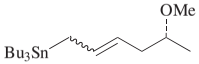
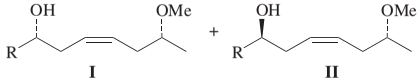
I **II**

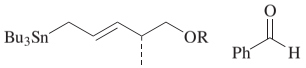
177

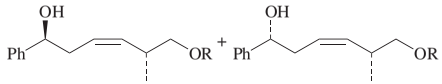
R	I+II	I:II
c-C_6H_{11}	(45)	84:16
n-C_7H_{13}	(54)	43:57

R

TABLE 12B. ADDITION OF OTHER ALLYLSTANNANES TO ALDEHYDES VIA TRANSMETALATION

Allylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 		$SnBr_4$, –78°		R: Ph (58); *p*-ClC_6H_4 (59); *p*-$MeOC_6H_4$ (35); Et (30); *i*-Pr (58)	197
C_6 		$SnBr_4$, CH_2Cl_2 –78°	 **I** + **II**	R: Me (72) 91:9; Et (67) 84:16; *i*-Pr (80) 85:15; Ph (75) 96:4; *p*-ClC_6H_4 (61) 92:8; *p*-$MeOC_6H_4$ (65) 93:7;  (73) 88:12;  (87) 76:24	198



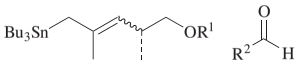


198

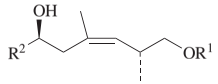
I **II**

	R	I+II	I:II
$SnCl_4$	H	(58)	80:20
$BuSnCl_3$	Bn	(8)	96:4
$SnBr_4$	Bn	(40)	95:5
Bu_2SnCl_2	Bn	(75)	99:1
$SnCl_4$	Bn	(low)	—
$SnCl_4$	PMB	(80)	95:5
$SnCl_4$	MOM	(66)	93:7
$SnCl_4$	SEM	(71)	80:20
$SnCl_4$	TBDMS	(60)	81:19
$SnCl_4$	TBDPS	(61)	80:20

C_7



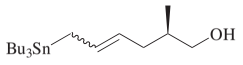
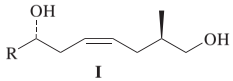
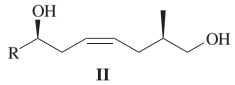
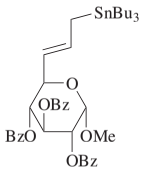
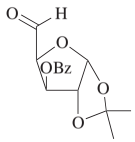
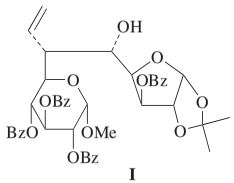
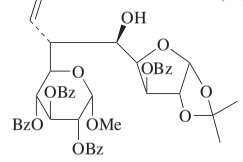
1. SnX_4
2. R^2CHO



199

	R^1	R^2	
$SnBr_4$	H	Ph	(92)
$SnBr_4$	H	MeCH=CH	(89)
$SnCl_4$	CH_2OMe	Ph	(69)
$SnCl_4$	CH_2OMe	*p*-$MeOC_6H_4$	(49)
$SnCl_4$	CH_2OMe	*i*-Pr	(57)
$SnCl_4$	CH_2OMe	MeCH=CH	(68)
$SnCl_4$	OBn	Ph	(78)

TABLE 12B. ADDITION OF OTHER ALLYLSTANNANES TO ALDEHYDES VIA TRANSMETALATION *(Continued)*

Allylstannane	Aldehyde	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 			 **I** +  **II**	200
		$SnBr_4$	R = Et; **I**+**II** (80); **I**:**II** 91:9	
		$SnBr_4$	R = *i*-Pr; **I**+**II** (58); **I**:**II** 91:9	
		$SnBr_4$	R = Ph; **I**+**II** (84); **I**:**II** 93:7	
		$SnBr_4$	R = *p*-$O_2NC_6H_4$; **I**+**II** (84); **I**:**II** 93:7	
		$SnBr_4$	R = *p*-$MeOC_6H_4$; **I**+**II** (76); **I**:**II** 91:9	
		$SnCl_4$	R = Ph; **I**+**II** (62); **I**:**II** 84:16	
C_8 		$TiCl_4$, CH_2Cl_2, 0°	 **I** +  **II** **I**+**II** (55); **I**:**II** = 78:22	201

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