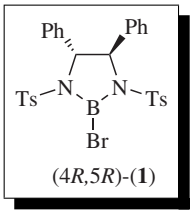
(4*R*,5*R*)-2-Bromo-1,3-bis-(4-methylphenyl sulfonyl)-4,5-diphenyl-1,3,2-diazaborolidine and (4*S*,5*S*)-2-Bromo-1,3-bis-(4-methylphenyl sulfonyl)-4,5-diphenyl-1,3,2-diazaborolidine

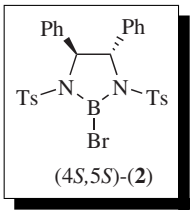


(4*R*,5*R*)-(**1**)

[121758-17-6] $C_{28}H_{26}BBrN_2O_4S_2$ (MW 609.36)

InChI = 1/C28H26BBrN2O4S2/c1-21-13-17-25(18-14-21)37(33,34)31-27(23-9-5-3-6-10-23)28(24-11-7-4-8-12-24)32(29(31)30)38(35,36)26-19-15-22(2)16-20-26/h3-20,27-28H,1-2H3/t27-,28-/m1/s1

InChIKey = PEEHKMHARMPWIU-VSGBNLITBC



(4*S*,5*S*)-(**2**)

[124600-99-3] $C_{28}H_{26}BBrN_2O_4S_2$ (MW 609.36)

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InChIKey = PEEHKMHARMPWIU-NSOVKSMOBN

(chiral bromoborane reagent used to control stereochemistry of enantioselective aromatic Claisen rearrangements, allylations of aldehydes, aldol reactions, and formation of chiral propa-1,2-dienyl and propargyl alcohols)

Alternate Names: 2-bromo-4,5-diphenyl-1,3-bis-(toluene-4-sulfonyl)-[1,3,2]diazaborolidine.

Physical Data: white solid.

Solubility: soluble in methylene chloride.

Preparative Methods: (1*R*,2*R*)−(+)-*N*,*N*′-bis-*p*-toluenesulfonyl-1,2-diphenylethylenediamine[1] was placed in a dry 25 mL round-bottom flask equipped with a magnetic stir bar and sealed with a septum. The flask was evacuated and flushed with argon three times. Freshly distilled dichloromethane (12 mL) was injected and the homogeneous solution was cooled to 0 °C for 10 min, warmed to 23 °C, kept at 23 °C for 40 min, and concentrated under vacuum (ca. 2 mm of Hg) using a metal tube inserted through the septum. Dryness of the vacuum line was maintained with a drying tube containing NaOH pellets and $CaSO_4$ to prevent possible hydrolysis of bromoborane **1**.[2]

Purification: solvent and HBr are removed under reduced pressure.

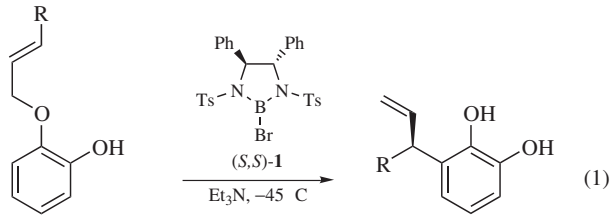
Handling, Storage, and Precautions: moisture sensitive.

Original Commentary

Andrea M. Pellerito & Robert E. Maleczka Jr
Michigan State University, East Lansing, MI, USA

General. Chiral 2-bromo-1,3-bis(4-methylphenyl sulfonyl)-4,5-diphenyl-1,3,2-diazaborolidine (**1**) is used to control the stereochemistry of enantioselective aromatic Claisen rearrangements, allylations of aldehydes, aldol reactions, and formation of chiral propa-1,2-dienyl and propargyl alcohols. Included is the discussion of both the (*R,R*) and the (*S,S*) chiral controllers.

Enantioselective Aromatic Claisen Rearrangements. Chiral boron reagent (**1**) can facilitate Claisen rearrangement of catechol monoallylic ether derivatives (**2**), affording catechol adducts (**3**)[3] (eq 1). Products formed by rearrangement of the allylic moiety to the *para* position and by abnormal Claisen rearrangement are not detected.



(**2**) (**3**) (1)

89–97% yield
94–95% ee

Rearrangement of a (*Z*)-allylic moiety requires higher reaction temperatures than do the corresponding (*E*)-allylic ethers, but affords *ent*-**3** in comparable yields and percent ee's. Trisubstituted allylic ether derivatives also afford benzofuran derivatives.

Replacement of the aromatic substituent of ligand **1** with 3,5-bis(trifluoromethyl)phenyl group increases the rate of reaction, but slightly lowers the enantioselectivity.

These reactions do not proceed in the absence of a hydroxy group in the *ortho* position. Thus, it is suggested that a rigid five-membered cyclic intermediate is formed (Figure 1). Reaction of catechol monoallylic ethers with **1** does not significantly decrease the Lewis acidity of the boron atom. Therefore, σ-bond formation between the phenolic hydroxy group and the boron complex followed by coordination of the allylic oxygen to the boron atom gives the five-membered cyclic complex. This model can explain the direction of the observed enantioselectivities. The *Re* site of the benzene ring of the substrate is likely shielded by one tolyl group of the sulfonamide ligand. Therefore, the allylic moiety should approach on the *Si* face, giving rise to the (*S*)-alcohol **3**.

Difluorovinyl allyl ethers can be similarly rearranged.[4] The preparation of β-substituted, α,α-difluorocarbonyl compounds (**5**) is possible upon treatment of **4** with 1.5 equiv of (*S,S*)-**1** in the presence of 1.5 equiv of Et_3N in CH_2Cl_2 at –78 °C, and then stirring at ambient temperature (eq 2).

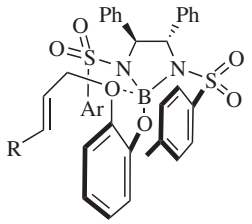
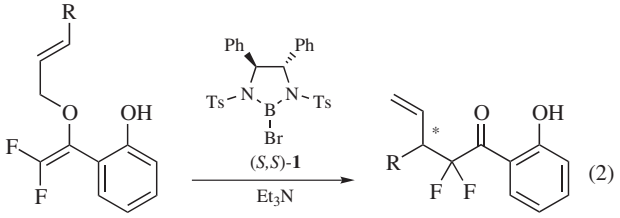


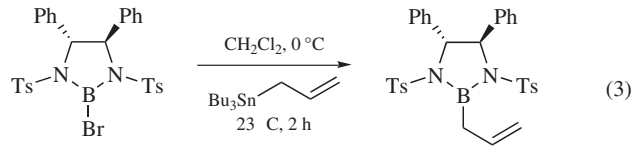
Figure 1



(**4**) (**5**)

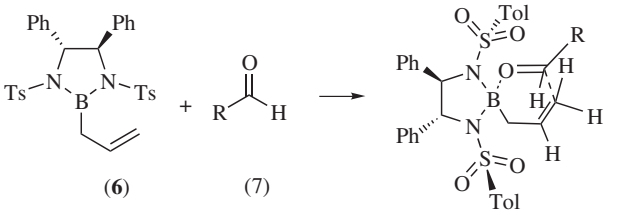
39–90% yield
41–85% ee

(2)

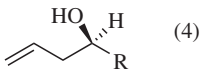


(*R,R*)-(**1**) (**6**)

(3)



(**6**) (7) (**8**)



(**9**)

(4)

Olefin geometry (*E* or *Z*) and steric bulkiness of the R substituent at the *Y*-position of **4** affect reaction temperature requirements and enantioselectivity. In the case of a *Z*-olefin bearing a bulky TMS group in the *Y*-position, the rearrangement proceeds at –78 °C and affords the product in 85% ee. With less bulky substituents on the olefin (both *E* and *Z*), higher reaction temperatures are required leading to a decrease in the enantiomeric excesses.

A postulated six-membered intermediate (Figure 2), formed by the attachment of the chiral boron reagent **1** to the phenolic hydroxy group, and the subsequent coordination of the ethereal oxygen to the boron atom can be used to explain the stereochemical outcome of the rearrangement. The *Si* face of the difluorovinyl ether moiety is shielded by the tolylsulfonyl groups; thus, the allylic moiety approaches preferably from the *Re* face to avoid steric interaction with the aromatic group in the chair-like transition state.

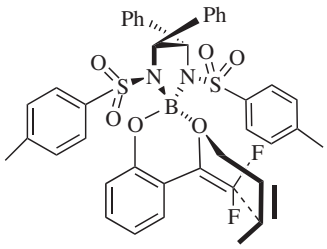


Figure 2

Allylation of Aldehydes. Bromoborane (*R,R*)-**1** reacts with allyltributylstannane to afford the chiral allylborane[2] **6** shown in eq 3.

Allylborane species **6** reacts with a variety of aldehydes to generate the corresponding homoallylic alcohol **9** in optical purities ranging from 90 to 98% ee (eq 4). Following the reaction, recovery of the (*R,R*)-bis-*p*-toluenesulfonamide can be achieved by precipitation upon the addition of Et_2O.

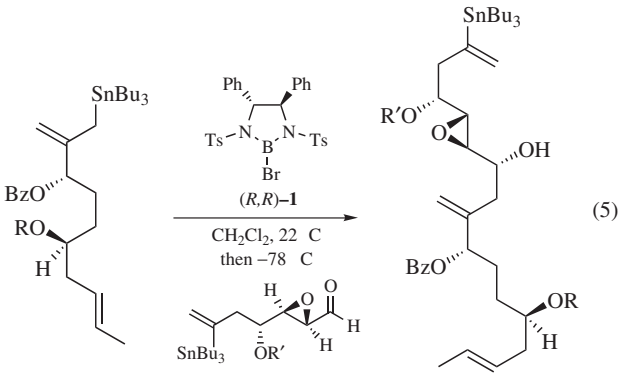
The observed enantioselectivities can be predicted on the basis of a chair-like transition structure that optimizes stereoelectronic interactions and minimizes steric repulsion between appendages on the five-membered ring, as shown in intermediate **8**.

Chiral aldehydes react with the allylborane reagent, affording homoallylic aldehydes in high stereoselectivity, via a putative chair-like transition structure. Substituted allyl groups, including 2-haloallyl groups, can also be used to produce a wide array of products.

This allylation protocol was used in the total synthesis of amphidinolide K.[5–7] to give homoallylic alcohol **12** in 72% yield and 17:1 dr (eq 5). Initial transmetallation of stannane **10** with (*R,R*)-**1** via allylic transposition yielded an intermediate borane. Introduction of aldehyde **11** at –78 °C provided for a facile condensation reaction leading to **12**. Stereocontrol was induced from the 1,2-diphenylethane sulfonamide auxiliary and could be predicted from a Zimmerman–Traxler model with minimized steric repulsions. The high level of selectivity obtained in this case was a result of a matched diastereomeric transition state featuring the inherent Felkin–Ahn selectivity for nucleophilic attack in aldehyde **11**, with the (*S*)-configuration of the benzoate of **10**, as well as the (*R,R*)-antipode of auxiliary **1**, resulting in threefold stereodifferentiation.

The bromoborane can also be prepared in situ. This was shown in synthetic studies toward phorboxazole A (eq 6),[8] where homoallylic alcohol **16** was formed in 98% yield (10:1 dr).

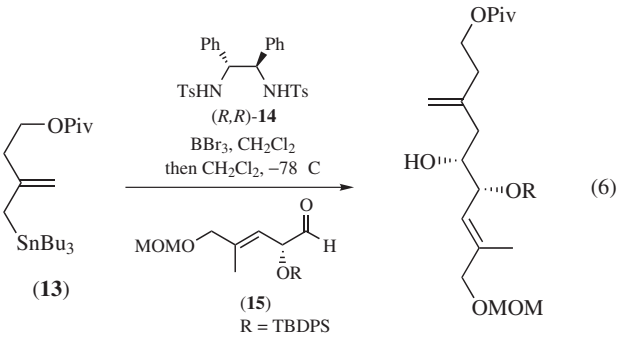
Aldol Reactions. *syn*-Aldol adducts can be formed enantioselectively from the reaction of diethyl ketone and various aldehydes using bromoborane (*R,R*)-**1** as a chiral controller (eq 7).[9] Reactions typically proceed in 85–91% yield with > 95% ee. This process led to the highly efficient synthesis of the rice and corn weevil aggregation pheromone sitophilure **19** (R = C_2H_5). Here the bis(tosyl)amide was easily recovered in high yield, since the aldol products were soluble in hexanes, but the chiral backbone was not.[1]



(**10**)
R = TBS

(**11**)
R′ = TIPS

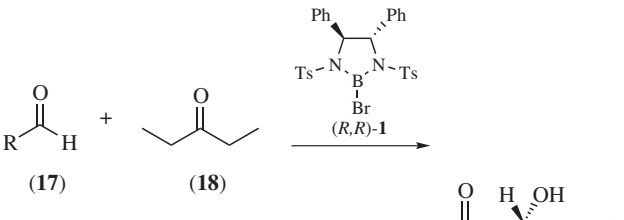
(**12**)
R = TBS, R′ = TIPS
72% yield, 17:1 dr



(**13**)

(**15**)
R = TBDPS

(**16**)
98% yield, 10:1 dr



(**17**) (**18**)

(**19**)
85–95% yield
>95% ee

Bromoborane (*R*,R)-**1** can also promote enantioselective aldol coupling between acetate esters or thioesters and aldehydes.[1]

The stereochemistry of the predominating aldol adducts follows the assumption that the phenyl groups of the ligand backbone force the vicinal *N*-sulfonyl substituents to occupy the opposite face of the five-membered ring to which they are attached. The optimum stereoelectronic and steric arrangement of the favored transition structure for the formation of aldol product is shown in Figure 3 and leads to the observed major product **19**.

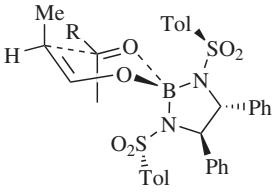
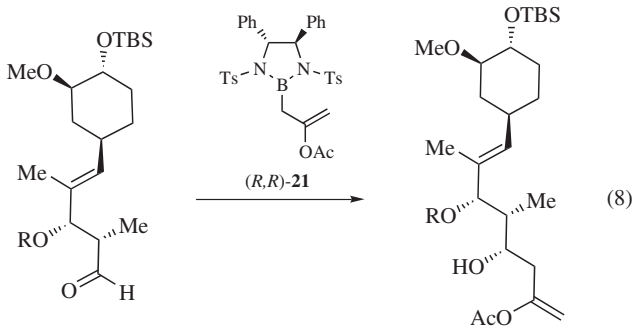


Figure 3

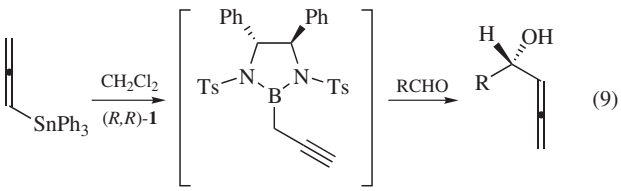
The aldol methodology was applied to the synthesis of FK-506.[7] Treatment of aldehyde **20** with cyclic borane **21** afforded homoallylic alcohol **22** in 17:1 diastereoselectivity (eq 8). Borane **21** was prepared from the reaction of (*S,S*)-**1** with 2-acetoxyallyltri-*n*-butylstannane in CH_2Cl_2 for 5 min at –78 °C, and then at 23 °C for 1.5 h. Reaction of the CH_2Cl_2 solution in situ with aldehyde **20** at –78 °C for 1 h produced homoallylic alcohol **22** as the major product. The bis(tosyl)amide from which reagent **21** was derived was efficiently recovered for reuse.



(**20**)
R = MOM

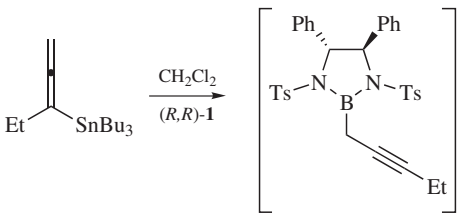
(**22**)
R = MOM
92% yield, 17:1 dr

Formation of Chiral Propa-1,2-dienyl and Propargyl Alcohols. Reaction of bromoborane (*R,R*)-**1** with propadienyltri-*n*-butylstannane **23** in CH_2Cl_2 at 0 °C for 4 h and 23 °C for 0.5 h produced the propargylborane derivative **24**, which reacts in situ with various aldehydes.[10] These reactions (eq 9) produce chiral propa-1,2-dienyl carbinols (**25**) in 72–82% yield with >99% ee. The products can be isolated with a purity of 98–99%, the impurity being the isomeric propargyl carbinol. In these cases, 90% of the bis-*p*-toluenesulfonamide of 1,2-diphenyl-1,2-diaminomethane (the chiral controller) is recovered. Use of (*S,S*)-**1** with the opposite enantiomer proceeded with similar efficiency.

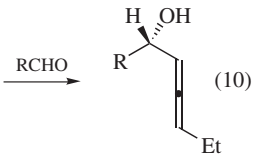


(**23**) (**24**) (**25**)
72–82% yield
>99% ee

This method can also be applied to 1,1-disubstituted allenes (**26**) to synthesize **28**, as shown in eq **10**.



(**26**) (**27**)

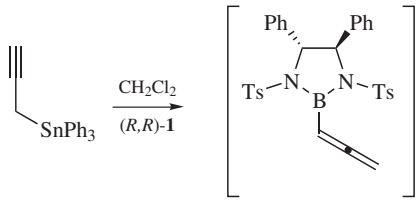


(10)

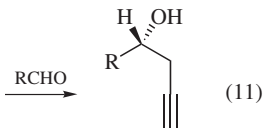
(**28**)

Derivatives of **1** can be used in the enantioselective propargylation of aldehydes (eq 11). Treatment of 2-propynyltriphenylstannane (**29**) with bromoborane **1** in CH_2Cl_2 at 0 °C for 4 h and 23 °C for 10 min produces allylborane **30**, which reacts with a variety of aldehydes to form propargyl carbinols (**31**). The enantioselection was excellent for the six substrates studied (91–98% ee) and chemical yields ranged from 74 to 81%. In each case, the chiral controller was separated from the propargylic alcohol for reuse by precipitation from 3:1 ether–hexane at 0 °C.

Attempted Enantioselective Enolborination. Some limitations to the scope of bromoborane **1** in asymmetric processes are documented. For example, attempts to desymmetrize C_s (or C_i) symmetric bifunctional substrates by selective enolborination have not been successful (eq 12).[11]



(**29**) (**30**)

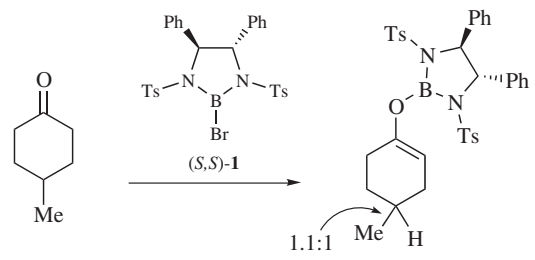


(11)

(**31**)

74–81% yield

91–98%ee



(12)

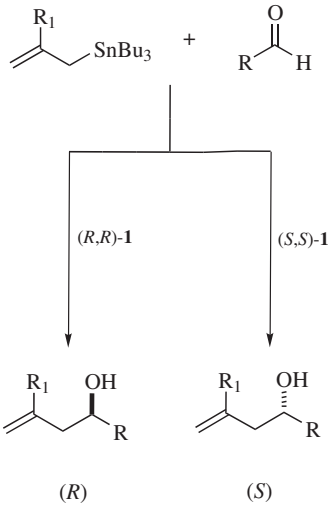
(**32**) (**33**)

First Update

David R. Williams & David C. Kammler
Indiana University, Bloomington, IN, USA

Carbonyl Allylations. Reagent **1** was originally introduced by Corey in 1989 for the asymmetric allylation of aldehydes with tri-*n*-butylallylstannane,[2] as previously reviewed.[1,12] Subsequent studies have demonstrated the utility of this reagent for the stereocontrolled generation of complex homoallylic alcohols via the convergent coupling of various functionalized, C_2-symmetric allylstannanes and substituted aldehydes.[5–8,13–17] The absolute stereochemistry of the newly formed alcohol stereocenter is predictable using a Zimmerman–Traxler model, and product formation is generally governed by the absolute stereochemistry of **1** (eq 13).

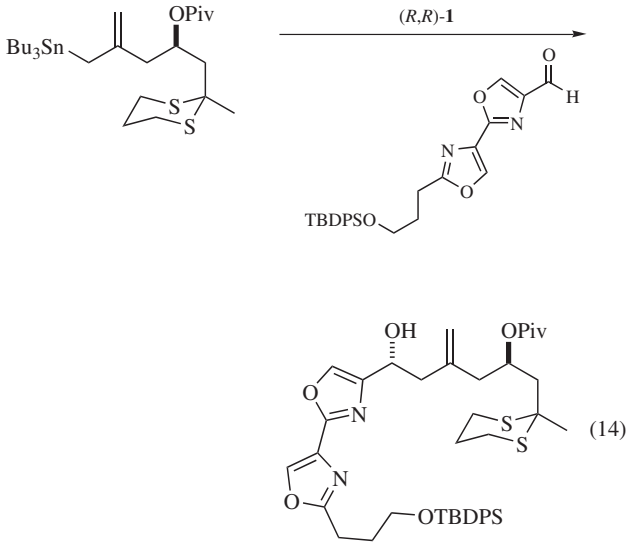
In situ transmetallation of the starting allylstannane to an intermediate allylic borane is rationalized via a 1,3-transposition pathway. In reactions with chiral aldehydes, matched and mismatched diastereotopic pathways are possible based upon the asymmetry of **1** and the intrinsic face selectivity exhibited for the carbonyl addition process. Yields are generally high (85–99%) with good to excellent stereoselectivity. Numerous functional groups are tolerated in the starting allylstannane, including esters, silyl and benzyl or *para*-methoxybenzyl ethers, dithioketals, and vinylstannanes. Lewis acid-sensitive functionalities (acetals, ketals, tetrahydropyranyl ethers) are not compatible. The aldehyde component may contain a wide variety of common protecting groups and additional functionality, including basic heteroaromatic systems such as pyridines and oxazoles.



(13)

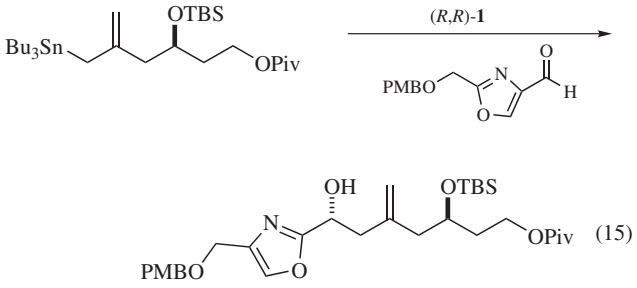
(*R*) (*S*)

Reactions of achiral aldehydes and homochiral stannanes exhibit stereoselectivity, which is predominantly dictated by the chiral auxiliary **1** if the preexisting asymmetry of the stannane is located at least two carbons or more (β) from the reactive allyl unit (eqs 14–16).[5,6]



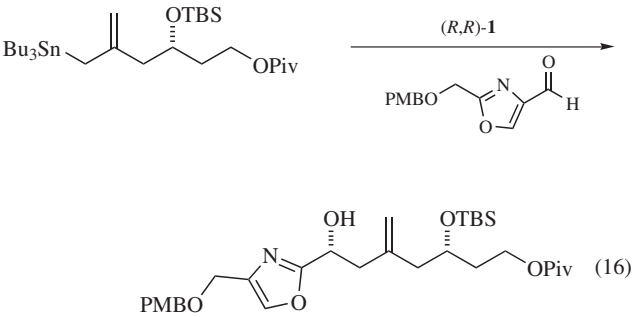
(14)

95%, 10.5:1 dr



(15)

92%, ≥20:1 dr

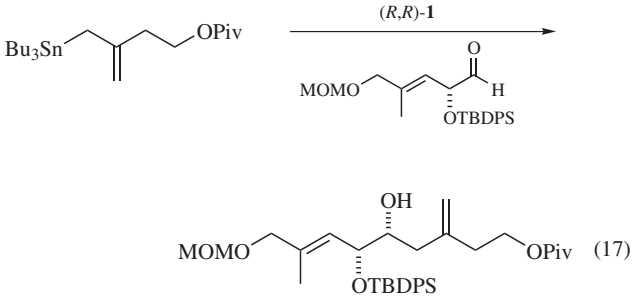


(16)

98%, ≥20:1 dr

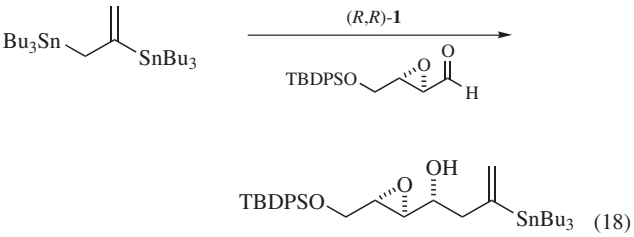
Achiral stannanes undergo reactions with aldehydes bearing α-asymmetry and provide examples of matched diastereoselectivity with respect to **1** (eq 17),[8] as well as cases of mismatched diastereoselection of these controlling factors (eq 18).[5]

In a similar fashion, asymmetric allylations with **1** and chiral aldehydes bearing β-substitution also display the expected behavior of diastereotopic transition states (eqs 19 and 20).[5]



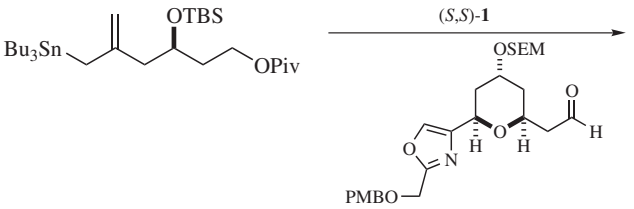
(17)

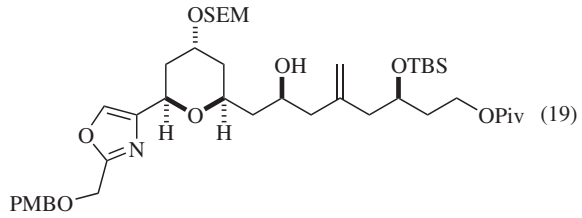
98%, 10:1 dr



(18)

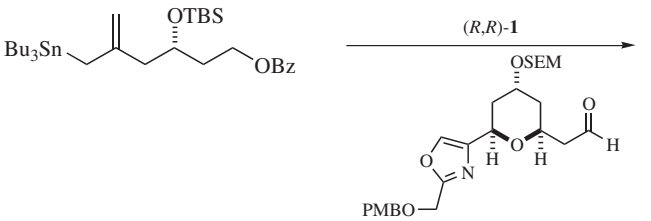
85%, 3.2:1 dr

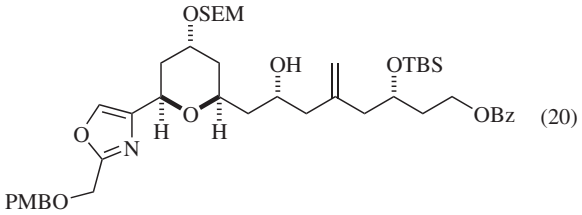




(19)

99%, 11.4:1 dr



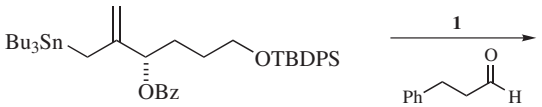


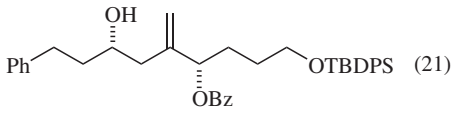
(20)

88%, 4:1 dr

The presence of α-asymmetry in the stannane component can have a dramatic impact on diastereoselection (eq 21).[5] The min-

imization of A[1,3] strain in the allylic component is a factor that influences the face selectivity enforced by the auxiliary **1**.

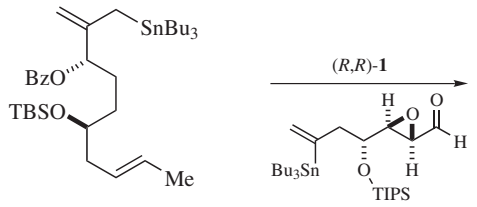


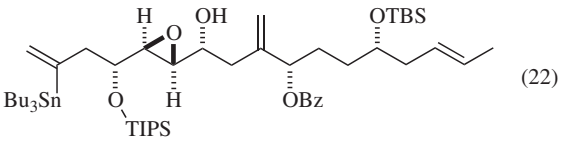


(21)

(*R*,*R*)-**1**: 96%, ≥20:1 dr
(*S*,*S*)-**1**: 94%, 1:1 dr

In complex examples, high levels of stereodifferentiation require the consideration of the conjoined influences of α-asymmetry in the allylstannane and chirality of the starting aldehyde, in addition to the choice of auxiliary **1** (eq 22).[4,8]





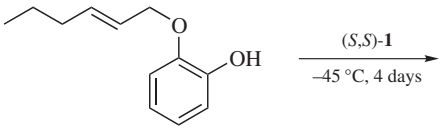
(22)

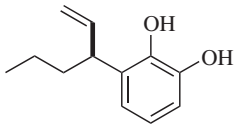
72%, 17:1 dr

Claisen Rearrangements. Claisen rearrangements of catechol allylic ethers, which avoid production of the 'abnormal' Claisen product, have been achieved using 1.5 equiv **1** and 1.5 equiv Et_3N at low temperature in dichloromethane with excellent (80–97%) yields and high (86–95%) enantioselectivities (eqs 23 and 24). The absolute configuration of the newly created benzylic stereocenter is dependent upon both the olefin geometry and the configuration of the controller. Lewis acid catalysis with (*S*,*S*)-**1** and *E*-olefins led to vinylic substituents bearing the *S*-configuration (eq 23), whereas (*S*,*S*)-**1** and *Z*-olefins yielded products with *R*-stereochemistry (eq 24).[3]

Similarly, Claisen rearrangements of difluorovinyl allyl ethers occurred with moderate to excellent yields (39–90%) and moderate enantioselectivities (eq 25). Simple alkyl-substituted olefins rearrange at –15 °C with modest stereocontrol (41–56% ee) whereas vinylsilanes rearrange at –78 °C with good (85% ee) selectivity. The absolute configuration of the newly formed benzylic stereocenter appears to depend upon both the geometry (*E* or *Z*) of the starting olefin and the configuration of (**1**), although the absolute stereochemistry of the product was proven only in the case cited below.[4]

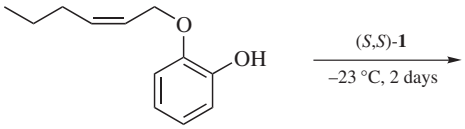
Other Uses. Reagent **1** has been used for enantioselective enolborination, albeit with poor (1.1:1) selectivity.[14] Similar bis-sulfonamide-derived boron Lewis acids have been used for aldol additions,[18–24] ester-Mannich reactions,[25] Diels–Alder reactions,[1,26,27] Ireland–Claisen reactions,[28,29] and [2,3]-Wittig rearrangements.[30,31] Similar bis-sulfonamide-derived aluminum Lewis acids have been used for aldol additions,[1] Diels–Alder reactions,[1,32–35] [2 + 2] ketene–aldehyde cycloadditions,[36,37] cyclopropanation of allylic alcohols,[38–40] and polymerization.[41,42]

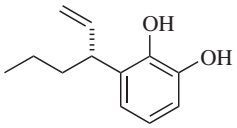




(23)

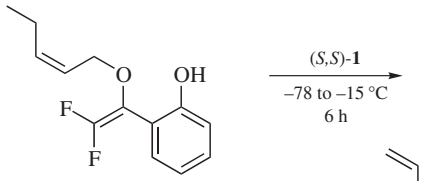
89%, 94% ee

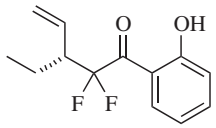




(24)

92%, 95% ee





(25)

58%, 43% ee

Related Reagents. Trifluorosulfonyl; *p*-Fluorophenylsulfonyl; Naphthylsulfonyl; Methylsulfonyl; phenylsulfonyl; 3,5-Bis(trifluoromethyl)phenylsulfonyl; *p*-Nitrosulfonyl Derivatives; Boron–bis-sulfonamide Lewis acids: (*R*,*R*)-1,3-Bis{[3,5-bis(trifluoromethyl) phenyl]sulfonyl}-2-bromo-4,5-diphenyl-1,3,2-diazaborolidine; (*R*, *R*)-1,3-Bis(methylsulfonyl)-2-bromo-4,5-diphenyl-1,3,2-diazabo rolidine; (*R*,*R*)-1,3-Bis[(trifluoromethyl)sulfonyl]-2-bromo 4,5-diphenyl-1,3,2-diazaborolidine; (*R*,*R*)-1,3-Bis(phenylsulfonyl)-2-bromo-4,5-diphenyl-1,3,2-diazaborolidine; (*R*,*R*)-1,3-Bis [(4-fluorophenyl)sulfonyl]-2-bromo-4,5-diphenyl-1,3,2-diazaborolidine; (*R*,*R*)-1,3-Bis[(4-nitrophenyl)sulfonyl]-2-bromo-4,5-diphenyl-1,3,2-diazaborolidine; (*R*,*R*)-1,3-Bis(2-naphthalenylsulfonyl)-2-bromo-4,5-diphenyl-1,3,2-diazaborolidine; (*R*,*R*)-1,3-bis(phenylsulfonyl)-2-bromooctahydro-1*H*-1,3,2-benzodiazaborole; (*R*, *R*)-1,3-bis-[(4-methylphenyl)sulfonyl]-2-bromooctahydro-1*H*-1,3,2-benzodiazaborole.

Aluminum–Bis-sulfonamide Lewis Acids: (*R*,*R*)-[*N*,*N*′(1,2-Diphenyl-1,2-ethanediyl)bis(1,1,1-trifluoromethanesulfona-

midato)](2-)-*N*,*N*′-methylaluminum; (*R*,*R*)-{[*N*,*N*′-(1,2-Diphenyl-1,2-ethanediyl)bis(1,1,1-trifluoromethanesulfonamidato)]-(2-)-*N*,*N*′}(2-methylpropyl)aluminum; (*R*, *R*)-{[*N*,*N*′-(1,2-diphenyl-1,2-ethanediyl)bis(4-methylbenzenesulfonamidato)](2-)-*N*,*N*′}chloroaluminum; (*R*,*R*)-{[*N*,*N*′-(1,2-Diphenyl-1,2-ethanediyl)bis[3,5-bis(trifluoromethyl)benzenesulfonamidato]](2-)-*N*,*N*′}ethylaluminum; (*S*,*S*)-[*N*,*N*′-(1,2-Diphenyl-1,2-ethanediyl)bis[2,4,6-trimethylbenzenesulfonamidato](2-)-*N*,*N*′]methylaluminum; (*S*,*S*)-[*N*,*N*′-(1,2-Diphenyl-1,2-Ethanediyl) (2,4,6-trimethylbenzenesulfonamidato)-2,4,6-tris(1-methylethyl)benzenesulfonamidato(2-)-*N*,*N*′]methylaluminum; (*S*,*S*)-{[*N*,*N*′-(1,2-Diphenyl-1,2-ethanediyl)bis[4-(1,1-dimethylethyl)-2,6-dimethylbenzenesulfonamidato]](2-)-*N*,*N*′}methylaluminum; (*S*,*S*)-{*N*,*N*′-(1,2-Diphenyl-1,2-ethanediyl)[(4-(1,1-dimethylethyl)-2,6-dimethylbenzenesulfonamidato]-2,4,6-tris(1-methylethyl)-benzenesulfonamidato(2-)-*N*,*N*′}methylaluminum; (*R*,*R*){(*N*,*N*′-(1,2-Diphenyl-1,2-ethanediyl)bis[2,4,6-tris(1-methylethyl)benzenesulfonamidato])(2-)-*N*,*N*′}ethylaluminum; (*S*,*S*)-{[*N*,*N*′-[1,2-Bis(3,5-dimethylphenyl)-1,2-ethanediyl]bis(1,1,1-trifluoromethanesulfonamidato)](2-)-*N*,*N*′}-methylaluminum; (*R*,*R*)-{[*N*,*N*′-1,2-Cyclohexanediylbis(1,1,1-trifluoromethanesulfonamidato)](2-)-*N*,*N*′}methylaluminum; (*R*,*R*)-{[*N*,*N*′-1,2-Cyclohexanediylbis(benzenesulfonamidato)](2-)-*N*, *N*′} (2-methylpropyl)aluminum; (*R*,*R*)-{[*N*,*N*′-1,2-Cyclohexanediyl-bis (4-nitrobenzenesulfonamidato)](2-)-*N*,*N*′}methylaluminum; (*R*,*R*)-{[*N*,*N*′-1,2-Cyclohexanediylbis(4-nitrobenzenesulfonamidato)]-(2-)-*N*,*N*′} ethylaluminum; (*R*,*R*)-{[*N*,*N*′-1,2-Cyclohexanediyl-bis(4-nitrobenzenesulfonamidato)](2-)-*N*,*N*′}(2-methylpropyl)-aluminum; (*R*,*R*)-{(*N*,*N*′-1,2-Cyclohexanediylbis[4-(trifluoromethyl) benzenesulfonamidato])(2-)-*N*,*N*′}(2-methylpropyl)-aluminum; (*R*,*R*){(*N*,-*N*′-1,2-Cyclohexanediylbis[3,5-bis(trifluoromethyl)benzenesulfonamidato])(2-)-*N*,*N*′}(2-methylpropyl)aluminum.

Other chiral controllers for allylation: (*R*)-[(1,1′-Binaphthalene)-2,2′-diolato(2-)-κO,$\kappa O'$]dichlorotitanium; (*R*)-[(1,1′-Binaphthalene)-2,2′-diolato(2-)-κO,$\kappa O'$]bis(2-propanolato)titanium; (*R*)-[(1,1′-Binaphthalene)-2,2′-diolato(2-)-κO,$\kappa O'$]bis(2-propanolato) zirconium; (*R*)-[(1,1′-Binaphthalene)-2,2′-diylbis(diphenylphosphine-κP)]trifluoromethanesulfonato-κO-silver; Chloro(η^5-cyclopentadienyl)[(4*R*, *trans*)-2,2-dimethylα,α,α',α'-tetraphenyl-1,3-dioxo-lane-4,5-dimethanolato(2-)-*O*α, *O*α']titanium; 2,2-dimethyl-α,α,α',α''-tetraphenyl-1,3-Dioxolane-4,5-dimethanolatotitanium diisopropoxide; chloro(cyclopentadienyl)bis[3-*O*-(1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranosyl)]titanium; {2,2′-Methylenebis-[(4*S*,5*R*)-4,5-dihydro-4,5-diphenyloxazole-κN3]}bis(trifluoromethanesulfonato-κO-zinc; Aqua{2,6-bis[(4*S*)-4,5-dihydro-4-(1-methylethyl)-2-oxazolyl-κN3]phenyl-κC}dichlororhodium; (*S*,*S*) -[2,6-Bis(1-methylethoxy)benzoyl]oxy-5-oxo-,3,2-dioxaborolane-4-acetic Acid; *B*-Methoxydiisopinocampheylborane; 1,3,2-Benzodioxastannol-2-ylidene Complex with Diisopropyl Tartrate; 2,2,2-Trifluoro-*N*-[(1*R*,2*R*)-1-methyl-2-phenyl-2-[(trimethylsilyl)oxy]ethylacetamide; (*R*,*R*)-Octahydro-1,3-dimethyl-2-(1-piperidinyl)-1*H*-1,3,2-benzodiazaphosphole-2-oxide.

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