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Diisopropyl Tartrate Modified (E)-γ-[(Cyclohexyloxy)dimethylsilyl]- and (E)-γ-(Dimethylphenylsilyl)allylboronates: Chiral Reagents for the Enantio- and Diastereoselective Synthesis of Anti 1,2-Diols and 2-Butene-1,4-diols via the Formal α- and γ-Hydroxyallylation of Aldehydes

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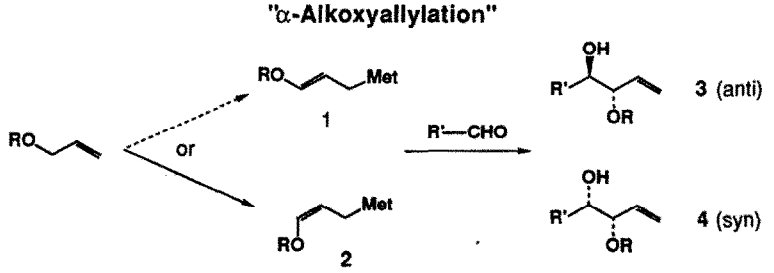
Key Words: Diastereoselective allylboration; enantioselective synthesis of anti 1,2-diols and 2-butene-1,4-diols

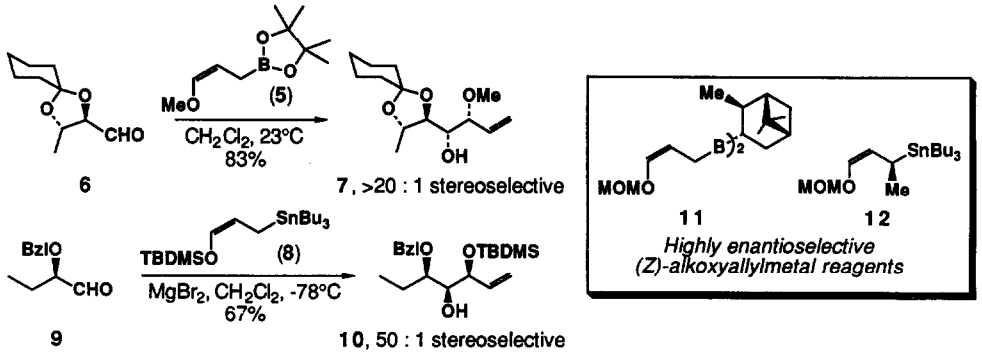
Abstract: *Enantioselective syntheses of 4-substituted (E)-2-butene-1,4-diols and anti 1,2-diols are described. Highly diastereoselective reactions of aldehydes and the chiral $PhMe_2Si$- and $(C_6H_{11}O)Me_2Si$-substituted allylboronates* **25** *and* **26** *provide anti homoallylic silanols* **29** *and* **50**, *respectively. Epoxidation of* **29** *with dimethyl dioxirane followed by acid catalyzed Petersen rearrangement of the intermediate epoxysilanols provides butene-1,4-diols* **27** *with excellent enantioselectivity (81-87% e.e.). Tamao oxidation of* **50** *provides anti diols* **22** *(64-72% e.e.). These procedures give excellent results especially in matched double asymmetric reactions with a range of oxygenated, chiral aldehydes (Figures 1 and 2). These methods promise to find application in diastereoselective syntheses of carbohydrates from acyclic precursors.*

The stereoselective synthesis of carbohydrates from acyclic precursors remains a topic of considerable current interest.[1] Procedures that enable syn or anti 1,2-diol units to be generated in concert with a C-C bond forming event are particularly attractive in this context, especially if the method is highly stereoselective. Among several different strategies that have been described, the "α-alkoxyallylation" of aldehydes via reactions with γ-alkoxyallylmetal reagents has received considerable attention as a preparative method.[2-7]

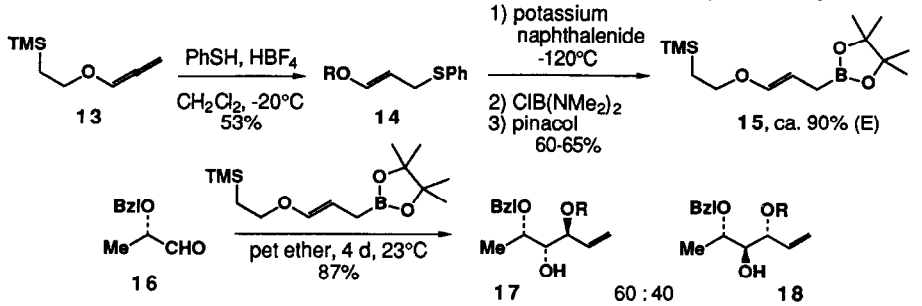


Thus far, the greatest success has been realized in the synthesis of syn diol monoether diastereomer **4** via reactions of aldehydes and (Z)-γ-alkoxyallylmetal reagents (**2**).[3,4] Several methods have been reported for the diastereoselective synthesis of racemic **4** via reactions of achiral aldehydes and achiral **2** (Met = B, Al, Sn).[2,3] In addition, excellent diastereoselectivity has been observed in the reactions of several (Z)-γ-alkoxyallylmetal reagents **2** and certain chiral aldehydes. For example, (Z)-γ-alkoxyallylboronates (e.g., **5**) exhibit outstanding diastereofacial selectivity in reactions with α,β-dialkoxy aldehydes like **6**.[3d,e] Diastereofacial selectivity,

however, is highly substrate dependent: analogous reactions with *O*-benzyl lactaldehyde proceed with only ca. 5 : 1 diastereoselectivity.[3f] Keck has shown that chelate controlled reactions of chiral α- or β- alkoxy substituted aldehydes and (Z)-γ-alkoxyallylstannanes give excellent stereoselectivity (e.g., **8** + **9** → **10**).[3i] This procedure is stereochemically complimentary to the (Z)-γ-alkoxyallylboronate sequence, but is restricted to substrates capable of participating in chelate mediated reactions. Finally, several chiral γ-alkoxyallylmetal reagents have been developed for the enantioselective synthesis of syn diol monoethers **4**.[4] Reagents **11** and **12**, in particular, have shown excellent levels of diastereoselectivity especially in matched double asymmetric reactions with chiral α-alkoxy aldehydes.[4d,5]

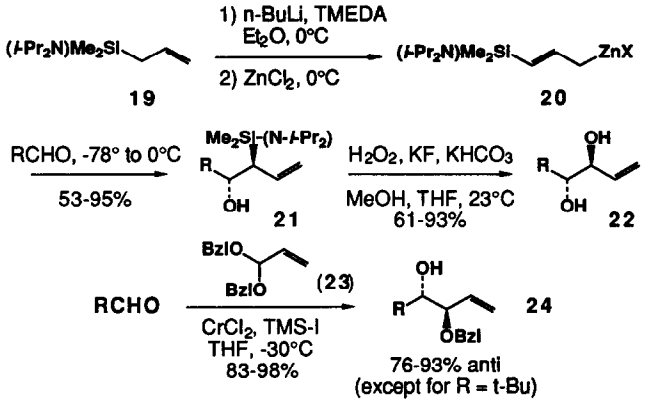


The stereocontrolled synthesis of the anti diol monoether diastereomer **3** has proven to be a more challenging problem.[2,6] (E)-γ-Alkoxyallylboron reagents have not been widely utilized owing to the difficulty of synthesis and the configurational instability of the (E)-alkoxyallyl anion precursors.[3c,f] While (Z)-γ-alkoxyallyllithium precursors to **6** and **11** are easily prepared with high isomeric purity directly from readily available allyl ethers,[8] an indirect route involving the addition of thiophenol to an allenyl ether (**13** → **14**) and reduction of the resulting (E)-allylic sulfide with potassium naphthalenide at -120°C (**14** → **15**) is necessary to gain access to the (E)-γ-alkoxyallyl potassium precursor to (E)-γ-alkoxyallylboronates such as **15**.[3c] Even so, reagents like **15** are obtained with only ca. 90% isomeric purity. In addition, reactions with chiral aldehydes proceed with poor diastereofacial selectivity (60 : 40), as illustrated by the example with *O*-benzyl lactaldehyde **16**.[3f]



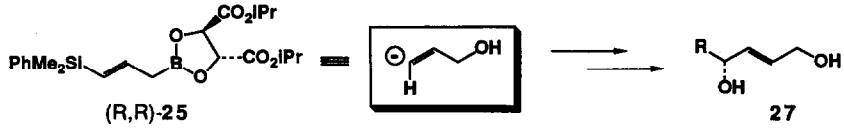
Two methods have been reported that show considerable promise as routes to anti 1,2-diols or the corresponding monoethers. First, Tamao and Ito reported that the γ-(dialkylamino)allyl zinc reagent **20** reacts smoothly with aldehydes to give anti silanol derivatives **21** that are then oxidized with retention of C-Si stereochemistry to anti diols **22**.[6e] This method nicely circumvents the problems noted above concerning the preparation of (E)-γ-alkoxyallyl anions since (E)-1-(trialklysilyl)allyl anions are considerably more stable than the (Z)-isomers, and are known to undergo electrophilic substitution at the γ-position to give products containing (E)-vinylsilane units (c.f., **19** → **20**).[9] The use of a silyl substituent as a hydroxyl surrogate is also a well established synthetic strategy.[10] The second new procedure for synthesis of anti 1,2-diol monoethers, reported by Takai and coworkers, involves a γ-alkoxyallylchromium species generated in situ via the reaction of an

acrolein acetal, TMS-I and $CrCl_2$.[6f] While this method is the most direct of any reported to date, it suffers from poor simple diastereoselectivity in a number of cases.

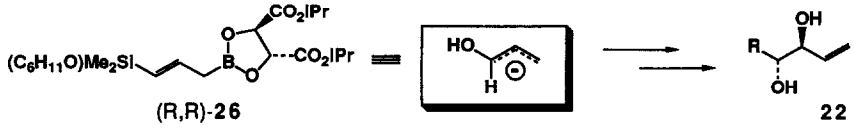


We report herein extensions of the Tamao-Ito strategy to the development of two new chiral silicon substituted allylboronates, **25** and **26**, that should prove useful in acyclic diastereoselective syntheses of carbohydrates and other polyoxygenated synthetic targets. Specifically, we describe a simple, highly enantio- and diastereoselective synthesis of 4-substituted-2-butene-1,4-diols **27** via the reactions of aldehydes and the γ-phenyldimethylsilyl substituted reagent **25**, and an enantioselective synthesis of anti diols **22** via a sequence involving γ-(cyclohexyloxy)dimethylsilylallylboronate **26**. Reagent **25** thus functions as a chiral allylic alcohol β-carbanion equivalent, while **26** is an enantioselective equivalent of an (E)-alkoxyallylmetal reagent (i.e., an allylic alcohol α-carbanion equivalent). Preliminary accounts of this work have appeared.[11]

A Chiral Allylic Alcohol β-Carbanion Equivalent:

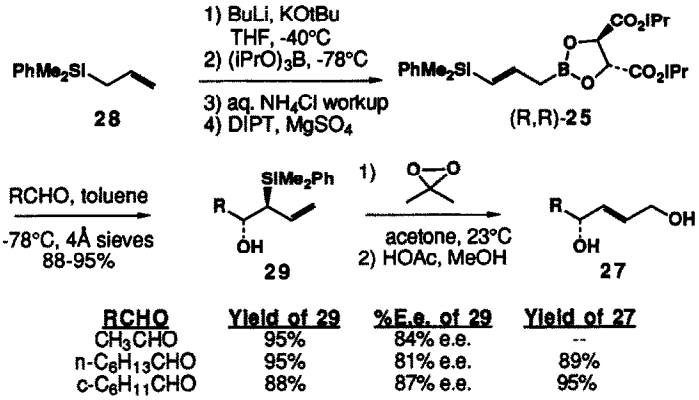


A Chiral Allylic Alcohol α-Carbanion Equivalent for Anti α-Hydroxyallylation of Aldehydes:



Diisopropyl Tartrate Modified (E)-γ-(Dimethylphenylsilyl)Allylboronate (25), A Chiral Allylic Alcohol β-Carbanion Equivalent for the Enantioselective Synthesis of 4-Substituted 2-Butene-1,4-Diols from Aldehydes. We initially targeted the $PhMe_2Si$- substituted allylboronate **25** as a reagent for the enantioselective synthesis of anti 1,2-diols **22** in anticipation that the phenyldimethylsilane unit of anti silanols **29** could be oxidized via one of the Fleming procedures.[10b,c] We quickly discovered, however, that electrophilic substitution reactions of the allylsilane unit are faster than protodesilylation or other Ph-Si cleavage reactions required as the first step in the Fleming oxidations.[10b,c] Nevertheless, useful chemistry was uncovered with the observation that silanols **29** are smoothly converted into 4-substituted butene-1,4-diols **27** via oxidation with dimethyl dioxirane[12] followed by the acid catalyzed Petersen elimination of the intermediate epoxysilanes. Allylboronate **25** thus functions as a chiral allylic alcohol β-carbanion equivalent capable of

controlling the absolute stereochemistry of the hydroxyl group generated at C(4) of **27**. As is shown subsequently, this method has considerable stereochemical generality in reactions with chiral aldehydes, and therefore is ideally suited for applications in organic synthesis.[13]



RCHO	Yield of 29	%E.e. of 29	Yield of 27
CH_3CHO	95%	84% e.e.	--
n-$C_6H_{13}CHO$	95%	81% e.e.	89%
c-$C_6H_{11}CHO$	88%	87% e.e.	95%

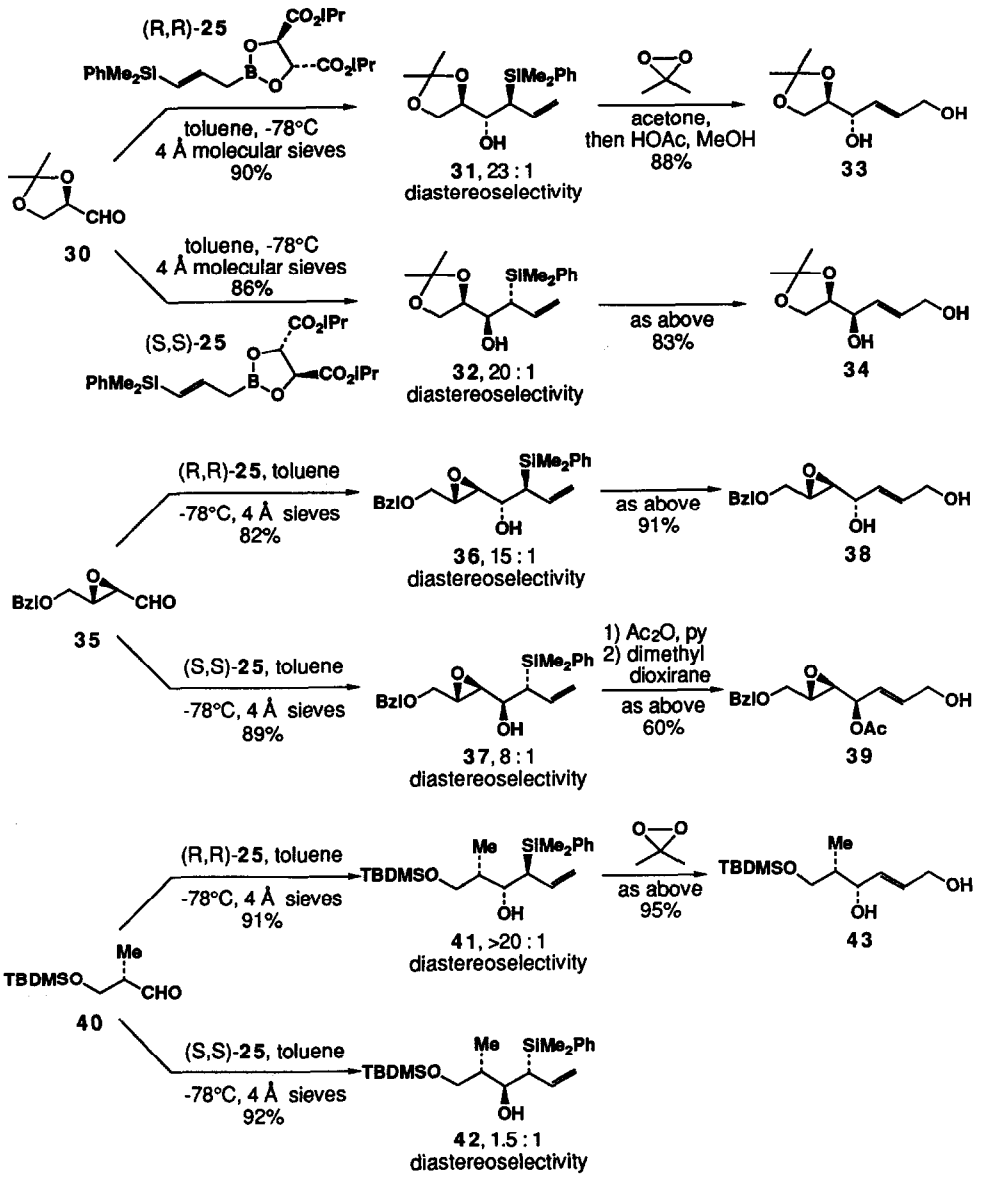
Allylboronate **25** was prepared from allyl(dimethylphenyl)silane **28** by using slight modifications of our standard allylboronate synthesis.[14] Thus, a THF solution of **28** was treated with 1.0 equiv. of n-BuLi and 1.0 equiv. of KOtBu at -40°C for 15 min followed by 1.0 equiv. of $(iPrO)_3B$ at -78°C for 15 min. This mixture was poured into aqueous NH_4Cl and extracted with ether. The extracts were immediately treated with 1.0 equiv. of DIPT, dried over $MgSO_4$ (2 h), and then concentrated to constant weight in vacuo. The crude product, consisting primarily of **25**, residual **28** and DIPT, is analyzed by ^1H NMR to determine the weight percentage of **25** in the mixture; the yield of **25** is generally 70-80%. Crude **25** was dissolved in toluene (ca. 1 M) and stored over 4Å molecular sieves at -20°C under Ar. Reactions with aldehydes were performed in toluene (0.3-0.5 M) at -78°C in the presence of 4Å molecular sieves.[15] A reaction (0.3 M) with cyclohexanecarboxaldehyde was essentially complete within 4 h, as determined by isolation of **29c** following the addition of a large excess of acetaldehyde to react with any unconsumed **25**.

The enantioselectivity of **25** was assessed via reactions with acetaldehyde, hexanal and cyclohexanecarboxaldehyde. The anti silanols **29** were obtained with excellent diastereoselectivity (the syn diastereomers were not detected) in 88-95% isolated yields and with enantiomeric purities of 81-87% e.e. (determined by the Mosher ester technique).[16] The enantioselectivity of **25** thus closely parallels that of the tartrate (E)-crotylboronates that we have previously studied.[14]

The epoxidation of anti silanols **29** and the subsequent acid catalyzed Petersen elimination constitutes the second stage of this method. While the epoxidation of allylsilanes has received considerable study,[17] we found that it was not possible to epoxidize the allylsilanols **29** cleanly by using either MCPBA or $VO(acac)_2$/TBHP. Evidently, the rate of these epoxidations is slow (vinyl groups are relatively unreactive) and Petersen eliminations of the intermediate epoxysilanes are probably competitive. The resulting allylic alcohols undoubtedly undergo a second epoxidation, leading ultimately to a mixture of products. This problem was solved by using an acetone solution of dimethyl dioxirane as the oxidant.[12,18] This reagent is neutral, the epoxidations are very fast, and competitive Petersen eliminations were not observed. The reaction mixtures were concentrated in vacuo and then treated with methanolic HOAc to effect the rearrangement to the desired allylic alcohols (88-95% overall yield). This study thus adds to the growing list of applications of dimethyl dioxirane as a mild, selective oxidant in organic synthesis.

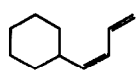
Several applications of this methodology in double asymmetric reactions with chiral aldehydes are summarized in Figure 1.[19] The reactions of (R,R)- and (S,S)-**25** with glyceraldehyde acetonide **30** display outstanding stereoselectivity, providing diastereomers **31** and **32** with ≥20 : 1 diastereoselectivity in each case.

Figure 1. Double Asymmetric Reactions of Chiral Aldehydes and γ-(Phenyldimethylsilyl)allylboronate 25.



This represents an almost perfect example of reagent controlled acyclic diastereoselection.[20] Similarly, the reactions of the two enantiomers of **25** and epoxyaldehyde **35** also exhibit excellent diastereoselectivity: the reaction with (R,R)-**25** provides **36** with 15 : 1 selectivity, while **37** is the major product of an 8 : 1 mixture when (S,S)-**25** is used. Because the enantiomeric purity of **35** is only 95% e.e., it can be calculated that the

diastereoselectivity of these reactions would be 20 : 1 and 1 : 10, respectively, if enantiomerically pure **35** were used.[21] It is also interesting to note that this pair of double asymmetric reactions are yet another set in which the matched case is less diastereoselective than the mismatched one (**37** is the major product in reactions with pinacol (E)-γ-(dimethylphenylsilyl)allylboronate)).[20,22] Finally, the reaction of α-methyl-β-alkoxy aldehyde **40** displays outstanding diastereoselectivity for **41** (>20 : 1) in the matched reaction with (R,R)-**25**, but poor selectivity (ca. 1.5 : 1) in the mismatched case leading leading to the anti, anti diastereomer **42**. Better selectivity for **42** undoubtedly can be obtained by using a more enantioselective chiral auxiliary.[23,24]



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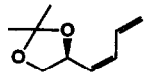

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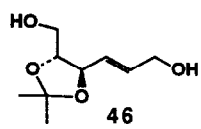

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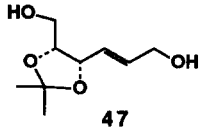

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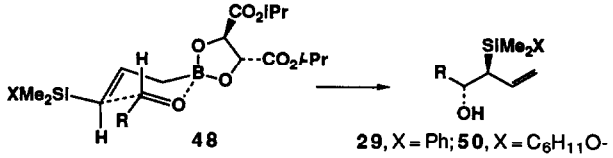
Stereochemical assignments were initially based on mechanistic considerations. Support for these assignments was obtained as follows. First, the anti stereochemistry of anti silanols **29c** (R = C_6H_{11}), **31** and **33** was established via base promoted (NaH, THF) Peterson eliminations to the corresponding (Z)-dienes **44** and **45**. The anti stereochemistry in these cases is thus consistent with expectations that the reactions of aldehydes and **25** would proceed by way of a cyclic, chair-like transition state analogous to that commonly invoked in reactions of crotylboronates and aldehydes.[2,14] Second, the sense of absolute stereochemical induction deriving from **25** was established by the acid catalyzed isomerization of allylic alcohols **33** and **34**. Treatment of **34** with catalytic p-TsOH in acetone provided exclusively trans acetonide **46**, isolated in 83% yield, while similar treatment of **33** provided a 3 : 1 mixture of **33** and cis acetonide **47**. The difference in thermodynamic stability of this pair of acetonides requires that **31** and **32** have 4,5-erythro and 4,5-threo configurations, respectively.[25] These assignments are fully consistent with major product formation via transition state **48**, and are in agreement with the sense of absolute stereochemical induction previously established for reactions of other tartrate ester modified allylboronates.[14,21-23] All other stereostructures in this series were assigned by analogy.

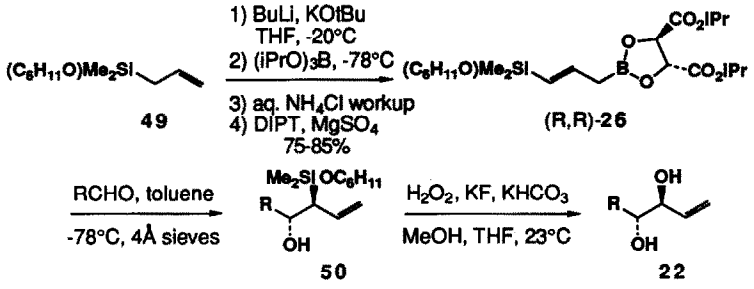


48

29, X = Ph; **50**, X = $C_6H_{11}O$-

Diisopropyl Tartrate Modified (E)-γ-[(Cyclohexyloxy)dimethylsilyl]allylboronate (26), A Chiral Allylic Alcohol α-Anion Equivalent for the Enantioselective Anti α–Hydroxyallylation of Aldehydes. In view of the difficulties encountered in attempts to perform Fleming oxidations of anti silanols **29** (vide supra), we turned to the development of alkoxysilyl substituted allylboronate **26** as a precursor of anti diols **22**. Reagent **26** was easily prepared in 75-85% yield from (cyclohexyloxy)-dimethylallylsilane **49**[26] by using the procedure described for the synthesis of **25**. A toluene solution of **26** was stored over 4Å molecular sieves at -20°C under Ar for 24 h before use. Reactions with aldehydes were performed in toluene (0.3-0.5 M) at -78°C in the presence of 4Å molecular sieves. A reaction (0.3 M) with cyclohexanecarboxaldehyde was essentially complete within a 4 h period under these conditions.

Reagent **26** is less enantioselective than other tartrate ester modified allylboronates that we have previously studied, including **25**.[14] For example, the reactions of **26** and CH_3CHO, n-$C_6H_{13}CHO$, and c-$C_6H_{11}CHO$ provided anti silanols **50** with enantioselectivity of only 64-72% e.e. as determined by Mosher ester analysis.[16] Nevertheless, the reactions with aldehydes exhibit outstanding diastereoselectivity (syn isomers were not detected) and anti silanols **50** are obtained in excellent yield. In comparison to the earlier study of Tamao and Ito,[6e] the aldehyde addition reactions of **26** are more efficient than those of the allylzinc



RCHO	Yield of 50	%E.e. of 50	Yield of 22
CH_3CHO	94%	69% e.e.	83%
n-$C_6H_{13}CHO$	86%	64% e.e.	95%
c-$C_6H_{11}CHO$	95%	72% e.e.	95%

reagent **20** since the "metal alkoxide" produced in the reactions of **26** is a nonbasic borate ester that shows no tendency to undergo Petersen elimination prior to workup.

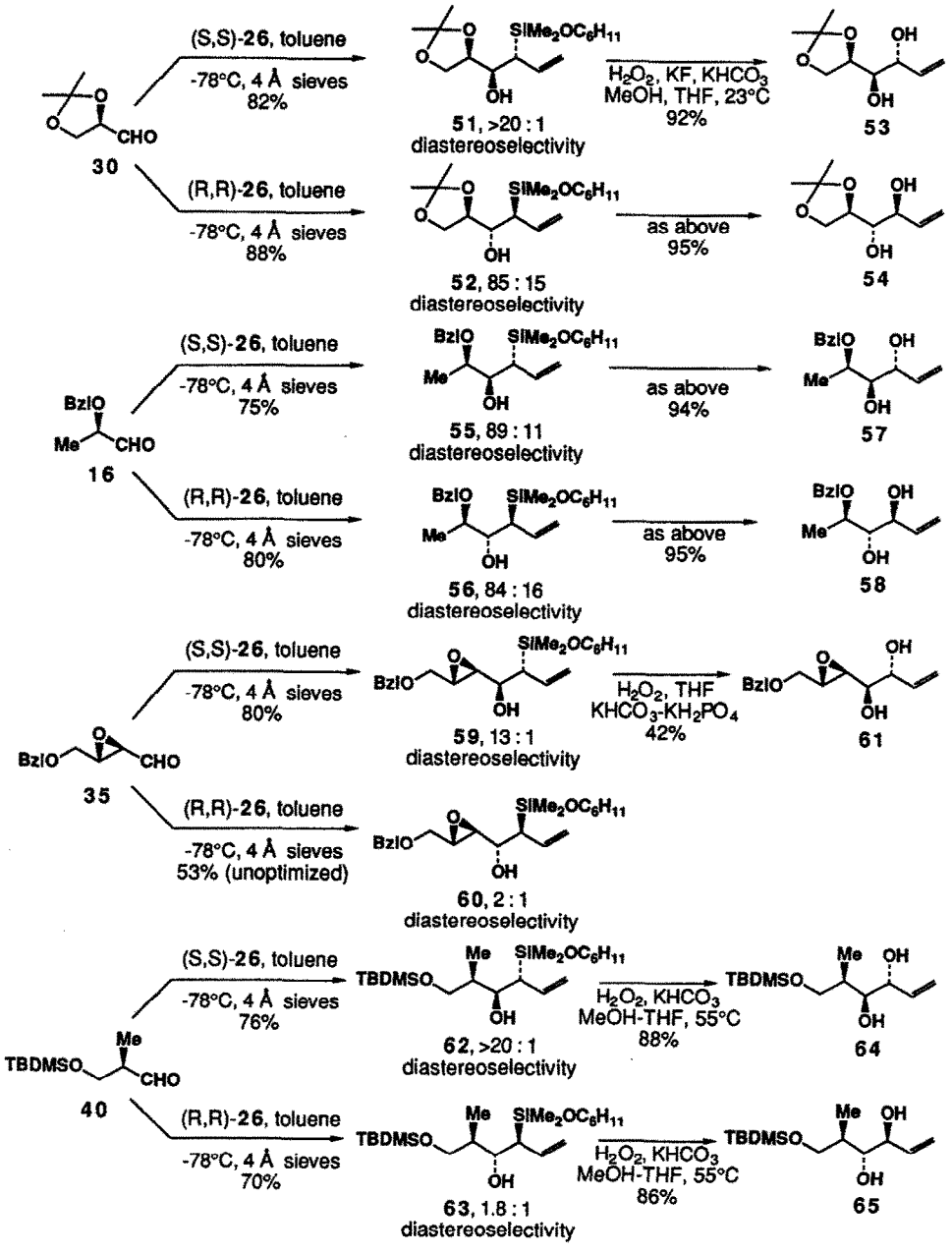
The diminished enantioselectivity of **26** compared to other tartrate allylboronates was unanticipated. In retrospect, however, this is reminiscent of and is perhaps related to the diminished enantioselectivity realized in the reactions of the tartrate allyl and crotylboronates and alkoxy-substituted aldehydes.[22] Nevertheless, it is probable that the enantioselectivity can be improved by using an alternative chiral auxiliary.[23,24,31]

In spite of the moderate enantioselectivity, reagent **26** displays very useful levels of stereoselectivity especially in matched double asymmetric reactions with chiral aldehydes.[19] Several examples are recorded in Figure 2. The most striking examples involve glyceraldehyde acetonide **30**: the reaction with (S,S)-**26** provides the 3,4-anti-4,5-syn diastereomer **51** with >20 : 1 stereoselectivity, while with (R,R)-**26** the 3,4-anti-4,5-anti diastereomer **52** is the major component of an 85 : 15 mixture. Excellent stereoselectivity was also realized in the pair of reactions involving benzyl lactaldehyde **16**: diastereomer **55** is the major product (89 : 11) of the matched double asymmetric reaction with (S,S)-**26**,[3e] while **56** predominates (84 : 16) in the mismatched reaction with (R,R)-**26**. These data are particularly gratifying in view of the modest enantioselectivity of **26** and the fact that aldehydes like **16** with conformationally unconstrained alkoxy substituents are generally poor asymmetric allylboration substrates.[22] Outstanding diastereoselectivity was also realized in the matched double asymmetric reactions of α,β-epoxyaldehyde **35** (93 : 7 selectivity for **59**, uncorrected for the enantiomeric purity of **35** (95% e.e.)), and β-alkoxy aldehyde **40** (>20 : 1 selectivity for **20**). That the mismatched double asymmetric reactions of **35** and **40** proceed with only ca. 2 : 1 selectivity reflects the moderate enantioselectivity of **26**, and reinforces the need to develop a second generation reagent with a more enantioselective chiral auxiliary.[23,24]

The oxidations of the alkoxysilanols generated in this study generally proceeded smoothly and in high yield by using Tamao's procedure (20 equiv of H_2O_2, 2 equiv of KF, 2 equiv of $KHCO_3$).[6e] If lesser quantities of H_2O_2 were used, then protodesilylated products, such as **66** in the case of **51**, are obtained in amounts inversely related to the quantity of H_2O_2 employed. This standard procedure worked well for all substrates except **59**, which is extremely sensitive towards base catalyzed Petersen elimination, and **62** and **63** which have TBDMS protecting groups that are cleaved under these conditions. We found, however, that the C(3)-silyloxy units of **62**-**63** are selectivity oxidized without interference of the TBDMS group if KF is omitted from the standard procedure. These reactions proceed at a considerably slower rate than those with KF, and it is necessary to compensate by heating to 50°C for 20 h. Nevertheless, diols **64** and **65** are obtained in 86-88% yield. Best results with the sensitive epoxyalcohol substrate **59** were obtained when KF was omitted and KH_2PO_4 was added as a buffer, but a significant amount of elimination to the (Z)-diene **67** still occurred.

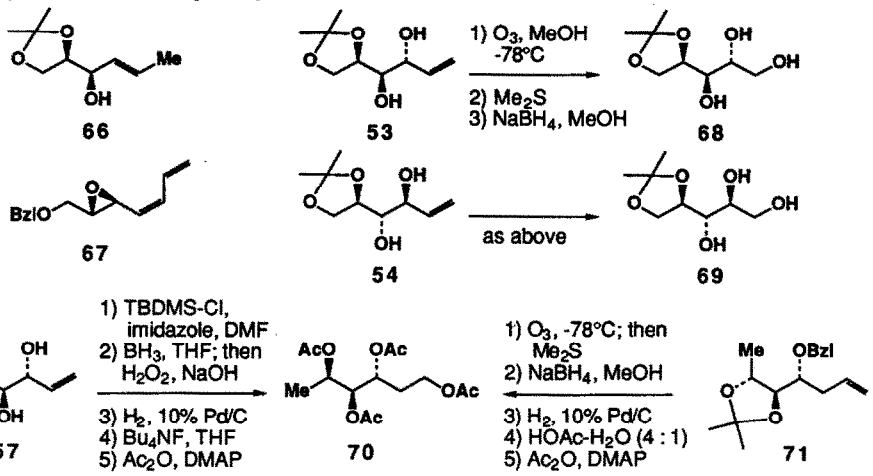
Stereochemical assignments, based initially on mechanistic considerations, are fully consistent with the following observations. First, the 3,4-anti stereochemistry of silanols **50c** (R = C_6H_{11}), **52** and **59** was

Figure 2. Double Asymmetric Reactions of 26 and Chiral Aldehydes.



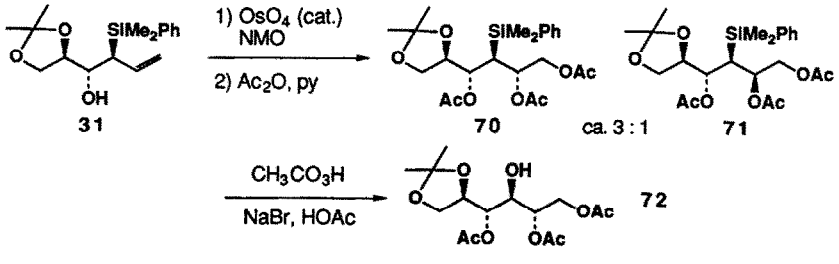
verified by treatment with NaH in THF which provided (Z)-dienes **44**, **45**, and **67**, respectively. Second, the *stereostructures of diols* **53** *and* **54**, *obtained by the Tamao oxidations of* **51** *and* **52**, were verified by the ozonolytic conversion to the known triols **68** and **69**, respectively.[27] Finally, the stereochemistry of *lyxo*-triol

derivative **57**, obtained by the Tamao oxidation of **55**, was confirmed by correlation with **71** via conversion to the tetraacetate **70**. Compound **71** is an intermediate in our synthesis of the olivomycin AB disaccharide and the stereochemistry is known unambiguously.[28]



These assignments agree fully with the sense of absolute stereochemical induction previously established for reactions of other tartrate ester modified allylboronates,[14,21-23] and thus are consistent with major product formation occurring by way of transition state **48** in the reactions of **26** with chiral and achiral aldehydes. All other stereostructures in this series are assigned by analogy.

Summary. Two new chiral allylboron reagents have been developed for use in acyclic diastereoselective syntheses of carbohydrates. γ-Phenyldimethylsilyl substituted reagent **25** is a chiral allylic alcohol β-carbanion equivalent that facilitates the enantio- and diastereoselective synthesis of substituted 2-butene-1,4-diols via aldehyde allylation and oxidation/Peterson elimination of the intermediate anti silanols (e.g., **29** → **27**). The allylic alcohols so obtained are ideally suited for further elaboration to carbohydrates via asymmetric epoxidation or osmylation sequences.[29,30] The γ-(cyclohexyloxy)dimethylsilyl substituted reagent **26**, on the other hand, is an enantioselective synthetic equivalent of an (E)-alkoxyallylmetal reagent (i.e., an allylic alcohol α-carbanion equivalent) that provides direct access to substituted anti-1-butene-3,4-diols **22** via aldehyde allylation and Tamao oxidation of the intermediate anti silanols (e.g., **50**). While **26** is only moderately enantioselective (64-72% e.e.) in reactions with achiral aldehydes, this reagent displays very useful stereoselectivity especially in matched double asymmetric reactions with chiral aldehydes (Figure 2). In contrast, reagent **25** is much more enantioselective (81-87% e.e.) and generally is more diastereoselective than **26** in both matched and mismatched double asymmetric reactions (compare Figures 1 and 2). While we have not yet developed conditions for directly oxidizing anti (phenyldimethyl)silanols **29** to anti diols **22** (vide supra), it is possible to oxidize the phenyldimethylsilane unit of **29** to an alcohol as long as the vinyl unit is



removed or modified in a prior step. One demonstration of this point is provided by the conversion of **31** to **74** summarized below.[10c] Thus, depending on the nature of the synthetic sequence under examination, either **25** or **26** may prove useful for the enantioselective anti α-hydroxyallylation of aldehydes.

Synthetic applications of this methodology will be reported in due course.

EXPERIMENTAL SECTION

General. ^1H NMR spectra were recorded on Varian XL 300 and 400 instruments using $CDCl_3$ as solvent. Residual $CHCl_3$ was assigned as δ 7.26. Infrared spectra were recorded on a Perkin Elmer Model 1420 Infrared Spectrophotometer and calibrated with the 1601 cm^{-1} absorption of polystyrene. Optical rotations were measured on a Rudolph Autopol III Polarimeter using a 1 mL cell with a 10 cm path length. Mass spectra were obtained using a Kratos GC/MS 80 RFA Mass Spectrometer. Elemental analyses were performed by Robertson Laboratories, Florham Park, NJ.

All reactions were conducted under dry N_2 or argon, using glassware dried at ca. 125°C. Ether, THF, and toluene were distilled from sodium benzophenone ketyl; CH_2Cl_2 and CH_3CN were distilled from CaH_2; methanol was distilled from Mg turnings. Most other solvents and reagents were dried over 4Å molecular sieves before use. Removal of solvents was accomplished on a rotary evaporator at reduced pressure.

Analytical thin layer chromatography (TLC) was performed by using Kieselgel 60 F_{254} glass plates precoated with a 0.25 mm layer of silica gel. Preparative TLC usually was performed on Kieselgel 60 F_{254} glass plates precoated with a 0.50 mm layer of silica gel. Flash column chromatography was performed by using Kieselgel 60 (230-400 mesh) silica gel. Compounds isolated by chromatography were freed of residual solvent under vacuum (<1.5 mm Hg) to constant weight, and generally were >95% pure by ^1H NMR.

Diisopropyl Tartrate Modified (E)-γ-(Dimethylphenylsilyl)Allylboronate (25). A 250 mL 3-neck flask containing allyl(dimethylphenyl)silane **28** (9.45 g, 53.7 mmol), KO^tBu (6.04 g, 53.6 mmol) and THF (50 mL) was flushed with Ar and cooled to -78°C. n-BuLi (2.5 M in hexane, 21.4 mL, 53.6 mmol) was then added dropwise via cannula. The cooling bath was removed and the mixture was allowed to warm to an internal temperature of -40°C. The solution was maintained at -40°C for 15 min and then recooled to -78°C. Triisopropylborate (10.1 g, 12.4 mL, 53.6 mmol) was added dropwise via cannula. Ten minutes later the mixture was poured into a separatory funnel containing 1 N HCl saturated with NaCl (100 mL). The aqueous layer was adjusted to pH 1 using 1 N HCl, and was extracted with additional ether (4 x 25 mL). The combined extracts were dried ($MgSO_4$) and then a solution of (R,R)-diisopropyl tartrate (12.6 g, 53.6 mmol) in ether (20 mL) was added. This mixture was stirred for at least 2 h, and then filtered through a fritted glass funnel under a N_2 blanket. The filtrate was concentrated on a rotary evaporator to a thick, colorless liquid, and then pumped to a constant weight (24.9 g) at 1.0 mm Hg. The crude product, consisting primarily of **25** with residual allyl(dimethylphenyl)silane **28** and DIPT, was analyzed by ^1H NMR to determine the weight percentage of **25** in the mixture; the yield of **25** is generally 70-80%. Crude **25** was dissolved in toluene (ca. 1 M) and stored over 4 Å molecular sieves: at -20°C under Ar: ^1H NMR δ 7.52 (m, 2 H), 7.34 (m, 3 H), 6.19 (dt, J=18.3, 7.1 Hz, 1 H), 5.81 (d, J=18.3 Hz, 1 H), 5.15 (m, 2 H), 4.79 (s, 2 H), 2.06 (dd, J=7.1, 1.8 Hz, 2 H), 1.29(d, J= 6.2 Hz, 12 H), 0.32 (s, 6 H).

Representative Procedure for Reactions of 25 and Aldehydes: (1R,2S)-1-Cyclohexyl-2-(dimethylphenyl)silylbut-3-ene-1-ol (29c). To a -78°C solution of (R,R)-**25** (0.96 mmol) in toluene (0.80 mL) under N_2 containing powdered 4Å molecular sieves (100 mg) was added a -78°C solution of freshly distilled cyclohexane carboxaldehyde (90 mg, 0.80 mmol) in toluene (0.20 mL) over a 10 min period. The mixture was stirred at -78°C for 5 h, and then was quenched with excess acetaldehyde (10 equiv.; to consume unreacted **25**). The solution was filtered through Celite, concentrated *in vacuo*, and chromatographed (30 x 150 mm column) using 8:1 hexane-ether as eluent to provide 202 mg (88%) of **29c** (87% e.e. by Mosher ester analysis): R_f = 0.30 (12% ether/hexane); $[\alpha]^{23}_D$ -14.3° (c = 0.85, $CHCl_3$); ^1H NMR δ 7.55 (m, 2 H), 7.37 (m, 3 H), 5.86 (ddd, J = 17.2, 10.6, 10.6 Hz, 1 H), 5.04 (dd, J = 10.6, 1.9 Hz, 1 H), 4.88 (dd, J = 17.2, 1.9 Hz, 1 H), 3.36 (dd, J = 7.4, 3.9 Hz, 1 H), 2.11 (dd, J = 10.6, 3.9 Hz, 1 H), 1.81-0.81 (m, 11 H), 0.37 (s, 3 H), 0.34 (s, 3 H); IR (neat) 3480, 3060, 2920, 2860, 1620, 1445, 1425, 1245, 1105, 970, 890, 830, 810, 725, 695 cm^{-1}; mass spectrum, calcd for $C_{18}H_{28}OSi$ (M^+) 288.1910, found 288.1917. *Anal.* Calcd for $C_{18}H_{28}OSi$: C, 74.93; H, 9.78. Found: C, 75.00; H, 9.92.

(3S,4R)-3-(Dimethylphenyl)silylpent-1-ene-4-ol (29a): R_f = 0.32 (25% ether/hexane); $[\alpha]^{23}_D$ + 1.5° (c = 0.8, $CHCl_3$); ^1H NMR δ 7.53 (m, 2 H), 7.37 (m, 3 H), 5.81 (ddd, J = 17.3, 9.9, 9.9 Hz, 1 H), 5.09 (dd, J = 9.9, 1.9 Hz, 1 H), 3.93 (m, 1 H), 1.85 (dd, J = 9.9, 5.9 Hz, 1 H), 1.61 (s, 1 H), 1.11 (d, J = 6.2 Hz, 3 H), 0.35 (s, 3 H), 0.33 (s, 3 H); IR (neat) 3440, 3060, 2960, 1630, 1425, 1245, 1110, 1045, 1000, 895, 695 cm^{-1}; mass spectrum, calcd for $C_{12}H_{17}OSi$ (M^+ - CH_3) 205.1048, found 205.1056. *Anal.* Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15. Found: C, 70.57, H, 9.47.

(3S,4R)-3-(Dimethylphenyl)silylnon-1-ene-4-ol (29b): R_f = 0.32 (12% ether/hexane); $[\alpha]^{23}_D$ -1.3° (c = 5.4, $CHCl_3$); ^1H NMR δ 7.53 (m, 2 H), 7.35 (m, 3 H), 5.83 (ddd, J = 17.2, 9.9, 9.9 Hz, 1 H), 5.07 (dd, J = 9.9, 1.9 Hz, 1 H), 4.91 (ddd, J = 17.2, 1.9, 1.3 Hz, 1 H), 3.72 (m, 1 H), 1.90 (dd, J=9.9, 4.3 Hz, 1 H), 1.42-1.12 (m, 9 H), 0.84 (t, J = 6.7 H, 3 H), 0.36 (s, 3 H), 0.33 (s, 3 H); IR (neat) 3600-3200 (br), 3070, 2960, 2930, 2860, 1625, 1460, 1250, 1110, 895, 830, 810, 700 cm^{-1}; mass spectrum, calcd for $C_{17}H_{28}OSi$ (M^+) 276.1909, found 276.1901 . *Anal.* Calcd for $C_{17}H_{28}OSi$: C, 73.85; H, 10.21. Found: C, 73.61; H, 10.31.

Representative Procedure for Dimethyl Dioxirane Oxidation/Peterson Elimination of Allyl(phenyldimethyl)silanes 29: (E)-(1R)-41-Cyclohexylbut-2-ene-1,4-diol (27c). Dimethyl dioxirane (1.6 mL, 0.16 mmol, 0.1 M in acetone) was added to a mixture of **29c** (27 mg, 0.09 mmol) and K_2CO_3 (0.67 g, 4.84 mmol). This mixture was stirred at 0°C for 1 h. Additional dimethyl dioxirane solution (0.93 mL, 0.093 mmol) was added (when an I_2 starch paper test indicated the absence of oxidant) until the reaction was complete (TLC analysis). The solution was filtered through a pad of Celite, concentrated, and then treated with a solution of HOAc in MeOH (1.78 mL of MeOH, 0.29 mL HOAc) for 10 minutes. The solution was diluted with ether and washed with aqueous $NaHCO_3$. The aqueous layer was extracted with ether (3 x 30 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Chromatography of the crude product (silica gel, 100 % ether) provided 16.8 mg (95%) of **27c** as a clear oil: R_f = 0.35 in 100% ether; $[\alpha]^{23}_D$ -11.1° (c = 2.5, $CHCl_3$); ^1H NMR δ 5.79 (dt, J = 15.6, 4.2 Hz, 1 H), 5.70 (dd, J = 15.6, 5.7 Hz, 1 H), 4.13 (d, J = 4.2 Hz, 2 H), 3.84 (dd, J = 5.7, 5.7 Hz, 1 H), 2.28 (br s, 2 H), 1.86-0.89 (m, 11 H); IR (neat) 3560-3060 (br), 2930, 2860, 1660, 1450, 1000, 940, 910, cm^{-1}; mass spectrum, calcd for $C_{10}H_{17}O$ (M^+ - OH) 153.1279, found 153.1199. *Anal.* Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.92; H, 10.67.

(E)-(4R)-Non-2-ene-1,4-diol (27b): R_f = 0.35 (ether); $[\alpha]^{23}_D$ -4.1° (c = 0.54, $CHCl_3$); ^1H NMR δ 5.83 (dt, J = 16.4, 5.1 Hz, 1 H), 5.72 (dd, J = 16.4, 6.4, Hz, 1 H), 4.14 (d, J = 4.1 Hz, 2 H), 4.15-4.08 (m, 1 H), 1.92 (s, 2 H), 1.20-1.56 (m, 8 H), 0.88 (t, J = 7.2 Hz, 3 H); IR (neat) 3700-3050 (br), 2995, 2940, 2890, 1460, 1385, 1375, 1260, 1215, 1115, 1070, 850 cm^{-1}; mass spectrum, calcd for $C_9H_{17}O$ (M^+ - OH) 141.1279 found 141.1271. *Anal.* Calcd for $C_9H_{18}O_2$: C, 68.29; H, 11.47. Found: C, 68.05; H, 11.27.

(3S,4R,5R)-5,6-O-Isopropylidene-3-(dimethylphenyl)silylhex-1-ene-4-ol (31). A -78°C solution of freshly distilled D-glyceraldehyde acetonide **30** (0.100 mg, 0.80 mmol) in toluene (0.30 mL) was added dropwise over a 10 min period to a -78°C solution of (R,R)-**25** (0.96 mmol, crude reagent) in toluene (1.45 mL) containing powdered 4Å molecular sieves (100 mg). The mixture was stirred overnight at -78°C and then was worked up as described for the preparation of **29c**. The product was purified by chromatography (30 x 150 mm column) with use of 8:1 hexane/ether as eluent to provide 221 mg (90%) of **31**: R_f = 0.27 in 25% (ether/hexane); $[\alpha]^{23}_D$ +20.7° (c= 1.05, $CHCl_3$); ^1H NMR δ 7.42 (m, 2 H), 7.31 (m, 3 H), 5.91 (ddd, J = 17.2, 10.7, 10.7 Hz, 1 H), 5.07 (dd, J = 10.7, 2.6 Hz, 1 H), 4.98 (dd, J = 17.2, 2.6 Hz, 1 H), 3.95 (m, 2 H), 3.87 (m, 2 H), 2.03 (dd, J = 10.7, 2.8 Hz, 1 H), 1.86 (s, 1 H), 1.39 (s, 3 H), 1.32 (s, 3 H), 0.43 (s, 3 H), 0.38 (s, 3 H); IR (neat) 3600-3200 (br), 3070, 2995, 2960, 2900, 1620, 1250, 1115, 1060, 835, 815, 790, 720, 700 cm^{-1}; mass spectrum, calcd for $C_{16}H_{23}O_3Si$ (M^+ - CH_3) 291.1416, found 291.1426. *Anal.* Calcd for $C_{17}H_{26}O_3Si$: C, 66.62; H, 8.55. Found: C, 66.93; H, 8.82.

(3R,4S,5R)-5,6-O-Isopropylidene-3-(dimethylphenyl)silylhex-1-ene-4-ol (32), obtained in 86% yield from the reaction of **30** and (S,S)-**25** (22 : 1 selectivity): R_f = 0.45 in 25% ether/hexanes; $[\alpha]^{23}_D$ +23.2° (c = 1.02, $CHCl_3$); ^1H NMR δ 7.56 (m, 2 H), 7.37 (m, 3 H), 5.97 (ddd, J = 17.1, 9.9, 9.9 Hz, 1 H), 4.97 (dd, J = 9.9, 2.0 Hz, 1 H), 4.78 (dd, J = 17.1, 2.0 Hz, 1 H), 4.05 (q, J = 6.5 Hz, 1 H), 3.92 (dd, J = 7.6, 6.5 Hz, 1 H), 3.59 (dd, J = 7.6, 6.5 Hz, 1 H), 3.46 (dd, J = 8.3, 6.5 Hz, 1 H), 2.60 (dd, J = 2.1, 2.0 Hz, 1 H), 1.70 (d, J = 9.9 Hz, 1 H), 1.35 (s, 3 H), 1.30 (s, 3 H), 0.40 (s, 3 H), 0.34 (s, 3 H); IR (neat) 3490, 3070, 2990, 2880, 1625, 1370, 1250, 1215, 1070, 835, 815, 700 cm^{-1}; mass spectrum, calcd for $C_{16}H_{23}O_3Si$ (M^+ - CH_3) 291.1416, found 291.1418. *Anal.* Calcd for $C_{17}H_{26}O_3Si$: C, 66.62; H, 8.55. Found: C, 66.90; H, 8.79.

(E)-(4S,5R)-5,6-O-Isopropylidene-hex-2-ene-1,4-diol (33), prepared from **31** in 88% yield: R_f = 0.35 (95% ether/hexane); $[\alpha]^{23}_D$ +4.7° (c = 0.7, $CHCl_3$); ^1H NMR δ 5.99 (dtd, J = 15.6, 4.6, 1.2 Hz, 1 H), 5.71 (ddt, J = 15.6, 5.8, 1.6 Hz, 1 H), 4.29 (m, 1 H), 4.17 (dd, J = 4.6, 1.6 Hz, 2 H), 4.12 (m, 1 H), 3.99 (dd, J = 8.1, 6.7 Hz, 1 H), 3.91 (dd, J = 8.1, 5.9 Hz, 1 H), 1.44 (s, 3 H), 1.36 (s, 3 H); IR ($CHCl_3$) 3600, 3520-3140 (br), 3005, 2950, 2930, 2890, 1650, 1450, 1380, 1370, 1220, 1150, 1060, 940, 850, 665 cm^{-1}; mass spectrum, calcd for $C_9H_{16}O_4$ (M^+) 188.1048, found 188.1038. *Anal.* Calcd for $C_9H_{16}O_4$: C, 57.43; H, 8.56. Found: C, 57.56; H, 8.51.

(E)-(4R,5R)-5,6-O-isopropylidene-hex-2-ene-1,4-ol (34), prepared from **32** in 83% yield: R_f = 0.35 (95% ether/MeOH); $[\alpha]^{23}_D$ +4.9° (c = 0.49, $CHCl_3$); ^1H NMR 5.97 (dtd, J = 15.5, 4.2, 1.4 Hz, 1 H), 5.67 (ddt, J = 15.5, 6.9, 1.5 Hz, 1 H), 4.15 (dd, J = 6.9, 1.5 Hz, 2 H), 4.09-3.96 (m, 3 H), 3.76 (ddd, J = 6.9, 5.0, 1.5 Hz, 1 H), 1.44 (s, 3 H), 1.36 (s, 3 H); IR (neat) 3300, 3180, 2960, 2905, 2890, 2860, 2840, 1660, 1440, 1365, 1355, 1305,

1145, 1120 cm^{-1}; mass spectrum, calcd for $C_8H_{13}O_4$ (M^+ - CH_3) 173.0814, found 173.0811. *Anal.* Calcd for $C_9H_{16}O_4$: C, 57.43; H, 8.56. Found: C, 57.56; H, 8.51.

(3S,4R,5R,6S)-7-Benzyloxy-5,6-epoxy-3-(dimethylphenyl)silylhept-1-ene-4-ol (36), prepared with 15 : 1 selectivity using (R,R)-**25**: R_f = 0.32 (25% ether/hexane); $[\alpha]^{23}_D$ -12.4° (c = 1.1, $CHCl_3$) ^1H NMR δ 7.55 (m, 2 H), 7.33 (m, 8 H), 5.86 (ddd, J = 17.9, 10.3, 10.3 Hz, 1 H), 4.98 (dd, J = 10.3, 2.0 Hz, 1 H), 4.87 (dd, J = 17.9, 2.0 Hz, 1 H), 4.56 (d, A of AB, J = 11.6 Hz, 1 H), 4.53 (d, B of AB, J = 11.6 Hz, 1 H), 3.95 (m, 1 H), 3.71 (d, J = 10.9 Hz, 1 H), 3.28 (m, 2 H), 2.99 (m, 1 H), 1.97 (dd, J = 10.3, 2.6 Hz, 1 H), 1.74 (s, 1 H), 0.39 (s, 3 H), 0.33 (s, 3 H); IR (neat) 3570, 3070, 2960, 2860, 1630, 1495, 1455, 1285, 1245, 1110, 900, 835, 695, 650 cm^{-1}; mass spectrum, calcd for $C_{22}H_{27}O_2Si$ (M^+ - OH) 351.1780, found 351.1800. *Anal.* Calcd for $C_{22}H_{28}O_3Si$: C, 71.70; H, 7.66. Found: C, 71.40; H, 7.65.

(3R,4S,5R,6S)-7-Benzyloxy-5,6-epoxy-3-(dimethylphenyl)silylhept-1-ene-4-ol (37), prepared with 8 : 1 selectivity using (S,S)-**25**: R_f = 0.32 (25% ether/hexane); $[\alpha]^{23}_D$ +10.3° (c = 0.6, $CHCl_3$); ^1H NMR δ 7.54 (m, 2 H), 7.35 (m, 8 H), 5.95 (ddd, J = 17.4, 10.7, 10.7 Hz, 1 H), 5.06 (dd, J = 10.7, 2.0 Hz, 1 H), 4.93 (dd, J = 17.4, 2.0 Hz, 1 H), 4.53 (d, A of AB, J = 12.2 Hz, 1 H), 4.49 (d, B of AB, J = 12.2 Hz, 1 H), 3.60 (dd, J = 11.9, 3.3 Hz, 1 H), 3.54 (dd, J = 5.7, 3.4 Hz, 1 H), 3.35 (dd, J = 11.9, 6.0 Hz, 1 H), 2.99(m, 1 H), 2.93 (dd, J = 5.7, 2.4 Hz, 1 H), 2.02 (dd, J = 10.7, 3.4 Hz, 1 H), 0.38 (s, 3 H), 0.33 (s, 3 H); IR (neat) 3570, 3070, 3030, 2960, 2870, 1960-1700 (Ar overtones), 1625, 1495, 1455, 1425, 1360, 1280, 1245, 1110, 900, 830, 695, 645 cm^{-1}; mass spectrum calcd for $C_{22}H_{27}O_2Si$ (M^+ - OH) 351.1780, found 351.1793. *Anal.* Calcd for $C_{22}H_{28}O_3Si$: C, 71.70; H, 7.66. Found: C, 71.43; H, 7.53.

(E)-(4S,5S,6S)-7-Benzyloxy-5,6-epoxy-hept-2-ene-1,4-diol (38), 91% yield from **36**: R_f = 0.20 (100% ether); $[\alpha]^{23}_D$ -7.3° (c = 1.5, $CHCl_3$); ^1H NMR δ 7.34 (m, 5 H), 5.99 (dtd, J = 15.6, 4.5, 1.3 Hz, 1 H), 5.82 (dd, J = 15.6, 4.3 Hz, 1 H), 4.59 (d, A of AB, J = 11.6 Hz, 1 H), 4.55 (d, B of AB, J = 11.6 Hz, 1 H), 4.20 (d, J = 4.5 Hz, 2 H), 4.13 (dd, J = 4.3, 1.6 Hz, 1 H), 3.78 (dd, J = 11.8, 2.6 Hz, 1 H), 3.52 (dd, J = 11.8,5.5 Hz, 1 H), 3.03 (m, 1 H); IR (neat) 3610, 3540-3040 (br), 1500, 1455, 1380, 1365, 1265, 1205, 1100, 980, 905, 790, 740, 700 cm; mass spectrum, calcd for $C_{13}H_{15}O_3$ (M^+ - OH) 219.1021, found 219.1005. *Anal.* Calcd for $C_{13}H_{16}O_4$: C, 67.18; H, 7.25. Found : C, 66.69; H, 7.19.

(3S,4R,5S)-6-(*tert*-Butyldimethyl)siloxy-3-(dimethylphenyl)silyl-5-methylhex-1-ene-4-ol (41), >20 : 1 selectivity from the double asymmetric reaction of **40** and (R,R)-**25**: R_f = 0.35 (8% ether-hexane); $[\alpha]^{23}_D$ -9.2° (c = 5.2, $CHCl_3$); ^1H NMR δ 7.52 (m, 2 H), 7.34 (m, 3 H), 5.90 (ddd, J = 17.2, 10.6, 10.6 Hz, 1 H), 5.00 (dd, J = 10.6, 2.0 Hz, 1 H), 4.90 (dd, J = 17.2, 2.0 Hz, 1 H), 3.86 (ddd, J = 5.8, 1.9, 1.9 Hz, 1 H), 3.54 (dd, J = 9.8, 4.7 Hz, 1 H), 3.52 (dd, J = 9.8, 4.8 Hz, 1 H), 2.41 (d, J = 3.2 Hz, 1 H), 2.09 (dd, J = 10.6, 5.9 Hz, 1 H), 1.69 (m, 1 H), 0.88 (s, 9 H), 0.79 (d, J = 6.4 Hz, 3 H), 0.36 (s, 3 H), 0.32 (s, 3 H), 0.02 (s, 6 H); IR (neat) 3600-3200 (br), 3040, 3020, 2940, 2900, 2820, 1610, 1455, 1410, 1240, 1100, 1000, 990, 820; mass spectrum, calcd for $C_{15}H_{33}O_2Si$ (M^+ - C_6H_5) 301.2019, found 301.1996. *Anal.* Calcd. for $C_{21}H_{38}O_2Si$: C, 66.60; H, 10.11. Found: C, 66.41; H, 9.96.

(3R,4S,5S)-6-(*tert*-Butyldimethyl)siloxy-3-(dimethylphenyl)silyl-5-methylhex-1-ene-4-ol (42), the major product of a 60 : 40 mixture from the mismatched reaction of **40** and (S,S)-**25**: R_f = 0.65 (8% ether/hexane); $[\alpha]^{23}_D$ + 8.4° (c = 1.10, $CHCl_3$); ^1H NMR δ 7.53 (m, 5 H), 6.02 (ddd, J = 17.7, 10.8, 10.8 Hz, 1 H), 4.97 (dd, J = 10.8, 2.5 Hz, 1 H), 4.78(dd, J = 17.7, 2.5 Hz, 1 H), 3.91 (dd, J = 2.0 Hz, 1 H), 3.70 (dd, J = 9.5, 3.8 Hz, 1 H), 3.54 (m, 1 H), 3.45 (dd, J = 9.5, 9.5 Hz, 1 H), 1.93 (d, J = 10.8 Hz, 1 H), 1.77 (m, 1 H), 0.89 (s, 9 H), 0.63 (d, J = 7.2 Hz, 3 H), 0.38 (s, 3 H), 0.33 (s, 3 H), 0.06 (s, 6 H); IR (CCl_4) 3690,3560-3200 (br), 3070, 3050, 2960, 2930, 2860, 1620, 1470, 1430, 1250, 1110, 1060, 1000, 830, 700 cm^{-1}; mass spectrum, calcd for $C_{15}H_{33}O_2Si$ (M^+ - C_6H_5) 301.2019, found 301.2008. *Anal.* Calcd for $C_{21}H_{38}O_2Si$: C, 66.60; H, 10.11. Found: C, 66.89; H, 10.22.

(E)-(4S,5S)-6-(*tert*-Butyldimethyl)siloxy-5-methylhex-2-ene-1,4-diol (43), prepared in 95% yield from **41**: R_f = 0.36 (70% ether/hexane); $[\alpha]^{23}_D$ -10.0° (c = 0.12, $CHCl_3$); ^1H NMR δ 5.87 (dt, J = 15.7, 5.1 Hz, 1 H), 5.73 (dd, J = 15.7, 5.4 Hz, 1 H), 4.29 (m, 1 H), 4.15 (d, J = 5.1 Hz, 2 H), 3.69 (dd, J = 10.4, 4.9 Hz, 1 H), 3.63 (dd, J = 10.4,6.4 Hz, 1 H), 1.90 (m, 1 H), 0.89 (s, 9 H), 0.85 (d, J = 7.0 Hz, 3 H), 0.06 (s, 6 H). IR (neat) 3600-3100 (br), 2940, 2900, 2840, 1460, 1450, 1375, 1345, 1240, 1080, 990 cm^{-1}; mass spectrum, calcd for $C_{13}H_{27}O_2Si$ (M^+ - OH) 243.1780, found, 243.1788. *Anal. Calcd for $C_{13}H_{28}O_3Si$: C, 59.95; H, 10.83. Found: C, 60.27; H, 10.57.*

1-Cyclohexylbut-1(Z),3-diene (44). A solution of 43 mg (0.138 mmol) of **29c** in dry THF (3.0 mL) was treated with NaH (0.172 g,0.40 mmol) under N_2 for 15 min. The mixture was then diluted with ether (20 mL), and poured into brine solution (20 mL). The aqueous layer was separated and extracted with ether (2 x 15 mL). The combined organic extracts were dried over $MgSO_4$. Filtration, concentration of the filtrate, and chromatography of the

product on silica gel using 9% ether/hexane as eluent gave 9.0 mg (53%) of the volatile diene **44**: R_f = 0.60 (100% hexane); ^{1}H NMR δ 6.64 (ddd, J = 17.5, 11.6, 11.6 Hz, 1 H), 5.89 (dd, J = 10.9, 10.9 Hz, 1 H), 5.30 (dd, J = 10.5, 10.5 Hz, 1 H), 5.17 (d, J = 16.7 Hz, 1 H), 5.06 (d, J = 10.5 Hz, 1 H), 2.43 (m, 1 H), 1.74-0.83 (m, 10 H); IR (CCl_4) 2930, 2850, 1655, 1455, 1370, 1115, 900 cm^{-1}; mass spectrum, calcd for $C_{10}H_{16}$ (M^+) 136.1270, found 136.1252.

(5R)-5,6-O-Isopropylidenehex-1,3-(Z)-diene (45) was prepared from **31** and **52** via the method described for **44**: R_f = 0.45 (14% ether/hexane); $[\alpha]^{23}_D$ + 3.0° (c = 0.40, $CHCl_3$); ^{1}H NMR δ 6.67 (ddd, J = 16.3, 10.9, 10.9 Hz, 1 H), 6.17 (dd, J = 9.5, 9.5, Hz, 1 H), 5.45 (dd, J = 9.5, 9.5 Hz, 1 H), 5.29 (ddd, J = 16.3, 1.4, 1.4 Hz, 1 H), 5.22 (dd, J = 10.2 Hz, 1 H), 4.97 (q, J = 6.4 Hz, 1 H), 4.12 (dd, J = 8.3, 6.4 Hz, 1 H), 3.55 (dd, J = 16.0, 8.3 Hz, 1 H), 1.44 (s, 3 H), 1.41 (s, 3 H); IR (CCl_4) 3070, 2960, 1625, 1425, 1380, 1370, 1250, 1115, 1065, 835, 700 cm^{-1}; mass spectrum, calcd for C_9H_{14} (M^+) 154.1013, found 154.0994.

(E)-(4R,5R)-O-Isopropylidenehex-2-ene-1,6-diol (46). A solution of 28 mg (0.148 mmol) of **34** in acetone (0.40 mL) was treated with p-toluenesulfonic acid monohydrate (0.003 mg, 0.015 mmol) for 6 h at 23°C. The solution was then diluted with aqueous $NaHCO_3$ (25.0 mL) and extracted with ether (3 x 20 mL). The organic extracts were dried ($MgSO_4$), filtered and concentrated The product was purified by flash chromatography using 5% MeOH/ether to give 23 mg (83%) of **46**: R_f = 0.35 (5% MeOH/ether); $[\alpha]^{23}_D$ +6.5° (c = 0.46, $CHCl_3$); ^{1}H NMR δ 6.01 (dtd, J = 15.6, 5.1, 0.8 Hz, 1 H), 5.74 (ddt, J = 15.6, 7.0, 1.2 Hz, 1 H), 4.38 (dd, J = 7.0, 7.0 Hz, 1 H), 4.19 (dd, J = 5.1, 1.2 Hz, 2 H), 3.83 (m, 2 H), 3.60 (dd, J = 12.5, 3.9 Hz, 1 H), 1.44 (s, 6 H); IR (CCl_4) 3700-3100 (br), 3000, 1600, 1460, 1380, 1375, 1220, 1165, 1105, 1075, 1045, 1000, 975, 855, 755 cm^{-1}; mass spectrum, calcd for $C_9H_{17}O_4$ (M^+ + 1) 189.1132, found 189.1126. *Anal.* Calcd for $C_9H_{16}O_4$: C, 57.43; H, 8.57. Found: C, 57.36; H, 8.53.

(E)-(4S,5R)-O-Isopropylidenehex-2-ene-1,6-diol (47). A solution of **33** (0.015 g, 0.079 mmol) in dry acetone (0.214 mL) was treated with p-TsOH as described for the conversion of **34** to **46**. The reaction was quenched by the addition of aqueous $NaHCO_3$ (15 mL) and extracted with ether (3 x 20 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated with use of 5% MeOH/ether to give 11 mg (72%) of recovered **33** and 2.9 mg (19%) of **47**: R_f = 0.32 in 5% MeOH/ether; ^{1}H NMR δ 6.01 (dt, J = 16.0, 5.5 Hz, 1 H), 5.79 (ddd, J = 16.0, 7.0 1.2 Hz, 1 H), 4.70 (t, J = 7.4 Hz, 1 H), 4.27 (q, J = 6.6 Hz, 1 H), 4.19 (d, J = 4.3 Hz, 2 H), 3.60 (d, J = 5.5 Hz, 2 H), 1.44 (s, 3 H); IR (CCl_4) 3540, 2940, 1460, 1380, 1260, 1110 cm^{-1}.

Diisopropyl Tartrate Modified (E)-γ-(Cyclohexyloxydimethylsilyl)Allylboronate (26). A mixture of allyldimethylsilyl cyclohexyl ether **42**[26] (3.77 g, 19.0 mmol), KO^{t}Bu (2.14g, 19.0 mmol) and THF (22 mL) was flushed with argon and cooled to -78°C. n-BuLi (7.62 mL, 19.05 mmol, 2.5 M in hexanes) was then added dropwise via cannula. The cooling bath was removed and the mixture was allowed to warm to -20°C for 30 min. The solution was recooled to -78°C and then triisopropylborate (3.58 g, 4.40 mL, 19.1 mmol) was added dropwise via cannula. The mixture was stirred for 10 min and then was poured into a 250 mL separatory funnel containing saturated aqueous NH_4Cl (70 mL). The phases were separated and the aqueous layer was extracted with additional ether (4 x 25 mL). The combined extracts were dried ($MgSO_4$) and then a solution of (R,R)-diisopropyl tartrate (4.46 g, 19.1 mmol) in ether (20 mL) was added. This mixture was stirred for 2 h, filtered through a fritted glass funnel under a nitrogen blanket and concentrated on a rotary evaporator to a colorless thick liquid that was pumped to constant weight (8.85 g) at 1.0 mm Hg. The crude product, consisting primarily of **26** and residual DIPT and unreacted **49**, was analyzed by ^{1}H NMR to determine the weight percentage of **40** in the mixture; the yield of **40** is generally 75-85%. Crude **26** was dissolved in toluene (ca. 1 M) and stored at -20°C under Ar over 4Å molecular sieves: ^{1}H NMR δ 6.21 (dt, J = 18.9, 7.0 Hz, 1 H), 5.68 (dd, J = 18.9, 1.0 Hz, 1 H), 5.11 (m, 2 H), 4.77 (s, 2 H), 3.54 (m, 1 H), 2.03 (dd, J = 7.0, 1.0 Hz, 2 H), 1.81-1.15 (m, 10 H), 1.30 (d, J = 6.2 Hz, 12 H), 0.15 (s, 6 H).

Representative Procedure for Reactions of 26 and Aldehydes: (1R,2S)-1-Cyclohexyl-2-(cyclohexyloxydimethyl)silylbut-3-ene-1-ol (50c). A -78°C solution of freshly distilled cyclohexanecarboxaldehyde (0.130 mL, 1.07 mmol) in toluene (1.0 mL) was added dropwise over 10 min to a -78°C mixture of (R,R)-**26** (1.39 mmol, crude reagent) in toluene (1.7 mL) and 4Å molecular sieves (280 mg) under N_2. The mixture was stirred at -78°C for ≥5 h and then was treated with acetaldehyde (10 eq) to consume any unreacted **26**. The resulting mixture was filtered through a pad of Celite, concentrated *in vacuo*, and chromatographed with use of 7% ether/hexane as eluant to provide 290 mg (93%) of **50c** (72% e.e. as determined by Mosher ester analysis): R_f = 0.32 (7% ether/hexane); $[\alpha]^{23}_D$ -9.7° (c = 0.69, $CHCl_3$); ^{1}H NMR δ 5.96 (ddd, J = 17.2, 10.6, 10.6 Hz, 1 H), 5.03 (dd, J = 10.6, 1.5 Hz, 1 H), 4.89 (dd, J = 17.2, 1.5 Hz, 1 H), 3.64 (m, 1 H), 3.57 (d, J = 8.6 Hz, 1 H), 3.25 (s, 1 H), 2.07 (d, J = 10.6 Hz, 1 H), 1.84-0.76 (m, 21 H), 0.19 (s, 3 H), 0.15 (s, 3 H); IR (neat) 3600-3300 (br), 3060, 3000, 2990, 2920, 2840, 1615, 1440, 1405, 1365, 1245, 1200, 1060, 1030, 985, 885, 830, 660 cm^{-1}; mass spectrum, calcd for $C_{18}H_{33}OSi$ (M^+ - OH) calcd 293.2301, found 293.2294. *Anal.* Calcd for $C_{18}H_{34}O_2Si$: C, 69.62; H, 11.04. Found: C, 69.42; H, 10.84.

(3S,4R)-3-(Cyclohexyloxydimethylsilyl)silylpent-1-ene-4-ol (50a) R_f = 0.30 (9% ether/hexane); $[\alpha]^{23}_D$ -8.6° (c = 3.9, $CHCl_3$); ^1H NMR δ 5.88 (ddd, J = 17.2, 9.9, 9.9 Hz, 1 H), 5.07 (dd, J = 9.9, 2.4 Hz, 1 H), 4.96 (ddd, J = 17.2, 2.4, 1.51 Hz, 1 H), 4.15 (m, 1 H), 3.65 (m, 1 H), 1.78-1.16 (m, 10 H), 1.70 (d, J = 9.9 Hz, 1 H), 1.22 (d, J = 6.3 Hz, 3 H), 0.18 (s, 3 H), 0.15 (s, 3 H); IR (neat) 3700-3100 (br), 3060, 3000-2840 (br), 1620, 1445, 1370, 1250, 1080, 1050, 1000, 860, 830, 780, 650 cm^{-1}; mass spectrum, calcd for $C_{13}H_{25}OSi$ (M^+ - OH) 225.1674, found 225.1674. *Anal.* Calcd for $C_{13}H_{26}O_2Si$: C, 64.42; H, 10.82. Found: C, 64.14; H, 10.95.

(3S,4R)-3-(Cyclohexyloxydimethyl)silylnon-1-ene-4-ol (50b): R_f = 0.56 (10% ether/hexane); $[\alpha]^{23}_D$ -6.4° (c = 1.69, $CHCl_3$); ^1H NMR δ 5.92 (ddd, J = 17.4, 9.7, 9.7 Hz, 1 H), 5.05 (dd, J = 9.7, 2.0 Hz, 1 H), 4.92 (dd, J = 17.4, 2.0 Hz, 1 H), 3.94 (m, 1 H), 3.66 (m, 1 H), 3.22 (m, 1 H), 1.82-1.18 (m, 19 H), 0.89 (t, J = 6.7 Hz, 3 H), 0.20 (s, 3 H), 0.16 (s, 3 H); IR (CCl_4) 3605, 3560-3300 (br), 2950, 2860, 1625, 1465, 1410, 1375, 1250, 1140, 950 cm^{-1}; mass spectrum, calcd for $C_{17}H_{33}OSi$ (M^+ - OH) 281.2301, found 281.2303. *Anal.* Calcd for $C_{17}H_{34}O_2Si$: C, 68.39; H, 11.48. Found: C, 68.51; H, 11.20.

Procedure for Tamao Oxidation of Alkoxyallylsilanols 50: (1R,2S)-1-Cyclohexylbut-3-ene-1,2-diol (22c). A mixture of 100 mg (0.32 mmol) of **50c**, $KHCO_3$ (0.065 g, 0.64 mmol), $KF{\cdot}2H_2O$ (0.060 g, 0.64 mmol) and 30% H_2O_2 (0.66 mL, 6.4 mmol) in MeOH (1 mL) and THF (1 mL) was stirred at 23°C for 24 h. Solid $Na_2S_2O_3$ (1.37 g, 8.7 mmol) was added and the mixture stirred for 30 min. It was then filtered and concentrated *in vacuo*. The crude product was purified by chromatography using 1:1 hexane/ether to provide 54 mg (98%) of the known diol **22c** as a colorless oil:[6e] R_f = 0.34 (50% ether/hexane); $[\alpha]^{23}_D$ +12.3° (c = 2.3, $CHCl_3$); ^1H NMR δ 5.98 (dddd, J = 17.2, 10.1, 5.4, 1.5 Hz, 1 H), 5.36 (dd, J = 17.2, 1.9 Hz, 1 H), 5.30 (d, J = 10.1 Hz, 1 H), 4.23 (dd, J = 5.4, 3.5 Hz, 1 H), 3.42 (dd, J = 8.2, 3.5 Hz, 1 H), 1.99-1.01 (m, 13 H); mass spectrum, calcd for $C_{10}H_{18}O_2$ (M^+) 170.1307, found 170.1325.

(3S,4R)-pent-1-ene-3,4-diol (22a), prepared in 83% yield by the Tamao oxidation of **50a**: R_f = 0.47 (ether); $[\alpha]^{23}_D$ -9.7° (c = 0.81, $CHCl_3$); ^1H NMR δ 5.88 (ddd, J = 17.0, 10.6, 6.2 Hz, 1 H), 5.28 (dd, J = 17.0, 2.4 Hz, 1 H), 5.24 (dd, J = 10.6, 2.4 Hz, 1 H), 4.08 (br s, 1 H), 3.87 (br s, 1 H), 2.68 (br s, 1 H), 2.55 (br s, 1 H), 1.12 (d, J = 9.7 Hz, 3 H), 1.11 (s, 3 H); IR (neat) 3650-3100 (br), 3080, 2980, 2930, 2870, 1640, 1445, 1425, 1380, 1115, 1070, 1035, 980, 925, 820 cm^{-1}; mass spectrum, calcd for $C_5H_9O_2$ (M^+ - 1) 101.0602, found 101.0595.

(3S,4R)-non-1-ene-3,4-diol (22b), prepared in 95% yield by the Tamao oxidation of **50b**: R_f = 0.32 (70% ether/hexane); ^1H NMR δ 5.93 (ddd, J = 17.4, 10.9, 6.2 Hz, 1 H), 5.33 (d, J = 17.4 Hz, 1 H), 5.28 (d, J = 10.9 Hz, 1 H), 4.10 (m, 1 H), 3.69 (m, 1 H), 2.11 (br s, 1 H), 1.99 (br s, 1 H), 1.08-0.83 (m, 8 H), 0.89 (t, J = 6.7 Hz, 3 H); IR (CCl_4) 3600-3100 (br s), 3070, 3000-2850 (br), 1620, 1450, 1420, 1375, 1210, 1100, 985, 925, 750 cm^{-1}; mass spectrum, calcd for $C_9H_{17}O$ (M^+ - OH) 141.1279, found 141.1265.

(3R,4S,5R)-3-(Cyclohexyloxydimethyl)silyl-5,6-O-isopropylidene-hex-1-ene-4-ol (51). A -78°C solution of freshly distilled D-glyceraldehyde acetonide **30** (0.13 g, 1.00 mmol) in toluene (0.24 mL) was added dropwise over 10 min to a -78°C mixture of (S,S)-**26** (1.30 mmol, crude reagent) and 4Å molecular sieves (280 mg) in toluene (0.93 mL) under N_2. The mixture was stirred at -78°C for 24 h and then was treated with acetaldehyde (10 eq) to quench unconsumed **26**. The solution was filtered through a pad of Celite, concentrated *in vacuo*, and chromatographed with use of 15% ether/hexane as eluant to provide 237 mg (72%) of **51** and 5.3 mg (2%) of **52**. The reaction stereoselectivity was determined to be >20:1 (**51** to **52**) by ^1H NMR analysis of the crude reaction product. Data for **51**: R_f = 0.45 (16% ether-hexane); $[\alpha]^{23}_D$ +13.3° (c = 0.78, $CHCl_3$); ^1H NMR δ 6.02 (ddd, J = 17.3, 10.8, 10.8 Hz, 1 H), 5.02 (dd, J = 10.8, 2.0 Hz, 1 H), 4.89 (dd, J = 17.3, 2.0 Hz, 1 H), 4.13 (q, 6.1 Hz, 1 H), 3.98 (dd, J = 8.1, 6.1 Hz, 1 H), 3.82 (dd, J = 6.1, 3.2 Hz, 1 H), 3.57 (dd, J = 8.1, 6.1 Hz, 1 H), 3.21 (s, 1 H), 1.82-1.13 (m, 10 H), 1.58 (dd, J = 10.8, 3.2 Hz, 1 H), 1.42 (s, 3 H), 1.35 (s, 3 H), 0.22 (s, 3 H), 0.15 (s, 3 H); IR (neat) 3600-3300 (br), 3050, 2960,2910, 2815, 1610, 1435, 1355, 1235, 1200, 1140, 1115, 1050, 855, 820, 780 cm^{-1}; mass spectrum, calcd for $C_{16}H_{29}O_4Si$ (M^+ - CH_3) 313.1835, found 313.1833. *Anal.* Calcd for $C_{17}H_{32}O_4Si$: C, 62.15; H, 9.82. Found: C, 62.09; H, 10.08.

(3S,4R,5R)-3-(Cyclohexyloxydimethyl)silyl-5,6-O-isopropylidene-hex-1-ene-4-ol (52). The reaction of **30** (0.15 g, 1.15 mmol) and (R,R)-**26** (1.15 mmol, crude reagent) was performed at -78°C as described for the preparation of **51**. The stereoselectivity was determined to be 85:15 (**52** to **51**) by high field ^1H NMR analysis of the reaction mixture. Chromatography of the product mixture with use of 14% ether/hexane as eluant provided 254 mg (67%) of **52** and 80 mg (21%) of **51**. Data for **52**: R_f = 0.34 in 20% ether/hexanes; $[\alpha]^{23}_D$ -7.6° (c = 0.46, $CHCl_3$); ^1H NMR δ 5.95 (ddd, J = 17.2, 10.7, 10.7 Hz, 1 H), 5.04 (dd, J = 10.7, 2.6 Hz, 1 H), 4.98 (dd, J = 17.2, 2.6 Hz, 1 H), 4.05-3.87 (m, 4 H), 3.59 (m, 1 H), 3.35 (s, 1 H), 1.80 (dd, J = 10.6, 2.3 Hz, 1 H), 1.82-1.15 (m, 10 H), 1.39 (s, 3 H), 1.32 (s, 3 H), 0.16 (s, 6 H); IR (neat) 3590, 3520-3200 (br), 3060, 2990, 2970, 2920, 2840, 1615, 1445, 1375, 1365,

1250, 1145, 1100, 1050, 905, 855, 830, 750, 650 cm^{-1}; mass spectrum, calcd for $C_{16}H_{29}O_4Si$ (M^+ - CH_3) 313.1835, found 313.1854. *Anal.* Calcd for $C_{17}H_{32}O_4Si$: C, 62.15; H, 9.82. Found: C, 62.40; H, 9.78.

(3S,4S,5R)-5-Benzyloxy-3-(Cyclohexyloxydimethyl)silylhex-1-ene-4-ol (55), 89 : 11 selectivity from **16** and (S,S)-**26**: R_f = 0.63 (15% ether/hexane); $[\alpha]^{23}_D$ -26.8° (c = 2.5, $CHCl_3$); ^1H NMR δ 7.32 (m, 5 H), 5.96 (ddd, J = 17.2, 10.7, 10.7 Hz, 1 H), 5.05 (dd, J = 10.7, 1.6 Hz, 1 H), 4.93 (dd, J = 17.2 Hz, 1 H), 4.63 (d, A of AB, J = 11.3 Hz, 1 H), 4.44 (d, B of AB, J = 11.3 Hz, 1 H), 3.72 (dd, J = 8.1, 2.3 Hz, 1 H), 3.63 (m, 1 H), 3.50 (m, 1 H), 2.95 (s, 1 H), 1.81-0.99 (m, 11 H), 1.11 (d, J = 5.9 Hz, 3 H), 0.19 (s, 3 H), 0.17 (s, 3 H); IR (neat) 3580, 3070, 3030, 2980, 2940, 1625, 1495, 1450, 1375, 1280, 1250, 1085, 900, 865, 830, 690 cm^{-1}; HRMS, calcd for $C_{15}H_{23}O_3Si$ (M^+ - C_6H_{11}) 279.1416, found 279.1410. *Anal.* Calcd for $C_{21}H_{34}O_3Si$: C, 69.56; H, 9.45. Found: C, 69.90; H, 9.23.

(3S,4R,5R)-5-Benzyloxy-3-(Cyclohexyloxydimethyl)silylhex-1-ene-4-ol (56), prepared with 84 : 16 selectivity from **16** and (R,R-**26**): R_f = 0.30 in 15% ether/hexane; $[\alpha]^{23}_D$ +6.8° (c = 2.6, $CHCl_3$); ^1H NMR δ 7.34 (m,5 H), 5.96 (ddd, J = 17.2, 10.6, 10.6 Hz, 1 H), 5.05 (dd, J = 10.6, 1.9 Hz, 1 H), 4.93 (dd, J = 17.2, 1.9 Hz, 1 H), 4.58 (d, A of AB, J = 11.3 Hz, 1 H), 4.43 (d, B of AB, J = 11.3 Hz, 1 H), 3.87 (dd, J = 6.9, 3.0 Hz, 1 H), 3.63 (m, 1 H), 3.53 (qd, J = 5.7, 3.7 Hz, 1 H), 3.34 (br s, 1 H), 2.11 (dd, J = 10.7, 3.7 Hz, 1 H), 1.75-1.15 (m, 13 H), 0.19 (s, 3 H), 0.13 (s, 3 H); IR (neat) 3580, 3070, 3030, 2940, 2860, 1625, 1450, 1375, 1250, 1085, 900, 865, 830, 690 cm^{-1}; mass spectrum, calcd for $C_{15}H_{22}O_2Si$ (M^+ - $C_6H_{12}O$) 262.1389, found 262.1370. *Anal.* Calcd for $C_{21}H_{34}O_3Si$: C, 69.56; H, 9.45. Found: C, 69.49; H, 9.20.

(3R,4S,5R,6S)-7-Benzyloxy-3-(cyclohexyloxydimethyl)silyl-5,6-epoxyhept-1-ene-4-ol (59), prepared with 13 : 1 selectivity from **35** and (S,S)-**26**: R_f = 0.30 (78% hexane/ether); $[\alpha]^{23}_D$ -2.0° (c = 0.59,$CHCl_3$); ^1H NMR δ 9.33 (m, 5 H), 5.95 (ddd, J = 16.5, 10.1, 10.1 Hz, 1 H), 5.06 (d, J = 10.1 Hz, 1 H), 5.00 (dd, J = 16.5, 1.3 Hz, 1 H), 4.59 (d, A of AB, J = 12.1 Hz, 1 H), 4.56 (d, B of AB, J = 12.1 Hz, 1 H), 3.76 (dd, J = 3.5, 2.4 Hz, 1 H), 3.72 (dd, J = 2.4, 1.3 Hz, 1 H), 3.65 (m, 1 H), 3.47 (ddd, J = 11.9, 5.3, 1.3 Hz, 1 H), 3.14 (m, 1 H), 3.07 (ddd, J = 4.8, 2.4, 1.3 Hz, 1 H), 2.95 (d, J = 3.5, 1.3 Hz, 1 H), 1.93 (dd, J = 10.1, 3.5 Hz, 1 H), 1.77-1.19 (m, 10 H), 0.18 (s, 6 H). IR (neat) 3620-3200 (br), 3050, 3010, 2920, 2840, 1630, 1485, 1440, 1350, 1240, 1080, 890, 825, 685 cm^{-1}; mass spectrum, calcd for $C_{16}H_{22}O_3Si$ (M^+ - $C_6H_{12}O$) 290.1338, found 290.1360. *Anal.* Calcd for $C_{22}H_{34}O_4Si$: C, 67.65; H, 8.77. Found: C, 67.15; H, 8.58.

(3S,4R,5R,6S)-7-Benzyloxy-3-(cyclohexyloxydimethyl)silyl-5,6-epoxyhept-1-ene-4-ol (60), obtained as an inseparable mixture with **59** from **35** and (R,R)-**26**: R_f = 0.30 (78% hexane/ether); $[\alpha]^{23}_D$ -0.6° (c = 2.8 for a 1:1 mixture of **60** and **59**, $CHCl_3$); ^1H NMR (on mixture) δ 7.40 (m, 5 H), 6.07-5.95 (m, 1 H), 5.14-5.03 (m, 2 H), 4.67 (d, A of AB, J = 11.8 Hz, 1 H), 4.63 (d, B of AB, J = 11.8 Hz, 1 H), 4.08 (m, 1 H), 3.92 (dd, J = 12.1, 1.9 Hz, 1 H), 3.65 (m, 1 H), 3.45 (ddd, J = 12.1, 6.2, 0.6 Hz, 1 H), 3.07 (m, 1 H), 3.01 (m, 1 H), 1.95 (m, 1 H), 1.80-1.19 (m, 10 H), 0.18 (s, 6 H).

(3R,4S,5R)-6-(tert-Butyldimethyl)siloxy-3-(cyclohexyloxydimethyl)silyl-5-methylhex-1-ene-4-ol (62), obtained with 20 : 1 selectivity from **40** and (S,S)-**26**: R_f = 0.40 (10% ether/hexane); $[\alpha]^{23}_D$ -19.2° (c = 2.3, $CHCl_3$); ^1H NMR δ 5.95 (ddd, J = 16.5, 10.6, 10.6 Hz, 1 H), 5.03 (dd, J = 10.6, 1.3 Hz, 1 H), 4.94 (dd, J = 16.5, 1.3 Hz, 1 H), 3.99 (m, 1 H), 3.63 (m, 1 H), 3.57 (d, J = 4.0 Hz, 1 H), 3.15 (d, J = 2.0 Hz, 1 H), 1.89 (dd, J = 10.6, 4.6 Hz, 1 H), 1.88-1.20 (m, 11 H), 1.00 (d, J = 6.5 Hz, 3 H), 0.89 (s, 9 H), 0.17 (s, 3 H), 0.14 (s, 3 H), 0.04 (s, 6 H); IR (neat) 3560-3420 (br), 2960, 2940, 2860, 1625, 1450, 1460, 1255, 1070, 1015, 970, 895, 835, 660 cm^{-1}; mass spectrum, calcd for $C_{21}H_{43}O_2Si_2$ (M^+ - OH) 383.2801, found 383.2784. *Anal.* Calcd for $C_{21}H_{44}O_3Si_2$: C, 62.94; H, 11.07. Found: C, 62.74; H, 10.54.

(3S,4R,5R)-6-(tert-Butyldimethyl)siloxy-3-(cyclohexyloxydimethyl)silyl-5-methylhex-1-ene-4-ol (63), obtained with 64 : 36 selectivity via the mismatched double asymmetric reaction of **40** and (R,R-**26**): R_f = 0.73 (10% ether/hexane); $[\alpha]^{23}_D$ -19.2° (c = 2.3, $CHCl_3$); ^1H NMR δ 6.00 (ddd, J = 17.2, 10.6, 10.6 Hz, 1 H), 5.09 (dd, J = 10.6, 2.3 Hz, 1 H), 4.92 (dd, J = 17.2, 2.3 Hz, 1 H), 3.86 (s, 1 H), 3.75 (dd, 10.2, 2.2 Hz, 1 H), 3.68 (d, A of AB, J = 5.1 Hz, 1 H), 3.64 (d, B of AB, J = 5.1 Hz, 1 H), 1.84-1.03 (m, 12 H), 0.89 (s, 9 H), 0.73 (d, J = 7.2 Hz, 3 H), 0.18 (s, 3 H), 0.17 (s, 3 H), 0.06 (s, 6 H); IR (CCl_4) 3580-3340 (br), 2940, 2860, 1630, 1475, 1470, 1460, 1260, 1230, 1070, 910, 830, 670 cm^{-1}; mass spectrum, calcd for $C_{20}H_{41}O_3Si_2$ (M^+ - CH_3) 385.2594, found 385.2614. *Anal.* Calcd for $C_{21}H_{44}O_3Si_2$: C, 62.94; H, 11.07. Found: C, 62.73; H, 10.70.

(3R,4R,5R)-5,6-O-Isopropylidenehex-1-ene-3,4-diol (53), 92% yield from the Tamao oxidation of **51**: R_f = 0.32 (20% hexane/ether); $[\alpha]^{23}_D$ +13.3° (c = 0.72, $CHCl_3$); ^1H NMR δ 5.94 (dddd, J = 17.2, 10.5, 5.6, 1.4 Hz, 1 H), 5.39 (ddd, J = 17.2, 1.6, 1.6 Hz, 1 H), 5.27 (ddd, J = 10.5, 3.1, 1.0 Hz, 1 H), 4.30-4.20 (m, 2 H), 4.03 (ddd, J = 6.9, 6.9, 1.5 Hz, 1 H), 3.88 (ddd, J = 6.9, 6.9, 1.5 Hz, 1 H), 3.52 (m, 1 H), 2.64 (d, J = 7.0 Hz, 1 H), 2.49

(d, J = 7.0 Hz, 1 H), 1.44 (s, 3 H), 1.37 (s, 3 H); IR (CCl_4) 3660-3100 (br), 3060, 2970, 2920, 2870, 1630, 1440, 1360, 1440, 1360, 1230, 1200, 1140, 910, 840, 780, 720 cm^{-1}; mass spectrum, calcd for $C_8H_{13}O_4$ (M^+ - CH_3) 173.0813, found 173.0817. *Anal.* Calcd for $C_9H_{16}O_4$: C, 57.43; H, 8.57. Found: C, 57.38; H, 8.56.

(3S,4S,5R)-5,6-O-isopropylidenehex-1-ene-3,4-diol (54), 95% yield from the Tamao oxidation of **52**: R_f = 0.32 (20% hexane/ether); $[\alpha]^{23}_D$ +7.0° (c = 0.95, $CHCl_3$); ^1H NMR δ 5.39 (ddd, J = 17.2, 1.35, 0.5 Hz, 1 H), 5.29 (ddd, J = 9.9, 1.1, 0.5 Hz, 1 H), 4.30 (dd, J = 9.0, 4.5 Hz, 1 H), 4.06 (m, 2 H), 3.97 (m, 1 H), 3.71 (d, J = 0.5 Hz, 1 H), 2.64 (s, 1 H), 2.37 (d, J = 1.6 Hz, 1 H), 1.42 (s, 3 H), 1.34 (s, 3 H); IR (neat) 3560-3200 (br), 2990, 2940, 2880, 1640, 1450, 1380, 1370, 1250, 1210, 1155, 1060, 990, 930, 850 cm^{-1}; mass spectrum, calcd for $C_9H_{15}O_3$ (M^+ - OH) 171.1021, found 171.1033. *Anal.* Calcd for $C_9H_{16}O_4$: C, 57.43; H, 8.57. Found: C, 57.42; H, 8.65.

(3R,4S,5R)-5-Benzyloxyhex-1-ene-3,4-diol (57), 94% yield from the Tamao oxidation of **55**: R_f = 0.36 (50% ether/hexane); $[\alpha]^{23}_D$ -38.3° (c = 1.9, $CHCl_3$); ^1H NMR δ 7.34 (m, 5 H), 5.92 (ddd, J = 17.1, 10.5, 5.5 Hz, 1 H), 5.33 (ddd, J = 17.1, 1.6, 1.6 Hz, 1 H), 5.23 (10.5, 1.6, 1.6 Hz, 1 H), 4.40 (d, A of AB, J = 11.3 Hz, 1 H), 4.21 (d, B of AB, J = 11.3 Hz, 1 H), 4.21 (dd, J = 5.5, 5.5 Hz, 1 H), 3.76 (m, 1 H), 3.46 (dd, J = 5.5, 4.5 Hz, 1 H), 1.28 (d, J = 6.2 Hz, 3 H); IR (neat) 3600-3200, 3090, 3070, 3040, 2980, 2940, 2880, 2000-1800 (Ar overtones), 1650, 1500, 1450, 1375, 1205, 1155-1020, 990, 920 cm^{-1}; mass spectrum, calcd for $C_{13}H_{18}O_3$ (M^+) 222.1256, found 222.1268. *Anal.* Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.21; H, 7.97.

(3S,4R,5R)-5-Benzyloxyhex-1-ene-3,4-diol (58), prepared in 95% yield by the Tamao oxidation of **56**: R_f = 0.30 (45% ether/hexane); $[\alpha]^{23}_D$ -58.6° (c = 0.50, $CHCl_3$); ^1H NMR δ 7.33 (m, 5 H), 5.96 (ddd, J = 17.1, 10.6, 6.1 Hz, 1 H), 5.34 (ddd, J = 17.1, 1.7, 1.7 Hz, 1 H), 5.27 (ddd, J = 10.6, 1.7, 1.7 Hz, 1 H), 4.64 (d, A of AB, J = 11.2 Hz, 1 H), 4.44 (d, B of AB, J = 11.2 Hz, 1 H), 4.28 (dd, J = 5.5, 5.5 Hz, 1 H), 3.64 (m, 2 H), 2.50 (br s, 1 H), 2.20 (br s, 1 H), 1.32 (d, J = 6.5 Hz, 3 H); IR (neat) 3600, 3520-3200 (br), 3080, 3040, 2980, 2930, 2880, 1640, 1500, 1450, 1380, 1080, 980, 925, 905, 690 cm^{-1}; mass spectrum, calcd for $C_{13}H_{18}O_3$ (M^+) 222.1256, found 222.1271. *Anal.* Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.10, 7.89.

(3R,4R,5R,6S)-7-Benzyloxy-5,6-epoxyhept-1-ene-3,4-diol (61). A mixture of **59** (33 mg, 0.084 mmol), $KHCO_3$ (8.4 mg, 0.084 mmol), KH_2PO_4 (11.5 mg, 0.084 mmol) and 30% H_2O_2 (0.336 mL, 3.36 mmol) in THF (1 mL) was stirred at 38°C for 5 h. The solution was then treated with $Na_2S_2O_3$ (0.35 g, 2.26 mmol) and stirred for 30 min. The mixture was filtered and the solvent removed *in vacuo*. The crude product was purified by chromatography using 20% hexane/ether giving 9 mg (49%) of **61** and 9 mg (42%) of (Z)-diene **67**: ^1H NMR δ 7.33 (m, 5 H), 6.83 (ddd, J = 16.6, 10.7, 10.7 Hz, 1 H), 6.34 (d, J = 10.7 Hz, 1 H), 5.40 (d, J = 16.6 Hz, 1 H), 5.33 (d, J = 10.7 Hz, 1 H), 4.68 (d, A of AB, J = 11.8 Hz, 1 H), 4.65 (d, B of AB, J = 11.8 Hz, 1 H), 3.85 (dd, J = 11.5, 3.0 Hz, 1 H), 3.74 (ddd, J = 8.9, 2.2, 0.8 Hz, 1 H), 3.63 (dd, J = 11.5 Hz, 5.4 Hz, 1 H), 3.21 (ddd, J = 5.4, 3.0, 2.2 Hz, 1 H). Data for **61**: R_f = 0.34 (80% ether/hexane); $[\alpha]^{23}_D$ -3.3° (c = 0.18, $CHCl_3$); ^1H NMR δ 7.33 (m, 5 H), 5.96 (dddd, J = 17.2, 10.5, 5.4, 1.3 Hz, 1 H), 5.42 (dd, J = 17.2, 1.7 Hz, 1 H), 5.31 (dd, J = 10.5, 1.7 Hz, 1 H), 4.58 (d, A of AB, J = 11.6 Hz, 1 H), 4.55 (d, J = B of AB, J = 11.6, 1 H), 4.32 (m, 1 H), 3.77 (dd, J = 11.7, 1.2 Hz, 1 H), 3.65 (m, 1 H), 3.48 (dd, J = 11.7, 6.0 Hz, 1 H), 3.18 (m, 1 H), 2.20 (s, 2 H); IR (CCl_4) 3560-3140 (br), 2930, 2860, 1650, 1450, 1380, 1360, 1110, 1100, 990, 925, 905, 690 cm^{-1}; mass spectrum, calcd for $C_{14}H_{17}O_4$ (M^+ - 1) 149.1126, found 149.1141.

(2R,3R,4R)-4,5-O-Isopropylidene-pent-1,2,3-triol (68). A -78°C solution of diol **53** (37 mg, 0.2 mmol) in dry MeOH (1 mL) and CH_2Cl_2 (1 mL) was treated with a stream of O_3 in O_2 until **53** was consumed (TLC analysis). The solution was purged with N_2 to remove O_3 before Me_2S (1 mL) was added. The solution was stirred at 23°C overnight. The volatile components were removed *in vacuo* and the crude aldehyde was treated with $NaBH_4$ (74 mg, 0.2 mmol) in MeOH (1 mL) at 0°C for 10 min. The known triol **68**[27] was purified by chromatography (1 x 0.5 mm preparative TLC plate, 100% MeOH): R_f = 0.30 in 100% MeOH; $[\alpha]^{23}_D$ -0.4° (c = 0.43, EtOH); lit.[27] $[\alpha]^{25}_D$ -0.42° (c = 1.92, EtOH); ^1H NMR δ 4.34 (dt, J = 6.8, 3.9 Hz, 1 H), 4.09 (dd, J = 8.8, 6.8 Hz, 1 H), 3.92 (dd, J = 8.8, 7.3 Hz, 1 H), 3.81 (m, 2 H), 3.66 (m, 1 H), 3.57 (m, 1 H), 2.92 (s, 1 H), 2.68 (d, J = 6.3 Hz, 1 H), 2.55 (s, 1 H), 1.45 (s, 3 H), 1.39 (s, 3 H); mass spectrum, calcd for $C_8H_{15}O_3$ (M^+ - OH) 175.0971, found 175.0978.

(2S,3S,4R)-4,5-O-Isopropylidenepent-1,2,3-triol (69) was prepared using the procedure for **68**. Data for **69**: R_f = 0.30 (100% MeOH); $[\alpha]^{23}_D$ +14.0° (c = 2.6, EtOH); lit.[27] $[\alpha]^{23}_D$ +13.7° (c = 2.35, EtOH); ^1H NMR δ 4.15 (m, 2 H), 3.99 (m, 1 H), 3.81 (m, 1 H), 3.77 (m, 2 H), 3.70 (m, 2 H), 3.40 (s, 1 H), 3.35 (s, 1 H), 1.43 (s, 3 H), 1.36 (s, 3 H); mass spectrum, calcd for $C_8H_{15}O_5$ (M^+ - 1) 191.0921, found 191.1039.

(3R,4S,5R)-1,3,4,5-tetraacetoxyhexane (70). A solution of diol **57** (65 mg, 0.29 mmol) in dry DMF (1 mL) was treated with imidazole (87 mg, 1.9 mmol) and TBDMS-Cl (96 mg, 0.64 mmol) overnight at 23°C. The solution was diluted with ether and washed with aqueous $NaHCO_3$. The aqueous layer was extracted with ether (3 x 30 mL).

The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude material was treated with BH_3-THF (0.11 mL, 1 M) at ambient temperature for 1 h. The mixture was then cooled to 0°C and treated with H_2O (0.3 mL), 30% H_2O_2 (0.30 mL), and 1 mL of 2 N NaOH. The reaction was added to a separatory funnel, diluted with 5 mL of H_2O and extracted with ether (3 x 30 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The product was chromatographed using 20% ether/hexane and hydrogenated over 10% Pd-C at 23°C for 24 h. The reaction was filtered through a pad of Celite and concentrated *in vacuo*. The crude product was purified by chromatography with use of 25% ether/hexane to provide 12 mg of the intermediate diol bis-TBDMS ether [^{1}H NMR δ 3.94 (m, 1 H), 3.75 (m, 3 H), 3.51 (dd, J = 5.1, 2.2 Hz, 1 H), 1.80 (m, 1 H), 1.79 (d, J = 6.2 Hz, 3 H), 0.93 (s, 9 H), 0.91 (s, 9 H), 0.12 (s, 6 H), 0.11 (s, 6 H)]. This intermediated was treated with a 1 M solution of nBu_4NF (0.16 mL, 0.16 mmol) in THF at 23°C for 1 h. The resulting solution was concentrated *in vacuo*, and treated with Ac_2O (0.024 mL, 0.25 mmol), pyridine (0.25 mL), and DMAP (5.0 mg) at 23°C. After being stirred for 20 min, the resulting solution was concentrated *in vacuo*, and chromatographed (10 x 150 mm column) with use of 45% ether/hexane to provide 10 mg of tetraacetate **70**. A reference sample of **70** was prepared from acetonide **71**[28] as described in text: R_f = 0.18 (45% ether/hexane); $[\alpha]^{23}_D$ +39.4° (c = 0.53, $CHCl_3$); ^{1}H NMR δ 5.34 (m, 1 H), 5.21 (m, 2 H), 4.01 (m, 2 H), 1.75-1.65 (m, 2 H), 1.75 (s, 3 H), 1.72 (s, 3 H), 1.66 (s, 3 H), 1.65 (s, 3 H), 1.02 (d, J = 6.2 Hz, 3 H); IR (CCl_4) 2900, 2960, 2930, 1745, 1430, 1370, 1225, 1050, 950 cm^{-1}; mass spectrum, calcd for $C_{12}H_{19}O_6$ (M^+ - $C_2H_3O_2$) 259.1181, found 259.1135. *Anal.* Calcd for $C_{14}H_{22}O_8$: C, 52.82; H, 6.96. Found: C, 53.10; H, 6.92.

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