Articles

Synthesis of Chiral α,δ-Dioxygenated Allylic Stannanes as Reagents for Carbohydrate Synthesis and Homologation

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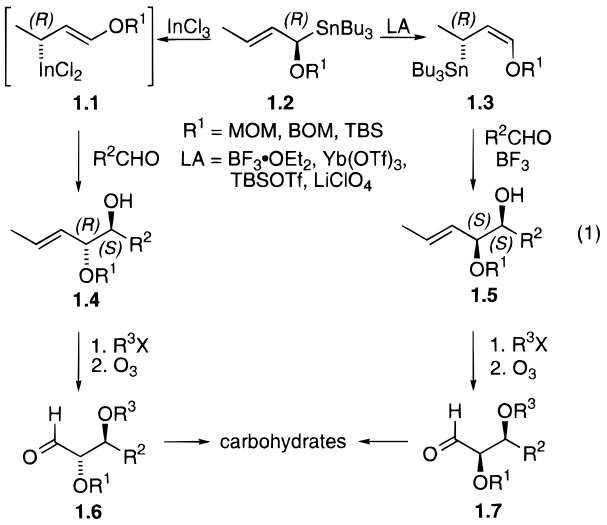
The δ-oxygenated allylic stannanes **4.4** and **4.5**, prepared through addition of Bu_3SnLi to γ-OTBS crotonaldehyde **4.3c** followed by etherification of the adduct with TBS-Cl or MOM-Cl, undergo transmetalation with $InCl_3$ and *in situ* addition to aldehydes leading to mainly *anti* adducts **5.1** or **5.2**, accompanied by varying amounts of *syn* diastereomers. Selectivities of >95:5 can be realized with the MOM reagent **4.5** and ynals **4.3d** and **4.3e** or cyclohexanecarboxaldehyde **4.3a**. With enals **4.3b** and **4.3c**, 80:20 mixtures of *anti* and *syn* adducts are formed. The *S* enantiomer **10.1** of stannane **4.5** has also been prepared as a reagent for carbohydrate synthesis. Accordingly, addition to α-ODPS acetaldehyde **10.2** in the presence of $InCl_3$ leads to the adduct **10.3** as an inseparable 90:10 mixture of *anti* and *syn* diastereomers. Dihydroxylation of the OTBS derivative **10.4** affords the potential altrose precursor **10.5** in 81% yield.

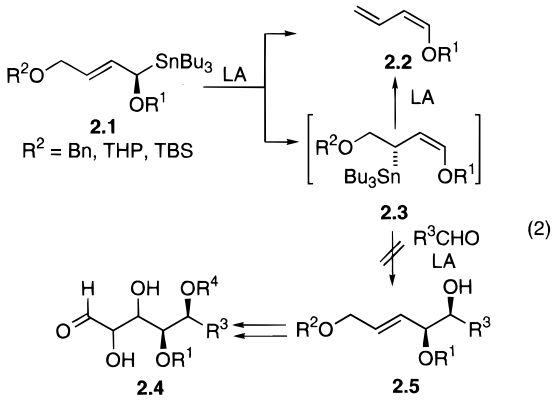
In recent years we have devised methodology for the synthesis of carbohydrates by a homologation strategy that employs chiral γ-oxygenated allylic stannanes and more recently, indium reagents (eq 1).[1−3]



(1)

The approach lends itself to the preparation of any given isomer of a differentially protected carbohydrate target by relatively modest changes in Lewis acid, stannane chirality, and aldehyde substrate. Our recent synthesis of precursors to the eight diastereomeric hexoses in both the D and L series illustrates the efficiency of the approach.[3] The use of a common precursor stannane **1.2** to access both *anti*- and *syn*-1,2-diol derivatives **1.4** and **1.5** is of particular interest.

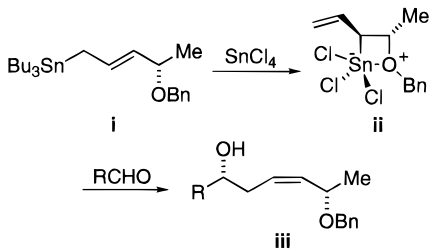
In related studies, we have been examining chiral α,δ-dioxygenated stannanes, such as **2.1**, for possible applications along lines similar to those of stannane **1.2**. Such reagents have the advantage that all carbons are utilized in the homologation process leading to the polyol derivative **2.4**. However, attempts to effect 1,3-isomerization of the α- to the γ-isomer **2.3** with BF_3•OEt_2 and other Lewis acids were unsuccessful owing to a facile elimination leading to 1,3-dienes **2.2** or decomposition of the stannane.[4]



(2)

We decided to explore the potential of transmetalation with the milder Lewis acid, $InCl_3$ as a possible route to

(4) Thomas has prepared β-oxygenated allylic trichlorostannanes (e.g., **ii**) *in situ* through treatment of δ-oxygenated allylic tributylstannanes **i** with $SnCl_4$. These intermediates were found to react with aldehydes through a chelated bicyclic transition state to afford monoprotected 1,5-diols **iii**. Evidently, 1,2-elimination (as in **2.3** → **2.2**) is less favorable in this case, possibly owing to chelation between the $SnCl_3$ and adjacent OR substituents as in **ii**. Our attempts at transmetalation of α-oxygenated allylic stannanes with $SnCl_4$ or $TiCl_4$ led to rapid decomposition, even at −78 °C.[1]

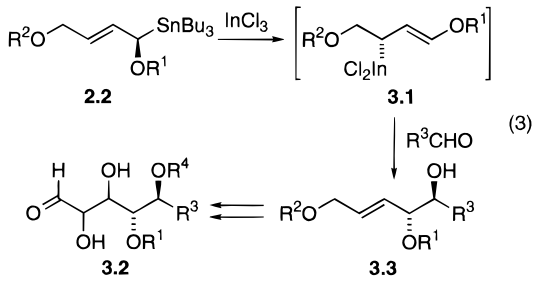


[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1996.

(1) Marshall, J. A. *Chem. Rev.* **1996**, *96*, 31.
(2) Marshall, J. A.; Hinkle, K. W. *J. Org. Chem.* **1995**, *60*, 1920.
(3) Marshall, J. A.; Hinkle, K. W. *J. Org. Chem.* **1996**, *61*, 105.

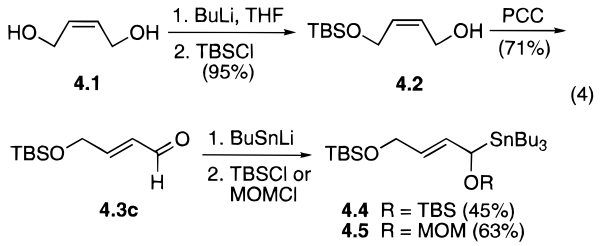
S0022-3263(96)01671-4 CCC: $12.00

a γ-indium intermediate such as **3.1**, which, by virtue of chelation, might be less inclined than the fugative tin analogue **2.3** to undergo β-elimination. The expected product of aldehyde homologation would be the *anti* adduct **3.3** (eq 3).



(3)

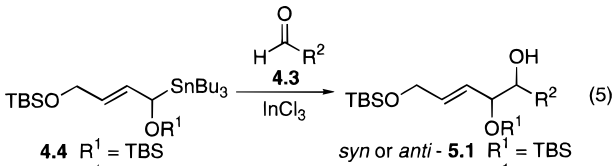
Two α,δ-dioxygenated allylic stannanes, **4.4** and **4.5**, were prepared for these studies starting from *(Z)*-2-butene-1,4-diol (**4.1**), as outlined in eq 4. Monosilylation



(4)

was easily effected,[5] and the resulting intermediate allylic alcohol was oxidized with attendant $Z \rightarrow E$ isomerization by PCC.[6] Our exploratory studies were conducted with racemic stannanes secured through addition of Bu_3SnLi to enal **4.3c**, followed by addition of MOM-Cl or TBS-Cl, respectively, to afford the α-oxygenated allylic stannane product **4.4** or **4.5**.[1]

Transmetalation of these stannane reagents with $InCl_3$ was carried out at −78 to 0 °C in the presence of various representative aldehydes. The results, summarized in eq 5, revealed several interesting trends. Reaction of the

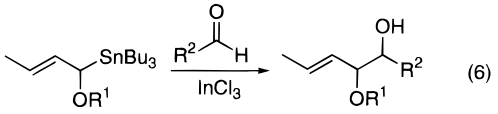


(5)

stannane	4.3	R^2	yield, %	5.1/5.2	*anti:syn*
4.4	**4.3a**	*c*-C_6H_{11}	99	**5.1a**	99:1
4.5	**4.3a**	*c*-C_6H_{11}	99	**5.2a**	99:1
4.4	**4.3b**	*(E)*-$CH_3CH{=}CH$	64	**5.1b**	67:33
4.5	**4.3b**	*(E)*-$CH_3CH{=}CH$	58	**5.2b**	80:20
4.4	**4.3c**	*(E)*-$TBSOCH_2CH{=}CH$	81	**5.1c**	42:58
4.5	**4.3c**	*(E)*-$TBSOCH_2CH{=}CH$	81	**5.2c**	80:20
4.4	**4.3d**	*n*-$C_6H_{13}C{\equiv}C$	87	**5.1d**	93:7
4.5	**4.3d**	*n*-$C_6H_{13}C{\equiv}C$	65	**5.2d**	97:3
4.4	**4.3e**	$TBSOCH_2C{\equiv}C$	74	**5.1e**	80:20
4.5	**4.3e**	$TBSOCH_2C{\equiv}C$	92	**5.2e**	96:4

branched aldehyde, cyclohexanecarbaldehyde (**4.3a**), with the bis(silyloxy) reagent **4.4** proceeded in near-quantitative yield with excellent *anti*:*syn* diastereoselectivity. Additions to crotonaldehyde (**4.3b**) and the γ-silyloxycrotonaldehyde (**4.3c)** were distinctly less selective. The latter actually showed a slight preference for the *syn* adduct, *syn*-**5.1c**. The α-OMOM reagent **4.5**, on the other hand, favored the *anti* adduct, *anti*-**5.2c**, by 80:20 with aldehyde **4.3c**. A higher *anti* diastereoselectivity of the MOM vs the TBS reagent was also noted with the alkynals **4.3d** and **4.3e**. Surprisingly, the overall *anti* preference was greater in additions to the ynals than with the related enals. In general, the α-OMOM reagent **4.5** proved superior to the α-OTBS analogue **4.4** for the production of *anti* adducts. At this point it appeared that the decreased *anti:syn* ratios were a function of both the δ-OTBS and the α-OR^1 substituent of stannanes **4.4** and **4.5**. Interestingly the γ-subsituent of the enal or ynal also influenced the selectivity (compare **5.1b** with **5.1c** and **5.1d** with **5.1e**).

To evaluate the influence of the α-OR^1 substituent, we carried out additions of the indium reagent derived from α-OTBS crotylstannane **6.1** and the α-OMOM analogue **6.2**[2] to representative aldehydes. The results of these studies are presented in eq 6. In all cases, the reagent



(6)

R^2	**6.3** yield, %	**6.3** *anti:syn*	**6.4** yield, %	**6.4** *anti:syn*	series
n-C_6H_{13}	91	75:25	99	95:5[a]	**a**
c-C_6H_{11}	98	93:7	95	98:2[a]	**b**
(E)-$CH_3CH{=}CH$	98	80:20	85	94:6	**c**
(E)-$TBSOCH_2CH{=}CH$	82	70:30	79	91:9	**d**
n-$C_6H_{13}C{\equiv}C$	82	77:23	85	90:10[a]	**e**

[a] ref 3

derived from the α-MOM stannane **6.2** gave higher *anti:syn* product ratios compared to the TBS counterpart **6.1** with a given aldehyde. The differences are particularly striking for heptanal (95:5 vs 75:25), *(E)*-2-butenal (94:6 vs 80:20), the δ-OTBS butenal (91:9 vs 70:30), and 2-nonynal (90:10 vs 77:23). By comparison, the γ-OTBS allylic stannane **1.3** (R^1 = TBS)shows higher diastereoselectivity than the OMOM (R^1 = MOM) reagent in BF_3-promoted additions, where the favored products are *syn*-**6.3** and -**6.4**.[7] Furthermore, enals give the highest *syn:anti* product ratios in those additions.

The relative stereochemistry of the major adducts **5.1** and **5.2** may be assigned by analogy with the findings summarized in eq 6 for the crotyl analogues. Additional support for the cyclohexyl adduct, *anti*-**5.1a**, was secured as shown in eq 7. Thus, the bis(TBS) ether **7.1**, derived from the known adduct *syn*-**6.3b** of cyclohexanecarbaldehyde and stannane **8.1** (BF_3),[7] was converted to aldehyde *syn*-**7.2** by ozonolysis. Analogous treatment of the bis(TBS) ether **7.3**, derived from the adduct *anti*-**5.1a**, afforded the diastereomeric aldehyde *anti*-**7.2**

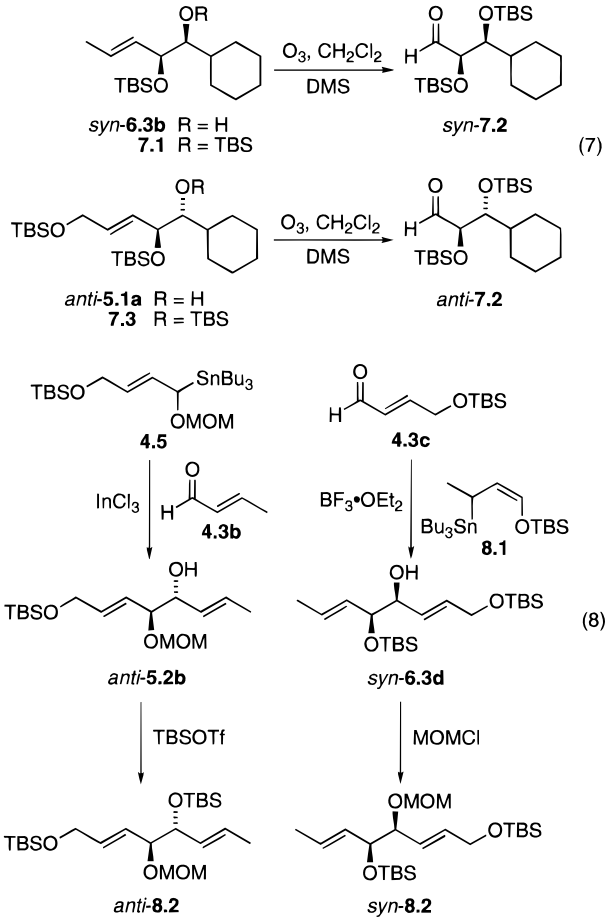
The stereochemistry of adduct *anti*-**5.2b** was confirmed through comparison of the derived TBS ether, *anti*-**8.2**, with the analogous ether, *syn*-**8.2**, prepared from *syn*-**6.3d**, as outlined in eq 8.[7]

Adduct *anti*-**5.1d** was converted, via the bis TBS ether **9.1**, to the aldehyde *anti*-**9.3** through dihydroxylation

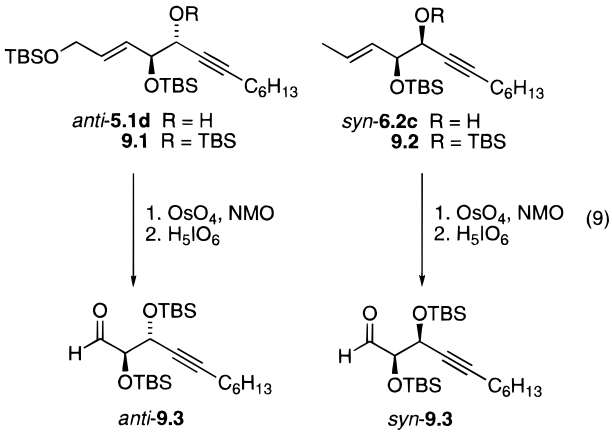
(5) McDougal, P. M.; Rico, J. G.; Oh, Y. I.; Condon, B. D. *J. Org. Chem.* **1986**, *51*, 3388.

(6) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647.

(7) Marshall, J. A.; Welmaker, G. S. *J. Org. Chem.* **1992**, *57*, 7158.



with OsO_4 and oxidative cleavage with H_5IO_6. The diastereomeric aldehyde, *syn*-**9.3**, was secured in a like manner from the adduct, *syn*-**6.2c**, prepared from stannane **8.1** and 2-nonynal with BF_3•OEt_2 (eq 9).[8]



Additional support for the *syn*/*anti* assignments of the foregoing adducts came from the relative chemical shifts of the OH proton as shown in Table 1. In all cases, this proton was deshielded in the *syn* isomer in comparison to the *anti* as a consequence of more effective internal hydrogen bonding. A similar trend was previously noted by Landmann and Hoffmann.[9]

The differing selectivities exhibited by the MOM and TBS indium reagents may result from interactions

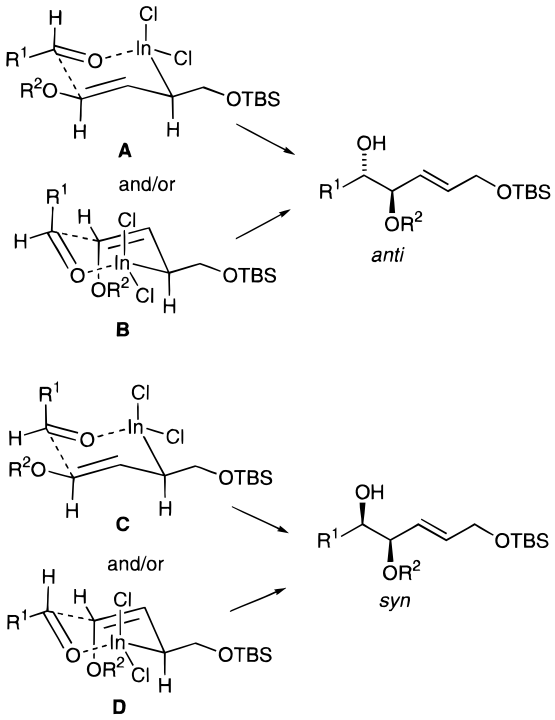
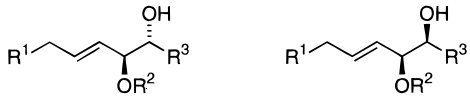


Figure 1. Chairlike transition states leading to *syn* and *anti*-1,2-diol derivatives.

Table 1. Chemical Shift Comparisons for the OH Proton of Adducts



				δ_{OH}	
R^1	R^2	R^3	adduct	*syn*	*anti*
OTBS	TBS	(*E*)-MeCH=CH	**5.1b**	2.55	2.22
OTBS	TBS	(*E*)-$TBSOCH_2CH$=CH	**5.1c**	2.56	2.21
OTBS	TBS	*n*-$C_6H_{13}C$≡C	**5.1d**	2.55	2.29
OTBS	TBS	$TBSOCH_2C$≡C	**5.1e**	2.37	2.13
OTBS	MOM	*c*-C_6H_{11}	**5.2a**	2.37	2.09
OTBS	MOM	(*E*)-MeCH=CH	**5.2b**	2.67	2.40
OTBS	MOM	(*E*)-$TBSOCH_2CH$=CH	**5.2c**	2.67	2.42
H	TBS	*n*-C_6H_{13}	**6.3a**	2.39	2.35
H	TBS	*c*-C_6H_{11}	**6.3b**	2.70	2.57
H	TBS	*n*-$C_6H_{13}C$≡C	**6.3e**	2.55	2.33
H	MOM	(*E*)-MeCH=CH	**6.4c**	2.53	2.23
H	MOM	(*E*)-$TBSOCH_2CH$=CH	**6.4d**	2.58	2.29

between the enol ether substituent R^2 and the aldehyde substituent R^1 in the presumed chairlike transition state **A** leading to the *anti* product (Figure 1). The effect would be greater for OTBS than for OMOM. In transition state **C**, leading to the *syn* adducts, this interaction is diminished. However, in **C** larger R^1 groups such as cyclohexyl may experience unfavorable steric opposition by ligands on the indium. The relative importance of these opposing effects will vary with the extent of bonding in the transition state. The interactions depicted in **A** would be less important in an early transition state as might be expected for a more reactive aldehyde.

An alternative rationale for the enhanced *anti*:*syn* product ratios from alkynals and cyclohexanecarboxaldehyde as opposed to the enals, depicted in eq 5, is also based on relative reactivities. It is known that allylindium species derived from allylic bromides and indium

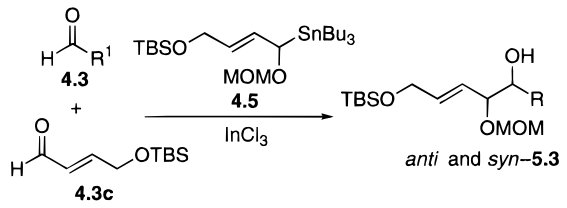
(8) Marshall, J. A.; Jablonowski, J. A.; Elliott, L. M. *J. Org. Chem.* **1995**, *60*, 2662.
(9) Landmann, B.; Hoffman, R. W. *Chem. Ber.* **1987**, *120*, 331.

metal undergo facile *E*/*Z* isomerization.[10] Assuming *E*/*Z* interconversion also takes place with the oxygenated analogues,[11] the relative transition state energies for the additions of the *E* vs *Z* (**B** vs **D** in Figure 1) reagents may differ for the various aldehydes, with **B** being significantly lower for alkynal and cyclohexyl aldehydes and less so with the alkenyl aldehydes. In actuality, both pathways may be operative with the *anti* adducts being formed via **A** and the *syn* via **D**.[12]

To estimate the relative reactivities of representative aldehydes with the α-OMOM, δ-OTBS allylic stannane **4.5** in the $InCl_3$-promoted additions, we carried out competition experiments. Accordingly, the two competing aldehydes, the allylic stannane **4.5**, and $InCl_3$ were mixed in the ratio 1:1:1:1 under the standard conditions. After complete consumption of stannane, the reaction was quenched and the products were isolated, along with any unreacted aldehyde(s). The results, summarized in Table 2, clearly show that **4.3a** and the acetylenic aldehyde **4.3e** are more reactive that the conjugated aldehyde **4.3c**. These findings are qualitatively consistent with the above transition state analysis.

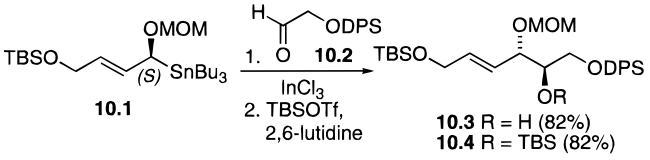
The foregoing experiments serve to establish the feasibility of utilizing α,δ-dioxygenated crotylstannanes for the synthesis of *anti* monoprotected 1,2-diol adducts from aldehydes. To complete this phase of our investigation, we elected to apply the methodology to a potential precursor of the rare hexose D-(+)-altrose (eq 10).[13] The *S* enantiomer **10.1** of the α-OMOM, δ-OTBS crotylstannane reagent of >95% ee was prepared by our standard procedure involving reduction of the acylstannane with *(R)*-BINAL-H followed by treatment of the resulting *S* alcohol with MOM-Cl and $(i\text{-Pr})_2NEt$.[14] Addition to α-ODPS acetaldehyde **10.2** afforded the adduct **10.3** as a 90:10 mixture of *anti* and *syn* diastereomers. The TBS derivative **10.4** was separated from the *syn* isomer and dihydroxylated with OsO_4-NMO[15] to afford diol **10.5**. This intermediate has the stereochemistry of D-(+)-altrose.

Table 2. Competition Experiments Between Aldehydes 4.3e vs 4.3c and 4.3a vs 4.3c for Stannane 4.5[a]

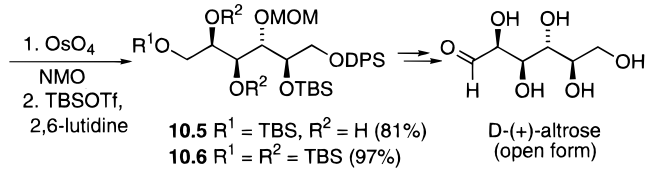


R^1	product(s)	ratio
c-C_6H_{11} (**4.3e**)	**5.3a/5.3c**	80:20
$TBSOCH_2C{\equiv}C$ (**4.3e**)	**5.3e/5.3c**	100:0

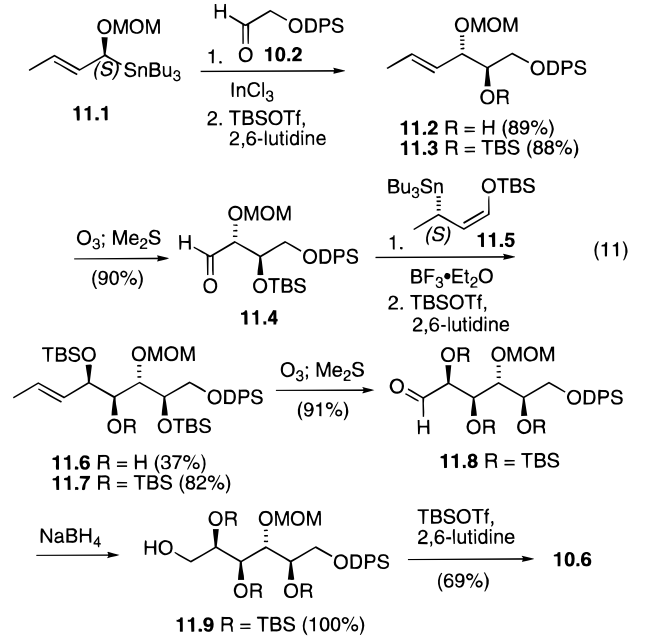
[a] Equimolar quantities of the stannane and each of the two aldehydes were subjected to the standard reaction conditions. The less reactive aldehyde was recovered.



(10)

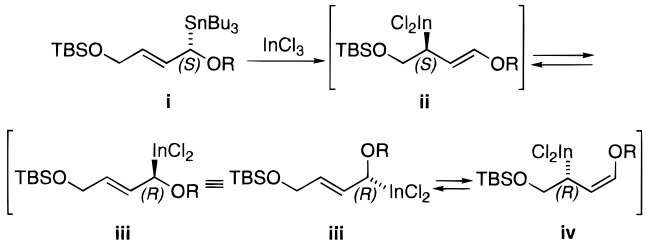


An independent synthesis of the TBS ether **10.6** derived from diol **10.5** was carried out as outlined in eq 11 with our established α- and γ-oxygenated crotylstannane reagents **11.1** and **11.5**.[1] Thus, $InCl_3$-mediated addition of the *(S)*-α-OMOM stannane **11.1** to aldehyde **10.2** afforded the *anti* adduct **11.2**. Protection as the TBS ether and ozonolysis yielded the aldehyde **11.4**, which was homologated with the *(S)*-γ-silyloxy allylic stannane **11.5** by the *syn*-selective BF_3 protocol.[1] This addition was performed several times, but in each case, the adduct **11.6** was formed in relatively low yield. The TBS derivative **11.7** was converted to aldehyde **11.8** by ozo-



(10) Isaac, M. B.; Chan, T.-H. *Tetrahedron Lett.* **1995**, *36*, 8957.

(11) It is assumed that the intial transmetalation (**i** → **ii**) takes place by an *anti* S_E2' process and the subsequent isomerization (**ii** → **iii**) occurs with *syn* stereochemistry. *Cf.*: Marshall, J. A.; Yu, R. H.; Perkins, J. F. *J. Org. Chem.* **1995**, *60*, 5550. The indium intermediates are most likely unsymmetrical Cl-bridged dimers but are depicted as monomers to simplify the analysis.



(12) A reviewer has suggested that *syn* adducts may arise via a noncyclic transition state in which $InCl_3$ is coordinated to the aldehyde carbonyl. Because of their increased basicity, enals would be more likely to follow this pathway. A similar explanation has been advanced to account for the formation of *anti* aldol adducts from the reaction of β-SPh enals and aromatic aldehydes with the Bu_2BOTf-derived boron enolate of a chiral *N*-propionyloxazolidinone: Danda, H.; Hansen, M. M.; Heathcock, C. H. *J. Org. Chem.* **1990**, *55*, 173. This point will be addressed in a future study with allylic indium intermediates in which *E*/*Z* isomerism is not an issue.

(13) This hexose is listed at $799.50/g in the 1996 Aldrich Catalog (Aldrich No. 86,226-6): *Aldrich Catalog Handbook of Fine Chemicals*; Aldrich Chemical Co.: Milwaukee, WI.

(14) Marshall, J. A.; Welmaker, G. S.; Gung, B. W. *J. Am. Chem. Soc.* **1991**, *113*, 647.

(15) VanRheenen, V.; Kelly, R. C.; Cha, D. Y. *Tetrahedron Lett.* **1976**, 1973.

nolysis, as before. Reduction and subsequent silylation yielded the protected hexitol **10.6** identical to the previously prepared sample according to comparison of ^{13}C and ^{1}H NMR spectra.

To complete our intended synthesis of D-altrose, we attempted to selectively cleave the primary OTBS ether (R^1) of intermediate **10.6**. Unfortunately, we were unable to effect this conversion under a variety of conditions (TBAF; HOAc, THF, H_2O; PPTS; HF; MeCN; to name a few). In each case a mixture of polyols was produced. Thus it would appear that a successful realization of this goal will require a change in protecting group strategy. Efforts along these lines and additional applications of this methodology to rare carbohydrates will be the subject of future studies.

Experimental Section[16]

***(Z)*-4-[(*tert*-Butyldimethylsilyl)oxy]-2-buten-1-ol (4.2).** A solution of 20.4 g (239 mmol) of *cis*-2-butene-1,4-diol in 400 mL of dry THF was stirred at 0 °C as 96.0 mL (240 mmol) of 2.5 M *n*-BuLi in hexanes was slowly added.[5] The mixture was stirred for 1 h, and 36.1 g (240 mmol) of TBS-Cl was added. The reaction mixture was allowed to slowly warm to room temperature over 3 h, quenched with saturated aqueous NH_4Cl, and extracted with Et_2O. The organic layer was dried over $MgSO_4$, and the solvent was removed by distillation under reduced pressure. Bulb to bulb distillation of the crude product (85 °C 1.0 mmHg)) afforded 46.1 g (95%) of alcohol **4.2**: ^{1}H NMR δ 5.68 (m, 2H), 4.24 (d, J = 4.9 Hz, 2H), 4.18 (t, J = 5.6 Hz, 2H), 1.99 (t, J = 5.9 Hz, 1H), 0.89 (s, 9H), 0.07 (s, 6H).

***(E)*-4-[(*tert*-Butyldimethylsilyl)oxy]-2-butenal (4.3c).** A solution of 18.6 g (91.9 mmol) of alcohol **4.2** in 200 mL of dry CH_2Cl_2 was stirred at 0 °C as 19.2 g of powdered 4 Å sieves followed by 20.3 g (94.0 mmol) of PCC was added.[6] The reaction mixture was allowed to slowly warm to room temperature. After 16 h, the solvent was removed by distillation under reduced pressure and the resulting brown solid was triturated with ether and filtered through a plug of silica. The filtrate was concentrated under reduced pressure. Bulb to bulb distillation of the crude product (1.0 mm, 65 °C) afforded 13.2 g (71%) of aldehyde **4.3c**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.58 (d, J = 8.1 Hz, 1H), 6.87 (dt, J = 15.4, 3.3 Hz, 1H), 6.38 (ddt, J = 15.4, 8.1, 2.2 Hz, 1H), 4.43 (dd, J = 3.2, 2.2 Hz, 2H), 0.90 (s, 9H), 0.07 (s, 6H).

***(E)*-1,4-[Bis(*tert*-butyldimethylsilyl)oxy]-1-tri-*n*-butylstannyl-2-butene (4.4).** A solution of 0.45 mL (3.2 mmol) of diisopropylamine in 12 mL of dry THF was stirred at 0 °C as 1.2 mL (3.0 mmol) of 2.5 M *n*-BuLi in hexanes was added. The solution was stirred for 15 min and then 0.73 mL (2.7 mmol) of Bu_3SnH was added. The resulting solution was stirred for 15 min and then cooled to −78 °C. To this mixture was added 0.50 g (2.5 mmol) of **4.3c**. The reaction mixture was stirred for 45 min, quenched with saturated aqueous NH_4Cl, and extracted with Et_2O. The organic layer was dried over $MgSO_4$, and the solvent was removed by distillation under reduced pressure. The crude hydroxy stannane was dissolved in 12 mL of dry CH_2Cl_2. The solution was stirred at rt and 0.20 g (3.0 mmol) of imidazole followed by 0.38 g (2.5 mmol) of chlorotrimethylsilane was added. After 2 h, the reaction was quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2. The organic extract was dried over $MgSO_4$, and the solvent was removed by distillation under reduced pressure. Chromatography of the crude product on a silica gel column with 1:49 EtOAc/hexanes as eluant afforded 0.68 g (45%) of silyl ether **4.4**: ^{1}H NMR δ 5.85 (dd, J = 15.0, 4.8 Hz, 1H), 5.47 (ddt, J = 15.0, 5.5, 1.8 Hz, 1H), 4.68 (m, 1H), 4.16 (m, 1H), 1.59−1.40 (m, 2H), 1.35−1.23 (m, 2H), 0.92−0.85 (m, 11H), 0.06 (s, 6H), 0.02 (s, 3H), 0.01 (s, 3H). Anal. Calcd for $C_{28}H_{62}O_2Si_2Sn$: C, 55.53; H, 10.32. Found: C, 55.80; H, 10.41.

***(E)*-4-[(*tert*-Butyldimethylsilyl)oxy]-1-(methoxymethoxy)-1-(tri-*n*-butylstannyl)-2-butene (4.5).** The procedure described for **4.4** was employed with 3.0 mL (17 mmol) of diisopropylamine in 80 mL of dry THF, 7.9 mL (20 mmol) of 2.5 M *n*-BuLi in hexanes, 4.9 mL (18 mmol) of Bu_3SnH, and 3.3 g (17 mmol) of **4.3c**. The crude hydroxy stannane was dissolved in 80 mL of dry CH_2Cl_2. The solution was stirred at 0 °C, and 1.4 mL (18 mmol) of *i*-Pr_2NEt followed by 3.2 mL (18 mmol) of chloromethyl methyl ether was added. The reaction was allowed to warm to rt and quenched after 16 h with saturated aqueous NH_4Cl. The mixture was extracted with CH_2Cl_2. The organic extract was dried over $MgSO_4$, and the solvent was removed by distillation under reduced pressure. Chromatography of the crude product on a silica gel column with 1:9 EtOAc/hexanes as eluant afforded 5.0 g (56%) of MOM ether **4.5**: ^{1}H NMR δ 5.80 (dd, J = 15.4, 6.7 Hz, 1H), 5.50 (ddt, J = 15.4, 5.0, 1.5 Hz, 1H), 4.66, 4,52 (ABq, J = 6.2 Hz, 2H), 4.63 (m, 1H), 4.17 (d, J = 5.0 Hz, 1H), 3.34 (s, 3H), 1.59-1.44 (m, 2H), 1.38−1.23 (m, 2H), 0.96−0.86 (m, 14H), 0.06 (s, 6H). Anal. Calcd for $C_{24}H_{52}O_3SiSn$: C, 53.84; H, 9.79. Found: C, 54.00; H, 9.72.

***(E,rel*-1*R*,2*S*)-2,5-[Bis(*tert*-butyldimethylsilyl)oxy]-1-cyclohexyl-3-penten-1-ol (*anti*-5.1a).** A solution of 0.07 g (0.33 mmol) of indium(III) chloride in 9.0 mL of EtOAc was stirred at rt as 0.04 mL (0.30 mmol) of **4.3a** was added. The solution was then cooled to −78 °C, and a solution of 0.18 g (0.30 mmol) of allylstannane **4.4** in 0.5 mL of EtOAc was added. The reaction mixture was allowed to slowly warm to rt, quenched with saturated aqueous $NaHCO_3$, and extracted with Et_2O. The organic extract was dried over $MgSO_4$, and the solvent was removed by distillation under reduced pressure. Chromatography of the crude product on a silica gel column with 1:9 EtOAc/hexanes as eluant afforded 0.07 g (99%) of *anti*-**5.1a**: ^{1}H NMR ($CDCl_3$, 360 MHz) δ 5.76 (dd, J = 15.4, 3.5 Hz, 1H), 5.71 (dd, J = 15.4, 5.3 Hz, 1H), 4.19 (m, 3H), 3.28 (ddd, J = 7.9, 4.0, 2.2 Hz, 1H), 2.36 (d, J = 2.2 Hz, 1H), 1.72−0.94 (m, 14H), 0.90 (s, 9H), 0.89 (s, 9H), 0.06 (s, 9H), 0.04 (s, 3H). Anal. Calcd for $C_{23}H_{48}O_3Si_2$: C, 64.42; H, 11.28. Found: C, 64.31; H, 11.31.

***(E,rel*-1*R*,2*S*)-5-[(*tert*-Butyldimethylsilyl)oxy]-1-cyclohexyl-2-(methoxymethoxy)-3-penten-1-ol (*anti*-5.2a).** The procedure described for *anti*-**5.1a** was employed with 0.03 g (0.14 mmol) of indium(III) chloride in 3.0 mL of EtOAc, 0.02 mL (0.13 mmol) of **4.3a** and 0.08 g (0.14 mmol) of allylstannane **4.5**. Chromatography of the crude product on a silica gel column with 1:9 EtOAc/hexanes as eluant afforded 0.02 g (99%) of *anti*-**5.2a**: ^{1}H NMR δ 5.84 (dt, J = 15.8, 4.6 Hz, 1H), 5.68 (dd, J = 15.8, 8.1 Hz, 1H), 4.72, 4.55 (ABq, J = 6.6 Hz, 2H), 4.22 (d, J = 4.6 Hz, 2H), 4.14 (dd, J = 8.1, 4.2 Hz, 1H), 3.45 (ddd, J = 7.3, 4.2, 3.1 Hz, 1H), 3.36 (s, 3H), 2.09 (d, J = 3.1 Hz, 1H), 1.81−0.95 (m, 11H), 0.91 (s, 9H), 0.07 (s, 6H). Anal. Calcd for $C_{19}H_{38}O_4Si$: C, 63.64; H, 10.68. Found: C, 63.75; H, 10.72.

***(E,rel*-4*S*,5*R*)-4-[(*tert*-Butyldimethylsilyl)oxy]-2-undecen-5-ol (6.3a).** The procedure described for *anti*-**5.1a** was followed with 0.11 g (0.51 mmol) of indium(III) chloride in 4.0 mL of EtOAc, 0.07 mL (0.47 mmol) of heptanal, and a solution of 0.29 g (0.61 mmol) of crotylstannane **6.1** in 0.5 mL of EtOAc. Chromatography of the crude product on a silica gel column with 1:9 EtOAc/hexanes as eluant afforded 0.13 g (91%) of adduct **6.3a** as a 75:25 mixture of *anti* and *syn* diastereomers: ^{1}H NMR *anti* δ 5.67 (dq, J = 15.4, 6.2 Hz, 1H), 5.50 (dd, J = 15.4, 7.3 Hz, 1H), 4.00 (dd, J = 7.3, 4.0 Hz, 1H), 3.56 (m, 1H), 2.57 (d, J = 3.8 Hz, 1H), 1.76 (d, J = 6.2 Hz, 3H), 1.52−1.32 (m, 13H), 0.94 (s, 9H), 0.10 (s, 3H), 0.08 (s, 3H).

***(E,E,4R,5S)*-5-(Methoxymethoxy)-2,6-octadien-4-ol (6.4c).** The procedure described for *anti*-**5.1a** was employed with 0.15 g (0.66 mmol) of indium(III) chloride in 9.0 mL of EtOAc, 0.05 mL (0.60 mmol) of **4.3b**, and 0.32 g (0.79 mmol) of allylstannane **6.2**. Chromatography of the crude product on a silica gel column with 1:9 EtOAc/hexanes as eluant afforded 0.10 g (85%) of adduct **6.4c** as an 94:6 mixture of *anti* and *syn* diastereomers: $[\alpha]^{23}_D$ 117.4 (*c* 1.0, CH_2Cl_2); ^{1}H NMR *anti* δ 5.66 (m, 2H), 5.40 (dd, J = 15.4, 7.0 Hz, 1H), 5.30 (dd, J = 15.4,

(16) For typical experimental protocols, see: Marshall, J. A.; Wang, X-j. *J. Org. Chem.* **1991**, *56*, 960. Unless otherwise stated, ^{1}H and ^{13}C NMR spectra were determined at 300 and 75 MHz, respectively, as dilute solutions in $CDCl_3$.

8.1 Hz, 1H), 4.63, 4.48 (ABq, J = 6.6 Hz, 2H), 3.99 (m, 1H), 3.88 (dd, J = 8.1, 4.0 Hz, 1H), 3.28 (s, 3H), 2.23 (br, 1H), 1.65 (d, J = 6.6, Hz, 3H), 1.63 (d, J = 6.6 Hz, 3H). Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 64.29; H, 9.69.

(*E*,*rel*-1*S*,2*R*)-1,2-[Bis(*tert*-butyldimethylsilyl)oxy]-1-cyclohexyl-3-propene (7.1). A solution of 0.27 g (0.92 mmol) of alcohol *syn*-**6.3b** in 10 mL of dry CH_2Cl_2 was stirred at 0 °C as 0.16 mL (1.4 mmol) of 2,6-lutidine followed by 0.25 mL of *tert*-butyldimethysilyl trifluoromethanesulfonate was added. After 40 min, the reaction was quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2. The organic extract was dried over $MgSO_4$, and the solvent was removed by distillation under reduced pressure. Chromatography of the crude product on a silica gel column with hexanes as eluant afforded 0.36 g (95%) of TBS ether **7.1**: ^{1}H NMR δ 5.58 (m, 2H), 4.09 (m, 1H), 3.28 (m, 1H), 1.81−0.94 (m, 14H), 0.90 (s, 9H), 0.89 (s, 9H), 0.05 (s, 6H), 0.03 (s, 3H), 0.01 (s, 3H).

(*rel*-2*R*,3*S*)-2,3-[Bis(*tert*-butyldimethylsilyl)oxy]-3-cyclohexylpropanal (*syn*-7.2). A solution of 0.15 g (0.37 mmol) of unsaturated diether **7.1** in 8.0 mL of dry CH_2Cl_2 was stirred at −78 °C as ozone was bubbled through the solution. After 4 min the solution acquired the blue characteristic of ozone, and 0.10 mL of dimethyl sulfide was added. The solution was allowed to warm to rt and stirred for 40 min. The solvent was removed by distillation under reduced pressure. Chromatography of the crude product on a silica gel column with 1:9 EtOAc/hexanes as eluant afforded 0.13 g (86%) of aldehyde *syn*-**7.2**: ^{1}H NMR δ 9.83 (s, 1H), 4.07 (d, J = 5.0 Hz, 1H), 3.67 (dd (apparent t), J = 5.0 Hz, 1H), 1.73−1.62 (m, 6H), 1.23−0.88 (m, 5H), 0.92 (s, 9H), 0.91 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H), 0.04 (s, 3H). Anal. Calcd for $C_{21}H_{44}O_3Si_2$: C, 62.94; H, 11.07. Found: C, 61.62; H, 11.00.

(*rel*-2*R*,3*R*)-2,3-[Bis(*tert*-butyldimethylsilyl)oxy]propanal (*anti*-7.2). The ozonolysis procedure described for aldehyde *syn*-**7.2** was employed with 0.11 g (0.20 mmol) of unsaturated diether **7.3** in 8.0 mL of dry CH_2Cl_2. Chromatography of the crude product on a silica gel column with 1:9 EtOAc/hexanes as eluant afforded 0.07 g (84%) of aldehyde *anti*-**7.2**: ^{1}H NMR δ 9.60 (d, J = 1.5 Hz, 1H), 4.03 (dd, J = 2.7, 1.5 Hz, 1H), 3.62 (dd, J = 6.9, 2.7 Hz, 1H), 1.89−1.54 (m, 6H), 1.26−1.08 (m, 5H), 0.92 (s, 9H), 0.88 (s, 9H), 0.08 (br, 9H), 0.06 (s, 3H).

(*E*,*rel*-1*R*,2*S*)-1,2,5-[Tris(*tert*-Butyldimethylsilyl)oxy]-1-cyclohexyl-3-pentene (7.3). A solution of 0.19 g (0.44 mmol) of alcohol *anti*-**5.1a** in 2.0 mL of dry CH_2Cl_2 was stirred at rt as 0.08 mL (0.64 mmol) of 2,6-lutidine followed by 0.12 mL (0.52 mmol) of *tert*-butyldimethysilyl trifluoromethanesulfonate was added. After 30 min, the reaction was quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2. The organic extract was dried over $MgSO_4$, and the solvent was removed by distillation under reduced pressure. Chromatography of the crude product on a silica gel column with 1:49 EtOAc/hexanes as eluant afforded 0.22 g (92%) of TBS ether **7.3**: ^{1}H NMR δ 5.69 (dd, J = 15.4, 6.6 Hz, 1H), 5.60 (dt, J = 15.4, 4.0 Hz, 1H), 4.15 (d, J = 4.0 Hz, 2H), 4.10 (dd, J = 6.6, 4.4 Hz, 1H), 3.34 (dd (apparent t), J = 4.4 Hz, 1H), 1.83−1.44 (m, 6H), 1.27−0.97 (m, 5H), 0.90 (s, 9H), 0.88 (s, 9H), 0.87 (s, 9H), 0.06 (s, 6H), 0.05 (s, 3H), 0.04 (s, 3H), 0.03 (s, 3H), 0.02 (s, 3H).

(*E*, *E*,*rel*-4*S*,5*R*)-1,5-[Bis(*tert*-butyldimethylsilyl)oxy]-4-(methoxymethoxy)-2,6-octadiene (*anti*-8.2). The procedure described for **7.1** was employed with 0.14 g (0.31 mmol) of alcohol *anti*-**5.2b** in 5.0 mL of dry CH_2Cl_2, 0.06 mL (0.50 mmol) of 2,6-lutidine and 0.12 mL (0.50 mmol) of *tert*-butyldimethylsilyl trifluoromethanesulfonate. Chromatography of the crude product on a silica gel column with 1:9 EtOAc/hexanes as eluant afforded 0.13 g (65%) of silyl ether *anti*-**8.2**: ^{1}H NMR δ 5.75 (dt, J = 15.4, 4.4 Hz, 1H), 5.65−5.44 (m, 3H), 4.68, 4.56 (ABq, J = 6.6 Hz, 2H), 4.18 (d, J = 4.4 Hz, 2H), 4.03 (dd (apparent t), J = 5.7 Hz, 1H), 3.94 (dd, J = 7.7, 5.1 Hz, 1H), 3.34 (s, 3H), 1.69 (d, J = 6.2 Hz, 3H), 0.90 (s, 9H), 0.87 (s, 9H), 0.06 (s, 6H), 0.03 (s, 3H), 0.01 (s, 3H). Anal. Calcd for $C_{22}H_{46}O_4Si_2$: C, 61.34; H, 10.76. Found: C, 61.51; H, 10.69.

(*E*,*E*,*rel*-4*S*,5*S*)-1,5-[Bis(*tert*-butyldimethylsilyl)oxy]-4-(methoxymethoxy)-2,6-octadiene (*syn*-8.2). A solution of 2.6 g (0.68 mmol) of alcohol *syn*-**6.3b** in 7.0 mL of dry CH_2Cl_2 was stirred at 0 °C as 0.12 mL (0.69 mmol) of *N*,*N*-diisopropylethylamine was added followed by 0.06 mL (0.72 mmol) of chloromethyl methyl ether. The reaction was allowed to warm to rt. After 16 h, TLC analysis still showed the presence of unreacted alcohol. An additional 0.12 mL (0.69 mmol) of *N*,*N*-diisopropylethylamine and 0.06 mL (0.72 mmol) chloromethyl methyl ether were added. After 24 h the reaction was quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2. The organic extract was dried over $MgSO_4$, and the solvent was removed by distillation under reduced pressure. Chromatography of the crude product on a silica gel column with 1:9 EtOAc/hexanes as eluant afforded 0.24 g (81%) of adduct *syn*-**8.2** and 0.02 g (6%) of unreacted alcohol, *syn*-**6.3b**: ^{1}H NMR δ 5.76 (dt, J = 15.4, 4.4 Hz, 1H), 5.60 (m, 2H), 5.46 (dd, J = 15.4, 6.6 Hz, 1H), 4.69, 4.62 (ABq, J = 6.6 Hz, 2H), 4.18 (d, J = 4.4 Hz, 2H), 4.11 (dd (apparent t), J = 5.9 Hz, 1H), 3.97 (dd (apparent t), J = 5.9 Hz, 1H), 3.36 (s, 3H), 1.68 (d, J = 6.2 Hz, 3H), 0.90 (s, 9H), 0.88 (s, 9H), 0.06 (s, 9H), 0.03 (s, 3H). Anal. Calcd for $C_{22}H_{46}O_4Si_2$: C, 61.34; H, 10.76. Found: C, 61.12; H, 10.68.

2-[(*tert*-Butyldiphenylsilyl)oxy]ethanal (10.2). A suspension of 0.56 g (23 mmol) of sodium hydride in 200 mL of dry THF was stirred at 0 °C as 1.2 g (20 mmol) of ethylene glycol was slowly added. The reaction mixture was allowed to warm to rt. After 40 min, 6.2 g (23 mmol) of *tert*-butylchlorodiphenylsilane was added. After 16 h, the reaction was quenched with saturated aqueous NH_4Cl and extracted with ether. The organic extract was dried over $MgSO_4$, and the solvent was removed by distillation under reduced pressure. Bulb to bulb distillation of the crude product (129 °C (0.5 mmHg)) afforded 5.6 g (94%) of 2-[(*tert*-butyldiphenylsilyl)oxy]-1-ethanol: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.68 (m, 4H), 7.41 (m, 6H), 3.77 (m, 2H), 3.69 (m, 2H), 2.12 (m, 1H).

A solution of 1.8 mL (21 mmol) of oxalyl chloride in 70 mL of dry CH_2Cl_2 was stirred at −78 °C as 3.0 mL (42 mmol) of dimethyl sulfoxide followed by a solution of 5.6 g (19 mmol) of the above prepared alcohol in 10 mL of CH_2Cl_2 was added. After 15 min, 13 mL of triethylamine was added and the reaction mixture was allowed to warm to rt. The solvent was then removed by distillation under reduced pressure to afford a white solid. The solid was triturated with 250 mL of 1:4 EtOAc/hexanes and filtered through a plug of silica gel. Solvent was removed from the filtrate by distillation under reduced pressure. Bulb to bulb distillation of the crude product (120 °C (0.6 mmHg)) afforded 5.0 g (89%) of aldehyde **10.2**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.73 (m, 1H), 7.66 (m, 4H), 7.41 (m, 6H), 4.22 (m, 2H), 1.10 (s, 9H).

(*E*,2*R*,3*S*)-6-[(*tert*-Butyldimethylsilyl)oxy]-1-[(*tert*-butyldiphenylsilyl)oxy]-3-(methoxymethoxy)-4-hexen-2-ol (10.3). The procedure described for *anti*-**5.1a** was employed with 0.23 g (1.1 mmol) of indium(III) chloride in 8.0 mL of EtOAc, 0.29 g (1.0 mmol) of aldehyde **10.2** in 1.0 mL of EtOAc, and 0.29 g (0.54 mmol) of (*S*)-allylstannane **10.1** in 1.0 mL of EtOAc. Chromatography of the crude product on a silica gel column with 1:4 EtOAc/hexanes as eluant afforded 0.43 g (82%) of alcohol **10.3** as a 10:1 mixture of *anti* and *syn* diastereomers: $[\alpha]^{23}_D$ 43.5 (*c* 0.8, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.66 (m, 4H), 7.39 (m, 6H), 5.81 (dt, J = 15.4, 4.4 Hz, 1H), 5.63 (dd, J = 15.4, 7.7 Hz, 1H), 4.68, 4.53 (ABq, J = 6.6 Hz, 2H), 4.17 (d, J = 4.4 Hz, 2H), 4.15 (m, 1H), 3.85−3.67 (m, 3H), 3.28 (s, 3H), 2.47 (d, J = 4.0 Hz, 1H), 1.07 (s, 9H), 0.89 (s, 9H), 0.04 (s, 6H). Anal. Calcd for $C_{30}H_{48}O_5Si_2$: C, 66.13; H, 8.88. Found: C, 66.39; H, 8.95.

(*E*,4*S*,5*R*)-1,5-[Bis(*tert*-butyldimethylsilyl)oxy]-6-[(*tert*-butyldiphenylsilyl)oxy]-4-(methoxymethoxy)-4-hexene (10.4). The procedure described for **7.1** was employed with 0.43 g (0.79 mmol) of alcohol **10.3** in 8.0 mL of dry CH_2Cl_2, 0.14 mL (1.2 mmol) of 2,6-lutidine, and 0.24 mL (1.0 mmol) of *tert*-butyldimethysilyl trifluoromethanesulfonate. Chromatography of the crude product on a silica gel column with 1:9 EtOAc/hexanes as eluant afforded 0.43 g (83%) of adduct **10.4**: $[\alpha]^{23}_D$ 32.9 (*c* 0.4, CH_2Cl_2); ^{1}H NMR δ 7.56 (m, 4H), 7.30 (m, 6H), 5.64 (dt, J = 15.4, 4.0 Hz, 1H), 5.55 (dd, J = 15.4, 8.1 Hz, 1H), 4.59, 4.42 (ABq, J = 6.6 Hz, 2H), 4.17 (dd, J = 8.1, 2.9 Hz, 1H), 4.07 (m, 2H), 3.77 (ddd (apparent dt), J = 6.2, 2.9

Hz, H2), 3.45 (m, 2H), 3.22 (s, 3H), 0.96 (s, 9H), 0.80 (s, 9H), 0.73 (s, 9H), −0.05 (s, 6H), −0.07 (s, 3H), −0.15 (s, 3H). Anal. Calcd for $C_{36}H_{62}O_5Si_3$: C, 65.60; H, 9.48. Found: C, 65.54; H, 9.52.

(2R,3R,4R,5R)-1,5-[Bis(*tert*-butyldimethylsilyl)oxy]-6-[(*tert*-butyldiphenylsilyl)oxy]-4-(methoxymethoxy)-2,3-hexanediol (10.5). A solution of 0.07 g (0.10 mmol) of unsaturated ether **10.4** in 5.0 mL of acetone and 0.5 mL of water was stirred at rt as 0.04 g (0.32 mmol) of *N*-methylmorpholine *N*-oxide was added followed by 0.21 mL (0.02 mmol) of a 2.5 wt % solution of OsO_4 in isobutyl alcohol. After 22 h, the reaction was quenched with cold, saturated aqueous $NaHSO_3$ and stirred for 1 h. The mixture was then extracted with EtOAc. The organic extract was dried over $MgSO_4$, and the solvent was removed by distillation under reduced pressure. Chromatography of the crude product on a silica gel column with 1:9 EtOAc/hexanes afforded 0.06 g (81%) of diol **10.5**: $[\alpha]^{23}_D$ −14.9 (*c* 3.4, CH_2Cl_2); ^{1}H NMR δ 7.61 (m, 4H), 7.31 (m, 6H), 4.69, 4.59 (ABq, J = 5.9 Hz, 2H), 4.07 (m, 1H), 3.85−3.61 (m, 6H), 3.52 (dd, J = 10.3, 5.5 Hz, 1H), 3.30 (s, 3H), 3.00 (br, 1H), 2.70 (br, 1H), 0.97 (s, 9H), 0.82 (s, 9H), 0.76 (s, 9H), −0.01 (s, 6H), −0.04 (s, 3H), −0.13 (s, 3H). Anal. Calcd for $C_{36}H_{64}O_7Si_3$: C, 62.38; H, 9.31. Found: C, 62.53; H, 9.37.

(2*R*,3*R*,4*R*,5*R*) 2,4,5,6-[tetrakis(*tert*-Butyldimethylsilyl)oxy]-1-[(*tert*-butyldiphenylsilyl)oxy]-3-(methoxymethoxy)hexane (10.6). A. From Diol 10.5. The procedure described for **7.1** was employed with 0.05 g (0.06 mmol) of diol **10.5** in 1.0 mL of dry CH_2Cl_2, 0.03 mL (0.21 mmol) of 2,6-lutidine, and 0.04 mL (0.16 mmol) of *tert*-butyldimethysilyl trifluoromethanesulfonate. Chromatography of the crude product on a silica gel column with 1:9 EtOAc/hexanes as eluant afforded 0.06 g (97%) of silyl ether **10.6**: ^{1}H NMR δ 7.65 (m, 4H), 7.29 (m, 6H), 4.71, 4.59 (ABq, J = 5.9 Hz, 2H), 4.16 (dd, J = 7.3, 2.9 Hz, 1H), 3.75−3.41 (m, 7H), 3.19 (s, 3H), 0.96 (s, 9H), 0.85 (s, 9H), 0.78 (s, 18H), 0.75 (s, 9H), 0.06 (s, 3H), 0.04 (s, 3H), −0.03 (s, 3H), −0.04 (s, 3H), −0.05 (s, 3H), −0.07 (s, 3H), −0.08 (s, 3H), −0.09 (s, 3H); ^{13}C NMR δ 135.82 (2C), 135.79 (2C), 133.58, 133.51, 129.52, 129.34, 127.59 (2C), 127.43 (2C), 97.38, 80.54, 74.72, 73.88, 72.32, 64.97, 63.89, 55.97, 29.71, 27.05 (3C), 26.07 (6C), 25.92 (3C), 25.89 (3C), 19.02, 18.44, 18.18, 18.12, −3.57, −3.87, −4.06, −4.29, −4.88, −4.92, −5.29, −5.40. Anal. Calcd for $C_{48}H_{92}O_7Si_5$: C, 62.55; H, 10.06. Found: C, 62.44; H, 9.96.

B. From Alcohol 11.9. The procedure described for **7.1** was employed with 0.03 g (0.04 mmol) of alcohol **11.9** in 3.0 mL of dry CH_2Cl_2, 0.01 mL (0.09 mmol) of 2,6-lutidine, and 0.01 mL (0.05 mmol) of *tert*-butyldimethysilyl trifluoromethanesulfonate. Chromatography of the crude product on a silica gel column with 1:9 EtOAc/hexanes as eluant afforded 0.02 g (69%) of silyl ether **10.5** identified by comparison of the ^{1}H NMR spectrum with that of the material prepared above in part A. The $[\alpha]_D$ of this sample and that derived from part A was nearly zero and varied [±1] from run to run.

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Supporting Information Available: Experimental procedures for **5.1b**−**e**, **5.2b**, **5.2c**, **5.2e**, **6.3b**−**e**, **6.4d**, **9.1**, *anti*-**9.3**, **10.1**, **11.2**−**11.4**, and **11.6**−**11.9** and ^{1}H NMR spectra for **4.2**, **4.3c**, **5.1c**, **5.1d**, **6.3a**, **6.3b**, **6.4c**, **6.4d**, **7.1**, *anti*-**7.2**, **7.3**, **9.1** *anti*-**9.3**, **10.1**, **10.1** *(R)*-mandelate, **10.1** *(S)*-mandelate, **10.2**, **10.3**, **10.3** *(R)*-mandelate, **10.3** *(S)*-mandelate, **10.6**, and **11.6**−**11.9** (37 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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