Stereoselective S_E2' Additions of Enantioenriched Allylic Tin and Indium Reagents to Protected Threose and Erythrose Aldehydes: A General Strategy for the Stereocontrolled Synthesis of Precursors to the Eight Diastereomeric Hexoses and Their Enantiomers

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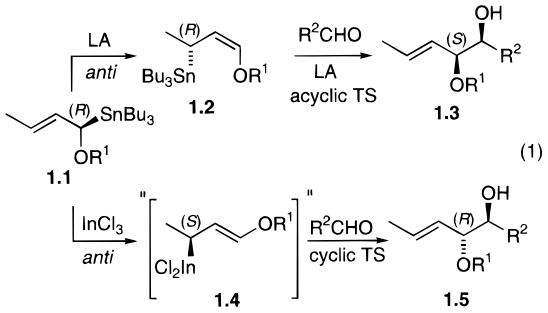
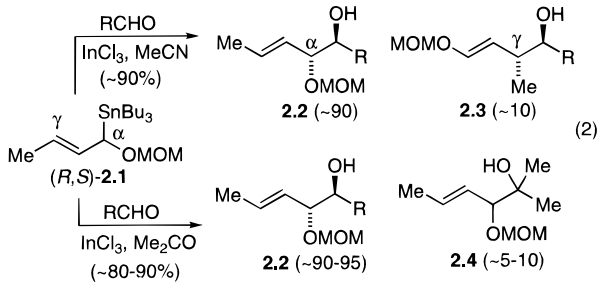
The enantioenriched (~90−95% ee) α-alkoxy allylic stannanes *(S)*- and *(R)*-**2.1** undergo *in situ* transmetallation with $InCl_3$ in EtOAc and subsequent S_E2' addition to aldehydes to afford *anti* adducts **3.2a**−**d** stereospecifically with excellent diastereoselectivity (90:10−98:2). Additions to the protected threose and erythrose aldehydes **4.2** and **4.4** are reagent controlled, yielding the *anti* adducts **5.1**−**5.4** with high stereoselectivity. These adducts are potential precursors of differentially protected L-talose, D-allose, L-glucose, and D-mannose.

In studies over the past several years, we have developed reliable routes to enantioenriched α-alkoxy and silyloxy allylic stannanes **1.1**.[1] These stannanes are readily transformed to the γ-isomers **1.2** by a stereospecific intermolecular *anti* process catalyzed by $BF_3{\cdot}OEt_2$ and other mild Lewis acids.[2] Treatment of stannanes **1.2** with various aldehydes in the presence of stoichiometric $BF_3{\cdot}OEt_2$ or, in some cases, $MgBr_2$, leads to differentially protected *syn* 1,2-diols **1.3**. With few exceptions, the additions proceed stereospecifically by an *anti* S_E2' pathway with high diastereoselectivity for the *syn* adduct.[1,2]



Until recently, attempts to utilize these reagents for the synthesis of *anti* adducts **1.5** have failed. Attempted transmetallation of α-oxygenated allylic stannanes with $SnCl_4$ or $TiCl_4$, or derivatives thereof, along precedented lines for simple crotyl analogues, led to total decomposition of the reagents.[3] Quite recently we discovered that $InCl_3$ effects a stereospecific *anti* S_E2' transmetallation of alkoxy stannanes **1.1** to give a transient indium reagent **1.4**[4,5] which effects a stereospecific and highly diastereoselective *syn* S_E2' addition to aldehydes leading to the *anti* adducts **1.5**.[4]

In our initial studies, we examined various solvents and found that reactions in acetonitrile and acetone were faster and more selective than those carried out in aqueous EtOH, THF, or DMF.[4] However, neither of these two solvents was completely satisfactory. In the former a small amount of γ-adduct **2.3** was generally produced along with the major α-adduct **2.2**. Such regioisomers were not found in acetone. However, competitive addition was a problem, leading to contamination by the acetone adduct **2.4**. Fortunately, this was usually separable from the major *anti* adduct **2.2**.



We have now found that ethyl acetate is a superior solvent for these reactions. In general, yields are higher and γ-adducts **2.3** are not formed. Some representative additions are summarized in eq 3. Use of the enantioenriched stannane *(R)*-**2.1** (ee >90%) with aldehydes **3.1b** and **3.1c** led to the adducts **3.2b/3.3b** and **3.2c/3.3c** of comparable ee.

The γ-alkoxy allylic stannanes *(S)*- and *(R)*-**4.1** have shown good potential as reagents for carbohydrate homologation. As illustrated in eq 4, additions to the protected threose or erythrose derivatives **4.2** or **4.4** can be carried out under conditions favoring Felkin−Ahn (BF_3 reactions) or chelation control ($MgBr_2$ reactions) to

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(1) For recent reviews, see: Marshall, J. A. *Chemtracts: Org. Chem.* **1992**, 75. Yamamoto, Y.; Sheda, N. *Advances in Detailed Reaction Mechanisms*; JAI Press Inc.: Greenwich, CT, 1994; Vol. 3, pp 1−44. Marshall, J. A. *Chem. Rev.*, in press.

(2) Marshall, J. A.; Welmaker, G. S.; Gung, B. W. *J. Am. Chem. Soc.* **1991**, *113*, 647. Marshall, J. A.; Jablonowski, J. A.; Elliott, L. M. *J. Org. Chem.* **1995**, *60*, 2662.

(3) For previous work in this area, see: Keck, G. E.; Abbott, D. E.; Boden, E. P.; Enholm, E. J. *Tetrahedron Lett.* **1984**, *25*, 3927. Boaretto, A.; Marton, D.; Tagliavini, G. *J. Organomet. Chem.* **1985**, *297*, 149. Denmark, S. E.; Wilson, T.; Willson, T. M. *J. Am. Chem. Soc.* **1988**, *110*, 984. Keck, G. E.; Andrus, M. B.; Castellino, S. *J. Am. Chem. Soc.* **1989**, *111*, 8136. Naruta, Y.; Nishigaichi, Y.; Maruyama, K. *Tetrahedron* **1989**, *45*, 1067. Zschage, O.; Schwark, J-R.; Krämer, T.; Hoppe, D. *Tetrahedron* **1992**, *48*, 8377. Thomas, E. J. *Chemtracts: Org. Chem.* **1994**, *7*, 207.

(4) Marshall, J. A.; Hinkle, K. W. *J. Org. Chem.* **1995**, *60*, 1920. The exact structure of this reagent is unknown. For some possibilities, see ref 5b.

(5) For previous applications of allylic indium reagents, see: (a) Kim, E.; Gordon, D. M.; Schmid, W.; Whitesides, G. M. *J. Org. Chem.* **1993**, *58*, 5500. (b) Araki, S.; Shimizu, T.; Johar, P. S.; Jin, S-J.; Butsugan, Y. *J. Org. Chem.* **1991**, *56*, 2538 and references cited therein.

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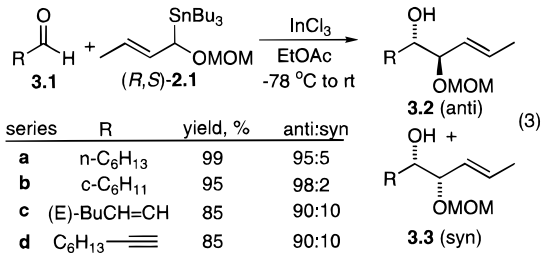
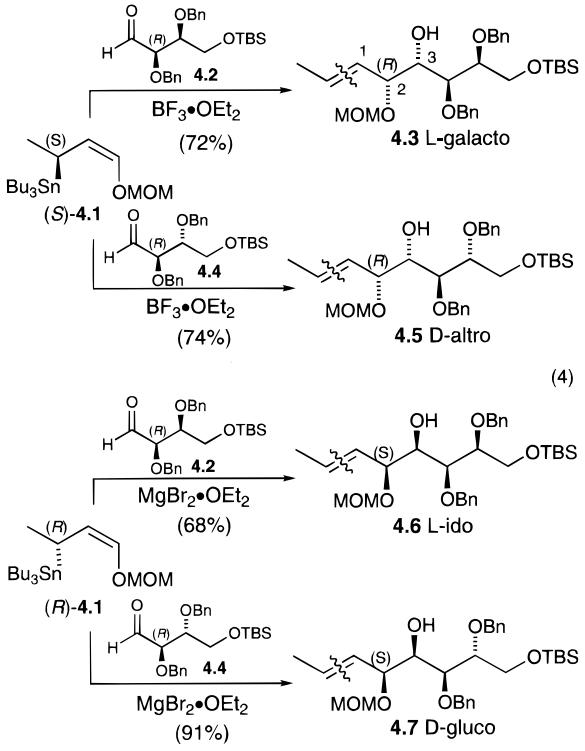


series	R	yield, %	anti:syn
a	n-C_6H_{13}	99	95:5
b	c-C_6H_{11}	95	98:2
c	(E)-BuCH=CH	85	90:10
d	C_6H_{13}—≡	85	90:10

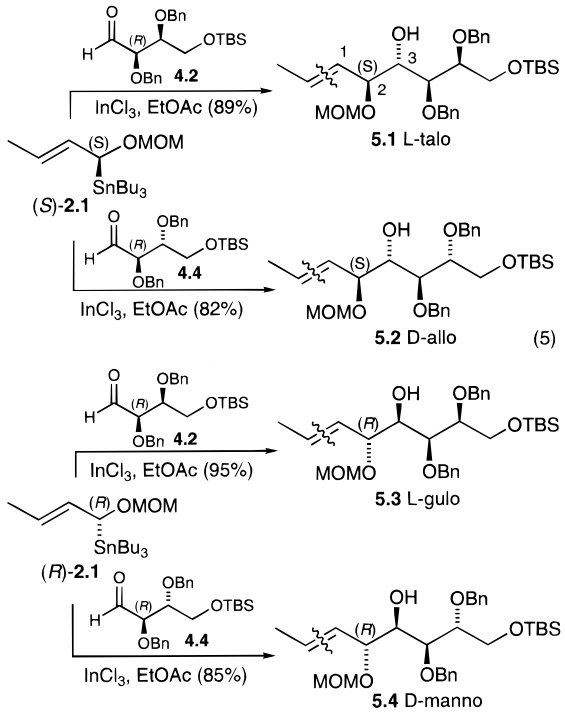
(3)

give four of the eight possible hexose precursors **4.3**, **4.5**, **4.6**, and **4.7**.[6,7] Each of these *syn* adducts is formed by an *anti* S_E2' process. The stereochemistry at the allylic center (*cf.* C2 in **4.3**) derives from the stannane, and the carbinyl center, from preferential facial attack on the aldehyde carbonyl.



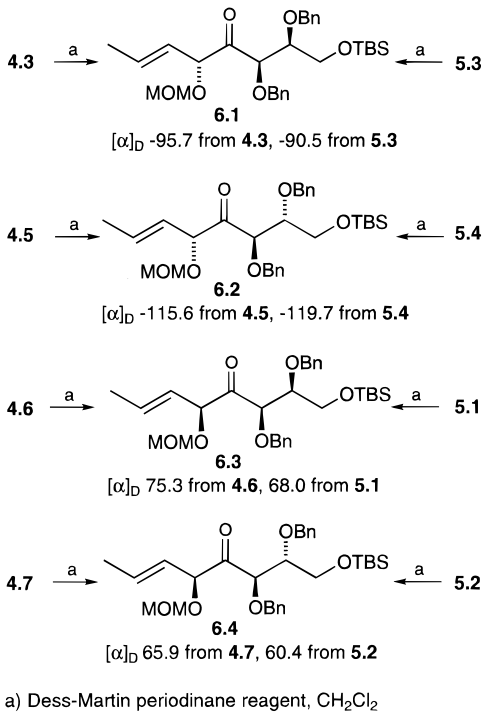
(4)

In an extension of these previous studies we examined reactions between the α-alkoxy stannanes *(S)*- and *(R)*-**2.1** and the protected threose and erythrose aldehydes **4.2** and **4.4** in the presence of $InCl_3$. Our initial studies were conducted in acetone. However, as noted above, EtOAc was later found to be a more satisfactory solvent. Each combination of stannane and aldehyde led to a discrete adduct (**5.1**−**5.4**) with little or no significant byproduct. It should be noted that a small amount of diastereomeric adducts would be formed from the 2−5% of enantiomeric stannanes present in our enantioenriched reagents **2.1**. The ^{1}H NMR spectra of adducts **5.1**−**5.4** were clearly different from those of their respective *syn* counterparts **4.3** and **4.5**−**4.7**. The stereochemistry of adducts **5.1**−**5.4** was tentatively assigned on the basis of previous results with stannane *(R)*-**2.1** and representative achiral aldehydes.[4]



(5)

Support for these assignments was secured through correlation with the *syn* adducts **4.3** and **4.5**−**4.7** as indicated in eq 6. Accordingly, Dess−Martin oxidation[8] of the *syn* and *anti* counterparts yielded the corresponding ketones **6.1**−**6.4**. The identity of the ketone obtained from each pair of alcohol diastereomers was confirmed by comparison of the ^{1}H NMR spectra and optical rotations.



(6)

a) Dess-Martin periodinane reagent, CH_2Cl_2

A priori the allylindium additions of eq 5 would expectedly show matched/mismatched characteristics.[9]

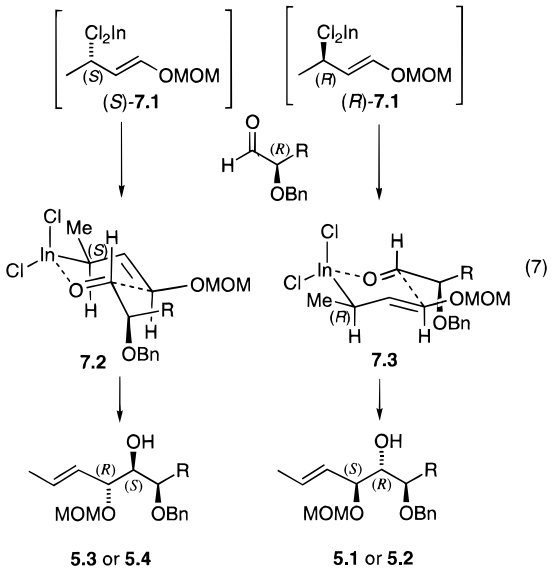
(6) Marshall, J. A.; Seletsky, B. M.; Luke, G. P. *J. Org. Chem.* **1994**, *59*, 3413.

(7) For other approaches to carbohydrate homologation, see: McGarvey, G. J.; Kimura, M.; Oh, T.; Williams, J. M. *J. Carbohydr. Chem.* **1984**, *3*, 125. Danishefsky, S. J.; DeNinno, S. L.; Chen, S.; Boisvert, L.; Barbachyn, M. *J. Am. Chem. Soc.* **1989**, *111*, 5810. Ramza, J.; Zamojski, A. *Tetrahedron* **1992**, *48*, 6123. Dondoni, A.; Perrone, D. *J. Org. Chem.* **1995**, *60*, 4749. Casiraghi, G.; Rassu, G. *Synthesis* **1995**, 607.

(8) Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4155.

(9) Reviews: Heathcock, C. H. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, 1991; Vol. 2, pp 181−238. Kim, B. M.; Williams, S. F.; Masamune, S. *Ibid.* pp 239−275.

Possible transition state arrangements are depicted in eq 7. The *(S)/(R)* combination **7.2** would appear sterically more accessible than the *(R)/(R)* arrangement **7.3**. This would be true for both chelation and Felkin−Ahn orientations. As both reagent/substrate combinations proceed with high diastereoselectivity, these reactions must be largely reagent directed.[9] Their apparent insensitivity to the steric environment of the aldehyde carbonyl may reflect an early transition state. In accord



with these conclusions the racemic stannane *(R,S)*-**2.1** afforded a nearly 1:1 mixture of adducts **5.1** and **5.3** with aldehyde **4.2**.

The methodology described in this and our preceding paper[6] provides efficient access to differentially protected hexose precursors of any desired stereochemistry from a single set of substrate aldehydes, their enantiomers, and the enantiomeric stannanes *(S)*- and *(R)*-**2.1**. Presumably the BOM analogues of **2.1** would serve equally well. We have not examined this possiblity with aldehydes **4.2** and **4.4**, but we have found that the OTBS derivatives give lower yields of adducts with $InCl_3$. Accordingly, at this point the methodology appears more suited to alkoxy stannanes.

Experimental Section[10]

General Procedure with $InCl_3$. One molar equivalent of $InCl_3$ as a 0.04 M solution in EtOAc at rt was placed in a sonication bath for 15 min. The solution was removed from the bath, and the aldehyde (1 mol equiv) was added with stirring. The solution was cooled to −78 °C followed by addition of the allylic stannane reagent (1.5 equiv). The reaction mixture was allowed to slowly warm to rt, and the progress of the reaction was monitored by TLC. When the aldehyde was no longer present, the reaction was quenched at rt with cold 1 M HCl and extracted with ether. The organic extracts were dried over $MgSO_4$, and Et_3N (approximately 2 equivs) was added to remove tin byproducts. The solvent was removed under reduced pressure, and the product was purified by elution column chromatography on silica gel with Et_2O−hexanes as the eluant.

(*E*)-*anti*-4-(Methoxymethoxy)-2-undecen-5-ol (3.2a). The general procedure was employed with 55 mg (0.25 mmol) of $InCl_3$ in 6 mL of EtOAc, 26 mg (0.23 mmol) of heptaldehyde, and 158 mg (0.38 mmol) of racemic stannane (*R,S*)-**2.1**. After 5 h, the reaction was quenched at rt with 1 M HCl and processed as described to afford 51 mg (99%) of a 95:5 mixture of adducts **3.2a** and **3.3a**. ^{1}H NMR: major isomer δ 5.71 (dq, J = 15.5, 6.5 Hz, 1H), 5.42 (ddq, J = 15.5, 8.5, 1.6 Hz, 1H), 4.72, 4.53 (ABq, J = 6.6 Hz, 2H), 3.89 (dd, J = 8.5, 3.9 Hz, 1H), 3.65 (dd, J = 8.1, 3.9 Hz, 1H), 3.33 (s, 3H), 2.20 (bs, 1H), 1.72 (dd, J = 6.5, 1.6 Hz, 3H), 1.47−1.34 (m, 2H), 1.26 (bs, 8H), 0.85 (t, J = 6.4 Hz, 3H); minor isomer δ 3.25 (dd, J = 8.5, 6.3 Hz, 1H). Anal. Calcd for $C_{13}H_{26}O_3$: C, 67.79; H, 11.38. Found: C, 67.63; H, 11.30.

(*E*)-*anti*-1-Cyclohexyl-2-(methoxymethoxy)-3-penten-1-ol (3.2b). The general procedure was employed with 55 mg (0.25 mmol) of $InCl_3$ in 6 mL of EtOAc, 28 mg (0.25 mmol) of cyclohexanecarboxaldehyde, and 150 mg (0.37 mmol) of racemic stannane (*R,S*)-**2.1**. After 5 h, the reaction was quenched at rt with 1 M HCl and processed as described to afford 58 mg (95%) of a 98:2 mixture of adducts **3.2b** and **3.3b**. ^{1}H NMR: major isomer δ 5.73 (dq, J = 15.5, 6.4 Hz, 1H), 5.43 (ddq, J = 15.5, 8.7, 1.6 Hz, 1H), 4.60, 4.50 (AB q, J = 6.6 Hz, 2H), 4.03 (dd, J = 8.7, 4.2 Hz, 1H), 3.41 (dd, J = 7.5, 4.2 Hz, 1H), 3.33 (s, 3H), 2.10 (bs, 1H), 2.05−1.94 (m, 1H), 1.74 (dd, J = 6.4, 1.6 Hz, 3H), 1.71−1.55 (m, 5H), 1.44−1.36 (m, 2H), 1.21−1.11 (m, 2H), 1.05−0.90 (m, 2H); minor isomer δ 3.25 (dd, J = 8.5, 6.3 Hz, 1H). Anal. Calcd for $C_{13}H_{24}O_3$: C, 68.38; H, 10.59. Found: C, 68.48; H, 10.59.

When the above reaction was conducted with stannane (*R*)-**2.1** [157 mg (0.38 mmol), $[\alpha]_D$ +55.9 (*c* 1.5, CH_2Cl_2), ee >90%], the (1*S*,2*R*) adduct **3.2b** was obtained in 98% yield as a 98:2 mixture with **3.3b** [$[\alpha]_D$ −112.2 (*c* 2.1, CH_2Cl_2)].[4]

(2*E*,6*E*)-*anti*-4-(Methoxymethoxy)-2,6-undecadien-5-ol (3.2c). The general procedure was employed with 53 mg (0.24 mmol) of $InCl_3$ in 6 mL of EtOAc, 27 mg (0.24 mmol) of heptenal, and 151 mg (0.37 mmol) of racemic stannane (*R,S*)-**2.1**. After 5 h, the reaction was quenched at rt with 1 M HCl and processed as described to afford 47 mg (85%) of a 90:10 mixture of adducts **3.2c** and **3.3c**. ^{1}H NMR: major isomer δ 5.76−5.66 (m, vinyl 2H), 5.46−5.33 (m, vinyl 2H), 4.70, 4.55 (AB q, J = 6.7 Hz, 2H), 4.09 (dd, J = 7.0, 4.0 Hz, 1H), 3.95 (dd, J = 8.2, 4.0 Hz, 1H), 3.35 (s, 3H), 2.30 (bs, 1H), 2.06−2.00 (m, 2H), 1.72 (dd, J = 6.5, 1.6 Hz, 3H), 1.37−1.26 (m, 4H), 0.86 (t, J = 7.1 Hz, 3H); minor isomer δ 3.38 (dd, J = 7.8, 7.5 Hz, 1H).

When the above reaction was conducted with stannane (*R*)-**2.1** [150 mg (0.37 mmol), $[\alpha]_D$ +55.9 (*c* 1.5, CH_2Cl_2), ee >90%], the (4*R*,5*S*) adduct **3.2c** was obtained in 87% yield as a 90:10 mixture with **3.3c** [$[\alpha]_D$ −96.7 (*c* 1.8, CH_2Cl_2)].[4]

(*E*)-*anti*-4-(Methoxymethoxy)-6-tridecyn-2-en-5-ol (3.2d). The general procedure was employed with 55 mg (0.25 mmol) of $InCl_3$ in 6 mL of EtOAc, 36 mg (0.25 mmol) of 2-nonynal, and 150 mg (0.38 mmol) of racemic stannane (*R,S*)-**2.1**. After 5 h, the reaction was quenched at rt with 1 M HCl and processed as described to afford 63 mg (95%) of a 90:10 mixture of adducts **3.2d** and **3.3d**. ^{1}H NMR: major isomer δ 5.78 (dq, J = 15.4, 6.5 Hz, 1H), 5.47 (ddq, J = 15.4, 7.9, 1.2 Hz, 1H), 4.73, 4.61 (AB q, J = 6.8 Hz, 2H), 4.33 (dt, J = 3.7, 2.1 Hz, 1H), 4.06 (dd, J = 7.9, 3.7 Hz, 1H), 3.39 (s, 3H), 2.75 (bs, 1H), 2.20 (dt, J = 7.0, 2.1 Hz, 2H), 1.73 (dd, J = 6.5, 1.5 Hz, 3H), 1.51−1.44 (m, 2H), 1.39−1.22 (m, 4H), 0.86 (t, J = 6.8 Hz, 3H); minor isomer δ 4.28 (dd, J = 4.0, 2.0 Hz, H1). Anal. Calcd for $C_{15}H_{27}O_3$: C, 70.83; H, 10.30. Found: C, 70.85; H, 10.20.

(6*E*,2*S*,3*R*,4*S*,5*S*)-2,3-Bis(benzyloxy)-1-[(*tert*-butyldimethylsilyl)oxy]-5-(methoxymethoxy)-6-octen-4-ol (5.1). The general procedure described above was employed with 55 mg (0.25 mmol) of $InCl_3$ in 6 mL of EtOAc, 108 mg (0.26 mmol) of aldehyde **4.2**, and 151 mg (0.37 mmol) of stannane (*S*)-**2.1** [$[\alpha]_D$ −60.0 (*c* 1.5, CH_2Cl_2), ee >95%]. After 5 h, the reaction was quenched at rt with 1 M HCl and processed as described to afford 124 mg (89%) of adduct **5.1**[6] [$[\alpha]_D$ 36.3 (*c* 2.0, CH_2Cl_2)]. ^{1}H NMR: δ 7.32−7.25 (m, 10H), 5.57 (dq, J = 15.5, 6.1 Hz, 1H), 5.47 (ddq, J = 15.5, 8.1, 1.3 Hz, 1H), 4.75 and 4.65, 4.68 and 4.51, 4.52 and 4.50 (AB q's, J = 11.9, 6.7, 11.5 Hz, 6H), 4.13 (dd, J = 8.2, 3.9 Hz, 1H), 4.00 (dd, J = 8.0, 4.4 Hz, 1H), 3.90−3.77 (m, 3H), 3.59 (dd, J = 7.8, 2.8 Hz, 1H), 3.32 (s, 3H), 3.17 (d, J = 4.5 Hz, 1H), 1.70 (dd, J = 6.1, 1.2 Hz, 3H), 0.87 (s, 9H), 0.02 (s, 3H), 0.01 (s, 3H). Anal. Calcd for $C_{30}H_{46}O_6Si$: C, 67.89; H, 8.74. Found: C, 67.65; H, 8.71.

(10) Unless otherwise stated ^{1}H NMR specta were recorded as dilute solutions in $CDCl_3$ at 300 MHz. For typical experimental protocols, see: Marshall, J. A.; Wang, X.-J. *J. Org. Chem.* **1991**, *56*, 960.

(6*E*,2*R*,3*R*,4*S*,5*S*)-2,3-Bis(benzyloxy)-1-[(*tert*-butyldimethylsilyl)oxy]-5-(methoxymethoxy)-6-octen-4-ol (5.2). The general procedure described above was employed with 53 mg (0.24 mmol) of $InCl_3$ in 6 mL of EtOAc, 108 mg (0.26 mmol) of aldehyde **4.4**, and 151 mg (0.37 mmol) of stannane (*S*)-**2.1** [[α]$_D$ −60.0 (*c* 1.5, CH_2Cl_2), ee >95%]. After 5 h, the reaction was quenched at rt with 1 M HCl and processed as described to afford 112 mg (82%) of adduct **5.2** [[α]$_D$ 22.2 (*c* 2.0, CH_2Cl_2)]. ^{1}H NMR: δ 7.36−7.26 (m, 10H), 5.53 (dq, *J* = 15.5, 6.0 Hz, 1H), 5.49 (ddq, *J* = 15.5, 8.1, 1.0 Hz, 1H), 4.76−4.41 (m, 6H), 4.22 (dd, *J* = 8.2, 3.2 Hz, 1H), 3.98−3.63 (m, 5H), 3.31 (s, 3H), 2.80 (br s, 1H), 1.69 (dd, *J* = 5.9, 0.9 Hz, 3H), 0.89 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H). Anal. Calcd for $C_{30}H_{46}O_6Si$: C, 67.89; H, 8.74. Found: C, 68.09; H, 8.67.

(6*E*,2*S*,3*R*,4*R*,5*R*)-2,3-Bis(benzyloxy)-1-[(*tert*-butyldimethylsilyl)oxy]-5-(methoxymethoxy)-6-octen-4-ol (5.3). The general procedure described above was employed with 55 mg (0.25 mmol) of $InCl_3$ in 6 mL of EtOAc, 101 mg (0.25 mmol) of aldehyde **4.2**, and 150 mg (0.37 mmol) of stannane (*R*)-**2.1** [[α]$_D$ +55.9 (*c* 1.5, CH_2Cl_2), ee >90%]. After 5 h, the reaction was quenched at rt with 1 M HCl and processed as described to afford 122 mg (95%) of adduct **5.3** [[α]$_D$ −25.0 (*c* 1.9, CH_2Cl_2)]. ^{1}H NMR: δ 7.34−7.24 (m, 10H), 5.69 (dq, *J* = 15.4, 6.4 Hz, 1H), 5.39 (ddq, *J* = 15.4, 8.4, 1.6 Hz, 1H), 4.74 −4.46 (m, 6H), 4.04 (dd, *J* = 14.6, 6.4 Hz, 1H), 3.83−3.75 (m, 4H), 3.67−3.60 (m, 1H), 3.32 (s, 3H), 2.60 (d, *J* = 6.8 Hz, 1H), 1.72 (dd, *J* = 6.4, 1.5 Hz, 3H), 0.88 (s, 9H), 0.03 (s, 3H), 0.02 (s, 3H). Anal. Calcd for $C_{30}H_{46}O_6Si$: C, 67.89; H, 8.74. Found: C, 67.93; H, 8.70.

(6*E*,2*R*,3*R*,4*R*,5*R*)-2,3-Bis(benzyloxy)-1-[(*tert*-butyldimethylsilyl)oxy]-5-(methoxymethoxy)-6-octen-4-ol (5.4). The general procedure described above was employed with 48 mg (0.21 mmol) of $InCl_3$ in 6 mL of EtOAc, 80 mg (0.19 mmol) of aldehyde **4.4**, and 122 mg (0.28 mmol) of stannane (*R*)-**2.1** [[α]$_D$ +55.9 (*c* 1.5, CH_2Cl_2), ee >90%]. After 5 h, the reaction was quenched at rt with 1 M HCl and processed as described to afford 86 mg (85%) of adduct **5.4** [[α]$_D$ −31.1 (*c* 1.9, CH_2Cl_2)]. ^{1}H NMR: δ 7.34−7.26 (m, 10H), 5.73 (dq, *J* = 15.4, 6.4 Hz, 1H), 5.43 (ddq, *J* = 15.4, 8.4, 1.6 Hz, 1H), 4.75 −4.46 (m, 6H), 4.07 (apparent t, *J* = 8.0 Hz, 1H), 3.92−3.71 (m, 5H), 3.32 (s, 3H), 2.99 (d, *J* = 6.2 Hz, 1H), 1.73 (dd, *J* = 6.4, 1.5 Hz, 3H), 0.89 (s, 9H), 0.04 (s, 3H), 0.04 (s, 3H). Anal. Calcd for $C_{30}H_{46}O_6Si$: C, 67.89; H, 8.74. Found: C, 68.04; H, 8.64.

(6*E*,2*S*,3*R*,4*R*,5*R*)-2,3-Bis(benzyloxy)-1-[(*tert*-butyldimethylsilyl)oxy]-5-(methoxymethoxy)-6-octen-4-ol (5.1) and (6*E*,2*S*,3*R*,4*S*,5*S*)-2,3-Bis(benzyloxy)-1-[(*tert*-butyldimethylsilyl)oxy]-5-(methoxymethoxy)-6-octen-4-ol (5.3). The general procedure described above was employed with 53 mg (0.24 mmol) of $InCl_3$ in 6 mL of acetone, 108 mg (0.26 mmol) of aldehyde **4.2**, and 308 mg (0.75 mmol, 3 equiv) of racemic stannane (*R*,*S*)-**2.1**. After 5 h the reaction was quenched at rt with 1 M HCl and processed as described to afford 86 mg (62%) of a *ca.* 1:1 mixture of adducts **5.1** and **5.3** as determined by ^{1}H NMR analysis.

(6*E*,2*S*,3*R*,5*R*)-2,3-Bis(benzyloxy)-1-[(*tert*-butyldimethylsilyl)oxy]-5-(methoxymethoxy)-6-octen-4-one (6.1). A. From Alcohol 4.3. To a solution of 40 mg of alcohol **4.3**[6] (0.08 mmol) in 2.0 mL of CH_2Cl_2 was added 64 mg (0.15 mmol) of Dess−Martin periodinane reagent[8] at rt. The reaction was monitored by TLC (30% Et_2O in hexanes) until the starting material was consumed. Upon completion, the reaction mixture was diluted with Et_2O (10 mL), solid $Na_2S_2O_3$ (7 equiv relative to periodinane reagent) in saturated aqueous $NaHCO_3$ was added, and the mixture was stirred vigorously. After the layers became clear and colorless (approximately 20 min), they were separated, and the aqueous layer was reextracted with Et_2O. The organic extracts were combined, dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure, and the product was purified by column chromatography on silica gel with 30% Et_2O in hexanes as the eluant to afford 33 mg (83%) of adduct **6.1** [[α]$_D$ −95.7 (*c* 2.2, CH_2Cl_2)]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.30−7.24 (m, 10H), 5.79 (dq, *J* = 15.3, 6.6 Hz, 1H), 5.30 (ddq, *J* = 15.3, 7.8, 1.6 Hz, 1H), 4.72 (d, *J* = 7.8 Hz, 1H), 4.67−4.38 (m, 7H), 3.88 (m, 1H), 3.75 (dd, *J* = 10.5, 6.2 Hz, 1H), 3.60 (dd, *J* = 10.6, 6.2 Hz, 1H), 3.26 (s, 3H), 1.61 (dd, *J* = 6.6, 1.0 Hz, 3H), 0.85 (s, 9H), −0.01 (s, 3H), −0.01 (s, 3H). Anal. Calcd for $C_{30}H_{44}O_6Si$: C, 68.15; H, 8.39. Found: C, 67.92; H, 8.27.

B. From Alcohol 5.3. The procedure described for **6.1** was employed with 37 mg (0.07 mmol) of alcohol **5.3** in 2 mL of CH_2Cl_2 and 44 mg (0.10 mmol) of Dess−Martin periodinane reagent.[8] After 20 min, the reaction was processed as described to afford 34 mg (94%) of adduct **6.1** [[α]$_D$ −90.5 (*c* 2.2, CH_2Cl_2)]. Anal. Calcd for $C_{30}H_{44}O_6Si$: C, 68.15; H, 8.39. Found: C, 68.18; H, 8.36.

(6*E*,2*R*,3*R*,5*S*)-2,3-Bis(benzyloxy)-1-[(*tert*-butyldimethylsilyl)oxy]-5-(methoxymethoxy)-6-octen-4-one (6.2). A. From Alcohol 4.5. The procedure described for **6.1** was employed with 46 mg (0.08 mmol) of alcohol **4.5**[6] in 2 mL of CH_2Cl_2 and 73 mg (0.17 mmol) of Dess−Martin periodinane reagent.[8] After 20 min, the reaction was processed as described to afford 32 mg (88%) of adduct **6.2** [[α]$_D$ −115.6 (*c* 1.3, CH_2Cl_2)]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32−7.24 (m, 10H), 5.86 (dq, *J* = 15.3, 6.6 Hz, 1H), 5.22 (ddq, *J* = 15.3, 8.5, 1.6 Hz, 1H), 4.80 (d, *J* = 8.5 Hz, 1H), 4.64−4.40 (m, 7H), 3.83−3.72 (m, 3H), 3.16 (s, 3H), 1.64 (dd, *J* = 6.6, 1.6 Hz, 3H), 0.87 (s, 9H), 0.02 (s, 3H), 0.02 (s, 3H). Anal. Calcd for $C_{30}H_{44}O_6Si$: C, 68.15; H, 8.39. Found: C, 68.27; H, 8.44.

B. From Alcohol 5.4. The procedure described for **6.1** was employed with 36 mg (0.07 mmol) of alcohol **5.4** in 2 mL of CH_2Cl_2 and 43 mg (0.10 mmol) of Dess−Martin periodinane reagent.[8] After 20 min, the reaction was processed as described to afford 28 mg (78%) of adduct **6.2** [[α]$_D$ −119.7 (*c* 2.1, CH_2Cl_2)].

(6*E*,2*S*,3*R*,5*S*)-2,3-Bis(benzyloxy)-1-[(*tert*-butyldimethylsilyl)oxy]-5-(methoxymethoxy)-6-octen-4-one (6.3). A. From Alcohol 4.6. The procedure described for **6.1** was employed with 53 mg (0.10 mmol) of alcohol **4.6**[6] in 2 mL of CH_2Cl_2 and 84 mg (0.20 mmol) of Dess−Martin periodinane reagent.[8] After 20 min, the reaction was processed as described to afford 47 mg (90%) of adduct **6.3** [[α]$_D$ +75.3 (*c* 2.1, CH_2Cl_2)]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32−7.24 (m, 10 H), 5.74 (dq, *J* = 15.4, 6.5 Hz, 1H), 5.33 (ddq, *J* = 15.4, 8.1, 1.6 Hz, 1H), 4.72 (d, *J* = 8.1 Hz, 1H), 4.64−4.40 (m, 7H), 3.96 (m, 1H), 3.73−3.61 (m, 2H), 3.23 (s, 3H), 1.68 (dd, *J* = 6.5, 1.5 Hz, 3H), 0.84 (s, 9H), −0.02 (s, 3H), −0.03 (s, 3H).

B. From Alcohol 5.1. The procedure described for **6.1** was employed with 45 mg (0.08 mmol) of alcohol **5.1** in 2 mL of CH_2Cl_2 and 73 mg (0.17 mmol) of Dess−Martin periodinane reagent. After 20 min, the reaction was processed as described to afford 22 mg (61%) of adduct **6.3** [[α]$_D$ +68.0 (*c* 2.1, CH_2Cl_2)].

(6*E*,2*R*,3*R*,5*S*)-2,3-Bis(benzyloxy)-1-[(*tert*-butyldimethylsilyl)oxy]-5-(methoxymethoxy)-6-octen-4-one (6.4). A. From Alcohol 4.7. The procedure described for **6.1** was employed with 31 mg (0.06 mmol) of alcohol **4.7**[6] in 2 mL of CH_2Cl_2 and 50 mg (0.11 mmol) of Dess−Martin periodinane reagent.[8] After 20 min, the reaction was processed as described to afford 30 mg (95%) of adduct **6.4** [[α]$_D$ +65.9 (*c* 2.1, CH_2Cl_2)]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33−7.24 (m, 10H), 5.67 (dq, *J* = 15.4, 7.3 Hz, 1H), 5.32 (ddq, *J* = 15.4, 6.3, 1.6 Hz, 1H), 4.72 (d, *J* = 6.3 Hz, 1H), 4.66−4.41 (m, 7H), 3.91−3.75 (m, 3H), 3.23 (s, 3H), 1.66 (dd, *J* = 6.6, 1.3 Hz, 3H), 0.86 (s, 9H), 0.02 (s, 6H). Anal. Calcd for $C_{30}H_{44}O_6Si$: C, 68.15; H, 8.39. Found: C, 68.04; H, 8.34.

B. From Alcohol 5.2. The procedure described for **6.1** was employed with 30 mg (0.06 mmol) of alcohol **5.2** in 2 mL of CH_2Cl_2 and 48 mg (0.11 mmol) of Dess−Martin periodinane reagent. After 20 min, the reaction was processed as described to afford 24 mg (83%) of adduct **6.4** [[α]$_D$ +60.4 (*c* 2.1, CH_2Cl_2)].

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Supporting Information Available: ^{1}H NMR spectra for **3.2a−d**, **4.3**, **4.5−4.7**, **5.1−5.4**, and **6.1−6.4** (21 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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