detector (EG&G model 1421) forming part of an EG&G OMA-III data handling system. For the spectra shown in Figure 3 the detector gate width was set at 5 ns, while the delay of the gate pulse was incremented in steps of 10 ns with respect to the laser pulse.

Acknowledgment. We acknowledge the award of a National Research Fellowship (to A.M.O.) and support from the Australian Research Council. This work was supported in part by the Netherlands Foundation for Chemical Research (SON) with the financial aid from the Netherlands Organization for the Advancement of Scientific Research (NWO).

π-Facial Selectivity in Catalytic Osmylation Reactions of Chiral C1-Oxygenated Allylic Silanes

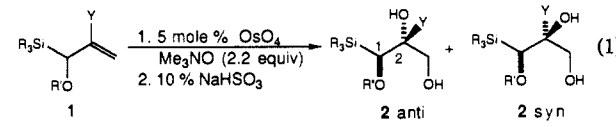
James S. Panek* and Pier F. Cirillo

Contribution from the Department of Chemistry, Metcalf Center for Science and Engineering, Boston University, Boston, Massachusetts 02215. *Received September 28, 1989*

Abstract: Oxygen-substituted allylic and crotyl silanes undergo vicinal hydroxylations with unprecedented levels of diastereofacial selectivities in the presence of catalytic amounts of osmium tetroxide to predominantly form 1,2-anti-1,2,3-triol units. The magnitude of face selectivity was influenced by two factors: the steric bulk of the silicon group and the type of substituent on the C1-oxygen. As the size of the silicon group increased [$Me_3Si- \rightarrow Et_3Si- \rightarrow PhMe_2Si- \rightarrow {}^tBuMe_2Si- \rightarrow Ph_2MeSi-$] the anti selectivity improved. Allylic silanes containing ethers and esters gave moderate to good anti selectivity. (*E*)-crotylsilanes gave higher selectivities than the corresponding *Z* stereoisomers. When a hydroxyl group is present the vicinal hydroxylation proceeded with virtual face specificity for the allylic and (*E*)-crotylsilanes producing the triol products with anti/syn selectivities reaching 147:1. Lower but still significant selectivities were obtained for the *Z* stereoisomers. These experiments present evidence supporting the notion that the steric effects of trialkyl silyl group are as important as σ donor effects in these electrophilic addition reactions.

Studies on electrophilic addition reactions to π systems adjacent to stereogenic carbon atoms have been the subject of considerable experimental and theoretical interest.[1] A fascinating aspect of this chemistry is the manner by which the asymmetric center can alter the relative rates of additions to either face (k_{anti}/k_{syn}) of the π system. It has been well-documented that chiral allylic metals can promote and direct the regio- and stereochemical outcome of many addition reactions.[2] Initial investigations by Kishi and co-workers[3] have shown that chiral allylic alcohols and ethers undergo diastereoselective osmylation reactions preferentially away from the oxygen function. This pattern has been confirmed in conformationally rigid systems.[4a] More recently Vedejs[4c] and Fleming[2g,h] have reported that allylic silanes participate in vicinal hydroxylation reactions with useful levels of selectivity. Here we disclose our results of a study to determine the *influence of a geminally substituted alkoxy-trialkylmetal center* on the π-facial selectivity in catalytic osmylation reactions. Our experiments present evidence supporting the notion that the steric influence[4] of the silicon group is as important as σ donor effects.[5a] The oxygen-substituted allylic silanes undergo vicinal hydroxylations with very high levels of diastereofacial selectivities

Table I. Diastereoselective Vicinal Hydroxylations of Chiral C1-Oxygenated Allylic Silanes[a]



(1)

chiral silane	R′	R_3Si	Y	ratio **2** anti/syn[b]	% yield[c,d]
1a	Ac	$SiMe_3$	H	6.5:1	57
1b	Ac	$SiEt_3$	H	7.5:1	67
1c	Ac	$SiMe_2Ph$	H	7.0:1	70
1d	Ac	Si^tBuMe_2	H	11.3:1	70
1e	Ac	$SiPh_2Me$	H	11.5:1	58
1f	$SiEt_3$	$SiMe_2{}^tBu$	H	12.6:1	36
1g	PhCO	$SiMe_3$	H	4.0:1	75
1h	Ac	$SiMe_3$	CH_3	3.5:1	63
1i	H	$SiMe_3$	CH_3	>97:3	65[e]

[a] The osmylation reactions were run in acetone/water [8:1; 5.0 mol % OsO_4; Me_3NO (2.2 equiv)] 0.2–0.5 M in substrate. [b] All products were isolated as anti/syn diastereomers, and ratios were determined by integration of the C1 methine protons at 93.94 KG (400 MHz NMR) or by capillary GC analysis after acetylation (Ac_2O, NEt_3, catalyst DMAP, CH_2Cl_2). [c] All products exhibited the expected ^1H NMR (400 MHz), IR, and mass spectral characteristics. [d] All yields are based on pure materials isolated by chromatography on SiO_2. [e] Crude yield.

(1) (a) Symposia in print, *Control of Acyclic Stereochemistry*: Mukaiyama, T. *Tetrahedron* **1984**, *40*, 2197. (b) Khan, S. D.; Pau, C. F.; Chamberlin, A. R.; Hehre, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 650. (c) Solladié, G.; Frechou, C.; Demailly, G. *Tetrahedron Lett.* **1986**, *27*, 2867. (d) McGarvey, G. J.; Williams, J. M. *J. Am. Chem. Soc.* **1985**, *107*, 1435. (e) Labelle, M.; Guindon, Y. *J. Am. Chem. Soc.* **1989**, *111*, 2204. (f) Stork, G.; Kahn, M. *Tetrahedron Lett.* **1983**, *24*, 3951.

(2) Organosilanes in synthesis, see inter alia: (a) Colvin, E. *Silicon in Organic Synthesis*; Butterworths: London, 1981. (b) Sakurai, H. *Organosilicon and Bioorganosilicon Chemistry*; Ellis Horwood: Chichester, 1985. (c) Symposia in print, *Organosilicon Chemistry in Organic Synthesis*: Fleming, I. *Tetrahedron* **1988**, *44*, 3760. (d) Hayashi, T.; Konishi, M.; Ito, H.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 4962. (e) Hayashi, T.; Konishi, M.; Kumada, M. *Ibid.* **1982**, *104*, 4963. (f) Curran, D. P.; Gothe, S. A. *Tetrahedron* **1988**, *44*, 3945. (g) Fleming, I.; Sarkar, A. S.; Thomas, A. P. *J. Chem. Soc., Chem. Commun.* **1987**, 157. (h) Fleming, I.; Lawrence, N. J. *Tetrahedron Lett.* **1988**, *29*, 2077. For the use of allylic stannanes, see: (j) Pratt, A. J.; Thomas, E. J. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1521. (k) Jephcote, V. J.; Pratt, A. J.; Thomas, E. *J. ibid.* **1989**, 1529 and references therein. (l) Marshall, J. A.; Crooks, S. L.; DeHoff, B. S. *J. Org. Chem.* **1988**, *53*, 1616. (m) Marshall, J. A.; Markwalder, J. A. *Tetrahedron Lett.* **1988**, *29*, 4814.

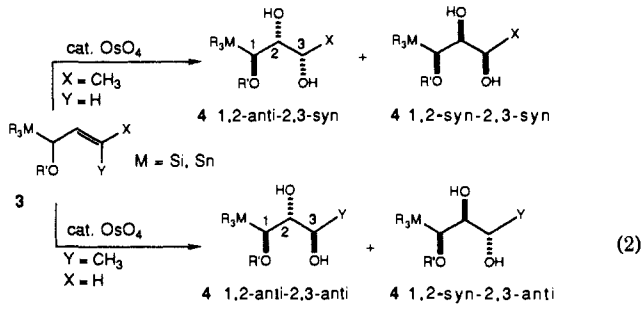
(3) For examples which follow the empirical rule, see: (a) Christ, W. J.; Cha, J. K.; Kishi, Y. *Tetrahedron Lett.* **1983**, *24*, 3947. (b) Christ, W. J.; Cha, J. K.; Kishi, Y. *Tetrahedron* **1984**, *40*, 2247.

(4) (a) Vedejs, E.; Dent, W. H., III *J. Am. Chem. Soc.* **1989**, *111*, 6861. (b) Danishefsky, S. J.; DiNinno, M. P.; Schulte, G. *J. Am. Chem. Soc.* **1988**, *110*, 3925. (c) Vedejs, E.; McClure, C. K. *J. Am. Chem. Soc.* **1986**, *108*, 1094.

(5) (a) Houk, K. N.; Duh, H.-Y.; Wu, Y.-D.; Moses, S. R. *J. Am. Chem. Soc.* **1986**, *108*, 2754. (b) Houk, K. N.; Moses, S. R.; Wu, Y.-D.; Rondan, N. G.; Jager, V.; Schohe, R.; Fronczek, F. *J. Am. Chem. Soc.* **1984**, *106*, 3880.

0002-7863/90/1512-4873$02.50/0

Table II. Diastereoselective Vicinal Hydroxylation of Chiral C1-Oxygenated (*E*)- and (*Z*)-Crotylsilanes/-Stannanes[a]



(2)

chiral silane	R′	R_3Si/SnR_3	X	Y	ratio **4** anti/syn[b]	% yield[c,d]
3a	Ac	$SiMe_3$	CH_3	H	4.5:1	63
3b	Ac	$SiEt_3$	CH_3	H	4.6:1	91
3c	Ac	Si^tBuMe_2	CH_3	H	7.0:1	61
3d	Ac	Si^tBuMe_2	H	CH_3	1.4:1	94
3e	H	$SiMe_3$	CH_3	H	27:1	60[e]
3f	H	Si^tBuMe_2	CH_3	H	120–147:1	62[e]
3g	H	Si^tBuMe_2	H	CH_3	4.7:1	45[e]
3h	H	$SiPhMe_2$	CH_3	H	33:1	77[e]
3i	Ac	$SnBu_3$	CH_3	H	7.0:1	72
3j	CH_2OCH_3	$SnBu_3$	CH_3	H	3.2:1	80[e]
3k	Si^tBuMe_2	$SiMe_3$	CH_3	H	10.3:1	92

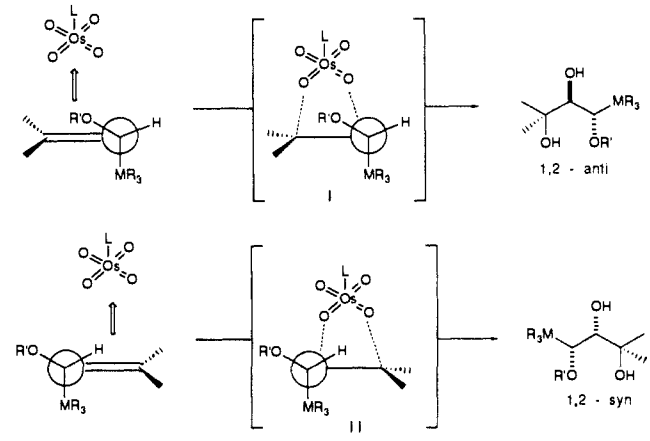
[a] The osmylation reactions were run in acetone/water [8:1; 5.0 mol % OsO_4; Me_3NO (2.2 equiv)] 0.2–0.5 M in substrate, and hydrolysis was carried out with an aqueous 10% $NaHSO_3$ solution. [b] All products were isolated as anti/syn diastereomers, and ratios were determined by integration of the C1 methine protons at 93.94 KG (400 MHz NMR) or by capillary GC analysis after acetylation. [c] All products exhibited the expected ^1H NMR (400 MHz), IR, and mass spectral characteristics. [d] All yields are based on pure materials isolated by chromatography on SiO_2 unless otherwise indicated. [e] Crude yield.

in the presence of catalytic amounts of osmium tetroxide to predominantly form 1,2-anti-1,2,3-triol units (eq 1 and 2). Interestingly, the magnitude but not the sense of induction was dramatically influenced by the type of substituent on the C1-oxygen. When R′ = H, the hydroxylation proceeded with virtual face specificity producing the triol products with anti/syn selectivities reaching 147:1 (see Tables I and II).[6]

To ensure steric bulk and strong σ electronic donation at the stereocenter, we examined the effect of trialkylsilane[7a] and tri-*n*-butylstannane groups.[7b] The operationally useful levels of selectivity obtained with these allylic metals may be more easily understood by considering the nature of the groups that compose the stereocenter and the principles that control the relative rates. The trialkylsilane (or stannane) being the largest and best σ donor group adopts an orientation antiperiplanar to the p-orbitals of the π system (and anti to the approaching electrophile), while the OR′ group adopts a position "inside" placing the remaining hydrogen substituent in the sterically least demanding position.[5a,b] Thus, the groups that compose the stereocenter are providing a conformational environment that provides a significant $\Delta\Delta G^{\ddagger}$ between the transition state structures I and II (Scheme I). As a result the relative rate for $k_{anti} \gg k_{syn}$ resulting in strong π-facial differentiation and the predominant formation of the anti product (Scheme I). These models can be used to describe the approach of the osmium reagent and the stereochemical outcome. Transition-state model I predicts the anti stereochemistry regardless of olefin geometry.[5]

The results obtained on a range of oxygen-substituted allylic silanes are summarized in Tables I and II. Under catalytic conditions [5.0 mol % OsO_4, $Me_3N \rightarrow O$ (2.2 equiv) in a solution

Scheme I



of acetone/water 8:1, 25 °C][3b,8] good yields and facial selectivities were obtained. The magnitude of π-face selectivity was shown to be dependent upon the size of the silyl group and the type of substituent on the oxygen atom. Highest anti stereoselection was obtained for the silanes with a free hydroxyl (R′ = H) and good to moderate selectivities for esters and silyl ethers. We began our study with 1-(acetyloxy)-2-propenyltrimethylsilane[9] (Scheme II and Table I, entry **1a**), which gave a 6.5:1 ratio (anti/syn) of diastereomers.[10] The reaction of 1-(acetyloxy)-2-propenyl-*tert*-butyldimethylsilane[11] (**1d**) under the standard conditions produced the expected triol products (**2**) in a combined yield of 68% as an 11.3:1 mixture of diastereomers (Table I).[12] An examination of a range of allylic systems with different silicon groups (Table I, entries **1a–g**) revealed that the anti stereoselectivities improved as the size of the trialkylsilicon group increased [$Me_3Si- \rightarrow Et_3Si- \rightarrow PhMe_2Si- \rightarrow {}^tBuMe_2Si- \rightarrow Ph_2MeSi-$]. A remarkable increase in selectivity (>97:3 anti/syn) was observed when the methallyl derivative bearing a free hydroxyl group was subjected to the osmylation conditions (compare entries **1h** and **1i**, Table I).

Osmium-catalyzed vicinal hydroxylations of *E* and *Z* disubstituted olefins **3** (eq 2) were also investigated.[13] For the cases

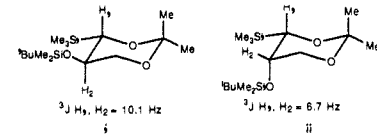
(6) The triacetates resulting from acylation (Ac_2O/NEt_3)/catalyst DMAP/CH_2Cl_2) of acetate diol **4c** and of triol **4f** revealed identical major diastereomers by ^1H NMR (400 MHz) and capillary GC.

(7) (a) Wierschke, S. G.; Chandraselchar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496. (b) Traylor, T. G.; Berwin, H. G.; Jerkunica, J.; Hall, M. L. *Pure Appl. Chem.* **1972**, *30*, 599.

(8) Ray, R.; Matteson, D. S. *Tetrahedron Lett.* **1980**, *21*, 449.

(9) (a) Panek, J. S.; Sparks, M. A. *Tetrahedron Lett.* **1987**, *28*, 4649. (b) Panek, J. S.; Sparks, M. A. *J. Org. Chem.* **1989**, *54*, 2034. (c) For the preparation of 1-hydroxyallylic silanes, see: Danheiser, R. L.; Fink, D. M.; Okano, K.; Tsai, Y.-H.; Szczepanski, S. W. *Org. Synth.* **1987**, *66*, 14. Danheiser, R. L.; Fink, D. M.; Okano, K.; Tsai, Y.-H.; Szczepanski, S. W. *J. Org. Chem.* **1985**, *50*, 5393.

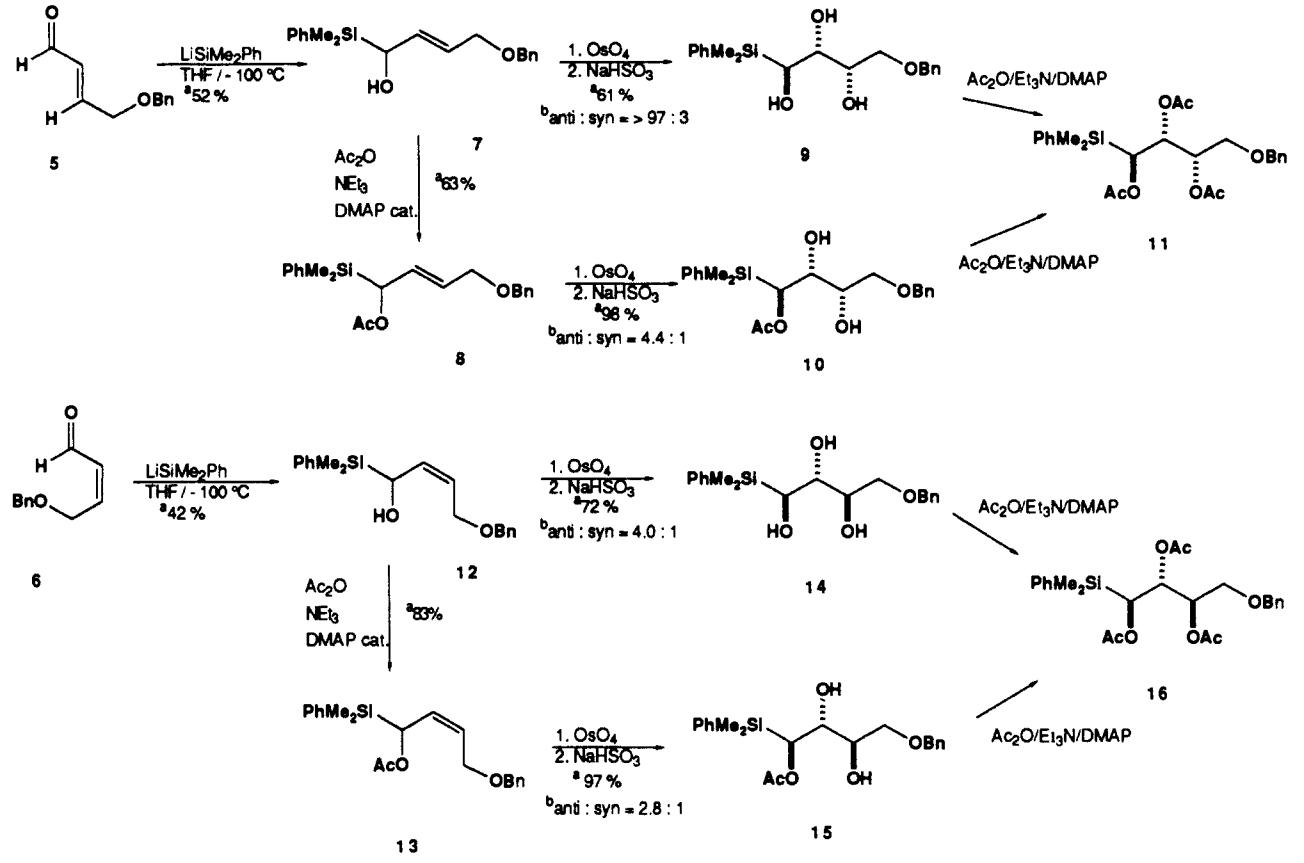
(10) The stereochemistry of the major (1,2-anti) and minor (1,2-syn) stereoisomers was determined by measurement and comparison of the $^3J_{H1,H2}$ values for the 1,3-dioxanes *trans*-**i** and *cis*-**ii** prepared from the vicinal hydroxylation products of 1-(benzoyloxy)-1-(trimethylsilyl)-2-propene (see Table I, entry **1g**; dioxane *trans*-**i** was prepared from compound *anti*-**2g** and dioxane *cis*-**ii** was prepared from *syn*-**2g**.



(11) Prepared in 50% yield from the *tert*-butyldimethylsilyl ether by reverse Brook rearrangement (*tert*-butyllithium 1.5 equiv; 0.2 M THF, 10% TMEDA; −78 → −30 °C; 40 min) and acylation (Ac_2O/catalyst DMAP/NEt_3/CH_2Cl_2; 85% yield). See (a) Brook, A. G.; Bassindale, A. R. Molecular Rearrangements of Organosilicon Compounds. In Rearrangements in Ground and Excited States; de Mayo, P., Ed.; New York, 1980; Essay 9, (b) Ireland, R. E.; Varney, M. D. *J. Am. Chem. Soc.* **1984**, *106*, 3668. (c) Scheller, M. E.; Frei, B. *Helv. Chim. Acta* **1985**, *68*, 44. (d) Scheller, M. E.; Schweitzer, W. B.; Frei, B. *Ibid.* **1989**, *72*, 264.

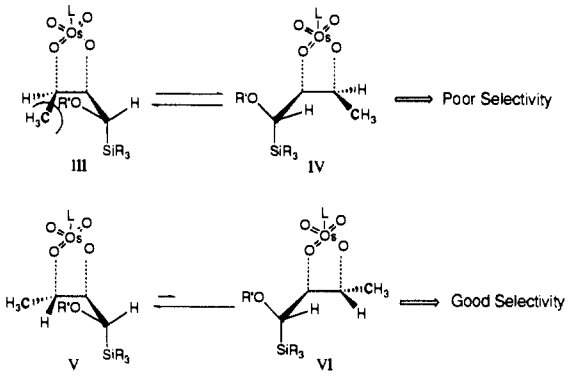
(12) To underscore the unusual nature of the osmylation reactions, when the experiment was conducted under the Sharpless "slow addition conditions", the expected triol was produced but with reduced stereoselectivity (1-(benzoyloxy)-2-propenyltrimethylsilane underwent vicinal hydroxylation with 4.0:1 anti:syn diastereoselectivity when subjected to standard conditions but with 2.7:1 selectivity under the Sharpless conditions). See: Wai, J. S. M.; Markó, I.; Svendsen, J. S.; Finn, M. G.; Jacobsen, E. N.; Sharpless, K. B. *J. Am. Chem. Soc.* **1989**, *111*, 1123.

Scheme II[a]



[a] Legend: (a) all yields are based on pure materials isolated by chromatography on SiO_2; (b) ratios determined by ^1H NMR or capillary GC analyses.

Scheme III



examined, the anti stereochemistry predominated, and substrates possessing larger silyl groups gave higher selectivities. Once again, excellent levels of selectivity were obtained for (*E*)-crotylsilanes bearing a free hydroxyl group (Table II, entries **3e**, **3f**, **3h**). The (*Z*)-crotylsilanes gave lower selectivities (Table II, entries **3d**, **3g**). The eroded facial selectivities for the *Z* stereoisomers may have resulted from a steric destabilizing interaction between the vinyl methyl and the C–OR' substituent eclipsing the π-system (see Scheme III). The facial bias is presumably arising from the stabilization of conformer V. Therefore, steric interaction for the (*Z*)-alkenes (**3d** and **3g**, Table II) lowers the $\Delta\Delta G^{\ddagger}$ between rotamers III and IV resulting in diminished face selectivity. This destabilizing interaction is less severe for the E stereoisomers (see rotamers V and VI).

Scheme II describes the vicinal hydroxylation of hetero-substituted allylic systems that contain an additional oxygenation at the C4-position. In these examples both *E* and *Z* disubstituted olefins were readily available through the addition of lithium dimethylphenylsilane[14] to the corresponding (*E*)- and (*Z*)-4-(benzyloxy)-2-butenals.[15] For the C4-oxygenated cases, the same trend and similar selectivities were observed. The sense of diastereoface selectivity was confirmed for both *E* allylic silanes **7** and **8** and *Z* allylic silanes **12** and **13**. Under standard acylation conditions [Ac_2O (6 equiv), Et_3N (8 equiv), catalytic DMAP, CH_2Cl_2], triol **9** and diol **10** were converted to the identical major 1,2-*anti*-2,3-*syn*-triacetate **11**. Similarly, **12** and **13** afforded the identical major 1,2-*anti*-2,3-*anti*-triacetate **16** after osmylation and acylation. This strategy represents a simple way in which the double bond stereochemistry helps to transform one stereocenter into 1,2-*anti*-2,3-*syn*- and 1,2-*anti*-2,3-*anti*-1,2,3,4-tetraol units **11** and **16** that are completely differentiated at each terminus.

In conclusion, the vicinal hydroxylation of chiral hetero-substituted allylic silanes by osmium tetroxide provides convenient access to an intriguing and potentially useful class of polyoxygenated organometallic compounds with excellent levels of stereoselectivity. Our results indicate that the size of the silyl group affects the level of selectivity although to a much lesser extent than when a free hydroxyl is present at the C-1 stereocenter. Our transition-state model (Scheme I) is somewhat different than that

(13) The (*E*)-crotyl compounds were obtained from commercially available *trans*-2-buten-1-ol (*E*:*Z* = 95:5 by capillary GC, Fluka); the (*Z*)-crotyl compounds were obtained via silylation of 2-butyn-1-ol (trialkylchlorosilane/imidazole/DMF/room temperature), followed by reduction with Lindlar's catalyst (10% by weight/1 atm H_2/hexane/room temperature, *Z*:*E* = 82:18 by capillary GC), before [1,2]-silyl-Wittig rearrangement.

(14) (a) Ager. D. J.; Fleming, I.; Patel, S. K. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2520. (b) Burke, S. D.; Saunders, J. O.; Oplinger, J. A.; Murtiashaw, C. W. *Tetrahedron Lett.* **1985**, *26*, 1131.

(15) Danishefsky, S. J.; Regan, J. *Tetrahedron Lett.* **1981**, *22*, 3919. The starting (*E*)-aldehyde was prepared by oxidation of the corresponding (*Z*)-alcohol with PCC on silica gel (1:2 w/w) in CH_2Cl_2 (64–75% yield; see: Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, *16*, 2647) or by Swern oxidation (99% yield; see: Swern, D.; Omura, K. *Tetrahedron* **1978**, *34*, 1651). Oxidation with MnO_2 in CH_2Cl_2 proceeded slowly to give variable mixtures of both (*E*)- and (*Z*)-aldehydes. Through the Swern oxidation isomerically pure (*Z*)-aldehyde could be obtained if the reaction was stopped promptly (10.0 min) after quenching with triethylamine.

of Vedejs[4] and closely resembles the staggered transition-state model used by Houk[5] and Curran[2f] to rationalize selectivities in nitrile oxide cycloadditions. It also does not fit the pattern of "oxygen avoidance" originally deduced by Kishi.[3] In addition, by positioning the largest group (R_3M) perpendicular to the adjacent π system and anti to the approaching electrophile it resembles the Felkin–Anh variant of Cram's[16] rule for *nucleophilic additions* to carbonyl compounds. Clearly, the stereoselectivities are not solely a function of hyperconjugative effects but rather a combination of several factors. The continued exploration of the utility of heteroatom-substituted allylic silanes and their applications are currently underway and will be reported in due course.

Experimental Section[17]

General Experimental Procedure for the Catalytic Osmylations of Chiral C1-Oxygenated Allylic Silanes 1a–h, 3a–d, 3i–k (Tables I and II), Depicted for 1a. A solution of the 1-(acetyloxy)-1-(trimethylsilyl)-2-propene (**1a**) (1.0 mmol) in acetone/water (8:1, 2.5 mL) was stirred at room temperature and treated with trimethylamine-*N*-oxide dihydrate (2.2 mmol, 244.5 mg). To this biphasic reaction system a 0.157 M solution of osmium tetroxide in distilled *tert*-butyl alcohol[17b] (0.05 mmol, 0.32 mL) was added. A yellow/orange color formed almost immediately after the addition of the osmium reagent. The reaction mixture was left stirring at room temperature for 1–2 h before being diluted with a 10% aqueous solution of sodium bisulfite (Aldrich, 5 mL). This new solution was left stirring for 10 min before extraction with ethyl acetate (3 × 10 mL). The combined organic layers were washed once with saturated brine, dried with magnesium sulfate, and filtered, and the solvent was removed under reduced pressure. The crude reaction mixture was flash-chromatographed on silica gel (petroleum ether/ethyl acetate eluant, 10–30% gradient) to afford 1-(acetyloxy)-1-(trimethylsilyl-2,3-propanediol (**2a**) as a mixture of 1,2-anti/syn diastereomers in 57% yield.

Experimental Procedure for the Catalytic Osmylation of Chiral C1-Oxygenated Allylic Silanes 1i, 3e–h, 7, 8, 12, and 13 (Tables I and II and Scheme II). For the 1-hydroxy allylic silanes an identical procedure was followed except that the extraction was performed with a 10% solution of isopropyl alcohol in chloroform. The resulting crude triols were pure by ^{1}H NMR (400 MHz) and were converted to their triacetates [$Ac_2O/Et_3N/CH_2Cl_2$/catalytic DMAP] before capillary GC analysis.

Spectral Data for Compounds 1a–i and 2a–i (Table I). 1-(Acetyloxy)-1-(trimethylsilyl)-2-propene (1a). See: Panek, J. S.; Sparks, M. A. *Tetrahedron Lett.* **1987**, *28*(*40*), 4649. Panek, J. S.; Sparks, M. A. *J. Org. Chem.* **1989**, *54*, 2034.

1-(Acetyloxy)-1-(trimethylsilyl)-2,3-propanediol (2a): 57% yield from **1a**; ^{1}H NMR (400 MHz, $CDCl_3$) (1,2-anti diastereomer) δ 4.67 (d, 1 H, H1, J = 8.4 Hz), 3.81 (ddd, 1 H, H2), 3.63 (dd, 1 H, H3a, $J_{H3a,H3b}$ = 12.1, $J_{H2,H3a}$ = 2.9 Hz), 3.48 (dd, 1 H, H3b, $J_{H2,H3b}$ = 5.5 Hz), 2.09 (s, 3 H, CH_3COO–), 0.12 (s, 9 H, Si-CH_3); (syn diastereomer) 4.85 (d, 1 H, H1, J = 3.6 Hz), 3.89 (ddd, 1 H, H2), 2.13 (s, 3 H, CH_3COO–), 0.13 (s, 9 H, Si-CH_3).

1-(Acetyloxy)-1-(triethylsilyl)-2-propene (1b): 81% yield from 1-(triethylsilyl)-2-propen-1-ol. See: Curran, D. P.; Gothe, S. A. *Tetrahedron* **1988**, *44*(*13*), 3945.

1-(Acetyloxy)-1-(triethylsilyl)-2,3-propanediol (2b): 67% yield from **1b**; ^{1}H NMR (400 MHz, $CDCl_3$) δ (1,2-anti diastereomer) 4.80 (d, 1 H, H1, $J_{H1,H2}$ = 7.9 Hz), 3.80 (ddd, 1 H, H2, $J_{H2,H3a}$ = 2.7, 4.9 Hz), 3.60 (dd, 1 H, H3a, $J_{H3a,H3b}$ = 12.0 Hz), 3.46 (dd, 1 H, H3b), 2.80 (2 br s, 2H, –OH), 2.08 (s, 3 H, CH_3COO–), 0.97 (q, 6 H, Si–CH_2–Me, J = 8.1 Hz), 0.67 (t, 9 H, $SiCH_2$–CH_3), (syn diastereomer) 5.01 (d, 1 H, H1, $J_{H1,H2}$ = 3.5 Hz); IR ($CHCl_3$) ν_{max} (cm^{-1}) (mixture of diastereomers) 3450, 2970, 2940, 2880, 1730, 1470, 1380, 1300, 1240, 1125, 1080, 1045, 620.

1-(Acetyloxy)-1-(dimethylphenylsilyl)-2-propene (1c): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.55 (m, 2 H, Ar-H), 7.36–7.41 (m, 3 H, Ar-H), 5.76–5.85 (ddd, 1 H, H2, $J_{H2,H1}$ = 5.68, $J_{H2,H3a}$ = 17.5, $J_{H2,H3b}$ = 1.6 Hz), 5.40 (dt, 1 H, H1, $J_{H1,H3}$ = 1.88 Hz), 4.99 (dd, 1 H, H3b, $J_{H3a,H3b}$ = 10.4 Hz), 4.96 (dd, 1 H, H3a), 2.07 (s, 3 H, CH_3COO–), 0.36 (s, 6 H, CH_3–Si).

1-(Acetyloxy)-1-(dimethylphenylsilyl)-2,3-propanediol (2c): 70% yield from **1c**; ^{1}H NMR (400 MHz, $CDCl_3$) δ (1,2-anti diastereomer) 7.55–7.52 (m, 2 H, Ar-H), 7.38–7.32 (m, 3 H, Ar-H), 4.82 (d, 1 H, H1, $J_{H2,H1}$ = 8.0 Hz), 3.75–3.70 (m, 1 H, H2), 3.51 (dd, 1 H, H3a, J =; J = Hz), 3.39 (dd, 1 H, H3b, J =; J = Hz), 2.04 (s, 3 H, CH_3COO–), 0.41, 0.38 (2s, 2 × 3H, CH_3–Si), (syn diastereomer) 5.05 (d, 1 H, H1, $J_{H2,H1}$ = 4.2 Hz).

1-(Acetyloxy)-1-(*tert*-butyldimethylsilyl)-2-propene (1d): 45% yield overall based on ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 (ddd, 1 H, H2, $J_{H1,H2}$ = 1.8, J = 1.5 Hz), 5.35 (dt, 1 H, H3a, $J_{H3a,H3b}$ = 5.6 Hz), 5.01 (dd, 1 H, H3b, J = 6.6 Hz), 4.98 (d, 1 H, H1), 2.10 (s, 3 H, CH_3COO–), 0.93 (s, 9 H, t-Bu), 0.04 (s, 3 H, CH_3^a–Si), 0.01 (s, 3 H, CH_3^b–Si); ^{13}C NMR (400 MHz, $CDCl_3$) δ 170.68 135.59 111.17 68.80 26.78 25.63 –3.62 –7.48 –8.64; IR ($CHCl_3$) ν_{max} (cm^{-1}) 2960, 2940, 2890, 2860, 1700, 1640, 1475, 1375, 1260, 1240, 1020, 990, 910, 890, 850, 810, 800, 780, 675.

1-(Acetyloxy)-1-(*tert*-butyldimethylsilyl)-2,3-propanediol (2d): 70% yield from **3a**; ^{1}H NMR (400 MHz, $CDCl_3$) δ (1,2-anti diastereomer) 4.86 (d, 1 H, H1, $J_{H1,H2}$ = 6.5 Hz), 3.83 (td, 1 H, H2, J = 6.4 Hz), 3.60 (dd, 1 H, H3a, $J_{H3a,H2}$ = 2.8, $J_{H3a,H3b}$ = 12.0 Hz), 3.48 (dd, 1 H, H3b, J = 5.6 Hz), 2.08 (s, 3 H, CH_3COO–), 0.90 (s, 9 H, t-Bu), 0.08–0.11 (2s, 6 H, CH_3–Si), (syn diastereomer) 5.04 (d, 1 H, H1, $J_{H1,H2}$ = 2.1 Hz); IR ($CHCl_3$) ν_{max} (cm^{-1}) (mixture of diastereomers) 3400, 2940, 2890, 2860, 1730, 1470, 1420, 1400, 1250, 1100, 1030, 970, 945, 855, 810, 780, 670.

1-(Acetyloxy)-1-(diphenylmethylsilyl)-2-propene (1e): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.64 (2m, 4 H, Ar-H), 7.37–7.48 (2m, 6 H, Ar-H), 5.89 (ddd, 1 H, H2, $J_{H1,H2}$ = 5.3, $J_{H2,H3a}$ = 1.54, $J_{H2,H3b}$ = 1.54 Hz), 5.82 (dt, 1 H, H3, $J_{H3a,H3b}$ = 5.4 Hz), 5.05 (dt, 1 H, H1, $J_{H1,H3a}$ = 1.2, $J_{H1,H3b}$ = 1.8 Hz), 5.01 (dt, 1 H, H3), 2.06 (s, 3 H, CH_3COO–), 0.67 (s, 3 H, CH_3-Si).

1-(Acetyloxy)-1-(diphenylmethylsilyl)-2,3-propanediol (2e): 58% yield from **1e**; ^{1}H NMR (400 MHz, $CDCl_3$) δ (1,2-anti diastereomer) 7.5–7.7 (m, 4 H, Ar-H), 7.3–7.5 (m, 6 H, Ar-H), 5.25 (d, 1 H, H1, $J_{H1,H2}$ = 8.1 Hz), 3.83 (ddd, 1 H, H3a, $J_{H3a,H3b}$ = 12.0 Hz), 2.70 (br s, 2 H, –OH), 1.92 (s, 3 H, CH_3COO–), 0.75 (s, 3 H, CH_3–Si), (syn diastereomer) 5.45 (d, 1 H, H1, $J_{H1,H2}$ = 3.1 Hz), IR ($CHCl_3$) ν_{max} (cm^{-1}) (mixture of diastereomers) 3450, 3080, 3060, 3020, 2960, 2900, 1730, 1595, 1430, 1375, 1260, 1240, 1120, 1070, 1050, 1030, 975, 840, 795, 740, 705, 655.

1-[(Triethylsilyl)oxy]-1-(*tert*-butyldimethylsilyl)-2-propene (1f): 82% yield overall based on methallyl alcohol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 (ddd, 1 H, H2), 4.98 (dd, 1 H, H3b, $J_{H3a,H3b}$ = 14.4 Hz), 4.84 (dd, 1 H, H3a), 4.07 (d, 3 H, H1, $J_{H1,H2}$ = 6.4 Hz), 0.8–1.0 (m, 15H, $-CH_2$–Si and t-BuSi), 0.4–0.6 (q, 6 H, CH_3–), –0.02, –0.06 (2s, 2 × 3H, CH_3–Si).

1-[(Triethylsilyloxy]-1-(*tert*-butyldimethylsilyl)-2,3-propanediol (2f): 36% yield from **1f**; ^{1}H NMR (400 MHz, $CDCl_3$) δ (1,2-anti diastereomer) 3.90 (d, 1 H, H1, $J_{H1,H2}$ = 2.2 Hz), 3.81 (m, 1 H), 3.68 (m, 1 H), 2.68 (br s, 1 H, –OH), 2.57 (br s, 1 H, –OH), 1.05–0.95 (t, 9 H, CH_3–C–Si), 0.92 (s, 9 H, t-BuSi), 0.63–0.71 (q, 6H, $-CH_2$–Si), 0.05, 0.03 (2s, 2 × 3H, CH_3–Si).

1-(Trimethylsilyl)-1-(benzoyloxy)-2-propene (1g): 60.2% yield from standard acylation [benzoyl chloride/pyridine/THF/catalytic DMAP] of 1-hydroxy-2-propenetrimethylsilane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.12 (s, 9 H, CH_3–Si), 5.02 (d, 1 H, H3b, J = 10.8), 5.09 (dd, 1 H, H3a, J = 17.2), 5.45 (m, 1 H, H1, J = 1.8, 2.0, 5.5 Hz), 5.96 (ddd, 1 H, H2, J = 6.0 Hz), 7.45 (m, 1 H, Ar-H), 7.55 (m, 2 H, Ar-H), 8.08 (d, 2 H, Ar-H).

***anti*-1-(Trimethylsilyl)-1-(benzoyloxy)propane-2,3-diol (2g):** 67.5% yield from catalytic osmylation of olefin under Sharpless slow addition conditions—see Wai, J. S. M.; Marko', I.; Svendsen, J. S.; Finn, M. G.; Jacobsen, E. N.; Sharpless, K. B. *J. Am. Chem. Soc.* **1989**, *111*(*3*), 1123; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.19 (s, 9 H, CH_3–Si), 2.55–2.63 (2 br s, 2 H, –OH), 3.57 (dd, 1 H, H3a, $J_{H3a,H2}$ = 4.8 Hz), 3.69 (dd, 1 H, H3b, $J_{H3a,H3b}$ = 12.1 Hz, $J_{H3b,H2}$ = 2.8 Hz), 3.96 (m, 1 H, H2), 4.92 (d, 1 H, H1, $J_{H1,H2}$ = 7.9 Hz), 7.46 (m, 2 H, *o*-Ar-H), 7.59 (m, 1 H, *p*-Ar-H), 8.03 (d, 2 H, *m*-Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.09; 133.33, 129.72, 129.68, 128.52, 80.53, 72.35, 68.50, 63.13, –2.67; IR ($CHCl_3$) ν_{max} (cm^{-1}) 3420, 2975, 2920, 1740, 1460, 1335, 1280, 1260, 1190, 1145, 1080, 1040, 900, 720.

(16) (a) Eliel, E. L. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academis Press: New York, 1983; Vol. 2, pp 125–156. (b) Morrision, J. D.; Mosher, H. S. *Asymmetric Organic Reactions*; American Chemical Society: Washington, DC, 1976.

(17) (a) Proton NMR spectra were obtained on either a Varian XL-400 or a JOEL GSX-270, and carbon-13 spectra were recorded on a Varian XL-400 at 100.00 MHz. Infrared spectra (IR) were recorded on a Perkin-Elmer 1310 infrared spectrophotometer. Electron impact mass spectral [EIMS], chemical ionization mass spectra [CIMS], and FAB (in a *p*-nitrobenzyl alcohol matrix) measurements were obtained on a Finnegan MAT-90. Melting points were recorded on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Gas chromatographic analysis was performed on a Hewlett-Packard 5890A chromatograph. All extraction and chromatographic solvents, acetone, ethyl acetate, ether, methylene chloride, chloroform, and isopropyl alcohol were distilled prior to use. Benzene, tetrahydrofuran, and ether were distilled from benzophenone ketyl before use. *tert*-Butyl alcohol was distilled from $KMnO_4$ prior to use in the osmium tetraoxide solutions.[17b] All other solvents and reagents were used as received from commercial sources. (b) Daniels, R.; Fisher, J. L. *J. Org. Chem.* **1963**, *28*, 321.

***syn*-1-(Trimethylsilyl)-1-(benzoyloxy)propane-2,3-diol (2g)**: 25.0% yield from catalytic osmylation of olefin under Sharpless slow addition conditions—see Wai, J. S. M.; Marko', I.; Svendsen, J. S.; Finn, M. G.; Jacobsen, E. N.; Sharpless, K. B. *J. Am. Chem. Soc.* **1989**, *111(3)*, 1123; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.20 (s, 9 H, CH_3–Si), 2.98–3.92 (2 br s, 2 H, –OH), 3.49 (dd, 1 H, H3a, $J_{H3a,H2}$ = 5.9 Hz), 3.57 (dd, 1 H, H3b, $J_{H3a,H3b}$ = 11.2 Hz, $J_{H3b,H2}$ = 6.8 Hz), 4.01 (m, 1 H, H2), 5.11 (d, 1 H, H1, $J_{H1,H2}$ = 3.5 Hz), 7.45–7.49 (m, 2 H, Ar-H), 7.58–7.62 (m, 1 H, Ar-H), 8.07 (d, 2 H, *m*-Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.62, 133.10, 129.88, 129.74, 129.65, 129.58, 80.47, 72.99, 70.14, 63.53, –2.66; IR ($CHCl_3$) ν_{max} (cm^{-1}) 3420, 2975, 2920, 1720, 1630, 1610, 1460, 1410, 1335, 1280, 1260, 1190, 1145, 1105, 1080, 1035, 900, 720.

1-(Acetyloxy)-1-(trimethylsilyl)-2-methyl-2-propene (1h): see Panek, J. S.; Sparks, M. A. *J. Org. Chem.* **1989**, *54*, 2034; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.98 (s, 1 H, H1), 4.70–4.67 (2d superimposed, H3a and b, J = 7.8 Hz), 2.05 (s, 3 H, CH_3COO–), 1.68 (s, 3 H, CH_3–), 0.04 (s, 9 H, CH_3–Si).

1-(Acetyloxy)-1-(trimethylsilyl)-2-methyl-2,3-propanediol (2h): 63% yield from **1h**; ^{1}H NMR (400 MHz, $CDCl_3$) δ (1,2-anti diastereomer) 4.70 (s, 1 H, H1), 3.34 (d, 1 H, H3a, $J_{H3a,H3b}$ = 10.6 Hz), 3.17 (d, 1 H, H3b), 2.11 (s, 3 H, CH_3COO–), 1.15 (s 3 H, CH_3), 0.15 (s, 9 H, CH_3–Si), 3.0 (br s, –OH), 2.63 (br s, –OH), (syn diastereomer) 4.88 (s, 1 H, H1), 3.33 (d, 1 H, H3a, $J_{H3a,H3b}$ = 7.5 Hz), 3.17 (d, not seen), 2.15 (s, 3 H, CH_3COO–), 1.24 (s 3 H, CH_3), 0.16 (s, 9 H, CH_3–Si).

1-(Trimethylsilyl)-2-methyl-2-propene-1-ol (1i): 92% yield from methallyl alcohol; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.79 (d, 1 H, H3a), 4.75 (d, 1 H, H3b, $J_{H3a,H3b}$ = 1.35 Hz), 3.87 (s, 1 H, H1), 1.71 (s, 3 H, CH_3–), 0.07 (s, 9 H, CH_3–Si), IR (neat) ν_{max} (cm^{-1}) (mixture of diastereomers) 3450, 2960, 2920, 2900, 2860, 2830, 1640, 1450, 1420, 1180, 1290, 1250, 1150, 1040, 1030, 1010, 990, 960, 870, 850, 780, 755, 725, 695, 655, 605.

1-(Trimethylsilyl)-2-methyl-1,2,3-propanetriol (2i): 65% yield from **1i**; ^{1}H NMR (400 MHz, $CDCl_3$) δ (1,2-anti diastereomer) 3.76 (d, 1 H, H3a, $J_{H3a,H3b}$ = 11.0 Hz), 3.46 (d, 1 H, H3b), 3.32 (s, 1 H, H1), 1.28 (s, 3 H, CH_3–), 0.15 (s, 9 H, CH_3–Si), IR ($CHCl_3$) ν_{max} (cm^{-1}) (mixture of diasteromers) 3600, 3450, 2960, 2880, 1470, 1380, 1355, 1250, 1120, 1045, 1000, 915, 860, 850, 820, 620.

Spectral Data for Compounds 3a–k and 4a–k (Table II). (*E*)-1-(Acetyloxy)-1-(trimethylsilyl)-2-butene (3a): 86% overall yield from silyl ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.46 (m, 2 H, H1 and H2), 5.10 (m, 1 H, H3), 2.07 (s, 3 H, CH_3COO–), 1.69 (d, 3 H, CH_3–, $J_{H3,H4}$ = 3.4 Hz), 0.05 (s, 9 H, CH_3–Si).

1-(Acetyloxy)-1-(trimethylsilyl)-2,3-butanediol (4a): 62% yield from **3a**; ^{1}H NMR (400 MHz, $CDCl_3$) δ (1,2-anti-2,3-syn diastereomer) 4.58 (d, 1 H, H1, $J_{H1,H2}$ = 9.7 Hz), 3.63 (q, 1 H, H3), 3.48 (dd, 1 H, H2, $J_{H2,H3}$ = 1.5 Hz), 2.10 (s, 3 H, CH_3COO–), 1.24 (d, 3 H, CH_3–, $J_{H3,H4}$ = 6.51 Hz), 0.12 (s, 9 H, CH_3–Si), (syn-syn diastereomer) 4.90 (d, 1 H, H1, $J_{H1,H2}$ = 3.1 Hz), 3.70 (t, 1 H, H1), 1.20 (d, 3 H, CH_3–, J = 7.2 Hz), 0.13 (s, 9 H, CH_3–Si); IR ($CHCl_3$) ν_{max} (cm^{-1}) (mixture of diastereomers) 3450, 2930, 2900, 2875, 1700, 1355, 1235, 1110, 1040, 1010, 980, 950, 830, 740, 680, 600; EIHRMS required 220.1131, found 220.1113.

(*E*)-1-(Acetyloxy)-1-(triethylsilyl)-2-butene (3b): 66% overall yield from silyl ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.47 (m, 2 H, H1 and H2 superimposed), 5.26 (m, 1 H, H3), 2.04 (s, 3 H, CH_3COO–), 1.67 (d, 3 H, CH_3–, $J_{H3,H4}$ = 3.6 Hz), 0.95 (t, 9 H, CH_3–C–Si), 0.58 (q, 6 H, CH_2–Si); ^{13}C NMR (100 MHz, $CDCl_3$) d 170.84, 127.97, 124.06, 68.66, 21.18, 17.86, 7.21, 1.69; IR (neat) ν_{max} (cm^{-1}) 2960, 2920, 2880, 1750, 1470, 1440, 1420, 1370, 1230, 1070, 1075, 1015, 970, 810, 740, 690, 610.

1-(Acetyloxy)-1-(triethylsilyl)-2,3-butanediol (4b): 91% yield from **3b**; ^{1}H NMR (400 MHz, $CDCl_3$) (1,2-anti-2,3-syn diastereomer) δ 4.67 (d, 1 H, H1, $J_{H1,H2}$ = 10.1 Hz), 3.54 (q, 1 H, H3, $J_{H3,H4}$ = 6.45 Hz), 3.43 (br d, 1 H), 2.07 (s, 3 H, CH_3COO–), 1.21 (d, 3 H, CH_3–), 0.95 (t, 9 H, CH_3–C–Si, J = 7.8 Hz), 0.65 (q, 6 H, CH_2–Si, J = 8.0 Hz), (syn-syn diastereomer) 5.04 (d, 1 H, H1, $J_{H1,H2}$ = 2.5 Hz), IR ($CHCl_3$) ν_{max} (cm^{-1}) 3550, 2960, 2940, 2920, 2880, 1720, 1465, 1375, 1295, 1245, 1185, 1130, 1105, 1070, 1050, 1020, 1010, 1000, 980, 915, 830, 610.

(*E*)-1-(Acetyloxy)-1-(*tert*-butyldimethylsilyl)-2-butene (3c): 62% yield overall from silyl ether—see Ireland, R. E.; Varney, M. D. *J. Am. Chem. Soc.* **1984**, *106*, 3668; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.51–5.47 (m, 2 H), 5.30–5.25 (m, 1 H), 2.05 (s, 3 H, CH_3COO–), 169 (d, 3 H, CH_3–, J = 3.5 Hz), 0.90 (s, 9 H, t-Bu), 0.02, –0.01 (2s, 2 × 3 H, CH_3–Si).

1-(Acetyloxy)-1-(*tert*-butyldimethylsilyl)butane-2,3-diol (4c): 61% yield from **3c**; ^{1}H NMR (400 MHz, $CDCl_3$) (1,2-anti-2,3-syn diastereomer) δ 4.71 (d, 1 H, H1, $J_{H1,H2}$ = 9.7 Hz), 3.62 (dq, 1 H, H3, $J_{H3,H4}$ = 8.0 Hz), 3.49 (dd, 1 H, H2), 2.17 (s, 3 H, CH_3COO–), 1.23 (d, 3 H, CH_3–), 0.91 (s, 9 H, t-Bu), 0.09, 0.11 (2s, 6 H, CH_3–Si), (syn-syn diastereomer) 5.08 (d, 1 H, H1, $J_{H1,H2}$ = 2.6 Hz), 3.41 (dd, 1 H, H2, $J_{H2,H3}$ = 4.4 Hz); IR ($CHCl_3$) ν_{max} (cm^{-1}) (mixture of diastereomers) 3550, 3060, 2990, 2960, 2940, 2900, 2860, 1720, 1470, 1425, 1375, 1270, 1260, 1185, 1125, 1100, 1070, 1050, 1025, 1000, 980, 900, 850, 830, 810, 610.

(*Z*)-1-(Acetyloxy)-1-(*tert*-butyldimethylsilyl)-2-butene (3d): 65% yield overall from silyl ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.59 (d, 1 H, H1, $J_{H1,H2}$ = 10.3 Hz), 5.47 (dq, 1 H, H3, $J_{H3,H4}$ = 6.3 Hz), 5.37 (ddd, 1 H, H2, $J_{H2,H3}$ = 1.5, $J_{H2,H4}$ = 0.54 Hz), 2.00 (s, 3 H, CH_3COO–), 169 (d, 3 H, CH_3–), 0.90 (s, 9 H, t-Bu), 0.02, –0.05 (2s, 2 × 3H, CH_3–Si).

1-(Acetyloxy)-1-(*tert*-butyldimethylsilyl)butane-2,3-diol (4d): 94% yield from **3d**; ^{1}H NMR (400 MHz, $CDCl_3$) (1,2-anti-2,3-anti diastereomer) δ 4.96 (d, 1 H, H1, $J_{H1,H2}$ = 6.2 Hz), 3.74–3.84 (2m, 2 H, H2 and H3), 2.03 (s, 3 H, CH_3COO–), 1.17 (d, 3 H, CH_3, $J_{H3,H4}$ = 6.4 Hz), 0.88 (s, 9 H, t-Bu), 0.09, 0.06 (2s, 2 × 3H, CH_3–Si); (syn-anti diastereomer) 5.18 (d, 1 H, H1, $J_{H1,H2}$ = 1.1 Hz), 3.23–3.37 (m, 2 H, H2 and H3), 2.11 (s, 3 H, CH_3COO–), 1.24 (d, 3 H, CH_3–, $J_{H3,H4}$ = 5.8 Hz), 0.86 (s, 9 H, t-Bu), 0.13, 0.06 (2s, 2 × 3 H, CH_3–Si); IR ($CHCl_3$) ν_{max} (cm^{-1}) (mixture of diastereomers) 3450, 2960, 2940, 2900, 2860, 1730, 1720, 1470, 1410, 1400, 1350, 1250, 1160, 1070, 1025, 1000, 970, 930, 900, 840, 830, 810, 780, 670.

1-(Trimethylsilyl)-2-buten-1-ol (3e): 89% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.63 (dd, 1H, H2, $J_{H2,H3}$ = 15.2 Hz), 5.55–5.46 (m, 1 H, H3), 3.92 (d, 1 H, H1, $J_{H2,H1}$ = 6.7 Hz), 1.72 (d, 3 H, CH_3–, $J_{H3,H4}$ = 5.8 Hz), 0.04 (s, 9 H, CH_3–Si).

1-(Trimethylsilyl)-1,2,3-butanetriol (4e): (60% yield from **3e**; ^{1}H NMR (400 MHz, $CDCl_3$) δ (1,2-anti-2,3-syn diastereomer) 0.09 (s, 9 H, H3a, CH_3–Si), 1.22 (d, 3 H, CH_3–, J = 6.4 Hz), 3.55 (m, 1 H), 3.58 (d, 1 H, J = 4.3 Hz), 4.05 (m, 1 H, J = 60 Hz), IR ($CHCl_3$) ν_{max} (cm^{-1}) 3450, 2960, 2900, 2260, 1380, 1250, 1180, 1125, 1100, 1055, 985, 915, 850, 650, 620; ^{13}C NMR (67.9 MHz, $CDCl_3$) d 75.15, 70.50, 69.41, 20.00 –3.03; FABMS (*p*-nitrobenzyl alcohol matrix) M^+ = 178.

(*E*)-1-(*tert*-Butyldimethylsilyl)-2-buten-1-ol (3f): 66% yield overall from silyl ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.70–5.60 (m, 1 H), 5.53–5.43 (m, 1 H), 4.05 (d, 1 H, H1, $J_{H1,H2}$ = 6.9 Hz), 1.71 (d, 3 H, CH_3–, $J_{H3,H4}$ = 6.4 Hz), 0.95 (s, 9 H, t-Bu), 0.01, –0.06 (2s, 2 × 3 H, CH_3–Si).

1-(*tert*-Butyldimethylsilyl)-1,2-*anti*-2,3-*syn*-butanetriol (4f): 61% yield from **3f**; ^{1}H NMR (400 MHz, $CDCl_3$) (1,2-anti-2,3-syn diastereomer) δ 4.11 (q, 1 H, H3, $J_{H3,H4}$ = 6.4 Hz), 3.83 (d, 1 H, J = 3.2 Hz), 3.43 (d, 1 H, J = 2.25 Hz), 1.22 (d, 3 H, CH_3–), 0.91 (s, 9 H, t-Bu), 0.11, –0.03 (2s, 2 × 3 H, CH_3–Si).

(*Z*)-1-(*tert*-Butyldimethylsilyl)-2-buten-1-ol (3g): 68% yield overall from silyl ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.56 (t, 1 H, J = 9.3 Hz), 5.44 (m, 1 H), 4.46 (d, 1 H, H1, $J_{H1,H2}$ = 10.3 Hz), 1.62 (dd, 3 H, CH_3–, $J_{H3,H4}$ = 6.7 Hz), 0.94 (s, 9 H, t-Bu), 0.03, –0.07 (2s, 2 × 3 H, CH_3–Si), IR ($CHCl_3$) ν_{max} (cm^{-1}) 3450, 2980, 2950, 2900, 2875, 1715, 1700, 1670, 1650, 1480, 1475, 1450, 1415, 1400, 1375, 1265, 1100, 1015, 980, 850, 820, 800, 770, 690.

1-(*tert*-Butyldimethylsilyl)butane-1,2,3-triol (4g): 61% yield from **3g**; ^{1}H NMR (400 MHz, $CDCl_3$) (1,2-anti-2,3-anti diastereomer) δ 3.98 (m, 1 H), 3.72 (d, 1 H, H1, J < 1 Hz), 3.74–3.70 (m, 1 H), 2.90–2.65 (3 br s, 3 × 1 H, –OH), 1.30 (d, 3 H, CH_3–), 0.96 (s, 9 H, t-Bu), 0.11, 0.06 (2s, 2 × 3 H, CH_3–Si).

(*E*)-1-(Phenyldimethylsilyl)-2-buten-1-ol (3h): 60% yield; see Burke, S. D.; Saunders, J. O.; Oplinger, J. A.; Murtiashaw, C. W. *Tetrahedron Lett.* **1985**, *26(9)*, 1131.

1-(Phenyldimethylsilyl)-1,2,3-butanetriol (4h): 77% yield from **3h**; ^{1}H NMR (400 MHz, $CDCl_3$) (1,2-anti diastereomer) δ 7.59–7.57 (m, 2 H, Ar-H), 7.41–7.36 (m, 3 H, Ar-H), 3.98 (m, 1 H, H3, J = 6.4, 1.7, 2.1 Hz), 3.76 (d, 1 H, H1, J = 5.1 Hz), 3.45 (m, 1 H, H2, J = 0.7 Hz), 2.60, 2.20, 1.66 (3 br s, 3 × 3H, –OH), 1.17 (d, 3 H, CH_3–, J = 6.4 Hz), 0.43, 0.42 (2s, 2 × 3 H, CH_3–Si); IR ($CHCl_3$) ν_{max} (cm^{-1}) 3460, 2960, 2900, 1360, 1285, 1250, 1110, 1050, 985, 900, 845, 820, 760, 710.

(*E*)-1-(Acetyloxy)-1-(tri-*n*-butylstannyl)-2-butene (3i): 53% yield overall based on crotonaldehyde; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73–5.65 (m, 1 H), 5.45–5.34 (m, 1 H), 5.21 (dt, 1 H, H1, $J_{H1,H2}$ = 7.3, $J_{H1,H3}$ = 0.72 Hz), 2.07 (s, 3 H, CH_3COO–), 1.71 (d, 3 H, CH_3–), 1.64–1.57 (m), 1.35–1.25 (m), 1.93–1.84 (m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.05, 130.47, 119.92, 72.02, 29.20, 28.85, 27.29, 20.87, 17.60, 13.60, 13.55, 9.84.

1-(Acetyloxy)-1-(tri-*n*-butylstannyl)-2,3-butanediol (4i): 72% yield from **3i**; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.93 (d, 1 H, H1, $J_{H1,H2}$ = 6.8 Hz), 3.68–3.62 (m, 2 H, H2 and H3), 2.65, 2.63 (2s, 2 × 1 H, –OH), 2.07 (s, 3 H, CH_3COO–), 1.54–1.47 (m), 1.39–1.28 (m), 1.24 (d, 3 H, CH_3–), 1.02–0.90 (m); IR ($CHCl_3$) ν_{max} (cm^{-1}) 3060, 3000, 2940, 2880, 2860, 1720, 1550, 1430, 1280, 1260, 1160, 1130, 905.

(*E*)-1-(Methoxymethoxy)-1-(tri-*n*-butylstannyl)-2-butene (3j): see Pratt, A. J.; Thomas, E. J. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1521; Jephcote, V. J.; Pratt, A. J.; Thomas, E. J. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1529 and references therein; Marshall, J. A.; Crooks, S. L.;

DeHoff, B. S. J. Org. Chem. 1988, 53, 1616.

1-(Methoxymethoxy)-1-(tri-*n*-butylstannyl)-2,3-butanediol (4j): 80% yield from **3j**; ^{1}H NMR (400 MHz, $CDCl_3$) (1,2-anti diastereomer) δ 4.64 (d, 1 H, MeO–CH–O, J = 6.6 Hz), 4.56 (d, 1 H, MeO–CH–O, J = 6.6 Hz), 4.14 (d, 1 H, H1, $J_{H1,H2}$ = 3.5 Hz), 3.82 (m, 1 H), 3.63 (m, 1 H), 3.18 (s, 3 H, MeO–), 1.60–1.80 (m), 1.21–1.42 (m), 0.87 (m); (syn diastereomer) 4.26 (d, 1 H, H1, $J_{H1,H2}$ = 3.2 Hz), 3.40 (s, 3 H, MeO–); IR ($CHCl_3$) ν_{max} (cm^{-1}) 2960, 2920, 2875, 2855, 1645, 1470, 1380, 1320, 1170–1080, 1020, 965, 870, 830, 660, 610.

(*E*)-1-[(*tert*-Butyldimethylsilyl)oxy]-1-(trimethylsilyl)-2-butene (3k): 68% yield overall from silyl ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.50–5.35 (m, 2 H, H2 and H3), 3.32 (d, 1 H, H1, $J_{H1,H2}$ = 6.0 Hz), 1.65 (d, 3 H, CH_3–, J = 7.2 Hz), 0.87 (s, 9 H, t-Bu), –0.01, –0.02 (2s, 2 × 3 H, CH_3–Si), –0.04 (s, 9 H, CH_3–Si).

1-[(*tert*-Butyldimethylsilyl)oxy]-1-(trimethylsilyl)-2,3-butanediol (4k): 92% yield from **3k**; ^{1}H NMR (400 MHz, $CDCl_3$) (1,2-anti diastereomer) δ 4.07 (m, 1 H, J = 7.5, 2.4 Hz), 3.78 (d, 1 H, H1, $J_{H1,H2}$ = 3.2 Hz), 3.45–3.40 (m, 1 H), 2.60, 2.58 (2s, 2 × 1 H, –OH), 1.21 (d, 3 H, CH_3–), 0.94 (s, 9 H, t-Bu), 0.16, 0.10 (2s, 2 × 3 H, CH_3–Si), 0.11 (s, 9 H, CH_3–Si), (syn diastereomer) d 4.14–4.04 (m, 1 H), 3.75 (d, 1 H, H1, $J_{H1,H2}$ = 4.1 Hz), 3.44–3.40 (m, 1 H), 2.78, 2.74 (2s, 2 × 1 H, –OH), 1.16 (d, 3 H, CH_3–), 0.93 (s, 9 H, t-Bu); IR (neat) ν_{max} (cm^{-1}) 3440 2960, 2930, 2900, 2860, 1480, 1470, 1410, 1395, 1365, 1260, 1100, 1060, 1040, 1010, 1000, 920, 840, 780, 690.

Spectral Data for Compounds 7–16 (Scheme II). (*E*)-1-(Phenyldimethylsilyl)-4-(benzyloxy)-but-2-en-1-ol (7): 52% yield from (*E*)-4-(benzyloxy)-2-butenal;[15] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.59 (m, 2 H, Ar-H), 7.44–7.31 (m, 8 H, Ar-H), 5.92 (dd, 1 H, H2, $J_{H1,H2}$ = 5.6, $J_{H3,H2}$ = 15.6 Hz), 5.68 (dtd, 1 H, H3, $J_{H3,H1}$ = 1.9, $J_{H3,H4}$ = 6.2 Hz), 4.50 (s, 2 H, Ph-CH_2-O), 4.25 (d, 1 H, H1); 4.06, 4.04 (2s, 2 H, H4a and b), 2.05 (br s, 1 H, OH–), 0.40, 0.38 (2s, 6 H, 2 × CH_3–Si); IR ($CHCl_3$) ν_{max} (cm^{-1}) 3400, 3080, 3040, 2960, 2900, 2860, 1500, 1460, 1430, 1365, 1310, 1250, 1210, 1115, 1065, 1030, 975, 840, 820, 780, 740, 700.

1-(Phenyldimethylsilyl)-4-(benzyloxy)-1,2-*anti*-2,3-*syn*-butanetriol (9): 61% yield from **7**; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.57 (m, 2 H, Ar-H), 7.40–7.28 (m, 8 H, Ar-H), 4.53 (dd, 2 H, Ph–CH_2–O, J = 12.0, 14.4 Hz), 3.98 (m, 1 H), 3.74 (d, 1 H, J = 6.4 Hz), 3.69 (d, 1 H, J = 6.5 Hz), 3.61 (d, 2 H, J = 4.6 Hz), 3.00, 2.05, 1.62 (3 br s, 1 H, –OH), 0.43 (s, 3 H, CH_3–Si), 0.42 (s, 3 H, CH_3–Si).

(*E*)-1-(Phenyldimethylsilyl)-1-(acetyloxy)-4-(benzyloxy)-but-2-ene (8): 63% yield from **7**; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.53 (m, 2 H, Ar-H), 7.43–7.28 (m, 8 H, Ar-H), 5.75 (ddd, 1 H, H2, J = 0.9; $J_{H1,H2}$ = 5.9, $J_{H3,H2}$ = 15.4 Hz), 5.58 (dt, 1 H, H3, J = 5.2 Hz), 5.47 (d, 1 H, H1), 4.46 (s, 2 H, Ph–CH_2–O), 4.04 (d, 2 H, H4, J = 5.2 Hz), 2.09 (s, 3 H, CH_3COO–), 0.40 (s, 6 H, CH_3–Si).

1-(Phenyldimethylsilyl)-1-(acetyloxy)-4-(benzyloxy)-2,3-*syn*-butanediol (10): 98% yield from **8**; ^{1}H NMR (400 MHz, $CDCl_3$) (1,2-anti-2,3-syn diastereomer) δ 7.60–7.55 (m, 2 H, Ar-H), 7.40–7.28 (m, 8 H, Ar-H), 4.91 (d, 1 H, H1, $J_{H1,H2}$ = 9.6 Hz), 4.51 (s, 2 H, Ph–CH_2–O), 4.06 (t, 1 H, J = 6.4 Hz), 3.77 (d, 1 H, J = 10 Hz), 3.57 (d, 2 H), 2.03 (s, 3 H, CH_3COO–), 0.44 (s, 3 H, CH_3–Si), 0.41 (s, 3 H, CH_3–Si), (syn-syn diastereomer) d 7.52–7.50 (m, 2 H, Ar-H), 7.40–7.28 (m, 8 H, Ar-H), 5.91 (d, 1 H, H1, $J_{H1,H2}$ = 3.6 Hz), 4.50 (d, 1 H), 3.70 (m, 1 H), 3.61 (d, 2 H), 3.52 (m, 1 H).

1-(Phenyldimethylsilyl)-1,2-*anti*-2,3-*syn*-(triacetyloxy)-4-(benzyloxy)butane (11): 76% yield from **9**, 92% yield from **10**; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.48 (m, 2 H, Ar-H), 7.37–7.24 (m, 8 H, Ar-H), 5.44 (dd, 1 H, H2, J = 9.2, J = 4.0 Hz), 5.23–5.18 (m, 2 H, H1 and H3), 4.47 (d, 1 H, Ph–CH_a–O), 4.38 (d, 1 H, Ph–CH_b–O, J = 11.2 Hz), 3.45–3.37 (m, 2 H, H4a and H4b, 2.06, 1.97, 1.62 (3 s, 3 × 3 H, CH_3COO–), 0.43, 0.33 (2 s, 2 × 3 H, CH_3–Si).

(*Z*)-1-(Phenyldimethylsilyl)-4-(benzyloxy)-but-2-en-1-ol (12): 42% yield from (*Z*)-4-(benzyloxy)-2-butenal;[15] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.57 (m, 2 H, Ar-H), 7.51–7.30 (m, 8 H, Ar-H), 5.65 (dd, 1 H, H2, J = 10.3 Hz), 5.58–5.50 (m, 1 H, H3), 4.41, 4.40 (2s, 2 H, Ph–CH_2–O), 4.32 (d, 1 H, H1, $J_{H1,H2}$ = 8.8 Hz), 3.89 (dd, 1 H, H4a, J = 7.7, J = 12.2 Hz), 3.75 (dd, 1 H, H4b, J = 4.5 Hz), 1.80 (br s, 1 H, –OH), 0.35, 0.31 (2s, 6 H, 2 × CH_3–Si); IR ($CHCl_3$) ν_{max} (cm^{-1}) 3400, 3060, 3030, 2920, 2860, 1680, 1495, 1450, 1425, 1250, 1205, 1115, 1070, 1025, 975, 840, 815, 740, 700.

1-(Phenyldimethylsilyl)-4-(benzyloxy)-1,2-*anti*-2,3-*anti*-butanetriol (14): 72% crude yield from **12**; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.61 (m, 2 H, Ar-H), 7.42–7.29 (m, 8 H, Ar-H), 4.72–4.41 (m, 4 H), 3.81–3.78 (m, 1 H), 3.72–3.68 (m, 1 H), 3.61–3.55 (m, 1 H), 2.9–2.4 (br s, 3 H, HO–), 0.44 (s, 6 H, CH_3–Si); IR ($CHCl_3$) ν_{max} (cm^{-1}) 3400, 3000, 2960, 2920, 2880, 2860, 1210, 1120, 1000, 910, 860, 835, 700, 645.

(*Z*)-1-(Phenyldimethylsilyl)-1-(acetyloxy)-4-(benzyloxy)-but-2-ene (13): 83% yield from **1d**; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.50 (m, 2 H, Ar-H), 7.40–7.28 (m, 8 H, Ar-H), 5.57–5.50 (m, 3 H, H1 and H2 and H3), 4.44 (d, 1 H, Ph–CH_2–O, J = 11.7 Hz), 4.36 (d, 1 H, Ph–CH_2–O, J = 11.8 Hz), 4.01 (dd, 1 H, H4a, J = 12.2 Hz), 3.69 (dd, 1 H, H4b, J = 3.7, J = 5.3 Hz), 2.02 (s, 3 H, CH_3COO–), 0.36 (s, 6 H, CH_3–Si).

1-(Phenyldimethylsilyl)-1-(acetyloxy)-4-(benzyloxy)-2,3-*anti*-butanediol (15): 97% yield from **13**; ^{1}H NMR (400 MHz, $CDCl_3$) (1,2-anti-2,3-anti diastereomer) δ 7.59–7.56 (m, 2 H, Ar-H), 7.41–7.23 (m, 8 H, Ar-H), 5.01 (d, 1 H, H1, $J_{H1,H2}$ = 7.8 Hz), 4.50 (s, 2 H, Ph–CH_2–O), 3.95 (dd, 1 H, J = 4.8, J = 7.8 Hz), 3.70–3.60 (m, 3 H), 1.94 (s, 3 H, CH_3COO–), 0.43 (s, 3 H, CH_3–Si), 0.42 (s, 3 H, CH_3–Si), (1,2-syn-2,3-anti diastereomer) δ 7.58–7.51 (m, 2 H, Ar-H), 7.41–7.23 (m, 8 H, Ar-H), 5.16 (d, 1 H, H1, $J_{H1,H2}$ = 1.7 Hz), 4.56 (2s, 2 H, Ph–CH_2–O), 3.76–3.70 (m), 3.70–3.60 (m), 2.10 (s, 3 H, CH_3COO–), 0.47 (s, 3 H, CH_3–Si), 0.45 (s, 3 H, CH_3–Si).

1-(Phenyldimethylsilyl)-1,2,3-(2,3-*anti*)-(triacetyloxy)-4-(benzyloxy)butane (16): 80% yield from **14**, 88% yield from **15**; ^{1}H NMR (400 MHz, $CDCl_3$) (1,2-anti-2,3-anti diastereomer) δ 7.56–7.54 (m, 2 H, Ar-H), 7.38–7.27 (m, 8 H, Ar-H), 5.34–5.32 (m, 1 H), 5.24 (d, 1 H, H1, J = 5.6 Hz), 5.19–5.16 (m, 1 H), 4.45–4.33 (2d, 2 H, Ph–CH_2–O), 3.62 (dd, 1 H, H4a, J = 3.2, 11.0 Hz), 3.52 (dd, 1 H, H4b, J = 11.0, 7.5 Hz), 2.03, 1.95, 1.80 (3 s, 3 × 3 H, CH_3COO–), 0.42, 0.39 (2 s, 2 × 3 H, CH_3–Si), (1,2-syn-2,3-anti diastereomer) δ 7.56–7.53 (m, 2 H, Ar-H), 7.38–7.27 (m, 8 H, Ar-H), 5.48–5.44 (m, 1 H), 5.15–5.09 (m, 1 H), 4.45–4.33 (2d, 2 H, Ph–CH_2–O), 3.44 (m, 2 H, H4), 2.07, 2.05, 1.53 (3 s, 3 × 3 H, CH_3COO–), 0.42, 0.32 (2 s, 2 × 3 H, CH_3–Si).

Acknowledgment. We thank Shawn Williams for providing valuable technical assistance. Financial support was provided by American Cancer Society, Grant No. IN-97K and the National Institutes of Health-NCI (CA47249).

Supplementary Material Available: Experimental procedures for the preparation of *trans*- and *cis*-1,3-dioxanes i and ii along with spectroscopic data (5 pages). Ordering information is given on any current masthead page.