

Enantioselective Synthesis of Carbohydrate Precursors via 1,2:2,3-Bis-Epoxy Intermediates

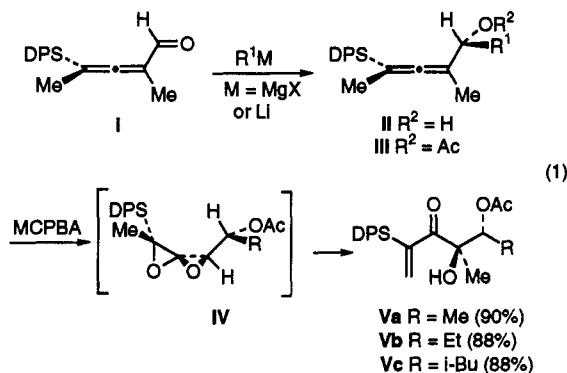
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Bis-epoxidation of the DPS-substituted allenylcarbinyl acetates **9**, **13**, **19**, **22**, and **30** afforded the enones **10**, **36**, **20**, **23**, and **31**, respectively, in 80–90% yield with excellent stereoselectivity. Treatment with DBU effected C to O DPS transfer leading to the methyl-branched hexose precursors, enones **11**, **37**, **21**, and **24**. The higher homologue **33** gave the branched 7-deoxyheptose precursor **33**. Reduction of enones **11**, **37**, and **33** with NaBH₄-CeCl₃ yielded the α -(S) alcohols **12**, **38**, and **35** in high yield. Alcohol **38** was converted to the 1-deoxy-4-methylpyranose tetraacetate **48** by epoxidation, base treatment, desilylation, and acetylation. An acyclic analogue of **48**, acetonide **53**, could be prepared from epoxide **39** by treatment with PhSH and NaOH, followed by silyl ether cleavage, acetonide formation, and Pummerer rearrangement-reduction. On the other hand, hydroxylation of alcohol **38** with OsO₄-NMO led to the selectively protected branched hexitol **59**, with high diastereoselectivity. The allylic alcohol benzoate **63** was likewise converted to diol **64**.

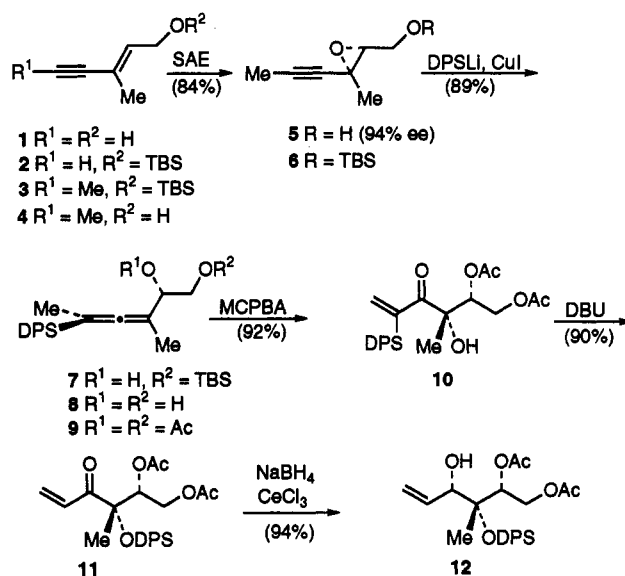
We recently disclosed a method for the substrate controlled diastereoselective synthesis of allenylcarbinols **II** by addition of Grignard reagents to chiral allenals such as **I** (eq 1).¹ The diphenyl-*tert*-butylsilyl (DPS) substit-



uent of **I** was found to be an effective steric directing group for these additions. In the course of studies on the chemistry of the allenyl products, we found that treatment of the acetate derivatives **III** with 2 equiv of *m*-ClC₆H₄-CO₂H (*m*-CPBA) led to the formation of enones **Va-c** in high yield.¹ In each case a single isomer was produced, presumably *via* the bis-epoxide **IV**. The present study was initiated to further develop this methodology for use in carbohydrate syntheses.

Our starting material for this project was the readily available allylic alcohol **1**.² Protection as the *tert*-butyldimethylsilyl (TBS) ether and then methylation and desilylation led to the homologue **4**. Sharpless asymmetric epoxidation (SAE) with the D-(-)-tartrate complex afforded the alkyloxirane **5** of 94% ee.³ The derived silyl ether **6** underwent smooth S_N2' displacement with the Gilman DPS cuprate⁴ giving allenylcarbinol **7** in 89% yield

as a single diastereoisomer. We have previously shown that such reactions proceed by an anti pathway.⁵



Desilylation of the adduct **7** followed by acetylation provided the diacetate **9**. This, on treatment with 2 equiv of *m*-CPBA buffered with NaH₂PO₄, afforded the enone **10** in 92% yield. Exposure of enone **10** to 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in CH₂Cl₂ gave rise to the isomeric enone **11**, the result of C to O silyl migration, in 90% yield. Reduction of this enone with NaBH₄ in the presence of CeCl₃⁶ led to alcohol **12** in 94% yield. The stereochemistry of this alcohol was initially assigned from chemical shift differences in the ¹H NMR spectra of the (S)- and (R)-*O*-methyl mandelates⁷ and later confirmed by single-crystal X-ray structure analysis.⁸

The acetate derivative **13** of alcohol **7** afforded the rearranged acetate **14** upon desilylation with TBAF.

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(1) Marshall, J. A.; Tang, Y. *J. Org. Chem.* 1993, 58, 3233.

(2) Available from Aldrich Chemical Co., Milwaukee, WI.

(3) Gao, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* 1987, 109, 5765.

(4) Cuadaro, P.; Gonzalez, A. M.; Gonzalez, B.; Pulido, F. J. *Synth. Commun.* 1989, 19, 275. Fleming, I.; Terrett, N. K. *Tetrahedron Lett.* 1983, 24, 4151.

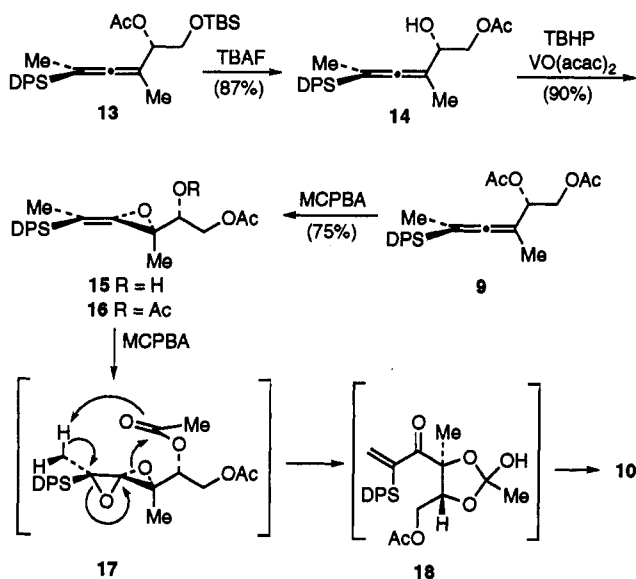
(5) Marshall, J. A.; Pinney, K. G. *J. Org. Chem.* 1993, 58, 0000.

(6) Cf. Fuche, J.-L. *J. Am. Chem. Soc.* 1978, 100, 2226.

(7) Trost, B. M.; Belletire, J. L.; Godleski, S.; McDougal, P. G.; Balkovec, J. M.; Baldwin, J. J.; Christy, M. E.; Ponticello, G. S.; Varga, S. L.; Springer, J. D. *J. Org. Chem.* 1986, 51, 2370.

(8) The analysis was carried out by Dr. Krzysztof Lewinski of this department. Details will be published elsewhere.

Hydroxyl-directed epoxidation led to the isoable allene monoepoxide 15.⁹ The derived acetate 16 could also be

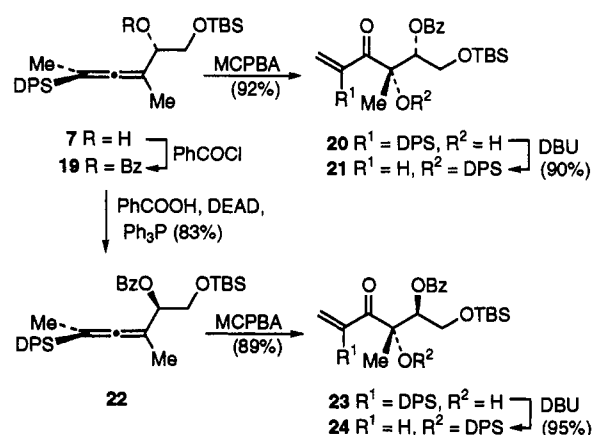


prepared by monoepoxidation of allene diacetate 9 with 1 equiv of *m*-CPBA buffered with NaH_2PO_4 . In both 14 and 9 epoxidation takes place *trans* to the bulky DPS grouping.

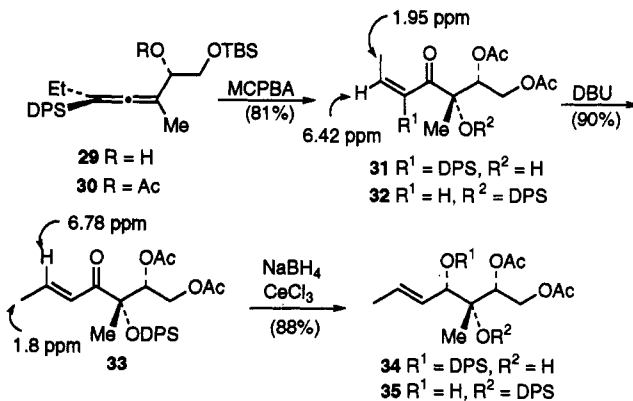
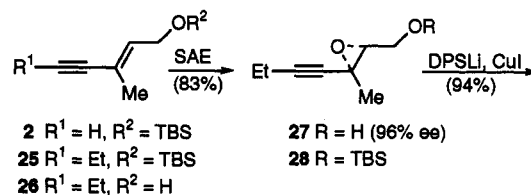
Epoxidation of the allene mono epoxide 16 with *m*-CPBA yielded enone 10. We were unable to isolate the presumed intermediate bis-epoxide 17 from this or any other experiment.¹⁰ Although we did not examine this point in detail, the bis-epoxidation of allenylcarbinols such as 14, lacking an allylic alkoxy carbonyl grouping, afforded the enone products in low yield. Thus, an assisted elimination pathway, as depicted in 17 \rightarrow 18, may facilitate the overall process. Presumably the secondary acetate 10 is favored over the alternative tertiary isomer on steric grounds (*cf.* 13 \rightarrow 14). We assume that the second epoxidation step occurs *trans* to the larger epoxide substituent of the alkylidene precursor 16.

In further studies of the methodology, we carried out the bis-epoxidation of the diastereomeric benzoates 19 and 22. Both are available from alcohol 7, the former through direct esterification and the latter by Mitsunobu inversion.¹¹ As expected, both cleanly led to the respective diastereomeric enones 20 and 23 upon epoxidation with *m*-CPBA. Treatment with DBU effected silyl migration,

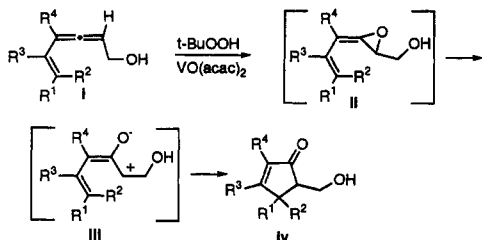
as with acetate 10, giving the ODPS enones 21 and 24, respectively.



It was of interest to examine a higher homologue of allenyl acetate 9 for the possible synthesis of heptose and other longer chain carbohydrate derivatives. To that end we prepared the ethyl derivative 29 by a parallel sequence starting from enyne 2, which was alkylated with ethyl iodide and then desilylated, epoxidized and resilylated. $\text{S}_{\text{N}}2'$ displacement of the resulting alkynloxirane with the DPS cuprate gave the allenyl carbinol 29.



(9) Monoepoxy allenes have been proposed as biogenetic precursors to prostanoids. Kim and Cha (Kim, S. J.; Cha, J. K. *Tetrahedron Lett.* 1988, 29, 5613) have shown that these generally nonisolable highly reactive intermediates can be trapped through intramolecular additions to the derived dipolar species (iii \rightarrow iv). In the present case, the analogous dipolar species (*cf.* iii) would be disfavored by the presence of the silicon substituent ($\text{R}^4 = \text{DPS}$).



(10) For previous studies of allene bis-epoxides, see: Crandall, J. K.; Woodrow, W. W.; Komin, J. B.; Machleder, W. H. *J. Org. Chem.*, 1974, 39, 1723. Chan, T. H.; Ong, B. B. *Tetrahedron* 1980, 36, 2269.

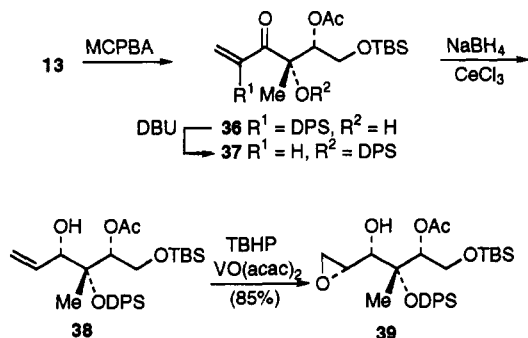
(11) Mitsunobu, O. *Synthesis* 1981.

The acetate derivative 30 was converted to enone 31, a single stereoisomer, with *m*-CPBA. Silyl transfer was effected with DBU affording enone 33 in high yield. The ^1H NMR spectrum of this substance showed coupling of the two vinyl protons typical of (*E*)-enones. The stereochemistry of the enone precursor 31 was not rigorously established, but the chemical shift differences for the vinylic β -H and CH_3 substituents are suggestive of the depicted (*E*)-isomer. Furthermore, a consideration of likely transition state arrangements for the bis-epoxide elimination (Figure 1) suggests preferential formation of the (*E*) product. Additional support for this assignment came from experiments in which mixtures of enones 32 and 33 were detected in the early stages of the DBU reaction.

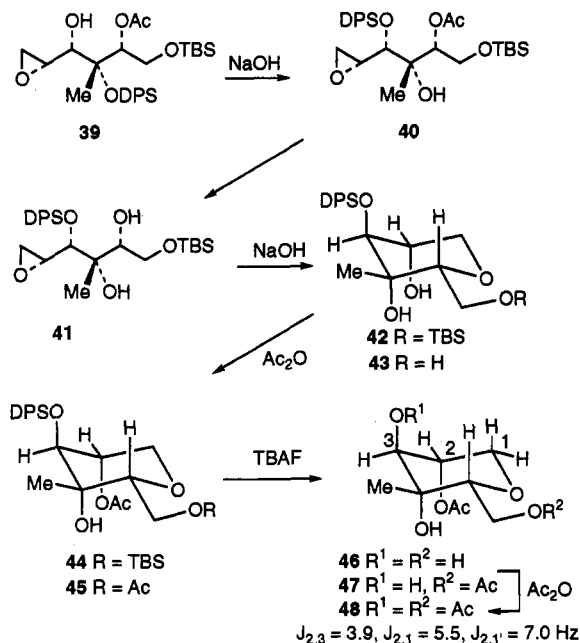
Reduction of enone 33 with NaBH_4 - CeCl_3 led initially to alcohol 34, which isomerized to 35 upon prolonged

exposure to the reduction conditions. The stereochemistry of alcohol **34** is assigned by analogy to **12**.

Preliminary studies on the synthesis of branched hexose derivatives by this methodology were conducted with the differentially protected alcohol **38**, prepared from allene **13** via enone **36** along the lines described for the acetate analogue **12**. Epoxidation of allylic alcohol **38** led to a single epoxy alcohol **39** in 85% yield.



Attempted cleavage of epoxide **39** with NaOH in aqueous *tert*-butyl alcohol at reflux¹² unexpectedly afforded a mixture of cyclic diol **42** and triol **43**. When this reaction was carried out at room temperature, alcohol **40**, the product of DPS migration, was the sole product. This alcohol afforded mainly the cyclized diol **42** upon further exposure to NaOH in aqueous *t*-BuOH at reflux. This reaction must proceed by a disfavored 6-*endo-tet* cyclization.¹³ Presumably, the usually preferred 5-*exo-tet* process is sterically blocked in this system.



Although diol **42** and triol **43** could be easily separated, it was more convenient to acetylate the mixture, whereupon a mixture of acetates **44** and **45** was obtained. Cleavage of the silyl ethers with TBAF led to the alcohols **46** and **47**. Acetylation of this mixture gave rise to a single

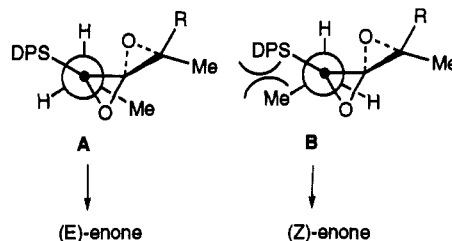
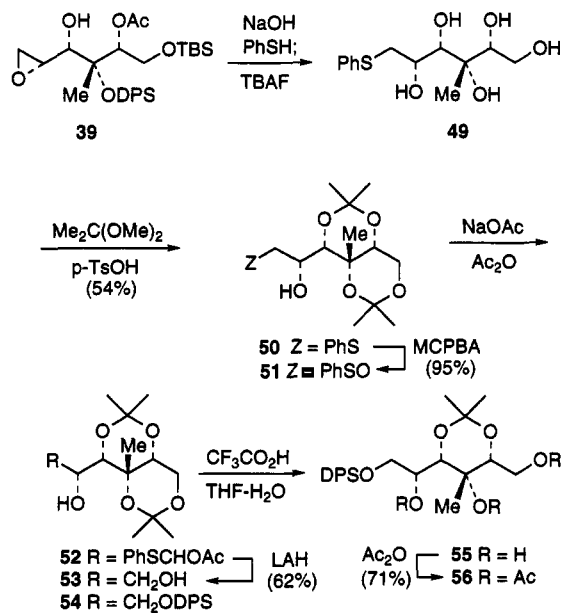


Figure 1. Transition-state arrangements for conversion of the bis-epoxide derived from allene **30** to the (*E*)-enone **31**.

triacetate **48**, a crystalline solid, in 65% overall yield for the four steps. The ¹H NMR spectrum of **48** confirmed the assigned stereochemistry.

An open chain analogue of the branched deoxyribose **48** was prepared from epoxide **39** along the lines of Sharpless and Masamune.¹⁴ Thus, treatment of **39** with PhSH and NaOH effected epoxide opening and acetate cleavage. Subsequent desilylation with TBAF led to the pentol **49**. Ketalization with excess 2,2-dimethoxypropane afforded the bis-acetonide **50** in 54% overall yield for the three steps. The structure of acetonide **50** was confirmed by ¹H NMR homodecoupling and D₂O exchange. Appli-



cation of the Pummerer sequence¹⁴ and subsequent reduction with LAH gave rise to diol **53** in 60% yield. The DPS ether **54** could be selectively hydrolyzed to the mono acetonide **55**, characterized as the diacetate derivative **56**.

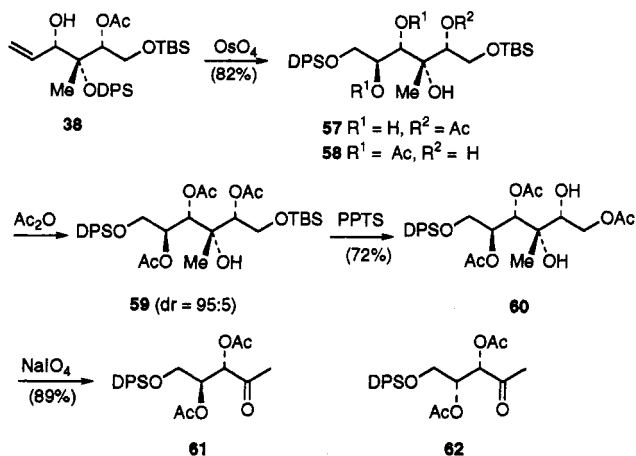
Direct hydroxylation of allylic alcohol **38** with catalytic OsO₄ and *N*-methylmorpholine *N*-oxide (NMO) proceeded with DPS migration to the terminal OH and partial acetate migration leading to a mixture of acetates **57** and **58**. Acetylation of this mixture afforded triacetate **59**, a 95:5 mixture of diastereoisomers. We assume that the hydroxylation affords mainly the anti isomer, as is the case for other acyclic allylic alcohols.¹⁵ Support for this assignment was secured through periodate cleavage of the diol **60**, obtained from triacetate **59** by selective TBS cleavage and concomitant acetate migration. The cleavage product, ketone **61**, was found to be isomeric with ketone

(12) Behrens, C. H.; Sharpless, K. B. *Aldrichim. Acta* 1983, 16, 67.

(13) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* 1976, 734. Stork, G.; Cama, L.D.; Coulson, D. R. *J. Am. Chem. Soc.* 1974, 96, 5268. For a recent example involving antibody catalysis see: Na, J.; Houk, K. N.; Sheulin, C. G.; Janda, K.D.; Lerner, R. A. *J. Am. Chem. Soc.* 1993, 115, 8453.

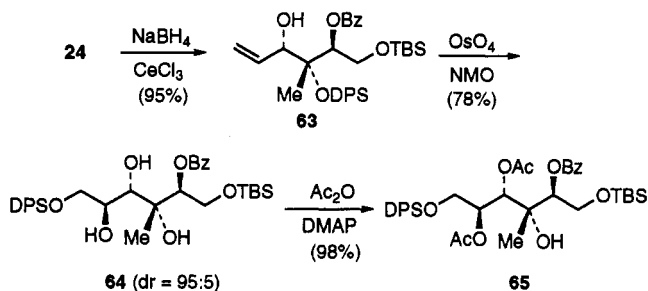
(14) Ko, S. Y.; Lee, A. W. M.; Masamune, S.; Reed, L. A., III; Sharpless, K. B. *Science* 1983, 220, 949.

(15) Cf. Cha, J. K.; Christ, W. J.; Kishi, Y. *Tetrahedron* 1984, 40, 2247.

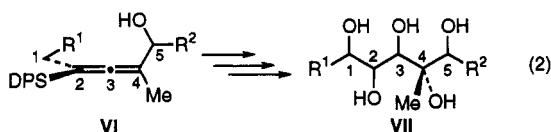


62 prepared by dihydroxylation of the obvious enone precursor.¹⁶

By an analogous sequence of reactions, the benzoate derivate 24, obtained through Mitsunobu inversion of alcohol 7 then bis-epoxidation and DPS migration, was reduced to the allylic alcohol 63. Hydroxylation with OsO₄-NMO proceeded with DPS migration, but in contrast to 38, acyl migration did not occur. The hydroxylation product 64 was obtained as a 95:5 mixture of diastereoisomers.



In summary, we have demonstrated that readily available nonracemic DPS-substituted allenylcarbinols VI can be transformed to potential precursors of branched carbohydrates (eq 2).

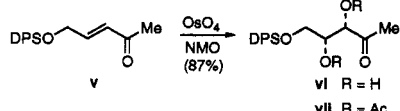


Our methodology allows for considerable variation in the stereocenters at C1–C5 of the ultimate polyol products VII. Additional studies along these lines as well as applications to natural product synthesis are in progress.¹⁸

Experimental Section¹⁹

(*E*)-1-[(*tert*-Butyldimethylsilyl)oxy]-3-methyl-2-penten-4-yne (2). To a solution of 5.6 mL (52.0 mmol) of (*E*)-3-methyl-

(16) The following sequence was employed for the racemic diacetate:



The use of AD mix β ¹⁷ afforded nonracemic diacetate vii in lower purity, possibly because of epimerization and/or elimination.

(17) Sharpless, K. B.; Amberg, W.; Bennai, Y. L.; Crispino, G. A.; Hartung, J.; Jeong, K.-S.; Kwong, H.-L.; Morikawa, K.; Wang, Z.-M.; Xu, D.; Zhang, X.-L. *J. Org. Chem.* 1992, 57, 2768.

2-penten-4-yn-1-ol (1)²⁰ in 170 mL of CH₂Cl₂ was added 5.31 g (78.0 mmol) of imidazole, 8.62 g (57.2 mmol) of TBSCl, and 0.10 g of DMAP. After 4 h, the reaction mixture was quenched with aqueous NH₄Cl and extracted with ether. The ether layer was dried over MgSO₄ and concentrated. The residue was chromatographed on a silica gel column using 1:20 ether–hexanes as eluant to afford 12.0 g (100%) of silyl ether 2 as a yellow oil: IR (cm⁻¹, film) 2929, 1067; ¹H NMR (CDCl₃, 300 MHz) δ 5.99 (t, *J* = 6.0 Hz), 4.23 (d, *J* = 6.0 Hz), 2.77 (s), 1.77 (s), 0.88 (s), 0.05 (s); ¹³C NMR (75 MHz, CDCl₃) 138.4, 117.7, 86.0, 74.6, 59.8, 25.8, 18.3, 17.3, -5.2; HRMS calcd for C₁₂H₂₁OSi (M⁺) 209.1362, found 209.1357.

(*E*)-1-[(*tert*-Butyldimethylsilyl)oxy]-3-methyl-2-hexen-4-yne (3). To a solution of 10.0 g (47.52 mmol) of enyne 2 in 160 mL of THF at -78 °C was added dropwise 20.9 mL (52.27 mmol) of 2.5 M *n*-BuLi in hexanes. The reaction mixture was stirred at -78 °C for 1 h, and then 20.2 g (142.6 mmol) of MeI was added. The reaction mixture was stirred at 0 °C for 8 h, quenched with aqueous NH₄Cl, and extracted with ether. The ether layer was dried over MgSO₄ and concentrated. The residue was chromatographed on a silica gel column using 1:20 ether–hexanes as eluant to afford 10.4 g (98%) of enyne 3 as a clear oil. IR (cm⁻¹, film) 2930, 836; ¹H NMR (CDCl₃, 300 MHz) δ 5.80 (t, *J* = 6.3 Hz), 4.22 (d, *J* = 6.3 Hz), 1.91 (s), 1.73 (s), 0.87 (s), 0.04 (s); ¹³C NMR (75 MHz, CDCl₃) 135.7, 119.6, 83.5, 82.5, 60.3, 26.3, 18.7, 18.1, 4.4, -4.8. Anal. Calcd for C₁₃H₂₄OSi: C, 69.58; H, 10.78. Found: C, 69.65; H, 10.83.

(*E*)-3-Methyl-2-hexen-4-yn-1-ol (4). To a solution of 5.6 g (24.95 mmol) of enyne 3 in 100 mL of THF at rt was added dropwise 37.4 mL (37.4 mmol) of 1.0 M TBAF in THF. The reaction mixture was stirred for 20 min and then quenched with aqueous NH₄Cl and extracted with ether. The ether layer was dried over MgSO₄ and concentrated. The residue was chromatographed on a silica gel column using 1:2 ether–hexanes as eluant to afford 2.47 g (90%) of alcohol 4 as a clear oil: IR (cm⁻¹, film) 3332, 2918; ¹H NMR (CDCl₃, 300 MHz) δ 5.88 (t, *J* = 6.3 Hz), 4.18 (t, *J* = 6.3 Hz), 1.92 (s), 1.79 (s); ¹³C NMR (75 MHz, CDCl₃) 133.9, 121.3, 84.0, 81.9, 59.0, 17.7, 4.10; HRMS calcd for C₇H₁₀O (M⁺) 110.0732, found 110.0728.

(2*S*,3*R*)-2,3-Epoxy-3-methyl-4-hexyn-1-ol (5). To a solution of 3.0 g of 4A powdered, activated molecular sieves in 100 mL of dry CH₂Cl₂ at -20 °C was added sequentially with stirring 0.69 mL (3.27 mmol) of D-(-)-diisopropyl tartrate and 0.81 mL (2.72 mmol) of Ti(O-*i*-Pr)₄.³ The reaction mixture was stirred at -20 °C as 6.60 mL (36.32 mmol) of 5.5 M TBHP was added by syringe at a moderate rate. The resulting mixture was stirred at -20 °C for 30 min. A solution of 2.0 g (18.16 mmol) of enyne alcohol 4 in 20 mL of CH₂Cl₂ was added dropwise. The reaction mixture was stirred for 12 h at -20 °C, warmed to 0 °C, and quenched with 15 mL of water. The mixture was stirred at 0 °C for 60 min, and 4.0 mL of 30% aqueous NaOH saturated with sodium chloride was added. The mixture was stirred vigorously, and phase separation occurred after 30–60 min. The mixture was transferred to a separatory funnel, and the organic phase was separated. The aqueous phase was extracted with CH₂Cl₂, and the combined organic extracts were dried over MgSO₄ and concentrated. The residue was chromatographed on a silica gel column using 1:2 ether–hexanes as eluant to afford 1.92 g (84%) of epoxide 5 as a clear oil: [α]_D²³ -2.79 (c 1.36, CHCl₃); IR (cm⁻¹, film) 3324, 1032; ¹H NMR (CDCl₃, 300 MHz) δ 3.78 (ddd, *J* = 12.1, 7.0 and 4.5 Hz), 3.63 (ddd, *J* = 12.1, 6.4 and 5.3 Hz), 3.25 (dd, *J* = 6.4 and 4.5 Hz), 2.63 (dd, *J* = 5.3 and 7.0 Hz), 1.77 (s), 1.45 (s); ¹³C NMR (75 MHz, CDCl₃) 79.2, 60.7, 64.1, 60.5, 51.6, 18.9, 3.5. The ee of this alcohol was found to be 94% by ¹H NMR analysis of the (*R*)- and (*S*)-*O*-methyl mandelate derivatives.

(4*S*,5*R*)-1-[(*tert*-Butyldimethylsilyl)oxy]-4,5-epoxy-4-methyl-2-hexyne (6). The procedure described for silyl ether 1 was employed with 1.50 g (11.89 mmol) of epoxy alcohol 5 in 60 mL of CH₂Cl₂ at rt and 2.15 g (14.27 mmol) of TBSCl, 1.21 g (17.84 mmol) of imidazole, and a catalytic amount of DMAP. After 4

(18) Cf. Wetteler, F.-J.; Welzel, P.; Duddeck, H.; Hofle, G.; Riemer, W.; Budzikiewicz, H. *Tetrahedron Lett.* 1979, 3493.

(19) For typical experimental protocols, see: Marshall, J. A.; Welmaker, G. S.; Gung, B. W., *J. Am. Chem. Soc.* 1991, 113, 647.

(20) Aldrich Chemical Co., Milwaukee, WI.

h, isolation as described, followed by chromatography on a silica gel column using 1:20 ether-hexanes as eluant, afforded 2.86 g (100%) of silyl ether 6 as a clear oil: $[\alpha]_D^{25} +5.77$ (c 1.30, CHCl_3); IR (cm^{-1} , film) 2930, 838; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 3.69 (d, $J = 5.4$ Hz), 3.23 (t, $J = 5.4$ Hz), 1.80 (s), 1.45 (s), 0.89 (s), 0.07 (s), 0.06 (s); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) 80.0, 78.9, 64.7, 61.9, 51.4, 26.2, 19.2, 18.7, 3.9, -4.8, -5.0; HRMS calcd for $\text{C}_{12}\text{H}_{21}\text{O}_2\text{Si}$ ($\text{M}^+ - \text{CH}_3$) 225.1311, found 225.1297. Anal. Calcd for $\text{C}_{13}\text{H}_{24}\text{O}_2\text{Si}$: C, 64.95; H, 10.06. Found: C, 64.69; H, 10.03.

(3R,5S)-6-[(*tert*-Butyldimethylsilyloxy)-2-(*tert*-butyldiphenylsilyl)-4-methyl-2,3-hexadien-5-yl] (7). To a solution of 3.33 g (17.47 mmol) of CuI in 50 mL of THF at -20°C was added dropwise 34.94 mL (34.94 mmol) of 1.0 M *t*-BuPh₂SiLi in THF (prepared by addition of *t*-BuPh₂SiCl to a solution of Li shot in THF. After being stirred at rt for 12 h, the brown-green solution was used directly. It can be stored in freezer before use if necessary). The reaction mixture was stirred at -20°C for 4 h, and then a solution of 2.0 g (8.32 mmol) of epoxide 6 in 30 mL of THF was added over 1 h. After 30 min the reaction mixture was quenched with 3% NH_4OH in aqueous NH_4Cl , stirred at rt for 20 min, and extracted with ether. The ether layer was dried over MgSO_4 and concentrated. The residue was chromatographed on a silica gel column using 1:40 ether-hexanes as eluant to afford 3.56 g (89%) of allenic alcohol 7 as a clear oil: $[\alpha]_D^{25} +0.26$ (c 5.60, CHCl_3); IR (cm^{-1} , film) 3446, 1944; $^1\text{H NMR}$ (CDCl_3 , 500 MHz) δ 7.25–7.65 (m), 4.00 (t, $J = 5.9$ Hz), 3.31 (d, $J = 5.9$ Hz), 2.18 (bs), 1.73 (s), 1.65 (s), 1.12 (s), 0.87 (s), 0.05 (s), 0.02 (s); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) 208.0, 136.55, 136.53, 134.9, 134.5, 129.59, 129.54, 128.08, 127.9, 92.9, 88.8, 73.4, 66.1, 28.6, 26.3, 19.2, 19.0, 18.7, 14.9, -4.92, -4.94; HRMS calcd for $\text{C}_{29}\text{H}_{44}\text{O}_2\text{Si}_2$ (M^+) 480.2880, found 480.2870. Anal. Calcd for $\text{C}_{29}\text{H}_{44}\text{O}_2\text{Si}_2$: C, 72.44; H, 9.22. Found: C, 72.54; H, 9.22.

(3R,5S)-2-(*tert*-Butyldiphenylsilyl)-4-methyl-2,3-hexadiene-5,6-diol (8). To a solution of 2.0 g (4.16 mmol) of allenic alcohol 7 in 12 mL of EtOH at rt was added 31 mg (1.25 mmol) of PPTS. The reaction mixture was stirred at rt overnight and quenched with saturated NaHCO_3 . The aqueous phase was extracted with ether. The ether layer was dried over MgSO_4 and concentrated. The residue was chromatographed on a silica gel column using 3:1 ether-hexanes as eluant to afford 1.37 g (90%) of diol 8 as a clear oil: $[\alpha]_D^{25} -0.44$ (c 4.55, CHCl_3). IR (cm^{-1} , film) 3398, 1940; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 7.24–7.65 (m), 3.82 (m), 3.40 (m), 1.81 (s), 1.61 (s), 1.14 (s); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) 207.2, 136.48, 136.46, 135.0, 134.3, 130.0, 128.2, 128.0, 93.5, 90.9, 73.5, 65.5, 28.8, 19.2, 19.1, 15.6; HRMS calcd for $\text{C}_{29}\text{H}_{40}\text{O}_2\text{Si}$ (M^+) 366.2015 found 366.2014. Anal. Calcd for $\text{C}_{29}\text{H}_{40}\text{O}_2\text{Si}$: C, 75.36; H, 8.25. Found: C, 75.25; H, 8.31.

(3R,5S)-5,6-Diacetoxy-2-(*tert*-butyldiphenylsilyl)-4-methyl-2,3-hexadiene (9). To a solution of 0.80 g (2.18 mmol) of diol 8 in 10 mL of CH_2Cl_2 at rt was added 0.50 mL (5.24 mmol) of Ac_2O , 0.53 mL (6.54 mmol) of pyridine, and a catalytic amount of DMAP. After 5 h, the reaction mixture was quenched with aqueous NH_4Cl and extracted with ether. The ether layer was dried over MgSO_4 and concentrated. The residue was chromatographed on a silica gel column using 1:3 ether-hexanes as eluant to afford 0.98 g (100%) of allenic diacetate 9 as a clear oil: $[\alpha]_D^{25} +40.3$ (c 3.21, CHCl_3); IR (cm^{-1} , film) 1946, 1747; $^1\text{H NMR}$ (CDCl_3 , 500 MHz) δ 7.25–7.65 (m), 5.40 (dd, $J = 3.8$ and 8.3 Hz), 4.07 (dd, $J = 3.8$ and 11.7 Hz), 4.00 (dd, $J = 8.3$ and 11.7 Hz), 1.99 (s), 1.94 (s), 1.70 (s), 1.66 (s), 1.08 (s); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) 207.9, 170.6, 170.3, 136.15, 136.13, 133.8, 133.7, 129.3, 127.8, 127.6, 89.5, 89.3, 72.3, 64.4, 28.0, 21.0, 20.8, 18.8, 18.6, 15.6. Anal. Calcd for $\text{C}_{27}\text{H}_{34}\text{O}_4\text{Si}$: C, 71.96; H, 7.60. Found: C, 71.85; H, 7.57.

(4S,5R)-5,6-Diacetoxy-2-(*tert*-butyldiphenylsilyl)-4-hydroxy-4-methyl-1-hexen-3-one (10). A. From Allene 9. To a solution of 0.70 g (1.55 mmol) of allenic diacetate 9 in 15 mL of CH_2Cl_2 at rt was added 1.07 g of Na_2HPO_4 followed by 1.07 g (3.10 mmol) of 50% *m*-CPBA. After 6 h, the reaction mixture was diluted with ether and aqueous 1 N NaOH. The aqueous layer was extracted with ether, and the combined organic layers were washed with brine, dried over MgSO_4 , and concentrated. The residue was chromatographed on a silica gel column using 1:3 ether-hexanes as eluant to afford 0.69 g (92%) of enone 10 as a clear oil: $[\alpha]_D^{25} +15.5$ (c 3.12, CHCl_3); IR (cm^{-1} , film) 3455, 1747; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 7.25–7.53 (m), 6.73 (s), 6.23

(s), 5.55 (dd, $J = 3.0$ and 7.9 Hz), 4.56 (dd, $J = 3.0$ and 12.1 Hz), 4.10 (dd, $J = 7.9$ and 12.1 Hz), 3.88 (s), 2.00 (s), 1.96 (s), 1.33 (s), 1.12 (s); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) 206.2, 170.8, 169.9, 146.4, 141.2, 136.2, 136.1, 133.64, 133.60, 129.5, 127.8, 79.3, 74.7, 62.6, 29.0, 23.0, 20.84, 20.80, 18.6. Anal. Calcd for $\text{C}_{27}\text{H}_{34}\text{O}_6\text{Si}$: C, 67.19; H, 7.10. Found: C, 66.96; H, 7.16.

B. From Allene Oxide 16. To a solution of 0.20 g (0.43 mmol) of allene oxide 16 in 1.2 mL of CH_2Cl_2 at rt was added 148 mg of Na_2HPO_4 followed by 148 mg (0.43 mmol) of 50% *m*-CPBA. After 6 h, the reaction mixture was diluted with ether and aqueous 1 N NaOH. The aqueous layer was extracted with ether, and the combined organic layers were washed with brine, dried over MgSO_4 , and concentrated. The residue was chromatographed on a silica gel column using 1:3 ether-hexanes as eluant to afford 0.19 g (91%) of enone 10 as a clear oil.

(4S,5R)-5,6-Diacetoxy-4-[(*tert*-butyldiphenylsilyloxy)-4-methyl-1-hexen-3-one (11). To a solution of 150 mg (0.31 mmol) of enone 10 in 0.5 mL of CH_2Cl_2 at rt was added 10 mg of DBU. The reaction mixture was stirred for 6 h and then quenched with aqueous NH_4Cl and extracted with ether. The ether layer was washed with brine and dried over MgSO_4 . After removal of solvent under reduced pressure, the residue was chromatographed on a silica gel column using 1:10 ether-hexanes as eluant to afford 135 mg (90%) of enone 11 as a clear oil: $[\alpha]_D^{25} -1.29$ (c 1.40, CHCl_3); IR (cm^{-1} , film) 1750, 1708; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 7.28–7.73 (m), 6.85 (dd, $J = 10.4$ and 17.1 Hz), 6.20 (dd, $J = 1.9$ and 17.1 Hz), 5.62 (dd, $J = 1.9$ and 10.4 Hz), 5.37 (dd, $J = 3.2$ and 7.8 Hz), 4.43 (dd, $J = 3.2$ and 12.0 Hz), 3.46 (dd, $J = 7.8$ and 12.0 Hz), 2.02 (s), 1.97 (s), 1.28 (s), 1.04 (s); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) 197.1, 170.6, 169.9, 136.2, 135.9, 134.3, 130.7, 129.8, 129.6, 129.5, 127.5, 127.3, 82.5, 74.9, 62.5, 27.4, 21.3, 20.9, 20.7, 19.8. Anal. Calcd for $\text{C}_{27}\text{H}_{34}\text{O}_6\text{Si}$: C, 67.19; H, 7.10. Found: C, 67.30; H, 7.13.

(3S,4R,5R)-5,6-Diacetoxy-4-[(*tert*-butyldiphenylsilyloxy)-4-methyl-1-hexen-3-ol (12). To a solution of 50 mg (0.10 mmol) of enone 11 in 0.5 mL of MeOH at 0°C was added 37.3 mg (0.10 mmol) of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ and 3.8 mg (0.10 mmol) of NaBH_4 . The reaction mixture was stirred for 3 h at 0°C and then quenched with aqueous NH_4Cl and extracted with ether. The ether layer was washed with brine and dried over MgSO_4 . After removal of solvent under reduced pressure, the residue was chromatographed on a silica gel column using 1:5 ether-hexanes as eluant to afford 47 mg (94%) of allylic alcohol 12 as white needles: mp 118–120 $^\circ\text{C}$; $[\alpha]_D^{25} -8.70$ (c 1.78, CHCl_3); IR (cm^{-1} , film) 3477, 1748; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 7.34–7.80 (m), 5.97 (ddd, $J = 5.2$, 10.7 and 17.2 Hz), 5.19 (dt, $J = 1.6$ and 17.2 Hz), 5.13 (dt, $J = 1.6$ and 10.7 Hz), 5.09 (dd, $J = 2.4$ and 8.8 Hz), 4.60 (dd, $J = 2.4$ and 12.0 Hz), 4.21 (dd, $J = 8.8$ and 12.0 Hz), 4.00 (d, $J = 5.2$ Hz), 2.00 (s), 1.97 (s), 1.14 (s), 1.04 (s); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) 170.8, 170.4, 136.2, 136.1, 134.7, 134.3, 129.9, 129.8, 127.63, 127.62, 116.4, 79.9, 75.6, 75.4, 63.6, 27.4, 21.7, 21.1, 20.9, 19.7. Anal. Calcd for $\text{C}_{27}\text{H}_{36}\text{O}_6\text{Si}$: C, 66.91; H, 7.49. Found: C, 66.85; H, 7.44.

(3R,5S)-5-Acetoxy-6-[(*tert*-butyldimethylsilyloxy)-2-(*tert*-butyldiphenylsilyl)-4-methyl-2,3-hexadiene (13). To a solution of 0.50 g (1.04 mmol) of allenic alcohol 7 in 4 mL of CH_2Cl_2 at rt was added 0.12 mL (1.25 mmol) of Ac_2O , 0.13 mL (1.56 mmol) of pyridine, and a catalytic amount of DMAP. After 5 h, the reaction mixture was quenched with aqueous NH_4Cl and extracted with ether. The ether layer was dried over MgSO_4 and concentrated. The residue was chromatographed on a silica gel column using 1:8 ether-hexanes as eluant to afford 0.54 g (100%) of allenic acetate 13 as a clear oil: $[\alpha]_D^{25} +34.34$ (c 3.76, CHCl_3); IR (cm^{-1} , film) 1944, 1743; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 7.29–7.67 (m), 5.27 (dd, $J = 4.1$ and 8.2 Hz), 3.57 (dd, $J = 8.2$ and 11.1 Hz), 3.50 (dd, $J = 4.1$ and 11.1 Hz), 1.93 (s), 1.69 (s), 1.66 (s), 1.09 (s), 0.85 (s), -0.01 (s), -0.12 (s); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) 208.0, 170.4, 136.4, 136.1, 134.1, 133.9, 129.2, 127.7, 127.5, 89.9, 88.6, 75.3, 64.1, 28.0, 25.8, 21.1, 18.8, 18.6, 18.3, 15.8, -5.35. Anal. Calcd for $\text{C}_{31}\text{H}_{46}\text{O}_3\text{Si}_2$: C, 71.21; H, 8.87. Found: C, 70.98; H, 8.96.

(2S,4R)-1-Acetoxy-5-(*tert*-butyldiphenylsilyl)-3-methyl-3,4-hexadien-2-ol (14). To a solution of 0.57 g (1.09 mmol) of allenic acetate 13 in 5 mL of THF at rt was added 63 mg (1.05 mmol) of acetic acid and 1.14 mL (1.05 mmol) of 1.0 M TBAF in THF. After 5 h, the reaction mixture was quenched with aqueous NH_4Cl and extracted with ether. The ether layer was dried over MgSO_4 and concentrated. The residue was chro-

matographed on a silica gel column using 1:8 ether-hexanes as eluant to afford 0.39 g (87%) of allenic alcohol 14 as a clear oil: $[\alpha]_D^{25} -11.98$ (c 1.36, CHCl_3); IR (cm^{-1} , film) 3417, 1945, 1738; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 7.31–7.64 (m), 3.92 (m), 2.04 (s), 1.79 (s), 1.62 (s), 1.14 (s); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) 207.1, 171.4, 136.5, 136.4, 134.9, 134.3, 129.8, 128.2, 128.0, 93.4, 91.4, 71.2, 67.3, 28.8, 21.3, 19.2, 19.0, 15.7. Anal. Calcd for $\text{C}_{25}\text{H}_{32}\text{O}_3$: Si: C, 73.49; H, 7.89. Found: C, 73.50; H, 7.84.

Allene Oxide 15. To a solution of 0.21 g (0.51 mmol) of allenic alcohol 14 in 2 mL of C_6H_6 at rt was added 0.11 mL (0.62 mmol) of 5.5 M TBHP in 2,2,4-trimethylpentane and a catalytic amount of VO(acac) $_2$. After 2 h, the reaction mixture was quenched with water and extracted with ether. The ether layer was dried over MgSO_4 and concentrated. The residue was chromatographed on a silica gel column using 1:4 ether-hexanes as eluant to afford 0.21 g (90%) of allene oxide 15 as a clear oil: $[\alpha]_D^{25} -14.86$ (c 0.74, CHCl_3); IR (cm^{-1} , film) 3448, 1744; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 7.30–7.57 (m), 3.87 (m), 3.03 (m), 2.04 (s), 2.01 (s), 1.18 (s), 0.95 (s).

Allene Oxide 16. A. From Alcohol 15. To a solution of 0.12 g (0.28 mmol) of allene oxide 15 in 2 mL of CH_2Cl_2 at rt was added 31 mg (0.30 mmol) of Ac_2O , 24 mg (0.30 mmol) of pyridine and a catalytic amount of DMAP. After 5 h, the reaction mixture was quenched with aqueous NH_4Cl and extracted with ether. The ether layer was dried over MgSO_4 and concentrated. The residue was chromatographed on a silica gel column using 1:6 ether-hexanes as eluant to afford 0.12 g (95%) of allene oxide 16 as a clear oil: $[\alpha]_D^{25} -25.66$ (c 4.15, CHCl_3); IR (cm^{-1} , film) 1749, 1238; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 7.29–7.68 (m), 4.57 (dd, $J = 3.1$ and 6.9 Hz), 3.96 (dd, $J = 3.1$ and 12.2 Hz), 3.74 (dd, $J = 6.9$ and 12.2 Hz), 2.05 (s), 1.95 (s), 1.90 (s), 1.15 (s), 0.92 (s); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) 170.4, 169.5, 148.7, 136.1, 136.0, 134.7, 129.4, 127.92, 127.87, 84.1, 70.3, 68.1, 62.2, 29.0, 20.8, 20.7, 18.8, 18.7, 15.0; HRMS calcd for $\text{C}_{23}\text{H}_{25}\text{O}_5\text{Si}$ ($\text{M}^+ - \text{Bu}$) 409.1471, found 409.1460.

B. From Diacetate 9. To a solution of 0.10 g (0.22 mmol) of allenic diacetate 9 in 2 mL of CH_2Cl_2 at 0 °C was added 76 mg (0.22 mmol) of 50% *m*-CPBA. After 4 h, the reaction mixture was diluted with ether and aqueous 0.5 N NaOH. The aqueous layer was extracted with ether, and the combined organic layers were washed with brine, dried over MgSO_4 and concentrated. The residue was chromatographed on a silica gel column using 1:6 ether-hexanes as eluant to afford 78 mg (75%) of allene oxide 16 as a clear oil.

(3*R*,5*S*)-5-(Benzoyloxy)-6-[(*tert*-butyldimethylsilyloxy)-2-(*tert*-butyldiphenylsilyloxy)-4-methyl-2,3-hexadiene (19). To a solution of 0.20 g (0.42 mmol) of allenic alcohol 7 in 3 mL of CH_2Cl_2 at rt was added 0.15 mL (1.26 mmol) of BzCl , 0.23 mL (1.68 mmol) of pyridine, and a catalytic amount of DMAP. After 24 h, the reaction mixture was quenched with aqueous NH_4Cl and extracted with ether. The ether layer was dried over MgSO_4 and concentrated. The residue was chromatographed on a silica gel column using 1:10 ether-hexanes as eluant to afford 0.24 g (98%) of allenic benzoate 19 as a clear oil: $[\alpha]_D^{25} +16.18$ (c 0.72, CHCl_3); IR (cm^{-1} , film) 1944, 1721; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 7.29–8.00 (m), 5.63 (dd, $J = 4.2$ and 7.9 Hz), 3.75 (dd, $J = 7.9$ and 11.0 Hz), 3.69 (dd, $J = 4.2$ and 11.0 Hz), 1.76 (s), 1.75 (s), 1.12 (s), 0.81 (s), 0.00 (s), -0.05 (s); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) 208.0, 166.1, 136.2, 134.0, 133.8, 132.7, 130.6, 129.7, 129.3, 129.2, 128.2, 127.8, 127.6, 90.0, 88.7, 75.6, 64.1, 28.1, 25.8, 18.9, 18.6, 18.2, 15.9, -5.33, -5.36. Anal. Calcd. for $\text{C}_{36}\text{H}_{48}\text{O}_5\text{Si}_2$: C, 73.92; H, 8.27. Found: C, 73.64; H, 8.35.

(4*S*,5*R*)-5-(Benzoyloxy)-6-[(*tert*-butyldimethylsilyloxy)-2-(*tert*-butyldiphenylsilyloxy)-4-methyl-4-hydroxy-1-hexen-3-one (20). The procedure described for 10 was employed with 0.30 g (0.51 mmol) of allenic benzoate 19 in 5 mL of CH_2Cl_2 at rt and 0.35 g of Na_2HPO_4 followed by 0.35 g (1.03 mmol) of 50% *m*-CPBA. After 6 h, isolation as described, followed by chromatography on a silica gel column using 1:10 ether-hexanes as eluant, afforded 0.29 g (92%) of enone 20 as a clear oil: $[\alpha]_D^{25} -13.41$ (c 0.82, CHCl_3); IR (cm^{-1} , film) 3449, 1723; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 7.27–8.10 (m), 7.04 (d, $J = 1.5$ Hz), 6.26 (d, $J = 1.5$ Hz), 5.62 (dd, $J = 4.0$ and 5.0 Hz), 4.50 (s), 4.16 (dd, $J = 4.0$ and 11.3 Hz), 4.02 (dd, $J = 5.0$ and 11.3 Hz), 1.42 (s), 1.07 (s), 0.85 (s), 0.03 (s), 0.02 (s); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) 206.9, 165.4, 146.1, 142.3, 136.2, 136.1, 134.1, 134.0, 133.2, 129.9, 129.3, 129.2,

128.4, 127.63, 127.61, 80.9, 77.1, 62.2, 29.1, 25.8, 24.2, 18.6, 18.1, -5.52, -5.54. Anal. Calcd for $\text{C}_{36}\text{H}_{48}\text{O}_5\text{Si}_2$: C, 70.09; H, 7.84. Found: C, 70.07; H, 7.98.

(4*S*,5*R*)-5-(Benzoyloxy)-6-[(*tert*-butyldimethylsilyloxy)-4-[(*tert*-butyldiphenylsilyloxy)-4-methyl-1-hexen-3-one (21). The procedure described for 11 was employed with 0.10 g (0.16 mmol) of enone 20 in 0.5 mL of CH_2Cl_2 at rt and 5 mg of DBU. After 2 h, isolation as described, followed by chromatography on a silica gel column using 1:10 ether-hexanes as eluant, afforded 90 mg (90%) of enone 21 as a clear oil: $[\alpha]_D^{25} -12.04$ (c 1.08, CHCl_3); IR (cm^{-1} , film) 1722, 1268; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 7.21–8.01 (m), 6.96 (dd, $J = 10.4$ and 17.1 Hz), 6.15 (d, $J = 1.9$ and 17.1 Hz), 5.55 (dd, $J = 1.9$ and 10.4 Hz), 5.50 (dd, $J = 5.0$ and 6.4 Hz), 3.99 (dd, $J = 5.0$ and 11.1 Hz), 3.85 (dd, $J = 6.4$ and 11.1 Hz), 1.33 (s), 1.03 (s), 0.77 (s), -0.04 (s), -0.07 (s); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) 197.5, 165.6, 136.2, 136.0, 134.46, 136.43, 133.0, 131.4, 130.2, 129.8, 128.6, 129.5, 128.9, 128.4, 127.4, 127.3, 82.8, 78.2, 61.5, 27.4, 25.7, 21.3, 19.7, 18.1, -5.59. Anal. Calcd for $\text{C}_{36}\text{H}_{48}\text{O}_5\text{Si}_2$: C, 70.09; H, 7.84. Found: C, 70.11; H, 8.06.

(3*R*,5*R*)-5-(Benzoyloxy)-6-[(*tert*-butyldimethylsilyloxy)-2-(*tert*-butyldiphenylsilyloxy)-4-methyl-2,3-hexadiene (22). To a solution of 0.50 g (1.04 mmol) of allenic alcohol 7, 190 mg (1.56 mmol) of PhCOOH , and 0.41 g (1.56 mmol) of PPh_3 in 5 mL of C_6H_6 at 0 °C was added a solution of 271 mg (1.56 mmol) of DEAD in 0.2 mL of C_6H_6 . After 5 min, the reaction mixture was quenched with aqueous NH_4Cl and extracted with ether. The ether layer was dried over MgSO_4 and concentrated. The residue was chromatographed on a silica gel column using 1:40 ether-hexanes as eluant to afford 0.50 g (83%) of allenic benzoate 22 as a clear oil: $[\alpha]_D^{25} -54.29$ (c 1.05, CHCl_3); IR (cm^{-1} , film) 1945, 1723; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 7.25–8.14 (m), 5.40 (t, $J = 5.8$ Hz), 3.57 (d, $J = 5.8$ Hz), 1.76 (s), 1.62 (s), 1.10 (s), 0.81 (s), -0.02 (s), -0.04 (s); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) 208.0, 166.3, 136.5, 134.6, 134.2, 133.1, 130.0, 129.6, 129.5, 128.6, 128.1, 127.8, 91.2, 89.9, 76.4, 64.1, 28.5, 26.2, 19.2, 18.8, 18.6, 16.1, -4.92, -4.97. Anal. Calcd for $\text{C}_{36}\text{H}_{48}\text{O}_5\text{Si}_2$: C, 73.92; H, 8.27. Found: C, 73.91; H, 8.32.

(4*S*,5*S*)-5-(Benzoyloxy)-6-[(*tert*-butyldimethylsilyloxy)-2-(*tert*-butyldiphenylsilyloxy)-4-methyl-4-hydroxy-1-hexen-3-one (23). The procedure described for 10 was employed with 0.30 g (0.51 mmol) of allenic benzoate 22 in 5 mL of CH_2Cl_2 at rt and 0.35 g of Na_2HPO_4 followed by 0.35 g (1.03 mmol) of 50% *m*-CPBA. After 6 h, isolation as described, followed by chromatography on a silica gel column using 1:10 ether-hexanes as eluant, afforded 0.28 g (89%) of enone 23 as a clear oil: $[\alpha]_D^{25} -2.20$ (c 1.01, CHCl_3); IR (cm^{-1} , film) 3451, 1723; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 7.27–8.10 (m), 7.04 (d, $J = 1.7$ Hz), 6.29 (d, $J = 1.7$ Hz), 5.62 (t, $J = 4.5$ Hz), 4.62 (s), 3.87 (dd, $J = 4.5$ and 11.3 Hz), 3.83 (dd, $J = 4.5$ and 11.3 Hz), 1.17 (s), 1.14 (s), 0.83 (s), -0.02 (s), -0.03 (s); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) 208.6, 166.1, 147.3, 140.5, 140.5, 136.40, 136.35, 133.8, 133.3, 129.9, 129.8, 129.42, 129.39, 128.4, 127.8, 127.6, 81.6, 75.4, 62.6, 29.0, 25.7, 23.7, 18.9, 18.1, -5.58, -5.62. Anal. Calcd for $\text{C}_{36}\text{H}_{48}\text{O}_5\text{Si}_2$: C, 70.09; H, 7.84. Found: C, 69.91; H, 7.90.

(4*S*,5*S*)-5-(Benzoyloxy)-6-[(*tert*-butyldimethylsilyloxy)-4-[(*tert*-butyldiphenylsilyloxy)-4-methyl-1-hexen-3-one (24). The procedure described for 11 was employed with 0.30 g (0.49 mmol) of enone 23 in 1.0 mL of CH_2Cl_2 and 15 mg of DBU. After 2 h, isolation as described, followed by chromatography on a silica gel column using 1:10 ether-hexanes as eluant, afforded 0.29 g (95%) of enone 24 as a clear oil: $[\alpha]_D^{25} +7.50$ (c 2.80, CHCl_3); IR (cm^{-1} , film) 1726, 1701, 1106; $^1\text{H NMR}$ (CDCl_3 , 500 MHz) δ 7.27–8.03 (m), 7.10 (dd, $J = 10.4$ and 17.2 Hz), 6.27 (d, $J = 1.9$ and 17.2 Hz), 5.65 (d, $J = 1.9$ and 10.4 Hz), 5.49 (dd, $J = 4.8$ and 7.0 Hz), 3.88 (dd, $J = 4.8$ and 11.0 Hz), 3.77 (dd, $J = 7.0$ and 11.0 Hz), 1.24 (s), 1.03 (s), 0.76 (s), -0.06 (s), -0.08 (s); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) 199.2, 166.2, 136.6, 136.5, 135.0, 133.4, 132.1, 130.5, 130.2, 130.0, 129.1, 128.8, 127.9, 127.8, 83.4, 79.1, 61.8, 27.7, 26.1, 22.1, 20.0, 18.5, 15.7, -5.17. Anal. Calcd for $\text{C}_{36}\text{H}_{48}\text{O}_5\text{Si}_2$: C, 70.09; H, 7.84. Found: C, 70.16; H, 7.88.

(*E*)-(5*S*,6*R*)-6-Acetoxy-7-[(*tert*-butyldimethylsilyloxy)-3-(*tert*-butyldiphenylsilyloxy)-5-hydroxy-5-methyl-2-hepten-4-one (31). The procedure described for enone 10 was employed with 0.30 g (0.56 mmol) of allenic acetate 30 in 6 mL of CH_2Cl_2 , 0.39 g of Na_2HPO_4 , and 0.39 g (1.12 mmol) of 50% *m*-CPBA. After 6 h, isolation as described, followed by chromatography on

a silica gel column using 1:8 ether-hexanes as eluant, afforded 0.26 g (81%) of enone **31** as a clear oil: $[\alpha]_D^{25}$ -14.87 (c 3.16, CHCl_3); IR (cm^{-1} , film) 3468, 1745, 1686; $^1\text{H NMR}$ (CDCl_3 , 500 MHz) δ 7.26–7.75 (m), 6.39 (q, $J = 6.8$ Hz), 5.05 (dd, $J = 3.0$ and 4.3 Hz), 3.86 (dd, $J = 3.0$ and 11.8 Hz), 3.74 (dd, $J = 4.3$ and 11.8 Hz), 3.37 (s), 1.99 (s), 1.92 (d, $J = 6.8$ Hz), 1.09 (s), 0.82 (s), 0.65 (s), -0.08 (s); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) 212.4, 170.6, 145.5, 141.2, 136.95, 136.93, 134.9, 134.8, 129.6, 128.1, 127.9, 81.9, 75.3, 62.6, 29.2, 26.2, 22.4, 21.4, 20.1, 18.9, 18.4, -5.24, -5.26. Anal. Calcd for $\text{C}_{32}\text{H}_{48}\text{O}_6\text{Si}_2$: C, 67.56; H, 8.50. Found: C, 67.78; H, 8.20.

(E)-(5S,6R)-6-Acetoxy-7-[(tert-butylidimethylsilyloxy]-5-[(tert-butylidiphenylsilyloxy)-5-methyl-2-hepten-4-one (33). The procedure described for enone **11** was employed with 200 mg (0.35 mmol) of enone **31** in 0.5 mL of CH_2Cl_2 and 10 mg of DBU. After 3 h, isolation as described, followed by chromatography on a silica gel column using 1:10 ether-hexanes as eluant, afforded 180 mg (90%) of enone **33** as a clear oil: $[\alpha]_D^{25}$ +28.57 (c 0.77, CHCl_3); IR (cm^{-1} , film) 1750, 1631; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 7.26–7.70 (m), 6.74 (dq, $J = 6.8$ Hz), 6.62 (d, $J = 16.6$ Hz), 5.28 (dd, $J = 4.3$ and 7.3 Hz), 3.73 (dd, $J = 4.3$ and 11.0 Hz), 3.65 (dd, $J = 7.3$ and 11.0 Hz), 2.00 (s), 1.79 (d, $J = 6.5$ Hz), 1.24 (s), 1.03 (s), 0.82 (s), -0.01 (s); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) 197.4, 170.2, 143.7, 136.6, 136.4, 135.2, 135.1, 129.9, 129.8, 127.7, 127.0, 83.0, 78.0, 61.9, 27.7, 26.1, 21.4, 21.3, 20.1, 18.6, 18.5, -5.15; HRMS calcd for $\text{C}_{28}\text{H}_{39}\text{O}_6\text{Si}_2$ ($\text{M}^+ - \text{Bu}$) 511.2334, found 511.2336. Anal. Calcd for $\text{C}_{32}\text{H}_{48}\text{O}_6\text{Si}_2$: C, 67.56; H, 8.50. Found: C, 67.72; H, 8.57.

(2R,3S,4R,5R)-5-Acetoxy-6-[(tert-butylidimethylsilyloxy]-4-[(tert-butylidiphenylsilyloxy)-1,2-epoxy-4-methyl-3-hexanol (39). To a solution of 400 mg (0.72 mmol) of alcohol **38** in 2 mL of toluene at rt was added 0.79 mL (4.32 mmol) of 5.5 M TBHP in 2,2,4-trimethylpentane and 92 mg of $\text{VO}(\text{acac})_2$. After 5 h, the reaction mixture was quenched with water and extracted with ether. The ether layer was dried over MgSO_4 and concentrated. The residue was chromatographed on a silica gel column using 1:4 ether-hexanes as eluant to afford 350 mg (85%) of epoxide **39** as a clear oil: $[\alpha]_D^{25}$ -12.8 (c 4.60, CHCl_3); IR (cm^{-1} , film) 3464, 1747; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 7.30–7.76 (m), 4.86 (dd, $J = 4.1$ and 5.3 Hz), 3.91 (dd, $J = 5.3$ and 11.2 Hz), 3.81 (dd, $J = 4.1$ and 11.2 Hz), 3.54 (t, $J = 4.8$ Hz), 3.20 (dt, $J = 4.8$ and 3.4 Hz), 2.97 (d, $J = 4.8$ Hz), 2.69 (d, $J = 3.4$ Hz), 1.96 (s), 1.19 (s), 1.04 (s), 0.85 (s), 0.01 (s), 0.00 (s); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) 169.9, 136.2, 136.1, 134.8, 134.6, 129.9, 129.8, 127.7, 127.5, 79.6, 77.8, 73.4, 61.0, 51.2, 44.3, 27.4, 25.7, 22.1, 21.1, 19.8, 18.1, -5.56. Anal. Calcd for $\text{C}_{31}\text{H}_{48}\text{O}_8\text{Si}_2$: C, 64.99; H, 8.45. Found: C, 64.88; H, 8.52.

(2R,3R,4S,5R)-2-Acetoxy-1-[(tert-butylidimethylsilyloxy]-4-[(tert-butylidiphenylsilyloxy)-5,6-epoxy-3-methyl-3-hexanol (40). A solution of 200 mg (0.35 mmol) of epoxide **39** in 1.0 mL of 1 N $\text{NaOH}/t\text{-BuOH}$ (1:6) was stirred at rt for 3 h. The reaction mixture was quenched with aqueous NH_4Cl and extracted with ether. The ether layer was dried over MgSO_4 and concentrated. The residue was chromatographed on a silica gel column using 1:4 ether-hexanes as eluant to afford 140 mg (70%) of alcohol **40** as a clear oil: $[\alpha]_D^{25}$ -2.39 (c 1.17, CHCl_3); IR (cm^{-1} , film) 3455, 1741; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 7.35–7.74 (m), 5.38 (dd, $J = 3.2$, and 6.9 Hz), 3.72 (dd, $J = 3.2$ and 11.3 Hz), 3.61 (dd, $J = 6.9$ and 11.3 Hz), 3.45 (d, $J = 7.7$ Hz), 3.03 (ddd, $J = 2.6$, 3.9 and 7.7 Hz), 2.90 (s), 2.11 (dd, $J = 3.9$ and 4.9 Hz), 2.04 (s), 1.76 (dd, $J = 2.6$ and 4.9 Hz), 1.19 (s), 1.06 (s), 0.87 (s), 0.04 (s), 0.03 (s); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) 171.2, 136.0, 135.9, 133.4, 132.4, 130.2, 129.9, 127.9, 127.6, 78.0, 76.3, 76.1, 61.9, 50.7, 46.1, 26.9, 25.7, 21.1, 19.7, 18.5, 18.1, -5.39, -5.45. Anal. Calcd for $\text{C}_{31}\text{H}_{48}\text{O}_8\text{Si}_2$: C, 64.99; H, 8.45. Found: C, 65.07; H, 8.52.

(1R,2S,3S,4R)-1-(Acetoxymethyl)-3,4-diacetoxy-2-methyltetrahydropyran-2-ol (48). A. From Epoxide **39**. A solution of 300 mg (0.52 mmol) of epoxide **39** in 1.0 mL of 1 N $\text{NaOH}/t\text{-BuOH}$ (1:3) was heated to reflux for 48 h. The reaction mixture was quenched with aqueous NH_4Cl and extracted with ether. The ether layer was dried over MgSO_4 and concentrated. The residue was chromatographed on a silica gel column using 1:4 ether-hexanes as eluant to afford a separable mixture of 160 mg (58%) of diol **42** and 20 mg (10%) of triol **43**. Diol **42**: IR (cm^{-1} , film) 3428, 1108; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 7.33–7.70 (m), 4.30 (dd, $J = 4.3$ and 6.5 Hz), 3.82–4.62 (m), 3.77 (d, $J = 3.8$

Hz), 3.64 (bs), 1.30 (s), 1.01 (s), 0.91 (s), 0.08 (s), 0.08 (s). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) 136.2, 136.1, 134.8, 134.6, 129.9, 127.8, 127.5, 86.3, 85.5, 81.2, 78.4, 62.7, 62.2, 27.3, 26.1, 19.5, 18.5, -5.15, -5.22. Triol **43**: IR (cm^{-1} , film) 3388, 1112; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 7.32–7.71 (m), 4.25 (t, $J = 6.7$ Hz), 3.40–4.00 (m), 1.43 (s), 1.08 (s); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) 135.8, 135.7, 133.6, 133.1, 130.08, 130.03, 127.87, 127.82, 82.0, 79.8, 79.2, 71.6, 71.1, 64.4, 26.9, 19.3, 16.8.

The procedure described for diol **9** was employed with 50 mg (0.094 mmol) of diol **42** in 0.3 mL of CH_2Cl_2 , 10 mg (0.095 mmol) of Ac_2O , 9.0 mg (0.105 mmol) of pyridine, and a catalytic amount of DMAP. Likewise, 20 mg (0.048 mmol) of diol **43** in 0.15 mL of CH_2Cl_2 , 10 mg (0.096 mmol) of Ac_2O , 8.0 mg (0.10 mmol) of pyridine, and a catalytic amount of DMAP were subjected to the same procedure. After 5 h, isolation as described, followed by chromatography on a silica gel column using 1:6 ether-hexanes as eluant, afforded 51 mg (95%) of acetate **44**. Analogous isolation afforded 22 mg (98%) of diacetate **45** as a clear oil.

To a solution of 50 mg (0.087 mmol) of acetate **44** in 0.2 mL of THF was added 0.26 mL (0.262 mmol) of 1.0 M TBAF in THF. Likewise, 20 mg (0.040 mmol) of diacetate **45** in 0.1 mL of THF and 0.06 mL (0.06 mmol) of 1.0 M TBAF in THF were subjected to the same procedure. The mixture was stirred at rt for 12 h, quenched with aqueous NH_4Cl , and extracted with ether. The ether layer was dried over MgSO_4 and concentrated to afford crude triol **46**. Analogous isolation afforded diacetate **47**.

To a solution of triol **46** in 0.3 mL of CH_2Cl_2 was added 2.0 equivs. of Ac_2O , 2.1 equivs. of pyridine and a catalytic amount of DMAP. Likewise diacetate **47** in 0.1 mL of CH_2Cl_2 , 1.0 equiv. of Ac_2O , 1.1 equivs. of pyridine and a catalytic amount of DMAP was subjected to the same procedure. After 5 h, the reaction mixture was quenched with aqueous NH_4Cl and extracted with ether. The ether layer was dried over MgSO_4 and concentrated. The residue was chromatographed on a silica gel column using 1:1 ether-hexanes as eluant to afford 20 mg (80%) of triacetate **48** as white needles. Analogous isolation starting from diacetate **47** afforded 95 mg (78%) of triacetate **48**, mp 93–95 °C. $[\alpha]_D^{25}$ +16.30 (c 0.81, CHCl_3). IR (cm^{-1} , film) 3484, 1743; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 5.19 (d, $J = 3.9$ Hz), 4.56 (ddd, $J = 3.9$, 5.5 and 7.0 Hz), 4.38 (dd, $J = 4.3$ and 12 Hz), 4.17 (d, $J = 5.5$ and 11.4 Hz), 4.14 (dd, $J = 6.8$ and 12 Hz), 4.06 (d, $J = 7.0$ and 11.4 Hz), 3.98 (dd, $J = 4.3$ and 6.8 Hz), 2.78 (s), 2.08 (s), 2.06 (s), 2.02 (s), 1.27 (s). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) 171.6, 171.2, 170.3, 82.3, 80.4, 80.3, 77.3, 63.4, 62.7, 21.3, 21.2, 21.1, 19.2. Anal. Calcd for $\text{C}_{13}\text{H}_{20}\text{O}_8$: C, 51.31; H, 6.62. Found: C, 51.42; H, 6.64.

B. From Epoxide 40. A solution of 350 mg (0.61 mmol) of epoxide **40** in 1.0 mL of 0.5 N $\text{NaOH}/t\text{-BuOH}$ (1:3) was heated to reflux for 36 h. The reaction mixture was quenched with aqueous NH_4Cl and extracted with ether. The ether layer was dried over MgSO_4 and concentrated. The residue was chromatographed on a silica gel column using 1:4 ether-hexanes as eluant to afford 200 mg (62%) of diol **42** as the major product. Diol **42** was transformed into triacetate **48** in 82% yield by acetylation, desilylation and acetylation as described above.

(2S,3S,4S,5R)-3,5:4,6-Bis(isopropylidenedioxy)-4-methyl-1-(phenylthio)-2-hexanol (50). To a solution of 250 mg (0.44 mmol) of epoxide **39** in 2 mL of dioxane and 2 mL of 0.5 N NaOH was added 0.13 mL (1.31 mmol) of benzenethiol. The reaction mixture was stirred at 65 °C for 5 h and then quenched with aqueous NH_4Cl and extracted with ether. The ether layer was dried over MgSO_4 and concentrated. The aqueous phase was extracted with ether. The ether layer was dried over MgSO_4 and concentrated to afford a mixture of products as a yellow oil. To a solution of the crude products in 2 mL of THF was added 1.31 mL (1.31 mmol) of 1.0 M TBAF in THF. The reaction mixture was stirred at rt for 6 h, quenched with aqueous NH_4Cl , and extracted with ether. The ether layer was dried over MgSO_4 and concentrated to afford crude pentol **49** as a yellow oil.

To a solution of the crude pentol **49** in 1.5 mL of 2,2-dimethoxypropane was added a catalytic amount of *p*-TsOH. The mixture was stirred at rt for 5 h and then quenched with aqueous NH_4Cl and extracted with ether. The ether layer was dried over MgSO_4 and concentrated. The aqueous phase was extracted with ether. The ether layer was dried over MgSO_4 and concentrated. The residue was chromatographed on a silica gel column using 1:1 ether-hexanes as eluant to afford 89 mg (54%

for three steps) of sulfide **50** as a clear oil: $[\alpha]_D^{25}$ -6.10 (c 0.56, CHCl_3); IR (cm^{-1} , film) 3448, 1212; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 7.16–7.42 (m), 4.12 (dd, $J = 6.8$ and 8.2 Hz), 4.00 (dd, $J = 6.8$ and 8.2 Hz), 3.97 (d, $J = 9.2$ Hz), 3.93 (t, $J = 8.2$ Hz), 3.74 (dddd, $J = 9.2$, 8.2, 3.8 and 2.6 Hz), 3.48 (dd, $J = 2.6$ and 14.0 Hz), 2.99 (dd, $J = 8.2$ and 14.0 Hz), 2.82 (d, $J = 3.8$ Hz), 1.40 (s), 1.38 (s), 1.37 (s), 1.26 (s), 1.13 (s); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) 135.4, 129.7, 129.0, 126.5, 109.5, 108.1, 82.2, 79.1, 78.8, 68.3, 65.6, 40.3, 28.7, 26.7, 26.1, 25.8, 19.2.

(2*S*,3*S*,4*S*,5*R*)-3,5:4,6-Bis(isopropylidenedioxy)-4-methyl-1-(phenylsulfinyl)-2-hexanol (51). To a solution of 70 mg (0.19 mmol) of sulfide **50** in 1.0 mL of CH_2Cl_2 was added 79 mg (0.22 mmol) of *m*-CPBA at -20°C . After 1.5 h, the reaction mixture was quenched with 0.1 N NaOH and extracted with CH_2Cl_2 . The organic layer was dried over MgSO_4 and concentrated. The residue was chromatographed on a silica gel column using 2:1 ether–hexanes as eluant to afford 69 mg (95%) of sulfoxide **51** as a separable 1:1 mixture of diastereoisomers: IR (cm^{-1} , film) 3484, 1211. Isomer one: $^1\text{H NMR}$ (CDCl_3 , 500 MHz) δ 7.56–7.93 (m), 4.28 (t, $J = 2.1$ and 9.9 Hz), 4.10 (dd, $J = 6.8$ and 8.1 Hz), 4.00 (dd, $J = 6.8$ and 8.1 Hz), 3.94 (d, $J = 9.2$ Hz), 3.91 (t, $J = 8.1$ Hz), 3.62 (d, $J = 2.1$ Hz), 3.55 (dd, $J = 2.1$ and 14.1 Hz), 3.27 (dd, $J = 9.9$ and 14.1 Hz), 1.37 (s), 1.35 (s), 1.31 (s), 1.25 (s), 1.13 (s). Isomer two: $^1\text{H NMR}$ (CDCl_3 , 500 MHz) δ 7.50–7.66 (m), 4.47 (td, $J = 1.0$ and 9.9 Hz), 4.13 (dd, $J = 6.8$ and 8.0 Hz), 4.00 (dd, $J = 6.8$ and 8.0 Hz), 3.96 (d, $J = 9.9$ Hz), 3.94 (t, $J = 8.0$ Hz), 3.14 (dd, $J = 1.0$ and 12.0 Hz), 3.27 (dd, $J = 9.9$ and 12.0 Hz), 1.39 (s), 1.38 (s), 1.36 (s), 1.28 (s), 1.21 (s).

(2*R*,3*S*,4*S*,5*R*)-3,5:4,6-Bis(isopropylidenedioxy)-4-methyl-1,2-hexanediol (53). To a solution of 70 mg (0.13 mmol) of sulfoxides **51** in 1.5 mL of Ac_2O was added 63 mg (0.76 mmol) of NaOAc. The reaction mixture was stirred at reflux for 15 h and quenched with 1.0 N NaOH. The aqueous layer was extracted with CH_2Cl_2 . The combined organic layer was dried over MgSO_4 and concentrated to afford the α -acetoxy sulfide as a mixture of diastereoisomers.

To a solution of the crude products in 0.5 mL of ether was added 23 mg (0.59 mmol) of LAH in one portion at 0°C . The mixture was stirred at 0°C for 1 h and quenched with saturated Na_2SO_4 . The aqueous phase was extracted with ether. The ether layer was dried over MgSO_4 and concentrated. The residue was chromatographed on a silica gel column using 2:1 ether–hexanes as eluant to afford 22 mg (62% for two steps) of diol **53** as a clear oil: $[\alpha]_D^{25}$ +6.30 (c 1.0, CHCl_3); IR (cm^{-1} , film) 3426, 1212; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 4.17 (dd, $J = 6.8$ and 7.4 Hz), 3.80–4.15 (m), 1.42 (s), 1.40 (s), 1.37 (s), 1.33 (s), 1.23 (s); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) 109.8, 108.3, 82.0, 78.9, 69.9, 65.6, 64.9, 28.7, 26.9, 26.0, 25.5, 20.0.

(2*R*,3*S*,4*S*,5*R*)-1-[(*tert*-Butyldiphenylsilyloxy)-3,5:4,6-bis(isopropylidenedioxy)-4-methyl-2-hexanol (54). To a solution of 20 mg (0.073 mmol) of diol **53** in 0.5 mL of CH_2Cl_2 was added 60 mg (0.086 mmol) of imidazole and 22 mg (0.080 mmol) of DPSCl. After 8 h, the reaction mixture was quenched with aqueous NH_4Cl and extracted with ether. The ether layer was dried over MgSO_4 and concentrated. The residue was chromatographed on a silica gel column using 1:3 ether–hexanes as eluant to afford 32 mg (88%) of alcohol **54** as a clear oil: $[\alpha]_D^{25}$ +8.10 (c 0.80, CHCl_3); IR (cm^{-1} , film) 3456, 1114; $^1\text{H NMR}$ (CDCl_3 , 500 MHz) δ 7.20–7.70 (m), 4.24 (d, $J = 9.4$ Hz), 4.14 (dd, $J = 6.7$ and 8.2 Hz), 4.02 (dd, $J = 6.7$ and 8.2 Hz), 3.96 (t, $J = 8.2$ Hz), 3.88 (dd, $J = 2.0$ and 10.2 Hz), 3.81 (dd, $J = 4.6$ and 10.2 Hz), 3.70 (ddd, $J = 2.0$, 4.6 and 9.4 Hz), 2.68 (s), 1.41 (s), 1.37 (s), 1.36 (s), 1.32 (s), 1.16 (s), 1.06 (s); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) 136.0, 135.9, 133.7, 133.4, 130.2, 128.2, 128.1, 109.6, 108.3, 82.5, 79.4, 76.7, 70.6, 66.05, 66.03, 29.0, 27.2, 27.0, 26.5, 26.6, 26.3, 19.7, 19.2.

(2*R*,3*S*,4*S*,5*R*)-1-[(*tert*-Butyldiphenylsilyloxy)-3,5-(isopropylidenedioxy)-4-methyl-2,4,6-triacetoxyhexane (56). To a solution of 24 mg (0.047 mmol) of alcohol **54** in 0.3 mL of THF– H_2O (4:1) was added 10 mL of TFA. The reaction mixture was stirred at rt for 5 h, quenched with saturated NaHCO_3 , and extracted with ether. The ether layer was dried over MgSO_4 and concentrated to afford the triol **55** as a clear oil. To a solution of triol **55** in 0.2 mL of CH_2Cl_2 was added 22 mg (0.21 mmol) of Ac_2O and 19 mg (0.24 mmol) of pyridine. After 5 h, the reaction mixture was quenched with aqueous NH_4Cl and extracted with ether. The ether layer was dried over MgSO_4 and concentrated. The residue was chromatographed on a silica gel column using 1:1 ether–hexanes as eluant to afford 20 mg (71% for two steps) of triacetate **56** as a clear oil: IR (cm^{-1} , film) 2948, 1737; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ 7.30–7.70 (m), 5.14 (dd, $J = 2.8$ and 9.2 Hz), 4.86 (dt, $J = 2.5$ and 9.9 Hz), 4.56 (dd, $J = 2.8$ and 11.9 Hz), 4.50 (d, $J = 9.9$ Hz), 4.06 (dd, $J = 9.2$ and 11.9 Hz), 3.88 (d, $J = 2.5$ Hz), 2.06 (s), 2.04 (s), 2.00 (s), 1.56 (s), 1.40 (s), 1.15 (s), 1.02 (s); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) 171.2, 170.4, 170.2, 135.91, 135.87, 133.70, 133.66, 130.13, 130.09, 128.08, 128.04, 108.6, 82.2, 73.8, 72.9, 72.4, 63.9, 63.5, 28.8, 27.0, 26.6, 21.24, 21.21, 21.17, 20.1, 19.7.

(2*R*,3*S*,4*S*,5*S*)-1-[(*tert*-Butyldimethylsilyloxy)-6-[(*tert*-butyldiphenylsilyloxy)-3-methyl-2,4,5-triacetoxy-3-hexanol (59). To a solution of 300 mg (0.54 mmol) of allylic alcohol **38** in 2.0 mL of acetone– H_2O (3:1) was added 132 mg (1.13 mmol) of NMO and a catalytic amount of OsO_4 . The reaction mixture was stirred at rt for 48 h and then quenched with saturated NaHSO_3 . The aqueous phase was extracted with ether. The ether layer was dried over MgSO_4 and concentrated. The residue was chromatographed on a silica gel column using 2:1 ether–hexanes as eluant to afford a 3:1 mixture of triols **57** and **58** as a clear oil.

To a solution of triols **57** and **58** in 1.0 mL of CH_2Cl_2 was added 115 mg (1.13 mmol) of Ac_2O and 107 mg (1.35 mmol) of pyridine. After 5 h, the reaction mixture was quenched with aqueous NH_4Cl and extracted with ether. The ether layer was dried over MgSO_4 and concentrated. The residue was chromatographed on a silica gel column using 1:1 ether–hexanes as eluant to afford 290 mg (81%) of triacetate **59** as a clear oil: $[\alpha]_D^{25}$ -0.86 (c 2.10, CHCl_3); IR (cm^{-1} , film) 3469, 1744; $^1\text{H NMR}$ (CDCl_3 , 500 MHz) δ 7.32–7.65 (m), 5.29 (d, $J = 4.6$ Hz), 5.17 (ddd, $J = 3.1$, 4.6 and 7.3 Hz), 4.78 (dd, $J = 4.6$ and 6.0 Hz), 3.99 (dd, $J = 3.1$ and 11.6 Hz), 3.78 (dd, $J = 3.6$ and 11.1 Hz), 3.75 (dd, $J = 7.3$ and 11.6 Hz), 3.65 (d, $J = 6.0$ and 11.1 Hz), 2.97 (s), 2.06 (s), 2.00 (s), 1.96 (s), 1.11 (s), 1.01 (s), 0.84 (s), 0.02 (s), 0.01 (s); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) 171.2, 170.7, 170.4, 136.1, 136.0, 133.7, 133.5, 130.2, 130.1, 128.12, 128.07, 76.2, 74.9, 73.8, 73.5, 62.5, 62.0, 27.1, 26.1, 21.4, 21.3, 21.1, 19.9, 19.5, 18.5, -5.22; HRMS calcd for $\text{C}_{31}\text{H}_{45}\text{O}_9\text{Si}_2$ ($\text{M}^+ - \text{Bu}$) 617.2602, found 617.2601. Anal. Calcd for $\text{C}_{35}\text{H}_{54}\text{O}_9\text{Si}_2$: C, 62.28; H, 8.06. Found: C, 62.42; H, 8.12.

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Supplementary Material Available: Experimental procedures for compounds **25–30**, **35–58**, and **61–65**; $^1\text{H NMR}$ spectra for compounds **3–5**, **7**, **10**, **12–14**, **16**, **25–27**, **33**, **35**, **36**, **40**, **42**, **43**, **48**, **50**, **51**, **53**, **54**, **56**, **61**, and **62**, and selected $^{13}\text{C NMR}$ spectra (57 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.