A Stereochemically General Synthesis of 2-Deoxyhexoses via the Asymmetric Allylboration of 2,3-Epoxy Aldehydes

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A stereochemically general strategy for the synthesis of 2-deoxyhexoses is described. This new approach involves the asymmetric allylboration of epoxy aldehydes **12** and **13**, prepared via the Sharpless asymmetric epoxidation reaction, as a means of establishing the stereochemistry of the sugar backbone. Thus, the matched double asymmetric allylborations of **12** and **13** using tartrate allylboronates (*R,R*)- and (*S,S*)-**7**, respectively, provide *erythro* epoxy alcohols **14** and **16** with excellent diastereoselectivity (>96:4) and enantioselectivity (≥96% ee). The mismatched double asymmetric reactions of **12** and **13** using (*S,S*)- and (*R,R*)-**7**, respectively, provided the diastereomeric *threo* epoxy alcohols **15** and **17** with lower (ca. 75:25) but still synthetically useful selectivity. The enantiomeric purity of the major diastereomer in each of these reactions was determined to be greater than that of the epoxy aldehyde precursors. Epoxy alcohols **14** and **16** were converted with excellent selectivity to the *l-arabino* (**21**) and *l-xylo* (**26**) tetrols via neighboring group assisted α-substitution reactions of the derived phenylurethane derivatives **18** and **23**. Stereochemically complementary β-opening reactions were accomplished by treating primary alcohols **38**, **40**, **42**, and **44** [prepared from **14–17**, respectively, by ethoxyethylation of C(4)-OH and removal of the C(7)-*tert*-butyldiphenylsilyl (TBDPS) ethers] with NaOH in aqueous *t*-BuOH at reflux. Acid-catalyzed hydrolysis of the C(4)-ethoxyethyl ethers then provided tetrols *d*-**35** (from **14**), *d*-**21** (from **15**), *d*-**30** (from **16**), and *d*-**26** (from **17**), each with excellent stereoselectivity. These tetrols were isolated and fully characterized as the tetraacetate derivatives **36**, **22**, **31**, and **27**, respectively. These β-opening reactions proceed by way of an epoxide migration (**29** to **33**) that inverts the stereochemistry at C(6) and activates C(7) toward nucleophilic attack. It is necessary that the C(4) hydroxyl be protected in three of the four stereoisomeric series to minimize competitive epoxide migration pathways (cf. **29** to **32a**). *arabino* tetrol **21** and *lyxo* tetrol **30** were converted to 2-deoxyglucose and 2-deoxygalactose, respectively, by a standard ozonolytic sequence and then to 2-deoxyglucitol pentaacetate (**45**) and 2-deoxygalactitol pentaacetate (**46**) via $NaBH_4$ reduction of the 2-deoxy sugars, thereby confirming all stereochemical assignments. The epoxide β-opening technology was also applied to epoxy benzyl ether **47** (prepared from **14**) and epoxy BOM ether **49** (deriving from **16**). These reactions provide tetrol derivatives **48** and **50**, respectively, in which the C(4)- and C(5)-hydroxyl functionality are suitably differentiated for use in subsequent synthetic sequences.

Introduction

The synthesis of carbohydrates and other polyhydroxylated materials from acyclic precursors remains a topic of considerable interest.[3] Rare monosaccharides are important structural components of numerous antibiotics, and highly functionalized carbohydrate derivatives continue to find widespread application as intermediates in natural products synthesis.[4] Of the many different strategies that have been explored, syntheses that proceed by way of epoxide intermediates have proven very popular.[5] For example, we have previously described syntheses of several 2,6-dideoxyhexoses proceeding by way of epoxy alcohol intermediates (cf. **2**) prepared via the Sharpless kinetic resolution/enantioselective epoxidation technology.[6,7] Two stereochemically complementary methods were employed for the regioselective manipulation of the epoxide units. In one, epoxy alcohols such as **2** were treated with aqueous acid to give triol derivatives with very high selectivity for attack of water at C(6), the epoxide carbon furthest removed from the carbinol center (Scheme I). This "β-mode" reactivity was applied in the synthesis of digitoxose summarized below. Alternatively, neighboring group assistance was employed for the delivery of oxygen nucleophiles to C(5), as illustrated in the olivose synthesis. We found that phenylurethanes were the best source of "tethered" oxygen nucleophiles and that these "α-mode" epoxide substitutions were best performed under anhydrous conditions in the presence of Lewis acids such as Et_2AlCl.[7]

Although this strategy for the synthesis of 2,6-dideoxyhexoses proved to be reasonably direct and efficient,[7] it suffers from several significant drawbacks: (i) because a resolution is involved, the maximum yield of useable nonracemic intermediates is 50%, and the separation of epoxy alcohol from the unreacted, kinetically resolved allylic alcohol is tedious, especially for large-scale work; (ii) the generality of this method is restricted since the efficiency of the kinetic resolution (that is, the relative rate of epoxidation of the two allylic alcohol enantiomers) and the diastereoselectivity of the epoxidation step are poor for secondary (*Z*)-allylic alcohols,[8] an important class of substrates; (iii) the α-opening methodology is unattractive in cases where the intended role of the carbohyrate frag-

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(2) Portions of this work are described in the Ph.D. Thesis of J. A. Straub, M.I.T., Cambridge, MA, 1987.
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ment is as an intermediate in subsequent reaction sequences, since the intrinsic differentiation of the C(4) and C(5) oxygen functionality in the epoxy alcohol substrate is lost in the course of the α-opening process (e.g., **2** to **3**). This is undesirable since 2-deoxy sugars with undifferentiated hydroxyl groups at C(3) and C(4) are produced, and the selective manipulation of this functionality is not always trivial.

We conclude that if sugars are to be synthesized de novo, it is imperative that the method be direct, efficient, completely general, and provide access to intermediates in which all of the hydroxyl functionality is completely differentiated for use in subsequent synthetic schemes.

We reasoned that these criteria might be satisfied by using the asymmetric allylboration of epoxy aldehydes as a means of establishing the stereochemistry of the sugar backbone.[9-13] This new approach, which promises to be exceptionally general and highly stereoselective, relies on two asymmetric transformations: (i) the Sharpless asymmetric epoxidation that provides epoxy alcohols generally with excellent enantioselectivity[6] and (ii) the asymmetric allylboration reaction that presumably can be used to achieve diastereoface selection in the addition of allyl or γ-alkoxyallyl units to the epoxy aldehydes.[11-14] Control of stereochemistry at C(3) relative to C(4) in **10** and **11** should be possible by selecting the appropriate (γ-alkoxyallyl)metal reagent **8** or **9**.[9,15] Given the ability to rationally manipulate the epoxide functionality, all possible hexoses of either absolute configuration should be easily accessible. In addition, as long as epoxide β-opening reactions are employed, the intrinsic differentiation of the C(4) and C(5) oxygen functionality already present in epoxy alcohols **10** and **11** can be carried through to strategic synthetic intermediates if the parent sugars themselves are not the ultimate targets (Scheme II).

We describe herein the results of the asymmetric allylborations of epoxy aldehydes **12** and **13** using tartrate allylboronates (*R,R*)- and (*S,S*)-**7** and applications of this chemistry to the highly diastereoselective synthesis of the four hept-1-ene-4,5,6,7-tetrol stereoisomers. The conversion of the *arabino* and *lyxo* diastereomers to 2-deoxyglucose and 2-deoxygalactose, respectively, is also described.

Results and Discussion

We began by studying the reactions of epoxy aldehydes **12** and **13** with both enantiomers of tartrate allylboronate **7** (Scheme III). The aldehydes were prepared by oxidation of the corresponding epoxy alcohols with NaOAc-buffered PCC (92–95% yield; see Experimental Section). When **12** was treated with achiral pinacol allylboronate, *erythro* epoxy alcohol **14** was produced as the major component of a 60:40 mixture.[16] The reaction of **12** and (*R,R*)-**7** therefore constitutes a matched pair since the selectivity for **14** increases to 96:4.[14] *erythro* epoxy alcohol **16** similarly is the major product (96:4) of a matched double asymmetric reaction of cis epoxy aldehyde **13** and (*S,S*)-**7**. Thus, two of the four epoxy alcohol diastereomers are available with excellent diastereoselectivity. The second pair of diastereomers, *threo* epoxy alcohols **15** and **17**, are available with lower but still synthetically useful selectivity (70–74:30–26) via the mismatched double asymmetric reactions of **12** and **13** with (*S,S*)- and (*R,R*)-**7**, respectively. The pairs of diastereomers produced in these reactions are easily separated chromatographically, and improved selectivity for **15** and **17** in the mismatched double asymmetric reactions presumably can be achieved by using a more highly enantioselective chiral allylmetal reagent.[12,17] The enantiomeric purity of the starting epoxy aldehydes, however, provides an upper limit of the diastereoselectivity that can be achieved in such reactions (vide infra).

An interesting aspect of these results is that the enantiomeric purities of the two products are different in each of the asymmetric allylboration reactions summarized here. This is a consequence of double stereodifferentiation involving distinctly different pathways for the reactions of **7** and the two epoxy aldehyde enantiomers, both of which are present since the Sharpless epoxidation provides the epoxy alcohol precursors to **12** and **13** in only 95% and 90% ee, respectively. For example, while the reaction of **13** with (*S,S*)-**7** is a matched pair that is highly stereoselective for **16**, the reaction of *ent*-**13**, the minor enantiom-

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(13) Chiral ((*Z*)-γ-alkoxyallyl)metal metal reagents: (a) Wuts, P. G. M.; Bigelow, S. S. *J. Chem. Soc., Chem. Commun.* **1984**, 736. (b) Brown, H. C.; Prabhakar, K. J.; Bhat, K. S. *J. Am. Chem. Soc.* **1988**, *110*, 1535. (c) Marshall, J. A.; Gung, W. Y. *Tetrahedron Lett.* **1989**, *30*, 2183.

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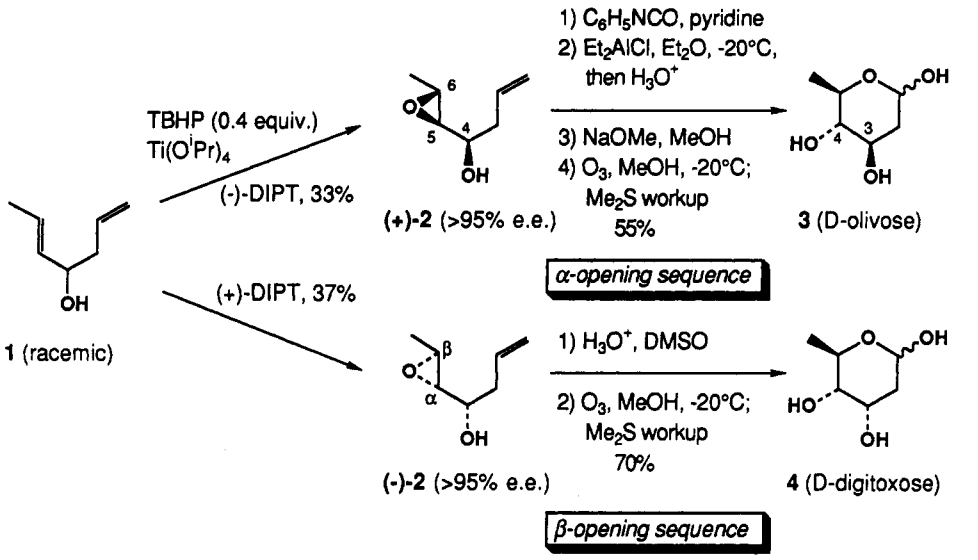
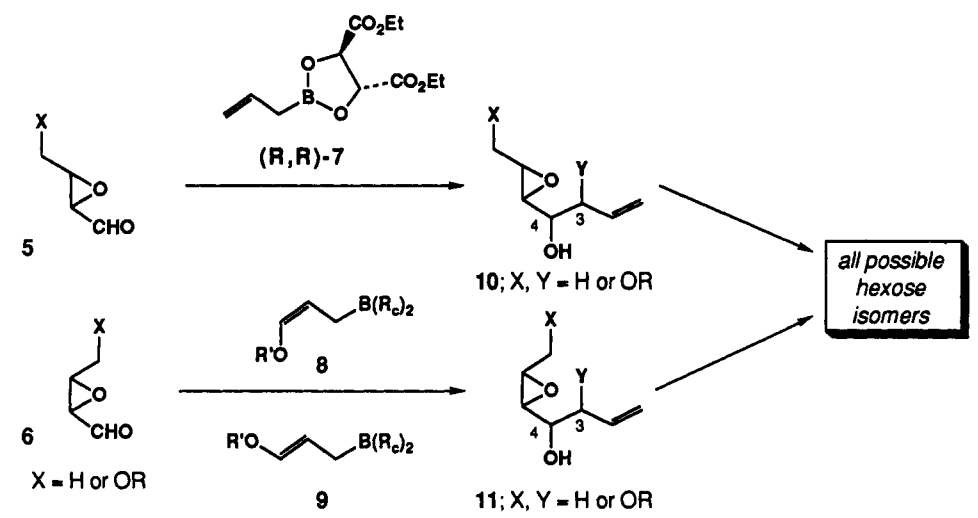
Scheme I



Scheme II



eric impurity present in **13**, with (*S,S*)-**7** is a mismatched combination that leads preferentially to *ent*-**17** (Scheme IV). *Thus, owing to the stereochemical preferences of the double asymmetric processes, the minor enantiomer of the epoxy aldehyde starting material is converted preferentially to the minor product diastereomer.* As a consequence, the enantiomeric purity of the major product is greater than that of the starting material, while the enantiomeric purity of the minor diastereomer is significantly less so. This is strikingly demonstrated by the reaction of **13** and (*S,S*)-**7**, where *the major enantiomer of the minor reaction product, ent-17, in fact derives from the minor enantiomer of 13.*

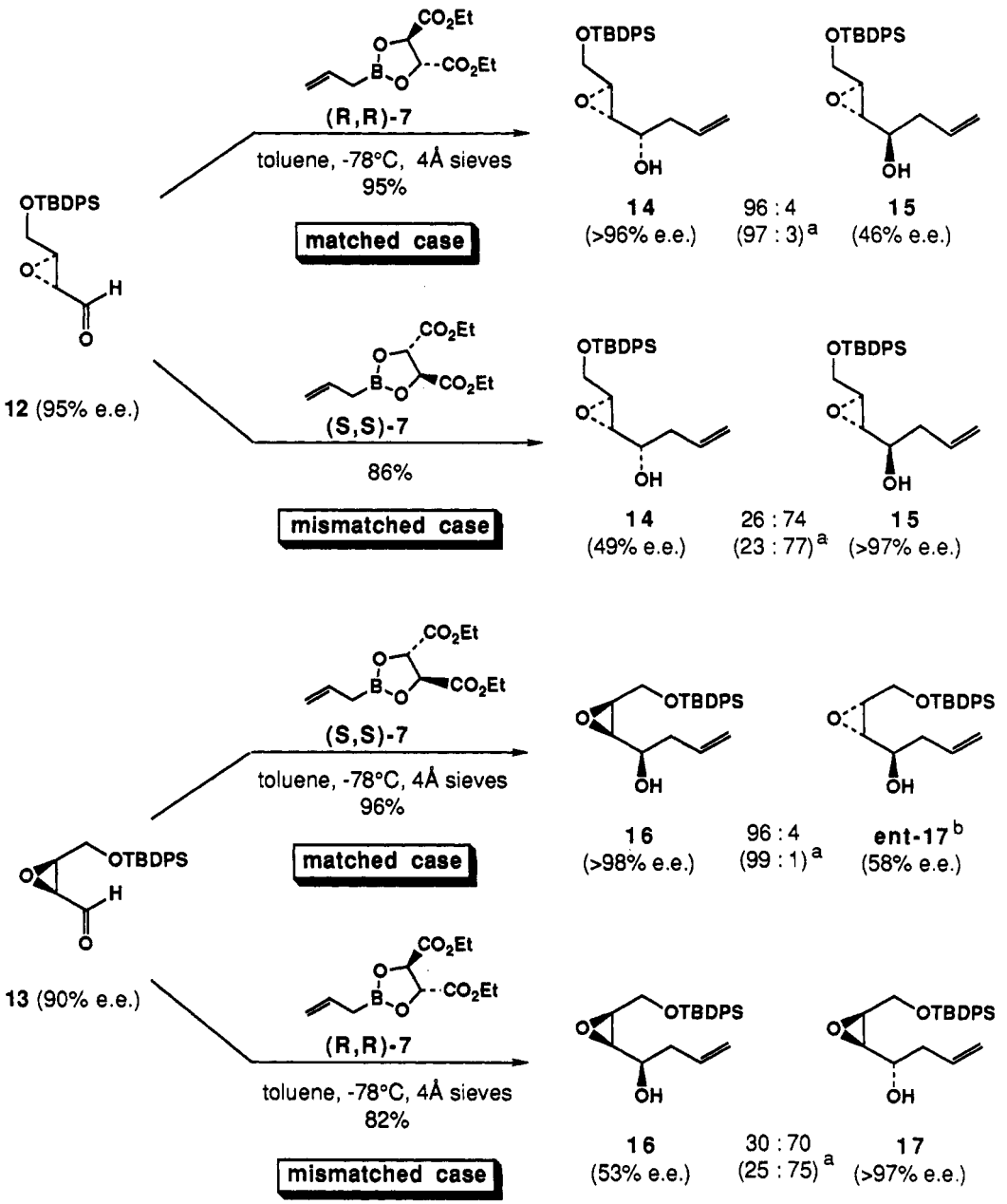
The enantiomeric purities of all reaction products are included in Scheme III. These data enable one to estimate the diastereoselectivity that should be obtained if the epoxy aldehydes were used in enantiomerically pure form. The total energy swings ($\Sigma\Delta\Delta G^{\ddagger}_{reagent}$) calculated for these pairs of double asymmetric reactions,[11g] that is, the total contribution of tartrate allylboronate **7** to the stereoselectivity of these reactions in energetic terms, is 1.8 kcal mol^{-1} for **12** and almost 2.1 kcal mol^{-1} for **13**, values well within the range that we consider normal for the reactions of **7** and well-behaved substrates.

The enhancement of the enantiomeric purity of the major diastereomer relative to that of the epoxy aldehyde starting materials has important ramifications in organic synthesis. These examples, along with those described by other investigators,[18] clearly demonstrate that products with very high enantiomeric purity can be prepared by linking multiple double asymmetric transformations in a synthetic pathway. *The enantiomeric purity of the major product diastereomer from a double asymmetric reaction will always be greater than that of its precursors as long as reagent-controlled mismatched double asymmetric pathways are accessible.* A direct implication is that, although desirable, it is not necessary to use chiral reagents with "overwhelmingly large" enantioselectivities in order to synthesize molecules with multiple asymmetric centers and high enantiomeric purity.

With the diastereofacial selectivity issue of the allylborations of epoxy aldehydes **12** and **13** now resolved, we

(18) (a) Hoye, T. R.; Suhadolnik, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5312. (b) Hoye, T. R.; Suhadolnik, J. C. *Tetrahedron* **1986**, *42*, 2855. (c) Schreiber, S. L.; Schreiber, T. S.; Smith, D. B. *J. Am. Chem. Soc.* **1987**, *109*, 1525. (d) Merifield, E.; Steel, P. G.; Thomas, E. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1826. (e) Enhancement of enantiomeric purity is also known to occur in coupling reactions in two chiral but not enantiomerically pure fragments: Kogure, T.; Eliel, E. L. *J. Org. Chem.* **1984**, *49*, 576. Midland, M. M.; Gabriel, J. *Ibid.* **1985**, *50*, 1143. Stafford, J. A.; Heathcock, C. H. *Ibid.* **1990**, *55*, 5433. We thank Prof. Heathcock for bringing these references to our attention.

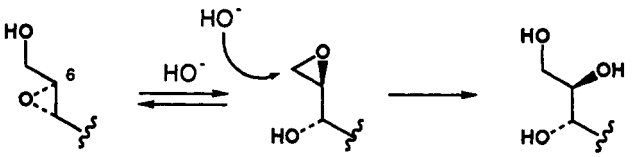
Scheme III[a,b]



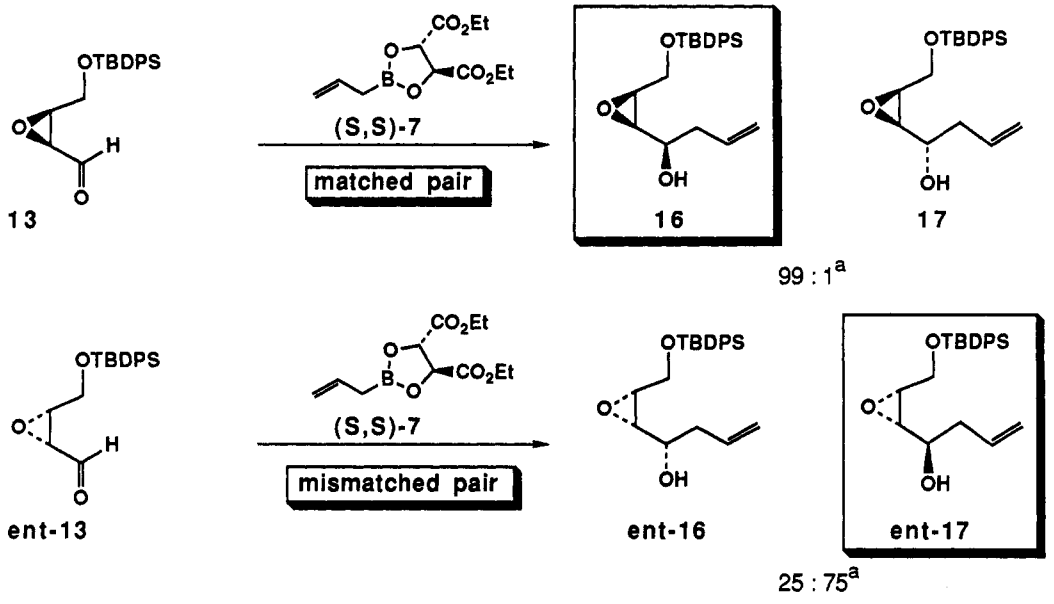
[a] Selectivity expected if epoxy aldehyde is 100% ee. [b] The major enantiomer of 17 in this case derives from the minor enantiomer of 13.

turned to an exploration of routes for the elaboration of **14–17** to the targeted 2-deoxyhexoses (Scheme V). As expected from our earlier studies,[7] neighboring group assisted "α-openings" proceeded smoothly via the intermediacy of phenylurethane derivatives. Thus, for example, phenylurethane **18** prepared from **14** was converted to carbonate **19** in greater than 95% isolated yield upon exposure to Et_2AlCl in Et_2O at −20 °C. Removal of the TBDPS protecting group was accomplished by exposure of **19** to Bu_4NF in tetrahydrofuran (THF) (53% yield), and then **20** was subjected to a standard methanolysis reaction to provide the L-*arabino* tetrol **21** (83%) that was characterized as the tetraacetate derivative **22**. This sequence was also performed by starting from epoxy alcohol **16**, leading ultimately to the L-*xylo* tetrol **26** and the tetraacetate derivative **27**. A mixture of carbonates **24a** and **24b** resulting from acyl transfer following epoxide opening was generally obtained. These isomers were separated chromatographically, but when treated with Bu_4NF to remove the TBDPS protecting group, each provided a mixture of diols **25a** and **25b**. Nevertheless, this sequence was highly stereoselective as only one tetraacetate (**27**) was obtained from the **25a,b** mixture.

Our original objective was to develop highly stereoselective β-opening reactions for the manipulation of **14–17** since this would permit the intrinsic functional group differentiation of C(4) and C(5), destined to become C(3) and C(4) in the targeted 2-deoxyhexoses, to be preserved via protection of C(4)-OH prior to the β-opening sequence. The presence of a protected hydroxymethyl group at C(7) suggested the possibility of a base-catalyzed epoxide migration sequence that would permit inversion of configuration at C(6) with subsequent nucleophilic ring opening at the most reactive primary position (cf. C(7)).[19]

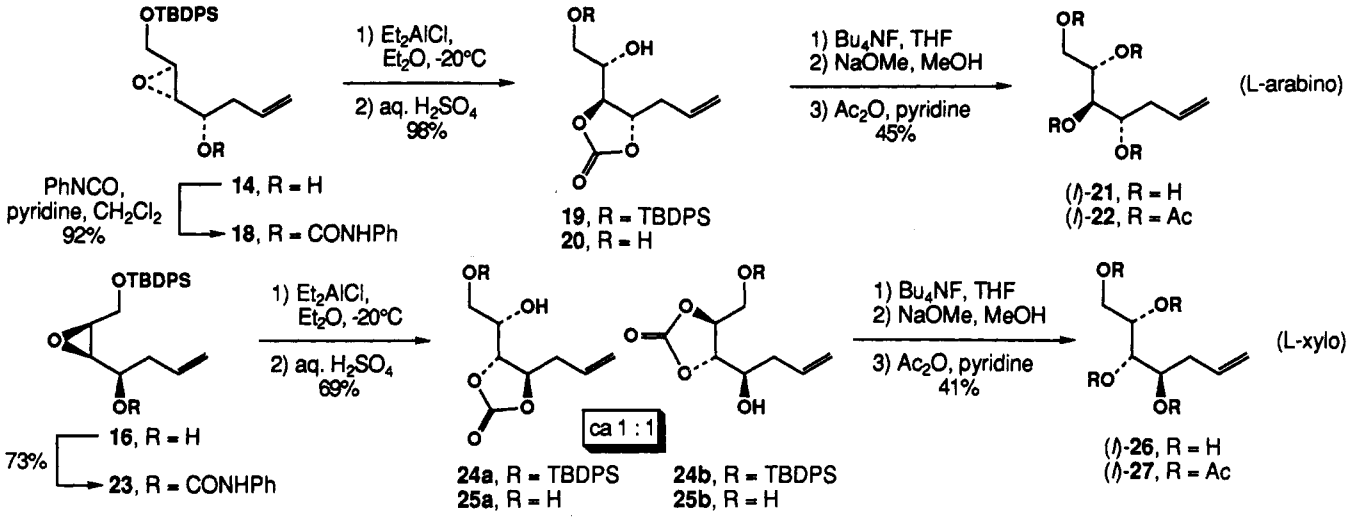


Scheme IV[a]



[a] Selectivity expected if **13** and *ent*-**13** are enantiomerically pure.

Scheme V

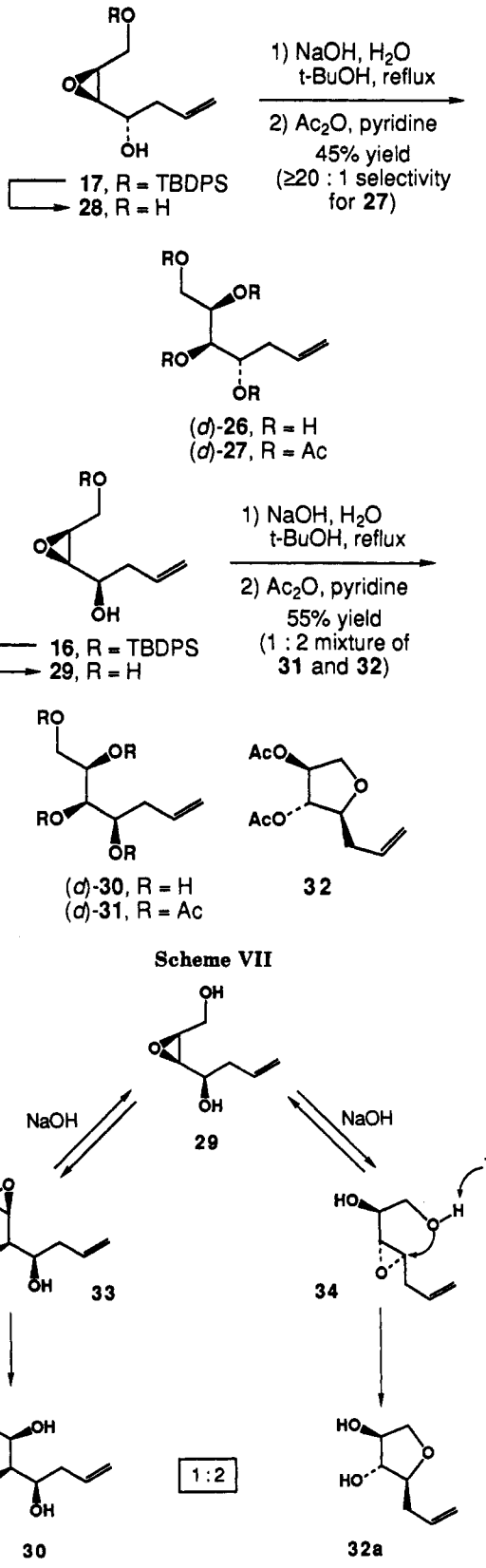


Initial experiments aimed at determining the feasibility of this strategy were performed by treating the epoxy diols corresponding to **14**–**17** (generated by treatment with Bu_4NF in THF, 78–85%) with NaOH in aqueous *t*-BuOH at reflux.[19b] Surprisingly, only the reaction of **28** (deriving from **17**) proceeded with good regioselectivity, providing *d*-**27**, the enantiomer of the tetraacetate generated by the α-opening of phenylurethane **23**, with ≥20:1 selectivity (Scheme VI). In contrast, the diol prepared from **15** provided a 9:1 mixture of two tetrols (**21** and a compound subsequently identified as **35**) that proved impossible to separate, and the reactions of the diols prepared from **14** and especially from **16** gave rise to significant amounts of byproducts believed to be tetrahydrofurans (cf. **29** to **31** and **32**). In the case of epoxy diol **29**, the unwanted tetrahydrofuran **32** presumably derives from a competitive epoxide migration pathway via epoxy alcohol isomer **34** that undergoes intramolecular cyclization faster than the terminal epoxide isomer **33** undergoes bimolecular nucleophilic substitution at C(7). Partial support for this hypothesis derives from the observation that treatment of **29** with NaOH in THF at ambient temperature provides the 4,5-epoxide isomer **34** in 79% isolated yield (Scheme VII).

It was clear from these results that it would be necessary to protect the free C(4)-OH so as to prevent competitive side reactions during the epoxide migration–hydrolysis sequence. For the purposes of synthesizing the parent 2-deoxyhexoses, we turned to intermediates possessing C(4)-ethoxyethyl (EE) ethers owing to their ease of introduction and subsequent removal. Thus, **14**–**17** were smoothly converted to diastereomeric mixtures of ethoxyethyl ethers **37**, **39**, **41**, and **44** [ethyl vinyl ether, pyridinium *p*-toluenesulfonate (PPTS), CH_2Cl_2, 85–95% yield], and then the TBDPS ethers were removed by treatment with Bu_4NF in THF (≥94% yield) (Scheme VIII). Alcohols **38**, **40**, **42**, and **44** were then subjected to the standard epoxide migration–nucleophilic substitution conditions. The ethoxyethyl ether protecting groups were hydrolyzed as part of the reaction workup, and tetrols **35**, **21**, **30**, and **26** were isolated and characterized as the tetraacetate derivatives **36**, **22**, **31**, and **27**, respectively.

(19) (a) Payne, G. B. *J. Org. Chem.* **1962**, *27*, 3819. (b) Katsuki, T.; Lee, A. W. M.; Ma, P.; Martin, V. S.; Masamune, S.; Sharpless, K. B.; Tuddenham, D.; Walker, F. J. *J. Org. Chem.* **1982**, *47*, 1373.

Scheme VI

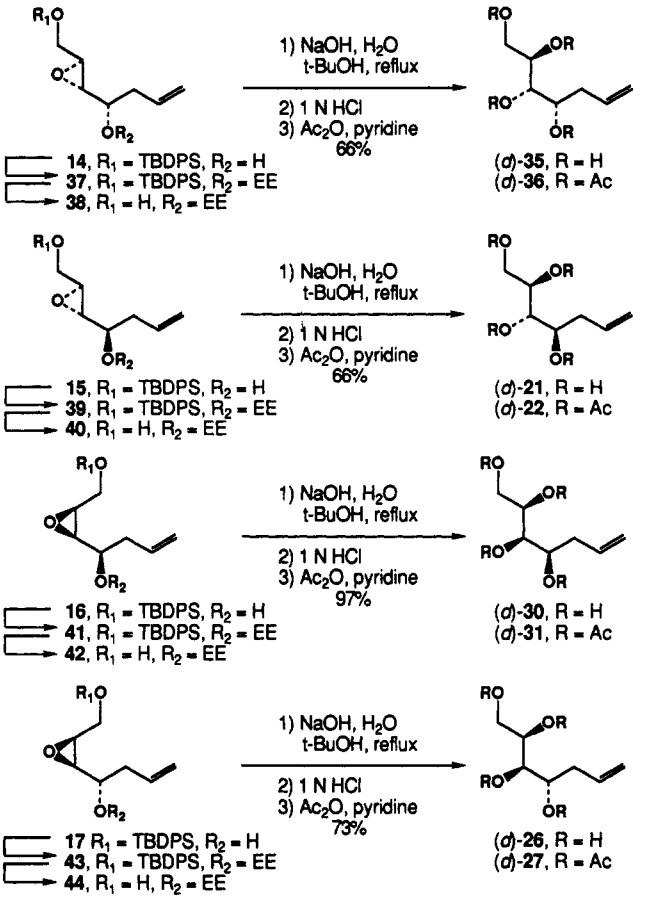


Scheme VII

High field ^1H NMR analysis revealed that each was produced with very high diastereoselectivity (≥98%).

Stereochemical assignments rest on the conversion of tetrols **21** and **30** to 2-deoxyglucose and 2-deoxygalactose, respectively. Thus, tetrols **21** and **30**, generated either by methanolysis of the corresponding tetraacetates or more directly by omitting the acylation steps in the previously described epoxide hydrolysis experiments, were treated

Scheme VIII



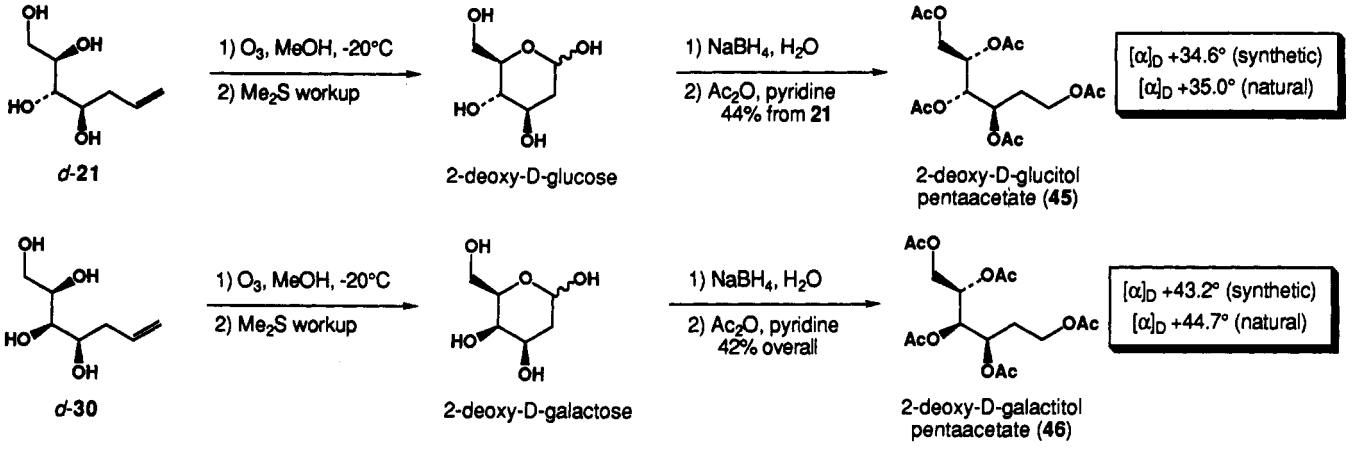
with O_3 in MeOH at −20 °C, and the resulting α-methoxy hydroperoxides were reduced by exposure to excess Me_2S (Scheme IX). In this way, *l*-**21** (deriving from the α-opening of epoxy urethane **18**) was converted into 2-deoxy-L-glucose ($[\alpha]^{20}_D$ −43° (*c* = 0.17, H_2O)) in 74% yield, while *d*-**21** (deriving from the β-opening of **40**) was similarly converted into 2-deoxy-D-glucose ($[\alpha]^{20}_D$ +36.3° (*c* = 0.43, H_2O). By way of comparison, the optical rotation of commercially available 2-deoxy-D-glucose was determined to be $[\alpha]^{20}_D$ +45° (*c* = 0.56, H_2O). It was subsequently determined that this ozonolysis procedure provided variable amounts of methyl 2-deoxyglucopyranoside, which proved difficult to separate from the synthetic sugar. Tetrol *d*-**30** deriving from the β-opening of **42** was similarly transformed into 2-deoxy-D-galactose (($[\alpha]^{20}_D$ +35.8° (*c* = 0.5, MeOH); $[\alpha]^{20}_D$ +44.4° (*c* = 0.5, MeOH) was measured for an authentic sample). Here again, variable amounts of methyl 2-deoxygalactosides were obtained, a factor no doubt contributing to the poor correlation of optical rotations.

Because purification of the synthetic sugars proved difficult, samples of the synthetic and natural materials were reduced with $NaBH_4$ in H_2O, and the resulting 2-deoxyhexitols were acylated to give the corresponding 2-deoxyhexitol pentaacetates that were easily purified and were fully characterized.[20] In this way, 2-deoxy-D-glucitol pentaacetate (**45**) and 2-deoxy-D-galactitol pentaacetate (**46**) were prepared, and the correlation between the synthetic and naturally derived materials was excellent.

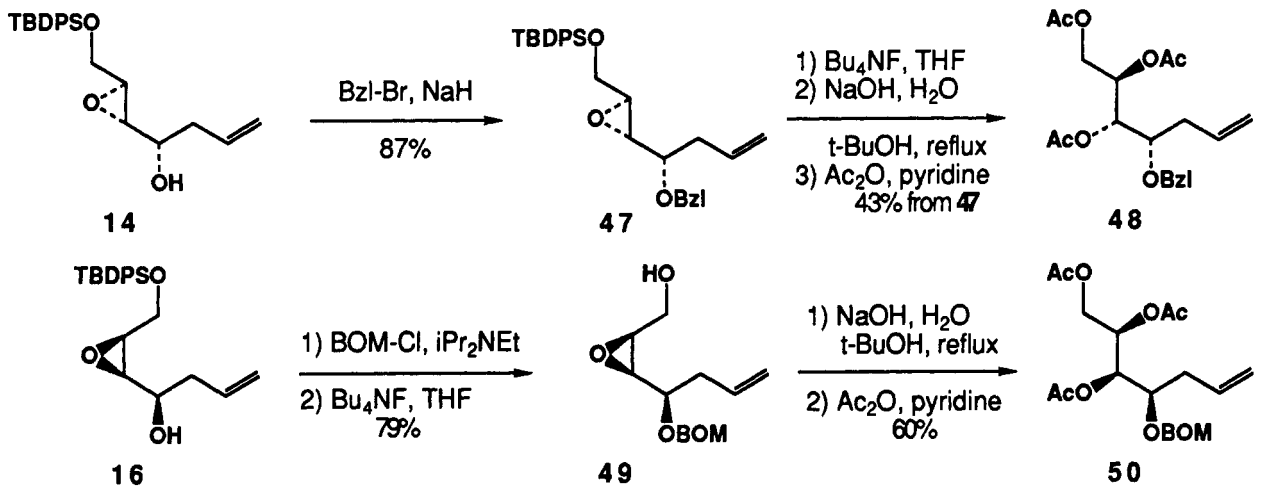
One of our stated objectives was to develop a simple preparative route to monosaccharides and other poly-

(20) Moore, R. E.; Barchi, J. J., Jr.; Bartolini, G. *J. Org. Chem.* **1985**, *50*, 374. ^1H NMR data for 2-deoxyglucitol pentaacetate (**45**) and 2-deoxygalactitol pentaacetate (**46**) are reported in this paper.

Scheme IX



Scheme X



hydroxylated intermediates that permits the intrinsic functional group differentiation that exists between C(4) and C(5) of epoxy alcohols **14–17** to be maintained in subsequent manipulations. While this objective is clearly met by use of intermediates **38**, **40**, **42**, and **44** possessing C(4) ethoxyethyl ethers, this protecting group is not the most desirable one for many purposes. That it is introduced as a mixture of diastereomers is among the least favorable of its attributes. Several additional experiments were performed in order to demonstrate that other protecting group combinations are compatible with the β-opening technology. Thus, compounds **47** and **49**, which are easily prepared by starting from **14** and **16**, respectively, were smoothly converted to **48** and **50** by using the standard β-opening sequence (Scheme X).

In summary, we have established that the 2-deoxyhexoses or their immediate precursors are easily prepared by a sequence involving the asymmetric allylborations of 2,3-epoxy aldehydes. This sequence is extremely flexible, as each of the four diastereomeric tetrols **21**, **26**, **30**, and **35** can be synthesized in principle by two stereochemically independent methods, depending on the method of epoxide manipulation that is employed. The β-mode of epoxide substitution promises to be the most useful synthetically since this permits the C(3) and C(4) hydroxyl groups of the target monosaccharides to be differentiated as a direct consequence of the synthetic sequence. Equally important, complete control over the absolute configuration of the polyol intermediates can be achieved simply by selecting the appropriate enantiomer of the epoxyallylic alcohol starting material. Extensions of this chemistry to the synthesis of the parent hexoses themselves via the reactions of epoxy aldehydes **12** and **13** and (γ-alkoxyallyl)boronates **8** and **9** or their surrogates will be reported in due course.

Experimental Section

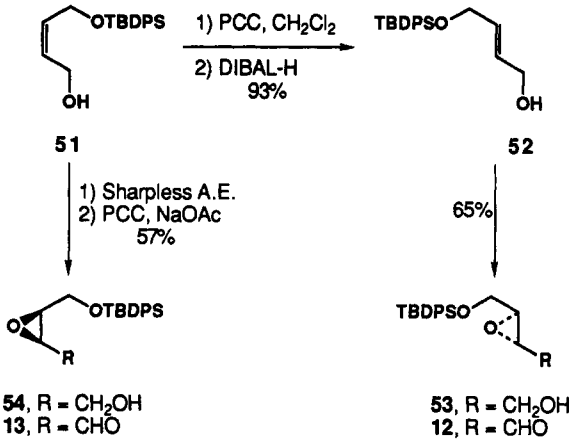
General. All reactions were conducted in oven-dried (125 °C) or flame-dried glassware under atmospheres of dry argon or nitrogen. All solvents were purified before use. Ether, tetrahydrofuran (THF), and toluene were distilled from sodium benzophenone ketyl. Methylene chloride was distilled from CaH_2.

^1H NMR spectra were measured at 250, 300, 360, 400, and 500 MHz on commercially available instruments. Residual chloroform (δ 7.26) was used as internal reference for spectra measured in $CDCl_3$. ^1H NMR spectra measured in CD_3OD were referenced against the CHD_2OD (δ 3.30) resonance. ^{13}C NMR spectra were recorded at 75.4 MHz and were referenced with the δ 77.0 resonance of $CDCl_3$. Low and high resolution mass spectra were measured at 70 eV.

Analytical HPLC was performed by using a 4.6 × 250 mm ChemcoPak column packed with 3-μm Chemcosorb silica gel. Analytical thin-layer chromatography (TLC) was performed by using 2.5 × 10 cm plates coated with a 0.25-mm thickness of silica gel containing PF 254 indicator (Analtech). Preparative thin-layer chromatography (PTLC) was performed by using 20 × 20 cm plates coated with 0.25- or 0.5-mm thickness of silica gel containing PF 254 indicator (Analtech). Flash chromatography was performed as described by Still using kieselgel 60 (230–400 mesh) or kieselgel 60 (70–230 mesh).[21] Unless otherwise noted, all compounds purified by chromatography are sufficiently pure (>95% by ^1H analysis) for use in subsequent reactions.

(21) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

Scheme XI. Synthesis of Epoxy Aldehydes 12 and 13



(4*S*,5*S*)-2-Allyl-1,3,2-dioxaborolane-4,5-dicarboxylic Acid Diethyl Ester [(*S*,*S*)-7]. Tartrate allylboronate **7** was prepared by using diethyl tartrate (DET) rather than diisopropyl tartrate in our standard procedure.[11a,f] This reagent was purified by distillation through a short path column (90–180 °C, 0.07–1.1 mmHg) for use in all initial allylboration experiments [65% yield based on DET; 45% based on $(MeO)_3B$ as per our original method].[11a] The purity of distilled (*S*,*S*)-**7** is determined by capillary GC analysis (0.25 mm × 12 m dimethylsilicone on a fused silica column, 70 °C for 40 min and then temperature increased at 10 °C/min to a final temperature of 200 °C). Under these conditions, DET elutes at 10.6 min and (*S*,*S*)-**7** at 12.8 min. Subsequent to our development of an improved method of synthesis,[11f] we have routinely employed standardized solutions crude **7** in the allylborations of epoxy aldehydes **12** and **13**. Partial data for (*S*,*S*)-**7**: ^{1}H NMR ($CDCl_3$) δ 5.88 (m, 1 H), 5.06 (d, J = 15.9 Hz, 1 H), 5.02 (d, J = 10 Hz, 1 H), 4.86 (s, 2 H), 4.27 (m, 4 H), 1.92 (d, J = 7 Hz, 2 H), 1.32 (m, 6 H).

***cis*-4-(*tert*-Butyldiphenylsiloxy)but-2-en-1-ol (51)** (Scheme XI). *n*-Butyllithium (2.2 mL, 2.7 M in hexane, 5.9 mmol) was added dropwise to a solution of 2-butene-1,4-diol (0.5 mL, 6.06 mmol) in 10 mL of THF at −78 °C. TBDPS-Cl (1.5 mL, 5.8 mmol) was added, the reaction was allowed to warm to 25 °C over 30 min and then was heated at reflux for 3.5 h. The solution was concentrated in vacuo and chromatographed silica gel (gradient elution using 5:1 hexane–ether to ether), giving 1.88 g (quantitative yield) of **51** as a pale green liquid:[22] ^{1}H NMR ($CDCl_3$) δ 7.68 (m, 4 H, Ar), 7.41 (m, 6 H, Ar), 5.66 (m, 2 H, H_2, H_3), 4.25 (d, J = 5.3 Hz, 1 H, OH), 1.04 (s, 9 H, *t*-Bu); IR ($CHCl_3$) 3620, 2920, 2880, 1462, 1422, 1422, 1200, 1080, 695 cm^{-1}; mass spectrum, m/e 327 (M^+ + H). Anal. Calcd for $C_{20}H_{26}O_2Si$: C, 73.57; H, 8.03. Found: C, 73.69; H, 8.14.

***trans*-4-(*tert*-Butyldiphenylsiloxy)-2-butenol (52).** A solution of cis allylic alcohol **51** (10.0 g, 30.6 mmol) in 4 mL of CH_2Cl_2 was added to a mixture of PCC (9.7 g, 45 mmol) and Celite (50 g) in 200 mL of CH_2Cl_2. The reaction was stirred at 25 °C for 2 h. Ether (200 mL) was then added, and the solids were removed by filtration through a pad of Celite–Florisil (1:1). The resulting solution was concentrated in vacuo, filtered through silica gel (eluting with Et_2O), and concentrated in vacuo to give 9.8 g (99% yield) of the corresponding *E* enal as a pale yellow solid: mp 80–84 °C; ^{1}H NMR ($CDCl_3$) δ 9.59 (d, J = 7.8 Hz, 1 H, H_1) 7.63 (d with fine coupling, J = 8.6 Hz, 4 H, Ar), 7.38 (m, 6 H), Ar), 6.83 (ddd, J = 1.5, 1.5, 15.7 Hz, 1 H, H_3), 6.55 (dddd, J = 2, 2, 7.7, 16.0 Hz, 1 H, H_2), 4.27 (dd, J = 1.7, 3.7 Hz, 2 H, H_4), 1.06 (s, 9 H, *t*-Bu); IR ($CHCl_3$) 2935, 2860, 1690, 1468, 1430, 1100, 690 cm^{-1}; mass spectrum, m/e 324 (parent ion).

To a −78 °C solution of the above enal (9.05 g, 27.9 mmol) in 200 mL of Et_2O was added diisobutylaluminum hydride (DIBAL-H, 31 mL, 1 M in hexane, 31 mmol) dropwise via an addition funnel. The reaction was stirred at −78 °C for 25 min and then at 25 °C for 1 h. MeOH (40 mL) was added and the solution stirred for 1.5 h. Saturated aqueous sodium potassium tartrate (250 mL) was added, and the mixture was stirred until two clear layers formed. The organic phase was separated, and the aqueous layer was extracted with ether (5 × 75 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated in vacuo. The crude product was purified by chromatography (silica gel, 1:1 ether–hexane), giving 8.50 g (93% yield) of **52** as a yellow liquid: ^{1}H NMR ($CDCl_3$) δ 7.66 (dd, J = 7.8, 2.0 Hz, 4 H, Ar), 7.39 (m, 6 H, Ar), 6.91 (ddd, J = 4.2, 4.2, 16 Hz, 1 H), 6.77 (ddd, J = 1.9, 1.9, 16 Hz, 1 H), 4.22 (m, 2 H, H_4), 4.13 (br s, 2 H, H_1), 1.26 (s, 1 H, OH), 1.06 (s, 9 H, *t*-Bu); IR ($CHCl_3$) 3610, 2940, 2860, 1428, 1100, 970, 690 cm^{-1}; mass spectrum, m/e 327 (M^+ + H). Anal. Calcd for $C_{20}H_{26}O_2Si$: C, 73.57; H, 8.03. Found: C, 73.28; H, 8.25.

***threo*-(2*S*,3*S*)-4-(*tert*-Butyldiphenylsiloxy)-2,3-epoxy-1-butanol (53).** $Ti(OiPr)_4$ (0.5 mL, 1.7 mmol) was added to a mixture (+)-(*R*,*R*)-DET (490 mg, 2.4 mmol) and 200 mg of 4-Å molecular sieves in 30 mL of CH_2Cl_2 at −20 °C. The solution was stirred for 10 min, and then allylic alcohol **52** (3.84 g, 11.8 mmol) was added. The mixture was stirred at −20 °C for 30 min. A solution of *tert*-butyl hydroperoxide (TBHP) in CH_2Cl_2 (3.0 mL, 4.26 M, 12.8 mmol) was added, and the mixture was stirred at −20 °C for 30 min and then stored at −20 °C for 3 days. The crude reaction mixture was filtered through Celite and concentrated in vacuo. Gradient elution chromatography (silica gel, pure hexane to 1:1 hexane–ether to pure ether) yielded a mixture consisting of **53** (2.85 g, 71% yield, ≥95% ee by Mosher ester analysis)[23] and 0.12 g of (+)-DET. Volatility problems prevented additional purification at this stage without substantial loss of material, and so this mixture was used directly in the next reaction. A small sample was fully purified for characterization purposes: $[\alpha]^{23}_D$ = −15.3° (c = 0.64, CH_2Cl_2); ^{1}H NMR ($CDCl_3$)δ 7.65 (m, 4 H, Ar), 7.40 (m, 6 H, Ar), 3.91 (m, 1 H, H_{1a}), 3.88 (dd, J = 4, 12 Hz, 1 H, H_{4a}), 3.77 (dd, J = 5, 12 Hz, 1 H, H_{4b}), 3.61 (ddd, J = 4, 8, 12 Hz, 1 H, H_{1b}), 3.17 (m, 1 H), 3.08 (m, 1 H), 1.61 (d, J = 8 Hz, 1 H, OH), 1.04 (s, 9 H, *t*-Bu); IR (neat) 3600–3100, 2935, 2880, 1465, 1430, 1390, 1255, 1100, 930, 860, 785, 690 cm^{-1}; mass spectrum, m/e 341 (M^+ − H). Anal. Calcd for $C_{20}H_{26}O_3Si$: C, 70.14; H, 7.65. Found: C, 69.81; H, 7.77.

***erythro*-(2*R*,3*S*)-4-(*tert*-Butyldiphenylsiloxy)-2,3-epoxy-1-butanol (54).** $Ti(OiPr)_4$ (0.6 mL, 2.0 mmol) was added to a mixture of (−)-(*S*,*S*)-DET (580 mg, 2.8 mmol) and 4-Å molecular sieves (200 mg) in 35 mL of CH_2Cl_2 at −20 °C. The solution was stirred at −20 °C for 25 min, and then allylic alcohol **51** (4.52 g, 13.9 mmol) was added. Thirty minutes later, a solution of TBHP in CH_2Cl_2 (3.5 mL, 4.26 M, 14.9 mmol) was added, and the reaction was then stored at −20 °C for 4 days. At this point the reaction appeared very close to completion according to TLC analysis. The crude reaction was filtered through a pad of 1:1 Celite–Florisil, concentrated in vacuo, and chromatographed (silica gel, pure hexane to 1:1 ether–hexane to pure ether), yielding 111 mg of recovered **51** (2%) and 2.72 g of **54** (57% yield, 90% ee by Mosher ester analysis)[23] as a pale yellow liquid: $[\alpha]^{23}_D$ = +5.4° (c = 0.39, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 7.67 (m, 4 H, Ar), 7.41 (m, 6 H, Ar), 3.90 (dd, J = 6.0, 11.7 Hz, 1 H, H_{4a}), 3.73 (dd, J = 5.3, 11.8 Hz, 1 H, H_{4b}), 3.66 (m, 2 H, H_1), 3.21 (m, 2 H, H_2, H_3), 1.81 (t, J = 6 Hz, 1 H, OH), 1.05 (s, 9 H, *t*-Bu); IR (neat) 3600–3100, 2940, 2865, 1465, 1428, 1080, 812, 729, 690 cm^{-1}; mass spectrum, m/e 281 (M^+ − $C_2O_2H_6$), no parent ion observed. Anal. Calcd for $C_{20}H_{26}O_3Si$: C, 70.14; H, 7.65. Found: C, 70.35; H, 7.91.

***threo*-(2*R*,3*S*)-4-(*tert*-Butyldiphenylsiloxy)-2,3-epoxybutanal (12).** A solution of epoxy alcohol **53** [a mixture of 2.43 g (8.5 mmol) of **53** and 0.12 g of (+)-DET] in 20 mL of CH_2Cl_2 was added to a mixture of PCC (2.74 g, 12.8 mmol), NaOAc (767 mg, 9.4 mmol), 4-Å molecular sieves (5 g), and Celite (5 g) in 50 mL of CH_2Cl_2. The reaction mixture was stirred for 30 min at 25 °C and then Et_2O (100 mL) was added. The resulting mixture was stirred for an additional 30 min and then was filtered through a pad of Celite–Florisil (1:1). The crude product was chromatographed (silica gel, 1:1 ether–pentane), giving **12** as a hydrate. This material was dehydrated by refluxing a CH_2Cl_2 solution in a Soxhlet apparatus containing 4-Å molecular sieves in the Soxhlet

(22) For the selective monosilylation of symmetrical diols, see: (a) Roush, W. R.; Blizzard, T. A. *J. Org. Chem.* **1984**, *49*, 1772 (cf. ref 23 therein). (b) Roush, W. R.; Gillis, H. R.; Essenfeld, A. P. *Ibid.* **1984**, *49*, 4674 (cf. procedure for the syntheses of **49**–**51** therein). (c) McDougal, P. G.; Rico, J. G.; Oh, Y.-I.; Condon, B. D. *Ibid.* **1986**, *51*, 3388.

(23) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543.

bulb. In this way, epoxy aldehyde **12** (2.22 g, 92% yield) was obtained as a pale greenish liquid: $[\alpha]^{25}_D = -2.4°$ (c = 1.4, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 9.06 (d, J = 5.7 Hz, 1 H, H_1), 7.65 (m, 4 H, Ar), 7.40 (m, 6 H, Ar), 3.96 (dd, J = 2.5, 12.1 Hz, 1 H, H_{4a}), 3.81 (dd, J = 3.5, 12.3 Hz, 1 H, H_{4b}), 3.39 (m, 2 H, H_2, H_3), 1.04 (s, 9 H, t-Bu); IR (neat) 3030, 2940, 1730, 1430, 1100, 1000, 820, 734, 692 cm^{-1}; mass spectrum, m/e 283 ($M^+ - t$-Bu), no parent ion observed; HRMS for $C_{16}H_{15}O_3Si$, calcd 283.0791, found 283.0790.

***erythro*-(2*S*,3*S*)-4-(*tert*-Butyldiphenylsiloxy)-2,3-epoxybutanal (13).** Epoxy alcohol **54** (2.56 g, 7.49 mmol) was oxidized to epoxy aldehyde **13** according to the procedure used to prepare **12**. Drying of **13** via the 4-Å molecular sieves–Soxhlet method was not required, as **13** did not hydrate readily. Chromatographic purification of the crude product (silica, 1:1 ether–pentane) provided **13** (2.55 g, quantitative yield) as a pale greenish liquid: $[\alpha]^{23}_D = -29.8°$ (c = 1.2, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 9.46 (d, J = 4.2 Hz, 1 H, H_1), 7.63 (m, 4 H, Ar), 7.40 (m, 6 H, Ar), 3.93 (m, 2 H, H_4), 3.40 (m, 2 H, H_2, H_3), 1.02 (s, 9 H, t-Bu); IR (neat) 3030, 2940, 2860, 1725, 1467, 1430, 1100, 810, 732, 690 cm^{-1}; mass spectrum, m/e 283 ($M^+ - t$-Bu), no parent ion observed; HRMS for $C_{16}H_{15}O_3Si$, calcd 283.0791, found 283.0790.

(−)-*lyxo*-(4*S*,5*S*,6*S*)-7-(*tert*-Butyldiphenylsiloxy)-5,6-epoxyhept-1-en-4-ol (14). Tartrate allylboronate (*R*,*R*)-**7** (1.0 g, 3.9 mmol) was added to a −78 °C solution of epoxy aldehyde **12** (506 mmol, 1.49 mmol) and 4-Å molecular sieves (300 mg) in 30 mL of dry toluene. The reaction was stirred overnight in a −78 °C freezer. The mixture was then allowed to warm to 23 °C and was filtered. Saturated aqueous $NaHCO_3$ (25 mL) was added, the mixture was stirred for 30 min, and then the organic phase was separated. The aqueous phase was extracted with additional ether. The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated in vacuo. The ratio of *lyxo* (**14**) to *xylo* (**15**) diastereomers was 96:4 as determined by HPLC analysis (19:1 $CHCl_3$–CH_3CN, Chemcosorb on 3-μm silica, 0.9 mL/min flow rate, *lyxo* R_f 9.0 min, *xylo* R_f 11.9 min). Purification of the crude product by chromatography (flash silica gel, 20:1 CH_2Cl_2–ether) provided **14** (503 mg, 89% yield, >96% ee by Mosher ester analysis)[23] and **15** (47 mg, 8% yield, contaminated with **14**, 46% ee by Mosher ester analysis). Data for **14**: $[\alpha]^{23}_D = -6.5°$ (c = 0.43 CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 7.65 (d, J = 6.6 Hz, 4 H, Ar), 7.37 (m, 6 H, Ar), 5.83 (m, 1 H, H_2), 5.2–5.0 (m, 2 H, H_1), 3.86 (dd, J = 12.5, 3.8 Hz, 1 H, H_{7a}) overlapping with 3.86 (m, 1 H, H_4), 3.72 (dd, J = 4.2, 11.4 Hz, 1 H, H_{7b}), 3.12 (ddd, J = 3, 3, 4 Hz, 1 H, H_6), 2.99 (dd, J = 2.8, 2.5 Hz, 1 H, H_5), 2.37 (ddd, J = 6, 6, 12 Hz, 1 H, H_{3a}), 2.27 (ddd, J = 8, 8, 12 Hz, 1 H, H_{3b}), 1.85 (d, J = 2.5 Hz, 1 H, OH), 1.03 (s, 9 H, t-Bu); IR (neat) 3700–3200, 3075, 2920, 2860, 1645, 1590, 1467, 1428, 1390, 1360, 1100, 992, 909, 828, 731, 690 cm^{-1}; mass spectrum, m/e 307 ($M^+ - t$-Bu–H_2O), no parent ion. Anal. Calcd for $C_{23}H_{30}O_3Si$: C, 72.21; H, 7.90. Found: C, 72.50; H, 7.63.

(−)-*xylo*-(4*R*,5*S*,6*S*)-7-(*tert*-Butyldiphenylsiloxy)-5,6-epoxyhept-1-en-4-ol (15). A solution of epoxy aldehyde **12** (316 mg, 0.93 mmol) in 20 mL of toluene was treated with (*S*,*S*)-**7** (614 mg, 2.40 mmol) according to the procedure described for the synthesis of **14**. The ratio of *xylo* (**15**) to *lyxo* (**14**) diastereomers was 74:26 (HPLC analysis). Purification of the crude product by chromatography (3 × 0.5 mm preparative TLC plates, 20:1 CH_2Cl_2–ether) provided **15** (232 mg, 65% yield, R_f = 0.31, 97% ee by Mosher ester analysis)[23] and **14** (75 mg, 21% yield, R_f = 0.38, 49% ee by Mosher ester analysis). Data for **15**: $[\alpha]^{23}_D = -9.4°$ (c = 0.47, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 7.65 (m, 4 H, Ar), 7.40 (m, 6 H, Ar), 5.82 (m, 1 H, H_2), 5.20–5.00 (m, 2 H, H_1), 3.84 (dd, J = 3.6, 12.5 Hz, 1 H, H_{7a}), 3.73 (dd, J = 4.4, 12.4 Hz, 1 H, H_{7b}), 3.57 (m, 1 H, H_4), 3.12 (m with small couplings, 1 H, H_6), 2.95 (dd, J = 2.7, 4.3 Hz, 1 H, H_5), 2.36 (dd, J = 6.6, 7.2 Hz, 2 H, H_3), 1.85 (d, J = 5.6 Hz, 1 H, OH), 1.04 (s, 9 H, t-Bu); IR (neat) 3600–3100, 3080, 2940, 2860, 1470, 1430, 1390, 1100, 910, 818, 731, 692 cm^{-1}; mass spectrum, m/e 307 ($M^+ - t$-Bu – H_2O), no parent ion. Anal. Calcd for $C_{23}H_{30}O_3Si$: C, 72.21; H, 7.90. Found: C, 72.31; H, 7.63.

(+)-*ribo*-(4*R*,5*R*,6*S*)-7-(*tert*-Butyldiphenylsiloxy)-5,6-epoxyhept-1-en-4-ol (16). A solution of epoxy aldehyde **13** (676 mg, 1.99 mmol) in 20 mL of toluene was treated with (*S*,*S*)-**7** (1.09 g, 4.29 mmol) according to the procedure described for **14**. The ratio of *ribo* (**16**) to *arabino* (**17**) diastereomers in the crude product was 96:4 as determined by HPLC analysis (19:1 $CHCl_3$–CH_3CN, Chemcosorb on 3-μm silica, 0.9 mL/min flow rate, R_f(**16**) 6.3 min, R_f(**17**) 15.3 min). Chromatography (flash silica gel, 20:1 CH_2Cl_2–ether) of this mixture gave (+)-**16** (703 mg, 93% yield, ≥98% ee by Mosher ester analysis)[23] and (+)-**17** (40 mg, 5% yield, 58% ee by Mosher ester analysis; *the major enantiomer of 17 derives from the minor enantiomer of epoxy aldehyde 13*). Data for **16**: $[\alpha]^{23}_D = +2.1°$ (c = 1.13, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 7.65 (m, 4 H, Ar), 7.42 (m, 6 H, Ar), 5.85 (m, 1 H, H_2), 5.18 (d with fine coupling, J = 17.1 Hz, 1 H, H_{1Z}), 5.13 (d with fine coupling, J = 9.5 Hz, 1 H, H_{1E}), 3.98 (dd, J = 4.7, 11.8 Hz, 1 H H_{7a}), 3.77 (dd, J = 5.6, 11.8 Hz, 1 H, H_{7b}), 3.54 (m, 1 H, H_4), 3.16 (ddd, J = 4.5, 4.5, 6.6 Hz, 1 H, H_6), 2.97 (dd, J = 4.5, 8.7 Hz, 1 H, H_5), 2.50–2.30 (m, 3 H, H_3, OH), 1.05 (s, 9 H, t-Bu); IR (neat) 3600–3200, 2940, 2860, 1465, 1430, 1080, 912, 810, 592 cm^{-1}; mass spectrum, m/e 365 (M^+ – OH), no parent ion. Anal. Calcd for $C_{23}H_{30}O_3Si$: C, 72.21; H, 7.90. Found: C, 72.34; H, 7.98.

(−)-*arabino*-(4*S*,5*R*,6*S*)-7-(*tert*-Butyldiphenylsiloxy)-5,6-epoxyhept-1-en-4-ol (17). A solution of epoxy aldehyde **13** (355 mg, 1.04 mmol) in 20 mL of toluene was treated with (*R*,*R*)-**7** (650 mg, 2.54 mmol) according to the procedure used to prepare **14**. The ratio of *arabino* (**17**) to *ribo* (**16**) isomers in the crude product was 70:30 by HPLC analysis (condition defined above). Purification of the crude product by chromatography (flash silica, 20:1 CH_2Cl_2–ether) afforded 222 mg of (−)-**17** (56% yield, 98% ee by Mosher ester analysis)[23] and 105 mg of (+)-**16** (26% yield, 53% ee by Mosher ester analysis). Data for **17**: $[\alpha]^{23}_D = -15.6°$ (c = 0.59, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 7.65 (m, 4 H, Ar), 7.41 (m, 6 H, Ar), 5.74 (m, 1 H, H_2), 5.10 (d, J = 19.5 Hz, 1 H, H_{1Z}), 5.08 (d, J = 9 Hz, 1 H, H_{1E}), 3.79 (m, 2 H, H_7), 3.44 (m, 1 H), 3.24 (m, 1 H), 2.97 (m, 1 H), 2.32 (dd, J = 5.5, 5.5 Hz, 2 H, H_3), 1.97 (d, J = 2.7 Hz, 1 H, OH), 1.05 (s, 9 H, t-Bu); IR (neat) 3600–3100, 3080, 2930, 2860, 1645, 1460, 1430, 1075, 1000, 910, 810, 690 cm^{-1}; mass spectrum, m/e 365 (M^+ – OH), no parent ion; HRMS for $C_{19}H_{19}O_2Si$ ($M^+ - H_2O - t$-Bu), calcd 307.1154, found 307.1153.

(−)-*lyxo*-(4*S*,5*S*,6*S*)-7-(*tert*-Butyldiphenylsiloxy)-5,6-epoxy-4-[(phenylcarbamoyl)oxy]hept-1-ene (18). A solution of epoxy alcohol **14** (139 mg, 0.36 mmol) in 1 mL of pyridine and 5 mL of CH_2Cl_2 was treated with phenyl isocyanate (0.90 mL, 0.83 mmol). The solution was stirred at 25 °C for 2 days, and then water (0.5 mL) and acetone (4.5 mL) were added. The solution was concentrated in vacuo and the residue was redissolved in $CHCl_3$, filtered to remove solids, and again concentrated. The crude product was then purified by chromatography (2 × 0.5 mm preparative TLC plates, 3:1 hexane–ether), giving **18** (168 mg, 92% yield) as a white solid: mp 82–83 °C; $[\alpha]^{23}_D$ −15.6° (c = 0.93, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 7.65 (m, 4 H, Ar), 7.36 (m, 3 H, Ar), 7.06 (t, J = 7.5 Hz, 1 H, Ar), 6.57 (s, 1 H, NH), 5.82 (m, 1 H, H_2), 5.15 (d, J = 15.6 Hz, 1 H, H_{1Z}), 5.11 (d, J = 9.8 Hz, 1 H, H_{1E}), 4.84 (ddd, J = 6, 6, 6 Hz, 1 H, H_4), 3.83 (dd, J = 2.9, 11.6 Hz, 1 H, H_{7a}), 3.72 (dd, J = 4.5, 11.6 Hz, 1 H, H_{7b}), 3.22 (s, 1 H, H_6), 3.03 (dd, J = 1.9, 5.5 Hz, 1 H, H_5), 2.48 (m, 2 H, H_3), 1.02 (s, 9 H, t-Bu); IR (CH_2Cl_2) 3430, 3040, 2940, 2860, 1741, 1601, 1441, 1311, 1209, 1100, 817, 687 cm^{-1}; mass spectrum, m/e 501 (parent ion); HRMS for $C_{30}H_{35}O_4NSi$, calcd 501.2335, found 501.2336.

(−)-*arabino*-(4*S*,5*S*,6*S*)-7-(*tert*-Butyldiphenylsiloxy)-hept-1-ene-4,5,6-triol 4,5-Carbonate (19). A solution of epoxy urethane **18** (108 mg, 0.22 mmol) in 2 mL of ether at −20 °C was treated with Et_2AlCl (0.25 mL, in 1 M in hexane, 0.25 mmol). The solution was stirred at −20 °C for 2 h and then aqueous H_2SO_4 (5 mL, 1M) was added. This mixture was stirred at 25 °C for 5 h and then was worked up by a standard extraction sequence. Chromatography of the crude product (0.5 mm silica gel preparative plate, 20:1 CH_2Cl_2–Et_2O) provided 89 mg (98% yield) of **19** as a colorless oil: $[\alpha]^{23}_D = -21.6°$ (c = 1.15, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 7.63 (d, J = 6.5 Hz, 4 H, Ar), 7.42 (m, 6 H, Ar), 5.77 (m, 1 H, H_2), 5.24 (d, J = 11.8 Hz, 1 H, H_{1E}), 5.23 (d, J = 16.2 Hz, 1 H, H_{1Z}), 4.78 (dt, J = 7, 7 Hz, 1 H, H_3), 4.36 (narrow m, with fine coupling, 1 H), 3.79 (s, 3 H, H_7, H_6), 2.53 (s, 3 H, H_3, OH), 1.08 (s, 9 H, t-Bu); IR ($CHCl_3$) 3000, 2937, 2870, 1800, 1447, 1382, 1110, 932, 842, 701, 662 cm^{-1}; mass spectrum, m/e 407 (M^+ – H_2O), no parent ion observed.

(−)-*arabino*-(4*S*,5*S*,6*S*)-Hept-1-ene-4,5,6,7-tetrol 4,5-Carbonate (20). n-Bu_4NF (0.25 mL, 1 M in THF, 0.25 mmol) was added to a solution of **19** (87 mg, 0.20 mmol) in 1 mL of THF. The reaction was stirred at 23 °C for 3 h. The mixture was then diluted with CH_2Cl_2 and was washed with saturated aqueous

NH_4Cl. The aqueous layer was back extracted with CH_2Cl_2. Due to a low mass recovery, the aqueous layer was concentrated and the residue was triturated with $CHCl_3$. The resulting material was combined with the organic extracts, and the crude product was purified by chromatography (0.5-mm silica gel preparative TLC plate ether), providing 20.3 mg (53% yield) of **20**: $[\alpha]^{23}_D$ −80° (c = 0.20, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 5.77 (m, 1 H, H_2), 5.24 (d, J = 15.8 Hz, 1 H, H_{1Z}), 5.23 (d, J = 11.7 Hz, 1 H, H_{1E}), 4.82 (ddd, J = 5.3, 5.3, 5.3 Hz, 1 H, H_4), 4.33 (dd, J = 5.1, 5.1 Hz, 1 H, H_5), 3.88 (ddd, J = 5.4, 5.4, 5.4 Hz, 1 H, H_6), 3.78 (dd, J = 3.3, 11.0 Hz, 1 H, H_{7a}), 3.67 (dd, J = 5.7, 11.9 Hz, 1 H, H_{7b}), 2.97 (m, 1 H, OH), 2.52 (complex m, 2 H, H_3), 2.38 (t, J = 7 Hz, 1 H, OH); IR (neat) 3400, 2940, 1790, 1380, 1180, 1050, 920, 762 cm^{-1}; mass spectrum, m/e 142 ($M^+ - CO_2 - H_2$), no parent ion; HRMS for $C_7H_{10}O_3$, calcd 142.0630, found 142.0629.

(−)-*arabino*-(4*S*,5*R*,6*S*)-Hept-1-ene-4,5,6,7-tetrol [(−)-*l*-21]. A solution of carbonate **20** (14.4 mg, 0.77 mmol) and NaOMe (10 mg, 0.42 mmol) in 1 mL of MeOH was stirred at 23 °C for 2 days. Excess Dowex 50W-XB (H^+) resin was added and the mixture was stirred for 10 min. The solution was filtered and concentrated, giving 10.7 mg (86%) of *l-arabino* tetrol (−)-**21** as a white solid: mp 100–103 °C; $[\alpha]^{25}_D$ = −9.9° (c = 0.74, MeOH); ^1H NMR (300 MHz, CD_3OD) δ 5.87 (m, 1 H), 5.10 (dd, J = 18.0, 1.4 Hz, 1 H), 5.02 (ddd, J = 10.2 1.3, 1.2 Hz, 1 H), 3.86 (ddd, J = 6.9, 6.9, 2.0 Hz, 1 H), 3.78 (dd, J = 11.0, 3.7 Hz, 1 H), 3.61 (m, 2 H), 3.37 (dd, J = 7.7, 2.2 Hz, 1 H), 2.30 (m, 2 H); ^{13}C NMR (75.4 MHz, CD_3OD) δ 136.74, 117.21, 73.89, 73.15, 71.19, 65.13, 39.42; IR (CH_3CN) 3520 (br), 2970, 1730, 1270, 1240, 1155, 1125; HRMS for $C_7H_{15}O_4$ (M + H^+), calcd 163.0970, found 163.0964. *arabino* tetrol **21** was fully characterized as the tetraacetate derivative **22**.

(+)-*arabino*-(4*R*,5*S*,6*R*)-Hept-1-ene-4,5,6,7-tetrol 4,5,6,7-Tetraacetate (22). A solution of epoxy alcohol **40** (31 mg, 0.14 mmol) in H_2O/*t*-BuOH (5:1, 2.5 mL) was treated with 1 N NaOH (0.5 mL) by using the procedure described for the synthesis of **31**. This provided crude (+)-*arabino* tetrol **21** that was acylated by using standard conditions (see procedure for synthesis of **31**) to facilitate chromatographic purification (silica gel, 30% Et_2O in hexanes). *arabino* tetraacetate **22** (31 mg, 66%) was obtained as a clear oil: $[\alpha]^{25}_D$ = +24.6° (c = 1.1, CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$) δ 5.70 (m, 1 H), 5.31 (dd, J = 8.7, 2.9 Hz, 1 H), 5.21 (ddd, J = 8.7, 5.7, 2.9 Hz, 1 H), 5.11 (m, 3 H), 4.24 (dd, J = 3.3, 12.5 Hz, 1 H), 4.13 (dd, J = 5.1, 12.5 Hz, 1 H), 2.26 (m, 2 H), 2.14 (s, 3 H), 2.06 (s, 3 H), 2.05 (s, 3 H), 2.04 (s, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 170.51, 170.15, 169.80, 169.71, 132.29, 118.58, 70.09, 69.72, 68.37, 61.88, 35.41, 20.73, 20.73, 20.61, 20.61; IR ($CDCl_3$) 3060, 2980, 1700 (br), 1645, 1435, 1370, 1225 (br), 1145 cm^{-1}; mass spectrum, m/e 270 (M^+ − HOAc). Anal. Calcd for $C_{15}H_{22}O_8$: C, 54.53; H, 6.71. Found: C, 54.72; H, 6.99.

(+)-*arabino*-(4*R*,5*S*,6*R*)-Hept-1-ene-4,5,6,7-tetrol (21). A solution of tetraacetate **22** (31 mg, 0.09 mmol) in MeOH (1.5 mL) was treated with a catalytic amount of K_2CO_3 at 23 °C for 1 h. The solution was filtered and then acidified by treatment with Dowex 50x8-400 ion exchange resin. After collection of the resin, the filtrate was concentrated at reduced pressure to give the tetrol **21** (15 mg, 98%) as a clear oil: $[\alpha]_D$ = +13.9° (c = 0.6, MeOH). The spectroscopic properties of this sample were in complete agreement with those of (−)-**21** prepared as described above by the hydrolysis of carbonate **20**.

(−)-*ribo*-(4*R*,5*R*,6*S*)-7-(*tert*-Butyldiphenylsiloxy)-5,6-epoxy-4-[(phenylcarbamoyl)oxy]hept-1-ene (23). Epoxy alcohol **16** (152 mg, 0.04 mmol) was treated with phenyl isocyanate (0.10 mL, 0.92 mmol) according to the procedure used to prepare **18**. Chromatographic purification of the crude product (2 × 0.5 mm PTLC plates, 3:1 hexane–ether) gave **23** (145 mg, 73% yield) as a colorless oil: $[\alpha]^{23}_D$ = −3.1° (c = 0.51, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 7.65 (m, 4 H, Ar), 7.38 (m, 6 H, Ar), 7.28 (m, 4 H, Ar), 7.04 (m, 1 H, Ar), 6.44 (br s, 1 H, NH), 5.79 (m, 1 H, H_2), 5.15 (d, J = 16.1 Hz, 1 H, H_{1Z}), 5.10 (d, J = 10.2 Hz, 1 H, H_{1E}), 4.57 (m, 1 H, H_4), 4.05 (dd, J = 3, 11.5 Hz, 1 H, H_{7a}), 3.78 (dd, J = 7.0, 12.4 Hz, 1 H, H_{7b}), 3.23 (ddd, J = 3, 3, 7 Hz, 1 H, H_6), 3.03 (dd, J = 4.7, 8.6 Hz, 1 H, H_5), 2.00 (m, 2 H, H_3), 1.03 (s, 9 H, *t*-Bu); IR (CH_2Cl_2) 3430, 3030, 2940, 2860, 1740, 1601, 1428, 1207, 1080, 820, 680 cm^{-1}; mass spectrum, m/e 501 (parent ion). Anal. Calcd for $C_{30}H_{35}O_4NSi$: C, 71.82; H, 7.03. Found: C, 71.59; H, 6.82.

(+)-*xylo*-(4*R*,5*R*,6*S*)-7-(*tert*-Butyldiphenylsiloxy)hept-1-ene-4,5,6-triol 4,5-Carbonate (24a) and (−)-*xylo*-(4*R*,5*S*,6*S*)-7-(*tert*-Butyldiphenylsiloxy)hept-1-ene-4,5,6-triol 5,6-Carbonate (24b). Epoxy urethane **23** (90 mg, 0.18 mmol) was treated with Et_2AlCl and the intermediate imino carbonate was hydrolyzed with aqueous H_2SO_4 according to the procedure used to prepare carbonate **19**. The mixture of **24a** and **24b** so obtained was separated chromatographically (0.5-mm silica preparative TLC, 20:1 CH_2Cl_2–ether), giving 33 mg of **24a** (43% yield, R_f = 0.28) and 31 mg of **24b** (43% yield, R_f = 0.19), each a colorless oil. In more recent runs, isomer **24a** was the only product observed.

Data for **24a**: $[\alpha]^{23}_D$ +25.4° (c = 0.57, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 7.64 (m, 4 H, Ar), 7.40 (m, 6 H, Ar), 5.72 (m, 1 H, H_2), 5.22 (d, J = 9.9 Hz, 1 H, H_{1E}), 5.20 (d, J = 18.9 Hz, 1 H, H_{1Z}), 4.75 (ddd, J = 6.5, 6.5, 6.5 Hz, 1 H, H_4), 4.38 (dd, J = 1.3, 5.8 Hz, 1 H, H_5), 3.72 (complex m, 3 H, H_6, H_7), 2.50 (m, 2 H, H_3), 2.26 (d, J = 5.5 Hz, 1 H, OH), 1.05 (s, 9 H, *t*-Bu). Irradiation at δ 4.75 caused δ 4.38 to collapse to a singlet and δ 2.50 to collapse to two doublets: (i) 2.52 (d, J = 5.6 Hz), and (ii) 2.49 (d, J = 5.8 Hz); IR (neat) 3480, 2940, 2860, 1790, 1470, 1385, 1170, 1100, 920, 810, 730, 695 cm^{-1}; mass spectrum, m/e 307 (M^+ − *t*-Bu − CO_2 − H_2O), no parent ion; HRMS for $C_{19}H_{20}O_2Si$, calcd 307.1154, found 307.1153.

Data for **24b**: $[\alpha]^{23}_D$ −34.3° (c = 0.98, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 7.64 (m, 4 H, Ar), 7.42 (m, 6 H, Ar), 5.80 (m, 1 H, H_2), 5.21 (d, J = 11.2 Hz, 1 H, H_{1E}), 5.20 (d, J = 15.8 Hz, 1 H, H_{1Z}), 4.64 (dd, J = 2.9, 2.9 Hz, 1 H, H_5), 4.61 (ddd, J = 1.6, 1.6, 1.6 Hz, 1 H, H_6), 3.93 (d with fine coupling, J = 11.8 Hz, 1 H, H_{7a}), 3.70 (d with fine coupling, J = 11.8 Hz, 1 H, H_{7a}), 3.70 (d with fine coupling, J = 11.7 Hz, 2 H, H_{7b}, H_4), 2.41 (dd, J = 6.4, 6.4 Hz, 2 H, H_3), 1.88 (d, J = 5.9 Hz, 1 H, OH), 1.07 (s, 9 H, *t*-Bu); IR (neat) 3460, 2940, 2860, 1790, 1465, 1430, 1380, 1170, 1100, 1045, 920, 820, 695 cm^{-1}; mass spectrum, m/e 369 (M^+ − *t*-Bu), no parent ion; HRMS for $C_{20}H_{21}O_5Si$, calcd 369.1158, found 369.1158.

(−)-*xylo*-(4*R*,5*R*,6*S*)-Hept-1-ene-4,5,6,7-tetrol 4,5-Carbonate (25a) and *xylo*-(4*R*,5*S*,6*S*)-Hept-1-ene-4,5,6,7-tetrol 5,6-Carbonate (25b). *n*-Bu_4F (0.03 mL, 1 M in THF, 0.03 mmol) was added to a solution of **24a** (12 mg, 0.03 mmol) in 0.5 mL of THF. The reaction was treated and worked up as in the synthesis of **20**. Chromatography (0.5-mm silica PTLC plate, ether) of the crude product provided 4.3 mg (81% yield) of a ca. 1:2 mixture of **25a** and **25b** (not separated). A comparable mixture was obtained (81% yield) from the isomeric carbonate **24b**: $[\alpha]^{23}_D$ = −60.5° (c = 0.2, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 5.77 (m, 1 H, H_{2a}, H_{2b}), 5.21 (m, 2 H, H_{Za}, H_{Zb}, H_{Ea}, H_{Eb}), 4.75 (m, 1 H, H_{4a}, H_{6b}), 4.60 (dd, J = 2.6, 5.9 Hz, 0.4 H, H_{5b}), 4.38 (dd, J = 2, 6 Hz, 0.6 H, H_{5a}), 3.96 (dd, J = 3.5, 12.7 Hz, 0.4 H, $H_{7'b}$), 3.71 (m, 2.4 H, $H_{7''b}$, $H_{7'a}$, H_{6a}, H_{4b}), 2.51 (m, 0.6 H, H_{3a}), 2.42 (dd, J = 7.6, 7.6 Hz, 1.4 H, H_{3b}), 1.8 (br s, OH); IR (neat) 3400, 2935, 1780, 1385, 1180, 1060, 920, 767 cm^{-1}; mass spectrum, m/e 142 (M^+ − CO_2 − H_2), no parent ion observed.

(+)-*xylo*-(4*R*,5*S*,6*S*)-Hept-1-ene-4,5,6,7-tetrol [(+)-26]. A mixture of carbonates **25a** and **25b** (11.8 mg, 0.063 mmol) and NaOMe (10 mg, 0.42 mmol) in 1 mL of MeOH was stirred at 23 °C for 2 days. Excess Dowex 50W-XB (H^+) resin was added, and the reaction was stirred for 10 min. The mixture was filtered and concentrated, giving 8.6 mg (85%) of *xylo* tetrol (+)-**26** as a colorless oil: $[\alpha]^{25}_D$ +7.6° (c = 0.25, MeOH); ^1H NMR (CD_3OD) δ 5.88 (m, 1 H, H_2), 5.12 (dd, J = 2.3, 18.5 Hz, 1 H, H_{1Z}), 5.06 (dd, J = 10.2, 2.0 Hz, 1 H, H_{1E}), 3.73 (m, 1 H), 3.63 (m, 2 H), 3.48 (dd, J = 4.2, 5.2 Hz, 1 H), 2.37 (ddd, J = 7.6, 7.6, 15.8 Hz, 1 H, H_{3a}), 2.29 (ddd, J = 7.4, 7.4, 14.9 Hz, 1 H, H_{3b}); IR (neat) 3350, 2930, 1400, 1080, 912 cm^{-1}; mass spectrum, m/e 121 (M^+ − $CH_2CH{=}CH_2$); HRMS for $C_4H_9O_4$, calcd 121.0501, found 121.0501. *xylo* tetrol **26** was fully characterized as the tetraacetate derivative **27**.

Tetrol (+)-**26** deriving from carbonates **25a,b** is the enantiomer of **26** prepared by the hydrolysis of diol **28** or the ethoxy ethyl ether derivative **44**.

(+)-*xylo*-(4*S*,5*R*,6*R*)-Hept-1-ene-4,5,6,7-tetrol 4,5,6,7-Tetraacetate (27). A solution of epoxy alcohol **44** (97 mg, 0.45 mmol) in H_2O/*t*-BuOH (5:1, 9.0 mL) was treated with NaOH (1.5 mL of 1 M solution) at 70 °C for 12 h according to the procedure described for the preparation of **31**. The crude tetrol **26** was acylated according to the standard procedure (cf. as for **31**), providing tetraacetate **27** (109 mg, 73% yield) as a clear oil following chromatographic purification (silica gel, 20% EtOAc in hexanes): $[\alpha]^{25}_D$ = +11.2° (c = 1.38, CH_2Cl_2); ^1H NMR (300 MHz,

C_6D_6) δ 5.70 (m, 1 H), 5.55 (ddd, J = 5.9, 5.9, 3.9 Hz, 1 H) 5.45 (dd, J = 5.9, 4.7 Hz, 1 H), 5.34 (ddd, J = 4.7, 4.3, 7.0 Hz, 1 H), 4.46 (dd, J = 11.3, 3.9 Hz, 1 H), 4.01 (dd, J = 11.3, 5.9 Hz, 1 H), 2.29 (m, 2 H), 2.10 (s, 3 H), 2.07 (s, 3 H), 2.06 (s, 3 H), 2.04 (s, 3 H); ^{13}C NMR (75.4 MHz, C_6D_6) δ 169.81, 169.63, 169.58, 169.39, 132.69, 118.72, 71.33, 70.75, 69.94, 62.25, 35.70, 20.34, 20.17, 20.11, 20.03; IR (neat) 3060, 2980, 1740 (br), 1640, 1365 (br), 1220 (br) cm^{-1}; HRMS for $C_{13}H_{19}O_6$ (M^+ – OAc), calcd. 271.1181, found 271.1187. Anal. Calcd for $C_{15}H_{22}O_8$: C, 54.53; H, 6.71. Found: C, 54.53; H, 6.68.

A similar procedure was used for the hydrolysis of diol **28**. Tetraacetate **27** so obtained, however, contained ca. 5% of another diastereomer.

(+)-*lyxo*-(4*R*,5*R*,6*R*)-Hept-1-ene-4,5,6,7-tetrol 4,5,6,7-Tetraacetate (31). To a solution of epoxy alcohol **42** (70 mg, 0.32 mmol) in H_2O/*t*-BuOH (5:1, 6 mL) was added 1 N NaOH (1 mL), and the resulting solution was heated at 70 °C for 12 h. After being cooled to ambient temperature, the solution was acidified to approximately pH 1 with 1 N HCl and heated again at 70 °C for 12 h. The mixture was allowed to cool, the pH was adjusted to pH 4 by using 2 N NaOH, and then the solution was concentrated in vacuo. Residual water removed by repeated azeotropic evaporation with CH_3CN. The crude tetrol (**30**) was suspended in CH_2Cl_2 (8 mL) and treated with acetic anhydride (0.25 mL, 2.6 mmol), triethylamine (0.46 mL, 3.3 mmol), and catalytic DMAP. This mixture was heated at reflux for 12 h; then the solution was filtered through a plug of Florisil and the filtrate concentrated at reduced pressure. Purification by silica gel chromatography (20% Et_2O in hexanes) gave *lyxo* tetraacetate **31** (103 mg, 97%) as a clear oil: $[\alpha]^{25}_D$ = +24.9° (c = 0.4, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.67 (m, 1 H), 5.36 (ddd, J = 6.9, 5.1, 3.3 Hz, 1 H), 5.24 (dd, J = 8.4, 3.3 Hz, 1 H), 5.07 (m, 3 H), 4.22 (dd, J = 12.3, 5.1 Hz, 1 H), 3.92 (dd, J = 12.3, 6.9 Hz, 1 H), 2.32 (m, 2 H), 2.11 (s, 3 H), 2.07 (s, 3 H), 2.03 (s, 3 H), 2.01 (s, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 170.30, 169.95, 169.80, 169.69, 132.35, 118.38, 70.86, 69.03, 68.08, 61.94, 35.19, 20.74, 20.60, 20.60, 20.53; IR (neat) 3060, 2960, 1745 (br), 1640, 1430, 1365, 1220 cm^{-1}; HRMS for $C_{15}H_{22}O_8$ (M^+), calcd 331.1393, found 331.1415. Anal. Calcd for $C_{15}H_{22}O_8$: C, 54.53; H, 6.71. Found: C, 54.46; H, 6.75.

A similar procedure was used for the hydrolysis of epoxy diol **29**. In this case, however, a 1:2 mixture of **31** and a byproduct diacetate tentatively identified as tetrahydrofuran **32** was obtained.

(+)-*lyxo*-(4*R*,5*R*,6*R*)-Hept-1-ene-4,5,6,7-tetrol (30). A solution of tetraacetate **31** (45 mg, 0.14 mmol) in MeOH (10 mL) was treated with a catalytic amount of potassium carbonate and the resulting solution was stirred at 23 °C for 1 h. Excess potassium carbonate was removed by filtration and the filtrate was acidified by treatment with Dowex 50x8-400 ion exchange resin. After removal of the resin, the filtrate was concentrated at reduced pressure to give *lyxo* tetrol **30** (16 mg. 73%) as a clear oil: $[\alpha]^{25}_D$ = +0.5° (c = 0.8, MeOH); ^{1}H NMR (300 MHz, CD_3OD) δ 5.92 (m, 1 H), 5.10 (dd, J = 17.6, 1 Hz, 1 H), 5.05 (dd, J = 10.7, 1 Hz, 1 H), 3.89 (ddd, J = 6.3, 6.3, 2.0 Hz, 1 H), 3.67 (ddd, J = 8.2, 8.2, 4.2 Hz, 1 H), 3.60 (d, J = 6.3 Hz, 1 H), 3.35 (dd, J = 8.2, 2.0 Hz, 1 H), 2.49 (m, 1 H), 2.19 (m, 1 H); ^{13}C NMR (75.4 MHz, CD_3OD) δ 136.84, 117.25, 74.55, 72.36, 71.96, 67.18, 39.30; IR (neat) 3400 (br), 2940, 1640, 1430 cm^{-1}; HRMS for $C_7H_{15}O_4$ (M + H$^+$), calcd 163.0970, found 163.0930.

(+)-*ribo*-(4*S*,5*S*,6*R*)-Hept-1-ene-4,5,6,7-tetrol 4,5,6,7-Tetraacetate (36). A solution of the epoxy alcohol **38** (19 mg, 0.09 mmol) in H_2O/*t*-BuOH (5:1, 2.4 mL) was treated with NaOH (0.35 mL of 1 M solution) according to the procedure described for the synthesis of **31**. The crude tetrol **35** was acylated by following the usual procedure, giving **36** (31 mg, 66%) as a clear oil: $[\alpha]^{25}_D$ = +13.3° (c = 0.2, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.70 (m, 1 H), 5.27 (m, 2 H), 5.09 (m, 3 H), 4.38 (dd, J = 12.1, 3.5 Hz, 1 H, A of AB), 4.14 (dd, J = 12.1, 6.2 Hz, 1 H, B of AB), 2.31 (m, 2 H), 2.05 (s, 3 H), 2.04 (s, 3 H), 2.03 (s, 3 H), 2.01 (s, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 170.71, 170.27, 170.27, 170.08, 134.14, 118.32, 71.85, 71.61, 70.34, 62.60, 35.12, 20.79, 20.73, 20.62, 20.54; IR (neat) 3070, 2970, 1740 (br), 1640, 1430, 1370, 1220 (br), 1040; mass spectrum, m/e 207 (M^+ – HOAc). Anal. Calcd for $C_{15}H_{22}O_8$: C, 54.53; H, 6.71. Found: C, 54.28; H, 7.00.

***lyxo*-(4*S*,5*S*,6*S*)-5,6-Epoxy-4-(1′-ethoxyethoxy)hept-1-en-7-ol (38).** A solution of epoxy alcohol **14** (615 mg, 1.6 mmol) in CH_2Cl_2 (8 mL) was treated with ethyl vinyl ether (0.31 mL, 3.2 mmol) and catalytic pyridinium *p*-toluenesulfonate (PPTS) according to the procedure used to prepare **41**. Ethoxyethyl ether **37** (729 mg, 99% yield) was obtained as a pale yellow oil that was used in the next reaction without further purification: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (m, 4 H), 7.40 (m, 6 H), 5.89 (m, 1 H), 5.13 (dd, J = 17.0, 1.0 Hz, 1 H), 5.09 (ddd, J = 11.0, 1.0, 1.0 Hz, 1 H), 4.82 (q, 1 H, diastereomer a), 4.75 (q, 1 H, diastereomer b), 3.90–3.40 (m, 5 H), 3.17 (m, 1 H), 2.96 (dd, 1 H, diastereomer a), 2.89 (dd, 1 H, diastereomer b), 2.40 (m, 2 H), 1.29 (dd, 3 H), 1.17 (dt, 3 H), 1.06 (s, 9 H); IR (neat) 3060, 2920, 1645, 1575, 1420, 1105 cm^{-1}; HRMS for $C_{25}H_{33}O_3Si$ (M^+ – OEt), calcd 409.2199, found 409.2187. Anal. Calcd for $C_{27}H_{38}O_4Si$: C, 71.32; H, 8.42. Found: C, 72.00; H, 8.15.

Ethoxyethyl ether **37** (611 mg, 1.35 mmol) in CH_3CN (13 mL) was treated with TBAF (1.6 mL of 1 M solution, 1.6 mmol) according to the procedure used to prepare **40**. Purification of the crude product by silica gel chromatography (20% EtOAc in CH_2Cl_2) provided **38** (234 mg, 80%) as a clear oil: $[\alpha]^{25}_D$ = –7.5° (c = 0.8, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88 (m, 1 H), 5.15 (m, 2 H), 4.75 (m, 1 H), 3.89 (m, 2 H), 3.68 (m, 2 H), 3.52 (m, 1 H), 3.24 (m, 1 H, diastereomer a), 3.17 (m, 1 H, diastereomer b), 3.10 (m, 1 H, diastereomer a), 2.97 (m, 1 H, diastereomer b), 2.37 (m, 2 H), 1.30 (m, 3 H), 1.19 (m, 3 H); IR (neat) 3440 (br), 2980, 2920, 1640, 1380, 1120, 1080, 1050, 750 cm^{-1}; HRMS for $C_7H_{11}O_2$ (M^+ – OEE), calcd 127.0759, found 127.0768. Anal. Calcd for $C_{11}H_{20}O_4$: C, 61.09; H, 9.32. Found: C, 60.80; H, 9.44.

***xylo*-(4*R*,5*S*,6*S*)-5,6-Epoxy-4-(1′-ethoxyethoxy)hept-1-en-7-ol (40).** A solution of epoxy alcohol **15** (580 mg, 1.5 mmol) in dry CH_2Cl_2 (20 mL) was treated with ethyl vinyl ether (0.29 mL, 3.0 mmol) and a catalytic amount of pyridinium *p*-toluenesulfonate, using the procedure described for the synthesis of **41**. Ethoxyethyl ether **39** (600 mg, 88%) was obtained as a pale yellow oil that was used without additional purification: $[\alpha]^{25}_D$ +5.4° (c = 0.9, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (m, 4 H), 7.41 (m, 6 H), 5.80 (m, 1 H), 5.06 (m, 2 H), 4.92 (q, 1 H, diastereomer a), 4.84 (q, 1 H, diastereomer b), 3.86–3.33 (m, 5 H), 2.99 (d, 1 H), 2.87 (m, 1 H), 2.34 (m, 2 H), 1.48 (d, 3 H, diastereomer a), 1.42 (d, 3 H, diastereomer b), 1.20 (m, 3 H), 1.05 (s, 9 H); IR (neat) 3060, 2920, 2850, 1615, 1580, 1410, 1105 cm–1; HRMS for $C_{25}H_{33}O_3Si$ (M^+ – OEt), calcd 409.2199, found 409.2187. Anal. Calcd for $C_{27}H_{38}O_4Si$: C, 71.32; H, 8.42. Found: C, 71.87; H, 8.51.

A solution of ethoxyethyl ether **39** (933 mg, 0.65 mmol) in dry THF (10 mL was treated with tetrabutylammonium fluoride (TBAF; 2.5 mL of 1 M solution in THF, 2.5 mmol) by using the procedure described for the synthesis of **42**. Epoxy alcohol **40** (443 mg, 99%) was obtained as a clear liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.81 (m, 1 H), 5.12 (d, 1 H), 5.07 (d, 1 H), 4.91 (q, 1 H, diastereomer a), 4.82 (q, 1 H, diastereomer b), 3.90 (dd, 1 H), 3.78–3.38 (m, 4 H), 3.06 (m, 1 H), 2.97 (m, 1 H), 2.35 (m, 2 H), 1.96 (t, 1 H), 1.35 (d, 3 H, diastereomer a), 1.30 (d, 3 H, diastereomer b), 1.20 (m, 5 H); IR (neat) 3430 (br), 3060, 2970, 2920, 1618, 1085 cm^{-1}; HRMS for $C_{11}H_{21}O_4$ (M + H$^+$), calcd 217.1439, found 217.1479. Anal. Calcd for $C_{11}H_{20}O_4$: C, 61.90; H, 9.32. Found: C, 61.14; H, 9.12.

***ribo*-(4*R*,5*R*,6*S*)-7-(*tert*-Butyldiphenylsiloxy)-5,6-epoxy-4-(1′-ethoxyethoxy)hept-1-ene (41).** To a solution of epoxy alcohol **16** (990 mg, 2.6 mmol) in dry CH_2Cl_2 (10 mL) was added ethyl vinyl ether (0.50 mL, 5.2 mmol) followed by a catalytic amount of PPTS. The solution was stirred at 23 °C for 2 h and then was filtered through a plug of Florisil, using ethyl acetate as eluant. The solution was concentrated under reduced pressure, giving ethoxyethyl ether **41** (1.13 g, 96%) as a clear oil (diastereomers at the acetal center): $[\alpha]^{25}_D$ = –5.6° (c = 2.3, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (m, 4 H), 7.42 (m, 6 H), 5.88 (m, 1 H), 5.13 (dd, J = 19, 1 Hz, 1 H), 5.08 (dd, J = 10, 1 Hz, 1 H), 4.76 (q, 1 H, diastereomer a), 4.74 (q, 1 H, diastereomer b), 4.01 (dd, 2 H, diastereomer a), 3.93 (dd, 2 H, diastereomer b), 3.81 (dd, 2 H, diastereomer a), 3.72 (dd, 2 H, diastereomer b), 3.56–3.20 (m, 4 H), 2.98 (dd, 1 H, diastereomer a), 2.93 (dd, 1 H, diastereomer b), 2.40 (m, 2 H), 1.22 (d, 3 H), 1.09 (s, 9 H), 1.02 (t, 3 H); IR (neat) 3060, 2920, 2845, 1620, 1590, 1410, 1100 cm^{-1}; HRMS for $C_{23}H_{29}O_2Si$ (M^+ – OEE), calcd 365.1937, found 365.1930. Anal. Calcd for $C_{27}H_{38}O_4Si$: C, 71.32; H, 8.42. Found: C, 71.62; H, 8.37.

***ribo*-(4*R*,5*R*,6*S*)-5,6-Epoxy-4-(1′-ethoxyethoxy)hept-1-en-7-ol (42).** To a solution of ethoxyethyl ether **41** (1.13 g, 2.48 mmol) in dry CH_3CN (25 mL) was added a 1 M solution of TBAF in THF

(3.0 mL, 3.0 mmol), and the resulting solution was stirred at 23 °C for 12 h. The reaction solution was diluted with EtOAc (75 mL), washed with saturated NH_4Cl (3 × 30 mL), and dried over $MgSO_4$. After removal of solvent at reduced pressure, the crude product was purified by silica gel chromatography (20% EtOAc in CH_2Cl_2), yielding epoxy alcohol **42** (503 mg, 94%) as a clear liquid: $[\alpha]^{25}_D$ = +2.8° (*c* = 11.3, CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$) δ 5.88 (m, 1 H), 5.10 (m, 2 H), 5.05 (q, 1 H, diastereomer a), 4.78 (q, 1 H, diastereomer b), 3.94 (m, 1 H), 3.54 (m, 5 H), 3.23 (m, 1 H), 2.97 (dd, 1 H, diastereomer a), 2.92 (dd, 1 H diastereomer b), 2.46 (m, 2 H), 1.33 (dd, 3 H), 1.21 (dt, 3 H); IR (neat) 3440 (br), 3060, 2970, 1625, 1120, 1085, 1045 cm^{-1}; HRMS for $C_7H_{11}O_2$ (M^+ – OEE), calcd 127.0759, found 127.0767. Anal. Calcd for $C_{11}H_{20}O_4$: C, 61.09; H, 9.32. Found: C, 60.74; H, 9.50.

***arabino*-(4*S*,5*R*,6*S*)-7-(*tert*-Butyldiphenylsiloxy)-5,6-epoxy-4-(1′-ethoxyethoxy)hept-1-ene (43).** Epoxy alcohol **17** (278 mg, 0.73 mmol) in CH_2Cl_2 (7 mL) was treated with ethyl vinyl ether (0.10 mL, 1.1 mmol) and catalytic PPTS according to the procedure used to prepare ethoxyethyl ether **41**. Ethoxyethyl ether **43** (300 mg, 91% yield) was obtained as a pale yellow oil: $[\alpha]^{25}_D$ = −24.5° (*c* = 1.0, CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$) δ 7.70 (m, 4 H), 7.42 (m, 6 H), 5.80 (m, 1 H), 5.06 (dd, *J* = 17.0, 1.0 Hz, 1 H), 5.01 (dd, *J* = 9.0, 1.0 Hz, 1 H), 4.88 (q, 1 H, diastereomer a), 4.79 (q, 1 H, diastereomer b), 3.76 (m, 2 H), 3.65–3.32 (m, 3 H), 3.18 (m, 1 H), 3.05 (dd, 1 H, diastereomer a), 2.98 (dd, 1 H, diastereomer b), 2.34 (m, 2 H), 1.34 (d, 3 H, diastereomer a), 1.27 (d, 3 H, diastereomer b), 1.18 (t, 3 H, diastereomer a), 1.13 (t, diastereomer b), 1.07 (s, 9 H); IR (neat) 3060, 2940, 1643, 1581, 1153 (br) cm^{-1}; HRMS for $C_{23}H_{29}O_2Si$ (M^+ – OEE), calcd 365.1937, found 365.1951. Anal. Calcd for $C_{27}H_{38}O_4Si$: C, 71.32; H, 8.42. Found: C, 71.17; H, 8.43.

***arabino*-(4*S*,5*R*,6*S*)-5,6-Epoxy-4-(1′-ethoxyethoxy)hept-1-en-7-ol (44).** A solution of ethoxyethyl ether **43** (1.14 g, 2.5 mmol) in CH_3CN (25 mL) was treated with TBAF (3.0 mL of 1.0 M solution in THF, 3.0 mmol) according to the procedure used to prepare epoxy alcohol **42**. Epoxy alcohol **44** (531 mg, 98% yield) was obtained as a clear oil following chromatographic purification (silica gel, 20% EtOAc in CH_2Cl_2): $[\alpha]^{25}_D$ = −33.4° (*c* = 1.2, CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$) δ 5.81 (m, 1 H), 5.13 (dd, *J* = 15.6, 1.0 Hz, 1 H), 5.08 (ddd, *J* = 6.5, 1.0, 1.0 Hz, 1 H), 4.96 (q, 1 H, diastereomer a), 4.82 (q, 1 H, diastereomer b), 3.83 (m, 1 H), 3.75–3.40 (m, 4 H), 3.11 (m, 2 H), 2.32 (m, 2 H), 2.08 (t, 1 H), 1.35 (d, 3 H, diastereomer a), 1.33 (d, 3 H, diasteromer b), 1.19 (m, 3 H); IR (neat) 3450 (br), 3080, 1645, 1100 cm^{-1}; HRMS for $C_{11}H_{19}O_3$ ($M + H^+ - H_2O$), calcd 199.1334, found 199.1356. Anal. Calcd for $C_{11}H_{20}O_4$: C, 61.09; H, 9.32. Found: C, 60.97; H, 9.63.

2-Deoxy-L-glucose. L-*arabino* tetrol (−)-**22** (2.3 mg, 0.014 mmol, prepared from carbonate **20**) in 1 mL of MeOH at −20 °C was treated with excess ozone (a stream of O_3 in O_2, 2 min). Residual ozone was removed by bubbling N_2 through the solution for 20 min, and then 0.10 mL of Me_2S was added. The reaction allowed to warm to 23 °C and stirred for 6 h. The solvent and resulting DMSO were removed in vacuo, giving 1.7 mg (74% yield) of crude 2-deoxy-L-glucose as a syrup: $[\alpha]^{20}_D$ = −43° (*c* = 0.17, H_2O). The structure was confirmed by comparison of ^1H NMR spectral data with those of a sample of commercially available 2-deoxy-D-glucose ($[\alpha]^{20}_D$ = +45°, *c* = 0.58, H_2O).

(+)-2-Deoxy-D-glucitol 1,3,4,5,6-Pentaacetate (45). A solution of *d-arabino* tetrol **21** (31 mg, 0.19 mmol; from the alkaline hydrolysis of epoxy alcohol **40**) in 6 mL of CH_2Cl_2/MeOH (1:1) at −78 °C was treated with ozone, using the procedure described for the synthesis of 2-deoxy-L-glucose. The crude sugar ($[\alpha]^{20}_D$ = +36.3° (*c* = 0.43, H_2O)) so obtained was contaminated with the corresponding methyl glycoside (high field NMR analysis) and was used without further purification in the following experiment.

The crude 2-deoxyglucose was dissolved in H_2O (2 mL), treated with $NaBH_4$ (13 mg, 0.36 mmol) and stirred at room temperature for 16 h. The reaction was quenched with HOAc (1 mL) and concentrated in vacuo. The crude product was dried by repeated coevaporated from MeCN (5 × 15 mL) and MeOH (5 × 15 mL). The crude tetrol was suspended in pyridine (2 mL) and treated with Ac_2O (136 μL, 1.4 mmol) and a catalytic amount of DMAP. After being stirred at 23 °C for 16 h, the mixture was diluted with EtOAc (10 mL) and washed with saturated $CuSO_4$ solution (3 × 10 mL). The organic extracts were dried ($MgSO_4$) and concentrated in vacuo, and the crude tetraacetate was purified by silica gel chromatography (10% EtOAc in hexanes). 2-Deoxyglucitol pentaacetate **45** (30 mg, 44%) was obtained as a clear oil: $[\alpha]^{25}_D$ = +34.6° (*c* = 0.1, CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$) δ 5.25 (m, 2 H), 5.07 (m, 1 H), 4.18 (dd, *J* = 12.5, 2.5 Hz, 1 H), 4.09 (dd, *J* = 12.5 4.8 Hz, 1 H), 4.01 (t, 2 H), 2.09 (s, 3 H), 2.02 (s, 3 H), 2.01 (s, 3 H), 2.00 (s, 3 H), 1.99 (s, 3 H), 1.78 (m, 2 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 170.65, 170.42, 170.03, 169.72, 169.72, 70.45, 68.24, 67.57, 61.72, 60.18, 30.05, 20.69, 20.69, 20.58, 20.53, 20.50; IR (neat) 3020, 2960, 1745 (br), 1370, 1230 (br), 1040, 750 cm^{-1}; HRMS for $C_{16}H_{25}O_{10}$ ($M + H^+$), calcd 377.1447, found 377.1443. Anal. Calcd for $C_{16}H_{24}O_{10}$: C, 51.04; H, 6.43. Found: C, 50.74; H, 6.60.

The structure of **45** was confirmed by comparison of the spectral data with those of an authentic sample similarly prepared (86%) from commercially available 2-deoxy-D-glucose. This reference sample of **45** had $[\alpha]_D$ = +35.0° (*c* = 3.8, CH_2Cl_2).

(+)-2-Deoxy-D-galactitol 1,3,4,5,6-Pentaacetate (46). A −78 °C solution of (+)-*lyxo* tetrol **30** (21 mg, 0.13 mmol) in 3 mL of CH_2Cl_2/MeOH (1:1) was treated with a stream of O_3 in O_2 until the solution remained blue (ca. 5 min.). Residual ozone was removed by bubbling N_2 through the solution for 20 min. Dimethyl sulfide (0.5 mL) was then added and the resulting solution stirred at 23 °C for 16 h. Concentration of this solution in vacuo provided a mixture of 2-deoxy-D-galactose and the corresponding methyl glycoside(s) as determined by 300-MHz NMR analysis. This mixture was dissolved in 10% HOAc (3 mL) and heated at 65 °C for 14 h. After being concentrated in vacuo and dried by repeated evaporation from MeCN (5 × 20 mL), crude 2-deoxy-D-galactose was obtained as a clear syrup: $[\alpha]_D$ = +35.8° (*c* = 0.5, MeOH). The purity of the synthetic 2-deoxygalactose was judged to be 90–95% by high field NMR analysis. The optical rotation of a commercially available sample of 2-deoxy-D-galactose was determined to be $[\alpha]_D$ = +44.4° (*c* = 0.5, MeOH). The synthetic sugar was used without further purification in the following experiment.

The crude synthetic 2-deoxy-D-galactose was dissolved in H_2O (2 mL) and treated with excess $NaBH_4$ (~50 mg) at 23 °C for 16 h. After being quenched with HOAc (1 mL), the crude mixture was evaporated from MeCN (5 × 10 mL) and MeOH (5 × 10 mL). The crude pentol was suspended in pyridine (2 mL) and treated with Ac_2O (90 μL, 0.96 mmol) and a catalytic amount of DMAP. After being stirred for 6 h at room temperature, the solution was diluted with EtOAc (10 mL) and washed with saturated $CuSO_4$ solution (3 × 10 mL). The organic phase was dried ($MgSO_4$) and concentrated in vacuo. The crude product was purified by silica gel chromatography (10% EtOAc in hexanes) to give pure synthetic 2-deoxygalactitol pentaacetate **46** (19 mg, 42%) as a clear oil: $[\alpha]^{25}_D$ = +43.2° (*c* = 0.3, CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$) δ 5.32 (m, 2 H), 5.13 (m, 1 H), 4.23 (dd, *J* = 11.0, 5.0 Hz, 1 H), 4.07 (t, *J* = 7.0 Hz, 2 H), 3.98 (dd, *J* = 12.0, 6.0 Hz, 1 H), 2.06 (m, 17 H); ^{13}C NMR (75.4 M Hz, $CDCl_3$) δ 170.75, 170.33, 169.96, 169.89, 169.79, 71.01, 68.25, 67.57, 61.83, 60.04, 29.17, 20.73, 20.70, 20.62, 20.55, 20.55; IR (neat) 3020, 2960, 1745 (br), 1430, 1370, 1225 (br), 1045 cm^{-1}; HRMS for $C_{14}H_{21}O_8$ ($M + H^+$ – HOAc), calcd 317.1236, found 317.1269. Anal. Calcd for $C_{16}H_{24}O_{10}$: C, 51.04; H, 6.43. Found: C, 50.79; H, 6.60.

The structure of **46** was confirmed by comparison of spectral data with that of an authentic sample similarly prepared (76% yield) by the reduction of commercially available 2-deoxy-D-galactose. This reference sample of **46** had $[\alpha]^{25}_D$ = +44.7° (*c* = 0.8, CH_2Cl_2).

***(−)-lyxo*-(4*S*,5*S*,6*S*)-7-(*tert*-Butyldiphenylsiloxy)-5,6-epoxy-4-(benzyloxy)hept-1-en-7-ol (47).** To a solution of benzyl bromide (0.21 mL, 1.8 mmol) and sodium hydride (56.8% in mineral oil, 135 mg, 3.20 mmol) in THF (10 mL) was added a solution of epoxy alcohol **14** (610 mg, 1.60 mmol) in THF (5 mL). This mixture was stirred for 12 h at 23 °C and then was quenched by addition of ether and water (20 mL, 1:1). The aqueous phase was separated and extracted with Et_2O (2 × 30 mL). The combined extracts were dried over $MgSO_4$, filtered, and concentrated in vacuo to provide the crude benzyl ether that was purified by chromatography (silica gel, 30% Et_2O in hexanes), giving the pure benzyl ether derivative (660 mg, 87%) as a clear oil: $[\alpha]^{25}_D$ = −13.4° (*c* = 0.8, CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$) δ 7.68 (m, 4 H), 7.38 (m, 11 H), 5.92 (m, 1 H), 5.14 (dd, *J* = 17.1, 1.0 Hz,

1 H), 5.09 (dd, J = 10.2, 1.0 Hz, 1 H), 4.66 (A of AB, J_{AB} = 11.7 Hz, 1 H), 4.53 (B of AB, J_{AB} = 11.7 Hz, 1 H), 3.76 (A of ABX, J_{AB} = 17.8, J_{AX} = 4.3 Hz, 1 H), 3.71 (B of ABX, J_{AB} = 17.8, J_{BX} = 4.3 Hz, 1 H), 3.36 (dd, J = 12.2, 6.6 Hz, 1 H), 3.13 (ddd, J = 4.3, 4.3, 3.8 Hz, 1 H), 2.92 (dd, J = 6.3, 2.7 Hz, 1 H), 2.44 (m, 2 H), 1.07 (s, 9 H); IR (neat) 3060, 2920, 2860, 1640, 1580, 1420, 1110, 700 cm^{-1}; mass spectrum, m/e 241, 181, 91. Anal. Calcd for $C_{30}H_{36}O_3Si$: C, 76.22; H, 7.67. Found: C, 76.36; H, 7.66.

(+)-*ribo*-(4*S*,5*S*,6*R*)-4-(Benzyloxy)hept-1-ene-5,6,7-triol 5,6,7-Triacetate (48). A solution of benzyl ether **47** (604 mg, 1.28 mmol) in THF (13 mL) was treated with TBAF (1.50 mL of 1 M solution in THF, 1.50 mmol) for 12 h at 23 °C. The reaction mixture was diluted with EtOAc (50 mL), washed with saturated NH_4Cl (3 × 20 mL), and dried over $MgSO_4$. Concentration of the filtrate in vacuo and purification of the crude product (silica gel, 20% EtOAc in CH_2Cl_2) provided the desired epoxy alcohol (215 mg, 65%) as a clear oil: $[\alpha]^{25}_D$ = −10.9° (c = 2.1, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (m, 5 H), 5.89 (m, 1 H), 5.15 (dd, J = 17.3, 1.5 Hz, 1 H), 5.11 (dd, J = 11.6, 2.0 Hz, 1 H), 4.60 (s, 2 H), 3.85 (dd, J = 12.2, 2.2 Hz, 1 H), 3.56 (dd, J = 13.0, 4.3 Hz, 1 H), 3.43 (q, 1 H), 3.12 (m, 1 H), 2.98 (dd, J = 4.9, 1.7 Hz, 1 H), 2.45 (m, 2 H), 1.68 (s, br, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 138.25, 133.66, 128.21, 128.21, 127.53, 127.42, 127.42, 127.42, 117.38, 72.13, 61.27, 59.96, 56.50, 36.93; IR ($CHCl_3$) 3060, 2920, 1635, 1580, 1420, 1110 cm^{-1}; HRMS for $C_{11}H_{13}O_3$ (M^+ − allyl), calcd 193.0865, found 193.0870.

A solution of the above epoxy alcohol (9 mg, 0.04 mmol) in t-BuOH (200 μL) was treated with 0.5 N NaOH (1 mL) and heated at 70 °C for 24 h. The cooled solution was acidified to approximately pH 6 by using Dowex 50x8-400 ion exchange resin. After filtration, the mixture was concentrated in vacuo and residual water was removed by repeated azeotropic evaporation from CH_3CN. The crude tetrol was suspended in CH_2Cl_2 (2 mL) and treated with Et_3N (0.39 mL, 2.8 mmol), Ac_2O (0.132 μL, 1.4 mmol), and a catalytic amount of DMAP. This mixture was heated at reflux for 12 h, diluted with EtOAc (10 mL), washed with H_2O (2 × 10 mL), and dried over $MgSO_4$. Concentration in vacuo and chromatographic purification of the crude product (silica gel, 20% EtOAc in hexanes) provided triacetate **48** (10 mg, 66% yield) as a clear oil: $[\alpha]^{25}_D$ = +14.0° (c = 0.7, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (m, 5 H), 5.82 (m, 1 H), 5.41 (m, 1 H), 5.24 (dd, J = 4.7, 5.1 Hz, 1 H), 5.13 (dd, J = 10.5, 1.5 Hz, 1 H), 5.08 (d, J = 9 Hz, 1 H), 4.58 (s, 2 H), 4.36 (dd, J = 2.8, 12.1 Hz, 1 H), 4.22 (dd, J = 7.6, 12.1 Hz, 1 H), 3.62 (q, 1 H), 2.38 (m, 2 H), 2.05 (s, 3 H), 2.04 (s, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 170.64, 169.95, 169.95, 137.64, 133.63, 128.37, 128.14, 128.02, 127.91, 127.87, 127.79, 117.87, 72.10, 71.90, 70.27, 65.55, 34.89, 20.88, 20.84, 20.74; IR (CH_2Cl_2) 3050, 2980, 1740 (br), 1365, 1220, 730 cm^{-1}; HRMS for $C_{18}H_{23}O_5$ (M^+ − OAc), calcd 319.1545, found 319.1534. Anal. Calcd for $C_{20}H_{26}O_7$: C, 63.48; H, 9.93. Found: C, 63.93; H, 9.74.

(−)-(4*R*,5*R*,6*S*)-5,6-Epoxy-4-[[(benzyloxy)methyl]oxy]-hept-1-en-7-ol (49). A mixture of epoxy alcohol **16** (575 mg, 1.5 mmol), i-Pr_2NEt (0.63 mL, 3.6 mmol), and BOM-Cl (0.25 mL, 1.8 mmol) in CH_2Cl_2 (3 mL) was heated at reflux for 26 h. After being allowed to cool, the solution was diluted with additional CH_2Cl_2 (50 mL), washed with H_2O (3 × 20 mL), dried over $MgSO_4$, and concentrated in vacuo. The crude product was dissolved in THF (3 mL) and treated with TBAF (1.0 M in THF, 2.0 mL, 2.0 mmol) at 23 °C for 16 h. This mixture was diluted with EtOAc (30 mL) and washed with saturated NH_4Cl (3 × 15 mL). The organic solution was dried over $MgSO_4$ and concentrated in vacuo. Chromatographic purification (silica gel, 20% EtOAc in CH_2Cl_2) provided epoxy alcohol **49** (312 mg, 79%) as a clear oil: $[\alpha]^{25}_D$ = −11.0° (c = 0.8, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (m, 5 H), 5.91 (m, 1 H), 5.18 (dd, J = 18.0, 1.0 Hz, 1 H), 5.13 (dd, J = 10.2, 1.0 Hz, 1 H), 4.93 (dd, J = 7.5, 2.4 Hz, 1 H), 4.76 (d, J = 6.6 Hz, 1 H), 4.66 (d, J = 3.6 Hz, 1 H), 3.88 (ddd, J = 8.4, 4.8, 4.2 Hz, 1 H), 3.53 (m, 2 H), 3.19 (m, 1 H), 3.01 (m, 2 H), 2.50 (m, 2 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 136.66, 133.59, 128.55, 128.55, 128.14, 128.14, 128.14, 117.82, 93.58, 73.55, 69.95, 59.97, 57.57, 56.60, 37.78; IR (neat) 3450 (br), 2960, 2900, 1640, 1500, 1100, 1040 cm^{-1}; mass spectrum, m/e 263 (M^+ − H). Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.15; H, 7.63. Found: C, 68.10; H, 7.67.

(+)-*lyxo*-(4*R*,5*R*,6*R*)-4-[[(Benzyloxy)methyl]oxy]hept-1-ene-5,6,7-triol 5,6,7-Triacetate (50). A solution of epoxy alcohol **49** (27 mg, 0.10 mmol) in t-BuOH (150 μL) was treated with 0.5 N NaOH (750 μL) and heated at 70 °C for 24 h. After being allowed to cool ambient temperature, the solution was acidified to approximately pH 6 with Dowex 50x8-400 ion exchange resin. The solution was filtered and concentrated, and residual water was removed by repeated azeotropic evaporation from CH_3CN. The crude tetrol was suspended in CH_2Cl_2 (1.5 mL) and treated with Et_3N (0.28 mL, 2.0 mmol), Ac_2O (94 μL, 1.0 mmol), and a catalytic amount of DMAP. After being heated at reflux for 12 h, the solution was diluted with EtOAc (10 mL), washed with H_2O (2 × 15 mL), and dried over $MgSO_4$. Concentration in vacuo and chromatographic purification (silica gel, 20% EtOAc in hexanes) provided triacetate **50** (24 mg, 60% yield) as a clear oil: $[\alpha]^{25}_D$ = +20.7° (c = 2.6, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (m, 5 H), 5.83 (m, 1 H), 5.43 (m, 1 H), 5.23 (dd, J = 5.1, 4.7 Hz, 1 H), 5.13 (d, J = 4.7 Hz, 1 H), 5.10 (d, J = 11.3 Hz, 1 H), 4.77 (A of AB, J_{AB} = 7.8 Hz, 1 H), 4.73 (B of AB, J_{AB} = 7.8 Hz, 1 H), 4.66 (A′ of AB′, $J_{AB'}$ = 11.3 Hz, 1 H), 4.58 (B′ of AB′, $J_{AB'}$ = 11.3 Hz, 1 H), 4.28 (dd, J = 4.7, 11.7 Hz, 1 H), 4.08 (dd, J = 6.2, 11.7 Hz, 1 H), 3.87 (q, 1 H), 2.42 (m, 2 H), 2.08 (s, 3 H), 2.06 (s, 3 H), 2.03 (s, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 170.48, 170.01, 169.91, 137.60, 133.54, 128.43, 128.43, 127.76, 127.76, 127.76, 118.02, 94.17, 75.35, 71.42, 69.92, 69.10, 35.40, 20.81, 20.71, 20.65; IR (CH_2Cl_2) 3070, 3020, 2940, 2900, 1745 (br), 1640, 1365, 1220 cm^{-1}; HRMS for $C_{19}H_{24}O_6$ (M^+ − HOAc), calcd 348.1573, found 348.1568. Anal. Calcd for $C_{21}H_{28}O_8$: C, 61.75; H, 6.91. Found: C, 62.02; H, 7.20.

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Registry No. (*R*,*R*)-**7**, 99417-58-0; (*S*,*S*)-**7**, 127851-95-0; **12**, 131486-44-7; **13**, 131380-35-3; *ent*-**13**, 131484-50-9; **14**, 131380-36-4; **15**, 131484-24-7; **16**, 131484-25-8; *ent*-**16**, 131484-42-9; **17**, 131484-26-9; *ent*-**17**, 131484-43-0; **18**, 131380-37-5; **19**, 131380-38-6; **20**, 131380-39-7; (*d*)-**21**, 131484-44-1; (*l*)-**21**, 131484-27-0; (*d*)-**22**, 131484-45-2; (*l*)-**22**, 131380-40-0; **23**, 131484-28-1; **24a**, 131484-29-2; **24b**, 131380-50-2; **25a**, 131484-30-5; **25b**, 131380-51-3; (*d*)-**26**, 131484-46-3; (*l*)-**26**, 131484-31-6; (*d*)-**27**, 131484-47-4; (*l*)-**27**, 131484-32-7; **28**, 131380-41-1; **29**, 131484-33-8; (*d*)-**30**, 131484-48-5; (*d*)-**31**, 131484-49-6; **32**, 131380-52-4; (*l*)-**35**, 58902-30-0; (*d*)-**36**, 131484-51-0; **37** (isomer 1), 131380-42-2; **37** (isomer 2), 131484-52-1; **38** (isomer 1), 131380-43-3; **38** (isomer 2), 131484-53-2; **39** (isomer 1), 131484-34-9; **39** (isomer 2), 131484-54-3; **40** (isomer 1), 131484-35-0; **40** (isomer 2), 131484-55-4; **41** (isomer 1), 131484-36-1; **41** (isomer 2), 131484-56-5; **42** (isomer 1), 131484-37-2; **42** (isomer 2), 131484-57-6; **43** (isomer 1), 131484-38-3; **43** (isomer 2), 131484-58-7; **44** (isomer 1), 131484-39-4; **44** (isomer 2), 131484-59-8; **45**, 15086-09-6; **46**, 49560-35-2; **47**, 131380-44-4; **47** desilyl derivative, 131380-49-9; **48**, 131380-45-5; **49**, 131380-46-6; **50**, 131380-47-7; **51**, 87770-83-0; **52**, 92808-78-1; **52** aldehyde derivative, 131380-48-8; **53**, 131484-40-7; **54**, 131484-41-8; 2-butene-1,4-diol, 110-64-5; 2-deoxy-L-glucose, 25029-33-8; 2-deoxy-D-glucose, 154-17-6; 2-deoxy-D-galactose, 1949-89-9.

Supplementary Material Available: ^{1}H NMR spectra of **7**, **12**, **13**, **17**, **18**, **19**, **20**, **21**, **24a**, **24a–24b** mixture, **25a–25b** mixture, **26**, and **30** (13 pages). Ordering information is given on any current masthead page.