# Enantio- and Diastereoselective Transformations of Cycloheptatriene to Sugars and Related Products†

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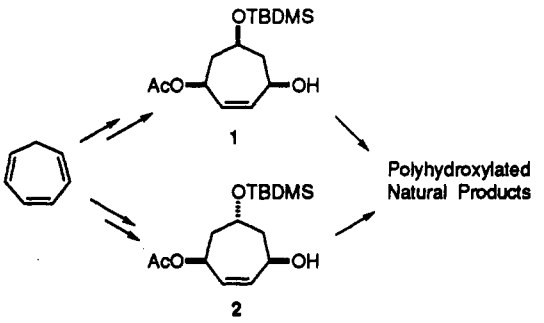
Both meso diastereomers of 6-[(*tert*-butyldimethylsilyl)oxy]-2-cycloheptene-1,4-diol, prepared from cycloheptatriene, have been enzymatically asymmetrized by conversion to monoacetates using *Pseudomonas cepacia* lipase in isopropenyl acetate. A study of protecting group manipulations, diastereoselective oxidations, and regioselective ring openings utilizing these enantiopure monacetates which results in the synthesis of all possible methyl 2,4-dideoxyhexopyranosides is described.

## Introduction

Sugars as a class of compounds have one of the highest densities of chiral centers, making them challenging targets in organic synthesis.[1-4] The obvious choices for starting materials are other readily available hexoses (D-glucose, D-galactose, D-mannose, D-fructose) or pentoses (D-ribose, D-arabinose, D-xylose).[5] The need for selective deoxygenated, modified or unnatural sugars calls for the development of new diastereoselective transformations and the use of other chiral starting materials such as tartaric acid,[6] D-glyceraldehyde,[7] and α-amino acids.[8,9] Enantioselective syntheses of sugars have been developed recently based on 7-oxanorbornenes.[10] The application of Sharpless asymmetric epoxidation to the synthesis of all L-hexoses is a very important achievement in this field.[11]

The use of enzymes in organic synthesis has brought a new powerful tool for enantioselective syntheses.[12-23] Recent developments on the use of enzymes in organic solvents, including resolutions as well as asymmetrization of meso or prochiral compounds[24] make this an attractive approach for the generation of new chiral, enantiopure starting materials for natural product synthesis. In the synthesis of carbohydrates, aldolases[15,21-23] and lipases[21,25] have been found to be the most useful. We have provided preliminary reports on asymmetrizations of cycloheptatriene-derived *meso*-diols **5** and **8**[26] and on the conversion of enzymatic reaction products **1** and **2** into the 2,4-dideoxyhexopyranose systems.[27a] Compound **1** has also been transformed to the fully oxygenated hexose, L-glucose.[27b]

**Scheme I**




In this paper we present our studies on diastereoselective oxidations of acetates **1** and **2** into appropriate precursors of various deoxy hexoses and heptoses (Scheme I) as well as details of the synthesis of 2,4-dideoxyhexopyranoses. Related stereocontrolled functionalization of cycloheptadiene using organometallic chemistry has recently been reported by Pearson and co-workers.[28-32]

† This paper is dedicated to Prof. A. Fava, University of Bologna, on the occasion of his 70th birthday.

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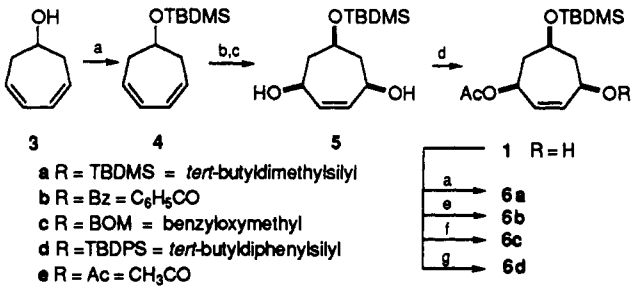
**Scheme II**[a]




[a] (a) TBDMSCl, imidazole, DMF (4, 88%; **6a**, 96%); (b) $^1O_2$, $CH_2Cl_2$, MeOH, and then silica gel chromatography (76%); (c) Zn, HOAc, $CH_2Cl_2$, 0 °C (98%); (d) Amano P-30 lipase, isopropenyl acetate, 50 °C (98%); (e) BzCl, $Et_3N$, $CH_2Cl_2$ (94%); (f) BOMCl, diisopropylethylamine, $CH_2Cl_2$ (76%); (g) TBDPSCl, imidazole, DMF (97%).

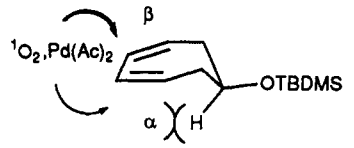



**Figure 1.** Conformational drawing of 4 illustrating preference for addition synto the OTBDMS substituent.

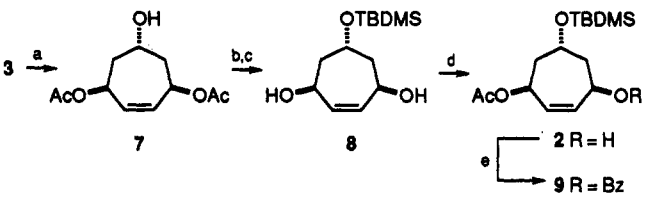
## Results and Discussion

**1. Synthesis of Optically Pure Monoacetates 1 and 2.** Cycloheptatriene was transformed[33] into cycloheptadienol (3)which was protected as its TBS ether 4 (Scheme II).

The latter was subjected to [4 + 2] addition of singlet oxygen[34] at 0 °C to form a separable mixture of peroxide diastereoisomers (5:1, the all-*syn* isomer being predominate). The selectivity for this reaction can be explained using the conformational model depicted in Figure 1. It is believed that the proton geminal to the silyloxy group hinders approach from the $\alpha$ face of the diene thereby resulting in a reaction from the $\beta$ face leading to the all-*syn* product.[34-37] Reduction of the peroxide with zinc and acetic acid provided diol **5**, which was treated with *Pseudomonas cepacia* (Amano P-30) lipase in isopropenyl acetate at 50 °C for 48 h. Removal of the enzyme by filtration followed by evaporation of the solvent in *vacuo* provided mono acetate **1** (>95% ee, 95% yield). Silylation of **1** led to product **6a**, which was identical to a compound that had previously been stereochemically correlated to a known mevinic acid analogue.[38]

The diastereomeric acetate **2** was synthesized via stereoselective palladium-catalyzed 1,4-diacetoxylation of diene **3** (Scheme III).[39] Since palladium(II) coordinates to the less-hindered $\beta$ face of the diene, acetate displaces the palladium complex from the $\alpha$ face to form a $\pi$-allyl palladium complex which in turn is attacked by another acetate from the $\alpha$ face providing diacetate **7**. Silylation and subsequent basic hydrolysis of the acetates afforded

**Scheme III**[a]




[a] (a) $Pd(OAc)_2$, $LiOAc{\cdot}2H_2O$, LiCl, $MnO_2$, benzoquinone, HOAc (75%); (b) TBDMSCl, imidazole, DMF; (c) KOH, MeOH, (88% from **7**); (d) Amano P-30 lipase, isopropenyl acetate, 50 °C (94%); (e) BzCl, $Et_3N$, $CH_2Cl_2$ (96%).

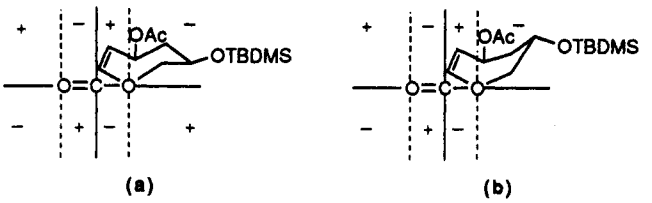



**Figure 2.** (a) Sector diagram of benzoate **6b**. (b) Sector diagram of benzoate **9**.

diol **8**, which was treated with Amano P-30 lipase in isopropenyl acetate at 50 °C for 5 days to produce acetate **2**. The alcohol **2** was converted to a Mosher ester which appeared to be a single diastereoisomer by $^1H$, $^{13}C$, and $^{19}F$ NMR spectroscopy.[40]

As noted above, the absolute configuration of **1** was determined by comparison to a common intermediate **6a** which had been prepared in our laboratory in a sequence involving acetylcholinesterase-catalyzed hydrolysis of a related *meso*-diacetate. The benzoate sector rule has been formulated by Nakanishi for the determination of the absolute configuration of cyclic secondary alcohols.[41] Benzoate **6b**, prepared from **1**, exhibited a positive Cotton effect in it's CD spectrum determined in methanol. This observation points to an absolute stereochemistry of (*S*) at the benzoyloxy substituted carbon of **6b** (see benzoate sector diagram, Figure 2a). Bonds in the positive and negative sectors of the diagram will make positive and negative contributions to the Cotton effect. The contribution of the more polarizable flanking carbon-carbon double bond is greater than that of the carbon–carbon single bond, and the former sector will dominate the Cotton effect. The absolute stereochemical assignment made in this way is consistent with the correlation noted above. Benzoate **9** also exhibited a positive Cotton effect and, according to the sector diagram (Figure 2b), can be assigned *S* stereochemistry at the benzoyloxy carbon. As confirmatory evidence of the absolute configuration of **2**, benzoates **6b** and **9** where desilylated ($nBu_4NF$, THF) and the resultant alcohols were oxidized with PCC in dichloromethane. In each case the same ketone **10** was obtained.

**2. Selective Introduction of Protecting Groups. Access to Both Enantiomeric Series.** Various protected derivatives in both enantiomeric series (**11a–d** and **13a–d**) were prepared from monoacetate **1** (Scheme IV). Protection of the hydroxy function, followed by basic

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(40) Racemic Mosher derivative: $^{19}F$ NMR (300 Mz, $CDCl_3$) $\delta$ -70.559, -70.603. Optically pure Mosher derivative: $^{19}F$ NMR (300 Mz, $CDCl_3$) $\delta$ -70.509. No trace of the other diastereomeric signals was found. Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543.
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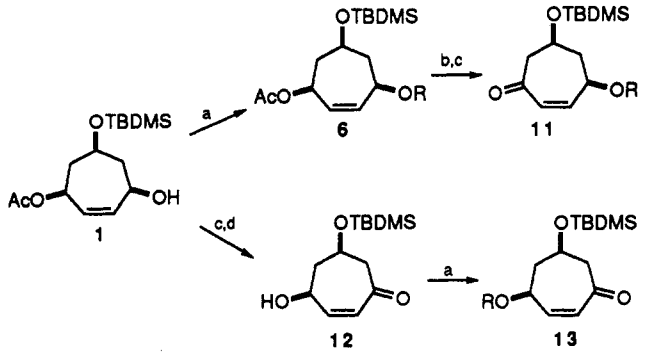
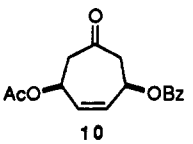
**Scheme IV**[a]




[a](a) (R = TBS) TBDMSCl, imidazole, DMF (**6a**, 96%; 13a, 75%); (R = Bz) BzCl, $Et_3N$, $CH_2Cl_2$ (**6b**, 94%); (R = BOM) BOMCl, diisopropylethylamine, $CH_2Cl_2$ (**6c**, 76%; **13c**, 77%); (R = TBDPS) TBDPSCl, imidazole, DMF (6d, 97%); (b) (R = TBDMS, TBDPS or BOM) KOH, MeOH; (R = Bz) $NH_3$, MeOH; (c) PDC, 4-Å molecular sieves, $CH_2Cl_2$ (**11a**, 96%; **11b**, 85%; **11c**, 86%; **11d**, 92% from **6**); (d) $Ti(Pr^iO)_4$, $Pr^iOH$, 60 °C, 84%

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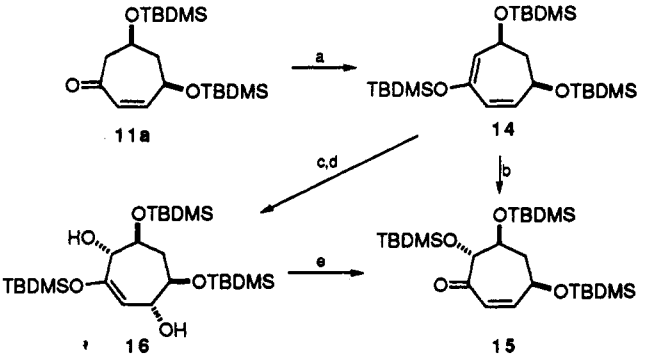
hydrolysis or ammonolysis[42] of the acetate and subsequent oxidation of the allylic alcohol (PDC, molecular sieves, 4 Å),[43] led to the enones 11. The opposite enantiomeric series was synthesized by oxidation of the allylic alcohol, followed by deprotection of the acetate using conditions described by Seebach.[44] This led to the γ-hydroxy enone 12 which was protected as a TBS or BOM derivative 13.

**3. Studies on the Diastereoselective Oxidation of Cycloheptane Ring System.** We envisioned that enones 11 and 13 would be the promising starting materials for diastereoselective oxidation of "deoxy" positions (Scheme V). An initial attempt to oxidize the position α to the carbonyl using lead tetraacetate gave a low yield of α-acetoxy product with no diastereeoselectivty. We then turned our attention to silyloxy dienes such as 14 (obtained from the enone 11a). Rubbotom oxidation[45] of diene 14 gave α-silyloxy enone 15. It is possible to observe initial formation of a 2:1 mixture of diastereoisomers but the cis-oxidation product equilibrated spontaneously or during chromatography on $SiO_2$ to the pure (by $^1H$ and $^{13}C$ NMR; >20:1) *trans*-diastereoisomer 15. Evidence for the stereochemistry of 15 was obtained by $^1H$ NMR as well as X-ray studies.

The [4 + 2] cycloaddition of singlet oxygen to silyloxy diene 14 resulted in the formation of one product (assumed to be the *anti*-peroxide for steric reasons). Reductive opening (Zn, HOAc) of the peroxide led to the diol 16. Under silylation conditions (TBSOTf, 2,6-lutidine), elimination of one of the hydroxyl groups resulted in regenerating an enone system (15).

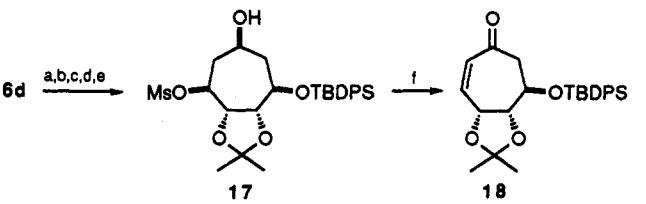
The third procedure for the functionalization of "deoxy" positions involved osmium-mediated cis-hydroxylation of 6d. Protection of the diol as the acetonide, hydrolysis of the acetate, mesylation, and acidic cleavage of the silyl ether gave, after chromatographic separation, alcohol 17 (Scheme VI). Swern oxidation led directly to enone 18.

**Scheme V**[a]



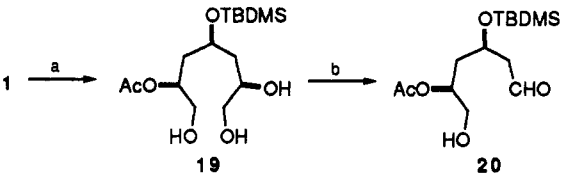

[a](a) TBDMSOTf, 2,6-lutidine, $CH_2Cl_2$; (b) mCPBA, $CH_2Cl_2$ (15, 83% from **11a**); (c) $^1O_2$, $CH_2Cl_2$, MeOH (98% from **11a**); (d) Zn, HOAc, $CH_2Cl_2$, 97%; (e) TBDMSOTf, 2,6-lutidine, $CH_2Cl_2$ (85%).

**Scheme VI**[a]




[a](a) $OsO_4$, NMO, acetone, $H_2O$; (b) dimethoxypropane, *p*-TsOH; (c) KOH, MeOH; (d) MsCl, $Et_3N$, $CH_2Cl_2$; (e) *p*-TsOH, MeOH, 55% from **6d**; (f) $(COCl)_2$, DMSO, $Et_3N$, 61%.

**Scheme VII**[a]




[a](a) $O_3$, DMS and then $NaBH_4$, $CH_2Cl_2$/MeOH (1:1), −78 °C, 90%; (b) $NaIO_4$, $SiO_2$, $CH_2Cl_2$, rt, 95%.

Compounds 15, 16, and 18 are appropriate precursors for the production of various deoxy hexoses and higher sugars. The utilization of these and related intermediates in the synthesis of such targets will be described in future publications. These syntheses are made possible by use of selective ring opening reactions such as those described in the section 4 and utilized in specific examples in section 5.

**4. Studies on the Regioselective Ring Opening Reactions.** The first possibility investigated was ozonolysis, followed by reductive workup, of the direct enzyme product 1 leading to the triol 19. Subsequent reaction with silica-gel-supported $NaIO_4$ gave aldehyde 20 (a2,4-dideoxy hexose in protected form) (Scheme VII).[46]

The second procedure for regioselective ring opening started with reduction of the enone 11d with $Et_3SiH$ in the presence of Wilkinson's catalyst[47] which led to the silyl enol 21 in excellent yield. Ozonolysis of enol 21, followed by reductive workup (DMS) and esterification with diazomethane gave aldehyde ester 22 in very good yield (Scheme VIII).

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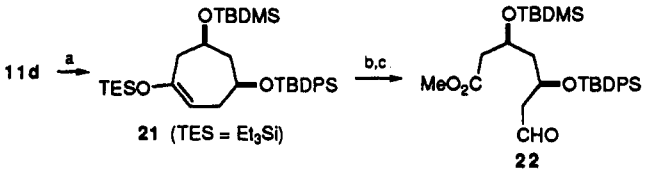
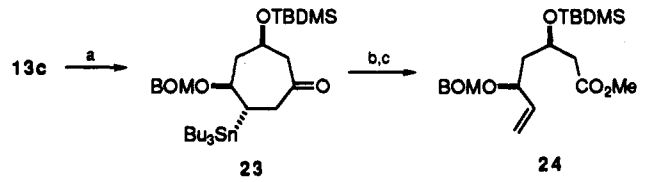
**Scheme VIII**[a]




[a](a) $Et_3SiH$, $Rh(Ph_3P)_3Cl$, 50 °C, 96%; (b) $O_3$, $CH_2Cl_2$/MeOH (1:1), −78 °C, and then DMS; (c) $CH_2N_2$, $Et_2O$, 94% from **21**.

**Scheme IX**[a]




[a](a) See ref 39; (b) mCPBA, $NaHCO_3$, $CH_2Cl_2$; (c) $CH_2N_2$, $Et_2O$, 65% from **23**.

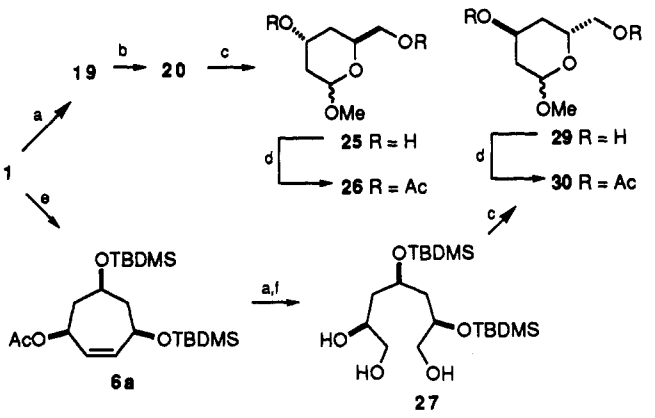
Pyranose ring systems should be easily formed from this compound by either acidic deprotection of the hydroxy group followed by *in situ* trapping formed product as a methyl glycoside or by selective reduction ($NaBH_4$) of the aldehyde functionality and deprotection followed by δ-lactone formation.

Our recently developed tin-directed Baeyer–Villiger reaction[48] provided another attractive method for the regioselective opening of the ring system. Conjugate addition of the tributylstannyl group to enone **13c** using the higher order cuprate developed by Lipshutz,[49] followed by treatment with 3-chloroperoxybenzoic acid in dichloromethane overnight, resulted in an oxidative fragmentation to give an olefinic carboxylic acid isolated as its methyl ester (**24**) (Scheme IX).

**5. Synthesis of 2,4-Dideoxy Hexoses.** To demonstrate the utility of these intermediates for the synthesis of carbohydrates, we have transformed enzyme asymmetrization products into methyl 2,4-dideoxy-*erythro*- and -*threo*-hexopyranosides[50–55] in both L and D forms.

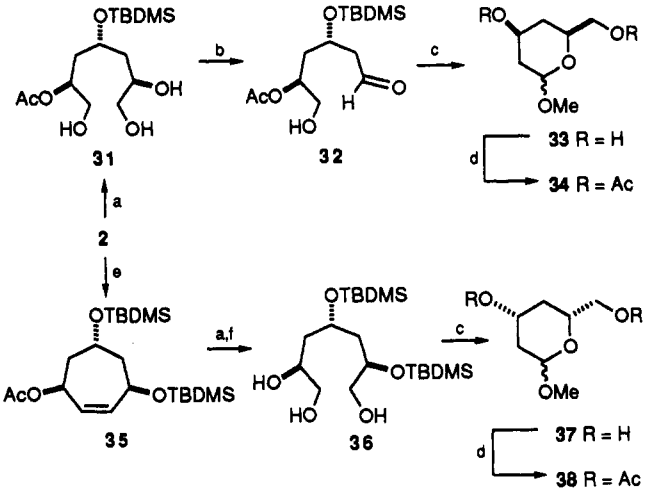
Ozonolysis of acetate **1** in methanol/dichloromethane (1:1) at −78 °C followed by reductive workup with DMS and sodium borohydride gave triol **19**. A minor product resulting from acyl migration to the primary vicinal hydroxyl group was observed. This phenomena occurred in all subsequent ozonolysis reactions. The triol was treated with silica-gel-supported[46] $NaIO_4$ in dichloromethane to give aldehyde **20**. Deprotection of the acetate and silyl group with Dowex acidic resin in methanol led to methyl 2,4-dideoxy-D-*erythro*-hexopyranoside (**25**) in 70% yield as a mixture of α and β anomers. The free hydroxyl groups were acetylated upon treatment with acetic anhydride and DMAP in pyridine to give methyl 3,6-di-*O*-acetyl-2,4-dideoxy-D-*erythro*-hexopyranoside **26** as a 2:1 mixture (by HPLC) of α and β anomers, which were separable by column chromatography (Scheme X).

**Scheme X**[a]




[a](a) $O_3$, DMS and then $NaBH_4$, $CH_2Cl_2$/MeOH (1:1), −78 °C, 90%; (b) $NaIO_4$, $SiO_2$, $CH_2Cl_2$, rt, 95%; (c) Dowex, MeOH, rt, 75%; (d) $Ac_2O$, pyridine, DMAP cat., $CH_2Cl_2$, rt, 95%; (e) TBSCl, imidazole, DMF, 96%; (f) KOH, MeOH, 75% from **6a**.

**Scheme XI**[a]




[a](a) $O_3$, DMS and then $NaBH_4$, $CH_2Cl_2$/MeOH (1:1), −78 °C, 76%; (b) $NaIO_4$, $SiO_2$, $CH_2Cl_2$, rt; (c) Dowex, MeOH, rt, 68% from **31**; (d) $Ac_2O$, pyridine, DMAP cat., $CH_2Cl_2$, rt, 82%; (e) TBSCl, imidazole, DMF, 93%; (f) KOH, MeOH, 62% from **35**.

The L-hexopyranoside series was synthesized by silylation of **1** followed by ozonolysis and reductive workup to give triol **27** as above (Scheme X). Oxidative cleavage with silica-gel-supported $NaIO_4$ in dichloromethane gave aldehyde **28**. Removal of the silyl groups with Dowex acidic resin in methanol gave methyl 2,4-dideoxy-L-*erythro*-hexopyranoside (**29**) as a mixture of anomers. Acetylation of the free hydroxyl provided methyl 3,6-di-*O*-acetyl-2,4-dideoxy-L-*erythro*-hexopyranoside (**30**) in a 1:2 ratio (by HPLC) of α and β anomers, which were separable by column chromatography.

The *threo* series of sugars was approached from acetate **2** in much the same manner as the *erythro* series (Scheme XI). Compound **2** was oxidatively cleaved with ozone followed by reductive workup to produce triol **31**. The vicinal diol was oxidatively cleaved using silica-gel-supported $NaIO_4$ in dichloromethane affording aldehyde **32**. The hydroxyl protecting groups were cleaved upon treatment with Dowex acidic resin in methanol to produce methyl 2,4-dideoxy-D-*threo*-hexopyranoside (**33**) as a

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mixture of anomers. Acetylation gave methyl 3,6-di-O-acetyl-2,4-dideoxy-D-*threo*-hexopyranoside (**34**) in a 5:1 mixture of $\alpha$ and $\beta$ anomers which were separable by column chromatography.

Silylation of acetate **2** followed by ozonolysis and reductive workup to give triol **36** as above (Scheme XI). Oxidative cleavage with silica-gel-supported $NaIO_4$ in methylene chloride gave aldehyde which after silyl groups removal with Dowex acidic resin in methanol gave methyl 2,4-dideoxy-L-*threo*-hexopyranoside (**37**) as a mixture of anomers. Acetylation of the free hydroxyl group provided methyl 3,6-di-*O*-acetyl-2,4-dideoxy-L-*threo*-hexopyranoside (**38**) in a 1:6 mixture of $\alpha$ and $\beta$ anomers which were separable by column chromatography.

## Conclusions

Enantio- and diastereoselective transformations of cycloheptatriene afforded enantiopure acetates **1** and **2**. Selective oxidations of the seven-membered ring systems followed by regioselective ring openings led to several direct precursors of hexoses and heptoses. The synthesis of all possible methyl 2,4-dideoxyhexopyranosides testifies to the versatility of methodology herein presented.

## Experimental Section

$^1H$ NMR (300 MHz) and $^{13}C$ NMR (75 MHz) spectra were recorded on a GE QE-300 spectrometer with $CDCl_3$ as the solvent and internal standard unless otherwise stated. Infrared spectra were recorded on a Nicloet 20D-FT spectrometer. Optical rotations were determined with a Perkin-Elmer 241 MC polarimeter. All chromatographic separations were carried out with Merck Kieselgel (230–400 mesh) and were monitored by TLC analyses, performed on Merck DC Alufolien Kieselgel 60F-254. Yields are reported for chromatographically pure compounds. Amano PS-30 lipase was obtained from the Amano International Enzyme Co., Troy, VA. Acetate **1** was synthesized according to the literature procedure.[27b]

**(1*R*,4*S*,6*R*)-4-Acetoxy-6-[(*tert*-butyldimethylsilyl)oxy]-2-cyclohepten-1-ol (2).** Diol **8** (2.198 g, 8.51 mmol) was taken up in isopropenyl acetate (250 mL) and to this solution was added Amano P-30 lipase (8.0 g) and the reaction mixture stirred at 50 °C for 168 h. The enzyme was filtered off and the solvent removed *in vacuo*. Purification of the residue using column chromatography (2:1; petroleum ether/ethyl acetate) yielded monoacetate **2** (2.394 g, 7.97 mmol, 94% yield) as a clear oil. $[\alpha]^{25}_D$ +4.1° (*c* 1.0, $CHCl_3$); IR (neat) 3430, 2931, 2859, 1743, 1372, 1243, 1047, 1031, 838 $cm^{-1}$; $^1H$ NMR $\delta$ 5.81–5.68 (m, 2H), 5.63–5.55 (m, 1H), 4.85–4.76 (m, 1H), 4.24 (ddd, J = 7.5, 5.0, 2.0 Hz, 1H), 2.41 (s, 3H), 1.98–1.86 (m, 2H), 1.82–1.72 (m, 2H), 0.91 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H); $^{13}C$ NMR $\delta$ 170.1, 136.9, 131.7, 69.0, 66.7, 65.8, 43.8, 40.0, 25.6, 21.3, 18.0, –4.9. Anal. Calcd for $C_{15}H_{28}O_4Si$: C, 59.96; H, 9.39. Found: C, 59.93; H, 9.57.

**(3*S*,5*S*,7*R*)-3-Acetoxy-5,7-bis-[(*tert*-butyldimethylsilyl)-oxy]cycloheptene (6a).** Acetate **1** (3.00 g, 10 mmol) was dissolved in DMF (20 mL). Imidazole (884 mg, 13 mmol) was added, followed by *tert*-butyldimethylsilyl chloride (1.80 g, 12 mmol). The reaction mixture was stirred at room temperature for 2 h then 0.1 N HCl (100 mL) and diethyl ether (100 mL) were added. After separation the water layer was extracted with diethyl ether (2 × 50 mL). Combined organics were washed with saturated $NaHCO_3$ (2 × 50 mL) and dried ($MgSO_4$). Evaporation of solvents, followed by coevaporation with toluene gave product **6a** (3.97 g, 96% yield), which was purified by flash chromatography (hexane/ethyl acetate; 95:5). **6a**: oil, $[\alpha]^{25}_D$ +13.9° (*c* 1.5, $CHCl_3$); IR ($CHCl_3$) 2932, 2885, 2858, 1733, 1470, 1461, 1373, 1258, 1249, 1064 $cm^{-1}$; $^1H$ NMR $\delta$ 5.69 (m, 1H), 5.50 (m, 1H), 5.21 (dd, *J* = 11.5, 2.5 Hz, 1H), 4.18 (bd, *J* = 11.0 Hz, 1H), 3.83 (dddd, *J* = 11.0, 11.0, 4.0, 4.0 Hz, 1H), 2.05 (s, 3H), 2.05–1.90 (m, 2H), 1.72 (m, 2H), 0.89 (s, 9H), 0.88 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H), 0.06 (s, 6H); $^{13}C$ NMR $\delta$ 170.1, 137.6, 129.7, 69.0, 68.8, 67.4, 46.5, 42.1, 25.8, 21.2, 18.1, 18.0, 0.9, –4.8, –4.9; HRMS *m/e* calcd for $C_{17}H_{33}Si_2O_4$ (M – $C_4H_9$) 357.1917, found 357.1920.

**(3*S*,5*S*,7*R*)-3-Acetoxy-7-(benzoyloxy)-5-[(*tert*-butyldimethylsilyl)oxy]cycloheptene (6b).** Acetate **1** (300 mg, 1 mmol) was dissolved in dichloromethane (10 mL). Pyridine (158 mg, 161 $\mu$L, 2 mmol) was added followed by benzoyl chloride (210 mg, 173 $\mu$L, 1.5 mmol). A catalytic amount of 4-(dimethylamino)-pyridine (12 mg, 0.1 mmol) was added and the reaction mixture was stirred at room temperature for 10 h. Then 0.1 N HCl (50 mL) and diethyl ether (50 mL) were added. After separation the water layer was extracted with diethyl ether (2 × 25 mL). Combined organics were washed with saturated $NaHCO_3$ (2 × 50 mL), dried ($MgSO_4$), and evaporated. The oily product was purified by flash chromatography (hexane/ethyl acetate; 97:3 to 95:5) to give 380 mg of acetate **6b** (94% yield) as an oil: $[\alpha]^{25}_D$ +13.2° (*c* 1.2, $CHCl_3$); IR ($CHCl_3$) 2955, 2931, 1742, 1722, 1273, 1240, 1094, 836 $cm^{-1}$; $^1H$ NMR $\delta$ 8.06 (m, 2H), 7.55 (m, 1H), 7.43 (m, 2H), 5.75 (m, 2H), 5.53 (bd, *J* = 12.0 Hz, 1H), 5.33 (bd, *J* = 11.0 Hz, 1H), 4.06 (m, 1H), 2.24–2.06 (m, 2H), 2.08 (s, 3H), 1.92–1.72 (m, 2H), 0.86 (s, 9H); $^{13}C$ NMR $\delta$ 170.0, 165.5, 133.0, 132.8, 132.1, 131.8, 131.7, 130.1, 129.6, 128.3, 102.2, 69.3, 69.0, 68.9, 68.2, 42.1, 42.0, 25.7, 21.2, 18.0, –4.8. Anal. Calcd for $C_{22}H_{32}O_5Si$: C 65.31; H 7.97. Found: C 65.51; H 8.18.

**(3*S*,5*S*,7*R*)-3-Acetoxy-7-[(benzoyloxy)methoxy]-5-[(*tert*-butyldimethylsilyl)oxy]cycloheptene (6c).** Acetate **1** (3.00 g, 10 mmol) was dissolved in dichloromethane (20 mL). Diisopropylethylamine (3.88 g, 5.21 mL, 30 mmol) was added, followed by benzyl chloromethyl ether (60% pure, 3.90 g, 3.46 mL, 15 mmol). The reaction mixture was stirred at room temperature for 24 h and then 0.1 N HCl (100 mL) and diethyl ether (100 mL) were added. After separation the water layer was extracted with diethyl ether (2 × 50 mL). Combined organics were washed with saturated $NaHCO_3$ (2 × 50 mL) and dried ($MgSO_4$). Evaporation of solvents gave an oily product which was purified by flash chromatography (hexane/ethyl acetate; 95:5 to 9:1) to give acetate **6c** (3.19 g, 76% yield) as an oil: $[\alpha]^{25}_D$ +20.5° (*c* 1.3, $CHCl_3$); IR (neat) 2925, 1738, 1242, 1090, 1040, 837 $cm^{-1}$; $^1H$ NMR $\delta$ 7.40–7.29 (m, 5H), 5.79 (m, 1H), 5.62 (m, 1H), 5.22 (m, 1H), 4.81 (s, 2H), 4.63 (d, *J* = 2.1 Hz, 2H), 4.26 (m, 1H), 3.91 (m, 1H), 2.08 (s, 3H), 2.17–2.00 (m, 2H), 1.73–1.60 (m, 2H), 0.98 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H); $^{13}C$ NMR $\delta$ 170.1, 137.5, 134.1, 131.5, 128.4, 127.9, 127.8, 92.7, 70.8, 69.5, 68.9, 42.8, 42.0, 25.7, 21.2, 18.0, –4.8. Anal. Calcd for $C_{23}H_{36}O_5Si$: C, 65.67; H, 8.63. Found: C, 65.84; H, 8.89.

**(3*S*,5*S*,7*R*)-3-Acetoxy-5-[(*tert*-butyldimethylsilyl)oxy]-7-[(*tert*-butyldiphenylsilyl)oxy]cycloheptene (6d).** Acetate **1** (3.00 g, 10 mmol) was dissolved in DMF (20 mL). Imidazole (884 mg, 13 mmol) was added, followed by *tert*-butyldiphenylsilyl chloride (3.01 g, 2.81 mL, 11 mmol). The reaction mixture was stirred at room temperature for 8 h and then 0.1 N HCl (100 mL) and diethyl ether (100 mL) were added. After separation the water layer was extracted with diethyl ether (2 × 50 mL). Combined organics were washed with saturated $NaHCO_3$ (2 × 50 mL) and dried ($MgSO_4$). Evaporation of solvents gave an oily product which was purified by flash chromatography (hexane/ethyl acetate; 97:3) to give acetate **6d** (5.24 g, 97 % yield) as an oil: $[\alpha]^{25}_D$ –1.5° (*c* 0.9, $CHCl_3$); IR (neat) 2955, 2930.9, 2858, 1740, 1428, 1370, 1112, 1070, 1059, 837 $cm^{-1}$; $^1H$ NMR $\delta$ 7.74 (m, 4H), 7.49–7.37 (m 6H), 5.92 (bd, *J* = 12.0 Hz, 1H), 5.55 (ddd, *J* = 12.0, 2.8, 2.6 Hz, 1H), 5.08 (dd, *J* = 11.3, 2.1 Hz, 1H), 4.31 (dd, *J* = 11.0, 1.9 Hz, 1H), 3.60 (dddd, *J* = 10.7, 10.6, 3.5, 3.4 Hz, 1H), 2.06 (s, 3H), 1.95 (bdd, *J* = 15.2, 13.2 Hz, 2H), 1.75 (m, 1H), 1.61 (m, 1H), 1.12 (s, 9H), 0.84 (s, 9H), –0.05 (s, 3H); –0.07 (s, 3H); $^{13}C$ NMR $\delta$ 170.3, 137.4, 135.9, 134.1, 133.7, 129.9, 129.8, 127.9, 69.1, 68.6, 68.3, 46.2, 42.1, 27.1, 25.9, 21.4, 19.3, 18.1, –4.6, –4.7. Anal. Calcd for $C_{31}H_{48}O_4Si_2$: C, 68.84; H, 8.95. Found: C, 69.07; H, 8.82.

***meso*-(1*R*,4*R*,6*R*)-3,6-Diacetoxy-4-cyclohepten-1-ol (7).** 3,5-Cycloheptadienol (**3**) (165 mg, 1.5 mmol), palladium acetate (16.8 mg, 0.075 mmol), lithium acetate dihydrate (765 mg, 7.5 mmol), manganese(IV) oxide (150 mg, 1.7 mmol), and *p*-benzoquinone (32 mg, 0.3 mmol) were taken up in acetic acid (2.5 mL) and stirred at room temperature for 41 h. The reaction mixture was then poured into a saturated sodium chloride solution (20 mL) and extracted with pentane (3 × 25 mL) and with diethyl ether (2 × 30 mL). The organic layers were combined, dried over

magnesium sulfate, filtered, and concentrated *in vacuo*. Purification of the residue using column chromatography (1:1, hexane/ethyl acetate) yielded the corresponding diacetate **7** (257 mg, 1.126 mmol, 75%) as a clear oil: IR (neat) 3448, 2936, 1744, 1368, 1240, 1024 $cm^{-1}$; $^1H$ NMR $\delta$ 5.70–5.63 (m, 4H), 4.24 (br s, 1H), 3.25 (br s, 1H), 2.01–1.82 (m, 4H), 1.98 (s, 6H); $^{13}C$ NMR $\delta$ 170.2, 132.6, 68.4, 65.1, 39.0, 21.0. Anal. Calcd for $C_{11}H_{16}O_5$: C, 57.89; H, 7.07. Found: C, 57.77; H, 7.07.

***meso*-(1*R*,4*R*,6*R*)-6-[(*tert*-Butyldimethylsilyl)oxy]-2-cycloheptene-1,4-diol (8).** Diacetate **7** (2.216 g, 9.71 mmol), *tert*-butyldimethylsilyl chloride (1.743 g, 11.57 mmol), and imidazole (1.64 g, 24.1 mmol) were dissolved in DMF (5 mL) and stirred at room temperature overnight. The reaction mixture was then poured into ethyl acetate (50 mL) and washed with water (3 × 25 mL). The organic layer was dried over magnesium sulfate, filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (10:1, petroleum ether/ethyl acetate) yielded the corresponding diacetate (3.4 g) as a clear oil: IR (neat) 2944, 2912, 2838, 1740, 1364, 1228, 1090, 1050, 850, 838 $cm^{-1}$; $^1H$ NMR $\delta$ 5.79–5.71 (m, 2H), 5.61 (br s, 2H), 4.25–4.16 (m, 1H), 1.98 (s, 6H), 1.98–1.86 (m, 2H), 1.79–1.69 (m, 2H), 0.87 (s, 9H), 0.03 (s, 6H); $^{13}C$ NMR $\delta$ 169.6, 132.6, 68.8, 66.3, 40.0, 25.6, 21.1, 17.9, -5.2. Anal. Calcd for $C_{17}H_{30}O_5Si$: C, 59.62; H, 8.83. Found: C, 59.59; H, 8.63.

The above diacetate (3.4 g) was taken up in methanol to which powdered potassium hydroxide (555 mg, 9.90 mmol) was added. After stirring for *ca.* 15 min the solvent was removed *in vacuo* and the residue was dissolved in ethyl acetate and washed with water. The organic layer was dried over magnesium sulfate, filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (1:1, petroleum ether/ethyl acetate) yielded the diol **8** (2.2 g, 8.51 mmol, 88% from **7**) as a white solid (mp 165–166 °C): IR (KBr pellet) 3263, 2927, 1471, 1381, 1341, 1252, 1086, 1049, 837 $cm^{-1}$; $^1H$ NMR ($CD_3OD$) $\delta$ 5.66 (s, 2H), 4.65 (br d, $J$ = 11.0 Hz, 2H), 4.24 (br s, 1H), 1.96-1.84 (m, 2H), 1.66 (dd, $J$ = 12.0, 12.0 Hz, 2H), 0.93 (s, 9H), 0.13 (s, 6H); $^{13}C$ NMR $\delta$ 135.8, 67.5, 65.0, 43.2, 25.0, 17.6, -6.1. Anal. Calcd for $C_{13}H_{26}O_3Si$: C, 60.42; H, 10.14. Found: C, 60.36; H, 9.98.

**(3*S*,5*R*,7*R*)-3-Acetoxy-7-(benzoyloxy)-5-[(*tert*-butyldimethylsilyl)oxy]cycloheptene (9).** Alcohol **2** (570 mg, 1.90 mmol) was dissolved in pyridine (0.5 mL). Benzoyl chloride (0.33 mL, 2.84 mmol) was added dropwise, followed by a catalytic amount of 4-(dimethylamino)pyridine. The reaction mixture was stirred at room temperature for 14 h and then poured into ethyl actate (15 mL) and washed with saturated ammonium chloride solution (2 × 10 mL) and with brine (10 mL). The organic layer was dried over magnesium sulfate and filtered and the solvent removed *in vacuo*. Purification of the residue by column chromatography (2:1, petroleum ether/ethyl acetate) yielded benzoate **9** (740 mg, 1.83 mmol, 96%) as a clear oil: $[\alpha]^{25}_D$ +10.3° (*c* 1.0, $CHCl_3$); IR (neat) 2954, 2930, 2858, 1744, 1723, 1273, 1241, 1119, 1027, 838 $cm^{-1}$; $^1H$ NMR $\delta$ 8.07–8.00 (m, 2H), 7.58–7.50 (m, 1H), 7.46–7.38 (m, 2H), 6.10–6.00 (m, 1H), 5.90–5.68 (m, 3H), 4.36–4.27 (m, 1H), 2.16–1.80 (m, 4H), 2.04 (s, 3H), 0.95 (s, 9H), 0.10 (s, 6H); $^{13}C$ NMR $\delta$ 169.7, 165.2, 132.9, 132.6, 130.4, 129.5, 128.2, 69.4, 68.9, 66.4, 40.3, 25.7, 21.2, 18.0, -5.1, -5.2. Anal. Calcd for $C_{22}H_{32}O_5Si$: C, 65.25; H, 7.97. Found: C, 65.25; H, 7.88.

**(3*S*,6*R*)-3-Acetoxy-6-(benzoyloxy)-4-cyclohepten-1-one (10).** *tert*-Butyldimethylsilyl ether **6b** (124 mg, 0.307 mmol) was taken up in THF (5 mL) and cooled to 0 °C. 1 M solution of tetrabutylammonium fluoride (0.38 mL, 0.38 mmol) was added to the reaction mixture which was allowed to warm to room temperature over 1.5 h. The reaction mixture was poured into ethyl acetate and washed twice with water and once with brine. Purification of the residue by column chromatography (2:1, petroleum ether/ethyl acetate) yielded the corresponding alcohol (80 mg, 0.276 mmol, 90%), which was taken up in dichloromethane (15 mL) along with crushed 4-Å molecular sieves (500 mg) and pyridinium chlorochromate (PCC) (223 mg, 1.033 mmol). The reaction mixture was stirred for 2.5 h, filtered through a short pad of silica gel, and eluted with diethyl ether. Purification of the residue obtained after removal of the solvent *in vacuo* by column chromatography (2:1, petroleum ether/ethyl acetate) yielded the ketone **10** (69 mg, 0.31 mmol, 90% yield) as a clear oil: $[\alpha]^{25}_D$ +42.4° (*c* 1.1, $CHCl_3$); IR (neat) 3066, 3039, 2975, 2930, 1742, 1718, 1374, 1271, 1238, 1110, 1026, 714 $cm^{-1}$; $^1H$ NMR $\delta$ 8.01 (d, $J$ = 7.5 Hz, 2H), 7.56 (dd, $J$ = 7.5, 7.5 Hz, 1H), 7.43 (dd, $J$ = 7.5, 7.5 Hz, 2H), 6.03 (dd, $J$ = 12.0, 3.5 Hz, 1H), 5.93 (dd, $J$ = 12.0, 3.5 Hz, 1H), 5.93–5.86 (m, 1H), 5.76–5.67 (m, 1H), 3.08–2.92 (m, 4H), 2.07 (s, 3H); $^{13}C$ NMR $\delta$ 203.7, 169.2, 165.2, 133.3, 131.7, 131.3, 129.6, 129.4, 128.4, 67.2, 66.7, 47.8, 47.7, 20.9. Anal. Calcd for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found: C, 66.51; H, 5.59.

**(4*R*,6*S*)-Bis-[(*tert*-butyldimethylsilyl)oxy]-2-cyclohepten-1-one (11a) Procedure I.** A solution of acetate **6a** (2.07 g, 5 mmol) in methanol (20 mL) was treated with KOH (56 mg, 1.0 mmol) and stirred 1 h. Diethyl ether (200 mL) and water (200 mL) were added. The aqueous layer was extracted with diethyl ether (50 mL), and the combined organics were washed with water (50 mL) and brine (50 mL) and dried ($MgSO_4$). Evaporation of solvents gave a colorless, solid product which was dissolved in dichloromethane (50 mL). Crushed molecular sieves (4-Å, ca. 5 g) and pyridinium dichromate (3.76 g, 10 mmol), were added and the reaction mixture was stirred for 6 h. Hexane and ethyl acetate (9:1, 300 mL) were added, and the reaction mixture was filtered through a pad of Celite. Removal of the solvent under reduced pressure gave a brown oil which was chromatographed on silica gel (hexane/ethyl acetate, 8:2) to give (**11a**) (948.5 mg, 96% yield) as a colorless oil: $[\alpha]^{25}_D$ +54.5° (*c* 0.9, $CHCl_3$); IR ($CCl_4$) 2957, 2930, 2859, 1680, 1472, 1258 $cm^{-1}$; $^1H$ NMR $\delta$ 6.59 (d, $J$ = 12.3 Hz, 1H), 5.93 (dd, $J$ = 12.3, 2.1 Hz, 1H), 4.50 (m, 1H), 4.20 (m, 1H), 2.81 (dd, $J$ = 15.0, 7.2 Hz, 1H), 2.69 (dd, $J$ = 15.1, 2.8 Hz, 1H), 2.35 (m, 1H), 2.02 (ddd, $J$ = 16.2, 11.0, 6.7 Hz, 1H), 0.91 (s, 9H), 0.86 (s, 9H), 0.10 (s, 3H), 0.07 (s, 6H), 0.05 (s, 3H); $^{13}C$ NMR $\delta$ 198.7, 152.4, 130.1, 68.4, 64.2, 51.9, 46.8, 25.7, 25.6, 18.1, 17.9, 0.9, -4.8, -4.9; HRMS *m/e* calcd for $C_{15}H_{29}Si_2O_3$ (M - $C_4H_9$) 313.1655, found 313.1659.

**(4*R*,6*S*)-4-(Benzoyloxy)-6-[(*tert*-butyldimethylsilyl)oxy]-2-cyclohepten-1-one (11b).** Acetate **6b** (404 mg, 1 mmol) was dissolved in saturated solution of ammonia in methanol (20 mL) and left for 6 h at room temperature. The solvent was evaporated in vacuo, dichloromethane (10 mL) was added, and procedure I was followed to give 306 mg of enone **11b** (85% yield) as a white solid: mp 72 °C; $[\alpha]^{25}_D$ +47.3° (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) 2968, 2940, 1734, 1721, 1716, 1405, 1271, 1240, 1099, 879 $cm^{-1}$; $^1H$ NMR $\delta$ 8.13–8.03 (m, 2H), 7.65–7.55 (m, 1H), 7.55–7.41 (m, 2H), 6.70 (dd, $J$ = 12.4, 1.1 Hz, 1H), 6.10 (d, $J$ = 12.4 Hz, 1H), 5.82 (m, 1H), 4.38 (m, 1H), 2.87 (m, 1H), 2.60 (m, 1H), 2.18 (m, 1H), 0.86 (s, 9H), 0.08 (s, 3H), 0.06 (s, 3H); $^{13}C$ NMR $\delta$ 198.8, 167.0, 146.9, 133.6, 132.2, 129.9, 128.6, 70.0, 64.0, 51.9, 42.9, 25.8, 18.5, -4.8. Anal. Calcd for $C_{20}H_{28}O_4Si$: C, 66.63; H, 7.83. Found: C, 66.70; H, 7.99.

**(4*R*,6*S*)-4-[(Benzyloxy)methoxy]-6-(*tert*-butyldimethylsilyloxy)-2-cyclohepten-1-one (11c).** Using procedure I (see **11a** above), acetate **6c** (4.21 g, 10 mmol) was transformed into enone **11c** (3.31 g, 86% yield): $[\alpha]^{25}_D$ +44.0° (*c* 0.8, $CHCl_3$); IR ($CDCl_3$) 2957, 2860, 1673, 1259 $cm^{-1}$; $^1H$ NMR $\delta$ 7.34 (s, 5H), 6.67 (dd, $J$ = 12.0, 1.9 Hz, 1H), 5.99 (dd, $J$ = 12.0, 2.0 Hz, 1H), 4.83 (s, 2H), 4.66 (s, 2H), 4.49 (dt, $J$ = 11.0, 2.0 Hz, 1H), 4.23 (tt, $J$ = 8.6, 2.0 Hz, 1H), 2.79 (dd, $J$ = 15.0, 6.0 Hz, 1H), 2.67 (dd, $J$ = 15.0, 3.0 Hz, 1H), 2.48 (m, 1H), 1.98 (m, 1H), 0.87 (s, 9H), 0.11 (s, 6H); $^{13}C$ NMR $\delta$ 198.7, 149.9, 137.4, 131.6, 128.7, 128.0, 93.1, 72.3, 70.1, 64.3, 51.7, 43,5, 25.8, 18.1, -4.8. Anal. Calcd for $C_{21}H_{32}SiO_4$: C, 66.98; H, 8.57. Found: C, 66.85; H, 8.81.

**(4*R*,6*S*)-6-[(*tert*-Butyldimethylsilyl)oxy]-4-[(*tert*-butyldiphenylsilyl)oxy]-2-cyclohepten-1-one (11d).** Using procedure I, acetate **6d** (5.40 g, 10 mmol) was transformed into enone **11d** (4.54 g, 92% yield). **11d**: oil, $[\alpha]^{25}_D$ +26.1° (*c* 1.1, $CHCl_3$); IR (neat) 2956, 2931, 2858, 1677, 1472, 1428, 1257, 1112, 1082, 836 $cm^{-1}$; $^1H$ NMR $\delta$ 7.73-7.60 (m, 4H), 7.58–7.40 (m, 6H), 6.75 (bd, $J$ = 12.3 Hz, 1H), 5.91 (bd, $J$ = 12.3 Hz, 1H), 4.52 (m, 1H), 3.90 (m, 1H), 2.70 (dd, $J$ = 14.8, 6.6 Hz, 1H), 2.48 (dd, $J$ = 14.8, 2.9 Hz, 1H), 2.25 (m, 1H), 2.05 (m, 1H), 1.11 (s, 9H), 0.82 (s, 9H), -0.05 (s, 3H), -0.06 (s, 3H); $^{13}C$ NMR $\delta$ 198.8, 152.4, 135.7, 130.1, 130.0, 127.8, 69.1, 64.0, 51.8, 46.5, 26.8, 25.6, 19.0, 17.8, -4.9, -5.1. Anal. Calcd for $C_{29}H_{42}O_3Si_2$: C, 70.39; H, 8.56. Found: C, 70.31; H, 8.56.

**(4*S*,6*R*)-6-[(*tert*-Butyldimethylsilyl)oxy]-4-hydroxy-2-cyclohepten-1-one (12).** A solution of acetate enone **1** (948 mg, 3.17 mmol) in 2-isopropanol (10 mL) was treated with titanium isopropoxide (416 $\mu$L, 1.39 mmol) and heated to 60 °C under an atmosphere of dry argon for 3.5 h. After cooling to room temperature, the solution was diluted with dichloromethane (50

mL) and washed with 1 N HCl (50 mL) followed by saturated sodium bicarbonate (50 mL). The organics were dried over sodium sulfate and solvent removed under reduced pressure to give a pale oil which was chromatographed on silica gel eluting with 30% EtOAc/petroleum ether to give **12** (685 mg, 84%) as a clear oil: IR ($CDCl_3$) 2963, 2871, 1672, 1257 $cm^{-1}$; $^1H$ NMR $\delta$ 6.62 (dd, $J$ = 12.5, 4.0 Hz, 1H), 5.93 (d, $J$ = 12.5 Hz, 1H), 4.47 (m, 1H), 4.27 (tt, $J$ = 9.0, 4.0 Hz, 1H), 3.67 (d, $J$ = 7.0 Hz, 1H), 2.80 (dd, $J$ = 14.5, 6.0 Hz, 1H), 2.67 (dd, $J$ = 14.5, 3.0 Hz, 1H), 2.33 (dt, $J$ = 14.0, 4.0 Hz, 1H), 2.17 (dt, $J$ = 14.0, 7.0 Hz, 1H), 0.91 (s, 9H), 0.13 (s, 3H), 0.09 (s, 3H); $^{13}C$ NMR $\delta$ 199.7, 149.7, 130.6, 67.9, 65.4, 52.2, 44.0, 25.7, 18.0, -4.9.

**(4*S*,6*R*)-4,6-Bis-(*tert*-butyldimethylsilyloxy]-2-cyclohepten-1-one (13a).** A solution of alcohol enone **12** (104 mg, 0.406 mmol) in DMF (2 mL) was treated with imidazole (52.5 mg, 0.77 mmol) and *tert*-butyldimethylchlorosilane (73.4 mg, 0.487 mmol) and stirred overnight. The solution was diluted with dichloromethane (25 mL) and washed with water (3 × 100 mL). The organics were separated and dried over sodium sulfate, and solvent was removed under reduced pressure to give a clear oil which was chromatographed on silica gel (hexane/ethyl acetate, 9:1) to give **13a** (113mg, 75%) as a low-melting waxy solid: $[\alpha]^{20}_D$ -54.7° (*c* 0.9, $CHCl_3$); IR ($CDCl_3$) 2987, 2850, 1668, 1255 $cm^{-1}$; $^1H$ NMR $\delta$ 6.60 (dd, $J$ = 12.0, 1.6 Hz, 1H), 5.94 (dd, $J$ = 12.0, 1.8 Hz, 1H), 4.51 (dt, $J$ = 8.5, 1.5 Hz, 1H), 4.20 (tt, $J$ = 9.0, 1.5 Hz, 1H), 2.81 (dd, $J$ = 15.0, 7.0 Hz, 1H), 2.70 (dd, $J$ = 15.0, 3.0 Hz, 1H), 2.35 (dt, $J$ = 13.0, 4.5 Hz, 1H), 2.05 (m, 1H), 0.92 (s, 9H), 0.84 (s, 9H), 0.13 (s, 6H), 0.06 (s, 6H); $^{13}C$ NMR $\delta$ 198.8, 152.6, 130.1, 68.4, 64.2, 51.9, 46.8, 25.7, 25.6, 18.1, 17.9, -4.8, -4.9, -4.9, -5.1. Anal. Calcd for $C_{19}H_{38}Si_2O_3$: C, 60.82; H, 10.34. Found: C, 60.51; H, 10.39.

**(4*S*,6*R*)-4-[(Benzyloxy)methoxy]-6-[(*tert*-butyldimethylsilyl)oxy]-2-cyclohepten-1-one (13c).** A solution of alcohol enone **12** (564 mg, 2.199 mmol) in dichloromethane (5 mL) was treated with diisopropylethylamine (766 $\mu$L, 4.398 mmol) followed by benzyl chloromethyl ether (459 $\mu$L, 3.299 mmol) under an atmosphere of dry argon and heated to 65 °C overnight. The solution was diluted with dichloromethane (50 mL) and washed with saturated sodium bicarbonate (25 mL). The organics were separated and dried over sodium sulfate, and solvent was removed under reduced pressure to give an orange oil which was chromatographed on silica gel (hexane/ethyl acetate, 8:2) to give **13c** (638 mg, 77% yield) as a clear oil: $[\alpha]^{20}_D$ -38.7° (c 1.0, $CHCl_3$); IR ($CDCl_3$) 2957, 2860, 1673, 1259 $cm^{-1}$; $^1H$ NMR $\delta$ 7.34 (s, 5H), 6.67 (dd, $J$ = 12.0, 1.9 Hz, 1H), 5.99 (dd, $J$ = 12.0, 2.0 Hz, 1H), 4.83 (s, 2H), 4.66 (s, 2H), 4.49 (dt, $J$ = 11.0, 2.0 Hz, 1H), 4.23 (tt, $J$ = 8.6, 2.0 Hz, 1H), 2.79 (dd, $J$ = 15.0, 6.0 Hz, 1H), 2.67 (dd, $J$ = 15.0, 3.0 Hz, 1H), 2.48 (m, 1H), 1.98 (m, 1H), 0.87 (s, 9H), 0.11 (s, 6H); $^{13}C$ NMR $\delta$ 198.7, 149.9, 137.4, 131.6, 128.7, 128.0, 93.4, 72.3, 70.1, 64.3, 51.7, 43.5, 25.8, 18.1, -4.8. Anal. Calcd for $C_{21}H_{32}SiO_4$: C, 66.98; H, 8.57. Found: C, 67.13; H, 8.60.

**(4*S*,6*R*)-4-Acetoxy-6-[(*tert*-butyldimethylsilyl)oxy]-2-cyclohepten-1-one (13e).** A solution of acetate **2** (1.0 g, 3.33 mmol) in dichloromethane (20 mL) was treated with PDC (1.88 g, 5.00 mmol) and crushed sieves (3.0 g) and stirred for 2 h. Hexane and ethyl acetate (8:2, 250 mL) were added, and the reaction mixture was filtered through a pad of Celite and washed with another portion of hexane/ethyl acetate (8:2) mixture (2 × 50 mL). Removal of the solvent under reduced pressure gave an oil which was chromatographed on silica gel (hexane/ethyl acetate, 8:2) to give **13c** (948.5 mg, 96% yield) as a colorless oil: $[\alpha]^{20}_D$ -30.0°(c 1.0, $CHCl_3$); IR ($CDCl_3$) 2867, 1736, 1677 $cm^{-1}$; $^1H$ NMR $\delta$ 6.50 (dt, $J$ = 12.4, 1.7 Hz, 1H), 6.00 (dd, $J$ = 12.4, 1.0 Hz, 1H), 5.53 (dt, $J$ = 11.0, 1.7 Hz, 1H), 4.27 (tt, $J$ = 10.0, 5.0 Hz, 1H), 2.79 (dd, $J$ = 14.0, 4.3 Hz, 1H), 2.72 (dd, $J$ = 14.0, 4.3 Hz, 1H), 2.42 (m, 1H), 2.06 (s, 3H), 1.98 (m, 1H), 0.81 (s, 9H), 0.02 (s, 3H), 0.01 (s, 3H); $^{13}C$ NMR $\delta$ 198.2, 170.1, 146.9, 132.0, 69.5, 63.9, 51.8, 42.8, 25.7, 21.1, 18.0, -4.9. Anal. Calcd for $C_{15}H_{26}SiO_4$: C, 60.37; H, 8.78. Found: C, 60.50; H, 8.82.

**(4*R*,6*S*,7*R*)-4,6,7-Tris-[(*tert*-butyldimethylsilyl)oxy]-2-cyclohepten-1-one (15). Method A.** To the solution of enone **11a** (370 mg, 1 mmol) in dry diethyl ether (15 mL) were added triethylamine (302 mg, 418 $\mu$L, 3 mmol) followed by *tert*-butyldimethylsilyl trifluoromethanesulfonate (396 mg, 344 $\mu$L, 1.5 mmol) under argon atmosphere. After 1 h the reaction mixture was decanted. The remaining oil was washed with ethyl ether (3 × 20 mL), and combined organics were extracted with sodium bicarbonate-saturated water solution (100 mL), dried ($MgSO_4$), and evaporated. The slightly yellow, oily product **14** [$^1H$ NMR $\delta$ 5.72 (d, $J$ = 12.2 Hz, 1H), 5.42 (ddd, $J$ = 12.2, 2.0, 2.0 Hz, 1H), 5.01 (s, 1H), 4.66 (ddd, $J$ = 10.6, 3.8, 3.7 Hz, 1H), 4.53 (dd, $J$ = 11.0, 2.6 Hz, 1H), 2.33 (dd, $J$ = 23.4, 11.0 Hz, 1H), 2.05 (m, 1H), 0.93 (s, 9H), 0.91 (bs, 18H), 0.15 (s, 3H), 0.14 (s, 3H), 0.09 (s, 6H); 0.08 (s, 6H); $^{13}C$ NMR $\delta$ 145.3, 139.3, 124.7, 117.5, 68.1, 67.1, 44.8, 26.0, 25.8, 25.4, 18.3, 18.1, -4.6 (3C), -4.7 (3C)] was dissolved in pentane (10 mL) and added to a stirred slurry of *m*-chloroperoxybenzoic acid (60% pure, 344 mg, ca. 1.2 mmol) and $MgSO_4$ (ca. 0.5 g) in pentane (40 mL) cooled to -20 °C ($CCl_4$–dry ice bath, drying tube). After 5 min the cooling bath was removed and the stirring was continued for additional 20 min. Then the reaction mixture was filtered, solvent was evaporated in vacuo, and the semicrystalline product was purified by flash chromatography (hexane/ethyl acetate; 97:3) to give enone **15** (416 mg, 83% yield) as a white solid: mp 103–106 °C; $[\alpha]^{25}_D$ +54.5° (*c* 0.9, $CHCl_3$); IR ($CDCl_3$) 2958, 2935, 1742, 1267 $cm^{-1}$; $^1H$ NMR $\delta$ 6.70 (dd, $J$ = 12.2 Hz, 1H), 5.82 (ddd, $J$ = 12.2, 2.6, 1.6 Hz, 1H), 4.96 (m, 1H), 4.10 (dd, $J$ = 3.7, 1.5 Hz, 1H), 4.01 (ddd, $J$ = 7.4, 7.4, 4.0 Hz, 1H), 2.33 (m, 1H), 1.90 (ddd, $J$ = 18.4, 10.8, 7.5 Hz, 1H), 0.87 (s, 9H), 0.83 (s, 9H), 0.82 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H), 0.06 (s, 3H), 0.01 (s, 3H), 0.00 (s, 3H); $^{13}C$ NMR $\delta$ 199.4, 155.3, 126.5, 83.7, 70.0, 66.8, 46.4, 25.9, 25.7, 25.7, -4.7, -4.8, -4.9, -5.0, -5.2, -5.3. Anal. Calcd for $C_{25}H_{52}Si_3O_4$: C, 59.94; H, 10.46. Found: C, 59.68; H, 10.46.

**Method B.** To the solution of diol **16** (220 mg, 0.45 mmol) in dry dichloromethane (5 mL), 2,6-lutidine (214 mg, 2 mmol) was added followed by *tert*-butyldimethylsilyl trifluoromethanesulfonate (264 mg, 1 mmol) at -78 °C under argon atmosphere. After 5 min, the cooling bath was removed and stirring was continued for additional 15 min. Then reaction mixture was partitioned between diethyl ether (30 mL) and 0.1 N HCl (30 mL). The organic layer was washed with saturated $NaHCO_3$ (2 × 35 mL), dried ($MgSO_4$), filtered, and evaporated. The oily residue was purified by chromatography (hexane/ethyl acetate, 97:3) to yield 181 mg (85% yield) of enone **15**. All analytical data was the same as for the compound obtained via first route.

**(1*R*,7*R*,5*S*,4*R*)-2,6,7-Tris-[(tert-butyldimethylsilyl)oxy]-2-cycloheptene-1,4-diol (16).** Diene **14** (968 mg, 2 mmol) was dissolved in dichloromethane (50 mL). A catalytic amount (10 mg) of 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine (TPP) was added. The reaction mixture was cooled to 0 °C and was irradiated with a broad-band lamp while bubbling $O_2$ through the reaction mixture. When the reaction was completed (TLC, hexane/ethyl acetate, 97:3; ca. 15 min) solvent was removed and the oily residue was chromatographed (hexane/ethyl acetate, 97:3 to 95:5) to give 1.01 g (98% yield) of pure peroxide **14'**. [$^1H$ NMR $\delta$ 5.23 (dd, $J$ = 8.0, 2.0 Hz, 1H), 4.58 (d, $J$ = 7.8 Hz, 1H), 4.23 (s, 1H), 3.90 (ddd, $J$ = ddd, $J$ = 11.0, 5.1, 1.2 Hz, 1H), 3.83 (ddd, $J$ = 10.3, 5.6, 2.1 Hz, 1H), 1.95 (m, 1H), 1.49 (dd, $J$ = 22.0, 10.8 Hz, 1H), 0.93 (s, 9H), 0.87 (s, 9H), 0.86 (s, 9H), 0.24 (s, 6H), 0.07 (s, 3H), 0.06 (s, 3H), 0.05 (s, 6H); $^{13}C$ NMR $\delta$ 151.6, 96.2, 86.3, 81.0, 70.1, 68.9, 38.2, 25.8 (2C), 25.7, 18.1, 18.0, -4.2, -4.6, -4.72 (2C), -4.8 (2C)].

To a suspension of freshly activated zinc (1.0 g) in the solution of peroxide **14'** (774 mg, 1.5 mmol) in dichloromethane (50 mL) was added (ice–water bath) acetic acid (0.20 mL). When the reduction was done by TLC (hexane/ethyl acetate, 97:3) (ca. 15 min), the reaction mixture was filtered through Celite and the solvent was removed. The resulting white solid was purified by chromatography (hexane/ ethyl acetate, 95:5) to yield 750 mg (97% yield) of diol **16** as a low-melting waxy solid: $[\alpha]^{25}_D$ +14.0° (*c* 1, $CHCl_3$); IR ($CDCl_3$) 2955, 2941, 2881, 1649, 1478, 1453, 1252, 1053, 874 $cm^{-1}$; $^1H$ NMR $\delta$ 4.84 (dd, $J$ = 3.9, 0.9 Hz, 1H), 4.00 (dd, $J$ = 8.9, 3.9 Hz, 1H), 3.95 (bd, $J$ = 9.3 Hz, 1H), 3.42 (ddd, $J$ = 10.2, 10.0, 3.6 Hz, 1H), 3.32 (ddd, $J$ = 10.7, 10.5, 4.0 Hz, 1H), 2.77 (d, $J$ = 3.1 Hz, 1H), 2.73 (s, 1H), 2.21 (ddd, $J$ = 13.7, 4.0, 3.8 Hz, 1H), 1.68 (ddd, $J$ = 13.5, 10.6, 10.5 Hz, 1H), 0.93 (s, 9H), 0.89 (bs, 18H), 0.19 (s, 3H), 0.18 (s, 3H), 0.09 (bs, 9H), 0.07 (s, 3H); $^{13}C$ NMR $\delta$ 149.3, 107.6, 73.5, 72.9, 71.9, 71.1, 44.9, 25.9, 25.8, 18.3, -4.2, -4.5 (2C), -4.6, -4.7 (2C). Anal. Calcd for $C_{25}H_{54}Si_3O_5$: C, 57.86; H, 10.49. Found: C, 57.99; H, 10.38.

**(1*S*,3*R*,4*R*,5*S*,6*S*)-3-[(*tert*-Butyldiphenylsilyl)oxy]-4,5-(isopropylidenedioxy)-6-[(methylsulfonyl)oxy]cycloheptan-**

1-ol (17). To a solution of olefin 6d (836 mg, 1.55 mmol) in THF (30 mL) were added a 0.039 M solution of osmium tetroxide in THF (4.1 mL, 0.16 mmol), a 60% aqueous solution (by wt) of *N*-methylmorpholine *N*-oxide (1.55 mL), and water (0.75 mL). The reaction mixture was stirred until the starting material was no longer visible by TLC (10:1 chloroform/methanol). Sodium bisulfite (250 mg), Florisil (1 g), and magnesium sulfate (2 g) were then added about 10 min apart, and the reaction mixture was stirred for an additional h. The reaction mixture was filtered and the solvent removed *in vacuo*. The residue was then dissolved in 2,2-dimethoxypropane (25 mL) containing a catalytic amount of *p*-toluenesulfonic acid and the reaction mixture stirred overnight. Sodium bicarbonate (15 mg) was added and the solvent removed *in vacuo*. Residue was taken up in methanol and a catalytic amount of potassium hydroxide was added. The reaction mixture was stirred until the starting material disappeared as judged by TLC (2:1 hexanes/ethyl acetate). The solvent was removed *in vacuo*, the residue dissolved in diethyl ether (100 mL), and washed with water (3 × 15 mL). The organic layer was dried over magnesium sulfate and filtered and the solvent removed *in vacuo*. Purification of the residue using column chromatography (10% methanol in chloroform) yielded the corresponding alcohol as a mixture (ca. 4:1) of diastereoisomers (717 mg, 1.26 mmol, 81% from 6d). The mixture of alcohols was dissolved in dichloromethane (40 mL). Triethylamine (191 mg, 1.89 mmol) followed by methanesulfonyl chloride (0.12 mL, 1.51 mmol) were added, and the reaction mixture was stirred at room temperature for 1 h. The reaction mixture was then poured into diethyl ether (150 mL) and washed with water (2 × 20 mL) and with brine (20 mL). The organic layer was dried over magnesium sulfate and filtered and the solvent removed *in vacuo*. Purification of the residue using column chromatography (5:1, hexane/ethyl acetate) yielded (803 mg, 1.24 mmol, 98%) a mixture of diasteroisomers. This mixture was dissolved methanol (10 mL). *p*-Toluenesulfonic acid (10 mg) was added and the reaction mixture was stirred for 36 h at room temp. The reaction mixture was then poured into ethyl acetate (30 mL) and washed with a saturated sodium bicarbonate solution (2 × 10 mL). The aqueous layers were combined and extracted with ethyl acetate (10 mL). The combined organic layers were dried over magnesium sulfate and filtered and the solvent removed *in vacuo*. Purification of the residue using column chromatography (2:1 hexane/ethyl acetate) produced a convienent separation of the diastereoisomers and afforded 17 (453 mg, 0.85 mmol, 55 % from 6d) as a white solid: mp 135–136 °C; $[\alpha]^{25}_D$ +45.1° (*c* 1.1, $CHCl_3$); $^1H$ NMR δ 7.36 (dd, $J_1$ = 14.4 Hz, $J_2$ = 6.6 Hz, 4H), 7.46–7.34 (m, 6H), 4.31 (br dd, $J_1 = J_2$ = 9.9 Hz, 1H), 4.22–4.08 (m, 2H), 3.82 (dd, $J_1$ = 8.7 Hz, $J_2$ = 7.8 Hz, 1H), 3.56 (dddd, $J_1 = J_2$ = 9.0 Hz, $J_3 = J_4$ = 4.5 Hz, 1H), 3.03 (s, 3H), 2.32 (dd, $J_1$ = 13.2 Hz, $J_2$ = 4.5 Hz, 1H), 1.90–1.70 (m, 3H), 1.36 (s, 3H), 1.22 (s, 3H), 1.09 (s, 9H); $^{13}C$ NMR δ 136.1, 135.8, 133.7, 133.3, 129.9, 129.9, 127.7, 127.5, 108.3, 80.2, 79.1, 78.5, 69.8, 66.1, 41.5, 41.1, 38.6, 27.0, 26.9, 24.3, 19.2. Anal. Calcd for $C_{27}H_{38}O_7SSi$: C, 60.65; H, 7.16. Found: C, 60.71, H, 7.26. The diastereoisomer resulting from *syn-periplanar cis*-hydroxylation (106 mg, 0.19 mmol, 12%) was also isolated.

**(4*R*,5*R*,6*R*)-6-[(*tert*-Butyldiphenylsilyl)oxy]-4,5-(isopropylidenedioxy)-2-cyclohepten-1-one (18).** To a solution of oxalyl chloride (0.07 mL, 0.81 mmol) in dichloromethane (10 mL) maintained at −60 °C was added dimethyl sulfoxide (0.12 mL, 1.618 mmol) dropwise and stirred for 15 min. The above alcohol 17 (300 mg, 0.561 mmol), dissolved in dichloromethane (0.5 mL), was added dropwise and stirred for 20 min. Triethylamine (0.47 mL, 3.37 mmol) was added and stirring continued for 10 min at which time the reaction mixture was allowed to warm to room temperature. After stirring for 2 h, the reaction mixture was quenched with water, poured into diethyl ether (50 mL), and washed with water (3 × 10 mL). The organic layer was dried over magnesium sulfate and filtered and the solvent removed *in vacuo*. Purification of the residue using column chromatography (2:1 hexane/ethyl acetate) produced enone 18 (150 mg, 0.344 mmol, 61%) as a clear oil: $[\alpha]^{25}_D$ −38.3° (*c* 1.27, $CHCl_3$); IR (neat) 3074.7, 2933, 2859, 1678, 1428, 1382, 1113, 1047, 881, 822.7 $cm^{-1}$; $^1H$ NMR δ 7.70–7.61 (m, 4H), 7.49–7.34 (m, 6H), 6.39 (dd, $J_1$ = 12.3 Hz, $J_2$ = 3.6 Hz, 1H), 5.92 (d, $J$ = 12.6 Hz, 1H), 4.89–4.84 (m, 1H), 4.34 (dd $J_1 = J_2$ = 6.0 Hz, 1H), 4.17 (ddd, $J_1 = J_2$ = 6.0 Hz, $J_3$ = 0.9 Hz, 1H), 2.89 (d, $J$ = 16.2 Hz, 1H), 2.71 (dd, $J_1$ = 16.5 Hz, $J_2$ = 9.0 Hz, 1H), 1.37 (s, 3H), 1.31 (s, 3H), 1.05 (s, 9H); $^{13}C$ NMR δ 198.7, 143.2, 135.9, 133.3, 133.0, 130.5, 130.0, 129.8, 127.7, 109.5, 80.4, 74.5, 69.1, 46.9, 27.3, 26.8, 25.4, 19.2. Anal. Calcd for $C_{26}H_{32}O_4Si$: C, 71.52; H, 7.39. Found: C, 71.71; H, 7.51.

**(2*S*,4*S*,6*R*)-2-Acetoxy-4-[(*tert*-butyldimethylsilyl)oxy]-1,6,7-heptanetriol (19).** Acetate 1 (601 mg, 2 mmol) was dissolved in methanol/methylene chloride (1:1; 25 mL) mixture. Ozone/oxygen (ca. 4% wt) was bubbled at −78 °C, until saturation of the solvent (blue color). Then the solution was purged with argon (still at −78 °C) until all blue color disappeared. Dimethyl sulfide (1 mL) followed by sodium borohydride (378 mg, 10 mmol) were added, and the cooling bath was removed. After stirring at room temperature for 0.5 h, the reaction mixture was poured into a mixture of ethyl ether (100 mL) and water (150 mL). After separation of phases, the aqueous layer was extracted with ethyl ether (2 × 50 mL). The combined extracts were dried over magnesium sulfate, and solvent was removed under reduced pressure to give a clear oil which was chromatographed on silica gel eluting with 5–10% EtOAc/ petroleum ether to give 19 (604 mg, 1.80 mmol, 90% yield) as a clear oil. The second fraction (27 mg, 0.08 mmol, 4% yield) was the product of acetate migration to the primary hydroxyl. 19: Oil, $[\alpha]^{28}_D$ −2.6° (*c* 1.4, $CHCl_3$); IR (neat) 3403, 2955, 2934, 2860, 1728, 1473, 1464, 1375, 1257, 1103, 1043, 939, 837 $cm^{-1}$; $^1H$ NMR δ 4.16 (dddd, $J$ = 6.1, 6.1, 6.0, 6.0 Hz, 1H), 4.10–3.35 (m, 9H), 2.07 (s, 3H), 1.72–1.60 (m, 4H), 0.86 (s, 9H), 0.09 (s, 6H); $^{13}C$ NMR δ 171.5, 70.0, 69.5, 68.8, 67.5, 66.8, 40.1, 39.8, 25.9, 21.0, 17.9, −4.3. Anal. Calcd for $C_{15}H_{32}SiO_6$: C, 53.54; H, 9.59. Found: C, 53.19; H, 9.69.

**(3*R*,5*S*)-5-Acetoxy-3-[(*tert*-butyldimethylsilyl)oxy]-6-hydroxyhexanal (20).** Sodium periodate (400 mg, 1.87 mmol) dissolved in water (2.7 mL) was added to a stirred suspension of silica gel (3.0 g) in dichloromethane (20 mL). Triol 19 (337 mg, 1 mmol) dissolved in dichloromethane (3 mL) was added, and the reaction mixture was stirred 1 h. The reaction mixture was filtered, and the silica gel was washed with dichloromethane (2 × 30 mL) and again filtered. Combined filtrates were concentrated in vacuo to give crude aldehyde 20 (287 mg, 0.95 mmol, 95%) as a clear oil. The crude aldehyde, which existed in hemiacetal form was carried forward to derivatives 25 and 26.

**(4*R*,6*S*)-6-[(*tert*-Butyldimethylsilyl)oxy]-4-[(*tert*-butyldiphenylsilyl)oxy]-1-[(triethylsilyl)oxy]cycloheptene (21).** To the solution of enone 11b (988 mg, 2 mmol) in triethylsilane (5 mL) was added a catalytic amount of tris(triphenylphosphine)-rhodium(I) chloride (Wilkinson's catalyst) (10 mg). The reaction mixture was stirred for 10 min, under argon at ca. +70 °C. When the reaction was done by TLC (hexane/ethyl acetate, 97:3) all volatile organics were evaporated *in vacuo* and the dark oily residue was purified by chromatography (hexane/ethyl acetate, 97:3) to give 1.17 g of product 21 (96% yield) as an oil: $[\alpha]^{25}_D$ −10.9° (*c* 1.2, $CHCl_3$); IR (neat) 2955, 2932, 2878, 1653, 1473, 1458, 1254, 1113, 1064, 837 $cm^{-1}$; $^1H$ NMR δ 7.75–7.60 (m, 4H), 7.45–7.30 (m, 6H), 4.70 (dd, $J$ = 9.8, 2.1 Hz, 1H), 3.62–3.45 (m, 2H), 2.63 (ddd, $J$ = 13.6, 12.6, 1.2 Hz, 1H), 2.30–2.00 (m, 3H), 1.85–1.72 (m, 1H), 1.10 (s, 9H), 0.95 (t, $J$ = 7.8 Hz, 3H), 0.61 (q, $J$ = 7.8 Hz, 2H), 0.00 (s, 3H), −0.01 (s, 3H); $^{13}C$ NMR δ 152.0, 135.8, 134.3, 129.5, 127.5, 102.5, 69.7, 67.7, 51.9, 44.6, 34.7, 27.0, 25.8, 19.1, 18.2, 6.8, 6.6, 6.4, 4.9, −4.8–5.0. Anal. Calcd for $C_{35}H_{58}Si_3O_3$: C, 68.79; H, 9.57. Found: C, 68.74; H, 9.84.

**(3*R*,6*S*)-Methyl 3-[(*tert*-Butyldimethylsilyl)oxy]-5-[(*tert*-butyldiphenylsilyl)oxy]-7-oxoheptanoate (22).** Through the solution of silyl enol 21 (916 mg, 1.5 mmol) in methanol/dichloromethane chloride mixture (1:1, 25 mL) was bubbled ozone/oxygen (ca. 4% Wt) at −78 °C, until saturation of the reaction mixture (blue color). Then the solution was purged with argon (still at −78 °C) until all blue color disappeared. Dimethyl sulfide (620 mg, 732 μL, 10 mmol) was added and the cooling bath was removed. After stirring at room temperature for 5 h, all volatile organics were removed in vacuo, and the oily residue was redissolved in diethyl ether (20 mL). Diazomethane solution (in ethyl ether, ca. 1 mL of 1.5 M solution) was added until a pale yellow color persisted longer than 1 min. Then solvent was evaporated in vacuo, and the crude oily product was purified by flash chromatography (hexane/ethyl acetate, 9:1) to afford aldehyde ester 22 (764 mg, 1.41 mmol, 94% yield) as an oil: $[\alpha]^{25}_D$ −3.8° (*c*, 1.7 $CHCl_3$); IR (neat) 3450, 2990, 2950, 1757, 1728, 1453,

1185, 1102, 860 cm$^{-1}$; $^1$H NMR $\delta$ 9.68 (bs, 1H), 7.72–7.65 (m, 4H), 7.48-7.30 (m, 6H), 4.34 (dddd, $J_1 = J_2 = J_3 = J_4 = 5.8$ Hz, 1H), 4.23 (dddd, $J_1 = J_2 = J_3 = J_4 = 5.8$ Hz, 1H), 3.64 (s, 3H), 2.55 (dddd, $J = 1.5, 5.2, 16.5, 21.6$ Hz, 1H), 2.26 (m, 1H), 1.97–1.87 (m, 1H), 1.87–1.73 (m, 1H), 1.07 (s, 9H), 1.00–0.92 (m, 1H), 0.63–0.50 (m, 1H), 0.01 (s, 3H), –0.01 (s, 3H); $^{13}$C NMR $\delta$ 201.3, 171.5, 135.8, 133.4, 133.2, 129.8, 127.7, 66.5, 66.4, 51.4, 50.2, 44.7, 42.1, 26.9, 25.6, 19.2, 17.7, –4.6, –4.9.

**(3*S*,4*S*,6*R*)-4-[(Benzyloxy)methoxy]-6-[(*tert*-butyldimethylsilyl)oxy]-3-(tributylstannyl)cycloheptanone (23).** Copper cyanide (129 mg, 1.44 mmol) in a 100-mL round-bottom flask was flushed with dry argon, flame-dried, and evacuated three times. After allowing the flask to cool, the copper cyanide was suspended in dry THF (5 mL) and cooled to –78 °C under an atmosphere of dry argon. The suspension was treated with 2.5 M *n*-BuLi (1.153 mL, 2.88 mmol) dropwise, warmed slightly until the solution became homogeneous, and cooled back to –78 °C. The solution was then treated with tri-*n*-butyltin hydride (0.775 mL, 2.88 mmol) dropwise which caused the solution to turn from clear to yellow. After 0.5 h, enone **13** (495 mg, 1.31 mmol) in dry tetrahydrofuran (5 mL) was added dropwise to the cuprate solution at –78 °C. After the addition was complete, the orange solution was treated with saturated ammonium chloride (5 mL) and allowed to warm to ambient temperature. The mixture was then treated with a solution of 1:1 concentrated ammonium hydroxide/saturated ammonium chloride (20 mL) and extracted with ether (3 × 25 mL). The combined extracts were dried over sodium sulfate, and solvent was removed under reduced pressure to give a clear oil which was chromatographed on silica gel eluting with 10% EtOAc/petroleum ether to give **23** (850 mg, 1.27 mmol, 97% yield) as a clear oil. $^1$H NMR $\delta$ 7.34 (s, 5H), 4.85 and 4.75 (ABq, $J = 7.5$ Hz, 2H), 4.71 and 4.49 (ABq, $J = 13.0$ Hz, 2H), 3.91 (tt, $J = 11.0$ Hz, $J = 4.0$ Hz, 1H), 3.45 (m, 1H), 2.53 (m, 1H), 3.05 (dd, $J = 13.5$ Hz, $J = 11.0$ Hz, 1H), 2.82 (m, 1H), 2.53 (m, 3H), 1.96 (ddd, $J = 14.0$ Hz, $J = 10.0$ Hz, $J = 4.0$ Hz, 1H), 1.80 (q, $J = 11.4$ Hz, 1H), 1.95 (m, 6H), 1.25 (m, 6H), 0.85 (m, 24H), 0.08 (s, 3H), 0.07 (s, 3H); $^{13}$C NMR $\delta$ 211.3, 131.7, 128.6, 127.9, 94.8, 81.1, 69.8, 67.6, 52.8, 49.0, 44.8, 30.3, 29.5, 29.4, 36.3, 29.2, 27.7, 27.3, 25.9, 18.7, 13.8, 9.6, –4.7; HRMS *m/e* calcd for $C_{29}H_{51}SiSnO_4$ (M – $C_4H_9$) 611.2577, found 611.2588.

**(3*R*,5*S*)-Methyl 5-[(Benzyloxy)methoxy]-3-[(*tert*-butyldimethylsilyl)oxy]-6-heptenoate (24).** A solution of $\beta$-tributylstannyl ketone **23** (268 mg, 0.40 mmol) in dichloromethane (5 mL) was treated with *m*-chloroperoxybenzoic acid (50–60% pure, 276 mg, ca. 0.80 mmol) in dichloromethane (5 mL) and dried over magnesium sulfate and sodium bicarbonate under an atmosphere of dry argon at ambient temperature. After 2 h, the solution was evaporated under reduced pressure to give a white solid which was dissolved in ether (50 mL) and treated with diazomethane etherate while stirring at room temperature. Removal of the excess diazomethane and solvent under reduced pressure gave a pale oil which was chromatographed on silica gel eluting with 5% EtOAc/petroleum ether to give **24** (106 mg, 0.26 mmol, 65% yield) as a clear oil: $[\alpha]^{20}_D$ –76.8° (*c* 0.9, $CHCl_3$); IR ($CDCl_3$) 2956, 2855, 2255, 1736, 1260, 1237 cm$^{-1}$; $^1$H NMR $\delta$ 7.39 (s, 5H), 5.70 (ddd, *J* 12.5 Hz, $J = 10.0$ Hz, $J = 8.0$ Hz, 1H), 5.25 (m, 2H), 4.79 and 4.69 (ABq, $J = 6.5$ Hz, 1H), 4.73 and 4.56 (ABq, $J = 11.5$ Hz, 2 H), 4.35 (m, 1H), 4.24 (m, 1H), 3.68 (s, 3H), 2.61 (ABq, d, $J = 15.0$ Hz, $J = 5.0$ Hz, 1H), 2.52 (ABq, d, $J = 15.0$ Hz, $J = 7.9$ Hz, 1H), 1.91 (ddd, $J = 13.4$ Hz, $J = 7.5$ Hz, $J = 5.0$ Hz, 1 H), 1.71 (ddd, $J = 12.2$ Hz, $J = 7.0$ Hz, $J = 5.0$ Hz, 1H), 0.87 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H); $^{13}$C NMR $\delta$ 172.2, 137.6, 128.5, 128.0, 118.0, 91.7, 74.4, 69.8, 66.8, 51.5, 43.4, 42.5, 28.9, 18.0, –4.4, –4.7. Anal. Calcd for $C_{22}H_{36}SiO_5$: C, 64.67; H, 8.88. Found: C, 64.37; H, 8.51.

**Methyl 2,4-Dideoxy-D-*erythro*-hexopyranoside (25).** To the solution of crude aldehyde **20** (274 mg, 0.90 mmol) in methanol (15 mL) was added Dowex-50 (100 mg). After 20 h, the reaction mixture was filtered, methanol was evaporated, and the crude product was purified by chromatography (ethyl acetate) to give product **25** (as a 2:1, mixture of $\alpha$ and $\beta$ anomers, 98.5 mg, 0.68 mmol, 75% yield) as an oil which was carried on to acetates **26**. **25**$\alpha$: $^{13}$C NMR $\delta$ 99.4, 65.9, 64.2, 63.9, 55.3, 35.1, 33.8. **25**$\beta$: $^{13}$C NMR $\delta$ 99.6, 71.2, 65.8, 65.0, 56.6, 38.4, 33.8.

**Methyl 3,6-Diacetyl-2,4-dideoxy-D-$\alpha$- and $\beta$-*erythro*-hexopyranoside (26).** To the solution of of diol **25** (162 mg, 1 mmol) in dichloromethane (5 mL) were added pyridine (158 mg, 161 $\mu$L, 2 mmol) followed by acetic anhydride (153 mg, 141 $\mu$L, 1.5 mmol) and a catalytic amount (ca. 2 mg) of 4-(dimethylamino)pyridine. After 15 h, all volatile organics were evaporated *in vacuo* and the oily residue was purified by flash chromatography (hexane/ethyl acetate, 7:3 to 6:4) to give 156 mg of $\alpha$ and 79 mg of $\beta$ anomer (95% total yield) of diacetylated product **26**. Spectral data on the anomers **26**$\alpha$ and **26**$\beta$ matched data from the racemic compounds reported in ref 50. **26**$\alpha$ oil, $[\alpha]^{23}_D$ –50.9° (*c* 1.4, $CHCl_3$); $^1$H NMR $\delta$ 5.25 ("t", $J = 3.1$ Hz, 1H), 4.62 (dd, $J = 9.6$, 2.0 Hz, 1H), 4.17–4.05 (m, 2H), 4.03–3.93 (m, 1H), 3.47 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.02–1.87 (m, 1H), 1.75–1.50 (m, 3H); $^{13}$C NMR $\delta$ 171.0, 170.1, 99.6, 69.0, 68.0, 66.4, 56.4, 35.3, 31.4, 21.3, 20.9. **26**$\beta$: Oil, $[\alpha]^{23}_D$ +105.1° (*c* 0.8, $CHCl_3$); $^1$H NMR $\delta$ 5.09 (dddd, $J = 3.2, 3.2, 3.1, 3.1$ Hz, 1H), 4.79 (d, $J = 4.1$ Hz, 1H), 4.26 (ddd, $J = 9.7, 9.6, 4.2$ Hz, 1H), 4.12 (bs, 1H), 4.11(d, $J = 2.8$ Hz, 1H), 3.35 (s, 3H), 2.09 (s, 3H), 2.06 (s, 3H), 2.00–1.67 (m, 4H); $^{13}$C NMR $\delta$ 171.1, 170.9, 97.7, 66.6, 61.8, 55.1, 32.2, 30.9, 21.5, 20.9.

**(2*R*,4*R*,6*S*)-2,4-Bis[(*tert*-butyldimethylsilyl)oxy]-1,6,7-heptanetriol (27).** Acetate **6a** (820 mg, 2 mmol) was dissolved in methanol (20 mL). Ozone/oxygen (ca. 4%) was passed at –78 °C, until a blue color persisted. Then the solution was purged with argon (still at –78 °C) until all blue color disappeared. Dimethyl sulfide (1 mL) followed by sodium borohydride (378 mg, 10 mmol) was added and the cooling bath was removed. After 2 h, potassium hydroxide (56 mg, 1 mmol) was added and stirring was continued for 1 h. Then the reaction mixture was poured into a mixture of diethyl ether (100 mL) and water (150 mL). After separation of phases, the aqueous layer was extracted with diethyl ether (3 × 50 mL). The combined extracts were dried over magnesium sulfate and solvent was removed under reduced pressure to give a clear oil which was chromatographed on silica gel, eluting with 40–50% EtOAc/ petroleum ether, to give **27** (612 mg, 1.50 mmol, 75% yield) as a clear oil: $[\alpha]^{23}_D$ +17.4° (*c* 1.2, $CHCl_3$); IR (neat) 3400, 2962, 2928, 1470, 1258, 1109 cm$^{-1}$; $^1$H NMR $\delta$ 4.20–4.10 (m, 1H), 3.90–3.20 (m, 8H), 2.85 (d, $J = 2.9$ Hz, 1H), 1.76–1.48 (m, 4H), 0.86 (s, 9H), 0.85 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H), 0.03 (s, 6H); $^{13}$C NMR $\delta$ 70.6, 69.7, 69.1, 67.6, 66.8, 44.5, 39.4, 26.0, 25.9, 18.3, 17.9, –4.2, –4.5, -5.3. Anal. Calcd for $C_{19}H_{44}Si_2O_5$: C, 55.83; H, 10.85. Found: C, 55.90; H 10.86.

**Methyl 2,4-dideoxy-L-$\alpha$- and -$\beta$-*erythro*-hexopyranoside 29** as a mixture of anomers were obtained by the same method as for **25** (75% yield).

**Methyl 3,6-Di-*O*-acetyl-2,4-dideoxy-L-$\alpha$- and $\beta$-*erythro*-hexopyranoside (30).** Diol **29** (162 mg, 1 mmol) was acetylated, using described procedure above to give 152 mg of $\alpha$ and 77 mg of $\beta$ anomer (94% total yield) of diacetylated product **30**. All spectral data were identical to those for compound **26**. **30**$\alpha$: $[\alpha]^{25}_D$ +51.8° (*c* 1, $CHCl_3$). **30**$\beta$: $[\alpha]^{25}_D$ –107.6° (*c* 1, $CHCl_3$).

**(2*S*,4*R*,6*R*)-2-(Acetoxy)-4-(*tert*-butyldimethylsilyloxy)-1,6,7-heptanetriol (31).** Acetate **2** (520 mg, 1.73 mmol) was taken up in a 1:1 mixture of methanol and dichloromethane (25 mL). The reaction mixture was cooled to –78 °C and purged with oxygen. Ozone was bubbled through the reaction mixture until the faint blue color of ozone was detected. The reaction mixture was then purged with oxygen until the blue color dissipated. Dimethyl sulfide (1 mL) followed by sodium borohydride (196 mg, 5.19 mmol) were introduced into the reaction mixture which was then warmed to room temperature. The reaction mixture was poured into water (50 mL) and the aqueous layer washed with dichloromethane (5 × 20 mL). The combined organics were dried over magnesium sulfate and filtered, and the solvent was removed *in vacuo*. Purification of the residue by column chromatography (10% methanol in chloroform) yielded triol **31** (440 mg, 1.31 mmol, 76%) as a clear oil: $[\alpha]^{25}_D$ +3.2° (*c* 1.6, $CHCl_3$); IR (neat) 3396, 2956, 2931, 1743, 1388, 1255, 1043, 838 cm$^{-1}$; $^1$H NMR ($CD_3OD$) $\delta$ 4.14 (ddd, $J_1 = 12.0$ Hz, $J_2 = J_3 = 6.3$ Hz, 1H), 4.01–3.90 (m, 2H), 3.79–3.70 (m, 1H), 3.48–3.26 (m, 3H), 2.04 (s, 3H), 1.69–1.47 (m, 4H), 0.89 (s, 9H), 0.12 (s, 3H), 0.11 (s, 3H); $^{13}$C NMR $\delta$ 68.6, 68.3, 66.9, 66.4, 65.7, 41.2, 41.1, 25.0, 19.3, –5.6, –5.7. Anal. Calcd for $C_{15}H_{32}O_6Si$: C, 53.54; H, 9.58. Found: C, 53.06; H, 9.43. A mixture of **31** and the product resulting from acyl migration to the primary alcohol (111 mg, 0.33 mmol, 19%) was also obtained.

**Methyl 2,4-Dideoxy-D-*threo*-hexopyranoside (33).** To a

vigorously stirred suspension of silica gel (4.0 g) in dichloromethane (25 mL) was added dropwise sodium periodate (534 mg, 2.5 mmol) dissolved in water (2.0 mL). To this was added triol **31** (420 mg, 1.25 mmol) dissolved in dichloromethane (1 mL). After 2 h the reaction mixture was filtered and the solid washed with dichloromethane (2 × 30 mL). The filtrate was concentrated *in vacuo*. Crude aldehyde **32** was then taken up in methanol (15 mL), Dowex 50 (100 mg) added, and the reaction mixture stirred overnight. The reaction mixture was filtered and the solvent removed *in vacuo*. Purification of the residue by column chromatography (10% methanol in chloroform) yielded diol **33** (137 mg, 0.84 mmol, 68%) as a mixture of anomers which were carried directly to the acetate **34**.

**Methyl 3,6-Di-*O*-acetyl-2,4-dideoxy-D-*threo*-hexopyranoside (34).** Diol **33** (91 mg, 0.56 mmol), acetic anhydride (229 mg, 2.24 mmol), and 4-(dimethylamino)pyridine were dissolved in pyridine (5 mL) and stirred until no starting material was detected by TLC (5% methanol in chloroform). The reaction mixture was then poured into diethyl ether (30 mL) and washed with brine (3 x 10 mL). The organic layer was dried over magnesium sulfate and filtered, and the solvent was removed *in vacuo*. Purification of the residue by column chromatography (5% methanol in chloroform) followed by separation of the anomers using HPLC (20% ethyl acetate in hexanes using a silica gel column) afforded the less-polar **34**$\alpha$ anomer (113 mg, 0.46 mmol, 82%) as a clear oil. $[\alpha]^{25}_D$ +131.6° (*c* 1.0, $CHCl_3$); $^1$H NMR $\delta$ 5.11 (dddd, $J_1 = J_2 = 11.4$ Hz, $J_3 = J_4 = 4.8$ Hz, 1H), 4.83 (d, $J = 3.0$ Hz, 1H), 4.11–3.90 (m, 3H), 3.26 (s, 3H), 2.06–1.93 (m, 2H), 2.02 (s, 3H), 1.96 (s, 3H), 1.57 (ddd, $J_1 = J_2 = 11.7$ Hz, $J_3 = 3.6$ Hz, 1H), 1.34 (ddd, $J_1 = J_2 = J_3 = 11.7$ Hz, 1H); $^{13}$C NMR $\delta$ 170.6, 170.0, 98.7, 66.3, 66.2, 65.3, 54.5, 35.2, 33.0, 21.0, 20.7. **34**$\beta$ (23 mg, 0.09 mmol, 16%) as a clear oil: $[\alpha]^{25}_D$ −32.0° (*c* 0.8, $CHCl_3$); $^1$H NMR $\delta$ 4.91 (dddd, $J_1 = J_2 = 11.4$ Hz, $J_3 = J_4 = 4.8$ Hz, 1H), 4.36 (dd, $J_1 = 9.8$ Hz, $J_2 = 2.0$ Hz, 1H), 4.20 (dd, $J_1 = 11.7$ Hz, $J_2 = 6.0$ Hz, 1H), 4.10 (dd, $J_1 = 11.7$ Hz, $J_2 = 4.5$ Hz, 1H), 3.64 (dddd, $J_1 = 12.0$ Hz, $J_2 = 6.3$ Hz, $J_3 = 4.5$ Hz, $J_4 = 2.1$ Hz, 1H), 3.49 (s, 3H), 2.18 (dddd, $J_1 = 12.0$ Hz, $J_2 = 4.8$ Hz, $J_3 = J_4 = 1.8$ Hz, 1H), 2.07 (s, 3H), 2.04 (s, 3H), 2.02–1.93 (m, 1H), 1.47 (ddd, $J_1 = 12.0$ Hz, $J_2 = J_3 = 9.9$ Hz, 1H), 1.35 (dd, $J_1 = J_2 = 12.0$ Hz, 1H). Spectral data on the anomers **34**$\alpha$ and **34**$\beta$ matched data from the racemic compounds reported in ref 50.

**(3*S*,5*S*,7*R*)-3-Acetoxy-5,7-bis[(*tert*-butyldimethylsilyl)oxy]cycloheptene (35).** Alcohol **2** (920 mg, 3.06 mmol), *tert*-butyldimethylsilyl chloride (553 mg, 3.67 mmol), and imidazole (521 mg, 7.66 mmol) were dissolved in DMF (15 mL). The reaction mixture was stirred overnight, poured into diethyl ether (100 mL), and washed with water (2 × 25 mL). The organic layer was dried over magnesium sulfate and filtered and the solvent removed in vacuo. Purification of the residue by column chromatography (10:1; hexanes/ethyl acetate) afforded **35** (1.175 mg, 2.83 mmol, 93%) as a clear oil: $[\alpha]^{25}_D$ +5.2° (*c* 1.0, $CHCl_3$); IR (neat) 2955, 2930, 2858, 1743, 1371, 1241, 1098, 1066, 837 cm$^{-1}$; $^1$H NMR $\delta$ 5.78–5.68 (m, 2H), 5.58–5.50 (m, 1H), 4.82–4.72 (m, 1H), 4.21 (ddd, $J = 5.5$, 3.0, 3.0 Hz, 1H), 2.03 (s, 3H), 1.92–1.70 (m, 4H), 0.92 (s, 9H), 0.88 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H), 0.06 (s, 3H), 0.05 (s, 3H); $^{13}$C NMR $\delta$ 169.9, 138.5, 130.8, 69.0, 67.0, 66.3, 44.1, 40.1, 25.8, 21.2, 18.0, −4.8, −4.9, -5.1. Anal. Calcd for $C_{21}H_{42}O_4Si_2$: C, 60.82, H, 10.21. Found: C, 60.95, H, 10.10.

**(2*R*,4*S*,6*S*)-2,4-Bis-[(*tert*-butyldimethylsilyl)oxy]-1,2,7-cycloheptanetriol (36).** Acetate **35** (920 mg, 2.22 mmol) was dissolved in a 1:1 mixture of methanol and dichloromethane (30 mL). The reaction mixture was cooled to −78 °C and purged with oxygen. Ozone was bubbled through the reaction mixture until a faint blue color was detected and then oxygen was bubbled through the reaction mixture until the color dissipated. Dimethyl sulfide (1 mL) followed by solid sodium borohydride (170 mg, 4.5 mmol) was added to the reaction mixture, which was allowed to warm to room temperature. After stirring at room temperature for 0.5 h, the reaction mixture was poured into a mixture of diethyl ether (150 mL) and water (150 mL). After separation of the phases, the aqueous layer was extracted with diethyl ether (3 × 50 mL). The combined extracts were dried over magnesium sulfate and filtered and the solvent removed *in vacuo*. The crude diol (979 mg, 2.17 mmol) was taken up in methanol (20 mL) and powdered potassium hydroxide (50 mg) added. The reaction mixture was stirred at room temperature until no starting material was detected by TLC (1:1 hexanes/ethyl acetate). The reaction mixture was then poured into diethyl ether (150 mL) and washed with water (3 × 50mL). The organic layer was dried over magnesium sulfate, filtered, and concentrated *in vacuo*. Purification of the residue using column chromatography (1:1 hexanes/ethyl acetate) yielded triol **36** (564 mg, 1.38 mmol, 62%) as a clear oil: $[\alpha]^{25}_D$ +2.0° (*c* 1.1, $CHCl_3$); IR (neat) 3403, 2954, 2929, 2857, 1472, 1463, 1257, 1104, 837 cm$^{-1}$; $^1$H NMR $\delta$ 4.30–4.20 (m, 1H), 4.01–3.91 (m, 1H), 3.83–3.71 (m, 2H), 3.61–3.50 (m, 2H), 3.45–3.34 (m, 2H), 2.98–2.78 (m, 2H), 1.80–1.49 (m, 4H), 0.87 (s, 18H), 0.10 (s, 6H), 0.04 (s, 6H); $^{13}$C NMR $\delta$ 69.1, 68.6, 67.5, 67.0, 39.3, 38.9, 25.8, 18.2, 17.8, −4.7, −4.9, −5.4. Anal. Calcd for $C_{19}H_{44}O_5Si_2$: C, 55.83; H, 10.85. Found: C, 55.63; H, 10.63.

**Methyl 2,4-Dideoxy-L-*threo*-hexopyranoside (37).** Triol **36** (459 mg, 1.123 mmol) was taken up in diethyl ether (25 mL). Sodium periodate (480 mg, 2.246 mmol) dissolved in water (2 mL) was added and the reaction mixture stirred overnight. The reaction mixture was then poured into diethyl ether (100 mL) and washed with water (50 mL). The aqueous layer was washed with diethyl ether (25 mL), and the organic layers were combined and concentrated *in vacuo*. Crude aldehyde was then taken up in methanol (20 mL), Dowex 50 (100 mg) added, and the reaction mixture stirred overnight. The Dowex 50 resin was filtered away and the solvent removed *in vacuo* to yield methyl glycoside **37** (156 mg, 0.962 mmol, 86%) as a mixture of anomers.

**Methyl 3,6-Di-*O*-acetyl-2,4-dideoxy-L-*threo*-hexopyranoside (38).** Crude **37** (156 mg, 0.962 mmol), acetic anhydride (393 mg, 3.90 mmol), and 4-(dimethylamino)pyridine were dissolved in pyridine (8 mL) and stirred at room temperature overnight. The reaction mixture was then poured into diethyl ether (30 mL) and washed with brine (3 × 10 mL). The organic layer was dried over magnesium sulfate and filtered and the solvent removed *in vacuo*. Purification of the residue by column chromatography (5% methanol in chloroform) followed by separation of the anomers using HPLC (20% ethyl acetate in hexanes using a silica gel column) afforded **38**$\alpha$ (128 mg, 0.52 mmol, 54%) as a clear oil: $[\alpha]^{25}_D$ −126.5° (*c* 1.1, $CHCl_3$). **38**$\beta$ (22 mg, 0.089 mmol, 9%) was also isolated as a clear oil: $[\alpha]^{25}_D$ +23.3° (*c* 0.8, $CHCl_3$). All spectral data were the same as for compound **34**.

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