Syntheses of Chiral Dispiroacetals from Carbohydrates

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The syntheses of trioxadispiroacetals from carbohydrates are described. (5*R*,7*S*,13*R*)-13-Methoxy-1,6,8-trioxadispiro[4.1.5.3]pentadecane (**23**) and (5*S*,7*S*,13*R*)-13-methoxy-1,6,8-trioxadispiro[4.1.5.3]-pentadecane (**24**) were prepared starting from D-galactose. The construction of the lateral tetrahydrofuran and tetrahydropyran rings was realized by homologation at C_1 and C_6 by appropriate tethers possessing a terminal primary alcohol. The cyclization of these alcohols at C_1 and C_5, respectively, was performed with (diacetoxyiodo)benzene and iodine in order to generate the alkoxy radicals which undergo an intramolecular hydrogen abstraction reaction. The diastereoisomers (5*R*,7*S*,13*S*)-13-methoxy-1,6,8-trioxadispiro[4.1.5.3]pentadecane (**37**) and (5*S*,7*S*,13*S*)-13-methoxy-1,6,8-trioxadispiro[4.1.5.3]pentadecane (**38**) were prepared starting from tri-*O*-acetyl-D-glucal using a suitable methodology in which homologation and intramolecular hydrogen abstraction were again the key steps. We believe that this protocol could be easily extended to other tricyclic dispiroacetal ring systems.

The widespread occurrence of the substituted spiroacetal ring system as a substructure in a large range of natural products has promoted considerable interest in the development of synthetic routes to these compounds.[1] Of special interest is the 1,6,8-trioxadispiro[4.1.5.3]-pentadecane arrangement which appears in nature in a small number of very important polyether ionophores such as narasin,[2] salinomycin[3] and noboritomycin[4] and the antibiotics CP 44,661[5] and X 14766A.[6] Recently, other molecular systems containing dispiro arrangements of the 1,7,9-trioxadispiro[5.1.5.2]pentadecane[7] and 1,6,8-trioxadispiro[4.1.5.2]tetradecane[8] types have been isolated from marine organisms. To study the configuration and conformation of the system, some other simpler models of trioxadispiroacetals have also been prepared and in a few cases X-ray crystallographic analysis has been used.[9]

We have recently reported on a method for the synthesis of optically active bicyclic spiroacetals from carbohydrates in which the spirocenter is achieved by an

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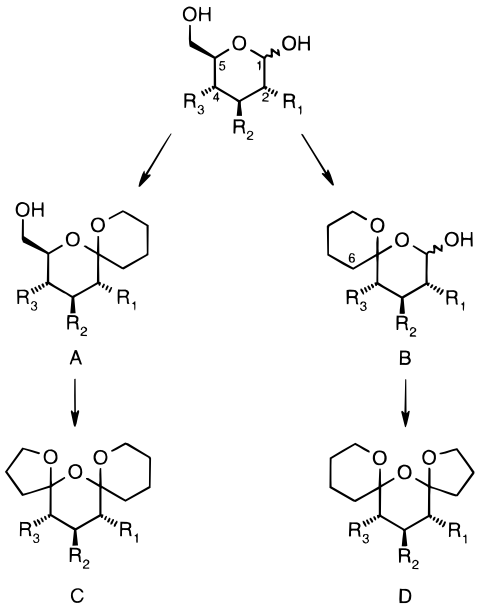
Scheme 1



intramolecular hydrogen abstraction (IHA) reaction promoted by alkoxy radicals.[10a] We wish to report here on an extension of this methodology to the synthesis of tricyclic dispiroacetals of the 1,6,8-trioxadispiro[4.1.5.3]-pentadecane type from carbohydrates.[11]

As shown in Scheme 1, the construction of the terminal tetrahydropyran ring on the anomeric center via C-glycosylation and an IHA reaction from the appropriate alcohol would give intermediate A. Two-carbon homologation of the C_5 tether and a second IHA reaction would afford tricyclic dispiroacetal C. If we change the position of the lateral heterocyclic rings and introduce the tetrahydropyran ring at C_5 and the tetrahydrofuran at C_1, we can obtain the tricyclic dispiroacetal D via intermediate B.

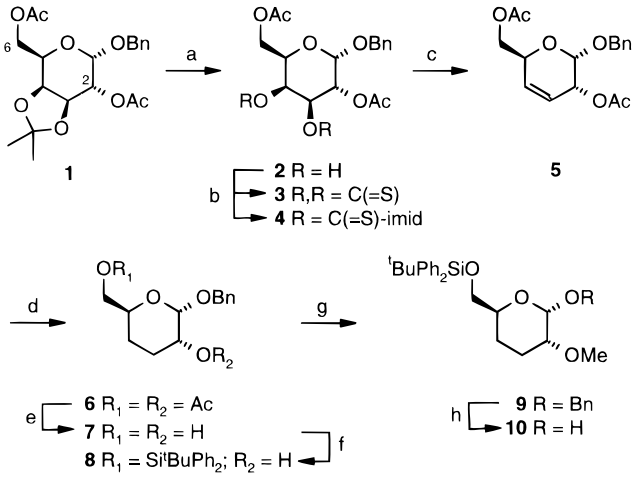
This methodology would allow us the preparation of both enantiomeric dispiroacetals from the same carbohydrate in an enantiodivergent synthesis with the sole condition that the groups at C_2 and C_4 (R_1 and R_3) are enantiomorphic, as is the case when D-glucose ($R_1 = R_2 = R_3 = OH$) is used as starting material.

Using this protocol and in order to devise simpler models, we have prepared two tricyclic dispiroacetals C ($R_1 = OMe$, $R_2 = R_3 = H$) and D ($R_1 = R_2 = H$, $R_3 = OMe$) starting from two appropriate dideoxysugars.

Results and Discussion

In our first synthesis, we decided to prepare the key intermediate **10** for the construction of the right-hand tetrahydropyran ring via C-glycosidation. We chose benzyl α-D-galactopyranoside[12] as our starting material because its structure allows the selective protection of the C_3 and C_4 hydroxyl groups as an isopropylidene while leaving the C_2 and C_6 hydroxyl groups unprotected.[13] The acetylation of these alcohols gave compound **1**. Acetic acid hydrolysis of the acetonide gave the corresponding diol **2** which was transformed into the cyclic thionocarbonate **3**, in 90% yield[14] (Scheme 2). A small amount (10%) of the 3,4-dithionoimidazole derivative **4** was also obtained. Reduction with trimethyl phosphite produced olefin **5** in 80% yield.[15] Hydrogenation of the double bond was accomplished using $Pd(OH)_2/C$ as catalyst to give **6** in 85% yield. Hydrogenolysis of the benzyl ether at C_1 was not observed under these conditions, but a very small amount (2%) of the 2-deoxy compound was found in the reaction mixture. Deprotection of the C_2 and C_6 hydroxyl groups was followed by selective protection of the primary alcohol with $^tBuPh_2SiCl$ to give **8** in 79% yield. O-Methylation of the alcohol at C_2 provided **9** which underwent selective cleavage of the anomeric benzyl ether when submitted to the $BCl_3{\cdot}SMe_2$ complex.[16] This alternative procedure was necessary since, as commented previously, the anomeric benzyl ether was inert under the more usual hydrogenolytic cleavage over Pd/C or $Pd(OH)_2/C$.

Scheme 2[a]



[a] Key: (a) AcOH (80%), 50 °C, 4 h, 80%; (b) 1,1′-thiocarbonyldiimidazole, MeCN, rt, 5 h 90%; (c) trimethyl phosphite, reflux, 4.5 h, 80%; (d) $Pd(OH)_2/C$, H_2, EtOH, 5 h, 85%; (e) K_2CO_3, MeOH, rt, 3 h, 100%; (f) TBDPSCl, imidazole, DMF, rt, 5 min, 79%; (g) dimethyl sulfate, NaOH, acetone, 45 °C → reflux, 2 h, 87%; (h) $BCl_3{\cdot}SMe_2$, CH_2Cl_2, rt, 14 h, 74%.

The resulting anomeric mixture **10** was transformed into the glycosyl chloride[17] and alkylated with 4-pentenylmagnesium bromide yielding the *C*-glycosides **11** and **12** as a (β:α, 1:3.7) mixture that was separated by chromatography (Scheme 3).[18] The stereochemistry at C_1 was determined by careful analysis of the corresponding coupling constants of the ddd systems at C_2. The alcohols **13** and **14** were obtained by ozonolysis followed by *in situ* reduction with $NaBH_4$. The intramolecular hydrogen abstraction reaction was then carried out by treating **13** with the (diacetoxyiodo)benzene (DIB)/iodine system to yield the spiroacetal isomers **15** and **16**. The

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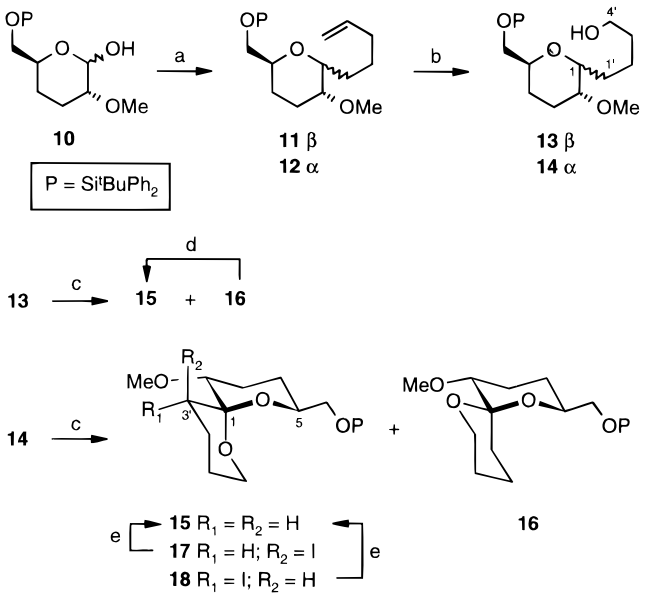
Scheme 3[a]



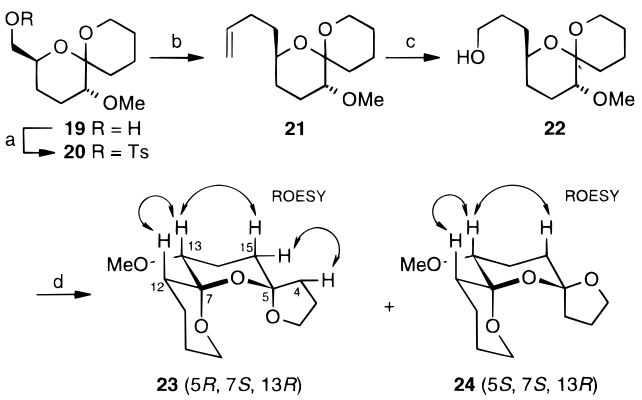
[a] Key: (a) (1) Ph_3P, CCl_4, THF, reflux, 3 h, (2) CH_2=CH-$(CH_2)_3$MgBr, Et_2O, 0 °C, 1 h, 74%; (b) O_3, CH_2Cl_2/MeOH, −78 °C, then $NaBH_4$, rt, 4 h, 95%; (c) DIB, I_2, cyclohexane, *hν*, 40 °C, 70 min; (d) HCl, AcOH, rt, 2 h, 100%; (e) $^nBu_3SnH$, AIBN, PhH, reflux, 35 min.

reaction proceeded in good yield (87%, **16**:**15**, 1:1.4), the minor isomer **16** being thermodynamically less stable, as indicated by the acid-catalyzed quantitative isomerization of **16** to **15**.

The stereochemistry of the spirocenter of this dioxaspiro-[5.5]undecanyl ring system was confirmed by X-ray crystallographic analysis of compound **15**.[19] As expected, the preferred conformation of the rings is determined principally by the maximum number of anomeric effects.[20] A study by molecular mechaniscs using the MMX force field[21] is in accord with the stability observed for the pair of stereoisomers obtained, **15** being favored over **16** by 3.9 kcal/mol of MMX steric energy.

Interestingly, when the hydrogen abstraction reaction was performed with the isomeric alcohol **14**, a pair of isomeric iodine compounds **17** and **18** was obtained, although in low yield (15%), apart from the expected spiroacetals **15** and **16** (51%). Both iodine compounds were reduced with $^nBu_3SnH$/AIBN to the same spiroacetal **15** in good yield, indicating an identical stereochemistry at the spirocenter. The position and configuration of the iodine atoms were established by ^1H NMR spectroscopy, the chemical shifts and coupling constants being in accord with the axial and equatorial orientation proposed for **17** and **18**, respectively. Although the formation of these iodine compounds is unclear, one possibility is that a hydrogen abstraction has taken place at $C_{1'}$ of **14** through a six-membered cyclic transition state. The loss of a hydrogen atom would give a 1,1′-olefin which upon 6-*endo*-*trig* iodocyclofunctionalization would yield the observed iodine compounds. Nevertheless, the possibility of a double hydrogen abstraction cannot be totally discarded. In any case, these mechanisms do not explain why the iodine compounds are only observed during the IHA reaction of diastereoisomer **14**. Attempts to calculate the energy of the possible transition states by using a MM2 force field model does not throw any light either.[22]

Scheme 4[a]



[a] Key: (a) TsCl, Py, rt, 15 h, 100%; (b) CH_2=$CHCH_2$MgBr, Et_2O, rt, 2 h, 85%; (c) O_3, CH_2Cl_2/MeOH, −78 °C, then $NaBH_4$, rt, 3 h, 98%; (d) DIB, I_2, cyclohexane, *hν*, rt, 4 h, 56%.

Deprotection and subsequent tosylation of compound **15** afforded tosylate **20**, which, as shown in Scheme 4, was subjected to the reaction with allylmagnesium bromide to afford olefin **21** in 85% yield. Ozonolysis followed by a reductive workup yielded alcohol **22**, which was submitted to a second hydrogen abstraction reaction with DIB/iodine to give a mixture of the 1,6,8-trioxadispiro-[4.1.5.3]pentadecane derivatives **23** and **24** in a ratio of 1:1.4. The stereochemistries at C_5 and C_7 were clearly assigned on the basis of the ROESY spectra (principal correlations shown by arrows in Scheme 4). The minor compound **23** is the thermodynamically more stable (by 4.1 kcal/mol),[21] the stereochemistries of the chiral centers being established as 5*R*,7*S*,13*R* for **23** and 5*S*,7*S*,13*R* for its C_5 isomer **24**. Unfortunately, attempts at acid-catalyzed equilibration of **24** were unsuccessful. The molecule seems to be very sensitive to these conditions, and a chroman derivative, formed by an intramolecular aldolic reaction, was the only isolated product.[23]

The second synthesis began as outlined in Scheme 5. The starting material chosen was the known compound **25**, prepared from tri-*O*-acetyl-D-glucal using a previously reported methodology.[24] Hydrogenation and deprotection of the acetonide cleanly gave the corresponding diol **27** in 70% overall yield, which was transformed into compound **28** by selective tosylation of the primary hydroxyl group. Alkylation of tosylate **28** with allylmagnesium

(19) The author has deposited the atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, upon request, from the Director, Cambridge Cystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

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(21) MMX force field as implemented in PCMODEL (v. 4.0), Serena Software, Bloomington, IN 47402-3076. See: Gajewski, J. J.; Gilbert, K. E.; McKelvey, J. *Advances in Molecular Modelling*; JAI Press: Greenwich, CT, 1992; Vol. 2.

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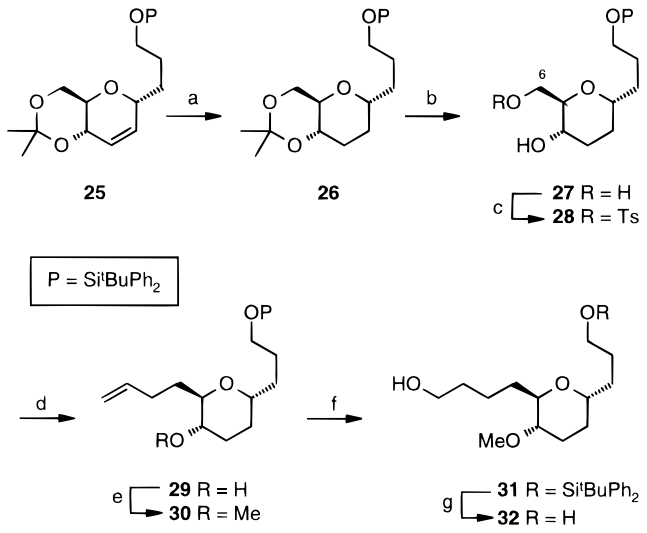
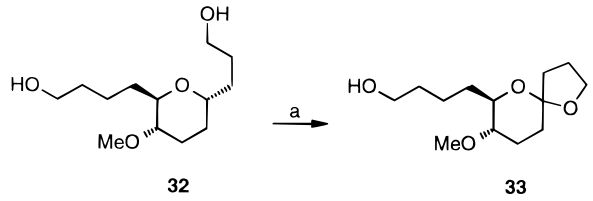
Scheme 5[a]



[a] Key: (a) $Pd(OH)_2/C$, H_2, EtOAc, 80%; (b) Amberlyst-15 (H^+), MeOH, rt, 1 h, 88%; (c) TsCl, Py, 0 °C, 4 h, 88%; (d) CH_2=CH-CH_2MgBr, Et_2O, 0 °C, 3 h, 80%; (e) dimethyl sulfate, NaOH, acetone, 50 °C, 4 h, 73%; (f) BH_3·THF, THF, 0 °C, 1 h, 73%; (g) TBAF, THF, rt, 2 h, 95%.

Scheme 6[a]

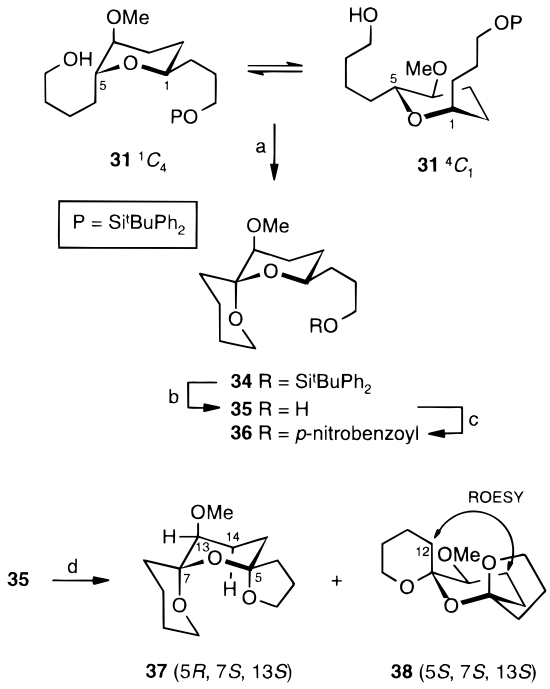


[a] Key: (a) DIB, I_2, cyclohexane, rt, 30 min, 60%.

bromide elongated the side chain at C_6 by a three-carbon unit necessary for the construction of the tetrahydropyran ring. O-Methylation of the secondary alcohol **29** with dimethyl sulfate/NaOH afforded methyl ether **30** in 73% yield. Hydroboration of the terminal olefin **30** with BH_3·THF followed by oxidative workup furnished the key intermediate alcohol **31** which was desilylated with TBAF to give diol **32**. This molecule contains the numbers of carbons and convenient functionality for subsequent elaboration of the trioxadispiro compound. Unfortunately, attempts to elaborate the trioxadispiro system directly from diol **32** by simultaneous double hydrogen abstraction reaction were unsuccessful and produced the dioxaspiro[4.5]decane ring system derivative **33** as the sole reaction product (Scheme 6). As expected, the tetrahydrofuran ring was formed first and the 1,3-diaxial interaction with the group at C_1 seemed to hinder the radical abstraction of the C_5 hydrogen through a less-favored seven-membered cyclic transition state.[10a]

Scheme 7 outlines a more efficient strategy involving first the formation of the dioxadispiro[5.5]undecane ring system. This was accomplished by reaction of alcohol **31** with the DIB/iodine reagent which gave compound **34** as the sole product in 43% yield. The presence of a triplet at δ 2.92 (J = 2.5 Hz) clearly indicated an axial disposition of the methoxyl group at C_{13}. A study by molecular mechanics indicated that the steric energy for both chair conformers of **31** ($^1C_4$ and $^4C_1$) is similar (Δ = 0.09 kcal/mol) allowing an equilibrium between them, the hydrogen abstraction and subsequent cyclization occurring

Scheme 7[a]



[a] Key: (a) DIB, I_2, CCl_4, rt, 90 min, 43%; (b) TBAF, THF, rt, 2 h, 86%; (c) *p*-nitrobenzoyl choride, Py/CH_2Cl_2, rt, 14 h, 97%; (d) DIB, I_2, cyclohexane, rt, 140 min, 78%.

from the conformation $^1C_4$ that avoids the 1,3-diaxial interactions between the hydrogen at C_5 and the side chain at C_1. Furthermore, the calculated energy[22] of the seven-membered transition state for the conformation $^1C_4$ is approximately 1 kcal/mol lower than the corresponding energy of the transition state for the abstraction reaction in the conformation $^4C_1$. The structure and stereochemistry of spiro **34** were deduced from its spectroscopic data, COSY, TOCSY, HMBC, and HMQC experiments, and confirmed by X-ray crystallographic analysis of a crystalline *p*-nitrobenzoate ester derivative **36**.[19] Both rings adopt a chair conformation with a maximum number of anomeric effects, leaving the methoxy group in the axial orientation.

Treatment of silyl ether derivative **34** with TBAF gave rise to alcohol **35**, which underwent intramolecular hydrogen abstraction to give the desired trioxadispiroacetals **37** and **38** in 78% yield. These compounds, as in the case of the other trioxadispiro prepared above, are also highly sensitive to traces of acid, and it was necessary to isolate them very carefully. The ^{1}H NMR spectrum of **37** showed a proton at δ 3.22 as a triplet of J = 2.9 Hz, indicating the axial disposition for the methoxyl group at C_{13}, and a strong deshielding for the axial proton at C_{14} (δ 2.67) owing to the 1.3-diaxial interactions with the oxygen atoms of the two adjacent rings.[9c,g] This confirmed that the central ring adopted the same chair conformation as that of its precursor alcohol, the stereochemistry of the chiral centers being established as 5*R*,7*S*,13*S*.

For compound **38**, we observed that the proton at C_{13} appears as a double doublet at δ 3.12 (J = 3.9, 9.5 Hz), indicating an equatorial orientation for the methoxyl group. The ROESY spectrum showed a spatial connectivity between H_{12} and H_{14} revealing the preference for this compound to exist in the conformation $^4C_1$ for

the central ring with two anomeric effects and the methoxyl group in equatorial position. The other conformation, $^1C_4$, with the same number of anomeric effects but with an axial methoxyl group, is less favored by 1.6 kcal/mol as determined by molecular mechanics. Compound **38** is then a C_5 epimer of **37**, and its stereochemistry is consequently 5*S*,7*S*,13*S*.

In conclusion, we have prepared four of eight possible isomers of the target molecule demonstrating the usefulness of a double IHA reaction to construct the lateral heterocyclic rings in this type of compounds. Despite the fact that the acid-sensitive nature of the models precluded the equilibration of the acetalic centers and, hence, the synthesis of the pair of enantiomers proposed, this methodology is particularly convenient when a specific stereochemistry is required at the spirocenters, since thermodynamically less stable isomers can also be obtained.

Experimental Section

General. Melting points were determined with a hot-stage apparatus and are uncorrected. Optical rotation measurements were recorded at room temperature in $CHCl_3$. IR spectra were recorded in $CHCl_3$ solutions unless otherwise stated. NMR spectra were determined at 200, 400, or 500 MHz for ^1H and 50.3 or 100.6 MHz for ^{13}C for $CDCl_3$ solutions unless otherwise stated in the presence of TMS as internal standard. Phase-sensitive ROESY spectra were measured with a mixing time of 700 ms. Mass spectra were determined at 70 eV unless otherwise specified. Merck silica gel 60 PF_{254} and 60 (0.063−0.2 mm) were used for preparative thin-layer chromatography (TLC) and column chromatography, respectively, unless otherwise stated. Circular layers of 1 mm of Merck silica gel 60 PF_{254} were used on a Chromatotron for centrifugally assisted chromatography. Commercial reagents and solvents were analytical grade or were purified by standard procedures prior to use.[25] All reactions involving air- or moisture-sensitive materials were carried out under a nitrogen atmosphere. The spray reagent for TLC was vanillin (1 g) in H_2SO_4−EtOH (4:1; 200 mL). (Diacetoxyiodo)benzene (DIB) 98% was purchased from Aldrich.

Benzyl 2,6-Di-*O*-acetyl-3,4-*O*-isopropylidene-α-D-galactopyranoside (1). To a solution of compound benzyl α-D-galactopyranoside (3.1 g, 11.5 mmol) in dry acetone (94 mL) were added, under nitrogen at 0 °C, 2,2-dimethoxypropane (4.24 mL, 34.5 mmol) and TsOH (200 mg, 1.15 mmol), and the solution was stirred for 7 h at this temperature. The reaction mixture was allowed to warm to room temperature and treated with triethylamine (2.6 mL, 18.4 mmol) and pyridine (30 mL). The solution was stirred for a further 15 min and concentrated under reduced pressure. The residue was dissolved in dry pyridine (30 mL), acetic anhydride (15 mL) was added, and the solution was stirred at room temperature for 20 h. Water was then added and the mixture extracted with CH_2Cl_2. The combined extracts were washed with dilute HCl (10%), saturated solution of $NaHCO_3$, and water, dried over Na_2SO_4, and concentrated under reduced pressure. Dry column chromatography of the residue (hexanes−EtOAc, 80:20) gave the title compound **1** (2.5 g, 6.34 mmol, 56%): mp 95.5−96.7 °C (from acetone−*n*-hexane); $[\alpha]_D$ +177.6° (*c* = 0.500); IR 1740, 1370, 1240 cm^{-1}; ^1H NMR 1.33 (3H, s), 1.51 (3H, s), 2.08 (3H, s), 2.11 (3H, s), 4.22−4.28 (2H, m), 4.32−4.42 (3H, m), 4.51 (1H, d, *J* = 12.1 Hz), 4.71 (1H, d, *J* = 12.1 Hz), 4.91 (1H, dd, *J* = 3.7, 8.0 Hz), 5.03 (1H, d, *J* = 3.7 Hz), 7.30−7.33 (5H, m); ^{13}C NMR 20.84 (2 × q), 26.26 (q), 27.79 (q), 63.55 (t), 65.86 (d), 69.54 (t), 71.55 (d), 73.25 (d), 73.34 (d), 95.06 (d), 109.91 (s), 127.69 (2 × d), 127.95 (d), 128.41 (2 × d), 136.83 (s), 170.35 (s), 170.68 (s); MS (EI) *m*/*z* (rel intensity) 379 ([M − CH_3]$^+$, 22), 303 (2), 287 (38), 245 (16), 228 (49), 215 (100), 174 (24), 157 (62). Anal. Calcd for $C_{20}H_{26}O_8$: C, 60.90; H, 6.64. Found: C, 61.02; H, 6.30.

Benzyl 2,6-Di-*O*-acetyl-α-D-galactopyranoside (2). A solution of compound **1** (2.42 g, 6.1 mmol) in AcOH (80%, 170 mL) was stirred at 50 °C for 4 h and then concentrated under reduced pressure. Dry column chromatography of the residue (hexanes−EtOAc, 35:65) gave the title compound **2** (1.75 g, 4.94 mmol, 80%): mp 132.5−133.9 °C (from acetone−*n*-hexane); $[\alpha]_D$ +181.4° (*c* = 0.290); IR 3565, 1736, 1236 cm^{-1}; ^1H NMR 2.10 (3H, s), 2.11 (3H, s), 3.00 (2H, br s), 3.97−4.10 (3H, m), 4.20 (1H, dd, *J* = 6.6, 11.3 Hz), 4.40 (1H, dd, *J* = 5.9, 11.3 Hz), 4.53 (1H, d, *J* = 12.1 Hz), 4.72 (1H, d, *J* = 12.1 Hz), 5.01 (1H, dd, *J* = 3.8, 10.0 Hz), 5.09 (1H, d, *J* = 3.8 Hz), 7.32−7.36 (5H, m); ^{13}C NMR 20.80 (q), 20.89 (q), 63.18 (t), 67.98 (2 × d), 69.41 (d), 69.56 (t), 71.36 (d), 95.53 (d), 127.76 (2 × d), 127.92 (d), 128.41 (2 × d), 137.04 (s), 171.11 (s), 171.44 (s); MS (EI) *m*/*z* (rel intensity) 337 ([M − OH]$^+$, 1), 287 (7), 263 (29), 229 (5), 203 (22), 187 (33), 169 (31), 91 (100). Anal. Calcd for $C_{17}H_{22}O_8$: C, 57.62; H, 6.26. Found: C, 57.59; H, 5.94.

Benzyl 2,6-Di-*O*-acetyl-3,4-*O*-thiocarbonyl-α-D-galactopyranoside (3). To a solution of diol **2** (1.71 g, 4.83 mmol) in dry acetonitrile (28 mL) was added under nitrogen 1,1′-thiocarbonyldiimidazole (2.58 g, 14.5 mmol), and the solution was stirred at room temperature for 5 h. The reaction mixture was then poured into brine and extracted with $CHCl_3$. The organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. Dry column chromatography of the residue (hexanes−EtOAc, 75:25 → 35:65) gave compound **3** (1.72 g, 4.34 mmol, 90%) and benzyl 2,6-di-*O*-acetyl-3,4-di-*O*-(1′*H*-imidazol-1′-ylthiocarbonyl)-α-D-galactopyranoside (**4**) (280 mg, 0.488 mmol, 10%). Compound **3**: $[\alpha]_D$ +123.1° (*c* = 0.316); IR 1748, 1231, 1134 cm^{-1}; ^1H NMR 2.08 (3H, s), 2.11 (3H, s), 4.29−4.41 (3H, m), 4.54 (1H, d, *J* = 12.0 Hz), 4.71 (1H, d, *J* = 12.0 Hz), 4.96 (1H, dd, *J* = 4.1, 7.2 Hz), 4.97 (1H, dd, *J* = 1.7, 7.0 Hz), 5.11 (1H, t, *J* = 7.1 Hz), 5.18 (1H, d, *J* = 4.0 Hz), 7.29−7.37 (5H, m); ^{13}C NMR 20.48 (q), 20.65 (q), 61.93 (t), 64.26 (d), 68.84 (d), 70.33 (t), 78.08 (d), 78.85 (d), 93.95 (d), 127.81 (2 × d), 128.32 (d), 128.54 (2 × d), 135.97 (s), 169.44 (s), 170.23 (s), 189.80 (s); MS (EI) *m*/*z* (rel intensity) 397 ([M + H]$^+$, 3), 305 (1), 289 (4), 263 (3), 230 (2), 187 (3), 139 (19), 107 (21), 91 (100). Anal. Calcd for $C_{18}H_{20}O_8S$: C, 54.53; H, 5.09; S, 8.07. Found: C, 54.81; H, 5.24; S, 8.03. Compound **4**: IR 1748, 1395, 1288, 1240 cm^{-1}; ^1H NMR 2.02 (3H, s), 2.03 (3H, s), 4.15 (2H, d, *J* = 6.7 Hz), 4.54 (1H, t, *J* = 6.5 Hz), 4.67 (1H, d, *J* = 12.2 Hz), 4.83 (1H, d, *J* = 12.2 Hz), 5.31 (1H, d, *J* = 3.7 Hz), 5.45 (1H, dd, *J* = 3.8, 10.7 Hz), 6.26 (1H, dd, *J* = 3.3, 10.7 Hz), 6.60 (1H, d, *J* = 3.1 Hz), 6.97 (1H, d, *J* = 2.0 Hz), 7.11 (1H, d, *J* = 2.0 Hz), 7.34 (1H, t, *J* = 1.5 Hz), 7.38−7.41 (5H, m), 7.62 (1H, t, *J* = 1.4 Hz), 8.17 (1H, s), 8.35 (1H, s); ^{13}C NMR 20.47 (q), 20.52 (q), 61.27 (t), 66.46 (d), 67.52 (d), 70.32 (t), 75.90 (d), 76.03 (d), 95.36 (d), 117.29 (d), 117.71 (d), 127.98 (2 × d), 128.34 (d), 128.55 (2 × d), 131.15 (d), 131.51 (d), 136.03 (s), 136.98 (d), 137.05 (d), 169.86 (s), 170.01 (s), 182.35 (s), 183.08 (s).

Benzyl 2,6-Di-*O*-acetyl-3,4-dideoxy-α-D-*erythro*-hex-3-enopyranoside (5). A solution of compound **3** (1.63 g, 4.12 mmol) in trimethyl phosphite (100 mL) was heated at reflux temperature for 4.5 h. The reaction mixture was then concentrated under high vacuum (1 mmHg), and the residue was purified by dry column chromatography (hexanes−EtOAc, 85:15) to give the title compound **5** (1.05 g, 3.28 mmol, 80%): IR 1736, 1372, 1228 cm^{-1}; ^1H NMR 2.08 (3H, s), 2.10 (3H, s), 4.17 (2H, d, *J* = 5.0 Hz), 4.41 (1H, m), 4.65 (1H, d, *J* = 12.3 Hz), 4.80 (1H, d, *J* = 12.3 Hz), 5.27 (1H, dd, *J* = 0.8, 4.3 Hz), 5.31 (1H, dddd, *J* = 1.7, 1.7, 3.5, 4.3 Hz), 5.75 (1H, dddd, *J* = 1.6, 1.6, 1.6, 10.6 Hz), 5.85 (1H, ddd, *J* = 1.4, 1.8, 10.6 Hz), 7.29−7.36 (5H, m); ^{13}C NMR 20.81 (2 × q), 65.24 (t), 66.26 (d), 67.06 (d), 70.12 (t), 93.88 (d), 124.34 (d), 127.79 (d), 127.87 (d), 127.92 (2 × d), 128.35 (2 × d), 137.27 (s), 170.31 (s), 170.73 (s); MS (EI) *m*/*z* (rel intensity) 247 ([M − CH_3COOCH_2]$^+$, 4), 229 (2), 213 (34), 184 (100), 169 (19), 142 (100), 108 (77), 91 (98). Anal. Calcd for $C_{17}H_{20}O_6$: C, 63.72; H, 6.30. Found: C, 63.82; H, 6.64.

(25) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: New York, 1988.

Benzyl 2,6-Di-*O*-acetyl-3,4-dideoxy-α-D-*erythro*-hexopyranoside (6). A suspension of **5** (100 mg, 0.312 mmol) and 20% $Pd(OH)_2$ on charcoal (40 mg) in EtOH (10 mL) was stirred at room temperature for 5 h under a hydrogen atmosphere. After the catalyst was filtered off, the solvent was removed under reduced pressure. Chromatotron chromatography (hexanes−EtOAc, 90:10) of the residue gave compound **6** (86 mg, 0.267 mmol, 85%) and benzyl 6-*O*-acetyl-2,3,4-trideoxy-α-D-*glycero*-hexopyranoside (2 mg, 0.007 mmol, 2%): $[\alpha]_D$ +92.4° (c = 0.840); IR 1732, 1240, 1023 cm^{-1}; ^1H NMR 1.33−2.08 (6H, m), 2.10 (3H, s), 4.06 (1H, m), 4.07 (2H, d, J = 1.6 Hz), 4.49 (1H, d, J = 11.8 Hz), 4.73 (1H, d, J = 11.8 Hz), 4.96 (1H, br s), 7.28−7.37 (5H, m); ^{13}C NMR 17.56 (t), 20.81 (q), 28.96 (t), 29.27 (t), 66.94 (d), 67.13 (t), 68.46 (t), 96.42 (d), 127.49 (d), 127.77 (2 × d), 128.30 (2 × d), 138.10 (s), 170.87 (s). MS (EI) m/z (rel intensity) 265 ([M + H]$^+$, 3), 264 (M$^+$, 1), 191 (5), 181 (11), 173 (8), 157 (100), 137 (37), 113 (25), 97 (100). Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.24; H, 7.80. Compound **6**: $[\alpha]_D$ +138.7° (c = 0.380); IR 1738, 1232, 1045 cm^{-1}; ^1H NMR 1.54−2.12 (4H, m), 2.05 (3H, s), 2.09 (3H, s), 4.03 (1H, m), 4.06 (2H, s), 4.57 (1H, d, J = 12.3 Hz), 4.77 (1H, d, J = 12.3 Hz), 4.79 (1H, ddd, J = 3.5, 5.0, 11.6 Hz), 4.98 (1H, d, J = 3.4 Hz), 7.30−7.37 (5H, m); ^{13}C NMR 20.72 (q), 20.90 (q), 22.70 (t), 26.31 (t), 66.02 (t), 66.22 (d), 68.90 (t), 69.90 (d), 94.91 (d), 127.65 (3 × d), 128.24 (2 × d), 137.44 (s), 170.23 (s), 170.68 (s); MS (EI) m/z (rel intensity) 323 ([M + H]$^+$, 1), 263 (1), 231 (1), 215 (100), 181 (15), 156 (34), 143 (99), 129 (31), 91 (98). Anal. Calcd for $C_{17}H_{22}O_6$: C, 63.34; H, 6.88. Found: C, 63.33; H, 6.93.

Benzyl 3,4-Dideoxy-α-D-*erythro*-hexopyranoside (7). To a solution of diacetate **6** (1.05 g, 3.26 mmol) in MeOH (45 mL) was added K_2CO_3 (901 mg, 6.52 mmol), and the solution was stirred at room temperature for 3 h. The reaction mixture was then poured into brine and extracted with $CHCl_3$. The organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure to give the title compound **7** (776 mg, 3.26 mmol, 100%): $[\alpha]_D$ +116.1° (c = 0.260); IR 3582, 2944, 1048 cm^{-1}; ^1H NMR 1.39−1.98 (6H, m), 3.51 (1H, dd, J = 6.5, 11.5 Hz), 3.62 (1H, dd, J = 3.3, 11.5 Hz), 3.64 (1H, m), 3.84 (1H, dddd, J = 0, 3.2, 6.4, 9.7 Hz), 4.56 (1H, d, J = 11.7 Hz), 4.80 (1H, d, J = 11.7 Hz), 4.94 (1H, d, J = 3.6 Hz), 7.31−7.39 (5H, m); ^{13}C NMR 25.91 (t), 26.98 (t), 65.28 (t), 68.11 (d), 69.06 (d), 69.38 (t), 97.70 (d), 127.89 (d), 127.95 (2 × d), 128.46 (2 × d), 137.45 (s); MS (EI) m/z (rel intensity) 239 ([M + H]$^+$, 7), 238 (M$^+$, 1), 237 ([M − H]$^+$, 3), 221 (54), 203 (6), 147 (2), 131 (25), 129 (47), 91 (100). Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.29; H, 7.62.

Benzyl 6-*O*-(*tert*-Butyldiphenylsilyl)-3,4-dideoxy-α-D-*erythro*-hexopyranoside (8). To a solution of diol **7** (365 mg, 1.53 mmol) in dry DMF (22 mL) were added *tert*-butyldiphenylsilyl chloride (0.92 mL, 3.53 mmol) and imidazole (480 mg, 7.06 mmol), and the solution was stirred at room temperature for 5 min. The reaction mixture was then poured into 10% HCl and extracted with CH_2Cl_2. The extracts were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography (hexanes−EtOAc, 97:3 → 80:20) to give compound **8** (578 mg, 1.21 mmol, 79%) and benzyl 2,6-di-*O*-(*tert*-butyldiphenylsilyl)-3,4-dideoxy-α-D-*erythro*-hexopyranoside (230 mg, 0.322 mmol, 21%): $[\alpha]_D$ +46.3° (c = 0.438); IR 3072, 2930, 1112 cm^{-1}; ^1H NMR 1.03 (9H, s), 1.04 (9H, s), 1.09−1.37 (2H, m), 1.57−1.67 (1H, m), 1.95−2.14 (1H, m), 3.45 (1H, dd, J = 5.0, 10.4 Hz), 3.58 (1H, dd, J = 6.1, 10.4 Hz), 3.73 (1H, ddd, J = 3.6, 3.6, 11.4 Hz), 3.83 (1H, dddd, J 1.9, 5.8, 5.8, 10.5 Hz), 4.47 (1H, d, J = 12.3 Hz), 4.57 (1H, d, J = 3.3 Hz), 4.74 (1H, d, J = 12.3 Hz), 7.28−7.44 (17H, m), 7.57−7.67 (8H, m); ^{13}C NMR 19.19 (2 × q), 26.62 (t), 26.80 (3 × q), 26.88 (3 × q), 27.08 (t), 66.75 (t), 68.22 (t), 68.74 (d), 70.40 (d), 97.21 (d), 127.37 (d), 127.53 (4 × d), 127.57 (4 × d), 127.95 (2 × d), 128.21 (2 × d), 129.57 (4 × d), 133.58 (2 × s), 134.06 (2 × s), 135.57−135.75 (8 × d), 138.16 (s); MS (EI) m/z (rel intensity) 549 ([M − BnOH − ^{t}Bu]$^+$, 1), 489 (Bu, 1), 411 (2), 401 (1), 363 (11), 267 (20), 239 (18), 213 (24), 199 (82), 91 (100). Anal. Calcd for $C_{45}H_{54}O_4Si_2$: C, 75.58; H, 7.61. Found: C, 75.25; H, 7.95. Compound **8**: $[\alpha]_D$ +47.9° (c = 0.196); IR 3576, 3070, 2932, 1063 cm^{-1}; ^1H NMR 1.08 (9H, s), 1.37−1.51 (1H, m), 1.64−1.97 (4H, m), 3.58 (1H, dd, J = 5.0, 10.3 Hz), 3.68 (1H, m), 3.71 (1H, dd, J = 5.8, 10.3 Hz), 3.86 (1H, dddd, J = 1.7, 5.4, 5.4, 11.0 Hz), 4.54 (1H, d, J = 11.7 Hz), 4.82 (1H, d, J = 11.7 Hz), 4.91 (1H, d, J = 3.5 Hz), 7.33−7.48 (11H, m), 7.67−7.74 (4H, m); ^{13}C NMR 19.24 (s), 26.81 (3 × q), 26.81 (t), 27.34 (t), 66.62 (t), 68.23 (d), 68.77 (t), 69.27 (d), 97.27 (d), 127.62 (4 × d), 127.78 (d), 127.98 (2 × d), 128.43 (2 × d), 129.63 (2 × d), 133.55 (2 × s), 135.60 (4 × d), 137.63 (s); MS (EI) m/z (rel intensity) 401 ([M − ^{t}Bu − H_2O]$^+$, 1), 311 (32), 291 (4), 251 (15), 233 (43), 207 (14), 91 (100). Anal. Calcd for $C_{29}H_{36}O_4Si$: C, 73.07; H, 7.61. Found: C, 73.23; H, 7.73.

Benzyl 6-*O*-(*tert*-Butyldiphenylsilyl)-3,4-dideoxy-2-*O*-methyl-α-D-*erythro*-hexopyranoside (9). To a solution of alcohol **8** (1.62 g, 3.40 mmol) in dry acetone (44 mL) was added, under nitrogen, pulverized NaOH (1.24 g, 0.031 mol). The reaction mixture was heated at 45 °C, and dimethyl sulfate (1.61 mL, 0.017 mol) was added dropwise. The solution was heated at reflux temperature for 2 h, poured into 10% aqueous solution of HCl, and extracted with CH_2Cl_2. The organic extracts were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography (hexanes−EtOAc, 95:5) to give the title compound **9** (1.45 g, 2.96 mmol, 87%): $[\alpha]_D$ +58° (c = 0.238); IR 3071, 2932, 2830, 1105 cm^{-1}; ^1H NMR 1.11 (9H, s), 1.32−1.53 (1H, m), 1.70−1.97 (3H, m), 3.34 (1H, m), 3.34 (3H, s), 3.59 (1H, dd, J = 4.9, 10.4 Hz), 3.70 (1H, dd, J = 5.8, 10.4 Hz), 3.91 (1H, dddd, J = 2.1, 5.4, 5.4, 11.5 Hz), 4.64 (1H, d, J = 12.2 Hz), 4.83 (1H, d, J = 12.2 Hz), 4.99 (1H, d, J = 3.3 Hz), 7.29−7.50 (11H, m), 7.70−7.76 (4H, m); ^{13}C NMR 19.23 (s), 23.30 (t), 26.81 (3 × q), 26.81 (t), 56.24 (q), 66.67 (t), 68.10 (t), 69.18 (d), 77.27 (d), 94.54 (d), 127.52 (d), 127.60 (4 × d), 128.12 (2 × d), 128.24 (2 × d), 129.60 (2 × d), 133.57 (2 × s), 135.61 (4 × d), 137.75 (s); MS (EI) m/z (rel intensity) 433 ([M − ^{t}Bu]$^+$, 3), 401 (5), 355 (3), 325 (78), 297 (14), 265 (19), 239 (28), 233 (76), 91 (100). Anal. Calcd for $C_{30}H_{38}O_4Si$: C, 73.43; H, 7.81. Found: C, 73.37; H, 7.95.

6-*O*-(*tert*-Butyldiphenylsilyl)-3,4-dideoxy-2-*O*-methyl-D-*erythro*-hexopyranose (10). To a solution of compound **9** (370 mg, 0.755 mmol) in dry CH_2Cl_2 (20 mL) was added, under nitrogen, the complex boron trichloride−dimethyl sulfide (812 mg, 4.53 mmol), and the solution was stirred at room temperature for 14 h. The reaction mixture was then poured into an aqueous saturated solution of $NaHCO_3$ and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated under reduced pressure. Chromatotron chromatography (hexanes−EtOAc, 80:20) of the residue gave the title compound **10** (225 mg, 0.562 mmol, 74%) as an anomeric mixture (α:β, 1:1): IR 3598, 3072, 2835, 1112 cm^{-1}; ^1H NMR 1.07 (18H, s), 1.28−1.55 (3H, m), 1.68−1.98 (4H, m), 2.15−2.24 (1H, m), 2.89−3.01 (2H, m), 3.26−3.35 (2H, m), 3.41 (3H, s), 3.47 (3H, s), 3.51−3.83 (3H, m), 4.04 (1H, dddd, J = 2.0, 5.3, 5.3, 11.0 Hz), 4.53 (1H, d, J = 7.4 Hz), 5.29 (1H, d, J = 3.3 Hz), 7.34−7.48 (12H, m), 7.65−7.71 (8H, m); ^{13}C NMR 19.15 (s), 19.19 (s), 22.22 (t), 26.56 (t), 26.77 (6 × q), 26.92 (t), 27.29 (t), 56.14 (q), 57.59 (q), 66.32 (t), 66.55 (t), 68.57 (d), 75.99 (d), 77.18 (d), 79.74 (d), 90.47 (d), 98.34 (d), 127.54 (8 × d), 129.53 (4 × d), 133.51 (4 × s), 135.49 (4 × d), 135.55 (4 × d); MS (EI) m/z (rel intensity) 383 ([M − OH]$^+$, 8), 343 (5), 325 (8), 305 (92), 265 (13), 249 (16), 221 (91), 199 (100). Anal. Calcd for $C_{23}H_{32}O_4Si$: C, 68.96; H, 8.05. Found: C, 69.13; H, 8.18.

6-*O*-(*tert*-Butyldiphenylsilyl)-1,3,4-trideoxy-2-*O*-methyl-1-(4′-pentenyl)-β-D-*erythro*-hexopyranose (11) and 6-*O*-(*tert*-Butyldiphenylsilyl)-1,3,4-trideoxy-2-*O*-methyl-1-(4′-pentenyl)-α-D-*erythro*-hexopyranose (12). To a solution of compound **10** (100 mg, 0.25 mmol) in dry THF (2 mL) were added, under nitrogen, CCl_4 (0.290 mL, 3 mmol) and Ph_3P (328 mg, 1.25 mmol), and the solution was stirred at reflux temperature for 3 h. The reaction mixture was cooled at room temperature, filtered over Celite 545, and concentrated under reduced pressure. The residue (105 mg) was dissolved in dry Et_2O (2.5 mL) and treated at 0 °C under nitrogen with a freshly prepared solution of 4-pentenylmagnesium bromide in Et_2O (2.73 mL, 0.3 mmol) and the reaction kept at 0 °C for 1 h. The reaction mixture was then poured into an aqueous solution of

ammonium chloride and extracted with Et_2O. The organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. Chromatotron chromatography (hexanes−EtOAc, 98:2) of the residue gave compounds **11** (18 mg, 0.04 mmol, 16%) and **12** (66 mg, 0.146 mmol, 58%). Compound **11**: $[\alpha]_D$ −33.7° (c = 0.326); IR 3072, 1639 cm^{-1}; ^1H NMR 1.06 (9H, s), 1.27−1.52 (3H, m), 1.54−1.91 (4H, m), 2.08 (2H, ddd, J = 0, 6.6, 13.3 Hz), 2.28 (1H, m), 2.84 (1H, ddd, J = 4.5, 9.6, 9.6 Hz), 3.11 (1H, ddd, J = 2.5, 8.7, 8.7 Hz), 3.36 (3H, s), 3.43 (1H, m), 3.56 (1H, dd, J = 5.1, 10.2 Hz), 3.73 (1H, dd, J = 5.7, 10.2 Hz), 4.94 (1H, br dd, J = 1.2, 10.1 Hz), 5.01 (1H, br dd, J = 1.2, 17.1 Hz), 5.83 (1H, dddd, J = 6.6, 6.6, 10.1, 17.0 Hz), 7.34−7.46 (6H, m), 7.68−7.73 (4H, m); ^{13}C NMR 1.21 (s), 24.78 (t), 26.76 (3 × q), 27.37 (t), 28.32 (t), 31.80 (t), 33.91 (t), 56.42 (q), 66.83 (t), 77.63 (d), 79.29 (d), 80.40 (d), 114.16 (t), 127.53 (4 × d), 129.50 (2 × d), 133.69 (s), 133.74 (s), 135.60 (4 × d), 139.06 (d); MS (EI) m/z (rel intensity) 451 ([M − H]$^+$, 2), 421 (5), 395 (97), 375 (48), 363 (100), 343 (32), 267 (40), 239 (21), 213 (25), 199 (57). Anal. Calcd for $C_{28}H_{40}O_3Si$: C, 74.29; H, 8.91. Found: C, 74.03; H, 8.93. Compound **12**: $[\alpha]_D$ +16.0° (c = 0.300); IR 3073, 1639 cm^{-1}; ^1H NMR 1.06 (9H, s), 1.35−1.89 (8H, m), 2.11 (2H, ddd, J = 0, 6.7, 13.3 Hz), 3.34 (3H, s), 3.37 (1H, m), 3.51−3.71 (3H, m), 3.94 (1H, ddd, J = 4.2, 4.2, 10.8 Hz), 4.96 (1H, br dd, J = 1.7, 10.2 Hz), 5.02 (1H, br dd, J = 1.8, 17.1 Hz), 5.82 (1H, dddd, J = 6.8, 6.8, 10.2, 17.0 Hz), 7.30−7.48 (6H, m), 7.65−7.72 (4H, m); ^{13}C NMR 19.18 (s), 23.44 (t), 24.07 (t), 24.54 (t), 26.13 (t), 26.81 (3 × q), 33.70 (t), 56.34 (q), 66.46 (t), 69.36 (d), 73.61 (d), 77.04 (d), 114.44 (t), 127.58 (4 × d), 129.56 (2 × d), 133.58 (2 × s), 135.58 (4 × d), 138.85 (d); MS (EI) m/z (rel intensity) 451 ([M − H]$^+$, 1), 421 (9), 395 (90), 375 (57), 363 (100), 343 (49), 267 (33), 239 (16), 213 (21), 199 (43), 147 (93). Anal. Calcd for $C_{28}H_{40}O_3Si$: C, 74.29; H, 8.91. Found: C, 74.17; H, 8.81

6-*O*-(*tert*-Butyldiphenylsilyl)-1,3,4-trideoxy-1-(4′-hydroxybutyl)-2-*O*-methyl-*β*-D-*erythro*-hexopyranose (13). A solution of compound **11** (102 mg, 0.226 mmol) in CH_2Cl_2/MeOH (15 mL, 1:1) was cooled at −78 °C, and ozone was introduced into the solution until it became blue. Then nitrogen was bubbled through the solution to expel excess ozone, and the mixture was allowed to warm to 0 °C. $NaBH_4$ (68 mg, 1.808 mmol) was added and the solution stirred for 12 h at room temperature. The reaction mixture was then poured into an aqueous solution of 10% HCl, extracted with $CHCl_3$, dried over Na_2SO_4, and concentrated under reduced pressure. Chromatotron chromatography of the residue (hexanes−EtOAc, 80:20) gave the title compound **13** (92 mg, 0.202 mmol, 89%): $[\alpha]_D$ −43.6° (c = 0.204); IR 3618, 3072, 1112 cm^{-1}; ^1H NMR 1.06 (9H, s), 1.26−1.87 (10H, m), 2.27 (1H, m), 2.84 (1H, ddd, J = 4.3, 9.8, 9.8 Hz), 3.11 (1H, ddd, J = 2.5, 8.8, 8.8 Hz), 3.36 (3H, s), 3.43 (1H, m), 3.55 (1H, dd, J = 5.2, 10.3 Hz), 3.63 (2H, t, J = 6.3 Hz), 3.72 (1H, dd, J = 5.9, 10.3 Hz), 7.33−7.47 (6H, m), 7.67−7.73 (4H, m); ^{13}C NMR 19.18 (s), 21.56 (t), 26.72 (3 × q), 27.32 (t), 28.23 (t), 31.74 (t), 32.69 (t), 56.38 (q), 62.75 (t), 66.76 (t), 77.64 (d), 79.24 (d), 80.40 (d), 127.52 (4 × d), 129.51 (2 × d), 133.62 (s), 133.65 (s), 135.56 (4 × d); MS (EI) m/z (rel intensity) 399 ([M − ^{t}Bu]$^+$, 17), 367 (24), 321 (6), 289 (21), 241 (22), 199 (100), 151 (55). Anal. Calcd for $C_{27}H_{40}O_4Si$: C, 71.01; H, 8.83. Found: C, 71.22; H, 8.89.

6-*O*-(*tert*-Butyldiphenylsilyl)-1,3,4-trideoxy-1-(4′-hydroxybutyl)-2-*O*-methyl-α-D-*erythro*-hexopyranose (14). A solution of compound **12** (240 mg, 0.531 mmol) in CH_2Cl_2/MeOH (35 mL, 1:1) was cooled at −78 °C, and ozone was introduced into the solution until it became blue. Then nitrogen was bubbled through the solution to expel excess ozone, and the mixture was allowed to warm to 0 °C. $NaBH_4$ (81 mg, 2.12 mmol) was added and the solution stirred for 4 h at room temperature. The reaction mixture was then poured into an aqueous solution of 10% HCl, extracted with $CHCl_3$, dried over Na_2SO_4, and concentrated under reduced pressure. Chromatotron chromatography of the residue (hexanes−EtOAc, 90:10 → 75:25) gave the title compound **14** (230 mg, 0.50 mmol, 95%): $[\alpha]_D$ +16.3° (c = 0.166); IR 3626, 1112 cm^{-1}; ^1H NMR 1.06 (9H, s), 1.26−1.69 (10H, m), 1.74−1.88 (2H, m), 3.34 (3H, s), 3.36 (1H, m), 3.52−3.73 (3H, m), 3.63 (2H, t, J = 6.4 Hz), 3.93 (1H, ddd, J = 3.8, 3.8, 10.9 Hz), 7.33−7.47 (6H, m), 7.65−7.71 (4H, m); ^{13}C NMR 19.21 (s), 21.48 (t), 23.35 (t), 24.63 (t), 25.92 (t), 26.83 (3 × q), 32.67 (t), 56.39 (q), 62.83 (t), 66.34 (t), 69.54 (d), 73.64 (d), 77.01 (d), 127.62 (4 × d), 129.62 (2 × d), 133.59 (2 × s), 135.61 (4 × d); MS (EI) m/z (rel intensity) 399 ([M − ^{t}Bu]$^+$, 17), 367 (48), 349 (9), 321 (23), 289 (66), 241 (22), 199 (51), 151 (100). Anal. Calcd for $C_{27}H_{40}O_4Si$: C, 71.01; H, 8.83. Found: C, 71.16; H, 8.90.

Reaction of 6-*O*-(*tert*-Butyldiphenylsilyl)-1,3,4-trideoxy-1-(4′-hydroxybutyl)-2-*O*-methyl-*β*-D-*erythro*-hexopyranose (13) with DIB/I_2. A solution of alcohol **13** (72 mg, 0.158 mmol) in cyclohexane (7 mL) containing DIB (72 mg, 0.221 mmol) and iodine (40 mg, 0.158 mmol) under nitrogen was irradiated at 40 °C for 1 h with two 100 W tungsten-filament lamps at 40 °C for 70 min. The reaction mixture was then poured into aqueous saturated $Na_2S_2O_3$, extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated. Chromatotron chromatography of the reaction residue (hexanes−EtOAc, 94:6) gave (1*R*)-6-*O*-(*tert*-butyldiphenylsilyl)-1,3,4-trideoxy-2-*O*-methyl-D-*erythro*-hexopyranose-1-spiro-2′-tetrahydropyran (**16**) (23.7 mg, 0.052 mmol, 33%) and (1*S*)-6-*O*-(*tert*-butyldiphenylsilyl)-1,3,4-trideoxy-2-*O*-methyl-D-*erythro*-hexopyranose-1-spiro-2′-tetrahydropyran (**15**) (34.5 mg, 0.076 mmol, 48%). Compound **16**: $[\alpha]_D$ −29.5° (c = 0.220); IR 3072, 2950, 1113 cm^{-1}; ^1H NMR 1.07 (9H, s), 1.25−1.81 (8H, m), 1.93−2.05 (2H, m), 3.03 (1H, dd, J = 4.7, 10.8 Hz), 3.44 (3H, s), 3.54−3.83 (4H, m), 4.10 (1H, ddd, J = 2.6, 11.4, 11.4 Hz), 7.34−7.44 (6H, m), 7.66−7.73 (4H, m); ^{13}C NMR 17.25 (t), 19.15 (s), 22.64 (t), 24.80 (t), 25.31 (t), 26.75 (3 × q), 26.75 (t), 57.95 (q), 61.42 (t), 66.80 (t), 72.67 (d), 81.81 (d), 99.16 (s), 127.60 (4 × d), 129.57 (2 × d), 133.57 (2 × s), 135.55 (4 × d); MS (EI) m/z (rel intensity) 454 (M$^+$, 1), 423 (4), 397 (7), 365 (100), 345 (26), 267 (40), 239 (36), 199 (38), 183 (36). Anal. Calcd for $C_{27}H_{38}O_4Si$: C, 71.33; H, 8.43. Found: C, 71.35; H, 8.44. Compound **15**: mp 100.2−101.8 °C (from acetone−n-hexane); $[\alpha]_D$ +5.3° (c = 0.304); IR 3072, 2933, 1113 cm^{-1}; ^1H NMR 1.07 (9H, s), 1.27−1.48 (3H, m), 1.56−1.84 (4H, m), 1.89−2.14 (3H, m), 2.93 (1H, dd, J = 4.8, 11.0 Hz), 3.38 (3H, s), 3.60 (1H, dd, J = 4.5, 10.0 Hz), 3.66−3.85 (3H, m), 3.70 (1H, dd, J = 5.9, 10.1 Hz), 7.36−7.44 (6H, m), 7.70−7.78 (4H, m); ^{13}C NMR 18.26 (t), 19.23 (s), 22.43 (t), 24.93 (t), 26.78 (3 × q), 27.03 (t), 30.64 (t), 57.19 (q), 60.57 (t), 66.87 (t), 69.43 (d), 81.57 (d), 96.47 (s), 127.61 (2 × d), 127.72 (2 × d), 129.57 (d), 129.58 (d), 133.76 (2 × s), 135.66 (2 × d), 135.68 (2 × d); MS (EI) m/z (rel intensity) 423 ([M − MeO]$^+$, 1), 397 (7), 365 (100), 345 (10), 267 (67), 239 (59), 199 (42), 183 (41). Anal. Calcd for $C_{27}H_{38}O_4Si$: C, 71.33; H, 8.43. Found: C, 71.61; H, 8.05.

Isomerization of (1*R*)-6-*O*-(*tert*-Butyldiphenylsilyl)-1,3,4-trideoxy-2-*O*-methyl-D-*erythro*-hexopyranose-1-spiro-2′-tetrahydropyran (16). To a solution of spiro compound **16** (25 mg, 0.055 mmol) in acetic acid (2 mL) was added a 0.3 M solution of HCl in acetic acid (0.25 mL). The mixture was stirred at room temperature for 2 h, poured into an aqueous solution of NaOH (10%), and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated under reduced pressure to give spiro compound **15** (25 mg, 0.055 mmol, 100%).

Reaction of 6-*O*-(*tert*-Butyldiphenylsilyl)-1,3,4-trideoxy-1-(4′-hydroxybutyl)-2-*O*-methyl-α-D-*erythro*-hexopyranose (14) with DIB/I_2. A solution of alcohol **14** (75 mg, 0.164 mmol) in cyclohexane (7.5 mL) containing DIB (85 mg, 0.262 mmol) and iodine (41 mg, 0.164 mmol) under nitrogen was irradiated in a manner similar to that described above for **13**. Chromatotron chromatography (hexanes−EtOAc, 95:5) of the residue gave (1*R*,3′*S*)-6-*O*-(*tert*-butyldiphenylsilyl)-1,3,4-trideoxy-2-*O*-methyl-D-*erythro*-hexopyranose-1-spiro-2′-[(3′-iodo)tetrahydropyran] (**18**) (2 mg, 0.003 mmol, 2%), compound **16** (16.5 mg, 0.036 mmol, 22%), (1*R*,3′*R*)-6-*O*-(*tert*-butyldiphenylsilyl)-1,3,4-trideoxy-2-*O*-methyl-D-*erythro*-hexopyranose-1-spiro-2′-[(3′-iodo)tetrahydropyran] (**17**) (11.6 mg, 0.02 mmol, 12%), and compound **15** (22 mg, 0.048 mmol, 29%). Compound **18**: $[\alpha]_D$ +11.3° (c = 0.142); IR 3068, 2931, 1104 cm^{-1}; ^1H NMR 1.05 (9H, s), 1.32−1.49 (2H, m), 1.61−1.80 (2H, m), 1.97−2.19 (3H, m), 2.61 (1H, m), 3.17 (1H, dd, J = 4.9, 10.5 Hz), 3.36 (3H, s), 3.56 (1H, dd, J = 4.4, 10.5 Hz), 3.66 (1H, dd, J = 6.0, 10.5 Hz), 3.78−3.90 (3H, m), 4.09 (1H, t, J = 4.3 Hz), 7.34−7.44

(6H, m), 7.67−7.73 (4H, m); ^{13}C NMR 19.18 (s), 22.66 (t), 23.56 (t), 26.44 (t), 26.74 (3 × q), 28.83 (d), 31.93 (t), 56.21 (q), 60.76 (t), 66.59 (t), 70.78 (d), 81.49 (d), 95.11 (s), 127.64 (4 × d), 129.62 (2 × d), 133.52 (2 × s), 135.61 (4 × d); MS (EI) *m*/*z* (rel intensity) 523 ([M − ^{t}Bu]$^+$, 2), 491 (18), 453 (6), 421 (3), 395 (92), 363 (33), 267 (34), 239 (12), 169 (100). Anal. Calcd for $C_{27}H_{37}O_4SiI$: C, 55.86; H, 6.42. Found: C, 55.71; H, 6.65. Compound **17**: $[\alpha]_D$ +38.1° (*c* = 0.304); IR 3072, 2932, 1104 cm^{-1}; ^{1}H NMR 1.06 (9H, s), 1.27−1.50 (2H, m), 1.58−1.75 (2H, m), 1.79−2.04 (2H, m), 2.31 (1H, m), 2.67 (1H, dddd, *J* = 4.1, 12.9, 12.9, 12.9 Hz), 3.46 (3H, s), 3.63 (1H, dd, *J* = 3.2, 9.9 Hz), 3.68−3.98 (5H, m), 4.71 (1H, dd, *J* = 4.5, 12.9 Hz), 7.39−7.48 (6H, m), 7.74−7.83 (4H, m); ^{13}C NMR 19.09 (s), 22.54 (t), 26.04 (t), 26.69 (3 × q), 28.90 (t), 30.96 (d), 32.84 (t), 57.27 (q), 60.13 (t), 66.31 (t), 71.14 (d), 79.34 (d), 96.59 (s), 127.69 (2 × d), 127.77 (2 × d), 129.51 (d), 129.59 (d), 133.36 (s), 133.55 (s), 135.68 (4 × d); MS (EI) *m*/*z* (rel intensity) 523 ([M − ^{t}Bu]$^+$, 1), 491 (5), 453 (5), 421 (4), 395 (83), 363 (20), 267 (33), 239 (29), 71 (100). Anal. Calcd for $C_{27}H_{37}O_4SiI$: C, 55.86; H, 6.42. Found: C, 55.72; H, 6.44.

Reduction of (1*R*,3′*R*)-6-*O*-(*tert*-Butyldiphenylsilyl)-1,3,4-trideoxy-2-*O*-methyl-D-*erythro*-hexopyranose-1-spiro-2′-[(3′-iodo)tetrahydropyran] (17). To a solution of iodide **17** (51 mg, 0.088 mmol) in dry benzene (8 mL) were added under nitrogen tributyltin hydride (0.118 mL, 0.440 mmol) and 2,2′-azobis(isobutironitrile) (AIBN) (2 mg, 0.013 mmol). The mixture was stirred at reflux temperature for 35 min, poured into water, and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated under reduced pressure. Chromatotron chromatography of the residue (hexanes−EtOAc, 94:6) gave the spiroacetal **15** (38.8 mg, 0.085 mmol, 97%).

Reduction of (1*R*,3′*S*)-6-*O*-(*tert*-Butyldiphenylsilyl)-1,3,4-trideoxy-2-*O*-methyl-D-*erythro*-hexopyranose-1-spiro-2′-[(3′-iodo)tetrahydropyran] (18). To a solution of iodide **18** (6.5 mg, 0.011 mmol) in dry benzene (1 mL) were added under nitrogen tributyltin hydride (15.1 μL, 0.056 mmol) and AIBN (1 mg, 0.006 mmol). The mixture was stirred at reflux temperature for 35 min, poured into water, and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated under reduced pressure. Chromatotron chromatography of the residue (hexanes−EtOAc, 94:6) gave the spiroacetal **15** (4.1 mg, 0.009 mmol, 80%).

(1*S*)-1,3,4-Trideoxy-2-*O*-methyl-D-*erythro*-hexopyranose-1-spiro-2′-tetrahydropyran (19). To a solution of spiro compound **15** (63 mg, 0.139 mmol) in dry THF (4 mL) was added under nitrogen tetrabutylammonium fluoride (91 mg, 0.347 mmol). The mixture was stirred at room temperature for 2.5 h, poured into a saturated solution of $NaHCO_3$, and extracted with $CHCl_3$. The organic layer was washed with brine, dried with Na_2SO_4, and concentrated under reduced pressure. Chromatotron chromatography (hexanes−EtOAc, 70:30) of the residue gave the title compound **19** (26.4 mg, 0.122 mmol, 88%): mp 88.0−89.2 °C (from Et_2O); $[\alpha]_D$ +43.3° (*c* = 0.164); IR 3600, 2944, 1066 cm^{-1}; ^{1}H NMR 1.37−2.12 (11H, m), 2.92 (1H, dd, *J* = 4.7, 11.2 Hz), 3.37 (3H, s), 3.50 (1H, dd, *J* = 7.0, 11.3 Hz), 3.64 (1H, dd, *J* = 3.3, 11.3 Hz), 3.69−3.82 (3H, m); ^{13}C NMR 18.75 (t), 21.95 (t), 24.63 (t), 26.16 (t), 30.26 (t), 57.08 (q), 60.59 (t), 65.51 (t), 68.93 (d), 81.27 (d), 96.37 (s); MS (EI) *m*/*z* (rel intensity) 217 ([M + H]$^+$, 23), 216 (M$^+$, 3), 215 ([M − H]$^+$, 7), 199 (2), 185 (34), 167 (3), 153 (17), 117 (26), 101 (100). Anal. Calcd for $C_{11}H_{20}O_4$: C, 61.09; H, 9.32. Found: C, 61.39; H, 9.11.

(1*S*)-1,3,4-Trideoxy-2-*O*-methyl-6-*O*-tosyl-D-*erythro*-hexopyranose-1-spiro-2′-tetrahydropyran (20). To a solution of alcohol **19** (69 mg, 0.319 mmol) in dry pyridine (7 mL) was added under nitrogen TsCl (244 mg, 1.276 mmol). The reaction mixture was stirred at room temperature for 15 h, poured into an aqueous solution of HCl (10%), and extracted with CH_2Cl_2. The combined extracts were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Chromatotron chromatography of the residue (hexanes−EtOAc, 85:15) gave the title compound **20** (118 mg, 0.319 mmol, 100%): $[\alpha]_D$ +18.5° (*c* = 0.362); IR 1363, 1176, 1099 cm^{-1}; ^{1}H NMR 1.26−1.82 (8H, m), 1.88−2.04 (2H, m), 2.45 (3H, s), 2.86 (1H, dd, *J* = 4.8, 11.1 Hz), 3.35 (3H, s), 3.54−3.70 (2H, m), 3.85 (1H, m), 3.99 (2H, d, *J* = 4.7 Hz), 7.35 (2H, d, *J* = 8.1 Hz), 7.81 (2H, d, *J* = 8.2 Hz); ^{13}C NMR 17.76 (t), 21.35 (q), 21.75 (t), 24.47 (t), 26.27 (t), 29.99 (t), 56.96 (q), 60.55 (t), 66.04 (d), 71.92 (t), 80.64 (d), 96.39 (s), 127.59 (2 × d), 129.54 (2 × d), 132.83 (s), 144.49 (s); MS (EI) *m*/*z* (rel intensity) 371 ([M + H]$^+$, 3), 370 (M$^+$, 2), 369 ([M − H]$^+$, 3), 339 (19), 198 (3), 167 (10), 155 (8), 101 (17), 58 (100).

(1*S*)-6-Allyl-1,3,4,6-tetradeoxy-2-*O*-methyl-D-*erythro*-hexopyranose-1-spiro-2′-tetrahydropyran (21). To a solution of *p*-toluenesulfonate **20** (83 mg, 0.224 mmol) in dry Et_2O (6 mL) was added, under nitrogen at 0 °C, allylmagnesium bromide in Et_2O (1.14 mL, 1.12 mmol). The mixture was stirred at room temperature for 2 h, poured into an aqueous solution of ammonium chloride, and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated under reduced pressure. Chromatotron chromatography (hexanes−EtOAc, 95:5) of the residue gave the title compound **21** (46 mg, 0.192 mmol, 85%): ^{1}H NMR 1.26−2.37 (14H, m), 2.91 (1H, dd, *J* = 4.8, 11.1 Hz), 3.37 (3H, s), 3.54−3.71 (3H, m), 4.97 (1H, dddd, *J* = 1.7, 1.7, 1.7, 10.5 Hz), 5.04 (1H, dddd, *J* = 1.7, 1.7, 1.7, 17.1 Hz), 5.87 (1H, dddd, *J* = 6.6, 6.6, 10.3, 16.9 Hz); ^{13}C NMR 18.26 (t), 22.57 (t), 24.93 (t), 30.29 (t), 30.70 (t), 30.97 (t), 34.97 (t), 57.06 (q), 60.60 (t), 67.77 (d), 81.54 (d), 96.28 (s), 114.34 (t), 138.62 (d); MS (EI) *m*/*z* (rel intensity) 239 ([M − H]$^+$, 3), 209 (1), 158 (34), 153 (2), 101 (22), 58 (100). Anal. Calcd for $C_{14}H_{24}O_3$: C, 69.96; H, 10.06. Found: C, 69.84; H, 9.93.

(1*S*)-1,3,4,6-Tetradeoxy-6-(2″-hydroxyethyl)-2-*O*-methyl-D-*erythro*-hexopyranose-1-spiro-2′-tetrahydropyran (22). A solution of compound **21** (40 mg, 0.167 mmol) in CH_2Cl_2/MeOH (11 mL, 1:1) was cooled at −78 °C, and ozone was introduced into the solution until it became blue. Then nitrogen was bubbled through the solution to expel excess ozone, and the mixture was allowed to warm to 0 °C. $NaBH_4$ (19 mg, 0.50 mmol) was added and the solution stirred for 3 h at room temperature. The reaction mixture was then poured into an aqueous solution of 10% HCl, extracted with $CHCl_3$, dried over Na_2SO_4, and concentrated under reduced pressure. Chromatotron chromatography of the residue (hexanes−EtOAc, 70:30 → 60:40) gave the title compound **22** (39.8 mg, 0.163 mmol, 98%): $[\alpha]_D$ +39.2° (*c* = 0.51); IR 3636, 3457 cm^{-1}; ^{1}H NMR 1.23−2.07 (14H, m), 2.18 (1H, br s), 2.88 (1H, dd, *J* = 4.8, 11.1 Hz), 3.34 (3H, s), 3.53−3.71 (3H, m), 3.64 (2H, t, *J* = 6.2 Hz); ^{1}H NMR (C_6D_6) 1.20−1.35 (2H, m), 1.47−1.71 (7H, m), 1.74−1.79 (1H, m), 1.83−2.03 (3H, m), 2.16 (1H, ddd, *J* = 4.1, 13.4, 13.4 Hz), 2.85 (1H, dd, *J* = 4.6, 11.6 Hz), 3.17 (1H, br s), 3.19 (3H, s), 3.58−3.65 (1H, m), 3.66−3.72 (4H, m); ^{13}C NMR 18.18 (t), 22.51 (t), 24.81 (t), 29.17 (t), 30.51 (t), 30.82 (t), 32.02 (t), 57.07 (q), 60.65 (t), 62.84 (t), 68.38 (d), 81.41 (d), 96.49 (s); ^{13}C NMR (100.6, C_6D_6) 18.73 (t), 22.93 (t), 25.31 (t), 29.61 (t), 30.99 (t), 31.31 (t), 32.46 (t), 56.61 (q), 60.67 (t), 62.55 (t), 68.61 (d), 81.90 (d), 96.75 (s); MS (EI) *m*/*z* (rel intensity) 245 ([M + H]$^+$, 4), 244 (M$^+$, 1), 243 ([M − H]$^+$, 4), 227 (10), 211 (19), 195 (31), 184 (100), 158 (100). Anal. Calcd for $C_{13}H_{24}O_4$: C, 63.89; H, 9.91. Found: C, 63.83; H, 9.61.

Reaction of (1*S*)-1,3,4,6-Tetradeoxy-6-(2″-hydroxyethyl)-2-*O*-methyl-D-*erythro*-hexopyranose-1-spiro-2′-tetrahydropyran (22) with DIB/I_2. A solution of alcohol **22** (20 mg, 0.082 mmol) in dry cyclohexane (5 mL) containing DIB (32 mg, 0.099 mmol) and iodine (21 mg, 0.082 mmol) under nitrogen was irradiated at room temperature for 4 h in a manner similar to that described above for **13**. Column chromatography of the reaction residue (hexanes−Et_2O, 85:15 → 70:30) gave (5*S*,7*S*,13*R*)-13-methoxy-1,6,8-trioxadispiro[4.1.5.3]pentadecane (**24**) (4.6 mg, 0.019 mmol, 23%) and (5*R*,7*S*,13*R*)-13-methoxy-1,6,8-trioxadispiro[4.1.5.3]pentadecane (**23**) (6.6 mg, 0.027 mmol, 33%). Compound **23**: ^{1}H NMR (C_6D_6) 1.27 (1H, d, *J* = 11.8 Hz), 1.42−1.49 (1H, m), 1.50−1.62 (3H, m), 1.75 (1H, br d, *J* = 12.7 Hz), 1.82−1.89 (1H, m), 1.91−2.00 (4H, m), 2.04−2.12 (2H, m), 2.31 (1H, ddd, *J* = 3.1, 7.9, 12.3 Hz), 3.25 (3H, s), 3.26 (1H, dd, *J* = 5.4, 8.8 Hz), 3.63−3.69 (1H, m), 3.73 (1H, ddd, *J* = 7.3, 7.3, 7.3 Hz), 3.86 (1H, ddd, *J* = 2.4, 12.5, 12.5 Hz), 4.02 (1H, ddd, *J* = 4.8, 8.3, 8.3 Hz); ^{13}C NMR (C_6D_6) 19.1 (t), 21.4 (t), 24.8 (t), 25.7 (t), 31.9 (t), 32.8 (t), 37.4

(t), 57.2 (q), 60.8 (t), 67.4 (t), 80.4 (d), 98.0 (s), 107.0 (s). Anal. Calcd for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15. Found: C, 64.32; H, 9.04. Compound **24**: ^{1}H NMR (C_6D_6) 1.36 (1H, br d, J = 14.3 Hz), 1.52−1.75 (7H, m), 1.93 (1H, ddd, J = 2.7, 2.7, 13.2 Hz), 1.97−2.07 (3H, m), 2.30 (1H, ddd, J = 4.4, 13.3, 13.3 Hz), 2.63 (1H, dddd, J = 3.3, 11.7, 13.8, 13.8 Hz), 2.97 (1H, dd, J = 3.8, 11.7 Hz), 3.28 (3H, s), 3.80−3.89 (2H, m), 4.01−4.08 (2H, m); ^{13}C NMR (C_6D_6) 19.3 (t), 19.8 (t), 24.7 (t), 25.8 (t), 32.3 (t), 34.9 (t), 40.0 (t), 56.03 (q), 61.5 (t), 69.2 (t), 82.5 (d), 97.6 (s), 105.9 (s); MS (EI) *m*/*z* (rel intensity) 241 ([M − H]$^+$, 1), 225 ([M − OH]$^+$, 1), 211 (1), 183 (1), 169 (2), 85 (20), 57 (100). Anal. Calcd for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15. Found: C, 64.23; H, 9.21.

1-[3′-(*tert*-Butyldiphenylsilyl)propyl]-1,2,3-trideoxy-4,6-*O*-isopropylidene-α-D-*erythro*-hexopyranose (26). A stirred solution of olefin **25** (1.95 g, 4.2 mmol) in EtOAc (20 mL) was treated with 20% $Pd(OH)_2$/C (195 mg, 10 wt %). A hydrogen atmosphere was introduced by using a hydrogen-filled balloon (repeated evacuation with aspirator). After consummation of starting material (monitored by TLC), the hydrogen was replaced with nitrogen. The reaction mixture was filtered through a Celite pad, and the filtrate was concentrated, followed by chromatography (hexanes−EtOAc, 95:5) to afford the reduced product **26** (1.569 g, 80%) along with the isomeric enol−ether 1-[3′-(*tert*-butyldiphenylsilyl)-propyl]-1,2,3-trideoxy-4,6-*O*-isopropylidene-D-*erythro*-hex-1-enopyranose (279 mg, 14%): $[\alpha]_D$ +32.6° (c = 2.1); IR (CCl_4) 3072, 2931, 1957−1823, 1671, 1428, 1103 cm^{-1}; ^{1}H NMR 1.06 (9H, s), 1.44 (3H, s), 1.54 (3H, s), 1.65−1.78 (2H, m), 2.05−2.20 (4H, m), 3.54 (1H, ddd, J = 5.4, 9.1, 10.7 Hz), 3.66 (2H, t, J = 6.3 Hz), 3.77 (1H, dd, J = 10.8, 10.8 Hz), 3.87 (1H, ddd, J = 6.2, 9.2, 9.2 Hz), 3.96 (1H, dd, J = 5.5, 10.8 Hz), 4.44 (1H, dd, J = 2.0, 5.0 Hz), 7.35−7.44 (6H, m), 7.65−7.70 (4H, m); ^{13}C NMR 19.09 (q), 19.19 (s) 26.84 (3 × q), 27.26 (t), 29.21 (q), 29.77 (t), 29.81 (t), 62.40 (t), 63.07 (t), 67.46 (d), 70.85 (d), 93.47 (d), 99.26 (s), 127.56 (4 × d), 129.51 (2 × d), 133.95 (2 × s), 135.53 (4 × d), 153.50 (s); MS (EI) *m*/*z* (rel intensity) 451 ([M − CH$_3$]$^+$, 6), 409 (100), 351 (100), 295 (64), 273 (47), 255 (24), 211 (35), 199 (100). Anal. Calcd for $C_{28}H_{38}O_4Si$: C, 72.06; H, 8.21. Found: C, 71.96; H, 7.88. Compound **26**: $[\alpha]_D$ +18.2° (c = 1.46); IR (CCl_4) 3072, 2946, 1957−1823, 1428, 1200, 1094 cm^{-1}; ^{1}H NMR 1.09 (9H, s) 1.43−1.72 (7H, m), 1.50 (3H, s), 1.56 (3H, s), 1.88−2.05 (1H, m), 3.37 (1H, ddd, J = 5.7, 9.1, 9.1 Hz), 3.55−3.72 (5H, m, 4-H), 3.85 (1H, m), 7.37−7.45 (6H, m), 7.66−7.71 (4H, m); ^{13}C NMR 19.16 (q), 19.16 (s), 24.76 (t), 26.09 (t), 26.85 (3 × d), 28.05 (t), 28.88 (t), 29.35 (q), 63.30 (t), 63.46 (t), 66.77 (d), 71.28 (d), 72.80 (d), 99.27 (s), 127.57 (4 × d), 129.52 (2 × d), 133.89 (2 × s), 135.49 (4 × d); MS (EI) *m*/*z* (rel intensity) 453 ([M − CH$_3$]$^+$, 7), 411 (30), 353 (14), 275 (21), 255 (4), 213 (7), 199 (100). Anal. Calcd for $C_{28}H_{40}O_4Si$: C, 71.75; H, 8.60. Found: C, 71.63; H, 8.67.

1-[3′-(*tert*-Butyldiphenylsilyl)propyl]-1,2,3-trideoxy-α-D-*erythro*-hexopyranose (27). A mixture of the acetonide **26** (2.04 g, 4.36 mmol), Amberlyst-15 (H^+) ion-exchange resin (600 mg), and MeOH (40 mL) was stirred at room temperature for 1 h. The Amberlyst resin was removed by filtration, the filtrate was concentrated, and the residue was chromatographed (hexanes−Et_2O, 10:90) to afford the diol **27** (1.64 g, 88%): $[\alpha]_D$ +20.2° (c = 1.03); ^{1}H NMR 1.07 (9H, s), 1.47−1.91 (8H, m), 2.22 (2H, bs), 3.44 (1H, m), 3.56 (1H, m), 3.68−3.79 (5H, m), 7.36−7.44 (6H, m), 7.65−7.70 (4H, m); ^{13}C NMR 19.15 (s), 26.84 (3 × d), 26.99 (t), 27.22 (t), 27.38 (t), 28.83 (t), 62.65 (t), 63.56 (t), 66.94 (d), 71.64 (d), 74.33 (d), 127.57 (4 × d), 129.53 (2 × d), 133.89 (2 × s), 135.50 (4 × d); MS (EI) *m*/*z* (rel intensity) 371 ([M − ^{t}Bu]$^+$, 2), 323 (1), 293 (93), 275 (36), 255 (7), 245 (18), 199 (100). Anal. Calcd for $C_{25}H_{36}O_4Si$: C, 70.05; H, 8.47. Found: C, 70.33; H, 8.65.

1-[3′-(*tert*-Butyldiphenylsilyl)propyl]-1,2,3-trideoxy-6-*O*-tosyl-α-D-*erythro*-hexopyranose (28). To a stirred solution of the diol **27** (1.52 g, 3.55 mmol) in dry pyridine (6.5 mL) at 0 °C was added TsCl (1 g, 5.25 mmol). After 4 h at 0 °C the excess TsCl was quenched with MeOH (1.2 mL), and the heterogeneous mixture was stirred for 20 min. The reaction mixture was diluted with Et_2O and sequentially washed with H_2O and brine. Drying (Na_2SO_4), concentration, and chromatography (hexanes−EtOAc, 90:10) gave the monotosylate **28** (1.8 g, 88%) and the ditosylate (214 mg, 8%): $[\alpha]_D$ +23.7° (c = 1.29); IR (CCl_4) 3071, 2931, 1956−1823, 1376, 1180 cm^{-1}; ^{1}H NMR (C_6D_6) 1.10−1.62 (6H, m), 1.22 (9H, s), 1.66−1.71 (2H, m), 1.88 (3H, s), 1.93 (3H, s), 3.22 (1H, m), 3.62 (2H, t, J = 6.0 Hz), 3.75 (1H, ddd, J = 5.4, 5.4, 5.4 Hz), 3.92 (1H, dd, J = 5.6, 10.5 Hz), 4.05 (1H, dd, J = 4.8, 10.5 Hz), 4.56 (1H, ddd, J = 5.6, 5.6, 5.6 Hz), 6.75 (2H, d, J = 8.1 Hz), 6.83 (2H, d, J = 8.1 Hz), 7.27−7.33 (6H, m), 7.76−7.88 (8H, m); ^{13}C NMR 19.14 (s), 21.62 (2 × d), 25.17 (t), 25.95 (t), 26.83 (3 × q), 28.30 (t), 28.41 (t), 63.34 (t), 67.75 (t), 70.56 (d), 71.50 (2 × d), 74.80 (d), 127.59 (4 × d), 127.67 (2 × d), 127.90 (2 × d), 129.55 (2 × d), 129.75 (2 × d), 129.97 (2 × d), 132.68 (s), 133.55 (s), 133.83 (2 × s), 135.47 (4 × d), 144.86 (s), 145.07 (s). Anal. Calcd for $C_{39}H_{48}O_8S_2Si$: C, 63.56; H, 6.57; S, 8.69. Found: C, 63.31; H, 6.55; S, 9.02. Compound **28**: $[\alpha]_D$ +8.1° (c = 0.54); IR (CCl_4) 3564, 3071, 2944, 1956−1823, 1371, 1178 cm^{-1}; ^{1}H NMR (C_6D_6) 1.24 (9H, s), 1.56−1.68 (9H, m), 1.86 (3H, s), 3.32−3.58 (3H, m), 3.66 (2H, t, J = 6.2 Hz), 4.14 (1H, dd, J = 2.5, 10.4 Hz), 4.32 (1H, dd, J = 4.9, 10.4 Hz), 6.72 (2H, d, J = 8.1 Hz), 7.28−7.34 (6H, m), 7.79−7.86 (6H, m); ^{13}C NMR 19.16 (s), 21.59 (q), 26.85 (3 × q), 26.98 (t), 27.18 (t), 28.70 (t), 63.48 (t), 65.58 (d), 69.35 (t), 71.90 (d), 72.97 (d), 127.59 (4 × d), 127.91 (2 × d), 129.54 (2 × d), 129.79 (2 × d), 132.88 (s), 133.92 (2 × s), 135.50 (4 × d), 144.84 (s); MS (EI, 30 eV) *m*/*z* (rel intensity) 525 ([M − ^{t}Bu]$^+$, 3), 353 (100), 293 (71), 275 (50), 199 (77), 155 (8). Anal. Calcd for $C_{32}H_{42}O_6SSi$: C, 65.95; H, 7.27; S, 5.49. Found: C, 65.84; H, 7.37; S, 5.52.

6-Allyl-1-[3′-(*tert*-butyldiphenylsilyl)propyl]-1,2,3,6-tetradeoxy-α-D-*erythro*-hexopyranose (29). To a solution of tosylate **28** (1.8 g, 3.09 mmol) in dry Et_2O (50 mL) was added, under nitrogen at 0 °C, allylmagnesium bromide (7 mL, 7 mmol, 1 M in Et_2O). The reaction mixture was stirred at 0 °C for 3 h, the cooling bath removed, and stirring continued at room temperature for 1 h. The reaction mixture was poured into aqueous saturated ammonium chloride and extracted with Et_2O, followed by washing with aqueous saturated $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated under reduced pressure. Column chromatograpy (hexanes−EtOAc, 90:10) of the residue gave the title compound **29** (1.12 g, 80%): $[\alpha]_D$ +22.3° (c = 0.68); IR (CCl_4) 3626, 3593, 3072, 2932, 1956−1823, 1640, 1112 cm^{-1}; ^{1} NMR (C_6D_6) 1.23 (9H, s), 1.28−1.84 (11H, m), 2.08−2.28 (2H, m), 3.22 (1H, ddd, J = 5.2, 5.2, 5.2 Hz), 3.40−3.49 (2H, m), 3.75 (2H, t, J = 6.0 Hz), 5.05 (1H, dd, J = 1.1, 10.2 Hz), 5.12 (1H, dd, J = 1.4, 17.1 Hz), 5.85 (1H, dddd, J = 6.6, 6.6, 10.3, 17.0 Hz), 7.28−7.32 (6H, m), 7.81−7.88 (4H, m); ^{13}C NMR 19.19 (s), 26.58 (t), 26.77 (t), 26.86 (3 × d), 28.73 (t), 29.47 (t), 29.76 (t), 30.18 (t), 63.68 (t), 68.63 (d), 69.60 (d), 76.12 (d), 114.85 (t), 127.57 (4 × d), 129.50 (2 × d), 133.98 (2 × s), 135.53 (4 × d), 138.18 (d); MS (EI) *m*/*z* (rel intensity) 435 ([M − OH]$^+$, 2), 395 ([M − ^{t}Bu]$^+$, 40), 377 (5), 317 (6), 299 (5), 275 (17), 199 (100). Anal. Calcd for $C_{28}H_{40}O_3Si$: C, 74.29; H, 8.91. Found: C, 74.20; H, 8.79.

6-Allyl-1-[3′-(*tert*-butyldiphenylsilyl)propyl]-1,2,3,6-tetradeoxy-4-*O*-methyl-α-D-*erythro*-hexopyranose (30). To a vigorously stirred suspension of the alcohol **29** (890 mg, 1.98 mmol) and pulverized sodium hydroxide (712 mg, 17.82 mmol) in dry acetone (7 mL) was added dropwise dimethyl sulfate (0.943 mL, 9.9 mmol) at 30 °C, after which the temperature was raised to 50 °C and maintained for 4 h. The cooled mixture was poured into ice−water and extracted with $CHCl_3$. Drying over Na_2SO_4 and concentration followed by chromatography (hexanes−EtOAc, 99:1) furnished the methyl ether **30** (669 mg, 73%) and starting alcohol **29** (232 mg, 25%) which was recycled. Compound **30**: $[\alpha]_D$ +26.0° (c = 0.48); IR (CCl_4) 3072, 2941, 2830, 1956−1823, 1640, 1111 cm^{-1}; ^{1}H NMR (C_6D_6) 1.23 (9H, s), 1.37−1.87 (10H, m), 2.16−2.36 (2H, m), 2.78 (1H, ddd, J = 4.1, 5.9, 5.9 Hz), 3.51 (3H, s), 3.55 (1H, m), 3.71 (1H, m), 3.74 (2H, t, J = 6.0 Hz), 5.05 (1H, dd, J = 1.0, 10.2 Hz), 5.15 (1H, dd, J = 1.7, 17.0 Hz), 5.92 (1H, dddd, J = 6.6, 6.6, 10.3, 16.9 Hz), 7.26−7.32 (6H, m), 7.80−7.87 (4H, m); ^{13}C NMR 19.19 (s), 23.27 (t), 26.85 (3 × d), 27.85 (t), 28.84 (t), 29.80 (t), 29.97 (2 × t), 56.24 (q), 63.76 (t), 69.95 (d), 73.14 (d), 77.88 (d), 114.67 (t), 127.55 (4 × d), 129.47 (2 × d), 134.02 (2 × s), 135.53 (4 × d), 138.42 (d); MS (EI) *m*/*z* (rel intensity) 467 ([M + H]$^+$, 2], 409 ([M − ^{t}Bu]$^+$, 55), 377 (100), 331 (9), 295 (17),

269 (24), 213 (56), 199 (100). Anal. Calcd for $C_{29}H_{42}O_3Si$: C, 74.63; H, 9.07. Found: C, 74.79; H, 8.79.

1-[3′-(*tert*-Butyldiphenylsilyl)propyl]-1,2,3,6-tetradeoxy-6-(3″-hydroxypropyl)-4-*O*-methyl-α-D-*erythro*-hexopyranose (31). To a solution of olefin **30** (315 mg, 0.676 mmol) in dry THF (1.5 mL) at 0 °C and under nitrogen was added dropwise a solution of BH_3.THF complex (0.6 mL, 0.6 mmol, 1 M in THF). After 1 h of stirring, the excess borane was quenched carefully by adding a drop of water. Dropwise addition of a mixture of 3 N NaOH (0.5 mL) and 30% hydrogen peroxide (0.25 mL), removal of the cooling bath, and continued stirring for 20 min resulted in a white heterogeneous mixture. Dilution with Et_2O, followed by washing with H_2O and brine, drying over Na_2SO_4, concentration, and concentrated. Chromatotron chromatography (hexanes−EtOAc, 60:40), gave the alcohol **31** (238 mg, 73%): $[\alpha]_D$ +25.8° (c = 0.84); IR (CCl_4) 3626, 3072, 2940, 2820, 1956−1823, 1111 cm^{-1}; ^{1}H NMR (C_6D_6) 1.24 (9H, s), 1.38−1.85 (15H, m), 2.81 (1H, ddd, J = 4.3, 4.3, 4.3 Hz), 3.17 (3H, s), 3.55 (2H, t, J = 5.7 Hz), 3.56 (1H, m), 3.73 (1H, m), 3.75 (2H, t, J = 6.0 Hz), 7.29−7.33 (6H, m), 7.82−7.87 (4H, m); ^{13}C NMR 19.15 (s), 21.89 (t), 23.16 (t), 26.82 (t), 26.82 (3 × q), 28.77 (t), 29.58 (t), 30.32 (t), 32.53 (t), 56.17 (q), 62.67 (t), 63.72 (t), 70.05 (d), 73.59 (d), 77.87 (d), 127.53 (4 × d), 129.45 (2 × d), 133.96 (2 × s), 135.48 (4 × d); MS (EI) m/z (rel intensity) 427 ([M − ^{t}Bu]$^+$, 7), 395 (12), 317 (11), 269 (7), 229 (3), 199 (57), 161 (39), 58 (100). Anal. Calcd for $C_{29}H_{44}O_4Si$: C, 71.86; H, 9.16. Found: C, 72.01; H, 9.19.

1-(3′-Hydroxypropyl)-1,2,3,6-tetradeoxy-6-(3″-hydroxypropyl)-4-*O*-methyl-α-D-*erythro*-hexopyranose (32). To a deoxygenated solution of compound **31** (27 mg, 0.056 mmol) in dry THF (1.5 mL) was added tetrabutylammonium fluoride (80 mg, 0.254 mmol), and the mixture was stirred at room temperature for 2 h. The solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2, washed with aqueous saturated $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated. Chromatotron chromatography (EtOAc → EtOAc−MeOH, 95:5) gave the alcohol **32** (13 mg, 95%): $[\alpha]_D$ +42° (c = 0.16); IR (CCl_4) 3636, 3402, 2941, 2868 cm^{-1}; ^{1}H NMR (C_6D_6) 1.26−1.50 (2H, m), 1.56−1.70 (13H, m), 2.33−2.40 (1H, m), 2.77−2.80 (1H, m), 3.16 (3H, s), 3.49−3.60 (5H, m), 3.76−3.79 (1H, m); ^{13}C NMR (C_6D_6) 22.46 (t), 23.72 (t), 27.28 (t), 29.79 (t), 30.52 (t), 30.70 (t), 32.91 (t), 55.80 (q), 62.49 (t), 62.76 (t), 70.28 (d), 73.44 (d), 78.44 (d); MS (EI) m/z (rel intensity) 247 ([M + H]$^+$, 3), 214 ([M − MeOH]$^+$, 2), 196 (27), 178 (6), 162 (10), 155 (32), 141 (26), 129 (100). Anal. Calcd for $C_{13}H_{26}O_4$: C, 63.37; H, 10.64. Found: C, 63.07; H, 10.96.

Reaction of 1-(3′-Hydroxypropyl)-1,2,3,6-tetradeoxy-6-(3″-hydroxypropyl)-4-*O*-methyl-α-D-*erythro*-hexopyranose (32) with DIB/I_2. A solution of alcohol **32** (13 mg, 0.053 mmol) in dry CCl_4 (1.5 mL) containing DIB (27 mg, 0.063 mmol) and iodine (18 mg, 0.053 mmol) under nitrogen was stirred at room temperature for 30 min. The reaction mixture was then poured into aqueous saturated $Na_2S_2O_3$ and extracted with Et_2O (previously filtered through K_2CO_3). The organic extracts were dried over Na_2SO_4, concentrated, and chromatographed on basic aluminum oxide 60 (70−230 mesh ASTM) Merck, activity grade I (hexanes−Et_2O, 50:50) to give **33** (7.7 mg, 60%): ^{1}H NMR (C_6D_6) 1.45−1.60 (8H, m), 1.74−1.78 (2H, m), 1.96−2.00 (4H, m), 2.14 (1H, m), 2.91 (1H, ddd, J = 1.3, 9.2, 9.2 Hz), 3.21 (3H, s), 3.50 (2H, t, J = 6.1 Hz), 3.82 (1H, ddd, J = 5.3, 8.0, 8.0 Hz), 3.88 (1H, ddd, J = 5.8, 7.9, 7.9 Hz), 3.96 (1H, ddd, J = 2.3, 9.1, 9.1 Hz); ^{13}C NMR (C_6D_6) 22.16 (t), 24.06 (t), 25.75 (t), 31.97 (t), 32.65 (t), 33.17 (t), 37.30 (t), 55.85 (q), 62.68 (t), 66.88 (t), 73.22 (d), 79.38 (d), 105.10 (s). Anal. Calcd for $C_{13}H_{24}O_4$: C, 63.90; H, 9.90. Found: C, 64.12; H, 9.78.

(5*S*)-1-[3′-(*tert*-Butyldiphenylsilyl)propyl]-1,2,3-trideoxy-4-*O*-methyl-α-D-*glycero*-pentopyranose-5-spiro-2″-tetrahydropyran (34). A solution of the alcohol **31** (50 mg, 0.103 mmol) in dry CCl_4 (5 mL) containing DIB (40 mg, 0.124 mmol) and iodine (13 mg, 0.051 mmol) under nitrogen was stirred at room temperature for 90 min. The reaction mixture was then poured into aqueous saturated $Na_2S_2O_3$, extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated. Chromatotron chromatography of the residue (hexanes−EtOAc, 97:3) yielded **34** (21.5 mg, 43%): $[\alpha]_D$ +47.1° (c = 0.78); IR (CCl_4) 3072, 2932, 2820, 1956−1823, 1112 cm^{-1}; ^{1}H NMR (C_6D_6) 1.08−1.12 (1H, m), 1.17 (9H, s), 1.20−1.95 (12H, m), 2.25 (1H, brd, J = 12.0 Hz), 2.92 (1H, t, J = 2.5 Hz), 3.07 (3H, s), 3.50 (1H, m), 3.58−3.62 (2H, m), 3.71−3.77 (2H, m), 7.21−7.23 (6H, m), 7.78−7.81 (4H, m); ^{13}C NMR (C_6D_6) 18.62 (t), 19.21 (s), 21.82 (t), 25.54 (t), 25.67 (t), 26.81 (3 × q), 29.23 (t), 32.19 (t), 32.64 (t), 56.56 (q), 60.04 (t), 64.35 (t), 68.80 (d), 78.61 (d), 96.36 (s), 127.74 (4 × d), 129.58 (2 × d), 134.25 (s), 134.28 (s), 135.99 (4 × d); MS (EI) m/z (rel intensity) 483 ([M + H]$^+$, 1), 451 ([M − MeO]$^+$, 1), 393 (31), 387 (13), 325 (8), 267 (22), 177 (56), 111 (19), 58 (100). Anal. Calcd for $C_{29}H_{42}O_4Si$: C, 72.16; H, 8.77. Found: C, 72.13; H, 8.40.

(5*S*)-1-(3′-Hydroxypropyl)-1,2,3-trideoxy-4-*O*-methyl-α-D-*glycero*-pentopyranose-5-spiro-2″-tetrahydropyran (35). To a deoxygenated solution of compound **34** (30 mg, 0.062 mmol) in dry THF (1 mL) was added tetrabutylammonium fluoride (50 mg, 0.165 mmol), and the mixture was stirred at room temperature for 2 h. The solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2, washed with aqueous saturated $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated. Chromatotron chromatography (hexanes−EtOAc, 70:30) gave the alcohol **35** (13 mg, 86%): $[\alpha]_D$ +72.1° (c = 0.49); IR (CCl_4) 3646, 3460, 2941, 2822, 1116 cm^{-1}; ^{1}H NMR (C_6D_6) 1.33−2.02 (13H, m), 2.35 (1H, dddd, J = 2.7, 2.7, 2.7, 13.2 Hz), 2.97 (1H, t, J = 2.7 Hz), 3.12 (3H, s), 3.53−3.71 (6H, m); ^{13}C NMR (C_6D_6) 18.78 (t), 21.96 (t), 25.56 (t), 25.84 (t), 29.57 (t), 32.36 (t), 33.00 (t), 56.82 (q), 60.34 (t), 62.93 (t), 69.32 (d), 78.79 (d), 96.75 (s); MS (EI) m/z (rel intensity) 245 ([M + H]$^+$, 4), 227 ([M − OH]$^+$, 2), 213 (2), 195 (10), 184 (18), 158 (31), 128 (18), 101 (100). Anal. Calcd for $C_{13}H_{24}O_4$: C, 63.91; H, 9.90. Found: C, 64.06; H, 9.83.

(5*S*)-1-[3′-(*p*-Nitrobenzoyl)propyl]-1,2,3-trideoxy-4-*O*-methyl-α-D-*glycero*-pentopyranose-5-spiro-2″-tetrahydropyran (36). To a solution of the alcohol **35** (3 mg, 0.012 mmol) in CH_2Cl_2 (0.1 mL) were added *p*-nitrobenzoyl chloride (6 mg, 0.032 mmol) and dry pyridine (4 μL), and the mixture was stirred at room temperature for 14 h. The reaction mixture was poured into ice−water and extracted with EtOAc. The organic extracts were washed with dilute HCl (10%) and aqueous saturated $NaHCO_3$, dried over Na_2SO_4, and concentrated under reduced pressure. Chromatography (hexanes−EtOAc 85:15) gave the *p*-nitrobenzoyl derivative **36** (4.7 mg, 97%) which crystallized from MeOH: mp 82.0−82.3 °C; ^{1}H NMR (C_6D_6) 1.19−2.05 (13H, m), 2.35 (1H, br d, J = 13.0 Hz), 2.99 (1H, t, J = 2.7 Hz), 3.13 (3H, s), 3.57−3.71 (3H, m), 4.21−4.30 (2H, m), 7.71 (2H, d, J = 9.0 Hz), 7.80 (2H, d, J = 9.1 Hz).

Reaction of (5*S*)-1-(3′-Hydroxypropyl)-1,2,3-trideoxy-4-*O*-methyl-α-D-*glycero*-pentopyranose-5-spiro-2″-tetrahydropyran (35) with DIB/I_2. A solution of alcohol **35** (20 mg, 0.082 mmol) in dry cyclohexane (5 mL) containing DIB (32 mg, 0.099 mmol) and iodine (21 mg, 0.082 mmol) under nitrogen was stirred at room temperature for 140 min. The reaction mixture was then poured into aqueous saturated $Na_2S_2O_3$ and extracted with Et_2O (previously filtered through K_2CO_3). The organic extracts were dried over Na_2SO_4, concentrated, and chromatographed on basic aluminum oxide 60 (70−230 mesh ASTM) Merck, activity grade I (*n*-pentane−Et_2O, 85:15) to give **37** (11.6 mg, 58%)and **38** (4 mg, 20%). Compound **37**: $[\alpha]_D$ +38.6° (c = 0.18); IR (CCl_4) 2931, 1618, 1440, 1378, 1207, 1121 cm^{-1}; ^{1}H NMR (C_6D_6) 1.41−1.55 (1H, m), 1.59−1.66 (6H, m), 1.76 (1H, dddd, J = 13.6, 3.7, 3.7, 3.7 Hz), 2.00−2.09 (2H, m), 2.14 (1H, dd, J = 8.0, 8.3 Hz), 2.26 (1H, ddd, J = 13.3, 13.3, 4.0 Hz), 2.36 (1H, br d, J = 13.3 Hz), 2.67 (1H, m), 3.18 (3H, s), 3.22 (1H, dd, J = 2.8, 3.1 Hz), 3.79−3.89 (2H, m), 4.07−4.15 (2H, m); ^{13}C NMR (C_6D_6) 19.1 (2 × t), 24.7 (t), 26.3 (t), 28.4 (t), 33.4 (t), 40.1 (t), 56.6 (q), 61.1 (t), 69.0 (t), 79.1 (d), 97.3 (s), 106.3 (s); MS (EI) m/z (rel intensity) 243 ([M + H]$^+$, 12), 242 (M$^+$, 16), 241 ([M − H]$^+$, 20), 225 (35), 211 (8), 209 (16), 193 (16), 142 (31), 84 (100). Anal. Calcd for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15. Found: C, 64.68; H, 8.78. Compound **38**: $[\alpha]_D$ +22.2° (c = 0.18); ^{1}H NMR (C_6D_6) 1.28−1.68 (6H, m), 1.84−2.03 (6H, m), 2.17 (1H, ddd, J = 2.7, 7.6, 7.6 Hz), 2.48 (1H, br d, J = 7.7 Hz), 3.12 (1H, dd, J = 3.9, 9.5 Hz), 3.38

(3H, s), 3.58−3.63 (1H, m), 3.70 (1H, ddd, J = 7.9, 7.9, 7.9 Hz), 3.99 (1H, ddd, J = 4.4, 8.2, 8.2 Hz), 4.06 (1H, ddd, J = 3.0, 11.0, 11.0 Hz); ^{13}C NMR (C_6D_6) 1.91 (t), 23.2 (t), 24.7 (t), 26.1 (t), 29.1 (t), 32.5 (t), 38.4 (t), 58.0 (q), 61.5 (t), 68.0 (t), 81.9 (d), 98.0 (s), 106.8 (s). Anal. Calcd for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15. Found: C, 64.21; H, 8.89.

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Supporting Information Available: X-ray crystallographic details for **15** (8 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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