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Synthesis of the monodeoxy derivatives of 2-(trimethylsilyl)ethyl β-lactoside *

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ABSTRACT

Monodeoxy derivatives of 2-(trimethylsilyl)ethyl (Me_3SiEt) β-lactoside were synthesized, by deoxygenation at the disaccharide level, for the 2′-, 3′-, 4′-, and 6′-monodeoxylactosides. The 2-, 3-, and 6-deoxy derivatives were synthesized by β-D-galactosylation of suitably protected monodeoxygenated Me_3SiEt glucosides. Silver silicate was shown to be an efficient glycosylation promoter in the preparation of the 2- and 3-deoxylactosides.

INTRODUCTION

The lactose moiety (β-D-Gal*p*-(1 → 4)-D-Glc*p*) occurs frequently in glycolipids, where it is located close to the lipid part. Several lactose-binding proteins have been identified, including lactosylceramide-binding adhesins on many bacteria and yeasts[1,2], antibodies directed to lactosylceramide[3,4], and lactose-binding endogenous lectins[5]. Several of these proteins recognize internal lactose epitopes of glycosphingolipids[1,4b]. Since lactose seems to be a common binder for many different proteins, monodeoxylactosides are of value for the investigation of hydrogen-bonding patterns in interactions between lactose and protein.

We now report the synthesis of seven monodeoxy analogues[6] (**2–8**) of Me_3SiEt lactoside (**1**). Methyl deoxy-β-lactosides were recently reported[7] with some experimental details for their preparation. Although simple methyl glycosides are relatively inexpensive and readily available starting materials, the oligosaccharides synthesized from them are not easily transformed into useful glycoconjugates. We have instead employed the Me_3SiEt group for anomeric protection because it is stable to most reaction conditions used in carbohydrate synthesis (several new conditions are reported here), and Me_3SiEt glycosides can been converted, typi-

* 2-(Trimethylsilyl)ethyl glycosides, Part 8. For Part 7, see ref. 10.
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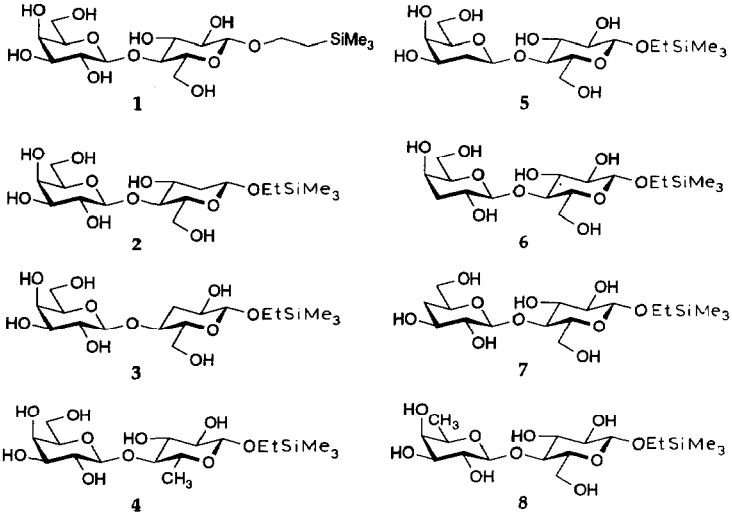


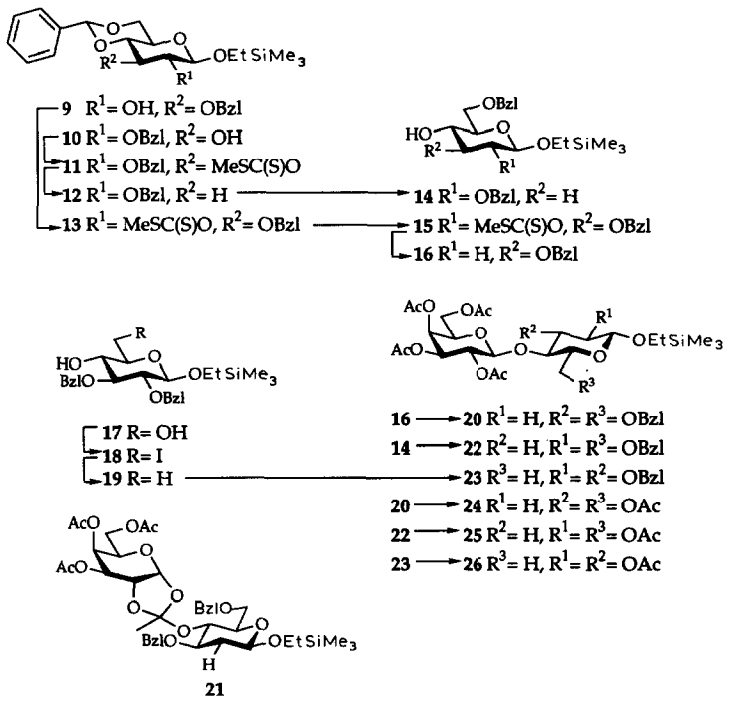
cally in better than 90% yield, into the corresponding 1-*O*-acyl-, 1-chloro-1-deoxy-, and hemiacetal sugars, en route to glycoconjugates[8–10]. Normally, these transformations occur late in multistep syntheses, thus making high yields important.

RESULTS AND DISCUSSION

The protected Me_3SiEt glucosides **9**[8] and **10**[8] were treated with sodium hydride–carbon disulfide–methyl iodide in tetrahydrofuran[11] to give the methylthio(thiocarbonyl) sugars **13** (90%) and **11** (93%). Tributyltin hydride-mediated reduction[11] of **11** gave **12** (98%). Reductive cleavage of the 4,6-*O*-benzylidene group[12] in **12** yielded the monodeoxyglycoside acceptor **14** (75%). The 4,6-*O*-benzylidene group of **13** was reductively cleaved[12] to give **15** (74%). Deoxygenation with tributyltin hydride[11] gave **16** (70%). The reason for the reversed order of reactions (**13** → **15** → **16** as compared to **11** → **12** → **14** above) was that the acidic conditions used in the reductive cleavage[12] ($NaBH_3CN$–HCl–tetrahydrofuran) might otherwise break the labile glycosidic bond of the 2-deoxyglycoside.

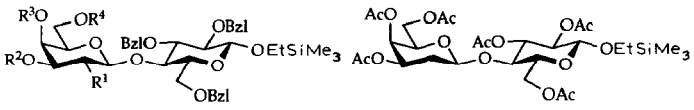
2-(Trimethylsilyl)ethyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside[8] was treated with iodine in refluxing methanol[13] to give the diol **17** (84%). Treatment of **17** with iodine–triphenylphosphine–imidazole in toluene[14] at 80°C gave the deoxyiodo sugar **18** (80%), which was hydrogenolyzed to give the 6-deoxyglucoside **19** (90%).

Silver triflate-promoted glycosylation of **19** with 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (acetobromogalactose) gave the disaccharide **23** (77%), whereas glycosylation with the alcohols **14** and **16** under similar conditions resulted in low yields of the desired deoxylactosides **22** and **20**, respectively. Thus, glycosyla-



tion of **14** with acetobromogalactose (1.5 equiv) and silver triflate (1.5 equiv) in dichloromethane in the presence of molecular sieve and tetramethylurea gave, in addition to recovered **14, 22** (31%), 2-(trimethylsilyl)ethyl 4-*O*-acetyl-2,6-di-*O*-benzyl-3-deoxy-β-D-*ribo*-hexopyranoside (10%), and, according to TLC, several slower moving products (not isolated). Formation of trans-acylation products during glycosylations with reactive alcohols is a well-known side reaction[15]. Compound **16** was consumed instantaneously when treated with silver triflate and acetobromogalactose, even at low temperature. According to TLC, several products were formed and the average yield of **20** was estimated to be below 10%.

The yields of **20** and **22** increased when the less reactive silver silicate[16] was used to promote the glycosylation. The reactions proceeded smoothly at room temperature when 2–2.5 equivalents of acetobromogalactose were used. The yields of **20** and **22** were typically in the range 65–70%. No trans-acetylation products were detected by TLC. The ortho-ester **21** was formed (67%) when tetramethylurea was used with **16**, acetobromogalactose, silver silicate, and molecular sieve in dichloromethane. Hydrogenolysis of the benzyl groups in **20, 22**, and **23**, followed by acetylation gave **24** (58%), **25** (97%), and **26** (77%). *O*-Deacetylation of **24–26** with methanolic sodium methoxide gave the deoxylactosides **2, 3**, and **4** in 94, 97, and 96% yield, respectively.



27 R^1 = OAc, R^2 = R^3 = R^4 = Ac
28 R^1 = OH, R^2 = R^3 = R^4 = H
29 R^1 = MeSC(S)O, R^2, R^3 = $(CH_3)_2C$, R^4 = $CH_3OC(CH_3)_2O$
30 R^1 = H, R^2 = R^3 = R^4 = H
5

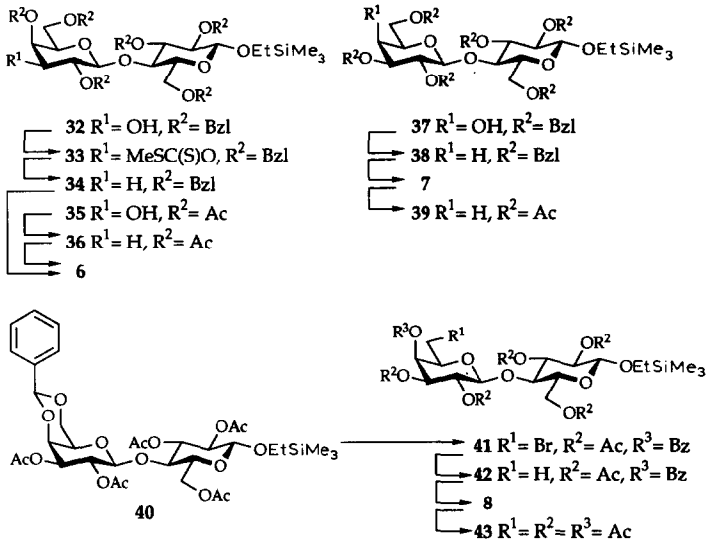
31

Silver triflate-mediated glycosylation of 2-(trimethylsilyl)ethyl 2,3,6-tri-*O*-benzyl-β-D-glucopyranoside[8] with acetobromogalactose gave **27** (87%), which was *O*-deacetylated to give **28**. Isopropylidenation of **28**, using 2,2-dimethoxypropane and camphorsulfonic acid, followed by treatment of the crude product with sodium hydride–carbon disulfide–methyl iodide gave the xanthate **29**, which was deoxygenated without previous purification. Removal of the isopropylidene protecting groups, using aqueous acetic acid (80%) at 60°C, yielded the monodeoxylactoside **30** (45% from **28**). The benzyl groups in **30** were hydrogenolyzed to furnish the deoxylactoside **5** (85%). The acetate **31** was prepared in order to aid the structure determination of **5**.

Regioselective allylation[17] of the lactoside **1**[8], followed by conventional benzylation and deallylation with palladium chloride in methanol[18], gave the alcohol **32** (39% from **1**). Compound **32** was converted into the xanthate **33** (87%), which was then treated with tributyltin hydride in refluxing toluene to give the 3′-deoxylactoside **34** (36%). In one experiment, **34** and **32** were formed from **33** in a ratio of ~5:4; a more reliable alternative was thus needed. Deoxygenation of the hexaacetate **35** (obtained in 51% yield from **1** by stannylation–benzylation–acetylation–hydrogenolysis) by sequential treatment with 1,1′-thiocarbonyldiimidazole[11] in 1,2-dimethoxyethane and tributyltin hydride in refluxing toluene allowed a quantitative conversion of **35** into **36**. *O*-Deacetylation of **36** gave the 3′-deoxylactoside **6** (97%). This seems to be the most efficient of the routes leading to **6**.

The known hexa-*O*-benzylated Me_3SiEt lactoside **37**[8] was readily converted into the 4′-deoxylactoside **38** (99%) by treatment of the corresponding xanthate with tributyltin hydride in refluxing toluene. This excellent result should be compared with the moderate yield obtained in the deoxygenation of compound **33**. The benzyl groups in **38** were removed by hydrogenolysis to give the 4′-deoxylactoside **7** (75%), which was acetylated to give **39** (98%).

Finally, treatment of compound **40**[8] with *N*-bromosuccinimide in refluxing carbon tetrachloride[19] gave the 6′-bromo-6′-deoxylactoside **41** in quantitative yield. Reduction of **41** with tributyltin hydride gave the 6′-deoxylactoside **42** (96%).



O-Deacylation of **42** gave **8** (97%), which was acetylated to give the hexa-acetate **43** (98%). It is noteworthy that **40** was converted into **43** in ~ 90% overall yield.

EXPERIMENTAL

General methods.—NMR spectra were recorded with a Varian XL-300 spectrometer. The solvent was used as internal reference unless otherwise stated. Optical rotations were measured with a Perkin–Elmer 141 polarimeter. TLC was performed on Kieselgel 60 F_{254} (Merck) with detection by UV light and/or by charring with sulfuric acid. Column chromatography was performed on Kieselgel 60 (Grace, 35–70 μm). Powdered molecular sieves were activated by heating with a flame until no more water condensed on the inside of the flask. Chloroform and CH_2Cl_2 were dried by passage through alumina (Merck, neutral, activity grade 1) immediately before use. Compounds **9**, **10**, **37**, and **40** were synthesized as reported[8].

*2-(Trimethylsilyl)ethyl 2-deoxy-4-O-(β-D-galactopyranosyl)-β-D-*arabino*-hexopyranoside* (**2**).—Compound **24** (7 mg, 10 μmol) was dissolved in dry MeOH (1 mL) and a catalytic amount of solid NaOMe was added. The solution was stirred overnight at room temperature. According to TLC (EtOAc–MeOH 9:1 and $CHCl_3$–MeOH–H_2O 200:150:3), **24** was completely converted into one product. The solution was neutralized by addition of silica gel, filtered (Celite), and concentrated. The residue was redissolved in water and freeze-dried to give **2** (4 mg, 94%); $[\alpha]_D^{25}$ −20° (*c* 0.4, CD_3OD). ^1H NMR data (D_2O): δ 4.74 (dd, 1 H, *J* 9.5, 1.1 Hz, H-1), 4.42 (d, 1 H, *J* 7.7 Hz, H-1′), 3.90 (d, 1 H, *J* 3.2 Hz, H-4′), 2.25 (ddd, 1 H, *J* 12.0, 4.2, 1.0 Hz, H-3*e*), 1.46 (ddd, 1 H, *J* 12.0, 10.0, 9.0 Hz, H-2*a*),

0.95 (m, 2 H, CCH_2Si), 0.00 [s, 9 H, $Si(CH_3)_3$]. ^{13}C NMR data (CD_3OD): δ 106.8, 102.2, 84.1, 78.6, 78.1, 76.4, 74.2, 72.6, 71.9, 69.1, 64.0, 63.9, 41.1, 20.5, 0.2.

*2-(Trimethylsilyl)ethyl 3-deoxy-4-O-(β-D-galactopyranosyl)-β-D-*ribo*-hexopyranoside* (**3**).—Compound **25** (42 mg, 62 μmol) was dissolved in dry MeOH (1 mL), a catalytic amount of solid NaOMe was added, and the solution was stirred at room temperature overnight. Neutralization with Duolite (H^+) resin, filtration, concentration, and lyophilization gave **3** (26 mg, 99%); $[\alpha]_D^{25}$ −14° (*c* 0.32, MeOH). ^1H NMR data (CD_3OD): δ 4.33 (d, 1 H, *J* 7.6 Hz, H-1′), 4.2 (d, 1 H, *J* 7.7 Hz, H-1), 4.00, 3.62 (2 ddd, 1 H each, 2 × CHCSi), 2.54 (dt, 1 H, *J* 12.3, 5.2, 4.0 Hz, H-3*e*), 1.58 (dd, 1 H, *J* 12.3 Hz, H-3*a*), 1.0 (m, 2 H, CCH_2Si), 0.03 [s, 9 H, $Si(CH_3)_3$]. ^{13}C NMR data (CD_3OD): δ 107.5, 88.4, 81.8, 78.2, 76.8, 76.5, 74.2, 71.8, 70.9, 69.4, 64.0, 41.3, 20.7, 0.2.

2-(Trimethylsilyl)ethyl 6-deoxy-4-O-(β-D-galactopyranosyl)-β-D-glucopyranoside (**4**).—Compound **26** (18 mg, 28 μmol) was treated with solid NaOMe in MeOH as described for **2** and **3**, yielding **4** (11 mg, 96%); $[\alpha]_D^{25}$ −12° (*c* 1.0, MeOH). ^1H NMR data (CD_3OD): δ 4.33, 4.26 (2 d, 1 H each, *J* 7.3 and 7.8 Hz, H-1′,1), 3.94 (ddd, 1 H, CHCSi), 3.82 (d, 1 H, *J* 2.8 Hz, H-4′), 3.48 (dd, 1 H, *J* 9.6, 3.2 Hz, H-3′), 3.22 (dd, 1 H, *J* 9.3, 7.8 Hz, H-2), 3.18 (t, 1 H, *J* 9.1 Hz, H-3 or H-4), 1.36 (d, 3 H, *J* 6.1 Hz, H-6), 1.00 (m, 2 H, CCH_2Si), 0.04 [s, 9 H, $Si(CH_3)_3$]. ^{13}C NMR data (CD_3OD): δ 105.4, 103.5, 86.4, 77.0, 76.4, 75.0, 74.8, 72.6, 72.0, 70.3, 68.1, 62.5, 19.1, 18.0, 1.4.

*2-(Trimethylsilyl)ethyl 4-O-(2-deoxy-β-D-*lyxo*-hexopyranosyl)-β-D-glucopyranoside* (**5**).—Compound **30** (500 mg, 0.72 mmol) was dissolved in AcOH (20 mL) and hydrogenolyzed (H_2, 1 atm, 345 mg Pd–C, 10%; room temperature) during 48 h. The mixture was filtered (Celite) and concentrated. Column chromatography of the residue (SiO_2, EtOAc–MeOH 9 : 1) gave **5** (260 mg, 85%); $[\alpha]_D^{25}$ −18° (*c* 1.1, MeOH). ^1H NMR data (D_2O): δ 4.50 (dd, 1 H, *J* 8.6, 1.2 Hz, H-1′), 4.2 (d, 1 H, *J* 8.1 Hz, H-1), 3.83 (ddd, 1 H, CHCSi), 3.7 (m, 2 H, H-3′ and H-6 or H-6′), 3.34 (m, 1 H, H-5), 3.11 (dd, 1 H, *J* 9.2, 8.1 Hz, H-2), 1.9 (m, 1 H, H-2′*e*), 1.5 (bdd, 1 H, *J* 12.1 Hz, H-2′*a*), 0.85 (m, 1 H, CCH_2Si), 0.02 [s, 9 H, $Si(CH_3)_3$]. ^{13}C NMR data (CD_3OD): δ 105.4, 103.6, 81.9, 78.9, 78.0, 76.4, 71.2, 70.3, 69.7, 64.4, 63.4, 37.2, 20.7, 0.1.

*2-(Trimethylsilyl)ethyl 4-O-(3-deoxy-β-D-*xylo*-hexopyranosyl)-β-D-glucopyranoside* (**6**).—(*a*) Compound **34** (172 mg, 0.18 mmol) was dissolved in AcOH (15 mL) and hydrogenolyzed (H_2, 1 atm, 118 mg Pd–C, 10%; room temperature) during 5 days. The mixture was filtered and concentrated, and the residue was chromatographed (SiO_2, EtOAc–MeOH 5 : 1) to give **6** (56 mg, 74%).

(*b*) Compound **36** (20 mg, 29 μmol) was treated with methanolic NaOMe. Neutralization with Duolite (H^+) resin, filtration, and evaporation of the solvent gave **6** (12 mg, 97%); $[\alpha]_D^{25}$ −16° (*c* 1.0, MeOH). ^1H NMR data (CD_3OD): δ 4.34 (d, 1 H, *J* 7.8 Hz, H-1′), 4.30 (d, 1 H, *J* 7.8 Hz, H-1), 4.00 (ddd, 1 H, CHCSi), 3.40 (m, 1 H, H-5), 3.20 (bt, 1 H, H-2), 2.08 (ddd, 1 H, *J* 13.6, 5.3, 3.2 Hz, H-3′*e*), 1.62 (ddd, 1 H, *J* 13.5, 10.1, 3.4 Hz, H-3′*a*), 1.00 (m, 2 H, CCH_2Si), 0.04 [s, 9 H,

$Si(CH_3)_3$]. ^{13}C NMR data (CD_3OD): δ 107.1, 103.7, 80.7, 80.2, 76.5, 76.4, 74.8, 68.2, 67.1, 66.7, 62.8, 62.0, 39.4, 19.1, −1.4.

*2-(Trimethylsilyl)ethyl 4-O-(4-deoxy-β-*D*-xylo-hexopyranosyl)-β-*D*-glucopyranoside* (**7**).—Compound **38** (1.6 g, 1.7 mmol) was dissolved in AcOH (15 mL) and hydrogenolyzed (1 atm, 806 mg Pd–C, 10%; 45°C) during 48 h. Filtration of the reaction mixture (Celite), concentration of the solution, and flash chromatography of the residue (SiO_2, CH_2Cl_2–MeOH 7:1) gave **7** (515 mg, 75%); $[\alpha]_D^{25}$ −15° (*c* 1.0, MeOH). ^1H NMR data (CD_3OD): δ 4.33, 4.30 (2 d, 1 H each, *J* 7.8 and 7.8 Hz, H-1,1′), 4.00 (m, 1 H, CHCSi), 3.87 (2 ddABq, 1 H each, *J* 2.5, 12.5 Hz and 4.0, 12.2 Hz, H-6′), 3.40 (m, 1 H, H-5), 3.23 (dd, 1 H, *J* 7.8, 9.2 Hz, H-2), 3.12 (dd, 1 H, *J* 7.9, 9.1 Hz, H-2′), 1.90 (ddd, 1 H, *J* 13.0, 5.1, 2.0 Hz, H-4′*e*), 1.41 (q, 1 H, *J* 13.0 Hz, H-4′*a*), 1.00 (m, 2 H, CH_2Si). ^{13}C NMR data (CD_3OD): δ 106.7, 105.2, 82.9, 78.4, 78.1, 79.0, 78.5, 75.9, 73.6, 69.7, 66.8, 63.6, 37.6, 20.7, 0.15.

*2-(Trimethylsilyl)ethyl 4-O-(6-deoxy-β-*D*-galactopyranosyl)-β-*D*-glucopyranoside* (**8**).—Compound **42** (26.5 mg, 36 μmol) was treated with methanolic NaOMe at room temperature for 12 h, then neutralized with Duolite (H^+) resin, and concentrated. The residue was chromatographed (SiO_2, EtOAc–MeOH 4:1) to give **8** (15 mg, 97%); $[\alpha]_D^{25}$ −17° (*c* 1.1, D_2O). ^1H NMR data (D_2O): δ 4.45 and 4.38 (2 d, 1 H each, *J* 8.0, 7.8 Hz, H-1,1′), 4.00 (ddd, 1 H, CHCSi), 3.93 (dABq, 1 H, H-6A), 3.82-3.68 (m, 3 H, H-6B,4′,5′), 3.63 (dd, 1 H, *J* 10.0, 3.6 Hz, H-3′), 3.45 (dd, 1 H, *J* 9.8, 7.9 Hz, H-2′), 3.25 (bt, 1 H, *J* 8.2 Hz, H-2), 1.23 (d, 3 H, *J* 5.2 Hz, H-6′), 1.00 (m, 2 H, CCH_2Si), 0.00 [s, 9 H, $Si(CH_3)_3$]. ^{13}C NMR data (CD_3OD): δ 106.6, 105.2, 82.6, 77.9, 76.4, 74.4, 74.0, 73.7, 69.8, 63.4, 20.7, 18.2, 0.2.

*2-(Trimethylsilyl)ethyl 2-O-benzyl-4,6-O-benzylidene-3-O-(methylthio)thiocarbonyl-β-*D*-glucopyranoside* (**11**).—To a solution of **10**[8] (3.16 g, 6.9 mmol) in THF (20 mL) were added NaH (461 mg, 10.6 mmol, 55% in oil) and a catalytic amount of imidazole[11]. After stirring the mixture for 40 min at room temperature, CS_2 (1.9 mL, 13.7 mmol) was added. The stirring was continued for 50 min, MeI (0.8 mL, 12.8 mmol) was added, and the stirring was continued until **10** was consumed according to TLC (~ 30 min). Excess of NaH was destroyed by addition of water, and Et_2O (20 mL) was added. The organic layer was washed with satd aq $NaHCO_3$, dried (Na_2SO_4), and concentrated. Flash chromatography of the residue (SiO_2, heptane–EtOAc 8:1) gave **11** (3.5 g, 93%); $[\alpha]_D^{25}$ −28° (*c* 1.0, $CHCl_3$). ^1H NMR data ($CDCl_3$): δ 6.35 (t, 1 H, *J* 9.3 Hz, H-3), 5.5 (s, 1 H, PhC*H*), 4.84, 4.70 (ABq, 2 H, *J* 11.3 Hz, PhCH_2), 4.64 (d, 1 H, *J* 7.6 Hz, H-1), 4.38 (dd, 1 H, *J* 4.9, 10.5 Hz, H-6), 4.02 (ddd, 1 H, *J* 1.9, 9.1, 9.3 Hz, CHCSi), 3.77 (dd, 1 H, *J* 9.3, 10.3 Hz, H-4), 3.75 (m, 1 H, *J* 10.3 Hz, H-6), 3.65 (ddd, 1 H, *J* 1.9, 8.8, 9.4 Hz, CHCSi), 3.65 (m, 1 H, *J* 4.6, 10.0 Hz, H-5), 3.58 (dd, 1 H, *J* 7.6, 9.0 Hz, H-2), 2.56 (s, 3 H, SMe), 1.06 (t, 2 H, *J* 9.1 Hz, CCH_2Si), 0.05 [s, 9 H, $Si(CH_3)_3$]. Anal. Calcd for $C_{27}H_{36}O_6S_2Si$: C, 59.1; H 6.6. Found: C, 59.2; H, 6.6.

*2-(Trimethylsilyl)ethyl 2-O-benzyl-4,6-O-benzylidene-3-deoxy-β-*D*-ribo-hexopyranoside* (**12**).—A solution of **11** (3.3 g, 6.0 mmol) in dry toluene (70 mL) was added to a refluxing solution of tributyltin hydride (3.0 mL, 12 mmol) during

80 min[11]. A catalytic amount of azo-bisisobutyronitrile (AIBN) was added, and the reflux was continued overnight. The mixture was concentrated and the residue was flash-chromatographed (SiO_2, heptane–EtOAc 10:1) to give **12** (2.6 g, 98%); $[\alpha]_D^{25}$ −32° (*c* 1.0, $CHCl_3$). ^1H NMR data ($CDCl_3$): δ 5.50 (s, 1 H, PhC*H*), 4.84, 4.64 (2 d, 1 H each, *J* 12.0 Hz, PhCH_2), 4.50 (d, 1 H, *J* 7.6 Hz, H-1), 4.33 (dd, 1 H, *J* 4.9, 10.5 Hz, H-6), 4.01 (m, 1 H, CHCSi), 3.77-3.60 (m, 2 H, H-6 and CHCSi), 3.52 (dt, 1 H, *J* 11.6, 7.4, 4.8 Hz, H-4), 3.42 (m, 2 H, H-2,5), 2.43 (ddd, 1 H, *J* 4.7, 9.3, 11.8 Hz, H-3*e*), 1.75 (q, 1 H, *J* 11.5 Hz, H-3*a*), 1.06 (ddd, 2 H, *J* 1.6, 6.8, 9.5 Hz, CCH_2Si), 0.05 [s, 9 H, $Si(CH_3)_3$]. Anal. Calcd for $C_{25}H_{34}O_5Si$: C, 67.8; H 7.7. Found: C, 67.8; H, 7.9.

*2-(Trimethylsilyl)ethyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-(methylthio)thiocarbonyl-β-*D*-glucopyranoside* (**13**).—Compound **9**[8] (3.1 g, 6.7 mmol) was treated with NaH, CS_2, and MeI as described in the preparation of **11**. Flash chromatography (SiO_2, EtOAc–heptane 1:5) gave **13** (3.3 g, 90%); mp 120–121°C, $[\alpha]_D^{25}$ −29° (*c* 1.0, $CHCl_3$). ^1H NMR data ($CDCl_3$): δ 6.04 (dd, 1 H, *J* 7.9, 8.3 Hz, H-2), 5.58 (s, 1 H, PhC*H*), 4.82, 4.62 (Abq, 2 H, *J* 11.9 Hz, PhCH_2), 4.62 (d, 1 H, *J* 7.8 Hz, H-1), 4.38 (dABd, 1 H, *J* 10.5, 5.0 Hz, H-6), 3.95, 3.57 (2 m, 1 H each, CH_2CSi), 3.90–3.77 (m, 3 H, H-3,4,6), 3.47 (m, 1 H, H-5), 2.58 (s, 3 H, CH_3), 0.9 (m, 2 H, CH_2Si), 0.00 [s, 9 H, $Si(CH_3)_3$]. Anal. Calcd for $C_{27}H_{36}O_6S_2Si$: C, 59.1; H 6.6. Found: C, 59.2; H, 6.7.

*2-(Trimethylsilyl)ethyl 2,6-di-*O*-benzyl-3-deoxy-β-*D*-ribo-hexopyranoside* (**14**).—A saturated solution of HCl in Et_2O was added to a mixture of **12** (2.4 g, 5.2 mmol), $NaBH_3CN$ (4.3 g, 58 mmol)[12], and activated molecular sieve (8.2 g, 3A) in THF (80 mL). The addition was continued until the organic phase became acidic (pH paper). The reaction was monitored by TLC and was shown to be complete within 5 min after the final addition of HCl. Solid $NaHCO_3$, CH_2Cl_2, and satd aq $NaHCO_3$ were added, the mixture was filtered, and the organic phase was dried ($MgSO_4$) and concentrated. Flash chromatography of the residue (SiO_2, EtOAc–heptane 2.5:1 → 1:1) gave **14** (1.8 g, 75%); $[\alpha]_D^{25}$ −28° (*c* 1.0, $CHCl_3$). ^1H NMR data ($CDCl_3$): δ 4.81, 4.65 (ABq, 2 H, *J* 11.9 Hz, PhCH_2), 4.57 (s, 2 H, PhCH_2), 4.40 (d, 1 H, *J* 7.1 Hz, H-1), 3.96 (ddd, 1 H, *J* 1.6, 7.3, 9.7 Hz, CHCSi), 3.77 (dABd, 1 H, *J* 4.9, 9.6 Hz, H-6), 3.67 (dABd, 1 H, *J* 6.8, 9.6 Hz, H-6), 3.63 {m, 1 H, H-4 [acetylated **14**: δ 4.73 (ddd, 1 H, *J* 4.9, 9.1, 11.2 Hz, H-4)]}, 3.57 (ddd, 1 H, *J* 1.9, 6.9, 9.6 Hz, CHCSi), 3.32 (ddd, 1 H, *J* 4.7, 7.0, 11.5 Hz, H-2), 3.02 (d, 1 H, *J* 3.0 Hz, HO-4), 2.34 (ddd, 1 H, *J* 4.7, 4.7, 12.7 Hz, H-3*e*), 1.6 (dd, 1 H, *J* 11.0, 12.2 Hz, H-3*a*), 1.02 (ddd, 2 H, *J* 1.7, 6.8, 9.5 Hz, CCH_2Si), 0.00 [s, 9 H, $Si(CH_3)_3$]. Anal. Calcd for $C_{25}H_{36}O_5Si$: C, 67.5; H 8.2. Found: C, 67.3 H, 8.0.

*2-(Trimethylsilyl)ethyl 3,6-di-*O*-benzyl-2-*O*-(methylthio)thiocarbonyl-β-*D*-glucopyranoside* (**15**).—Compound **13** (2.03 g, 3.7 mmol) was treated with $NaBH_3CN$ and HCl-satd Et_2O in THF as described in the preparation of **11**. Flash chromatography (SiO_2, EtOAc–heptane 1:1) gave **15** (1.5 g, 74%); $[\alpha]_D^{25}$ −34° (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 5.98 (dd, 1 H, *J* 9.1, 7.9 Hz, H-2), 4.79–4.55 (m, 4 H, CH_2Ph), 4.54 (d, 1 H, *J* 8.0 Hz, H-1), 3.96 (ddd, 1 H, *J* 10.1, 9.3, 6.2 Hz, CHCSi),

3.82–3.59 (m, 3 H, H-3,4,6), 3.57–3.48 (m, 2 H, H-5, CHCSi), 2.78 (OH), 2.59 (s, 3 H, SCH_3), 0.92 (m, 2 H, CCH_2Si), −0.01 [s, 9 H, $Si(CH_3)_3$]. Anal. Calcd for $C_{27}H_{38}O_6S_2Si$: C, 58.9; H 7.0. Found: C, 58.8; H, 7.0.

2-(Trimethylsilyl)ethyl 3,6-di-O-benzyl-2-deoxy-β-D-arabino-hexopyranoside (**16**). —A solution of tributyltin hydride (352 μL, 1.40 mmol) in dry toluene (15 mL) was added dropwise under Ar to a refluxing solution of **15** (567 mg, 1.03 mmol) in toluene (20 mL). A catalytic amount of AIBN was added, the mixture was stirred overnight, then concentrated, and the residue was chromatographed (SiO_2, toluene–EtOAc 4:1) to give **16** (320 mg, 70%); $[\alpha]_D^{25}$ −50° (*c* 1.0, $CHCl_3$). ^1H NMR data ($CDCl_3$): δ 4.70–4.57 (m, 4 H, PhC*H*), 4.48 (dd, 1 H, *J* 9.70, 2.0 Hz, H-1), 3.99 (m, 1 H, CHCSi), 3.80 (dABq, 2 H, *J* 10.3, 4.3, 10.3, 5.3 Hz, H-6), 3.59–3.38 (m, 4 H, H-3,4,5, CHCSi), 2.29 (ddd, 1 H, *J* 12.3, 4.8, 2.1 Hz, H-2*e*), 1.57 (m, 1 H, H-2*a*), 0.94 (m, 2 H, CCH_2Si), 0.03 (s, 9 H, $Si(CH_3)_3$); acetylated **16**: δ 4.9 (t, 1 H, *J* 9.3 Hz, H-4), 4.47 (dd, 1 H, *J* 9.6 and 2.0 Hz, H-1), 3.22 (ddd, 1 H, *J* 12.6, 5.0, 2.1 Hz, H-2*e*), 1.70 (ddd, 1 H, *J* 12.2, 9.8, 9.8 Hz, H-2*a*). Anal. Calcd for $C_{25}H_{36}O_5Si$: C, 67.5; H 8.2. Found: C, 67.6; H, 8.1.

2-(Trimethylsilyl)ethyl 2,3-di-O-benzyl-β-D-glucopyranoside (**17**).—2-(Trimethylsilyl)ethyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside[8] (995 mg, 1.8 mmol) was treated with iodine (100 mg) in refluxing MeOH (100 mL)[13]. The reaction was quenched after 18 h by addition of solid $Na_2S_2O_3$ and water. Filtration and concentration of the clear solution yielded a white solid, which was purified by flash chromatography (SiO_2, EtOAc–heptane 1:1) to give **17** (650 mg, 84%); $[\alpha]_D^{25}$ −22° (*c* 0.9, $CHCl_3$). ^1H NMR data ($CDCl_3$): δ 5.00–4.60 (m, 4 H, PhC*H*), 4.46 (d, 1 H, *J* 7.4 Hz, H-1), 3.99 (dd, 1 H, *J* 10.1, 8.1 Hz, CHCSi), 3.95–3.70 (2 m, 2 H, H-6), 3.64 (dd, 1 H, *J* 10.9, 8.5 Hz, H-3), 3.52 (bt, 1 H, *J* 11.0 Hz, H-4), 3.50–3.25 (m, 2 H, H-5, CHCSi), 3.42 (dd, 1 H, *J* 8.6, 7.3 Hz, H-2), 1.04 (dd, 2 H, *J* 10.1, 8.8 Hz, CCH_2Si), 0.04 [s, 9 H, $Si(CH_3)_3$]. Anal. Calcd for $C_{25}H_{36}O_6Si$: C, 65.2; H, 7.9. Found: C, 65.1; H, 8.4.

2-(Trimethylsilyl)ethyl 2,3-di-O-benzyl-6-deoxy-6-iodo-β-D-glucopyranoside (**18**). —Compound **17** (503 mg, 1.09 mmol) was dissolved in dry toluene (20 mL). Triphenylphosphine (430 mg, 1.64 mmol), iodine (388 mg, 1.53 mol), and imidazole (217 mg, 3.28 mmol) were added and the mixture was heated at 75°C under vigorous stirring for 30 min[14]. The reaction mixture was diluted with toluene, and solids were dissolved in acetone. The organic phases were pooled and washed three times with aq satd $NaHCO_3$, dried (Na_2SO_4), filtered, and concentrated. The residue was flash-chromatographed (SiO_2, EtOAc–heptane 1:3) to give **18** (496 mg, 80%); $[\alpha]_D^{25}$ −15° (*c* 0.8, $CHCl_3$). ^1H NMR data ($CDCl_3$): δ 5.05–4.60 (m, 4 H, PhC*H*), 4.45 (dd, 1 H, *J* 7.6, 3.4 Hz; virtual coupling to H-3; H-1), 4.05 (m, 1 H, CHCSi), 3.69 (m, 1 H, CHCSi), 3.56 (dABd, 1 H, *J* 9.8, 0.9 Hz, H-6), 3.42 (m, 2 H, H-2,3), 3.32 (bt, 1 H, H-5), 3.20 (m, 2 H, H-4,6). ^{13}C NMR data ($CDCl_3$): δ 103.0, 83.4, 82.0, 75.2, 74.6, 74.3, 73.5, 67.6, 18.5, 6.0, −1.4. Anal. Calcd for $C_{25}H_{35}IO_5Si$: C, 52.6; H 6.2. Found: C, 52.7; H, 6.1.

2-(Trimethylsilyl)ethyl 2,3-di-O-benzyl-6-deoxy-β-D-glucopyranoside (**19**).—Com-

pound **18** (445 mg, 0.78 mmol) was hydrogenolyzed (H_2, 1 atm, 190 mg Pd–C, 10%; room temperature) in EtOAc (25 mL) for 6 h. The mixture was filtered (Celite) and the solution was concentrated. The residue was flash-chromatographed (SiO_2, EtOAc–heptane 1 : 5) to give **19** (311 mg, 90%) as a colorless syrup; $[\alpha]_D^{25}$ −24° (*c* 0.9, $CHCl_3$). ^1H NMR data ($CDCl_3$): δ 5.00–4.60 (m, 4 H, PhC*H*), 4.40 (d, 1 H, *J* 7.4 Hz, H-1), 4.00, 3.60 (2 m, 1 H each, CH_2CSi), 3.40 (m, 2 H, H-2,3), 3.3 (m, 1 H, *J* 6.0 Hz, H-5), 5.20 (bt, *J* 9.5 Hz, H-4), 1.31 (d, 3 H, *J* 5.8 Hz, H-6), 1.02 (m, 2 H, CCH_2Si), 0.02 [s, 9 H, $Si(CH_3)_3$]. Anal. Calcd for $C_{25}H_{36}O_5Si$: C, 67.5; H 8.2. Found: C, 67.4 H, 8.0.

*2-(Trimethylsilyl)ethyl 3,6-di-*O*-benzyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-β-*D*-*arabino*-hexopyranoside* (**20**).—Compound **16** (70 mg, 0.16 mmol) and 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (120 mg, 0.29 mmol) were dissolved in CH_2Cl_2 (0.8 mL, distilled from CaH_2). Activated molecular sieve (350 mg, 3A) was added and the mixture was stirred under Ar at room temperature for 1 h. Silver silicate[16] (200 mg) was added, the mixture was protected from light, and the stirring was continued for 5 h. The mixture was filtered and concentrated, and the residue was chromatographed (SiO_2, EtOAc–heptane 2 : 1) to give **20** (80 mg, 66%); $[\alpha]_D^{25}$ −14.8° (*c* 0.7, $CHCl_3$). ^1H NMR data ($CDCl_3$): δ 5.27 (d, 1 H, *J* 3.4 Hz, H-4′), 5.13 (dd, 1 H, *J* 10.5, 8.0 Hz, H-2′), 4.86 (dd, 1 H, *J* 10.5, 3.5 Hz, H-3′), 4.74 (d, 1 H, *J* 8.0 Hz, H-1′), 4.73, 4.66, 4.52 (PhC*H*), 4.43 (dd, 1 H, *J* 9.6, 1.8 Hz, H-1), 4.09–3.86 (m, 3 H, *J* 11.1, 8.0, 11.2, 5.7 Hz, H-6, CHCSi), 3.79 (t, 1 H, *J* 8.9 Hz, H-4), 3.71, 3.72 (2 s, 1 H each, H-6′), 3.68–3.45 (m, 3 H, H-5,5′, CHCSi), 3.36 (ddt, 1 H, *J* 10.2, 9.4, 3.2 Hz, H-3), 2.30 (ddd, 1 H, *J* 12.7, 1.8, 5.0 Hz, H-2*e*), 2.11–1.90 (4 s, 3 H each, OAc), 1.64 (ddABq, 1 H, *J* 12.5, 9.6 Hz, H-2*a*), 0.96 (dd, 2 H, *J* 8.8, 8.0 Hz, CCH_2Si), 0.03 (s, 9 H, $Si(CH_3)_3$). Anal. Calcd for $C_{39}H_{54}O_{14}Si$: C, 60.5; H 7.0. Found: C, 60.3; H, 7.2.

*3,4,6-Tri-*O*-acetyl-α-D-galactopyranose 1,2-{[2-(trimethylsilyl)ethyl 3,6-di-*O*-benzyl-2,4-dideoxy-β-D-*arabino*-hexopyranosid-4-yl] orthoacetate}* (**21**).—Compound **16** (60 mg, 0.13 mmol) and 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (85 mg, 0.21 mmol) were dissolved in CH_2Cl_2 (1.5 mL, distilled from CaH_2). Tetramethylurea (30 μL, 0.25 mmol) and activated molecular sieve (300 mg, 3A) were added and the mixture was stirred under Ar at room temperature for 1 h. Silver silicate[16] (200 mg) was added, the mixture was protected from light, and the stirring was continued for 15 h. A second portion of 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (50 mg, 0.12 mmol) was added and the stirring was continued for 10 h. The mixture was filtered and concentrated, and the residue was chromatographed (SiO_2, EtOAc–heptane 1 : 3) to give **21** (70 mg, 67%); $[\alpha]_D^{25}$ +27° (*c* 0.6, $CHCl_3$). ^1H NMR data ($CDCl_3$): δ 5.80 (d, 1 H, *J* 4.6 Hz, H-1′), 5.40 (t, 1 H, *J* 2.7 Hz, H-4′), 4.90 (dd, 1 H, *J* 3.3, 3.0 Hz, H-3′), 4.70–4.50 (m, 4 H, PhC*H*), 4.45 (dd, 1 H, *J* 9.4, 1.8 Hz, H-1), 4.28 (m, 2 H, H-2′,5′), 4.1 (m, 3 H, H-6′ and CHCSi), 3.82 (dABd, 1 H, *J* 10.7, 2.2 Hz, H-6), 3.70–3.42 (m, 4 H, H-3,4,6, CHCSi), 3.36 (m, 1 H, H-5), 2.30 (ddd, 1 H, *J* 12.9, 5.4, 1.6 Hz, H-2*e*), 2.06, 2.05, 1.98 (3 s, 3 H each, OAc), 1.7 (s, 3 H, CH_3CO_3), 1.68 (m, 1 H, H-2*a*), 0.96 (m, 2 H,

CCH_2Si), 0.01 [s, 9 H, $Si(CH_3)_3$]. Anal. Calcd for $C_{39}H_{54}O_{14}Si$: C, 60.5; H 7.0. Found: C, 60.3; H, 7.1.

*2-(Trimethylsilyl)ethyl 2,6-di-*O*-benzyl-3-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-β-*D*-ribo-hexopyranoside* (**22**).—Compound **14** (65 mg, 0.15 mmol) and 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (112 mg, 0.27 mmol) were dissolved in CH_2Cl_2 (1.0 mL, distilled from CaH_2). Activated molecular sieve (200 mg, 3A) was added and the mixture was stirred under Ar at room temperature for 1 h. Silver silicate[16] (250 mg) was added, the mixture was protected from light, and the stirring was continued for 17 h. The mixture was filtered and concentrated, and the residue was chromatographed (SiO_2, EtOAc–heptane 2:1) to give **22** (80 mg, 71%); $[\alpha]_D^{25}$ −12° (*c* 1.0, $CHCl_3$). ^1H NMR data ($CDCl_3$): δ 5.43 (d, 1 H, *J* 5.3 Hz, H-4′), 5.13 (dd, 1 H, *J* 3.4, 10.4 Hz, H-3′), 4.82, 4.51 (ABq, 1 H each, *J* 12.0 and 11.8 Hz, PhCH_2), 4.67, 4.63 (ABq, 2 H, *J* 6.2 and 5.9 Hz, PhCH_2), 4.44 (d, 1 H, *J* 8.0 Hz, H-1′), 4.22 (d, 1 H, *J* 7.6 Hz, H-1), 4.20, 4.05 (dABq, 2 H, *J* 11.1, 6.6 Hz, H-6′), 4.02 (m, 1 H, CHCSi), 3.78 (dt, 1 H, *J* 1.0, 6.8, Hz, H-5′), 3.63 (m, 2 H, H-6), 3.40 (m, 1 H, H-5), 3.30 (ddd, 1 H, *J* 5.1, 7.6, 9.4 Hz, H-2), 2.46 (ddd, 1 H, *J* 4.4, 4.9, 12.3 Hz, H-3*e*), 2.15, 2.01, 1.97, 1.96 (4 s, 3 H each, OAc), 1.68 (m, 1 H, *J* 11.8 Hz, H-3*a*), 0.05 [s, 9 H, $Si(CH_3)_3$]. Anal. Calcd for $C_{39}H_{54}O_{14}Si$: C, 60.5; H, 7.0. Found: C, 60.5; H, 7.0.

*2-(Trimethylsilyl)ethyl 2,3-di-*O*-benzyl-6-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-β-*D*-glucopyranoside* (**23**).—Compound **19** (103 mg, 23 mmol) and 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (226 mg, 0.55 mmol) were dissolved in CH_2Cl_2 (4 mL), and silver trifluoromethanesulfonate (252 mg, 0.98 mmol), tetramethylurea (110 μL, 0.92 mmol), and molecular sieve (450 mg, 4A) were added. The mixture was stirred for 28 h, then filtered, and concentrated. The residue was chromatographed (SiO_2, EtOAc–heptane 1:3) to give **23** (138 mg, 77%); $[\alpha]_D^{25}$ +6° (*c* 1.0, $CHCl_3$). ^1H NMR data ($CDCl_3$): δ 5.28 (d, 1 H, *J* 3.4 Hz, H-4′), 5.18 (dd, 1 H, *J* 10.2, 7.6 Hz, H-2′), 4.98–4.83 (m, 4 H, PhC*H*, H-3′), 4.82 (d, 1 H, *J* 8.1 Hz, H-1′), 4.67 (ABd, 1 H, *J* 11.2 Hz, PhC*H*), 4.36 (d, 1 H, *J* 7.8 Hz, H-1), 3.97 (m, 2 H, CHCSi and H-6′), 3.77 (dABq, 1 H, *J* 10.8, 5.6 Hz, H-6′), 3.58 (m, 3 H, H-3,4,5′), 3.39 (m, 3 H, H-2,5, CHCSi), 2.10–1.90 (4 s, 3 H each, OAc), 1.30 (d, 3 H, *J* 5.4 Hz, H-6), 0.85 (m, 2 H, CCH_2Si), 0.00 [s, 9 H, $Si(CH_3)_3$]. Anal. Calcd for $C_{39}H_{54}O_{14}Si$: C, 60.5; H 7.0. Found: C, 60.6; H, 7.0.

*2-(Trimethylsilyl)ethyl 3,6-di-*O*-acetyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-β-*D*-arabino-hexopyranoside* (**24**).—Compound **20** (46.7 mg, 60.2 μmol) was subjected to hydrogenolysis (H_2, 1 atm, 46 mg Pd–C, 10%; room temperature) in MeOH (1.0 mL, containing 3 drops of AcOH). The reaction was complete after 4 h (TLC; EtOAc–MeOH 8:1). The reaction mixture was diluted with toluene, filtered (Celite), and concentrated. The crude material was dissolved in 1:1 Ac_2O–pyridine (2 mL), and the solution was stirred overnight at room temperature. Evaporation of the reagents and flash chromatography of the residue (Et_2O–toluene 1:1) gave **24** (23.7 mg, 58%); $[\alpha]_D^{25}$ −10° (*c* 1.1, $CDCl_3$). ^1H NMR data ($CDCl_3$): δ 5.35 (d, 1 H, *J* 3.5 Hz, H-4′), 5.15 (dd, 1 H, *J* 10.5, 7.8 Hz, H-2′),

5.05 (ddd, 1 H, *J* 11.6, 8.7, 5.7 Hz, H-3), 4.96 (dd, 1 H, *J* 10.6, 3.4 Hz, H-3′), 4.55 (d, 1 H, *J* 8.2 Hz, H-1′), 4.51 (dd, 1 H, *J* 9.6, 1.7 Hz, H-1), 4.40 (dABd, 1 H, *J* 11.9, 2.0 Hz, H-6), 4.20–4.00 (m, 3 H, H-6,6′), 3.98–3.83 (m, 2 H, H-5′, CHCSi), 3.65 (dd, 1 H, *J* 9.3, 8.8 Hz, H-4), 3.58–3.48 (m, 2 H, H-5, CHCSi), 2.30 (ddd, 1 H, *J* 12.6, 5.7, 1.8 Hz, H-2*e*), 2.15, 2.10, 2.08, 2.06, 1.97 (5 s, 18 H, OAc), 1.56 (m, H-2*a*), 0.93 (m, 2 H, CCH_2Si), 0.03 [s, 9 H, $Si(CH_3)_3$]. Anal. Calcd for $C_{29}H_{46}O_{16}Si$: C, 51.3; H, 6.8. Found: C, 50.8; H, 6.9.

*2-(Trimethylsilyl)ethyl 2,6-di-*O*-acetyl-3-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-β-*D*-*ribo*-hexopyranoside* (**25**).—Compound **22** (417 mg, 0.54 mmol) was hydrogenolyzed (H_2, 1 atm, 178 mg Pd–C, 10%; room temperature) in AcOH (15 mL). The reaction was monitored by TLC (EtOAc–heptane 1:1) The reaction mixture was filtered (Celite) and concentrated, and the crude material was acetylated in 1:1 Ac_2O–pyridine (10 mL). Flash chromatography (SiO_2, EtOAc–heptane 1:1) gave **25** (357 mg, 97%); $[\alpha]_D^{25}$ −11.0° (*c* 1.1, $CDCl_3$). ^1H NMR data ($CDCl_3$): δ 5.33 (d, 1 H, *J* 3.2 Hz, H-4′), 5.17 (dd, 1 H, *J* 10.5, 7.9 Hz, H-2′), 5.08 (dd, 1 H, *J* 10.4, 3.4 Hz, H-3′), 4.65 (ddd, 1 H, *J* 11.5, 7.8, 5.0 Hz, H-2), 4.50 (d, 1 H, *J* 7.9 Hz, H-1′), 4.41 (d, 1 H, *J* 7.8 Hz, H-1), 4.28 (dABd, 1 H, *J* 11.6, 1.7 Hz, H-6), 4.19–3.92 (m, 4 H, H-6,6′, CHCSi), 3.91 (dt, 1 H, *J* 6.4, 0.8 Hz, H-5′), 3.70–3.45 (m, 3 H, H-4,5, CHCSi), 2.64 (ddd, 1 H, *J* 11.3, 4.9, 4.5 Hz, H-2*e*), 2.14, 2.09, 2.07, 2.06, 2.05, 1.97 (6 s, 3 H each, OAc), 1.68 (q, 1 H, *J* 12.0 Hz, H-3*a*), 0.90 (m, 2 H, CCH_2Si), 0.009 [s, 9 H, $Si(CH_3)_3$]. Anal. Calcd for $C_{29}H_{46}O_{16}Si$: C, 51.3; H 6.8. Found: C, 51.7; H, 6.5.

*2-(Trimethylsilyl)ethyl 2,3-di-*O*-acetyl-6-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-β-*D*-glucopyranoside* (**26**).—Compound **23** (86 mg, 0.11 mmol) was dissolved in AcOH (4 mL) and hydrogenolyzed (H_2, 1 atm, 200 mg Pd–C, 10%; room temperature). The reaction mixture was filtered through Celite and concentrated. The crude material was acetylated overnight in 1:1 Ac_2O–pyridine. Flash chromatography (SiO_2, EtOAc–heptane 1:1) gave **26** (58 mg, 77%); $[\alpha]_D^{25}$ −24° (*c* 1.1, $CDCl_3$). ^1H NMR data ($CDCl_3$): δ 5.34 (d, 1 H, *J* 3.4 Hz, H-4′), 5.13 (m, 2 H, H-3,2′), 4.97 (dd, 1 H, *J* 10.3, 3.5 Hz, H-3′), 4.86 (dd, 1 H, *J* 9.8, 7.9 Hz, H-2), 4.54, 4.44 (2 d, 1 H each, *J* 7.9 Hz, H-1′,1), 4.10 (m, 2 H, H-6′), 3.93 (m, 2 H, H-5′, CHCSi), 3.50 (m, 3 H, H-4,5, CHCSi), 2.15, 2.06, 2.04, 2.03, 2.025, 1.97 (6 s, 3 H each, OAc), 1.34 (d, 3 H, *J* 5.5 Hz, CH_3), 0.91 (m, CCH_2Si), 0.00 [s, 9 H, $Si(CH_3)_3$]. Anal. Calcd for $C_{29}H_{46}O_{16}Si$: C, 51.3; H 6.8. Found: C, 51.0; H, 6.8.

*2-(Trimethylsilyl)ethyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galacto-pyranosyl)-β-*D*-glucopyranoside* (**27**).—2-(Trimethylsilyl)ethyl 2,3,6-tri-*O*-benzyl-β-*D*-glucopyranoside[8] (4.9 g, 8.9 mmol), silver trifluoromethanesulfonate (3.5 g, 13.6 mmol), and tetramethylurea (1.8 mL, 15 mmol) were dissolved in dry CH_2Cl_2 (60 mL) and molecular sieve (4 g, 3A) was added. The mixture was stirred at room temperature for 30 min, then cooled to −20°C. Freshly prepared 2,3,4,6-tetra-*O*-acetyl-α-*D*-galactopyranosyl bromide (5.5 g, 13.4 mmol) in CH_2Cl_2 (30 mL) was added dropwise during 15 min. The mixture was allowed to reach room temperature. The reaction was complete within 5 h according to TLC analysis. The

reaction mixture was filtered (Celite) and concentrated. Flash chromatography of the residue (EtOAc–heptane 1:3) gave **27** (6.8 g, 87%); $[\alpha]_D^{25}$ −3.4° (*c* 1.3, $CHCl_3$). ^1H NMR data ($CDCl_3$): δ 5.26 (d, 1 H, *J* 3.2 Hz, H-4′), 5.12 (dd, 1 H, *J* 10.4, 8. 1 Hz, H-2′), 4.95–4.75 (m, 6 H, H-3′, C*H*Ph), 4.67 (d, 1 H, *J* 8.1 Hz, H-1 or H-1′), 4.50 (m, 1 H, C*H*Ph), 4.37 (d, 1 H, *J* 7.7 Hz, H-1 or H-1′), 2.10, 1.98, 1.97 (3 s, 12 H, OAc), 1.03 (m, 2 H, CCH_2Si), 0.03 [s, 9 H, $Si(CH_3)_3$]. Anal. Calcd for $C_{46}H_{60}O_{15}Si$: C, 62.7; H, 6.9. Found: C, 62.2; H, 6.9.

*2-(Trimethylsilyl)ethyl 2,3,6-tri-*O*-benzyl-4-*O*-(β-*D*-galactopyranosyl)-β-*D*-glucopyranoside* (**28**).—Compound **27** (6.3 g, 7.2 mmol) was stirred with methanolic NaOMe overnight. The mixture was neutralized with Duolite (H^+) resin, then filtered, and concentrated to give **28** (5.1 g, 99%); $[\alpha]_D^{25}$ +26° (*c* 1.3, $CDCl_3$). ^1H NMR data ($CDCl_3$): δ 4.98–4.56 (m, 6 H, C*H*Ph), 4.52, 4.40 (2 d, 1 H each, *J* 7.7 Hz, H-1,1′), 1.03 (m, 2 H, CCH_2Si), 0.03 [s, 9 H, $Si(CH_3)_3$]. Anal. Calcd for $C_{38}H_{52}O_{11}Si$: C, 64.0; H, 7.4. Found: C, 63.9; H, 7.4.

*2-(Trimethylsilyl)ethyl 2,3,6-tri-*O*-benzyl-4-*O*-(2-deoxy-β-*D*-lyxo-hexopyranosyl)-β-*D*-glucopyranoside* (**30**).—Compound **28** (500 mg, 0.70 mmol) was suspended in 2,2-dimethoxypropane (25 mL), a catalytic amount of *p*-toluenesulfonic acid was added, and the reaction mixture was stirred overnight. Triethylamine was added and the solution was concentrated. The crude material was immediately dissolved in dry THF (3 mL, distilled from benzophenone ketyl). Sodium hydride (62 mg, 1.30 mmol) was added and the system was stirred at room temperature. After 40 min, CS_2 (0.4 mL, 2.9 mmol) and a catalytic amount of imidazole were added. The stirring was continued for 95 min, then MeI (140 μL, 2.4 mmol) was added. The reaction was monitored by TLC (EtOAc–heptane 1:2 + 0.1% of triethylamine). Excess of NaH was destroyed by addition of silica gel, the mixture was filtered and concentrated, and the residue was chromatographed (SiO_2, EtOAc–heptane 2:1 + triethylamine) to yield **29** (429 mg) as a syrup. A solution of **29** in dry toluene (4 mL) was added during 35 min to a refluxing solution of tributyltin hydride (180 μL, 0.67 mmol) in dry toluene (3 mL) under Ar. The solution was refluxed for 10 h, then concentrated, and the resulting syrup was chromatographed (SiO_2, EtOAc–heptane 6:1) to give 2-(trimethylsilyl)ethyl 2,3,6-tri-*O*-benzyl-2-deoxy-4-*O*-(3,4-*O*-isopropylidene-6-*O*-(2-methoxypropyl)-β-*D*-*lyxo*-hexopyranosyl)-β-*D*-glucopyranoside (277 mg, 69%). A portion (220 mg, 0.29 mmol) of this compound was dissolved in aq AcOH (80 vol%, 10 mL). The solution was heated at 60° for 45 min and concentrated. The resulting syrup was chromatographed (SiO_2, EtOAc–MeOH 9:1) to give **30** (173 mg, 83%; 45% overall yield from **27**); $[\alpha]_D^{25}$ +15° (*c* 1.3, $CHCl_3$). ^1H NMR data ($CDCl_3$): δ 4.95–4.48 (m, 6 H, PhCH_2), 4.47 (dd, 1 H, *J* 8.3, 2.2 Hz, H-1′), 4.39 (d, 1 H, *J* 7.6 Hz, H-1), 1.82 (ddd, 1 H, *J* 11.8, 4.7, 2.4 Hz, H-2′*e*), 1.60 (dd, 1 H, *J* 11.8, 10.3 Hz, H-2′*a*), 1.05 (m, 2 H, CCH_2Si), 0.03 [s, 9 H, $Si(CH_3)_3$]. Anal. Calcd for $C_{38}H_{52}O_{10}Si$: C, 65.5; H, 7.5. Found: C, 65.4; H, 7.5.

*2-(Trimethylsilyl)ethyl 2,3,6-tri-*O*-acetyl-4-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-lyxo-hexopyranosyl)-β-*D*-glucopyranoside* (**31**).—Compound **5** (256 mg, 0.60 mmol) was stirred overnight in 1:1 Ac_2O–pyridine (20 mL). The solution was co-concentrated

with toluene to yield **31** (431 mg, 99%); $[\alpha]_D^{25}$ −15° (*c* 0.7, $CHCl_3$). ^1H NMR data ($CDCl_3$): δ 5.20 (d, 1 H, *J* 3.1 Hz, H-4′), 5.80 (t, 1 H, *J* 9.4 Hz, H-3), 4.92 (m, 2 H, H-2,3′), 4.55 (dd, 1 H, *J* 8.1, 3.8 Hz, H-1′), 4.45 (d, 1 H, *J* 8.0 Hz, H-1), 4.43, 4.20 (dABq, 2 H, *J* 12.2, 4.8, 2.3 Hz, H-6), 4.10 (m, 2 H, H-6′), 3.95, 3.58 (2 m, 1 H each, CH_2CSi), 3.83 (t, 1 H, *J* 9.47 Hz, H-4), 3.67 (dt, 1 H, *J* 5.9, 1.0 Hz, H-5′), 3.65 (m, 1 H, H-5), 2.06–1.99 (m, 18 H, OAc), 2.08, (m, 1 H, *J* 11.2 Hz, H-2′*e*), 1.88 (q, 1 H, *J* 11.23, 8.0 Hz, H-2′*a*), 0.90 (m, 2 H, CCH_2Si), 0.0 [s, 9 H, $Si(CH_3)_3$]. Anal. Calcd for $C_{29}H_{46}O_6Si$: C, 51.3; H 6.8. Found: C, 51.2; H, 6.9.

*2-(Trimethylsilyl)ethyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,4,6-tri-*O*-benzyl-β-*D*-galacto-pyranosyl)-β-*D*-glucopyranoside* (**32**).—Compound **1**[8] (2.32 g, 5.24 mmol) and dibutyltin oxide (1.41 g, 5.66 mmol) were suspended in benzene (130 mL) and the mixture was refluxed for 14 h with azeotropic removal of water. Tetrabutylammonium bromide (1.71 g, 5.24 mmol) and allyl bromide (8.9 mL, 104 mmol) were added and the reflux was continued for 8 h. The solution was concentrated and the residue was chromatographed (SiO_2, EtOAc–heptane 10:1) to give 1.8 g of a white solid {$[\alpha]_D^{25}$ −5.3° (*c* 0.6, CD_3OD)}. The white solid (1.69 g) was treated with NaH (1.25 g, 29 mmol) in DMF (13 mL) for 2 h. Benzyl bromide (5 mL, 42 mmol) was added and the stirring was continued for 4 h. The reaction was quenched with water (9 mL), and the aqueous phase was extracted with Et_2O (4 × 15 mL). The ether layers were pooled, washed with water, dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, EtOAc–heptane 5:1) to give 2.2 g of a colorless syrup {$[\alpha]_D^{25}$ +0.5° (*c* 1.0, $CHCl_3$)}, which was treated as follows: The syrup (2.0 g) was dissolved in a suspension of palladium(II) chloride (100 mg) in 3:2 EtOH–MeOH (20 mL), and the mixture was stirred at room temperature for 6.5 h, then filtered (Celite), and concentrated. The crude product was chromatographed (SiO_2, EtOAc–heptane 1:5) to give **32** (1.67 g, 1.7 mmol; 32% overall yield from **1**); $[\alpha]_D^{25}$ +0.1° (*c* 2.0, CH_2Cl_2). ^1H NMR data ($CDCl_3$): δ 5.04–4.24 (m, 14 H, H-1,1′, PhCH_2), 4.06–3.91 (m, 2 H, H-5′, CHCSi). ^{13}C NMR data ($CDCl_3$): δ 139.8, 138.8, 138.5, 138.4, 138.1, 103.2, 102.8, 82.9, 81.9, 80.7, 77.3, 77.2, 76.9, (2 C), 75.3, 75.2, 75.1, 75.0 (2 C), 73.4, 73.21, 73.16, 68.0, 67.4, 18.5, −1.4. Anal. Calcd for $C_{59}H_{72}O_{11}Si$: C, 71.9; H, 7.1. Found: C, 72.2; H, 7.2.

*2-(Trimethylsilyl)ethyl 2,3,6-tri-*O*-benzyl-4-*O*-[2,4,6-tri-*O*-benzyl-3-*O*-(methyl-thio)thiocarbonyl-β-*D*-galactopyranosyl]-β-*D*-glucopyranoside* (**33**).—Compound **32** (129 mg, 0.13 mmol) was dissolved in THF (0.5 mL), NaH (14 mg, 0.29 mmol) and imidazole (1 mg, 10 μmol) were added, and the mixture was stirred for 65 min. Carbon disulfide (60 μL, 0.43 mmol) was added, the mixture was stirred for 1.5 h, and MeI (20 μL, 0.32 mmol) was added. The reaction was complete (TLC; Et_2O–toluene 1:5) after 2 h. The mixture was diluted with CH_2Cl_2, then washed consecutively with water, 2 M HCl, satd aq $NaHCO_3$, and water. Drying (Na_2SO_4), filtration, evaporation, and column chromatography of the crude product (SiO_2, EtOAc–heptane 1:19 → 1:9) gave **33** (122 mg, 87%) as a syrup; $[\alpha]_D^{25}$ +11.0° (*c* 1.6, $CDCl_3$). ^1H NMR data ($CDCl_3$): δ 5.65 (dd, 1 H, *J* 10.0, 3.0 Hz, H-3′); 4.45, 4.38 (2 d, 1 H each, *J* 7.84, 7.87 Hz, H-1,1′); 2.55 (s, 3 H, CH_3S); 1.05 (m, 2 H,

CCH_2Si). ^{13}C NMR data ($CDCl_3$): δ 139.9, 139.2, 138.4, 138.3 (2 C), 138.0, 128.4–127.1 (30 C), 103.2, 102.6, 84.4, 83.0, 81.9, 77.7, 77.3, 75.4, 75.0, 73.5, 73.4, 73.3, 72.5, 68.3, 67.7, 67.4, 19.2, 18.5, −1.4. Anal. Calcd for $C_{61}H_{74}O_{11}S_2Si$: C, 68.1; H, 6.9. Found: C, 68.5; H, 6.7.

2-(Trimethylsilyl)ethyl 2,3,6-tri-O-benzyl-4-O-(2,4,6-tri-O-benzyl-3-deoxy-β-D-xylo-hexopyranosyl)-β-D-glucopyranoside (**34**).—Compound **33** (497 mg, 0.46 mmol) in toluene (4 mL, distilled from CaH_2) was added dropwise under Ar to a refluxing solution of tributyltin hydride (160 μL, 0.60 mmol) during 1 h[11]. The solution was refluxed overnight and concentrated. The residue was chromatographed (SiO_2, EtOAc–heptane 1:4) to give **34** (160 mg, 36%); $[\alpha]_D^{25}$ −7° (*c* 0.2, $CHCl_3$). ^1H NMR data ($CDCl_3$): δ 2.35 (ddd, 1 H, *J* 12.3, 4.45, 2.9 Hz, H-3*e*), 1.36 (ddd, 1 H, *J* 13.7, 11.8, 2.6 Hz, H-3*a*). ^{13}C NMR data ($CDCl_3$): δ 139.3, 138.9, 138.73, 138.69, 138.5, 138.4, 104.5, 103.1, 83.2, 82.1, 77.2, 76.8, 76.4, 75.3, 74.9, 74.2, 73.4, 73.1, 72.6, 72.5, 71.4, 68.5, 67.3, 32.7, 18.5, −1.4. Anal Calcd for $C_{59}H_{72}O_{10}Si$: C, 73.1; H 7.5. Found: C, 73.2 H, 7.3.

2-(Trimethylsilyl)ethyl 2,3,6-tri-O-acetyl-4-O-(2,4,6-tri-O-acetyl-β-D-galacto-pyranosyl)-β-D-glucopyranoside (**35**).—Compound **1**[8] (970 mg, 2.19 mmol), and dibutyltin oxide (580 mg, 2.33 mmol) were dissolved in benzene (50 mL). The mixture was refluxed overnight and the water formed was removed with a Dean–Stark trap. The mixture was cooled to room temperature and benzyl bromide (5.1 mL, 42.8 mmol) and tetrabutylammonium bromide (700 mg, 2.14 mmol) were added. The mixture was refluxed for 4.5 h, the solvent was removed, and the residue was chromatographed to give 2-(trimethylsilyl)ethyl 4-*O*-(3-*O*-benzyl-β-D-galactopyranosyl)-β-D-glucopyranoside (820 mg), which was treated with Ac_2O–pyridine (15 mL, 2:1) at room temperature overnight. The mixture was concentrated to give a residue (1.1 g), which was hydrogenolyzed (H_2, 1 atm., 150 mg Pd–C, 10%; room temperature) in AcOH (20 mL). The mixture was filtered (Celite) and concentrated, and the residue was chromatographed (SiO_2, EtOAc–heptane 1:1) to give **35** (780 mg, 51%); $[\alpha]_D^{25}$ −14° (*c* 1.2, $CHCl_3$). ^1H NMR data ($CDCl_3$): δ 5.29 (dd, 1 H, *J* 2.8, 0.3 Hz, H-4′), 5.18 (dd, 1 H, *J* 9.5, 9.1 Hz, H-3), 4.89 (2 dd, 1 H each, *J* 9.7, 7.9, and 10.0, 7.8 Hz, H-2,2′), 4.48 (d, 1 H, *J* 7.9 Hz, H-1′), 4.42 (d, 1 H, *J* 7.8 Hz, H-1), 4.50 (dABd, H-6), 4.18 (dABd, 1 H, *J* 11.9, 5.3 Hz, H-6), 4.10 (m, 2 H, H-6′), 2.00–2.20 (5 s, 18 H, OAc). Anal. Calcd for $C_{29}H_{46}O_{17}Si$: C, 50.2; H, 6.7. Found: C, 50.3; H, 6.7.

2-(Trimethylsilyl)ethyl 2,3,6-tri-O-acetyl-4-O-(2,4,6-tri-O-acetyl-3-deoxy-β-D-xylo-hexopyranosyl)-β-D-glucopyranoside (**36**).—Compound **35** (522 mg, 0.75 mmol) and 1,1′-thiocarbonyldiimidazole (227 mg, 1.24 mmol) were dissolved in 1,2-dimethoxyethane (35 mL), and the mixture was refluxed for 2.5 h, then allowed to attain room temperature, and concentrated. The residue was dissolved in CH_2Cl_2, the solution was washed with aq 1 M HCl and satd aq $NaHCO_3$, dried ($MgSO_4$), and concentrated. The residue was dissolved in dry toluene (40 mL), heated to reflux, and a solution of tributyltin hydride (400 μL, 1.46 mmol) in toluene (10 mL) was added dropwise under Ar[11] during 30 min. A catalytic amount of AIBN was

added and the mixture was refluxed overnight. The reaction was monitored by TLC. The mixture was concentrated, and the residue was flash-chromatographed (SiO_2, EtOAc–heptane 5:1) to give **36** (508 mg, 99%); $[\alpha]_D^{25}$ −34° (*c* 1.0, $CHCl_3$). ^1H NMR data ($CDCl_3$): δ 5.18 (dd, 1 H, *J* 9.2, 9.6 Hz, H-3), 5.02 (bd, 1 H, *J* 1.0 Hz, H-4), 4.9 (dd, 1 H, *J* 8.0, 9.6 Hz, H-2), 4.76 (ddd, 1 H, *J* 5.6, 8.0, 11.3 Hz, H-2′), 4.47 (d, 1 H, *J* 8.0 Hz, H-1 or 1′), 4.44 (d, 1 H, *J* 8.1 Hz, H-1 or 1′), 4.20 (dABq, 1 H, *J* 5.3, 11.9 Hz, H-6), 4.50 (dABq, 1 H, *J* 2.2, 11.9 Hz, H-6), 4.10 (d, 2 H, *J* 6.7 Hz, H-6′), 3.95 (dt, 1 H, CHCSi), 3.84 (bdd, 1 H, *J* 1.4, 6.5 Hz, H-5′), 3.79 (t, 1 H, *J* 9.3 Hz, H-4), 3.64 (m, 1 H, H-5), 3.56 (dt, 1 H, CHCSi), 2.44 (ddd, 1 H, *J* 2.9, 5.1, 13.8 Hz, H-3′*e*), 2.04–2.12 (5 s, 18 H, OAc), 1.62 (ddd, 1 H, *J* 3.2, 11.7, 14.4 Hz, H-3′*a*), 0.9 (m, 2 H, CCH_2Si), 0.00 [s, 9 H, $Si(CH_3)_3$]. Anal. Calcd for $C_{29}H_{46}O_{16}Si$: C, 51.3; H 6.8. Found: C, 51.6; H, 6.6.

*2-(Trimethylsilyl)ethyl 2,3,6-tri-O-benzyl-4-O-(2,3,6-tri-O-benzyl-4-deoxy-β-*D*-xylo-hexopyranosyl)-β-*D*-glucopyranoside* (**38**).—A solution of **37**[8] (2.2 g, 2.2 mmol) in THF (10 mL) was added to a mixture of NaH (173 mg, 3.9 mmol) and imidazole (catalytic amount) in THF (5 mL). The mixture was stirred for 30 min, CS_2 (650 μL, 4.7 mmol) was added, the mixture was stirred for 35 min, and MeI (290 μL, 4.7 mmol) was added[11]. The reaction was complete (TLC; EtOAc–heptane 1:5) after 1.5 h. The mixture was diluted with Et_2O (100 mL), then washed consecutively with water, satd aq $NaHCO_3$, and water. Drying (Na_2SO_4), filtration, evaporation, and column chromatography of the crude product (SiO_2, EtOAc–heptane 1:5) gave 2.4 g of a colorless syrup; {$[\alpha]_D^{25}$ +2.9° (*c* 1.5, $CHCl_3$)}. A portion (2.14 g) of the syrup dissolved in dry toluene (20 mL) was added dropwise (~ 10 drops/min) to a refluxing solution of tributyltin hydride (1.0 mL, 3.66 mmol) in dry toluene[11] (20 mL). A catalytic amount of AIBN was added, and the mixture was refluxed under Ar. When the reaction was complete (TLC; Et_2O–toluene 1:9), the reaction mixture was concentrated, and the residue was flash-chromatographed (SiO_2, Et_2O–toluene 1:18) to give **38** (1.91 g, 99% from **37**); $[\alpha]_D^{25}$ +10.9° (*c* 1.4, $CDCl_3$). ^1H NMR data ($CDCl_3$): δ 2.18 (ddd, 1 H, *J* 12.1, 5.6, 1.5 Hz, H-3*e*), 1.37 (q, 1 H, *J* 12.5 Hz, H-3*a*). ^{13}C NMR data ($CDCl_3$): δ 139.3, 138.8 (2 C), 138.6, 138.5, 138.4, 103.2, 102.7, 83.4, 83.1, 82.0, 78.9, 76.8, 75.3, 75.1, 75.0, 74.9, 73.5, 73.2, 72.4, 72.0, 70.7, 68.5, 67.4, 34.2, 18.6, −1.3. Anal. Calcd for $C_{59}H_{72}O_{10}Si$: C, 73.1; H, 7.5. Found: C, 72.9; H, 7.1.

*2-(Trimethylsilyl)ethyl 2,3,6-tri-O-acetyl-4-O-(2,3,6-tri-O-acetyl-4-deoxy-β-*D*-xylo-hexopyranosyl)-β-*D*-glucopyranoside* (**39**).—Compound **7** (173 mg, 0.41 mmol) was stirred at room temperature for 48 h in 1:1 pyridine–Ac_2O (5 mL). The mixture was co-concentrated with toluene, and the residue was flash-chromatographed (SiO_2, EtOAc–heptane 1:1) to give **39** (274 mg, 98%); $[\alpha]_D^{25}$ +14° (*c* 1.1, $CHCl_3$). ^1H NMR data ($CDCl_3$): δ 5.17 (dd, 1 H, *J* 9.6, 9.0 Hz, H-3), 4.93 (ddd, 1 H, *J* 9.6, 4.1, 1.7 Hz, H-3′), 4.9 (dd, 1 H, *J* 9.6, 7.8 Hz, H-2′), 4.8 (dd, 1 H, *J* 7.7 Hz, H-2), 4.50 (dd, 1 H, *J* 11.9, 2.2 Hz, H-6), 4.50 (d, 1 H, *J* 7.9 Hz, H-1′), 4.40 (d, 1 H, *J* 7.7 Hz, H-1), 4.10 (d, 1 H, *J* 12.0 Hz, H-6), 4.20, 4.10 (dABq, 1 H each, *J* 11.7, 5.5, 4.5 Hz, H-6), 3.90 (m, 1 H, CHCSi), 3.80 (t, 1 H, *J* 9.9 Hz, H-4), 3.70 (m, 1 H, H-5′),

3.55 (m, 2 H, H-5, CHCSi), 2.15–1.90 (m, 19 H, H-4′*e* and OAc), 1.55 (m, H-4′*a*), 0.90 (m, 2 H, CCH_2Si), −0.10 [s, 9 H, $Si(CH_3)_3$]. Anal. Calcd for $C_{29}H_{46}O_{16}Si$: C, 51.3; H 6.8. Found: C, 51.6; H, 7.0.

*2-(Trimethylsilyl)ethyl 2,3,6-tri-*O*-acetyl-4-*O*-(2,3-di-*O*-acetyl-4-*O*-benzoyl-6-bromo-6-deoxy-β-*D*-galactopyranosyl)-β-*D*-glucopyranoside* (**41**).—Compound **40**[8] (1.30 g, 1.78 mmol) was dissolved in CCl_4 (100 mL). Moisture was removed by azeotropic distillation of ~25 mL of the solvent. *N*-Bromosuccinimide (334 mg, 2.2 mmol) and $BaCO_3$ (3 g) were added[19], and the mixture was refluxed under N_2. The brown colour (bromine) had disappeared after 25 min and after 50 min, a new product was formed (TLC). The mixture was filtered (elution with CH_2Cl_2), and the organic phase was washed with satd aq $NaHCO_3$, dried (Na_2SO_4), and concentrated. The residue was chromatographed (SiO_2, EtOAc–heptane 1:1) to give **41** (1.5 g, 100%); $[\alpha]_D^{25}$ +7.5° (*c* 1.1, $CDCl_3$). ^1H NMR data ($CDCl_3$): δ 8.07, 7.62, 7.51 (5 H, Ar-H), 5.79 (d, 1 H, *J* 3.1 Hz, H-4′), 5.25 (dd, 1 H, *J* 9.4, 9.1 Hz, H-3), 5.19 (dd, 1 H, *J* 10.3, 7.4 Hz, H-2′), 5.08 (dd, 1 H, *J* 10.4, 3.3 Hz, H-3′), 4.58 (d, 1 H, *J* 8.0 Hz, H-1′), 4.52 (m, 2 H, H-1,6), 4.12 (dd, 1 H, *J* 12.1, 5.1 Hz, H-6), 3.80-4.00 (m, 3 H, CHCSi, H-4,5′), 3.66 (m, 1 H, H-5), 3.56 (m, 1 H, CHCSi), 3.45 (2 H, H-6′), 2.13, 2.04, 2.03, 1.94 (4 s, 15 H, OAc), 0.90 (m, 2 H, CCH_2Si), 0.00 [s, 9 H, $Si(CH_3)_3$]. Anal. Calcd for $C_{34}H_{47}BrO_{16}Si$: C, 49.8; H, 5.8. Found: C, 50.2; H, 5.9.

*2-(Trimethylsilyl)ethyl 2,3,6-tri-*O*-acetyl-4-*O*-(2,3-di-*O*-acetyl-4-*O*-benzoyl-6-deoxy-β-*D*-*galactopyranosyl)-β-*D*-glucopyranoside* (**42**).—Compound **41** (1.17 g, 1.43 mmol) was dissolved in dry toluene (50 mL), the mixture was heated (reflux), and tributyltin hydride (1.16 mL, 3.9 mmol) was added dropwise under Ar. A catalytic amount of AIBN was added and the solution was refluxed overnight. The solvent was removed and the residue was chromatographed (SiO_2, EtOAc–heptane 1:2) to give **42** (1.02 g, 96%); $[\alpha]_D^{25}$ +17° (*c* 1.5, $CHCl_3$). ^1H NMR data ($CDCl_3$): δ 8.10, 7.60, 7.50 (5 H, Ar-H), 5.43 (d, 1 H, *J* 3.3 Hz, H-4′), 5.22 (t, 1 H, *J* 9.2 Hz, H-3), 5.19 (dd, 1 H, *J* 10.5, 7.8 Hz, H-2′), 5.05 (dd, 1 H, *J* 10.4, 3.4 Hz, H-3′), 4.90 (dd, 1 H, *J* 9.6, 8.0 Hz, H-2), 4.50 (m, 3 H, H-1,1′,6), 4.12 (dABd, 1 H, *J* 12.0, 5.0 Hz, H-6), 3.95 (ddd, 1 H, *J* 10.1, 9.7, 5.6 Hz, CHCSi), 3.86 (bq, 1 H, *J* 6.5 Hz, H-5′), 3.81 (t, 1 H, *J* 9.8 Hz, H-4), 3.60 (m, 2 H, H-5, CHCSi), 2.12, 2.04, 2.01, 1.93 (4 s, 15 H, OAc), 1.25 (d, 3 H, *J* 6.4 Hz, H-6′), 0.90 (m, 2 H, CCH_2Si), 0.01 [s, 9 H, $Si(CH_3)_3$]. Anal. Calcd for $C_{34}H_{48}O_{16}Si$: C, 55.1; H, 6.5. Found: C, 54.6; H, 6.8.

*2-(Trimethylsilyl)ethyl 2,3,6-tri-*O*-acetyl-4-*O*-(2,3,4-tri-*O*-acetyl-6-deoxy-β-*D*-galactopyranosyl)-β-*D*-glucopyranoside* (**43**).—Compound **8** (10 mg, 23 μmol) was acetylated in 1:1 Ac_2O–pyridine (0.5 mL). The mixture was concentrated and the residue was flash-chromatographed (SiO_2, EtOAc–heptane 1:1) to give **43** (16 mg, 100%); $[\alpha]_D^{25}$ −10° (*c* 1.0, $CHCl_3$). ^1H NMR data ($CDCl_3$): δ 5.17 (d, 1 H, *J* 3.3 Hz, H-4′), 5.18 (t, 1 H, *J* 9.2 Hz, H-3), 5.08 (dd, 1 H, *J* 10.5, 7.9 Hz, H-2′), 4.94 (dd, 1 H, *J* 10.4, 3.5 Hz, H-3′), 4.87 (dd, 1 H, *J* 9.5, 8.0 Hz, H-2), 4.47 (d, 1 H, *J* 8.1 Hz, H-1), 4.43 (d, 1 H, *J* 7.9 Hz, H-1′), 4.47, 4.10 (dABq, 2 H, *J* 11.8, 5.12 Hz, H-6), 3.87 (ddd, 1 H, *J* 9.9, 9.7, 6.1 Hz, CHCSi), 3.76 (t, 1 H, *J* 9.4 Hz, H-4), 3.72

(bq, 1 H, *J* 6.6 Hz, H-5'), 3.60 (m, 1 H, H-5), 3.54 (dt, 1 H, *J* 9.7, 6.8 Hz, CHCSi), 2.16, 2.10, 2.04, 2.03, 1.96 (5 s, 18 H, OAc), 1.19 (d, 3 H, *J* 6.4 Hz, H-6'), 0.90 (m, 2 H, CCH_2Si), 0.00 [s, 9 H, $Si(CH_3)_3$]. Anal. Calcd for $C_{29}H_{46}O_{16}Si$: C, 51.3; H 6.8. Found: C, 51.5; H, 6.9.

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