Synthesis of Double-Chain Bis-sulfone Neoglycolipids of the 2′-, 3′-, and 6′-Deoxyglobotrioses

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Partially protected 2-(trimethylsilyl)ethyl deoxylactosides (deoxygenated in the 2-, 3-, and 6-positions of the galactose unit) were synthesized via various routes and glycosylated with galactosyl donors to give the corresponding deoxytrisaccharides. Removal of the protecting groups gave the 2-(trimethylsilyl)ethyl 2′-, 3′-, and 6′-deoxyglobotriosides. Transformation of the protected trisaccharides into trichloroacetimidates, via the corresponding hemiacetals, proceeded in 86–96% overall yield. Glycosylation of 3-(hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]propanol with the trisaccharidic trichloroacetimidates, in 37–68% yield, followed by removal of protecting groups, gave the title neoglycolipids.

Introduction

Globotriose (Galα1-4Galβ1-4Glc) is presented as globotriosylceramide (Gb_3, P^k antigen, CD77; Figure 1) on the outside of eucaryotic cells. Gb_3 functions as an antigen of the P blood group system[1] and is also used by pathogenic *Esherichia coli*[2] and *Streptococcus suis*[3] bacteria as attachment sites necessary for colonization. Bacterial toxins, such as the shiga toxin[4] and verotoxin,[5] utilize Gb_3 to exert their toxic actions. Furthermore, Gb_3 and other glycolipids of the globoseries are tumor-associated antigens on the surface of Burkitt lymphoma cells,[6] human teratocarcinoma cells,[7] and other tumor cells[8] and are also enriched in the body fluids of patients suffering from Fabry's disease.[9]

Within collaborative projects with several research groups, we have investigated carbohydrate–protein interactions, aiming at a deeper understanding of the fine molecular details of bacterial protein attachment to saccharides of the globoseries of glycolipids. Collections of synthetic saccharides and analogs were used as soluble inhibitors in these investigations. Thus, using all the globoseries di- through pentasaccharide fragments and the monodeoxy analogs of galabiose (Galα1-4Gal; the common epitope of the natural globoseries saccharides), the receptor sites of the adhesion proteins (adhesins) of uropathogenic *E. coli*[10] and *S. suis*[11] were probed. It was found that the *E. coli* adhesin (PapG) formed intramolecular hydrogen bonds with the galabiose hydroxyl groups in positions 6, 2′, 3′, 4′, and 6′, whereas the *S. suis* adhesin used the hydroxyl groups in positions 2, 3, 4′, and 6′. This constitutes the first example where two bacterial organisms of different origin recognize the same cell-surface saccharide by different binding mechanisms. The conformations of the various globoseries saccharides, including the monodeoxy analogs, were found to be very similar, which strongly indicates that their different binding potencies to the bacterial proteins have a configurational rather than a conformational origin.[12]

In order to widen the the scope of such receptor mappings beyond the use of soluble inhibitors, we have synthesized standardized neoglycolipids,[13] based on a double-chain bis-sulfone aglycon as depicted in Figure 1. This type of glycolipid was designed[14] to mimic the natural glycosyl ceramides and thereby function as a general structural platform for the synthesis and biological evaluation of neoglycolipids based on saccharide analogs. The nature of the aglycon in neoglycolipids was recently shown to be important for the presentation of saccharide to the bacterial protein verotoxin.[15] It was found that synthetic Gb_3–bis-sulfone lipid and the corresponding Gb_3–ceramide, when presented in a lipid matrix, were equally effective binders of verotoxin, whereas the corresponding bis-sulfide lipid was a nonbinder.

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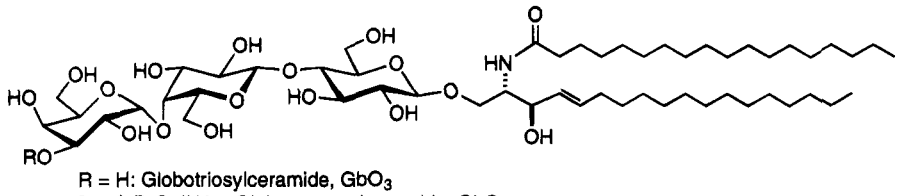
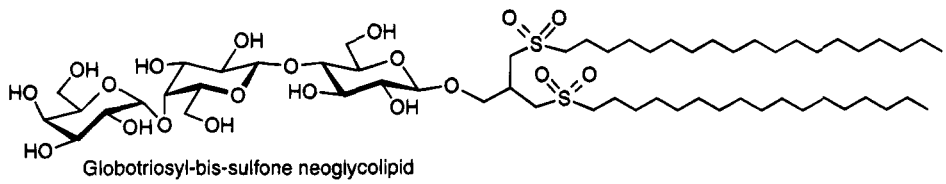


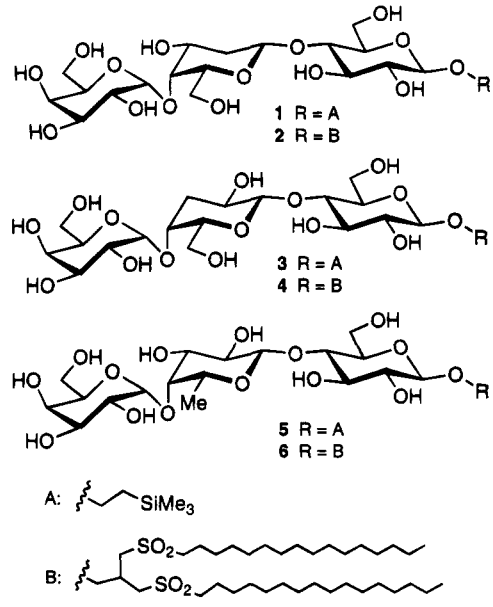
R = H: Globotriosylceramide, GbO_3
R = β-D-GalNAc: Globotetraosylceramide, GbO_4
R = α-D-GalNAc(1-3)-β-D-GalNAc: Globopentaosylceramide, GbO_5, Forssman antigen



Globotriosyl-bis-sulfone neoglycolipid

Figure 1. Structure of globotriosylceramide (GbO_3) and its double-chain bis-sulfone mimetic.

Scheme 1. Structures of the Synthetic Deoxyglobotriosides



We have recently initiated the synthesis of all the monodeoxy analogs of GbO_3–bis-sulfone lipids in order to obtain a comprehensive collection of compounds for identification of the binding sites of GbO_3-binding proteins. Deoxygenations in the terminal galactose moiety gave the 2″-, 3″-, 4″-, and 6″-deoxyglobotriose lipids.[16] We now report the synthesis of the three deoxyglobotriose lipids, where deoxygenations were performed in the central galactose moiety (compounds **2**, **4**, and **6**; Scheme 1).

Results and Discussion

I. Synthesis of the 2′-Deoxylactoside Acceptor 8. The acceptor **8** was synthesized by two different routes (Scheme 2). The first route employed the triol **7**,[17] which was synthesised via an improved method, using an imidazole thiocarbonate, instead of xanthate, for the Bu_3SnH-induced deoxygenation step (see the Experimental Section). The synthesis of **8** was based on partial benzoylation of **7** via an intermediary stannylene complex, a method that has been used to advantage for regioselective allylation, benzylation, and esterfication in the 3-position of galactose derivatives.[18] When dibutyltin oxide and benzoyl chloride both were used in 3-fold excess in methanol/toluene as solvent, the desired dibenzoate **8** was obtained in 89% yield. When less of the reagents was used, the selectivity dropped, and **8** was isolated in only 50–60% yield.

The second route employed the galactal derivative **9** as donor in the NIS-induced iodoglycosylation of **10**, which gave **11** (76%). Although NIS-promoted glycosylation usually gives α-glycosides,[19] an exception has been observed for 3,4-*O*-isopropylidenegalactal derivatives.[20] Under these conditions, the β-glycoside **11** was obtained in 76% yield. Hydrogenolysis of the carbon–iodine bond in **11** gave the deoxylactoside **12** (97%), which was deprotected to give the diol **13** (85%). Attempted selective benzoylation of **13** gave, in 91% yield, a mixture (12:6:1) of dibenzoate **8**, the isomeric dibenzoate **14**, and the tribenzoate **15**.

II. Synthesis of the 3′-Deoxylactoside Acceptors 28 and 31. Treatment of the 3′,4′-diol **16**[21] (Scheme 3) with dibutyltin oxide and allyl bromide gave the 3′-*O*-allyl-protected lactoside **17** (91%), which was acetylated to give **18** (99%). Deallylation of **18** with palladium in methanol[22] gave **19** (76%), which was treated with (thiocarbonyl)diimidazole to give the thiocarbamate **20** (85%). Reduction of **20** with tributyltin hydride gave the desired 3′-deoxylactoside **21** (42%) together with the byproducts **19**, **22**, and **16**. The yield of **21** is similar to what is found in other deoxygenations in the 3-position of benzyl-protected galactosides.[16,17,23] The hypothetical route to **21**, via formation of a 3′-thiocarbamate directly from **16** and deoxygenation, was not attempted since tributyltin hydride-mediated deoxygenation requires protection of vicinal substituents.[23]

The low overall yield of **21** (**16** → **21**, 23%) made us search for an alternative route. The *p*-methoxyben-

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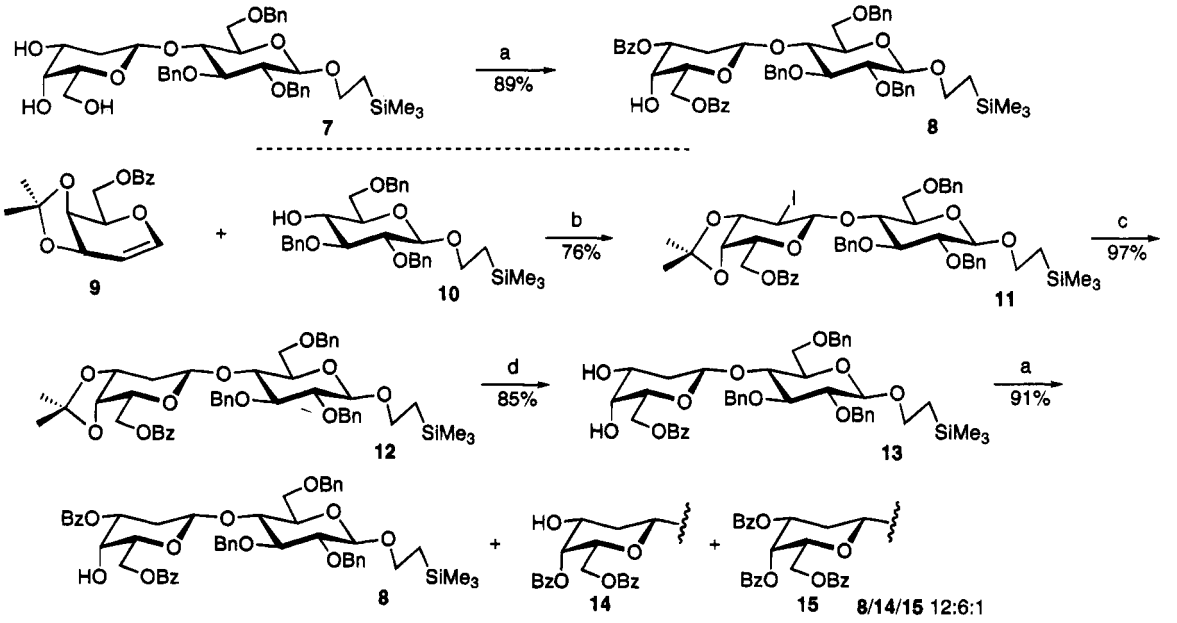
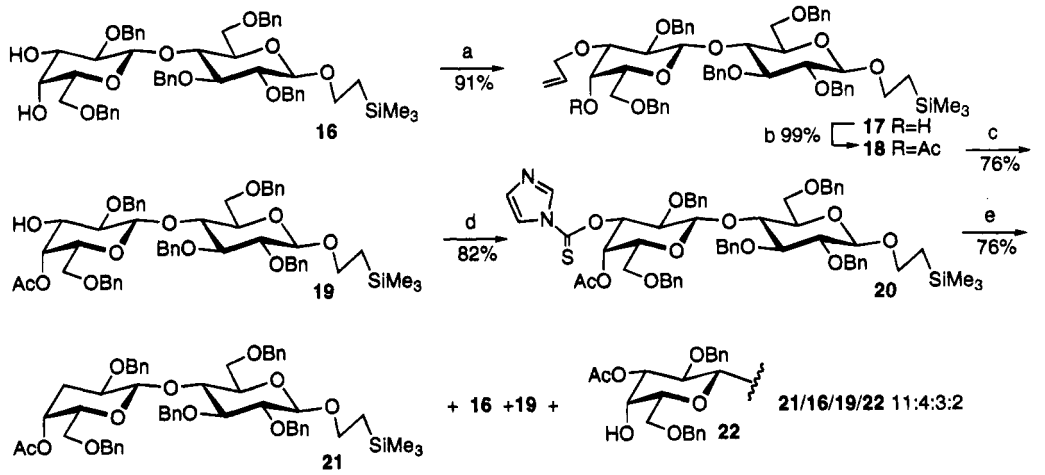
Scheme 2[a]



[a] Key: (a) Bu_2SnO, MeOH, then BzCl, toluene; (b) NIS, MeCN; (c) H_2, Pd/C, MeOH/EtOAc (5:1), Et_3N; (d) aqueous AcOH, 50 °C.

Scheme 3[a]



[a] Key: (a) Bu_2SnO, allylBr, Bu_4NI, toluene, 80 °C; (b) Ac_2O/pyridine; (c) $PdCl_2$, MeOH; (d) $imidaz_2CS$, $ClCH_2CH_2Cl$; (e) Bu_3SnH, AIBN, toluene.

zylidene derivative **23**[16] (Scheme 4) was treated with dibutyltin oxide and (thiocarbonyl)imidazole to give the thiocarbamate **24** (47%) as the main product. However, attempted acetylation of **24** caused breakage of the carbon–oxygen bond in the thiocarbamate group, and only the corresponding penta-*O*-acetate was isolated from the reaction mixture. Instead, **23** was treated with dibutyltin oxide and phenyl chlorodithioformate, which gave the xanthate **25** (87%). In contrast to compound **24**, **25** could be acetylated to give **26** (87%), and deoxygenation gave the 3′-deoxylactoside **27** (85%).

Opening of the *p*-methoxybenzylidene ring of **27** was first attempted by reduction with sodium cyanoborohydride and trifluoroacetic acid in *N*,*N*-dimethylformamide.[24] However, this gave a virtually unseparable mixture (~3:1) of the HO-4′ and HO-6′ derivatives. We have recently found that 4,6-(*p*-methoxybenzylidene)-protected pyranosides can be oxidatively opened with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to give compounds having mainly unprotected secondary and *p*-methoxybenzoyl-protected primary hydroxyl groups, respectively. Similar oxidative opening has been reported with furanose derivatives.[25] Treatment of **27** with DDQ in toluene at 80 °C gave a separable mixture of **28** and **29** (96%, 7:3). In a third attempt toward a 3′-deoxylactoside acceptor, we removed the 4′,6′-protecting group in **27** by hydrolysis in aqueous acetic acid, giving **30** (97%). Subsequent silylation of **30** with *tert*-butyldimethylsilyl chloride gave the second useful donor **31** (88%).

In summary, three routes to 3′-deoxylactoside acceptors have been developed. Both the first (**16** → **21**: 24%; **21**/**19**/**22**/**16** 11:3:2:4) and second (**23** → **28**: 40%; **28**/**29** 7:3) route produced a separable mixture from which the desired compound was isolated. However, the third route

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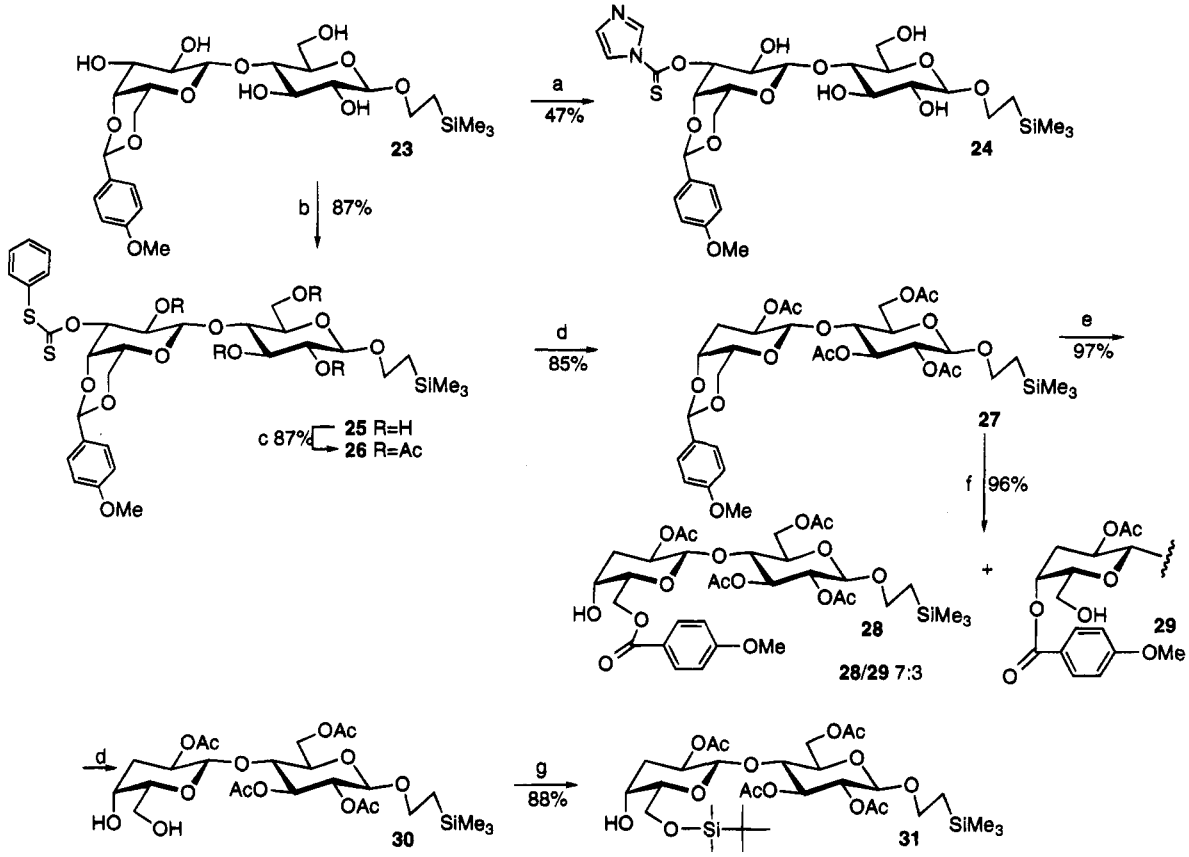
Scheme 4[a]



[a] Key: (a) Bu_2SnO, MeOH, then $imidaz_2CS$, DMAP, $ClCH_2CH_2Cl$; (b) Bu_2SnO, MeOH, then PhSCSCl, Bu_4NCl, toluene; (c) Ac_2O/pyridine; (d) Bu_3SnH, AIBN, toluene; (e) aqueous AcOH, 50 °C; (f) DDQ, $NaHSO_4$, 18-crown-6, toluene; (g) TBDMS-Cl, imidazole, CH_2Cl_2.

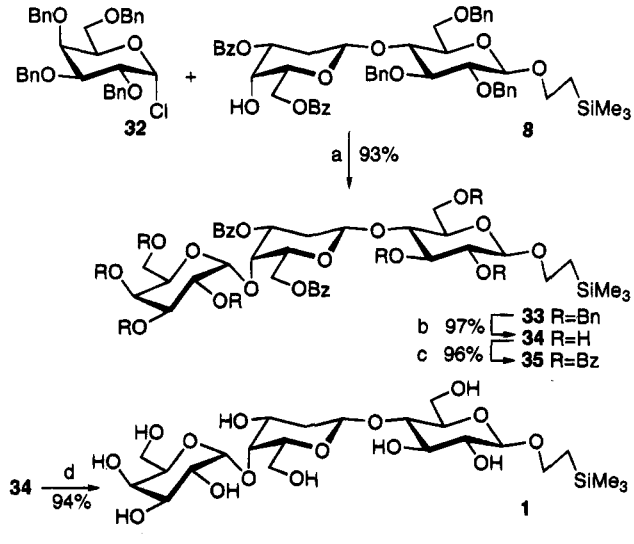
(**23** → **31**; 53%) was superior in that separation of byproducts was not needed, and furthermore, the overall yield was higher.

III. Synthesis of the 2′-Deoxyglobotrioside 1. The 2′-deoxylactoside acceptor **8** was treated with the galactosyl donor **32**,[26] using silver trifluoromethanesulfonate as promoter, to give trisaccharide **33** (93%) in a clean α-glycosylation reaction (Scheme 5). The high yield and stereoselectivity is attributed to the long reaction time and the low reaction temperature. The benzyl protecting groups of **33** were removed by hydrogenolysis to give **34** (97%), and treatment of **34** with benzoyl chloride in pyridine gave the fully benzoylated compound **35** (96%), suitable for transformation into the 2′-deoxyglobotriosyl neoglycolipid **2**, as depicted in Scheme 8. Debenzoylation of **34** gave the corresponding TMSEt 2′-deoxyglobotrioside **1** (94%).

IV. Synthesis of the 3′-Deoxyglobotrioside 3. The 3′-deoxylactoside acceptor **31** was treated with the galactosyl donor **32**[26] (Scheme 6), essentially as in the preparation of **33**, to give trisaccharide **36** (82%). The *tert*-butyldimethylsilyl protecting group was removed by treatment with tetrabutylammonium fluoride in tetrahydrofuran to give **37** (99%). Hydrogenolytic debenzylation of **37** gave **38** (92%), and subsequent deacetylation gave the TMSEt 3′-deoxyglobotrioside **3** (92%).

Glycosylation of the 3′-deoxylactoside acceptor **28** as above gave the trisaccharide **39** (66%), together with the corresponding β-glycoside (~5%). Hydrogenolytic debenzylation of **39** gave **40** (99%), and subsequent acetylation gave **41** (98%), suitable for transformation into the 3′-deoxyglobotriosyl neoglycolipid **4**, as depicted in Scheme 8.

Scheme 5[a]

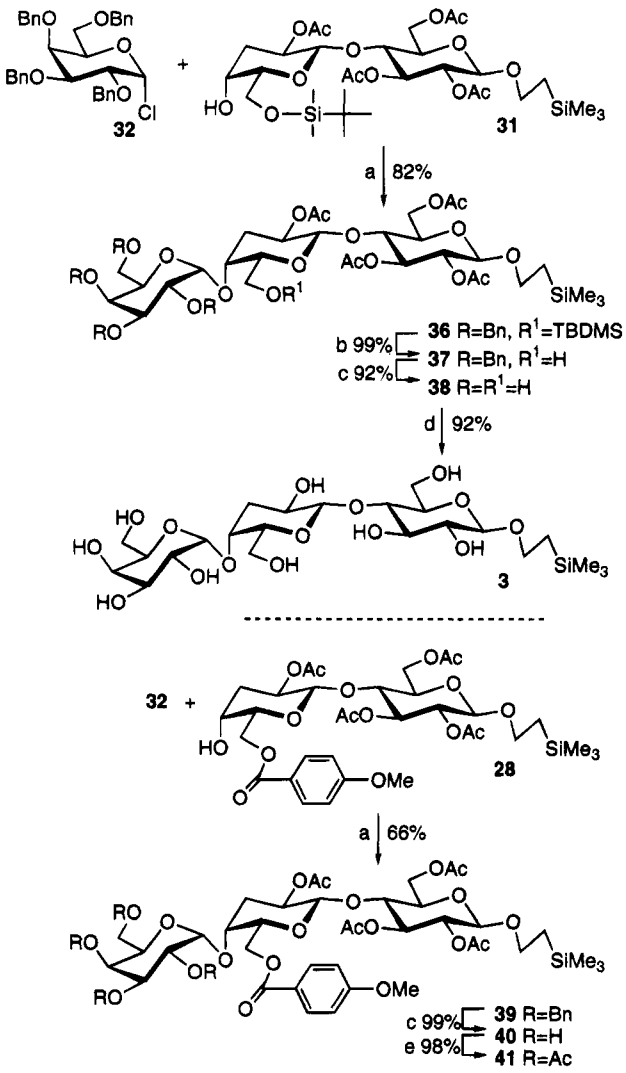


[a] Key: (a) AgOTf, collidine, MS AW-300, CH_2Cl_2; (b) H_2, Pd/C, AcOH; (c) BzCl, pyridine; (d) NaOMe, MeOH.

V. Synthesis of the 6′-Deoxyglobotrioside 5. In contrast to the deoxygenations of lactosides leading to the 2′- and 3′-deoxy compounds, the 6′-deoxy function was introduced on the trisaccharide level. This required that the HO-6′-substitution pattern of the lactoside acceptor

(26) Kihlberg, J.; Frejd, T.; Jansson, K.; Sundin, A.; Magnusson, G. *Carbohydr. Res.* **1988**, *176*, 271–286.

Scheme 6[a]



[a] Key: (a) AgOTf, collidine, MS AW-300, CH_2Cl_2; (b) Bu_4NF, THF; (c) H_2, Pd/C, AcOH; (d) NaOMe, MeOH; (e) Ac_2O, pyridine.

could be manipulated after the α-galactosylation step, without affecting the remaining protecting groups. A *p*-methoxybenzyl group can often be selectively removed by treatment with DDQ, which suggested **42**[16] as a suitable starting material (Scheme 7). The lactoside acceptor **42** was galactosylated with the 2-thiopyridyl galactoside **45**,[27] using silver trifluoromethanesulfonate and a trace of *p*-toluenesulfonic acid as promoter. In the absence of *p*-toluenesulfonic acid, the donor **45** seemed to be quite unreactive, which is in sharp contrast to our earlier experience with deoxy analogs of **45**.[16] The crude reaction mixture was difficult to purify, and therefore, it was treated with DDQ in order to remove the *p*-methoxybenzyl group prior to purification. The two-step procedure thus yielded the trisaccharide **46** (64%).

In a second attempt, **42** was glycosylated with the galactosyl donor **32** in the presence of silver trifluoromethanesulfonate, which gave a low yield of **48** (37%).

In a third attempt, the lactoside **43**[16] (Scheme 7) was transformed into the *tert*-butyldimethylsilyl-protected acceptor **44** (97%). Treatment of **44** with galactosyl donor **32**,[26] using silver trifluoromethanesulfonate as promoter, gave an easily separated mixture of **47** (72%) and the corresponding β-anomer (~5%). Removal of the *tert*-butyldimethylsilyl group with tetrabutylammonium fluoride gave **46** (94%). We prefer this third route because it gave the highest yield of **46** and the procedures were simpler than in the other two routes.

The 6′-deoxygenation was performed by treating **46** with iodine–triphenylphosphine–imidazole to give **49** (96%), followed by regioselective hydrogenolysis in a methanol–triethylamine mixture, thus yielding the desired 6′-deoxy compound **50** (98%). Hydrogenolytic debenzylation of **50** gave **51** (96%), which was subsequently debenzoylated to give the TMSEt 6′-deoxyglobotrioside **5** (99%). Acetylation of **51** gave **52** (97%), suitable for transformation into the 6′-deoxyglobotriosyl neoglycolipid **6**, as depicted in Scheme 8.

VI. Synthesis of the 2′-, 3′-, and 6′-Deoxyneoglycolipids 2, 4, and 6. The double-chain bis-sulfone neoglycolipids[14] were designed to emulate natural glycosphingolipids and to permit a flexible synthesis of compounds with different alkyl chain lengths. In the original paper,[14] we described the synthesis of neoglycolipids by displacement of bromide from 3-bromo-2-bromomethylpropyl glycosides by alkyl thiols. The bis-sulfide lipids were then easily transformed into the corresponding bis-sulfones. The synthesis of neoglycolipids has been reviewed recently.[13]

When only one kind of lipid (e.g., C_{16}-alkyl chains) is needed, glycosylation of the bis-sulfone alcohol leads directly to the desired compound, as demonstrated in our syntheses of the 2″-, 3″-, 4″-, and 6″-deoxyglobotrioside analogs.[16] Here, we utilized the generally high-yielding transformations of TMSEt glycosides into the corresponding 1-*O*-acetate or hemiacetal, suitable for conversion into other glycosides.[21] However, it was found[16] that boron trifluoride etherate/acetic anhydride-induced transformation of some of the TMSEt glycosides into the corresponding 1-*O*-acetyl trisaccharide donors caused partial deterioration of the saccharide, whereas transformation into hemiacetals and subsequent formation of trichloroacetimidates took place without problems. Therefore, we used the latter method in the synthesis of compounds **2**, **4**, and **6** (Scheme 8).

The TMSEt glycosides **35**, **41**, and **52** were transformed into the hemiacetals **53** (99%), **56** (91%), and **59** (99%) by treatment with trifluoroacetic acid in dichloromethane.[21] The hemiacetals were then transformed into the corresponding α-trichloroacetimidates **54** (87%), **57** (98%), and **60** (96%) by treatment with trichloroacetonitrile and DBU in dichloromethane.[28] 3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]propan-1-ol[16,29] was glycosylated with the trichloroacetimidates **54**, **57**, and **60** to give the acylated compounds **55** (57%), **58** (37%), and **61** (68%). Removal of the protecting acyl groups gave the desired neoglycolipids **2** (98%), **4** (98%), and **6** (99%). The yields in the glycosylations (step c, Scheme 8) seemed to depend on the protecting groups, in that a benzoyl group in the 2-position was a more efficient participating group than an acetyl group. Similar observations have been reported.[30,31] In the preparations of **55** and **61**, only

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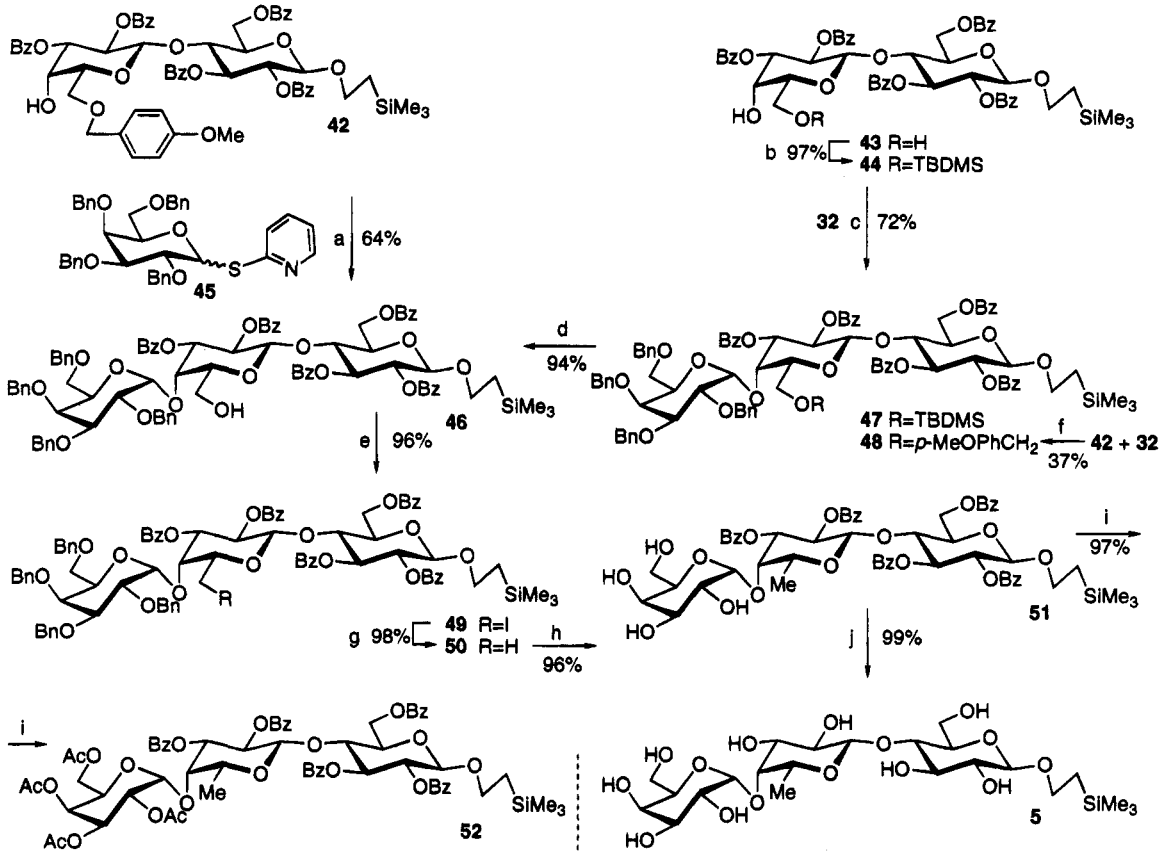
Scheme 7[a]



[a] Key: (a) AgOTf, CH_2Cl_2, MS AW-300, then DDQ, CH_2Cl_2–H_2O 18:1; (b) TBDMS-Cl, imidazole, CH_2Cl_2, 4 °C; (c) AgOTf, collidine, MS AW-300, CH_2Cl_2; (d) Bu_4NF, THF; (e) I_2, Ph_3P, imidazole, toluene, 80 °C; (f) AgOTf, TMU, MS AW-300, toluene/ether 10:1; (g) H_2, Pd/C, MeOH/EtOAc 5:1, Et_3N; (h) H_2, Pd/C, AcOH; (i) Ac_2O, pyridine; (j) NaOMe, MeOH.

the hemiacetals **53** and **59** were isolated as byproducts, whereas with **58**, additional byproducts were formed.

Experimental Section

General experimental procedures were as previously reported.[14] Molecular sieves were activated before use by heating with a flame under vacuum for 10 min and kept under vacuum for an additional 60 min.

2-(Trimethylsilyl)ethyl 4-*O*-[2-Deoxy-4-*O*-(α-D-galactopyranosyl)-β-D-*lyxo*-hexopyranosyl]-β-D-glucopyranoside (1). Compound **34** (122 mg, 0.153 mmol) was treated with NaOMe/MeOH (1 M, 0.2 mL) in MeOH (5 mL) at room temperature. The reaction was monitored by TLC (SiO_2, EtOAc/MeOH 3:1) After 6 h, the mixture was neutralized (AcOH) and concentrated. The residue was chromatographed (SiO_2–C_{18}, H_2O/MeOH 1:0 → 0:1) to give **1** (84 mg, 94%): $[\alpha]^{25}_D$ +27° (*c* 1.0, MeOH); ^1H NMR data (D_2O) δ 4.93 (d, 1 H, *J* = 3.7 Hz), 4.46 (d, 1 H, *J* = 8.0 Hz), 4.29 (t, 1 H, *J* = 6.4 Hz), 3.24 (t, 1 H, *J* =8.2 Hz), 2.07 (bd, 1 H, 11.2 Hz), 1.74 (q, 1 H, *J* = 11.3 Hz), 1.00 (m, 2 H), 0.03 (s, 9 H); ^{13}C NMR data (D_2O) δ 104.1, 103.5, 102.9, 81.4, 78.7, 78.5, 77.4, 77.3, 75.6, 73.6, 71.9, 71.7, 71.4, 71.2, 70.5, 63.5, 63.3, 62.9, 38.0, 20.3, 0.2.

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]-propyl 4-*O*-[2-Deoxy-(4-*O*-α-D-galactopyranosyl)-β-D-*lyxo*-hexopyranosyl]-β-D-glucopyranoside (2). Compound **55** (62 mg, 0.030 mmol) was dissolved in $CHCl_3$/MeOH (10 mL, 3:2), and NaOMe/MeOH (1 M, 0.2 mL) was added. The reaction was monitored by TLC ($CHCl_3$/MeOH/AcOBu/H_2O 12:8:8:1). After 16 h, the mixture was neutralized with Duolite (H^+) resin, filtered, washed with hot (~50 °C) MeOH, and concentrated. The residue was dissolved in hot (~50 °C) MeOH, and the solution was cooled to room temperature and kept at −25 °C overnight, which formed a precipitate of **2** (29.5 mg, 87%). The mother liquid was concentrated, and the residue was dissolved in MeOH/toluene (1:1). The solution was added to a silica gel column that was packed with the help of toluene and chromatographed (SiO_2, MeOH/toluene 1:1 → 3:1, then $CHCl_3$/MeOH/H_2O 13:7:1) to give an additional amount of **2** (3.7 mg, 11%; total yield 98%): $[\alpha]^{25}_D$ +31° (*c* 0.5, $CHCl_3$/MeOH/H_2O 13:7:1); ^1H NMR data ($CDCl_3$/CD_3OD/D_2O 13:7:1) δ 4.95 (bs, 1 H), 4.66 (dd, 1 H, *J* = 1.7, 9.8 Hz), 4.36 (d, 1 H, *J* = 7.8 Hz), 3.12 (m, 4 H), 3.02 (m, 1 H), 2.03 (bd, 1 H, *J* = 12.1 Hz), 0.90 (t, 6 H, *J* = 6.8 Hz).

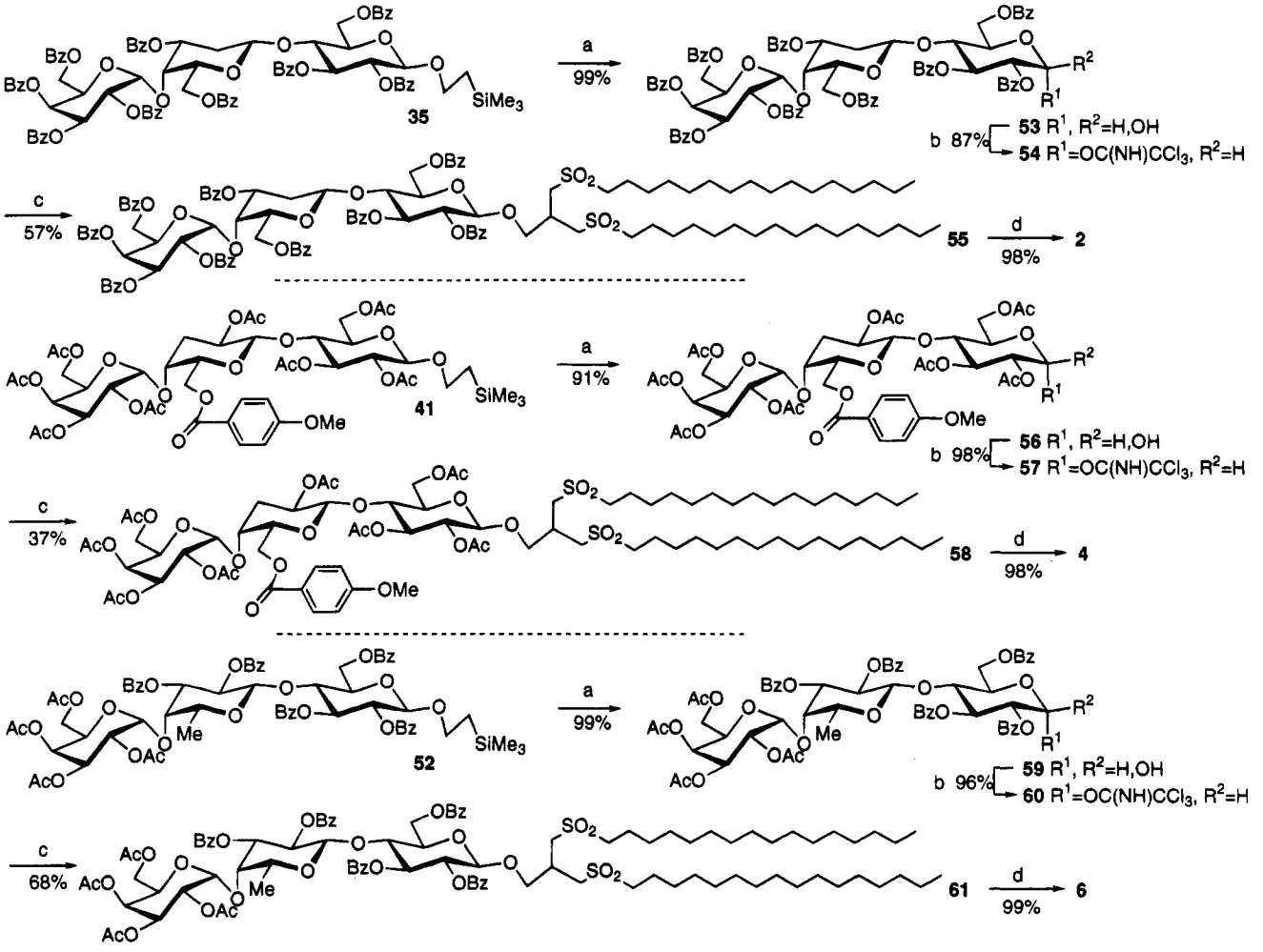
2-(Trimethylsilyl)ethyl 4-*O*-[3-Deoxy-4-*O*-(α-D-galactopyranosyl)-β-D-*xylo*-hexopyranosyl]-β-D-glucopyranoside (3). Compound **38** (210 mg, 0.277 mmol) was deacetylated as described above (**34** → **1**), and the crude product was chromatographed (SiO_2–C_{18}, H_2O/MeOH 1:0 → 0:1) to give **3** (150 mg, 92%): $[\alpha]^{25}_D$ +18° (*c* 1.0, MeOH); ^1H NMR data (D_2O) δ 4.97 (d, 1 H, *J* = 3.7 Hz), 4.47 (2 d, 1 H each, *J* = 8.0, 8.1 Hz), 2.38 (dt, 1 H, *J* = 3.9, 13.9 Hz), 1.72 (bt, 1 H, *J* = 12.3 Hz), 1.00 (m, 2 H), 0.00 (s, 9 H); ^{13}C NMR data (D_2O) δ 107.54 104.1, 103.4, 81.3, 81.2, 77.7, 77.5, 77.3, 75.7, 74.5, 72.0, 72.0, 71.3, 71.2, 68.8, 64.0, 63.5, 62.8, 38.6, 20.3, 0.3.

3-Hexadecylsulfonyl-2-[(hexadecylsulfonyl)methyl]propyl 4-*O*-[3-Deoxy-4-*O*-(α-D-galactopyranosyl)-β-D-*xylo*-hexopyranosyl]-β-D-glucopyranoside (4). Compound **58** (41 mg, 0.026 mmol) was deacylated and purified as described above (**55** → **2**) to give **4** (29 mg, 98%): $[\alpha]^{25}_D$ +14° (*c* 1.0, $CHCl_3$/MeOH/H_2O 13:7:1) ^1H NMR data ($CDCl_3$/CD_3OD/D_2O 13:7:1): δ 4.96 (bs, 1 H), 4.42, 4.38 (d, 1 H each, *J* = 7.9, 7.8 Hz), 3.12 (m, 4 H), 3.02 (m, 1 H), 2.43 (bd, 1 H, *J* = 12.7 Hz), 1.68 (bt, 1 H, *J* = 12.7 Hz), 0.89 (bt, 6 H, *J* = 7.2 Hz).

2-(Trimethylsilyl)ethyl 4-*O*-[4-*O*-(α-D-galactopyranosyl)-β-D-fucopyranosyl]-β-D-glucopyranoside (5). Compound **51** (98 mg, 0.088 mmol) was debenzoylated as described

(31) Elofsson, M.; Broddefalk, J.; Ekberg, T.; Kihlberg, J. *Carbohydr. Res.* **1994**, *258*, 123–133.

Scheme 8[a]



[a] Key: (a) CF_3CCOOH/CH_2Cl_2 2:1; (b) DBU, Cl_3CCN, CH_2Cl_2; (c) 3-(hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]propan-1-ol,[28] BF_3Et_2O, MS 4 Å, CH_2Cl_2; (d) NaOMe, MeOH/$CHCl_3$ 2:3.

above (**34** → **1**), and the crude product was chromatographed (SiO_2–C_{18}, H_2O/MeOH 1:0 → 0:1) to give **5** (48 mg, 93%): $[\alpha]^{25}_D$ +45° (*c* 1.2 , MeOH); ^1H NMR data (D_2O) δ 5.02 (d, 1 H, *J* = 3.7 Hz), 4.46 (2 d, 1 H each, *J* = 8.0, 7.6 Hz), 4.40 (bt, 1 H, *J* = 6.6 Hz), 1.34 (d, 3 H, *J* = 6.4 Hz), 1.00 (m, 2 H), 0.00 (s, 9 H); ^{13}C NMR data (D_2O) δ 106.0, 104.1, 103.3, 81.9, 81.8, 77.5, 77.3, 75.7, 75.0, 74.0, 73.3, 73.2, 71.9, 71.7, 71.6, 71.2, 63.2, 62.8, 20.3, 18.3, 0.2.

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]-propyl 4-*O*-[4-*O*-(α-D-Galactopyranosyl)-β-D-fucopyranosyl]-β-D-glucopyranoside (6). Compound **61** (110 mg, 0.061 mmol) was debenzoylated and purified as described above (**55** → **2**) to give **6** (67 mg, 99%): $[\alpha]^{25}_D$ +31° (*c* 1.0, $CHCl_3$/MeOH/H_2O 13:7:1) ^1H NMR data ($CDCl_3/CD_3OD/D_2O$ 13:7:1): δ 4.94 (bs, 1 H), 4.38, 4.36 (d, 1 H each, *J* = 7.6, 7.8 Hz), 3.12 (m, 4 H), 3.00 (m, 1 H), 1.85 (m, 4 H), 1.39 (d, 3 H, *J* = 6.4 Hz), 0.89 (bt, 6 H, *J* = 6.9 Hz).

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzyl-4-*O*-(2-deoxy-β-D-*lyxo*-hexopyranosyl)-β-D-glucopyranoside (7). A mixture of 2-(trimethylsilyl)ethyl 2,3,6-tri-*O*-benzyl-4-*O*-(β-D-galactopyranosyl)-β-D-glucopyranoside[17] (500 mg, 0.702 mmol), 2,2-dimethylpropane (25 mL), and a catalytic amount of *p*-toluenesulfonic acid was stirred for 2 days at room temperature. Triethylamine (0.5 mL) was added, and the solvent was removed. A mixture of the residue, 1,1′-(thiocarbonyl)diimidazole (250 mg, 1.404 mmol), and dry $ClCH_2CH_2Cl$ (20 mL) was kept at 60 °C overnight and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc/Et_3N 10:10:1), toluene (30 mL) and tributyltin hydride (0.440 mL, 1.64 mmol) were added to the crude material, the mixture was heated to reflux, and a solution of AIBN (5 mg) in dry toluene (3 mL) was added during 10 min under Ar. The mixture was refluxed overnight and concentrated. The resulting syrup was hydrolyzed in aqueous AcOH (80%, 10 mL) at 60 °C overnight and concentrated. The residue was chromatographed (SiO_2, heptane, 200 mL, then toluene/MeOH 15:1) to give **7** (255 mg, 52%). The physical data of **7** were in agreement with those reported earlier.[17]

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzyl-4-*O*-(3,6-di-*O*-benzoyl-2-deoxy-β-D-*lyxo*-hexopyranosyl)-β-D-glucopyranoside (8), 2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzyl-4-*O*-(4,6-di-*O*-benzoyl-2-deoxy-β-D-*lyxo*-hexopyranosyl)-β-D-glucopyranoside (14), and 2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzyl-4-*O*-(3,4,6-tri-*O*-benzoyl-2-deoxy-β-D-*lyxo*-hexopyranosyl)-β-D-glucopyranoside (15). (a) Compound **7**[17] (63 mg, 0.091 mmol) and dibutyltin oxide (68 mg, 0.272 mmol) were dissolved in MeOH (5 mL), and the mixture was heated at reflux for 5 h and then concentrated under argon. The residue was kept under vacuum (oil pump) for 1.5 h, dissolved in dry toluene (5 mL) under Ar, and cooled (−25 °C). To the cold solution was added benzoyl chloride (0.032 mL, 0.270 mmol), and the mixture was left at 4 °C for 17 h and at room temperature for 0.5 h. The mixture was diluted with toluene/H_2O (80 mL, 5:3) and filtered (Celite). The organic phase was dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 5:1) to give **8** (72 mg, 89%): $[\alpha]^{25}_D$ −3° (*c* 1.0, $CHCl_3$) ^1H NMR data ($CDCl_3$): δ 4.97 (m, 1 H), 4.73 (m, 1 H), 4.50 (dd, 1 H, *J* = 7.6, 11.3 Hz), 4.39 (d, 1 H, *J* = 7.8 Hz), 4.17 (dd, 1 H, *J* = 5.9, 11.1 Hz), 1.99 (m, 2 H), 0.15 (s, 9 H); ^{13}C NMR data ($CDCl_3$) δ 166.4, 165.6, 139.0, 138.6, 138.0, 133.4, 133.2, 129.8–127.4, 103.3, 99.7, 83.0, 82.0, 76.5, 75.2, 74.9, 74.6, 73.5, 72.4, 71.1,

68.7, 67.5, 65.0, 62.4, 31.7, 18.6, −1.4 (3C). Anal. Calcd for $C_{52}H_{60}O_{12}Si$: C, 69.0; H, 6.7. Found: C, 68.9; H, 6.5.

(b) Compound **13** (213 mg, 0.266 mmol), dibutyltin oxide (100 mg, 0.399 mmol), and benzoyl chloride (0.044 mL, 0.372 mmol) were treated as above to give **8** (137 mg, 57%), **14** (70 mg, 29%), and **15** (15 mg, 5%). Compound **14**: $[\alpha]^{25}_D$ −44° (*c* 1.0 , $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 8.20−7.15 (25 H), 5.38 (d, 1 H, *J* = 2.9 Hz), 4.41 (d, 1 H, *J* = 7.8 Hz), 4.35 (dd, 1 H, *J* = 6.4, 11.2 Hz), 4.26 (dd, 1 H, *J* = 7.2, 11.0 Hz), 3.82 (m, 1 H), 1.96 (bdd, 1 H, *J* = 4.2, 12.4 Hz), 1.78 (dt, 1 H, *J* = 9.7, 12.1 Hz), 0.05 (s, 9 H). Compound **15**: $[\alpha]^{25}_D$ −30° (*c* 1.0 , $CHCl_3$) ^1H NMR data ($CDCl_3$): δ 5.66 (d, 1 H, *J* =2.4 Hz), 5.17 (m, 1 H), 4.84 (m, 1 H), 4.41 (d, 1 H, *J* = 7.7 Hz), 4.37 (dd, 1 H, *J* = 6.3, 11.2 Hz), 4.23 (dd, 1 H, *J* = 7.5, 11.1 Hz), 2.08 (m, 2 H), 1.06 (m, 2 H), 0.02 (s, 9 H).

6-*O*-Benzoyl-3,4-*O*-isopropylidene-D-galactal (9). To a cold (0 °C) solution of 3,4-*O*-isopropylidene-D-galactal[32] (1.00 g, 5.41 mmol) and pyridine (1.5 mL) in dry CH_2Cl_2 (10 mL) was added benzoyl chloride (1.25 mL, 10.81 mmol), and the mixture was stirred for 2 h. CH_2Cl_2 (100 mL) was added, and the mixture was washed with aqueous H_2SO_4 (30 mL, 2 M), water (30 mL), and saturated aqueous $NaHCO_3$ (30 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 5:1) to give **9** (1.56 g, 99%): $[\alpha]^{25}_D$ −11° (*c* 1.0, $CHCl_3$) ^1H NMR data ($CDCl_3$): δ 6.42 (d, 1 H, *J* = 6.4 Hz) 4.85 (ddd, 1 H, *J* = 1.4, 2.9 and 6.3 Hz), 4.70 (dd, 1 H, *J* = 3.1, 6.2 Hz), 4.64, 4.63 (d, 1 H each, *J* = 7.3, 5.0 Hz), 4.37 (m, 1 H), 4.27 (m, 1 H); HRMS calcd for $C_{16}H_{18}O_5$-Na (M + Na) 313.1052, found 313.1052.

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzyl-4-*O*-(6-*O*-benzoyl-2-deoxy-2-iodo-3,4-*O*-isopropylidene-β-D-galactopyranosyl)-β-D-glucopyranoside (11). To a cold (0 °C) solution of 2-(trimethylsilyl)ethyl 2,3,6-tri-*O*-benzyl-β-D-glucopyranoside[21] (**10**) (380 mg, 0.690 mmol) and **9** (299 mg, 1.030 mmol) in dry MeCN (10 mL) was added a solution of *N*-iodosuccinimide (268 mg, 1.19 mmol) in dry MeCN (2 mL) under Ar and exclusion from light. The mixture was stirred at 0 °C for 1 h and at room temperature for 16 h and concentrated. The residue was dissolved in CH_2Cl_2 (70 mL), and the mixture was washed with aqueous $Na_2S_2O_3$ (30 mL, 10%) and saturated aqueous $NaHCO_3$ (30 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, heptane/CH_2Cl_2/AcOEt 42:14:1) to give **11** (510 mg, 76%): $[\alpha]^{25}_D$ +26° (*c* 1.0, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 4.55 (d, 1 H, *J* = 9.4 Hz), 4.50 (dd, 1 H, *J* = 5.4, 11.5 Hz), 4.41 (d, 1 H, *J* = 7.8 Hz), 4.34 (dd, 1 H, *J* = 5.1, 9.0 Hz), 4.28 (dd, 1 H, *J* = 7.4, 11.4 Hz), 3.39 (dd, 1 H, *J* = 7.9, 9.1 Hz), 1.52, 1.37 (s, 3 H each), 0.06 (s, 9 H); ^{13}C NMR data ($CDCl_3$) δ 166.1, 139.0, 138.8, 138.3, 133.1, 129.8−127.3, 111.4, 103.2, 99.2, 82.6, 82.1, 82.0, 75.5, 75.1, 74.9, 74.6, 73.6, 73.3, 71.1, 68.9, 67.4, 33.6, 28.3, 26.1, 18.5, −1.3 (3C); HRMS calcd for $C_{48}H_{59}O_{11}ISiNa$ (M + Na) 989.2769, found 989.2758.

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzyl-4-*O*-(6-*O*-benzoyl-2-deoxy-3,4-*O*-isopropylidene-β-D-*lyxo*-hexopyranosyl)-β-D-glucopyranoside (12). Compound **11** (400 mg, 0.414 mmol) was hydrogenated (H_2, 10% Pd/C, 103 mg) in a mixture of MeOH/EtOAc (12 mL, 5:1) and Et_3N (0.073 mL) for 1 h and then filtered (Celite) and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 5:1) to give **12** (338 mg, 97%): $[\alpha]^{25}_D$ +11° (*c* 1.0, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 4.57 (dd, 1 H, *J* = 5.4, 11.4 Hz), 4.53 (dd, 1 H, *J* = 2.0, 9.7Hz), 4.39 (m, 2 H), 3.41 (dd, 1 H, *J* = 7.9, 9.0 Hz), 1.97 (ddd, 1 H, *J* = 2.1, 6.9, 12.9 Hz), 1.60 (m, 1 H), 1.51, 1.33 (s, 3 H each), 0.05 (s, 9 H); ^{13}C NMR data ($CDCl_3$) δ 166.3, 139.0, 138.7, 138.1, 133.0−127.3, 109.7, 103.2, 99.1, 82.7, 82.1, 76.1, 75.1, 74.9, 74.7, 73.5, 72.2, 71.1, 71.0, 68.7, 67.4, 64.0, 35.7, 28.3, 26.4, 18.6, −1.4. Anal. Calcd for $C_{48}H_{60}O_{11}Si$: C, 68.5; H, 7.2. Found: C, 68.4; H, 7.0.

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzyl-4-*O*-(6-*O*-benzoyl-2-deoxy-β-D-*lyxo*-hexopyranosyl)-β-D-glucopyranoside (13). Compound **12** (283 mg, 0.336 mmol) was treated with aqueous AcOH (80%, 5 mL) at 50 °C for 4.5 h, and the mixture was concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 1:1) to give **13** (228 mg, 85%): $[\alpha]^{25}_D$ +12° (*c* 1.0, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 4.58 (dd, 1 H, *J* = 1.8, 9.8 Hz), 4.40 (d, 1 H, *J* = 7.7 Hz), 3.95 (t, 1 H, *J* = 9.4 Hz), 1.90 (ddd, 1 H, *J* = 1.6, 4.5, 12.5 Hz), 1.60 (ddd, 1H, *J* = 9.6, 12.2, 9.7 Hz), 0.07 (s, 9 H); ^{13}C NMR data ($CDCl_3$) δ 166.6, 139.1, 138.7, 138.1, 133.3−127.4 (21C), 103.3, 100.0, 82.8, 82.0, 76.4, 74.9, 74.9, 74.7, 73.5, 72.6, 68.8, 68.2, 67.5, 66.8, 62.9, 35.4, 18.6, −1.3 (3C); HRMS calcd for $C_{45}H_{56}O_{11}SiNa$ (M + Na) 823.3489, found 823.3480.

2-(Trimethylsilyl)ethyl 2,3,6-tri-*O*-benzyl-4-*O*-(3-*O*-allyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-β-D-glucopyranoside (17). A mixture of compound **16**[21] (200 mg, 0.224 mmol), dibutyltin oxide (67 mg, 0.268 mmol), and toluene (15 mL) was refluxed for 1 h. Part of the toluene (5 mL) was removed by distillation under Ar. The residue was cooled to 80 °C, and tetrabutylammonium iodide (50 mg) and allyl bromide (0.154 mL, 1.79 mmol) were added. The mixture was stirred overnight at 90 °C and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 4:1) to give **17** (189 mg, 91%): $[\alpha]^{25}_D$ +6° (*c* 1.5, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 6.02−5.88 (m, 1 H), 5.33−5.21 (m, 2 H), 1.05 (m, 2 H); ^{13}C NMR data δ 139.3, 138.9, 138.7, 138.5, 138.3, 134.7, 134.7, 117.3, 103.2, 102.7, 102.7, 18.6, −1.3; HRMS calcd for $C_{55}H_{68}O_{11}SiNa$ (M + Na) 955.4429, found 955.4423.

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzyl-4-*O*-(4-*O*-acetyl-3-*O*-allyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-β-D-glucopyranoside (18). Compound **17** (1.00 g, 1.072 mmol) was acetylated with Ac_2O/pyridine (9 mL, 1:1) at room temperature for 20 h. The mixture was diluted with CH_2Cl_2 (150 mL), washed with aqueous H_2SO_4 (50 mL, 1 M), water (2 × 70 mL), saturated aqueous $NaHCO_3$ (70 mL), and water (70 mL), dried (Na_2SO_4), and concentrated to give crude **18** (1.04 g, 99%): $[\alpha]^{25}_D$ +3° (*c* 1.0, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 5.88 (m, 1 H), 5.44 (d, 1 H, *J* = 3.5 Hz), 4.47, 4.42 (d, 1 H each, *J* = 7.4, 7.8 Hz), 2.03 (s, 3 H), 1.04 (m, 2 H); ^{13}C NMR data δ 170.2, 139.2, 138.8, 138.7, 138.3, 137.9, 134.6, 134.5, 133.7, 117.1, 103.2, 102.4, 20.9, 18.5, −1.4 (3C); HRMS calcd for $C_{57}H_{70}O_{12}SiNa$ (M + Na) 997.4534, found 997.4542.

2-(Trimethylsilyl)ethyl 2,3,6-tri-*O*-benzyl-4-*O*-(4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-β-D-glucopyranoside (19). Compound **18** (970 mg, 0.995 mmol) was treated with $PdCl_2$ (59 mg, 0.333 mmol) in MeOH (20 mL) at room temperature for 4 h. The mixture was filtered (Celite) and concentrated. The residue was chromatographed to give **19** (702 mg, 76%): $[\alpha]^{25}_D$ −5° (*c* 1.0, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 5.37 (d, 1 H, *J* = 3.4Hz), 4.53, 4.44 (d, 1 H each, *J* = 7.6, 7.9 Hz), 2.07 (s, 3 H), 1.09 (m, 2 H); ^{13}C NMR data δ 171.0, 139.1, 138.8, 138.3, 138.2, 137.9, 103.2, 102.4, 20.8, 18.5, −1.4 (3C); HRMS calcd for $C_{54}H_{66}O_{12}SiNa$ (M + Na) 957.4221, found 957.4246.

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzyl-4-*O*-{4-*O*-acetyl-2,6-di-*O*-benzyl-3-*O*-[imidazol-1-yl(thiocarbonyl)]-β-D-galactopyranosyl}-β-D-glucopyranoside (20). A mixture of **19** (240 mg, 0.257 mmol), 1,1′-(thiocarbonyl)diimidazole (132 mg, 0.744 mmol), and dry $ClCH_2CH_2Cl$ (5 mL) was heated at 80 °C for 19 h. The mixture was diluted with CH_2Cl_2 (50 mL), washed with saturated aqueous $NaHCO_3$ (20 mL) and water (20 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, toluene/EtOAc 12:1) to give **20** (221 mg, 82%): $[\alpha]^{25}_D$ −1° (*c* 0.7, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 7.95 (s, 1 H), 6.99 (s, 1 H), 5.62−5.57 (m, 2 H), 4.59 (d, 1 H *J* = 7.8 Hz), 4.41 (d, 1 H, *J* = 7.3 Hz), 1.90 (s, 3 H), 1.05 (m, 2 H); ^{13}C NMR data δ 169.5, 139.0, 138.8, 138.1, 137.7, 137.4, 128.5, 128.4, 128.4, 128.4, 128.3, 128.0−127.4, 103.3, 102.3, 82.8, 81.9, 80.9, 76.7, 75.3, 75.0, 74.7, 73.4, 71.2, 68.1, 67.5, 66.7, 66.5, 20.4, 18.5, −1.4; HRMS calcd for $C_{58}H_{68}O_{12}$-SSiNa (M + Na) 1067.4160, found 1067.4150.

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzyl-4-*O*-(4-*O*-acetyl-2,6-di-*O*-benzyl-3-deoxy-β-D-*xylo*-hexopyranosyl)-β-D-glucopyranoside (21) and 2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzyl-4-*O*-(3-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-β-D-glucopyranoside (22). To a refluxing solution of compound **20** (135 mg, 0.129 mmol) and tributyltin hydride (0.116 mL, 0.387 mmol) in dry toluene (10 mL) was added during 5 min a solution of AIBN (~5 mg) in dry toluene (1 mL) under Ar. The mixture was refluxed for 23 h and

(32) Alonso, R. A.; Vite, G. D.; McDevitt, R. E.; Fraser-Reid, B. *J. Org. Chem.* **1992**, *57*, 573−584.

concentrated. The residue was chromatographed (SiO_2, heptane/toluene/EtOAc 9:1:0 → 9:1:2) to give **21** (49 mg, 42%), **22** (9 mg, 8%), **19** (13 mg, 11%), and **16**[21] (17 mg, 15%). Compound **21**: $[\alpha]^{25}_D$ −23° (*c* 1.0, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 5.04 (m, 1 H), 4.55, 4.41 (d, 1 H each *J* = 7.8, 7.8 Hz), 2.34 (ddd, 1 H, *J* = 3.1, 4.9, 14.0 Hz), 1.64 (m, 1 H), 2.02 (s, 3 H), 0.15 (s, 9 H); ^{13}C NMR data δ 170.2, 139.23, 138.8, 138.4, 138.1, 128.4−127.2, 104.2, 103.2, 83.1, 82.0, 75.2, 74.9, 74.9, 74.0, 73.3, 73.2, 72.5, 68.6, 67.9, 67.6, 67.4, 33.6, 21.0, 18.5, −1.4. Anal. Calcd for $C_{54}H_{66}O_{11}Si$: C, 70.6; H, 7.2. Found: C, 70.2; H, 6.9. Compound **22**: $[\alpha]^{25}_D$ +12° (*c* 0.8, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 4.78 (dd, 1 H, *J* = 3.0, 9.9 Hz), 4.51 (d, 1H *J* = 7.8 Hz), 2.58 (d, 1 H, *J* = 4.2 Hz), 2.01 (s, 3 H), 0.15 (s, 9 H). Compound **16**: $[\alpha]^{25}_D$ +12° (*c* 1.0, $CHCl_3$).

2-(Trimethylsilyl)ethyl 4-*O*-{3-*O*-[Imidazol-1-yl(thiocarbonyl)]-4,6-*O*-(*p*-methoxybenzylidene)-β-D-galactopyranosyl}-β-D-glucopyranoside (24). A mixture of **23**[16] (600 mg, 1.070 mmol), dibutyltin oxide (300 mg, 1.180 mmol), and MeOH (30 mL) was refluxed for 10 h. The solvent was removed, and toluene (2 mL) was added and removed (oil pump). A mixture of the residue, 1,1′-(thiocarbonyl)diimidazole (304 mg, 1.711 mmol), DMAP (10 mg), actived molecular sieves 3Å (1 g), and dry $ClCH_2CH_2Cl$ (50 mL) was stirred at 35 °C under Ar for 4 days. The mixture was filtered (Celite) and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 10:1) to give **24** (335 mg, 47%): ^1H NMR data ($CDCl_3$) δ 8.30, 7.61, 6.98 (s, 1 H each), 5.63 (dd, 1 H, *J* = 3.6, 10.0 Hz), 5.43 (s, 1 H), 4.71 (d, 1 H, *J* = 7.9 Hz), 4.57 (d, 1 H, *J* = 3.7 Hz), 4.38−4.31 (m, 2 H), 3.79 (s, 3 H), 0.00 (s, 9 H).

2-(Trimethylsilyl)ethyl 4-*O*-{3-*O*-[(Phenylthio)(thiocarbonyl)]-4,6-*O*-(*p*-methoxybenzylidene)-β-D-galactopyranosyl}-β-D-glucopyranoside (25). Compound **23** (1.00 g, 1.783 mmol), dibutyltin oxide (676 mg, 2.674 mmol), phenylthiochlorothiocarbonate (0.379 mL, 2.674 mmol), tetrabutylammonium chloride (258 mg, 0.892 mmol), and dry toluene were treated at 35 °C for 24 h as described in the preparation of **8**. The solvent was removed, and the residue was chromatographed (SiO_2, heptane/EtOAc 1:10) to give **25** (1.10g, 87%): $[\alpha]^{25}_D$ +30° (*c* 1.4, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 5.69 (dd, 1 H, *J* = 3.7, 10.0 Hz), 5.37 (s, 1 H), 4.61 (d, 1 H, *J* = 8.0 Hz), 4.50 (d, 1 H, *J* = 3.4 Hz), 4.31 (d, 1 H, *J* = 7.7 Hz), 3.82 (s, 3 H), 0.00 (s, 9 H); HRMS calcd for $C_{32}H_{44}O_{12}S_2SiNa$ (M + Na) 735.1941, found 735.1951.

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-acetyl-4-*O*-{2-*O*-acetyl-3-*O*-[(phenylthio)(thiocarbonyl)]-4,6-*O*-(*p*-methoxybenzylidene)-β-D-galactopyranosyl}-β-D-glucopyranoside (26). Compound **25** (380 mg, 0.533 mmol) was acetylated as described in the preparation of **17**. The crude product was chromatographed (SiO_2, heptane/EtOAc 2:1) to give **26** (409 mg, 87%): $[\alpha]^{25}_D$ +25° (*c* 1.5, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 5.69 (dd, 1 H, *J* = 3.7, 10.1 Hz), 5.41 (s, 1 H), 5.22−5.14 (m, 2 H), 4.88 (dd, 1H, *J* = 7.9, 9.8 Hz), 4.51−4.44 (m, 3 H), 2.09, 2.02, 1.99 (3 s, 12 H), 0.01 (s, 9 H); HRMS calcd for $C_{40}H_{52}O_{16}S_2SiNa$ (M + Na) 903.2364, found 903.2350.

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-acetyl-4-*O*-[2-*O*-acetyl-3-deoxy-4,6-*O*-(*p*-methoxybenzylidene)-β-D-*xylo*-hexopyranosyl]-β-D-glucopyranoside (27). A mixture of compound **26** (430 mg, 0.466 mmol), tributyltin hydride (0.448 mL, 1.399 mmol), AIBN (5 mg), and dry toluene (22 mL) was treated as described in the preparation of **20**. The crude product was chromatographed (SiO_2, heptane/EtOAc 2:1 → 1:1) to give **27** (297 mg, 85%): $[\alpha]^{25}_D$ −22° (*c* 1.0, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 5.43 (s, 1 H), 5.20 (t, 1 H, *J* = 9.8 Hz), 4.74 (dd, 1 H, *J* = 8.0, 9.9 Hz), 4.88 (m, 1 H), 4.50, 4.40 (d, 1 H each, *J* = 7.9, 8.1 Hz), 2.50 (ddd, 1 H, *J* = 2.7, 5.3, 13.7 Hz), 2.11, 2.08, 2.04, 2.02 (s, 3 H each), 1.61 (m, 1 H), 0.01 (s, 9 H). Anal. Calcd for $C_{33}H_{48}O_{15}Si$ C, 55.6; H, 6.8. Found: C, 55.5; H, 6.8.

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-acetyl-4-*O*-[2-*O*-acetyl-3-deoxy-6-*O*-(*p*-methoxybenzoyl)-β-D-*xylo*-hexopyranosyl]-β-D-glucopyranoside (28) and 2-(trimethylsilyl)-ethyl 2,3,6-Tri-*O*-acetyl-4-*O*-[2-*O*-acetyl-3-deoxy-4-*O*-(*p*-methoxybenzoyl)-β-D-*xylo*-hexopyranosyl]-β-D-glucopyranoside (29). A mixture of **27** (80 mg, 0.112 mmol), DDQ (40 mg, 0.169 mmol), 18-crown-6 ether (3 mg), $NaHSO_4$ (69 mg, 0.507 mmol), molecular sieves 4 Å (0.01 mL H_2O added to 200 mg of sieve), and $ClCH_2CH_2Cl$ (5 mL) was stirred at 70 °C overnight and then diluted with CH_2Cl_2 /H_2O (70 mL, 5:2) and filtered (Celite). The organic phase was washed with saturated aqueous $NaHCO_3$ (2 × 20 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, toluene/CH_3CN 9:1 → 7:1) to give **28** (53 mg, 65%) and **29** (25 mg, 31%). Compound **28**: $[\alpha]^{25}_D$ −6° (*c* 1.2, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 5.20 (t, 1 H, *J* = 9.5 Hz), 4.93 (dd, 1 H, *J* = 8.1, 9.6 Hz), 4.89 (m, 1 H), 4.66 (dd, 1 H, *J* = 6.1, 11.6 Hz) 4.51 (dd, 1 H, *J* = 1.7, 11.9 Hz) 4.47, 4.39 (d, 1 H each, *J* = 7.9, 8.1 Hz), 4.27 (dd, 1 H, *J* = 7.1, 11.5 Hz), 4.20 (dd, 1 H, *J* = 5.1, 12.0 Hz), 3.87 (s, 3 H), 2.44 (ddd, 1 H, *J* = 3.0, 5.2, 13.5 Hz), 2.08, 2.04 (s, 6 H each), 1.57 (m, 1 H), 0.90 (m, 2 H), 0.00 (s, 9 H); HRMS calcd for $C_{33}H_{48}O_{16}SiNa$ (M + Na) 751.2609, found 751.2612. Compound **29**: $[\alpha]^{25}_D$ +4° (*c* 1.0 , $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 5.32 (t, 1 H, *J* = 2.0 Hz), 5.20, (t, 1 H, *J* = 9.6 Hz), 4.94 (m, 1 H), 4.92 (dd, 1 H, *J* = 8.0, 9.6 Hz), 4.56−4.48 (m, 3 H), 4.20 (dd, 1 H, *J* = 5.5, 11.9 Hz), 3.87 (s, 3 H), 2.53 (ddd, 1 H, *J* = 3.2, 5.3, 14.1 Hz), 2.12, 2.07, 2.03, 1.95 (s, 3 H each), 1.57 (m, 1 H), 0.92 (m, 2 H), 0.00 (s, 9 H); HRMS calcd for $C_{33}H_{48}O_{16}SiNa$ (M + Na) 751.2609, found 751.2621.

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-acetyl-4-*O*-(2-*O*-acetyl-3-deoxy-β-D-*xylo*-hexopyranosyl)-β-D-glucopyranoside (30). Compound **27** (309 mg, 0.433 mmol) was treated with aqueous AcOH (80%) at 50 °C for 4 h. The solvent was removed, and the residue was chromatographed to give **30** (250 mg, 97%): $[\alpha]^{25}_D$ −31° (*c* 1.0, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 5.17 (t, 1 H, *J* = 9.4 Hz), 4.93−4.83 (m, 2 H), 4.48, 4.44 (d, 1 H each, *J* = 7.9, 8.0 Hz), 2.38 (ddd, 1 H, *J* = 3.2, 5.3, 13.6 Hz), 2.10, 2.07, 2.04, 2.03 (s, 3 H each), 1.57 (m, 1 H), 0.01 (s, 9 H); HRMS calcd for $C_{25}H_{42}O_{14}SiNa$ (M + Na) 617.2242, found 617.2249.

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-acetyl-4-*O*-[2-*O*-acetyl-6-*O*-(*tert*-butyldimethylsilyl)-3-deoxy-β-D-*xylo*-hexopyranosyl]-β-D-glucopyranoside (31). To a cold (0 °C) mixture of **30** (250 mg, 0.421 mmol), imidazole (86 mg, 1.26 mmol), and CH_2Cl_2 (9 mL) was added *tert*-butyldimethylsilyl chloride (98 mg, 0.631 mmol). The mixture was stirred at 4 °C overnight and then diluted with CH_2Cl_2 (100 mL), washed with saturated aqueous $NaHCO_3$ (30 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 3:1) to give **31** (261 mg, 88%): $[\alpha]^{25}_D$ −34° (*c* 0.5, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 5.16 (t, 1 H, *J* = 9.5 Hz), 4.88 (dd, 1 H, *J* = 8.1, 9.8 Hz), 4.85 (m, 1 H), 4.48 (dd, 1 H, *J* = 2.0, 11.8 Hz), 4.46, 4.38 (d, 1 H each, *J* = 8.1, 7.8), 4.21 (dd, 1 H, *J* = 5.3, 11.9 Hz), 2.43 (ddd, 1 H, *J* = 3.3, 5.2, 13.8 Hz), 2.09 (s, 3 H), 2.02 (s, 9 H), 1.51 (m, 1 H), 0.88 (m, 11 H), 0.07 (s, 6 H), 0.01 (s, 9 H); HRMS calcd for $C_{31}H_{56}O_{14}Si_2$-Na (M + Na) 731.3106, found 731.3115.

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzyl-4-*O*-[3,6-di-*O*-benzoyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-β-D-*lyxo*-hexopyranosyl]-β-D-glucopyranoside (33). To a cold (−60 °C) mixture of **8** (195 mg, 0.215 mmol), silver trifluoromethanesulfonate (112 mg, 0.431 mmol), collidine (0.086 mL, 0.762 mmol), molecular sieves (AW-300, 600 mg), and dry CH_2Cl_2 (7 mL) was added a solution of **32**[26] (245 mg, 0.438 mmol) in dry CH_2Cl_2 (2 mL), under Ar. After 1.5 h, the temperature was allowed to raise to 20 °C. After 6 h, Et_3N was added, and the mixture was diluted with CH_2Cl_2 (200 mL) and filtered (Celite). The mixture was washed with saturated aqueous $NaHCO_3$ (100 mL) and water (100 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 10:1) to give **33** (285 mg, 93%): $[\alpha]^{25}_D$ +18° (*c* 1.0, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 4.63 (d, 1 H, *J* = 3.6 Hz), 4.38 (d, 1 H, *J* = 7.8 Hz), 2.12 (m, 1 H), 1.94 (bd, 1 H, *J* = 10.2 Hz); ^{13}C NMR data ($CDCl_3$) δ 166.2, 165.0, 139.1, 138.8, 138.8, 138.7, 138.3, 138.1, 133.2, 132.9, 130.1−127.3, 103.2, 100.5, 99.9, 82.9, 82.0, 79.2, 76.4, 75.2, 75.1, 74.9, 74.9, 74.7, 74.4, 73.7, 73.5, 73.3, 73.1, 72.8, 71.9, 70.3, 68.9, 68.3, 67.4, 63.5, 32.6, 18.6, −1.4. Anal. Calcd for $C_{86}H_{94}O_{17}Si$: C, 72.3; H, 6.6. Found: C, 72.2; H, 6.6.

2-(Trimethylsilyl)ethyl 4-*O*-[3,6-Di-*O*-benzoyl-2-deoxy-4-*O*-(α-D-galactopyranosyl)-β-D-*lyxo*-hexopyranosyl]-β-D-glucopyranoside (34). Compound **33** (280 mg, 0.196 mmol) was hydrogenated (H_2, 10% Pd/C, 85 mg) in acetic acid (7 mL) for 10 h. The mixture was filtered (Celite) and concentrated, and the residue was chromatographed (SiO_2, CH_2Cl_2 /MeOH

20:1) to give **34** (152 mg, 97%): $[\alpha]^{25}_D$ +45° (*c* 1.0, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 5.08 (d, 1 H, *J* = 9.8 Hz), 4.99 (s, 1 H), 4.31 (d, 1 H, *J* =7.6 Hz), 2.28–2.07 (m, 2 H), 0.03 (s, 9 H); ^{13}C NMR data ($CDCl_3$) δ 166.5, 165.9, 133.6, 133.3, 129.9–128.4, 102.1, 101.0, 100.3, 78.6, 74.6, 74.4, 73.7, 72.8, 71.0, 70.6, 69.9, 69.9, 69.8, 69.2, 67.7, 63.1, 62.0, 62.0, 61.1, 32.2, 18.3, −1.4; HRMS calcd for $C_{37}H_{52}O_{17}SiNa$ (M + Na) 819.2871, found 819.2850.

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzoyl-4-*O*-[3,6-di-*O*-benzoyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-benozyl-α-D-galactopyranosyl)-β-D-*lyxo*-hexopyranosyl]-β-D-glucopyranoside (35). To a cold (0 °C) mixture of compound **34** (72 mg, 0.090 mmol) and pyridine (2 mL) was added benzoyl chloride (0.092 mL, 0.97 mmol). The mixture was left at room temperature overnight and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 3:1) to give **35** (131 mg, 96%): $[\alpha]^{25}_D$ +48° (*c* 1.0, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 6.06 (dd, 1 H, *J* = 1.0, 3.4 Hz), 5.97 (dd, 1 H, *J* = 3.3, 10.9 Hz), 5.84 (t, 1 H, *J* = 9.5 Hz), 5.70 (dd, 1 H, *J* = 3.4, 10.8 Hz), 5.60 (d, 1 H, *J* = 3.5 Hz), 5.50 (dd, 1 H, *J* = 7.9, 9.7 Hz), 5.05 (ddd, 1 H, *J* = 2.2, 4.7, 12.3 Hz), 4.80 (m, 2 H), 4.77 (d, 1 H, *J* = 7.9 Hz), 4.55 (dd, 1 H, *J* = 5.1, 12.0 Hz), 2.26 (ddd, 1 H, *J* = 8.8, 9.3, 8.9, Hz), 2.02 (bd, 1 H, *J* = 9.7 Hz), 0.03 (s, 9 H); ^{13}C NMR data ($CDCl_3$) δ 166.3, 166.1, 165.8, 165.8, 165.7, 165.5, 165.3, 165.2, 165.2, 133.8–128.2, 100.6, 99.4, 98.0, 75.9, 74.1, 73.7, 73.1, 73.0, 72.3, 71.0, 70.3, 69.5, 68.1, 68.0, 67.5, 63.2, 62.7, 61.9, 32.6, 18.0, −1.5; HRMS calcd for $C_{87}H_{80}O_{24}SiNa$ (M + Na) 1547.4707, found 1547.4738.

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-acetyl-4-*O*-[2-*O*-acetyl-6-*O*-(*tert*-butyldimethylsilyl)-3-deoxy-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-β-D-*xylo*-hexopyranosyl]-β-D-glucopyranoside (36). A mixture of compound **31** (325 mg, 0.458 mmol), **32** (522 mg, 0.934 mmol), silver trifluoromethanesulfonate (238 mg, 0.920 mmol), collidine (0.184 mL, 1.38 mmol), and CH_2Cl_2 (13 mL) was treated as descibed in the preparation of **33**. The crude product was chromatographed (SiO_2, heptane/EtOAc 10:1 → 7:1) to give **36** (465 mg, 82%): $[\alpha]^{25}_D$ +17° (*c* 0.9, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 5.12 (m, 2 H), 4.90 (dd, 1 H, *J* = 7.8, 9.8 Hz), 4.34 (d, 1 H, *J* = 8.0 Hz), 2.62 (dt, 1 H, *J* = 5.8, 13.3 Hz), 2.10, 2.03, 1.96, 1.83 (s, 3 H each), 1.50 (m, 1 H), 0.87 (m, 11 H), 0.01 (s, 15 H); ^{13}C NMR data ($CDCl_3$) δ 170.5, 170.3, 169.6, 169.3, 138.9, 138.7, 138.7, 138.6, 128.3–127.3, 102.0, 100.3, 79.3, 78.7, 76.8, 75.4, 75.0, 74.7, 73.4, 73.3, 73.2, 72.9, 72.6, 71.4, 70.0, 70.0, 69.8, 69.5, 67.4, 62.5, 60.5, 34.3, 25.8, 20.9, 20.9, 20.8, 18.0, 17.9, −1.4; HRMS calcd for $C_{65}H_{90}O_{19}Si_2Na$ (M + Na) 1253.5513, found 1253.5529.

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-acetyl-4-*O*-[2-*O*-acetyl-3-deoxy-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-β-D-*xylo*-hexopyranosyl]-β-D-glucopyranoside (37). To a solution of compound **36** (445 mg, 0.361 mmol) in THF (18 mL) was added a solution of tetrabutylammonium fluoride trihydrate (226 mg, 0.718 mmol) in THF (2 mL). After 5.5 h, the mixture was diluted with toluene (150 mL), washed with saturated aqueous $NaHCO_3$ (50 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 3:1–1:1) to give **37** (400 mg, 99%): $[\alpha]^{25}_D$ −2° (*c* 1.1, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 5.18 (t, 1 H, *J* = 9.2 Hz), 4.92–4.86 (m, 3 H), 4.79 (m, 1 H), 4.39 (d, 1 H, *J* =7.8 Hz), 2.61 (bdt, 1 H, *J* = 4.0, 14.0 Hz), 2.10, 2.04, 1.99, 1.98 (s, 3 H each), 1.49 (ddd, 1 H, *J* = 2.7, 14.0, 2.4 Hz), 0.01 (s, 9 H); ^{13}C NMR data ($CDCl_3$) δ 170.6, 170.1, 169.7, 169.1, 138.8, 138.5, 137.7, 128.5–127.4, 102.7, 101.2, 100.0, 79.2, 77.2, 76.4, 76.1, 75.7, 74.8, 74.6, 74.5, 73.5, 74.4, 72.8, 72.3, 71.8, 70.2, 68.9, 68.3, 67.4, 62.6, 60.9, 33.5, 21.0, 20.9, 20.8, 17.9, −1.4; HRMS calcd for $C_{59}H_{76}O_{19}SiNa$ (M + Na) 1139.4648, found 1139.4672.

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-acetyl-4-*O*-[2-*O*-acetyl-3-deoxy-4-*O*-(α-D-galactopyranosyl)-β-D-*xylo*-hexopyranosyl]-β-D-glucopyranoside (38). Compound **37** (386 mg, 0.346 mmol) was hydrogenolyzed as described in the preparation of **34**. The crude product was chromatographed (SiO_2, EtOAc/MeOH 20:1 → 15:1) to give **38** (241 mg, 92%): $[\alpha]^{25}_D$ +4° (*c* 1.1, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 5.16 (t, 1 H, *J* = 9.2 Hz), 4.98 (d, 1 H, *J* = 2.6 Hz), 4.86 (dd, 1 H, *J* = 7.9, 9.3 Hz), 4.68 (m, 1 H). 4.50, 4.44 (2 d, 1 H each, *J* = 7.9, 8.1 Hz), 2.60 (bd, 1 H, *J* = 12.5 Hz), 2.09, 2.05, 2.04, 2.02 (s, 3 H each), 1.53 (bt, 1 H, *J* = 12.0 Hz), 0.00 (s, 9 H); HRMS calcd for $C_{31}H_{52}O_{19}SiNa$ (M + Na) 779.2770, found 779.2780.

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-acetyl-4-*O*-[2-*O*-acetyl-3-deoxy-6-*O*-(*p*-methoxybenzoyl)-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-β-D-*xylo*-hexopyranosyl]-β-D-glucopyranoside (39). To a cold (−60 °C) mixture of **28** (160 mg, 0.220 mmol), silver trifluoromethanesulfonate (114 mg, 0.440 mmol), collidine (0.086 mL, 0.660 mmol), molecular sieves (AW-300, 800 mg), and dry CH_2Cl_2 (5 mL) was added a solution of **32** (250 mg, 0.447mmol) in dry CH_2Cl_2 (3 mL), under Ar. After 30 min at −60 °C, the temperature was allowed to rise to room temperature. After 11 h, Et_3N (0.5 mL) was added, and the mixture was diluted with CH_2Cl_2 (100 mL) and filtered (Celite). The mixture was washed with saturated aqueous $NaHCO_3$ (40 mL) and water (40 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 7:1) to give **39** (180 mg, 66%): $[\alpha]^{25}_D$ +9° (*c* 1.0, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 5.18 (t, 1 H, *J* = 9.1 Hz), 5.03 (d, 1 H, *J* = 2.5 Hz), 4.47 (d, 1 H, *J* = 8.0 Hz), 4.39 (d, 1 H, *J* = 7.8 Hz), 2.64 (ddd, 1 H, *J* = 3.5, 5.1, 13.8 Hz), 2.07, 2.04, 1.98, 1.92 (s, 3 H each), 1.47 (bt, 1 H, *J* = 13.9 Hz), 0.01 (s, 9 H); ^{13}C NMR data ($CDCl_3$) δ 170.5, 170.4, 169.4, 169.3, 165.9, 163.8, 138.8, 138.7, 138.5, 138.4, 131.7–114.0, 102.1, 101.0, 100.3, 79.5, 76.5, 75.7, 75.6, 75.3, 74.7, 74.1, 74.0, 73.3, 73.1, 72.9, 72.7, 71.5, 70.3, 69.5, 69.0, 67.4, 62.4, 62.0, 55.5, 34.2, 20.8, 20.8, 20.7, 17.9, −1.4.

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-acetyl-4-*O*-[2-*O*-acetyl-3-deoxy-6-*O*-(*p*-methoxybenzoyl)-4-*O*-(α-D-galactopyranosyl)-β-D-*xylo*-hexopyranosyl]-β-D-glucopyranoside (40). Compound **39** (145 mg, 0.116 mmol) was hydrogenolyzed as described in the preparation of **34**. The crude product was chromatographed (SiO_2, EtOAc/MeOH 10:1) to give **22** (103 mg, 99%): $[\alpha]^{25}_D$ +7° (*c* 0.9, $CDCl_3$); ^1H NMR data ($CDCl_3$) δ 5.20 (t, 1 H, *J* = 9.5 Hz), 5.01 (bs, 1 H), 4.92 (dd, 1 H, *J* = 8.0, 9.7 Hz), 4.73 (m, 1 H), 4.62 (dd, 1 H, *J* = 7.5, 11.1 Hz), 4.54 (dd, 1 H, *J* = 1.7, 11.9 Hz), 4.70 (dd, 2 H, *J* = 7.9, 8.0 Hz), 2.69 (m, 1 H), 2.11, 2.09, 2.06, 2.05 (s, 3 H each), 1.53 (m, 1 H), 0.01 (s, 9 H); HRMS calcd for $C_{39}H_{58}O_{21}SiNa$ (M + Na) 913.3138, found 913.3129.

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-acetyl-4-*O*-[2-*O*-acetyl-3-deoxy-6-*O*-(*p*-methoxybenzoyl)-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-β-D-*xylo*-hexopyranosyl]-β-D-glucopyranoside (41). Compound **40** (89 mg, 0.10 mmol) was treated with Ac_2O/pyridine (5 mL, 1:1) at room temperature overnight. The solvent was removed, and the residue was chromatographed (SiO_2, heptane/EtOAc 1:2) to give **22** (104 mg, 98%): $[\alpha]^{25}_D$ +18° (*c* 1.0, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 5.55 (d, 1 H, *J* = 2.4 Hz), 5.39 (dd, 1 H, *J* = 3.2, 10.8 Hz), 5.25–5.14 (m, 3 H), 4.90 (dd, 1 H, *J* = 8.1, 9.5 Hz), 4.74 (m, 1 H), 4.48 (m, 5 H), 3.86 (s, 3 H), 2.62 (bdt, 1 H, *J* = 3.7 13.9 Hz), 2.11, 2.07, 2.04, 2.02, 1.99, 1.97 (24 H), 1.53 (bt, 1 H, *J* = 11.8 Hz), 0.01 (s, 9 H); HRMS calcd for $C_{47}H_{66}O_{25}$-SiNa (M + Na) 1081.3560, found 1081.3552.

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzoyl-4-*O*-[2,3-di-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (44). To a cold (4 °C) mixture of compound **43**[16] (300 mg, 0.311 mmol), imidazole (42 mg, 0.622 mmol), and dry CH_2Cl_2 (10 mL) was added *tert*-butyldimethylsilyl chloride (97%, 72 mg, 0.467 mmol) under Ar. The mixture was stirred at 4 °C overnight and then diluted with CH_2Cl_2 (50 mL) and washed with saturated aqueous $NaHCO_3$ (20 mL) and saturated aqueous NaCl (20 mL). The organic phase was dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 6:1 → 3:1) to give **44** (327 mg, 98%): $[\alpha]^{25}_D$ +57° (*c* 1.0, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 5.73–5.64 (m, 2 H), 5.37 (dd, 1 H, *J* = 7.9, 9.6 Hz), 5.13 (dd, 1 H, *J* = 3.1, 10.4 Hz), 4.73, 4.68 (d, 1 H each, *J* = 7.9, 7.8 Hz), 4.57 (dd, 1 H, *J* = 2.7, 12.0 Hz), 4.40 (dd, 1 H, *J* = 4.67, 12.0 Hz), 0.80 (s, 9 H), 0.08, 0.07 (s, 3 H each), −0.15 (s, 9 H); HRMS calcd for $C_{58}H_{68}O_{16}Si_2Na$ (M + Na) 1099.3944, found 1099.3997.

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzoyl-4-*O*-[2,3-di-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (46). (a) To a cold (−30 °C) mixture of **42**[16] (226 mg, 0.209 mmol), silver

trifluoromethanesulfonate (77 mg, 0.293 mmol), molecular sieves (AW-300, 300 mg), and dry toluene (7 mL) was added a mixture of **45**[27] (198 mg, 0.313 mmol), *p*-toluenesulfonic acid (5 mg), and dry toluene (2 mL) under Ar. The mixture was allowed to rise to room temperature. After 12 h, a second portion of the mixture of **45** (40 mg, 0.063 mmol), silver trifluoromethanesulfonate (16.5 mg, 0.063 mmol), and toluene (1 mL) was added, and the stirring was continued for another 12 h. The mixture was diluted with CH_2Cl_2 (50 mL), solid $NaHCO_3$ (~1 g) was added, and the mixture was filtered (Celite). The filtrate was washed with saturated aqueous $NaHCO_3$ (20 mL) and water (20 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 8:1 → 3:1) to give **46** (83 mg, 27%) and a slightly impure mixture of **46** and **48**. The mixture of **46** and **48** was dissolved in CH_2Cl_2/H_2O (8 mL, 18:1), and DDQ (97%, 68 mg, 0.92 mmol) was added. The mixture was left overnight and concentrated. The residue was chromatographed (SiO_2, heptane/CH_2Cl_2/EtOAc 10:5:3) to give **46** (116 mg, 37%, the total yield of **46** was 64%): $[\alpha]^{25}_D$ +51° (*c* 0.9, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 5.77 (t, 1 H, J = 9.2 Hz), 5.65 (dd, 1 H, J = 7.8, 10.9 Hz), 5.34 (dd, 1 H, J = 7.8, 9.5 Hz), 5.16 (dd, 1 H, J = 2.5, 10.7 Hz), 4.85 (d, 1 H, J = 7.9 Hz), 4.66 (d, 1 H, J = 7.3 Hz), -.013 (s, 9 H); ^{13}C NMR data ($CDCl_3$) δ 166.1, 165.7, 165.3, 165.1, 165.0, 138.8, 138.7, 138.5, 137.0, 133.2–127.2, 101.7, 100.6, 100.1, 79.3, 76.8, 75.5, 75.1, 74.7, 74.4, 74.1, 73.8, 73.5, 72.9, 72.7, 72.4, 70.2, 70.0, 67.7, 67.3, 62.5, 59.1, 17.9, −1.5; HRMS calcd for $C_{86}H_{88}O_{21}SiNa$ (M + Na) 1507.5485, found 1507.5481.

(b) Compound **47** (239 mg, 0.149 mmol) was treated with tetrabutylammonium fluoride trihydrate (98%, 94 mg, 0.299 mmol) in THF as described in the preparation of **37**. The crude product was chromatographed (SiO_2, heptane/EtOAc 3:1 → 1:1) to give **46** (207 mg, 94%).

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzoyl-4-*O*-[2,3-di-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (47). To a cold (−55 °C) mixture of **44** (264 mg, 0.245 mmol), silver trifluoromethanesulfonate (132 mg, 0.517 mmol), collidine (0.102 mL, 0.762 mmol), molecular sieves (AW-300, 800 mg), and dry CH_2Cl_2 (5 mL) was added a solution of **32**[26] (289 mg, 0.508) in dry CH_2Cl_2 (3 mL) under Ar. The mixture was kept at −55 °C for 30 min, at 0 °C for 2 h, and at room temperature for 6 h and then diluted with CH_2Cl_2 (100 mL) and filtered (Celite). The filtrate was washed with saturated aqueous $NaHCO_3$ (40 mL) and water (40 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, toluene/MeCN 40:1) to give **47** (282 mg, 72%): $[\alpha]^{25}_D$ +64° (*c* 1.0, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 5.82–5.75 (m, 2 H), 5.36 (dd, 1 H, J = 7.8, 9.6 Hz), 5.10 (dd, 1 H, J = 2.7, 9.8 Hz), 4.93 (d, 1 H, J = 3.2 Hz), 4.88, 4.71 (d, 1 H each, J = 7.7, 7.8 Hz), 4.51 (dd, 1 H, J = 5.0, 11.8 Hz), 0.83 (m, 11 H), −0.10, −0.12, −0.13 (s, 15 H); ^{13}C NMR data ($CDCl_3$) δ 166.4, 165.8, 165.2, 165.2, 139.1, 139.1, 138.8, 138.6, 133.0–127.2, 101.4, 100.1, 99.8, 78.5, 76.8, 76.0, 75.8, 75.1, 74.9, 74.7, 73.9, 73.4, 73.1, 72.8, 72.8, 72.6, 72.5, 70.4, 69.4, 67.5, 67.3, 62.8, 59.9, 25.9, 18.0, 17.9–1.5; HRMS calcd for $C_{92}H_{102}O_{21}Si_2Na$ (M + Na) 1621.6350, found 1621.6329.

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzoyl-4-*O*-[2,3-di-*O*-benzoyl-6-*O*-(*p*-methoxybenzyl)-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (48). A mixture of compound **42**[16] (482 mg, 0.445 mmol), silver trifluoromethanesulfonate (344 mg, 1.34 mmol), tetramethylurea (0.176 mL, 1.47 mmol), molecular sieves (AW-300, 1.0 g), and dry toluene/Et_2O (22 mL, 10:1) was stirred at −70 °C for 30 min. A solution of **32**[26] (420 mg, 0.751 mmol) in dry toluene/Et_2O (15mL, 10:1) was added under Ar. The mixture was left at room temperature for 2 days and then diluted with CH_2Cl_2 (200 mL), filtered (Celite), and washed with saturated aqueous $NaHCO_3$ (100 mL). The mixture was dried (Na_2SO_4) and concentrated. The residue was chromatographed (SiO_2, heptane/CH_2Cl_2/EtOAc 10:5:2) to give **48** (262 mg, 37%): $[\alpha]^{25}_D$ +48° (*c* 1.0, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 5.81–5.71 (m, 2 H), 5.32 (dd, 1 H, J = 7.8, 9.4 Hz), 5.07 (dd, 1 H, J = 2.7, 10.8 Hz), 4.87 (d, 1 H, J = 7.6 Hz), 4.78 (d, 1 H, J = 3.1 Hz), 4.69 (d, 1 H, J = 7.9 Hz), 3.77 (s, 3 H), 3.00 (dd, 1 H, J = 4.9, 9.3 Hz), 2.93 (dd, 1 H, J = 5.3, 8.3 Hz), −0.15 (s, 9 H); HRMS calcd for $C_{94}H_{96}O_{22}SiNa$ (M + Na) 1627.6060, found 1627.6084.

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzoyl-4-*O*-[2,3-di-*O*-benzoyl-6-deoxy-6-iodo-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (49). A mixture of compound **46** (330 mg, 0.222 mmol) and toluene (8 mL) was heated to 80 °C, and triphenylphosphine (145 mg, 0.555 mmol), imidazole (54 mg, 0.777 mmol), and iodine (141 mg, 0.555 mmol) were added. After 1.5 h, the mixture was diluted with toluene (40 mL), which caused a small part of the material to precipitate. The solid material was dissolved in acetone (2 mL). The combined organic phases were washed with saturated aqueous $NaHCO_3$ (30 mL) and aqueous $Na_2S_2O_3$ (30 mL, 10%), dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 4:1) to give **49** (340 mg, 96%): $[\alpha]^{25}_D$ +68° (*c* 1.0, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 5.80 (t, 1 H, J = 9.1 Hz), 5.69 (dd, 1 H, J = 7.8, 10.7 Hz), 5.33 (dd, 1 H, J = 7.9, 9.3 Hz), 4.95 (dd, 1 H, J = 2.5, 11.0 Hz), 4.86 (d, 1 H, J = 7.8 Hz), 4.70 (d, 1 H, J = 2.2 Hz), 2.94 (dd, 1 H, J = 4.7, 8.3 Hz), 2.77 (dd, 1 H, J = 4.9, 9.4 Hz), −0.14 (s, 9 H); ^{13}C NMR data ($CDCl_3$) δ 166.5, 165.7, 165.3, 165.2, 165.1, 138.9, 138.8, 138.5, 138.3, 133.2–127.3, 101.5, 100.8, 100.2, 79.0, 76.9, 76.8, 76.8, 75.9, 75.9, 74.9, 74.5, 74.5, 74.1, 73.7, 73.0, 72.8, 72.5, 72.3, 69.7, 69.7, 67.4, 67.3, 62.5, 17.9, −1.5; HRMS calcd for $C_{86}H_{87}O_{20}ISiNa$ (M + Na) 1617.4502, found 1617.4551.

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzoyl-4-*O*-[2,3-di-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-β-D-fucopyranosyl]-β-D-glucopyranoside (50). A mixture of compound **49** (374 mg, 0.234 mmol), MeOH/EtOAc (12 mL, 5:1), and Et_3N (0.041 mL) was hydrogenated (H_2, 10% Pd/C, 100 mg) for 3 h at room temperature. The reaction was monitored by TLC (toluene/EtOAc 10:1). The mixture was filtered (Celite) and concentrated, and the residue was chromatographed (SiO_2, heptane/EtOAc 4:1) to give **50** (338 mg, 98%): $[\alpha]^{25}_D$ +85° (*c* 1.0, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 5.82 (t, 1 H, J = 9.3 Hz), 5.73 (dd, 1 H, J = 7.8, 10.1 Hz), 5.36 (dd, 1 H, J = 7.8, 9.3 Hz), 5.05 (dd, 1 H, J = 2.7, 10.9 Hz), 4.85 (d, 1 H, J = 7.8 Hz), 4.74 (d, 1 H, J = 7.8 Hz), 0.99 (d, 3 H, J = 6.3 Hz), −0.14 (s, 9 H); ^{13}C NMR data ($CDCl_3$): δ 166.6, 165.7, 165.3, 165.2, 165.0, 139.0–127.34, 101.7, 100.7, 100.1, 78.9, 78.4, 76.9, 75.0, 75.0, 74.8, 74.2, 73.4, 73.1, 72.9, 72.8, 72.5, 71.6, 70.1, 69.7, 67.6, 67.3, 62.7, 17.9, 16.2, −1.5; HRMS calcd for $C_{86}H_{88}O_{20}SiNa$ (M + Na) 1491.5536, found 1491.5538.

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzoyl-4-*O*-[2,3-di-*O*-benzoyl-4-*O*-(α-D-galactopyranosyl)-β-D-fucopyranosyl]-β-D-glucopyranoside (51). Compound **50** (312 mg, 0.212 mmol) was hydrogenated as described in the preparation of **34.** The crude product was chromatographed (SiO_2, heptane/EtOAc 1:15) to give **51** (225 mg, 96%): $[\alpha]^{25}_D$ +92° (*c* 1.2, $CDCl_3$); ^1H NMR data ($CDCl_3$) δ 5.73 (t, 1 H, J = 9.5 Hz), 5.67 (dd, 1 H, J = 7.8, 10.7 Hz), 5.37 (dd, 1 H, J = 7.8, 9.6 Hz), 5.09 (dd, 1 H, J = 2.8, 10.9 Hz), 4.90 (d, 1 H, J = 3.8 Hz), 4.75, 4.69 (d, 1 H each, J = 7.8, 7.9 Hz), 4.55 (dd, 1 H, J = 2.1, 12.2 Hz), 4.43 (dd, 1 H, J = 4.9, 12.2 Hz), 0.77 (d, 3 H, J = 6.3 Hz), −0.15 (s, 9 H); HRMS calcd for $C_{58}H_{64}O_{20}SiNa$ (M + Na) 1131.3658, found 1131.3674.

2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzoyl-4-*O*-[2,3-di-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-β-D-fucopyranosyl]-β-D-glucopyranoside (52). Compound **51** (130 mg, 0.117 mmol) was acetylated as described in the preparation of **18**. The crude product was chromatographed (SiO_2, heptane/EtOAc 1:1) to give **52** (144 mg, 97%): $[\alpha]^{25}_D$ +124° (*c* 1.0, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 5.76 (t, 1 H, J = 9.2 Hz), 5.61 (dd, 1 H, J = 7.8, 9.9 Hz), 5.42 (dd, 1 H, J = 1.0, 3.2 Hz), 5.38 (dd, 1 H, J = 3.2, 10.6 Hz), 5.31 (dd, 1 H, J = 7.8, 9.5 Hz), 5.12 (dd, 1 H, J = 2.9, 10.8 Hz), 5.06 (dd, 1 H, J = 3.6, 10.5 Hz), 5.01 (d, 1 H, J = 3.7 Hz), 4.80, 4.70 (d, 1 H each, J = 7.8, 7.7 Hz), 2.03, 1.99, 1.95, 1.90 (s, 3 H each), −0.15 (s, 9 H); HRMS calcd for $C_{66}H_{72}O_{24}SiNa$ (M + Na) 1299.4081, found 1299.4073.

2,3,6-Tri-*O*-benzoyl-4-*O*-[3,6-di-*O*-benzoyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-benozyl-α-D-galactopyranosyl)-β-D-*lyxo*-hexopyranosyl]-β-D-glucopyranose (53). To a cold (0 °C) mixture of compound **35** (119 mg, 0.078 mmol) and CH_2Cl_2

(0.5 mL) was added trifluoroacetic acid (1 mL). The mixture was stirred at 0 °C for 30 min and at 10 °C for 30 min, *n*-propyl acetate (3 mL) was added, and the mixture was coconcentrated with toluene (3 × 2 mL). The residue was chromatographed (SiO_2, heptane/EtOAc 1:1) to give **53** (111 mg, 100%), which was used without further characterization.

2,3,6-Tri-*O*-benzoyl-4-*O*-[3,6-di-*O*-benzoyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-benozyl-α-D-galactopyranosyl)-β-D-*lyxo*-hexopyranosyl]-α-D-glucopyranosyl trichloroacetimidate (54). To a cold (0 °C) solution of compound **53** (111 mg, 0.078 mmol) in CH_2Cl_2 (2 mL) were added trichloroacetonitrile (0.258 mL) and diazabicycloundecane (DBU, 0.01 mL). The reaction was monitored by TLC (heptane/EtOAc 1:1). The solvent was removed, and the residue was chromatographed (SiO_2, heptane/EtOAc/Et_3N 1:1:0.05) to give **54** (106 mg, 87%) and **53** (13 mg, 12%). Compound **54**: $[\alpha]^{25}_D$ +75° (*c* 0.9, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 8.60 (s, 1 H), 6.77 (d, 1 H, *J* = 3.7 Hz), 6.21 (t, 1 H, *J* = 9.8 Hz), 5.95 (d, 1 H, *J* = 3.6 Hz), 5.91 (dd, 1 H, *J* = 3.4, 10.6 Hz), 5.66 (dd, 1 H, *J* = 3.4, 10.6 Hz), 5.58 (d, 1 H, *J* = 3.9 Hz), 5.55 (dd, 1 H, *J* = 3.7, 10.1 Hz), 5.04 (m, 1 H), 4.83 (d, 1 H, *J* = 8.9 Hz), 2.28 (bq, 1 H, *J* = 12.8 Hz); HRMS calcd for $C_{83}H_{68}O_{24}NCl_3Na$ (M + Na) 1590.3095, found 1590.3118.

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]-propyl 2,3,6-Tri-*O*-benzoyl-4-*O*-[3,6-di-*O*-benzoyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-benozyl-α-D-galactopyranosyl)-β-D-*lyxo*-hexopyranosyl]-β-D-glucopyranoside (55). To a mixture of 3-(hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]-propan-1-ol[16] (202 mg, 0.310 mmol), $BF_3{\cdot}Et_2O$ (0.010 mL, 0.074 mmol), and actived molecular sieves in CH_2Cl_2 (5 mL) was added dropwise a cold (−50 °C) solution of **54** (99.0 mg, 0.063 mmol) in CH_2Cl_2 (2.5 mL) under Ar. After 4 h, an additional portion of $BF_3{\cdot}Et_2O$ (0.0067 mL, 0.050 mmol) was added, and the mixture was stirred for 4 h. The reaction was quenched with Et_3N (0.3 mL), and the mixture was diluted with CH_2Cl_2 (70 mL), filtered (Celite), washed with saturated aqueous $NaHCO_3$ (30 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was dissolved in hot EtOAc. Unreacted 3-(hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]propan-1-ol precipitated on cooling to −4 °C overnight. The precipitate was removed by filtration and washed with cold EtOAc. The solvent was removed, and the residue was chromatographed (SiO_2, toluene/EtOAc 5:1 → 3:1) to give **55** (74 mg, 57%): $[\alpha]^{25}_D$ +34° (*c* 0.8, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 6.00 (d, 1 H, *J* = 3.2 Hz), 5.93 (dd, 1 H, *J* = 3.3, 10.8 Hz), 5.79 (t, 1 H, *J* = 9.6 Hz), 5.65 (dd, 1 H, *J* = 3.5, 10.9 Hz), 5.56 (d, 1 H, *J* = 3.4 Hz), 5.42 (dd, 1 H, *J* = 8.0, 9.8 Hz), 5.02 (bd, 1 H, *J* = 12.7 Hz), 4.74 (d, 1 H, *J* = 7.8 Hz), 3.26−2.66 (m, 9 H), 2.22 (bq, 1 H, *J* = 12.1 Hz), 1.97 (bd, 1 H, *J* = 10.5 Hz), 0.88 (t, 6 H, *J* = 6.5 Hz); HRMS calcd for $C_{117}H_{140}O_{28}S_2Na$ (M + Na) 2079.8870, found 2079.8879.

2,3,6-Tri-*O*-acetyl-4-*O*-[2-*O*-acetyl-3-deoxy-6-*O*-(*p*-methoxybenzoyl)-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-β-D-*xylo*-hexopyranosyl]-β-D-glucopyranose (56). Compound **41** (100 mg, 0.0944 mmol) was treated with trifluoroacetic acid as described in the preparation of **53**. The crude product was chromatographed (SiO_2, heptane/EtOAc 1:1) to give **56** (82.4 mg, 91%), which was used without further characterization.

2,3,6-Tri-*O*-acetyl-4-*O*-[2-*O*-acetyl-3-deoxy-6-*O*-(*p*-methoxybenzoyl)-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-β-D-*xylo*-hexopyranosyl]-β-D-glucopyranosyl Trichloroacetimidate (57). Compound **56** (80.0 mg, 0.0834 mmol) was treated with trichloroacetonitrile (0.275 mL) and DBU (0.010 mL) as described in the preparation of **54**. The crude product was chromatographed (SiO_2, heptane/EtOAc/Et_3N 1:1:0.5) to give **57** (90 mg, 98%): $[\alpha]^{25}_D$ +63° (*c* 0.9, $CDCl_3$); ^1H NMR data ($CDCl_3$) δ 8.65 (s, 1 H), 6.50 (d, 1 H *J* = 4.0 Hz) 5.61 (t, 1 H, *J* = 9.8 Hz), 5.57 (d, 1 H, *J* = 3.1 Hz), 5.42 (dd, 1 H, *J* = 3.2, 10.7 Hz), 5.21−5.16 (m, 2 H), 5.07 (dd, 1 H, *J* = 3.8, 10.2 Hz), 4.74 (m, 1 H), 3.88 (s, 3 H), 2.69 (bd, 1 H, *J* = 12.5 Hz), 2.16, 2.13, 2.08, 2.06, 2.03, 2.02, 2.01, 1.99 (s, 3 H each); HRMS calcd for $C_{44}H_{54}O_{25}NCl_3Na$ (M + Na) 1124.1948, found 1124.1930.

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]-propyl 2,3,6-Tri-*O*-acetyl-4-*O*-[2-*O*-acetyl-3-deoxy-6-*O*-(*p*-methoxybenzoyl)-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-β-D-*xylo*-hexopyranosyl]-β-D-glucopyranoside (58). Compound **57** (86 mg, 0.0780 mmol) was treated with 3-(hexadecylsulfonyl)-2-[(hexadecylsulfonyl)-methyl]propan-1-ol[16] (250 mg, 0.385 mmol) and $BF_3{\cdot}Et_2O$ in CH_2Cl_2 as described in the preparation of **55**. Attempted chromatography of the crude product (SiO_2, heptane/EtOAc 2:1 → 1:2) was unsuccessful. The chromatographed material was dissolved in hot MeOH, and the temperature was gradually lowered overnight until it reached −25 °C. Compound **58** (20 mg, 16%) precipitated and was collected. The mother liquid was concentrated, and the residue was chromatographed (SiO_2−C_{18}, H_2O/MeOH 1:0 → 0:1) to give **58** (27 mg, 21%; total yield of **58**: 37%): $[\alpha]^{25}_D$ +16° (*c* 1.4, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 5.57 (d, 1 H, *J* = 3.0 Hz), 5.41 (dd, 1 H, *J* = 3.3, 10.9 Hz), 5.24 (t, 1 H, *J* = 9.5 Hz), 5.20 (m, 2 H), 4.90 (dd, 1 H, *J* = 7.8, 9.8 Hz), 4.75 (m, 1 H), 3.88 (s, 3 H), 3.40−2.90 (m, 9H), 2.65 (m, 1 H), 2.13, 2.13, 2.11, 2.07, 2.05, 2.03, 2.01, 1.99 (s, 3 H each). 0.88 (t, 6 H, *J* = 6.4 Hz); HRMS calcd for $C_{78}H_{126}O_{29}S_2Na$ (M + Na) 1613.7724, found 1613.7723.

2,3,6-Tri-*O*-benzoyl-4-*O*-[2,3-di-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-β-D-fucopyranosyl]-β-D-glucopyranoside (59). Compound **52** (138 mg, 0.108 mmol) was treated with trifluoroacetic acid as described in the preparation of **53**. The crude product was chromatographed (SiO_2, heptane/EtOAc 1:1) to give **59** (126 mg, 99%), which was used without further characterization.

2,3,6-Tri-*O*-benzoyl-4-*O*-[2,3-di-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-β-D-fucopyranosyl]-β-D-glucopyranosyl Trichloroacetimidate (60). Compound **59** (126 mg, 0.107 mmol) was treated with trichloroacetonitrile (0.355 mL) and DBU (0.014 mL) as described in the preparation of **54**. The crude product was chromatographed (SiO_2, heptane/EtOAc/Et_3N 1:1:0.5) to give **60** (135 mg, 96%): $[\alpha]^{25}_D$ +167° (*c* 1.1, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 8.53 (s, 1 H), 6.65 (d, 1 H,*J* = 3.6 Hz), 6.19 (t, 1 H, *J* = 10.0 Hz), 5.66 (dd, 1 H, *J* = 7.8, 10.9 Hz), 5.43−5.37 (m, 3 H), 5.15 (dd, 1 H, *J* = 2.9, 10.8 Hz), 5.07 (dd, 1 H, *J* = 3.6, 9.9 Hz), 5.04 (d, 1 H, *J* = 3.7 Hz), 4.90 (d, 1 H, *J* = 7.8 Hz), 2.04, 2.00, 1.98, 1.88 (s, 3 H each), 0.84 (d, 3 H, *J* = 6.6 Hz); HRMS calcd for $C_{63}H_{60}O_{24}NCl_3Na$ (M + Na) 1342.2469, found 1342.2487.

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]-propyl 2,3,6-Tri-*O*-benzoyl-4-*O*-[2,3-di-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-β-D-fucopyranosyl]-β-D-glucopyranoside (61). Compound **60** (130 mg, 0.0984 mmol) was treated with 3-(hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]propan-1-ol[16] (313 mg, 0.482 mmol) and $BF_3{\cdot}Et_2O$ in CH_2Cl_2 as described in the preparation of **55**. The residue was chromatographed (SiO_2, toluene/EtOAc 7:1) to give **61** (121 mg, 68%): $[\alpha]^{25}_D$ +89° (*c* 0.9, $CHCl_3$); ^1H NMR data ($CDCl_3$) δ 5.79 (t, 1 H, *J* = 9.3 Hz), 5.61 (dd, 1 H, *J* = 7.8, 10.7 Hz), 5.41 (dd, 1 H, *J* = 1.2, 3.2 Hz), 5.38 (dd, 1 H, *J* = 3.4, 10.3 Hz), 5.28 (dd, 1 H, *J* = 7.9, 9.7 Hz), 5.14 (dd, 1 H, *J* = 2.9, 11.9 Hz), 5.07 (dd, 1 H, *J* = 3.6, 10.3 Hz), 5.02 (d, 1 H, *J* = 3.7 Hz), 4.82, 4.73 (d, 1 H each, *J* = 7.8, 7.9 Hz), 3.18−2.63 (m, 9 H), 2.04, 2.00, 1.97, 1.90 (s, 3 H each), 0.88 (t, 6 H, *J* = 6.5 Hz), 0.83 (d, 3 H, *J* = 6.3 Hz); HRMS calcd for $C_{97}H_{132}O_{18}S_2Na$ (M + Na) 1831.8244, found 1831.8273.

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Supporting Information Available: ^1H NMR spectra and ^1H NMR data with assigned signals for all title compounds described in the Experimental Section (93 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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