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Synthesis of double-chain bis-sulfone neoglycolipids of the 2″-, 3″-, 4″-, and 6″-deoxyglobotrioses

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Abstract

2-(Trimethylsilyl)ethyl ($Me_3SiCH_2CH_2$) 2,3,6-tri-*O*-benzoyl-4-*O*-(2,3-di-*O*-benzoyl-6-*O*-*p*-methoxybenzyl-β-D-galactopyranosyl-β-D-glucopyranoside was glycosylated with different 2-, 3-, 4-, or 6-"deoxy-D-galactose" derivatives to give the corresponding deoxytrisaccharides. Removal of the protecting groups gave the $Me_3SiCH_2CH_2$ 2″-, 3″-, 4″-, and 6″-deoxyglobotriosides. Transformation of the protected $Me_3SiCH_2CH_2$ globotriosides into the corresponding trichloroacetimidates proceeded, via the hemiacetals, in 91–96% over-all yield. Glycosylation of 3-(hexadecylsulfonyl-2-[hexadecylsulfonyl)methyl]propanol with the trichloroacetimidates, followed by removal of protecting groups, gave the title neoglycolipids.

Key words: Deoxyglobotriosides; Neoglycolipids; 2-Trimethylsilyl(ethyl)glycosides

1. Introduction

Globotriosyl ceramide (GbO_3, P^k-antigen) is present on red blood cells where it is one of the glycolipid antigens of the P-blood-group system [1]. Together with globotetraosyl ceramide and the Forssman antigen, GbO_3 seems to function as a carbohydrate receptor for several proteins from pathogenic bacteria such as the pilus-associated PapG adhesin protein of uropathogenic *Escherichia coli* [2], verotoxin from *E. coli* [3], Shiga toxin from *Shigella dysenteriae* [4], and the adhesin from *Streptococcus suis* [5]. Furthermore, glycolipids of the globoseries have been suggested to be tumor-associated antigens on Burkitt lymphoma cells [6], human

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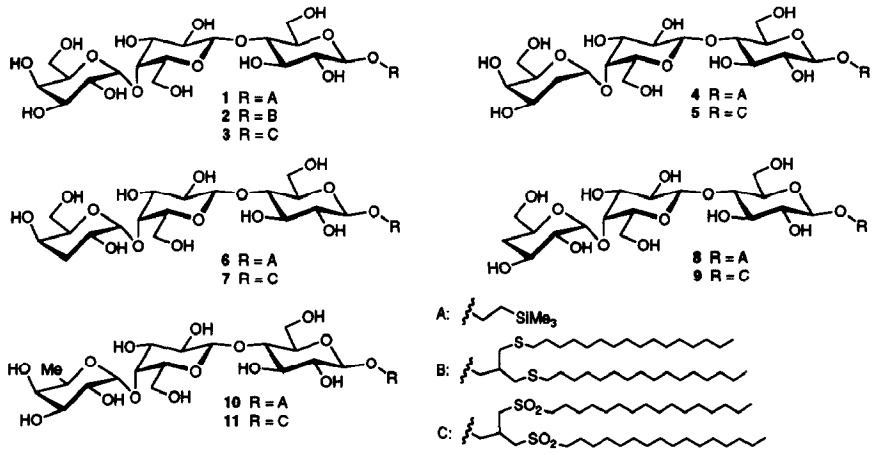


Scheme 1.

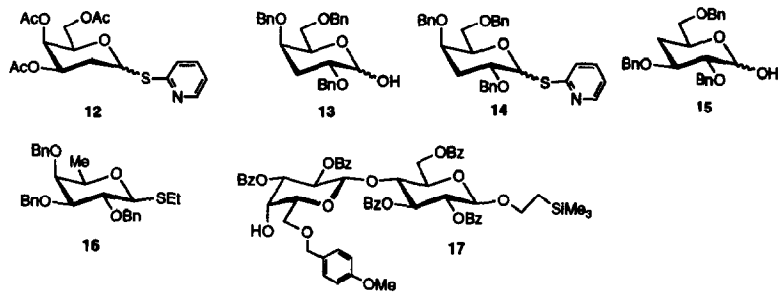
teratocarcinoma cells [7], and other tumor cells [8], and are also enriched in the body fluids of patients suffering from Fabry's disease [9].

We have reported the synthesis of GbO_3-containing neoglycoproteins [10], glycosides [10,11], and neoglycolipids [10,12] including compounds **1–3**, as well as deoxy- and *C*-methyl analogues for use in the probing of carbohydrate–protein combining sites [13]. The synthesis of the di → penta-saccharidic fragments of GbO_5 (Forssman antigen) was recently completed [14,15] and a compilation of references to all syntheses of Forssman fragments (except lactosides) was included [14]. We now report the synthesis of four monodeoxy derivatives of GbO_3 in the form of $Me_3SiCH_2CH_2$ glycosides and bis-sulfone neoglycolipids (**4–11**) as well as improved syntheses of the lipids **2** [12] and **3** [12] (Scheme 1). These compounds are potentially useful for specificity studies with GbO_3-binding proteins and cells, both by direct binding to glycolipid-coated surfaces and by inhibition of binding with the soluble glycosides.

2. Results and discussion

Deoxyglycosyl donors require more subtle anomeric activation than normal saccharides. We and others have observed that the stability and ease of handling of glycosyl halides increases in the series Br → Cl → F [16]. Therefore, glycosyl fluorides [17] were tested as glycosyl donors in the case of 3- and 4-"deoxy-D-galactose" (cf. **13** [16] and **15** [16]) whereas with 2- and 6-"deoxy-D-galactose" (cf. **12** [18] and **16** [19]), thioglycosides were chosen as glycosyl donors. A higher glycosylation yield was obtained with the thioglycoside **14** than with the glycosyl fluoride obtained from **13**.

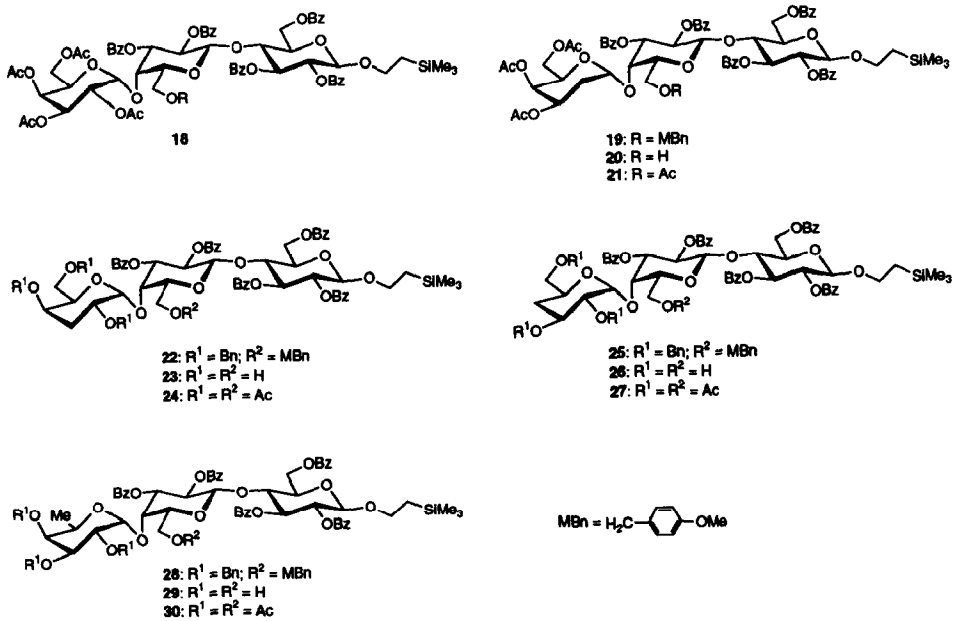
Lactoside **17** was used as glycosyl acceptor in reactions with the donors mentioned above. The $Me_3SiCH_2CH_2$ anomeric blocking group [11,20,21] was used



Scheme 2.

because of the ease of removal [11] and transformation into 1-*O*-acyl [11] and 1-chloro-1-deoxy groups [21] suitable for further anomeric activation. The *p*-methoxybenzyl group was chosen for protection of the 6′-position because it is easily removed under oxidative conditions, thereby avoiding potential problems with hydrogenolytic cleavage in the presence of sulfur-containing residues from, for example, glycosylations with thioglycosides. The synthesis of compounds **12–17** (Scheme 2) is discussed towards the end of the paper.

Compound **18** (Scheme 3) was synthesised as described [11] and used for the synthesis of **1–3** as discussed later.



Scheme 3.

The 2″-deoxy trisaccharide **19** was obtained in 65% yield and high α-selectivity (no β isomer was detected) by treating a mixture of **17** and **12** with silver triflate in dichloromethane. Silver triflate has been reported to give α-selectivity in the synthesis of *C*-glycosyl compounds [22]. The synthesis of **19** seems to be the first example of an α-selective O-glycoside synthesis with silver triflate as promoter. Attempted activation of **12** with iodomethane [18] was unsuccessful. Initial attempts to condense **17** (or the more reactive 2-(trimethylsilyl)ethyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,6-tri-*O*-benzyl-β-D-galactopyranosyl)-β-D-glucopyranoside) with 3,4,6-tri-*O*-acetyl-D-galactal in the presence of iodosuccinimide [23] were unsuccessful.

The 3″-deoxy trisaccharide **22** was obtained in 84% yield (no β isomer was detected) by treating a mixture of **17** and **14** with silver triflate as above. Using the fluorosugar obtained from **13** as donor gave **22** in only 33% yield.

The 4″-deoxy trisaccharide **25** was obtained in 57% yield by treating a mixture of **17** and the glycosyl fluoride obtained from **15** with stannous chloride–silver perchlorate in tetrahydrofuran [24]. The corresponding β isomer was isolated in 7% yield.

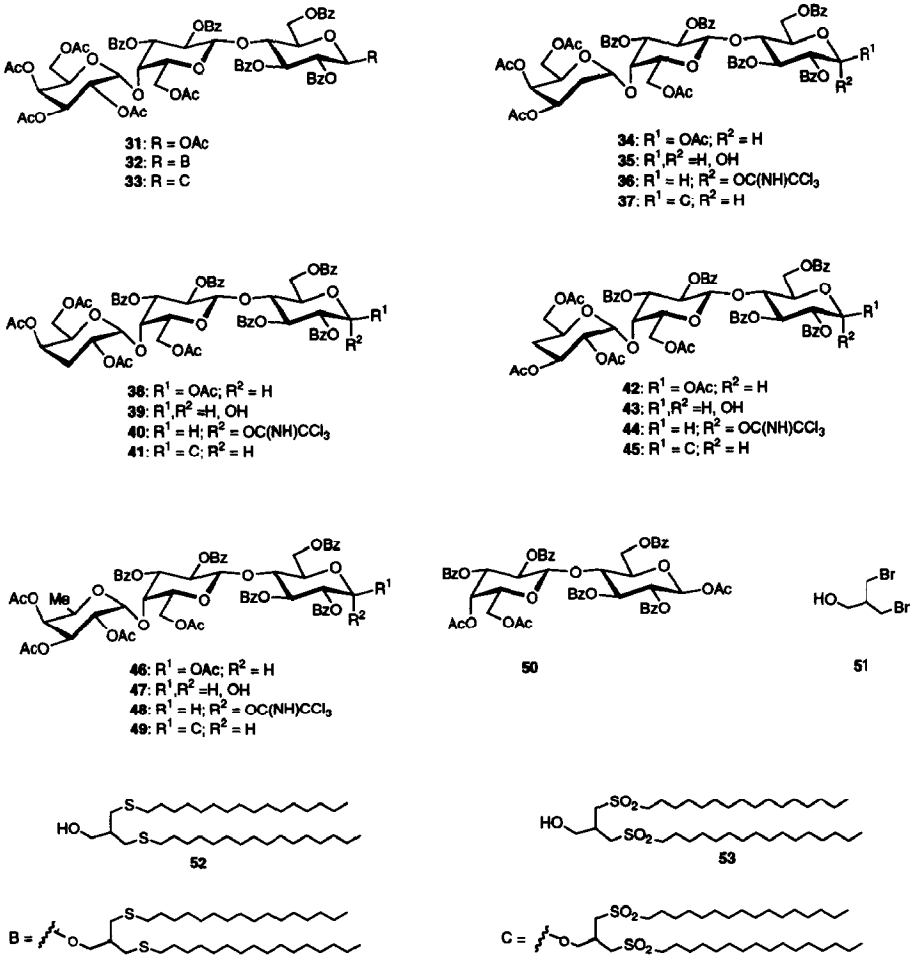
The 6″-deoxy trisaccharide **28** was obtained in 55% yield by treating a mixture of **17** and thioglycoside **16** [19] with silver triflate–copper(II) bromide–tetrabutylammonium bromide in nitromethane [25].

The *p*-methoxybenzyl (MBn) protecting group in **19** was removed by treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in aqueous dichloromethane [26], which gave **20** in 97% yield. Hydrogenolytic cleavage of the benzyl and MBn groups in **22**, **25**, and **28** gave **23** (91%), **26** (80%), and **29** (59%), and acetylation of the unprotected hydroxyl groups in **20**, **23**, **26**, and **29** gave the acylated $Me_3SiCH_2CH_2$ trisaccharides **21** (99%), **24** (92%), **27** (98%), and **30** (91%).

The 2″- and 3″-deoxy $Me_3SiCH_2CH_2$-GbO_3 were obtained by debenzoylation in methanolic sodium methoxide of **20** (→ **4**, 99%) and **23** (→ **6**, 99%). The 4″- and 6″-deoxy $Me_3SiCH_2CH_2$-GbO_3 were obtained by debenzoylation followed by hydrogenolytic cleavage of the benzyl protecting groups in **25** (→ **8**, 94%) and **28** (→ **10**, 97%).

We have reported the synthesis of bis-sulfone neoglycolipids via the corresponding 3-bromo-2-bromomethylpropyl (dibromoisobutyl, DIB) glycosides, using an alkanethiol for nucleophilic displacement of bromide, followed by oxidation of the resulting bis-sulfide to the corresponding bis-sulfone [12]. This stepwise approach is practical for the preparation of neoglycolipids having different chain-lengths. However, when only one lipid is desired, glycosylation of the corresponding bis-sulfone (or-sulfide) alcohol would be preferred, provided that the glycosylation step can be performed in high yield and stereoselectivity. It should be noted that glycosylation of DIBOL (**51**) can normally be done by a Lewis acid (e.g., boron trifluorideetherate) promoted reaction of a sugar β-peracetate. The resulting DIB β-glycoside is unusually stable towards anomerisation to the α isomer under the Lewis acid conditions [12].

The $Me_3SiCH_2CH_2$ glycosides **21**, **24**, **27**, and **30** were treated with boron trifluoride etherate and acetic anhydride [11], in order to obtain the corresponding



Scheme 4.

β-acetates. Whereas the 4″-deoxy compound **42** (Scheme 4) was formed in 91% yield and thus behaved normally [11,20], the remaining 2″- (**34**), 3″- (**38**), and 6″-deoxy (**46**) compounds were formed in unusually low yields, 44, 50, and 37%, respectively. The lactose derivative **50** was isolated in ~50% yield in each case, clearly showing that deoxyglycosides may in some cases undergo cleavage of interglycosidic bonds on treatment with the $BF_3 \cdot Et_2O$–Ac_2O mixture. In contrast, we recently reported the successful $BF_3 \cdot Et_2O$–Ac_2O-mediated transformation of $Me_3SiCH_2CH_2$ monodeoxyfluorolactosides into the corresponding anomeric acetates [27], and earlier experiments [11] with $Me_3SiCH_2CH_2$ 3′-*C*-methyl and -ethyl GbO_3 derivatives gave the desired acetates in good yield although, in the latter cases, the $\beta:\alpha$ ratio of 1-acetates was reduced to ca. 4:1 as compared to the normal ratio of $>20:1$. As shown below, $BF_3 \cdot Et_2O$ *per se* is not harmful. A more

probable candidate would be the acylium ion present in the mixture which would affect some, but not all, deoxy-sugar glycosides.

Fortunately, the $Me_3SiCH_2CH_2$ blocking group gives further options for deprotection–activation of the anomeric position [11,20]. Treatment of the glycosides **21**, **24**, **27**, and **30** with trichloroacetic acid in dichloromethane [11] gave the corresponding hemiacetals **35** (98%), **39** (95%), **43** (96%), and **47** (98%). Conversion into the corresponding trichloroacetimidates [28] gave **36** (98%), **40** (96%), **44** (99%), and **48** (97%), ready for glycosylation of the bis-sulfone alcohol **53**.

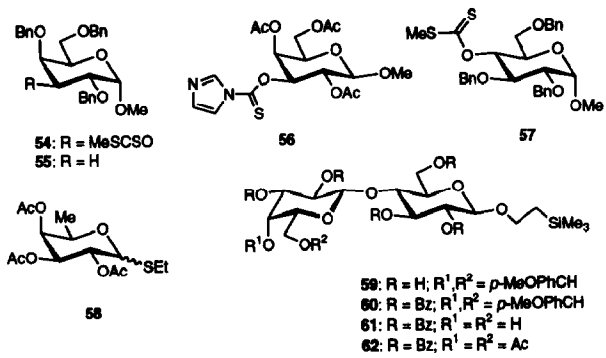
The solubility of **53** in dichloromethane is highly temperature dependent and is acceptable at +30°C but too low at −50°C, which is the desired reaction temperature. To solve this problem, we added dropwise a cold (−50°C) solution of the saccharide to a mixture of **53** and $BF_3 \cdot Et_2O$ in dichloromethane (kept at 30°C) under slow stirring, hoping to keep a low local reaction temperature without lowering the solubility of **53**. Under these conditions, compounds **37** (73%), **41** (59%), **45** (55%), and **49** (60%) were obtained without the formation of α isomers. Such unexpectedly high β-selective glycosylation was also observed with DIBOL (**51**) and the resulting DIB glycosides were quite stable towards anomerisation, even under acidic conditions [12]. *O*-Deacylation of **37**, **41**, **45**, and **49** with sodium methoxide in methanol–chloroform and chromatographic purification gave the desired lipids **5** (89%), **7** (82%), **9** (77%), and **11** (66%).

In contrast to some of the deoxy compounds discussed above, the trisaccharide β-1-acetate **31** (obtained in 95% yield, $\beta:\alpha$ 97:3, by $BF_3 \cdot Et_2O$–Ac_2O-treatment of **18**) underwent facile $BF_3 \cdot Et_2O$-mediated glycosylation of the bis-sulfide and bis-sulfone alcohols **52** and **53**, giving the known [12] neoglycolipids **32** and **33**. Glycosylation of **52** with **31** in the presence of 5 equiv of $BF_3 \cdot Et_2O$ and molecular sieves (6% of the solvent weight) in dichloromethane proceeded slowly to give **32** (42%). In the absence of molecular sieves a byproduct (probably an α,β-mixture of the glycoside having undergone *O*-deacetylation in the 2-position) was formed that could not be removed efficiently from the desired **32**. After some experimentation, it was found that a good yield and excellent stereoselectivity was obtained by using a trace of molecular sieves (a few grains) and 3 equiv of $BF_3 \cdot Et_2O$. Thus, compound **32** was obtained in 76% yield without the formation of isomers. Under the same conditions, the bis-sulfone lipid **33** was obtained pure in only 48% yield, probably due to the low solubility of **53**. *O*-Deacetylation [12] of **32** and **33** gave the bis-sulfide and bis-sulfone neoglycolipids **2** (70%) and **3** (95%), respectively.

3. Synthesis of the starting materials 52, 53, and 12–17

Treatment of DIBOL (**51**) [29] with 2 equiv of hexadecanethiol and cesium carbonate in *N*,*N*-dimethylformamide gave the bis-sulfide **52** (93%) which was oxidised with *m*-chloroperoxybenzoic acid (MCPBA) to give the bis-sulfone alcohol **53** in 99% yield.

2-Pyridyl 3,4,6-tri-*O*-acetyl-2-deoxy-1-thio-D-*lyxo*-hexopyranoside (**12**, Scheme 5)



Scheme 5.

was prepared (93%, $\alpha:\beta$ 4.5:1) by addition of 2-mercaptopyridine to tri-*O*-acetyl-D-galactal, using *p*-toluenesulfonic acid as catalyst [18].

2,4,6-Tri-*O*-benzyl-3-deoxy-D-*xylo*-hexopyranoside [16] (**13**) was prepared from methyl 3-*O*-allyl-2,4,6-tri-*O*-benzyl-α-D-galactopyranoside [30]. Thus, deallylation [31] (93%) gave methyl 2,4,6-tri-*O*-benzyl-α-D-galactopyranoside [32] which was transformed into the xanthate **54** (99%) by using sodium hydride–carbon disulfide–imidazole–iodomethane in tetrahydrofuran [33]. Reduction [33] of **54** with tributyltin hydride gave the 3-deoxygalactoside **55** (46%) and hydrolysis with aqueous acetic acid–HCl gave the hemiacetal **13** [16] (89%).

In an alternative route to **13**, methyl 2,4,6-tri-*O*-acetyl-β-D-galactopyranoside [34] was transformed [35] into the corresponding imidazolylthiocarbonyl derivative **56** (99%), reduction of which [35] with tributyltin hydride gave methyl 2,4,6-tri-*O*-acetyl-3-deoxy-β-D-*xylo*-hexopyranoside [36] (72%). *O*-Deacetylation and benzylation gave methyl 2,4,6-tri-*O*-benzyl-3-deoxy-β-D-*xylo*-hexopyranoside [16] (99%), which was hydrolysed to give **13** [16] (80%). Compound **13** was transformed into the corresponding glycosyl chloride [16] and treatment with 2-mercaptopyridine [37] gave the thioglycoside **14** (93%).

2,3,6-Tri-*O*-benzyl-4-deoxy-D-*xylo*-hexopyranose (**15**) was prepared from methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside [38]. Thus, transformation [33] to the xanthate **57** (97%) and reduction with tributyltin hydride gave methyl 2,3,6-tri-*O*-benzyl-4-deoxy-α-D-*xylo*-hexopyranoside [39] (95%), which was hydrolysed to give **15** (80%).

Ethyl 2,3,4-tri-*O*-benzyl-1-thio-β-D-fucopyranoside [19] (**16**) was prepared from D-fucose by acetylation followed by treatment of the tetra-acetate with ethanethiol–boron trifluoride etherate, which gave the thioglycoside **58** (89%). *O*-Deacetylation of **58** followed by *O*-benzylation gave **16** (79%).

The glycosyl acceptor **17** was prepared by conversion of 2-(trimethylsilyl)ethyl β-lactoside [11] into the corresponding 4′,6′-*p*-methoxybenzylidene acetal [40] **59** (77%) followed by benzoylation to give **60** (90%), and reductive opening of the *p*-methoxybenzylidene group with sodium cyanoborohydride–trifluoroacetic acid

[40] to give **17** (88%). When ethereal hydrochloric acid [41] was used instead of trifluoroacetic acid, the *p*-methoxybenzylidene group was removed and the corresponding 4′,6′-deprotected compound **61** was obtained (92%) and characterised as the diacetate **62**.

4. Experimental

General experimental procedures were as previously reported [12]. Compounds **1** [11], **2** [12], **3** [12], **18** [11], **31** [11], and **51** [29] were prepared as described.

3-Hexadecylthio-2-[(hexadecylthio)methyl]propyl 4-O-[4-O-α-D-galactopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (**2**).—Compound **32** (95 mg, 0.064 mmol) was deacylated as described [12], to give **2** (48 mg, 70%).

3-Hexadecylsulfonyl-2-[(hexadecylsulfonyl)methyl]propyl 4-O-[4-O-α-D-galactopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (**3**).—Compound **33** (38 mg, 0.024 mmol) was deacylated as described [12], to give **3** (26 mg, 95%).

2-(Trimethylsilyl)ethyl 4-O-[4-O-(2-deoxy-α-D-lyxo-hexopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (**4**).—Compound **20** (35.0 mg, 0.027 mmol) was treated with NaOMe—MeOH (1 M, 0.2 mL) in MeOH (2 mL) at room temperature overnight, neutralised with Amberlite IR-120 (H^+) resin, filtered, concentrated, and chromatographed (SiO_2, 1:2 MeOH–EtOAc) to give **4** (16.0 mg, 99%); $[\alpha]_D^{25}$ +24.5° (*c* 0.80, MeOH); ^{1}H NMR (D_2O): δ 5.03 (bs, 1 H, H-1″), 4.51, 4.49 (d, 1 H each, *J* 7.9, 7.8 Hz, H-1,1′), 1.90 (bd, 2 H, *J* 7.6 Hz, H-2″), 1.00 (m, 2 H CH_2Si), 0.30 (s, 9 H, $SiCH_3$).

3-Hexadecylsulfonyl-2-[(hexadecylsulfonyl)methyl]propyl 4-O-[4-O-(2-deoxy-α-D-lyxo-hexopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (**5**).—Compound **37** (26.0 mg, 0.0143 mmol) was dissolved in 3:2 $CHCl_3$–MeOH (5 mL), and NaOMe–MeOH (1 M, 0.2 mL) was added. The reaction was monitored by TLC (SiO_2, 65:35:10:5 $CHCl_3$–MeOH–acetone–H_2O). After 18 h, **37** was consumed and the mixture was neutralised by Amberlite IR-120 (H^+) resin, filtered, and concentrated. The residue was suspended in 2:1 H_2O–EtOAc and the suspension was chromatographed (SiO_2-C_{18}, H_2O, MeOH, and 65:35:10 $CHCl_3$–MeOH–H_2O) to give **5** (14.8 mg, 92%); $[\alpha]_D^{25}$ +18.0° (*c* 0.41, 65:35:5 $CHCl_3$–MeOH–H_2O); ^{1}H NMR ($CDCl_3$): δ 4.74 (bd, 1 H, *J* 2.6 Hz, H-1″), 4.15, 4.12 (d, 1 H each, *J* 7.5, 8.0 Hz, H-1,1′), 2.92–2.83 (m, 4 H, SCH_2), 2.77 (m, 1 H, $CHCH_2S$), 1.74–1.54 (m, 4 H, SCH_2CH_2), 0.64 (t, 6 H, *J* 6.7 Hz, CH_3).

2-(Trimethylsilyl)ethyl 4-O-[4-O-(3-deoxy-α-D-xylo-hexopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (**6**).—Compound **23** (31 mg, 0.028 mmol) was debenzoylated as in the preparation of **4**. The crude material was chromatographed (SiO_2, 1:2 MeOH–EtOAc) to give **6** (16.2 mg, 99%); $[\alpha]_D^{25}$ +21.6° (*c* 0.50, MeOH); ^{1}H NMR (D_2O): δ 4.88 (d, 1 H, *J* 3.5 Hz, H-1″), 4.50 (bt, 2 H, *J* 6.9, 7.1 Hz, H-1,1′), 2.05–1.95 (m, 2 H, H-3″), 0.02 (s, 9 H, $SiCH_3$).

3-Hexadecylsulfonyl-2-[(hexadecylsulfonyl)methyl]propyl 4-O-[4-O-(3-deoxy-α-D-xylo-hexopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (**7**).—Compound **41** (31.5 mg, 0.0174 mmol) was deacylated as in the preparation of **5**, to give **7** (14.2

mg, 85%); $[\alpha]_D^{25}$ +27.4° (*c* 0.34, 65:35:5 $CHCl_3$–MeOH–H_2O; ^1H NMR (65:35:5 $CDCl_3$–CD_3OD–D_2O): δ 4.62 (d, 1 H, *J* 3.4 Hz, H-1″), 4.19 (d, 1 H, *J* 7.1 Hz, H-1′), 4.12 (d, 1 H, *J* 7.6 Hz, H-1), 2.87 (m, 4 H, SCH_2), 2.76 (m, 1 H, OCH_2CH), 0.65 (t, 6 H, *J* 6.7 Hz, CH_3).

*2-(Trimethylsilyl)ethyl 4-O-[4-O-(4-deoxy-α-*D*-xylo-hexopyranosyl)-β-*D*-galacto-pyranosyl]-β-*D*-glucopyranoside* (**8**).—Compound **25** (58 mg, 0.387 mmol) was debenzoylated with NaOMe–MeOH for 5 h. The mixture was neutralised with Amberlite IR-120 (H^+) resin and concentrated. The residue was dissolved in AcOH (5 mL) and hydrogenated (H_2, Pd–C 10%, 50 mg) for 14 h, and the mixture was filtered (Celite) and concentrated. The residue was chromatographed (SiO_2, 3:2 MeOH–EtOAc) to give **8** (21.5 mg, 94%); $[\alpha]_D^{25}$ +24.5° (*c* 0.90, MeOH); ^1H NMR (D_2O): δ 4.95 (d, 1 H, *J* 3.7 Hz, H-1″), 4.51, 4.49 (d, 1 H each, *J* 7.8, 8.1 Hz, H-1,1′), 2.00 (m, 1 H, H-4″*e*), 1.48 (bq, 1 H, *J* 12.1 Hz, H-4″*a*), 0.03 (s, 9 H, $SiMe_3$).

*3-Hexadecylsulfonyl-2-[(hexadecylsulfonyl)methyl]propyl-4-O-[4-O-(4-deoxy-α-*D*-xylo-hexopyranosyl)-β-*D*-galactopyranosyl]-β-*D*-glucopyranoside* (**9**).—Compound **45** (31.8 mg, 0.0173 mmol) was deacylated as in the preparation of **5**, to give **9** (15.4 mg, 79%); $[\alpha]_D^{25}$ +24.3° (*c* 0.36, 65:35:5 $CHCl_3$–MeOH–H_2O); ^1H NMR (65:35:5 $CDCl_3$–CD_3OD–D_2O): δ 4.70 (d, 1 H, *J* 3.7 Hz, H-1″), 4.10, 4.07 (d, 1 H each, *J* 7.8 Hz, H-1,1′), 2.87 (m, 4 H, SCH_2), 2.76 (m, 1 H, OCH_2CH), 0.65 (t, 6 H, *J* 6.7 Hz, CH_3).

*2-(Trimethylsilyl)ethyl 4-O-[4-O-(α-*D*-fucopyranosyl)-β-*D*-galactopyranosyl]-β-*D*-glucopyranoside* (**10**).—Compound **28** (50 mg, 0.033 mmol) was debenzoylated and hydrogenated as in the preparation of **8**. The crude material was chromatographed (SiO_2, 1:2 MeOH–EtOAc) to give **10** (19.0 mg, 97%); $[\alpha]_D^{25}$ +26.2° (*c* 0.82, MeOH); ^1H NMR (CD_3OD): δ 4.88 (d, 1 H, *J* 3.7 Hz, H-1″), 4.43, 4.39 (d, 1 H each, *J* 7.2, 7.8 Hz, H-1,1′), 1.21 (d, 3 H, *J* 6.5 Hz, H-6″), 0.02 (s, 9 H, $SiCH_3$).

*3-Hexadecylsulfonyl-2-[(hexadecylsulfonyl)methyl]propyl 4-O-[4-O-(α-*D*-fucopyr-anosyl)-β-*D*-galactopyranosyl]-β-*D*-glucopyranoside* (**11**).—Compound **49** (19.5 mg, 0.0108 mmol) was deacylated, as in the preparation of **5**, to give **11** (8.2 mg, 68%); $[\alpha]_D^{25}$ +8.5° (*c* 0.6, 65:35:5 $CHCl_3$–MeOH–H_2O); ^1H NMR (65:35:5 $CDCl_3$–CD_3OD–D_2O): δ 4.65 (bs, 1 H, H-1″), 4.18, 4.13 (d, 1 H each, *J* 7.5, 7.8 Hz, H-1,1′), 2.92–2.83 (m, 4 H, SCH_2), 2.79 (m, 1 H, $CHCH_2S$), 1.74–1.54 (m, 4 H, SCH_2CH_2), 0.64 (t, 6 H, *J* 6.7 Hz, CH_3).

*2-Pyridyl 3,4,6-tri-O-acetyl-2-deoxy-1-thio-*D*-lyxo-hexopyranoside* (**12**).—A mixture of 3,4,6-tri-*O*-acetyl-D-galactal (690 mg, 2.53 mmol), 2-mercaptopyridine (774 mg, 6.96 mmol), and *p*-toluenesulfonic acid (200 mg, 1.16 mmol) in CH_2Cl_2 (15 mL) was refluxed until TLC showed the reaction to be completed (2 days). The mixture was poured into 3:4 H_2O–CH_2Cl_2 (70 mL), the water phase was extracted with CH_2Cl_2 (20 mL), and the combined extract was washed with aq KOH (2%, 30 mL), dried (Na_2SO_4), and concentrated. The residue was chromatographed (SiO_2, 3:1 heptane–EtOAc) to give **12** (908 mg, 93%, α:β 4.5:1); ^1H NMR ($CDCl_3$): δ (α anomer) 6.50 (d, 1 H, *J* 5.2 Hz, H-1), 4.54 (t, 1 H, *J* 6.2 Hz, H-5), 2.60 (dt, 1 H, *J* 5.5, 12.7 Hz, H-2*e*); (β anomer) 5.70 (dd, 1 H, *J* 2.3, 11.5 Hz, H-1), 5.14 (m, 1 H, H-3). Mass spectrum: calcd for $C_{17}H_{21}NO_{17}S$ (M + 1): *m/z* 384.1117; found: *m/z* 384.1125.

2,4,6-Tri-O-benzyl-3-deoxy-D-xylo-hexopyranose (**13**).—(*a*) Methyl 2,4,6-tri-*O*-benzyl-3-deoxy-β-D-*xylo*-hexopyranoside [16] (500 mg, 1.11 mmol) was treated at 80°C with 4:1 AcOH–1 M HCl (10 mL) for 4.5 h. The mixture was diluted with 7:2 CH_2Cl_2–H_2O (90 mL), the water phase was extracted with CH_2Cl_2 (2 × 30 mL), and the combined organic phase was washed with water (2 × 40 mL) and satd aq $NaHCO_3$ (2 × 40 mL), dried (Na_2SO_4), and concentrated. The residue was chromatographed (6:1 heptane–EtOAc) to give **13** (388 mg, 80%).

(*b*) Methyl 2,4,6-tri-*O*-benzyl-3-deoxy-α-D-*xylo*-hexopyranoside (300 mg, 0.70 mmol) was treated as above to give **13** (257 mg, 89%). Mass spectrum: calcd for $C_{27}H_{30}O_5$ (M + 1): *m/z* 435.2171; found: *m/z* 435.2206.

2-Pyridyl 2,4,6-tri-O-benzyl-3-deoxy-1-thio-D-xylo-hexopyranoside (**14**).—Compound **13** (100 mg, 0.23 mmol) and DMF (100 μL) were dissolved in CH_2Cl_2 (2 mL) and oxalyl chloride (100 μL, 1.16 mmol) was added over 10 min. The reaction was monitored by TLC (2:1 heptane–EtOAc). When the reaction was completed, toluene (10 mL) was added, and the mixture was filtered (Celite), concentrated to a volume of 2 mL, and then added to a mixture of 2-mercaptopyridine (5 mg, 0.46 mmol) and K_2CO_3 (64 mg, 0.46 mmol) in dry acetone (1.5 mL), which had been kept at 40°C for 1 h. The mixture was stirred for 16 h at 40°C, then diluted with toluene (40 mL), washed with aq NaOH (1%, 10 mL) and water (20 mL), dried (Na_2SO_4), and concentrated. The residue was chromatographed (SiO_2, 20:1 toluene–Et_2O) to give **14** (111 mg, 92.0%, α:β 3:7); ^1H NMR ($CDCl_3$): δ 6.5 (d, *J* 5.2 Hz, H-1α), 5.4 (d, *J* 9.8 Hz, H-1β). Mass spectrum: calcd for $C_{32}H_{33}NO_4S$ (M + 1): *m/z* 528.2209; found: *m/z* 528.2250.

2,3,6-Tri-O-benzyl-4-deoxy-D-xylo-hexopyranose (**15**).—Compound **57** (5.1 g, 9.20 mmol) and a catalytic amount of azobis(isobutyronitrile) (AIBN) were dissolved in toluene (150 mL) and added over 1.5 h to a refluxing solution of tributyltin hydride (5.4 g, 18.4 mmol) in toluene (200 mL), kept under Ar. The mixture was refluxed overnight and then concentrated. The residue was chromatographed (SiO_2, 4:1 heptane–EtOAc) to give methyl 2,3,6-tri-*O*-benzyl-4-deoxy-α-D-*xylo*-hexopyranoside (3.9 g, 95%) as a syrup; [^1H NMR ($CDCl_3$): δ 3.93 (m, 2 H, H-3,5), 3.47 (d, 2 H, *J* 5.1 Hz, H-6), 3.38 (s, 1 H, OCH_3), 2.07 (m, 1 H, H-4*e*), 1.51 (bq, 1 H, *J* 12.1 Hz, H-4*a*]. The syrup (100 mg, 0.22 mmol) was treated with an acid mixture as in the preparation of **13**, and the crude material was chromatographed (SiO_2, 5:1 heptane–EtOAc) to give **15** (76 mg, 80%) and unreacted material (19 mg, 19%). Mass spectrum (**15**): calcd for $C_{27}H_{30}O_5$ (M + 1): *m/z* 435.2171; found: *m/z* 435.2153.

Ethyl 2,3,4-tri-O-benzyl-1-thio-β-D-fucopyranoside (**16**).—Compound **58** (4.00 g, 11.95 mmol) was deacetylated with NaOMe–MeOH (1 M, 0.5 mL) in MeOH (100 mL). The solvent was removed and the residue was stirred with NaH (80%, 2.54 g, 84.7 mmol) in DMF (300 mL) for 40 min, then cooled with an ice–water bath. $PhCH_2Br$ (10.1 mL, 84.7 mmol) was added during 10 min and the ice–water bath was removed. After 2.5 h, MeOH (7 mL) was added in order to destroy unreacted NaH. After 10 min, the mixture was poured into a cold, stirred mixture of 3:1 CH_2Cl_2–H_2O (300 mL). The water phase was extracted with CH_2Cl_2 (100 mL), and the combined organic phase was washed with water (200 mL), dried (Na_2SO_4),

and concentrated. The residue was chromatographed (SiO_2, 5:1 heptane–EtOAc) to give **16** (4.12 g, 72%); $[\alpha]_D^{25}$ −3.8° (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 4.40 (d, 1 H, *J* 9.5 Hz, H-1), 3.80 (t, 1 H, *J* 9.5 Hz, H-2), 3.62 (d, 1 H, *J* 2.8 Hz, H-4), 3.36 (dd, 1 H, *J* 2.9, 9.3 Hz, H-3), 1.30 (t, 3 H, *J* 7.5 Hz, SCH_2CH_3), 1.20 (d, 3 H, *J* 6.4 Hz, H-6). Mass spectrum: calcd for $C_{29}H_{34}O_4S$ (M − 1): *m/z* 477.2100; found: *m/z* 477.2093.

*2-(Trimethylsilyl)ethyl 2,3,6-tri-*O*-benzoyl-4-*O*-(2,3-di-*O*-benzoyl-6-*O*-*p*-methoxybenzyl-β-*D*-galactopyranosyl)-β-*D*-glucopyranoside* (**17**).—A mixture of compound **60** (5.4 g, 4.99 mmol), 3A molecular sieves (7 g), and DMF (50 mL) was stirred for 10 min, then $NaCNBH_3$ (95%, 3.30 g, 50.0 mmol) was added and the mixture was stirred for 20 min. A cooled (~ 0°C) solution of CF_3CO_2H (3.87 mL, 50.0 mmol) in DMF (40 mL) was added dropwise over 20 min. The reaction was monitored by TLC (6:1 toluene–Et_2O); when the hydrolysis product **61** started to form, the reaction was quenched by addition of solid $NaHCO_3$ (10 g). CH_2Cl_2 (400 mL) was added, the mixture was poured into cold water (300 mL), the water phase was extracted with CH_2Cl_2 (2 × 150 mL), and the combined organic phase was washed with satd aq $NaHCO_3$ (300 mL) and water (200 mL), dried (Na_2SO_4), and concentrated. The residue was recrystallised (EtOAc–heptane) to give **17** (2.78 g). The mother liquid was concentrated and chromatographed (SiO_2, 20:1 toluene–Et_2O) to give **17** (2.00 g) and unreacted **60** (0.5 g, 9%). The total yield of **17** was 4.78 g (88%); $[\alpha]_D^{25}$ +57.8° (*c*, 0.77, $CHCl_3$); ^1H NMR (CD_3COCD_3): δ 5.38 (dd, 1 H, *J* 7.9, 9.6 Hz, H-2), 5.08 (dd, 1 H, *J* 3.1, 10.4 Hz, H-3′), 4.73, 4.68 (d, 1 H each, *J* 7.8, 7.9 Hz, H-1,1′), 4.58, 4.39 (dd, 1 H, each, *J* 1.5, 4.8, 12.0 Hz, H-6), 3.80 (s, 3 H, OCH_3), 3.45 (dt, 1 H, *J* 6.6, 10.0 Hz, OCH_2CH_2), −0.15 (s, 9 H, $SiCH_3$). Anal. Calcd for $C_{60}H_{62}O_{17}Si$: C, 66.5; H, 5.7. Found: C, 66.4; H, 5.9.

*2-(Trimethylsilyl)ethyl 2,3,6-tri-*O*-benzoyl-4-*O*-[2,3,-di-*O*-benzoyl-6-*O*-*p*-methoxybenzyl-4-*O*(3,4,6-tri-*O*-acetyl-2-deoxy-α-*D*-lyxo-hexopyranosyl)-β-*D*-galactopyranosyl]-β-*D*-glucopyranoside* (**19**).—Compounds **12** (23 mg, 0.060 mmol) and **17** (62 mg, 0.057 mmol) were dissolved in CH_2Cl_2 (2.5 mL), 3A molecular sieves (0.20 g) were added, and the mixture was stirred under N_2 for 4 h, then cooled to −15°C. Silver trifluoromethanesulfonate (23 mg, 0.09 mmol) in CH_2Cl_2 (2.5 mL) was added with exclusion of light and the mixture was stirred for 1 h at < −5°C and for 5 h at room temperature. CH_2Cl_2 (40 mL) was added, and the mixture was filtered (Celite), washed with satd aq $NaHCO_3$ (20 mL), dried (Na_2SO_4), and concentrated. The residue was chromatographed (SiO_2, 15:1 toluene–Et_2O) to give **19** (50.0 mg, 65%); $[\alpha]_D^{25}$ +51.0° (*c*, 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.66 (t, 1 H, *J* 9.4 Hz, H-3), 5.62 (dd, 1 H, *J* 7.9, 10.8 Hz, H-2′), 4.79 (d, 1 H, *J* 3.2 Hz, H-1″), 4.73, 4.68 (d, 1 H each, *J* 7.9, 7.5 Hz, H-1,1′), 3.82 (s, 3 H, OCH_3), 2.03, 2.02, 1.77 (3 s, 3 H each, OAc), 0.13 (s, 9 H, $SiCH_3$).

*2-(Trimethylsilyl)ethyl 2,3,6-tri-*O*-benzoyl-4-*O*-[2,3-di-*O*-benzoyl-4-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-α-*D*-lyxo-hexopyranosyl)-β-*D*-galactopyranosyl]-β-*D*-glucopyranoside* (**20**).—Compound **19** (100 mg, 0.074 mmol) and DDQ (~ 97%, 27 mg, ~ 0.114 mmol) were dissolved in 18:1 CH_2Cl_2–H_2O (2 mL), and the mixture was stirred at room temperature for 6 h, then poured into 5:1 CH_2Cl_2–H_2O (60 mL) and filtered (Celite). The organic phase was dried (Na_2SO_4) and concentrated. The

residue was flash-chromatographed (SiO_2, 2:1 heptane–EtOAc) to give **20** (89 mg, 97%); $[\alpha]_D^{25}$ +107.5° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.42 (dd, 1 H, *J* 7.8, 9.3 Hz, H-2), 5.23 (m, 1 H, H-3″), 4.81 (d, 1 H, *J* 3.3 Hz, H-1″), 4.79 (d, 1 H, *J* 8.1 Hz, H-1′), 4.70 (d, 1 H, *J* 7.6 Hz, H-1), 2.03, 2.02, 1.80 (3 s, 3 H each, OAc), 1.91 (ddd, 1 H, *J* 3.7, 3.2, 12.2 Hz, H-2″), 0.14 (s, 9 H, $SiCH_3$). Mass spectrum: calcd for $C_{64}H_{70}O_{23}Si$ (M + Na): *m/z* 1257.3975; found: *m/z* 1257.3962.

*2-(Trimethylsilyl)ethyl 4-*O*-[6-*O*-acetyl-2,3-di-*O*-benzoyl-4-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-α-*D*-lyxo-hexopyranosyl)-β-*D*-galactopyranosyl]-2,3,6-tri-*O*-benzoyl-β-*D*-gluco-pyranoside* (**21**).—Compound **19** (100 mg, 0.074 mmol) was treated with DDQ (~ 97%, 36 mg, ~ 1.54 mmol) in AcOH (2 mL) at room temperature for 22 h, then Ac_2O (1 mL) and pyridine (1 mL) were added. After 2 h, TLC analysis (1:1 heptane–EtOAc) showed that the starting compound **19** had been consumed. MeOH (0.5 mL) was added and the mixture was co-concentrated with toluene to remove pyridine. The residue was flash-chromatographed (SiO_2, 2:1 heptane–EtOAc) to give **21** (94 mg, 99%); $[\alpha]_D^{25}$ +124.3° (*c* 1.2, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.73 (t, 1 H, *J* 9.5 Hz, H-3), 5.63 (dd, 1 H, *J* 7.9, 10.6 Hz H-2′), 5.38 (dd, 1 H, *J* 7.9, 9.6 Hz, H-2), 5.23 (m, 1 H, H-3″), 5.10 (dd, 1 H, *J*, 3.5, 10.0 Hz, H-2″), 4.76 (d, 1 H, *J* 7.8 Hz, H-1′), 4.70 (d, 1 H, *J* 7.4 Hz, H-1), 2.03, 2.02, 2.01, 1.80 (4 s, 3 H each, $OCCH_3$), 1.91 (ddd, 1 H, *J* 3.7, 3.2, 12.2 Hz, H-2″), 0.14 (s, 9 H $SiCH_3$). Mass spectrum: calcd for $C_{66}H_{72}O_{24}Si$ (M + Na): *m/z* 1299.4081; found: *m/z* 1299.4075.

*2-(Trimethylsilyl)ethyl 2,3,6-tri-*O*-benzoyl-4-*O*-[2,3-di-*O*-benzoyl-6-*O*-p-meth-oxybenzyl-4-*O*-(2,4,6-tri-*O*-benzyl-3-deoxy-α-*D*-xylo-hexopyranosyl)-β-*D*-galactopyr-anosyl]-β-*D*-glucopyranoside* (**22**).—(*a*) Compound **17** (467 mg, 0.43 mmol), $SnCl_2$ (92 mg, 0.492 mmol), $AgClO_4$ (103 mg, 0.49 mmol), and 3A molecular sieves (0.5 g) were added to dry THF (8 mL). The mixture was protected from light and stirred for 1 h under N_2, then cooled to −30°C. A solution of 2,4,6-tri-*O*-benzyl-3-deoxy-α,β-*D*-*xylo*-hexopyranosyl fluoride [~ 0.41 mmol, prepared immediately before use from **13** (178 mg, 0.41 mmol) as described in the preparation of **25**] was added. After 30 min, the mixture was gradually allowed to reach room temperature. The reaction was monitored by TLC (4:1 toluene–Et_2O). After 20 h, CH_2Cl_2 (30 mL) was added, and the mixture was filtered (Celite) and concentrated. The residue was chromatographed (SiO_2, 20:1 toluene–Et_2O) to give **22** (200 mg, 33%); $[\alpha]_D^{25}$ +43.3° (*c* 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.74 (m, 2 H, H-3,2′), 5.32 (dd, 1 H, *J* 8.0, 9.4 Hz, H-2), 5.07 (dd, 1 H, *J* 2.7, 10.8 Hz, H-3′), 4.83 (d, 1 H, *J* 7.8 Hz, H-1′), 4.76 (d, 1 H, *J* 3.2 Hz, H-1″), 4.70 (d, 1 H, *J* 7.8 Hz, H-1), 3.80 (s, 3 H, OCH_3), 2.02–1.74 (m, 2 H, H-3), − 0.15 (s, 9 H, $SiCH_3$). Mass spectrum: calcd for $C_{87}H_{90}O_{21}Si$ (M − 1): *m/z* 1497.5666; found: *m/z* 1497.5667.

(*b*) Compound **17** (70 mg, 0.065 mmol), **14** (36 mg, 0.068 mmol), 3A molecular sieves (0.3 g), and CH_2Cl_2 (3 mL) were stirred under N_2 for 30 min, then cooled to −5°C. Silver trifluoromethanesulfonate (24 mg, 0.091 mmol) was added and the mixture was protected from light and kept below 0°C for 5 h. The reaction was quenched by adding solid K_2CO_3 (30 mg), CH_2Cl_2 (5 mL) was added, and the mixture was filtered (Celite) and concentrated. The residue was chromatographed (toluene–Et_2O) to give **22** (81 mg, 84%).

*2-(Trimethylsilyl)ethyl 2,3,6-tri-*O*-benzoyl-4-*O*-[2,3-di-*O*-benzoyl-4-*O*-(3-deoxy-α-*D*-xylo-hexopyranosyl)-β-*D*-galactopyranosyl]-β-*D*-glucopyranoside* (**23**).—Compound **22** (100 mg, 0.067 mmol) was dissolved in AcOH (7 mL) and hydrogenated (H_2; Pd–C 10%, 140 mg) and purified, as described for **26**, to give **23** (67 mg, 91%); $[\alpha]_D^{25}$ +65.1° (*c* 0.83, MeOH); ^{1}H NMR ($CDCl_3$): δ 5.70 (t, 1 H, *J* 9.3 Hz, H-3), 5.63 (dd, 1 H, *J* 7.8, 10.7 Hz, H-2′), 4.80 (d, 1 H, *J* 7.7 Hz, H-1′), 4.73 (d, 1 H, *J* 3.1 Hz, H-1″), 4.68 (d, 1 H, *J* 7.9 Hz, H-1), 1.91 (m, 1 H, H-3″*e*), 1.71 (dt, 1 H, *J* 2.1, 12.4 Hz, H-3″*a*), −0.15 (s, 9 H, $SiCH_3$). Mass spectrum: calcd for $C_{58}H_{64}O_{20}Si$ (M + Na): *m/z* 1131.3658; found: *m/z* 1131.3677.

*2-(Trimethylsilyl)ethyl 4-*O*-[6-*O*-acetyl-2,3-di-*O*-benzoyl-4-*O*-(2,4,6-tri-*O*-acetyl-3-deoxy-α-*D*-xylo-hexopyranosyl)-β-*D*-galactopyranosyl]-2,3,6-tri-*O*-benzoyl-β-*D*-glucopyranoside* (**24**).—Compound **23** (162 mg, 0.146 mmol) was acetylated (1:1 Ac_2O–pyridine, 3 mL) and the crude product was chromatographed (SiO_2, 3:2 heptane–EtOAc) to give **24** (172 mg, 92%); $[\alpha]_D^{25}$ +58.0° (*c* 0.74, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.74 (t, 1 H, *J* 9.3 Hz, H-3), 5.63 (dd, 1 H, *J* 7.8, 10.9 Hz, H-2′), 4.88 (dq, 1 H, *J* 3.1, 5.3, 11.4 Hz, H-2″), 4.82 (d, 1 H, *J* 7.8 Hz, H-1′), 4.76 (d, 1 H, *J* 2.9 Hz, H-1″), 4.69 (d, 1 H, *J* 7.8 Hz, H-1), 2.05, 2.03, 1.96, 1.90 (4 s, 3 H each, OAc). Mass spectrum: calcd for $C_{66}H_{72}O_{24}Si$ (M + Na): *m/z* 1299.4081; found: *m/z* 1299.4097.

*2-(Trimethylsilyl)ethyl 2,3,6-tri-*O*-benzoyl-4-*O*-[2,3-di-*O*-benzoyl-6-*O*-p-methoxybenzyl-4-*O*-(2,3,6-tri-*O*-benzyl-4-deoxy-α-*D*-xylo-hexopyranosyl)-β-*D*-galactopyranosyl]-β-*D*-glucopyranoside* (**25**).—Compound **15** (1.11 g, 2.56 mmol) was dissolved in THF (9 mL) and diethylaminosulfur trifluoride (335 μL, 2.80 mmol) was added at −30°C under N_2-protection. The mixture was allowed to attain room temperature and, after 2.5 h, the reaction was quenched by adding MeOH (350 mL). The solvent was removed, and the crude 2,3,6-tri-*O*-benzyl-4-deoxy-α-*D*-*xylo*-hexopyranosyl fluoride was dissolved in dry THF before use. Compound **17** (2.19 g, 2.02 mmol) was dissolved in dry THF (35 mL) and $SnCl_2$ (479 mg, 2.5 mmol), $AgClO_4$ (525 mg, 2.53 mmol), and actived 3A molecular sieves (3.5 g) were added, and the mixture, under N_2, was stirred for 3 h with exclusion of light, then cooled to −10°C. The solution of crude fluoride (~ 2.5 mmol in 15 mL of THF) was added dropwise and the mixture was stirred at < −5°C for 2 h and at room temperature for 48 h, then quenched with Et_3N (468 mL, 3.33 mmol) and filtered (Celite). CH_2Cl_2 (200 mL) was added and the mixture was washed with aq HCl (1 M, 50 mL) and satd aq $NaHCO_3$ (2 × 50 mL), dried (Na_2SO_4), and concentrated. The residue was chromatographed (SiO_2, 20:1 toluene–Et_2O) to give **25** (1.74 g, 57%); $[\alpha]_D^{25}$ +56.6° (*c* 0.69, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.76 (t, 1 H, *J* 9.2 Hz, H-3), 5.69 (dd, 1 H, *J* 7.7, 10.9 Hz, H-2′), 5.31 (dd, 1 H, *J* 7.9, 9.4 Hz, H-2), 4.95 (dd, 1 H, *J* 2.8, 10.8 Hz, H-3′), 4.84 (d, 1 H, *J* 7.8 Hz, H-1′), 4.81 (d, 1 H, *J* 3.3 Hz, H-1″), 3.77 (s, 3 H, OCH_3), 3.35 (dd, 1 H, *J* 9.7, 3.5 Hz, H-2″), 2.13–2.04 (m, 1 H, H-4″*e*), 1.63 (bq, 1 H, *J* 12.3 Hz, H-4″*a*), 0.85 (m, 2 H, OCH_2CH_2). Mass spectrum: calcd for $C_{87}H_{90}O_{21}Si$ (M − 1): *m/z* 1497.5666; found: *m/z* 1497.5641.

*2-(Trimethylsilyl)ethyl 2,3,6-tri-*O*-benzoyl-4-*O*-[2,3-di-*O*-benzoyl-4-*O*-(4-deoxy-α-*D*-xylo-hexopyranosyl)-β-*D*-galactopyranosyl]-β-*D*-glucopyranoside* (**26**).—Compound **25** (1.48 g, 0.99 mmol) was dissolved in AcOH and hydrogenated as described in

the preparation of **23**. The crude material was chromatographed (20:1 EtOAc–heptane) to give **26** (879 mg, 80%); $[\alpha]_D^{25}$ +78.8° (*c* 0.72, $CHCl_3$); ^1H NMR data ($CDCl_3$): δ 5.72 (t, 1 H, *J* 9.3 Hz, H-3), 5.63 (dd, 1 H, *J* 7.9, 10.7 Hz, H-2′), 4.83–4.78 (2 H, H-1′,1″), 4.69 (d, 1 H, *J* 7.8 Hz, H-1), 1.92 (m, 1 H, H-4″*e*), 1.47 (bq, 1 H, *J* 12.3 Hz, H-4″*a*), −0.16 (s, 9 H, $SiCH_3$). Mass spectrum: calcd for $C_{58}H_{64}O_{20}Si$ (M + Na): *m/z* 1131.3658; found: *m/z* 1131.3677.

2-(Trimethylsilyl)ethyl 4-O-[6-O-acetyl-2,3-di-O-benzoyl-4-O-(2,3,6-tri-O-acetyl-4-deoxy-α-D-xylo-hexopyranosyl)-β-D-galactopyranosyl]-2,3,6-tri-O-benzoyl-β-D-gluco-pyranoside (**27**).—Compound **26** (851 mg, 0.768 mmol) was acetylated as described in the preparation of **24**. The crude material was chromatographed (SiO_2, 3:1 heptane–EtOAc) to give **27** (963 mg, 98%); $[\alpha]_D^{25}$ +85.0° (*c* 0.70, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.76 (t, 1 H, *J* 9.3 Hz, H-3), 5.63 (dd, 1 H, *J* 7.9, 11.0 Hz, H-2′), 5.36 (dd, 1 H, *J* 7.8, 9.5 Hz, H-2), 5.21 (dt, 1 H, *J* 4.8, 10.6 Hz, H-3″), 5.02 (dd, 1 H, *J* 2.6, 10.9 Hz, H-3′), 4.85 (d, 1 H, *J* 3.7 Hz, H-1″), 4.70 (d, 1 H, *J* 7.8 Hz, H-1), 4.61 (dd, 1 H, *J* 2.1, 12.2 Hz, H-6), 4.44 (dd, 1 H, *J* 4.6, 11.7 Hz, H-6), 1.90, 1.96, 1.94, 2.05 (4 s, 3 H each, OAc), −0.17 (s, 9 H, $SiMe_3$). Mass spectrum: calcd for $C_{66}H_{72}O_{24}Si$ (M + Na): *m/z* 1299.4081; found: *m/z* 1299.4075.

2-(Trimethylsilyl)ethyl 2,3,6-tri-O-benzoyl-4-O-[2,3-di-O-benzoyl-6-O-p-methoxy-benzyl-4-O-(2,3,4-tri-O-benzyl-α-D-fucopyranosyl)-β-D-galactopyranosyl]-β-D-gluco-pyranoside (**28**).—A solution of compounds **16** (859 mg, 1.79 mmol) and **17** (1.55 g, 1.43 mmol) in CH_2Cl_2 (2 mL) was added with a syringe to a mixture of $CuBr_2$ (683 mg, 3.06 mmol), tetrabutylammonium bromide (1.16 g, 3.60 mmol), silver trifluoromethanesulfonate (786 mg, 3.06 mmol), 4A molecular sieves (2.5 g), and dry nitromethane (20 mL), that had been stirred for 1 h at room temperature and then cooled to −10°C. The temperature was kept at −10°C for 1 h and then gradually raised to room temperature. After 20 h, the mixture was filtered, the solid material was washed with CH_2Cl_2 (20 mL), and the solvent was removed. The residue was chromatographed (SiO_2, 5:1 heptane–EtOAc) to give **28** (1.19 g, 56%); $[\alpha]_D^{25}$ +61.2° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.78 (t, 1 H, *J* 9.2 Hz, H-3), 5.70 (dd, 1 H, *J* 7.7, 10.9 Hz, H-2′), 5.32 (dd, 1 H, *J* 7.8, 9.4 Hz, H-2), 5.09 (dd, 1 H, *J* 2.8, 10.9 Hz, H-3′), 3.70 (s, 3 H, OCH_3), 0.66 (d, 3 H, *J* 6.5 Hz, H-6″), −0.15 (s, 9 H, $SiCH_3$). Anal. Calcd for $C_{87}H_{90}O_{21}Si$: C, 69.6; H, 6.0. Found: C, 69.2; H, 6.1.

2-(Trimethylsilyl)ethyl 2,3,6-tri-O-benzoyl-4-O-[2,3-di-O-benzoyl-4-O-(α-D-fuco-pyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (**29**).—Compound **28** (99.5 mg, 0.066 mmol) was dissolved in AcOH (4 mL) and hydrogenated (H_2, Pd–C, 10%, 100 mg) at room temperature. The reaction did not proceed to completion, even after addition of an extra aliquot (100 mg) of Pd–C and 2 days of reaction time. The mixture was filtered (Celite), washed with MeOH (10 mL), and concentrated. The residue was chromatographed (SiO_2 20:1 EtOAc–heptane) to give **29** (44 mg, 59%); $[\alpha]_D^{25}$ +71.5° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.73 (t, 1 H, *J* 9.0 Hz, H-3), 5.64 (dd, 1 H, *J* 8.0, 10.7 Hz, H-2′), 5.32 (dd, 1 H, *J* 7.8, 9.6 Hz, H-2), 5.09 (dd, 1 H, *J* 2.9, 10.8 Hz, H-3′), 4.80 (d, 1 H, *J* 7.9 Hz, H-1′), 4.74 (d, 1 H, *J* 3.4 Hz, H-1″), 4.69 (d, 1 H, *J* 7.8 Hz, H-1), 0.95 (d, 3 H, *J* 6.5 Hz, H-6″), −0.15 (s, 9 H, $SiCH_3$). Mass spectrum: calcd for $C_{58}H_{64}O_{20}Si$ (M + Na): *m/z* 1131.3658; found: *m/z* 1131.3657.

2-(Trimethylsilyl)ethyl 4-O-[6-O-acetyl-2,3-di-O-benzoyl-4-O-(2,3,4-tri-O-acetyl-α-D-fucopyranosyl)-β-D-galactopyranosyl-2,3,6-tri-O-benzoyl-β-D-glucopyranoside (**30**). —Compound **29** (360 mg, 0.325 mmol) was acetylated as described in the preparation of **24**. The crude material was chromatographed (SiO_2, 3:1 heptane–EtOAc) to give **30** (375 mg, 91%); $[\alpha]_D^{25}$ +92.1° (*c* 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.76 (t, 1 H, *J* 9.2 Hz, H-3), 5.64 (dd, 1 H, *J* 7.8, 10.7 Hz, H-2′), 5.35 (dd, 1 H, *J* 7.9, 9.6 Hz, H-2), 5.10 (dd, 1 H, *J* 3.7, 12.0 Hz, H-2″), 5.01 (dd, 1 H, *J* 2.8, 10.9 Hz, H-3′), 4.86 (d, 1 H, *J* 3.7 Hz, H-1″), 4.81 (d, 1 H, *J* 7.8 Hz, H-1′), 4.69 (d, 1 H, *J* 7.8 Hz, H-1), 2.07, 1.99, 1.96, 1.92 (4 s, 3 H each, OAc), 0.70 (d, 3 H, *J* 6.5 Hz, H-6″), −0.15 (s, 9 H, $SiCH_3$). Mass spectrum: calcd for $C_{66}H_{72}O_{24}Si$ (M + Na): *m/z* 1299.4081; found: *m/z* 1299.4086.

3-(Hexadecylthio)-2-[(hexadecylthio)methyl]propyl 4-O-[6-O-acetyl-2,3-di-O-benzoyl-4-O-(2,3,4,6-tetra-O-acetyl-α-D-galactopyranosyl)-β-D-galactopyranosyl]-2,3,6-tri-O-benzoyl-β-D-glucopyranoside (**32**).—The β-acetate **31** [11] (52 mg, 0.041 mmol) and the bis-sulfide alcohol **52** (60 mg, 0.102 mmol) were dissolved in CH_2Cl_2 (5 mL) and cooled to 0°C. Approximately 3 grains of 3A molecular sieve (AW-300) and $BF_3 \cdot Et_2O$ (19 μL, 0.12 mmol) were added, the cooling was interrupted after 30 min, and the mixture was stirred at room temperature for 24 h. Et_3N (20 μL) and CH_2Cl_2 (5 mL) were added, and the mixture was filtered (Celite) and concentrated. The residue was chromatographed (SiO_2, 1:1 → 3:1 CH_2Cl_2–heptane) to give **32** [12] (54 mg, 76%). Physical data were in accord with those published [12].

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]propyl 4-O-[6-O-acetyl-2,3-di-O-benzoyl-4-O-(2,3,4,6-tetra-O-acetyl-α-D-galactopyranosyl)-β-D-galactopyranosyl-2,3,6-tri-O-benzoyl-β-D-glucopyranoside (**33**).—The β-acetate **31** [11] (53 mg, 0.042 mmol) and the bis-sulfone alcohol **53** (60 mg, 0.087 mmol) were suspended in CH_2Cl_2 (8 mL) and treated as in the preparation of **32**, to give **33** (36 mg, 48%). Physical data were in accord with those published [12].

1-O-Acetyl-4-O-[6-O-acetyl-2,3-di-O-benzoyl-4-O-(3,4,6-tri-O-acetyl-2-deoxy-α-D-lyxo-hexopyranosyl)-β-D-galactopyranosyl]-2,3,6-tri-O-benzoyl-β-D-glucopyranose (**34**).—Compound **21** (86 mg, 0.067 mmol) and Ac_2O (65 μL, 0.69 mmol) were dissolved in toluene (1 mL) and $BF_3 \cdot Et_2O$ (7 μL) was added at room temperature. After 3 h, TLC (1:2 heptane–EtOAc) showed that the starting material was consumed. The mixture was poured into 5:2 CH_2Cl_2–H_2O (70 mL), the water phase was extracted with CH_2Cl_2 (20 mL), and the combined organic phase was washed with satd aq $NaHCO_3$ (20 mL), dried (Na_2SO_4), and concentrated. The residue was chromatographed (SiO_2, 3:1 heptane–EtOAc) to give **34** (36 mg, 44%) and **50** (34 mg, 51%). Compound **34** had $[\alpha]_D^{25}$ +99.1° (*c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.91 (d, 1 H, *J* 8.2 Hz, H-1), 5.79 (t, 1 H, *J* 9.3 Hz, H-3), 5.63 (dd, 1 H, *J* 7.8, 10.6 Hz, H-2′), 5.53 (dd, 1 H, *J* 8.3, 9.6 Hz, H-2), 5.23 (m, 1 H, H-3″), 5.10 (dd, 1 H, *J* 3.4, 10.6 Hz, H-3′), 4.76 (d, 1 H, *J* 7.8 Hz, H-1′), 4.70 (d, 1 H, *J* 3.2 Hz, H-1″), 2.05, 2.03, 2.02, 2.01, 1.99 (5 s, 3 H each, OAc). Mass spectrum: calcd for $C_{63}H_{62}O_{25}$ (M + Na): *m/z* 1241.3478; found: *m/z* 1241.3440.

4-O-[6-O-Acetyl-2,3-di-O-benzoyl-4-O-(3,4,6-tri-O-acetyl-2-deoxy-α-D-lyxo-hexopyranosyl)-β-D-galactopyranosyl]-2,3,6-tri-O-benzoyl-D-glucopyranose (**35**).—Com-

pound **21** (51 mg, 0.040 mmol) was dissolved in 2:1 CF_3CO_2H–CH_2Cl_2 (0.75 mL) and the mixture was stirred at 10°C for 30 min. Propyl acetate (1.5 mL) was added and, after 5 min, the mixture was co-concentrated with toluene (2 × 3 mL). The residue was chromatographed (SiO_2, 2:1 heptane–EtOAc) to give **35** (46 mg, 98%), which was used without further characterisation.

*4-O-[6-O-Acetyl-2,3-di-O-benzoyl-4-O-(3,4,6-tri-O-acetyl-2-deoxy-α-*D*-lyxo-hexopyranosyl)-α-*D*-galactopyranosyl]-2,3,6-tri-O-benzoyl-β-*D*-glucopyranosyl trichloroacetimidate* (**36**).—Compound **35** (50.0 mg, 0.0425 mmol) was dissolved in trichloroacetonitrile (144 μL), the mixture was cooled to 0°C, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (5.5 μL) was added. TLC (1:2 heptane–EtOAc) showed that the reaction was finished after 30 min. The solvent was removed and the residue was chromatographed (SiO_2, 3:2 heptane–EtOAc) to give **36** (55 mg, 98%); $[\alpha]_D^{25}$ +131.0° (*c* 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.53 (s, 1 H, NH), 6.70 (d, 1 H, *J* 3.7 Hz, H-1), 6.11 (dd, 1 H, *J* 8.7, 10.1 Hz, H-3), 5.66 (dd, 1 H, *J* 7.8, 10.2 Hz, H-2′), 5.49 (dd, 1 H, *J* 3.7, 10.2 Hz, H-2), 5.24 (m, 1 H, H-3″), 5.11 (dd, 1 H, *J* 3.1, 10.7 Hz, H-3′), 4.85 (d, 1 H, *J* 7.9 Hz, H-1′), 4.73 (d, *J* 2.9 Hz, H-1″), 2.04, 2.03, 2.01, 2.00 (4 s, 3 H each, OAc). Mass spectrum: calcd for $C_{63}H_{60}Cl_3NO_{24}$ (M + 1): *m/z* 1320.2649; found: *m/z* 1320.2614.

*3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]propyl 4-O-[6-O-acetyl-2,3-di-O-benzoyl-4-O-(3,4,6-tri-O-acetyl-2-deoxy-α-*D*-lyxo-hexopyranosyl)-β-*D*-galactopyranosyl]-2,3,6-tri-O-benzoyl-β-*D*-glucopyranoside* (**37**).—Compound **36** (30 mg, 0.023 mmol) was dissolved in CH_2Cl_2 (1.5 mL). The mixture was cooled to −50°C and added dropwise to a mixture of **53** (48.0 mg, 0.072 mmol), $BF_3 \cdot Et_2O$ (4.0 μL), 3A molecular sieves (A.W.-300, 0.5 g), and CH_2Cl_2 (3 mL), at 30°C under N_2. The resulting mixture was stirred at room temperature for 3 h, then quenched with Et_3N (5.0 μL), diluted with CH_2Cl_2 (10 mL), and filtered (Celite). The solid material was washed with CH_2Cl_2 (10 mL) and the combined organic phase was concentrated to give a semicrystalline mass, which was dissolved in hot EtOAc. Crystalline **53** (formed on cooling to room temperature) was filtered off and washed with cold EtOAc. The mother liquid was concentrated, and flash-chromatographed (SiO_2, 2:1 heptane–EtOAc) to give **37** (30.0 mg, 73%); $[\alpha]_D^{25}$ +68.9° (*c* 0.91, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.75 (t, 1 H, *J* 9.4 Hz, H-3), 5.63 (dd, 1 H, *J* 7.6, 10.5 Hz, H-2′), 5.36 (dd, 1 H, *J* 8.2, 9.6 Hz, H-2), 5.19 (bs, 1 H, H-4″), 5.11 (dd, 1 H, *J* 2.7, 10.5 Hz, H-3′), 4.78 (d, 1 H, *J* 7.8 Hz, H-1′), 4.72, 4.69 (d, 1 H each, *J* 8.3, 4.0 Hz, H-1,1″), 3.19–2.60 (m, 9 H, $CHCH_2SO_2CH_2$). Mass spectrum: calcd for $C_{97}H_{132}O_{28}S_2$ (M + Na): *m/z* 1831.8244; found: *m/z* 1831.8213.

*1-O-Acetyl-4-O-[6-O-acetyl-2,3-di-O-benzoyl-4-O-(2,4,6-tri-O-acetyl-3-deoxy-α-*D*-xylo-hexopyranosyl)-β-*D*-galactopyranosyl]-2,3,6-tri-O-benzoyl-β-*D*-glucopyranose* (**38**).—Compound **24** (95 mg, 0.074 mmol) was treated with Ac_2O–$BF_3 \cdot Et_2O$ as described in the preparation of **34**. The crude product was chromatographed (SiO_2, 3:1 heptane–EtOAc) to give **38** (45 mg, 50%); ^{1}H NMR ($CDCl_3$): δ 5.90 (d, 1 H, *J* 8.1 Hz, H-1), 5.78 (t, 1 H, *J* 9.3 Hz, H-3), 5.62 (dd, 1 H, *J* 7.8, 10.8 Hz, H-2′), 4.79 (d, 1 H, *J* 7.6 Hz, H-1′), 4.68 (bd, 1 H, *J* 2.4 Hz, H-1″), 1.98–1.85 (15 H, OAc).

*4-O-[6-O-Acetyl-2,3-di-O-benzoyl-4-O-(2,4,6-tri-O-acetyl-3-deoxy-α-*D*-xylo-hexo-*

pyranosyl)-β-D-galactopyranosyl]-2,3,6-tri-O-benzoyl-D-glucopyranose (**39**).—Compound **24** (178 mg, 0.139 mmol) was treated with 2:1 CF_3CO_2H–CH_2Cl_2 as described in the preparation of **35**. The crude product was chromatographed (SiO_2, 1:1 heptane–EtOAc) to give **39** (155 mg, 95%), which was used without further characterisation.

4-O-[6-O-Acetyl-2,3-di-O-benzoyl-4-O-(2,4,6-tri-O-acetyl-3-deoxy-α-D-xylo-hexopyranosyl)-β-D-galactopyranosyl]-2,3,6-tri-O-benzoyl-β-D-glucopyranosyl trichloroacetimidate (**40**).—Compound **39** (145 mg, 0.123 mmol) was treated with trichloroacetonitrile and DBU as described in the preparation of **36**. The crude product was chromatographed (SiO_2, 1:1 heptane–EtOAc) to give **40** (156 mg, 96%); $[\alpha]_D^{25}$ +83.4° (*c* 0.70, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.53 (s, 1 H, NH), 6.68 (d, 1 H, *J* 3.7 Hz, H-1), 6.13 (t, 1 H, *J* 9.3 Hz, H-3), 5.67 (dd, 1 H, *J* 8.0, 10.7 Hz, H-2′), 5.43 (dd, 1 H, *J* 3.8, 10.1 Hz, H-2), 5.07 (m, 2 H, H-3′,4″), 4.76 (d, 1 H, *J* 3.1 Hz, H-1″), 2.04, 2.02, 1.95, 1.91 (4 s, 3 H each, OAc). Mass spectrum: calcd for $C_{63}H_{60}Cl_3NO_{24}$ (M + Na): *m/z* 1342.2469; found: *m/z* 1342.2439.

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]propyl 4-O-[6-O-acetyl-2,3-di-O-benzoyl-4-O-(2,3,6-tri-O-acetyl-3-deoxy-α-D-xylo-hexopyranosyl)-β-D-galactopyranosyl]-2,3,6-tri-O-benzoyl-β-D-glucopyranoside (**41**).—Compound **40** (40.0 mg, 0.030 mmol) was treated with **53** (78.6 mg, 0.120 mmol) and $BF_3 \cdot Et_2O$ in CH_2Cl_2, as described in the preparation of **37**, to give **41** (33 mg, 59%); $[\alpha]_D^{25}$ +36.7° (*c* 1.0, $CDCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.76 (t, 1 H, *J* 9.4 Hz, H-3), 5.62 (dd, 1 H, *J* 7.9, 10.6 Hz, H-2′), 5.34 (dd, 1 H, *J* 7.9, 9.9 Hz, H-2), 5.19 (m, 2 H, H-3′, 4″), 4.88 (m, 1 H, H-2″), 4.83 (d, 1 H, *J* 7.8 Hz, H-1′), 4.77 (d, 1 H, *J* 2.9 Hz, H-1″), 4.72 (d, 1 H, *J* 8.0 Hz, H-1), 3.19–2.62 (m, 9 H, $CHCH_2SO_2CH_2$), 2.05, 2.03, 1.99, 1.91 (4 s, 3 H each, OAc), 0.87 (t, 6 H, *J* 6.7 Hz, CH_2CH_3). Mass spectrum: calcd for $C_{97}H_{132}O_{28}S_2$ (M + Na): *m/z* 1831.8244; found: *m/z* 1831.8333.

1-O-Acetyl-4-O-[6-O-acetyl-2,3-di-O-benzoyl-4-O-(2,3,6-tri-O-acetyl-4-deoxy-α-D-xylo-hexopyranosyl)-β-D-galactopyranosyl]-2,3,6-tri-O-benzoyl-β-D-glucopyranose (**42**).—Compound **27** (100 mg, 0.080 mmol) was treated with Ac_2O–$BF_3 \cdot Et_2O$ as described in the preparation of **34**. The crude product was chromatographed (SiO_2, 3:1 heptane–EtOAc) to give **42** (86 mg, 91%); $[\alpha]_D^{25}$ +101.0° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.92 (d, 1 H, *J* 8.1 Hz, H-1), 5.81 (t, 1 H, *J* 9.0 Hz, H-3), 5.64 (dd, 1 H, *J* 7.7, 10.6 Hz, H-2′), 5.51 (dd, 1 H, *J* 8.2, 9.3 Hz, H-2), 5.19 (dt, 1 H, *J* 4.9, 11.2 Hz, H-3″), 5.03 (dd, 1 H, *J* 2.7, 11.0 Hz, H-3′), 4.86 (d, 1 H, *J* 3.7 Hz, H-1″), 4.58, 4.47 (dd, 1 H each, *J* 1.8, 3.9, 12.3 Hz, H-6), 2.21 (m, 1 H, H-4″*e*), 1.56 (bq, 1 H, *J* 11.7 Hz, H-4″*a*), 2.05, 2.03, 1.98, 1.97, 1.94, 1.92 (5 s, 3 H each, OAc). Anal. Calcd for $C_{63}H_{62}O_{15}$: C, 62.1; H, 5.1. Found: C, 61.7; H, 5.3.

4-O-[6-O-Acetyl-2,3-di-O-benzoyl-4-O-(2,3,6-tri-O-acetyl-4-deoxy-α-D-xylo-hexopyranosyl)-β-D-galactopyranosyl]-2,3,6-tri-O-benzoyl-D-glucopyranose (**43**).—Compound **27** (200 mg, 0.157 mmol) was treated with 2:1 CF_3CO_2H–CH_2Cl_2 as described in the preparation of **35**. The crude product was chromatographed (SiO_2, 2:1 heptane–EtOAc) to give **43** (177 mg, 96.0%), which was used without further characterisation.

4-O-[6-O-Acetyl-2,3-di-O-benzoyl-4-O-(2,3,6-tri-O-acetyl-4-deoxy-α-D-xylo-hexopyranosyl)-β-D-galactopyranosyl]-2,3,6-tri-O-benzoyl-β-D-glucopyranosyl trichloro-

acetimidate (**44**).—Compound **43** (165 mg, 0.14 mmol) was treated with trichloroacetonitrile and DBU as described in the preparation of **36**. The crude product was chromatographed (SiO_2, 2:1 heptane–EtOAc) to give **44** (183 mg, 99%); $[\alpha]_D^{25}$ +161.0° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.55 (s, 1 H, NH), 6.67 (d, 1 H, *J* 3.7 Hz, H-1), 6.17 (t, 1 H, *J* 9.5 Hz, H-3), 5.68 (dd, 1 H, *J* 9.8, 11.0 Hz, H-2′), 5.46 (dd, 1 H, *J* 3.7, 10.3 Hz, H-2″), 5.21 (dt, 1 H, *J* 4.7, 10.5 Hz, H-3″), 5.04 (dd, 1 H, *J* 2.9, 10.9 Hz, H-3′), 4.89 (d, 1 H, *J* 8.1 Hz, H-1′), 4.86 (d, 1 H, *J* 3.5 Hz, H-1″), 4.81 (dd, 1 H, *J* 3.5, 10.4 Hz, H-2″), 2.25 (m, 1 H, H-4″*e*), 2.10–1.90 (4 s, 3 H each, OAc), 1.56 (bq, 1 H, *J* 11.8 Hz, H-4″*a*). Mass spectrum: calcd for $C_{63}H_{60}Cl_3NO_{24}$ (M + Na): *m/z* 1342.2469; found: *m/z* 1342.2415.

*3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]propyl 4-*O*-[6-*O*-acetyl-2,3-di-*O*-benzoyl-4-*O*-(2,3,6-tri-*O*-acetyl-4-deoxy-α-*D*-xylo-hexopyranosyl)-β-*D*-galactopyranosyl]-2,3,6-tri-*O*-benzoyl-β-*D*-glucopyranoside* (**45**).—Compound **44** (20.0 mg, 0.0151 mmol) was dissolved in CH_2Cl_2 (1 mL). The mixture was cooled to −5°C and added dropwise to a mixture of **53** (32.0 mg, 0.048 mmol), $BF_3 \cdot Et_2O$ (4.2 μL, 0.031 mmol), 3A molecular sieves (A.W.-300, 0.3 g), and CH_2Cl_2 (2 mL), at 40°C under N_2. The resulting mixture was stirred at −5°C for 30 min and at room temperature for 4 h, then quenched with Et_3N (20 μL), diluted with CH_2Cl_2 (20 mL), filtered (Celite), and concentrated to give a semicrystalline mass, which was dissolved in hot EtOAc. Crystalline **53** (formed on cooling to room temperature) was filtered off and washed with cold EtOAc. The mother liquid was concentrated, and the residue was chromatographed (SiO_2, 3:2 heptane–EtOAc) to give **45** (15.0 mg, 55%); $[\alpha]_D^{25}$ +44.0° (*c* 0.25, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.78 (t, 1 H, *J* 9.3 Hz, H-3), 5.62 (td, 1 H, *J* 7.8, 10.6 Hz, H-2′), 5.33 (dd, 1 H, *J* 8.0, 9.6 Hz, H-2), 5.19 (td, 1 H, *J* 5.1, 10.6 Hz, H-3″), 4.86 (d, 1 H, *J* 3.5 Hz, H-1″), 4.73 (d, 1 H, *J* 7.9 Hz, H-1), 3.19–2.62 (m, 9 H, $CHCH_2SO_2CH_2$), 2.25–2.16 (m, 1 H, H-4″*e*), 2.04, 1.97, 1.94, 1.93 (4 s, 3 H each, OAc), 0.87 (t, 6 H, *J* 6.7 Hz, CH_2CH_3). Mass spectrum: calcd for $C_{97}H_{132}O_{28}S_2$ (M + Na): *m/z* 1831.8244; found: *m/z* 1831.8213.

*1-*O*-Acetyl-4-*O*-[6-*O*-acetyl-2,3-di-*O*-benzoyl-4-*O*-(2,3,4-tri-*O*-acetyl-α-*D*-fucopyranosyl)-β-*D*-galactopyranosyl]-2,3,6-tri-*O*-benzoyl-β-*D*-glucopyranose* (**46**).—Compound **30** (65 mg, 0.051 mmol) was treated with Ac_2O–$BF_3 \cdot Et_2O$ as described in the preparation of **34**. The crude product was chromatographed (SiO_2, 3:1 heptane–EtOAc) to give **46** (23 mg, 37%), **50** (16 mg, 32%), and the $Me_3SiCH_2CH_2$ glycoside corresponding to **50** (7 mg, 13%). Compound **46** had $[\alpha]_D^{25}$ +110.5° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.93 (d, 1 H, *J* 8.1 Hz, H-1), 5.81 (t, 1 H, *J* 9.1 Hz, H-3), 5.65 (dd, 1 H, *J* 7.8, 10.4 Hz, H-2′), 4.87 (d, 1 H, *J* 3.7 Hz, H-1″), 4.82 (d, 1 H, *J* 7.8 Hz, H-1′), 2.07, 1.99, 1.98, 1.97, 1.91 (5 s, 3 H each, OAc), 0.71 (d, 3 H, *J* 6.5 Hz, H-6″). Mass spectrum: calcd for $C_{63}H_{62}O_{25}$ (M + Na): *m/z* 1241.3478; found: *m/z* 1241.3500.

*4-*O*-[6-*O*-Acetyl-2,3-di-*O*-benzoyl-4-*O*-(2,3,4-tri-*O*-acetyl-α-*D*-fucopyranosyl)-β-*D*-galactopyranosyl]-2,3,6-tri-*O*-benzoyl-β-*D*-glucopyranose* (**47**).—Compound **30** (223 mg, 0.175 mmol) was treated with 2:1 CF_3CO_2H–CH_2Cl_2 as described in the preparation of **35**. The crude product was chromatographed (SiO_2, 1:1 heptane–EtOAc) to give **47** (201 mg, 98%), which was used without further characterisation.

4-O-[6-O-Acetyl-2,3-di-O-benzoyl-4-O-(2,3,4-tri-O-acetyl-α-D-fucopyranosyl)-α-D-galactopyranosyl]-2,3,6-tri-O-benzoyl-β-D-glucopyranosyl trichloroacetimidate (**48**). —Compound **47** (100 mg, 0.085 mmol) was treated with trichloroacetonitrile and DBU as described in the preparation of **36**. The crude product was chromatographed (SiO_2, 1:1 heptane–EtOAc) to give **48** (109 mg, 97%); $[\alpha]_D^{25}$ +87.0° (*c* 0.6, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.53 (s, 1 H, NH), 6.66 (d, 1 H, *J* 3.7 Hz, H-1), 6.16 (d, 1 H, *J* 8.9 Hz, H-3), 5.69 (dd, 1 H, *J* 7.7, 10.8 Hz, H-2′), 5.44 (dd, 1 H, *J* 3.7, 10.1 Hz, H-2), 5.11 (dd, 1 H, *J* 3.6, 10.4 Hz, H-2″), 4.89 (d, 1 H, *J* 7.9 Hz, H-1′), 4.87 (d, 1 H, *J* 3.7 Hz, H-1″), 2.07, 1.99, 1.95, 1.92 (4 s, 3 H each, OAc). Mass spectrum: calcd for $C_{63}H_{60}Cl_3NO_{24}$ (M + Na): *m/z* 1342.2469; found: *m/z* 1342.2416.

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]propyl 4-O-[6-O-acetyl-2,3-di-O-benzoyl-4-O-(2,3,4-tri-O-acetyl-α-D-fucopyranosyl)-β-D-galactopyranosyl]-2,3,6-tri-O-benzoyl-β-D-glucopyranoside (**49**).—Compound **48** (57 mg, 0.043 mmol) was treated with **53** (61 mg, 0.092 mmol) and $BF_3 \cdot Et_2O$ in CH_2Cl_2 as described in the preparation of **37**. The crude product was chromatographed (3:1 heptane–EtOAc), to give **49** (46.7 mg, 59%); $[\alpha]_D^{25}$ +66.0° (*c* 0.58, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.77 (t, 1 H, *J* 9.3 Hz, H-3), 5.65 (dd, 1 H, *J* 7.7, 10.1 Hz H-2′), 5.10 (dd, 1 H, *J* 3.3, 11.4 Hz, H-2″), 5.03 (dd, 1 H, *J* 2.7, 10.9 Hz, H-3′), 4.78 (d, 1 H, *J* 3.4 Hz, H-1″), 4.83 (d, 1 H, *J* 8.0 Hz, H-1′), 4.72 (d, 1 H, *J* 8.0 Hz, H-1), 3.19–2.60 (m, 9 H, $CHCH_2SO_2CH_2$), 2.08, 1.99, 1.97, 1.92 (4 s, 3 H each, OAc), 0.70 (d, 3 H, *J* 6.4 Hz, H-6″). Anal. Calcd for $C_{97}H_{132}O_{28}S_2$: C, 64.4; H, 7.3. Found: C, 63.8; H, 7.7.

1-O-Acetyl-2,3,6-tri-O-benzoyl-4-O-(4,6-di-O-acetyl-2,3-di-O-benzoyl-β-D-galactopyranosyl)-β-D-glucopyranose (**50**), *isolated as a byproduct in the preparation of* **34**, **38**, *and* **46**.—Compound **50** had $[\alpha]_D^{25}$ +66.2° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.91 (d, 1 H, *J* 8.2 Hz, H-1), 5.79 (t, 1 H, *J* 9.3 Hz, H-3), 5.58 (dd, 1 H, *J* 7.7, 10.3 Hz, H-2′), 5.55 (dd, 1 H, *J* 8.2, 9.8 Hz, H-2), 5.39 (d, 1 H, *J* 3.4 Hz, H-4′), 5.19 (dd, 1 H, *J* 3.3, 10.4 Hz, H-3′), 4.77 (d, 1 H, *J* 7.8 Hz, H-1′), 2.00, 1.98, 1.92 (3 s, 3 H each, OAc). Mass spectrum: calcd for $C_{53}H_{48}O_{19}$ (M − 1): *m/z* 987.2712; found: *m/z* 987.2740.

3-Hexadecylthio-2-(hexadecylthiomethyl)propan-1-ol (**52**).—Compound **51** [29] (97%, 5.0 g, 21.6 mmol), hexadecanethiol (20.5 mL, 65.1 mmol), and DMF (150 mL) were cooled to 0°C and Cs_2CO_3 (95%, 22.3 g, 65 mmol) was added. The mixture was stirred at room temperature, under N_2, for 24 h, then poured into 3:5 ice–water–CH_2Cl_2 (800 mL). The water phase was extracted with CH_2Cl_2 (3 × 300 mL), the combined organic phase was washed with satd aq NaCl (2 × 300 mL) and dried (Na_2SO_4), and CH_2Cl_2 was removed. MeOH (200 mL) was added to force the crystallisation of **52**, which was isolated by filtration to give 11.7 g (93%). ^1H NMR ($CDCl_3$): δ 3.77 (t, 2 H, *J* 5.5 Hz, OCH_2), 2.65 (bt, 4 H, *J* 6.7 Hz, CH_2S), 2.52 (bt, 4 H, *J* 7.4 Hz, SCH_2), 1.94 (m, 1 H, CH_2CH), 1.57 (m, 4 H, SCH_2CH_2), 0.88 (bt, 6 H, *J* 6.7 Hz, CH_2CH_3). Mass spectrum: calcd for $C_{36}H_{74}OS_2$ (M + 1): *m/z* 587.5259; found: *m/z* 587.5266.

3-Hexadecylsulfonyl-2-(hexadecylsulfonylmethyl)propan-1-ol (**53**).—Compound **52** (200 mg, 0.34 mmol) was dissolved in CH_2Cl_2 (10 mL) and MCPBA (85%, 276 mg, 1.36 mmol) was added in portions. After 17 h, the mixture was diluted with

CH_2Cl_2 (100 mL), washed with aq Na_2SO_3 (1 M, 30 mL) and satd aq NaCl (30 mL), dried (Na_2SO_4), and concentrated to give **53** (220 mg, 99%). Recrystallisation from EtOAc gave an analytical sample; ^{1}H NMR ($CDCl_3$): δ 3.93 (brd, 2 H, J 5.3 Hz, OCH_2), 3.42 (dd, 2 H, J 6.8, 14.1 Hz, CH_2SO_2), 3.24 (dd, 2 H, J 5.7, 14.0 Hz, CH_2SO_2), 3.06–2.93 (5 H, SO_2CH_2, CH), 1.83 (m, 4 H, $SO_2CH_2CH_2$), 0.87 (t, 6 H, J 6.7 Hz, CH_2CH_3). Mass spectrum: calcd for $C_{36}H_{74}O_5S_2$ (M + 1): m/z 651.5056; found m/z 651.5053.

*Methyl 2,4,6-tri-*O*-benzyl-3-*O*-(methylthio)thiocarbonyl-α-*D*-galactopyranoside* (**54**).—A mixture of methyl 2,4,6-tri-*O*-benzyl-α-D-galactopyranoside [30] (1.54 g, 3.32 mmol), NaH (80% in oil, 203 mg, 6.63 mmol), and THF (10 mL) was stirred for 2 h and imidazole (10 mg, 0.15 mmol) was added. After 5 min, CS_2 (1.7 mL) was added and the mixture was stirred for 2.5 h. MeI (0.41 mL, 6.63 mmol) was added and the reaction was monitored by TLC (1:1 heptane–EtOAc). After 3 h, the mixture was diluted with CH_2Cl_2 (100 mL), washed with satd aq $NaHCO_3$ (50 mL) and water (50 mL), dried (Na_2SO_4), and concentrated. The residue was flash-chromatographed (SiO_2, 2:1 heptane–EtOAc) to give **54** (1.82 g, 99%); $[\alpha]_D^{25}$ +64.9° (c 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 6.10 (dd, 1 H, J 3.1, 10.2 Hz, H-3), 4.28 (d, 1 H, J 2.9 Hz, H-4), 4.19 (dd, 1 H, J 3.7, 10.3 Hz, H-2), 4.04 (t, 1 H, J 6.5 Hz, H-5), 3.39 (s, 3 H, OCH_3), 2.59 (s, 3 H, SCH_3). Mass spectrum: calcd for $C_{30}H_{34}O_6S_2$ (M + 1): m/z 555.1875; found: m/z 555.1839.

*Methyl 2,4,6-tri-*O*-benzyl-3-deoxy-α-*D*-xylo-hexopyranoside* (**55**).—A solution of compound **54** (1.80 g, 3.24 mmol) and azobis(isobutyronitrile) (43 mg) in toluene (55 mL) was added to a refluxing solution of Bu_3SnH (> 98%, 1.72 mL, ~ 6.49 mmol) in toluene (70 mL), kept under Ar. The mixture was refluxed for 30 h, then cooled, filtered (Celite), and concentrated. The residue was chromatographed (SiO_2, 5:1 → 2:1 heptane–EtOAc) to give **55** (605 mg, 42%) and methyl 2,4,6-tri-*O*-benzyl-α-D-galactopyranoside (461 mg, 31%). Compound **55** had $[\alpha]_D^{25}$ +13.8° (c 0.5, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 4.75 (d, 1 H, J 3.4 Hz, H-1), 3.94 (dt, 1 H, J 1.3, 6.2 Hz, H-4), 3.87 (dt, 1 H, J 3.5, 4.3, 12.0 Hz, H-2), 3.44 (s, 3 H, OCH_3), 2.23 (dt, 1 H, J 4.0, 13.5 Hz, H-3a), 1.86 (dt, 1 H, J 2.4, 12.8 Hz, H-3e). Anal. Calcd for $C_{28}H_{32}O_5$: C, 74.9; H, 7.1. Found: C, 74.4; H, 7.1.

*Methyl 2,4,6-tri-*O*-acetyl-3-*O*-(imidazol-1-ylthiocarbonyl)-β-*D*-galactopyranoside* (**56**).—A mixture of methyl 2,4,6-tri-*O*-acetyl-β-D-galactopyranoside [32] (570 mg, 1.78 mmol), *N*,*N*′-thiocarbonyldiimidazole (635 mg, 3.56 mmol), and dry 1,2-dimethoxyethane (30 mL) was refluxed under Ar overnight, then concentrated. The residue was chromatographed (SiO_2, 2:3 heptane–EtOAc) to give **56** (765 mg, 99%); $[\alpha]_D^{25}$ +12.5° (c 1.0 $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.23 (d, 1 H J 1.0 Hz, N=CHN), 7.48 (t, 1 H, J 1.5 Hz, =CHN), 7.00 (dd, 1 H, J 0.9, 1.7 Hz, NCH=C), 5.44 (dd, 1 H, J 8.0, 9.9 Hz, H-2), 4.46 (d, 1 H, J 7.9 Hz, H-1), 4.00 (t, 1 H, J 6.6 Hz, H-5), 3.55 (s, 3 H, OCH_3), 2.11, 2.06, 2.03 (3 s, 3 H each, OAc). Mass spectrum: calcd for $C_{17}H_{22}N_2O_9S$ (M + 1): m/z 431.1124; found: m/z 431.1115.

*Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(methylthio)thiocarbonyl-α-*D*-glucopyranoside* (**57**).—A mixture of methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside [36] (4.50 g, 9.49 mmol), NaH (80% in oil, 592 mg, ~ 19.4 mmol), imidazole (18 mg, 0.27 mmol), and THF (27 mL) was stirred for 2 h, then CS_2 (5.1 mL, 85.0 mmol) was added. After

1.5 h, MeI (1.21 mL, 19.6 mmol) was added and the reaction was monitored by TLC (2:1 heptane–EtOAc). The mixture was diluted with CH_2Cl_2 (60 mL) and washed with water (25 mL). The water phase was extracted with CH_2Cl_2 (30 mL), and the combined organic phase was washed with aq HCl (0.2 M, 30 mL), satd aq $NaHCO_3$ (30 mL), and water (30 mL), dried (Na_2SO_4), and concentrated. The residue was chromatographed (SiO_2, 2:1 heptane–EtOAc) to give **57** (5.22 g, 97%); $[\alpha]_D^{25}$ +27° (*c* 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 6.15 (dd, 1 H, *J* 9.2, 10.1 Hz, H-4), 4.09 (t, 1 H, *J* 9.3 Hz, H-3), 3.80 (ddd, 1 H, *J* 2.4, 5.4, 9.8 Hz, H-5), 3.42 (s, 3 H, OMe). Mass spectrum: calcd for $C_{30}H_{34}O_6S_2$ (M + 1): *m/z* 555.1875; found: *m/z* 555.1837.

*Ethyl 2,3,4-tri-*O*-acetyl-1-thio-*D*-fucopyranoside* (**58**).—D-Fucose (3.47 g, 21.2 mmol) was treated with 1:1 Ac_2O–pyridine (50 mL) to give crude 1,2,3,4-tetra-*O*-acetyl-D-fucose (7.0 g, 99.5%). A mixture of 1,2,3,4-tetra-*O*-acetyl-D-fucose (5.0 g, ~ 15 mmol), $HSCH_2CH_3$ (2.23 mL, 30.1 mmol), and CH_2Cl_2 (80 mL) was cooled (ice bath) and $BF_3 \cdot Et_2O$ (2.80 mL, 22.6 mmol) was added. The mixture was stirred at room temperature for 6 h, then washed rigorously with aq NaOH (1 M, 30 mL), satd aq $NaHCO_3$ (30 mL), and water (20 mL), dried (Na_2SO_4), and concentrated. The residue was chromatographed (SiO_2, 2:1 heptane–EtOAc) to give **58** (4.5 g, 89%, $\alpha:\beta$ 1:7); ^1H NMR ($CDCl_3$): δ 5.70 (d, *J* 5.1 Hz, H-1α), 4.48 (d, *J* 9.8 Hz, H-1β). Mass spectrum: calcd for $C_{14}H_{22}O_7S$ (M + 1): *m/z* 335.1165; found: *m/z* 335.1169.

*2-(Trimethylsilyl)ethyl 4-*O*-(4,6-*O*-p-methoxybenzylidene-β-*D*-galactopyranosyl)-β-*D*-glucopyranoside* (**59**).—A mixture of 2-(trimethylsilyl)ethyl β-D-lactoside [11] (14.4 g, 32.5 mmol), *p*-methoxy-α,α-dimethoxytoluene (12.4 g, 68.2 mmol), *p*-toluenesulfonic acid (240 mg, 1.40 mmol), and dry CH_3CN (450 mL) was stirred at room temperature for 38 h. Et_3N (1.5 mL) was added and the solvent was removed. The residue was extracted with hot EtOAc (200 mL), the extract was filtered, and heptane was added to give crystalline **59** (4.51 g, 25%). The mother liquid was concentrated and the residue was chromatographed (SiO_2, 5:1 EtOAc–MeOH) to give additional **59** (10.1 g, 56%). Compound **59** was obtained in a total yield of 81%; $[\alpha]_D^{25}$ −39.6° (*c* 0.7, MeOH); ^1H NMR ($CDCl_3$): δ 7.45 (dd, 2 H, *J* 1.7, 2.8 Hz, Ar-H), 6.92 (dd, 2 H, *J* 2.1, 6.8 Hz, Ar-H), 5.58 (s, 1 H, Ar-C*H*), 4.55 (d, 1 H, *J* 7.6 Hz, H-1′), 4.31 (d, 1 H, *J* 7.8 Hz, H-1), 3.80 (s, 3 H, OCH_3), 0.96 (m, 2 H, CH_2CH_2), 0.03 (s, 9 H, $SiCH_3$). Mass spectrum: calcd for $C_{25}H_{40}O_{12}Si$ (M − OMe): *m/z* 529.2105; found: *m/z* 529.2134.

*2-(Trimethylsilyl)ethyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3-di-*O*-benzoyl-4,6-*O*-p-methoxybenzylidene-β-*D*-galactopyranosyl)-β-*D*-glucopyranoside* (**60**).—A mixture of compound **59** (14.2 g, 25.3 mmol) and pyridine (70 mL) was cooled (ice bath) and benzoyl chloride (29.4 mL, 253 mmol) was added during 12 min. After 10 min, the cooling bath was removed and the mixture was stirred at room temperature. When TLC (toluene–Et_2O) indicated that the reaction was completed, water (2.5 mL) was added and the stirring was continued for 20 min. CH_2Cl_2 (400 mL) was added, and the mixture was filtered (Celite), washed with aq H_2SO_4 (2 M, 200 mL), water (200 mL), and satd aq $NaHCO_3$ (200 mL), dried (Na_2SO_4), and concentrated. The residue was chromatographed (SiO_2, 20:1 toluene–Et_2O) to give **60** (24.7 g, 90%);

$[\alpha]_D^{25}$ +115.9° (*c* 0.67, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.83 (t, 1 H, *J* 9.1 Hz, H-3), 5.78 (dd, 1 H, *J* 7.9, 10.6 Hz, H-2'), 5.31 (dd, 1 H, *J* 7.8, 9.4 Hz, H-2), 5.22 (s, 1 H, Ar-C*H*), 5.14 (dd, 1 H, *J* 3.6, 10.3 Hz, H-3'), 4.83 (d, 1 H, *J* 8.0 Hz, H-1'), 4.70 (d, 1 H, *J* 7.8 Hz, H-1), 4.61, 4.37 (dd, 1 H each, *J* 2.4, 4.5, 11.7 Hz, H-6), 4.28 (d, 1 H, *J* 3.7 Hz, H-4'), 4.20 (t, 1 H, *J* 9.2 Hz, H-4), 3.80 (s, 3 H, OCH_3), −0.16 (s, 9 H, $SiCH_3$). Mass spectrum: calcd for $C_{60}H_{60}O_{17}Si$ (M + 1): *m/z* 1081.3678; found: *m/z* 1081.3623.

*2-(Trimethylsilyl)ethyl 2,3,6-tri-*O*-benzoyl-4-*O*-(2,3-di-*O*-benzoyl-β-*D*-galactopyranosyl)-β-*D*-glucopyranoside* (**61**).—A mixture of compound **60** (1.80 g, 1.66 mmol), $NaCNBH_3$ (870 mg, 13.9 mmol), 4A molecular sieves (1 g), and THF (20 mL) was stirred for 30 min, then cooled with an ice bath. An ice-cold solution of satd ethereal HCl (~ 1 mL) was added dropwise until no more gas was evolved. The reaction was monitored by TLC (4:1 toluene–Et_2O). After 9 h, solid $NaHCO_3$ (~ 0.5 g) was added and the mixture was stirred for 10 min. CH_2Cl_2 (60 mL) was added and the mixture was washed with satd aq $NaHCO_3$ (20 mL) and water (25 mL), dried (Na_2SO_4), and concentrated. The residue was chromatographed (SiO_2, 3:1 heptane–EtOAc) to give **61** (1.48 g, 92%); $[\alpha]_D^{25}$ +77.2° (*c* 0.84, $CHCl_3$). Mass spectrum: calcd for $C_{52}H_{54}O_{16}Si$ (M + Na): *m/z* 985.3079; found: *m/z* 985.3060.

*2-(Trimethylsilyl)ethyl 2,3,6-tri-*O*-benzoyl-4-*O*-(4,6-di-*O*-acetyl-2,3-di-*O*-benzoyl-β-*D*-galactopyranosyl)-β-*D*-glucopyranoside* (**62**).—Compound **61** was acetylated (1:1 Ac_2O–pyridine) to give **62**; $[\alpha]_D^{25}$ +56.9° (*c* 1.12, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.73 (t, 1 H, *J* 9.5 Hz, H-3), 5.57 (dd, 1 H, *J* 7.9, 9.6 Hz, H-2'), 5.37 (d, 1 H, *J* 3.5 Hz, H-4'), 1.98, 1.93 (2 s, 3 H each, OAc). Mass spectrum: calcd for $C_{56}H_{58}O_{18}Si$ (M + 1): *m/z* 1047.3471; found: *m/z* 1047.3499.

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