on the Ratio of 3-Azido-2-hydroxybutanal Hydrate (9·H_2O) to Hydroxyacetone Phosphate (DHAP, 1) Employed (see Figure 1). 1 (60 mM), variable concentrations of 9·H_2O, and RAMA (4 units/mL) were incubated for 2 days at pH 6.2 and 25 °C as described above. The barium salts **11a/11b** were precipitated by addition of a solution of $BaCl_2 \cdot 2H_2O$ (0.2 mmol/mL) and ethanol (1 mmol/mL), and hydrolyzed with PASE. The reaction mixture was evaporated, and aliquots of the residue were persilylated. The diastereoisomer ratio of the TMS_4 derivatives of **12/13** was determined by capillary GC (OV 1701; 20 m; 40–300 °C, 5°/min; on-column injection).

2,6,7-Trideoxy-2,6-imino-D-*glycero*-D-*manno*-heptitol (14) and 2,6,7-Trideoxy-2,6-imino-D-*glycero*-D-*gluco*-heptitol (15). A suspension of $PtO_2 \cdot 2H_2O$ (200 mg) and activated charcoal (700 mg) in demineralized water (60 mL) was stirred and saturated twice with H_2 (100 bar) at 25 °C for 7 min. A solution of **13** (1.0 g, 4.56 mmol) in glacial acetic acid (1 mL) and demineralized water (15 mL) was added rapidly. The mixture was hydrogenated at 25 °C for 12 h (50–80 bar H_2) and filtered over Celite. The filtrate was adjusted to pH 2 with 1 N HCl, the solvent was evaporated in vacuo, and the residue was dissolved in ethanol. By addition of ether, **14**·HCl/**15**·HCl were precipitated (855 mg, 88%). The colorless oil was applied to a WOLFATIT H^+ column, which was washed with water and eluted with 10% ammonia. The eluate was evaporated in vacuo. Anal. Calcd for $C_7H_{15}N_4 \cdot 0.2H_2O$: C, 46.50; H, 8.47; N, 7.75. Found: C, 46.33; H, 8.51; N, 7.60. High-resolution mass spectrum (EI): calcd for $C_7H_{15}NO_4$ 177.1001, found 177.1000. MS (EI, 70 eV): *m/z* (%) 177 (1.5) $[M]^{+\cdot}$, 160 (1.6) $[M - OH]^+$, 159 (1.5) $[M - H_2O]^{+\cdot}$, 146 (100) $[M - CH_2OH]^+$. CI(CH_4)-3,4,5,7-tetrakis(trimethylsilyl) derivatives of **14** and **15** (obtained from the mixture **14**·HCl/**15**·HCl): *m/z* (%) 466 (7) $[MH]^+$, 464 (4) $[M - H]^+$, 450 (19) $[MH - CH_4]^+$, 378 (2.4), 362 (6.6), 286 (11.7), 216 (6), besides 75 (100) $[HOSiMe_2]^+$ and 73 (83) $[SiMe_3]^+$. The mixture of **14**·HCl/**15**·HCl in water (2 mL) was acidified with diluted formic acid and separated on DOWEX 50 W×8 NH_4^+ (200–400 mesh; 2.5 × 50 cm; conditioned with 0.75 M ammonium formate, pH 4.0; eluent 0.75 M ammonium formate buffer, applied with a gradient: 50 mL pH 4.0, 75 mL pH 5.0, 180 mL pH 5.0–5.6; polarimetric detection). The individual fractions were applied to a WOLFATIT H^+ column (2 × 15 cm), washed with water, and eluted with 10% ammonia. The eluates were concentrated in vacuo, yielding **15** as an oil and **14** as colorless crystals. **15**. $[\alpha]^{20}_D$: +38.7° (*c* 1, H_2O). ^1H NMR see Table I. ^{13}C NMR (D_2O): δ 20.02 (C-7), 52.64 (C-6), 56.92, 64.12, 72.39, 73.64, 74.17. **14** (dried over P_2O_5 and potassium hydroxide). Mp 141 °C. $[\alpha]^{20}_D$: −11.3° (*c* 1, H_2O). ^1H NMR see Table I. ^{13}C NMR (D_2O): δ 17.06 (C-7), 55.15 (C-6), 57.28, 63.32, 71.33, 73.91, 75.80.

2,6,7-Trideoxy-2,6-imino-L-*glycero*-L-*gulo*-heptitol (16). A mixture of **12/13** (1.0 g, 4.56 mmol) was hydrogenated, and the reaction mixture was worked up chromatographically as described for **14/15**. The products were eluted from the DOWEX NH_4^+ column in the order **14**, **16**, **15**. The fraction containing **16** was concentrated in vacuo, yielding pure **16** as a colorless oil. $[\alpha]^{20}_D$: +17.3° (*c* 1, H_2O). ^1H NMR see Table I. ^{13}C NMR (D_2O): δ 19.81 (C-7), 57.14 (C-6), 62.82, 64.42, 74.61, 79.11, 80.87.

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Prespacer Glycosides in Glycoconjugate Chemistry. Dibromoisobutyl Glycosides for the Synthesis of Neoglycolipids, Neoglycoproteins, Neoglycoparticles, and Soluble Glycosides

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3-Bromo-2-(bromomethyl)propyl (dibromoisobutyl or DIB) mono- to tetrasaccharide glycosides were prepared in moderate to high yields by treatment of the corresponding 1-*O*-acetyl saccharides with 3-bromo-2-(bromomethyl)propanol (DIBOL) and boron trifluoride etherate. Treatment of the DIB glycosides with alkyl- and ω-methoxycarbonylalkyl thiols gave the corresponding bis-sulfide glycolipids and spacer arm sugars, respectively. Oxidation of the sulfides with *m*-chloroperbenzoic acid gave the corresponding bis-sulfones. Treatment of the DIB glycosides with tetrabutylammonium fluoride gave the corresponding allylic bromide glycosides, and addition of thiols gave the allylic sulfides. Prolonged fluoride treatment gave the allylic fluorides. Hydrogenation of DIB glycosides under basic conditions gave the corresponding isobutyl glycosides. Spacer arm and allylic bromide glycosides were coupled to bovine serum albumin and derivatized silica gel, thereby providing artificial glycoproteins and glycoparticles.

The aim of the present report is to show that the combination of 2-(trimethylsilyl)ethyl (TMSET) glycosides for anomeric blocking during oligosaccharide synthesis,[1] followed by transformation into 3-bromo-2-(bromomethyl)-propyl (dibromoisobutyl or DIB) glycosides and further conversion to glycolipids, spacer glycosides, and soluble glycosides, represents a coherent and systematic approach to the rational synthesis of glycoconjugates. By this strategy, the number of synthesis steps can be minimized and the desired glycoconjugates can be obtained in high yield. The general concept is depicted in Scheme I.

Biochemical and medical research on the function of glycolipids and glycoproteins depends to a great extent on the availability of synthetic glycoconjugates both with the sugar portion intact and in the form of analogues that emulate the natural compounds. For example, synthetic glycolipids are useful for the coating of cells and surfaces

† Symbicom AB.

(1) Jansson, K.; Ahlfors, S.; Frejd, T.; Kihlberg, J.; Magnusson, G.; Dahmén, J.; Noori, G.; Stenvall, K. *J. Org. Chem* **1988**, *53*, 5629.

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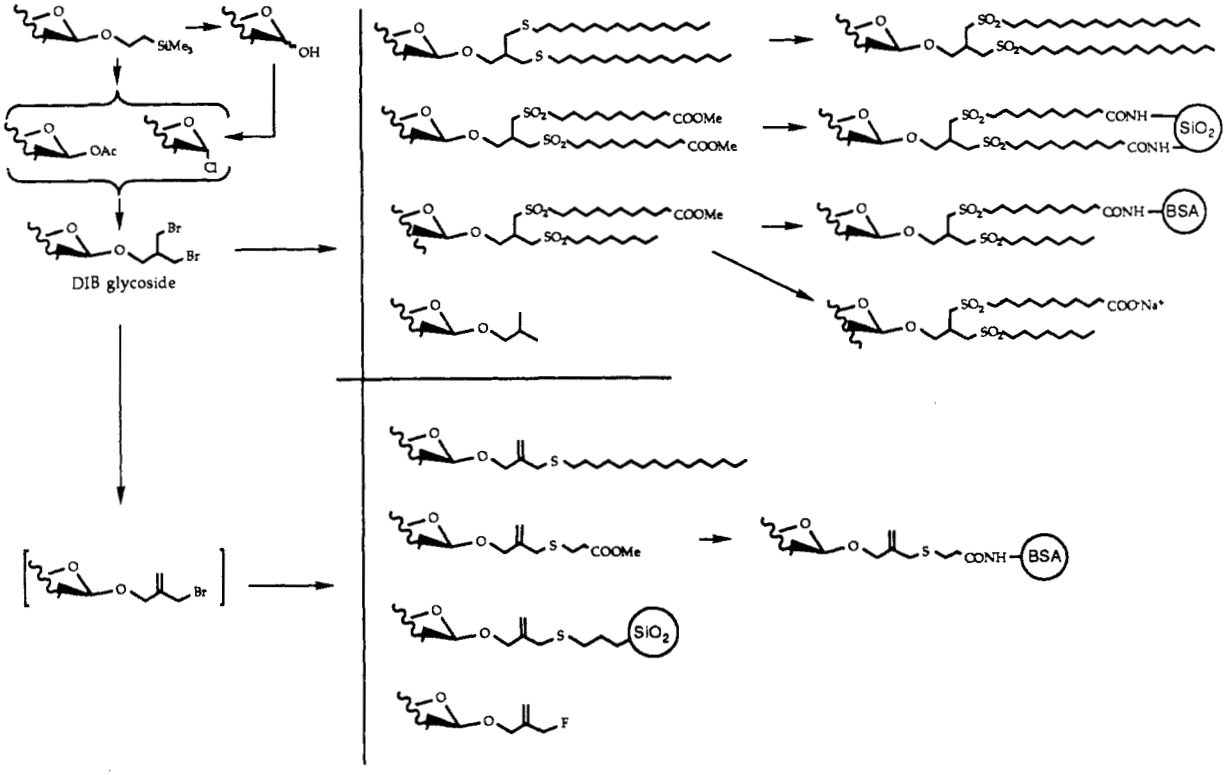
Scheme I



and for the formation of micelles and liposomes of value as antigens and for drug targeting; synthetic glycoproteins have been used extensively as antigens in the preparation of anti-carbohydrate antibodies; glycoparticles have been used in affinity purification of lectins and as active components of diagnostic kits; soluble glycosides have been used as inhibitors of carbohydrate–protein aggregation. It should be noted that many oligosaccharidic moieties are only present in glycolipids and not in glycoproteins and vice versa. Synthetic carbohydrate chemistry can provide "mismatched" conjugates, for example glycolipid-derived sugars in the form of glycoproteins for immunization purposes and glycoprotein-derived sugars in the form of glycolipids for coating experiments. Finally, synthetic glycoconjugates might be more stable toward enzymic breakdown than the natural counterparts, which could be of value in the development of carbohydrate-based drugs. It is for such reasons we have developed the general methods for rational glycoconjugate synthesis depicted in Scheme I.

The ideal anomeric blocking group should be stable toward all possible reaction conditions during the build up of oligosaccharides and then allow specific removal (→ hemiacetals) or transformation into anomerically activated sugars. 2-(Trimethylsilyl)ethyl (TMSET) glycosides fulfill most of these criteria. They were converted into hemiacetal sugars, 1-*O*-acyl sugars (with conservation of the anomeric configuration), and 1-chloro sugars.[1,2] Most of the investigated TMSET glycosides (mono- to tetrasaccharides) underwent these transformations in practically quantitative yields. An alternative to a removable anomeric blocking group is to use a prespacer aglycon all the way through the oligosaccharide synthesis and then transform it into the final spacer glycoside or neoglycolipid. We have reported the use of 2-bromoethyl[3,4] and DIB[5]

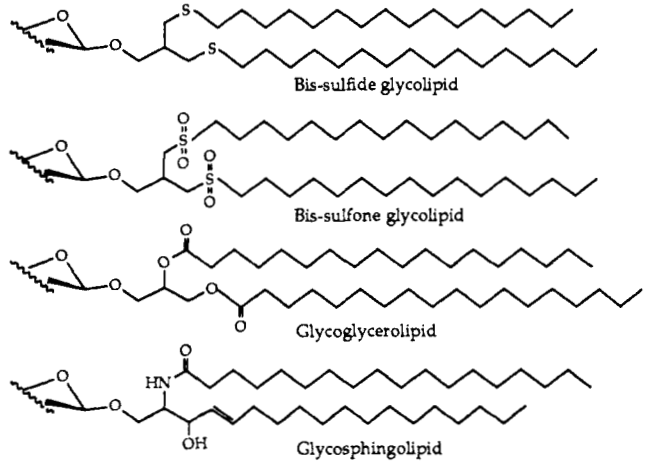


Figure 1.

glycosides for this type of approach, which is, however, somewhat limited due to the rather sensitive nature of the bromine-containing aglycons, especially under the strongly basic conditions used in for example O-benzylations.

The preparation and use of DIB glycosides in glycoconjugate synthesis is the main topic of this report; the general features are depicted in Scheme I. The DIB glycosides were originally conceived out of the need for synthetic glycolipids that mimic the natural ones. The aglycon should encompass a methylene group connecting the anomeric oxygen and the branch-point carbon, two hydrocarbon tails of variable length, and an intermediate region of high polarity. The structural similarities between

(2) (a) Jansson, K.; Magnusson, G. *Tetrahedron* **1990**, *46*, 59. (b) Jansson, K.; Noori, G.; Magnusson, G. *J. Org. Chem.* **1990**, *55*, 3181.

(3) Magnusson, G. In *Protein-Carbohydrate Interactions in Biological Systems*; Lark, D., Ed.; Academic Press: London, 1986; p 215.

(4) Dahmén, J.; Frejd, T.; Magnusson, G.; Noori, G.; Carlström, A.-S. *Carbohydr. Res.* **1984**, *129*, 63 and references cited therein.

(5) Ansari, A. A.; Frejd, T.; Magnusson, G. *Carbohydr. Res.* **1987**, *161*, 225.

Table I. Isolated Yields of Various Products Depicted in Chart I

DIB glycosides		bis-sulfide lipids		bis-sulfone lipids		allylic derivatives	
compd	%	compd	%	compd	%	compd	%
1[5]	54	2[5]	70	3	80	5	88
8[5]	60	6[5]	79	7	76	19	73
25	75	9[5]	88	10	69	20	76
30	48	26	81	28	80	21	79
35	35	31	97	33	97	23	74
37[5]	43	36	66	41	99	45	72
52	56	38[5]	51	43	92	46	78
58	75	39	63	55	86	47	82
64	71	53	93	61	91		
70	41	59	76	67	89		
76	90	65	87	73	83		
79	91	71	66				
82	45	77	70				
		80	52				
		83	61				

the natural and the synthetic glycolipids are shown in Figure 1. DIB glycosides are well suited as prespacer glycosides in that they are suitable starting materials for the synthesis of a wide array of glycoconjugates (Scheme I and Chart I).

We have recently found that DIB β-glycosides (and 2-bromoethyl β-glycosides[3,4]) are more stable than other alkyl β-glycosides toward Lewis acid catalyzed anomerization as exemplified with DIB and isobutyl β-glucopyranoside (Figure 2). The reason for this stability is as yet unknown. It should be noted that β-1-*O*-acetates (1,2-trans configuration) are more reactive than α-acetates and therefore more efficient glycosyl donors.[6] TMSET β-glycosides[1] provide β-1-*O*-acetates in high yield by treatment with BF_3Et_2O/Ac_2O. Since β-glycosides (1,2-trans configuration) are formed first when a participating protecting group is present in the 2-position, it is of value that no subsequent anomerization occurs. Thereby difficult separation of anomeric glycosides is avoided. All DIB glycosides of the present report (Chart I) were prepared by BF_3Et_2O-mediated glycosylation of 3-bromo-2-(bromomethyl)propanol (DIBOL)[5] using mono- to tetrasaccharide acetates as glycosyl donors. The reaction was especially rapid and high yielding with deoxy, deoxyalkyl, and 2-*N*-phthalimido[7] glycosyl donors as exemplified in the synthesis of compounds **25**, **58**, **76**, and **79** (Table I). The major byproduct in glycosylations of sugar acetates carrying a 2-OAc group, is the corresponding α/β-DIB glycoside with an unprotected 2-OH group. Transformation of these compounds into the fully acetylated derivatives may raise the yield of the desired DIB glycoside. A further advantage is that DIBOL is a nonchiral compound which means that diastereomers will not be obtained. DIBOL is a new compound and should find use as a general synthon both as such and in the form of protected derivatives.[5]

The DIB glycosides were transformed into a host of different glycoconjugates as shown in Scheme I and Chart I. Being primary alkyl bromides, DIB glycosides are well suited for nucleophilic substitution reactions, and treatment with alkyl thiols in *N,N*-dimethylformamide in the presence of cesium carbonate[8] gave the corresponding bis-sulfide lipids (B and C substituents in Chart I; Table I). The yields are normally high, and variations seem to depend on the workup conditions since different compounds are variously prone to formation of emulsions; care should be taken to break such emulsion before separation of phases during extraction and washing procedures.

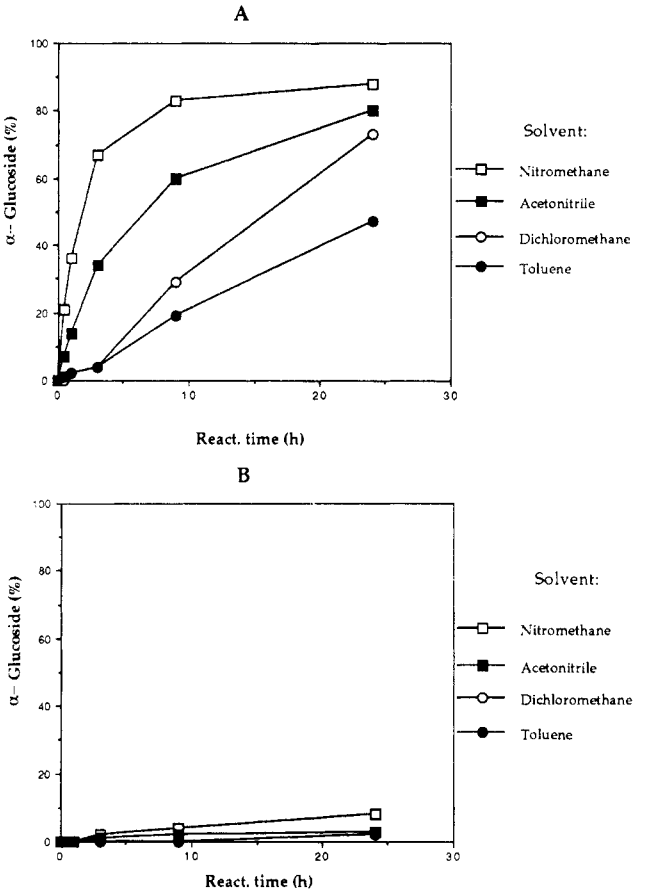
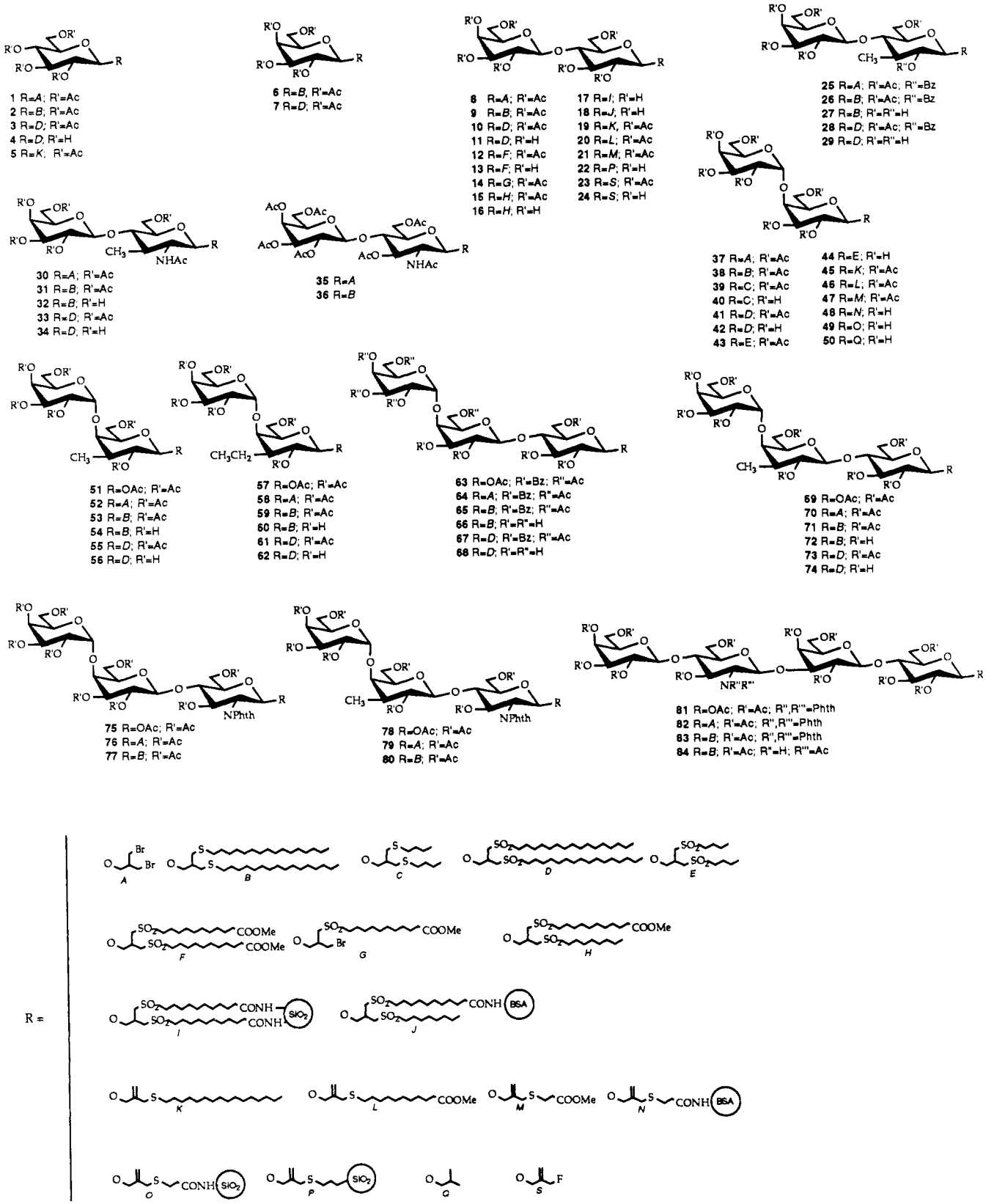


Figure 2. Amount of α-glucoside formed in BF_3Et_2O-mediated anomerization, in different solvents, of isobutyl (A) and DIB (B) 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (see the Experimental Section).

Oxidation of the bis-sulfides with 4 equiv of *m*-chloroperbenzoic acid gave the corresponding bis-sulfone lipids in high yield in a very clean reaction (D and E substituents in Chart I; Table I). The variation of the isolated yields can be attributed to the different ease with which the compounds form emulsions during workup, as discussed above for the bis-sulfide lipids. Alternatively, the reaction mixture can be purified by filtration through a short column of alumina in order to remove the *m*-chlorobenzoic acid formed as a byproduct. This procedure often gave a higher yield of the desired bis-sulfone glycolipid. When 2 equiv of *m*-chloroperbenzoic acid is used, bis-sulfoxide (diastereomeric) lipids were obtained in low yield together with various under- and over-oxidized products; here di-

(6) Paulsen, H.; Paal, M. *Carbohydr. Res.* **1984**, *135*, 53.
(7) Dahmén, J.; Frejd, T.; Magnusson, G.; Noori, G. *Carbohydr. Res.* **1983**, *114*, 328.
(8) Buter, J.; Kellogg, R. M. *J. Org. Chem.* **1981**, *46*, 4481.

Chart I



astereomers were probably formed.[9]

The bis-sulfone glycolipids are useful mimics of natural glycolipids since they both carry a polar portion in the aglycon close to the sugar residue (see Figure 1). The bis-sulfone aglycon is furthermore nonchiral, and, therefore, difficult separation of diastereomers is avoided. Variation of the hydrocarbon chain length permitted tuning of the solubility and other characteristics of the lipids. For example, the galabiose derivative **44** that carries two butyl chains was soluble in the aqueous buffer used in inhibition experiments[10] whereas the bis-hexadecyl lipid

(9) Jansson, K.; Magnusson, G., unpublished observation.

(10) Kihlberg, J.; Hultgren, S. J.; Normark, S.; Magnusson, G. *J. Am. Chem. Soc.* **1989**, *111*, 6364.

Table II. Amount of Sugar Bound in Various Glycosylated Silica Gels and Glycoproteins

glyco-conjugate	degree of binding	glyco-conjugate	degree of binding
17	0.13 mmol/g[a]	48	17.5 mol/mol[b]
18	21 mol/mol[b]	49	0.19 mmol/g[a]
22	0.23 mmol/g[a]		

[a] Millimole of sugar per gram of glycosylated silica gel. [b] Mole of sugar per mole of glycoprotein.

42 was practically insoluble. Sonication of the bis-hexadecyl lactose lipid **11** in the presence of lecithin in water gave a clear solution, probably by way of liposome formation.[11] We observed a drastic difference in receptor activity between the sulfide (deacetylated **9**[5]) and sulfone (**11**) lipids when these were coated on thin-layer plates. The latter bound radioactively labeled Sendai virus with the same affinity as the natural receptor lactosyl ceramide, whereas deacetylated **9** showed no receptor activity.[12] The reason may be that the receptor epitope includes the polar part of the aglycon or simply that lipids with such a polar part are more effectively exposed to the virus particles.

Alkyl thiols that carry ester groups gave compounds that are suitable for coupling to proteins and particles (see below). Treatment of the DIB lactoside **8** with 1 equiv of methyl 11-mercaptoundecanoate[13] followed by the somewhat shorter octyl thiol and deacetylation gave compound **16** which, after hydrolysis of the methyl ester, was soluble in water at pH >7. Such compounds are soluble mimics of glycolipids in that the shorter alkyl chain should stick to the carboxylic acid containing chain due to the hydrophobic effect. The complete aglycon might have a rodlike shape in the same way as the natural glycolipids.[14] Hydrolysis of the methyl esters of **13** provided the corresponding water-soluble diacid. This compound might not have the rodlike shape (at ionizing pH) but rather would the two anions repel each other and the hydrophobic interaction between the two alkyl chains should be interrupted at some point along the two chains.

Treatment of DIB glycosides with base gave strongly alkylating allylic bromide glycosides that were captured by addition of suitable thiols, thus forming allylic sulfides (Table I). With diazabicycloundecane (DBU) as base, the yield of allylic sulfide was consistently in the range 40–50%, whereas with tetrabutylammonium fluoride (F^- as base), the yields were in the range 70–80% and the reaction was rapid (ca. 5 min). Only the latter procedure is reported in the Experimental Section. A wide selection of allylic sulfides is thus available from DIB glycosides as exemplified by the single-chain lipids **5**, **19**, and **45**, the spacer arm glycosides **20**, **21**, **46**, and **47**, and the glycosylated silica gel **22** (Table II). It has been shown that single-chain lipids, for geometrical reasons,[15] give rise to micelles instead of liposomes on sonication in water.

Prolonged treatment of the DIB lactoside **8** with tetrabutylammonium fluoride caused substitution of the allylic bromine by fluorine, and the allylic fluoride **23** was obtained. Deacetylation gave the soluble allylic fluoride **24** of use in inhibition experiments. With positron-emitting $^{18}F^-$, radioactively labeled glycosides would be obtained. These are potentially useful for inter alia pharmacokinetic tracer experiments in humans since ^{18}F has a short half-life (112 min).

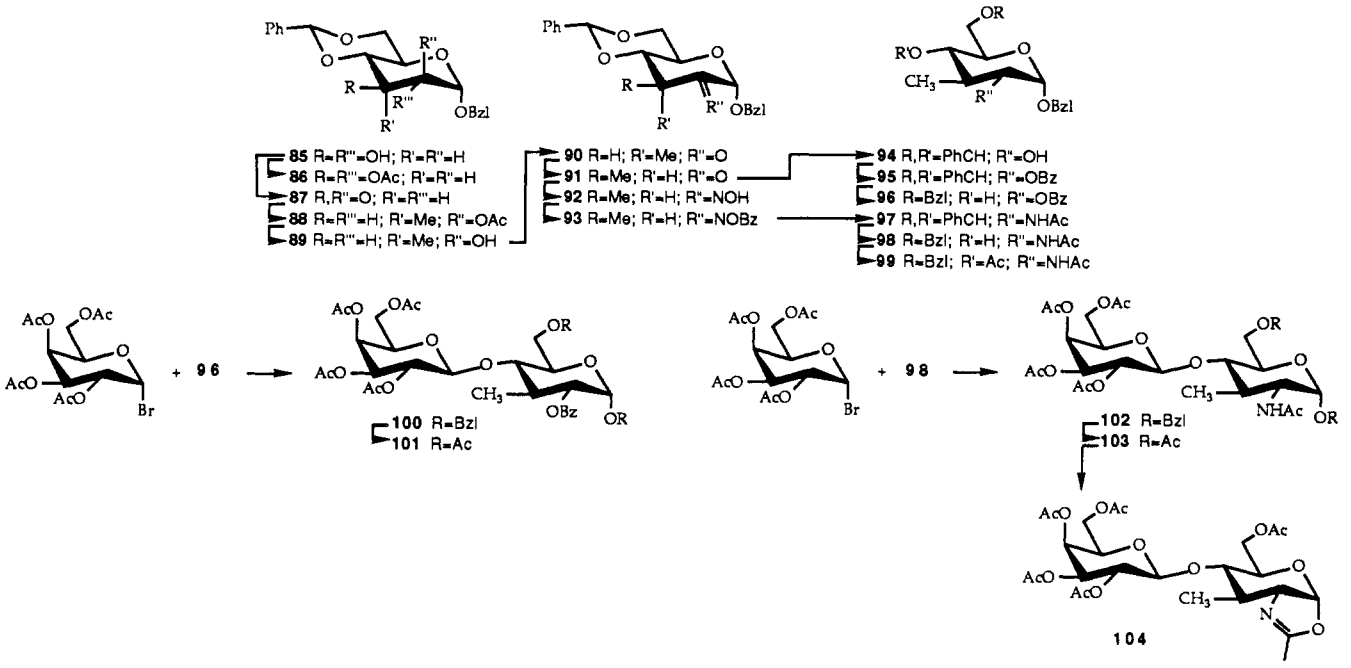
Hydrogenolysis of DIB glycosides under basic conditions leads to isobutyl glycosides, as exemplified by compound **50**. This compound was used as a soluble inhibitor in the mapping of the receptor site of the PapG adhesin of uropathogenic *Escherishia coli* bacteria.[10] It should be noted that under acidic conditions, benzylic protecting groups were removed by hydrogenolysis, leaving the DIB aglycon intact, which is similar to the debenzylation of 2-bromoethyl glycosides.[16]

Finally, the preparation of artificial glycoproteins and glycoparticles (Table II) was performed via the esters **13**, **16**, and **47** and the allylic bromide obtained by treatment of **8** with tetrabutylammonium fluoride or diazabicycloundecane. The latter reagent gave however lower yields (ca. 50%) of the allylic bromide. The esters were transformed into the corresponding, strongly acylating, acyl azides,[17-19] and bovine serum albumin (BSA) was added. Acylation presumably occurred on the primary amino groups of the lysine residues of the protein. Dialysis of the reaction mixture and freeze-drying of the residue gave the artificial glycoproteins **18** and **48** of use as antigens. With aminated silica gel instead of BSA, the carbohydrate-coated silica gels **17** and **49** were obtained. Treatment of alkylthiol-derivatized silica gel with the allylic bromide obtained from **8** by treatment with diazabicycloundecane gave the lactose-coated silica gel **22**. The degree of binding of sugar to the carrier was in the expected range and compared well with our earlier results with 2-bromoethyl glycoside derived spacer arm sugars.[3,13,19] The coupling of allylic bromide glycosides to silica gel carrying alkyl thiol spacers is a new rapid and efficient procedure. Finally, it should be emphasized that the use of sulfur-containing aglycons makes it possible to determine the amount of sugar bound to the carrier by simple sulfur combustion analysis.[19] In the case of thiolated silica (**22**), carbon analysis revealed the degree of binding.

The syntheses of most of the 1-*O*-acetyl saccharides and some DIB glycosides of Chart I have been reported in some of our previous papers (see the Experimental Section). The syntheses of the lactose and *N*-acetyllactosamine derivatives **101** and **104** were performed as shown in Scheme II. The monosaccharide starting materials **96** and **98** were prepared by opening of the epoxide ring of **87** with methylmagnesium chloride, followed by oxidation of HO-2 and epimerization of Me-3 to give the ketone **91**. This reaction sequence was used by Sinaÿ and co-workers for the preparation of methyl 4,6-*O*-benzylidene-3-deoxy-3-*C*-methyl-α-D-altropyranoside.[20] Reduction of the keto function of **91**, benzoylation of the hydroxyl group formed, and reductive opening[21] of the benzylidene ring of **95** gave the partially protected 3-deoxymethyl glucose derivative **96**. Treatment of **91** with hydroxylamine and benzoylation of the oxime gave **93**, which was reduced by diborane,[22] and the amine formed was acetylated to give **97**. Reductive opening of the benzylidene ring then gave the partially protected 3-deoxymethyl-*N*-acetylglucosamine derivative

(11) Magnusson, G., unpublished results.
(12) Karlsson, K.-A.; Magnusson, G.; Norrby, E.; Wadell, G., unpublished results.
(13) Dahmén, J.; Frejd, T.; Magnusson, G.; Noori, G.; Carlström, A.-S. *Carbohydr. Res.* **1984**, *127*, 27.
(14) Pasher, I.; Sundell, S. *Chem. Phys. Lipids* **1977**, *20*, 175.
(15) Israelachvili, I. N.; Marcelja, S.; Horn, R. G. *Q. Rev. Biophys.* **1980**, *13*, 121.
(16) Dahmén, J.; Frejd, T.; Grönberg, G.; Lave, T.; Magnusson, G.; Noori, G. *Carbohydr. Res.* **1983**, *118*, 292.
(17) Inman, J. K.; Merchant, B.; Claflin, L.; Tacey, S. E. *Immunochemistry* **1973**, *10*, 165.
(18) Lemieux, R. U.; Bundle, D. R.; Baker, D. A. *J. Am. Chem. Soc.* **1975**, *97*, 4076.
(19) Dahmén, J.; Frejd, T.; Magnusson, G.; Noori, G.; Carlström, A.-S. *Carbohydr. Res.* **1984**, *127*, 15.
(20) Pougny, J.-R.; Sinaÿ, P. *J. Chem. Res. (M)* **1982**, 0186–0196.
(21) Garegg, P. J.; Hultberg, H. *Carbohydr. Res.* **1981**, *93*, c10.
(22) Lemieux, R. U.; James, K.; Nagabuhshan, T. L.; Ito, Y. *Can. J. Chem.* **1973**, *51*, 33.

Scheme II



98. Glycosylation of **96** and **98** with acetobromogalactose, hydrogenolytic cleavage of the benzyl aglycon, and acetylation gave the disaccharides **101** and **103**. Compound **103** was transformed into the oxazoline derivative **104**. Compounds **101** and **104** were then used for synthesis of the DIB glycosides **25** and **30**. The *N*-acetyllactosamine-derived oxazolin[23] was transformed into the DIB glycoside **35**.

Experimental Section

NMR spectra were recorded in $CDCl_3$, CMD ($CDCl_3$/CD_3OD/D_2O), or Me_2SO-d_6 at 300 MHz. Chemical shifts and coupling constants were obtained from a first-order analysis of the spectra. Melting points are uncorrected. Concentrations were made using rotary evaporation with bath temperature at or below 40 °C. Anhydrous Na_2SO_4 was used as drying agent for the organic extracts in the workup procedures. TLC was performed on Kiselgel 60 F_{254} plates (Merck). Column chromatography was performed in the gravity mode using SiO_2 (Matrex LC-Gel; 60 A, 35-70 MY, Grace). Gas chromatography was performed on a semipolar DB-17+ capillary column (J&W Scientific). The following abbreviations were used: *m*-chloroperbenzoic acid, MCPBA; tetrabutylammonium fluoride trihydrate, TBAF; boron trifluoride etherate, BF_3·Et_2O.

Anomerization Reactions (cf. Figure 2). Isobutyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside and the DIB glucoside **1** (0.1 mmol) were added to separate cylindrical reaction flasks containing a magnetic stirring bar, and the flasks were dried at room temperature under vacuum (oil pump). The solvent (0.7 mL) and BF_3·Et_2O (39 μL, 0.3 mmol) was added with a syringe. The mixture was stirred at room temperature, and samples (50 μL) were collected after 0.5, 1, 3, 9, and 24 h. The sample was partitioned between saturated aqueous sodium hydrogencarbonate (0.5 mL) and diethyl ether (200 μL). TLC analysis showed that only the α- and β-glycosides were present. Samples were taken from the organic phase and submitted to quantitative GC analysis. The relative amount of α-glycosides are shown in Figure 2.

Starting materials:[1,5] **1**, **2**, **6**, **8**, **9**, and **37** (ref 5); **51**, **57**, **63**, **69**, **75**, **78**, and **81** (ref 1).

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]propyl 2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranoside (3). The bis-sulfide glycolipid **2**[5] (1.6 g, 1.74 mmol) was dissolved in ethyl acetate (60 mL) by heating to ca. 40 °C, and MCPBA (1.35 g, 7.83 mmol) was added. The mixture was stirred for 3 h, dichloromethane was added in order to dissolve the precipitated MCPBA, and the solution was filtered through a column (i.d. 40 mm) of alumina (30 g) to remove acids. The column was eluted with dichloromethane (the eluate was checked for aromatic compounds by spotting on TLC plates and UV visualization). Removal of solvent from the combined eluates gave crude **3** (1.5 g), which was chromatographed (SiO_2, EtOAc/heptane, 1:2 → EtOAc → MeOH) to give **3** (1.37 g, 80%): $[\alpha]^{23}_D$ −6° (*c* 0.7, $CDCl_3$); ^{1}H NMR ($CDCl_3$) δ 5.21 (t, 1 H, *J* = 9.5 Hz, H-3), 5.05 (t, 1 H, *J* = 10.0 Hz, H-4), 4.97 (dd, 1 H, H-2), 4.54 (d, 1 H, *J* = 8.1 Hz, H-1), 4.27, 4.13 (dAB q, *J* = 12.5, 4.9, 2.4 Hz, H-6), 4.01, 3.99 (AB q, 1 H each, *J* = 12 Hz, $OCHOCH_2$), 3.70 (m, 1 H, H-5).

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]propyl β-D-Glucopyranoside (4). The bis-sulfone glycolipid **3** (900 mg, 0.92 mmol) was dissolved in dichloromethane (70 mL), and methanolic sodium methoxide (50 mL, ca. 1 mg of Na) was added. The reaction was monitored by TLC (SiO_2, $CHCl_3$/MeOH/H_2O, 65:35:10). After 24 h, **3** was consumed and a single new compound was detected. The reaction mixture was neutralized by Duolite (H^+) resin, and the solvent was removed to give a quantitative yield of **4**: $[\alpha]^{23}_D$ −3.9° (*c* 0.9, CMD, 65:35:10). ^{1}H NMR (CMD, 65:35:10) δ 4.34 (d, 1 H, *J* = 7.3 Hz, H-1), 0.89 (t, 6 H, *J* = 6.8 Hz, CH_3).

2-[(Hexadecylthio)methyl]-2-propenyl 2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranoside (5). A solution of TBAF in acetonitrile (0.4 M, 2 mL, 0.8 mmol of Bu_4NF) was added to the DIB glucoside **1**[5] (112 mg, 0.20 mmol), and the mixture was stirred for 7 min (TLC showed that **1** had been consumed). Hexadecylmercaptan (82 μL, 0.26 mmol) was added, and the mixture was stirred for 45 min and then filtered through a column of silica gel (35 × 25 mm, 40–63 μm, EtOAc as eluent) to remove tetrabutylammonium salts. The eluate was concentrated, and the residue was chromatographed (SiO_2, EtOAc/heptane, 1:2) to give **5** (115 mg, 88%). Crystallization from methanol gave pure **5** (109 mg, 83%): mp 92–93 °C (MeOH); $[\alpha]_D$ −15° (*c* 1.4, $CDCl_3$); ^{1}H NMR ($CDCl_3$) δ 5.21 (t, 1 H, *J* = 9.4 Hz, H-3), 5.10 (t, 1 H, *J* = 9.8 Hz, H-4), 5.097, 5.03 (s, 1 H each, $=CH_2$), 5.04 (dd, 1 H, *J* = 9.5, 8.1 Hz, H-2), 4.54 (d, 1 H, *J* = 8.1 Hz, H-1), 4.41, 4.20 (AB q, 1 H each, *J* = 15.0 Hz, $OCH_2C=$), 4.27, 4.15 (dAB q, 1 H each, *J* = 12.0, 4.6, 2.4 Hz, H-6), 3.69 (octet, 1 H, *J* = 9.8, 4.6, 2.2 Hz, H-5), 3.15, 3.11 (AB q, 1 H each, *J* = 13.9 Hz, $=CCH_2S$), 2.36 (t, 2 H, *J* = 7 Hz, SCH_2CH_2). Anal. Calcd for $C_{34}H_{58}O_{10}S$: C, 62.0; H, 8.9. Found: C, 62.2; H, 8.9.

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]-

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propyl 2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranoside (7). The bis-sulfide glycolipid **6**[5] (85 mg, 0.09 mmol) was treated as in the preparation of **3** to give **7** (69 mg, 76%): $[\alpha]^{23}_D$ −2.3° (*c* 1, $CDCl_3$); ^1H NMR ($CDCl_3$) δ 5.39 (dd, 1 H, *J* = 1.0 Hz, H-4), 5.15 (dd, 1 H, *J* = 10.5 Hz, H-2), 5.01 (dd, 1 H, *J* = 3.4 Hz, H-3), 4.50 (d, 1 H, *J* = 7.7 Hz, H-1).

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]propyl 2,3,6-Tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-glucopyranoside (10). The bis-sulfide glycolipid **9**[5] (431 mg, 0.36 mmol) was treated as in the preparation of **3** to give **10** (311 mg, 69%): $[\alpha]^{23}_D$ −7° (*c* 0.8, $CDCl_3$); ^1H NMR ($CDCl_3$) δ 5.35 (dd, 1 H, *J* = 1 Hz, H-4′), 5.19 (t, 1 H, *J* = 9.4 Hz, H-2), 5.11 (dd, 1 H, *J* = 10.1 Hz, H-2′), 4.96 (dd, 1 H, *J* = 3.2 Hz, H-3′), 4.88 (dd, 1 H, *J* = 7.9 Hz, H-3), 4.50, 4.48 (d, 1 H each, *J* = 7.6 Hz, H-1, 1′), 3.97, 3.96 (AB q, 1 H each, *J* = 12 Hz, $OCHOCH_2$). Anal. Calcd for $C_{62}H_{108}O_{22}S_2$: C, 58.6; H, 8.6. Found: C, 58.0; H, 8.4.

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]propyl 4-*O*-β-D-Galactopyranosyl-β-D-glucopyranoside (11). The bis-sulfone glycolipid **10** (900 mg, 0.71 mmol) was deacetylated, as described in the preparation of **4** to give a quantitative yield of **11**: $[\alpha]^{23}_D$ −1° (*c* 0.5, CMD, 65:35:10); ^1H NMR (CMD, 65:35:10) δ 4.39, 4.41 (d, 1 H each, *J* = 7.6, 7.8 Hz, H-1,1′), 2.71 (d, 4 H, *J* = 6.6 Hz, $CHCH_2SO_2$), 2.53 (t, 4 H, *J* = 7.3 Hz, $SO_2CH_2CH_2$).

3-[[10-(Methoxycarbonyl)decyl]sulfonyl]-2-[[[10-(methoxycarbonyl)decyl]sulfonyl]methyl]propyl 2,3,6-Tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-glucopyranoside (12). The DIB lactoside **8**[5] (2.6 g, 3 mmol) was dissolved in dry *N*,*N*-dimethylformamide (29 mL), and methyl 11-mercaptoundecanoate[13] (2 mL) was added, followed by cesium carbonate (1.5 g). The reaction was monitored by TLC (SiO_2, EtOAc/heptane, 1:1). After 40 h at 20 °C, water was added, and the mixture was extracted with dichloromethane. The extract was dried and the solvent was removed. The residue was dissolved in ethyl acetate (80 mL), and *m*-chloroperbenzoic acid (2.7 g, 12.2 mmol) was added. After 18 h, the mixture was filtered through a column of aluminum oxide (70 g, activity grade II–III), and the column was eluted with dichloromethane (300 mL). The solvent was removed, and the residue was chromatographed (SiO_2, EtOAc/heptane 3:2) to give 2-(bromomethyl)-3-[[10-(methoxycarbonyl)decyl]sulfonyl]propyl 2,3,6-tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-glucopyranoside (**14**, 1.10 g, 36%; $[\alpha]_D$ −6° (*c* 0.7, $CHCl_3$)) followed by **12** (1.12 g, 31%): $[\alpha]_D$ −7° (*c* 1.1, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.35 (dd, 1 H, *J* = 3.4, 1.0 Hz, H-4′), 5.19 (t, 1 H, *J* = 9.0 Hz, H-3), 5.11 (dd, 1 H, *J* = 10.3, 7.8 Hz, H-2′), 4.95 (dd, 1 H, *J* = 9.0, 3.4 Hz, H-3′), 4.88 (dd, 1 H, *J* = 9.8, 7.8 Hz, H-2), 4.50, 4.48 (d, 1 H each, *J* = 7.8 and 7.6 Hz, H-1,1′), 3.66 (s, 6 H, OMe), 2.30 (t, 4 H, *J* = 7.6 Hz, CH_2COO).

3-[[10-(Methoxycarbonyl)decyl]sulfonyl]-2-[[[10-(methoxycarbonyl)decyl]sulfonyl]methyl]propyl 4-*O*-β-D-Galactopyranosyl-β-D-glucopyranoside (13). The bis-sulfone diester **12** (900 mg, 0.74 mmol) was deacetylated, as described in the preparation of **4**, to give a quantitative yield of **13**: $[\alpha]^{23}_D$ −3° (*c* 0.5, $CHCl_3/CH_3OH/H_2O$, 65:35:10).

3-[[10-(Methoxycarbonyl)decyl]sulfonyl]-2-[(octylsulfonyl)methyl]propyl 2,3,6-Tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-glucopyranoside (15). Compound **14** (820 mg, 0.79 mmol; from the preparation of **12**) was dissolved in dry *N*,*N*-dimethylformamide (20 mL), and octanethiol (174 mg, 1.2 mmol) was added, followed by cesium carbonate (240 mg, 0.74 mmol). The reaction was monitored by TLC (SiO_2, EtOAc/heptane, 1:1). After 20 h at 20 °C, water was added and the mixture was extracted with dichloromethane. The extract was dried, the solvent was removed, and the residue was chromatographed (SiO_2, EtOAc/heptane, 1:1) to give 3-[[10-(methoxycarbonyl)decyl]sulfonyl]-2-[(octylthio)methyl]propyl 2,3,6-tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-glucopyranoside [830 mg, 96%; $[\alpha]_D$ −5° (*c* 0.9, $CHCl_3$)], 800 mg (0.74 mmol) of which was dissolved in ethyl acetate (25 mL). MCPBA (320 mg, 1.85 mmol) was added, and the mixture was stirred for 18 h, concentrated, dissolved in dichloromethane, and then filtered through aluminum oxide (15 g) using dichloromethane (75 mL) as eluent. Removal of the solvent gave **15** (667 mg, 80%): $[\alpha]_D$ −14° (*c* 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.34 (dd, 1 H, *J* = 3.4, 1.0 Hz, H-4′), 5.19 (t, 1 H, *J* = 9.5 Hz, H-3), 5.10 (dd, 1 H, *J* = 10.3, 7.8 Hz, H-2′), 4.95 (dd, 1 H, *J* = 10.3, 3.4 Hz, H-3′), 4.87 (dd, 1 H, *J* = 9.5, 7.8 Hz, H-2), 4.49, 4.47 (d, 1 H each, *J* = 7.8 Hz, H-1,1′), 3.66 (s, 3 H, OMe), 2.30 (t, 2 H, *J* = 7.6 Hz, CH_2COO), 0.87 (t, 3 H, *J* = 6.4 Hz, CH_2CH_3).

3-[[10-(Methoxycarbonyl)decyl]sulfonyl]-2-[(octylsulfonyl)methyl]propyl 4-*O*-β-D-Galactopyranosyl-β-D-glucopyranoside (16). The bis-sulfone monoester **15** (600 mg, 0.53 mmol) was deacetylated, as described in the preparation of **4**, to give a quantitative yield of **16**: $[\alpha]^{23}_D$ −1° (*c* 0.9, $CHCl_3/CH_3OH/H_2O$, 65:35:10).

Silica Gel–Lactoside Conjugate 17. The diester **13** (50 mg, 0.054 mmol) was dissolved in ethanol (4 mL). Hydrazine hydrate (99.5%, 0.5 mL) was added, the mixture was left overnight, and the volatile material was thoroughly removed by repeated additions and evaporations of dichloromethane. The resulting dihydrazide was dissolved in dry methyl sulfoxide (1 mL), and hydrogen chloride in 1,4-dioxane (130 μL, 4.5 M) was added followed by a solution of *tert*-butyl nitrite (26 μL) in dry methyl sulfoxide (100 μL). The mixture was stirred at room temperature for 30 min, and a solution of sulfamic acid (15 mg) in methyl sulfoxide (150 μL) was added. After 15 min, the crude azide was added dropwise, with stirring, to a suspension of aminated silica gel (166 mg, Spherisorb 5 μm, 0.6 mmol amino groups/g; Phase Sep, Deeside Ind. Est., Queensferry, Clwyd, UK) in sodium tetraborate–potassium hydrogen carbonate buffer (3 mL, 0.08 M $Na_2B_4O_7$ and 0.35 M $KHCO_3$). The pH was maintained at 9.0–9.3 by additions of sodium hydroxide (1 M). The mixture was stirred at room temperature overnight, washed (centrifugation) with two portions of water, methanol, and dichloromethane, and dried to give the conjugate **17**. Combustion analysis of **17** showed the sulfur content to be 0.82%, which corresponds to a degree of binding of 0.13 mmol of sugar per gram of silica gel conjugate.

BSA–Lactoside Conjugate 18. The methyl ester **16** (50 mg, 0.07 mmol) was dissolved in ethanol (2 mL) by heating to 50 °C. Hydrazine hydrate (99.5%, 0.25 mL) was added, the mixture was left overnight, and the volatile material was thoroughly removed by repeated additions and evaporations of toluene. The resulting hydrazide was dissolved in dry methyl sulfoxide (1 mL), and hydrogen chloride in 1,4-dioxane (100 μL, 4.5 M) was added followed by a solution of *tert*-butyl nitrite (18 μL) in dry methyl sulfoxide (100 μL). The mixture was stirred at room temperature for 30 min, and a solution of sulfamic acid (10 mg) in methyl sulfoxide (200 μL) was added. After 25 min, the mixture was added dropwise, with stirring, to a solution of bovine serum albumin (BSA; 65 mg, 1 μmol) in sodium tetraborate–potassium hydrogen carbonate buffer (2.5 mL, 0.08 M $Na_2B_4O_7$ and 0.35 M $KHCO_3$). The pH was maintained at 9.0–9.3 by additions of sodium hydroxide (1 M). The mixture was stirred at room temperature overnight and then dialyzed for 48 h against distilled water (4 × 5 L). Freeze-drying of the dialyzed material gave the conjugate **18**. Combustion analysis of BSA and **18** showed the sulfur content to be 1.71% and 3.08%, respectively. The difference (1.37%) corresponds to a degree of binding (number of sugar molecules per molecule of protein) of 21.

2-[(Hexadecylthio)methyl]-2-propenyl 2,3,6-Tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-glucopyranoside (19). The DIB lactoside **8**[5] (170 mg, 0.20 mmol), TBAF in acetonitrile (0.4 M, 2 mL), and hexadecanethiol (82 μL, 0.26 mmol) were treated, essentially as described in the preparation of **5**, to give **19** (138 mg, 73%): $[\alpha]_D$ −11° (*c* 1.4, $CDCl_3$); ^1H NMR ($CDCl_3$) δ 5.34 (dd, 1 H, *J* = 2.7, 1.0 Hz, H-4′), 5.20 (t, 1 H, *J* = 9.0 Hz, H-2), 5.08, 5.02 (bs, 1 H each, $=CH_2$), 5.11 (dd, 1 H, *J* =10.1, 7.9 Hz, H-2′), 4.95 (dd, 1 H, *J* = 9.8, 3.7 Hz, H-3′), 4.93 (t, 1 H, *J* = 8.1 Hz, H-3), 4.51, 4.48 (d, 1 H each, *J* = 7.8 Hz, H-1,1′), 4.38, 4.16 (AB q, 1 H each, *J* = 12.0 Hz, $OCH_2C=$), 3.14, 3.10 (AB q, 1 H each, *J* = 4.3 Hz, $=CCH_2S$), 2.37 (t, 2 H, *J* = 7.4 Hz, SCH_2CH_2).

2-[[[10-(Methoxycarbonyl)decyl]thio]methyl]-2-propenyl 2,3,6-Tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-glucopyranoside (20). The DIB lactoside **8**[5] (170 mg, 0.20 mmol), TBAF in acetonitrile (0.4 M, 2 mL), and methyl 11-mercaptoundecanoate[13] (63 mg, 0.26 mmol) were treated, essentially as described in the preparation of **5**, to give **20** (140 mg, 76%): $[\alpha]_D$ −9° (*c* 0.4, $CDCl_3$); ^1H NMR ($CDCl_3$) δ 5.35 (dd, 1 H, *J* = 3.4, 0.7 Hz, H-4′), 5.20 (t, 1 H, *J* = 9.0 Hz, H-2),

5.11 (dd, 1 H, J = 10.3, 7.6 Hz, H-2'), 5.08, 5.02 (bs, 1 H, each, $=CH_2$), 4.95 (dd, 1 H, J = 10.5, 3.7 Hz, H-3'), 4.94 (t, 1 H, J = 8.5 Hz, H-3), 4.50, 4.48 (d, 1 H, each, J = 7.8 Hz, H-1,1'), 4.38, 4.16 (AB q, 1 H each, J = 12.0 Hz, $OCH_2C=$), 3.67 (s, 3 H, OMe), 3.14, 3.10 (AB q, 1 H each, J = 14.5 Hz, $=CCH_2S$), 2.37 (t, 2 H, J = 7.5 Hz, SCH_2CH_2), 2.30 (t, 2 H, J = 7.5 Hz, CH_2COO). Anal. Calcd for $C_{42}H_{64}O_2S$: C, 54.8; H, 7.0. Found: C, 54.7; H, 7.1.

2-[[[2-(Methoxycarbonyl)ethyl]thio]methyl]-2-propenyl 2,3,6-Tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-glucopyranoside (21). The DIB lactoside 8[5] (170 mg, 0.20 mmol), TBAF in acetonitrile (0.4 M, 2 mL), and methyl 3-mercaptopropionate (30 μL, 0.26 mmol) were treated, essentially as described in the preparation of **5**, to give **21** (128 mg, 79%): $[\alpha]_D$ −12° (c 0.8, $CDCl_3$); ^1H NMR ($CDCl_3$, Me_4Si) δ 5.35 (dd, 1 H, J = 3.4, 0.7 Hz, H-4'), 5.20 (t, 1 H, J = 9.3 Hz, H-2), 5.12, 5.07 (bs, 1 H each, $=CH_2$), 5.11 (dd, 1 H, J = 10.3, 7.8 Hz, H-2'), 4.95 (dd, 1 H, J = 9.8, 3.4 Hz, H-3'), 4.93 (t, 1 H, J = 8.1 Hz, H-3), 4.51, 4.48 (d, 1 H each, J = 7.8 Hz, H-1,1'), 4.37, 4.17 (AB q, 1 H each, J = 12.0 Hz, $OCH_2C=$), 3.70 (s, 3 H, OMe), 3.17, 3.14 (AB q, 1 H each, J = 14.2 Hz, $=CCH_2S$).

Silica Gel–Lactoside Conjugate 22. The DIB lactoside 8[5] (85 mg, 0.1 mmol) was dissolved in dry ethyl acetate (1.5 mL), and diazabicycloundecane (46 mg, 45 μL, 0.3 mmol) was added. The mixture was stirred for 3 h, and alkylthiol-derivatized silica gel (114 mg, prepared by treating Lichrosorb, Merck, 10 μm, ca 300 m^2/g, with 3-(trimethoxysilyl)propane-1-thiol which gave a material carrying ca. 0.9 mmol of thiol/g) was added. After 2 h, the allyl bromide glycoside was consumed according to TLC analysis. The solid material was washed with dichloromethane, water, and methanol on a glass filter, deacetylated with methanolic sodium methoxide (1 mL, 0.02 M) overnight, washed with water, methanol, dichloromethane, and ether, and dried in vacuo to give the conjugate **22**. The degree of binding was 0.23 mmol of sugar per gram of silica gel conjugate as determined by carbon combustion analysis.

2-(Fluoromethyl)-2-propenyl 2,3,6-Tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-glucopyranoside (23). The DIB lactoside 8[5] (3.57 g, 4.2 mmol) and TBAF (5.2 g, 16.5 mmol) were dissolved in acetonitrile (20 mL). The mixture was stirred at room temperature for 20 min, refluxed for 50 min, cooled, and partitioned between ethyl acetate and saturated aqueous sodium hydrogen carbonate. The organic phase was washed with water and saturated aqueous sodium chloride and then concentrated. The residue was chromatographed (SiO_2, EtOAc/heptane 2:3) to give **23** (2.21 g, 74%): $[\alpha]^{23}_D$ −17° (c 1.3, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.35 (dd, 1 H, J = 3.5, 1 Hz, H-4'), 5.28 (m, 1 H, J = 1 Hz, =CH), 5.24 (bs, 1 H, =CH), 5.20 (t, 1 H, J = 9.5 Hz, H-3), 5.11 (dd, 1 H, J = 10.5, 8 Hz, H-2'), 4.95 (dd, 1 H, J = 10.5, 3.5 Hz, H-3'), 4.93 (dd, 1 H, J = 9.5, 8 Hz, H-2), 4.83 (bd, 2 H, J = 47.2 Hz, CH_2F), 4.45–4.53 (3 H, inter alia H-1, 1'), 4.35, 4.15 (AB q, 2 H, J = 13 Hz, $OCH_2C=$), 4.03–4.18 (m, 4 H), 3.87 (td, 1 H, J = 7.5, 1 Hz, H-5'), 3.80 (t, 1 H, J = 10 Hz, H-6), 3.60 (ddd, 1 H, J = 10, 5, 2 Hz, H-5); ^{13}C NMR ($CDCl_3$) δ 170.7 (2 C), 170.5, 170.4, 170.1, 169.9, 169.4, 140.4 (d, J = 14.9 Hz, CCH_2F), 116.5 (d, J = 9.7 Hz, $C=CH_2$), 101.2, 99.6, 83.0 (d, J = 167.1 Hz, CH_2F), 76.2, 72.7 (2 C), 71.6, 70.9, 70.7, 69.13 (d, J = 2.5 Hz, $OCH_2C=$), 69.07, 66.6, 61.8, 60.7, 20.6, 20.4 (4 C), 20.3.

2-(Fluoromethyl)-2-propenyl 4-*O*-β-D-galactopyranosyl-β-D-glucopyranoside (24). Compound **23** (2.1 g, 2.96 mmol) was deacetylated in methanolic sodium methoxide (3.9 mM, 102 mL) for 64 h. The mixture was neutralized with Duolite C-26 (H^+) resin, filtered, and concentrated. The residue was chromatographed ($CHCl_3$/MeOH/H_2O, 65:35:10, lower phase) to give **24** (1.64 g, 95%): $[\alpha]^{23}_D$ −9° (c 1.5, $CHCl_3$); ^1H NMR [D_2O, $Me_3Si(CD_2)_2COONa$] δ 5.44 (bs, 2 H, $=CH_2$), 5.01 (d, 2 H, J = 46.8 Hz, CH_2F), 4.82 (HDO), 4.53 (d, 1 H, J = 8 Hz, H-1 or -1'), 4.47, 4.33 (AB q, 1 H each, J = 13 Hz, $OCH_2C=$), 4.46 (d, 1 H, J = 7.5 Hz, H-1' or -1), 3.30–4.01 (12 H); ^{13}C NMR δ 143.3 (d, J = 14.5 Hz, CCH_2F), 121.5 (d, J = 10.2 Hz, $C=CH_2$), 106.2, 104.3, 87.1 (d, J = 160.7 Hz, CH_2F), 81.5, 78.5, 77.9, 77.5, 75.9, 75.7, 74.1, 72.4 (d, J = 2.2 Hz, $OCH_2C=$), 71.7, 64.1, 63.2.

3-Bromo-2-(bromomethyl)propyl 6-*O*-Acetyl-2-*O*-benzoyl-3-deoxy-3-*C*-methyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-glucopyranoside (25). The epimeric mixture **101** (1.26 g, 1.8 mmol) and 3-bromo-2-(bromomethyl)-propanol[5] (1.05 g, 4.5 mmol) were dissolved in dry dichloromethane (45 mL), and BF_3·Et_2O (1.55 mL, 12.6 mmol) was added at 0 °C. The mixture was stirred at room temperature for 12 h and was then diluted with dichloromethane and poured into saturated cold aqueous sodium hydrogen carbonate. The aqueous phase was extracted with dichloromethane, and the combined organic extract was washed with saturated aqueous sodium hydrogen carbonate and saturated aqueous sodium chloride, dried, filtered, and concentrated. The residue was chromatographed (SiO_2, EtOAc/heptane, 2:1) to give amorphous **25** (1.17 g, 75%): $[\alpha]^{22}_D$ −1° (c 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.38 (dd, 1 H, J = 3.5, 1 Hz, H-4'), 5.19 (dd, 1 H, J = 10.5, 8.0 Hz, H-2'), 4.98 (dd, 1 H, J = 10.5, 3.5 Hz, H-3'), 4.88 (dd, 1 H, J = 11.0, 8.0 Hz, H-2), 4.52, 4.47 (d, 1 H each, J = 8.0 Hz, H-1,1'), 1.11 (d, 3 H, J = 6.5 Hz, CH_3CH). Anal. Calcd for $C_{34}H_{44}Br_2O_{16}$: C, 47.0; H, 5.1. Found: C, 46.3; H, 5.0.

3-(Hexadecylthio)-2-[(hexadecylthio)methyl]propyl 6-*O*-Acetyl-2-*O*-benzoyl-3-deoxy-3-*C*-methyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-glucopyranoside (26). Compound **25** (100 mg, 0.12 mmol), hexadecanethiol (177 μL, 0.58 mmol), and cesium carbonate (94 mg, 0.29 mmol) were suspended in dry N,N-dimethylformamide (3 mL) and stirred at room temperature for 3.5 h. The mixture was then diluted with ethyl acetate, washed with water and saturated aqueous sodium chloride, dried, filtered, and concentrated. The residue was chromatographed (ethyl acetate/heptane, 1:3) to give amorphous **26** (114 mg, 81%): $[\alpha]^{22}_D$ −1.2° (c 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.37 (dd, 1 H, J = 3.5, 1 Hz, H-4'), 5.19 (dd, 1 H, J = 10.5, 8.0 Hz, H-2'), 4.98 (dd, 1 H, J = 10.5, 3.5 Hz, H-3'), 4.89 (dd, 1 H, J = 11.0, 8.0 Hz, H-2), 4.50, 4.46 (d, 1 H each, J = 8.0 Hz, H-1,1') 1.11 (d, 3 H, J = 6.5 Hz, CH_3CH).

3-(Hexadecylthio)-2-[(hexadecylthio)methyl]propyl 3-Deoxy-3-*C*-methyl-4-*O*-β-D-galactopyranosyl-β-D-glucopyranoside (27). Methanolic sodium methoxide (0.2 M, 4 mL) was added to a solution of **26** (81 mg, 0.07 mmol) in a mixture of dry methanol (4 mL) and dry dichloromethane (8 mL). The mixture was stirred at reflux temperature for 11 h and then neutralized with Duolite C-26 (H^+) resin, filtered, and concentrated. The residue was subjected to chromatography ($CHCl_3$/MeOH/H_2O, 65:35:10, lower phase) to give amorphous **27** (51 mg, 85%): $[\alpha]^{22}_D$ −5.1° (c 0.8, $CHCl_3$/MeOH/H_2O, 65:35:8); ^1H NMR (CMD, 65:35:8) δ 4.34 (d, 1 H, J = 7.5 Hz with virtual coupling: entry 19 in ref 24, H-1 or -1'), 4.26 (d, 1 H, J = 8.0 Hz, H-1' or -1), 1.20 (d, 3 H, J = 6.5 Hz, CH_3CH).

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]propyl 6-*O*-Acetyl-2-*O*-benzoyl-3-deoxy-3-*C*-methyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-glucopyranoside (28). To a solution of compound **26** (118 mg, 0.096 mmol) in ethyl acetate (6 mL) was added MCPBA (93 mg, 0.43 mmol). The mixture was stirred at room temperature for 1 h and was then diluted with ethyl acetate, washed subsequentely with aqueous sodium bisulfite (15%), saturated aqueous sodium hydrogen carbonate, and saturated aqueous sodium chloride, dried, filtered, and concentrated. Chromatography (SiO_2, EtOAc/heptane 3:2) gave amorphous **28** (100 mg, 80%): $[\alpha]^{22}_D$ −3.1° (c 0.9, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.38 (dd, 1 H, J = 3.5, 1 Hz, H-4'), 5.19 (dd, 1 H, J = 10.5, 8.0 Hz, H-2'), 4.99 (dd, 1 H, J = 10.5, 3.5 Hz, H-3'), 4.86 (dd, 1 H, J = 11.0, 8.0 Hz, H-2), 4.55, 4.47 (d, 1 H each, J = 8.0 Hz, H-1,1'), 1.10 (d, 3 H, J = 6.5 Hz, CH_3-3). Anal. Calcd for $C_{66}H_{110}O_{20}S_2$: C, 61.6; H, 8.6. Found: C, 61.6; H, 8.8.

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]propyl 3-Deoxy-3-*C*-methyl-4-*O*-β-D-galactopyranosyl-β-D-glucopyranoside (29). Compound **28** (100 mg, 0.08 mmol) was deacetylated essentially as in the preparation of **27** but with reflux for 48 h to give after chromatography ($CHCl_3$/MeOH/H_2O, 65:35:10, lower phase, and CH_2Cl_2/MeOH, 9:1) amorphous **29** (60 mg, 79%): $[\alpha]^{22}_D$ −4.3° (c 0.8, CMD, 65:35:8); ^1H NMR (CMD, 65:35:8) δ 4.33 (d, 1 H, J = 8 Hz with virtual coupling: entry 19 in ref 24, H-1 or -1'), 4.30 (d, 1 H, J = 7.5 Hz, H-1' or -1), 1.20 (d, 3 H, J = 6.5 Hz, CH_3CH).

3-Bromo-2-(bromomethyl)propyl 2-Acetamido-6-*O*-acetyl-2,3-dideoxy-3-*C*-methyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-glucopyranoside (30). Crude **104** (701 mg, 1.2 mmol) was stirred for 5.5 h in 3-bromo-2-(bromomethyl)propanol[5] (5 mL) containing anhydrous p-toluenesulfonic acid (25 mg). Pyridine (0.63 mL) was added, and excess pyridine was evaporated. The residue was washed with three portions of

a mixture (10:45) of diethyl ether/heptane (50, 25 and 25 mL). The residual pale yellow oil was chromatographed ($CHCl_3$/MeOH, 75:1, and EtOAc/heptane, 6:1) to remove the 1'-α isomer and give amorphous **30** (490 mg, 48% from crude **104**): $[\alpha]^{20}_D$ -4.9° (*c* 1.1, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.42 (bd, 1 H, J = 9 Hz, NH), 5.37 (dd, 1 H, J = 3.5, 0.5 Hz, H-4'), 5.17 (dd, 1 H, J = 10.5, 8 Hz, H-2'), 4.97 (dd, 1 H, J = 10.5, 3.5 Hz, H-3'), 4.44 (d, 1 H, J = 8 Hz, H-1'), 2.16, 2.12, 2.06, and 1.98 (s, 3 H each), 2.05 (s, 6 H), 1.14 (d, 3 H, J = 6.5 Hz, CH_3CH). Anal. Calcd for $C_{29}H_{43}NO_{15}$: C, 43.2; H, 5.3; N, 1.8. Found: C, 43.1; H, 5.3; N, 1.8.

3-(Hexadecylthio)-2-[(hexadecylthio)methyl]propyl 2-Acetamido-6-*O*-acetyl-2,3-dideoxy-3-*C*-methyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-glucopyranoside (31). Compound **30** (438 mg, 0.54 mmol), hexadecanethiol (460 μL, 1.5 mmol), and cesium carbonate (345 mg, 1.06 mmol) were suspended in *N,N*-dimethylformamide (2.1 mL) and stirred under a nitrogen atmosphere at room temperature for 45 h. The mixture was partitioned between ice–water and diethyl ether. The aqueous phase was extracted twice with diethyl ether, and the combined organic phase was washed with water, dried, filtered, and concentrated to give crude **31**. Chromatography (SiO_2, EtOAc/heptane, 5:6 → 1:1) gave **31** (610 mg, 97%). An analytical sample was crystallized from methanol: mp 115.3–117.3 °C; $[\alpha]^{20}_D$ +3.1° (*c* 1.1, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.37 (dd, 1 H, J = 3.5, 1 Hz, H-4'), 5.33 (d, 1 H, J = 9.5 Hz, NH), 5.17 (dd, 1 H, J = 10.5, 8 Hz, H-2'), 4.97 (dd, 1 H, J = 10.5, 3.5 Hz, H-3'), 4.43 (d, 1 H, J = 8 Hz, H-1'), 4.32 (d, 1 H, J = 7.5 Hz, H-1), 2.65–2.53 (4 H, CH_2S), 2.51–2.43 (4 H, CH_2S), 2.16, 2.12, 2.06, 2.05, 2.03, and 1.97 (s, 3 H each), 1.10 (d, 3 H, J = 6.5 Hz, CH_3CH), 0.88 (t, 6 H, J = 6.5 Hz, CH_3CH_2). Anal. Calcd for $C_{61}H_{109}NO_{15}S_2$: C, 63.1; H, 9.4; N, 1.2. Found: C, 63.1; H, 9.5; N, 1.2.

3-(Hexadecylthio)-2-[(hexadecylthio)methyl]propyl 2-Acetamido-2,3-dideoxy-3-*C*-methyl-4-*O*-β-D-galactopyranosyl-β-D-glucopyranoside (32). Compound **31** (257 mg, 0.19 mmol) was dissolved in a mixture of methanolic sodium methoxide (3 mM, 132 mL), dichloromethane (80 mL), tetrahydrofuran (17 mL), and water (0.5 mL) and stirred at room temperature with occasional warming to dissolve precipitated material. After 22 h the mixture was heated to give a clear solution which, while still warm, was rapidly neutralized with Duolite C-26 (H^+) resin, filtered, and concentrated. The residue was chromatographed (SiO_2, $CHCl_3$/MeOH/H_2O, 65:35:10, lower phase) to give, after lyophilization, amorphous **32** (148 mg, 70%): $[\alpha]^{20}_D$ -7.0° (*c* 1.0, $CHCl_3$/MeOH/H_2O, 6:4:1); ^1H NMR (CMD, 65:35:8) δ 4.36, 4.30 (d, 1 H each, J = 7, 8 Hz, H-1,1'), 2.00 (s, 3 H, CH_3CO), 1.08 (d, 3 H, J = 6.5 Hz, CH_3CH), 0.89 (t, 6 H, J = 7 Hz, CH_3CH_2). Anal. Calcd for $C_{51}H_{99}NO_{10}S_2$: C, 64.4; H, 10.5; N, 1.5. Found: C, 63.5; H, 10.1; N, 1.4.

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]propyl 2-Acetamido-6-*O*-acetyl-2,3-dideoxy-3-*C*-methyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-glucopyranoside (33). The bis-sulfide glycolipid **31** (280 mg, 0.24 mmol) was treated as in the preparation of **28** to give after chromatography (SiO_2, EtOAc/heptane, 4:1) **33** (288 mg, 97%). An analytical sample was recrystallized from methanol: mp 74.5–76.5 °C; $[\alpha]^{20}_D$ -1.5° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.51 (d, 1 H, J = 9.5 Hz, NH), 5.37 (dd, 1 H, J = 3.5, 1 Hz, H-4'), 5.17 (dd, 1 H, J = 10.5, 8 Hz, H-2'), 4.97 (dd, 1 H, J = 10.5, 3.5 Hz, H-3'), 4.44 (d, 1 H, J = 8 Hz, H-1'), 4.30 (d, 1 H, J = 8 Hz, H-1), 2.75–3.20 (4 H, SO_2CH_2), 2.15, 2.12, 2.06, 2.05, 2.04, 1.97 (s, 3 H each, CH_3CO), 1.10 (d, 3 H, J = 6.5 Hz, CH_3CH), 0.88 (t, 6 H, J = 6.5 Hz, CH_3CH_2).

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]propyl 2-Acetamido-2,3-dideoxy-3-*C*-methyl-4-*O*-β-D-galactopyranosyl-β-D-glucopyranoside (34). Compound **33** (257 mg, 0.19 mmol) was O-deacetylated in a mixture of methanolic sodium methoxide (4 mM, 51 mL) and dichloromethane (10 mL) at room temperature for 25 h. The solution was neutralized with Duolite C-26 (H^+) resin, filtered, and concentrated. The residue was chromatographed (SiO_2, $CHCl_3$/MeOH/H_2O, 65:35:10, lower phase), and the fraction containing **34** was concentrated. The residue was suspended in water and lyophilized to give a quantitative yield of amorphous **34**: $[\alpha]^{20}_D$ -9.0° (*c* 0.6, $CHCl_3$/MeOH/H_2O, 6:4:1); ^1H NMR (CMD, 65:35:8) δ 4.34, 4.33 (d, 1 H each, J = 7, 8.5 Hz, H-1,1'), 2.01 (s, 3 H, CH_3CO), 1.09 (d, 3 H, J = 6.5 Hz, CH_3CH), 0.89 (t, 6 H, J = 6.5 Hz, CH_3CH_2). Anal. Calcd for $C_{51}H_{99}NO_{14}S_2$: C, 60.4; H, 9.8; N, 1.4. Found: C, 58.8; H, 9.4; N, 1.3.

3-Bromo-2-(bromomethyl)propyl 2-Acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-glucopyranoside (35). A mixture of the oxazoline obtained from *N*-acetyllactosamine[23] (840 mg, 1.36 mmol), 3-bromo-2-(bromomethyl)propanol[5] (948 mg, 4.08 mmol), and toluene-*p*-sulfonic acid monohydrate (80 mg) in dry 1,2-dichloromethane (30 mL) was heated at reflux for 45 min. The mixture was then cooled to room temperature, diluted with a mixture of chloroform (120 mL) and pyridine (1.5 mL), washed with aqueous 10% hydrochloric acid, water, and saturated sodium hydrogen carbonate, dried, and concentrated. The residue was chromatographed (SiO_2, toluene/EtOAc/Et_3N, 100:200:1) to afford crystalline **35** (400 mg, 35%): mp 157.5–158.5 °C (aqueous EtOH); $[\alpha]^{20}_D$ -11° (*c* 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.64 (bs, 1 H, NH), 5.36 (d, 1 H, J = 2.7 Hz, H-4'), 5.12 (dd, 1 H, J = 7.9, 10.5 Hz, H-2'), 4.97 (dd, 1 H, J = 10.5, 2.7 Hz, H-3') 4.50 (d, 2 H, J = 8.1 Hz, H-1,1'), 2.15, 2.13, 2.09, 2.06, 1.97 (s, 21 H, $COCH_3$ and $NHCOCH_3$). Anal. Calcd for $C_{30}H_{43}Br_2NO_{17}$: C, 42.4; H, 5.1; N, 1.7. Found: C, 42.3; H, 5.0; N, 1.5.

3-(Hexadecylthio)-2-[(hexadecylthio)methyl]propyl 2-Acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-glucopyranoside (36). Cesium carbonate (153 mg, 0.47 mmol) was added to a solution of **35** (100 mg, 0.12 mmol) and hexadecylthiol (122 mg, 0.47 mmol) in dry DMF (10 mL), and the mixture was stirred at room temperature for 16 h under N_2. Hexadecanethiol (61 mg, 0.23 mmol) and cesium carbonate (72 mg, 0.23 mmol) were added, and the stirring was continued for 3 h. The mixture was partitioned between dichloromethane and water, and the organic extract was washed with three portions of water, dried, and concentrated. The residue was chromatographed (EtOAc/heptane, 1:1) to give amorphous **36** (95 mg, 66%): $[\alpha]^{20}_D$ -7° (*c* 1.5, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.62 (d, 1 H, J = 9.8 Hz, NH), 5.35 (dd, 1 H, J = 3.4, 1.0 Hz, H-4'), 5.12 (dd, 1 H, J = 7.8, 10.5 Hz, H-2'), 5.02 (dd, 1 H, J = 8.3, 9.8 Hz, H-2), 4.97 (dd, 1 H, H-3), 4.49 (d, 1 H, J = 7.8 Hz, H-1), 4.36 (d, 1 H, J = 7.8 Hz, H-1'), 2.44–2.63 (m, 8 H, CH_2S), 2.15, 2.12, 2.08, 2.06, 2.057, 1.98, 1.97 (s, 3 H each, $COCH_3$ and $NHCOCH_3$). Anal. Calcd for $C_{62}H_{109}NO_{17}S_2$: C, 61.8; H, 9.1; N, 1.2. Found: C, 61.3; H, 9.3; N, 1.1.

3-(Butylthio)-2-[(butylthio)methyl]propyl 2,3,6-Tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-β-D-galactopyranoside (39). A mixture of **37**[5] (220 mg, 0.259 mmol), butylmercaptan (70 mg, 83 μL, 0.78 mmol), cesium carbonate (202 mg, 0.621 mmol), and dry *N,N*-dimethylformamide (2.5 mL) was stirred overnight and then worked up essentially as described[5] in the preparation of **38**. The residue was chromatographed (SiO_2, EtOAc/heptane, 3:2) to give **39** (141 mg, 63%): $[\alpha]^{25}_D$ +72° (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.58 (dd, 1 H, J = 1.2, 3.3 Hz, H-4'), 5.38 (dd, 1 H, J = 3.3, 11.0 Hz, H-2'), 5.20 (dd, 1 H, J = 3.6, 11.1 Hz, H-3'), 5.16 (dd, 1 H, J = 7.7, 10.9 Hz, H-2), 4.99 (d, 1 H, J = 3.7 Hz, H-1'), 4.80 (dd, 1 H, J = 2.8, 10.8 Hz, H-3), 4.45 (d, 1 H, J = 7.8 Hz, H-1) 2.55–2.70, 2.45–2.55 (m, 4 H each, CH_2S), 1.50–1.63, 1.34–1.47 (m, 4 H each, $SCH_2CH_2CH_2$), 0.91 (t, 6 H, J = 7.3 Hz, CH_3). Anal. Calcd for $C_{38}H_{60}O_{18}S_2$: C, 52.5; H, 7.0. Found: C, 52.6; H, 6.9.

3-(Butylthio)-2-[(butylthio)methyl]propyl 4-*O*-α-D-Galactopyranosyl-β-D-galactopyranoside (40). Compound **39** (85 mg, 0.098 mmol) was deacetylated as described in the preparation of **4** and then chromatographed (SiO_2, $CHCl_3$/CH_3OH/H_2O, 65:35:10) and freeze-dried to give **40** (36 mg, 64%): $[\alpha]^{25}_D$ +72° (*c* 0.8, Me_2SO-d_6); ^1H NMR (Me_2SO-d_6) δ 4.81 (d, 1 H, J = 3.8 Hz, H-1'), 4.08 (d, 1 H, J = 7.5 Hz, H-1), 0.86 (t, 6 H, J = 7.3 Hz, CH_3); ^{13}C NMR (Me_2SO-d_6) δ 104.3, 100.9, 77.5, 74.5, 73.1, 71.3, 71.0, 70.0, 69.4, 68.9, 68.8, 60.5, 59.3, 32.3, 32.0, 31.44, 31.38, 31.2, 21.2, 13.4.

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]propyl 2,3,6-Tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-β-D-galactopyranoside (41). The bis-sulfide glycolipid **38** (235 mg, 0.195 mmol) was oxidized as in the preparation of **3** to give **41** (246 mg, 99%): $[\alpha]^{23}_D$ +47.2° (*c* 0.6, $CDCl_3$); ^1H NMR ($CDCl_3$) δ 5.58 (dd, 1 H, J = 3.7, 1.2 Hz, H-4'), 5.39 (dd, 1 H, J = 11.0, 3.7 Hz, H-2'), 5.21 (dd, 1 H, J = 11.2, 3.4 Hz, H-3'), 5.15 (dd, 1 H, J = 11.0, 7.8 Hz, H-2), 4.97 (d, 1 H, J = 3.9 Hz, H-1'), 4.79 (dd, 1 H, J = 11.0, 2.7 Hz, H-3), 4.51 (d, 1 H, J = 7.8

Hz, H-1). Anal. Calcd for $C_{62}H_{108}O_{22}S_2$: C, 58.6; H, 8.6. Found: C, 58.7; H, 8.7.

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]propyl 4-*O*-α-D-Galactopyranosyl-β-D-galactopyranoside (42). The bis-sulfone glycolipid **41** (215 mg, 0.17 mmol) was deacetylated, as described in the preparation of **4**, to give a quantitative yield of **42**: $[\alpha]^{23}_D$ +27° (*c* 0.8, CMD, 65:35:10); ^{1}H NMR (CMD, 65:35:10) δ 4.34 (d, 1 H, *J* = 7.3 Hz, H-1), 0.89 (t, 1 H, *J* = 6.8 Hz, CH_2CH_3).

3-(Butylsulfonyl)-2-[(butylsulfonyl)methyl]propyl 2,3,6-Tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-β-D-galactopyranoside (43). The bis-sulfide glycolipid **39** (368 mg, 0.424 mmol) was treated essentially as in the preparation of **3** to give after chromatography (SiO_2, EtOAc/heptane, 3:2) **43** (364 mg, 92%): $[\alpha]^{25}_D$ +61° (*c* 1, $CDCl_3$); ^{1}H NMR ($CDCl_3$) δ 5.57 (dd, 1 H, *J* = 1.2, 3.2 Hz, H-4′), 5.39 (dd, 1 H, *J* = 3.2, 11.1 Hz, H-3′), 5.21 (dd, 1 H, *J* = 3.5, 11.1 Hz, H-2′), 5.15 (dd, 1 H, *J* = 7.8, 10.9 Hz, H-2), 4.97 (d, 1 H, *J* = 3.5 Hz, H-1′), 4.78 (dd, 1 H, *J* = 2.8, 10.9 Hz, H-3), 4.51 (d, 1 H, *J* = 7.8 Hz, H-1), 3.80 (bt, 1 H, *J* = 6.3 Hz, H-5), 3.41 (dd, 1 H, *J* = 5.2, 14.4 Hz, $CHCH_2SO_2$), 3.34 (dd, 1 H, *J* = 7.5, 14.4 Hz, $CHCH_2SO_2$), 3.21 (dd, 1 H, *J* = 7.5, 14.2 Hz, $CHCH_2SO_2$), 3.17 (dd, 1 H, *J* = 5.0, 14.2 Hz, $CHCH_2SO_2$), 3.08–3.00 (m, 4 H, $SO_2CH_2CH_2$), 0.973 (t, 3 H, *J* = 7.4 Hz, CH_3), 0.969 (t, 3 H, *J* = 7.4 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 101.5, 99.7, 72.6, 72.3, 70.7, 68.6, 68.5, 67.8, 67.4, 67.2, 62.2, 60.6, 53.9, 53.6, 52.9, 51.4, 13.5. Anal. Calcd for $C_{38}H_{60}O_{22}S_2$: C, 48.9; H, 6.5. Found: C, 48.4; H, 6.4.

3-(Butylsulfonyl)-2-[(butylsulfonyl)methyl]propyl 4-*O*-α-D-Galactopyranosyl-β-D-galactopyranoside (44). Compound **43** (332 mg, 0.356 mmol) was deacetylated as described in the preparation of **40** to give **44** (215 mg, 94%): $[\alpha]^{25}_D$ +58° (*c* 1.3, Me_2SO-d_6); ^{1}H NMR (Me_2SO-d_6) δ 4.82 (d, 1 H, *J* = 3.8 Hz, H-1′), 4.13 (d, 1 H, *J* = 7.2 Hz, H-1), 0.90 (t, 6 H, *J* = 7.3 Hz, CH_2CH_3); ^{13}C NMR (Me_2SO-d_6) δ 104.1, 100.6, 77.1, 74.5, 72.7, 71.1, 70.8, 69.6, 69.2, 68.8, 68.7, 60.4, 59.1, 52.23, 52.19, 51.6, 51.4, 29.0, 23.32, 23.26, 20.9 (2 C), 13.4 (2 C).

2-[(Hexadecylthio)methyl]-2-propenyl 2,3,6-Tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-β-D-galactopyranoside (45). The DIB galabioside **37**[5] (170 mg, 0.20 mmol), TBAF in acetonitrile (0.4 M, 2 mL), and hexadecanethiol (82 μL, 0.26 mmol) were treated essentially as described in the preparation of **5** to give **45** (137 mg, 72%): $[\alpha]_D$ +56° (*c* 0.5, $CDCl_3$); ^{1}H NMR ($CDCl_3$) δ 5.57 (dd, 1 H, *J* = 3.2, 1.0 Hz, H-4′), 5.38 (dd, 1 H, *J* = 11.0, 3.2 Hz, H-2′), 5.21 (dd, 1 H, *J* = 11.2, 7.1 Hz, H-2), 5.20 (dd, 1 H, *J* = 11.0, 3.2 Hz, H-3′), 5.12, 5.03 (bs, 1 H each, $=CH_2$), 5.00 (d, 1 H, *J* = 3.7 Hz, H-1′), 4.82 (dd, 1 H, *J* = 10.7, 2.7 Hz, H-3), 4.51 (d, 1 H, *J* = 7.8 Hz, H-1), 4.42, 4.20 (AB q, 1 H, each, *J* = 12.3 Hz, $OCH_2C=$), 3.17, 3.14 (AB q, 1 H each, *J* = 14.2 Hz, CCH_2S), 2.39 (t, 2 H, *J* = 7.3 Hz, SCH_2CH_2).

2-[[[10-(Methoxycarbonyl)decyl]thio]methyl]-2-propenyl 2,3,6-Tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-β-D-galactopyranoside (46). The DIB galabioside **37**[5] (170 mg, 0.20 mmol), TBAF in acetonitrile (0.4 M, 2 mL), and methyl 11-mercaptoundecanoate[13] (63 mg, 0.26 mmol) were treated essentially as described in the preparation of **5** to give **46** (144 mg, 78%): $[\alpha]_D$ +55° (*c* 1.1, $CDCl_3$); ^{1}H NMR ($CDCl_3$) δ 5.57 (dd, 1 H, *J* = 3.4, 1.2 Hz, H-4′), 5.38 (dd, 1 H, *J* = 11.0, 3.2 Hz, H-2′), 5.21 (dd, 1 H, *J* = 10.5, 7.1 Hz, H-2), 5.20 (dd, 1 H, *J* = 11.0, 3.2 Hz, H-3′), 5.12, 5.03 (bs, 1 H each, $=CH_2$), 5.00 (d, 1 H, *J* = 3.7 Hz, H-1′), 4.82 (dd, 1 H, *J* = 10.7, 2.9 Hz, H-3), 4.51 (d, 1 H, *J* = 7.8 Hz, H-1), 4.42, 4.20 (AB q, 1 H, each, *J* = 12.7 Hz, $OCH_2C=$), 3.67 (s, 3 H, OMe), 3.17, 3.14 (AB q, 1 H each, *J* = 14.2 Hz, CCH_2S), 2.39 (t, 2 H, *J* = 7.3 Hz, SCH_2CH_2), 2.30 (t, 2 H, *J* = 7.8 Hz, CH_2COO). Anal. Calcd for $C_{42}H_{64}O_{20}S$: C, 54.7; H, 7.0. Found: C, 54.0; H, 7.1.

2-[[[2-(Methoxycarbonyl)ethyl]thio]methyl]-2-propenyl 2,3,6-Tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-β-D-galactopyranoside (47). The DIB galabioside **37**[5] (170 mg, 0.20 mmol), TBAF in acetonitrile (0.4 M, 2 mL), and methyl 3-mercaptopropionate (30 μL, 0.26 mmol) were treated essentially as described in the preparation of **5** to give **47** (133 mg, 82%): $[\alpha]_D$ +53° (*c* 0.8, $CDCl_3$); ^{1}H NMR ($CDCl_3$) δ 5.57 (dd, 1 H, *J* = 3.4, 1.2 Hz, H-4′), 5.38 (dd, 1 H, *J* = 11.0, 3.2 Hz, H-2′), 5.21 (dd, 1 H, *J* = 10.7, 7.8 Hz, H-2), 5.20 (dd, 1 H, *J* = 11.0, 3.7 Hz, H-3′), 5.16, 5.07 (bs, 1 H each, $=CH_2$), 5.00 (d, 1 H, *J* = 3.7 Hz, H-1′), 4.82 (dd, 1 H, *J* = 10.8, 2.9 Hz, H-3), 4.51 (d, 1 H, *J* = 7.6 Hz, H-1), 4.41, 4.20 (AB q, 1 H, each, *J* = 12.3 Hz, $OCH_2C=$), 3.70 (s, 3 H, OMe), 3.21, 3.17 (AB q, 1 H each, *J* = 14.1 Hz, CCH_2S). Anal. Calcd for $C_{34}H_{48}O_{20}S$: C, 50.5; H, 6.0. Found: C, 51.2; H, 6.3.

BSA–Galabioside Conjugate 48. The methyl ester **47** (120 mg) was deacetylated as described in the preparation of **4** to give crude 2-[[[2-(methoxycarbonyl)ethyl]thio]methyl]propenyl 4-*O*-α-D-galactopyranosyl-β-D-galactopyranoside (80 mg). Part of the crude material (36 mg, 0.07 mmol) was coupled to BSA as described in the preparation of the BSA–lactoside conjugate **18**. The degree of binding was 17.5 as determined by differential sulfur combustion analysis.

Silica Gel–Galabioside Conjugate (49). Crude 2-[[[2-(methoxycarbonyl)ethyl]thio]methyl]propenyl 4-*O*-α-D-galactopyranosyl-β-D-galactopyranoside (46 mg, 0.09 mmol) was transformed into the corresponding azide essentially as described in the preparation of **17**, using hydrazine hydrate (0.25 mL) and *tert*-butyl nitrite (40 μL), and the azide was coupled to aminated silica gel (see **17**) to give the conjugate **49**. Combustion analysis of **49** showed the sulfur content to be 0.35%, which corresponds to a degree of binding of 0.19 mmol of sugar per gram of silica gel conjugate.

Isobutyl 4-*O*-α-D-Galactopyranosyl-β-D-galactopyranoside (50). Compound **37**[5] (129 mg, 0.152 mmol) was dissolved in methanolic sodium methoxide (0.05 M, 2 mL), and the solution was stirred at room temperature for 2 h. Methanolic sodium methoxide (1 M, 0.3 mL) and Pd/C (10%, 80 mg) were added, and the mixture was hydrogenated (1 atm) for 3 h and then filtered (Celite), and the filtrate was neutralized with Duolite (H^+) resin and concentrated. Column chromatography (SiO_2, EtOH/CH_2Cl_2, 2:3) of the residue gave, after freeze-drying, amorphous **50** (51 mg, 84%): $[\alpha]^{25}_D$ +95° (*c* 0.9, H_2O); ^{1}H NMR (D_2O) δ 4.94 (d, 1 H, *J* = 3.8 Hz, H-1′), 4.42 (d, 1 H, *J* = 7.7 Hz, H-1), 4.37 (bt, 1 H, *J* = 7.0 Hz, H-5′), 4.01 (bd, 2 H, *J* = 3.0 Hz, H-4 and H-4′), 3.53 (dd, 1 H, *J* = 10.2, 7.7 Hz, H-2), 3.44 [dd, 1 H, *J* = 9.6, 6.6 Hz, $OCH_2CH(CH_3)_2$], 1.88 [m, 1 H, *J* = 6.7 Hz, $OCH_2CH(CH_3)_2$], 0.89 [d, 1 H, *J* = 6.7 Hz, $OCH_2CH(CH_3)_2$].

3-Bromo-2-(bromomethyl)propyl 2,6-Di-*O*-acetyl-3-deoxy-3-*C*-methyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-β-D-galactopyranoside (52). Compound **51**[1] (400 mg, 0.63 mmol, α/β 80:20) and 3-bromo-2-(bromomethyl)propanol[5] (731 mg, 3.15 mmol) were dissolved in dry dichloromethane (5 mL) and BF_3·Et_2O (775 μL, 6.3 mmol) was added at 0 °C. The mixture was stirred at room temperature until **51** was consumed (1.5 h) and dichloromethane (20 mL) was added. The mixture was washed with saturated aqueous sodium hydrogen carbonate (10 mL) and water (10 mL), dried, and concentrated. Column chromatography (SiO_2, EtOAc/heptane, 1:2) gave amorphous **52** (287 mg, 56%): $[\alpha]_D$ +59° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 5.52 (dd, 1 H, *J* = 3.1, 1.4 Hz, H-4′), 5.36 (dd, 1 H, *J* = 11.1, 3.1 Hz, H-3′), 5.28 (dd, 1 H, *J* = 11.1, 3.5 Hz, H-2′), 5.08 (d, 1 H, *J* = 3.5 Hz, H-1′), 4.85 (dd, 1 H, *J* = 11.6, 7.7 Hz, H-2), 4.50–4.44 (m, 1 H, H-5), 4.38 (d, 1 H, *J* = 7.7 Hz, H-1), 4.36 (dd, 1 H, *J* = 11.8, 7.0 Hz, H-6), 4.19 (dd, 1 H, *J* = 11.2, 6.2 Hz, H-6), 4.15–4.05 (m, 2 H, H-6′), 3.97 (dd, 1 H, *J* = 11.7, 4.9 Hz, CH_2CH), 3.70–3.75 (2 H, H-4,5), 3.64 (dd, 1 H, *J* = 10.4, 4.6 Hz, CH_2CH), 3.58 (dd, 1 H, *J* = 9.7, 7.1 Hz, CH_2CH), 3.56 (dd, 1 H, *J* = 10.4, 5.5 Hz, CH_2CH), 3.50–3.45 (m, 2 H, CH_2CH), 2.40–2.31 (m, 1 H, CH_2CH), 2.13–1.98 (6 s, 3 H each, OAc), 1.96–1.83 (m, 1 H, H-3), 1.12 (d, 3 H, *J* = 7.0 Hz, CH_3). Anal. Calcd for $C_{29}H_{42}Br_2O_{16}$: C, 43.2; H, 5.2. Found: C, 43.1; H, 5.4.

3-(Hexadecylthio)-2-[(hexadecylthio)methyl]propyl 2,6-Di-*O*-acetyl-3-deoxy-3-*C*-methyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-β-D-galactopyranoside (53). Compound **52** (255 mg, 0.32 mmol), hexadecanethiol (317 μL, 0.95 mmol) and cesium carbonate (175 mg, 0.54 mmol) were suspended in dry *N*,*N*-dimethylformamide (2 mL) and stirred at room temperature for 6 h. The mixture was then diluted with dichloromethane (25 mL), washed with water (10 mL), dried, and concentrated. Column chromatography (SiO_2, EtOAc/heptane, 1:3) gave amorphous **53** (340 mg, 93%): $[\alpha]_D$ +48° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 5.53 (dd, 1 H, *J* = 2.9, 1.2 Hz, H-4′), 5.35 (dd, 1 H, *J* = 11.2, 2.9 Hz, H-3′), 5.27 (dd, 1 H, *J* = 11.2, 3.4 Hz, H-2′), 5.08 (d, 1 H, *J* = 3.5 Hz, H-1′), 4.85 (dd, 1 H, *J* = 11.2, 7.6 Hz, H-2), 4.50–4.45 (m, 1 H, H-5′), 4.36 (d, 1 H, *J* = 7.6 Hz, H-1),

4.39–4.32 (m, 1 H, H-6), 4.03–4.23 (3 H, H-6,6′), 3.96 (dd, 1 H, J = 9.7, 4.5 Hz, CH_2CH), 3.68–3.74 (2 H, H-5,4), 3.58 (dd, 1 H, J = 9.6, 5.9 Hz, CH_2CH), 2.73–2.53 (m, 4 H, CHCH_2S), 2.13–1.97 (6 s, 3 H each, OAc), 1.94–1.82 (m, 1 H, H-3), 1.11 (d, 3 H, J = 7.0 Hz, CHCH_3), 0.88 (t, 6 H, J 6.7 Hz, CH$_2$CH_3). Anal. Calcd for $C_{61}H_{108}O_{16}S_2$: C, 63.1; H, 9.4. Found: C, 62.7; H, 9.3.

3-(Hexadecylthio)-2-[(hexadecylthio)methyl]propyl 3-Deoxy-3-*C*-methyl-4-*O*-α-D-galactopyranosyl-β-D-galactopyranoside (54). Compound **53** (23 mg, 0.02 mmol) was deacylated essentially as in the preparation of **4** to give after chromatography (CH$_2$Cl$_2$/MeOH, 10:1) and lyophilization amorphous **54** (13 mg, 73%): $[\alpha]_D$ +7° (c 0.2, CHCl$_3$/MeOH, 5:1); ^{1}H NMR (CMD, 65:35:10) δ 4.98 (bs, 1 H, H-1′), 4.27 (d, 1 H, J = 7.6 Hz, H-1), 4.10–3.62 (m, 13 H), 2.74–2.68 (m, 4 H, CHCH_2S), 2.56–2.50 (m, 4 H, SCH_2CH$_2$), 2.06–2.00 (m, 1 H, CHCH_2), 1.81–1.64 (m, 1 H, H-3), 1.23 (d, 3 H, J = 6.7 Hz, CHCH_3), 0.89 (t, 6 H, J = 6.9 Hz, CH$_2$CH_3).

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]propyl 2,6-Di-*O*-acetyl-3-deoxy-3-*C*-methyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-β-D-galactopyranoside (55). The bis-sulfide glycolipid **53** (150 mg, 0.13 mmol) was treated essentially as in the preparation of **28** to give after column chromatography (SiO$_2$, EtOAc/heptane, 1:1) amorphous **55** (136 mg, 86%): $[\alpha]_D$ +43° (c 1.0, CHCl$_3$); ^{1}H NMR (CDCl$_3$) δ 5.52 (dd, 1 H, J = 2.9, 1.2 Hz, H-4′), 5.37 (dd, 1 H, J = 11.2, 3.0 Hz, H-3′), 5.29 (dd, 1 H, J = 11.2, 3.3 Hz, H-2′), 5.06 (d, 1 H, J = 3.4 Hz, H-1′), 4.83 (dd, 1 H, J = 11.6, 7.7 Hz, H-2), 4.50–4.43 (m, 1 H, H-5′), 4.42 (d, 1 H, J = 7.7 Hz, H-1), 4.33 (dd, 1 H, J = 11.5, 7.1 Hz, H-6), 4.19 (dd, 1 H, J = 11.5, 5.6 Hz, H-6), 4.16–4.04 (m, 2 H, H-6′), 3.98 (d, 2 H, J = 4.2 Hz, CH_2CH), 3.75–3.68 (m, 2 H, H-5,4), 3.45–3.12 (m, 4 H, CHCH_2S), 3.08–2.94 (m, 5 H, SCH_2CH$_2$, CH_2CH), 2.14–1.99 (6 s, 3 H each, OAc), 1.94–1.77 (m, 5 H), 1.12 (d, 3 H, J = 7.0 Hz, CHCH_3), 0.88 (t, 6 H, J = 6.7 Hz, CH$_2$CH_3). Anal. Calcd for $C_{61}H_{108}O_{20}S_2$: C, 59.8; H, 8.9. Found: C, 60.0; H, 9.0.

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]propyl 3-Deoxy-3-*C*-methyl-4-*O*-α-D-galactopyranosyl-β-D-galactopyranoside (56). Compound **55** (18 mg, 0.015 mmol) was deacylated and neutralized as described in the preparation of **4**. Column chromatography (SiO$_2$, CHCl$_3$/MeOH, 7:1) and lyophilization gave amorphous **56** (12 mg, 86%): $[\alpha]_D$ +20° (c 0.3, CHCl$_3$/MeOH 5:1); ^{1}H NMR (CMD, 65:35:10) δ 4.95 (d, 1 H, J = 2.1 Hz, H-1′), 4.32 (d, 1 H, J = 7.5 Hz, H-1), 4.16–3.62 (m, 12 H), 3.53–3.34 (m, 4 H, CHCH_2S), 3.16–3.08 (m, 4 H, SCH_2CH$_2$), 3.05–2.94 (m, 1 H, CHCH$_2$), 1.91–1.70 (5 H), 1.23 (d, 1 H, J = 6.8 Hz, CHCH_3), 0.89 (t, 6 H, J = 6.7 Hz, CH$_2$CH_3).

3-Bromo-2-(bromomethyl)propyl 2,6-Di-*O*-acetyl-3-deoxy-3-*C*-ethyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-β-D-galactopyranoside (58). Compound **57**[1] (150 mg, 0.23 mmol, α/β 80:20) was treated with 3-bromo-2-(bromomethyl)propanol[5] (163 mg, 0.70 mmol) and BF$_3$·Et$_2$O (284 μL, 2.30 mmol) as described in the preparation of **52**. Column chromatography (SiO$_2$, EtOAc/heptane, 1:2) gave amorphous **58** (141 mg, 75%): $[\alpha]_D$ +62° (c 0.5, CHCl$_3$); ^{1}H NMR (CDCl$_3$) δ 5.53 (dd, 1 H, J = 2.9, 1.4 Hz, H-4′), 5.35 (dd, 1 H, J = 11.1, 3.0 Hz, H-3′), 5.27 (dd, 1 H, J = 11.1, 3.5 Hz, H-2′), 5.09 (d, 1 H, J = 3.4 Hz, H-1′), 4.89 (dd, 1 H, J = 11.0, 7.7 Hz, H-2), 4.44–4.39 (m, 1 H, H-5′), 4.38 (dd, 1 H, J = 11.3, 7.2 Hz, H-6), 4.37 (d, 1 H, J = 7.7 Hz, H-1), 4.19 (dd, 1 H, J = 11.2, 6.2 Hz, H-6), 4.12 (dd, 1 H, J = 11.2, 7.2 Hz, H-6′), 4.04 (dd, 1 H, J = 11.3, 6.4 Hz, H-6′), 3.97 (dd, 1 H, J = 9.6, 4.8 Hz, CH_2CH), 3.85 (bs, 1 H, H-4), 3.71–3.65 (m, 1 H, H-5), 3.65–3.45 (m, 5 H, CH_2CH), 2.41–2.30 (m, 1 H, CH_2CH), 2.13–1.98 (6 s, 3 H each, OAc), 1.62–1.42 (m, 3 H, H-3 and CH_2CH$_3$), 0.95 (t, 3 H, J = 7.1 Hz, CH$_2$CH_3). Anal. Calcd for $C_{30}H_{44}Br_2O_{16}$: C, 43.9; H, 5.4. Found: C, 43.8; H, 5.4.

3-(Hexadecylthio)-2-[(hexadecylthio)methyl]propyl 2,6-Di-*O*-acetyl-3-deoxy-3-*C*-ethyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-β-D-galactopyranoside (59). Compound **58** (129 mg, 0.16 mmol) was treated with hexadecanethiol (158 μL, 0.47 mmol) and cesium carbonate (89 mg, 0.27 mmol) as described in the preparation of **53**. Column chromatography (SiO$_2$, EtOAc/heptane, 1:3) gave amorphous **59** (143 mg, 76%): $[\alpha]_D$ +46° (c 1.0, CHCl$_3$); ^{1}H NMR (CDCl$_3$) δ 5.53 (dd, 1 H, J = 2.9, 1.1 Hz, H-4′), 5.34 (dd, 1 H, J = 11.3, 2.8 Hz, H-3′), 5.26 (dd, 1 H, J = 11.3, 3.4 Hz, H-2′), 5.09 (d, 1 H, J = 3.4 Hz, H-1′), 4.88 (dd, 1 H, J = 10.5, 7.6 Hz, H-2), 4.45–4.39 (m, 1 H, H-5′), 4.38 (dd, 1 H, J = 11.2, 6.8 Hz, H-6), 4.35 (dd, 1 H, J = 7.6 Hz, H-1), 4.20 (dd, 1 H, J = 11.3, 6.4 Hz, H-6), 4.12 (dd, 1 H, J = 11.3, 7.0 Hz, H-6′), 4.04 (dd, 1 H, J = 11.0, 6.4 Hz, H-6′), 3.95 (dd, 1 H, J = 9.5, 4.4 Hz, CH_2CH), 3.84 (bs, 1 H, H-4), 3.70–3.64 (m, 1 H, J = 6.8 Hz, H-5), 3.58 (dd, 1 H, J = 9.6, 6.0 Hz, CH_2CH), 2.72–2.54 (m, 4 H, CHCH_2S), 2.53–2.46 (m, 4 H, SCH_2CH$_2$), 2.13–1.98 (6 s, 3 H each, OAc), 1.61–1.40 (m, 7 H), 0.94 (t, 3 H, J = 7.2 Hz, CH$_2$CH_3), 0.88 (t, 6 H, J = 6.7 Hz, CH$_2$CH_3). Anal. Calcd for $C_{62}H_{110}O_{16}S_2$: C, 63.3; H, 9.4. Found: C, 63.3; H, 9.4.

3-(Hexadecylthio)-2-[(hexadecylthio)methyl]propyl 3-Deoxy-3-*C*-ethyl-4-*O*-α-D-galactopyranosyl-β-D-galactopyranoside (60). Compound **59** (25 mg, 0.02 mmol) was deacetylated and neutralized as described in the preparation of **4**. Column chromatography (SiO$_2$, CHCl$_3$/MeOH, 15:1) and lyophilization gave amorphous **60** (16 mg, 84%): $[\alpha]_D$ +28° (c 0.1, CHCl$_3$); ^{1}H NMR (CMD, 65:35:10) δ 5.0 (d, 1 H, J = 2.9 Hz, H-1′), 4.26 (d, 1 H, J = 7.6 Hz, H-1), 4.05–3.56 (m, 13 H), 2.74–2.68 (m, 4 H, CHCH_2S), 2.56–2.50 (m, 4 H, SCH_2CH$_2$), 2.12–2.01 (m, 1 H, CH_2CH), 1.02 (t, 3 H, J = 7.1 Hz, CH_2CH$_3$), 0.89 (t, 6 H, J = 6.6 Hz, CH$_2$CH_3).

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]propyl 2,6-Di-*O*-acetyl-3-deoxy-3-*C*-ethyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-β-D-galactopyranoside (61). Compound **59** (70 mg, 0.06 mmol) was treated essentially as described in the preparation of **28** to give after column chromatography (SiO$_2$, EtOAc/heptane, 1:2) amorphous **61** (67 mg, 91%): $[\alpha]_D^{22}$ +42° (c 1, CHCl$_3$); ^{1}H NMR (CDCl$_3$) δ 5.52 (dd, 1 H, J = 2.9, 1.2 Hz, H-4′), 5.36 (dd, 1 H, J = 11.1, 3.0 Hz, H-3′), 5.28 (dd, 1 H, J = 10.9, 3.4 Hz, H-2′), 5.07 (d, 1 H, J = 3.4 Hz, H-1′), 4.86 (dd, 1 H, J = 11.2, 7.8 Hz, H-2), 4.41 (d, 1 H, J = 7.5 Hz, H-1), 4.45–4.32 (m, 2 H, H-5′,6), 4.18 (dd, 1 H, J = 11.5, 5.9 Hz, H-6), 4.13–4.01 (m, 2 H, H-6′), 4.15 (d, 2 H, J = 4.2 Hz, CH_2CH), 3.83 (bs, 1 H, H-4), 3.71–3.65 (m, 1 H, J = 6.5 Hz, H-5), 3.45–3.15 (m, 4 H, CHCH_2S), 3.07–2.94 (5 H, SCH_2CH$_2$ and CH_2CH), 2.14–1.98 (6 s, 3 H each, OAc), 0.95 (t, 3 H, J = 7.1 Hz, CH_2CH$_3$), 0.88 (t, 6 H, J = 6.7 Hz, CH$_2$CH$_3$). Anal. Calcd for $C_{62}H_{110}O_{20}S_2$: C, 60.1; H, 8.9. Found: C, 60.4; H, 9.3.

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]propyl 3-Deoxy-3-*C*-ethyl-4-*O*-α-D-galactopyranosyl-β-D-galactopyranoside (62). Compound **61** (25 mg, 0.02 mmol) was deacetylated and neutralized as described in the preparation of **4**. Column chromatography (SiO$_2$, CHCl$_3$/MeOH, 15:1) and lyophilization gave amorphous **62** (18 mg, 90%): $[\alpha]_D$ +28° (c 0.4, CHCl$_3$/MeOH, 5:1). ^{1}H NMR (CMD, 65:35:10) δ 4.98 (d, 1 H, J = 3.4 Hz, H-1′), 4.30 (d, 1 H, J = 7.5 Hz, H-1), 4.18–3.36 (m, 17 H), 3.15–3.07 (m, 4 H, SCH_2CH$_2$), 3.06–2.97 (m, 1 H, CH$_2$CH), 1.02 (t, 3 H, J = 6.7 Hz, CH$_2$CH_3), 0.88 (t, 6 H, J = 6.7 Hz, CH$_2$CH_3).

3-Bromo-2-(bromomethyl)propyl 2,3,6-Tri-*O*-benzoyl-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]-β-D-glucopyranoside (64). The acetate **63**[1] (520 mg, 0.41 mmol) was treated with 3-bromo-2-(bromomethyl)propanol[5] (290 mg, 1.25 mmol) and BF$_3$·Et$_2$O (300 mg, 2.11 mmol, 270 μL) in dichloromethane essentially as described in the preparation of **52**. Column chromatography (SiO$_2$, EtOAc/heptane, 45:55) gave **64** (418 mg, 51%): $[\alpha]_D$ +90° (c 1.1, CHCl$_3$); ^{1}H NMR (CDCl$_3$) δ 5.76 (t, 1 H, J = 9.4 Hz, H-3), 5.64 (dd, 1 H, J = 10.9, 7.7 Hz, H-2′), 5.48 (dd, 1 H, J = 3.4, 1.5 Hz, H-4″), 5.35 (dd, 1 H, J = 9.4, 7.7 Hz, H-2), 5.31 (dd, 1 H, J = 11.1, 3.3 Hz, H-3′), 5.10 (dd, 1 H, J = 11.0, 3.7 Hz, H-2″), 5.06 (dd, 1 H, J = 10.6, 2.6 Hz, H-3″), 4.95 (d, 1 H, J = 3.4 Hz, H-1″), 4.84 (d, 1 H, J = 8.0 Hz, H-1′), 4.69 (d, 1 H, J = 7.7 Hz, H-1). Anal. Calcd for $C_{67}H_{68}Br_2O_{26}$: C, 55.5; H, 4.7. Found: C, 55.3; H, 4.7.

3-(Hexadecylthio)-2-[(hexadecylthio)methyl]propyl 2,3,6-Tri-*O*-benzoyl-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]-β-D-glucopyranoside (65). Compound **64** (42 mg, 0.030 mmol) was treated with hexadecanethiol essentially as described in the preparation of **26** to give after chromatography (SiO$_2$, EtOAc/heptane, 1:2) **65** (46 mg, 87%): $[\alpha]_D$ +32° (c 0.5, CHCl$_3$); ^{1}H NMR (CDCl$_3$) δ 5.76 (t, 1 H, J = 9.3 Hz, H-3), 5.64 (dd, 1 H, J = 11.2, 7.5 Hz, H-2′), 5.48 (dd, 1 H, J = 3.9, 1.5 Hz, H-4″), 5.35 (dd, 1 H, J = 9.5, 7.9 Hz, H-2), 5.30 (dd, 1 H, J = 11.2, 3.3 Hz, H-3′), 5.10 (dd, 1 H, J = 11.4, 3.3 Hz, H-2″), 5.03 (dd, 1 H, J = 11.0, 2.7 Hz, H-3″), 4.94 (d, 1 H, J = 3.5 Hz, H-1″), 4.82

(d, 1 H, J = 7.8 Hz, H-1'), 4.68 (d, 1 H, J = 7.6 Hz, H-1). Anal. Calcd for $C_{99}H_{134}O_{26}S_2$: C, 65.9; H, 7.5. Found: C, 65.5; H, 7.5.

3-(Hexadecylthio)-2-[(hexadecylthio)methyl]propyl 4-*O*-(4-*O*-α-D-Galactopyranosyl-β-D-galactopyranosyl)-β-D-glucopyranoside (66). Compound **65** (95 mg, 0.064 mmol) was deacylated as described in the preparation of **4** to give **66** (48 mg, 70%): $[\alpha]^{25}_D$ +29° (c 0.4, CMD, 65:35:5); ^{1}H NMR (CMD, 65:35:5) δ 4.70 (d, 1 H, J = 2.7 Hz, H-1''), 4.07 (d, 1 H, J = 7.6 Hz, H-1 or H-1'), 2.47 (bd, 4 H, J = 6.3 Hz, $CHCH_2S$), 2.29 (t, 4 H, J = 7.4 Hz, SCH_2CH_2), 1.82 (m, 1 H, OCH_2CH), 1.36 (m, 4 H, SCH_2CH_2), 0.65 (t, 6 H, J = 6.6 Hz, CH_2CH_3).

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]propyl 2,3,6-Tri-*O*-benzoyl-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]-β-D-glucopyranoside (67). The bis-sulfide glycolipid **65** (25 mg, 0.0137 mmol) was oxidized with MCPBA (17 mg) as described in the preparation of **28** to give **67** (23 mg, 89%): $[\alpha]_D$ +67° (c 1, $CDCl_3$); ^{1}H NMR ($CDCl_3$) δ 5.77 (t, 1 H, J = 8.9 Hz, H-3), 5.64 (dd, 1 H, J = 10.9, 7.7 Hz, H-2'), 5.47 (dd, 1 H, J = 3.3, 1.3 Hz, H-4''), 5.33 (dd, 1 H, J = 9.6, 7.9 Hz, H-2), 5.30 (dd, 1 H, J = 11.1, 3.3 Hz, H-3'), 5.10 (dd, 1 H, J = 11.0, 3.5 Hz, H-2''), 5.05 (dd, 1 H, J = 10.9, 2.7 Hz, H-3''), 4.95 (d, 1 H, J = 3.7 Hz, H-1''), 4.83 (d, 1 H, J = 7.9 Hz, H-1'), 4.72 (d, 1 H, J = 7.9 Hz, H-1). Anal. Calcd for $C_{99}H_{134}O_{30}S_2$: C, 63.6; H, 7.2. Found: C, 63.3; H, 7.3.

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]propyl 4-*O*-(4-*O*-α-D-Galactopyranosyl-β-D-galactopyranosyl)-β-D-glucopyranoside (68). Compound **67** (38 mg, 0.024 mmol) was deacylated as described in the preparation of **4** to give **68** (26 mg, 95%): $[\alpha]_D^{61}$ +34° (c 0.9, Me_2SO-d_6 + 3 dr, D_2O, 61 °C); ^{1}H NMR (Me_2SO-d_6 + 3 dr D_2O, 61 °C) δ 4.81 (d, 1 H, J = 3.7 Hz, H-1''), 4.28 (d, 1 H, J = 7.3 Hz, H-1), 4.23 (d, 1 H, J = 7.8 Hz, H-1').

3-Bromo-2-(bromomethyl)propyl 2,3,6-Tri-*O*-acetyl-4-*O*-[2,6-di-*O*-acetyl-3-deoxy-3-*C*-methyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (70). Compound **69**[1] (200 mg, 0.2 mmol, β/α 95:5) and 3-bromo-2-(bromomethyl)propanol[5] (360 mg, 1.54 mmol) was dissolved in dry dichloromethane (2 mL), and BF_3·Et_2O (320 μL, 2.60 mmol) was added at 0 °C. The mixture was stirred at 0 °C for 1.5 h, diluted with dichloromethane (20 mL), washed with saturated aqueous sodium hydrogen carbonate (10 mL), and water (10 mL), dried, and concentrated. Column chromatography (SiO_2, EtOAc/heptane, 1:1) of the residue gave **70** (145 mg, 41%) as a syrup: $[\alpha]_D^{25}$ +32° (c 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 5.53 (dd, 1 H, J = 3.1, 1.3 Hz, H-4''), 5.36 (dd, 1 H, J = 11.1, 3.1 Hz, H-3''), 5.25 (dd, 1 H, J = 11.1, 3.6 Hz, H-2''), 5.19 (dd, 1 H, J = 9.5, 8.9 Hz, H-3), 5.07 (d, 1 H, J = 3.6 Hz, H-1''), 4.90 (dd, 1 H, J = 9.5, 7.9 Hz, H-2), 4.79 (dd, 1 H, J = 11.6, 7.7 Hz, H-2'), 4.47 (d, 1 H, J = 7.9 Hz, H-1), 4.39 (d, 1 H, J = 7.8 Hz, H-1'), 2.39–2.27 (m, 1 H, CH_2CH), 2.13–1.98 (9 s, 3 H each, OAc), 1.91–1.78 (m, 1 H, H-3'), 1.09 (d, 3 H, J = 7.0 Hz, CH_2CH_3).

3-(Hexadecylthio)-2-[(hexadecylthio)methyl]propyl 2,3,6-Tri-*O*-acetyl-4-*O*-[2,6-di-*O*-acetyl-3-deoxy-3-*C*-methyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (71). Compound **70** (65 mg, 0.06 mmol) was treated with hexadecanethiol overnight, essentially as described in the preparation of **26** to give after chromatography (EtOAc/heptane, 1:2) **71** (56 mg, 66%) as a syrup: $[\alpha]^{22}_D$ +28° (c 0.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 5.53 (dd, 1 H, J = 3.1, 1.3 Hz, H-4''), 5.35 (dd, 1 H, J = 11.1, 3.1 Hz, H-3''), 5.26 (dd, 1 H, J = 11.1, 3.6 Hz, H-2''), 5.18 (dd, 1 H, J = 9.5, 9.0 Hz, H-3), 5.07 (d, 1 H, J = 3.6 Hz, H-1''), 4.90 (dd, 1 H, J = 9.6, 7.9 Hz, H-2), 4.79 (dd, 1 H, J = 11.5, 7.6 Hz, H-2''), 4.46 (d, 1 H, J = 7.9 Hz, H-1), 4.38 (d, 1 H, J = 7.6 Hz, H-1'), 2.65–2.51 (m, 4 H, $CHCH_2S$), 2.51–2.44 (m, 4 H, SCH_2CH_2), 2.13–1.97 (9 s, 3 H each, OAc), 1.89–1.78 (m, 1 H, H-3), 1.09 (d, 3 H, J = 7.0 Hz, $CHCH_3$), 0.88 (t, 6 H, J = 6.7 Hz, CH_2CH_3).

3-(Hexadecylthio)-2-[(hexadecylthio)methyl]propyl 4-*O*-(3-Deoxy-3-*C*-methyl-4-*O*-α-D-galactopyranosyl-β-D-galactopyranosyl)-β-D-glucopyranoside (72). Compound **71** (48 mg, 0.03 mmol) was dissolved in a 3:2 mixture (2.5 mL) of dichloromethane and methanolic sodium methoxide (0.04 M), and the mixture was stirred at room temperature for 7 h and then neutralized with Duolite (H^+) resin. The resin was washed ($CHCl_3$/MeOH/H_2O, 65:35:6), and the solvent was removed. Column chromatography ($CHCl_3$/MeOH/H_2O, 65:35:6) of the residue and lyophilization gave amorphous **72** (33 mg, 95%): $[\alpha]^{22}_D$ +31° (c 0.3, $CHCl_3$/MeOH/H_2O, 65:35:6); ^{1}H NMR (CMD, 65:35:6) δ 4.89 (d, 1 H, J = 3.3 Hz, H-4''), 4.41, 4.31 (d, 1 H, J = 7.7 Hz, H-1,1'), 2.77–2.65 (m, 4 H, $CHCH_2S$), 2.56–2.49 (m, 4 H, SCH_2CH_2), 2.10–2.01 (m, 1 H, CH_2CH), 1.83–1.72 (m, 1 H, H-3), 1.22 (t, 3 H, J = 6.8 Hz, $CHCH_3$), 0.89 (t, 6 H, J = 6.7 Hz, CH_2CH_3).

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]propyl 2,3,6-Tri-*O*-acetyl-4-*O*-[2,6-di-*O*-acetyl-3-deoxy-3-*C*-methyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (73). Compound **71** (45 mg, 0.03 mmol) was oxidized with MCPBA (30 mg, 0.14 mmol) and chromatographed as described in the preparation of **55** to give **73** (38 mg, 83%) as a syrup: $[\alpha]^{22}_D$ +15° (c 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 5.53 (dd, 1 H, J = 3.1, 1.2 Hz, H-4''), 5.36 (dd, 1 H, J = 11.1, 3.1 Hz, H-3''), 5.25 (dd, 1 H, J = 11.1, 3.5 Hz, H-2''), 5.18 (dd, 1 H, J = 9.6, 8.8 Hz, H-3), 5.07 (d, 1 H, J = 3.5 Hz, H-1''), 4.89 (dd, 1 H, J = 9.6, 8.0 Hz, H-2), 4.79 (dd, 1 H, J = 11.6, 7.6 Hz, H-2'), 4.50 (d, 1 H, J = 8.0 Hz, H-1), 4.39 (d, 1 H, J = 7.6 Hz, H-1'), 3.38–3.09 (m, 4 H, $CHCH_2S$), 3.05–2.91 (5 H, SCH_2CH_2) and CH_2CH), 2.13–1.98 (9 s, 3 H each, OAc), 1.89–1.76 (m, 5 H), 1.09 (t, 3 H, J = 7.0 Hz, $CHCH_3$), 0.88 (t, 6 H, J = 6.7 Hz, CH_2CH_3).

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]propyl 4-*O*-(3-Deoxy-3-*C*-methyl-4-*O*-α-D-galactopyranosyl-β-D-galactopyranosyl)-β-D-glucopyranoside (74). Compound **73** (31 mg, 0.02 mmol) was deacetylated and chromatographed as described in the preparation of **72**. Lyophilization gave amorphous **74** (20 mg, 85%): $[\alpha]^{22}_D$ +13° (c 0.7, Me_2SO); ^{1}H NMR (CMD, 65:35:10) δ 4.88 (d, 1 H, J = 3.3 Hz, H-1''), 4.39, 4.36 (d, 1 H each, J = 7.7 Hz, H-1,1'), 3.14–3.07 (m, 4 H, SCH_2CH_2), 3.06–2.95 (m, 1 H, CH_2CH), 1.90–1.71 (5 H), 1.22 (t, 3 H, J = 6.8 Hz, $CHCH_3$), 0.89 (t, 6 H, J = 6.7 Hz, CH_2CH_3).

3-Bromo-2-(bromomethyl)propyl 3,6-Di-*O*-acetyl-2-deoxy-2-phthalimido-4-*O*-[2,3,6-tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (76). Compound **75**[1] (47 mg, 0.044 mmol) and 3-bromo-2-(bromomethyl)propanol[5] (65 mg, 0.28 mmol) were dissolved in dry dichloromethane (2 mL), and BF_3·Et_2O (60 μL, 0.49 mmol) was added at 0 °C. The mixture was stirred at room temperature for 1.5 h, diluted with dichloromethane, and poured into cold, saturated aqueous sodium hydrogen carbonate. The aqueous phase was extracted with dichloromethane, and the combined organic extract was washed with saturated aqueous sodium hydrogen carbonate and saturated aqueous sodium chloride, dried, filtered, and concentrated. The residue was chromatographed (SiO_2, EtOAc/heptane, 3:2) to give amorphous **76** (49 mg, 90%): $[\alpha]^{22}_D$ +43° (c 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 5.75 (dd, 1 H, J = 10.5, 8.5 Hz, with virtual coupling, H-3), 5.57 (dd, 1 H, J = 3.5, 1.0 Hz, H-4''), 5.37 (d, 1 H, J = 8.5 Hz, H-1), 5.36 (dd, 1 H, J = 11.0, 3.5 Hz, H-3''), 5.16 (dd, 1 H, J = 11.0, 4.0 Hz, H-2''), 4.97 (d, 1 H, J = 4.0 Hz, H-1''), 4.57 (d, 1 H, J = 7.5 Hz, H-1'). Anal. Calcd for $C_{48}H_{59}Br_2NO_{26}$: C, 47.0; H, 4.9. Found: C, 46.7; H, 4.8.

3-(Hexadecylthio)-2-[(hexadecylthio)methyl]propyl 3,6-Di-*O*-acetyl-2-deoxy-2-phthalimido-4-*O*-[2,3,6-tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (77). Compound **76** (246 mg, 0.2 mmol) was treated with hexadecanethiol for 20 h essentially as described in the preparation of **26** to give after chromatography (EtOAc/heptane, 1:15) amorphous **77** (223 mg, 70%): $[\alpha]^{22}_D$ +38° (c 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.70–7.90 (4 H), 5.75 (dd, 1 H, J = 10.5, 8.0 Hz, H-2), 5.57 (dd, 1 H, J = 3.5, 1.0 Hz, H-4''), 5.36 (dd, 1 H, J = 11.0, 3.5 Hz, H-3''), 5.34 (d, 1 H, J = 8.5 Hz, H-1), 5.16 (dd, 1 H, J = 11.0, 3.5 Hz, H-2''), 5.11 (dd, 1 H, J = 11.0, 7.5 Hz, H-2'), 4.97 (d, 1 H, J = 3.5 Hz, H-1''), 4.73 (dd, 1 H, J = 11.0, 2.5 Hz, H-3'), 4.56 (d, 1 H, J = 7.5 Hz, H-1'), 0.84 (t, 16 H, J = 7.0 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 101.1, 99.6, 98.3 (C-1,1',1'').

3-Bromo-2-(bromomethyl)propyl 3,6-Di-*O*-acetyl-2-deoxy-2-phthalimido-4-*O*-[2,6-di-*O*-acetyl-3-deoxy-3-*C*-methyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (79). Compound **78**[1] (62 mg, 0.06 mmol) was treated with 3-bromo-2-(bromomethyl)propanol[5] (85 mg, 0.37 mmol) and BF_3·Et_2O (83 μL, 0.67

mmol) as described in the preparation of **70**. Column chromatography (SiO_2, EtOAc/heptane, 1:1) gave **79** (66 mg, 91%): $[\alpha]^{22}_D$ +36° (*c* 0.7, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.73 (dd, 1 H, *J* = 10.6, 8.4 Hz, with virtual coupling, H-3), 5.51 (dd, 1 H, *J* = 3.1, 1.3 Hz, H-4″), 5.36 (d, 1 H, *J* = 8.6 Hz, H-1), 5.32 (dd, 1 H, *J* = 11.2, 3.1 Hz, H-3″), 5.23 (dd, 1 H, *J* = 11.2, 3.5 Hz, H-2″), 5.05 (d, 1 H, *J* = 3.5 Hz, H-1″), 4.88 (dd, 1 H, *J* = 11.6, 7.7 Hz, H-2′), 4.44 (d, 1 H, *J* = 7.7 Hz, H-1′), 4.21 (dd, 1 H, *J* = 10.6, 8.5 Hz, H-2), 2.29–2.19 (m, 1 H, CH_2CH), 2.14–1.94 (8 s, 3 H each, OAc), 1.92–1.78 (m, 1 H, H-3′), 1.08 (d, 3 H, *J* = 7.0 Hz, CH_3).

3-(Hexadecylthio)-2-[(hexadecylthio)methyl]propyl 3,6-Di-*O*-acetyl-2-deoxy-2-phthalimido-4-*O*-[2,6-di-*O*-acetyl-3-deoxy-3-*C*-methyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (80). Compound **79** (48 mg, 0.04 mmol), hexadecanethiol (40 μL, 0.12 mmol), and cesium carbonate (23 mg, 0.07 mmol) were suspended in dry *N*,*N*-dimethylformamide (0.05 mL) and the mixture was stirred at room temperature overnight. Hexadecanethiol (80 μL, 0.24 mmol) and cesium carbonate (46 mg, 0.14 mmol) were added, and the mixture was kept at room temperature for 4 h, diluted with dichloromethane (20 mL), washed with water (10 mL), dried, and concentrated. Column chromatography (SiO_2, EtOAc/heptane, 1:2) of the residue gave **80** (32 mg, 52%) as a syrup: $[\alpha]^{25}_D$ +33° (*c* 0.9, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.73 (dd, 1 H, *J* = 10.6, 8.3 Hz, H-3), 5.51 (dd, 1 H, *J* = 3.1, 1.2 Hz, H-4″), 4.33 (dd, 1 H, *J* = 8.4 Hz, H-1), 4.32 (dd, 1 H, *J* = 11.2, 3.1 Hz, H-3″), 5.23 (dd, 1 H, *J* = 11.2, 3.5 Hz, H-2″), 5.05 (d, 1 H, *J* = 3.6 Hz, H-1″), 4.80 (dd, 1 H, *J* = 11.4, 7.6 Hz, H-2′), 4.43 (d, 1 H, *J* = 7.7 Hz, H-1′), 4.20 (dd, 1 H, *J* = 10.6, 8.5 Hz, H-2), 2.47–2.29 (m, 4 H, $CHCH_2S$), 2.28–2.21 (m, 4 H, SCH_2CH_2), 2.14–1.93 (8 s, 3 H each, OAc), 1.92–1.80 (m, 1 H, H-3), 1.08 (d, 3 H, *J* = 6.9 Hz, $CHCH_3$), 0.88 (t, 6 H, *J* = 6.7 Hz, CH_2CH_3). Anal. Calcd for $C_{79}H_{125}NO_{24}S_2$: C, 61.7; H, 8.2. Found: C, 61.3; H, 8.4.

3-Bromo-2-(bromomethyl)propyl 2,3,6-Tri-*O*-acetyl-4-*O*-[2,4,6-tri-*O*-acetyl-3-*O*-[3,6-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-2-deoxy-2-phthalimido-β-D-glucopyranosyl]-β-D-galactopyranosyl]-β-D-glucopyranoside (82). $BF_3{\cdot}Et_2O$ (1.21 g, 8.52 mmol) was added to a cooled (0 °C), stirred solution of **81**[1] (771 mg, 0.57 mmol), and 3-bromo-2-(bromomethyl)propanol[5] (202 mg, 0.87 mmol) in dry dichloromethane (11 mL). The mixture was allowed to attain room temperature over a period of 2 h, chloroform was added, and the mixture was washed with saturated sodium hydrogen carbonate and water, dried, and concentrated. The residue was chromatographed (SiO_2, toluene/EtOAc, 1:1) to give **82** (388 mg, 45%): $[\alpha]^{25}_D$ +5° (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.71–7.82 (m, 4 H, aromatic), 5.70 (dd, 1 H, *J* = 8.8, 10.8 Hz, H-4″), 5.35 (d, 1 H, *J* = 8.2 Hz, H-1″), 4.59, 4.40, 4.28 (d, *J* = 7.8, 7.9, 8.0 Hz, H-1,1′,1‴), 2.19–1.81 (12 s, 36 H, $COCH_3$).

3-(Hexadecylthio)-2-[(hexadecylthio)methyl]propyl 2,3,6-Tri-*O*-acetyl-4-*O*-[2,4,6-tri-*O*-acetyl-3-*O*-[3,6-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-2-deoxy-2-phthalimido-β-D-glucopyranosyl]-β-D-galactopyranosyl]-β-D-glucopyranoside (83). A solution of **82** (325 mg, 0.21 mmol) and hexadecanethiol (217 mg, 0.84 mmol) in dry *N*,*N*-dimethylformamide (6.5 mL) was treated with cesium carbonate (205 mg, 0.63 mmol) under N_2 for 22 h at room temperature. The mixture was partitioned between ethyl ether and water. The organic extract was washed with four portions of water, dried, and concentrated. The residue was chromatographed (SiO_2, EtOAc/heptane, 1:1) to afford amorphous **83** (238 mg, 61%): $[\alpha]^{20}_D$ +6° (*c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.69 (dd, 1 H, *J* = 8.7, 10.8 Hz, H-3″), 5.34 (d, 1 H, *J* = 8.2 Hz, H-1″), 5.32 (dd, 1 H, *J* = 0.9 Hz, H-4′ or H-4‴), 5.29 (bd, 1 H, *J* = 4.1 Hz, H-4′ or H-4‴), 4.58, 4.37, 4.26 (d, *J* = 7.9, 7.9, 8.0 Hz, H-1,1′,1‴), 2.42–2.62 (m, 8 H, CH_2S), 2.18–1.80 (12 s, 36 H, $COCH_3$); ^{13}C NMR ($CDCl_3$) δ 170.6–168.6 (CO), 101.1, 100.9, 100.5, 97.4 (C-1,1′,1″,1‴), 62.0, 61.6, 60.6, 60.0 (C-6,6′,6″,6‴), 54.9 (C-2″). Anal. Calcd for $C_{92}H_{141}NO_{34}S_2$: C, 59.1; H, 7.6; N, 0.8. Found: C, 59.3; H, 7.7; N, 0.7.

3-(Hexadecylthio)-2-[(hexadecylthio)methyl]propyl 2,3,6-Tri-*O*-acetyl-4-*O*-[2,4,6-tri-*O*-acetyl-3-*O*-[2-acetamido-3,6-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-2-deoxy-β-D-glucopyranosyl]-β-D-galactopyranosyl]-β-D-glucopyranoside (84). A solution of **83** (200 mg, 0.11 mmol) and hydrazine hydrate (2 mL) in aqueous 90% ethanol (15 mL) was heated at reflux for 16 h. The mixture was concentrated, water was added and removed, and pyridine was added and removed four times. The residue was acetylated in pyridine/acetic anhydride (10 mL, 1:1) at room temperature for 1.5 h and then at 50 °C for 3 h. The mixture was concentrated, and toluene was added and removed from the residue three times. The yellow, syrupy residue was partitioned between chloroform and aqueous 5% hydrochloric acid. The organic phase was washed with water, saturated sodium hydrogen carbonate, and water, dried, and concentrated. The residue was chromatographed (SiO_2, EtOAc/heptane, 3:1) to give **84** (150 mg, 78.5%): $[\alpha]^{20}_D$ +6° (*c* 0.6, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.32 (d, 1 H, *J* = 9.0 Hz, $NHCOCH_3$), 4.67 (d, 1 H, *J* = 8.2 Hz, H-1″), 4.54, 4.44, 4.33 (d, *J* = 7.9, 8.1, 8.1 Hz, H-1,1′,1‴), 2.63–2.42 (m, 8 H, CH_2S), 2.15–1.90 (12 s, 39 H, $COCH_3$). Anal. Calcd for $C_{86}H_{141}NO_{33}S_2$: C, 58.0; H, 8.0; N, 0.8. Found: C, 58.1; H, 8.0; N, 0.7.

Benzyl 4,6-*O*-Benzylidene-α-D-glucopyranoside (85). D-Glucose (36 g, 0.2 mol) was suspended in toluene (500 mL) containing benzyl alcohol (250 mL, 2.4 mol) and *p*-toluenesulfonic acid monohydrate (0.5 g). The mixture was heated at reflux for 21 h with continuous removal of water, cooled to room temperature, and filtered through solid sodium hydrogen carbonate. The filtrate was partitioned between diethyl ether and water. The organic phase was extracted twice with water, and the combined aqueous phase was washed twice with diethyl ether and concentrated to give crude benzyl D-glucopyranoside (21.3 g), which was then stirred with α,α-dimethoxytoluene (49 g) and *p*-toluenesulfonic acid monohydrate (320 mg) in acetonitrile (250 mL) for 75 min at room temperature. Triethylamine (0.9 mL) was added, the mixture was concentrated, and the residue was crystallized from ethanol to give **85** (6.3 g). Chromatography of the mother liquor (SiO_2, EtOAc/heptane, 1:1 → 2:1) gave benzyl 4,6-*O*-benzylidene-β-D-glucopyranoside (4.7 g) and a second fraction containing **85** (3.9 g). The total yield of **85** was 10.2 g (36% from benzyl D-glucopyranoside): mp 161.5–163 °C (EtOH); $[\alpha]^{20}_D$ +99° (*c* 1.2, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.53 (s, 1 H, PhCH), 5.02 (d, 1 H, *J* = 4 Hz, H-1), 4.78 4.57 (AB q, 2 H, *J* = 11.5 Hz, $PhCH_2$), 3.97 (t, 1 H, *J* = 9 Hz, H-3), 3.64 (dd, 1 H, *J* = 9, 4 Hz, H-2), 3.51 (t, 1 H, *J* = 9 Hz, H-4).

Benzyl 2,6-Di-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranoside (86). A sample of **85** was acetylated in pyridine/acetic anhydride (1:1) at room temperature for 27 h, and the reaction mixture was then concentrated. The residue was repeatedly co-concentrated with toluene, and the residue was crystallized from methanol to give **86**: mp 107–109 °C; $[\alpha]^{20}_D$ +104° (*c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.65 (t, 1 H, *J* = 10 Hz, H-3), 5.50 (s, 1 H, PhCH), 5.12 (d, 1 H, *J* = 4 Hz, H-1), 4.90 (dd, 1 H, *J* = 10, 4 Hz, H-2), 4.76, 4.56 (AB q, 2 H, *J* = 12 Hz, $PhCH_2$), 3.65 (t, 1 H, *J* = 10 Hz, H-4).

Benzyl 2,3-Anhydro-4,6-*O*-benzylidene-α-D-mannopyranoside (87). To a stirred suspension of sodium hydride (60% in mineral oil, 4.4 g, 110 mmol) in *N*,*N*-dimethylformamide (250 mL) was added a solution of **85** (17.9 g, 50 mmol) in *N*,*N*-dimethylformamide (100 mL). The mixture was stirred for 2 h, and (*p*-tolylsulfonyl)imidazole (12.3 g, 55 mmol) was added. The stirring was continued for 1 h, and the reaction mixture was poured on ice–water (500 mL) and extracted three times with diethyl ether/dichloromethane (5:1; 600, 300, and 125 mL). The combined organic extract was washed with saturated aqueous sodium chloride (25 mL), dried, filtered, and concentrated. The residue was crystallized from methanol to give **87** (12.1 g, 72%): mp 127–129 °C; $[\alpha]^{20}_D$ +98° (*c* 1.1, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.57 (s, 1 H, PhCH), 5.12 (s, 1 H, H-1), 4.81, 4.65 (AB q, 2 H, *J* = 11.5 Hz, $PhCH_2$), 3.50 (d, 1 H, *J* = 3.5 Hz, H-2 or H-3), 3.24 (d, 1 H, *J* = 3.5 Hz, H-2 or H-3).

Benzyl 2-*O*-Acetyl-4,6-*O*-benzylidene-3-deoxy-3-*C*-methyl-α-D-altropyranoside (88). To a suspension of **87** (15.5 g, 45.5 mmol) in diethyl ether (1 L) was added a solution of methylmagnesium chloride in tetrahydrofuran (3.0 M, 150 mL, 450 mmol), and the mixture was heated at reflux under nitrogen for 5 days. The reaction mixture was then slowly concentrated by allowing diethyl ether to boil off through a hypodermic needle during 3 days. The progress of the reaction was monitored by TLC (SiO_2, EtOAc/heptane, 2:3). The mixture was diluted with diethyl ether (750 mL), saturated aqueous ammonium chloride solution (60 mL) was carefully added, and the mixture was filtered

and concentrated to give crude **89** (15.9 g). The crude product was acetylated in pyridine/acetic anhydride (400 mL, 5:3) at room temperature for 18 h, the mixture was concentrated, and the residue was crystallized from methanol to give **88** (14.1 g). Chromatography (SiO_2, EtOAc/heptane, 1:3) and crystallization of the mother liquor gave additional **88**: total yield of **88** 15.4 g (85%); mp 123–125 °C; $[\alpha]^{20}_D$ +95° (*c* 1.3, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.60 (s, 1 H, PhCH), 4.91 (dd, 1 H, *J* = 2.5, 1 Hz, H-2), 4.77 (s, 1 H, H-1), 4.75, 4.53 (AB q, 2 H, *J* = 12 Hz, $PhCH_2$), 2.43–2.32 (m, 1 H, H-3), 1.32 (d, 3 H, *J* = 7.5 Hz, CH_3).

Benzyl 4,6-*O*-Benzylidene-3-deoxy-3-*C*-methyl-α-D-altropyranoside (89). Compound **88** (18.4 g, 46 mmol) was suspended in methanol (750 mL), and methanolic sodium methoxide (0.2 M, 5 mL) was added. The mixture was stirred at room temperature for 20 h (during which time a clear solution was obtained), neutralized by rapid filtration through a short column of Duolite C-26 (H^+) resin, and concentrated. The residue was chromatographed (SiO_2, EtOAc/heptane, 2:3 → 1:1) to give **89** (15.2 g, 92%): mp 104.5–106.5 °C (toluene/heptane); $[\alpha]^{20}_D$ +124° (*c* 1.4, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.59 (s, 1 H, PhCH), 4.79 (d, 1 H, *J* = 1 Hz, with virtual coupling, H-1), 4.77, 4.51 (AB q, 2 H, *J* = 12 Hz, $PhCH_2$), 3.85 (dd, 1 H, *J* = 2, 1 Hz, H-2), 2.46–2.34 (m, 1 H, H-3), 1.27 (d, 3 H, *J* = 7.5 Hz, CH_3). Anal. Calcd for $C_{21}H_{24}O_5$: C, 70.8; H, 6.7. Found: C, 70.7; H, 6.8.

Benzyl 4,6-*O*-Benzylidene-3-deoxy-3-*C*-methyl-α-D-*ribo*-hexopyranosid-2-ulose (90). A solution of trifluoroacetic anhydride (9.0 mL, 63.7 mmol) in dichloromethane (25 mL) was added dropwise during 15 min to a stirred and cooled (−65 °C) solution of methyl sulfoxide (5.93 mL, 84.3 mmol) in dichloromethane (90 mL). A solution of **89** (15.2 g, 42.7 mmol) in dichloromethane (145 mL) was then added during 40 min while keeping the temperature of the reaction mixture at approximately −60 °C. Stirring was continued for 1.5 h, and triethylamine (17 mL, 122 mmol) was added. The reaction mixture was allowed to attain room temperature during 1 h and was then diluted with diethyl ether (1 L) and washed with aqueous hydrochloric acid (4 × 125 mL), saturated aqueous sodium hydrogen carbonate, water, and saturated aqueous sodium chloride. The mixture was dried, filtered, and concentrated to give crude, crystalline **90** (15.2 g). An analytical sample was crystallized from diethyl ether/heptane: mp 76–77 °C; $[\alpha]^{20}_D$ +98° (*c* 1.2, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.57 (s, 1 H, PhCH), 4.82 (bs, 1 H, H-1), 4.81, 4.66 (AB q, 2 H, *J* = 12 Hz, $PhCH_2$), 3.10 (pentet, 1 H, *J* = 7 Hz, H-3), 1.43 (d, 3 H, *J* = 7.5 Hz, CH_3).

Benzyl 4,6-*O*-Benzylidene-3-deoxy-3-*C*-methyl-α-D-*arabino*-hexopyranosid-2-ulose (91). Crude **90** (14.2 g, 40.1 mmol) was stirred with triethylamine (25 mL) in *N*,*N*-dimethylformamide (85 mL) for 20 h at room temperature. The reaction mixture was then partitioned between dichloromethane and water, and the organic phase was washed with water, dried, filtered, and concentrated to give crude **91** (13.8 g). Recrystallization from ethanol (600 mL) gave **91** (11.4 g, 80% from **89**): mp 163–165 °C; $[\alpha]^{20}_D$ +98° (*c* 1.1, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.52 (s, 1 H, PhCH), 4.84 (s, 1 H, H-1), 4.82, 4.65 (AB q, 2 H, *J* = 12 Hz, $PhCH_2$), 3.45 (dd, 1 H, *J* = 11.5, 9 Hz, H-4), 3.12 (dq, 1 H, *J* = 11.5, 6.5 Hz, H-3), 1.22 (d, 3 H, *J* = 6.5 Hz, CH_3).

Benzyl 4,6-*O*-Benzylidene-3-deoxy-3-*C*-methyl-2-oximido-α-D-*arabino*-hexopyranoside (92). Hydroxylamine hydrochloride (35 g, 0.5 mol) and sodium hydroxide (17 g, 0.43 mol) were dissolved in water (200 mL), and the pH was adjusted to 7.0 with aqueous sodium hydroxide (5 M). A solution of **91** (12.0 g, 33.9 mmol) in methanol (1.1 L) was added. The mixture was heated to reflux temperature which gave an essentially clear solution that was cooled to room temperature. Water was added, and methanol was evaporated at reduced pressure. The aqueous residue was extracted twice with dichloromethane, and the combined organic phase was washed with water, dried, filtered, and concentrated to give a quantitative yield of **92**. An analytical sample was crystallized from toluene: mp 159–160.5 °C; $[\alpha]^{20}_D$ +88° (*c* 1.1, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 6.07 (s, 1 H, H-1), 5.54 (s, 1 H, PhCH), 4.81, 4.68 (AB q, 2 H, *J* = 12 Hz, $PhCH_2$), 3.36 (dd, 1 H, *J* = 11, 9 Hz, H-4), 2.97 (dq, 1 H, *J* = 11, 6.5 Hz, H-3), 1.23 (d, 3 H, *J* = 6.5 Hz, CH_3).

Benzyl 4,6-*O*-Benzylidene-3-deoxy-3-*C*-methyl-2-(benzoyloximido)-α-D-*arabino*-hexopyranoside (93). A solution of benzoyl chloride (11 mL, 94.6 mmol) in pyridine (50 mL) was added during 10 min to a stirred solution of compound **92** (13.0 g, 35.5 mmol) in pyridine (200 mL) at 0 °C, and the mixture was allowed to attain room temperature. After 3 h, the mixture was partitioned between ice–water and dichloromethane. The organic phase was washed with water, dried, filtered, and concentrated. The residue was crystallized from ethanol (550 mL) to give **93** (12.4 g, 74%): mp 159–160.5 °C; $[\alpha]^{20}_D$ +114° (*c* 1.3, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.75–7.26 (15 H, aromatic H), 6.00 (s, 1 H, H-1), 5.58 (s, 1 H, PhCH), 4.85, 4.71 (AB q, 2 H, *J* = 12 Hz, $PhCH_2$), 3.48 (dd, 1 H, *J* = 11, 9 Hz, H-4), 3.19 (dq, 1 H, *J* = 11, 6.5 Hz, H-3), 1.44 (d, 3 H, *J* = 6.5 Hz, CH_3). Anal. Calcd for $C_{28}H_{29}NO_5$: C, 71.0; H, 5.7; N, 3.0. Found: C, 71.1; H, 5.7; N, 3.0.

Benzyl 4,6-*O*-Benzylidene-3-deoxy-3-*C*-methyl-α-D-glucopyranoside (94). Compound **91** (8.7 g, 24.6 mmol) was suspended in dry diethyl ether (450 mL), and lithium aluminum hydride (0.93 g, 24.6 mmol) was added. The mixture was stirred for 4 h at 0 °C, and water (1 mL), aqueous sodium hydroxide (15%, 1 mL), and water (3 mL) were added.[25] The solid that was obtained was filtered off and washed with toluene. The filtrate was washed with water and saturated aqueous sodium chloride, dried, filtered, and concentrated to give crude **94** (7.26 g). Crystallization from toluene/heptane gave pure **94** (6.31 g, 74%): mp 157.2–157.6 °C; $[\alpha]^{20}_D$ +82° (*c* 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.51–7.31 (10 H, aromatic H), 5.00 (s, 1 H, PhCH), 4.93 (d, 1 H, *J* = 4.0 Hz, H-1), 4.81–4.56 (AB q, 2 H, *J* = 11.5 Hz, $PhCH_2$), 3.37 (dd, 1 H, *J* = 10.5, 4.0 Hz, H-2), 2.12–1.98 (m, 1 H, H-3), 1.20 (d, 3 H, *J* = 6.5 Hz, CH_3).

Benzyl 2-*O*-Benzoyl-4,6-*O*-benzylidene-3-deoxy-3-*C*-methyl-α-D-glucopyranoside (95). Compound **94** (2.0 g, 5.6 mmol) was dissolved in dry dichloromethane (25 mL) and pyridine (1.8 mL). Benzoyl chloride (1.3 mL, 11.2 mmol) was added dropwise with stirring at 0 °C, and the mixture was allowed to attain room temperature. When **94** had been consumed, water (ca. 2 mL) was added, and the mixture was stirred for 15 min, diluted with dichloromethane, washed with dilute aqueous hydrochloric acid, water, and saturated aqueous sodium hydrogen carbonate, dried, filtered, and concentrated. The crude material was crystallized from methanol to give pure **95** (1.65 g, 64%): mp 118.5–119.5 °C; $[\alpha]^{22}_D$ +119° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 8.10–7.14 (15 H, aromatic H), 5.60 (s, 1 H, PhCH), 5.13 (d, 1 H, *J* = 3.5 Hz, H-1), 4.87 (dd, 1 H, *J* = 11.5, 3.5 Hz, H-2), 4.78, 4.56 (AB q, 2 H, *J* = 12.5 Hz, $PhCH_2$), 2.68–2.53 (m, 1 H, H-3), 1.15 (d, 3 H, *J* = 7 Hz, CH_3).

Benzyl 2-*O*-Benzoyl-6-*O*-benzyl-3-deoxy-3-*C*-methyl-α-D-glucopyranoside (96). Saturated etheral hydrogen chloride was added at room temperature to a mixture of **95** (2.0 g, 4.3 mmol), sodium cyanoborohydride (3.3 g, 52.4 mmol), and powdered molecular sieve (3 Å, 3.5 g) in dry tetrahydrofuran (80 mL). The addition was discontinued when the solution became acidic (pH paper). The reaction was monitored by TLC (SiO_2, EtOAc/heptane, 1:1), and when **95** had been consumed, dichloromethane was added. The mixture was filtered, washed with saturated aqueous sodium hydrogen carbonate and saturated aqueous sodium chloride, dried, filtered, and concentrated. The residue was chromatographed (SiO_2, EtOAc/heptane, 1:4) to give **96** (1.57 g, 79%): syrup; $[\alpha]^{20}_D$ +107° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 8.15–7.15 (15 H, aromatic H), 5.42 (d, 1 H, *J* = 3.5 Hz, H-1), 4.80 (dd, 1 H, *J* = 2, 3.5 Hz, H-2), 4.75, 4.55 (AB q, 2 H, *J* = 12.5 Hz, $PhCH_2$), 4.64, 4.56 (AB q, 2 H, *J* = 12 Hz, $PhCH_2$), 2.44–2.29 (m, 1 H, H-3), 1.14 (d, 3 H, *J* = 7 Hz, CH_3). Anal. Calcd for $C_{28}H_{30}O_6$: C, 72.7; H, 6.5. Found: C, 72.0; H, 6.6.

Benzyl 2-Acetamido-4,6-*O*-benzylidene-2,3-dideoxy-3-*C*-methyl-α-D-glucopyranoside (97). A solution of diborane in tetrahydrofuran (1 M, 200 mL) was added to a cooled (0 °C) solution of **93** (4.73 g, 10 mmol) in tetrahydrofuran (50 mL) under nitrogen. The mixture was allowed to attain room temperature, and the stirring was continued for 16 h. Methanol (160 mL) was added followed by acetic anhydride (40 mL). After being stirred for 1.5 h, the reaction mixture was concentrated and then repeatedly co-concentrated with methanol followed by co-concentration twice with toluene to give crude **97**. Crystallization from ethanol (500 mL) gave **97** (3.3 g, 83%): mp 260–263 °C; $[\alpha]^{20}_D$ +85° (*c* 1.1, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.63 (d, 1 H, *J* = 10 Hz,

(25) Fieser, L. F.; Fieser, M. *Reagents for organic synthesis*; Wiley: New York, 1967; Vol. 1, p 583.

NH), 5.54 (s, 1 H, PhCH), 4.78 (d, 1 H, J = 3 Hz, H-1), 4.77, 4.49 (AB q, 2 H, J = 12 Hz, $PhCH_2$), 4.12–4.03 (m, 1 H, H-2), 3.30 (dd, 1 H, J = 10.5, 9.5 Hz, H-4), 2.15–1.95 (m, 1 H, H-3), 1.98 (s, 3 H, CH_3CO), 1.06 (d, 3 H, J = 6.5 Hz, CH_3). Anal. Calcd for $C_{23}H_{27}NO_5$: C, 69.5; H, 6.8; N, 3.5. Found: C, 69.8; H, 7.2; N, 3.6.

Benzyl 2-Acetamido-6-*O*-benzyl-2,3-dideoxy-3-*C*-methyl-α-D-glucopyranoside (98). Compound **97** (3.35 g, 8.4 mmol) was dissolved in tetrahydrofuran (200 mL), and molecular sieve (3 Å, 11 g) and sodium cyanoborohydride (2.9 g, 46 mmol) were added. A saturated solution (18 mL) of hydrogen chloride in diethyl ether was added during 15 min. The mixture was stirred for 1 h, and sodium cyanoborohydride (0.4 g) and saturated ethereal hydrogen chloride (3 mL) were added. The stirring was continued for 45 min, and the reaction mixture was filtered and partitioned between dichloromethane (500 mL) and water (100 mL). The aqueous phase was extracted twice with dichloromethane (100 and 50 mL), and the combined organic phase was washed with water (50 mL) and saturated aqueous sodium chloride, dried, filtered, and concentrated. The residue was chromatographed (SiO_2, EtOAc/MeOH, 40:1), and the product was crystallized from ethyl acetate to give **98** (2.05 g, 61%): mp 172.5–174.5 °C (toluene); $[\alpha]^{20}_D$ +98° (c 1.2, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.40–7.27 (10 H, aromatic H), 5.50 (d, 1 H, J = 9.5 Hz, NH), 4.75 (d, 1 H, J = 3.5 Hz, H-1), 4.74, 4.47 (AB q, 2 H, J = 11.5 Hz, $PhCH_2$), 4.62, 4.55 (AB q, 2 H, J = 12.0 Hz, $PhCH_2$), 3.96 (ddd, 1 H, J = 11.5, 9.5, 3.5 Hz, H-2), 3.81–3.71 (2 H, H-5, H-6), 3.67–3.60 (m, 1 H, H-6), 3.39 (t, 1 H, J = 9.5 Hz, H-4), 2.83 (bs, 1 H, OH), 1.95 (s, 3 H, CH_3CO), 1.90–1.75 (m, 1 H, H-3), 1.05 (d, 3 H, J = 6.5 Hz, CH_3). Anal. Calcd for $C_{23}H_{29}NO_5$: C, 69.2; H, 7.3; N, 3.5. Found: C, 69.1; H, 7.4; N, 3.5.

Benzyl 2-Acetamido-4-*O*-acetyl-6-*O*-benzyl-2,3-dideoxy-3-*C*-methyl-α-D-glucopyranoside (99). A sample of **98** was acetylated in a mixture of acetic anhydride and pyridine (1:1) for 2.5 h at room temperature. The temperature was raised to 50 °C, and the mixture was stirred for 1.5 h. Co-concentration of the mixture with toluene and ethanol followed by crystallization from ethanol gave **99**: mp 159.8–160.3 °C; $[\alpha]^{20}_D$ +114° (c 1.2, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.50 (d, 1 H, J = 10 Hz, NH), 4.81 (d, 1 H, J = 3.5 Hz, H-1), 4.79 (t, 1 H, J = 10 Hz, H-4), 4.79, 4.49 (AB q, 2 H, J = 11.5 Hz, $PhCH_2$), 4.54 (s, 2 H, $PhCH_2$), 2.05–1.89 (m, 1 H, H-3), 1.96, 1.95 (s, 3 H each, CH_3CO), 0.90 (d, 3 H, J = 6.5 Hz, CH_3).

Benzyl 2-*O*-Benzoyl-6-*O*-benzyl-3-deoxy-3-*C*-methyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-D-glucopyranoside (100). A solution of **96** (0.92 g, 2.0 mmol), tetramethylurea (0.79 mL, 6.6 mmol), and silver trifluoromethanesulfonate (1.54 g, 6.0 mmol) in dry dichloromethane (20 mL) was cooled to −65 °C, and acetobromogalactose (2.1 g, 5.0 mmol) in dry dichloromethane (5 mL) was added dropwise. The mixture was protected from light and was allowed to slowly attain room temperature. After being stirred for 16 h, the reaction mixture was partitioned between dichloromethane and saturated aqueous sodium hydrogen carbonate, and both phases were filtered through Celite. The aqueous phase was extracted with dichloromethane, and the combined organic phase was washed with saturated aqueous sodium chloride, dried, filtered, and concentrated. Chromatography (SiO_2, EtOAc/toluene, 20:3) gave amorphous **100** (1.17 g, 74%): $[\alpha]^{22}_D$ +63° (c 1.1, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 8.1–7.1 (15 H, aromatic H), 5.29 (dd, 1 H, J = 3.5, 1.0 Hz, H-4′), 5.13 (d, 1 H, J = 3.5 Hz, H-1), 5.07 (dd, 1 H, J = 10.5, 8.0 Hz, H-2′), 4.80 (dd, 1 H, J = 11.5, 3.5 Hz, H-2), 4.75 (dd, 1 H, J = 10.5, 3.5 Hz, H-3′), 3.36 (d, 1 H, J = 8.0 Hz, H-1′), 2.44–2.28 (m, 1 H, H-3), 1.08 (d, 3 H, J = 6.5 Hz, CH_3). Anal. Calcd for $C_{42}H_{48}O_{15}$: C, 63.6; H, 6.1. Found: C, 63.7; H, 6.3.

1,6-Di-*O*-acetyl-2-*O*-benzoyl-3-deoxy-3-*C*-methyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-D-glucopyranose (101). Compound **100** (0.5 g, 0.66 mmol) was hydrogenolyzed (H_2, Pd/C, 10%, 250 mg) in acetic acid (100 mL) for 2 h. The catalyst was filtered off, and the filtrate was co-concentrated with toluene. The residue was acetylated using acetic anhydride/pyridine (1:2, 7.5 mL) for 4 h at room temperature. The mixture was co-concentrated with toluene and chromatographed (SiO_2, EtOAc/heptane, 4:1) to give amorphous **101** (434 mg, 94.5%, 1-α/1-β 1:1): ^1H NMR ($CDCl_3$) δ 6.29 (d, J = 3.5 Hz, H-1$_\alpha$), 5.76 (d, J = 8.5 Hz, H-1$_\beta$).

Benzyl 2-Acetamido-6-*O*-benzyl-2,3-dideoxy-3-*C*-methyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α/β-D-galactopyranosyl)-α-D-glucopyranoside (102). A solution of **98** (200 mg, 0.5 mmol), tetramethylurea (120 mg, 1.0 mmol), and silver trifluoromethanesulfonate (230 mg, 0.9 mmol) in dichloromethane (4 mL) was cooled to −78 °C, and solid acetobromogalactose (308 mg, 0.75 mmol) was added. The mixture was protected from light. After being stirred for 16 h at room temperature, the reaction mixture was partitioned between dichloromethane and saturated aqueous sodium hydrogen carbonate. The aqueous phase was extracted with dichloromethane, and the combined organic phase was washed with water and saturated aqueous sodium chloride, dried, filtered, and concentrated. The residue was chromatographed (SiO_2, EtOAc/heptane, 3:1) to give **102** (295 mg, 80%) as a mixture of 1′-anomers (1′-α/1′-β, 1:6): ^1H NMR ($CDCl_3$, 1′-β isomer) δ 5.45 (d, 1 H, J = 10 Hz, NH), 5.27 (dd, 1 H, J = 3.5, 1 Hz, H-4′), 5.05 (dd, 1 H, J = 10.5, 8 Hz, H-2′), 4.79 (d, 1 H, J = 12 Hz, PhCH), 4.79 (d, 1 H, J = 4.5 Hz, H-1), 4.75 (dd, 1 H, J = 10.5, 3.5 Hz, H-3′), 4.71 (d, 1 H, J = 12 Hz, PhCH), 4.50 (d, 1 H, J = 12 Hz, $PhCH_2$), 4.42 (d, 1 H, J = 12 Hz, $PhCH_2$), 4.36 (d, 1 H, J = 8 Hz, H-1′), 2.12, 2.05, 1.97, 1.95, 1.94 (s, 3 H each, CH_3CO) 1.90–1.75 (m, 1 H, H-3), 1.00 (d, 3 H, J = 7 Hz, CH_3).

2-Acetamido-1,6-di-*O*-acetyl-2,3-dideoxy-3-*C*-methyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α/β-D-galactopyranosyl)-α/β-D-glucopyranose (103). The disaccharide mixture **102** (2.1 g, 2.88 mmol) was hydrogenolyzed (H_2, 40 psi, Pd/C, 10%, 500 mg) in acetic acid (10 mL) at room temperature for 3.5 h, and the mixture was filtered and concentrated. The residue was acetylated with acetic anhydride/pyridine (1:1, 100 mL) for 24 h at room temperature followed by co-concentration with toluene. The residue was chromatographed (SiO_2, $CHCl_3$/MeOH, 30:1) to give **103** (1.71 g, 94%) as an anomeric mixture (1-α/1-β, 1:2 and 1′-α/1′-β, 1:6): ^1H NMR ($CDCl_3$, 1′-β isomer) δ 5.96 (d, 1 H, J = 3.5 Hz, H-1$_\alpha$), 5.54 (d, 1 H, J = 8.5 Hz, H-1$_\beta$), 1.13 (d, 3 H, J = 6.5 Hz, CH_3CH_β), 1.09 (d, 3 H, J = 6.5 Hz, CH_3CH_α).

2-Methyl-[4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-6-*O*-acetyl-3-deoxy-3-*C*-methyl-α-D-glucopyrano][2′,1′:4,5]-2-oxazoline (104). A mixture of **103** (800 mg, 1.26 mmol), acetic acid (2.2 mL), acetic anhydride (0.2 mL), and zinc chloride (1.2 g, 8.8 mmol) in 1,2-dichloroethane (45 mL) was heated at reflux for 3.25 h and then cooled and partitioned between ice-cold saturated aqueous sodium hydrogen carbonate and dichloromethane. The aqueous phase was extracted once with dichloromethane, and the combined organic phase was washed with saturated aqueous sodium hydrogen carbonate, dried, filtered, and concentrated to give **104** (749 mg: 1′-α/1′-β, 1:6) containing traces of starting material. This material was used without purification in the glycosidation leading to the DIB glycoside **30**. Compound **104** had: ^1H NMR ($CDCl_3$, 1′-β isomer) δ 5.85 (d, 1 H, J = 7.5 Hz, H-1), 5.36 (dd, 1 H, J = 3.5, 1 Hz, H-4′), 5.19 (dd, 1 H, J = 10.5, 8 Hz, H-2′), 4.97 (dd, 1 H, J = 10.5, 3.5 Hz, H-3′), 4.50 (d, 1 H, J = 8 Hz, H-1′), 2.16, 2.11, 2.04, 1.97 (s, 3 H each), and 2.05 (s, 6 H), 1.18 (d, 3 H, J = 7.5 Hz, CH_3CH).

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Supplementary Material Available: ^1H and/or ^{13}C NMR spectra for compounds **3**, **4**, **7**, **11**, **12**, **15**, **19**, **21**, **23**, **24**, **26**, **27**, **29**, **33**, **45**, **54**, **56**, **60**, **62**, **70–74**, **77**, **79**, **82**, **87**, **88**, **90**, **94**, **95**, **99**, and **102–104** (39 pages). Ordering information is given on any current masthead page.