Restriction of Conformation in Galabiosides Via an $O^6-O^{2'}$-Methylene Bridge†

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Treatment of 2-(trimethylsilyl)ethyl 2,3-di-*O*-acetyl-4-*O*-(3,4,6-tri-*O*-acetyl-α-D-galactopyranosyl)-*β*-D-galactopyranoside (**12**) and 2-(trimethylsilyl)ethyl 2,3-di-*O*-benzyl-*β*-D-glucopyranoside (**15**) with the novel reagent combination formaldehyde diphenylmercaptal−*N*-iodosuccinimide−trifluoromethanesulfonic acid [$(PhS)_2CH_2$/NIS/TfOH], gave the corresponding 6,2′-*O*- and 4,6-*O*-methylidene acetals **13** and **16** in 52% and 53% yield, respectively. Deacetylation of **13** gave 2-(trimethylsilyl)ethyl 4-*O*-α-D-galactopyranosyl-*β*-D-galactopyranoside (**1**). The conformation of **1** was similar to that of the non-acetalated parent glycoside.

Introduction

Galabiose (Galα1-4Gal) is an integral part of a number of biologically important glycolipids of the globo series.[1] These glycolipids function *inter alia* as adhesion receptors for bacterial surface (pilus) proteins and toxins, as summarized in a recent publication from our laboratory.[2] Our current research is directed toward the development of efficient water soluble inhibitors of bacterial adhesion, based on the structural motifs found in the naturally occurring glycolipids.[3]

Oligosaccharides and their analogs are subject to enzymic hydrolysis. Therefore it can be anticipated that their half-life *in vivo* is decreased, which reduces their potential as bacterial adhesion inhibitors. Various methods to avoid enzymic hydrolysis have been suggested, such as substitution of the intersaccharidic oxygen atom by a sulfur atom (S-glycosides) or a methylene group (C-glycosides). While this seems to work in some cases,[4] the inhibitory function can be severely impaired. For example, a thiogalabioside of the above-mentioned type was 30 times less efficient than the parent compound in inhibiting the binding of purified bacterial pilus protein to covalently immobilized galabiose and globotriose.[5]

An alternative method for stabilizing the intersaccharidic glycosidic bond might be by formation of a bridge between the monosaccharide units. It is important that the overall shape of the bioactive epitope of such a molecule is conserved and that the bridge does not interfere sterically with the binding site of the receptor. The intersaccharidic bridge would in such cases introduce a conformational bias and even contribute to the stability of the saccharide−receptor complex by a favorable entropic factor.

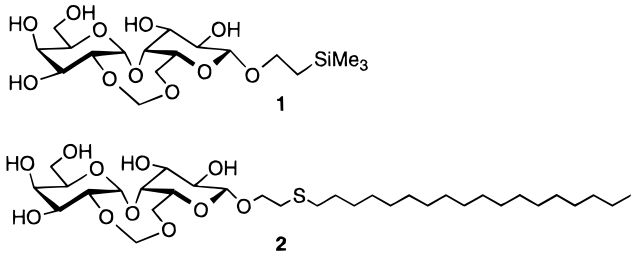

Figure 1.

All galabiose-containing oligosaccharides studied so far, including most of the synthetic analogs, have very similar conformations,[6] with the two galabiose-derived hydroxyl groups HO-6 and HO-2′ situated close together. The presence of an intramolecular hydrogen bond between these two hydroxyls was determined by NMR.[5,6] It occurred to us that a methylene bridge might be an acceptable substitute for the hydrogen bond and that the bioactive conformation of galabiose would not be severely altered. Furthermore, formaldehyde acetals are much more stable than, for example, acetone acetals.[7] However, as discussed below, the binding efficacy of the bridged compound to bacterial receptor proteins was reduced, despite reasonable conservation of the overall conformation.

Methods for the creation of saccharide analogs with a stable intersaccharidic bridge seem to be available only for ganglioside lactams.[8] We now report the formation of a methylene bridge (Figure 1) between two closely situated hydroxyl groups, using the novel reagent combination $(PhS)_2CH_2$/NIS/TfOH.

Synthesis of Methylene-Bridged Galabiosides. The synthesis of the bridged disaccharide **1** was envisioned either via bridge-formation in a suitably semiprotected galabioside, or by intramolecular glycoside

† Dedicated to Professor Hans Paulsen on the occasion of his 75th birthday.

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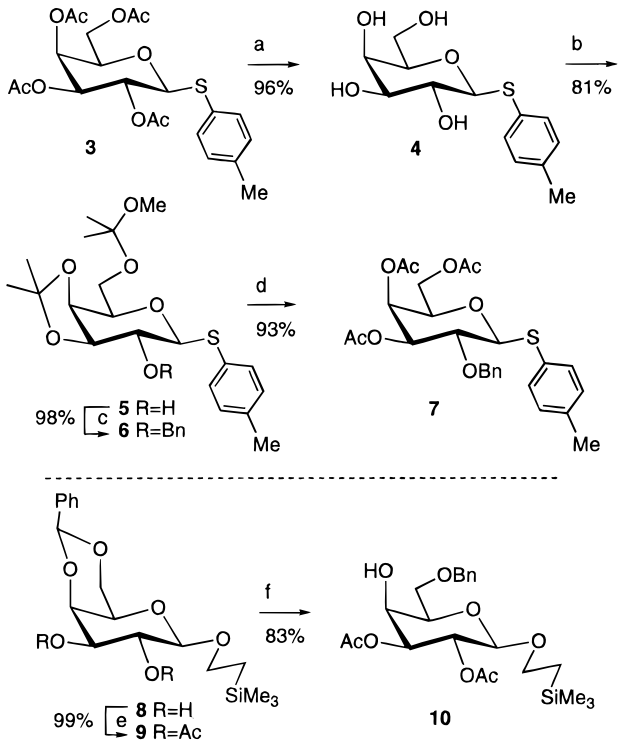
Scheme 1



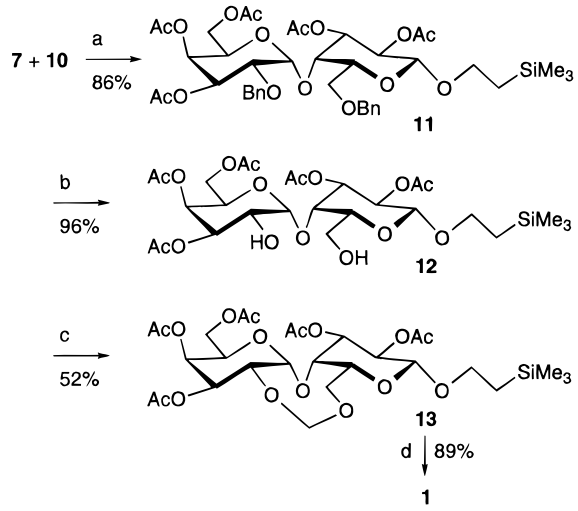
Legend: (a) MeONa, MeOH. (b) $(MeO)_2CMe_2$, *p*-TsOH. (c) NaH, BnBr, DMF, Ar, 22 °C, 3.5 h. (d) Aqueous AcOH, 90 °C, 90 min, then Ac_2O, pyridine, 15 h. (e) Ac_2O, pyridine. (f) $NaCNBH_3$, molecular sieves 4 Å, THF, $HCl{\cdot}Et_2O$, 22 °C.

formation of two methylene-linked galactose residues. The former route was chosen because we already had considerable experience of galabiose chemistry, and we considered it to be a more general route, potentially useful for other oligosaccharides. The 2-(trimethylsilyl)-ethyl (TMSEt) group was chosen for anomeric protection, due to its easy and high-yielding removal toward the end of a synthesis.[9]

Synthesis of the building blocks needed for assembly of **11** was performed via rather traditional, high-yielding reactions, as shown in Scheme 1. Thus, the galactosyl donor **7** was prepared from the known[10] thioglycoside **3**, deacetylation of which (→**4**; 96%) and isopropylidenation[9] of the product with 2,2-dimethoxypropane/PTSA gave **5** (81%) having only position 2 unprotected. Benzylation of **5** (→**6**; 98%), followed by removal of the isopropylidene groups and acetylation of the liberated hydroxyls, gave the glycosyl donor **7** (93%). Acetylation of the known[9] 4,6-*O*-benzylidene acetal **8** (→**9**; 99%), followed by reductive opening[11] of the benzylidene ring, gave the glycosyl acceptor **10** (83%).

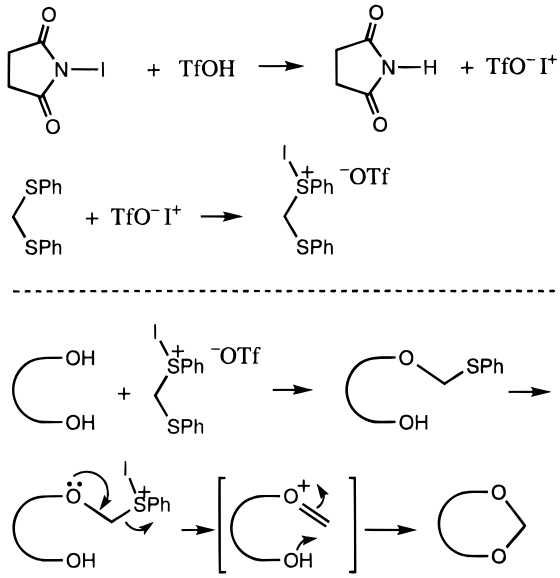
The glycosyl acceptor **10** was α-galactosylated with the donor **7** under activation with *N*-iodosuccinimide/trifluoromethanesulfonic acid,[12] giving the TMSEt-galabioside **11** (86%). No corresponding *β*-glycoside was isolated. Hydrogenolysis of the two benzyl groups of **11** gave **12**

Scheme 2



Legend: (a) NIS, molecular sieves 300 AW, Et_2O, CH_2Cl_2, Ar, −45 °C, TfOH. (b) H_2, Pd/C, AcOH, 22 °C, 17 h. (c) $(PhS)_2CH_2$, molecular sieves 300 AW, MeCN, CH_2Cl_2, Ar, −35 °C, NIS, TfOH, 3.8 h. (d) MeONa, MeOH.

Scheme 3. Reasonable Route from Diols to Formaldehyde Acetals, Using the Reagent Combination $(PhS)_2CH_2$/NIS/TfOH



(96%), with HO-6 and HO-2′ exposed for methylidenation (Scheme 2).

Standard acid-catalyzed activation of dimethoxymethane[13] (or formaldehyde) in the presence of **12** failed to produce the bridged saccharide **13**; only a mixture of the corresponding 6-*O*-methoxymethyl and 6,2′-*O*-bis-(methoxymethyl) derivatives was obtained in low (∼20%) yield. In contrast, activation of formaldehyde diphenylmercaptal by *N*-iodosuccinimide and trifluoromethanesulfonic acid [$(PhS)_2CH_2$/NIS/TfOH], essentially as in the glycosylation reaction described above, gave a reactive species that converted **12** into the 9-membered ring methylene-bridged galabioside **13** (52%). The novel methylidenation reaction is supposed to proceed via the intermediates depicted in Scheme 3. Removal of the acetyl groups of **13** gave the bridged TMSEt−galabioside **1** (89%).

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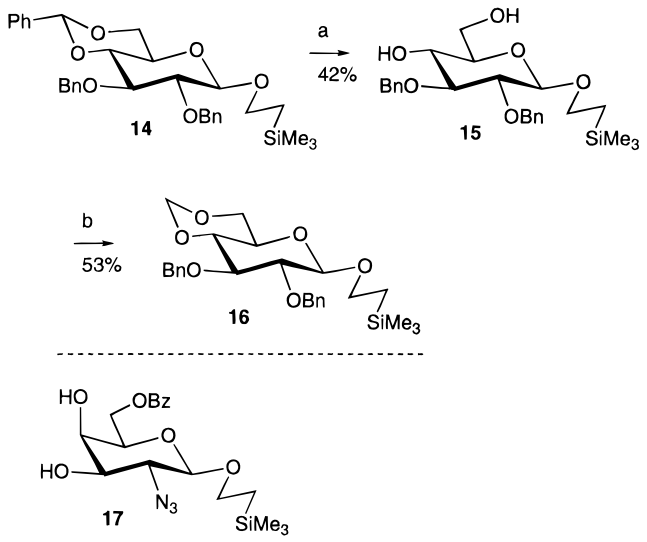
Scheme 4



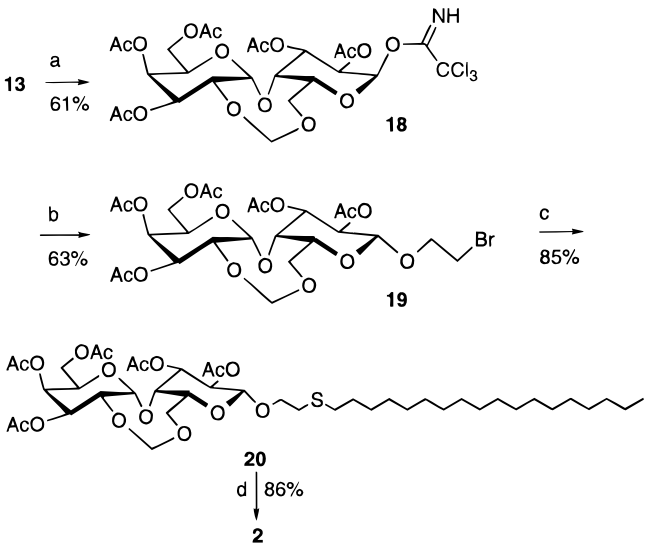
Legend: (a) Aqueous AcOH, 90 °C, 3 h. (b) $(PhS)_2CH_2$, molecular sieves 300 AW, MeCN, CH_2Cl_2, Ar, −35 °C, NIS, TfOH, 3.8 h.

Possible ring-size limitations of the methylidenation reaction were investigated using the diols **15** and **17** (Scheme 4). Compound **15** was obtained by hydrolysis (in unexpectedly low yield; 42%) of the known[9] 4,6-*O*-benzylidene acetal **14**. Treatment of **15** under the methylidenation conditions described provided the 4,6-*O*-methylidene acetal **16** (53%), whereas attempted methylidenation of the vicinal diol **17**[8b] failed; only degraded starting material was obtained after prolonged reaction. The outcome of these two attempts can be explained by the so-called Baldwin rules, stating that a "6-*endo*-trig" mechanism is favored (cf. Scheme 3), whereas a "5-*endo*-trig" mechanism is disfavored.[14]

It was rewarding to find that the 4,6-*O*-methylidene acetal **16** could be formed, since methods are scarce for conformational restriction of the hydroxymethyl group of pyranosidic hexoses, which is often desired in receptor studies with carbohydrates.[15] The methylidenation reaction described here introduces minimal steric bulk in the molecule, and formyl acetals are generally more stable against hydrolysis than other acetals.[13]

In addition to soluble glycosides (such as **1**) for use as inhibitors of proteins that bind to natural glycoconjugates,[16] well-defined neoglycolipids[17] are useful for coating of microtiter plates or for presentation on TLC plates. The TMSEt galabioside **13** was transformed into the neoglycolipid **2** (Scheme 5). Treatment of **13** with trifluoroacetic acid in dichloromethane[9] gave the corresponding hemiacetal (quantitative yield), which was converted without purification to the imidate[18] **18** (61%). Glycosylation of 2-bromoethanol with **18** gave the 2-bromoethyl glycoside **19** (63%), treatment of which with

Scheme 5



Legend: (a) CF_3COOH, CH_2Cl_2, 22 °C, 30 min, and then CCl_3CN, DBU, 0 °C, 1 h. (b) $HOCH_2CH_2Br$, $BF_3{\cdot}Et_2O$, CH_2Cl_2, 0 °C, Ar, 50 min. (c) $C_{18}H_{37}SH$, Cs_2CO_3, DMF, Ar, 22 °C, 20 h. (d) MeONa, MeOH, CH_2Cl_2, 22 °C, 90 min.

octadecanethiol and cesium carbonate in DMF[19] gave the glycolipid **20** (85%). Removal of the acetyl groups of **20** furnished the neoglycolipid **2** (86%).

Conformation of Compound 1. Conformational analysis of a large number of galabiose-containing di→pentasaccharides and their derivatives (e.g., monodeoxy analogs) by X-ray crystallography,[20] NMR,[6] and computational methods[6] showed that they generally retain the overall shape of the parent compound (e.g., **B** in Figure 2). In short, they all show a strong NOE effect between H-4 and H-1′ of the galactose residues and, more importantly, a strong (∼0.5 ppm) downfield shift (compared to methyl α-D-galactopyranoside; **A** in Figure 2) of the ^{1}H-NMR signal for H-5′, due to the close proximity of H-5′ and O-3 in galabiosides. The downfield shift is absent in the 3-deoxy- and 3-C-methyl analogs of methyl *β*-galabioside.[6a]

The conformations of **1** and its parent compound **B** (Figure 2) were investigated by ^{1}H-NMR and molecular mechanics (MM3 force field)[21] calculations. The ^{1}H-NMR signal was deshielded in both compounds, 0.2 ppm for **1** and 0.58 ppm for **B**. The difference in deshielding indicates that the average H-5′−O-3 distance in **1** is somewhat longer than in **B**. Compound **1** had strong NOE contacts between one methylene-bridge hydrogen and both H-1′ and H-2′, which is in agreement with the calculated low-energy conformations (Figure 2).

Molecular mechanics calculations[21] of **1**, using reasonable starting conformations for the nine-membered ring, all converged to one of the two low-energy conformers shown in Figure 2. The conformers of lowest energy had a H-5′−O-3 distance of 2.7 and 3.1 Å and O_2CH_2−H-1′ and −H-2′ distances of 2.2−2.7 Å, respectively. These

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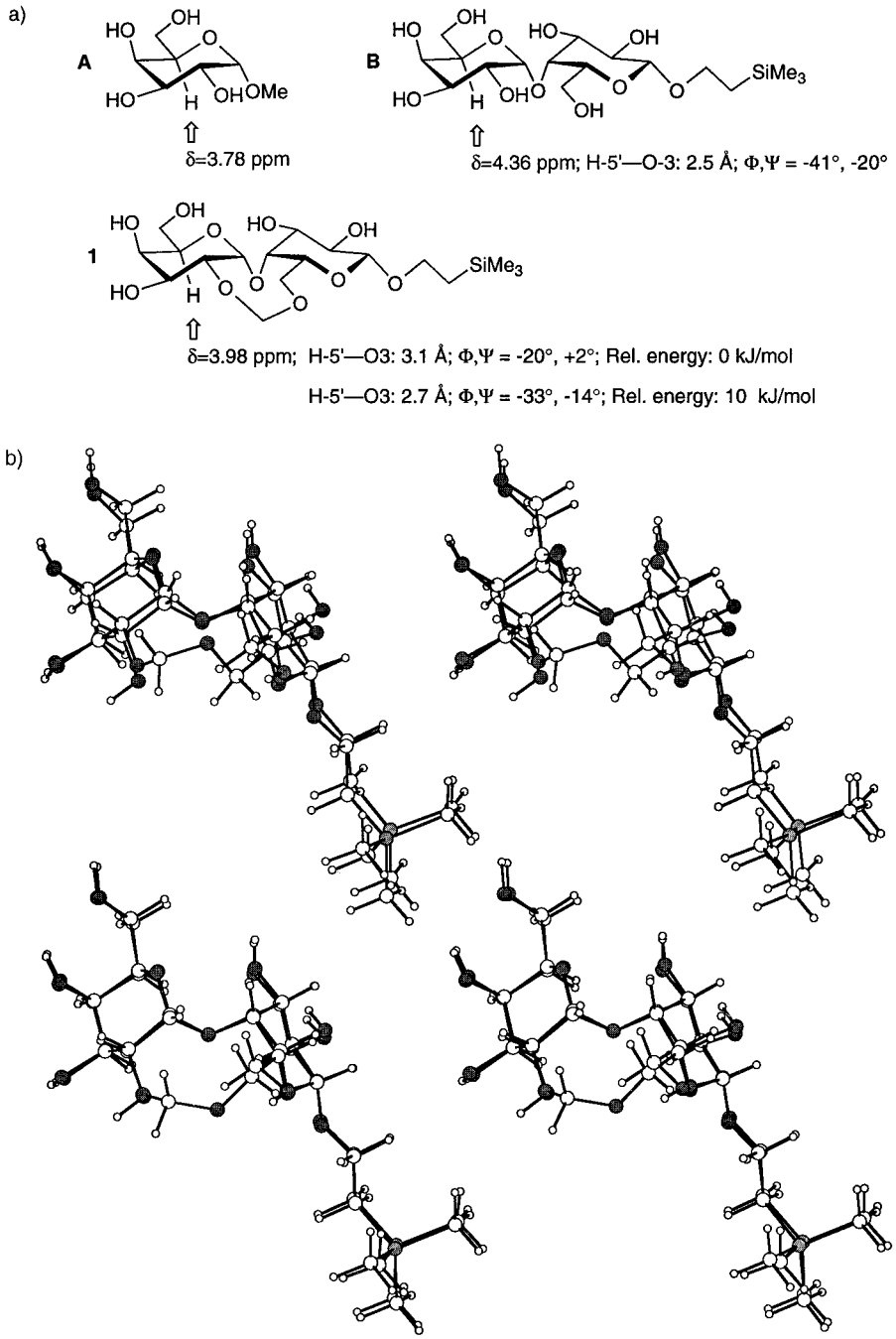

Figure 2. (a) H-5′ chemical shifts, calculated H-5′−O-3 distances, and calculated interglycosidic torsional angles (Φ,Ψ). (b) Stereorepresentation of the least-squares fit between low-energy conformations of compounds **1** and **B**; (top) lowest energy conformation of **1**; (bottom) next-lowest energy conformation of **1**.

distances agree[22] with the modest deshielding of H-5′ and the strong NOE contacts between O_2CH_2 and H-1′/H-2′. A comparison between the low-energy conformers of **1** and **B** was performed by a least-squares fit of the coordinates for all pyranose ring atoms (Figure 2).[21] The two low-energy conformers of **1** gave, in comparison with **B**, root mean square (RMS) values of 0.4 and 0.1 Å, respectively.

Recognition of 1 by Bacterial Proteins. Three bacterial proteins are known to use galabiose-containing glycolipids as attachment points for the infectious process: (i) the *Escherichia coli* pilus protein PapG in complex with its chaperone PapD;[23] (ii) Verotoxin[24] produced by enterotoxic *E. coli*; and (iii) the *Streptococcus suis* bacterium[25] that carries a galabiose-recognizing surface protein. A comparative binding study of the 6,2′-*O*-methylidene galabiosides **1** and **2** and of the parent, nonbridged, compound **B** was performed using the three bacterial proteins.

Attempted inhibition by **1** of binding of the PapG/PapD protein complex to a covalently anchored galabioside[5] failed, as expected, since the PapG protein requires the presence of intact HO-6 and HO-2′. Attempted binding

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of verotoxin[3e,24] to the neoglycolipid **2** was also unsuccessful for the same reason.

Compound **1** showed a reduced (compared with **B**), but still significant, inhibition of hemagglutination of *S. suis* bacteria (S. Haataja, J. Finne, M. Wilstermann, and G. Magnusson, unpublished results). *S. suis* uses HO-2, -3, -4′, and -6′ for binding to galabiosides but not HO-6, -2′, and -3′.[3d] Thus, the inhibitory efficiency of **1** is consistent with a slightly altered conformation, which carries the important hydroxyls somewhat differently positioned than in the efficient inhibitor **B**. The calculated (MM3) positional differences for HO-2, -3, -4′, and 6′, as measured in the least-squares-fitted low-energy conformations of **1** and **B** (Figure 2) were 0.7, 0.8, 0.2, and 1.0 Å and 0.2, 0.3, 0.1, and 0.4 Å, respectively.

We reported earlier that exchange of the intersaccharidic oxygen atom in compound **B** for a sulfur atom caused a 30-fold drop in inhibitory efficiency (PapG/PapD binding).[5] In the present investigation, introduction of the methylene bridge caused a similar decrease in inhibitor efficency of **1**, although the conformational change in the galabiose moiety was rather limited. This gives reason for contemplating the structural preciseness needed in the design of analogs of natural ligands.

Experimental Section

Melting points are uncorrected. NMR spectra were recorded at 500, 400, or 300 MHz. ^{1}H-NMR spectral assignments were made by the double-resonance techniques COSY, HETCOR, and TOCSY. Concentrations were made using rotary evaporation with bath temperature at or below 40 °C. TLC was performed on Kieselgel 60 F_{254} plates (Merck). Column chromatography was performed using SiO_2 (Matrex LC-gel: 60A, 35−70 MY, Grace). Compounds **3**,[10] **8**,[9] **14**,[9] and **17**[8b] were prepared essentially as described.

2-(Trimethylsilyl)ethyl 6,2′-*O*-Methylidene-4-*O*-α-D-galactopyranosyl-β-D-galactopyranoside (1). Sodium methoxide (1.1 M, 0.050 mL) was added to a solution of **13** (61 mg, 0.092 mmol) in dry MeOH (2.5 mL), and the mixture was stirred for 90 min and then neutralized with Duolite C-26 (H^+) resin, filtered, and concentrated. The residue was chromatographed (SiO_2, CH_2Cl_2/MeOH 6:1 + 0.1% Et_3N) to give **1** (37 mg, 89%); $[\alpha]^{22}_D$ +23 (*c* 0.5, H_2O); ^{1}H NMR data (D_2O), δ 5.12 (d, 1 H, *J* 4.5 Hz, H-1′), 4.79 (d, 1 H, *J* 7.5 Hz, OCH_2O), 4.75 (d, 1 H, *J* 7.5 Hz, OCH_2O), 4.28 (d, 1 H, *J* 7.9 Hz, H-1), 4.00−3.74 (m, 9 H), 3.63−3.58 (m, 3 H), 3.55 (dd, 1 H, *J* 10.1, 4.0 Hz, H-3), 3.33 (dd, 1 H, *J* 10.1, 7.9 Hz, H-2), 0.90 (m, 2 H, CH_2Si), −0.10 (s, 9 H, $SiMe_3$); ^{13}C NMR data (D_2O), δ 103.9, 102.4, 94.6, 84.0, 78.1, 73.2, 72.7, 72.1, 69.7, 69.2, 69.1, 64.0, 61.8, 18.4, −1.7; HRMS calcd for $C_{18}H_{34}O_{11}SiNa$ (M + Na), 477.1768; found, 477.1775.

2-(Octadecylthio)ethyl 6,2′-*O*-Methylidene-4-*O*-α-D-galactopyranosyl-β-D-galactopyranoside (2). Sodium methoxide (1.1 M, 0.013 mL) was added to a solution of **20** (23 mg, 0.026 mmol) in dry MeOH (1 mL) and dry CH_2Cl_2 (0.2 mL). After 90 min, aqueous acetic acid (0.040 mL, 0.87 M) was added, immediately followed by Et_3N (0.25 mL), and the mixture was concentrated. The residue was chromatographed (SiO_2, CH_2Cl_2/MeOH 8:1+0.1% Et_3N) to give **2** (15 mg, 86%); $[\alpha]^{23}_D$ +8 (*c* 1.0, $CHCl_3$/MeOH 1:1); ^{1}H NMR data ($CDCl_3$/CD_3OD 2:1), δ 5.09 (d, 1 H, *J* 4.4 Hz, H-1′), 4.82 (d, 1 H, *J* 7.2 Hz, OCH_2O), 4.75 (d, 1 H, *J* 7.2 Hz, OCH_2O), 4.18 (d, 1 H, *J* 7.5 Hz, H-1), 4.04 (t, 1 H, *J* 8.7 Hz), 3.96−3.60 (m, 11 H), 3.50 (dd, 1 H, *J* 10.0, 3.9 Hz, H-3), 3.42 (dd, 1 H, *J* 10.0, 7.4 Hz, H-2), 2.72 (t, 2 H, *J* 7.0 Hz, CH_2S), 2.51 (t, 2 H, *J* 7.4 Hz, SCH_2), 1.55 (m, 2 H), 1.37−1.16 (m, 30 H), 0.84 (t, 3 H, *J* 6.9 Hz, CH_3); ^{13}C NMR data ($CDCl_3$), δ 104.3, 103.2, 93.9, 84.1, 78.4, 73.0, 72.5, 72.0, 71.9, 69.7, 69.3, 62.7, 62.3, 32.6, 32.2, 31.6, 30.0−29.2, 23.0, 14.2; HRMS calcd for $C_{33}H_{62}O_{11}SNa$ (M + Na), 689.3911; found, 689.3914.

4-Methylphenyl 1-thio-β-D-galactopyranoside (4). Sodium methoxide (2 M, 3 mL) was added to a solution of **3**[10] (12.5 g, 28.6 mmol) in dry MeOH (120 mL). The mixture was stirred overnight and then neutralized with Duolite C-26 (H^+) resin, filtered, and concentrated to give **4** (7.90 g, 96%); $[\alpha]^{22}_D$ −65 (*c* 1.0, MeOH); ^{1}H NMR data (D_2O), δ 7.44 (m, 2 H, Ar), 7.21 (m, 2 H, Ar), 4.64 (d, 1 H, *J* 9.5 Hz, H-1), 3.93 (d, 1 H, *J* 3.2 Hz, H-4), 3.75−3.51 (m, 5 H), 2.28 (s, 3 H, CH_3); HRMS calcd for $C_{13}H_{19}O_5S$ (M + H), 287.0953; found, 287.0940.

4-Methylphenyl 3,4-*O*-Isopropylidene-6-*O*-(2-methoxyisopropyl)-1-thio-β-D-galactopyranoside (5). To a solution of **4** (7.85 g, 27.4 mmol) in 2,2-dimethoxypropane (280 mL) was added a catalytic amount of *p*-toluenesulfonic acid. The mixture was stirred for 20 h and then neutralized with Et_3N and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 2:1→1:1 + 0.2% Et_3N) to give **5** (8.81 g, 81%); $[\alpha]^{25}_D$ −10 (*c* 1.1, $CHCl_3$); ^{1}H NMR data ($CDCl_3$), δ 7.46 (m, 2 H, Ar), 7.12 (m, 2 H, Ar), 4.39 (d, 1 H, *J* 10.2 Hz, H-1), 4.19 (dd, 1 H, *J* 5.4, 2.1 Hz, H-4), 4.07 (dd, 1 H, *J* 6.9, 5.5 Hz, H-3), 3.86 (ddd, 1 H, *J* 7.1, 5.5, 2.2 Hz, H-5), 3.74 (dd, 1 H, *J* 9.8, 6.7 Hz, H-6), 3.67 (dd, 1 H, *J* 9.8, 5.5 Hz, H-6), 3.54 (dd, 1 H, *J* 10.2, 6.9 Hz, H-2), 3.23 (s, 3 H, OMe), 2.33 (s, 3 H, $PhCH_3$), 1.41, 1.38, 1.37, 1.33 (s, 3 H each, CCH_3); HRMS calcd for $C_{20}H_{30}O_8S$ (M), 398.1763; found, 398.1771.

4-Methylphenyl 2-*O*-Benzyl-3,4-*O*-isopropylidene-6-*O*-(2-methoxyisopropyl)-1-thio-β-D-galactopyranoside (6). To a solution of **5** (8.71 g, 21.9 mmol) in dry DMF (70 mL) under Ar was added sodium hydride (1.76 g, 44 mmol, 60% in mineral oil). The mixture was stirred for 1 h and then cooled to 0 °C, and benzyl bromide (5.2 mL, 44 mmol) was added dropwise. The mixture was left at room temperature for 3.5 h, and excess sodium hydride was destroyed by addition of MeOH (5 mL). The mixture was partitioned between ether and water, the aqueous phase was extracted with ether, and the combined organic phases were dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 3:1 + 0.2% Et_3N) to give **6** (10.5 g, 98%); $[\alpha]^{25}_D$ −13 (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$), δ 7.48−7.07 (m, 9 H, Ar), 4.81 (d, 1 H, *J* 11.4 Hz, CH_2Ph), 4.68 (d, 1 H, *J* 11.4 Hz, CH_2Ph), 4.58 (d, 1 H, *J* 9.7 Hz, H-1), 4.22 (m, 2 H), 3.82 (ddd, 1 H, *J* 7.0, 5.3, 1.9 Hz, H-5), 3.74 (dd, 1 H, *J* 9.8, 6.7 Hz, H-6), 3.67 (dd, 1 H, *J* 9.8, 5.5 Hz, H-6), 3.50 (dd, 1 H, *J* 9.7, 2.2 Hz, H-2), 3.19 (s, 3 H, OMe), 2.32 (s, 3 H, $PhCH_3$), 1.40, 1.36, 1.35, 1.34 (s, 3 H each, CCH_3); HRMS calcd for $C_{27}H_{36}O_6S$ (M), 488.2233; found, 488.2244.

4-Methylphenyl 3,4,6-Tri-*O*-acetyl-2-*O*-benzyl-1-thio-β-D-galactopyranoside (7). Compound **6** (10.3 g, 21.1 mmol) was dissolved in aqueous acetic acid (120 mL, 80%), and the mixture was kept at 90 °C for 90 min and then concentrated and co-concentrated with toluene. The residue was acetylated with acetic anhydride−pyridine (80 mL, 1:1) overnight. The mixture was concentrated and co-concentrated with toluene. The residue was chromatographed (SiO_2, heptane/EtOAc 2:1) to give **7** (9.9 g, 93%). An analytical sample was crystallized from heptane; mp 139−140 °C; $[\alpha]^{25}_D$ +8 (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$), δ 7.50−7.12 (m, 9 H, Ar), 5.40 (d, 1 H, *J* 3.3 Hz, H-4), 5.01 (dd, 1 H, *J* 9.6, 3.3 Hz, H-3), 4.86 (d, 1 H, *J* 11.0 Hz, CH_2Ph), 4.67 (d, 1 H, *J* 9.7 Hz, H-1), 4.58 (d, 1 H, *J* 11.0 Hz, CH_2Ph), 4.18 (dd, 1 H, *J* 11.2, 7.0 Hz, H-6), 4.10 (dd, 1 H, *J* 11.2, 6.3 Hz, H-6), 3.87 (t, 1 H, *J* 6.7 Hz, H-5), 3.72 (t, 1 H, *J* 9.7 Hz, H-2), 2.35 (s, 3 H, $PhCH_3$), 2.13, 2.04, 1.93 (s, 3 H each, OAc); ^{13}C NMR data ($CDCl_3$), δ 170.4, 170.1, 169.9, 138.1, 137.9, 132.8, 129.7, 129.3, 128.4, 127.9, 88.2, 75.5, 75.3, 74.2, 74.1, 67.7, 61.7, 21.2, 20.71, 20.70; HRMS calcd for $C_{26}H_{30}O_8SNa$ (M + Na), 525.1559; found, 525.1569.

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-acetyl-4,6-*O*-benzylidene-β-D-galactopyranoside (9). Compound **8**[9] (307 mg, 0.83 mmol) was acetylated with acetic anhydride/pyridine (20 mL, 1:1) overnight. The mixture was concentrated and co-concentrated with toluene, and the residue was chromatographed (SiO_2, heptane/EtOAc 1:1 + 0.1% Et_3N) to give **9** (371 mg, 99%); $[\alpha]^{25}_D$ +46 (*c* 1.1, $CHCl_3$); ^{1}H NMR data ($CDCl_3$), δ 7.55−7.35 (m, 5 H, Ar), 5.52 (s, 1 H, CHPh), 5.39 (dd, 1 H, *J* 10.4, 8.0 Hz, H-2), 4.97 (dd, 1 H, *J* 10.4, 4.7 Hz, H-3), 4.53 (d, 1 H, *J* 8.0 Hz, H-1), 4.40−4.32 (m, 2 H), 4.10−4.00 (m, 2 H), 3.61−3.51 (m, 2 H), 2.08, 2.06, (s, 3 H each, OAc), 0.97 (m, 2

H, CH_2Si), 0.01 (s, 9 H, $SiMe_3$); ^{13}C NMR data ($CDCl_3$), δ 170.9, 169.3, 137.5, 129.1, 128.2, 126.4, 101.1, 100.5, 73.5, 72.2, 69.0, 68.7, 66.8, 66.3, 20.9, 17.9, −1.4; HRMS calcd for $C_{22}H_{34}O_8SiNa$ (M + Na), 477.1920; found, 477.1915.

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-acetyl-6-*O*-benzyl-*β*-D-galactopyranoside (10). Compound **9** (6.94 g, 15.3 mmol), $NaCNBH_3$ (9.6 g, 153 mmol), and molecular sieves (7 g, 4 Å) were suspended in dry THF (160 mL). Saturated etheral HCl was added dropwise until the gas evolution ceased and TLC showed that **9** had been consumed. Solid $NaHCO_3$, CH_2Cl_2 (300 mL), and saturated aqueous $NaHCO_3$ (50 mL) were added, the mixture was filtered (Celite), and the phases were separated. The aqueous phase was extracted with CH_2Cl_2, and the combined organic phases were dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, toluene/EtOAc 5:1 → 3:1) to give **10** (5.78 g, 83%); $[\alpha]^{25}_D$ −9 (*c* 1.0, $CHCl_3$); ^1H NMR data ($CDCl_3$), δ 7.35−7.29 (m, 5 H, Ar), 5.25 (dd, 1 H, *J* 10.3, 7.9 Hz, H-2), 4.93 (dd, 1 H, *J* 10.3, 3.2 Hz, H-3), 4.60 (d, 1 H, *J* 11.1 Hz, CH_2Ph), 4.55 (d, 1 H, *J* 11.1 Hz, CH_2Ph), 4.46 (d, 1 H, *J* 7.9 Hz, H-1), 4.14 (brt, 1 H, *J* 3.7 Hz, H-5), 4.00 (m, 1 H), 3.82−3.67 (m, 3 H), 3.55 (dt, 1 H, *J* 9.9, 6.6 Hz, OCH_2), 2.09, 2.04, (s, 3 H each, OAc), 0.93 (m, 2 H, CH_2Si), 0.00 (s, 9 H, $SiMe_3$); ^{13}C NMR data ($CDCl_3$), δ 170.3, 169.5, 137.6, 128.5, 127.9, 127.8, 100.7, 73.8, 73.6, 73.1, 69.5, 69.1, 68.1, 67.2, 20.93, 20.87, 18.0, −1.4; HRMS calcd for $C_{22}H_{32}O_8SiNa$ (M + Na), 475.1764; found, 475.1773.

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-acetyl-6-*O*-benzyl-4-*O*-(3,4,6-tri-*O*-acetyl-2-*O*-benzyl-α-D-galactopyranosyl)-*β*-D-galactopyranoside (11). A mixture of **7** (1.44 g, 2.86 mmol), **10** (1.00 g, 2.20 mmol), molecular sieves (800 mg, AW 300), *N*-iodosuccinimide (742 mg, 3.30 mmol), dry Et_2O (60 mL), and dry CH_2Cl_2 (20 mL) was stirred at room temperature for 1 h under Ar and then cooled to −45 °C. Trifluoromethanesulfonic acid (0.029 mL, 0.33 mmol) was added to the cooled mixture. After 2.5 h, Et_3N (1 mL) was added, the mixture was filtered (Celite), diluted with CH_2Cl_2 and successively washed with saturated aqueous $Na_2S_2O_3$, saturated aqueous $NaHCO_3$, and water, dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, toluene/EtOAc 4:1→1:1) to give **11** (1.56 g, 86%); $[\alpha]^{25}_D$ +42 (*c* 0.9, $CHCl_3$); ^1H NMR data ($CDCl_3$), δ 7.32−7.22 (m, 10 H, Ar), 5.52 (dd, 1 H, *J* 3.4, 1.3 Hz, H-4′), 5.41 (dd, 1 H, *J* 10.6, 3.3 Hz, H-3′), 5.18 (dd, 1 H, *J* 10.6, 7.8 Hz, H-2), 4.89 (d, 1 H, *J* 4.0 Hz, H-1′), 4.86 (dd, 1 H, *J* 10.6, 2.9 Hz, H-3), 4.65 (d, 1 H, *J* 12.0 Hz, CH_2Ph), 4.57 (m, 2 H), 4.46 (d, 1 H, *J* 7.8 Hz, H-1), 4.32 (d, 1 H, *J* 11.8 Hz, CH_2Ph), 4.25 (d, 1 H, *J* 11.8 Hz, CH_2Ph), 4.18−4.12 (m, 2 H), 4.07 (dd, 1 H, *J* 10.8, 5.8 Hz, H-6′), 4.00 (m, 1 H), 3.86 (dd, 1 H, *J* 9.7, 6.0 Hz, H-6) 3.85 (dd, 1 H, *J* 10.5, 3.5 Hz, H-2′), 3.72 (t, 1 H, *J* 6.1 Hz, H-5′), 3.63 (dd, 1 H, *J* 9.8, 6.1 Hz, H-6), 3.54 (dt, 1 H, *J* 9.8, 6.8 Hz, OCH_2), 2.11, 2.05, 2.03, 1.98 (s, 3 H each, OAc), 0.97 (m, 2 H, CH_2Si), 0.02 (s, 9 H, $SiMe_3$); ^{13}C NMR data ($CDCl_3$), δ 171.1, 171.0, 170.5, 170.2, 169.5, 138.6, 138.5, 128.84, 128.77, 128.2, 128.1, 128.03, 128.00, 101.0, 100.8, 74.9, 74.2, 73.9, 73.7, 73.5, 70.2, 69.8, 68.9, 68.8, 67.5, 67.3, 61.2, 21.4, 21.24, 21.23, 21.13, 21.12, 18.4, −1.0; HRMS calcd for $C_{41}H_{56}O_{16}SiNa$ (M + Na), 855.3235; found, 855.3226.

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-acetyl-4-*O*-(3,4,6-tri-*O*-acetyl-α-D-galactopyranosyl)-*β*-D-galactopyranoside (12). Compound **11** (1.50 g, 1.82 mmol) was hydrogenated (H_2, Pd/C, 10%, 500 mg, 1 atm) in acetic acid (40 mL) overnight. The mixture was filtered (Celite) and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 1:2) to give **12** (1.14 g, 96%); $[\alpha]^{25}_D$ +84 (*c* 1.0, $CHCl_3$); ^1H NMR data ($CDCl_3$), δ 5.48 (dd, 1 H, *J* 3.3, 1.2 Hz, H-4′), 5.20 (m, 2 H), 4.94 (d, 1 H, *J* 3.1 Hz, H-1′), 4.84 (dd, 1 H, *J* 10.7, 2.9 Hz, H-3), 4.52 (d, 1 H, *J* 7.8 Hz, H-1), 4.51 (m, 1 H, H-5′), 4.30 (dd, 1 H, *J* 3.0, 1.0 Hz, H-4), 4.17 (dd, 1 H, *J* 10.9, 7.8 Hz, H-6′), 4.08 (dd, 1 H, *J* 10.8, 6.0 Hz, H-6′), 4.03−3.94 (m, 4 H), 3.85 (m, 1 H), 3.68 (m, 1 H, H-5), 3.55 (dt, 1 H, *J* 9.9, 6.2 Hz, OCH_2), 3.08 (brs, 1 H), 2.12, 2.08, 2.06, 2.05, 2.04 (s, 3 H each, OAc), 0.96 (m, 2 H, CH_2Si), 0.02 (s, 9 H, $SiMe_3$); ^{13}C NMR data ($CDCl_3$), δ 171.2, 171.03, 171.02, 170.6, 169.5, 102.5, 101.2, 78.4, 73.43, 73.42, 70.8, 69.4, 68.6, 68.2, 68.0, 61.4, 61.2, 21.32, 21.28, 21.2, 21.11, 21.09, 18.4, −1.0; HRMS calcd for $C_{27}H_{44}O_{16}SiNa$ (M + Na), 675.2296; found, 675.2293.

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-acetyl-6,2′-*O*-methylidene-4-*O*-(3,4,6-tri-*O*-acetyl-α-D-galactopyranosyl)-*β*-D-galactopyranoside (13). A mixture of **12** (50 mg, 0.077 mmol), formaldehyde diphenylmercaptal (21 mg, 0.092 mmol), molecular sieves (100 mg, AW 300), dry MeCN (1.7 mL), and dry CH_2Cl_2 (0.66 mL) was stirred at room temperature for 1 h under Ar, then cooled to −35 °C. To the cooled mixture was added dropwise a solution of *N*-iodosuccinimide (86 mg, 0.383 mmol) and trifluoromethanesulfonic acid (0.002 mL, 0.023 mmol) in dry MeCN (0.4 mL). After 3 h 50 min, Et_3N (0.05 mL) was added and the mixture was filtered (Celite), diluted with CH_2Cl_2, and successively washed with saturated aqueous $Na_2S_2O_3$, saturated aqueous $NaHCO_3$, and water, dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 1:1 + 0.1% Et_3N) to give **13** (26 mg, 52%); $[\alpha]^{22}_D$ +71 (*c* 1.0, $CHCl_3$); ^1H NMR data ($CDCl_3$), δ 5.52 (dd, 1 H, *J* 3.4, 1.1 Hz, H-4′), 5.32 (dd, 1 H, *J* 10.4, 3.4 Hz, H-3′), 5.18 (dd, 1 H, *J* 10.8, 7.6 Hz, H-2), 5.12 (d, 1 H, *J* 4.2 Hz, H-1′), 4.85 (dd, 1 H, *J* 10.8, 3.7 Hz, H-3), 4.78 (d, 1 H, *J* 7.2 Hz, OCH_2O), 4.72 (d, 1 H, *J* 7.2 Hz, OCH_2O), 4.43 (m, 1 H, H-5′), 4.41 (d, 1 H, *J* 7.6 Hz, H-1), 4.21−4.09 (m, 3 H), 4.00−3.91 (m, 4 H), 3.85 (dd, 1 H, *J* 9.5, 7.5 Hz, H-5), 3.50 (dt, 1 H, *J* 9.8, 6.6 Hz, OCH_2), 2.12, 2.10, 2.07, 2.05, 2.03 (s, 3 H each, OAc), 0.95 (m, 2 H, CH_2Si), 0.01 (s, 9 H, $SiMe_3$); ^{13}C NMR data ($CDCl_3$), δ 170.8, 170.5, 170.1, 169.9, 169.3, 103.9, 100.3, 93.0, 81.1, 74.9, 72.3, 69.2, 68.8, 67.9, 67.1, 66.7, 62.0, 60.8, 21.1, 20.9, 20.8, 20.7, 20.6, 17.9, −1.4; HRMS calcd for $C_{28}H_{44}O_{16}SiNa$ (M + Na), 687.2296; found, 687.2282.

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-benzyl-*β*-D-glucopyranoside (15). Compound **14**[9] (224 mg, 0.408 mmol) was dissolved in aqueous acetic acid (80%, 7.5 mL), and the mixture was kept at 90 °C for 3 h and then concentrated and co-concentrated with toluene. The residue was chromathographed (SiO_2, heptane/EtOAc 1:1) to give **15** (79 mg, 42%); $[\alpha]^{22}_D$ −21 (*c* 1, $CHCl_3$); ^1H NMR data ($CDCl_3$), δ 7.45−7.24 (m, 10 H, Ar), 4.99 (d, 1 H, *J* 11.0 Hz, CH_2Ph), 4.97 (d, 1 H, *J* 11.6 Hz, CH_2Ph), 4.74 (d, 1 H, *J* 11.1 Hz, CH_2Ph), 4.69 (d, 1 H, *J* 11.5 Hz, CH_2Ph), 4.48 (d, 1 H, *J* 7.4 Hz, H-1), 4.02 (m, 1 H, OCH_2), 3.93−3.74 (m, 2 H, H-6), 3.64 (m, 1 H, OCH_2), 3.56 (m, 1 H, H-4), 3.46 (t, 1 H, *J* 8.8 Hz, H-3), 3.44 (brt, 1 H, *J* 8.2 Hz, H-2), 3.35 (m, 1 H, H-5), 2.44 (d, 1 H, *J* 2.4 Hz, OH), 2.14 (t, 1 H, *J* 3.5 Hz, OH), 1.05 (m, 1 H, CH_2Si), 0.04 (s, 9 H, $SiMe_3$); ^{13}C NMR data ($CDCl_3$), δ 138.9, 138.8, 129.1, 128.9, 128.5, 128.4, 128.2, 103.8, 84.3, 82.4, 75.6, 75.2, 75.1, 70.8, 68.3, 63.1, 19.1, −1.0; HRMS calcd for $C_{25}H_{36}O_6SiNa$ (M + Na), 483.2179; found, 483.2165.

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-benzyl-4,6-*O*-methylidene-*β*-D-glucopyranoside (16). Compound **15** (40 mg, 0.087 mmol) was treated as descibed in the preparation of **13**. Column chromathography (SiO_2, heptane/EtOAc 8:1) gave **16** (22 mg, 53%); $[\alpha]^{22}_D$ +4 (*c* 1.0, $CHCl_3$); ^1H NMR data ($CDCl_3$), δ 7.39−7.25 (m, 10 H, Ar), 5.10 (d, 1 H, *J* 6.2 Hz, OCH_2O), 4.92 (d, 1 H, *J* 11.0 Hz, CH_2Ph), 4.89 (d, 1 H, *J* 11.4 Hz, CH_2Ph), 4.80 (d, 1 H, *J* 11.4 Hz, CH_2Ph), 4.76 (d, 1 H, *J* 11.0 Hz, CH_2Ph), 4.64 (d, 1 H, *J* 6.3 Hz, OCH_2O), 4.49 (d, 1 H, *J* 7.7 Hz, H-1), 4.23 (dd, 1 H, *J* 10.4, 4.8 Hz, H-6), 3.98 (m, 1 H, OCH_2), 3.68 (t, 1 H, *J* 9.0 Hz, H-3), 3.63 (m, 1 H, OCH_2), 3.51 (t, 1 H, *J* 10.2 Hz, H-6), 3.45−3.38 (m, 2 H, H-2,4), 3.32 (dt, 1 H, *J* 9.7, 4.5 Hz, H-5), 1.04 (dd, 2 H, *J* 9.3, 7.9 Hz, CH_2Si), 0.04 (s, 9 H, $SiMe_3$); ^{13}C NMR data ($CDCl_3$), δ 142.7, 138.5, 138.4, 129.1, 128.34, 128.30, 128.1, 127.9, 127.7, 127.6, 103.6, 93.6, 82.3, 81.4, 80.9, 75.3, 75.0, 68.6, 68.0, 66.2, 18.6, −1.4; HRMS calcd for $C_{26}H_{36}O_6SiNa$ (M + Na), 495.2179; found, 495.2180.

2,3-Di-*O*-acetyl-6,2′-*O*-methylidene-4-*O*-(3,4,6-tri-*O*-acetyl-α-D-galactopyranosyl)-α-D-galactopyranosyl Trichloroacetimidate (18). Compound **13** (100 mg, 0.150 mmol) was dissolved in CH_2Cl_2 (0.75 mL), trifluoroacetic acid (1.5 mL) was added,[9] and the mixture was stirred for 30 min. *n*-Propyl acetate (5 mL) and toluene (10 mL) were added, and the mixture was concentrated. The residue was dissolved in a mixture of dry CH_2Cl_2 (3 mL) and trichloroacetonitrile (0.485 mL, 4.8 mmol) at 0 °C under Ar. Diazabicycloundecane (DBU, 0.033 mL, 0.22 mmol) was added, and after 1 h the mixture was concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 1:1 + 0.1% Et_3N) to give **18** (65 mg, 61%); $[\alpha]^{22}_D$

+128 (*c* 1.0, $CHCl_3$); ^1H NMR data ($CDCl_3$), δ 8.62 (s, 1 H, NH), 6.63 (d, 1 H, *J* 3.4 Hz, H-1), 5.52 (dd, 1 H, *J* 3.7, 1.1 Hz, H-4′), 5.40 (dd, 1 H, *J* 11.2, 3.4 Hz, H-2), 5.33 (dd, 1 H, *J* 10.4, 3.4 Hz, H-3′), 5.28 (dd, 1 H, *J* 11.2, 3.5 Hz, H-3), 5.15 (d, 1 H, *J* 4.2 Hz, H-1′), 4.77 (d, 1 H, *J* 7.2 Hz, OCH_2O), 4.72 (d, 1 H, *J* 7.2 Hz, OCH_2O), 4.42 (m, 2 H), 4.36 (dd, 1 H, *J* 3.4, 1.8 Hz, H-4), 4.16 (dd, 1 H, *J* 10.8, 9.0 Hz), 4.08−4.02 (m, 2 H), 3.99 (dd, 1 H, *J* 10.4, 4.1 Hz, H-2′), 3.82 (dd, 1 H, *J* 9.8, 7.4 Hz, H-3′), 2.12, 2.10, 2.07, 2.05, 2.03 (s, 3 H each, OAc); ^{13}C NMR data ($CDCl_3$), δ 171.1, 170.8, 170.53, 170.51, 170.4, 161.4, 104.4, 94.3, 93.4, 81.6, 75.3, 71.0, 69.2, 69.1, 68.1, 67.5, 67.2, 62.2, 61.1, 21.7, 21.3, 21.13, 21.07; HRMS calcd for $C_{25}H_{32}O_{16}NCl_3Na$ (M + Na), 730.0684; found, 730.0675.

2-Bromoethyl 2,3-Di-*O*-acetyl-6,2′-*O*-methylidene-4-*O*-(3,4,6-tri-*O*-acetyl-α-D-galactopyranosyl)-*β*-D-galactopyranoside (19). Boron trifluoride etherate (0.0027 mL, 0.021 mmol) was added to a mixture of **18** (50 mg, 0.070 mmol), 2-bromoethanol (0.0075 mL, 0.106 mmol), and dry CH_2Cl_2 (1 mL) at 0 °C under Ar. After 50 min, the mixture was diluted with CH_2Cl_2, washed with saturated aqueous $NaHCO_3$, dried (Na_2SO_4), filtered, and concentrated. Column chromatography (SiO_2, heptane/EtOAc 1:1 + 0.1% Et_3N) gave **19** (30 mg, 63%); $[\alpha]^{25}_D$ +79 (*c* 1.0, $CHCl_3$); ^1H NMR data ($CDCl_3$), δ 5.51 (dd, 1 H, *J* 3.4, 1.1 Hz, H-4′), 5.32 (dd, 1 H, *J* 10.4, 3.4 Hz, H-3′), 5.22 (dd, 1 H, *J* 10.8, 7.7 Hz, H-2), 5.13 (d, 1 H, *J* 4.2 Hz, H-1′), 4.86 (dd, 1 H, *J* 10.8, 3.7 Hz, H-3), 4.78 (d, 1 H, *J* 7.2 Hz, OCH_2O), 4.73 (d, 1 H, *J* 7.2 Hz, OCH_2O), 4.49 (d, 1 H, *J* 7.7 Hz, H-1), 4.42 (m, 1 H), 4.21−4.05 (m, 4 H), 4.01−3.93 (m, 3 H), 3.86 (dd, 1 H, *J* 9.4, 7,2 Hz), 3.79 (dt, 1 H, *J* 11.0, 6.9 Hz, OCH_2), 3.48 (dd, 2 H, *J* 6.8, 5.6 Hz, CH_2Br), 2.12, 2.11, 2.10, 2.05, 2.04 (s, 3 H each, OAc); ^{13}C NMR data ($CDCl_3$), δ 171.1, 170.9, 170.5, 170.4, 169.9, 104.3, 101.3, 93.4, 81.2, 75.3, 73.0, 72.4, 69.5, 69.1, 68.2, 67.2, 62.4, 61.2, 30.6, 21.5, 21.34, 21.26, 21.13, 21.07; HRMS calcd for $C_{25}H_{35}O_{16}BrNa$ (M + Na), 693.1006; found, 693.0993.

2-(Octadecylthio)ethyl 2,3-Di-*O*-acetyl-6,2′-*O*-methylidene-4-*O*-(3,4,6-tri-*O*-acetyl-α-D-galactopyranosyl)-*β*-D-galactopyranoside (20). Compound **19** (30 mg, 0.045 mmol), octadecanethiol (25.6 mg, 0.090 mmol), and cesium carbonate (17.5 mg, 0.054 mmol) were dissolved in dry DMF (2 mL) under Ar. After 20 h, the mixture was diluted with ether, washed with water, dried (Na_2SO_4), filtered, and concentrated. Column chromatography (SiO_2, heptane/EtOAc 1:1 + 0.1% Et_3N) gave **20** (33.4 mg, 85%); $[\alpha]^{22}_D$ +56 (*c* 1.0, $CHCl_3$); ^1H NMR data ($CDCl_3$), δ 5.51 (brd, 1 H, *J* 2.5 Hz, H-4′), 5.32 (dd, 1 H, *J* 10.3, 3.4 Hz, H-3′), 5.20 (dd, 1 H, *J* 10.8, 7.7 Hz, H-2), 5.12 (d, 1 H, *J* 4.1 Hz, H-1′), 4.85 (dd, 1 H, *J* 10.7, 3.7 Hz, H-3), 4.78 (d, 1 H, *J* 7.2 Hz, OCH_2O), 4.73 (d, 1 H, *J* 7.2 Hz, OCH_2O), 4.46 (d, 1 H, *J* 7.7 Hz, H-1), 4.42 (m, 1 H, H-5′), 4.21−4.14 (m, 2 H), 4.10 (t, 1 H, *J* 8.9 Hz), 4.01−3.93 (m, 4 H), 3.85 (dd, 1 H, *J* 9.3, 7,2 Hz), 3.62 (dt, 1 H, *J* 10.1, 7.5 Hz, OCH_2), 2.70 (m, 2 H, CH_2S), 2.53 (t, 2 H, *J* 7.4 Hz, SCH_2), 2.12, 2.11, 2.09, 2.05, 2.04 (s, 3 H each, OAc), 0.89 (t, 3 H, *J* 6.8 Hz, CH_3); ^{13}C NMR data ($CDCl_3$), δ 171.1, 170.9, 170.5, 170.4, 169.8, 104.3, 101.2, 93.4, 81.4, 75.3, 72.9, 72.5, 69.5, 69.3, 69.2, 68.2, 67.1, 62.4, 61.2, 33.0, 32.3, 31.8, 30.2−29.3, 23.1, 21.5, 21.3, 21.2, 21.12, 21.06, 14.6; HRMS calcd for $C_{43}H_{72}O_{16}SNa$ (M + Na), 899.4439; found, 899.4425.

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Supporting Information Available: ^1H NMR spectra and ^1H NMR data with peak assignments for all title compounds described in the experimental section (16 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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