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

Zhiyuan Zhang and Göran Magnusson*

Organic Chemistry 2, Chemical Center, The Lund Institute of Technology, University of Lund, P. O. Box 124, S-221 00 Lund, Sweden

Received October 26, 1995[⊗]

Partially protected 2-(trimethylsilyl)ethyl 2- and 3-deoxyglucosides and 6-deoxylactoside were synthesised via various routes and glycosylated with galabiosyl and galactosyl donors to give the corresponding deoxytrisaccharides. Removal of the protecting groups gave the 2-(trimethylsilyl)-ethyl 2-, 3-, and 6-deoxyglobotriosides. Transformation of the protected trisaccharides into trichloroacetimidates, via the corresponding hemiacetals, proceeded in ∼80% overall yield. Glycosylation of 3-(hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]propanol with the trisaccharidic trichloroacetimidates, in 72−79% yield, followed by removal of protecting groups, gave the title neoglycolipids.

Introduction

Globotriose (Galα1−4Galβ1−4Glc) is present as globotriosylceramide (GbO_3, P^k antigen, CD77; Figure 1) on the outside of eucaryotic cells, where it plays important biological roles, as summarized in our previous publication on the synthesis of deoxyglobotriosides.[1]

The present publication describes the synthesis of the final three TMSEt deoxyglobotriosides and the corresponding neoglycolipids, where deoxygenations were performed in the reducing-end glucose moiety (compounds **1**, **3**, **5** and **2**, **4**, **6**, respectively, Figure 2). The corresponding deoxyglobotriose derivatives, where deoxygenations were performed in the non-reducing-terminal[2] and the central[1] galactose moieties, were reported earlier. The complete set of deoxyglobotriose derivatives constitutes, together with the parent compounds, a valuable collection of molecular probes useful for identification of binding epitopes in GbO_3-binding proteins. The collection of deoxytrisaccharides constitutes an addition to the deoxydisaccharides previously used by us for receptor mapping of surface adhesive proteins of pathogenic *Escherichia coli* and *Streptococcus suis* bacteria.[3]

Our bis-sulfone neoglycolipids[4] were designed to emulate the natural glycosyl ceramides (cf. Figure 1) and thereby constitute a standardized platform for the synthesis and biological evaluations of receptor-active saccharides and their analogs. We have recently shown that GbO_3-bis-sulfone neoglycolipid and its natural counterpart GbO_3-ceramide were equally effective binders of the bacterial protein verotoxin.[5]

Results and Discussion

I. Synthesis of the 2- and 3-Deoxyglucoside Acceptors 13 and 19. Glycosyl acceptors carrying an unprotected hydroxyl group in the 4-position are normally prepared by reductive ring-opening of the corresponding 4,6-*O*-benzylidene derivative, using sodium cyanoborohydride in the presence of hydrogen chloride or trifluoroacetic acid.[6] In order to avoid the strongly acidic conditions that are potentially harmful to glycosides, especially of deoxygenated sugars, we have developed an alternative method[7] based on oxidative cleavage of 4,6-*O*-*p*-methoxybenzylidene acetals under neutral or slightly acidic conditions. The cleavage is regioselective and leads preferentially to the corresponding 6-*O*-*p*-methoxybenzoate, leaving HO-4 unprotected for the ensuing glycosylation. In contrast to the 6-*O*-benzylated acceptors obtained by the reductive cleavage route, the oxidative route gives acylated acceptors, which often means that the overall synthetic scheme can be shortened by a hydrogenolysis and an ensuing acylation step. It seems as if this oxidative cleavage is the first generally useful route to fully acylated glycosyl acceptors.

2-(Trimethylsilyl)ethyl β-D-glucopyranoside[8] was treated with *p*-methoxy-α,α-dimethoxytoluene in the presence of a catalytic amount of *p*-toluenesulfonic acid to give the *O*-*p*-methoxybenzylidene-protected glycoside **7** (94%). Partial benzoylation of **7**, either directly with benzoyl chloride or via the stannylene derivative,[9] gave easily separated mixtures of mono and dibenzoylated compounds (**8**−**10**) in different ratios (Scheme 1).

The monobenzoates **8** and **9** were treated with thiocarbonyldiimidazole to give the thiocarbamates[10] **11** (93%) and **16** (94%). Reductive cleavage of the 2-thiocarbamoyl group of **11** with tributyltin hydride[11] proceeded in quantitative yields to give the 2-deoxy glucoside

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1996.

(1) Zhang, Z.; Magnusson, G. *J. Org. Chem.* **1995**, *60*, 7304−7315.
(2) Zhiyuan, Z.; Magnusson, G. *Carbohydr. Res.* **1994**, *262*, 79−101.
(3) (a) Kihlberg, J.; Hultgren, S. J.; Normark, S.; Magnusson, G. *J. Am. Chem. Soc.* **1989**, *111*, 6364−6368. (b) Haataja, S.; Tikkanen, K.; Nilsson, U.; Magnusson, G.; Karlsson, K.-A.; Finne, J. *J. Biol. Chem.* **1994**, *269*, 27466−27472. (c) Magnusson, G.; Hultgren, S. J.; Kihlberg, J. *Methods in Enzymolology*; Doyle, R. J.; Ofek, I., Eds.; Academic Press, San Diego, 1995; Vol. 253, pp 105−114. (d) Striker, R.; Nilsson, U.; Stonecipher, A.; Magnusson, G.; Hultgren, S.J. *Mol. Microbiol.* **1995**, *16*, 1021−1029. (e) Kihlberg, J.; Magnusson, G. *Pure Appl. Chem.*, in press.
(4) Magnusson, G.; Ahlfors, S.; Dahmén, J.; Jansson, K.; Nilsson, U.; Noori, G.; Stenvall, K.; Tjörnebo, A. *J. Org. Chem.* **1990**, *55*, 3933−3946.
(5) Boyd, B.; Magnusson, G.; Zhiuyan, Z.; Lingwood, C. A. *Eur. J. Biochem.* **1994**, *223*, 873−878.
(6) (a) Garegg, P. J.; Hultberg, H.; Wallin, S. *Carbohydr. Res.* **1982**, *108*, 97−101. (b) Johansson, R.; Samuelsson, B. *J. Chem. Soc. Perkin Trans.* 1 **1984**, 2371−2374.
(7) Zhang, Z.; Magnusson, G. *J. Org. Chem.* **1996**, *61*, 2394.
(8) Jansson, K.; Ahlfors, S.; Frejd, T.; Kihlberg, J.; Magnusson, G. *J. Org. Chem.* **1988**, *53*, 5629−5647.
(9) (a) David, S.; Hanessian, S. *Tetrahedron* **1985**, *41*, 643−663. (b) Ogawa, T.; Kaburagi, T. *Carbohydr. Res.* **1982**, *103*, 53−64.
(10) Rasmussen, J. R.; Slinger, C. J.; Kordish, R. J.; Newman-Evans, D. D. *J. Org. Chem.* **1981**, *46*, 4843−4846.
(11) Barton, D. H. R.; McCombie, S. W. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1574−1585.

0022-3263/96/1961-2383$12.00/0

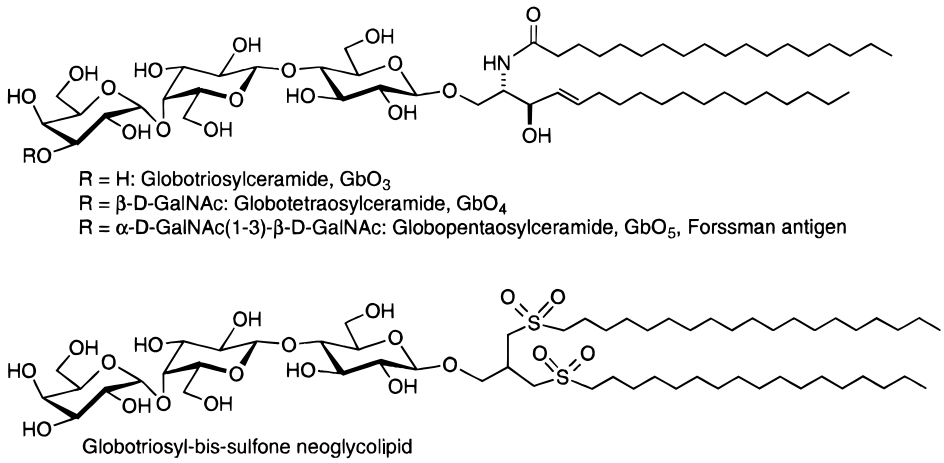


Figure 1. Structure of globotriosylceramide (GbO_3) and its double-chain bis-sulfone mimetic.

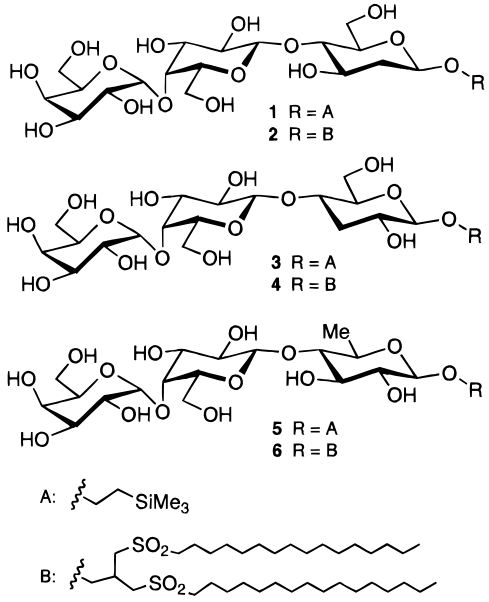


Figure 2. Structures of the synthetic deoxyglobotriosides.

12. According to TLC analysis, the reduction was equally efficient with compound **16**, but on chromatography of the reaction product consisting almost exclusively of **17**, the *p*-methoxybenzylidene group was partly removed to give **18**, probably due to the increased acid sensitivity introduced by the 3-deoxy function. This problem was circumvented by the addition of a small amount of triethylamine to the eluent. Treatment of **18** with *p*-methoxy-α,α-dimethoxytoluene as above restored the desired compound **17** (99%).

Regioselective oxidative cleavage of the *p*-methoxybenzylidene groups of **12** and **17** was performed by treatment with DDQ. Compound **12** gave a mixture of the 6- and 4-*O*-*p*-methoxybenzoates **13** and **14**, together with a small amount of **15** in the ratio 24:10:1, using DDQ and 0.2 equiv of acetic acid. It is known that acyl groups migrate on treatment with silver fluoride.[12] Treatment of **14** with silver nitrate/potassium fluoride gave a 3:1 mixture of **13** and **14**, and the pure glycosyl acceptor **13** was obtained in 69% yield. Treatment of **17** with DDQ in the absence of acetic acid gave a mixture of the 6- and 4-*O*-*p*-methoxybenzoates **19** and **20** in the ratio 3:2. Treatment of the crude mixture with silver nitrate/potassium fluoride caused the 4-*O*-*p*-methoxybenzoyl group to migrate to the 6-position, and the ratio of **19** and **20** changed to 14:1. Pure glycosyl acceptor **19** was obtained after chromatography in 85% yield from **17**.

II. Synthesis of the 6-Deoxylactoside acceptor 25. Since lactose is an integrated part of GbO_3, we decided to investigate the possibility of regioselective functionalization of the 6-position in the known[2] lactoside **21** (Scheme 2). If successful, one glycosylation step and several protection/deprotection steps would be avoided en route to 6-deoxy-GbO_3 derivatives. Thus, treatment of **21** with iodine/imidazole/triphenylphosphine[13] furnished the 6-deoxyiodolactoside **22** (80%) and hydrogenolysis of the carbon−iodine bond gave the 6-deoxylactoside **23** (92%). Treatment of **23** with benzoyl chloride and pyridine/DMAP gave the tetrabenzoate **24** (91%). Oxidative cleavage of the *p*-methoxybenzylidene group of **24** with DDQ essentially as above but with an excess of acetic acid, gave a mixture of the 6- and 4-*p*-methoxybenzoates **25** and **26** in the ratio 5:1. Pure 6-deoxylactoside acceptor **25** was obtained in 83% yield after chromatography.

III. Synthesis of the Galabiosyl Donors 36−38. Synthesis of glycosyl donors requires that the anomeric protecting group is compatible with the methods used in carbohydrate synthesis and that it can be transformed into suitable anomeric activating groups. The 2-(trimethylsilyl)ethyl (TMSEt) group fulfills most of these criteria in that it permits highly yielding and stereoselective transformations into the corresponding hemiacetal, 1-O-acyl, and chloro sugar.[8,14] As an alternative, we have investigated the *p*-methoxyphenyl glycosides and their conversion into various anomerically activated derivatives. It is known[15] that the *p*-methoxyphenyl group can be removed by treatment with ceric ammonium nitrate (CAN). In addition, we have found that *p*-methoxyphenyl glycosides can be converted directly into the corresponding chloro and bromo sugars as well as thioglycosides.

Galactose β-pentaacetate was treated with *p*-methoxyphenol in the presence of boron trifluoride etherate to

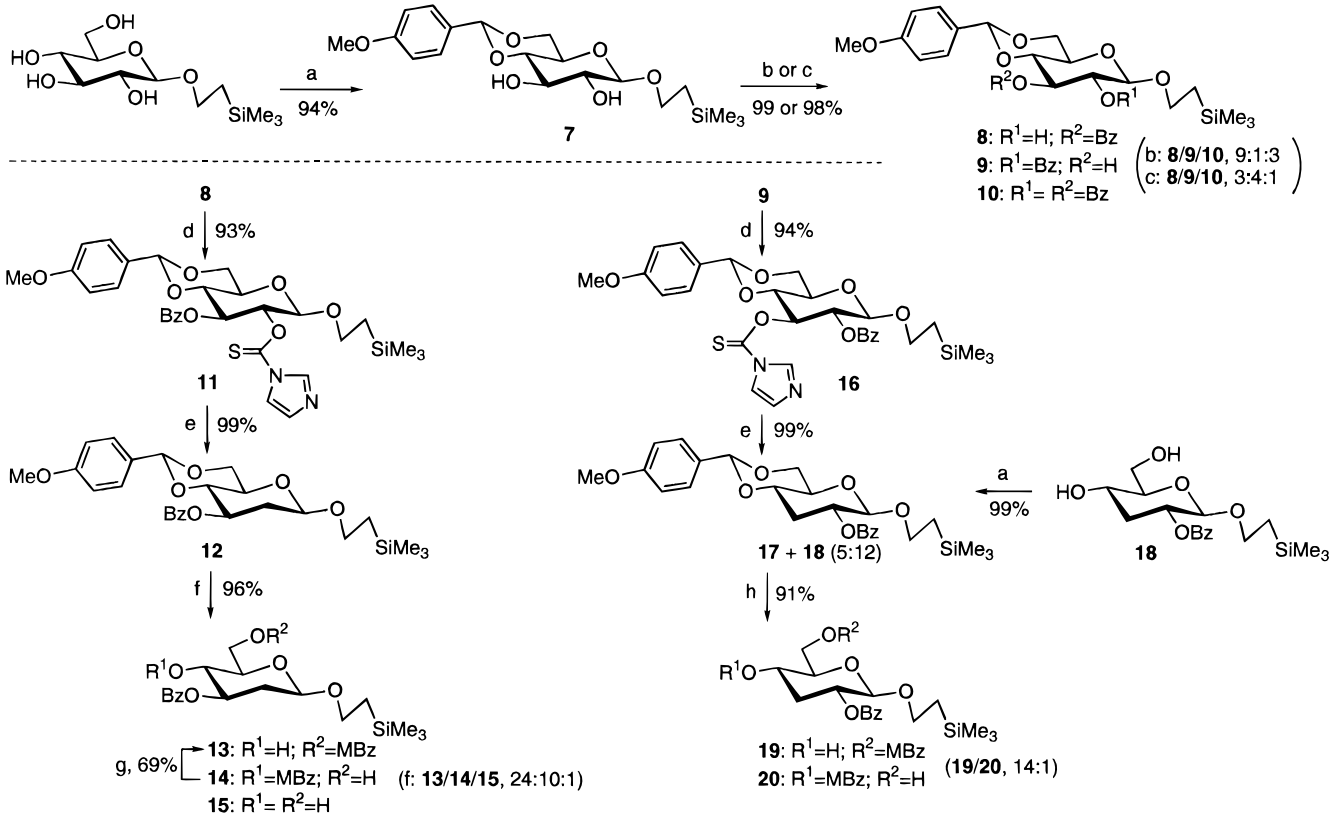
(12) Yasumori, T.; Sato, K.; Hashimoto, H.; Yoshimura, J. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2538−2542.

(13) Garegg, P. J.; Johansson, R.; Ortega, C.; Samuelsson, B. *J. Chem. Soc., Perkin Trans. 1* **1982,** 681−683.

(14) Jansson, K.; Noori, G.; Magnusson, G. *J. Org. Chem.* **1990**, *55*, 3181−3185.

(15) (a) Murakata, C.; Ogawa, T. *Carbohydr. Res.* **1992**, *235*, 95−114. (b) Jacob, P., III; Callery, P. S.; Shulgin, A. T.; Castagnoli, N., Jr. *J. Org. Chem.* **1976**, *41*, 3627−3629. (c) Fukuyama, T., Laird, A. A., Hotchkiss, L. M. *Tetrahedron Lett.* **1985**, *26*, 6291−6292.

Scheme 1[a]



[a] (a) *p*-$MeOC_6H_4CH(OMe)_2$, TsOH, MeCN; (b) BzCl, Et_3N, CH_2Cl_2; (c) Bu_2SnO, toluene/benzene, and then BzCl, toluene; (d) $(imidaz)_2CS$, benzene, reflux; (e) Bu_3SnH, AIBN, toluene, reflux; (f) DDQ, AcOH (0.2 equiv), mol sieves (3 Å), toluene, 80 °C; (g) $AgNO_3$, KF, pyridine, H_2O, 100 °C; (h) DDQ, mol sieves (3 Å), toluene, 80 °C, and then $AgNO_3$, KF, pyridine, H_2O, 100 °C.

furnish crystalline **27**[15a] in 81% yield (Scheme 3). Deacetylation of **27** gave crude **28**[15a] (99%), which was treated with α,α-dimethoxytoluene and *p*-toluenesulfonic acid to give the solid 4,6-*O*-benzylidene derivative **29**, which was isolated by precipitation. Compound **29** was benzoylated to give crystalline **30** in 85% yield. Reductive opening[6a] of the benzylidene ring of **30** gave the *p*-methoxyphenyl glycoside acceptor **31** in 91% yield after chromatography. In summary, galactose β-pentaacetate was transformed in five steps into **31** in >60% overall yield and with only one (the last step) chromatographic purification.

The acceptor **31** was glycosylated with 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl chloride[16] in the presence of silver triflate to give the galabioside **32** (81%). Hydrogenolysis of the benzyl groups of **32**, followed by acetylation of the crude material gave the fully acylated glycoside **34** in 89% overall yield.

Compound **34** was converted into the three galabiose donors **36**, **37**, and **38**. Treatment of **34** with CAN gave the hemiacetal **35** (88%), and treatment of the crude hemiacetal with trichloroacetonitrile gave the trichloroacetimidate **36** (91%), suitable[17] for use as a galabiosyl donor. Compound **34** was easily converted in one step and high stereoselectivity into the thioglycoside **37** (93%) by treatment with thiophenol and boron trifluoride etherate. Treatment of **34** with acetyl bromide and a catalytic amount of zinc bromide gave the galabiosyl bromide **38** in 93% yield.

IV. Synthesis of the 2-, 3-, and 6-deoxyglobotriosides 1, 3, and 5. Glycosides with a deoxy function in the 2-position are quite sensitive to anomerization, especially in the presence of acids. Initial attempts to glycosylate acceptor **13** with the trichloroacetimidate **36** or the thio glycoside **37** were essentially unsuccessful (Scheme 4). With donor **36** and TfOTMS,[17] the desired **39** was not formed and most of **36** was converted into the hemiacetal **35**. Changing to silver triflate[18] gave **39**, albeit in low yield, partly due to rapid anomerization at the TMSEt-anomeric center. The sensitivity of 2-deoxyglycosides to anomerization is further witnessed by the anomerization of acceptor **13** into **40**. Attempted glycosylation of **13** with the thioglycoside donor **37** was also largely unsuccessful, due to the propensity for anomerization under the glycosylation conditions.

Finally, compound **39** was successfully prepared by glycosylation of **13** with the galabiosyl bromide **38** with silver silicate[19] as promoter in 86% isolated yield. This reagent is mild enough not to cause anomerization of the TMSEt glycosides; unreacted **13** was isolated (12%) without anomerization into **40**. Deacetylation of **39** gave the 2-deoxyglobotrioside **2** in 88% yield.

In contrast to the attempted preparations of 2-deoxyglobotriosides, the 3-deoxy analog **41** could be prepared from both the trichloroacetimidate **36** and the thioglycoside **37**, using the acceptor **19**. In the former case, activation with 1 equiv of silver triflate[18] gave **41** in 63% yield. When an excess of silver triflate was used, the furanoside **42** was also formed, probably due to the

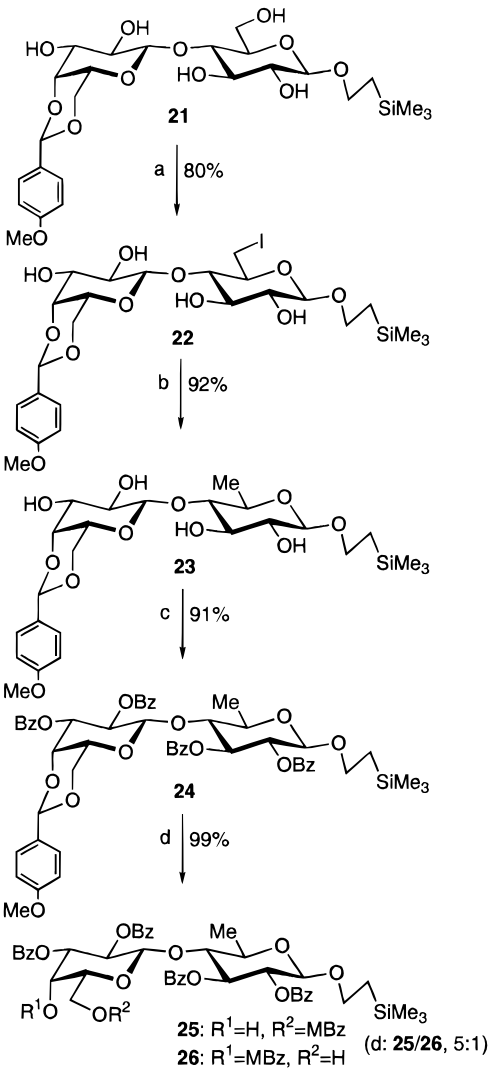
(16) Kihlberg, J.; Frejd, T.; Jansson, K.; Sundin, A.; Magnusson, G. *Carbohydr. Res.* **1988**, *176*, 271−286.

(17) Schmidt, R. R.; Michel, J. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 731−732.

(18) Douglas, S. P.; Whitfield, D. M.; Krepinsky, J. J. *J. Carbohydr. Chem.* **1993**, *12*, 131−136.

(19) Paulsen, H.; Lockhoff, O. *Chem. Ber.* **1981**, *114*, 3102−3114.

Scheme 2[a]



[a] (a) I_2, imidazole, Ph_3P, toluene/MeCN (5:2), reflux; (b) H_2, Pd/C, EtOAc/EtOH/Et_3N (1:5:0.01); (c) BzCl, pyridine, DMAP; (d) DDQ, AcOH (5 equiv), H_2O, mol sieves (3 Å), toluene, 80 °C.

flexibility of the pyranose ring of **19**, which might permit a boatlike conformation, where HO-4 can reach the anomeric position. Glycosylation of **19** with the thioglycoside donor **37** at −30 °C gave the desired **41** in 92% yield, using *N*-iodosuccinimide/silver triflate[20] as promoter. No anomerization occurred and the furanosidic byproduct **42** was not detected in the reaction mixture. Deacetylation of **41** gave the 3-deoxyglobotrioside **3** in 95% yield.

Clean α-galactosylation of the 6-deoxylactoside acceptor **25** with 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl chloride[16] in the presence of silver triflate gave **43** in 76% yield. Hydrogenolysis of the benzyl protecting groups gave **44** (93%), and deacylation of **44** gave the 6-deoxyglobotrioside **5** in 98% yield. Acetylation of **44** gave the fully acylated **45** (99%).

V. Synthesis of the 2-Deoxyglobotriosyl Neoglycolipid 2. Cleavage of the TMSEt group by trifluoroacetic acid[8] to produce hemiacetal sugars is widely used, especially with large synthetic oligosaccharides, where reliability and high yields are of crucial importance. Furthermore, this cleavage reaction proceeded without problems in our previous preparations of deoxyglobotriosides.[1,2] However, attempted cleavage of the TMSEt group in the 2-deoxysaccharide **39** by treatment with trifluoroacetic acid gave the desired hemiacetal in only 15% yield together with 78% of a mixture of the three corresponding trehaloses (data not shown). Furthermore, attempted conversion of a 2-deoxylactoside[21] to the corresponding chlorosugar[14] was somewhat unpredictable; no attempt to transform **39** into the corresponding 1-chlorosugar was therefore made. In addition, the expected low β/α−selectivity in the planned glycosylations made us consider an alternative route to the neoglycolipid **2**.

Addition[22] of hydrogen chloride to 3,4,6-tri-*O*-benzoylglucal[23] gave the desired 3,4,6-tri-*O*-benzoyl-2-deoxy-α-D-glucopyranosyl chloride in quantitative yield according to ^{1}H NMR analysis. When the same reaction was attempted with 3,4,6-tri-*O*-acetylglucal, several byproducts were formed. Treatment of the chloro sugar with 3-(hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]propan-1-ol[2] (**46**) and silver silicate gave an easily separated anomeric mixture of **47** and **48** (69%) (Scheme 5). Debenzoylation of **47** gave crude **49**, which was converted into the acceptor **50** by regioselective benzoylation via the corresponding stannylene intermediate. When 2 equiv of dibutyltin oxide was used for the stannylation, **50** was obtained in only 30% yield together with the corresponding tri-*O*-benzoate and other byproducts. However, increasing the amount of dibutyltin oxide to 4 equiv raised the yield of **50** to 84%. It seems as if the latter procedure leads to highly selective benzoylations, without the need for rigorously dry reaction conditions. Glycosylation of acceptor **50** with the galabiosyl bromide **38**, using silver silicate[19] as promoter, gave **51** in 83% yield. Finally, deacetylation of **51** furnished the desired 2-deoxyglobotriosyl neoglycolipid **2** (98%).

VI. Synthesis of the 3- and 6-Deoxyglobotriosyl Neoglycolipids 4 and 6. In contrast to the attempted formation of hemiacetal from **39**, the 3- and 6-deoxyglycosides **41** and **45** smoothly underwent trifluoroacetic acid-induced cleavage[8] of the TMSEt group to give the hemiacetals **52** (98%) and **55** (94%), respectively (Scheme 6). Treatment of **52** with trichloroacetonitrile[17] gave the corresponding trichloroacetimidate **53** (79%) as an α/β mixture (2:1), whereas the same conditions converted **55** into pure **56** (81%). Silver triflate-promoted[18] glycosylation of the lipid alcohol **46** with trichloroacetimidates **53** and **56** gave **54** (72%) and **57** (79%). Deacetylation of **54** and **57** then gave the desired 3- and 6-deoxyglobotriosyl neoglycolipids **4** (98%) and **6** (96%), respectively.

Experimental Section

General experimental procedures were as previously reported.[4] Toluene and dichloromethane were distilled from calcium hydride under N_2. Activated molecular sieves and silver silicate[18] were flame-dried under vacuum for 5 min and then kept under vacuum (oil pump) for approximately 1 h.

2-(Trimethylsilyl)ethyl 2-Deoxy-4-*O*-[4-*O*-(α-D-galactopyranosyl)-β-D-galactopyranosyl]-β-D-*arabino*-hexopyranoside (1). Compound **39** (60 mg, 0.048 mmol) was treated with MeONa/MeOH (1 M, 0.2 mL) in MeOH (5 mL) at room

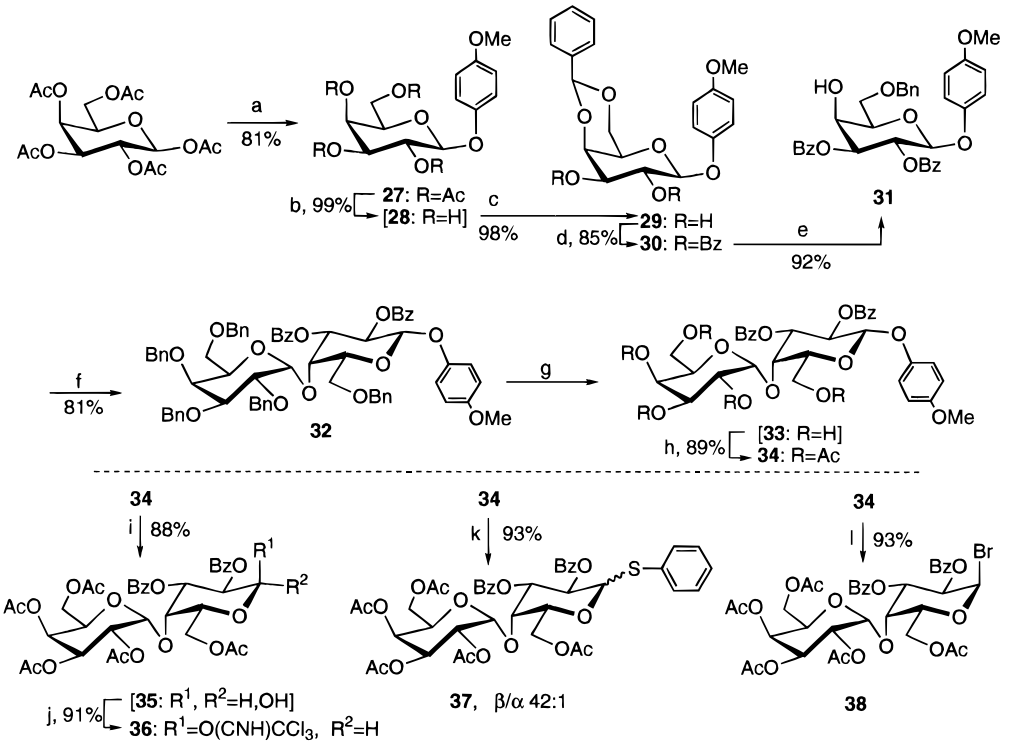
(20) Konradsson, P.; Udodong, U. E.; Fraser-Reid, B. *Tetrahedron Lett.* **1990**, *31*, 4313−4316.

(21) Ekberg, T.; Magnusson, G. Unpublished results.

(22) Lancelin, J.-M.; Morin-Allory, L.; Sinaÿ, P. *J. Chem. Soc., Chem. Commun.* **1984**, 355−356.

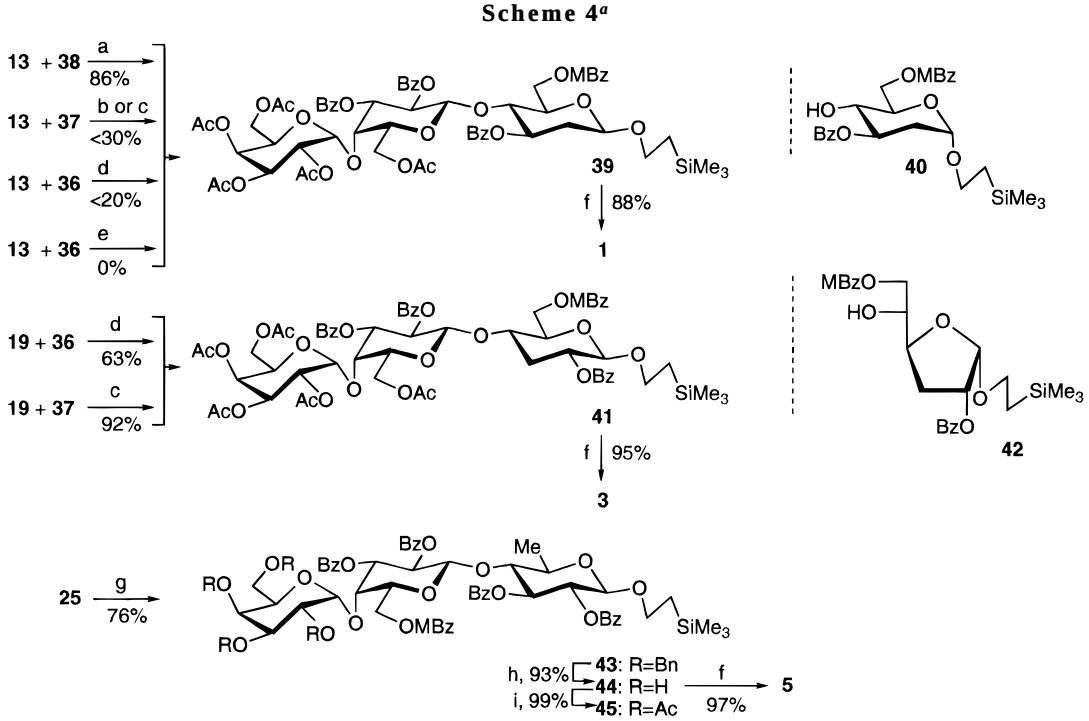
(23) Lundt, I.; Pedersen, C. *Acta Chem. Scand.* **1966**, *20*, 1369−1375.

Scheme 3[a]



[a] (a) $MeOC_6H_4OH$, $BF_3{\cdot}Et_2O$, CH_2Cl_2; (b) MeONa, MeOH; (c) $C_6H_5CH(OMe)_2$, TsOH, MeCN; (d) BzCl, pyridine; (e) $NaBH_3CN$, HCl, THF, mol sieves (3 Å); (f) 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl chloride, AgOTf, collidine, acid washed mol sieves (3 Å), CH_2Cl_2; (g) H_2, Pd/C, AcOH; (h) Ac_2O, pyridine; (i) $(NH_4)_2Ce(NO_3)_6$, acetone, H_2O; (j) Cl_3CCN, DBU, CH_2Cl_2; (k) C_6H_5SH, $BF_3{\cdot}Et_2O$, $ClCH_2CH_2Cl$; (l) AcBr, $ZnBr_2$, $CHCl_3$.

Scheme 4[a]

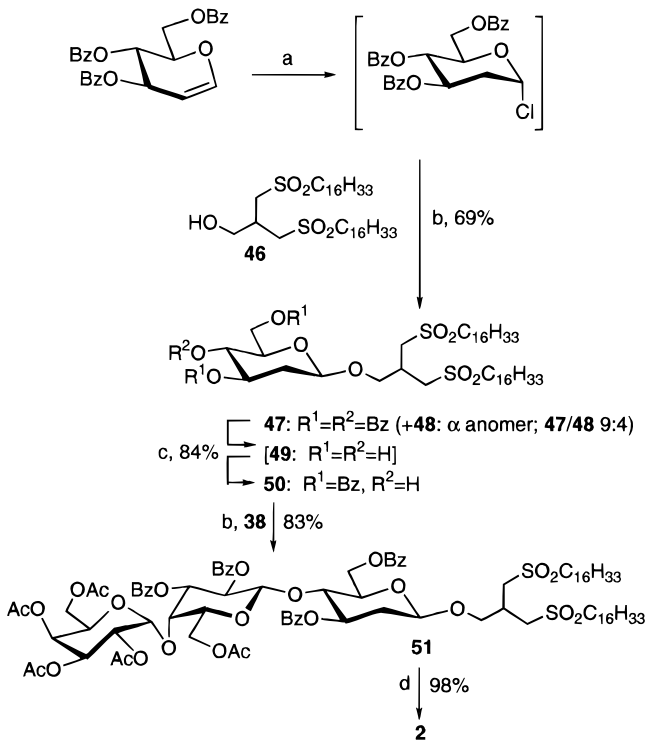


[a] (a) Ag−SiO_2, CH_2Cl_2; (b) NIS, TfOH, CH_2Cl_2; (c) NIS, TfOAg, CH_2Cl_2; (d) TfOAg, CH_2Cl_2; (e) TfOTMS, MeCN; (f) MeONa, MeOH; (g) 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl chloride, TfOAg, collidine, CH_2Cl_2; (h) H_2, Pd/C, AcOH; (i) Ac_2O, pyridine.

temperature. The reaction was monitored by TLC (SiO_2, EtOAc/MeOH 3:1). After 5 h, the mixture was neutralized with Duolite (H^+) resin, filtered, and concentrated. The residue was chromatographed (SiO_2-C_{18}, H_2O/MeOH 1:0 → 0:1) to give **1** (25 mg, 88%); $[\alpha]^{25}_D$ +47.4° (*c* 1.0, MeOH); ^{1}H NMR data (D_2O): δ 4.90 (d, 1 H, *J* = 3.4 Hz), 4.47 (d, 1 H, *J* = 7.8 Hz), 4.31 (t, 1 H, *J* = 6.1 Hz), 2.34 (bd, 1 H, *J* = 5.2, 12.5 Hz), 1.45 (bq, 1 H, *J* = 11.6 Hz), 0.95 (m, 2 H), −0.02 (s, 9 H); ^{13}C NMR data (D_2O): δ 106.1, 103.1, 101.6, 83.2, 83.1, 80.1, 78.1, 77.6, 74.9, 73.7, 73.6, 72.1, 71.9, 71.7, 71.3, 70.4, 63.3, 63.1, 40.5, 20.2, 0.2.

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]-propyl 2-Deoxy-4-*O*-[4-*O*-(α-D-galactopyranosyl)-*β*-D-galactopyranosyl]-*β*-D-*arabino*-hexopyranoside (2). Com-

Scheme 5[a]



[a] (a) HCl, toluene, 0 °C; (b) Ag−SiO_2, CH_2Cl_2; (c) MeONa, MeOH, and then Bu_2SnO, BzCl, toluene, 100 °C, 2 min; (d) MeONa, MeOH, $CHCl_3$.

pound **51** (27 mg, 0.016 mmol) was dissolved in $CHCl_3$/MeOH (5 mL, 3:2), and MeONa/MeOH (1 M, 0.2 mL) was added. The reaction was monitored by TLC ($CHCl_3$/MeOH/BuOAc/H_2O 12:8:8:1). After 11 h, the mixture was neutralized with AcOH and concentrated. The residue was chromatographed (SiO_2, CH_2Cl_2/MeOH → CH_2Cl_2/MeOH/H_2O; 2:1 → 2:1:0.05) to give **2** (17.6 mg, 98%); $[\alpha]^{25}_D$ +37.5° (*c* 0.6, $CHCl_3$/MeOH/H_2O 13:7:1); ^{1}H NMR data ($CDCl_3$/CD_3OD/D_2O 13:7:1): δ 4.97 (d, 1 H, J = 2.5 Hz), 4.61 (dd, 1 H, J = 9.5, 1.2 Hz), 4.42 (d, 1 H, J = 7.3 Hz), 4.12 (dd, 1 H, J = 10.1, 4.2 Hz), 4.42 (d, 1 H, J = 1.6 Hz), 3.95 (bs, 1 H), 3.12 (m, 4 H), 2.99 (m, 1 H), 2.25 (bdd, 1 H, J = 10.2, 4.5 Hz), 0.89 (t, 6 H, J = 6.8 Hz).

2-(Trimethylsilyl)ethyl 3-Deoxy-4-*O*-[4-*O*-(α-D-galactopyranosyl)-*β*-D-galactopyranosyl]-*β*-D-*ribo*-hexopyranoside (3). Compound **43** (60 mg, 0.048 mmol) was deacylated as described above (**39** → **1**) and the crude product was chromatographed (SiO_2-C_{18}, H_2O/MeOH 1:0 → 0:1) to give **3** (27 mg, 95%); $[\alpha]^{25}_D$ +51.5° (*c* 1.0, MeOH); ^{1}H NMR data (D_2O): δ 4.91 (d, 1 H, J = 3.8 Hz), 4.48 (d, 1 H, J = 7.6 Hz), 4.38 (d, 1 H, J = 7.7 Hz), 2.52 (m, 1 H), 1.60 (q, 1 H, J = 12.0 Hz), 1.00 (m, 2 H), −0.02 (s, 9 H); ^{13}C NMR data (D_2O): δ 106.7, 106.1, 102.9, 81.0, 79.4, 77.9, 76.6, 74.9, 73.6, 71.9, 71.7, 71.5, 70.8, 70.3, 63.2, 62.6, 40.5, 20.3, 0.2.

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]-propyl 3-Deoxy-4-*O*-[4-*O*-(α-D-galactopyranosyl)-*β*-D-galactopyranosyl]-*β*-D-*ribo*-hexopyranoside (4). Compound **54** (65 mg, 0.037 mmol) was deacylated as described above (**51** → **2**). After 12 h, the mixture was neutralized with Duolite (H^+) resin, filtered, and concentrated. The crude product was chromatographed (SiO_2-C_{18}, H_2O/MeOH 1:0 → 0:1) to give **4** (40 mg, 98%); $[\alpha]^{25}_D$ +27.8° (*c* 1.0, $CHCl_3$/MeOH/H_2O 13:7:1); ^{1}H NMR data ($CDCl_3$/CD_3OD/D_2O 13:7:1): δ 5.00 (d, 1 H, J = 2.4 Hz), 4.43, 4.29 (d, 1 H each, J = 7.6 and 7.5 Hz), 4.03 (d, 1 H, J = 1.6 Hz), 3.97 (bs 1 H), 3.11 (m, 4 H), 3.00 (m, 1 H), 2.52 (m, 1 H), 1.63 (q, 1 H, J = 12.0 Hz), 0.89 (t, 6 H, J = 6.8 Hz).

2-(Trimethylsilyl)ethyl 6-Deoxy-4-*O*-[4-*O*-(α-D-galactopyranosyl)-*β*-D-galactopyranosyl]-*β*-D-glucopyranoside (5). Compound **44** (80 mg, 0.070 mmol) was deacylated as described above (**39** → **1**), and the crude product was chromatographed (SiO_2-C_{18}, H_2O/MeOH 1:0 → 0:1) to give **3** (40 mg, 97%); $[\alpha]^{25}_D$ +50.0° (*c* 1.0, MeOH); ^{1}H NMR data (D_2O): δ 4.91 (d, 1 H, J = 3.8 Hz), 4.52 (d, 1 H, J = 8.0 Hz), 4.44 (d, 1 H, J = 8.2 Hz), 4.32 (t, 1 H, J = 5.9 Hz), 1.34 (d, 3 H, J = 6.3 Hz), 1.00 (m, 2 H), −0.01 (s, 9 H); ^{13}C NMR data (D_2O): δ 106.2, 103.9, 103.1, 86.7, 80.2, 78.1, 77.2, 75.9, 74.9, 73.8, 73.7, 73.6, 71.9, 71.7, 71.3, 71.1, 63.3, 63.1, 20.4, 19.5, 0.2.

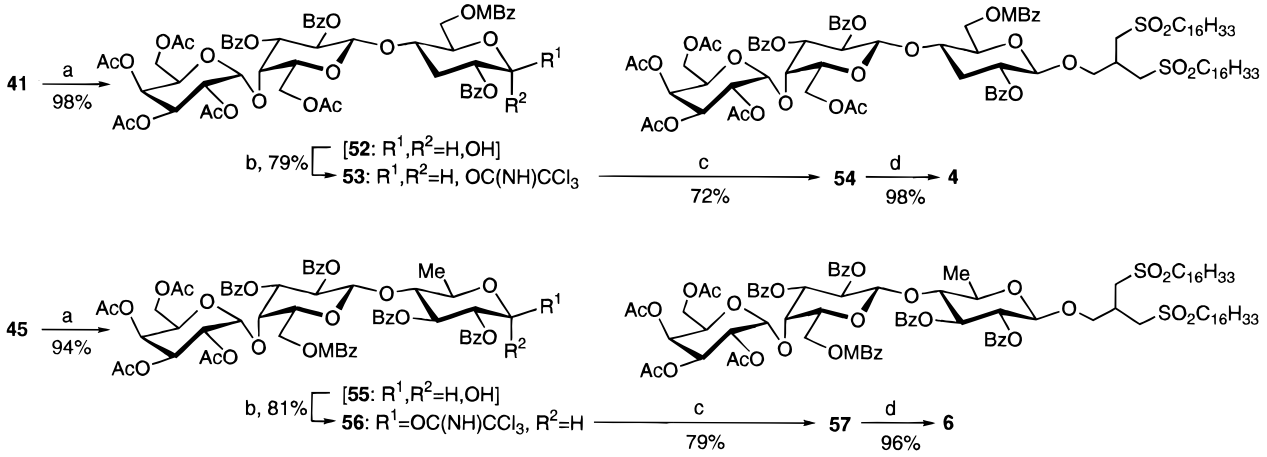
3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]-propyl 6-Deoxy-4-*O*-[4-*O*-(α-D-galactopyranosyl)-*β*-D-galactopyranosyl]-*β*-D-glucopyranoside (6). Compound **57** (84 mg, 0.046 mmol) was deacylated as described above (**51** → **2**), and the crude product was chromatographed (SiO_2-C_{18}, H_2O/MeOH 1:0 → 0:1) to give **6** (49 mg, 96%); $[\alpha]^{25}_D$ +24.7° (*c* 1.0, $CHCl_3$/MeOH/H_2O 13:7:1); ^{1}H NMR data ($CDCl_3$/CD_3OD/D_2O 13:7:1): δ 4.95 (bd, 1 H, J = 2.7 Hz), 4.39, 4.33 (d, 1 H each, J = 7.1 and 7.8 Hz), 4.00 (d, 1 H, J = 2.1 Hz), 3.96 (bs, 1 H), 3.11 (m, 4 H), 3.01 (m, 1 H), 1.39 (d, 3 H, J = 6.2 Hz), 0.89 (t, 6 H, J = 6.4 Hz).

2-(Trimethylsilyl)ethyl 4,6-*O*-*p*-Methoxybenzylidene-*β*-D-glucopyranoside (7). A mixture of 2-(trimethylsilyl)-ethyl *β*-D-glucopyranoside[8] (3.8 g, 13.57 mmol), *p*-methoxy-α,α-dimethoxytoluene (3.1 mL, 20.4 mmol), dry CH_3CN (100 mL), and *p*-toluenesulfonic acid (50 mg) was stirred at room temperature for 3 h and then neutralized with Et_3N (1 mL) and concentrated. The residue was chromatographed (SiO_2, toluene/CH_3CN 4:1) to give **7** (5.10g, 94%); $[\alpha]^{25}_D$ -44.2° (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 7.42, 6.89 (d, 2 H each, J = 8.7 Hz), 5.49 (s, 1 H), 4.41 (d, 1 H, J = 7.8 Hz), 4.33 (dd, 1 H, J = 10.5, 4.6 Hz), 2.85, 2.67 (s, 1 H each), 0.03 (s, 3 H). ^{13}C NMR ($CDCl_3$) δ 160.3, 129.5, 127.6, 113.7, 102.7, 101.9, 80.6, 74.6, 73.2, 68.7, 67.9, 66.4, 55.3, 18.3, −1.4. HRMS calcd for $C_{19}H_{31}O_7Si$ (M + H): 399.1839; found: 399.1847.

2-(Trimethylsilyl)ethyl 3-*O*-Benzoyl-4,6-*O*-(*p*-methoxybenzylidene)-*β*-D-glucopyranoside (8), 2-(Trimethylsilyl)-ethyl 2-*O*-Benzoyl-4,6-*O*-(*p*-methoxybenzylidene)-*β*-D-glucopyranoside (9), and 2-(Trimethylsilyl)ethyl 2,3-Di-*O*-benzoyl-4,6-*O*-(*p*-methoxybenzylidene)-*β*-D-glucopyranoside (10). (a) Compound **7** (1.5 g, 3.77 mmol) and Et_3N (5.23 mL, 37.7 mmol) were dissolved in CH_2Cl_2 (30 mL). The mixture was cooled (ice−water bath), and benzoyl chloride (2.21 mL, 18.84 mmol) was added dropwise under Ar. After 1 h, the reaction was quenched by adding MeOH (2 mL), and the mixture was diluted with CH_2Cl_2 (100 mL) and washed with saturated aqueous $NaHCO_3$ (2 × 50 mL). The organic phase was dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, heptane/toluene/EtOAc 6:1:1 → 5:1:1) to give **10** (0.54 g, 23%), **8** (1.28 g, 68%), and **9** (0.16 g, 8%). Compound **10**: $[\alpha]^{25}_D$ −4.5° (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.76 (t, 1 H, J = 9.6 Hz), 5.51 (s, 1 H), 5.46 (dd, 1 H, J = 9.5, 7.9 Hz), 4.81 (d, 1 H, J = 7.9 Hz), 4.43 (dd, 1 H, J = 10.3, 5.0 Hz), 3.77 (s, 3 H), −0.07 (s, 9 H); HRMS calcd for $C_{33}H_{38}O_9SiNa$ (M + Na): 629.2183; found: 629.2186. Compound **8**: $[\alpha]^{25}_D$ -83.0° (*c* 1.5, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.49 (s, 1 H), 5.48 (t, 1 H, J = 9.5 Hz), 4.55 (d, 1 H, J = 7.7 Hz), 4.38 (dd, 1 H, J = 10.5, 5.0 Hz), 3.76 (s, 3 H), 0.04 (s, 9 H); HRMS calcd for $C_{26}H_{35}O_8Si$ (M + H): 503.2109; found: 503.2101. Compound **9**: $[\alpha]^{25}_D$ -34.2° (*c* 2.0 $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.53 (s, 1 H), 5.17 (dd, 1 H, J = 9.2, 7.9 Hz), 4.69 (d, 1 H, J = 7.8 Hz), 4.38 (dd, 1 H, J = 10.5, 4.9 Hz), 4.02 (t, 1 H, J = 9.1 Hz), 3.80 (s, 3 H), −0.07 (s, 9 H); HRMS calcd for $C_{26}H_{35}O_8Si$ (M + H): 503.2109; found: 503.2101.

(b) Compound **7** (2.0 g, 5.03 mmol) and dibutyltin oxide (2.00 g, 8.04 mmol) were dissolved in toluene/benzene (120 mL 5:1), the mixture was refluxed under Ar for 1 h, and approximately 30 mL of the solvent was distilled off. The mixture was cooled to −25 °C, and benzoyl chloride (875 μL, 7.54 mmol) was added. The mixture was kept at −25 °C overnight, a second portion of benzoyl chloride (875 μL, 7.54 mmol) was added, the mixture was stirred at room temperature for 2 h and at 40 °C for 1 h, MeOH (5 mL) was added, and the mixture was concentrated. The residue was dissolved in hot CH_3CN (50 mL), and the mixture was allowed to cool to room temperature. The resulting precipitate was filtered off, and the filtrate was concentrated. The residue was chromatographed (SiO_2, hep-

Scheme 6[a]



[a] (a) TFA, CH_2Cl_2, 0 °C; (b) Cl_3CCN, DBU, CH_2Cl_2; (c) **46**, TfOAg, CH_2Cl_2; (d) MeONa, MeOH, $CHCl_3$.

tane/toluene/EtOAc 6:1:1) to give **10** (0.44 g, 14%), **8** (1.00 g, 39%), and **9** (1.15 g, 46%).

2-(Trimethylsilyl)ethyl 3-*O*-Benzoyl-2-*O*-(imidazol-1-ylthiocarbonyl)-4,6-*O*-(*p*-methoxybenzylidene)-*β*-D-glucopyranoside (11). A mixture of compound **8** (1.16 g, 2.31 mmol), 1,1'-thiocarbonyldiimidazole (>97%, 847 mg, 4.61 mmol), and dry benzene (20 mL) was refluxed for 4 h and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 5: 2) to give **11** (1.31 g, 93%); $[\alpha]^{25}_D$ −31.6° (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 8.27, 7.55, 6.99 (s, 1 H each), 6.03 (dd, 1 H, J = 9.5, 7.8 Hz), 5.81 (t, 1 H, J = 9.5 Hz), 5.51 (s, 1 H), 4.86 (d, 1 H, J = 7.8 Hz), 4.43 (dd, 1 H, J = 10.4, 4.9 Hz), 3.76 (s, 3 H), −0.04 (s, 9 H); HRMS calcd for $C_{30}H_{36}O_8N_2SSiNa$ (M + Na^+): 635.1859; found: 635.1864.

2-(Trimethylsilyl)ethyl 3-*O*-Benzoyl-2-deoxy-4,6-*O*-(*p*-methoxybenzylidene)-*β*-D-*arabino*-hexopyranoside (12). A solution of compound **8** (1.28 g, 2.10 mmol) and a catalytic amount of azobis(isobutyronitrile) in toluene (20 mL) was added dropwise to a boiling solution of Bu_3SnH (98%, 1.48 mL, 5.50 mmol) in toluene (35 mL) under Ar. The mixture was refluxed for 4 h and concentrated. The residue was chromatographed (SiO_2, toluene 250 mL → heptane/EtOAc 3: 1) to give **12** (1.01 g, 99%); $[\alpha]^{25}_D$ -97.9° (*c* 1.0 $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.55 (s, 1 H), 5.35 (m, 1 H), 4.75 (dd, 1 H, J = 9.6, 2.2 Hz), 4.36 (dd, 1 H, J = 10.5, 4.9 Hz), 3.77 (s, 3 H), 2.51 (ddd, 1 H, J = 12.4, 5.3, 1.9 Hz), 1.80 (bq, 1 H, J = 11.8 Hz), 0.02 (s, 9 H); Anal. calcd for $C_{26}H_{34}O_7Si$: C 64.2, H 7.1; found: C 63.8, H 7.1.

2-(Trimethylsilyl)ethyl 3-*O*-Benzoyl-2-deoxy-6-*O*-(*p*-methoxybenzoyl)-*β*-D-*arabino*-hexopyranoside (13), 2-(Trimethylsilyl)ethyl 3-*O*-Benzoyl-2-deoxy-4-*O*-(*p*-methoxybenzoyl)-*β*-D-*arabino*-hexopyranoside (14), and 2-(Trimethylsilyl)ethyl 3-*O*-Benzoyl-2-deoxy-*β*-D-*arabino*-hexopyranoside (15). A mixture of compound **12** (779 mg, 1.60 mmol), DDQ (751 mg, 3.21 mmol), AcOH (17 μL, 0.48 mmol), molecular sieves (300 mg, 4 Å), and toluene (30 mL) was stirred at 80 °C overnight. The mixture was diluted with EtOAc (150 mL), filtered, and washed with saturated aqueous $NaHCO_3$ (2 × 70 mL) and saturated aqueous NaCl (50 mL). The organic phase was dried ($NaSO_4$), filtered, and concentrated. Column chromatography (SiO_2, heptane/EtOAc 6:1 → 4:1) of the residue gave **13** (533 mg, 66%), **14** (220 mg, 27%), and **15** (16 mg, 3%). Compound **13**: $[\alpha]^{25}_D$ -12.4° (*c* 1.4, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.17 (m, 1 H), 4.74 (dd, 1 H, J = 12.0, 4.6 Hz), 4.67 (dd, 1 H, J = 9.7, 2.0 Hz), 4.58 (dd, 1 H J = 12.0, 2.2 Hz), 3.87 (s, 3 H), 2.41 (ddd, 1 H, J = 12.5, 5.3, 1.8 Hz), 1.80 (dt, 1 H, J = 12.0, 9.7 Hz), 0.02 (s, 9 H); HRMS calcd for $C_{26}H_{34}O_8$ SiNa (M + Na): 525.192; found: 525.1938; Compound **14**: $[\alpha]^{25}_D$ -103.3° (*c* 1.5, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.48 (m, 1 H), 5.33 (t, 1 H, J = 9.6 Hz), 4.76 (dd, 1 H, J = 9.7, 2.0 Hz), 3.81 (s, 3 H), 2.60−2.48 (m, 2 H), 1.91 (ddd, 1 H, J = 9.6, 9.1, 9.7 Hz), 0.03 (s, 9 H); HRMS calcd for $C_{26}H_{34}O_8$ SiNa (M + Na): 525.1921; found: 525.1938. Compound **15**: $[\alpha]^{25}_D$ -15.6° (*c* 0.8, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.12 (m, 1 H), 4.68 (dd, 1 H, J = 9.7, 2.0 Hz), 3.79 (t, 1 H, J = 9.1 Hz), 3.44 (m, 1 H), 2.40 (ddd, 1 H, J = 12.5, 5.2, 1.9 Hz), 1.78 (dt, 1 H, J = 12.1, 9.8 Hz), 0.03 (s, 9 H); HRMS calcd for $C_{18}H_{28}O_6$ SiNa (M + Na): 391.1553; found: 391.1546.

14 → 13. To a solution of compound **14** (219 mg, 0.44 mmol) in pyridine/H_2O (4 mL, 5:1) were added $AgNO_3$ (30 mg, 0.18 mmol) and KF (50 mg, 0.86 mmol). The mixture was stirred at 100 °C for 8 h, poured into a stirred mixture of EtOAc/H_2O (115 mL, 75:40), and filtered through Celite. The water phase was extracted with EtOAc (20 mL), and the combined organic phases were dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 5:1 → 1:2) to give **13** (152 mg, 69%) and **14** (47 mg, 22%).

2-(Trimethylsilyl)ethyl 2-*O*-Benzoyl-3-*O*-(imidazol-1-ylthiocarbonyl)-4,6-*O*-(*p*-methoxybenzylidene)-*β*-D-glucopyranoside (16). Compound **9** (1.21 g, 2.41 mmol) was treated as described in the preparation of **11**. The crude product was chromatographed (SiO_2, heptane/EtOAc 2:1) to give **16** (1.38 g, 94%): $[\alpha]^{25}_D$ -10.8° (*c* 1.5, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 6.32 (t, 1 H, J = 9.3 Hz), 5.52 (m, 2 H, H-2), 4.85 (d, 1 H, J = 7.6 Hz), 4.45 (dd, 1 H, J = 10.6, 4.9 Hz), 3.89 (t, 1 H J = 10.2 Hz), 3.78 (s, 3 H), −0.07 (s, 9 H). Anal. Calcd for $C_{30}H_{36}O_8N_2SSi$: C 58.8, H 5.9, N 4.6; found: C 59.0, H 5.8, N 4.5.

2-(Trimethylsilyl)ethyl 2-*O*-Benzoyl-3-deoxy-4,6-*O*-(*p*-methoxybenzylidene)-*β*-D-*ribo*-hexopyranoside (17) and 2-(Trimethylsilyl)ethyl 2-*O*-Benzoyl-3-deoxy-*β*-D-*ribo*-hexopyranoside (18). Compound **16** (1.36 g, 2.22 mmol) was treated with Bu_3SnH and AIBN as described in the preparation of **12**. The crude product was chromatographed (SiO_2, toluene/EtOAc 7:1) to give **17** (312 mg, 29%) and **18** (568 mg, 70%). Compound **17**: $[\alpha]^{25}_D$ -50.0° (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.08 (m, 1 H), 4.71 (d, 1 H, J = 7.9 Hz), 4.36 (dd, 1 H, J = 10.5, 4.8 Hz), 3.80 (s, 3 H), 2.66 (m, 1 H), 1.88 (q, 1 H, J = 11.6 Hz), −0.04 (s, 9 H); HRMS calcd for $C_{26}H_{35}O_7Si$ (M + H): 487.2152; found: 487.2146. Compound **18**: $[\alpha]^{25}_D$ -61.6° (*c* 1.5, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 4.93 (m, 1 H), 4.64 (d, 1 H, J = 7.8 Hz), 3.59 (m, 2 H), 3.43 (m, 1 H), 2.57 (dt, 1 H, J = 12.2, 5.1 Hz), 1.72 (q, 1 H, J = 11.5 Hz), −0.07 (s, 9 H); HRMS calcd for $C_{18}H_{29}O_6Si$ (M + H^+): 369.1733; found: 369.1733.

18 → 17. Compound **18** (450 mg, 1.22 mmol) was treated as described in the preparation of **7**. The crude product was chromatographed (SiO_2, toluene/Et_3N 100: 1) to give **17** (587 mg, 99%).

2-(Trimethylsilyl)ethyl 2-*O*-Benzoyl-3-deoxy-6-*O*-(*p*-methoxybenzoyl)-*β*-D-*ribo*-hexopyranoside (19) and 2-(Trimethylsilyl)ethyl 2-*O*-Benzoyl-3-deoxy-4-*O*-*p*-methoxybenzoyl-*β*-D-*ribo*-hexopyranoside (20). A mixture of compound **17** (150 mg, 0.31 mmol), DDQ (192 mg, 0.82 mmol), molecular sieves (50 mg, unactivated), and toluene (5 mL) was stirred at 80 °C for 24 h, diluted with EtOAc (70 mL), washed

with saturated aqueous $NaHCO_3$ (2 × 40 mL), dried (Na_2SO_4), and concentrated. The ^{1}H-NMR spectrum of the crude product showed a mixture of **19** and **20** (3:2). The mixture was dissolved in pyridine/H_2O (4.5 mL 10:1), and $AgNO_3$ (55 mg, 0.32 mmol) and KF (19 mg, 0.33 mmol) were added. The mixture was stirred at 100 °C for 16 h and concentrated. The residue was chromatographed (SiO_2, toluene/CH_2Cl_2/THF 20:10:3) to give **19** (132 mg, 85%) and **20** (10 mg, 6.4%). Compound **19**: $[\alpha]^{25}_D$ -70.5° (*c* 2.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 4.95 (m, 1 H), 4.75 (dd, 1 H, J = 12.1, 4.4 Hz), 4.64 (d, 1 H, J = 7.7 Hz), 4.50 (dd, 1 H, J = 12.0, 2.4 Hz), 3.85 (s, 3 H), 2.60 (dt, 1 H, J = 12.3, 4.7 Hz), 1.75 (q, 1 H, J = 11.2 Hz), −0.06 (s, 9 H); HRMS calcd for $C_{26}H_{34}O_8SiNa$ (M + Na^+): 525.1921; found: 525.1929. Compound **20**: $[\alpha]^{25}_D$ -33.3° (*c* 0.9, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.20−5.00 (m, 2 H), 4.76 (d, 1 H, J = 7.1 Hz), 3.86 (s, 3 H), 2.79 (dt, 1 H, J = 12.7, 4.9 Hz), 1.97 (ddd, 1 H, J = 10.2, 7.1, 10.1 Hz), −0.03 (s, 9 H); HRMS calcd for $C_{26}H_{34}O_8SiNa$ (M + Na): 525.1921; found: 525.1938.

2-(Trimethylsilyl)ethyl 6-Deoxy-6-iodo-4-*O*-[4,6-*O*-(*p*-methoxybenzylidene)-*β*-D-galactopyranosyl]-*β*-D-glucopyranoside (22). Compound **21**[2] (500 mg, 0.89 mmol), Ph_3P (463 mg, 1.77 mmol), and imidazole (243 mg, 0.51 mmol) were dissolved in toluene/CH_3CN (70 mL 5:2). I_2 (408 mg, 1.61 mmol) was carefully added, and the mixture was refluxed. After 5 h, the mixture was cooled to room temperature, MeOH (20 mL) was added, and the mixture was concentrated. The residue was extracted with hot EtOAc (3 × 30 mL), and the organic phase was concentrated. The residue was chromatographed (SiO_2, EtOAc/toluene 15:1 → 1:0 and then EtOAc/MeOH 20:1) to give **22** (480 mg, 80%); $[\alpha]^{25}_D$ -17.9° (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.42 (s, 1 H), 4.40, 4.31 (d, 1 H each, J = 7.9 and 7.8 Hz), 4.22 (d, 1 H, J = 12.0 Hz), 4.08 (d, 1 H, J = 3.4 Hz), 3.78 (s, 3 H), 3.57 (dd, 1 H, J = 9.8, 3.5 Hz), 0.03 (s, 9 H); ^{13}C NMR data ($CDCl_3$): δ 160.3, 129.9, 127.7, 113.7, 103.0, 101.6, 101.2, 82.4, 75.2, 74.1, 74.0, 73.4, 72.4, 70.4, 68.9, 67.6, 66.8, 55.4, 18.2, 6.51, −1.4; HRMS calcd for $C_{25}H_{39}O_{11}SiINa$ (M + Na^+): 693.1204; found: 693.1212.

2-(Trimethylsilyl)ethyl 6-Deoxy-4-*O*-[4,6-*O*-(*p*-methoxybenzylidene)-*β*-D-galactopyranosyl]-*β*-D-glucopyranoside (23). Compound **22** (450 mg, 0.67 mmol) was dissolved in EtOH/EtOAc/Et_3N (50 mL 5:1:0.01), and the mixture was hydrogenated (H_2, Pd/C 10%, 250 mg). After 3 h, the mixture was filtered through Celite, the solid residue was washed with EtOAc (30 mL), and the filtrate was concentrated. The residue was chromatographed (SiO_2, EtOAc/toluene 20:1 → 1:0 and then EtOAc/EtOH 10:1) to give **23** (337 mg, 92%); $[\alpha]^{25}_D$ -28.7° (*c* 1.5, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.44 (s, 1 H), 4.34, 4.28 (d, 1 H each, J = 7.6 and 7.8 Hz), 4.24 (d, 1 H, J = 12.0 Hz), 4.12 (d, 1 H, J = 4.1 Hz), 3.80 (s, 3 H), 3.18 (t, 1 H, J = 9.0 Hz), 1.38 (d, 3 H, J = 6.2 Hz), 0.02 (s, 9 H); ^{13}C NMR data ($CDCl_3$): δ 160.3, 130.0, 127.8, 113.7, 103.4, 101.8, 101.2, 85.6, 75.0, 74.5, 73.9, 72.6, 71.2, 70.7, 68.8, 67.4, 66.9, 55.3, 18.3, 17.7, −1.4; HRMS calcd for $C_{25}H_{40}O_{11}SiNa$ (M + Na^+): 567.2238; found: 567.2249.

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-benzoyl-6-deoxy-4-*O*-[2,3-di-*O*-benzoyl-4,6-*O*-(*p*-methoxybenzylidene)-*β*-D-galactopyranosyl]-*β*-D-glucopyranoside (24). Compound **23** (308 mg, 0.57 mmol) and a catalytic amount of DMAP were dissolved in pyridine (10 mL), and the mixture was cooled (ice-water bath). Benzoyl chloride (437 μL, 3.75 mmol) was added dropwise, and the mixture was left at room temperature overnight. The solvent was removed, and the residue was redissolved in CH_2Cl_2 (70 mL), washed with saturated aqueous $NaHCO_3$ (2 × 50 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 3:2) to give **24** (491 mg, 91%): $[\alpha]^{25}_D$ +125.0° (*c* 1.1, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.81−5.72 (m, 2 H), 5.27 (dd, 1 H, J = 9.7, 8.0 Hz), 5.24 (s, 1 H), 5.15 (dd, 1 H, J = 3.6, 10.4 Hz), 4.86, 4.62 (d, 1 H each, J = 7.9 and 8.0 Hz), 4.28 (d, 1 H, J = 3.6 Hz), 3.80 (s, 3 H), 1.15 (d, 3 H, J = 6.0 Hz), 0.12 (s, 9 H).

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-benzoyl-6-deoxy-4-*O*-[2,3-di-*O*-benzoyl-6-*O*-(*p*-methoxybenzoyl)-*β*-D-galactopyranosyl]-*β*-D-glucopyranoside (25) and 2-(Trimethylsilyl)ethyl 2,3-Di-*O*-benzoyl-6-deoxy-4-*O*-[2,3-di-*O*-benzoyl-4-*O*-(*p*-methoxybenzoyl)-*β*-D-galactopyranosyl]-*β*-D-glucopyranoside (26). Compound **24** (259 mg, 0.27 mmol) was treated with DDQ (134 mg, 0.57 mmol), AcOH (81.5 μL, 1.43 mmol), molecular sieves (250 mg), and H_2O (10 μL, 0.57 mmol), as described in the preparation of **13**. The crude product was chromatographed (SiO_2, heptane/EtOAc 3:1 → 1:1) to give **25** (218 mg, 83%) and **26** (43.9 mg, 16%). Compound **25**: $[\alpha]^{25}_D$ +34.0° (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.71 (dd, 1 H, J = 10.4, 7.9 Hz), 5.65 (t, 1 H, J = 9.0 Hz), 5.36 (dd, 1 H, J = 9.9, 8.0 Hz), 5.20 (dd, 1 H, J = 10.4, 3.2 Hz), 4.80, 4.61 (d, 1 H each, J = 7.9 and 8.0 Hz), 3.87 (s, 3 H), 1.25 (d, 3 H, J = 6.0 Hz), −0.11 (s, 9 H); HRMS calcd for $C_{53}H_{56}O_{16}SiNa$ (M + Na^+): 999.3235; found: 999.3245. Compound **26**: $[\alpha]^{25}_D$ +91.9° (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.78 (dd, 1 H, J = 10.4, 7.9 Hz), 5.62 (t, 1 H, J = 9.0 Hz), 5.53 (d, 1 H, J = 3.2 Hz), 5.42 (dd, 1 H, J = 10.4, 3.4 Hz), 5.38 (dd, 1 H, J = 9.9, 8.0 Hz), 4.87, 4.62 (d, 1 H each, J = 7.8 and 7.9 Hz), 3.91 (s, 3 H), 2.90, 2.72 (m, 1 H each), 1.27 (d, 3 H, J = 6.1 Hz), −0.11 (s, 9 H); HRMS calcd for $C_{53}H_{56}O_{16}SiNa$ (M + Na^+): 999.3235; found: 999.3224.

***p*-Methoxyphenyl 2,3,4,6-Tetra-*O*-acetyl-*β*-D-galactopyranoside (27).** Galactose pentaacetate (10.0 g, 25.64 mmol) and *p*-methoxyphenol (3.38 g, 30.77 mmol) were dissolved in CH_2Cl_2 (50 mL), the mixture was cooled (ice−water bath), and $BF_3{\cdot}Et_2O$ (3.85 mL, 28.11 mmol) was added dropwise. After 7 h, the mixture was diluted with CH_2Cl_2 (250 mL) and washed with water (200 mL), saturated aqueous $NaHCO_3$ (200 mL), and water (2 × 150 mL), dried (Na_2SO_4), filtered, and concentrated. The crude product was kept under vacuum (oil pump) for 5 h. The partly crystalline residue was recrystallized from EtOAc/heptane first at room temperature and then at −20 °C overnight. Filtration gave crystalline **27** (9.40 g, 81%): mp 109−110 °C; $[\alpha]^{25}_D$ +3.2° (*c* 0.9, $CHCl_3$), [lit.[15a] $[\alpha]_D$ +9.6° (*c* 0.54)]; ^{1}H NMR data ($CDCl_3$): δ 6.96, 6.82 (d, 2 H each, J = 9.2 Hz), 5.50 (dd, 1 H, J = 10.5, 8.0 Hz), 5.48 (dd, 1 H, J = 3.5, 1.0 Hz), 5.09 (dd, 1 H, J = 10.5, 3.4 Hz), 4.92 (d, 1 H, J = 8.0 Hz), 4.24 (dd, 1 H, J = 11.3, 7.0 Hz), 4.16 (dd, 1 H, J = 11.2, 6.4 Hz), 4.01 (m, 1 H), 3.77 (s, 3 H), 2.18, 2.09, 2.06, 2.01 (s, 3 H each).

***p*-Methoxyphenyl 4,6-*O*-Benzylidene-*β*-D-galactopyranoside (29).** Compound **27** (14.25 g, 31.39 mmol) was deacetylated as described in the preparation of **1** to give **28** (18.91 g, 99%). The crude product (4.15 g, 14.51 mmol) was dissolved in dry acetonitrile (100 mL), and α,α-dimethoxytoluene (7.9 mL, 29.02 mmol) and a catalytic amount of PTSA were added. The mixture was stirred at room temperature for 30 min and then cooled (ice−water bath), and the crystalline material was collected. The mother liquid was concentrated, and the residue was triturated with hot heptane/EtOAc (60 mL 5:2). The solution was cooled to room temperature, and the crystalline material was collected. The combined crystalline material was washed with heptane/EtOAc (5:2) and dried to give **29** (5.28 g, 98%): mp 229−231 °C; $[\alpha]^{25}_D$ -88.4° (*c* 1.0, MeOH/$CHCl_3$ 1:1); ^{1}H NMR data ($CDCl_3$): δ 5.58 (s, 1 H), 4.80 (d, 1 H, J = 7.7 Hz), 4.38 (dd, 1 H, J = 12.5, 1.5 Hz), 4.28 (dd, 1 H, J = 3.8, 1.2 Hz), 4.12 (dd, 1 H, J = 12.5, 1.9 Hz), 4.01 (dd, 1 H, J = 9.3, 7.9 Hz), 3.59 (m, 1 H). HRMS calcd for $C_{20}H_{22}O_7Na$ (M + Na): 397.1263; found: 397.1273.

***p*-Methoxyphenyl 2,3-Di-*O*-benzoyl-4,6-*O*-benzylidene-*β*-D-galactopyranoside (30).** Compound **29** (5.08 g, 13.58 mmol) was benzoylated as described in the preparation of **24**. The crude product was recrystallized from MeOH to give **30** (6.68 g, 85%): mp 198−199 °C; $[\alpha]^{25}_D$ +115.6° (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 6.10 (dd, 1 H, J = 9.5, 8.1 Hz), 5.58 (s, 1 H), 5.43 (dd, 1 H, J = 10.5, 3.5 Hz), 5.20 (d, 1 H, J = 8.0 Hz), 4.65 (d, 1 H, J = 2.9 Hz), 4.46 (dd, 1 H, J = 12.5, 1.5 Hz), 4.17 (dd, 1 H, J = 12.5, 1.7 Hz), 3.74 (s, 1 H); HRMS calcd for $C_{34}H_{30}O_9Na$ (M + Na): 605.1788; found: 605.1770.

***p*-Methoxyphenyl 2,3-Di-*O*-benzoyl-6-*O*-benzyl-*β*-D-galactopyranoside (31).** To a mixture of compound **30** (6.00 g, 10.31 mmol), $NaCNBH_3$ (85%, 5.75 g, 77.72 mmol), molecular sieves (7 g), and dry THF (150 mL) was added dropwise a cold saturated solution of HCl in Et_2O until no more gas was formed. The reaction was stopped after 2 h by adding solid $NaHCO_3$ (~10 g). The mixture was diluted with CH_2Cl_2 (300 mL) and H_2O (100 mL) and filtered through Celite. The

organic phase was washed with saturated aqueous $NaHCO_3$ (150 mL) and saturated aqueous NaCl (150 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 4:1 → 3:2) to give **31** (5.56 g, 92%): $[\alpha]^{25}_D$ +71.4° (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 6.01 (dd, 1 H, J = 10.3, 8.0 Hz), 5.35 (dd, 1 H, J = 10.3, 3.2 Hz), 5.13 (d, 1 H, J = 8.0 Hz), 4.61 (s, 2 H), 4.44 (bt, 1 H, J = 3.8 Hz), 3.74 (s, 1 H); ^{13}C NMR data ($CDCl_3$): δ 165.9, 165.6, 119.0, 114.5, 101.4, 74.4, 73.9, 73.7, 69.6, 69.3, 69.2, 68.0, 55.6; HRMS calcd for $C_{34}H_{32}O_9Na$ (M + Na): 607.1944; found: 607.1933.

***p*-Methoxyphenyl 2,3-Di-*O*-benzoyl-6-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-*β*-D-galactopyranoside (32).** A mixture of **31** (1.28 g, 2.19 mmol), TfOAg (817 mg, 3.15 mmol), CH_2Cl_2 (40 mL), and activated acid-washed molecular sieve AW-300 (4 g) was stirred at −70 °C for 30 min. Collidine (626 μL, 4.73 mmol) and a solution of 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl chloride[17] (1.60 g, 2.87 mmol) in CH_2Cl_2 (10 mL) was added. The mixture was kept at −40 °C for 2 h and allowed to attain room temperature. After 4 h, the temperature was lowered to −40 °C and an additional portion of TfOAg (371 mg, 0.46 mmol) was added. The mixture was stirred at room temperature overnight, and solid $NaHCO_3$ (2 g) was added. The mixture was diluted with CH_2Cl_2/H_2O (250 mL 4:1) and filtered through Celite. The organic phase was washed with saturated aqueous $NaHCO_3$ (70 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, toluene/Et_2O 30:1) to give **32** (1.95 g, 81%): $[\alpha]^{25}_D$ +78.0° (*c* 1.5, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 6.02 (dd, 1 H, J = 10.7, 7.8 Hz), 5.28 (dd, 1 H, J = 10.7, 2.8 Hz), 5.15 (d, 1 H, J = 7.8 Hz), 4.96 (d, 1 H, J = 3.5 Hz), 4.46 (dd, 1 H, J = 2.9 Hz), 4.39 (dd, 1 H, J = 9.5, 5.5 Hz), 4.49 (dd, 1 H, J = 10.3, 2.5 Hz), 3.74 (s, 1 H), 3.43 (t, 1 H, J = 9.2 Hz), 3.02 (dd, 1 H, J = 8.3, 5.1 Hz); ^{13}C NMR data ($CDCl_3$): δ 166.5, 165.4, 155.5, 151.4, 118.9, 114.5, 101.23, 101.20, 101.16, 100.7, 100.6, 79.0, 76.5, 75.51, 75.47, 75.0, 74.8, 74.8, 74.4, 73.9, 73.2, 73.0, 72.5, 69.7, 69.6, 68.7, 67.6, 67.5, 55.64, 55.59; HRMS calcd for $C_{68}H_{66}O_{14}Na$ (M + Na): 1129.4350; found: 1129.4358.

***p*-Methoxyphenyl 2,3-Di-*O*-benzoyl-4-*O*-(α-D-galactopyranosyl)-*β*-D-galactopyranoside (33) and *p*-Methoxyphenyl 6-*O*-Acetyl-2,3-di-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-*β*-D-galactopyranoside (34).** A mixture of compound **32** (1.47 g, 1.33 mmol) and AcOH (5 mL) was hydrogenated (H_2, Pd/C 10%, 210 mg) for 6.5 h. The mixture was filtered and concentrated to give crude **33**: $[\alpha]^{25}_D$ +111.9° (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.86 (dd, 1 H, J = 10.1, 8.3 Hz), 5.46 (bd, 1 H, J = 10.5 Hz), 5.13 (d, 1 H, J = 7.8 Hz), 5.00 (s, 1 H), 4.49 (s, 1 H), 3.68 (s, 1 H); HRMS calcd for $C_{33}H_{36}O_{14}Na$ (M + Na^+): 679.2003; found: 679.2023.

Crude **33** was acetylated with Ac_2O/pyridine (8 mL, 1:1). The mixture was coconcentrated with toluene (2 × 3 mL), and the residue was chromatographed (SiO_2, heptane/EtOAc 2:1 → 1:1) to give **34** (1.023 g, 89%); $[\alpha]^{25}_D$ +115.3° (*c* 0.9, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.90 (dd, 1 H, J = 10.5, 7.8 Hz), 5.51 (dd, 1 H, J = 3.2, 1.4 Hz), 5.47 (dd, 1 H, J = 10.8, 3.3 Hz), 5.31 (dd, 1 H, J = 10.5, 2.8 Hz), 5.23 (dd, 1 H, J = 10.7, 3.6 Hz), 5.17 (d, 1 H, J = 7.7 Hz), 5.12 (d, 1 H, J = 3.7 Hz), 4.39 (d, 1 H, J = 2.4 Hz), 3.76 (s, 1 H), 2.14, 2.11, 2.08, 1.99 and 1.91 (s, 3 H each). Anal. Calcd for $C_{43}H_{46}O_{19}$: C 59.6, H 5.4. Found: C 59.9, H 5.4.

6-*O*-Acetyl-2,3-di-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-D-galactopyranose (35) and 6-*O*-Acetyl-2,3-di-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-α-D-galactopyranosyl Trichloroacetimidate (36). Compound **34** (960 mg, 1.11 mmol) was dissolved in acetone−H_2O (40 mL 3:1), and the mixture was cooled (ice−water bath). A solution of CAN (4.3 g, 7.84 mmol) in acetone/H_2O (5 mL 3:1) was added, and the mixture was stirred at room temperature for 30 min. The mixture was concentrated to a volume of 20 mL, diluted with CH_2Cl_2 (150 mL), washed with saturated aqueous $NaHCO_3$ (2 × 70 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 1:1 → 1:2) to give crude **35** (740 mg, 88%).

Crude **35** (250 mg, 0.329 mmol) was dissolved in CH_2Cl_2 (10 mL), the mixture was cooled (ice−water bath), and trichloroacetonitrile (1.09 mL) and DMU (53.9 μL, 0.36 mmol) were added. After 5 h, the mixture was concentrated, and the residue was chromatographed (SiO_2, heptane/EtOAc/Et_3N 20:10:0.1 → 10:10:0.1) to give **36** (270 mg, 91%); $[\alpha]^{25}_D$ +145.0° (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 8.64 (s, 1 H), 6.80 (d, 1 H, J = 3.6 Hz), 5.92 (dd, 1 H, J = 11.0, 3.7 Hz), 5.77 (dd, 1 H, J = 11.0, 2.7 Hz), 5.26 (dd, 1 H, J = 10.7, 3.5 Hz), 5.14 (d, 1 H, J = 3.6 Hz), 4.39 (dd, 1 H, J = 11.2, 6.9 Hz), 4.25 (dd, 1 H, J = 11.2, 6.1 Hz), 3.82 (dd, 1 H, J = 11.0, 7.8 Hz), 3.53 (dd, 1 H, J = 11.1, 6.2 Hz), 2.15, 2.09, 2.06, 2.00, 1.79 (s 3 H each). HRMS calcd for $C_{38}H_{40}O_{18}Cl_3NNa$ (M + Na): 926.1209; found: 926.1215.

Phenyl 6-*O*-Acetyl-2,3-di-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-1-thio-*β*-D-galactopyranoside (37). Compound **34** (800 mg, 0.92 mmol) was dissolved in $ClCH_2CH_2Cl$/toluene (20 mL 1:1), and thiophenol (379 μL, 3.70 mmol) and $BF_3{\cdot}Et_2O$ (127 μL) were added. The mixture was heated at 65 °C for 10 h and then poured into a mixture of CH_2Cl_2 (150 mL) and saturated aqueous Na_2CO_3 (75 mL). The organic phase was washed with saturated aqueous NaCl (2 × 70 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 2:1 → 1:1) to give **37** (β:α ~42:1, 721 mg, 93%). **37**β had $[\alpha]^{25}_D$ +97.3° (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.52 (t, 1 H, J = 10.1 Hz), 5.37 (bd, 1 H, J = 3.2 Hz), 5.15 (dd, 1 H, J = 11.0, 3.4 Hz), 4.99 (d, 1 H, J = 3.6 Hz), 4.90 (d, 1 H, J = 9.7 Hz), 4.52 (dd, 1 H, J = 11.4, 7.0 Hz), 2.15, 2.13, 2.07, 2.02, 1.97 (s, 3 H each). HRMS calcd for $C_{42}H_{44}O_{17}SNa$ (M + Na): 875.2197; found: 875.2197.

6-*O*-Acetyl-2,3-di-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-*β*-D-galactopyranosyl Bromide (38). Compound **34** (100 mg, 0.12 mmol) was dissolved in CH_2Cl_2 (3 mL), and AcBr (26 mL, 0.35 mmol) and a catalytic amount of $ZnBr_2$ (~2 mg) were added. The mixture was stirred at room temperature for 4.5 h and chromatographed (SiO_2, heptane/EtOAc 5:1 → 3:2) to give **38** (88 mg, 93%); $[\alpha]^{25}_D$ +201.8° (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 6.89 (d, 1 H, J = 3.9 Hz), 5.74 (dd, 1 H, J = 10.8, 2.5 Hz), 5.60 (dd, 1 H, J = 10.7, 3.9 Hz), 5.48 (bd, 1 H, J = 2.9 Hz), 5.42 (dd, 1 H, J = 11.0, 3.2 Hz), 5.25 (dd, 1 H, J = 10.7, 3.7 Hz), 5.11 (d, 1 H, J = 3.6 Hz), 4.39 (dd, 1 H, J = 11.5, 7.1 Hz), 4.28 (dd, 1 H, J = 11.5, 5.6 Hz), 3.82 (dd, 1 H, J = 11.0, 7.6 Hz), 3.54 (dd, 1 H, J = 11.0, 6.3 Hz), 2.14, 2.11, 2.08, 1.99, 1.95 (s, 3 H each); HRMS calcd for $C_{36}H_{39}O_{17}BrNa$ (M + Na): 845.1268; found: 845.1262.

2-(Trimethylsilyl)ethyl 3-*O*-Benzoyl-2-deoxy-6-*O*-(*p*-methoxybenzoyl)-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-*arabino*-hexopyranoside (39). Acceptor **13** (139 mg, 0.28 mmol), donor **38** (342 mg, 0.42 mmol), acid-washed molecular sieves (AW-300, 500 mg), and CH_2Cl_2 (5 mL) were stirred for 40 min under Ar. Silver silicate (400 mg) was added, and the mixture was stirred at room temperature under protection from light. After 24 h, an additional portion of silver silicate (50 mg) was added, and stirring was continued for another 24 h. The mixture was filtered through Celite, and the solid residue was washed with hot CH_2Cl_2 (25 mL). The combined filtrate was concentrated, and the residue was chromatographed (SiO_2, heptane/EtOAc 2:1 → 1:1) to give **39** (297 mg, 86%); $[\alpha]^{25}_D$ +83.8° (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.64 (dd, 1 H, J = 10.7, 7.8 Hz), 5.43 (dd, 1 H, J = 3.1, 1.3 Hz), 5.36 (m, 1 H), 5.30 (dd, 1 H, J = 11.0, 3.4 Hz), 5.16−5.06 (m, 2 H), 4.95 (d, 1 H, J = 3.5 Hz), 4.89 (d, 1 H, J = 7.8 Hz), 4.19 (d, 1 H, J = 2.5 Hz), 2.51 (bdd, 1 H, J = 12.9, 5.5 Hz), 2.09 (m, 1 H), 2.02, 1.98, 1.96, 1.91, 1.86 (s, 3 H each). Anal. Calcd for $C_{62}H_{72}O_{25}Si$: C 59.8, H 5.8. Found: C 59.7, H 5.6.

2-(Trimethylsilyl)ethyl 3-*O*-Benzoyl-2-deoxy-6-*O*-(*p*-methoxybenzoyl)-α-D-*arabino*-hexopyranoside (40). Compound **40** was obtained as a byproduct (presumably via anomerization of acceptor **13**) during the largely unsuccessful attempts to prepare **39** from **36** or **37** (see text). Compound **40**: $[\alpha]^{25}_D$ +57.0° (*c* 0.4, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.46 (m, 1 H), 5.01 (d, 1 H, J = 3.2 Hz), 5.54 (dd, 1 H, J = 12.0, 4.9 Hz), 4.56 (dd, 1 H, J = 12.0, 2.0 Hz), 4.03 (m, 1 H), 3.68 (m, 1

H), 2.32 (bdd, 1 H, J = 13.4, 5.5 Hz), 1.92 (bddd, 1 H, J = 3.4, 3.1, 3.2 Hz); HRMS calcd for $C_{26}H_{34}O_8SiNa$ (M + Na^+): 525.1921; found: 525.1938.

2-(Trimethylsilyl)ethyl 2-*O*-Benzoyl-3-deoxy-6-*O*-(*p*-methoxybenzoyl)-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-*ribo*-hexopyranoside (41) and 2-(Trimethylsilyl)ethyl 2-*O*-Benzoyl-3-deoxy-6-*O*-*p*-methoxybenzoyl-α-D-*ribo*-hexofuranoside (42). (a) A mixture of compound **36** (305 mg, 0.34 mmol), **19** (203 mg, 0.41 mmol), acid-washed molecular sieves (AW-300, 300 mg), and CH_2Cl_2 (5 mL) was cooled (ice−water bath), and the mixture was stirred under Ar for 20 min. Silver triflate (76 mg, 0.34 mmol) was added under protection from light. The mixture was stirred at 0 °C for 4.5 h. The cooling bath was removed, and stirring was continued for 20 h. An additional portion of silver triflate (30 mg, 0.13 mmol) was added, and the mixture was stirred for 3 h. The reaction was quenched by adding Et_3N (250 μL), and the mixture was diluted with CH_2Cl_2 (75 mL), filtered through Celite, washed with saturated aqueous $NaHCO_3$ (30 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 3:2) to give **42** (37 mg, 18%) and **41** (264 mg, 63%). Compound **42**: $[\alpha]^{25}_D$ -17.5° (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.36 (d, 1 H, J = 5.1 Hz), 5.14 (s, 1 H), 4.62 (dt, 1 H, J = 7.6, 3.9, Hz), 4.44 (dd, 1 H, J = 11.7, 4.6 Hz), 4.35 (dd, 1 H, J = 11.7, 6.6 Hz), 4.18 (bq, 1 H, J = 4.4 Hz), 3.86 (s, 3 H), 3.21 (s, 1 H), 2.57 (m, 1 H), 2.18 (dd, 1 H, J = 14.2, 7.1 Hz), 0,03 (s, 9 H); ^{13}C NMR δ 166.4, 165.8, 163.6, 122.1, 113.7, 105.4, 81.0, 78.7, 71.2, 66.1, 65.3, 55.5, 29.5, 18.2, −1.4; HRMS calcd for $C_{26}H_{34}O_8SiNa$ (M + Na): 525.1921; found: 525.1908.

Compound **41**: $[\alpha]^{25}_D$ +68.8° (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.64 (dd, 1 H, J = 10.6, 7.9 Hz), 5.49 (dd, 1 H, J = 3.0, 1.0 Hz), 5.42 (dd, 1 H, J = 11.0, 3.2 Hz), 5.18 (dd, 1 H, J = 11.0, 3.4 Hz), 5.01 (d, 1 H, J = 3.8 Hz), 4.97 (m, 1 H), 4.81, 4.60 (d, 1 H each, J = 7.8 and 7.9 Hz), 4.29 (d, 1 H, J = 2.3 Hz), 2.88 (dt, 1 H, J = 12.6, 5.1 Hz), 2.09, 2.05, 2.01, 1.96, 1.88 (s, 3 H each). Anal. Calcd for $C_{62}H_{72}O_{25}Si$: C 59.8, H 5.8. Found: C 59.8, H 5.7.

(b) A mixture of compound **37** (224 mg, 0.26 mmol), **19** (88 mg, 0.18 mmol), NIS (77 mg, 0.342 mmol), acid-washed molecular sieves (AW-300, 300 mg), and CH_2Cl_2 (5 mL) was cooled to −50 °C. The mixture was stirred under Ar for 60 min, and then silver triflate (6.8 mg, 0.026 mmol) was added under protection from light. The mixture was stirred at −50 °C for 40 min and at −30 °C for 3 h. Et_3N (200 μL) was added, and the mixture was diluted with CH_2Cl_2 (75 mL), filtered through Celite, washed with 10% aqueous $Na_2S_2O_3$ (40 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 3:2) to give **41** (201 mg, 92%).

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-benzoyl-6-deoxy-4-*O*-[2,3-di-*O*-benzoyl-6-*O*-(*p*-methoxybenzoyl)-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-*β*-D-galactopyranosyl]-*β*-D-glucopyranoside (43). A mixture of compound **25** (300 mg, 0.31 mmol), silver trifluoromethanesulfonate (120 mg, 0.46 mmol), collidine (92 mL, 0.69 mmol), acid-washed molecular sieves (AW-300, 150 mg), and CH_2Cl_2 (5 mL) was cooled to −60 °C. A solution of 2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl chloride[16] (265 mg, 0.64 mmol) in CH_2Cl_2 (3 mL) was added under Ar and protection from light. The mixture was kept at −50 °C for 2 h and at room temperature for 20 h. The mixture was diluted with CH_2Cl_2 (70 mL), filtered through Celite, washed with saturated aqueous $NaHCO_3$ (40 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, toluene/Et_2O 20:1) to give **43** (350 mg, 76%); $[\alpha]^{25}_D$ +35.7° (*c* 1.0 $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.77−5.68 (m, 2 H), 5.31 (dd, 1 H, J = 9.8, 7.9 Hz), 5.10 (dd, 1 H, J = 10.7, 2.7 Hz), 4.89 (d, 1 H, J = 7.9 Hz), 4.61 (d, 1 H, J = 8.0 Hz), 3.98 (dd, 1 H, J = 10.5, 2.2 Hz), 3.76 (t, 1 H, J = 9.2 Hz), 3.35 (t, 1 H, J = 9.4 Hz), 2.98 (dd, 1 H, J = 5.2 and 8.3 Hz), 1.28 (d, 3 H, J = 6.1 Hz), 0.10 (s, 9 H); ^{13}C NMR data ($CDCl_3$): δ 166.6, 165.4, 165.3, 165.1, 163.6, 122.3, 113.9, 101.8, 101.72, 101.68, 101.3, 101.2, 100.3, 100.2, 82.1, 79.1, 75.8, 75.5, 75.01, 74.95, 74.9, 74.5, 73.54, 73.47, 73.42, 73.39, 73.3, 73.0, 72.8, 72.72, 72.65, 71.2, 70.3, 69.8, 67.5, 61.7, 55.52, 55.48, 18.1, 17.7, −1.40, −1.42; HRMS calcd for $C_{87}H_{90}O_{21}SiNa$ (M + Na^+): 1521.5642; found: 1521.5654.

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-benzoyl-6-deoxy-4-*O*-[2,3-di-*O*-benzoyl-6-*O*-(*p*-methoxybenzoyl)-4-*O*-(α-D-galactopyranosyl)-*β*-D-galactopyranosyl]-*β*-D-glucopyranoside (44). Compound **43** (300 mg, 0.20 mmol) was dissolved in AcOH (5 mL), and the mixture was hydrogenated (H_2, Pd/C 10%, 50 mg) for 2 h. The mixture was filtered and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 1:20 → 0:1) to give **44** (212 mg, 93%); $[\alpha]^{25}_D$ +51.0° (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.70 (dd, 1 H, J = 10.7, 7.8 Hz), 5.65 (t, 1 H, J = 9.5 Hz), 5.36 (dd, 1 H, J = 9.8, 8.0 Hz), 5.23 (dd, 1 H, J = 10.7, 2.7 Hz), 4.93 (d, 1 H, J = 3.2 Hz), 4.83 (d, 1 H, J = 7.8 Hz), 4.61 (d, 1 H, J = 8.1 Hz), 4.25 (d, 1 H, J = 2.7 Hz), 3.84 (s, 3 H), 1.24 (d, 3 H, J = 5.9 Hz), −0.12 (s, 9 H); ^{13}C NMR data ($CDCl_3$): δ 166.0, 165.6, 165.4, 165.2, 102.04, 102.01, 101.98, 100.13, 100.08, 100.00, 82.6, 18.0, 17.4, −1.49, −1.51; HRMS calcd for $C_{59}H_{66}O_{21}SiNa$ (M + Na^+): 1161.3764; found: 1161.3740.

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-benzoyl-6-deoxy-4-*O*-[2,3-di-*O*-benzoyl-6-*O*-(*p*-methoxybenzoyl)-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-*β*-D-galactopyranosyl]-*β*-D-glucopyranoside (45). Compound **44** (105 mg, 0.092 mmol) was acetylated as described in the preparation of **34**. The crude product was chromatographed (SiO_2, heptane/EtOAc 1:1) to give **45** (119 mg, 99%); $[\alpha]^{25}_D$ +77.5° (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.73−5.63 (m, 2 H), 5.47 (dd, 1 H, J = 3.1, 1.0 Hz), 5.03 (d, 1 H, J = 3.4 Hz), 4.87 (d, 1 H, J = 7.8 Hz), 4.60 (d, 1 H, J = 8.0 Hz), 4.46 (bt, 1 H, J = 7.3 Hz), 4.22 (d, 1 H, J = 2.4 Hz), 3.86 (s, 3 H), 2.04, 2.00, 1.96, 1.90 (s, 3 H each), 1.25 (d, 3 H, J = 6.1 Hz), −0.12 (s, 9 H). Anal. Calcd for $C_{67}H_{74}O_{25}Si$: C 61.5, H 5.7. Found: C 61.3, H 5.6.

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]-propyl 3,4,6-Tri-*O*-benzoyl-2-deoxy-*β*-D-*arabino*-hexopyranoside (47) and 3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]propyl 3,4,6-Tri-*O*-benzoyl-2-deoxy-α-D-*arabino*-hexopyranoside (48). HCl (g) was bubbled into a cold (ice−water bath) solution of 3,4,6-tri-*O*-benzoyl-D-glucal[23] (100 mg, 0.22 mmol) in dry toluene (4 mL) for 40 min. The mixture was coconcentrated with $CHCl_3$ (2 × 2 mL) to remove unreacted HCl. The crude product was kept under vacuum (oil pump) overnight. A mixture of the crude 3,4,6-*O*-tribenzoyl-2-deoxy-α-D-*arabino*-hexopyranosyl chloride, compound **46** (150 mg, 0.23 mmol), acid-washed molecular sieves (3 Å, 300 mg), and CH_2Cl_2 (8 mL) was stirred for 30 min under Ar and then cooled (ice−water bath), and silver silicate (200 mg) was added under protection from light. The mixture was stirred at 0 °C for 0.5 h and at room temperature for 30 h and then filtered through Celite using hot CH_2Cl_2 (30 mL). The filtrate was concentrated, and the residue was chromatographed (SiO_2, heptane/EtOAc/CH_2Cl_2 8:1:2 → 5:1:2) to give **48** (50 mg, 21%) and **47** (115 mg, 48%). Compound **47**: $[\alpha]^{25}_D$ -5.3° (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.58 (t, 1 H, J = 9.6 Hz), 5.42 (m, 1 H), 4.83 (dd, 1 H, J = 9.4, 1.9 Hz), 4.65 (dd, 1 H, J = 12.1, 2.8 Hz), 4.46 (dd, 1 H, J = 12.0, 5.3 Hz), 2.62 (ddd, 1 H, J = 12.3, 5.2, 1.8 Hz), 0.88 (t, 6 H, J = 6.4 Hz); ^{13}C NMR data ($CDCl_3$): δ 166.1, 165.7, 165.5, 99.7. Anal. Calcd for $C_{63}H_{96}O_{12}S_2$: C 68.2, H 8.7. Found: C 68.3, H 8.6.

Compound **48**: $[\alpha]^{25}_D$ +19.4° (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.64 (m, 1 H), 5.57 (t, 1 H, J = 9.5 Hz), 5.11 (d, 1 H, J = 3.1 Hz), 4.58 (dd, 1 H, J = 12.1, 3.1 Hz), 4.47 (dd, 1 H, J = 12.2, 5.2 Hz), 4.36 (m, 1 H), 4.06 (dd, 1 H, J = 10.0, 4.6 Hz), 3.77 (dd, 1 H, J = 10.0, 4.8 Hz), 3.46 (dd, 2 H, J = 14.1, 6.4 Hz), 3.25 (dq, 2 H, J = 13.7, 6.0, 3.4 Hz), 3.12−2.98 (m, 5 H), 2.55 (dd, 1 H, J = 13.4, 4.9 Hz), 2.04 (m, 1 H), 0.88 (t, 6 H, J = 6.4 Hz); HRMS calcd for $C_{63}H_{96}O_{12}S_2Na$ (M + Na^+): 1131.6241; found: 1131.6251.

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]-propyl 2-Deoxy-*β*-D-*arabino*-hexopyranoside (49) and 3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]propyl 3,6-Di-*O*-benzoyl-2-deoxy-*β*-D-*arabino*-hexopyranoside (50). Compound **47** (129 mg, 0.12 mmol) was debenzoylated to give **49**, as described in the preparation of **1**. Without further characterization, the crude **49** and dibutyltin oxide (123 mg, 0.49 mmol) were refluxed in toluene/benzene (13 mL, 10:3); approximately 2 mL of the solvent was removed by

distillation. Benzoyl chloride (36 μL, 0.31 mmol) was added, and after 3 min, the mixture was cooled and diluted with CH_2Cl_2 (20 mL) and then cooled with an ice−water bath to crystallize the stannylene byproducts, filtered and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 4:1 → 3:1) to give **50** (98.2 mg, 84%): $[\alpha]^{25}_D$ −2.7° (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.15 (m, 1 H), 4.77 (dd, 1 H, *J* = 12.2, 4.2 Hz), 4.72 (dd, 1 H, *J* = 9.6, 1.9 Hz), 4.63 (dd, 1 H, *J* = 12.1, 2.0 Hz), 4.02, 3.96 (dd, 1 H each, *J* = 10.0, 5.0, 4.8 Hz), 2.45 (ddd, 1 H, *J* = 12.3, 5.1, 1.7 Hz), 0.88 (t, 6 H, *J* = 6.6 Hz); HRMS calcd for $C_{56}H_{92}O_{11}S_2Na$ (M + Na^+): 1027.5979; found: 1027.5958.

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]-propyl 3,6-Di-*O*-benzoyl-2-deoxy-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-*arabino*-hexopyranoside (51). Compound **50** (86 mg, 0.086 mmol) and compound **38** (100 mg, 0.12 mmol) were treated with silver silicate (240 mg) in CH_2Cl_2 (5 mL) as described in the preparation of **41**. After 48 h, the reaction mixture was worked up, and the crude product was chromatographed (SiO_2, heptane/EtOAc/CH_2Cl_2 2:1:1 → 3:2:2) to give **51** (124 mg, 83%): $[\alpha]^{25}_D$ +65.5° (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.65 (dd, 1 H, *J* = 10.8, 7.8 Hz), 5.44 (dd, 1 H, *J* = 3.1, 1.2 Hz), 5.35 (m, 1 H), 5.32 (dd, 1 H, *J* = 11.2, 3.2 Hz), 5.14 (dd, 1 H, *J* = 11.2, 3.5 Hz), 4.96 (d, 1 H, *J* = 3.4 Hz), 4.92 (d, 1 H, *J* = 7.8 Hz), 4.6 (bd, 1 H, *J* = 9.8 Hz), 4.19 (d, 1 H, *J* = 2.7 Hz), 3.51 (bt, 1 H, *J* = 6.8 Hz), 2.54 (bdd, 1 H, *J* = 12.2, 5.1 Hz), 2.03, 1.97, 1.96, 1.94, 1.85 (s, 3 H each), 0.88 (t, 6 H, *J* = 6.6 Hz); HRMS calcd for $C_{92}H_{130}O_{28}S_2Na$ (M + Na^+): 1769.8089; found: 1760.8059.

2-*O*-Benzoyl-3-deoxy-6-*O*-(*p*-methoxybenzoyl)-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]-D-*ribo*-hexopyranose (52). To a cold (-10 °C) solution of compound **41** (135 mg, 0.11 mmol) in CH_2Cl_2 (0.5 mL) was added trifluoroacetic acid (1 mL).[8] The mixture was stirred at −10 °C for 30 min, at 0 °C for 60 min, and 10 °C for 30 min, *n*-propyl acetate (3 mL) was added, and the mixture was coconcentrated with toluene (3 × 1 mL). The residue was chromatographed (SiO_2, heptane/EtOAc/CH_2Cl_2 4:3:2 → 2:3:1) to give **52** (121 mg, 98%), which was used without full characterization. HRMS calcd for $C_{59}H_{60}O_{25}Na$ (M + Na): 1167.3321; found: 1167.3333.

2-*O*-Benzoyl-3-deoxy-6-*O*-*p*-methoxybenzoyl-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]-α,*β*-D-*ribo*-hexopyranosyl Trichloroacetimidate (53). To a cold (0 °C) solution of compound **52** (113 mg, 0.099 mol) in CH_2Cl_2 (2 mL) was added trichloroacetonitrile (0.347 mL) and diazabicycloundecane (DMU, 0.014 mL). The reaction was monitored by TLC (heptane/EtOAc 1:1). The solvent was removed, and the residue was chromatographed (SiO_2, heptane/EtOAc/Et_3N 30:20:1) to give **53** (101 mg, 79% α/*β* ~2:1): ^{1}H NMR data ($CDCl_3$): δ 8.61 (s), 8.56 (s), 6.50 (d, *J* = 4.4 Hz), 5.99 (d, *J* = 7.9 Hz); HRMS calcd for $C_{59}H_{60}OSiNa$ (M + Na): 1310.2418; found: 1310.2412.

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]-propyl 2-*O*-Benzoyl-3-deoxy-6-*O*-(p-methoxybenzoyl)-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-*ribo*--hexopyranoside (54). A mixture of compound **53** (91 mg, 0.71 mmol), **46** (140 mg, 0.22 mmol), acid-washed molecular sieves (AW-300, 250 mg), and CH_2Cl_2 (5 mL) was stirred for 30 min under Ar and then cooled (ice−water bath), and TfOAg (56 mg, 0.070 mmol) was added. The mixture was stirred at 0 °C for 1 h under protection from light and then at room temperature for 5 h. Solid $NaHCO_3$ (0.5 g) and CH_2Cl_2 (25 mL) were added, and the mixture was stirred for 10 min and then filtered through Celite using hot CH_2Cl_2 (5 mL). The combined organic phase was washed with aqueous 10% $NaHCO_3$/10% NaCl (25 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 3:2) to give **54** (90.5 mg, 72%): $[\alpha]^{25}_D$ +48.5° (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.65 (dd, 1 H, *J* = 10.6, 7.8 Hz), 5.49 (dd, 1 H, *J* = 2.9, 1.0 Hz), 5.43 (dd, 1 H, *J* = 11.0, 3.3 Hz), 5.19 (m, 2 H), 5.04 (d, 1 H, *J* = 3.4 Hz), 4.97 (m, 1 H), 4.82 (d, 1 H, *J* = 7.8 Hz), 4.63 (d, 1 H, *J* = 7.8 Hz), 4.56 (bt, 1 H, *J* = 6.6 Hz), 4.30 (d, 1 H, *J* = 2.7 Hz), 3.50−2.72 (m, 10 H), 2.10, 2.06, 2.02, 1.96, 1.89 (s, 3 H each), 0.87 (t, 6 H, *J* = 6.5 Hz); HRMS calcd for $C_{93}H_{132}O_{29}S_2Na$ (M + Na^+): 1799.8193; found: 1799.8234.

2,3-Di-*O*-benzoyl-6-deoxy-4-*O*-[2,3-di-*O*-benzoyl-6-*O*-(*p*-methoxybenzoyl)-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-*β*-D-galactopyranosyl]-D-glucopyranose (55). Compound **45** (122 mg, 0.093 mmol) was treated with trifluoroacetic acid as described in the preparation of **52**. The crude product was chromatographed (SiO_2, heptane/EtOAc 1:1) to give **55** (106 mg, 94%), which was used without further characterization. HRMS calcd for $C_{62}H_{62}O_{25}Na$ (M + Na^+): 1229.3478; found: 1229.3447.

2,3-Di-*O*-benzoyl-6-deoxy-4-*O*-[2,3-di-*O*-benzoyl-6-*O*-(*p*-methoxybenzoyl)-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-*β*-D-galactopyranosyl]-*β*-D-glucopyranosyl Trichloroacetimidate (56). Compound **55** (102 mg, 0.085 mmol) was treated with trichloroacetonitrile (0.274 mL) and DBU (0.011 mL) as described in the preparation of **53**. The residue was chromatographed (SiO, heptane/EtOAc/Et_3N 1:1:0.05) to give **56** (92 mg, 81%); $[\alpha]^{25}_D$ +96.8° (*c*, 1.3 $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 8.49 (s, 1 H), 6.59 (d, 1 H, *J* = 3.9 Hz), 6.09 (t, 1 H, *J* = 9.3 Hz), 5.70 (dd, 1 H, *J* = 10.9, 7.8 Hz), 5.46 (bd, 1 H, *J* = 2.1 Hz), 5.40 (dd, 1 H, *J* = 10.2, 3.4 Hz), 5.14 (dd, 1 H, *J* = 11.2, 3.0 Hz), 5.15 (m, 2 H), 5.05 (d, 1 H, *J* = 3.5 Hz), 4.93 (d, 1 H, *J* = 8.0 Hz), 4.47 (bt, 1 H, *J* = 6.4 Hz), 4.23 (d, 1 H, *J* = 2.0 Hz), 3.50−2.72 (m, 10 H), 2.04, 2.00, 1.95, 1.89 (s, 3 H each), 1.24 (d, 3 H, *J* = 6.6 Hz); HRMS calcd for $C_{64}H_{62}O_{25}SiNa$ (M + Na): 1372.2574; found: 1372.2566.

3-(Hexadecylsulfonyl)-2-[(hexadecylsulfonyl)methyl]-propyl 2,3-Di-*O*-benzoyl-6-deoxy-4-*O*-[2,3-di-*O*-benzoyl-6-*O*-(*p*-methoxybenzoyl)-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-*β*-D-galactopyranosyl]-*β*-D-glucopyranoside (57). Compound **56** (82 mg, 0.061 mmol) was treated with **46** (119 mg, 0.18 mmol) and TfOAg (48 mg, 0.061 mmol) as described in the preparation of **54**. The crude product was chromatographed (SiO_2, heptane/EtOAc/CH_2Cl_2 14:7:4) to give **57** (88 mg, 79%): $[\alpha]^{25}_D$ +53.2° (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.74−5.62 (m, 2 H), 5.46 (dd, 1 H, *J* = 3.0, 1.2 Hz), 5.03 (d, 1 H, *J* = 3.7 Hz), 4.86 (d, 1 H, *J* = 7.7 Hz), 4.62 (d, 1 H, *J* = 8.1 Hz), 4.46 (bt, 1 H, *J* = 6.7 Hz), 4.23 (d, 1 H, *J* = 2.3 Hz), 3.15 (m, 2 H), 2.89 (m, 4 H), 2.68 (m, 1 H), 2.05, 2.00, 1.96, 1.90 (s, 3 H each), 0.88 (t, 6 H, *J* = 6.4 Hz); HRMS calcd for $C_{98}H_{134}O_{29}S_2Na$ (M + Na^+): 1861.8450; found: 1861.8301.

Acknowledgment. This work was supported by the Swedish Natural Science Research Council.

Supporting Information Available: ^{1}H NMR spectra and ^{1}H NMR data with peak assignments for all title compounds described in the Experimental Section (73 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.

JO951914K