Synthesis of XylβCer, Galβ1−4XylβCer, NeuAcα2−3Galβ1−4XylβCer and the Corresponding Lactone and Lactam Trisaccharides

Michael Wilstermann and Göran Magnusson*

Organic Chemistry 2, Center for Chemistry and Chemical Engineering, Lund University, P.O. Box 124, S-221 00 Lund, Sweden

Received February 18, 1997[⊗]

2-(Trimethylsilyl)ethyl 2-*O*-benzoyl- and 2,3-di-*O*-acetyl-β-D-xylopyranosides (**12** and **14**) were synthesized in high yields and subjected to glycosylation with various glycosyl donors. Galactosylation of **12** gave the xylose analogue of TMSEt lactoside (**3**), which was transformed into the glycosyl acceptor **19**. Sialylation then gave the xylose analogue of G_{M3} trisaccharide (**5**). The TMSEt glycosides **10**, **25**, and **32** were transformed into the corresponding trichloroacetimidates, which were used for glycosylation of an azidosphingosine derivative. The resulting sphingosyl glycosides were transformed into the title ceramides. Treatment of NeuAcα2−3Galβ1−4XylβCer (**5**) with acetic acid gave the corresponding 1″→2′-lactone **7**. Glycosylation of **12** or **14** with a G_{M4}-lactam donor (**40**) gave the xylose analogue of G_{M3}-lactam (**42**). There was a 3-fold increase in the formation of GAG chains in the presence of 0.5 μM XylβCer (**2**) in the medium.

Introduction

Glycosaminoglycan (GAG) chains are anchored to specific core proteins via a xylosyl-serine glycosidic linkage.[1] Xylosides carrying hydrophobic aglycons can function as competitive inhibitors of proteoglycan biosynthesis by serving as primers for free (not protein-bound) GAG-chain assembly. While certain monoxylosides are taken up by cells,[2] disaccharides carrying the hydrophobic naphthyl aglycon on the xylose moiety were not taken up unless the saccharide moiety was partially methylated or acetylated.[3] The xyloside naroparcil was recently shown to have an in vivo effect on GAG biosynthesis in rabbits.[4]

In addition to the inhibitory effect of xylosides on protein-bound GAG-chain assembly, treatment of human melanoma cells or Chinese hamster ovary cells with 4-methylumbelliferyl-β-D-xylopyranoside (Xylβ4MU) caused the expected free GAG-chain synthesis to transgress to a substantial degree into the glycolipid biosynthetic pathway, resulting in the formation of the novel trisaccharide NeuAcα2−3Galβ1−4Xylβ4MU,[5] a xylose analogue of the ganglioside G_{M3} trisaccharide. However, further sialylation into the G_{D3} analogue NeuAcα2−8NeuAcα2−3Galβ1−4Xylβ4MU was not observed. It thus seems as if the sialyl-2,3-transferase involved in G_{M3} synthesis does not discriminate between its substrates Galβ1−4GlcβCer and Galβ1−4XylβMU, whereas the sialyl-2,8-transferase of G_{D3} synthesis cannot use NeuAcα2−3Galβ1−4Xylβ4MU as a substrate. It is not clear if the Xyl or the MU moiety is responsible for this lack of recognition by the sialyl-2,8-transferase.

Gangliosides are known to lactonize upon treatment with acid in vitro.[6] The question of lactonization in vivo has been debated for decades, and experimental evidence has come from investigations such as reductive radiolabeling with tritium[6b] and immunostaining of cells with antibodies raised against ganglioside lactones.[7] However, the hydrolytic lability of the lactones has made it difficult to draw any safe conclusions about their presence in vivo, especially since the antibodies cross-reacted with the nonlactonized form of the ganglioside. Ganglioside lactones are in practice poor immunogens because of the easy hydrolysis of the lactone ring. We have synthesized ganglioside lactams, which are quite stable against hydrolysis and have conformations very similar to those of the ganglioside lactones.[8] Antibodies, raised against the G_{M3}-lactam, were found to cross-react with G_{M3}-lactone in vitro, but not with the open form G_{M3}-ganglioside.[9] Mouse melanoma cells that are known to carry large amounts of surface-bound G_{M3}-ganglioside, were stained by the anti-G_{M3}-lactam antibodies, which strongly indicates that G_{M3}-lactone is present on the cell surface.[10]

Xylose and ceramide are intrinsic components of proteoglycans and glycosphingolipids, respectively. The XylβCer-containing hybrids presented here might well be taken up by cells in a more efficient way than other glycosides and would therefore be of use for investigations of the specificity of the glycosyl transferases involved in glycoprotein and glycolipid biosynthesis. We now report

[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1997.

(1) (a) Muir, H.; Hardingham, T. E. In *Biochemistry of Carbohydrates,* Whelan, W. J., Ed., M. T. P. Internat. Rev. Sci. Biochem., Ser. 1, Butterworths: London, 1975; Vol. 5. (b) Schwartz, N. B. *Trends Glycosci. Glycotechnol.* **1995**, *7*, 429−445.

(2) (a) Okayama, M.; Kimata, K.; Suzuki, S. *J. Biochem. (Tokyo)* **1973**, *74*, 1069−1073. (b) Sobue, M.; Habuchi, H.; Ito, K.; Yonekura, H.; Oguri, K.; Sakurai, K.; Kamohara, S.; Ueno, Y.; Noyori, R.; Suzuki, S. *Biochem. J.* **1987**, *241*, 591−601.

(3) Sarkar, A. K.; Fritz, T. A.; Taylor, W. H.; Esko, J. D. *Proc. Natl. Acad. Sci. U.S.A.* **1995**, *92*, 3323−3327.

(4) Masson, P. J.; Coup, D.; Millet, J.; Brown, N. L. *J. Biol. Chem.* **1995**, *270*, 2662−2668.

(5) (a) Freeze, H. H.; Sampath, D.; Varki, A. *J. Biol. Chem.* **1993**, *268*, 1618−1627. (b) Freeze, H. H.; Etchison, J. R. *Trends Glycosci. Glycotechnol.* **1996**, *8*, 65−77.

(6) (a) Wiegandt, H. *Physiol. Biol. Chem. Exp. Pharmacol.* **1966**, *57*, 190−222. (b) Gross, S. K.; Williams, M. A.; McCluer, R. H. *J. Neurochem.* **1980**, *34*, 1351−1361. (c) Riboni, L.; Sonnino, S.; Acquotti, D.; Malesci, A.; Ghidoni, R.; Egge, H.; Mingrino, S.; Tettamanti, G. *J. Biol. Chem.* **1986**, *261*, 8514−8519. (d) Bassi, R.; Riboni, L.; Sonnino, S.; Tettamanti, G. *Carbohydr. Res.* **1989**, *193*, 141−146. (e) Maggio, B.; Ariga, T.; Yu, R. K. *Biochemistry* **1990**, *29*, 8729−8734.

(7) (a) Nores, G. A.; Dohi, T.; Taniguchi, M.; Hakomori, S. *J. Immunol.* **1987**, *139*, 3171−3176. (b) Bouchon, B.; Levery, S. B.; Clausen, H.; Hakomori, S. *Glycoconj. J.* **1992**, *9*, 27−38.

(8) (a) Ray, A. K.; Nilsson, U.; Magnusson, G. *J. Am. Chem. Soc.* **1992**, *114*, 2256−2257. (b) Wilstermann, M.; Kononov, L. O.; Nilsson, U.; Ray, A. K.; Magnusson, G. *J. Am. Chem. Soc.* **1995**, *117*, 4742−4754.

(9) Ding, K.; Rosén, A.; Ray, A. K.; Magnusson, G. *Glycoconj. J.* **1993**, *9*, 303−306.

(10) Magnusson, G.; Ding, K.; Nilsson, U.; Ray, A. K.; Rosén, A.; Sjögren, H.-A. In *Complex Carbohydrates in Drug Research*; Alfred Benzon Symposium 36, Bock, K., Clausen, H., Eds.; Munksgaard: Copenhagen, 1994; pp 89−100.

S0022-3263(97)00298-3 CCC: $14.00

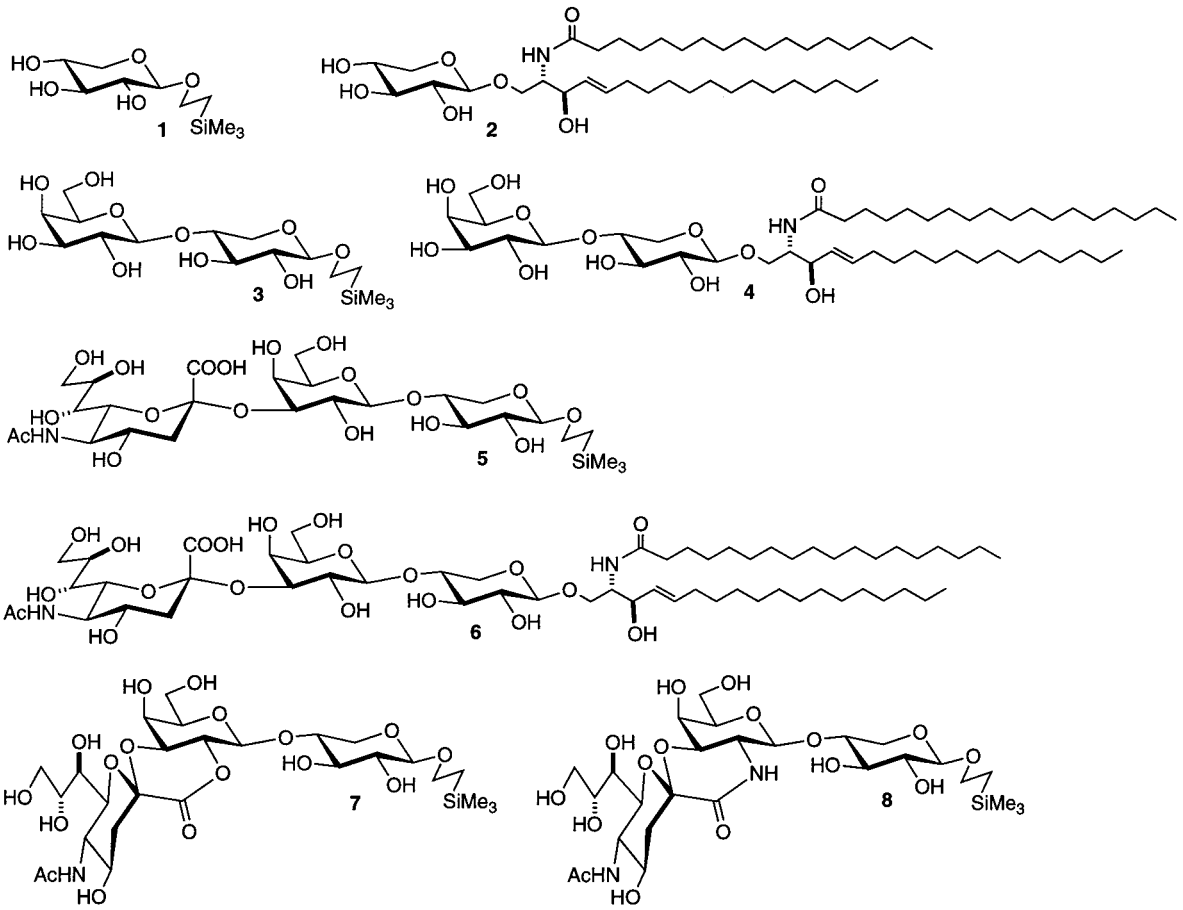


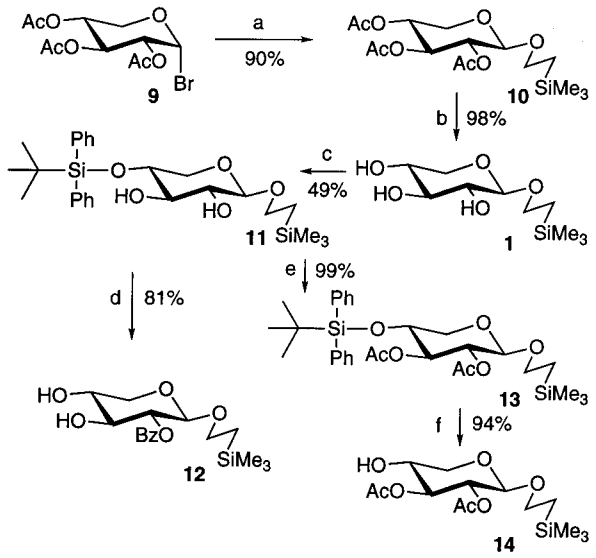
Figure 1. Synthetic xylosides.

the chemical synthesis of the novel TMSEt xylosides **1**, **3**, and **5**, and the glycolipids XylβCer (**2**), Galβ1−4XylβCer (**4**), and NeuAcα2−3Galβ1−4XylβCer (**6**) (Figure 1), with potential for further investigations of GAG and glycolipid biosynthesis. XylβCer (**2**) was found to initiate the biosynthesis of GAG chains in cell culture, as discussed below. Furthermore, the G_{M3}-lactone and -lactam analogues **7** and **8** were synthesized (Figure 1) for intended use in investigations of the possible in vivo sialylation of ganglioside lactones (e.g. G_{M3}-lactone → G_{D3}-lactone), a question that has not been addressed in the literature.

Results and Discussion

I. Synthesis of Glycosyl Acceptor Xylosides. Glycosylation of 2-(trimethylsilyl)ethanol with acetobromoxylose[11] (**9**, Scheme 1) gave **10** (90%), and the acetyl groups were removed to give the TMSEt xyloside **1** (98%). Attempted isopropylidenation, as well as regioselective acylation and allylation via stannylene complexes as described for the corresponding methyl xyloside,[12] were unsuccessful. Instead, silylation of **1** with *tert*-butylchlorodiphenylsilane provided the 4-*O*-silylated compound **11** (49%) together with the corresponding 2-*O*- (27%) and 3-*O*- (trace) silylated isomers. The diol **11** was *O*-benzoylated by benzoyl chloride (1.3 equiv) at the 2-position in a completely regioselective reaction. The same result was obtained with 3 equiv of benzoyl chloride,

Scheme 1[a]

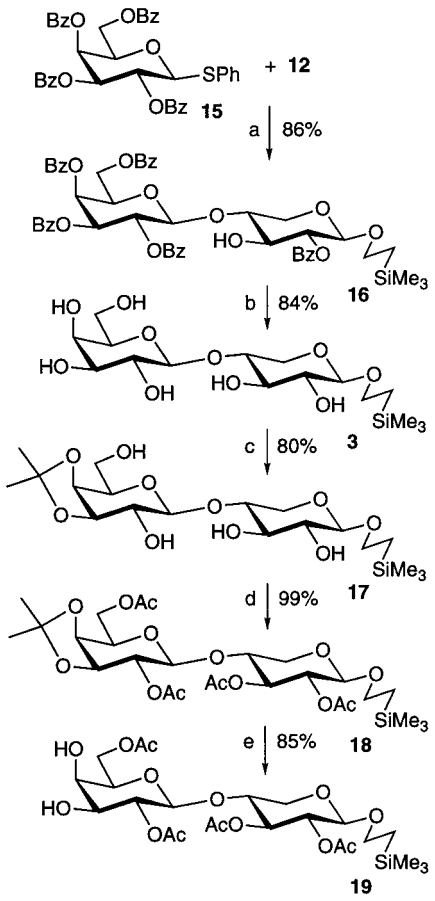


[a] (a) HgO, $HgBr_2$, TMSEtOH, CH_2Cl_2, MS 4 Å; (b) MeONa, MeOH; (c) TBDPSCl, Et_3N, DMAP, $CHCl_3$; (d) PhCOCl, pyridine, then $Bu_4NF{\cdot}3H_2O$, HOAc, THF; (e) Ac_2O, pyridine; (f) $Bu_4NF{\cdot}3H_2O$, HOAc, THF.

showing that HO-3 of 2-*O*-benzoylated **11** is highly unreactive. Removal of the silyl protecting group with Bu_4NF/acetic acid in THF provided the diol **12** (81% overall yield from **11**). In contrast to the benzoylation of **11**, acetylation with an excess of acetic anhydride furnished the diacetate **13** (99%), and desilylation of **13** as above gave **14** (94%). Attempted desilylation of **13**

(11) Weygand, F. *Methods in Carbohydrate Chemistry*; Academic Press: New York and London, 1962; Vol. 1, pp 182−185.
(12) Helm, R. F.; Ralph, J. *J. Org. Chem.* **1991**, *56*, 7015−7021.

Scheme 2[a]



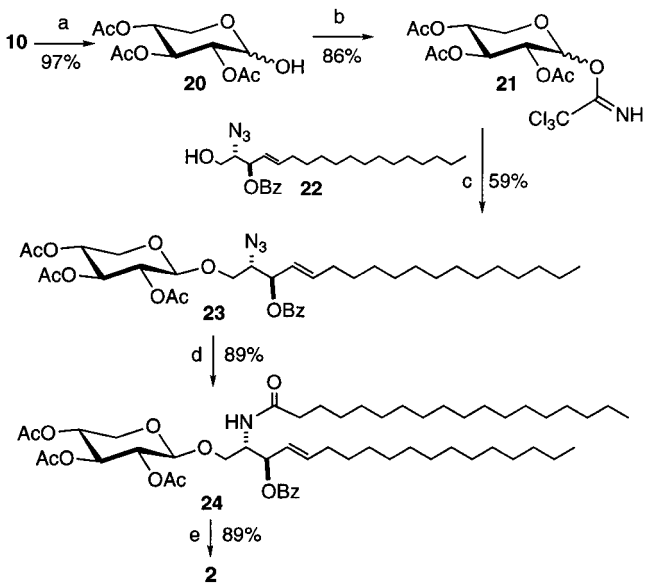
[a] (a) NIS, TfOH, MeCN, CH_2Cl_2, MS 300AW, −45 °C; (b) MeONa, MeOH; (c) $Me_2C(OMe)_2$, $MePhSO_3H$; (d) Ac_2O, pyridine; (e) AcOH, H_2O, 50 °C.

with Bu_4NF in THF resulted in partial acetyl migration from position 3 to position 4. Compounds **12** and **14** were used as glycosyl acceptors in the ensuing reactions, as shown below.

II. Synthesis of Gal*β*1−4Xyl*β*OTMSEt. The diol acceptor **12** was glycosylated with the thiogalactoside **15**,[13] under activation with *N*-iodosuccinimide (NIS) and trifluoromethanesulfonic acid (TfOH),[14] to provide the disaccharide derivative **16** (86%, Scheme 2), contaminated with approximately 10% of the corresponding *β*-1,3 regioisomer. De-*O*-benzoylation with methanolic sodium methoxide gave a mixture of two disaccharides; chromatographic purification permitted the isolation of pure **3** (84%). Treatment of **3** with 2,2-dimethoxypropane and *p*-toluenesulfonic acid gave the 3,4-*O*-isopropylidene derivative **17** (80%), and subsequent *O*-acetylation afforded **18** (99%). De-*O*-isopropylidenation of **18** with aqueous acetic acid at 50 °C gave the glycosyl acceptor **19**. When the reaction was performed at 90 °C, the 6′-*O*-acetyl group migrated partially to the 4′-position.

III. Synthesis of Xyl*β*Cer, Gal*β*1−4Xyl*β*Cer, and NeuAcα2−3Gal*β*1−4Xyl*β*Cer. Transformation of the TMSEt glycosides **10**, **25**, and **32** into the corresponding glycosyl ceramides was performed as depicted in Schemes

Scheme 3[a]



[a] (a) CF_3COOH, CH_2Cl_2; (b) Cl_3CCN, DBU, CH_2Cl_2, 0 °C; (c) $BF_3{\cdot}Et_2O$, CH_2Cl_2, MS 300AW, −33 °C; (d) H_2S, pyridine, H_2O, then $C_{17}H_{35}COOH$, EDC·HCl, CH_2Cl_2; (e) MeONa, MeOH, CH_2Cl_2

3-5. Acetylation of the TMSEt disaccharide **3** gave **25** (95%) (Scheme 4). Sialylation of **19** with the sialyl xanthate donor **30**[15] (Scheme 5) gave the trisaccharide **31** (56%), and *O*-acetylation of **31** permitted isolation of the per-*O*-acetate **32** (99%).

Treatment of **10**, **25**, and **32** with trifluoroacetic acid[16] (TFA) furnished the hemiacetals **20** (97%), **26** (100%), and **33** (100%), respectively (Schemes 3−5), and subsequent treatment of the hemiacetals with trichloroacetonitrile[17] provided the trichloroacetimidates **21**[18] (84%), **27** (92%), and **34** (81%) as α,*β* mixtures. Glycosylation of the azidosphingosine derivative **22**[19] with imidates **21**, **27**, and **34** gave the glycosides **23** (59%), **28** (70%), and **35** (66%), respectively. An excess of boron trifluoride etherate (10 equiv) was used in all these glycosylations in order to avoid contamination of the product by the corresponding ortho esters. The azidosphingosine glycosides were reduced with hydrogen sulfide, and the resulting amines were acylated with octadecanoic acid in the presence of 1-ethyl-3-[3-(dimethylamino)propyl]carbodiimide, to give the protected glycosyl ceramides **24** (89%), **29** (80%), and **36** (88%). Removal of the acetyl groups in **24** and **29** by treatment with methanolic sodium methoxide provided Xyl*β*Cer (**2**, 89%, Scheme 3) and Gal*β*1−4Xyl*β*Cer (**4**, 95%, Scheme 4). Treatment of **36** with methanolic sodium methoxide, followed by aqueous sodium hydroxide, gave NeuAcα2−3Gal*β*1−4Xyl*β*Cer (**6**, 53%; Scheme 5).

IV. Synthesis of NeuAcα2−3Gal*β*1−4Xyl*β*TMSEt-lactone and -lactam. Ganglioside lactones, in equilibrium with the parent gangliosides, have been found to

(13) Ferrier, R. J.; Furneaux, R. H. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1993−1996.

(14) (a) Konradsson, P.; Mootoo, D. R.; McDewitt, R. E.; Fraser-Reid, B. *J. Chem. Soc., Chem. Commun.* **1990**, 270−272. (b) Veeneman, G. H.; van Leeuwen, S. H.; van Boom, J. H. *Tetrahedron Lett.* **1990**, *31*, 1331−1334.

(15) Marra, A. Sinaÿ, P. *Carbohydr. Res.* **1990**, *195*, 303−308.

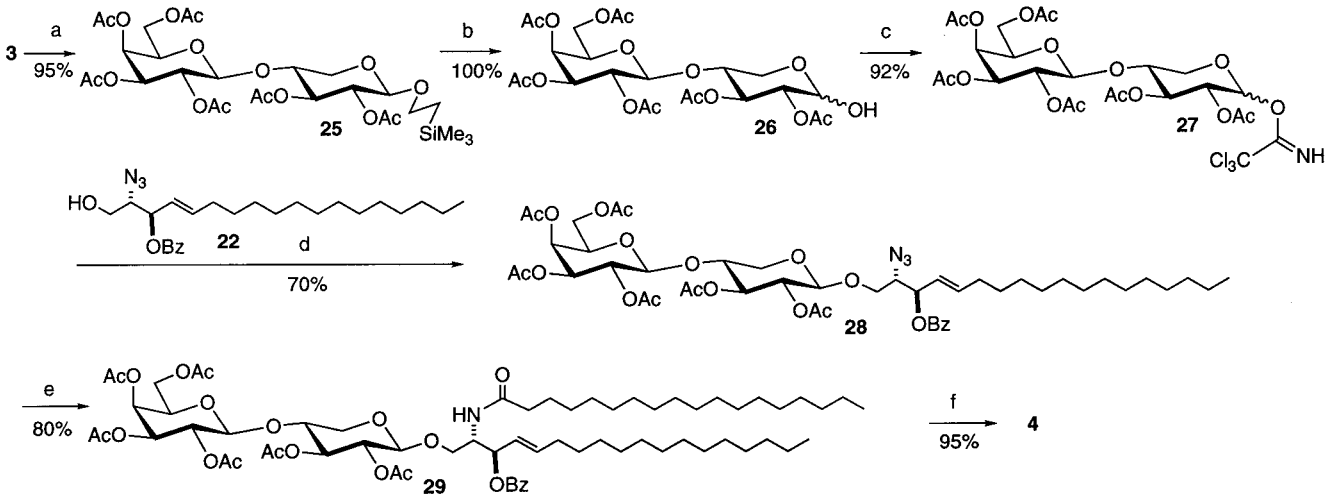
(16) Jansson, K.; Ahlfors, S.; Frejd, T.; Kihlberg, J.; Magnusson, G.; Dahmén, J.; Noori, G.; Stenvall, K. *J. Org. Chem.* **1988**, *53*, 5629−5647.

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

(18) Mori, M.; Ito, Y.; Ogawa, T. *Carbohydr. Res.* **1990**, *195*, 199−224.

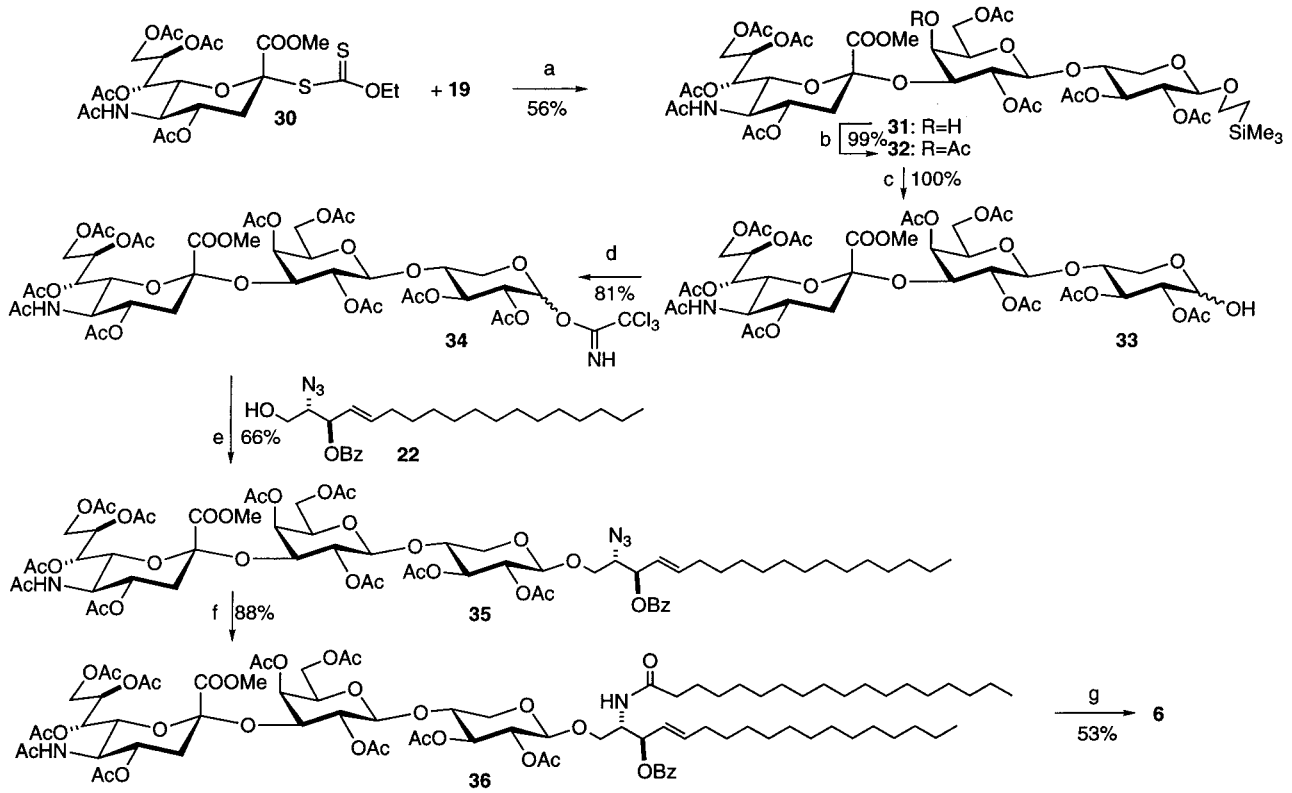
(19) (a) Schmidt, R. R.; Zimmermann, P.; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 725−726. (b) Ito, Y.; Kiso, M.; Hasegawa, A. *J. Carbohydr. Chem.* **1989**, *8*, 285−294.

Scheme 4[a]



[a] (a) Ac_2O, pyridine; (b) CF_3COOH, CH_2Cl_2; (c) Cl_3CCN, DBU, CH_2Cl_2, 0 °C; (d) $BF_3{\cdot}Et_2O$, CH_2Cl_2, MS 300AW, −33 °C; (e) H_2S, pyridine, H_2O, then $C_{17}H_{35}COOH$, EDC·HCl, CH_2Cl_2; (f) MeONa, MeOH, CH_2Cl_2.

Scheme 5[a]



[a] (a) MeSBr, TfOAg, MeCN, CH_2Cl_2, MS 3 Å, −72 °C; (b) Ac_2O, pyridine; (c) CF_3COOH, CH_2Cl_2; (d) Cl_3CCN, DBU, CH_2Cl_2, 0 °C; (e) $BF_3{\cdot}Et_2O$, CH_2Cl_2, MS 300AW, −33 °C; (f) H_2S, pyridine, H_2O, then $C_{17}H_{35}COOH$, EDC·HCl, CH_2Cl_2; (g) MeONa, NaOH (aq), MeOH, CH_2Cl_2.

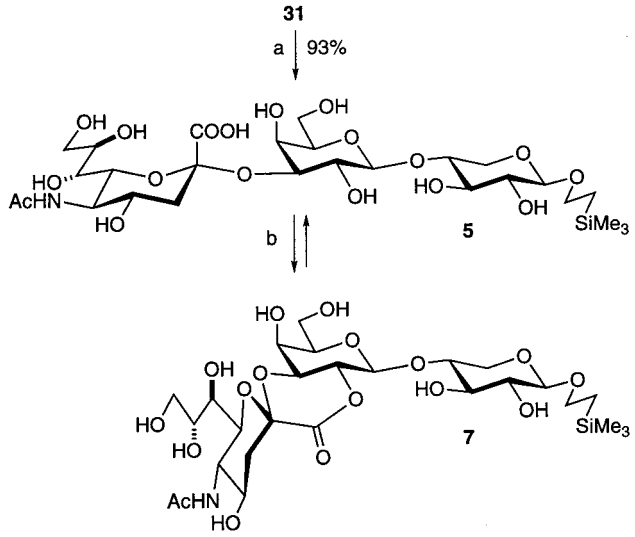
be present on the surface of inter alia tumor cells, as discussed in the Introduction. The corresponding lactams have conformations very similar to those of the lactones and are much more stable against hydrolysis.[8] Therefore, ganglioside lactams can be used as well-defined antigens for the production of antibodies that recognize ganglioside lactones.[9,10]

Compound **31** was treated with methanolic sodium methoxide followed by aqueous sodium hydroxide, to furnish the xylose analogue (**5**, 93%) of the G_{M3} TMSEt trisaccharide (Scheme 6).[8] Treatment of **5** with acetic acid caused formation of the 1″→2′ lactone **7** as the main product (Scheme 6), together with unreacted **5** (**7**/**5** ∼3:1) and a small amount (∼5%) of the corresponding 1″→4′ lactone.

The G_{M4}-lactam disaccharide **37**[8b] was acetylated to give **38** (91%). Removal of the TMSEt protecting group with trifluoroacetic acid[16] provided the hemiacetal **39** (100%), and treatment of the latter with oxalyl bromide gave the glycosyl bromide **40** (61%). Compound **40** was transformed into the xanthate **41** by treatment with potassium ethylxanthate (Scheme 7).

The substituent in the 2-position of glycosyl donors **40** and **41** is unable (for steric reasons) to participate in

Scheme 6[a]



[a] (a) MeONa, MeOH, then H_2O, NaOH, MeOH; (b) AcOH.

stabilizing a positive charge at the anomeric carbon. Therefore, it was anticipated that **40** and **41** might give α/β mixtures on glycosylation. However, this was not the case with silver silicate-promoted[20] glycosylation of xyloside **14** with the bromide donor **40**, and the desired trisaccharide **42** was obtained, albeit in low yield (24%). In an attempt to raise the yield, the less hindered diol acceptor **12** was used, but this led to a mixture of the desired **43** and it's O-3 regioisomer **44** (45%; 1:2). In another attempt, glycosylation of **14** with the xanthate donor **41** also failed. De-*O*-acetylation of **42** gave the xylose analogue (**8**, 95%) of the G_{M3}-lactam[8] TMSEt trisaccharide.

The preponderant formation of the O-3 regioisomer **44** in the glycosylation of **12** with **40**, as discussed above, is in sharp contrast to the glycosylation of **12** with the galactose donor **15**, where the O-4:O-3 ratio of regioisomers was 10:1 (Scheme 2). However, glycosylation of **12** with the donor 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl bromide[21] proceeded with the same O-4: O-3 ratio (1:2) as in the glycosylation with the donor **40**; both donors carry a nonparticipating group in the 2-position.

VII. Induction of GAG Chain Biosynthesis. In a preliminary investigation, it was found that the xylosylceramide **2** induced the biosynthesis of GAG chains.[22] The test was performed by incubating skin fibroblasts with ^{35}S-sulfate-containing medium in the presence of various concentrations of **2** in fetal calf serum, sonicated to improve uptake by the fibroblasts. Radiosulfated xyloside-primed and secreted GAGs were recovered from the medium, using methods described in detail elsewhere.[23] There was a 3-fold increase in the formation of GAG chains at a 0.5 μM concentration of **2** in the medium. A full account of the induction of GAG chains by the xylose-containing ceramides **2** and **4** will be reported in due course.

(20) van Boeckel, C. A. A.; Beetz, T. *Rec. Trav. Chim. Pays-Bas* **1987**, *106*, 596−598.
(21) (a) Sabesan, S.; Lemieux, R. U. *Can. J. Chem.* **1984**, *62*, 644−654. (b) Broddefalk, J.; Nilsson, U.; Kihlberg, J. *J. Carbohydr. Chem.* **1994**, *13*, 129−132.
(22) Fransson, L.-Å., personal communication.
(23) (a) Fransson, L.-Å.; Havsmark, B.; Sakuari, K.; Suzuki, S. *Glycoconj. J.* **1992**, *9*, 45−55. (b) Fransson, L.-Å.; Karlsson, P.; Schmidtchen, A. *Biochim. Biophys. Acta 1992*, *1137*, 287−297.

Experimental Section

Melting points are uncorrected. ^{1}H NMR spectra were recorded at 300, 400, and 500 MHz. Assignment of ^{1}H signals was based on COSY and HETCOR 2D-techniques. Reactions were performed at room temperature unless stated otherwise. Concentrations were made by rotary evaporation with bath temperature at or below 40 °C. TLC was performed on Kiselgel 60 F_{254} plates (Merck) and column chromatography on SiO_2 (Matrex LC-gel: 60A, 35−70 MY, Grace).

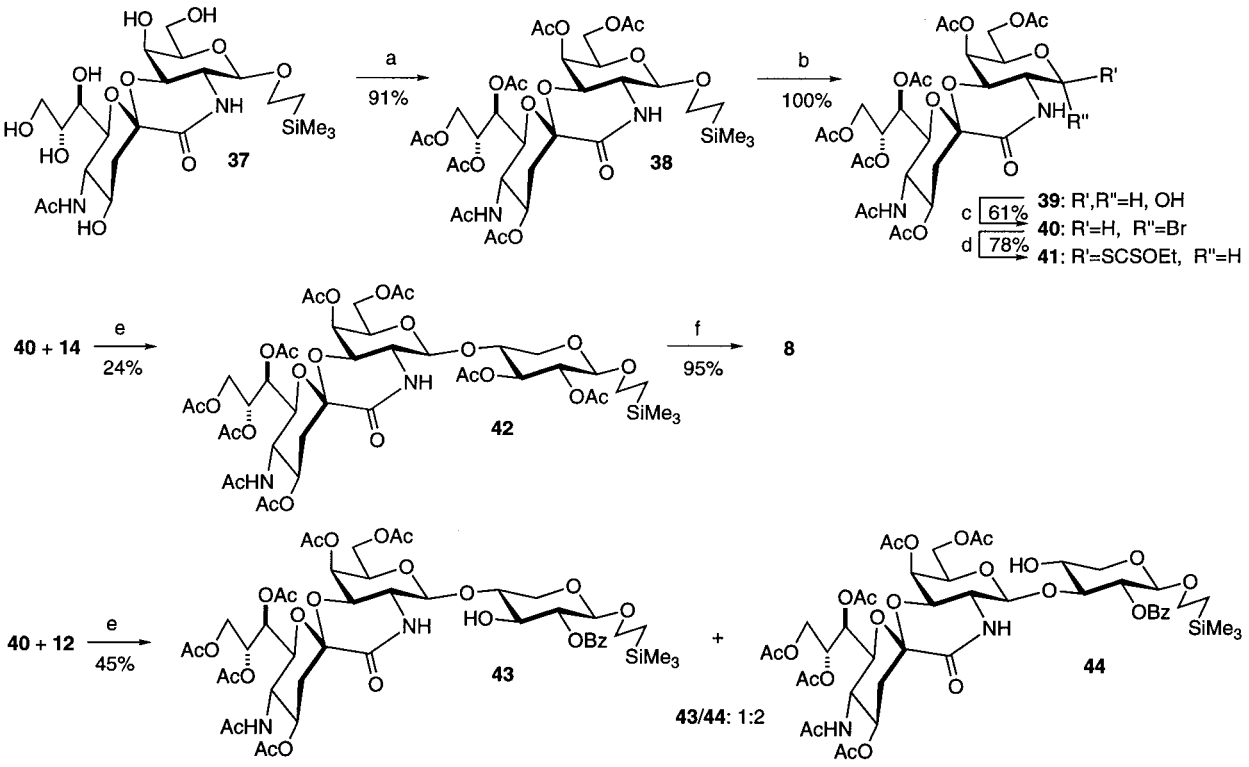
2-(Trimethylsilyl)ethyl β-D-Xylopyranoside (1). Methanolic sodium methoxide (2 M, 10 mL) was added to a solution of compound **10** (13.9 g, 37.0 mmol) in dry MeOH (200 mL), and the mixture was stirred for 2 h and then neutralized with Amberlite IR 120 (H^+) resin, filtered, and concentrated. The residue was chromatographed (SiO_2, CH_2Cl_2/EtOH 8:1) to give **1** (9.1 g, 98%); $[\alpha]^{25}_D$ −33 (*c* 1.0, MeOH); ^{1}H NMR data (D_2O): δ 4.28 (d, 1 H, J = 7.9 Hz, H-1), 3.89−3.75 (m, 2 H), 3.61 (m, 1 H, OCH_2), 3.47 (m, 1 H, OCH_2), 3.28 (t, 1 H, J = 9.2 Hz, H-3), 3.20−3.12 (m, 2 H), 0.89 (m, 2 H, CH_2Si), −0.11 (s, 9 H, $SiMe_3$); HRMS calcd for $C_{10}H_{23}O_5Si$ (M + H): 251.1315; found: 251.1309.

(2*S*,3*R*,4*E*)-3-Hydroxy-2-octadecanamidooctadec-4-enyl β-D-Xylopyranoside (2). Methanolic sodium methoxide (1.1 M, 0.010 mL) was added to a solution of compound **24** (10.5 mg, 0.011 mmol) in dry MeOH (0.5 mL) and dry CH_2Cl_2 (0.5 mL) under Ar. The mixture was stirred for 3 h and then neutralized with acetic acid and concentrated. The residue was chromatographed (SiO_2, CH_2Cl_2/MeOH 15:1) to give **2** (7.1 mg, 89%); $[\alpha]^{22}_D$ −16 (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$ + 2% CD_3OD): δ (assignment of aglycon protons are shown in italic) 5.71 (m, 1 H, *H-5*), 5.44 (dd, 1 H, J = 15.4, 6.4 Hz, *H-4*), 4.23 (d, 1 H, J = 6.9 Hz, H-1), 4.15−4.00 (m, 3 H), 3.96 (dd, 1 H, J = 11.6, 4.9 Hz, H-5), 3.64−3.55 (m, 2 H), 3.44 (t, 1 H, J = 8.2 Hz, H-3), 3.28 (dd, 1 H, J = 8.2, 7.0 Hz, H-2), 3.25 (dd, 1 H, J = 11.7, 9.3 Hz, H-5), 2.18 (t, 2 H, J = 7.2 Hz, *H-2′*), 1.71−1.15 (m, 54 H, CH_2), 0.86 (t, 6 H, J = 6.9 Hz, CH_3); ^{13}C NMR data ($CDCl_3$ + 2% CD_3OD): δ 174.7, 134.7, 128.9, 104.0, 75.8, 73.6, 72.9, 69.8, 69.3, 65.4, 53.3, 32.7, 32.3, 30.1−29.5, 26.2, 23.1, 14.5; HRMS calcd for $C_{41}H_{79}O_7NNa$ (M + Na): 720.5754; found 720.5756.

2-(Trimethylsilyl)ethyl 4-*O*-(β-D-Galactopyranosyl)-β-D-xylopyranoside (3). Compound **16** (200 mg, 0.217 mmol) was deacylated as described in the preparation of **1**, to give **3**, contaminated with approximately 10% of the corresponding 3-*O* regioisomer. Column chromatography (SiO_2, CH_2Cl_2/MeOH 5:1) gave pure **3** (75 mg, 84%); $[\alpha]^{24}_D$ −32 (*c* 1.0, MeOH); ^{1}H NMR data (D_2O): δ 4.33 (d, 1 H, J = 7.8 Hz, H-1′), 4.30 (d, 1 H, J = 7.8 Hz, H-1), 3.94 (dd, 1 H, J = 11.7, 5.3 Hz), 3.84 (m, 1 H), 3.78 (d, 1 H, J = 3.4 Hz), 3.75−3.54 (m, 5 H), 3.51 (dd, 1 H, J = 10.0, 3.4 Hz, H-3′), 3.44 (t, 1 H, J = 11.1 Hz, H-3), 3.37 (dd, 1 H, J = 10.0, 7.7 Hz, H-2′), 3.25 (t, 1 H, J = 11.5 Hz, H-5), 3.12 (dd, 1 H, J = 9.2, 7.9 Hz, H-2), 0.88 (m, 2 H, CH_2Si), −0.11 (s, 9 H, $SiMe_3$); ^{13}C NMR data (D_2O): δ 103.0, 102.6, 73.7, 73.5, 71.5, 69.5, 69.2, 67.4, 63.8, 61.9, 18.4, −1.7; HRMS calcd for $C_{16}H_{33}O_{10}Si$ (M + H): 413.1843; found: 413.1844. 2-(Trimethylsilyl)ethyl 3-*O*-(β-D-galactopyranosyl)-β-D-xylopyranoside: $[\alpha]^{24}_D$ −30 (*c* 1.0, MeOH); ^{1}H NMR data (D_2O): δ 4.55 (d, 1 H, J = 7.7 Hz, H-1), 4.36 (d, 1 H, J = 7.9 Hz, H-1′), 3.92−3.86 (m, 2 H), 3.82 (brd, 1 H, J = 3.2 Hz, H-4′), 3.73−3.56 (m, 7 H), 3.50 (dd, 1 H, J = 9.9, 7.7 Hz, H-2′), 3.34 (t, 1 H, J = 8.4 Hz, H-3), 3.24 (t, 1 H, J = 10.7 Hz, H-5), 0.92 (m, 2 H, CH_2Si), −0.07 (s, 9 H, $SiMe_3$).

(2*S*,3*R*,4*E*)-3-Hydroxy-2-octadecanamidooctadec-4-enyl 4-*O*-(β-D-galactopyranosyl)-β-D-xylopyranoside (4). Methanolic sodium methoxide (1.1 M, 0.008 mL) was added to a solution of compound **29** (10.4 mg, 0.0086 mmol) in dry MeOH (0.2 mL) and dry CH_2Cl_2 (0.8 mL) under Ar. The mixture was stirred overnight and then neutralized with acetic acid and concentrated. The residue was chromatographed (SiO_2, CH_2Cl_2/MeOH 5:1) to give **4** (7.0 mg, 95%); $[\alpha]^{22}_D$ −3 (*c* 0.4, $CHCl_3$/MeOH 4:1); ^{1}H NMR data ($CDCl_3$/CD_3OD 4:1): δ (assignment of aglycon protons are shown in italic) 5.66 (m, 1 H, *H-5*), 5.40 (m, 1 H, *H-4*), 4.25 (d, 1 H, J = 7.6 Hz, H-1′), 4.17 (d, 1 H, J = 7.4 Hz, H-1), 4.09−4.02 (m, 2 H, *H-2,3*), 3.99−3.94 (m, 2 H,

Scheme 7[a]



[a] (a) Ac_2O, pyridine; (b) CF_3COOH, CH_2Cl_2; (c) $(COBr)_2$, DMF, CH_2Cl_2, 0 °C; (d) KSCSOEt, EtOH; (e) Ag-silicate, CH_2Cl_2, MS 4 Å; (f) MeONa, MeOH.

H-1, H-5), 3.81 (d, 1 H, J = 2.2 Hz, H-4′), 3.79 (dd, 1 H, J = 11.8, 7.2 Hz, H-6′), 3.68 (dd, 1 H, J = 11.8, 4.2 Hz, H-6′), 3.64 (m, 1 H, H-4), 3.53 (dd, 1 H, J = 10.3, 3.2 Hz, *H-1*), 3.51−3.48 (m, 3 H), 3.44 (dd, 1 H, J = 9.7, 3.2 Hz, H-3′), 3.29−3.23 (m, 2 H), 2.13 (t, 2 H, J = 7.6 Hz, *H-2′*), 1.97 (dd, 2 H, J = 14.1, 7.0 Hz, *H-6*), 1.53 (m, 2 H, *H-3′*), 1.47−1.07 (m, 50 H, CH_2), 0.83 (t, 6 H, J = 7.0 Hz, CH_3); ^{13}C NMR data ($CDCl_3/CD_3OD$ 4:1): δ 174.5, 134.1, 128.9, 103.5, 102.6, 75.3, 74.1, 73.2, 72.7, 72.3, 70.7, 68.9, 68.8, 63.3, 61.5, 53.0, 37.3, 32.2, 31.7, 29.5−29.0, 25.7, 22.5, 13.8; HRMS calcd for $C_{47}H_{89}O_{12}NNa$ (M + Na): 882.6282; found 882.6265.

2-(Trimethylsilyl)ethyl 4-*O*-[3-*O*-(5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonic acid)-β-D-galactopyranosyl]-β-D-xylopyranoside (5). Methanolic sodium methoxide (2 M, 0.013 mL) was added to a solution of compound **31** (26 mg, 0.025 mmol) in dry MeOH (1 mL) under Ar. The mixture was stirred at room temperature for 1 h 45 min and then neutralized with Duolite C-26 (H^+) resin and concentrated. The residue was dissolved in water (1 mL), and MeOH (1 mL) and aqueous sodium hydroxide (1 M, 0.078 mL) were added. The mixture was stirred for 3.5 h and then neutralized with Duolite C-26 (H^+) resin and concentrated. The residue was chromathographed (SiO_2, CH_2Cl_2/MeOH/H_2O + 0.1% AcOH 5:5:1) to give **5** (15.5 mg, 93%); $[\alpha]^{22}_D$ −23 (*c* 1.0, MeOH); ^{1}H NMR data (D_2O): δ 4.61 (d, 1 H, J = 7.9 Hz, H-1′), 4.49 (d, 1 H, J = 7.9 Hz, H-1), 4.16 (m, 2 H), 4.06−4.00 (m, 2 H), 3.96−3.88 (m, 4 H), 3.82−3.77 (m, 7 H), 3.65 (t, 1 H, J = 7.7 Hz, H-3), 3.64 (m, 1 H), 3.61 (dd, 1 H, J = 9.8, 7.9 Hz, H-2′), 3.44 (dd, 1 H, J = 11.7, 10.5 Hz, H-5), 3.33 (dd, 1 H, J = 9.3, 7.9 Hz, H-2), 2.80 (dd, 2 H, J = 12.5, 4.6 Hz, H-3″eq), 2.10 (s, 3 H, NHAc), 1.88 (t, 1 H, J = 12.2 Hz, H-3″ax), 1.07 (m, 2 H, CH_2Si), 0.15 (s, 9 H, $SiMe_3$); ^{13}C NMR data (D_2O): δ 175.8, 174.4, 102.9, 102.2, 100.5, 77.1, 76.4, 75.9, 75.0, 73.7, 72.4, 69.9, 69.3, 69.1, 68.9, 68.3, 63.7, 63.4, 61.9, 52.5, 40.3, 22.9, 18.4, −1.7; HRMS calcd for $C_{27}H_{49}O_{18}NSiNa$ (M + Na): 726.2617; found: 726.2643.

(2*S*,3*R*,4*E*)-3-Hydroxy-2-octadecanamidooctadec-4-enyl 4-*O*-[3-*O*-(5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonic acid)-β-D-galactopyranosyl]-β-D-xylopyranoside (6). Methanolic sodium methoxide (1.1 M, 0.0028 mL) was added to a solution of compound **36** (5.1 mg, 0.0031 mmol) in dry MeOH (1 mL) and dry CH_2Cl_2 (0.1 mL) under Ar. The mixture was stirred for 4.5 h and then aqueous sodium hydroxide (0.1 M, 0.062 mL) was added, and the mixture was stirred for 1 h. Aqueous acetic acid (0.4 M, 0.1 mL) was added, and the mixture was immediately chromatographed (SiO_2, CH_2Cl_2/MeOH/H_2O + 0.1% AcOH 65:35:1 → 65:35:5) to give **6** (1.9 mg, 53%); $[\alpha]^{22}_D$ −20 (*c* 0.15, $CHCl_3$/MeOH 1:1); ^{1}H NMR data ($CDCl_3/CD_3OD$ 1:1): δ (assignments of aglycon protons are shown in italic) 5.66 (dt, 1 H, J = 14.9, 6.8 Hz, *H-5*), 5.42 (dd, 1 H, J = 15.3, 7.3 Hz, *H-4*), 4.34 (d, 1 H, J = 7.7 Hz, H-1′), 4.20 (d, 1 H, J = 7.3 Hz, H-1), 4.11 (dd, 1 H, J = 10.3, 4.6 Hz), 4.07−3.46 (m, 21 H), 2.79 (brd, 1 H, J = 10.1 Hz, H-3″eq), 2.15 (t, 2 H, J = 7.6 Hz, *H-2′*), 1.72 (t, 1 H, J = 10.4 Hz, H-3″ax), 1.60−1.20 (m, 54 H, CH_2), 0.85 (t, 6 H, J = 6.8 Hz, CH_3); ^{13}C NMR data ($CDCl_3/CD_3OD$ 1:1): δ 175.1, 174.1, 165.4, 134.6, 130.9, 104.0, 102.9, 99.3, 76.5, 75.8, 74.6, 73.9, 73.3, 72.3, 71.7, 69.4, 69.3, 69.1, 68.1, 67.9, 63.7, 63.6, 61.9, 53.5, 53.0, 37.0, 32.8, 32.3, 30.0−29.5, 26.3, 23.9, 22.3, 14.1; HRMS calcd for $C_{58}H_{106}O_{20}N_2Na$ (M + Na): 1173.7237; found: 1173.7224.

2-(Trimethylsilyl)ethyl 4-*O*-[3-*O*-(5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosyloyl-1″→2′-lactone)-β-D-galactopyranosyl]-β-D-xylopyranoside (7). A mixture of compound **5** (4.10 mg, 0.0058 mmol) and AcOH (1 mL) was stirred overnight and then concentrated. The residue was chromatographed (SiO_2, CH_2Cl_2/MeOH/H_2O + 0.1% AcOH 65:35:4) to give a mixture (2.57 mg, 64%) of **7** and residual **5** (3:1), and a small amount (∼5%) of the corresponding 1″→4′-lactone. Compound **7**: ^{1}H NMR data (selected, D_2O): δ 4.73 (d, 1 H, J = 7.8 Hz, H-1′), 4.30 (d, 1 H, J = 7.9 Hz, H-1), 4.17 (dt, 1 H, J = 10.7, 5.4 Hz, H-4″), 4.07 (dd, 1 H, J = 10.6, 2,9 Hz, H-3′), 4.01 (brd, 1 H, J = 3.0 Hz, H-4′), 3.99 (dd, 1 H, J = 11.8, 5.3 Hz, H-5), 3.79 (t, 1 H, J = 10.3 Hz, H-5″), 3.46 (t, 1 H, J = 9.2 Hz, H-3), 3.28 (dd, 1 H, J = 11.7, 10.5 Hz, H-5), 3.15 (dd, 1 H, J = 9.3, 7.9 Hz, H-2), 2.50 (dd, 1 H, J = 13.4, 5.3 Hz, H-3″eq), 1.91 (s, 3 H, NHAc), 1.63 (dd, 1 H, J = 13.4, 11.2 Hz, H-3″ax), 0.96−0.78 (m, 2 H, CH_2Si), −0.12 (s, 9 H, $SiMe_3$); HRMS calcd for $C_{27}H_{47}O_{17}NSiNa$ (M + Na): 708.2511; found: 708.2504.

2-(Trimethylsilyl)ethyl 4-*O*-[2-Amino-2-deoxy-3-*O*-(5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosyloyl-1″→2′-lactam)-β-D-galactopyranosyl]-β-D-xylopyranoside (8). Compound **42** (3.14 mg, 0.0031 mmol) was deacetylated as described in the preparation of **1** (neutralization was made with Duolite C-26 (H^+) resin). Column chromatography (SiO_2, CH_2Cl_2/MeOH/H_2O 65:35:5) gave **8** (2.0 mg, 95%); $[\alpha]^{22}_D$ −30 (*c* 0.16, MeOH); ^{1}H NMR data (D_2O): δ 4.58 (d, 1 H, *J* = 8.1 Hz, H-1′), 4.31 (d, 1 H, *J* = 7.8 Hz, H-1), 4.21 (dt, 1 H, *J* = 11.0, 5.5 Hz, H-4″), 3.99 (dd, 1 H, *J* = 11.6, 5.4 Hz, H-5), 3.92 (brd, 1 H, *J* = 2.5 Hz, H-4′), 3.81−3.56 (m, 13 H), 3.50 (dd, 1 H, *J* = 11.8, 5.4 Hz, H-9″), 3.47 (t, 1 H, *J* = 9.2 Hz, H-3), 3.39 (dd, 1 H, *J* = 9.5, 1.1 Hz, H-7″), 3.31 (dd, 1 H, *J* = 11.6, 10.5 Hz, H-5), 3.16 (dd, 1 H, *J* = 9.3, 7.9 Hz, H-2), 2.45 (dd 1 H, *J* = 13.4, 5.5 Hz, H-3″eq), 1.91 (s, 3 H, NHAc), 1.56 (dd, 1 H, *J* = 13.4, 11.2 Hz, H-3″ax), 0.88 (m, 2 H, CH_2-Si), −0.12 (s, 9 H, $SiMe_3$); ^{13}C NMR data (D_2O): δ 175.9, 169.5, 102.9, 99.4, 98.8, 77.3, 76.9, 76.5, 74.7, 73.7, 73.1, 70.9, 69.3, 68.7, 68.6, 66.3, 64.2, 63.6, 61.8, 52.6, 51.0, 40.1, 22.9, 18.4, −1.7; HRMS calcd for $C_{27}H_{48}O_{16}N_2SiNa$ (M + Na): 707.2670; found: 707.2672.

2-(Trimethylsilyl)ethyl 2,3,4-Tri-*O*-acetyl-β-D-xylopyranoside (10). To a mixture of compound **9**[11] (14.0 g, 41.4 mmol), HgO (8.95 g, 41.4 mmol), $HgBr_2$ (80 mg, 0.22 mmol), molecular sieves (6 g, 3 Å), and dry CH_2Cl_2 (150 mL) under Ar and protected from light was added 2-(trimethylsilyl)-ethanol (8.88 mL, 70 mmol). After 1 h, the mixture was diluted with CH_2Cl_2, filtered (Celite), and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 3:1) to give **10** (14.0 g, 90%); $[\alpha]^{23}_D$ −62 (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.15 (t 1 H, *J* = 8.7 Hz, H-3), 4.92 (m, 2 H, H-2,4), 4.48 (d, 1 H, *J* = 6.8 Hz, H-1), 4.10 (dd, 1 H, *J* = 11.8, 5.1 Hz, H-5), 3.92 (dt, 1 H, *J* = 9.6, 6.3 Hz, OCH_2), 3.53 (dt, 1 H, *J* = 9.7, 6.8 Hz, OCH_2), 3.34 (dd, 1 H, *J* = 11.7, 9.0 Hz, H-5), 2.04, 2.04, 2.03 (s, 3 H each, OAc), 0.92 (m, 2 H, CH_2Si), 0.00 (s, 9 H, $SiMe_3$); ^{13}C NMR data ($CDCl_3$): δ 170.2, 169.9, 169.4, 100.2, 71.7, 71.0, 70.0, 69.0, 67.1, 62.0, 20.7 17.9, −1.4; HRMS calcd for $C_{16}H_{28}O_8SiNa$ (M + Na): 399.1451; found: 399.1440.

2-(Trimethylsilyl)ethyl 4-*O*-(*tert*-Butyldiphenylsilyl)-β-D-xylopyranoside (11). *tert*-Butylchlorodiphenylsilane (3.32 mL, 12.8 mmol) was added to a mixture of **1** (1.60 g, 6.39 mmol), DMAP (860 mg, 7.03 mmol), triethylamine (1.78 mL, 12.8 mmol), and dry $CHCl_3$ (100 mL). After 48 h, MeOH (5 mL) was added and the mixture was concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 5:1) to give **11** (1.53 g, 49%), the 2-silylated analogue (839 mg, 27%), and trace amounts of the 3-silylated analogue. Compound **11**: $[\alpha]^{22}_D$ −68 (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 7.71−7.36 (m, 10 H, Ar), 4.66 (brd, 1 H, *J* = 3.4 Hz, H-1), 3.88−3.70 (m, 4 H), 3.60−3.45 (m, 3 H), 3.28 (dd, 1 H, *J* = 12.3, 4.6 Hz, H-5), 3.19 (d, 1 H, *J* = 7.3 Hz), 1.10 (s, 9 H, CMe_3), 0.94 (m, 2 H, CH_2Si), 0.00 (s, 9 H, $SiMe_3$); HRMS calcd for $C_{26}H_{40}O_5Si_2$-Na (M + Na): 511.2312; found: 511.2321. 2-(Trimethylsilyl)-ethyl 2-*O*-{*tert*-butyldiphenylsilyl)-β-D-xylopyranoside: $[\alpha]^{24}_D$ −11 (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 7.73−7.38 (m, 10 H, Ar), 4.42 (brd, 1 H, *J* = 2.9 Hz, H-1), 4.05 (dd, 1 H, *J* = 10.7, 1.6 Hz, H-5), 3.87 (m, 1 H, H-3), 3.74−3.57 (m, 5 H), 3.23 (m, 1 H, OCH_2), 3.16 (d, 1 H, *J* = 8.7 Hz), 1.11 (s, 9 H, CMe_3), 0.67 (m, 2 H, CH_2Si), −0.05 (s, 9 H, $SiMe_3$).

2-(Trimethylsilyl)ethyl 2-*O*-Benzoyl-β-D-xylopyranoside (12). To a solution of compound **11** (1.51 g, 3.09 mmol) in dry pyridine (70 mL) at 0 °C was added benzoyl chloride (0.470 mL, 4.02 mmol). After 3.5 h, MeOH (5 mL) was added, and the mixture was diluted with CH_2Cl_2 and successively washed with saturated aqueous $NaHCO_3$ and water, dried (Na_2SO_4), and concentrated. The residue was desilylated as described in the preparation of **14**. The crude product was chromatographed (SiO_2, heptane/EtOAc 1:1) to give **12** (890 mg, 81%): $[\alpha]^{22}_D$ −40 (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CHCl_3$): δ 8.05−7.43 (m, 15 H, Ar), 4.97 (dd, 1 H, *J* = 6.9, 5.2 Hz, H-2), 4.74 (d, 1 H, *J* = 5.1 Hz, H-1), 4.14 (dd, 1 H, *J* = 11.9, 3.3 Hz, H-5), 3.93 (m, 1 H, OCH_2), 3.80 (m, 2 H, H-3,4), 3.58 (dt, 1 H, *J* = 10.2, 6.5 Hz, OCH_2), 3.48 (dd, 1 H, *J* = 11.9, 6.9 Hz, H-5), 0.95 (m, 2 H, CH_2Si), −0.02 (s, 9 H, $SiMe_3$); ^{13}C NMR data ($CDCl_3$): δ 166.2, 133.4, 129.9, 129.6, 128.4, 99.9, 73.8, 73.4, 69.9, 67.1, 64.0, 18.1, −1.5; HRMS calcd for $C_{17}H_{26}O_6SiNa$ (M + Na): 377.1396; found: 377.1389.

2-(Trimethylsilyl)ethyl 2,3-di-*O*-Acetyl-4-*O*-(*tert*-butyldiphenylsilyl)-β-D-xylopyranoside (13). Compound **11** (400 mg, 0.818 mmol) was acetylated overnight with acetic anhydride (10 mL), pyridine (10 mL), and DMAP (catalytic amount). The mixture was concentrated and coconcentrated with toluene, and the residue was chromatographed (SiO_2, heptane/EtOAc 6:1) to give **13** (473 mg, 99%): $[\alpha]^{22}_D$ −22 (*c* 0.9, $CHCl_3$); ^{1}H NMR data ($CHCl_3$): δ 7.65−7.34 (m, 10 H, Ar), 5.17 (t, 1 H, *J* = 9.2 Hz, H-3), 4.68 (dd, 1 H, *J* = 9.5, 7.8 Hz, H-2), 4.40 (d, 1 H, *J* = 7.8 Hz, H-1), 3.85 (m, 2 H), 3.67 (dd, 1 H, *J* = 11.5, 5.4 Hz, H-5), 3.48 (dt, 1 H, *J* = 9.8, 6.8 Hz, OCH_2), 3.25 (t, 1 H, *J* = 11.0 Hz, H-5), 2.01, 1.82 (s, 3 H each, OAc), 1.02 (s, 9 H, $(CH_3)_3C$), 0.89 (m, 2 H, CH_2Si), −0.03 (s, 9 H, $SiMe_3$); HRMS calcd for $C_{30}H_{44}O_7Si_2Na$ (M + Na): 595.2523; found: 595.2523.

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-acetyl-β-D-xylopyranoside (14). To a solution of **13** (1.23 g, 2.15 mmol) and HOAc (0.49 mL, 8.61 mmol) in THF (90 mL) was added tetrabutylammonium fluoride trihydrate (2.03 g, 6.46 mmol). After 12 h, the mixture was diluted with CH_2Cl_2 and successively washed with saturated aqueous $NaHCO_3$ and water, dried (Na_2SO_4), and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 3:2) to give **14** (679 mg, 94%): $[\alpha]^{22}_D$ −58 (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CHCl_3$): δ 4.90 (m, 2 H), 4.46 (m, 1 H), 4.07 (dd, 1 H, *J* = 11.7, 4.8 Hz), 3.93 (dt, 1 H, *J* = 9.9, 6.1 Hz), 3.80 (m, 1 H), 3.54 (dt, 1 H, *J* = 9.7, 6.7 Hz), 3.36 (dd, 1 H, *J* = 11.8, 8.8 Hz), 2.55 (d, 1 H, *J* = 6.0 Hz), 2.10, 2.06 (s, 3 H each), 0.93 (m, 2 H), 0.01 (s, 9 H); ^{13}C NMR data ($CDCl_3$): δ 171.6, 169.5, 100.2, 75.5, 70.7, 68.6, 67.1, 64.8, 20.9, 20.8, 18.0, −1.4; HRMS calcd for $C_{14}H_{26}O_7SiNa$ (M + Na): 357.1346; found: 357.1362.

2-(Trimethylsilyl)ethyl 2-*O*-Benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-β-D-xylopyranoside (16). A mixture of the thiogalactoside **15**[13] (116 mg, 0.169 mmol), compound **12** (40 mg, 0.113 mmol), molecular sieves (130 mg, AW 300), dry MeCN (1.7 mL), and dry CH_2Cl_2 (0.66 mL) was stirred for 1 h under Ar and then cooled to −45 °C. A solution of *N*-iodosuccinimide (41 mg, 0.181 mmol) and trifluoromethanesulfonic acid (0.003 mL, 0.03 mmol) in dry MeCN (0.3 mL) was added dropwise to the cooled mixture. After 45 min, triethylamine (0.25 mL) was added, and the mixture was filtered (Celite), diluted with CH_2Cl_2, washed with saturated aqueous $NaHCO_3$, dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, toluene/EtOAc 10:1) to give **16** (91 mg, 86%), contaminated with approximately 10% of the corresponding 3-*O* regioisomer. Compound **16**: ^{1}H NMR data ($CDCl_3$): δ 8.13−7.19 (m, 25 H, Ar), 5.97 (d, 1 H, *J* = 3.4 Hz, H-4′), 5.82 (dd, 1 H, *J* = 10.5, 7.9 Hz, H-2′), 5.60 (dd, 1 H, *J* = 10.5, 3.4 Hz, H-3′), 5.15 (dd, 1 H, *J* = 9.1, 7.6 Hz, H-2), 4.96 (d, 1 H, *J* = 8.1 Hz, H-1′), 4.62 (m, 1 H), 4.50 (d, 1 H, *J* = 7.5 Hz, H-1), 4.39 (m, 2 H), 4.13 (d, 1 H, *J* = 2.2 Hz), 3.99−3.73 (m, 4 H), 3.49 (dt, 1 H, *J* = 9.8, 6.4 Hz, OCH_2), 3.33 (m, 1 H, H-5), 0.83 (m, 2 H, CH_2Si), −0.10 (s, 9 H, $SiMe_3$); HRMS calcd for $C_{51}H_{52}O_{15}SiNa$ (M + Na): 955.2973; found: 955.2961. An analytical sample was acetylated in order to simplify determination of the regioselectivity. ^{1}H NMR gave H-3 at 5.39 ppm (t, 1 H, *J* = 8.3 Hz) and a new singlet at 1.93 ppm (3 H, OAc).

2-(Trimethylsilyl)ethyl 4-*O*-(3,4-*O*-Isopropylidene-β-D-galactopyranosyl)-β-D-xylopyranoside (17). To a mixture of **3** (25 mg, 0.061 mmol) and 2,2-dimethoxypropane (1 mL) was added *p*-toluenesulfonic acid (catalytic amount), and the mixture was stirred overnight and then neutralized with triethylamine. The mixture was concentrated, and the residue was dissolved in MeOH (3 mL) and water (0.3 mL) and stirred for 6 h at 80 °C. The mixture was concentrated, and the residue was chromatographed (SiO_2, CH_2Cl_2/EtOH 15:1 + 0.1% Et_3N) to give **17** (22 mg, 80%): $[\alpha]^{26}_D$ −13 (*c* 1.0, MeOH); ^{1}H NMR data (CD_3OD): δ 4.32 (d, 1 H, *J* = 8.2 Hz, H-1′), 4.23 (d, 1 H, *J* = 7.6 Hz, H-1), 4.18 (dd, 1 H, *J* = 5.5, 2.1 Hz, H-4′), 4.05−3.97 (m, 2 H, H-5, H-3′), 3.95−3.88 (m, 2 H, H-5′, OCH_2), 3.80 (dd, 1 H, *J* = 11.6, 7.8 Hz, H-6′), 3.73 (dd, 1 H, *J* = 11.6, 4.2 Hz, H-6′), 3.68 (m, 1 H, H-4), 3.62 (m, 1 H, OCH_2), 3.45 (m, 2 H, H-3, H-2′), 3.28 (dd, 1 H, *J* = 11.6, 10.2 Hz, H-5),

3.19 (dd, 1 H, J = 9.1, 7.6 Hz), 1.47, 1.32 (s, 3 H each, CCH_3), 0.99 (m, 2 H, CH_2Si), 0.03 (s, 9 H, $SiMe_3$); HRMS calcd for $C_{19}H_{37}O_{10}Si$ (M + H): 453.2156; found: 453.2182.

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-acetyl-4-*O*-(2,6-di-*O*-acetyl-3,4-*O*-isopropylidene-*β*-D-galactopyranosyl)-*β*-D-xylopyranoside (18). Compound **17** (200 mg, 0.442 mmol) was acetylated as described in the preparation of **13**. The crude product was chromatographed (SiO_2, heptane/EtOAc 1:1 + 0.1% Et_3N) to give **18** (272 mg, 99%): $[\alpha]^{22}_D$ −13 (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.10 (t, 1 H, J = 8.5 Hz, H-3), 4.83 (m, 2 H, H-2,2′), 4.43 (d, 1 H, J = 7.0 Hz, H-1), 4.41 (d, 1 H, J = 7.4 Hz, H-1′), 4.35−4.10 (m, 4 H), 4.01−3.85 (m, 3 H), 3.81 (dd, 1 H, J = 8.4, 3.7 Hz), 3.52 (dt, 1 H, J = 9.6, 7.1 Hz, OCH_2), 3.31 (dd, 1 H, J = 11.7, 9.1 Hz, H-5), 2.10, 2.06, 2.04, 2.03 (s, 3 H, each OAc), 1.53, 1.31 (s, 3 H each, $C(CH_3)_3$), 0.90 (m, 2 H, CH_2Si), 0.00 (s, 9 H, $SiMe_3$); HRMS calcd for $C_{27}H_{45}O_{14}Si$ (M + H): 643.2398; found: 643.2401.

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-acetyl-4-*O*-(2,6-di-*O*-acetyl-*β*-D-galactopyranosyl)-*β*-D-xylopyranoside (19). Compound **18** (150 mg, 0.242 mmol) was dissolved in aqueous acetic acid (5 mL, 80%), and the mixture was kept at 50 °C for 8 h and then concentrated and co-concentrated with toluene. The residue was chromatographed (SiO_2, CH_2Cl_2/EtOH 20:1) to give **19** (120 mg, 85%): $[\alpha]^{23}_D$ −34 (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.11 (t, 1 H, J = 8.6 Hz, H-3), 4.85 (m, 2 H, H-2,2′), 4.43 (d, 1 H, J = 7.0 Hz, H-1), 4.39 (d, 1 H, J = 7.9 Hz, H-1′), 4.36 (dd, 1 H, J = 11.5, 6.0 Hz, H-6′), 4.22 (dd, 1 H, J = 11.4, 6.7 Hz, H-6′), 3.98 (dd, 1 H, J = 11.8, 5.0 Hz, H-5), 3.91 (m, 1 H, OCH_2), 3.86 (d, 1 H, J = 3.4 Hz, H-4′), 3.80 (m, 1 H, H-4), 3.66 (t, 1 H, J = 6.7 Hz, H-5′), 3.61 (dd, 1 H, J = 9.7, 3.5 Hz, H-3′), 3.53 (dt, 1 H, J = 9.8, 6.7 Hz, OCH_2), 3.32 (dd, 1 H, J = 11.9, 9.5 Hz, H-5), 2.11, 2.10, 2.039, 2.036 (s, 3 H each, OAc), 0.91 (m, 2 H, CH_2Si), 0.00 (s, 9 H, $SiMe_3$); ^{13}C NMR data ($CDCl_3$): δ 171.7, 171.5, 170.9, 170.1, 101.3, 100.8, 76.3, 73.8, 73.0, 72.7, 71.5, 68.9, 67.7, 63.4, 63.1, 21.4, 21.3, 21.2, 18.4, −1.0; HRMS calcd for $C_{24}H_{40}O_{14}NSiNa$ (M + Na): 603.2085; found: 603.2079.

2,3,4-Tri-*O*-acetyl-α,*β*-D-xylopyranose (20). Compound **10** (56 mg, 0.149 mmol) was treated with trifluoroacetic acid,[16] as described in the preparation of **33**, to give **20** (41 mg, 97%). The crude product was used, without further purification, in the preparation of **21**.

2,3,4-Tri-*O*-acetyl-α*β*-D-xylopyranosyl Trichloroacetimidate (21). Compound **20** (35 mg, 0.127 mmol) was treated as described in the preparation of **34**. The crude product was chromatographed (SiO_2, heptane/EtOAc 2:1) to give **21** (46 mg, 84%). Analytical data were in full accordance with those previously published.[18]

(2*S*,3*R*,4*E*)-2-Azido-3-(benzoyloxy)octadec-4-enyl 2,3,4-Tri-*O*-acetyl-*β*-D-xylopyranoside (23). A mixture of compound **21** (21 mg, 0.050 mmol), azidosphingosine **22**[19] (42 mg, 0.099 mmol), and molecular sieves (100 mg, 300 AW) in dry CH_2Cl_2 (1 mL) was stirred for 1 h under Ar and then cooled to −33 °C. Boron trifluoride etherate (0.062 mL, 0.495 mmol) and, after 90 min, Et_3N (0.2 mL) were added, and the mixture was filtered (Celite) and concentrated. The residue was chromatographed (SiO_2, heptane/EtOAc 4:1) to give **23** (20 mg, 59%): $[\alpha]^{22}_D$ −57 (*c* 0.9, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ (assignment of aglycon protons are shown in italic) 8.06−7.45 (m, 5 H, *Ar*), 5.92 (dt, 1 H, J = 14.4, 6.9 Hz,*H-5*), 5.62−5.53 (m, 2 H, *H-3,4*), 5.50 (t, 1 H, J = 7.9 Hz, H-3), 4.94 (dd, 1 H, J = 7.9, 6.1 Hz, H-2), 4.92 (m, 1 H, H-4), 4.56 (d, 1 H, J = 6.1 Hz, H-1), 4.12 (dd, 1 H, J = 12.0, 4.7 Hz, H-5), 3.95−3.83 (m, 2 H, *H-1,2*), 3.59 (dd, 1 H, J = 10.0, 4.9 Hz, *H-1*), 3.40 (dd, 1 H, J = 12.1, 7.8 Hz, H-5), 2.11, 2.08, 2.07 (s, 3 H each, OAc), 1.48−1.15 (m, 24 H, CH_2), 0.89 (t, 3 H, J = 6.9 Hz, CH_3); ^{13}C NMR data ($CDCl_3$): δ 170.5, 170.2, 169.8, 165.6, 139.5, 133.7, 130.3, 130.2, 128.9, 123.2, 100.4, 75.0, 71.1, 70.5, 68.9, 68.3, 64.0, 62.0, 32.8, 32.3, 30.1−29.1, 23.1, 21.2, 21.1, 14.6; HRMS calcd for $C_{36}H_{53}O_{10}N_3Na$ (M + Na): 710.3629; found 720.3625.

(2*S*,3*R*,4*E*)-3-(Benzoyloxy)-2-octadecanamidooctadec-4-enyl 2,3,4-Tri-*O*-acetyl-*β*-D-xylopyranoside (24). Hydrogen sulfide was bubbled through a mixture of compound **23** (14.5 mg, 0.021 mmol) and aqueous pyridine (5 mL, Pyr/H_2O ~6:1) for 1 h at 0 °C. The mixture was kept under H_2S at 22 °C for 48 h. N_2 was bubbled through the mixture for 1 h, and then it was concentrated and coconcentrated with toluene. The residue was dissolved in dry CH_2Cl_2 (1 mL), and octadecanoic acid (24 mg, 0.084 mmol) and 1-ethyl-3-[3-(dimethylamino)-propyl]carbodiimide hydrochloride (16 mg, 0.084 mmol) were added. After 3 h, the mixture was chromatographed (SiO_2, heptane/EtOAc 3:2) to give **24** (17.5 mg, 89%): $[\alpha]^{23}_D$ −13 (*c* 0.6, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ (assignment of aglycon protons are shown in italic) 8.05−7.42 (m, 5 H, *Ar*), 5.88 (dt, 1 H, J = 14.6, 6.8 Hz, *H-5*), 5.79 (d, 1 H, J = 7.3 Hz, *NH*), 5.57−5.45 (m, 2 H, *H-3,4*), 5.14 (t, 1 H, J = 8.1 Hz, H-3), 4.89 (dd, 1 H, J = 8.4, 6.1 Hz, H-2), 4.88 (m, 1 H, H-4), 4.51 (m, 1 H, *H-2*), 4.48 (d, 1 H, J = 6.3 Hz, H-1), 4.03 (dd, 1 H, J = 10.0, 3.6 Hz, *H-1*), 3.98 (dd, 1 H, J = 12.0, 4.7 Hz, H-5), 3.60 (dd, 1 H, J = 10.1, 4.1 Hz, *H-1*), 3.30 (dd, 1 H, J = 12.0, 7.9 Hz, H-5), 2.36 (t, 2 H, J = 7.6 Hz, *H-2′*), 2.08, 2.06, 2.05 (s, 3 H each, OAc), 1.70−1.15 (m, 54 H, CH_2), 0.89 (t, 6 H, J = 6.5 Hz, CH_3); ^{13}C NMR data ($CDCl_3$): δ 173.1, 170.4, 170.2, 170.0, 165.7, 138.1, 133.5, 130.7, 130.1, 128.8, 125.2, 100.8, 74.6, 71.2, 71.0, 69.1, 67.6, 62.1, 51.0, 37.3, 33.9, 32.7, 32.4, 30.1−29.3, 26.2, 25.2, 23.1, 21.18, 21.16, 14.6; HRMS calcd for $C_{54}H_{89}O_{11}NNa$ (M + Na): 950.6333; found 950.6335.

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl)-*β*-D-xylopyranoside (25). Compound **3** (15 mg, 0.036 mmol) was acetylated with acetic anhydride (5 mL) and pyridine (5 mL) overnight. The mixture was concentrated and coconcentrated with toluene, and the residue was chromathographed (SiO_2, heptane/EtOAc 1:1) to give **25** (23 mg, 95%); $[\alpha]^{21}_D$ −34 (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 5.36 (d, 1 H, J = 2.6 Hz, H-4′), 5.15−5.07 (m, 2 H, H-2′,3), 4.98 (dd, 1 H, J = 10.4, 3.4 Hz, H-3′), 4.83 (dd, 1 H, J = 8.6, 7.0 Hz, H-2), 4.51 (d, 1 H, J = 7.9 Hz, H-1′), 4.45 (d, 1 H, J = 7.0 Hz, H-1), 4.11 (d, 2 H, J = 6.6 Hz, H-6′), 3.97 (dd, 1 H, J = 11.9, 5.1 Hz, H-5), 3.94−3.88 (m, 2 H), 3.82 (dt, 1 H, J = 5.3, 4.7 Hz, H-4), 3.54 (dt, 1 H, J = 9.9, 6.5 Hz, OCH_2), 3.33 (dd, 1 H, J = 11.8, 9.3 Hz, H-5), 2.16, 2.07, 2.05, 1.98 (s, 3 H each, OAc), 0.91 (m, 2 H, CH_2Si), −0.01 (s, 9 H, $SiMe_3$); ^{13}C NMR data ($CDCl_3$): δ 170.4, 170.2, 170.1, 170.0, 169.7, 169.0, 101.2, 100.3, 75.9, 72.2, 71.1, 70.9, 69.0, 67.2, 66.8, 62.7, 61.2, 20.8, 20.7, 20.6, 18.0, −1.4; HRMS calcd for $C_{28}H_{44}O_{16}SiNa$ (M + Na): 687.2296; found 687.2297.

2,3-Di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl)-α*β*-D-xylopyranose (26). Compound **25** (53 mg, 0.080 mmol) was treated as described in the preparation of **33** to give **26** (45 mg, 100%). The crude product was used without further purification in the preparation of **27**.

2,3-Di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl)-α*β*-D-xylopyranosyl Trichloroacetimidate (27). Compound **26** (45 mg, 0.080 mmol) was treated as described in the preparation of **34**. The crude product was chromatographed (SiO_2, heptane/EtOAc 1:1) to give **27** (52 mg, 92%) as an anomeric mixture (α/*β* 3:1). Selected ^{1}H NMR data ($CDCl_3$): δ 8.68 (s, 1 H), 8.64 (s, 1 H), 6.41 (d, 1 H, J = 3.7 Hz), 6.00 (d, 1 H, J = 3.8 Hz), 5.48 (t, 1 H, J = 9.6 Hz), 5.36 (d, 1 H, J = 3.2 Hz), 4.57 (d, 1 H, J = 8.0 Hz), 4.51 (d, 1 H, J = 7.8 Hz); HRMS calcd for $C_{25}H_{32}O_{16}NCl_3Na$ (M + Na): 730.0684; found 730.0689.

(2*S*,3*R*,4*E*)-2-Azido-3-(benzoyloxy)octadec-4-enyl 2,3-Di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl)-*β*-D-xylopyranoside (28). Compound **27** (22 mg, 0.031 mmol) and **22**[19] (33 mg, 0.078 mmol) were treated as described in the preparation of **23**. Column chromatography (SiO_2, heptane/EtOAc 3:2) gave **28** (21 mg, 70%); $[\alpha]^{22}_D$ −41 (*c* 1.0, $CHCl_3$); δ (assignment of aglycon protons are shown in italic) 8.07−7.44 (m, 5 H, *Ar*), 5.93 (dt, 1 H, J = 14.6, 6.7 Hz, *H-5*), 5.62−5.51 (m, 2 H, *H-3,4*), 5.37 (d, 1 H, J = 2.6 Hz, H-4′), 5.17−5.10 (m, 2 H, H-3, H-2′), 5.00 (dd, 1 H, J = 10.4, 3.4 Hz, H-3′), 4.86 (dd, 1 H, J = 7.4, 5.8 Hz, H-2), 4.54 (d, 1 H, J = 5.8 Hz, H-1), 4.52 (d, 1 H, J = 7.9 Hz, H-1′), 4.12 (d, 2 H, J = 6.7 Hz, H-6′), 3.98 (dd, 1 H, J = 12.0, 4.4 Hz, H-5), 3.93−3.77 (m, 4 H), 3.59 (dd, 1 H, J = 10.0, 4.7 Hz, *H-1*), 3.37 (dd, 1 H, J = 12.1, 7.8 Hz, H-5), 2.16, 2.11, 2.08, 2.07, 2.03, 1.99 (s, 3 H each, OAc), 1.45−1.12 (m, 24 H, CH_2), 0.89 (t, 3 H, J = 6.8 Hz, CH_3); ^{13}C NMR data ($CDCl_3$): δ 170.9, 170.6, 170.5, 170.3, 170.1, 169.4, 165.6, 139.4, 133.7, 130.3, 130.2, 128.9, 123.3, 101.6, 100.4, 75.6, 74.9, 71.34, 71.28, 71.2, 70.5, 69.4, 68.4, 67.3, 64.0, 62.2, 61.6, 32.8, 32.3, 30.1−29.1, 23.1, 21.22, 21.20, 21.11,

21.08, 20.99, 14.5; HRMS calcd for $C_{48}H_{69}O_{18}N_3Na$ (M + Na): 998.4474; found 998.4481.

(2*S*,3*R*,4*E*)-3-(Benzoyloxy)-2-octadecanamidooctadec-4-enyl 2,3-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl)-*β*-D-xylopyranoside (29). Compound **28** (16.4 mg, 0.0174 mmol) was treated as described in the preparation of **24**. Column chromatography (SiO_2, heptane/EtOAc 1:1) gave **29** (17 mg, 80%); $[\alpha]^{22}_D$ −14 (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): *δ* (assignment of aglycon protons are shown in italic) 8.04−7.43 (m, 5 H, *Ar*), 5.88 (dt, 1 H, *J* = 14.4, 6.8 Hz, *H-5*), 5.75 (d, 1 H, *J* = 9.4 Hz, *NH*), 5.54−5.43 (m, 2 H, *H-3,4*), 5.36 (d, 1 H, *J* = 2.6 Hz, H-4′), 5.15−5.07 (m, 2 H, H-3, H-2′), 4.98 (dd, 1 H, *J* = 10.4, 3.5 Hz, H-3′), 4.83 (dd, 1 H, *J* = 7.7, 5.9 Hz, H-2), 4.51 (m, 1 H, *H-2*), 4.48 (d, 1 H, *J* = 7.9 Hz, H-1′), 4.45 (d, 1 H, *J* = 5.9 Hz, H-1), 4.11 (d, 2 H, *J* = 6.6 Hz, H-6′), 4.01 (dd, 1 H, *J* = 9.8, 3.0 Hz, *H-1*), 3.90 (t, 1 H, *J* = 6.8 Hz, H-5′), 3.82−3.72 (m, 2 H, H-4,5), 3.55 (dd, 1 H, *J* = 10.0, 3.9 Hz, *H-1*), 3.22 (m, 1 H, H-5), 2.15, 2.10, 2.07, 2.06, 1.98, 1.97 (s, 3 H each, OAc), 1.70−1.15 (m, 54 H, CH_2), 0.89 (t, 6 H, *J* = 6.8 Hz, CH_3); ^{13}C NMR data ($CDCl_3$): *δ* 173.1, 170.9, 170.6, 170.5, 170.3, 170.2, 169.4, 165.7, 136.4, 133.5, 130.7, 130.0, 128.9, 125.3, 101.5, 100.5, 75.6, 74.5, 71.30, 71.26, 71.20, 70.9, 69.3, 67.7, 67.3, 62.1, 61.6, 50.9, 37.3, 32.7, 32.4, 30.1−29.3, 26.2, 23.1, 21.2, 21.1, 21.0, 14.6; HRMS calcd for $C_{66}H_{105}O_{19}NNa$ (M + Na): 1238.7179; found 1238.7191.

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-acetyl-4-*O*-[2,6-di-*O*-acetyl-3-*O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylate)-*β*-D-galactopyranosyl]-*β*-D-xylopyranoside (31). A mixture of compound **30**[15] (205 mg, 0.344 mmol), compound **19** (100 mg, 0.172 mmol), molecular sieves (100 mg, 3 Å), dry MeCN (1.3 mL), and dry CH_2Cl_2 (1.33 mL) was stirred under Ar for 2.5 h. The mixture was protected from light, silver trifluoromethanesulfonate (91 mg, 0.353 mmol) in dry MeCN (0.7 mL) was added, and the mixture was cooled to −72 °C. Methylsulfenyl bromide (0.086 mL, 4 M, 0.344 mmol, dissolved in $ClCH_2CH_2Cl$) was added in four portions over 15 min. After 4 h, diisopropylamine (0.15 mL) was added, and the stirring was continued for 1 h at −72 °C. The mixture was diluted with CH_2Cl_2, filtered (Celite), successively washed with saturated aqueous $NaHCO_3$ and water, dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, toluene/EtOH 15:1 → 5/1) to give **31** (102 mg, 56%): $[\alpha]^{22}_D$ −26 (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): *δ* 5.58 (ddd, 1 H, *J* = 9.4, 7.2, 2.5 Hz, H-8″), 5.31 (dd, 1 H, *J* = 9.1, 2.6 Hz, H-7″), 5.12 (d, 1 H, *J* = 10.1 Hz, NH″), 5.08 (t, 1 H, *J* = 8.9 Hz, H-3), 4.95 (dd, 1 H, *J* = 9.9, 8.0 Hz, H-2′), 4.82 (dd, 1 H, *J* = 9.1, 7.4 Hz, H-2), 4.77 (m, 1 H, H-4″), 4.56 (d, 1 H, *J* = 8.0 Hz, H-1′), 4.41 (d, 1 H, *J* = 7.3 Hz, H-1), 4.37 (m, 1 H), 4.24 (m, 3 H), 4.04 (m, 2 H), 3.94−3.80 (m, 4 H), 3.79 (s, 3 H, OMe), 3.63 (t, 1 H, *J* = 6.0 Hz), 3.52 (dt, 1 H, *J* = 9.8, 6.4 Hz, OCH_2), 3.38 (brd, 1 H, *J* = 2.6 Hz, H-4′), 3.28 (dd, 1 H, *J* = 11.8, 9.9 Hz, H-5), 2.63 (dd, 1 H, *J* = 12.7, 4.5 Hz, H-3″eq), 2.19, 2.13, 2.09, 2.07, 2.04, 2.02, 2.013, 2.012, 1.85 (s, 3 H each, OAc, NHAc), 1.82 (t, 1 H, *J* = 12.5 Hz, H-3″ax), 0.90 (m, 2 H, CH_2Si), −0.01 (s, 9 H, $SiMe_3$); ^{13}C NMR data ($CDCl_3$): *δ* 170.9, 170.64, 170.60, 170.4, 170.3, 169.8, 169.7, 169.5, 168.4 ($J_{C1''-H3''ax}$ = 6.6 Hz[24]), 101.1, 100.5, 97.0, 76.1, 73.7, 72.8, 72.4, 71.9, 71.5, 69.3, 68.8, 67.8, 67.5, 67.4, 67.2, 63.3, 63.1, 63.0, 57.0, 53.1, 49.1, 37.7, 23.1, 21.3, 20.86, 20.79, 20.77, 20.73, 18.0, −1.4; HRMS calcd for $C_{44}H_{67}O_{26}NSiNa$ (M + Na): 1076.3618; found: 1076.3635.

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-acetyl-4-*O*-[2,4,6-tri-*O*-acetyl-3-*O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylate)-*β*-D-galactopyranosyl]-*β*-D-xylopyranoside (32). Compound **31** (60 mg, 0.057 mmol) was acetylated as described in the preparation of **25**. Column chromatography (SiO_2, CH_2Cl_2/EtOH 20:1) gave **32** (62 mg, 99%): $[\alpha]^{22}_D$ −23 (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): *δ* 5.63 (ddd, 1 H, *J* = 9.5, 7.3, 2.4 Hz, H-8″), 5.30 (dd, 1 H, *J* = 9.4, 2.8 Hz, H-7″), 5.09 (t, 1 H, *J* = 9.0 Hz, H-3), 5.08 (d, 1 H, *J* = 10.2 Hz, NH″), 4.92 (dd, 1 H, *J* = 10.1, 8.0 Hz, H-2′), 4.85 (m, 3 H), 4.63 (d, 1 H, *J* = 7.9 Hz, H-1′), 4.48 (dd, 1 H, *J* = 10.2, 3.4 Hz, H-3′), 4.42 (d, 1 H, *J* = 7.5 Hz, H-1), 4.38 (dd, 1 H, *J* = 12.0, 2.4 Hz, H-9″), 4.15−3.77 (m, 11 H), 3.63 (dd, 1 H, *J* = 10.7, 2.7 Hz, H-6″), 3.52 (dt, 1 H, *J* = 9.8, 6.6 Hz, OCH_2), 3.30 (dd, 1 H, *J* = 11.6, 10.0 Hz, H-5), 2.57 (dd, 1 H, *J* = 12.6, 4.5 Hz, H-3″eq), 2.23, 2.18, 2.09, 2.08, 2.06, 2.05, 2.03, 2.00, 1.85 (s, 3 H each, OAc, NHAc), 1.82 (t, 1 H, *J* = 12.5 Hz, H-3″ax), 0.89 (m, 2 H, CH_2Si), −0.01 (s, 9H, $SiMe_3$); HRMS calcd for $C_{46}H_{69}O_{27}NSiNa$ (M + Na): 1118.3724; found: 1118.3748.

2,3-Di-*O*-acetyl-4-*O*-[2,4,6-tri-*O*-acetyl-3-*O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylate)-*β*-D-galactopyranosyl]-αβ-D-xylopyranose (33). Compound **32** (52 mg, 0.047 mmol) was dissolved in CH_2Cl_2 (0.27 mL), trifluoroacetic acid (0.54 mL) was added, and the mixture was stirred for 1 h.[16] *n*-Propyl acetate (1.6 mL) and toluene (3.2 mL) were added, and the mixture was concentrated to give **33** (47 mg, 100%). The crude product was used without further purification in the preparation of **34**.

2,3-Di-*O*-acetyl-4-*O*-[2,4,6-tri-*O*-acetyl-3-*O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylate)-*β*-D-galactopyranosyl]-αβ-D-xylopyranosyl Trichloroacetimidate (34). DBU (0.0031 mL, 0.021 mmol) was added to a solution of compound **33** (26 mg, 0.026 mmol) and Cl_3CCN (0.085 mL, 0.84 mmol) in dry CH_2Cl_2 (0.5 mL) at 0 °C under Ar. After 75 min, the mixture was concentrated, and the residue was chromatographed (SiO_2, CH_2Cl_2/EtOH 20:1) to give **34** (24 mg, 81%) as an anomeric mixture (α/*β* 3:1); $[\alpha]^{20}_D$ +12 (*c* 1.1, $CHCl_3$); Selected ^{1}H NMR data ($CDCl_3$): *δ* 8.69, 8.63 (s), 6.44 (d, *J* = 3.7 Hz), 5.99 (d, *J* = 4.7 Hz). HRMS calcd for $C_{43}H_{57}O_{27}N_2Cl_3Na$ (M + Na): 1161.2112; found: 1161.2085.

(2*S*,3*R*,4*E*)-2-Azido-3-(benzoyloxy)octadec-4-enyl 2,3-Di-*O*-acetyl-4-*O*-[2,4,6-tri-*O*-acetyl-3-*O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylate)-*β*-D-galactopyranosyl]-*β*-D-xylopyranoside (35). Boron trifluoride etherate (0.021 mL, 0.167 mmol) was added to a mixture of compound **34** (19 mg, 0.0167 mmol), azidosphingosine **22**[19] (17.9 mg, 0.0417 mmol), and molecular sieves (40 mg, 300 AW) in dry CH_2Cl_2 (0.5 mL) at −33 °C under Ar. After 90 min, Et_3N (0.06 mL) was added, and the mixture was immediately chromatographed (SiO_2, CH_2Cl_2/EtOH 30:1) to give **35** (15.4 mg, 66%); $[\alpha]^{23}_D$ −26 (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): *δ* (assignments of aglycon protons are shown in italic) 8.05−7.41 (m, 5 H, *Ar*), 5.91 (dt, 1 H, *J* = 14.2, 6.8 Hz, *H-5*), 5.63 (ddd, 1 H, *J* = 9.4, 7.5, 2.7 Hz, H-8″), 5.65−5.50 (m, 2 H, *H-3,4*), 5.30 (dd, 1 H, *J* = 9.3, 2.8 Hz, H-7″), 5.12 (t, 1 H, *J* = 8.3 Hz, H-3), 5.03 (d, 1 H, *J* = 10.2 Hz), 4.93 (dd, 1 H, *J* = 10.2, 7.9 Hz, H-2′), 4.88−4.82 (m, 3 H), 4.62 (d, 1 H, *J* = 8.0 Hz, H-1′), 4.50 (dd, 1 H, *J* = 10.2, 3.4 Hz, H-3′), 4.47 (d, 1 H, *J* = 6.7 Hz, H-1), 4.05 (m, 4 H), 3.90−3.79 (m, 5 H), 3.84 (s, 3 H, OMe), 3.62 (dd, 1 H, *J* = 10.8, 2.8 Hz, H-6″), 3.57 (dd, 1 H, *J* = 10.0, 5.0 Hz, *H-1*), 3.35 (dd, 1 H, *J* = 11.9, 8.0 Hz, H-5), 2.57 (dd, 1 H, *J* = 12.5, 4.7 Hz, H-3″eq), 2.22, 2.17, 2.09, 2.08, 2.07, 2.05, 2.02, 2.00, 1.84 (s, 3 H each, OAc, NHAc), 1.70 (t, 1 H, *J* = 12.4 Hz, H-3″ax), 1.39−1.24 (m, 22 H, CH_2), 0.87 (t, 1 H, *J* = 7.0 Hz, CH_3); ^{13}C NMR data ($CDCl_3$): *δ* 170.9, 170.7, 170.6, 170.4, 170.3, 170.2, 169.9, 169.8, 169.7, 169.4, 167.9, 165.1, 139.0, 133.2, 129.9, 129.7, 128.4, 122.8, 101.4, 100.5, 96.8, 75.9, 74.6, 72.1, 72.0, 71.3, 70.8, 70.7, 69.7, 69.3, 68.1, 67.6, 67.3, 63.6, 63.0, 62.8, 61.9, 53.1, 49.0, 37.4, 32.4, 31.9, 29.7, 29.66, 29.64, 29.63, 29.62, 29.56, 29.4, 29.3, 29.1, 28.7, 23.1, 22.7, 21.5, 20.9, 20.8, 20.74, 20.69, 20.6, 14.1; HRMS calcd for $C_{66}H_{94}O_{29}N_4Na$ (M + Na): 1429.5901; found: 1429.5896.

(2*S*,3*R*,4*E*)-3-(Benzoyloxy)-2-octadecanamidooctadec-4-enyl 2,3-Di-*O*-acetyl-4-*O*-[2,4,6-tri-*O*-acetyl-3-*O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylate)-*β*-D-galactopyranosyl]-*β*-D-xylopyranoside (36). Hydrogen sulfide was bubbled through a mixture of compound **35** (7.92 mg, 0.00563 mmol) and aqueous pyridine (5 mL, 83%) for 1 h at 0 °C. The mixture was kept under H_2S at 22 °C for 48 h. N_2 was bubbled through the mixture for 1 h, and then it was concentrated and

(24) (a) Hori, H.; Nakajima, T.; Nishida, Y.; Ohrui, H.; Meguro, H. *Tetrahedron Lett.* **1988**, *29*, 6317−6320. (b) Prytulla, S.; Lauterwein, J.; Klessinger, M.; Thiem, J. *Carbohydr. Res.* **1991**, *215*, 345−349. (c) Ercégovic, T.; Magnusson, G. *J. Chem. Soc., Chem. Commun.* **1994**, 831−832.

coconcentrated with toluene. The residue was dissolved in dry CH_2Cl_2 (0.5 mL), and octadecanoic acid (6.4 mg, 0.0225 mmol) and 1-ethyl-3-[3-(dimethylamino)propyl]carbodiimide hydrochloride (4.3 mg, 0.0225 mmol) were added. After 2.5 h, the mixture was chromatographed (SiO_2, CH_2Cl_2/EtOH 30:1) to give **36** (8.2 mg, 88%); $[\alpha]^{23}_D$ −14 (*c* 0.8, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ (assignments of aglycon protons are shown in italic) 8.07−7.42 (m, 5 H, *Ar*), 5.87 (dt, 1 H, *J* = 14.5, 6.9 Hz, *H-5*), 5.74 (d, 1 H, *J* = 9.3 Hz, NH″), 5.62 (ddd, 1 H, *J* = 9.5, 7.0, 2.6 Hz, H-8″), 5.48 (m, 2 H), 5.32 (dd, 1 H, *J* = 9.4, 2.8 Hz, H-7″), 5.13 (t, 1 H, *J* = 8.3 Hz, H-3), 5.03 (d, 1 H, *J* = 10.3 Hz, NH′), 4.95−4.81 (m, 4 H), 4.62 (d, 1 H, *J* = 7.9 Hz, H-1′), 4.50 (m, 2 H), 4.43 (d, 1 H, *J* = 6.6 Hz, H-1), 4.39 (dd, 1 H, *J* = 12.2, 2.5 Hz, H-9″), 4.03 (m, 5 H), 3.94−3.79 (m, 6 H), 3.64 (dd, 1 H, *J* = 10.8, 2.8 Hz, H-6″), 3.56 (dd, 1 H, *J* = 9.9, 4.2 Hz, *H-1*), 3.27 (dd, 1 H, *J* = 12.1, 8.9 Hz, H-5), 2.58 (dd, 1 H, *J* = 12.6, 4.6 Hz, H-3″eq), 2.21, 2.19, 2.11, 2.09, 2.08, 2.07, 2.05, 2.02, 2.00, 1.86 (s, 3 H each, OAc, NHAc), 1.71 (t, 1 H, *J* = 12.5 Hz, H-3″ax), 1.30−1.20 (m, 54 H, CH_2), 0.89 (m, 6 H, CH_3); ^{13}C NMR data ($CDCl_3$): δ 173.0, 171.3, 171.1, 171.0, 170.8, 170.75, 170.70, 170.3, 170.2, 169.9, 168.3, 165.7, 138.2, 133.4, 130.7, 130.0, 128.8, 125.2, 101.7, 101.1, 97.2, 76.2, 74.7, 72.4, 72.2, 71.3, 71.2, 70.0, 69.7, 68.0, 67.8, 67.6, 63.4, 63.0, 62.3, 53.6, 50.9, 49.4, 37.3, 32.8, 32.4, 30.1−29.7, 30.0, 29.4, 26.2, 23.6, 23.1, 21.9, 21.29, 21.25, 21.19, 21.18, 21.16, 21.1, 14.6; HRMS calcd for $C_{84}H_{130}O_{30}N_2Na$ (M + Na): 1669.8606; found: 1669.8579.

2-(Trimethylsilyl)ethyl 4,6-Di-*O*-acetyl-2-amino-2-deoxy-3-*O*-(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosyloyl-1′→2-lactam)-*β*-D-galactopyranoside (38). Compound **37**[8b] (34 mg, 0.062 mmol) was acetylated as described in the preparation of **13**. The crude product was chromathographed (SiO_2, CH_2Cl_2/EtOAc 1:4) to give **38** (45 mg, 91%); $[\alpha]^{27}_D$ −47 (*c* 1.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 7.39 (s, 1 H, NH), 6.37 (d, 1 H, *J* = 10.3 Hz, NH′), 5.51 (dd, 1 H, *J* = 3.4, 2.3 Hz, H-7′), 5.40 (dd, 1 H, *J* = 2.8, 1.6 Hz, H-4), 5.21 (dt, 1 H, *J* = 10.8, 5.4 Hz, H-4′), 5.05 (ddd, 1 H, *J* = 5.1, 3.2, 1.7 Hz, H-8′), 4.55 (dd, 1 H, *J* = 12.3, 1.6 Hz, H-9′), 4.37 (d, 1 H, *J* = 7.7 Hz, H-1), 4.31 (dd, 1 H, *J* = 12.3, 4.8 Hz, H-9′), 4.27−4.20 (m, 2 H, H-6, H-5′), 4.12 (dd, 1 H, *J* = 11.3, 6.5 Hz, H-6), 4.03 (dd, 1 H, *J* = 10.4, 2.2 Hz, H-6′), 4.00−3.91 (m, 2 H, H-5, OCH_2), 3.89 (dd, 1 H, *J* = 11.1, 3.1 Hz, H-3), 3.81 (dd, 1 H, *J* = 11.0, 7.5 Hz, H-2), 3.62 (m, 1 H, OCH_2), 2.50 (dd, 1 H, *J* = 13.1, 5.5 Hz, H-3′eq), 2.26, 2.13, 2.09, 2.05, 1.94, 1.89, (s, 3 H each, OAc, NHAc), 1.88 (dd, 1 H, *J* = 13.0, 11.3 Hz, H-3′ax), 0.98 (m, 2 H, CH_2-Si), 0.02 (s, 9 H, $SiMe_3$); HRMS calcd for $C_{34}H_{52}O_{18}N_2SiNa$ (M + Na): 827.2882; found: 827.2889.

4,6-Di-*O*-acetyl-2-amino-2-deoxy-3-*O*-(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosyloyl-1′→2-lactam)-α*β*-D-galactopyranose (39). Compound **38** (367 mg, 0.456 mmol) was treated as described in the preparation of **33** to give **39** (327 mg, 100%). The crude product was used without further purification in the preparation of compound **40**.

4,6-Di-*O*-acetyl-2-amino-2-deoxy-3-*O*-(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosyloyl-1′→2-lactam)-α-D-galactopyranosyl Bromide (40). Oxalyl bromide (0.031 mL, 0.328 mmol) was dissolved in dry CH_2Cl_2 (1.7 mL), and the mixture was added to a cooled (0 °C) solution of compound **39** (77 mg, 0.109 mmol) in dry CH_2Cl_2 (2.5 mL) and dry DMF (0.024 mL, 0.306 mmol) under Ar. The mixture was stirred at 0 °C for 1 h and for 12 h at 22 °C and then diluted with CH_2Cl_2, washed with saturated aqueous $NaHCO_3$ and water, dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, CH_2Cl_2/EtOH 20:1) to give **40** (51 mg, 61%), contaminated with a trace of DMF; $[\alpha]^{27}_D$ +74 (*c* 1.2, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 6.88 (s, 1 H, NH), 6.64 (d, 1 H, *J* = 2.7 Hz, H-1), 6.08 (d, 1 H, *J* = 10.2 Hz, NH′), 5.49 (brs, 1 H, H-4), 5.35−5.18 (m, 3 H), 4.44−4.05 (m, 8 H), 3.80 (dd, 1 H, *J* = 10.5, 1.8 Hz, H-6′), 2.48 (dd, 1 H, *J* = 13.1, 5.6 Hz, H-3′eq), 2.26, 2.13, 2.11, 2.07, 2.02, 2.00, 1.89, (s, 3 H each, OAc, NHAc), 1.76 (dd, 1 H, *J* = 12.9, 11.4 Hz, H-3′ax); HRMS calcd for $C_{29}H_{39}O_{17}N_2BrNa$ (M + Na): 789.1330; found: 789.1305.

4,6-Di-*O*-acetyl-2-amino-2-deoxy-3-*O*-(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosyloyl-1′→2-lactam)-*β*-D-galactopyranosyl Ethyl Xanthate (41). Potassium ethylxanthate (7.5 mg, 0.047 mmol) was added to a solution of compound **40** (24 mg, 0.031 mmol) in EtOH (1 mL). The mixture was stirred for 16 h while protected from light and then diluted with CH_2Cl_2, washed with water, dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (SiO_2, CH_2Cl_2/EtOH 20:1) to give **41** (20 mg, 78%); $[\alpha]^{25}_D$ −7 (*c* 1.1, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 7.21 (s, 1 H, NH), 6.30 (d, 1 H, *J* = 10.0 Hz, NH′), 5.49 (brd, 1 H, *J* = 1.8 Hz, H-4), 5.44 (d, 1 H, *J* = 10.4 Hz, H-1), 5.37 (dd, 1 H, *J* = 3.8, 2.2 Hz, H-7′), 5.23 (dt, 1 H, *J* = 11.0, 5.4 Hz, H-4′), 5.11 (m, 1 H, H-8′), 4.68 (m, 2 H, OCH_2), 4.44 (dd, 1 H, *J* = 12.2, 1.7 Hz, H-9′), 4.25−4.00 (m, 7 H), 3.93 (dd, 1 H, *J* = 10.5, 2.1 Hz, H-6′), 2.52 (dd, 1 H, *J* = 13.1, 5.4 Hz, H-3′eq), 2.25, 2.12, 2.09, 2.07, 2.04, 1.96, 1.89, (s, 3 H each, OAc, NHAc), 1.45 (t, 3 H, *J* = 7.1 Hz, CH_3); ^{13}C NMR data ($CDCl_3$): δ 209.5, 170.8, 170.4, 170.1, 169.9, 166.6, 98.4, 85.6, 78.0, 75.9, 73.2, 71.9, 71.1, 70.7, 68.3, 65.4, 63.3, 61.7, 48.4, 48.3, 37.0, 29.7, 23.2, 21.04, 21.01, 20.9, 20.7, 20.5, 13.8; HRMS calcd for $C_{32}H_{44}O_{18}N_2S_2Na$ (M + Na): 831.1928; found: 831.1945.

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-acetyl-4-*O*-[4,6-di-*O*-acetyl-2-amino-2-deoxy-3-*O*-(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosyloyl-1″→2′-lactam)-*β*-D-galactopyranosyl]-*β*-D-xylopyranoside (42). A solution of compound **40** (40 mg, 0.052 mmol), compound **14** (14.5 mg, 0.043 mmol), and molecular sieves (30 mg, 4 Å) in dry CH_2Cl_2 (0.5 mL) was stirred under Ar for 1 h. Silver silicate[20] (73 mg) was added, and the mixture was protected from light and stirred for 3 days and then filtered (Celite) and concentrated. The residue was chromatographed (SiO_2, CH_2Cl_2/EtOH 20:1) to give **42** (10.7 mg, 24%); $[\alpha]^{23}_D$ −60 (*c* 0.6, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 6.57 (s, 1 H, NH′), 5.55 (d, 1 H, *J* = 10.6 Hz, NH″), 5.46 (dt, 1 H, *J* = 10.8, 5.1 Hz, H-4″), 5.39 (brs, 1 H, H-4′), 5.28 (dd, 1 H, *J* = 6.0, 2.1 Hz, H-7″), 5.13 (m, 2 H), 4.85 (dd, 1 H, *J* = 7.9, 6.3 Hz, H-2), 4.51 (d, 1 H, *J* = 6.3 Hz, H-1), 4.45 (brd, 1 H, *J* = 7.4 Hz, H-1′), 4.31 (dd, 1 H, *J* = 12.3, 2.6 Hz, H-9″), 4.20−4.05 (m, 5 H), 4.00 (dt, 1 H, *J* = 7.8, 4.5 Hz, H-4), 3.95−3.80 (m, 5 H), 3.54 (dt, 1 H, *J* = 9.8, 6.4 Hz, OCH_2), 3.49 (dd, 1 H, *J* = 12.2, 8.1 Hz, H-5), 2.44 (dd, 1 H, *J* = 13.2, 5.6 Hz, H-3″eq), 2.22, 2.10, 2.09, 2.07, 2.063, 2.062, 2.059, 1.99, 1.87, (s, 3 H each, OAc, NHAc), 1.81 (dd, 1 H, *J* = 13.1, 11.5 Hz, H-3″ax), 0.91 (m, 2 H, CH_2Si), 0.01 (s, 9 H, $SiMe_3$); ^{13}C NMR data ($CDCl_3$): δ 170.9, 170.7, 170.51, 170.47, 170.40, 170.2, 170.1, 170.0, 169.9, 169.5, 100.0, 99.0, 98.0, 75.4, 73.6, 72.9, 72.0, 71.6, 70.9, 70.6, 70.2, 67.9, 67.2, 65.1, 62.6, 61.6, 61.4, 57.0, 50.3, 50.2, 49.14, 49.06, 37.4, 29.7, 23.2, 20.93, 20.86, 20.81, 20.79, 20.74, 20.72, 20.66, 20.5, 17.9, −1.4; HRMS calcd for $C_{43}H_{64}O_{24}N_2SiNa$ (M + Na): 1043.3516; found: 1043.3512.

2-(Trimethylsilyl)ethyl 2-*O*-Benzoyl-4-*O*-[4,6-di-*O*-acetyl-2-amino-2-deoxy-3-*O*-(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosyloyl-1″→2′-lactam)-*β*-D-galactopyranosyl]-*β*-D-xylopyranoside (43) and 2-(Trimethylsilyl)ethyl 2-*O*-Benzoyl-3-*O*-[4,6-di-*O*-acetyl-2-amino-2-deoxy-3-*O*-(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosyloyl-1″→2′-lactam)-*β*-D-galactopyranosyl]-*β*-D-xylopyranoside (44). Compound **40** (40 mg, 0.052 mmol) and compound **12** (15.4 mg, 0.0434 mmol) were treated as described in the preparation of **42**. The crude product was chromatographed (SiO_2, toluene/EtOH 10:1) to give almost pure **43** (6.9 mg, 15%) and pure **44** (13.6 mg, 30%). Compound **43**: ^{1}H NMR data ($CDCl_3$): δ 8.06−7.40 (m, 5 H, Ar), 5.91 (d, 1 H, *J* = 10.4 Hz, NH″), 5.40 (m, 2 H), 5.31 (dd, 1 H, *J* = 6.4, 1.9 Hz, H-7″), 5.21 (dt, 1 H, *J* = 6.7, 2.4 Hz, H-8″), 5.12 (dd, 1 H, *J* = 9.5, 7.8 Hz, H-2), 4.60 (d, 1 H, *J* = 7.3 Hz, H-1′), 4.55 (d, 1 H, *J* = 7.8 Hz, H-1), 4.38 (dd, 1 H, *J* = 12.4, 2.5 Hz, H-9″), 4.30−3.80 (m, 13 H), 3.56 (dt, 1 H, *J* = 10.1, 6.0 Hz, OCH_2), 3.43 (dd, 1 H, *J* = 11.6, 10.0 Hz, H-5), 2.48 (dd, 1 H, *J* = 13.2, 5.5 Hz, H-3″eq), 2.25, 2.14, 2.13, 2.09, 2.04, 1.91, 1.89, (s, 3 H each, OAc, NHAc), 1.81 (dd, 1 H, *J* = 13.3, 11.4 Hz, H-3″ax), 0.90 (m, 2 H, CH_2Si), −0.04 (s, 9 H, $SiMe_3$); HRMS calcd for $C_{46}H_{64}O_{23}N_2SiNa$ (M + Na): 1063.3567; found: 1063.3607.

Compound **44**: $[\alpha]^{25}_{D}$ +2 (*c* 1.0, $CHCl_3$); ^1H NMR data ($CDCl_3$): δ 8.08−7.45 (m, 5 H, Ar), 6.61 (brs, 1 H, NH′), 5.54 (dt, 1 H, J = 10.9, 5.3 Hz, H-4″), 5.34 (m, 2 H), 5.28 (dd, 1 H, J = 2.7, 1.4 Hz, H-4′), 5.08 (m, 2 H), 4.58 (d, 1 H, J = 7.5 Hz, H-1), 4.32 (dd, 1 H, J = 12.5, 3.0 Hz, H-9″), 4.20−4.10 (m, 5 H), 4.01 (dd, 1 H, J = 12.5, 4.8 Hz, H-9″), 3.97 (m, 1 H, OCH_2), 3.92 (ddd, 1 H, J = 10.0, 8.2, 5.5 Hz, H-4), 3.86 (m, 1 H, H-5′), 3.81 (dd, 1 H, J = 10.5, 2.0 Hz, H-6″), 3.77 (dd, 1 H, J = 11.0, 7.7 Hz, H-2′), 3.73 (t, 1 H, J = 8.4 Hz, H-3), 3.62 (dd, 1 H, J = 11.1, 3.0 Hz, H-3′), 3.59 (m, 1 H, OCH_2), 3.34 (dd, 1 H, J = 11.8, 10.0 Hz, H-5), 2.32 (dd, 1 H, J = 13.2, 5.5 Hz, H-3″eq), 2.23, 2.22, 2.09, 2.05, 2.04, 1.99, 1.88, (s, 3 H each, OAc, NHAc), 1.75 (dd, 1 H, J = 13.0, 11.5 Hz, H-3″ax), 0.89 (m, 2 H, CH_2-Si), −0.15 (s, 9 H, $SiMe_3$); ^{13}C NMR data ($CDCl_3$): δ 171.1, 170.64, 170.57, 170.54, 170.0, 169.8, 169.6, 167.1, 165.7, 134.1, 130.0, 129.0, 128.8, 100.5, 97.9, 84.7, 75.1, 73.7, 71.9, 71.8, 70.3, 68.8, 68.3, 67.5, 67.0, 65.2, 64.9, 61.8, 61.5, 56.9, 50.3, 49.2, 37.4, 29.7, 23.3, 21.0, 20.9, 20.77, 20.75, 20.6, 20.5, 18.1, −1.4; HRMS calcd for $C_{46}H_{64}O_{23}N_2SiNa$ (M + Na): 1063.3567; found: 1063.3544.

Acknowledgment. This work was supported by the Swedish Research Council for Engineering Sciences and the Swedish Natural Science Research Council.

JO970298K