# Synthesis of Ganglioside Lactams Corresponding to $G_{M1}$-, $G_{M2}$-, $G_{M3}$-, and $G_{M4}$-Ganglioside Lactones

**Michael Wilstermann, Leonid O. Kononov, Ulf Nilsson, Asim K. Ray, and Göran Magnusson***

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

*Received January 18, 1995*[⊗]

**Abstract:** Ganglioside lactams are potentially useful analogs of ganglioside lactones, which are highly immunogenic derivatives of gangliosides. The lactam corresponding to the $G_{M3}$-lactone saccharide has been synthesized by sialylation of a suitably protected lactose derivative carrying an azido group in the 2′-position, followed by reduction and ring closure to form $G_{M3}$-lactam. Glycosylation in the 4-position of the central saccharide unit gave the $G_{M2}$- and $G_{M1}$-lactam saccharides. By a similar route, a 2-azido-Gal derivative was sialylated and treated as above to give the $G_{M4}$-lactam saccharide. Deprotection gave the $G_{M2-4}$-lactam saccharides in water soluble form, whereas attempted deprotection of the $G_{M1}$-lactam caused its degradation. The $G_{M3}$-lactam saccharide was coupled to ceramide, to afford the ganglioside lactam analog, and via a spacer to bovine serum albumin (BSA). The BSA conjugate was used as immunogen to raise monoclonal antibodies that cross-reacted with $G_{M3}$-lactone. The antibodies were used in a histological staining of murine melanoma cells, clearly showing the presence of $G_{M3}$-lactone on the cell surface. Keeping the $G_{M2-4}$-lactam saccharides in $D_2O$ at 37 °C for 1 month caused marginal (0−11%) hydrolysis of the lactam ring.

Gangliosides are sialic acid-containing glycosphingolipids that are present in the outer membrane of living cells.[1] Their saccharide moieties are exposed to the medium surrounding the cell, thereby permitting recognition by saccharide-binding proteins. Gangliosides are tumor-associated antigens[2,3] and also important cell-surface receptors, where they *inter alia* mediate the recruitment of leucocytes to sites of inflammation.[4] Furthermore, gangliosides are efficient receptors for the adhesion of bacteria and viruses to cells, a prerequisite for infection.[5]

The carboxylic acid group of gangliosides may enter into lactone formation with suitably placed hydroxyl groups in neighboring saccharide moieties, thus leading to the formation of δ-lactone rings. This is a facile process *in vitro* in acid medium.[6] It has been discussed for decades if ganglioside lactones are also present *in vivo*, thus being able to permit fine tuning of the ganglioside's receptor activity. Indirect evidence for the existence of ganglioside lactones has been obtained by sodium borotritide reduction of cells and detection of radioactive glycolipid products on chromatographic plates.[6b] However, the possibility that the lactones are artifacts from manipulation of the cells cannot be ruled out. Additional evidence has been obtained by immunostaining of cells, using antibodies raised against preformed ganglioside lactones.[7] However, in most cases the antibodies were not lactone-specific but cross-reacted with the native ganglioside. For this reason, safe conclusions about the presence of ganglioside lactones on living cells could not be drawn, although recent studies seem to support their existence.[8] It has also been suggested that ganglioside lactones are more immunogenic than their native counterparts, suggesting that the lactones may be of value as immunogens for raising tumor-specific antibodies and even for vaccination against tumors.[7] However, the hydrolytic lability of the lactones makes them less suited as immunogens, since it is difficult to maintain a high plasma concentration for the time needed to obtain a strong immune response. Hydrolytically stable and structurally similar lactone analogs are thus desired.

In a preliminary paper[9] we described the synthesis of a lactam analog of the trisaccharide corresponding to ganglioside $G_{M3}$-lactone. Conformational analysis revealed a striking similarity between $G_{M3}$-lactam and $G_{M3}$-lactone [RMS = 0.097 Å according to molecular mechanics (MM2) calculations]. The $G_{M3}$-lactam was coupled, via a spacer, to bovine serum albumin (BSA), and the resulting neoglycoprotein was used as immunogen to raise monoclonal antibodies.[10] $G_{M3}$-lactam−BSA was highly immunogenic, giving more than 300 hybridomas from immunization of one mouse. Random selection of eight of the hybridomas gave monoclonal antibodies that all were of the IgG type. Three of these antibodies recognized $G_{M3}$-lactone but not native $G_{M3}$-ganglioside. Immunohistochemical staining

[⊗] Abstract published in *Advance ACS Abstracts*, April 15, 1995.

(1) (a) Hakomori, S. *Annu. Rev. Biochem.* **1981**, *50*, 733−764. (b) Karlsson, K.-A. In *Biological Membranes;* Chapman, D., Ed.; Academic Press: London, 1982; Vol. 4, pp 1−74. (c) Gigg, J.; Gigg, R. *Topics Curr. Chem.* **1990**, *154*, 77−138. (d) Sweeley, C. C. In *Biochemistry of Lipids, Lipoproteins and Membranes;* Vance, D. E., Vance, J., Eds.; Elsevier Science Publishers: Oxford, U.K., 1991, pp 327−361.

(2) Hakomori, S. *Chem. Phys. Lipids* **1986**, *42*, 209−233.

(3) Yogeeswaran, G. *Adv. Cancer Res.* **1983**, *38*, 289−350.

(4) (a) Phillips, M. L.; Nudelman, E.; Gaeta, F. C. A.; Perez, M.; Singhal, A. K.; Hakomori, S.; Paulson, J. C. *Science* **1990**, *250*, 1130−1132. (b) Walz, G.; Aruffo, A.; Kolanus, W.; Bevilacqua, M.; Seed, B. *Science* **1990**, *250*, 1132−1135. (c) Lowe, J. B.; Stoolman, L. M.; Nair, R. P.; Larsen, R. D.; Berhend, T. L.; Marks, R. M. *Cell* **1990**, *63*, 475−484.

(5) *Microbial Lectins and Agglutinins*; Mirelman, D., Ed.; Wiley: New York, 1986.

(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) Nores, G. A.; Dohi, T.; Taniguchi, M.; Hakomori, S. *J. Immunol.* **1987**, *139*, 3171−3176.

(8) Bouchon, B.; Levery, S. B.; Clausen, H.; Hakomori, S. *Glycoconj. J.* **1992**, *9*, 27−38.

(9) Ray, A. K.; Nilsson, U.; Magnusson, G. *J. Am. Chem. Soc.* **1992**, *114*, 2256−2257.

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

0002-7863/95/1517-4742$09.00/0 

of murine melanoma B16 cells (known to carry large amounts of $G_{M3}$-ganglioside on their surface) with one of the antibodies clearly demonstrated that $G_{M3}$-lactone was present on the cells.[11] We now disclose the full details of the synthesis of $G_{M3}$-lactam and its derivatives (including $G_{M3}$-ganglioside lactam), as well as the synthesis of $G_{M4}$, $G_{M2}$, and $G_{M1}$-lactam glycosides.

**Synthesis of $G_{M3}$-Lactam.** Glycosylation of the partially benzylated TMSEt glucoside **2**[12] with the bromosugar **1**,[13] using silver silicate[14] as promotor, gave the lactose azide derivative **3** (61%). It should be noted that despite the nonparticipating character of the azide group in **1**, a $\beta$-glycosidic linkage was formed in excess over the corresponding $\alpha$-linkage, which is in accordance with the proposed mode of action of silver silicate. Compound **3** ($\beta/\alpha$ mixture) was de-*O*-acetylated (→**4**, 97%), **4** was *O*-isopropylidenated (→**5**, 78%), **5** was *O*-benzylated (→**6**, 86%), and **6** was de-*O*-isopropylidenated (→**7**, 94%). Compounds **6** and **7** were obtained as the pure $\beta$-linked compounds after chromatography, wheras **4** and **5** were mixtures of isomers (see Experimental Section).

Regioselective sialylation with the sialyl donor **8**[15] at the 3′-position of **7** gave, after chromatography, the $G_{M3}$-trisaccharide analog **9** (71%). The corresponding $\beta$-sialoside was isolated in 4% yield from the reaction mixture; no material from sialylation at the 4′-position was obtained. Similar selective sialylations of acceptors having two or even three unprotected hydroxyl groups are well-known; a recent review covers such reactions.[16]

Reduction of the azide group in **9** was initially[9] performed with "nickel boride". However, we now favor the use of hydrogen sulfide because it gives a cleaner reaction and higher yield and the workup procedure is simpler. Thus, treatment of **9** with hydrogen sulfide, followed by treatment with methanolic sodium methoxide (deacetylation) of the crude product, gave in a one-pot reaction the desired lactam **10** (97%). When the sodium methoxide treatment was omitted, **11** was obtained, albeit in lower yield (70%). Compound **11** is a valuable precursor for *inter alia* the synthesis of the $G_{M2}$- and $G_{M1}$-lactams (see below). Hydrogenolytic removal of the *O*-benzyl groups in **10** gave the lactam glycoside **12** (94%), which is useful for biochemical studies[10] and as precursor for the preparation of the BSA conjugate **46** (Scheme 6) and the $G_{M3}$-ganglioside lactam **56** (Scheme 7).

The reason for the low yield of **11** is probably as follows. Reduction of **9** gives an intermediary amino ester, which cyclizes either to the desired lactam (**11**) or to the amino lactone (corresponding to **15**), which is lost during the chromatographic purification of **11**. This is supported by the fact that the azido lactone **14** (as well as the azido ester **13**) gives a mixture of the lactam **10** and the amino lactone **15** on reduction with hydrogen sulfide (Scheme 1). Treatment of **15** with sodium methoxide caused its complete transformation into the lactam **10** (probably via the corresponding amino methyl ester). In summary, when the lactam **10** (and not **11**) is desired, treatment of the crude reduction product with sodium methoxide produces **10** in practically quantitative yield (97%). When **11** is desired, a reagent that could transform the amino lactone byproduct into the lactam **11** without removing the acetate protecting groups would be beneficial.

**Synthesis of $G_{M2}$-Lactam.** Glycosylation of the $G_{M3}$-lactam acceptor **11** with the galactosamine donor **16**[17] gave the desired $G_{M2}$-tetrasaccharide **20** (61%) in an acceptable $\beta/\alpha$ ratio (93:7). In an attempt to raise the yield and also to obtain a tetrasaccharide with a protecting group pattern that would permit further glycosylation to the $G_{M1}$-pentasaccharide lactam, additional thioglycoside donors (**17**–**19**) were investigated. The two isopropylidene-protected donors **18** and **19**[17] gave a much improved glycosylation yield, but the $\beta/\alpha$ ratio dropped to an unacceptable level, as shown in Scheme 2. A reason for the low $\beta/\alpha$ ratio with **17**–**19** might be that a "phthaloxonium" ion (a possible intermediate) cannot be developed as efficiently as with the more successful donor **16**.

Refurbishing of **20** was performed via a four-step procedure (hydrogenolysis of the benzyl groups, hydrazinolysis of the phthaloyl group, *N*- and *O*-acetylation, and de-*O*-acetylation), which gave **24** in 48% overall yield. Compound **24** was *inter alia* used in specificity testing of monoclonal anti-$G_{M3}$-lactam antibodies.[10]

Using a slightly altered sequence of events in the refurbishing procedure gave the fully acetylated $G_{M2}$-lactam **25** (42%). Treatment of this TMSEt glycoside with acetic anhydride–boron trifluoride etherate[12] gave the corresponding anomeric acetate **26** in high yield and stereoselectivity (96%, $\beta/\alpha$ 14:1). Compound **26** was then transformed into the spacer thioglycoside **27** (50%, $\beta/\alpha$ 4:1), suitable for coupling to proteins and other carriers. As for the $G_{M3}$-lactam spacer glycoside **45** (Scheme 6), **27** carries a sulfur atom, which permits easy determination of the number of sugar residues in glycoconjugates by sulfur combustion analysis.[18]

In an attempt to raise the yield and $\beta/\alpha$ ratio in the glycosylation reaction, the azide ester **9** was treated with **16** (Scheme 3). Thus, the yield increased to 66% and only the $\beta$-glycoside was isolated. However, the ensuing azide reduction–lactamization sequence gave the $G_{M2}$-lactam **29** in only 29% yield.

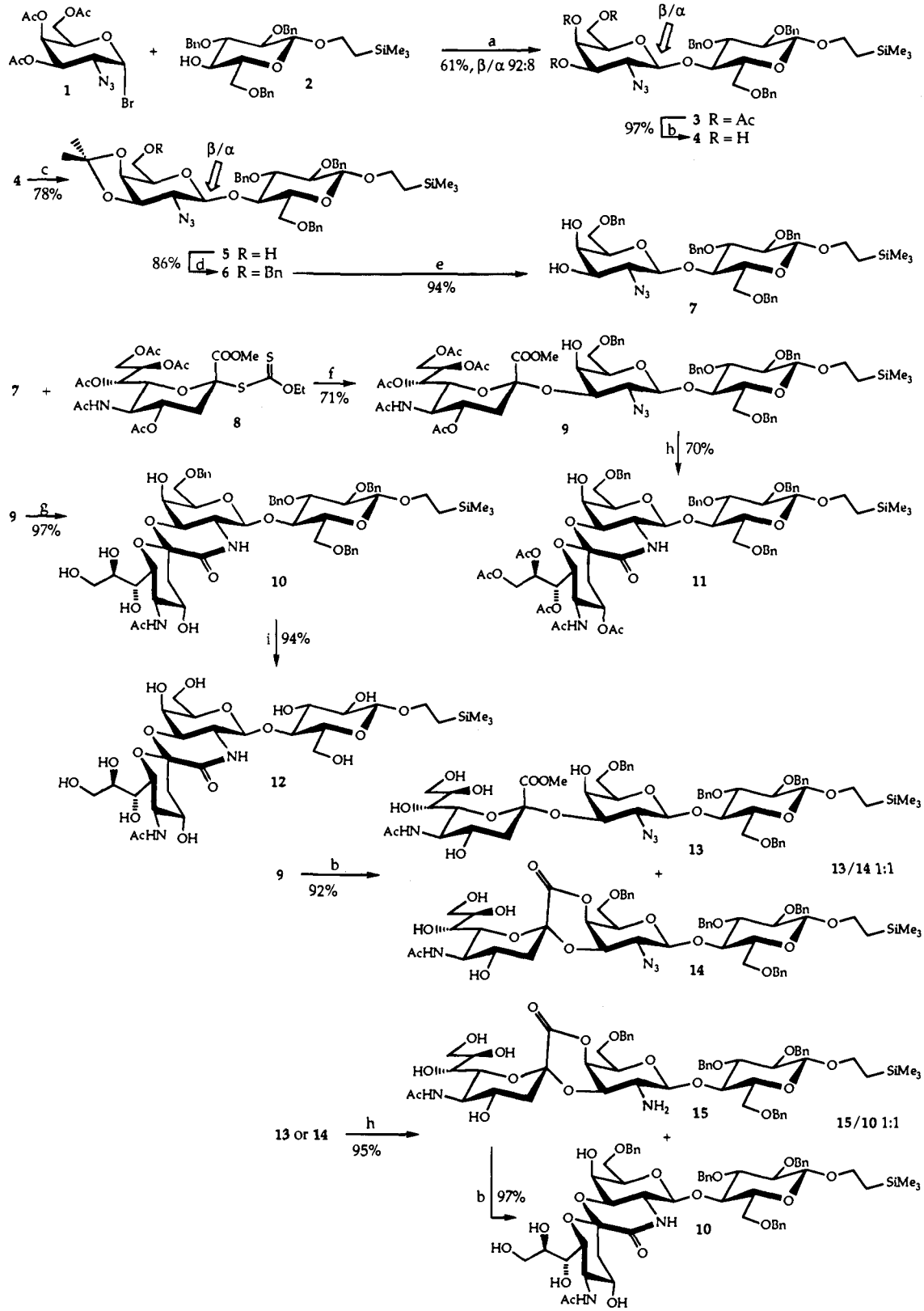
**Synthesis of $G_{M1}$-Lactam.** Glycosylation of the $G_{M3}$-lactam acceptor **11** with the disaccharide **30**[19] gave the fully protected $G_{M1}$-lactam **31** (free of the corresponding $\alpha$-glycoside) in a notoriously unpredictable reaction (Scheme 4). The reaction was performed several times, and the yields varied between 0 and 45%. Furthermore, attempted deblocking of **31** was unsuccessful and only degradation products were observed. An extreme chemical shift (6.49 ppm) for the anomeric proton of the GalNPhth unit (H-1‴) indicates that the compound is sterically strained. This strain might constitute a driving force for the degradation.

**Synthesis of $G_{M4}$-Lactam.** The known[19] glycoside **32** was *O*-isopropylidenated to give **33** (90%), which in turn was *O*-benzoylated and de-*O*-isopropylidenated to give the acceptor **34** (98%) as shown in Scheme 5. Sialylation of **34** with the xanthate donor **8**[15] followed by chromatography permitted isolation, in 6% yield, of the $\beta$-sialoside corresponding to **35**. Acetylation of the rest of the eluate and chromatography gave the desired $G_{M4}$ analog **35** (61%). As with **7** (Scheme 1), **34** carries two unprotected hydroxyl groups and the sialylation reaction is nevertheless completely regioselective.

Deacetylation of **35** gave a 2:1 mixture of the azido ester **36**

(11) 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.
(12) Jansson, K.; Ahlfors, S.; Frejd, T.; Kihlberg, J.; Magnusson, G.; Dahmén, J.; Noori, G.; Stenvall, K. *J. Org. Chem.* **1988**, *53*, 5629–5647.
(13) Lemieux, R. U.; Sabesan, S. *Can. J. Chem.* **1984**, *62*, 644–654.
(14) van Boeckel, C. A. A.; Beetz, T. *Recl. Trav. Chim. Pay-Bas* **1987**, *106*, 596–598.
(15) Marra, A.; Sinaÿ, P. *Carbohydr. Res.* **1990**, *195*, 303–308.
(16) Magnusson, G. *Adv. Drug Deliv. Rev.* **1994**, *13*, 267–284.
(17) Hasegawa, A.; Nagahama, T.; Ohki, H.; Kiso, M. *J. Carbohydr. Chem.* **1992**, *11*, 699–714.
(18) Magnusson, G.; Ahlfors, S.; Dahmén, J.; Jansson, K.; Nilsson, U.; Noori, G.; Stenvall, K.; Tjörnebo, A. *J. Org. Chem.* **1990**, *55*, 3932–3946.
(19) Wilstermann, M.; Magnusson, G. *Carbohydr. Res.* **1995**, in press.

**Scheme 1**

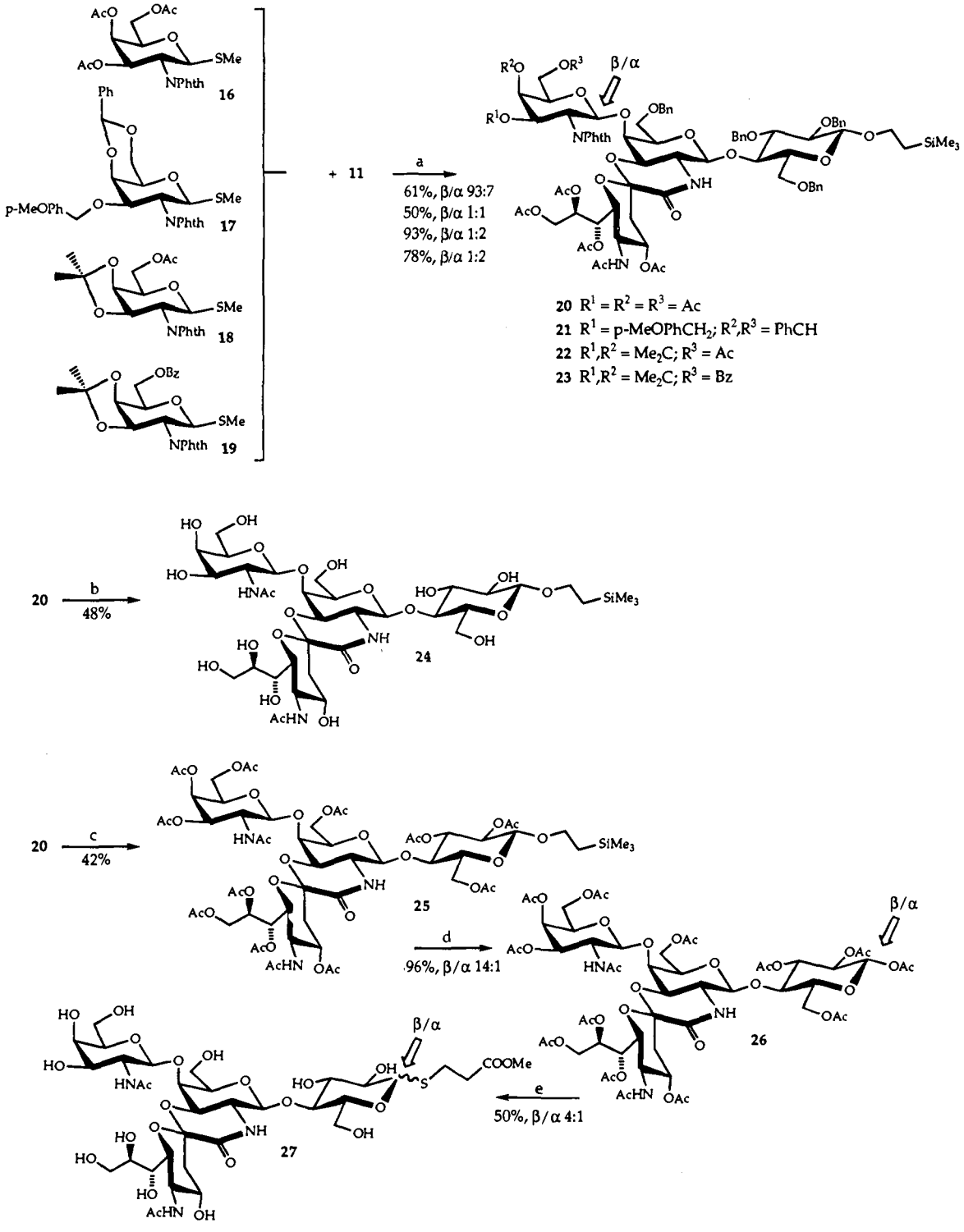


[a] Ag-silicate, $CH_2Cl_2$, MS 4 Å. [b] MeONa, MeOH. [c] $(MeO)_2CMe_2$, camphor-$SO_3H$. [d] $PhCH_2Br$, NaH, DMF. [e] 85% aqueous HOAc. [f] MeSBr, $CF_3SO_3Ag$, MeCN, $CH_2Cl_2$, −78 °C. [g] $H_2S$, pyridine, $Et_3N$, $H_2O$, then MeONa, MeOH. [h] $H_2S$, pyridine, $Et_3N$, MeOH. [i] $H_2$, Pd/C, AcOH.

and the azido lactone **37**. Reduction of the **36/37** mixture with hydrogen sulfide, followed by treatment with sodium methoxide gave the desired $G_{M4}$-lactam **38** (96%). The behavior of the $G_{M4}$ analogs is similar to that of the $G_{M3}$ analogs (cf. **9**−**15**, Scheme 1). Compound **38** was used in the characterization of anti-$G_{M3}$-lactam monoclonal antibodies.[10]

Treatment of the **36/37** mixture with aqueous sodium hydroxide gave the azido acid **39** (99%). Reduction of **39** with hydrogen sulfide under slightly basic conditions furnished the amino acid **40** (53%), which was used as NMR standard in an investigation of the hydrolytic stability of the $G_{M2-4}$-lactams (see below).

**Scheme 2**




[a] MeSBr, $CF_3SO_3Ag$, MeCN, $CH_2Cl_2$, MS 3 Å, −25 °C. [b] $H_2$, Pd/C, HOAc, then $H_2NNH_2{\cdot}H_2O$, EtOH, 85 °C, then $Ac_2O$, pyridine, then MeONa, MeOH. [c] $H_2$, Pd/C, HOAc, then MeONa, MeOH, then $H_2NNH_2{\cdot}H_2O$, EtOH, 85 °C, then $Ac_2O$, pyridine. [d] $Ac_2O$, $BF_3Et_2O$, $CH_2Cl_2$. [e] $HSCH_2CH_2COOMe$, $BF_3Et_2O$, $CH_2Cl_2$, then MeONa, MeOH.

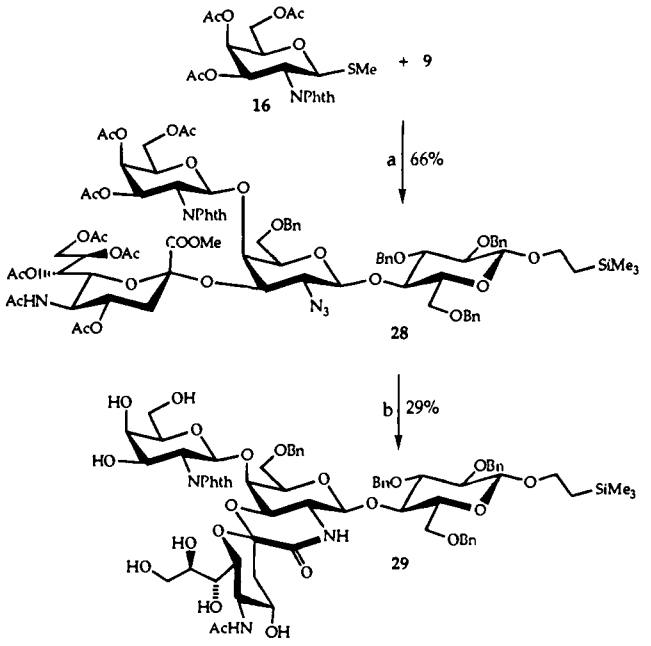
**Synthesis of $G_{M3}$-Lactam−BSA and $G_{M3}$-Ganglioside Lactam.** The $G_{M3}$-lactam−BSA conjugate **46** was prepared as follows. The unprotected $G_{M3}$-saccharide **12** was acetylated to give **41** (90%) as shown in Scheme 6. Activation of the TMSEt group of **41** with α,α-dichloromethyl methyl ether[20] furnished the α-chlorosugar **42** in quantitative yield. Glycosylation of 2-bromoethanol[21] with the donor **42** gave the 2-bromoethyl glycoside **43** (54%) as an inseparable β/α mixture (6:1). Treatment of **43** with methyl mercaptopropionate and cesium carbonate[22] gave **44** (82%), and deacetylation of **44** gave the spacer glycoside **45** (86%). Transformation of **45** to the corresponding acyl azide and addition of BSA furnished the

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

(21) Dahmén, J.; Frejd, T.; Magnusson, G.; Noori, G.; Carlström, A.-S. *Carbohydr. Res.* **1984**, *129*, 63−71, and references cited therein.

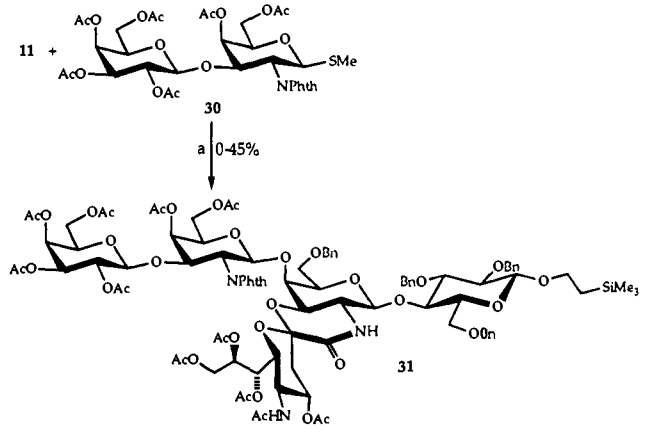
(22) (a) Dahmén, J.; Frejd, T.; Magnusson, G.; Noori, G.; Carlström, A.-S. *Carbohydr. Res.* **1984**, *127*, 15−25. (b) Buter, J.; Kelogg, R. M. *J. Org. Chem.* **1981**, *46*, 4481−4485.

**Scheme 3**



[a] MeSBr, $CF_3SO_3Ag$, MeCN, $CH_2Cl_2$, MS 3 Å, −25 °C. [b] MeONa, MeOH, then $H_2S$, pyridine, $Et_3N$, MeOH, then DMAP, pyridine, 50 °C.

**Scheme 4**



[a] NIS, $CF_3SO_3H$, MeCN, $CH_2Cl_2$, MS 3 Å, −45 °C.

$G_{M3}$-lactam−BSA conjugate **46**. This coupling method has been used by us and others for coupling of a number of different saccharides to various proteins.[18,23] The number of saccharide molecules per molecule of BSA was determined by differential sulfur combustion analysis[18] to be ~24. The conjugate **46** was used as immunogen to raise monoclonal antibodies[10] that cross-reacted with $G_{M3}$-ganglioside lactone (but not with $G_{M3}$-ganglioside), thereby showing that these entities are present on murine malignant melanoma cells.[11]

As shown in Scheme 6, the BSA conjugate **46** is a β/α mixture (6:1). Therefore, an alternative route to a pure β-glycosidic spacer saccharide was investigated. Treatment of the TMSEt glycoside **41** with acetic anhydride−boron trifluoride etherate gave the anomeric acetate **47** (100%) as a β/α mixture (10:1). Treatment of **47** with methyl mercaptopropionate−boron trifluoride etherate[24] gave **48** (85%, β/α 96:4). Deacetylation of **48** gave the $G_{M3}$-lactam spacer saccharide **49** (74%), useful for coupling to different types of carriers.

(23) Lemieux, R. U.; Bundle, D. R.; Baker, D. A. *J. Am. Chem. Soc.* **1975**, *97*, 4076−4083.

(24) Dahmén, J.; Frejd, T.; Magnusson, G.; Noori, G. *Carbohydr. Res.* **1983**, *114*, 328−330.

The $G_{M3}$-ganglioside lactam **56** was also prepared from the key intermediate **41** (Scheme 7). Thus, treatment of **41** with trifluoroacetic acid[12] gave the hemiacetal **50** (100%), which was used without purification in the preparation of the trichloroacetimidate[25] donor **51** (96%, α/β 3:1). Glycosylation of the azidosphingosine derivative **52**[26] with **51** gave a mixture (96:4) of the desired glycoside **53** and the corresponding orthoester **54**. Treatment of the mixture with aqueous acetic acid followed by chromatography gave pure **53** (44%). Reduction of the azide group of pure **53** with hydrogen sulfide and acylation of the corresponding amine with stearoyl chloride gave the ceramide derivative **55** (91%). Deacylation of **55** gave the $G_{M3}$-ganglioside lactam **56** (92%), useful for coating of cells and hydrophobic surfaces and as a component of liposomes and other biologically valuable aggregates.

**Stability of $G_{M2-4}$-Lactams in Aqueous Solution.** The $G_{M2-4}$-lactams **12**, **24**, and **38** were submitted to an investigation of their hydrolytic stability. The compounds were dissolved in $D_2O$, and the solutions were kept at 37 °C for 1 month. The NMR spectra were recorded at intervals. The $G_{M3}$-lactam **12** suffered hydrolysis (~11% after one month) somewhat more readily than the $G_{M4}$-lactam **38**, whereas the $G_{M2}$-lactam **24** was stable during the whole period of investigation. Since long-term studies of hydrolytic stability might be sensitive to traces of acids or bases, we realize that the differences observed might be insignificant. However, the fact that the bulk of the lactams was left unchanged for a month at 37 °C indicates the possibility that they also remain unchanged under truly physiological conditions.

## Experimental Section

The structures of all new compounds were determined by careful NMR analyses, including sophisticated 2D methods such as COSY, TOCSY, HETCOR, long-range HETCOR, and NOESY. NMR spectra were recorded with a Bruker ARX 500 MHz or a Varian XL 300 MHz spectrometer. Melting points are uncorrected. Optical rotations were measured with a Perkin-Elmer 141 polarimeter. High-resolution mass spectra were obtained on a JEOL JMS SX 102 spectrometer. Concentrations were made using rotary evaporation with bath temperature at or below 40 °C. TLC was performed on Kieselgel 60 $F_{254}$ plates (Merck). Column chromatography was performed using $SiO_2$ (Matrex LC-gel, 60A, 35−70 MY, Grace).

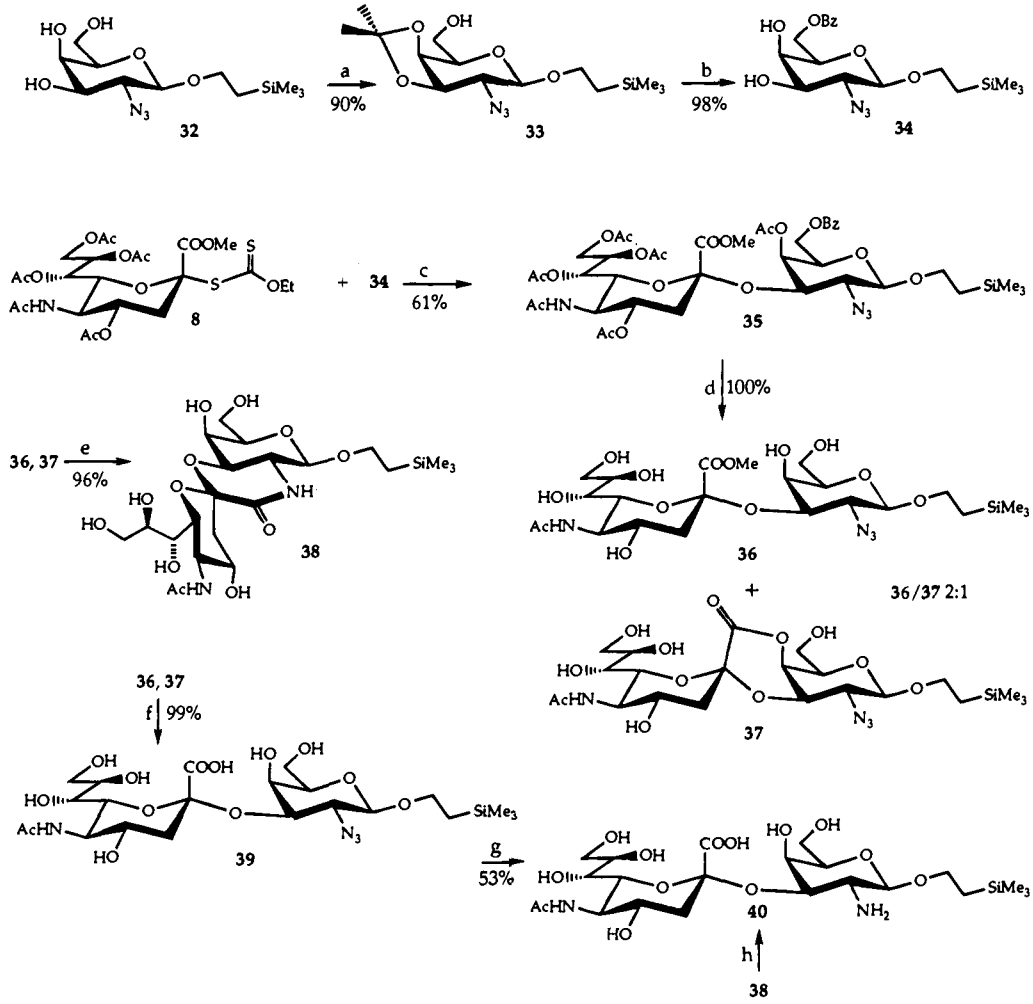
**2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzyl-4-*O*-(3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-β-D-galactopyranosyl)-β-D-glucopyranoside (3).** A mixture of **1**[13] (4.52 g, 8.22 mmol), **2**[12] (2.90 g, 7.36 mmol), powdered molecular sieves (3 g, 4 Å), and dry dichloromethane (50 mL) was stirred for 1 h under $N_2$ with protection from light, and then silver silicate[14] (8 g) was added. After 48 h, the mixture was filtered (Celite) and concentrated. The residue was chromatographed ($SiO_2$, heptane/EtOAc, 6:1→4:1) to give **3** (3.87 g, 61%), contaminated with 8% of the corresponding α anomer. **3**: $^1H$ NMR ($CDCl_3$) δ 7.40−7.28 (m, 15 H, PhH), 5.19 (brd, 1 H, $J$ = 3.4 Hz, H-4'), 4.92 (d, 1 H, $J$ = 11.2 Hz, $CH_2Ph$), 4.90 (d, 1 H, $J$ = 10.5 Hz, $CH_2Ph$), 4.79 (d, 1 H, $J$ = 11.2 Hz, $CH_2Ph$), 4.75 (d, 1 H, $J$ = 12.0 Hz, $CH_2Ph$), 4.71 (d, 1 H, $J$ = 10.0 Hz, $CH_2Ph$), 4.60 (dd, 1 H, $J$ = 3.3, 10.8 Hz, H-3'), 4.48 (d, 1 H, $J$ = 12.0 Hz, $CH_2Ph$), 4.41 (d, 1 H, $J$ = 7.6 Hz, H-1), 4.39 (d, 1 H, $J$ = 8.1 Hz, H-1'), 2.09−1.99 (3 s, 3 H each, OAc), 1.04 (m, 2 H, $CH_2Si$), 0.04 (s, 9 H, $SiMe_3$); *m/z* calcd for $C_{44}H_{57}O_{13}N_3Si$ (M + H) 864.3738, found 864.3734.

**2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzyl-4-*O*-(2-azido-2-deoxy-β-D-galactopyranosyl)-β-D-glucopyranoside (4).** Methanolic sodium methoxide (2 M, 0.5 mL) was added to a solution of **3** (3.70 g, 4.28 mmol) in methanol (50 mL), and the mixture was stirred for 6 h and then neutralized with Duolite C-26 ($H^+$) resin, filtered, and concentrated

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

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

**Scheme 5**



[a] $(MeO)_2CMe_2$, $MePhSO_3H$. [b] BzCl, pyridine, 0 °C, then 80% aqueous HOAc, 80 °C. [c] MeSBr, $CF_3SO_3Ag$, MeCN, $CH_2Cl_2$, MS 3 Å, −78 °C, then $Ac_2O$, pyridine, DMAP. [d] MeONa, MeOH. [e] $H_2S$, pyridine, $Et_3N$, MeOH, then MeONa, MeOH. [f] NaOH, $H_2O$. [g] $H_2S$, pyridine, $Et_3N$, MeOH. [h] $D_2O$, 37 °C, 30 days.

to give **4** (3.06 g, 97%), contaminated with 8% of the corresponding α anomer. **4**: $^1H$ NMR ($CDCl_3$) δ 7.36−7.21 (m, 15 H, PhH), 4.42 (d, 1 H, $J$ = 7.7 Hz, H-1), 4.28 (d, 1 H, $J$ = 8.1 Hz, H-1′), 1.05 (m, 2 H, $CH_2Si$), 0.00 (s, 9 H, $SiMe_3$); *m/z* calcd for $C_{38}H_{51}O_{10}N_3Si$ (M + H) 738.3422, found 738.3452.

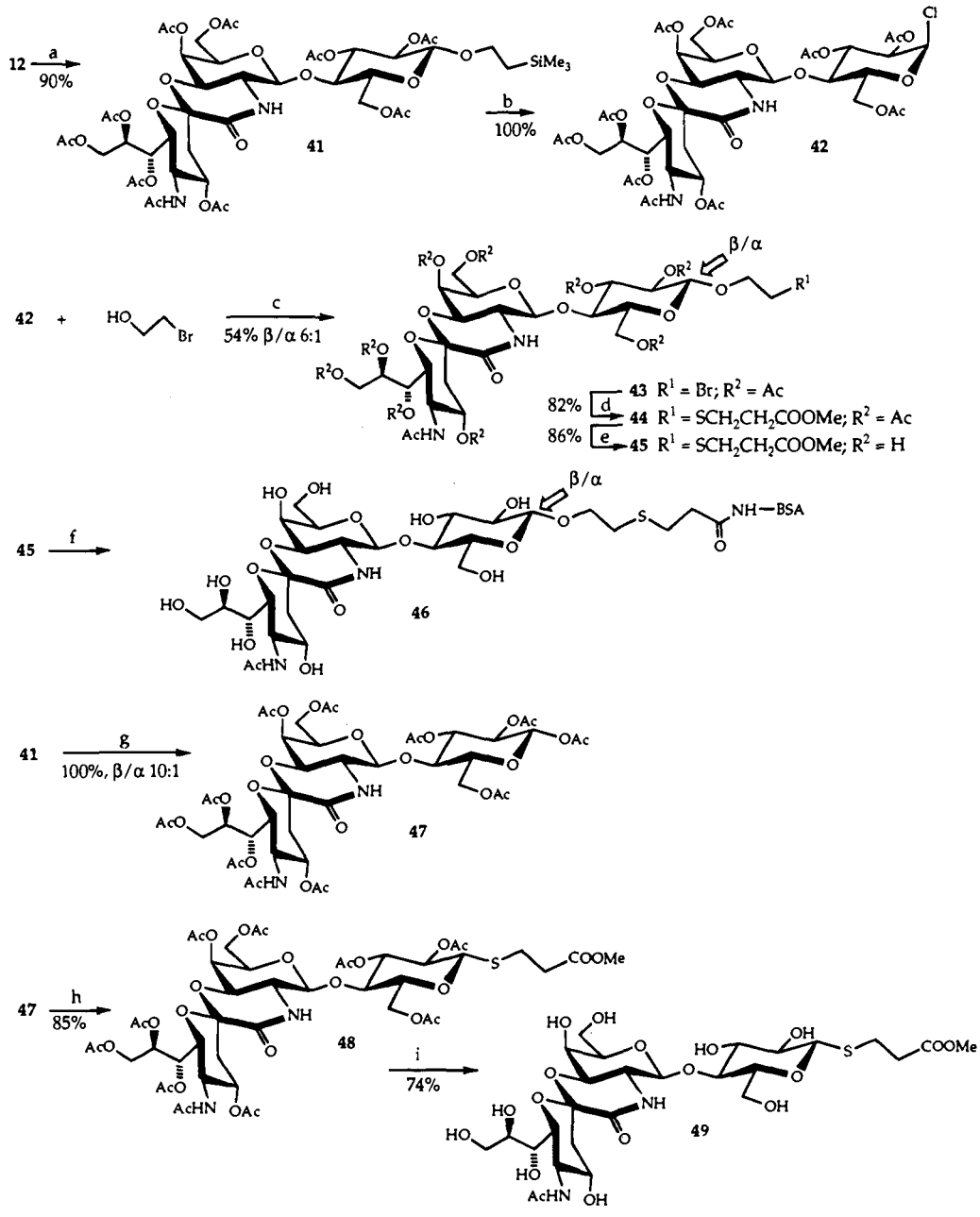
**2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzyl-4-*O*-(2-azido-2-deoxy-3,4-*O*-isopropylidene-β-D-galactopyranosyl)-β-D-glucopyranoside (5).** To a mixture of **4** (750 mg, 1.02 mmol, α/β 8:92) and 2,2-dimethoxypropane (25 mL) was added camphor-10-sulfonic acid (15 mg), and the mixture was stirred for 48 h at room temperature and then neutralized with triethylamine (0.15 mL). The mixture was concentrated, and the residue was dissolved in methanol (40 mL) and water (4 mL), kept for 3 h at 85 °C, and then concentrated and coconcentrated with toluene. The residue was chromatographed ($SiO_2$, heptane/EtOAc, 4:1→1:2) to give **5** (620 mg, 78%), contaminated with 9% of the corresponding 4,6-*O*-isopropylidene derivative. **5**: $^1H$ NMR ($CDCl_3$) δ 7.40−7.26 (m, 15 H, PhH), 4.94 (d, 1 H, $J$ = 10.9 Hz, $CH_2Ph$), 4.87 (d, 1 H, $J$ = 10.5 Hz, $CH_2Ph$), 4.79 (d, 1 H, $J$ = 10.3 Hz, $CH_2Ph$), 4.75 (d, 1 H, $J$ = 11.0 Hz, $CH_2Ph$), 4.74 (d, 1 H, $J$ = 12.2 Hz, $CH_2Ph$), 4.48 (d, 1 H, $J$ = 12.2 Hz, $CH_2Ph$), 4.40 (d, 1 H, $J$ = 7.8 Hz, H-1), 4.21 (d, 1 H, $J$ = 8.5 Hz, H-1′), 1.55 (s, 3 H, $CCH_3$), 1.33 (s, 3 H, $CCH_3$), 1.05 (m, 2 H, $CH_2Si$), 0.04 (s, 9 H, $SiMe_3$); *m/z* calcd for $C_{41}H_{55}O_{10}N_3Si$ (M − H) 776.3578, found 776.3558.

**2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzyl-4-*O*-(2-azido-6-*O*-benzyl-2-deoxy-3,4-*O*-isopropylidene-β-D-galactopyranosyl)-β-D-glucopyranoside (6).** To a solution of **5** (2.35 g, 3.02 mmol) in *N,N*-dimethylformamide (40 mL) was added sodium hydride (300 mg, 6.20 mmol, 50% in mineral oil). The mixture was stirred for 1 h, and benzyl bromide (600 μL, 5.0 mmol) was added dropwise. After 16 h, excess sodium hydride was destroyed by addition of methanol (5 mL), and the mixture was diluted with dichloromethane, washed (saturated aqueous NaCl), dried ($Na_2SO_4$), and concentrated. The residue was chromatographed ($SiO_2$, heptane/EtOAc, 7:1→1:1) to give **6** (2.24 g, 86%): $[\alpha]^{25}_D$ +21° (*c* 1.4, $CDCl_3$); $^1H$ NMR ($CDCl_3$) δ 7.40−7.22 (m, 20 H, PhH), 4.92 (d, 1 H, $J$ = 11.0 Hz, $CH_2Ph$), 4.89 (d, 1 H, $J$ = 10.5 Hz, $CH_2Ph$), 4.75 (d, 1 H, $J$ = 10.7 Hz, $CH_2Ph$), 4.73 (d, 1 H, $J$ = 12.2 Hz, $CH_2Ph$), 4.72 (d, 1 H, $J$ = 11.0 Hz, $CH_2Ph$), 4.51 (d, 1 H, $J$ = 12.0 Hz, $CH_2Ph$), 4.49 (d, 1 H, $J$ = 12.1 Hz, $CH_2Ph$), 4.40 (d, 1 H, $J$ = 7.8 Hz, H-1), 4.32 (d, 1 H, $J$ = 10.9 Hz, $CH_2Ph$), 4.29 (d, 1 H, $J$ = 8.4 Hz, H-1′), 1.59 (s, 3 H, $CCH_3$), 1.36 (s, 3 H, $CCH_3$), 1.04 (m, 2 H, $CH_2Si$), 0.04 (s, 9 H, $SiMe_3$); *m/z* calcd for $C_{48}H_{62}O_{13}N_3Si$ (M + H) 868.4204, found 868.4216.

**2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzyl-4-*O*-(2-azido-6-*O*-benzyl-2-deoxy-β-D-galactopyranosyl)-β-D-glucopyranoside (7).** Compound **6** (2.20 g, 2.54 mmol) was dissolved in aqueous acetic acid (50 mL, 85%), and the mixture was kept at 85 °C for 90 min and then concentrated and coconcentrated with toluene. The residue was chromatographed ($SiO_2$, heptane/EtOAc, 4:1→2:1) to give **7** (1.96 g, 94%): $[\alpha]^{25}_D$ +19° (*c* 1.2, $CDCl_3$); $^1H$ NMR ($CDCl_3$) δ 7.36−7.21 (m, 20 H, PhH), 4.93 (d, 1 H, $J$ = 11.0 Hz, $CH_2Ph$), 4.92 (d, 1 H, $J$ = 11.0 Hz, $CH_2Ph$), 4.79 (d, 1 H, $J$ = 11.2 Hz, $CH_2Ph$), 4.51 (d, 1 H, $J$ = 12.2 Hz, $CH_2Ph$), 4.40 (d, 1 H, $J$ = 7.6 Hz, H-1), 4.31 (d, 1 H, $J$ = 8.1 Hz, H-1′), 2.76 (d, 1 H, $J$ = 3.7 Hz, OH), 2.56 (d, 1 H, $J$ = 8.0 Hz, OH), 1.05 (m, 2 H, $CH_2Si$), 0.04 (s, 9 H, $SiMe_3$); *m/z* calcd for $C_{45}H_{57}O_{10}N_3Si$ (M + Na) 850.3710, found 850.3732.

**2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzyl-4-*O*-[2-azido-6-*O*-benzyl-2-deoxy-3-*O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylate)-β-D-galacto-**

**Scheme 6**



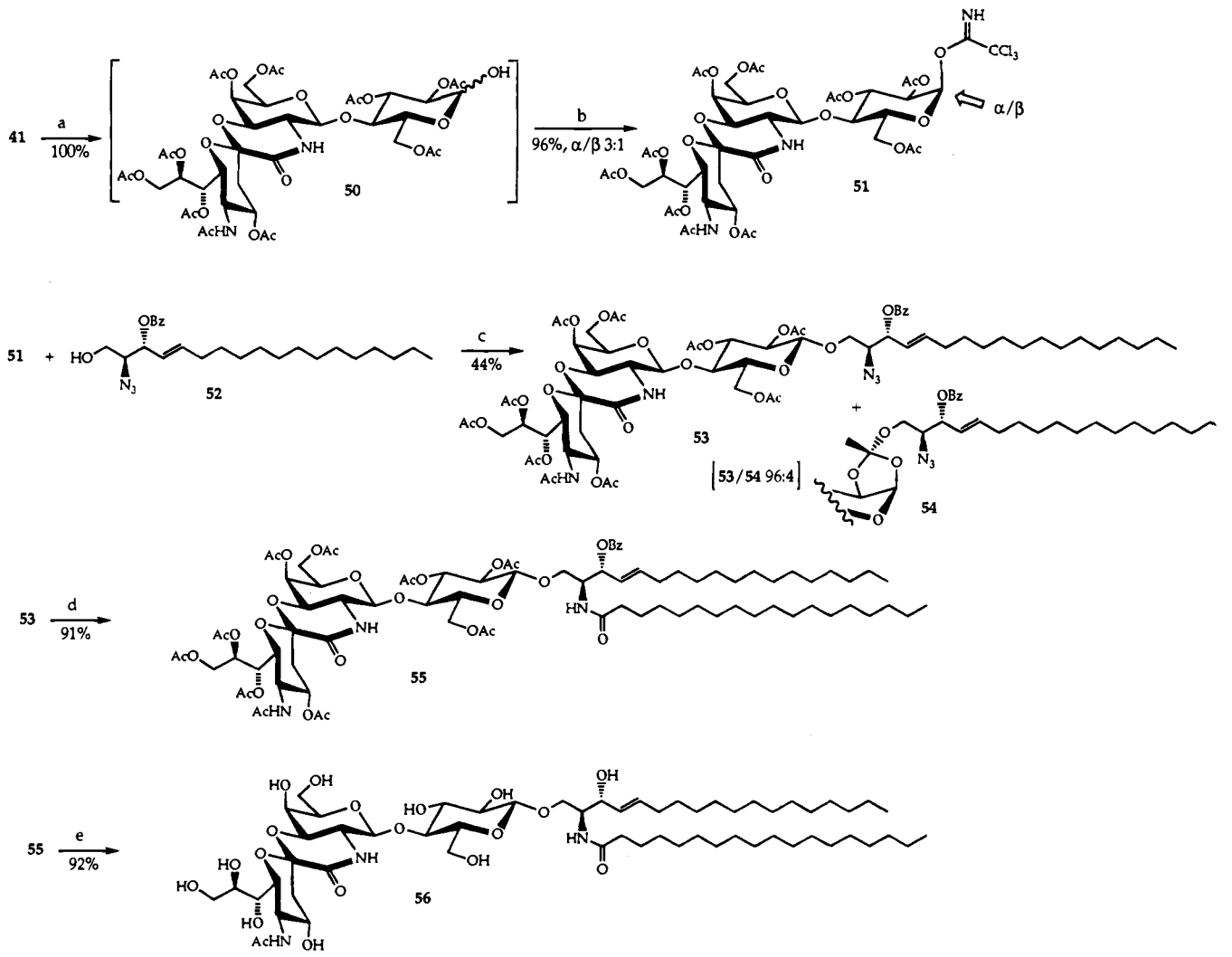

[a] $Ac_2O$, pyridine, DMAP. [b] $Cl_2CHOMe$, $ZnCl_2$, $CHCl_3$. [c] $CF_3SO_3Ag$, $CH_2Cl_2$, MS 3 Å, −28 °C→room temperature. [d] $HSCH_2CH_2COOMe$, $Cs_2CO_3$, DMF. [e] MeONa, MeOH. [f] $H_2NNH_2{\cdot}H_2O$, EtOH, then t-$BuNO_2$, DMSO, HCl, $H_2NSO_3H$, then BSA, buffer. [g] $BF_3Et_2O$, $Ac_2O$, $CH_2Cl_2$. [h] $BF_3Et_2O$, $HSCH_2CH_2COOMe$, $CH_2Cl_2$. [i] MeONa, MeOH.

**pyranosyl]-β-D-glucopyranoside (9).** A mixture of **7** (610 mg, 0.74 mmol), **8**[15] (880 mg, 1.48 mmol), powdered molecular sieves (1.5 g, 3 Å), dry acetonitrile (15 mL), and dry dichloromethane (10 mL) was stirred under $N_2$ for 90 min. Silver triflate (385 mg, 1.50 mmol) was added, and the mixture was cooled to −78 °C and kept protected from light. Methanesulfenyl bromide (395 μL, 3.7 M in $ClCH_2CH_2Cl$, 1.48 mmol) was added in four portions. After 2 h, diisopropylamine (500 μL) was added and the stirring was continued for 1 h at −78 °C. The mixture was diluted with dichloromethane, filtered (Celite), washed (saturated aqueous $NaHCO_3$ and water), dried ($Na_2SO_4$), and concentrated. The residue was chromatographed ($SiO_2$, heptane/EtOAc, 1:1, then toluene/EtOAc, 1:1→1:5) to give **9** (681 mg, 71%) and the corresponding β anomer (37 mg, 4%). **9**: $[\alpha]^{25}_D$ −13° (*c* 1.1, $CDCl_3$); $^1H$ NMR ($CDCl_3$) δ 7.37−7.19 (m, 20 H, PhH), 5.55 (ddd, 1 H, *J* = 2.7, 5.8, 8.6 Hz, H-8″), 5.32 (dd, 1 H, *J* = 1.2, 8.7 Hz, H-7″), 5.12 (d, 1 H, *J* = 9.7 Hz, NH), 4.97 (d, 1 H, *J* = 11.2 Hz, $CH_2Ph$), 4.94 (m, 1 H, H-4″), 4.92 (d, 1 H, *J* = 11.1 Hz, $CH_2Ph$), 4.84 (d, 1 H, *J* = 11.1 Hz, $CH_2Ph$), 4.69 (d, 1 H, *J* = 11.1 Hz, $CH_2Ph$), 4.64 (d, 1 H, *J* = 12.1 Hz, $CH_2Ph$), 4.62 (d, 1 H, *J* = 12.1 Hz, $CH_2Ph$), 4.51 (d, 1 H, *J* = 8.1 Hz, H-1′), 4.41 (d, 1 H, *J* = 7.8 Hz, H-1), 4.36 (d, 1 H, *J* = 11.9 Hz, $CH_2Ph$), 4.31 (d, 1 H, *J* = 11.9 Hz, $CH_2Ph$), 4.30 (dd, 1 H, *J* = 2.7, 12.5 Hz, H-9″a), 4.18 (dd, 1 H, *J* = 3.2, 10.0 Hz, H-3′), 3.97 (brt, 1 H, *J* = 9.3 Hz, H-4), 3.76 (s, 3 H, OMe), 3.44 (brt, 1 H, *J* = 5.6 Hz, H-5′), 3.40 (dd, 1 H, *J* = 7.8, 9.1 Hz, H-2), 2.65 (dd, 1 H, *J* = 4.4, 12.0 Hz, H-3″eq), 2.10−1.89 (5 s, 3 H each, OAc, NHAc), 1.04 (m, 2 H, $CH_2Si$), 0.03 (s, 9 H, $SiMe_3$); $^{13}C$ NMR δ 168 (C-1″, $J_{C\text{-}1'':H\text{-}3''ax}$ = 4.5 Hz[27]). Anal. Calcd for $C_{65}H_{84}O_{22}N_4Si$: C, 60.0; H, 6.5; N, 4.3. Found: C, 59.9; H, 6.5; N, 4.2.

**2-(Trimethylsilyl)ethyl 2,3,6-Tri-O-benzyl-4-*O*-[2-amino-6-*O*-benzyl-2-deoxy-3-*O*-(5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosyloyl-1″→2′-lactam)-β-D-galactopyranosyl]-β-D-glucopyranoside (10).** Hydrogen sulfide was bubbled through a mixture of **9** (30 mg, 0.023 mmol), pyridine (1.5 mL), triethylamine (0.75 mL), and methanol (0.75 mL) for 1 h at 0 °C. The mixture was kept under

(27) (a) Prytulla, S.; Lauterwein, J.; Klessinger, M.; Thiem, J. *Carbohydr. Res.* **1991**, *215*, 345−349. (b) Hori, H.; Nakajima, T.; Nishida, Y.; Ohrui, H.; Meguro, H. *Tetrahedron Lett.* **1988**, *29*, 6317−6320.

**Scheme 7**



[a] $CF_3COOH$, $CH_2Cl_2$. [b] $Cl_3CCN$, DBU, $CH_2Cl_2$. [c] $BF_3Et_2O$, $CH_2Cl_2$. [d] $H_2S$, pyridine, $H_2O$, then $C_{17}H_{35}COOH$, EDC, $CH_2Cl_2$. [e] MeONa, MeOH.

$H_2S$ at room temperature for 24 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 methanol (1.2 mL), methanolic sodium methoxide (2 M, 8 $\mu$L) was added under argon, and the mixture was stirred for 2 h 30 min, then neutralized with Duolite C-26 ($H^+$) resin, and concentrated. The residue was chromatographed ($SiO_2$, $CH_2Cl_2$/MeOH, 10:1→5:1) to give **10** (24 mg, 97%); $[\alpha]^{22}_D$ −9° (*c* 0.98, MeOH); $^1H$ NMR ($CD_3OD$) $\delta$ 7.41−7.18 (m, 20 H, PhH), 4.72 (d, 1 H, $J$ = 11.0 Hz, $CH_2Ph$), 4.67 (d, 1 H, $J$ = 12.5 Hz, $CH_2Ph$), 4.65 (d, 1 H, $J$ = 10.8 Hz, $CH_2Ph$), 4.61 (d, 1 H, $J$ = 11.9 Hz, $CH_2Ph$), 4.48 (d, 1 H, $J$ = 8.0 Hz, H-1′), 4.42 (d, 1 H, $J$ = 7.8 Hz, H-1), 4.28 (d, 1 H, $J$ = 12.0 Hz, $CH_2Ph$), 3.81 (t, 1 H, $J$ = 10.2 Hz, H-3), 2.50 (dd, 1 H, $J$ = 5.5, 13.0 Hz, H-3″eq), 2.00 (s, 3 H, NHAc), 1.65 (dd, 1 H, $J$ = 11.0, 13.0 Hz, H-3″ax), 0.04 (s, 9 H, $SiMe_3$); *m/z* calcd for $C_{56}H_{74}O_{17}N_2Si$ (M + Na) 1097.4654, found 1097.4662.

**2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzyl-4-*O*-[2-amino-6-*O*-benzyl-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-glucopyranoside (11).** Hydrogen sulfide was bubbled through a mixture of **9** (1.60 g, 1.23 mmol), pyridine (70 mL), triethylamine (35 mL), and methanol (35 mL) for 90 min at 0 °C. The mixture was kept under $H_2S$ at room temperature for 16 h. $N_2$ was bubbled through the mixture for 1 h and then it was concentrated and coconcentrated with toluene. The residue was chromatographed ($SiO_2$, toluene/EtOAc, 1:1→1:2) to give **11** (1.07 g, 70%): $[\alpha]^{22}_D$ −5° (*c* 1.1, $CHCl_3$); $^1H$ NMR ($CDCl_3$) $\delta$ 7.40−7.20 (m, 20 H, PhH), 5.65 (dt, 1 H, $J$ = 5.6, 10.6 Hz, H-4″), 5.29 (dd, 1 H, $J$ = 2.3, 5.9 Hz, H-7″), 5.20 (dt, 1 H, $J$ = 2.6, 6.6, Hz, H-8″), 4.98 (d, 1 H, $J$ = 11.5 Hz, $CH_2Ph$), 4.92 (d, 1 H, $J$ = 10.8 Hz, $CH_2Ph$), 4.91 (d, 1 H, $J$ = 12.1 Hz, $CH_2Ph$), 4.80 (d, 1 H, $J$ = 12.4 Hz, $CH_2Ph$), 4.74 (d, 1 H, $J$ = 12.3 Hz, $CH_2Ph$), 4.67 (d, 1 H, $J$ = 10.9 Hz, $CH_2Ph$), 4.51 (d, 1 H, $J$ = 8.0 Hz, H-1′), 4.39 (d, 1 H, $J$ = 7.8 Hz, H-1), 4.39 (dd, 1 H, $J$ = 2.5, 12.4 Hz, H-9″a), 4.22 (dd, 1 H, $J$ = 10.3, 20.5 Hz, H-5″), 4.07 (dd, 1 H, $J$ = 6.7, 12.4 Hz, H-9″b), 3.86 (dd, 1 H, $J$ = 8.1, 12.5 Hz, H-2′), 3.73 (dd, 1 H, $J$ = 3.1, 11.6 Hz, H-6a), 3.52 (dd, 1 H, $J$ = 2.6, 10.7 Hz, H-3′), 3.44 (dd, 1 H, $J$ = 7.8, 8.9 Hz, H-2), 3.37 (m, 1 H, H-5′), 3.31 (dd, 1 H, $J$ = 5.2, 9.4 Hz, H-6′a), 2.52 (dd, 1 H, $J$ = 5.5, 13.1 Hz, H-3″eq), 2.15−1.90 (5 s, 3 H each, OAc, NHAc), 1.88 (dd, 1 H, $J$ = 11.1, 13.1 Hz, H-3″ax), 1.04 (m, 2 H, $CH_2Si$), 0.03 (s, 9 H, $SiMe_3$). Anal. Calcd for $C_{64}H_{82}O_{21}N_2Si$: C, 61.8; H, 6.6; N, 2.3. Found: C, 61.6; H, 6.7; N, 2.3.

**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-glucopyranoside (12).** Compound **10** (164 mg, 0.16 mmol) was hydrogenated ($H_2$, Pd/C, 10%, 300 mg, 1 atm) in acetic acid (13 mL) for 4 h. The mixture was filtered (Celite) and concentrated. The residue was chromatographed ($SiO_2$, $CH_2Cl_2$/MeOH/$H_2O$, 65:35:5) to give **12** (106 mg, 94%): $[\alpha]^{24}_D$ −22° (*c* 0.70, MeOH); $^1H$ NMR ($D_2O$) $\delta$ 4.71 (d, 1 H, $J$ = 8.1 Hz, H-1′), 4.48 (d, 1 H, $J$ = 8.0 Hz, H-1), 4.34 (ddd, 1 H, $J$ = 5.4, 10.0, 10.9 Hz, H-4″), 4.06 (d, 1 H, $J$ = 2.6 Hz, H-4′), 4.02 (dd, 1 H, $J$ = 2.6, 10.8 Hz, H-3′), 3.93 (dd, 1 H, $J$ = 3.0, 12.3 Hz, H-6a), 3.89 (t, 1 H, $J$ = 10.2 Hz, H-5″), 3.84 (dd, 1 H, $J$ = 8.1, 10.8 Hz, H-2′), 3.79 (t, 1 H, $J$ = 9.9 Hz, H-4), 3.74 (dd, 1 H, $J$ = 1.1, 10.5 Hz, H-6″), 3.70 (m, 1 H, H-8″), 3.67 (t, 1 H, $J$ = 9.2 Hz, H-3), 3.62 (m, 1 H, H-5), 3.62 (dd, 1 H, $J$ = 5.6, 12.0 Hz, H-9″a), 3.52 (dd, 1 H, $J$ = 1.1, 9.4 Hz, H-7″), 3.28 (dd, 1 H, $J$ = 8.0, 9.2 Hz, H-2), 2.59 (dd, 1 H, $J$ = 5.4, 13.3 Hz, H-3″eq), 2.02 (s, 3 H, NHAc), 1.68 (dd, 1 H, $J$ = 11.1, 13.3 Hz, H-3″ax), 1.00

(m, 2 H, $CH_2Si$), 0.02 (s, 9 H, $SiMe_3$); $^{13}C$ NMR $\delta$ 175.9, 169.6, 102.4, 100.7, 98.8, 78.9, 78.9, 77.0, 74.9, 74.8, 73.9, 73.2, 71.0, 69.3, 68.6, 68.6, 66.3, 64.1, 61.8, 61.5, 52.6, 51.6, 40.1, 22.9, 18.4, −1.7; *m/z* calcd for $C_{28}H_{50}O_{17}N_2Si$ (M + H) 715.2957, found 715.2958.

**2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzyl-4-*O*-[2-azido-6-*O*-benzyl-2-deoxy-3-*O*-(methyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylate)-β-D-galactopyranosyl]-β-D-glucopyranoside (13) and 2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzyl-4-*O*-[2-azido-6-*O*-benzyl-2-deoxy-3-*O*-(5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosyloyl-1″→4′-lactone)-β-D-galactopyranosyl]-β-D-glucopyranoside (14).** Methanolic sodium methoxide (2 M, 75 μL) was added to a solution of **9** (232 mg, 0.18 mmol) in dry methanol (3 mL), and the mixture was stirred for 23 h and then neutralized with Duolite C-26 ($H^+$) resin, filtered, and concentrated. The residue was chromatographed ($SiO_2$, toluene/EtOH, 5:1) to give **13** (89 mg, 44%) and **14** (94 mg, 48%). **13**: $^1H$ NMR ($CD_3OD$) $\delta$ 7.45−7.18 (m, 20 H, PhH), 4.43 (d, 1 H, $J$ = 8.0 Hz, H-1), 4.37 (d, 1 H, $J$ = 8.1 Hz, H-1′), 3.81 (s, 3 H, OMe), 3.26 (dd, 1 H, $J$ = 8.0, 9.1 Hz, H-2), 2.77 (dd, 1 H, $J$ = 4.5, 12.8 Hz, H-3″eq), 2.01 (s, 3 H, NHAc), 1.97 (dd, 1 H, $J$ = 11.5, 12.7 Hz, H-3″ax), 0.04 (s, 9 H, $SiMe_3$). **14**: $^1H$ NMR ($CD_3OD$) $\delta$ 7.42−7.17 (m, 20 H, PhH), 5.24 (brd, 1 H, $J$ = 4.0 Hz, H-4′), 4.43 (d, 1 H, $J$ = 7.8 Hz, H-1), 4.37 (d, 1 H, $J$ = 8.2 Hz, H-1′), 3.24 (dd, 1 H, $J$ = 7.9, 9.2 Hz, H-2), 2.53 (dd, 1 H, $J$ = 5.4, 13.2 Hz, H-3″eq), 2.03 (s, 3 H, NHAc), 1.74 (dd, 1 H, $J$ = 11.2, 13.1 Hz, H-3″ax), 0.04 (s, 9 H, $SiMe_3$).

**2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzyl-4-*O*-[2-amino-6-*O*-benzyl-2-deoxy-3-*O*-(5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosyloyl-1″→4′-lactone)-β-D-galactopyranosyl]-β-D-glucopyranoside (15) and 2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzyl-4-*O*-[2-amino-6-*O*-benzyl-2-deoxy-3-*O*-(5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosyloyl-1″→2′-lactam)-β-D-galactopyranosyl]-β-D-glucopyranoside (10).** (a) Hydrogen sulfide was bubbled through a mixture of **14** (94 mg, 0.086 mmol), pyridine (5 mL), triethylamine (2.5 mL), and methanol (2.5 mL) for 3.5 h at 0 °C. The mixture was kept under $H_2S$ at room temperature for 3 days. $N_2$ was bubbled through the mixture for 1 h and then it was concentrated and coconcentrated with toluene. The residue was chromatographed ($SiO_2$, toluene/EtOH, 5:1) to give **10** (47 mg, 51%) and **15** (44 mg, 47%). **15**: $^1H$ NMR ($CD_3OD$) $\delta$ 7.39−7.20 (m, 20 H, PhH), 5.25 (d, 1 H, $J$ = 3.9 Hz, H-4′), 4.43 (d, 1 H, $J$ = 7.8 Hz, H-1), 4.39 (d, 1 H, $J$ = 8.1 Hz, H-1′), 3.25 (dd, 1 H, $J$ = 7.9, 9.1 Hz, H-2), 2.80 (dd, 1 H, $J$ = 8.1, 10.1 Hz, H-2′), 2.52 (dd, 1 H, $J$ = 5.5, 13.1 Hz, H-3″eq), 2.02 (s, 3 H, NHAc), 1.77 (dd, 1 H, $J$ = 11.0, 13.2 Hz, H-3″ax), 0.04 (s, 9 H, $SiMe_3$). (b) Compound **13** (89 mg, 0.078 mmol) was treated as above, which gave **10** (42 mg, 49%) and **15** (39 mg, 46%).

**Methyl 4,6-*O*-Benzylidene-2-deoxy-3-*O*-(*p*-methoxybenzyl)-2-phthalimido-1-thio-β-D-galactopyranoside (17).** A mixture of methyl 2-deoxy-2-phthalimido-1-thio-β-D-galactopyranoside[17] (292 mg, 0.86 mmol), α,α-dimethoxytoluene (205 μL, 1.37 mmol), *p*-toluenesulfonic acid monohydrate (catalytic amount), and acetonitrile (10 mL) was stirred overnight. Triethylamine (1 mL) was added and the solution concentrated. The residue was chromatographed ($SiO_2$, heptane/EtOAc, 1:1 + 0.1% $Et_3N$) to give methyl 4,6-*O*-benzylidene-2-deoxy-2-phthalimido-1-thio-β-D-galactopyranoside (320 mg, 87%): $[\alpha]^{25}_D$ +42° (*c* 0.97, $CHCl_3$); $^1H$ NMR ($CDCl_3$) $\delta$ 7.88−7.42 (m, 9 H, PhH), 5.61 (s, 1 H, CHPh), 5.28 (d, 1 H, $J$ = 9.8 Hz, H-1), 4.60 (m, 2 H, H-2,3), 4.43 (dd, 1 H, $J$ = 1.5, 12.5 Hz, H-6a), 4.34 (dd, 1 H, $J$ = 1.0, 3.3 Hz, H-4), 4.10 (dd, 1 H, $J$ = 1.8, 12.5 Hz, H-6b), 3.74 (brs, 1 H, H-5), 2.24 (s, 3 H, SMe).

To a mixture of methyl 4,6-*O*-benzylidene-2-deoxy-2-phthalimido-1-thio-β-D-galactopyranoside (15 mg, 0.035 mmol), *p*-methoxybenzyl chloride (48 μL, 0.35 mmol), and dry *N,N*-dimethylformamide (3 mL) was added NaH (4 mg, 0.14 mmol, 80% in mineral oil), and the mixture was kept at 50 °C for 6 h. Another portion of NaH (4 mg) was added, and the mixture was kept at 70 °C for 2 h; then methanol (1 mL) was added to destroy excess NaH. The mixture was partitioned between dichloromethane and water, the aqueous layer was extracted with dichloromethane, and the extract was washed (saturated aqueous $NaHCO_3$ and water), dried ($Na_2SO_4$), and concentrated. The residue was chromatographed ($SiO_2$, heptane/EtOAc, 1:1 + 0.1% triethylamine) to give **17** (11.8 mg, 61%): $[\alpha]^{25}_D$ +61° (*c* 0.60, $CHCl_3$); $^1H$ NMR ($CDCl_3$) $\delta$ 7.86−7.38 (m, 9 H, PhH), 7.02−6.55 (m, 4 H, PhH), 5.52 (s, 1 H, CHPh), 5.18 (d, 1 H, $J$ = 10.4 Hz, H-1), 4.82 (t, 1 H, $J$ = 10.5 Hz, H-2), 4.56 (d, 1 H, $J$ = 12.5 Hz, $CH_2Ph$), 4.48 (dd, 1 H, $J$ = 3.4, 10.6 Hz, H-3), 4.38 (d, 1 H, $J$ = 12.5 Hz, $CH_2Ph$), 4.37 (dd, 1 H, $J$ = 1.6, 12.4 Hz, H-6a), 4.25 (brd, 1 H, $J$ = 3.6 Hz, H-4), 4.04 (dd, 1 H, $J$ = 1.7, 12.4 Hz, H-6b), 3.70 (s, 1 H, OMe), 2.24 (s, 3 H, SMe); *m/z* calcd for $C_{30}H_{29}O_7NS$ (M + H) 548.1743, found 548.1732.

**Methyl 6-*O*-Acetyl-2-deoxy-3,4-*O*-isopropylidene-2-phthalimido-1-thio-β-D-galactopyranoside (18).** Methyl 2-deoxy-3,4-*O*-isopropylidene-2-phthalimido-1-thio-β-D-galactopyranoside[17] (638 mg, 1.68 mmol) was acetylated with acetic anhydride−pyridine (30 mL, 1:1) for 17 h. The mixture was concentrated and coconcentrated with toluene, and the residue was chromatographed ($SiO_2$, heptane/EtOAc, 2:1) to give **18** (682 mg, 96%); $[\alpha]^{25}_D$ +77° (*c* 0.96, $CHCl_3$); $^1H$ NMR ($CDCl_3$) $\delta$ 7.84−7.71 (m, 4 H, PhH), 5.08 (d, 1 H, $J$ = 10.6 Hz, H-1), 4.84 (dd, 1 H, $J$ = 5.0, 8.9 Hz, H-3), 4.40 (m, 2 H, H-6a,b), 4.37 (dd, 1 H, $J$ = 8.8, 10.6 Hz, H-2), 4.19 (m, 1 H, H-5), 2.14, 2.11 (2s, 3 H each, SMe, OAc), 1.63, 1.33 (2s, 3 H each, $CCH_3$); *m/z* calcd for $C_{20}H_{23}O_7NS$ (M + H) 422.1273, found 422.1286.

**2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzyl-4-*O*-[2-amino-6-*O*-benzyl-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)-4-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (20).** A mixture of **16** (297 mg, 0.30 mmol), **11** (400 mg, 0.32 mmol), powdered molecular sieves (300 mg, 3 Å), dry acetonitrile (2 mL), and dry dichloromethane (8 mL) was stirred under argon for 90 min. The mixture was protected from light and cooled to −25 °C, and silver triflate (169 mg, 0.66 mmol) in dry acetonitrile (2 mL) was added, followed by methanesulfenyl bromide (161 μL, 4 M in $ClCH_2CH_2Cl$, 0.64 mmol) in four portions. After 4 h, diisopropylamine (2 mL) was added and the stirring was continued for 1 h at −25 °C. The mixture was diluted with dichloromethane, filtered (Celite), and successively washed (saturated aqueous $NaHCO_3$ and water), dried ($Na_2SO_4$), and concentrated. The residue was chromatographed ($SiO_2$, toluene/EtOAc, 1:3, then toluene/EtOH, 30:1→10:1) to give **20** (306 mg, 57%) and the corresponding α-glycoside (23 mg, 4%). **20**: $[\alpha]^{25}_D$ −18° (*c* 0.70, $CHCl_3$); $^1H$ NMR ($CDCl_3$) $\delta$ 7.90−7.18 (m, 24 H, PhH), 5.83 (d, 1 H, $J$ = 8.5 Hz, H-1‴), 5.55 (dd, 1 H, $J$ = 3.3, 11.4 Hz, H-3‴), 5.42 (dt, 1 H, $J$ = 5.7, 10.6 Hz, H-4″), 5.37 (brd, 1 H, $J$ = 3.2 Hz, H-4‴), 5.32 (m, 2 H, H-7″,8″), 5.17 (d, 1 H, $J$ = 10.1 Hz, NH), 4.86 (d, 1 H, $J$ = 11.1 Hz, $CH_2Ph$), 4.58 (d, 1 H, $J$ = 10.9 Hz, $CH_2Ph$), 4.52 (dd, 1 H, $J$ = 8.4, 11.4 Hz, H-2‴), 4.34 (d, 1 H, $J$ = 7.8 Hz, H-1′), 4.31 (d, 1 H, $J$ = 7.8 Hz, H-1), 3.63 (dd, 1 H, $J$ = 7.9, 10.8 Hz, H-2′), 3.50 (t, 1 H, $J$ = 8.9 Hz, H-3), 3.38 (dd, 1 H, $J$ = 2.3, 10.7 Hz, H-3′), 3.35 (dd, 1 H, $J$ = 7.7, 8.9 Hz, H-2), 2.37−1.82 (8 s, 3 H each, OAc, NHAc), 1.00 (m, 2 H, $CH_2Si$), 0.58 (t, 1 H, $J$ = 12.0 Hz, H-3″ax), 0.04 (s, 9 H, $SiMe_3$). Anal. Calcd for $C_{85}H_{101}O_{30}N_3Si$: C, 61.5; H, 6.1; N, 2.5. Found: C, 61.4; H, 6.4; N, 2.5.

**Compounds 21−23.** Treatment of **11** with **17−19** as above gave the $G_{M2}$-related saccharides **21** (50%, β/α 1:1), **22** (93%, β/α 1:2), and **23** (78%, β/α 1:2). The $^1H$ NMR spectra were in full accordance with the proposed structures.

**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)-4-*O*-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (24).** Compound **20** (90 mg, 0.054 mmol) was hydrogenated ($H_2$, Pd/C, 10%, 50 mg, 1 atm) in acetic acid (3 mL) overnight. The mixture was filtered (Celite) and concentrated. The residue was dissolved in a mixture of ethanol (3 mL) and hydrazine hydrate (300 μL), and the solution was kept at 85 °C for 80 min, and then diluted with ethanol (20 mL), concentrated, and coconcentrated with EtOH five times. The residue was acetylated with acetic anhydride−pyridine (3.5 mL, 1.5:2) for 1 h. The mixture was concentrated and coconcentrated with toluene, then stirred in methanolic sodium methoxide (0.05 M, 2 mL) for 2 h, and neutralized with Duolite C-26 ($H^+$) resin, filtered, and concentrated. The residue was chromatographed ($SiO_2$, $CH_2Cl_2$/MeOH/$H_2O$, 10:5:1) to give **24** (24 mg, 48%): $[\alpha]^{24}_D$ −29° (*c* 0.80, MeOH); $^1H$ NMR ($D_2O$) $\delta$ 4.71 (d, 1 H, $J$ = 8.6 Hz, H-1‴), 4.64 (d, 1 H, $J$ = 8.1 Hz, H-1′), 4.48 (d, 1 H, $J$ = 8.1 Hz, H-1), 4.35 (dd, 1 H, $J$ = 9.2, 11.1 Hz, H-5″), 4.32 (brd, 1 H, $J$ = 3.1 Hz, H-4′), 4.22 (dd, 1 H, $J$ = 0.9, 11.2 Hz, H-6″), 4.18 (ddd, 1 H, $J$ = 5.6, 6.6, 9.1 Hz, H-4″), 4.13 (dd, 1 H, $J$ = 2.5, 10.3 Hz,

H-3′), 3.97 (dd, 1 H, $J$ = 8.5, 10.9 Hz, H-2‴), 3.94 (d, 1 H, $J$ = 3.4 Hz, H-4‴), 3.90 (dd, 1 H, $J$ = 2.6, 12.5 Hz, H-6a), 3.87 (dd 1 H, $J$ = 2.6, 11.8 Hz, H-9″a), 3.79 (t, 1 H, $J$ = 9.4 Hz, H-4), 3.66 (dd, 1 H, $J$ = 3.4, 10.9 Hz, H-3‴), 3.65 (t, 1 H, $J$ = 9.2 Hz, H-3), 3.63 (dd 1 H, $J$ = 6.2, 11.8 Hz, H-9″b), 3.60 (m, 1 H, H-5), 3.54 (dd, 1 H, $J$ = 0.9, 9.7 Hz, H-7″), 3.45 (dd, 1 H, $J$ = 8.1, 10.3 Hz, H-2′), 3.27 (dd, 1 H, $J$ = 8.1, 9.2 Hz, H-2), 2.65 (dd, 1 H, $J$ = 6.7, 15.0 Hz, H-3″eq), 2.02–2.01 (2 s, 3 H each, NHAc), 2.15 (dd, 1 H, $J$ = 4.8, 14.9 Hz, H-3″ax), 1.00 (m, 2 H, $CH_2Si$), 0.00 (s, 9 H, $SiMe_3$); $^{13}C$ NMR ($D_2O$) $\delta$ 175.9, 175.4, 171.4, 103.2, 102.4, 100.6, 100.0, 78.4, 76.5, 75.9, 75.2, 74.9, 74.0, 73.9, 73.1, 73.0, 71.8, 70.7, 69.3, 69.1, 68.6, 68.3, 64.0, 61.9, 61.6, 61.3, 53.5, 53.2, 52.0, 37.3, 23.4, 22.9, 18.5, −1.6; *m/z* calcd for $C_{36}H_{63}O_{22}N_3Si$ (M + H) 918.3751, found 918.3729.

**2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-acetyl-4-*O*-[6-*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)-4-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (25).** Compound **20** (278 mg, 0.17 mmol) was hydrogenated ($H_2$, Pd/C, 10%, 210 mg, 1 atm) in acetic acid (20 mL) overnight. The mixture was filtered (Celite) and concentrated. The residue was dissolved in methanol (10 mL), methanolic sodium methoxide (2 M, 0.4 mL) was added, and the mixture was stirred for 4 h, neutralized with Duolite C-26 ($H^+$) resin, filtered, and concentrated. The residue was dissolved in a mixture of ethanol (9 mL) and hydrazine hydrate (0.9 mL), and the solution was kept at 85 °C for 80 min, then diluted with ethanol (20 mL), concentrated, and coconcentrated with EtOH five times. The residue was acetylated with acetic anhydride (10 mL), pyridine (10 mL), and DMAP (catalytic amount) overnight and then concentrated and coconcentrated with toluene. The residue was chromatographed ($SiO_2$, $CH_2Cl_2$/EtOH, 25:1→15:1) to give **25** (96 mg, 42%): $[\alpha]^{24}_D$ −22° (*c* 1.0, $CHCl_3$); $^1H$ NMR ($CDCl_3$) $\delta$ 5.58 (ddd, 1 H, $J$ = 5.5, 9.9, 11.1 Hz, H-4″), 5.39 (d, 1 H, $J$ = 2.7 Hz, H-4‴), 5.25 (d, 1 H, $J$ = 8.4 Hz, H-1‴), 5.05 (dd, 1 H, $J$ = 3.3, 11.4 Hz, H-3‴), 4.88 (dd, 1 H, $J$ = 7.9, 9.5 Hz, H-2), 4.51 (t, 1 H, $J$ = 9.3 Hz, H-3), 4.48 (d, 1 H, $J$ = 7.9 Hz, H-1), 4.21 (d, 1 H, $J$ = 8.1 Hz, H-1′), 3.58 (m, 1 H, $OCH_2$), 2.47 (dd, 1 H, $J$ = 5.3, 13.2 Hz, H-3″eq), 2.19–1.89 (13 s, 3 H each, OAc, NHAc), 1.80 (dd, 1 H, $J$ = 11.5, 12.9 Hz, H-3″ax), 0.93 (m, 2 H, $CH_2Si$), 0.01 (s, 9 H, $SiMe_3$); $^{13}C$ NMR $\delta$ 100.1 (C-1′), 99.9 (C-1), 98.8 (C-1‴), 97.6 (C-1″), 38.4 (C-3″), −1.4 ($SiMe_3$). Anal. Calcd for $C_{58}H_{85}O_{33}N_3Si$: C, 50.5; H, 6.2; N, 3.0. Found: C, 50.3; H, 6.2; N, 2.8.

**1,2,3,6-Tetra-*O*-acetyl-4-*O*-[6-*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)-4-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranose (26).** To a solution under argon of **25** (30.5 mg, 0.022 mmol) in dry dichloromethane (1 mL) was added acetic anhydride (94 μL, 0.99 mmol) and boron trifluoride etherate (28 μL, 0.22 mmol). After 2 h 10 min, the mixture was diluted with dichloromethane, washed (saturated aqueous $NaHCO_3$), dried ($Na_2SO_4$), and concentrated to give crude **26** (28 mg, 96%, β/α 14:1): $^1H$ NMR ($CDCl_3$) $\delta$ 6.27 (d, 1 H, $J$ = 4.3 Hz, H-1α), 5.70 (d, 1 H, $J$ = 8.3 Hz, H-1β), 5.39 (brd, 1 H, $J$ = 2.4 Hz, H-4‴), 5.23 (d, 1 H, $J$ = 8.4 Hz, H-1‴), 5.04 (dd, 1 H, $J$ = 8.3, 9.5 Hz, H-2), 4.20 (d, 1 H, $J$ = 7.3 Hz, H-1′), 2.44 (dd, 1 H, $J$ = 5.6, 12.7 Hz, H-3″eq), 2.18–1.89 (14 s, 3 H each, OAc, NHAc), 1.76 (dd, 1 H, $J$ = 11.7, 12.9 Hz, H-3″ax).

**2-(Methoxycarbonyl)ethyl 4-*O*-[2-Amino-2-deoxy-3-*O*-(5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosyloyl-1″→2′-lactam)-4-*O*-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-β-D-galactopyranosyl]-1-thio-αβ-D-glucopyranoside (27).** To a solution of crude **26** (28 mg, 0.021 mmol) in dry dichloromethane (0.5 mL) was added methyl mercaptopropionate (12 μL, 0.11 mmol) and boron trifluoride etherate (28 μL, 0.22 mmol) under argon. After 2 h 10 min, the mixture was diluted with dichloromethane, washed (saturated aqueous $NaHCO_3$), dried ($Na_2SO_4$), and concentrated. The residue was passed through a short column ($SiO_2$, $CH_2Cl_2$/EtOH, 20:1→10:1), and the eluate was dissolved in dry methanol (1 mL). Methanolic sodium methoxide (2 M, 8 μL) was added, and after 3 h, the mixture was neutralized with Duolite C-26 ($H^+$) resin and concentrated. The residue was chromatographed ($SiO_2$, $CH_2Cl_2$/MeOH/$H_2O$, 5:5:1) to give **27** (9.5 mg, 50%) as an α/β mixture (1:4): $^1H$ NMR ($D_2O$) $\delta$ 5.42 (d, 1 H, $J$ = 5.5 Hz, H-1α), 4.63 (d, 1 H, $J$ = 8.6 Hz, H-1‴), 4.57 (d, 1 H, $J$ = 8.1 Hz, H-1′), 4.50 (d, 1 H, $J$ = 9.9 Hz, H-1β), 4.27 (dd, 1 H, $J$ = 10.0, 10.8 Hz, H-5″), 4.25 (brd, 1 H, $J$ = 3.1 Hz, H-4′), 4.15 (brd, 1 H, $J$ = 10.7 Hz, H-6″), 4.11 (m, 1 H, H-4″), 4.05 (dd, 1 H, $J$ = 2.4, 10.3 Hz, H-3′), 3.89 (dd, 1 H, $J$ = 8.8, 11.3 Hz, H-2‴), 3.65 (s, 3 H, OMe), 3.38 (dd, 1 H, $J$ = 8.3, 10.1 Hz, H-2′), 3.27 (dd, 1 H, $J$ = 9.2, 9.5 Hz, H-2), 2.90 (m, 2 H, $SCH_2$), 2.72 (t, 2 H, $J$ = 7.0 Hz, $CH_2$-COO), 2.58 (dd, 1 H, $J$ = 6.4, 14.8 Hz, H-3″eq), 2.06 (dd, 1 H, $J$ = 5.2, 14.7 Hz, H-3″ax), 2.03–2.01 (2 s, 3 H each, NHAc); *m/z* calcd for $C_{35}H_{57}O_{23}N_3S$ (M + H) 920.3182, found 920.3199.

**2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzyl-4-*O*-[2-azido-6-*O*-benzyl-2-deoxy-3-*O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylate)-4-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (28).** A mixture of **16** (36 mg, 0.077 mmol), **9** (50 mg, 0.038 mmol), powdered molecular sieves (0.1 g, 3 Å), dry acetonitrile (0.5 mL), and dry dichloromethane (2 mL) was stirred under $N_2$ for 2 h. The mixture was protected from light and kept at −25 °C. Silver triflate (21 mg, 0.081 mmol) and dry acetonitrile (0.5 mL) were added, followed by methanesulfenyl bromide (20 μL, 4 M in $ClCH_2CH_2Cl$, 0.08 mmol), added in four portions. After 4 h 20 min, diisopropylamine (250 μL) was added, and the stirring was continued for 30 min at −25 °C. The mixture was diluted with dichloromethane, filtered (Celite), washed (saturated aqueous $NaHCO_3$ and water), dried ($Na_2SO_4$), and concentrated. The residue was chromatographed ($SiO_2$, $CH_2Cl_2$/MeOH, 50:1) to give **28** (44 mg, 66%): $[\alpha]^{22}_D$ +4° (*c* 0.98, $CHCl_3$); $^1H$ NMR ($CDCl_3$) $\delta$ 7.92–7.17 (m, 24 H, PhH), 6.14 (dd, 1 H, $J$ = 3.4, 11.6 Hz, H-3‴), 5.52 (m, 1 H, H-8″), 5.50 (brd, 1 H, $J$ = 3.6 Hz, H-4‴), 5.38 (d, 1 H, $J$ = 8.4 Hz, H-1‴), 5.32 (dd, 1 H, $J$ = 2.1, 9.2 Hz, H-7″), 4.93 (d, 1 H, $J$ = 11.0 Hz, $CH_2Ph$), 4.84 (d, 1 H, $J$ = 10.0 Hz, $CH_2Ph$), 4.81 (m, 1 H, H-4″), 4.78 (d, 1 H, $J$ = 11.1 Hz, $CH_2Ph$), 4.59 (d, 1 H, $J$ = 11.8 Hz, $CH_2$-Ph), 4.58 (dd, 1 H, $J$ = 8.3, 11.7 Hz, H-2‴), 4.51 (d, 1 H, $J$ = 11.9 Hz, $CH_2Ph$), 4.39 (d, 1 H, $J$ = 7.8 Hz, H-1), 4.37 (d, 1 H, $J$ = 8.0 Hz, H-1′), 4.29 (d, 1 H, $J$ = 12.0 Hz, $CH_2Ph$), 4.20 (d, 1 H, $J$ = 12.0 Hz, $CH_2Ph$), 4.17 (dd, 1 H, $J$ = 2.7, 10.2 Hz, H-3′), 3.91 (dd, 1 H, $J$ = 2.1, 10.7 Hz, H-6″), 3.82 (s, 3 H, OMe), 3.35 (dd, 1 H, $J$ = 7.9, 9.1 Hz, H-2), 2.88 (dd, 1 H, $J$ = 4.1, 13.0 Hz, H-3″eq), 2.85 (dd, 1 H, $J$ = 7.9, 10.1 Hz, H-2′), 2.23–1.85 (8 s, 3 H each, OAc, NHAc), 1.71 (t, 1 H, $J$ = 12.8 Hz, H-3″ax), 1.03 (m, 2 H, $CH_2Si$), 0.01 (s, 9 H, $SiMe_3$).

**2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzyl-4-*O*-[2-amino-6-*O*-benzyl-2-deoxy-3-*O*-(5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosyloyl-1″→2′-lactam)-4-*O*-(2-deoxy-2-phthalimido-β-D-galactopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (29).** Methanolic sodium methoxide (2 M, 8 μL) was added to a solution of **28** (24.5 mg, 0.014 mmol) in methanol (1 mL), and the mixture was stirred for 1 h 30 min, then neutralized with Duolite C-26 ($H^+$) resin, filtered, and concentrated. The residue was dissolved in pyridine (2 mL), triethylamine (1 mL), and methanol (1 mL). Hydrogen sulfide was bubbled through the mixture for 1 h at 0 °C, and the mixture was then kept at room temperature overnight. $N_2$ was bubbled through the mixture for 1 h and then it was concentrated. The residue was passed through a short column ($SiO_2$, toluene/MeOH, 4:1). The eluate was concentrated and dissolved in pyridine (5 mL), DMAP (catalytic amount) was added, and the mixture was kept at 50 °C for 25 h and then concentrated and coconcentrated with toluene. Column chromatography ($SiO_2$, toluene/MeOH, 4:1) gave **29** (6.0 mg, 29%). The structure of **29** was proven by acetylation, which gave **20**.

**2-(Trimethylsilyl)ethyl 2,3,6-Tri-*O*-benzyl-4-*O*-{2-amino-6-*O*-benzyl-2-deoxy-3-*O*-[5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosyloyl-1″→2′-lactam)-4-*O*-[4,6-di-*O*-acetyl-2-deoxy-2-phthalimido-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-galactopyranosyl]-β-D-galactopyranosyl}-β-D-glucopyranoside (31).** A mixture of **11** (30 mg, 0.024 mmol), **30**[19] (24 mg, 0.032 mmol), powdered molecular sieves (0.2 g, 3 Å), dry acetonitrile (3 mL), and dry dichloromethane (1 mL) was stirred at room temperature for 1 h under $N_2$ and then cooled to −45 °C. *N*-Iodosuccinimide (8 mg, 0.036 mmol) in dry acetonitrile (200 μL) was added, followed by trifluoromethanesulfonic acid (1 μL, 0.011 mmol). After 2 h 40 min, triethylamine (250 μL) was added, and the mixture was filtered (Celite), washed (saturated aqueous $Na_2S_2O_4$ and saturated aqueous $NaHCO_3$), dried ($Na_2SO_4$), and concentrated. The residue was chromatographed

($SiO_2$, toluene/EtOH, 30:1) to give **31** (21 mg, 45%): $[\alpha]^{25}_D$ +27° (*c* 0.95, $CHCl_3$); $^1H$ NMR ($CDCl_3$) $\delta$ 7.86−7.13 (m, 24 H, PhH), 6.49 (d, 1 H, $J$ = 9.1 Hz, H-1‴), 5.41 (dt, 1 H, $J$ = 5.7, 10.8 Hz, H-4″), 5.24 (brd, 1 H, $J$ = 3.0 Hz, H-4⁗), 5.01 (dd, 1 H, $J$ = 7.8, 10.3 Hz, H-2⁗), 4.81 (dd, 1 H, $J$ = 3.4, 8.3 Hz, H-3‴), 4.48 (d, 1 H, $J$ = 7.8 Hz, H-1′), 4.45 (d, 1 H, $J$ = 7.8 Hz, H-1⁗), 4.38 (d, 1 H, $J$ = 7.8 Hz, H-1), 3.10 (t, 1 H, $J$ = 9.6 Hz, H-5″), 2.67 (dd, 1 H, $J$ = 5.3, 12.7 Hz, H-3″eq), 2.19−1.45 (11 s, 3 H each, OAc, NHAc), 1.56 (dd, 1 H, $J$ = 11.8, 13.0 Hz, H-3″ax), 1.03 (m, 2 H, $CH_2Si$), 0.02 (s, 9 H, $SiMe_3$); *m/z* calcd for $C_{96}H_{117}O_{38}N_3Si$ (M + Na) 1970.6982, found 1970.6992.

**2-(Trimethylsilyl)ethyl 2-Azido-2-deoxy-3,4-*O*-isopropylidene-β-D-galactopyranoside (33).** To a solution of **32**[19] (6.50 g, 21.3 mmol) and 2,2-dimethoxypropane (95 mL) was added *p*-toluenesulfonic acid (catalytic amount) and the mixture was stirred overnight and then neutralized with triethylamine. The mixture was concentrated, dissolved in methanol (65 mL) and water (6.5 mL), and stirred for 5 h at 80 °C. The mixture was concentrated and the residue was chromatographed ($SiO_2$, heptane/EtOAc, 2:1→1:1 + 0.1% triethylamine) to give **33** (6.66 g, 90%). An analytical sample was recrystallized from heptane. **33**: $[\alpha]^{25}_D$ +40° (*c* 0.9, $CHCl_3$); mp 82−83 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 4.25 (d, 1 H, $J$ = 8.5 Hz, H-1), 4.10 (dd, 1 H, $J$ = 2.0, 5.4 Hz, H-4), 3.62 (m, 1 H, $OCH_2$), 1.54 (s, 3 H, $CCH_3$), 1.34 (s, 3 H, $CCH_3$), 1.05 (m, 2 H, $CH_2Si$), 0.04 (s, 9 H, $SiMe_3$). Anal. Calcd for $C_{14}H_{27}O_5N_3Si$: C, 48.7; H, 7.9; N, 12.2. Found: C, 48.4; H, 7.6; N, 12.2.

**2-(Trimethylsilyl)ethyl 2-Azido-6-*O*-benzoyl-2-deoxy-β-D-galactopyranoside (34).** Compound **33** (5.48 g, 15.9 mmol) was dissolved in pyridine (60 mL), and benzoyl chloride (2.40 mL, 20.6 mmol) was added at 0 °C. After 1 h, water (2 mL) was added and the mixture was stirred for 10 min, then diluted with dichloromethane, washed (saturated aqueous $NaHCO_3$ and saturated aqueous NaCl), dried ($Na_2SO_4$), and concentrated. The residue was dissolved in aqueous acetic acid (100 mL, 80%), and the mixture was kept at 80 °C for 100 min and then concentrated and coconcentrated with toluene. The residue was chromatographed ($SiO_2$, heptane/EtOAc, 3:2) to give **34** (6.69 g, 98%). An analytical sample was recrystallized from ether−heptane. **34**: $[\alpha]^{25}_D$ +38° (*c* 1.0, $CHCl_3$); mp 55−57 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 7.42−8.05 (m, 5 H, PhH), 4.63 (dd, 1 H, $J$ = 6.9, 11.4 Hz, H-6a), 4.50 (dd, 1 H, $J$ = 6.6, 11.4 Hz, H-6b), 4.32 (d, 1 H, $J$ = 7.6 Hz, H-1), 4.01 (m, 1 H, $OCH_2$), 3.93 (dd, 1 H, $J$ = 1.0, 3.2 Hz, H-4), 3.77 (m, 1 H, H-5), 3.64 (m, 1 H, $OCH_2$), 3.55 (dd, 1 H, $J$ = 7.7, 10.1 Hz, H-2), 3.47 (dd, 1 H, $J$ = 3.2, 10.1 Hz, H-3), 1.05 (m, 2 H, $CH_2Si$), 0.01 (s, 9 H, $SiMe_3$); *m/z* calcd for $C_{18}H_{30}O_6N_3Si$ (M + $NH_4$) 427.2013, found 427.2012.

**2-(Trimethylsilyl)ethyl 4-*O*-Acetyl-2-azido-6-*O*-benzoyl-2-deoxy-3-*O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylate)-β-D-galactopyranoside (35).** A mixture of **34** (100 mg, 0.244 mmol), **8** (218 mg, 0.366 mmol), powdered molecular sieves (300 mg, 3 Å), dry acetonitrile (4.2 mL), and dry dichloromethane (3.2 mL) was stirred under argon for 2 h. The mixture was protected from light, silver triflate (95 mg, 0.371 mmol) in dry acetonitrile (0.6 mL) was added, and the mixture was cooled to −72 °C. Methanesulfenyl bromide (133 μL, 2.75 M in $ClCH_2CH_2Cl$, 0.366 mmol) was added in four portions. After 2 h, diisopropylamine (200 μL) was added and the stirring was continued for 1 h at −72 °C. The mixture was diluted with dichloromethane, filtered (Celite), washed (saturated aqueous $NaHCO_3$ and water), dried ($Na_2SO_4$), and concentrated. The residue was chromatographed to give the β anomer corresponding to **35** (13 mg, 6%). The remaining fractions were pooled and concentrated, and the residue was acetylated with pyridine−acetic anhydride (20 mL, 1:1) and DMAP (catalytic amount) for 5 h. The solvent was removed, and the residue was chromatographed ($SiO_2$, toluene/EtOH, 20:1) to give pure **35** (139 mg, 61%): $[\alpha]^{25}_D$ −45° (*c* 1.0, $CHCl_3$); $^1H$ NMR ($CDCl_3$) $\delta$ 7.40−8.05 (m, 5 H, PhH), 5.61 (m, 1 H, H-8′), 5.35 (dd, 1 H, $J$ = 2.0, 9.3 Hz, H-7′), 5.06 (d, 1 H, $J$ = 10.0 Hz, NH), 4.98 (m, 2 H, H-4,4′), 4.62 (dd, 1 H, $J$ = 3.4, 10.1 Hz, H-3), 4.37 (d, 1 H, $J$ = 8.1 Hz, H-1), 4.31 (dd, 1 H, $J$ = 2.5, 12.7 Hz, H-9′a), 4.24 (dd, 1 H, $J$ = 6.2, 11.4 Hz, H-6a), 4.10 (dd, 1 H, $J$ = 4.8, 12.7 Hz, H-9′b), 3.81 (s, 3 H, OMe), 3.64 (m, 1 H, $OCH_2$), 2.64 (dd, 1 H, $J$ = 4.6, 12.5 Hz, H-3′eq), 2.02−2.13 (9 s, 3 H each, OAc, NHAc), 1.95 (t, 1 H, $J$ = 12.5 Hz, H-3′ax), 1.06 (m, 2 H, $CH_2Si$), 0.01 (s, 9 H, $SiMe_3$); $^{13}C$ NMR ($CDCl_3$) $\delta$ 170.8, 170.5, 170.4, 170.2, 170.1, 170.0, 167.9 ($J_{C1'-H3'ax}$ = 3.7 Hz[27]), 165.8, 133.1, 129.7, 129.6, 128.3, 100.5, 96.7, 72.5, 71.9, 70.5, 69.0, 68.0, 67.6, 67.1, 67.0, 62.4, 62.2, 62.0, 53.0, 49.2, 37.0, 23.2, 21.3, 20.8, 20.7, 20.6, 18.1, −1.5. Anal. Calcd for $C_{40}H_{56}O_{19}N_4Si$: C, 51.9; H, 6.1; N, 6.1. Found: C, 51.9; H, 6.1; N, 5.8.

**2-(Trimethylsilyl)ethyl 2-Amino-2-deoxy-3-*O*-(5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosyloyl-1′→2-lactam)-β-D-galactopyranoside (38).** Methanolic sodium methoxide (2 M, 75 μL) was added to a solution of **35** (150 mg, 0.162 mmol) in dry methanol (10 mL) under argon. The mixture was stirred for 4 h, then neutralized with Duolite C-26 ($H^+$) resin, and concentrated to give a mixture (2:1) of **36** and **37** (99 mg, 100%). A portion of the mixture (31.2 mg, 0.051 mmol) was dissolved in pyridine (3 mL), triethylamine (1.5 mL), and methanol (1.5 mL), and hydrogen sulfide was bubbled through the solution for 1 h at 0 °C. The mixture was kept under $H_2S$ at room temperature overnight. $N_2$ was bubbled through the mixture for 1 h, and then it was concentrated and coconcentrated with toluene. The residue was dissolved in dry methanol (1.2 mL), methanolic sodium methoxide (2 M, 8 μL) was added under argon, and the mixture was stirred for 150 min, then neutralized with Duolite C-26 ($H^+$) resin, and concentrated. The residue was chromatographed ($SiO_2$, $CH_2Cl_2$/MeOH/$H_2O$, 65:35:5) to give **38** (27 mg, 96%): $[\alpha]^{25}_D$ −13° (*c* 0.98, $H_2O$); $^1H$ NMR ($D_2O$) $\delta$ 4.58 (d, 1 H, $J$ = 8.1 Hz, H-1), 4.34 (ddd, 1 H, $J$ = 5.4, 10.2, 11.1 Hz, H-4′), 4.04 (d, 1 H, $J$ = 2.8 Hz, H-4), 3.98 (dd, 1 H, $J$ = 2.8, 10.8 Hz, H-3), 3.88 (t, 1 H, $J$ = 10.3 Hz, H-5′), 3.70 (ddd, 1 H, $J$ = 2.7, 5.3, 11.4 Hz, H-8′), 3.68 (dd, 1 H, $J$ = 1.1, 10.5 Hz, H-6′), 3.62 (dd, 1 H, $J$ = 5.4, 11.9 Hz, H-9′a), 3.52 (dd, 1 H, $J$ = 1.1, 9.5 Hz, H-7′), 2.57 (dd, 1 H, $J$ = 5.4, 13.3 Hz, H-3′eq), 2.02 (s, 3 H, NHAc), 1.68 (dd, 1 H, $J$ = 11.1, 13.3 Hz, H-3′ax), 1.03 (m, 2 H, $CH_2$-Si), 0.01 (s, 9 H, $SiMe_3$); *m/z* calcd for $C_{22}H_{40}O_{12}N_2Si$ (M + H) 553.2429, found 553.2444.

**2-(Trimethylsilyl)ethyl 2-Azido-2-deoxy-3-*O*-(5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonic acid)-β-D-galactopyranoside (39).** Methanolic sodium methoxide (2 M, 75 μL) was added to a solution of **35** (150 mg, 0.162 mmol) in dry methanol (10 mL) under argon, and the mixture was stirred for 4 h, then neutralized with Duolite C-26 ($H^+$) resin, and concentrated to give a mixture (2:1) of **36** and **37** (99 mg, 100%). A portion of the mixture (20 mg, 0.033 mmol) was dissolved in water (1 mL), and sodium hydroxide (2 M, 49 μL) was added. After 90 min, the mixture was neutralized with Duolite C-26 ($H^+$) resin, filtered, and concentrated. The residue was chromatographed ($SiO_2$, $CH_2Cl_2$/MeOH/$H_2O$, 65:35:5 + 0.1% acetic acid) to give **39** (19 mg, 98%): $[\alpha]^{22}_D$ −24° (*c* 1.0, $H_2O$); $^1H$ NMR ($D_2O$) $\delta$ 4.41 (d, 1 H, $J$ = 8.3 Hz, H-1), 4.18 (dd, 1 H, $J$ = 3.1, 10.4 Hz, H-3), 4.02 (m, 1 H, $OCH_2$), 3.50 (dd, 1 H, $J$ = 8.4, 10.3 Hz, H-2), 2.77 (dd, 1 H, $J$ = 4.6, 12.6 Hz, H-3′eq), 2.01 (s, 3 H, NHAc), 1.82 (t, 1 H, $J$ = 12.1 Hz, H-3′ax), 1.01 (m, 2 H, $CH_2Si$), 0.00 (s, 9 H, $SiMe_3$); *m/z* calcd for $C_{22}H_{40}O_{13}N_4Si$ (M + Na) 619.2259, found 619.2241.

**2-(Trimethylsilyl)ethyl 2-Amino-2-deoxy-3-*O*-(5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonic acid)-β-D-galactopyranoside (40).** Hydrogen sulfide was bubbled through a mixture of **39** (10.6 mg, 0.018 mmol), pyridine (2 mL), triethylamine (1 mL), and methanol (1 mL) for 1 h at 0 °C. The mixture was kept under $H_2S$ at room temperature 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 chromatographed ($SiO_2$-C18, MeOH/$H_2O$ 1:9→1:1) to give **40** (5.4 mg, 53%): $[\alpha]^{22}_D$ −21° (*c* 0.37, MeOH); $^1H$ NMR ($D_2O$) $\delta$ 4.42 (d, 1 H, $J$ = 8.3 Hz, H-1), 4.05 (dd, 1 H, $J$ = 3.1, 10.6 Hz, H-3), 4.03 (m, 1 H, $OCH_2$), 3.91 (d, 1 H, $J$ = 3.2 Hz, H-4), 3.89 (m, 1 H, H-8′), 3.85 (dd, 1 H, $J$ = 2.6, 12.0 Hz, H-9′a), 3.83 (t, 1 H, $J$ = 10.1 Hz, H-5′), 3.75 (m, 1 H, $OCH_2$), 3.68 (m, 1 H, H-4′), 3.63 (dd, 1 H, $J$ = 6.3, 12.0 Hz, H-9′b), 2.93 (dd, 1 H, $J$ = 8.4, 10.4 Hz, H-2), 2.76 (dd, 1 H, $J$ = 4.6, 12.4 Hz, H-3′eq), 1.75 (t, 1 H, $J$ = 12.1 Hz, H-3′ax), 1.00 (m, 2 H, $CH_2Si$), 0.00 (s, 9 H, $SiMe_3$); $^{13}C$ NMR ($D_2O$) $\delta$ 176.6, 175.2 (NHAc, CO), 104.0 (C-2′), 101.2 (C-1), 76.5 (C-5), 76.1 (C-3), 74.4 (C-6′), 73.2 (C-8′), 70.0 ($OCH_2$), 69.9 (C-4′), 69.7 (C-7′), 67.8 (C-4), 64.3 (C-9′), 62.6 (C-6), 53.3 (C-5′), 53.0 (C-2), 41.6 (C-3′), 23.6 ($CH_3$), 19.2 ($CH_2Si$), −0.9 ($SiMe_3$); *m/z* calcd for $C_{22}H_{42}O_{13}N_2Si$ (M + H) 571.2534, found 571.2535.

**2-(Trimethylsilyl)ethyl 2,3,6-Tri-*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-glucopyranoside (41).** Compound **12** (106 mg, 0.148 mmol) was acetylated with acetic anhydride (5 mL), pyridine (5 mL), and DMAP (catalytic amount) overnight. The mixture was concentrated and coconcentrated with toluene, and the residue was chromatographed ($SiO_2$, toluene/EtOH, 5:1) to give **41** (146 mg, 90%): $[\alpha]^{25}_D$ −32° (*c* 0.80, $CHCl_3$); $^1H$ NMR ($CHCl_3$) δ 5.46 (dt, 1 H, *J* = 5.5, 10.8 Hz, H-4″), 5.38 (brs, 1 H, H-4′), 5.29 (dt, 1 H, *J* = 3.0, 7.0 Hz, H-8″), 5.23 (t, 1 H, *J* = 9.1 Hz, H-3), 5.21 (dd, 1 H, *J* = 1.8, 7.0 Hz, H-7″), 4.86 (dd, 1 H, *J* = 7.9, 9.3 Hz, H-2), 4.56 (d, 1 H, *J* = 7.9 Hz, H-1), 4.40 (d, 1 H, *J* = 8.0 Hz, H-1′), 4.25 (dd, 1 H, *J* = 3.0, 12.0 Hz, H-9″a), 4.18 (dd, 1 H, *J* = 6.1, 11.0 Hz, H-6′a), 4.16 (t, 1 H, *J* = 10.2 Hz, H-5″), 4.11 (dd, 1 H, *J* = 7.2, 11.2 Hz, H-6′b), 4.05 (dd, 1 H, *J* = 7.0, 12.2 Hz, H-9″b), 3.88 (t, 1 H, *J* = 9.4 Hz, H-4), 3.53 (m, 1 H, $OCH_2$), 2.41 (dd, 1 H, *J* = 5.5, 13.2 Hz, H-3″eq), 2.21−1.90 (10 s, 3 H each, OAc, NHAc), 1.80 (dd, 1 H, *J* = 11.2, 13.2 Hz, H-3″ax), 0.92 (m, 2 H, $CH_2Si$), 0.01 (s, 9 H, $SiMe_3$); $^{13}C$ NMR ($CDCl_3$) δ 100.6 (C-1′), 99.7 (C-1), 97.8 (C-2″), 73.4 (C-3), 72.2 (C-2), 70.2 (C-4″), 69.2 (C-8″), 67.4 (C-7″), 65.0 (C-4′), 1.4 ($SiMe_3$); *m/z* calcd for (M + H) 1093.3908, found 1093.3920. Anal. Calcd for $C_{46}H_{68}O_{26}N_2Si$: C, 50.5; H, 6.3; N, 2.6. Found: C, 50.8; H, 6.4; N, 2.5.

**2,3,6-Tri-*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-glucopyranosyl Chloride (42).** Compound **41** (167 mg, 0.153 mmol) was dissolved in dry chloroform (4 mL) under nitrogen. Zinc chloride (fused, 20 mg, 0.144 mmol) was added followed by dichloromethyl methyl ether (105 μL, 1.18 mmol). The mixture was stirred at room temperature overnight, then diluted with chloroform, washed (saturated aqueous $NaHCO_3$ and water), dried ($Na_2SO_4$), and concentrated to give **42** (156 mg, 100%). The crude product was used without further purification in the preparation of compound **43**.

**2-Bromoethyl 2,3,6-Tri-*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-glucopyranoside (43).** A solution of **42** (156 mg, 0.154 mmol) in dry dichloromethane (1 mL) was added to a stirred, cooled (−28 °C) mixture of bromoethanol (100 μL, 1.4 mmol), silver trifluoromethanesulfonate (52 mg, 0.202 mmol), and molecular sieves (0.1 g, 3 Å) in dry dichloromethane (1 mL). The mixture was kept under nitrogen and protected from light. After 4 h, the mixture was allowed to attain room temperature, the stirring was continued overnight, and the mixture was filtered (Celite), washed (saturated aqueous $NaHCO_3$ and water), dried ($Na_2SO_4$), and concentrated. The residue was chromatographed ($SiO_2$, toluene/EtOH, 10:1) to give **43** (90 mg, 54%) as an inseparable mixture (α/β 1:6): $^1H$ NMR ($CDCl_3$) δ 5.04 (d, 1 H, *J* = 4.3 Hz, H-1α), 4.90 (dd, 1 H, *J* = 8.0, 9.4 Hz, H-2), 4.69 (d, 1 H, *J* = 8.0 Hz, H-1β), 3.42 (brt, 2 H, *J* = 5.8 Hz, $CH_2Br$), 2.39 (dd, 1 H, *J* = 5.6, 13.2 Hz, H-3″eq), 2.21−1.89 (10 s, 3 H each, OAc, NHAc); *m/z* calcd for $C_{43}H_{59}O_{26}N_2Br$ (M + H) 1099.2617, found 1099.2600.

**2-[[2-(Methoxycarbonyl)ethyl]thio]ethyl 2,3,6-Tri-*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-glucopyranoside (44).** Methyl mercaptopropionate (37 μL, 0.33 mmol) was added to a mixture of **43** (90 mg, 0.082 mmol) and cesium carbonate (32 mg, 0.100 mmol) in dry dimethylformamide (1.5 mL) under nitrogen. After 2.5 h, the mixture was diluted with dichloromethane, washed (water), dried ($Na_2SO_4$), and concentrated. The residue was chromatographed ($SiO_2$, toluene/EtOH, 15:1→10:1) to give **44** (77 mg, 82%) as an inseparable mixture (α/β 1:6). **44β**: $^1H$ NMR ($CDCl_3$) δ 4.88 (dd, 1 H, *J* = 8.0, 9.5 Hz, H-2), 4.62 (d, 1 H, *J* = 8.0 Hz, H-1), 3.69 (s, 3H, OMe), 2.78 (brt, 2 H, *J* = 7.3 Hz, $SCH_2$), 2.69 (brt, 2 H, *J* = 7.0 Hz, $CH_2S$), 2.58 (brt, 2 H, *J* = 8.6 Hz, $CH_2CO$), 2.38 (dd, 1 H, *J* = 5.8, 13.4 Hz, H-3″eq), 2.19−1.89 (10 s, 3 H each, OAc, NHAc), 1.74 (t, 1 H, *J* = 12.4 Hz, H-3″ax); *m/z* calcd for $C_{47}H_{66}O_{28}N_2S$ (M + H) 1139.3601, found 1139.3610.

**2-[[2-(Methoxycarbonyl)ethyl]thio]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-glucopyranoside (45).** Methanolic sodium methoxide (2 M, 20 μL) was added to a solution of **44** (49 mg, 0.043 mmol) in dry methanol (2 mL), and the mixture was stirred for 4 h, then neutralized with Duolite C-26 ($H^+$) resin, and concentrated. The residue was chromatographed ($SiO_2$, $CH_2Cl_2$/MeOH/$H_2O$, 10:5:1) to give **45** (28 mg, 86%) as an inseparable mixture (α/β 1:6): $^1H$ NMR ($D_2O$) δ 5.92 (d, 1 H, *J* = 4.1 Hz, H-1α), 4.70 (d, 1 H, *J* = 8.1 Hz, H-1′), 4.49 (d, 1 H, *J* = 8.1 Hz, H-1β), 3.70 (s, 3H, OMe), 3.50 (brd, 1 H, *J* = 9.3 Hz, H-7″), 3.31 (t, 1 H, *J* = 7.6 Hz, H-2), 2.58 (dd, 1 H, *J* = 5.4 13.2 Hz, H-3″eq), 2.02 (s, 3 H, NHAc), 1.68 (dd, 1 H, *J* = 10.3, 13.2 Hz, H-3″ax); $^{13}C$ NMR ($D_2O$) δ 175.9, 169.6, 103.1, 100.7, 98.2, 78.7, 78.7, 77.0, 75.0, 74.6, 73.8, 73.2, 71.0, 69.9, 68.6, 66.2, 64.1, 61.8, 61.5, 53.1, 52.6, 51.6, 40.1, 35.0, 31.6, 27.3, 22.9, 12.9, 12.9; *m/z* calcd for $C_{29}H_{48}O_{19}N_2S$ (M + H) 761.2650, found 761.2664.

**$GM_3$-Lactam−BSA Conjugate (46).** A solution of **45** (22 mg, 0.029 mmol) and hydrazine hydrate (85%, 0.25 mL) in ethanol (2 mL) was stirred overnight. The mixture was concentrated, and the residue was lyophilized and dissolved in dimethyl sulfoxide (0.5 mL). Hydrogen chloride in dioxane (4 M, 53 μL) and a solution of *tert*-butyl nitrite (9 μL, 0.075 mmol) in dimethyl sulfoxide (0.05 mL) were added. The mixture was stirred at room temperature for 30 min, and a solution of sulfamic acid (5 mg, 0.055 mmol) in dimethyl sulfoxide (0.05 mL) was added. After 15 min, the mixture was added dropwise, with stirring, to a solution of BSA (27 mg, 0.00041 mmol) in sodium tetraborate−potassium hydrogen carbonate buffer (1 mL, 0.08 M $Na_2B_4O_7$ and 0.35 M $KHCO_3$) at 4 °C. The pH was maintained at 8.5−9.5 by addition of 1 M sodium hydroxide. The mixture was stirred at 4−15 °C for 1 h and at room temperature overnight, then dialyzed ($H_2O$, 96 h), and lyophilized to give **46**. The degree of binding (number of hapten molecules per molecule of protein) was 24, as determined by differential sulfur combustion analysis.[18]

**1,2,3,6-Tetra-*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-glucopyranose (47).** To a solution of **41** (25.5 mg, 0.023 mmol) in dry dichloromethane (1 mL) was added acetic anhydride (99 μL, 1.05 mmol) and boron trifluoride etherate (29 μL, 0.233 mmol) under argon. After 1 h, the mixture was diluted with dichloromethane, washed (saturated aqueous $NaHCO_3$), dried ($Na_2SO_4$), and concentrated to give crude **47** (24 mg, 100%, β/α 91:9): $^1H$ NMR ($CDCl_3$) δ 6.25 (d, 1 H, *J* = 4.1 Hz, H-1α), 5.82 (d, 1 H, *J* = 8.5 Hz, H-1β), 5.29 (m, 1 H, H-8″), 5.03 (dd, 1 H, *J* = 8.3, 9.4 Hz, H-2), 2.28 (dd, 1 H, *J* = 5.2, 13.2 Hz, H-3″eq), 2.22−1.89 (11 s, 3 H each, OAc, NHAc), 1.76 (dd, 1 H, *J* = 11.2, 13.3 Hz, H-3″ax).

**2-(Methoxycarbonyl)ethyl 2,3,6-Tri-*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]-1-thio-β-D-glucopyranoside (48).** To a solution of crude **47** (24 mg, 0.023 mmol) in dry dichloromethane (0.5 mL) was added methyl mercaptopropionate (12.6 μL, 0.116 mmol) and boron trifluoride etherate (29 μL, 0.233 mmol) under argon. After 1.3 h, the mixture was diluted with dichloromethane, washed (saturated aqueous $NaHCO_3$), dried ($Na_2SO_4$), and concentrated. The residue was chromatographed ($SiO_2$, $CH_2Cl_2$/EtOH, 20:1) to give **48** (21.7 mg, 85%) containing traces of **47α** and **48α**: $^1H$ NMR ($CDCl_3$) δ 4.94 (t, 1 H, *J* = 9.8 Hz, H-2), 4.67 (d, 1 H, *J* = 10.0 Hz, H-1), 4.13 (d, 1 H, *J* = 8.0 Hz, H-1′), 3.68 (s, 3 H, OMe), 2.90 (m, 2 H, $SCH_2$), 2.72 (t, 2 H, *J* = 7.0 Hz, $CH_2COO$), 2.38 (dd, 1 H, *J* = 6.0, 13.8 Hz, H-3″eq), 2.20−1.89 (10 s, 3 H each, OAc, NHAc); *m/z* calcd for $C_{45}H_{62}O_{27}N_2S$ (M + H) 1095.3339, found 1095.3319.

**2-(Methoxycarbonyl)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]-1-thio-β-D-glucopyranoside (49).** Methanolic sodium methoxide (2 M, 7 μL) was added to a solution of **48** (16.2 mg, 0.015 mmol) in dry methanol (2 mL) under argon, and the mixture was stirred for 2 h 40 min, then neutralized with Duolite C-26 ($H^+$) resin, and concentrated. The residue was chromatographed ($SiO_2$, $CH_2Cl_2$/MeOH/$H_2O$, 65:35:5) to give **49** (7.6 mg, 74%) as an inseparable mixture (α/β 4:96): $^1H$ NMR ($D_2O$) δ 5.44 (d, 1 H, *J* = 5.6 Hz, H-1α), 4.70 (d, 1 H, *J* = 8.1 Hz, H-1′), 4.55 (d, 1 H, *J* = 10.0 Hz, H-1β), 4.32 (dt, 1 H, *J* = 5.2, 10.3 Hz, H-4″), 3.70 (s, 3H, OMe), 3.50 (brd, 1 H, *J* = 9.3 Hz, H-7″), 3.33 (t, 1 H, *J* = 8.9, 9.9 Hz, H-2), 2.97 (m, 2 H, $CH_2S$), 2.77 (t, 2 H, *J* = 7.0 Hz, $CH_2CO$), 2.58 (dd, 1 H, *J* = 5.4, 13.4 Hz, H-3″eq), 2.02 (s, 3 H, NHAc), 1.68 (dd, 1 H, *J*

= 11.1, 13.3 Hz, H-3″ax); *m/z* calcd for $C_{27}H_{44}O_{18}N_2S$ (M + H) 717.2398, found 717.2371.

**2,3,6-Tri-*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]-αβ-D-glucopyranose (50).** Compound **41** (59 mg, 0.054 mmol) was dissolved in dichloromethane (270 μL), trifluoroacetic acid (540 μL) was added, and the mixture was stirred for 1.3 h. *n*-Propyl acetate (1.6 mL) and toluene (3.2 mL) were added, and the mixture was concentrated to give **50** (60 mg, 100%). The crude product was used without further purification in the preparation of **51**.

**2,3,6-Tri-*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]-αβ-D-glucopyranosyl Trichloroacetimidate (51).** DBU (6.4 μL, 0.043 mmol) was added to a solution of **50** (60 mg, 0.054 mmol) and trichloroacetonitrile (170 μL, 1.7 mmol) in dry dichloromethane (0.8 mL) at 0 °C under argon. After 50 min, the mixture was concentrated and the residue was chromatographed ($SiO_2$, toluene/EtOH, 5:1) to give **51** (59 mg, 96%) as an α/β mixture (3:1): $^1$H NMR ($CDCl_3$) δ 8.71 (s, 1 H, NHα), 8.60 (s, 1 H, NHβ), 6.48 (d, 1 H, *J* = 3.7 Hz, H-1α), 5.90 (d, 1 H, *J* = 7.8 Hz, H-1β), 5.58 (d, 1 H, *J* = 9.8 Hz, NH), 5.48 (dt, 1 H, *J* = 5.2, 10.7 Hz, H-4″), 5.26 (dd, 1 H, *J* = 1.8, 7.2 Hz, H-7″), 5.19 (m, 1 H, H-8″), 5.08 (dd, 1 H, *J* = 3.7, 10.0 Hz, H-2α), 3.76 (dd, 1 H, *J* = 1.8, 10.4 Hz, H-6″), 2.39 (dd, 1 H, *J* = 5.6, 13.4 Hz, H-3″eq), 2.35−1.88 (10 s, 3 H each, OAc, NHAc), 1.78 (dd, 1 H, *J* = 11.5, 13.2 Hz, H-3″ax). Anal. Calcd for $C_{43}H_{56}O_{26}N_3Cl_3$: C, 45.4; H, 5.0; N, 3.7. Found: C, 45.0; H, 4.9; N, 3.6.

**(2*S*,3*R*,4*E*)-2-Azido-3-(benzoyloxy)octadec-4-enyl 2,3,6-Tri-*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-glucopyranoside (53).** Boron trifluoride etherate (46 μL, 0.365 mmol) was added to a mixture of **51** (45.1 mg, 0.037 mmol), the azidosphingosine derivative **52** (31.5 mg, 0.073 mmol), and powdered, acid-washed molecular sieves (0.1 g, AW 300) in dry dichloromethane (1.1 mL) at −33 °C under argon. After 1 h 35 min, triethylamine (100 μL) was added, and the mixture was immediately chromatographed ($SiO_2$, $CH_2Cl_2$/EtOH, 35:1) to give **53** and the corresponding orthoester **54** as an inseparable mixture (22.8 mg, **53**/**54**, 96:4). The mixture was dissolved in aqueous acetic acid (5 mL, 90%). After 1.5 h, toluene was added, and the mixture was concentrated. The residue was chromatographed ($SiO_2$, $CH_2Cl_2$/EtOH, 20:1) to give pure **53** (22.3 mg, 44%): $[\alpha]^{25}_D$ −37° (*c* 0.90, $CHCl_3$); $^1$H NMR ($CDCl_3$) δ (assignments of aglycon protons are shown in italic type) 8.06−7.32 (m, 5 H, PhH), 5.92 (dt, 1 H, *J* = 6.8, 15.0 Hz, *H-5*), 5.71 (d, 1 H, *J* = 6.4 Hz, NH), 5.60 (dd, 1 H, *J* = 4.2, 8.0 Hz, *H-3*), 5.55 (m, 1 H, *H-4*), 5.42 (dt, 1 H, *J* = 5.5, 10.7 Hz, H-4″), 5.37 (brs, 1 H, H-4′), 5.29 (dt, 1 H, *J* = 3.1, 6.9 Hz, H-8″), 5.26 (t, 1 H, *J* = 8.8 Hz, H-3), 4.92 (dd, 1 H, *J* = 7.6, 8.8 Hz, H-2), 4.64 (d, 1 H, *J* = 7.5 Hz, H-1), 4.39 (d, 1 H, *J* = 7.1 Hz, H-1′), 4.24 (dd, 1 H, *J* = 3.1, 12.1 Hz, H-9″a), 4.17 (dd, 1 H, *J* = 6.3, 11.2 Hz, H-6′a), 4.14 (t, 1 H, *J* = 10.3 Hz, H-5″), 4.12 (dd, 1 H, *J* = 7.1, 11.3 Hz, H-6′a), 4.04 (dd, 1 H, *J* = 6.9, 12.1 Hz, H-9″b), 3.87 (dd, 1 H, *J* = 6.8, 10.0 Hz, *H-1*), 3.77 (m, 1 H, H-5), 3.69 (dd, 1 H, *J* = 1.7, 10.4 Hz, H-6″), 3.59 (dd, 1 H, *J* = 5.3, 10.0 Hz, *H-1*), 2.41 (dd, 1 H, *J* = 5.6, 13.3 Hz, H-3″eq), 2.21−1.89 (10 s, 3 H each, OAc, NHAc), 1.78 (dd, 1 H, *J* = 11.3, 13.2 Hz, H-3″ax), 1.40−1.20 (m, 22 H, $CH_2$), 0.88 (t, 3 H, *J* = 7.0 Hz, $CH_3$). Anal. Calcd for $C_{66}H_{93}O_{28}N_5$: C, 56.4; H, 6.7; N, 5.0. Found: C, 56.4; H, 6.4; N, 4.8.

**(2*S*,3*R*,4*E*)-3-(Benzoyloxy)-2-(octadecanamido)octadec-4-enyl 2,3,6-Tri-*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-glucopyranoside (55).** Hydrogen sulfide was bubbled through a mixture of **53** (22.3 mg, 0.016 mmol) and aqueous pyridine (5 mL, 83%) for 1 h 45 min at 0 °C. This mixture was kept under $H_2S$ at room temperature 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 dichloromethane (0.5 mL) and octadecanoic acid (13.2 mg, 0.053 mmol), and 1-ethyl-3-[3-(dimethylamino)propyl]carbodiimide hydrochloride (EDC) (9.5 mg, 0.053 mmol) was added. After 1 h 50 min, the mixture was chromatographed ($SiO_2$, $CH_2Cl_2$/EtOH, 25:1) to give **55** (23.9 mg, 91%): $[\alpha]^{25}_D$ −20° (*c* 0.79, $CHCl_3$); $^1$H NMR ($CDCl_3$) δ (assignments of aglycon protons are shown in italic type) 8.06−7.45 (m, 5 H, PhH), 5.88 (dt, 1 H, *J* = 6.8, 15.1 Hz, *H-5*), 5.71 (d, 1 H, *J* = 9.3 Hz, NH), 5.53 (brt, 1 H, *J* = 7.3 Hz, *H-3*), 5.46 (m, 1 H, *H-4*), 5.39 (m, 1 H, H-4″), 5.37 (brs, 1 H, H-4′), 5.27 (dt, 1 H, *J* = 2.8, 6.7 Hz, H-8″), 5.21 (dd, 1 H, *J* = 1.7, 6.9 Hz, H-7″), 5.18 (t, 1 H, *J* = 9.2 Hz, H-3), 4.88 (dd, 1 H, *J* = 7.8, 9.4 Hz, H-2), 4.55 (d, 1 H, *J* = 7.8 Hz, H-1), 4.32 (d, 1 H, *J* = 7.3 Hz, H-1′), 4.22 (dd, 1 H, *J* = 3.0, 12.1 Hz, H-9″a), 3.83 (t, 1 H, *J* = 9.4 Hz, H-4), 3.59 (dd, 1 H, *J* = 4.5, 10.0 Hz, *H-1*), 2.35 (dd, 1 H, *J* = 5.6, 13.3 Hz, H-3″eq), 2.21−1.89 (10 s, 3 H each, OAc, NHAc), 1.74 (dd, 1 H, *J* = 11.5, 13.0 Hz, H-3″ax), 1.58 (m, 2 H, *H-3a*), 1.30−1.20 (m, $CH_2$), 0.88 (m, 6 H, $CH_3$). Anal. Calcd for $C_{84}H_{129}O_{29}N_3$: C, 61.3; H, 7.9; N, 2.5. Found: C, 63.0; H, 8.1; N, 2.3.

**(2*S*,3*R*,4*E*)-3-Hydroxy-2-(octadecanamido)octadec-4-enyl 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-glucopyranoside (56).** Methanolic sodium methoxide (2 M, 5 μL) was added to a solution of **55** (13.8 mg, 0.0084 mmol) in dry methanol (2 mL) and dry dichloromethane (0.2 mL), and the mixture was stirred overnight, then neutralized with Duolite C-26 ($H^+$) resin, and concentrated. The residue was chromatographed ($SiO_2$, $CH_2Cl_2$/MeOH, 4:1) to give **56** (9.0 mg, 92%): $[\alpha]^{25}_D$ − 6° (*c* 0.56, $CHCl_3$/MeOH, 1:1); $^1$H NMR ($D_2O$) δ (assignments of aglycon protons are shown in italic type) 5.66 (dt, 1 H, *J* = 6.8, 15.0 Hz, *H-5*), 5.42 (brd, 1 H, *J* = 7.7, 15.3 Hz, *H-4*), 4.56 (d, 1 H, *J* = 8.1 Hz, H-1′), 4.35 (dt, 1 H, *J* = 5.5, 10.4 Hz, H-4″), 4.26 (d, 1 H, *J* = 7.7 Hz, H-1), 4.04 (t, 1 H, *J* = 7.9 Hz, *H-1*), 3.97 (dd, 1 H, *J* = 8.1, 10.8 Hz, H-2′), 3.93 (brs, 1 H, H-4′), 3.56 (t, 1 H, *J* = 9.1 Hz, H-3), 3.52 (dd, 1 H, *J* = 3.2, 10.1 Hz, *H-1*), 2.48 (dd, 1 H, *J* = 5.4, 13.1 Hz, H-3″eq), 2.14 (t, 2 H, *J* = 7.6 Hz, *H-2′*), 2.00 (s, 3 H, NHAc), 1.62 (dd, 1 H, *J* = 11.0, 13.1 Hz, H-3″ax), 1.55 (m, 2 H, *H-3′*), 1.36−1.07 (m, 50 H, $CH_2$), 0.86 (t, 6 H, *J* = 6.9 Hz, $CH_3$); $^{13}$C NMR ($D_2O$) δ 174.1, 173.7, 167.3, 133.6, 128.9, 102.6, 100.4, 97.3, 78.8, 77.3, 75.8, 73.8, 73.7, 72.8, 72.1, 71.2, 69.5, 68.1, 67.9, 66.8, 65.3, 63.4, 60.8, 60.6, 52.6, 52.1, 49.4, 48.2−47.2, 39.6, 35.7, 31.7, 31.2, 29.0, 28.8, 28.7, 28.6, 25.3, 22.0, 21.3, 13.0; *m/z* calcd for $C_{59}H_{107}O_{19}N_3$ (M + Na) 1184.7396, found 1184.7401.

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

JA9501833