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Synthesis of neoglycolipids containing a mucin-type core unit

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Abstract

The unnatural glycolipids *O*-β-D-galactopyranosyl-(1→4)-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→3)-*O*-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-(1→1)-ceramide (**1**), *O*-β-D-galactopyranosyl-(1→4)-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→6)-*O*-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-(1→1)-ceramide (**2**), and *O*-β-D-galactopyranosyl-(1→4)-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→3)-*O*-[*O*-β-D-galactopyranosyl-(1→4)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→6)]-*O*-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-(1→1)-ceramide (**3**), and their β-(1→1)-linked isomers, were synthesized. The precursor oligosaccharides for **1**, **2**, and **3** were made by coupling *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-acetyl-2-deoxy-2-phthalimido-α,β-D-glucopyranosyl trichloroacetimidate with *tert*-butyldiphenylsilyl 2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranoside, *tert*-butyldiphenylsilyl 2-azido-3-*O*-benzoyl-2-deoxy-β-D-galactopyranoside, and *tert*-butyldiphenylsilyl *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-*O*-(3,6-di-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-2-azido-2-deoxy-β-D-galactopyranoside, respectively. These oligosaccharides were converted into their trichloroacetimidates, which were coupled with 3,2′-di-*O*-benzoyl ceramide. Deprotection of the coupling products gave the title compounds **1**, **2**, and **3**.

Keywords: Neoglycolipids, synthesis of; Mucin-type core unit in neoglycolipids

1. Introduction

The cores of mucin-type carbohydrate chains have unique structures that have not been found in glycolipids. Typical structures such as T [1,2], Tn [3,4], and sialosyl Tn [5] have been chemically identified and considered to be tumor-associated antigens. In contrast

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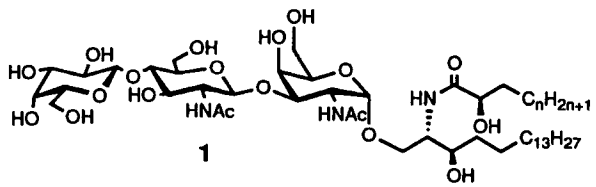

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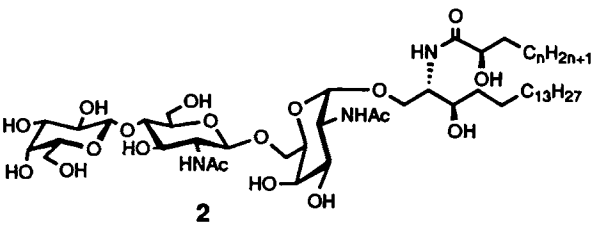

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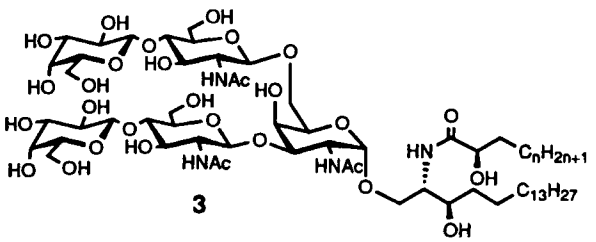

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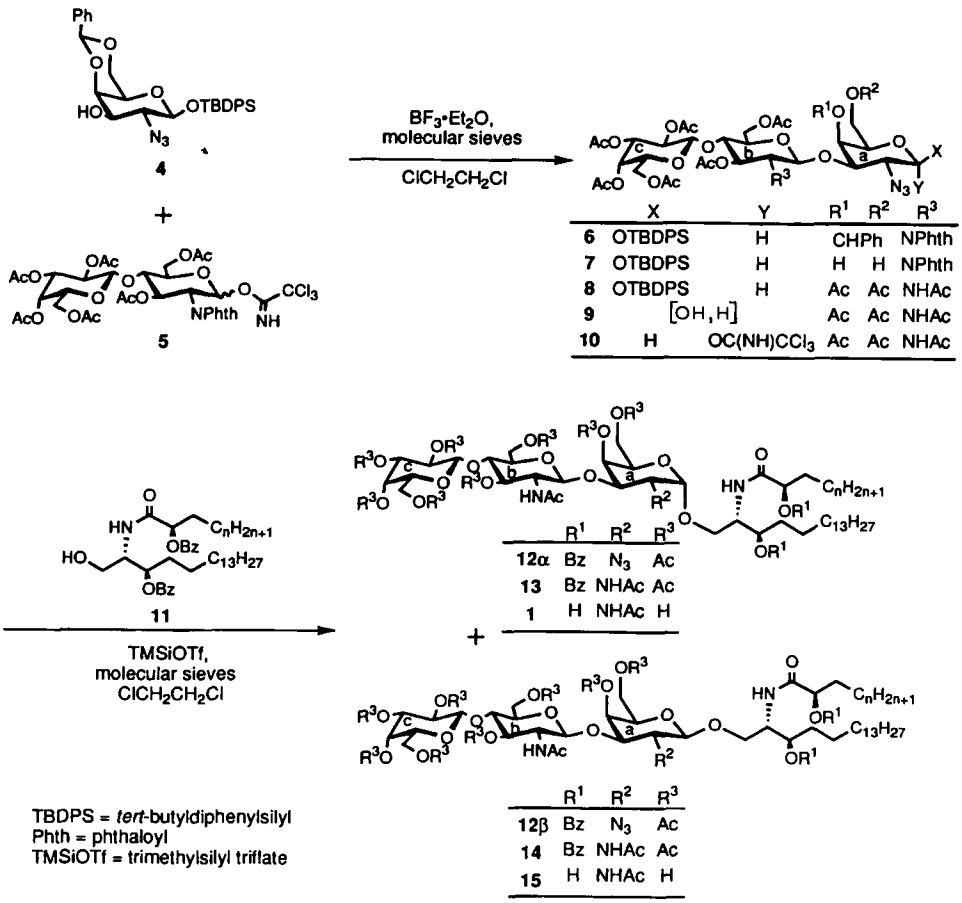
to the situation with the glycolipids, however, it is difficult to determine the distinct structure that is recognized by monoclonal antibodies against mucin-type antigens. To make the characterization of such monoclonal antibodies easier we have established a synthetic route to neoglycolipid [6] antigens such as **1**, **2**, and **3**, which were designed to carry a mucin-type core unit on a ceramide foundation [7]. The characteristic feature of a mucin-type core unit is an *N*-acetyl-α-D-galactosamine residue linked to L-serine or L-threonine. Since the configuration of the functionalized portion of the ceramides is the same as that of L-serine these neoglycolipids are expected to be good analogues of glycoproteins carrying mucin-type carbohydrate chains.

2. Results and discussion

Boron trifluoride etherate-promoted glycosylation [8] of the 2-azido-2-deoxy-D-galactose derivative [9] **4** with lactosamine donor **5** in 1,2-dichloroethane was performed (Scheme 1) in the presence of activated, powdered molecular sieves AW-300 at −20°C to give an 84% yield of **6**. Removal of the benzylidene group [10] of **6** with trifluoroacetic acid in dichloromethane gave an 80% yield of **7**, which was converted into **8** in two steps (*i*, hydrazine hydrate–ethanol [11]; *ii*, Ac_2O–pyridine, 95% overall). The TBDPS protective group was removed with tetrabutylammonium fluoride in the presence of acetic acid [12] to give an anomeric mixture **9**, which on treatment with 1,8-diazabicyclo[5.4.0]undec-



	X	Y	R^1	R^2	R^3
6	OTBDPS	H	CHPh		NPhth
7	OTBDPS	H	H	H	NPhth
8	OTBDPS	H	Ac	Ac	NHAc
9	[OH,H]		Ac	Ac	NHAc
10	H	$OC(NH)CCl_3$	Ac	Ac	NHAc

	R^1	R^2	R^3
12α	Bz	N_3	Ac
13	Bz	NHAc	Ac
1	H	NHAc	H

	R^1	R^2	R^3
12β	Bz	N_3	Ac
14	Bz	NHAc	Ac
15	H	NHAc	H

Scheme 1.

7-ene and trichloroacetonitrile afforded a trisaccharide imidate **10** (54% overall yield from **8**), as evidenced by ^{1}H NMR signals at δ 8.76 (s, 1 H, C=N*H*) and 6.44 (d, 1 H, *J* 3.4 Hz, H-1aα). To serve as a glycosyl acceptor the protected ceramide **11** was prepared in 4 steps from natural ceramide, type IV, (*i*, reduction of the double bond by hydrogenation; *ii*, tritylation; *iii*, benzoylation; and *iv*, removal of the trityl group). The resultant compound was purified by reversed-phase HPLC (Fig. 1), and resolved into 8 peaks. Each peak was analyzed by FD-MS and 500 MHz NMR. The results showed that the material was 3,2′-di-*O*-benzoylated ceramide in which the α-hydroxy fatty acid was mainly 24:0, with smaller amounts of 18:0, 22:0, 23:0, 25:0, 26:0, 27:0, and 28:0.

The glycosylation of the protected ceramide **11** with **10** was promoted with trimethylsilyl triflate in 1,2-dichloroethane at room temperature to give a mixture of **12**α and **12**β. As judged from the intensities of the NMR signals of H-1a (**12**α, δ_H 4.79, *J* 3.4 Hz; **12**β, 4.02, *J* 7.8 Hz), the ratio of the α and β glycosides was 2:3. The anomers were not separated in this stage; instead the azido groups of **12**α and **12**β were transformed into acetamido groups in two steps (*i*, $NaBH_4$–$NiCl_2$ in ethanol [13]; *ii*, Ac_2O–pyridine) to give compounds **13** and **14**. These were resolved by PLC on silica gel to give 17% of **13** and 24% of **14**, based

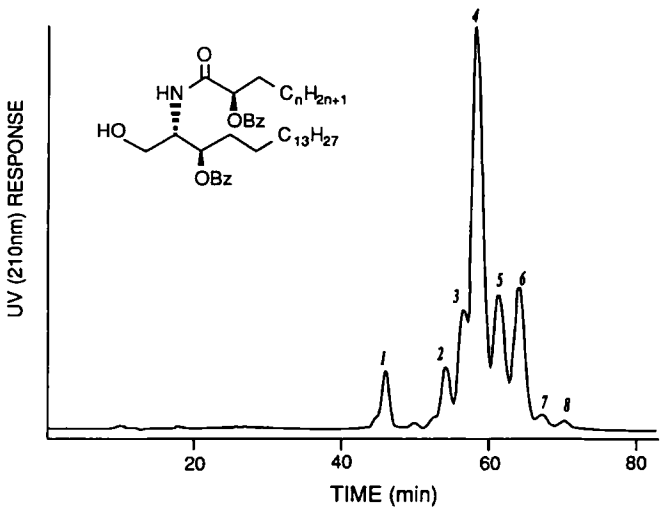


Fig. 1. Reversed-phase HPLC analysis of 3,2′-di-*O*-benzoylceramide (**11**) on TSK ODS-80TM. The solvent was 10:3 THF–H_2O, pumped at a flow rate of 5 mL/min; temperature 45°C; column, 30 cm × 21.5 mm i.d.; sample, 21.3 mg.

on **11**. Deprotection of both compounds **13** and **14** was carried out by treatment with sodium methoxide to give compound **1** and the β isomer **15**. The structures of **1** and **15** were assigned from the reaction sequence, and established by their NMR data (Fig. 2; pyridine-d_6–D_2O, 50°C): **1**, δ 5.36 (d, 1 H, J 3.9 Hz, H-1a); **15**, δ 5.16 (d, 1 H, J 8.3 Hz, H-1a).

For the synthesis of the trisaccharide glycolipid **2** (Scheme 2), the 4,6-unprotected 2-azido-2-deoxygalactose derivative **16**, obtained from **4** in two steps (*i*, benzoyl chloride–pyridine; *ii*, F_3CCO_2H–CH_2Cl_2), was used as the acceptor. The glycosylation by **5** was promoted with boron trifluoride etherate in the presence of activated, powdered molecular sieves AW-300 in 1,2-dichloroethane at room temperature to give a 29% yield of **17**. The 4-*O*-glycosylated regioisomer was not found in this reaction mixture. Conversion of **17** into

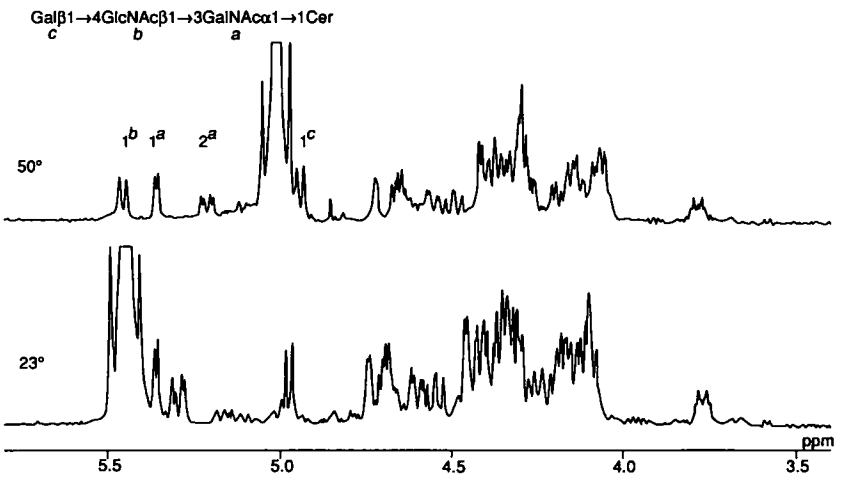
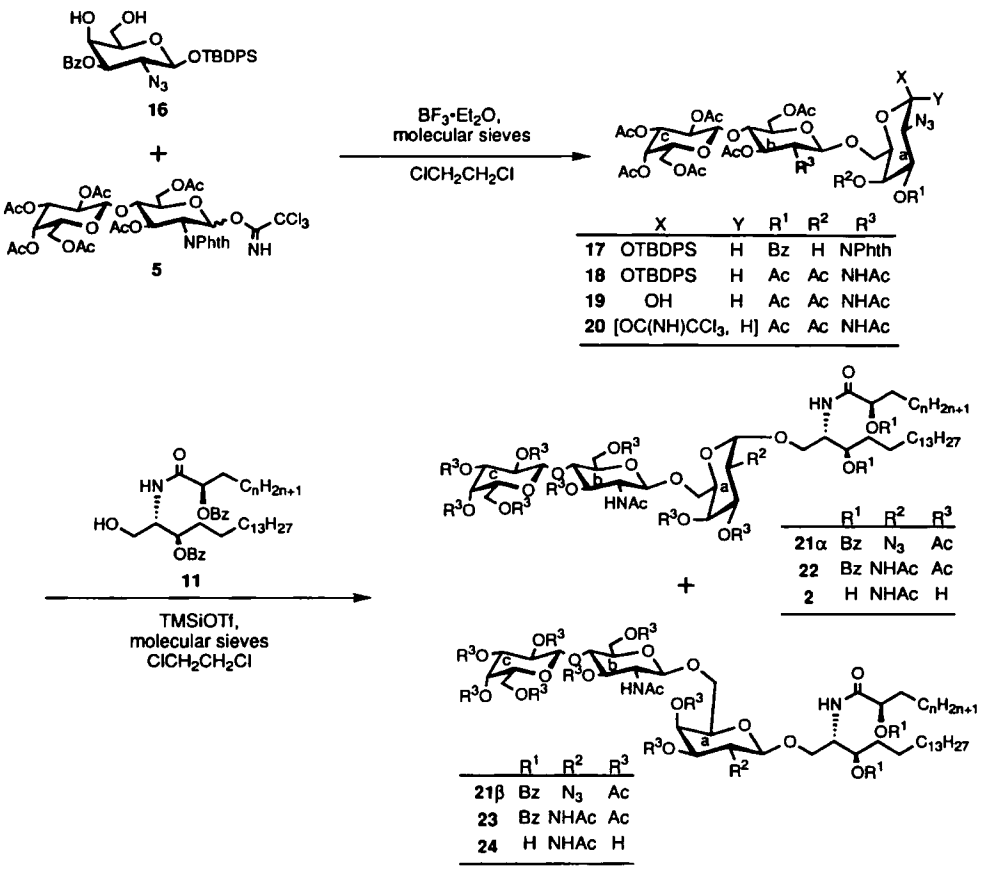


Fig. 2. 400 MHz ^1H NMR spectrum of compound **1** in pyridine-d_6–D_2O.



Scheme 2.

glycotriosyl donor **20** was carried out (56% overall yield) as described for the preparation of **10** from **7**. The coupling of **20** and protected ceramide **11** was promoted with trimethylsilyl triflate in 1,2-dichloroethane at room temperature to give a mixture of **21**α and **21**β, which were not separated in this step. As judged from the intensities of the NMR signals of H-1a (**21**α, δ_H 4.93, J 3.9 Hz; **21**β, 4.17, J 8.3 Hz), the ratio of the a and β glycosides was 4:3. The azido groups of **21**α and **21**β were converted into acetamido groups, and the products were resolved by silica-gel column chromatography to give 11% of **22** and 9% of **23**, based on **11**. Deprotection of both compounds **22** and **23** was achieved by treatment with sodium methoxide, to give compound **2** and the β isomer **24**. The structures of **2** and **24** were supported by their NMR data (Fig. 3; 2:1 $CDCl_3$–CD_3OD): **2**, δ 4.52 (d, 1 H, J 3.4 Hz, H-1a); **24**, δ 4.07 (d, 1 H, J 7.3 Hz, H-1a).

Boron trifluoride etherate-promoted glycosylation of the 2a-azido-2a-deoxy glycotriosyl derivative **7** with lactosamine donor **5** in 1,2-dichloroethane was performed (Scheme 3) in the presence of activated, powdered molecular sieves AW-300 at −20°C to give compound **25**. Compound **25** was converted into **26** in two steps(*i*, hydrazine hydrate–ethanol; *ii*, Ac_2O–pyridine) in 68% overall yield. Assignment of NMR signals to the b and b′ rings was confirmed by observation of an NOE between H-1b and H-6a, and comparison of

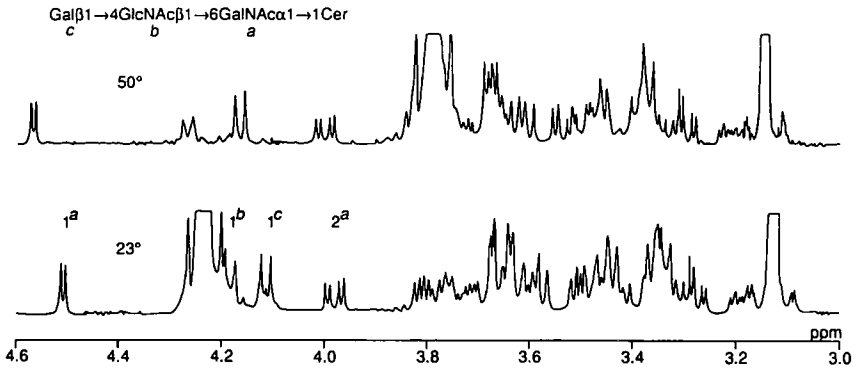
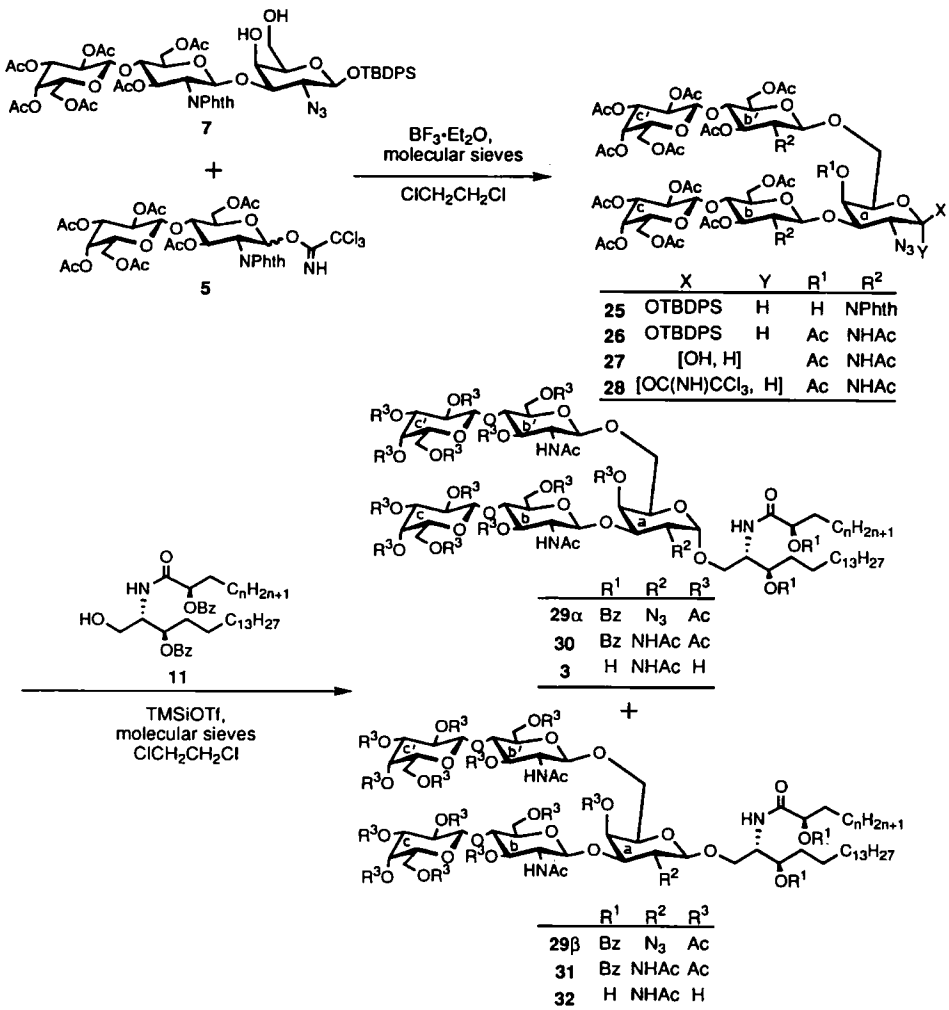


Fig. 3. 400 MHz ^{1}H NMR spectrum of compound **2** in 2:1 $CDCl_3$–CD_3OD.



Scheme 3.

Table 1
^{1}H NMR data

Compound	Chemical shifts (δ) at 400 MHz in $CDCl_3$								
	GalNAc			GlcNAc			Gal		
	H-1a	H-2a	H-3a	H-1b	H-2b	H-3b	H-1c	H-2c	H-3c
8	4.21	3.64	3.40	4.55	3.94	5.02	4.54	5.10	4.97
18	4.48	3.79–3.65	4.66	4.27	3.75	4.97	4.45	5.12	4.95
26	4.34	3.62	3.47–3.32	4.54	3.96	5.01	4.53	5.10	4.97
				4.30	3.64	5.04	4.46	5.12	4.95

chemical shifts with those of compounds **8** and **18** (Table 1). Compound **26** was converted into the pentasaccharide imidate **28** via **27** (85% overall yield from **26**); δ_H 9.25 (s, 0.5 H, C=N*H*α), 8.79 (s, 0.5 H, C=N*H*β), 5.30 (d, 0.5 H, *J* 3.5 Hz, H-1aα), and 5.23 (d, 0.5 H, *J* 8.2 Hz, H-1aβ). The glycosylation of protected ceramide **11** with **28**, as with **10** and **20** was promoted with trimethylsilyl triflate in 1,2-dichloroethane at −5°C to give a mixture of **29**α and **29**β. As judged from the intensities of the NMR signals of H-1a (**29**α, δ_H 4.83, *J* 3.4 Hz; **29**β, 4.58, *J* 7.8 Hz), the ratio of the α and β glycosides was 2:1. The azido groups of compounds **29**α and **29**β were transformed into acetamido groups, and the products were separated by silica-gel column chromatography to give 13% of **30** and 6% of **31**, based on **28.** Deprotection of both **30** and **31** was accomplished by treatment with sodium methoxide, to give compounds **3** and **32**. The structures of **3** and **32** were assigned from the reaction sequence, and established by their NMR data (Fig. 4; Me_2SO-d_6–D_2O): **3**, δ_H 4.63 (d, 1 H, *J* 3.0 Hz, H-1a); **32**, δ 4.27 (d, 1 H, *J* 8.0 Hz, H-1a).

In conclusion, we have established a facile route to the synthesis of mucin-type neoglycolipids **1**, **2**, and **3**, and now we are in a position to generate specific monoclonal antibodies against mucin-type carbohydrate chains.

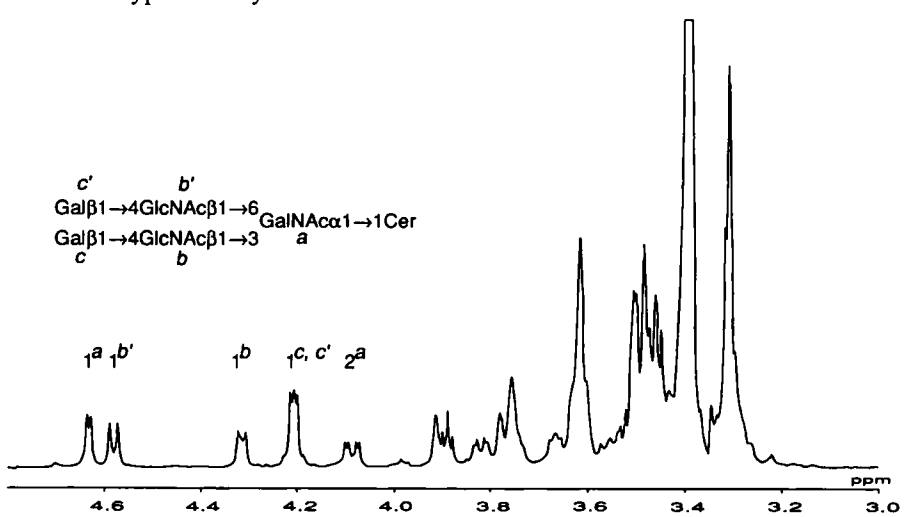


Fig. 4. 400 MHz ^{1}H NMR spectrum of compound **3** in Me_2SO-d_6–D_2O.

3. Experimental

General methods.—^{1}H NMR spectra were recorded at 200 MHz with a Varian Gemini 200 and at 400 MHz with a Jeol GX400 instrument for samples dissolved in the solvents noted. Field desorption mass spectra (FD-MS) were recorded with a Hitachi M-80B spectrometer. Column chromatography was carried out on silica gel (Merck Silica 60), with the solvent systems noted. TLC and high performance TLC were performed on Silica Gel 60 F_{254} (Merck). HPLC analysis was performed on columns of TSK gel Silica 60 and ODS-80TM (TOSOH Corporation, Japan).

tert-*Butyldiphenylsilyl* O-*(2,3,4,6-tetra*-O-*acetyl-β*-D-*galactopyranosyl)-(1→4)*-O-*(3,6-di*-O-*acetyl-2-deoxy-2-phthalimido-β*-D-*glucopyranosyl)-(1→3)-2-azido-4,6*-O-*benzylidene-2-deoxy-β*-D-*galactopyranoside* (**6**).—To a stirred mixture of *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-acetyl-2-deoxy-2-phthalimido-α,β-D-glucopyranosyl trichloroacetimidate [8] (**5**, 0.869 g, 1.00 mmol), *tert*-butyldiphenylsilyl 2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranoside [9] (**4**, 0.426 g, 0.80 mmol), and molecular sieves AW-300 (1.00 g) in 1,2-dichloroethane (11 mL) was added 1.0 M $BF_3 \cdot E t_2O$ (0.20 mL) at −20°C. The mixture was stirred for 2 h at −20°C, then filtered, and the solids were washed with $CHCl_3$. The filtrate was washed with aq $NaHCO_3$ and aq NaCl, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by chromatography on silica gel using 3:1 hexane–EtOAc to afford compound **6** (0.827 g, 0.67 mmol, 84%). NMR (400 MHz, $CDCl_3$): δ_H 5.51 (d, 1 H, $J_{1,2}$ 8.3 Hz, H-1b), 5.46 (s, 1 H, PhC*H*), 4.98 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3c), 4.76 (dd, 1 H, $J_{5,6}$ 2.4 Hz, H-6b), 4.59 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1c), 4.30 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1a), 4.28 (dd, 1 H, $J_{2,3}$ 10.3 Hz, H-2b), 4.11 (dd, 1 H, $J_{4,5}$ 0.5 Hz, H-4a), 4.09–4.01 (m, 2 H, H-6c,6′c), 4.02 (dd, 1 H, $J_{6,6}$ 12.2 Hz, H-6′b), 3.91–3.81 (m, 4 H, H-6a,6′a,4b,5c), 3.71 (m, 1 H, $J_{5,6'}$ 3.9 Hz, H-5b), 3.67 (dd, 1 H, $J_{2,3}$ 10.7 Hz, H-2a), 3.18 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3a), 2.87 (dt, 1 H, H-5a), 2.14, 2.05, 2.04, 2.03, 1.96, 1.92 (6 s, 18 H, Ac), and 1.01 (s, 9 H, *t*-Bu); FD-MS: *m/z* 1236.8 (M^+). Anal. Calcd for $C_{61}H_{68}N_4O_{22}Si$: C, 59.21; H, 5.54; N, 4.53. Found: C, 59.3; H, 5.5; N, 4.5.

tert-*Butyldiphenylsilyl* O-*(2,3,4,6-tetra*-O-*acetyl-β*-D-*galactopyranosyl)-(1→4)*-O-*(3,6-di*-O-*acetyl-2-deoxy-2-phthalimido-β*-D-*glucopyranosyl)-(1→3)-2-azido-2-deoxy-β*-D-*galactopyranoside* (**7**).—To a stirred solution of **6** (0.800 g, 0.65 mmol) in CH_2Cl_2 (15 mL) was added aq 60% CF_3COOH (0.5 mL) at 0°C, and the mixture was stirred overnight at room temperature. It was then added to aq $NaHCO_3$ (50 mL), and extraction was completed after dilution with $CHCl_3$. The organic layer was washed with aq $NaHCO_3$ and aq NaCl, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by chromatography on silica gel using 3:1 hexane–EtOAc to yield compound **7** (0.593 g, 0.52 mmol, 80%). NMR (400 MHz, $CDCl_3$): δ_H 5.75 (dd, 1 H, $J_{3,4}$ 8.3 Hz, H-3b), 5.49 (d, 1 H, $J_{1,2}$ 8.8 Hz, H-1b), 5.34 (d, 1 H, $J_{4,5}$ 1.0 Hz, H-4c), 5.12 (dd, 1 H, $J_{2,3}$ 10.3 Hz, H-2c), 4.98 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3c), 4.58 (dd, 1 H, H-6b), 4.56 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1c), 4.32 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1a), 4.27 (dd, 1 H, $J_{2,3}$ 10.7 Hz, H-2b), 4.12–4.01 (m, 3 H, H-6′b,6c,6′c), 3.89–3.79 (m, 4 H, H-4a,4b,5b,5c), 3.64 (dd, 1 H, $J_{6,6'}$ 11.7 Hz, H-6a), 3.50 (dd, 1 H, $J_{2,3}$ 10.3 Hz, H-2a), 3.44 (dd, 1 H, $J_{5,6'}$ 3.9 Hz, H-6′a), 3.20 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3a), 3.04 (dt, 1 H, $J_{5,6}$ 7.3 Hz, H-5a), 2.14, 2.09, 2.05, 2.04, 1.96, 1.93 (6 s, 18 H, Ac), and 1.01 (s, 9 H, *t*-Bu); FD-MS: *m/z* 1148.8 (M^+). Anal. Calcd for $C_{54}H_{64}N_4O_{22}Si \cdot H_2O$: C, 55.57; H, 5.70; N, 4.80. Found: C, 55.1; H, 5.3; N, 4.4.

tert-*Butyldiphenylsilyl* O-*(2,3,4,6-tetra*-O-*acetyl-β*-D-*galactopyranosyl)-(1→4)*-O-*(2-acetamido-3,6-di*-O-*acetyl-2-deoxy-β*-D-*glucopyranosyl)*-(1→3)-4,6-*di*-O-*acetyl*-2-*azido*-2-*deoxy-β-D-galactopyranoside* (**8**).—A solution of **7** (0.254 g, 0.22 mmol) in 50:1 EtOH–$H_2NNH_2 \cdot H_2O$ (12.5 mL) was stirred under reflux overnight and then concentrated in vacuo. The residue was dissolved in pyridine (5 mL), and to the solution was added Ac_2O (2 mL) and a trace of 4-dimethylaminopyridine. The solution was stirred overnight at room temperature, then diluted with $CHCl_3$, successively washed with aq $NaHCO_3$ and aq NaCl, dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by chromatography on silica gel using 1:2 hexane–EtOAc to yield compound **8** (0.241 g, 0.21 mmol, 95%). NMR (400 MHz, $CDCl_3$): δ_H 5.34 (d, 1 H, $J_{4,5}$ 1.0 Hz, H-4c), 5.45 (d, 1 H, $J_{2,NH}$ 9.5 Hz, N*H*-b), 5.20 (dd, 1 H, $J_{4,5}$ 0.6 Hz, H-4a), 5.10 (dd, 1 H, $J_{2,3}$ 10.5 Hz, H-2c), 5.02 (dd, 1 H, $J_{3,4}$ 8.9 Hz, H-3b), 4.97 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3c), 4.55 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1b), 4.54 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1c), 4.45 (dd, 1 H, H-6b), 4.31 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1a), 4.10 (dd, 1 H, H-6c), 4.09 (dd, 1 H, H-6′c), 3.98–3.91 (m, 4 H, H-6a,6′a,2b,6′b), 3.86 (dt, 1 H, H-5c), 3.82 (dd, 1 H, $J_{4,5}$ 9.3 Hz, H-4b), 3.64 (dd, 1 H, $J_{2,3}$ 10.3 Hz, H-2a), 3.49–3.42 (m, 2 H, H-5a,5b), 3.40 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3a), 2.15, 2.11, 2.07, 2.06, 2.03, 1.96, 1.94, 1.92, 2.01 (9 s, 27 H, Ac), and 1.01 (s, 9 H, *t*-Bu); FD-MS: *m/z* 1167 $(M+Na)^+$. Anal. Calcd for $C_{52}H_{68}N_4O_{23}Si$: C, 54.54; H, 5.98; N, 4.89. Found: C, 54.6; H, 6.0; N, 5.1.

O-*(2,3,4,6-Tetra*-O-*acetyl-β*-D-*galactopyranosyl)-(1→4)*-O-*(2-acetamido-3,6-di*-O-*acetyl-2-deoxy-β*-D-*glucopyranosyl)-(1→3)-4,6-di*-O-*acetyl-2-azido-2-deoxy-α,β*-D-*galactopyranose* (**9**).—A solution of compound **8** (0.240 g, 0.21 mmol) and AcOH (14 μL, 0.24 mmol) in dry THF (5 mL) was cooled to −10°C. Tetrabutylammonium fluoride (1 M in THF, 0.55 mL) was added dropwise. The mixture was stirred for 2 h at −10°C, then diluted with H_2O (50 mL). The mixture was extracted with $CHCl_3$, and the organic layer was washed with aq NaCl, dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by chromatography on silica gel using 1:2 hexane–EtOAc to yield compound **9** (0.125 g, 0.14 mmol, 66%). NMR (400 MHz, $CDCl_3$): δ_H 5.78 (d, 0.2 H, $J_{2,NH}$ 9.3 Hz, N*H*-bα), 5.74 (d, 0.8 H, $J_{2,NH}$ 9.3 Hz, N*H*-bβ), 4.65 (d, 0.8 H, $J_{1,2}$ 6.8 Hz, H-1bβ), 4.54 (d, 1 H, $J_{1,2}$ 8.3 Hz, H-1c), 4.07 (bd, 0.8 H, $J_{1,2}$ 8.6 Hz, H-1aβ), and 4.05 (d, 0.2 H, $J_{1,2}$ 3.5 Hz, H-1aα); FD-MS: *m/z* 906.9 (M^+). Anal. Calcd for $C_{36}H_{50}N_4O_{23} \cdot 2H_2O$: C, 45.86; H, 5.77; N, 5.94. Found: C, 46.0; H, 5.4; N, 5.6.

3-O-*Benzoyl-2*-N-*[(2R)-2-benzoyloxyalkanoyl]sphinganine (3,2′-di*-O-*benzoylceramide)* (**11**).—A mixture of ceramide (0.248 g, type IV, purchased from Sigma Chemical Co., St. Louis, MO) and 10% Pd–C (0.020 g) in THF (30 mL) was stirred for 15 h at room temperature under H_2, and filtered through Celite. The filtrate was concentrated in vacuo to give hydrogenated ceramide (0.205 g). The residue and trityl chloride (0.189 mg, 0.678 mmol) were dissolved in pyridine (5 mL) and the mixture was stirred for 6 days, then benzoyl chloride (0.095 mg, 0.678 mmol) was added. This mixture was stirred overnight, and poured into 1 M $NaHCO_3$. The product was recovered by extraction with $CHCl_3$, and the extract was washed with H_2O, dried ($MgSO_4$), and concentrated in vacuo. Chromatography of the residue over silica gel in 10:1 hexane–EtOAc gave 3,2′-di-*O*-benzoyl-1-*O*-trityl ceramide (0.337 mg). This compound was dissolved in CH_2Cl_2 (10 mL), and added to aq 60% CF_3COOH (1 mL). The mixture was stirred for 2 h, then poured into 1 M $NaHCO_3$. The product was recovered by extraction with $CHCl_3$, and the extract was

washed with H_2O, dried ($MgSO_4$), and concentrated in vacuo. Chromatography of the residue over silica gel in 4:1 hexane–EtOAc gave **11** (0.114 g). NMR (400 MHz, $CDCl_3$): δ_H 7.06 (d, 1 H, $J_{2,NH}$ 8.5 Hz, N*H*), 5.41 (t, 1 H, $J_{2',3'A} = J_{2',3'B} = 5.5$ Hz, H-2') [1], 5.14 (ddd, 1 H, $J_{2,3}$ 7.0, $J_{3,4A}$ 9.5, $J_{3,4B}$ 3.5 Hz, H-3), 4.19 (m, 1 H, $J_{1,2}$ 3.0, $J_{1,2}$ 11.5, $J_{2,3}$ 7.0 Hz, H-2), 3.65 (ddd, 2 H, $J_{1A,2}$ 3.0, $J_{1B,2}$ 11.5, $J_{1,1}$ 25.0 Hz, H-1A,1B), 2.85 (m, 1 H, O*H*), 2.01 (m, 2 H, H-3'A,3'B), 1.84 (ddd, 1 H, $J_{3,4A}$ 9.5, $J_{4A,5}$ 5.0, $J_{4A,4B}$ 18.5 Hz, H-4A), 1.69 (ddd, 1 H, $J_{3,4B}$ 3.5, $J_{4B,5}$ 8.5, $J_{4A,4B}$ 18.5 Hz, H-4B), 1.25 (m, CH_2), and 0.88 (t, 6 H, J 6.5 Hz, CH_3).

Reversed-phase HPLC of the 3,2'-di-*O*-benzoyl ceramide was performed on TSK gel ODS-80TM (Fig. 1). The mixture was resolved into 8 peaks, which gave the following FD-MS: 1 (18:0, $C_{50}H_{81}NO_6$), *m/z* 792 $(M)^+$; 2 (22:0, $C_{54}H_{89}NO_6$), *m/z* 848 $(M)^+$; 3 (23:0, $C_{55}H_{91}NO_6$), *m/z* 862 $(M)^+$; 4 (24:0, $C_{56}H_{93}NO_6$), *m/z* 876 $(M)^+$; 5 (25:0, $C_{57}H_{95}NO_6$), *m/z* 890 $(M)^+$; 6 (26:0, $C_{58}H_{97}NO_6$), *m/z* 904 $(M)^+$; 7 (27:0, $C_{59}H_{99}NO_6$), *m/z* 918 $(M)^+$; 8 (28:0, $C_{60}H_{101}NO_6$), *m/z* 932 $(M)^+$. All spectra showed a peak at *m/z* 105 (Bz).

O-*(2,3,4,6-Tetra*-O-*acetyl-β*-D-*galactopyranosyl)-(1→4)*-O-*(2-acetamido-3,6-di*-O-*acetyl-2-deoxy-β*-D-*glucopyranosyl)-(1→3)*-O-*(4,6-di*-O-*acetyl-2-azido-2-deoxy-α*-D-*galactopyranosyl)-(1→1)-3*-O-*benzoyl-2*-N-*[(2R)-2-benzoyloxyalkanoyl]sphinganine* (**12α**) *and* O-*(2,3,4,6-tetra*-O-*acetyl-β*-D-*galactopyranosyl)-(1→4)*-O-*(2-acetamido-3,6-di*-O-*acetyl-2-deoxy-β*-D-*glucopyranosyl)-(1→3)*-O-*(4,6-di*-O-*acetyl-2-azido-2-deoxy-β*-D-*galactopyranosyl)-(1→1)-3*-O-*benzoyl-2*-N-*[(2R)-2-benzoyloxyalkanoyl]-sphinganine* (**12β**).—To a solution of **9** (0.100 g, 0.11 mmol) in 1,2-dichloroethane (1.0 mL) was added CCl_3CN (0.11 mL) and 1,8-diazabicyclo[5.4.0]undec-7-ene (0.02 mL, 0.13 mmol). The mixture was stirred for 3 h, and directly subjected to column chromatography on silica gel using 1:2 toluene–EtOAc to afford α-trichloroacetimidate **10** (0.095 g, 0.090 mmol, 82%). NMR (200 MHz, $CDCl_3$): δ_H 8.76 (s, 1 H, C=N*H*), 6.44 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1a), 5.53 (dd, 1 H, H-4a), 5.50 (d, 1 H, $J_{2,NH}$ 9.8 Hz, N*H*-b), 5.35 (dd, 1 H, $J_{4,5}$ 1.0 Hz, H-4c), 5.11 (dd, 1 H, $J_{2,3}$ 10.7 Hz, H-2c), 5.05 (dd, 1 H, $J_{3,4}$ 8.8 Hz, H-3b), 4.97 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3c), 4.68 (dd, 1 H, H-6b), 4.67 (d, 1 H, $J_{1,2}$ 8.3 Hz, H-1b), 4.52 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1c), 4.30 (dt, 1 H, H-5a), 4.16–3.95 (m, 8 H, H-2a,3a,6a,6'a,2b, 6'b,6c,6'c), 3.88 (dt, 1 H, H-5c), 3.83 (dd, 1 H, $J_{4,5}$ 9.3 Hz, H-4b), 3.59 (m, 1 H, H-5b), 2.15, 2.11, 2.07, 2.06, 2.03, 1.96, 1.94, 1.92 (8 s, 27 H, Ac), and 1.09 (s, 9 H, *t*-Bu).

To a stirred mixture of **10** (0.091 g, 0.087 mmol), **11** (0.069 g, 0.079 mmol), and powdered molecular sieves AW-300 (0.12 g) in 1,2-dichloroethane (2.0 mL) was added M TMSiOTf in 1,2-dichloroethane (0.20 mL) at −20°C. The mixture was stirred overnight at room temperature, diluted with $CHCl_3$, and filtered through Celite. The filtrate was washed with aq $NaHCO_3$ and aq NaCl, dried over $MgSO_4$, and concentrated in vacuo. The resulting residue was purified on silica gel using 1:2 hexane–EtOAc to yield a mixture of anomers **12α** and **12β** (0.068 g, 0.39 mmol, 49%). NMR (400 MHz, $CDCl_3$): δ_H 6.95 (d, 0.6 H, Cer N*H*-β), 6.91 (d, 0.4 H, Cer N*H*-α), 4.79 (d, 0.4 H, $J_{1,2}$ 3.4 Hz, H-1aα), 4.55 (d, 0.6 H, $J_{1,2}$ 7.8 Hz, H-1cβ), 4.53 (d, 0.4 H, $J_{1,2}$ 7.8 Hz, H-1cα), 4.36 (d, 0.6 H, $J_{1,2}$ 8.3 Hz, H-1bβ), 4.28 (d, 0.4 H, $J_{1,2}$ 7.8 Hz, H-1bα), 4.02 (d, 0.6 H, $J_{1,2}$ 7.8 Hz, H-1aβ), 1.20 (m, CH_2), and 0.85 (t, CH_3).

[1] The letters A and B are used to designate the two magnetically nonequivalent protons of the pairs attached to C-3 of the ceramide fatty acyl group (i.e., C-3') and to C-1 and C-4 of the sphinganine chain.

O-*(2,3,4,6-Tetra*-O-*acetyl-β*-D-*galactopyranosyl)-(1→4)*-O-*(2-acetamido-3,6-di*-O-*acetyl-2-deoxy-β*-D-*glucopyranosyl)-(1→3)*-O-*(2-acetamido-4,6-di*-O-*acetyl-2-deoxy-α*-D-*galactopyranosyl)-(1→1)-3*-O-*benzoyl-2*-N-*[(2*R*)-2-benzoyloxyalkanoyl]sphinganine* (**13**) *and* O-*(2,3,4,6-tetra*-O-*acetyl-β*-D-*galactopyranosyl)-(1→4)*-O-*(2-acetamido-3,6-di*-O-*acetyl-2-deoxy-β*-D-*glucopyranosyl)-(1→3)*-O-*(2-acetamido-4,6-di*-O-*acetyl-2-deoxy-β*-D-*galactopyranosyl)-(1→1)-3*-O-*benzoyl-2*-N-*[(2*R*)-2-benzoyloxy-alkanoyl]sphinganine* (**14**).—A mixture of **12**α and **12**β (0.083 g, 0.047 mmol) was dissolved in a solution of $NiCl_2 \cdot 6H_2O$ (0.183 g, 0.77 mmol) and H_3BO_3 (0.093 g, 1.50 mmol) in EtOH (4 mL). To this solution was added $NaBH_4$ (0.050 g, 1.32 mmol) at room temperature, the mixture was stirred for 1.5 h at room temperature, then Ac_2O was added, and stirring was continued overnight at room temperature. Methanol was then added to the mixture, and it was concentrated in vacuo. The residue was dissolved in $CHCl_3$, and the organic layer was washed with aq $NaHCO_3$ and aq NaCl, dried over $MgSO_4$, and concentrated in vacuo. The resulting residue was purified by chromatography on silica gel using 1:2 hexane–EtOAc to afford a mixture of compounds **13** and **14** (0.077 g). This mixture was purified by PLC on silica gel to afford **13** (0.029 g, 0.016 mmol) and **14** (0.040 g, 0.022 mmol) (25% and 48%, respectively, from the mixture **12**α + **12**β). NMR data for **13** (400 MHz, $CDCl_3$): δ_H 7.32 (d, 1 H, Cer N*H*), 5.35 (dd, 1 H, H-4c), 5.33 (t, 1 H, Cer H-2′), 5.22 (dd, 1 H, Cer H-3), 5.16 (dd, 1 H, H-4a), 5.15 (dd, 1 H, $J_{3,4}$ 8.8 Hz, H-3b), 5.12 (dd, 1 H, $J_{2,3}$ 10.3 Hz, H-2c), 4.97 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3b), 4.70 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1b), 4.69 (dd, 1 H, H-6b), 4.63 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1a), 4.54 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1c), 4.44 (m, 1 H, Cer H-2), 4.40 (dd, 1 H, $J_{2,3}$ 10.8 Hz, H-2a), 4.12 (m, 2 H, H-6c,6′c), 4.04 (dd, 1 H, H-6′b), 4.01 (dt, 1 H, H-5a), 3.95 (dd, 1 H, $J_{3,4}$ 2.9 Hz, H-3a), 3.92 (m, 2 H, H-6a,6′a), 3.88 (dt, 1 H, H-5c), 3.84–3.80 (m, 2 H, Cer H-1A, H-4b), 3.66 (dd, 1 H, $J_{2,3}$ 10.3 Hz, H-2b), 3.58 (m, 1 H, H-5b), 3.26 (dd, 1 H, Cer H-1B), 2.15, 2.14, 2.08, 2.06, 2.05, 2.01, 1.97, 1.95 (8 s, 30 H, Ac), 1.24 (m, CH_2), and 0.84 (t, CH_3).

NMR data for **14** (400 MHz, $CDCl_3$): δ_H 6.88 (d, 1 H, J 8.1 Hz, Cer N*H*), 5.35 (dd, 1 H, H-4c), 5.32 (t, 1 H, Cer H-2′), 5.29 (dd, 1 H, H-4a), 5.17 (t, 1 H, Cer H-3), 5.11 (dd, 1 H, $J_{2,3}$ 10.3 Hz, H-2c), 5.01 (dd, 1 H, $J_{3,4}$ 8.8 Hz, H-3b), 4.97 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3c), 4.82 (d, 1 H, $J_{1,2}$ 8.3 Hz, H-1a), 4.58 (dd, 1 H, H-6b), 4.51 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1b), 4.51 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1c), 4.51 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3a), 4.37 (m, 1 H, Cer H-2), 4.10 (m, 2 H, H-6c,6′c), 4.00 (dd, 1 H, H-6′b), 3.99–3.76 (m, 5 H, H-6a,4b,5c, Cer H-1A,1B), 3.97 (dd, 1 H, H-6′a), 3.91 (dd, 1 H, $J_{2,3}$ 10.3 Hz, H-2b), 3.72 (dt, 1 H, H-5a), 3.52 (m, 1 H, H-5b), 3.09 (dd, 1 H, $J_{2,3}$ 10.7 Hz, H-2a), 2.15, 2.14, 2.06, 2.05, 2.04, 1.99, 1.97, 1.95 (8 s, 30 H, Ac), 1.24 (m, CH_2), and 0.84 (t, CH_3).

O-*β*-D-*Galactopyranosyl-(1→4)*-O-*(2-acetamido-2-deoxy-β*-D-*glucopyranosyl)-(1→3)*-O-*(2-acetamido-2-deoxy-α*-D-*galactopyranosyl)-(1→1)-2*-N-*[(2*R*)-2-hydroxy-alkanoyl]sphinganine* (**1**).—A solution of compound **13** (0.016 g, 0.0086 mmol) in 1:1 MeOH–THF (3 mL) containing M NaOMe–MeOH (0.1 mL) was stirred overnight at room temperature, and made neutral with Dowex 50W-X8. The suspension was filtered, and the filtrate was concentrated in vacuo. The resultant residue was purified by PLC on silica gel using 55:40:10 $CHCl_3$–MeOH–H_2O afford to **1** (0.004 g, 0.032 mmol, 37%). NMR (400 MHz, pyridine-d_6–D_2O, 50°C): δ_H 5.47 (d, 1 H, $J_{1,2}$ 8.3 Hz, H-1b), 5.36 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1a), 5.29 (dd, 1 H, H-2a), 4.97 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1c), 4.74 (m, 1 H, H-4a), 4.73–4.64 (m, 3 H, Cer H-2,3,2′), 4.61 (dd, 1 H, H-3a), 4.55 (dd, 1 H, H-3b),

4.46 (dd, 1 H, H-4c), 4.44–4.05 (m, 14 H, H-5a,6a,6'a,2b,4b,6b,6'b,2c,3c,5c,6c,6'c, Cer H-1A,1B), 3.77 (m, 1 H, H-5b), 2.45, 2.20 (2 s, 6 H, Ac), 1.30 (m, CH_2), and 0.88 (t, CH_3).

O-*β*-D-*Galactopyranosyl-(1→4)*-O-*(2-acetamido-2-deoxy-β*-D-*glucopyranosyl)-(1→3)*-O-*(2-acetamido-2-deoxy-β*-D-*galactopyranosyl)-(1→1)*-2-N-*[(2R)-2-hydroxyalkanoyl]sphinganine* (**15**).—A solution of compound **14** (0.029 g, 0.016 mmol) in 1:1 MeOH–THF (6 mL) containing 0.1 M NaOMe–MeOH (0.17 mL) was stirred overnight at room temperature, then made neutral with Dowex 50W-X8. The suspension was filtered, and the filtrate was concentrated in vacuo. The resultant residue was purified by PLC on silica gel using 55:40:10 $CHCl_3$–MeOH–H_2O to afford **15** (0.007 g, 0.0057 mmol, 35%). NMR (400 MHz, pyridine-d_6–D_2O, 50°C): δ_H 5.52 (d, 1 H, $J_{1,2}$ 8.3 Hz, H-1b), 5.16 (d, 1 H, $J_{1,2}$ 8.3 Hz, H-1a), 4.98 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1c), 4.75 (dd, 1 H, H-2a), 4.72 (m, 1 H, H-4a), 4.68 (m, 1 H, Cer H-2), 4.67 (dd, 1 H, H-3a), 4.65–4.56 (m, 3 H, H-3b, Cer H-1A,2'), 4.46 (dd, 1 H, H-4c), 4.44 (dd, 1 H, H-2c), 4.41–4.02 (m, 13 H, H-3,5a,6a,6'a,2b,4b,6b,6'b,3c,5c,6c,6'c, Cer H-1B), 3.82 (m, 1 H, H-5b), 2.40, 2.15 (2 s, 6 H, Ac), 1.25 (m, CH_2), and 0.88 (t, CH_3).

tert-*Butyldiphenylsilyl 2-azido-3*-O-*benzoyl-2-deoxy-β*-D-*galactopyranoside* (**16**).—To a stirred mixture of compound **4** (0.300 g, 0.56 mmol) and 4-dimethylaminopyridine (12 mg) in CH_2Cl_2 20 mL) was added pyridine (0.9 mL) and benzoyl chloride (95 mg, 0.68 mmol). The solution was stirred for 20 h at room temperature, then diluted with CH_2Cl_2, successively washed with aq $NaHCO_3$, and aq NaCl, dried over $MgSO_4$, and concentrated in vacuo. The resulting residue was subjected to column chromatography on silica gel using 4:1 hexane–EtOAc to give a yellow syrup. This residue was dissolved in CH_2Cl_2 (15 mL), aq 60% CF_3COOH (0.5 mL) was added at 0°C, and the mixture was stirred overnight at room temperature. It was then poured into aq $NaHCO_3$ (50 mL), and extraction was completed after dilution with CH_2Cl_2. The organic layer was washed with aq $NaHCO_3$ and aq NaCl, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by chromatography on silica gel using 3:2 hexane–EtOAc to yield compound **16** (0.168 g, 0.31 mmol, 54% based on **4**). NMR (200 MHz, $CDCl_3$): δ_H 4.80 (dd, 1 H, $J_{3,4}$ 3.0 Hz, H-3), 4.66 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 4.10 (d, 1 H, H-4), 4.03 (dd, 1 H, $J_{2,3}$ 10.8 Hz, H-2), 3.65 (dd, 1 H, $J_{5,6}$ 5.8, $J_{6,6'}$ 12.0 Hz, H-6), 3.48 (dd, 1 H, $J_{5,6'}$ 3.8 Hz, H-6'), 3.21 (m, 1 H, H-5), and 1.11 (s, 9 H, *t*-Bu). Anal. Calcd for $C_{29}H_{33}N_3O_6Si \cdot H_2O$: C, 61.58; H, 6.23; N, 7.43. Found: C, 61.63; H, 6.50; N, 7.22.

tert-*Butyldiphenylsilyl* O-*(2,3,4,6-tetra*-O-*acetyl-β*-D-*galactopyranosyl)-(1→4)*-O-*(2-acetamido-3,6-di*-O-*acetyl-2-deoxy-β*-D-*glucopyranosyl)-(1→6)-3,4-di*-O-*acetyl-2-azido-2-deoxy-β*-D-*galactopyranoside* (**18**).—To a stirred mixture of **5** (2.26 g, 2.64 mmol), **16** (1.100 g, 2.01 mmol), and 1.00 g of molecular sieves AW-300 in 1,2-dichloroethane was added M $BF_3 \cdot Et_2O$ (0.65 mL) at −20°C, then the suspension was filtered, and the solids were washed with $CHCl_3$. The filtrate was washed with aq $NaHCO_3$ and aq NaCl, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by chromatography on silica gel using 3:1 hexane–EtOAc to yield compound **17** (0.783 g, 0.59 mmol, 29%). NMR (400 MHz, $CDCl_3$): δ_H 5.67 (dd, 1 H, $J_{3,4}$ 8.3 Hz, H-3b), 5.33 (d, 1 H, $J_{1,2}$ 8.8 Hz, H-1b), 5.31 (d, 1 H, H-4c), 5.11 (dd, 1 H, $J_{2,3}$ 10.7 Hz, H-2c), 4.95 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3c), 4.76 (dd, 1 H, $J_{5,6}$ 1.9 Hz, H-6b), 4.70 (dd, 1 H, $J_{3,4}$ 2.9 Hz, H-3a), 4.54 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1c), 4.40 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1a), 4.10–3.96 (m, 5 H, H-2a,4a,2b,6c,6'c),

3.93 (dd, 1 H, $J_{6,6'}$ 12.2 Hz, H-6'b), 3.86 (t, 1 H, $J_{5,6}$ 9.3 Hz, H-6a), 3.83 (dt, 1 H, H-5c), 3.78 (dd, 1 H, $J_{4,5}$ 10.3 Hz, H-4b), 3.70 (m, 1 H, H-5b), 3.45 (dd, 1 H, $J_{5,6'}$ 4.4, $J_{6,6'}$ 9.3 Hz, H-6'a), 3.26 (d, 1 H, J 5.4 Hz, OH-4a), 3.22 (dd, 1 H, H-5a), 2.35, 2.13, 2.03, 1.95, 1.88, 1.86 (6 s, 18 H, Ac), and 1.06 (s, 9 H, *t*-Bu).

A solution of **17** (0.783 g, 0.59 mmol) in 50:1 EtOH–$H_2NNH_2 \cdot H_2O$ (40 mL) was stirred under reflux overnight and then concentrated in vacuo. The residue was dissolved in pyridine (15 mL), and to the solution Ac_2O (5 mL) and a trace of 4-dimethylaminopyridine was added. The solution was stirred overnight at room temperature, then diluted with $CHCl_3$, successively washed with aq $NaHCO_3$, and aq NaCl, dried over Na_2SO_4, and concentrated in vacuo. The resulting residue was purified on silica gel using 1:2 hexane–EtOAc to afford compound **18** (0.592 g, 0.52 mmol, 88%). NMR (400 MHz, $CDCl_3$): δ_H 5.35 (dd, 1 H, H-4c), 5.22 (dd, 1 H, $J_{4,5}$ 0.5 Hz, H-4a), 5.13 (d, 1 H, $J_{2,NH}$ 10.3 Hz, N*H*-b), 5.12 (dd, 1 H, $J_{2,3}$ 10.3 Hz, H-2c), 5.00–4.93 (m, 2 H, H-3b,3c), 4.66 (dd, 1 H, $J_{3,4}$ 2.9 Hz, H-3a), 4.48 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1a), 4.45 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1c), 4.40 (dd, 1 H, H-6b), 4.27 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1b), 4.12 (dd, 1 H, H-6c), 4.09 (dd, 1 H, H-6'c), 4.03 (dd, 1 H, H-6'b), 3.86 (dt, 1 H, $J_{5,6'}$ 6.8 Hz, H-5c), 3.79–3.65 (m, 3 H, H-2a,2b,4b), 3.61 (dd, 1 H, H-6a), 3.47 (dt, 1 H, H-5a), 3.44–3.34 (m, 2 H, H-6'a,5b), 2.16, 2.15, 2.08, 2.07, 2.05, 2.03, 2.01, 1.97, 1.73 (9 s, 27 H, Ac), and 1.09 (s, 9 H, *t*-Bu); FD-MS: m/z 1144.7 $(M+1)^+$. Anal. Calcd for $C_{52}H_{68}N_4O_{23}Si$: C, 54.54; H, 5.98; N, 4.89. Found: C, 54.3; H, 5.9; N, 4.8.

O-*(2,3,4,6-Tetra*-O-*acetyl*-β-D-*galactopyranosyl)*-*(1→4)*-O-*(2-acetamido-3,6-di*-O-*acetyl-2-deoxy*-β-D-*glucopyranosyl)*-*(1→6)*-*3,4-di*-O-*acetyl-2-azido-2-deoxy*-β-D-*galactopyranose* (**19**).—Compound **18** (0.592 g, 0.52 mmol) was desilylated as described for synthesis of compound **9**, and the product was purified by chromatography on silica gel using 99:1 CH_2Cl_2–MeOH to yield **19** (0.378 g, 0.40 mmol, 81%). Compound **19** NMR data (400 MHz, $CDCl_3$): δ_H 6.13 (d, 1 H, $J_{2,NH}$ 9.3 Hz, N*H*-b), 6.10 (bs, 1 H, OH-1a), 4.85 (d, 1 H, $J_{1,2}$ 6.8 Hz, H-1b), 4.72 (bd, 1 H, $J_{1,2}$ 8.6 Hz, H-1a), and 4.48 (d, 1 H, $J_{1,2}$ 8.3 Hz, H-1c); FD-MS: m/z 906.9 $(M+1)^+$. Anal. Calcd. for $C_{36}H_{50}N_4O_{23} \cdot CH_3OH$: C, 47.34; H, 5.79; N, 5.97. Found: C, 47.27; H, 5.55; N, 5.73.

O-*(2,3,4,6-Tetra*-O-*acetyl*-β-D-*galactopyranosyl)*-*(1→4)*-O-*(2-acetamido-3,6-di*-O-*acetyl-2-deoxy*-β-D-*glucopyranosyl)*-*(1→6)*-O-*(3,4-di*-O-*acetyl-2-azido-2-deoxy*-α-D-*galactopyranosyl)*-*(1→1)*-*3*-O-*benzoyl-2*-N-*[(2R)-2-benzoyloxyalkanoyl]sphinganine* (**21**α) *and* O-*(2,3,4,6-tetra*-O-*acetyl*-β-D-*galactopyranosyl)*-*(1→4)*-O-*(2-acetamido-3,6-di*-O-*acetyl-2-deoxy*-β-D-*glucopyranosyl)*-*(1→6)*-O-*(3,4-di*-O-*acetyl-2-azido-2-deoxy*-β-D-*galactopyranosyl)*-*(1→1)*-*3*-O-*benzoyl-2*-N-*[(2R)-2-benzoyloxyalkanoyl]-sphinganine* (**21**β).—Compound **17** (0.100 g, 0.11 mmol) was converted into **20** (0.091 g, 0.087 mmol, 79%) as described for synthesis of **10**. NMR (200 MHz, $CDCl_3$): δ_H 9.30 (s, 0.5 H, C=N*H*), 8.78 (s, 0.5 H, C=N*H*), 6.40 (d, 0.5 H, $J_{1,2}$ 3.4 Hz, H-1aα), 5.65 (d, 0.5 H, $J_{1,2}$ 7.8 Hz, H-1aβ).

To a stirred mixture of **20** (0.145 g, 0.22 mmol), **11** (0.100 g, 0.11 mmol), and powdered molecular sieves (0.200 g) in 1,2-dichloroethane (2.5 mL) was added TMSiOTf (0.03 mL, 0.16 mmol) at −20°C. The mixture was stirred overnight at room temperature, diluted with $CHCl_3$, and filtered through Celite. The filtrate was washed with aq $NaHCO_3$ and aq NaCl, dried over $MgSO_4$, and concentrated in vacuo. The resulting residue was purified on silica gel using 1:2 hexane–EtOAc to yield a mixture of anomers **21**α and **21**β (0.114 g,

0.065 mmol, 57%). A part of mixture was purified with PLC to separate the anomers. NMR data for **21**α (400 MHz, $CDCl_3$): δ_H 6.88 (d, Cer N*H*), 6.20 (d, 1 H, N*H*-b), 4.93 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1a), 4.54 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1b), 4.49 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1c), 1.30 (m, CH_2), and 0.85 (t, CH_3). NMR data for **21**β (400 MHz, $CDCl_3$): δ_H 7.08 (d, Cer N*H*), 6.15 (d, 1 H, N*H*-b), 4.65 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1b), 4.51 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1c), 4.17 (d, 1 H, $J_{1,2}$ 8.3 Hz, H-1a), 1.30 (m, CH_2), and 0.85 (t, CH_3).

*O-(2,3,4,6-Tetra-*O*-acetyl-β-*D*-galactopyranosyl)-(1→4)-*O*-(2-acetamido-3,6-di-*O*-acetyl-2-deoxy-β-*D*-glucopyranosyl)-(1→6)-*O*-(2-acetamido-3,4-di-*O*-acetyl-2-deoxy-α-*D*-galactopyranosyl)-(1→1)-3-*O*-benzoyl-2-*N*-[(2R)-2-benzoyloxyalkanoyl]sphinganine* (**22**) *and* *O-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-(1→4)-*O*-(2-acetamido-3,6-di-*O*-acetyl-2-deoxy-β-*D*-glucopyranosyl)-(1→6)-2-acetamido-3,4-di-*O*-acetyl-2-deoxy-β-*D*-galactopyranosyl)-(1→1)-3-*O*-benzoyl-2-*N*-[(2R)-2-benzoyloxyalkanoyl]-sphinganine* (**23**).—A mixture of compounds **21**α and **21**β (0.026 g, 0.015 mmol) was dissolved in a solution of $NiCl_2 \cdot 6H_2O$ (0.056 g, 0.24 mmol) and H_3BO_3 (28 mg, 0.45 mmol) in EtOH (1.4 mL). To this solution was added $NaBH_4$ (0.014 g, 0.37 mmol) at room temperature. The mixture was stirred for 1 h at room temperature, AcOH and EtOH were added, and the solvents were evaporated in vacuo. The residue was dissolved in pyridine and Ac_2O, and the mixture was stirred overnight at room temperature, diluted with MeOH, and concentrated in vacuo. The residue was dissolved in $CHCl_3$, the organic layer was washed with aq $NaHCO_3$ and aq NaCl, dried over $MgSO_4$, and concentrated in vacuo. The resulting residue was purified on silica gel using 1:2 hexane–EtOAc, and then by HPLC on a TOSOH Silica-60 column (25 cm×4.6 mm) using EtOAc at a flow rate of 1 mL/min to yield compounds **22** (0.005 g, 0.0028 mmol) and **23** (0.004 g, 0.0022 mmol) (19% and 15%, respectively, from the mixture **21**α+**21**β). NMR data for **22** (400 MHz, $CDCl_3$): δ_H 6.80 (d, 1 H, *J* 9.8 Hz, Cer N*H*), 6.06 (d, 1 H, $J_{2,NH}$ 9.8 Hz, N*H*-a), 5.89 (d, 1 H, $J_{2,NH}$ 8.8 Hz, N*H*-b), 5.49 (t, 1 H, Cer H-2′), 5.35–5.27 (m, 2 H, H-4c, Cer H-3), 5.13 (dd, 1 H, H-3b), 5.06 (dd, 1 H, H-2c), 4.93 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3c), 4.85 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3a), 4.76 (dd, 1 H, H-4a), 4.55 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1a), 4.48 (d, 1 H, $J_{1,2}$ 6.8 Hz, H-1b), 4.47 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1c), 4.50–4.40 (m, 3 H, H-2a,6b, Cer H-2), 4.16–4.00 (m, 3 H, H-6′b,6c,6′c), 3.84 (dt, 1 H, H-5c), 3.80–3.67 (m, 4 H, H-5a,2b,4b, Cer H-1A), 3.58 (m, 1 H, H-5b), 3.35 (dd, 1 H, Cer H-1B), 3.33 (dd, 1 H, H-6a), 3.26 (dd, 1 H, H-6′a), 2.18, 2.17, 2.10, 2.09, 2.08, 2.03, 1.98, 1.85 (8 s, 30 H, Ac), 1.25 (m, CH_2), and 0.88 (t, CH_3).

NMR data for **23** (400 MHz, $CDCl_3$): δ_H 7.10 (d, 1 H, *J* 8.1 Hz, Cer N*H*), 6.11 (d, 1 H, $J_{2,NH}$ 9.3 Hz, N*H*-b), 5.67 (d, 1 H, $J_{2,NH}$ 8.3 Hz, N*H*-a), 5.37 (t, 1 H, Cer H-2′), 5.34 (dd, 1 H, H-4c), 5.25 (dd, 1 H, H-4a), 5.22–5.15 (m, 3 H, H-3a,3b, Cer H-3), 5.11 (dd, 1 H, $J_{2,3}$ 10.3 Hz, H-2c), 4.97 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3c), 4.71 (d, 1 H, $J_{1,2}$ 8.3 Hz, H-1a), 4.57 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1b), 4.49 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1c), 4.47 (dd, 1 H, H-6b), 4.41 (m, 1 H, Cer H-2), 4.15–4.03 (m, 3 H, H-6′b,6c,6′c), 3.92–3.80 (m, 3 H, H-2b,5c, Cer H-1A), 3.79–3.50 (m, 7 H, H-2a,5a,6a,6′a,4b,5b, Cer H-1B), 2.18, 2.13, 2.08, 2.06, 2.05, 1.90, 1.88, 1.86 (8 s, 30 H, Ac), 1.25 (m, CH_2), and 0.88 (t, CH_3).

*O-β-*D*-Galactopyranosyl-(1→4)-*O*-(2-acetamido-2-deoxy-β-*D*-glucopyranosyl)-(1→6)-*O*-(2-acetamido-2-deoxy-α-*D*-galactopyranosyl)-(1→1)-2-*N*-[(2R)-2-hydroxyalkanoyl]sphinganine* (**2**).—Compound **22** (0.020 g, 11.2 μmol) was converted into **2** (0.010 g, 8.09 μmol, 72%) as described for the synthesis of **1**. NMR (400 MHz, 2:1

$CDCl_3$–CD_3OD): δ_H 4.52 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1a), 4.19 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1b), 4.11 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1c), 3.96 (dd, 1 H, H-2a), 3.79 (dd, 1 H, Cer H-2′), 3.74 (dd, 1 H, H-6c), 3.69 (m, 1 H, Cer H-2), 3.67–3.52 (m, 6 H, H-4a,5a,6b,6′b,5c, Cer H-1A), 3.51–3.37 (m, 5 H, H-3a,6a,2b,3b,6′c), 3.36–3.27 (m, 5 H, H-6′a,4b,2c, Cer H-1B, 3), 3.26 (dd, 1 H, H-3c), 3.17 (m, 1 H, H-5b), 1.79, 1.75 (2 s, 6 H, Ac), 1.08 (m, CH_2), and 0.63 (t, CH_3).

O-*β*-D-*Galactopyranosyl-(1→4)*-O-*(2-acetamido-2-deoxy-β*-D-*glucopyranosyl)-(1→6)*-O-*(2-acetamido-2-deoxy-β*-D-*galactopyranosyl)-(1→1)-2*-N-*[(2R)-2-hydroxyalkanoyl]sphinganine* (**24**).—Compound **23** (0.020 g, 11.2 μmol) was converted into **24** (0.002 g, 1.62 μmol, 14%) as described for synthesis of **15**. NMR (400 MHz, 2:1 $CDCl_3$–CD_3OD): δ_H 4.20 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1b), 4.09 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1c), 4.07 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1a), 1.73, 1.70 (2 s, 6 H, Ac), 0.99 (m, CH_2), and 0.57 (t, CH_3).

tert-*Butyldiphenylsilyl* O-*(2,3,4,6-tetra*-O-*acetyl-β*-D-*galactopyranosyl)-(1→4)*-O-*(3,6-di*-O-*acetyl-2-deoxy-2-phthalimido-β*-D-*glucopyranosyl)-(1→3)*-O-*[*O-*(2,3,4,6-tetra*-O-*acetyl-β*-D-*galactopyranosyl)-(1→4)-(3,6-di*-O-*acetyl-2-deoxy-2-phthalimido-β*-D-*glucopyranosyl)-(1→6)]-2-azido-2-deoxy-β*-D-*galactopyranoside* (**25**).—To a stirred mixture of compound **5** (0.272 g, 0.31 mmol), **7** (0.334 g, 0.29 mmol), and molecular sieves AW-300 (0.80 g) in 1,2-dichloroethane (6 mL) was added M $BF_3 \cdot Et_2O$ (0.06 mL) at −20°C. The mixture was stirred for 2 h at −20°C. The suspension was filtered, and the solids were washed with $CHCl_3$. The filtrate was washed with aq $NaHCO_3$ and aq NaCl, and the organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by chromatography on silica gel using 3:1 toluene–EtOAc to afford compound **25** (0.123 g, 0.066 mmol, 23%) and mixture of compounds **5** and **25** (0.245 g). NMR data for **25** (400 MHz, $CDCl_3$): δ_H 5.58 (dd, 1 H, $J_{2,3}$ 10.8, $J_{3,4}$ 8.3 Hz, H-3b′), 5.46 (dd, 1 H, $J_{2,3}$ 11.2, $J_{3,4}$ 8.8 Hz, H-3b), 5.35 (dd, 1 H, H-4c), 5.34 (dd, 1 H, H-4c′), 5.28 (d, 1 H, $J_{1,2}$ 8.3 Hz, H-1b′), 5.16 (dd, 1 H, $J_{2,3}$ 10.3 Hz, H-2c), 5.14 (dd, 1 H, $J_{2,3}$ 10.2 Hz, H-2c′), 4.97 (dd, 1 H, $J_{3,4}$ 3.9 Hz, H-3c), 4.96 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3c′), 4.95 (d, 1 H, $J_{1,2}$ 8.3 Hz, H-1b), 4.54 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1c′), 4.48 (dd, 1 H, H-6b′), 4.45 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1c), 4.22 (dd, 1 H, H-6b), 4.17–3.98 (m, 8 H, H-2b,6′b,2b′,6′b′,6c,6′c,6c′,6′c′), 4.12 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1a), 3.91–3.80 (m, 4 H, H-6a,4b,5c,5c′), 3.83 (dd, 1 H, $J_{4,5}$ 8.8 Hz, H-4b′), 3.78 (m, 1 H, H-5b′), 3.54 (dd, 1 H, $J_{4,5}$ 0.5 Hz, H-4a), 3.38 (dd, 1 H, $J_{5,6'}$ 4.4, $J_{6,6'}$ 10.7 Hz, H-6′a), 3.45 (dd, 1 H, $J_{2,3}$ 10.3 Hz, H-2a), 3.04 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3a), 2.98 (dd, 1 H, $J_{5,6'}$ 8.8 Hz, H-5a), 2.75 (m, 1 H, H-5b), and 0.95 (s, 9 H, *t*-Bu). Anal. Calcd for $C_{86}H_{99}N_5O_{39}Si \cdot 0.5$toluene: C, 56.55; H, 5.46; N, 3.68. Found: C, 56.30; H, 5.90; N, 3.18.

tert-*Butyldiphenylsilyl* O-*(2,3,4,6-tetra*-O-*acetyl-β*-D-*galactopyranosyl)-(1→4)*-O-*(2-acetamido-3,6-di*-O-*acetyl-2-deoxy-β*-D-*glucopyranosyl)-(1→3)*-O-*[*O-*(2,3,4,6-tetra*-O-*acetyl-β*-D-*galactopyranosyl)-(1→4)-(2-acetamido-3,6-di*-O-*acetyl-2-deoxy-β*-D-*glucopyranosyl)-(1→6)]-4*-O-*acetyl-2-azido-2-deoxy-β*-D-*galactopyranoside* (**26**).—Compound **25** (0.132 g, 0.070 mmol) was converted into **26** (0.082 g, 0.048 mmol, 68%) as described for the synthesis of **8**. Compound **26** had NMR data (400 MHz, $CDCl_3$): δ_H 5.48 (d, 1 H, *J* 9.8 Hz, N*H*-b′), 5.34 (m, 2 H, H-4c,4c′), 5.30 (d, 1 H, *J* 9.3 Hz, N*H*-b), 5.18 (d, 1 H, $J_{3,4}$ 3.4 Hz, H-4a), 5.12 (dd, 1 H, $J_{2,3}$ 10.3 Hz, H-2c), 5.10 (dd, 1 H, $J_{2,3}$ 10.8 Hz, H-2c′), 5.04 (dd, 1 H, $J_{3,4}$ 8.8, $J_{4,5}$ 10.2 Hz, H-3b), 5.01 (dd, 1 H, $J_{2,3}$ 10.2, $J_{3,4}$ 9.3 Hz, H-3b′), 4.98–4.93 (m, 2 H, H-3c,3c′), 4.67 (dd, 1 H, H-6b′), 4.54 (d, 1 H, $J_{1,2}$ 8.3 Hz, H-

1b′), 4.53 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1c′), 4.46 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1c), 4.41 (dd, 1 H, H-6b), 4.34 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1a), 4.30 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1b), 4.14–4.05 (m, 4 H, H-6c,6′c,6c′,6′c′), 4.03 (dd, 1 H, H-6′b), 3.98–3.92 (m, 2 H, H-2b′,6′b′), 3.90–3.85 (m, 2 H, H-5c,5c′), 3.82 (dd, 1 H, $J_{4,5}$ 9.3 Hz, H-4b′), 3.70–3.59 (m, 3 H, H-5a,2b,4b), 3.62 (d, 1 H, $J_{2,3}$ 10.2 Hz, H-2a), 3.45–3.33 (m, 5 H, H-3a,6a,6′a,5b,5b′), and 1.10 (s, 9 H, *t*-Bu). Anal. Calcd for $C_{76}H_{101}N_5O_{38}Si$: C, 53.05; H, 5.91; N, 4.07. Found: C, 52.83; H, 5.97; N, 4.06.

O-(2,3,4,6-Tetra-O-acetyl-β-D-galactopyranosyl)-(1→4)-O-(2-acetamido-3,6-di-O-acetyl-2-deoxy-β-D-glucopyranosyl)-(1→3)-O-[O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-(1→4)-(2-acetamido-3,6-di-O-acetyl-2-deoxy-β-D-glucopyranosyl)-(1→6)]-4-O-acetyl-2-azido-2-deoxy-α,β-D-galactopyranose (**27**).—Compound **26** (0.120 g, 0.070 mmol) was desilylated to **27** as described for the conversion of **8** into **9**. The yield of **27** was 0.085 g (0.052 mmol, 85% based on **26** consumed). NMR (400 MHz, $CDCl_3$): δ_H 4.85 (d, 0.5 H, $J_{1,2}$ 3.5 Hz, H-1aα), 4.53 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1b′), 4.53 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1b), 4.48 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1c′), 4.44 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1c), and 4.29 (d, 0.5 H, $J_{1,2}$ 8.2 Hz, H-1aβ). Anal. Calcd for $C_{60}H_{83}N_5O_{38}\cdot 3C_2H_5OH$: C, 48.92; H, 6.28; N, 4.32. Found: C, 49.09; H, 6.68; N, 4.30.

O-(2,3,4,6-Tetra-O-acetyl-β-D-galactopyranosyl)-(1→4)-O-(2-acetamido-3,6-di-O-acetyl-2-deoxy-β-D-glucopyranosyl)-(1→3)-O-[O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-(1→4)-(2-acetamido-3,6-di-O-acetyl-2-deoxy-β-D-glucopyranosyl)-(1→6)]-O-(4-O-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl)-(1→1)-3-O-benzoyl-2-N-[(2R)-2-benzoyloxyalkanoyl]sphinganine (**29α**) *and O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-(1→4)-O-(2-acetamido-3,6-di-O-acetyl-2-deoxy-β-D-gluco-pyranosyl)-(1→3)-O-[O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-(1→4)-(2-acetamido-3,6-di-O-acetyl-2-deoxy-β-D-glucopyranosyl)-(1→6)]-O-(4-O-acetyl-2-azido-2-deoxy-β-D-galactopyranosyl)-(1→1)-3-O-benzoyl-2-N-[(2R)-2-benzoyloxyalkanoyl]-sphinganine* (**29β**).—The above preparation of **27** was converted into the trichloroacetimidate **28** as described for the transformation of **9** into **10**. NMR data for **28** (200 MHz, $CDCl_3$): δ_H 9.25 (s, 0.5 H, C=N*H*β), 8.79 (s, 0.5 H, C=N*H*α), 5.30 (d, 0.5 H, $J_{1,2}$ 3.5 Hz, H-1aα), 5.23 (d, 0.5 H, $J_{1,2}$ 8.2 Hz, H-1aβ), 4.55 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1b′), 4.49 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1b), 4.63 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1c′), and 4.60 (d, 1 H, $J_{1,2}$ 8.6 Hz, H-1c).

To a stirred mixture of **28** (0.082 g, 0.050 mmol), **11** (0.050 g, 0.057 mmol), and powdered molecular sieves (0.100 g) in 1,2-dichloroethane (2.0 mL) was added 0.1 M TMSiOTf in 1,2-dichloroethane (0.5 mL, 0.05 mmol) at −5°C. The mixture was stirred for 1.5 h, diluted with $CHCl_3$, and filtered through Celite. The filtrate was washed with aq $NaHCO_3$ and aq NaCl, dried over $MgSO_4$, and concentrated in vacuo. The resulting residue was purified on silica gel using 4:1 CH_2Cl_2–acetone to afford a mixture of compounds **29α** and **29β** (0.029 g, 0.012 mmol, 25%). NMR (400 MHz, $CDCl_3$): δ_H 4.83 (d, 0.67 H, $J_{1,2}$ 3.4 Hz, H-1aα), 4.63 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1b), 4.58 (d, 0.33 H, $J_{1,2}$ 7.8 Hz, H-1aβ), 4.52 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1c′), 4.49 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1c), 4.23 (d, 1 H, $J_{1,2}$ 8.3 Hz, H-1b′), 1.22 (m, C*H*$_2$), and 0.86 (t, C*H*$_3$).

O-(2,3,4,6-Tetra-O-acetyl-β-D-galactopyranosyl)-(1→4)-O-(2-acetamido-3,6-di-O-acetyl-2-deoxy-β-D-glucopyranosyl)-(1→3)-O-[O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-(1→4)-(2-acetamido-3,6-di-O-acetyl-2-deoxy-β-D-glucopyranosyl)-(1→6)]-O-(2-acetamido-4-O-acetyl-2-deoxy-α-D-galactopyranosyl)-(1→1)-3-O-benzoyl-2-N-

[(2R)-2-benzoyloxyalkanoyl]sphinganine (**30**) *and* O-*(2,3,4,6-tetra*-O-*acetyl-β*-D-*galactopyranosyl)-(1→4)*-O-*(2-acetamido-3,6-di*-O-*acetyl-2-deoxy-β*-D-*glucopyranosyl)-(1→3)*-O-*[*O-*(2,3,4,6-tetra*-O-*acetyl-β*-D-*galactopyranosyl)-(1→4)-(2-acetamido-3,6-di*-O-*acetyl-2-deoxy-β*-D-*glucopyranosyl)-(1→6)]*-O-*(2-acetamido-4*-O-*acetyl-2-deoxy-β*-D-*galactopyranosyl)-(1→1)-3*-O-*benzoyl-2*-N-*[(2R)-2-benzoyloxy-alkanoyl]sphinganine* (**31**).—A mixture of compounds **29**α and **29**β (38 mg, 0.016 mmol) was converted into **30** (19 mg, 0.008 mmol) and **31** (9 mg, 0.004 mmol) (50% and 24%, respectively, from the mixed precursor) as described for the synthesis of **13** and **14**. Compound **30** had NMR data (400 MHz, $CDCl_3$): δ_H 5.39–5.31 (m, 3 H, H-4c,4c', Cer H-2'), 5.31–5.24 (m, 1 H, Cer H-3), 5.24–5.03 (m, 5 H, H-4a,3b,3b',2c,2c'), 5.03–4.90 (m, 2 H, H-3c,3c'), 4.66 (d, 1 H, $J_{1,2}$ 3.0 Hz, H-1a), 4.65–4.42 (m, 3 H, H-6b,6b', Cer H-2), 4.56 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1b'), 4.52 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1b), 4.49 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1c), 4.49 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1c'), 4.35 (dd, 1 H, H-2a), 4.19–3.96 (m, 6 H, H-6'b,6'b',6c,6'c,6c',6'c'), 3.94–3.60 (m, 10 H, H-3a,6a,6'a,2b,4b,2b',4b',5c,5c', Cer H-1A), 3.59–3.46 (m, 2 H, H-5b,5b'), 3.36–3.26 (m, 2 H, H-5a, Cer H-1B), 1.30 (m, CH_2), and 0.90 (t, CH_3).

NMR data for **31**: δ_H 6.84 (d, 1 H, *J* 8.0 Hz, Cer N*H*), 6.36 (d, 1 H, N*H*-b'), 6.34 (d, 1 H, *J* 8.4 Hz, N*H*-a), 5.79 (d, 1 H, N*H*-b), 5.28 (dd, 2 H, $J_{4,5}$ 0.4 Hz, H-4c,4c'), 5.26–5.16 (m, 2 H, H-3b', Cer H-2'), 5.22 (dd, H-4a), 5.14 (m, 1 H, Cer H-3), 5.06 (dd, 1 H, $J_{2,3}$ 10.4 Hz, H-2c'), 5.04 (dd, 1 H, $J_{2,3}$ 10.4 Hz, H-2c), 4.91 (m, 1 H, H-3b), 4.90 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3c), 4.89 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3c'), 4.73 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1a), 4.55 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1b'), 4.53 (dd, 1 H, H-6b), 4.45 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1b), 4.45 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1c'), 4.43 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1c), 4.48–4.35 (m, 2 H, H-3a,6b'), 4.28 (m, 1 H, Cer H-2), 4.10–3.98 (m, 5 H, H-6'b',6c,6'c,6c',6'c'), 3.95 (dd, 1 H, H-6'b), 3.91–3.50 (m, 11 H, H-6a,6'a,2b,4b,2b',4b',5b',5c,5c', Cer H-1A,1B), 3.48–3.34 (m, 2 H, H-5a,5b), 3.05 (m, 1 H, H-2a), 1.19 (m, CH_2), and 0.80 (t, CH_3).

O-*β*-D-*Galactopyranosyl-(1→4)*-O-*(2-acetamido-2-deoxy-β*-D-*glucopyranosyl)-(1→3)*-O-*[*O-*β*-D-*galactopyranosyl-(1→4)-(2-acetamido-2-deoxy-β*-D-*glucopyranosyl)-(1→6)]*-O-*(2-acetamido-2-deoxy-α*-D-*galactopyranosyl)-(1→1)-2*-N-*[(2R)-2-hydroxy-alkanoyl]sphinganine* (**3**).—Compound **30** (0.008 g, 3.5 μmol) was converted into **3** (0.004 g, 2.7 μmol, 75%) as described for synthesis of **1**. Compound **3** had NMR (400 MHz, Me_2SO-d_6): δ_H 4.63 (d, 1 H, $J_{1,2}$ 3.0 Hz, H-1a), 4.57 (d, 1 H, $J_{1,2}$ 8.5 Hz, H-1b'), 4.31 (d, 1 H, $J_{1,2}$ 7.0 Hz, H-1b), 4.20 (d, 2 H, $J_{1,2}$ 7.5 Hz, H-1c,1c'), 4.08 (dd, 1 H, $J_{2,3}$ 11.0 Hz, H-2a), 1.85, 1.81, 1.78 (3 s, 9 H, Ac), 1.22 (m, CH_2), and 0.85 (t, CH_3).

O-*β*-D-*Galactopyranosyl-(1→4)*-O-*(2-acetamido-2-deoxy-β*-D-*glucopyranosyl)-(1→3)*-O-*[*O-*β*-D-*galactopyranosyl-(1→4)-(2-acetamido-2-deoxy-β*-D-*glucopyranosyl)-(1→6)]*-O-*(2-acetamido-2-deoxy-β*-D-*galactopyranosyl)-(1→1)-2*-N-*[(2R)-2-hydroxy-alkanoyl]sphinganine* (**32**).—Compound **31** (0.008 g, 3.5 μmol) was converted into **32** (0.004 g, 2.7 μmol, 75%) as described for synthesis of **15**. Compound **32** had NMR (400 MHz, Me_2SO-d_6): δ_H 4.57 (d, 1 H, $J_{1,2}$ 8.3 Hz, H-1b'), 4.40 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1b), 4.27 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1a), 4.23 (d, 2 H, $J_{1,2}$ 7.0 Hz, H-1c,1c'), 1.83, 1.81, 1.80 (3 s, 9 H, Ac), 1.23 (m, CH_2), and 0.84 (t, CH_3).

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