Pergamon

Bioorganic & Medicinal Chemistry, Vol. 4, No. 11, pp 1833–1847, 1996

PII: S0968-0896(96)00165-4
0968-0896/96 $15.00+0.00

Synthesis And Biological Activities of Three Sulfated Sialyl Le^x Ganglioside Analogues for Clarifying the Real Carbohydrate Ligand Structure of L-Selectin†

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Abstract—Sulfated sialyl Le^x ganglioside analogues at C-6 of D-galactose, *N*-acetyl-D-glucosamine, and of both D-galactose and *N*-acetyl-D-glucosamine residues have been synthesized, in order to clarify the structure of the real carbohydrate ligand of L-selectin. Coupling of the suitably protected *N*-acetyl-D-glucosaminyl-β(1→3)-lactose derivatives **13** and **16** with the sialyl α(2→3)-D-galactopyranosyl trichloroacetimidates **10** and **12** (glycosyl donors), via glycosylation of 2-(trimethylsilyl)ethyl 4,6-*O*-benzylidene-β-D-galactopyranoside (**1**) with the phenyl 2-thioglycoside derivative (**2**) of *N*-acetylneuraminic acid (Neu5Ac) using *N*-iodosuccinimide/TfOH, *O*-benzoylation, removal of the benzylidene group affording **5**, selective 6-*O*-levulinoylation, *O*-benzoylation, removal of the 2-(trimethylsilyl)ethyl group, and imidate formation, or via *O*-acetylation of **5**, removal of the 2-(trimethylsilyl)ethyl group, then imidate formation, gave the pentasaccharides **18–20**. The glycosylation of the pentasaccharide acceptors (**21–23**) derived from **18–20** by removal of the 4-methoxybenzyl group, with phenyl 1-thioglycoside derivative **27** of L-fucose using dimethyl(methylthio)sulfonium triflate (DMTST) afforded the corresponding hexasaccharides **28–30**, which were transformed in good yields, via reductive removal of their benzyl groups, *O*-acetylation, selective removal of the 2-(trimethylsilyl)ethyl group, imidate formation, coupling with (2*S*,3*R*,4*E*)-2-azido-*O*-benzoyl-4-octadecene-1,3-diol (**35**) in the presence of boron trifluoride etherate, selective reduction of the azido group, coupling with octadecanoic acid, selective removal of the levulinoyl groups, treatment with sulfur trioxide–pyridine complex, then removal of the protecting groups, into the desired sulfated sialyl Le^x ganglioside analogues **50–52**. Copyright © 1996 Elsevier Science Ltd

Introduction

Selectins (E-, P-, and L-)[2–8] are a class of recently discovered cell adhesion molecules which act to localize spatially and temporally the binding of specific leukocytes to certain vascular endothelial cells. All selectins possess a similar arrangement of their protein parts which are calcium-dependent lectin domains, an epidermal growth factor domain and a discrete number of sequence modules similar to those found in complement-binding proteins. The lectin domains of selectins mediate cell adhesion through recognition and binding of cell-specific oligosaccharide ligands on a variety of glycoconjugates such as glycoproteins, gangliosides and glycosaminoglycans. Although each selectin may have its own optimum carbohydrate ligand, there is now general agreement that all three selectins can efficiently recognize sialyl Lewis x (sLe^x), sialyl Lewis^a (sLe^a), and structurally related Lewis blood group oligosaccharides.[9] It has been known[10–19] that L- and P-selectins can efficiently bind to sulfated carbohydrates such as fucoidan, sulfatides, sulfated glucuronic acid (HNK-1) epitope, heparin, and sulfo-Le^x-like structures. In order to clarify (the structure of) the real carbohydrate ligands for each selectin, we have synthesized[20–26] a variety of sialylated, sulfated and phosphated Le^x and Le^a oligosacharides and their analogues. L-selectin has been discovered as a lymphocyte homing receptor involved in the binding of lymphocytes to the high endothelial venules of limph nodes. One of the endothelial-derived ligands for L-selectin is GlyCAM-1, a mucin-like glycoprotein with sulfated, sialylated, and fucosylated oligosaccharides. Very recently, Rosen and co-workers[27–30] have isolated the presence of sulfated Gal and GlcNAc residues at C-6, and Galβ(1→4)6-*O*-sulfo-GlcNAc and 6-*O*-sulfo-Galβ(1→4)GlcNAc by a mild hydrolysis of GlyCAM-1, and suggested that sulfated sLe^x structure may comprise a recognition determinant on GlyCAM-1. On the other hand, Jacob and co-workers[31a] have enzymatically synthesized a 6-*O*-sulfo-Galβ(1→4)GlcNAc residue containing sLe^x-pentasaccharide and compared its inhibition ability with L-selectin binding with an sLe^x tetrasaccharide, and it displayed a stronger activity. Very recently, Matta and co-workers[31b,c] have chemically synthesized 6-*O*-sulfo-Galβ(1→4)GlcNAc residue containing sLe^a and sLe^x oligosaccharides.

In view of these facts, and as a part of our continuing efforts on the chemical synthesis, biological functions, structural determination of carbohydrate ligands of cell-adhesion molecules, and for the development of the selectin blocker, we describe herein the synthesis of the sulfated sLe^x ganglioside analogues at C-6 of the Gal or GlcNAc, and of both Gal and GlcNAc residues, for clarifying the structure of the real carbohydrate ligand of L-selectin, and their binding activities not only to L-selectin but also to E- and P-selectins.

†Synthetic Studies on Sialoglycoconjugates. Part 87. For Part 86, see ref. 1.

Results and Discussion

For the synthesis of the three desired, sulfated sLe^x gangliosides **50–52**, the core oligosaccharides **21–23** were selected as the glycosyl acceptors. Compounds **21–23** each have a free hydroxy group at C-3 of the GlcNAc residue for α-fucosylation, and also levulinoyl groups at the desired positions and provide selectively the free hydroxy group at C-6 of the Gal (d) or GlcNAc, and of both Gal and GlcNAc residues for further sulfation.

The glycosyl acceptors **21–23** were prepared as follows: glycosylation[32] of 2-(trimethylsilyl)ethyl 4,6-*O*-benzylidene-β-D-galactopyranoside (**1**)[33] with the phenyl 2-thioglycoside derivative (**2**)[34] (1.5 equiv., relative to the acceptor) of *N*-acetylneuraminic acid (Neu5Ac) in acetonitrile for 3 h at −30 °C in the presence of *N*-iodosuccinimide (NIS;[32c,35] 2.3 equiv., relative to the donor) trifluoromethanesulfonic acid (TfOH), gave the expected α-glycoside **3** in 65% yield. The observed chemical shift and coupling constants [δ 2.75, $J_{gem}=12.6$, $J_{3(eq),4}=4.4$ Hz, 4.88 (m) and 5.35 ($J_{6,7}=1.2$, $J_{7,8}=8.0$ Hz] for H-3*eq*, H-4, and H-7 in the Neu5Ac moiety are characteristic for α-glycosidic linkages.[36]

Treatment of **3** with benzoic anhydride in the presence of 4-dimethylaminopyridine afforded the 2-benzoate **4** in 86% yield, which was converted *via* reductive removal (**5**, 94%) of the benzylidene group (10% Pd-C), selective 6-*O*-levulinoylation (**6**, 85%) with levulinic anhydride in pyridine in the presence of 4-dimethylaminopyridine at −50 °C, and 4-*O*-benzoylation into 2-(trimethylsilyl)ethyl *O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-galacto-2-nonulopyranosylonate)-(2→3)-2,4-di-*O*-benzoyl-6-*O*-levulinoyl-β-D-galactopyranoside (**7**, 82%). Acetylation of **5** gave the 4,6-di-*O*-acetate **8** (91%), which was used for the synthesis of a sulfated sLe^x ganglioside at C-6 of the GlcNAc residue. Compounds **7** and **8** were transformed into the corresponding trichloroacetimidates **10** and **12** in good yields by selective removal[20a,33] of the 2-(trimethylsilyl)ethyl group with trifluoroacetic acid and subsequent imidate formation.[37]

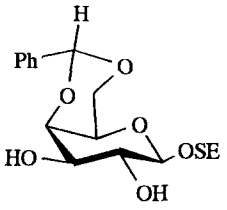
The glycosylation of **13**[38] or **16** derived from **14**[38] by reductive removal (**15**, 82%) of the benzylidene group followed by selective levulinoylation in 81% yield, with **10** in dichloromethane in the presence of TMS-triflate for 12 h at 7 °C, afforded the corresponding pentasaccharides **18** (50%) and **20** (45%), respectively. In essentially the same way, coupling of **12** and **16** gave pentasaccharide **19** in 77% yield. The β-configurations of **18**, **19**, and **20** were assigned from their ^{1}H NMR data that showed the signals at δ 5.46 (t, 1H, $J_{1,2}=J_{2,3}=8.1$ Hz, **18**), 5.36 (t, 1H, $J_{1,2}=J_{2,3}=8.4$ Hz, **19**), and 5.46 (dd, 1H, $J_{1,2}=9.9$, $J_{2,3}=7.7$ Hz, **20**) for H-2d of the obtained pentasaccharides. Removal of the 4-methoxybenzyl group in **18–20** in acetonitrile–water in the presence of ceric ammonium nitrate (CAN)[25d,39] for 1–3 h at room temperature afforded the desired glycosyl acceptors **21** (98%), **22** (90%), and **23** (68%), respectively. The glycosylation of **21**, **22**, or **23** was effected with phenyl 2,3,4-tri-*O*-benzyl-1-thio-β-L-fucopyranoside **27** which was newly prepared from tetra-*O*-acetyl-β-L-fucopyranose via replacement of the anomeric acetoxy group with a phenylthio group using thiophenol in the presence of boron trifluoride etherate, *O*-deacetylation with sodium methoxide in methanol, and subsequent *O*-benzylation with benzyl bromide in the presence of sodium hydride in *N*,*N*-dimethylformamide (DMF). Reaction in the presence of dimethyl(methylthio)sulfonium triflate (DMTST)[32a,40] and molecular sieves 4 Å (MS-4 Å) in benzene for 48–72 h at 7 °C gave the desired hexasaccharides **28** (58%), **29** (90%), and **30** (50%), respectively, showing in their ^{1}H NMR spectra, signals at δ 5.15 (d, $J_{1,2}=3.6$ Hz, H-1f of **28**), 5.03 (d, $J_{1,2}=3.3$ Hz, H-1f of **29**) and 5.17 (d, $J_{1,2}=3.5$ Hz, H-1f of **30**), characteristic of the α-fucopyranosyl unit.

Removal of the benzyl groups from **28**, **29**, and **30** by catalytic hydrogenolysis over 10% Pd-C in ethanol:acetic acid (5:1) for 24–40 h at 40 °C, and subsequent acetylation gave the per-*O*-acylated hexasaccharide **31** (89%), **32** (94%), and **33** (82%), respectively. Selective removal of the 2-(trimethylsilyl)ethyl group from **31**, **32**, and **33** as described in the preparation of **9** gave the corresponding 1-hydroxy compounds which, on treatment[37] with trichloroacetonitrile in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) for 2 h at 0 °C, gave the corresponding α-trichloroacetimidates **34** (91%), **38** (98%), and **41** (89%), respectively.

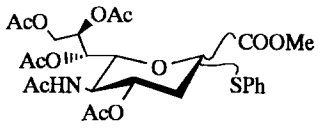
The ^{1}H NMR spectra of these compounds showed signals at δ 6.47 (d, 1H, $J_{1,2}=3.5$–3.7 Hz, H-1a) and 8.65–8.67 (s, 1H, C=NH), indicating the trichloroacetimidates to be α. The final glycosylation[41,42a] of (2*S*,3*R*,4*E*)-2-azido-3-*O*-benzoyl-4-octadecene-1,3-diol (**35**)[42] with **34**, **38**, or **41** thus obtained, in dichloromethane for 5 h at 0 °C in the presence of boron trifluoride etherate and MS-4 Å, gave only the expected β-glycosides **36** (63%), **39** (58%), and **42** (48%), respectively. The ^{1}H NMR spectra of **36**, **39**, and **42** showed a one-proton doublet at δ 4.43 ~ 4.49 ($J_{1,2}=7.0$ ~ 7.7 Hz, H-1a), showing the newly formed glycosidic linkages to be β. Selective reduction[37b,43] of the azido group in **36**, **39**, or **42** with hydrogen sulfide in aq. 83% pyridine for 72 h at 0 °C, and subsequent condensation with octadecanoic acid using 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (water-soluble carbodiimide, WSC) in dichloromethane, furnished the corresponding ganglioside derivatives **37** (54%), **40** (60%), and **43** (60%). Selective removal[25a,44] of the levulinoyl group from **37**, **40**, or **43** was carried out in ethanol with hydrazine monoacetate at room temperature to give **44** (70%), **46** (50%), and **48** (49%), respectively. Treatment[25a] of compounds **44**, **46**, or **48** with sulfur trioxide–pyridine complex in DMF for 2 ~ 4 h at room temperature afforded the corresponding sulfates **45** (98%), **47** (91%), and **49** (91%) as their pyridine salts. *O*-Deacylation of **45**, **47**, or **49** with sodium methoxide in methanol, with subsequent saponification of the sialic acid methyl ester group, yielded the desired sulfated sLe^x gangliosides **50–52** in almost quantitative yields as

their sodium salts. FABMS spectra (negative ion mode) showed the base peaks at *m/z* $(M-Na)^-$ 1794 and $(M-2Na)^{2-}$ 1771 for **50** and **51**, and *m/z* $(M-Na)^-$ 1896 for **52**.

This work reports the first stereocontrolled synthesis of the sulfated sLe^x ganglioside analogues which will be candidate structures for the L-selectin ligand, using the selectively levulinoylated pentasaccharide acceptors **21**,



1



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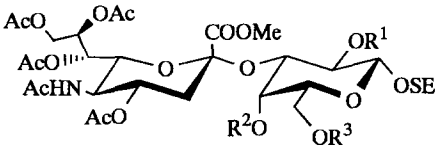
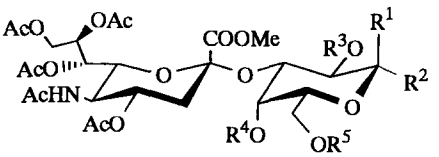
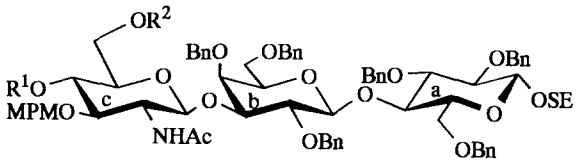


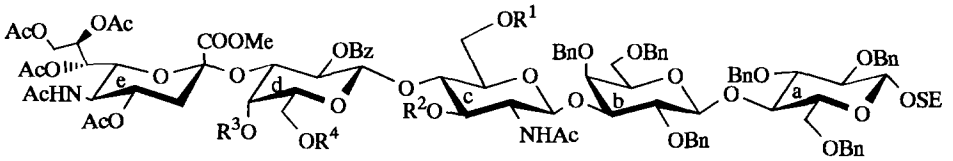
	R^1	R^2	R^3
3	H	benzylidene	
4	Bz	benzylidene	
5	Bz	H	H
6	Bz	H	Lev
7	Bz	Bz	Lev
8	Bz	Ac	Ac



	R^1	R^2	R^3	R^4	R^5
9	OH, H		Bz	Bz	Lev
10	$OC(=NH)CCl_3$, H		Bz	Bz	Lev
11	OH, H		Bz	Ac	Ac
12	$OC(=NH)CCl_3$, H		Bz	Ac	Ac



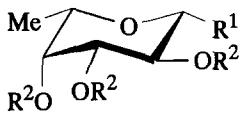
	R^1	R^2
13	H	OBn
14	benzylidene	
15	H	H
16	H	Lev
17	Ac	Lev



		R^1	R^2	R^3	R^4
10 + 13 ⟶	**18**	Bn	MPM	Bz	Lev
12 + 16 ⟶	**19**	Lev	MPM	Ac	Ac
10 + 16 ⟶	**20**	Lev	MPM	Bz	Lev
	21	Bn	H	Bz	Lev
	22	Lev	H	Ac	Ac
	23	Lev	H	Bz	Lev

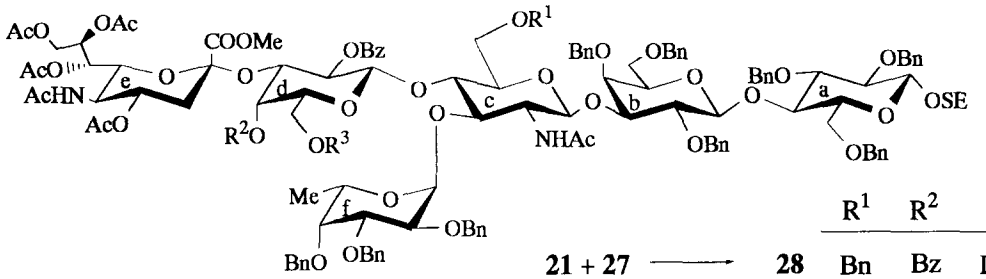
Chart 1.

22, and **23**. The binding activities to E-, P-, and L-selectins of these sulfated sLe^x ganglioside analogues were examined[45] by H. Kondo and co-workers of Kanebo Ltd, Japan (unpublished report). Interestingly, the introduction of a sulfo group on the 6-OH of Gal, or on both the Gal and GlcNAc residues completely abolished the binding to E-selectin. Compound **51** containing a sulfo group on the 6-OH of the GlcNAc residue bound to E-selectin almost as well as the sLe^x ganglioside. These results show that the introduction of the sulfo group (anionic substituent) on the 6-OH of the Gal residue abolishes E-selectin recognition. On

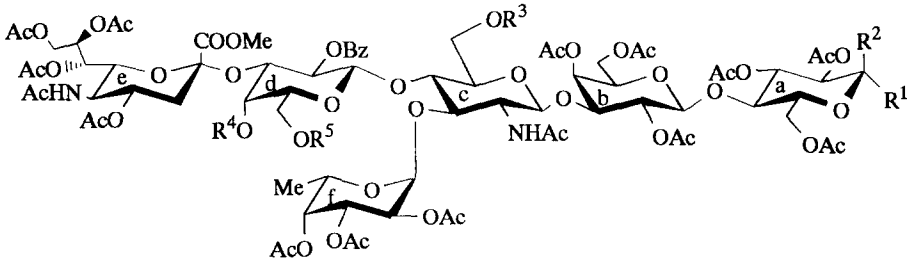


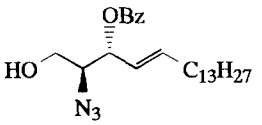
	R^1	R^2
24	OAc	Ac
25	SPh	Ac
26	SPh	H
27	SPh	Bn

SE = 2-(trimethylsilyl)ethyl
Bz = benzoyl
Bn = benzyl
Lev = levulinoyl
MPM = 4-methoxybenzyl



		R^1	R^2	R^3
21 + **27**	→ **28**	Bn	Bz	Lev
22 + **27**	→ **29**	Lev	Ac	Ac
23 + **27**	→ **30**	Lev	Bz	Lev

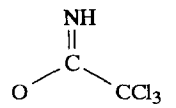




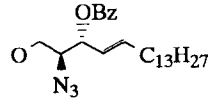
35

	R^1	R^2	R^3	R^4	R^5
31	OSE	H	Ac	Bz	Lev
32	OSE	H	Lev	Ac	Ac
33	OSE	H	Lev	Bz	Lev
34	H	X	Ac	Bz	Lev
36	Y	H	Ac	Bz	Lev
37	Z	H	Ac	Bz	Lev
38	H	X	Lev	Ac	Ac
39	Y	H	Lev	Ac	Ac
40	Z	H	Lev	Ac	Ac
41	H	X	Lev	Bz	Lev
42	Y	H	Lev	Bz	Lev
43	Z	H	Lev	Bz	Lev

X=



Y=



Z =

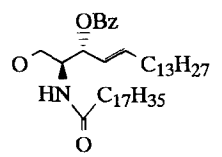


Chart 2.

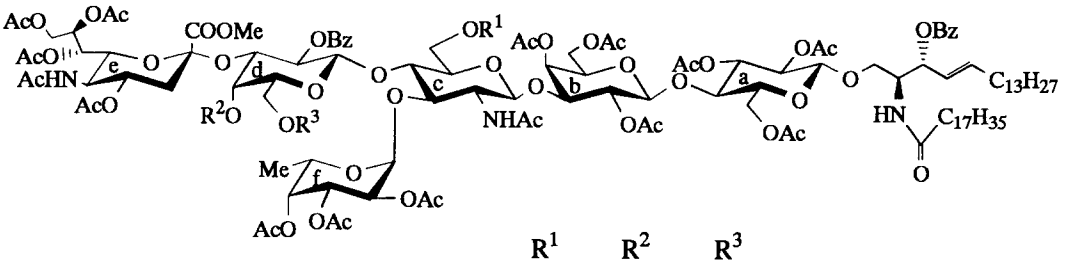
the contrary, for P-selectin, binding to **50–52** appeared to be equivalent to sLe^x ganglioside, indicating the introduction of sulfo group at the 6-OH positions did not affect for the recognition. Very interestingly, for L-selectin, binding to **52** was different from that of **50**, **51**, and the sLe^x ganglioside (hexasaccharide).[20b] Binding to **50** or **51** appeared to be equivalent to that of the sLe^x ganglioside, while binding to disulfated sLe^x **52** was effectively distinct from those of **50**, **51**, and sLe^x ganglioside, suggesting strongly that the real carbohydrate ligand structure of L-selectin is a disufated molecule. Details of this biological investigation will be appearing in the near future.

Experimental

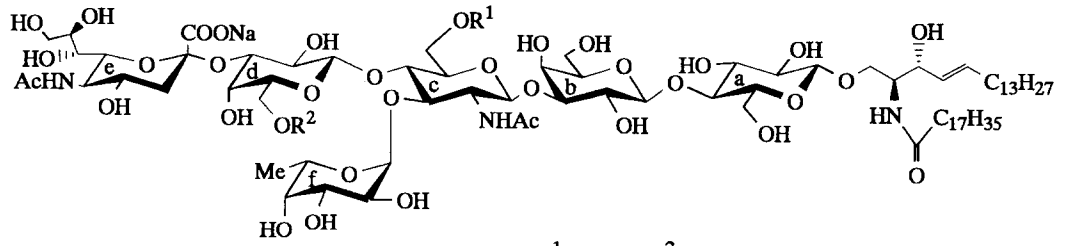
General methods

Optical rotations were determined with a Union PM-201 polarimeter at 25 °C, and IR spectra were recorded with a Jasco IRA-100 spectrophotometer. ^{1}H NMR spectra were recorded at 270 MHz with a Jeol JNM-GX 270 spectrometer. FAB-MS spectra were determined with a Jeol JMS-SX 102A mass spectrometer/JMA-DA 7000 data system. Each sample was mixed with diethylamine matrix on a target. The ion accelerating voltage was 8.0 KV, and the primary beam for the bombardment was 6.0 KeV of xenon. Preparative chromatography was performed on silica gel (Wako Chemical Co., 200 mesh) with the solvent systems specified. Concentrations were conducted in vacuo.

2-(Trimethylsilyl)ethyl *O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-4,6-*O*-benzylidene-β-D-galactopyranoside (3). To a solution of phenyl (methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-thio-D-glycero-D-galacto-2-nonulopyranosid)onate (**2**, 8.79 g, 15.1 mmol) and 2-(trimethylsilyl)ethyl 4,6-*O*-benzylidene-β-D-galactopyranoside (**1**, 3.61 g, 9.8 mmol) in dry acetonitrile (15 mL) was added molecular sieves 3 Å (MS-3 Å, 12.5 g), and the mixture was stirred for 5 h at room temperature, then cooled to −30 °C. To the cooled suspension were added, with stirring, NIS (7.7 g, 34.2 mmol) and TfOH (360 μL, 4.1 mmol), and the stirring was continued for 3 h at



	R^1	R^2	R^3
44	Ac	Bz	H
45	Ac	Bz	SO_3•pyr.
46	H	Ac	Ac
47	SO_3•pyr.	Ac	Ac
48	H	Bz	H
49	SO_3•pyr.	Bz	SO_3•pyr.



	R^1	R^2
50	H	SO_3Na
51	SO_3Na	H
52	SO_3Na	SO_3Na

Chart 3.

−30 °C. The solids were filtered off and washed with CH_2Cl_2, and the filtrate and washings were combined and washed with M Na_2CO_3, M $Na_2S_2O_3$ and water, dried (Na_2SO_4) and concentrated. Column chromatography (toluene:MeOH 5:1) of the residue on silica gel afforded the α-glycoside **3** (5.26 g, 65%) as an amorphous mass; $[\alpha]_D$ +4.2° (*c* 0.8, $CHCl_3$); IR (KBr): 3500–3200, 1750, 1680, 1550, 1220, 860, 840, 700 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.08 (m, 2H, $Me_3SiCH_2CH_2$), 1.89 (s, 3H, AcN), 2.02, 2.05, 2.16, 2.20 (4s, 12H, 4AcO), 2.75 [dd, 1H, J_{gem}=12.6, $J_{3b(eq),4}$=4.4 Hz, H-3b(*eq*)], 3.59 (s, 3H, MeO), 4.47 (d, 1H, $J_{1,2}$=7.7 Hz, H-1a), 4.88 (m, 1H, H-4b), 5.25 (m, 1H, $J_{6,7}$=2.1, $J_{7,8}$=8.0 Hz, H-7b), 5.38 (s, 1H, PhCH), 5.43 (m, 1H, H-8b), 7.28–7.64 (m, 5H, Ph). Anal.: calcd for $C_{37}H_{53}NO_{18}Si$: C, 53.68; H, 6.45; N, 1.69; found: C, 53.43; H, 6.45; N, 1.65%.

2-(Trimethylsilyl)ethyl *O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-2-*O*-benzyl-4,6-*O*-benzylidene-β-D-galactopyranoside (4). To a solution of **3** (510 mg, 0.62 mmol) in pyridine (5 mL) were added benzoic anhydride (270 mg) and 4-dimethylaminopyridine (22 mg), and the mixture was stirred overnight at room temperature, concentrated and extracted with CH_2Cl_2. The extract was washed with 2 M HCl and water, dried (Na_2SO_4) and concentrated. Column chromatography (ethyl acetate:hexane 4:1) of the residue on silica gel gave **4** (500 mg, 86%) as an amorphous mass; $[\alpha]_D$ +18.8° (*c* 2.1, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.97 (m, 2H, $Me_3SiCH_2CH_2$), 1.82 [t, 1H, J_{gem}=$J_{3b(ax),4}$=12.6 Hz, H-3b(*ax*)], 1.92, 1.95, 2.03, 2.16, 2.31 (5s, 15H, 4AcO, AcN), 2.69 [dd, 1H, $J_{3b(eq),4}$= 4.4 Hz, H-3b(*eq*)], 3.64 (s, 3H, MeO), 4.46 (dd, 1H, J_{gem}=12.1, $J_{8,9'}$=2.4 Hz, H-9′), 4.64 (dd, 1H, $J_{2,3}$=10.1, $J_{3,4}$=3.7 Hz, H-3a), 4.82 (d, 1H, $J_{1,2}$=7.9 Hz, H-1a), 5.35 (d, 1H, $J_{NH,5}$=9.3 Hz, NH), 5.50 (s, 1H, PhCH), 5.55 (dd, 1H, $J_{2,3}$=10.1 Hz, H-2), 5.64 (m, 1H, H-8), 7.38–7.67 (m, 10H, 2Ph). Anal.: calcd for $C_{45}H_{59}NO_{19}Si$: C, 57.13; H, 6.29; N, 1.48; found: C, 56.90; H, 6.00; N, 1.43%.

2-(Trimethylsilyl)ethyl *O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-2-*O*-benzoyl-β-D-galactopyranoside (5). A solution of **4** (830 mg, 0.88 mmol) in AcOH (10 mL) was hydrogenolysed in the presence of 10% Pd-C (1 g) for 7 h at room temperature then filtered, and the solids were washed with CH_2Cl_2. The filtrate and washings were combined and concentrated. Column chromatography (toluene:MeOH 50:1) of the residue on silica gel gave **5** (710 mg, 94%) as an amorphous mass; $[\alpha]_D$ −1.4° (*c* 1.3, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.83 (m, 2H, $Me_3SiCH_2CH_2$), 1.65 (s, 3H, AcN), 1.82, 1.96, 2.06, 2.16 (4s, 12H, 4AcO), 2.51 [dd, 1H, J_{gem}=12.8, $J_{3b(eq),4}$=4.6 Hz, H-3b(*eq*)], 3.79 (s, 3H, MeO), 4.32 (dd, 1H, J_{gem}=12.5, $J_{8,9'}$=2.4 Hz, H-9′), 4.40 (dd, 1H, $J_{2,3}$=9.9, $J_{3,4}$=3.3 Hz, H-3a), 4.67 (d, 1H, $J_{1,2}$=7.9 Hz, H-1a), 4.79 (m, 1H, H-4b), 5.20 (dd, 1H, $J_{6,7}$=1.7, $J_{7,8}$=9.0 Hz, H-7), 5.31 (dd, 1H, H-2a), 5.36 (d, 1H, $J_{NH,5}$=8.4 Hz, NH), 5.50 (m, 1H, H-8), 7.29–8.14 (m, 5H, Ph). Anal.: calcd for $C_{38}H_{55}NO_{19}Si$: C, 53.20; H, 6.46; N, 1.63; found: C, 53.18; H, 6.19; N, 1.39%.

2-(Trimethylsilyl)ethyl *O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-2-*O*-benzoyl-6-*O*-levulinoyl-β-D-galactopyranoside (6). To a solution of **5** (360 mg, 0.42 mmol) in pyridine (4.5 mL) and CH_2Cl_2 (1.5 mL), cooled to −50 °C, was added dropwise a solution of levulinic anhydride (110 mg) in CH_2Cl_2 (3 mL), and the mixture was stirred for 18 min at −50 °C. After completion of the reaction, MeOH (2 mL) was added to the mixture and concentrated then extracted with CH_2Cl_2. The extract was successively washed with 2 M HCl and water, dried (Na_2SO_4) and concentrated. Column chromatography (CH_2Cl_2:MeOH 25:1) of the residue on silica gel gave **6** (340 mg, 85%) as an amorphous mass; $[\alpha]_D$ +6.6° (*c* 0.9, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.85 (m, 2H, $Me_3SiCH_2CH_2$), 1.60 (s, 3H, AcN), 1.81, 1.97, 2.07, 2.17 (4s, 12H, 4AcO), 2.20 (s, 3H, $MeCOCH_2CH_2$), 2.66–2.85 (m, 4H, $MeCOCH_2CH_2$), 3.80 (s, 3H, MeO), 4.28 (dd, 1H, J_{gem}=12.5, $J_{8,9'}$=2.4 Hz, H-9′), 4.35 (m, 2H, H-6a), 4.42 (dd, 1H, $J_{2,3}$=9.9, $J_{3,4}$=3.1 Hz, H-3a), 4.65 (d, 1H, $J_{1,2}$=7.9 Hz, H-1a), 4.78 (m, 1H, H-4b), 5.28 (dd, 1H, H-2a), 5.52 (m, 1H, H-8), 7.28–8.20 (m, 5H, Ph). Anal.: calcd for $C_{43}H_{61}NO_{21}Si$: C, 54.02; H, 6.43; N, 1.47; found: C, 53.79; H, 6.24; N, 1.32%.

2-(Trimethylsilyl)ethyl *O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-2,4-di-*O*-benzoyl-6-*O*-levulinoyl-β-D-galactopyranoside (7). To a solution of **6** (580 mg, 0.61 mmol) in pyridine (5 mL) and 4-dimethylaminopyridine (22 mg) was added benzoic anhydride (270 mg, 1.2 mmol) and the mixture was stirred for 12 h at room temperature, MeOH (0.5 mL) was added to the mixture, and this was concentrated then extracted with CH_2Cl_2. The extract was successively washed with 2 M HCl and water, dried (Na_2SO_4) and concentrated. Column chromatography (toluene:MeOH 50:1) of the residue on silica gel gave **7** (530 mg, 82%) as an amorphous mass; $[\alpha]_D$ +40.5° (*c* 1.6, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.87 (m, 2H, $Me_3SiCH_2CH_2$), 1.46 (s, 3H, AcN), 1.67 [t, 1H, J_{gem}=$J_{3b(ax),4}$=12.5 Hz, H-3b(*ax*)], 1.78, 1.92, 2.09, 2.18 (4s, 12H, 4AcO), 2.24 (s, 3H, $MeCOCH_2CH_2$), 2.45 [dd, 1H, $J_{3b(eq),4}$=4.6 Hz, H-3b(*eq*)], 2.51–2.79 (m, 4H, $MeCOCH_2CH_2$), 3.89 (s, 3H, MeO), 4.35 (dd, 1H, J_{gem}=12.5, $J_{8,9'}$=2.4 Hz, H-9′), 4.80 (dd, 1H, $J_{2,3}$=10.1, $J_{3,4}$=3.3 Hz, H-3a), 4.81 (m, 1H, H-4b), 4.83 (d, 1H, $J_{1,2}$=7.9 Hz, H-1a), 5.23 (d, 1H, H-4a), 5.39 (dd, 1H, H-2a), 5.63 (m, 1H, H-8), 7.28–8.21 (m, 10H, 2Ph). Anal.: calcd for $C_{50}H_{65}NO_{22}Si$: C, 56.65; H, 6.18; N, 1.32; found: C, 56.63; H, 6.08; N, 1.03%.

2-(Trimethylsilyl)ethyl *O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-4,6-di-*O*-acetyl-2-*O*-benzoyl-β-D-galactopyranoside (8). To a solution of **5** (930 mg, 1.1 mmol) in pyridine (10 mL) was added

acetic anhydride (4 mL) and the mixture was stirred for 3 h at room temperature and concentrated. Column chromatography (toluene:MeOH 50:1) of the residue on silica gel gave **8** (930 mg, 91%) as an amorphous mass; $[\alpha]_D$ +23.0° (*c* 1.1, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$): δ 0.87 (m, 2H, $Me_3SiCH_2CH_2$), 1.43 (s, 3H, AcN), 1.79, 1.97, 2.06, 2.08, 2.14, 2.22 (6s, 18H, 6AcO), 2.55 [dd, 1H, J_{gem} = 12.5, $J_{3b(eq),4}$ = 4.4 Hz, H-3b(*eq*)], 3.86 (s, 3H, MeO), 4.33 (dd, 1H, J_{gem} = 12.5, $J_{8,9'}$ = 2.2 Hz, H-9'), 4.69 (dd, 1H, $J_{2,3}$ = 10.1, $J_{3,4}$ = 3.2 Hz, H-3a), 4.76 (d, 1H, $J_{1,2}$ = 7.9 Hz, H-1a), 4.85 (m, 1H, H-4b), 4.99 (d, 1H, H-4a), 5.60 (m, 1H, H-8), 7.29–8.17 (m, 5H, Ph). Anal.: calcd for $C_{42}H_{59}NO_{21}Si$: C, 53.55; H, 6.31; N, 1.49; found: C, 53.46; H, 6.23; N, 1.38%.

***O*-(Methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-2,4-di-*O*-benzoyl-6-*O*-levulinoyl-D-galactopyranose (9).** To a solution of **7** (1.0 g, 0.94 mmol) in CH_2Cl_2 (20 mL), cooled to 0 °C, was added CF_3CO_2H (10 mL) and the mixture was stirred for 30 min at room temperature and concentrated. Column chromatography (ethyl acetate:hexane 4:1) of the residue on silica gel gave **9** (810 mg, 90%) as an amorphous mass; IR (KBr): 3600–3300, 1750, 1670, 1550, 1225, 720 cm $^{-1}$. Anal.: calcd for $C_{45}H_{53}NO_{22}$: C, 56.31; H, 5.57; N, 1.46; found: C, 56.24; H, 5.53; N, 1.33%.

***O*-(Methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-2,4-di-*O*-benzoyl-6-*O*-levulinoyl-D-galactopyranosyl trichloroacetimidate (10).** To a solution of **9** (400 mg, 0.42 mmol) in CH_2Cl_2 (4 mL), cooled to 0 °C, were added trichloroacetonitrile (1.26 mL) and DBU (62 μL, 0.42 mmol), and the mixture was stirred for 1 h at 0 °C then concentrated. Column chromatography (ethyl acetate:hexane 4:1) of the residue on silica gel gave **10** (450 mg, 98%) as an amorphous mass; IR (KBr): 3450–3200, 1740, 1680, 1540, 1220, 710 cm^{-1}. The anomeric ratio (α:β) was estimated as ~5:6 from the ratio of the intensities of the anomeric proton signals of galactose residue in the ^1H NMR spectrum. Anal.: calcd for $C_{47}H_{53}N_2O_{22}Cl_3$: C, 51.12; H, 4.84; N, 2.54; found: C, 50.82; H, 4.69; N, 2.48%.

***O*-(Methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-4,6-di-*O*-acetyl-2-*O*-benzoyl-D-galactopyranose (11).** To a solution of **8** (880 mg, 0.93 mmol) in CH_2Cl_2 (10 mL), cooled to 0 °C, was added CF_3CO_2H (9 mL) and the mixture was stirred for 1 h at room temperature, then work up as described for **9** gave **11** (780 mg, 98%) as an amorphous mass; IR (KBr): 3600–3300, 1750, 1680, 1540, 1220, 710 cm^{-1}. Anal.: calcd for $C_{37}H_{47}NO_{21}$: C, 52.79; H, 5.63; N, 1.66; found: C, 52.61; H, 5.53; N, 1.37%.

***O*-(Methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-nonulopyranosylonate)-(2→3)-4,6-di-*O*-acetyl-2-*O*-benzoyl-D-galactopyranosyl trichloroacetimidate (12).** To a solution of **11** (250 mg, 0.3 mmol) in CH_2Cl_2 (3 mL), cooled to 0 °C, were added trichloroacetonitrile (0.89 mL) and DBU (44 μL, 0.3 mmol) and the mixture was stirred for 1.5 h at 0 °C, then work up as described for **10** gave **12** (233 mg, 80%) as an amorphous mass. The anomeric ratio (α:β) was estimated as ~3:4 from the ratio of the intensities of the anomeric proton signals of galactose residue in the ^1H NMR spectrum. Anal.: calcd for $C_{39}H_{47}N_2O_{21}Cl_3$: C, 47.50; H, 4.80; N, 2.84; found: C, 47.79; H, 4.74; N, 2.82%.

2-(Trimethylsilyl)ethyl *O*-(2-acetamido-2-deoxy-3-*O*-4-methoxybenzyl-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (15). A solution of **14** (100 mg, 72 μmol) in AcOH (8 mL) and water (2 mL) was heated for 36 h at 40 °C and concentrated. Column chromatography (ethyl acetate:hexane 3:2) of the residue on silica gel gave **15** (77.6 mg, 82%) as an amorphous mass; $[\alpha]_D$ −19.1° (*c* 1.6, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$): δ 1.01 (m, 2H, $Me_3SiCH_2CH_2$), 1.49 (s, 3H, AcN), 3.75 (s, 3H, MeO), 6.80–7.38 (m, 34H, 6Ph, MeOPh). Anal.: calcd for $C_{75}H_{91}NO_{17}Si$: C, 68.94; H, 7.02; N, 1.07; found: C, 68.77; H, 7.01; N, 0.87%.

2-(Trimethylsilyl)ethyl *O*-(2-acetamido-2-deoxy-6-*O*-levulinoyl-3-*O*-methoxybenzyl-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (16). To a solution of **15** (480 mg, 0.37 mmol) and 4-dimethylaminopyridine (45 mg, 0.37 mmol) in pyridine (40 mL) and CH_2Cl_2 (10 mL), cooled to −50 °C, was dropwise added, with stirring, a solution of levulinic anhydride (90 mg) in CH_2Cl_2 (34 mL). The mixture was stirred for 2 h at −50 °C then MeOH (2 mL) was added to the mixture. The solution was stirred for 30 min and concentrated then extracted with CH_2Cl_2. The extract was successively washed with 2M HCl and water, dried (Na_2SO_4) and concentrated. Column chromatography (ethyl acetate:hexane 1:1) of the residue on silica gel gave **16** (420 mg, 81%) as an amorphous mass; $[\alpha]_D$ −11.6° (*c* 1.0, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$): δ 1.01 (m, 2H, $Me_3SiCH_2CH_2$), 1.44 (s, 3H, AcN), 2.04 (s, 3H, $MeCOCH_2CH_2$), 2.53 (m, 4H, $MeCOCH_2CH_2$), 3.73 (s, 3H, MeO), 6.80–7.32 (m, 34H, 6Ph, MeOPh). Anal.: calcd for $C_{80}H_{97}NO_{19}Si$: C, 68.40; H, 6.96; N, 1.00; found: C, 68.39; H, 6.71; N, 0.97%.

2-(Trimethylsilyl)ethyl *O*-(2-acetamido-4-*O*-acetyl-2-deoxy-3-*O*-4-methoxybenzyl-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (17). A solution of **16** (50.7 mg, 36 μmol) in pyridine (1 mL)-acetic anhydride (1 mL) was kept for 2 h at room temperature and concentrated. Column chromatography (ethyl acetate:hexane 1:2) of the residue on silica gel gave **17** (51 mg, 98%) as an amorphous mass; $[\alpha]_D$ +2.0° (*c* 1.0, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$): δ 1.01 (m, 2H, $Me_3SiCH_2CH_2$), 1.42 (s, 3H, AcN), 2.01, 2.06 (2s, 6H, AcO, $MeCOCH_2CH_2$), 2.51 (m, 4H, $MeCOCH_2CH_2$), 3.77 (s, 3H, MeO), 5.01 (t, 1H, $J_{3,4} = J_{4,5}$ = 8.1 Hz, H-4c),

6.81–7.36 (m, 34H, 6Ph, MeOPh). Anal.: calcd for $C_{82}H_{99}NO_{20}Si$: C, 68.08; H, 6.90; N, 0.97; found: C, 67.80; H, 6.79; N, 0.70%.

2-(Trimethylsilyl)ethyl *O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-*O*-(2,4-di-*O*-benzoyl-6-*O*-levulinoyl-β-D-galactopyranosyl)-(1→4)-*O*-(2-acetamido-6-*O*-benzyl-2-deoxy-3-*O*-4-methoxybenzyl-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (18). To a solution of **13** (251 mg, 0.18 mmol) and **10** (297 mg, 0.27 mmol) in dry CH_2Cl_2 (1 mL) was added MS-4 Å (AW-300, 400 mg), and the mixture was stirred for 5 h at room temperature, then cooled to 0 °C. Trimethylsilyl trifluoromethanesulfonate (TMS•OTf, 16 μL, 83 μmol) was added to the mixture and this was stirred for 12 h at 7 °C, neutralized with Et_3N and filtered, and the residue was washed with CH_2Cl_2. The combined filtrate and washings were washed with water, dried (Na_2SO_4) and concentrated. Column chromatography (ethyl acetate:hexane 2:1) of the residue on silica gel gave **18** (206 mg, 50%) as an amorphous mass; $[\alpha]_D$ +13.5° (*c* 1.3, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$): δ 1.01 (m, 2H, $Me_3SiCH_2CH_2$), 1.44, 1.49 (2s, 6H, 2AcN), 1.78, 1.92, 1.97, 2.10, 2.21 (5s, 15H, 4AcO, $MeCOCH_2CH_2$), 2.39–2.63 (m, 4H, $MeCOCH_2CH_2$), 3.68 (s, 3H, MeOPh), 3.89 (s, 3H, MeO), 5.24 (d, 1H, $J_{3,4}$=2.9 Hz, H-4d), 5.46 (t, 1H, $J_{1,2}=J_{2,3}$=8.1 Hz, H-2d), 5.68 (m, 1H, H-8e), 6.62–8.24 (m, 49H, 9Ph, MeOPh). Anal.: calcd for $C_{127}H_{148}N_2O_{38}Si$: C, 65.28; H, 6.38; N, 1.20; found: C, 65.04; H, 6.17; N, 1.02%.

2-(Trimethylsilyl)ethyl *O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-*O*-(4,6-di-*O*-acetyl-2-*O*-benzoyl-β-D-galactopyranosyl)-(1→4)-*O*-(2-acetamido-2-deoxy-6-*O*-levulinoyl-3-*O*-4-methoxybenzyl-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (19). Glycosylation of **16** (310.5 mg, 0.022 mmol) with **12** (326.5 mg, 0.33 mmol) in dry CH_2Cl_2 (1 mL) in the presence of TMS•OTf (19 μL, 98 μmol) and MS-4 Å (AW-300, 300 mg) for 12 h at 7 °C and workup as described for **18** gave **19** (377 mg, 77%) as an amorphous mass; $[\alpha]_D$ +7.6° (*c* 1.2, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$): δ 1.01 (m, 2H, $Me_3SiCH_2CH_2$), 1.42, 1.50 (2s, 6H, 2AcN), 1.80, 1.96, 2.01, 2.05, 2.06 2.11, 2.19 (7s, 21H, 6AcO, $MeCOCH_2CH_2$), 2.47–2.56 (m, 4H, $MeCOCH_2CH_2$), 3.75 (s, 3H, MeOPh), 3.85 (s, 3H, MeO), 5.02 (d, 1H, $J_{3,4}$=3.1 Hz, H-4d), 5.30 (t, 1H, $J_{1,2}=J_{2,3}$=8.4 Hz, H-2d), 5.60 (m, 1H, H-8e), 6.76–8.19 (m, 39H, 7Ph, MeO*Ph*). Anal.: calcd for $C_{117}H_{142}N_2O_{39}Si$: C, 63.06; H, 6.42; N, 1.26; found: C, 62.92; H, 6.17; N, 1.21%.

2-(Trimethylsilyl)ethyl *O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-*O*-(2,4-di-*O*-benzoyl-6-*O*-levulinoyl-β-D-galactopyranosyl)-(1→4)-*O*-(2-acetamido-2-deoxy-6-*O*-levulinoyl-3-*O*-4-methoxybenzyl-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (20). Glycosylation of **16** (420.5 mg, 0.3 mmol) with **10** (485.6 mg, 0.44 mmol) in dry CH_2Cl_2 (1 mL) in the presence of TMS•OTf (26 μL, 0.13 mmol) and MS-4 Å (AW-300, 300 mg) for 12 h at 7 °C and workup as described for **18** gave **20** (315.6 mg, 45%) as an amorphous mass; $[\alpha]_D$ +25.5° (*c* 1.0, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$): δ 1.01 (m, 2H, $Me_3SiCH_2CH_2$), 1.41, 1.51 (2s, 6H, 2AcN), 1.79, 1.91, 2.07, 2.09, 2.13, 2.22 (6s, 18H, 4AcO, $2MeCOCH_2CH_2$), 2.44–2.70 (m, 8H, $2MeCOCH_2CH_2$), 3.68 (s, 3H, MeOPh), 3.89 (s, 3H, MeO), 5.25 (d, 1H, $J_{3,4}$=3.3 Hz, H-4d), 5.46 (dd, 1H, $J_{1,2}$=9.9 Hz, $J_{2,3}$=7.7 Hz, H-2d), 5.62 (m, 1H, H-8e), 6.63–8.21 (m, 44H, 8Ph, MeOPh). Anal.: calcd for $C_{125}H_{148}N_2O_{40}Si$: C, 63.98; H, 6.36; N, 1.19; found: C, 63.73; H, 6.27; N, 1.09%.

2-(Trimethylsilyl)ethyl *O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-*O*-(2,4-di-*O*-benzoyl-6-*O*-levulinoyl-β-D-galactopyranosyl)-(1→4)-*O*-(2-acetamido-6-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (21). To a solution of **18** (63.8 mg, 27 μmol) in CH_3CN (0.9 mL) and water (0.1 mL) was added ceric ammonium nitrate (CAN, 33 mg, 60 μmol), and the mixture was stirred for 3.5 h at room temperature and extracted with CH_2Cl_2. The extract was successively washed with M $NaHCO_3$ and water, dried (Na_2SO_4) and concentrated. Column chromatography (ethyl acetate:hexane 4:1) of the residue on silica gel gave **21** (56.5 mg, 98%) as an amorphous mass; $[\alpha]_D$ +22.2° (*c* 1.1, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$): δ 0.92 (m, 2H, $Me_3SiCH_2CH_2$), 1.49, 1.56 (2s, 6H, 2AcN), 1.77, 1.90, 2.04, 2.11, 2.22 (5s, 15H, 4AcO, $MeCOCH_2CH_2$), 2.43 [dd, 1H, J_{gem}=12.6, $J_{3e(eq),4}$=4.4 Hz, H-3e(*eq*)], 2.54–2.72 (m, 4H, $MeCOCH_2CH_2$), 3.86 (s, 3H, MeO), 5.20 (d, 1H, $J_{3,4}$=3.1 Hz, H-4d), 5.50 (dd, 1H, $J_{1,2}$=9.7, $J_{2,3}$=8.3 Hz, H-2d), 5.65 (m, 1H, H-8e), 7.05–8.27 (m, 45H, 9Ph). Anal.: calcd for $C_{119}H_{140}N_2O_{37}Si$: C, 64.43; H, 6.36; N, 1.26; found: C, 64.27; H, 6.16; N, 1.22%.

2-(Trimethylsilyl)ethyl *O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-*O*-(4,6-di-*O*-acetyl-2-*O*-benzoyl-β-D-galactopyranosyl)-(1→4)-*O*-(2-acetamido-2-deoxy-6-*O*-levulinoyl-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (22). To a solution of **19** (253.2 mg, 0.11 mmol) in CH_3CN (2.7 mL) and water (0.3 mL) was added CAN (250 mg, 0.45 mmol), and the mixture was stirred for 1 h at room temperature. Workup as described for **21** gave **22** (216.5 mg, 90%) as an amorphous mass; $[\alpha]_D$ +20.1° (*c* 1.6, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$): δ 1.00 (m, 2H, $Me_3SiCH_2CH_2$), 1.49, 1.52 (2s, 6H, 2AcN), 1.78, 1.95, 2.01, 2.04, 2.07, 2.14, 2.18 (7s, 21H, 6AcO, $MeCOCH_2CH_2$), 2.34–2.51 (m, 4H, $MeCOCH_2CH_2$), 3.83 (s, 3H, MeO), 5.24 (dd, 1H, $J_{6,7}$=2.6, $J_{7,8}$=9.4 Hz, H-7e), 5.33 (dd, 1H, $J_{1,2}$=9.9, $J_{2,3}$=8.1 Hz, H-2d), 5.60

(m, 1H, H-8e), 7.05–8.20 (m, 35H, 7Ph). Anal.: calcd for $C_{109}H_{134}N_2O_{38}Si$: C, 62.10; H, 6.41; N, 1.33; found: C, 61.93; H, 6.26; N, 1.22%.

2-(Trimethylsilyl)ethyl *O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-*O*-(2,4-di-*O*-benzoyl-6-*O*-levulinoyl-β-D-galactopyranosyl)-(1→4)-*O*-(2-acetamido-2-deoxy-6-*O*-levulinoyl-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (23). Selective removal of the 4-methoxybenzyl group in **20** (190 mg, 81 μmol) with CAN (116 mg, 0.21 mmol) in CH_3CN (1.8 mL) and water (0.2 mL) for 3 h at room temperature and workup as described for **21** gave **23** (120 mg, 68%) as an amorphous mass; $[\alpha]_D$ +22.6° (*c* 1.6, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$): δ 1.00 (m, 2H, $Me_3SiCH_2CH_2$), 1.49, 1.54 (2s, 6H, 2AcN), 1.77, 1.90, 2.03, 2.09, 2.13, 2.22 (6s, 18H, 4AcO, 2MeCOCH$_2$CH$_2$), 2.33–2.73 (m, 8H, 2MeCOCH$_2$CH$_2$), 3.86 (s, 3H, MeO), 5.21 (d, 1H, $J_{3,4}$=3.3 Hz, H-4d), 5.48 (dd, 1H, $J_{1,2}$=9.7, $J_{2,3}$=8.2 Hz, H-2d), 5.62 (m, 1H, H-8e), 7.05–8.21 (m, 40H, 8Ph). Anal.: calcd for $C_{117}H_{140}N_2O_{39}Si$: C, 63.12; H, 6.34; N, 1.26; found: C, 62.93; H, 6.25; N, 1.24%.

Phenyl 2,3,4-tri-*O*-acetyl-1-thio-β-L-fucopyranoside (25). To a solution of **24** (59.2 g, 178 mmol) in CH_2Cl_2 (620 mL), cooled to 0 °C, were added, with stirring, thiophenol (37.7 mL, 367 mmol) and boron trifluoride etherate (59 mL, 220 mmol), and the mixture was stirred for 2 h at room temperature and CH_2Cl_2 (300 mL) was added. The solution was successively washed with M Na_2CO_3 and water, dried (Na_2SO_4) and concentrated. Column chromatography (ethyl acetate:hexane 1:4) of the residue on silica gel gave **25** (58.5 g, 86%) as an amorphous mass; $[\alpha]_D$ −3.0° (*c* 0.9, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$): δ 1.24 (d, 3H, $J_{5,6}$=6.2 Hz, H-6), 1.97, 2.08, 2.14 (3s, 9H, 3AcO), 3.84 (q, 1H, $J_{5,6}$=6.4 Hz, H-5), 4.71 (d, 1H, $J_{1,2}$=9.9 Hz, H-1), 5.04 (dd, 1H, $J_{2,3}$=9.9, $J_{3,4}$=3.3 Hz, H-3), 5.23 (t, 1H, H-2), 5.27 (d, 1H, H-4), 7.28–7.53 (m, 5H, Ph). Anal.: calcd for $C_{18}H_{22}O_7S$: C, 56.53; H, 5.80; found: C, 56.42; H, 5.74%.

Phenyl 1-thio-β-L-fucopyranoside (26). To a solution of **25** (51 g, 0.13 mmol) in MeOH (250 mL) was added NaOMe (1.5 g, 28% NaOMe in MeOH), and the mixture was stirred for 5 h at room temperature and neutralized with Amberlite IR-120 (H^+) resin, then filtered and concentrated to a crystalline mass. Recrystallization from ether:hexane gave **26** (32.5 g, 95%) as needles; mp 91–92 °C; $[\alpha]_D$ +68° (*c* 0.6, MeOH); ^1H NMR (270 MHz, $CDCl_3$): δ 1.34 (d, 3H, $J_{5,6}$=6.5 Hz, H-6), 7.30–7.54 (m, 5H, Ph). Anal.: calcd for $C_{12}H_{16}O_4S$: C, 56.23; H, 6.29; found: C, 56.18; H, 6.19%.

Phenyl 2,3,4-tri-*O*-benzyl-1-thio-β-L-fucopyranoside (27). To a solution of **26** (1.0 g, 3.9 mmol) in *N*,*N*-dimethylformamide (DMF, 30 mL), cooled to 0 °C, was added NaH in oil suspension (1.2 g, 60% NaH weight), the mixture was stirred for 30 min at 0 °C, and then benzyl bromide (2 mL) was added. The stirring was continued for 1.5 h at room temperature, and MeOH (1 mL) was added and concentrated then extracted with ethyl acetate. The extract was washed with water, dried (Na_2SO_4) and concentrated to a crystalline mass. Recrystallization from ether:hexane gave **27** (1.7 g, 84%) as needles; mp 107–109 °C; $[\alpha]_D$ −14.0° (*c* 0.7, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$): δ 1.26 (d, 3H, $J_{5,6}$=6.4 Hz, H-6), 3.52 (q, 1H, $J_{5,6}$=6.4 Hz, H-5), 3.59 (dd, 1H, $J_{2,3}$=11.7, $J_{3,4}$=2.8 Hz, H-3), 3.93 (dd, 1H, $J_{1,2}$=9.5 Hz, H-2), 4.60 (d, 1H, H-1), 4.73, 4.76, 4.83 (6H, 3CH$_2$Ph), 7.18–7.60 (m, 20H, 4Ph). Anal.: calcd for $C_{33}H_{30}O_4S$: C, 75.83; H, 5.79; found: C, 75.56; H, 5.53%.

2-(Trimethylsilyl)ethyl *O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-*D-glycero*-α-D-galacto-2-nonulopyranosylonate)-(2→3)-*O*-(2,4-di-*O*-benzoyl-6-*O*-levulinoyl-β-D-galactopyranosyl)-(1→4)-*O*-[(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→3)]-*O*-(2-acetamido-6-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (28). To a solution of **21** (161.5 mg, 76 μmol) and **27** (45.2 mg, 87 μmol) in dry benzene (1 mL) was added powdered MS-4 Å (300 mg), and the mixture was stirred for 5 h at room temperature, then cooled to 0 °C. Dimethyl(methylthio)sulfonium triflate (DMTST, 68 mg, 0.26 mmol) and MS-4 Å (45 mg) were added to the mixture, and this was stirred for 48 h at 7 °C and neutralized with Et_3N. After dilution with CH_2Cl_2 (50 mL), the solids were collected and washed with CH_2Cl_2, and the combined filtrate and washings was washed with water, dried (Na_2SO_4) and concentrated. Column chromatography (ethyl acetate:hexane 3:1) of the residue on silica gel gave **28** (116 mg, 58%) as an amorphous mass; $[\alpha]_D$ −17.5° (*c* 1.8, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$): δ 1.02 (m, 2H, $Me_3SiCH_2CH_2$), 1.16 (d, 3H, $J_{5,6}$=6.4 Hz, H-6f), 1.51, 1.79 (2s, 6H, 2AcN), 1.91, 1.97, 2.03, 2.09, 2.22 (5s, 15H, 4AcO, MeCOCH$_2$CH$_2$), 2.41–2.62 (m, 4H, MeCOCH$_2$CH$_2$), 3.83 (s, 3H, MeO), 5.15 (d, 1H, $J_{1,2}$=3.6 Hz, H-1f), 5.42 (dd, 1H, $J_{1,2}$=9.9, $J_{2,3}$=8.1 Hz, H-2d), 5.67 (m, 1H, H-8e), 7.08–8.21 (m, 60H, 12Ph). Anal.: calcd for $C_{146}H_{168}N_2O_{41}Si$: C, 66.55; H, 6.43; N, 1.06; found: C, 66.50; H, 6.34; N, 0.91%.

2-(Trimethylsilyl)ethyl *O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-*O*-(4,6-di-*O*-acetyl-2-*O*-benzoyl-β-D-galactopyranosyl)-(1→4)-*O*-[(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→3)]-*O*-(2-acetamido-2-deoxy-6-*O*-levulinoyl-β-D-glucopyranosyl)-(1h3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (29). Glycosylation of **22** (294.3 mg, 0.14 mmol) with **27** (87 mg, 0.17 mmol) in dry benzene (1 mL) in the presence of DMTST (130 mg, 0.5 mmol) and MS-4 Å (386 mg) for 72 h at 7 °C, then workup as described for **28** gave **29** (317 mg, 90%) as an amorphous mass; $[\alpha]_D$ −12.3° (*c* 1.5, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$): δ 1.01 (m, 2H, $Me_3SiCH_2CH_2$), 1.22 (d, 3H, $J_{5,6}$=6.4 Hz, H-6f),

1.34, 1.52 (2s, 6H, 2AcN), 1.79, 1.92, 1.95, 2.02, 2.04, 2.06, 2.18 (7s, 21H, 6AcO, MeCOCH$_2$CH$_2$), 2.47–2.55 (m, 4H, MeCOCH$_2$CH$_2$), 3.84 (s, 3H, MeO), 5.03 (d, 1H, $J_{1,2}$=3.3 Hz, H-1f), 5.22 (dd, 1H, $J_{1,2}$=10.1, $J_{2,3}$=8.1 Hz, H-2d), 5.29 (dd, 1H, $J_{6,7}$=2.8, $J_{7,8}$=9.5 Hz, H-7e), 7.04–8.15 (m, 50H, 10Ph). Anal.: calcd for $C_{136}H_{162}N_2O_{42}Si$: C, 64.70; H, 6.47; N, 1.11; found: C, 64.54; H, 6.34; N, 0.82%.

2-(Trimethylsilyl)ethyl *O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-nonulopyranosylonate)-(2→3)-*O*-(2,4-di-*O*-benzoyl-6-*O*-levulinoyl-β-D-galactopyranosyl)-(1→4)-*O*-[(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→3)]-*O*-(2-acetamido-2-deoxy-6-*O*-levulinoyl-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (30). Glycosylation of **23** (276 mg, 0.12 mmol) with **27** (77 mg, 0.15 mmol) in dry benzene (1 mL) in the presence of DMTST (116 mg, 0.45 mmol) and MS-4 Å (375 mg) for 72 h at 7 °C, then work up as described for **28** gave **30** (159 mg, 50%) as an amorphous mass; $[\alpha]_D$ −14.3° (*c* 1.7, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.01 (m, 2H, $Me_3SiCH_2CH_2$), 1.21 (d, 3H, $J_{5,6}$=6.4 Hz, H-6f), 1.41, 1.54 (2s, 6H, 2AcN), 1.79, 1.91, 2.06, 2.08, 2.11, 2.22 (6s, 18H, 4AcO, 2MeCOCH$_2$CH$_2$), 2.42–2.68 (m, 8H, 2MeCOCH$_2$CH$_2$), 3.84 (s, 3H, MeO), 5.17 (d, 1H, $J_{1,2}$=3.5 Hz, H-1f), 5.24 (d, 1H, $J_{3,4}$=2.9 Hz, H-4d), 5.29 (dd, 1H, $J_{6,7}$=2.4, $J_{7,8}$=9.3 Hz, H-7e), 5.43 (dd, 1H, $J_{1,2}$=10.1, $J_{2,3}$=8.3 Hz, H-2d), 5.62 (m, 1H, H-8e), 7.05–8.19 (m, 55H, 11Ph). Anal.: calcd for $C_{144}H_{168}N_2O_{43}Si$: C, 65.44; H, 6.41; N, 1.06; found: C, 65.16; H, 6.27; N, 0.88%.

2-(Trimethylsilyl)ethyl *O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-*O*-(2,4-di-*O*-benzoyl-6-*O*-levulinoyl-β-D-galactopyranosyl)-(1→4)-*O*-[(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-(1→3)]-*O*-(2-acetamido-6-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (31). A solution of **28** (112.2 mg, 43 μmol) in EtOH (20 mL) and AcOH (4 mL) was hydrogenolysed in the presence of 10% Pd-C (120 mg) for 24 h at 40 °C, then filtered and concentrated. The residue was acetylated with Ac_2O (1 mL) in pyridine (5 mL) for 24 h at 40 °C. The product was dissolved in CH_2Cl_2 (50 mL) and the solution was washed with 2M HCl and water, dried (Na_2SO_4) and concentrated. Column chromatography (ethyl acetate:hexane 4:1) of the residue on silica gel gave **31** (81.5 mg, 89%) as an amorphous mass; $[\alpha]_D$ −10.2° (*c* 1.5, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.92 (m, 2H, $Me_3SiCH_2CH_2$), 1.19 (d, 3H, $J_{5,6}$=6.6 Hz, H-6f), 1.57, 1.78, 1.85, 1.90, 1.91, 2.00, 2.02, 2.03, 2.07, 2.09 (9H), 2.10, 2.11, 2.17, 2.22 2.24 (15s, 51H, 2AcN, 14AcO, MeCOCH$_2$CH$_2$), 2.62–2.82 (m, 4H, MeCOCH$_2$CH$_2$), 3.87 (s, 3H, MeO), 5.07 (d, 1H, $J_{1,2}$=2.6 Hz, H-1f), 5.37 (dd, 1H, $J_{1,2}$=9.7, $J_{2,3}$=8.6 Hz, H-2d), 5.68 (m, 1H, H-8e), 7.16–8.17 (m, 10H, 2Ph). Anal.: calcd for $C_{96}H_{128}N_2O_{51}Si$: C, 53.53; H, 5.99; N, 1.30; found: C, 53.39; H, 5.94; N, 1.19%.

2-(Trimethylsilyl)ethyl *O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-*O*-(4,6-di-*O*-acetyl-2-*O*-benzoyl-β-D-galactopyranosyl)-(1→4)-*O*-[(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-(1→3)]-*O*-(2-acetamido-2-deoxy-6-*O*-levulinoyl-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (32). Hydrogenolysis of **29** (317 mg, 0.13 mmol) in EtOH (40 mL) and AcOH (8 mL) in the presence of 10% Pd-C (320 mg) for 48 h at 40 °C, and subsequent acetylation with Ac_2O (2 mL) in pyridine (5 mL) as described for **31** gave **32** (247 mg, 94%) as an amorphous mass; $[\alpha]_D$ −18.0° (*c* 1.2, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.92 (m, 2H, $Me_3SiCH_2CH_2$), 1.24 (d, 3H, $J_{5,6}$=7.2 Hz, H-6f), 1.49, 1.78 (2s, 6H, 2AcN), 1.90, 1.95, 1.96, 1.99, 2.02, 2.05, 2.08 (6H), 2.09, 2.10, 2.15, 2.17, 2.18 (9H), 2.20 (13s, 48H, 15AcO, MeCOCH$_2$CH$_2$), 2.51 (dd, 1H, J_{gem}=12.5, $J_{3e(eq),4}$=4.6 Hz, H-3e(*eq*)), 2.64–2.79 (m, 4H, MeCOCH$_2$CH$_2$), 3.85 (s, 3H, MeO), 5.07 (d, 1H, $J_{1,2}$=3.1 Hz, H-1f), 5.60 (m, 1H, H-8e), 7.32–8.14 (m, 5H, Ph). Anal.: calcd for $C_{91}H_{126}N_2O_{51}Si$: C, 52.25; H, 6.07; N, 1.34; found: C, 52.07; H, 5.77; N, 1.17%.

2-(Trimethylsilyl)ethyl *O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-*O*-(2,4-di-*O*-benzoyl-6-*O*-levulinoyl-β-D-galactopyranosyl)-(1→4)-*O*-[(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-(1→3)]-*O*-(2-acetamido-2-deoxy-6-*O*-levulinoyl-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (33). Hydrogenolysis of **30** (159 mg, 60 μmol) in EtOH (20 mL) and AcOH (4 mL) in the presence of 10% Pd-C (160 mg) for 48 h at 40 °C, and subsequent acetylation with Ac_2O (2 mL) in pyridine (5 mL) as described for **31** gave **33** (109 mg, 82%) as an amorphous mass; $[\alpha]_D$ −11.0° (*c* 1.2, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.92 (m, 2H, $Me_3SiCH_2CH_2$), 1.19 (d, 3H, $J_{5,6}$=6.4 Hz, H-6f), 1.57, 1.78 (2s, 6H, 2AcN), 1.85, 1.90, 1.91, 1.99, 2.02, 2.08 (12H), 2.09 (6H), 2.18 (6H), 2.20, 2.22 (10s, 45H, 13AcO, 2MeCOCH$_2$CH$_2$), 2.38 [dd, 1H, J_{gem}=13.0, $J_{3e(eq),4}$=4.9 Hz, H-3e(*eq*)], 2.61–2.86 (m, 8H, 2MeCOCH$_2$CH$_2$), 3.87 (s, 3H, MeO), 5.66 (m, 1H, H-8e), 7.28–8.17 (m, 10H, 2Ph). Anal.: calcd for $C_{99}H_{132}N_2O_{52}Si$: C, 53.80; H, 6.02; N, 1.27; found: C, 53.70; H, 5.93; N, 1.12%.

***O*-(Methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-*O*-(2,4-di-*O*-benzoyl-6-*O*-levulinoyl-β-D-galactopyranosyl)-(1→4)-*O*-[(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-(1→3)]-*O*-(2-acetamido-6-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl trichloroacetimidate (34).** To a solution of **31** (72.6 mg, 34 μmol) in CH_2Cl_2 (4.5 mL), cooled to 0 °C, was added CF_3CO_2H (1.25 mL), and the mixture was stirred for 2 h at room temperature and concentrated. The product was purified by chromatography on a column of silica gel with ethyl acetate:hexane 4:1 to give the 1-hydroxy compound (63 mg). To a solution of

this in CH_2Cl_2 (0.8 mL), cooled to 0 °C, were added trichloroacetonitrile (92 μL, 0.92 mmol) and DBU (5.5 μL, 36 μmol), the mixture was stirred for 2 h at 0 °C, and the progress of the reaction was monitored by TLC. The mixture was concentrated. Column chromatography (ethyl acetate:hexane 4:1) of the residue on silica gel gave **34** (67 mg, 91%) as an amorphous mass; $[\alpha]_D$ +6.6° (*c* 1.4, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$): δ 1.19 (d, 3H, $J_{5,6}=6.6$ Hz, H-6f), 1.57–2.23 (13s, 51H, 14AcO, 2AcN, MeCOCH$_2$CH$_2$), 2.38 (dd, 1H, $J_{gem}=12.5$, $J_{3e(eq),4}=4.4$ Hz, H-3e(*eq*)), 2.62–2.86 (m, 4H, MeCOCH$_2$CH$_2$), 3.87 (s, 3H, MeO), 6.47 (d, 1H, $J_{1,2}=3.5$ Hz, H-1a), 7.28–8.17 (m, 10H, 2Ph), 8.66 (s, 1H, C=NH). Anal.: calcd for $C_{93}H_{116}N_3O_{51}Cl_3$: C, 50.81; H, 5.32; N, 1.91; found: C, 50.78; H, 5.13; N, 1.88%.

***O*-(Methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-*O*-(2,4-di-*O*-benzoyl-6-*O*-levulinoyl-β-D-galactopyranosyl)-(1→4)-*O*-[(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-(1→3)]-*O*-(2-acetamido-6-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl)-(1→1)-(2*S*,3*R*,4*E*)-2-azido-3-*O*-benzoyl-4-octadecene-1,3-diol (36).** To a solution of **34** (83.6 mg, 38 μmol) and (2*S*,3*R*,4*E*)-2-azido-3-*O*-benzoyl-4-octadecene-1,3-diol (**35**, 32.5 mg, 76 μmol) in dry CH_2Cl_2 (1 mL) was added MS 4 Å (AW-300, 300 mg), and the mixture was stirred for 5 h at room temperature, then cooled to 0 °C. BF_3•OEt_2 (10 μL, 37 μmol) was added, and the mixture was stirred for a further 5 h at 0 °C. The solids were filtered off and washed with CH_2Cl_2. The combined filtrate and washings were washed with M Na_2CO_3 and water, dried (Na_2SO_4) and concentrated. Column chromatography (ethyl acetate:hexane 3:1) of the residue on silica gel gave **36** (59.5 mg, 63%) as an amorphous mass; $[\alpha]_D$ −7.5° (*c* 1.2, $CHCl_3$); IR (KBr): 3300, 2100, 1750, 1680, 1540, 1230, 710 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 0.88 (t, 3H, $J_{Me,CH2}=6.8$ Hz, MeCH$_2$), 1.24 (s, 22H, 11CH$_2$), 1.58, 1.78 (2s, 6H, 2AcN), 1.85–2.23 (15s, 45H, 14AcO, MeCOCH$_2$CH$_2$), 2.38 [dd, 1H, $J_{gem}=12.6$, $J_{3e(eq),4}=4.2$ Hz, H-3e(*eq*)], 2.62–2.81 (m, 4H, MeCOCH$_2$CH$_2$), 3.87 (s, 3H, MeO), 4.46 (d, 1H, $J_{1,2}=7.0$ Hz, H-1a), 5.92 (dt, 1H, $J_{4,5}=14.7$, $J_{5,6}=J_{5,6'}=6.8$ Hz, H-5 of sphingosine), 7.28–8.17 (m, 15H, 3Ph). Anal.: calcd for $C_{116}H_{153}N_5O_{53}$: C, 56.51; H, 6.26; N, 2.84; found: C, 56.32; H, 5.96; N, 2.56%.

***O*-(Methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-*O*-(2,4-di-*O*-benzoyl-6-*O*-levulinoyl-β-D-galactopyranosyl)-(1→4)-*O*-[(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-(1→3)]-*O*-(2-acetamido-6-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl)-(1→1)-(2*S*,3*R*,4*E*)-2-octadecanamido-4-octadecene-1,3-diol (37).** Hydrogen sulfide was bubbled through a stirred solution of **36** (72.5 mg, 29 μmol) in aq 83% pyridine (10 mL) for 3 days at 0 °C, with the progress of the reaction being monitored by TLC. The mixture was concentrated, and the residue was stirred with octadecanoic acid (17 mg, 60 μmol) and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (WSC, 17 mg, 89 μmol) in dry CH_2Cl_2 (2 mL) for 12 h at room temperature. After completion of the reaction, CH_2Cl_2 (30 mL) was added to the mixture, and the solution was washed with water, dried (Na_2SO_4) and concentrated to a syrup that was chromatographed on a column of silica gel with ethyl acetate:hexane 4:1, to give **37** (43.2 mg, 54%) as an amorphous mass; $[\alpha]_D$ −5.1° (*c* 0.9, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$): δ 0.88 (t, 6H, $J_{Me,CH2}=7.0$ Hz, 2MeCH$_2$), 1.26 (s, 52H, 26CH$_2$), 1.57, 1.78 (2s, 6H, 2AcN), 1.85–2.23 (15s, 45H, 14AcO, MeCOCH$_2$CH$_2$), 2.38 (dd, 1H, $J_{gem}=12.5$, $J_{3e(eq),4}=4.2$ Hz, H-3e(*eq*)), 2.62–2.81 (m, 4H, MeCOCH$_2$CH$_2$), 3.87 (s, 3H, MeO), 5.87 (dt, 1H, $J_{4,5}=13.7$, $J_{5,6}=J_{5,6'}=6.8$ Hz, H-5 of sphingosine), 7.27–8.17 (m, 15H, 3Ph). Anal.: calcd for $C_{134}H_{189}N_3O_{54}$: C, 59.48; H, 7.07; N, 1.50; found: C, 59.45; H, 6.88; N, 1.29%.

***O*-(Methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-*O*-(4,6-di-*O*-acetyl-2-*O*-benzoyl-β-D-galactopyranosyl)-(1→4)-*O*-[(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-(1→3)]-*O*-(2-acetamido-2-deoxy-6-*O*-levulinoyl-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl trichloroacetimidate (38).** Selective removal of the 2-(trimethylsilyl)ethyl group in **32** (220.5 mg, 0.11 μmol) with CF_3CO_2H (4 mL) in CH_2Cl_2 (12 mL) for 2.5 h at room temperature, and subsequent reaction of the product with trichloroacetonitrile (0.32 μL, 3.2 mmol) in CH_2Cl_2 (1.8 mL) in the presence of DBU (19 μL, 0.13 mmol) for 2 h at 0 °C as described for **34** gave **38** (218.7 mg, 98%) as an amorphous mass; $[\alpha]_D$ +8.3° (*c* 1.7, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$): δ 1.24 (d, 3H, $J_{5,6}=7.1$ Hz, H-6f), 1.49, 1.78 (2s, 6H, 2AcN), 1.91–2.20 (16s, 48H, 15AcO, MeCOCH$_2$CH$_2$), 2.51 [dd, 1H, $J_{gem}=12.8$, $J_{3e(eq),4}=4.4$ Hz, H-3e(*eq*)], 2.69–2.79 (m, 4H, MeCOCH$_2$CH$_2$), 3.86 (s, 3H, MeO), 6.47 (d, 1H, $J_{1,2}=3.7$ Hz, H-1a), 7.30–8.15 (m, 5H, Ph), 8.67 (s, 1H, C= NH). Anal.: calcd for $C_{88}H_{114}N_3O_{51}Cl_3$: C, 49.48; H, 5.38; N, 1.97; found: C, 49.41; H, 5.16; N, 1.71%.

***O*-(Methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-*O*-(4,6-di-*O*-acetyl-2-*O*-benzoyl-β-D-galactopyranosyl)-(1→4)-*O*-[(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-(1→3)]-*O*-(2-acetamido-2-deoxy-6-*O*-levulinoyl-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl)-(1→1)-(2*S*,3*R*,4*E*)-2-azido-3-*O*-benzoyl-4-octadecene-1,3-diol (39).** Coupling of **38** (218.7 mg, 0.1 mmol) with **35** (88 mg, 0.21 mmol) in CH_2Cl_2 (2 mL) in the presence of BF_3•OEt_2 (28 μL, 0.1 mmol) and MS-4 Å (AW-300, 600 mg) as described for **36** gave **39** (142 mg, 58%) as an amorphous mass; $[\alpha]_D$ −18.6° (*c* 1.8, $CHCl_3$); IR (KBr): 3350, 2100, 1750, 1680, 1550, 1220, 710 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 0.88 (t, 3H, $J_{Me,CH2}=6.8$ Hz, MeCH$_2$), 1.24 (s, 22H, 11CH$_2$),

1.49, 1.78 (2s, 6H, 2AcN), 1.90–2.20 (16s, 48H, 15AcO, MeCOCH$_2$CH$_2$), 2.51 [dd, 1H, J_{gem} = 12.6, $J_{3e(eq),4}$ = 4.6 Hz, H-3e(*eq*)], 3.86 (s, 3H, MeO), 4.49 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1a), 5.91 (dt, 1H, $J_{4,5}$ = 14.1, $J_{5,6}$ = $J_{5,6'}$ = 7.0 Hz, H-5 of sphingosine), 7.30–8.15 (m, 10H, 2Ph). Anal.: calcd for $C_{111}H_{151}N_5O_{53}$: C, 55.47; H, 6.33; N, 2.91; found: C, 55.21; H, 6.24; N, 2.73%.

***O*-(Methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-*O*-(4,6-di-*O*-acetyl-2-*O*-benzoyl-β-D-galactopyranosyl)-(1→4)-*O*-[(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-(1→3)]-*O*-(2-acetamido-2-deoxy-6-*O*-levulinoyl-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl)-(1→1)-(2*S*,3*R*,4*E*)-3-*O*-benzoyl-2-octadecanamido-4-octadecene-1,3-diol (40).** Selective reduction of the azido group in **39** (142 mg, 59 μmol) with H_2S in aq 83% pyridine (20 mL), followed by coupling of the product with octadecanoic acid (34 mg, 0.12 mmol) in the presence of WSC (34 mg, 0.18 mmol) and workup as described for **37** gave **40** (91.5 mg, 60%) as an amorphous mass; $[\alpha]_D$ −9.8° (*c* 1.8, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.88 (t, 6H, $J_{Me,CH2}$ = 6.8 Hz, 2MeCH$_2$), 1.26 (s, 52H, 26CH$_2$), 1.49, 1.78 (2s, 6H, 2AcN), 1.89–2.20 (16s, 48H, 15AcO, MeCOCH$_2$CH$_2$), 2.51 [dd, 1H, J_{gem} = 12.3, $J_{3e(eq),4}$ = 4.2 Hz, H-3e(*eq*)], 2.63–2.81 (m, 4H, MeCOCH$_2$CH$_2$), 3.86 (s, 3H, MeO), 5.07 (d, 1H, $J_{1,2}$ = 2.9 Hz, H-1f), 5.86 (dt, 1H, $J_{4,5}$ = 14.7, $J_{5,6}$ = $J_{5,6'}$ = 7.3 Hz, H-5 of sphingosine), 7.30–8.14 (m, 10H, 2Ph). Anal.: calcd for $C_{129}H_{187}N_3O_{54}$: C, 58.60; H, 7.13; N, 1.59; found: C, 58.40; H, 6.93; N, 1.38%.

***O*-(Methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-*O*-(2,4-di-*O*-benzoyl-6-*O*-levulinoyl-β-D-galactopyranosyl)-(1→4)-*O*-[(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-(1→3)]-*O*-(2-acetamido-2-deoxy-6-*O*-levulinoyl-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl trichloroacetimidate (41).** Selective removal of the 2-(trimethylsilyl)ethyl group in **33** (109 mg, 50 μmol) with CF_3CO_2H (2 mL) in CH_2Cl_2 (6 mL) for 2.5 h at room temperature, followed by treatment of the 1-hydroxy compound with trichloroacetonitrile (0.143 mL, 1.4 mmol) in CH_2Cl_2 (0.9 mL) in the presence of DBU (8.5 μL, 57 μmol) for 2 h at 0 °C and work up as described for **34** gave **41** (99.5 mg, 89%) as an amorphous mass; $[\alpha]_D$ +8.3° (*c* 1.7, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.19 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6f), 1.58, 1.78 (2s, 6H, 2AcN), 1.85–2.32 (15s, 45H, 13AcO, 2MeCOCH$_2$CH$_2$), 2.61–2.85 (m, 8H, 2MeCOCH$_2$CH$_2$), 3.87 (s, 3H, MeO), 5.64 (m, 1H, H-8e), 6.47 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1a), 7.28–8.17 (m, 10H, 2Ph), 8.65 (s, 1H, C= NH). Anal.: calcd for $C_{96}H_{120}N_3O_{52}Cl_3$: C, 51.15; H, 5.37; N, 1.86; found: C, 51.02; H, 5.30; N, 1.62%.

***O*-(Methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-*O*-(2,4-di-*O*-benzoyl-6-*O*-levulinoyl-β-D-galactopyranosyl)-(1→4)-*O*-[(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-(1→3)]-*O*-(2-acetamido-2-deoxy-6-*O*-levulinoyl-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl)-(1→1)-(2*S*,3*R*,4*E*)-2-azido-3-*O*-benzoyl-4-octadecene-1,3-diol (42).** Coupling of **41** (99.5 mg, 44 μmol) with **35** (38 mg, 89 μmol) in CH_2Cl_2 (1 mL) in the presence of BF_3•OEt_2 (12 μL, 44 μmol) and MS-4 Å (AW-300, 300 mg) as described for **36** gave **42** (53 mg, 48%) as an amorphous mass; $[\alpha]_D$ −12.8° (*c* 1.1, $CHCl_3$); IR (KBr) 3350, 2100, 1750, 1690, 1540, 1220, 710 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.86 (t, 3H, $J_{Me,CH2}$ = 7.0 Hz, MeCH$_2$), 1.24 (s, 22H, 11CH$_2$), 1.58, 1.78 (2s, 6H, 2AcN), 1.85–2.23 (15s, 45H, 13AcO, 2MeCOCH$_2$CH$_2$), 2.38 (dd, 1H, J_{gem} = 12.3, $J_{3e(eq),4}$ = 4.8 Hz, H-3e(*eq*)), 2.63–2.78 (m, 8H, 2MeCOCH$_2$CH$_2$), 3.87 (s, 3H, MeO), 4.43 (d, 1H, $J_{1,2}$ = 7.6 Hz, H-1a), 5.91 (dt, 1H, $J_{4,5}$ = 13.6, $J_{5,6}$ = $J_{5,6'}$ = 6.8 Hz, H-5 of sphingosine), 7.28–8.17 (m, 15H, 3Ph). Anal.: calcd for $C_{119}H_{157}N_5O_{54}$: C, 56.68; H, 6.28; N, 2.78; found: C, 56.62; H, 6.14; N, 2.51%.

***O*-(Methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-*O*-(2,4-di-*O*-benzoyl-6-*O*-levulinoyl-β-D-galactopyranosyl)-(1→4)-*O*-[(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-(1→3)]-*O*-(2-acetamido-2-deoxy-6-*O*-levulinoyl-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-(2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl)-(1→1)-(2*S*,3*R*,4*E*)-3-*O*-benzoyl-2-octadecanamido-4-octadecene- 1,3-diol (43).** Selective reduction of the azido group in **42** (53 mg, 21 μmol) with H_2S in aq 83% pyridine (10 mL), followed by coupling of the product with octadecanoic acid (12 mg, 42 μmol) in the presence of DBU (12 mg, 63 μmol) and workup as described for **37** gave **43** (34.5 g, 60%) as an amorphous mass; $[\alpha]_D$ −6.0° (*c* 0.7, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.88 (t, 6H, $J_{Me,CH2}$ = 6.8 Hz, 2*Me*$_2$CH$_2$), 1.26 (s, 52H, 26CH$_2$), 1.58, 1.78 (2s, 6H, 2AcN), 1.85–2.24 (15s, 45H, 13AcO, 2MeCOCH$_2$CH$_2$), 2.38 [dd, 1H, J_{gem} = 12.8, $J_{3e(eq),4}$ = 4.8 Hz, H-3e(*eq*)], 2.61–2.78 (m, 8H, 2MeCOCH$_2$CH$_2$), 3.87 (s, 3H, MeO), 5.86 (dt, 1H, $J_{4,5}$ = 14.4, $J_{5,6}$ = $J_{5,6'}$ = 7.2 Hz, H-5 of sphingosine), 7.27–8.17 (m, 15H, 3Ph). Anal.: calcd for $C_{137}H_{193}N_3O_{55}$: C, 59.58; H, 7.04; N, 1.52; found: C, 59.41; H, 6.80; N, 1.26%.

***O*-(Methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-*O*-(2,4-di-*O*-benzoyl-β-D-galactopyranosyl)-(1→4)-*O*-[(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-(1→3)]-*O*-(2-acetamido-6-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl)-(1→1)-(2*S*,3*R*,4*E*)-3-*O*-benzoyl-2-octadecanamido-4-octadecene-1,3-diol (44).** To a solution of **37** (10.7 mg, 3.9 μmol) in EtOH (0.3 mL) was added hydrazine monoacetate (0.4 mg, 4.3 μmol), and the mixture was stirred for 30 min at room temperature then concentrated. Column chromatography (CH_2Cl_2:MeOH 20:1) of the residue on silica gel gave **44** (7.0 mg, 70%) as an amorphous mass; $[\alpha]_D$ −6.4° (*c* 0.5, $CHCl_3$); ^{1}H NMR

(270 MHz, $CDCl_3$): δ 0.88 (t, 6H, $J_{Me,CH2}=7.0$ Hz, 2MeCH$_2$), 1.26 (s, 52H, 26CH$_2$), 1.54, 1.78 (2s, 6H, 2AcN), 1.86–2.22 (14s, 42H, 14AcO), 2.38 [dd, 1H, $J_{gem}=12.1$, $J_{3e(eq),4}=4.2$ Hz, H-3e(*eq*)], 3.77 (s, 3H, MeO), 5.86 (dt, 1H, $J_{4,5}=13.4$, $J_{5,6}=J_{5,6'}=6.7$ Hz, H-5 of sphingosine), 7.27–8.18 (m, 15H, 3Ph). Anal.: calcd for $C_{127}H_{183}N_3O_{52}$: C, 59.41; H, 7.07; N, 1.61; found: C, 59.32; H, 6.99; N, 1.47%.

***O*-(Methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-*O*-(2,4-di-*O*-benzoyl-6-*O*-sulfo-β-D-galactopyranosyl)-(1→4)-*O*-[(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-(1→3)]-*O*-(2-acetamido-6-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-(2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl)-(1→1)-(2*S*,3*R*,4*E*)-3-*O*-benzoyl-2-octadecanamido-4-octadecene-1,3-diol pyridine salt (45)**. To a solution of **44** (23.5 mg, 8.9 μmol) in DMF (0.5 mL) was added sulfur trioxide–pyridine complex (7 mg, 44 μmol) and the mixture was stirred for 4 h at room temperature. MeOH (2 mL) was added, and the mixture was concentrated. Column chromatography ($CHCl_3$:MeOH 5:1) of the residue on Sephadex LH-20 (20 g) gave the crude product, and this was purified by column chromatography on silica gel (20 g) with CH_2Cl_2:MeOH 15:1, to give **45** (24.2 mg, 98%) as an amorphous mass; $[\alpha]_D$ −3.3° (*c* 0.5, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.88 (t, 6H, $J_{Me,CH2}=7.0$ Hz, 2MeCH$_2$), 1.26 (s, 52H, 26CH$_2$), 1.55, 1.78 (2s, 6H, 2AcN), 1.88–2.24 (14s, 42H, 14AcO), 3.82 (s, 3H, MeO), 5.86 (dt, 1H, $J_{4,5}=14.7$, $J_{5,6}=J_{5,6'}=7.3$ Hz, H-5 of sphingosine), 7.27–8.15 (m, 20H, 3Ph, C_5H_5N). Anal.: calcd for $C_{134}H_{187}N_4O_{55}S$: C, 58.19; H, 6.81; N, 2.03; found: C, 58.10; H, 6.65; N, 1.98%.

***O*-(Methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-*O*-(4,6-di-*O*-acetyl-2-*O*-benzoyl-β-D-galactopyranosyl)-(1→4)-*O*-[(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-(1→3)]-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl)-(1→1)-(2*S*,3*R*,4*E*)-3-*O*-benzoyl-2-octadecanamido-4-octadecene-1,3-diol (46)**. Selective hydrolysis of the levulinoyl group in **40** (91.1 mg, 34 μmol) with hydrazine monoacetate (3.8 mg, 41 μmol) in EtOH (2.1 mL) and workup as described for **44** gave **46** (44.5 mg, 50%) as an amorphous mass; $[\alpha]_D$ −13.0° (*c* 0.6, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.88 (t, 6H, $J_{Me,CH2}=6.8$ Hz, 2MeCH$_2$), 1.26 (s, 52H, 26CH$_2$), 1.48, 1.78 (2s, 6H, 2AcN), 1.88–2.21 (15s, 45H, 15AcO), 2.53 [dd, 1H, $J_{gem}=12.3$, $J_{3e(eq),4}=4.4$ Hz, H-3e(*eq*)], 3.87 (s, 3H, MeO), 5.87 (dt, 1H, $J_{4,5}=13.4$, $J_{5,6}=J_{5,6'}=6.7$ Hz, H-5 of sphingosine), 7.27–8.18 (m, 10H, 2Ph). Anal.: calcd for $C_{124}H_{181}N_3O_{52}$: C, 58.50; H, 7.17; N, 1.65; found: C, 58.34; H, 7.12; N, 1.64%.

***O*-(Methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-*O*-(4,6-di-*O*-acetyl-2-*O*-benzoyl-β-D-galactopyranosyl)-(1→4)-*O*-[(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-(1→3)]-*O*-(2-acetamido-2-deoxy-6-*O*-sulfo-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-(2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl)-(1→1)-(2*S*,3*R*,4*E*)-3-*O*-benzoyl-2-octadecanamido-4-octadecene-1,3-diol pyridine salt (47)**. To a solution of **46** (29 mg, 11 μmol) in DMF (0.5 mL) was added sulfur trioxide–pyridine complex (9 mg, 57 μmol), and the mixture was stirred for 2 h at room temperature and work up as described for **45** gave **47** (28 mg, 91%) as an amorphous mass; $[\alpha]_D$ −18.7° (*c* 0.6, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.88 (t, 6H, $J_{Me,CH2}=7.0$ Hz, 2MeCH$_2$), 1.26 (s, 52H, 26CH$_2$), 1.48, 1.80 (2s, 6H, 2AcN), 1.85–2.18 (15s, 45H, 15AcO), 3.80 (s, 3H, MeO), 5.86 (dt, 1H, $J_{4,5}=13.2$, $J_{5,6}=J_{5,6'}=6.6$ Hz, H-5 of sphingosine), 7.27–8.24 (m, 15H, 2Ph, C_5H_5N). Anal.: calcd for $C_{129}H_{185}N_4O_{55}S$: C, 57.30; H, 6.90; N, 2.07; found: C, 57.04; H, 6.87; N, 1.80%.

***O*-(Methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-*O*-(2,4-di-*O*-benzoyl-β-D-galactopyranosyl)-(1→4)-*O*-[(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-(1→3)]-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl)-(1→1)-(2*S*,3*R*,4*E*)-3-*O*-benzoyl-2-octadecanamido-4-octadecene-1,3-diol (48)**. Selective hydrolysis of the levulinoyl groups in **43** (34.2 mg, 12 μmol) with hydrazine monoacetate (2.7 mg, 29 μmol) in EtOH (0.7 mL) for 3 h at room temperature and workup as described for **44** gave **48** (16 mg, 49%) as an amorphous mass; $[\alpha]_D$ −6.3° (*c* 0.3, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.88 (t, 6H, $J_{Me,CH2}=7.0$ Hz, 2MeCH$_2$), 1.26 (s, 52H, 26CH$_2$), 1.55, 1.78 (2s, 6H, 2AcN), 1.82–2.24 (13s, 39H, 13AcO), 3.77 (s, 3H, MeO), 5.86 (dt, 1H, $J_{4,5}=14.8$, $J_{5,6}=J_{5,6'}=7.4$ Hz, H-5 of sphingosine), 7.32–8.30 (m, 15H, 3Ph). Anal.: calcd for $C_{127}H_{181}N_3O_{51}$: C, 59.45; H, 7.11; N, 1.64; found: C, 59.43; H, 7.07; N, 1.50%.

***O*-(Methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate)-(2→3)-*O*-(2,4-di-*O*-benzoyl-6-*O*-sulfo-β-D-galactopyranosyl)-(1→4)-*O*-[(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-(1→3)]-*O*-(2-acetamido-2-deoxy-6-*O*-sulfo-β-D-glucopyranosyl)-(1→3)-*O*-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl)-(1→1)-(2*S*,3*R*,4*E*)-3-*O*-benzoyl-2-octadecanamido-4-octadecene-1,3-diol dipyridine salt (49)**. To a solution of **48** (10.5 mg, 4 μmol) in DMF (0.5 mL) was added sulfur trioxide–pyridine complex (6.4 mg, 40 μmol) and the mixture was stirred for 2 h at room temperature and work up as described for **45** gave **49** (10.6 mg, 91%) as an amorphous mass; $[\alpha]_D$ −8.0° (*c* 0.4, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.88 (t, 6H, $J_{Me,CH2}=6.8$ Hz, 2MeCH$_2$), 1.26 (s, 52H, 26CH$_2$), 1.60–2.24 (15s, 45H, 13AcO, 2AcN), 3.78 (s, 3H, MeO), 5.86 (m, 1H, H-5 of sphingosine), 7.26–8.25 (m, 25H, 3Ph, 2C_5H_5N). Anal.: calcd for $C_{137}H_{189}N_5O_{57}S_2$: C, 57.09; H, 6.61; N, 2.43; found: C, 57.02; H, 6.53; N, 2.23%.

***O*-(5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonic acid)-(2→3)-*O*-(6-*O*-sulfo-β-D-galactopyranosyl)-(1→4)-*O*-[α-L-fucopyranosyl-(1→3)]-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→3)-*O*-β-D-galactopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→1)-(2*S*,3*R*,4*E*)-2-octadecanamido-1,3-diol disodium salt (50).** To a solution of **45** (24.2 mg, 8.7 μmol) in MeOH (2 mL) and 1,4-dioxane (1 mL) was added NaOMe (600 mg, 28% NaOMe in MeOH), and the mixture was stirred for 48 h at 20 °C then water (1 mL) was added. After completion of the reaction (24 h), the mixture was concentrated. Column chromatography ($CHCl_3$:MeOH:H_2O:Et_3N 5:4:0.7:0.07) of the residue on Sephadex (40 g) gave **50** (15.5 mg, 98%) as an amorphous mass; $[\alpha]_D$ −5.7° (*c* 0.5, $CHCl_3$:MeOH:H_2O 5:4:0.7); ^1H NMR (270 MHz, $CDCl_3$:CD_3OD 1:1): δ 0.89 (t, 6H, $J_{Me,CH2}$ = 7.0 Hz, 2MeCH_2), 1.27 (s, 52H, 26CH_2), 2.31 [dd, 1H, J_{gem} = 11.0, $J_{3e(eq),4}$ = 4.0 Hz, H-3e(*eq*)], 5.46 (dd, 1H, $J_{3,4}$ = 6.8, $J_{4,5}$ = 15.9 Hz, H-4 of sphingosine), 5.69 (dt, 1H, $J_{5,6}$ = $J_{5,6'}$ = 7.7 Hz, H-5 of sphingosine); IR (KBr) 3600–3200, 2920, 2850, 1700, 1660, 1550 cm $^{-1}$; The mass spectrum of **50** (negative ion mode) showed the base peak at m/z 1794 $(M\text{-}Na)^-$ and 1771 $(M\text{-}2Na)^{2-}$.

***O*-(5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonicacid)-(2→3)-*O*-β-D-galactopyranosyl-(1→4)-*O*-[α-L-fucopyranosyl-(1→3)]-*O*-(2-acetamido-2-deoxy-6-*O*-sulfo-β-D-glucopyranosyl)-(1→3)-*O*-β-D-galactopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→1)-(2*S*,3*R*,4*E*)-2-octadecanamido-1,3-diol disodium salt (51).** To a solution of **47** (28 mg, 10 μmol) in MeOH (2 mL) and 1,4-dioxane (1 mL) was added NaOMe (600 mg, 28% NaOMe in MeOH), and work up as described for **50** gave **51** (18.2 mg, 98%) as an amorphous mass; $[\alpha]_D$ −8.7° (*c* 0.6, $CHCl_3$:MeOH:H_2O 5:7:2); IR (KBr) 3600–3200, 2920, 2850, 1700, 1660, 1550 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$:CD_3OD 1:1): δ 0.89 (t, 6H, J_{Me,CH_2} = 6.8 Hz, 2MeCH_2), 1.28 (s, 52H, 26CH_2), 2.31 [m, 1H, H-3e(*eq*)], 5.46 (m, 1H, H-4 of sphingosine), 5.69 (dt, 1H, J_{gem} = 15.5, $J_{5,6}$ = $J_{5,6'}$ = 7.0 Hz, H-5 of sphingosine). The mass spectrum of **51** (negative ion mode) showed the base peaks at m/z 1794 (M-Na) and 1771 $(M\text{-}2Na)^{2-}$.

***O*-(5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonic acid)-(2→3)-*O*-(6-*O*-sulfo-β-D-galactopyranosyl)-(1→4)-*O*-[α-L-fucopyranosyl-(1→3)]-*O*-(2-acetamido-2-deoxy-6-*O*-sulfo-β-D-glucopyranosyl)-(1→3)-*O*-β-D-galactopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→1)-(2*S*,3*R*,4*E*)-2-octadecanamido-4-octadecene-1,3-diol trisodium salt (52).** To a solution of **49** (10.6 mg, 3.6 μmol) in MeOH (2 mL) and 1,4-dioxane (1 mL) was added NaOMe (600 mg, 28% NaOMe in MeOH), and work up as described for **50** gave **52** (6.8 mg, 98%) as an amorphous mass; $[\alpha]_D$ −10.3° (*c* 0.2, $CHCl_3$:MeOH:H_2O 5:4:0.7); IR (KBr): 3600–3250, 2920, 2850, 1700, 1660, 1550 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$:CD_3OD 1:1): δ 0.89 (t, 6H, J_{Me,CH_2} = 6.8 Hz, 2MeCH_2), 1.27 (s, 52H, 26CH_2), 1.97, 2.03 (2s, 6H, 2AcN), 2.30 [m, 1H, H-3e(*eq*)], 5.45 (m, 1H, H-4 of sphingosine), 5.70 (dt, 1H, $J_{4,5}$ = 14.5, $J_{5,6}$ = $J_{5,6'}$ = 6.8 Hz, H-5 of sphingosine). The MS of **52** (negative ion mode) showed the base peak at *m/z* 1895 $(M\text{-}Na)^-$.

Acknowledgment

This work was supported in part by grant-in-aid for Scientific Research on Priority Areas from the Japanese Ministry of Education, Science and Culture (No. 07273226 and 05274102).

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(*Received in U.S.A.* 17 *January* 1996; *accepted* 16 *May* 1996)