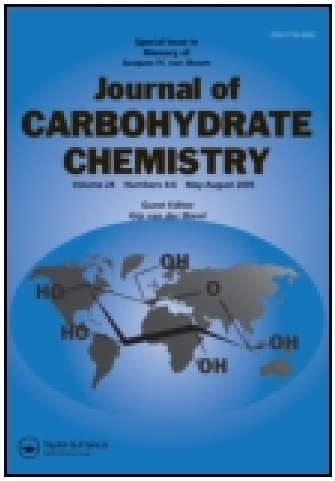

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Synthesis and Antigenic Property of a Novel Sialyl 6-*O*-Sulfo Lewis X Neo-glycolipid Containing Lactamized Neuraminic Acid[#]

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CONTENTS

[#]Synthetic Studies on Sialoglycoconjugates, Part 136. For part 135, see Ref.[1].

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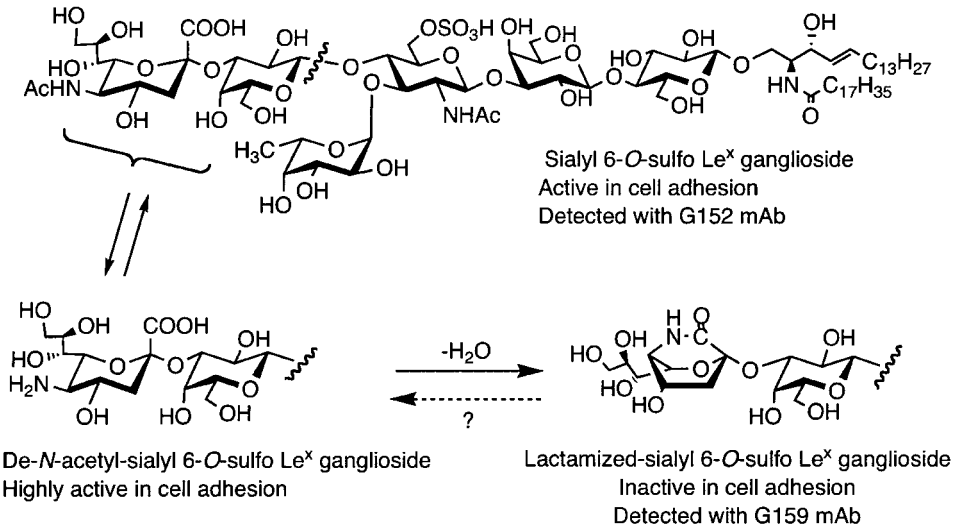
ABSTRACT

Synthesis and antigenic property of a novel 6-*O*-sulfated sLe^x neo-glycolipid containing lactamized neuraminic acid are described. Coupling of methyl (methyl 4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-5-trifluoroacetamido-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2 $\rightarrow$ 3)-4,6-di-*O*-acetyl-2-*O*-benzoyl-1-thio-β-D-galactopyranoside **(3)** with 2-(tetradecyl)hexadecyl (2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1 $\rightarrow$ 3)-2-acetamido-2-deoxy-6-*O*-4-methoxyphenyl-β-D-glucopyranoside **(7)** gave a protected sLe^x tetrasaccharide glycolipid **(8)**. Removal of all the acyl protecting groups and subsequent lactamization afforded the lactamized sLe^x derivative**(10)**, which was converted to the target compound **(14)** by selective removal of the 4-methoxyphenyl group and 6-*O*-sulfation of the GlcNAc residue, and removal of all protective groups under the basic conditions furnished the target molecule. The antigenic property of the synthesized neo-glycolipid was examined by TLC-immunostaining with G159 monoclonal antibody.

Key Words: Selectin; Sialic acid; Sialyl Lewis X; Glycolipid.

INTRODUCTION

L-selectin mediates the attachment of lymphocytes to specialized high endothelial venules (HEV) in the course of their migration from the blood to lymphoid tissues.[2] We have shown that the sialyl 6-*O*-sulfo Lewis X serves as the major endogenous ligand for L-selectin on HEV in human lymph nodes,[3,4] and proposed the ligand processing pathway involving "activation" by de-*N*-acetylation of sialic acid and "inactivation" by lactamization (Fig. 1). The G159 mAb has newly been cloned as the monoclonal antibody which specifically recognizes the lactamized-sialyl 6-*O*-sulfo Le^x ganglioside.[5]



Figrure 1. Proposed ligand processing pathway and binding reactivity for human L-selectin.

To investigate the structure required for recognition by G159 monoclonal antibody, we have synthesized lactamized GM4[6] and sLe^x[7] analogs containing lactamized neuraminic acid. However, these compounds were not recognized by G159 mAb, suggesting that the antibody may specifically recognize the structure involving the 6-*O*-sulfated GlcNAc residue. We here describe the synthesis of lactamized-sialyl 6-*O*-sulfo Lewis X tetrasaccharide glycolipid **(14)** containing both lactamized neuraminic acid and the 6-*O*-sulfated GlcNAc residue being expected as the minimal structure defined by G159 mAb (Fig. 2).

RESULTS AND DISCUSSION

The main problems to be solved in the synthesis of the title compound **14** are (i) suitable protection of the amino group at C-5 of neuraminic acid and 6-OH of the GlcNAc residue, which undergo lactamization and sulfation, respectively, and (ii) efficient introduction of the lipid part and fucose. To solve the first problem, we designed the suitably protected sialyl Lewis X tetrasaccharide glycolipid **8** (Sch. 1) as the key intermediate,

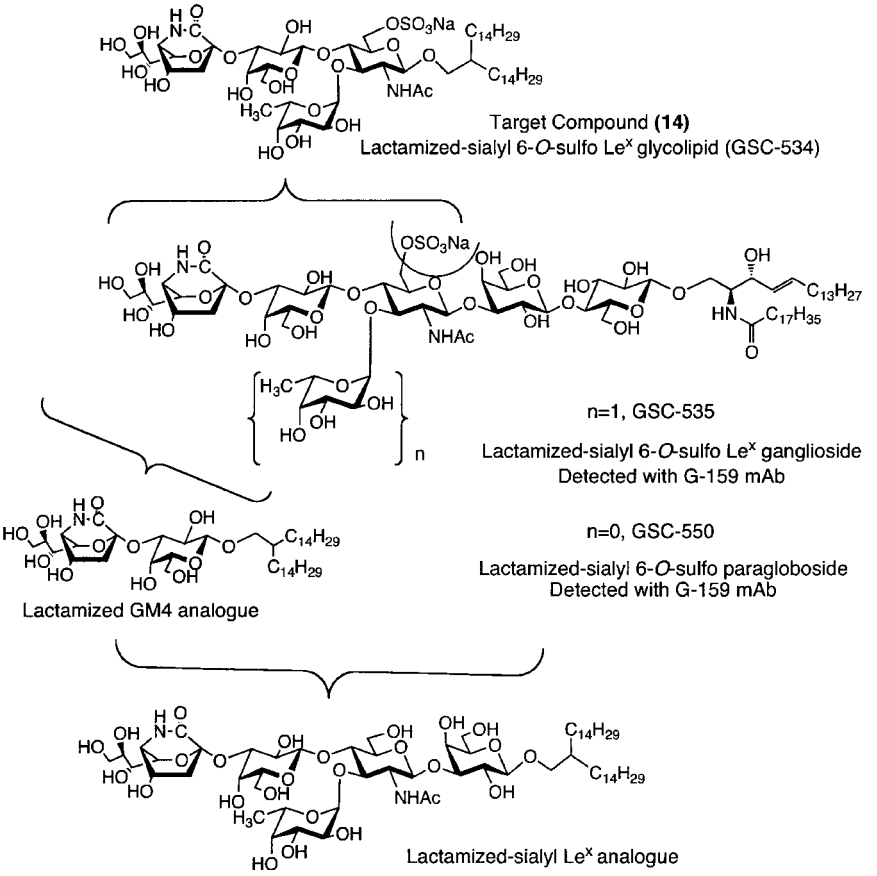
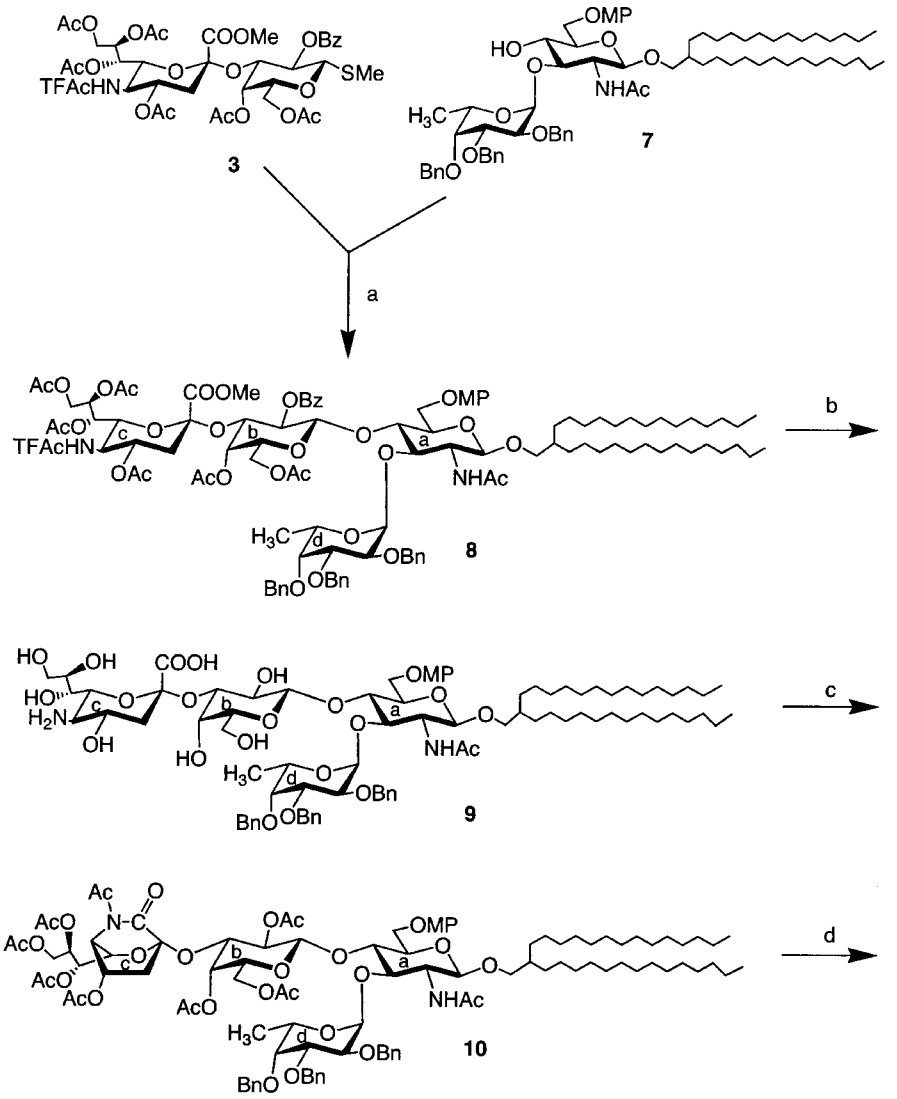
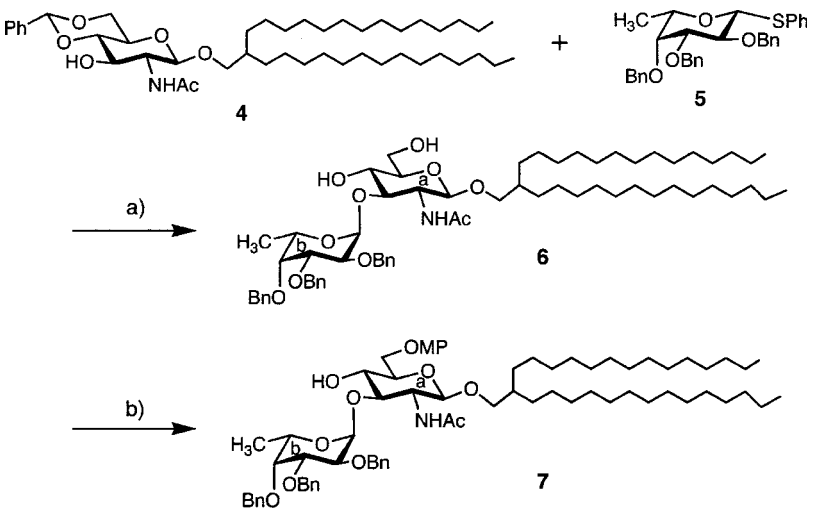


Figure 2. Lactamized-sialyl Le^x analog.



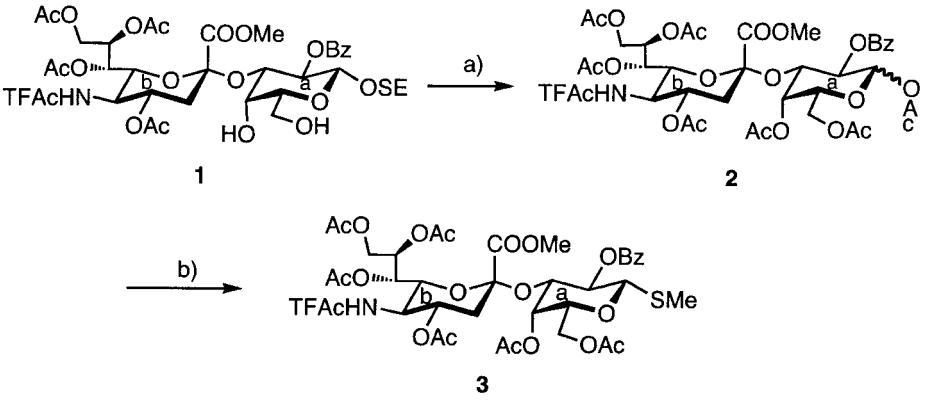
Scheme 1. (a) DMTST/CH_2Cl_2, MS4A, 0°C, 57%; (b) NaOMe/MeOH, then H_2O, 45°C, 95%; (c) 1, HBTU, HOBt/DMF, 65°C, 2, Ac_2O/Pyr, 76.2% (two steps); (d) 1, H_2, $Pd(OH)_2$/EtOH, 2, Ac_2O/Pyr, 93% (two steps).

in which the amino group of neuraminic acid and 6-OH of the GlcNAc residue are protected by the trifluoroacetyl (TFAc) and 4-methoxyphenyl (MP) groups, respectively. The TFAc protected sialic acid is equivalent to the *N*-deacetylated and lactamized sialic acids, and the MP group can be chemoselectively cleaved by ceric ammonium nitrate (CAN). For the second problem, we examined the efficient construction of 2-(tetradecyl)hexadecyl (2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1 $\rightarrow$ 3)-2-acetamido-6-*O*-4-methoxyphenyl-2-deoxy-β-D-glucopyranoside **(7)** (Sch. 2).



Scheme 2. (a) 1, NIS, TfOH/benzene, 7°C; 2, 80% AcOHaq, 45°C, 51%, two steps and (b) MPOH, PPh_3, DEAD/THF, 80°C, 88%.

The suitably protected sialyl galactose donor **3** was prepared by treatment of **1**[8] with boron trifluoride etherate in dichloromethane–acetic anhydride, giving the acetate **2** (97%, $\alpha/\beta = 5/1$),[9] and successive treatment of **2** with methylthiotrimethylsilane (TMSSMe) and trimethylsilyl trifluoromethanesulfonate (TMSOTf) in dichloroethane for 72 hr at 50°C (Sch. 3). For the synthesis of acceptor **7**, compound **4** was first synthesized by using the established method,[10] and then coupled with the fucose donor **5**.[11] The resulting crude disaccharide was treated with 80% AcOH at 45°C to afford **6** in 51% yield in two steps (Sch. 2). The low yield of this reaction was owing to a cleavage of the tri-*O*-benzylated fucoside during the acidic hydrolysis of the benzylidene acetal. In the ^{1}H NMR spectrum of **6**, the anomeric proton of fucose appeared at δ 4.94 (d, $J_{1,2} = 3.8$ Hz, H-1b), indicating the newly formed glycoside linkage to be α. The regioselective 4-methoxyphenylation

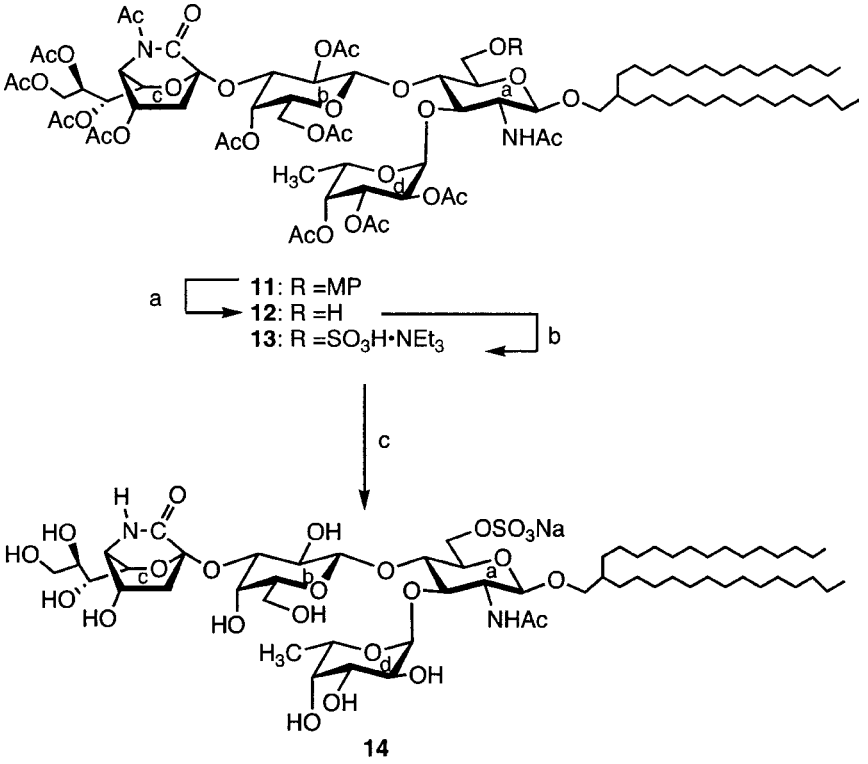


Scheme 3. (a) $BF_3 \cdot OEt_2$, Ac_2O/CH_2Cl_2, 97% and (b) TMSSMe, TMSOTf/CH_2ClCH_2Cl, 50°C, 89%.

at *O*-6 of **6** was carried out by treatment with *p*-methoxyphenol (MPOH), PPh_3, and diethylazodicarboxylate (DEAD) in THF,[12,13] to give **7** in 88% yield.

Coupling of **3** and **7**, promoted by dimethyl(methylthio)sulfonium triflate (DMTST),[14,15] gave the desired tetrasaccharide glycolipid **8** in 57% yield (Sch. 1). The partial *N*,*O*-deacylation of **8** with sodium methoxide in methanol for 72 hr at 45°C, and subsequent saponification of the methylester group afforded *N*-deacetylated sLe^x derivative **9** in 95% yield, which upon treatment with HBTU[16] and HOBt in DMF at 65°C, followed by acetylation to afford the desired **10** in good yield (76%, two steps). The ^1H NMR spectrum of **10** showed signals at δ 2.32 (dd, 1H, $J_{3\beta,4} = 10.1$ Hz, $J_{gem} = 14.6$ Hz, H-3cβ), and δ 2.41 (dd, 1H, $J_{3\alpha,4} = 5.5$ Hz, $J_{gem} = 14.6$ Hz, H-3cα), which are characteristic of the $B^{5,2}$ boat conformation of sialic acid.[6] Hydrogenolytic removal of the benzyl (Bn) groups in **10** and the following acetylation gave **11** (93%, two steps). Selective cleavage of the MP group in **11** and the subsequent 6-*O*-sulfation of **12** with a sulfur trioxide–pyridine ($SO_3 \cdot$ Pyr.) complex in DMF, followed by an addition of triethylamine to stabilize the sulfate group during the column chromatography, gave **13** in good yield. Removal of all protective groups in **13** under alkaline conditions furnished the target compound **14** (GSC-534) in high yield (Sch. 4).

As shown in Fig. 3, the compound **14** (GSC-534) was not stained with G159 antibody in TLC-immunostaining, in contrast with the lactamized-sialyl 6-*O*-sulfo Le^x ganglioside



Scheme 4. (a) CAN/CH_3CN, H_2O, 0°C, 75%; (b) $SO_3 \cdot$ Pyr complex/DMF, then Et_3N, r.t., 78%; and (c) NaOMe/MeOH, r.t., 98%.

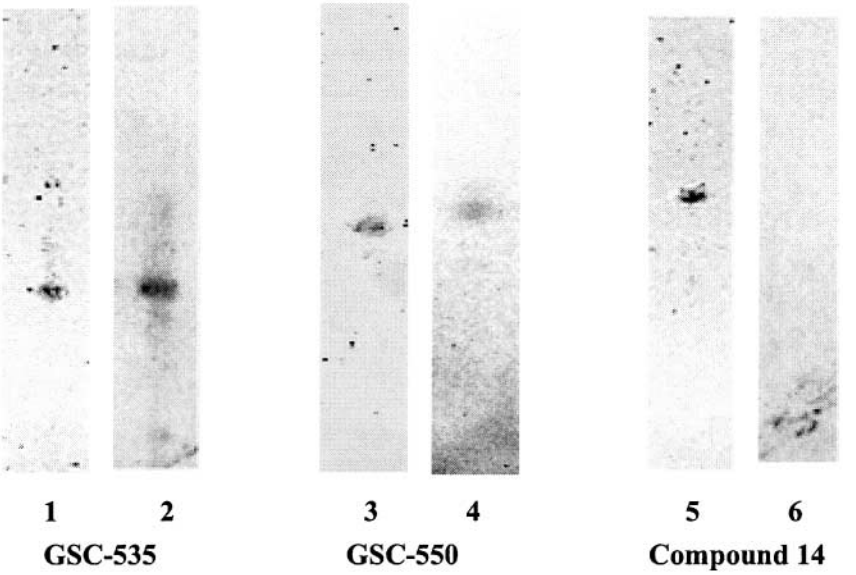


Figure 3. TLC-immunostaining patterns of synthesized glycolipids. Lanes 1, 3, and 5 are Orcinol/H_2SO_4 staining. Lanes 2, 4, and 6 are G159 mAb staining. Lactamized-sialyl 6-*O*-sulfo Lewis X ganglioside (GSC-535) and lactamized-sialyl 6-*O*-sulfo paragloboside (GSC-550) were detected with G159 mAb, but compound **14** was not.

(GSC-535)[1] as well as the corresponding paragloboside derivative (GSC-550)[1] (Fig. 2). These results suggest that the lactose moiety could be critical for the recognition by G159 mAb either as the essential component of the G159-defined determinant or as a spacer to keep the determinant apart from the lipid moiety adsorbed on TLC sheets. The difference in the structures of the ceramide and the artificial ceramide (B30) also may affect the recognition by G159 mAb. A further study to elucidate the details of the recognition mapping defined by G159 mAb is now under investigation.

In summary, we have successfully synthesized a novel 6-*O*-sulfated sLe^x neo-glycolipid, which was designed as a probe to determine the minimum structure required for the recognition by G159 mAb. Utilizing this synthetic probe, the significance of the lactose moiety for the recognition by G159 mAb was suggested.

EXPERIMENTAL

General Methods

TLC was conducted on E. Merck silica gel 60 F-254 aluminum plate. Compounds were visualized by exposure to UV light or by spraying with a solution of 10% H_2SO_4 in ethanol. Column chromatography on silica gel (Fuji Silysia Co., 300 mesh) was performed with the solvent systems (v/v) specified. Specific rotations were determined with a Horiba SEPA-300 high-sensitive polarimeter at 25°C. ^1H NMR and ^{13}C NMR spectra were recorded

at 300 K with a Varian Unity Inova 500 (500 MHz) or Varian Unity Inova 400 (100.6 MHz) spectrometer, respectively. The values (ppm) are given relative to Me_4Si as the internal standard. MALDI-TOF mass spectra were recorded on a BRUKER Daltonics Autoflex-G MALDI-TOF Mass spectrometer instrument using a 2,5-dihydroxybenzoic acid matrix. Dichloromethane, methanol, ethanol, benzene, and DMF were kept dry over 4 Å MS, while pyridine and acetonitrile were kept dry over 3 Å MS.

Methyl (methyl 4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-5-trifluoroacetamido-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2 → 3)-4,6-di-*O*-acetyl-2-*O*-benzoyl-1-thio-β-D-galactopyranoside (3). To a solution of **1** (108 mg, 0.118 mmol) in Ac_2O (0.5 mL) and dry CH_2Cl_2 (1 mL) was added $BF_3 \cdot OEt_2$ (130 μL, 0.47 mmol), and the mixture was stirred for 24 hr at room temperature and extracted with chloroform. The extract was successively washed with $NaHCO_3$ and water, dried (Na_2SO_4), and concentrated. Column chromatography (70 : 1 $CHCl_3$–MeOH) of the residue on silica gel gave **2** (108.1 mg, 97.3%) as an amorphous mass ($\alpha/\beta = 5/1$).

To a solution of **2** (108.1 mg, 0.12 mmol) in dry CH_2ClCH_2Cl (1 mL) were added TMSSMe (57.4 μL, 0.45 mmol) and TMSOTf (77.8 μL, 0.4 mmol). The mixture was stirred for 72 hr at 50°C. After dilution with chloroform, the extract was successively washed with 1 M sodium carbonate and water, dried (Na_2SO_4), and concentrated. Column chromatography (100 : 1 $CHCl_3$–MeOH) of the residue on silica gel afforded **3** (94.5 mg, 88.6%) as an amorphous mass; $[\alpha]_D + 31.2°$ (*c* 0.18, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.42 (s, 3H, MeS), 1.71 (t, 1H, $J_{gem} = J_{3ax,4} = 12.5$ Hz, H-3b*ax*), 1.94, 2.05, 2.056, 2.12, 2.16, 2.18 (6s, 18H, 6AcO), 2.57 (dd, 1H, $J_{3eq,4} = 4.5$ Hz, $J_{gem} = 12.5$ Hz, H-3b*eq*), 3.84 (s, 3H, COOMe), 4.34 (dd, 1H, $J_{8,9} = 2.8$ Hz, $J_{gem} = 12.5$ Hz, H-9b), 4.69 (d, 1H, $J_{1,2} = 9.8$ Hz, H-1a), 4.76 (dd, $J_{2,3} = 9.6$ Hz, $J_{3,4} = 3.2$ Hz, H-3a), 4.96 (m, 1H, H-4b), 5.03 (d, 1H, H-4a), 5.18 (dd, $J_{6,7} = 2.0$, $J_{7,8} = 8.9$ Hz, H-7b), 5.35 (t, 1H, H-2a), 5.52 (m, 1H, H-8b), 6.48 (d, 1H, $J_{5,NH} = 9.1$ Hz, NH of b), 7.46–8.14 (m, 5 H, 1Ph).

^{13}C NMR ($CDCl_3$) δ 11.40, 11.99, 20.45, 20.70, 20.74, 20.79, 21.48, 37.29, 49.63, 53.29, 62.10, 62.24, 66.30, 67.95, 68.48, 68.62, 71.10, 72.20, 74.36, 83.22, 96.84, 128.46, 130.06, 130.26, 133.53, 157.67, 165.53 (C═O), 167.82 (C═O), 169.77 (C═O), 170.22 (C═O), 170.52 (C═O), 170.73 (C═O), 170.74 (C═O), 170.79 (C═O).

Anal. Calcd for $C_{38}H_{46}F_3NO_{20}S$ (925.83): C, 49.30; H, 5.01; N, 1.51. Found: C, 49.12; H, 4.83; N, 1.25.

2-(Tetradecyl)hexadecyl (2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1 → 3)-2-acetamido-2-deoxy-β-D-glucopyranoside (6). To a solution of **4** (105 mg, 0.14 mmol) and **5** (113.6 mg, 0.21 mmol) in dry benzene (5 mL) was added molecular sieves 4 Å (300 mg), and the mixture was stirred for 6 hr at room temperature, then cooled to 0°C. *N*-Iodosuccinimide (NIS; 145 mg, 0.64 mmol) and TMSOTf (8.3 μL, 42 μmol) were added to the mixture, and the resultant mixture was stirred for 2 hr at 7°C and neutralized with Et_3N. After dilution with chloroform, the precipitate was filtered off, and washed with chloroform. The filtrate and washings were combined, and successively washed with 1 M sodium carbonate and sodium thiosulfate, dried (Na_2SO_4), and concentrated.

The residue was dissolved in AcOH (8 mL) and water (2 mL), and the reaction mixture was stirred for 48 hr at 45°C, and then concentrated. Column chromatography (200 : 1 $CHCl_3$–MeOH) of the residue on silica gel gave **6** (82.8 mg, 51%, two steps) as an amorphous mass; $[\alpha]_D -26.8°$ (*c* 0.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.87 (t, 6H, $J = 6.6$ Hz, $2CH_3$), 1.16 (d, 3H, $J_{5,6} = 6.4$ Hz, H-6b), 1.22–1.52 (m, 53H, $26CH_2$ and CH), 1.58 (s, 3H, AcN), 3.25 (dd, 1H, $J_{1,2} = 7.8$ Hz, $J_{2,3} = 9.2$ Hz, H-2a), 3.31

(dd, 1H, OCH_2C of alkyl part), 3.41 (dd, 1H, H-4a), 3.68 (s, 1H, H-4b), 3.74–3.79 (m, 3H, H-5a, H-6′a and OCH_2C of alkyl part), 3.86–3.90 (m, 2H, H-3a and H-6a), 3.94 (dd, 1H, $J_{2,3} = 10.5$ Hz, $J_{3,4} = 2.1$ Hz, H-3b), 4.09 (dd, 1H, $J_{1,2} = 3.8$ Hz, $J_{2,3} = 10.5$ Hz, H-2b), 4.84 (d, 1H, $J_{1,2} = 7.8$ Hz, H-1a), 4.94 (d, 1H, $J_{1,2} = 3.8$ Hz, H-1b), 5.52 (d, 1H, $J_{NH,2} = 7.3$ Hz, NH), 7.25–7.40 (m, 15H, 3Ph).

^{13}C NMR ($CDCl_3$) δ 14.14, 16.71, 22.69, 23.05, 26.63, 26.79, 29.37, 29.66, 29.71, 30.10, 30.16, 30.87, 31.13, 31.92, 38.09, 56.12, 62.73, 68.14, 70.98, 72.86, 73.08, 74.08, 74.72, 75.00, 75.94, 76.73, 79.06, 83.96, 99.27, 100.62, 127.46, 127.61, 127.67, 127.75, 127.98, 128.21, 128.28, 128.35, 128.46, 128.57, 138.22, 138.28, 138.43, 170.58 (C═O).

Anal. Calcd for $C_{65}H_{103}NO_{10}$ (1057.76): C, 73.75; H, 9.81; N, 1.32. Found: C, 73.60; H, 9.58; N, 1.23.

2-(Tetradecyl)hexadecyl (2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1 → 3)-2-acetamido-2-deoxy-6-*O*-4-methoxyphenyl-β-D-glucopyranoside (7). To a solution of **6** (82.8 mg, 0.078 mmol) in THF (5 mL) were added PPh_3 (102.1 mg, 0.39 mmol), DEAD (123.1 μL, 0.28 mmol), and MPOH (58.8 mg, 0.47 mmol), and the mixture was stirred under reflux for 17 hr. After completion of the reaction, the mixture was concentrated. Column chromatography (200 : 1 $CHCl_3$–MeOH) of the residue on silica gel afforded **7** (80.1 mg, 88%) as an amorphous mass; $[\alpha]_D$ −24.0° (*c* 0.86, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.87 (t, 6H, $J = 6.9$ Hz, $2CH_3$), 1.15 (d, 3H, $J_{5,6} = 6.4$ Hz, H-6b), 1.21–1.52 (m, 53H, $26CH_2$ and CH), 1.59 (s, 3H, AcN), 3.27 (dd, 1H, $J_{gem} = 9.6$ Hz, $J_{vic} = 6.6$ Hz, OCH_2C of alkyl part), 3.32 (dd, 1H, $J_{2,3} = 10.0$ Hz, H-2a), 3.49 (t, 1H, H-4a), 3.61 (m, 1H, H-5a), 3.69 (s, 1H, H-4b), 3.75 (s, 3H, *Me*OPh), 3.79 (dd, 1H, OCH_2C of alkyl part), 3.95 (m, 2H, H-3a and H-3b), 4.09 (dd, 1H, $J_{1,2} = 3.6$ Hz, $J_{2,3} = 10.2$ Hz, H-2b), 4.09 (m, 1H, H-5b), 4.10–4.14 (m, 2H, H-6a and H-6′a), 4.86 (d, 1H, $J_{1,2} = 8.5$ Hz, H-1a), 4.98 (d, 1H, $J_{1,2} = 3.6$ Hz, H-1b), 5.51 (d, 1H, $J_{NH,2} = 7.1$ Hz, NH), 6.79–7.40 (m, 19H, MeO*Ph*, 3Ph).

^{13}C NMR ($CDCl_3$) δ 11.34, 14.38, 20.39, 20.83, 24.34, 24.47, 27.07, 27.37, 27.42, 27.83, 27.88, 28.62, 28.87, 29.63, 35.73, 53.37, 54.08, 65.75, 66.28, 68.03, 70.52, 70.60, 71.66, 71.80, 72.68, 73.62, 74.41, 74.73, 74.94, 75.05, 76.78, 81.68, 96.80, 97.94, 112.17, 113.89, 125.18, 125.37, 125.44, 125.62, 125.97, 126.06, 126.16, 126.24, 135.95, 136.02, 136.15, 150.94, 151.62, 168.20 (C═O).

Anal. Calcd for $C_{72}H_{109}NO_{11}$ (1163.80): C, 74.25; H, 9.43; N, 1.20. Found: C, 74.09; H, 9.18; N, 1.01.

2-(Tetradecyl)hexadecyl (methyl 4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-5-trifluoroacetamido-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2 → 3)-(4,6-di-*O*-acetyl-2-*O*-benzoyl-β-D-galactopyranosyl)-(1 → 4)-[(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1 → 3)]-2-acetamido-2-deoxy-6-*O*-4-methoxyphenyl-β-D-glucopyranoside (8). To a solution of **3** (44.8 mg, 0.048 mmol) and **7** (37 mg, 0.031 mmol) in dry CH_2Cl_2 (0.6 mL) was added molecular sieves 4 Å (38 mg), and the mixture was stirred for 3 hr at room temperature, then cooled to 0°C. DMTST (89.5 mg, 0.18 mmol) was added to the mixture, and the resultant mixture was stirred for 3 days at 0°C and neutralized with Et_3N. After dilution with chloroform, the precipitate was filtered off, and washed with chloroform. The filtrate and washings were combined, and successively washed with 1 M sodium carbonate and water, dried (Na_2SO_4), and concentrated. Column chromatography (80 : 1 $CHCl_3$–MeOH) of the residue on silica gel afforded **8** (37.1 mg, 57.2%) as an amorphous mass; $[\alpha]_D$ +10.5° (*c* 0.7, $CHCl_3$); ^{1}H NMR

($CDCl_3$) δ 0.88 (t, 6H, $J = 6.9$ Hz, $2CH_3$), 1.05 (d, 3H, $J_{5,6} = 6.4$ Hz, H-6d), 1.14–1.41 (m, 53H, $26CH_2$ and CH), 1.51 (s, 3H, AcN), 1.71 (t, 1H, $J_{gem} = J_{3ax,4} = 12.5$ Hz, H-3*cax*), 1.957, 1.959, 1.96, 1.98, 2.06, 2.18 (6s, 18H, 6AcO), 2.59 (dd, 1H, $J_{3eq,4} = 4.6$ Hz, $J_{gem} = 12.5$ Hz, H-3*ceq*), 2.82 (dd, 1H, $J_{gem} = 8.7$, $J_{vic} = 6.6$ Hz, OCH_2C of alkyl part), 3.34 (s, 1H, H-4d), 3.43 (dd, 1H, $J_{gem} = 9.4$ Hz, $J_{vic} = 5.7$ Hz, OCH_2C of alkyl part), 3.63 (dd, 1H, $J_{2,3} = 9.8$ Hz, $J_{3,4} = 2.5$ Hz, H-3d), 3.68 (s, 3H, *Me*OPh), 3.74 (t, 1H, H-2a), 3.87 (s, 3H, COO*Me*), 3.95–3.98 (m, 2H, H-9c and H-5d), 4.00 (dd, 1H, H-4d), 4.36 (dd, 1H, H-9′c), 4.80 (dd, 1H, $J_{2,3} = 10.0$ Hz, $J_{3,4} = 3.4$ Hz, H-3b) 4.93 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1b), 4.99 (m, 1H, H-4c), 5.04 (d, 1H, H-4b), 5.08 (d, 1H, $J_{1,2} = 3.6$ Hz, H-1d), 5.20 (dd, 1H, $J_{6,7} = 2.1$ Hz, $J_{7,8} = 9.2$ Hz, H-7c), 5.28 (dd, 1H, $J_{1,2} = 8.0$ Hz, $J_{2,3} = 10.0$ Hz, H-2b), 5.58 (m, 1H, H-8c), 6.10 (d, 1H, $J_{NH,5} = 8.9$ Hz NH of c), 6.21 (d, 1H, $J_{NH,2} = 9.15$ Hz, NH), 6.71–8.15 (m, 24H, 4Ph, MeO*Ph*).

^{13}C NMR ($CDCl_3$) δ 14.13, 16.54, 20.16, 20.45, 20.61, 20.59, 20.70, 21.43, 22.70, 23.12, 26.72, 26.89, 29.38, 29.67, 29.72, 29.79, 30.23, 30.92, 31.11, 31.93, 37.97, 49.74, 53.38, 55.57, 61.62, 62.06, 66.38, 66.74, 67.48, 67.61, 67.87, 68.50, 70.88, 70.93, 71.06, 71.14, 72.66, 73.08, 73.40, 74.31, 74.50, 96.89, 97.28, 99.39, 100.41, 114.51, 115.37, 127.21, 127.31, 127.43, 127.51, 127.93, 128.14, 128.27, 128.29, 128.40, 128.62, 129.93, 130.12, 133.41, 138.57, 138.76, 139.02, 152.79, 153.93, 166.10 (C═O), 167.73 (C═O), 169.54 (C═O), 169.80 (C═O), 170.11 (C═O), 170.27 (C═O), 170.54 (C═O), 170.60 (C═O), 170.69 (C═O).

Anal. Calcd for $C_{109}H_{151}F_3N_2O_{31}$ (2041.03): C, 64.10; H, 7.45; N, 1.37; O, 24.28. Found: C, 63.83; H, 7.41; N, 1.33.

2-(Tetradecyl)hexadecyl (5-amino-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonic acid)-(2 → 3)-(β-D-galactopyranosyl)-(1 → 4)-[(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1 → 3)]-2-acetamido-2-deoxy-6-*O*-4-methoxyphenyl-β-D-glucopyranoside (9). To a solution of **8** (35.8 mg, 71 μmol) in methanol (4 mL) was added catalytic amount of 28% sodium methoxide in methanol, and the mixture was stirred for 72 hr at 45°C. Water (0.1 mL) was added and the mixture was stirred for 48 hr at room temperature. The mixture was neutralized with Amberlite IR-120 (H^+) resin and filtered. The resin was washed with methanol, and the combined filtrate and washings were concentrated. Column chromatography (MeOH) of the residue on Sephadex LH-20 gave **9** (26.3 mg, 95%) as an amorphous mass; $[\alpha]_D$ −43.2° (*c* 0.52, $CHCl_3$); ^1H NMR (CD_3OD) δ 0.79 (t, 6H, $J = 6.9$ Hz, $2CH_3$), 1.04 (d, 3H, $J_{5,6} = 6.4$ Hz, H-6d), 1.10–1.42 (m, 53H, $26CH_2$ and CH), 1.60 (t, 1H, $J_{gem} = J_{3ax,4} = 12.1$ Hz, H-3*cax*), 1.87 (s, 3H, AcN of a), 2.72 (dd, 1H, H-3*ceq*), 2.93 (t, 1H, H-5c), 3.14 (dd, 1H, $J_{6,7} = 2.9$ Hz, $J_{7,8} = 8.0$ Hz H-7c), 3.19 (dd, 1H, $J = 9.6$ Hz, $J_{vic} = 6.2$ Hz, OCH_2C of alkyl part), 3.41 (dd, 1H, $J_{1,2} = 7.8$ Hz, $J_{2,3} = 9.4$ Hz, H-2b), 3.42 (m, 1H, H-8c), 3.60 (m, 1H, H-4c), 3.65 (s, 3H, *Me*OPh), 3.80–3.83 (m, 2H, H-6c and H-3b), 3.86 (dd, 1H, $J_{1,2} = 3.7$ Hz, $J_{2,3} = 10.3$ Hz, H-2d), 4.01 (dd, 1H, $J_{2,3} = 10.3$ Hz, $J_{3,4} = 2.9$ Hz, H-3d), 4.25 (d, 1H, $J_{1,2} = 7.8$ Hz, H-1b), 4.71 (m, 1H, H-5d), 5.22 (d, 1H, $J_{1,2} = 3.7$ Hz, H-1d), 6.76–7.31 (m, 19H, 3Ph, MeO*Ph*).

^{13}C NMR (CD3OD) δ 13.09, 15.51, 22.22, 22.37, 26.37, 26.54, 29.11, 29.39, 29.74, 30.68, 30.81, 31.71, 37.98, 40.55, 52.82, 54.83, 62.01, 66.41, 69.85, 71.98, 72.27, 74.01, 74.34, 75.04, 78.43, 95.62, 97.81, 99.78, 100.74, 114.48, 115.89, 123.84, 126.95, 127.07, 127.77, 127.90, 128.06, 128.23, 136.32, 138.85, 154.26, 157.04, 171.50 (C═O), 173.03 (C═O).

Anal. Calcd for $C_{87}H_{134}N_2O_{23}$ (1574.94): C, 66.30; H, 8.57; N, 1.78. Found: C, 66.05; H, 8.54; N, 1.55.

2-(Tetradecyl)hexadecyl (5-acetylamino-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl 1,5-lactam)-(2 → 3)-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1 → 4)-[(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1 → 3)]-2-acetamido-2-deoxy-6-*O*-4-methoxyphenyl-β-D-glucopyranoside (10). To a solution of **9** (26.3 mg, 16.6 μmol) in DMF (3 mL) were added HBTU (19.5 mg, 50 μmol) and HOBt (6.83 mg, 50 μmol), and the mixture was stirred for 4 hr at 65°C, and then concentrated. Column chromatography (MeOH) of the residue on Sephadex LH-20 gave the lactamized sLe^x derivative. The residue was treated with acetic anhydride (1.5 mL) and pyridine (3 mL) for 12 hr at room temperature, then cooled to 0°C. Methanol (1 mL) was added and the mixture was concentrated, and the residue was extracted with chloroform and successively washed with cold 2 M hydrochloric acid and water, dried (Na_2SO_4), and concentrated. Column chromatography (100 : 1 $CHCl_3$–MeOH) of the residue on silica gel gave **10** (24.1 mg, 76.2%, two steps) as an amorphous mass; $[\alpha]_D$ −17.6° (*c* 0.48, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 6H, J = 6.9 Hz, $2CH_3$), 0.98 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6d), 1.19–1.50 (m, 53H, $26CH_2$ and CH), 1.97, 1.98, 2.06, 2.07, 2.10, 2.13, 2.14, 2.21 (8s, 7OAc, AcN of a), 2.32 (dd, 1H, $J_{3\beta,4}$ = 10.1 Hz, J_{gem} = 14.6 Hz, H-3cβ), 2.41 (dd, 1H, $J_{3\beta,4}$ = 5.5 Hz, J_{gem} = 14.6 Hz, H-3cα), 2.57 (s, 3H, AcN of c), 3.28 (dd, 2H, OCH_2C of alkyl part and H-4d), 3.57 (dd, 1H, $J_{2,3}$ = 10.0 Hz, $J_{3,4}$ = 3.0 Hz, H-3d), 3.63 (dd, 1H, J_{gem} = 9.8 Hz, J_{vic} = 6.6 Hz, OCH_2C of alkyl part), 3.68 (s, 3H, *Me*OPh), 3.80 (m, 1H, H-5d), 3.94 (dd, 1H, $J_{1,2}$ = 3.4 Hz, $J_{2,3}$ = 10.1 Hz, H-2d), 4.13–4.16 (m, 2H, H-2a and H-3b), 4.19 (dd, 1H, $J_{8,9}$ = 5.3 Hz, J_{gem} = 11.8 Hz, H-9c), 4.27 (dd, 1H, $J_{8,9'}$ = 6.4 Hz, J_{gem} = 11.2 Hz, H-9′c), 4.49 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1a), 4.55 (t, 1H, H-3a), 4.63 (d, 1H, H-4b), 4.85 (m, 1H, H-4c), 5.03 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1d), 5.12 (dd, 1H, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 10.6 Hz, H-2b), 5.36 (m, 1H, H-5c), 5.43 (m, 1H, H-8c), 5.77 (dd, 1H, $J_{6,7}$ = 3.7 Hz, $J_{7,8}$ = 9.8 Hz, H-7c), 6.40 (d, 1H, $J_{NH,2}$ = 9.2 Hz, NH), 6.74–7.39 (m, 19H, 3Ph, MeO*Ph*).

^{13}C NMR ($CDCl_3$) δ 14.14, 16.47, 20.62, 20.67, 20.72, 20.87, 21.03, 22.69, 23.09, 26.33, 26.84, 26.95, 29.38, 29.67, 29.72, 30.26, 31.04, 31.15, 31.93, 35.69, 38.19, 47.93, 55.21, 61.29, 61.80, 66.81, 67.55, 68.59, 69.44, 69.88, 71.24, 72.58, 72.95, 73.27, 74.50, 76.02, 79.59, 95.84, 97.70, 99.64, 100.64, 114.62, 115.30, 127.13, 127.31, 127.43, 127.51, 127.78, 128.12, 128.26, 128.32, 128.46, 138.48, 138.77, 138.98, 152.46, 154.07, 164.80 (C═O), 168.96 (C═O), 169.04 (C═O), 169.56 (C═O), 169.78 (C═O), 169.84 (C═O), 170.13 (C═O), 170.36 (C═O), 170.58 (C═O).

Anal. Calcd for $C_{103}H_{148}N_2O_{30}$ (1893.01): C, 65.31; H, 7.88; N, 1.48. Found: C, 65.04; H, 7.87; N, 1.43.

2-(Tetradecyl)hexadecyl (5-acetylamino-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl 1,5-lactam)-(2 → 3)-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1 → 4)-[(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-(1 → 3)]-2-acetamido-2-deoxy-6-*O*-4-methoxyphenyl-β-D-glucopyranoside (11). A solution of **10** (20.1 mg, 10.6 μmol) in ethanol (2 mL) was vigorously stirred over $Pd(OH)_2$ (40 mg) for 24 hr at room temperature under hydrogen. The catalyst was collected and washed with methanol. The combined filtrate and washings were concentrated, and the residue was treated with acetic anhydride (2.5 mL) and pyridine (4 mL) for 12 hr at room temperature, then cooled to 0°C. Methanol (1.5 mL) was added and the mixture was concentrated, and the residue was extracted with chloroform and successively washed with cold 2 M

hydrochloric acid and water, dried (Na_2SO_4), and concentrated. Column chromatography (70 : 1 $CHCl_3$–MeOH) of the residue on silica gel gave **10** (17.3 mg, 93%) as an amorphous mass; $[\alpha]_D$ −17.1° (*c* 0.35, $CHCl_3$), ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 6H, $J = 6.7$ Hz, $2CH_3$), 1.09 (d, 3H, $J_{5,6} = 6.4$ Hz, H-6d), 1.24–1.52 (m, 53H, $26CH_2$ and CH), 1.96, 1.98, 2.04, 2.06, 2.07, 2.11, 2.12, 2.13, 2.16, 2.17, 2.20 (11s, 33H, 10OAc, AcN of a), 2.24 (dd, 1H, $J_{3\beta,4} = 10.5$ Hz, $J_{gem} = 13.9$ Hz, H-3cβ), 2.29 (dd, 1H, $J_{3\alpha,4} = 5.3$ Hz, $J_{gem} = 13.9$ Hz, H-3cα), 2.56 (s, 3H, AcN of c), 3.22 (dd, 1H, $J_{gem} = 9.4$ Hz, $J_{vic} = 6.2$ Hz, OCH_2C of alkyl part), 3.71 (dd, 1H, $J_{gem} = 9.4$ Hz, $J_{vic} = 5.3$ Hz, OCH_2C of alkyl part), 3.76 (s, 3H, *Me*OPh), 3.93 (dd, 1H, $J_{2,3} = 10.3$ Hz, $J_{3,4} = 3.4$ Hz, H-3b), 4.18 (dd, 1H, $J_{8,9} = 6.2$ Hz, $J_{gem} = 11.8$ Hz, H-9c), 4.20 (d, 1H, H-6c), 4.30 (dd, 1H, $J_{8,9'} = 5.7$ Hz, $J_{gem} = 11.4$ Hz, H-9′c), 4.50 (d, 1H, $J_{1,2} = 8.2$ Hz, H-1b), 4.84 (m, 1H, H-4c), 5.02 (dd, 1H, H-2d), 5.07 (dd, 1H, $J_{1,2} = 8.2$ Hz, $J_{2,3} = 10.3$ Hz, H-2b), 5.18 (d, 1H, $J_{1,2} = 3.4$ Hz, H-1d), 5.24 (d, 1H, H-4b), 5.34–5.37 (m, 2H, H-5c and H-3d), 5.43 (m, 1H, H-8c), 5.69 (d, 1H, $J_{NH,2} = 9.6$ Hz, NH), 5.74 (dd, 1H, $J_{6,7} = 3.7$ Hz, $J_{7,8} = 9.6$ Hz, H-7c), 6.85–6.93 (m, 4H, MeO*Ph*).

^{13}C NMR ($CDCl_3$) δ 14.14, 15.78, 20.63, 20.69, 20.77, 20.83, 20.99, 22.70, 23.31, 26.32, 26.67, 26.89, 29.37, 29.67, 29.72, 30.12, 30.19, 30.90, 31.14, 31.93, 35.51, 38.09, 47.92, 55.55, 61.33, 61.96, 64.46, 67.39, 67.65, 68.08, 68.60, 69.40, 69.98, 71.23, 71.43, 71.73, 72.16, 72.67, 73.54, 73.96, 74.47, 95.86, 96.04, 99.88, 100.85, 114.82, 115.97, 152.39, 154.31, 164.84 (C═O), 169.05 (C═O), 169.37 (C═O), 169.47 (C═O), 169.69 (C═O), 169.75 (C═O), 169.83 (C═O), 170.18 (C═O), 170.42 (C═O), 170.48 (C═O), 170.64 (C═O), 170.68 (C═O), 171.03 (C═O).

Anal. Calcd for $C_{88}H_{136}N_2O_{33}$ (1748.90): C, 60.40; H, 7.83; N, 1.60. Found: C, 60.10; H, 7.69; N, 1.46.

2-(Tetradecyl)hexadecyl (5-acetylamino-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl 1,5-lactam)-(2 → 3)-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1 → 4)-[(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-(1 → 3)]-2-acetamido-2-deoxy-β-D-glucopyranoside (12). To a solution of **11** (17.3 mg, 9.9 μmol) in acetonitrile (1.8 mL) and water (0.2 mL) was added CAN (16.8 mg, 0.03 mmol), and the mixture was stirred for 2.5 hr at 0°C and extracted with chloroform. The extract was successively washed with 1 M sodium carbonate and water, dried (Na_2SO_4), and concentrated. Column chromatography (100 : 1 $CHCl_3$–MeOH) of the residue on silica gel gave **12** (12.1 mg, 74.6%) as an amorphous mass; $[\alpha]_D$ −8.2° (*c* 0.24, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 6H, $J = 6.6$ Hz, $2CH_3$), 1.22–1.52 (m, 56H, $26CH_2$, CH and H-6d), 1.94, 1.95, 2.02, 2.05, 2.08, 2.09, 2.10, 2.14, 2.16, 2.18, 2.21 (11s, 33H, 10OAc, AcN of a), 2.27 (dd, 1H, $J_{3\beta,4} = 10.5$ Hz, $J_{gem} = 14.4$ Hz, H-3cβ), 2.38 (dd, 1H, $J_{3\alpha,4} = 5.4$ Hz, $J_{gem} = 14.4$ Hz, H-3cα), 2.56 (s, 3H, AcN of c), 3.20 (dd, 1H, $J_{gem} = 9.3$ Hz, $J_{vic} = 6.6$ Hz, OCH_2C of alkyl part), 3.28 (br-d, 1H, H-6a), 3.73 (dd, 1H, OCH_2C of alkyl part), 3.85 (dd, 1H, H-2a), 4.13 (dd, 1H, $J_{2,3} = 9.8$ Hz, $J_{3,4} = 3.6$ Hz, H-3b), 4.18 (dd, 1H, $J_{8,9} = 5.5$ Hz, $J_{gem} = 11.6$ Hz, H-9c), 4.22 (br-d, 1H, H-6c), 4.26 (dd, 1H, $J_{8,9'} = 6.4$ Hz, $J_{gem} = 11.6$ Hz, H-9′c), 4.37 (d, 1H, $J_{1,2} = 7.6$ Hz, H-1a) 4.60 (d, 1H, $J_{1,2} = 8.2$ Hz, H-1b), 4.85 (m, 1H, H-4c), 4.97–5.00 (m, 2H, H-2d and H-5d), 5.05 (dd, 1H, $J_{1,2} = 8.2$ Hz, $J_{2,3} = 10.0$ Hz, H-2b), 5.21(dd, 1H, $J_{2,3} = 10.9$ Hz, $J_{3,4} = 3.2$ Hz, H-3d), 5.29 (d, 1H, H-4b), 5.36 (m, 1H, H-5c), 5.43 (m, 2H, H-8c and H-1d), 5.76 (dd, 1H, $J_{6,7} = 3.8$ Hz, $J_{7,8} = 8$ Hz, H-7c).

^{13}C NMR ($CDCl_3$) δ 14.13, 15.77, 20.45, 20.62, 20.69, 20.70, 20.77, 20.83, 20.98, 22.70, 23.30, 26.63, 26.79, 26.89, 29.37, 29.68, 29.71, 30.13, 30.18, 30.91, 31.13,

31.92, 35.71, 39.12, 48.29, 61.58, 62.02, 64.52, 67.68, 68.28, 68.66, 69.47, 69.82, 71.28, 71.35, 71.46, 71.77, 72.18, 72.54, 72.62, 73.58, 73.62, 73.99, 74.39, 75.62, 96.88, 97.27, 99.48, 100.72, 169.21 (C═O), 168.37 (C═O), 169.12 (C═O), 169.58 (C═O), 169.84 (C═O), 170.12 (C═O), 170.27 (C═O), 170.42 (C═O), 170.51 (C═O), 170.55 (C═O), 170.63 (C═O), 170.77 (C═O), 171.05 (C═O).

Anal. Calcd for $C_{81}H_{130}N_2O_{32}$ (1642.86): C, 59.18; H, 7.97; N, 1.70. Found: C, 59.10; H, 7.85; N, 1.63.

2-(Tetradecyl)hexadecyl (5-acetylamino-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl 1,5-lactam)-(2 → 3)-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1 → 4)-[(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-(1 → 3)]-2-acetamido-2-deoxy-6-*O*-sulfo-β-D-glucopyranoside triethylammonium salt (13). To a solution of **12** (12.1 mg, 7.4 μmol) in DMF (1 mL) was added sulfur trioxide pyridine complex (7.1 mg, 44 μmol), and the mixture was stirred for 6 hr at room temperature. Triethylamine (0.1 mL) was added and the mixture was concentrated. Column chromatography (1 : 1 $CHCl_3$–MeOH) of the residue on Sephadex LH-20 gave the crude sulfated product, and this was purified by column chromatography (30:1 $CHCl_3$–MeOH) on silica gel to afford **13** (10.5 mg, 78%) as an amorphous mass; $[\alpha]_D$ −28.9° (*c* 0.04, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 6H, $J = 6.6$ Hz, $2CH_3$), 1.22 (d, 3H, $J_{5,6} = 6.4$ Hz, H-6d), 1.25–1.30 (m, 52H, $26CH_2$), 1.40 (t, 9H, NCH_2CH_3), 1.45 (m, 1H, CH), 1.94, 1.95, 2.05, 2.06, 2.07, 2.091, 2.094, 2.14, 2.160, 2.165, 2.23 (11s, 33H, 10OAc, AcN of a), 2.29 (dd, 1H, $J_{3\beta,4} = 10.8$ Hz, $J_{gem} = 14.3$ Hz, H-3cβ), 2.46 (dd, 1H, $J_{3\alpha,4} = 5.3$ Hz, $J_{gem} = 14.3$ Hz, H-3cα), 2.56 (s, 3H, AcN of c), 3.16 (m, 7H, NCH_2CH_3 and OCH_2C of alkyl part), 3.68 (dd, 1H, $J_{gem} = 9.6$ Hz, $J_{vic} = 5.5$ Hz, OCH_2C of alkyl part), 3.96 (t, 1H, H-2a), 4.20 (br-d, 1H, H-6c), 4.24–4.28 (m, 3H, H-9c, H-9′c and H-3b), 4.85 (m, 2H, H-4c and H- 5d), 4.89 (d, 1H, $J_{1,2} = 8.2$ Hz, H-1b), 5.02 (dd, 1H, $J_{1,2} = 3.4$ Hz, $J_{2,3} = 10.5$ Hz, H-2d), 5.04 (dd, 1H, $J_{1,2} = 8.2$ Hz, $J_{2,3} = 10.1$ Hz, H-2b), 5.24 (dd, 1H, $J_{2,3} = 10.5$ Hz, H-3d), 5.34 (m, 1H, H-8c), 5.37 (d, 1H, $J_{1,2} = 3.2$ Hz, H-1d), 5.43 (d, 1H, H-4b), 5.51 (d, 1H, $J_{NH,2} = 8.5$ Hz, NH), 5.77 (dd, 1H, $J_{6,7} = 4.1$ Hz, $J_{7,8} = 8.6$ Hz, H-7c).

Anal. Calcd for $C_{87}H_{145}N_3O_{35}S$ (1823.94): C, 57.25; H, 8.01; N, 2.30. Found: C, 56.98; H, 7.72; N, 2.25.

2-(Tetradecyl)hexadecyl (5-amino-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosyl 1,5-lactam)-(2 → 3)-(β-D-galactopyranosyl)-(1 → 4)-[(α-L-fucopyranosyl)-(1 → 3)]-2-acetamido-2-deoxy-6-*O*-sulfo-β-D-glucopyranoside sodium salt (14). To a solution of **13** (5.6 mg, 3.1 μmol) in methanol (3 mL) and dioxane (1 mL) was added catalytic amount of 28% sodium methoxide in methanol, and the mixture was stirred for 30 hr at room temperature and then concentrated. Column chromatography (1 : 1 $CHCl_3$–MeOH) of the residue on Sephadex LH-20 gave the target molecule **14** (3.9 mg, 98%) as an amorphous mass; $[\alpha]_D$ +3.2° (*c* 0.07, 1 : 1 $CHCl_3$–MeOH); ^{1}H NMR (CD_3OD) δ 0.86 (t, 6H, $J = 7.6$ Hz, $2CH_3$), 1.07 (d, 3H, $J_{5,6} = 6.6$ Hz, H-6d), 1.19–1.43 (m, 53H, $26CH_2$ and CH), 1.84 (s, 3H, AcN of a), 2.01 (dd, 1H, $J_{3\alpha,4} = 5.0$ Hz, $J_{gem} = 13.6$ Hz, H-3cα), 2.30 (dd, 1H, $J_{3\beta,4} = 10.3$ Hz, $J_{gem} = 13.4$ Hz, H-3cβ), 3.43 (m, 1H, H-8c), 3.46 (m, 1H, H-5c), 3.48 (dd, 1H, $J_{1,2} = 7.5$ Hz, $J_{2,3} = 9.6$ Hz, H-2b), 3.54 (dd, 1H, H-2d), 3.58 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1a), 3.61 (m, 2H, H-9c and H-4d), 3.64 (dd, 1H, $J_{gem} = 14.4$ Hz, H-9′c), 3.70 (t, 1H, $J_{1,2} = 8.0$ Hz, H-2a), 3.78 (dd, 1H, $J_{2,3} = 10.0$ Hz, $J_{3,4} = 3.2$ Hz, H-3d), 3.98 (m, 2H, H-3b and H-4c), 4.10 (br-d, 1H, H-4b), 4.37 (br-d, 1H, H-6c), 4.56 (d, 1H, $J_{1,2} = 7.5$ Hz, H-1b), 4.74 (m, 1H, H-5d), 4.92 (d, 1H, $J_{1,2} = 4.1$ Hz, H-1d).

MALDI-TOF MS (positive-ion mode, DHB, MeCN) Calcd for $C_{59}H_{107}N_2NaO_{24}S$ $[M + Na]^+$ 1282.6832. Found: 1282.5850.

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