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Synthesis of α-series ganglioside GM1α containing C20-sphingosine

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Abstract—A synthesis of α-series ganglioside GM1α (III^{6}Neu5AcGgOse$_4$Cer) containing C20-sphingosine(d20:1) is described. Glycosylation of 2-(trimethylsilyl)ethyl 2,3,6-tri-*O*-benzyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside with the glucosamine donor ethyl 3-*O*-acetyl-2-deoxy-4,6-*O*-[(4-methoxyphenyl)methylene]-2-phthalimido-1-thio-β-D-glucopyranoside furnished a β-(1→4)-linked trisaccharide. Reductive cleavage of the *p*-methoxybenzylidene group followed by intramolecular inversion of its triflate afforded the desired trisaccharide, which was transformed into a trisaccharide acceptor via removal of the phthaloyl and *O*-acetyl groups followed by *N*-acetylation. A tetrasaccharide acceptor was obtained by glycosylation of the trisaccharide acceptor with dodecyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-β-D-galactopyranoside, followed by removal of the *p*-methoxybenzyl group. Coupling of the tetrasaccharide acceptor with ethyl (methyl 4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-1-thio-5-trichloroacetamido-D-*glycero*-D-*galacto*-2-nonulopyranosid)onate and subsequent radical reduction gave the desired GM1α saccharide derivative, which was coupled with (2*S*,3*R*,4*E*)-2-azido-3-*O*-benzoyl-4-eicosene-1,3-diol after conversion into the imidate.

Keywords: α-Series gangliosides; Cholinergic-specific ganglioside antigen; Chol-1; GM1α; Intramolecular inversion; α-Sialylation; *N*-Trichloroacetylneuraminic acid; Eicosene

1. Introduction

Gangliosides are ubiquitously located in vertebrate cell and are particularly abundant in the nervous system. However, α-series gangliosides containing a common sialyl α(2→6)*N*-acetylgalactosamine residue are exclusively localized on cholinergic neurons[1] and are well known as a cholinergic-specific ganglioside antigen (Chol-1).[2] There have been several reports suggesting putative roles of α-series gangliosides in the nervous system such as the specific association of GT1aα and GQ1bα with cholinergic neuron of rat brain,[3] the specific cell adhesion of GQ1bα mediated by myelin-associated glycoprotein[4] and the potent neuritogenic activity of GT1aα towards cultured neuronal cells (Neuro-2A).[5] Three extremely minor but novel Chol-1 antigens isolated from bovine brain were identified as GM1α, GD1aα and GT1bα; each ganglioside was composed of various ceramides; two major components were sphingosines (d18:1 and d20:1).[6] One interesting fact is that the sphingosine d20:1 was not found in brain sphingomyelin but only brain gangliosides. These variations in ceramide structure are generally expressed in a cell-type-specific and developmentally regulated manner, implying that they have some specific purposes. For elucidating the specific purposes, it is necessary to examine the physicochemical characters of some gangliosides having a different ceramide. The synthesis of GM1α containing sphingosine d18:1 and fatty acid C18:0 has been reported.[7] We present herein the synthesis of GM1α comprised of sphingosine d20:1 and octadecanoic acid C18:0.

2. Results and discussion

Because gangliosides having many variations in ceramide structure would be in demand, we decided to

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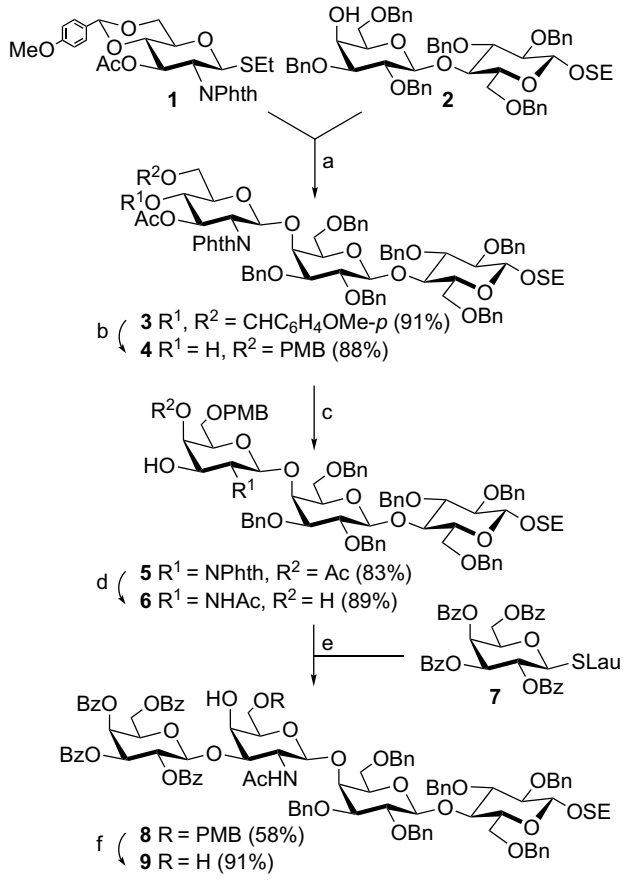


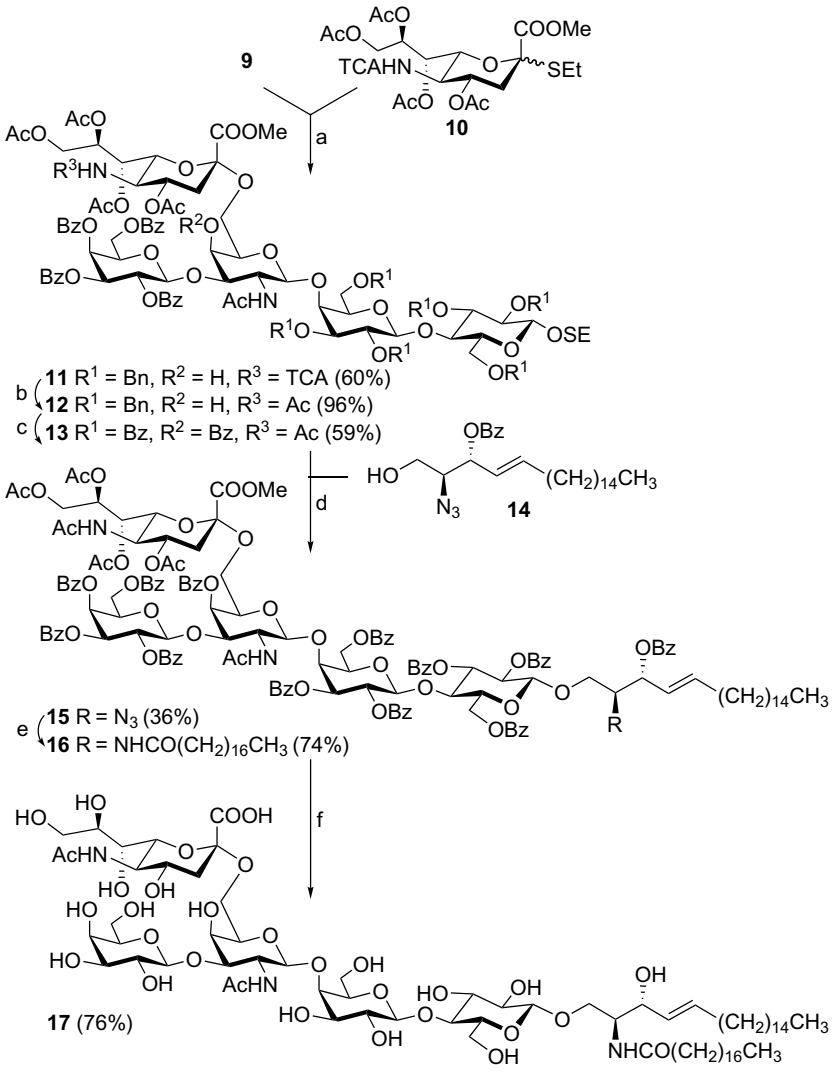
Scheme 1. Reagents and conditions: (a) NIS–TfOH, MS 4 Å, CH_2Cl_2, −40 °C; (b) $NaB(CN)H_3$, TFA, MS 4 Å, DMF, 0 °C to rt; (c) Tf_2O, CH_2Cl_2–pyridine, 0 °C to rt; DMF, 60 °C; (d) $NH_2NH_2{\cdot}H_2O$, EtOH, reflux; Ac_2O, pyridine, rt; (e) NIS–TfOH, MS 4 Å, CH_2Cl_2, 0 °C; (f) CAN, CH_3CN, rt. SE: 2-(trimethylsilyl)ethyl; PMB: *p*-methoxybenzyl; NPhth: phthalimide; Lau: laulyl.

use a glucosamine derivative as a starting material for the galactosamine moiety. As shown in Scheme 1, condensation of the lactose acceptor 2-(trimethylsilyl)-ethyl 2,3,6-tri-*O*-benzyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (**2**)[8] with the glucosamine donor ethyl 3-*O*-acetyl-2-deoxy-4,6-*O*-[(4-methoxyphenyl)methylene]-2-phthalimido-1-thio-β-D-glucopyranoside (**1**)[9] in CH_2Cl_2 in the presence of *N*-iodosuccinimide (NIS)-TfOH and molecular sieves (4 Å) afforded the β-linked trisaccharide **3** in 91% yield. The signal at 5.48 (d, $J_{1,2}$ 8.2 Hz, H-1^{III}) ppm in the ^1H NMR spectrum of **3** proves the β-configuration of the newly synthesized linkage. Reductive cleavage of the *p*-methoxybenzylidene group of **3** by $NaB(CN)H_3$ and CF_3CO_2H offered the 6-*O*-*p*-methoxybenzyl derivative **4** (88%). Intramolecular inversion by the acetyl group of **4** via the triflate yielded the target intermediate **5** having *galacto*-configuration in a high yield (83%). The signal 5.49 (d, $J_{3,4}$ 3.4 Hz, H-4^{III}) ppm in the ^1H NMR spectrum of **5** proves the formation of galactosamine moiety. *O*-Deacetylation and cleavage of phthalimide group with hydrazine monohydrate followed by *N*-acetylation yielded the trisaccharide acceptor **6** (89%). Condensation of **6** with the galactosyl donor **7** obtained from dodecyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside[10] by deacetylation and benzoylation afforded the β-linked tetrasaccharide **8** (58%). The signal at 4.92 (d, $J_{1,2}$ 7.9 Hz, H-1^{IV}) ppm in the ^1H NMR spectrum of **8** proves the β-configuration of the newly synthesized linkage. Removal of the *p*-methoxybenzyl group with ammonium cerium(IV) nitrate produced the tetrasaccharide acceptor **9** in 91% yield.

Our earlier experience with a sialyl donor having 5-*N*-trichloroacetyl group had shown that the sialyl donor ethyl (methyl 4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-1-thio-5-trichloroacetamido-D-*glycero*-D-*galacto*-2-nonulopyranosid)onate (**10**) gave preferentially the α-glycoside in CH_2Cl_2 or CH_2Cl_2–Et_2O.[11] Consequently, when we started to couple the donor **10** with the acceptor **9**, CH_2Cl_2 was tried as a solvent. The amount of TfOH required for the beginning of the reaction was unsettled because of low solubility of TfOH in CH_2Cl_2, though the α-linked pentasaccharide **11** was obtained in 50% yield. This problem was solved by the use of CH_3CN in which TfOH is completely soluble. Sialylation of **9** with the donor **10** by use of NIS–TfOH in CH_3CN afforded stereoselectively the α-linked pentasaccharide **11** in 60% yield (Scheme 2). Radical reduction with *t*-BuSnH and AIBN gave the sialopentasacccharide **12** (96%). The signals at 4.82 (H-4^V), 2.54 (H-3eq^V) and 1.85 (H-3ax^V) ppm and the value of δ |H-9a^V–H-9b^V| = 0.22 ppm in the ^1H NMR spectrum of **12** prove the α-configuration of the newly synthesized linkage. Removal of the benzyl group with $NaBrO_3$ and $Na_2S_2O_4$ followed by benzoylation afforded the GM1α oligosaccharide derivative **13** (59%).

Removal of the 2-(trimethylsilyl)ethyl group and subsequent trichloroacetimidate formation gave the pentasaccharide donor; its condensation with (2*S*,3*R*,4*E*)-2-azido-3-*O*-benzoyl-4-eicosene-1,3-diol (**14**)[12] afforded the β-linked glycosyl sphingosine derivative **15** (36%). The signal at 4.54 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1^I) ppm in the ^1H NMR spectrum of **15** proves the β-configuration of the newly synthesized linkage. Reduction of the azido group of **15** with Zn powder and subsequent coupling of the amino group with octadecanoic acid using *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride gave the ganglioside derivative **16** in 74% yield.

One-pot deprotection of **16** through methanolysis and saponification of the methyl ester group gave the title ganglioside GM1α **17** comprised of sphingosine d20:1 and fatty acid C18:0 in 76% yield. The signals at 4.63 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1^{IV}), 4.37 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1^{II}), 4.35 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1^{III}), 4.31 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1^I), 2.35 (H-3eq^V), 1.78 (H-3ax^V) ppm in the



Scheme 2. Reagents and conditions: (a) NIS–TfOH, MS 3 Å, CH_3CN, −40 °C; (b) BuSnH, AIBN, C_6H_6, reflux; (c) $NaBrO_3$, $Na_2S_2O_4$, AcOEt–H_2O, rt; BzCl, pyridine; (d) TFA, CH_2Cl_2, 0 °C; CCl_3CN, DBU, CH_2Cl_2, rt; $BF_3{\cdot}Et_2O$, MS 4 Å, CH_2Cl_2, 0 °C; (e) Zn powder, AcOH–CH_2Cl_2, rt; $CH_3(CH_2)_{16}COOH$, $Me_2HN(CH_2)_3N{=}C{=}NEtCl$, CH_2Cl_2, rt; (f) MeONa, MeOH, rt; H_2O, rt. TCA: CCl_3CO.

^{1}H NMR spectrum of **17** clearly prove the desired anomeric configuration of the synthesized linkages.

3. Experimental

3.1. General procedures

Optical rotations were measured at 25 °C with a JASCO DIP-370 polarimeter. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-600 spectrometer at 600 and 125 MHz, respectively. In $CDCl_3$, the δ_H-value is relative to internal Me_4Si and the δ_C-value is referenced to the solvent [δ_C ($CDCl_3$) 77.0]. Assignments were aided by COSY, TOCSY and ^{1}H–^{13}C correlation spectroscopy. High-resolution mass spectra were recorded on a JEOL JMS-700 under FAB conditions. Elemental analyses were performed on a Perkin-Elmer 2400 II elemental analyzer. All reactions were monitored by TLC on aluminium sheets coated with silica gel $60F_{254}$ (0.2 mm thickness, E. Merck, Darmstadt, Germany). Column chromatography was carried out using Wako gel C-300E (Wako). Solvent extracts were dried with anhydrous $MgSO_4$ unless otherwise specified.

3.2. 2-(Trimethylsilyl)ethyl *O*-[3-*O*-acetyl-2-deoxy-4,6-*O*-[(4-methoxyphenyl)methylene]-2-phthalimido-β-D-glucopyranosyl]-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (3)

To a solution of **2**[8] (428 mg, 0.44 mmol) and **1**[9] (380 mg, 0.74 mmol) in anhyd CH_2Cl_2 (5 mL) were added molecular sieves 4 Å (480 mg) and NIS (343 mg, 1.52 mmol), then cooled to −40 °C. To the

mixture was added TfOH (10 μL, 0.11 mmol), and stirring was continued for 40 min at −40 °C. The reaction was quenched with Et_3N (50.0 μL). The precipitate was filtered off and washed with CH_2Cl_2. The filtrate and washings were combined, and the solution was successively washed with satd aq $NaHCO_3$, M $Na_2S_2O_3$ and satd aq NaCl, dried and concentrated. Purification by flash column chromatography (1:4 EtOAc–hexane) gave **3** (567 mg, 91%) as an amorphous mass. $[\alpha]_D$ +10.5 (*c* 1.00, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.85–6.84 (m, 38H, 6Ph, NPhth, *p*-MeOC$_6H_4$), 6.11 (t, 1H, H-3^{III}), 5.52 (s, 1H, *p*-MeOC$_6$H$_4$C*H*), 5.48 (d, 1H, $J_{1,2}$ 8.2 Hz, H-1^{III}), 5.10 (d, 1H, J_{gem} 10.2 Hz, C*H*HPh), 4.89 (d, 1H, J_{gem} 10.8 Hz, C*H*HPh), 4.79 (d, 1H, J_{gem} 10.2 Hz, C*H*HPh), 4.77 (d, 1H, J_{gem} 10.8 Hz, C*H*HPh), 4.46 (d, 1H, J_{gem} 11.8 Hz, C*H*HPh), 4.40 (d, 1H, J_{gem} 12.1 Hz, C*H*HPh), 4.32 (d, 1H, $J_{1,2}$ 8.8 Hz, H-1^{I}), 4.33 (d, 1H, $J_{1,2}$ 8.2 Hz, H-2^{III}), 4.22 (d, 1H, $J_{1,2}$ 8.8 Hz, H-1^{II}), 4.19 (H-5^{III}), 4.17 (H-6a^{III}), 3.97 (m, 1H, C*H*HCH$_2$Si), 3.82 (t, 1H, $J_{3,4}$ 9.6 Hz, H-4^{I}), 3.80 (OC*H*$_3$), 3.75 (H-6b^{III}), 3.72 (H-4^{III}), 3.71 (H-4^{II}), 3.61 (H-6a^{I}), 3.56 (t, 1H, $J_{2,3}$ 9.5 Hz, $J_{3,4}$ 9.6 Hz, H-3^{I}), 3.55 (H-6a^{II}, H-6b^{I}), 3.54 (m, 1H, C*H*HCH$_2$Si), 3.33 (t, 1H, $J_{1,2}$ 8.8 Hz, $J_{2,3}$ 9.5 Hz, H-2^{I}), 3.32 (H-6b^{II}), 3.27 (m, 1H, H-5^{I}), 3.12 (H-5^{II}), 3.10 (t, 1H, $J_{2,3}$ 8.8 Hz, H-3^{II}), 3.02 (t, 1H, $J_{2,3}$ 8.8 Hz, H-2^{II}), 1.88 (s, 3H, COC*H*$_3$), 1.01 (m, 2H, CH$_2$C*H*$_2$Si), 0.00 (s, 9H, 3SiC*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 190.80, 170.07, 160.11, 139.49, 138.90, 138.34, 138.27, 137.83, 131.94, 129.34, 128.89, 128.62, 128.47, 128.35, 128.30, 128.26, 128.20, 128.12, 128.05, 127.86, 127.76, 127.72, 127.63, 127.52, 127.40, 127.29, 127.16, 127.04, 114.23, 113.56, 103.08 (C-1^{I}), 101.87 (C-1^{II}), 101.51 (*C*HC$_6$H$_4$OMe-*p*), 99.67 (C-1^{III}), 82.81 (C-3^{I}), 81.71 (C-2^{I}), 80.41 (C-3^{II}), 80.08 (C-2^{II}), 79.35 (C-4^{II}), 76.41 (C-4^{I}), 75.63, 75.01 (C-5^{I}), 74.93, 74.69, 73.18, 73.02, 72.96, 72.66 (C-5^{III}), 72.30 (C-5^{II}), 69.25, 68.59, 68.18 (C-6^{I}), 68.06, 67.25 (O*C*H$_2$CH$_2$Si), 65.50 (C-4^{III}), 60.34 (C-6^{II}), 55.52, 55.32, 55.23 (O*C*H$_3$), 20.66 (CO*C*H$_3$), 18.38 (*C*H$_2$Si), 14.14, −1.45 (Si*C*H$_3$). Anal. Calcd for $C_{83}H_{91}NO_{19}Si$: C, 69.48; H, 6.39; N, 0.98. Found: C, 69.55; H, 6.56; N, 1.04.

3.3. 2-(Trimethylsilyl)ethyl *O*-[3-*O*-acetyl-2-deoxy-6-*O*-[(4-methoxyphenyl)methyl]-2-phthalimido-β-D-glucopyranosyl]-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (4)

A solution of **3** (721 mg, 0.50 mmol) and molecular sieves 4 Å AW300 (2.7 g) in anhyd DMF (4.2 mL) was cooled to 0 °C and $NaB(CN)H_3$ (333 mg, 5.0 mmol) was added. A solution of TFA (135 μL) in anhyd DMF (7.9 mL) was then added dropwise and the mixture was allowed to stir at rt for 24 h. The reaction mixture was poured into cold satd aq $NaHCO_3$ and extracted with CH_2Cl_2. The organic layer was successively washed with satd aq NaCl, dried and concentrated. Purification by flash column chromatography (1:2 EtOAc–hexane) gave **4** (637 mg, 88%) as an amorphous mass. $[\alpha]_D$ +13.9 (*c* 1.00, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.65–6.82 (m, 38H, 6Ph, NPhth, *p*-MeOC$_6H_4$), 5.94 (dd, 1H, $J_{2,3}$ 11.0 Hz, $J_{3,4}$ 9.0 Hz, H-3^{III}), 5.39 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1^{III}), 5.08 (d, 1H, J_{gem} 9.8 Hz, C*H*HPh), 4.89 (d, 1H, J_{gem} 11.0 Hz, C*H*HPh), 4.79 (d, 1H, J_{gem} 11.0 Hz, C*H*HPh), 4.76 (d, 1H, J_{gem} 9.8 Hz, C*H*HPh), 4.46 (d, 1H, J_{gem} 12.1 Hz, C*H*HPh), 4.45 (d, 1H, J_{gem} 11.1 Hz, C*H*HPh), 4.44 (d, 1H, J_{gem} 12.1 Hz, C*H*HPh), 4.43 (d, 1H, J_{gem} 11.1 Hz, C*H*HPh), 4.34 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1^{I}), 4.33 (t, 1H, $J_{1,2}$ 8.3 Hz, $J_{2,3}$ 11.0 Hz, H-2^{III}), 4.20 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1^{II}), 4.14 (d, 1H, J_{gem} 10.8 Hz, *p*-MeOC$_6$H$_4$CH*H*), 3.98 (m, 1H, C*H*HCH$_2$Si), 3.90 (t, 1H, $J_{3,4}$ 9.0 Hz, H-4^{III}), 3.82 (t, 1H, $J_{3,4}$ 9.3 Hz, $J_{4,5}$ 9.6 Hz, H-4^{I}), 3.76 (H-6a^{III}), 3.76 (s, 3H, OC*H*$_3$), 3.73 (d, 1H, $J_{3,4}$ 2.3 Hz, H-4^{II}), 3.69 (H-6b^{III}), 3.69 (H-5^{III}), 3.68 (H-6a^{II}), 3.62 (H-6a^{I}), 3.59 (H-6b^{I}), 3.55 (m, 1H, C*H*HCH$_2$Si), 3.53 (t, 1H, $J_{2,3}$ 9.1 Hz, $J_{3,4}$ 9.3 Hz, H-3^{I}), 3.47 (d, 1H, J_{gem} 10.8 Hz, *p*-MeOC$_6$H$_4$CH*H*), 3.35 (dd, 1H, $J_{5,6b}$ 5.1 Hz, H-6b^{II}), 3.31 (dd, 1H, $J_{1,2}$ 7.8 Hz, $J_{2,3}$ 9.1 Hz, H-2^{I}), 3.27 (ddd, 1H, $J_{4,5}$ 9.6 Hz, H-5^{I}), 3.13 (dd, 1H, $J_{5,6b}$ 5.1 Hz, H-5^{II}), 3.10 (dd, 1H, $J_{2,3}$ 9.6 Hz, $J_{3,4}$ 2.3 Hz, H-3^{II}), 3.01 (dd, 1H, $J_{1,2}$ 7.6 Hz, $J_{2,3}$ 9.6 Hz, H-2^{II}), 1.91 (s, 3H, COC*H*$_3$), 1.01 (m, 2H, CH$_2$C*H*$_2$Si), 0.00 (s, 9H, 3SiC*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 171.31, 159.28, 139.07, 138.93, 138.66, 138.29, 138.26, 137.95, 129.54, 129.33, 129.25, 128.38, 128.20, 128.11, 128.05, 127.96, 127.84, 127.67, 127.41, 127.36, 127.31, 127.26, 113.83, 103.08 (C-1^{I}), 101.81 (C-1^{II}), 99.19 (C-1^{III}), 82.78 (C-3^{I}), 81.74 (C-2^{I}), 80.48 (C-3^{II}), 80.10 (C-2^{II}), 76.26 (C-4^{I}), 75.93, 75.05, 74.96 (C-5^{I}), 74.91 (C-4^{II}), 74.65, 73.38, 73.21 (C-5^{III}), 72.98, 72.95 (C-3^{III}), 72.86, 72.73 (C-5^{II}), 72.44, 71.51 (C-4^{III}), 69.68 (C-6^{III}), 68.47 (C-6^{II}), 68.15 (C-6^{I}), 67.25 (O*C*H$_2$), 55.19 (O*C*H$_3$), 54.58 (C-2^{III}), 20.76 (CO*C*H$_3$), 18.38 (*C*H$_2$Si), −1.46 (Si*C*H$_3$). Anal. Calcd for $C_{83}H_{93}NO_{19}Si$: C, 69.39; H, 6.52; N, 0.97. Found: C, 69.27; H, 6.71; N, 0.88.

3.4. 2-(Trimethylsilyl)ethyl *O*-[4-*O*-acetyl-2-deoxy-6-*O*-[(4-methoxyphenyl)methyl]-2-phthalimido-β-D-galactopyranosyl]-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (5)

A solution of **4** (733 mg, 0.51 mmol) in anhyd CH_2Cl_2 (16 mL) and anhyd pyridine (3.1 mL) was cooled to 0 °C and Tf_2O (257 μL, 1.5 mmol) added dropwise. The mixture was stirred at rt for 1 h, then diluted with anhyd CH_2Cl_2, successively washed with 2 M HCl and satd aq NaCl, dried and the residue was co-evaporated with toluene (three times) at rt. The residue was dissolved in anhyd DMF (100 mL). The solution was heated to 60 °C and kept for 1 h and concentrated. Purification by flash column chromatography (1:3 EtOAc–

hexane) gave **5** (606 mg, 83%) as an amorphous mass. $[\alpha]_D$ −2.3 (*c* 1.00, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.85–6.82 (m, 38H, 6Ph, NPhth, *p*-$MeOC_6H_4$), 5.49 (d, 1H, $J_{3,4}$ 3.4 Hz, H-4^{III}), 5.26 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1^{III}), 5.04 (d, 1H, J_{gem} 9.4 Hz, C*H*HPh), 4.98 (dd, 1H, $J_{2,3}$ 11.0 Hz, $J_{3,4}$ 3.4 Hz, H-3^{III}), 4.91 (d, 1H, J_{gem} 11.1 Hz, C*H*HPh), 4.82 (d, 1H, J_{gem} 11.1 Hz, C*H*HPh), 4.79 (d, 1H, J_{gem} 9.4 Hz, C*H*HPh), 4.45 (d, 1H, J_{gem} 12.3 Hz, C*H*HPh), 4.43 (dd, 1H, $J_{1,2}$ 8.3 Hz, $J_{2,3}$ 11.0 Hz, H-2^{III}), 4.42 (d, 1H, J_{gem} 12.3 Hz, C*H*HPh), 4.40 (d, 1H, J_{gem} 11.3 Hz, C*H*HPh), 4.34 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1^{I}), 4.30 (d, 1H, J_{gem} 11.3 Hz, C*H*HPh), 4.28 (d, 1H, J_{gem} 12.3 Hz, C*H*HPh), 4.27 (d, 1H, J_{gem} 12.3 Hz, C*H*HPh), 4.26 (d, 1H, J_{gem} 12.1 Hz, C*H*HPh), 4.16 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1^{II}), 4.14 (d, 1H, J_{gem} 11.0 Hz, *p*-$MeOC_6H_4CH$*H*), 4.10 (d, 1H, J_{gem} 12.1 Hz, C*H*HPh), 3.98 (m, 1H, C*H*HCH_2Si), 3.93 (m, 1H, $J_{5,6b}$ 5.7 Hz, H-5^{III}), 3.76 (s, 3H, OCH_3), 3.76 (H-4^{I}), 3.70 (d, 1H, $J_{3,4}$ 2.6 Hz, H-4^{II}), 3.64 (H-$6a^{II}$), 3.60 (H-$6a^{I}$, H-$6b^{I}$), 3.54 (H-$6a^{III}$), 3.54 (m, 1H, C*H*HCH_2Si), 3.53 (H-3^{I}), 3.49 (m, 1H, $J_{5,6b}$ 5.7 Hz, H-$6b^{III}$), 3.41 (d, 1H, J_{gem} 11.0 Hz, *p*-$MeOC_6H_4CH$*H*), 3.31 (dd, 1H, $J_{1,2}$ 7.9 Hz, H-2^{I}), 3.28 (H-$6b^{II}$), 3.27 (H-5^{I}), 3.10 (m, 1H, H-5^{II}), 3.08 (dd, 1H, $J_{2,3}$ 9.4 Hz, $J_{3,4}$ 2.6 Hz, H-3^{II}), 3.03 (dd, 1H, $J_{1,2}$ 7.6 Hz, $J_{2,3}$ 9.4 Hz, H-2^{II}), 2.12 (s, 3H, $COCH_3$), 1.01 (m, 2H, CH_2CH_2Si), 0.00 (s, 9H, $3SiCH_3$). ^{13}C NMR ($CDCl_3$): δ 171.59, 168.74, 167.82, 159.24, 139.02, 138.95, 138.79, 138.29, 138.26, 137.96, 133.72, 133.45, 132.54, 131.77, 129.70, 129.57, 129.48, 128.28, 128.23, 128.18, 128.14, 128.10, 128.02, 127.95, 127.81, 127.64, 127.41, 127.37, 127.32, 127.25, 127.21, 127.16, 127.01, 123.16, 122.84, 113.76, 103.05 (C-1^{I}), 102.02 (C-1^{II}), 99.87 (C-1^{III}), 82.70 (C-3^{I}), 81.74 (C-2^{I}), 80.42 (C-3^{II}), 79.99 (C-2^{II}), 76.57 (C-4^{I}), 76.09, 75.28 (C-4^{II}), 75.06 (C-5^{I}), 74.96, 74.51, 73.06 (C-5^{II}), 72.99, 72.94, 72.38, 71.56 (C-5^{III}), 69.89 (C-4^{III}), 68.65 (C-6^{II}), 68.11 (C-6^{I}), 67.44 (C-6^{III}), 67.23, 66.74 (C-3^{III}), 55.17 (OCH_3), 54.47 (C-2^{III}), 29.62, 21.00 ($COCH_3$), 18.36 (CH_2Si), −1.46 ($SiCH_3$). Anal. Calcd for $C_{83}H_{93}NO_{19}Si$: C, 69.39; H, 6.52; N, 0.97. Found: C, 69.36; H, 6.69; N, 0.81.

3.5. 2-(Trimethylsilyl)ethyl *O*-[2-acetamido-2-deoxy-6-*O*-[(4-methoxyphenyl)methyl]-β-D-galactopyranosyl]-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (6)

A solution of **5** (686 mg, 0.48 mmol) in 95% EtOH (14.3 mL) and hydrazine monohydrate (0.49 mL) heated under reflux for 2 h. The mixture were evaporated and co-evaporated several times with toluene to give a residue, which was dissolved in MeOH (24 mL) and Ac_2O (3.5 mL), and stirred overnight at rt. After pyridine (7 mL) was added, the mixture was concentrated and solution of the residue in CH_2Cl_2 was successively washed with 2 M HCl, satd aq NaCl, dried and concentrated. Purification by flash column chromatography (5:7 EtOAc–hexane) gave **6** (553 mg, 89%) as an amorphous mass. $[\alpha]_D$ +8.2 (*c* 1.00, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.41–7.17 (m, 34H, 6Ph, *p*-$MeOC_6H_4$), 4.90 (d, 1H, J_{gem} 10.4 Hz, C*H*HPh), 4.89 (d, 1H, J_{gem} 10.8 Hz, C*H*HPh), 4.84 (d, 1H, J_{gem} 11.3 Hz, C*H*HPh), 4.74 (d, 1H, J_{gem} 10.8 Hz, C*H*HPh), 4.73 (d, 1H, J_{gem} 10.4 Hz, C*H*HPh), 4.72 (d, 1H, J_{gem} 9.8 Hz, C*H*HPh), 4.64 (d, 1H, J_{gem} 9.8 Hz, C*H*HPh), 4.57 (2 d, 2H, J_{gem} 11.3 Hz, J_{gem} 12.3 Hz, 2C*H*HPh), 4.43 (d, 1H, J_{gem} 11.9 Hz, C*H*HPh), 4.42 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1^{II}), 4.39 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1^{III}), 4.38 (d, 1H, J_{gem} 11.9 Hz, C*H*HPh), 4.37 (d, 1H, J_{gem} 12.3 Hz, C*H*HPh), 4.36 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1^{I}), 4.34 (d, 1H, J_{gem} 12.3 Hz, *p*-$MeOC_6H_4CH$*H*), 4.27 (d, 1H, J_{gem} 12.3 Hz, *p*-$MeOC_6H_4CH$*H*), 4.01 (d, 1H, $J_{3,4}$ 2.3 Hz, H-4^{II}), 3.98 (m, 1H, C*H*HCH_2Si), 3.93 (t, 1H, $J_{3,4}$ 9.3 Hz, H-4^{I}), 3.85 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4^{III}), 3.73–3.69 (m, 6H, OCH_3, H-$6a^{I}$, H-$6b^{I}$, H-2^{III}), 3.55 (m, 1H, C*H*HCH_2Si), 3.53 (t, 1H, $J_{3,4}$ 9.3 Hz, H-3^{I}), 3.47 (m, 2H, H-2^{II}, H-3^{II}), 3.42 (dd, 1H, $J_{2,3}$ 9.0 Hz, $J_{3,4}$ 3.2 Hz, H-3^{III}), 3.36 (m, 2H, H-2^{I}, H-5^{I}), 1.50 (s, 3H, $NCOCH_3$), 1.01 (m, 2H, CH_2CH_2Si), 0.00 (s, 9H, $3SiCH_3$). ^{13}C NMR ($CDCl_3$): δ 173.94, 159.16, 138.64, 138.59, 138.51, 138.22, 138.12, 136.24, 129.85, 129.38, 128.97, 128.82, 128.68, 128.42, 128.22, 128.18, 128.13, 127.95, 127.75, 127.57, 127.47, 127.40, 127.36, 113.73, 103.07 (C-1^{II}), 102.72 (C-1^{III}), 102.29 (C-1^{I}), 82.39 (C-3^{I}), 82.08, 81.87, 80.59, 76.46, 75.58 (C-4^{II}), 75.49 (C-4^{I}), 75.26, 74.99, 74.93, 74.86, 73.72, 73.25, 73.19, 73.10, 68.82, 68.55, 68.10, 67.31, 67.15, 56.27, 55.14 (OCH_3), 22.14 ($COCH_3$), 18.38 (CH_2Si), −1.47 ($SiCH_3$). Anal. Calcd for $C_{75}H_{91}NO_{17}Si$: C, 68.94; H, 7.02; N, 1.07. Found: C, 68.91; H, 6.87; N, 1.01.

3.6. Dodecyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-β-D-galactopyranoside (7)

Dodecyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside[10] (10.4 g, 19.5 mmol) was suspended in a solution of anhyd MeOH (16 mL), anhyd CH_2Cl_2 (24 mL) and M NaOMe (3.7 mL), the mixture was stirred at rt for 4 h. This solution was then treated with ion-exchange resin Amberlite IR-120 (H+) for about 5 min. The resin was filtered off, and the solvent was removed under diminished pressure to quantitatively give a white solid (7.1 g). To a stirred solution of the solid in anhyd pyridine (60 mL) and anhyd CH_2Cl_2 (40 mL) was added a solution of benzoyl chloride (12.9 mL, 111 mmol) dropwise at 0 °C. The reaction was stirred at rt for 6 h. The reaction mixture was then diluted with anhyd CH_2Cl_2 (250 mL) and sequentially washed with 2 M HCl, satd aq $NaHCO_3$ and then satd aq NaCl. The organic layer was dried and concentrated. Purification by flash column chromatography (1:10 EtOAc–hexane) gave **7** (13.8 g, 91%) as a colourless syrup. $[\alpha]_D$ +60.0 (*c* 1.00,

$CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.01–7.15 (m, 20H, 4Ph), 5.97 (d, 1H, $J_{3,4}$ 3.4 Hz, H-4), 5.78 (t, 1H, $J_{1,2}$ 10.0 Hz, $J_{2,3}$ 10.0 Hz, H-2), 5.58 (dd, 1H, $J_{2,3}$ 10.0 Hz, $J_{3,4}$ 3.4 Hz, H-3), 4.79 (d, 1H, $J_{1,2}$ 10.0 Hz, $J_{2,3}$ 10.0 Hz, H-1), 4.60 (dd, 1H, H-6a), 4.34–4.29 (m, 2H, H-5, 6b), 2.79–2.66 (m, 2H, SCH_2), 1.67–1.50 (m, 2H, SCH_2CH_2), 1.25–1.13 (m, 18H, $9CH_2$), 0.79 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 165.95, 165.44, 165.38, 165.26 (4*C*=O), 133.60, 133.30, 133.27, 129.88, 129.73, 129.66, 129.16, 128.95, 128.79, 128.57, 128.53, 128.38, 128.31, 128.22, 84.30 (C-1), 74.77 (C-5), 72.53 (C-3), 68.15 (C-4), 68.00 (C-2), 62.08 (C-6), 31.85, 30.33, 29.71, 29.60, 29.57, 29.52, 29.48, 29.30, 29.08, 28.82, 22.64, 14.13. Anal. Calcd for $C_{46}H_{52}O_9S$: C, 70.74; H, 6.71; S, 4.11. Found: C, 70.52; H, 6.90; S, 3.95.

3.7. 2-(Trimethylsilyl)ethyl *O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-(1→3)-*O*-[2-acetamido-2-deoxy-6-*O*-[(4-methoxyphenyl)methyl]-β-D-galactopyranosyl]-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (8)

To a solution of **6** (543 mg, 0.42 mmol) and **7** (466 mg, 0.60 mmol) in anhyd CH_2Cl_2 (11 mL) were added molecular sieves 4 Å AW300 (500 mg) and NIS (242 mg, 1.08 mmol), then cooled to 0 °C. To the mixture was added TfOH (5.3 μL, 0.06 mmol), and the stirring was continued for 30 min at 0 °C. The reaction was quenched with Et_3N (50.0 μL). The precipitate was filtered off and washed with CH_2Cl_2. The filtrate and washings were combined, and the solution was successively washed with satd aq $NaHCO_3$, M $Na_2S_2O_3$ and satd aq NaCl, dried and concentrated. Purification by flash column chromatography (1:4 EtOAc–hexane) gave **8** (453 mg, 58%) as an amorphous mass. $[\alpha]_D$ +61.8 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.08–6.79 (m, 54H, 10Ph, *p*-$MeOC_6H_4$), 5.95 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4^{IV}), 5.77 (dd, 1H, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 10.4 Hz, H-2^{IV}), 5.56 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.2 Hz, H-3^{IV}), 5.14 (d, 1H, $J_{2,NH}$ 6.4 Hz, N*H*), 5.07 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1^{III}), 4.92 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1^{IV}), 4.89–4.18 (14d, 14H, 12C*H*HPh, *p*-$MeOC_6H_4CH_2$), 4.52 (m, 1H, $J_{3,4}$ 3.0 Hz, H-3^{III}), 4.37 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1^{II}), 4.35 (d, 1H, $J_{1,2}$ 8.1 Hz, H-1^{I}), 4.16 (d, 1H, $J_{3,4}$ 3.0 Hz, H-4^{III}), 4.00 (d, 1H, $J_{3,4}$ 2.6 Hz, H-4^{II}), 3.97 (m, 1H, C*H*HCH$_2$Si), 3.86 (t, 1H, $J_{3,4}$ 9.3 Hz, H-4^{I}), 3.71 (s, 3H, OCH_3), 3.57 (m, 1H, C*H*HCH$_2$Si), 3.50 (t, 1H, $J_{3,4}$ 9.3 Hz, H-3^{I}), 3.38 (H-2^{II}), 3.37 (H-2^{III}), 3.34 (H-5^{I}), 3.33 (H-2^{I}), 3.28 (H-3^{II}), 1.04 (s, 3H, $COCH_3$), 1.01 (m, 2H, CH_2CH_2Si), 0.00 (s, 9H, $3SiCH_3$). ^{13}C NMR ($CDCl_3$): δ 165.94, 165.57, 165.47, 159.20, 138.85, 138.79, 138.55, 138.35, 138.08, 133.65, 133.33, 133.28, 130.19, 130.02, 129.78, 129.72, 129.30, 129.24, 128.90, 128.67, 128.55, 128.50, 128.42, 128.35, 128.26, 128.21, 128.14, 128.10, 127.99, 127.92, 127.74, 127.60, 127.53, 127.48, 127.37, 127.25, 113.80, 103.13 (C-1^{I}), 102.41 (C-1^{II}), 102.33 (C-1^{IV}), 99.32 (C-1^{III}), 82.98 (C-3^{I}), 81.89, 81.68, 80.13 (C-3^{III}), 79.86, 76.48 (C-4^{I}), 75.21, 75.18, 75.13, 74.93, 73.73, 73.25, 73.11, 73.03, 72.83, 72.36, 72.25 (C-4^{II}), 71.55, 71.44 (C-3^{IV}), 69.53 (C-2^{IV}), 69.33, 69.09, 68.36 (C-4^{III}), 68.00 (C-4^{IV}), 67.29 (CH_2CH_2Si), 62.11, 55.19 (OCH_3), 54.18 (C-2^{III}), 22.77 ($COCH_3$), 18.47 (CH_2CH_2Si), −1.42 ($SiCH_3$). Anal. Calcd for $C_{109}H_{117}NO_{26}Si$: C, 69.45; H, 6.26; N, 0.74. Found: C, 69.73; H, 6.18; N, 0.65.

3.8. 2-(Trimethylsilyl)ethyl *O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-(1→3)-*O*-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (9)

To a solution of **8** (488 mg, 0.26 mmol) in CH_3CN (4.6 mL) and water (1.1 mL) was added dropwise ammonium cerium(IV) nitrate (426 mg, 0.78 mmol) in CH_3CN (6.8 mL) and the mixture was stirred for 1 h at rt. The reaction mixture was diluted with EtOAc and was successively washed with satd aq $NaHCO_3$, dried and concentrated. Purification by flash column chromatography (1:1 EtOAc–hexane) gave **9** (415 mg, 91%) as an amorphous mass. $[\alpha]_D$ +68.0 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.85–6.82 (m, 50H, 10Ph), 5.94 (d, 1H, $J_{3,4}$ 3.6 Hz, H-4^{IV}), 5.77 (dd, 1H, $J_{1,2}$ 7.8 Hz, $J_{2,3}$ 10.5 Hz, H-2^{IV}), 5.55 (dd, 1H, $J_{2,3}$ 10.5 Hz, $J_{3,4}$ 3.6 Hz, H-3^{IV}), 5.18 (d, 1H, N*H*), 4.92 (d, 1H, $J_{1,2}$ 8.1 Hz, H-1^{III}), 4.91 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1^{IV}), 4.90 (d, 1H, J_{gem} 11.0 Hz, C*H*HPh), 4.87 (d, 1H, J_{gem} 10.0 Hz, C*H*HPh), 4.74 (d, 1H, J_{gem} 11.0 Hz, C*H*HPh), 4.69 (d, 1H, J_{gem} 10.0 Hz, C*H*HPh), 4.66 (d, 1H, J_{gem} 11.0 Hz, C*H*HPh), 4.58 (t, 1H, $J_{3,4}$ 2.8 Hz, H-3^{III}), 4.35 (d, 1H, $J_{1,2}$ 8.1 Hz, H-1^{I}), 4.30 (d, 1H, $J_{1,2}$ 8.1 Hz, H-1^{II}), 4.05 (d, 1H, $J_{3,4}$ 2.8 Hz, H-4^{III}), 3.98 (m, 1H, C*H*HCH$_2$Si), 3.86 (d, 1H, $J_{3,4}$ 2.8 Hz, H-4^{II}), 3.84 (t, 1H, $J_{3,4}$ 9.3 Hz, $J_{4,5}$ 9.4 Hz, H-4^{I}), 3.71 (dd, 1H, $J_{5,6a}$ 4.2 Hz, $J_{6a,6b}$ 10.8 Hz, H-6a^{I}), 3.66 (m, 1H, $J_{5,6b}$ 10.6 Hz, $J_{6a,6b}$ 10.8 Hz, H-6b^{I}), 3.57 (m, 1H, C*H*HCH$_2$Si), 3.50 (t, 1H, $J_{3,4}$ 9.3 Hz, H-3^{I}), 3.40 (H-2^{III}), 3.38 (H-2^{I}), 3.38 (H-2^{II}), 3.33 (m, 1H, $J_{4,5}$ 9.4 Hz, $J_{5,6a}$ 4.2 Hz, $J_{5,6b}$ 10.6 Hz, H-5^{I}), 3.19 (dd, 1H, $J_{3,4}$ 2.8 Hz, H-3^{II}), 1.00 (m, 5H, $COCH_3$, CH_2CH_2Si), 0.00 (s, 9H, $3SiCH_3$). ^{13}C NMR ($CDCl_3$): δ 165.95, 165.52, 165.40, 164.79, 138.81, 138.61, 138.45, 138.38, 138.16, 138.06, 133.66, 133.51, 133.31, 133.26, 129.98, 129.75, 129.66, 129.22, 129.07, 128.77, 128.64, 128.54, 128.43, 128.34, 128.32, 128.25, 128.23, 128.19, 128.15, 128.10, 127.96, 127.78, 127.65, 127.62, 127.56, 127.54, 127.51, 127.49, 127.47, 127.36, 103.13 (C-1^{I}), 102.54 (C-1^{II}), 102.23 (C-1^{III}), 100.01 (C-1^{IV}), 82.96 (C-3^{I}), 81.88, 81.14 (C-3^{IV}), 80.32, 79.82, 76.73 (C-4^{I}), 75.69, 75.18, 75.12, 74.93, 74.00, 73.35, 73.13, 73.05, 72.34, 71.80, 71.44, 71.40, 69.37, 68.32, 68.25, 68.08, 67.66, 67.28, 62.42, 62.32, 54.06 (C-2^{III}), 22.64 ($COCH_3$),

18.44 (CH_2CH_2Si), −1.45 ($SiCH_3$). Anal. Calcd for $C_{101}H_{109}NO_{25}Si$: C, 68.73; H, 6.22; N, 0.79. Found: C, 68.59; H, 6.48; N, 0.67.

3.9. 2-(Trimethylsilyl)ethyl *O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-(1→3)-[*O*-(methyl 4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-5-trichloroacetamido-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2→6)]-*O*-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (11)

To a solution of **9** (253 mg, 0.14 mmol) and ethyl (methyl 4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-1-thio-5-trichloroacetamido-D-*glycero*-D-*galacto*-2-nonulopyranosid)onate[11] (**10**, 269 mg, 0.42 mmol) in anhyd CH_3CN (3.5 mL) were added molecular sieves 3 Å AW300 (380 mg) and NIS (190 mg, 0.84 mmol), then cooled to −40 °C. To the mixture was added TfOH (9.3 μL, 0.11 mmol), and stirring was continued for 1.5 h at −40 °C. The reaction was quenched with Et_3N (100 μL). The precipitate was filtered off and washed with CH_2Cl_2. The filtrate and washings were combined, and the solution was successively washed with satd aq $NaHCO_3$, M $Na_2S_2O_3$ and satd aq NaCl, dried and concentrated. Purification by flash column chromatography (1:3 EtOAc–hexane) gave **11** (200 mg, 60%) as an amorphous mass. $[\alpha]_D$ +36.8 (*c* 1.00, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.08–7.15 (m, 50H, 10Ph), 6.63 (d, 1H, N*H*^{V}), 5.97 (d, 1H, $J_{3,4}$ 3.1 Hz, H-4^{IV}), 5.76 (dd, 1H, $J_{1,2}$ 8.5 Hz, $J_{2,3}$ 10.0 Hz, H-2^{IV}), 5.59 (dd, 1H, $J_{2,3}$ 10.0 Hz, $J_{3,4}$ 3.1 Hz, H-3^{IV}), 5.32 (H-8^V), 5.29 (H-7^V), 5.17 (d, 1H, $J_{NH,2}$ 6.4 Hz, N*H*^{III}), 5.13 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1^{III}), 5.06 (ddd, 1H, $J_{3ax,4}$ 12.2 Hz, $J_{4,5}$ 4.5 Hz, H-4^V), 4.95 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1^{IV}), 4.88 (d, 1H, J_{gem} 11.3 Hz, C*H*HPh), 4.85 (d, 1H, J_{gem} 11.3 Hz, C*H*HPh), 4.56 (H-3^{III}), 4.47 (d, 1H, J_{gem} 12.1 Hz, C*H*HPh), 4.38 (d, $J_{1,2}$ 7.6 Hz, H-1^{II}), 4.35 (d, $J_{1,2}$ 8.7 Hz, H-1^I), 4.29 (H-6^V), 4.20 (H-4^{III}), 4.19 (H-9a^V), 4.00 (H-9b^V), 3.98 (m, 1H, C*H*HCH$_2$Si), 3.88 ($J_{4,5}$ 4.5 Hz, H-5^V), 3.87 ($J_{4,5}$ 9.1 Hz, H-4^I), 3.77 (s, 3H, COOC*H*$_3$), 3.58 (m, 1H, C*H*HCH$_2$Si), 3.50 (t, 1H, $J_{3,4}$ 9.1 Hz, H-3^I), 3.38 (H-2^{II}), 3.36 (H-5^I), 3.34 (H-3^{II}), 3.32 (H-2^{III}), 3.30 (H-2^I), 2.60 (m, 1H, J_{gem} 12.2 Hz, H-3eq^V), 2.10, 2.09, 1.95, 1.91, 1.10 (s, each 3H, 5COC*H*$_3$), 1.83 (t, 1H, $J_{gem} = J_{3ax,4}$ = 12.2 Hz, H-3ax^V), 1.00 (m, 2H, CH$_2$C*H*$_2$Si), 0.00 (s, 9H, 3SiC*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 177.60, 170.62, 170.49, 170.31, 169.88, 169.69, 167.81, 165.84, 165.49, 165.44, 164.84, 161.95, 138.92, 138.84, 138.78, 138.54, 138.33, 138.12, 133.59, 133.33, 133.25, 129.96, 129.76, 129.66, 129.25, 129.21, 128.97, 128.62, 128.50, 128.44, 128.36, 128.21, 128.17, 128.11, 128.06, 128.00, 127.93, 127.81, 127.72, 127.64, 127.57, 127.44, 127.30, 127.20, 103.09, (C-1^I), 102.37 (C-1^{II}), 102.33 (C-1^{IV}), 99.24 (C-1^{III}), 98.92, 92.06, 82.98 (C-3^I), 81.91, 81.87, 79.82, 79.62 (C-3^{III}), 76.35, 75.47, 75.20, 75.14, 74.88, 73.85, 73.44, 73.24, 73.07, 73.02, 72.31, 72.07, 72.00, 71.79, 71.42, 71.28, 69.60, 69.01, 68.53, 68.44, 68.37, 67.91, 67.79, 67.52, 67.43, 67.22, 63.06, 62.00 (C-9^V), 61.60, 54.25 (C-2^{III}), 52.93 (OC*H*$_3$), 51.67, 37.65, 29.62, 29.51, 22.81, 20.94, 20.65, 20.58, 18.43, −1.45 ($SiCH_3$). Anal. Calcd for $C_{121}H_{133}Cl_3N_2O_{37}Si$: C, 62.06; H, 5.72; N, 1.20. Found: C, 5.49; H, 5.89; N, 1.06.

3.10. 2-(Trimethylsilyl)ethyl *O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-(1→3)-[*O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2→6)]-*O*-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (12)

A solution of **11** (193 mg, 82.5 μmol), tributyltin hydride (197 μL, 0.74 mmol), *N*,*N*-dimethylacetamide (0.54 mL) and 2,2′-azobisisobutyronitrile (AIBN; 3.3 mg) in anhyd benzene (3.3 mL) heated under reflux for 15 min. The reaction mixture was then cooled and concentrated under diminished pressure. Purification by flash column chromatography (2:1 EtOAc–hexane) gave **12** (178 mg, 96%) as an amorphous mass. $[\alpha]_D$ +38.5 (*c* 1.00, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.15–7.10 (m, 50H, 10Ph), 5.97 (d,1H, $J_{3,4}$ 3.4 Hz, H-4^{IV}), 5.76 (dd, 1H, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 10.2 Hz, H-2^{IV}), 5.58 (dd, 1H, $J_{2,3}$ 10.2 Hz, $J_{3,4}$ 3.4 Hz, H-3^{IV}), 5.34–5.28 (m, 3H, H-7^V, H-8^V, N*H*), 5.11 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1^{III}), 4.96 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1^{IV}), 4.82 (m, 1H, H-4^V), 4.52 (m, 1H, H-3^{III}), 4.38 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1^{II}), 4.35 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1^I), 4.21–4.17 (m, 2H, H-4^{III}, H-9a^V), 4.12 (d, 1H, $J_{3,4}$ 2.2 Hz, H-4^{II}), 3.99–3.93 (m, 2H, H-9b^V, C*H*HCH$_2$Si), 3.86 (t, 1H, $J_{3,4}$ 9.1 Hz, H-4^I), 3.75 (s, 3H, COOC*H*$_3$), 3.69–3.67 (m, 3H, H-6a^I, H-6b^I, H-6a^{II}), 3.56 (m, 1H, C*H*HCH$_2$Si), 3.49 (t, 1H, $J_{3,4}$ 9.1 Hz, H-3^I), 3.43 (m, 1H, H-5^{II}), 3.40–3.27 (m, 6H, H-2^{II}, H-2^{III}, H-5^I, H-3^{II}, H-2^I, H-6b^{II}), 2.54 (dd, 1H, J_{gem} 12.8 Hz, $J_{3eq,4}$ 4.5 Hz, H-3eq^V), 1.85 (m, 1H, J_{gem} 12.8 Hz, H-3ax^V), 2.08, 2.07, 1.95, 1.92, 1.84, 1.10 (6s, each 3H, 6COC*H*$_3$), 1.00 (m, 2H, CH$_2$C*H*$_2$Si), 0.00 (s, 9H, 3SiC*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 170.75, 170.65, 170.54, 170.21, 169.96, 169.60, 168.00, 165.83, 165.50, 165.41, 164.82, 38.97, 138.86, 138.77, 138.58, 138.35, 138.13, 133.58, 133.33, 133.23, 133.20, 129.95, 129.78, 129.75, 129.68, 129.26, 128.99, 128.62, 128.58, 128.51, 128.44, 128.36, 128.31, 128.22, 128.19, 128.18, 128.11, 128.08, 128.06, 128.01, 127.95, 127.89, 127.85, 127.73, 127.71, 127.69, 127.62, 127.57, 127.48, 127.44, 127.42, 127.31, 127.18, 103.10 (C-1^I), 102.34 (C-1^{II}, C-1^{IV}), 98.95 (C-1^{III}), 82.98 (C-3^I), 81.93, 81.90, 79.84, 79.72 (C-3^{III}), 76.38, 75.49, 75.22, 75.15, 74.89, 73.95, 73.28, 73.08, 72.64, 72.30, 72.05, 71.43, 71.30, 69.63, 69.07, 69.02, 68.59, 68.39, 67.91, 67.45, 67.38, 67.23 (*C*H$_2$CH$_2$Si), 62.91, 62.17 (C-9^V), 61.60, 54.23 (C-2^{III}),

52.75 (O*C*H$_3$), 49.45 (C-5^V), 37.59 (C-3^V), 23.11, 22.80, 20.96, 20.76, 20.74, 20.65, 18.44 (CH$_2$*C*H$_2$Si), −1.45 (Si*C*H$_3$). Anal. Calcd for $C_{121}H_{136}N_2O_{37}Si$: C, 62.92; H, 6.12; N, 1.25. Found: C, 62.83; H, 6.26; N, 1.25.

3.11. 2-(Trimethylsilyl)ethyl *O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-(1→3)-[*O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2→6)]-*O*-(2-acetamido-4-*O*-benzoyl-2-deoxy-β-D-galactopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzoyl-β-D-glucopyranoside (13)

Compound **12** (136 mg, 60.8 μmol) was dissolved in EtOAc (5.4 mL) and then a solution of sodium bromate (165 mg, 1.1 mmol) in water (3.7 mL) was added. To the well stirred two-phase system an aqueous solution of sodium hydrosulfite (80% pure, 203 mg, dissolved in 7.7 mL water) was added dropwise over 20 min at rt. The mixture was diluted with EtOAc and the organic phase was successively washed with M $Na_2S_2O_3$ and satd aq NaCl, dried ($MgSO_4$) and concentrated under diminished pressure. To the solution of the residue in pyridine (2.5 mL) added dropwise benzoyl chloride for 2.5 h at rt. The reaction was quenched with MeOH (60 μL) and diluted with CH_2Cl_2, successively washed with satd aq $NaHCO_3$ and satd aq NaCl, dried and concentrated. Purification by flash column chromatography (1:80 MeOH–CH_2Cl_2) gave **13** (80 mg, 59%) as an amorphous mass. $[\alpha]_D$ +21.1 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.31–7.02 (m, 55H, 11Ph), 6.07 (d, 1H, $J_{3,4}$ 3.4 Hz, H-4^{IV}), 5.84 (dd, 1H, $J_{1,2}$ 7.7 Hz, $J_{2,3}$ 10.2 Hz, H-2^{IV}), 5.74 (t, 1H, $J_{2,3}$ 9.6 Hz, $J_{3,4}$ 9.8 Hz, H-3^I), 5.69 (dd, 1H, $J_{2,3}$ 10.2 Hz, $J_{3,4}$ 3.4 Hz, H-3^{IV}), 5.59 (dd, 1H, $J_{1,2}$ 7.8 Hz, $J_{2,3}$ 10.5 Hz, H-2^{II}), 5.51 (dd, 1H, $J_{2,3}$ 9.6 Hz, $J_{1,2}$ 7.9 Hz, H-2^I), 5.40 (dd, 1H, $J_{2,3}$ 10.5 Hz, $J_{3,4}$ 2.3 Hz, H-3^{II}), 5.35 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1^{III}), 5.25 (d, 1H, N*H*), 5.20 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1^{IV}), 4.91 (d, 1H, $J_{1,2}$ 7.8 Hz, H-1^{II}), 4.87 (m, 1H, $J_{3eq,4}$ 4.7 Hz, H-4^V), 4.74 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1^I), 4.59 (d, 1H, $J_{3,4}$ 2.3 Hz, H-4^{II}), 4.35 (t, 1H, $J_{3,4}$ 9.8 Hz, H-4^I), 4.33 (t, 1H, $J_{1,2}$ 7.8 Hz, $J_{2,3}$ 12.8 Hz, H-2^{III}), 4.09 (dd, 1H, $J_{2,3}$ 12.8 Hz, H-3^{III}), 4.03–3.97 (m, 2H, H-5^V, C*H*HCH$_2$Si), 3.88 (m, 1H, H-5^I), 3.43 (s, 3H, COOC*H*$_3$), 2.48 (dd, 1H, J_{gem} 13.0 Hz, $J_{3eq,4}$ 4.5 Hz, H-3eq^V), 1.78 (m, 1H, H-3ax^V), 2.16, 2.08, 2.07, 20.6, 2.01, 1.94 (6s, each 3H, 6COC*H*$_3$), 0.95 (m, 2H, CH$_2$C*H*$_2$Si), 0.00 (s, 9H, 3SiC*H*$_3$). ^{13}C NMR ($CDCl_3$): δ 170.87, 170.42, 170.09, 169.96, 169.61, 167.48, 165.90, 165.84, 165.56, 165.46, 165.43, 164.96, 164.86, 133.54, 133.48, 133.27, 133.23, 133.11, 132.62, 130.99, 130.26, 130.15, 130.12, 130.02, 129.94, 129.91, 129.79, 129.75, 129.69, 129.63, 129.53, 129.50, 129.43, 129.29, 129.25, 129.17, 128.96, 128.95, 128.89, 128.72, 128.68, 128.61, 128.55, 128.51, 128.43, 128.35, 128.23, 128.18, 101.53 (C-1^{IV}), 100.54 (C-1^I), 99.42 (C-1^{II}), 98.41 (C-1^{III}), 96.38 (C-1^V), 74.28, 74.10 (C-4^I), 73.59 (C-3^{II}), 73.16 (C-3^I), 73.08, 72.56, 71.81 (C-2^I), 71.76 (C-3^{IV}), 71.63, 70.72, 70.30 (C-2^{II}), 70.07 (C-2^{IV}), 69.73, 69.01, 68.99, 68.77 (C-4^{II}), 67.81, 67.49, 67.38 (*C*H$_2$CH$_2$Si), 63.65, 62.56, 62.00, 61.89, 61.83 (O*C*H$_3$), 56.52, 55.04, 53.38, 52.39, 49.60, 37.31, 29.65, 23.11, 20.78, 20.74, 20.69, 20.65, 17.84 (CH$_2$*C*H$_2$Si), −1.58 (Si*C*H$_3$). Anal. Calcd for $C_{128}H_{128}N_2O_{44}Si$: C, 63.36; H, 5.32; N, 1.15. Found: C, 63.24; H, 5.60; N, 1.02.

3.12. *O*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl)-(1→3)-[*O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2→6)]-*O*-(2-acetamido-4-*O*-benzoyl-2-deoxy-β-D-galactopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→1)-(2*S*,3*R*,4*E*)-2-azido-3-*O*-benzoyl-4-eicosene-1,3-diol (15)

To a solution of **13** (131 mg, 54.0 μmol) in anhyd CH_2Cl_2 (2.0 mL) was added TFA (2.5 mL) at 0 °C and the mixture was stirred for 30 min at 0 °C, quenched with propylacetate (5.0 mL) and concentrated. The residue was then dissolved in anhyd CH_2Cl_2 (2.0 mL) and CCl_3CN (126 μL, 1.25 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 13 μL, 87.0 μmol) were added at rt. The mixture was stirred for 1 h at rt, then concentrated. The residue was filtered through short pad of silica gel and concentrated. To a solution of the residue and (2*S*,3*R*,4*E*)-2-azido-3-*O*-benzoyl-4-eicosene-1,3-diol[12] (**14**, 40 mg, 87.4 μmol) in anhyd CH_2Cl_2 were added molecular sieves 4 Å AW300 (130 mg) and $BF_3{\cdot}Et_2O$ (8.5 μL, 67.0 μmol). The mixture was stirred for 2 h at 0 °C and diluted with anhyd CH_2Cl_2 and successively washed with satd aq $NaHCO_3$ and satd aq NaCl, dried and concentrated. Purification by flash column chromatography (1:80 MeOH–CH_2Cl_2) gave **15** (54 mg, 36%) as an amorphous mass. $[\alpha]_D$ +14.4 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.04–6.93 (m, 60H, 12Ph), 5.87 (d, 1H, $J_{3,4}$ 3.8 Hz, H-4^{IV}), 5.64 (dd, 1H, $J_{1,2}$ 7.7 Hz, $J_{2,3}$ 10.4 Hz, H-2^{IV}), 5.60 (m, 1H, $J_{4,5}$ 15.9 Hz, $J_{5,6} = J_{5,6'}$ 6.8 Hz, H-5 of sphingosine), 5.56 (t, 1H, $J_{2,3}$ 9.4 Hz, $J_{3,4}$ 9.4 Hz, H-3^I), 5.49 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.8 Hz, H-3^{IV}), 5.43 (t, 1H, $J_{3,4}$ 7.9 Hz, H-3 of sphingosine), 5.39 (dd, 1H, $J_{1,2}$ 7.6 Hz, $J_{2,3}$ 10.6 Hz, H-2^{II}), 5.34 (m, 1H, $J_{3,4}$ 7.9 Hz, $J_{4,5}$ 15.9 Hz, H-4 of sphingosine), 5.33 (dd, 1H, $J_{1,2}$ 7.6 Hz, $J_{2,3}$ 9.4 Hz, H-2^I), 5.21 (dd, 1H, $J_{2,3}$ 10.6 Hz, $J_{3,4}$ 2.5 Hz, H-3^{II}), 5.16 (d, 1H, $J_{3,4}$ 2.1 Hz, H-4^{III}), 5.15 (d, 1H, $J_{1,2}$ 5.3 Hz, H-1^{III}), 4.99 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1^{IV}), 4.98 (d, 1H, $J_{NH,5}$ 9.8 Hz, N*H*^{V}), 4.71 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1^{II}), 4.64 (m, 1H, H-4^V), 4.54 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1^I), 4.40 (d, 1H, $J_{3,4}$ 2.5 Hz, H-4^{II}), 4.17 (t, 1H, $J_{3,4}$ 9.4 Hz, H-4^I), 4.13 (dd, 1H, $J_{2,3}$ 12.5 Hz, $J_{3,4}$ 2.1 Hz, H-3^{III}), 3.89 (dd, 1H, $J_{1,2}$ 5.3 Hz, $J_{2,3}$ 12.5 Hz, H-2^{III}), 3.68 (m, 1H, H-5^I), 3.22 (s, 3H,

COOCH_3), 2.28 (dd, 1H, J_{gem} 12.9 Hz, H-3eq^{V}), 1.96, 1.88, 1.87, 1.86, 1.79, 1.74 (6s, each 3H, 6COCH_3), 1.57 (t, 1H, J_{gem} 12.9 Hz, H-3ax^{V}), 1.40–1.04 (m, 26H, 13CH_2), 0.80 (t, 3H, CH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 140.45 (C-5 of sphingosine), 136.25–128.86 (arom-C), 124.02 (C-4 of sphingosine), 103.12 (C-1^{IV}), 102.55 (C-1^{I}), 100.00 (C-1^{II}), 97.99 (C-1^{III}), 76.26, 75.88 (C-4^{III}), 75.34 (C-4^{I}), 75.15 (C-3^{II}), 74.96, 74.32 (C-3^{I}), 74.14, 73.34, 73.23 (C-3^{IV}), 73.14 (C-2^{I}), 72.30, 71.84 (C-2^{IV}), 71.66, 70.57, 70.36, 69.80, 69.73, 69.39 (C-4^{IV}), 68.96, 64.99, 63.88, 63.59, 63.49, 63.47, 63.44, 63.41, 63.88 (C-3^{III}), 63.59, 63.49, 63.47 (C-2^{III}), 63.44, 63.41, 58.01, 54.07, 51.19, 38.80, 33.86, 24.78, 24.77, 22.27, 22.19, 15.66. The carbonyl carbons and the quaternary carbon (C-2^{V}) of **15** could not be assigned, because these chemical shifts of the carbons were recorded by ^{1}H–^{13}C correlation spectroscopy. Anal. Calcd for $C_{150}H_{157}N_5O_{46}$: C, 65.14; H, 5.72; N, 2.53. Found: C, 64.09; H, 5.81; N, 2.61.

3.13. *O*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl)-(1→3)-[*O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2→6)]-*O*-(2-acetamido-4-*O*-benzoyl-2-deoxy-β-D-galactopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→1)-(2*S*,3*R*,4*E*)-3-*O*-benzoyl-4-eicosene-2-octadecanamido-1,3-diol (16)

A mixture of **15** (46 mg, 16.6 μmol), zinc powder (370 mg) and acetic acid (27 μL) in anhyd CH_2Cl_2 (2.6 mL) was stirred at rt for 4 h and then filtered through Celite. The filtrate was concentrated under diminished pressure and remaining AcOH was co-evaporated with toluene. The residue filtered through short pad of silica gel and concentrated. To a solution of the residue (34 mg) and octadecanoic acid (35 mg, 0.12 mmol) in anhyd CH_2Cl_2 (2.5 mL) was added *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (12 mg, 0.06 mmol) and stirred for 12 h at rt. The reaction mixture was diluted with anhyd CH_2Cl_2 and was successively washed with water, dried and concentrated. Purification by flash column chromatography (1:80 MeOH–CH_2Cl_2) gave **16** (37 mg, 74%). $[\alpha]_D$ +24.2 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.17–6.96 (m, 60H, 12Ph), 5.95 (d, 1H, $J_{3,4}$ 3.8 Hz, H-4^{IV}), 5.82 (m, 1H, $J_{4,5}$ 15.2 Hz, $J_{5,6} = J_{5,6'} = 7.6$ Hz, H-5 of sphingosine), 5.71 (dd, 1H, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 10.4 Hz, H-2^{IV}), 5.62 (t, 1H, $J_{2,3}$ 9.7 Hz, H-3^{I}), 5.59 (d, 1H, $J_{NH,2}$ 9.4 Hz, N*H* of sphingosine), 5.55 (dd, 1H, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.8 Hz, H-3^{IV}), 5.47 (t, 1H, $J_{3,4}$ 7.7 Hz, H-3 of sphingosine), 5.43 (dd, 1H, $J_{1,2}$ 7.5 Hz, $J_{2,3}$ 10.6 Hz, H-2^{II}), 5.40 (dd, 1H, $J_{3,4}$ 7.7 Hz, $J_{4,5}$ 15.2 Hz, H-4 of sphingosine), 5.34 (dd, 1H, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2^{I}), 5.27 (dd, 1H, $J_{2,3}$ 10.6 Hz, $J_{3,4}$ 2.4 Hz, H-3^{II}), 5.09 (d, 1H, $J_{NH,5}$ 9.2 Hz, N*H*^{V}), 5.06 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1^{IV}), 4.74 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1^{II}), 4.71 (m, 1H, $J_{3eq,4}$ 4.7 Hz, H-4^{V}), 4.51 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1^{I}), 4.46 (d, 1H, $J_{3,4}$ 2.4 Hz, H-4^{II}), 3.68 (m, 1H, H-5^{I}), 3.26 (s, 3H, OCH_3), 2.35 (dd, 1H, J_{gem} 13.2 Hz, $J_{3eq,4}$ 4.7 Hz, H-3^{V}eq), 2.03 (s, 3H, COCH_3), 1.96 (m, 2H, H-6 of sphingosine), 1.95, 1.94, 1.93, 1.86, 1.82 (6s, each 3H, 5COCH_3), 1.78 (t, 1H, J_{gem} 13.2 Hz, H-3ax^{V}), 1.40–1.04 (m, 54H, 27CH_2 of sphingosine and octadecanamide), 0.88 (t, 6H, 2CH_2CH_3 of sphingosine and octadecanamide). ^{13}C NMR ($CDCl_3$): δ 172.54, 172.23, 170.93, 170.48, 170.11, 169.95, 169.60, 167.38, 165.89, 165.79, 165.66, 165.54, 165.50, 165.44, 165.41, 165.03, 165.00, 164.95, 164.67, 164.40, 137.44 (C-5 of sphingosine), 133.61, 133.58, 133.50, 133.34, 133.31, 133.24, 133.18, 133.13, 132.79, 132.66, 130.89, 130.16, 130.11, 130.08, 129.92, 129.89, 129.77, 129.74, 129.66, 129.59, 129.49, 129.41, 129.27, 129.25, 129.18, 129.09, 129.08, 128.82, 128.80, 128.70, 128.60, 128.56, 128.51, 128.46, 128.44, 128.31, 128.19, 128.18, 124.75 (C-4 of sphingosine), 101.50 (C-1^{IV}), 100.90 (C-1^{I}), 99.14 (C-1^{II}), 96.24 (C-1^{III}), 74.30, 73.85, 73.46, 73.43, 73.21, 72.48, 72.42, 72.39, 72.01, 71.60, 70.58, 70.14, 69.99, 69.59, 68.80, 68.70, 68.55, 68.52, 67.69, 67.51, 67.22, 63.61, 61.92, 61.76, 61.71, 56.39, 52.38, 50.27, 49.49, 37.26, 36.43, 33.53, 32.27, 31.90, 29.68, 29.67, 29.64, 29.61, 29.51, 29.48, 29.45, 29.34, 29.25, 29.23, 29.16, 29.06, 28.91, 25.48, 24.76, 23.32, 23.15, 22.66, 20.81, 20.77, 20.70, 14.12. The carbonyl carbons and the quaternary carbon (C-2^{V}) of **16** could not be assigned, because these chemical shifts of the carbons were recorded by ^{1}H–^{13}C correlation spectroscopy. HRFABMS: calcd for $C_{168}H_{193}N_3O_{47}$ $[M+H]^+$: *m*/*z* 3005.2883, found 3005.2188.

3.14. *O*-(β-D-Galactopyranosyl)-(1→3)-[*O*-(5-acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2→6)]-*O*-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→4)-*O*-(β-D-galactopyranosyl)-(1→4)-*O*-(β-D-glucopyranosyl)-(1→1)-(2*S*,3*R*,4*E*)-4-eicosene-2-octadecanamido-1,3-diol (17)

To a solution of **16** (15 mg, 5.0 μmol) in anhyd MeOH (1.5 mL) was added 0.5 M NaOMe in anhyd MeOH (70.0 μL), and the mixture was stirred for 24 h at rt, and water (0.5 mL) was added. The solution was stirred for 17 h at rt, then acidified with Amberlite IR-120 (H^+) resin until pH 4 (pH-indicator paper), and the mixture was filtered. The resin was washed with MeOH, and combined filtrate and washings were concentrated. Purification by column chromatography (7:40:50 H_2O–MeOH–$CHCl_3$) of the residue on Sephadex LH-20 (8 g) gave **17** (6 mg, 76%). $[\alpha]_D$ −11.0 (*c* 0.34, 7:40:50 H_2O–MeOH–$CHCl_3$); ^{1}H NMR (1:3:3 D_2O–CD_3OD–$CDCl_3$): δ 5.70 (m, 1H, $J_{4,5}$ 14.8 Hz, H-5 of sphingosine), 5.44 (dd, 1H, $J_{3,4}$ 8.0 Hz, $J_{4,5}$ 14.8 Hz, H-4 of sphingosine), 4.63 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1^{IV}), 4.37 (d,

1H, $J_{1,2}$ 7.7 Hz, H-1^{II}), 4.35 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1^{III}), 4.31 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1^{I}), 4.12 (d, 1H, $J_{3,4}$ 2.8 Hz, H-4^{IV}), 4.08 (t, 1H, $J_{3,4}$ 8.0 Hz, H-3 of sphingosine), 4.04 (d, 1H, $J_{3,4}$ 2.5 Hz, H-4^{II}), 4.00 (dd, 1H, $J_{1,2}$ 8.5 Hz, $J_{2,3}$ 10.8 Hz, H-2^{IV}), 3.83 (d, 1H, $J_{3,4}$ 3.0 Hz, H-4^{III}), 3.75 (dd, 1H, $J_{2,3}$ 10.8 Hz, $J_{3,4}$ 2.8 Hz, H-3^{IV}), 3.64 (dd, 1H, $J_{2,3}$ 10.1 Hz, $J_{3,4}$ 2.5 Hz, H-3^{II}), 3.54 (dd, 1H, $J_{2,3}$ 9.7 Hz, $J_{1,2}$ 7.6 Hz, H-2^{III}), 3.49 (dd, 1H, $J_{2,3}$ 9.7 Hz, $J_{3,4}$ 3.0 Hz, H-3^{III}), 3.43 (dd, 1H, $J_{1,2}$ 7.7 Hz, $J_{2,3}$ 10.1 Hz, H-2^{II}), 2.77 (dd, 1H, J_{gem} 12.0 Hz, $J_{3eq,4}$ 4.2 Hz, H-3eq^{V}), 2.18 (t, 2H, $COCH_2$), 2.04, 2.02 (2 s, each 3H, $2NCOCH_3$), 2.03 (m, 2H, H-6, 6′ of sphingosine), 1.61 (t, 1H, J_{gem} 12.0 Hz, H-3ax^{V}), 1.58 (m, 2H, $COCH_2CH_2$), 1.33–1.23 (m, 54H, $27CH_2$ of sphingosine and octadecanamide), 0.89 (t, 6H, $2CH_2CH_3$ of sphingosine and octadecanamide). Signals overlapping with the signal of solvents could not be assigned. ^{13}C NMR (1:3:3 D_2O–CD_3OD–$CDCl_3$): δ 135.37 (C-5 of sphingosine), 129.96 (C-4 of sphingosine), 105.58 (C-1^{III}), 103.92 (C-1^{II}), 103.49 (C-1^{I}), 103.18 (C-1^{IV}), 80.90, 79.74, 76.80, 75.69, 75.58, 73.80, 73.75, 73.58, 73.53, 72.53, 72.19, 71.75, 71.58, 70.75, 69.64, 69.36, 68.87, 68.81, 64.32, 64.21, 63.87, 63.82, 61.60, 61.54, 61.26, 60.88, 53.66, 52.83, 52.22, 41.36, 41.06, 36.97, 33.05, 30.07, 26.58, 22.78, 23.14, 18.93, 14.27. The carbonyl carbons and the quaternary carbon (C-2^{V}) of **17** could not be assigned, because these chemical shifts of the carbons were recorded by ^{1}H–^{13}C correlation spectroscopy. HRFABMS: calcd for $C_{168}H_{193}N_3O_{47}$ $[M+H]^+$: *m*/*z* 1573.9080, found 1573.9091.

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