Synthetic Studies on Glycosphingolipids from Protostomia Phyla: Synthesis of Glycosphingolipids from the Parasite *Schistosoma mansoni*

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Synthetic access to three neutral glycosphingolipids from the parasite *Schistosoma mansoni* adult worm has been achieved. These structures differ significantly from those of other parasites and exhibit a unique structural motif termed "schisto-core" consisting of GalNAcβ1→4Glcβ1→sequence. We have synthesized glycosphingolipids, β-D-GalNAc*p*-(1→4)-β-D-Glc*p*-(1→1)Cer (1), β-D-GlcNAc*p*-(1→3)-β-D-GalNAc*p*-(1→4)-β-D-Glc*p*-(1→1)Cer (2) and β-D-Gal*p*-(1→4)-β-D-GlcNAc*p*-(1→3)-β-D-GalNAc*p*-(1→4)-β-D-Glc*p*-(1→1)Cer (3).

Key words glycosphingolipid; *Schistosoma mansoni*; schisto-core; chemical synthesis

Investigation of the functional roles of mammalian carbohydrates in biological processes have been an area of intense study in recent years.[1)] In contrast, much less time has been devoted to structures of glycosphingolipids (GSLs) from invertebrates that differ significantly from mammalian glycans. Due to these differences in the glycan structure we have been interested in the relationships between the structure and biological activity of GSLs from invertebrate species and have synthesized oligosaccharides found in various Protostomia phyla.[2—9)] In the course of our studies, we paid attention to the presence of unique GSLs found in the parasite, *Schistosoma mansoni*.[10)] Makaaru *et al.* identified a novel glycan core structure termed "schisto-core" in the GSLs isolated from *S. mansoni* adult worm and they can be extended to other unique glycan sequences (Fig. 1: **A**—**F**).[11)] Moreover, the parasite egg and the cercariae are a rich source of highly antigenic, multifucosylated GSLs.[10,12,13)] Studies on the glycobiology of parasitic helminthes can contribute to a better understanding of glycolipid-mediated host–parasite interactions including species specific- and organ-specific infections but also will provide useful information how changes in the glycan structure relate to different stages in the parasite development. Based on this background, we have initiated synthetic research efforts to prepare GSLs (**A**—**F**). In this paper we report on the synthesis of GSLs (**A**—**C**; **1**—**3**) this time. Disaccharide **1** contains the schisto-core sequence GalNAcβ1→4Glcβ1→Cer while trisaccharide **2** and tetrasaccharide **3** are elongated glycan sequences that contain a terminal schisto-core. Oligosaccharides **1**—**3** serve as molecular probes to explore glycosphingolipid-mediated interactions containing the schisto core in *S. mansoni*. The syntheses of di- and trisaccharide derivatives were conducted by stepwise synthesis of suitably protected monosaccharide-based glycosyl donors and acceptors. The tetrasaccharide derivative was conducted by block synthesis of a disaccharide acceptor and disaccharide donor.

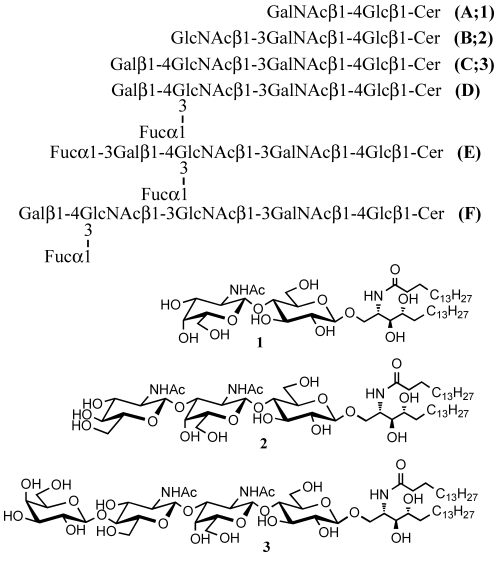
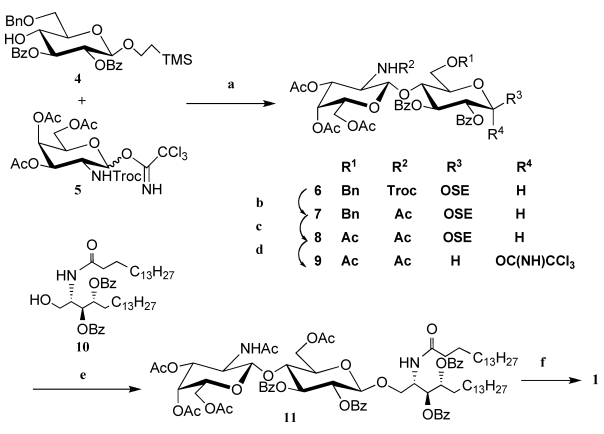


Fig. 1. Structures of Glycosphingolipids from the Parasite *S. mansoni* and Target Compounds **1**—**3**

Results and Discussion

The synthetic scheme for the synthesis of target compounds **1**—**3** are shown in Charts 1—3. Initially, the per-*O*-acylated 2-(trimethylsilyl)ethyl glycoside derivatives **8**, **16** and **27** were prepared that serve as synthetic intermediates



Reagents and conditions: (a) TMSOTf, MS 4 Å, CH_2Cl_2, 97%; (b) Zn, Ac_2O, AcOH, 85%; (c) 1), Pd–C/H_2, THF–MeOH 2), Ac_2O, Pyr., 95%; (d) 1), TFA, CH_2Cl_2 2), CCl_3CN, DBU, CH_2Cl_2, 73%; (e) TMSOTf, MS 4 Å, CH_2Cl_2, 57%; (f) MeONa, dioxane/MeOH, 67%.

Chart 1

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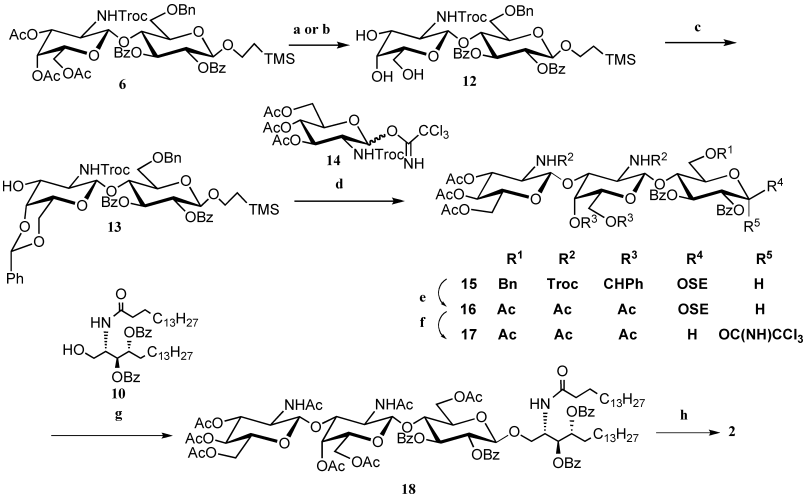
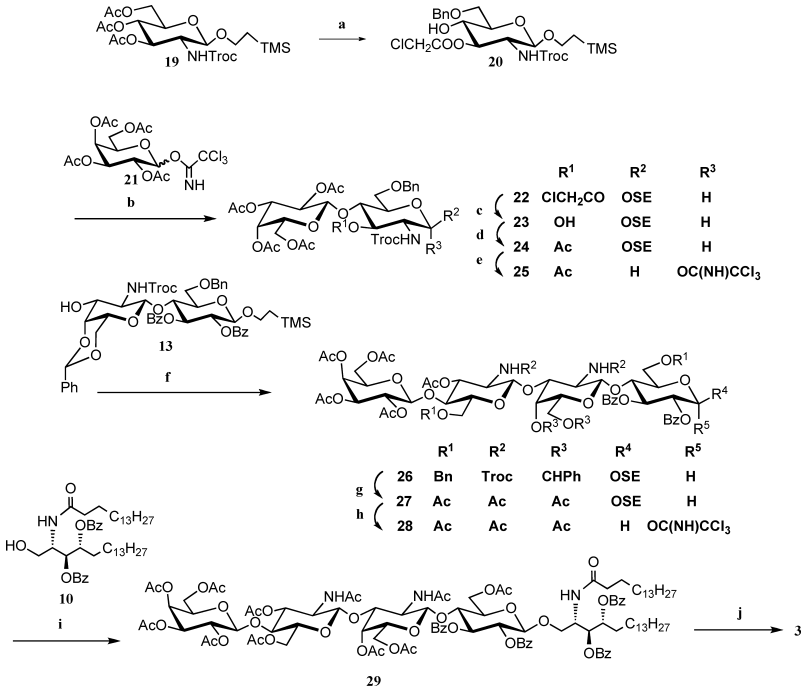


Reagents and conditions: (a) TsOH, $CHCl_3$–MeOH, 60%; (b) guanidine nitrate, NaOMe, CH_2Cl_2/MeOH, 89%; (c) BDA, $NaHSO_4 \cdot SiO_2$, CH_3CN, 89%; (d) TMSOTf, MS 4 Å, CH_2Cl_2, 85%; (e) 1), Zn, Ac_2O, AcOH 2), Pd–C/H_2, MeOH, AcOH 3) Ac_2O, Pyr., 62% (3 steps); (f) 1), TFA, CH_2Cl_2 2), CCl_3CN, DBU, CH_2Cl_2, 78%; (g) TMSOTf, MS 4 Å, CH_2Cl_2, 52%; (h) MeONa, dioxane/MeOH, 86%.

Chart 2



Reagents and conditions: (a) 1) Et_3N, MeOH 2) BDA, CSA, CH_3CN, MS 3 Å, 72% (2 steps) 3) ClAcCl, CH_2Cl_2–Pyr., 75% 4) $NaBH_3CN$, MS 3 Å, HCl–Et_2O, 86%; (b) TMSOTf, MS 4 Å, CH_2Cl_2, 86%; (c) thiourea, Pyr., EtOH, 85%; (d) Ac_2O, Pyr., 82%; (e) 1), TFA, CH_2Cl_2 2), CCl_3CN, DBU, CH_2Cl_2, 74%, (f) TMSOTf, MS 4 Å, CH_2Cl_2, 83%; (g) 1), Zn, Ac_2O, AcOH 2), Pd–C/H_2, MeOH, AcOH 3), Ac_2O, Pyr., 42% (3 steps); (h) 1), TFA, CH_2Cl_2 2), CCl_3CN, DBU, CH_2Cl_2, 61%; (i) TMSOTf, MS 4 Å, CH_2Cl_2, 34%; (j) MeONa, dioxane/MeOH, 55%.

Chart 3

for the installation of the ceramide moiety. Glycosylation of **4**[14] with **5**[15] in the presence of trimethylsilyl trifluoromethanesulfonate (TMSOTf)[16] and 4 Å molecular sieves (MS 4 Å) in CH_2Cl_2 gave the desired disaccharide (**6**) after purification in 97% yield. The anomeric proton of the GalNAc unit appeared as a doublet at δ 4.30 (d, J=8.5 Hz). Subsequently, the 2,2,2-trichloroethoxycarbonyl (Troc) group was converted to an acetamido moiety by reduction and *N*-acetylation with Zn–Ac_2O–AcOH to afford **7** in 85% yield. Removal of benzyl group from **7** by catalytic hydrogenolysis over 10% Pd/C in MeOH and *O*-acetylation provided **8**. Disaccharide derivative **6** was selected as precursor for the synthesis of trisaccharide **16**. Two methods were studied for the selective deacetylation of **6** in the presence of benzoyl- and Troc-protecting groups. Initially, we attempted to selectively saponify the acetyl groups with *p*-toluenesulfonic acid[17] in $CHCl_3$–MeOH to provide disaccharide **12** in 60% yield. However, the yield could be significantly improved by using guanidine/guanidinium nitrate reagent (G/$GHNO_3$)[18] that provided **12** in 89% yield. Benzylidenation[19] of disaccharide **12** produced acceptor **13**, which was subjected to glycosylation with donor **14**[20] using TMSOTf as promoter to afford

the desired trisaccharide **15** in 85% yield. The β-glycosidic linkage was assigned on the basis of homonuclear coupling constants (H-1 of GlcNAc, δ=4.96 ppm, $J_{H1,H2}$=8.0 Hz). Removal of the Troc-protecting group was achieved with Zn in a mixture containing Ac_2O and AcOH, followed by catalytic hydrogenation over 10% Pd–C in MeOH–AcOH and acetylation to provide trisaccharide intermediate **16**. Tetrasaccharide intermediate **26** was prepared by block synthesis of a disaccharide acceptor **13** and disaccharide donor **25**. Glycosyl acceptor **20** was obtained from **19**[21] by deacetylation, benzylidenation, chloroacetylation, and reductive ring-opening of the benzylidene acetal as previously described.[3] TMSOTf-promoted glycosylation of acceptor **20** with donor **21**[22] was carried out in the presence of 4 Å MS in CH_2Cl_2 and afforded the desired disaccharide **22** as the sole product in 86% yield. The β-glycosidic linkage in **22** was confirmed by ^{1}H-NMR spectroscopy. The anomeric proton of the galactose moiety appeared as a doublet with a homonuclear coupling constant of 7.9 Hz. Deblocking of the 3-*O*-chloroacetyl group in **22** was achieved with thiourea and the resulting alcohol **23** was converted into ester **24** by acetylation. Selective removal of the 2-(trimethylsilyl)ethyl group in **24** was achieved with trifluoroacetic acid in CH_2Cl_2, and treatment with CCl_3CN in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)[23] to provide the corresponding α-trichloroacetimidate **25** in 74% yield. Tetrasaccharide derivative **26** was synthesized by coupling of donor **25** with disaccharide acceptor **13** in 83% yield. Deblocking of **26** was achieved using the same conditions as described for trisaccharide **16** produced the per-*O*-acylated tetrasaccharide derivative **27**.

Next, for the selective removal of the 2-(trimethylsilyl)ethyl group, the fully acylated oligosaccharides **8**, **16** and **27** were converted to the glycosyl imidate **9**, **17** and **28**. TMSOTf-promoted glycosylation of phytoceramide acceptor **10**[24] with glycosyl donors **9**, **17** and **28** afforded the desired β-glycosides **11** (57%), **18** (52%) and **29** (34%) yields, respectively. Finally, standard deacetylation and purification by column chromatography on Sephadex LH-20 furnished glycolipids **1**—**3**.

Conclusion

In summary, a systematic and integrated approach for the synthesis of three glycosphingolipids **1**—**3** found in the parasite, *Schistosoma mansoni* has been accomplished. The synthetic strategy described may also find use for conjugation of the glycan portion of *S. mansoni* to other non-lipid-based carrier molecules. Biological testing for schistosomasis using GSLs **1**—**3** is currently in progress and results will be reported in detail elsewhere. It is expected that the prepared glycosphingolipids will find use in future studies designed to reveal the relationships between the structure and biological activity for specific antibody detection in patients with schistosomasis.

Experimental

General Methods Optical rotations were measured with a Jasco P-1020 digital polarimeter. ^{1}H- and ^{13}C-NMR spectra were recorded with a JMN A500 FT NMR spectrometer and a JEOL JNM-ECP600 with Me_4Si as the internal standard for solutions in $CDCl_3$. Matrix assisted laser desorption/ionization-time of flight (MALDI-TOF)-MS was recorded on an Applied Biosystems Voyager RP mass spectrometer. High-resolution mass spectra were recorded on a JEOL JMS-700 under FAB conditions. TLC was performed on Silica Gel 60 F254 (E. Merck) with detection by quenching of UV fluorescence and by charring with 10% H_2SO_4. Column chromatography was carried out on Silica Gel 60 (E. Merck). 2-(Trimethylsilyl)ethyl 2,3-di-*O*-benzoyl-6-*O*-benzyl-β-D-glucopyranoside (**4**),[14] 3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-1-*O*-D-galactopyranosyl trichloroacetimidate (**5**),[15] 3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-1-*O*-D-glucopyranosyl trichloroacetimidate (**14**),[19] 2-(trimethylsilyl)ethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (**19**)[20] and 2,3,4,6-tetra-*O*-acetyl-1-*O*-D-galactopyranosyl trichloroacetimidate (**21**)[21] were prepared as reported. Benzoylceramide **10** was prepared from phytosphingosine, which was purchased from Degussa (The Netherlands) by the conventional four-step procedure.[24]

2-(Trimethylsilyl)ethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzoyl-6-*O*-benzyl-β-D-glucopyranoside (6) A solution of **4** (1.77 g, 3.06 mmol) and **5** (2.85 g, 4.57 mmol) containing activated 4 Å MS (5.0 g) in dry CH_2Cl_2 (25.0 ml) was stirred under an atmosphere of argon for 18 h at room temperature, then cooled to −40 °C. TMSOTf (62.3 μl, 0.34 mmol) was added, and the mixture was stirred for 3 h at −40 °C, then neutralized with Et_3N. The solids were filtrated off and washed with $CHCl_3$. The combined filtrate and washings were successively washed with brine, dried ($MgSO_4$) and concentrated. The product was purified by silica gel column chromatography using 2 : 1 hexane–ethyl acetate as eluent to give **6** as an amorphous powder (3.10 g, 97%). $[\alpha]_D^{25}$ −16.2 (c=1.2, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.01—7.40 (15H, m, 3Ph), 5.64 (1H, t, $J_{2,3}$=$J_{3,4}$=9.8 Hz, H-3 of Glc), 5.46 (1H, dd, $J_{1,2}$=7.9 Hz, H-2 of Glc), 5.10 (1H, d, $J_{3,4}$=3.7 Hz, H-4 of GalN), 4.94, 4.49 (2H, each d, benzylmethylene), 4.78—4.67 (4H, m, H-1 of Glc, H-3 of GalN, C$\underline{H}_2$CCl$_3$), 4.30 (1H, d, $J_{1,2}$=8.5 Hz, H-1 of GalN), 4.21 (1H, t, $J_{4,5}$=9.8 Hz, H-4 of Glc), 4.11—4.06 (2H, m, N$\underline{H}$, C$\underline{H}_2$CH$_2$Si(CH$_3$)$_3$), 3.86 (1H, dd, H-6a of Glc), 3.75 (1H, d, H-6b of Glc), 3.66—3.61 (3H, m, H-5 of Glc, H-2 of GalN, C$\underline{H}_2$CH$_2$Si(CH$_3$)$_3$), 3.50 (1H, t, $J_{5,6}$=8.9 Hz, H-5 of GalN), 3.54 (2H, d, H-6 of GalN), −0.01 (9H, s, Si(C$\underline{H}_3$)$_3$). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 170.0×2, 165.3, 165.1, 153.7, 137.5, 132.9×3, 130.1, 129.7×3, 129.6×3, 129.2×3, 129.0, 128.7×3, 128.2, 128.1×3, 100.7 (C-1 of Glc), 100.2 (C-1 of GalN), 95.6, 74.9, 74.4, 74.3, 73.6, 73.2, 71.8, 70.1, 69.9, 67.4, 67.2, 65.9, 60.4, 52.3, 20.6, 20.44, 20.36, 17.9, 14.1, −1.52. MALDI-TOF-MS: Calcd for $C_{47}H_{56}Cl_3NO_{17}SiNa$: ([M+Na]$^+$) m/z 1062.2. Found 1062.3. HR-FAB-MS: Calcd for $C_{47}H_{56}Cl_3NO_{17}SiNa$: ([M+Na]$^+$) m/z 1062.2280. Found 1062.2239.

2-(Trimethylsilyl)ethyl 2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzoyl-6-*O*-benzyl-β-D-glucopyranoside (7) To a solution of **6** (1.0 g, 0.18 mol) in Ac_2O (10 ml) and AcOH (5 ml) was added zinc powder (400 mg). The reaction mixture was stirred for 18 h at 40 °C. After completion of the reaction, the mixture was filtered and extracted with $CHCl_3$. The solution was washed with water, dried ($MgSO_4$), and concentrated. The filtrate was concentrated and purified by silica gel column chromatography using 3 : 1 toluene–acetone as the eluent to give **7** as syrup (737 mg, 85%). $[\alpha]_D^{25}$ −1.0 (c=9.9, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.96—7.33 (15H, m, 3 Ph), 5.60 (1H, t, $J_{2,3}$=$J_{3,4}$=9.2 Hz, H-3 of Glc), 5.39 (1H, dd, $J_{1,2}$=7.9 Hz, H-2 of Glc), 5.06 (1H, d, $J_{3,4}$=3.7 Hz, H-4 of GalN), 4.92 (1H, dd, $J_{2,3}$=10.0 Hz, H-3 of GalN), 4.85—4.83 (2H, m, NH, benzylmethylene), 4.67 (1H, d, H-1 of Glc), 4.55 (1H, d, $J_{1,2}$=7.9 Hz, H-1 of GalN), 4.51 (1H, d, benzylmethylene), 4.17 (1H, t, $J_{4,5}$=9.2 Hz, H-4 of Glc), 4.04—3.98 (1H, m, C$\underline{H}_2$CH$_2$Si(CH$_3$)$_3$), 3.77—3.66 (4H, m, H-5, 6 of Glc, H-2 of GalN), 3.60—3.55 (1H, m, C$\underline{H}_2$CH$_2$Si(CH$_3$)$_3$), 3.48 (1H, t, $J_{5,6}$=7.3 Hz, H-5 of GalN), 3.40—3.32 (2H, m, H-6 of GalN), 0.95—0.82 (m, 2H, CH$_2$C$\underline{H}_2$Si(CH$_3$)$_3$), −0.07 (9H, s, Si(C$\underline{H}_3$)$_3$). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 170.1, 170.0, 169.8, 165.3, 165.1, 137.9, 132.9, 129.9, 129.7×3, 129.6×3, 128.7×2, 128.6×2, 128.3×3, 128.2×2, 128.1×3, 100.5 (C-1 of Glc), 99.9 (C-1 of GalN), 74.8, 74.5, 73.6, 73.3, 71.9, 70.2, 69.8, 67.5, 67.4, 66.0, 60.5, 51.4, 23.2, 20.6, 20.5, 20.4, 17.9, −1.55. MALDI-TOF-MS: Calcd for $C_{46}H_{57}NO_{16}SiNa$, ([M+Na]$^+$) m/z 930. Found 930. HR-FAB-MS: Calcd for $C_{46}H_{57}NO_{16}SiNa$, ([M+Na]$^+$) m/z 930.3525. Found 930.3539.

2-(Trimethylsilyl)ethyl 2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranosyl-(1→4)-6-*O*-acetyl-2,3-di-*O*-benzoyl-β-D-glucopyranoside (8) To a solution of **7** (340 mg, 0.37 mmol) in MeOH (4.0 ml) was hydrogenolysed under hydrogen in the presence of 10% Pd/C (400 mg) for 18 h at room temperature, then filtered and concentrated. The residue was acetylated with Ac_2O (3.0 ml) in pyridine (4.5 ml). The reaction mixture was poured into ice H_2O and extracted with $CHCl_3$. The extract was washed sequentially with 5% HCl, aq $NaHCO_3$, and brine, dried ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography using 2 : 1 toluene–acetone as eluent to give **8** as syrup (305 mg, 95%). $[\alpha]_D^{25}$ +16.3 (c=7.5, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.04—7.36 (15H,

m, 3Ph), 6.01 (1H, d, NH), 5.74 (1H, t, $J_{2,3}$=$J_{3,4}$=9.2 Hz, H-3 of Glc), 5.43 (1H, t, $J_{1,2}$=7.9 Hz, H-2 of Glc), 5.24—5.21 (2H, m, H-3, 4 of GalN), 4.83 (1H, d, $J_{1,2}$=7.9 Hz, H-1 of GalN), 4.78 (1H, d, H-1 of Glc), 4.57 (1H, br d, H-6a of Glc), 4.36 (1H, m, H-6b of Glc), 4.09—4.03 (2H, m, H-4 of Glc, $CH_2CH_2Si(CH_3)_3$), 3.95—3.89 (2H, m, H-5 of Glc, H-2 of GalN), 3.69—3.64 (2H, m, H-5 of GalN, $CH_2CH_2Si(CH_3)_3$), 3.51—3.42 (2H, m, H-6 of GalN), 1.02—0.88 (2H, m, $CH_2CH_2Si(CH_3)_3$), −0.01 (9H, s, $Si(CH_3)_3$). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 171.0, 170.5, 170.2, 170.0, 169.8, 165.3, 165.1, 133.0, 129.7×3, 129.6×3, 129.4, 128.3×2, 128.2×3, 100.4 (C-1 of Glc), 100.3 (C-1 of GalN), 76.1, 73.1, 72.9, 71.9, 70.3, 69.7, 67.5, 66.0, 62.4, 60.3, 51.8, 23.1, 20.9, 20.5×2, 20.4, 17.8, −1.59. MALDI-TOF-MS: Calcd for $C_{41}H_{53}NO_{17}SiNa$ ([M+Na]$^+$) m/z 882.3. Found 882.8. HR-FAB-MS: Calcd for $C_{41}H_{53}NO_{17}SiNa$ ([M+Na]$^+$) m/z 882.2980. Found 882.2968.

2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranosyl-(1→4)-6-*O*-acetyl-2,3-di-benzoyl-1-*O*-α-D-glucopyranosyl Trichloroacetimidate (9) To a solution of **8** (300 mg, 0.35 mmol) in CH_2Cl_2 (3.0 ml), cooled to 0 °C was added CF_3CO_2H (1.5 ml), and the mixture was stirred for 3 h at room temperature and concentrated. EtOAc and toluene (1 : 2) were added and evaporated to give the reducing sugar. To a solution of the residue in CH_2Cl_2 (3.0 ml) cooled at 0 °C were added DBU (53.1 μl, 0.35 mmol) and CCl_3CN (0.36 ml, 3.49 mmol). The reaction mixture was stirred for 6 h at room temperature. After completion of the reaction, the mixture was concentrated. The residue was purified by silica gel column chromatography using 15 : 1 chloroform–methanol as eluent to give **9** as an amorphous powder (230 mg, 73%). $[\alpha]_D^{25}$ +9.5 (c=1.0, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.61 (1H, s, C(NH)CCl_3), 8.54—8.13 (10H, m, 2Ph), 6.71 (1H, d, $J_{1,2}$=3.7 Hz, H-1 of Glc), 6.07 (1H, t, $J_{2,3}$=$J_{3,4}$=9.2 Hz, H-3 of Glc), 5.88 (1H, d, NH), 5.47 (1H, dd, H-2 of Glc), 5.27 (1H, dd, $J_{2,3}$=11.0 Hz, $J_{3,4}$=3.1 Hz, H-3 of GalN), 5.16 (1H, d, H-4 of GalN), 4.97 (1H, d, $J_{1,2}$=8.5 Hz, H-1 of GalN), 4.52 (1H, br d, H-6a of Glc), 4.35—4.28 (1H, m, H-5, 6b of Glc), 4.15—4.11 (1H, t, $J_{4,5}$=9.8 Hz, H-4 of Glc), 3.78—3.72 (1H, dd, H-2 of GalN), 3.60 (1H, t, $J_{5,6}$=7.3 Hz, H-5 of GalN), 3.52—3.41 (2H, m, H-6 of GalN). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 170.8, 170.6, 170.1, 170.0, 169.8, 165.4, 165.2, 160.5, 133.5, 133.4, 129.9×2, 129.8×2, 129.6, 129.51, 129.45×2, 128.7, 128.4, 128.3, 100.1 (C-1 of GalN), 92.9 (C-1 of Glc), 77.2, 75.5, 71.2, 70.5, 70.4, 70.1, 69.4, 66.0, 61.9, 60.2, 52.3, 23.1, 20.8, 20.5, 20.4. MALDI-TOF-MS: Calcd for $C_{38}H_{41}Cl_3N_2O_{17}Na$: ([M+Na]$^+$) m/z 925.1. Found 925.8.

2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranosyl-(1→4)-6-*O*-acetyl-2,3-di-*O*-benzoyl-β-D-glucopyranosyl-(1→1)-(2*S*,3*S*,4*R*)-3,4-di-*O*-benzoyl-2-palmitoylamidooctadecane-1,3,4-triol (11) A solution of **9** (37.5 mg, 44.2 mmol) and (2*S*,3*S*,4*R*)-3,4-di-*O*-benzoyl-2-palmitoylamidooctadecane-1,3,4-triol **10** (47.1 mg, 66.2 mmol) containing activated 4 Å MS (200 mg) in dry CH_2Cl_2 (0.4 ml) was stirred under an atmosphere of argon for 18 h at room temperature, then cooled to 0 °C. TMSOTf (97 μl, 35.4 μmol) was added, and the mixture was stirred for 3 h at room temperature, then neutralized with Et_3N. The solids were filtrated off and washed with $CHCl_3$. The combined filtrate and washings were successively washed with brine, dried ($MgSO_4$) and concentrated. The product was purified by flash silica gel column chromatography using 100 : 1 chloroform–methanol as eluent to give **11** as an amorphous powder (35.6 mg, 57%). $[\alpha]_D^{25}$ +23.5 (c=1.0, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.06—7.36 (20H, m, 4 Ph), 6.01 (1H, d, ceramide-NH), 5.69—5.66 (1H, m, NH of GalN), 5.60 (1H, t, $J_{2,3}$=$J_{3,4}$=9.1 Hz, H-3 of Glc), 5.34—5.32 (1H, m, ceramide-H-4), 5.28 (1H, t, $J_{1,2}$=8.2 Hz, H-2 of Glc), 5.11 (1H, d, $J_{3,4}$=3.3 Hz, H-4 of GalN), 5.06 (1H, dd, $J_{2,3}$=11.0 Hz, H-3 of GalN), 4.64 (1H, d, H-1 of Glc), 4.61 (1H, d, $J_{1,2}$=7.1 Hz, H-1 of GalN), 4.60—4.57 (1H, m, ceramide-H-2), 4.22—4.20 (1H, m, H-6a of Glc), 4.01—3.95 (3H, m, H-4, 6b of Glc, ceramide-H-1a), 3.86 (1H, dd, H-2 of GalN), 3.73—3.71 (1H, m, H-5 of Glc), 3.61 (1H, dd, ceramide-H-1b), 3.52 (1H, t, $J_{5,6}$=7.3 Hz, H-5 of GalN), 3.44 (1H, dd, $J_{6a,6b}$=7.8 Hz, H-6a of GalN), 3.34 (1H, dd, H-6b of GalN), 1.95—0.86 (62H, m, alkyl). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 173.3, 172.9, 170.9, 170.5, 170.3, 170.1, 169.9, 166.3, 165.3, 165.2, 165.1, 163.5, 133.8, 133.43, 133.39, 133.2, 133.0, 130.1, 129.9, 129.8, 129.73, 129.66, 129.6, 129.5, 128.9, 128.7, 128.5, 128.3, 100.8 (C-1 of Glc), 99.9 (C-1 of GalN), 91.9, 76.0, 73.9, 73.7, 72.9, 72.7, 72.2, 72.1, 70.4, 69.9, 67.0, 65.9, 62.5, 61.6, 60.3, 51.4, 49.9, 47.8, 36.8, 36.4, 31.9, 29.69, 29.66, 29.6, 29.5, 29.3, 29.2, 25.8, 25.7, 25.5, 25.4, 23.1, 22.7, 20.7, 20.6, 20.5, 14.1. MALDI-TOF-MS: Calcd for $C_{84}H_{116}N_2O_{22}Na$: ([M+Na]$^+$) m/z 1528. Found 1528. HR-FAB-MS: Calcd for $C_{84}H_{116}N_2O_{22}Na$: ([M+Na]$^+$) m/z 1527.7917. Found 1527.7946.

2-Acetamido-2-deoxy-β-D-galactopyranosyl-(1→4)-β-D-glucopyranosyl-(1→1)-(2*S*,3*S*,4*R*)-2-palmitoylamidooctadecane-1,3,4-triol (1) To a solution of **10** (35.6 mg) in MeOH (1.5 ml) was added dioxane (1.5 ml) and NaOMe (15.0 mg) at 45 °C. The mixture was stirred for 5 h and then neutralized with Amberlite IR 120 [H$^+$]. The mixture was filtered and concentrated. The product was purified by Sephadex LH-20 column chromatography in MeOH to give **1** as white solid (14.5 mg, 67%). $[\alpha]_D^{25}$ −26.4 (c=0.4, 1 : 1 $CHCl_3$-MeOH). mp 128—129 °C. ^{1}H-NMR (600 MHz, 1 : 1 $CDCl_3$-CD_3OD) δ: 4.48 (1H, d, J=8.0 Hz, H-1 of GalN), 4.30 (1H, d, J=7.7 Hz, H-1 of Glc). MALDI-TOF-MS: Calcd for $C_{48}H_{92}N_2O_{14}Na$: ([M+Na]$^+$) m/z 944. Found 944. HR-FAB-MS: Calcd for $C_{48}H_{93}N_2O_{14}$: ([M+H]$^+$) m/z 921.6446. Found 921.6465.

2-(Trimethylsilyl)ethyl 2-Deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzoyl-6-*O*-benzyl-β-D-glucopyranoside (12) (a) To a solution of **6** (1.75 g, 1.68 mmol) was added TsOH (0.97 g, 3.36 mmol, 2.0 eq) in $CHCl_3$/MeOH (18.0 ml, 9 : 1). The reaction mixture was stirred for 48 h at room temperature then neutralized with Et_3N. The filtrate was washed with brine, dried ($MgSO_4$), and concentrated. The filtrate was concentrated and purified by silica gel column chromatography using 20 : 1 chloroform–methanol as the eluent to give **12** as syrup (0.93 g, 60.4%).

(b) To a solution of **6** (1.08 g, 1.04 mmol) was added guanidinium nitrate (622 mg) and MeONa (54.2 mg) in MeOH/$CHCl_3$ (50 ml, 9 : 1). The reaction mixture was stirred for 1 h at room temperature then neutralized with Amberlite IR 120 [H$^+$]. The filtrate was washed with brine, dried ($MgSO_4$), and concentrated. The filtrate was concentrated and purified by silica gel column chromatography using 20 : 1 chloroform–methanol as the eluent to give **12** as syrup (0.85 g, 89%). $[\alpha]_D^{25}$ +13.6 (c=1.5, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.93—7.32 (15H, m, 3Ph), 5.57 (1H, t, $J_{2,3}$=$J_{3,4}$=9.2 Hz, H-3 of Glc), 5.39 (1H, t, $J_{1,2}$=7.9 Hz, H-2 of Glc), 4.87 (1H, d, NH), 4.80, 4.49 (2H, each d, 2 benzylmethylene), 4.72 (1H, d, CH_2CCl_3), 4.65 (1H, d, H-1 of Glc), 4.60 (1H, d, CH_2CCl_3), 4.21 (1H, d, $J_{1,2}$=7.9 Hz, H-1 of GalN), 4.07 (1H, t, $J_{4,5}$=10.0 Hz, H-4 of Glc), 4.03—3.98 (2H, m, $CH_2CH_2Si(CH_3)_3$), 3.85 (1H, br d, H-6a of Glc), 3.77—3.69 (2H, m, H-6b of Glc, H-4 of GalN), 3.65 (1H, br d, H-5 of Glc), 3.59—3.54 (2H, m, $CH_2CH_2Si(CH_3)_3$), 3.49 (1H, dd, $J_{2,3}$=11.0 Hz, H-2 of GalN), 3.28, (1H, br s, H-3 of GalN), 3.12, (2H, br s, H-5 of GalN, OH), 3.02 (2H, br s, H-6a of GalN, OH), 2.93 (2H, br s, H-6 of GalNb, OH), 0.94—0.81 (2H, m, $CH_2CH_2Si(CH_3)_3$), −0.07 (9H, s, $Si(CH_3)_3$). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 166.3, 165.2, 155.2, 137.6×3, 133.4, 133.0×2, 129.7, 129.5×3, 129.0, 128.8×3, 128.5, 128.2×3, 100.9 (C-1 of GalN), 100.3 (C-1 of Glc), 95.6, 76.6, 74.6, 74.5, 74.4, 74.0, 73.6, 71.9×2, 68.2, 68.0, 67.4, 61.1, 55.1, 17.9×3, −1.51. MALDI-TOF-MS: Calcd for $C_{41}H_{50}Cl_3NO_{14}SiNa$: ([M+Na]$^+$) m/z 936.2. Found 937.3. HR-FAB-MS: Calcd for $C_{41}H_{50}Cl_3NO_{14}SiNa$: ([M+Na]$^+$) m/z 936.1964. Found 936.1919.

2-(Trimethylsilyl)ethyl 4,6-*O*-Benzylidene-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzoyl-6-*O*-benzyl-β-D-glucopyranoside (13) To a solution of **12** (756 mg, 0.83 mmol) in CH_3CN (10 ml) was added $NaHSO_4 \cdot SiO_2$ (1.5 g) and benzaldehyde dimethyl acetal (BDA) (0.25 ml, 1.66 mmol, 2.0 eq). The reaction mixture was stirred for 2 h at room temperature, then neutralized with Et_3N. The solids were filtrated off and the filtrated was concentrated. The product was purified by silica gel column chromatography using 10 : 1 toluene–acetone as eluent to give **13** as white solid (734 mg, 89%). $[\alpha]_D^{25}$ −13.0 (c=7.7, $CHCl_3$). mp 164—165 °C ^{1}H-NMR ($CDCl_3$) δ: 8.03—7.25 (20H, m, 4Ph), 5.75 (1H, t, $J_{2,3}$=$J_{3,4}$=8.8 Hz, H-3 of Glc), 5.41 (1H, dd, $J_{1,2}$=7.9 Hz, H-2 of Glc), 5.33 (1H, s, PhCH), 5.14 (1H, d, NH), 4.87 (1H, d, benzylmethylene), 4.78—4.66 (3H, m, H-1 of Glc, CH_2CCl_3, benzylmethylene), 4.46 (1H, d, $J_{1,2}$=7.9 Hz, H-1 of GalN), 4.21 (1H, t, $J_{4,5}$=8.8 Hz, H-4 of Glc), 4.10—4.03 (2H, m, H-6a of Glc, $CH_2CH_2Si(CH_3)_3$), 3.94 (1H, d, $J_{3,4}$=1.8 Hz, H-4 of GalN), 3.86 (1H, dd, H-6b of Glc), 3.77—3.75 (1H, m, H-5 of Glc), 3.74—3.50 (4H, m, H-2, 3, 6a of GalN, $CH_2CH_2Si(CH_3)_3$), 3.46 (1H, d, H-6b of GalN), 2.95 (1H, s, H-5 of GalN), 1.01—0.88 (1H, m, $CH_2CH_2Si(CH_3)_3$), −0.01 (9H, s, $Si(CH_3)_3$) . ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 165.3, 154.8, 137.9, 137.5, 132.9, 132.7, 129.8×2, 129.7×2, 129.6, 129.0×2, 128.6×3, 128.5×2, 128.2×2, 128.1×2, 128.0×2, 126.5×2, 101.0 (C-1 of GalN), 100.5 (C-1), 95.5, 74.6×2, 74.5, 73.7, 73.6, 72.4, 71.0, 68.3, 68.0, 67.4, 66.4, 55.6, 17.9, −1.49. MALDI-TOF-MS: Calcd for $C_{48}H_{54}Cl_3NO_{14}SiNa$: ([M+Na]$^+$) m/z 1024. Found 1024. HR-FAB-MS: Calcd for $C_{48}H_{54}Cl_3NO_{14}SiNa$: ([M+Na]$^+$) m/z 1024.2277. Found 1024.2218.

2-(Trimethylsilyl)ethyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzoyl-6-*O*-benzyl-β-D-glucopyranoside (15) Compound **15** was prepared from **13** (1.42 g, 1.42 mmol) and **14** (1.30 g, 2.13 mmol) by the same method described for preparation of **6**. The product was purified by silica chromatography using 3 : 2 hexane–ethyl acetate as

eluent to give **15** as an amorphous powder (1.75 g, 85%). $[\alpha]_D^{25}$ +35.7 (c=4.4, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 4.96 (1H, d, $J_{1,2}$=8.0 Hz, H-1 of GlcN), 4.80 (1H, d, $J_{1,2}$=9.3 Hz, H-1 of GalN), 4.72 (1H, d, $J_{1,2}$=9.3 Hz, H-1 of Glc). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 170.4, 170.2, 169.3, 165.4, 165.2, 153.8, 138.3, 137.5, 134.4, 132.84, 132.76, 129.7×2, 129.6×2, 128.94, 128.87, 128.6, 128.5×2, 128.4, 128.1×2, 128.0×2, 127.9, 127.8, 127.7, 126.3, 100.7, 100.4 (C-1 of Glc), 100.4 (C-1 of GalN), 99.1 (C-1 of GlcN), 95.5, 95.4, 75.5, 75.10, 74.99, 74.8, 74.4, 74.2, 73.8, 73.2, 72.4, 71.8, 68.4, 68.3, 67.3, 66.2, 61.9, 56.1, 53.8, 20.7, 20.52, 20.48, 17.9×2, −1.68. MALDI-TOF-MS: Calcd for $C_{63}H_{72}Cl_6N_2O_{23}SiNa$: ([M+Na]$^+$) m/z 1485.2. Found 1486.3.

2-(Trimethylsilyl)ethyl 2-Acetamido-*O*-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-gluctopyranosyl-(1→3)-2-acetamide-4,6-di-*O*-acetyl-2-deoxy-β-D-galactopyranosyl-(1→4)-6-*O*-acetyl-2,3-di-*O*-benzoyl-β-D-glucopyranoside (16) To a solution of **15** (1.75 g, 0.13 mmol) in Ac_2O (10.0 ml) and AcOH (20.0 ml) was added zinc powder (3.0 g). The reaction mixture was stirred for 18 h at 45 °C. After completion of the reaction, the mixture was filtered and the filtrate was diluted with $CHCl_3$, washed with water, dried ($MgSO_4$) and concentrated to give the intermediate. To a solution of the residue in MeOH (10.0 ml) was added AcOH (5.0 ml) and hydrogenolysed under hydrogen in the presence of 10% Pd/C (500 mg) for 18 h at room temperature, then filtered and concentrated. The residue was acetylated with acetic anhydride (20.0 ml) in pyridine (30.0 ml). The reaction mixture was added toluene and concentrated. The residue was purified by silica gel column chromatography using 3 : 1 toluene–acetone as eluent to give **16** as syrup (855 mg, 62%). $[\alpha]_D^{25}$ +31.3 (c=2.5, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 4.91 (1H, d, $J_{1,2}$=8.2 Hz, H-1 of GlcN), 4.88 (1H, d, $J_{1,2}$=8.2 Hz, H-1 of GalN), 4.79 (1H, d, $J_{1,2}$=7.7 Hz, H-1 of Glc). ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 100.4 (C-1 of Glc), 100.3 (C-1 of GalN), 99.2 (C-1 of GlcN). MALDI-TOF-MS: Calcd for $C_{53}H_{70}N_2O_{24}SiNa$: ([M+Na]$^+$) m/z 1169.4. Found 1170.2. HR-FAB-MS: Calcd for $C_{53}H_{70}N_2O_{24}SiNa$: ([M+Na]$^+$) m/z 1169.3986. Found 1169.3945.

2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-gluctopyranosyl-(1→3)-2-acetamido-4,6-di-*O*-acetyl-2-deoxy-β-D-galactopyranosyl-(1→4)-6-*O*-acetyl-2,3-di-*O*-benzoyl-1-*O*-α-D-glucopyranosyl Trichloroacetimidate (17) Compound **17** was prepared from **16** (130 mg, 0.11 mmol) by the same method described for preparation of **9**. The product was purified by silica chromatography using 40 : 1 chloroform–methanol as eluent to give **17** (105 mg, 78%). $[\alpha]_D^{25}$ +42.6 (c=0.5, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.62 (1H, s, OC(N<u>H</u>)CCl_3), 7.99—7.33 (10H, m, 2Ph), 6.70 (1H, d, $J_{1,2}$=3.6 Hz, H-1 of Glc), 6.55 (1H, d, N<u>H</u> of GalN), 6.35 (1H, d, N<u>H</u> of GlcN), 5.98 (1H, t, $J_{2,3}$=$J_{3,4}$=9.9 Hz, H-3 of Glc), 5.48 (1H, dd, H-2 of Glc), 5.25 (1H, d, $J_{3,4}$=9.7 Hz, H-3 of GlcN), 5.20 (1H, d, $J_{3,4}$=3.2 Hz, H-4 of GalN), 5.00 (1H, t, $J_{4,5}$=9.7 Hz, H-4 of GlcN), 4.96 (1H, d, $J_{1,2}$=8.2 Hz, H-1 of GalN) , 4.80 (1H, d, $J_{1,2}$=8.2 Hz, H-1 of GlcN), 4.55 (1H, d, H-6a), 4.39 (1H, dd, $J_{2,3}$=7.2 Hz, H-3 of GalN), 4.30—4.27 (1H, m, H-5 of Glc), 4.19—4.05 (4H, m, H-4, 6b of Glc, H-6 of GlcN), 3.67—3.53 (4H, m, H-6a of Glc, H-5 of GalN, H-2, 5 of GlcN), 3.34—3.31 (2H, m, H-6b of Glc, H-2 of GalN). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 171.5, 170.7, 170.6, 170.2, 169.4, 169.3, 165.4, 165.3, 160.5, 133.5, 133.3, 129.8×3, 129.6×3, 128.4×2, 128.33×2, 128.26×2, 100.4 (C-1 of GlcN), 98.9 (C-1 of GalN), 93.0 (C-1 of Glc), 90.6, 74.5, 74.4, 72.1, 71.5, 71.3, 71.0, 70.3, 70.1, 68.3, 68.1, 62.0, 61.5, 61.4, 55.0, 54.5, 23.4, 23.2, 20.8, 20.64, 20.59, 20.55×2, 20.5×2, 20.4. MALDI-TOF-MS: Calcd for $C_{50}H_{58}Cl_3N_3O_{24}Na$: ([M+Na]$^+$) m/z 1212.2. Found 1212.7.

2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-gluctopyranosyl-(1→3)-2-acetamido-4,6-di-*O*-acetyl-2-deoxy-β-D-galactopyranosyl-(1→4)-6-*O*-acetyl-2,3-di-*O*-benzoyl-β-D-glucopyranosyl-(1→1)-(2*S*,3*S*,4*R*)-3,4-di-*O*-benzoyl-2-palmitoylamidooctadecane-1,3,4-triol (18) Compound **18** was prepared from **17** (110 mg, 93.0 mmol) and **10** (106 mg, 140 μmol) by the same method described for preparation of **11**. The product was purified by silica chromatography using 60 : 1 chloroform–methanol as eluent to give **18** as syrup (85.8 mg, 52%). $[\alpha]_D^{25}$ +28.9 (c=1.0, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 5.00 (1H, d, $J_{1,2}$=8.5 Hz, H-1 of GlcN), 4.77 (1H, d, $J_{1,2}$=8.3 Hz, H-1 of GalN), 4.56 (1H, d, $J_{1,2}$=7.7 Hz, H-1 of Glc). ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 100.4 (C-1 of Glc), 100.2 (C-1 of GalN), 97.7 (C-1 of GlcN). MALDI-TOF-MS: Calcd for $C_{96}H_{133}N_3O_{29}Na$: ([M+Na]$^+$) m/z 1815. Found 1815.

2-Acetamido-2-deoxy-β-D-gluctopyranosyl-(1→3)-2-acetamido-2-deoxy-β-D-galactopyranosyl-(1→4)-β-D-glucopyranosyl-(1→1)-(2*S*,3*S*,4*R*)-2-palmitoylamidooctadecane-1,3,4-triol (2) Compound **2** was prepared from **18** (38.2 mg) by the same method described for preparation of **1**. The product was purified by Sephadex LH-20 column chromatography in MeOH to give **2** as white solid 20.6 mg (86%). $[\alpha]_D^{25}$ −8.4 (c=0.16, 1 : 1 $CHCl_3$–CD_3OH). mp 145—146 °C. ^{1}H-NMR (600 MHz, 1 : 1 $CDCl_3$–CD_3OD) δ: 4.89 (1H, d, $J_{1,2}$=8.5 Hz, H-1 of GlcN), 4.60 (1H, d, $J_{1,2}$=8.0 Hz, H-1 of GalN), 4.57 (1H, d, $J_{1,2}$=7.7 Hz, H-1 of Glc). MALDI-TOF-MS: Calcd for $C_{56}H_{105}N_3O_{19}Na$: ([M+Na]$^+$) m/z 1146.7. Found 1146.1. HR-FAB-MS: Calcd for $C_{56}H_{105}N_3O_{19}Na$: ([M+Na]$^+$) m/z 1146.7240. Found 1146.7185.

2-(Trimethylsilyl)ethyl 6-*O*-Benzyl-3-*O*-chloroacetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (20) To a solution of compound **19** (3.0 g, 5.16 mmol) in MeOH (30.0 ml) was added Et_3N (6.0 ml). The reaction mixture was stirred for 18 h at room temperature and concentrated to give the reducing sugar. To a solution of the residue in CH_3CN (16.0 ml) was added Camphor-10-sulfonic acid (CSA) (369 mg, 1.55 mmol, 0.3 eq), 3 Å MS (2.5 g) and BDA (1.6 ml, 10.3 mmol, 2.0 eq). The reaction mixture was stirred under an atmosphere of argon for 5 h at room temperature. The solids were filtrated off and washed with $CHCl_3$. The combined filtrate was concentrated. The product was purified by silica gel column chromatography using 4 : 1 hexane–ethyl acetate as eluent to give 2-(trimethylsilyl)ethyl 4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside as white solid (2.05 g, 72%). To a solution of this compound (1.62 mg, 2.98 mmol) in CH_2Cl_2 (30.0 ml) was added pyridine (6.0 ml) then cooled to 0 °C. ClAcCl (0.48 ml, 5.97 mmol, 2.0 eq) was added, and the mixture was stirred for 5 h at room temperature. The mixture was diluted with $CHCl_3$, washed with aq. 5% HCl, aq. $NaHCO_3$ and brine, dried ($MgSO_4$) and concentrated. The product was purified by silica gel column chromatography using 3 : 1 hexane–ethyl acetate as eluent to give 2-(trimethylsilyl)ethyl 4,6-*O*-benzylidene-3-*O*-chloroacetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside as an amorphous powder (1.39 g, 75%). To a solution of this compound (474 mg, 0.77 mmol) in THF (8.0 ml) was added 3 Å MS (500 mg) and $NaBH_3CN$ (386 mg, 6.16 mmol, 8.0 eq). The reaction mixture was stirred under an atmosphere of argon for 3 h at room temperature, then cooled to 0 °C. HCl–Et_2O (12.0 ml) was added. The addition was discontinued when the solution became acidic, and the mixture was stirred for 30 min at 0 °C. The solids were filtrated off and washed with $CHCl_3$. The combined filtrate and washings were successively washed with aq. $NaHCO_3$ and brine, dried ($MgSO_4$) and concentrated. The product was purified by silica gel column chromatography using 3 : 1 hexane–ethyl acetate as eluent to give **20** as syrup (410 mg, 86%). $[\alpha]_D^{25}$ −26.3 (c=5.67, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.35—7.25 (5H, m, Ph), 5.43 (1H, d, N<u>H</u>), 5.20 (1H, t, $J_{2,3}$=$J_{3,4}$=9.8 Hz, H-3), 4.76 (1H, d, C<u>H</u>$_2CCl_3$), 4.65—4.54 (3H, m, C<u>H</u>$_2CCl_3$, 2 benzylmethylene), 4.54 (1H, d, $J_{1,2}$=8.5 Hz, H-1), 4.11 (2H, q, C<u>H</u>$_2$Cl), 3.97—3.92 (1H, m, C<u>H</u>$_2CH_2Si$), 3.80—3.72 (3H, m, H-4, 6), 3.63 (1H, dd, H-2), 3.57—3.52 (2H, m, H-5, C<u>H</u>$_2CH_2Si$), 3.25 (1H, d, O<u>H</u>), −0.01 (9H, s, $Si(CH_3)_3$). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 168.1, 154.32, 137.5, 128.5×3, 128.0, 127.7×2, 101.8, 100.1 (C-1), 95.4, 74.5, 73.7×2, 70.7, 70.1, 67.4, 56.0, 40.8, 18.0×2, −1.5. MALDI-TOF-MS: Calcd for $C_{23}H_{33}Cl_4NO_9SiNa$, ([M+Na]$^+$) 642.0, Found 642.8.

2-(Trimethylsilyl)ethyl 2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-6-*O*-benzyl-3-*O*-chloroacetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (22) Compound **22** was prepared from **20** (715 mg, 1.20 mmol) and **21** (851 mg, 1.73 mmol) by the same method described for preparation of **6**. The product was purified by silica chromatography using 3 : 1 chloroform–methanol as eluent to give **22** as an amorphous powder (952 mg, 86%). $[\alpha]_D^{25}$ −4.34 (c=4.3, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.37—7.28 (5H, m, Ph), 5.28 (1H, d, N<u>H</u>), 5.24 (1H, d, $J_{3,4}$=3.7 Hz, H-4 of Gal), 5.16 (1H, t, $J_{3,4}$=9.2 Hz, H-3 of GlcN), 4.93 (1H, t, $J_{1,2}$=7.9 Hz H-2 of Gal), 4.78—4.63 (4H, m, H-3 of Gal, CH_2CCl_3, benzylmethylene), 4.48 (1H, d, $J_{1,2}$=8.6 Hz, H-1 of GlcN), 4.44 (1H, d, benzylmethylene), 4.40 (1H, d, H-1 of Gal), 4.10—4.02 (3H, m, H-6 of Gal, ClC<u>H</u>$_2$CO), 3.96—3.88 (2H, m, H-4 of GlcN, C<u>H</u>$_2CH_2Si(CH_3)_3$), 3.70 (1H, d, H-6 of GlcN), 3.66—3.59 (2H, m, H-2 of GlcN, H-5 of Gal), 3.54—3.49 (1H, m, C<u>H</u>$_2CH_2Si(CH_3)_3$), 3.44 (1H, br d, H-5 of GlcN), −0.03 (9H, s, $Si(C\underline{H}_3)_3$). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 170.3, 170.2, 170.0, 168.8, 167.0, 154.2, 137.6, 128.6×2, 128.1, 128.0×2, 100.4 (C-1 of GlcN), 100.1 (C-1 of Gal), 95.4, 74.5×2, 74.3, 73.6, 70.9×2, 70.6×2, 69.1, 67.3, 67.2, 66.9, 61.1, 55.9, 40.8, 20.6, 20.5, 18.0, −1.5. MALDI-TOF-MS: Calcd for $C_{37}H_{51}Cl_4NO_{17}SiNa$: ([M+Na]$^+$) m/z 972.2. Found 972.5. HR-FAB-MS: Calcd for $C_{37}H_{51}Cl_4NO_{17}SiNa$: ([M+Na]$^+$) m/z 972.1578. Found 972.1601.

2-(Trimethylsilyl)ethyl 2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (23) To a solution of **22** (780 mg, 0.82 mmol) in EtOH (5.0 ml) was added pyridine (3.0 ml) and thiourea (509 mg, 6.56 mmol). The reaction mixture was stirred for 4 h at 80 °C. The mixture was diluted with $CHCl_3$, washed with aq. 5% HCl, aq. $NaHCO_3$ and brine, dried ($MgSO_4$)

and concentrated. The product was purified by silica gel column chromatography using 3 : 2 hexane–ethyl acetate as eluent to give **23** as a white solid (624 mg, 85%). $[\alpha]_D^{25}$ −4.3 (c=4.3, $CHCl_3$). mp 125—126 °C. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.38—7.29 (5H, m, Ph), 5.34 (1H, d, $J_{3,4}$=3.7 Hz, H-4 of Gal), 5.18—5.15 (2H, m, H-2 of Gal, NH), 4.92 (1H, dd, $J_{2,3}$=9.2 Hz, H-3 of Gal), 4.74—4.67 (3H, m, CH_2CCl_3, benzylmethylene), 4.60 (1H, br, H-1 of GlcN), 4.50 (1H, d, benzylmethylene), 4.48 (1H, d, $J_{1,2}$=10.4 Hz, H-1 of Gal), 4.14—4.07 (2H, m, H-6 of Gal), 3.99—3.88 (4H, m, H-3 of GlcN, H-5 of Gal, $CH_2CH_2Si(CH_3)_3$, OH), 3.70—3.61 (2H, m, H-4, 6 of GlcN), 3.56—3.51 (1H, m, $CH_2CH_2Si(CH_3)_3$), 4.47 (1H, m, H-5 of GlcN), 3.32 (1H, q, $J_{2,3}$=8.3 Hz, H-2 of GlcN), −0.01 (9H, s, $Si(CH_3)_3$). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 170.4, 170.1, 169.9, 169.1, 154.1, 138.0×2, 128.5, 127.9×2, 127.8, 101.3 (C-1 of Gal), 99.9 (C-1 of GlcN), 95.5, 81.4, 74.5, 73.9, 73.6×2, 71.8, 71.2, 70.7, 68.7, 67.9, 67.2, 66.9, 61.4×2, 57.8, 20.7×2, 20.6, 20.5, 18.0, −1.4. MALDI-TOF-MS: Calcd for $C_{35}H_{50}Cl_3NO_{16}SiNa$: ($[M+Na]^+$) m/z 896. Found 896. HR-FAB-MS: Calcd for $C_{35}H_{50}Cl_3NO_{16}SiNa$: ($[M+Na]^+$) m/z 896.1862. Found 896.1827.

2-(Trimethylsilyl)ethyl 2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (24) Compound **23** was acetylated with acetic anhydride (3.0 ml) in pyridine (4.5 ml) for 18 h. The reaction mixture was poured into ice H_2O and extracted with $CHCl_3$. The extract was washed sequentially with 5% HCl, aq. $NaHCO_3$, and brine, dried ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography using 2 : 1 hexane–ethyl acetate as eluent to give **24** as an amorphous powder (263 mg, 82%). $[\alpha]_D^{25}$ −8.5 (c=6.6, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.40—7.26 (5H, m, Ph), 5.28 (1H, d, $J_{3,4}$=3.7 Hz, H-4 of Gal), 5.15 (1H, d, NH), 5.09 (1H, m, $J_{3,4}$=9.8 Hz, H-3 of GlcN), 5.10 (1H, dd, $J_{1,2}$=7.8 Hz, $J_{2,3}$=9.7 Hz, H-2 of Gal), 4.82 (1H, dd, H-3 of Gal), 4.79—4.71 (2H, m, CH_2CCl_3, benzylmethylene), 4.66 (1H, d, CH_2CCl_3) 4.48 (1H, d, benzylmethylene), 4.44 (2H, d, H-1 of GlcN, H-1 of Gal), 4.06 (1H, dd, H-6 of Gal), 3.98—3.90 (2H, m, H-4 of GlcN, $CH_2CH_2Si(CH_3)_3$), 3.74—3.63 (4H, m, H-2, 5, 6 of GlcN), 3.56—3.50 (1H, m, $CH_2CH_2Si(CH_3)_3$), 3.44 (1H, br s, H-5 of Gal), 0.95—0.89 (2H, m, $CH_2CH_2Si(CH_3)_3$), −0.01 (9H, s, $Si(CH_3)_3$). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 170.5, 170.3, 170.1, 170.0, 168.8, 154.2, 137.7×2, 128.5×2, 128.0×2, 100.7 (C-1 of Gal), 100.3 (C-1 of GlcN), 95.5, 74.9, 74.7, 74.4, 73.6, 72.3, 70.9, 70.5, 69.1, 67.4, 67.2, 66.8, 60.9, 56.1, 20.8, 20.6×2, 20.5×2, 18.0, −1.46. MALDI-TOF-MS: Calcd for $C_{37}H_{52}Cl_3NO_{17}SiNa$: ($[M+Na]^+$) m/z 938.2. Found 938.5. HR-FAB-MS: Calcd for $C_{37}H_{52}Cl_3NO_{17}SiNa$: ($[M+Na]^+$) m/z 938.1968. Found 938.1988.

2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-1-*O*-α-D-glucopyranosyl Trichloroacetimidate (25) Compound **25** was prepared from **24** (263 mg, 0.29 mmol) by the same method described for preparation of **9**. The product was purified by silica chromatography using 2 : 1 hexane–ethyl acetate as eluent to give **25** as an amorphous powder (202 mg, 74%). $[\alpha]_D^{25}$ +37.6 (c=1.2, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.74 (1H, s, C(NH)CCl_3), 7.43—7.34 (5H, m, Ph), 6.41 (1H, d, $J_{1,2}$=3.7 Hz, H-1 of GlcN), 5.29 (1H, d, $J_{3,4}$=3.7 Hz, H-4 of Gal), 5.28—5.24 (2H, m, H-3 of GlcN, NH), 5.01 (1H, dd, $J_{1,2}$=7.9 Hz, $J_{2,3}$=10.4 Hz, H-2 of Gal), 4.81—4.76 (2H, m, H-3 of Gal, benzylmethylene), 4.74—4.67 (2H, m, CH_2CCl_3), 4.44 (1H, d, benzylmethylene), 4.43 (1H, d, H-1 of Gal), 4.20—4.05 (4H, m, H-2, 4 of GlcN, H-6 of Gal), 3.86 (1H, br d, H-5 of Gal), 3.79 (1H, dd, H-6a of GlcN), 3.70—3.66 (2H, m, H-5, 6b of GlcN). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 171.0, 170.3, 170.1, 170.0, 168.8, 160.7, 154.2, 137.4, 128.7×2, 128.3, 128.2×2, 100.4 (C-1 of Gal), 95.2, 94.9 (C-1 of GlcN), 90.7, 74.5, 74.0, 73.8, 72.9, 71.0, 70.5, 70.2, 69.1, 66.8, 66.7, 60.9, 54.1, 20.8, 20.7, 20.62, 20.56, 20.5.

2-(Trimethylsilyl)ethyl 2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzoyl-6-benzyl-β-D-glucopyranoside (26) A solution of **13** (176 mg, 0.18 mmol) and **25** (202 mg, 0.21 mmol) containing activated 4 Å MS (400 mg) in dry CH_2Cl_2 (4.0 ml) was stirred under an atmosphere of argon for 2 h at room temperature, then cooled to −40 °C. TMSOTf (3.2 μl, 0.02 mmol) was added, and the mixture was stirred for 2 h at −40 °C, then neutralized with Et_3N. The solids were filtrated off and washed with $CHCl_3$. The combined filtrate and washings were successively washed with brine, dried ($MgSO_4$) and concentrated. The product was purified by silica gel column chromatography using 6 : 1 toluene–acetone as eluent to give **26** as an amorphous powder (262 mg, 83%). $[\alpha]_D^{25}$ +10.3 (c=1.6, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.01—7.23 (25H, m, 5Ph), 5.77 (1H, t, $J_{2,3}$=$J_{3,4}$=9.8 Hz, H-3 of Glc), 5.55 (1H, br, NH), 5.40—5.33 (4H, m, H-2 of Glc, H-3 of GlcN, H-4 of Gal, CHPh), 5.09—5.06 (2H, m, H-2 of Gal, benzylmethylene), 4.97 (1H, d, $J_{1,2}$=7.9 Hz, H-1 of GlcN), 4.98—4.90 (2H, m, H-3 of Gal, NH), 4.82—4.67 (7H, m, $J_{1,2}$=7.9 Hz, H-1 of Glc, 3 benzylmethylene, $3CH_2CCl_3$), 4.54 (1H, d, CH_2CCl_3), 4.47 (2H, d, $J_{1,2}$=7.9 Hz, H-1 of GalN, H-1 of Gal), 4.29 (1H, t, $J_{4,5}$=9.8 Hz, H-4 of Glc), 4.12—4.04 (5H, m, H-6a of Glc, H-4 of GlcN, H-6 of Gal, $CH_2CH_2Si(CH_3)_3$), 3.89—3.61 (10H, m, H-5, 6b of Glc, H-2, 3, 4 of GalN, H-2, 6 of GlcN, H-5 of Gal, $CH_2CH_2Si(CH_3)_3$), 3.56—3.42 (3H, m, H-6 of GalN, H-5 of GlcN), 2.84 (1H, s, H-5 of GalN), −0.01 (9H, s, $Si(CH_3)_3$). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 170.3, 170.1, 170.0, 168.7, 165.2, 153.8, 138.3, 137.5, 132.8, 132.7, 129.7, 129.6, 129.0, 128.9, 128.6, 128.4, 128.2, 128.0, 127.8, 127.7, 126.3, 125.2, 100.7, 100.5 (C-1), 100.3 (C-1 of GalN, C-1 of Gal), 99.1 (C-1 of GlcN), 95.5, 75.3, 74.8, 74.4, 74.3, 74.2, 73.82, 73.76, 73.2, 72.4, 72.2, 70.9, 70.5, 69.1, 68.4, 68.2, 67.3, 66.7, 66.2, 60.9, 56.0, 53.9, 21.4, 20.7, 20.6, 20.5, 17.9, −1.51. MALDI-TOF-MS: Calcd for $C_{80}H_{92}Cl_6N_2O_{30}SiNa$: ($[M+Na]^+$) m/z 1821.4. Found 1822.1.

2-(Trimethylsilyl)ethyl 2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-2-acetamido-3,6-di-*O*-acetyl-2-deoxy-β-D-glucopyranosyl-(1→3)-2-acetamido-4,6-di-*O*-acetyl-2-deoxy-β-D-galactopyranosyl-(1→4)-6-*O*-acetyl-2,3-di-*O*-benzoyl-β-D-glucopyranoside (27) Compound **27** was prepared from **26** (363 mg, 0.20 mmol) by the same method described for preparation of **16**. The product was purified by silica chromatography using 2 : 1 toluene–acetone as eluent to give **27** as syrup (120 mg, 42%). $[\alpha]_D^{25}$ +9.5 (c=0.98, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 6.07 (1H, d, NH of GlcN), 5.87 (1H, d, NH of GalN), 4.90 (1H, d, $J_{1,2}$=8.0 Hz, H-1 of GlcN), 4.69 (1H, d, $J_{1,2}$=7.7 Hz, H-1 of Glc), 4.55 (1H, d, $J_{1,2}$=6.9 Hz, H-1 of GalN), 4.48 (1H, d, $J_{1,2}$=8.0 Hz, H-1 of Gal). ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 101.0 (C-1 of Gal), 100.6 (C-1 of GalN), 100.4 (C-1 of Glc), 98.9 (C-1 of GlcN). MALDI-TOF-MS: Calcd for $C_{65}H_{86}N_2O_{32}SiNa$ ($[M+Na]^+$) m/z 1457.4. Found 1456.3.

2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-2-acetamido-3,6-di-*O*-acetyl-2-deoxy-β-D-glucopyranosyl-(1→3)-2-acetamido-4,6-di-*O*-acetyl-2-deoxy-β-D-galactopyranosyl-(1→4)-6-*O*-acetyl-2,3-di-*O*-benzoyl-1-*O*-α-D-glucopyranosyl Trichloroacetimidate (28) Compound **28** was prepared from **27** (120 mg, 0.08 mmol) by the same method described for preparation of **9**. The product was purified by silica chromatography using 30 : 1 chloroform–methanol as eluent to give **28** as amorphous powder (76 mg, 61%). $[\alpha]_D^{25}$ +45.0 (c=1.0, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.60 (1H, s, OC(NH)CCl_3), 6.07 (1H, d, $J_{1,2}$=3.9 Hz, H-1 of Glc), 6.17 (1H, d, NH of GlcN), 5.86 (1H, d, NH of GalN), 5.02 (1H, d, $J_{1,2}$=8.2 Hz, H-1 of GlcN), 4.53 (1H, d, $J_{1,2}$=7.7 Hz, H-1 of GalN), 4.48 (1H, d, $J_{1,2}$=7.7 Hz, H-1 of Gal). ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 100.9 (C-1 of Gal), 100.8 (C-1 of GalN), 98.9 (C-1 of GlcN), 93.0 (C-1 of Glc), 90.7 (OC(NH)CCl_3).

2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-2-acetamido-3,6-di-*O*-acetyl-2-deoxy-β-D-glucopyranosyl-(1→3)-2-acetamido-4,6-di-*O*-acetyl-2-deoxy-β-D-galactopyranosyl-(1→4)-6-*O*-acetyl-2,3-di-*O*-benzoyl-β-D-glucopyranosyl-(1→1)-(2*S*,3*S*,4*R*)-3,4-di-*O*-benzoyl-2-palmitoylamidooctadecane-1,3,4-triol (29) Compound **29** was prepared from **28** (76 mg, 51.1 μmol) and **10** (78 mg, 102 μmol) by the same method described for preparation of **11**. The product was purified by silica chromatography using 30 : 1 chloroform–methanol as eluent to give **29** as syrup (35 mg, 34%). $[\alpha]_D^{25}$ +11.1 (c=0.3, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 6.21 (1H, d, NH of ceramide), 5.99 (1H, d, NH of GlcN), 5.73 (1H, d, NH of GalN), 4.81 (1H, d, $J_{1,2}$=8.2 Hz, H-1 of GlcN), 4.56 (1H, d, $J_{1,2}$=7.4 Hz, H-1 of Glc), 4.52 (1H, d, $J_{1,2}$=8.4 Hz, H-1 of GalN), 4.47 (1H, d, $J_{1,2}$=7.7 Hz, H-1 of Gal). ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 101.0 (C-1 of Gal), 100.6 (C-1 of Glc), 100.3 (C-1 of GalN), 98.9 (C-1 of GlcN). MALDI-TOF-MS: Calcd for $C_{108}H_{149}N_3O_{37}Na$: ($[M+Na]^+$) m/z 2103. Found 2103.

β-D-Galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-2-acetamido-2-deoxy-β-D-galactopyranosyl-(1→4)-β-D-glucopyranosyl-(1→1)-(2*S*,3*S*,4*R*)-2-hexadecanamido-4-octadecane-1,3,4-triol (3) Compound **3** was prepared from **29** (12.0 mg) by the same method described for preparation of **1**. The product was purified by Sephadex LH-20 column chromatography in MeOH to give **3** as white solid (4.1 mg, 55%). $[\alpha]_D^{25}$ +4.8 (c=0.13, 1 : 1 $CHCl_3$–CD_3OH). mp 185—186 °C. ^{1}H-NMR (600 MHz, 1 : 1 $CDCl_3$–CD_3OD) δ: 4.60 (1H, d, $J_{1,2}$=8.5 Hz, H-1 of GlcN), 4.48 (1H, d, $J_{1,2}$=8.5 Hz, H-1 of GalN), 4.40 (1H, d, $J_{1,2}$=7.7 Hz, H-1 of Gal), 4.30 (1H, d, $J_{1,2}$=7.5 Hz, H-1 of Glc). MALDI-TOF-MS: Calcd for $C_{62}H_{115}N_3O_{24}Na$: ($[M+Na]^+$) 1309, Found 1309. HR-FAB-MS: Calcd for $C_{62}H_{115}N_3O_{24}Na$: ($[M+Na]^+$) m/z 1308.7768. Found 1308.7742.

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