SUPPORTING INFORMATION

Mycobacterium tuberculosis β-gentiobiosyl diacylglycerides signal through the pattern recognition receptor Mincle: Total synthesis and structure activity relationships

Mark B. Richardson,[a] Shota Torigoe,[b] Sho Yamasaki,[b]* and Spencer J. Williams*[a]

[a] School of Chemistry and Bio21 Molecular Science and Biotechnology Institute, University of Melbourne, Victoria 3010, Australia. E-mail: sjwill@unimelb.edu.au

[b] Division of Molecular Immunology, Medical Institute of Bioregulation, Kyushu University, Fukuoka 812-8582, Japan. E-mail: yamasaki@bioreg.kyushu-u.ac.jp

Table of Contents

Supplementary Figures

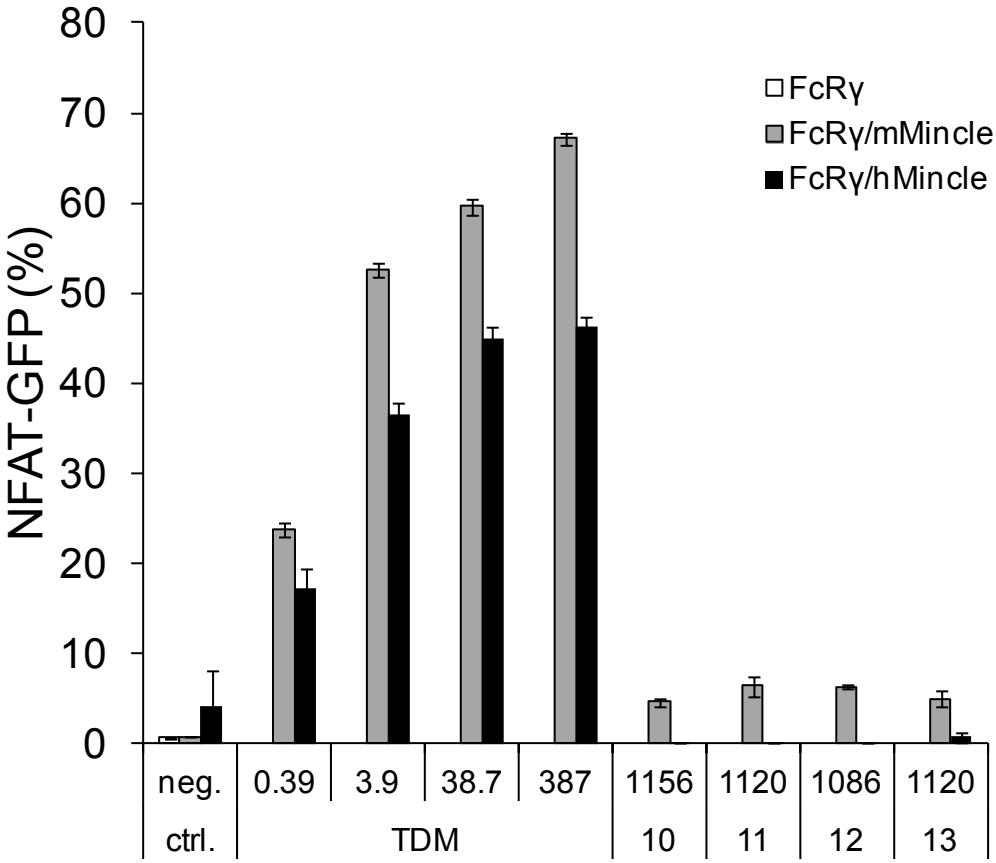

Figure S1.

Data from Figure 2, replotted according to molecular weight. Amounts correspond to pmol of glycolipid per well. Molar quantity of TDM was calculated using an estimated molecular mass of 2582 g mol^{-1}.

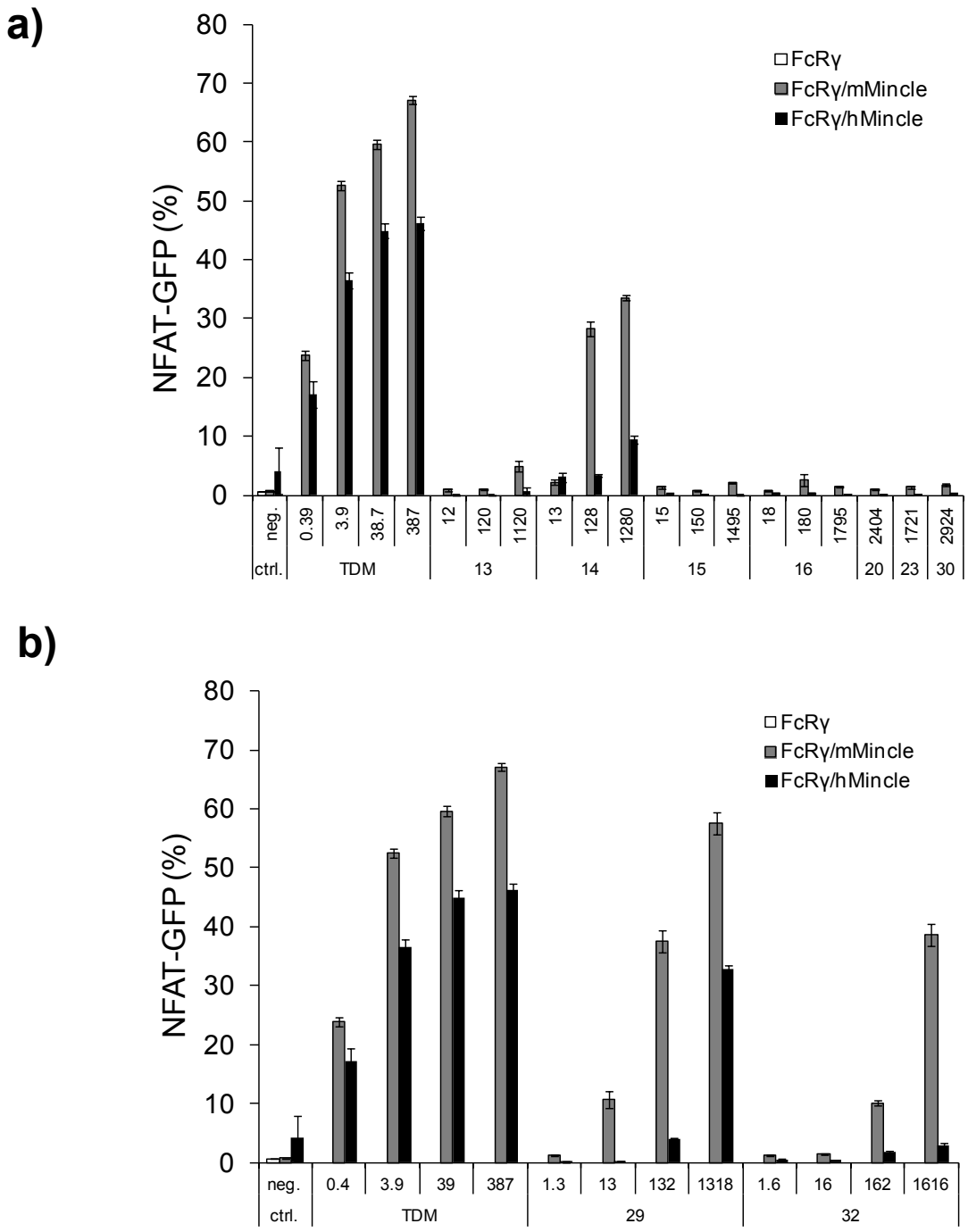

Figure S2.

Data from Figure 3, replotted according to molecular weight. Amounts correspond to pmol of glyco(lipid) per well. Molar quantity of TDM was calculated using an estimated molecular mass of 2582 g mol^{-1}. a) Structure-activity variations in the diacylglyceride fragment. **30** = gentiobiose. b) Glucosyl diglycerides.

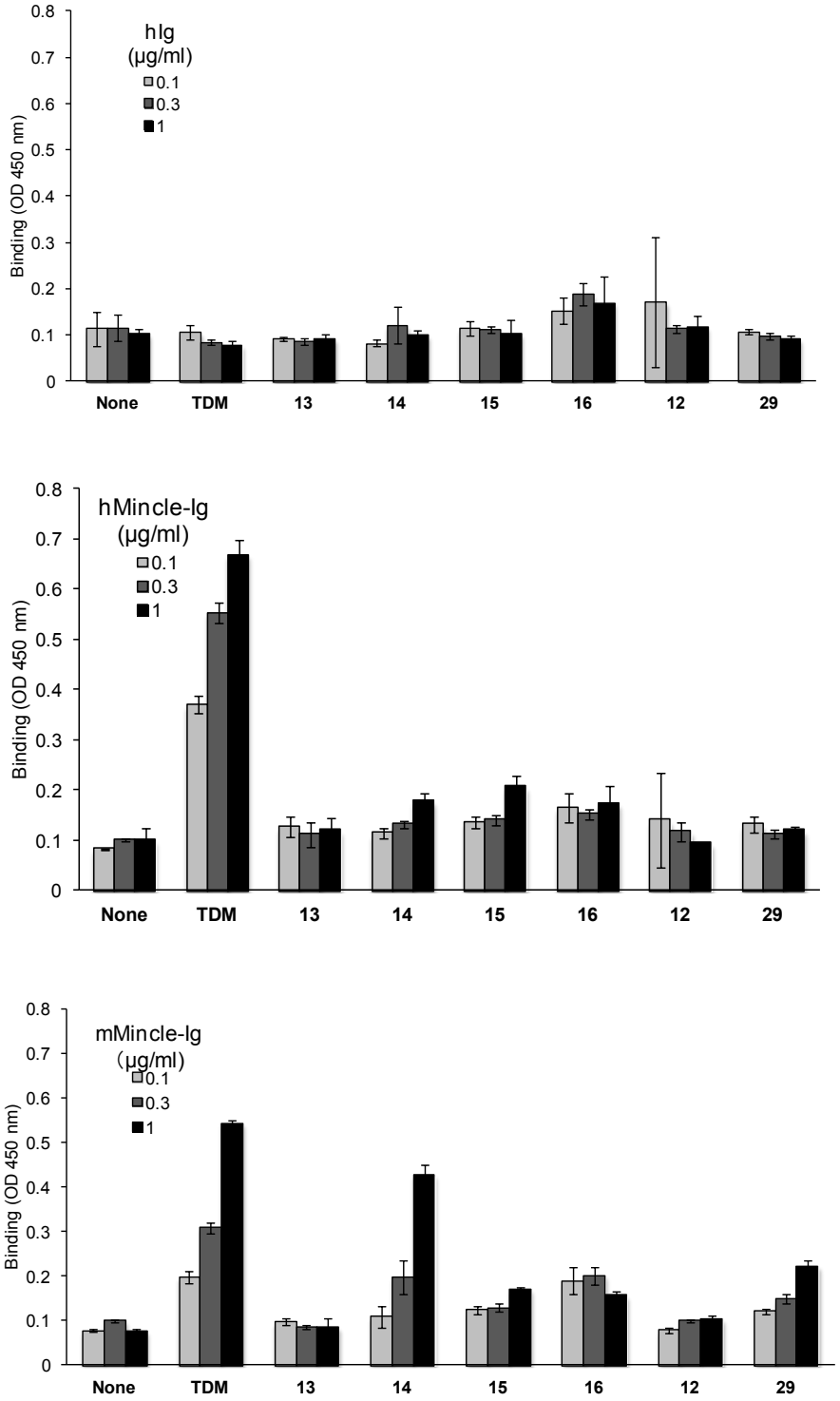

Figure S3. ELISA-based detection of glycosyl diglycerides by mouse (mMincle) and human (hMincle) Ig fusions.

Top: hIgG1-Fc (hIg); **middle**: hMincle-Ig; and **bottom**: mMincle-Ig were incubated with plate-coated glycolipid (0.6 μg/well). Bound Ig-fusion protein was detected with anti–hIgG-HRP followed by the addition of colorimetric substrate. The data are the means ± SD for triplicate assays and representative results from two independent experiments with similar results are shown.

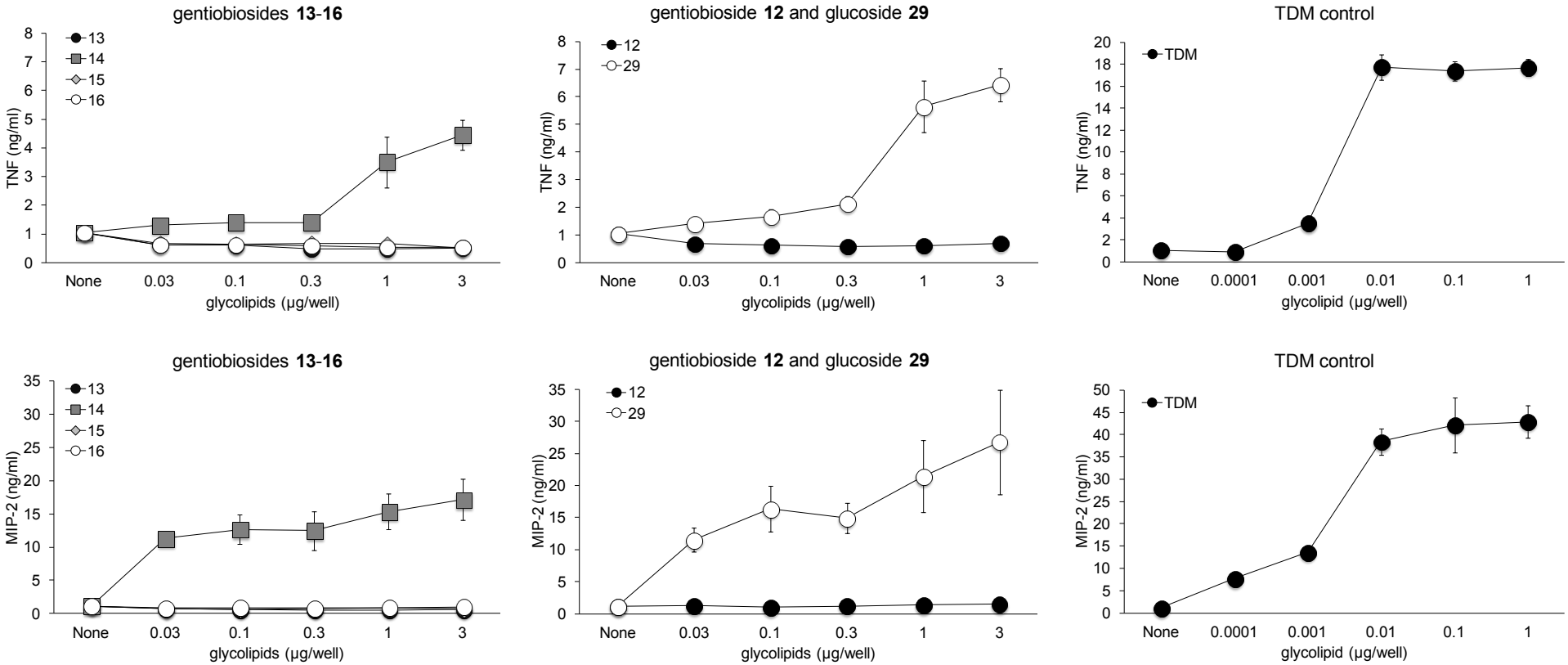

Figure S4. Stimulation of murine BMDCs with glycolipids.

Bone marrow derived dendritic cells (BMDCs) were stimulated with plate-coated glycolipids. The culture supernatants were collected at 48 hrs and the concentrations of tumor necrosis factor (TNF) and macrophage inflammatory protein 2 (MIP-2) were determined by ELISA. The data are the means ± SD for triplicate assays and representative results from two independent experiments with similar results are shown. TDM control data are plotted with a different vertical scale.

Mincle reporter assay

2B4-NFAT-GFP reporter cells expressing mouse Mincle/FcRγ or human Mincle/FcRγ were prepared as previously described.[1] In order to stimulate the cells, glycolipids were dissolved in chloroform:methanol (2:1) at 1 mg/ml were diluted in isopropanol and added to 96-well plates at 20 μl/well, followed by evaporation of the solvent as previously described.[2] Activation of NFAT-GFP was monitored by flow cytometry.

Preparation of bone marrow-derived dendritic cells (BMDCs)

Bone marrow was suspended in RPMI 1640 medium supplemented with 10 % (v/v) fetal calf serum (FCS), β-mercaptoethanol and culture supernatant of MGM-5 (provided by Dr. S. Nagata) as a source of granulocyte macrophage colony-stimulating factor (GM-CSF) and cultured at 5×10^5 cells/well for 10 d at 37 °C in 6-well plates.

Ig-fusion proteins

Murine and human Mincle-Ig fusion proteins were prepared as previously described.[1] The extracellular domain of murine (46-214 aa) and human (46-214 aa) Mincle was fused to hIgG1 Fc region.

Synthetic chemistry

General Synthetic Methods

Proton nuclear magnetic resonance spectra (^{1}H NMR, 500 MHz) and proton decoupled carbon nuclear magnetic resonance spectra (^{13}C NMR, 125 MHz) were obtained in deuterated chloroform, methanol-d_4 (CD_3OD) and DMSO-d_6 with residual protonated solvent as internal standard. Abbreviations for multiplicity are s, singlet; d, doublet; t, triplet; q, quartet; p, pentet. Fourier-transform infrared spectra were obtained as neat samples on an attenuated total reflectance instrument using a diamond-coated zinc selenide sample accessory. Flash chromatography was carried out on silica gel 60 according to the procedure of Still *et al*.[3] Analytical thin layer chromatography (t.l.c.) was conducted on aluminium-backed 2 mm thick silica gel 60 GF_{254} and chromatograms were visualized with ceric ammonium molybdate (Hanessian's stain) or orcinol/$FeCl_3$ (Bial's reagent). High resolution mass spectra (HRMS) were obtained by ionizing samples using electro-spray ionization (ESI) and a time-of-flight mass analyzer. Dry DMF was obtained by drying over 4 Å molecular sieves. Hexanes refers to petroleum ether, boiling range 40-60 °C. Dichloromethane and THF were dried over alumina according to the method of Pangborn *et al*.[4]

(R)-α-Cyanobenzyl 2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl-(1,6)-2,3,6-tri-O-benzoyl-β-D-glucopyranoside (2)

Benzoyl chloride (5.02 mL, 44.8 mmol) was added slowly to a stirred solution of amygdalin (2.00 g, 4.37 mmol) and DMAP (53.4 mg, 437 μmol) in anhydrous pyridine (16 mL) at 0 °C, then the mixture was warmed to rt and stirred under nitrogen for 1 h. When the reaction mixture solidified, additional pyridine (14 mL) was added and the slurry was stirred for a further 2.5 h. The reaction mixture was concentrated in vacuo then diluted into water and extracted with CH_2Cl_2 (2 × 100 mL). The combined organic phases were washed sequentially with 10% aq. HCl (1 ×100 mL), sat. aq. $NaHCO_3$ (2 × 100 mL), and dried ($MgSO_4$), filtered and the solvent evaporated in vacuo to give an

amorphous white solid. The residue was crystallized from EtOH (750 mL), affording **5** as a white powder (4.83 g, 93%); mp 229-230 °C (lit.[5] 235); $[\alpha]^{24}_{D}$ -12.3 (*c* 1.10 in $CHCl_3$) (lit.[5] -10.7 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.86-3.97 (2 H, m, H5',6'), 4.04-4.13 (1 H, m, H6'), 4.19 (1 H, ddd, *J* 9.9, 5.0, 3.1 Hz, H5''), 4.42 (1 H, dd, *J* 12.2, 5.0 Hz, H6''), 4.48 (1 H, d, *J* 7.9 Hz, H1'), 4.60 (1 H, dd, *J* 12.2, 3.1 Hz, H6''), 5.13 (1 H, d, *J* 7.8 Hz, H1''), 5.18 (1 H, s, H1), 5.28-5.33 (1 H, m, H4'), 5.46 (1 H, dd, *J* 9.6, 7.9 Hz, H2'), 5.57 (1 H, dd, *J* 9.7, 7.8 Hz, H2''), 5.66 (1 H, dd, *J* 9.6, 9.6 Hz, H3'), 5.68 (1 H, dd, *J* 9.9, 9.7 Hz, H4''), 6.01 (1 H, dd, 9.7, 9.7 Hz, H3''), 7.20-7.59 (36 H, m, Ar), 7.74-7.78 (2 H, m, Ar), 7.79-7.84 (6 H, m, Ar), 7.87-7.92 (2 H, m, Ar), 7.95-8.03 (4 H, m, Ar). These assignments differ from those reported by Ziegler and Seidl.[5] ^{13}C NMR (125 MHz, $CDCl_3$) δ 63.1 (C6''), 67.9 (C6'), 68.6 (C1), 69.58 (C4'), 69.62 (C4''), 71.3 (C2'), 72.37 (C2''), 72.45 (C5''), 72.7 (C3'), 72.9 (C3''), 74.6 (C5'), 98.0 (C1'), 101.3 (C1''), 117.2 (CN), 128.0-130.4 (40 C, Ar), 132.0, 133.2, 133.37, 133.43, 133.5, 133.6, 133.7, 133.8 (8 C, ipso-Ph), 164.8, 165.3, 165.46, 165.48, 165.7, 165.9, 166.2 (7 C, Ph*C*O_2). These assignments differ from that reported by Ziegler and Seidl.[5] IR ν 705.3, 729.0, 772.2, 906.6, 1026.1, 1067.5, 1090.0, 1258.4, 1451.6, 1602.0, 1725.4 cm^{-1}; HRMS (ESI^+) calcd for $C_{69}H_{56}NO_{18}$ $[M+H]^+$ *m/z* 1186.3492, found 1186.3556.

2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1,6)-2,3,6-tri-*O*-benzoyl-β-D-glucopyranosyl chloride (3)

A mixture of **2** (6.00 g, 5.06 mmol), fused $ZnCl_2$ (483 mg, 3.54 mmol), powdered mol. sieves (4 Å, 5 g) and dichloromethyl methyl ether (2.3 mL, 25.3 mmol) in $CHCl_3$ (40 mL) was heated under reflux under N_2 for 14 h. The mixture was cooled to rt, diluted with toluene (100 mL), filtered, and evaporated in vacuo to give a brown foam. Purification by flash chromatography (2 ✂ 6% acetone/toluene) afforded **3** as a white foam (4.51 g, 82%); mp 65-75 °C; $[\alpha]^{25}_{D}$ +37.3 (*c* 1.10 in $CHCl_3$) (lit.[5] $[\alpha]_D$ -40.5 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.86 (1 H, dd, *J* 12.0, 5.8 Hz, H6), 4.13-4.19 (2 H, m, H6,5'), 4.49 (1 H, dd, *J* 12.1, 5.0 Hz, H6'), 4.56 (1 H, ddd, *J* 10.1, 5.8, 1.9 Hz, H5), 4.63 (1 H, dd, *J* 12.1, 3.2 Hz, H6'), 4.99 (1 H, d, *J* 7.8 Hz, H1'), 5.28 (1 H, dd, *J* 10.1, 4.0

Hz, H2), 4.49 (1 H, dd, *J* 10.1, 9.8 Hz, H4), 5.58 (1 H, dd, *J* 9.7, 7.8 Hz, H2'), 5.68 (1 H, dd, *J* 9.6, 9.6 Hz, H4'), 5.95 (1 H, dd, *J* 9.7, 9.6 Hz, H3'), 6.15 (1 H, dd, *J* 10.1, 9.8 Hz, H3), 6.36 (1 H, d, *J* 4.0 Hz, H1), 7.13-7.58 (21 H, m, Ph), 7.77-7.81 (2 H, m, Ph), 7.83-7.87 (4 H, m, Ph), 7.89-7.93 (2 H, m, Ph), 7.95-7.99 (2 H, m, Ph), 8.00-8.08 (4 H, m, Ph); ^{13}C NMR (125 MHz, $CDCl_3$) δ 63.1 (C6'), 67.4 (C6), 68.4 (C4), 69.77 (C4'), 69.84 (C3), 71.7 (C2), 71.8 (C2'), 72.3 (C5), 72.4 (C5'), 72.9 (C3'), 90.3 (C1), 101.6 (C1'), 128.4-130.1 (35 C, Ph), 133.20, 133.22, 133.34, 133.35, 133.5, 133.7, 133.8 (7 C, ipso-*Ph*CO_2), 165.1, 165.27, 165.30, 165.34, 165.6, 165.9, 166.2 (7 C, Ph*C*O_2); IR ν 704.8, 749.7, 770.7, 1026.2, 1067.8, 1090.3, 1259.4, 1451.7, 1602.1, 1725.0 cm^{-1}; HRMS (ESI^+) calcd for $C_{61}H_{50}ClO_{17}$ $[M+H]^+$ *m*/*z* 1089.2731, found 1089.2745.

4-Methylphenyl 2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl-(1,6)-2,3,4-tri-O-benzoyl-β-D-1-thio-glucopyranoside (4)

A solution of potassium thiocresolate (1.00 g, 6.14 mmol) in DMF (10 mL) was added to a solution of **3** (5.57 g, 5.11 mmol) in DMF (10 mL) and the reaction mixture was stirred at rt under nitrogen for 14 h. The solvent was evaporated in vacuo and the residue was dissolved in EtOAc (100 mL) and washed sequentially with 10% aq. HCl (2 × 50 mL), water (2 × 50 mL), and brine (2 × 50 mL), dried ($MgSO_4$), filtered and the solvent evaporated in vacuo to give a brown foam. Purification by flash chromatography (0 ⩽ 5% acetone/$CHCl_3$) and crystallization from hexanes/EtOAc afforded **4** as white flakes (5.82 g, 97%); mp 225-227 °C; $[\alpha]^{21}_D$ +16.3 (*c* 1.10 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.37 (3 H, s, CH_3), 3.90-4.04 (3 H, m, H5,6,6), 4.09 (1 H, ddd, *J* 9.8, 5.2, 3.0 Hz, H5'), 4.41 (1 H, dd, *J* 12.2, 5.2 Hz, H6'), 4.61 (1 H, dd, *J* 12.2, 3.0 Hz, H6'), 4.82 (1 H, d, *J* 10.0 Hz, H1), 5.02 (1 H, d, *J* 7.9 Hz, H1'), 5.25 (1 H, dd, *J* 9.7, 9.5 Hz, H4), 5.33 (1 H, dd, *J* 10.0, 9.7 Hz, H2), 5.50 (1 H, dd, *J* 9.7, 7.9 Hz, H2'), 5.61 (1 H, dd, *J* 9.8, 9.7 Hz, H4'), 5.78 (1 H, dd, *J* 9.7, 9.5 Hz, H3), 5.86 (1 H, dd, *J* 9.7, 9.7 Hz, H3'), 7.17-7.60 (25 H, m, Ar), 7.74-7.96 (12 H, m, Ar), 8.04-8.06 (2 H, m, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.4 (CH_3), 63.1 (C6'), 68.4 (C6), 69.7 (C4), 69.8 (C4'), 70.7 (C2), 72.0 (C2'), 72.5 (C5'), 73.1 (C3'), 74.3 (C3), 78.6 (C5), 86.1 (C1), 101.2 (C1'),

128.4-130.0 (39 C, Ar), 133.27, 133.30, 133.31, 133.34, 133.4, 133.57, 133.59, 134.1, 139.0 (9 C, *ipso*-Ar), 165.1, 165.30, 165.33, 165.5, 165.8, 165.9, 166.2 (7 C, Ph*C*O_2); IR ν 706.3, 771.5, 1026.3, 1067.8, 1089.9, 1259.0, 1451.5, 1725.9 cm^{-1}; HRMS (ESI^+) calcd for $C_{68}H_{56}O_{17}SNa$ $[M+Na]^+$ *m*/*z* 1199.3130, found 1199.3111.

1,2-Di-O-(4-bromobenzyl)-sn-glyceryl 2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl-(1,6)-2,3,6-tri-O-benzoyl-β-D-glucopyranoside (6)

A mixture of thioglycoside **4** (1.54 g, 1.31 mmol), glycerol **5** (619 mg, 430 mmol), powdered molecular sieves (4 Å, 2.50 g) and NIS (736 mg, 3.27 mmol) in anhydrous CH_2Cl_2 (40 mL) was stirred under nitrogen atmosphere at rt for 30 min, then cooled to 0 °C. TfOH in CH_2Cl_2 (0.01 M, 1.31 mL, 13.1 μmol) was added, and the mixture was stirred for 5 min at 0 °C, then diluted into CH_2Cl_2 (100 mL) and filtered. The filtrate was washed sequentially with sat. aq. $NaHCO_3$ (2 × 100 mL), aq. $Na_2S_2O_3$ (0.5 M, 2 × 50 mL), sat. aq. $NaHCO_3$ (2 × 100 mL), brine (2 × 100 mL), dried ($MgSO_4$), filtered, and the solvent was removed in vacuo. The residue was purified by flash chromatography (9:4:1 ✂ 5:4:1 hexanes/CH_2Cl_2/acetone) to give the glycosyl glyceride **6** as a white solid (1.91 g, 98%): mp 57-60 °C; $[\alpha]^{24}_D$ +6.2 (*c* 1.00 in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 3.39 (2 H, d, *J* 5.0 Hz, H1,1), 3.51-3.54 (2 H, m, H2,3), 3.76 (1 H, dd, *J* 12.2, 6.2 Hz, H3), 3.87 (1 H, dd, *J* 11.4, 7.6 Hz, H6'), 3.97 (1 H, ddd, *J* 9.7, 7.6, 2.0 Hz, H5'), 4.06 (1 H, dd, *J* 11.4, 2.0 Hz, H6'), 4.09 (1 H, ddd, *J* 9.7, 5.0, 3.2 Hz, H5''), 4.18 (1 H, d, *J* 12.2 Hz, *sn*-1 CH_2Ar), 4.22 (1 H, d, *J* 12.2 Hz, *sn*-1 CH_2Ar), 4.42 (1 H, dd, *J* 12.2, 5.0 Hz, H6''), 4.43 (1 H, d, *J* 12.2 Hz, *sn*-2 CH_2Ar), 4.50 (1 H, d, *J* 12.2 Hz, *sn*-2 CH_2Ar), 4.58 (1 H, dd, *J* 12.2, 3.2 Hz, H6''), 4.70 (1 H, d, *J* 7.9 Hz, H1'), 5.00 (1 H, d, *J* 7.9 Hz, H1''), 5.31 (1 H, dd, *J* 9.7, 9.7 Hz, H4'), 5.38 (1 H, dd, *J* 9.7, 7.9 Hz, H2'), 5.51 (1 H, dd, *J* 9.7, 7.9 Hz, H2''), 5.63 (1 H, dd, *J* 9.7, 9.7 Hz, H4''), 5.78 (1 H, dd, *J* 9.7, 9.7 Hz, H3'), 5.88 (1 H, dd, *J* 9.7, 9.6 Hz, H3''), 7.03-7.05, 7.12-7.16 (4 H, 2m, Ar), 7.24-7.62 (25 H, m, Ar), 7.76-8.01 (14 H, m, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 63.1 (C6''), 68.6 (C6'), 68.8 (C3), 69.7 (C4''), 70.0 (C4'), 70.2 (C1), 71.4 (*sn*-2 *C*H_2Ar), 72.0 (C2'), 72.1 (C2''), 72.4 (C5''),

72.6 (*sn*-1 *C*H_2Ar), 72.8 (C3'), 73.0 (C3"), 74.1 (C5'), 77.4 (C2), 101.2 (C1'), 101.5 (C1"), 121.4, 121.5 (2 C, C-Br), 128.4-130.0 (43 C, Ar,Ph), 133.28, 133.33, 133.37, 133.39, 133.40, 133.58, 133.64, 137.4, 137.7 (9 C, *ipso*-Ar), 165.1, 165.2, 165.3, 165.5, 165.8, 165.9, 166.2 (7 C, C=O); IR ν 706.1, 771.5, 1012.1, 1025.9, 1067.3, 1089.4, 1258.7, 1725.5 cm^{-1}; HRMS (ESI^+) calcd for $C_{78}H_{66}Br_2NaO_{20}$ $[M+Na]^+$ *m/z* 1503.2406, found 1503.2451.

1,2-Di-*O*-(4-bromobenzyl)-sn-glyceryl β-D-glucopyranosyl-(1,6)-β-D-glucopyranoside

Methanolic NaOMe (1.0 M, 169 μL, 169 μmol) was added to a suspension of **6** (2.50 g, 1.69 mmol) in MeOH (35 mL) at rt, and the mixture was stirred under an atmosphere of nitrogen for 16 h, then diluted into MeOH (100 mL), and neutralised with Amberlyst resin (H^+ form), then filtered. The filtrate was evaporated in vacuo, and the residue was purified by flash chromatography (17:2:1 ✂ 7:2:1 EtOAc/MeOH/H_2O) to give the heptaol as a white solid (1.16 g, 91%): mp 57-60 °C; $[\alpha]^{24}_D$ -18.7 (*c* 1.00 in MeOH); ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.95-2.99 (2 H, m, H2',2"), 3.05-3.10 (3 H, m, H4',4",5"), 3.12-3.19 (2 H, m, H3',3"), 3.29-3.33 (1 H, m, H5'), 3.41-3.46 (1 H, m, H6"), 3.51-3.69 (5 H, m, H1,3,3,6',6"), 3.73-3.79 (1 H, m, H2), 3.83 (1 H, dd, *J* 10.6, 5.5 Hz, H1), 3.97-3.99 (1 H, m, H6'), 4.17 (1 H, d, *J* 7.7 Hz, H1'), 4.26 (1 H, d, *J* 7.8 Hz, H1"), 4.44-4.50 (3 H, m, CH_2O*H*, *sn*-1 CH_2PhBr), 4.56 (1 H, d, *J* 12.5 Hz, *sn*-2 CH_2PhBr), 4.62 (1 H, d, *J* 12.5 Hz, *sn*-2 CH_2PhBr), 4.89 (1 H, d, *J* 4.5 Hz, 2"-OH'), 4.93-4.94 (2 H, m), 5.02-5.03 (2 H, m, 3'-OH, 4'-OH, 3"-OH, 4"OH), 5.05 (1 H, d, *J* 5.0 Hz, 2'-OH), 7.27-7.32, 7.50-7.54 (8 H, 2m, Ar); ^{13}C NMR (125 MHz, methanol-d_4) δ 62.7 (C6"), 69.8 (C6'), 70.1 (C3), 71.39 (C4'), 71.44 (C4"), 71.53 (C1), 72.3 (*sn*-2 *C*H_2Ar), 73.4 (*sn*-1 *C*H_2Ar), 75.00 (C2'), 75.03 (C2"), 77.0 (C5"), 77.8 (C5'), 77.9 (C3"), 78.0 (C3'), 78.8 (C2), 104.6 (C1'), 104.8 (C1"), 122.26, 122.29 (2 C, C-Br), 130.6, 130.9, 132.38, 132.44, 138.99, 139.23 (10 C, Ar); IR ν 772.5, 1010.3, 1067.1, 1220.0, 1487.7, 2882.0, 1360.6 cm^{-1}; HRMS (ESI^+) calcd for $C_{29}H_{39}Br_2O_{13}$ $[M+H]^+$ *m/z* 753.0752, found 753.0742.

1,2-Di-*O*-(4-bromobenzyl)-sn-glyceryl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl-(1,6)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (7)

A solution of the heptaol (1.00 g, 1.33 mmol) in DMF (5.0 mL) was added to a stirred suspension of NaH in mineral oil (60%, 195 mg, 19.8 mmol) and imidazole (18.0 mg, 265 μmol) in DMF (2.0 mL) at 0 °C, and the resulting mixture was warmed to rt and stirred under nitrogen for 30 min. After the mixture had solidified, it was cooled to 0 °C and BnBr (2.05 mL, 17.2 mmol) was added. The mixture was warmed to rt and stirred under nitrogen for 48 h. The reaction mixture was diluted by slow addition of MeOH (30 mL), then water (200 mL) at 0 °C. The mixture was extracted with Et_2O (5 × 50 mL) and the combined organic phase was washed with brine (100 mL), dried ($MgSO_4$), filtered and the solvent evaporated in vacuo. The residue was purified by flash chromatography (22:4:1 ✂ 11:4:1 hexanes/CH_2Cl_2/acetone) to give **7** as a white solid (1.71 g, 91%): mp 141-149 °C; $[\alpha]^{21}_D$ +13.5 (*c* 1.00 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.40-3.51 (4 H, m, H2',2",4",5'), 3.54-3.59 (3 H, 3, m, H1,1,3), 3.60-3.65 (3 H, m, H3',4',5"), 3.67-3.77 (5 H, m, H2,3",6',6",6"), 4.02 (1 H, dd, *J* 10.5, 4.9 Hz, H3), 4.24 (1 H, dd, *J* 11.5, 2.0 Hz, H6'), 4.392 (2 H, br s, *sn*-1 CH_2Ar), 4.393 (1 H, d, *J* 7.8 Hz, H1'), 4.51 (1 H, d, *J* 7.9 Hz, H1"), 4.52 (1 H, d, *J* 12.1 Hz, *sn*-2 CH_2Ar), 4.55-4.61 (4 H, m, CH_2Ph), 4.56 (1 H, d, *J* 12.1 Hz, *sn*-2 CH_2Ar), 4.64 (1 H, d, *J* 12.4 Hz, CH_2Ph), 4.70 (1 H, d, *J* 11.0 Hz, CH_2Ph), 4.77 (1 H, d, *J* 11.1 Hz, CH_2Ph), 4.78 (1 H, d, *J* 11.0Hz, CH_2Ph), 4.82 (1 H, d, *J* 10.9 Hz, CH_2Ph), 4.819 (1 H, d, *J* 11.0 Hz, CH_2Ph), 4.84 (1 H, d, *J* 11.0 Hz, CH_2Ph), 4.90 (1 H, d, *J* 11.1 Hz, CH_2Ph), 4.92 (1 H, d, *J* 10.9 Hz, CH_2Ph), 4.96 (1 H, d, *J* 11.0 Hz, CH_2Ph), 5.00 (1 H, d, *J* 11.0 Hz, CH_2Ph), 7.12-7.45 (43 H, m, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 68.7 (C6"), 69.0 (C6'), 69.1 (C3), 70.7 (C1), 71.3 (*sn*-2 *C*H_2Ar), 72.6 (*sn*-1 *C*H_2Ar), 73.6, 74.77, 74.84 (3 C, *C*H_2Ph), 74.98 (C4"), 75.04, 75.09 (2 C, *C*H_2Ph), 75.2 (C4'), 75.8 (2 C, *C*H_2Ph), 77.4 (C2), 77.9 (C5"), 78.3 (C5'), 82.2 (C2'), 82.3 (C2"), 84.7 (C3'), 84.9 (C3"), 103.8 (C1'), 104.1 (C1"), 121.4, 121.5 (2 C, para-Ar), 127.7-128.5 (35 C, Ar), 129.2, 129.3, 131.45, 131.54 (8 C, Ar-*CH*), 137.4, 137.7, 138.1, 138.25, 138.26, 138.5, 138.59, 138.64, 138.66 (9 C, *ipso*-Ar); IR ν 695.4,

732.0, 772.2, 1064.0, 1218.2, 1360.0, 1453.6, 1738.4, 2866.3 cm^{-1}; HRMS (ESI^+) calcd for $C_{78}H_{80}Br_2NaO_{13}$ $[M+H]^+$ *m*/z 1405.3858, found 1405.3876.

1,2-Di-O-[4-(N,N-methylphenylamino)benzyl]-sn-glyceryl 2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl-(1,6)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (8)

A mixture of **7** (490 mg, 354 μmol), *N*-methylaniline (119 μL, 1.10 mmol), $Pd(OAc)_2$ (15.9 mg, 70.7 μmol), XPhos (101 mg, 212 μmol) and K_3PO_4 (300 mg, 1.41 mmol) in toluene (5 mL) was heated to 85 °C and stirred for 2 d under a nitrogen atmosphere. The reaction mixture was cooled to rt, diluted with EtOAc (60 mL), washed with aq. NaOH (2.0 M, 2 × 30 mL), dried ($MgSO_4$), filtered, and the solvent was evaporated in vacuo. The residue was purified by flash chromatography (22:4:1:0.1 ✂ 11:4:1:0.1 hexanes/CH_2Cl_2/acetone/Et_3N) to give **8** as a yellow oil (500 mg, 98%): $[\alpha]^{24}_D$ +12.5 (*c* 1.00 in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 3.27, 3.32 (6 H, 2s, CH_3), 3.45-3.58 (4 H, m, H2',2",4",5'), 3.60-3.86 (11 H, m, H1,1,2,3,3',3",4',5",6',6",6"), 4.10 (1 H, dd, *J* 10.4, 4.8 Hz, H3), 4.28 (1 H, dd, *J* 11.4, 1.8 Hz, H6'), 4.45 (1 H, d, *J* 12.0 Hz, sn-1 CH_2Ar), 4.46 (1 H, d, *J* 7.7 Hz, H1'), 4.78 (1 H, d, *J* 12.0 Hz, sn-1 CH_2Ar), 4.55 (1 H, d, *J* 7.9 Hz, H1"), 4.59 (1 H, d, *J* 10.2 Hz, sn-2 CH_2Ar), 4.62 (1 H, d, *J* 10.2 Hz, sn-2 CH_2Ar), 4.57-4.77, 4.80-4.90 (10 H, m, 5 × CH_2Ph), 4.94-5.09 (4 H, m, 2 × CH_2Ph), 6.94-7.10 (10 H, m, 2 × N*Ph*), 7.20-7.44 (43 H, m, Ar,Ph); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.31, 40.32 (2 C, CH_3), 68.7 (C6"), 69.0 (C6'), 69.4 (C3), 70.4 (C1), 71.8 (sn-2 *C*H_2Ar), 73.2, (sn-1 *C*H_2Ar), 73.6, 74.77, 74.80 (3 C, *C*H_2Ph), 74.96 (C4"), 74.99, 75.03, 75.1, 75.8 (4 C, *C*H_2Ph), 77.0 (C2), 77.9 (C5"), 78.3 (C5'), 82.1 (C2'), 82.3 (C2"), 84.7 (C3'), 84.9 (C3"), 103.9 (C1'), 104.1 (C1"), 120.2, 120.3, 120.4, 120.6, 121.2, 121.4 (10 C, N-Ph), 127.6-129.3 (43 C, Ph, Ar), 131.1, 131.5, 138.16, 138.27, 138.29, 138.5, 138.6, 138.7, 148.4, 148.5, 149.0, 149.1 (13 C, *ipso*-Ar); IR ν 697.1, 735.4, 750.1, 1028.4, 1067.7, 1344.1, 1453.9, 1496.5, 1513.8, 1595.0, 2867.1 cm^{-1}; HRMS (ESI^+) calcd for $C_{92}H_{97}N_2O_{13}$ $[M+H]^+$ *m*/z 1437.6985, found 1437.6965.

sn-Glyceryl 3-O-[2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl-(1,6)-2,3,6-tri-O-benzyl-β-D-glucopyranoside] (9)

The diamine **8** (755 mg, 525 μmol) was dissolved in 5% TFA soln. in CH_2Cl_2 (54 mL) at rt under an atmosphere of nitrogen, and stirred for 30 min. The reaction mixture was diluted with CH_2Cl_2 (150 mL), and washed sequentially with sat. aq. NH_4OH (2 × 50 mL), water (4 × 50 mL), and brine (4 × 50 mL), then dried ($MgSO_4$), filtered, and the solvent was evaporated in vacuo. The residue was purified by flash chromatography (2.5% ✂ 5% MeOH/CH_2Cl_2) to give the diol **9** as a white solid (530 mg, 96%): mp 153-154 °C; $[\alpha]^{23}_D$ +15.4 (*c* 1.00 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.40-3.83 (16 H, m, H1,1,2,2',2",3,3',3',3",4',4",5',5",6',6",6"), 4.20 (1 H, dd, *J* 11.6, 2.0 Hz, H6'), 4.39 (1 H, d, *J* 7.8 Hz, H1'), 4.51 (1 H, d, *J* 7.8 Hz, H1"), 4.54-4.69 (4 H, m, C*H*$_2$Ph), 4.74-5.04 (10 H, m, C*H*$_2$Ph), 7.16-7.42 (35 H, m, Ph); ^{13}C NMR (125 MHz, $CDCl_3$) δ 63.6 (C1), 68.8 (C6"), 69.0 (C6'), 70.8 (C2), 72.5 (C3), 73.6, 74.9, 75.01 (3 C, *C*H_2Ph), 75.05 (C4"), 75.09, 75.13, 75.76, 75.79 (5 C, C4', *C*H_2Ph), 78.0 (C5"), 78.3 (C5'), 82.2 (C2'), 82.3 (C2"), 84.75 (C3'), 84.76 (C3"), 104.0 (C1'), 104.1 (C1"), 127.7-128.6 (35 C, Ph), 137.9, 138.2, 138.3, 138.4, 138.5, 138.7 (7 C, ipso-Ph); IR ν 696.1, 749.9, 910.2, 1027.8, 1066.0, 1108.2, 1357.4, 1453.8, 2867.4, 3031.1, 3407.1 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{64}H_{70}KO_{13}$ $[M+K]^+$ *m*/z 1085.4448, found 1085.4449.

1,2-Di-O-[13-methyltetradecanoyl]-sn-glyceryl 2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl-(1,6)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (iso-C_{15} heptabenzyl diglyceride)

A solution of the diol **9** (50.0 mg, 47.7 μmol) in anhydrous DMF (600 μL) was added to a stirred solution of COMU (81.8 mg, 191 μmol), 13-methyltetradecanoic acid[6] (34.7 mg, 143 μmol), Hunig's base (24.9 μL, 143 μmol) and DMAP (17.5 mg, 143 μmol) in DMF (600 μL) at rt under an atmosphere of nitrogen. The mixture was heated to 85 °C for 24 h, then was diluted with EtOAc (30 mL) and washed with water (5 × 15 mL), brine (2 × 15 mL), then dried ($MgSO_4$), filtered, and the solvent was removed in vacuo. The residue was purified by flash chromatography (1% ✂ 50% EtOAc/toluene) to give the iso-C_{15} heptabenzyl diglyceride as a white solid (73.2 mg, 99%): mp 88-

90 °C; $[\alpha]^{24}_D$ +7.7 (*c* 3.40 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (12 H, d, *J* 6.6 Hz, $CH(CH_3)_2$), 1.11-1.20 (4 H, m, $CH_2CH(CH_3)_2$), 1.20-1.34 (32 H, m), 1.45-1.71 (6 H, m, $CH(CH_3)_2$, acyl-β), 2.18-2.23 (2 H, m, *sn*-2 acyl-α), 2.23-2.27 (2 H, m, *sn*-1 acyl-α), 3.40-3.52 (5 H, m, H2',4',5',2",3), 3.53-3.60 (1 H, m, H4"), 3.60-3.76 (6 H, m, H3',6',3",5",6",6"), 3.94 (1 H, dd, *J* 10.9, 4.6 Hz, H3), 4.12 (1 H, dd, *J* 11.9, 7.1 Hz, H1), 4.18-4.26 (2 H, m, H6',1), 4.31 (1 H, d, *J* 8.0 Hz, H1'), 4.44 (1 H, d, *J* 7.9 Hz, H1"), 4.50-4.58 (3 H, m, CH_2Ph), 4.62 (1 H, d, *J* 12.2 Hz, CH_2Ph), 4.67 (1 H, d, *J* 11.0 Hz, CH_2Ph), 4.72-4.85 (5 H, m, CH_2Ph), 4.87-5.08 (4 H, m, CH_2Ph), 5.11-5.22 (1 H, m, H2), 7.13-7.43 (35 H, m, Ph); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.8 (4 C, $CH(CH_3)_2$), 25.00, 25.05, 27.6, 28.1, 29.2, 29.3, 29.46, 29.47, 29.66, 29.68, 29.8-29.9, 30.1, 39.2 (22 C, 2 × $(CH_2)_{10}CH$), 34.2 (*sn*-1 acyl-α), 34.4 (*sn*-2 acyl-α), 62.8 (C1), 68.1 (C3), 68.8 (C6'), 69.0 (C6"), 70.0 (C2), 73.7, 74.81, 74.84 (3 C, CH_2Ph), 75.00 (C5'), 75.07, 75.10 (2 C, CH_2Ph), 75.2 (C5"), 75.78, 75.83 (2 C, CH_2Ph), 78.0 (C4"), 78.2 (C4'), 82.1 (C2'), 82.2 (C2"), 84.7 (C3'), 84.9 (C3"), 103.8 (C1'), 104.2 (C1"), 127.7-128.6 (35 C, Ar), 138.1, 138.29, 138.31, 138.5, 138.60, 138.67, 138.72 (7 C, *ipso*-Ph), 173.1 (*sn*-2 C=O), 173.4 (*sn*-1 C=O); IR ν 703.4, 732.1, 786.4, 851.0, 1015.3, 1258.8, 1716.8, 2963.3 cm^{-1}; HRMS (ESI^+) calcd for $C_{94}H_{126}NaO_{15}$ $[M+Na]^+$ *m*/z 1517.8989, found 1517.8989.

1,2-Di-O-[13-methyltetradecanoyl]-sn-glyceryl β-D-glucopyranosyl-(1,6)-β-D-glucopyranoside (10)

A mixture of $Pd(OH)_2$ (20% w/w on carbon, 23.4 mg, 33.4 μmol) and iso-C_{15} heptabenzyl diglyceride (74.0 mg, 47.7 μmol) in 1:1:1 AcOH/MeOH/THF (9 mL) was stirred under H_2 (40 atm) at rt for 3 d. The reaction mixture was filtered through a PTFE pad, and the reaction vial was rinsed with 1:1:1 AcOH/MeOH/THF (5 × 15 mL) with sonication, and the washings were filtered through the same PTFE pad. The combined filtrates were concentrated in vacuo, and AcOH azeotropically removed with toluene (4 × 50 mL). The residue was purified by flash chromatography (110:10:1 ✂ 11:10:1 $CHCl_3$/MeOH/H_2O) to give the iso-C_{15}-glycolipid **10** as a white solid (25.2 mg, 61%): mp

110-114 °C, $[\alpha]^{23}_D$ -18.5 (*c* 0.60 in $CHCl_3$); ^{1}H NMR (500 MHz, 9:1 methanol-d_4/$CDCl_3$) δ 0.82 (12 H, d, *J* 6.6 Hz, CH(CH_3)$_2$), 1.07-1.16 (4 H, m, CH_2CH(CH$_3$)$_2$), 1.16-1.37 (32 H, m), 1.47 (2 H, t of sept, *J* 6.6, 6.6 Hz, CH(CH$_3$)$_2$), 1.53-1.62 (4 H, m, *β*), 2.28 (1 H, t, *J* 7.5 Hz, *sn*-1 acyl-*α*), 2.29 (1 H, t, *J* 7.4 Hz, *sn*-2 acyl-*α*), 3.21 (1 H, dd, *J* 9.2, 7.7 Hz, H2''), 3.23 (1 H, dd, *J* 9.0, 7.8 Hz, H2'), 3.27 (1 H, ddd, *J* 10.1, 5.4, 2.2 Hz, H5''), 3.31 (1 H, dd, *J* 9.2, 9.0 Hz, H3''), 3.35 (1 H, dd, *J* 9.2, 9.0 Hz, H3'), 3.37 (1 H, dd, *J* 9.2, 9.6 Hz, H4'), 3.38 (1 H, dd, *J* 10.1, 9.0 Hz, H4''), 3.43 (1 H, ddd, *J* 9.6, 5.4, 2.1 Hz, H5'), 3.67 (1 H, dd, *J* 11.9, 5.4 Hz, H6''), 3.74 (1 H, dd, *J* 11.0, 5.6 Hz, H3), 3.83 (1 H, dd, *J* 11.5, 5.4 Hz, H6'), 3.92 (1 H, dd, *J* 11.9, 2.2 Hz, H6''), 4.11 (1 H, dd, *J* 11.0, 5.4 Hz, H3), 4.15 (1 H, *J* 11.5, 2.1 Hz, H6'), 4.21 (1 H, dd, *J* 12.1, 6.9 Hz, H1), 4.23 (1 H, d, *J* 7.8 Hz, H1'), 4.30 (1 H, d, *J* 7.7 Hz, H1''), 4.34 (1 H, dd, *J* 12.0, 3.0 Hz, H1), 5.23 (1 H, dddd, *J* 6.9, 5.6, 5.4, 3.0 Hz, H2); ^{13}C NMR (125 MHz, 9:1 methanol-d_4/$CDCl_3$) δ 22.8 (4 C, CH(*C*H$_3$)$_2$), 25.19, 25.21, 27.7, 28.3, 29.41, 29.43, 29.61, 39.81, 29.82, 29.9-30.0, 30.2, 39.4 (26 C, 2 × (*C*H$_2$)$_{10}$*C*H), 34.4 (*sn*-1 acyl-*α*), 34.6 (*sn*-2 acyl-*α*), 62.0 (C6''), 63.1 (C3), 68.4 (C1), 69.0 (C6'), 70.1 (C3'), 70.5 (C3''), 70.6 (C2), 73.8 (C2''), 73.9 (C2'), 75.7 (C5'), 76.54 (C4''), 76.57 (C5''), 76.8 (C4'), 103.7 (C1'), 103.9 (C1''), 174.2 (*sn*-2 C=O), 174.5 (*sn*-1 C=O); IR ν 720.9, 800.0, 1016.1, 1167.0, 1260.2, 1735.4, 2850.9, 2919.5, 2957.7, 3361.4 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{45}H_{88}NO_{15}$ $[M+NH_4]^+$ *m*/z 882.6148, found 882.6131.

1,2-Di-O-[14-methylpentadecanoyl]-sn-glyceryl 2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl-(1,6)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (iso-C_{16} heptabenzyl diglyceride)

A solution of **9** (67.8 mg, 64.7 μmol) in DMF (800 μL) was added to a stirred solution of COMU (111 mg, 259 μmol), 14-methylpentadecanoic acid[6] (47.1 mg, 194 μmol), Hunig's base (33.8 μL, 194 μmol) and DMAP (23.4 mg, 194 μmol) in DMF (800 μL), using the same procedure as for the synthesis of the iso-C_{15} heptabenzyl diglyceride. The residue was purified by flash chromatography (1% ⩤ 50% EtOAc/toluene) to give the iso-C_{16} heptabenzyl diglyceride as a white solid (85.1 mg, 86%): mp 86-89 °C; $[\alpha]^{24}_D$ +6.4 (*c* 0.90 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (12 H, d, *J*

6.7 Hz, CH(CH_3)$_2$), 1.11-1.20 (4 H, m, CH_2CH(CH$_3$)$_2$), 1.20-1.32 (36 H, m), 1.46-1.65 (6 H, m, CH(CH$_3$)$_2$, acyl-β), 2.17-2.22 (2 H, m, *sn*-2 acyl-α), 2.22-2.28 (2 H, m, *sn*-1 acyl-α), 3.36-3.53 (5 H, m, H3,2',4',5',2''), 3.53-3.59 (1 H, m, H4''), 3.59-3.76 (6 H, m, H3',6',3'',5'',6'',6''), 3.94 (1 H, dd, *J* 10.9, 4.6 Hz, H3), 4.12 (1 H, dd, *J* 11.8, 7.1 Hz, H1), 4.18-4.25 (2 H, m, H6', H1), 4.31 (1 H, d, *J* 7.7 Hz, H1'), 4.44 (1 H, d, *J* 7.9 Hz, H1''), 4.50-4.58 (3 H, m, CH_2Ph), 4.62 (1 H, d, *J* 12.2 Hz, CH_2Ph), 4.67 (1 H, d, *J* 11.0 Hz, CH_2Ph), 4.72-4.85 (5 H, m, CH_2Ph), 4.87-5.08 (4 H, m, CH_2Ph), 5.09-5.19 (1 H, m, H2), 7.11-7.40 (35 H, m, Ph); ^{13}C NMR (125 MHz, CDCl$_3$) δ 22.8 (4 C, CH(*C*H$_3$)$_2$), 25.00, 25.05, 27.6, 28.1, 29.25, 29.30, 29.46, 29.47, 29.66, 29.67, 29.81-29.88, 30.1, 39.2 (24 C, 2 × (CH$_2$)$_{11}$CH), 34.2 (*sn*-1 acyl-α), 34.4 (*sn*-2 acyl-α), 62.8 (C1), 68.1 (C3), 68.8 (C6'), 69.0 (C6''), 70.0 (C2), 73.7, 74.81, 74.84 (3 C, *C*H$_2$Ph), 75.00 (C5'), 75.07, 75.10 (2 C, *C*H$_2$Ph), 75.17 (C5''), 75.79, 75.82 (2 C, *C*H$_2$Ph), 77.9 (C4''), 78.2 (C4'), 82.1 (C2'), 82.2 (C2''), 84.7 (C3'), 84.9 (C3''), 103.8 (C1'), 104.2 (C1''), 127.7-128.6 (35 C, Ar), 138.1, 138.29, 138.30, 138.5, 138.60, 138.67, 138.71 (7 C, ipso-*Ph*), 173.1 (*sn*-2 C=O), 173.4 (*sn*-1 C=O); IR ν 703.4, 732.3, 779.0, 848.0, 1016.6, 1259.2, 1716.0, 2963.4 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{96}H_{130}NaO_{15}$ [M+Na]$^+$ *m*/z 1545.9302, found 1545.9302.

1,2-Di-O-[14-methylpentadecanoyl]-sn-glyceryl β-D-glucopyranosyl-(1,6)-β-D-glucopyranoside (11)

The iso-C$_{16}$ heptabenzyl diglyceride (85.0 mg, 55.8 μmol) was treated with hydrogen, as described for the synthesis of **10**. The residue was purified by flash chromatography (110:10:1 ✂ 11:10:1 CHCl$_3$/MeOH/H$_2$O) to give the iso-C$_{16}$-glycolipid **11** as a white solid (24.5 mg, 49%): mp 105-112 ^{o}C, [α]$^{24}_D$ -19.8 (*c* 0.80 in CHCl$_3$); ^{1}H NMR (500 MHz, 9:1 methanol-d_4/CDCl$_3$) δ 0.87 (12 H, d, *J* 6.6 Hz, CH(CH_3)$_2$), 1.12-1.20 (4 H, m, CH_2CH(CH$_3$)$_2$), 1.22-1.37 (36 H, m), 1.52 (2 H, t of sept, *J* 6.6, 6.6 Hz, CH(CH$_3$)$_2$), 1.56-1.65 (4 H, m, β), 2.31 (1 H, t, *J* 7.5 Hz, *sn*-1 acyl-α), 2.33 (1 H, t, *J* 7.4 Hz, *sn*-2 acyl-α), 3.20 (1 H, dd, *J* 9.2, 7.7 Hz, H2''), 3.23 (1 H, dd, *J* 9.0, 7.8 Hz, H2'), 3.27 (1 H, ddd, *J* 10.1, 5.4, 2.2 Hz, H5''), 3.31 (1 H, dd, *J* 9.2, 9.0 Hz, H3''), 3.35 (1 H, dd, *J* 9.2, 9.0 Hz,

H3'), 3.37 (1 H, dd, *J* 9.2, 9.6 Hz, H4'), 3.38 (1 H, dd, *J* 10.1, 9.0 Hz, H4''), 3.43 (1 H, ddd, *J* 9.6, 5.4, 2.1 Hz, H5'), 3.67 (1 H, dd, *J* 11.9, 5.4 Hz, H6''), 3.74 (1 H, dd, *J* 11.0, 5.6 Hz, H3), 3.76 (1 H, dd, *J* 11.5, 5.4 Hz, H6'), 3.87 (1 H, dd, *J* 11.9, 2.2 Hz, H6''), 3.98 (1 H, dd, *J* 11.0, 5.4 Hz, H3), 4.15 (1 H, *J* 11.5, 2.1 Hz, H6'), 4.21 (1 H, dd, *J* 12.1, 6.9 Hz, H1), 4.27 (1 H, d, *J* 7.8 Hz, H1'), 4.35 (1 H, d, *J* 7.7 Hz, H1''), 4.42 (1 H, dd, *J* 12.0, 3.0 Hz, H1), 5.27 (1 H, dddd, *J* 6.9, 5.6, 5.4, 3.0 Hz, H2); ^{13}C NMR (125 MHz, 9:1 methanol-d_4/$CDCl_3$) δ 23.0 (4 C, $CH(CH_3)_2$), 25.91, 25.92, 28.4, 29.0, 29.9, 30.08, 30.10, 30.2, 30.34, 30.35, 30.5-30.7, 30.9, 40.1 (24 C, 2 × $(CH_2)_{11}CH$), 34.9 (*sn*-1 acyl-α), 35.1 (*sn*-2 acyl-α), 62.6 (C6''), 63.9 (C3), 68.8 (C1), 69.8 (C6'), 71.2 (C3'), 71.4 (C3''), 71.6 (C2), 74.7 (C2''), 74.9 (C2'), 76.9 (C5'), 77.6 (C4''), 77.8 (2 C, C4',5''), 104.5 (C1'), 104.7 (C1''), 174.8 (*sn*-2 C=O), 175.0 (*sn*-1 C=O); IR ν 801.6, 1019.2, 1167.4, 1260.7, 1367.2, 1457.0, 1466.9, 1542.2, 1735.2, 2850.9, 2920.0, 3362.0 cm^{-1}; HRMS (ESI^+) calcd for $C_{47}H_{88}KO_{15}$ $[M+K]^+$ *m*/z 931.5755, found 931.5778.

1,2-Di-O-[15-methylhexadecanoyl]-sn-glyceryl 2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl-(1,6)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (iso-C_{17} heptabenzyl diglyceride)

The iso-C_{17} heptabenzyl diglyceride was prepared from **9** (150 mg, 147 μmol) and 15-methylhexadecanoic acid[6] (119 mg, 441 μmol) using the same procedure as for the synthesis of the iso-C_{15} heptabenzyl diglyceride. The residue was purified by flash chromatography (1% ✂ 50% EtOAc/toluene) to give the iso-C_{17}-diglyceride as a white solid (206 mg, 90%): mp 85-87 °C; $[\alpha]^{25}_D$ +6.2 (*c* 1.20 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (12 H, d, *J* 6.6 Hz, $CH(CH_3)_2$), 1.11-1.19 (4 H, m, $CH_2CH(CH_3)_2$), 1.19-1.33 (40 H, m), 1.47-1.62 (6 H, m, $CH(CH_3)_2$, acyl-*β*), 2.18-2.23 (2 H, m, *sn*-2 acyl-α), 2.23-2.28 (2 H, m, *sn*-1 acyl-α), 3.36-3.51 (5 H, m, H3,2',4',5',2''), 3.53-3.59 (1 H, m, H4''), 3.59-3.77 (6 H, m, H3',6',3'',5'',6'',6''), 3.93 (1 H, dd, *J* 10.8, 4.7 Hz, H3), 4.12 (1 H, dd, *J* 11.9, 7.1 Hz, H1), 4.18-4.26 (2 H, m, H1,6'), 4.32 (1 H, d, *J* 7.8 Hz, H1'), 4.45 (1 H, d, *J* 7.6 Hz, H1''), 4.51-4.57 (3 H, m, CH_2Ph), 4.63 (1 H, d, *J* 12.4 Hz, CH_2Ph), 4.67 (1 H, d, *J* 11.0 Hz, CH_2Ph), 4.75-4.79 (3 H, m, CH_2Ph), 4.81 (1 H, d, *J* 11.0 Hz, CH_2Ph), 4.83 (1 H, d, *J* 10.9 Hz,

CH_2Ph), 4.87-4.99 (4 H, m, CH_2Ph), 5.10-5.16 (1 H, m, H2), 7.13-7.37 (35 H, m, Ph); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.8 (4 C, CH(*C*H_3)$_2$), 25.0, 25.1, 27.6, 28.1, 29.26, 29.31, 29.47, 29.48, 29.67, 29.68, 29.82, 29.84, 29.85, 29.87, 29.88, 29.89, 29.90, 30.1, 39.2 (26 C, $(CH_2)_{12}$CH), 34.2 (*sn*-1 acyl-α), 34.4 (*sn*-2 acyl-α), 62.9 (C1), 68.1 (C3), 68.8 (C6'), 69.1 (C6''), 70.0 (C2), 73.7, 74.81, 74.84 (3 C, *C*H_2Ph), 75.0 (C5'), 75.07, 75.11 (2 C, *C*H_2Ph), 75.2 (C5''), 75.79, 75.83 (2 C, *C*H_2Ph), 78.0 (C4''), 78.2 (C4'), 82.1 (C2'), 82.2 (C2''), 84.7 (C3'), 84.9 (C3''), 103.8 (C1'), 104.2 (C1''), 127.7-128.6 (35 C, Ar), 138.1, 138.31, 138.32, 138.5, 138.61, 138.68, 138.73 (7 C, ipso-*Ph*), 173.1 (*sn*-2 C=O), 173.4 (*sn*-1 C=O); IR ν 698.2, 737.3, 801.7, 1028.1, 1071.6, 1166.9, 1261.9, 1361.2, 1453.6, 1497.3, 1731.5, 2852.9, 2923.1 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{98}H_{134}NaO_{15}$ $[M+Na]^+$ *m*/z 1573.9615, found 1573.9615.

1,2-Di-O-[15-methylhexadecanoyl]-sn-glyceryl β-D-glucopyranosyl-(1,6)-β-D-glucopyranoside (12)

The iso-C_{17} heptabenzyl diglyceride (108 mg, 69.7 μmol) was treated with hydrogen, as described for the synthesis of **10**. The residue was purified by flash chromatography (110:10:1 ✂ 11:10:1 $CHCl_3$/MeOH/H_2O) to give the iso-C_{17}-glycolipid **12** as a white solid (43.2 mg, 67%): mp 106-107 ^{o}C, $[\alpha]^{25}_D$ -20.2 (*c* 1.00 in $CHCl_3$); ^{1}H NMR (500 MHz, 9:1 methanol-d_4/$CDCl_3$) δ 0.86 (12 H, d, *J* 6.6 Hz, CH(C*H*$_3$)$_2$), 1.12-1.18 (4 H, m, C*H*$_2$CH(CH$_3$)$_2$), 1.20-1.39 (40 H, m), 1.51 (2 H, t of sept, *J* 6.6, 6.6 Hz, C*H*(CH$_3$)$_2$), 1.56-1.64 (4 H, m, *β*), 2.31 (1 H, t, *J* 7.5 Hz, *sn*-1 acyl-α), 2.32 (1 H, t, *J* 7.4 Hz, *sn*-2 acyl-α), 3.20 (1 H, dd, *J* 9.2, 7.7 Hz, H2''), 3.24 (1 H, dd, *J* 9.0, 7.8 Hz, H2'), 3.27 (1 H, ddd, *J* 10.1, 5.4, 2.2 Hz, H5''), 3.31 (1 H, dd, *J* 9.2, 9.0 Hz, H3''), 3.35 (1 H, dd, *J* 9.2, 9.0 Hz, H3'), 3.37 (1 H, dd, *J* 9.2, 9.6 Hz, H4'), 3.38 (1 H, dd, *J* 10.1, 9.0 Hz, H4''), 3.43 (1 H, ddd, *J* 9.6, 5.4, 2.1 Hz, H5'), 3.67 (1 H, dd, *J* 11.9, 5.4 Hz, H6''), 3.74 (1 H, dd, *J* 11.0, 5.6 Hz, H3), 3.77 (1 H, dd, *J* 11.5, 5.4 Hz, H6'), 3.86 (1 H, dd, *J* 11.9, 2.2 Hz, H6''), 3.97 (1 H, dd, *J* 11.0, 5.4 Hz, H3), 4.15 (1 H, *J* 11.5, 2.1 Hz, H6'), 4.21 (1 H, dd, *J* 12.1, 6.9 Hz, H1), 4.27 (1 H, d, *J* 7.8 Hz, H1'), 4.35 (1 H, d, *J* 7.7 Hz, H1''), 4.41 (1 H, dd, *J* 12.0, 3.0 Hz, H1), 5.26 (1 H, dddd, *J* 6.9, 5.6, 5.4, 3.0 Hz, H2);

^{13}C NMR (125 MHz, 9:1 methanol-d_4/$CDCl_3$) δ 23.0 (4 C, $CH(CH_3)_2$), 25.76, 25.78, 28.3, 28.8, 29.9, 30.0, 30.17, 30.18, 30.35, 30.38, 30.48, 30.50, 30.52, 30.54, 30.8, 39.9 (26 C, $(CH_2)_{12}CH$), 34.8 (*sn*-1 acyl-α), 35.0 (*sn*-2 acyl-α), 62.5 (C6''), 63.7 (C3), 68.7 (C1), 69.6 (C6'), 70.9 (C3'), 71.2 (C3''), 71.3 (C2), 74.5 (C2''), 74.6 (C2'), 76.6 (C5'), 77.3 (C4''), 77.5 (C5''), 77.5 (C4'), 104.4 (C1'), 104.5 (C1''), 174.6 (*sn*-2 C=O), 174.9 (*sn*-1 C=O); IR ν 720.8, 800.2, 1016.6, 1167.0, 1260.3, 1467.2, 1733.7, 2850.7, 2919.0, 3364.8 cm^{-1}; HRMS (ESI^+) calcd for $C_{49}H_{92}KO_{15}$ $[M+K]^+$ *m*/z 959.6073, found 959.6050.

1,2-Di-O-hexadecanoyl-sn-glyceryl 2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl-(1,6)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (palmityl heptabenzyl diglyceride)

The diol **9** (71.2 mg, 68.0 μmol) and palmitic acid (49.4 mg, 204 μmol) were processed according to the procedure for the synthesis of the iso-C_{15} heptabenzyl diglyceride. The residue was purified by flash chromatography (1% ✂ 50% EtOAc/toluene) to give the heptabenzyl C_{16}-diglyceride as a white solid (79.1 mg, 76%): mp 93-94 °C; $[\alpha]^{25}_D$ +12.0 (*c* 1.10 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (6 H, t, *J* 7.0 Hz, CH_3), 1.20-1.35 (48 H, m), 1.47-1.61 (4 H, m, acyl-β), 2.17-2.22 (2 H, m, *sn*-2 acyl-α), 2.22-2.26 (2 H, m, *sn*-1 acyl-α), 3.36-3.50 (5 H, m, H3,2',4',5',2''), 3.53-3.59 (1 H, m, H4''), 3.59-3.76 (6 H, m, H3',6',3'',5'',6'',6''), 3.93 (1 H, dd, *J* 10.9, 4.7 Hz, H3), 4.12 (1 H, dd, *J* 11.9, 7.1 Hz, H1), 4.16-4.24 (2 H, m, H1,6'), 4.30 (1 H, d, *J* 7.8 Hz, H1'), 4.43 (1 H, d, *J* 7.9 Hz, H1''), 4.51-4.57 (3 H, m, CH_2Ph), 4.61 (1 H, d, *J* 12.2 Hz, CH_2Ph), 4.67 (1 H, d, *J* 11.1 Hz, CH_2Ph), 4.73-4.84 (5 H, m, CH_2Ph), 4.88-4.98 (4 H, m, CH_2Ph), 5.10-5.16 (1 H, m, H2), 7.14-7.35 (35 H, m, Ph); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.3 (2 C, CH_3), 22.8, 25.0, 25.1, 29.26, 29.31, 29.47, 29.48, 29.52, 29.67, 29.69, 29.8-29.9, 32.1 (26 C, $(CH_2)_{13}$), 34.2 (*sn*-1 acyl-α), 34.4 (*sn*-2 acyl-α), 62.9 (C1), 68.1 (C3), 68.8 (C6'), 69.1 (C6''), 70.0 (C2), 73.7, 74.81, 74.84 (3 C, CH_2Ph), 75.0 (C5'), 75.07, 75.11 (2 C, CH_2Ph), 75.2 (C5''), 75.79, 75.83 (2 C, CH_2Ph), 78.0 (C4''), 78.2 (C4'), 82.1 (C2'), 82.2 (C2''), 84.7 (C3'), 84.9 (C3''), 103.8 (C1'), 104.2 (C1''), 127.7-128.6 (35 C, Ar), 138.1, 138.31, 138.32, 138.5, 138.61, 138.68, 138.72 (7 C, ipso-*Ph*), 173.1 (*sn*-2 C=O), 173.4 (*sn*-1 C=O);

IR ν 696.2, 734.8, 753.0, 798.7, 911.3, 1015.9, 1067.4, 1164.5, 1206.1, 1260.0, 1307.7, 1360.8, 1453.9, 1497.3, 1731.2, 2851.1, 2919.4 cm^{-1}; HRMS (ESI^+) calcd for $C_{96}H_{130}NaO_{15}$ $[M+Na]^+$ *m*/z 1545.9302, found 1545.9302.

1,2-Di-O-hexadecanoyl-sn-glyceryl β-D-glucopyranosyl-(1,6)-β-D-glucopyranoside (13)

The heptabenzyl C_{16}-diglyceride (58.0 mg, 38.1 μmol) was treated with hydrogen as described for the synthesis of **10**. The residue was purified by flash chromatography (110:10:1 ✂ 11:10:1 $CHCl_3$/MeOH/H_2O) to give the C_{16}-diglyceride **13** as a white solid (32.9 mg, 97%): mp 200-205 °C, $[\alpha]^{25}_D$ +12.0 (*c* 1.10 in $CHCl_3$); ^1H NMR (500 MHz, 9:1 methanol-d_4/$CDCl_3$) δ 0.89 (6 H, t, *J* 6.9 Hz, CH_3), 1.15-1.41 (48 H, m), 1.55-1.66 (4 H, m, *β*), 2.32 (1 H, t, *J* 7.5 Hz, *sn*-1 acyl-*α*), 2.33 (1 H, t, *J* 7.4 Hz, *sn*-2 acyl-*α*), 3.21 (1 H, dd, *J* 9.2, 7.7 Hz, H2''), 3.25 (1 H, dd, *J* 9.0, 7.8 Hz, H2'), 3.28 (1 H, ddd, *J* 10.1, 5.4, 2.2 Hz, H5''), 3.31 (1 H, dd, *J* 9.2, 9.0 Hz, H3''), 3.35 (1 H, dd, *J* 9.2, 9.0 Hz, H3'), 3.37 (1 H, dd, *J* 9.2, 9.6 Hz, H4'), 3.38 (1 H, dd, *J* 10.1, 9.0 Hz, H4''), 3.43 (1 H, ddd, *J* 9.6, 5.4, 2.1 Hz, H5'), 3.68 (1 H, dd, *J* 11.9, 5.4 Hz, H6''), 3.76 (1 H, dd, *J* 11.0, 5.6 Hz, H3), 3.78 (1 H, dd, *J* 11.5, 5.4 Hz, H6'), 3.87 (1 H, dd, *J* 11.9, 2.2 Hz, H6''), 3.98 (1 H, dd, *J* 11.0, 5.4 Hz, H3), 4.15 (1 H, *J* 11.5, 2.1 Hz, H6'), 4.23 (1 H, dd, *J* 12.1, 6.9 Hz, H1), 4.28 (1 H, d, *J* 7.8 Hz, H1'), 4.36 (1 H, d, *J* 7.7 Hz, H1''), 4.42 (1 H, dd, *J* 12.0, 3.0 Hz, H1), 5.27 (1 H, dddd, *J* 6.9, 5.6, 5.4, 3.0 Hz, H2); ^{13}C NMR (125 MHz, 9:1 methanol-d_4/$CDCl_3$) δ 14.3 (2 C, CH_3), 23.4, 25.78, 25.80, 29.95, 29.97, 30.15, 30.17, 30.18, 30.4-30.6, 32.8 (26 C, $(CH_2)_{13}$), 34.9 (*sn*-1 acyl-*α*), 35.1 (*sn*-2 acyl-*α*), 62.6 (C6''), 63.8 (C3), 68.8 (C1), 69.8 (C6'), 71.2 (C3'), 71.4 (C3''), 71.5 (C2), 74.6 (C2''), 74.7 (C2'), 76.7 (C5'), 77.5 (C4''), 77.6 (C5''), 77.7 (C4'), 104.5 (C1'), 104.6 (C1''), 174.7 (*sn*-2 C=O), 174.9 (*sn*-1 C=O); IR ν 720.9, 803.9, 1072.1, 1167.5, 1260.4, 1734.5, 2850.4, 2917.6, 3364.5 cm^{-1}; HRMS (ESI^+) calcd for $C_{47}H_{88}KO_{15}$ $[M+K]^+$ *m/z* 915.6015, found 915.6023

1,2-Di-O-dodecanoyl-sn-glyceryl β-D-glucopyranosyl-(1,6)-β-D-glucopyranoside (14)

Lauryl chloride (43.4 μL, 172 μmol) was added to a solution of the diol **9** (30.0 mg, 28.6 μmol) and DMAP (3.50 mg, 28.6 μmol), in pyridine (6 mL), and the mixture was stirred at rt under an atmosphere of nitrogen for 24 h. The solvent was evaporated in vacuo, and the residue was dissolved into Et_2O (80 mL), and then washed sequentially with 0.1 M aq. HCl (5 × 50 mL), water (3 × 20 mL), sat. aq. $NaHCO_3$ (3 × 20 mL), and brine (2 × 20 mL), then dried ($MgSO_4$), filtered, and the solvent was evaporated in vacuo. The crude diglyceride was dissolved in 1:1:1 AcOH/MeOH/THF (5 mL), then $Pd(OH)_2$ (20% w/w on carbon, 14.1 mg, 20.0 μmol) was added and the mixture was stirred under H_2 (40 atm) at rt for 3 d. The reaction mixture was filtered through a PTFE pad, and the reaction vial was rinsed with 1:1:1 AcOH/MeOH/THF (5 × 15 mL) with sonication, and the washings were filtered through the same PTFE pad. The combined filtrates were concentrated in vacuo, and azeotropic removal of AcOH from the residue in vacuo was performed with toluene (4 × 50 mL). The residue was purified by flash chromatography (110:10:1 ✂ 11:10:1 $CHCl_3$/MeOH/H_2O) to give C_{12}-diglyceride **14** as a colourless oil (11.4 mg, 51%): $[\alpha]^{27}_D$ -9.7 (*c* 1.10 in 1:1 $CHCl_3$/MeOH); ^{1}H NMR (500 MHz, 9:1 methanol-d_4/$CDCl_3$) δ 0.87 (6 H, t, *J* 6.9 Hz, CH_3), 1.21-1.34 (32 H, m), 1.51-1.65 (4 H, m, *β*), 2.32 (2 H, t, *J* 7.5 Hz, *sn*-1 acyl-*α*), 2.33 (2 H, t, *J* 7.4 Hz, *sn*-2 acyl-*α*), 3.21 (1 H, dd, *J* 9.2, 7.7 Hz, H2"), 3.25 (1 H, dd, *J* 9.0, 7.8 Hz, H2'), 3.28 (1 H, ddd, *J* 10.1, 5.4, 2.2 Hz, H5"), 3.31 (1 H, dd, *J* 9.2, 9.0 Hz, H3"), 3.35 (1 H, dd, *J* 9.2, 9.0 Hz, H3'), 3.37 (1 H, dd, *J* 9.2, 9.6 Hz, H4'), 3.38 (1 H, dd, *J* 10.1, 9.0 Hz, H4"), 3.43 (1 H, ddd, *J* 9.6, 5.4, 2.1 Hz, H5'), 3.68 (1 H, dd, *J* 11.9, 5.4 Hz, H6"), 3.76 (1 H, dd, *J* 11.0, 5.6 Hz, H3), 3.78 (1 H, dd, *J* 11.5, 5.4 Hz, H6'), 3.87 (1 H, dd, *J* 11.9, 2.2 Hz, H6"), 3.96 (1 H, dd, *J* 11.0, 5.4 Hz, H3), 4.15 (1 H, *J* 11.5, 2.1 Hz, H6'), 4.23 (1 H, dd, *J* 12.1, 6.9 Hz, H1), 4.28 (1 H, d, *J* 7.8 Hz, H1'), 4.36 (1 H, d, *J* 7.7 Hz, H1"), 4.40 (1 H, dd, *J* 12.0, 3.0 Hz, H1), 5.26 (1 H, dddd, *J* 6.9, 5.6, 5.4, 3.0 Hz, H2); ^{13}C NMR (125 MHz, 9:1 methanol-d_4/$CDCl_3$) δ 14.5 (2 C, CH_3), 23.4, 25.43, 25.45, 29.91, 29.93, 30.13, 30.16, 30.4-30.6, 32.7 (18 C, $(CH_2)_9$), 34.9 (*sn*-1 acyl-*α*), 35.1 (*sn*-2 acyl-*α*), 62.5 (C6"), 63.6 (C3), 68.8 (C1), 69.6 (C6'), 70.9 (C3'), 71.1 (C3"), 71.3 (C2), 74.4 (C2"),

74.5 (C2'), 76.5 (C5'), 77.3 (C4''), 77.4 (C5''), 77.5 (C4'), 104.39 (C1'), 104.43 (C1''), 174.7 (*sn*-2 C=O), 175.0 (*sn*-1 C=O); HRMS (ESI^+) calcd for $C_{39}H_{76}NO_{15}$ $[M+NH_4]^+$ *m/z* 798.5210, found 798.5208.

1,2-Di-O-octanoyl-sn-glyceryl β-D-glucopyranosyl-(1,6)-β-D-glucopyranoside (15)

The diol **9** (30.0 mg, 28.6 μmol), caprylyl chloride (29.3 μL, 172 μmol), and DMAP (3.50 mg, 28.6 μmol) in pyridine (6 mL), followed by hydrogenolysis of the crude material over $Pd(OH)_2$ (20% w/w on carbon, 14.1 mg, 20.0 μmol) were processed using the same procedure as for the synthesis of **14**. The residue was purified by flash chromatography (110:10:1 ✂ 11:10:1 $CHCl_3$/MeOH/H_2O) to give the C_8-diglyceride **15** as a colourless oil (10.1 mg, 53%): $[\alpha]^{24}_D$ -8.6 (*c* 1.00 in 1:1 $CHCl_3$/MeOH); ^1H NMR (500 MHz, 9:1 methanol-d_4/$CDCl_3$) δ 0.87 (6 H, t, *J* 6.9 Hz, CH_3), 1.20-1.35 (16 H, m), 1.54-1.64 (4 H, m, *β*), 2.30 (2 H, t, *J* 7.5 Hz, *sn*-1 acyl-*α*), 2.31 (2 H, t, *J* 7.4 Hz, *sn*-2 acyl-*α*), 3.21 (1 H, dd, *J* 9.2, 7.7 Hz, H2''), 3.25 (1 H, dd, *J* 9.0, 7.8 Hz, H2'), 3.28 (1 H, ddd, *J* 10.1, 5.4, 2.2 Hz, H5''), 3.31 (1 H, dd, *J* 9.2, 9.0 Hz, H3''), 3.35 (1 H, dd, *J* 9.2, 9.0 Hz, H3'), 3.37 (1 H, dd, *J* 9.2, 9.6 Hz, H4'), 3.38 (1 H, dd, *J* 10.1, 9.0 Hz, H4''), 3.43 (1 H, ddd, *J* 9.6, 5.4, 2.1 Hz, H5'), 3.68 (1 H, dd, *J* 11.9, 5.4 Hz, H6''), 3.76 (1 H, dd, *J* 11.0, 5.6 Hz, H3), 3.78 (1 H, dd, *J* 11.5, 5.4 Hz, H6'), 3.87 (1 H, dd, *J* 11.9, 2.2 Hz, H6''), 3.95 (1 H, dd, *J* 11.0, 5.4 Hz, H3), 4.15 (1 H, *J* 11.5, 2.1 Hz, H6'), 4.23 (1 H, dd, *J* 12.1, 6.9 Hz, H1), 4.28 (1 H, d, *J* 7.8 Hz, H1'), 4.36 (1 H, d, *J* 7.7 Hz, H1''), 4.38 (1 H, dd, *J* 12.0, 3.0 Hz, H1), 5.25 (1 H, dddd, *J* 6.9, 5.6, 5.4, 3.0 Hz, H2); ^{13}C NMR (125 MHz, 9:1 methanol-d_4/$CDCl_3$) δ 14.5 (2 C, CH_3), 23.4, 25.75, 25.77, 29.8, 29.90, 29.92, 32.57, 32.58 (10 C, $(CH_2)_5$), 34.9 (*sn*-1 acyl-*α*), 35.1 (*sn*-2 acyl-*α*), 62.6 (C6''), 63.7 (C3), 68.8 (C1), 69.7 (C6'), 70.9 (C3'), 71.2 (C3''), 71.4 (C2), 74.5 (C2''), 74.6 (C2'), 76.5 (C5'), 77.3 (C4''), 77.45 (C5''), 77.54 (C4'), 104.46 (C1'), 104.49 (C1''), 174.7 (*sn*-2 C=O), 175.0 (*sn*-1 C=O); HRMS (ESI^+) calcd for $C_{31}H_{56}NaO_{15}$ $[M+Na]^+$ *m/z* 691.3512, found 691.3545.

1,2-Di-O-butanoyl-sn-glyceryl β-D-glucopyranosyl-(1,6)-β-D-glucopyranoside (16)

The diol **9** (30.0 mg, 28.6 μmol), butyric anhydride (28.7 μL, 172 μmol), and DMAP (3.50 mg, 28.6 μmol), in pyridine (6.00 mL), followed by hydrogenolysis of the crude material over $Pd(OH)_2$ (20% w/w on carbon, 14.1 mg, 20.0 μmol) were processed using the same procedure as for the synthesis of **14**. The residue was purified by flash chromatography (110:10:1 ✂ 11:10:1 $CHCl_3$/MeOH/H_2O) to give the C_4-diglyceride **16** as a colourless oil (8.6 mg, 54%): $[\alpha]^{24}_D$ -17.0 (*c* 0.50 in MeOH); ^{1}H NMR (500 MHz, methanol-d_4) δ 0.94 (3 H, t, *J* 7.3 Hz, CH_3), 0.95 (3 H, t, *J* 7.3 Hz, CH_3), 1.58-1.69 (4 H, m, *β*), 2.28-2.36 (4 H, m, α), 3.12-3.50 (8 H, m, H2',2",3',3",4',4",5',5"), 3.63-3.69 (1 H, m, H6"), 3.72-3.79 (2 H, m, H3,6'), 3.84-8.90 (1 H, m, H6"), 3.98 (1 H, dd, *J* 11.0, 5.6 Hz, H3), 4.12-4.18 (1 H, m, H6'), 4.22 (1 H, dd, *J* 12.2, 6.6 Hz, H1), 4.27 (1 H, d, *J* 7.8 Hz, H1'), 4.37 (1 H, d, *J* 7.8 Hz, H1"), 4.41 (1 H, dd, *J* 12.0, 3.2 Hz, H1), 5.23-5.29 (1 H, m, H2); ^{13}C NMR (125 MHz, methanol-d_4) δ 12.5 (2 C, CH_3), 17.96, 17.98 (2 C, *β*), 35.36, 35.58 (2 C, *α*), 61.3 (C6"), 62.5 (C3), 67.5 (C1), 68.5 (C6'), 70.0 (C3'), 70.2 (C3"), 70.3 (C2), 73.5 (C2"), 73.7 (C2'), 75.7 (C5'), 76.41 (C4"), 76.58 (2 H, C4', C5"), 103.22 (C1'), 103.51 (C1"), 173.3 (*sn*-2 C=O) 173.5 (*sn*-1 C=O); HRMS (ESI$^+$) calcd for $C_{23}H_{44}NO_{15}$ $[M+NH_4]^+$ *m/z* 574.2706, found 574.2693.

1,2,5,6-Tetra-O-(4-bromobenzyl)-3,4-O-isopropylidene-D-mannitol

A solution of 3,4-*O*-isopropylidene-D-mannitol[7] (750 mg, 3.37 mmol) in DMF (6 mL) was added to a stirred suspension of NaH in mineral oil (60%, 675 mg, 16.9 mmol) and imidazole (4.6 mg, 67.5 μmol) in DMF (4 mL) at 0 °C, and then the mixture was warmed to rt and stirred under nitrogen for 30 min. After the mixture had solidified, it was cooled to 0 °C and a solution of PBB-Br (5.27 g, 21.1 mmol) in DMF (6 mL) was added. The mixture was warmed to rt and stirred under nitrogen for 24 h. The reaction mixture was diluted by slow addition of MeOH (10 mL) at 0 °C, then the solvent was evaporated in vacuo. The residue was dissolved in EtOAc (50 mL) then washed with water (3 × 50 mL) and brine (3 × 50 mL), then dried ($MgSO_4$), filtered and evaporated in vacuo. The residue was purified by flash chromatography (22:4:1 ✂ 11:4:1 hexanes/CH_2Cl_2/acetone)

affording the product as a colourless oil (3.02 g, 100%); $[\alpha]^{22}_{D}$ +16.8 (*c* 1.00 in CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.36 (6 H, s, 2 × CH_3), 3.59 (2 H, dd, *J* 11.1, 6.8 Hz, H1,6), 3.69-3.73 (4 H, m, H1,6,2,5), 4.12-4.15 (2 H, m, H3,4), 4.39 (2 H, d, *J* 12.3 Hz, C*H*$_2$Ph), 4.41 (2 H, d, *J* 12.3 Hz, C*H*$_2$Ph), 4.50 (2 H, d, *J* 12.0 Hz, C*H*$_2$Ph), 4.65 (2 H, d, *J* 12.0 Hz, C*H*$_2$Ph), 7.11-7.17, 7.37-7.47 (16 H, 2m, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.4 (2 C, 2 × CH_3), 70.7 (2 C, C1,6), 72.2, 72.7 (4 C, *C*H$_2$Ph), 78.5 (2 C, C3,4), 79.6 (2 C, C2,5), 110.0 (*C*$(CH_3)_2$), 121.58, 121.61, 129.3, 129.5, 131.5, 131.6, 137.3, 137.5 (24 C, Ar); IR ν 666.7, 754.3, 771.8, 801.0, 832.7, 872.5, 1010.5, 1068.7, 1165.0, 1219.0, 1237.8, 1369.7, 1379.9, 1403.3, 1487.2, 1593.1, 1725.7, 2866.2, 2986.0 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{37}H_{39}Br_4O_6$ $[M+H]^+$ *m*/*z* 894.9475, found 894.9451.

1,2,5,6-Tetra-O-(4-bromobenzyl)-D-mannitol

A solution of 1,2,5,6-tetra-*O*-(4-bromobenzyl)-3,4-*O*-isopropylidene-D-mannitol (3.02 g, 3.36 mmol) in 70% aq. AcOH (30 mL) was heated under reflux in a nitrogen atmosphere for 3 h. After cooling to rt, the solvent was evaporated in vacuo, and residual aq. AcOH was removed from the residue through formation of an azeotrope with toluene (3 × 50 mL). The residue was purified by flash chromatography (17:2:1 ✂ 7:2:1 toluene/CH_2Cl_2/MeOH), affording the diol as a colourless oil (2.38 g, 82%); $[\alpha]^{25}_{D}$ -2.9 (*c* 1.00 in CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.90-3.07 (2 H, m, 3-O*H*, 4-O*H*), 3.65 (2 H, dd, *J* 9.8, 4.8 Hz, H1,6), 3.71 (2 H, dd, *J* 9.8, 4.0 Hz, H1,6), 3.71-3.76 (2 H, m, H2,5), 3.90-3.96 (2 H, m, H3,4), 4.47 (2 H, d, *J* 11.4 Hz, C*H*$_2$Ph), 4.49 (2 H, d, *J* 11.4 Hz, C*H*$_2$Ph), 4.54 (2 H, d, *J* 11.7 Hz, C*H*$_2$Ph), 4.66 (2 H, d, *J* 11.7 Hz, C*H*$_2$Ph), 7.13-7.21, 7.41-7.48 (16 H, 2m, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 69.9 (2 C, C3,4), 70.3 (2 C, C1,6), 72.5, 72.9 (4 C, *C*H$_2$Ph), 79.4 (2 C, C2,5), 121.8, 121.9, 129.4, 129.6, 131.69, 131.70, 137.0, 137.2 (24 C, Ar); IR ν 751.7, 771.0, 801.1, 1010.6, 1069.0, 1218.9, 1487.3, 1593.5, 2866.5, 2917.3, 3470.5 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{34}H_{35}Br_4O_6$ $[M+H]^+$ *m*/*z* 854.9162, found 854.9154.

1,2-Di-*O*-(4-bromobenzyl)-sn-glycerol (5)

A solution of $NaIO_4$ (3.26 g, 15.3 mmol) in water (8 mL) was added to a solution of 1,2,5,6-tetra-*O*-(4-bromobenzyl)-D-mannitol (2.38 g, 2.77 mmol) in THF (40 mL) and the reaction mixture was stirred at rt for 2.5 h, then diluted into EtOAc (160 mL). The organic phase was collected and washed with brine (3 × 100 mL) and water (3 × 100 mL) in cycles until the organic phase appeared clear. The organic phase was dried ($MgSO_4$), filtered and evaporated in vacuo. Water (11 mL) and $NaBH_4$ (2.51 g, 66.4 mmol) were added to a solution of the residue in EtOH (90 mL) at 0 °C, then the reaction mixture was warmed to rt and stirred under nitrogen for 3 h. The reaction mixture was neutralised by slow addition of 50% aq. AcOH at 0 °C, then was diluted into water (350 mL) and extracted with Et_2O (3 × 100 mL). The combined extracts were washed with sat. aq. $NaHCO_3$ (80 mL) and brine (80 mL), then dried ($MgSO_4$), filtered, and evaporated in vacuo. The residue was purified by flash chromatography (10:4:1 ✂ 5:4:1 hexanes/CH_2Cl_2/acetone), affording **5** as a colourless oil (2.03 g, 85%); $[\alpha]^{24}_D$ -8.1 (*c* 1.00 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.15 (1 H, s, CH_2OH), 3.58 (1 H, dd, *J* 9.9, 5.2 Hz, H1), 3.61 (1 H, dd, *J* 9.9, 4.9 Hz, H1), 3.67 (1 H, dd, *J* 13.6, 2.6 Hz, H3), 3.68 (1 H, dddd, *J* 6.4, 5.2, 4.9, 2.6 Hz, H2), 3.76 (1 H, dd, *J* 13.6, 6.4 Hz, H3), 4.46 (1 H, d, *J* 12.5 Hz, CH_2PhBr), 4.49 (1 H, d, *J* 12.5 Hz, CH_2PhBr), 4.58 (1 H, d, *J* 12.1 Hz, CH_2Ar), 4.63 (1 H, d, *J* 12.1 Hz, CH_2Ar), 7.16-7.23, 7.44-7.50 (8 H, 2m, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 63.0 (C3), 70.5 (C1), 71.6 (CHOCH_2Ph), 72.9 (CH_2OCH_2Ph), 78.4 (C2), 121.77, 121.80, 129.4, 129.5, 131.7, 137.0, 137.4 (12 C, Ar); IR ν 772.9, 793.5, 800.9, 1010.3, 1068.0, 1219.7, 1404.4, 1486.9, 1591.4, 1699.4, 2867.8, 3421.3 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{17}H_{19}Br_2O_3$ $[M+H]^+$ *m*/*z* 428.9696, found 428.9692.

1,2-Di-*O*-benzyl-sn-glyceryl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1,6)-2,3,6-tri-*O*-benzoyl-β-D-glucopyranoside (18)

A mixture of thioglycoside **4** (1.40 g, 1.19 mmol), 1,2-di-*O*-benzyl-sn-glycerol **17**[8] (389 mg, 1.43 mmol), powdered molecular sieves (4 Å, 2.50 g) and NIS (669 mg, 2.97 mmol) in CH_2Cl_2 (35 mL)

was stirred under nitrogen at rt for 30 min, then cooled to 0 °C. TfOH in CH_2Cl_2 (0.01 M, 1.19 mL, 11.9 μmol) was added, and the mixture was stirred for 5 min at 0 °C. The mixture was diluted into CH_2Cl_2 (100 mL) and filtered. The filtrate was washed sequentially with sat. aq. $NaHCO_3$ (2 × 100 mL), aq. $Na_2S_2O_3$ (0.5 M, 2 × 50 mL), sat. aq. $NaHCO_3$ (2 × 100 mL), brine (2 × 100 mL), dried ($MgSO_4$), filtered, and the solvent was removed in vacuo. The crude material was purified by flash chromatography (9:4:1 ✂ 5:4:1 hexanes/CH_2Cl_2/acetone) to give the glycosyl glyceride **18** as a white foam (1.55 g, 98%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.45 (2 H, d, *J* 4.8 Hz, H1,1), 3.55-3.62 (2 H, m, H2,3), 3.79 (1 H, dd, *J* 12.3, 6.1 Hz, H3), 3.89 (1 H, dd, *J* 11.4, 7.6 Hz, H6'), 3.96 (1 H, ddd, *J* 9.5, 7.6, 1.9 Hz, H5'), 4.04 (1 H, ddd, *J* 9.7, 5.0, 3.2 Hz, H5''), 4.08 (1 H, dd, *J* 11.5, 1.9 Hz, H6'), 4.28 (1 H, d, *J* 12.7 Hz, C*H*$_2$Ph), 4.30 (1 H, d, *J* 12.7 Hz, C*H*$_2$Ph), 4.40 (1 H, dd, *J* 12.2, 5.0 Hz, H6''), 4.53 (1 H, d, *J* 12.0 Hz, C*H*$_2$Ph), 4.56 (1 H, dd, *J* 12.2, 3.2 Hz, H6''), 4.58 (1 H, d, *J* 12.0 Hz, C*H*$_2$Ph), 4.73 (1 H, d, *J* 7.9 Hz, H1'), 5.04 (1 H, d, *J* 7.9 Hz, H1''), 5.34 (1 H, dd, *J* 9.7, 9.5 Hz, H4'), 5.42 (1 H, dd, *J* 9.8, 7.9 Hz, H2'), 5.53 (1 H, dd, *J* 9.7, 7.9 Hz, H2''), 5.63 (1 H, dd, *J* 9.7, 9.7 Hz, H4''), 5.79 (1 H, dd, *J* 9.7, 9.7 Hz, H3'), 5.90 (1 H, dd, *J* 9.7, 9.7 Hz, H3''), 7.20-7.58 (31 H, m, Ph), 7.77-8.05 (14 H, m, Ph); ^{13}C NMR (125 MHz, $CDCl_3$) δ 63.0 (C6''), 68.5 (C6'), 69.0 (C3), 69.7 (C4''), 70.0 (C4'), 70.2 (2 C, C1, *C*H_2Ph), 72.0 (C2'), 72.2 (C2''), 72.3 (C5''), 72.9 (*C*H_2Ph), 73.0 (C3'), 73.3 (C3''), 74.1 (C5'), 77.3 (C2), 101.2 (C1'), 101.4 (C1''), 127.5-130.0 (47 C, Ph), 128.8, 128.92, 128.94, 129.99, 129.4 129.5, 129.7 (7 C, ipso-Ph), 165.1, 165.24, 165.25, 165.5, 165.79, 165.83, 166.2 (7 C, C=O).

1,2-Di-*O*-benzyl-sn-glyceryl β-D-glucopyranosyl-(1,6)-β-D-glucopyranoside (19)

Methanolic NaOMe (1.0 M, 75.5 μL, 75.5 μmol) was added to a suspension of **18** (1.0 g, 755 μmol) in MeOH (15.0 mL) at rt, and the mixture was stirred under an atmosphere of nitrogen for 16 h, then diluted into MeOH (100 mL) neutralised with Amberlyst resin (H^+ form), then filtered. The filtrate was evaporated in vacuo, and the residue was purified by flash chromatography (17:2:1 ✂ 7:2:1 EtOAc/MeOH/H_2O) to give the heptaol **19** as a white solid (446 mg, 99%): mp 62-70 °C;

$[\alpha]^{26}_{D}$ -19.4 (*c* 3.35 in MeOH); ^{1}H NMR (500 MHz, methanol-d_4) δ 3.19-3.49 (8 H, m, H2',2",3',3",4',4",5',5"), 3.61-3.70 (3 H, m, H3,3,6"), 3.73 (1 H, dd, *J* 10.5, 4.8, H1), 3.79 (1 H, dd, *J* 11.5, 5.5 Hz, H6'), 3.82-3.89 (2 H, m, H2,6"), 3.99 (1 H, dd, *J* 10.5, 4.6 Hz, H1), 4.16 (1 H, dd, *J* 11.5, 1.8 Hz, H6'), 4.29 (1 H, d, *J* 7.7 Hz, H1'), 4.39 (1 H, d, *J* 7.7 Hz, H1"), 4.52 (1 H, d, *J* 12.6 Hz, CH_2Ph), 4.54 (1 H, d, *J* 12.6 Hz, CH_2Ph), 4.65 (1 H, d, *J* 12.6 Hz, CH_2Ph), 4.69 (1 H, d, *J* 12.6 Hz, CH_2Ph), 4.78-4.85 (7 H, br s, 7 × OH), 7.23-7.39 (10 H, m, 2 × Ph); ^{13}C NMR (500 MHz, methanol-d_4) δ 62.6 (C6"), 69.8 (C6'), 70.1 (C3), 71.2 (C4'), 71.3 (C4"), 71.4 (C1), 73.2, 74.2 (2 C, *C*H_2Ph), 74.9 (C2'), 75.0 (C2"), 76.9 (C5"), 77.7 (C5'), 77.80 (C3"), 77.85 (C3'), 78.6 (C2), 104.6 (C1'), 104.7 (C1"), 128.59, 128.64, 128.8, 129.1, 139.6, 139.7 (12 C, Ph); HRMS (ESI$^+$) calcd for $C_{29}H_{40}NaO_{13}$ $[M+Na]^+$ *m/z* 619.2361, found 619.2361.

sn-Glyceryl 3-*O*-[β-D-glucopyranosyl-(1,6)-β-D-glucopyranoside] (20)

A mixture of **19** (190 mg, 318 μmol) and $Pd(OH)_2$ (20% w/w on carbon, 22.4 mg, 31.8 μmol) in 1:1:1 AcOH/MeOH/THF (3.0 mL) was stirred under H_2 (40 atm) at rt for 20 min. The reaction mixture was filtered through a PTFE pad, and the reaction vial was rinsed with 1:1:1 AcOH/MeOH/THF (5 × 10 mL) with sonication, and the washings were filtered through the same PTFE pad. The combined filtrates were concentrated in vacuo, and azeotropic removal of AcOH from the residue in vacuo was performed with toluene (4 × 20 mL). The residue was purified by flash chromatography (110:10:1 ✂ 11:10:1 $CHCl_3$/MeOH/H_2O) to give **20** as a colourless gum (132 mg, 99%): $[\alpha]^{23}_{D}$ -30.8 (*c* 1.00 in MeOH); ^{1}H NMR (400 MHz, methanol-d_4) δ 3.14-3.88 (16 H, m), 4.17 (1 H, m, H6'), 4.28 (1 H, d, *J* 7.9 Hz, H1'), 4.35 (1 H, d, *J* 7.8 Hz, H1"); ^{13}C NMR (100 MHz, methanol-d_4) δ 62.6 (C6"), 63.9 (C1), 69.8 (C6'), 71.5 (2 C, C4',4"),72.3 (C2), 73.1 (C3), 74.9, 75.0 (2 C, C2',2"), 76.8, 77.6 (2 C, C5',5"), 77.8, 77.9 (2 C, C3',3"), 104.6, 104.8 (2 C, C1',1"); IR ν 925.6, 1011.3, 1165.9, 1228.7, 1365.8, 1643.9, 1748.3, 2887.9, 3310.2 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{15}H_{28}NaO_{13}$ $[M+Na]^+$ *m/z* 439.1423, found 439.1425.

15-Methylhexadecyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1,6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranoside (22)

A mixture of thioglycoside **4** (200 mg, 170 μmol), 15-methylhexadecanol **21**[6] (47.9 mg, 187 μmol), NIS (95.6 mg, 425 μmol), and powdered molecular sieves (4 Å, 2.50 g) in anhydrous CH_2Cl_2 (5 mL) was stirred under nitrogen atmosphere at rt for 30 min, then cooled to 0° C. A solution of TfOH in CH_2Cl_2 (0.01 M, 170 μL, 1.70 μmol) was added, and the mixture was stirred for 5 min at 0 °C, then diluted into CH_2Cl_2 (100 mL) and filtered. The filtrate was washed sequentially with sat. aq. $NaHCO_3$ (2 × 100 mL), aq. $Na_2S_2O_3$ (0.5 M, 2 × 50 mL), sat. aq. $NaHCO_3$ (2 × 100 mL), brine (2 × 100 mL), then dried ($MgSO_4$), filtered, and the solvent was removed in vacuo. The residue was purified by flash chromatography (9:4:1 ✂ 5:4:1 hexanes/CH_2Cl_2/acetone) to give iso-C_{17}-glucoside **22** as a colourless oil (170 mg, 77%): $[\alpha]^{23}_D$ -2.4 (*c* 1.00 in $CHCl_3$); ^{1}H NMR (500 MHz, 1:1 methanol-d_4/$CDCl_3$) δ 0.88 (6 H, d, *J* 6.7 Hz, 2 × CH_3), 0.90-1.40 (26 H, m), 1.53 (1 H, t of sept, *J* 6.7, 6.7 Hz, C*H*$(CH_3)_2$), 3.18 (1 H, ddd, *J* 9.8, 7.4, 5.4 Hz, OC*H*$_2$CH$_2$), 3.62 (1 H, ddd, *J* 9.8, 5.8, 5.8 Hz, OC*H*$_2$CH$_2$), 3.89 (1 H, dd, *J* 11.4, 8.0 Hz, H6), 4.02 (1 H, ddd, *J* 9.9, 8.0, 1.8 Hz, H5), 4.09 (1 H, dd, *J* 11.4, 1.8 Hz, H6), 4.15 (1 H, ddd, *J* 9.8, 5.1, 3.2 Hz, H5'), 4.44 (1 H, dd, *J* 12.2, 5.2 Hz, H6'), 4.61 (1 H, d, *J* 7.9 Hz, H1), 4.62 (1 H, dd, *J* 12.2, 3.1 Hz, H6'), 5.03 (1 H, d, *J* 7.8 Hz, H1'), 5.32 (1 H, dd, *J* 9.9, 9.7 Hz, H4), 5.40 (1 H, dd, *J* 9.8, 7.9 Hz, H2), 5.53 (1 H, dd, *J* 9.8, 7.8 Hz, H2'), 5.65 (1 H, dd, *J* 9.8, 9.7 Hz, H4'), 5.82 (1 H, dd, *J* 9.8, 9.7 Hz, H3), 5.90 (1 H, dd, *J* 9.7, 9.7 Hz, H3'), 7.23-7.59, 7.78-8.04 (35 H, m, Ph); ^{13}C NMR (125 MHz, 1:1 methanol-d_4/$CDCl_3$) δ 22.8 (2 C, CH_3), 25.9, 27.5, 28.1, 29.3-30.1, 39.2 (14 C, $(CH_2)_{13}$CH), 63.1 (C6'), 68.9 (C6), 69.6 (C4), 70.1 (2 C, C4', OCH_2CH$_2$), 71.99 (C2), 72.04 (C2'), 72.4 (C5'), 72.96 (C3'), 72.98 (C3), 74.1 (C5), 101.1 (C1), 101.5 (C1'), 128.3-128.6, 128.8, 128.86, 128.89, 129.0, 129.4, 129.5, 129.6, 129.8-130.0, 133.18, 133.240, 133.245, 133.33, 133.34, 133.54, 133.57 (Ph), 165.1, 165.2, 165.3, 165.5, 165.8, 165.9, 166.2 (7 C, C=O); IR ν 685.9, 706.4, 755.9, 801.8, 834.2, 854.7, 936.5, 975.3, 1027.1, 1068.4, 1093.6, 1105.5, 1177.7, 1260.8, 1315.2, 1367.2, 1451.5, 1492.4, 1584.9, 1602.5,

1724.1, 2853.9, 2924.6, 3063.4 cm^{-1}; HRMS (ESI^+) calcd for $C_{78}H_{88}NO_{18}$ $[M+NH_4]^+$ *m/z* 1326.5996, found 1326.5999.

15-Methylhexadecyl β-D-glucopyranosyl-(1,6)-β-D-glucopyranoside (23)

A suspension of **22** (170 mg, 130 μmol) in MeOH (5.00 mL) was treated with methanolic NaOMe (1.0 M, 50 μL, 50 μmol) using the same procedure as for the synthesis of **19**. The crude material was purified by flash chromatography (110:10:1 ✂ 11:10:1 $CHCl_3$/MeOH/H_2O) to give the heptaol **23** as a white solid (70.6 mg, 94%): mp 141-150 °C; $[\alpha]^{25}_D$ -25.7 (*c* 1.00 in 4:3 H_2O/EtOH); ^1H NMR (500 MHz, 1:1 methanol-d_4/$CDCl_3$) δ 0.83 (6 H, d, *J* 6.6 Hz, 2 × CH_3), 1.10-1.15 (2 H, m, CH_2CH(CH_3)$_2$), 1.18-1.38 (22 H, m), 1.48 (1 H, t of sept, *J* 6.6, 6.6 Hz, CH(CH_3)$_2$), 1.56-1.61 (2 H, m, OCH$_2$CH_2), 3.18-3.30 (3 H, m, H2,2',5), 3.33-3.44 (4 H, m, H3,3',4',5'), 3.45-3.54 (2 H, m, H4, OCH_2CH$_2$), 3.71 (1 H, dd, *J* 12.0, 4.8 Hz, H6'), 3.78-3.90 (3 H, m, H6,6', OCH_2CH$_2$), 4.10 (1 H, dd, *J* 11.0, 2.0 Hz, H6), 4.24 (1 H, d, *J* 7.8 Hz, H1), 4.33 (1 H, d, *J* 7.8 Hz, H1'); ^{13}C NMR (125 MHz, 1:1 methanol-d_4/$CDCl_3$) δ 22.8 (2 C, CH_3), 26.3, 27.8, 28.4, 29.95, 30.04, 30.05, 30.08, 30.11, 30.3, 39.5 (14 C, $(CH_2)_{13}CH$), 61.9 (C6'), 69.0 (C6), 70.2 (C4), 70.4 (C4'), 70.7 (O*C*H$_2$CH$_2$), 73.9 (2 C, C2,2'), 75.6 (C5), 76.8 (C5'), 76.7 (C3), 76.8 (C3'), 103.5 (C1), 103.8 (C1'); IR ν 800.2, 909.0, 1022.8, 1070.7, 1167.7, 1260.9, 1366.4, 1416.9, 1466.3, 1560.1, 1644.9, 2853.0, 2922.6, 3365.0 cm^{-1}; HRMS (ESI^+) calcd for $C_{29}H_{56}NaO_{11}$ $[M+Na]^+$ *m/z* 603.3715, found 603.3724.

1,2-Di-*O*-(4-bromobenzyl)-sn-glyceryl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (25)

4-Methylphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-1-thio-glucopyranoside **24**[9] (473 mg, 673 μmol) and 1,2-di-*O*-(4-bromobenzyl)-sn-glycerol **17** (318 mg, 740 μmol) were treated as for the synthesis of **6**. The crude material was purified by flash chromatography (9:4:1 ✂ 5:4:1 hexanes/CH_2Cl_2/acetone) to give the glycosyl glyceride **25** as a white foam (582 mg, 86%): mp 46-49 °C; $[\alpha]^{25}_D$ +14.1 (*c* 1.00 in CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$) δ 3.44 (1 H, dd, *J* 10.2, 5.4 Hz, H1), 3.49 (1 H, dd, *J* 10.2, 4.2 Hz, H1), 3.71 (1 H, dddd, *J* 5.4, 5.4, 5.0, 4.2 Hz, H2), 3.77 (1 H, dd, *J* 10.4, 5.4 Hz, H3), 4.04 (1

H, dd, *J* 10.4, 5.0 Hz, H3), 4.16 (1 H, ddd, *J* 10.0, 5.0, 3.2 Hz, H5'), 4.22 (1 H, d, *J* 12.0 Hz, C*H*$_2$Ar), 4.25 (1 H, d, *J* 12.0 Hz, C*H*$_2$Ar), 4.48 (1 H, d, *J* 12.2 Hz, C*H*$_2$Ar), 4.533 (1 H, d, *J* 12.2 Hz, C*H*$_2$Ar), 4.534 (1 H, dd, *J* 12.1, 5.0 Hz, H6'), 4.67 (1 H, dd, *J* 12.1, 3.2 Hz, H6'), 4.93 (1 H, d, *J* 7.8 Hz, H1'), 5.57 (1 H, dd, *J* 9.9, 7.8 Hz, H2'), 5.72 (1 H, dd, *J* 10.0, 9.5 Hz, H4'), 5.93 (1 H, dd, *J* 9.9, 9.5 Hz, H3'), 7.05 (2 H, d, *J* 8.2 Hz, *sn*-2 *ortho*-Ar), 7.11 (2 H, d, *J* 8.3 Hz, *sn*-1 *ortho*-Ar), 7.28-7.59, 7.85-8.05 (24 H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 63.2 (C6'), 69.1 (C3), 69.8 (C4'), 70.0 (C1), 71.4 (*C*H$_2$Ar), 72.0 (C2'), 72.4 (C5'), 72.6 (*C*H$_2$Ar), 72.9 (C3'), 77.0 (C2), 101.5 (C1'), 121.4, 121.48, 128.4, 128.50, 128.52, 128.53, 128.84, 128.86, 129.2, 129.26, 129.29, 129.6, 129.82, 129.84, 129.88, 129.92, 131.46, 131.50, 133.28, 133.37, 133.43, 133.6, 137.2, 137.5 (Ar), 165.1, 165.3, 165.9, 166.2 (4 C, C=O); IR ν 686.4, 708.2, 756.9, 803.0, 832.8, 937.9, 976.1, 1012.1, 1026.9, 1068.6, 1092.3, 1177.3, 1262.3, 1315.0, 1368.0, 1451.4, 1488.3, 1584.8, 1601.8, 1724.8, 2870.6, 3066.0 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{51}H_{48}Br_2NO_{12}$ $[M+ NH_4]^+$ *m/z* 1024.1538, found 1024.1534.

1,2-Di-*O*-(4-bromobenzyl)-sn-glyceryl β-D-glucopyranoside (26)

Tetrabenzoate **25** (582 mg, 577 μmol) was treated with methanolic NaOMe (1.0 M, 120 μL, 120 μmol) using the same procedure as for the synthesis of **19**. The crude material was purified by flash chromatography (17:2:1 ✂ 7:2:1 EtOAc/MeOH/H_2O) to give the tetraol **26** as a colourless oil (260 mg, 76%): $[\alpha]^{25}_D$ -6.3 (*c* 1.00 in MeOH); ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.22-3.26 (1 H, m, H2'), 3.27-3.37 (2 H, m, H4',5'), 3.39-3.43 (1 H, m, H3'), 3.66 (1 H, dd, *J* 10.4, 5.9 Hz, H1), 3.68-3.74 (1 H, m, H6'), 3.71 (1 H, dd, *J* 10.4, 3.7 Hz, H1), 3.76 (1 H, dd, *J* 10.6, 4.7 Hz, H3), 3.85-3.94 (2 H, m, H2, H6'), 4.03 (1 H, dd, *J* 10.6, 4.9 Hz, H3), 4.32 (1 H, d, *J* 7.6 Hz, H1'), 4.51 (2 H, s, C*H*$_2$Ar), 4.64 (1 H, d, *J* 12.1 Hz, C*H*$_2$Ar), 4.69 (1 H, d, *J* 12.1 Hz, C*H*$_2$Ar), 7.26 (2 H, d, *J* 8.2 Hz, *ortho*-Ar), 7.31 (2 H, d, *J* 8.1 Hz, *ortho*-Ar), 7.47 (2 H, d, *J* 8.1 Hz, *meta*-Ar), 7.49 (2 H, d, *J* 8.2 Hz, *meta*-Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 62.7 (C6'), 69.9 (C3), 71.4 (C1), 71.5 (C4'), 72.3, 73.4 (2 C, *C*H$_2$Ar), 74.98 (C2'), 77.86 (2 C, C3',5'), 78.8 (C2), 104.5 (C1'), 122.22, 122.24, 130.5, 130.7, 132.3, 132.4,

138.9, 139.1 (Ar); IR ν 794.6, 894.3, 1011.2, 1035.6, 1067.0, 1166.0, 1203.8, 1363.3, 1406.2, 1456.7, 1487.8, 1593.6, 1640.2, 2871.4, 3352.3 cm^{-1}; HRMS (ESI^+) calcd for $C_{23}H_{32}Br_2NO_8$ $[M+NH_4]^+$ *m/z* 608.0490, found 608.0485.

1,2-Di-*O*-(4-bromobenzyl)-sn-glyceryl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (27)

A solution of the tetraol **26** (260 mg, 439 μmol) in DMF (750 μL) was added to a stirred suspension of NaH in mineral oil (60%, 87.8 mg, 2.20 mmol) and imidazole (1.20 mg, 176 μmol) in DMF (500 μL) at 0 °C, and then the mixture was warmed to rt and stirred under nitrogen for 30 min. After the mixture had solidified, it was cooled to 0 °C and BnBr (326 μL, 2.74 mmol) was added. The mixture was warmed to rt and stirred under nitrogen for 48 h, and then was diluted by slow addition of MeOH (10 mL), then water (50 mL) at 0 °C. The mixture was extracted with Et_2O (3 × 30 mL) and the combined organic phases were washed with brine (50 mL), dried ($MgSO_4$), filtered and the solvent evaporated in vacuo. The residue was purified by flash chromatography (22:4:1 ✂ 11:4:1 hexanes/CH_2Cl_2/acetone) to give **27** as a colourless oil (270 mg, 65%): $[\alpha]^{26}_D$ +2.6 (*c* 1.00 in MeOH); ^1H NMR (600 MHz, $CDCl_3$) δ 3.43-3.48 (1 H, m, H5'), 3.46 (1 H, dd, *J* 10.0, 7.8 Hz, H2'), 3.628 (1 H, dd, *J* 10.0, 9.8 Hz, H4'), 3.634 (1 H, dd, *J* 10.3, 5.9 Hz, H1), 3.67-3.76 (2 H, m, H6',6'), 3.68 (1 H, dd *J* 10.3, 4.1 Hz, H1), 3.718 (1 H, dd, *J* 10.0, 9.8 Hz, H3'), 3.723 (1 H, dd, *J* 10.4, 5.4 Hz, H3), 3.83 (1 H, dddd, *J* 5.9, 5.4, 4.7, 4.1 Hz, H2), 4.07 (1 H, dd, *J* 10.4, 4.7 Hz, H3), 4.43 (1 H, d, *J* 7.8 Hz, H1'), 4.45 (2 H, s, CH_2Ar), 4.55 (1 H, d, *J* 12.2 Hz, CH_2Ph), 4.56 (1 H, d, *J* 10.8 Hz, CH_2Ph), 4.62 (1 H, d, *J* 12.2 Hz, CH_2Ph), 4.62 (1 H, d, *J* 12.3 Hz, CH_2Ar), 4.65 (1 H, d, *J* 12.3 Hz, CH_2Ar), 4.71 (1 H, d, *J* 11.1 Hz, CH_2Ph), 4.82 (1 H, d, *J* 11.0 Hz, CH_2Ph), 4.85 (1 H, d, *J* 10.8 Hz, CH_2Ph), 4.90 (1 H, d, *J* 11.1 Hz, CH_2Ph), 4.94 (1 H, d, *J* 11.0 Hz, CH_2Ph), 7.16-7.46 (28 H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 69.0 (C6'), 69.1 (C3), 70.7 (C1), 71.4, 72.7, 73.6, 74.8 (4 C, *C*H_2Ar), 75.0 (C5'), 75.1, 75.8 (2 C, *C*H_2Ar), 77.4 (C2), 77.9 (C4'), 82.3 (C2'), 84.7 (C3'), 104.0 (C1'), 121.46, 121.54, 127.73, 127.74, 127.8, 127.9, 128.00, 128.01, 128.1, 128.4, 128.49, 128.50, 128.51, 129.30, 129.34, 131.5, 131.6, 137.4, 137.7, 138.2, 138.2, 138.5, 138.7 (Ar); IR ν 697.6,

736.1, 804.0, 911.0, 1011.8, 1028.4, 1069.2, 1207.3, 1274.7, 1307.0, 1360.8, 1404.3, 1454.0, 1487.9, 1593.5, 1731.0, 2866.5, 3030.5, 3064.0 cm^{-1}; HRMS (ESI^+) calcd for $C_{51}H_{56}Br_2NO_8$ $[M+NH_4]^+$ *m/z* 968.2368, found 968.2342.

1,2-Di-*O*-[4-(*N*,*N*-methylphenylamino)benzyl]-sn-glyceryl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside

N-Methylaniline (91.7 μL, 846 μmol) was added to a stirred mixture of **27** (260 mg, 273 μmol), $Pd(OAc)_2$ (12.3 mg, 54.6 μmol), XPhos (78.1 mg, 164 μmol) and K_3PO_4 (232 mg, 1.09 mmol) in toluene (3.82 mL) at rt, under an atmosphere of nitrogen, then the mixture was heated to 85 °C and stirred for 2 d. After completion as judged by ESI-MS, the reaction mixture was cooled to rt, diluted with EtOAc (60 mL), washed with aq. NaOH (2.0 M, 2 × 30 mL), dried ($MgSO_4$), filtered, and the solvent was evaporated in vacuo. The residue was purified by flash chromatography (22:4:1:0.1 ✂ 11:4:1:0.1 hexanes/CH_2Cl_2/acetone/Et_3N) to give the diamine as a yellow oil (249 mg, 90%): $[\alpha]^{27}_D$ +3.3 (*c* 1.00 in $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 3.31, 3.32 (6 H, 2s, 2 × CH_3), 3.49 (1 H, ddd, *J* 9.0, 4.4, 2.2 Hz, H5'), 3.51 (1 H, dd, *J* 9.0, 7.8 Hz, H2'), 3.66 (1 H, dd, *J* 9.0, 9.0 Hz, H4'), 3.69 (1 H, dd, *J* 9.0, 9.0 Hz, H3'), 3.70 (1 H, dd, *J* 10.3, 5.6 Hz, H1), 3.742 (1 H, dd, *J* 10.3, 4.4 Hz, H1), 3.743 (1 H, dd, *J* 10.7, 4.4 Hz, H6'), 3.78 (1 H, dd, *J* 10.7, 2.2 Hz, H6'), 3.80 (1 H, dd, *J* 10.4, 5.4 Hz, H3), 3.92 (1 H, dddd, *J* 5.6, 5.4, 4.8, 4.4 Hz, H2), 4.12 (1 H, dd, *J* 10.4, 4.8 Hz, H3), 4.48 (1 H, d, *J* 7.8 Hz, H1'), 4.51 (2 H, s, CH_2Ar), 4.58 (1 H, d, *J* 12.2 Hz, CH_2Ph), 4.59 (1 H, d, *J* 10.8 Hz, CH_2Ph), 4.66 (1 H, d, *J* 12.2 Hz, CH_2Ph), 4.68 (2 H, s, CH_2Ar), 4.75 (1 H, d, *J* 11.0 Hz, CH_2Ph), 4.84 (1 H, d, *J* 11.0 Hz, CH_2Ph), 4.87 (1 H, d, *J* 10.8 Hz, CH_2Ph), 4.97 (1 H, d, *J* 11.0 Hz, CH_2Ph), 4.98 (1 H, d, *J* 11.0 Hz, CH_2Ph), 6.96-7.08, 7.19-7.40 (38 H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.3 (2 C, CH_3), 69.0 (C6'), 69.4 (C3), 70.3 (C1), 71.9, 73.3, 73.6, 74.8 (4 C, *C*H_2Ph), 75.0 (C5'), 75.1, 75.8 (2 C, *C*H_2Ph), 77.0 (C2), 77.92 (C4'), 82.33 (C2'), 84.75 (C3'), 104.01 (C1'), 120.1, 120.4, 120.5, 120.7, 121.3, 121.5, 127.67, 127.69, 127.8, 127.9, 128.0, 128.1, 128.2, 128.43, 128.45, 128.48, 129.0, 129.1, 129.27, 129.29, 138.25, 138.27, 138.6, 138.7, 148.56, 148.60, 149.05,

149.07 (Ar); IR ν 697.5, 750.2, 822.4, 869.9, 1070.3, 1253.6, 1343.6, 1454.0, 1496.6, 1514.1, 1595.2, 2862.4, 3033.0 cm^{-1}; HRMS (ESI^+) calcd for $C_{65}H_{68}KN_2O_8$ $[M+K]^+$ *m/z* 1043.4608, found 1043.4632.

sn-Glyceryl 3-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside) (28)

A solution of the above diamine (245 mg, 244 μmol) was dissolved into a solution of TFA in CH_2Cl_2 (5% v/v, 24.4 mL) at rt under an atmosphere of nitrogen, and the solution was stirred for 30 min. The reaction mixture was diluted with CH_2Cl_2 (75 mL), and washed sequentially with sat. aq. NH_4OH (2 × 25 mL), water (4 × 25 mL), and brine (4 × 25 mL), then dried ($MgSO_4$), filtered, and the solvent was evaporated in vacuo. The residue was purified by flash chromatography (2.5% ✂ 5% MeOH/CH_2Cl_2) to give the diol **28** as a white solid (90.0 mg, 60%): mp 67-69 °C; $[\alpha]^{24}_D$ +9.9 (*c* 0.50 in $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 3.45 (1 H, dd, *J* 7.8, 9.2 Hz, H2'), 3.50-3.58 (4 H, m, H1,4',5',6'), 3.62-3.71 (3 H, m, H1,3',6'), 3.75 (1 H, dd, *J* 11.5, 6.8 Hz, H3), 3.84-3.88 (1 H, m, H2), 3.93 (1 H, dd, *J* 11.5, 2.6 Hz, H3), 4.41 (1 H, d, *J* 7.8 Hz, H1'), 7.23-7.38 (20 H, Ph); ^{13}C NMR (125 MHz, $CDCl_3$) δ 63.5 (C1), 69.1 (C6'), 71.3 (C2), 73.7 (C3), 74.0 (CH_2Ph), 74.6 (C4'), 75.1, 75.2, 75.9 (3 C, *C*H_2Ph), 78.0 (C5'), 82.3 (C3'), 84.8 (C2'), 104.5 (C1'), 127.8, 127.94, 127.97, 128.00, 128.03, 128.15, 128.18, 128.19, 128.55, 128.56, 128.58, 137.8, 138.0, 138.4, 138.6 (Ph); IR ν 659.1, 693.9, 715.7, 751.8, 853.4, 910.3, 934.5, 999.0, 1028.1, 1044.8, 1065.6, 1087.2, 1120.9, 1148.3, 1207.5, 1280.6, 1342.5, 1362.0, 1400.4, 1452.1, 1469.7, 2875.5, 2911.7, 3030.0, 3063.6, 3385.1 cm^{-1}; HRMS (ESI^+) calcd for $C_{37}H_{46}NO_8$ $[M+NH_4]^+$ *m/z* 632.3218, found 632.3237.

1,2-Di-O-(15-methylhexadecanoyl)-sn-glyceryl 2,3,4,6-tetra-O-benzyl-β-D-glucopyranoside

A solution of the diol **28** (50.0 mg, 81.3 μmol) in anhydrous DMF (500 μL) was added to a stirred solution of COMU (174 mg, 407 μmol), 15-methylhexadecanoic acid[6] (88.0 mg, 325 μmol), Hunig's base (42.5 μL, 244 μmol) and DMAP (39.7 mg, 325 μmol) in DMF (1.50 mL) at rt under an atmosphere of nitrogen. The reaction mixture was heated to 85 °C for 2 d, then was diluted with

EtOAc (50 mL) and washed with water (3 × 25 mL), brine (2 × 25 mL), then dried ($MgSO_4$), filtered, and the solvent was removed in vacuo. The residue was purified by flash chromatography (1% ✂ 50% EtOAc/toluene) to give the tetrabenzyl iso-C_{17}-diglyceride as a white solid (62.0 mg, 68%): mp 49 °C sharp, $[\alpha]^{23}_D$ +6.6 (*c* 1.0 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (12 H, d, *J* 6.6 Hz, CH(C*H*$_3$)$_2$); 1.11-1.20 (4 H, m, C*H*$_2$CH(CH$_3$)$_2$), 1.20-1.34 (40 H, m), 1.47-1.68 (6 H, m, C*H*(CH$_3$)$_2$, acyl-*β*), 2.25-2.29 (2 H, m, *sn*-2 acyl-*α*), 2.27-2.31 (2 H, m, *sn*-1 acyl-*α*), 3.44 (1 H, ddd, *J* 9.0, 4.9, 2.1 Hz, H5'), 3.45 (1 H, dd, *J* 9.0, 7.8 Hz, H2'), 3.60 (1 H, dd, *J* 9.1, 9.0 Hz, H4'), 3.63 (1 H, dd, *J* 9.1, 9.0 Hz, H3'), 3.69 (1 H, dd, *J* 10.8, 4.4 Hz, H3), 3.71 (1 H, dd, *J* 10.9, 4.9 Hz, H6'), 3.73 (1 H, dd, *J* 10.9, 2.1 Hz, H6'), 4.07 (1 H, dd, *J* 10.8, 4.6 Hz, H3), 4.23 (1 H, dd, *J* 12.0, 6.7 Hz, H1), 4.39 (1 H, d, *J* 7.8 Hz, H1'), 4.41 (1 H, dd, *J* 12.0, 3.6 Hz, H1), 4.53 (1 H, d, *J* 10.8 Hz, C*H*$_2$Ph), 4.54 (1 H, d, *J* 12.2 Hz, C*H*$_2$Ph), 4.62 (1 H, d, *J* 12.2 Hz, C*H*$_2$Ph), 4.70 (1 H, d, *J* 11.0 Hz, C*H*$_2$Ph), 4.79 (1 H, d, *J* 11.0 Hz, C*H*$_2$Ph), 4.81 (1 H, d, *J* 10.8 Hz, C*H*$_2$Ph), 4.92 (1 H, d, *J* 11.0 Hz, C*H*$_2$Ph), 4.93 (1 H, d, *J* 11.0 Hz, C*H*$_2$Ph), 5.29 (1 H, dddd, *J* 6.7, 4.6, 4.4, 3.6 Hz, H2), 7.13-7.40 (20 H, Ph); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.8 (4 C, CH(*C*H$_3$)$_2$), 25.01, 25.06, 27.6, 28.1, 29.26, 29.31, 29.47, 29.48, 29.67, 29.68, 29.82, 29.84, 29.85, 29.87, 29.88, 29.89, 29.90, 30.1, 39.2 (26 C, (CH$_2$)$_{12}$CH), 34.2 (*sn*-1 acyl-*α*), 34.4 (*sn*-2 acyl-*α*), 62.8 (C1), 68.1 (C3), 68.9 (C6'), 70.1 (C2), 73.6, 74.9, 75.1 (3 C, *C*H$_2$Ph), 75.2 (C5'), 75.8 (*C*H$_2$Ph), 77.8 (C4'), 82.1 (C2'), 84.7 (C3'), 104.0 (C1'), 127.4-128.9, 138.21, 138.23, 138.5, 138.7 (Ph), 173.2 (*sn*-2 C=O), 173.5 (*sn*-1 C=O); IR ν 677.8, 698.4, 721.0, 739.0, 751.0, 909.1, 1017.1, 1070.1, 1100.1, 1130.8, 1150.1, 1167.5, 1198.1, 1212.2, 1245.5, 1268.4, 1308.4, 1362.2, 1383.1, 1414.5, 1454.5, 1468.4, 1497.3, 1605.5, 1743.0, 2850.2, 2918.6, 3032.4, 3065.2 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{71}H_{106}NaO_{10}$ $[M+Na]^+$ *m/z* 1141.7679, found 1141.7674.

1,2-Di-O-[15-methylhexadecanoyl]-sn-glyceryl β-D-glucopyranoside (29)

The above tetrabenzyl iso-C_{17}-diglyceride (62.0 mg, 55.4 μmol) and $Pd(OH)_2$ (20% w/w on carbon, 22.8 mg, 32.5 μmol) was hydrogenolyzed using the same procedure as for the synthesis of **10**. The

crude residue was purified by flash chromatography (110:10:1 ✂ 11:10:1 $CHCl_3$/MeOH/H_2O) to give the iso-C_{17}-diglyceride **29** as a white solid (24.6 mg, 59%):mp 135-140 °C; $[\alpha]^{25}_D$ -6.6 (*c* 0.30 in $CHCl_3$); ^{1}H NMR (500 MHz, 3:1 methanol-d_4/$CDCl_3$) δ 0.85 (12 H, d, *J* 6.6 Hz, CH(CH_3)$_2$), 1.12-1.18 (4 H, m, CH_2CH(CH_3)$_2$), 1.20-1.36 (40 H, m), 1.50 (2 H, t of sept, *J* 6.6, 6.6 Hz, CH(CH_3)$_2$), 1.55-1.65 (4 H, m, acyl-β), 2.30 (1 H, t, *J* 7.6 Hz, *sn*-1 acyl-α), 2.32 (1 H, t, *J* 7.3 Hz, *sn*-2 acyl-α), 3.20 (1 H, dd, *J* 9.0, 7.8 Hz, H2'), 3.27 (1 H, ddd, *J* 9.3, 5.4, 2.2 Hz, H5'), 3.33 (1 H, dd, *J* 9.3, 8.6 Hz, H4'), 3.35 (1 H, dd, *J* 9.0, 8.6 Hz, H3'), 3.67 (1 H, dd, *J* 12.0, 5.4 Hz, H6'), 3.73 (1 H, dd, *J* 10.9, 6.0 Hz, H3), 3.86 (1 H, dd, *J* 12.0, 2.2 Hz, H6'), 3.96 (1 H, dd, *J* 10.9, 5.3 Hz, H3), 4.20 (1 H, dd, *J* 12.1, 6.8 Hz, H1), 4.26 (1 H, d, *J* 7.8 Hz, H1'), 4.43 (1 H, dd, *J* 12.1, 2.9 Hz, H1), 5.26 (1 H, dddd, *J* 6.8, 6.0, 5.3, 2.9 Hz, H2); ^{13}C NMR (125 MHz, 3:1 methanol-d_4/$CDCl_3$) δ 23.0 (4 C, CH(CH_3)$_2$), 25.8, 28.3, 28.8, 29.9, 30.0, 30.16, 30.17, 30.35, 30.36, 30.48, 30.51, 30.54, 30.8, 39.9 (26 C, $(CH_2)_{12}$CH), 34.8 (*sn*-1 acyl-α), 35.0 (*sn*-2 acyl-α), 62.5 (C6'), 63.7 (C3), 68.5 (C1), 71.2 (C3'), 71.4 (C2), 74.6 (C2'), 77.5 (C5'), 77.6 (C4'), 104.4 (C1'), 174.6 (*sn*-2 C=O), 174.9 (*sn*-1 C=O); IR ν 721.7, 804.2, 885.1, 906.6, 996.5, 1031.1, 1064.5, 1111.1, 1144.2, 1166.0, 1231.2, 1246.3, 1266.9, 1286.0, 1338.9, 1383.6, 1415.6, 1466.8, 1715.7, 1737.3, 2445.9, 2849.7, 2916.6, 3300.2 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{43}H_{82}NaO_{10}$ $[M+Na]^+$ *m/z* 781.5801, found 781.5808.

1,2-Di-*O*-benzyl-sn-glyceryl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside

A solution of 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl trichloroacetimidate[10] (780 mg, 1.58 mmol), 1,2-di-*O*-benzyl-sn-glycerol[8] **17** (474 mg, 1.74 mmol) and powdered molecular sieves (4 Å, 2.50 g) in anhydrous CH_2Cl_2 (50 mL) was stirred under nitrogen atmosphere at rt for 30 min, then cooled to 0° C. TfOH (14.0 μL, 158 μmol) was added, and the mixture was stirred for 20 min at 0 °C, then diluted with CH_2Cl_2 (150 mL) and filtered. The filtrate was washed sequentially with sat. aq. $NaHCO_3$ (2 × 100 mL), brine (2 × 100 mL), then dried ($MgSO_4$), filtered, and the solvent was removed in vacuo. The residue was purified by flash chromatography (9:4:1 ✂ 5:4:1 hexanes/CH_2Cl_2/acetone) to give the glucoside as a colourless oil (541 mg, 52%): $[\alpha]^{27}_D$ -10.2 (*c*

1.00 in $CHCl_3$) (lit.[11] -12.5 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.92, 1.97, 1.99, 2.03 (12 H, 4s, 4 × Ac), 3.55 (1 H, dd, *J* 10.3, 5.1 Hz, H1), 3.58 (1 H, dd, *J* 10.3, 4.4 Hz, H1), 3.63 (1 H, ddd, *J* 9.8, 4.7, 2.2 Hz, H5'), 3.70 (1 H, dd, *J* 9.8, 5.3 Hz, H3), 3.73 (1 H, dddd, *J* 5.3, 5.1, 4.4, 4.2 Hz, H2), 3.94 (1 H, dd, *J* 9.8, 4.2 Hz, H3), 4.09 (1 H, dd, *J* 12.3, 2.2 Hz, H6'), 4.24 (1 H, dd, *J* 12.3, 4.7 Hz, H6'), 4.49 (1 H, d, *J* 12.0 Hz, C*H*$_2$Ph), 4.527 (1 H, d, *J* 7.9 Hz, H1'), 4.532 (1 H, d, *J* 12.0 Hz, C*H*$_2$Ph), 4.62 (1 H, d, *J* 12.1 Hz, C*H*$_2$Ph), 4.64 (1 H, d, *J* 12.1 Hz, C*H*$_2$Ph), 4.98 (1 H, dd, *J* 9.6, 7.9 Hz, H2'), 5.07 (1 H, dd, *J* 9.8, 9.5 Hz, H4'), 5.17 (1 H, dd, *J* 9.6, 9.5 Hz, H3'), 7.22-7.35 (10 H, Ph); ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.45, 20.47, 20.6 (4 C, 4 × CH_3), 61.8 (C6'), 68.3 (C4'), 69.1 (C1), 69.6 (C3), 71.2 (C2'), 71.6 (C2), 72.0 (*C*H$_2$Ph), 72.7 (C3'), 73.3 (*C*H$_2$Ph), 76.7 (C5'), 100.9 (C1'), 127.45, 127.50, 127.54, 128.2, 128.3, 138.1, 138.4 (Ph), 169.1, 169.3, 170.1, 170.4 (4 C, C=O); IR ν 667.1, 697.9, 715.3, 739.6, 905.7, 1034.6, 1174.4, 1213.6, 1366.4, 1431.7, 1454.0, 1496.7, 1496.7, 1603.2, 1745.8, 2871.3, 2941.9, 3030.8 cm^{-1}; HRMS (ESI$^+$) calcd for $C_{31}H_{42}NO_{12}$ $[M+NH_4]^+$ *m/z* 620.2702, found 620.2713.

sn-Glyceryl 3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside) (31)

A mixture of the above glucoside (500 mg, 830 μmol) and $Pd(OH)_2$ (20% w/w on carbon, 58.3 mg, 83.0 μmol) in EtOAc (4 mL) was stirred under H_2 (40 atm) at rt for 15 min. The reaction mixture was filtered through a PTFE pad, and the reaction vial was rinsed with EtOAc (5 × 10 mL) with sonication, and the washings were filtered through the same PTFE pad. The combined filtrates were concentrated in vacuo and the residue was purified by flash chromatography (1% ≯ 20% MeOH/$CHCl_3$) to give **31** as a glassy solid (348 mg, 99%): mp 116-118 °C (lit.[11] 115-116 °C); $[\alpha]^{28}_D$ -9.5 (*c* 1.00 in $CHCl_3$) (lit.[11] -14.9 in $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.94 (C3'-CO_2CH_3), 1.96 (C4'-CO_2CH_3), 1.99 (C2'-CO_2CH_3), 2.03 (C6'-CO_2CH_3), 3.50 (1 H, dd, *J* 11.4, 5.1 Hz, H1), 3.60 (1 H, dd, *J* 11.4, 3.7 Hz, H1), 3.65-3.70 (2 H, m, H5',3), 3.75-3.78 (2 H, m, H3,2), 4.11 (1 H, dd, *J* 12.4, 2.5 Hz, H6'), 4.17 (1 H, dd, *J* 12.4, 5.0 Hz, H6'), 4.50 (1 H, d, *J* 8.0 Hz, H1'), 4.92 (1 H, dd, *J* 9.6, 8.0 Hz, H2'), 5.00 (1 H, dd, *J* 9.7, 9.7 Hz, H4'), 5.15 (1 H, dd, *J* 9.7, 9.6 Hz,

H3'); ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.5, 20.6, 20.7 (4 C, CO_2CH_3), 61.9 (C6'), 63.3 (C1), 68.3 (C4'), 70.5 (C2), 71.2 (C2'), 71.83 (C5'), 72.1 (C3), 72.6 (C3'), 101.2 (C1'), 169.5, 169.7, 170.2, 170.8 (4 C, C=O); IR ν 677.4, 697.8, 759.6, 877.7, 911.1, 929.7, 959.7, 984.3, 1034.6, 1098.3, 1165.5, 1220.7, 1366.2, 1376.4, 1432.9, 1742.1, 2916.7, 2963.9, 3534.0 cm^{-1}; HRMS (ESI^+) calcd for $C_{17}H_{26}NaO_{12}$ $[M+Na]^+$ *m/z* 445.1316, found 445.1333.

1,2-Di-*O*-dodecanoyl-sn-glyceryl 2,3,4,6-*O*-acetyl-β-D-glucopyranoside

A solution of the diol **31** (348 mg, 824 μmol), lauryl chloride (457 μL, 1.81 mmol) and DMAP (20.1 mg, 165 μmol) in pyridine (16.5 mL) was stirred at rt under an atmosphere of nitrogen for 24 h. The solvent was evaporated in vacuo, and the residue was dissolved in Et_2O (80 mL), and then washed sequentially with 0.1 M aq. HCl (5 × 50 mL), water (3 × 20 mL), sat. aq. $NaHCO_3$ (3 × 20 mL), and brine (2 × 20 mL), then dried ($MgSO_4$), filtered, and the solvent was evaporated in vacuo. The residue was purified by flash chromatography (1% ✂ 20% EtOAc/toluene) to give the tetraacetyl C_{12}-diglyceride as a white solid (455 mg, 70 %): mp 79 °C sharp, $[\alpha]^{26}_D$ -6.5 (*c* 1.00 in CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.80 (6 H, t, *J* 7.1 Hz, $(CH_2)_8CH_3$), 1.11-1.29 (32 H, m, $CO_2CH_2CH_2(CH_2)_8$), 1.45-1.60 (4 H, m, $CO_2CH_2CH_2$), 1.92, 1.94, 1.97, 2.00 (12 H, 4s, 4 × Ac), 2.19-2.23 (4 H, m, CO_2CH_2), 3.60 (1 H, dd, *J* 11.0, 5.7 Hz, H3), 3.63 (1 H, ddd, *J* 9.6, 4.8, 2.4 Hz, H5'), 3.87 (1 H, dd, *J* 11.0, 5.0 Hz, H3), 4.04 (1 H, dd, *J* 12.0, 6.4 Hz, H1), 4.05 (1 H, dd, *J* 12.3, 2.4 Hz, H6'), 4.18 (1 H, dd, *J* 12.3, 4.8 Hz, H6'), 4.22 (1 H, dd, *J* 12.0, 3.5 Hz, H1), 4.46 (1 H, d, *J* 7.9 Hz, H1'), 4.90 (1 H, dd, *J* 9.7, 7.9 Hz, H2'), 4.99 (1 H, dd, *J* 10.0, 9.6 Hz, H4'), 5.11 (1 H, dddd, *J* 6.4, 5.7, 5.0, 3.5 Hz, H2), 5.12 (1 H, dd, *J* 9.7, 9.6 Hz, H3'); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0 (2 C, CH_2CH_3), 20.5, 20.6 (4 C, CO_2CH_3), 22.6, 24.8, 29.04, 29.06, 29.2, 29.3, 29.4, 29.6, 31.9 (18 C, $(CH_2)_9$, 34.0, 34.2 (2 C, CO_2CH_2), 61.8 (C6'), 62.1 (C1), 67.6 (C3), 68.3 (C4'), 69.6 (C2), 71.1 (C2'), 71.9 (C5'), 72.6 (C3'), 101.0 (C1'), 169.1, 169.2, 170.1, 170.5 (4 C, CO_2CH_3), 172.7 (*sn*-2 C=O), 173.1 (*sn*-1 C=O); IR ν 721.5, 840.5, 887.8, 905.4, 953.1, 982.8, 1047.7, 1070.3, 1085.5, 1099.4, 1113.0, 1137.8, 1170.6, 1227.3, 1257.3, 1328.3, 1368.7, 1442.8, 1467.1, 1745.0, 2851.0,

2919.3, 2957.4 cm^{-1}; HRMS (ESI^+) calcd for $C_{41}H_{74}NO_{14}$ $[M+NH_4]^+$ *m/z* 804.5104, found 804.5141.

1,2-Di-O-dodecanoyl-sn-glyceryl β-D-glucopyranoside (32)

A suspension of the above tetraacetyl C_{12}-diglyceride (40.0 mg, 50.8 μmol) and aqueous hydrazine hydrate (11.8 mM, 34.5 μL, 407 μmol) in 85% aq. EtOH (1.0 mL) was stirred at 37 °C for 3 h, then the solvent was evaporated in-vacuo. The residue was purified by flash chromatography (110:10:1 ✂ 11:10:1 $CHCl_3$/MeOH/H_2O) to give **32** as a white solid (17.3 mg, 55%): mp 121-129 °C; $[\alpha]^{27}_D$ -5.6 (*c* 0.90 in 1:1 $CHCl_3$/MeOH); ^1H NMR (500 MHz, $CDCl_3$) δ 0.83 (6 H, t, *J* 7.0 Hz, C*H*$_3$), 1.15-1.31 (32 H, m, $(CH_2)_8$), 1.51-1.61 (4 H, m, $CO_2CH_2CH_2$), 2.25-2.31 (4 H, m, CO_2CH_2), 3.21 (1 H, dd, *J* 9.1, 7.7 Hz, H2'), 3.25 (1 H, m, H5'), 3.32-3.34 (2 H, m, H3',4'), 3.68 (1 H, dd, *J* 10.8, 6.1 Hz, H3), 3.70 (1 H, dd, *J* 12.0, 5.2 Hz, H6'), 3.82 (1 H, dd, *J* 12.0 2.9 Hz, H6'), 3.88 (1 H, dd, *J* 10.8, 5.3 Hz, H3), 4.16 (1 H, dd, *J* 12.0, 6.7 Hz, H1), 4.24 (1 H, d, *J* 7.7 Hz, H1'), 4.35 (1 H, dd, *J* 12.0, 3.1 Hz, H1), 5.22 (1 H, dddd, *J* 6.7, 6.1, 5.3, 3.1, H2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1 (2 C, CH_3), 22.8, 25.03, 25.05, 29.2, 29.3, 29.4, 29.5, 29.6, 29.77, 29.79, 32.1 (18 C, $(CH_2)_9$), 34.3, 34.4 (2 C, CO_2CH_2), 62.0 (C6'), 63.0 (C1), 68.1 (C3), 70.3 (C3'), 70.5 (C2), 73.7 (C2'), 76.4 (C5'), 76.5 (C4'), 103.7 (C1'), 174.0 (*sn*-2 C=O), 174.3 (*sn*-1 C=O); IR ν 995.9, 1018.6, 1031.0, 1055.6, 1065.3, 1080.9, 1110.5, 1123.6, 1143.2, 1165.2, 1714.4, 1736.5, 2851.1, 2870.7, 2919.2, 2955.2, 3285.2, 3524.2 cm^{-1}; HRMS (ESI^+) calcd for $C_{33}H_{66}NO_{10}$ $[M+NH_4]^+$ *m/z* 636.4681, found 636.4679.

References

1 Y. Hattori, D. Morita, N. Fujiwara, D. Mori, T. Nakamura, H. Harashima, S. Yamasaki and M. Sugita, *J. Biol. Chem.*, 2014, **289**, 15405.
2 E. Ishikawa, T. Ishikawa, Y. S. Morita, K. Toyonaga, H. Yamada, O. Takeuchi, T. Kinoshita, S. Akira, Y. Yoshikai and S. Yamasaki, *J. Exp. Med.*, 2009, **206**, 2879.
3 W. C. Still, M. Kahn and A. M. Mitra, *J. Org. Chem.*, 1978, **43**, 2923.
4 A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, 1996, **15**, 1518.
5 T. Ziegler and U. Seidl, *J. Carbohydr. Chem.*, 1991, **10**, 813.
6 M. B. Richardson and S. J. Williams, *Beilstein J. Org. Chem.*, 2013, **9**, 1807.
7 L. F. Wiggins, *J. Chem. Soc.*, 1946, 13.
8 D. Mcadam, A. Perera and R. Stick, *Aust. J. Chem.*, 1987, **40**, 1901.

9 S.-S. Weng, C.-L. Li, C.-S. Liao, T.-A. Chen, C.-C. Huang and K.-T. Hung, *J. Carbohydr. Chem.*, 2010, **29**, 429.
10 R. R. Schmidt, J. Michel and M. Roos, *Liebigs Ann.*, 1984, 1343.
11 M. Kaneda, K. Mizutani and K. Tanaka, *Phytochemistry*, 1982, **21**, 891.