Electronic Supplementary Information

A General and Convergent Synthesis of Diverse Glycosylphosphatidylinositol Glycolipids

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General Information. All chemicals used were reagent grade and used as supplied except where noted. All reactions were performed in oven-dried glassware under an inert atmosphere (nitrogen or argon) unless noted otherwise. Reagent grade dichloromethane (DCM or CH₂Cl₂), tetrahydrofuran (THF), methanol (MeOH) *N*,*N*-dimethylformamide (DMF), toluene (PhMe) and acetonitrile (MeCN) were passed through activated neutral molecular sieves column prior to use. Reagent grade thiophene was dried over activated molecular sieves prior to use. Pyridine was distilled over CaH₂ prior to use. Analytical thin layer chromatography (TLC) was performed on Merck silica gel 60 F₂₅₄ plates (0.25mm). Compounds were visualized by UV irradiation or dipping the plate in a cerium sulfate-ammonium molybdate (CAM) solution or sulfuric acid ethanol solution. Triethylamine (TEA)/CO₂ buffer was prepared by filling TEA (7mL) in a measuring cylinder and adding water until the total volume reached 500mL. The solution was transferred to a flask and CO₂ was bubbled through the solution for 1 h at 0 °C. The buffer was stored at 4 °C. Flash column chromatography was carried out using a forced flow of the indicated solvent on Fluka silica gel 60 (230-400 mesh, for preparative column chromatography).

¹H, ¹³C and ³¹P NMR spectra were recorded on a BRUKER Avance 300 (300MHz), Varian 400 (400 MHz), Bruker ECP-500 (500MHz), Varian 600 (600 MHz) or BRUKER Avance-III (700MHz) spectrometer in CDCl₃ with chemical shifts referenced to internal standards CHCl₃ (7.26 ppm ¹H, 77.1 ppm ¹³C) and DMSO (2.50 ppm ¹H, 39.52 ppm ¹³C) unless otherwise stated. Coupling constants are reported in Hertz (Hz). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; br, broad singlet for ¹H NMR data. Signals were assigned by means of ¹H-¹H COSY, ¹H-¹H TOCSY, ¹H-¹³C HSQC and ¹H-¹³C HMBC spectra. ESI mass spectral analyses were performed by the MS-service at the Institute of Chemistry and Biochemistry at the Free University of Berlin using a modified MAT 711 spectrometer. Infrared (IR) spectra were recorded as thin films on a Perkin

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Elmer Spectrum 100 FTIR spectrophotometer. Optical rotations (OR) were measured with a Schmidt & Haensch UniPol L 1000 at a concentration (c) expressed in g/100 mL.



Synthesis of the key mannoside **1**. *Reaction conditions:* (a) NapBr, NaH, DMF, 99%; (b) 80% AcOH_(aq), 65 °C, 72%; (c) i. Bu₂SnO, PhMe, reflux; ii. BnBr, TBAB, 99% over 2 steps; (d) LevOH, DIC, DMAP, CH₂Cl₂, 82%; (e) DDQ, H₂O, CH₂Cl₂, 96%.

Allyl 2,3-*O*-isopropylidene-4-*O*-(2-naphthylmethyl)-6-*O*-*tert*butyldiphenylsilyl-α-D-mannopyranoside (1b)



To a solution of alcohol $1a^{[1]}$ (25.0 g, 50.1 mmol) in DMF (100 mL) was added NaH (3.61 g, 150 mmol, 60% in mineral oil) and 2-(bromomethyl)naphthalene (16.63 g, 75 mmol) at 0°C. After 5 h, the reaction mixture was quenched with water and neutralized with 1N HCl and extracted three times with dichloromethane. The combined organic layers were washed with brine, dried over MgSO₄, filtered and concentrated. The crude product was purified by silica gel column chromatography to give mannoside 1b (30.4 g, 47.6 mmol, 95% yield) as colorless oil: R_f (SiO₂, nhexane/ethyl acetate 7:1) = 0.60; $[\alpha]_D^{20}$: + 13.3 (c = 1.0, CHCl₃); ATR-FTIR (cm⁻¹): 3052, 2930, 2857, 1428, 1221, 1113, 1083, 817, 702; ¹H NMR (400 MHz, CDCl₃) δ 7.88 – 7.63 (m,8H), 7.54 – 7.29 (m, 9H), 5.89 (m, 1H, =CH-), 5.27 (m, 1H, CH₂=), 5.19 (m, 1H, CH₂=), 5.12 (s, 1H, Man-1), 5.04 (d, J = 11.6 Hz, 1H, -CH₂- of NAP), 4.73 (d, J = 11.6 Hz, 1H, -CH₂- of NAP), 4.40 (t, J = 8.0 Hz, 1H, Man-3), 4.28 – 4.14 (m, 2H, Man-2, -CH₂- of allyl), 4.09 – 3.94 (m, 2H, -CH₂- of allyl, Man-6), 3.88 (dd, J = 11.0, 5.0 Hz, 1H, Man-6), 3.76 (ddd, J = 10.2, 5.0, 1.6 Hz, 1H, Man-5), 3.68 $(dd, J = 10.2, 6.8 \text{ Hz}, 1H, \text{Man-4}), 1.53 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.05 (s, 9H, tBu);$ ¹³C NMR (101 MHz, CDCl₃) δ 135.99, 135.89, 135.75, 133.89 (=CH-), 133.80, 133.49, 133.35, 133.08, 129.86, 129.71, 129.68, 128.15, 128.04, 127.88, 127.78, 127.70, 126.75, 126.12, 126.07, 125.90, 117.95 (CH₂=), 109.45 (C(OMe)₂), 96.16 (C1), 79.20 (C3), 76.13 (C2), 75.83 (C4), 73.16 (-OCH₂ of NAP), 69.87 (C5), 67.70 (OCH₂ of allyl), 63.50 (C6), 28.14 (Me), 26.92 (Me of tBu), 26.57 (Me), 19.45 (CMe₃); ESI-MS: m/z [M+Na]⁺ cald 661.2956, obsd 661.2984.

Allyl 4-*O*-(2-naphthylmethyl)-6-*O*-tertbutyldiphenylsilyl-α-D-mannopyranoside (1c)



Acetal **1b** (32 mg, 0.05 mmol) was dissolved in a mixture of acetic acid (80% in water, 2 mL) and CHCl₃ (1 mL). This solution was heated to 50°C for 2 h. Afterwards the solution was heated to 65°C for another 2 h. The solvents were removed in vacuo to give an oil that was purified by flash column chromatography to give diol **1c** (21.7 mg, 0.036 mmol, 72% yield) as yellow oil: R_f (SiO₂, EtOAc/*n*-hexane 1:1) = 0.67; $[\alpha]_D^{20}$: + 26.4 (c = 1.0, CHCl₃); ATR-FTIR (cm⁻¹): 3422, 2927, 2856, 1427, 1220, 1112, 1068, 822, 810, 740, 702; ¹H NMR (400 MHz, CDCl₃) δ 7.88 – 7.63 (m, 8H), 7.54 – 7.44 (m, 2H), 7.44 – 7.31 (m, 7H), 5.88 (m, 1H, CH=), 5.26 (m, 1H, CH₂=), 5.18 (m, 1H, CH₂=), 4.93 (d, *J* = 11.5 Hz, 1H, CH₂ of NAP), 4.90 (d, *J* = 1.3 Hz, 1H, Man-1), 4.82 (d, *J* = 11.5 Hz, 1H, CH₂ of NAP), 4.18 (dd, *J* = 12.9, 5.1 Hz, 1H, CH₂ of Allyl), 4.09 – 3.90 (m, 5H, Man-2, 3, 6, CH₂ of Allyl), 3.82 (t, *J* = 9.4 Hz, 1H, Man-4), 3.73 (dt, *J* = 9.7, 3.1 Hz, 1H, Man-5), 1.09 (s, 1H, *t*Bu); ¹³C NMR (101 MHz, CDCl₃) δ 136.00, 135.80, 135.78, 133.76 (CH=), 133.42, 133.16, 129.79, 128.52, 128.10, 127.83, 127.74, 126.80, 126.28, 126.12, 125.94, 117.73 (CH₂=) , 98.47 (Man-1), 76.16 (Man-4), 75.04 (CH₂ of NAP), 72.33 (Man-5), 72.08, 71.36, 67.93 (CH₂ of Allyl), 63.26 (Man-6), 27.00 (*t*Bu), 19.49 (**C**(Me)₃); ESI-MS: m/z [M+Na]⁺ cald 621.2643, obsd 621.2686.

Allyl 3-*O*-benzyl-4-*O*-(2-naphthylmethyl)-6-*O*-tertbutyldiphenylsilyl-α-D-mannopyranoside (1d)



A mixture of diol **1c** (897 mg, 1.50 mmol) and Bu₂SnO (372 mg, 1.50 mmol) in toluene was refluxed for 4 h using a Dean-Stark apparatus. Benzyl bromide (178 µl, 1.50 mmol) and tetra-*n*-butylammonium bromide (967 mg, 3.00 mmol) were added. After 1 h, the solvent was removed under reduced pressure and the crude material was purified by silica gel column chromatography to give mannoside **1d** (914 mg, 1.33 mmol, 89% yield) as colorless oil: R_f (SiO₂, EtOAc/Hexane 1:5) = 0.49; $[\alpha]_D^{20}$: + 19.7 (c = 1.0, CHCl₃); ATR-FTIR (cm⁻¹): 3563, 3054, 2929, 2857, 1428, 1112, 1056, 822, 756, 702; ¹H NMR (400 MHz, CDCl₃) δ 7.85 – 7.78 (m, 1H), 7.78 – 7.67 (m, 6H), 7.63 (s, 1H), 7.51 – 7.44 (m, 2H), 7.44 – 7.26 (m, 12H), 5.89 (m, 1H, CH=), 5.26 (m, 1H, CH₂=), 5.18 (m, 1H,

CH₂=),), 5.01 (d, J = 11.1 Hz, 1H, CH₂ of Nap), 4.97 (d, J = 1.5 Hz, 1H, Man-1), 4.81 – 4.64 (m, 3H, CH₂ of NAP and Bn), 4.19 (ddt, J = 12.9, 5.2, 1.5 Hz, 1H, CH₂ of Allyl), 4.11 (dd, J = 3.1, 1.5 Hz, 1H, Man-2), 4.07 – 3.85 (m, 5H, Man-3,5,6 and CH₂ of Allyl), 3.78 (dt, J = 9.2, 3.3 Hz, 1H, Man-4), 2.43 (s, 1H, OH), 1.06 (s, 9H, *t*Bu); ¹³C NMR (101 MHz, CDCl₃) δ 138.11, 136.01, 135.94, 135.76, 133.90, 133.87 (CH=), 133.46, 133.41, 133.10, 129.70, 128.69, 128.23, 128.07, 128.04, 127.79, 127.69, 126.68, 126.13, 126.12, 125.97, 117.76 (CH₂=), 98.26 (Man-1), 80.56, 75.41(CH₂ of NAP), 74.49, 72.65 (Man-4), 72.22 (CH₂ of Bn), 68.68 (Man-2), 67.81 (CH₂ of Allyl), 63.35 (Man-6), 26.94 (*t*Bu), 19.45 (C(Me)₃); ESI-MS: m/z [M+Na]⁺ cald 711.3112, obsd 711.3099.

Allyl3-O-benzyl-2-O-levulinyl-4-O-(2-naphthylmethyl)-6-O-tertmannopyranoside (1)



To a solution of compound 1d (41 mg, 60 µmol) in DCM (2 mL) were added LevOH (10 mg, 89 μmol), DMAP (5.8 mg, 48 μmol) and N,N'-diisopropylcarbodiimide (11 mg, 89 μmol). After 4 h, the reaction mixture was filtered and the crude material was purified by flash column chromatography to afford compound 1 (45 mg, 57 µmol, 95% yield) as colorless syrup. Rf (SiO₂, EtOAc/Cyclohexane $1:5 = 0.48; [\alpha]_{D}^{20}: + 5.4$ (c = 1.04, CHCl₃); ATR-FTIR (cm⁻¹): 3052, 2930, 2857, 1740, 1720, 1427, 1362, 1138, 1104, 1059, 997, 740, 702; ¹H NMR (400 MHz, CDCl₃) δ 7.86 – 7.80 (m, 1H), 7.78 – 7.68 (m, 7H), 7.65 (s, 1H), 7.52 – 7.45 (m, 2H), 7.44 – 7.28 (m, 11H), 5.88 (m, 1H, =CH-), 5.44 (dd, J = 2.9, 1.7 Hz, 1H, Man-2), 5.26 (m, 1H, CH₂=), 5.19 (m, 1H, CH₂=), 5.07 (d, J = 11.0 Hz, 1H, CH₂ of NAP), 4.90 (d, J = 1.7 Hz, 1H, Man-1), 4.76 (m, 2H, CH₂ of NAP, CH₂ of Bn), 4.57 (d, J = 11.2 Hz, 1H, CH₂ of Bn), 4.15 (ddt, J = 12.8, 5.2, 1.4 Hz, 1H, CH₂ of Allyl), 4.11 – 3.90 (m, 5H, Man-3, Man-6, Man-5, CH₂ of Allyl), 3.77 (dd, J = 9.0, 2.7 Hz, 1H, Man-4), 2.87 – 2.62 (m, 4H, CH₂-CH₂), 2.14 (s, 3H, CH₃), 1.09 (s, 9H, tBu); ¹³C NMR (101 MHz, CDCl₃) δ 206.38 (ketone), 172.29 (ester of Lev), 138.26, 136.08, 136.05, 135.70, 133.96, 133.68, 133.43, 133.35, 133.08, 129.74, 128.50, 128.26, 128.18, 128.05, 127.82, 127.80, 127.68, 126.64, 126.13, 126.10, 125.92, 117.87 (CH₂=), 96.79 (Man-1), 78.47, 75.47, 74.37, 72.82, 71.85, 69.23, 68.02, 63.10, 38.16 (CH₂), 29.95 (CH₃), 28.30 (CH₂), 26.93 (*t*Bu), 19.52 (C(Me)₃); ESI-MS: m/z [M+Na]⁺ cald 809.3480, obsd 809.3459.

Allyl 3-O-benzyl-2-O-levulinyl-4-O-(2-naphthylmethyl)-α-D-mannopyranoside (9a)



To a solution of mannoside 1 (0.300 g, 0.381 mmol) in THF (1 mL) was added HF-pyridine (100 μ L, 3.85 mmol). After overnight stirring, the reaction mixture was quenched with NaHCO_{3(aq)} and extracted with DCM for three times. The combined organic layers were dried over Na₂SO₄, filtered and concentrated. The crude product was purified by silica gel column chromatography to give mannoside **9a** (0.200 g, 0.365 mmol, 96% yield) as a colorless oil: R_f (SiO₂, EtOAc/*n*-hexane 1:1) = 0.32; $[\alpha]_{D}^{20}$: + 7.0 (c = 1.00, CHCl₃); ATR-FTIR (cm⁻¹): 3486, 3059, 2922, 1740, 1719, 1365, 1137, 1081, 1057, 990; ¹H NMR (400 MHz, CDCl₃) δ 7.79 – 7.57 (m, 4H), 7.41 – 7.19 (m, 8H), 5.80 (m, 1H, =CH), 5.31 (dd, J = 3.3, 1.8 Hz, 1H, Man2), 5.19 (m, 1H, =CH₂), 5.12 (m, 1H, =CH₂), 4.99 (d, J = 11.1 Hz, 1H), 4.79 (d, J = 1.8 Hz, 1H, Man1), 4.73 (d, J = 11.1 Hz, 1H), 4.64 (d, J = 11.2 Hz, 1H), 4.48 (d, J = 11.2 Hz, 1H, -CH₂-), 4.08 (ddt, J = 12.8, 5.3, 1.5 Hz, 1H, -CH₂- of allyl), 3.98 (dd, J = 12.8, 5.3, 1.5 Hz, 9.3, 3.3 Hz, 1H, Man3), 3.90 (ddt, J = 12.8, 6.1, 1.3 Hz, 1H, -CH₂- of allyl), 3.83 - 3.71 (m, 3H, Man4, Man6), 3.67 (m, 1H, Man5), 2.75 – 2.54 (m, 4H, CH₂ of Lev), 2.08 (s, 3H, Me of Lev); ¹³C NMR (101 MHz, CDCl₃) δ 206.31 (ketone of Lev), 171.99 (ester of Lev), 138.01, 135.74, 133.36, 133.29 (vinyl), 132.98, 128.36, 128.15, 128.02, 127.91, 127.70, 127.68, 126.70, 126.08, 125.99, 125.90, 117.78 (=CH₂), 96.88 (C1), 78.02 (C3), 75.28 (-CH₂-), 74.18 (C4), 71.89 (C5), 71.63 (-CH₂-), 68.99 (C2), 68.24 (-CH₂- of allyl), 62.07 (C6), 38.02 (-CH₂- of Lev), 29.73 (Me of Lev), 28.15 (-CH₂- of Lev); ESI-MS: m/z [M+Na]⁺ cald 571.2308 for C₃₂H₃₆O₈, obsd 571.2300.

2,3,4-Tri-*O*-benzyl-6-*O*-triisopropylsilyl- α -D-mannopyranosyl- $(1 \rightarrow 2)$ -3,4,6-tri-*O*-benzyl- α -D-mannopyranosyl trichloroacetimidate (4)



Triphenylphosphine (0.15 g, 0.572 mmol) was added to a solution of $Pd(OAc)_2$ (25 mg, 0.111 mmol) in MeOH (3 mL) in the absence of light. After 3 h, diethylamine (1.0 mL, 9.67 mmol) and a solution of allyl 2,3,4-tri-*O*-benzyl-6-*O*-triisopropylsilyl- α -D-mannopyranosyl-(1 \rightarrow 2)-3,4,6-tri-*O*-benzyl- α -D-mannopyranoside^[2] (1.00 g, 0.926 mmol) in CH₂Cl₂ (10 mL) were added. After 16 h at room temperature, the solvent was removed to give brown oil that was purified by flash column chromatography (EtOAc/hexane 1:4) to yield lactol (0.93 g, 0.895 mmol, 97% yield) as an inseparable anomeric mixture.

The lactol (0.51 g, 0.491 mmol) was dissolved in dichloromethane (5 mL). DBU (8 μ L, 0.053 mmol) and 2,2,2-trichloroacetonitrile (0.50 mL, 4.99 mmol) were added at 0 °C. The reaction mixture was then allowed to warm up to room temperature over 2 h before the solvent was removed. The crude product was purified by silica gel column chromatography (EtOAc/hexane 1:9) to give glycosyl trichloroacetimidate **4** (0.56 g, 0.473 mmol, 96% yield) as colorless oil: R_f (SiO₂, EtOAc/Hexane 1:4) = 0.53; $[\alpha]^{20}_{D}$: + 26.1 (c = 2.31, CHCl3); ATR-FTIR (cm⁻¹) 3345, 3089, 3064, 3031, 2892, 2865, 1672, 1496, 1454, 1363, 1103, 1051, 1027; ¹H NMR (400 MHz, CDCl₃) δ 8.49 (s, 1H, NH), 7.26-7.08 (m, 30 H), 6.18 (d, *J* = 1.9 Hz, 1H, ManI-1), 5.22 (d, *J* = 1.6 Hz, 1H, ManII-1), 4.82 (d, *J* = 11.0 Hz, 1H), 4.77 (d, *J* = 10.7 Hz, 1H), 4.61-4.57 (m, 4H), 4.51 (d, *J* = 10.8 Hz, 1H), 4.47-4.38 (m, 5H), 4.13 (br, 1H), 3.98-3.81 (m, 7H), 3.76-3.61 (m, 4H), 1.02-0.97 (m, 21H, TIPS); ¹³C NMR (101 MHz, CDCl₃) δ 160.07 (C=NH), 138.91, 138.80, 138.57, 138.55, 138.32, 137.90, 128.58, 128.50, 128.45, 128.37, 128.31, 128.28, 128.24, 128.22, 128.12, 128.11, 128.05, 127.90, 127.83, 127.78, 127.65, 127.57, 127.49, 127.45, 98.94 (ManII-1), 97.04 (ManI-1), 91.13 (CCl₃), 79.88, 79.49, 75.46, 75.13, 75.10, 75.00, 74.75, 74.18, 74.11, 73.46, 72.66, 72.39, 72.18, 71.34, 68.89, 63.06, 18.19 (TIPS), 18.16 (TIPS), 12.18 (TIPS); ESI-MS: m/z [M+Na]+ cald 1204.4307, obsd 1204.4309.

Allyl 2,3,4-tri-*O*-benzyl-6-*O*-triisopropylsilyl- α -D-mannopyranosyl- $(1\rightarrow 2)$ -3,4,6-tri-*O*-benzyl- α -D-mannopyranosyl- $(1\rightarrow 6)$ -3-*O*-benzyl-2-*O*-levulinyl-4-*O*-(2-naphthylmethyl)- α -D-mannopyranoside (9)



A mixture of trichloroacetimidate **4** (94 mg, 0.080 mmol) and mannoside **9a** (38 mg, 0.069 mmol) was co-evaporated with toluene for three times and dried over vacuum for 30 min. To a solution of this mixture in DCM (0.8 mL) were added thiophene (0.5 mL), molecular sieves (4Å, 50 mg) and TBSOTf (2.0 μ L, 8.7 μ mol). After 60 min, pyridine (50 μ L) was added to quench the reaction and the reaction mixture was filtered. The solvents were evaporated to dryness to give a yellow oil that was purified by silica gel column chromatography to give trisaccharide **9** (0.100 g, 0.064 mmol, 92% yield) as colorless oil: R_f (SiO₂, EtOAc/Hexane 1:2) = 0.48; [α]²⁰_D: + 21.2 (c = 1.30, CHCl₃); ATR-

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> FTIR (cm⁻¹) 3063, 3031, 2924, 2865, 1738, 1721, 1454, 1362, 1085, 1052, 1027; ¹H NMR (600 MHz, CDCl₃) δ 7.73 (m, 1H), 7.69 – 7.60 (m, 3H), 7.41 – 7.35 (m, 2H), 7.31 – 7.05 (m, 36H), 5.81 (m, 1H, =CH), 5.37 (dd, J = 3.3, 1.5 Hz, 1H, ManI-2), 5.25 (d, J = 1.6 Hz, 1H, ManIII-1), 5.22 (ddd, *J* = 17.1, 2.8, 1.5 Hz, 1H), 5.12 (ddd, *J* = 10.5, 2.8, 1.3 Hz, 1H), 5.01 (d, *J* = 11.3 Hz, 1H), 4.85 (d, *J* = 11.5 Hz, 1H), 4.84 (d, J = 2.2 Hz, 1H, ManII-1), 4.78 (d, J = 1.5 Hz, 1H, ManI-1), 4.77 (d, J =11.0 Hz, 1H), 4.66 (d, J = 11.0 Hz, 1H), 4.62 (d, J = 11.3 Hz, 1H), 4.59 (d, J = 11.0 Hz, 1H), 4.56 (d, J = 11.2 Hz, 1H), 4.55 - 4.49 (m, 2H), 4.46 (d, J = 11.0 Hz, 1H), 4.45 - 4.36 (m, 5H), 4.29 (d, J = 11.0 Hz, 1H)= 12.2 Hz, 1H), 4.17 (dd, J = 2.3, 2.2 Hz, 1H, ManII-2), 4.08 (m, 1H, -CH₂- of allyl), 4.00 (dd, J =9.2, 3.3 Hz, 1H, ManI-3), 3.96 – 3.84 (m, 7H, -CH₂- of allyl, ManI-6, ManII-3, ManIII-3, ManIII-5, ManIII-6), 3.81 (ddd, J = 9.8, 5.7, 1.5 Hz, 1H, ManI-5), 3.75 - 3.64 (m, 5H, ManI-4, ManII-4, ManII-5, ManIII-2, ManIII-4), 3.61 (dd, J = 10.4, 1.5 Hz, 1H, ManI-6), 3.53 (dd, J = 11.0, 4.0 Hz, 1H,ManII-6), 3.45 (br-d, J = 11.0 Hz, 1H, ManII-6), 2.65 – 2.57 (m, 4H, CH₂ of Lev), 2.07 (s, 3H, Me of Lev), 1.00 (br, 21H, TIPS); ¹³C NMR (151 MHz, CDCl₃) δ 206.26 (ketone of Lev), 172.19 (ester of Lev), 138.90, 138.75, 138.65, 138.54, 138.48, 138.08, 137.90, 135.88, 133.31 (vinyl), 132.94, 128.53, 128.43, 128.35, 128.31, 128.28, 128.27, 128.15, 128.07, 128.03, 127.95, 127.90, 127.88, 127.84, 127.81, 127.80, 127.70, 127.58, 127.54, 127.51, 127.45, 127.39, 127.39, 126.14, 126.04, 125.80, 125.70, 118.31 (=CH₂), 98.99 (ManII-1), 98.53 (ManIII-1), 96.56 (ManI-1), 80.28, 79.75, 78.60 (ManI-3), 75.11, 75.10, 75.01, 74.95, 74.72, 74.36, 73.95, 73.18, 72.61, 72.20, 72.11, 71.90, 71.84, 71.68, 70.66 (ManI-5), 69.14 (ManII-6), 68.87 (ManI-2), 68.05 (-CH₂- of allyl), 66.38 (ManI-6), 63.20 (ManIII-6), 37.97 (-CH₂- of Lev), 29.87 (Me of Lev), 28.13 (-CH₂- of Lev), 18.11 (Me of TIPS), 12.07 (CHMe₂ of TIPS); ESI-MS: m/z [M+Na]⁺ cald 1591.7510, obsd 1591.7509.

> 2,3,4-Tri-*O*-benzyl-6-*O*-tri*iso*propylsilyl- α -D-mannopyranosyl- $(1\rightarrow 2)$ -3,4,6-tri-*O*-benzyl- α -D-mannopyranosyl- $(1\rightarrow 6)$ -3-*O*-benzyl-2-*O*-levulinyl-4-*O*-(2-naphthylmethyl)- α -D-mannopyranosyl- $(1\rightarrow 4)$ -2-azido-3,6-di-*O*-benzyl-2-deoxy- α -D-glucopyranosyl- $(1\rightarrow 6)$ -1-*O*-allyl-2,3,4,5-tetra-*O*-benzyl-D-*myo*-inositol (11)



A solution of $[IrCOD(PPh_2Me)_2]PF_6$ (22 mg, 26 µmol) in THF (5 mL) was stirred under hydrogen until the color turned from red to colorless to pale yellow. The hydrogen atmosphere was exchanged with argon. This solution was added into a flask with trisaccharide **9** (0.402 g, 0.256 mmol). After 65 h, the solvent was removed and the residue was dissolved in acetone (4.5 mL) and water (0.5 mL). Mercury(II) chloride (0.347 g, 1.28 mmol) and mercury(II) oxide (8.0 mg, 37 µmol) were added. After 1 h, NaHCO_{3(aq)} was added and the reaction mixture was extracted with dichloromethane for three times. The combined organic layers were dried over Na₂SO₄, filtered and concentrated. The residue was filtered through a pad of silica gel to yield the lactol **10a** as colorless oil.

To a solution of crude lactol in DCM (3 mL) were added 2,2,2-trichloroacetonitrile (0.15 mL, 1.5 mmol) and DBU (2.0 μ L, 13 μ mol) at 0 °C. After 1 h at 0 °C, the solvent was removed to give a brown oil that was purified by silica gel column chromatography to yield imidate **10** (0.235 g, 0.140 mmol, 55 % yield over two steps) as an inseparable mixture of anomers.

A mixture of imidate 10 (0.235 g, 0.140 mmol) and pseudodisaccharide $5^{[3]}$ (0.121 g, 0.128 mmol) was co-evaporated with toluene for three times and dried under vacuum for 30 min. To a solution of this mixture in toluene (3 mL) at -40°C were added molecular sieves (4Å, 100 mg) and TMSOTf (3.0 µL, 17 µmol). After 2 h at -40°C, pyridine (50 µL) was added to quench the reaction. The reaction mixture was filtered to give a vellow oil that was purified by silica gel column chromatography to afford pseudopentasaccharide **11** (0.310 g, 0.126 mmol, 98% yield): $[\alpha]_{D}^{20} = +18.7$ (c = 1.0, CHCl₃); ATR-FTIR (cm⁻¹): 3063, 3031, 2924, 2865, 2105, 1741, 1721, 1497, 1454, 1361, 1048, 1027; ¹H NMR (300 MHz, CDCl₃) δ 6.8-7.8 (m, 72H), 5.89-5.95 (m, 1H, -CH=), 5.43-5.71 (m, 5H), 3.59-5.10 (m, 38H), 3.14-3.59 (m, 12H), 2.38-2.58 (m, 4H, CH₂ of Lev), 2.06 (s, 3H, Me of Lev), 0.96 (s, 21 H, TIPS); ¹³C NMR (100 MHz, CDCl₃) δ 12.1, 18.1, 18.1, 28.0, 29.7, 37.9, 63.0, 63.5, 66.3, 68.6, 69.0, 69.1, 69.6, 73.7, 73.8, 74.0, 74.1, 74.5, 74.6, 74.7, 74.8, 75.0, 75.0, 75.1, 75.3, 75.3, 75.8, 78.6, 79.8, 80.2, 80.4, 80.9, 81.3, 81.9, 82.0, 97.5, 98.6, 99.0, 99.1, 117.2, 125.5, 125.6, 126.0, 127.1, 127.2, 127.2, 127.3, 127.4, 127.4, 127.5, 127.5, 127.6, 127.7, 127.7, 127.7, 127.8, 127.8, 127.9, 127.9, 128.0, 128.0, 128.1, 128.2, 128.3, 128.3, 128.4, 128.4, 137.9, 138.1, 138.2, 138.3, 138.4, 138.6, 138.7, 138.8, 138.8, 138.9, 139.1, 171.7, 205.7; HRMS-MALDI (*m/z*): [M+Na]⁺ Calcd for C₁₄₉H₁₆₇N₃O₂₇SiNa, 2481.1454; Found: 2481.1390.

2,3,4-Tri-*O*-benzyl-6-*O*-triisopropylsilyl- α -D-mannopyranosyl- $(1\rightarrow 2)$ -3,4,6-tri-*O*-benzyl- α -D-mannopyranosyl- $(1\rightarrow 6)$ -3-*O*-benzyl-2-*O*-levulinyl-4- α -D-mannopyranosyl- $(1\rightarrow 4)$ -2-azido-3,6-di-*O*-benzyl-2-deoxy- α -D-glucopyranosyl- $(1\rightarrow 6)$ -1-*O*-allyl-2,3,4,5-tetra-*O*-benzyl-D-*myo*-inositol (12)



Pseudopentasaccharide 11 (85.0 mg, 34.6 µmol) was dissolved in a mixture of DCM and water (v:v = 4:1, 10 mL). DDQ (24.0 mg, 0.104 mmol) was added at 0 °C. After 5 h, the reaction mixture was washed with saturated NaHCO_{3(aq)}, dried over MgSO₄, filtered and concentrated. The crude product was purified by silica gel column to give alcohol 12 (68.2 mg, 29.4 μ mol, 85% yield): $[\alpha]_D^{20} = +$ 40.2 (c = 0.80, CHCl₃); ATR-FTIR (cm⁻¹): 3064, 3031, 2927, 2865, 2105, 1742, 1721, 1497, 1454, 1361, 1053, 1028; ¹H NMR (400 MHz, CDCl₃) δ 7.39 – 6.80 (m, 65H), 5.85 (m, 1H), 5.64 (d, J =3.7 Hz, 1H), 5.36 – 5.26 (m, 2H), 5.26 – 5.15 (m, 2H), 5.10 (dd, J = 10.4, 1.5 Hz, 1H), 4.97 – 3.26 (m, 54H), 3.24 – 3.22 (m, 2H), 3.16 – 3.07 (m, 2H), 2.47 – 2.17 (m, 4H, CH₂ of Lev), 1.92 (s, 3H, Me of Lev), 0.99 (br, 21H, TIPS); ¹³C NMR (101 MHz, CDCl₃) δ 205.32 (ketone), 171.27 (ester), 138.72, 138.50, 138.46, 138.20, 138.12, 137.99, 137.90, 137.82, 137.52, 137.45, 134.33, 133.90, 128.07, 128.05, 128.03, 128.00, 127.95, 127.91, 127.88, 127.83, 127.76, 127.65, 127.63, 127.58, 127.55, 127.51, 127.39, 127.35, 127.30, 127.29, 127.20, 127.14, 127.10, 127.02, 126.97, 126.84, 126.66, 116.78 (=CH₂ of allyl), 98.84, 98.72, 98.11, 97.16, 81.63, 81.49, 80.95, 80.56, 80.07, 79.26, 75.39, 74.99, 74.77, 74.57, 74.45, 74.10, 73.74, 73.59, 73.48, 72.95, 72.51, 72.27, 72.05, 71.75, 71.55, 71.28, 70.46, 69.31, 68.92, 68.26, 65.49, 63.16, 62.50, 62.11, 37.53 (-CH₂- of Lev), 29.31 (-CH₃), 27.67 (-CH₂- of Lev), 17.73 (-CH₃ of TIPS), 17.69 (-CH₃ of TIPS), 11.73 (-CHMe₂ of TIPS); ESI-MS: m/z [M+Na]⁺ cald 2341.0822, obsd 2341.0870.

Allyl 3-O-benzyl-2-O-levulinyl-6-O-tertbutyldiphenylsilyl-α-D-mannopyranoside (15)



Mannoside 1 (2.50 g, 3.18 mmol) was dissolved in PBS buffer (1.0 M, 1 mL, pH 7.4) and dichloromethane (19 mL). DDQ (0.865 g, 3.81 mmol) was added at 0°C. After 5 h the reaction mixture was washed with sat. NaHCO₃ solution, dried over Na₂SO₄, filtered and concentrated. The crude product was purified by silica gel column chromatography to give mannoside 15 (1.83 g, 2.83 mmol, 89% yield) as colorless oil: R_f (SiO₂, EtOAc/Cyclohexane 1:2) = 0.20; $[\alpha]_D^{20}$: + 4.42 (c = 1.09, CHCl₃): ATR-FTIR (cm⁻¹): 3486, 3071, 2930, 2857, 1741, 1720, 1428, 1362, 1138, 1105, 1082, 1044, 741, 702; ¹H NMR (400 MHz, CDCl₃) δ 7.71-7.69 (m, 4H), 7.42-7.26 (m, 11H), 5.86 (m, 1H, =CH-), 5.35 (dd, J = 3.2, 1.7 Hz, 1H, Man-2), 5.24 (m, 1H, =CH₂), 5.17 (m, 1H, =CH₂), 4.84 (d, J = 1.7 Hz, 1H, Man-1), 4.69 (d, J = 11.2 Hz, 1H, CH₂ of Bn), 4.45 (d, J = 11.2 Hz, 1H, CH₂ of Bn), 4.14 (ddt, J = 13.0, 5.6, 1.5 Hz, 1H, CH₂ of allyl), 3.99 – 3.88 (m, 4H, CH₂ of allyl, Man-4, Man-6), 3.80 (dd, J = 9.4, 3.2 Hz, 1H, Man-3), 3.69 (dt, J = 9.4, 4.0 Hz, 1H, Man-5), 2.77 - 2.53 (m, 4H, CH₂ of Lev), 2.10 (s, 3H, Me of Lev), 1.05 (s, 9H, tBu); ¹³C NMR (101 MHz, CDCl₃) δ 206.15 (ketone), 172.00 (ester), 137.77, 135.70, 135.59, 133.50, 133.45, 133.26, 129.67, 129.66, 128.45, 128.14, 127.88, 127.65, 127.62, 117.67 (CH₂=), 96.83 (C1), 77.64 (C3), 72.35 (C5), 71.52 (-OCH₂-), 68.22 (C2), 67.93 (-OCH₂- of allyl), 67.26 (C4), 63.87 (C6), 37.94 (-CH₂CH₂- of Lev), 29.77 (Me), 28.07 (-CH₂CH₂- of Lev), 26.80 (Me of tBu), 19.31 (CMe₃); ESI-MS: $m/z [M+Na]^+$ cald 669.2854, obsd 669.2858.

Allyl3,4,6-tri-O-benzyl-2-deoxy-2-trichloracetamido- β -D-galactopyranosyl- $(1 \rightarrow 4)$ -3-O-benzyl2-O-levulinyl-6-O-tertbutyldiphenylsilyl- α -D-mannopyranoside (16)



Dibutyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-trichloracetamido- α -D-galactopyranosyl phosphate **8**^[4] (63 mg, 0.080 mmol) and alcohol **15** (40 mg, 0.062 mmol) were evaporated with toluene (3x2 mL) and placed under high vacuum for 30 min. The residue was dissolved in anhydrous DCM (3 mL) and molecular sieves (4Å, 150 mg) were added. The slurry was stirred for 15 min at r.t. before it was cooled down to -40°C. TMSOTf (14.5 µL, 0.080 mmol) was added dropwise and the yellow solution was stirred at -40°C for 1h before it was quenched with TEA (100 µL) and diluted with CHCl₃ (10

mL). The reaction mixture was filtered over Celite® and solvents were removed under reduced pressure. The residue was purified using flash column chromatography (n-hexane/ethyl acetate 5:1) to yield 16 (62 mg, 0.051 mmol, 82% yield) as white foam: R_f (SiO₂, *n*-hexane/ethyl acetate 3:1) = 0.55; $[\alpha]^{20}_{D}$: + 30.2 (c = 1.00, CHCl₃); ATR-FTIR (cm⁻¹): 3409, 3066, 3032, 2929, 2858, 1737, 1717. 1520. 1362. 1140. 1105. 1065cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.77 – 7.71 (m, 4H), 7.43 – 7.24 (m, 21H), 7.23 - 7.16 (m, 5H), 6.32 (d, J = 7.4 Hz, 1H, NH), 5.93 - 5.84 (m, 1H, CH of allyl), 5.34 (dd, J = 3.3, 1.5 Hz, 1H, Man-2), 5.26 (dd, J = 17.2, 1.5 Hz, 1H, CH₂ of allyl), 5.20 (dd, J =10.4, 1.2 Hz, 1H, CH₂ of allyl), 5.16 (d, J = 8.3 Hz, 1H, Gal-1), 4.89 (d, J = 11.2 Hz, 1H), 4.84 (d, J= 1.5 Hz, 1H, Man-1), 4.69 – 4.62 (m, 3H), 4.57 (d, J = 11.2 Hz, 1H), 4.47 (d, J = 11.3 Hz, 1H), 4.35 $(d, J = 11.8 \text{ Hz}, 1\text{H}), 4.27 (d, J = 11.8 \text{ Hz}, 1\text{H}), 4.18 (dd, J = 12.8, 5.3 \text{ Hz}, 1\text{H}), 4.09 - 4.03 (m, 2\text{H}), 4.09 (m, 2\text{H}), 4.09 (m, 2\text{H}), 4.09 (m, 2\text$ 4.01 - 3.94 (m, 4H), 3.86 (dd, J = 11.2, 5.4 Hz, 1H), 3.77 (dd, J = 9.8, 4.9 Hz, 1H), 3.70 (dt, J = 11.2, 5.4 Hz, 110, 3.70 (dt, J = 11.2, 3.8 Hz, 3.810.9, 7.9 Hz, 1H), 3.63 (t, J = 8.6 Hz, 1H), 3.45 (dd, J = 8.0, 5.4 Hz, 1H), 3.33 (dd, J = 9.0, 5.2 Hz, 1H), 2.65 – 2.53 (m, 2H, CH₂ of Lev), 2.53 – 2.46 (m, 1H, CH₂ of Lev), 2.46 – 2.40 (m, 1H, CH₂ of Lev), 2.05 (s, 3H, Me of Lev), 1.08 (s, 9H, tBu); 13 C NMR (151 MHz, CDCl₃) δ 206.33 (ketone), 172.10 (ester), 161.89 (CCl₃CONH), 138.76, 138.70, 138.05, 137.80, 136.10, 135.73, 133.85, 133.62, 133.34, 129.98, 129.88, 128.57, 128.49, 128.32, 128.24, 128.13, 128.01, 127.97, 127.87, 127.84, 127.83, 127.72, 127.69, 127.20, 127.05, 117.96 (CH₂ of Allyl), 98.55 (Gal-1), 96.49 (Man-1), 92.39 (CCl₃CONH), 77.20, 76.52, 74.92, 73.56, 73.24, 72.91, 72.67, 72.21, 72.07, 71.66, 69.22, 68.16, 68.09, 63.70, 56.76, 38.06, 29.81 (Me of Lev), 28.20, 26.81 (Me of tBu), 19.43 (C_{auart} of tBu); (ESI-MS): m/z [M+Na]⁺ cald 1244.3893 for C₆₆H₇₄Cl₃NO₁₃Si, obsd 1244.3875.

Allyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-trichloracetamido- β -D-galactopyranosyl-(1 \rightarrow 4)-3-*O*-benzyl-2-*O*-levulinyl- α -D-mannopyranoside (17)



Disaccharide **16** (62 mg, 0.051 mmol) was dissolved in THF (400 µL) in a 15 mL FalconTM tube and HF-pyridine (101 µL, 5.570 mmol) was added. The solution was stirred for 24 h at room temperature before it was quenched with sat. NaHCO₃ solution and extracted with ethyl acetate (2 x 15 mL). Solvents were removed under reduced pressure and the residue was purified using flash column chromatography (*n*-hexane/ethyl acetate 1:2->1:3) to yield 17 as yellow oil (40 mg, 0.041 mmol, 80% yield): R_f (SiO₂, *n*-hexane/ethyl acetate 1:3) = 0.24; $[\alpha]^{20}_{\text{D}}$: + 26.2 (c = 1.00, CHCl₃); ATR-FTIR (cm⁻¹): 3506, 3332, 3062, 2923, 2870, 1740, 1718, 1530, 1455, 1364, 1139, 1100, 1070, 1027; ¹H NMR (600 MHz, CDCl₃) δ 7.27 – 7.08 (m, 20H), 6.84 (d, *J* = 7.3 Hz, 1H, NH), 5.82 – 5.73 (m, 1H, CH of allyl), 5.24 (dd, *J* = 3.2, 1.4 Hz, 1H, Man-2), 5.18 (dd, *J* = 17.2, 1.5 Hz, 1H, CH₂= of al-

lyl), 5.14 – 5.10 (m, 2H, CH₂= of allyl and Gal-1), 4.81 (d, J = 11.4 Hz, 1H), 4.74 (d, J = 1.4 Hz, 1H, Man-1), 4.61 (d, J = 11.6 Hz, 1H), 4.55 (d, J = 11.2 Hz, 1H), 4.48 (d, J = 11.5 Hz, 2H), 4.40 (d, J = 11.2 Hz, 1H), 4.31 (d, J = 11.7 Hz, 1H), 4.22 (d, J = 11.7 Hz, 1H), 4.11 (dd, J = 10.9, 2.4 Hz, 1H), 4.08 – 4.02 (m, 2H), 3.93 – 3.84 (m, 4H), 3.75 (dd, J = 12.1, 3.4 Hz, 1H), 3.72 – 3.68 (m, 1H), 3.62 – 3.57 (m, 1H), 3.55 – 3.49 (m, 2H), 3.41 – 3.35 (m, 1H), 2.52 – 2.38 (m, 3H, CH₂ of Lev), 2.33 (dt, J = 16.7, 6.2 Hz, 1H, CH₂ of Lev), 1.99 (s, 3H, Me of Lev).; ¹³C NMR (151 MHz, CDCl₃) δ 206.47 (ketone), 172.00 (ester), 162.17 (amide), 138.63, 138.27, 137.88, 137.66, 133.42, 128.58, 128.54, 128.46, 128.35, 128.10, 128.06, 128.03, 127.94, 127.70, 127.45, 126.86, 118.05 (CH₂= of Allyl), 98.63 (Gal-1), 96.80 (Man-1), 92.73 (CCl₃CONH), 77.24, 76.45, 74.87, 73.61, 73.50, 72.24, 71.97, 71.71, 71.07, 68.87, 68.43, 68.40, 61.76, 56.29, 38.00, 29.82, 29.80 (Me of Lev), 28.11.; ESI-MS for C₅₀H₅₆Cl₃NO₁₃: m/z [M+Na]⁺ cald 1006.2715, obsd 1006.2714.

Allyl 2,3,4-tri-*O*-benzyl-6-*O*-triisopropylsilyl- α -D-mannopyranosyl- $(1\rightarrow 2)$ -3,4,6-tri-*O*-benzyl- α -D-mannopyranosyl- $(1\rightarrow 6)$ -3-*O*-benzyl-4-*O*-(3,4,6-tri-*O*-benzyl-2-deoxy-2-trichloracetamido- β -D-galactopyranosyl)-2-*O*-levulinyl- α -D-mannopyranoside (18a)



Disaccharide **17** (40 mg, 0.041 mmol) and dimannoside **4** (63 mg, 0.054 mmol) were co-evaporated with toluene (3 x 2 mL) and placed under high vacuum for 30 min. The residue was dissolved in an-hydrous diethyl ether (3 mL) and molecular sieves (4Å, 150 mg) were added. The slurry was stirred for 10 min at room temperature before it was cooled down to 0°C and TBSOTf (9.3 μ L, 0.041 mmol) was added. The reaction mixture was stirred for 1 h at 0°C before it was quenched with TEA (100 μ L) and filtered over Celite®. Solvents were evaporated under reduced pressure and the crude product was purified using flash column chromatography (*n*-hexane/ethyl acetate 4:1) to yield tetra-saccharide **18a** (60 mg, 0.030 mmol, 74% yield) as yellow oil: R_f (SiO₂, *n*-hexane/ethyl acetate 4:1) = 0.24; [α]²⁰_D: + 19.8 (c = 1.00, CHCl₃); ATR-FTIR (cm⁻¹): 3350, 2925, 2866, 1719, 1524, 1454, 1363, 1137, 1100, 1071, 1028; ¹H NMR (400 MHz, CDCl₃) δ 7.26 – 7.04 (m, 50H), 6.43 (s, 1H, NH {rotamer}), 6.08 (s, 1H, NH {rotamer}), 5.73 (m, 1H, =CH of allyl), 5.26 – 5.21 (m, 2H, ManI-2{5.24ppm}), 5.15 (d, *J* = 17.2 Hz, 1H, CH₂= of allyl), 5.08 (d, *J* = 8.3 Hz, 1H, Gal-1), 5.05 (d, *J* = 10.5 Hz, 1H, CH₂= of allyl), 4.83 (d, *J* = 10.9 Hz, 1H), 4.77 – 4.69 (m, 3H), 4.68 (d, *J* = 1.3 Hz, 1H,

ManI-1), 4.64 – 4.22 (m, 16H), 4.15 (d, J = 11.7 Hz, 1H), 4.10 – 3.93 (m, 5H), 3.91 – 3.53 (m, 17H), 3.53 – 3.40 (m, 2H), 3.29 (dd, J = 8.2, 4.7 Hz, 1H), 2.51 – 2.29 (m, 4H, CH₂ of Lev), 1.96 (s, 3H, Me of Lev), 1.04 – 0.98 (m, 21H, TIPS); ¹³C NMR (101 MHz, CDCl₃) δ 206.33 (ketone), 172.02 (ester), 163.47 (amide {rotamer}), 162.19 (amide {rotamer}), 139.10, 138.89, 138.65, 138.58, 138.55, 138.34, 138.17, 137.99, 137.71, 133.33, 128.54, 128.48, 128.46, 128.44, 128.38, 128.34, 128.28, 128.19, 128.14, 128.08, 128.07, 128.05, 127.93, 127.88, 127.84, 127.79, 127.75, 127.73, 127.62, 127.57, 127.54, 127.45, 127.40, 127.36, 127.26, 118.43 (CH₂= of Allyl), 98.68 (Gal-1), 98.55, 98.36, 96.33 (ManI-1), 92.71 (CCl₃CO), 80.90, 79.67, 77.36, 76.38, 75.26, 75.18, 74.98, 74.95, 74.72, 74.53, 73.85, 73.60, 73.47, 73.37, 72.43, 72.27, 72.19, 72.13, 71.70, 71.39, 69.99, 68.87 (ManI-2), 68.43, 67.99, 66.41, 63.03, 56.45, 37.99 (CH₂ of Lev), 29.82 (Me of Lev), 28.13 (CH₂ of Lev), 18.22 (TIPS), 18.17 (TIPS), 12.19 (TIPS); (ESI-MS): m/z [M+Na]⁺ cald 2026.7917 for C₁₁₃H₁₃₂Cl₃NO₂₃Si, obsd 2026.7891.

 $\label{eq:allyl2} Allyl2,3,4-tri-O-benzyl-6-O-triisopropylsilyl-α-D$-mannopyranosyl-(1$-$2)$-3,4,6-tri-O-benzyl-α-D$-mannopyranosyl-(1$-$6)$-4-O-(3,4,6-tri-O-benzyl-2-deoxy-2-acetamido-β-D$-galactopyranosyl)-$3$-$O$-benzyl-$2$-$O$-levulinyl-$\alpha$-D$-mannopyranoside (18)}$



Tetrasaccharide **18a** (60 mg, 0.030 mmol) was dissolved in acetic acid (1 mL) and heated to 55°C to give a colorless solution. Zinc (195 mg, 2.99 mmol) was added to this solution in three portions over 30 min. Afterwards the slurry was stirred for 2 h at 55°C before it was filtered, diluted with toluene (10 mL) and evaporated to dryness. The residue was purified using column chromatography (*n*-hexane/ethyl acetate 2:1) to yield tetrasaccharide **18** (42 mg, 0.022 mmol, 74% yield) as yellow oil: R_f (SiO₂, *n*-hexane/ethyl acetate 2:1) = 0.22; $[\alpha]^{20}_{\text{D}}$: + 22.6 (c = 1.00, CHCl₃); ATR-FTIR (cm⁻¹): 3349, 2924, 2865, 1741, 1721, 1675, 1454, 1364, 1136, 1064, 1028cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.03 (m, 50H), 6.21 (d, J = 7.4 Hz, 1H, NH), 5.74 (m, 1H, CH of allyl), 5.28 – 5.11 (m, 3H), 5.06 (t, J = 8.6 Hz, 2H), 4.85 (d, J = 10.8 Hz, 1H), 4.79 – 4.67 (m, 4H), 4.64 – 4.28 (m, 14H), 4.23 – 4.15 (m, 2H), 4.13 – 3.36 (m, 25H), 3.16 (dd, J = 8.2, 4.7 Hz, 1H), 2.51 – 2.31 (m, 4H, CH₂ of Lev), 1.96 (s, 3H, Me of Lev), 1.69 (s, 3H, Me of NHAc), 1.08 – 0.93 (m, 21H, TIPS); ¹³C

NMR (101 MHz, CDCl₃) δ 206.26 (ketone), 172.12 (ester), 170.95 (amide), 139.08, 138.93, 138.70, 138.57, 138.39, 138.30, 138.08, 137.80, 133.28 (CH of Allyl), 128.59, 128.54, 128.43, 128.41, 128.36, 128.32, 128.30, 128.21, 128.15, 128.14, 128.09, 128.00, 127.94, 127.89, 127.78, 127.74, 127.61, 127.59, 127.47, 127.37, 127.29, 127.18, 118.38 (CH₂= of allyl), 100.33, 98.43, 98.11, 96.50 (4x anomeric carbon), 80.78, 79.55, 78.31, 76.49, 75.51, 75.23, 75.04, 74.57, 74.50, 74.09, 73.98, 73.50, 73.36, 73.31, 72.40, 72.35, 72.28, 72.14, 71.81, 71.76, 71.47, 70.19, 69.48, 68.95, 68.59, 68.03, 65.83, 64.68, 63.03, 55.03, 37.98 (CH₂ of Lev), 29.82 (CH₃ of Lev), 28.14 (CH₂ of Lev), 23.55 (CH₃CONH), 18.22 (TIPS), 18.17 (TIPS), 12.20 (TIPS); ESI-MS for C₁₁₃H₁₃₅NO₂₃Si: m/z [M+Na]⁺ cald 1925.9125, obsd 1925.9080.



Hydrogen was bubbled for 20 min through a solution of [IrCOD(PPh₂Me)₂]PF₆ (10 mg, 0.012 mmol) in anhydrous THF (3 mL) to yield a pale yellow solution. The atmosphere was exchanged to nitrogen and the solution was added to tetrasaccharide **18** (40 mg, 0.021 mmol). The resulting reaction mixture was stirred for 12 h at room temperature before removal of solvents. The residue was dissolved in acetone (2.8 mL) and water (0.2 mL). HgCl₂ (34.2 mg, 0.126 mmol) and HgO (0.5 mg, 0.002 mmol) were added and the solution was stirred for 2 h at room temperature before it was diluted with ethyl acetate (15 mL) and washed with sat. NaHCO₃ solution (15 mL). The organic layer was dried over Na₂SO₄, filtered and concentrated. The residue was purified using column chromatography (*n*-hexane/ethyl acetate 2:1) to yield lactol **20a** (27 mg, 0.014 mmol, 69% yield) as color-less oil: R_f (SiO₂, *n*-hexane/ethyl acetate 3:2) = 0.20; $[\alpha]^{20}_{\text{D}}$: + 15.3 (c = 1.00, CHCl₃); ATR-FTIR (cm⁻¹): 3349, 2925, 2865, 1739, 1720, 1673, 1455, 1364, 1105, 1067, 1028; ¹H NMR (600 MHz, CDCl₃) δ 7.29 (d, *J* = 7.3 Hz, 2H), 7.26 – 7.10 (m, 44H), 7.07 – 7.02 (m, 4H), 6.28 (d, *J* = 7.1 Hz, 1H, NH), 5.12 (d, *J* = 8.3 Hz, 1H, GalNAc-1), 5.04 (s, 1H), 4.92 (s, 1H), 4.83 (d, *J* = 10.3 Hz, 1H), 4.76 (d, *J* = 3.8 Hz, 1H), 4.71 (d, *J* = 11.6 Hz, 1H), 4.63 – 4.40 (m, 12H), 4.35 (dd, *J* = 24.0, 11.8

Hz, 3H), 4.26 (dd, J = 11.4, 1.6 Hz, 2H), 4.14 – 3.93 (m, 8H), 3.87 – 3.74 (m, 5H), 3.67 (d, J = 6.5 Hz, 2H), 3.58 – 3.50 (m, 3H), 3.48 – 3.41 (m, 4H), 3.37 (dd, J = 8.1, 5.3 Hz, 1H), 3.30 (dd, J = 8.4, 6.6 Hz, 1H), 3.04 (dd, J = 8.7, 5.0 Hz, 1H), 2.53 – 2.35 (m, 4H, CH₂ of Lev), 1.99 (s, 3H, CH₃ of Lev), 1.73 (s, 3H, CH₃CONH), 1.05 – 0.99 (m, 21H, TIPS); ¹³C NMR (151 MHz, CDCl₃) δ 206.39 (ketone), 171.90 (ester), 171.24 (amide), 139.01, 138.94, 138.89, 138.67, 138.42, 138.20, 138.17, 138.13, 137.60, 128.71, 128.59, 128.57, 128.45, 128.43, 128.30, 128.24, 128.21, 128.11, 128.10, 128.03, 127.98, 127.97, 127.95, 127.90, 127.74, 127.70, 127.69, 127.63, 127.45, 127.45, 127.16, 126.70, 100.46 (GalNAc-1; $J_{CH} = 167$ Hz; β), 97.88 ($J_{CH} = 173$ Hz; α), 96.81($J_{CH} = 172$ Hz; α), 91.86 ($J_{CH} = 176$ Hz, α), 79.82, 77.78, 77.37, 77.16, 76.95, 76.65, 75.99, 75.79, 75.41, 75.15, 74.89, 74.64, 73.39, 73.36, 73.12, 72.71, 72.59, 72.51, 72.33, 72.26, 72.07, 72.01, 70.96, 70.07, 69.75, 69.01, 68.32, 67.58, 62.90, 55.93, 38.11 (CH₂ of Lev), 29.89 (CH₃ of Lev), 28.22 (CH₂ of Lev), 23.54 (CH₃CONH), 18.25 (TIPS), 18.19 (TIPS), 12.26 (TIPS); (ESI-MS): m/z [M+Na]⁺ cald 1885.8806 for C₁₁₀H₁₃₁NO₂₃Si, obsd 1885.8787.

 $\begin{array}{l} 2,3,4\text{-}\mathrm{Tri}\text{-}\textit{O}\text{-}\mathrm{benzyl-6-}\textit{O}\text{-}\mathrm{tri}iso propylsilyl-} \alpha\text{-}\mathrm{D}\text{-}\mathrm{mannopyranosyl-}(1\rightarrow2)\text{-}3,4,6\text{-}\mathrm{tri}\text{-}\textit{O}\text{-}\mathrm{benzyl-}\alpha\text{-}\mathrm{D}\text{-}\mathrm{mannopyranosyl-}(1\rightarrow6)\text{-}4\text{-}\textit{O}\text{-}(3,4,6\text{-}\mathrm{tri}\text{-}\textit{O}\text{-}\mathrm{benzyl-}2\text{-}\mathrm{acetamido-}\beta\text{-}\mathrm{D}\text{-}\mathrm{galactopyranosyl-}(1\rightarrow6)\text{-}4\text{-}O\text{-}(3,4,6\text{-}\mathrm{tri}\text{-}\textit{O}\text{-}\mathrm{benzyl-}2\text{-}\mathrm{acetamido-}\beta\text{-}\mathrm{D}\text{-}\mathrm{galactopyranosyl-}(1\rightarrow4)\text{-}2\text{-}\mathrm{azido-}3,6\text{-}\mathrm{di}\text{-}O\text{-}\mathrm{benzyl-}2\text{-}\mathrm{deoxy-}\alpha\text{-}\mathrm{D}\text{-}\mathrm{glucopyranosyl-}(1\rightarrow6)\text{-}1\text{-}O\text{-}\mathrm{allyl-}2,3,4,5\text{-}\mathrm{tetra}\text{-}O\text{-}\mathrm{benzyl-}D\text{-}myo\text{-}\mathrm{inositol}\ (20)\end{array}$



Lactol **20a** (27 mg, 0.014 mmol) was dissolved in anhydrous DCM (1mL) and trichloroacetonitrile (145 μ L, 1.449 mmol) was added. Afterwards DBU (1.1 μ L, 0.007 mmol) was added and the reaction mixture was stirred for 1 h at room temperature before removal of solvents. The residue was purified using column chromatography (*n*-hexane/ethyl acetate 2:1 containing 0.1% TEA) to yield imidate **19** (26 mg, 0.013 mmol, 89% yield) as an inseparable mixture of anomers.

Imidate **19** (26 mg, 0.013 mmol) and pseudodisaccharide **5** (10 mg, 0.011 mmol) were evaporated with toluene (3 x 2 mL) and the residue was placed under high vacuum for 30min. The residue was dissolved in anhydrous diethyl ether (1 mL) and molecular sieves (4Å, 50 mg) were added. The slurry was stirred for 10 min at room temperature before it was cooled down to 0°C and TBSOTf (2.4

µL, 0.011 mmol) was added. The reaction mixture was stirred for 1 h at 0°C before it was quenched with TEA (50 µL) and filtered over Celite[®]. Solvents were removed under reduced pressure and the crude product was purified using flash column chromatography (*n*-hexane/ethyl acetate 3:1) to yield pseudohexasaccharide 20 (24 mg, 0.009 mmol, 81% yield) as yellow oil: R_f (SiO₂, *n*-hexane/ethyl acetate 2:1) = 0.51; $[\alpha]_{D}^{20}$: + 25.3 (c = 1.00, CHCl₃); ATR-FTIR (cm⁻¹) 3353, 3088, 3064, 3031, 2924, 2864, 2106, 1741, 1721, 1676, 1454, 1362, 1095, 1055, 1028, 913; ¹H NMR (400 MHz. CDCl₃) δ 7.34-7.02 (m, 80H), 5.94 (d, J = 8.8 Hz, 1H, NH), 5.84 (m, 1H, =CH of allyl), 5.62 (d, J = 3.6 Hz, 1H, Glc-1), 5.29-5.28 (m, 2H, ManI-1, ManI-2), 5.18 (dd, J = 1.5, 17.2 Hz, 1H), 5.09-5.07 (m, 2H), 4.92 (d, J = 11.2 Hz, 1H), 4.84 (d, J = 10.6 Hz, 1H), 4.83 (d, J = 10.6 Hz, 1H), 4.79-3.13 (m, 68H), 2.21-2.12 (m, 4H, -CH₂- of Lev), 1.82 (s, Me of Lev, 3H), 1.57 (s, Me of -NHAc, 3H), 0.97 (br, 21H, TIPS); ¹³C NMR (101 MHz, CDCl₃) δ 205.84 (ketone of Lev), 171.75 (ester of Lev), 170.30 (amide), 138.97, 138.90, 138.86, 138.78, 138.61, 138.51, 138.48, 138.43, 138.30, 138.26, 138.20, 138.13, 137.97, 137.85, 137.63, 134.34 (=CH of allyl), 128.57, 128.54, 128.52, 128.50, 128.46, 128.40, 128.37, 128.34, 128.28, 128.25, 128.23, 128.21, 128.15, 128.06, 128.03, 127.98, 127.91, 127.79, 127.74, 127.71, 127.67, 127.63, 127.59, 127.58, 127.54, 127.52, 127.43, 127.39, 127.31, 127.23, 127.13, 126.88, 117.18 (=CH₂ of allyl), 100.80 (GalNHAc-1), 99.39 (ManII-1), 98.55 (ManIII-1), 98.38 (ManI-1), 97.51 (Glc-1), 82.03, 81.86, 81.23, 80.94, 80.58, 79.79, 79.17, 75.79, 75.65, 75.52, 75.34, 75.28, 75.05, 74.51, 74.32, 74.26, 74.09, 73.88, 73.80, 73.57, 73.50, 73.21, 72.90, 72.82, 72.64, 72.36, 72.25, 72.18, 72.04, 71.51, 71.42, 71.11, 70.90, 70.71, 69.90, 69.76, 68.98, 68.39, 66.64, 63.74, 62.87, 53.09, 37.82 (-CH₂- of Lev), 29.64 (-CH₃), 28.00 (-CH₂- of Lev), 23.19 (-CH₃), 18.17 (-CH₃ of TIPS), 18.12 (-CH₃ of TIPS), 12.11 (-CHMe₂ of TIPS); ESI-HRMS: m/z [M+Na]⁺ cald 2814.3025, obsd 2814.3069.

400/700 MHz NMR Data		20						
(n.d. = not determin)	GlcN	ManI	ManII	ManIII	GalNAc			
cheimcal shift (ppm)	$^{1}\mathrm{H}$	5.62	5.29	4.54	5.09	4.71		
	¹³ C	97.51	98.38	99.39	98.55	100.80		
coupling constant (Hz)	H-H	3.6	n.d.	n.d.	n.d.	n.d.		
	C-H	178	174	172	171	159		

 $2,3,4-Tri-O-benzyl-6-O-tri iso propylsilyl-a-D-mannopyranosyl-(1\rightarrow 2)-3,4,6-tri-O-benzyl-a-D-mannopyranosyl-(1\rightarrow 6)-4-O-(3,4,6-tri-O-benzyl-2-deoxy-2-acetamido-\beta-D-galactopyranosyl)-3-O-benzyl-2-O-levulinyl-a-D-mannopyranosyl-(1\rightarrow 4)-2-azido-3,6-di-O-benzyl-2-deoxy-a-D-glucopyranosyl-(1\rightarrow 6)-1-O-allyl-2,3,4,5-tetra-O-benzyl-D-myo-inositol (21a)$



A solution of [IrCOD(PPh₂Me)₂]PF₆ (25 mg, 0.030 mmol) in THF (2 mL) was stirred under hydrogen atmosphere until the color turned from red to colorless to pale yellow (ca. 10 min). The hydrogen atmosphere was exchanged with argon, pseudohexasaccharide 20 (0.870 g, 0.311 mmol) in THF (5 mL) was added. After 40 h, the solvent was removed and the residue was dissolved in acetone (6.5 mL). Water (0.5 mL), mercury(II) chloride (0.423 g, 1.56 mmol) and mercury(II) oxide (7.0 mg, 0.032 mmol) were added. After 20 min, NaHCO_{3(aq)} (15 mL) was added and the reaction mixture was extracted with DCM (3 x 10 mL). The combined organic layers were dried over Na_2SO_4 , filtered and concentrated. The crude product was purified by silica gel column chromatography to give alcohol **21a** (0.70 g, 0.254 mmol, 82% yield) as colorless oil: R_f (SiO₂, *n*-hexane/ethyl acetate 2:1) = $0.21 \ [\alpha]^{20}$:+ 24.6 (c = 0.71, CHCl₃); ATR-FTIR (cm⁻¹) 3349, 3089, 3064, 3031, 2924, 2865, 2107, 1739, 1720, 1675, 1454, 1362, 1094, 1053, 1028; ¹H NMR (400 MHz, CDCl₃) δ 7.30-7.02 (m, 80H), 5.94 (d, J = 8.6 Hz, 1H, NH), 5.28 (d, J = 3.5 Hz, 1H, Glc-1), 5.27-5.26 (m, 2H, ManI-1, ManI-2), 5.10 (br, 1H, ManIII-1), 4.90 (d, J = 11.6 Hz, 1H), 4.88 (d, J = 10.8 Hz, 1H), 4.83 (d, J = 10.7 Hz, 1H), 4.83 (d, J = 10.7 Hz, 1H), 4.75-4.35 (m, 20H), 4.27-4.19 (m, 7H), 4.10-3.76 (m, 17H), 3.74-3.68 (m, 2H), 3.63-3.26 (m, 17H), 2.19-3.11 (m, 2H), 2.23-2.15 (m, 4H, CH₂ of Lev), 1.82 (s, Me of Lev, 3H), 1.57 (s, Me of -NHAc, 3H), 0.99-0.96 (m, 21H, TIPS); ¹³C NMR (101 MHz, CDCl₃) δ 205.91 (ketone of Lev), 171.74 (ester of Lev), 170.52 (amide), 138.96, 138.91, 138.88, 138.72, 138.64, 138.49, 138.47, 138.42, 138.30, 138.26, 138.20, 137.98, 137.71, 137.61, 128.56, 128.55, 128.53, 128.50, 128.49, 128.44, 128.39, 128.37, 128.32, 128.27, 128.25, 128.19, 128.17, 128.08, 128.03, 127.98, 127.95, 127.84, 127.79, 127.77, 127.74, 127.70, 127.67, 127.64, 127.57, 127.51, 127.43, 127.31, 127.03, 100.76 (GalNHAc-1), 99.43 (ManII-1), 98.58 (ManIII-1), 98.22 (ManI-1), 98.04 (Glc-1), 82.00, 81.38, 81.00, 80.97, 80.92, 80.57, 79.53, 79.26, 77.23, 75.86, 75.79, 75.73, 75.31, 75.04, 74.91, 74.57, 74.38, 74.21, 73.89, 73.84, 73.58, 73.51, 73.30, 73.00, 72.79, 72.59, 72.39, 72.28, 72.22, 72.08, 71.58, 71.54, 70.73, 70.58, 69.85, 69.00, 68.57, 66.54, 64.61, 62.97, 53.33, 37.81 (-CH₂- of Lev), 29.69 (-CH₃), 28.01 (-CH₂- of Lev), 23.25 (-CH₃), 18.22 (-CH₃ of TIPS), 18.17 (-CH₃ of TIPS), 12.15 (-CHMe₂ of TIPS); ESI-MS: m/z [M+Na]⁺ cald 2775.2751, obsd 2775.2783.

Triethylammonium (S)-2,3-bis(stearoyloxy)propyl phosphonate (6)^[4]



Phosphorous acid was submitted to azeotropic drying with freshly distilled pyridine three times to produce pyridinium hydrogenphosphonate. The mixture of 1,2-distearoyl-sn-glycerol (380 mg, 0.608 mmol) and pyridinium hydrogenphosphonate (108 mg, 0.669 mmol) was co-evaporated with freshly distilled pyridine (3 x 5 mL of pyridine; last removal of pyridine was carried out overnight). The solid residue was dissolved in anhydrous pyridine (15 mL). Pivaloyl chloride (82 µL, 0.669 mmol) was added to the reaction mixture dropwise. The mixture was stirred under nitrogen at room temperature for 2 days. Volatile organics were removed under reduced pressure and the crude product was purified on a column of silica gel deactivated with triethylamine (eluting with 5% MeOH in CH₂Cl₂ and gradually increasing the polarity to 10% MeOH in CH₂Cl₂) to afford H-phosphonate 6 (451 mg, 94% yield) as a white greasy solid. If the product is contaminated with excess triethylammonium salts, the salts can be removed on a Sephadex LH-20 size exclusion column (eluting with 1:1 MeOH: CH₂Cl₂ containing 0.5 % Et₃N by volume) to give pure triethylammonium (S)-2,3bis(stearovloxy)propyl phosphonate: R_f (10% MeOH in CH_2Cl_2) = 0.3; $[\alpha]_D^{20} = +$ 2.5 (c = 1.2, CHCl₃); ATR-FTIR (cm⁻¹): 3290, 2911, 1743, 1489, 1237, 1190; ¹H NMR (400 MHz, CDCl₃) δ 12.55 (1H, $H(NEt_3)$), 6.86 (d, J = 668 Hz, 1H, H-P); 5.26 – 5.17 (m, 1H), 4.38 (dd, J = 11.9, 3.6 Hz, 1H), 4.18 (dd, J = 11.9, 6.4 Hz, 1H), 3.99 (dd, J = 7.9, 5.3 Hz, 2H), 3.07 (br d, 6H, 3CH₂-Et₃N), 2.26 (q, J= 6.8 Hz, 4H), 1.65-1.49 (m, 4H), 1.36 (t, J = 7.3 Hz, 9H, 3CH₃-Et₃N), 1.22-1.29 (m, 56H), 0.88 (t, J = 6.6 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 173.9, 173.0, 70.1, 62.4, 62.3, 45.7 (3C, (CH₃CH₂)₃N), [34.3, 34.1, 31.9, 29.7 - 29.1, 24.9, 22.7 (32C, CH₂lipid)] 14.1 (2C, CH₃lipid), 8.55(3C, (CH₃CH₂)₃N), ³¹P NMR (162 MHz, CDCl₃) δ 4.87; ESI-MS for C₃₉H₉₃NO₇P: m/z [M-H+2Na]⁺ cald 733.5119, obsd 733.5118.

Triethylammonium 2,3,4-tri-*O*-benzyl-6-*O*-tri*iso*propylsilyl-α-D-mannopyranosyl-(1 \rightarrow 2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1 \rightarrow 6)-4-*O*-(3,4,6-tri-*O*-benzyl-2-deoxy-2-acetamido-β-D-galactopyranosyl)-3-*O*-benzyl-2-*O*-levulinyl-α-D-mannopyranosyl-(1 \rightarrow 4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1 \rightarrow 6)-2,3,4,5-tetra-*O*-benzyl-1-*O*-(1,2-di-*O*-octadecanoyl-*sn*-glyceryl-phosphonato)-D-*myo*-inositol (21b)



Alcohol **21a** (48 mg, 0.017 mmol) and H-phosphonate **6** (20.7 mg, 0.026 mmol) were co-evaporated with anhydrous pyridine (3 x 2 mL) and placed under high vacuum for 30 min. The residue was dissolved in anhydrous pyridine (2 mL) and PivCl (5.4 µL, 0.044 mmol) was added. The reaction mixture was stirred for 2 h at room temperature before water (50 µL) and iodine (8.9 mg, 0.035 mmol) were added. The reaction mixture was stirred for 1 h before it was quenched with sat. Na₂S₂O_{3(aq)} dried over Na₂SO₄ and filtered. Solvents were evaporated and the residue was co-evaporated with toluene (3 x 2 mL). The crude product was purified using flash column chromatography (CHCl₃/MeOH from 100:0 -> 96:4). The fractions containing the desired product were pooled and washed with TEA/CO₂-Buffer (2x15 mL), dried over Na₂SO₄ and concentrated to yield lipidated pseudohexasaccharide 21b (56 mg, 0.016 mmol, 91% yield) as yellow oil: Rf (SiO₂, CHCl₃/MeOH 9:1) = 0.53; $\left[\alpha\right]^{20}$; + 30.8 (c = 1.00, CHCl₃); ATR-FTIR (cm⁻¹); 3089, 3031, 2924, 2854, 2108, 1739, 1678, 1454, 1362, 1094, 1052, 1028; ¹H NMR (600 MHz, CDCl₃) δ 7.44 (d, J = 7.7 Hz, 2H), 7.38 - 7.12 (m, 76H), 7.08 (dd, J = 6.6, 2.8 Hz, 2H), 6.03 (d, J = 8.8 Hz, 1H, NH), 5.90 (d, J = 3.7Hz, 1H, GlcNH₂-1), 5.36 - 5.33 (m, 2H, ManI-2), 5.25 (td, J = 8.8, 5.7 Hz, 1H, CH of glycerol), 5.17 (d, J = 1.0 Hz, 1H), 5.04 (d, J = 11.9 Hz, 1H), 4.98 - 4.91 (m, 3H), 4.90 - 4.74 (m, 9H), 4.73 - 4.91 (m, 3H), 4.90 - 4.74 (m, 9H), 4.73 - 4.91 (m, 3H), 4.90 - 4.74 (m, 9H), 4.73 - 4.91 (m, 3H), 4.90 - 4.74 (m, 9H), 4.73 - 4.91 (m, 3H), 4.90 - 4.74 (m, 9H), 4.73 - 4.91 (m, 3H), 4.90 - 4.74 (m, 9H), 4.73 - 4.91 (m, 3H), 4.90 - 4.74 (m, 9H), 4.73 - 4.91 (m, 3H), 4.90 - 4.74 (m, 9H), 4.73 - 4.91 (m, 3H), 4.90 - 4.74 (m, 9H), 4.73 - 4.91 (m, 3H), 4.90 - 4.74 (m, 9H), 4.73 - 4.91 (m, 3H), 4.90 - 4.74 (m, 9H), 4.73 - 4.91 (m, 9H), 4.91 (m, 9H), 4.91 (m, 9H), 4.73 - 4.91 (m, 9H), 4.94.58 (m, 6H), 4.57 – 4.48 (m, 4H), 4.46 – 4.28 (m, 12H), 4.19 – 4.00 (m, 12H), 4.00 – 3.96 (m, 1H), 3.94 - 3.85 (m, 4H), 3.83 (dd, J = 10.8, 3.1 Hz, 1H), 3.78 (dd, J = 9.4, 7.1 Hz, 1H), 3.71 - 3.39 (m, 16H), 3.36 - 3.32 (m, 2H), 3.13 (dd, J = 10.2, 3.7 Hz, 1H, GlcNH₂-2), 2.90 (dd, J = 14.0, 6.8 Hz,

6H, CH₂ of TEA), 2.32 – 2.19 (m, 8H, CH₂ of Lev; 2x O-COCH₂-CH₂), 1.92 (s, 3H, Me of Lev), 1.63 (s, 3H, Me of NHAc), 1.59 – 1.52 (m, 4H, 2x O-COCH₂-CH₂), 1.33 – 1.23 (m, 56H, CH₂ of lipid), 1.21 (t, J = 7.3 Hz, 9H, Me of TEA), 1.10 – 1.05 (m, 21H, TIPS), 0.89 (t, J = 7.0 Hz, 6H, Me of lipid); ¹³C NMR (126 MHz, CDCl₃) δ 205.90 (ketone), 173.46, 173.10 (2 x fatty acid ester), 171.77 (ester of Lev), 170.36 (amide), 139.89, 139.07, 138.98, 138.89, 138.83, 138.65, 138.62, 138.58, 138.56, 138.36, 138.27, 138.05, 138.02, 137.74, 128.64, 128.60, 128.58, 128.46, 128.43, 128.40, 128.38, 128.33, 128.32, 128.30, 128.27, 128.22, 128.18, 128.15, 128.09, 128.05, 128.02, 127.96, 127.86, 127.78, 127.73, 127.68, 127.66, 127.62, 127.57, 127.53, 127.50, 127.47, 127.45, 127.28, 127.26, 127.16, 127.10, 126.97, 100.64 (GalNAc-1), 99.51, 98.86, 98.71, 96.74 (GlcNH₂-1), 81.98, 81.55, 81.16, 80.44, 79.82, 79.27, 77.36, 75.93, 75.74, 75.59, 75.46, 75.34, 75.18, 74.88, 74.59, 74.41, 74.36, 73.93, 73.88, 73.63, 73.28, 73.17, 72.71, 72.49, 72.37, 72.26, 72.10, 71.61, 71.52, 71.13, 70.80, 70.79, 70.71, 70.68, 70.62, 69.96, 69.81, 69.01, 68.73, 66.76, 63.92, 63.68, 62.95, 62.86, 45.59 (CH₂ of TEA), 37.91(CH₂ of Lev), 34.40, 34.19 (2 x O-COCH₂-CH₂), 32.05, 29.84, 29.81, 29.79, 29.67, 29.65, 29.48, 29.45, 29.28, 28.07 (CH₂ of Lev), 25.02, 24.99 (2 x O-COCH₂-CH₂), 23.22 (Me of NHAc), 22.81, 18.23, 18.18 (2x TIPS), 14.23, 14.22 (2 x Me of lipid chain), 12.18 (TIPS), 8.57 (Me of TEA); ³¹P NMR (243 MHz, CDCl₃) δ -1.42; ESI-MS for C₂₀₃H₂₆₁N₄O₃₉PSi: m/z [M-H+3Na]²⁺ cald 1675.8204, obsd 1675.8225.

Triethylammonium2,3,4-tri-O-benzyl- α -D-mannopyranosyl- $(1\rightarrow 2)$ -3,4,6-tri-O-benzyl- α -D-
mannopyranosyl- $(1\rightarrow 6)$ -4-O-(3,4,6-tri-O-benzyl-2-deoxy-2-acetamido- β -D-galactopyranosyl-
3-O-benzyl-2-O-levulinyl- α -D-mannopyranosyl- $(1\rightarrow 4)$ -2-azido-3,6-di-O-benzyl-2-deoxy- α -D-
glucopyranosyl- $(1\rightarrow 6)$ -2,3,4,5-tetra-O-benzyl-1-O-(1,2-di-O-octadecanoyl-sn-glyceryl-
phosphonato)-D-myo-inositol (21)



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> Lipidated pseudohexasaccharide 21b (56 mg, 0.016 mmol) was dissolved in MeCN (3 mL). Water (11.4 µL, 0.633 mmol) and Sc(OTf)₃ (23.4 mg, 0.047 mmol) were added and the reaction mixture was stirred at 50 °C for 5 h before it was quenched with TEA (50 µL) and evaporated to drvness. The residue was purified using flash column chromatography (CHCl₃/MeOH from $100:0 \rightarrow 97:3$). The fractions containing the desired product were pooled and washed with TEA/CO₂-Buffer (2 x 15 mL), dried over Na₂SO₄ and concentrated to yield pseudohexasaccharide 21 (38 mg, 0.011 mmol, 71% yield) as white foam: $[\alpha]^{20}_{D} = +37.1$ (c = 1.00, CHCl₃); ATR-FTIR (cm⁻¹); 3298, 3089, 3063, 3031, 2924, 2854, 2108, 1740, 1674, 1454, 1362, 1211, 1096, 1049, 1028; ¹H NMR (400 MHz, CDCl₃) δ 12.25 (s, 1H, HNEt₃⁺), 7.33 (d, J = 7.1 Hz, 2H), 7.31 – 6.99 (m, 78H), 6.00 (d, J = 8.3 Hz, 1H, NH), 5.81 (d, J = 3.5 Hz, 1H, GlcNH₂-1), 5.30 – 5.19 (m, 2H), 5.15 (dq, J = 5.9, 3.3 Hz, 1H, CH of glycerol), 4.94 (dd, J = 6.6, 5.2 Hz, 2H), 4.88 - 4.63 (m, 11H), 4.61 - 4.14 (m, 20H), 4.11 - 3.34(m, 31H), 3.16 (q, J = 9.3 Hz, 1H), 3.05 (dd, J = 10.1, 3.6 Hz, 1H), 2.87 (dd, J = 13.4, 8.8 Hz, 6H, CH₂ of TEA), 2.29 – 2.09 (m, 8H, CH₂ of Lev; 2x O-COCH₂-CH₂), 1.85 (s, 3H, Me of Lev), 1.64 (s, 3H, Me of NHAc), 1.51 – 1.42 (m, 4H, 2x O-COCH₂-CH₂), 1.26 – 1.10 (m, 65H, Me of TEA; CH₂) of lipid), 0.81 (t, J = 6.8 Hz, 6H, Me of lipid); 13 C NMR (101 MHz, CDCl₃) δ 206.21 (ketone), 173.49, 173.12, 171.74, 170.73, 139.89, 139.03, 138.86, 138.70, 138.63, 138.53, 138.49, 138.44, 138.37, 138.21, 138.10, 138.02, 130.13, 129.86, 128.67, 128.56, 128.50, 128.47, 128.41, 128.37, 128.35, 128.34, 128.31, 128.28, 128.14, 128.12, 128.04, 128.02, 127.99, 127.84, 127.79, 127.76, 127.69, 127.67, 127.63, 127.61, 127.58, 127.54, 127.50, 127.46, 127.35, 127.28, 127.21, 127.12, 127.05, 100.79, 99.89, 99.38, 98.99, 96.60, 81.91, 81.60, 81.15, 80.04, 79.56, 79.12, 77.36, 76.03, 75.91, 75.72, 75.41, 75.28, 75.17, 75.12, 74.97, 74.84, 74.56, 74.34, 74.24, 74.12, 73.96, 73.54, 73.50, 73.45, 73.10, 73.06, 72.45, 72.32, 72.25, 72.18, 71.72, 71.34, 70.71, 70.64, 70.00, 69.70, 69.47, 68.87, 68.71, 67.21, 63.85, 63.36, 62.90, 62.41, 54.24, 45.64, 37.90, 34.41, 34.20, 32.06, 29.85, 29.82, 29.80, 29.72, 29.68, 29.66, 29.50, 29.46, 29.38, 29.34, 29.29, 28.02, 27.35, 27.30, 25.64, 25.03, 25.00, 23.45, 22.82, 14.26, 8.61; ³¹P NMR (243 MHz, CDCl₃) δ -1.58; ESI-MS for $C_{194}H_{241}N_4O_{39}P: m/z [M-H+3Na]^{2+} cald 1753.8871, obsd 1753.8871.$

Triethylammonium 2-[(N-benzyloxycarbonyl)amino]ethyl H-phosphonate (7) [4,8]



A mixture of benzyl (2-hydroxyethyl)carbamate (1.50 g, 7.68 mmol) and phosphonic acid (0.693 g, 8.45 mmol) was co-evaporated three times with pyridine. The mixture was dissolved in pyridine (50 mL) and PivCl (1.04 mL, 8.45 mmol) was added. After 12 h, the solvent was removed to give a colorless oil that was purified by silica gel column chromatography to give a white solid (ca. 2 g, mix-

ture of product and triethylammonium salts). The white residue was then dissolved in TEA/CO₂ buffer, and extracted with 5% trifluoroethanol in chloroform for three times. The combined organic layers were concentrated to give triethylammonium 2-[(*N*-benzyloxycarbonyl)amino]ethyl H-phosphonate **7** (1.66 g, 4.61 mmol, 60% yield) as a colorless oil: R_f (SiO₂, CHCl₃/MeOH 3:1 with 0.5% NEt₃) = 0.38; ATR-FTIR (cm⁻¹) 3237, 3033, 2984, 2950, 2886, 2335, 1712, 1537, 1455, 1260, 1207, 1146, 1051, 991; ¹H NMR (600 MHz, CDCl₃) δ 12.45 (s, 1H, Et₃NH⁺), 7.31 - 7.18 (m, 5H, Ph), 6.30 (br, 1H, NH), 6.26 (br, 1H, PH), 5.01 (s, 2H, -CH₂- of Cbz), 3.90 (m, 2H, -OCH₂-), 3.36 (dd, *J* = 9.5, 4.8 Hz, 2H, -NCH₂-), 2.92 (q, *J* = 7.2 Hz, 6H, -CH₂- of NEt₃), 1.20 (t, *J* = 7.2 Hz, 9H, Me of NEt₃); ¹³C NMR (151 MHz, CDCl₃) δ 156.52 (carbonyl), 136.83, 128.39, 128.13, 127.92, 66.40 (-CH₂- of Cbz), 62.34 (-OCH₂-), 45.39 (-CH₂- of NEt₃), 42.34 (-NCH₂-), 8.44 (Me of NEt₃); ³¹P NMR (243 MHz, CDCl₃) δ 5.66; ESI-MS: m/z [M-H]⁻ cald 258.0537, obsd 258.0538.

Bistriethylammonium (2,3,4-tri-*O*-benzyl-6-*O*-(2-(*N*-benzyloxycarbonyl)aminoethyl-phosphonato)- α -D-mannopyranosyl-(1 \rightarrow 2)-3,4,6-tri-*O*-benzyl- α -D-mannopyranosyl-(1 \rightarrow 6)-4-*O*-(3,4,6-tri-*O*-benzyl-2-deoxy-2-acetamido- β -D-galactopyranosyl)-3-*O*-benzyl- α -D-mannopyranosyl-(1 \rightarrow 4)-2-azido-3,6-di-*O*-benzyl-2-deoxy- α -D-glucopyranosyl-(1 \rightarrow 6)-2,3,4,5-tetra-*O*-benzyl-1-*O*-(1,2-di-*O*-octadecanoyl-*sn*-glycerylphosphonato)-D-*myo*-inositol (22)



Lipidated pseudohexasaccharide **21** (28 mg, 8.3 μ mol) and H-phosphonate **7** (13.4 mg, 37 μ mol) were evaporated with anhydrous pyridine (3 x 2 mL) and placed under high vacuum for 30 min. The residue was dissolved in anhydrous pyridine (2 mL) and PivCl (7.6 μ L, 62 μ mol) was added. The reaction mixture was stirred for 2 h at room temperature before water (50 μ L) and iodine (11.5 mg, 45 μ mol) were added. The reaction mixture was stirred for 1 h before acetic acid (95 μ L, 1.654mmol)

and hydrazine monohydrate (65 wt%, 40 µL, 0.827 mmol) were added. After 12 h the solvents were evaporated and the residue was evaporated with toluene (3 x 2 mL). The crude product was purified using flash column chromatography (CHCl₃/MeOH from 100:0 -> 90:10). The fractions containing the desired product were pooled and washed with TEA/CO₂-Buffer (2 x 15mL), dried over Na₂SO₄ and concentrated to yield bisphosphorylated pseudohexasaccharide 22 (24 mg, 6.6 µmol, 80% yield) as colorless oil: R_f (SiO₂, CHCl₃/MeOH 90:10) = 0.38; $[\alpha]_D^{20}$: + 28.2 (c = 1.00, CHCl₃); ATR-FTIR (cm⁻¹): 3254, 3030, 2924, 2853, 2107, 1737, 1672, 1497, 1454, 1362, 1215, 1052, 1028; ¹H NMR $(600 \text{ MHz}, \text{CDCl}_3) \delta 12.17 \text{ (s, 2H, HNEt}_3), 7.46 - 6.94 \text{ (m, 85H)}, 6.28 \text{ (s, 1H, NH)}, 5.84 \text{ (d, J} = 3.4 \text$ Hz, 1H, GlcNH₂-1), 5.29 – 5.13 (m, 2H, CH of glycerole), 4.99 – 4.16 (m, 41H), 4.15 – 4.00 (m, 5H), 3.99 – 3.39 (m, 32H), 3.28 – 3.22 (m, 1H), 3.14 (dd, J = 9.2, 4.6 Hz, 1H), 3.04 (dd, J = 10.2, 3.4 Hz, 1H, GlcNH₂-2), 2.80 (dd, J = 13.5, 6.5 Hz, 12H, CH₂ of TEA), 2.21 – 2.11 (m, 4H), 1.82 (s, 3H, Me of NHAc), 1.54 - 1.43 (m, 4H), 1.30 - 1.15 (m, 56H), 1.10 (t, J = 7.2 Hz, 18H, Me of TEA), 0.81 (t, J = 7.0 Hz, 6H, Me of lipid); ¹³C NMR (101 MHz, CDCl₃) δ 173.48, 173.11 (2x fatty acid ester), 170.88 (amide), 156.61 (Cbz), 139.90, 139.22, 139.02, 138.93, 138.87, 138.69, 138.56, 138.46, 138.30, 138.22, 137.95, 137.71, 137.12, 128.68, 128.50, 128.41, 128.37, 128.33, 128.29, 128.26, 128.24, 128.20, 128.09, 127.98, 127.91, 127.84, 127.81, 127.76, 127.68, 127.66, 127.61, 127.55, 127.42, 127.31, 127.11, 126.94, 102.02, 100.88, 99.89, 98.46, 96.49 (GlcNH₂-1), 81.89, 81.81, 81.08, 80.28, 80.11, 79.75, 79.72, 79.65, 79.60, 79.54, 78.20, 78.16, 76.31, 75.82, 75.63, 75.25, 75.14, 74.88, 74.78, 74.54, 74.40, 73.52, 73.40, 73.26, 73.04, 72.69, 72.42, 72.30, 72.24, 72.04, 71.98, 71.73, 70.75, 70.71, 70.07, 69.76, 69.42, 68.96, 66.38, 65.23, 64.23, 63.88, 63.43 (GlcNH₂-2), 61.85, 45.61 (CH₂ of TEA), 34.41, 34.20 (2x O-CO-CH₂-CH₂), 32.06, 29.85, 29.80, 29.67, 29.50, 29.30, 25.04, 25.00 (2x O-CO-CH2-CH2), 23.51 (Me of AcNH), 22.83, 14.26 (Me of lipid), 8.58 (Me of TEA); ³¹P NMR (243 MHz, CDCl₃) δ 0.16, -1.69; ESI-MS for C₁₉₉H₂₄₇N₅O₄₂P₂: $m/z [M-2H+3Na+K]^{2+}$ cald 1774.3026, obsd 1774.2933.

6-*O*-Aminoethylphosphonato-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→6)-4-*O*-(2-deoxy-2-acetamido-β-D-galactopyranosyl)-α-D-mannopyranosyl-(1→4)-2-amino-2-deoxy-α-D-glucopyranosyl-(1→6)-1-*O*-(1,2-di-*O*-octadecanoyl-*sn*-glycerylphosphonato)-D-*myo*-inositol (3) ^[4]



Bisphosphorylated pseudohexasaccharide **22** (7.0 mg, 1.9 μ mol) was dissolved in CHCl₃ (2mL) and Amberlite IR120 H (30 mg) was added. The slurry was stirred for 1 h, before it was filtered and evaporated to dryness. Afterwards the residue was dissolved in CHCl₃/MeOH/H₂O (4 mL, 9:7:2). Pd/C (10wt%, 20.4 mg, 19 μ mol) and HOAc (10 μ L) were added. Through this slurry was bubbled H₂ for 15 min, before the reaction mixture was stirred for 5 d under a hydrogen atmosphere. The solution was filtered through a syringe filter and evaporated to dryness. The residue was washed with CHCl₃ 86x5 mL) to yield GPI **3** (3.1 mg, 1.7 μ mol, 89 % yield) as white solid. Spectral data was in agreement with previously reported data.^[4]



Synthesis of galactoside **25**. Reagent and conditions: (a) TFA, Et₃SiH, 4Å MS, DCM, 92%; (b) NAP-Br, NaH, DMF, 99%; (c) i. PMe3, H2O, THF; ii. trichloroacetyl chloride, pyridine, 85%.

Phenyl 2-azido-3,6-di-O-benzyl-2-deoxy-1-seleno-α-D-galactopyranoside (25b)



Phenyl 2-azido-2-deoxy-4,6-di-*O*-benzyliden-1-seleno- α -D-galactopyranoside **25a**^[5] (8.66 g, 16.6 mmol) was dissolved in DCM (83 mL). Molecular sieves (4Å, 8.3 g), triethylsilane (10 mL, 133 mmol) and 2,2,2-trifluoroacetic acid (15.6 mL, 99 mmol) were added at 0°C. After 2 h at 0°C, the reaction mixture was filtered, washed with sat. NaHCO₃ solution (3 x 50 mL), dried over Na₂SO₄, filtered and concentrated to give galactoside **25b** (8.00 g, 15.3 mmol, 92% yield) as colorless oil. R_f (Hexanes/EtOAc = 3:1) = 0.33; $[\alpha]_D^{20} = +174.35$ (c = 1.00, CHCl₃); ATR-FTIR (cm⁻¹): 3480, 3061, 3031, 2871, 2110, 1578, 1497, 1477, 1454, 1438, 1367, 1297, 1265, 1208, 1091, 1064, 1027, 738, 696; ¹H NMR (600 MHz, CDCl₃) δ 7.53-7.51 (m, 2H), 7.34-7.10 (m, 13H), 5.85 (d, *J* = 5.4 Hz, 1H, GalNAc-1), 4.66 (d, *J* = 11.6 Hz, 1H), 4.63 (d, *J* = 11.6 Hz, 1H), 4.45 (d, *J* = 11.8 Hz, 1H), 4.41 (d, *J* = 11.8 Hz, 1H), 4.32 (br t, *J* = 5.5 Hz, 1H, GalNAc-5), 4.16 (dd, *J* = 5.4, 10.2 Hz, 1H, GalNAc-2), 4.08 (br, GalNAc-4), 3.66 (dd, *J* = 5.4, 10.2 Hz, 1H, GalNAc-6), 3.61-3.56 (m, 2H, GalNAc-3 & GalNAc-6); ¹³C NMR (151 MHz, CDCl₃) δ 137.76, 136.99, 134.77, 129.06, 128.69, 128.43, 128.30, 128.12, 128.04, 127.92, 127.78, 127.69, 85.22 (C1), 78.85 (C3), 73.57 (-CH₂-), 71.99 (-CH₂-), 71.23 (C5), 69.30 (C6), 66.39 (C4), 60.25 (C2); ESI-MS: m/z [M+Na]⁺ cald 548.1059, obsd 548.1064.

Phenyl2-azido-3,6-di-O-benzyl-2-deoxy-4-O-(2-naphthylmethyl)-1-seleno-α-D-galactopyranoside (25c)



Galactoside **25b** (8.00 g, 15.3 mmol) and 2-(bromomethyl)naphthalene (4.05 g, 18.3 mmol) were dissolved in DMF (30 mL) to give a colorless solution. Sodium hydride (0.44 g, 18.3 mmol) was added at 0°C. After 1 h, MeOH (1 mL) was added. The reaction mixture was neutralized with 1N HCl_(aq) and extracted three times with diethyl ether. The combined organic layers were dried over Na₂SO₄, filtered and concentrated. After recrystallization out of MeOH, galactoside **25c** (10.1 g, 15.2 mmol, 99% yield) was obtained as white solid: R_f (Hexanes/EtOAc = 9:1) = 0.25; $[\alpha]_D^{20} = +$ 158.55 (c = 1.00, CHCl₃); ATR-FTIR (cm⁻¹): 2868, 2108, 1578, 1497, 1477, 1454, 1438, 1365, 1298, 1264, 1208, 1091, 1097, 1080, 1064, 1028, 819, 737, 696; ¹H NMR (600 MHz, CDCl₃) δ

7.70-7.64 (m, 3H), 7.56 (br, 1H), 7.50-7.49 (m, 2H), 7.37-7.07 (m, 16H), 5.85 (d, J = 5.3 Hz, 1H, GalNAc-1), 4.94 (d, J = 11.6 Hz, 1H), 4.64 (s, 2H), 4.61 (d, J = 11.6 Hz, 1H), 4.33-4.30 (m, 2H, GalNAc-2 & GalNAc-5), 4.29 (d, J = 11.7 Hz, 1H), 4.24 (d, J = 11.7 Hz, 1H), 3.99 (br, GalNAc-4), 3.64 (d, J = 2.6, 10.6 Hz, 1H, GalNAc-3), 3.53 (dd, J = 7.2, 9.3 Hz, 1H, GalNAc-6), 3.37 (dd, J = 5.9, 9.3 Hz, 1H, GalNAc-6); ¹³C NMR (151 MHz, CDCl₃) δ 137.80, 137.43, 135.65, 134.77, 133.20, 133.03, 129.06, 128.63, 128.45, 128.38, 128.14, 128.07, 127.94, 127.88, 127.85, 127.82, 127.73, 126.80, 126.18, 126.13, 125.98, 85.55 (C1), 80.33 (C3), 74.95 (-CH₂-), 73.44 (-CH₂-), 72.97 (C4), 72.49 (-CH₂-), 71.97 (C5), 68.35 (C6), 61.11 (C2); ESI-MS: m/z [M+Na]⁺ cald 688.1687, obsd 688.1684.

Phenyl3,6-di-O-benzyl-2-deoxy-4-O-(2-naphthylmethyl)-1-seleno-2-trichloracetamido-α-D-galactopyranoside (25)



Galactoside 25c (8.77 g, 13.2 mmol) was dissolved in water (1.2 mL) and THF (22 mL). Trimethylphosphine (1.0 M in THF, 15.8 mL, 15.8 mmol) was added at 0°C. After 3 h, water was added and the reaction mixture was extracted three times with DCM. The combined organic layers were dried over Na₂SO₄, filtered and concentrated to give a white solid. The residue was re-dissolved in chloroform (22 mL). Pyridine (3.2 mL, 40 mmol) and 2,2,2-trichloroacetyl chloride (3.0 mL, 26 mmol) were added at 0°C. After 30 min, the solvent was removed and the residue was recrystallized from MeOH to give galactoside 25 (8.33 g, 11.3 mmol, 85% yield) as white solid: Rf (Hexanes/EtOAc = 4:1) = 0.38; $[\alpha]_{D}^{20}$ = + 136.73 (c = 1.00, CHCl₃); ATR-FTIR (cm⁻¹): 3331, 3059, 2887, 1685, 1531, 1497, 1475, 1454, 1439, 1371, 1312, 1146, 1104, 1079, 1068, 1028, 839, 821, 738, 689; ¹H NMR (600 MHz, CDCl₃) δ 7.72-7.68 (m, 3H), 7.63 (br, 1H), 7.39-7.38 (m, 3H), 7.45-7.44 (m, 2H), 7.40-7.37 (m, 3H), 7.30-7.10 (m, 13H), 6.73 (d, J = 7.1 Hz, 1H, NH), 6.03 (d, J = 4.8 Hz, 1H, GalNAc-1), 4.99 (d, J = 11.6 Hz, 1H, -CH₂-), 4.70 (m, 1H, GalNAc-2), 4.69 (d, J = 11.6 Hz, 1H), 4.62 (d, J = 12.0 Hz, 1H), 4.41 (d, J = 12.0 Hz, 1H), 4.38 (d, J = 11.6 Hz, 1H), 4.32 (d, J = 11.6Hz, 1H), 4.28 (br t, J = 6.6 Hz, GalNAc-5), 4.11 (br, GalNAc-4), 3.66 (dd, J = 7.5, 9.2 Hz, 1H, Gal-NAc-6), 3.54-3.50 (m, H GalNAc-3 & GalNAc-6); ¹³C NMR (151 MHz, CDCl₃) δ 161.57 (amide), 137.74, 137.06, 135.52, 134.36, 133.18, 133.04, 129.26, 128.81, 128.80, 128.49, 128.48, 128.26, 128.19, 128.04, 127.96, 127.92, 127.91, 127.90, 127.88, 127.86, 127.84, 127.71, 126.84, 126.23, 126.10, 125.95, 92.44 (CCl₃), 88.69 (C1), 77.99 (C3), 74.74 (-CH₂-), 73.58 (-CH₂-), 72.81 (C5), 71.64 C4), 71.33 (-CH₂-), 68.30 (C6), 52.20 (C2); ESI-MS: m/z [M+Na]⁺ cald 806.0722, obsd 806.0733.

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Phenyl 3,6-di-O-benzyl-2-deoxy-1-seleno-2-trichloracetamido-a-D-galactopyranoside (26)



Galactoside **25** (199 mg, 0.263 mmol) was dissolved in DCM/H₂O (10:1; 2 mL) and DDQ (71.7 mg, 0.316 mmol) was added. After 3 h the reaction mixture was diluted with ethyl acetate (15 mL) and washed with sat. NaHCO₃ solution (3 x 15 mL). The organic layer was dried over sodium sulfate and evaporated to dryness. The residue was purified using flash column chromatography (*n*-hexane/ethyl acetate 4:1) to yield **26** (147 mg, 0.228 mmol, 87% yield) as yellow solid: R_f (Hexanes/EtOAc = 6:1) = 0.24; $[\alpha]_D^{20} = +164.9$ (c = 1.00, CHCl₃); ATR-FTIR (cm⁻¹): 3486, 3364, 3062, 3031, 2917, 2871, 1708, 1512, 1096, 1081, 1065; ¹H NMR (400 MHz, CDCl₃) δ 7.50 – 7.41 (m, 2H), 7.35 – 7.01 (m, 13H), 6.75 (d, *J* = 7.8 Hz, 1H, NH), 5.92 (d, *J* = 4.9 Hz, 1H, GalNAc-1), 4.66 (d, *J* = 12.0 Hz, 1H), 4.55 (m, 1H, GalNAc-2), 4.51 (d, *J* = 11.8 Hz, 1H), 4.48 (d, *J* = 11.8 Hz, 1H), 4.46 (d, *J* = 10.1, 5.4 Hz, 1H, GalNAc-6), 3.69 (dd, *J* = 10.1, 5.9 Hz, 1H, GalNAc-6), 3.43 (dd, *J* = 10.9, 2.8 Hz, 1H, GalNAc-3), 2.75 (br, 1H, OH); ¹³C NMR (101 MHz, CDCl₃) δ 161.63 (amide), 137.81, 136.82, 134.43, 129.32, 128.83, 128.46, 128.39, 128.18, 127.94, 127.82, 127.77, 92.38 (CCl₃), 88.74 (C1), 76.76 (C3), 73.66 (-CH₂-), 72.32 (C5), 70.92 (-CH₂-), 69.20 (C6), 65.50 (C4), 51.33 (C2); ESI-MS: m/z [M+Na]⁺ cald 666.0085, obsd 666.0087.

Phenyl 2,3,4,6-tetra-*O*-benzyl- α -D-glucopyranosl- $(1\rightarrow 4)$ -2-deoxy-2-trichloracetamido-3,6-di-*O*-benzyl-1-seleno- α -D-galactopyranoside (29)



Galactoside **26** (68 mg, 0.106 mmol) and dibutyl 2,3,4,6-tetra-*O*-benzyl- α/β -D-glucopyranosyl phosphate **27**^[6] (85 mg, 0.116 mmol) were co-evaporated with anhydrous toluene (3x2 mL) and placed under high vacuum for 30 min. The residue was dissolved in anhydrous toluene (2 mL) and molecular sieves (4Å, 150 mg) were added. The reaction mixture was stirred for 15 min at room temperature before it was cooled down to -40°C and TMSOTf (21 µL, 0.116 mmol) was added. The reaction mixture was stirred for 1h at -40 °C before it was quenched with TEA (50 µL), diluted with

CHCl₃ (10 mL) and filtered over Celite®. Solvents were evaporated and the residue was purified using flash column chromatography (*n*-hexane/ethyl acetate 6:1) to yield **29** (97 mg, 0.083 mmol, 79% yield, $\alpha/\beta = 3:1$) as yellow solid. For α-anomer: R_f (*n*-hexane/ethyl acetate = 4:1) = 0.26; $[\alpha]_D^{20}$ = + 118.3 (c = 1.00, CHCl₃); ATR-FTIR (cm⁻¹): 3397, 3088, 3063, 3030, 2923, 2866, 1723, 1498, 1454, 1362, 1154, 1097, 1070, 1046, 1028; ¹H NMR (400 MHz, CDCl₃) δ 7.51 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.40 – 7.07 (m, 33H), 6.84 (d, *J* = 5.8 Hz, 1H, NH), 6.28 (d, *J* = 4.8 Hz, 1H, GalNAc-1), 5.09 (d, *J* = 3.5 Hz, 1H, Glc-1), 4.98 – 4.83 (m, 4H), 4.79 (d, *J* = 10.9 Hz, 1H), 4.71 (d, *J* = 12.0 Hz, 1H), 4.56 – 4.49 (m, 1H, GalNAc-2), 4.43 (dd, *J* = 11.4, 7.2 Hz, 3H), 4.34 – 4.28 (m, 2H), 4.25 (d, *J* = 8.1 Hz, 1H), 4.22 – 4.04 (m, 5H), 3.73 (t, *J* = 9.7 Hz, 1H), 3.60 (dd, *J* = 9.9, 3.5 Hz, 1H, Glc-2), 3.53 – 3.48 (m, 2H), 3.18 (dd, *J* = 10.6, 1.6 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 161.58 (amide), 138.93, 138.52, 138.49, 138.16, 137.99, 137.29, 134.74, 129.26, 128.90, 128.57, 128.55, 128.49, 128.42, 128.41, 128.18, 128.10, 127.99, 127.93, 127.91, 127.86, 127.74, 127.67, 127.60, 127.51, 100.39 (Glc-1), 92.48 (CCl₃), 88.14 (GalNAc-1), 82.01, 80.28, 78.00, 77.36, 75.65, 75.00, 74.24, 73.50, 73.22, 72.67, 71.11, 70.87, 68.07, 67.49, 52.39 (GalNAc-2); ESI-MS: m/z [M+K]⁺ cald 1204.2236, obsd 1204.2316.





Galactoside **25** (0.42 g, 0.536 mmol) and dibutyl phosphate (0.266 mL, 1.339 mmol) were dissolved in DCM (6.4 mL). *N*-Iodosuccinimide (0.145 g, 0.643 mmol) was added at 0 °C. After 30 min, sat. Na₂S₂O_{3(aq)} (10 mL) was added. The reaction mixture was extract with DCM for three times. The combined organic layers were dried over Na₂SO₄, filtered and concentrated. The crude product was purified by silica gel column chromatography to give glycosyl phosphate **32** (0.422 g, 0.504 mmol, 94% yield) as white solid: R_f (Hexanes/EtOAc = 2:1) = 0.32; ; $[\alpha]_D^{20} = +59.4$ (c= 2.10, CHCl₃); ATR-FTIR (cm⁻¹): 2961, 1710, 1512, 1455, 1272, 1102, 1028, 959; ¹H NMR (600 MHz, CDCl₃) δ 7.73-7.68 (m, 3H), 7.61 (br, 1H), 7.39-7.38 (m, 3H), 7.28-7.14 (m, 10H), 6.65 (d, *J* = 8.7 Hz, 1H, NH), 5.70 (dd, *J* = 3.5, 5.5 Hz, 1H, GalNAc-1), 5.01 (d, *J* = 11.7 Hz, 1H), 4.71 (m, 1H, GalNAc-2), 4.67 (d, *J* = 11.7 Hz, 1H), 4.61 (d, *J* = 12.0 Hz, 1H), 4.44 (d, *J* = 12.0 Hz, 1H), 4.35 (d, *J* = 11.6 Hz, 1H), 4.30 (d, *J* = 11.6 Hz, 1H), 4.10-4.08 (m, 2H, GalNAc-5 & GalNAc-4), 3.98-3.90 (m, 4H, -OCH₂Pr), 3.74 (d, *J* = 2.4, 10.9 Hz, 1H, GalNAc-3), 3.57 (dd, *J* = 7.8, 9.2 Hz, 1H, GalNAc-6), 3.49 (dd, *J* = 5.8, 9.2 Hz, 1H, GalNAc-6), 1.54-1.47 (m, 4H, -CH₂Et), 1.28-1.23 (m, 4H, -CH₂Me), 0.81 (t, *J* = 7.4 Hz, 6H, Me); ¹³C NMR (151 MHz, CDCl₃) δ 161.92 (amide), 137.55, 137.24, 135.42, 133.15, 133.03, 128.66, 128.44, 128.17, 128.05, 127.94, 127.91, 127.89, 127.68, 127.62, 126.96, 126.30, 126.07, 125.94, 96.43 (d, J = 6.7 Hz, C1), 92.38 (CCl₃), 76.12 (C3), 74.71 (-CH₂-), 73.55 (-CH₂-), 71.66 (C4 & C5), 71.57 (-CH₂-), 68.25 (C6), 68.07 (d, J = 5.9 Hz, -OCH₂Pr), 68.02 (d, J = 6.1 Hz, -OCH₂Pr), 51.12 (d, J = 8.0 Hz, C2), 32.16 (d, J = 7.0 Hz, -CH₂Et), 32.15 (d, J = 7.0 Hz, -CH₂Et), 18.58 (-CH₂Me*2), 13.59 (Me), 13.57 (Me); ³¹P NMR (243 MHz, CDCl₃) δ -2.43; ESI-MS: m/z [M+Na]⁺ cald 860.2117, obsd 860.2108.

Allyl 3,6-di-*O*-benzyl-2-deoxy-2-trichloracetamido- β -D-galactopyranosyl-(1 \rightarrow 4)-3-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-2-*O*-levulinyl- α -D-mannopyranoside (33)



A mixture of glycosyl phosphate 32 (0.625 g, 0.747 mmol) and mannoside 15 (0.402 g, 0.621 mmol) was co-evaporated three times with toluene and dried under vacuum for 30 min. The residue was dissolved in DCM (9.5 mL) and was cooled down to -40°C. TMSOTf (135 µL, 0.746 mmol) was added. After 1 h at -40°C, PBS buffer (1.0 M, pH 7.4, 1 mL) and DDQ (0.282 g, 1.24 mmol) were added, and the reaction mixture was kept at 20°C for 2 h. The reaction mixture was diluted with dichloromethane and washed with sat. NaHCO_{3(aq)}, dried over Na₂SO₄, filtered and concentrated. The crude product was purified by silica gel column chromatography to give disaccharide 34 (0.660 g, 0.582 mmol, 94% yield) as white foam: R_f (SiO₂, EtOAc/Hexane 1:2) = 0.33; $[\alpha]_D^{20} = +28.85$ (c = 1.00, CHCl₃); ATR-FTIR (cm⁻¹): 3407, 3067, 3031, 2930, 2858, 1718, 1520, 1497, 1454, 1427, 1364, 1138, 1105, 1072, 1028, 822, 741, 701; ¹H NMR (600 MHz, CDCl₃) δ 7.74-7.71 (m, 4H), 7.41-7.20 (m, 21H), 6.33 (d, J = 7.6 Hz, 1H, NH), 5.87 (m, 1H, =CH of allyl), 5.35 (dd, J = 1.9, 3.4 Hz, 1H, Man-2), 5.26 (dq, J = 17.1, 1.4 Hz, 1H, =CH₂), 5.19 (dq, J = 10.4, 1.4 Hz, 1H, =CH₂), 5.03 (d, J = 8.3 Hz, 1H, Gal-1), 4.84 (d, J = 1.9 Hz, 1H, Man-1), 4.67 (d, J = 11.6 Hz, 1H), 4.65 (d, J = 1.9 Hz, 1Hz, 1Hz), 4.65 (d, J = 1.9 Hz, 1Hz), 4.65 (d, J = 1.9 Hz, 1Hz), 4.65 (d, J = 1.9 Hz, 1Hz), 4.65 (d, J = 1.9 Hz), 4.65 (11.5 Hz, 1H), 4.63 (d, J = 11.6 Hz, 1H), 4.50 (d, J = 11.5 Hz, 1H), 4.45 (d, J = 12.0 Hz, 1H), 4.40 $(d, J = 12.0 \text{ Hz}, 1\text{H}), 4.18-4.15 \text{ (m, 2H, -OCH}_2 \text{ of allyl & Man-4}), 4.09 \text{ (br-d, } J = 3.1 \text{ Hz}, 1\text{H}, \text{ Gal-}$ 4), 3.99-3.94 (m, 3H, -OCH₂- of allyl, Man-3 & Man-6), 3.88 (dd, J = 3.1, 10.7 Hz, 1H, Gal-3), 3.83 (dd, J = 5.0, 11.3 Hz, 1H, Man-6), 3.74 (br-dd, J = 4.4, 10.0 Hz, 1H, Man-5), 3.68-3.63 (m, 2H, Gal-2 & Gal-6), 3.46 (dd, J = 5.3, 9.8 Hz, 1H, Gal-6), 3.42 (br-dd, J = 5.3, 6.0 Hz, 1H, Gal-5), 2.65-2.40 (m, 4H, CH₂ of Lev), 2.04 (s, 3H, Me of lev), 1.08 (s, 9H, *t*-Bu); 13 C NMR (151 MHz, CDCl₃) δ 206.39 (ketone), 171.99 (ester), 161.80 (amide), 138.62, 138.01, 137.33, 135.98, 135.63, 133.78, 133.49, 133.13, 129.86, 129.81, 128.60, 128.38, 128.20, 128.13, 127.90, 127.78, 127.73, 127.71, 127.65, 127.62, 127.22, 127.11, 117.87 (=CH₂), 98.29 (Gal-1), 96.39 (Man-1), 92.27 (CCl₃), 76.18 (Man-3), 75.92 (Gal-3), 73.56 (-CH₂-), 72.93 (Gal-5), 72.47 (Man-5), 72.37 (Man-4), 71.60 (-CH₂-), Electronic Supplementary Material (ESI) for Chemical Science This journal is © The Royal Society of Chemistry 2013

71.33 (-CH₂-), 69.18 (Man-2), 68.63 (Gal-6), 67.98 (-OCH₂- of allyl), 65.06 (Gal-4), 63.21 (Man-6), 55.71 (Gal-2), 37.93, 29.71, 28.04, 26.70, 19.33; ESI-MS: m/z [M+Na]⁺ cald 1154.3423, obsd 1154.3481.

Allyl 2,3,4,6-tetra-*O*-benzyl- α/β -D-glucopyranosyl- $(1\rightarrow 4)$ -3,6-di-*O*-benzyl-2-deoxy-2-trichloracetamido- β -D-galactopyranosyl-3-*O*-benzyl-6-*O*-tertbutyldiphenylsilyl-2-*O*-levulinyl- α -D-mannopyranoside (31)



Procedure A (Table 1): Selenoglycoside **29** (49 mg, 0.042 mmol, $\alpha/\beta = 3:1$), dibutyl phosphate (20.9 µL, 0.105 mmol) and molecular sieves (4Å, 100 mg) were suspended in anhydrous DCM (2 mL) and stirred for 10 min at room temperature, before the solution was cooled down to 0 °C and NIS (18.9 mg, 0.084 mmol) was added. After 1 h the reaction mixture was quenched with sat. sodium thiosulfate solution and diluted with CHCl₃ (10 mL). The organic layer was washed with sat. sodium bicarbonate solution (3 x15 mL), dried over sodium sulfate and concentrated in vacuo. The residue was purified by silica gel column chromatography to yield glycosylphosphate **30** (22 mg, 0.018 mmol, 43% yield) as an inseparable mixture of anomers: R_f (SiO₂, EtOAc/Hexane 2:3) = 0.35. Glycosylphosphate **30** (22 mg, 0.018 mmol) and mannoside **15** (9 mg, 0.014 mmol) were evaporated with anhydrous toluene (3x2 mL) and placed under high vacuum for 30 min. The residue was dissolved in anhydrous DCM (1 mL) and molecular sieves (4Å, 50 mg) was added. The slurry was stirred for 10 min at r.t. before the solution was cooled down to -40 °C and TMSOTf (3.3 µL, 0.018 mmol) was added. After 1 h at -40 °C the reaction was quenched with TEA (10 µL), diluted with CHCl₃ (10 mL) and filtered over Celite[®]. Solvents were removed in vacuo and the residue was purified by silica gel column chromatography to yield trisaccharide **31** (2.3 mg, 1.4 μ mol, 10% yield, α/β = 3:1) as colorless oil.

Procedure B (Table 2): Thioglucoside **34** (132 mg, 0.225 mmol), disaccharide **33** (170 mg, 0.15 mmol), DMF (0.104 mL, 1.350 mmol), and molecular sieves (4Å, 50 mg) were suspended in toluene (3 mL). *N*-Iodosuccinimide (50.6 mg, 0.225 mmol) and TMSOTF (0.041 mL, 0.225 mmol) were added at 0°C. The reaction mixture was placed in an ultrasonic device (Elma Elmasonic P) with an ultrasonic frequency of 80 kHz and the temperature was controlled by a cooler (Huber TC100E). After 16 h at 0°C, the reaction mixture was diluted with chloroform and washed with Na₂S₂O_{3(aq)},

NaHCO_{3(aq)}, dried over Na₂SO₄, filtered and concentrated. The crude product was purified by silica gel column chromatography to give trisaccharide **31** (0.240 g, 0.145 mmol, 97 % yield, $\alpha/\beta = 17.8:1$) as colorless oil: R_f (SiO₂, EtOAc/Hexane 1:3) = 0.35; For α -anomer: $\left[\alpha\right]_D^{20} = +54.95$ (c = 1.00, CHCl₃); ATR-FTIR (selective bands, cm⁻¹): 3410, 3064, 3031, 2929, 2858, 1739, 1717, 1519, 1497, 1454, 1428, 1362, 1262, 1208, 1140, 1103, 1072, 1028, 938, 822, 737, 698; ¹H NMR (600 MHz, CDCl₃) δ 7.76 – 7.50 (m, 4H), 7.39 – 7.01 (m, 39H), 7.00 – 6.86 (m, 2H), 6.25 (d, J = 7.1 Hz, 1H, NH), 5.77 (m, 1H, =CH of allyl), 5.21 (dd, J = 3.4, 1.7 Hz, 1H, Man-2), 5.17-5.14 (m, 2H, =CH₂ & Gal-1), 5.09 (dq, J = 10.4, 1.3 Hz, 1H, =CH₂), 4.99 (d, J = 3.4 Hz, 1H, Glc-1), 4.74 (d, J = 1.7 Hz, 1H, Man-1), 4.71 (d, J = 10.9 Hz, 1H), 4.68-4.61 (m, 7H), 4.58 (d, J = 12.3 Hz, 1H), 4.32 (d, J = 11.8 Hz, 1H), 4.31 (d, J = 12.1 Hz, 1H), 4.26 (d, J = 10.8 Hz, 1H), 4.12 – 3.85 (m, 12H), 3.80 (dd, J= 11.2, 5.4 Hz, 1H, Man-6), 3.71 (dd, J = 9.9, 5.4 Hz, 1H, Man-5), 3.63 (dd, J = 9.7, 9.6 Hz, 1H, Glc-4), 3.51 – 3.43 (m, 2H, Glc-2, Gal-2), 3.33 (dd, J = 8.6, 5.6 Hz, 1H, Gal-5), 3.27 – 3.17 (m, 2H, Gal-6, Glc-6), 2.85 (dd, J = 10.7, 1.8 Hz, 1H, Glc-6), 2.56 – 2.31 (m, 4H, CH₂ of Lev), 1.94 (s, 3H, Me), 0.97 (s, 9H, t-Bu); ¹³C NMR (151 MHz, CDCl₃) & 206.35 (ketone), 172.13 (ester), 161.83 (amide), 138.88, 138.83, 138.58, 138.45, 138.29, 138.09, 137.98, 136.16, 135.75, 133.80, 133.64, 133.28, 130.07, 129.89, 128.60, 128.49, 128.47, 128.39, 128.35, 128.32, 128.23, 128.17, 128.00, 127.90, 127.80, 127.73, 127.70, 127.59, 127.52, 127.32, 127.18, 126.96, 118.01 (=CH₂), 100.14 (Glc-1), 98.77 (Gal-1), 96.43 (Man-1), 92.22 (CCl₃), 82.20, 80.14 (Glc-2), 77.89 (Glc-3), 76.14, 76.00, 75.46, 75.05, 73.86, 73.69, 73.36, 73.32, 73.08, 72.68, 71.83 (-CH₂-), 71.29 (-CH₂-), 70.82, 69.22 (Man-2), 68.17 (-OCH₂- of allyl), 67.67 (Glc-6), 67.31 (Gal-6), 63.91 (Man-6), 56.94 (Gal-2), 38.05 (-CH₂CH₂- of Lev), 29.82 (Me), 28.22 (-CH₂CH₂- of Lev), 26.80 (Me of *t*Bu), 19.44 (CMe₃); ESI-MS: m/z [M+Na]⁺ cald 1678.5829, obsd 1678.5894.

600 MHz NMR Data	31 α-Anomer				31 β-Anomer				
(n.d. = not determined)		Man-1	Gal-1	Glc-1	NH	Man-1	Gal-1	Glc-1	NH
chemical shift (ppm)	$^{1}\mathrm{H}$	4.74	5.19	4.99	6.25	4.72	5.07	4.76	6.15
	¹³ C	96.43	98.77	100.14	-	96.54	98.70	102.88	-
coupling constant (Hz)	H-H	1.7	8.4	3.4	7.1	n.d.	8.1	n.d.	7.6
	C-H	172	163	170	-	173	164	164	-

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> Allyl 2,3,4,6-tetra-*O*-benzyl- α/β -D-glucopyranosyl- $(1\rightarrow 4)$ -3,6-di-*O*-benzyl-2-deoxy-2trichloracetamido- β -D-galactopyranosyl-3-*O*-benzyl-2-*O*-levulinyl- α -D-mannopyranoside (24)



Trisaccharide 31 (1.289 g, 0.778 mmol) was dissolved in THF (6 mL) and HF-pyridine complex (~70% HF, 0.202 mL, 7.78 mmol) was added. After 2 d saturated NaHCO_{3(aq)} was added to quench the reaction. The reaction mixture was extracted three times with dichloromethane. The combined organic layers were dried over Na₂SO₄, filtered and concentrated. The crude product was purified by silica gel column chromatography to give trisaccharide 24 (0.900 g, 0.635 mmol, 82% yield) as an anomeric mixture: R_f (SiO₂, EtOAc/Hexane 3:1) = 0.25; For α -anomer: $\left[\alpha\right]_D^{20} = +63.31$ (c = 1.00, CHCl₃): ATR-FTIR (selective bands, cm⁻¹): 3411, 3063, 3031, 2923, 2870, 1717, 1523, 1497, 1454, 1363, 1208, 1139, 1072, 1028, 930, 821, 737, 697; ¹H NMR (400 MHz, CDCl₃) δ 7.29 – 6.90 (m. 36H), 5.74 (m, 1H, =CH of allyl), 5.20 - 5.10 (m, 3H, Man-2, Gal-1 & =CH₂), 5.07 (d, J = 10.4 Hz, 1H, =CH₂), 4.96 (d, J = 3.3 Hz, 1H, Glc-1), 4.77 – 4.49 (m, 9H), 4.35 (d, J = 11.8 Hz, 1H), 4.31 (d, J = 12.2 Hz, 1H), 4.25 (d, J = 10.7 Hz, 1H), 4.11 – 3.91 (m, 10H), 3.88 (dd, J = 9.2, 3.4 Hz, 1H, Man-3), 3.83 (dd, J = 12.9, 6.2 Hz, 1H, CH₂ of allyl), 3.80 - 3.70 (m, 3H, Gal-2 & Man-6), 3.66 - 3.57(m, 2H, Man-5 & Glc-4), 3.48 - 3.45 (m, 2H, Gal-5 & Glc-2), 3.35 (dd, J = 9.4, 5.6 Hz, 1H, Gal-6), 3.24 (br-d, J = 9.3 Hz, 1H, Glc-6), 2.87 (br-d, J = 9.7 Hz, 1H, Glc-6), 2.44 – 2.30 (m, 4H, CH₂ of Lev), 1.92 (s, 3H, Me of Lev); ¹³C NMR (101 MHz, CDCl₃) δ 206.57 (ketone), 171.99 (ester), 162.00 (amide), 138.84, 138.45, 138.41, 138.34, 138.11, 137.92, 137.88, 133.37 (vinyl), 128.49, 128.45, 128.42, 128.40, 128.32, 128.29, 128.26, 128.23, 128.17, 128.14, 128.01, 127.98, 127.92, 127.76, 127.69, 127.63, 127.60, 127.55, 127.44, 127.37, 127.25, 127.02, 117.84 (=CH₂), 100.04 (Glc-1), 98.95 (Gal-1), 96.67 (Man-1), 92.64 (CCl₃), 82.04, 80.13, 77.79, 76.32, 75.81, 75.35, 74.95, 73.82, 73.65, 73.54, 73.25, 73.07, 73.01, 71.74, 71.56, 71.22, 70.76, 69.28 (Man-2), 68.30 (-OCH₂of allyl), 67.57 (br, Gal-6 & Glc-6), 61.75 (Man-6), 56.37 (Gal-2), 37.86 (CH₂ of Lev), 29.66 (Me), 28.07 (CH₂ of Lev); ESI-MS: m/z [M+Na]⁺ cald 1440.4622, obsd 1440.4645.

Allyl 2,3,4-tri-*O*-benzyl-6-*O*-triisopropylsilyl- α -D-mannopyranosyl- $(1\rightarrow 2)$ -3,4,6-tri-*O*-benzyl- α -D-mannopyranosyl- $(1\rightarrow 6)$ -3-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl- α -D-glucopyranosyl- $(1\rightarrow 4)$ -3,6-di-*O*-benzyl-2-deoxy-2-trichloracetamido- β -D-galactopyranosyl)-2-*O*-levulinyl- α -D-mannopyranoside (35)



A mixture of trichloroacetimidate 4 (0.571 g, 0.482 mmol) and trisaccharide 24 (0.57 g, 0.402 mmol) was co-evaporated three times with toluene. The residue was then dissolved in a mixture of thiophene (7 mL) and toluene (3.5 mL). Molecular sieves (4Å, 300 mg) and TBSOTf (18.5 µL, 0.081 mmol) were added. After 1 h, TEA (50 µL) was added and the reaction mixture was filtered through a pad of Celite[®]. The filtrate was evaporated to dryness to give a yellow oil that was purified by silica gel column chromatography to afford pentasaccharide **35** (0.830 g, 0.340 mmol, 85% yield): R_f (SiO₂, EtOAc/Hexane 1:3) = 0.33; $[\alpha]_D^{20} = +40.8$ (c = 1.00, CHCl₃); ATR-FTIR (selective bands, cm⁻¹): 3031, 2865, 1719, 1497, 1454, 1363, 1208, 1074, 821, 736; ¹H NMR (600 MHz, CDCl₃) δ 7.29-7.03 (m, 64H), 6.92-6.91 (m, 2H), 5.72 (m, 1H, =CH of allyl), 5.25 (d, J = 1.7 Hz, 1H, ManIII-1), 5.21 (dd, J = 1.9, 3.5 Hz, 1H, ManI-2), 5.14 (dg, J = 17.2, 1.5 Hz, 1H, =CH₂), 5.06 $(d, J = 8.4 \text{ Hz}, 1\text{H}, \text{Gal-1}), 5.04 (dq, J = 10.4, 1.2 \text{ Hz}, 1\text{H}, =\text{CH}_2), 4.91 (d, J = 3.5 \text{ Hz}, 1\text{H}, \text{Glc-1}),$ 4.84 (d, J = 10.7 Hz, 1H), 4.80 (d, J = 1.6 Hz, 1H, ManII-1), 4.75 (d, J = 10.5 Hz, 1H), 4.70 (d, 1.9 Hz, 1H, ManI-1), 4.66 (d, J = 11.0 Hz, 1H), 4.63-4.54 (m, 8H), 4.53 (d, J = 12.5 Hz, 1H), 4.52 (d, J = 10.7 Hz, 1H), 4.40 (d, J = 11.6 Hz, 1H), 4.37 (d, J = 10.7 Hz, 1H), 4.35 (d, J = 11.8 Hz, 1H),4.34 (d, J = 12.5 Hz, 1H), 4.30 (d, J = 12.3 Hz, 1H), 4.30 (d, J = 12.3 Hz, 1H), 4.28 (d, J = 12.2 Hz, 1H), 4.22 (d, J = 10.5 Hz, 1H), 4.21 (d, J = 11.4 Hz, 1H), 4.13-4.08 (m, 3H), 4.03-3.74 (m, 19H), 3.66 (dd, J = 1.7, 3.1 Hz, 1H, ManIII-2), 3.65-3.56 (m, 6H), 3.52 (br-dd, J = 6.2, 7.1 Hz, 1H, Gal-5),3.45 (dd, J = 3.5, 10.0 Hz, 1H, Glc-2), 3.39 (dd, J = 6.2, 9.8 Hz, 1H, Gal-6), 3.13 (dd, J = 1.8, 10.8 Hz)Hz, 1H, Glc-6), 2.76 (dd, J = 1.8, 10.8 Hz, 1H, Glc-6), 2.40-2.26 (m, 4H, CH₂ of Lev), 1.91 (s, 3H, Me of Lev), 1.01-1.00 (m, 21H, TIPS); ¹³C NMR (151 MHz, CDCl₃) δ 206.02 (ketone), 172.00 (ester), 161.85 (amide), 139.00, 138.78, 138.72, 138.51, 138.48, 138.44, 138.37, 138.36, 138.16, 138.09, 137.93, 137.82, 133.19, 128.43, 128.42, 128.35, 128.34, 128.28, 128.25, 128.21, 128.18, 128.16, 128.13, 128.06, 128.01, 127.95, 127.91, 127.88, 127.81, 127.73, 127.66, 127.58, 127.53,

127.46, 127.40, 127.33, 127.31, 127.21, 127.16, 126.96, 118.25 (=CH₂), 99.95 (Glc-1), 98.67 (Gal-1), 98.57 (ManII-1), 98.26 (ManIII-1), 96.17 (ManI-1), 92.50 (CCl₃), 82.03, 80.92, 79.95 (Glc-2), 79.61, 77.66, 76.39, 75.35, 75.28, 75.19, 75.05, 74.86, 74.84, 74.81, 74.43, 73.82, 73.78, 73.48, 73.34, 73.22, 73.17, 73.11, 72.27, 72.23, 72.13, 72.07, 71.66, 71.55, 71.21, 70.58, 69.86, 69.61, 69.12 (ManI-2), 67.89 (-OCH₂- of allyl), 67.64 (Gal-6), 67.36 (Glc-6), 66.10, 62.96, 56.25 (Gal-2), 37.75 (-CH₂- of Lev), 29.63 (Me of Lev), 27.96 (-CH₂- of Lev), 18.12 (TIPS), 18.07 (TIPS), 12.06 (TIPS); ESI-MS: m/z [M+Na]⁺ cald 2458.9854, obsd 2458.9827.

600 MHz NMR Data		35							
(n/a = not applicable)		ManI-1	ManII-1	ManIII-1	Gal-1	Glc-1			
chemcial shift (ppm)	$^{1}\mathrm{H}$	4.70	4.80	5.25	5.06	4.91			
	¹³ C	96.17	98.57	98.26	98.67	99.95			
coupling constant (Hz)	H-H	1.9	1.6	1.7	8.4	3.5			
	С-Н	170	174	170	165	170			

Allyl 2,3,4-tri-*O*-benzyl-6-*O*-triisopropylsilyl- α -D-mannopyranosyl- $(1\rightarrow 2)$ -3,4,6-tri-*O*-benzyl- α -D-mannopyranosyl- $(1\rightarrow 6)$ -3-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl- α -D-glucopyranosyl- $(1\rightarrow 4)$ -3,6-di-*O*-benzyl-2-deoxy-2-acetamido- β -D-galactopyranosyl)-2-*O*-levulinyl- α -D-mannopyranoside (36)



Pentasaccharide **35** (0.21 g, 0.086 mmol) was dissolved in acetic acid (3 mL). Zinc (0.563 g, 8.61 mmol) was added at 55°C in three portions over 30 min. After 2 h at 55°C, the reaction mixture was filtered through a pad of Celite®. The filtrate was concentrated to give an oil that was purified by silica gel column chromatography to yield pentasaccharide **36** (0.19 g, 0.081 mmol, 94% yield): R_f (SiO₂, EtOAc/Hexane 2:3) = 0.41; $[\alpha]_D^{20} = +30.5$ (c = 1.0, CHCl₃); ATR-FTIR (cm⁻¹): 3066, 3029, 2925, 2866, 1742, 1720, 1675, 1497, 1454, 1363, 1208, 1136, 1071, 1028, 736, 697; ¹H NMR (600 MHz, CDCl₃) δ 7.27-6.97 (m, 63H), 6.94-6.92 (m, 2H), 6.44 (d, J = 7.3 Hz, 1H, NH), 5.71 (m, 1H, =CH of allyl), 5.27 (d, J = 1.8 Hz, 1H, ManIII-1), 5.18 (dd, J = 1.9, 3.6 Hz, 1H, ManI-2), 5.14 (dq, J

 $= 17.2, 1.4 \text{ Hz}, 1\text{H}, =\text{CH}_2$, 5.04 (dq, $J = 10.4, 1.2 \text{ Hz}, 1\text{H}, =\text{CH}_2$), 5.01 (d, J = 8.4 Hz, 1H, GalNAc-1), 4.87 (d, J = 3.5 Hz, 1H, Glc-1), 4.84 (d, J = 10.9 Hz, 1H), 4.82 (d, J = 1.7 Hz, 1H, ManII-1), 4.73 (d, J = 11.2 Hz, 1H), 4.72 (d, J = 10.6 Hz, 1H), 4.71 (d, J = 1.9 Hz, 1H, ManI-1), 4.64-4.54 (m, J = 1.9 Hz, 1H), 4.64-4.54 (m, J = 1.9 Hz), 4.64-4.510H), 4.46 (d, J = 11.8 Hz, 1H), 4.44 (d, J = 13.0 Hz, 1H), 4.39 (d, J = 11.7 Hz, 1H), 4.35 (d, J = 11.712.6 Hz, 1H), 4.26-4.22 (m, 3H), 4.19 (d, J = 11.0 Hz, 1H), 4.16 (d, J = 1.7, 2.2 Hz, 1H, ManII-2), 4.07 (d, J = 12.0 Hz, 1H), 4.04 (t, J = 9.6 Hz, 1H, ManIII-4), 3.99-3.91 (m, 7H), 3.88-3.79 (m, 10H), 3.76 (br, 1H, GalNAc-4), 3.74-3.70 (m, 2H, ManI-6, ManII-5), 3.63 (dd, J = 1.8, 3.0 Hz, 1H, ManIII-2), 3.61-3.51 (m, 4H, ManII-6, ManIII-5, GalNAc-2, Glc-4), 3.44-3.42 (m, 2H, GalNAc-5, Glc-2), 3.34 (dd, J = 9.6, 9.7 Hz, 1H, ManII-4), 3.30 (dd, J = 7.1, 10.4 Hz, 1H, ManII-6), 3.20 (dd, J = 5.6, 9.6 Hz, 1H, GalNAc-6), 3.12 (dd, J = 1.7, 10.6 Hz, 1H, Glc-6), 2.76 (dd, J = 1.6, 10.4 Hz, 1H, Glc-6), 2.49-2.32 (m, 4H, CH₂ of Lev), 1.95 (s, 3H, Me), 1.80 (s, 3H, Me), 1.00-0.99 (m, 21H, TIPS): ¹³C NMR (151 MHz, CDCl₃) δ 206.11 (ketone), 172.01 (ester), 170.69 (amide), 138.92, 138.83, 138.70, 138.54, 138.44, 138.37, 137.96, 137.88, 137.33, 133.01, 128.48, 128.43, 128.37, 128.27, 128.24, 128.16, 128.13, 128.09, 128.07, 128.01, 127.89, 127.74, 127.71, 127.69, 127.68, 127.66, 127.62, 127.51, 127.43, 127.32, 127.28, 127.24, 127.14, 126.95, 126.88, 118.33 (=CH₂), 101.04 (GalNAc-1), 100.29 (Glc-1), 98.08 (ManIII-1), 97.77 (ManII-1), 96.27 (ManI-1), 81.93, 80.81, 80.11, 79.39, 77.84, 77.70 (Glc-4), 75.76, 75.46, 75.27, 75.08, 74.99, 74.64, 74.35, 73.88, 73.57, 73.44, 73.10, 72.87, 72.34, 72.29, 72.23, 71.65, 71.48, 71.20, 70.51, 70.10 (ManII-6), 68.93 (ManI-2), 68.81, 67.88 (-OCH₂- of allyl), 67.76 (GalNAc-6), 67.37 (Glc-6), 65.39 (ManI-6), 62.78 (ManIII-6), 54.70 (GalNAc-2), 37.79 (-CH₂- of Lev), 29.68 (Me of Lev), 27.98 (-CH₂- of Lev), 23.54 (Ac), 18.06 (TIPS), 18.02 (TIPS), 12.04 (TIPS); ESI-MS: m/z [M+Na]⁺ cald 2358.1062, obsd 2358.1058.

600 MHz NMR Data		36						
		ManI-1	ManII-1	ManIII-1	GalNAc-1	Glc-1		
chemical shift (ppm)	$^{1}\mathrm{H}$	4.71	4.82	5.27	5.01	4.87		
	¹³ C	96.27	97.77	98.08	101.04	100.29		
coupling constant (Hz)	H-H	1.9	1.7	1.8	8.4	3.5		
	C-H	170	171	174	165	170		

2,3,4-Tri-*O*-benzyl-6-*O*-tri*iso*propylsilyl- α -D-mannopyranosyl- $(1\rightarrow 2)$ -3,4,6-tri-*O*-benzyl- α -D-mannopyranosyl- $(1\rightarrow 6)$ -3-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl- α -D-glucopyranosyl- $(1\rightarrow 4)$ -3,6-di-*O*-benzyl-2-deoxy-2-acetamido- β -D-galactopyranosyl)-2-*O*-levulinyl- α -D-mannopyranosyl- $(1\rightarrow 4)$ -2-azido-3,6-di-*O*-benzyl-2-deoxy- α -D-glucopyranosyl- $(1\rightarrow 6)$ -1-*O*-allyl-2,3,4,5-tetra-*O*-benzyl-D-*myo*-inositol (38)



A solution of [IrCOD(PPh₂Me)₂]PF₆ (4.9 mg, 5.8 μ mol) in THF (3 mL) was stirred under hydrogen at 20 °C until the colour turned from red to colourless to pale yellow. The hydrogen atmosphere was exchanged with Ar. This solution was then added into a flask with pentasaccharide **36** (96 mg, 0.041 mmol). After overnight stirring, the solvent was removed and the residue was dissolved in a mixture of acetone (2.7 mL) and water (0.3 mL). Mercury(II) chloride (66.9 mg, 0.247 mmol) and mercury(II) oxide (2.0 mg, 9.2 μ mol) were added. After 1 h, the reaction mixture was diluted with chloroform and washed with saturated NaHCO_{3(aq)}, dried over Na₂SO₄, filtered and concentrated to give the crude lactol **37a**: R_f (SiO₂, EtOAc/Hexane 2:3 = 0.28). The crude lactol **37a** was dissolved in DCM (3mL) and 2,2,2-trichloroacetonitrile (0.20 mL, 2.0 mmol) and DBU (2.6 μ L, 0.017 mmol) were added. After 1 h, the solvent was removed to give a brown oil that was purified by flash column chromatography to give imidate **37** (83 mg, 0.034 mmol, 83% yield) as an inseparable mixture of anomers: R_f (SiO₂, EtOAc/Hexane 2:3) = 0.43.

A mixture of glycosylimidate **37** (83 mg, 0.034 mmol) and pseudodisaccharide **5** (32 mg, 0.034 mmol) was co-evaporated three times with toluene and dried under vacuum for 30 min. To a toluene (3 mL) solution of this mixture were added molecular sieves (4Å, 50 mg) and TMSOTf (3 μ L, 0.017 mmol) at -40°C. After 1 h at -40°C TEA (50 μ L) was added. The reaction mixture was filtered and the filtrate was concentrated to give a yellow oil that was purified by silica gel column chromatography to yield pseudoheptasaccharide **38** (87 mg, 0.027 mmol, 80% yield): R_f (SiO₂, EtOAc/Hexane 1:2) = 0.43; $[\alpha]_D^{20} = +$ 38.6 (c = 1.00, CHCl₃); ATR-FTIR (selective bands, cm⁻¹): 3030, 2865, 2105, 1720, 1497, 1454, 1362, 1208, 1072, 1028, 736, 697; ¹H NMR (600 MHz, CDCl₃) δ 7.34-6.94 (m, 95H), 6.04 (d, *J* = 9.2 Hz, 1H, NH), 5.83 (m, 1H, =CH of allyl), 5.58 (d, *J* = 3.7 Hz, 1H, GlcN-
1), 5.30 (d, J = 1.7 Hz, 1H, ManI-1), 5.28 (dd, J = 1.7, 3.2 Hz, 1H, ManI-2), 5.18 (dt, J = 17.2, 1.6 Hz, 1H, =CH₂), 5.10-5.08 (m, 2H, =CH₂, ManIII-1), 4.92 (d, J = 11.3 Hz, 1H) 4.84 (d, J = 10.7 Hz, 1H), 4.83 (d, J = 10.7 Hz, 1H), 4.76-4.74 (m, 5H), 4.70-4.68 (m, 3H), 4.65 (d, J = 12.3 Hz, 1H), 4.63-4.40 (m, 16H), 4.37 (d, J = 12.9 Hz, 1H), 4.28-4.16 (m, 9H), 4.13 (dd, J = 9.4, 9.6 Hz, 1H, Ino-6), 4.11 (d, J = 11.9 Hz, 1H), 4.08-3.69 (m, 22H), 3.67 (dd, J = 3.2, 8.6 Hz, 1H, ManI-3), 3.58-3.46 (m, 8H), 3.41 (dd, J = 3.5, 9.9 Hz, 1H, Glc-2), 3.38-3.24 (m, 8H), 3.14-3.08 (m, 2H), 2.99 (dd, J = 3.5, 3.99 Hz, 1 H, Glc-2), 3.38-3.24 (m, 8H), 3.14-3.08 (m, 2H), 2.99 (dd, J = 3.5, 3.99 Hz, 1 H, Glc-2), 3.38-3.24 (m, 8H), 3.14-3.08 (m, 2H), 2.99 (dd, J = 3.5, 3.99 Hz, 1 H, Glc-2), 3.38-3.24 (m, 8H), 3.14-3.08 (m, 2H), 3.99 (dd, J = 3.5, 3.99 Hz, 3.2.5, 11.6 Hz, 1H), 2.78 (dd, J = 1.8, 10.9 Hz, 1H), 2.24-2.07 (m, 4H, CH₂ of Lev), 1.81 (s, 3H, Me of Lev), 1.71 (s, 3H, Me), 0.98-0.97 (m, 21H, TIPS); ¹³C NMR (151 MHz, CDCl₃) δ 205.68 (ketone), 171.65 (ester), 169.99 (amide), 138.91, 138.85, 138.82, 138.80, 138.65, 138.53, 138.46, 138.38, 138.24, 138.16, 137.98, 137.89, 137.82, 137.41, 134.28 (=CH of allyl), 128.83, 128.61, 128.59, 128.48, 128.42, 128.38, 128.32, 128.27, 128.23, 128.17, 128.14, 128.11, 128.07, 128.02, 127.96, 127.93, 127.82, 127.78, 127.69, 127.67, 127.63, 127.57, 127.52, 127.48, 127.42, 127.33, 127.30, 127.21, 127.14, 126.30, 117.01 (=CH₂), 101.60 (GalNac-1), 100.71 (Glc-1), 99.45 (ManII-1), 98.48 (ManIII-1), 98.27 (ManI-1), 97.58 (GlcN-1), 82.08, 81.97, 81.74, 81.02, 80.94, 80.89, 80.62, 80.02 (Glc-2), 79.66, 79.01, 77.81, 75.67, 75.60, 75.42, 75.27, 75.20, 75.11, 75.01, 74.59, 74.39, 74.24, 73.99, 73.87, 73.79, 73.72, 73.48, 73.31, 73.07, 72.83, 72.77, 72.31, 71.95, 71.83, 71.39, 71.22, 70.82, 70.78, 70.66, 69.88 (ManI-2), 69.56, 68.52, 68.12, 67.62, 66.65, 63.74 (GlcN-2), 62.74 (ManIII-6), 52.75 (GalNAc-2), 37.67 (-CH₂- of Lev), 29.34 (Me of Lev), 27.91 (-CH₂- of Lev), 23.19 (Ac), 18.08 (TIPS), 18.03 (TIPS), 12.04 (TIPS); ESI-MS: m/z [M+2Na]²⁺ cald 1634.7427, obsd 1634.7484.

600 MHz NMR Data		38							
(n.d. = not determine	d)	GlcN-1	ManI-1	ManII-1	ManIII-1	GalNAc-1	Glc-1		
	1 H	5.58	5.30	4.52	5.08	4.69	4.74		
chemical shift (ppm)	¹³ C	97.58	98.27	99.45	98.48	101.60	100.71		
coupling constant (Hz)	H-H	3.7	1.7	n.d.	n.d.	n.d.	3.5		
	C-H	182	177	175	171	162	170		

2,3,4-Tri-*O*-benzyl-6-*O*-tri*iso*propylsilyl- α -D-mannopyranosyl- $(1\rightarrow 2)$ -3,4,6-tri-*O*-benzyl- α -D-mannopyranosyl- $(1\rightarrow 6)$ -3-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl- α -D-glucopyranosyl- $(1\rightarrow 4)$ -3,6-di-*O*-benzyl-2-deoxy-2-acetamido- β -D-galactopyranosyl)-2-*O*-levulinyl- α -D-mannopyranosyl- $(1\rightarrow 4)$ -2-azido-3,6-di-*O*-benzyl-2-deoxy- α -D-glucopyranosyl- $(1\rightarrow 6)$ -2,3,4,5-tetra-*O*-benzyl-D-*myo*-inositol (39)



A solution of [IrCOD(PPh₂Me)₂]PF₆ (4.0 mg, 4.7 µmol) in THF (1 mL) was stirred under hydrogen until the color turned from red to colorless to pale yellow. The hydrogen atmosphere was exchanged with Ar. This solution was added to a THF (0.5 mL) solution of pseudoheptasaccharide 38 (80 mg, 0.025 mmol). After three days, the solvent was removed and the residue was dissolved in a mixture of acetone (2.7 mL) and water (0.3 mL). Mercury(II) chloride (40.4 mg, 0.149 mmol) and mercury(II) oxide (2.0 mg, 9.2 µmol) were added. After 1 h, saturated NaHCO_{3(au)} was added and the reaction mixture was extracted three times with dichloromethane. The combined organic layers were dried over Na₂SO₄, filtered and concentrated. The crude product was purified by silica gel column chromatography to give pseudoheptasaccharide **39** (75 mg, 0.024 mmol, 95% yield) as a colorless oil. R_f (SiO₂, EtOAc/Hexane 1:2) = 0.36; $[\alpha]_D^{20} = +34.8$ (c = 1.00, CHCl₃); ATR-FTIR (selective bands, cm⁻¹): 2866, 2106, 1497, 1454, 1362, 1053, 735, 697; ¹H NMR (600 MHz, CDCl₃) δ 7.32-6.94 (m, 95H), 5.99 (d, J = 9.0 Hz, 1H, NH), 5.27-5.25 (m, 2H, ManI-1, ManI-2), 5.23 (d, J = 3.3 Hz, 1H, Glc-1), 5.08 (d, J = 1.4 Hz, 1H, ManIII-1), 4.90 (d, J = 11.6 Hz, 1H), 4.89 (d, J = 10.5 Hz, 1H), 4.84 (d, J = 10.7 Hz, 1H), 4.83 (d, J = 10.5 Hz, 1H), 4.76-4.74 (m, 2H, Glc-1), 4.72-4.52 (m, 17H,), 4.47-4.45 (m, 3H), 4.43 (d, J = 11.0 Hz, 1H), 4.39 (d, J = 12.1 Hz, 1H), 4.35 (d, J = 12.9 Hz, 1H), 4.26-4.15 (m, 8H), 4.13 (d, J = 12.0 Hz, 1H), 4.07-4.02 (m, 4H), 4.00-3.91 (m, 6H), 3.87-3.76 (m, 11H), 3.73 (dd, J = 3.4, 8.4 Hz, 1H, ManI-3), 3.69 (m, 1H, ManII-5), 3.58-3.53 (m, 7H), 3.50-3.45 (m, 2H, GalNAc-6, ManII-6), 3.43-3.35 (m, 4H), 3.33-3.29 (m, 3H), 3.26-3.24 (m, 2H, ManI-6, Glc-6), 3.17 (dd, J = 1.9, 11.1 Hz, 1H, GlcN-6), 3.12 (d, J = 6.3 Hz, 1H, OH), 3.08 (br-d, J = 11.1Hz, 1H, GlcN-6), 2.78 (dd, J = 1.7, 10.8 Hz, 1H, Glc-6), 2.26-2.10 (m, 4H, CH₂ of Lev), 1.82 (s, 3H, Me of Lev), 1.68 (s, 3H, Me), 0.98-0.97 (m, 21H, TIPS); ¹³C NMR (151 MHz, CDCl₃) δ 205.70 (ke-

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tone), 171.61 (ester), 170.11 (amide), 138.91, 138.88, 138.80, 138.71, 138.64, 138.53, 138.45, 138.25, 138.13, 137.95, 137.86, 137.51, 137.46, 128.62, 128.52, 128.45, 128.36, 128.33, 128.28, 128.24, 128.14, 128.09, 128.03, 127.94, 127.86, 127.77, 127.69, 127.61, 127.58, 127.47, 127.36, 127.30, 127.27, 127.20, 127.14, 126.36, 101.42 (GalNAc-1), 100.64 (Glc-1), 99.46 (ManII-1), 98.52 (ManIII-1), 98.13 (GlcN-1), 98.02 (ManI-1), 82.06, 81.94, 81.22, 81.00, 80.85, 80.81, 80.00, 79.28, 79.08, 77.80, 77.14, 75.67, 75.21, 74.99, 74.87, 74.79, 74.63, 74.42, 74.21, 74.05, 73.76, 73.49, 73.32, 73.18, 73.09, 72.90, 72.77, 72.66, 72.31, 72.00, 71.96, 71.43, 71.26, 70.66, 70.61, 70.61 (ManII-6), 69.94 (ManI-2), 68.51 (GalNAc-6), 68.27 (GlcN-6), 67.60 (Glc-6), 66.43 (ManI-6), 64.61 (GlcN-2), 62.80 (ManIII-6), 52.96 (GalNAc-2), 37.66 (-CH₂- of Lev), 29.54 (Me of Lev), 27.90 (-CH₂- of Lev), 23.20 (Ac), 18.09 (TIPS), 18.04 (TIPS), 12.04 (TIPS); ESI-MS: m/z $[M+2Na]^{2+}$ cald 1614.7270, obsd 1614.7344; $[M+H]^+$ cald 3184.4829, obsd 3184.4836.

600 MHz NMR Data		39					
(n.d. = not determined)		GlcN-1	ManI-1	ManII-1	ManIII-1	GalNAc-1	Glc-1
chemical shift (ppm)	$^{1}\mathrm{H}$	5.23	5.26	4.57	5.08	4.70	4.76
	¹³ C	98.13	98.02	99.46	98.52	101.42	100.64
coupling constant (Hz)	H-H	3.3	n.d.	n.d.	1.4	n.d.	n.d.
	C-H	173	174	171	171	160	170

Triethylammonium(2,3,4-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→6)-3-O-benzyl-4-O-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl-(1→4)-3,6-di-O-benzyl-2-deoxy-2-acetamido-β-D-galactopyranosyl)-2-O-levulinyl-α-D-mannopyranosyl-(1→4)-2-azido-3,6-di-O-benzyl-2-deoxy-α-D-glucopyranosyl-(1→6)-2,3,4,5-tetra-O-benzyl-1-O-(1,2-di-O-octadecanoyl-sn-glyceryl-phosphonato)-D-myo-inositol (40)



A mixture of pseudoheptasaccharide 39 (59 mg, 0.019 mmol) and H-phosphonate 6 (29 mg, 0.038 mmol) was co-evaporated three times with pyridine and dried under vacuum overnight. To a pyridine (1.5 mL) solution of this mixture was added PivCl (9.1 µL, 0.074 mmol). After 2 h, water (10 μ L) and iodine (9.4 mg, 0.038 mmol) were added. After 1 h, sat. Na₂S₂O_{3(aq)} was added to quench the reaction and the solvent was removed. The remaining residue was then dissolved in dichloromethane and washed three times with TEA/CO₂-buffer. The solvent was removed to give colorless oil, which was dissolved in a mixture of chloroform (1.5 mL) and methanol (1.5 mL) together with Dowex 50WX8 (Na⁺) resin (50 mg). After 30 min, the mixture was filtered and the filtrate was concentrated to give yellow oil. This residue was dissolved in a mixture of acetonitrile (2.5 mL), water (1.5 µL) and chloroform (1.5 mL). Sc(OTf)₃ (27 mg, 0.055 mmol) was added and the reaction mixture was kept at 40°C for 12 h before the reaction was quenched by the addition of pyridine (0.1 mL). The solvent was removed to give a brown oil that was purified by column chromatography using silica gel deactivated with TEA to afford mono-phosphate 40 (45 mg, 0.012 mmol, 64% yield). R_{f} (SiO₂, chloroform/MeOH 30:1) = 0.21; ¹H NMR (600 MHz, CDCl₃) δ 12.36 (s, 1H, HNEt₃⁺), 7.32 (d, J = 7.2 Hz, 2H), 7.29 – 6.96 (m, 91H), 6.93 (d, J = 6.9 Hz, 2H), 6.18 (d, J = 7.1 Hz, 1H, NH), 5.77 (br, 1H, GlcN-1), 5.21 (dd, J = 3.0, 1.4 Hz, 1H, ManI-2), 5.17 (d, J = 1.4 Hz, 1H, ManI-1), 5.15 (dt, J = 8.9, 5.7 Hz, 1H, sn-2 of glycerol), 4.95 – 4.91 (m, 2H), 4.90 (d, J = 1.6 Hz, 1H, ManIII-1), 4.88 (d, J = 3.4 Hz, 1H, Glc-1), 4.85 (d, J = 10.6 Hz, 1H), 4.83 (d, J = 10.6 Hz, 1H), 4.82 (br, 1H, ManII-1), 4.80 (d, J = 11.0 Hz, 1H), 4.76 (d, J = 10.7 Hz, 1H), 4.75 (d, J = 10.7 Hz, 1H), $4.70 \text{ (m, 3H)}, 4.66 \text{ (d, } J = 11.6 \text{ Hz}, 1\text{H}), 4.61 \text{ (m, 2H)}, 4.60 - 4.52 \text{ (m, 6H)}, 4.52 - 4.45 \text{ (m, 5H)}, 4.43 \text{ (m,$ -4.32 (m, 8H), 4.30 (s, 2H), 4.29 -4.23 (m, 5H), 4.09 (d, J = 12.0 Hz, 1H), 4.06 (br-d, J = 9.5 Hz, 1H, GlcN-5), 4.04 - 3.83 (m, 13H), 3.81 (dd, J = 9.3, 2.8 Hz, 1H), 3.78 - 3.62 (m, 13H), 3.61 - 3.51(m, 7H), 3.48 (dd, J = 9.9, 2.0 Hz, 1H), 3.46 - 3.34 (m, 5H), 3.28 (dd, J = 1.6, 10.8 Hz, 1H, Glc-6), 3.18 (dd, J = 9.5, 5.5 Hz, 1H), 3.03 (dd, J = 3.1, 10.3 Hz, 1H, GlcN-2), 2.88 (br-d, J = 10.6 Hz, 1H, 1H)Glc-6), 2.85 – 2.79 (m, 6H, CH₂ of TEA), 2.32 – 2.17 (m, 4H), 2.17 – 2.12 (m, 4H), 1.85 (s, 3H, Me of Lev), 1.75 (s, 3H, Me), 1.49 - 1.42 (m, 4H, lipid), 1.17 (d, J = 11.5 Hz, 56H, lipid), 1.12 (t, J =7.3 Hz, 9H, Me of TEA), 0.81 (t, J = 7.0 Hz, 6H, CH₃ of lipid); ¹³C NMR (151 MHz, cdcl₃) δ 206.05 (ketone), 173.32 (ester of lipid), 172.96 (ester of lipid), 171.54 (ester of Lev), 170.61 (amide), 139.66, 138.87, 138.85, 138.74, 138.67, 138.54, 138.47, 138.41, 138.34, 138.31, 138.08, 138.05, 137.96, 137.87, 128.68, 128.41, 128.33, 128.28, 128.25, 128.22, 128.18, 128.15, 128.02, 128.00, 127.90, 127.85, 127.81, 127.75, 127.67, 127.66, 127.63, 127.52, 127.47, 127.45, 127.42, 127.39, 127.36, 127.29, 127.20, 127.12, 126.99, 126.93, 126.77, 126.72, 101.32 (GalNAc-1), 100.28 (Glc-1), 99.89 (ManIII-1), 99.41 (ManII-1), 99.05 (ManI-1), 96.51 (GlcN-1), 82.01, 81.74, 81.40, 81.29, 80.97, 80.22, 79.85, 79.49, 78.19, 77.81, 76.66, 75.94, 75.65, 75.54, 75.42, 75.27, 75.23, 75.15, 74.98, 74.91, 74.78, 74.73, 74.01, 73.46, 73.23, 73.15, 72.86, 72.41, 72.32, 72.16, 72.01, 71.53, 71.06, 70.65, 69.72, 69.44, 69.13, 68.78 (GlcN-6), 67.86, 67.66 (Glc-6), 67.38, 63.83, 63.21 (GlcN-6), 67.86, 67.66 (Glc-6), 67.38, 63.83, 63.21 (GlcN-6), 67.86, 67.66 (Glc-6), 67.86, 63.83, 2), 62.67, 62.38, 54.56 (GalNAc-2), 45.40, 37.72, 34.25, 34.05, 31.92, 29.71, 29.69, 29.68, 29.66, 29.57, 29.53, 29.52, 29.36, 29.32, 29.15, 29.14, 27.88, 24.88, 24.85, 23.43, 22.68, 14.11, 8.41; ³¹P NMR (243 MHz, CDCl₃) δ -1.64; ESI-MS: m/z [M+2Na]²⁺ cald 1879.9229, obsd 1879.9222.

600 MHz NMR Data		40							
(n.d. = not determine	d)	GlcN-1	ManI-1	ManII-1	ManIII-1	GalNAc-1	Glc-1		
¹ H		5.77	5.17	4.82	4.90	4.93	4.87		
chemical shift (ppm)	¹³ C	96.51	99.05	99.41	99.89	101.32	100.28		
coupling constant (Hz)	H-H	n.d.	1.4	n.d.	1.6	8.8	3.4		
	C-H	179	177	175	170	164	170		

Bistriethylammonium (2,3,4-tri-*O*-benzyl-6-*O*-(2-(*N*-benzyloxycarbonyl)aminoethyl-phosphonato)- α -D-mannopyranosyl-(1 \rightarrow 2)-3,4,6-tri-*O*-benzyl- α -D-mannopyranosyl-(1 \rightarrow 6)-3-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl- α -D-glucopyranosyl-(1 \rightarrow 4)-3,6-di-*O*-benzyl-2-deoxy-2-acetamido- β -D-galactopyranosyl)- α -D-mannopyranosyl-(1 \rightarrow 4)-2-azido-3,6-di-*O*-benzyl-2-deoxy- α -D-glucopyranosyl-(1 \rightarrow 6)-2,3,4,5-tetra-*O*-benzyl-1-*O*-(1,2-di-*O*-octadecanoyl-*sn*-glycerylphosphonato)-D-*myo*-inositol (41)



A mixture of mono-phosphate 40 (25.0 mg, 6.55 µmol) and H-phosphonate 7 (13 mg, 0.036 mmol) was co-evaporated three times with pyridine and dried under vacuum for 30 min. To a pyridine (1.5 mL) solution of this mixture was added PivCl (7.5 µL, 0.061 mmol). After 2 h, water (10 µL) and iodine (10 mg, 0.039 mmol) were added. After 1 h, sat. Na₂S₂O_{3(aq)} was added to quench the reaction. The reaction mixture was diluted with chloroform, dried over Na₂SO₄, filtered and concentrated. The residue was then dissolved in a mixture of DCM (3 mL), pyridine (40 µL) and acetic acid $(20 \,\mu\text{L})$ before hydrazine (65 μL , 0.066 mmol) was added. After 12 h, the solvent was removed. The crude product was purified by column chromatography using TEA deactivated silica gel to afford bis-phosphate **41** (25.0 mg, 6.13 μ mol, 94% yield). R_f (SiO₂, chloroform/MeOH 10:1) = 0.44; ¹H NMR (600 MHz, CDCl₃) δ 12.14 (br, 2H), 7.34 – 6.88 (m, 100H), 6.27 (br, 1H, NH of NHCbz), 5.83 (br, 1H, GlcN-1), 5.17-5.14 (m, 2H, sn-2 of glycerol, GalNAc-1), 4.95-3.38 (m, 88H), 3.25-3.10 (m, 5H), 3.01 (br-d, J = 8.7 Hz, 1H, GlcN-2), 2.80 (br-d, J = 9.9 Hz, 1H), 2.70 (q, J = 7.3 Hz, 12H, CH₂ of TEA), 2.15-2.13 (m, 4H, lipid), 1.87 (s, 3H, Ac), 1.47 (br, 4H, lipid), 1.18-1.16 (m, 56H, lipid), 1.04 (t, J = 7.3 Hz, 18H, Me of TEA), 0.81 (d, J = 7.0 Hz, 6H, Me of lipid); ³¹P NMR (243 MHz, CDCl₃) δ 0.02, -1.89; ESI-MS: m/z [M+2Na]²⁺ cald 1959.9287, obsd 1959.9235; [M-2H]²⁻ cald 1935.4306, obsd 1935.4360.

6-*O*-Aminoethylphosphonato-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→6)-4-*O*-(α-D-glucopyranosyl-(1→4)-2-deoxy-2-acetamido-β-D-galactopyranosyl)-α-D-mannopyranosyl-(1→4)-2-amino-2-deoxy-α-D-glucopyranosyl-(1→6)-1-*O*-(1,2-di-*O*-octadecanoyl-*sn*-glycerylphosphonato)-D-*myo*-inositol (23)



Bisphosphate **41** (43 mg, 10 µmol) was dissolved in chloroform (1 mL), MeOH (1 mL) and water (0.3 mL). Acetic acid (10 µL) and palladium on activated charcoal (10% Pd, 45 mg) were added to this solution. The reaction mixture was kept under a hydrogen atmosphere for 3 d before filtration. Evaporation of the filtrate gave GPI **24** (15 mg, 7.5 µmol, 71% yield) as white solid. $[\alpha]_D^{20}$: + 36.4 (c = 0.20, DMSO); ATR-FTIR (cm⁻¹): 3363, 2958, 1640, 1456, 1398, 1049, 1025, 995; ¹H NMR (selected signals 600 MHz, DMSO-*d*₆) δ 5.26 (br, 1H), 5.12 (br, 1H), 4.98 (br, 1H), 2.29-2.18 (m, 4H), 1.87 (s, 3H, Ac), 1.55-1.47 (m, 4H), 1.26-1.22 (m, 56H), 0.86-0.84 (m, 6H, Me of lipid); ³¹P NMR (243 MHz, DMSO-*d*₆) δ 0.74, 0.27; ESI-MS: m/z [M-2H]²⁻ cald 999.9704, obsd 999.9725; [M-H]⁻ cald 2000.9492, obsd 2000.9538.

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> Allyl 3,4-di-*O*-benzyl-2-deoxy-2-trichloroacetamido- β -D-glucopyranosyl-(1 \rightarrow 4)-3-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-2-*O*-levulinyl- α -D-mannopyranoside (46)



A mixture of thioglucoside $44^{[7]}$ (0.542 g, 0.703 mmol) and allyl mannoside 15 (0.303 g, 0.468 mmol) was co-evaporated twice with anhydrous chloroform and dissolved in DCM (9.4 mL). Molecular sieves (4Å, 200 mg), NIS (0.158 g, 0.703 mmol) and TMSOTf (0.025 mL, 0.141 mmol) were added at -30°C. The reaction mixture was then allowed to warm up to 0°C over 45 min. After 45 min at 0°C, the reaction mixture was diluted with DCM and washed with $Na_2S_2O_{3(aq)}$ and $NaHCO_{3(aq)}$. The organic layer was dried over Na₂SO₄, filtered and concentrated. TEA (2 mL, 14.34 mmol) was added. After 16 h, the solvent was removed to give a yellow oil that was purified by silica gel column chromatography to give disaccharide 46 (0.507 g, 0.447 mmol, 95% yield) as white foam: R_f (SiO₂, EtOAc/Hexane 1:2) = 0.31; $[\alpha]_D^{20} = +19.32$ (c = 1.00, CHCl₃); ATR-FTIR (cm⁻¹): 3403, 3067, 3032, 2930, 2859, 1717, 1518, 1455, 1428, 1362, 1210, 1140, 1105, 1074, 1028, 994, 932, 823, 741, 701; ¹H NMR (400 MHz, CDCl₃) δ 7.66-7.60 (m, 4H), 7.35 – 7.13 (m, 21H), 6.28 (d, J = 7.9 Hz, 1H, NH), 5.73 (m, 1H, =CH of allyl), 5.26 (dd, J = 3.0, 1.8 Hz, 1H, Man-2), 5.12 (dd, J = 17.2, 1.4 Hz, 1H, =CH₂), 5.06 (dd, J = 10.4, 1.1 Hz, 1H, =CH₂), 4.73 (d, J = 1.8 Hz, 1H, Man-1), 4.71 (d, J = 10.8 Hz, 1H), 4.67 (d, J = 7.5 Hz, 1H, Glc-1), 4.67 (d, J = 11.4 Hz, 1H), 4.58 (d, J = 10.8 Hz, 1H), 4.58 (d, J = 11.2 Hz, 1H), 4.56 (d, J = 10.8 Hz, 1H), 4.52 (d, J = 11.2 Hz, 1H), 4.50 (d, J = 11.4 Hz, 1H), 4.28 (br-t, J = 9.6 Hz, 1H, Man-4), 4.04 - 3.93 (m, 1H, CH₂ of allyl), 3.85 - 3.81 (m, 3H, CH₂ of allyl), Man-3 & Man-6), 3.76 (dd, J = 11.6, 2.7 Hz, 1H, Man-6), 3.64-3.51 (m, 4H, Glc-2, Glc-3, Glc-6 & Man-5), 3.41 (dd, J = 9.1, 8.3 Hz, 1H, Glc-4), 3.28 (dd, J = 11.9, 5.3 Hz, 1H, Glc-6), 3.20 - 3.11 (m, 1H, Glc-5), 2.61 – 2.45 (m, 4H, CH₂ of Lev), 1.97 (s, 3H, Me of Lev), 1.01 (s, 9H, *t*-Bu); ¹³C NMR (101 MHz, CDCl₃) δ 206.44 (ketone), 172.07 (ester), 161.62 (amide), 138.42, 137.81, 137.78, 136.08, 135.77, 133.97, 133.51, 132.95, 130.07, 129.91, 128.58, 128.56, 128.35, 128.03, 128.00, 127.97, 127.85, 127.68, 127.61, 117.90 (=CH₂), 98.82 (Glc-1), 96.60 (Man-1), 92.47 (CCl₃), 80.58 (Glc-3), 78.84 (Glc-4), 75.75 (Man-3), 75.09 (Glc-5 & -CH₂-), 74.82 (-CH₂-), 72.48 (-CH₂-), 72.36 (Man-5), 72.23 (Man-4), 69.83 (Man-2), 68.15 (-OCH₂- of allyl), 62.22 (Man-6), 61.68 (Glc-6), 58.55 (Glc-2), 38.03 (-CH₂- of Lev), 29.75 (Me of Lev), 28.17 (-CH₂- of Lev), 26.88 (Me of tert-Bu), 19.46 (CMe₃); ESI-MS: m/z [M+Na]⁺ cald 1154.3418, obsd 1154.3411.

Allyl 2,3,4,6-tetra-O-benzyl- β -D-galactopyranosyl- $(1\rightarrow 6)$ -3,4-di-O-benzyl-2-deoxy-2-trichloroacetamido- β -D-glucopyranosyl- $(1\rightarrow 4)$ -3-O-benzyl-6-O-(*tert*-butyldiphenylsilyl)-2-O-levulinyl- α -D-mannopyranoside (47)



A mixture of phosphate 45^[6] (0.184 g, 0.251 mmol) and disaccharide 46 (0.190 g, 0.168 mmol) was co-evaporated with toluene (3x3 mL). This mixture was dissolved in EtCN (4.2 mL) and molecular sieves (4Å, 50 mg) was added. TMSOTf (0.049 mL, 0.268 mmol) was added at -78°C. After 7 h at -78°C, the reaction mixture was filtered, washed with NaHCO_{3(aq)}, dried over Na₂SO₄, filtered and concentrated. The crude product was purified by silica gel column chromatography to give trisaccharide **47** (0.224 g, 0.135 mmol, 81% yield) as white foam: R_f (SiO₂, EtOAc/Hexane 1:3) = 0.22; $\left[\alpha\right]_{D}^{20} = +13.70 \text{ (c} = 1.00, \text{ CHCl}_{3}); \text{ ATR-FTIR (cm}^{-1}): 3406, 3348, 3065, 3031, 2929, 2859, 1720$ 1588, 1519, 1497, 1455, 1428, 1362, 1260, 1208, 1140, 1103, 1067, 1028, 997, 916, 823, 738, 699; ¹H NMR (400 MHz, CDCl₃) δ 7.70 – 7.65 (m, 4H), 7.45 – 6.93 (m, 41H), 6.41 (d, J = 7.8 Hz, 1H, NH), 5.82 (m, 1H, =CH of allyl), 5.27 - 5.17 (m, 2H, Man-2 & =CH₂), 5.14 (dd, J = 10.4, 1.2 Hz, 1H, =CH₂), 5.05 (d, J = 7.8 Hz, 1H, Glc-1), 4.89 (d, J = 11.5 Hz, 1H), 4.84 (d, J = 11.1 Hz, 1H), 4.78 (d, J = 1.7 Hz, 1H, Man-1), 4.74 (d, J = 11.1 Hz, 1H), 4.67 (s, 2H), 4.64 – 4.57 (m, 3H), 4.54 (d, J = 11.6 Hz, 1H), 4.51 (d, J = 11.4 Hz, 1H), 4.47 (d, J = 11.0 Hz, 1H), 4.42 (d, J = 11.4 Hz, 1H),4.38 (d, J = 11.9 Hz, 1H), 4.34 (d, J = 11.9 Hz, 1H), 4.16 (d, J = 7.7 Hz, 1H, Gal-1), 4.14 - 4.09 (dd, J = 11.9 Hz, 1H), 4.16 (d, J = 11.9 Hz, 1H), 4.16J = 12.9, 5.2 Hz, 1H, CH₂ of allyl), 3.98 – 3.89 (m, 5H, CH₂ of allyl, Man-3, Man-4, Man-6 & Glc-6), 3.85 (br-d, J = 2.6 Hz, 1H, Gal-4), 3.83 – 3.76 (m, 3H, Man-6, Glc-3 & Gal-2), 3.74 (m, 1H, Man-5), 3.67 (t, J = 8.6 Hz, 1H, Glc-4), 3.55 (m, 1H, Gal-6), 3.52 – 3.45 (m, 2H, Glc-6 & Gal-6), 3.44 - 3.38 (m, 2H, Gal-3 & Gal-5), 3.33 (m, 1H, Glc-2), 3.25 (m, 1H, Glc-5), 2.65 - 2.45 (m, 4H, CH₂ of Lev), 2.03 (s, 3H, Me), 1.02 (s, 9H, *t*-Bu); ¹³C NMR (101 MHz, CDCl₃) δ 206.46 (ketone), 171.99 (ester), 161.55 (amide), 138.73, 138.64, 138.43, 138.40, 138.32, 138.00, 137.85, 135.99, 135.65, 133.71, 133.51, 133.31, 129.82, 129.79, 128.44, 128.34, 128.32, 128.25, 128.20, 128.09, 127.89, 127.87, 127.81, 127.79, 127.67, 127.60, 127.55, 127.51, 127.41, 127.37, 127.24, 127.17, 117.83 (=CH₂), 104.06 (Gal-1), 98.72 (Glc-1), 96.23 (Man-1), 92.12 (CCl₃), 82.40 (Gal-3), 79.69, 79.09, 77.83 (Glc-4), 76.25 (Man-3), 75.23 (-CH₂-), 74.66 (-CH₂-), 74.48 (-CH₂-), 74.08, 74.03, 73.62, 73.59, 73.47, 73.31 (Gal-5), 72.78 (-CH₂-), 72.42 (Man-5), 71.34 (-CH₂-), 69.02 (Man-2), 68.50 (Gal-6), 67.93 (-OCH₂- of allyl), 67.65 (Glc-6), 63.55 (Man-6), 59.03 (Glc-2), 38.00 (-CH₂- of Electronic Supplementary Material (ESI) for Chemical Science This journal is © The Royal Society of Chemistry 2013

Lev), 29.77 (Me of Lev), 28.16 (-CH₂- of Lev), 26.70 (Me of *tert*-Bu), 19.26 (CMe₃) ; ESI-MS: m/z [M+Na]⁺ cald 1676.5824, obsd 1676.5861.

Allyl 2,3,4,6-tetra-O-benzyl- β -D-galactopyranosyl- $(1\rightarrow 6)$ -3,4-di-O-benzyl-2-deoxy-2-trichloroacetamido- β -D-glucopyranosyl- $(1\rightarrow 4)$ -3-O-benzyl-2-O-levulinyl- α -D-mannopyranoside (48)



To a THF solution (2.5 mL) of trisaccharide 47 (0.447 g, 0.270 mmol) was added HF-pyridine (70% HF, 0.280 mL, 10.8 mmol). After 36 h, sat. NaHCO_{3(aq)} was added until no formation of bubbles. The reaction mixture was extracted with DCM for three times. The combined organic layers were concentrated and purified by silica gel column chromatography to give trisaccharide 48 (0.342 g, 0.241 mmol, 89 % yield) as a white foam: R_f (SiO₂, EtOAc/Hexane 3:2) = 0.33; $[\alpha]_D^{20} = +16.14$ (c $= 1.00, CHCl_3$; ATR-FTIR (cm⁻¹): 3335, 3064, 3031, 2925, 2871, 1740, 1718, 1527, 1497, 1455, 1364, 1209, 1140, 1066, 1028, 993, 919, 822, 737, 698; ¹H NMR (400 MHz, CDCl₃) δ 7.31 – 7.02 (m, 35H,), 7.00 (d, J = 7.7 Hz, 1H, NH), 5.76 (m, 1H, =CH of allyl), 5.22 (dd, J = 3.2, 2.0 Hz, 1H, Man-2), 5.17 (ddd, J = 17.2, 3.0, 1.5 Hz, 1H, =CH₂), 5.13 – 5.06 (m, 2H, =CH₂ & Glc-1), 4.88 – 4.78 (m, 2H), 4.75 - 4.72 (m, 2H), 4.63 (s, 2H), 4.61 (d, J = 11.6 Hz, 1H), 4.59 (d, J = 11.0 Hz, 1H),4.54 - 4.42 (m, 5H), 4.34 (d, J = 11.8 Hz, 1H), 4.30 (d, J = 11.8 Hz, 1H), 4.18 (d, J = 7.7 Hz, 1H, Gal-1), 4.09 – 3.96 (m, 4H), 3.93 – 3.74 (m, 5H), 3.70 – 3.36 (m, 11H), 2.51 – 2.36 (m, 4H, CH₂ of Lev), 1.98 (s, 3H, Me of Lev); ¹³C NMR (101 MHz, CDCl₃) δ 206.44 (ketone), 171.97 (ester). 161.83 (amide), 138.74, 138.73, 138.45, 138.03, 138.00, 137.94, 137.91, 133.37, 128.49, 128.45, 128.37, 128.36, 128.33, 128.19, 128.15, 128.06, 127.91, 127.88, 127.84, 127.81, 127.73, 127.67, 127.61, 127.57, 127.50, 126.92, 117.94 (=CH₂), 104.19 (Gal-1), 98.34 (Glc-1), 96.54 (Man-1), 92.57 (CCl₃), 82.37, 79.33, 79.23, 77.68, 76.33, 75.30, 74.62, 74.45, 74.33, 74.13, 73.53, 73.50, 73.38, 72.82, 71.79, 71.71, 70.69, 68.58, 68.53, 68.26, 61.50, 58.12 (Glc-2), 37.94 (-CH₂- of Lev), 29.73 (Me of Lev), 28.05 (-CH₂- of Lev); ESI-MS: m/z [M+Na]⁺ cald 1438.4646, obsd 1438.4681.

Allyl 2,3,4-tri-*O*-benzyl-6-*O*-tri*iso*propylsilyl- α -D-mannopyranosyl- $(1\rightarrow 2)$ -3,4,6-tri-*O*-benzyl- α -D-mannopyranosyl- $(1\rightarrow 6)$ -3-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl- β -D-galactopyranosyl- $(1\rightarrow 6)$ -3,4-di-*O*-benzyl-2-deoxy-2-trichloroacetamido- β -D-glucopyranosyl)-2-*O*-levulinyl- α -D-mannopyranoside (49)



A mixture of trichloroacetimidate 4 (0.304 g, 0.257 mmol) and trisaccharide 48 (0.280 g, 0.197 mmol) was co-evaporated three times with toluene. The residue was then dissolved in anhydrous diethyl ether (1 mL). Molecular sieves (4Å, 50 mg) were added, and the reaction mixture was cooled to 0 °C before the addition of TBSOTf (5.9 µL, 0.026 mmol). After 1 h at 0 °C, NEt₃ was added. The reaction mixture was filtered and the crude product was purified by silica gel column chromatography to give pentasaccharide 49 (0.403 g, 0.112 mmol, 84% yield) as a white foam: R_f (SiO₂, EtOAc/Hexane 1:3) = 0.24; $[\alpha]_D^{20} = +18.15$ (c = 1.00, CHCl₃); ATR-FTIR (cm⁻¹): 3340, 3064, 3031, 2926, 2865, 1741, 1720, 1519, 1497, 1454, 1363, 1208, 1137, 1098, 1070, 1028, 914, 833, 821, 736, 697; ¹H NMR (600 MHz, CDCl₃) δ 7.34 – 6.87 (m, 66H), 5.71 (m, 1H, =CH of allyl), 5.23 $(d, J = 1.3 \text{ Hz}, 1\text{H}, \text{ManIII-1}), 5.20 (br, 1\text{H}, \text{ManI-2}), 5.13 (dd, J = 17.3, 1.2 \text{ Hz}, 1\text{H}, =CH_2), 5.08 (d, J = 17.3, 1.2 \text{ Hz}, 1\text{Hz}, 1\text{H}, =CH_2), 5.08 (d, J = 17.3, 1.2 \text{ Hz}, 1\text{Hz}, 1\text{Hz},$ J = 7.9 Hz, 1H, Glc-1), 5.03 (br-d, J = 10.3 Hz, 1H, =CH₂), 4.84 (d, J = 11.7 Hz, 1H), 4.83 (d, J = 10.3 Hz, 1H, =CH₂), 4.84 (d, J = 11.7 Hz, 1H), 4.83 (d, J = 10.3 Hz, 1H, =CH₂), 4.84 (d, J = 11.7 Hz, 1H), 4.83 (d, J = 10.3 Hz, 1H, =CH₂), 4.84 (d, J = 11.7 Hz, 1H), 4.83 (d, J = 10.3 Hz, 1H, =CH₂), 4.84 (d, J = 10.3 10.6 Hz, 1H), 4.78 (d, J = 11.0 Hz, 1H), 4.74 – 4.69 (m, 3H), 4.68 (d, J = 1.3 Hz, 1H, ManI-1), 4.63 (s, 2H), 4.61 (d, J = 10.8 Hz, 1H), 4.59 – 4.55 (m, 2H), 4.53 – 4.46 (m, 6H), 4.43 – 4.30 (m, 10H), 4.11 (d, J = 7.7 Hz, 1H, Gal-1), 4.09 - 4.04 (m, 2H), 4.00 - 3.87 (m, 6H), 3.84 - 3.73 (m, 9H), 3.65-3.33 (m, 13H), 3.23 (br-d, J = 9.0 Hz, 1H, Glc-5), 2.54 -2.40 (m, 4H, CH₂ of Lev), 1.94 (s, 3H, Me of Lev), 1.04 - 0.98 (m, 21H, TIPS); ¹³C NMR (151 MHz, CDCl₃) δ 206.25 (ketone), 171.93 (ester), 161.86 (amide), 139.06, 138.86, 138.80, 138.69, 138.55, 138.53, 138.47, 138.34, 138.33, 138.13, 138.11, 138.02, 137.92, 133.30, 128.54, 128.49, 128.48, 128.41, 128.37, 128.36, 128.32, 128.28, 128.27, 128.26, 128.23, 128.22, 128.19, 128.18, 128.17, 128.15, 128.11, 128.09, 128.06, 128.03, 128.01, 127.99, 127.95, 127.93, 127.91, 127.86, 127.83, 127.80, 127.74, 127.71, 127.65, 127.61, 127.59, 127.59, 127.56, 127.52, 127.46, 127.42, 127.36, 127.26, 118.37 (=CH₂), 104.12 (Gal-1), 98.75 (Glc-1), 98.47 (ManII-1), 98.24 (ManIII-1), 96.10 (ManI-1), 92.55 (CCl₃), 82.48, 80.73, 79.61, 79.52, 79.22, 77.83, 76.24, 75.30, 75.16, 75.06, 74.89, 74.77, 74.66, 74.51, 74.41, 74.23, 74.19, 74.06, 73.76, 73.61, 73.51, 73.36, 73.27, 72.86, 72.33, 72.18, 72.13, 72.02, 71.64, Electronic Supplementary Material (ESI) for Chemical Science This journal is © The Royal Society of Chemistry 2013

71.06, 69.94, 69.65, 68.63, 68.59, 67.84, 67.74, 66.30, 62.91, 59.15 (Glc-2), 38.00 (-CH₂- of Lev), 29.76 (Me of Lev), 28.17 (-CH₂- of Lev), 18.18, 18.13, 12.14; ESI-MS: $m/z [M+Na]^+$ cald 2458.9854, obsd 2458.9940.

600 MHz NMR Data for 49		ManI-1	ManII-1	ManIII-1	Glc-1	Gal-1
	$^{1}\mathrm{H}$	4.68	4.72	5.23	5.08	4.11
chemical shift (ppm)	¹³ C	96.10	98.47	98.24	98.75	104.12
	H-H	1.3	-	1.3	7.9	7.7
coupling constant (Hz)	C-H	174	173	173	165	159

Allyl 2,3,4-tri-*O*-benzyl-6-*O*-tri*iso*propylsilyl- α -D-mannopyranosyl- $(1\rightarrow 2)$ -3,4,6-tri-*O*-benzyl- α -D-mannopyranosyl- $(1\rightarrow 6)$ -3-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl- β -D-galactopyranosyl- $(1\rightarrow 6)$ -3,4-di-*O*-benzyl-2-deoxy-2-acetamido- β -D-glucopyranosyl)-2-*O*-levulinyl- α -D-mannopyranoside (50)



To a solution of pentasaccharide **49** (0.274 g, 0.112 mmol) in acetic acid (3 mL) was added zinc powder (0.661 g, 10.1 mmol) in three portions over 30 min at 55°C. After 2 h at 55°C, the reaction mixture was filtered and concentrated. The crude product was purified by silica gel column chromatography to give pentasaccharide **50** (0.227 g, 0.097 mmol, 87% yield) as a colorless oil: R_f (SiO₂, EtOAc/Hexane 1:2) = 0.19; R_f (SiO₂, EtOAc/Hexane 2:3) = 0.29; $[\alpha]_D^{20} = + 23.80$ (c = 1.00, CHCl₃); ATR-FTIR (cm⁻¹): 3063, 3031, 2924, 2866, 1743, 1720, 1677, 1497, 1454, 1363, 1208, 1138, 1099, 1069, 1028, 914, 834, 736, 697; ¹H NMR (600 MHz, CDCl₃) δ 7.44 – 7.08 (m, 65H), 6.39 (d, *J* = 7.8 Hz, 1H, NH), 5.88 (m, 1H, =CH of allyl), 5.39 (br, 1H, ManIII-1), 5.31 – 5.28 (m, 2H, ManI-2 & =CH₂), 5.21 (br-d, *J* = 10.3 Hz, 1H, =CH₂), 5.13 (d, *J* = 7.9 Hz, 1H, Glc-1), 5.03 – 4.95 (m, 3H), 4.89 – 4.84 (m, 4H), 4.80 – 4.47 (m, 19H), 4.45 (d, *J* = 12.1 Hz, 1H), 4.42 (d, *J* = 11.9 Hz, 1H), 4.29 – 4.19 (m, 3H), 4.17 – 3.81 (m, 16H), 3.79 (br, 1H, ManIII-2), 3.75 – 3.67 (m, 3H), 3.65 – 3.45 (m, 8H), 3.34 (br-d, *J* = 9.4 Hz, 1H, Glc-5), 2.67 – 2.52 (m, 4H, CH₂ of Lev), 2.10 (s, 3H, Me of Lev), 1.88 (s, 3H, Me of Ac), 1.17 – 1.16 (m, 21H, TIPS); ¹³C NMR (151 MHz, CDCl₃) δ 206.22 (ketone), 172.01 (ester), 170.60 (amide), 138.99, 138.86, 138.80, 138.63, 138.52, 138.47, 138.24, 138.05, 137.97, 137.84, 133.27, 128.52, 128.49, 128.45, 128.40, 128.37, 128.30, 128.25,

128.23, 128.19, 128.11, 128.09, 128.06, 127.97, 127.95, 127.92, 127.84, 127.80, 127.75, 127.72, 127.71, 127.67, 127.64, 127.59, 127.57, 127.55, 127.52, 127.49, 127.46, 127.41, 127.35, 127.30, 118.22, 104.05 (Gal-1), 100.54 (Glc-1), 98.25 (ManIII-1), 98.14 (ManII-1), 96.27 (ManI-1), 82.53, 80.76, 80.59, 79.50, 79.20, 78.05, 76.37, 75.27, 75.20, 75.19, 75.06, 74.90, 74.85, 74.62, 74.43, 74.16, 74.10, 73.92, 73.87, 73.62, 73.49, 73.31, 73.13, 72.85, 72.31, 72.22, 72.14, 71.95, 71.66, 71.23, 69.99, 69.41, 68.77, 68.59, 67.95, 67.65, 65.86, 62.91, 57.72 (Glc-2), 37.89 (-CH₂- of Lev), 29.75 (Me of Lev), 28.12 (-CH₂- of Lev), 23.49 (Me of Ac), 18.18, 18.12, 12.15; ESI-MS: m/z $[M+Na]^+$ cald 2357.1023, obsd 2357.1092.

600 MHz NMR Data for 50		ManI-1	ManII-1	ManIII-1	Glc-1	Gal-1
chemical shift (ppm)	$^{1}\mathrm{H}$	4.70	4.74	5.39	5.13	4.11
	¹³ C	96.27	98.14	98.25	100.54	104.05
coupling constant (Hz)	H-H	-	-	-	7.9	-
	С-Н	170	172	175	164	159

2,3,4-Tri-O-benzyl-6-O-tri*iso*propylsilyl- α -D-mannopyranosyl- $(1\rightarrow 2)$ -3,4,6-tri-O-benzyl- α -D-mannopyranosyl- $(1\rightarrow 6)$ -3-O-benzyl-4-O-(2,3,4,6-tetra-O-benzyl- β -D-galactopyranosyl- $(1\rightarrow 6)$ -3,4-di-O-benzyl-2-deoxy-2-acetamido- β -D-glucopyranosyl)-2-O-levulinyl- α -D-mannopyranosyl- $(1\rightarrow 4)$ -2-azido-3,6-di-O-benzyl-2-deoxy- α -D-glucopyranosyl- $(1\rightarrow 6)$ -1-O-allyl-2,3,4,5-tetra-O-benzyl-D-*myo*-inositol (52)



To a solution of $[IrCOD(PPh_2Me)_2]PF_6$ (6.3 mg, 7.5 µmol) in THF (2 mL) was bubbled hydrogen for 10 min. The color of the solution changed from red to colorless to light pale yellow. The hydrogen atmosphere was exchanged with Ar. This solution was then added into a flask with pentasaccharide **50** (0.175 g, 0.075 mmol), and the reaction mixture was kept at 30°C for 17 h. The solvent was then removed, and the residue was dissolved in acetone (1.8 mL). Water (0.2 mL), mercury(II) chloride (0.102 g, 0.375 mmol) and mercury(II) oxide (1.6 mg, 7.5 µmol) were added. After 1 h, the reaction mixture was diluted with DCM and washed with NaHCO_{3(aq)}, dried over Na₂SO₄, filtered and concentrated. The residue was then dissolved in a mixture of EtOAc and hexane (1:1), and the solution was passed through a pad of silica gel. The filtrate was concentrated to give the crude lactol **51a** as colorless oil: R_f (SiO₂, EtOAc/Hexane 2:3) = 0.27.

To a solution of the crude lactol **51a** in DCM (2 mL) were added 2,2,2-trichloroacetonitrile (0.100 mL, 0.984 mmol) and a catalytic amount of DBU (1 drop). After 40 min, the solvent was removed to give a brown oil that was purified by silica gel column chromatography to give glycosyl imidate **51** (0.103 g, 0.042 mmol, 56% yield) as an inseparable mixture of anomers: R_f (SiO₂, EtOAc/Hexane 2:3) = 0.40.

A mixture of imidate **51** (103 mg, 0.042 mmol) and pseudodisaccharide **5** (40.0 mg, 0.042 mmol) was co-evaporated with toluene (3 x 2 mL). The residue was then dissolved in toluene (2 mL). Molecular sieves (4Å, 50 mg) and thiophene (0.034 mL, 0.42 mmol) were added. The reaction mixture was then cooled to -40°C before the addition of TMSOTf (3.1 µL, 0.017 mmol). After 1 h at -40°C, TEA (50 µL) was added and the reaction mixture was filtered. The crude product was purified by silica gel column chromatography to give pseudoheptasaccharide 52 (119 mg, 0.037 mmol, 87% vield) as a colorless oil: R_f (SiO₂, EtOAc/Hexane 1:2) = 0.22; $[\alpha]_D^{20} = +26.77$ (c = 1.00, CHCl₃); ATR-FTIR (cm⁻¹): 3031, 2865, 2106, 1741, 1678, 1497, 1454, 1361, 1053, 1027; ¹H NMR (600 MHz, CDCl₃) δ 7.39 – 6.92 (m, 95H), 6.12 (d, J = 8.5 Hz, 1H, NH), 5.82 (m, 1H, =CH of allyl), 5.60 $(d, J = 3.1 \text{ Hz}, 1\text{H}, \text{GlcN-1}), 5.27 (br, 1\text{H}, \text{ManI-1}), 5.17 (br-d, J = 17.3 \text{ Hz}, 1\text{H}, =\text{CH}_2), 5.14 - 5.04$ (m, 3H, ManI-2, ManIII-1 & =CH₂), 4.92 (d, J = 11.4 Hz, 1H), 4.88 – 4.15 (m, 40H), 4.09 – 4.01 (m, 3H), 4.00 – 3.64 (m, 21H), 3.57 (br, 1H, ManIII-2), 3.55 – 3.53 (m, 2H), 3.49 – 3.21 (m, 14H), 3.15 - 3.12 (m, 2H), 2.35 - 2.15 (m, 4H, CH₂ of Lev), 1.83 (s, 3H, Me of Lev), 1.66 (s, 3H, Me of Ac), 0.98 (br, 21H, TIPS); ¹³C NMR (151 MHz, CDCl₃) δ 206.04 (ketone), 171.72 (ester), 170.28 (amide), 139.13, 138.94, 138.87, 138.76, 138.70, 138.65, 138.42, 138.34, 138.20, 138.11, 138.04, 137.83, 134.44, 128.72, 128.52, 128.41, 128.32, 128.29, 128.13, 128.10, 128.04, 127.98, 127.86, 127.81, 127.77, 127.70, 127.58, 127.43, 127.28, 117.22 (=CH₂), 104.36 (Gal-1), 101.98 (GlcNAc-1), 99.36 (ManII-1), 98.50 (ManIII-1), 98.18 (ManI-1), 97.55 (GlcN-1), 82.58, 82.12, 81.96, 81.37, 81.00, 80.70, 80.48, 79.42, 76.29, 75.88, 75.61, 75.34, 75.08, 74.98, 74.70, 74.60, 74.39, 74.12, 73.84, 73.71, 73.52, 73.32, 73.27, 73.11, 73.05, 72.95, 72.89, 72.76, 72.41, 72.23, 72.06, 71.83, 71.55, 71.27, 70.98, 70.44, 69.82, 69.68, 68.65, 68.01, 66.66, 63.69 (GlcN-2), 62.86, 56.06 (Glc-NAc-2), 37.81 (-CH₂CH₂- of Lev), 29.74 (Me of Lev), 28.02 (-CH₂CH₂- of Lev), 23.38 (Me of Ac), 18.23, 18.18, 12.19; ESI-MS: m/z [M+2Na]²⁺ cald 1634.7427, obsd 1634.7444.

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600 MHz NMR Data for 52		GlcN- 1	ManI-1	ManII-1	ManIII-1	GlcNAc- 1	Gal-1
chemical shift (ppm) $\frac{1}{13}$	$^{1}\mathrm{H}$	5.60	5.27	4.51	5.07	4.67	4.08
	¹³ C	97.55	98.18	99.36	98.50	101.98	104.36
coupling constant (Hz)	H-H	3.1	-	-	-	-	-
	С-Н	179	173	172	170	163	161

2,3,4-Tri-*O*-benzyl-6-*O*-tri*iso*propylsilyl- α -D-mannopyranosyl- $(1\rightarrow 2)$ -3,4,6-tri-*O*-benzyl- α -D-mannopyranosyl- $(1\rightarrow 6)$ -3-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl- β -D-galactopyranosyl- $(1\rightarrow 6)$ -3,4-di-*O*-benzyl-2-deoxy-2-acetamido- β -D-glucopyranosyl)-2-*O*-levulinyl- α -D-mannopyranosyl- $(1\rightarrow 4)$ -2-azido-3,6-di-*O*-benzyl-2-deoxy- α -D-glucopyranosyl- $(1\rightarrow 6)$ -2,3,4,5-tetra-*O*-benzyl-D-*myo*-inositol (53)



Through a solution of $[IrCOD(PPh_2Me)_2]PF_6$ (2.5 mg, 3.0 µmol) in THF (3 mL) was bubbled hydrogen for 15 min. The hydrogen atmosphere was exchanged with Ar, and this solution was added into a flask with pseudoheptasaccharide **52** (97 mg, 0.030 mmol). The reaction mixture was kept at 30°C for 24 h. The solvent was removed and the residue was dissolved in acetone (1.8 mL). Water (0.2 mL), mercury(II) chloride (40.8 mg, 0.150 mmol) and mercury(II) oxide (1.3 mg, 6.0 µmol) were added. After 45 min, the reaction mixture was diluted with chloroform and washed with Na-HCO_{3(aq)}, dried over Na₂SO₄, filtered and concentrated. The crude product was purified by silica gel column chromatography to give pseudoheptasaccharide **53** (75.6 mg, 0.024 mmol, 79% yield) as a colorless oil: R_f (SiO₂, EtOAc/Hexane 1:2) = 0.29; R_f (SiO₂, EtOAc/Hexane 2:3) = 0.56; $[\alpha]_D^{20} = +$ 22.9 (c = 1.00, CHCl₃); ATR-FTIR (cm⁻¹): 3064, 3031, 2925, 2866, 2107, 1741, 1720, 1684, 1454, 1362, 1055, 1028; ¹H NMR (600 MHz, CDCl₃) δ 7.47 – 7.11 (m, 95H), 6.11 (br, 1H, NH), 5.42 (br, 1H, MaI-1), 5.30 (br, 1H, GlcN-1), 5.24 (br, 2H, MaI-2 & MaIII-1), 5.05 (d, *J* = 11.6 Hz, 1H), 5.02 – 4.91 (m, 5H), 4.87 (d, *J* = 7.7 Hz, 1H, GlcNAc-1), 4.86 – 4.31 (m, 33H), 4.26 (d, *J* = 7.6 Hz,

1H, Gal-1), 4.21 – 3.37 (m, 40H), 3.33 (d, J = 5.1 Hz, 1H), 2.48 – 2.29 (m, 4H, CH₂ of Lev), 1.98 (s, 3H, Me of Lev), 1.77 (s, 3H, Me of Ac), 1.12 (br, 21H, TIPS); ¹³C NMR (151 MHz, CDCl₃) δ 206.01 (ketone), 171.59 (ester), 170.29 (amide), 139.04, 138.80, 138.75, 138.66, 138.50, 138.43, 138.35, 138.21, 138.03, 137.98, 137.62, 104.26 (Gal-1), 101.29 (GlcNAc-1), 99.33 (ManII-1), 98.37 (ManIII-1), 97.94 (GlcN-1), 97.35 (ManI-1), 82.51, 82.01, 81.56, 81.47, 80.87, 80.77, 80.65, 79.48, 79.35, 76.29, 75.73, 75.27, 75.18, 74.99, 74.93, 74.84, 74.65, 74.58, 74.40, 74.36, 74.08, 73.82, 73.66, 73.43, 73.27, 73.15, 73.07, 72.91, 72.83, 72.53, 72.19, 72.00, 71.49, 70.55, 69.99, 69.75, 69.54, 68.69, 68.64, 67.99, 66.21, 64.36 (GlcN-2), 62.89, 56.41 (GlcNAc-2), 37.70 (-CH₂CH₂- of Lev), 29.66 (Me of Lev), 27.91 (-CH₂CH₂- of Lev), 23.30 (Me of Ac), 18.16, 18.11, 12.10; ESI-MS: m/z [M+2Na]²⁺ cald 1614.7271, obsd 1614.7286.

600 MHz NMR Data for 53		GlcN- 1	ManI-1	ManII-1	ManIII-1	GlcNAc- 1	Gal-1
chamical shift (ppm)	$^{1}\mathrm{H}$	5.30	5.42	4.61	5.24	4.87	4.26
chemical shift (ppm)	¹³ C	97.45	97.35	99.33	98.37	101.29	104.26
coupling constant (Hz)	H-H	-	-	-	-	7.7	7.6
	C-H	174	174	174	173	160	161

Triethylammonium 1,2-di-O-dimyristoyl-sn-glyceryl H-phosphonate (43)^[8]



Phosphorous acid (50 mg, 0.586 mmol) and 1,2-dimyristoyl-*sn*-glycerol (157 mg, 0.293 mmol) were co evaporated with anhydrous pyridine (3x2 mL). The residue was placed under high vacuum for 3 h and dissolved in anhydrous pyridine (5 mL). PivCl (75.4 μ L, 0.586 mmol) was added and the solution was stirred for 18 h. All solvents were removed in vacuo and column chromatography (CHCl₃/MeOH starting from 100%CHCl₃ to 90%) yielded a yellow solid that was further purified using a LH-20 column (1:1 DCM/MeOH +1%TEA) to yield **43** (80 mg, 0.118 mmol, 38% yield) as colorless solid: R_f (SiO₂, CHCl₃/MeOH 90:10) = 0.43 $[\alpha]_D^{20}$: + 3.7 (c = 1.0, CHCl₃); ATR-FTIR (cm⁻¹): 3380, 2957, 2917, 2850, 1738, 1468, 1227, 1203, 1171, 1061, 988; ¹H NMR (400 MHz, CDCl₃) δ 12.14 (s, 1H, **H**NEt₃⁺), 6.76 (d, *J* = 640.8 Hz, 1H), 5.20 – 5.13 (m, 1H), 4.32 (dd, *J* = 11.9, 3.6 Hz, 1H), 4.12 (dd, *J* = 11.9, 6.4 Hz, 1H), 3.97 (dd, *J* = 8.1, 5.2 Hz, 2H), 3.17 – 2.84 (m, 6H, CH₂ of TEA), 2.25 (dd, *J* = 15.2, 7.6 Hz, 4H), 1.60 – 1.49 (m, 4H), 1.37 – 1.09 (m, 49H), 0.83 (t, *J* = 6.8 Hz, 6H, CH₃ of lipid); ¹³C NMR (101 MHz, CDCl₃) δ 173.39, 173.01, 70.31 (d, *J* = 7.2 Hz), 62.48, 62.22 (d, *J* = 4.2 Hz), 45.64, 34.32, 34.13, 31.97, 29.75, 29.73, 29.71, 29.57, 29.41, 29.38, 29.37,

29.21, 29.18, 24.95, 24.93, 22.73, 14.16, 8.60; 31 P NMR (162 MHz, CDCl₃) δ 4.17; ESI-MS: m/z [M+Na]⁺ cald for C₃₁H₆₁O₇P 599.4 , obsd 599.3.

 $\label{eq:absolution} Triethylammonium 2,3,4-tri-O-benzyl-\alpha-D-mannopyranosyl-(1\rightarrow2)-3,4,6-tri-O-benzyl-\alpha-D-mannopyranosyl-(1\rightarrow6)-3-O-benzyl-4-O-(2,3,4,6-tetra-O-benzyl-\beta-D-galactopyranosyl-(1\rightarrow6)-3,4-di-O-benzyl-2-deoxy-2-acetamido-\beta-D-glucopyranosyl)-2-O-levulinyl-\alpha-D-mannopyranosyl-(1\rightarrow4)-2-azido-3,6-di-O-benzyl-2-deoxy-\alpha-D-glucopyranosyl-(1\rightarrow6)-1-O-(1,2-dimyristoyl-sn-glyceryl-phosphonato)-2,3,4,5-tetra-O-benzyl-D-myo-inositol (55a)$



Pseudoheptasaccharide 53 (51 mg, 16 µmol) and triethylammonium 1,2-dimyristoyl-sn-glycerole Hphosphonate 43 (21.7 mg, 32 µmol) were co-evaporated with anhydrous pyridine (3x2 mL) and placed under high vacuum for 2 h. The residue was dissolved in anhydrous pyridine (2 mL) and PivCl (6.9µL, 56µmol) was added. The solution was stirred for 2 h at room temperature before water (11.5 µL, 640 µmol) and iodine (10.2 mg, 40 µmol) were added. The reaction mixture was stirred for 1 h at room temperature before the reaction was quenched with sat. Na₂S₂O₃ solution (10 drops), dried over Na₂SO₄ and filtered over Celite©. Solvents were evaporated in vacuo and the residue was co-evaporated with toluene (3x5 mL). The residue was dissolved in chloroform and washed with 1N HCl (15 mL), sat. NaHCO₃ solution (15 mL) and brine (15 mL). The organic layer was dried over sodium sulfate, filtered and evaporated to dryness. Crude 54 was dissolved in MeCN (5 mL) and water (11.5 µL, 640 µmol). Sc(OTf)₃ (23.6 mg, 48 µmol) was added and the reaction mixture was heated to 50°C for 5 h. The reaction was guenched with pyridine (50 μ L) and solvents were removed under reduced pressure. The residue was purified with column chromatography on TEA deactivated SiO2 (CHCl3/MeOH from 0%MeOH to 5%). Fractions containing the product were pooled and washed with TEA/CO₂ buffer (2x15 mL), dried over Na₂SO₄ and concentrated to yield lipidated pseudoheptasaccharide 55a (44 mg, 12 µmol, 74% yield) as yellow foam: Rf (SiO₂, CHCl₃/MeOH

95:5 = 0.58; $[\alpha]^{20}_{D}$ = + 35.6 (c = 1.00, CHCl₃); ATR-FTIR (cm⁻¹): 3344, 2924, 2854, 2108, 1740, 1454, 1052, 696; ¹H NMR (600 MHz, CDCl₃) δ 12.18 (s, 1H, HNEt₃⁺), 7.42 – 6.93 (m, 95H), 6.36 $(d, J = 7.4 \text{ Hz}, 1\text{H}, \text{NH}), 5.84 (d, J = 3.6 \text{ Hz}, 1\text{H}, \text{GlcNH}_2-1), 5.21 - 5.07 (m, 3\text{H}), 4.94 (d, J = 12.0 \text{ Hz})$ Hz, 1H), 4.90 – 4.22 (m, 41H), 4.14 – 4.06 (m, 2H), 4.04 – 3.96 (m, 3H), 3.95 – 3.28 (m, 34H), 3.18 $(d, J = 9.2 \text{ Hz}, 1\text{H}), 3.01 (dd, J = 10.2, 3.6 \text{ Hz}, 1\text{H}, \text{GlcNH}_2-2), 2.82 (dd, J = 13.9, 6.8 \text{ Hz}, 6\text{H}, \text{CH}_2$ of TEA), 2.73 (s, 1H), 2.39 – 2.11 (m, 1H, 8H, CH₂ of Lev; 2x O-CO-CH₂-CH₂), 1.86 (s, 3H, Me of Lev), 1.71 (s, 3H, Me of NHAc), 1.47 (s, 4H, 2x O-CO-CH₂-CH₂), 1.27 – 1.07 (m, 53H, 22xCH₂ of lipids and CH₃ of TEA), 0.80 (t, J = 7.0 Hz, 6H, CH₃ of lipids); ¹³C NMR (151 MHz, CDCl₃) δ 206.34 (ketone of Lev), 173.50, 173.13 (2xCO of lipid ester), 171.65 (CO of Lev), 170.68 (CONH), 139.93, 138.85, 138.82, 138.81, 138.78, 138.73, 138.70, 138.68, 138.67, 138.60, 138.48, 138.46, 138.28, 138.21, 138.11, 138.04, 128.85, 128.55, 128.54, 128.47, 128.44, 128.40, 128.37, 128.36, 128.32, 128.30, 128.28, 128.23, 128.13, 128.09, 128.08, 128.04, 127.99, 127.90, 127.84, 127.80, 127.76, 127.75, 127.70, 127.65, 127.63, 127.61, 127.58, 127.56, 127.53, 127.46, 127.44, 127.41, 127.36, 127.33, 127.19, 127.03, 104.30, 101.73, 100.00, 99.44, 99.41, 96.45 (GlcNH₂-1), 82.58, 81.91, 81.75, 81.49, 81.14, 79.72, 79.62, 79.33, 77.84, 77.80, 76.25, 76.15, 75.74, 75.51, 75.48, 75.38, 75.33, 75.13, 75.10, 74.84, 74.77, 74.25, 74.17, 74.12, 74.05, 73.84, 73.70, 73.53, 73.32, 73.27, 73.14, 72.95, 72.92, 72.57, 72.46, 72.30, 71.99, 71.92, 71.26, 71.04, 70.75, 70.70, 69.58, 69.12, 69.11, 69.09, 68.60, 67.83, 67.82, 63.81, 63.78, 63.32 (GlcNH₂-2), 62.94, 62.65, 45.62 (CH₂ of TEA), 42.42, 37.88, 34.42, 34.21, 32.06, 29.84, 29.83, 29.82, 29.81, 29.76, 29.67, 29.66, 29.50, 29.46, 29.39, 29.29, 28.04, 25.03, 25.00, 23.52, 22.83, 17.85, 14.26, 12.43 (CH₃ of lipid), 8.66 (CH₃ of TEA); ³¹P NMR (162 MHz, CDCl₃) δ -1.66; ESI-MS: m/z [M+3Na-H]²⁺ cald 1835.8546, obsd 1835.8557.

Bistriethylammonium 2,3,4-tri-O-benzyl-6-O-(2-(N-benzyloxycarbonyl)aminoethyl-phosphonato)- α -D-mannopyranosyl-(1 \rightarrow 2)-3,4,6-tri-O-benzyl- α -D-mannopyranosyl-(1 \rightarrow 6)-3-O-benzyl-4-O-(2,3,4,6-tetra-O-benzyl- β -D-galactopyranosyl-(1 \rightarrow 6)-3,4-di-O-benzyl-2-deoxy-2-acetamido- β -D-glucopyranosyl)- α -D-mannopyranosyl-(1 \rightarrow 4)-2-azido-3,6-di-O-benzyl-2-deoxy- α -D-glucopyranosyl-(1 \rightarrow 6)-1-O-(1,2-dimyristoyl-*sn*-glyceryl-phosphonato)-2,3,4,5-tetra-O-benzyl-D-*myo*-inositol (55)



Pseudoheptasaccaride 55a (12 mg, 2.95 µmol) and H-phosphonate 7 (10.6 mg, 30 µmol) were coevaporated with anhydrous pyridine (3 x 2 mL) and the residue was placed under high vacuum for 1 h. The residue was dissolved in anhydrous pyridine (2 mL) and PivCl (6.1 µL, 50 µmol) was added. After stirring for 2 h at room temperature water (2.2 µL, 2.2 µmol) and iodine (8.3 mg, 33 µmol) were added. The solution was stirred for another hour before acetic acid (33.7 µL, 590 µmol) and hydrazine in THF (1 M, 295 µL, 295 µmol) were added. The solution was stirred for 14 h before solvents were removed in vacuo and the residue was purified with column chromatography on TEA deactivated SiO₂ (CHCl₃/MeOH from 0%MeOH to 5%). Fractions containing the product were pooled and washed with TEA/CO₂ buffer (2 x 15 mL), dried over Na₂SO₄ and concentrated to yield bisphosphorylated pseudoheptasaccharide 55 (9.6 mg, 2.4 µmol, 82% yeild) as yellow foam: R_f $(SiO_2, CHCl_3/MeOH 95:5) = 0.53; [\alpha]^{20}_{D}: + 28.3 (c = 0.96, CHCl_3); ATR-FTIR (cm^{-1}): 3352, 2925,$ 2855, 2107, 1732, 1454, 1049, 696 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.52 – 6.93 (m, 100H), 6.18 (s, 1H, NH), 5.93 (d, J = 3.3 Hz, 1H, GlcNH₂-1), 5.26 – 5.17 (m, 2H), 5.04 – 4.95 (m, 2H), 4.95 – 4.88 (m, 2H), 4.88 – 4.16 (m, 42H), 4.12 – 3.44 (m, 38H), 3.43 – 3.31 (m, 4H), 3.24 – 3.18 (m, 2H), $3.09 (dd, J = 10.2, 3.3 Hz, 1H, GlcNH_2-2), 2.70 (dd, J = 14.3, 7.1 Hz, 12H, CH_2 of TEA), 2.28 -$ 2.14 (m, 4H, 2x O-CO-CH₂-CH₂), 2.00 (s, 3H, CH₃ of NHAc), 1.54 (s, 4H, 2x O-CO-CH₂-CH₂),

1.30 – 1.21 (m, 44H, CH₂ of lipid), 1.12 (t, J = 7.2 Hz, 18H, CH₃ of TEA), 0.87 (t, J = 6.9 Hz, 6H, CH₃ of lipid); ¹³C NMR (151 MHz, CDCl₃) δ 173.50, 173.13 (2xCO of lipid ester), 170.58 (CO of NHAc), 156.52 (CO of NHCbz), 139.96, 139.20, 139.07, 139.05, 139.04, 138.98, 138.92, 138.83, 138.76, 138.70, 138.63, 138.61, 138.48, 138.48, 138.43, 138.42, 138.41, 138.19, 138.10, 137.78, 137.01, 128.83, 128.72, 128.50, 128.48, 128.46, 128.40, 128.38, 128.32, 128.31, 128.30, 128.28, 128.22, 128.10, 128.03, 127.96, 127.95, 127.93, 127.92, 127.91, 127.86, 127.84, 126.92, 103.78, 102.72, 102.37, 100.89, 98.30, 96.12 (Glc-NH₂-1), 83.25, 82.09, 81.82, 81.80, 81.71, 81.09, 80.05, 79.69, 79.59, 79.11, 78.44, 78.32, 77.87, 77.70, 77.54, 77.37, 77.16, 76.95, 76.05, 75.78, 75.54, 75.31, 74.84, 74.81, 74.76, 74.61, 74.27, 74.11, 73.89, 73.55, 73.42, 73.01, 72.92, 72.78, 72.73, 72.53, 72.41, 72.32, 72.21, 71.85, 70.96, 70.78, 70.73, 70.47, 70.02, 69.58, 69.48, 68.65, 68.19, 67.50, 66.47, 65.83, 64.07, 64.03, 63.82, 63.79, 63.30, 62.96 (Glc-NH₂-2), 46.03, 34.43, 34.22, 32.06, 29.84, 29.81, 29.67, 29.50, 29.47, 29.30, 25.04, 25.01, 23.44, 22.83, 14.26 (CH₃ of lipid), 10.24 (CH₃ of TEA); ³¹P NMR (243 MHz, CDCl₃) δ -0.92 (phosphoethanolamine), -1.68 (lipid); ESI-MS: m/z [M-2H]²⁻ cald 1880.3713, obsd 1880.3393.

 $\begin{array}{l} 6-O-(2-Aminoethyl-phosphonato)-α-D-mannopyranosyl-(1\rightarrow 2)-α-D-mannopyranosyl-(1\rightarrow 6)-4-\\ O-\beta-D-galactopyranosyl-(1\rightarrow 6)-2-deoxy-2-acetamido-\beta-D-glucopyranosyl-α-D-\\ mannopyranosyl-(1\rightarrow 4)-2-amino-2-deoxy-α-D-glucopyranosyl-(1\rightarrow 6)-1-O-(1,2-dimyristoyl-sn-glyceryl-phosphonato)-D-myo-inositol (42) \end{array}$



Pseudoheptasaccharide **55** (9.6 mg, 2.4 μ mol) was dissolved in CHCl₃/MeOH/H₂O (4 mL; 9:7:2). HOAc (10 μ L) and Pd/C (10wt%, 12.9 mg, 12 μ mol) was added. Then hydrogen was bubbled through this solution for 20 min and the resulting mixture was stirred for 5 d under hydrogen atmosphere. Finally the solution was filtered through a syringe filter and solvents were evaporated. The residue was washed with CHCl₃ (6x5 mL) to yield GPI **42** (3.9 mg, 2.1 µmol, 85% yield) as white solid: $[\alpha]^{20}_{D=}$ + 60.4 (c = 0.39, CHCl₃/MeOH/H₂O-9:7:2); ATR-FTIR (cm⁻¹): 3408, 2921, 2852, 1627, 1456, 1399, 1030; ¹H NMR (600 MHz, DMSO-d₆, selected signals) δ 6.68 (s, 1H, NHAc), 5.32 (t, *J* = 4.4 Hz, 1H), 5.15 – 5.04 (m, 1H), 4.87 (s, 1H), 4.79 (s, 1H), 4.70 (s, 1H), 2.88 (s, 2H), 2.33 – 2.24 (m, 2H), 2.21 (s, 3H, Me of NHAc), 2.03 – 1.96 (m, 2H), 1.88 – 1.81 (m, 2H), 1.57 – 1.42 (m, 4H, 2x O-CO-CH₂-CH₂), 1.29 – 1.20 (m, 44H, CH₂ of lipids), 0.85 (t, *J* = 6.8 Hz, 6H, CH₃ of lipids); ³¹P NMR (243 MHz, DMSO-d₆) δ -0.51(phosphoethanolamine), -1.33 (lipid); ESI-MS: *m/z* [M+Na]⁺ cald 1912.8205, obsd 1912.8207.



Synthesis of mannoside **57**. Reagents and conditions: (a) NaH, BnBr, DMF, 0 °C, 94%; (b) 70% AcOH_(aq), 70 °C, 88%; (c) i. MeC(OEt)₃, CSA, MeCN; ii. 80% AcOH_(aq), 95%.

Allyl 4-O-benzyl-6-O-(tert-butyldiphenylsilyl)-2,3-O-isopropylidene-α-D-manno-pyranoside (57a)



To a solution of mannoside **1a** ^[26] (3.37g, 6.80 mmol) and benzyl bromide (4.02 mL, 33.8mmol) in anhydrous DMF (40 mL) was added sodium hydride (811 mg, 33.8 mmol) at 0°C. After 1 h at 0°C, methanol (5 mL) was added. The reaction mixture was diluted with diethyl ether (150 mL). The organic layer was washed with brine (3 x 75 mL), dried over Na₂SO₄, filtered and concentrated. The crude product was purified by flash column chromatography to yield mannoside **57a** (3.75 g, 6.40 mmol, 94% yield) as a yellow oil: $[\alpha]_D^{20} = +15.5$ (c = 0.80, CHCl₃); ATR-FTIR (selective bands, cm⁻¹): v 3071, 2931, 2857, 1428, 1112, 1077, 1022, 995, 738; ¹H NMR (400 MHz, CDCl₃) δ 7.80 – 7.61 (m, 4H), 7.47 – 7.40 (m, 2H), 7.39 – 7.31 (m, 4H), 7.28 – 7.11 (m, 5H), 5.89 (m, 1H CH₂=CH), 5.27 (dq, J = 17.2, 1.6 Hz, 1H, CH₂=CH), 5.19 (ddd, J = 10.4, 2.8, 1.2 Hz, 1H, CH₂=CH), 5.12 (s, 1H, Man-1), 4.88 (d, J = 11.4 Hz, 1H, CH₂ of Bn), 4.56 (d, J = 11.4 Hz, 1H, CH₂ of Bn), 4.39 – 4.31 (t, J = 6.4 Hz, 1H, Man-3), 4.27 – 4.15 (m, 2H, CH₂ of Allyl, Man-2), 4.01 (ddt, J = 12.8, 6.4, 1.2 Hz, 1H), 3.94 (dd, J = 11.0, 1.9 Hz, 1H, Man-6), 3.86 (dd, J = 11.0, 5.2 Hz, 1H, Man-6), 3.73 (ddd, J Hz, 1H), 3.94 (dd, J = 11.0, 1.9 Hz, 1H, Man-6), 3.86 (dd, J = 11.0, 5.2 Hz, 1H, Man-6), 3.73 (ddd, J

= 10.2, 5.2, 1.8 Hz, 1H, Man-5), 3.63 (dd, J = 10.2, 6.9 Hz, 1H, Man-4), 1.53 (s, 3H, Me), 1.39 (s, 3H, Me), 1.05 (s, 9H, C(CH₃)₃); ¹³C NMR (101 MHz, CDCl₃) δ 138.45, 135.99, 135.76, 133.88, 133.79 (CH₂=CH-CH₂), 133.47, 129.70, 129.68, 128.38, 127.96, 127.78, 127.70, 127.65, 117.95 (CH₂=CH-CH₂), 109.41 (Cqu. isopropylidene), 96.13 (Man-1), 79.16 (Man-3), 76.11 (Man-2), 75.89 (Man-4), 73.10 (CH₂ of Bn), 69.86 (Man-5), 67.67(CH₂=CH-CH₂), 63.46 (Man-4), 28.13(Me), 26.92(C(CH₃)₃), 26.56 (Me), 19.44(CMe₃); ESI-MS: m/z [M+Na]⁺ cald 611.2805, obsd 611.2809.

Allyl 4-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranoside (57b)



A solution of mannoside **57a** (96 mg, 0.16 mmol) in aqueous acetic acid (70%, 3 mL) was kept at 70°C for 90 min. The reaction mixture was then diluted with chloroform (40 mL), and washed with NHCO_{3(aq)} (3x 20 mL). The organic layers were dried over Na₂SO₄, filtered and concentrated. The residue was purified by flash column chromatography to yield diol **57b** (79 mg, 0.14 mmol, 88% yield) as a yellow oil that crystallized upon standing: $[\alpha]_D^{20} = +32.8$ (c =1.00, CHCl₃); ATR-FTIR (selective bands, cm⁻¹): v 3424, 2930, 2857, 1427, 1104, 1055, 1006, 738; ¹H NMR (400 MHz, CDCl₃) δ 7.76 – 7.54 (m, 4H), 7.47 – 6.71 (m, 11H), 5.88 – 5.69 (m, 1H, CH₂=CH-CH₂), 5.17 (ddd, J = 17.2, 3.0, 1.3 Hz, 1H, CH₂=CH-CH₂), 5.08 (dd, J = 10.4, 1.3 Hz, 1H, CH₂=CH-CH₂), 4.80 (d, J = 1.5 Hz, 1H,Man-1), 4.68 (d, J = 11.2 Hz, 1H, CH₂ of Bn), 4.55 (d, J = 11.2 Hz, 1H, CH₂ of Bn), 4.09 (ddt, J = 12.8, 5.0, 1.3 Hz, 1H, CH₂=CH-CH₂), 3.93 – 3.76 (m, 5H, CH₂=CH-CH₂, Man-2, Man-6), 3.72 – 3.52 (m, 2H), 2.28 (s, 2H, OH), 1.00 (s, 9H, *t*Bu); ¹³C NMR (101 MHz, CDCl₃) δ 138.32, 135.95, 135.75, 133.76, 133.71, 133.39, 129.75, 128.64, 128.02, 127.96, 127.80, 127.72, 117.67 (CH₂=CH-CH₂), 98.46 (Man-1), 76.13, 74.95 (CH₂ of Bn), 72.34, 72.02, 71.28, 67.85 (CH₂=CH-CH₂), 63.26 (Man-6), 26.96 (C(CH₃)₃), 19.44; (CMe₃); ESI-MS: m/z [M+Na]⁺ cald 571.2492, obsd 571.2510.

Allyl 2-O-acetyl-4-O-benzyl-6-O-(*tert*-butyldiphenylsilyl)-α-D-mannopyranoside (57)



To a solution of diol **57b** (1.00 g, 1.82 mmol) and triethyl orthoacetate (1.00 mL, 5.47 mmol) in acetonitrile (20 mL) was added camphorsulfonic acid (85.0 mg, 0.364 mmol). After 3 h, NEt₃ was added and the solvents were evaporated to dryness. The residue was then dissolved in 80% $AcOH_{(aq)}$ (20 mL). After overnight, the solvents were evaporated to dryness and the residue was purified by silica gel column chromatography to give mannoside **57** (1.02 g, 1.73 mmol, 95%) as a colorless oil: R_f (SiO₂, EtOAc/Hexane 1:4) = 0.18; $[\alpha]_D^{20} = +31.1$ (c = 1.00, CHCl₃); ATR-FTIR (selective bands, cm⁻¹): v 3475, 3071, 2931, 2858, 1746, 1473, 1455, 1428, 1372, 1238, 1137, 1112, 1077, 982, 926, 824, 741, 702; ¹H NMR (600 MHz, CDCl₃) δ 7.82 – 7.63 (m, 4H), 7.47 – 7.19 (m, 11H), 5.85 (m, 1H, vinyl), 5.24 (dd, J = 17.2, 1.4 Hz, 1H, =CH₂), 5.16 (dd, J = 10.4, 1.4 Hz, 1H, =CH₂), 5.12 (dd, J = 3.1, 1.3 Hz, 1H, Man-2), 4.88 (d, J = 1.3 Hz, 1H, Man-1), 4.85 (d, J = 11.1 Hz, 1H, -CH₂- of Bn), 4.68 (d, J = 11.1 Hz, 1H, -CH₂- of Bn), 4.20 (dd, J = 9.3, 3.1 Hz, 1H, Man-3), 4.12 (m, 1H, -CH₂- of allyl), 4.00 (dd, J = 11.3, 4.0 Hz, 1H, Man-6), 3.97 – 3.89 (m, 3H, Man-4, Man-6, -CH₂- of allyl), 3.68 (dd, J = 9.7, 2.4 Hz, 1H, Man-5), 2.14 (s, 3H, Ac), 1.09 (s, 9H, *t*Bu); ¹³C NMR (151 MHz, CDCl₃) δ 170.81 (ester), 138.33, 135.92, 135.52, 133.84, 133.51 (vinyl), 133.11, 129.61, 129.59, 128.43, 127.78, 127.74, 127.65, 127.51, 117.53 (=CH₂), 96.28 (Man-1), 75.84 (Man-4), 75.05 (-CH₂- of Bn), 72.86 (Man-2), 72.37 (Man-5), 70.28 (Man-3), 67.87 (-CH₂- of allyl), 62.82 (Man-6), 26.76 (Me of *t*Bu), 21.01 (Me of Ac), 19.38 (CMe₃); ESI-MS: m/z [M+Na]⁺ cald 613.2592, obsd 613.2598.

Allyl 2,3,4,6-tetra-O-benzyl- α -D-galactopyranosyl- $(1\rightarrow 6)$ -2,3,4-tri-O-benzyl- α -D-galactopyranosyl- $(1\rightarrow 3)$ -2-O-acetyl-4-O-benzyl-6-O-(*tert*-butyldiphenylsilyl)- α -D-mannopyranoside (59)



A mixture of digalatoside **58**^[9] (449 mg, 0.442 mmol) and mannoside **57** (174 mg, 0.295 mmol) was co-evaporated three times with toluene. This mixture was dissolved in toluene (6.3 mL) and thiophene (2.1 mL). Molecular sieves (4Å, 100 mg), DMF (204 μ L, 2.65 mmol), NIS (99 mg, 0.442 mmol) and TMSOTf (80 μ L, 0.061 mmol) were added at 0 °C. The reaction mixture was placed in an ultrasonic device (Elma Elmasonic P) with an ultrasonic frequency of 80 kHz and the temperature was controlled by a cooler (Huber TC100E). After 12 h at 0 °C, NEt₃ was added. The reaction mixture was filtered and concentrated. The crude product was purified by silica gel column chromatography to give trisaccharide **59** (0.380 g, 0.246 mmol, 83 % yield) as a colorless oil: R_f (SiO₂, EtOAc/Hexane 1:4) = 0.38; $[\alpha]_D^{20} = +52.4$ (c = 1.00, CHCl₃); ATR-FTIR (selective bands, cm⁻¹): v 3064, 3031, 2929, 1744, 1497, 1454, 1428, 1361, 1238, 1136, 1102, 1058, 991, 824, 736, 697; ¹H NMR (600 MHz, CDCl₃) δ 7.68 – 7.61 (m, 2H), 7.60 – 7.54 (m, 2H), 7.36 – 6.97 (m, 46H), 5.73 (m,

1H, vinyl), 5.12 (dd, J = 17.2, 1.3 Hz, 1H, =CH₂), 5.10 – 5.04 (m, 3H, Man-2, GalI-1, -CH₂-), 5.03 $(dd, J = 10.4, 1.3 Hz, 1H, =CH_2), 4.85 (d, J = 11.4 Hz, 1H, -CH_2-), 4.80 (d, J = 11.2 Hz, 1H, -CH_2-),$ 4.77 - 4.77 (m, 2H, Man-1, GalII-1), 4.73 (d, J = 7.6 Hz, 1H), 4.74 - 4.67 (m, 3H, -CH₂-*3), 4.65 $(d, J = 12.1 \text{ Hz}, 1\text{H}, -\text{CH}_2-), 4.61 (d, J = 10.7 \text{ Hz}, 1\text{H}, -\text{CH}_2-), 4.61 (d, J = 10.7 \text{ Hz}, 1\text{H}, -\text{CH}_2-), 4.55$ $(d, J = 11.8 \text{ Hz}, 1\text{H}, -\text{CH}_2), 4.53 - 4.42 \text{ (m, 2H, -CH}_2-*5), 4.35 \text{ (d, } J = 11.8 \text{ Hz}, 1\text{H}, -\text{CH}_2-), 4.08$ (dd, J = 9.5, 3.2 Hz, 1H, Man-3), 4.02 – 3.92 (m, 9H, Man-4, GalI-2, GalI-3, GalI-4, GalI-5, GalII-2, GalII-4, GalII-5, -CH₂- of allyl), 3.89 (dd, *J* = 10.1, 2.7 Hz, 1H, GalII-2), 3.85 (dd, *J* = 11.3, 4.0 Hz, 1H, Man-6), 3.82 (dd, J = 12.9, 6.2 Hz, 1H, -CH₂- of allyl), 3.75 (m, 1H, Man-6), 3.62 - 3.52 (m, 4H, Man-5, GalI-6*2, GalII-6), 3.49 (dd, J = 9.1, 5.5 Hz, 1H, GalII-6), 1.99 (s, 1H, Ac), 1.00 (s, 9H, *t*Bu); ¹³C NMR (151 MHz, CDCl₃) δ 170.36 (Ac), 139.00, 138.94, 138.87, 138.86, 138.82, 138.68, 138.58, 138.23, 135.98, 135.58, 133.93, 133.68 (vinyl), 133.22, 129.61, 129.58, 128.44, 128.42, 128.37, 128.36, 128.34, 128.33, 128.31, 128.29, 128.29, 128.27, 128.26, 128.25, 128.24, 128.24, 128.23, 128.21, 128.20, 128.18, 128.16, 128.15, 128.14, 128.08, 127.93, 127.84, 127.80, 127.79, 127.77, 127.73, 127.67, 127.62, 127.57, 127.54, 127.53, 127.49, 127.47, 127.38, 127.35, 127.31, 127.23, 127.18, 117.63 (=CH₂), 100.52 (GalI-1), 99.01 (GalII-1), 95.96 (Man-1), 79.12, 78.74 (Man-3), 78.57, 76.45, 76.02, 74.98, 74.93, 74.83, 74.76, 74.20, 73.55, 73.35, 73.32, 73.22, 72.69, 72.60, 72.58, 72.26, 69.81, 69.27, 68.51 (GalII-6), 67.94 (-CH₂- of allyl), 66.64 (GalI-6), 62.81 (Man-6), 26.85 (Me of tBu), 21.21 (Me of Ac), 19.42 (CMe₃); ESI-MS: m/z [M+Na]⁺ cald 1568.6967, obsd 1568.6922.

 $\begin{array}{l} 2\text{-}O\text{-}Acetyl\text{-}4\text{-}O\text{-}benzyl\text{-}3\text{-}O\text{-}(2,3,4,6\text{-}tetra\text{-}O\text{-}benzyl\text{-}\alpha\text{-}D\text{-}galactopyranosyl\text{-}(1\rightarrow6)\text{-}2,3,4\text{-}tri\text{-}O\text{-}benzyl\text{-}\alpha\text{-}D\text{-}galactopyranosyl\text{-}(1\rightarrow4)\text{-}2\text{-}azido\text{-}3,6\text{-}di\text{-}O\text{-}benzyl\text{-}2\text{-}deoxy\text{-}\alpha\text{-}D\text{-}glucopyranosyl\text{-}(1\rightarrow6)\text{-}1\text{-}O\text{-}allyl\text{-}2,3,4,5\text{-}tetra\text{-}O\text{-}benzyl\text{-}D\text{-}myo\text{-}inositol (61) \end{array}$



Through a solution of $[IrCOD(PPh_2Me)_2]PF_6$ (4.4 mg, 5.2 µmol) in THF (2 mL) was bubbled hydrogen for 10 min. After the color changed from red to colorless to light pale yellow, the hydrogen atmosphere was exchanged with argon. This solution was then added into a flask with trisaccharide **59** (0.161 g, 0.104 mmol). After 22 h at 25 °C, the solvent was removed and the residue was redissolved in acetone (1.8 mL). Water (0.2 mL), mercury(II) chloride (0.141 g, 0.521 mmol) and

mercury(II) oxide (2.3 mg, 10 μ mol) were added. After 30 min, the reaction mixture was diluted with DCM and washed with NHCO_{3(aq)}, dried over Na₂SO₄, filtered and concentrated. The residue was filtered through a pad of silica gel (eluent EtOAc/Hex 1:2), and the filtrate was evaporated to dryness to yield the crude lactol **60a** as a colorless oil: R_f (SiO₂, EtOAc/Hexane 1:4) = 0.17.

To a solution of the crude lactol **60a** in CH₂Cl₂ (1.5 mL) were added 2,2,2-trichloroacetonitrile (0.10 mL, 0.98 mmol) and DBU (15 μ L, 98 μ mol). After 40 min, the solvent was removed to give a brown oil that was purified by silica gel column chromatography to give imidate **60** (0.160 g, 0.097 mmol, 93% yield) as a colorless oil and an inseparable mixture of anomers: R_f (SiO₂, EtOAc/Hexane 1:4) = 0.40.

A mixture of imidate 60 (0.160 g, 0.097 mmol) and pseudodisaccharide 5 (76.6 mg, 0.081 mmol) was co-evaporated three times with toluene. To a solution of this mixture in diethyl ether (2 mL) were added molecular sieves (4Å, 40 mg) and TBSOTf (7.4 µL, 32 µmol) at 0 °C. After 1 h at 0 °C, NEt₃ was added. The reaction mixture was filtered and concentrated. The crude product was purified by silica gel column chromatography to give pseudopentasaccharide 61 (0.190 g, 0.078 mmol, 97% yield) as a white foam: R_f (SiO₂, EtOAc/Hexane 1:4) = 0.22; R_f (SiO₂, EtOAc/Hexane 1:3) = 0.49; $[\alpha]_{D}^{20} = +71.6$ (c = 1.00, CHCl₃); ATR-FTIR (selective bands, cm⁻¹): v 3064, 3031, 2929, 2859, 2106, 1741, 1497, 1454, 1360, 1238, 1136, 1101, 1054, 1028, 823, 736, 697; ¹H NMR (600 MHz. CDCl₃) δ 7.64 (d, J = 6.9 Hz, 2H), 7.55 (d, J = 6.8 Hz, 2H), 7.43 – 6.83 (m, 76H), 5.90 (m, 1H, =CH-), 5.66 (d, J = 3.8 Hz, 1H, GlcN-1), 5.39 (d, J = 1.6 Hz, 1H, Man-1), 5.30 (dd, J = 2.3, 1.6 Hz, 10.4, 1.4 Hz, 1H, =CH₂), 5.01 (d, J = 3.4 Hz, 1H, GalI-1), 4.99 (d, J = 11.5 Hz, 1H, -CH₂-), 4.92 -4.84 (m, 4H, -CH₂-*4), 4.83 (d, J = 3.6 Hz, 1H, GalII-1), 4.82 – 4.64 (m, 11H, -CH₂-*11), 4.63 – 4.49 (m, 7H, $-CH_2-*7$), 4.45 (d, J = 11.8 Hz, 1H, $-CH_2-$), 4.33 (d, J = 11.8 Hz, 1H, $-CH_2-$), 4.23 – 4.17 (m, 2H, Ino-6, Man-4), 4.15 – 4.08 (m, 4H, Ino-4, GalI-3, -CH₂-*2), 4.07 – 3.94 (m, 10H, -CH2- of ally1*2, Ino-2, Man-3, GalI-2, GalI-4, GalI-5, GalII-2, GalII-4, GalII-5), 3.92 – 3.87 (m, 4H, GlcN-3, GlcN-4, GlcN-5, GalII-3), 3.73 – 3.65 (m, 2H, Man-6, GalI-6), 3.60 – 3.55 (m, 2H, GalI-6, GalII-6), 3.50 (dd, J = 8.8, 5.4 Hz, 1H, GalII-6), 3.45 (br-d, J = 10.7 Hz, 1H, Man-6), 3.41 – 3.35 (m, 2H, Ino-5, Man-5), 3.34 – 3.30 (m, 2H, Ino-1, Ino-3), 3.17 – 3.13 (m, 2H, GlcN-2, GlcN-6), 3.05 (m, 1H, GlcN-6), 1.95 (s, 1H, Ac), 1.02 (s, 9H, tBu); 13 C NMR (151 MHz, CDCl₃) δ 169.85 (Ac), 139.39, 139.12, 138.90, 138.74, 138.61, 138.56, 138.50, 138.48, 138.24, 138.20, 138.06, 138.01, 137.98, 135.88, 135.44, 134.21 (vinyl), 133.93, 132.89, 129.43, 129.39, 128.45, 128.33, 128.30, 128.25, 128.19, 128.16, 128.15, 128.10, 128.05, 128.00, 127.98, 127.95, 127.88, 127.78, 127.76, 127.72, 127.70, 127.67, 127.64, 127.61, 127.55, 127.52, 127.47, 127.46, 127.44, 127.39, 127.32, 127.29, 127.25, 127.21, 127.16, 127.10, 127.01, 126.98, 126.94, 126.83, 116.83 (=CH₂), 100.75 (GalI-1), 99.22 (GalII-1), 97.98 (Man-1), 97.75 (GlcN-1), 81.90, 81.70, 81.01, 80.80, 80.22, 79.96, 79.07, 78.49, 76.20, 76.14, 75.74, 75.64, 74.99, 74.94, 74.74, 74.63, 74.54, 74.47, 74.25, 74.05, 73.98, 73.57, 73.41, 73.32, 73.29, 73.23, 72.97, 72.75, 72.69, 72.36, 72.03, 70.64 (-CH₂- of allyl), 69.71, 69.61, 69.21, 68.20 (GalII-6), 68.08 (GlcN-6), 66.36 (GalI-6), 63.49 (GlcN-2), 62.06 (Man-6), 26.79 (Me of *t*Bu), 20.89 (Me of Ac), 19.32 (CMe₃); ESI-MS: m/z [M+Na]⁺ cald 2458.0906, obsd 2458.0955; [M+2Na]²⁺ cald 1240.5400, obsd 1240.5447.

 $\begin{array}{l} 4-O\text{-Benzyl-}3-O\text{-}(2,3,4,6\text{-tetra-}O\text{-benzyl-}\alpha\text{-}D\text{-}galactopyranosyl-}(1\rightarrow 6)\text{-}2,3,4\text{-}tri\text{-}O\text{-}benzyl\text{-}\alpha\text{-}D\text{-}galactopyranosyl-}(1\rightarrow 4)\text{-}2\text{-}azido\text{-}3,6\text{-}di\text{-}O\text{-}benzyl\text{-}2\text{-}deoxy\text{-}\alpha\text{-}D\text{-}glucopyranosyl-}(1\rightarrow 6)\text{-}1\text{-}O\text{-}allyl\text{-}2,3,4,5\text{-}tetra\text{-}O\text{-}benzyl\text{-}D\text{-}myo\text{-}inositol (62a)} \end{array}$



To a solution of pseudopentasaccharide 61 (212 mg, 0.087 mmol) in THF (1 mL) was added NaOMe (1.0 M in MeOH, 1.0 mL, 1.0 mmol). The reaction mixture was kept at 50 °C for 1 h before neutralized with Amberlite IR-120. The reaction mixture was filtered and concentrated, and the crude material was purified by silica gel column chromatography to afford the deacetylated pentasaccharide 62a (183 mg, 0.076 mmol, 88% yield): R_f (SiO₂, EtOAc/Hexane 1:4) = 0.19; R_f (SiO₂, EtOAc/Hexane 1:3) = 0.46; $[\alpha]_D^{20} = +61.7$ (c = 1.00, CHCl₃); ATR-FTIR (selective bands, cm⁻¹): v 2929, 2105, 1497, 1454, 1358, 1101, 1047, 737, 698; ¹H NMR (600 MHz, CDCl₃) δ 7.74 (d, *J* = 6.9 Hz, 2H), 7.68 (d, J = 6.9 Hz, 2H), 7.51 – 7.05 (m, 75H), 6.92 (t, J = 7.4 Hz, 1H), 5.97 (m, 1H, =CH-), 5.70 (d, J = 3.7 Hz, 1H, GlcN-1), 5.42 (d, J = 10.9 Hz, 1H, -CH₂-), 5.33 (dd, J = 17.2, 1.2 Hz, 1H, $=CH_2$), 5.25 (dd, J = 10.4, 1.2 Hz, 1H, $=CH_2$), 5.19 (br, 1H, Man-1), 5.08 (d, J = 3.4 Hz, 1H, Gall-1), 5.01 (d, J = 11.6 Hz, 1H, -CH₂-), 5.00 (d, J = 11.2 Hz, 1H, -CH₂-), 4.96 (d, J = 10.5 Hz, 1H, - CH_{2} -), 4.92 - 4.73 (m, 12H, $-CH_{2}$ -*12), 4.72 - 4.59 (m, 9H, $-CH_{2}$ -*7, GalI-5, GalII-1), 4.52 (d, J =12.2 Hz, 1H, $-CH_2$ -), 4.49 (d, J = 11.5 Hz, 1H, $-CH_2$ -), 4.43 (br, 1H, Man-2), 4.34 (d, J = 12.2 Hz, 1H, -CH₂-), 4.31 (dd, J = 9.6, 9.4 Hz, 1H, Ino-6), 4.28 – 4.23 (m, 2H, -CH₂-, Man-4), 4.20 (dd, J =10.2, 2.6 Hz, 1H, Gall-3), 4.16 – 3.11 (m, 3H, -CH₂-, Ino-4, Gall-2), 4.08 – 3.92 (m, 8H, -CH₂- of allyl*2, Ino-2, Man-3, Man-6, GlcN-5, GalI-4, GalII-2), 3.85 (dd, J = 10.0, 9.3 Hz, 1H, GlcN-3), 3.82 - 3.72 (m, 4H, GlcN-4, GalI-6, GalII-3, GalII-5), 3.68 (br, 1H, GalII-4), 3.65 (br-d, J = 10.6Hz, 1H, Man-6), 3.51 (br-d, J = 9.6 Hz, 1H, Man-5), 3.48 - 3.36 (m, 6H, Ino-1, Ino-3, Ino-5, GlcN-6*2, GalII-6), 3.35 - 3.30 (m, 2H, GalI-6, GalII-6), 2.82 (dd, J = 10.0, 3.7 Hz, 1H, GlcN-2), 1.10 (s, 9H, *t*Bu); ¹³C NMR (151 MHz, CDCl₃) δ 139.68, 138.99, 138.86, 138.84, 138.78, 138.72, 138.63, 138.60, 138.47, 138.32, 138.29, 137.95, 137.88, 135.91, 135.72, 134.30 (=CH-), 133.95, 133.31, 129.50, 129.48, 128.49, 128.47, 128.44, 128.42, 128.38, 128.36, 128.34, 128.30, 128.29, 128.25, 128.22, 128.22, 128.20, 128.06, 128.03, 128.01, 127.99, 127.96, 127.94, 127.92, 127.80, 127.74, 127.72, 127.71, 127.69, 127.67, 127.63, 127.58, 127.56, 127.48, 127.47, 127.45, 127.43, 127.38, 127.10, 127.01, 126.77, 116.93 (=CH₂), 104.05 (Man-1), 99.86 (GalI-1), 98.62 (GalII-1), 97.47 (GlcN-1), 83.14, 81.98, 81.85, 81.45, 80.88, 79.70, 79.56, 78.80, 78.58, 77.16, 75.77, 75.65, 75.37, 75.25, 75.14, 75.08, 74.90, 74.75, 74.55, 74.51, 74.01, 73.51, 73.47, 73.33, 73.30, 73.22, 72.94, 72.91, 72.84, 72.75, 70.76 (-CH₂- of Allyl), 70.53 (Man-2), 70.16, 69.95 (GalI-5), 69.69, 69.28 (Ga-III-6), 68.59 (GlcN-6), 67.32 (GalI-6), 63.13 (Man-6), 63.09 (GlcN-2), 26.99 (Me of *t*Bu), 19.43 (CMe₃); ESI-MS: m/z [M+Na]⁺ cald 2416.0800, obsd 2416.0728; [M+2Na]²⁺ cald 1219.5346, obsd 1219.5324.

2,4-*O*-Di-benzyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl- α -D-galactopyranosyl-(1 \rightarrow 6)-2,3,4-tri-*O*-benzyl- α -D-galactopyranosyl)-6-*O*-(*tert*-butyldiphenylsilyl)- α -D-mannopyranosyl-(1 \rightarrow 4)-2-azido-3,6-di-*O*-benzyl-2-deoxy- α -D-glucopyranosyl-(1 \rightarrow 6)-1-*O*-allyl-2,3,4,5-tetra-*O*-benzyl-D-*myo*-inositol (62b)



To a solution of the alcohol **62a** (0.100 g, 0.042 mmol) in DMF (2 mL) at 0 °C were added sodium hydride (18 mg, 0.75 mmol) and BnBr (60 μ L, 0.50 mmol). After 1 h at 0 °C, the reaction mixture was quenched with water and extracted three times with diethyl ether. The combined organic layers were dried over Na₂SO₄, filtered and concentrated. The material was purified by silica gel column chromatography to give the fully protected glycan **62b** (95 mg, 0.038 mmol, 92% yield): R_f (SiO₂, EtOAc/Hexane 1:4) = 0.30; $[\alpha]_D^{20} = +67.9$ (c = 1.00, CHCl₃); ATR-FTIR (selective bands, cm⁻¹): v 3031, 2929, 2105, 1497, 1454, 1358, 1208, 1100, 1053, 1028, 735, 697; ¹H NMR (600 MHz, CDCl₃) δ 7.70 (d, J = 6.9 Hz, 2H), 7.65 (d, J = 6.8 Hz, 2H), 7.52 – 7.04 (m, 80H), 6.91 (t, J = 7.4 Hz, 1H), 6.01 (m, 1H, =CH-), 5.82 (d, J = 3.7 Hz, 1H, GlcN-1), 5.42 (br, 1H, -CH₂-), 5.36 (br, 1H, Man-1), 5.35 (dd, J = 17.0, 1.4 Hz, 1H, =CH₂), 5.26 (dd, J = 10.5, 1.4 Hz, 1H, =CH₂), 5.15 (d, J = 10.5 Hz, 1H, GalI-1), 5.09 (d, J = 11.4 Hz, 1H, -CH₂-), 4.82 – 4.64 (m, 13H, -CH₂-), 4.88 (d, J = 3.5 Hz, 1H, GalII-1), 4.85 (d, J = 11.4 Hz, 1H, -CH₂-), 4.48 (d, J = 12.1 Hz, 1H, -CH₂-), 4.43 – 4.41 (m, 3H, -CH₂-, Man-4, GalI-5), 4.82 –

4.64 (m, 2H, -CH₂-, Ino-6), 4.27 (d, J = 12.2 Hz, 1H, -CH₂-), 4.24 – 4.03 (m, 12H, -CH₂-*4, Ino-2, Ino-4, GlcN-5, Man-3, GalI-2, GalI-3, GalI-4, GalII-2), 4.00 - 3.97 (m, 2H, GlcN-3, Man-2), 3.94 -3.86 (m, 2H, GlcN-4, Man-6), 3.82 (br, 1H, GalII-4), 3.80 (dd, J = 9.9, 9.4 Hz, 1H, GalI-6), 3.76 (dd, J = 10.1, 2.5 Hz, 1H, GalII-3), 3.64 (br, 1H, GalI-6), 3.58 (br-d, J = 10.7 Hz, 1H, Man-6), 3.54 - 3.39 (m, 7H, Ino-1, Ino-3, Ino-5, Man-5, GalII-5, GalII-6*2), 3.33 - 3.27 (m, 2H, GlcN-2, GlcN-6), 3.20 (dd, J = 10.8, 2.4 Hz, 1H, GlcN-6), 1.01 (s, 9H, tBu); ¹³C NMR (151 MHz, CDCl₃) δ 139.71, 139.32, 139.05, 138.97, 138.85, 138.77, 138.60, 138.33, 138.28, 138.24, 138.14, 137.94, 135.92, 135.70, 134.32 (=CH-), 133.89, 133.21, 129.48, 129.42, 128.53, 128.50, 128.47, 128.43, 128.40, 128.32, 128.27, 128.23, 128.21, 128.14, 128.09, 128.05, 128.01, 127.92, 127.84, 127.80, 127.74, 127.67, 127.63, 127.58, 127.51, 127.45, 127.40, 127.31, 127.27, 127.21, 127.14, 126.96, 126.80, 126.71, 116.96 (=CH₂), 100.38 (GalI-1), 99.54 (ManI-1), 99.21 (GalII-1), 97.87 (GlcN-1), 81.93, 81.90, 81.29, 80.93, 79.71, 79.28 (GalII-3), 78.94, 78.67, 76.63, 76.25, 75.79, 75.08, 74.79, 74.76, 74.58, 74.09, 73.88, 73.83, 73.47, 73.23, 73.06, 72.85, 72.76, 72.61, 71.30, 70.77 (-CH₂- of Allyl), 69.87, 69.73, 69.52, 68.90 (GalII-6), 68.34 (GlcN-6), 66.39 (GalI-6), 63.26 (GlcN-2), 62.65 (ManI-6), 26.82 (Me of tBu), 19.26 (CMe₃); ESI-MS: m/z [M+Na]⁺ cald 2507.1300, obsd 2507.1307; [M+2Na]²⁺ cald 1264.5581, obsd 1264.5611.

 $2,4-\text{Di-}O-\text{benzyl-}3-O-(2,3,4,6-\text{tetra-}O-\text{benzyl-}\alpha-\text{D-}galactopyranosyl-(1\rightarrow 6)-2,3,4-\text{tri-}O-\text{benzyl-}\alpha-\text{D-}galactopyranosyl)-\alpha-\text{D-}mannopyranosyl-(1\rightarrow 4)-2-azido-3,6-di-O-\text{benzyl-}2-deoxy-\alpha-\text{D-}glucopyranosyl-(1\rightarrow 6)-1-O-allyl-2,3,4,5-\text{tetra-}O-\text{benzyl-}D-myo-inositol (62)$



To a flask containing the fully protected glycan **62b** (0.237 g, 0.095 mmol) was added HF-pyridine (0.25 mL, 9.62 mmol). After 48 h, the reaction mixture was quenched with NaHCO_{3(aq)}, and extracted with DCM for three times. The organic layers were dried over Na₂SO₄, filtered and concentrated. The material was purified by silica gel column chromatography to give alcohol **62** (0.203 g, 0.090 mmol, 95 % yield) as a white foam: R_f (SiO₂, EtOAc/Hexane 1:S4) = 0.11; R_f (SiO₂, EtOAc/Hexane 1:2) = 0.47; $[\alpha]_D^{20} = +74.6$ (c = 1.00, CHCl₃); ATR-FTIR (selective bands, cm⁻¹): v 3501, 3064, 3030, 2922, 2869, 2105, 1729, 1497, 1454, 1358, 1255, 1209, 1127, 1098, 1053, 1028, 913, 736, 697; ¹H NMR (600 MHz, CDCl₃) δ 7.35 – 6.94 (m, 75H, Ph), 5.88 (m, 1H, =CH-), 5.61 (d, J = 3.6 Hz, 1H, GlcN-1), 7.23 – 5.12 (m, 3H), 4.97 (d, J = 11.0 Hz, 1H, -CH₂-), 4.89 (d, J = 10.7 Hz, 1H, -

CH₂-), 4.84 - 4.69 (m, 9H), 4.59 - 4.19 (m, 18H), 4.16 - 4.05 (m, 5H), 3.99 - 3.83 (m, 11H), 3.71 - 3.66 (m, 7H), 3.36 - 3.24 (m, 9H), 3.15 (dd, J = 9.7, 3.6 Hz, 1H, 1H, GlcN-2), 3.08 (br, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 139.09, 138.80, 138.77, 138.69, 138.62, 138.60, 138.50, 138.43, 138.25, 138.01, 134.32, 128.53, 128.46, 128.35, 128.32, 128.30, 128.27, 128.22, 128.21, 128.20, 128.19, 128.07, 128.00, 127.90, 127.86, 127.75, 127.68, 127.64, 127.60, 127.57, 127.54, 127.53, 127.46, 127.41, 127.31, 127.28, 127.25, 127.20, 117.15, 99.32 (Man-1, GalI-1, GalII-1), 97.75 (GlcN-1), 81.97, 81.83, 81.32, 80.95, 80.33, 79.33, 78.83, 76.31, 75.81, 74.83, 74.78, 74.66, 74.52, 74.31, 74.11, 73.98, 73.81, 73.38, 73.36, 73.21, 72.86, 72.77, 72.63, 72.33, 71.41, 70.90, 70.29, 69.64, 68.74, 67.65, 66.73, 63.71 (GlcN-2); ESI-MS for C₁₃₈H₁₄₅N₃O₂₅: m/z [M+Na]⁺ cald 2267.0059, obsd 2267.0051; [M+K]⁺ cald 2282.9799, obsd 2282.9834.

2,3,4-Tri-*O*-benzyl-6-*O*-tri*iso*propylsilyl- α -D-mannopyranosyl- $(1\rightarrow 2)$ -3,4,6-tri-*O*-benzyl- α -D-mannopyranosyl- $(1\rightarrow 6)$ -2,4-di-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl- α -D-galactopyranosyl- $(1\rightarrow 6)$ -2,3,4-tri-*O*-benzyl- α -D-galactopyranosyl)- α -D-mannopyranosyl- $(1\rightarrow 4)$ -2-azido-3,6-di-*O*-benzyl-2-deoxy- α -D-glucopyranosyl- $(1\rightarrow 6)$ -1-*O*-allyl-2,3,4,5-tetra-*O*-benzyl-D-*myo*-inositol (63)



A mixture of imidate **4** (34 mg, 0.029 mmol) and pseudopentasaccharide **62** (50 mg, 0.022 mmol) was co-evaporated three times with toluene. The residue was then dissolved in Et₂O (0.75 mL). Molecular sieves (4Å, 30 mg) and TBSOTf (6.7 μ L, 0.029 mmol) were added at 0 °C. After 1 h at 0 °C, the reaction mixture was filtered and concentrated. The crude product was purified by silica gel column chromatography to give pseudoheptasaccharide **63** (51 mg, 0.016 mmol, 70% yield): R_f (SiO₂, EtOAc/Hexane 1:4) = 0.29; $[\alpha]_D^{20} = +50.2$ (c = 1.00, CHCl₃); ATR-FTIR (selective bands, cm⁻¹): v 3064, 3031, 2925, 2865, 2106, 1733, 1587, 1497, 1454, 1360, 1209, 1098, 1053, 1028, 913, 824, 736, 697; ¹H NMR (400 MHz, CDCl₃) δ 7.47 – 6.91 (m, 105H), 5.92 (m, 1H, vinyl), 5.72 (br, 1H), 5.29 – 5.24 (m, 2H), 5.18 – 5.16 (m, 2H), 5.03 – 3.13 (m, 89H), 1.03 (br, 21H, TIPS); ¹³C NMR (101 MHz, CDCl₃) δ 139.13, 138.85, 138.81, 138.75, 138.67, 138.58, 138.48, 138.44, 138.32, 138.23, 138.13, 138.08, 137.96, 134.24, 128.56, 128.39, 128.33, 128.27, 128.24, 128.20, 128.15,

128.10, 128.00, 127.91, 127.86, 127.78, 127.76, 127.73, 127.70, 127.67, 127.61, 127.58, 127.46, 127.40, 127.35, 127.22, 127.17, 127.09, 127.06, 126.98, 126.63, 116.95, 99.38, 99.25, 98.98, 98.36, 97.66, 81.90, 81.82, 81.16, 80.90, 80.33, 80.02, 79.70, 79.25, 79.07, 76.13, 76.03, 75.70, 75.41, 75.00, 74.88, 74.74, 74.58, 74.49, 74.41, 74.31, 73.99, 73.85, 73.65, 73.40, 73.27, 73.17, 73.04, 72.77, 72.60, 72.54, 72.46, 72.00, 71.84, 71.60, 71.42, 71.02, 70.73, 69.76, 69.47, 68.77, 68.66, 68.43, 66.42, 64.55, 63.39, 62.81, 18.07, 18.02, 12.02; ESI-MS: m/z [M+2Na]²⁺ cald 1656.2612, obsd 1656.2666.

2,3,4-Tri-*O*-benzyl-6-*O*-tri*iso*propylsilyl- α -D-mannopyranosyl- $(1\rightarrow 2)$ -3,4,6-tri-*O*-benzyl- α -D-mannopyranosyl- $(1\rightarrow 6)$ -2,4-di-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl- α -D-galactopyranosyl- $(1\rightarrow 6)$ -2,3,4-tri-*O*-benzyl- α -D-galactopyranosyl)- α -D-mannopyranosyl- $(1\rightarrow 4)$ -2-azido-3,6-di-*O*-benzyl-2-deoxy- α -D-glucopyranosyl- $(1\rightarrow 6)$ -2,3,4,5-tetra-*O*-benzyl-D-*myo*-inositol (64)



To a solution of [IrCOD(PPh₂Me)₂]PF₆ (2.0 mg, 2.4 µmol) in THF (1 mL) was bubbled hydrogen for 10 min. After the color changed from red to colorless to light pale yellow, the hydrogen atmosphere was exchanged with argon. This solution was then added into a flask with pseudoheptasaccharide **63** (51 mg, 0.016 mmol), and the reaction mixture was kept at 20 °C for 24 h before removal of the solvent. The residue was dissolved in acetone (0.9 mL). Water (0.1 mL), mercury(II) chloride (21 mg, 0.078 mmol) and mercury(II) oxide (2.0 mg, 9.2 µmol) were added. After 1 h, the reaction mixture was diluted with DCM and washed with NaHCO_{3(aq)}, dried over Na₂SO₄, filtered and concentrated. The crude product was purified by silica gel column chromatography to give alcohol **64** (36 mg, 0.011 mmol, 72 % yield) as a colorless oil: R_f (SiO₂, EtOAc/Hexane 1:3) = 0.35; $[\alpha]_D^{20}$ = +47.5 (*c* = 1.00, CHCl₃); ATR-FTIR (selective bands, cm⁻¹): v 3483, 3064, 3030, 2926, 2865, 2108, 1733, 1497, 1454, 1360, 1254, 1209, 1126, 1098, 1052, 1028, 912, 883, 736, 697; ¹H NMR (400 MHz, CDCl₃) δ 7.44 – 6.93 (m, 105H), 5.42 (br, 1H), 5.29 (br, 1H), 5.17 (br, 1H), 5.05 –3.19 (m, 88H), 1.03 (br, 21H); ¹³C NMR (101 MHz, CDCl₃) δ 139.07, 138.81, 138.71, 138.63, 138.59, 138.57, 138.53, 138.51, 138.46, 138.31, 138.10, 137.96, 137.59, 128.44, 128.40, 128.38, 128.34, 128.30, 128.29, 128.24, 128.22, 128.18, 128.16, 128.11, 128.09, 128.03, 127.99, 127.94, 127.93, 127.89, 127.88, 127.86, 127.82, 127.73, 127.71, 127.66, 127.61, 127.60, 127.53, 127.49, 127.42, 127.41, 127.37, 127.29, 127.24, 127.21, 127.18, 127.12, 127.07, 127.02, 126.72, 108.42, 99.27, 99.21, 98.36, 97.89, 94.34, 81.85, 81.18, 80.89, 80.63, 80.37, 79.71, 79.27, 78.97, 77.21, 77.15, 76.25, 76.13, 75.70, 75.24, 75.07, 75.01, 74.82, 74.72, 74.56, 74.38, 73.82, 73.71, 73.40, 73.36, 73.17, 72.91, 72.68, 72.56, 72.52, 72.00, 71.91, 71.45, 71.21, 70.47, 69.70, 69.55, 68.77, 68.66, 66.64, 66.39, 64.55, 64.29, 62.89, 18.07, 18.03, 12.01; ESI-MS: m/z $[M+2Na]^{2+}$ cald 1636.2455, obsd 1636.2441; $[M+Na+K]^{2+}$ cald 1644.2324, obsd 1644.2306; $[M+2K]^{2+}$ cald 1652.2192, obsd 1652.2228.

Triethylammonium2,3,4-tri-O-benzyl- α -D-mannopyranosyl- $(1\rightarrow 2)$ -3,4,6-tri-O-benzyl- α -D-mannopyranosyl- $(1\rightarrow 6)$ -2,4-di-O-benzyl-3-O-(2,3,4,6-tetra-O-benzyl- α -D-galactopyranosyl- $(1\rightarrow 6)$ -2,3,4-tri-O-benzyl- α -D-galactopyranosyl)- α -D-manno-pyranosyl- $(1\rightarrow 4)$ -2-azido-3,6-di-O-benzyl-2-deoxy- α -D-glucopyranosyl- $(1\rightarrow 6)$ -1-O-(1,2-dimyristoyl-sn-glyceryl-phosphonato)-2,3,4,5-tetra-O-benzyl-D-myo-inositol (65)



Pseudoheptasaccharide **64** (24 mg, 7.4 µmol) and H-phosphonate **43** (10.1 mg, 15 µmol) were coevaporated with anhydrous pyridine (3x2 mL) and the residue was placed under high vacuum for 30 min. The residue was dissolved in dry pyridine (2 mL) and PivCl (2.8 µL, 22 µmol) was added. The solution was stirred for 2 h before water (20 µL) and iodine (4.7 mg, 19 µmol) were added. The solution was stirred for 1 h before it was quenched with sat. Na₂S₂O_{3(aq)}, dried over Na₂SO₄ and filtered. The solution was concentrated and co-evaporated with toluene (3x2 mL). The residue was dissolved in CHCl₃/MeOH (10:1) and passed over a small pad of silica gel. The resulting solution was evaporated to dryness and the residue was dissolved in MeCN (2 mL). Water (1 drop) and Sc(OTf)₃ (11 mg, 22 µmol) were added and the solution was kept at 50 °C for 5 h, before it was quenched with TEA (10 µL) and concentrated. The residue was purified using flash column chromatography on TEA deactivated silica gel (CHCl₃/MeOH starting from 0% MeOH to 3%) to yield the lipidated glycan **65** (20 mg, 5.3 µmol, 72% yield) as yellow foam: R_f (SiO₂, CHCl₃/MeOH 10:1) = 0.65; [α]²⁰_D: + 46.5 (c = 1.00, CHCl₃); ATR-FTIR (cm⁻¹): 3345, 3089, 3063, 3031, 2924, 2854, 2107,

1738, 1497, 1454, 1094, 1048, 1028; ¹H NMR (600 MHz, CDCl₃) δ 12.31 (s, 1H; HNEt₃⁺), 7.48 – 6.91 (m, 105H), 5.26 - 5.21 (m, 2H), 5.05 - 4.94 (m, 3H), 4.93 - 4.82 (m, 5H), 4.80 - 4.52 (m, 21H), 4.50 – 4.19 (m, 22H), 4.16 – 4.00 (m, 10H), 3.97 – 3.61 (m, 18H), 3.56 – 3.24 (m, 13H), 3.20 (m, 1H), 3.01 (bs, 6H, CH₂ of TEA), 2.23 (dd, J = 14.0, 6.8 Hz, 4H, O-CO-CH₂- CH₂), 1.59 – 1.50 (m, 4H, O-CO-CH₂- CH₂), 1.36 - 1.17 (m, 49H, CH₂ of lipid and Me of TEA), 0.88 (t, J = 7.0 Hz, 6H, Me of lipid); ¹³C NMR (151 MHz, CDCl₃) δ 173.41, 173.08 (2xester), 139.29, 138.96, 138.93, 138.86, 138.81, 138.78, 138.76, 138.71, 138.63, 138.53, 138.46, 138.32, 138.22, 138.14, 138.09, 128.74, 128.56, 128.50, 128.46, 128.44, 128.42, 128.38, 128.36, 128.35, 128.32, 128.30, 128.28, 128.20, 128.16, 128.00, 127.92, 127.91, 127.86, 127.80, 127.75, 127.64, 127.54, 127.47, 127.39, 127.36, 127.32, 127.21, 99.62, 99.51, 99.44, 81.90, 81.06, 80.95, 80.03, 79.89, 79.78, 79.39, 79.18, 78.40, 76.68, 76.31, 76.27, 75.78, 75.24, 75.11, 74.92, 74.88, 74.84, 74.72, 74.64, 74.56, 74.42, 74.35, 73.98, 73.55, 73.43, 73.37, 73.19, 72.78, 72.66, 72.58, 72.56, 72.35, 72.28, 71.97, 71.95, 71.17, 69.91, 69.61, 68.95, 68.86, 68.66, 66.49, 65.76, 62.22, 45.81 (CH₂ of TEA), 34.36, 34.18, 32.07, 29.85, 29.83, 29.81, 29.66, 29.51, 29.48, 29.45, 29.29, 29.26, 25.01, 22.84, 14.27, 8.71 (Me of TEA); ³¹P NMR (243 MHz, CDCl₃) δ -1.53; ESI-MS: m/z [M-H+3Na]²⁺ cald 1856.3699 for C₂₂₀H₂₅₆N₃O₄₂P, obsd 1856.3713.

Bistriethylammonium 2,3,4-tri-*O*-benzyl-6-*O*-(2-(*N*-benzyloxycarbonyl)aminoethylphosphonato)- α -D-mannopyranosyl-(1 \rightarrow 2)-3,4,6-tri-*O*-benzyl- α -D-mannopyranosyl-(1 \rightarrow 6)-2,4-di-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl- α -D-galactopyranosyl-(1 \rightarrow 6)-2,3,4-tri-*O*-benzyl- α -D-galactopyranosyl)- α -D-mannopyranosyl-(1 \rightarrow 4)-2-azido-3,6-di-*O*-benzyl-2-deoxy- α -Dglucopyranosyl-(1 \rightarrow 6)-1-*O*-(1,2-dimyristoyl-sn-glyceryl-phosphonato)-2,3,4,5-tetra-*O*-benzyl-D-*myo*-inositol (66)



Lipidated pseudoheptasaccharide **65** (14 mg, 3.7 μ mol) and H-phosphonate **7** (6.1 mg, 17 μ mol) were co evaporated with anhydrous pyridine (3x2 mL) and placed under high vacuum for 30 min. The residue was dissolved in anhydrous pyridine (2 mL) and PivCl (3.5 μ L, 28 μ mol) was added. The solu-

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tion was stirred 2 h before water (10 µL) and iodine (5.2 mg, 21µmol) were added. The solution was stirred for 1 h before it was quenched with sat. $Na_2S_2O_{3(aq)}$, dried over sodium sulfate, filtered and evaporated to dryness. The residue was co evaporated with toluene (3x 2 mL) and purified using flash column chromatography on TEA deactivated silica gel (CHCl₃/MeOH starting from 0% MeOH to 5%). The fractions containing the desired product were pooled and washed with TEA/CO₂ buffer (3x15 mL). The organic layer was dried over sodium sulfate, filtered and evaporated to dryness to yield bisphosphate 66 (12 mg, 2.9 μ mol, 78% yield) as yellow oil: R_f (SiO₂, CHCl₃/MeOH 10:1) = $0.50; [\alpha]_{D}^{20}$: + 42.6 (c = 1.20, CHCl₃); ATR-FTIR (cm⁻¹): 3403, 2925, 2855, 2108, 1735, 1454, 1215, 1093, 1044, 1028; ¹H NMR (600 MHz, CDCl₃) δ 11.51 (s, 2H, **H**NEt₃⁺), 7.38 (d, J = 7.5 Hz, 2H), 7.35 (d, J = 7.5 Hz, 2H), 7.33 – 7.04 (m, 102H), 7.03 – 6.94 (m, 4H), 6.59 (s, 1H, NH), 5.89 (d, J = 2.9 Hz, 1H), 5.39 - 5.28 (m, 2H), 5.24 (dt, J = 8.7, 5.6 Hz, 1H, CH of glycerol), 5.09 - 4.80 (m, 2H)11H), 4.80 - 4.64 (m, 8H), 4.64 - 4.19 (m, 27H), 4.18 - 3.59 (m, 36H), 3.54 (d, J = 10.5 Hz, 2H), 3.52 – 3.45 (m, 3H), 3.45 – 3.24 (m, 9H), 3.19 (d, J = 8.3 Hz, 1H), 3.00 (d, J = 6.8 Hz, 12H, CH₂ of TEA), 2.26 – 2.19 (m, 4H, O-CO-CH₂-CH₂), 1.57 – 1.49 (m, 4H, O-CO-CH₂-CH₂), 1.36 – 1.19 (m, 58H, CH₂ of lipid and Me of TEA), 0.87 (t, J = 6.8 Hz, 6H, Me of lipids); ¹³C NMR (151 MHz, CDCl₃) § 173.47, 173.10 (2xester), 156.69, 139.87, 139.32, 139.04, 138.97, 138.90, 138.83, 138.78, 138.69, 138.63, 138.59, 138.53, 138.49, 138.44, 138.32, 138.11, 137.17, 128.65, 128.48, 128.43, 128.36, 128.30, 128.18, 128.15, 128.10, 128.02, 127.96, 127.90, 127.83, 127.77, 127.70, 127.60, 127.51, 127.46, 127.43, 127.36, 127.28, 127.20, 127.04, 99.39, 99.33, 99.30, 98.90, 96.88, 81.85, 81.49, 81.16, 80.43, 80.00, 79.39, 79.17, 77.91, 76.28, 75.94, 75.68, 75.11, 74.93, 74.87, 74.78, 74.70, 74.54, 74.21, 73.96, 73.55, 73.37, 73.37, 73.33, 72.99, 72.71, 72.66, 72.65, 72.60, 72.46, 72.27, 72.27, 72.13, 71.80, 71.18, 70.72 (CH of glycerol), 70.49, 69.93, 69.57, 69.49, 68.84, 66.56, 66.46, 66.36, 64.53, 63.96, 63.12, 62.87, 61.86, 45.87 (CH₂ of TEA), 42.51, 34.40, 34.20, 32.06, 29.83, 29.80, 29.66, 29.50, 29.46, 29.29, 25.03, 25.00, 22.82, 14.26, 8.67 (Me of TEA); ³¹P NMR $(243 \text{ MHz}, \text{CDCl}_3) \delta 0.53, -2.07; \text{ESI-MS: } \text{m/z} [\text{M}-2\text{H}+4\text{Na}]^{2+} \text{ cald } 1995.8835 \text{ for } \text{C}_{230}\text{H}_{268}\text{N}_4\text{O}_{47}\text{P}_2,$ obsd 1995.8777.

6-*O*-(2-Aminoethyl-phosphonato)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→6)-3-*O*-(α-D-galactopyranosyl-(1→6)-α-D-galactopyranosyl)-α-D-mannopyranosyl-(1→4)-2-amino-2-deoxy-α-D-glucopyranosyl-(1→6)-1-*O*-(1,2-dimyristoyl-sn-glyceryl-phosphonato)-D-*myo*inositol (56)



Bisphosphate **66** (12 mg, 2.9 μ mol) was dissolved in CHCl₃ (5 mL) and Amberlite IR120 H (50 mg) was added. The slurry was stirred for 30 min, before it was filtered and evaporated to dryness. The residue was dissolved in CHCl₃/MeOH/H₂O (9:7:2; 5 mL) and Pd/C (10wt%, 31 mg, 29 μ mol) and acetic acid (2 drops) were added. Hydrogen was bubbled through this solution for 20 min and the reaction mixture was stirred for 4 d under a hydrogen atmosphere. The reaction mixture was filtered through a syringe filter and evaporated to dryness. The residue was washed with CHCl₃ (6x5 mL) to yield the GPI **56** (4.6 mg, 2.5 μ mol, 85% yield) as a white solid. Spectral data was in agreement with previously reported data.^[10]

Tristriethylammonium(2,3,4-tri-O-benzyl-6-O-(2-(N-benzyloxycarbonyl)aminoethyl-
phosphonato)- α -D-mannopyranosyl- $(1\rightarrow 2)$ -3,4,6-tri-O-benzyl- α -D-mannopyranosyl- $(1\rightarrow 6)$ -4-
O-(3,4,6-tri-O-benzyl-2-deoxy-2-acetamido- β -D-galactopyranosyl)-3-O-benzyl-2-O-(2-(N-
benzyloxycarbonyl)aminoethyl-phosphonato)- α -D-mannopyranosyl- $(1\rightarrow 4)$ -2-azido-3,6-di-O-
benzyl-2-deoxy- α -D-glucopyranosyl- $(1\rightarrow 6)$ -2,3,4,5-tetra-O-benzyl-1-O-(1,2-di-O-octadecanoyl-
sn-glycerylphosphonato)-D-myo-inositol (67)



Lipidated pseudohexasaccharide **22** (17 mg, 4.7 µmol) and H-phosphonate **7** (8.4 mg, 23 µmol) were evaporated with anhydrous pyridine (3 x 2 mL) and placed under high vacuum for 30 min. The residue was dissolved in anhydrous pyridine (2 mL) and PivCl (3.2 µL, 26 µmol) was added. The reaction mixture was stirred for 2 h at room temperature before water (50 µL) and iodine (7.1 mg, 28 µmol) were added. The reaction mixture was stirred for 18 h before it was quenched with sat. sodium thiosulfate solution and evaporated to dryness. The residue was purified using flash column chromatography (CHCl₃/MeOH from 95:5 -> 90:10). The fractions containing the desired product were pooled and washed with TEA/CO₂-Buffer (3 x 15mL), dried over Na₂SO₄ and concentrated to yield trisphosphorylated pseudohexasaccharide **67** (16 mg, 4.0 µmol, 86% yield) as yellow oil: R_f (SiO₂, CHCl₃/MeOH 90:10) = 0.20; $[\alpha]^{20}_{D}$: + 22.8 (c = 1.60, CHCl₃); ATR-FTIR (cm⁻¹): 3431, 2925, 2854, 2109, 1740, 1455, 1222, 1053; ¹H NMR (400 MHz, CDCl₃) δ 11.42 (s, 3H), 7.55 - 6.95 (m, 90H), 6.33 (s, 1H), 6.24 (s, 1H), 5.65 (s, 1H), 5.17 (s, 1H), 5.10 - 3.41 (m, 85H), 3.31 - 3.10 (m, 4H), 2.94 (q, J = 7.2 Hz, 18H, CH₂ of TEA), 2.22 - 1.90 (m, 7H, NHAc and 2x CH₂ next to fatty acid ester), 1.56 - 1.38 (m, 4H), 1.34 - 1.09 (m, 83H), 0.87 (t, J = 6.9 Hz, 6H, Me of lipids); ¹³C NMR (151 MHz, CDCl₃) δ 173.38, 173.03 (2x fatty acid ester), 171.06 (amide), 156.61 (Cbz),

139.67, 139.25, 139.13, 139.03, 139.00, 138.91, 138.87, 138.77, 138.66, 138.62, 138.40, 138.04, 137.19, 137.09, 128.51, 128.47, 128.39, 128.36, 128.34, 128.29, 128.26, 128.24, 128.18, 128.14, 128.06, 128.03, 128.00, 127.93, 127.89, 127.83, 127.68, 127.61, 127.60, 127.58, 127.44, 127.38, 127.28, 127.17, 127.13, 127.06, 82.01, 80.88, 75.63, 74.99, 74.89, 73.51, 73.03, 72.71, 72.42, 72.31, 70.76, 70.68, 70.48, 69.86, 68.30, 66.45, 66.25, 65.56, 64.57, 64.13, 62.63, 61.86, 45.80 (CH₂ of TEA), 42.32, 42.04, 34.28, 34.12, 32.06, 29.86, 29.83, 29.81, 29.80, 29.68, 29.67, 29.50, 29.47, 29.28, 29.24, 24.96, 22.82, 14.25, 8.64 (Me of TEA); ³¹P NMR (162 MHz, CDCl₃) δ -0.77, -2.13; ESI-MS for C₂₀₉H₂₅₉N₆O₄₇P₃: m/z [M-3H]³⁻ cald 1232.2374, obsd 1232.2412.

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