CHEMBIOCHEM

Supporting Information

Defining the Interaction of Human Soluble Lectin ZG16p and Mycobacterial Phosphatidylinositol Mannosides

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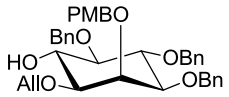
Synthetic procedures

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 CH_2Cl_2), tetrahydrofuran (THF), methanol (MeOH) *N*,*N*-dimethylformamide (DMF) and toluene were passed through activated neutral molecular sieves column prior to use. Pyridine was distilled over CaH_2 prior to use. Analytical thin layer chromatography (TLC) was performed on Merck silica gel 60 F_{254} plates (0.25 mm). 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)/CO_2 buffer was prepared by filling TEA (7 mL) in a measuring cylinder and adding water until the total volume reached 500mL. The solution was transferred to a flask and CO_2 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, ^{13}C and ^{31}P NMR spectra were recorded on a *Varian* MR-400 (400 MHz) and on a *Varian* PremiumCOMPACT 600 (600 MHz) spectrometer in $CDCl_3$ and D_2O with chemical shifts referenced to internal standards $CHCl_3$ (7.26 ppm ^1H, 77.1 ppm ^{13}C) and D_2O (4.79 ppm ^1H) 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-^{13}C HSQC, and ^1H-^{13}C 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 an Agilent 6210 ESI-TOF spectrometer. Infrared (IR) spectra were recorded as thin films on a Perkin 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.

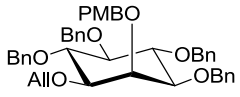
1-*O*-Allyl-2-*O*-*p*-methoxybenzyl-3,4,5-tri-*O*-benzyl-D-*myo*-inositol (4a)



Diol **3**[1](91 mg, 185 µmol, 1 equiv) and TBAI (69 mg, 185 µmol, 1 equiv) were dissolved in DMF (2 mL). The solution was cooled down to -20°C using ice/NaCl and NaH (22 mg, 930 µmol, 5 equiv) was added. The slurry was stirred for 5 min before PMBCl (25 µL, 190 µmol, 1 equiv) was added. The reaction mixture was stirred for 3 h at -20 °C before it was quenched with MeOH (200 µL). Water (7 mL) was added and the water phase was extracted with Et_2O (50 mL). The ether layer was washed with sat. $NaHCO_3$ solution (2 x 20mL), dried over Na_2SO_4 and evaporated to dryness. The residue was purified using column chromatography (*n*-hexane/ethyl acetate 3:1) to yield **4a** as yellow oil (46 mg, 75 µmol, 41%; 38 mg of starting material were recovered). The spectroscopic data was in agreement with the literature[2].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.13 (m, 17H), 6.75 (d, *J* = 8.4 Hz, 2H), 5.81 (ddd, *J* = 22.5, 10.7, 5.5 Hz, 1H, CH_2=C**H**-CH_2), 5.19 (d, *J* = 17.2 Hz, 1H, C**H**$_2$=CH-CH_2), 5.10 (d, *J* = 10.4 Hz, 1H, C**H**$_2$=CH-CH_2), 4.88 – 4.49 (m, 8H), 4.07 – 3.84 (m, 5H), 3.71 (s, 3H, OC**H**$_3$), 3.29 (t, *J* = 9.0 Hz, 2H), 3.01 (dd, *J* = 9.8, 1.6 Hz, 1H), 2.41 (bs, 1H, O**H**); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.16, 139.03, 138.96, 138.53, 134.67, 131.04, 129.54, 128.50, 128.42, 128.18, 127.94, 127.73, 127.67, 127.63, 117.42, 113.68, 83.58, 81.55, 81.28, 79.98, 77.48, 77.16, 76.84, 75.93, 75.42, 73.72, 72.96, 72.92, 72.88, 71.20, 55.38.

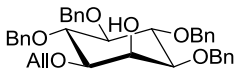
1-*O*-Allyl-2-*O*-*p*-methoxybenzyl-3,4,5,6-tetra-*O*-benzyl-D-*myo*-inositol (4b)



Inositol **4a**[2] (46 mg, 75 µmol, 1 equiv) was dissolved in DMF (2 mL). The solution was cooled down to 0°C and NaH (9 mg, 377 µmol, 5 equiv) was added. Afterwards BnBr (18 µL, 151 µmol, 2 equiv) was added and the reaction was stirred at 0°C for 3h. The reaction mixture was quenched with MeOH (200 µL) and water (10 mL) was added. The water phase was extracted with Et_2O (40 mL). The ether layer was washed with sat. $NaHCO_3$ solution (2 x 20 mL), dried over Na_2SO_4 and evaporated to dryness. The residue was purified using column chromatography (*n*-hexane/ethyl acetate 8:1) to yield **4b** as colorless solid (47.5 mg, 68 µmol, 90%).

$[\alpha]^{20}_D$: + 4.7 (*c* = 1.00, $CHCl_3$); FT-IR (neat) ν^{-1}: 3033, 2891, 1610, 1510, 1454, 1068 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.21 (m, 27H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.14 – 5.70 (m, 1H, CH_2=C**H**-CH_2), 5.30 (d, *J* = 17.1 Hz, 1H, C**H**$_2$=CH-CH_2), 5.17 (d, *J* = 10.9 Hz, 1H, C**H**$_2$=CH-CH_2), 4.93 – 4.85 (m, 4H), 4.84 – 4.75 (m, 4H), 4.62 (q, *J* = 11.6 Hz, 1H), 4.13 – 3.94 (m, 5H), 3.80 (s, 3H, OC**H**$_3$), 3.45 (t, *J* = 9.2 Hz, 1H), 3.34 (d, *J* = 10.1 Hz, 1H), 3.24 (d, *J* = 9.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.13, 139.04, 138.61, 135.08, 131.20, 129.57, 128.46, 128.42, 128.26, 128.20, 127.87, 127.64, 127.55, 116.73, 113.66, 83.81, 81.82, 81.07, 80.90, 75.97, 73.76, 72.86, 71.76, 55.39; *m/z* (ESI) Found: $[M+Na]^+$, 723.3303 $C_{38}H_{42}O_7$ requires $[M+Na]^+$, 723.3298.

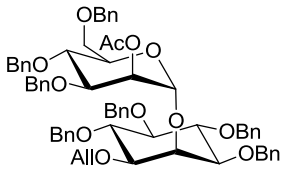
1-*O*-Allyl-3,4,5,6-tetra-*O*-benzyl-D-*myo*-inositol (4)



Fully protected inositol **4b** (38.8 mg, 55 µmol, 1 equiv) was dissolved in chloroform/TFA (1 mL, 9:1) and stirred for 30 min. The reaction mixture was diluted with toluene (3 mL) and solvents were evaporated. The residue was purified using column chromatography (*n*-hexane/ethyl acetate 4:1) to yield **4** as colorless oil (30 mg, 52 µmol, 93%). The spectroscopic data was in agreement with the literature[1].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.16 (m, 20H), 5.96 (ddd, *J* = 22.8, 10.9, 5.7 Hz, 1H, CH_2=C**H**-CH_2), 5.31 (dd, *J* = 17.2, 1.4 Hz, 1H, C**H**$_2$=CH-CH_2), 5.21 (d, *J* = 10.4 Hz, 1H, C**H**$_2$=CH-CH_2), 4.99 – 4.80 (m, 6H), 4.75 (s, 2H), 4.33 – 4.13 (m, 3H), 3.99 (dt, *J* = 15.2, 9.5 Hz, 2H), 3.53 – 3.38 (m, 2H), 3.32 (dd, *J* = 9.6, 2.6 Hz, 1H), 2.50 (bs, 1H, O**H**); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.86, 138.84, 138.83, 138.08, 134.80, 128.59, 128.47, 128.20, 128.14, 127.99, 127.95, 127.72, 127.70, 127.66, 117.57, 114.07, 83.23, 81.32, 81.30, 80.02, 79.73, 76.10, 76.08, 76.05, 72.92, 72.01, 67.81.

2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-1-*O*-allyl-3,4,5,6-tetra-*O*-benzyl-D-*myo*-inositol (6)

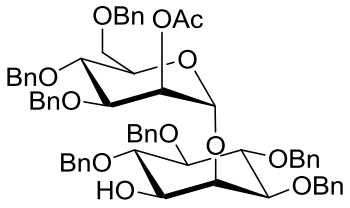


myo-Inositol **4** (30 mg, 52 µmol, 1.0 equiv) and phosphate **5**[3] (50.6 mg, 67 µmol, 1.3 equiv) were co evaporated with toluene (3 x 2 mL) and placed under HV for 30 min. The residue was dissolved in dry toluene (3 mL) and powdered MS4Å (100 mg) was added. The slurry was stirred at r.t. for 15 min before it was cooled down to -40°C. TMSOTf (12.1 µL, 67 µmol, 1.3 equiv) was added and the reaction was stirred at -40°C for 2 h. The reaction was quenched with TEA (100 µL) and filtered through a pad of Celite®. Solvents were removed *in vacuo* and the residue was purified using column chromatography (*n*-hexane/ethyl acetate 6:1) to yield **6** as colorless oil (46 mg, 44 µmol, 84%).

$[\alpha]^{20}_{D}$: + 26.3 (*c* = 1.00, $CHCl_3$); FT-IR (neat) ν^{-1}: 3031, 2921, 2864, 1746, 1497, 1454, 1070, 1052 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.20 (m, 33H), 7.17 – 7.12 (m, 2H), 5.89 (ddt, *J* = 17.2, 10.5, 5.2 Hz, 1H, CH_2=C**H**-CH_2), 5.51 (t, *J* = 2.1 Hz, 1H, Man-2), 5.33 – 5.23 (m, 2H, Man-1, C**H**$_2$=CH-CH_2), 5.15 (dd, *J* = 10.5, 1.6 Hz, 1H,

C**H**$_2$=CH-CH$_2$), 4.95 – 4.70 (m, 9H), 4.69 – 4.57 (m, 3H), 4.43 (d, *J* = 10.8 Hz, 1H), 4.37 – 4.29 (m, 2H), 4.23 – 4.17 (m, 1H), 4.15 (dt, *J* = 5.1, 1.5 Hz, 2H), 4.00 – 3.95 (m, 2H), 3.92 – 3.80 (m, 2H), 3.53 – 3.41 (m, 2H), 3.35 – 3.26 (m, 3H), 2.17 (s, 3H, C**H**$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.25 (CH$_3$**C**O), 138.83, 138.81, 138.77, 138.74, 138.29, 138.09, 134.60, 128.55, 128.51, 128.48, 128.45, 128.44, 128.33, 128.19, 128.09, 128.06, 128.03, 127.85, 127.73, 127.64, 127.60, 127.50, 127.33, 116.74, 110.12, 98.97 (Man-1, $J_{C,H}$ = 175.0Hz), 83.48, 81.37, 81.24, 80.63, 79.04, 77.82, 76.25, 75.97, 75.87, 75.14, 74.31, 73.54, 72.74, 72.63, 71.96, 71.75, 71.41, 68.89 (Man-2), 68.54, 21.31 (**C**H$_3$CO); *m/z* (ESI) Found: $[M+Na]^+$, 1077.4781 $C_{66}H_{70}O_{12}$ requires $[M+Na]^+$, 1077.4765.

2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,5,6-tetra-*O*-benzyl-D-*myo*-inositol (8a)

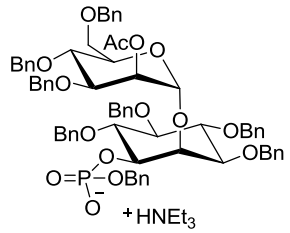


(1,5-Cyclooctadiene)bis(methyldiphenyl-phosphine)iridium(I) PF_6 (3 mg, 3.6 µmol, 0.1 equiv) was dissolved in dry THF (5 mL) and H_2 was bubbled through thesolution for 30 min (color change from red to slight yellow). Afterwards dry N_2 was bubbled through this solution for 15 min to remove dissolved H_2. This solution was then added to a solution of pseudodisaccharide **6** (42 mg, 40 µmol, 1 equiv) in dry THF (2 mL). The reaction mixture was stirred for 12 h before 1 M HCl (1 mL) was added to cleave the corresponding enol ether. The solution was stirred for 18 h before it was diluted with Et_2O (50 mL). The organic layer was washed with sat. $NaHCO_3$ solution (3 x 20 mL), dried over Na_2SO_4 and solvents were removed *in vacuo*. The residue was purified using

column chromatography (*n*-hexane/ethyl acetate 3:1) to yield **8a** as colorless oil (37 mg, 36 µmol, 92%).

$[\alpha]^{20}_{D}$: + 18.9 (*c* = 1.00, $CHCl_3$); FT-IR (neat) ν^{-1}: 3483, 2925, 2865, 1747, 1454, 1071 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.01 (m, 35H), 5.31 (s, 1H, Man-2), 5.20 (s, 1H, Man-1), 4.95 – 4.80 (m, 3H), 4.79 – 4.59 (m, 6H), 4.51 (d, *J* = 10.4 Hz, 3H), 4.35 (d, *J* = 10.7 Hz, 1H), 4.28 – 4.18 (m, 2H), 4.14 – 4.05 (m, 1H), 3.90 – 3.84 (m, 2H), 3.76 (t, *J* = 9.5 Hz, 1H), 3.65 (t, *J* = 9.5 Hz, 1H), 3.48 – 3.34 (m, 3H), 3.29 (d, *J* = 9.8 Hz, 1H), 3.22 (d, *J* = 10.8 Hz, 1H), 2.18 (bs, 1H, O**H**), 2.06 (s, 3H, C**H**$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.37 (CH_3**C**O), 138.78, 138.66, 138.50, 138.34, 138.30, 138.17, 138.12, 128.88, 128.58, 128.56, 128.47, 128.45, 128.34, 128.32, 128.21, 128.14, 128.09, 128.07, 128.01, 127.87, 127.66, 127.63, 127.60, 127.53, 127.36, 99.21 (Man-1), 83.79, 81.86, 81.24, 79.09, 77.87, 75.96, 75.89, 75.63, 75.21, 74.37, 74.22, 73.54, 72.30, 72.02, 71.57, 68.92, 68.57, 21.32 (**C**H_3CO); *m/z* (ESI) Found: $[M+Na]^+$, 1037.4424 $C_{66}H_{70}O_{12}$ requires $[M+Na]^+$, 1037.4452.

Triethylammonium 2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-1-*O*-monobenzylphospho-3,4,5,6-tetra-*O*-benzyl-D-*myo*-inositol (8)



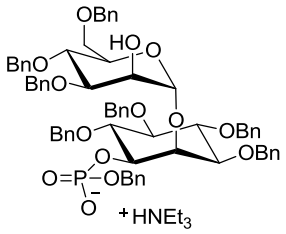
Alcohol **8a** (25 mg, 25 µmol, 1 equiv) and sodium benzyl phosphonate **7**[4] (10.5 mg, 54 µmol, 2.2 equiv) were co evaporated with dry pyridine (3 x 2mL) and placed under HV for 30 min. The residue was dissolved in dry pyridine (4 mL) and PivCl (10.6 µL, 86 µmol, 3.5 equiv) was added. The reaction mixture was stirred for 2 h before water (10

µL) and iodine (14.4 mg, 57 µmol, 2.3 equiv) were added. The solution was stirred for 18 h before it was quenched with sat. $Na_2S_2O_3$ solution (approx. 3 drops), dried with Na_2SO_4 and filtered. Solvents were removed *in vacuo* and the residue was co evaporated with toluene (3 x 2 mL). The residue was purified using column chromatography ($CHCl_3$/MeOH 95:5 to 90:10; SiO_2 was deactivated with 1% TEA in $CHCl_3$) to yield colorless oil. The residue was dissolved in $CHCl_3$ (30 mL), washed with TEA/CO_2 buffer (3 x 10 mL), dried over Na_2SO_4 and evaporated to dryness to yield **8** as colorless oil (25 mg, 19 µmol, 79%).

$[\alpha]^{20}_D$: + 32.1 (*c* = 1.00, $CHCl_3$); FT-IR (neat) ν^{-1}: 3032, 2926, 1746, 1454, 1236, 1051 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.47 (s, 1H, **H**N(CH_2CH_3)$_3$), 7.42 (d, *J* = 7.3 Hz, 2H), 7.36 (d, *J* = 7.3 Hz, 2H), 7.30 – 7.13 (m, 36H), 5.57 – 5.56 (m, 1H, Man-2), 5.55 (s, 1H, Man-1), 5.06 (d, *J* = 11.2 Hz, 1H), 4.97 (dd, *J* = 12.3, 6.5 Hz, 1H), 4.93 (dd, *J* = 12.4, 6.5 Hz, 1H), 4.90 – 4.76 (m, 8H), 4.69 (d, *J* = 11.9 Hz, 1H), 4.58 – 4.53 (m, 2H), 4.46 (dd, *J* = 22.9, 11.5 Hz, 2H), 4.26 (t, *J* = 8.6 Hz, 1H), 4.22 (d, *J* = 12.0 Hz, 1H), 4.17 (d, *J* = 9.5 Hz, 1H), 3.99 – 3.91 (m, 3H), 3.85 (t, *J* = 9.6 Hz, 1H), 3.49 (t, *J* = 9.2 Hz, 1H), 3.45 – 3.38 (m, 2H), 3.13 (d, *J* = 10.6 Hz, 1H), 2.89 – 2.83 (m, 6H, HN(C**H**$_2$CH$_3$)$_3$), 2.06 (s, 3H, C**H**$_3$), 1.15 (t, *J* = 7.3 Hz, 9H, HN(CH_2C**H**$_3$)$_3$); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.02 (CH_3**C**O), 139.28, 139.28, 139.01, 138.83, 138.81, 138.63, 138.53, 138.27, 128.54, 128.49, 128.43, 128.42, 128.34, 128.29, 128.27, 128.23, 128.19, 128.19, 128.16, 127.96, 127.94, 127.77, 127.74, 127.64, 127.56, 127.47, 127.28, 127.23, 127.19, 98.85 (Man-1), 83.32, 83.31, 81.24, 80.61, 80.57, 79.49, 78.15, 77.37, 77.16, 76.95, 76.22, 75.80, 75.10, 75.00, 74.34, 74.28, 73.35, 72.45, 71.99, 71.45, 69.04, 68.64, 67.43, 45.41 (HN(**C**H_2CH_3)$_3$), 21.31 (**C**H_3CO), 8.55 (HN(CH_2**C**H_3)$_3$); ^{31}P NMR (243 MHz, $CDCl_3$) δ -0.91; *m/z* (ESI) Found: $[M+Na]^+$, 1207.4628 $C_{70}H_{73}O_{15}P$ requires $[M+Na]^+$, 1207.4585.

Triethylammonium

3,4,6-Tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-1-*O*-monobenzylphospho-3,4,5,6-tetra-*O*-benzyl-D-*myo*-inositol (12)

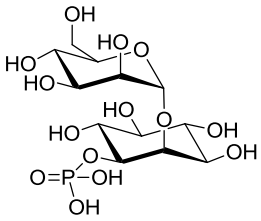


Phosphate **8** (25 mg, 19 µmol, 1 equiv) was dissolved in dry MeOH (3 mL) and NaH (2.3 mg, 97 µmol, 5 equiv) was added. The reaction mixture was stirred for 18 h before it was diluted with $CHCl_3$ (20 mL) and washed with TEA/CO_2 buffer (3 x 10 mL). The organic layer was dried over Na_2SO_4, filtered and evaporated to dryness to yield **12** as yellow oil (24 mg, 19 µmol, 99%).

$[\alpha]^{20}_D$: + 32.1 (*c* = 1.00, $CHCl_3$); FT-IR (neat) ν^{-1}: 3032, 2926, 1746, 1454, 1236, 1051 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.18 (s, 1H, **H**N(CH_2CH_3)$_3$), 7.32 (d, *J* = 7.9 Hz, 3H), 7.25 (t, *J* = 7.6 Hz, 2H), 7.23 – 7.08 (m, 35H), 5.49 (s, 1H, Man-1), 4.97 (d, *J* = 11.1 Hz, 1H), 4.87 – 4.81 (m, 3H), 4.80 – 4.77 (m, 4H), 4.74 (dd, *J* = 10.8, 7.2 Hz, 2H), 4.70 – 4.63 (m, 3H), 4.49 (d, *J* = 12.0 Hz, 1H), 4.42 (d, *J* = 10.9 Hz, 1H), 4.32 (d, *J* = 12.0 Hz, 1H), 4.16 (d, *J* = 12.0 Hz, 1H), 4.13 (s, 1H), 4.07 (ddd, *J* = 9.8, 7.7, 2.1 Hz, 1H), 4.03 (dt, *J* = 10.2, 2.0 Hz, 1H), 3.93 (t, *J* = 9.7 Hz, 1H), 3.83 – 3.76 (m, 3H), 3.40 (t, *J* = 9.3 Hz, 1H), 3.34 (dd, *J* = 10.0, 2.5 Hz, 1H), 3.32 (dd, *J* = 10.9, 2.5 Hz, 1H), 3.01 (d, *J* = 9.8 Hz, 1H), 2.87 (q, *J* = 7.3 Hz, 6H, HN(C**H**$_2$CH$_3$)$_3$), 1.13 (t, *J* = 7.3 Hz, 9H, HN(CH_2C**H**$_3$)$_3$); ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.23, 138.93, 138.88, 138.83, 138.68, 138.52, 138.39, 128.61, 128.45, 128.43, 128.36, 128.31, 128.25, 128.22, 128.19, 128.13, 128.04, 127.87, 127.67, 127.62, 127.56, 127.55, 127.37, 127.26, 127.15, 127.13, 100.92 (Man-1), 83.38, 81.20, 81.10, 81.05, 79.63, 79.46, 76.24, 75.82, 75.52, 75.14, 74.40, 74.31, 73.31, 72.14, 72.11, 71.10, 68.76, 68.69, 67.23, 67.20, 45.55 (HN(**C**H$_2$CH$_3$)$_3$),

8.61 ($HN(CH_2\mathbf{C}H_3)_3$); ^{31}P NMR (243 MHz, $CDCl_3$) δ -0.83; *m/z* (ESI) Found: $[M+HN(CH_2CH_3)_3]^+$, 1244.5867 $C_{68}H_{71}O_{14}P$ requires $[M+HN(CH_2CH_3)_3]^+$, 1244.5864.

α-D-Mannopyranosyl-(1→2)-1-*O*-phospho-D-*myo*-inositol (1)

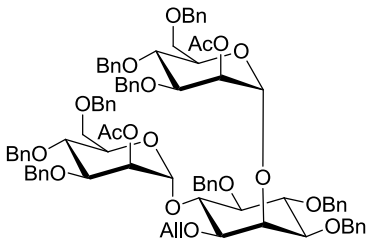


Phosphate salt **12** (24 mg, 19 µmol, 1 equiv) was dissolved in MeOH (5 mL) and washed Amberlite IR120 H resin (150 mg) was added. The slurry was stirred for 30 min to remove TEA. The solution was filtered through cotton and solvents were removed *in vacuo*. The residue was dissolved in MeOH (5 mL) and Pd/C 10wt% (20.5 mg, 19 µmol, 1 equiv) was added. H_2 was bubbled through the solution for 20 min before the reaction mixture was stirred for 18 h under 1 atm H_2. To remove dissolved H_2 dry N_2 was bubbled through the solution for 10 min. The slurry was filtered through a syringe filter and solvents were removed *in vacuo*. The residue was purified using a size exclusion column (140 mm x 10 mm; 5%EtOH in water, super fine G25; GE Healthcare) to yield **1** as colorless solid (8 mg, 19 µmol, 98%).

$[\alpha]^{20}_D$: + 28.9 (*c* = 0.80, H_2O); FT-IR (neat) ν^{-1}: 2929, 2450, 1394, 1032, 983 cm^{-1}; ^1H NMR (600 MHz, D_2O) δ 5.16 (d, *J* = 1.6 Hz, 1H, Man-1), 4.32 (t, *J* = 2.4 Hz, 1H, Ino-2), 4.11 (dd, *J* = 3.3, 1.9 Hz, 1H, Man-2), 4.05 (td, *J* = 9.7, 1.9 Hz, 1H, Ino-1), 4.01 (ddd, *J* = 10.0, 5.3, 2.3 Hz, 1H, Man-5), 3.88 – 3.83 (m, 2H, Man-6, Man-3), 3.80 – 3.76 (m, 2H, Man-6, Ino-6), 3.69 (t, *J* = 10.0 Hz, 1H, Ino-4), 3.66 – 3.64 (m, 1H, Man-4), 3.62 (dd, *J* = 10.1, 2.4 Hz, 1H, Ino-3), 3.34 (t, *J* = 9.1 Hz, 1H, Ino-5); ^{13}C NMR (151 MHz, D_2O) δ 101.31 (Man-1), 78.62 (Ino-2), 76.16 (Ino-1), 74.04 (Ino-5), 72.68 (Man-5), 72.35 (Ino-4), 71.70 (d, *J* = 5.6 Hz, Ino-6), 70.25 (Man-3), 70.03 (Man-2),

69.92 (Ino-3), 66.55 (Man-4), 60.78 (Man-6); ^{31}P NMR (243 MHz, D_2O) δ -0.54; *m/z* (ESI) Found: $[M-H]^-$, 421.0831 $C_{12}H_{23}O_{14}P$ requires $[M-H]^-$, 421.0752.

2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→6)-[2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)]-1-*O*-allyl-3,4,5,-tri-*O*-benzyl-D-*myo*-inositol (9)

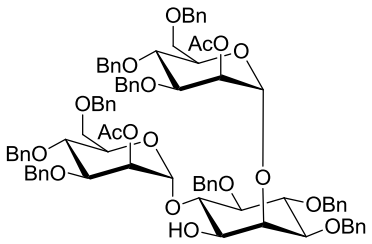


Diol **3**[1] (38 mg, 77 µmol, 1 equiv) and phosphate **5**[3] (152 mg, 201 µmol, 2.6 equiv) were co evaporated with toluene (3 x 2 mL) and placed under HV for 30 min. The residue was dissolved in dry toluene (4 mL) and powdered MS4Å (200 mg) was added. The slurry was stirred at r.t. for 15 min before it was cooled down to -40°C. TMSOTf (36.4 µL, 201 µmol, 2.6 equiv) was added and the reaction was stirred at -40°C for 2 h. The reaction was quenched with TEA (100 µL) and filtered through a pad of Celite®. Solvents were removed *in vacuo* and the residue was purified using column chromatography (*n*-hexane/ethyl acetate 3:1) to yield **9** as yellow oil (69 mg, 48 µmol, 62%).

$[\alpha]^{20}_D$: + 29.7 (*c* = 1.00, $CHCl_3$); FT-IR (neat) ν^{-1}: 3031, 2929, 2866, 1745, 1454, 1367, 1235, 1045 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 6.95 (m, 45H), 5.81 (ddt, *J* = 16.2, 10.8, 5.5 Hz, 1H, CH_2=C**H**-CH_2), 5.40 (s, 2H), 5.36 (s, 1H), 5.13 (d, *J* = 17.2 Hz, 1H, C**H**$_2$=CH-CH_2), 5.08 – 5.04 (m, 2H, C**H**$_2$=CH-CH_2), 4.84 (dd, *J* = 22.0, 10.6 Hz, 2H), 4.79 – 4.69 (m, 4H), 4.69 – 4.61 (m, 2H), 4.56 – 4.44 (m, 5H), 4.33 (d, *J* = 10.6 Hz, 2H), 4.26 – 4.18 (m, 2H), 4.13 – 3.92 (m, 7H), 3.91 – 3.83 (m, 4H), 3.76 (t, *J* = 9.6 Hz,

1H), 3.44 (dd, *J* = 10.6, 3.0 Hz, 1H), 3.30 – 3.13 (m, 6H), 2.04 (s, 3H, C**H**$_3$), 2.04 (s, 3H, C**H**$_3$); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.42, 169.91 (2xCH_3**C**O), 139.11, 138.85, 138.51, 138.30, 138.08, 138.06, 134.10, 128.71, 128.53, 128.46, 128.45, 128.43, 128.32, 128.30, 128.27, 128.20, 128.18, 128.17, 128.07, 128.06, 128.02, 127.98, 127.82, 127.78, 127.70, 127.62, 127.60, 127.57, 127.50, 127.47, 127.42, 127.36, 117.66 (**C**H_2=CH-CH_2), 99.29, 98.65 (2xMan-1; $J_{C,H}$ = 173.2Hz and $J_{C,H}$ = 175.7Hz) , 81.43, 81.02, 78.87, 78.37, 77.50, 76.28, 76.12, 75.80, 75.09, 75.07, 74.27, 74.15, 73.50, 73.42, 72.56, 72.26, 71.79, 71.61, 71.58, 71.55, 71.34, 68.77, 68.61, 68.51, 68.25, 67.49, 67.45, 60.50, 21.28, 21.24 (2x**C**H_3CO); *m/z* (ESI) Found: $[M+Na]^+$, 1461.6364 $C_{88}H_{94}O_{18}$ requires $[M+Na]^+$, 1461.6338.

2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→6)-[2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)]-3,4,5,-tri-*O*-benzyl-D-*myo*-inositol (10)

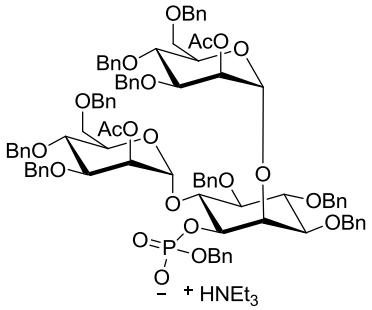


Pseudotrisaccharide **9** (68 mg, 47 µmol, 1 equiv) was dissolved in dry DCM/MeOH (1.4 mL; 1:1) and $PdCl_2$ (4.2 mg, 24 µmol, 0.5 equiv) was added. The slurry was stirred for 12 h at r.t. before it was filtered over Celite® and evaporated to dryness. The residue was purified using column chromatography (*n*-hexane/ethyl acetate 2:1) to yield **10** as yellow oil (42 mg, 30 µmol, 64%).

$[\alpha]^{20}_D$: + 43.4 (*c* = 1.00, $CHCl_3$); FT-IR (neat) ν^{-1}: 3470, 3031, 2925, 2862, 1745, 1454, 1236, 1048 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.12 (m, 45H), 5.51 (s, 1H), 5.38 (s, 1H), 5.35 – 5.29 (m, 2H), 4.98 – 4.89 (m, 2H), 4.86 (d, *J* = 10.9 Hz, 2H), 4.82 –

4.68 (m, 4H), 4.64 – 4.49 (m, 6H), 4.45 (dd, *J* = 10.9, 1.5 Hz, 2H), 4.33 (dd, *J* = 12.1, 4.7 Hz, 2H), 4.24 – 4.20 (m, 1H), 4.20 – 4.07 (m, 2H), 4.07 – 3.95 (m, 4H), 3.84 (dd, *J* = 20.3, 10.0 Hz, 2H), 3.65 (d, *J* = 8.9 Hz, 1H), 3.57 (dd, *J* = 10.8, 3.0 Hz, 1H), 3.52 – 3.26 (m, 5H), 3.13 (bs, 1H, O**H**), 2.15 (s, 3H, C**H**$_3$), 2.13 (s, 3H, C**H**$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.92, 170.31 (2xCH$_3$**C**O), 138.83, 138.73, 138.59, 138.55, 138.36, 138.12, 138.03, 138.01, 128.58, 128.54, 128.48, 128.45, 128.37, 128.35, 128.33, 128.30, 128.09, 128.07, 128.06, 127.99, 127.88, 127.81, 127.78, 127.70, 127.61, 127.48, 99.65, 96.22 (2xMan-1), 81.41, 80.76, 79.40, 78.66, 77.86, 77.69, 77.36, 76.51, 75.87, 75.73, 75.15, 74.96, 74.44, 74.22, 73.52, 73.49, 72.28, 72.18, 71.78, 71.76, 71.73, 71.67, 69.45, 68.79, 68.60, 21.31, 21.26 (2x**C**H$_3$CO); *m/z* (ESI) Found: $[M+H]^+$, 1399.6206 $C_{85}H_{90}O_{18}$ requires $[M+H]^+$, 1399.6205.

Triethylammonium
2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-*α*-D-mannopyranosyl-(1→6)-[2-*O*-acetyl-3,4,6-tri-*O*-benzyl-*α*-D-mannopyranosyl-(1→2)]-1-*O*-monobenzylphospho-3,4,5,-tri-*O*-benzyl-D-*myo*-inositol (11)



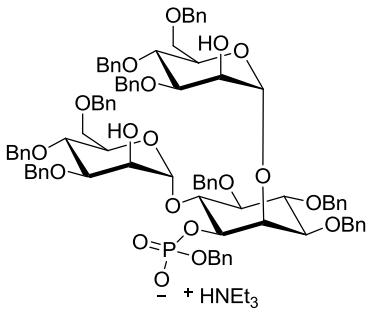
Alcohol **10** (42 mg, 30 µmol, 1 equiv) and sodium benzyl phosphonate **7**[4] (11.7 mg, 60 µmol, 2 equiv) were co evaporated with dry pyridine (3 x 2 mL) and placed under HV for 30 min. The residue was dissolved in dry pyridine (3 mL) and PivCl (12.9 µL, 105 µmol, 3.5 equiv) was added. The reaction mixture was stirred for 2 h before water (10 µL) and iodine (16 mg, 63 µmol, 2.1 equiv) were added. The solution was stirred for 18

h before it was quenched with sat. $Na_2S_2O_3$ solution (approx. 3 drops), dried with Na_2SO_4 and filtered. Solvents were removed *in vacuo* and the residue was co-evaporated with toluene (3 x 2 mL). The residue was purified using column chromatography ($CHCl_3$/MeOH 97:3; SiO_2 was deactivated with 1% TEA in $CHCl_3$) to yield colorless oil. The residue was dissolved in $CHCl_3$ (30 mL), washed with TEA/CO_2 buffer (3 x 10 mL), dried over Na_2SO_4 and evaporated to dryness to yield **11** as colorless oil (31.8 mg, 20 µmol, 68%).

$[\alpha]^{20}_D$: + 34.2 (*c* = 1.00, $CHCl_3$); FT-IR (neat) ν^{-1}: 2926, 2855, 1745, 1497, 1455, 1367, 1100, 1057 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.41 (s, 1H, **H**N(CH_2CH_3)$_3$), 7.36 (d, *J* = 7.3 Hz, 2H), 7.30 (d, *J* = 7.1 Hz, 2H), 7.24 – 7.04 (m, 42H), 6.99 (dd, *J* = 6.6, 2.9 Hz, 2H), 6.96 (t, *J* = 7.6 Hz, 2H), 5.63 (s, 1H), 5.55 (s, 1H), 5.52 (s, 1H), 5.41 (s, 1H), 4.89 (d, *J* = 7.1 Hz, 2H), 4.83 (t, *J* = 9.9 Hz, 2H), 4.77 – 4.65 (m, 7H), 4.57 – 4.40 (m, 6H), 4.35 (d, *J* = 10.9 Hz, 1H), 4.32 (d, *J* = 10.9 Hz, 1H), 4.17 – 4.04 (m, 5H), 4.01 (d, *J* = 9.7 Hz, 1H), 3.96 (dd, *J* = 9.5, 3.1 Hz, 1H), 3.93 (dd, *J* = 9.5, 3.0 Hz, 1H), 3.87 (dd, *J* = 20.9, 9.9 Hz, 2H), 3.79 (t, *J* = 9.6 Hz, 1H), 3.38 (dd, *J* = 11.0, 2.6 Hz, 2H), 3.34 – 3.24 (m, 3H), 3.04 (dd, *J* = 11.0, 1.4 Hz, 1H), 2.81 (q, *J* = 7.3 Hz, 6H, HN(C**H**$_2$CH$_3$)$_3$), 1.94 (s, 3H), 1.92 (s, 3H), 1.09 (t, *J* = 7.3 Hz, 9H, HN(CH_2C**H**$_3$)$_3$); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.00, 169.76 (2xCH$_3$**C**O), 139.24, 139.03, 138.66, 138.62, 138.51, 138.29, 138.20, 128.75, 128.48, 128.40, 128.34, 128.32, 128.26, 128.23, 128.19, 128.18, 128.13, 128.09, 128.00, 127.92, 127.84, 127.81, 127.67, 127.54, 127.51, 127.47, 127.45, 127.40, 127.34, 127.30, 127.25, 99.51, 98.48 (2xMan-1), 81.60, 79.60, 78.66, 77.92, 76.76, 76.74, 76.12, 75.79, 75.37, 75.04, 75.00, 74.32, 74.19, 73.36, 72.14, 71.66, 71.64, 71.56, 71.47, 68.55, 67.33, 45.33 (HN(**C**H_2CH_3)$_3$), 21.34, 21.21 (2x**C**H_3CO), 8.54 (HN(CH_2**C**H_3)$_3$); ^{31}P NMR (243 MHz, $CDCl_3$) δ -0.36; *m/z* (ESI) Found: $[M+Na]^+$, 1591.6152 $C_{92}H_{97}O_{21}P$ requires $[M+H]^+$, 1591.6158.

Triethylammonium

3,4,6-Tri-*O*-benzyl-α-D-mannopyranosyl-(1→6)-[3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)]-1-*O*-monobenzylphospho-3,4,5,-tri-*O*-benzyl-D-*myo*-inositol (13)

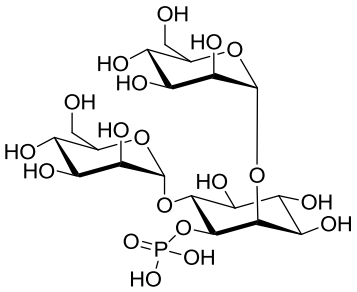


Phosphate salt **11** (31 mg, 19 µmol, 1 equiv) was dissolved in dry MeOH (5 mL) and NaH (2.2 mg, 93 µmol, 5 equiv) was added. The solution was stirred for 48 h at r.t. before it was diluted with $CHCl_3$ (25 mL) and washed with TEA/CO_2 buffer (3 x 10 mL). The organic layer was dried with Na_2SO_4 and evaporated to dryness. The residue was purified using column chromatography ($CHCl_3$/MeOH 95:5 to 90:10; SiO_2 was deactivated with 1% TEA in $CHCl_3$) to yield colorless oil. The residue was dissolved in $CHCl_3$ (30 mL), washed with TEA/CO_2 buffer (3 x 10 mL), dried over Na_2SO_4 and evaporated to dryness to yield **13** as colorless oil (23 mg, 14 µmol, 78%).

$[\alpha]^{20}_D$: + 51.6 (*c* = 1.00, $CHCl_3$); FT-IR (neat) ν^{-1}: 3319, 3030, 2930, 2863, 1454, 1363, 1210, 1048 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.4 Hz, 2H), 7.41 (d, *J* = 7.4 Hz, 2H), 7.37 – 7.13 (m, 42H), 7.12 – 7.06 (m, 4H), 5.56 (s, 1H), 5.53 (s, 1H), 5.04 (d, *J* = 6.7 Hz, 2H), 4.91 (dd, *J* = 10.6, 6.0 Hz, 2H), 4.82 (d, *J* = 10.8 Hz, 1H), 4.80 – 4.75 (m, 3H), 4.72 (d, *J* = 11.4 Hz, 1H), 4.66 (t, *J* = 9.8 Hz, 4H), 4.58 (d, *J* = 11.7 Hz, 1H), 4.51 – 4.44 (m, 4H), 4.41 – 4.35 (m, 2H), 4.28 – 4.20 (m, 2H), 4.19 – 4.09 (m, 4H), 4.01 – 3.84 (m, 6H), 3.43 – 3.37 (m, 2H), 3.33 (t, *J* = 9.3 Hz, 1H), 3.29 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.24 (d, *J* = 10.4 Hz, 1H), 3.15 (d, *J* = 10.5 Hz, 1H), 2.94 (qd, *J* = 7.2, 2.3 Hz, 6H, $HN(C\mathbf{H}_2CH_3)_3$), 1.23 (t, *J* = 7.3 Hz, 9H, $HN(CH_2C\mathbf{H}_3)_3$); ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.10, 138.91, 138.68, 138.45, 138.29, 128.64, 128.39, 128.34, 128.33,

128.31, 128.29, 128.20, 128.19, 128.18, 128.11, 128.09, 127.98, 127.90, 127.86, 127.64, 127.59, 127.51, 127.40, 127.35, 127.28, 127.21, 100.67 (2xMan-1; overlapping signals were resolved in ^{1}H-^{13}C-HSQC experiment), 81.49, 81.45, 79.79, 79.59, 79.28, 77.72, 77.68, 76.14, 75.75, 75.07, 74.60, 74.48, 74.42, 74.26, 73.39, 73.22, 71.98, 71.90, 71.38, 71.04, 68.70, 68.66, 68.44, 68.35, 67.47, 67.44, 45.58 (HN(**C**$H_2CH_3)_3$), 8.71 (HN(CH_2**C**$H_3)_3$); ^{31}P NMR (243 MHz, $CDCl_3$) δ -1.29; *m/z* (ESI) Found: $[M-H+2Na]^+$, 1529.5772 $C_{88}H_{93}O_{19}P$ requires $[M-H+2Na]^+$, 1529.5771.

α-D-Mannopyranosyl-(1→6)-[α-D-mannopyranosyl-(1→2)]-1-*O*-phospho-D-*myo*-inositol (2)



Pseudotrisaccahride **13** (23 mg, 14 µmol, 1 equiv) was dissolved in MeOH (5 mL) and washed Amberlite IR120 H resin (150 mg) was added. The slurry was stirred for 30 min to remove TEA. The solution was filtered through cotton and solvents were removed *in vacuo*. The residue was dissolved in MeOH (5 mL) and Pd/C 10wt% (15.4 mg, 14 µmol, 1 equiv) was added. H_2 was bubbled through the solution for 20 min before the reaction mixture was stirred for 18 h under 1 atm H_2. To remove dissolved H_2 dry N_2 was bubbled through the solution for 10 min. The slurry was filtered through a syringe filter and solvents were removed *in vacuo*. The residue was purified using a size exclusion column (140 mm x 10 mm; 5% EtOH in water; super fine G25, GE Healthcare) to yield **2** as colorless solid (7.8 mg, 13 µmol, 92%).

$[\alpha]^{20}_{D}$: +120.2 (*c* = 0.80, H_2O); FT-IR (neat) ν^{-1}: 3302, 2977, 1387, 1152, 1010, 809 cm^{-1}; ^{1}H NMR (600 MHz, D_2O) δ 5.18 (d, *J* = 1.6 Hz, 2H, 2xMan-1), 4.32 (t, *J* = 2.3 Hz, 1H, Ino-2), 4.16 – 4.14 (m, 2H, 2xMan-2), 4.13 (dd, *J* = 9.5, 2.0 Hz, 1H, Ino-1), 4.05 – 4.00 (m, 2H, 2xMan-5), 3.91 – 3.77 (m, 7H, Ino-6{3.90}, 2xMan-3, 2xMan-6), 3.76 – 3.66 (m, 3H, 2xMan-4, Ino-4{3.68}), 3.62 (dd, *J* = 10.2, 2.6 Hz, 1H, Ino-3), 3.38 (t, *J* = 9.2 Hz, 1H, Ino-5); ^{13}C NMR (101 MHz, D_2O) δ 101.29, 101.17 (2xMan-1), 78.54 (Ino-2), 77.86 (d, *J* = 6.2 Hz, Ino-6), 76.28 (d, *J* = 5.5 Hz, Ino-1), 72.88 (Ino-5), 72.67, 72.58, 72.53, 70.23, 70.21, 70.04, 69.90, 69.74, 66.55, 66.36 (2xMan-4), 60.78, 60.57 (2xMan-6); ^{31}P NMR (243 MHz, D_2O) δ -0.83; *m/z* (ESI) Found: $[M-H]^-$, 583.1286 $C_{18}H_{33}O_{19}P$ requires $[M-H]^-$, 583.1280.

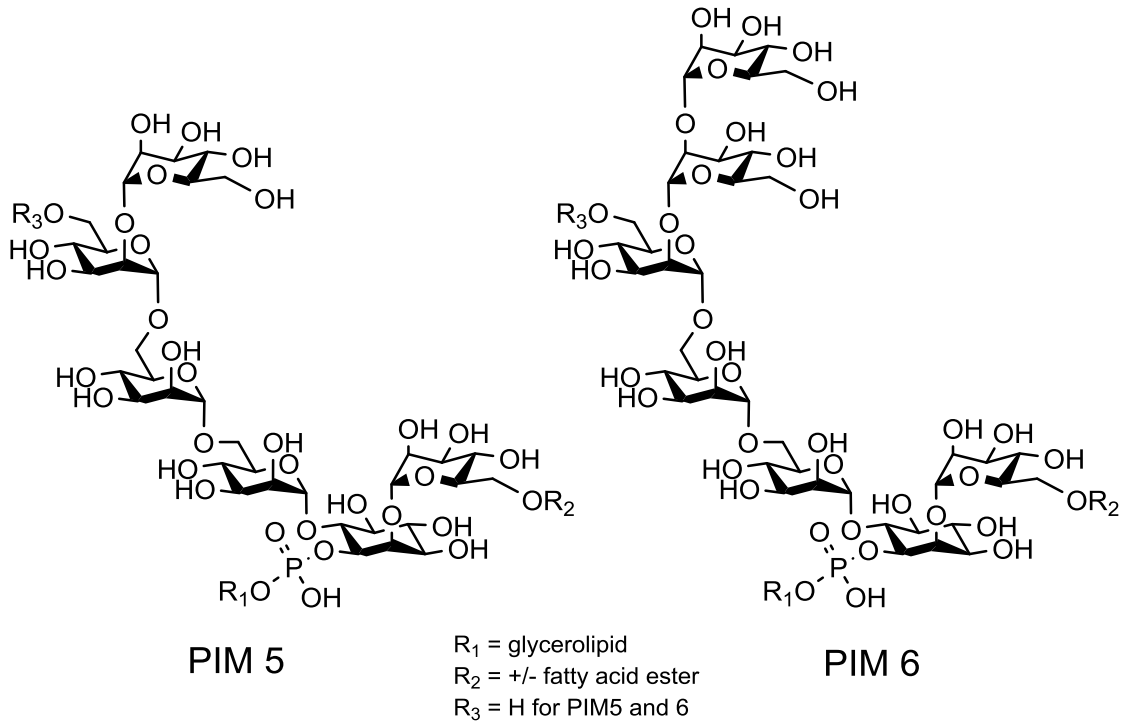


Figure S1. Chemical structures of PIM5 and 6. R_3 serves as a branching point for mycobacterial lipomannan (LM).

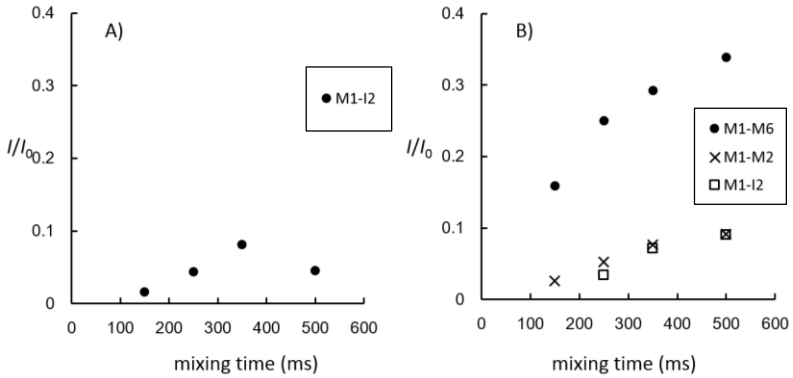


Figure S2. NOESY build-up curve of PIM1 **1** (A) and PIM2 **2** (B).

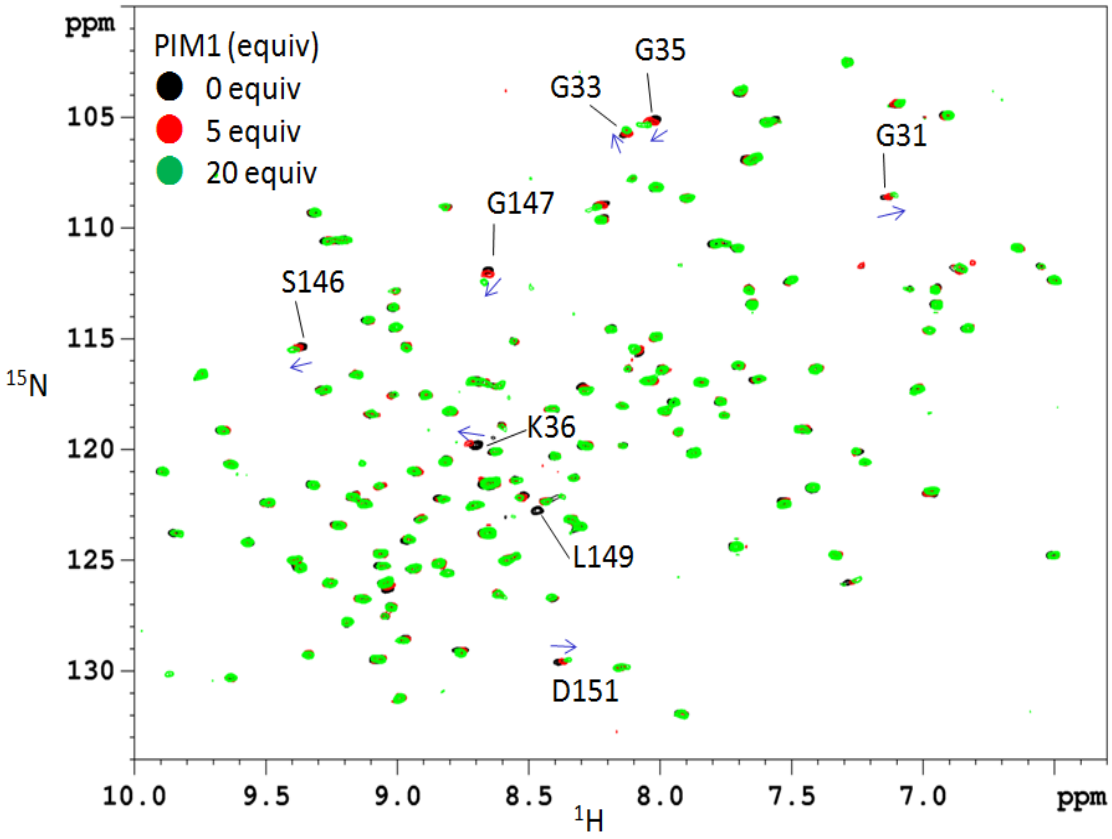


Figure S3. ^{1}H-^{15}N HSQC spectra of uniformly ^{15}N-labeled ZG16p in titration with PIM1 glycan **1**. Black signals are with no ligand, red signals are in the presence of 5 equiv of **1**, and blue signals are in the presence of 20 equiv of **1**. Blue arrows indicate direction of the chemical shifts change in the titrations of **1**.

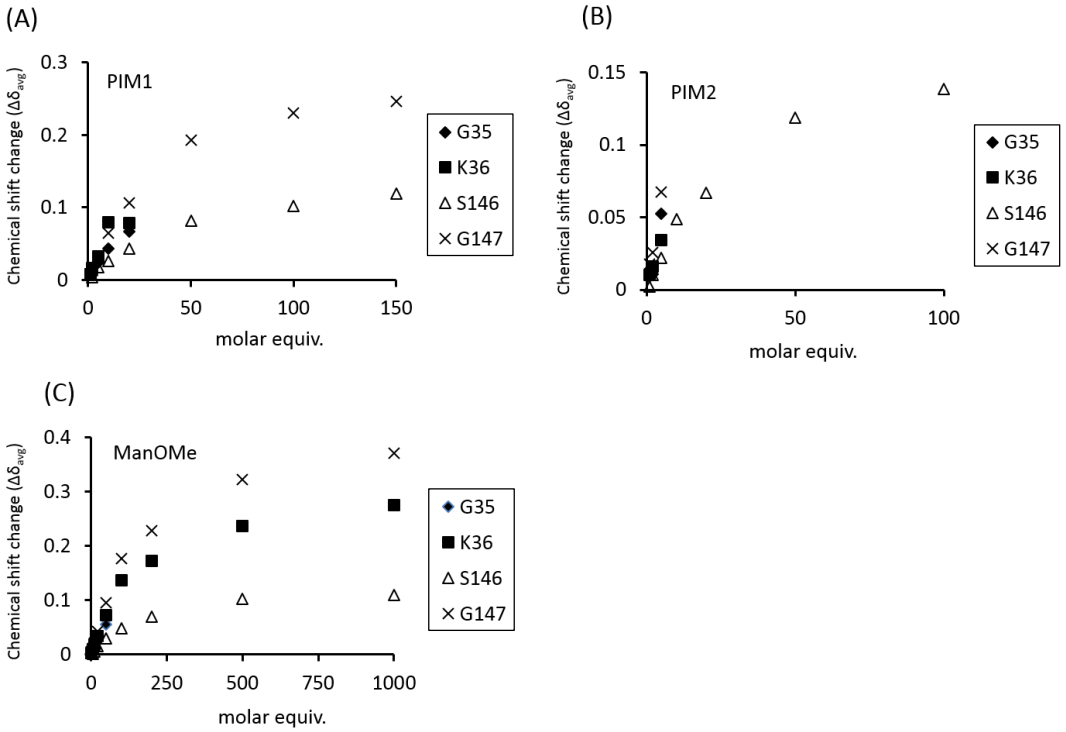


Figure S4. Dose-dependent chemical shift changes of the NMR signals (Gly35, Lys36, Ser146, Gly147) of ^{15}N-ZG16p during the titration with PIM1 **1** (A), PIM2 **2** (B), and ManOMe (C).

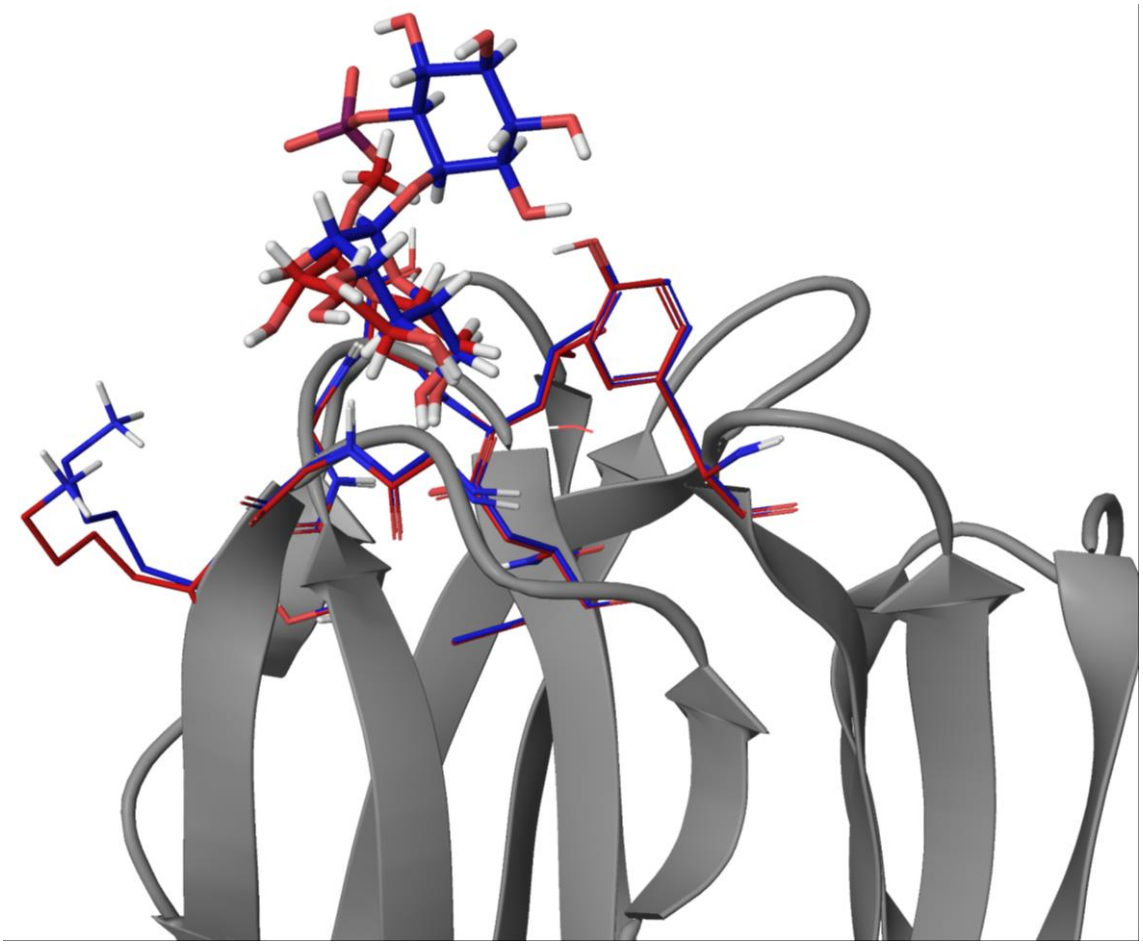


Figure S5. Superpose of PIM1 glycan **1** docking model (blue) obtained in this study and X-ray crystal structure with ManOMe (magenta) (PDB ID 3VZF).

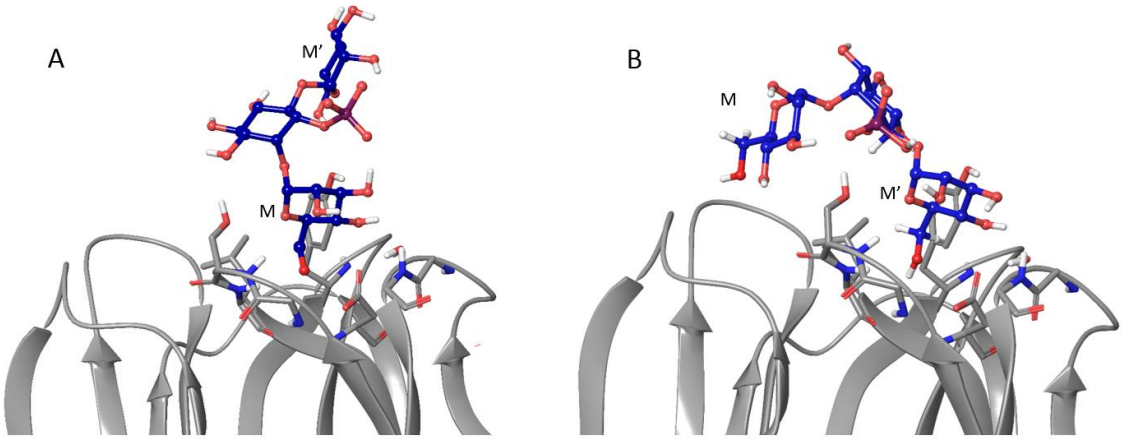


Figure S6. Possible models of two binding modes in PIM2. A; binding mode of PIM2 (M)-ZG16p, and B; binding mode of PIM2 (M')-ZG16p. Bound conformation of PIM2 is estimated based on TR NOE data using Macromodel. The PIM2-ZG16p complex models A and B are constructed based on the Glide model of PIM1 by manual superposition of PIM1 mannose at M and M' of PIM2, respectively.

Table S1. Summary of NMR parameters and conditions.

	machine/probe	TD1 (^{1}H)	TD2 (^{15}N)	TD3 (^{13}C)	scan	temp (°C)
^{1}H–^{15}N HSQC	800 MHz /cryo-TCI	1024	512	–	2	25
HN(CO)CA	600 MHz /cryo-TCI	1024	64	64	56	25
HNCA	800 MHz /cryo-TCI	1024	64	64	32	25
CBCA(CO)NH	600 MHz /cryo-TCI	1024	64	64	64	25
HNCACB	800 MHz /cryo-TCI	1024	64	72	64	25

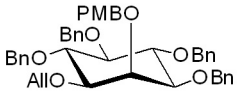
References

(1) Boonyarattanakalin, S.; Liu, X.; Michieletti, M.; Lepenies, B.; Seeberger, P. H. *J. Am. Chem. Soc.* **2008**, *130*, 16791.

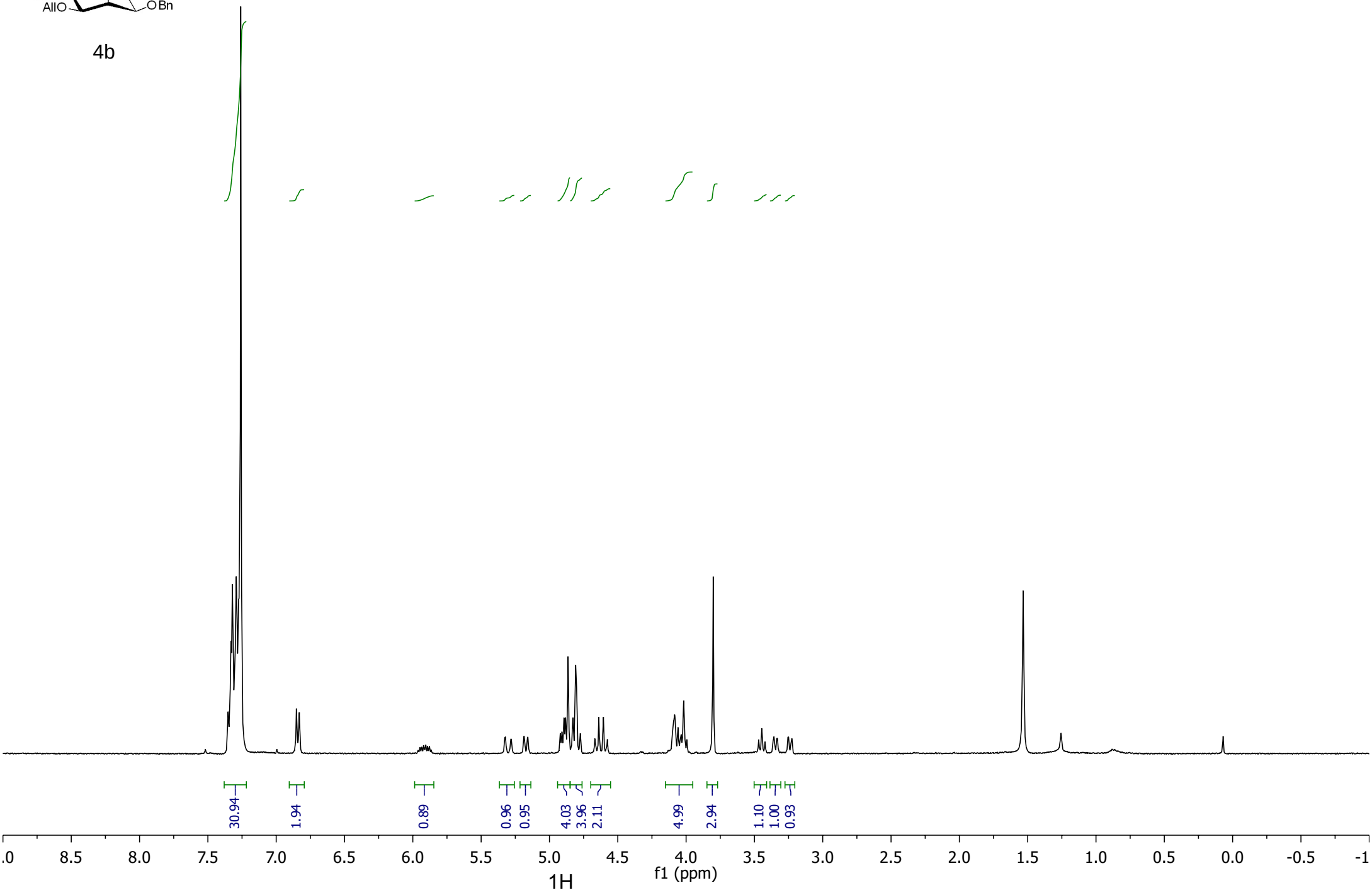
(2) Liu, X.; Kwon, Y. U.; Seeberger, P. H. *J. Am. Chem. Soc.* **2005**, *127*, 5004.

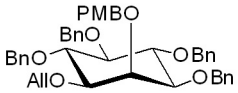
(3) Ravidà, A.; Liu, X.; Kovacs, L.; Seeberger, P. H. *Org. Lett.* **2006**, *8*, 1815.

(4) Knerr, L.; Pannecoucke, X.; Schmitt, G.; Luu, B. *Tetrahedron Lett.* **1996**, *37*, 5123.


PMBO
BnO
BnO
OBn
AllO
OBn

4b


30.94
1.94
0.89
0.96
0.95
4.03
3.96
2.11
4.99
2.94
1.10
1.00
0.93
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)
1H



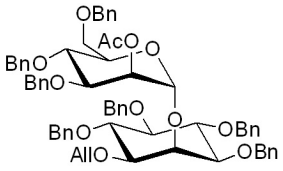
4b

159.13
139.04
138.61
135.08
131.20
129.57
128.46
128.42
128.26
128.20
127.87
127.64
127.55
116.73
113.66
83.81
81.82
81.07
80.90
75.97
73.76
72.86
71.76
55.39

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

13C



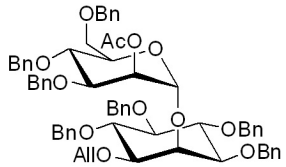
6

35.16 1.93 0.93 0.90 1.94 0.92 9.74 3.10 1.00 1.94 0.99 1.94 1.99 2.18 2.09 2.90 3.12

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1

f1 (ppm)

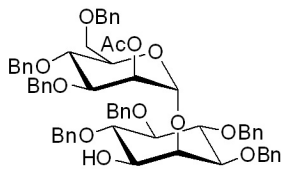
1H


OBn
AcO
O
BnO
BnO
BnO
O
BnO
OBn
AllO
OBn

6

170.25
138.83
138.81
138.77
138.74
138.29
138.09
134.60
128.48
128.45
128.44
110.12
98.97
83.48
81.37
81.24
80.63
79.04
77.82
76.25
75.97
75.87
75.14
74.31
73.54
72.74
72.63
71.96
71.75
71.41
68.89
68.54
21.31
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

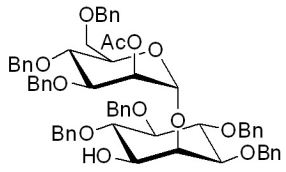
13C


OBn
AcO
O
BnO
BnO
BnO
O
BnO
OBn
HO
OBn

8a

34.18
0.82
0.82
3.14
6.09
2.64
0.94
1.75
1.14
1.77
1.05
1.02
3.14
1.00
0.94
0.64
2.49
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

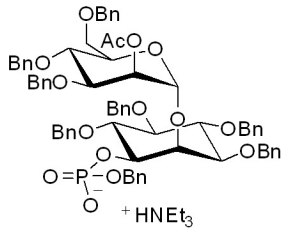
1H


OBn
AcO
O
BnO
BnO
BnO
O
BnO
OBn
HO
OBn

8a

170.37
138.78
138.66
138.50
138.34
138.30
138.17
138.12
128.58
128.56
128.47
128.45
128.34
128.32
128.14
128.09
128.07
128.01
127.36
99.21
83.79
81.86
81.24
79.09
77.87
75.96
75.89
75.63
75.21
74.37
74.22
73.54
72.30
72.02
71.57
68.92
68.57
21.32
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

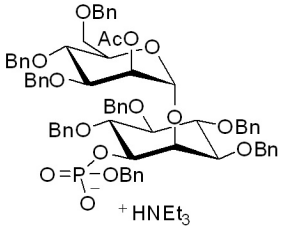
13C


OBn
AcO
O
BnO
BnO
BnO
BnO
O
OBn
OBn
O
O=P
OBn
O
+HNEt3

8

0.94
1.98
2.15
38.27
0.99
0.91
1.16
8.91
1.07
1.11
3.28
2.37
1.07
5.96
3.00
8.97
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

1H



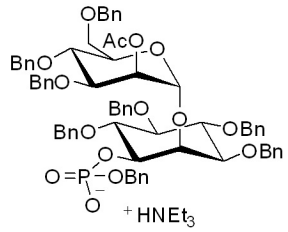
8

170.02
139.28
139.28
139.01
138.83
138.81
138.63
138.53
138.27
128.49
128.43
128.42
128.34
128.29
128.27
128.23
128.19
128.19
128.16
127.96
98.85
83.32
83.31
81.24
79.49
78.15
77.37
77.16
76.95
76.22
75.80
75.10
75.00
74.28
73.35
72.45
71.99
69.04
45.41
21.31
8.55

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

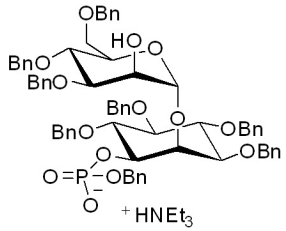
f1 (ppm)

13C


OBn
AcO
O
BnO
BnO
BnO
BnO
O
OBn
OBn
O
O=P
OBn
O
+HNEt3

8

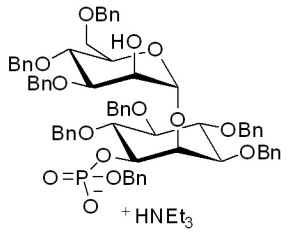
-0.91
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
31P
f1 (ppm)


OBn
HO
O
BnO
BnO
BnO
O
BnO
OBn
OBn
O
O=P
OBn
O
+HNEt3

12

0.73
3.48
1.76
31.11
0.92
2.08
3.14
1.01
1.02
0.99
0.98
6.51
9.51
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

1H



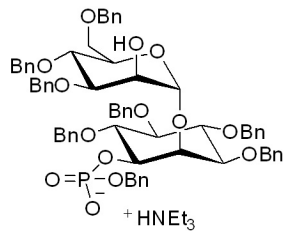
12

139.23
138.93
138.88
138.83
138.68
138.52
138.39
128.43
128.31
128.25
128.22
128.19
128.13
128.04
127.87
127.37
127.15
100.92
83.38
81.20
81.10
81.05
79.63
79.46
76.24
75.82
75.52
75.14
74.40
74.31
73.31
72.14
72.11
71.10
68.76
68.69
45.55
8.61

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

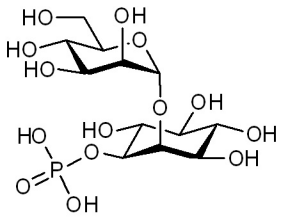
13C


OBn
HO
O
BnO
BnO
BnO
O
BnO
OBn
OBn
O
O=P
OBn
O
+HNEt3

12

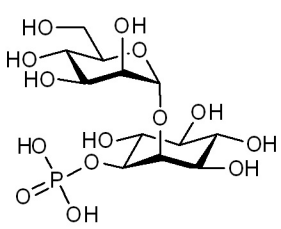
-0.83
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
f1 (ppm)

31P


HO
OH
HO
O
HO
O
OH
HO
HO
OH
OH
HO
O
P
O
OH

PIM 1

1.00
1.00
1.02
1.02
1.05
2.09
2.04
1.19
0.91
1.00
1.01
.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
1H
f1 (ppm)

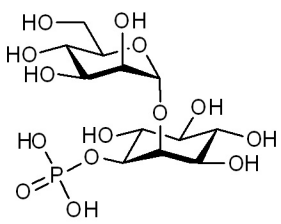


PIM 1

101.31
78.62
76.16
74.04
72.68
72.35
71.72
71.68
70.25
70.03
69.92
66.55
60.78

13C

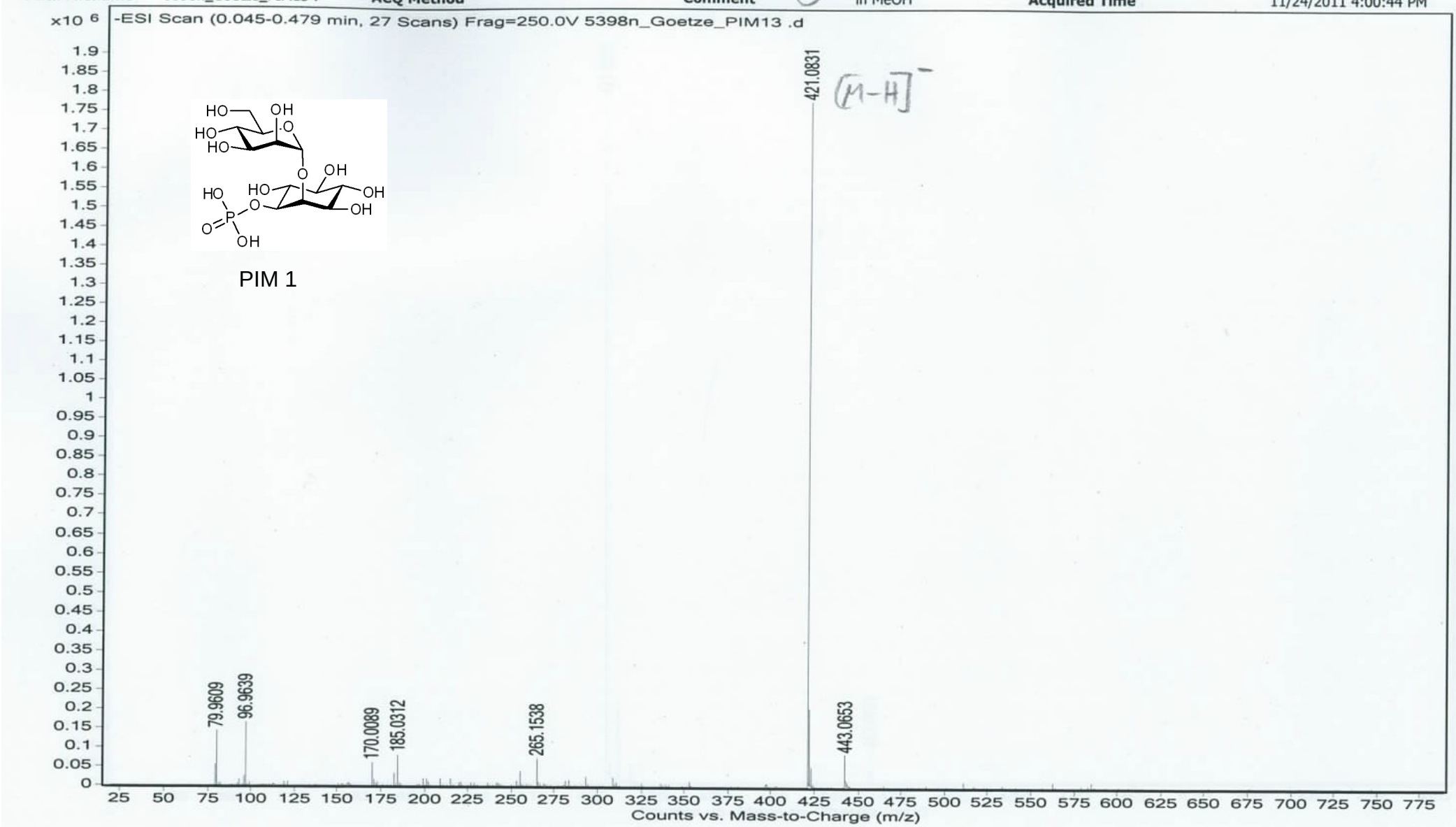
f1 (ppm)


HO
OH
HO
O
HO
O
OH
HO
HO
OH
OH
O
P
O
OH

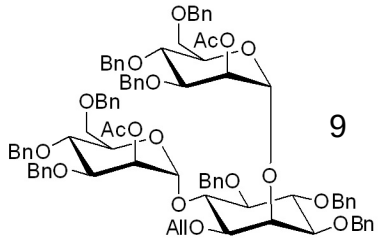
PIM 1

-0.54
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
-3.5
-4.0
-4.5
-5
f1 (ppm)
31P

Sample Name	PIM13	**Position**	Vial 1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-0.1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	5398n_Goetze_PIM13 .	**ACQ Method**		**Comment**	in MeOH	**Acquired Time**	11/24/2011 4:00:44 PM



PIM 1



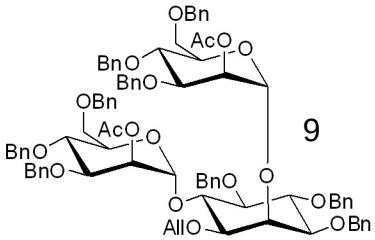
9

45.16 0.86 1.88 0.95 0.98 1.93 2.06 4.08 2.14 6.21 1.94 1.96 7.61 5.08 1.13 1.00 6.03 6.00

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1

1H

f1 (ppm)



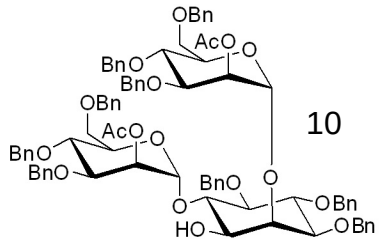
9

170.42
169.91
128.53
128.46
128.45
128.43
128.32
128.30
128.27
128.20
128.18
128.17
128.07
128.06
128.02
127.98
127.82
127.47
117.66
99.29
98.65
81.43
77.50
75.09
75.07
73.50
73.42
72.56
71.79
71.61
71.58
71.34
60.50
21.28
21.24

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

13C

f1 (ppm)



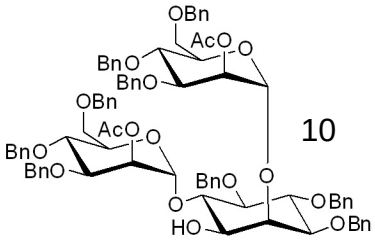
10

45.54 0.96 0.90 1.78 1.90 1.83 4.00 5.96 1.84 1.90 0.93 2.78 3.88 1.98 1.00 0.92 5.09 0.86 5.33

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1

1H

f1 (ppm)



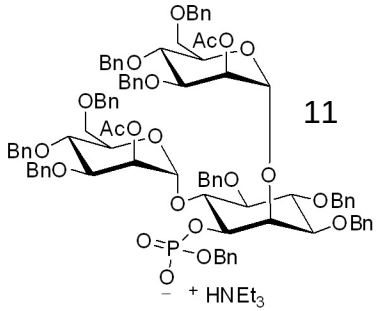
10

170.92
170.31
138.83
138.73
138.59
138.55
138.36
138.12
138.03
138.01
128.54
128.48
128.45
128.37
128.35
128.33
128.30
128.09
128.07
128.06
127.78
99.65
96.22
81.41
80.76
79.40
78.66
77.86
77.69
77.36
75.87
75.73
75.15
74.96
74.44
74.22
73.52
73.49
72.28
72.18
71.78
71.76
71.73
71.67
69.45
68.79
68.60
21.31
21.26

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

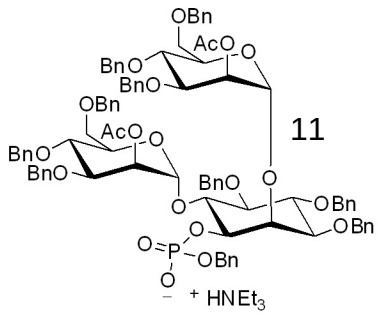
13C

f1 (ppm)


OBn
AcO
O
BnO
BnO
OBn
AcO
O
BnO
BnO
BnO
O
OBn
OBn
O
O=P
OBn
O
⁻ ⁺ HNEt3

11

1.92
1.99
40.16
1.88
1.97
0.99
0.95
0.93
1.02
1.91
2.09
7.03
6.22
0.99
1.06
5.11
0.99
0.99
1.01
2.03
1.02
2.00
2.96
1.00
6.07
6.12
9.23
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
1H
f1 (ppm)

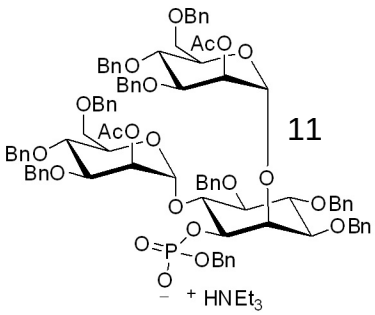


170.00
169.76
139.24
139.03
138.66
138.62
138.51
138.29
138.20
128.34
128.32
128.26
128.23
128.19
128.18
128.13
127.84
127.51
127.25
99.51
98.48
81.60
77.92
76.12
75.79
75.37
75.04
75.00
74.32
74.19
73.36
72.14
71.66
71.64
71.56
71.47
68.55
67.33
45.33
21.34
21.21
8.54

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

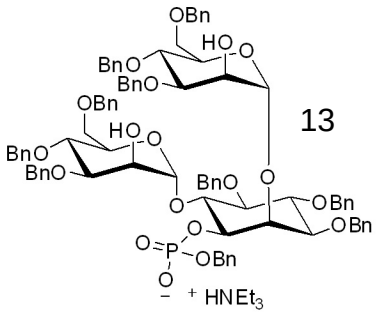
13C

f1 (ppm)


OBn
AcO
BnO
BnO
OBn
AcO
BnO
BnO
BnO
O
O
O
OBn
OBn
O
P
OBn
O
+ HNEt3

11

-0.36
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
31P
f1 (ppm)



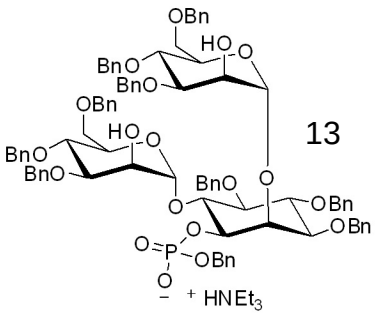
13

1.72 1.81 40.70 4.21 0.93 0.93 1.91 2.00 1.12 3.02 1.07 3.94 1.07 4.03 2.06 2.13 4.04 6.20 2.11 1.05 1.04 1.03 1.11 9.42 13.97

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1

1H

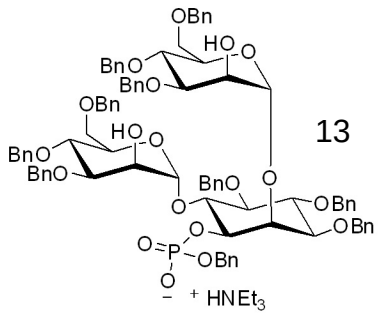
f1 (ppm)


OBn
HO
O
BnO
BnO
OBn
HO
O
BnO
BnO
BnO
O
O
OBn
OBn
O
P
OBn
O
HNEt3

13

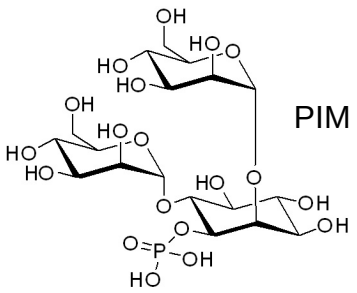
139.10
138.91
138.68
138.45
138.29
128.34
128.33
128.31
128.20
128.19
128.18
128.11
128.09
127.90
127.86
100.87
81.49
81.45
79.79
79.28
76.14
75.75
75.07
74.60
74.42
74.26
73.39
73.22
71.98
71.90
71.38
71.04
68.35
67.47
65.58
8.71
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

13C


OBn
HO
BnO
BnO
OBn
HO
BnO
BnO
BnO
O
O
OBn
OBn
O
O=P
OBn
O
HNEt3

13

1.29
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
31P
f1 (ppm)



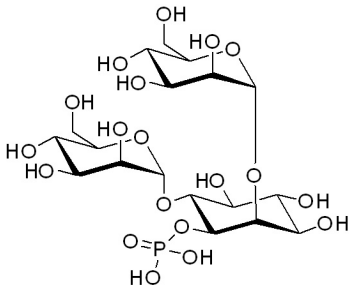
PIM 2

1.95 0.95 2.96 1.96 7.25 3.23 1.06 1.00

5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1

1H

f1 (ppm)



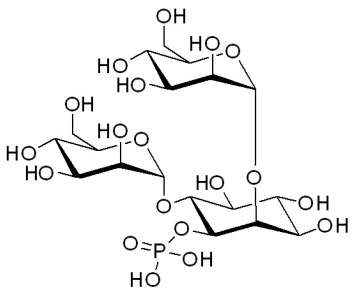
PIM 2

101.29
101.17
78.54
77.89
77.83
76.31
76.25
72.67
72.58
72.53
70.23
70.21
69.90
66.55
66.36
60.78
60.57

20 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 3

13C

f1 (ppm)



PIM 2

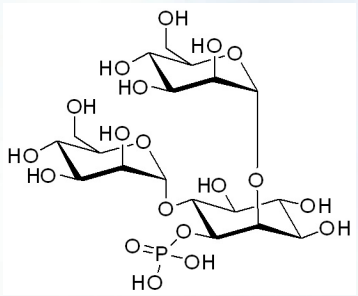
-0.83

3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2.5 -3.0 -3.5 -4.0 -4.5 -5

f1 (ppm)

31P

Sample Name	PIM11	**Position**	Vial 1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	-0.1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	5399_Goetze_PIM11.d	**ACQ Method**		**Comment**	in MeOH	**Acquired Time**	11/25/2011 10:22:29 AM



PIM 2