

Supporting Information

Synthesis of Glycosylphosphatidylinositol (GPI) Anchor Glycolipids Bearing Unsaturated Lipids

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General Methods

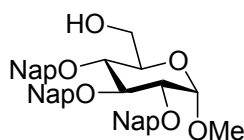
All chemicals used were reagent grade and used as acquired except where noted. All reactions were performed in oven-dried glassware under an inert atmosphere (nitrogen or argon) unless noted otherwise. Reagent grade dichloromethane (DCM or CH₂Cl₂), tetrahydrofuran (THF), methanol (MeOH) *N,N*-dimethylformamide (DMF), toluene (PhMe) and acetonitrile (MeCN) were dried with activated neutral molecular sieves column prior to use. Pyridine was distilled over CaH₂ prior to use. Analytical thin layer chromatography (TLC) was performed on Macherey Nagel silica gel 60 F₂₅₄ plates (0.25mm). Compounds were visualized by UV irradiation or dipping the TLC plates into a cerium sulfate-ammonium molybdate (CAM) solution or a solution of 3-methoxyphenol ethanol containing sulfuric acid. 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 Varian 400 (400 MHz), a 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 . MS/MS analysis were carried out on a Bruker amaZon ETD 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.

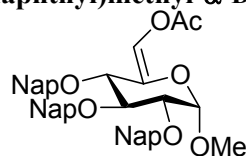
Normal phase LC analysis was performed on an Agilent 1200 HPLC system using a YMC® Diol column (4.6 x 100 mm), a gradient from 10 to 90 percent of ethyl acetate in n-hexane in 30 min, 1ml/min flow rate and ELSD detection.

Methyl 2,3,4-tri-*O*-(2-naphthyl)methyl- α -D-glucopyranoside (**9**)



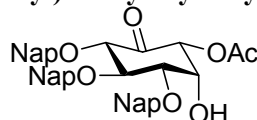
6-O-Trityl-1-O-methyl glucosamine **8**¹ (22 g, 50.4 mmol) was stirred overnight at room temperature in the presence of NapBr (39 g, 176 mmol) and NaH (8.06 g, 202 mmol, 60% in mineral oil) in DMF (500 mL). The reaction was quenched with aq. NH₄Cl, extracted with EtOAc, washed with brine, dried with Na₂SO₄, filtered, and evaporated. The residue was purified by flash chromatography (hexane/EtOAc = 5:1, *R_f* 0.4) to give the naphthylated compound in 85% yield (36.8 g, 42.9 mmol) as white solid. To a stirred solution of fully protected compound (19.1 g, 22.29 mmol) in MeOH (180 mL) *p*-TsOH (0.848 g, 4.46 mmol) was added at room temperature. The reaction mixture was neutralized with Et₃N after 14 h and concentrated in vacuo. The product was purified by silica gel column chromatography to give alcohol **9** in 90% yield (12.3 g, 20.01 mmol) as white solid; *R_f* = 0.2 (hexane/EtOAc = 2:1), [α]_D²⁰: -56.7 (c = 5.1, CHCl₃); ATR-FTIR (cm⁻¹): 3474, 3054, 3012, 2922, 1914, 1720, 1692, 1632, 1509, 1464, 1364, 1347, 1271, 1215, 1192, 1158, 1123, 1075, 1048, 1021, 953, 894, 854, 815, 748, 707; ¹H NMR (400 MHz, CDCl₃) δ 7.89-7.74 (m, 12H), 7.60-7.47 (m, 8H), 7.45 (dd, *J* = 8.4, 1.6 Hz, 1H), 5.28 & 5.11 (ABq, *J* = 11.3 Hz, 2H, -CH₂- of Nap), 5.12 & 4.90 (ABq, *J* = 11.0 Hz, 2H, -CH₂- of Nap), 5.02 & 4.93 (ABq, *J* = 12.2 Hz, 2H, -CH₂- of Nap), 4.69 (d, *J* = 3.5 Hz, 1H, Glc-1), 4.21 (t, *J* = 9.2 Hz, 1H, Glc-3), 3.90-3.76 (m, 3H, Glc-6, Glc-5), 3.74-3.65 (m, 2H, Glc-4, Glc-2), 3.45 (s, 3H, -OMe); ¹³C NMR (100 MHz, CDCl₃) δ 136.3, 135.7, 135.6, 133.4, 133.3, 133.2, 133.1, 133.0, 128.4, 128.3, 128.2, 128.01, 127.97, 127.74, 127.72, 127.0, 126.7, 126.5, 126.2, 126.13, 126.10, 126.05, 126.0, 125.86, 125.85, 98.2 (C1), 82.0 (C3), 80.0 (C2), 77.6 (C4), 75.8 (-CH₂- of Nap), 75.2 (-CH₂- of Nap), 73.5 (-CH₂- of Nap), 70.8 (C5), 61.9 (C6), 55.3 (-OMe); ESI-MS: *m/z* [M+Na]⁺ calcd 637.2566, obsd 637.2578.

(Z)-Methyl 6-O-acetyl-2,3,4-tri-O-(2-naphthyl)methyl- α -D-glucopyranoside (10)



To a solution of alcohol **9** (15.1 g, 24.56 mmol) and $\text{SO}_3 \cdot \text{Py}$ (31.3 g, 98 mmol) in CH_2Cl_2 (250 mL) was added DIPEA (30 mL, 172 mmol) at 0 °C under stirring. The reaction mixture was stirred at 0 °C for 10 min and then DMSO (24.4 mL, 344 mmol) was added to the mixture. After 1 h at 0 °C, the reaction was diluted with aq. NaHCO_3 , extracted with Et_2O , washed with brine, dried with Na_2SO_4 and concentrated in vacuo (Hex/EtOAc=3:2, R_f 0.15). The crude compound was dissolved in MeCN (240 mL). Then, Ac_2O (13.9 mL, 147 mmol) and K_2CO_3 (13.6 g, 98 mmol) were added; the reaction mixture was refluxed (85 °C) for 3-4 h and allowed to cool to room temperature, diluted with aq. NaHCO_3 , extracted with Et_2O , washed with brine, dried with Na_2SO_4 , and concentrated in vacuo. The product was purified by flash chromatography to give enol ester **10** in 80% yield (two steps, 12.8 g, 19.55 mmol) as white solid; R_f = 0.28 (hexane/EtOAc = 3:1), $[\alpha]_D^{20}$: -67.6 (c = 0.55, CHCl_3); ATR-FTIR (cm^{-1}): 3052, 2930, 2857, 1754, 1216, 1113, 1088, 817, 702; ^1H NMR (400 MHz, CDCl_3) δ 7.85-7.68 (m, 12H), 7.53-7.43 (m, 9H), 7.28 (d, J = 1.4 Hz, 1H, Glc-6), 5.13 & 5.06 (ABq, J = 11.3 Hz, 2H, $-\text{CH}_2-$ of Nap), 5.02 & 4.88 (ABq, J = 12.3 Hz, 2H, $-\text{CH}_2-$ of Nap), 4.98 & 4.94 (ABq, J = 11.6 Hz, 2H, $-\text{CH}_2-$ of Nap), 4.77 (d, J = 3.4 Hz, 1H, Glc-1), 4.14-4.08 (m, 2H, Glc-3, Glc-4), 3.74-3.70 (m, 1H, Glc-2), 3.52 (s, 3H, $-\text{OMe}$), 2.17 (s, 3H, $-\text{OAc}$); ^{13}C NMR (100 MHz, CDCl_3) δ 167.4 ($\text{O}=\text{C}-\text{O}-$ of AcO), 136.2 (C5), 135.5, 135.22, 135.15, 133.5, 133.4, 133.33, 133.25, 133.2, 133.1, 128.5, 128.4, 128.2, 128.14, 128.10, 128.05, 127.82, 127.79, 127.1, 126.9, 126.7, 126.3, 126.21, 126.18, 126.10, 126.06, 126.0, 125.9, 123.3 (C6), 99.9 (C1), 81.5 (C3), 79.3 (C2), 77.9 (C4), 75.8 ($-\text{CH}_2-$ of Nap), 74.6 ($-\text{CH}_2-$ of Nap), 74.0 ($-\text{CH}_2-$ of Nap), 56.5 ($-\text{OMe}$), 20.7 ($-\text{CH}_3$ of OAc); ESI-MS: m/z $[\text{M}+\text{Na}]^+$ calcd 677.2515, obsd 677.2507.

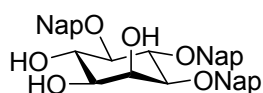
(1R,2R,3S,4R,5S)-3,4,5-Tri-O-(2-naphthyl)methoxy-2-hydroxy-6-oxocyclohexyl Acetate (11)



The enolate compound **10** (7.6 g, 11.6 mmol) was dissolved in a mixture of acetone/water (5:1, 120 mL). To this solution, $\text{Hg}(\text{OTf})_2$ (5.94 g, 13.93 mmol) was added at rt. After 1 h, the reaction solution was cooled to 0 °C. To this reaction, aq. NaOAc (3M, 11.6 mL) and brine (10 mL) were successively added. The reaction was allowed to slowly warm to room temperature and stirred at room temperature for 12 h. The reaction mixture was diluted with aq. NaHCO_3 and extracted with EtOAc. The combined organic layer was washed with brine, dried over Na_2SO_4 , concentrated in vacuo, and placed

under high vacuum. The product was crystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ to give ketone compound **11** as white solid; $R_f = 0.20$ (hexane/EtOAc = 3:2), $[\alpha]_D^{20}$: -61.0 ($c = 0.77$, CHCl_3); ATR-FTIR (cm^{-1}): 3488, 3051, 2930, 2857, 1750, 1508, 1365, 1347, 1237, 1173, 1125, 1089, 1032, 895, 854, 818, 784, 753; ^1H NMR (400 MHz, CDCl_3) δ 7.84-7.66 (m, 12H), 7.53-7.38 (m, 9H), 5.19 (d, $J = 2.6$ Hz, 1H, Ino-1), 5.14 & 5.02 (ABq, $J = 11.1$ Hz, 2H, $-\text{CH}_2-$ of Nap), 5.13 & 4.71 (ABq, $J = 11.7$ Hz, 2H, $-\text{CH}_2-$ of Nap), 4.96 & 4.92 (ABq, $J = 12.0$ Hz, 2H, $-\text{CH}_2-$ of Nap), 4.38 (t, $J = 2.5$ Hz, 1H, Ino-2), 4.27-4.18 (m, 2H, Ino-4, Ino-5), 3.94 (dd, $J = 8.5, 2.4$ Hz, 1H, Ino-3), 2.62 (brs, 1H, -OH), 2.25 (s, 3H, -OAc); ^{13}C NMR (100 MHz, CDCl_3) δ 198.0 ($-\text{C}=\text{O}-$), 169.9 ($\text{O}=\text{C}-\text{O}-$ of AcO), 135.9, 134.9, 134.8, 133.5, 133.4, 133.31, 133.29, 133.26, 133.2, 128.7, 128.4, 128.20, 128.17, 128.12, 128.07, 127.9, 127.82, 127.79, 127.3, 127.2, 126.8, 126.5, 126.4, 126.19, 126.17, 126.1, 126.0, 125.9, 83.5 (C5), 82.0 (C4), 78.9 (C3), 76.3 ($-\text{CH}_2-$ of Nap), 75.1 (C1), 73.7 ($-\text{CH}_2-$ of Nap), 73.6 ($-\text{CH}_2-$ of Nap), 69.6 (C2), 20.7 ($-\text{CH}_3$ of OAc); ESI-MS: m/z $[\text{M}+\text{Na}]^+$ calcd 663.2359, obsd 663.2386.

D-3,4,5-Tri-O-(2-naphthyl)methyl-*myo*-inositol (**12**)

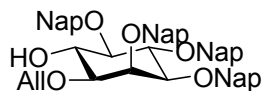


In the first step, the ketone compound **11** (5.85 g, 9.13 mmol) was dissolved in MeCN (50 ml) and this solution was transferred to a cooled (0 °C) solution of $\text{NaBH}(\text{OAc})_3$ (7.74 g, 36.5 mmol) in a mixture of AcOH/MeCN ($v/v = 1:1$, 100 mL). The reaction was allowed to warm to room temperature and stirred at room temperature for 12 h. The reaction mixture was diluted with aq. NaHCO_3 and extracted with EtOAc. The combined organic layer was washed with brine, dried over Na_2SO_4 , concentrated in vacuo, and placed under high vacuum. The crude product was crystallized by $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ to give diol compound intermediate **11a** in 68% yield (two steps, 5.10 g, 7.93 mmol) as white solid; $R_f = 0.20$ (hexane/EtOAc = 1:1), $[\alpha]_D^{20}$: -13.3 ($c = 0.56$, CHCl_3); ATR-FTIR (cm^{-1}): 3452, 3055, 2896, 1746, 1510, 1365, 1343, 1270, 1236, 1169, 1157, 1143, 1121, 1070, 1046, 1012, 951, 891, 852, 816, 774, 761, 743, 711; ^1H NMR (400 MHz, CDCl_3) δ 7.83-7.65 (m, 12H), 7.50-7.42 (m, 9H), 5.13 & 4.97 (ABq, $J = 11.5$ Hz, 2H, $-\text{CH}_2-$ of Nap), 5.12 & 5.04 (ABq, $J = 11.2$ Hz, 2H, $-\text{CH}_2-$ of Nap), 4.90 & 4.85 (ABq, $J = 11.6$ Hz, 2H, $-\text{CH}_2-$ of Nap), 4.78 (dd, $J = 10.3, 2.8$ Hz, 1H, Ino-1), 4.39 (t, $J = 2.7$ Hz, 1H, Ino-2), 4.20 (dd, $J = 10.2, 9.4$ Hz, 1H, Ino-6), 4.06 (t, $J = 9.5$ Hz, 1H, Ino-4), 3.68 (dd, $J = 9.5, 2.7$ Hz, 1H, Ino-3), 3.49 (t, $J = 9.4$ Hz, 1H, Ino-5), 2.18 (s, 3H, -OAc); ^{13}C NMR (100 MHz, CDCl_3) δ 170.9 ($\text{O}=\text{C}-\text{O}-$ of AcO), 136.2, 135.9, 135.0, 133.48, 133.45, 133.4, 133.3, 133.2, 133.1, 128.6, 128.5, 128.3, 128.1, 127.9, 127.83, 127.81, 127.0, 126.8, 126.6, 126.4, 126.29,

126.27, 126.2, 126.10, 126.07, 126.0, 125.94, 125.90, 83.1 (C5), 81.1 (C4), 80.2 (C3), 76.0 (-CH₂- of Nap), 75.9 (-CH₂- of Nap), 73.3 (C1), 73.1 (-CH₂- of Nap), 70.7 (C6), 68.0 (C2), 21.3 (-CH₃ of OAc); ESI-MS: m/z [M+Na]⁺ calcd 665.2515, obsd 665.2525.

Next, the diol compound **11a** (6.19 g, 9.63 mmol) was stirred at room temperature for 30 min in the presence of NaOMe (0.104 g, 1.93 mmol) in MeOH/CH₂Cl₂ (v/v = 1:1, 80 mL). After neutralization with resin, the mixture was dried by evaporation and passed through a short column of silica gel using MeOH/DCM (20:1) as eluent to deliver **12** as a white powder. [α]_D²⁰: -28.9 (c = 0.57, CHCl₃); ATR-FTIR (cm⁻¹): 3417, 3054, 3019, 2924, 2869, 1509, 1468, 1405, 1363, 1349, 1272, 1173, 1153, 1139, 1123, 1060, 1008, 991, 948, 893, 857, 818, 779, 756, 739, 715; ¹H NMR (400 MHz, CD₃OD) δ 7.82-7.69 (m, 7H), 7.66-7.58 (m, 4H), 7.54-7.32 (m, 10H), 5.07 & 4.95 (ABq, *J* = 11.0 Hz, 2H, -CH₂- of Nap), 5.06 & 4.99 (ABq, *J* = 11.3 Hz, 2H, -CH₂- of Nap), 4.94 & 4.81 (ABq, *J* = 12.0 Hz, 2H, -CH₂- of Nap), 4.22 (t, *J* = 2.6 Hz, 1H, Ino-2), 4.02 (t, *J* = 9.5 Hz, 1H, Ino-4), 3.89 (t, *J* = 9.5 Hz, 1H, Ino-6), 3.55 (dd, *J* = 9.7, 2.6 Hz, 1H, Ino-3), 3.41 (t, *J* = 9.3 Hz, 1H, Ino-5), 3.35 (dd, *J* = 9.8, 2.7 Hz, 1H, Ino-1); ¹³C NMR (100 MHz, CDCl₃) δ 135.9, 135.8, 132.91, 132.89, 132.87, 132.7, 132.55, 132.54, 127.6, 127.39, 127.37, 127.35, 127.09, 127.05, 126.2, 126.0, 125.9, 125.6, 125.53, 125.49, 125.4, 125.2, 83.0 (C5), 80.8 (C4), 79.7 (C3), 75.3 (-CH₂- of Nap), 75.0 (-CH₂- of Nap), 72.7 (C6), 71.7 (-CH₂- of Nap), 71.5 (C1), 68.9 (C2); ESI-MS: m/z [M+Na]⁺ calcd 623.2410, obsd 623.2405.

D-1-O-Allyl-2,3,4,5-tetra-O-(2-naphthyl)methyl-*myo*-inositol (**7**)



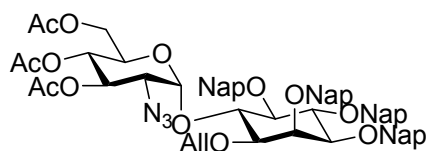
D-1-O-Allyl-3,4,5-tri-O-(2-naphthyl)methyl-*myo*-inositol

A mixture of triol compound **12** (5.8 g, 9.66 mmol) and bis(tributyltin)oxide (6.40 mL, 12.55 mmol) in toluene (150 mL) was refluxed using a Dean-Stark trap. After 5 h, TBAI (3.57 g, 9.66 mmol) and allyl bromide (4.18 g, 48.3 mmol) were added. The mixture was stirred at 65 °C overnight under Ar atmosphere. The solvent was evaporated in vacuo and the product was purified by flash chromatography to give allylated *myo*-inositol **12a** in 68% yield (two steps, 4.2 g, 6.55 mmol) as white solid; *R*_f = 0.35 (hexane/EtOAc = 2:1), [α]_D²⁰: -51.9 (c = 0.6, CHCl₃); ATR-FTIR (cm⁻¹): 3436, 3055, 2885, 2357, 2333, 2186, 2003, 1915, 1508, 1364, 1344, 1270, 1167, 1143, 1121, 1067, 1016, 1004, 971, 942, 927, 893, 883, 854, 814, 776, 753, 741, 705; ¹H NMR (400 MHz, CDCl₃) δ 7.84-7.65 (m, 12H), 7.53-7.42 (m, 9H), 6.00-5.87 (m, 1H, -CH= of allyl), 5.27 (dq, *J* = 17.2, 1.5 Hz, 1H, -CH₂- of allyl), 5.18 (ddd, *J* = 10.4, 2.5, 1.1 Hz, 1H, -CH₂- of allyl), 5.14 & 5.06 (ABq, *J* = 11.1 Hz, 2H, -

CH₂- of Nap), 5.10 & 5.04 (ABq, J = 11.5 Hz, 2H, -CH₂- of Nap), 4.95 & 4.92 (ABq, J = 12.0 Hz, 2H, -CH₂- of Nap), 4.31 (t, J = 2.6 Hz, 1H, Ino-2), 4.21 (ddt, J = 12.6, 5.8, 1.3 Hz, 1H, -CH₂- of allyl), 4.16-4.07 (m, 3H, Ino-4, Ino-6, -CH₂- of allyl), 3.55 (dd, J = 9.6, 2.7 Hz, 1H, Ino-3), 3.46 (t, J = 9.4 Hz, 1H, Ino-5), 3.20 (dd, J = 9.6, 2.7 Hz, 1H, Ino-1); ¹³C NMR (100 MHz, CDCl₃) δ 136.3, 136.2, 135.4, 134.5 (-CH= of allyl), 133.44, 133.41, 133.3, 133.2, 133.08, 133.05, 128.5, 128.4, 128.2, 128.1, 128.0, 127.82, 127.79, 127.77, 126.8, 126.7, 126.6, 126.3, 126.19, 126.17, 126.13, 126.08, 126.05, 126.0, 125.94, 125.90, 118.0 (=CH₂ of allyl), 82.9 (C5), 81.1 (C4), 80.0 (C3), 79.0 (C1), 76.1 (-CH₂- of Nap), 75.6 (-CH₂- of Nap), 72.9 (-CH₂- of Nap), 72.4 (C6), 71.5 (-CH₂- of allyl), 67.1 (C2); ESI-MS: m/z [M+Na]⁺ calcd 663.2723, obsd 663.2733.

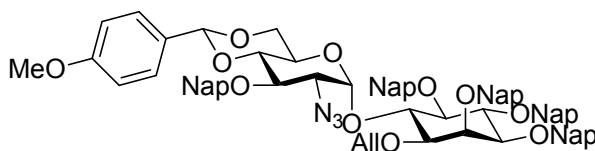
The obtained allyl myo-inositol (1.05 g, 1.64 mmol) was dissolved in DMF (15 mL). The solution was then cooled to 0 °C, and NaH (87 mg, 3.61 mmol) was added in one portion. After stirring for 30 min at 0 °C, the reaction mixture was cooled to -20 °C and 2-naphthylmethyl bromide (0.362 g, 1.64 mmol) in DMF was added dropwise. The reaction was stirred 2 h allowing it to warm to 0 °C. The reaction was quenched with water and extracted with EtOAc (50 mL). The combined organic layers were further washed with water and brine and dried over Na₂SO₄. The solvents were removed under reduced pressure and the crude product was purified by flash chromatography to give the *myo*-inositol building block **7** in 67% yield (0.86 g, 1.10 mmol) as white solid; R_f = 0.28 (hexane/EtOAc 3:1), [α]_D²⁰: -21.8 (c = 1.23, CHCl₃); ATR-FTIR (cm⁻¹): 3451, 3057, 3014, 2925, 2861, 1603, 1510, 1460, 1365, 1345, 1272, 1216, 1171, 1156, 1124, 1055, 952, 930, 892, 854, 815, 714; ¹H NMR (400 MHz, CDCl₃) δ 7.86-7.72 (m, 13H), 7.70-7.60 (m, 3H), 7.54-7.42 (m, 12H), 5.98-5.85 (m, 1H, -CH= of allyl), 5.29-5.22 (m, 1H, -CH₂- of allyl), 5.21-5.15 (m, 2H, -CH₂- of allyl, -CH₂- of Nap), 5.13-5.08 (m, 5H, -CH₂- of Nap), 4.90 & 4.84 (ABq, J = 11.9 Hz, 2H, -CH₂- of Nap), 4.33-4.23 (m, 2H, Ino-2, Ino-4), 4.19-4.16 (m, 1H, Ino-6), 4.12-3.98 (m, 2H, -CH₂- of allyl), 3.58-3.50 (m, 2H, Ino-3, Ino-5), 3.22-3.15 (m, 1H, Ino-1); ¹³C NMR (100 MHz, CDCl₃) δ 136.5, 136.4, 135.9, 134.6 (-CH= of allyl), 133.44, 133.36, 133.3, 133.1, 133.0, 128.29, 128.26, 128.2, 128.1, 128.0, 127.80, 127.78, 127.75, 126.7, 126.6, 126.4, 126.30, 126.28, 126.26, 126.08, 126.06, 126.0, 125.87, 125.85, 117.6 (=CH₂ of allyl), 83.5 (C5), 81.6 (C4), 81.2 (C3), 80.0 (C1), 76.0 (-CH₂- of Nap), 75.5 (-CH₂- of Nap), 74.2 (-CH₂- of Nap), 73.4 (C6), 73.2 (-CH₂- of Nap), 73.0 (C2), 71.4 (-CH₂- of allyl); ESI-MS: m/z [M+Na]⁺ calcd 803.3349, obsd 803.3372.

2-Azido-3,4,6-tri-*O*-acetyl-2-deoxy- α -D-glucopyranosyl-(1→6)-1-*O*-allyl-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (15**)**



A mixture of donor **6**² (1.34 g, 2.82 mmol) and acceptor **7** (1.47 g, 1.88 mmol) in Et₂O/CH₂Cl₂ (v/v = 6:1, 17.5 mL) was stirred at room temperature for 10 min. TMSOTf (0.102 mL, 0.563 mmol) was added to the stirred mixture at 0 °C. After stirring for 30 min at room temperature, the reaction was quenched with Et₃N and the solvent was removed in vacuo. The crude product was purified by flash chromatography to give disaccharide **16** (hexane/EtOAc = 3:1, R_f 0.38) in 91% yield (1.87 g, 1.71 mmol) as a colorless oil; [α]_D²⁰: 46.6 (c = 0.81, CHCl₃); ATR-FTIR (cm⁻¹): 3019, 2877, 2110, 1746, 1510, 1437, 1370, 1216, 1172, 1125, 1029, 933, 894, 855, 817, 718; ¹H NMR (400 MHz, CDCl₃) δ 7.84-7.58 (m, 16H), 7.50-7.31 (m, 12H), 5.97-5.87 (m, 1H, -CH= of allyl), 5.86 (d, *J* = 3.7 Hz, 1H, Glc-1), 5.41 (dd, *J* = 10.4, 9.6 Hz, 1H, Glc-3), 5.33 (d, *J* = 12.3 Hz, 1H, -CH₂- of Nap), 5.25-5.12 (m, 3H, =CH₂ of allyl, -CH₂- of Nap), 5.10-5.01 (m, 3H, -CH₂- of Nap), 4.98 (d, *J* = 13.1 Hz, 1H, -CH₂- of Nap), 4.90-4.77 (m, 3H, -CH₂- of Nap, Glc-4), 4.43-4.34 (m, 2H, Glc-5, Ino-5), 4.31 (t, *J* = 9.5 Hz, 1H, Ino), 4.14 (t, *J* = 2.1 Hz, 1H, Ino), 4.03 (dd, *J* = 12.2, 5.6 Hz, 1H, -CH₂- of allyl), 3.95 (dd, *J* = 12.2, 5.6 Hz, 1H, -CH₂- of allyl), 3.78 (dd, *J* = 12.6, 1.9 Hz, 1H, Glc-6), 3.59-3.50 (m, 3H, Glc-6, Ino-1, Ino-4), 3.45 (dd, *J* = 9.8, 1.8 Hz, 1H, Ino-6), 3.19 (dd, *J* = 10.7, 3.6 Hz, 1H, Glc-2); ¹³C NMR (100 MHz, CDCl₃) δ 170.6 (O=C-O- of AcO), 170.1 (O=C-O- of AcO), 169.6 (O=C-O- of AcO), 136.3, 136.2, 136.0, 135.8, 134.2 (-CH= of allyl), 133.39, 133.38, 133.34, 133.32, 133.2, 133.1, 133.0, 132.9, 128.4, 128.20, 128.15, 128.1, 128.00, 127.98, 127.95, 127.83, 127.78, 127.7, 126.9, 126.8, 126.5, 126.4, 126.32, 126.27, 126.24, 126.17, 126.1, 126.00, 125.97, 125.9, 124.8, 124.7, 117.6 (=CH₂ of allyl), 97.3 (C1, *J*_{CH} = 173.2 Hz), 82.0, 81.9, 81.6, 81.0, 76.1 (-CH₂- of Nap), 75.4 (-CH₂- of Nap), 74.9, 74.4 (-CH₂- of Nap), 73.2 (-CH₂- of Nap), 73.1, 71.1 (-CH₂- of allyl), 70.5 (C3), 68.0 (C4), 67.1, 61.4 (C6), 61.1 (C2), 20.9 (-CH₃ of OAc), 20.7 (-CH₃ of OAc), 20.0 (-CH₃ of OAc); ESI-MS: *m/z* [M+Na]⁺ calcd 1116.4259, obsd 1116.4228.

2-Azido-3-*O*-(2-naphthyl)methyl-4,6-*O*-(*p*-methoxybenzylidene)-2-deoxy- α -D-glucopyranosyl-(1→6)-1-*O*-allyl-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (17**)**



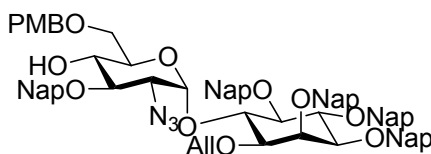
2-Azido-4,6-O-(p-methoxybenzylidene)-2-deoxy- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-1-O-allyl-2,3,4,5-tetra-O-(2-naphthyl)methyl-D-myo-inositol

The disaccharide **16** (1.75 g, 1.60 mmol) was stirred at room temperature for 30 min in the presence of NaOMe (17 mg, 0.320 mmol) in MeOH/CH₂Cl₂ (v/v = 5:1, 18 mL). After neutralization with resin, the mixture compound was removed by evaporation. The crude compound was dissolved in DMF (15 mL). Then, anisaldehyde dimethylacetal (0.329 mL, 1.93 mmol) and CSA (69 mg, 0.297 mmol) were added to the mixture and stirred overnight at room temperature. Then, the reaction mixture was quenched with aq. NH₄Cl and extracted three times with EtOAc. 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 *pseudo*-disaccharide **16a** in 86% yield (1.39 g, 1.28 mmol) as a colorless oil; R_f = 0.18 (hexane/EtOAc 3:1), $[\alpha]_D^{20}$: 69.9 (c = 0.89, CHCl₃); ATR-FTIR (cm⁻¹): 3018, 2866, 2110, 1616, 1520, 1466, 1367, 1347, 1305, 1252, 1216, 1172, 1125, 1087, 1029, 989, 928, 894, 856, 817, 745; ¹H NMR (400 MHz, CDCl₃) δ 7.89-7.74 (m, 11H), 7.71-7.66 (m, 3H), 7.63-7.60 (m, 1H), 7.56-7.37 (m, 12H), 7.30 (dd, J = 8.4, 1.2 Hz, 1H), 6.83-6.79 (m, 2H, PMB), 6.58-6.54 (m, 2H, PMB), 6.05-5.93 (m, 1H, -CH= of allyl), 5.84 (d, J = 3.7 Hz, 1H, Glc-1), 5.32 (s, 1H, -CH- of *p*-methoxybenzylidene), 5.31-5.25 (m, 1H, =CH₂ of allyl), 5.24-5.11 (m, 5H, =CH₂ of allyl, -CH₂- of Nap), 5.10 (d, J = 12.3 Hz, 1H, -CH₂- of Nap), 4.97 (d, J = 10.7 Hz, 1H, -CH₂- of Nap), 4.91 & 4.84 (ABq, J = 11.9 Hz, 2H, -CH₂- of Nap), 4.45 (t, J = 9.6 Hz, 1H), 4.36 (t, J = 9.6 Hz, 1H), 4.29-4.17 (m, 4H), 4.12-4.01 (m, 2H, -CH₂- of allyl), 3.74 (s, 3H, -OMe of PMB), 3.65-3.54 (m, 3H), 3.48 (dd, J = 9.7, 1.7 Hz, 1H), 3.41 (t, J = 9.4 Hz, 1H), 3.24 (dd, J = 10.1, 3.7 Hz, 1H, Glc-2), 2.69 (d, J = 1.6 Hz, 1H, -OH); ¹³C NMR (100 MHz, CDCl₃) δ 160.0 (Ph-O of PMB), 136.3, 136.2, 136.1, 135.8, 134.3 (-CH= of allyl), 133.6, 133.34, 133.29, 133.12, 133.07, 133.0, 132.9, 129.4, 128.2, 128.21, 128.15, 128.03, 128.01, 127.82, 127.80, 127.75, 127.7 (Ph of PMB), 127.6, 126.8, 126.7, 126.5, 126.4, 126.3, 126.23, 126.15, 126.1, 126.0, 125.92, 125.89, 125.85, 125.8, 125.6, 125.2, 125.1, 117.5 (=CH₂ of allyl), 113.4 (Ph of PMB), 101.9 (-CH- of *p*-methoxybenzylidene), 98.1 (C1, J_{CH} = 177.6 Hz), 82.04, 82.00, 81.7, 80.8, 76.0 (-CH₂- of Nap), 75.3 (-CH₂- of Nap), 75.2, 74.3 (-CH₂- of Nap), 73.2 (-CH₂- of Nap), 73.1, 71.2 (-CH₂- of allyl), 68.82 (C6), 68.79 (C3), 63.3 (C2), 62.3, 55.3 (OMe of PMB); ESI-MS: m/z [M+Na]⁺ calcd 1108.4360, obsd 1108.4437; m/z [M+K]⁺ calcd 1124.4100, obsd 1124.4168.

To a solution of obtained alcohol (1.67 g, 1.54 mmol) in DMF (15 mL) was added NaH (92 mg, 2.31 mmol, 60% in mineral oil), NapBr (0.680 g, 3.07 mmol) and TBAI (0.568 g, 1.54 mmol) at 0 °C. The reaction mixture was stirred overnight at room temperature. Then, the reaction was quenched with aq. NH₄Cl and extracted three times with EtOAc. 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 the fully protected compound **17** in 88% yield (1.66 g, 1.35 mmol) as a colorless oil; R_f = 0.25 (hexane/EtOAc 5:1), $[\alpha]_D^{20}$: 56.3 (c = 0.77, CHCl_3); ATR-FTIR (cm^{-1}): 3016, 2870, 2109, 1616, 1519, 1261, 1216, 1172, 1124, 1090, 1053, 1033, 927, 856, 802, 702; ^1H NMR (400 MHz, CDCl_3) δ 7.86-7.72 (m, 14H), 7.69 (dd, J = 8.5, 6.5 Hz, 1H), 7.65-7.56 (m, 4H), 7.53 (s, 1H), 7.50-7.35 (m, 14H), 7.30 (dd, J = 8.4, 1.5 Hz, 1H), 7.01-6.96 (m, 2H, PMB), 6.70-6.64 (m, 2H, PMB), 6.02-5.90 (m, 1H, -CH= of allyl), 5.79 (d, J = 3.8 Hz, 1H, Glc-1), 5.41 (s, 1H, -CH- of *p*-methoxybenzylidene), 5.28-5.21 (m, 1H, =CH₂ of allyl), 5.19-5.15 (m, 1H, =CH₂ of allyl), 5.15 & 4.95 (ABq, J = 10.9 Hz, 2H, -CH₂- of Nap), 5.10 & 5.06 (ABq, J = 12.4 Hz, 4H, -CH₂- of Nap), 5.01 & 4.89 (ABq, J = 11.5 Hz, 2H, -CH₂- of Nap), 4.86 & 4.80 (ABq, J = 11.9 Hz, 2H, -CH₂- of Nap), 4.39 (t, J = 9.6 Hz, 1H), 4.34-4.25 (m, 2H), 4.19 (dd, J = 10.1, 4.9 Hz, 1H, Glc-6), 4.14 (t, J = 1.8 Hz, 1H), 4.08-4.01 (m, 3H, -CH₂- of allyl, Glc-3), 3.79 (s, 3H, -OMe of PMB), 3.66 (t, J = 9.4 Hz, 1H, Glc-4), 3.63-3.54 (m, 2H), 3.52 (dd, J = 9.8, 2.2 Hz, 1H), 3.43 (dd, J = 9.7, 2.0 Hz, 1H), 3.36 (dd, J = 10.0, 3.8 Hz, 1H, Glc-6); ^{13}C NMR (100 MHz, CDCl_3) δ 159.9 (Ph-O of PMB), 136.4, 136.3, 136.0, 135.8, 135.6, 134.4 (-CH= of allyl), 133.6, 133.41, 133.39, 133.36, 133.2, 133.1, 133.01, 133.00, 130.1, 128.33, 128.29, 128.21, 128.19, 128.15, 128.12, 128.06, 128.0, 127.84, 127.82, 127.75, 127.71, 127.69, 127.6 (Ph of PMB), 127.1, 126.71, 126.66, 126.5, 126.4, 126.3, 126.2, 126.14, 126.10, 126.03, 125.95, 125.93, 125.90, 125.80, 125.78, 125.7, 125.6, 117.4 (=CH₂ of allyl), 113.4 (Ph of PMB), 101.4 (-CH- of *p*-methoxybenzylidene), 98.1 (C1, J_{CH} = 178.1 Hz), 83.0 (C4), 82.12, 82.10, 81.6, 81.0, 75.93 (-CH₂- of Nap), 75.92 (C3), 75.5 (-CH₂- of Nap), 75.3, 74.9 (-CH₂- of Nap), 74.4 (-CH₂- of Nap), 73.3, 73.2 (-CH₂- of Nap), 71.2 (-CH₂- of allyl), 69.0 (C6), 63.4 (C2), 62.7, 55.4 (OMe of PMB); ESI-MS: m/z $[\text{M}+\text{Na}]^+$ calcd 1248.4986, obsd 1248.5008.

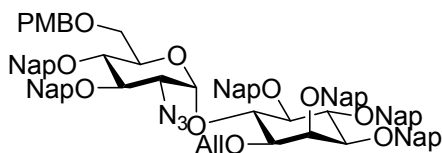
2-Azido-3-O-(2-naphthyl)methyl-6-O-(p-methoxybenzyl)-2-deoxy- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-1-O-allyl-2,3,4,5-tetra-O-(2-naphthyl)methyl-D-myo-inositol 16a



A mixture of the protected *pseudo*-disaccharide **17** (2.01 g, 1.64 mmol), NaBH_3CN (1.03 g, 16.4 mmol), and freshly activated 4 Å molecular sieves in dry $\text{THF}/\text{CH}_2\text{Cl}_2$ (v/v = 1:1, 32.8 mL) was stirred at room temperature and argon atmosphere for 40 min. Then $\text{CF}_3\text{CO}_2\text{H}$ (2.53 mL, 32.8 mmol) was added dropwise. After stirring during 9 h at room temperature, the reaction mixture was quenched by addition of a saturated aq. NaHCO_3 . The mixture was filtered through a pad of Celite. The organic phase was separated and the remaining aqueous phase was extracted with CH_2Cl_2 . The combined organic phase was washed with brine, dried with Na_2SO_4 , and then filtered and concentrated in vacuo.

The residue was purified by flash chromatography to give *pseudo*-disaccharide **19** (hexane/EtOAc = 3:1, R_f 0.35) in 80% yield (1.61 g, 1.31 mmol) as a colorless oil; $[\alpha]_D^{20}$: 23.2 (c = 0.86, CHCl_3); ATR-FTIR (cm^{-1}): 3012, 2947, 2872, 2839, 2107, 1613, 1587, 1512, 1465, 1442, 1364, 1347, 1304, 1248, 1216, 1173, 1124, 1034, 962, 928, 894, 855, 815, 747; ^1H NMR (400 MHz, CDCl_3) δ 7.87-7.74 (m, 15H), 7.68-7.60 (m, 5H), 7.56-7.33 (m, 15H), 6.91-6.87 (m, 2H, PMB), 6.73-6.69 (m, 2H, PMB), 6.01-5.89 (m, 1H, $-\text{CH}=\text{}$ of allyl), 5.77 (d, J = 3.7 Hz, 1H, Glc-1), 5.28-5.14 (m, 4H, $=\text{CH}_2$ of allyl, $-\text{CH}_2-$ of Nap), 5.09 (d, J = 12.4 Hz, 1H, $-\text{CH}_2-$ of Nap), 5.07-4.99 (m, 4H, $-\text{CH}_2-$ of Nap), 4.90 (d, J = 11.5 Hz, 1H, $-\text{CH}_2-$ of Nap), 4.85 & 4.80 (ABq, J = 11.9 Hz, 2H, $-\text{CH}_2-$ of Nap), 4.36 (t, J = 9.6 Hz, 1H), 4.31 (t, J = 9.6 Hz, 1H), 4.17-4.14 (m, 1H), 4.13 & 3.92 (ABq, J = 11.5 Hz, 2H, $-\text{CH}_2-$ of PMB), 4.10-4.02 (m, 3H, $-\text{CH}_2-$ of allyl, Glc-5), 3.88 (d, J = 10.1 Hz, 1H, Glc-3), 3.75 (s, 3H, $-\text{OMe}$ of PMB), 3.70 (td, J = 9.6, 3.2 Hz, 1H, Glc-4), 3.56 (t, J = 8.0 Hz, 1H), 3.53 (dd, J = 9.6, 2.2 Hz, 1H), 3.44 (dd, J = 9.7, 1.8 Hz, 1H), 3.29 (dd, J = 10.3, 3.7 Hz, 1H, Glc-2), 3.24 (dd, J = 10.3, 4.5 Hz, 1H, Glc-6), 3.08 (dd, J = 10.3, 3.4 Hz, 1H, Glc-6); ^{13}C NMR (100 MHz, CDCl_3) δ 159.1 (Ph-O of PMB), 136.4, 136.2, 136.1, 135.9, 135.8, 134.4 ($-\text{CH}=\text{}$ of allyl), 133.5, 133.41, 133.36, 133.35, 133.3, 133.2, 133.13, 133.09, 133.0, 132.9, 129.9, 129.4 (Ph of PMB), 128.4, 128.3, 128.2, 128.13, 128.10, 128.07, 128.06, 128.0, 127.9, 127.83, 127.79, 127.73, 127.70, 127.0, 126.72, 126.69, 126.5, 126.4, 126.3, 126.20, 126.18, 126.16, 126.12, 126.10, 126.04, 126.03, 125.98, 125.94, 125.89, 125.83, 125.78, 125.6, 117.2 ($=\text{CH}_2$ of allyl), 113.7 (Ph of PMB), 97.8 (C1 , J_{CH} = 174.9 Hz), 82.1, 81.7, 80.9, 79.4 (C3), 76.0 ($-\text{CH}_2-$ of Nap), 75.6 ($-\text{CH}_2-$ of Nap), 75.4, 75.0 ($-\text{CH}_2-$ of Nap), 74.3 ($-\text{CH}_2-$ of Nap), 73.1 ($-\text{CH}_2-$ of Nap), 73.00, 72.96 ($-\text{CH}_2-$ of PMB), 72.7 (C4), 71.2 ($-\text{CH}_2-$ of allyl), 69.4 (C5), 69.0 (C6), 63.0 (C2), 55.3 (OMe of PMB); ESI-MS: m/z $[\text{M}+\text{Na}]^+$ calcd 1250.5143, obsd 1250.5138.

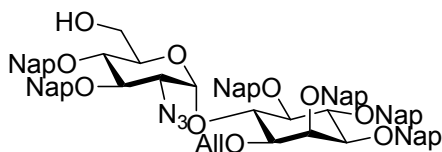
2-Azido-3,4-di-*O*-(2-naphthyl)methyl-6-*O*-(*p*-methoxybenzyl)-2-deoxy- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-1-*O*-allyl-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (3**)**



To a solution of alcohol **16a** (0.330 g, 0.269 mmol) in DMF (3 mL) was added NaH (16.0 mg, 0.403 mmol, 60% in mineral oil), Bu_4NI (99.0 mg, 0.269 mmol) and NapBr (89.0 mg, 0.403 mmol) at 0 °C. The reaction was stirred for 14h at room temperature, quenched with aq. NH_4Cl and diluted with ethyl acetate. The organic layer was washed with $\text{Na}_2\text{S}_2\text{O}_3$ (5% in water) and brine, dried over MgSO_4 , filtered and concentrated. The crude product was purified by silica gel column chromatography to give *pseudo*-dimer **3** in 82% yield (0.301 g, 0.220 mmol) as a colorless oil; R_f = 0.30 (hexane/EtOAc

4:1), $[\alpha]_{\text{D}}^{20}$: 38.9 ($c = 0.71$, CHCl_3); ATR-FTIR (cm^{-1}): 3057, 3013, 2929, 2860, 2107, 1511, 1464, 1365, 1347, 1304, 1249, 1216, 1172, 1125, 1080, 1035, 953, 893, 855, 815, 744; ^1H NMR (400 MHz, CDCl_3) δ 7.88-7.57 (m, 24H), 7.51-7.43 (m, 11H), 7.42-7.26 (m, 6H), 6.90 (dd, $J = 8.5, 1.5$ Hz, 1H), 6.88-6.85 (m, 2H, PMB), 6.61-6.57 (m, 2H, PMB), 6.03-5.91 (m, 1H, $-\text{CH}=\text{ of allyl}$), 5.83 (d, $J = 3.7$ Hz, 1H, Glc-1), 5.31-5.16 (m, 4H, $=\text{CH}_2$ of allyl, $-\text{CH}_2-$ of Nap), 5.11 (d, $J = 12.0$ Hz, 1H, $-\text{CH}_2-$ of Nap), 5.07 (d, $J = 12.3$ Hz, 1H, $-\text{CH}_2-$ of Nap), 5.07-4.99 (m, 3H, $-\text{CH}_2-$ of Nap), 4.91 (d, $J = 11.6$ Hz, 1H, $-\text{CH}_2-$ of Nap), 4.86 & 4.81 (ABq, $J = 11.8$ Hz, 2H, $-\text{CH}_2-$ of Nap), 4.70 & 4.22 (ABq, $J = 11.2$ Hz, 2H, $-\text{CH}_2-$ of Nap), 4.44 & 3.95 (ABq, $J = 11.8$ Hz, 2H, $-\text{CH}_2-$ of PMB), 4.41 (t, $J = 9.6$ Hz, 1H, Ino-6), 4.35 (t, $J = 9.5$ Hz, 1H), 4.18-4.10 (m, 2H), 4.08-4.01 (m, 3H, $-\text{CH}_2-$ of allyl, Glc-3), 3.74 (dd, $J = 10.0, 9.3$ Hz, 1H, Glc-4), 3.60-3.52 (m, 2H), 3.55 (s, 3H, $-\text{OMe}$ of PMB), 3.45 (dd, $J = 9.8, 1.9$ Hz, 1H, Ino-1), 3.39 (dd, $J = 10.4, 3.7$ Hz, 1H, Glc-2), 3.20 (dd, $J = 10.7, 1.5$ Hz, 1H, Glc-6), 3.03 (dd, $J = 10.7, 1.5$ Hz, 1H, Glc-6); ^{13}C NMR (100 MHz, CDCl_3) δ 159.1 (Ph-O of PMB), 136.4, 136.18, 136.15, 136.0, 135.81, 135.79, 134.4 ($-\text{CH}=\text{ of allyl}$), 133.40, 133.37, 133.3, 133.23, 133.15, 133.1, 132.98, 132.95, 132.8, 130.0 (Ph of PMB), 129.7, 128.3, 128.23, 128.18, 128.13, 128.09, 128.05, 128.0, 127.92, 127.85, 127.82, 127.75, 127.72, 127.68, 126.8, 126.7, 126.5, 126.4, 126.3, 126.2, 126.14, 126.13, 126.09, 126.08, 126.00, 125.96, 125.94, 125.91, 125.89, 125.84, 125.81, 125.66, 125.65, 125.0, 117.0 ($=\text{CH}_2$ of allyl), 113.7 (Ph of PMB), 98.0 (C1), 82.19, 82.15, 81.7, 80.9, 80.4 (C3), 78.2 (C4), 76.0 ($-\text{CH}_2-$ of Nap), 75.8 (Ino-6), 75.4 ($-\text{CH}_2-$ of Nap), 75.3 ($-\text{CH}_2-$ of Nap), 74.7 ($-\text{CH}_2-$ of Nap), 74.3 ($-\text{CH}_2-$ of Nap), 73.1 ($-\text{CH}_2-$ of Nap), 73.00, 72.98 ($-\text{CH}_2-$ of PMB), 71.1 ($-\text{CH}_2-$ of allyl), 70.3 (C5), 67.0 (C6), 63.6 (C2), 55.1 (OMe of PMB); ESI-MS: m/z $[\text{M}+\text{Na}]^+$ calcd 1390.5769, obsd 1390.5752.

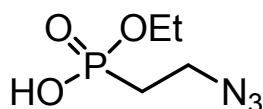
2-Azido-3,4-di-*O*-(2-naphthyl)methyl-2-deoxy- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-1-*O*-allyl-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (24**)**



A mixture of *pseudo*-disaccharide **3** (0.301 g, 0.220 mmol) and TFA (0.45 mL) in CH_2Cl_2 (3 mL) was stirred at 0 $^\circ\text{C}$ for 15 min. The solution was quenched with Et_3N and the solvent was removed in vacuo. The crude product was purified by silica gel column chromatography to give the alcohol **24** in 91% yield (0.249 g, 0.199 mmol) as a colorless oil; $R_f = 0.38$ (hexane/EtOAc 5:2), $[\alpha]_{\text{D}}^{20}$: 44.1 ($c = 0.75$, CHCl_3); ATR-FTIR (cm^{-1}): 3060, 3013, 2876, 2107, 1510, 1458, 1365, 1347, 1272, 1249, 1216, 1172, 1124, 1055, 1024, 953, 932, 893, 855, 815, 747; ^1H NMR (400 MHz, CDCl_3) δ 7.88-7.72 (m, 14H), 7.70-7.63 (m, 6H), 7.57-7.37 (m, 20H), 7.25-7.21 (m, 1H), 7.14 (dd, $J = 8.3, 1.5$ Hz, 1H), 6.07-

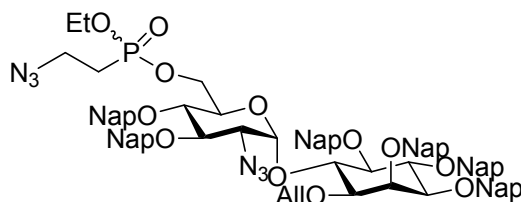
5.93 (m, 1H, -CH= of allyl), 5.80 (d, $J = 3.3$ Hz, 1H, Glc-1), 5.32-5.19 (m, 4H, =CH₂ of allyl, -CH₂- of Nap), 5.15-5.04 (m, 5H, -CH₂- of Nap), 4.97 (d, $J = 11.3$ Hz, 1H, -CH₂- of Nap), 4.92-4.80 (m, 3H, -CH₂- of Nap), 4.69 (d, $J = 11.3$ Hz, 1H, -CH₂- of Nap), 4.42-4.31 (m, 2H), 4.20-4.04 (m, 5H, -CH₂- of allyl, Glc-3, Glc-5, Ino), 3.68 (t, $J = 9.5$ Hz, 1H, Glc-4), 3.63-3.54 (m, 2H), 3.51-3.45 (m, 1H, Ino-1, Glc-6), 3.34 (dd, $J = 10.3, 3.4$ Hz, 1H, Glc-2), 3.23 (t, $J = 9.1$ Hz, 1H, Glc-6); ¹³C NMR (100 MHz, CDCl₃) δ 136.3, 136.2, 135.80, 135.76, 135.75, 135.6, 134.4 (-CH= of allyl), 133.38, 133.36, 133.34, 133.32, 133.30, 133.25, 133.12, 133.08, 133.01, 132.98, 132.9, 128.33, 128.29, 128.17, 128.15, 128.09, 128.08, 128.0, 127.84, 127.81, 127.79, 127.76, 127.7, 126.8, 126.74, 126.68, 126.6, 126.5, 126.4, 126.3, 126.2, 126.12, 126.07, 126.0, 125.9, 125.83, 125.75, 125.6, 117.4 (=CH₂ of allyl), 97.7 (C1), 82.2, 82.0, 81.7, 80.9, 80.1 (C3), 78.0 (C4), 76.0 (-CH₂- of Nap), 75.8 (-CH₂- of Nap), 75.5, 75.4 (-CH₂- of Nap), 75.1 (-CH₂- of Nap), 74.3 (-CH₂- of Nap), 73.1 (-CH₂- of Nap), 72.9, 71.2 (-CH₂- of allyl), 70.9 (C5), 63.7 (C2), 61.1 (C6); ESI-MS: m/z [M+Na]⁺ calcd 1270.5194, obsd 1270.5203; m/z [M+K]⁺ calcd 1286.4933, obsd 1286.4937.

***O*-Ethyl (2-azidoethyl)phosphonic acid (**22**)**



LiBr (0.341 g, 3.93 mmol) was added in one portion to a solution of diethyl 2-azidoethylphosphonate³ (0.678 g, 3.27 mmol) in 2-pentanone (5 mL). The mixture was heated at 105-110 °C for 2 h. Then the solvent was evaporated under reduced pressure, and the solid residue was washed with Et₂O. The crude lithium salt of product was suspended in CH₂Cl₂ (10 mL) and HCl (20% in water) was added to the suspension until pH 1 was reached. NaCl (2.0 g) was added to the two-phase mixture, the organic layer was separated and the aqueous layer extracted with CH₂Cl₂. The combined extracts were dried over Na₂SO₄, the solvent evaporated under reduced pressure and the rest of the volatile material was removed in vacuo to give analytically pure phosphonic acid **22** as a yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 10.58 (brs, 1H, OH), 4.12 (dq, $J = 14.4, 7.1$ Hz, 2H, OCH₂ of Et), 3.55 (dt, $J = 12.3, 7.7$ Hz, 2H, CH₂N₃), 2.15-2.02 (m, 2H, PCH₂), 1.35 (t, $J = 7.1$ Hz, 3H, CH₃ of Et); ¹³C NMR (100 MHz, CDCl₃) δ 61.78 (d, $J_{PC} = 6.7$ Hz, OCH₂ of Et), 45.35 (d, $J_{PC} = 1.5$ Hz, CH₂N₃), 26.31 (d, $J_{PC} = 143.4$ Hz, PCH₂), 16.43 (d, $J_{PC} = 6.5$ Hz, CH₃ of Et); ³¹P NMR (162 MHz, CDCl₃) δ 29.46; ESI-MS: m/z [M+H]⁺ calcd 180.0538, obsd 180.0545; m/z [M+Na]⁺ calcd 202.0357, obsd 202.0360; m/z [M+K]⁺ calcd 218.0097, obsd 218.0080.

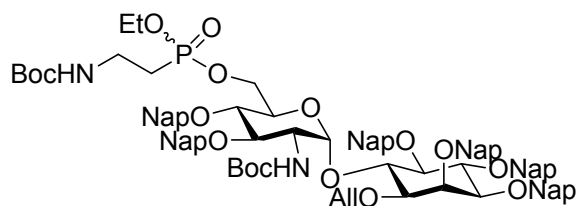
2-Azido-3,4-di-*O*-(2-naphthyl)methyl-6-*O*-((2-azidoethyl)phosphonic acid ethyl ester)-2-deoxy- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-1-*O*-allyl-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (25**)**



To a solution of phosphonic acid **22** (140 mg, 0.782 mmol) and dry DMF (6 μ L, 0.0782 mmol) in CH_2Cl_2 (3 mL) at 0 $^\circ\text{C}$ and argon atmosphere was added oxalylic chloride (75 μ L, 0.860 mmol) via syringe. After 1 h at room temperature, the reaction was monitored with ^{31}P -NMR, showing full conversion (^{31}P NMR (162 MHz, CDCl_3) δ 37.71). The reaction mixture was concentrated in vacuo to yield a brown oil. Due to the sensitivity and toxicity of this compound, the compound was used immediately. The solution of crude phosphonochloridate was added dropwise to a solution of pseudodimer **5** (97 mg, 0.078 mmol), DIPEA (0.271 mL, 1.55 mmol) and 1*H*-tetrazole (0.173 mL, 0.078 mmol, 0.45M solution in CH_3CN) in toluene (2 mL) at 0 $^\circ\text{C}$. The reaction was quenched after overnight at room temperature with water and diluted with EtOAc. The organic phase was washed with aq. NaHCO_3 and then brine, dried over MgSO_4 , filtered and concentrated in vacuo. The crude product was purified by flash chromatography to give ethyl phosphonate *pseudo*-disaccharide **25** in 72% yield (79 mg, 0.056 mmol, ~1:1 mixture of diastereomers) as a colorless oil; R_f = 0.25 (hexane/EtOAc 3:2), ^1H NMR (400 MHz, CDCl_3 , ~1:1 mixture of diastereomers) δ 7.88-7.74 (m, 28H), 7.70-7.63 (m, 12H), 7.59-7.38 (m, 40H), 7.30-7.27 (m, 1H), 7.26-7.22 (m, 1H), 7.16 (dd, J = 8.5, 1.1 Hz, 1H), 7.10 (dd, J = 8.4, 1.0 Hz, 1H), 6.06-5.94 (m, 2H, -CH= of allyl), 5.77 (d, J = 3.5 Hz, 2H, Glc-1), 5.31-5.19 (m, 8H, =CH₂ of allyl, -CH₂- of Nap), 5.15-5.05 (m, 10H, -CH₂- of Nap), 4.95-4.80 (m, 8H, -CH₂- of Nap), 4.71 (d, J = 11.2 Hz, 1H, -CH₂- of Nap), 4.65 (d, J = 11.3 Hz, 1H, -CH₂- of Nap), 4.39-4.32 (m, 4H), 4.25-4.00 (m, 10H, -CH₂- of allyl, Glc-3, Glc-5, Ino), 3.93-3.83 (m, 3H, OCH₂ of Et, Glc-6), 3.77-3.66 (m, 3H, OCH₂ of Et, Glc-6), 3.64-3.45 (m, 9H, Glc-4, Ino-1, Glc-6, Ino), 3.42-3.28 (m, 7H, Glc-6, Glc-2, CH₂N₃), 1.86-1.75 (m, 4H, PCH₂), 1.09 (t, J = 7.1 Hz, 3H, CH₃ of Et), 1.08 (t, J = 7.0 Hz, 3H, CH₃ of Et); ^{13}C NMR (100 MHz, CDCl_3 , ~1:1 mixture of diastereomers) δ 136.3, 136.09, 136.07, 136.0, 135.9, 135.72, 135.70, 135.61, 135.58, 135.44, 135.43, 134.4 (-CH= of allyl), 133.4, 133.33, 133.28, 133.26, 133.2, 133.13, 133.07, 133.04, 133.02, 132.97, 132.8, 128.34, 128.33, 128.32, 128.19, 128.17, 128.16, 128.15, 128.1, 128.02, 128.00, 127.98, 127.9, 127.82, 127.80, 127.77, 127.68, 127.67, 126.87, 126.85, 126.81, 126.78, 126.7, 126.6, 126.5, 126.4, 126.3, 126.20, 126.18, 126.15, 126.13, 126.07, 126.05, 126.01, 125.99, 125.97, 125.95, 125.93, 125.88, 125.85, 125.83, 125.78, 125.76, 125.7, 125.6, 125.5, 117.4 (=CH₂ of allyl), 117.3 (=CH₂ of

allyl), 97.73 (C1), 97.72 (C1), 82.2, 81.9, 81.5, 80.98, 80.97, 80.4 (C3), 80.3 (C3), 77.8 (C4), 77.7 (C4), 76.1 (-CH₂- of Nap), 76.0 (-CH₂- of Nap), 75.74, 75.68, 75.65 (-CH₂- of Nap), 75.54 (-CH₂- of Nap), 75.47 (-CH₂- of Nap), 75.4 (-CH₂- of Nap), 75.1 (-CH₂- of Nap), 75.0 (-CH₂- of Nap), 74.3 (-CH₂- of Nap), 74.2 (-CH₂- of Nap), 73.1 (-CH₂- of Nap*2), 72.7, 72.6, 71.21 (-CH₂- of allyl), 71.18 (-CH₂- of allyl), 69.47 (d, J_{PC} = 6.0 Hz, C5), 69.34 (d, J_{PC} = 6.3 Hz, C5), 63.97 (d, J_{PC} = 7.0 Hz, C6), 63.94 (d, J_{PC} = 6.7 Hz, C6), 63.62 (C2), 63.58 (C2), 61.91 (d, J_{PC} = 6.7 Hz, OCH₂ of Et), 61.82 (d, J_{PC} = 6.6 Hz, OCH₂ of Et), 45.27 (d, J_{PC} = 1.4 Hz, CH₂N₃), 45.20 (d, J_{PC} = 1.3 Hz, CH₂N₃), 25.79 (d, J_{PC} = 140.9 Hz, PCH₂), 25.55 (d, J_{PC} = 140.1 Hz, PCH₂), 16.37 (d, J_{PC} = 5.6 Hz, CH₃ of Et), 16.32 (d, J_{PC} = 5.9 Hz, CH₃ of Et); ³¹P NMR (162 MHz, CDCl₃, ~1:1 mixture of diastereomers) δ 27.13, 26.94; ESI-MS: m/z [M+Na]⁺ calcd 1431.5548, obsd 1431.5589; m/z [M+K]⁺ calcd 1447.5287, obsd 1447.5324.

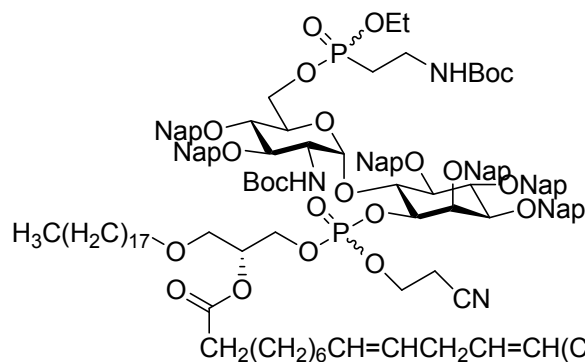
2-[N-(tert-butoxycarbonylamido]-3,4-di-O-(2-naphthyl)methyl-6-O-((2-N-(tert-butoxycarbonylaminoethyl)phosphonic acid ethyl ester)-2-deoxy-α-D-glucopyranosyl-(1→6)-1-O-allyl-2,3,4,5-tetra-O-(2-naphthyl)methyl-D-myo-inositol (26)



Dithiothreitol (41 mg, 0.267 mmol) and DIPEA (58 μL, 0.333 mmol) were added to a solution of phosphonate **25** (94 mg, 0.067 mmol) in MeCN/H₂O (v/v = 9:1, 2 mL) under argon atmosphere. The solution was stirred at room temperature for 2 h. The reaction mixture was diluted with toluene and evaporated. The solid remaining was treated with Boc₂O (62 μL, 0.268 mmol) and DIPEA (47 μL, 0.268 mmol) in MeOH (1mL). After 2.5 h at room temperature, the solvent was evaporated and the crude product chromatographed on silica gel to give product **26** in 86% yield (89 mg, 0.057 mmol, ~1:1 mixture of diastereomers) as a colorless oil; R_f = 0.38 (hexane/EtOAc = 1:1), ¹H NMR (400 MHz, CDCl₃, ~1:1 mixture of diastereomers) δ 7.85-7.72 (m, 14H), 7.69-7.62 (m, 6H), 7.60-7.36 (m, 20H), 7.32-7.27 (m, 1H), 7.23-7.16 (m, 1H), 5.94-5.80 (m, 1H, -CH= of allyl), 5.53-5.46 (m, 1H, Glc-1), 5.26-5.12 (m, 4H, =CH₂ of allyl, -CH₂- of Nap), 5.11-4.96 (m, 5H, =CH₂ of allyl, -CH₂- of Nap), 4.95-4.88 (m, 2H, -CH₂- of Nap), 4.84 (d, J = 11.9 Hz, 1H), 4.78 (d, J = 12.0 Hz, 1H), 4.72 (d, J = 11.1 Hz, 1H), 4.67 (d, J = 11.1 Hz, 1H), 4.34-4.26 (m, 2H), 4.19-4.09 (m, 2H), 4.07-3.95 (m, 3H Glc-2, Glc-6, -CH₂- of allyl), 3.91-3.62 (m, 6H, OCH₂ of Et, Glc-6, -CH₂- of allyl, C), 3.50-3.40 (m, 2H), 3.35-3.16 (m, 3H, C, CH₂NHBoc), 1.71-1.60 (m, 2H, PCH₂), 1.45-1.39 (m, 18H, CH₃- of Boc), 1.06 (t, J = 7.0 Hz, 3H, CH₃ of Et), 1.04 (t, J = 7.2 Hz, 3H, CH₃ of Et); ¹³C NMR (100 MHz, CDCl₃, ~1:1

mixture of diastereomers) δ 155.74 (-O=C-O- of Boc), 155.73 (-O=C-O- of Boc), 155.3 (-O=C-O- of Boc), 136.2, 136.13, 136.12, 136.03, 135.99, 135.96, 135.8, 135.71, 135.68, 134.2 (-CH= of allyl), 133.36, 133.35, 133.32, 133.30, 133.26, 133.2, 133.1, 133.04, 132.99, 132.87, 132.85, 128.3, 128.23, 128.17, 128.15, 128.1, 128.0, 127.83, 127.81, 127.75, 127.71, 127.69, 126.84, 126.80, 126.72, 126.71, 126.66, 126.6, 126.53, 126.51, 126.48, 126.45, 126.4, 126.3, 126.21, 126.15, 126.12, 126.08, 126.06, 126.02, 126.00, 125.97, 125.9, 125.81, 125.79, 125.76, 125.6, 118.2 (=CH₂ of allyl), 99.3 (C1), 99.1 (C1), 82.19, 82.16, 81.4, 81.3, 80.82, 80.76, 80.7, 79.5 (C of Boc), 79.3 (C of Boc), 77.6, 76.6, 76.4, 76.1 (-CH₂- of Nap), 76.0 (-CH₂- of Nap), 75.7 (-CH₂- of Nap), 75.5 (-CH₂- of Nap), 75.34 (-CH₂- of Nap), 75.29 (-CH₂- of Nap), 75.1 (-CH₂- of Nap), 75.0 (-CH₂- of Nap), 74.1 (-CH₂- of Nap), 74.0 (-CH₂- of Nap), 73.1 (-CH₂- of Nap*2), 72.3, 72.2, 71.0 (-CH₂- of allyl), 70.32 (C5), 70.26 (C5), 64.0 (d, J_{PC} = 4.0 Hz, C6), 63.8 (d, J_{PC} = 4.0 Hz, C6), 61.8 (d, J_{PC} = 7.1 Hz, OCH₂ of Et), 61.6 (d, J_{PC} = 7.0 Hz, OCH₂ of Et), 54.7 (C2), 54.6 (C2), 34.64 (CH₂NHBoc), 34.58 (CH₂NHBoc), 28.6 (CH₃ of Boc), 28.52 (CH₃ of Boc), 28.51 (CH₃ of Boc), 26.2 (d, J_{PC} = 141.1 Hz, PCH₂), 25.7 (d, J_{PC} = 140.3 Hz, PCH₂), 16.4 (CH₃ of Et), 16.3 (CH₃ of Et); ³¹P NMR (162 MHz, CDCl₃, ~1:1 mixture of diastereomers) δ 30.43, 29.81; ESI-MS: m/z [M+Na]⁺ calcd 1580.6820, obsd 1580.6711; m/z [M+K]⁺ calcd 1596.6559, obsd 1596.6466.

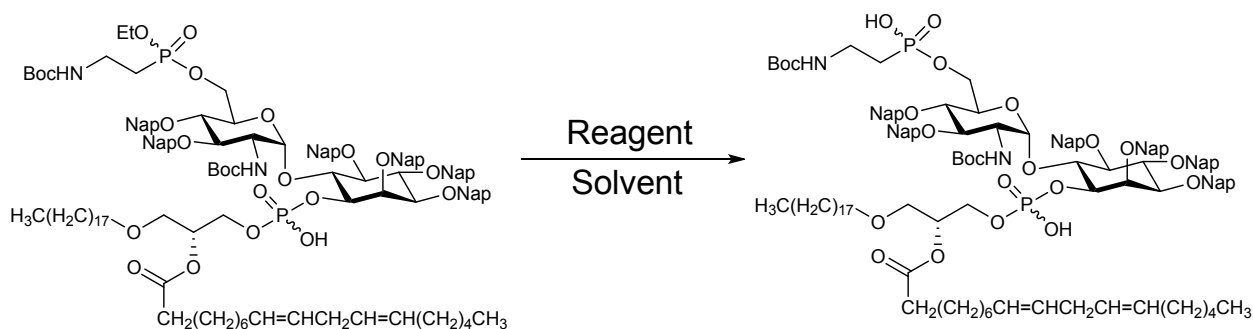
2-[*N*-(*tert*-butoxycarbonyl)amido]-3,4-di-*O*-(2-naphthyl)methyl-6-*O*-((2-*N*-(*tert*-butoxycarbonyl)aminoethyl)phosphonic acid ethyl ester)-2-deoxy- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-1-*O*-[1-*O*-(octadecyl)-2-*O*-(9*Z*,12*Z*-octadecanoyl)-*sn*-glycero-3-phosphocynoethyl]-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (28)



The *pseudo*-disaccharide **26** (90 mg, 0.058 mmol) and sodium acetate (2.84 mg, 0.035 mmol) were dissolved in a mixture of acetic acid (1 mL) and water (60 μ L). PdCl₂ (61 mg, 0.347 mmol) was added, and the reaction mixture was stirred for 9 h. The reaction mixture was filtered through Celite® and concentrated in vacuo. Then, the reaction mixture was poured into saturated aq. NaHCO₃, and the aqueous layer was extracted with ethyl acetate. The organic layers were combined and dried over Na₂SO₄, filtered and concentrated. The residue was purified by flash column chromatography to

afford alcohol compound **27** in 71% yield (62 mg, 0.041 mmol, R_f 0.18 (hexane/EtOAc 1:1), ^{31}P NMR (162 MHz, CDCl_3) δ 30.47, 29.77; ESI-MS: m/z $[\text{M}+\text{Na}]^+$ cald 1539.6473, obsd 1539.6439; m/z $[\text{M}+\text{K}]^+$ cald 1555.6213, obsd 1555.6179). Without further characterization the deallylated **27** (26.0 mg, 17.0 μmol) and tetrazole (0.45 M solution in acetonitrile, 0.381 mL, 0.171 mmol) were stirred in anhydrous $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (v/v = 3:1, 3 mL) for 10 min at room temperature. A solution of freshly prepared phosphoramidite **3** (69.0 mg, 86.0 μmol) in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (v/v = 3:1, 1 mL) was slowly added. The reaction was stirred at room temperature for 2 h, was cooled to -40°C and *tert*-butyl hydroperoxide (5.5 M solution in *n*-decane, 62 μL , 0.343 mmol) was added. After 1 h at -40°C , Me_2S (51 μL , 0.685 mmol) was added and the mixture was stirred for 1 h at -40°C . Then, the reaction mixture was poured into saturated NaHCO_3 , and extracted. The aqueous layer was extracted with CH_2Cl_2 ; the organic layers were combined, dried over Na_2SO_4 , filtered and concentrated. The residue was purified by flash column chromatography to afford the desired compound **28** in 64% yield (24.5 mg, 10.94 μmol , ~1:1 mixture of diastereomers) as a colorless oil; R_f = 0.15 ($\text{CH}_2\text{Cl}_2/\text{MeOH}$ 20:1), ^1H NMR (400 MHz, CDCl_3 ~1:1 mixture of diastereomers) δ 7.86 (s, 5H), 7.86 – 7.27 (m, 38H), 7.23 – 7.13 (m, 1H), 7.10 – 6.99 (m, 1H), 5.56 (d, J = 6.4 Hz, 1H), 5.43 – 5.24 (m, 1H), 5.23 – 4.59 (m, 1H), 4.07 (dd, J = 45.1, 19.7 Hz, 1H), 3.84 (s, 1H), 3.80 – 3.33 (m, 1H), 3.33 – 2.96 (m, 1H), 2.85 (dt, J = 11.3, 6.8 Hz, 1H), 2.74 (t, J = 10.9 Hz, 1H), 2.30 (d, J = 7.6 Hz, 1H), 2.15 (dd, J = 16.3, 8.4 Hz, 1H), 2.08 – 1.87 (m, 2H), 1.46 (s, 2H), 1.42 – 1.30 (m, 6H), 1.24 (s, 12H), 1.13 (t, J = 7.2 Hz, 6H), 0.86 (t, J = 6.4 Hz, 3H); ^{31}P NMR (162 MHz, CDCl_3 , ~1:1 mixture of diastereomers) δ : 30.24, 29.82, -1.95, -2.00, -2.18.

2-[*N*-(*tert*-butoxycarbonyl)amido]-3,4-di-*O*-(2-naphthyl)methyl-6-*O*-((2-*N*-(*tert*-butoxycarbonyl)aminoethyl)phosphonate)-2-deoxy- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-1-*O*-[1-*O*-(octadecyl)-2-*O*-(9*Z*,12*Z*-octadecanoyl)-*sn*-glycero-3-phosphocynoethyl]-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol



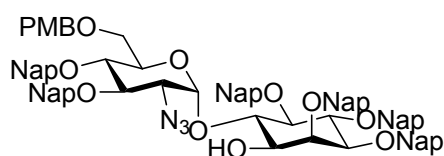
The phosphorylated and fully protected pseudo-disaccharide **28** (5 mg, 2.2 μmol) was treated with a

reagents and conditions described in the table below. The progress of the reaction was followed by TLC (Hexanes/EtOAc/CH₂Cl₂ (1:1:1). At the reaction time, the obtained products were analyzed by ³¹P and ¹H NMR spectroscopy.

Table 1. Various deethylation conditions² of ethylphosphonate of compound **28**

Solvent	Reagent	Temperature	Time	Result
1,4-Dioxane	PhSH, Et ₃ N	Room temp.	2 days	no reaction
THF	PhSH, Et ₃ N	Room temp.	2 days	no reaction
DMF	PhSH, Et ₃ N	Room temp.	2 days	no reaction
DMF	PhSH, Et ₃ N	60 °C	2 days	no reaction
DMF	PhSH, DIPEA	Room temp.	2 days	no reaction
DMF	PhSH, DIPEA	60 °C	overnight	decomposition
DMF	2-methyl-5- <i>tert</i> -butylthiophenol, DIPEA	Room temp.	2 days	no reaction
DMF	2-methyl-5- <i>tert</i> -butylthiophenol, DIPEA	60 °C	overnight	decomposition
Acetone	NaI	60 °C	overnight	no reaction
2-Pentanone	LiBr	110 °C	2 h	decomposition
Ethanol	1N HCl	reflux	2 h	no reaction
Ethanol	6N HCl	reflux	2 h	no reaction
Ethanol	12N HCl	reflux	2 h	decomposition

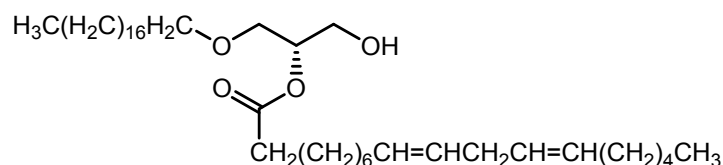
2-Azido-3,4-di-*O*-(2-naphthyl)methyl-6-*O*-(*p*-methoxybenzyl)-2-deoxy- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (29**)**



A solution of [IrCOD(PPh₂Me)₂]PF₆ (6.67 mg, 7.89 μ mol) in THF (0.5 mL) was stirred under hydrogen at room temperature until the colour turned from red to colourless to pale yellow. The hydrogen atmosphere was changed to an argon atmosphere and the solution was added into a THF (1 mL) solution of disaccharide **3** (0.108 g, 78.9 μ mol). The reaction was stirred at room temperature for 5 h, then the solvent was removed and the residue was dissolved in acetone/H₂O (v/v = 9:1, 3 mL). Mercury(II) chloride (0.129 g, 0.473 mmol) and mercury(II) oxide (1.71 mg, 7.89 μ mol) were added. After 1 h, the solvent was removed. The residue was dissolved in CH₂Cl₂ and washed with saturated NaHCO₃, dried over Na₂SO₄, filtered and concentrated. The crude product was purified by silica gel

column chromatography to give *pseudo*-dimer **29** in 91% yield (95.7 mg, 0.072 mmol) as a colorless oil; R_f = 0.20 (hexane/EtOAc 3:1), ^1H NMR (400 MHz, CDCl_3) δ 7.88-7.61 (m, 22H), 7.59-7.33 (m, 19H), 7.01 (d, J = 8.4 Hz, 1H), 6.82-6.75 (m, 2H, PMB), 6.62-6.56 (m, 2H, PMB), 5.52 (d, J = 3.6 Hz, 1H, Glc-1), 5.26 & 4.87 (ABq, J = 11.5 Hz, 2H, $-\text{CH}_2-$ of Nap), 5.24-5.17 (m, 2H, $-\text{CH}_2-$ of Nap), 5.08-5.00 (m, 4H, $-\text{CH}_2-$ of Nap), 4.88 (s, 2H, $-\text{CH}_2-$ of Nap), 4.73 (d, J = 11.0 Hz, 1H, $-\text{CH}_2-$ of Nap), 4.35-4.28 (m, 3H, $-\text{CH}_2-$ of Nap, $-\text{CH}_2-$ of PMB, Ino-6), 4.18 (t, J = 2.6 Hz, 1H), 4.14 (t, J = 9.5 Hz, 1H), 4.07 (t, J = 9.6 Hz, 1H), 3.99 (t, J = 10.2 Hz, 1H, Glc-5), 3.79-3.69 (m, 3H), 3.65-3.59 (m, 2H), 3.56 (s, 3H, $-\text{OMe}$ of PMB), 3.53 (t, J = 9.4 Hz, 1H), 3.45 (d, J = 5.8 Hz, 1H, OH), 3.10 (dd, J = 11.2, 2.2 Hz, 1H, Glc-6), 2.92 (dd, J = 11.2, 2.0 Hz, 1H, Glc-6); ^{13}C NMR (100 MHz, CDCl_3) δ 159.2 (Ph-O of PMB), 136.3, 136.10, 136.07, 135.70, 135.66, 135.5, 133.41, 133.36, 133.33, 133.25, 133.2, 133.10, 133.09, 133.0, 132.9, 130.0 (Ph of PMB), 129.5, 128.4, 128.3, 128.2, 128.12, 128.08, 128.06, 128.03, 127.9, 127.83, 127.76, 127.75, 127.7, 127.0, 126.8, 126.7, 126.6, 126.4, 126.3, 126.24, 126.22, 126.13, 126.11, 126.09, 126.04, 126.00, 125.98, 125.96, 125.90, 125.87, 125.8, 125.7, 125.5, 113.6 (Ph of PMB), 98.8 (C1), 82.1, 81.3, 80.97, 80.96, 80.9, 78.1, 76.8, 76.1 ($-\text{CH}_2-$ of Nap), 75.5 ($-\text{CH}_2-$ of Nap), 75.2 ($-\text{CH}_2-$ of Nap), 75.0 ($-\text{CH}_2-$ of Nap), 74.8 ($-\text{CH}_2-$ of Nap), 73.8, 73.1 ($-\text{CH}_2-$ of Nap), 72.9 ($-\text{CH}_2-$ of PMB), 71.0 (C5), 66.7 (C6), 64.3 (C2), 55.1 (OMe of PMB); ESI-MS: m/z $[\text{M}+\text{Na}]^+$ calcd 1350.5456, obsd 1350.5482; m/z $[\text{M}+\text{K}]^+$ calcd 1366.5195, obsd 1366.5208.

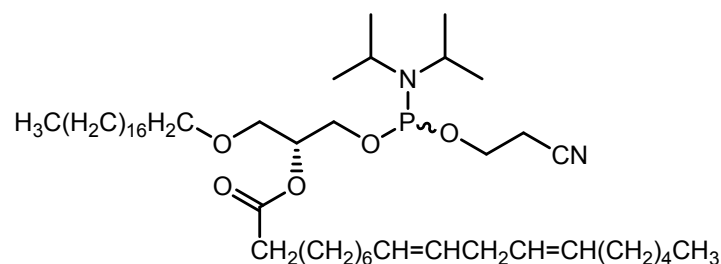
1-*O*-(Octadecyl)-2-*O*-(9*Z*,12*Z*-octadecanoyl)-*sn*-glycerol (**20**)



To a stirred solution of 1-*O*-octadecyl-3-*O*-*tert*-butyldimethylsilyl-*sn*-glycerol (**19**)⁴ (0.509 g, 1.11 mmol) and DMAP (13.5 mg, 0.111 mmol) in CH_2Cl_2 (11 mL) at room temperature was added linolenic acid (0.415 mL, 1.33 mmol) and DCC (0.275 mg, 1.33 mmol). The reaction mixture was stirred at room temperature for 5 h. The reaction was extracted with CH_2Cl_2 , washed with brine, dried with Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography to afford glycerol compound R_f = 0.13 (hexane/EtOAc 40:1). A mixture of the obtained glycerol (0.301 g, 0.220 mmol) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.45 mL) in CH_2Cl_2 (3 mL) was stirred at 0 °C for 15 min. The solution was quenched with Et_3N and then the solvent was removed in vacuo. The crude product was purified by flash chromatography to give 2-*O*-acylated glycerol derivative **20** (hexane/EtOAc = 6:1, R_f 0.20) in 60% yield (0.401 g, 0.661 mmol, 2 steps) as a colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 5.43-5.28 (m, 4H, $-\text{CH}=\text{}$), 5.03-4.97 (m, 1H, *sn*-2-CH-), 3.81 (d, J = 4.1 Hz, 2H, *sn*-3- CH_2-), 3.64 (dd,

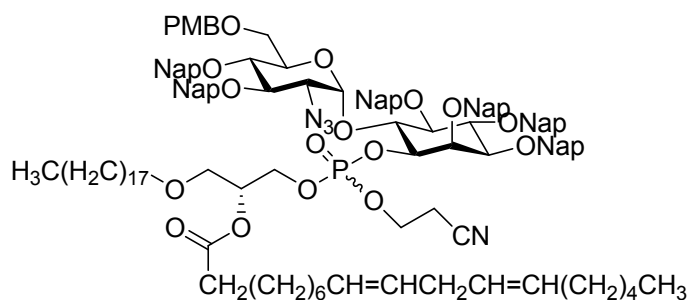
$J = 10.4, 4.9$ Hz, 1H, sn -1-CH_{2a}-), 3.59 (dd, $J = 10.7, 5.1$ Hz, 1H, sn -1-CH_{2b}-), 3.50-3.39 (m, 2H, -OCH₂-), 2.77 (t, $J = 6.4$ Hz, 2H, =CH-CH₂-CH=), 2.35 (t, $J = 7.5$ Hz, 2H, -COCH₂-), 2.22 (brs, 1H, -OH), 2.04 (t, $J = 6.8$ Hz, 4H, -CH₂-CH=), 1.66-1.51 (m, 4H, -COCH₂CH₂-, -OCH₂CH₂-), 1.35-1.22 (m, 44H), 0.91-0.85 (m, 6H, -CH₃*2); ¹³C NMR (100 MHz, CDCl₃) δ 173.8 (-O=C-O-), 130.4 (-CH=), 130.2 (-CH=), 128.2 (-CH=), 128.0 (-CH=), 72.9 (sn -2-CH-), 72.1 (-OCH₂- of octadecyl), 70.2 (sn -1-CH₂-), 63.2 (sn -3-CH₂-), 34.5 (-COCH₂-), 32.1, 31.7, 29.9, 29.83, 29.82, 29.78, 29.76, 29.7, 29.6, 29.52, 29.50, 29.34, 29.27, 29.2, 27.35 (-CH₂-CH=), 27.34 (-CH₂-CH=), 26.2, 25.8 (=CH-CH₂-CH=), 25.1 (-COCH₂CH₂-), 22.9, 22.7, 14.3 (-CH₃), 14.2 (-CH₃); ESI-MS: m/z [M+Na]⁺ calcd 629.5485, obsd 629.5498.

2-Cyanoethyl-*N,N*-diisopropylamine-(1-*O*-(octadecyl)-2-*O*-(9*Z*,12*Z*-octadecanoyl)-*sn*-glycero)-3-phosphoramidite (4)



To a solution of 2-*O*-acylated glycerol derivative **20** (0.108 g, 0.178 mmol) and commercially available bis(diisopropylamino)(2-cyanoethoxy)phosphine (0.068 mL, 0.214 mmol) in anhydrous CH₂Cl₂/MeCN (v/v = 2:1, 1.8 mL) was added 1*H*-tetrazole (0.593 mL, 0.267 mmol, 0.45M solution in CH₃CN). The reaction was stirred for 2 h at room temperature under argon atmosphere. Then, the reaction mixture was quenched with aq. NaHCO₃ and diluted with CH₂Cl₂. The reaction mixture was washed with aq. NaHCO₃, extracted with CH₂Cl₂, dried over Na₂SO₄, filtered and concentrated. Purification using a triethylamine neutralized silica gel column gave a 1:1 diastereomeric (originating at phosphorus) mixture of phosphoramidite **4** in 90% yield (0.129 g, 0.160 mmol) as a colorless oil; R_f = 0.58 (hexane/EtOAc 4:1), ¹H NMR (600 MHz, CDCl₃, ~1:1 mixture of diastereomers) δ 5.41-5.28 (m, 4H, -CH=), 5.15-5.09 (m, 1H, sn -2-CH-), 3.88-3.65 (m, 4H, -OCH₂CH₂CN, sn -3-CH₂-), 3.62-3.54 (m, 4H, HC-N, sn -1-CH₂-), 3.48-3.37 (m, 2H, -OCH₂- of octadecyl), 2.76 (t, $J = 6.8$ Hz, 2H, =CH-CH₂-CH=), 2.64-2.60 (m, 2H, -CH₂CN), 2.34-2.28 (m, 2H, -COCH₂-), 2.04 (q, $J = 7.0$ Hz, 4H, -CH₂-CH=), 1.65-1.58 (m, 2H, -COCH₂CH₂-), 1.56-1.50 (m, 2H, -OCH₂CH₂- of octadecyl), 1.37-1.23 (m, 44H), 1.19-1.16 (m, 12H, -CH(CH₃)₂*2), 0.88 (q, $J = 6.9$ Hz, 6H, -CH₃*2); ¹³C NMR (151 MHz, CDCl₃, ~1:1 mixture of diastereomers) δ 173.31 (-O=C-O-), 173.28 (-O=C-O-), 130.3 (-CH=), 130.1

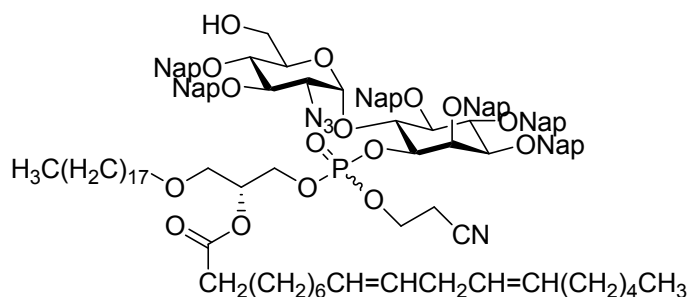
2-Azido-3,4-di-*O*-(2-naphthyl)methyl-6-*O*-(*p*-methoxybenzyl)-2-deoxy- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-1-*O*-[1-*O*-(octadecyl)-2-*O*-(9*Z*,12*Z*-octadecanoyl)-*sn*-glycero-3-phosphocynoethyl]-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (30)



20

Nap), 4.68 (d, $J = 11.1$ Hz, 1.8H, $-\text{CH}_2-$ of Nap), 4.62 (d, $J = 9.1$ Hz, 1.8H), 4.56-4.39 (m, 5.4H), 4.33-4.16 (m, 9H), 4.15-3.96 (m, 7.2H), 3.93 (dd, $J = 11.9$, 4.5 Hz, 1.8H), 3.76-3.68 (m, 3.6H), 3.59-3.29 (m, 18H), 3.18 (dd, $J = 10.0$, 4.8 Hz, 1.8H, Glc-6), 3.02 (dd, $J = 10.6$, 4.2 Hz, 1.8H, Glc-6), 2.80-2.64 (m, 5.4H), 2.52-2.24 (m, 5.4H), 2.08-1.99 (m, 7.2H), 1.58-1.44 (m, 7.2H), 1.28-1.23 (m, 75.6H), 0.90-0.86 (m, 10.8H, $-\text{CH}_3$); ^{13}C NMR (100 MHz, CDCl_3 , ~1:0.8 mixture of diastereomers) δ 173.3 ($-\text{O}=\text{C}-\text{O}-$), 173.2 ($-\text{O}=\text{C}-\text{O}-$), 159.1 (Ph-O of PMB), 136.41, 136.37, 135.9, 135.82, 135.77, 135.7, 135.64, 135.62, 133.4, 133.33, 133.30, 133.2, 133.11, 133.09, 133.06, 133.0, 132.8, 130.4 ($-\text{CH}=\text{}$), 130.18 ($-\text{CH}=\text{}$), 130.16 ($-\text{CH}=\text{}$), 130.0 (Ph of PMB), 129.5, 128.34, 128.26, 128.24, 128.21, 128.17, 128.15, 128.13, 128.11, 128.07, 128.04, 128.01, 127.9, 127.82, 127.80, 127.75, 127.73, 127.71, 127.68, 126.8, 126.74, 126.71, 126.67, 126.6, 126.5, 126.4, 126.34, 126.25, 126.23, 126.22, 126.19, 126.1, 126.04, 125.99, 125.98, 125.96, 125.93, 125.90, 125.86, 125.84, 125.76, 125.74, 125.73, 125.5, 116.52 ($-\text{CN}$), 116.51 ($-\text{CN}$), 113.7 (Ph of PMB), 97.1 ($\text{C}1$), 81.8, 81.7, 80.9, 80.63, 80.57, 79.6, 78.02 (d, $J_{\text{PC}} = 2.5$ Hz, $\text{sn}-2\text{-CH}-$), 78.00 (d, $J_{\text{PC}} = 2.5$ Hz, $\text{sn}-2\text{-CH}-$), 77.0, 76.09, 76.07, 76.0, 75.74, 75.73, 75.71, 75.6, 75.43, 75.42, 75.3, 75.2, 74.8, 73.32, 73.31, 73.2, 72.96, 72.954, 72.946, 72.02, 71.96, 70.77, 70.76, 70.70, 70.69, 70.58, 70.55, 70.54, 70.53, 68.53, 68.51, 68.50, 68.40, 68.39, 66.82, 66.81, 64.3, 63.2, 63.14, 63.09, 62.44, 62.38, 62.13, 62.08, 55.1 (OMe of PMB), 34.4, 34.3, 32.1, 31.67, 31.65, 29.9, 29.81, 29.77, 29.70, 29.66, 29.6, 29.51, 29.48, 29.42, 29.37, 29.31, 29.30, 29.29, 29.25, 29.24, 29.2, 27.34 ($-\text{CH}_2\text{-CH}=\text{}$), 27.33 ($-\text{CH}_2\text{-CH}=\text{}$), 26.7, 26.19, 26.17, 26.1, 25.8 ($=\text{CH-CH}_2\text{-CH}=\text{}$), 25.04, 24.98, 22.8, 22.72, 22.68, 22.67, 22.62, 22.61, 19.9 (d, $J_{\text{PC}} = 7.0$ Hz, $-\text{CH}_2\text{CN}$), 19.7 (d, $J_{\text{PC}} = 7.2$ Hz, $-\text{CH}_2\text{CN}$), 14.3 ($-\text{CH}_3$), 14.2 ($-\text{CH}_3$); ^{31}P NMR (162 MHz, CDCl_3 , ~1:1 mixture of diastereomers) δ -2.41, -2.69; ESI-MS: m/z $[\text{M}+\text{Na}]^+$ calcd 2073.0900, obsd 2073.0947; m/z $[\text{M}+\text{K}]^+$ calcd 2089.0639, obsd 2089.0686.

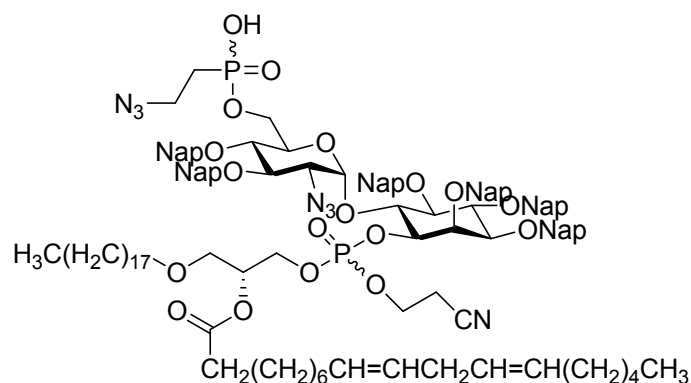
2-Azido-3,4-di-*O*-(2-naphthyl)methyl-2-deoxy- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-1-*O*-[1-*O*-(octadecyl)-2-*O*-(9*Z*,12*Z*-octadecanoyl)-*sn*-glycero-3-phosphocynoethyl]-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (31)



A mixture of the lipidated compound **30** (0.115 g, 0.056 mmol) and TFA (0.15 mL) in CH_2Cl_2 (1 mL) was stirred at 0 °C for 15 min. The reaction was quenched with Et_3N and the solvent was removed in

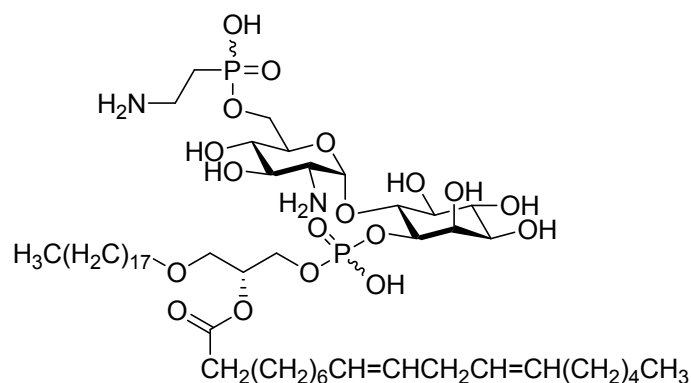
vacuo. The crude product was purified by flash chromatography to afford desired compound **31** in 80% yield (87 mg, 0.045 mmol, ~1:1 mixture of diastereomers) as a colorless oil; R_f = 0.28 (hexane/EtOAc = 3:2), ^1H NMR (600 MHz, CDCl_3 , ~1:1 mixture of diastereomers) δ 7.86-7.58 (m, 22H), 7.52-7.30 (m, 18H), 7.20 (t, J = 7.6 Hz, 1H), 7.12 (t, J = 8.3 Hz, 1H), 5.50-5.45 (m, 1H, Glc-1), 5.42-5.28 (m, 4H, -CH=), 5.26-5.14 (m, 4H, *sn*-2-CH-, -CH₂- of Nap), 5.06-4.84 (m, 8H, -CH₂- of Nap), 4.68-4.64 (m, 1H, -CH₂- of Nap), 4.61-4.56 (m, 1H), 4.55-4.49 (m, 1H), 4.44-4.38 (m, 1H), 4.32-3.25 (m, 5H), 4.22-4.15 (m, 1H), 4.14-4.07 (m, 2H), 4.05-3.96 (m, 1H), 3.73-3.70 (m, 1H), 3.69-3.64 (m, 1H), 3.60-3.55 (m, 1H), 3.52-3.18 (m, 8H), 3.27-3.22 (m, 1H), 2.79-2.66 (m, 2H), 2.36-2.20 (m, 2H), 2.08-1.97 (m, 2H), 1.61-1.46 (m, 6H), 1.28-1.23 (m, 42H), 0.89-0.87 (m, 6H, -CH₃); ^{13}C NMR (151 MHz, CDCl_3 , ~1:1 mixture of diastereomers) δ 173.28 (-O=C-O-), 173.25 (-O=C-O-), 136.3, 136.0, 135.70, 135.66, 135.61, 135.58, 135.53, 133.41, 133.39, 133.37, 133.36, 133.32, 133.29, 133.2, 133.13, 133.12, 133.08, 133.07, 133.02, 133.01, 132.92, 132.91, 130.4 (-CH=), 130.20 (-CH=), 130.17 (-CH=), 130.15 (-CH=), 128.37, 128.35, 128.30, 128.28, 128.21, 128.16, 128.14, 128.12, 128.101, 128.095, 128.05, 128.0, 127.9, 127.83, 127.81, 127.78, 127.72, 127.71, 127.69, 126.8, 126.7, 126.61, 126.60, 126.5, 126.4, 126.31, 126.26, 126.23, 126.19, 126.16, 126.13, 126.06, 126.0, 125.93, 125.87, 125.86, 125.8, 125.65, 125.64, 116.6 (-CN), 116.5 (-CN), 97.72 (C1), 97.69 (C1), 81.74, 81.69, 81.1, 80.8, 80.74, 80.70, 80.6, 79.7, 79.5, 77.9, 77.0, 76.2, 76.13, 76.06, 76.0, 75.6, 75.4, 75.29, 75.26, 75.2, 74.8, 74.73, 74.71, 74.6, 73.4, 73.3, 72.1, 72.0, 71.41, 71.36, 70.83, 70.79, 70.77, 70.74, 70.68, 70.67, 70.65, 70.63, 70.62, 68.54, 68.45, 68.4, 67.4, 67.12, 67.09, 63.5, 63.4, 62.5, 62.4, 62.2, 62.1, 62.1, 62.0, 34.4, 34.3, 32.1, 31.8, 31.7, 29.87, 29.86, 29.83, 29.81, 29.73, 29.70, 29.67, 29.65, 29.51, 29.49, 29.42, 29.37, 29.31, 29.29, 29.26, 29.19, 27.3, 26.22, 26.18, 26.15, 25.8 (=CH-CH₂-CH=), 25.1, 25.0, 22.8, 19.8 (d, J_{PC} = 7.2 Hz, -CH₂CN), 19.6 (d, J_{PC} = 6.9 Hz, -CH₂CN), 14.3 (-CH₃), 14.2 (-CH₃); ^{31}P NMR (243 MHz, CDCl_3 , ~1:1 mixture of diastereomers) δ 5.38, 5.33, -5.56, -5.66; ESI-MS: m/z $[\text{M}+\text{Na}]^+$ calcd 1953.0324, obsd 1953.0402; m/z $[\text{M}+\text{K}]^+$ calcd 1969.0064, obsd 1969.0161.

2-Azido-3,4-di-*O*-(2-naphthyl)methyl-6-*O*-((2-azidoethyl)phosphonic acid)-2-deoxy- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-1-*O*-[1-*O*-(octadecyl)-2-*O*-(9*Z*,12*Z*-octadecanoyl)-*sn*-glycero-3-phosphocynoethyl]-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (32)



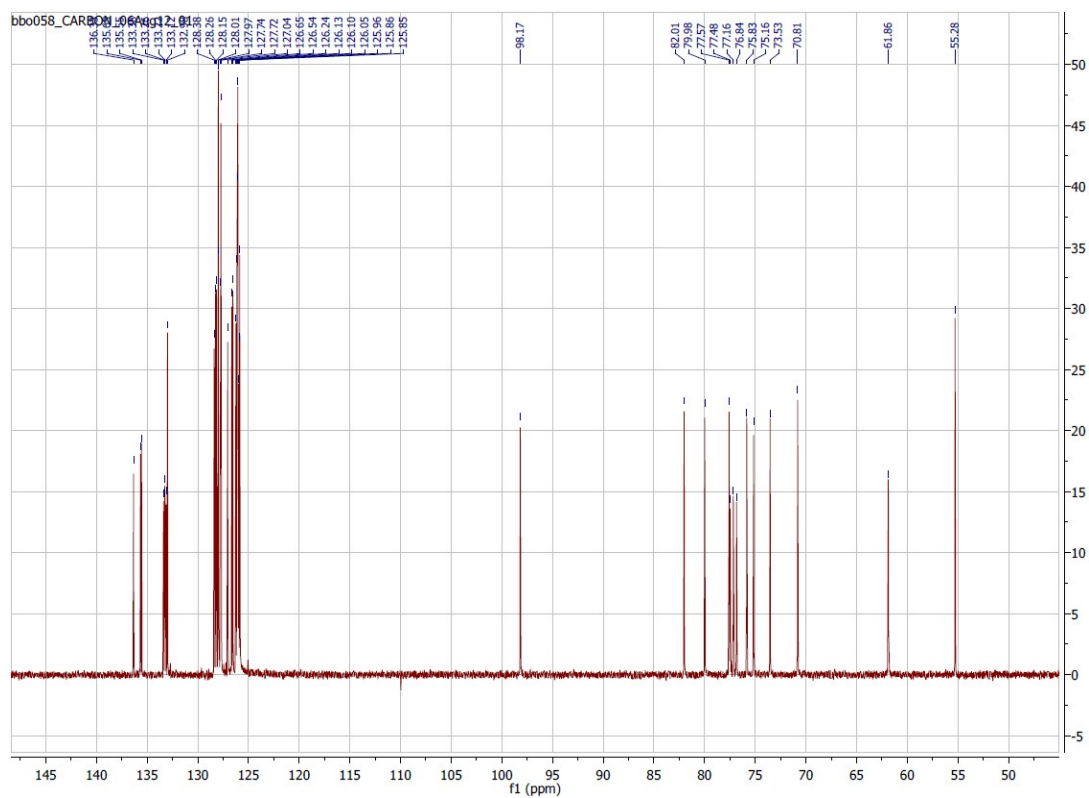
Diethyl 2-azidoethylphosphonate (45.0 mg, 0.217 mmol) was dissolved in CH_2Cl_2 (0.5 mL) and cooled to 0 °C. Then, bromotrimethylsilane (0.070 mL, 0.543 mmol) was added dropwise, the reaction mixture was warmed to room temperature and stirred for 14 h. the solvent was removed when the starting material was consumed. The obtained crude bis(trimethylsilyl) (2-azidoethyl)phosphonate was dissolved in CH_2Cl_2 (0.5 mL) and 2 drops of DMF. Then oxalyl chloride (0.076 mL, 0.867 mmol) was added dropwise and stirred vigorously for 1.5 h at room temperature. The reaction mixture was evaporated to yield the crude bis(chloro)(2-azidoethyl)phosphonate **5a**,⁵ which was directly used without further purification. The crude phosphonodichloridate **5a** was dissolved in toluene (0.5 mL) and then was added dropwise to a solution of pseudodimer **24** (42 mg, 0.022 mmol), DIPEA (0.076 mL, 0.435 mmol) and 1*H*-tetrazole (0.048 mL, 0.022 mmol, 0.45M solution in CH_3CN) in toluene (0.5 mL) at 0 °C. After 2 h at 0 °C, 1 drop of water was added to reaction mixture then stirred for 1 h at room temperature. The reaction was quenched with water and diluted with EtOAc. The organic phase was washed with aq. NaHCO_3 and brine, dried over MgSO_4 , filtered and concentrated in vacuo. The crude product was purified by flash chromatography to give phosphodiester compound **32** in 87% yield (39 mg, 0.019 mmol, ~1:1 mixture of diastereomers) as a colorless oil; R_f = 0.25 ($\text{CHCl}_3/\text{MeOH}$ 15:1), ^1H NMR (600 MHz, CDCl_3 , ~1:1 mixture of diastereomers) δ 7.88-7.26 (m, 40H), 7.19-7.15 (m, 1H), 7.13-7.09 (m, 1H), 5.46-5.30 (m, 5H, Glc-1, -CH=), 5.26-5.10 (m, 5H, *sn*-2-CH-, -CH₂- of Nap), 5.04-4.80 (m, 8H, -CH₂- of Nap), 4.72 (d, 1H, J = 11.2 Hz, -CH₂- of Nap), 4.66-4.45 (m, 2H), 4.36-4.02 (m, 9H), 3.92-3.86 (m, 1H), 3.77-3.71 (m, 2H), 3.59-3.23 (m, 9H), 2.78-2.50 (m, 6H), 2.36-2.25 (m, 2H), 2.08-1.94 (m, 4H), 1.61-1.45 (m, 4H), 1.34-1.15 (m, 42H), 0.91-0.85 (m, 6H, -CH₃); ^{31}P NMR (243 MHz, CDCl_3 , ~1:1 mixture of diastereomers) δ 18.32, 18.01, 17.10, -5.15, -5.79; ESI-MS: m/z $[\text{M}+\text{Na}]^+$ calcd 2086.0366, obsd 2086.0311; m/z $[\text{M}+\text{K}]^+$ calcd 2102.0105, obsd 2102.0025.

2-Amino-6-O-((2-aminoethyl)phosphonic acid)-2-deoxy- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-1-O-[1-O-(octadecyl)-2-O-(9*Z*,12*Z*-octadecanoyl)-*sn*-glycero-3-phosphate]-D-*myo*-inositol (2)

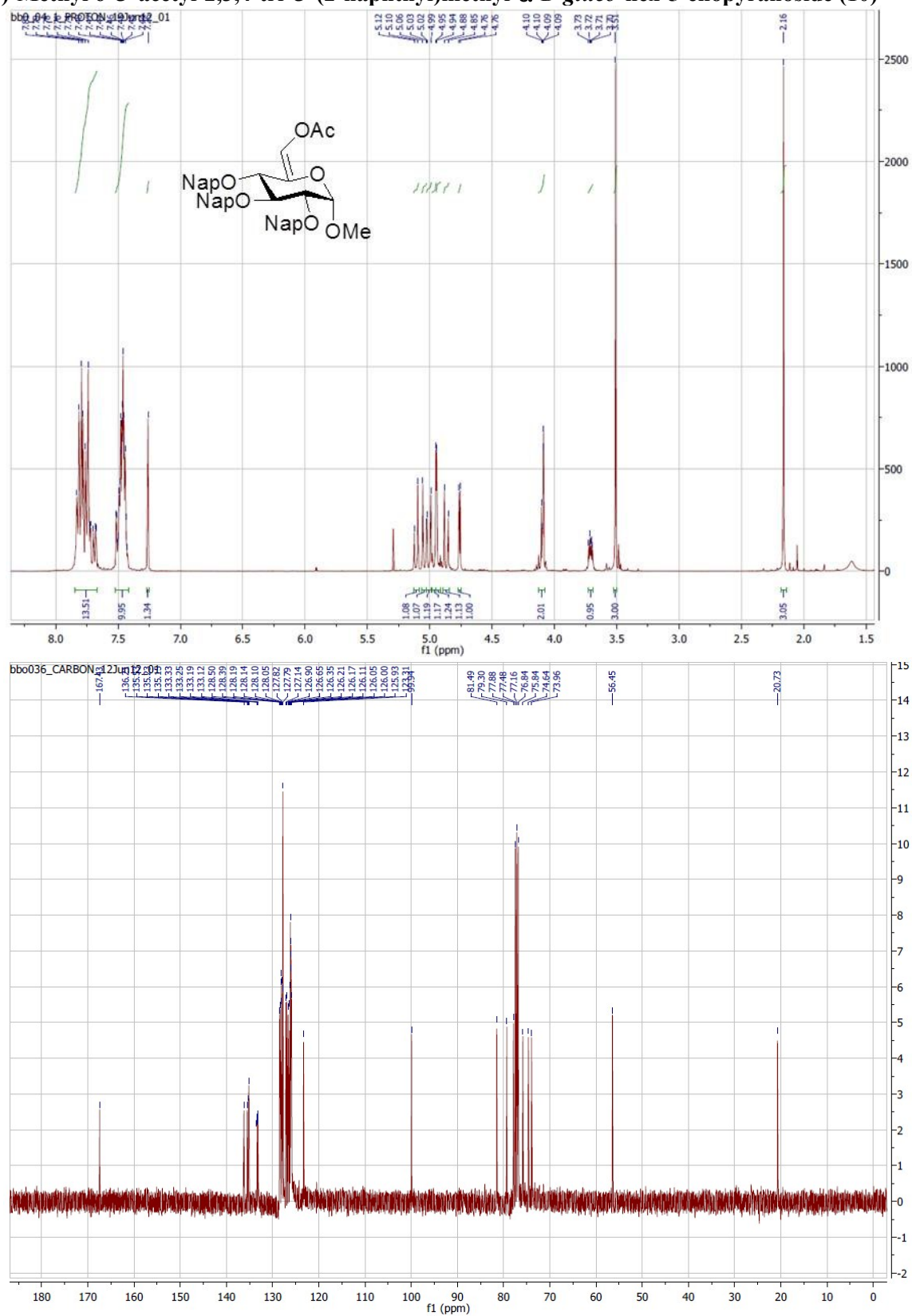


DBU (150 μL) was added to a solution of phosphodiester compound **32** (10 mg, 4.85 μmol) in anhydrous CH_2Cl_2 (0.5 mL) at room temperature.⁶ After 15 min, acetic acid (150 μL) was added to the reaction mixture and then the solution was evaporated to yield a crude glycerol phosphate. The resulted pseudo-disaccharide was dissolved in $\text{CH}_2\text{Cl}_2/\text{AcOH}$ (v/v = 1:1, 1.0 mL) and zinc powder (6.34 mg, 0.097 mmol) was added. After stirring for 2h, the mixture was filtered and condensed in vacuum to co-distilled with toluene to remove the acetic acid. The crude residue was dissolved in a mixture of TFA/toluene (v/v = 8:2, 1.0 mL) at 0 $^\circ\text{C}$ and was stirred at 0 $^\circ\text{C}$ for 2 h. Next the reaction was warmed to room temperature and stirred for additional 3 h. Finally, the mixture was then diluted with toluene (2 mL), concentrated in vacuo at room temperature. The crude product was purified on a Sephadex LH-20 size exclusion chromatography ($\text{CHCl}_3/\text{MeOH}/\text{H}_2\text{O}$ = 3:3:1) to give the desired compound **2** in 72% yield (3 steps, 3.88 mg, 3.47 μmol , ~1:1 mixture of diastereomers) as a white solid; ^1H NMR (400 MHz, CDCl_3 and MeOD, ~1:1 mixture of diastereomers) δ 5.54-5.14 (m, 5H, Glc-1, -CH=), 4.22-3.75 (m, 10H), 3.68-3.59 (m, 3H), 3.51-3.37 (m, 5H), 3.25-3.08 (m, 4H), 2.41-2.28 (m, 4H), 2.10-1.90 (m, 5H), 1.82-1.73 (m, 2H), 1.70-1.50 (m, 6H), 1.44-1.19 (m, 40H), 0.93-0.83 (m, 6H, - CH_3); ^{31}P NMR (162 MHz, CDCl_3 , ~1:1 mixture of diastereomers) δ 25.73, 4.10; ESI-MS: m/z $[\text{M}+\text{H}]^+$ calcd 1117.6681, obsd 1117.6997; m/z $[\text{M}+\text{H}_3\text{O}]^+$ calcd 1135.6787, obsd 1135.6882; m/z $[\text{M}+\text{Na}]^+$ calcd 1139.6501, obsd 1139.6636; m/z $[\text{M}+\text{Na}+\text{H}_2\text{O}]^{2+}$ calcd 1157.6606, obsd 1157.6682; m/z $[\text{M}-\text{H}]^-$ calcd 1115.6525, obsd 1115.6528; m/z $[\text{M}+\text{OH}]^-$ calcd 1133.6630, obsd 1133.6636; m/z $[\text{M}+\text{OH}+\text{Na}-\text{H}]^-$ calcd 1155.6450, obsd 1155.6447.

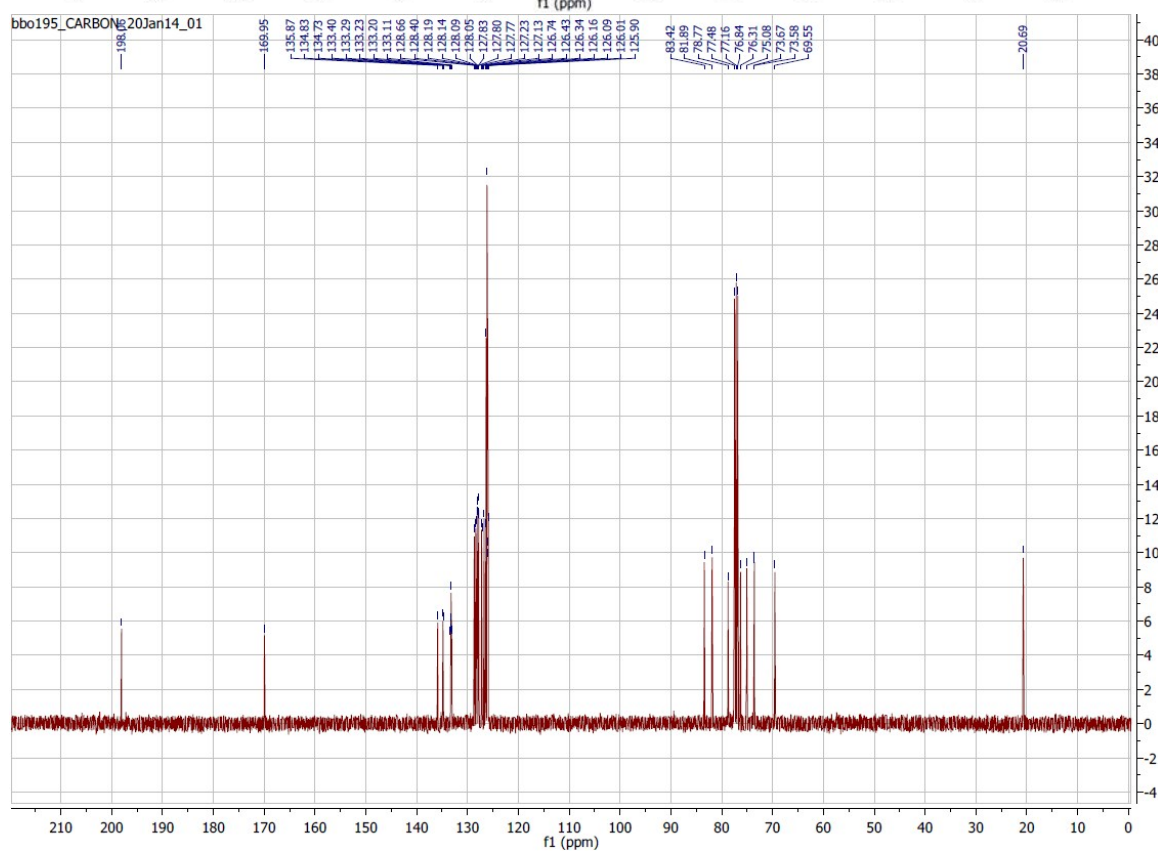
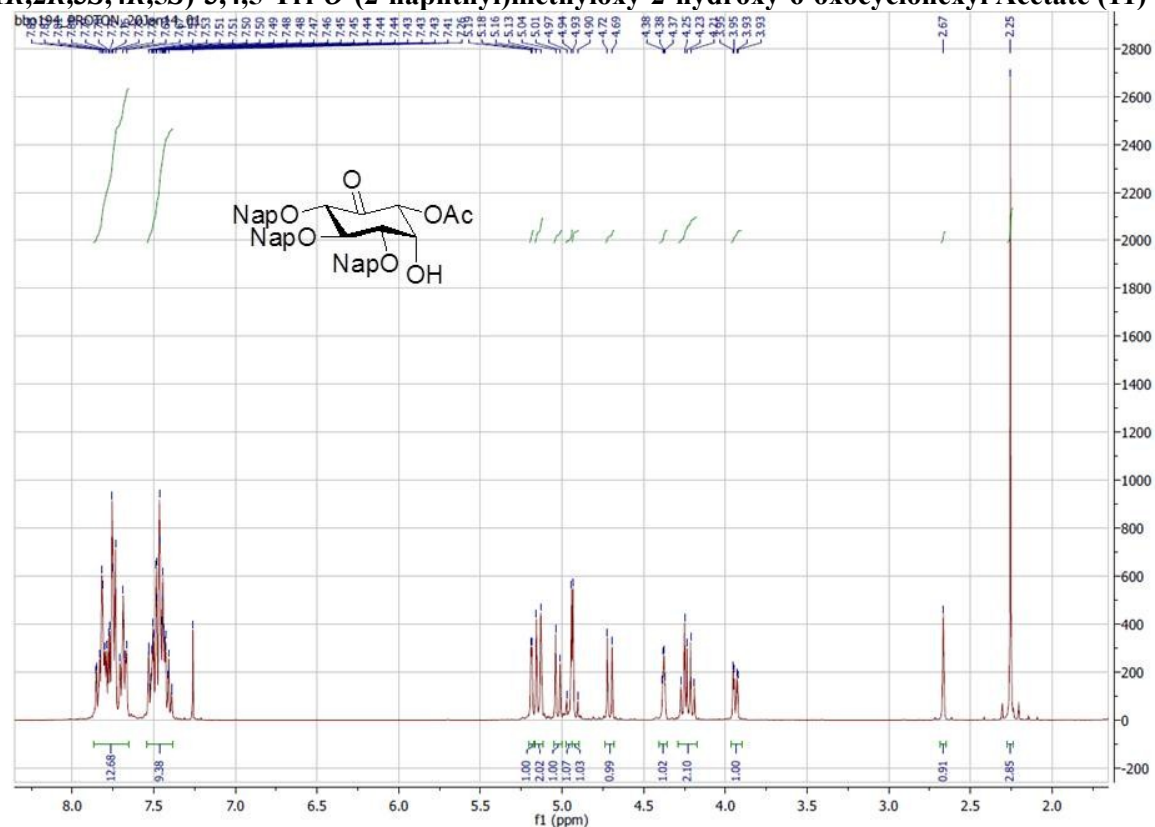
Methyl 2,3,4-tri-*O*-(2-naphthyl)methyl- α -D-glucopyranoside (9)



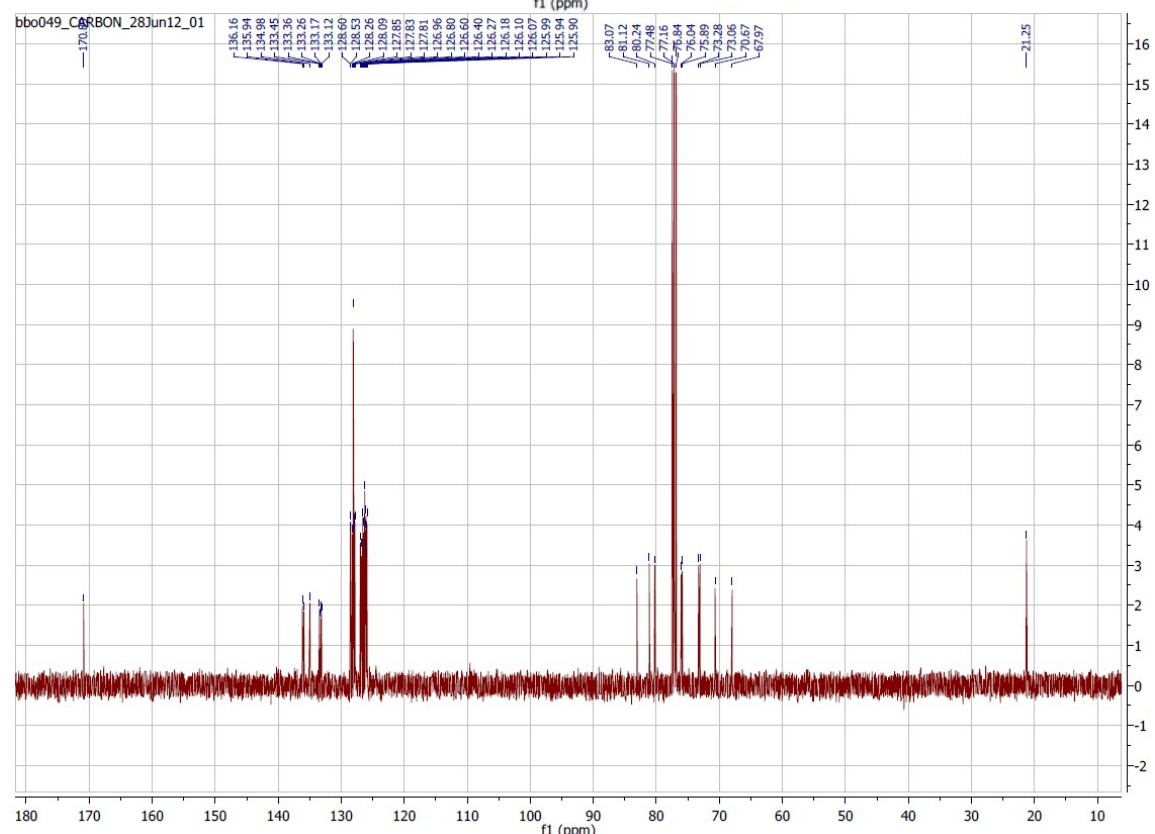
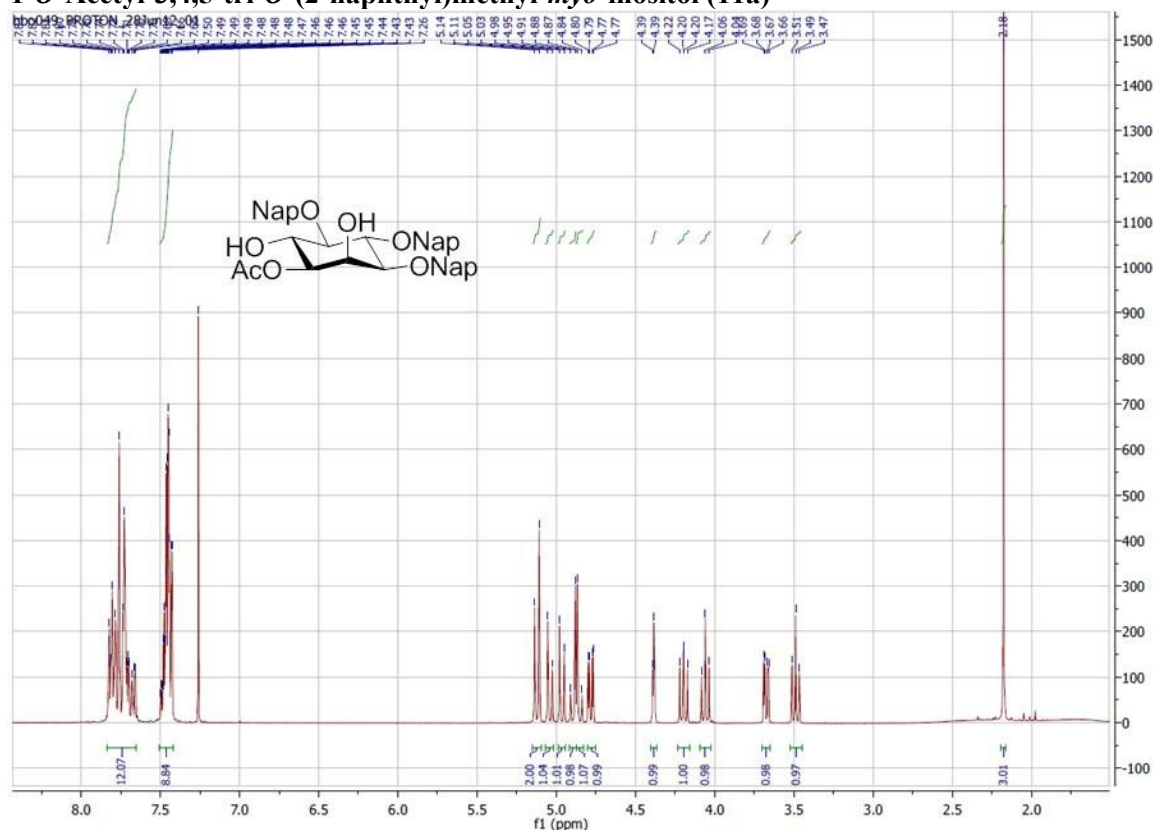
(Z)-Methyl 6-O-acetyl-2,3,4-tri-O-(2-naphthyl)methyl- α -D-glucopyranoside (10)



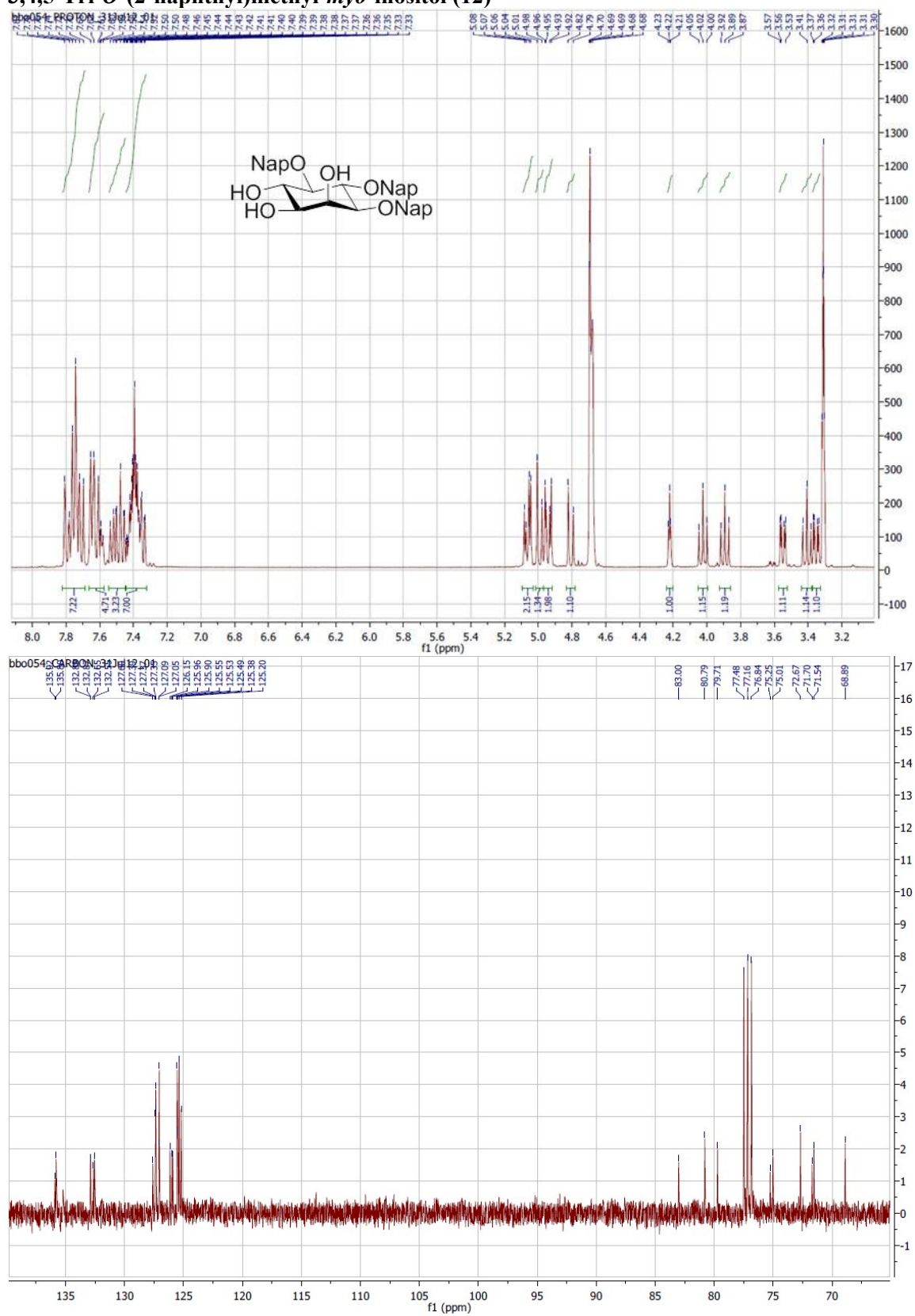
(1*R*,2*R*,3*S*,4*R*,5*S*)-3,4,5-Tri-*O*-(2-naphthyl)methoxy-2-hydroxy-6-oxocyclohexyl Acetate (11)



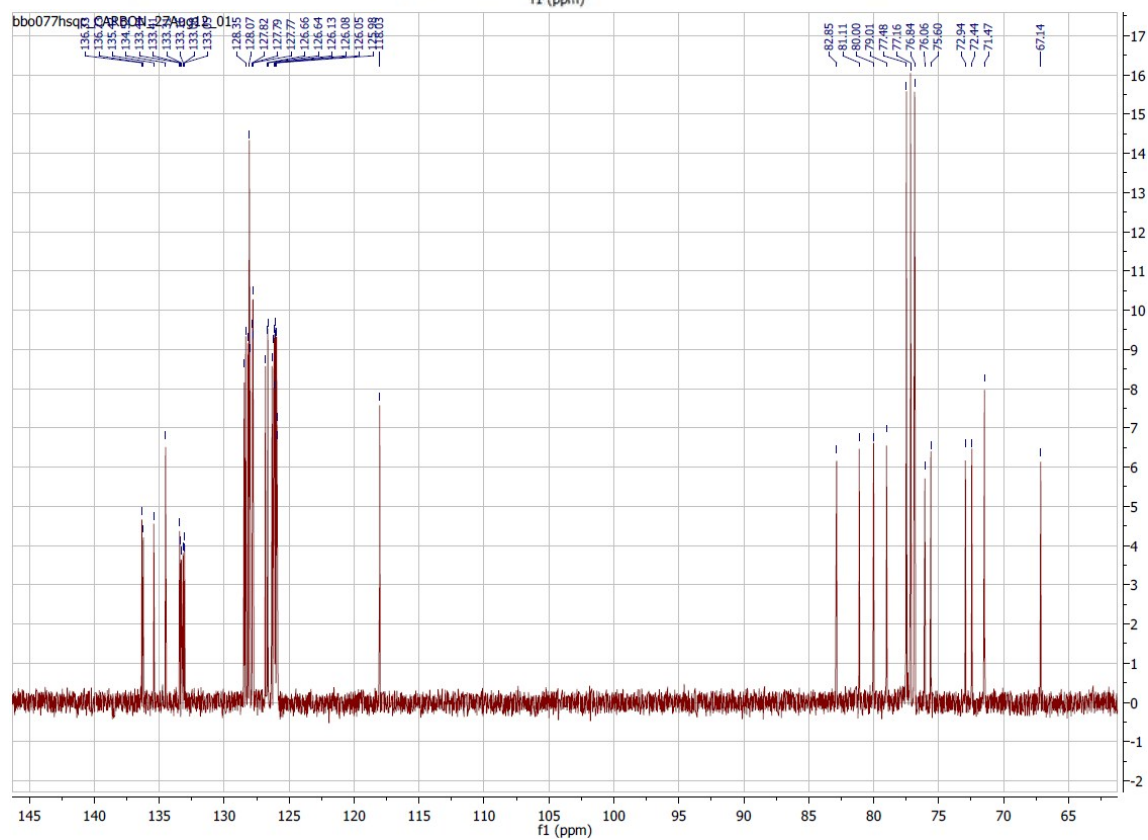
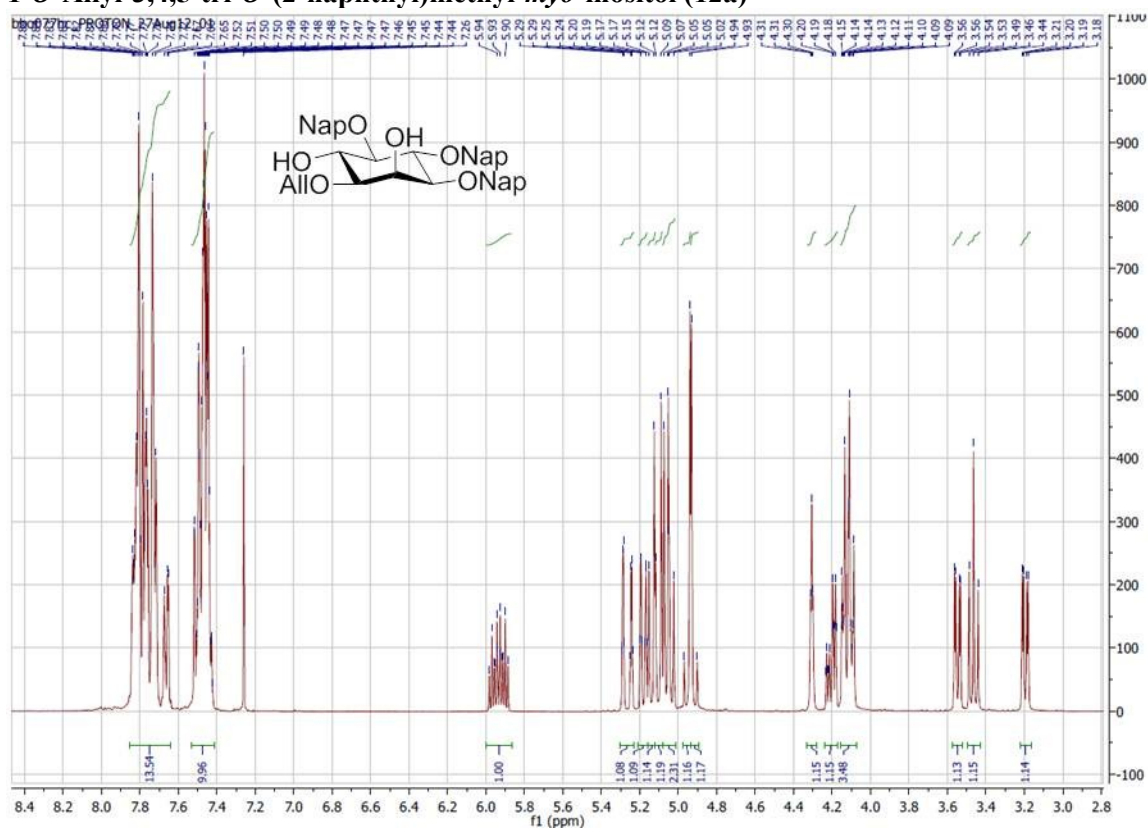
D-1-*O*-Acetyl-3,4,5-tri-*O*-(2-naphthyl)methyl-*myo*-inositol (11a)



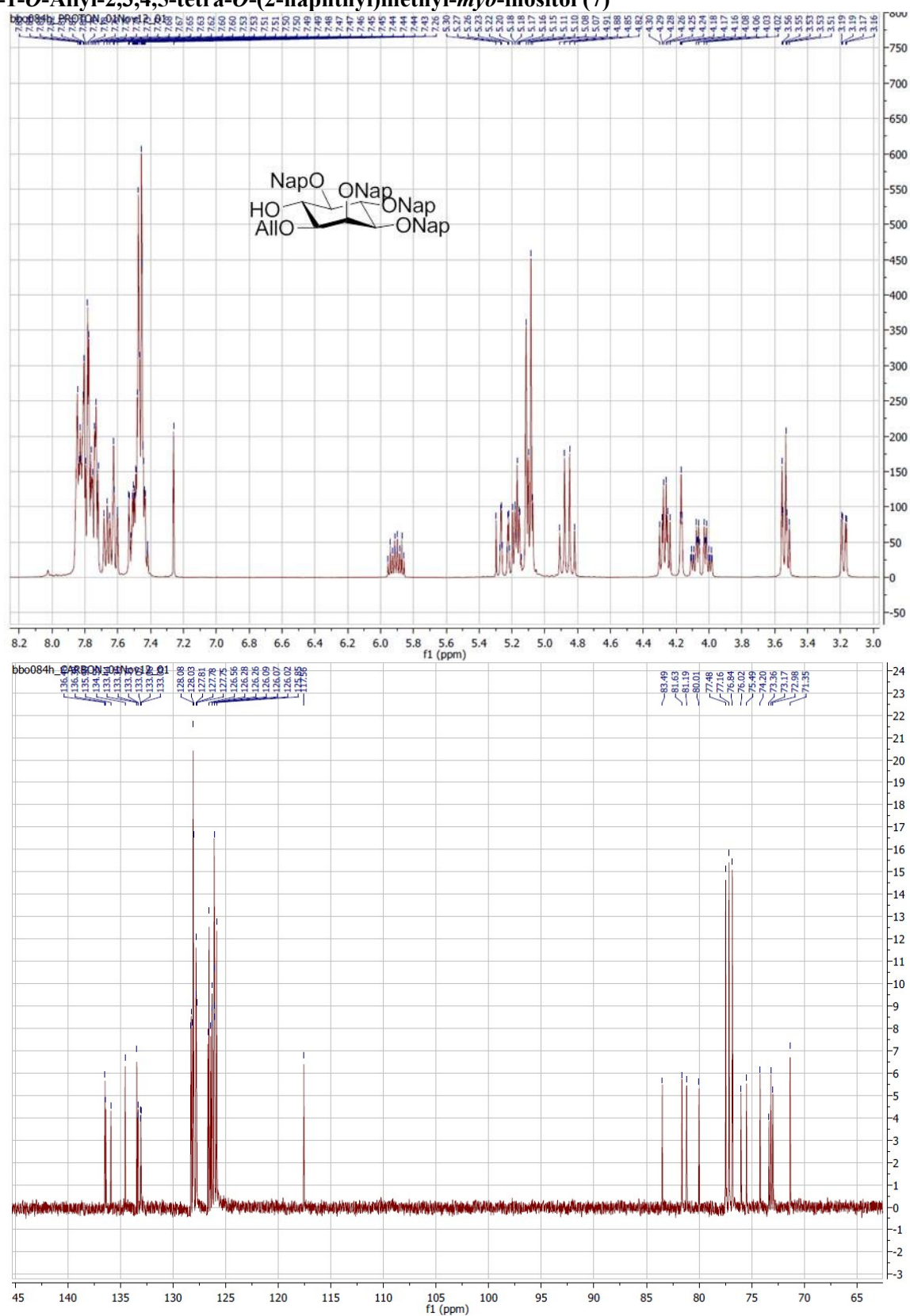
D-3,4,5-Tri-*O*-(2-naphthyl)methyl-*myo*-inositol (12)



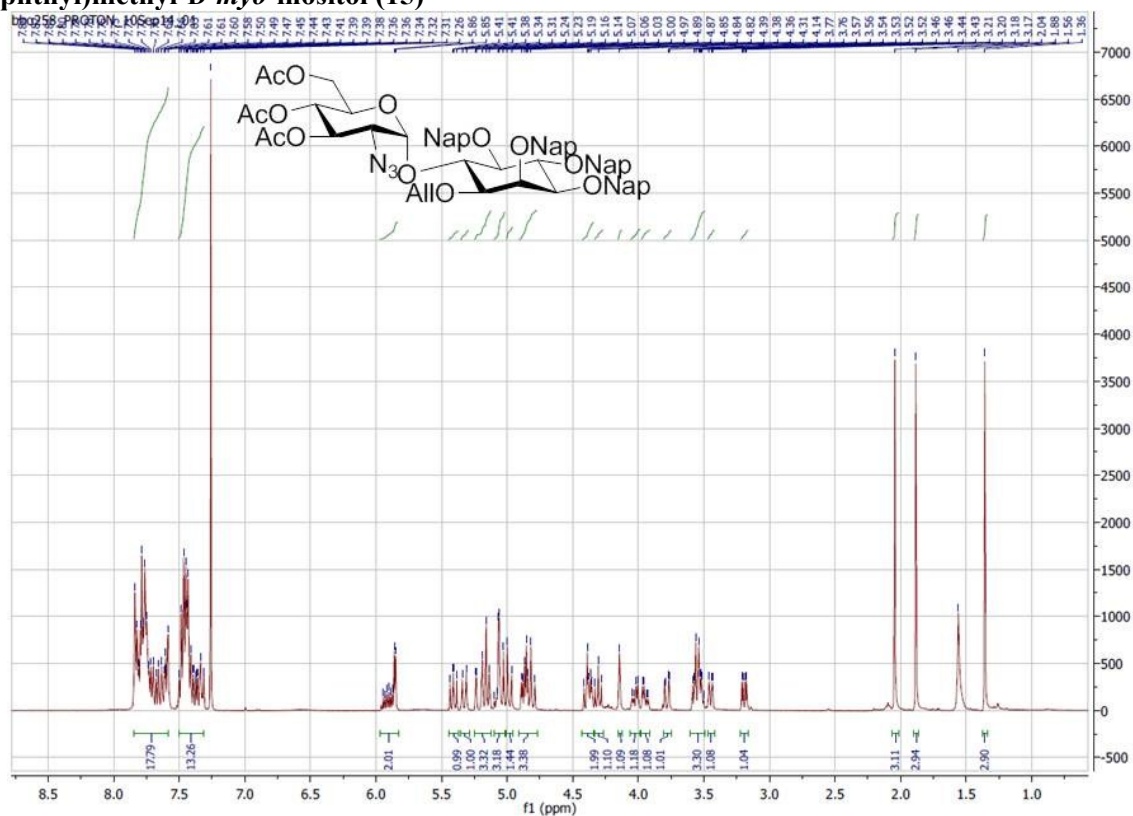
D-1-*O*-Allyl-3,4,5-tri-*O*-(2-naphthyl)methyl-*myo*-inositol (12a)

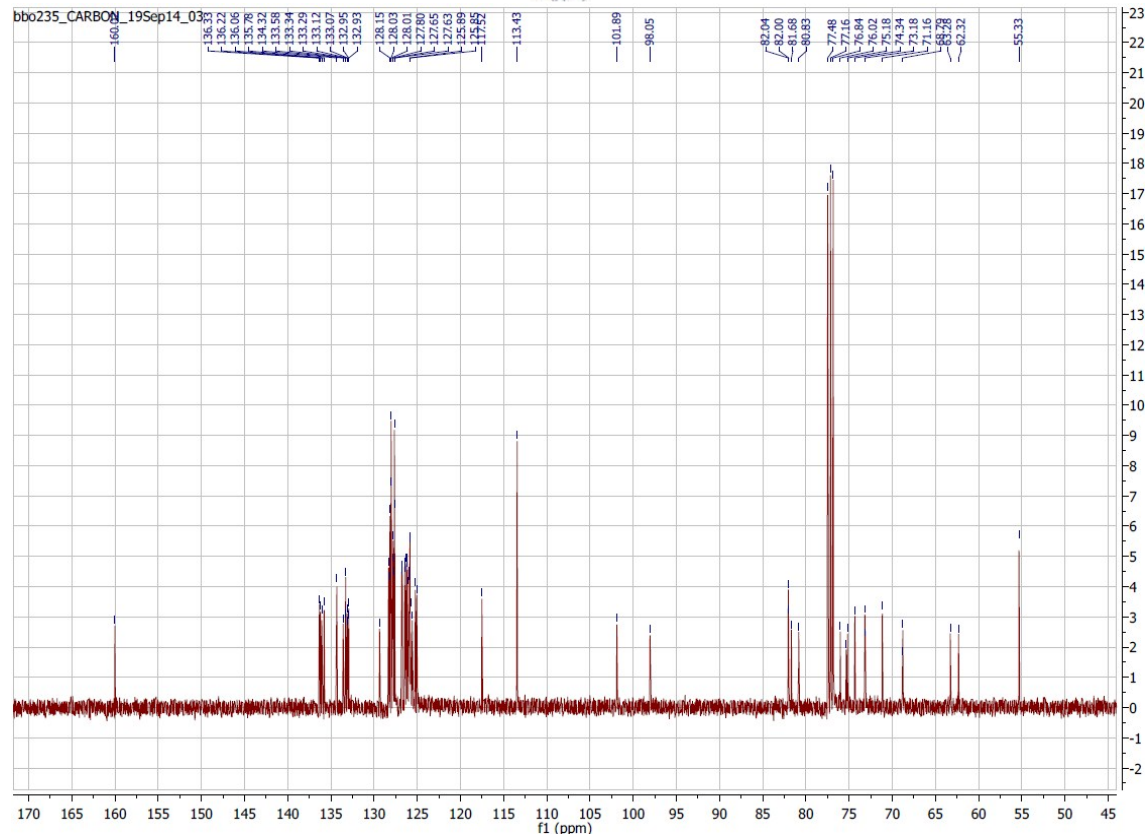
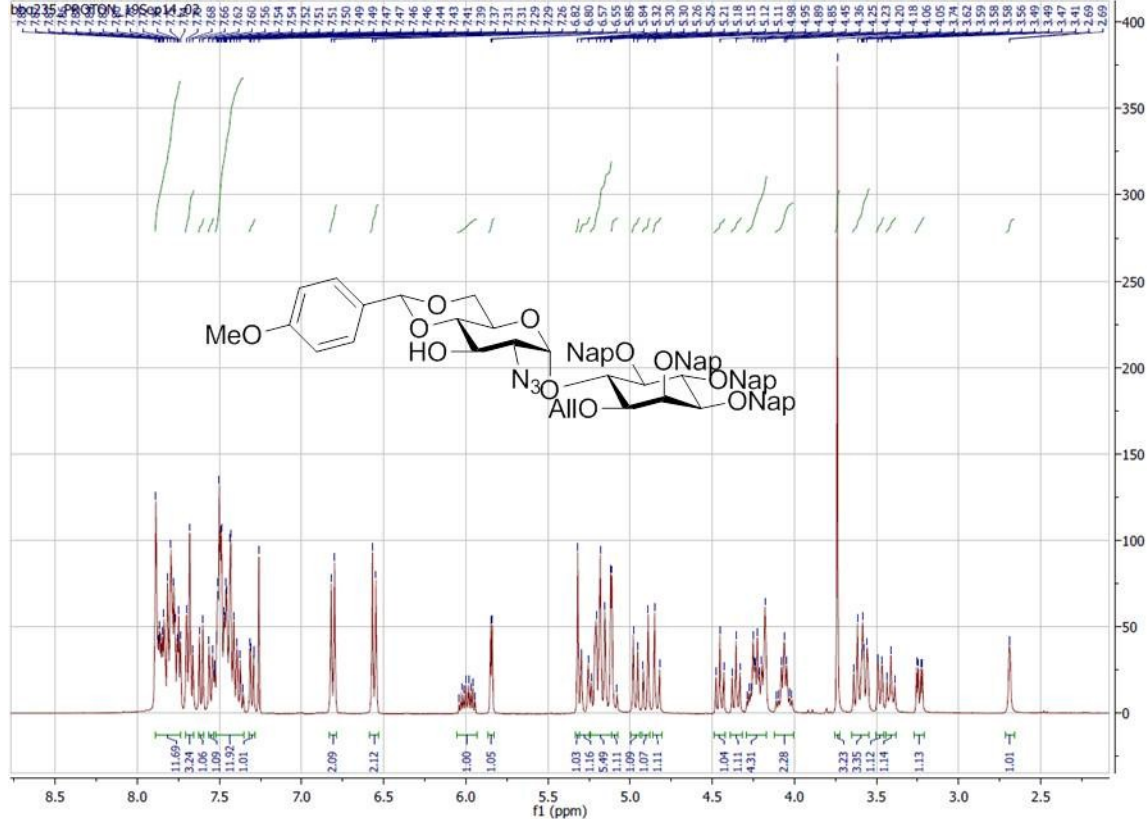


D-1-*O*-Allyl-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-*myo*-inositol (7)

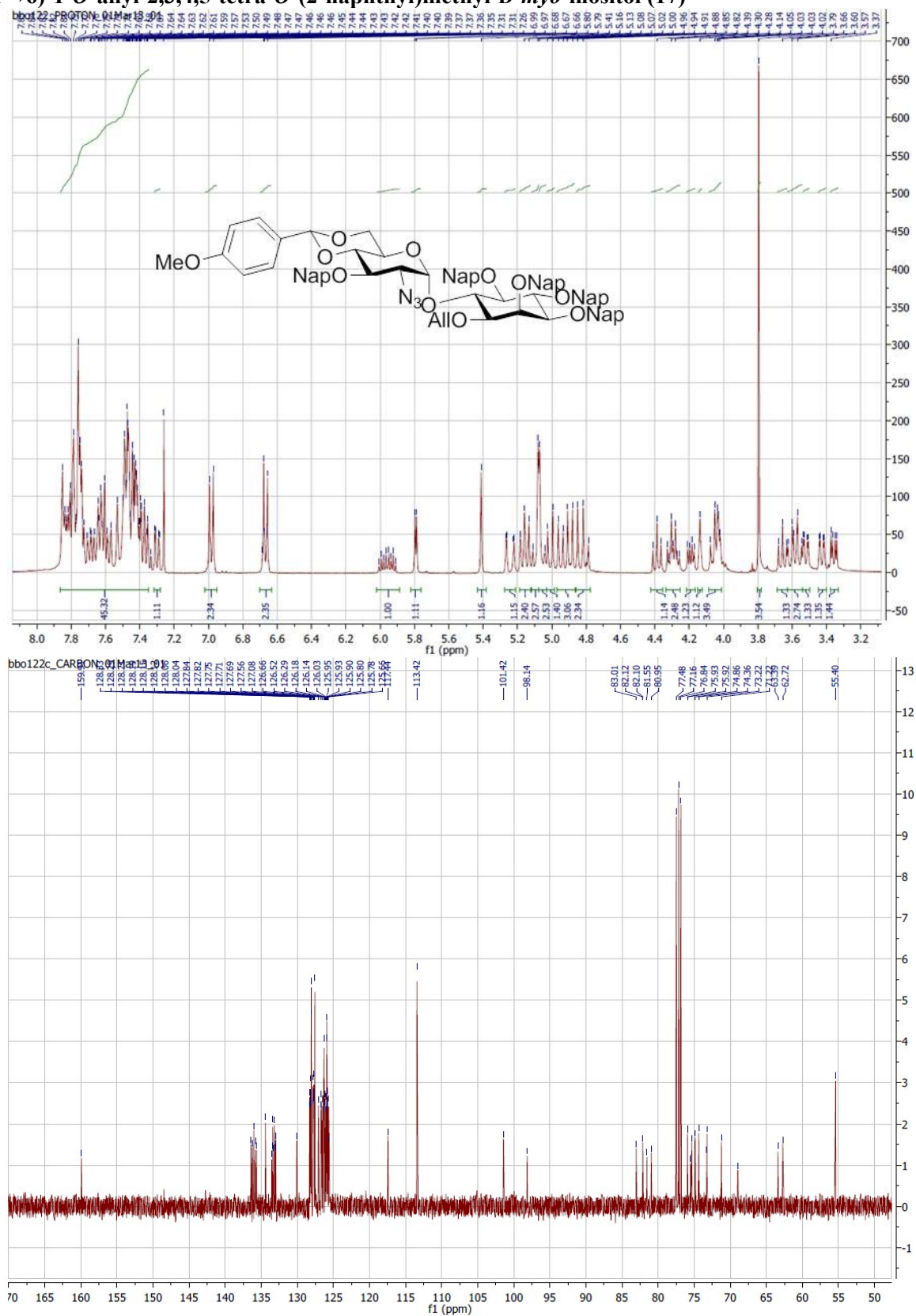


2-Azido-3,4,6-tri-*O*-acetyl-2-deoxy- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-1-*O*-allyl-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (15)

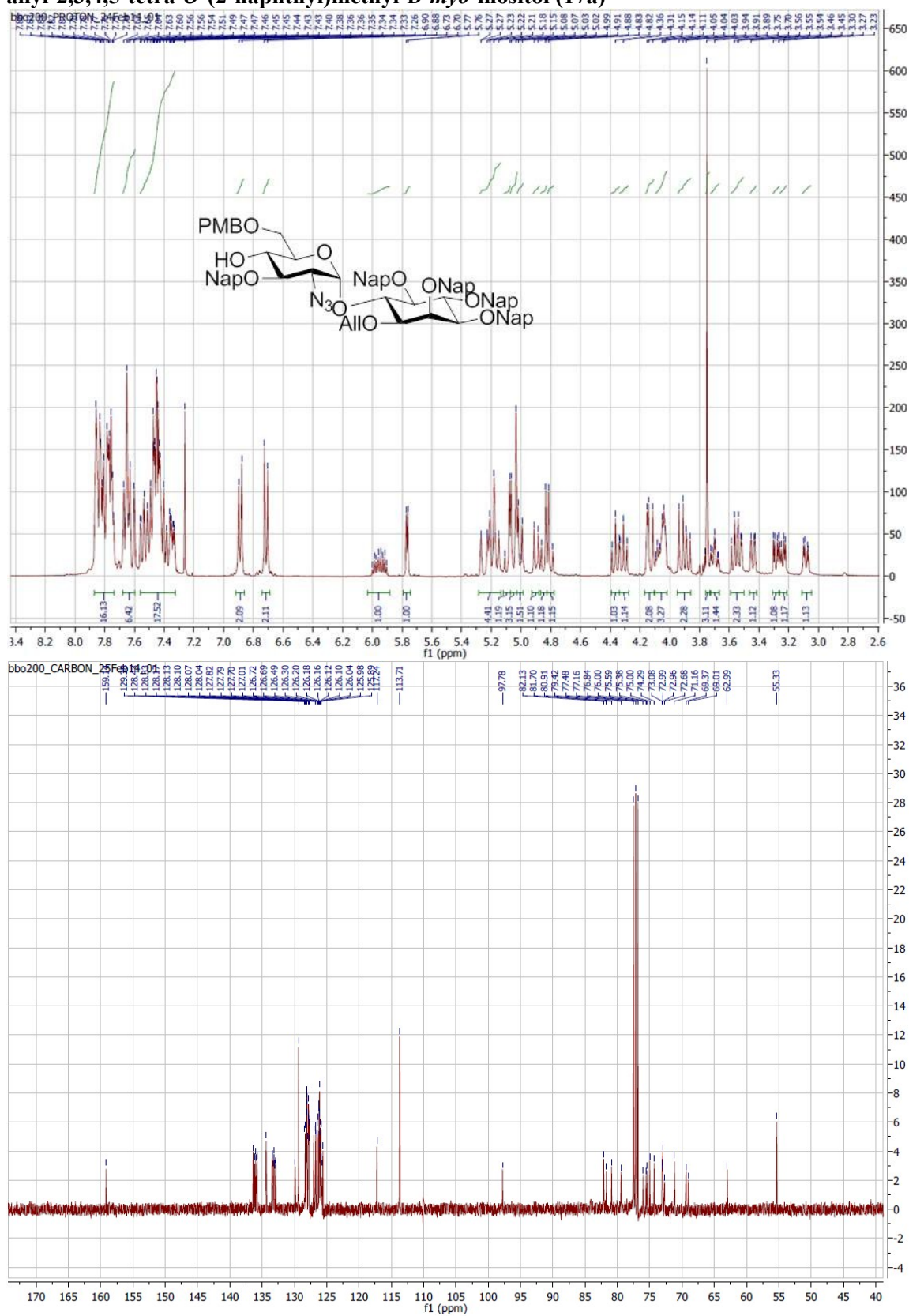




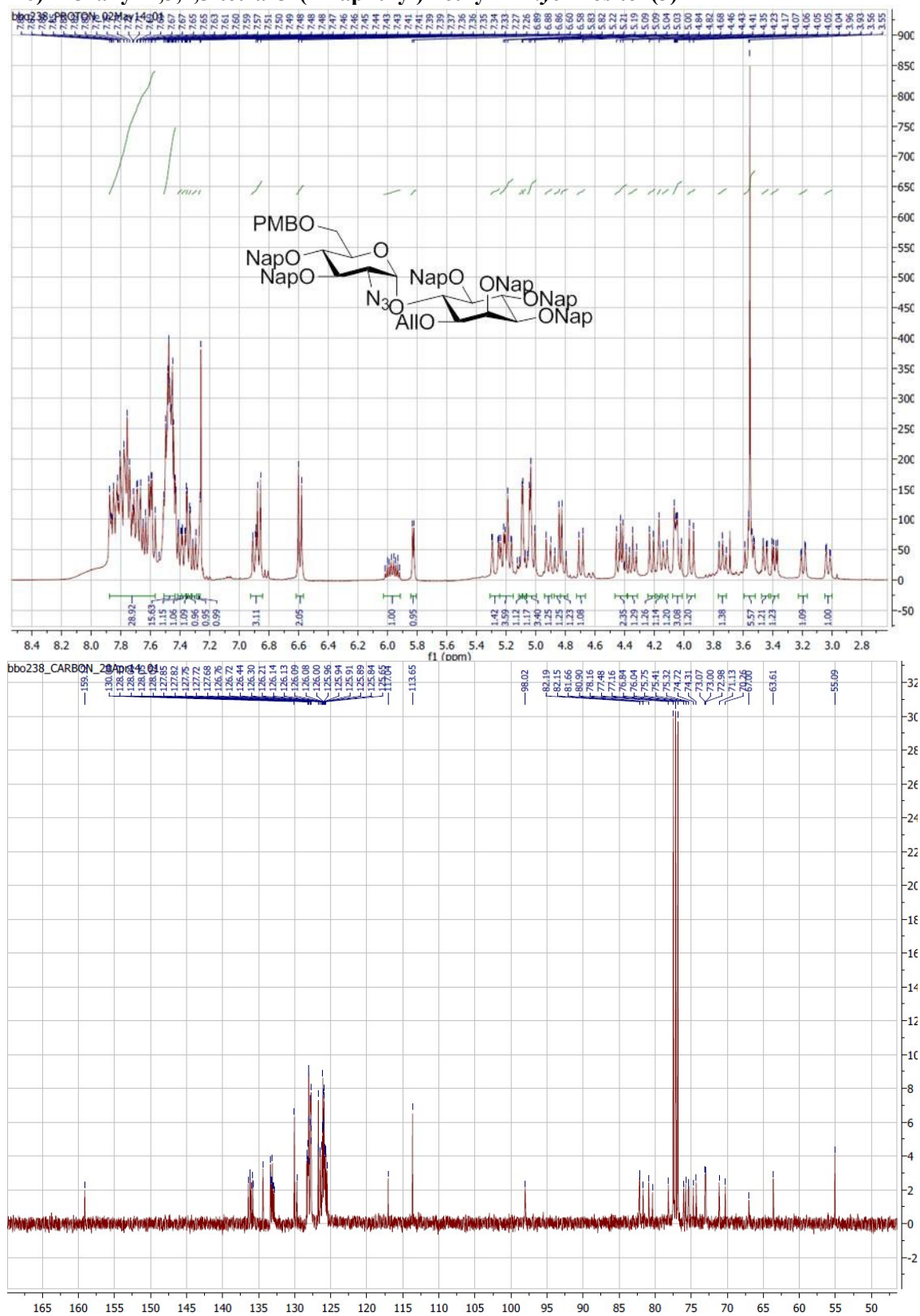
2-Azido-3-*O*-(2-naphthyl)methyl-4,6-*O*-(*p*-methoxybenzylidene)-2-deoxy- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-1-*O*-allyl-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (17)



2-Azido-3-*O*-(2-naphthyl)methyl-6-*O*-(*p*-methoxybenzyl)-2-deoxy- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-1-*O*-allyl-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (17a)



2-Azido-3,4-di-*O*-(2-naphthyl)methyl-6-*O*-(*p*-methoxybenzyl)-2-deoxy- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-1-*O*-allyl-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (3)



Chemical structure of compound 10 is shown above the spectrum. The structure is a bicyclic system with a hydroxyl group, a naproxen ether, and a diazo group.

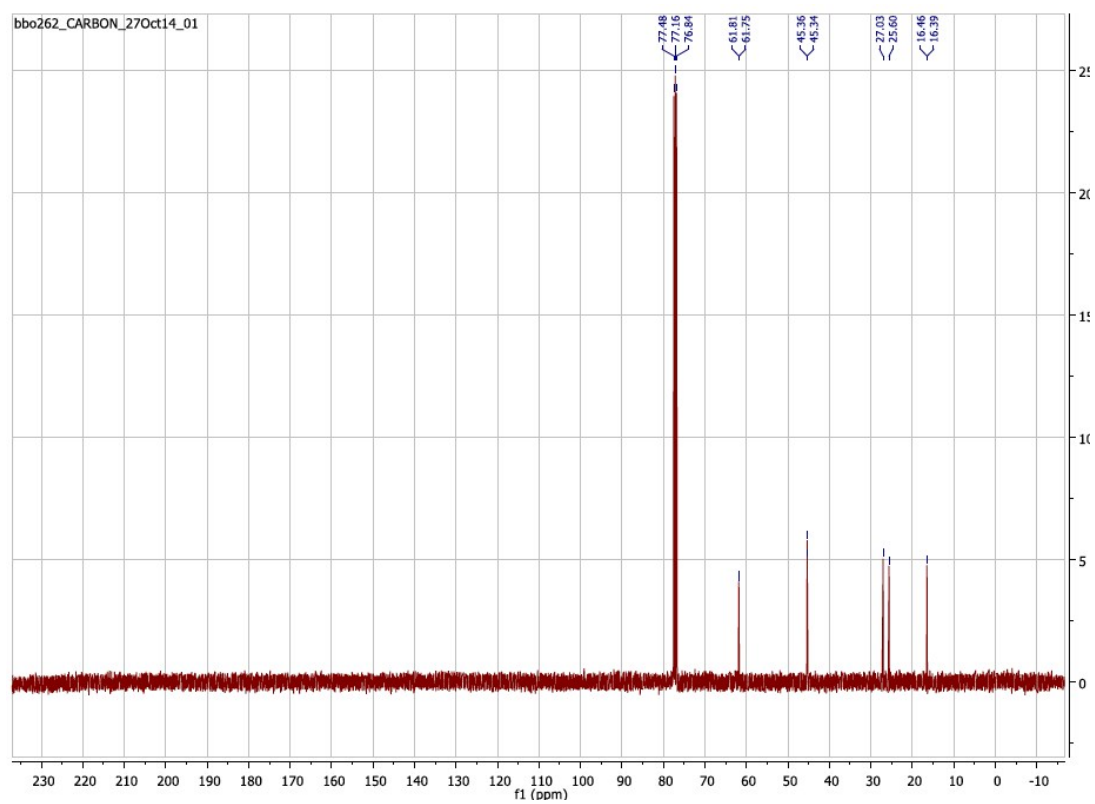
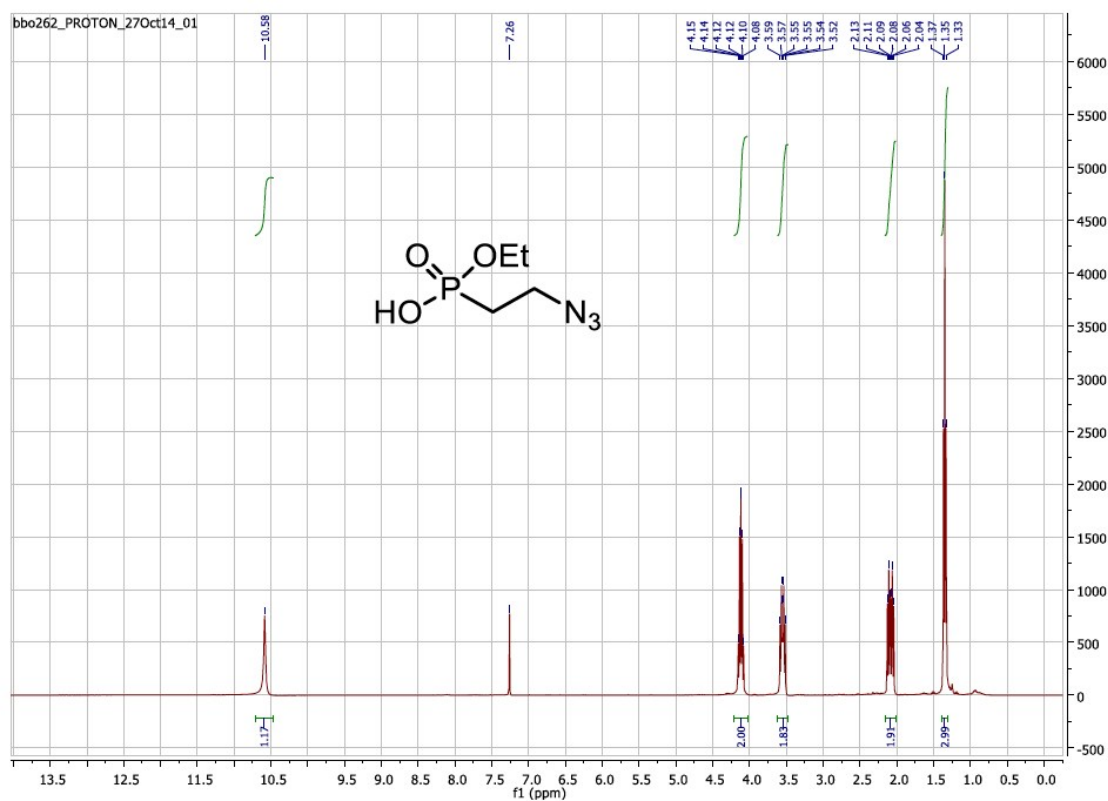
¹H NMR spectrum (CDCl₃) of compound 10. The x-axis represents the chemical shift in ppm (f1), ranging from 4.0 to 2.5. The y-axis represents the intensity. The spectrum shows several peaks, with integration values provided below the main signals.

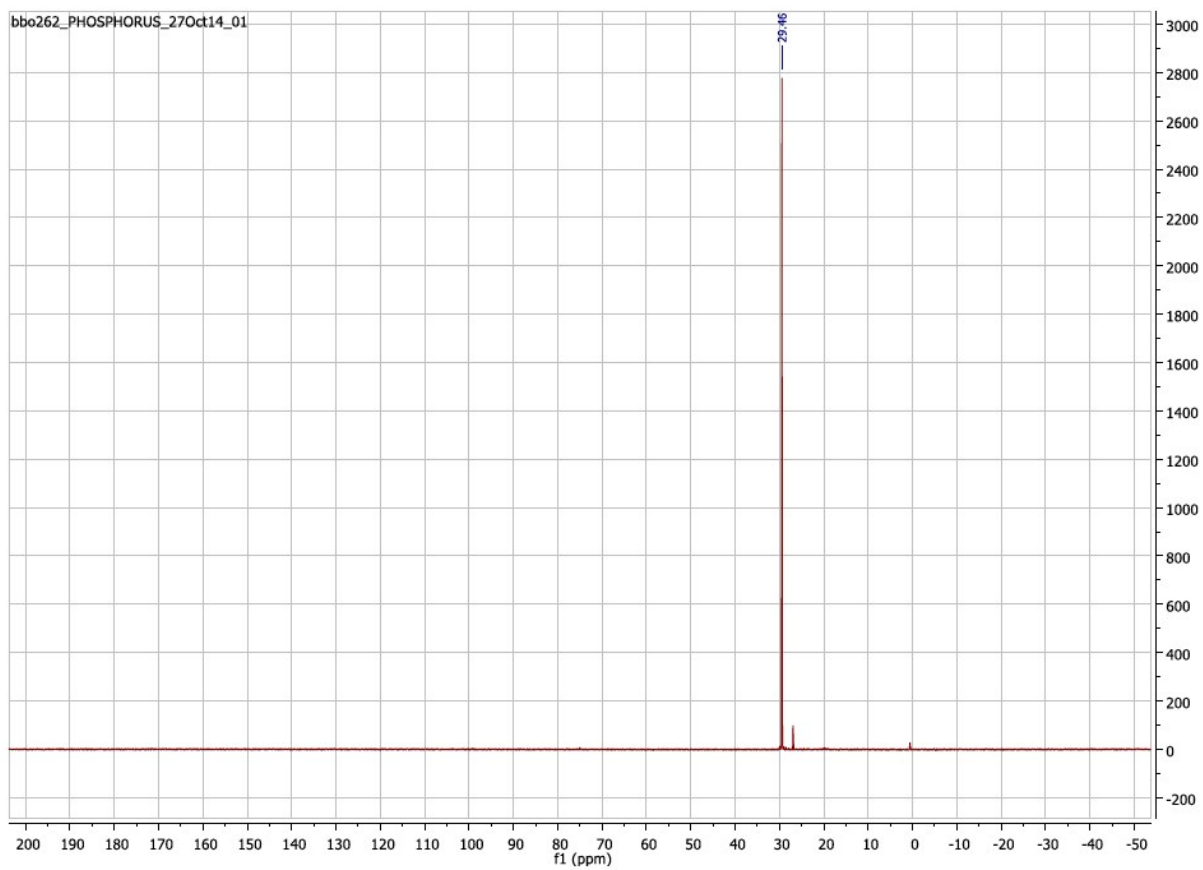
Integration values (from left to right):

- 16.16
- 7.46
- 21.74
- 0.94
- 1.06
- 1.00
- 1.03
- 4.53
- 5.59
- 3.65
- 1.12
- 2.19
- 5.52
- 1.17
- 2.20
- 2.07
- 1.06
- 1.10

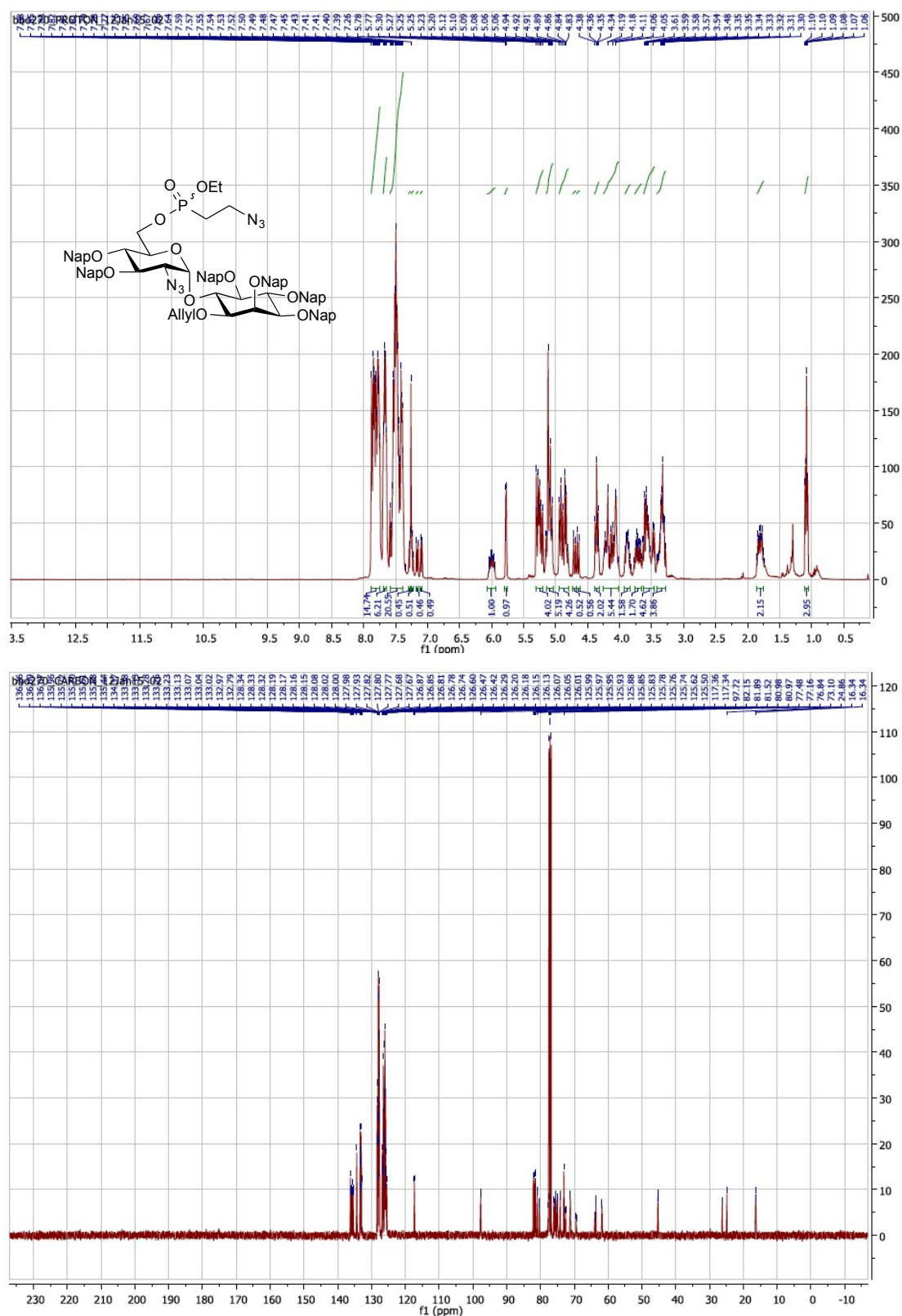


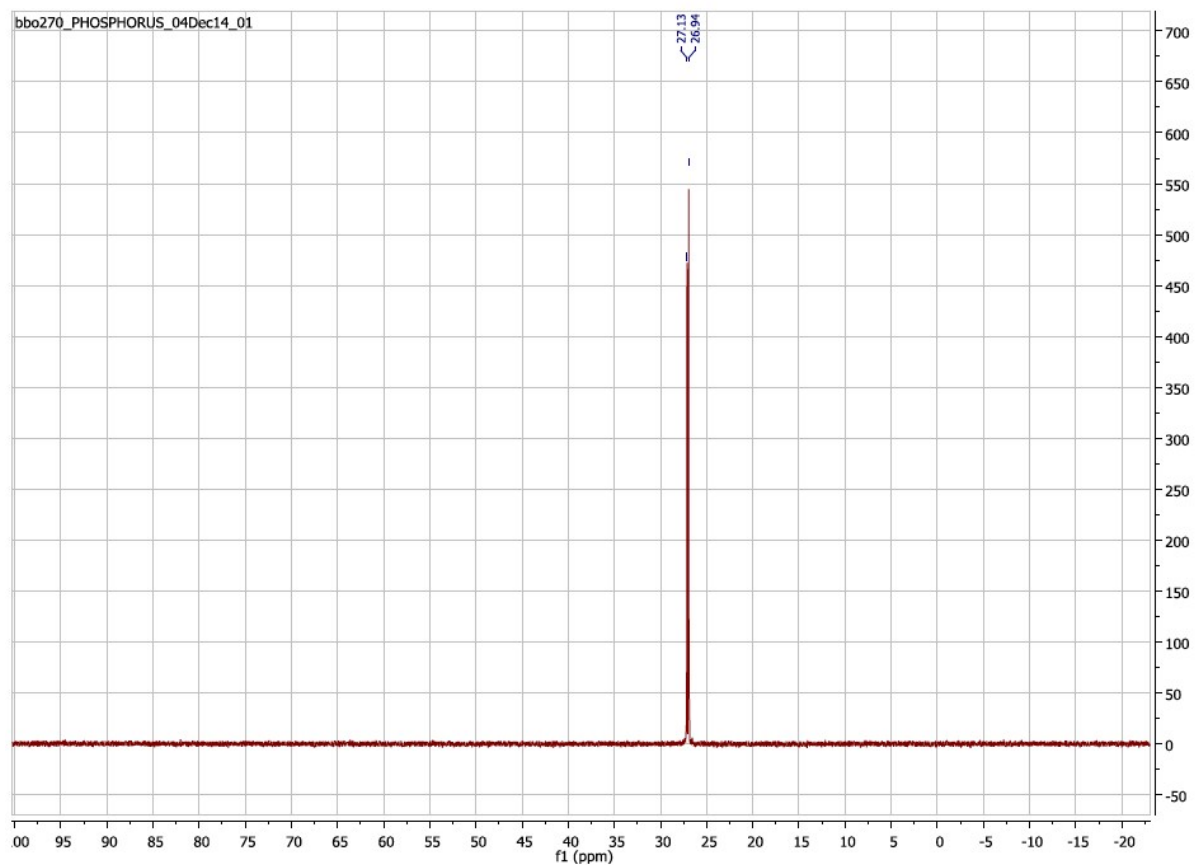
***O*-Ethyl (2-azidoethyl)phosphonic acid (22)**

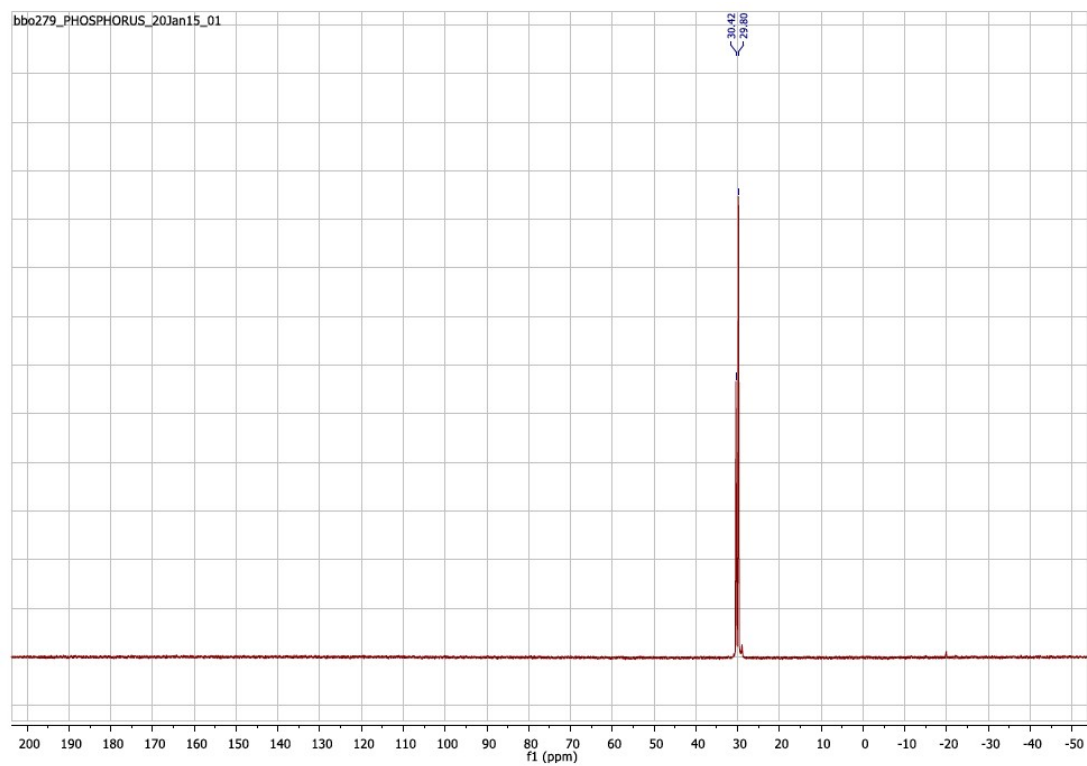


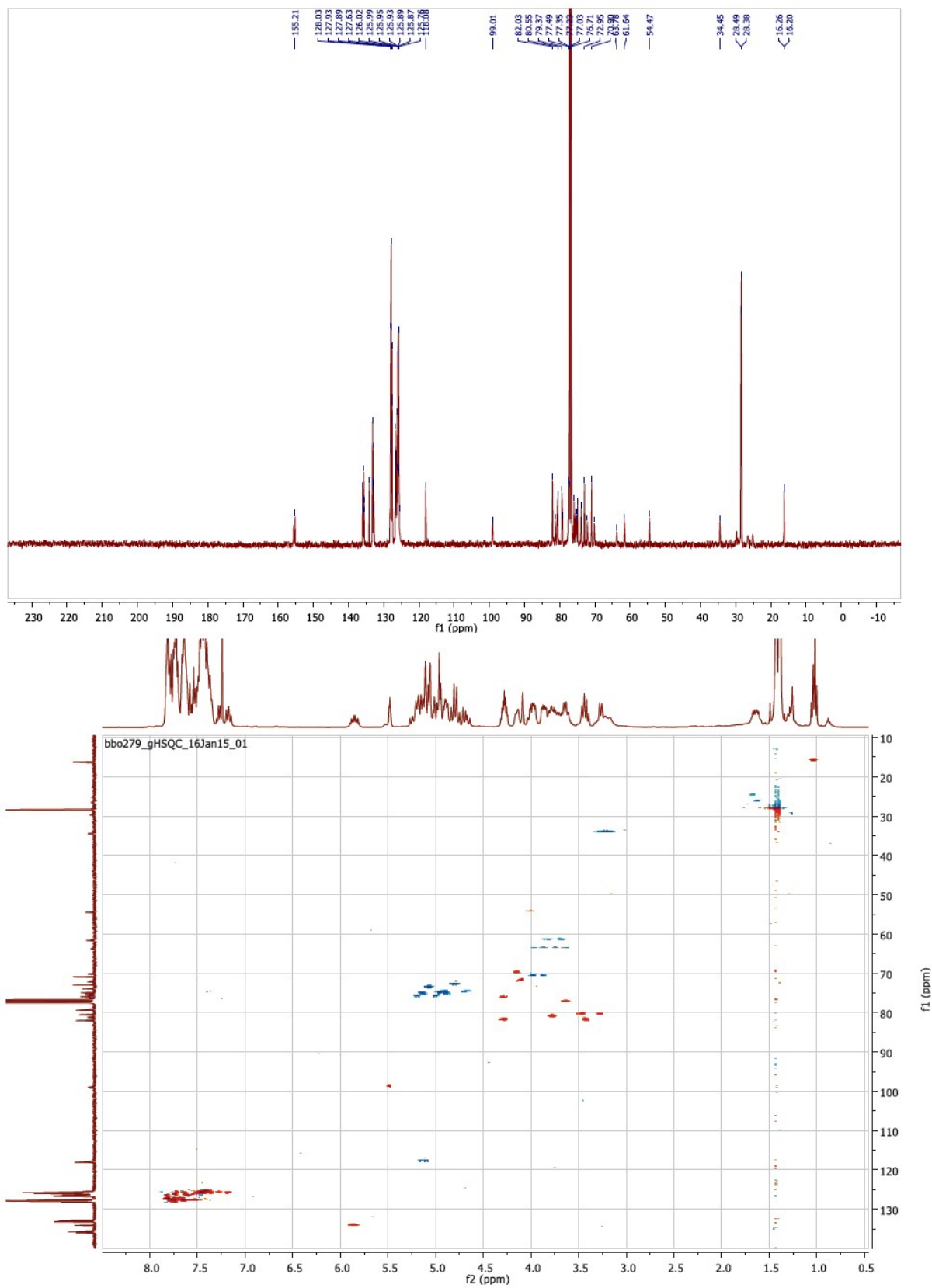


2-Azido-3,4-di-*O*-(2-naphthyl)methyl-6-*O*-((2-azidoethyl)phosphonic acid ethyl ester)-2-deoxy- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-1-*O*-allyl-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (25)

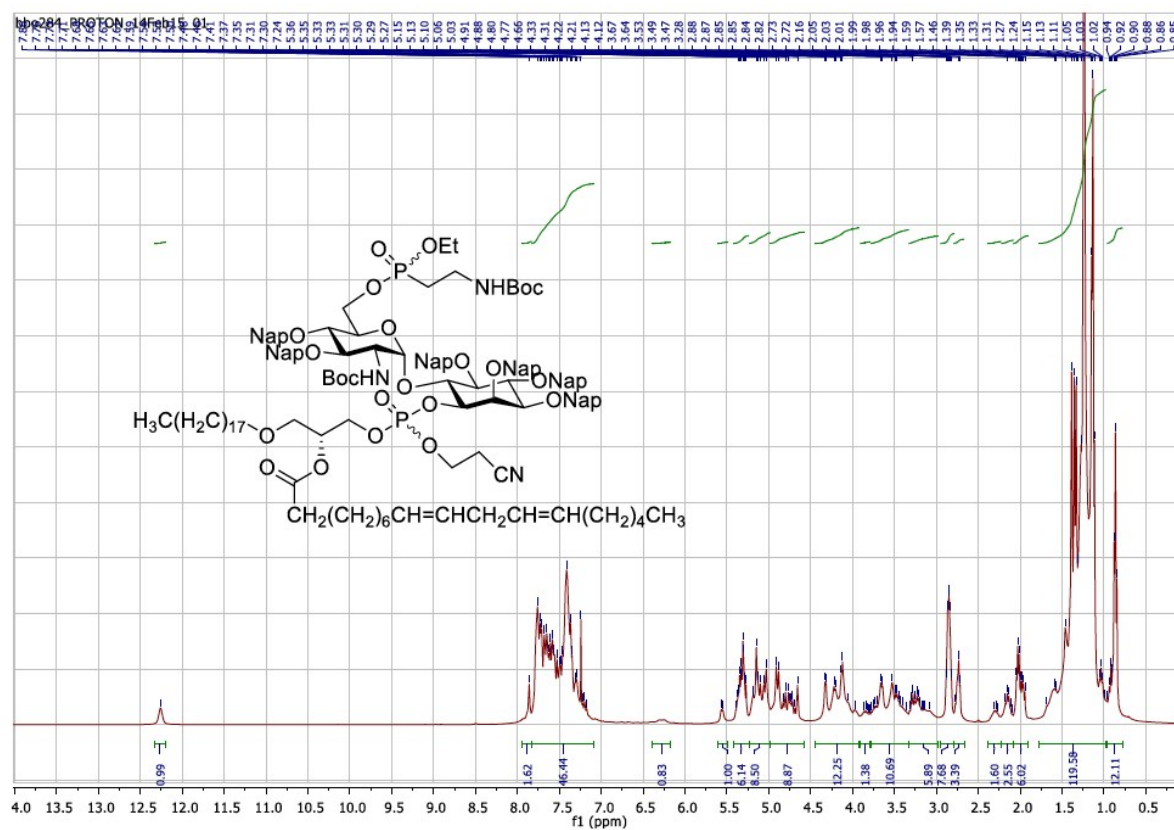


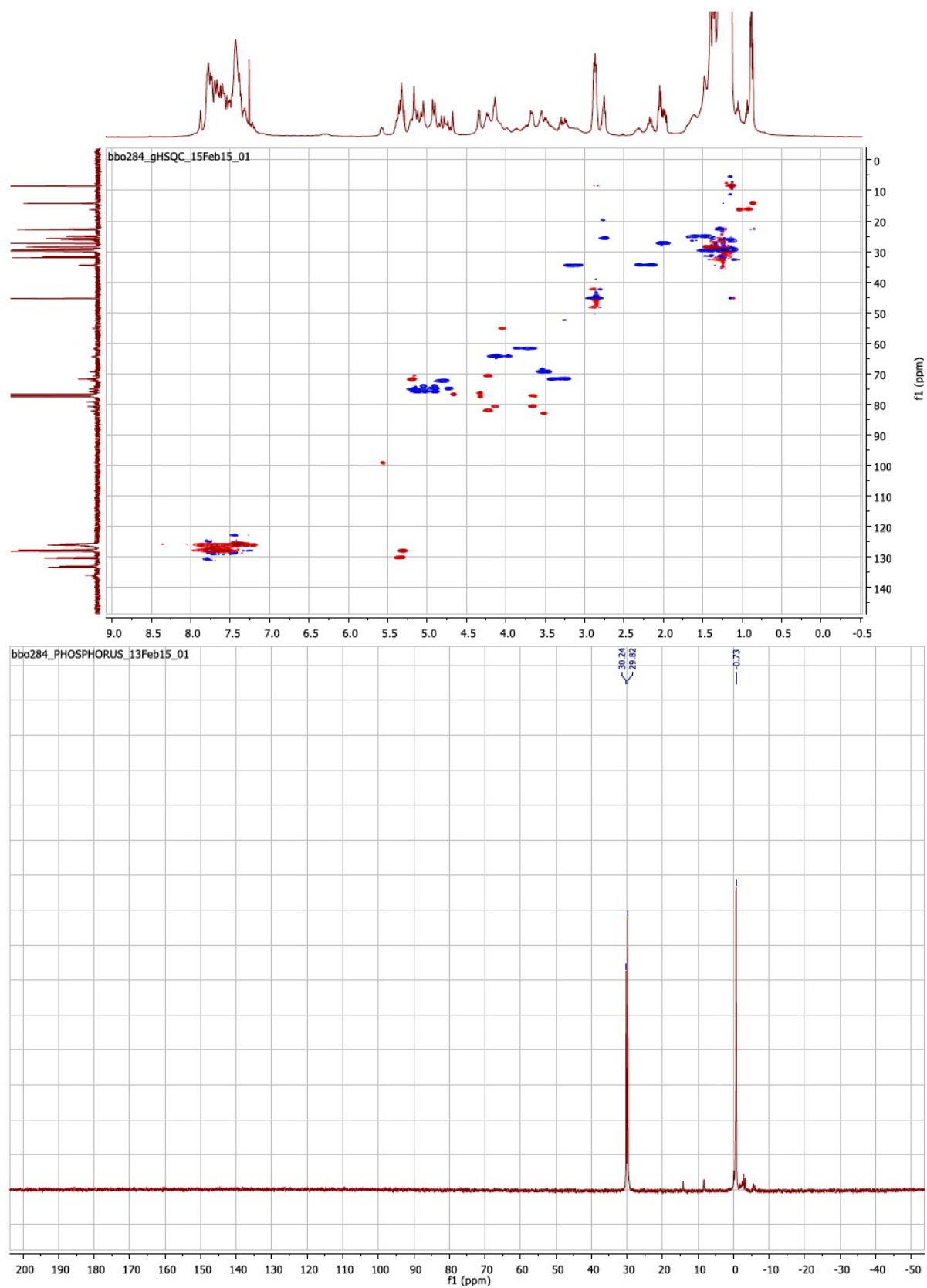




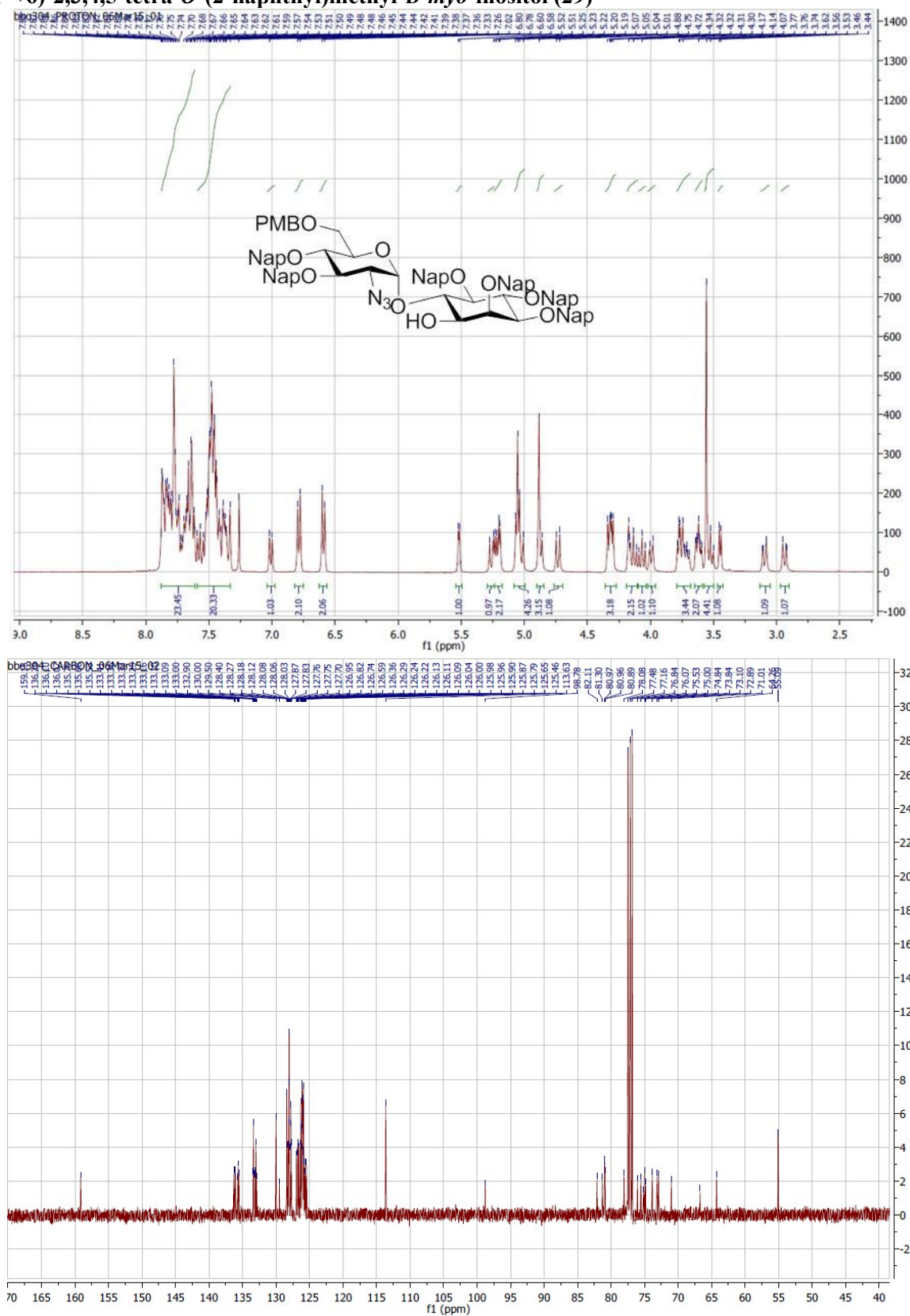


2-[*N*-(*tert*-butoxycarbonyl)amido]-3,4-di-*O*-(2-naphthyl)methyl-6-*O*-((2-*N*-(*tert*-butoxycarbonyl)aminoethyl)phosphonic acid ethyl ester)-2-deoxy- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-1-*O*-[1-*O*-(octadecyl)-2-*O*-(9*Z*,12*Z*-octadecanoyl)-*sn*-glycero-3-phosphocynoethyl]-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (28)

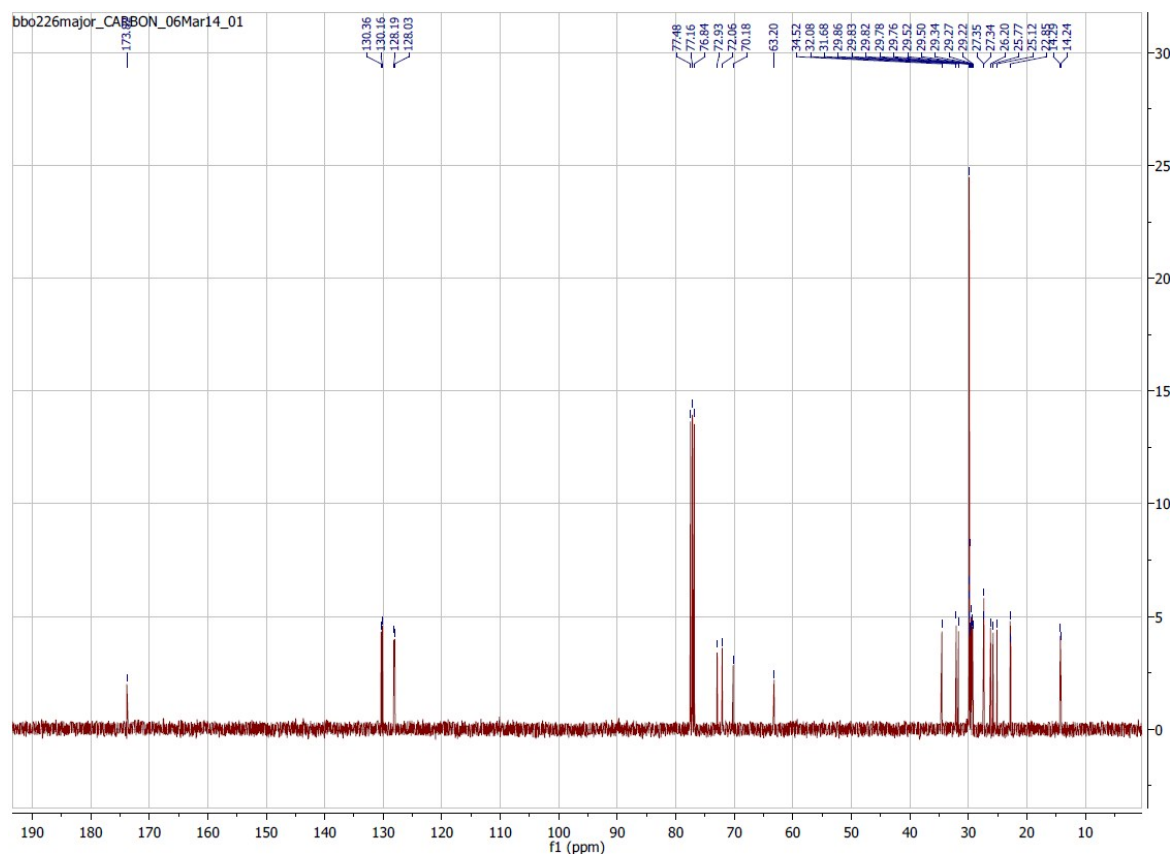
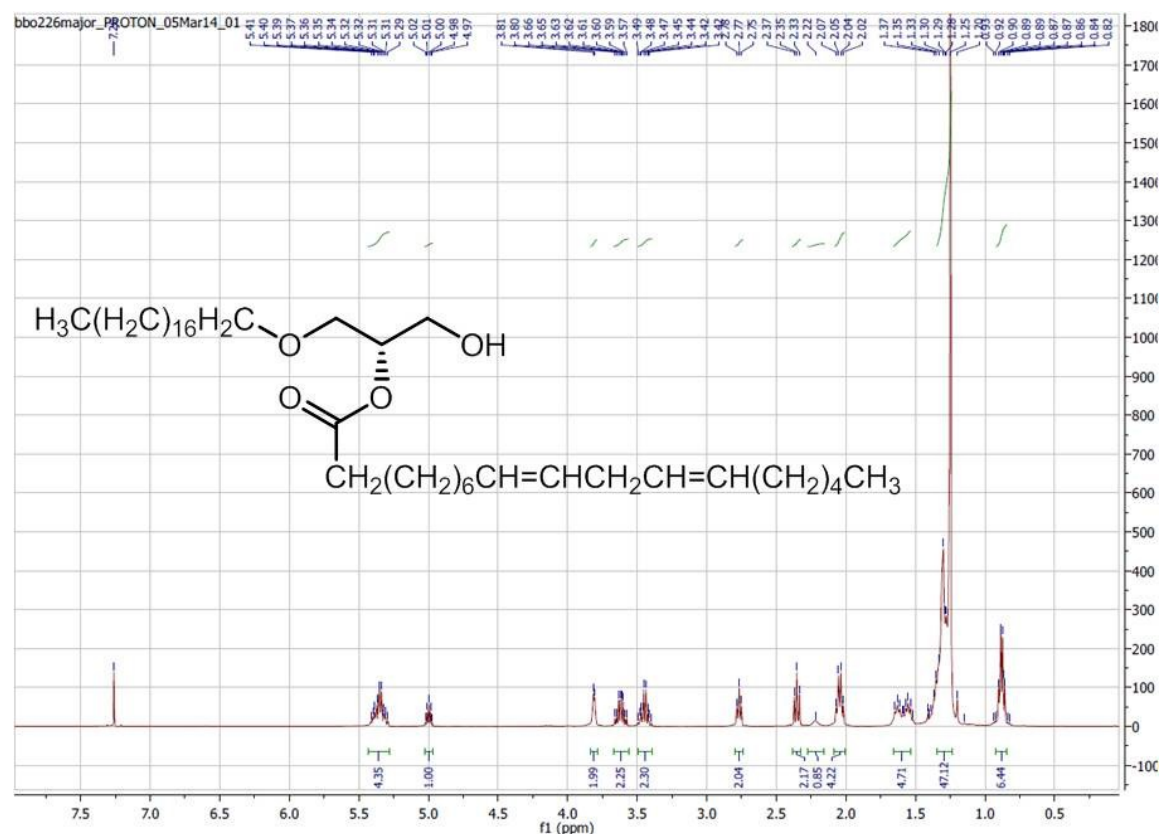




2-Azido-3,4-di-*O*-(2-naphthyl)methyl-6-*O*-(*p*-methoxybenzyl)-2-deoxy- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (29)



1-*O*-(Octadecyl)-2-*O*-(9*Z*,12*Z*-octadecanoyl)-*sn*-glycerol (20)

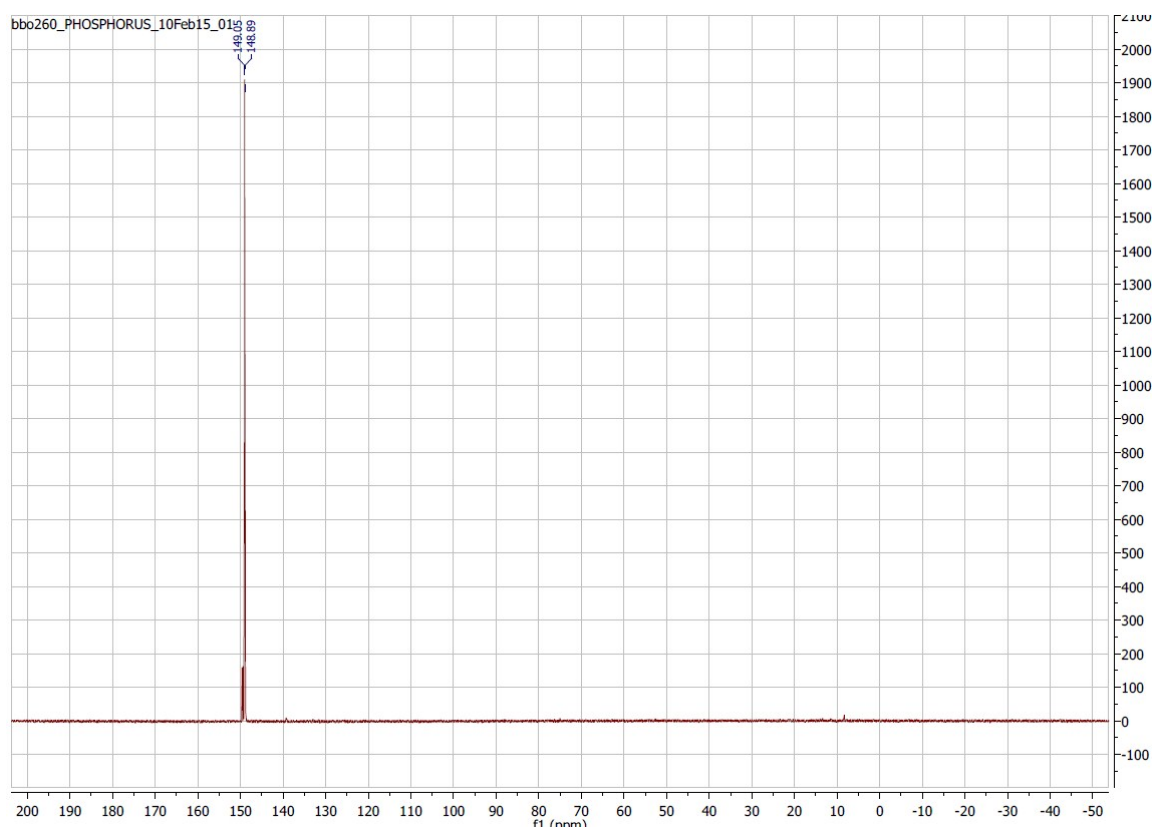


1H NMR (400 MHz, CDCl₃)

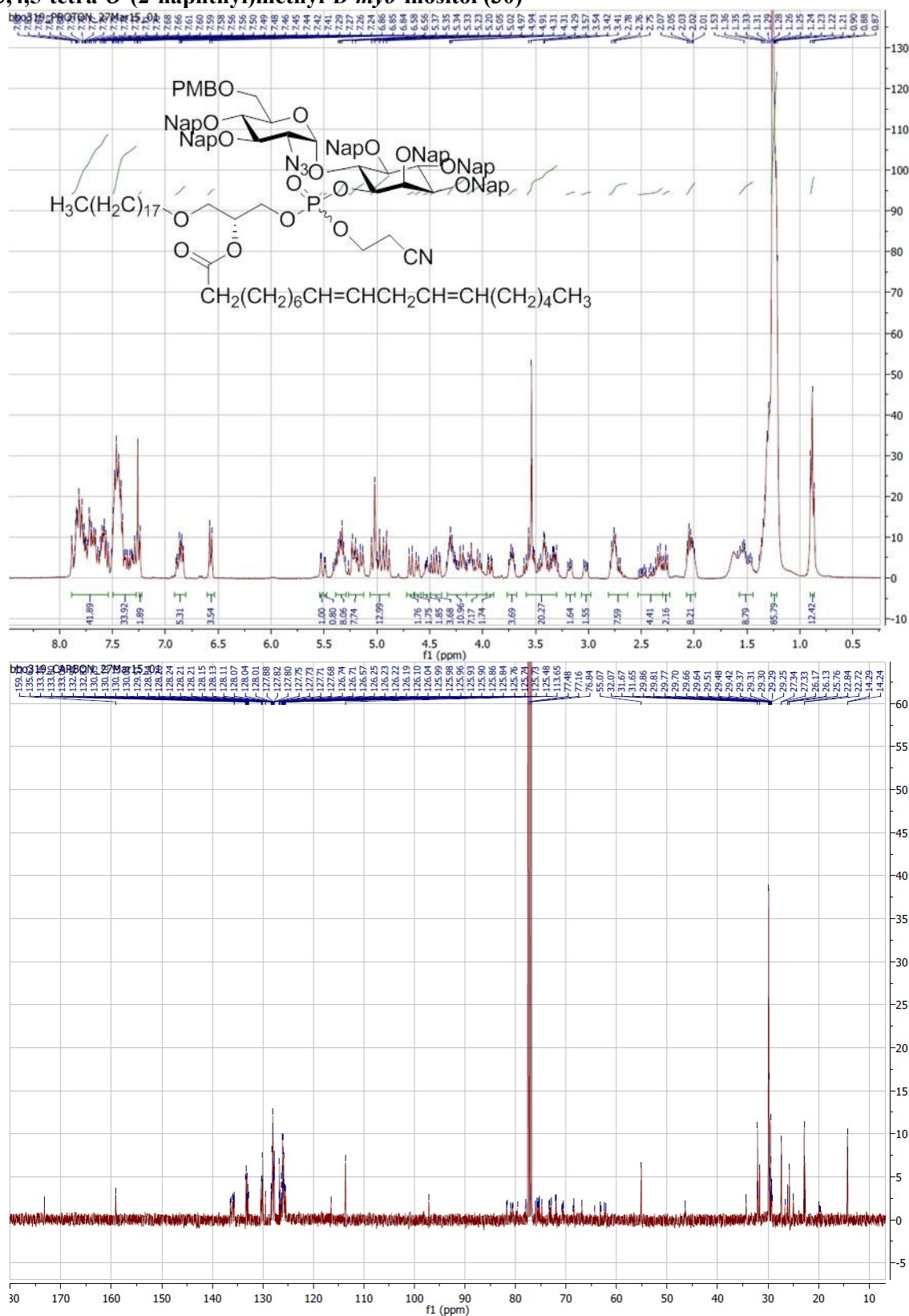
Chemical structure of compound 1:

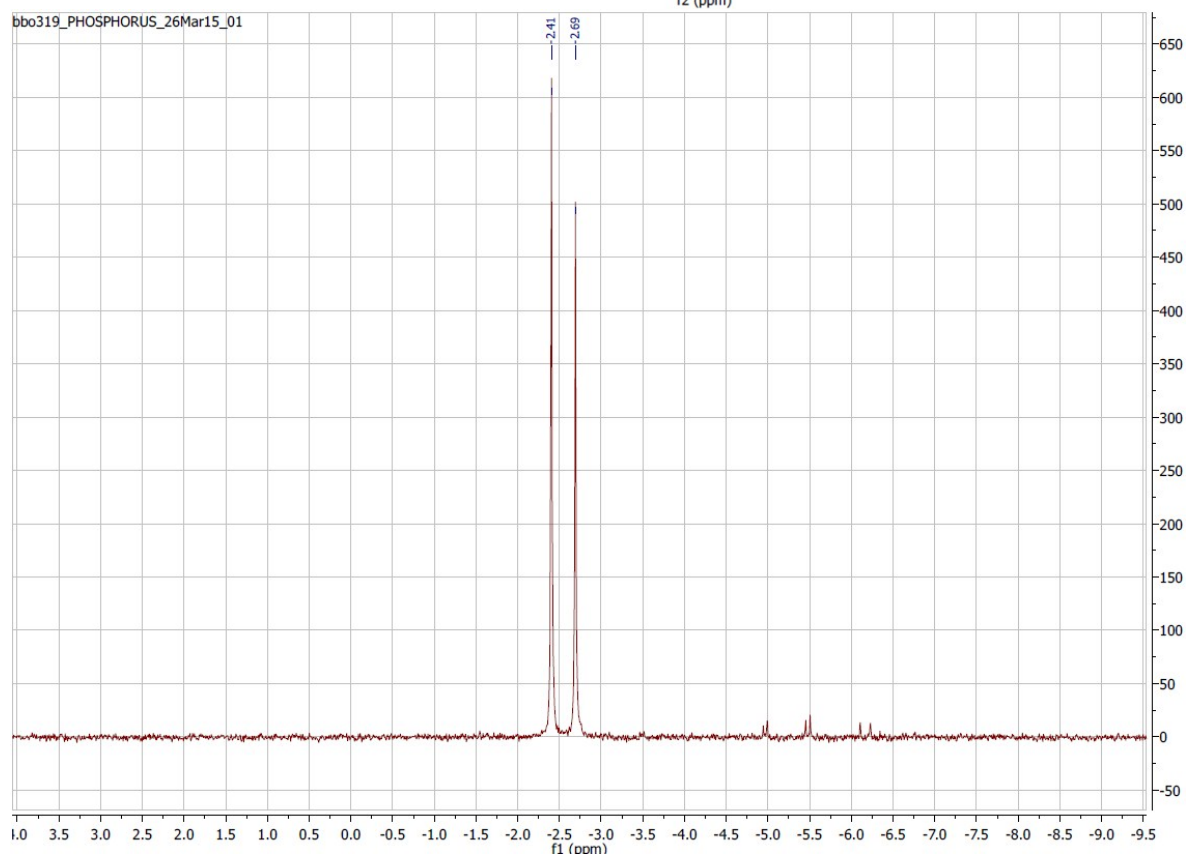
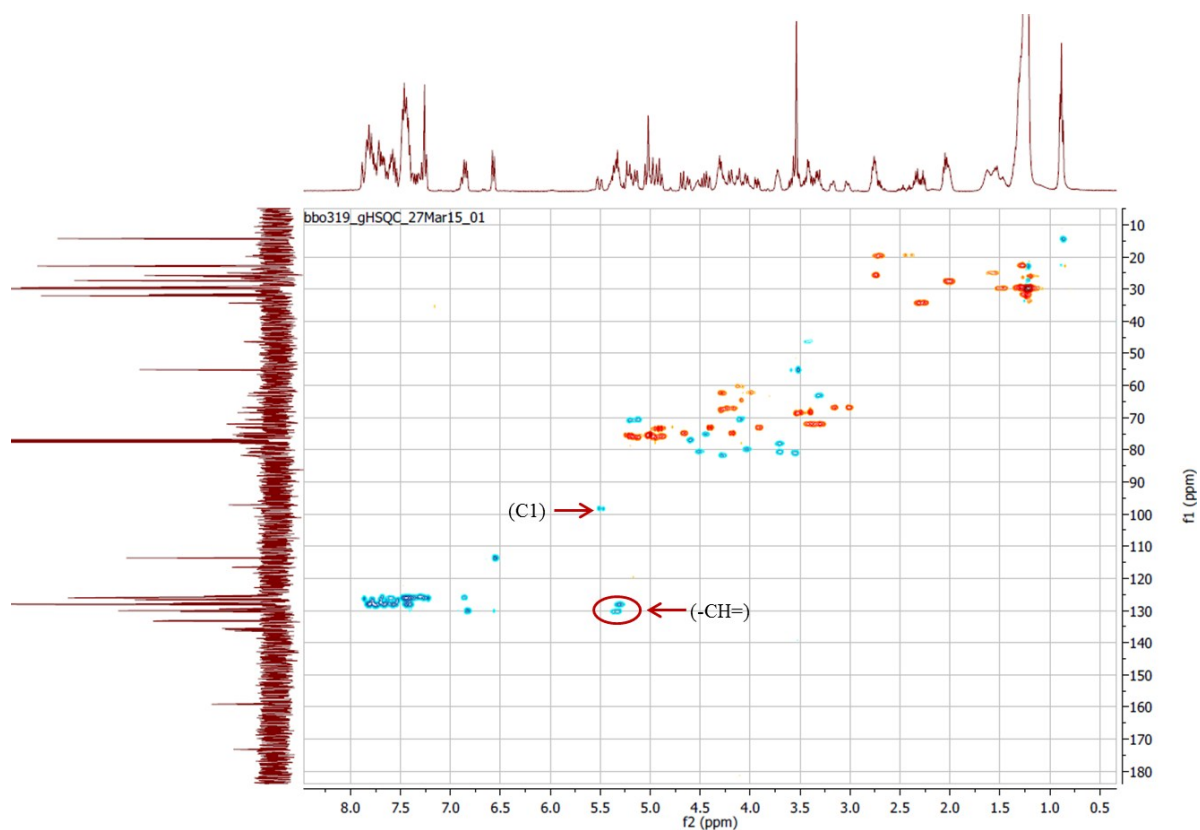
CCCCCCCCCCCCCCCCOC[C@H](C(=O)OCCCC=CCCC=CCCC)COP(C(C)C)C(C)COCC#N

Peak list (ppm): 7.32, 7.31, 7.29, 7.28, 7.27, 7.26, 7.25, 7.24, 7.23, 7.22, 7.21, 7.20, 7.19, 7.18, 7.17, 7.16, 7.15, 7.14, 7.13, 7.12, 7.11, 7.10, 7.09, 7.08, 7.07, 7.06, 7.05, 7.04, 7.03, 7.02, 7.01, 7.00, 6.99, 6.98, 6.97, 6.96, 6.95, 6.94, 6.93, 6.92, 6.91, 6.90, 6.89, 6.88, 6.87, 6.86, 6.85, 6.84, 6.83, 6.82, 6.81, 6.80, 6.79, 6.78, 6.77, 6.76, 6.75, 6.74, 6.73, 6.72, 6.71, 6.70, 6.69, 6.68, 6.67, 6.66, 6.65, 6.64, 6.63, 6.62, 6.61, 6.60, 6.59, 6.58, 6.57, 6.56, 6.55, 6.54, 6.53, 6.52, 6.51, 6.50, 6.49, 6.48, 6.47, 6.46, 6.45, 6.44, 6.43, 6.42, 6.41, 6.40, 6.39, 6.38, 6.37, 6.36, 6.35, 6.34, 6.33, 6.32, 6.31, 6.30, 6.29, 6.28, 6.27, 6.26, 6.25, 6.24, 6.23, 6.22, 6.21, 6.20, 6.19, 6.18, 6.17, 6.16, 6.15, 6.14, 6.13, 6.12, 6.11, 6.10, 6.09, 6.08, 6.07, 6.06, 6.05, 6.04, 6.03, 6.02, 6.01, 6.00, 5.99, 5.98, 5.97, 5.96, 5.95, 5.94, 5.93, 5.92, 5.91, 5.90, 5.89, 5.88, 5.87, 5.86, 5.85, 5.84, 5.83, 5.82, 5.81, 5.80, 5.79, 5.78, 5.77, 5.76, 5.75, 5.74, 5.73, 5.72, 5.71, 5.70, 5.69, 5.68, 5.67, 5.66, 5.65, 5.64, 5.63, 5.62, 5.61, 5.60, 5.59, 5.58, 5.57, 5.56, 5.55, 5.54, 5.53, 5.52, 5.51, 5.50, 5.49, 5.48, 5.47, 5.46, 5.45, 5.44, 5.43, 5.42, 5.41, 5.40, 5.39, 5.38, 5.37, 5.36, 5.35, 5.34, 5.33, 5.32, 5.31, 5.30, 5.29, 5.28, 5.27, 5.26, 5.25, 5.24, 5.23, 5.22, 5.21, 5.20, 5.19, 5.18, 5.17, 5.16, 5.15, 5.14, 5.13, 5.12, 5.11, 5.10, 5.09, 5.08, 5.07, 5.06, 5.05, 5.04, 5.03, 5.02, 5.01, 5.00, 4.99, 4.98, 4.97, 4.96, 4.95, 4.94, 4.93, 4.92, 4.91, 4.90, 4.89, 4.88, 4.87, 4.86, 4.85, 4.84, 4.83, 4.82, 4.81, 4.80, 4.79, 4.78, 4.77, 4.76, 4.75, 4.74, 4.73, 4.72, 4.71, 4.70, 4.69, 4.68, 4.67, 4.66, 4.65, 4.64, 4.63, 4.62, 4.61, 4.60, 4.59, 4.58, 4.57, 4.56, 4.55, 4.54, 4.53, 4.52, 4.51, 4.50, 4.49, 4.48, 4.47, 4.46, 4.45, 4.44, 4.43, 4.42, 4.41, 4.40, 4.39, 4.38, 4.37, 4.36, 4.35, 4.34, 4.33, 4.32, 4.31, 4.30, 4.29, 4.28, 4.27, 4.26, 4.25, 4.24, 4.23, 4.22, 4.21, 4.20, 4.19, 4.18, 4.17, 4.16, 4.15, 4.14, 4.13, 4.12, 4.11, 4.10, 4.09, 4.08, 4.07, 4.06, 4.05, 4.04, 4.03, 4.02, 4.01, 4.00, 3.99, 3.98, 3.97, 3.96, 3.95, 3.94, 3.93, 3.92, 3.91, 3.90, 3.89, 3.88, 3.87, 3.86, 3.85, 3.84, 3.83, 3.82, 3.81, 3.80, 3.79, 3.78, 3.77, 3.76, 3.75, 3.74, 3.73, 3.72, 3.71, 3.70, 3.69, 3.68, 3.67, 3.66, 3.65, 3.64, 3.63, 3.62, 3.61, 3.60, 3.59, 3.58, 3.57, 3.56, 3.55, 3.54, 3.53, 3.52, 3.51, 3.50, 3.49, 3.48, 3.47, 3.46, 3.45, 3.44, 3.43, 3.42, 3.41, 3.40, 3.39, 3.38, 3.37, 3.36, 3.35, 3.34, 3.33, 3.32, 3.31, 3.30, 3.29, 3.28, 3.27, 3.26, 3.25, 3.24, 3.23, 3.22, 3.21, 3.20, 3.19, 3.18, 3.17, 3.16, 3.15, 3.14, 3.13, 3.12, 3.11, 3.10, 3.09, 3.08, 3.07, 3.06, 3.05, 3.04, 3.03, 3.02, 3.01, 3.00, 2.99, 2.98, 2.97, 2.96, 2.95, 2.94, 2.93, 2.92, 2.91, 2.90, 2.89, 2.88, 2.87, 2.86, 2.85, 2.84, 2.83, 2.82, 2.81, 2.80, 2.79, 2.78, 2.77, 2.76, 2.75, 2.74, 2.73, 2.72, 2.71, 2.70, 2.69, 2.68, 2.67, 2.66, 2.65, 2.64, 2.63, 2.62, 2.61, 2.60, 2.59, 2.58, 2.57, 2.56, 2.55, 2.54, 2.53, 2.52, 2.51, 2.50, 2.49, 2.48, 2.47, 2.46, 2.45, 2.44, 2.43, 2.42, 2.41, 2.40, 2.39, 2.38, 2.37, 2.36, 2.35, 2.34, 2.33, 2.32, 2.31, 2.30, 2.29, 2.28, 2.27, 2.26, 2.25, 2.24, 2.23, 2.22, 2.21, 2.20, 2.19, 2.18, 2.17, 2.16, 2.15, 2.14, 2.13, 2.12, 2.11, 2.10, 2.09, 2.08, 2.07, 2.06, 2.05, 2.04, 2.03, 2.02, 2.01, 2.00, 1.99, 1.98, 1.97, 1.96, 1.95, 1.94, 1.93, 1.92, 1.91, 1.90, 1.89, 1.88, 1.87, 1.86, 1.85, 1.84, 1.83, 1.82, 1.81, 1.80, 1.79, 1.78, 1.77, 1.76, 1.75, 1.74, 1.73, 1.72, 1.71, 1.70, 1.69, 1.68, 1.67, 1.66, 1.65, 1.64, 1.63, 1.62, 1.61, 1.60, 1.59, 1.58, 1.57, 1.56, 1.55, 1.54, 1.53, 1.52, 1.51, 1.50, 1.49, 1.48, 1.47, 1.46, 1.45, 1.44, 1.43, 1.42, 1.41, 1.40, 1.39, 1.38, 1.37, 1.36, 1.35, 1.34, 1.33, 1.32, 1.31, 1.30, 1.29, 1.28, 1.27, 1.26, 1.25, 1.24, 1.23, 1.22, 1.21, 1.20, 1.19, 1.18, 1.17, 1.16, 1.15, 1.14, 1.13, 1.12, 1.11, 1.10, 1.09, 1.08, 1.07, 1.06, 1.05, 1.04, 1.03, 1.02, 1.01, 1.00, 0.99, 0.98, 0.97, 0.96, 0.95, 0.94, 0.93, 0.92, 0.91, 0.90, 0.89, 0.88, 0.87, 0.86, 0.85, 0.84, 0.83, 0.82, 0.

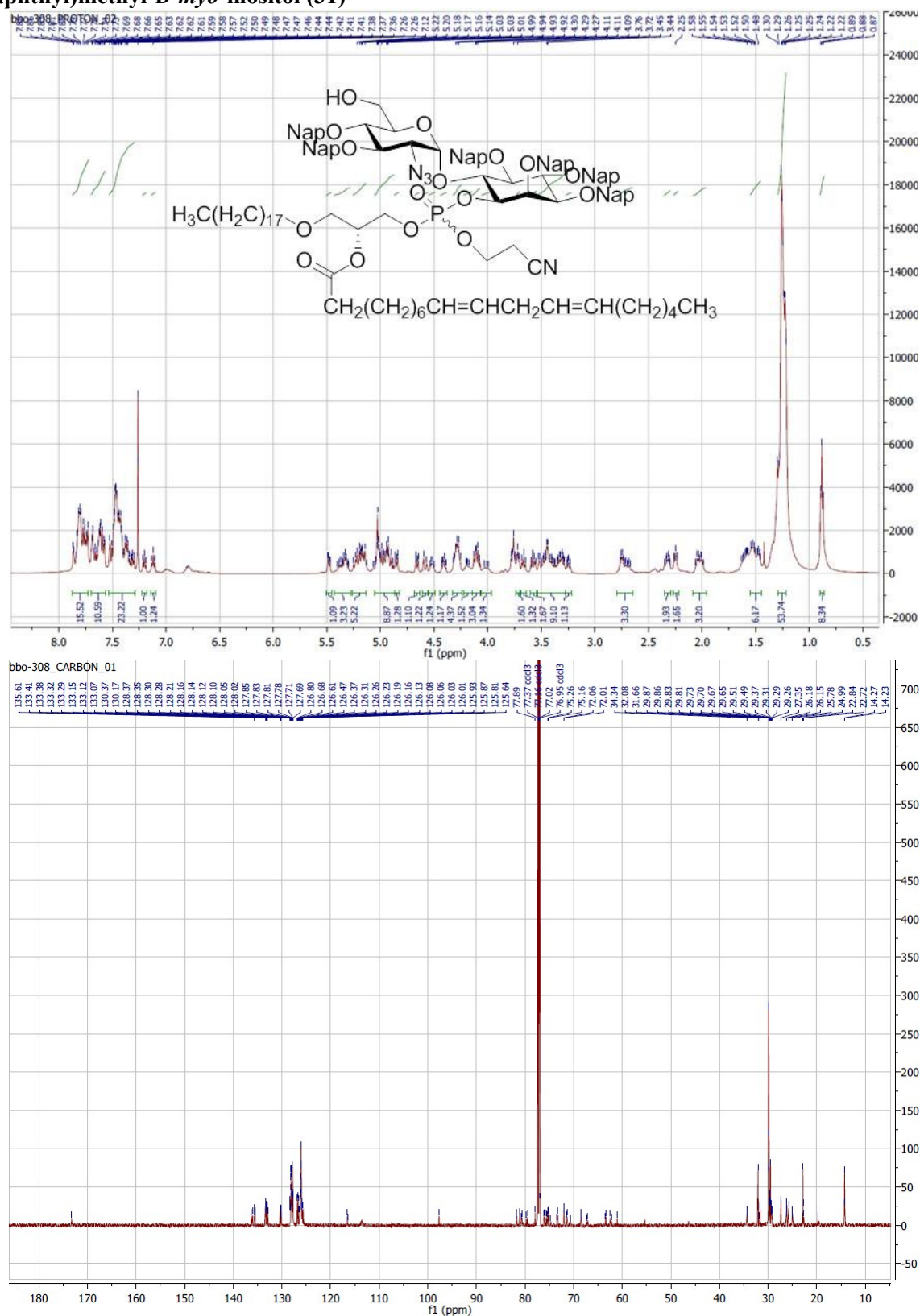


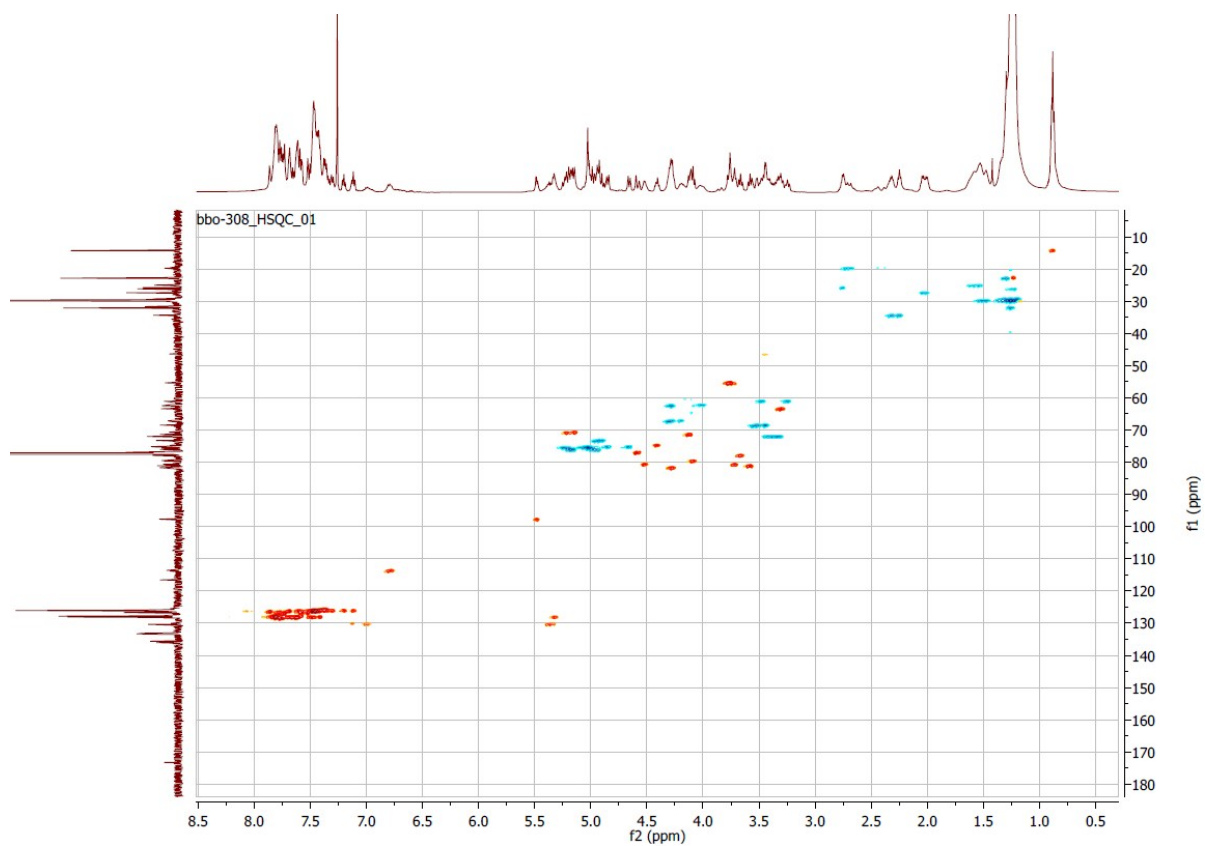
2-Azido-3,4-di-*O*-(2-naphthyl)methyl-6-*O*-(*p*-methoxybenzyl)-2-deoxy- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-1-*O*-[1-*O*-(octadecyl)-2-*O*-(9*Z*,12*Z*-octadecanoyl)-*sn*-glycero-3-phosphocynoethyl]-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (30)



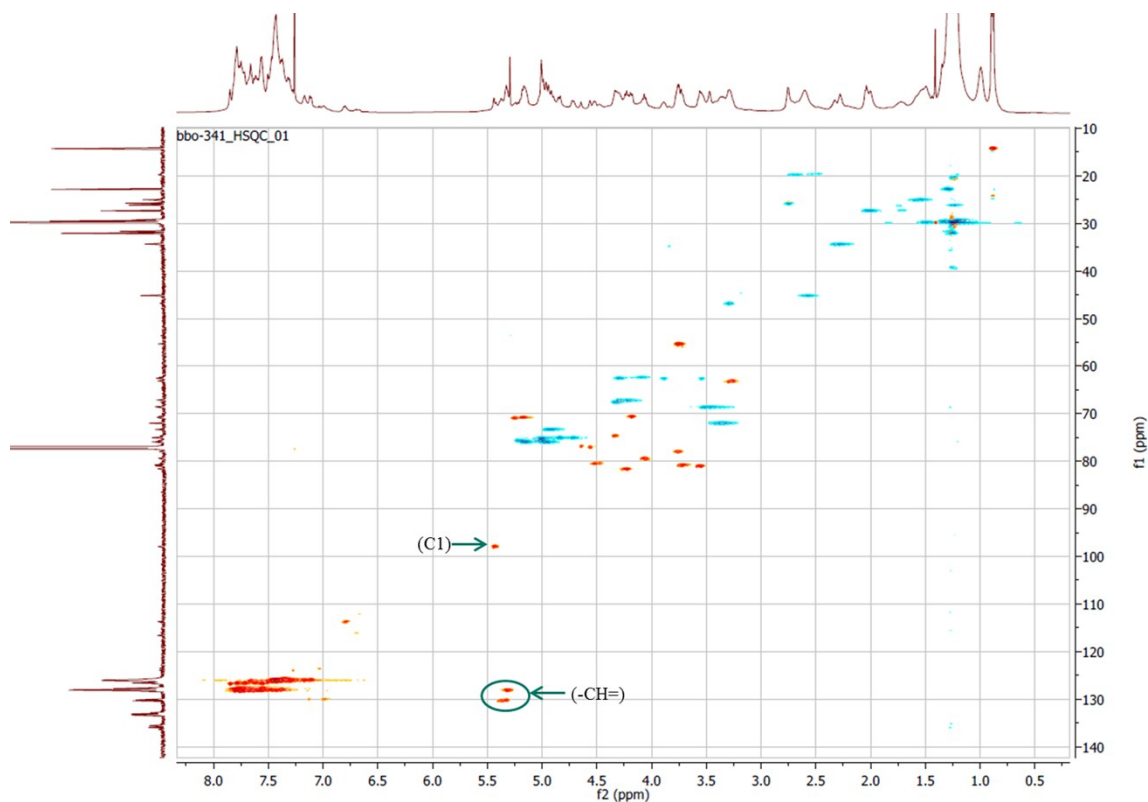
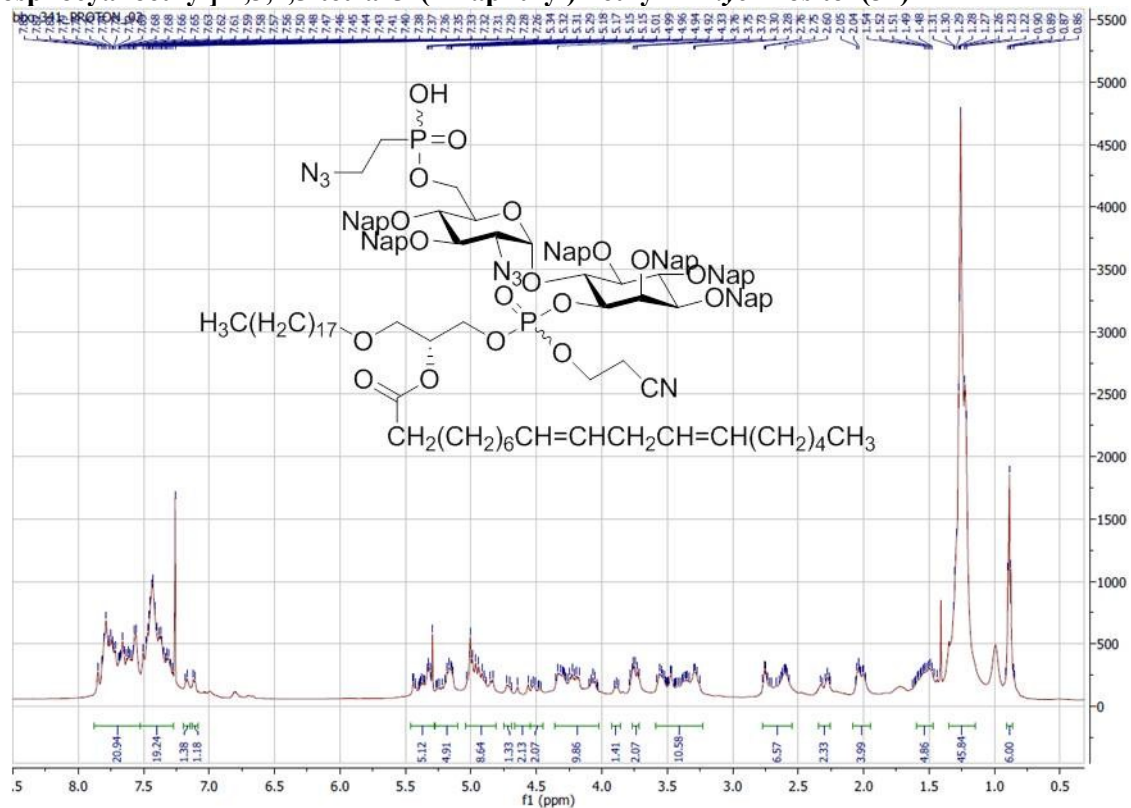


2-Azido-3,4-di-*O*-(2-naphthyl)methyl-2-deoxy- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-1-*O*-[1-*O*-(octadecyl)-2-*O*-(9*Z*,12*Z*-octadecanoyl)-*sn*-glycero-3-phosphocynoethyl]-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (31)

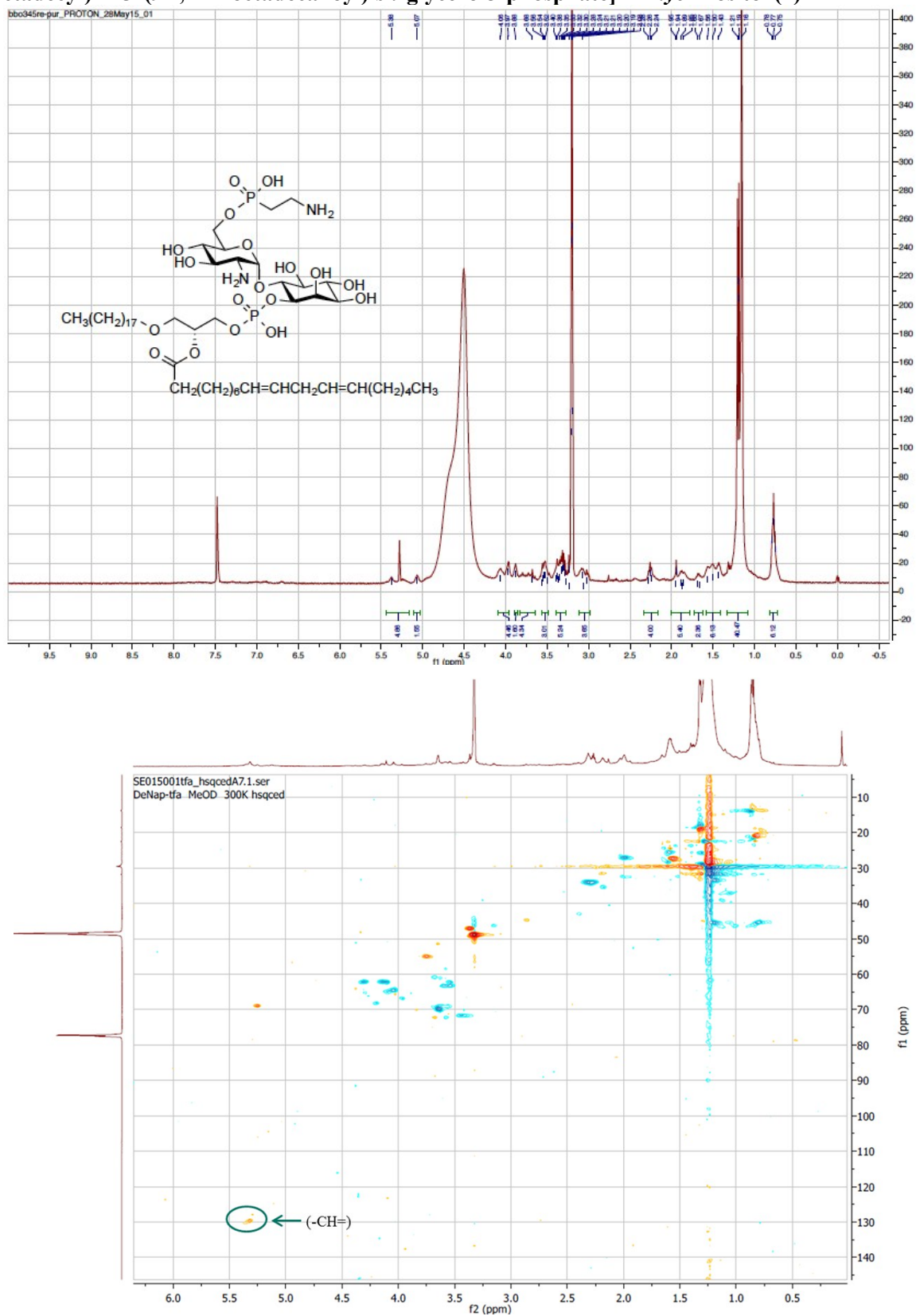


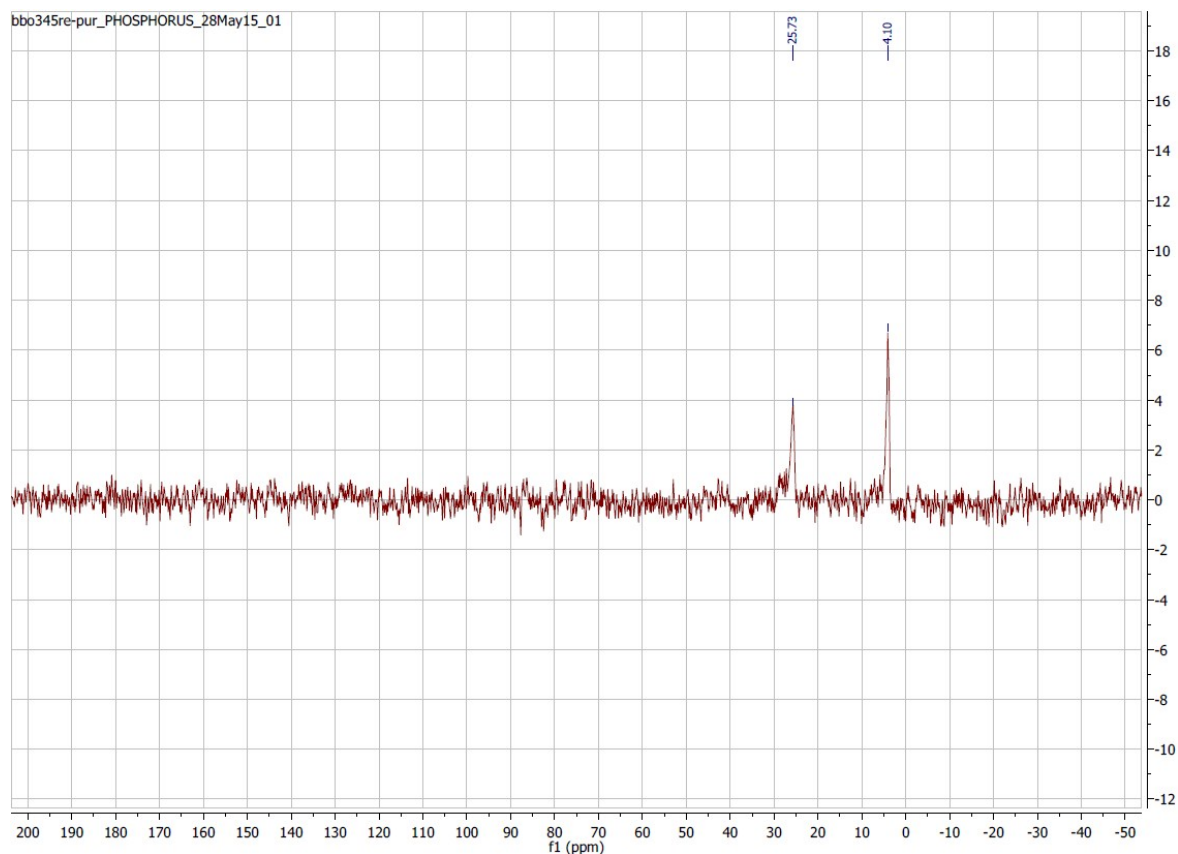


2-Azido-3,4-di-*O*-(2-naphthyl)methyl-6-*O*-(2-azidoethyl)phosphonic acid)-2-deoxy- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-1-*O*-[1-*O*-(octadecyl)-2-*O*-(9*Z*,12*Z*-octadecanoyl)-*sn*-glycero-3-phosphocynoethyl]-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (32)

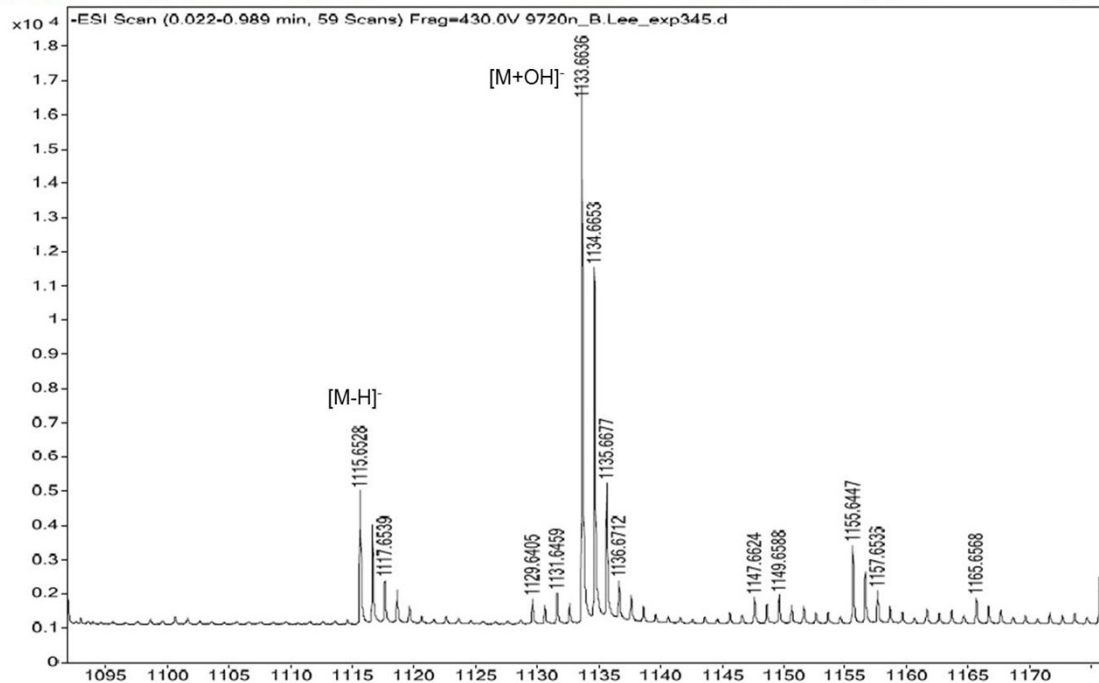


2-Amino-6-*O*-((2-aminoethyl)phosphonic acid)-2-deoxy- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-1-*O*-[1-*O*-(octadecyl)-2-*O*-(9*Z*,12*Z*-octadecanoyl)-*sn*-glycero-3-phosphate]-D-*myo*-inositol (2)

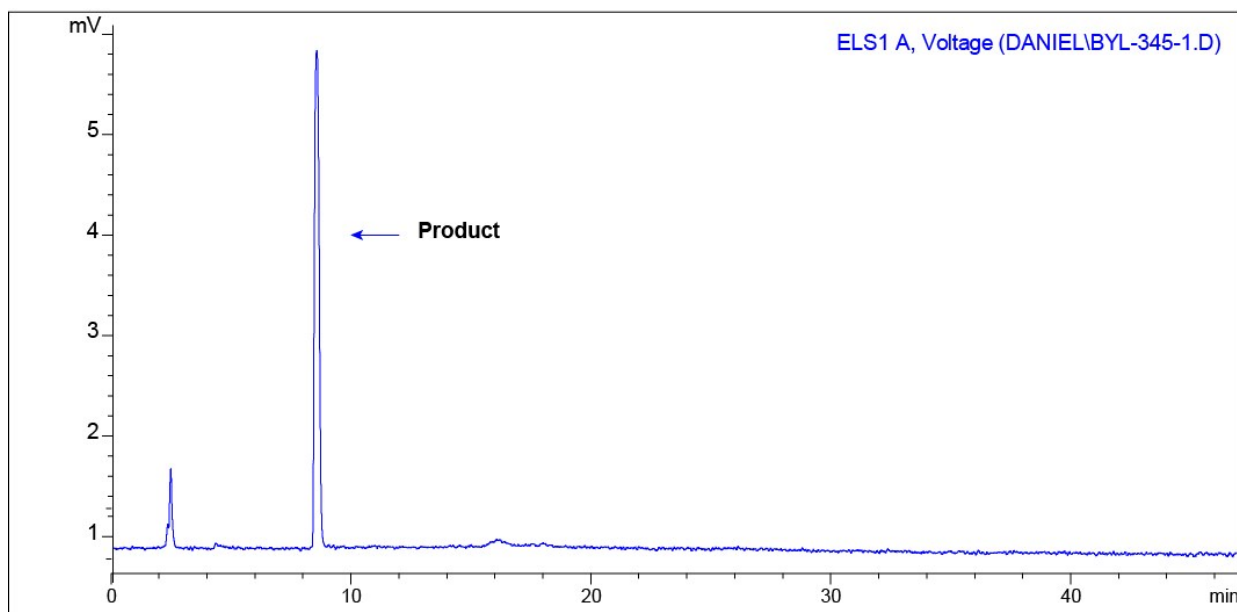
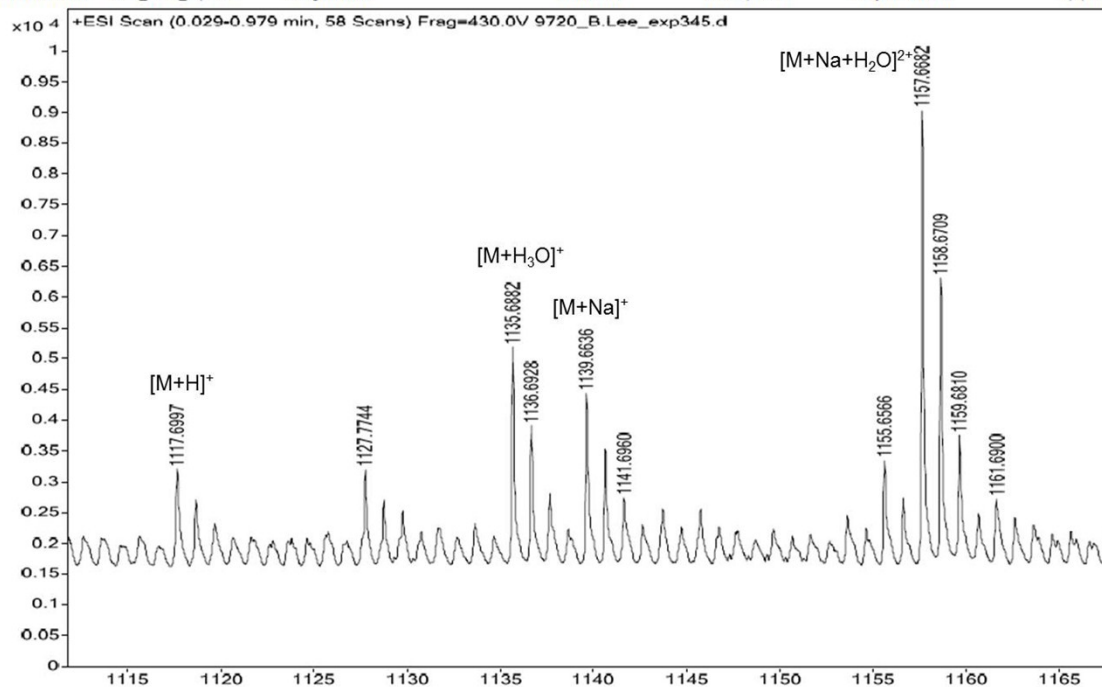




Sample Name	exp345	Position	Vial 1	Instrument Name	Instrument 1	User Name	
Inj Vol	5	InjPosition		SampleType	Sample	IRM Calibration Status	Success
Data Filename	9720n_B.Lee_exp345.d	ACQ Method		Comment	in DCM/MeOH	Acquired Time	6/9/2015 1:52:38 PM

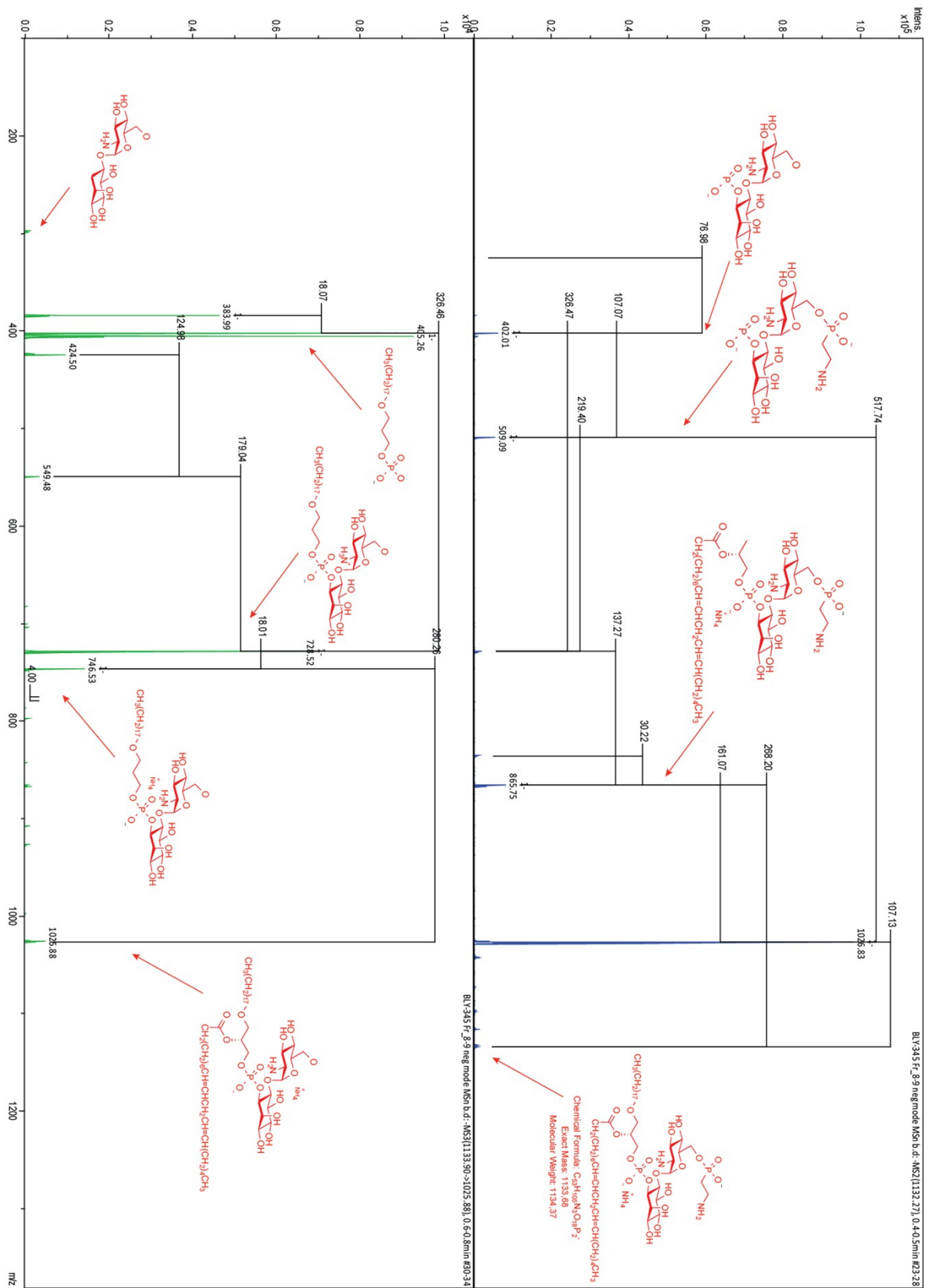


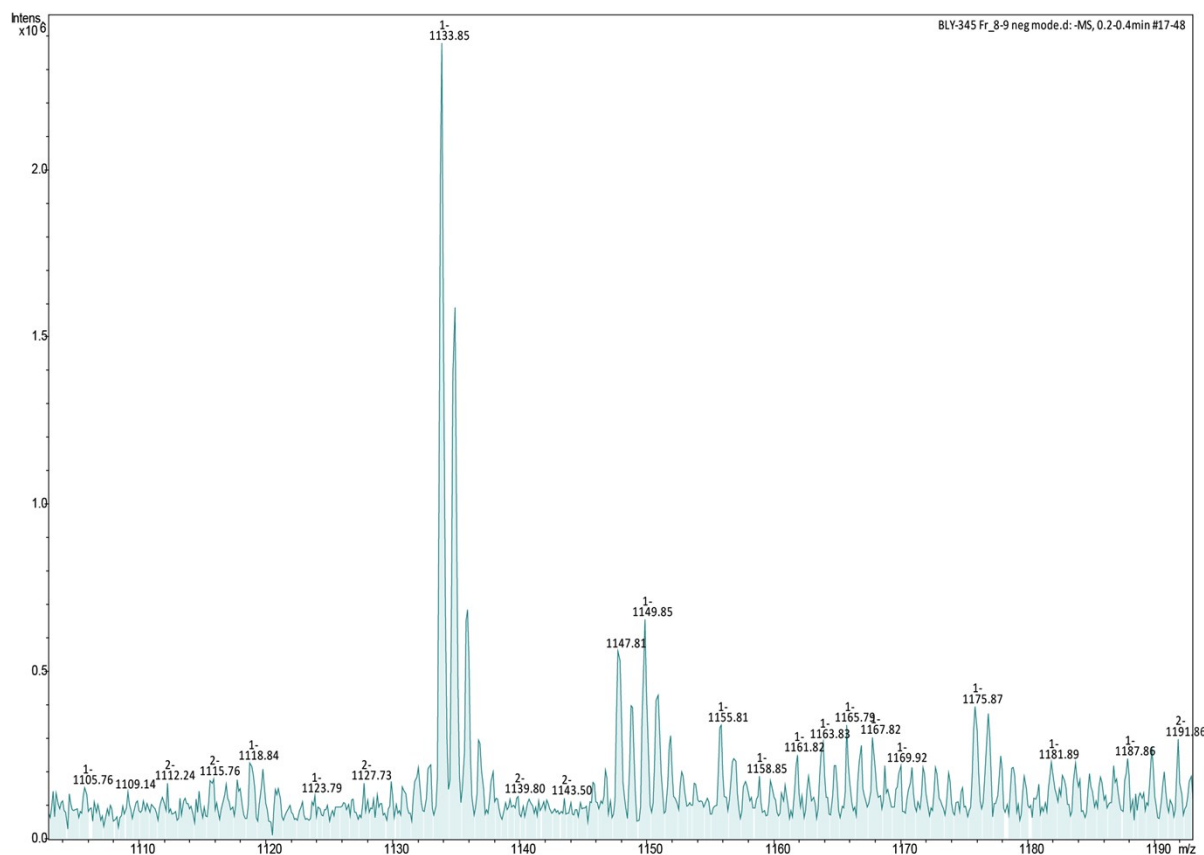
Sample Name	exp345	Position	Vial 1	Instrument Name	Instrument 1	User Name	
Inj Vol	5	InjPosition		SampleType	Sample	IRM Calibration Status	Success
Data Filename	9720_B.Lee_exp345.d	ACQ Method		Comment	in DCM/MeOH	Acquired Time	6/9/2015 1:36:28 PM



Normal Phase HPLC analysis of compound 2. The analysis was performed on a Agilent 1200 HPLC system using a YMC DIOL column (4,6 x 100 mm), a gradient of ethyl acetate in n-hexane from 10 to 90 % in 30 min, and 1 ml/min flow rate. The detection of the compounds was performed using an ELSD detector.

MS/MS analysis of compound 2.





ESI- MS Analysis of Compound 2 carried out on a Bruker amaZon Speed ETD mass spectrometer in negative mode. (M+OH)⁻ MS_{calculated} 1133.66, MS_{found} 1133.85.

References

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