Supporting Information

Synthesis of Glycosylphosphatidylinositol (GPI) Anchor Glycolipids Bearing Unsaturated Lipids

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General Methods

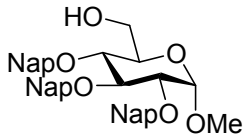
All chemicals used were reagent grade and used as adquired except where noted. All reactions were performed in oven-dried glassware under an inert atmosphere (nitrogen or argon) unless noted otherwise. Reagent grade dichloromethane (DCM or CH_2Cl_2), tetrahydrofuran (THF), methanol (MeOH) *N,N*-dimethylformamide (DMF), toluene (PhMe) and acetonitrile (MeCN) were dried with 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 Macherey Nagel silica gel 60 F_{254} 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, ^{13}C and ^{31}P NMR spectra were recorded on a Varian 400 (400 MHz), a Varian 600 (600 MHz) or BRUKER Avance-III (700MHz) spectrometer in $CDCl_3$ with chemical shifts referenced to internal standards $CHCl_3$ (7.26 ppm ^1H, 77.1 ppm ^{13}C) and DMSO (2.50 ppm ^1H, 39.52 ppm ^{13}C) 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-^{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 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.

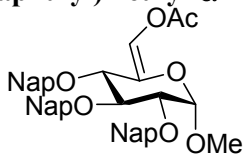
Normal phase LC analysis was performed on an Agilent 1200 HPLC system using a YMC® Diol column (4.6 x 100 mm), a gradient from 10 to 90 percent of ethyl acetate in n-hexane in 30 min, 1ml/min flow rate and ELSD detection.

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



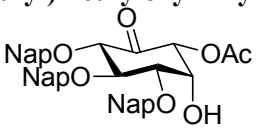
6-O-Trityl-1-O-methyl glucosamine **8**[1] (22 g, 50.4 mmol) was stired overnight at room temperature in the presence of NapBr (39 g, 176 mmol) and NaH (8.06 g, 202 mmol, 60% in mineral oil) in DMF (500 mL). The reaction was quenched with aq. NH_4Cl, extrated with EtOAc, washed with brine, dried with Na_2SO_4, filtered, and evaporated. The residue was purified by flash chromatography (hexane/EtOAc = 5:1, R_f 0.4) to give the naphtylated 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 Et_3N 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), $[\alpha]_D^{20}$: -56.7 (c = 5.1, $CHCl_3$); 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; ^{1}H NMR (400 MHz, $CDCl_3$) 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, -CH_2- of Nap), 5.12 & 4.90 (ABq, *J* = 11.0 Hz, 2H, -CH_2- of Nap), 5.02 & 4.93 (ABq, *J* = 12.2 Hz, 2H, -CH_2- 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 (-CH_2- of Nap), 75.2 (-CH_2- of Nap), 73.5 (-CH_2- of Nap), 70.8 (C5), 61.9 (C6), 55.3 (-OMe); ESI-MS: m/z $[M+Na]^+$ cald 637.2566, obsd 637.2578.

(*Z*)-Methyl 6-*O*-acetyl-2,3,4-tri-*O*-(2-naphthyl)methyl-α-D-*gluco*-hex-5-enopyranoside (10)



To a solution of alcohol **9** (15.1 g, 24.56 mmol) and $SO_3 \cdot Py$ (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, -CH_2- of Nap), 5.02 & 4.88 (ABq, *J* = 12.3 Hz, 2H, -CH_2- of Nap), 4.98 & 4.94 (ABq, *J* = 11.6 Hz, 2H, -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, -OMe), 2.17 (s, 3H, -OAc); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4 (O=C-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 (-CH_2- of Nap), 74.6 (-CH_2- of Nap), 74.0 (-CH_2- of Nap), 56.5 (-OMe), 20.7 (-CH_3 of OAc); ESI-MS: m/z $[M+Na]^+$ cald 677.2515, obsd 677.2507.

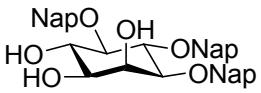
(1*R*,2*R*,3*S*,4*R*,5*S*)-3,4,5-Tri-*O*-(2-naphthyl)methyloxy-2-hydroxy-6-oxocyclohexyl Acetate (11)



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, $Hg(OTf)_2$ (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 crystalized from CH_2Cl_2/Et_2O 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, -CH_2- of Nap), 5.13 & 4.71 (ABq, *J* = 11.7 Hz, 2H, -CH_2- of Nap), 4.96 & 4.92 (ABq, *J* = 12.0 Hz, 2H, -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 (-C=O-), 169.9 (O=C-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 (-CH_2- of Nap), 75.1 (C1), 73.7 (-CH_2- of Nap), 73.6 (-CH_2- of Nap), 69.6 (C2), 20.7 (-CH_3 of OAc); ESI-MS: m/z $[M+Na]^+$ cald 663.2359, obsd 663.2386.

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

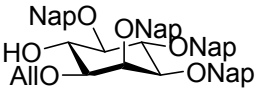


In the first step, the ketone compound **11** (5.85 g, 9.13 mmol) was dissolved in MeCN (50 ml) and this solution was transfered to a cooled (0 °C) solution of $NaBH(OAc)_3$ (7.74 g, 36.5 mmol) in a mixture of AcOH/MeCN (v/v = 1:1, 100 mL). The reaction was allowed to warm to room temperature and stirred 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 crystalized by CH_2Cl_2/Et_2O 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, -CH_2- of Nap), 5.12 & 5.04 (ABq, *J* = 11.2 Hz, 2H, -CH_2- of Nap), 4.90 & 4.85 (ABq, *J* = 11.6 Hz, 2H, -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 (O=C-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 (-CH_2- of Nap), 75.9 (-CH_2- of Nap), 73.3 (C1), 73.1 (-CH_2- of Nap), 70.7 (C6), 68.0 (C2), 21.3 (-CH_3 of OAc); ESI-MS: m/z $[M+Na]^+$ cald 665.2515, obsd 665.2525.

Next, the diol compound **11a** (6.19 g, 9.63 mmol) was stired at room temperature for 30 min in the presence of NaOMe (0.104 g, 1.93 mmol) in MeOH/CH_2Cl_2 (v/v = 1:1, 80 mL). After neutralization with resin, the mixture was dried by evaporation and passed throught a short column of silica gel using MeOH/DCM (20:1) as eluent to deliver **12** as a white powder. $[\alpha]_D^{20}$: -28.9 (c = 0.57, $CHCl_3$); 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; ^{1}H NMR (400 MHz, CD_3OD) 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, -CH_2- of Nap), 5.06 & 4.99 (ABq, *J* = 11.3 Hz, 2H, -CH_2- of Nap), 4.94 & 4.81 (ABq, *J* = 12.0 Hz, 2H, -CH_2- 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 (-CH_2- of Nap), 75.0 (-CH_2- of Nap), 72.7 (C6), 71.7 (-CH_2- of Nap), 71.5 (C1), 68.9 (C2); ESI-MS: m/z $[M+Na]^+$ cald 623.2410, obsd 623.2405.

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



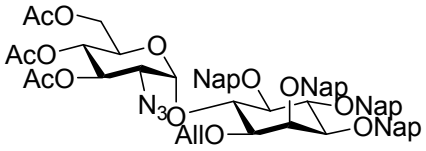
D-1-O-Allyl-3,4,5-tri-O-(2-naphthyl)methyl-myo-inositol

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), $[\alpha]_D^{20}$: -51.9 (c = 0.6, $CHCl_3$); 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; ^{1}H NMR (400 MHz, $CDCl_3$) 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, -CH_2- of allyl), 5.18 (ddd, *J* = 10.4, 2.5, 1.1 Hz, 1H, -CH_2- of allyl), 5.14 & 5.06 (ABq, *J* = 11.1 Hz, 2H, -

CH_2- of Nap), 5.10 & 5.04 (ABq, *J* = 11.5 Hz, 2H, -CH_2- of Nap), 4.95 & 4.92 (ABq, *J* = 12.0 Hz, 2H, -CH_2- of Nap), 4.31 (t, *J* = 2.6 Hz, 1H, Ino-2), 4.21 (ddt, *J* = 12.6, 5.8, 1.3 Hz, 1H, -CH_2- of allyl), 4.16-4.07 (m, 3H, Ino-4, Ino-6, -CH_2- 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 (=CH_2 of allyl), 82.9 (C5), 81.1 (C4), 80.0 (C3), 79.0 (C1), 76.1 (-CH_2- of Nap), 75.6 (-CH_2- of Nap), 72.9 (-CH_2- of Nap), 72.4 (C6), 71.5 (-CH_2- of allyl), 67.1 (C2); ESI-MS: m/z $[M+Na]^+$ cald 663.2723, obsd 663.2733.

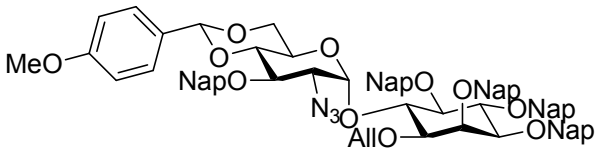
The obtained allyl myo-inositol (1.05 g, 1.64 mmol) was dissolved in DMF (15 mL). The solution was then cooled to 0 °C, and NaH (87 mg, 3.61 mmol) was added in one portion. After strirring for 30 min at 0 °C, the reaction mixture was cooled to -20 °C and 2-naphthylmethyl bromide (0.362 g, 1.64 mmol) 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 Na_2SO_4. 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), $[\alpha]_D^{20}$: -21.8 (c = 1.23, $CHCl_3$); 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; ^{1}H NMR (400 MHz, $CDCl_3$) 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, -CH_2- of allyl), 5.21-5.15 (m, 2H, -CH_2- of allyl, -CH_2- of Nap), 5.13-5.08 (m, 5H, -CH_2- of Nap), 4.90 & 4.84 (ABq, *J* = 11.9 Hz, 2H, -CH_2- 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, -CH_2- of allyl), 3.58-3.50 (m, 2H, Ino-3, Ino-5), 3.22-3.15 (m, 1H, Ino-1); ^{13}C NMR (100 MHz, $CDCl_3$) 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 (=CH_2 of allyl), 83.5 (C5), 81.6 (C4), 81.2 (C3), 80.0 (C1), 76.0 (-CH_2- of Nap), 75.5 (-CH_2- of Nap), 74.2 (-CH_2- of Nap), 73.4 (C6), 73.2 (-CH_2- of Nap), 73.0 (C2), 71.4 (-CH_2- of allyl); ESI-MS: m/z $[M+Na]^+$ cald 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 Et_2O/CH_2Cl_2 (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 Et_3N 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; $[\alpha]_D^{20}$: 46.6 (c = 0.81, $CHCl_3$); ATR-FTIR (cm^{-1}): 3019, 2877, 2110, 1746, 1510, 1437, 1370, 1216, 1172, 1125, 1029, 933, 894, 855, 817, 718; ^1H NMR (400 MHz, $CDCl_3$) 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, $-CH_2-$ of Nap), 5.25-5.12 (m, 3H, $=CH_2$ of allyl, $-CH_2-$ of Nap), 5.10-5.01 (m, 3H, $-CH_2-$ of Nap), 4.98 (d, *J* = 13.1 Hz, 1H, $-CH_2-$ of Nap), 4.90-4.77 (m, 3H, $-CH_2-$ 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, $-CH_2-$ of allyl), 3.95 (dd, *J* = 12.2, 5.6 Hz, 1H, $-CH_2-$ 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 ($=CH_2$ of allyl), 97.3 (C1, J_{CH} = 173.2 Hz), 82.0, 81.9, 81.6, 81.0, 76.1 ($-CH_2-$ of Nap), 75.4 ($-CH_2-$ of Nap), 74.9, 74.4 ($-CH_2-$ of Nap), 73.2 ($-CH_2-$ of Nap), 73.1, 71.1 ($-CH_2-$ of allyl), 70.5 (C3), 68.0 (C4), 67.1, 61.4 (C6), 61.1 (C2), 20.9 ($-CH_3$ of OAc), 20.7 ($-CH_3$ of OAc), 20.0 ($-CH_3$ of OAc); ESI-MS: m/z $[M+Na]^+$ cald 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)



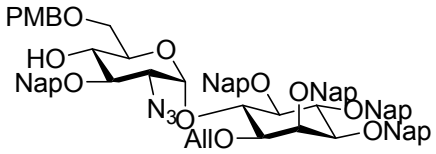
2-Azido-4,6-O-(p-methoxybenzylidene)-2-deoxy-α-D-glucopyranosyl-(1→6)-1-O-allyl-2,3,4,5-tetra-O-(2-naphthyl)methyl-D-myo-inositol

The disaccharide **16** (1.75 g, 1.60 mmol) was stired at room temperature for 30 min in the presence of NaOMe (17 mg, 0.320 mmol) in MeOH/CH_2Cl_2 (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. NH_4Cl and extracted three times with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$, 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, $CHCl_3$); 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; ^{1}H NMR (400 MHz, $CDCl_3$) 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, =CH_2 of allyl), 5.24-5.11 (m, 5H, =CH_2 of allyl, -CH_2- of Nap), 5.10 (d, *J* = 12.3 Hz, 1H, -CH_2- of Nap), 4.97 (d, *J* = 10.7 Hz, 1H, -CH_2- of Nap), 4.91 & 4.84 (ABq, *J* = 11.9 Hz, 2H, -CH_2- 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, -CH_2- 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 (=CH_2 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 (-CH_2- of Nap), 75.3 (-CH_2- of Nap), 75.2, 74.3 (-CH_2- of Nap), 73.2 (-CH_2- of Nap), 73.1, 71.2 (-CH_2- of allyl), 68.82 (C6), 68.79 (C3), 63.3 (C2), 62.3, 55.3 (OMe of PMB); ESI-MS: m/z $[M+Na]^+$ cald 1108.4360, obsd 1108.4437; m/z $[M+K]^+$ cald 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. NH_4Cl and extracted three times with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$, 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; ^{1}H 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, $=CH_2$ of allyl), 5.19-5.15 (m, 1H, $=CH_2$ of allyl), 5.15 & 4.95 (ABq, *J* = 10.9 Hz, 2H, $-CH_2-$ of Nap), 5.10 & 5.06 (ABq, *J* = 12.4 Hz, 4H, $-CH_2-$ of Nap), 5.01 & 4.89 (ABq, *J* = 11.5 Hz, 2H, $-CH_2-$ of Nap), 4.86 & 4.80 (ABq, *J* = 11.9 Hz, 2H, $-CH_2-$ 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, $-CH_2-$ 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 ($=CH_2$ 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 ($-CH_2-$ of Nap), 75.92 (C3), 75.5 ($-CH_2-$ of Nap), 75.3, 74.9 ($-CH_2-$ of Nap), 74.4 ($-CH_2-$ of Nap), 73.3, 73.2 ($-CH_2-$ of Nap), 71.2 ($-CH_2-$ of allyl), 69.0 (C6), 63.4 (C2), 62.7, 55.4 (OMe of PMB); ESI-MS: m/z $[M+Na]^+$ cald 1248.4986, obsd 1248.5008.

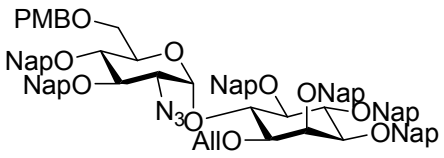
2-Azido-3-O-(2-naphthyl)methyl-6-O-(p-methoxybenzyl)-2-deoxy-α-D-glucopyranosyl-(1→6)-1-O-allyl-2,3,4,5-tetra-O-(2-naphthyl)methyl-D-myo-inositol 16a



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 THF/CH_2Cl_2 (v/v = 1:1, 32.8 mL) was stirred at room temperature and argon atmosphere for 40 min. Then CF_3CO_2H (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; ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H 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, -CH= of allyl), 5.77 (d, *J* = 3.7 Hz, 1H, Glc-1), 5.28-5.14 (m, 4H, =CH_2 of allyl, -CH_2- of Nap), 5.09 (d, *J* = 12.4 Hz, 1H, -CH_2- of Nap), 5.07-4.99 (m, 4H, -CH_2- of Nap), 4.90 (d, *J* = 11.5 Hz, 1H, -CH_2- of Nap), 4.85 & 4.80 (ABq, *J* = 11.9 Hz, 2H, -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, -CH_2- of PMB), 4.10-4.02 (m, 3H, -CH_2- of allyl, Glc-5), 3.88 (d, *J* = 10.1 Hz, 1H, Glc-3), 3.75 (s, 3H, -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 (-CH= 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 (=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 (-CH_2- of Nap), 75.6 (-CH_2- of Nap), 75.4, 75.0 (-CH_2- of Nap), 74.3 (-CH_2- of Nap), 73.1 (-CH_2- of Nap), 73.00, 72.96 (-CH_2- of PMB), 72.7 (C4), 71.2 (-CH_2- of allyl), 69.4 (C5), 69.0 (C6), 63.0 (C2), 55.3 (OMe of PMB); ESI-MS: m/z $[M+Na]^+$ cald 1250.5143, obsd 1250.5138.

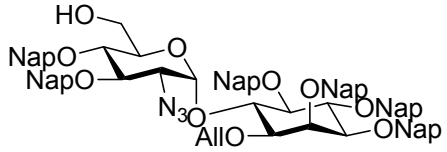
2-Azido-3,4-di-*O*-(2-naphthyl)methyl-6-*O*-(*p*-methoxybenzyl)-2-deoxy-α-D-glucopyranosyl-(1→6)-1-*O*-allyl-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (3)



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 $Na_2S_2O_3$ (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), $[\alpha]_D^{20}$: 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, -CH= of allyl), 5.83 (d, *J* = 3.7 Hz, 1H, Glc-1), 5.31-5.16 (m, 4H, $=CH_2$ of allyl, $-CH_2$- of Nap), 5.11 (d, *J* = 12.0 Hz, 1H, $-CH_2$- of Nap), 5.07 (d, *J* = 12.3 Hz, 1H, $-CH_2$- of Nap), 5.07-4.99 (m, 3H, $-CH_2$- of Nap), 4.91 (d, *J* = 11.6 Hz, 1H, $-CH_2$- of Nap), 4.86 & 4.81 (ABq, *J* = 11.8 Hz, 2H, $-CH_2$- of Nap), 4.70 & 4.22 (ABq, *J* = 11.2 Hz, 2H, $-CH_2$- of Nap), 4.44 & 3.95 (ABq, *J* = 11.8 Hz, 2H, $-CH_2$- 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, $-CH_2$- 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, -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 (-CH= 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 ($=CH_2$ 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 ($-CH_2$- of Nap), 75.8 (Ino-6), 75.4 ($-CH_2$- of Nap), 75.3 ($-CH_2$- of Nap), 74.7 ($-CH_2$- of Nap), 74.3 ($-CH_2$- of Nap), 73.1 ($-CH_2$- of Nap), 73.00, 72.98 ($-CH_2$- of PMB), 71.1 ($-CH_2$- of allyl), 70.3 (C5), 67.0 (C6), 63.6 (C2), 55.1 (OMe of PMB); ESI-MS: m/z $[M+Na]^+$ cald 1390.5769, obsd 1390.5752.

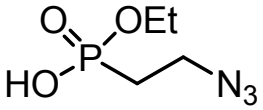
2-Azido-3,4-di-*O*-(2-naphthyl)methyl-2-deoxy-α-D-glucopyranosyl-(1→6)-1-*O*-allyl-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (24)



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 °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), $[\alpha]_D^{20}$: 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-

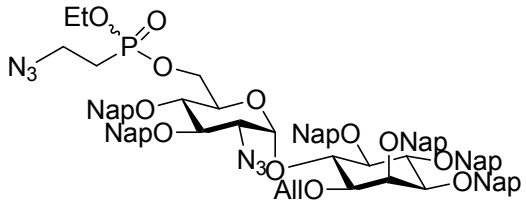
5.93 (m, 1H, -CH= of allyl), 5.80 (d, J = 3.3 Hz, 1H, Glc-1), 5.32-5.19 (m, 4H, =CH_2 of allyl, -CH_2- of Nap), 5.15-5.04 (m, 5H, -CH_2- of Nap), 4.97 (d, J = 11.3 Hz, 1H, -CH_2- of Nap), 4.92-4.80 (m, 3H, -CH_2- of Nap), 4.69 (d, J = 11.3 Hz, 1H, -CH_2- of Nap), 4.42-4.31 (m, 2H), 4.20-4.04 (m, 5H, -CH_2- 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 (=CH_2 of allyl), 97.7 (C1), 82.2, 82.0, 81.7, 80.9, 80.1 (C3), 78.0 (C4), 76.0 (-CH_2- of Nap), 75.8 (-CH_2- of Nap), 75.5, 75.4 (-CH_2- of Nap), 75.1 (-CH_2- of Nap), 74.3 (-CH_2- of Nap), 73.1 (-CH_2- of Nap), 72.9, 71.2 (-CH_2- of allyl), 70.9 (C5), 63.7 (C2), 61.1 (C6); ESI-MS: m/z $[M+Na]^+$ cald 1270.5194, obsd 1270.5203; m/z $[M+K]^+$ cald 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-azidoethylphosphonate[3] (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 Et_2O. The crude lithium salt of product was suspended in CH_2Cl_2 (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 CH_2Cl_2. The combined extracts were dried over Na_2SO_4, 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; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.58 (brs, 1H, OH), 4.12 (dq, J = 14.4, 7.1 Hz, 2H, OCH_2 of Et), 3.55 (dt, J = 12.3, 7.7 Hz, 2H, CH_2N_3), 2.15-2.02 (m, 2H, PCH_2), 1.35 (t, J = 7.1 Hz, 3H, CH_3 of Et); ^{13}C NMR (100 MHz, $CDCl_3$) δ 61.78 (d, J_{PC} = 6.7 Hz, OCH_2 of Et), 45.35 (d, J_{PC} = 1.5 Hz, CH_2N_3), 26.31 (d, J_{PC} = 143.4 Hz, PCH_2), 16.43 (d, J_{PC} = 6.5 Hz, CH_3 of Et); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.46; ESI-MS: m/z $[M+H]^+$ cald 180.0538, obsd 180.0545; m/z $[M+Na]^+$ cald 202.0357, obsd 202.0360; m/z $[M+K]^+$ cald 218.0097, obsd 218.0080.

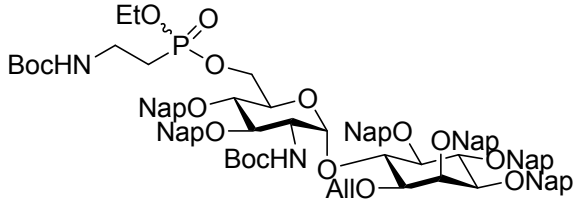
2-Azido-3,4-di-*O*-(2-naphthyl)methyl-6-*O*-((2-azidoethyl)phosphonic acid ethyl ester)-2-deoxy-α-D-glucopyranosyl-(1→6)-1-*O*-allyl-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (25)



To a solution of phosphonic acid **22** (140 mg, 0.782 mmol) and dry DMF (6 μL, 0.0782 mmol) in CH_2Cl_2 (3 mL) at 0 °C and argon atmosphere was added oxalylic chloride (75 μL, 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 phosponochloridate 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 °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), ^{1}H 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, =CH_2 of allyl, -CH_2- of Nap), 5.15-5.05 (m, 10H, -CH_2- of Nap), 4.95-4.80 (m, 8H, -CH_2- of Nap), 4.71 (d, *J* = 11.2 Hz, 1H, -CH_2- of Nap), 4.65 (d, *J* = 11.3 Hz, 1H, -CH_2- of Nap), 4.39-4.32 (m, 4H), 4.25-4.00 (m, 10H, -CH_2- of allyl, Glc-3, Glc-5, Ino), 3.93-3.83 (m, 3H, OCH_2 of Et, Glc-6), 3.77-3.66 (m, 3H, OCH_2 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, CH_2N_3), 1.86-1.75 (m, 4H, PCH_2), 1.09 (t, *J* = 7.1 Hz, 3H, CH_3 of Et), 1.08 (t, *J* = 7.0 Hz, 3H, CH_3 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 (=CH_2 of allyl), 117.3 (=CH_2 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 (-CH_2- of Nap), 76.0 (-CH_2- of Nap), 75.74, 75.68, 75.65 (-CH_2- of Nap), 75.54 (-CH_2- of Nap), 75.47 (-CH_2- of Nap), 75.4 (-CH_2- of Nap), 75.1 (-CH_2- of Nap), 75.0 (-CH_2- of Nap), 74.3 (-CH_2- of Nap), 74.2 (-CH_2- of Nap), 73.1 (-CH_2- of Nap*2), 72.7, 72.6, 71.21 (-CH_2- of allyl), 71.18 (-CH_2- 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, OCH_2 of Et), 61.82 (d, J_{PC} = 6.6 Hz, OCH_2 of Et), 45.27 (d, J_{PC} = 1.4 Hz, CH_2N_3), 45.20 (d, J_{PC} = 1.3 Hz, CH_2N_3), 25.79 (d, J_{PC} = 140.9 Hz, PCH_2), 25.55 (d, J_{PC} = 140.1 Hz, PCH_2), 16.37 (d, J_{PC} = 5.6 Hz, CH_3 of Et), 16.32 (d, J_{PC} = 5.9 Hz, CH_3 of Et); ^{31}P NMR (162 MHz, $CDCl_3$, ~1:1 mixture of diastereomers) δ 27.13, 26.94; ESI-MS: m/z $[M+Na]^+$ cald 1431.5548, obsd 1431.5589; m/z $[M+K]^+$ cald 1447.5287, obsd 1447.5324.

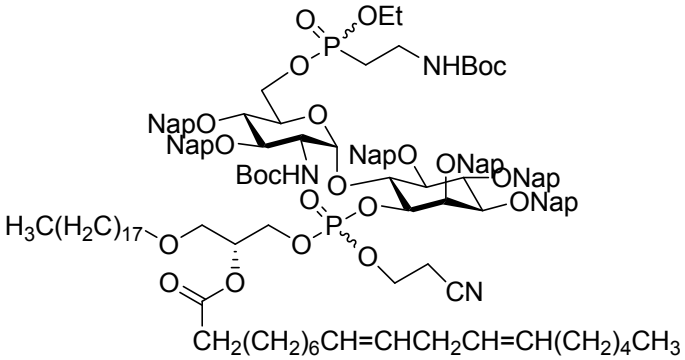
2-[*N-(tert*-butoxycarbonyl)amido]-3,4-di-*O*-(2-naphthyl)methyl-6-*O*-((2-*N-(tert*-butoxycarbonyl)aminoethyl)phosphonic acid ethyl ester)-2-deoxy-α-D-glucopyranosyl-(1→6)-1-*O*-allyl-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (26)



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/H_2O (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 Boc_2O (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), ^{1}H NMR (400 MHz, $CDCl_3$, ~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, =CH_2 of allyl, -CH_2- of Nap), 5.11-4.96 (m, 5H, =CH_2 of allyl, -CH_2- of Nap), 4.95-4.88 (m, 2H, -CH_2- 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, -CH_2- of allyl), 3.91-3.62 (m, 6H, OCH_2 of Et, Glc-6, -CH_2- of allyl, C), 3.50-3.40 (m, 2H), 3.35-3.16 (m, 3H, C, CH_2NHBoc), 1.71-1.60 (m, 2H, PCH_2), 1.45-1.39 (m, 18H, CH_3- of Boc), 1.06 (t, J = 7.0 Hz, 3H, CH_3 of Et), 1.04 (t, J = 7.2 Hz, 3H, CH_3 of Et); ^{13}C NMR (100 MHz, $CDCl_3$, ~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 (=CH_2 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 (-CH_2- of Nap), 76.0 (-CH_2- of Nap), 75.7 (-CH_2- of Nap), 75.5 (-CH_2- of Nap), 75.34 (-CH_2- of Nap), 75.29(-CH_2- of Nap), 75.1 (-CH_2- of Nap), 75.0 (-CH_2- of Nap), 74.1 (-CH_2- of Nap), 74.0 (-CH_2- of Nap), 73.1 (-CH_2- of Nap*2), 72.3, 72.2, 71.0 (-CH_2- 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, OCH_2 of Et), 61.6 (d, J_{PC} = 7.0 Hz, OCH_2 of Et), 54.7 (C2), 54.6 (C2), 34.64 (CH_2NHBoc), 34.58 (CH_2NHBoc), 28.6 (CH_3 of Boc), 28.52 (CH_3 of Boc), 28.51 (CH_3 of Boc), 26.2 (d, J_{PC} = 141.1 Hz, PCH_2), 25.7 (d, J_{PC} = 140.3 Hz, PCH_2), 16.4 (CH_3 of Et), 16.3 (CH_3 of Et); ^{31}P NMR (162 MHz, $CDCl_3$, ~1:1 mixture of diastereomers) δ 30.43, 29.81; ESI-MS: m/z $[M+Na]^+$ cald 1580.6820, obsd 1580.6711; m/z $[M+K]^+$ cald 1596.6559, obsd 1596.6466.

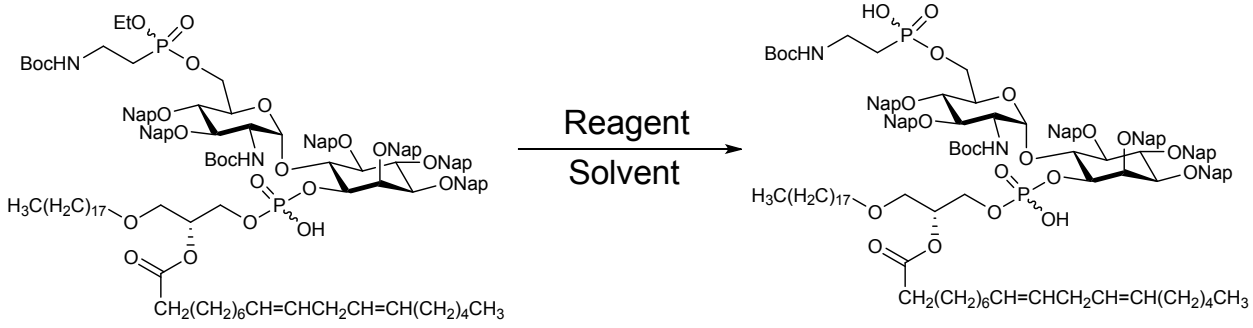
2-[*N-(tert*-butoxycarbonyl)amido]-3,4-di-*O*-(2-naphthyl)methyl-6-*O*-((2-*N*-*(tert*-butoxycarbonyl)aminoethyl)phosphonic acid ethyl ester)-2-deoxy-α-D-glucopyranosyl-(1→6)-1-*O*-[1-*O*-(octadecyl)-2-*O*-(9Z,12Z-octadecanoyl)-*sn*-glycero-3-phosphocyanoethyl]-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (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 μL). $PdCl_2$ (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. $NaHCO_3$, and the aqueous layer was extracted with ethyl acetate. The organic layers were combined and dried over Na_2SO_4, 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 $[M+Na]^+$ cald 1539.6473, obsd 1539.6439; m/z $[M+K]^+$ 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 CH_2Cl_2/CH_3CN (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 CH_2Cl_2/CH_3CN (v/v = 3:1, 1 mL) was slowly added. The reaction was stirred at room temperature for 2 h, was cooled to -40 ºC and *tert*-butyl hydroperoxide (5.5 M solution in n-decane, 62 μL, 0.343 mmol) was added. After 1 h at -40 ºC, Me_2S (51 μL, 0.685 mmol) was added and the mixture was stirred for 1 h at -40 ºC. 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 (CH_2Cl_2/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→6)-1-*O*-[1-*O*-(octadecyl)-2-*O*-(9Z,12Z-octadecanoyl)-*sn*-glycero-3-phosphocyanoethyl]-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol



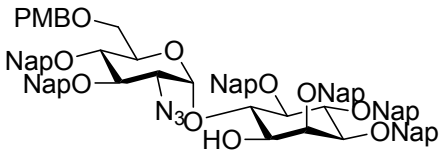
The phosphorylated and fully protected pseudo-disaccharide **28** (5 mg, 2,2 μmol) was treated with a

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 ^{31}P and ^{1}H NMR spectroscopy.

Table 1. Various deethylation conditions[2] of ethylphosphonate of compound **28**

Solvent	Reagent	Temperature	Time	Result
1,4-Dioxane	PhSH, Et_3N	Room temp.	2 days	no reaction
THF	PhSH, Et_3N	Room temp.	2 days	no reaction
DMF	PhSH, Et_3N	Room temp.	2 days	no reaction
DMF	PhSH, Et_3N	60 °C	2 days	no reaction
DMF	PhSH, DIPEA	Room temp.	2 days	no reaction
DMF	PhSH, DIPEA	60 °C	overnight	decompostion
DMF	2-methyl-5-*tert*-butylthiophenol, DIPEA	Room temp.	2 days	no reaction
DMF	2-methyl-5-*tert*-butylthiophenol, DIPEA	60 °C	overnight	decompostion
Acetone	NaI	60 °C	overnight	no reaction
2-Pentanone	LiBr	110 °C	2 h	decompostion
Ethanol	1N HCl	reflux	2 h	no reaction
Ethanol	6N HCl	reflux	2 h	no reaction
Ethanol	12N HCl	reflux	2 h	decompostion

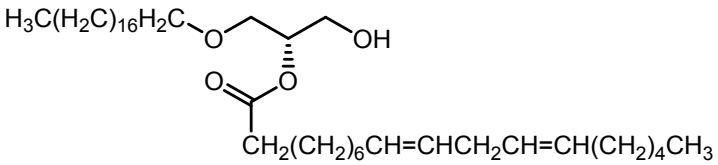
2-Azido-3,4-di-*O*-(2-naphthyl)methyl-6-*O*-(*p*-methoxybenzyl)-2-deoxy-α-D-glucopyranosyl-(1→6)-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (29)



A solution of $[IrCOD(PPh_2Me)_2]PF_6$ (6.67 mg, 7.89 μmol) 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 μmol). The reaction was stirred at room temperature for 5 h, then the solvent was removed and the residue was dissolved in acetone/H_2O (v/v = 9:1, 3 mL). Mercury(II) chloride (0.129 g, 0.473 mmol) and mercury(II) oxide (1.71 mg, 7.89 μmol) were added. After 1 h, the solvent was removed. The residue was dissolved in CH_2Cl_2 and washed with saturated $NaHCO_3$, dried over Na_2SO_4, 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), ^{1}H 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, -CH_2- of Nap), 5.24-5.17 (m, 2H, -CH_2- of Nap), 5.08-5.00 (m, 4H, -CH_2- of Nap), 4.88 (s, 2H, -CH_2- of Nap), 4.73 (d, *J* = 11.0 Hz, 1H, -CH_2- of Nap), 4.35-4.28 (m, 3H, -CH_2- of Nap, -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, -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 (-CH_2- of Nap), 75.5 (-CH_2- of Nap), 75.2 (-CH_2- of Nap), 75.0 (-CH_2- of Nap), 74.8 (-CH_2- of Nap), 73.8, 73.1 (-CH_2- of Nap), 72.9 (-CH_2- of PMB), 71.0 (C5), 66.7 (C6), 64.3 (C2), 55.1 (OMe of PMB); ESI-MS: m/z $[M+Na]^+$ cald 1350.5456, obsd 1350.5482; m/z $[M+K]^+$ cald 1366.5195, obsd 1366.5208.

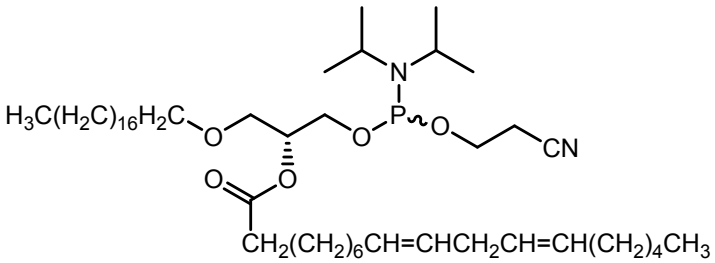
1-*O*-(Octadecyl)-2-*O*-(9Z,12Z-octadecanoyl)-*sn*-glycerol (20)



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 $BF_3{\cdot}Et_2O$ (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; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43-5.28 (m, 4H, -CH=), 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, -OCH_2-), 2.77 (t, *J* = 6.4 Hz, 2H, =CH-C*H*$_2$-CH=), 2.35 (t, *J* = 7.5 Hz, 2H, -COC*H*$_2$-), 2.22 (brs, 1H, -OH), 2.04 (t, *J* = 6.8 Hz, 4H, -C*H*$_2$-CH=), 1.66-1.51 (m, 4H, -$COCH_2$C*H*$_2$-, -OCH_2C*H*$_2$-), 1.35-1.22 (m, 44H), 0.91-0.85 (m, 6H, -CH_3*2); ^{13}C NMR (100 MHz, $CDCl_3$) 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 (-OCH_2- of octadecyl), 70.2 (*sn*-1-CH_2-), 63.2 (*sn*-3-CH_2-), 34.5 (-CO*C*H$_2$-), 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 (-*C*H_2-CH=), 27.34 (-*C*H_2-CH=), 26.2, 25.8 (=CH-*C*H_2-CH=), 25.1 (-$COCH_2$*C*H_2-), 22.9, 22.7, 14.3 (-CH_3), 14.2 (-CH_3); ESI-MS: m/z $[M+Na]^+$ cald 629.5485, obsd 629.5498.

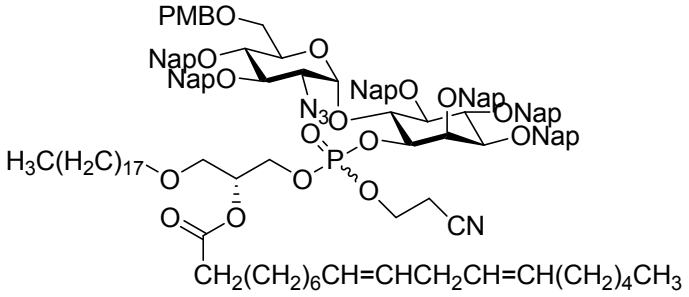
2-Cyanoethyl-*N*,*N*-diisopropylamine-(1-*O*-(octadecyl)-2-*O*-(9Z,12Z-octadecanoyl)-*sn*-glycero)-3-phosphoamidite (4)



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 CH_2Cl_2/MeCN (v/v = 2:1, 1.8 mL) was added 1*H*-tetrazole (0.593 mL, 0.267 mmol, 0.45M solution in CH_3CN). The reaction was stirred for 2 h at room temperature under argon atmosphere. Then, the reaction mixture was quenched with aq. $NaHCO_3$ and diluted with CH_2Cl_2. The reaction mixture was washed with aq. $NaHCO_3$, extracted with CH_2Cl_2, dried over Na_2SO_4, 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), ^{1}H NMR (600 MHz, $CDCl_3$, ~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, -OC*H*$_2$$CH_2$CN, *sn*-3-$CH_2$-), 3.62-3.54 (m, 4H, HC-N, *sn*-1-CH_2-), 3.48-3.37 (m, 2H, -OCH_2- of octadecyl), 2.76 (t, *J* = 6.8 Hz, 2H, =CH-C*H*$_2$-CH=), 2.64-2.60 (m, 2H, -CH_2CN), 2.34-2.28 (m, 2H, -COC*H*$_2$-), 2.04 (q, *J* = 7.0 Hz, 4H, -C*H*$_2$-CH=), 1.65-1.58 (m, 2H, -$COCH_2$C*H*$_2$-), 1.56-1.50 (m, 2H, -OCH_2C*H*$_2$- of octadecyl), 1.37-1.23 (m, 44H), 1.19-1.16 (m, 12H, -$CH(CH_3)_2$*2), 0.88 (q, *J* = 6.9 Hz, 6H, -CH_3*2); ^{13}C NMR (151 MHz, $CDCl_3$, ~1:1 mixture of diastereomers) δ 173.31 (-O=C-O-), 173.28 (-O=C-O-), 130.3 (-CH=), 130.1

(-CH=), 128.2 (-CH=), 128.0 (-CH=), 117.7 (-CN), 72.1 (d, J_{PC} = 2.9 Hz, *sn*-2-CH-), 72.0 (d, J_{PC} = 2.9 Hz, *sn*-2-CH-), 71.78 (-OCH_2- of octadecyl), 71.77 (-OCH_2- of octadecyl), 69.2 (*sn*-1-CH_2-), 69.1 (*sn*-1-CH_2-), 62.2 (d, J_{PC} = 12.2 Hz, *sn*-3-CH_2-), 62.1 (d, J_{PC} = 12.3 Hz, *sn*-3-CH_2-), 58.7 (d, J_{PC} = 7.6 Hz, -OCH_2CH_2CN), 58.5 (d, J_{PC} = 7.9 Hz, -OCH_2CH_2CN), 43.3 (HC-N), 43.2 (HC-N), 34.6 (-COCH_2-), 32.1, 31.7, 29.84, 29.79, 29.78, 29.76, 29.6, 29.49, 29.48, 29.36, 29.35, 29.3, 29.2, 27.3 (-CH_2-CH=), 26.2, 25.8 (=CH-CH_2-CH=), 25.1 (-$COCH_2CH_2$-), 24.8 (-CH_3 of diisopropylamine), 24.70 (-CH_3 of diisopropylamine), 24.67 (-CH_3 of diisopropylamine), 24.66 (-CH_3 of diisopropylamine), 22.8, 22.7, 20.5 (d, J_{PC} = 6.5 Hz, -CH_2CN), 14.24 (-CH_3), 14.20 (-CH_3); ^{31}P NMR (243 MHz, $CDCl_3$, ~1:1 mixture of diastereomers) δ 149.05, 148.89; ESI-MS: m/z $[M+Na]^+$ cald 829.6563, obsd 829.6567; m/z $[M+K]^+$ cald 845.6303, obsd 845.6320.

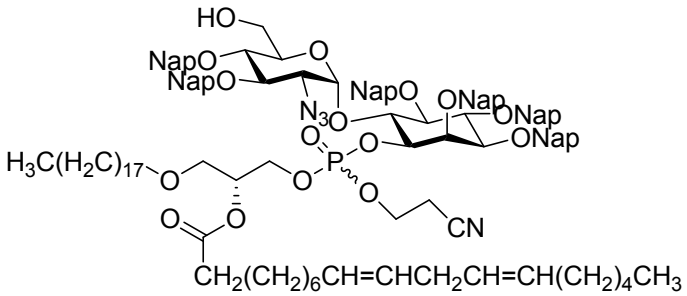
2-Azido-3,4-di-*O*-(2-naphthyl)methyl-6-*O*-(*p*-methoxybenzyl)-2-deoxy-α-D-glucopyranosyl-(1→6)-1-*O*-[1-*O*-(octadecyl)-2-*O*-(9Z,12Z-octadecanoyl)-*sn*-glycero-3-phosphocyanoethyl]-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (30)



To a solution of the *pseudo*-disaccharide **29** (0.101 g, 0.076 mmol) and tetrazole (0.45 M solution in acetonitrile, 1.01 mL, 0.456 mmol) in anhydrous CH_2Cl_2 (3 mL) under stiring and at room temperature was slowly added a solution of freshly prepared phosphoramidite **4** (0.184 g, 0.228 mmol) in CH_2Cl_2 (3 mL). After the reaction was stirred for 30 min at room temperature, the reaction was cooled to -40 ºC and treated with *tert*-butyl hydroperoxide (5.5 M solution in decane, 0.166 mL, 0.912 mmol). The reaction was stirred for 1 h at -40 ºC, then Me_2S (0.135 mL, 1.825 mmol) was added and the resulting mixture was stirred for additional 1 h at -40 ºC. The reaction mixture was poured into saturated $NaHCO_3$ and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography to afford the desired compound **30** (hexane/EtOAc = 2:1, R_f 0.18) in 87% yield (0.135 g, 0.066 mmol, ~1:1 mixture of diastereomers) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, ~1:0.8 mixture of diastereomers) δ 7.88-7.54 (m, 39.6H), 7.50-7.24 (m, 34.2H), 6.90-6.81 (m, 5.4H), 6.60-6.54 (m, 3.6H), 5.53 (d, *J* = 3.8 Hz, 1H, Glc-1), 5.49 (d, *J* = 3.8 Hz, 0.8H, Glc-1), 5.40-5.29 (m, 7.2H, -CH=), 5.27-5.12 (m, 7.2H, *sn*-2-CH-, -CH_2- of Nap), 5.06-4.87 (m, 12.6H, -CH_2- of

Nap), 4.68 (d, J = 11.1 Hz, 1.8H, -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, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, ~1:0.8 mixture of diastereomers) δ 173.3 (-O=C-O-), 173.2 (-O=C-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 (-CH=), 130.18 (-CH=), 130.16 (-CH=), 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 (-CN), 116.51 (-CN), 113.7 (Ph of PMB), 97.1 (C1), 81.8, 81.7, 80.9, 80.63, 80.57, 79.6, 78.02 (d, J_{PC} = 2.5 Hz, *sn*-2-CH-), 78.00 (d, J_{PC} = 2.5 Hz, *sn*-2-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 (-$C$$H_2$-CH=), 27.33 (-$C$$H_2$-CH=), 26.7, 26.19, 26.17, 26.1, 25.8 (=CH-$C$$H_2$-CH=), 25.04, 24.98, 22.8, 22.72, 22.68, 22.67, 22.62, 22.61, 19.9 (d, J_{PC} = 7.0 Hz, -$C$$H_2$CN), 19.7 (d, J_{PC} = 7.2 Hz, -$C$$H_2$CN), 14.3 (-$CH_3$), 14.2 (-$CH_3$) ; ^{31}P NMR (162 MHz, $CDCl_3$, ~1:1 mixture of diastereomers) δ -2.41, -2.69); ESI-MS: m/z $[M+Na]^+$ cald 2073.0900, obsd 2073.0947; m/z $[M+K]^+$ cald 2089.0639, obsd 2089.0686.

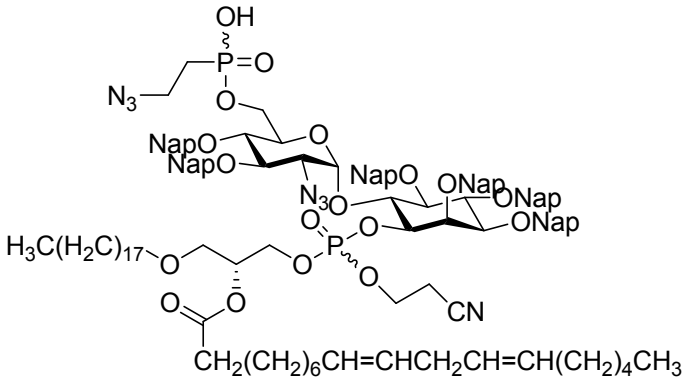
2-Azido-3,4-di-*O*-(2-naphthyl)methyl-2-deoxy-α-D-glucopyranosyl-(1→6)-1-*O*-[1-*O*-(octadecyl)-2-*O*-(9Z,12Z-octadecanoyl)-*sn*-glycero-3-phosphocyanoethyl]-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (31)



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

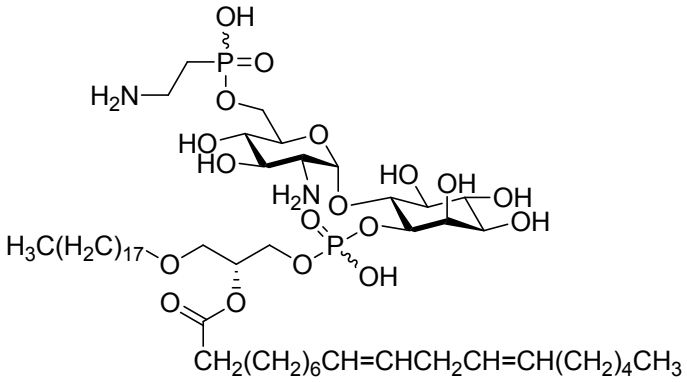
vacuo. The crude product was purified by flash chromatography to afford desired compound **31** in 80% yield (87 mg, 0.045 mmol, ~1:1 mixture of diastereomers) as a colorless oil; R_f = 0.28 (hexane/EtOAc = 3:2), ^{1}H NMR (600 MHz, $CDCl_3$, ~1:1 mixture of diastereomers) δ 7.86-7.58 (m, 22H), 7.52-7.30 (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-, -CH_2- of Nap), 5.06-4.84 (m, 8H, -CH_2- of Nap), 4.68-4.64 (m, 1H, -CH_2- 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, -CH_3); ^{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-*C*H_2-CH=), 25.1, 25.0, 22.8, 19.8 (d, J_{PC} = 7.2 Hz, -*C*H_2CN), 19.6 (d, J_{PC} = 6.9 Hz, -*C*H_2CN), 14.3 (-CH_3), 14.2 (-CH_3); ^{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 $[M+Na]^+$ cald 1953.0324, obsd 1953.0402; m/z $[M+K]^+$ cald 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→6)-1-*O*-[1-*O*-(octadecyl)-2-*O*-(9*Z*,12*Z*-octadecanoyl)-*sn*-glycero-3-phosphocyanoethyl]-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 phosponodichloridate **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 ($CHCl_3$/MeOH 15:1), ^{1}H 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-, -CH_2- of Nap), 5.04-4.80 (m, 8H, -CH_2- of Nap), 4.72 (d, 1H, *J* = 11.2 Hz, -CH_2- 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, -CH_3); ^{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 $[M+Na]^+$ cald 2086.0366, obsd 2086.0311; m/z $[M+K]^+$ cald 2102.0105, obsd 2102.0025.

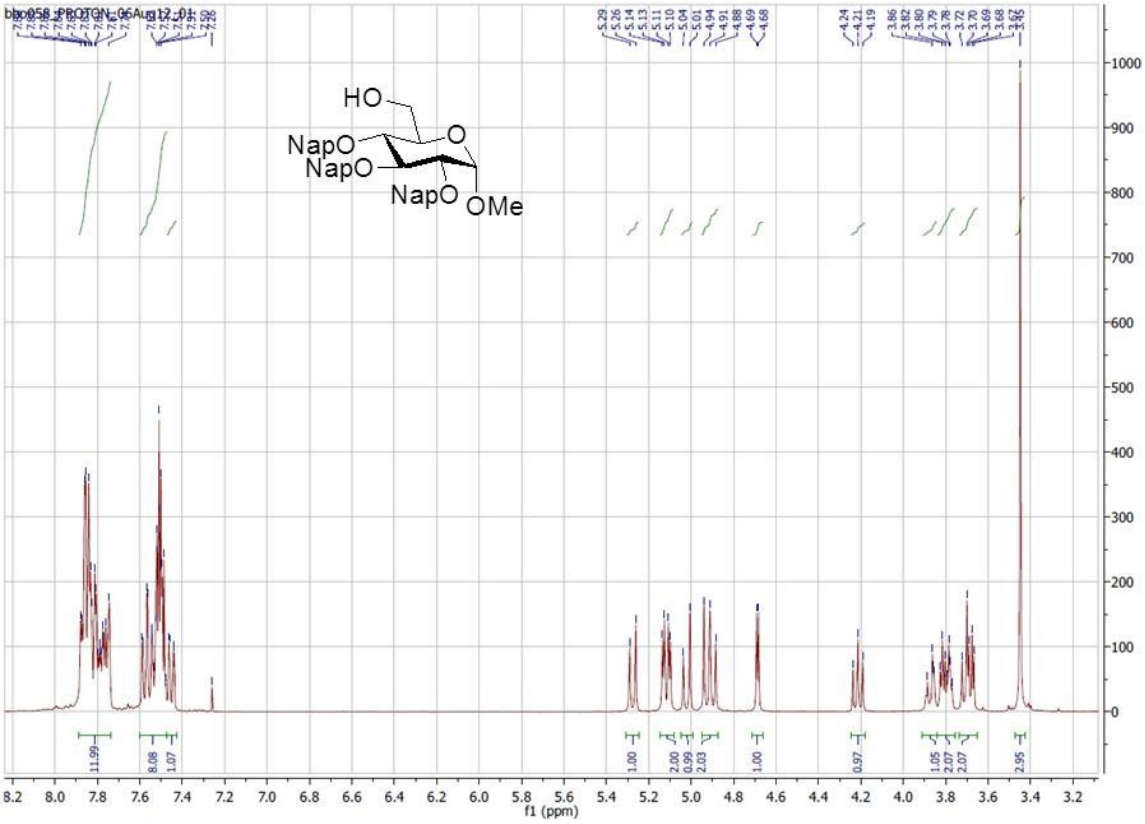
2-Amino-6-*O*-((2-aminoethyl)phosphonic acid)-2-deoxy-α-D-glucopyranosyl-(1→6)-1-*O*-[1-*O*-(octadecyl)-2-*O*-(9Z,12Z-octadecanoyl)-*sn*-glycero-3-phosphate]-D-*myo*-inositol (2)

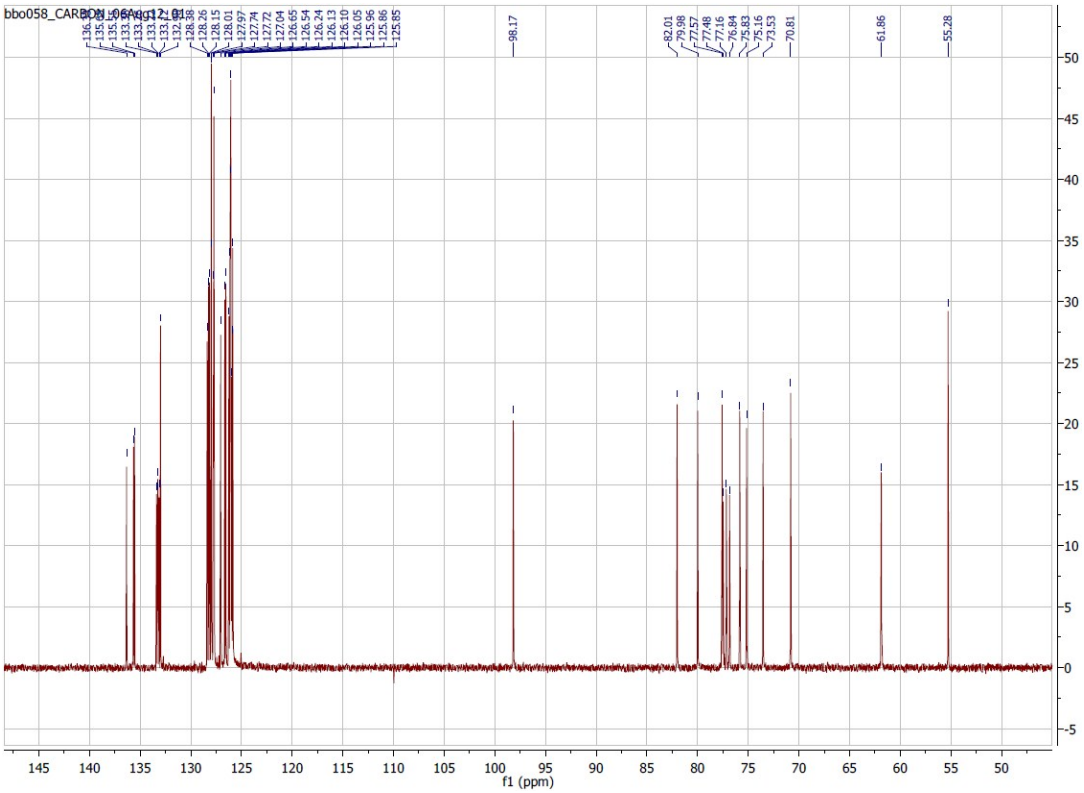


DBU (150 μL) was added to a solution of phosphodiester compound **32** (10 mg, 4.85 μmol) in anhydrous CH_2Cl_2 (0.5 mL) at room temperature.[6] After 15 min, acetic acid (150 μL) was added to the reaction mixture and then the solution was evaporated to yield a crude glycerol phosphate. The resulted pseudo-disaccharide was disolved in CH_2Cl_2/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-detilled 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 ºC and was stirred at 0 ºC 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 ($CHCl_3$/MeOH/H_2O = 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; ^{1}H 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 $[M+H]^+$ cald 1117.6681, obsd 1117.6997; m/z $[M+H_3O]^+$ cald 1135.6787, obsd 1135.6882; m/z $[M+Na]^+$ cald 1139.6501, obsd 1139.6636; m/z $[M+Na+H_2O]^{2+}$ cald 1157.6606, obsd 1157.6682; m/z $[M-H]^-$ cald 1115.6525, obsd 1115.6528; m/z $[M+OH]^-$ cald 1133.6630, obsd 1133.6636; m/z $[M+OH+Na-H]^-$ cald 1155.6450, obsd 1155.6447.

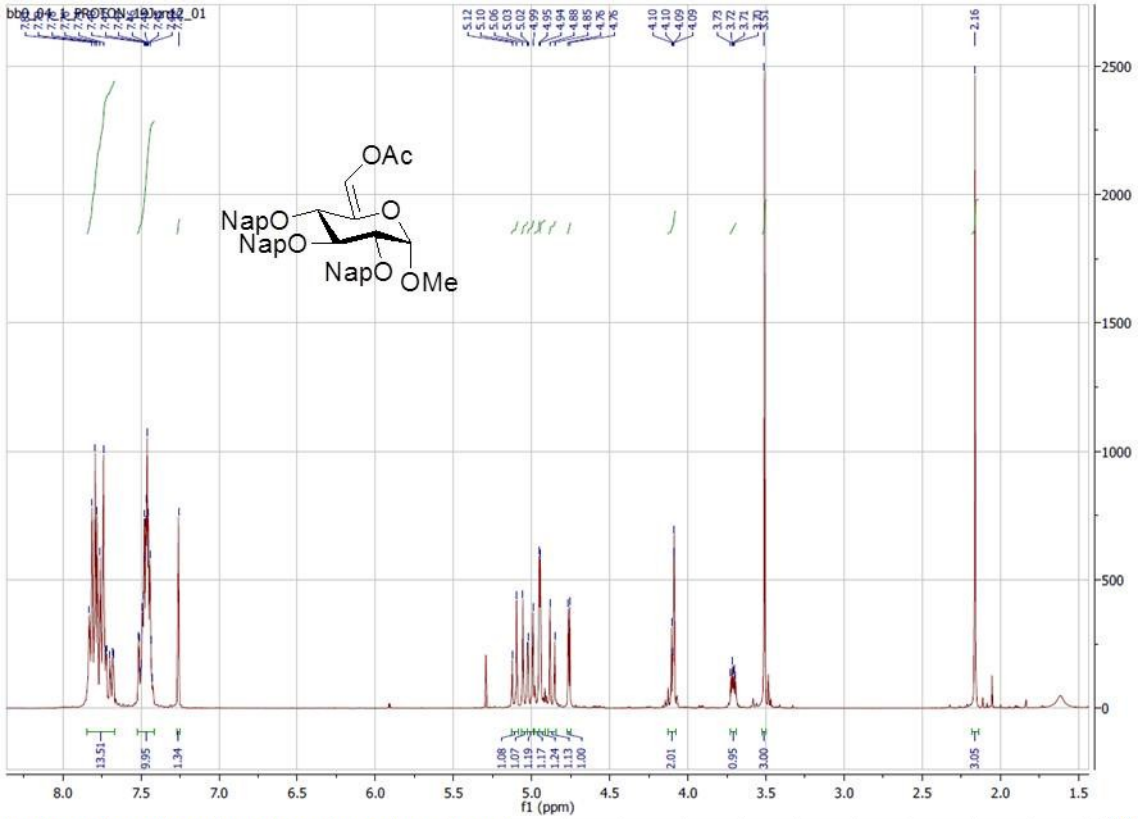
NMR and MS Spectra

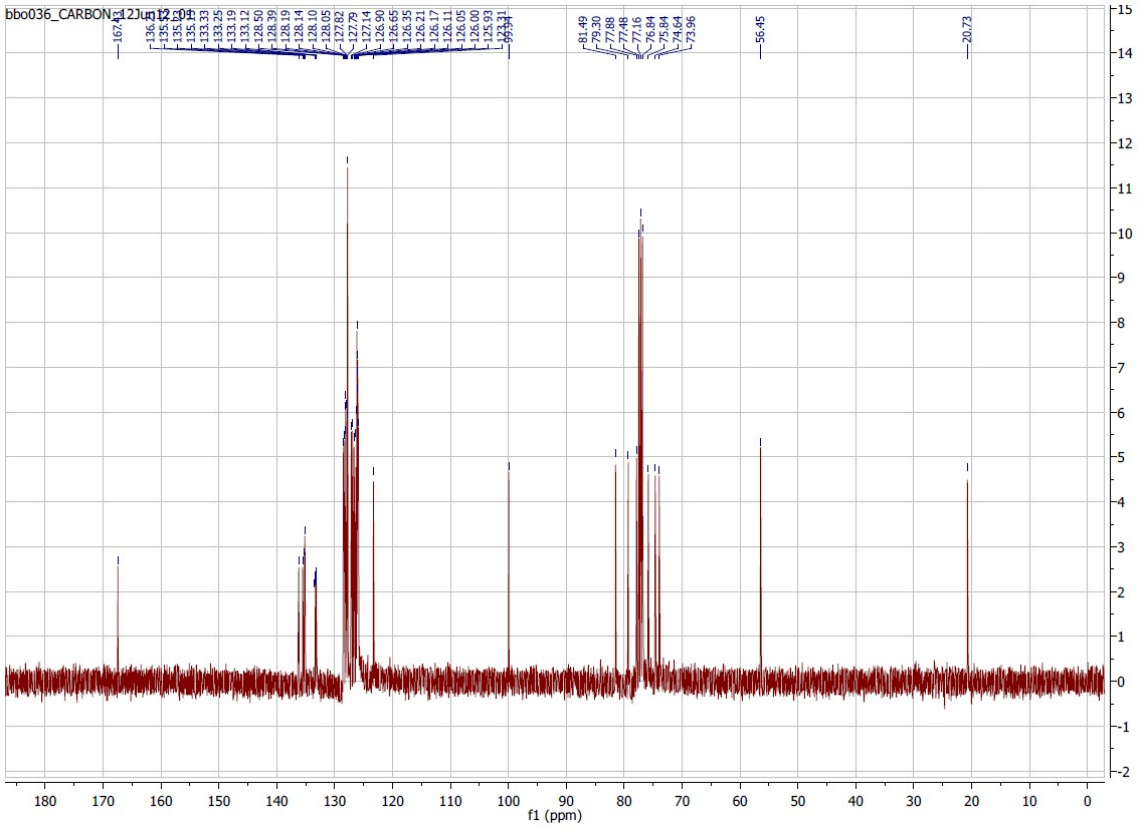
Methyl 2,3,4-tri-*O*-(2-naphthyl)methyl-α-D-glucopyranosiede (9)



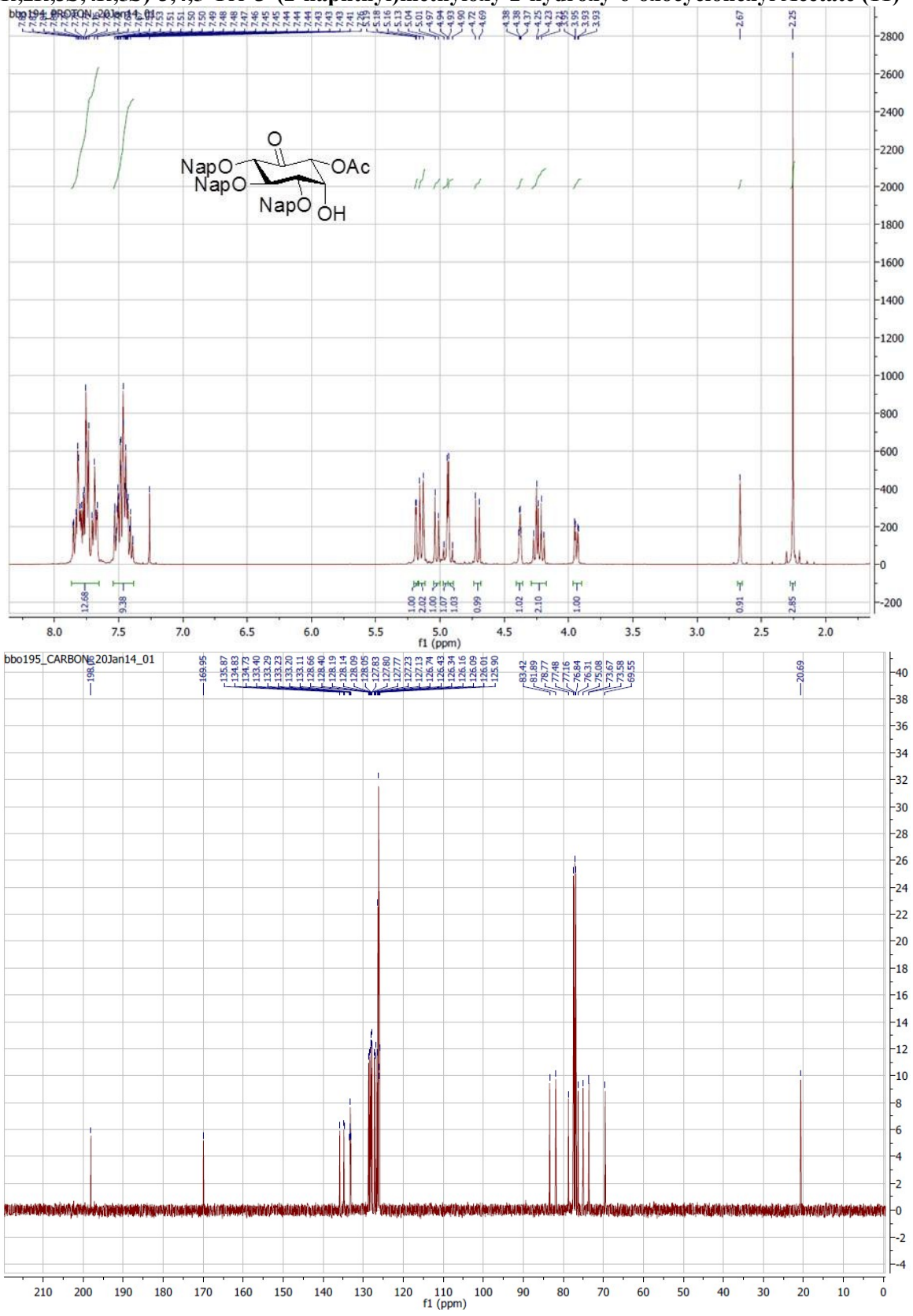


(*Z*)-Methyl 6-*O*-acetyl-2,3,4-tri-*O*-(2-naphthyl)methyl-α-D-*gluco*-hex-5-enopyranoside (10)

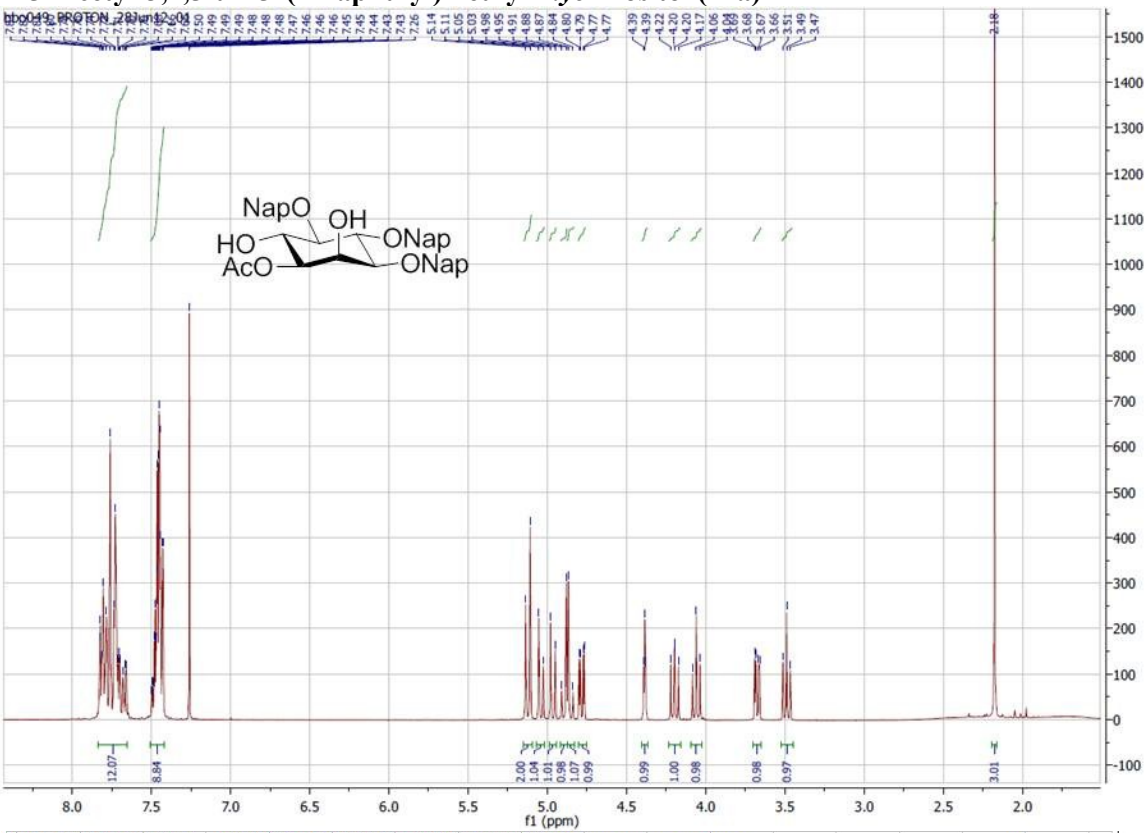


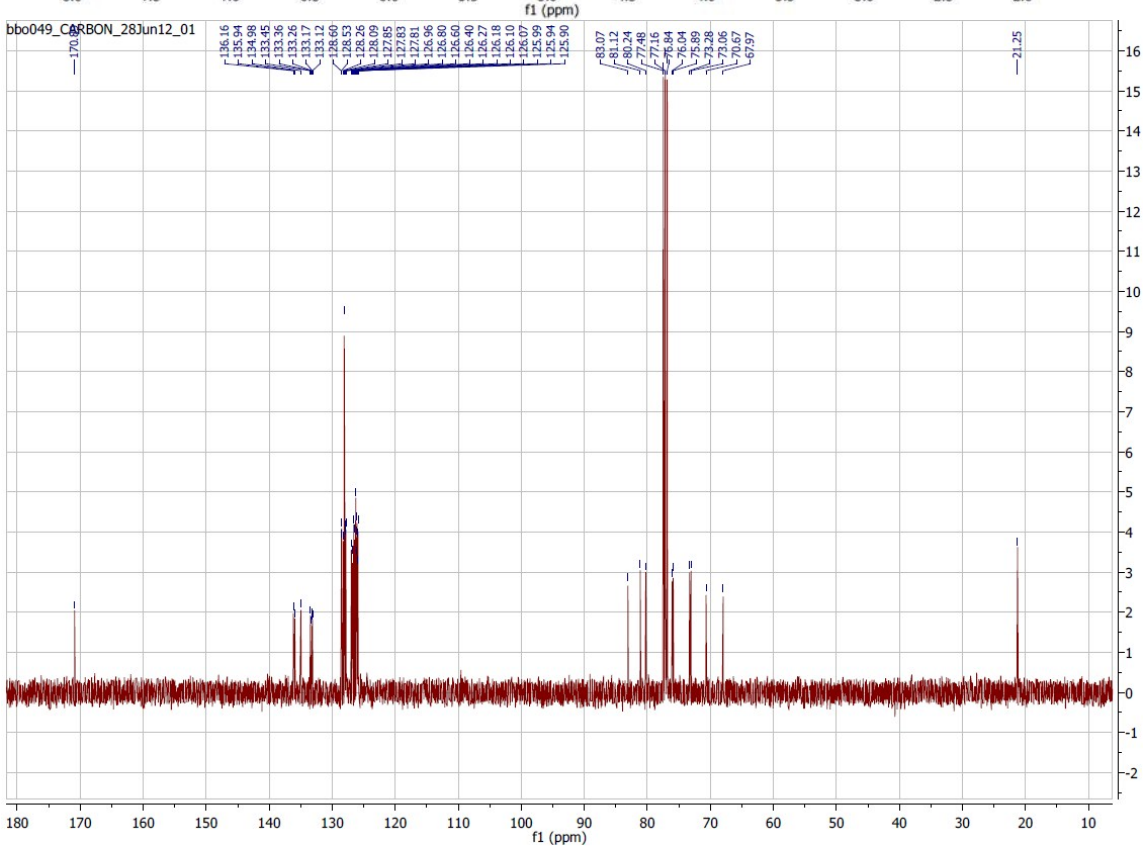


(1*R*,2*R*,3*S*,4*R*,5*S*)-3,4,5-Tri-*O*-(2-naphthyl)methyloxy-2-hydroxy-6-oxocyclohexyl Acetate (11)

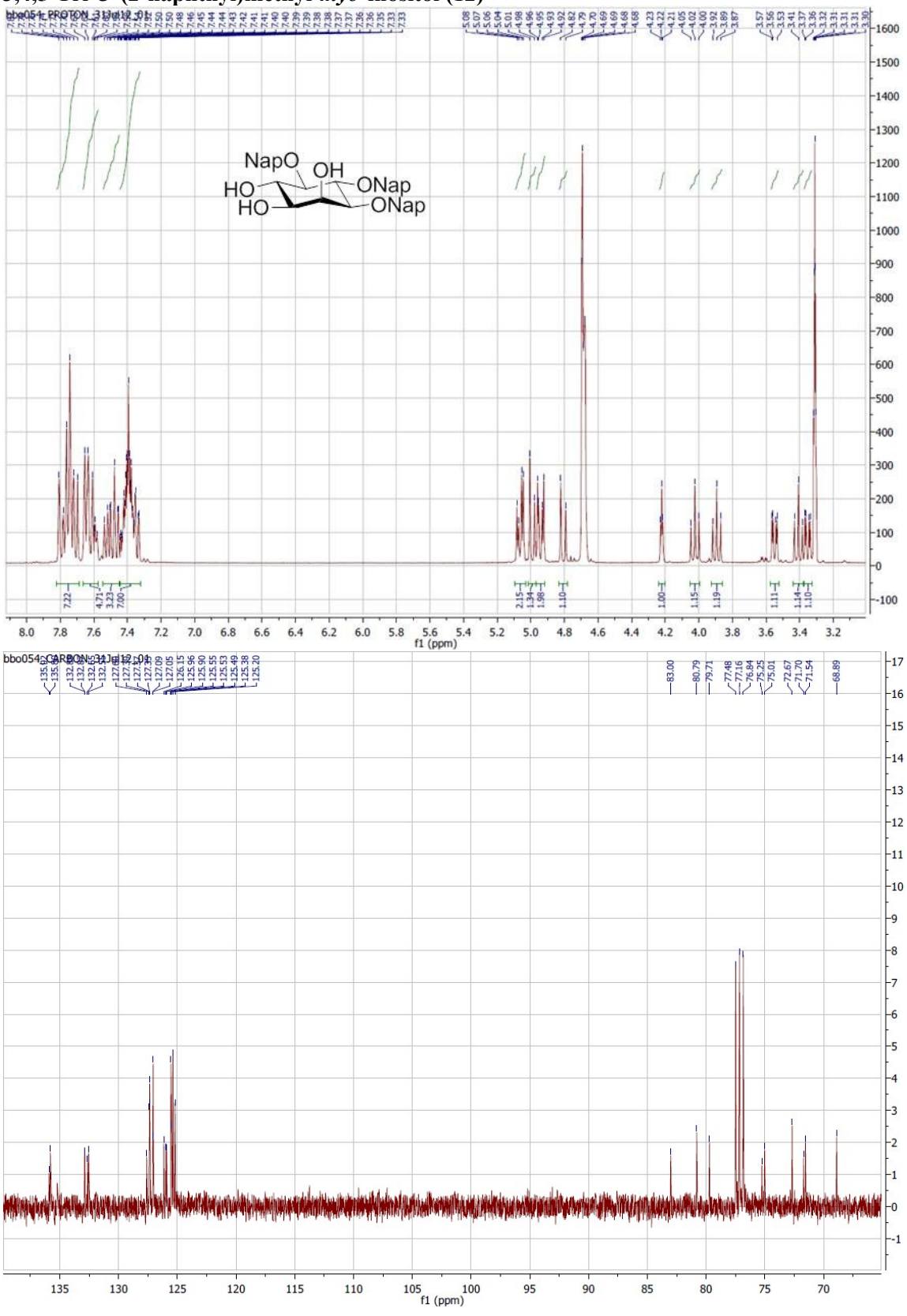


D-1-*O*-Acetyl-3,4,5-tri-*O*-(2-naphthyl)methyl-*myo*-inositol (11a)

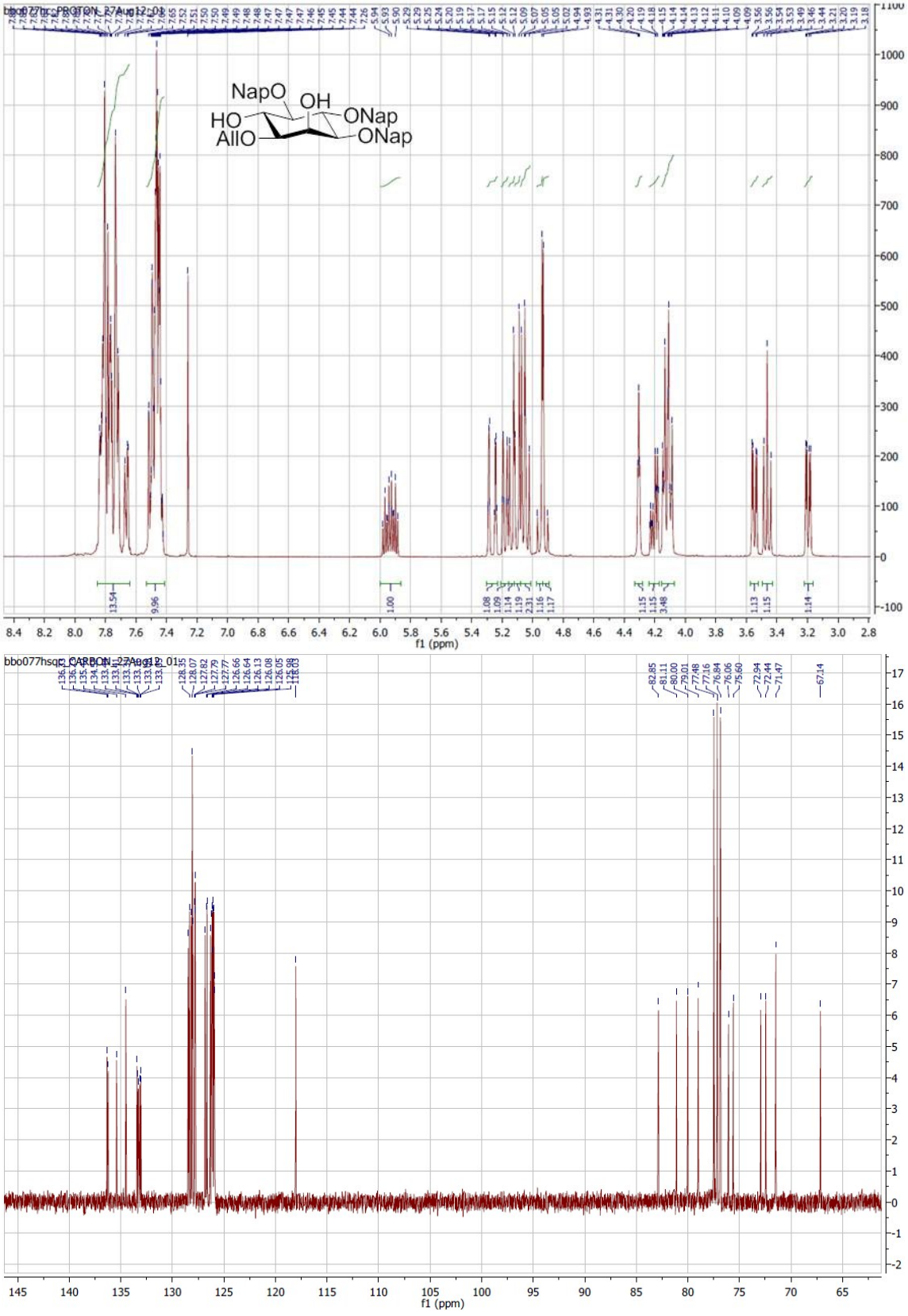




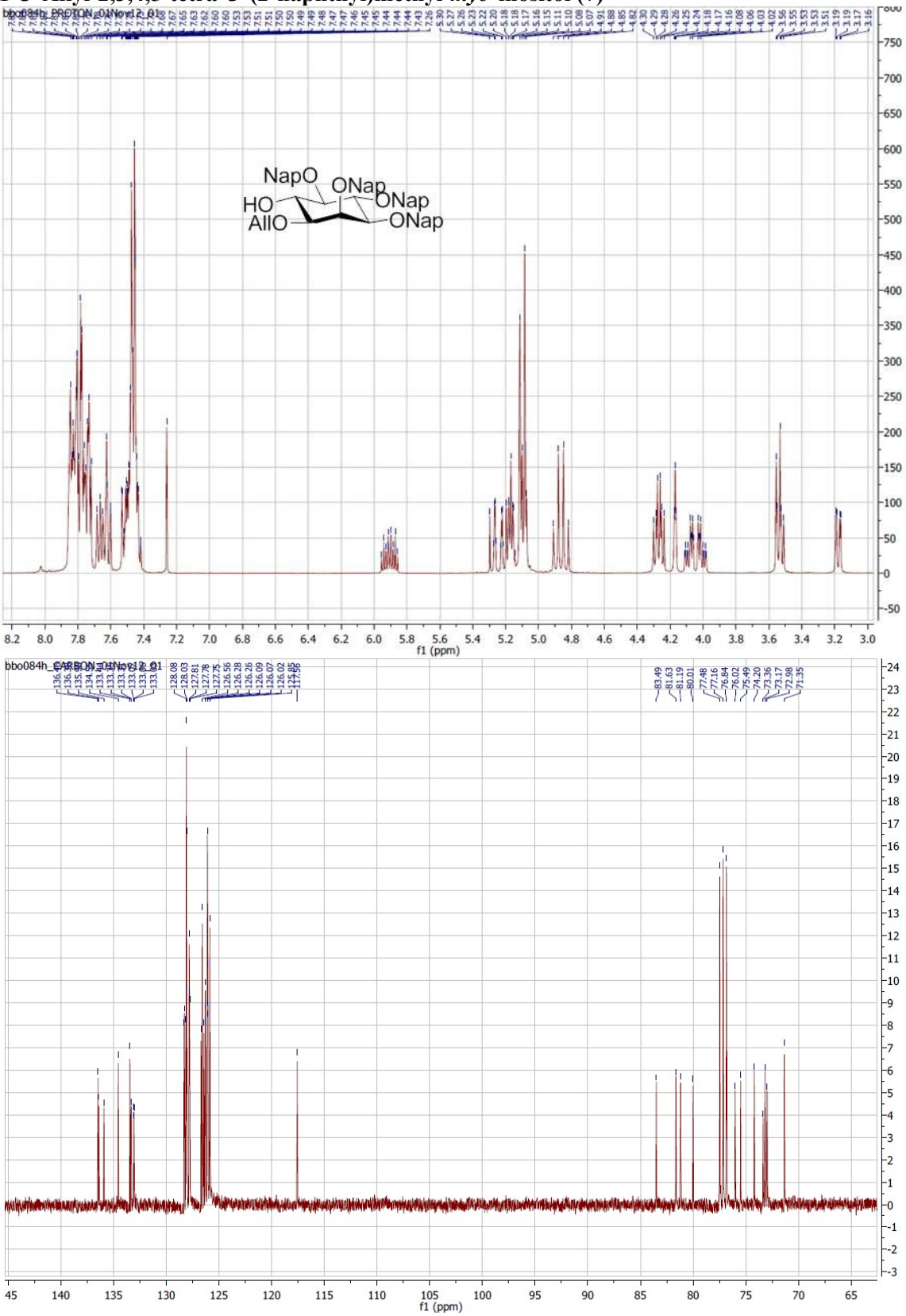
D-3,4,5-Tri-*O*-(2-naphthyl)methyl-*myo*-inositol (12)



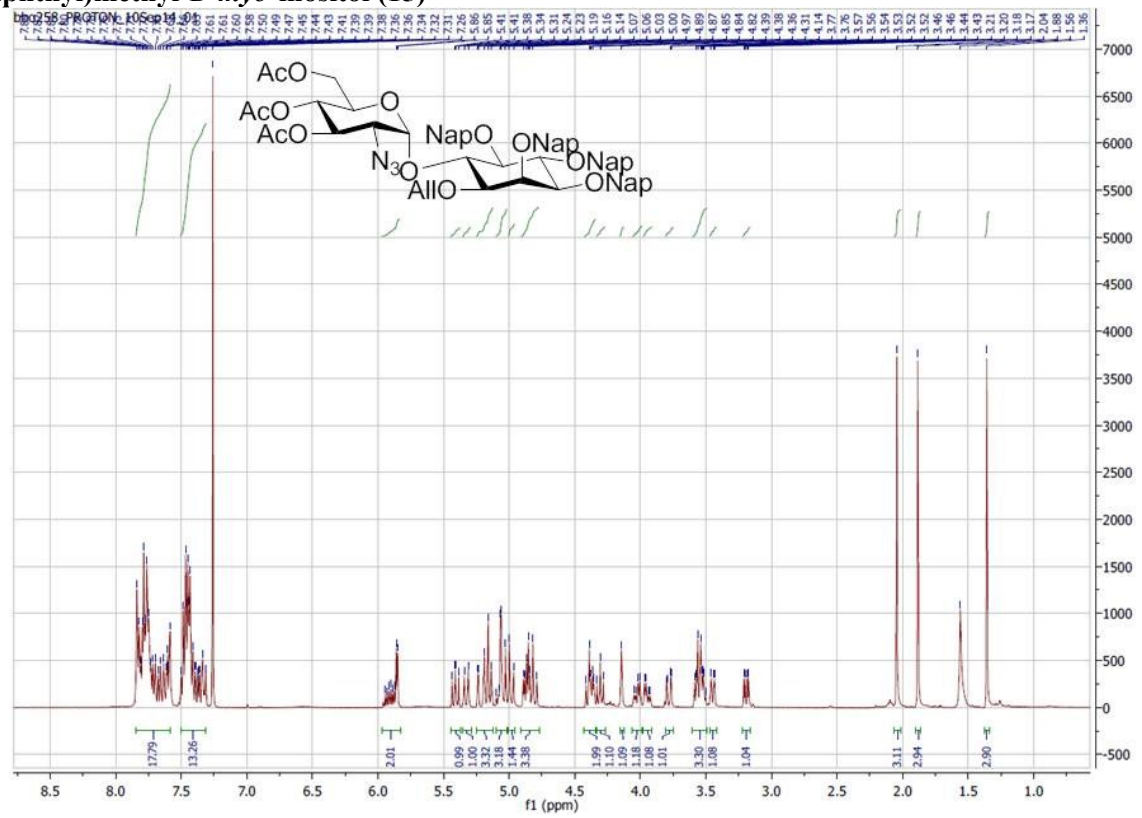
D-1-*O*-Allyl-3,4,5-tri-*O*-(2-naphthyl)methyl-*myo*-inositol (12a)

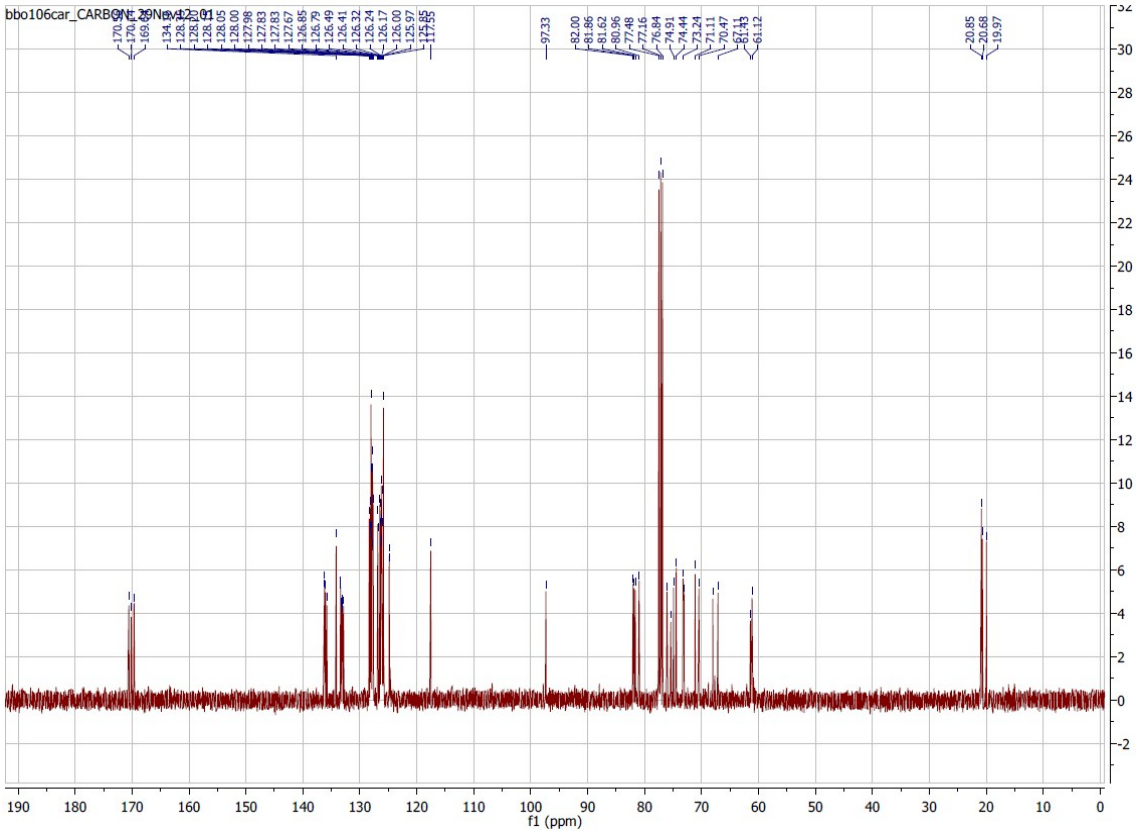


D-1-*O*-Allyl-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-*myo*-inositol (7)

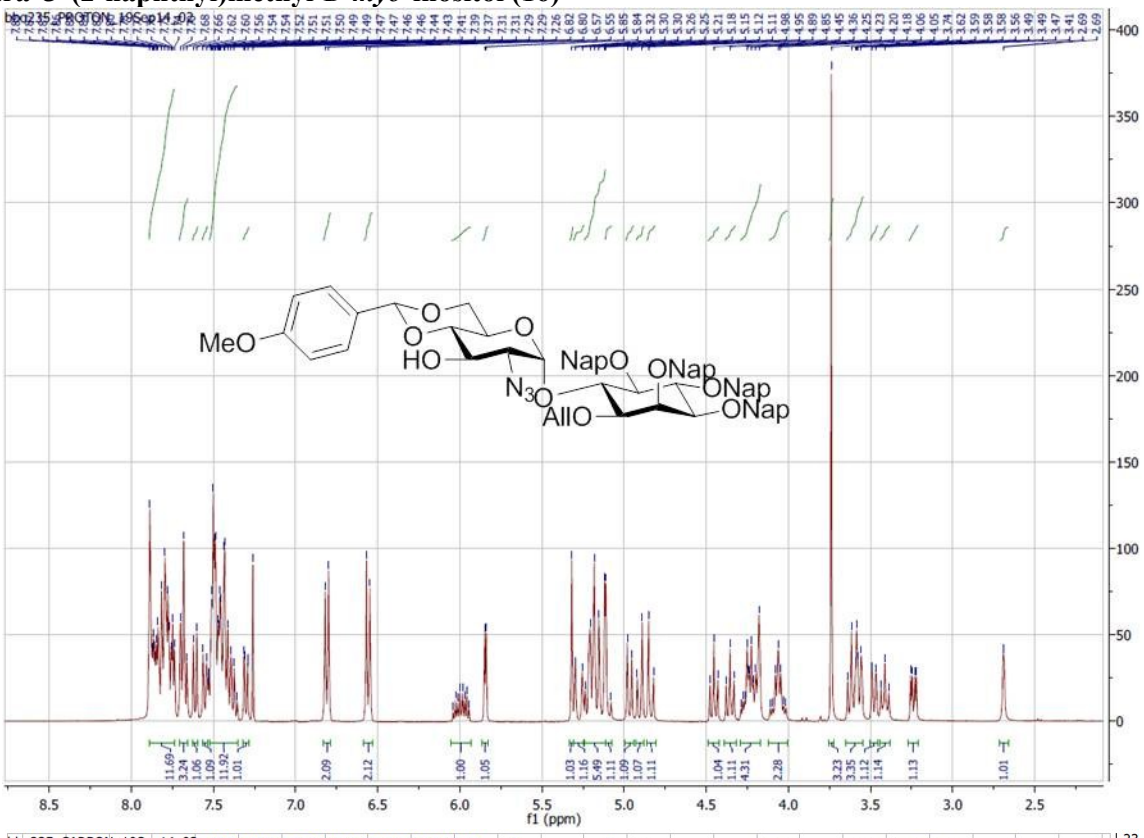


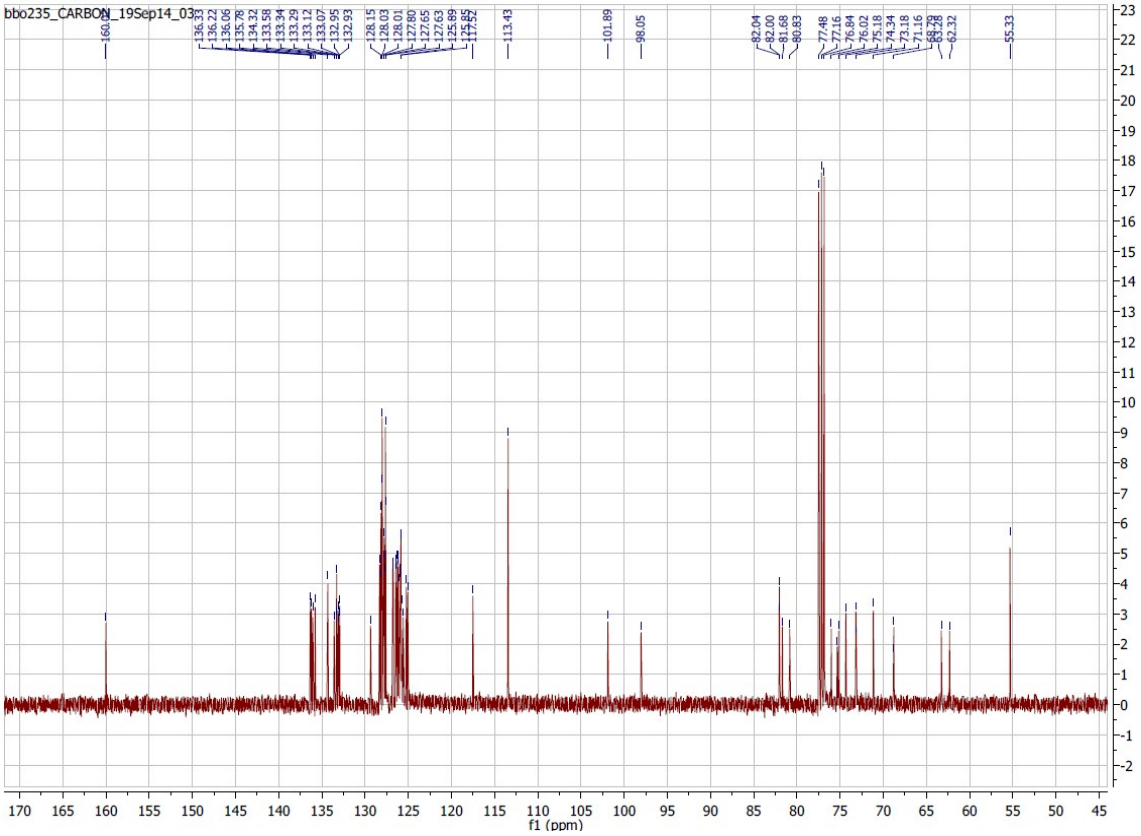
2-Azido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl-(1→6)-1-*O*-allyl-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (15)



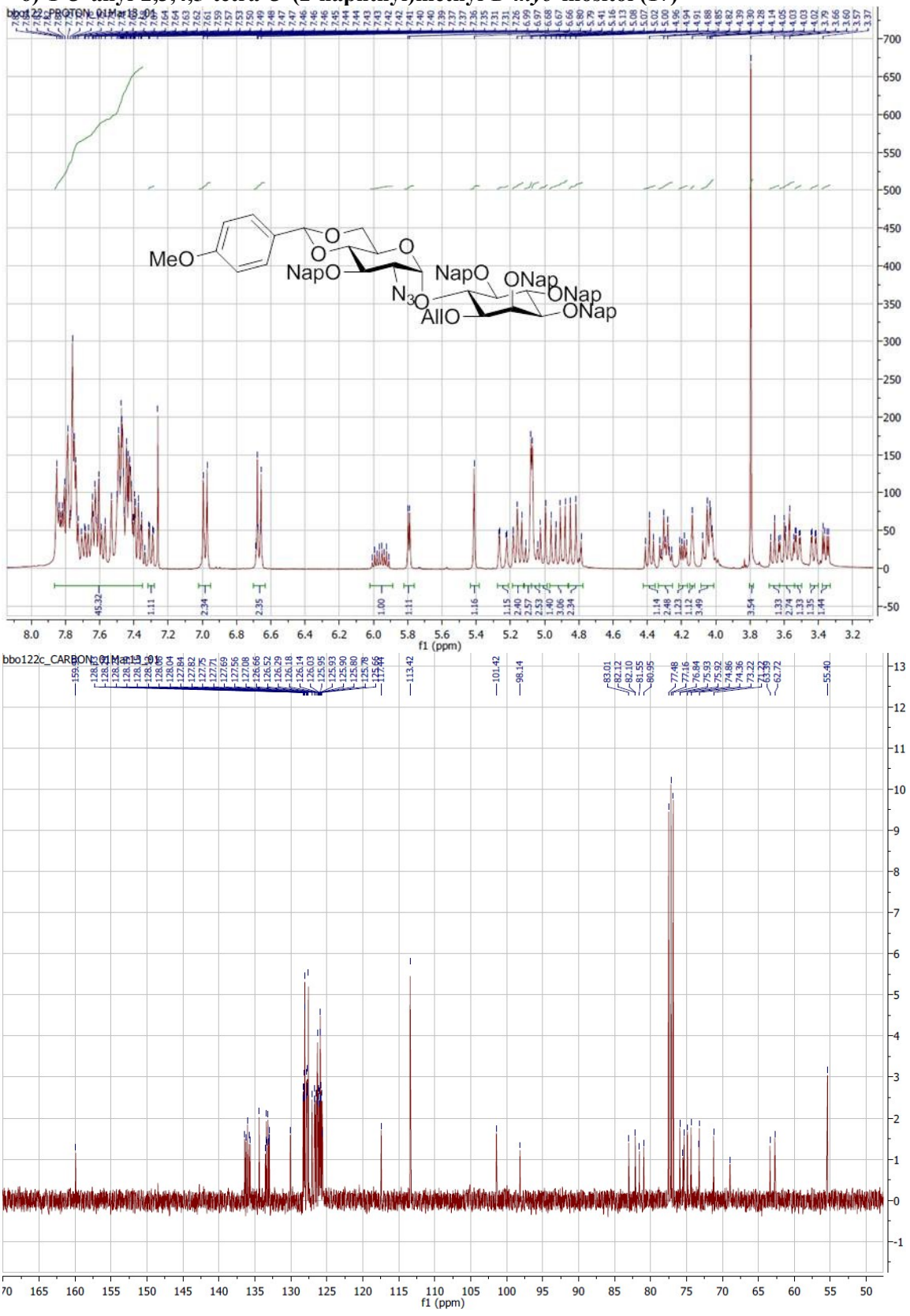


2-Azido-4,6-*O*-(*p*-methoxybenzylidene)-2-deoxy-α-D-glucopyranosyl-(1→6)-1-*O*-allyl-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (16)

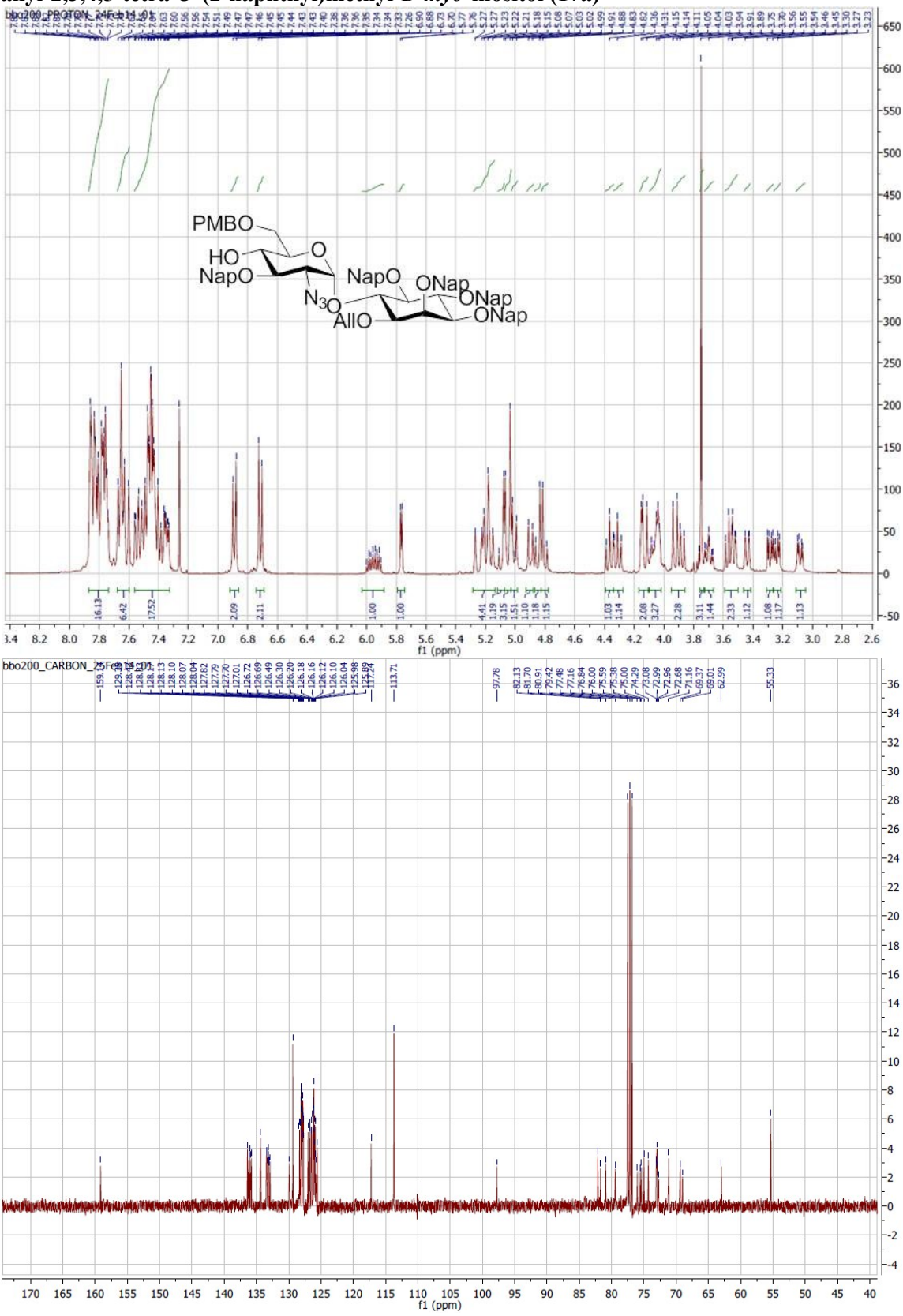




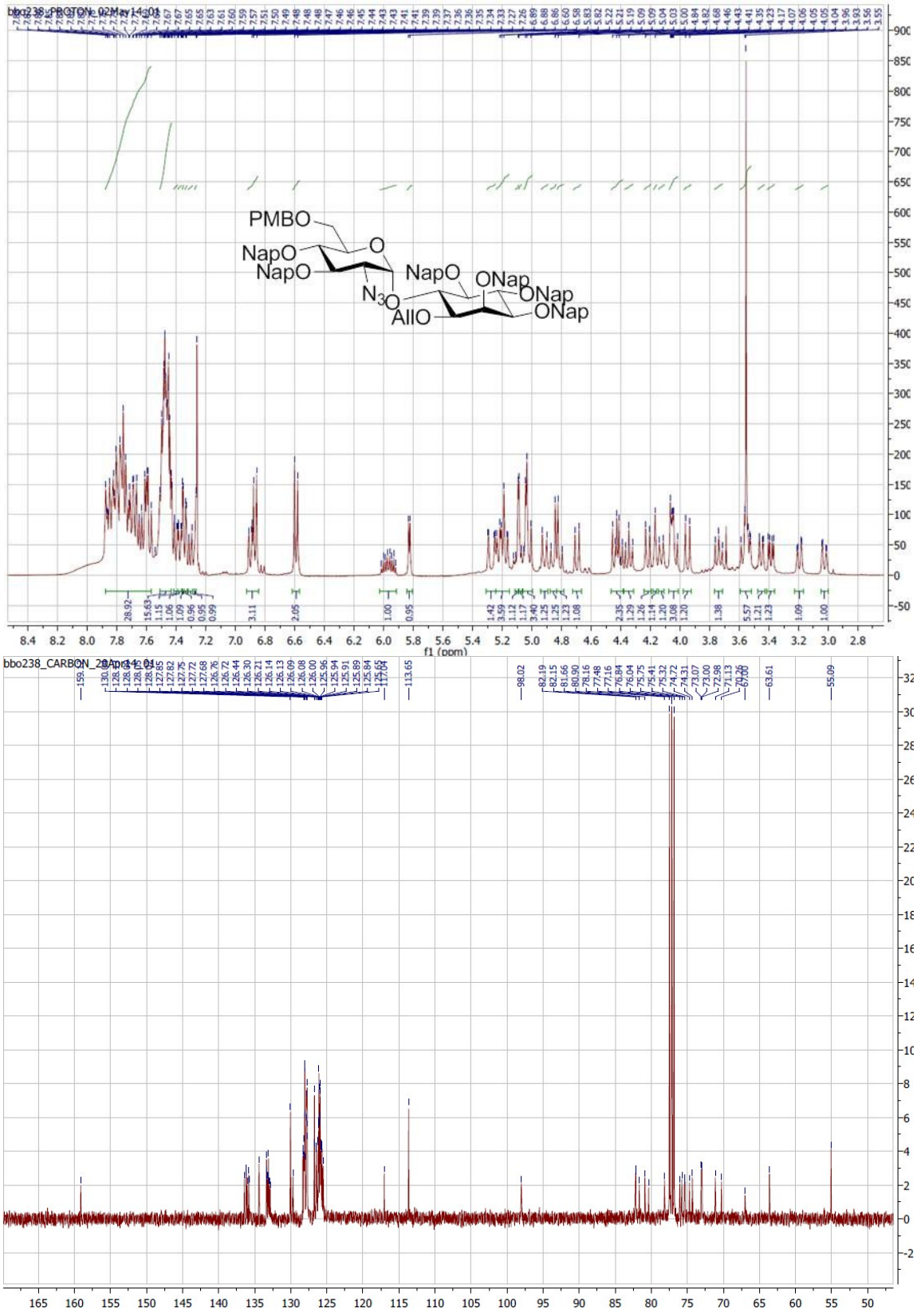
2-Azido-3-*O*-(2-naphthyl)methyl-4,6-*O*-(*p*-methoxybenzylidene)-2-deoxy-α-D-glucopyranosyl-(1→6)-1-*O*-allyl-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (17)



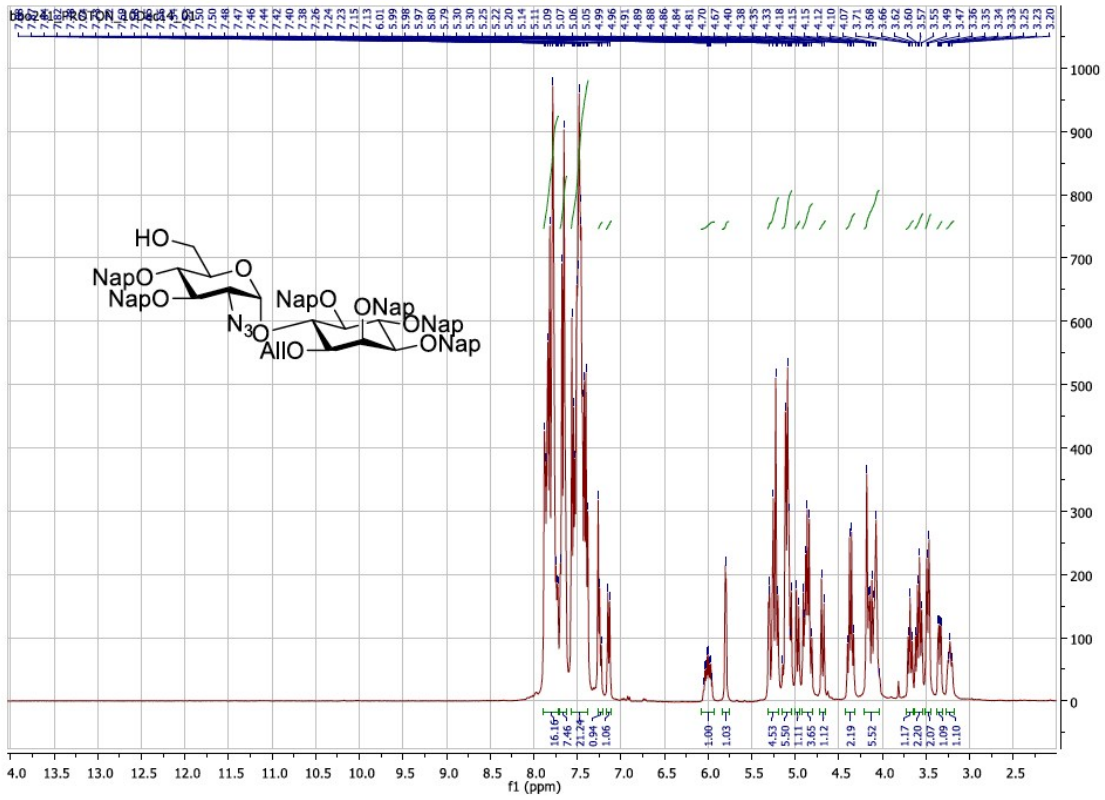
2-Azido-3-*O*-(2-naphthyl)methyl-6-*O*-(*p*-methoxybenzyl)-2-deoxy-α-D-glucopyranosyl-(1→6)-1-*O*-allyl-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (17a)

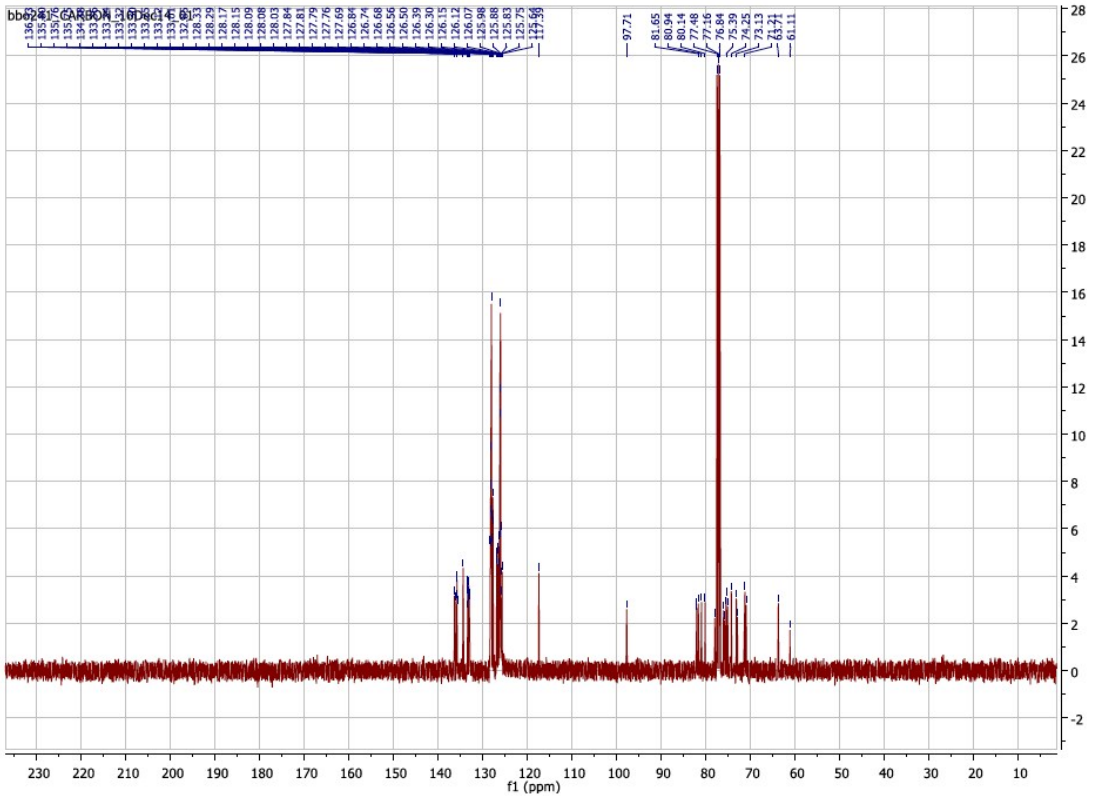


2-Azido-3,4-di-*O*-(2-naphthyl)methyl-6-*O*-(*p*-methoxybenzyl)-2-deoxy-α-D-glucopyranosyl-(1→6)-1-*O*-allyl-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (3)

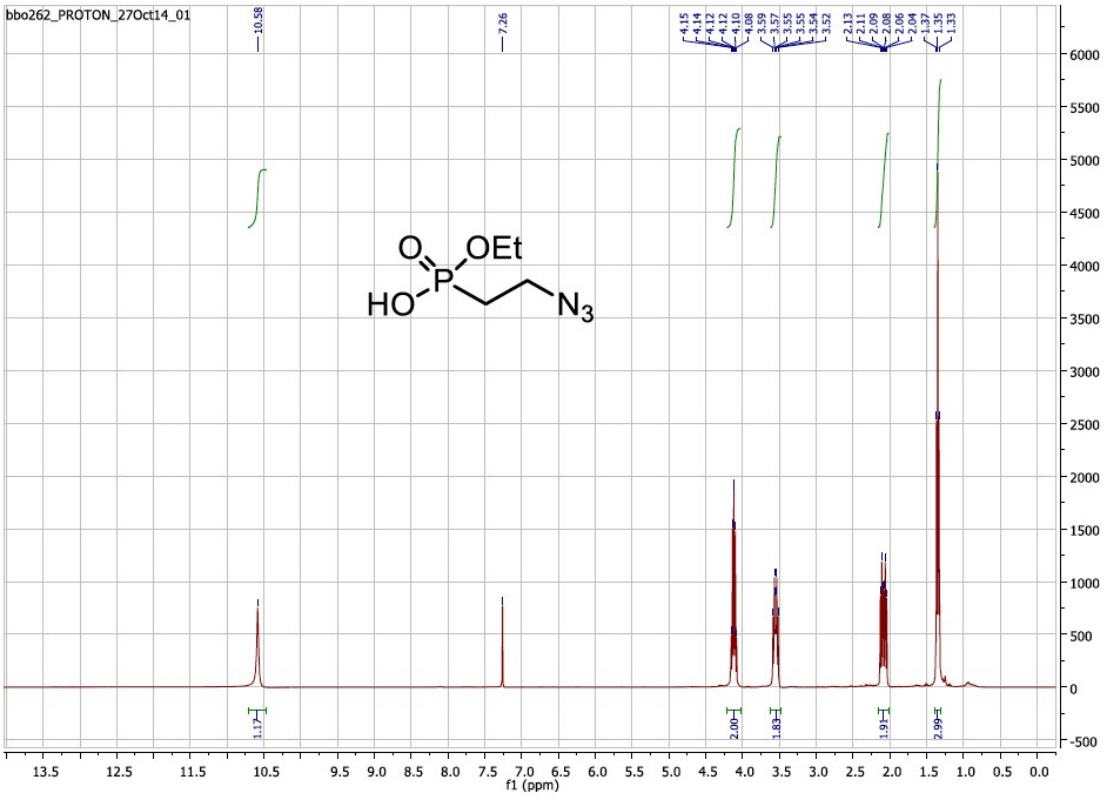


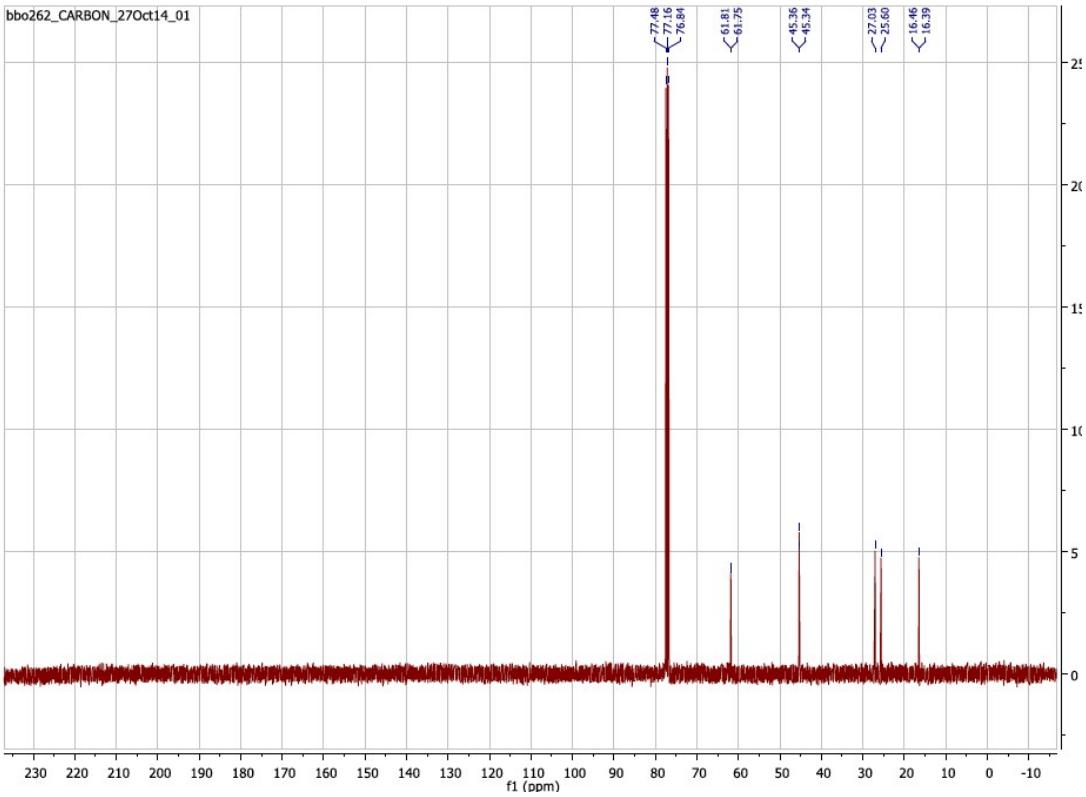
2-Azido-3,4-di-*O*-(2-naphthyl)methyl-2-deoxy-α-D-glucopyranosyl-(1→6)-1-*O*-allyl-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (24)

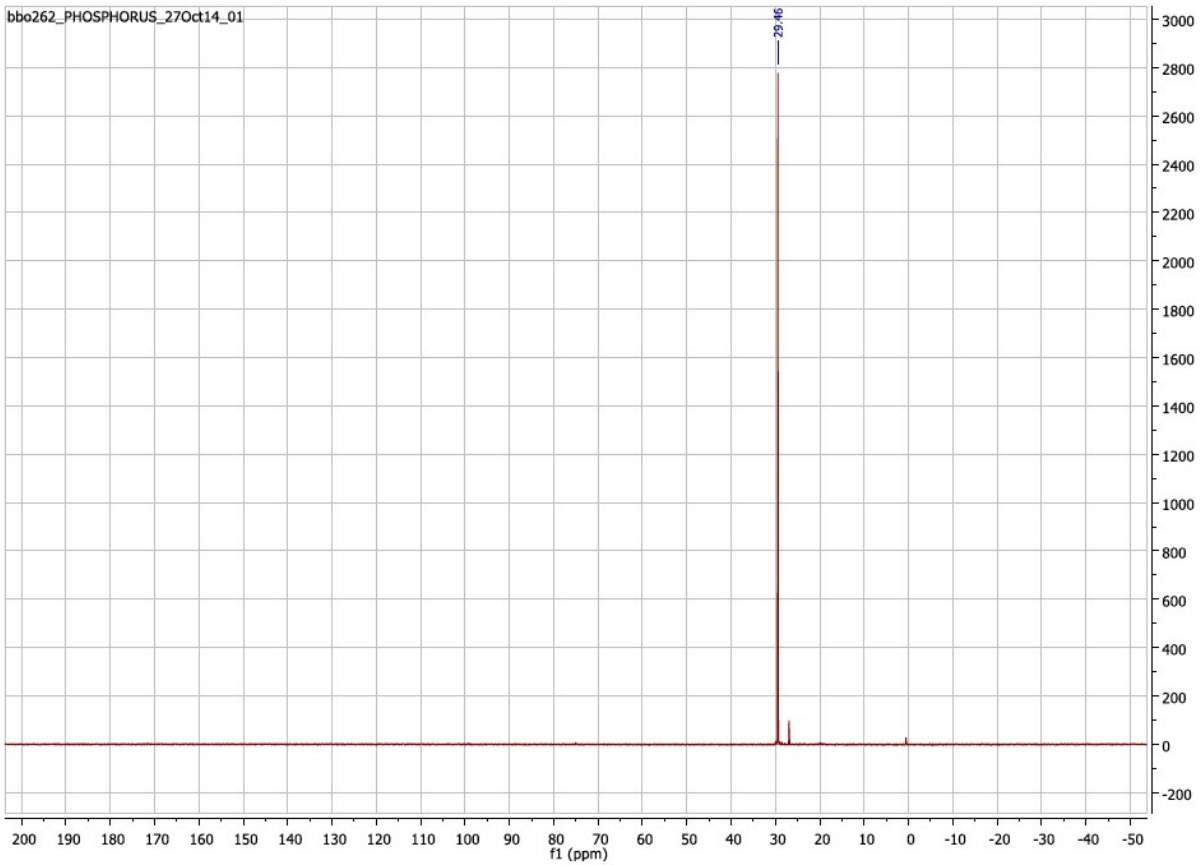




O-Ethyl (2-azidoethyl)phosphonic acid (22)



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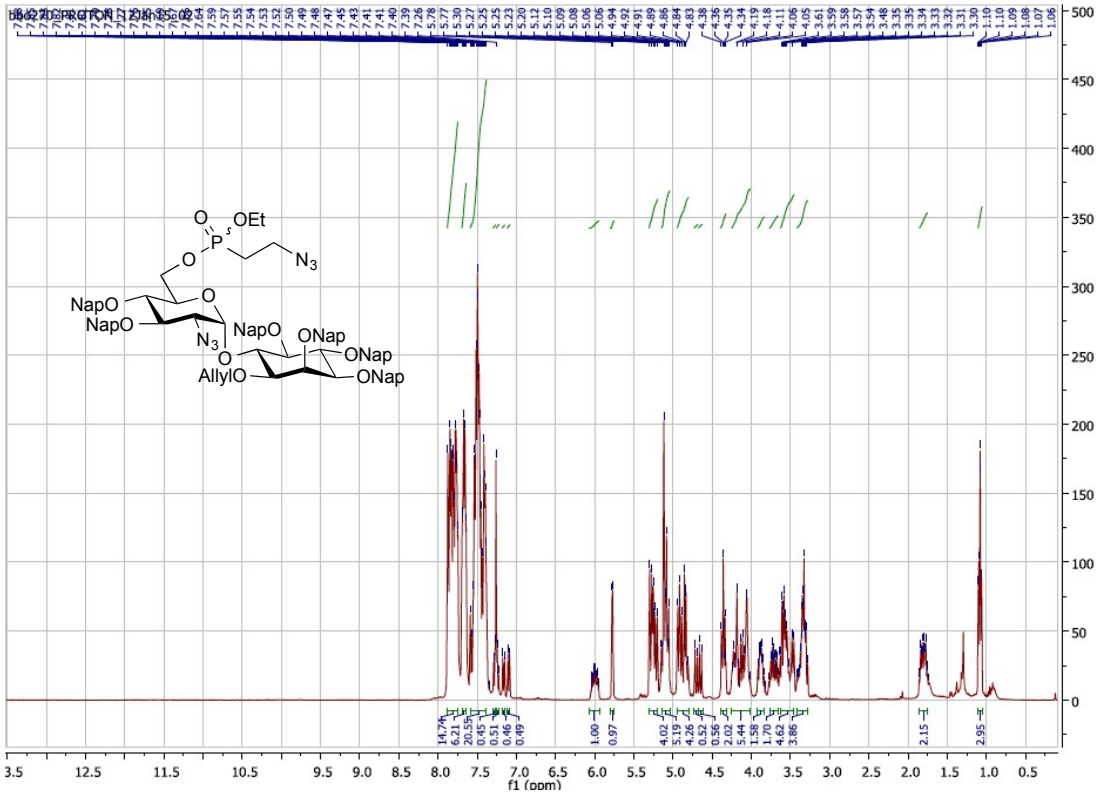
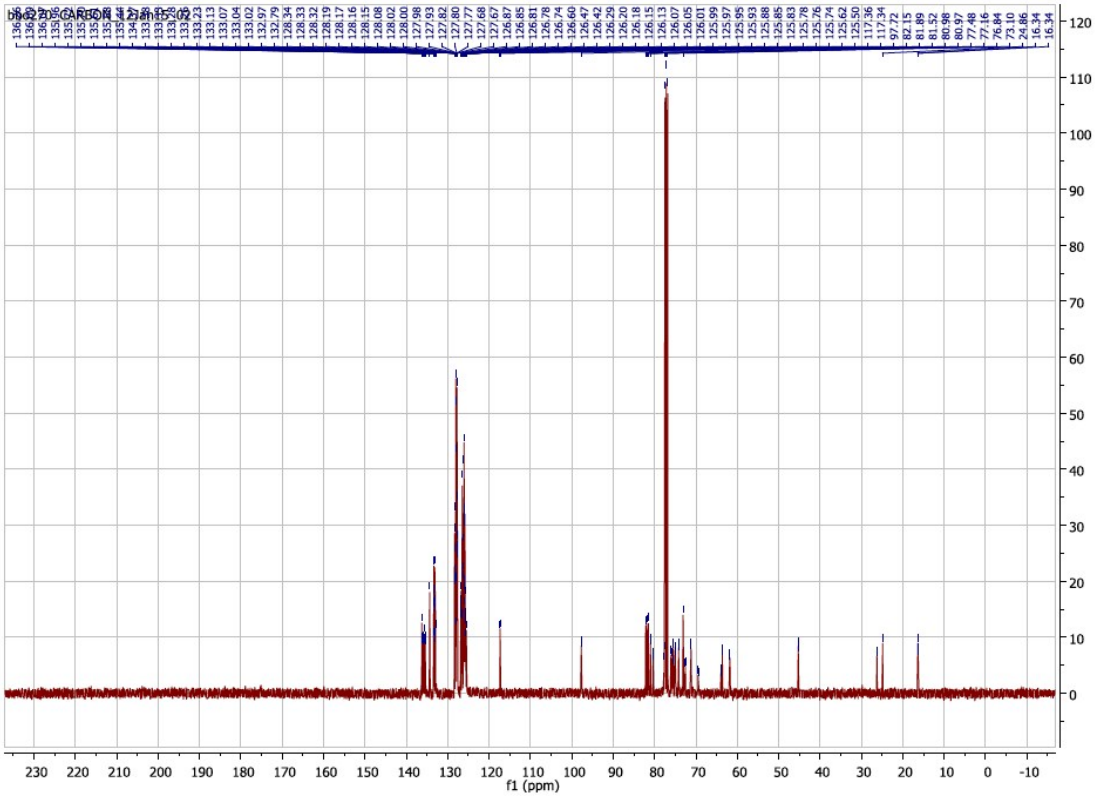
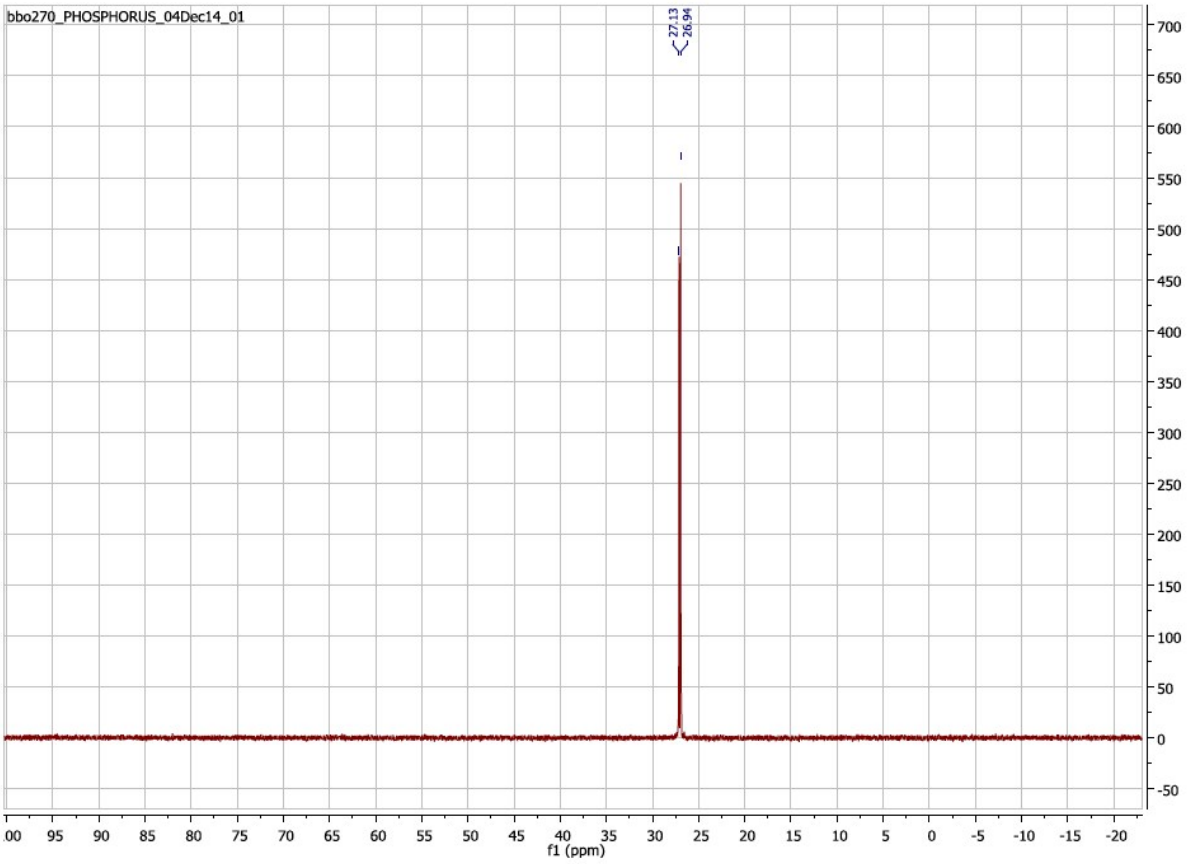
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

2-Azido-3,4-di-*O*-(2-naphthyl)methyl-6-*O*-((2-azidoethyl)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 (25)



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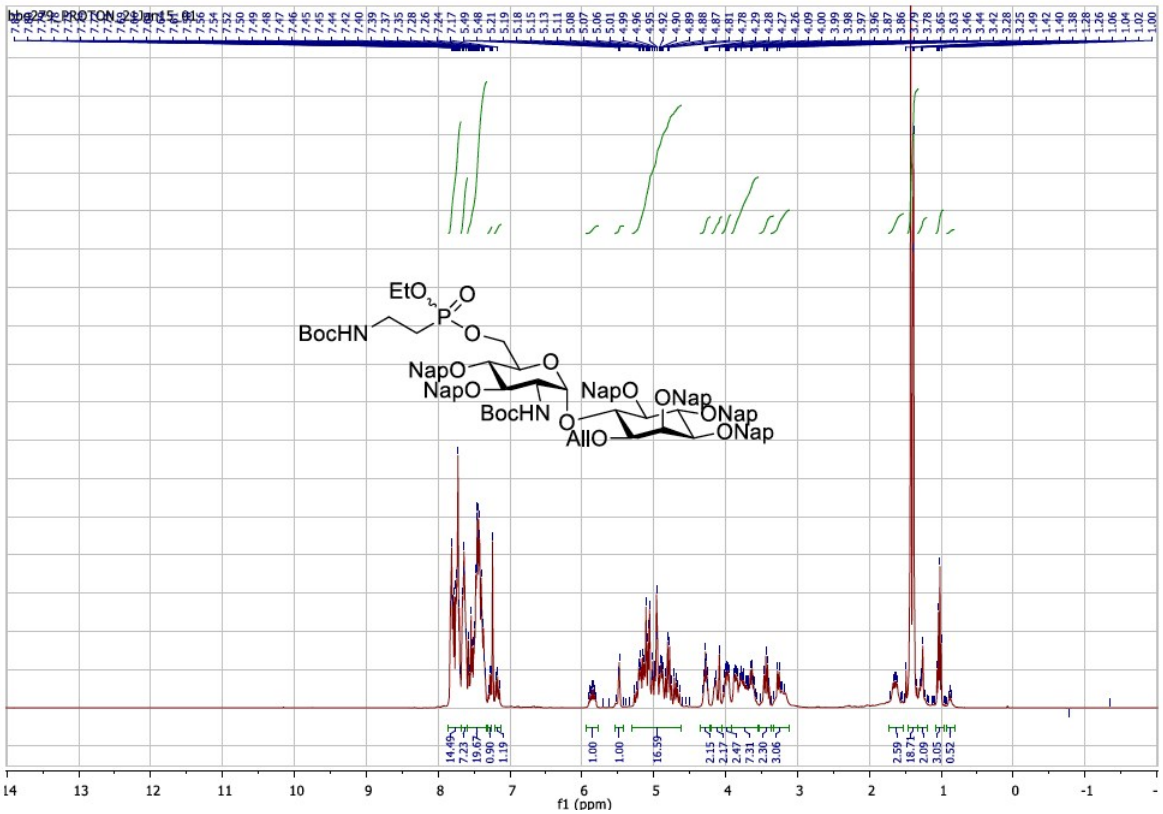
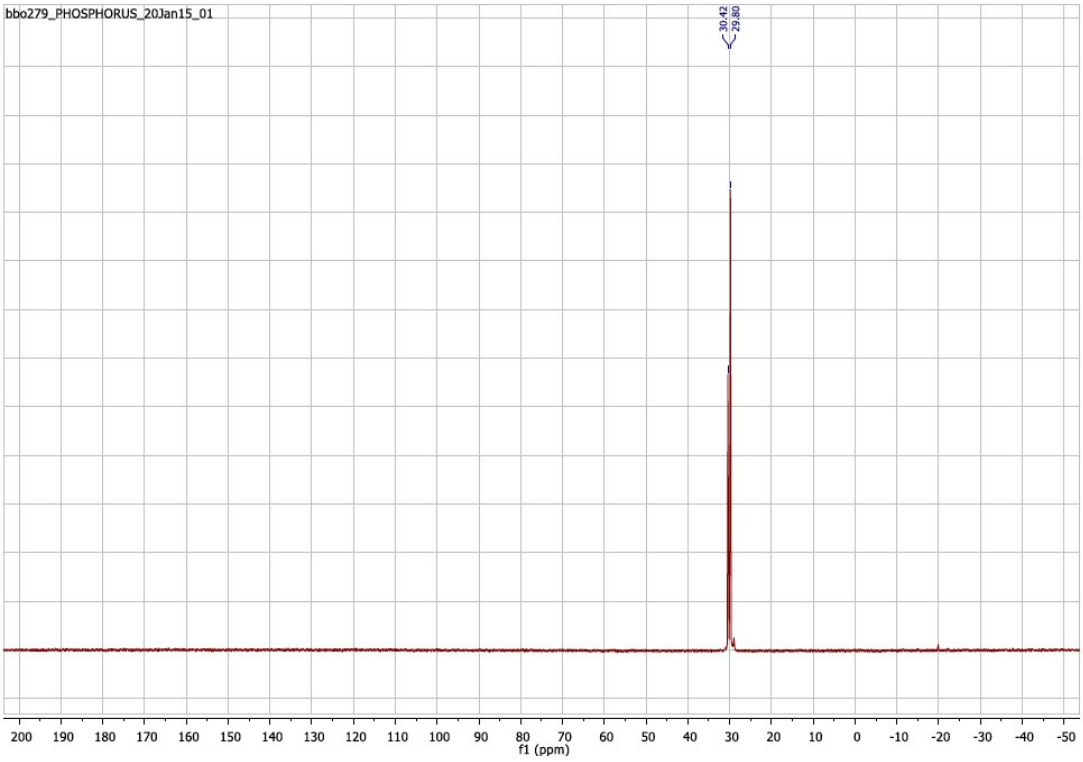
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
00 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20
f1 (ppm)

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→6)-1-*O*-allyl-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (26)




bbo279_PHOSPHORUS_20Jan15_01
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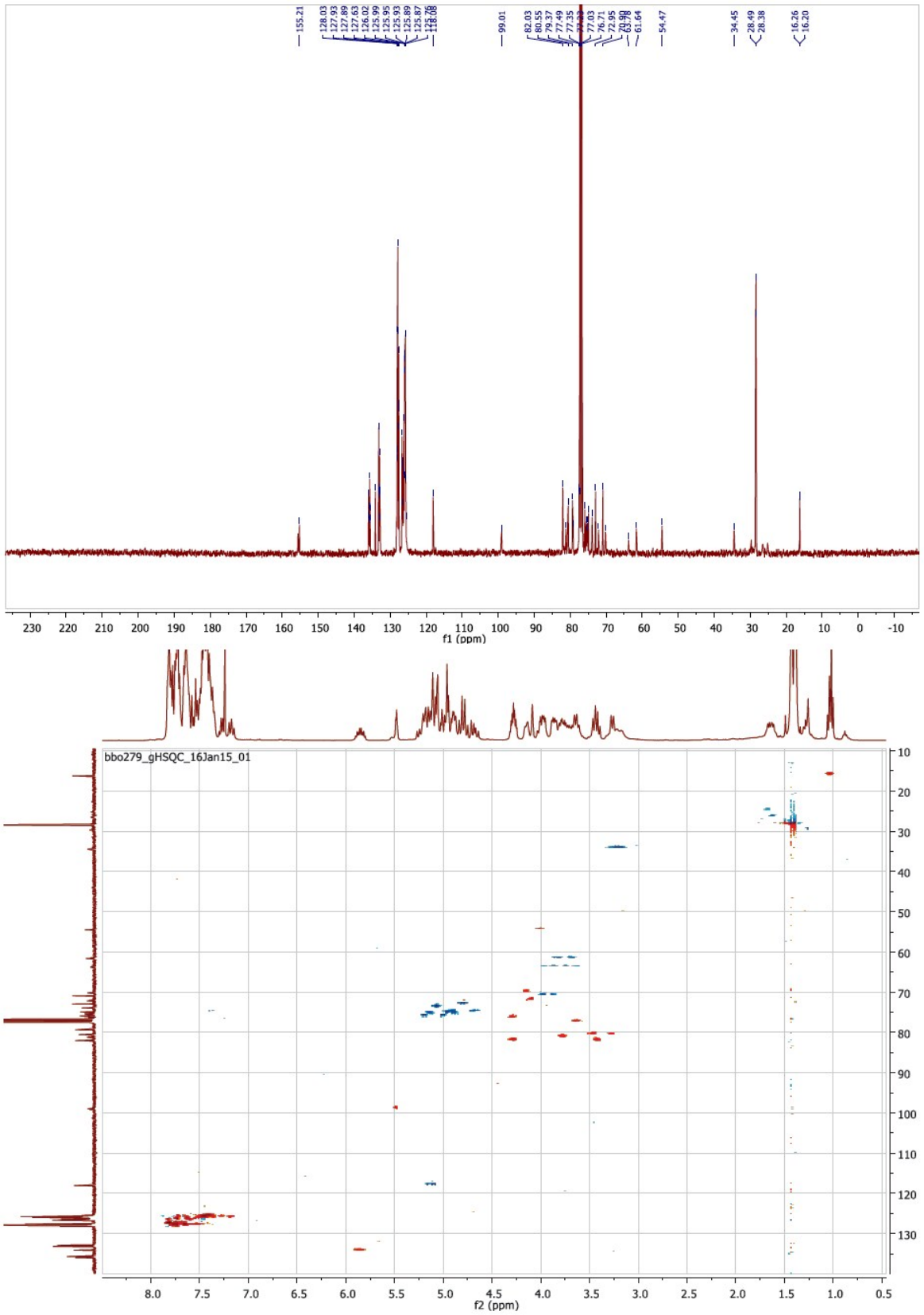
29.80
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)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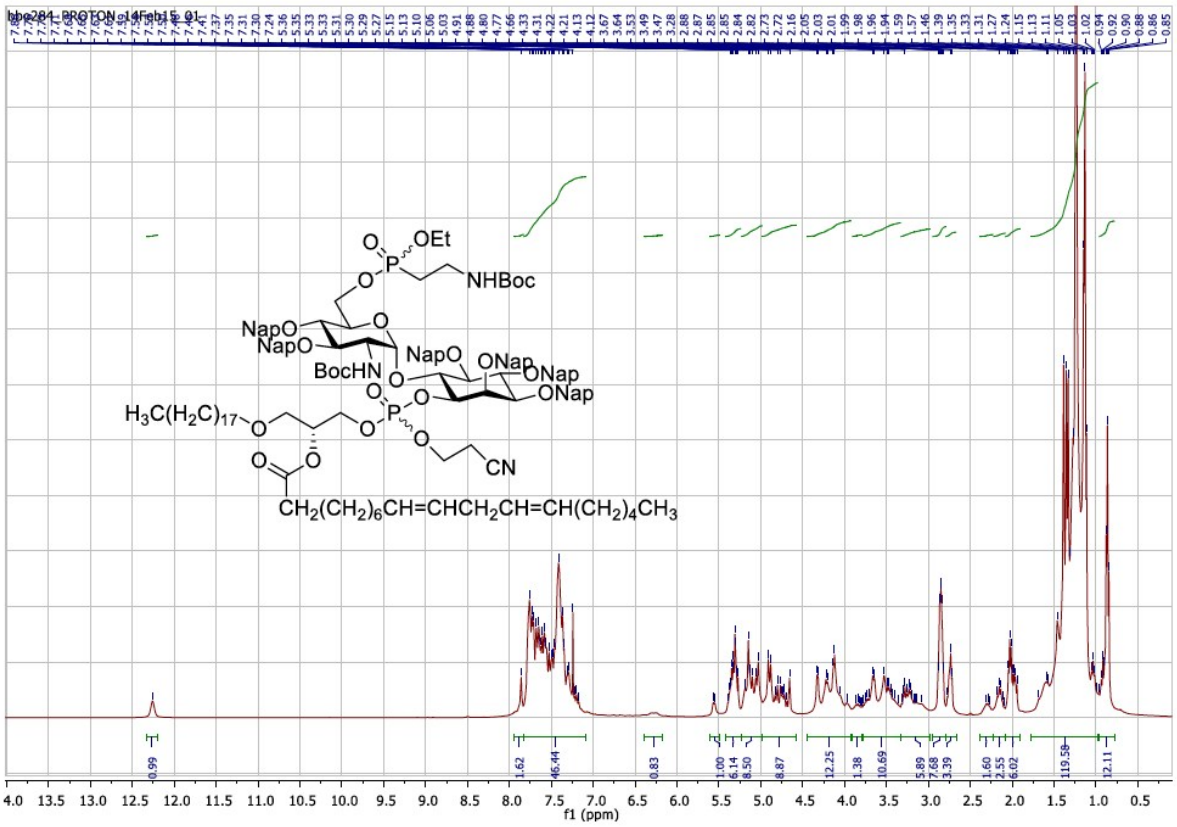
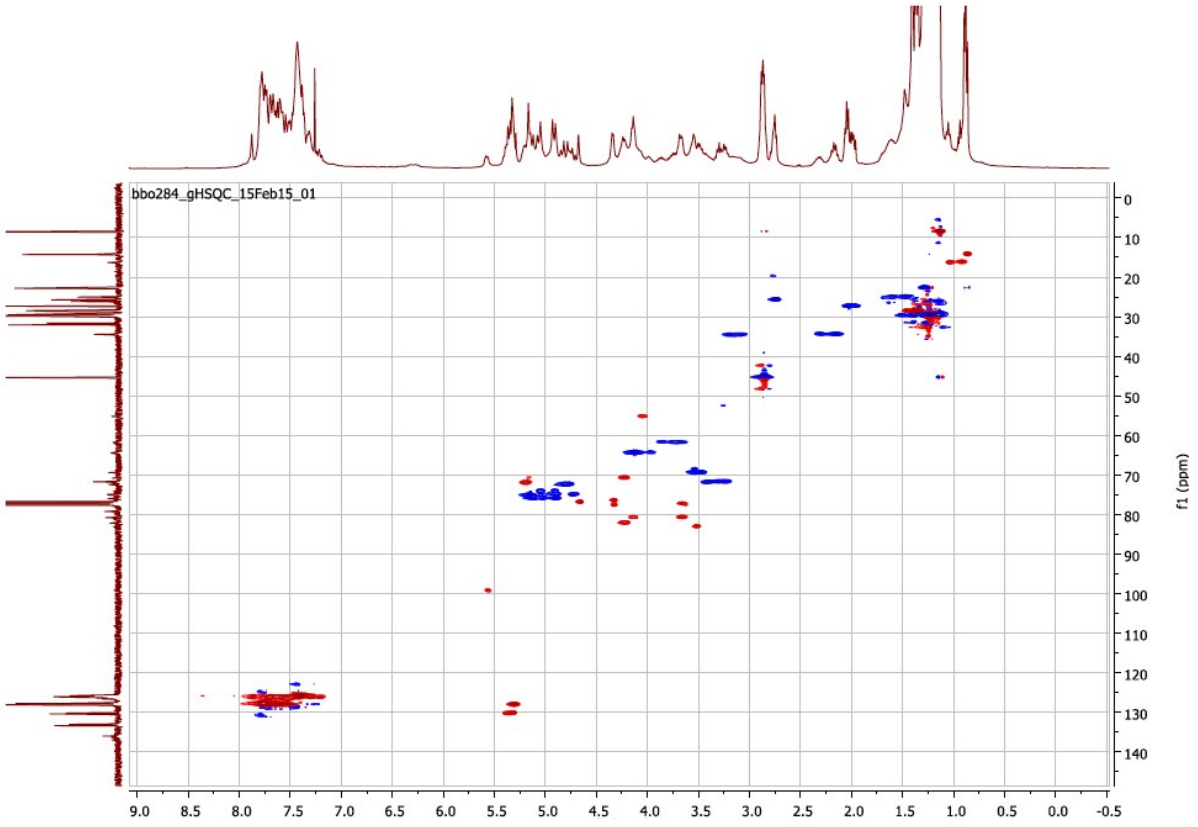
77.35
77.03
76.71
76.65
70.90
63.78
61.64
54.47
34.45
28.49
28.38
16.26
16.20
f1 (ppm)
bbo279_gHSQC_16Jan15_01
f2 (ppm)
f1 (ppm)

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→6)-1-*O*-[1-*O*-(octadecyl)-2-*O*-(9Z,12Z-octadecanoyl)-*sn*-glycero-3-phosphocyanoethyl]-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (28)

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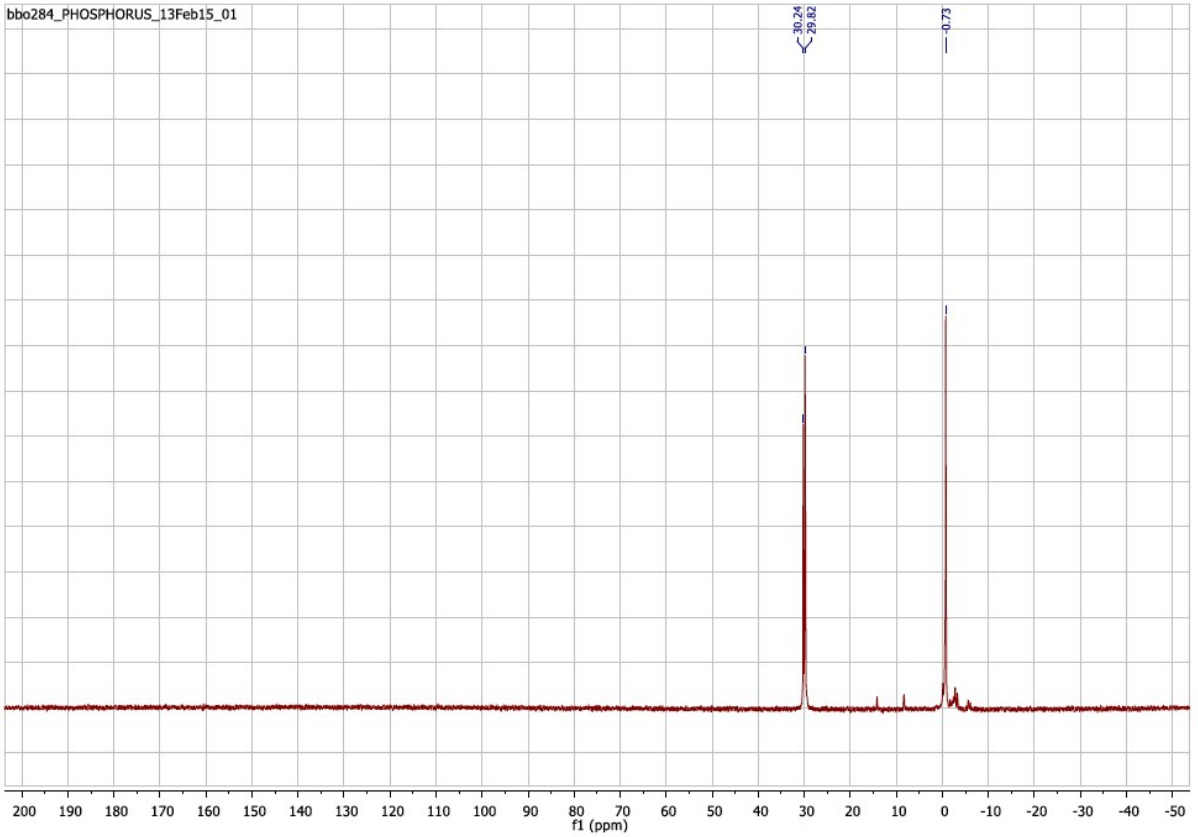
f1 (ppm)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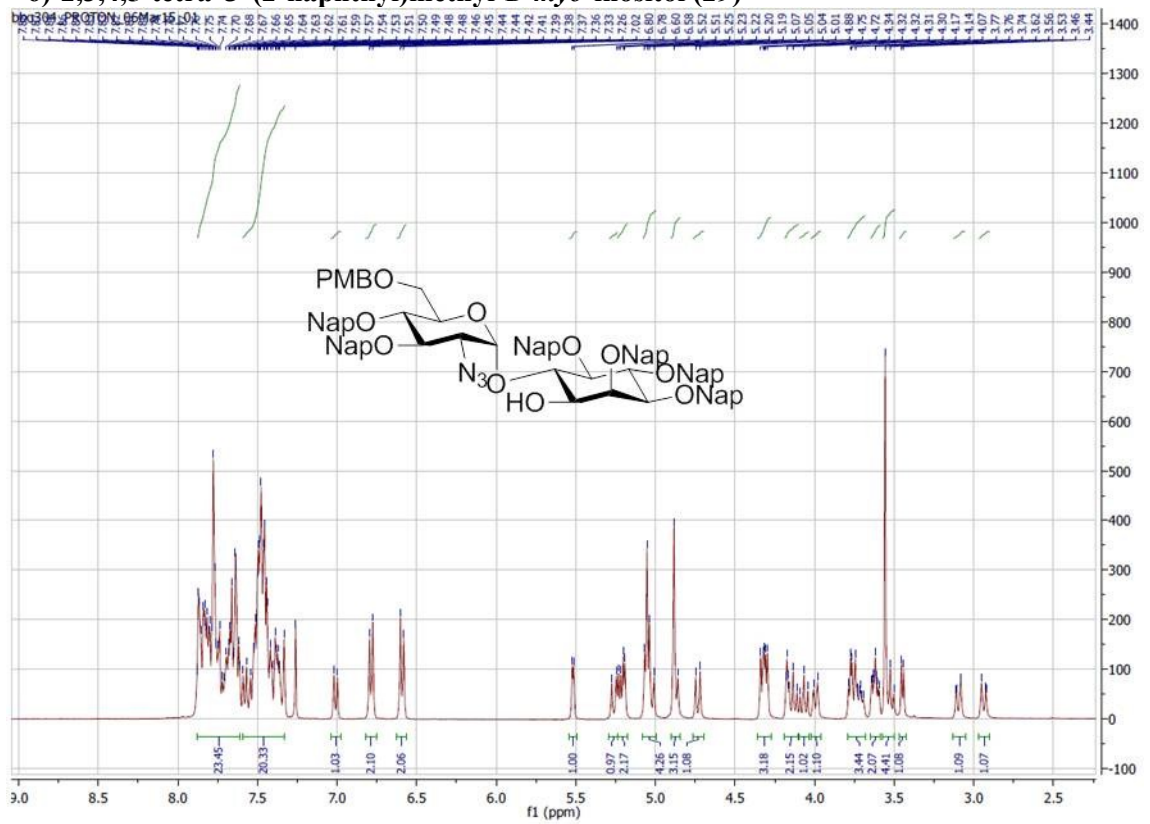
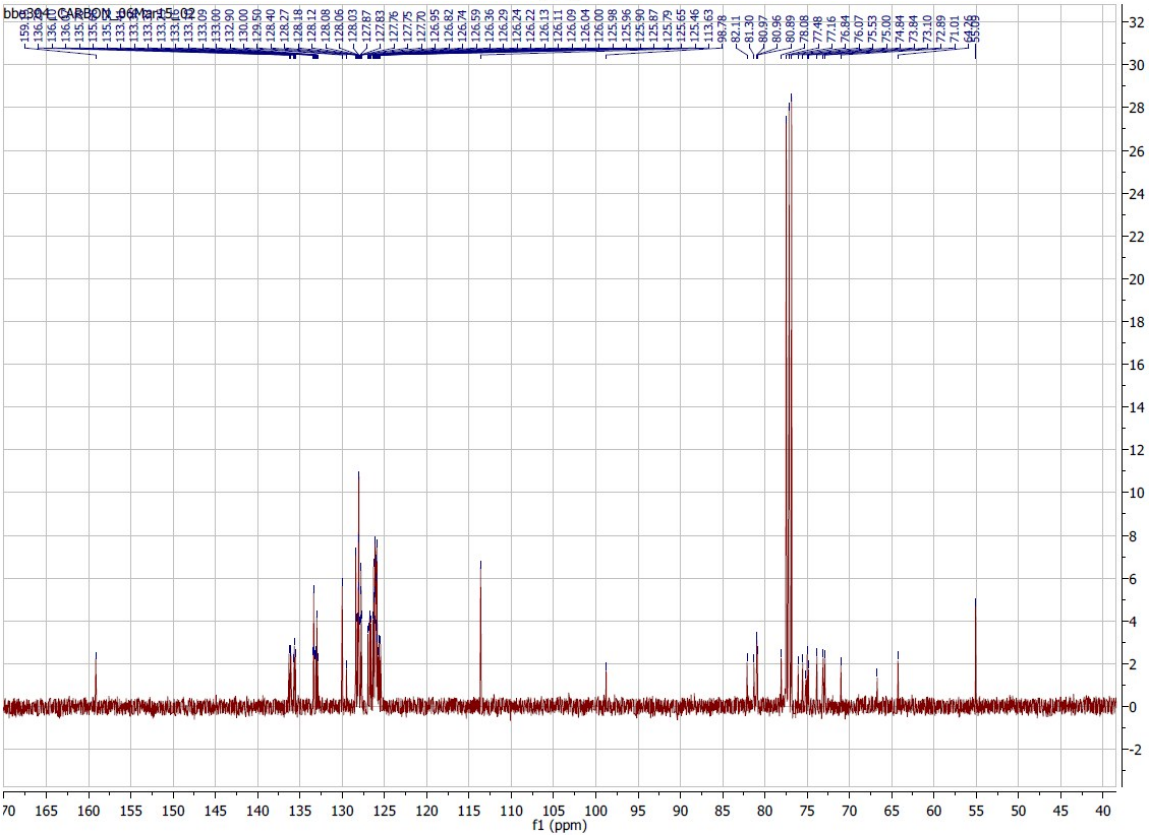
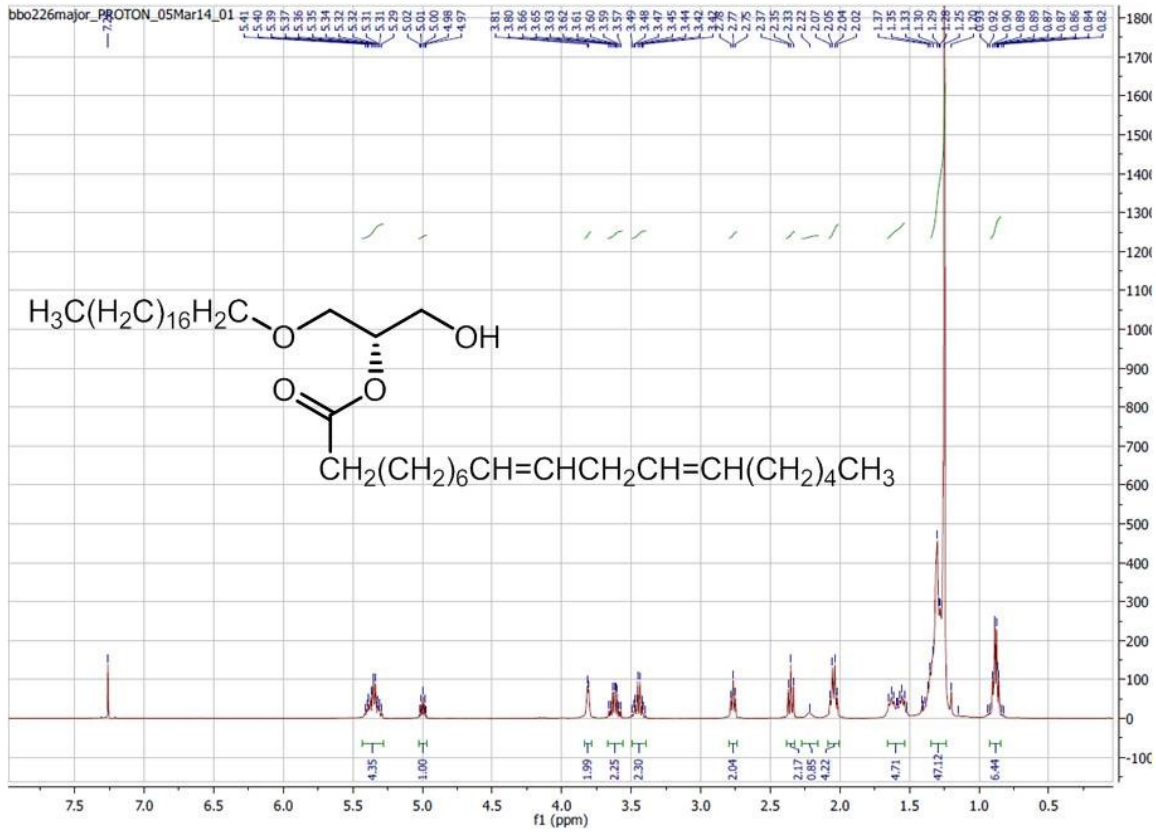
-0.73
f1 (ppm)

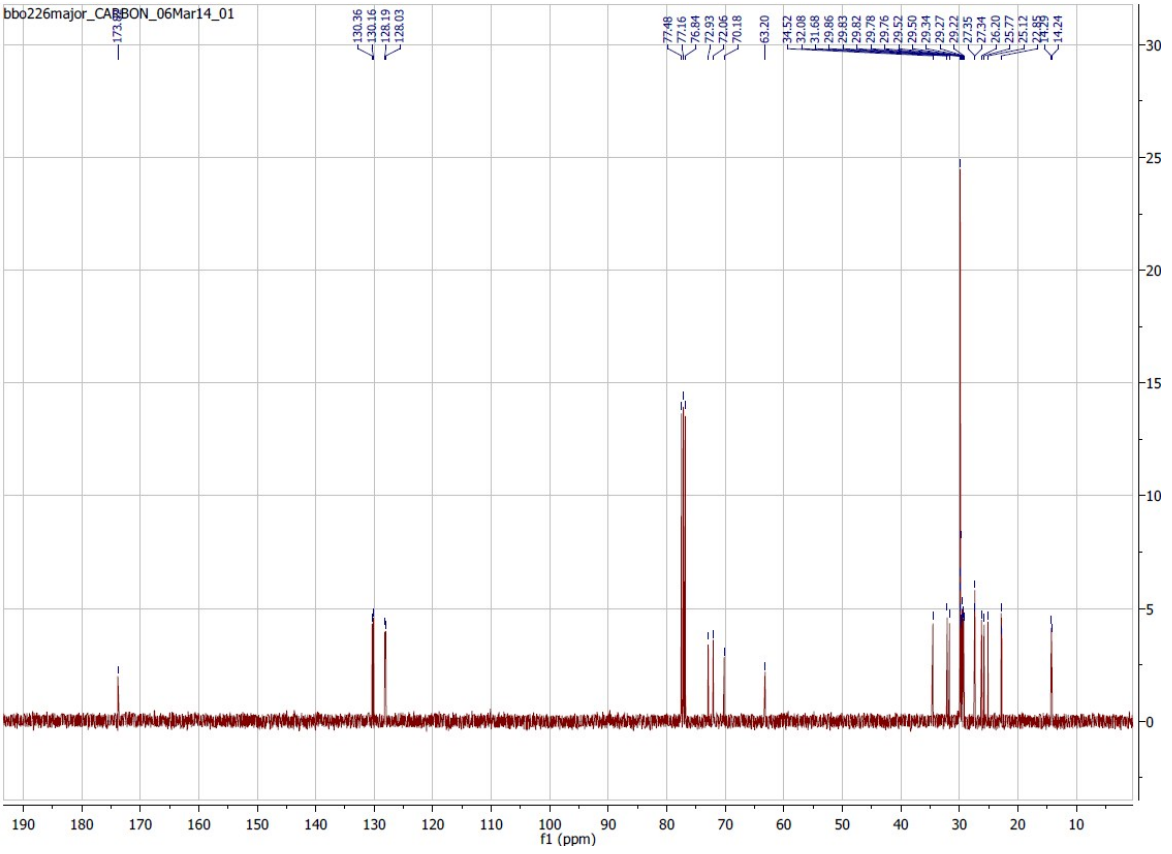
2-Azido-3,4-di-*O*-(2-naphthyl)methyl-6-*O*-(*p*-methoxybenzyl)-2-deoxy-α-D-glucopyranosyl-(1→6)-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (29)



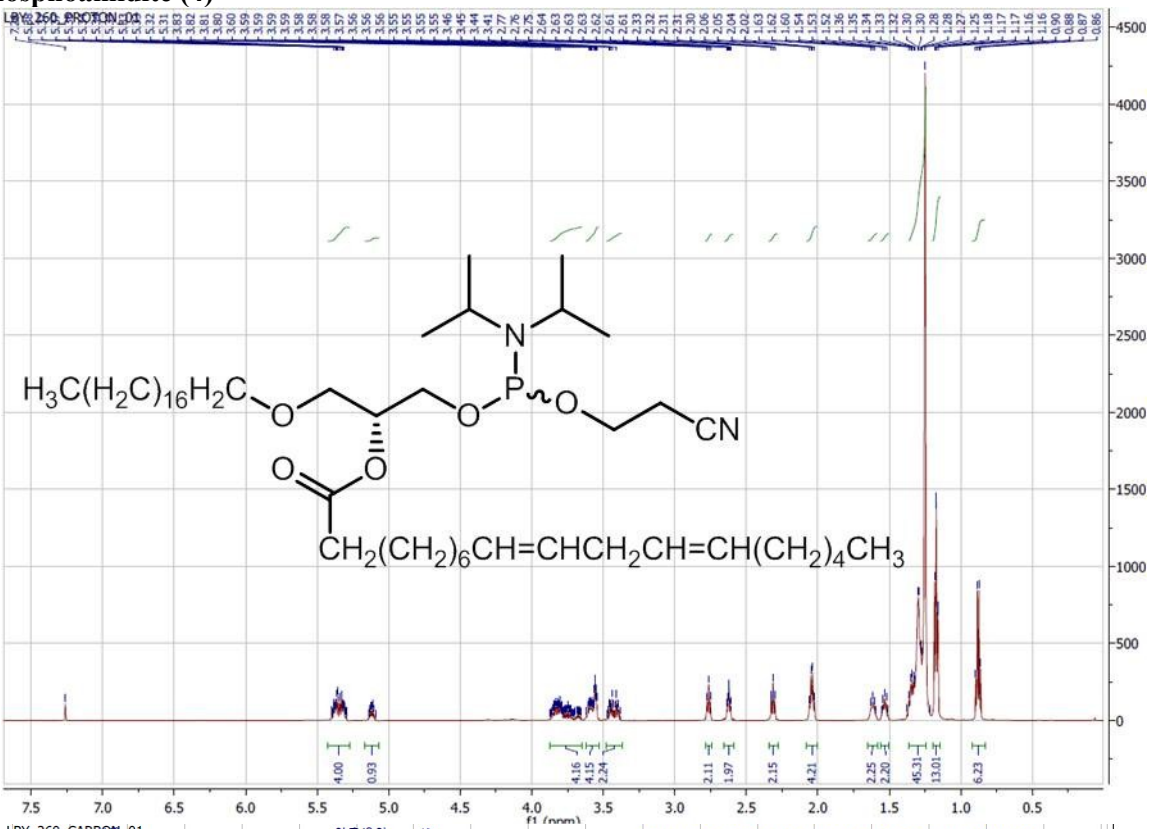


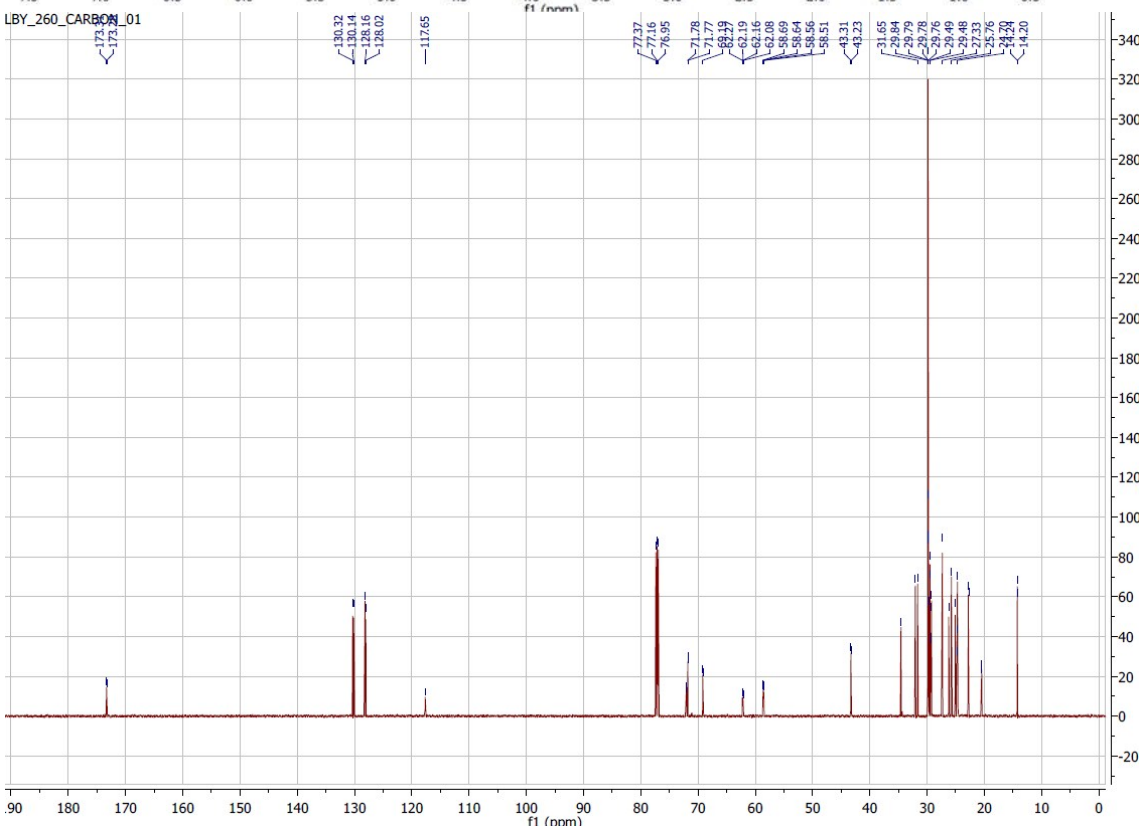
1-*O*-(Octadecyl)-2-*O*-(9Z,12Z-octadecanoyl)-*sn*-glycerol (20)

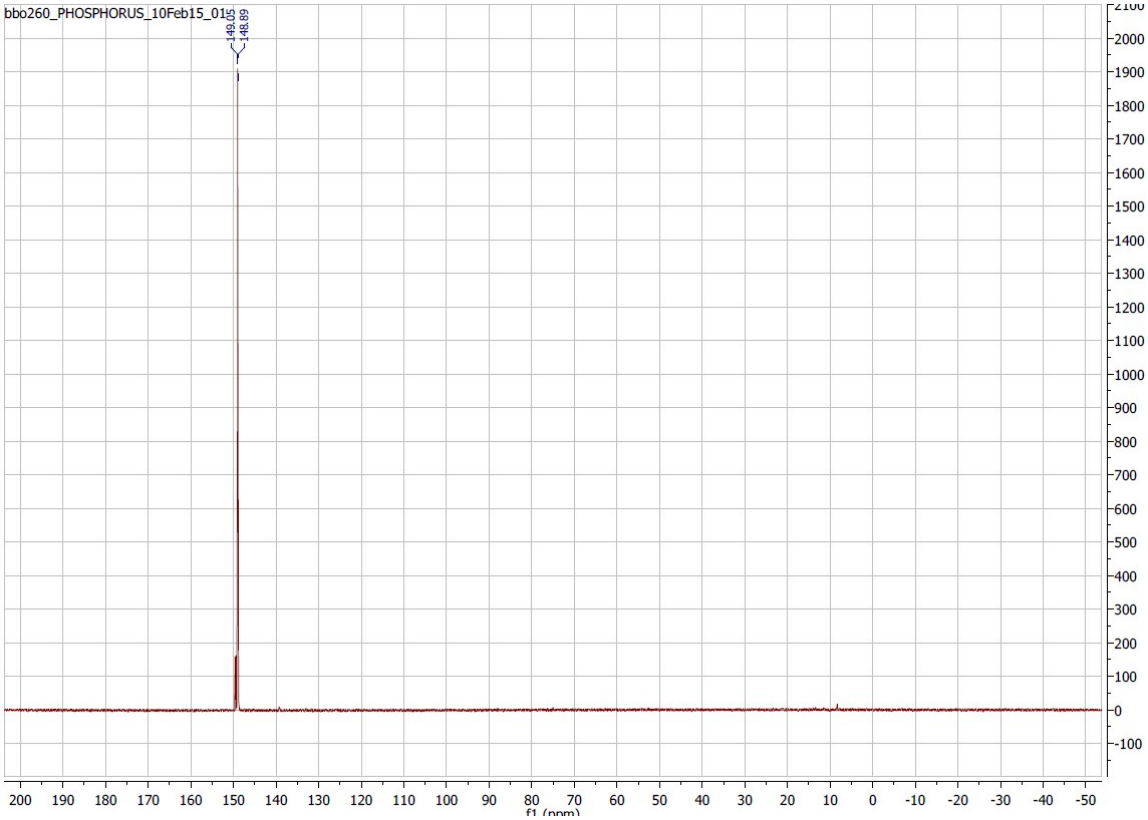




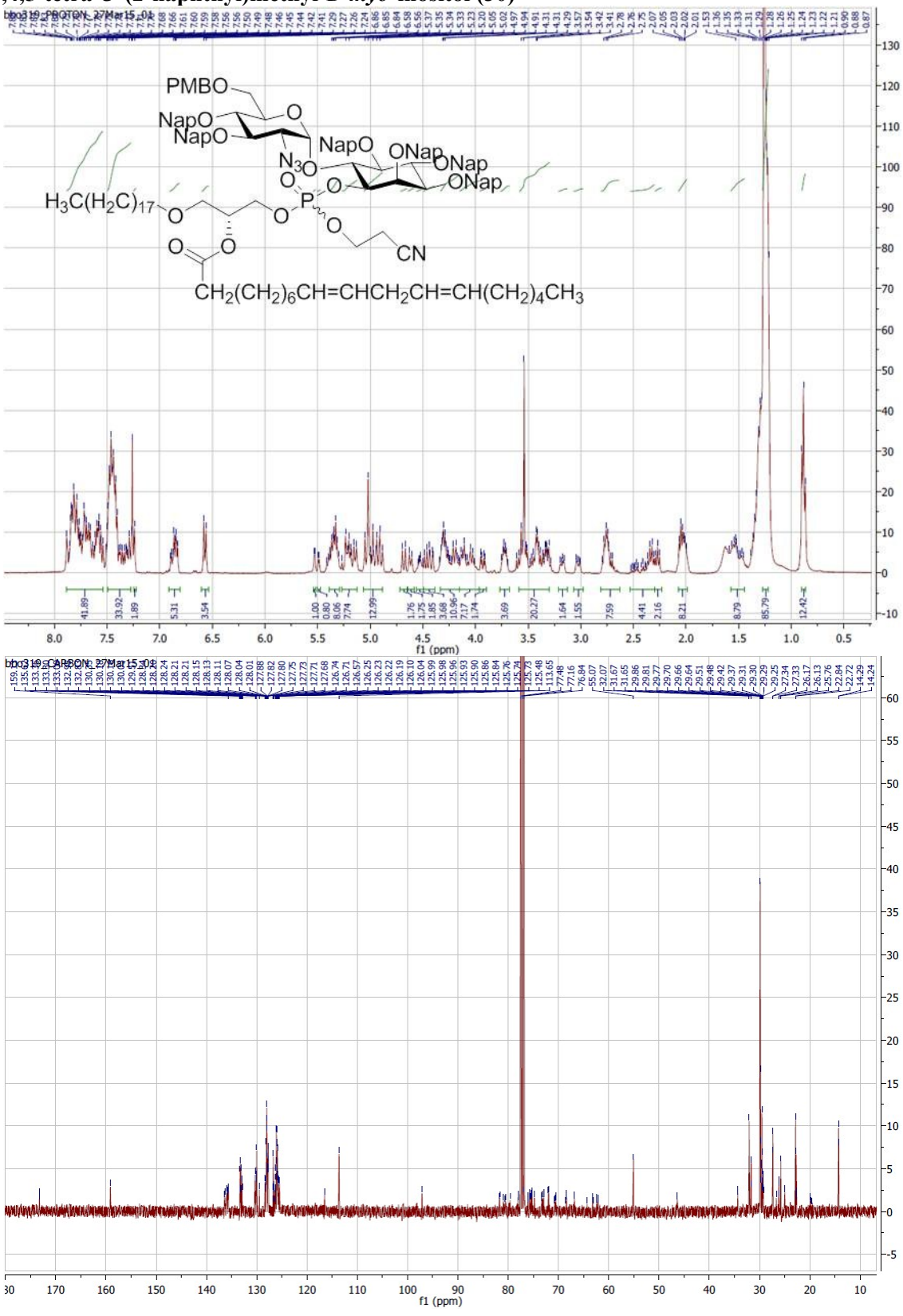
2-Cyanoethyl-*N,N*-diisopropylamine-(1-*O*-(octadecyl)-2-*O*-(9Z,12Z-octadecanoyl)-*sn*-glycero)-3-phosphoamidite (4)

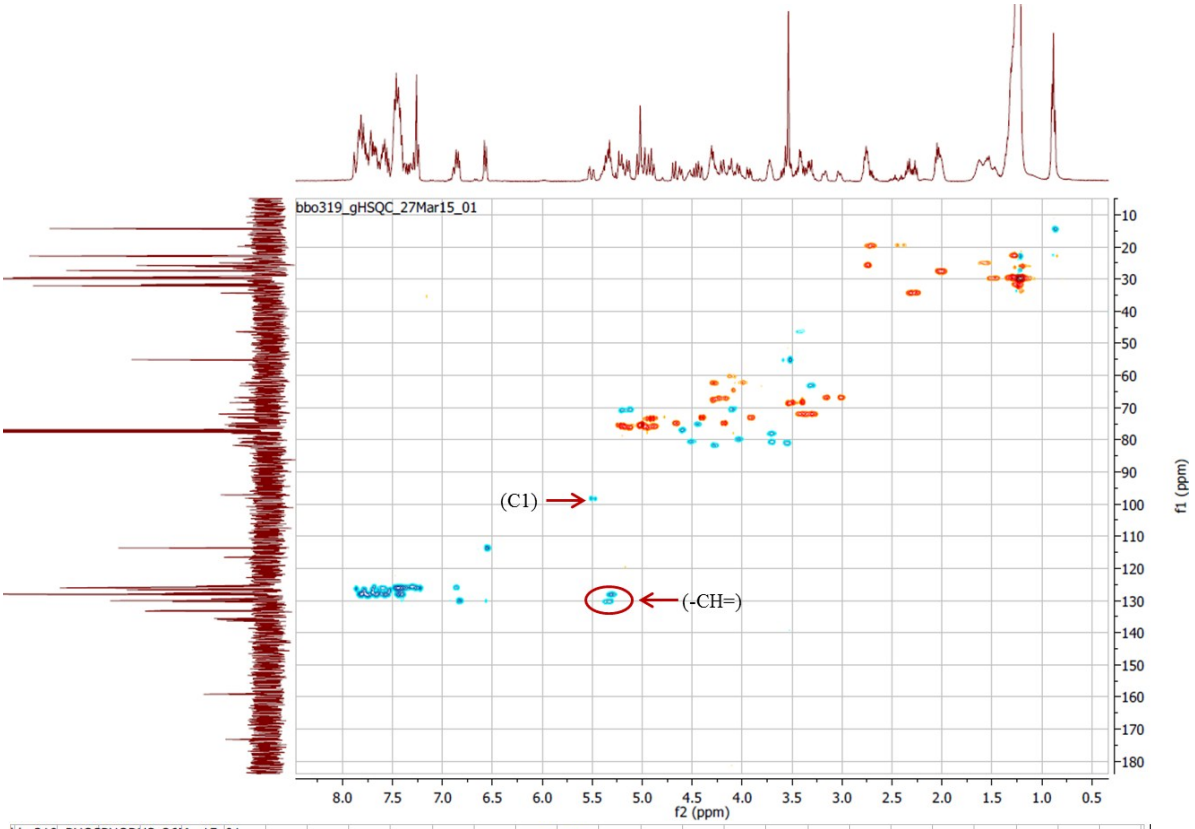


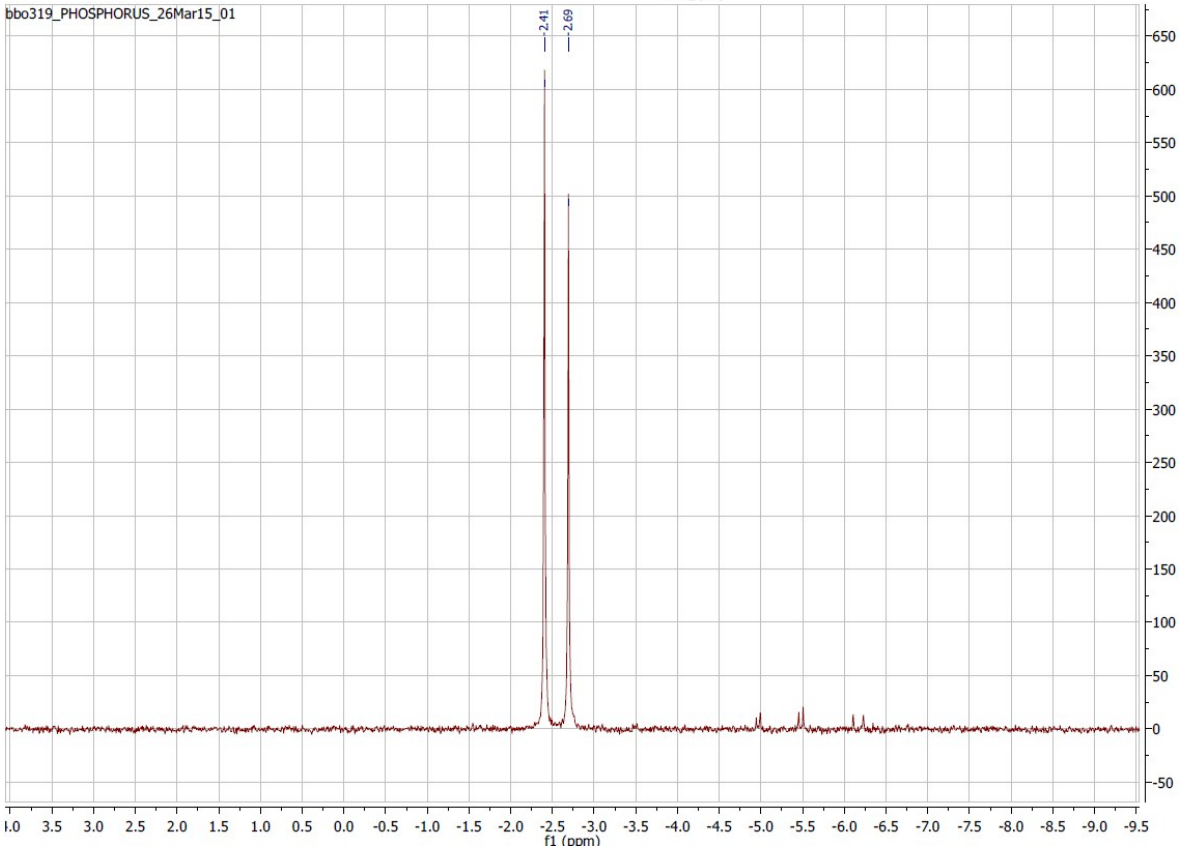



bbo260_PHOSPHORUS_10Feb15_01
149.05
148.89
f1 (ppm)

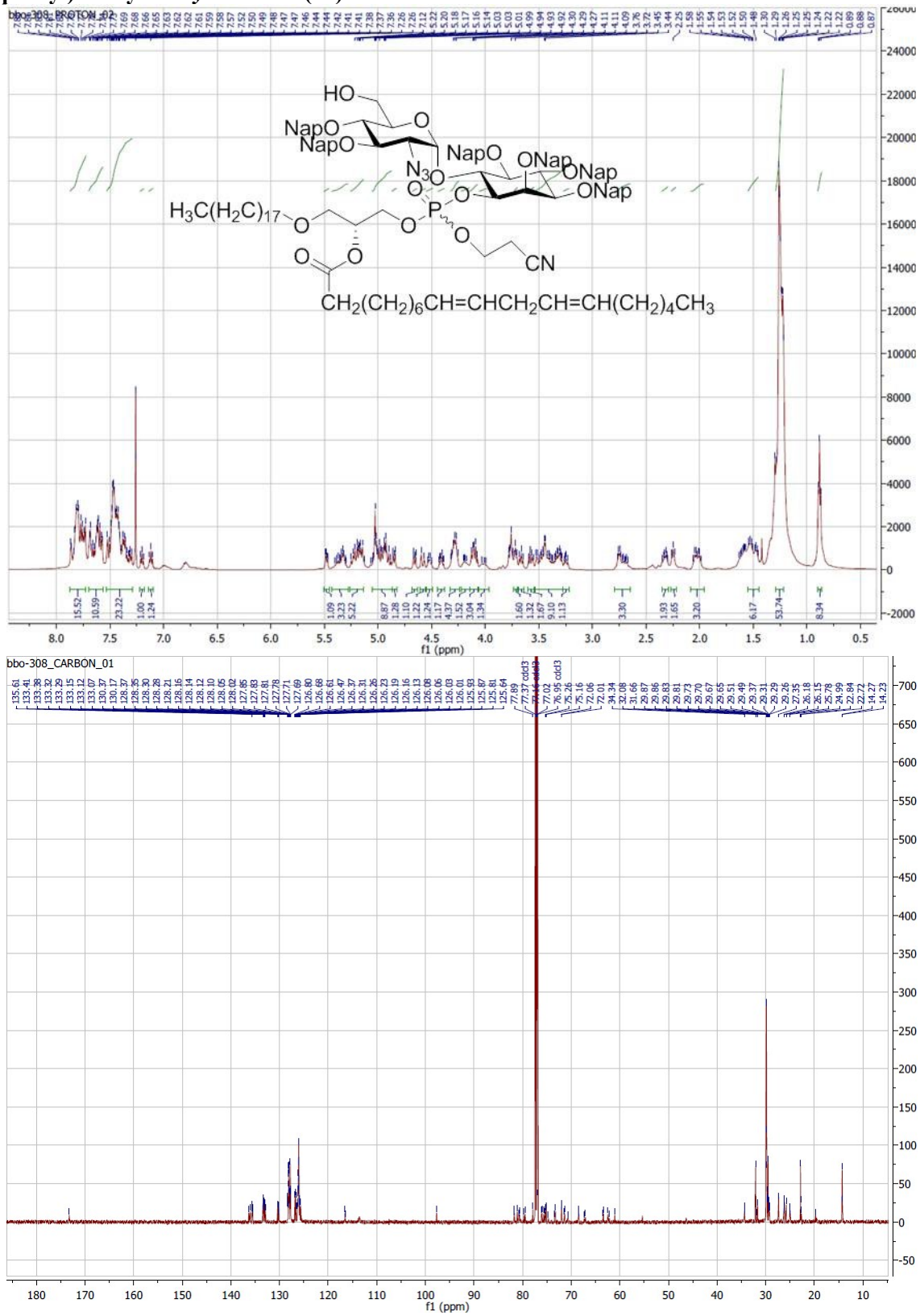
2-Azido-3,4-di-*O*-(2-naphthyl)methyl-6-*O*-(*p*-methoxybenzyl)-2-deoxy-α-D-glucopyranosyl-(1→6)-1-*O*-[1-*O*-(octadecyl)-2-*O*-(9*Z*,12*Z*-octadecanoyl)-*sn*-glycero-3-phosphocyanoethyl]-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (30)

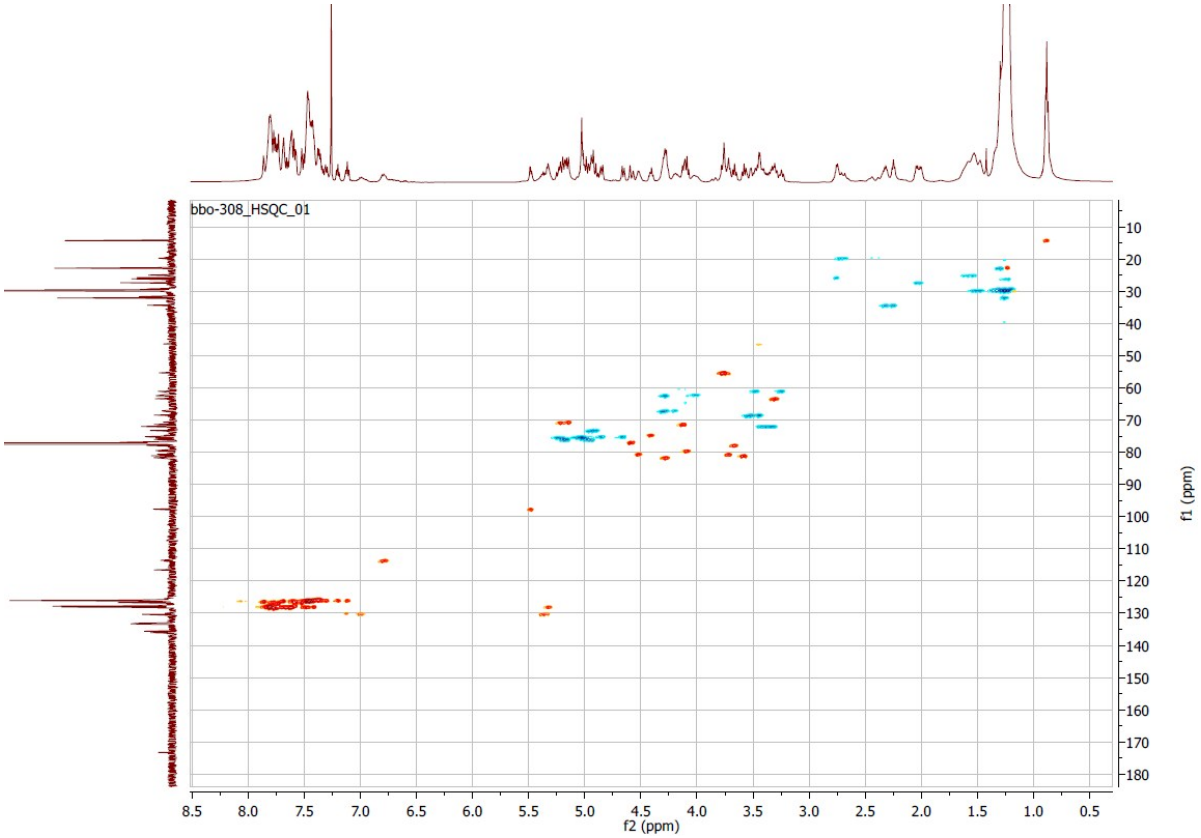



bbo319_gHSQC_27Mar15_01
(C1)
(-CH=)
f2 (ppm)
f1 (ppm)

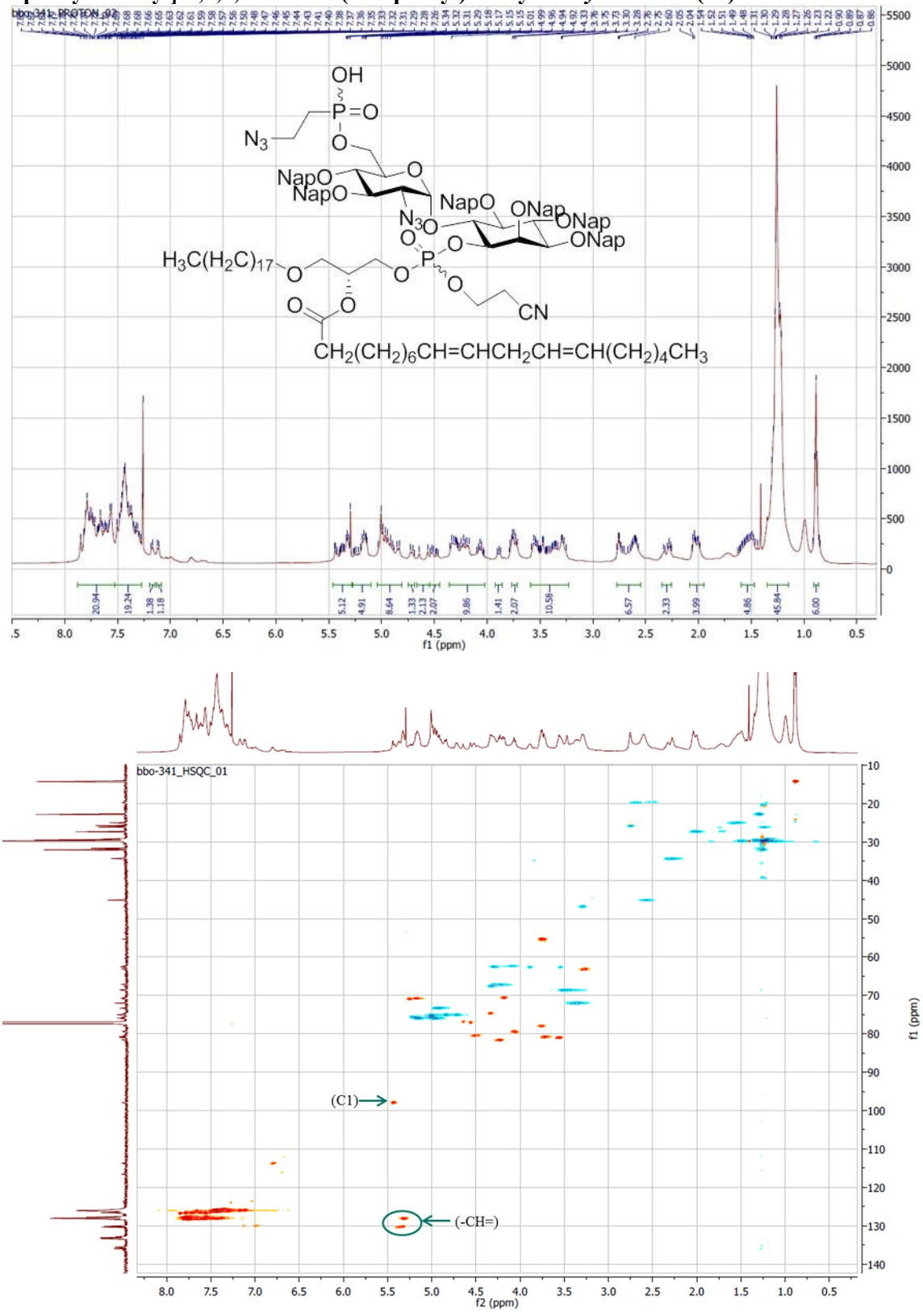

bbo319_PHOSPHORUS_26Mar15_01
2.41
2.69
f1 (ppm)

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

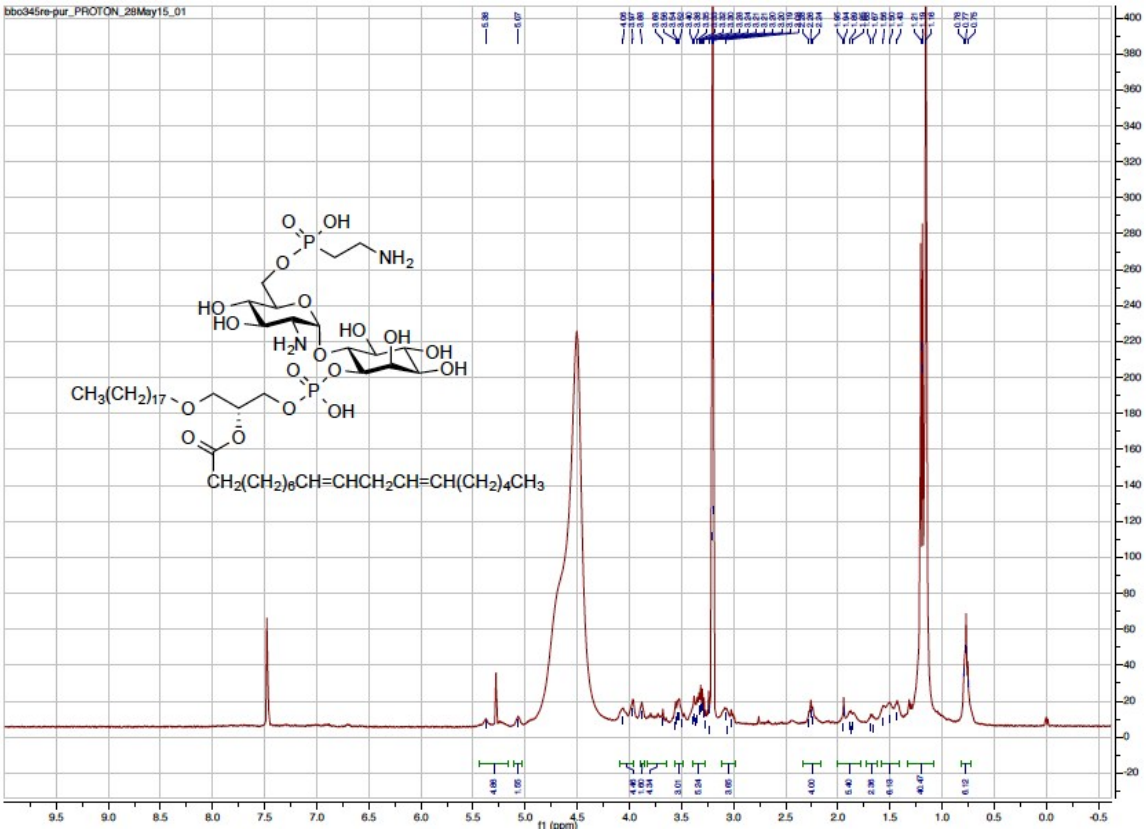


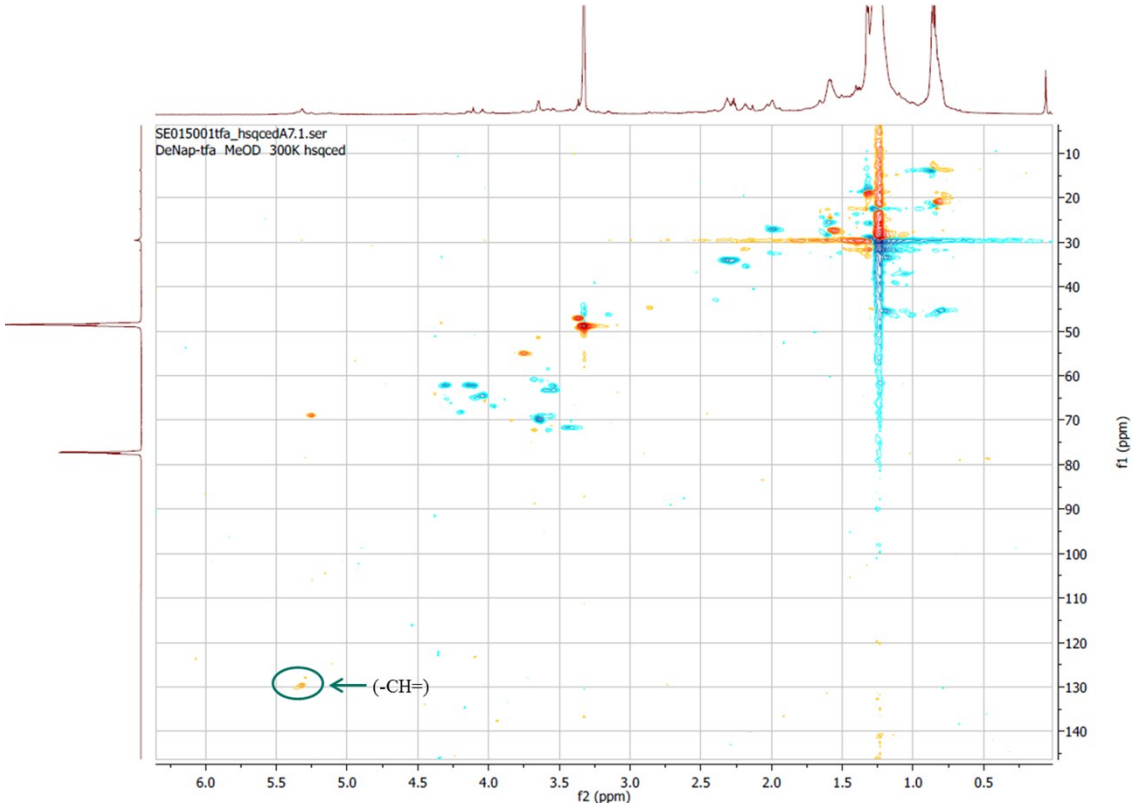

bbo-308_HSQC_01
f2 (ppm)
f1 (ppm)

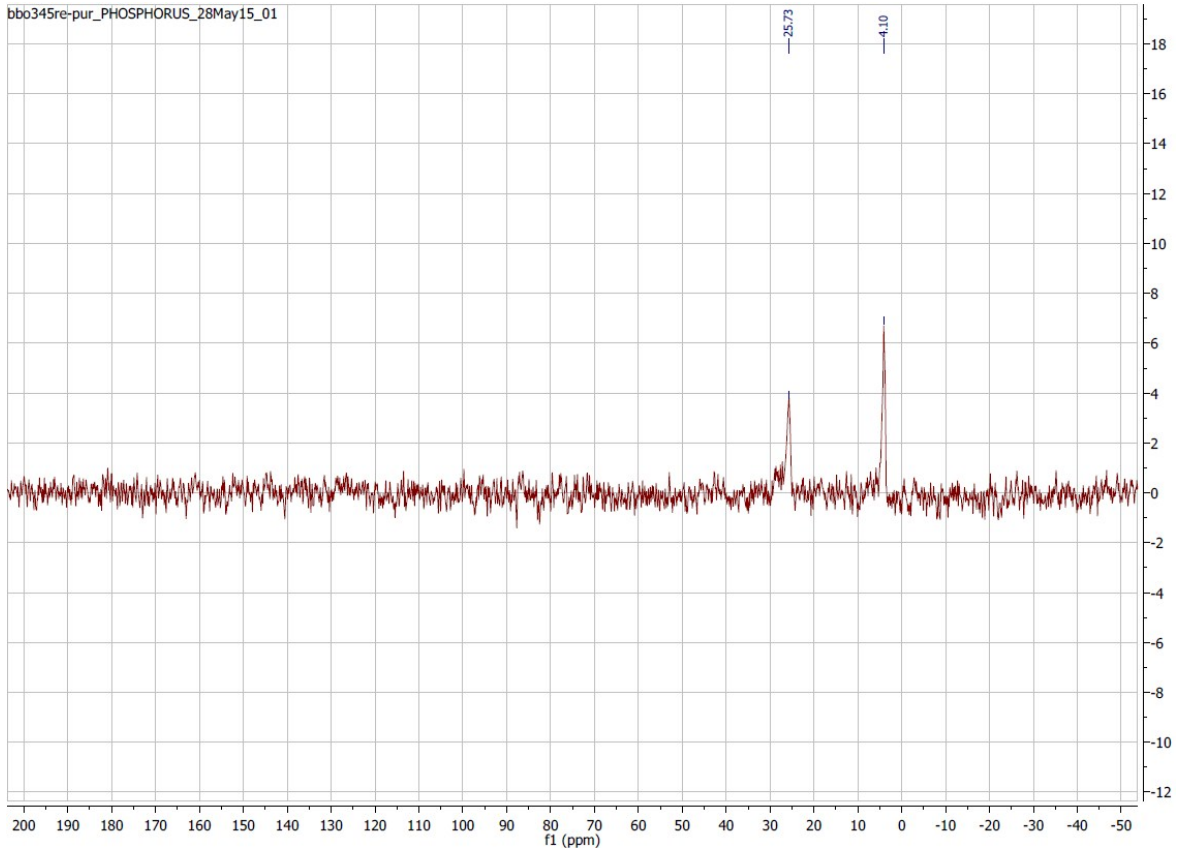
2-Azido-3,4-di-*O*-(2-naphthyl)methyl-6-*O*-((2-azidoethyl)phosphonic acid)-2-deoxy-α-D-glucopyranosyl-(1→6)-1-*O*-[1-*O*-(octadecyl)-2-*O*-(9*Z*,12*Z*-octadecanoyl)-*sn*-glycero-3-phosphocyanoethyl]-2,3,4,5-tetra-*O*-(2-naphthyl)methyl-D-*myo*-inositol (32)



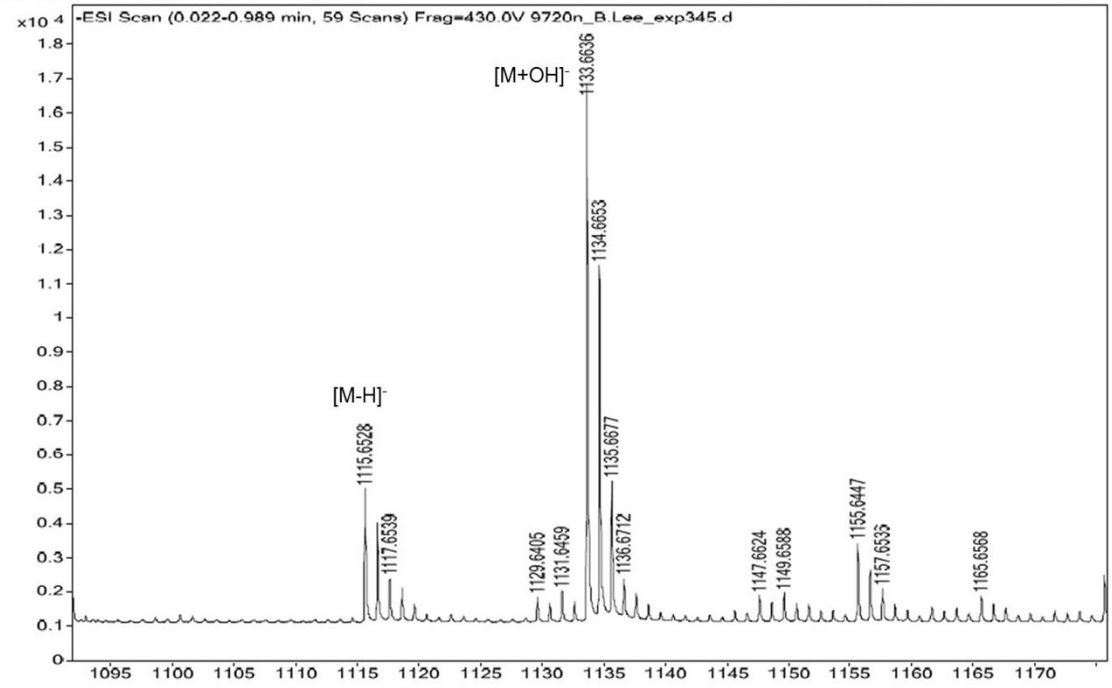
2-Amino-6-*O*-((2-aminoethyl)phosphonic acid)-2-deoxy-α-D-glucopyranosyl-(1→6)-1-*O*-[1-*O*-(octadecyl)-2-*O*-(9Z,12Z-octadecanoyl)-*sn*-glycero-3-phosphate]-D-*myo*-inositol (2)

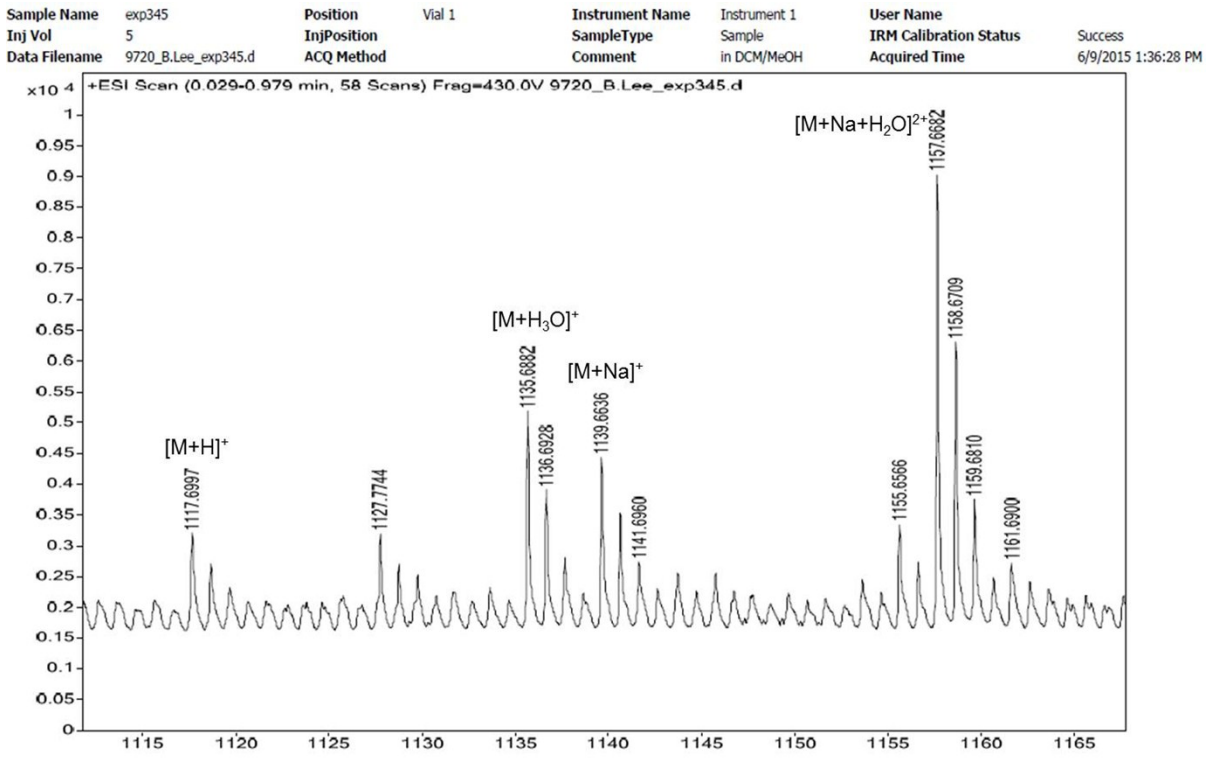


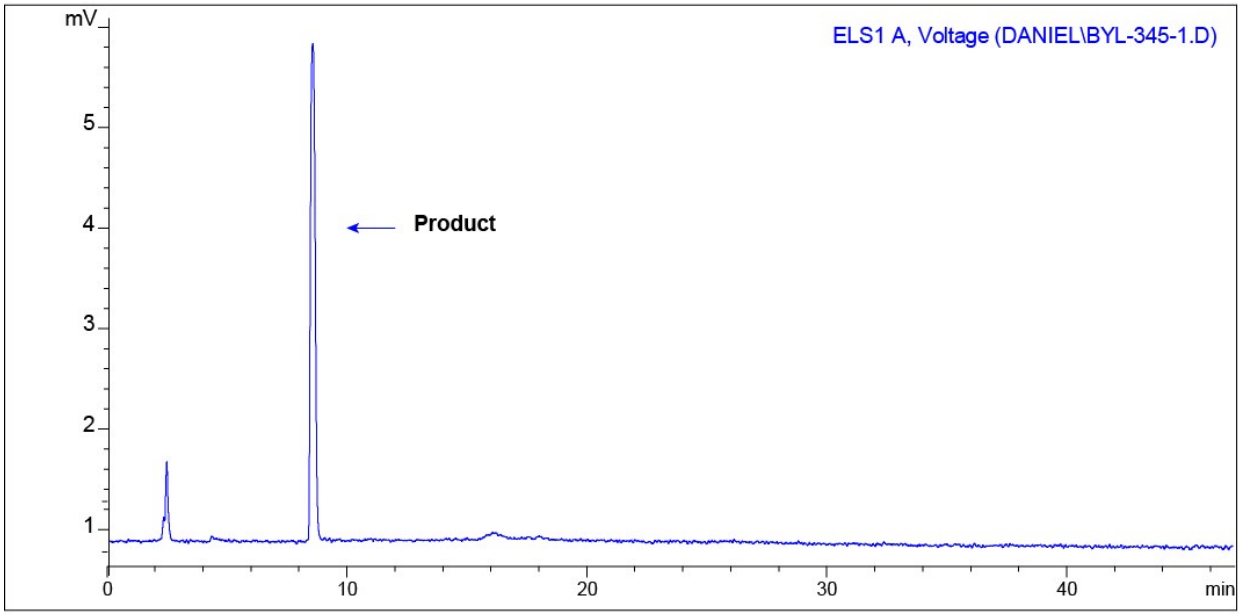




Sample Name	exp345	**Position**	Vial 1	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	5	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	9720n_B.Lee_exp345.d	**ACQ Method**		**Comment**	in DCM/MeOH	**Acquired Time**	6/9/2015 1:52:38 PM

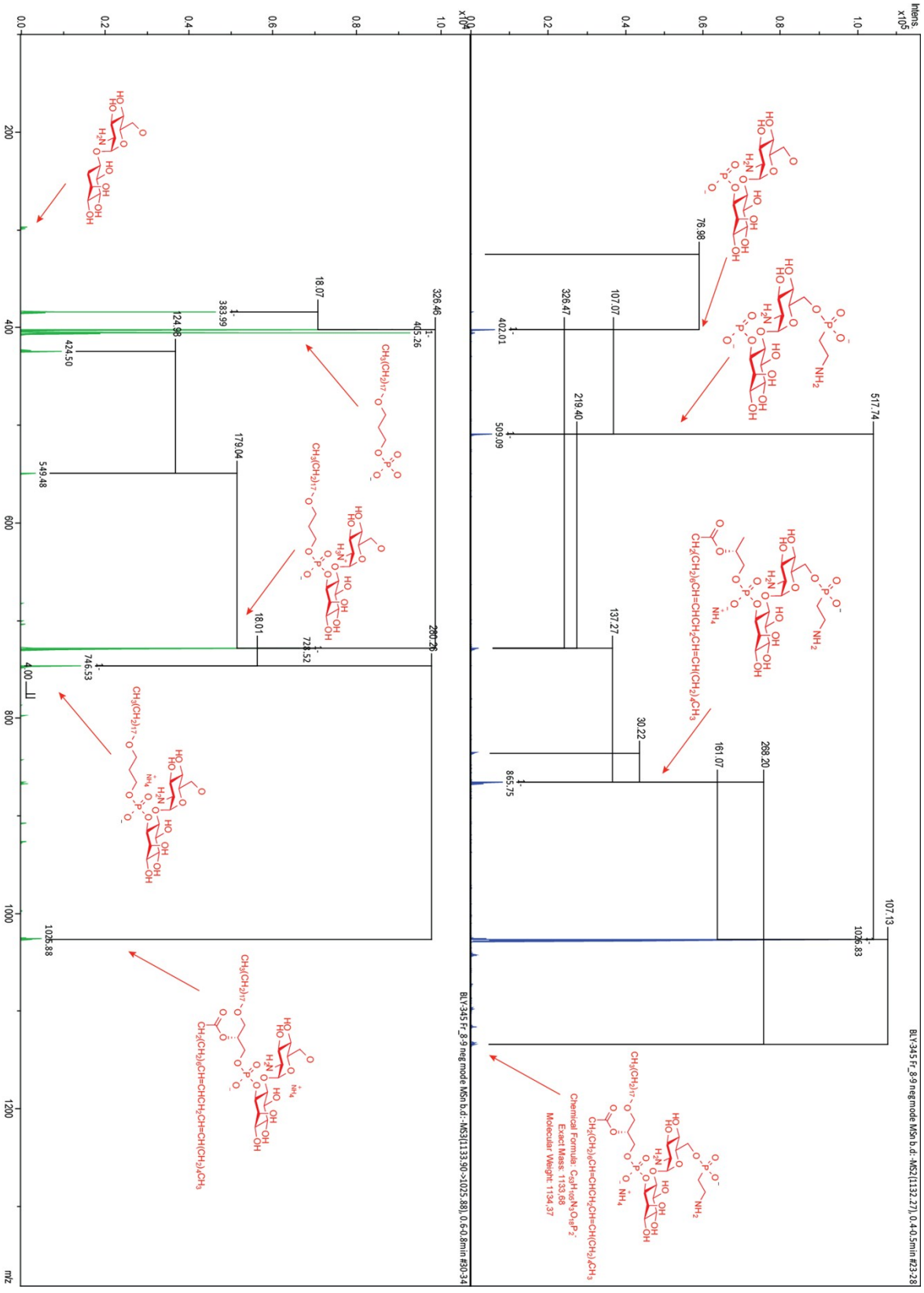


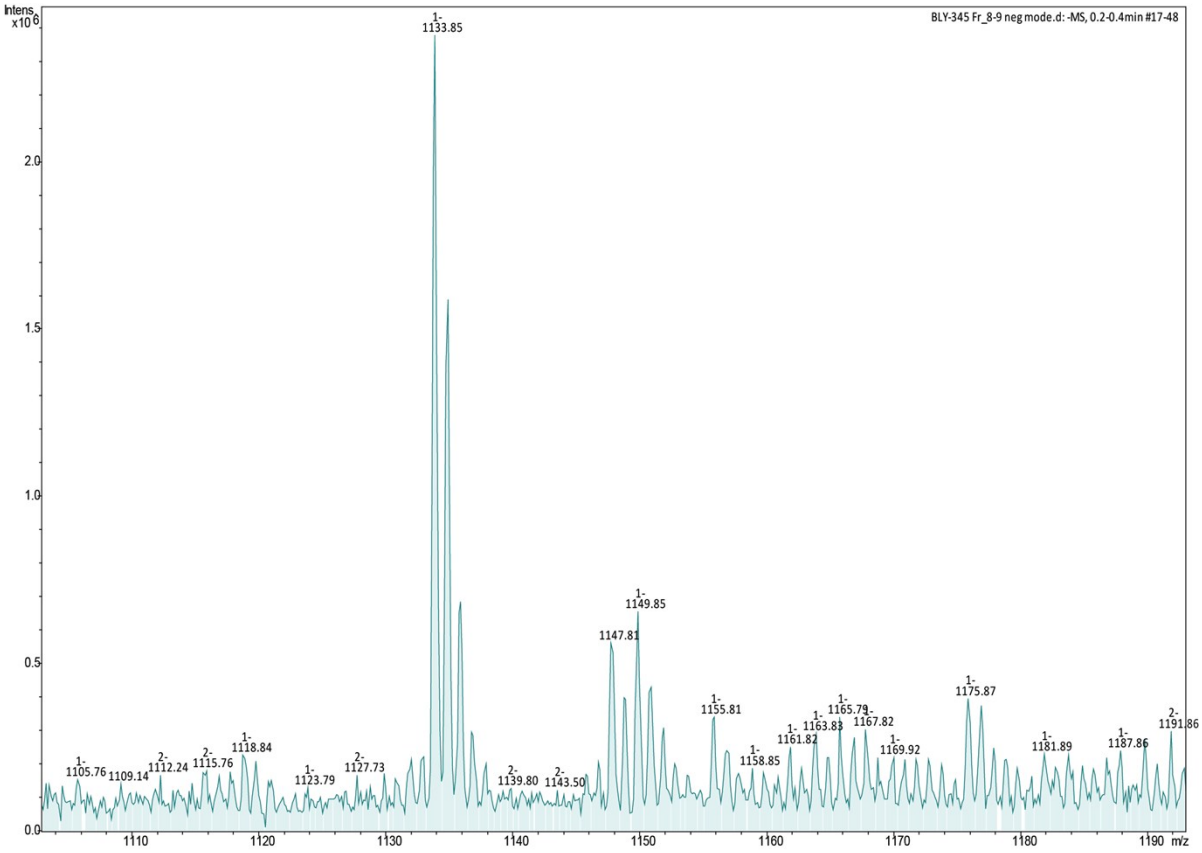




***Normal Phase HPLC analysis of compound* 2.** The analysis was performed on a Agilent 1200 HPLC system using a YMC DIOL column (4,6 x 100 mm), a gradient of ethyl acetate in n-hexane from 10 to 90 % in 30 min, and 1 ml/min flow rate. The detection of the compounds was performed using an ELSD detector.

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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