Dissecting the Influence of Oxazolidinones and Cyclic Carbonates in Sialic Acid Chemistry

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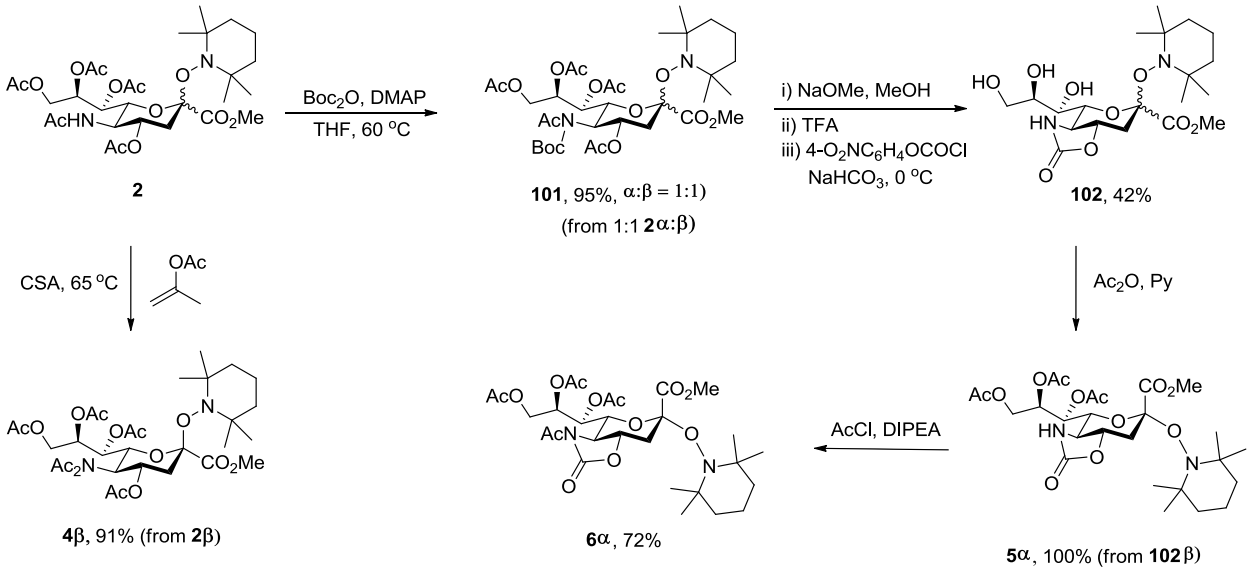
[a] Compounds **2**-**19** are numbered as they appear in the Communication. Compounds **101**-**106** do not appear in the Communication and are numbered as they appear in the Supporting Information.

General Experimental: Unless otherwise stated all NMR spectra were recorded in CDCl3 solution. Specific rotations were recorded in CH_2Cl_2 solution unless otherwise specified. All solvents were dried using standard protocols. All reactions were performed in an atmosphere of dry nitrogen. All organic extracts were dried over sodium sulfate and concentrated under aspirator vacuum. Chromatographic purifications were carried out over silica gel/neutral alumina. Sialyl xanthate **1** was prepared according to a literature procedure.[1] Stereochemical assignments of coupled sialosides are based on $^3JC1\text{-}H3\text{-}ax$ values.

Standard procedure for the equilibration experiments: A solution of the TEMPO sialoside (0.05-0.1 M) in deuterated dichloroethane in an NMR tube was degassed, filled with nitrogen and was heated at 90 ^oC. With periodic monitoring of the reaction mixture using 1H NMR spectroscopy, heating was continued until the reaction reached equilibrium. The solution was then concentrated under reduced pressure and purified by silica gel chromatography eluting with ethyl acetate/hexanes. Compounds **4α**, **101α**, **5β**, **6β** were synthesized using this protocol from corresponding **4β**, **101β**, **5α**, **6α** respectively.

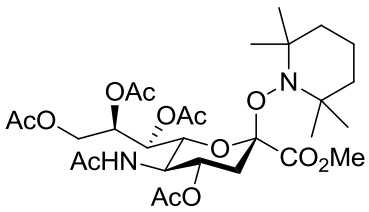


Scheme: Synthesis of TEMPO sialosides

Preparation of TEMPO sialoside (2): A solution of sialyl xanthate **1** (1.20 g, 2.01 mmol, 16:1, α:β) and 20 equivalents of TEMPO (6.29 g, 40.3 mmol) in 50 mL of anhydrous dichloroethane

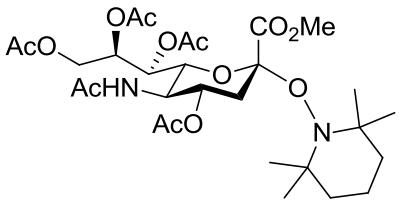
was degassed, purged with nitrogen and photolyzed (254 nm, Rayonnet® photoreactor, Pyrex®) for 3 days. After the completion of the reaction the solution was concentrated and the residue was purified by neutral alumina column chromatography (1:1, ethyl acetate/hexane) to obtain **2** (875 mg, 69 %) as a separable mixture of diastereomers **2α** and **2β** in 1:2 ratio respectively, along with (100 mg, 10%) glycal **3**.

Methyl (1-(1,1,5,5-tetramethylpiperidinyloxy) 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-di deoxy-2-thio-D-glycero-β-D-galacto-non-2-ulopyranoside)onate 2β):



$[\alpha]^{24}_{D}$ = -3.4 (*c* = 1, CH_2Cl_2), 1H NMR (500 MHz, $CDCl_3$) δ: 5.58 (d, *J* = 10.0 Hz, 1H), 5.44 (m, 1H), 5.28 (dt, *J* = 10.5, 4.5 Hz, 1H), 5.19 (d, *J* = 8.5 Hz, 1H), 4.95 (dd, *J* = 12.5, 2.0 Hz, 1H), 4.32 (dd, *J* = 10.5, 2.5 Hz, 1H), 4.13-4.04 (m, 2H), 3.73 (s, 3H), 2.90 (dd, *J* = 12.5, 4.0 Hz, 1H), 2.11 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.87 (s, 3H), 1.80 (t, *J* = 12.5 Hz, 1H), 1.58-1.42 (m, 2H), 1.40-1.22 (m, 4H), 1.19 (s, 3H), 1.16 (s, 3H), 1.15 (s, 3H), 1.11 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.4, 170.9, 170.5, 170.2, 170.1, 165.8 (C-1, $^{3}J_{\text{C-1, H-3ax}}$ = 0 Hz), 103.8, 74.0, 73.0, 69.2, 68.9, 63.0, 61.7, 60.7, 51.7, 49.1, 40.7, 40.4, 38.5, 33.8, 33.6, 23.2, 21.8, 21.3, 21.0, 20.9, 20.7, 16.7. ESIHRMS Calcd. For $C_{29}H_{46}N_2O_{13}Na$ $[M + Na]^+$, 653.2898; found: 653.2888.

Methyl (1-(1,1,5,5-tetramethylpiperidinyloxy) 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-thio-D-glycero-α-D-galacto-non-2-ulopyranoside)onate (2α):



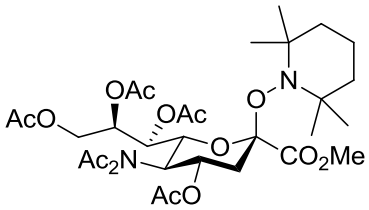
$[\alpha]^{24}_D$ = -7.0 (*c* = 1, CH_2Cl_2), 1H NMR (500 MHz, $CDCl_3$) δ: 5.32 (d, *J* = 10.0 Hz, 1H), 5.25 (br s, 2H), 5.02 (m, 1H), 4.52 (dd, *J* = 11.0, 3.5 Hz, 1H), 4.22 (m, 1H), 3.96 (m, 1H), 3.80 (s, 3H), 3.60 (d, *J* = 11.0 Hz, 1H), 2.55 (d, *J* = 11.0 Hz, 1H), 2.07 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 2.02

(s, 3H), 1.84 (s, 3H), 1.58-1.40 (m, 6H), 1.32 (s, 3H), 1.13 (s, 3H), 1.04 (s, 3H), 1.02 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.0, 170.6, 170.4, 170.1, 169.9, 168.0 (C-1, *t*, $^3J_{C\text{-}1,\ H\text{-}3ax}$ = 4.6 Hz), 103.3, 73.1, 71.1, 70.3, 68.2, 62.1, 60.7, 60.6, 52.6, 49.2, 41.0, 40.3, 33.7, 33.3, 33.2, 23.1, 21.0, 20.9, 20.8, 20.69, 20.66, 20.5, 16.8. ESIHRMS Calcd. For $C_{29}H_{46}N_2O_{13}Na$ $[M + Na]^+$, 653.2898; found: 653.2893.

Preparation of glycal (3): A solution of sialyl xanthate **1α** (100 mg, 0.16 mmol, 16:1, α:β) in 1 mL of anhydrous dichloroethane was degassed, purged with nitrogen, and irradiated with canard-hanovia 450 W medium-pressure mercury vapour lamp for 15 h. The reaction mixture was then concentrated and the residue was purified by silica gel column chromatography (6:4, ethyl acetate/hexane) to obtain pure glycal **3** (55 mg, 66 %) as a colorless oil. The spectral data of the compound is in absolute match with the literature data.[2]

Methyl (1-(1,1,5,5-tetramethylpiperidinyloxy) 5-acetylacetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-thio-D-glycero-β-D-galacto-non-2-ulopyranoside)onate (4β): To a solution of

compound **2β** (96 mg, 0.15 mmol) in isopropenyl acetate (2.8 mL), was added camphorsulfonic acid (35 mg, 0.15 mmol). The reaction mixture was stirred for 5 h at 65 ^oC. The reaction mixture was then quenched with triethylamine, cooled to room temperature and concentrated under reduced pressure. The crude residue was filtered through a short plug of silica gel to obtain pure **4β** (93 mg, 91%) as colorless foam.

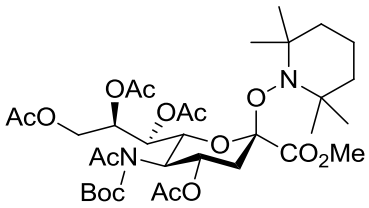


$[\alpha]^{24}_D$ = +9.6 (*c* = 0.6, CH_2Cl_2), 1H NMR (500 MHz, $CDCl_3$) δ: 5.92 (dt, *J* = 11.0, 4.5 Hz, 1H), 5.32-5.26 (m, 2H), 5.15 (td, *J* = 2.0, 8.0 Hz, 1H), 4.83 (dd, *J* = 12.5, 2.0 Hz, 1H), 4.20-4.13 (m, 2H), 3.73 (s, 3H), 3.05 (dd, *J* = 12.5, 4.5 Hz, 1H), 2.38 (s, 3H), 2.31 (s, 3H), 2.12 (s, 3H), 2.01 (s,

3H), 2.00 (s, 3H), 1.97 (s, 3H), 1.69 (t, *J* = 11.5 Hz, 1H), 1.58-1.46 (m, 4H), 1.38-1.31 (m, 2H), 1.25 (s, 3H), 1.22 (s, 3H), 1.15 (s, 3H), 1.11 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 174.3, 173.9, 170.6, 170.5, 170.3, 169.7, 166.0, 103.6, 73.2, 69.4, 69.1, 67.0, 62.6, 61.7, 60.8, 57.0, 51.6, 40.7, 40.5, 39.5, 33.8, 33.6, 27.9, 25.8, 21.4, 21.19, 20.8, 20.7, 16.7. ESIHRMS Calcd. For $C_{31}H_{48}N_2O_{14}Na$ $[M + Na]^+$, 695.3003; found: 695.3005.

Methyl (1-(1,1,5,5-tetramethylpiperidinyloxy) 5-acetamido-5-*N*-(1,1-dimethylethoxy) carbonyl-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-thio-D-glycero-β-D-galacto-non-2-ulopyranoside)onate (101β):

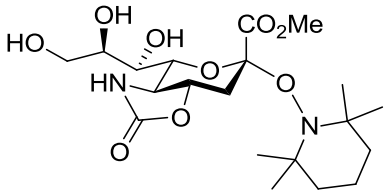
To a solution of compound **2** (600 mg (1:1, α:β), 0.9 mmol) in anhydrous THF (4 mL), were added di-*tert*-butyl dicarbonate (1.960 g, 9 mmol) and DMAP (40 mg, 0.3 mmol) at room temperature. The mixture was stirred for 10 h at 60 ^{o}C under N_2 before it was cooled to room temperature. The reaction mixture was concentrated under reduced pressure and the residue was purified by silica gel chromatography eluting with ethyl acetate/hexane (1:4) to obtain 175 mg of pure **101β** as foam along with 485 mg as a mixture of **101α** and **101β** with a combined 95 % yield.



$[\alpha]^{24}_D$ = +19.5 (*c* = 0.8, CH_2Cl_2), 1H NMR (400 MHz, $CDCl_3$) δ: 5.93 (dt, *J* = 13.5, 6.0 Hz, 1H, minor), 5.71 (dt, *J* = 13.5, 6.4 Hz, 1H, minor), 5.34 (dd, *J* = 10.0, 2.0 Hz, 1H, minor), 5.29 (br s, 1H, both rotamers), 5.20 (m, 1H, both rotamers), 5.06 (dd, *J* = 10.4, 2.0 Hz, 1H, major), 4.93 (m, 1H, both rotamers), 4.80 (t, *J* = 10.4 Hz, 1H, major), 4.35 (t, *J* = 10.4 Hz, 1H, minor), 4.14 (m, 1H, both rotamers), 3.73 (s, 3H, both rotamers), 3.04 (dd, *J* = 12.8, 4.4 Hz, 1H, minor), 2.35 (s, 3H, minor), 2.29 (s, 3H), 2.21 (s, 3H, minor), 2.07 (s, 3H, major), 2.03 (s, 3H, major), 2.01 (s, 3H, minor), 2.00 (s, 3H, both rotamers), 1.96 (s, 3H, minor), 1.95 (s, 3H, major), 1.80 (t, *J* = 12.0 Hz, 1H, major), 1.66 (t, *J* = 12.0 Hz, 1H, minor), 1.57-1.11 (s, 9H, major), 1.55-1.53 (m, 3H, both rotamers), 1.50 (s, 9H, minor), 1.46 (m, 1H, both rotamers), 1.37-1.34 (m, 2H, both rotamers), 1.27-1.11 (m, 12H, both rotamers). ^{13}C NMR (125 MHz, $CDCl_3$, both rotamers) δ:

173.7, 173.3, 170.6, 170.5, 170.4, 170.3, 169.9, 169.7, 166.1, 153.3, 152.09, 152.05, 104.1, 103.7, 84.9, 84.3, 80.9, 73.9, 73.5, 71.8, 69.4, 69.2, 69.1, 67.3, 66.5, 63.0, 62.9, 61.7, 60.7, 60.3, 56.3, 52.6, 51.5, 40.7, 40.5, 39.9, 39.5, 33.8, 33.69, 33.65, 29.6, 28.2, 28.0, 27.9, 27.86, 27.82, 27.76, 27.68, 27.39, 27.34, 27.31, 26.4, 22.0, 21.4, 21.1, 20.9, 20.89, 20.81, 20.77, 20.70, 16.7. ESIHRMS Calcd. For $C_{34}H_{54}N_2O_{15}Na$ $[M + Na]^+$, 753.3396; found: 753.3422.

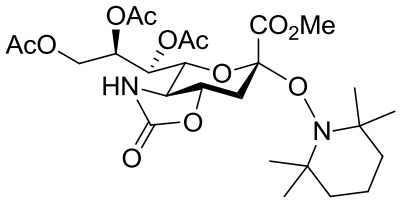
Methyl (1-(1,1,5,5-tetramethylpiperidinyloxy) 5-*N*,4-*O*-carbonyl-3,5-dideoxy-2-thio-D-glycero-α-D-galacto-non-2-ulopyranoside)onate (102*α*): To a solution of a mixture of compounds **101** (290 mg, (2.8:1, α:β), 0.39 mmol) in methanol was added a catalytic amount of sodium methoxide. The solution was stirred for 1 h at room temperature and then quenched with Amberlyst 15 ion-exchange resin. The reaction mixture was filtered through Celite® and concentrated under reduced pressure. The residue was treated with 3 mL of trifluoroacetic acid for 1 h at room temperature and concentrated under reduced pressure. The concentrate and $NaHCO_3$ (230 mg, 2.73 mmol) were taken in a mixture of acetonitrile (1.5 mL) and water (3 mL), cooled to 0 ^oC. To a vigorously stirred solution of the mixture was added 4-nitrophenylchloroformate (195 mg, 0.96 mmol) in acetonitrile (1.5 mL) dropwise and the reaction mixture was stirred continuously for 3 h. The reaction mixture was extracted with EtOAc (20 mL x 3), and the combined extracts were washed with brine and then dried over Na_2SO_4 and concentrated. The residue was purified by silica gel chromatography eluting with EtOAc/MeOH from to 1/0 to 5/1 to give pure **102α** (55 mg, 42 % from **101α** over 3 steps) as colorless foam.



$[\alpha]^{24}_D$ = -36.6 (*c* = 1, CH_2Cl_2), 1H NMR (500 MHz, $CDCl_3$) δ: 6.85 (br s, 1H), 4.05 (m, 1H), 3.90-3.80 (m, 6H), 3.66 (br s, 2H), 3.56 (t, *J* = 9.5, 1H), 2.98 (d, *J* = 9.5, 1H), 2.72 (t, *J* = 12.5, 1H), 1.58-1.36 (m, 5H), 1.28 (m, 1H), 1.24 (s, 3H), 1.11 (s, 6H), 1.06 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 168.4, 160.8, 105.0, 79.1, 76.4, 71.4, 69.5, 62.8, 60.9, 56.7, 53.2, 40.9, 40.5,

33.68, 33.62, 33.49, 33.48, 33.1, 20.88, 20.80, 16.8. ESIHRMS Calcd. For $C_{20}H_{34}N_2O_9Na$ [M + Na]$^+$, 469.6164; found: 469.2162.

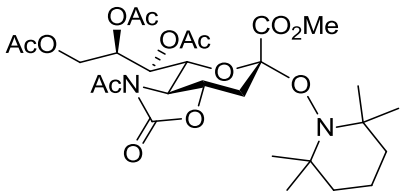
Methyl (1-(1,1,5,5-tetramethylpiperidinyloxy) 7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-2-thio-D-glycero-α-D-galacto-non-2-ulopyranoside)onate (5α): Compound **102α** (55 mg, 0.096 mmol) was treated with 2 mL of pyridine and Ac_2O (1:1) at room temperature overnight, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography eluting with EtOAc/hexane (4:6) to give product **5α** (69 mg, quantitative) as foam.



$[\alpha]^{24}_D$ = -27.5 (*c* = 1, CH_2Cl_2), 1H NMR (500 MHz, $CDCl_3$) δ: 5.41 (m, 1H), 5.28 (s, 1H), 5.07 (dd, *J* = 8.5, 1.0 Hz, 1H), 4.47 (dd, *J* = 13.0, 2.0 Hz, 1H), 4.35 (dd, *J* = 12.5, 4.0 Hz, 1H), 4.11 (m, 1H), 3.81 (dd, *J* = 9.5, 0.5 Hz, 1H), 3.77 (s, 3H), 2.98, (t, *J* = 10.0 Hz, 1H), 2.86 (dd, *J* = 12.5, 4.0 Hz, 1H), 2.79 (t, *J* = 12.5 Hz, 1H), 2.12 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H), 1.55-1.14 (m, 5H), 1.29 (m, 1H), 1.24 (s, 3H), 1.14 (s, 3H), 1.06 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.5, 170.5, 169.5, 167.8 (C-1, $^3J_{C\text{-}1,\ H\text{-}3ax}$ = 6.75 Hz),, 159.6, 104.6, 78.2, 73.4, 69.2, 68.5, 61.4, 61.0, 60.7, 57.3, 52.8, 41.0, 40.4, 33.3, 33.2, 33.0, 20.9, 20.8, 20.7, 20.5, 16.8. ESIHRMS Calcd. For $C_{26}H_{40}N_2O_{12}Na$ [M + Na]$^+$, 595.2479; found: 595.2463.

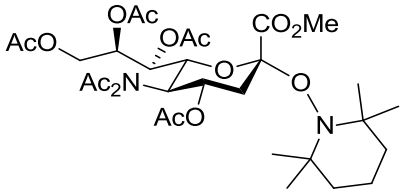
Methyl (1-(1,1,5,5-tetramethylpiperidinyloxy) 5-acetamido-7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-2-thio-D-glycero-α-D-galacto-non-2-ulopyranoside)onate (6α): To a solution of compound **5α** (30 mg, 0.05 mmol) in anhydrous CH_2Cl_2 (0.7 mL), was added EtN(*i*-Pr)$_2$ (0.8 mL, 0.5 mmol), and cooled to 0 ^{o}C, followed by the addition of acetyl chloride (0.03 mL, 0.4 mmol). After completion of the reaction, the resulting solution was poured into saturated $NaHCO_3$ solution. The organic layer was separated and the aqueous layer was extracted twice with CH_2Cl_2 (2 x 5 mL). The combined organic extracts were washed with brine, dried over

Na_2SO_4, concentrated under reduced pressure. The residue was purified by silica gel chromatography eluting with EtOAc/hexane (1:1) to give pure **6α** (23 mg, 71%) as foam.



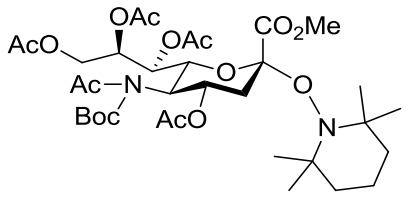
$[\alpha]^{24}_D$ = -10.7 (*c* = 0.7, CH_2Cl_2), 1H NMR (500 MHz, $CDCl_3$) δ: 5.48 (dd, *J* = 4.5, 1.5 Hz, 1H), 5.33 (m, 1H), 4.53 (dd, *J* = 12.0, 3.0 Hz, 1H), 4.17 (dd, *J* = 11.5, 7.0 Hz, 1H), 4.10 (d, *J* = 9.0 Hz, 1H), 3.66 (dd, *J* = 11.0, 9.5 Hz, 1H), 2.89 (dd, *J* = 12.5, 4.0 Hz, 1H), 2.83 (t, *J* = 13.0 Hz, 1H), 2.46 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 1.62-1.42 (m, 6H), 1.35 (s, 3H), 1.15 (s, 3H), 1.07 (s, 3H), 1.06 (s 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 172.3, 170.7, 170.5, 169.7, 167.9 (C-1, $^3J_{\text{C-1, H-3ax}}$ = 6.5 Hz),, 153.9, 103.9, 76.5, 76.3, 73.1, 71.7, 62.6, 60.9, 60.8, 58.5, 53.0, 41.0, 40.4, 33.28, 33.22, 32.1, 29.7, 24.7, 21.1, 20.8, 20.66, 20.62, 16.8. ESIHRMS Calcd. For $C_{28}H_{42}N_2O_{13}Na$ $[M + Na]^+$, 637.2573; found: 637.2585.

Methyl (1-(1,1,5,5-tetramethylpiperidinyloxy) 5-acetylacetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-thio-D-glycero-β-D-galacto-non-2-ulopyranoside)onate (4α):



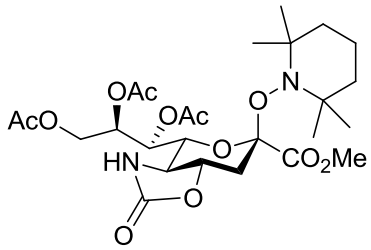
$[\alpha]^{24}_D$ = +12.4 (*c* = 0.25, CH_2Cl_2), 1H NMR (400 MHz, $CDCl_3$) δ: 5.62 (dt, *J* = 11.2, 5.2 Hz, 1H), 5.27 (m, 1H), 5.11 (d, *J* = 5.6 Hz, 1H), 4.66 (d, *J* = 10.0 Hz, 1H), 4.52 (dd, *J* = 12.0, 2.0 Hz, 1H), 4.29 (dd, *J* = 12.0, 6.4 Hz, 1H), 3.95 (t, *J* = 10.4 Hz, 1H), 3.85 (s, 3H), 2.73 (dd, *J* = 13.2, 5.6 Hz, 1H), 2.44 (t, *J* = 12.0 Hz, 1H), 2.34 (s, 3H), 2.27 (s, 3H), 2.11 (s, 3H), 2.09 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H), 1.57-1.44 (m, 6H), 1.32 (s, 3H), 1.16 (s, 3H), 1.07 (s, 6H). ^{13}C NMR δ: 174.3, 173.8, 170.6, 170.09, 170.04, 169.5, 167.6, 103.4, 70.6, 69.8, 67.76, 67.71, 61.7, 60.8, 60.6, 57.4, 52.6, 40.9, 40.3, 35.0, 33.3, 25.7, 20.9, 20.8, 20.77, 20.72, 20.6, 16.9. ESIHRMS Calcd. For $C_{31}H_{48}N_2O_{14}Na$ $[M + Na]^+$, 695.3003; found: 695.3008.

Methyl (1-(1,1,5,5-tetramethylpiperidinyloxy) 5-acetamido-5-*N*-(1,1-dimethylethoxy) carbonyl-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-thio-D-glycero-α-D-galacto-non-2-ulopyranoside)onate (101α):



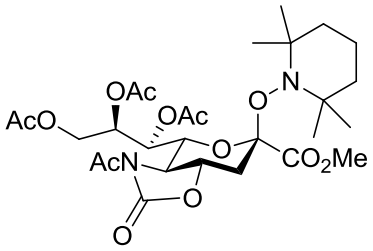
$[\alpha]^{24}_{D}$ = +15.7 (*c* = 0.75, CH_2Cl_2), 1H NMR (400 MHz, $CDCl_3$) δ: 5.49 (dt, *J* = 11.2, 5.2 Hz, 1H), 5.25 (m, 1H), 5.14 (d, *J* = 5.2 Hz, 1H), 4.74 (t, *J* = 10.0 Hz, 1H), 4.63 (dd, *J* = 12.4, 2.8 Hz, 1H), 4.34 (d, *J* = 10.0 Hz, 1H), 4.21 (dd, *J* = 12.4, 7.2 Hz, 1H), 3.80 (s, 3H), 2.68 (dd, *J* = 12.8, 5.2 Hz, 1H), 2.57 (t, *J* = 11.2 Hz, 1H), 2.35 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.96 (s, 3H), 1.55 (s, 9H), 1.35 (s, 3H), 1.15 (s, 3H), 1.05 (s, 3H), 1.03 (s, 3H). ^{13}C NMR δ: 173.9, 170.6, 170.0, 169.9, 168.2, 151.7, 103.4, 84.7, 71.8, 71.2, 67.69, 67.65, 61.8, 60.7, 60.6, 52.5, 52.3, 41.0, 40.3, 34.7, 33.3, 27.9, 27.88, 27.80, 26.7, 21.0, 20.79, 27.73, 20.5, 16.9. ESIHRMS Calcd. For $C_{34}H_{54}N_2O_{15}Na$ $[M + Na]^+$, 753.3396; found: 753.3392.

Methyl (1-(1,1,5,5-tetramethylpiperidinyloxy) 7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-2-thio-D-glycero-β-D-galacto-non-2-ulopyranoside)onate (5β):



$[\alpha]^{24}_{D}$ = -15.0 (*c* = 0.5, CH_2Cl_2), 1H NMR (400 MHz, CDCl3) δ: 5.43 (s, 1H), 5.25 (m, 1H), 5.20 (t, *J* = 4.0 Hz, 1H), 4.67 (dd, *J* = 12.0, 2.0 Hz, 1H), 4.55 (m, 1H), 4.29 (dd, *J* = 9.6, 3.6 Hz, 1H), 4.23 (dd, *J* = 12.8, 6.8 Hz, 1H), 3.75 (s, 3H), 3.16 (t, *J* = 10.5 Hz, 1H), 3.17-3.09 (m, 2H), 2.15 (s, 1H), 2.08 (s, 3H), 2.05-2.02 (m, 4H), 1.54-1.47 (m,2H), 1.40-1.33 (m, 2H), 1.29-1.21 (m, 1H), 1.18 (s, 3H), 1.12 (s, 6H), 1.10 (s, 3H). ^{13}C NMR δ: 170.8, 170.4, 170.3, 165.5, 159.5, 104.5, 76.6, 72.8, 71.2, 71.0, 61.9, 61.7, 60.8, 58.7, 51.8, 40.7, 40.5, 38.6, 34.0, 33.5, 21.6, 21.0, 21.0, 20.6, 16.6. ESIHRMS Calcd. For $C_{26}H_{40}N_2O_{12}Na$ $[M + Na]^+$, 595.2479; found: 595.2473.

Methyl (1-(1,1,5,5-tetramethylpiperidinyloxy) 5-acetamido-7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-2-thio-D-glycero-β-D-galacto-non-2-ulopyranoside)onate (6β):

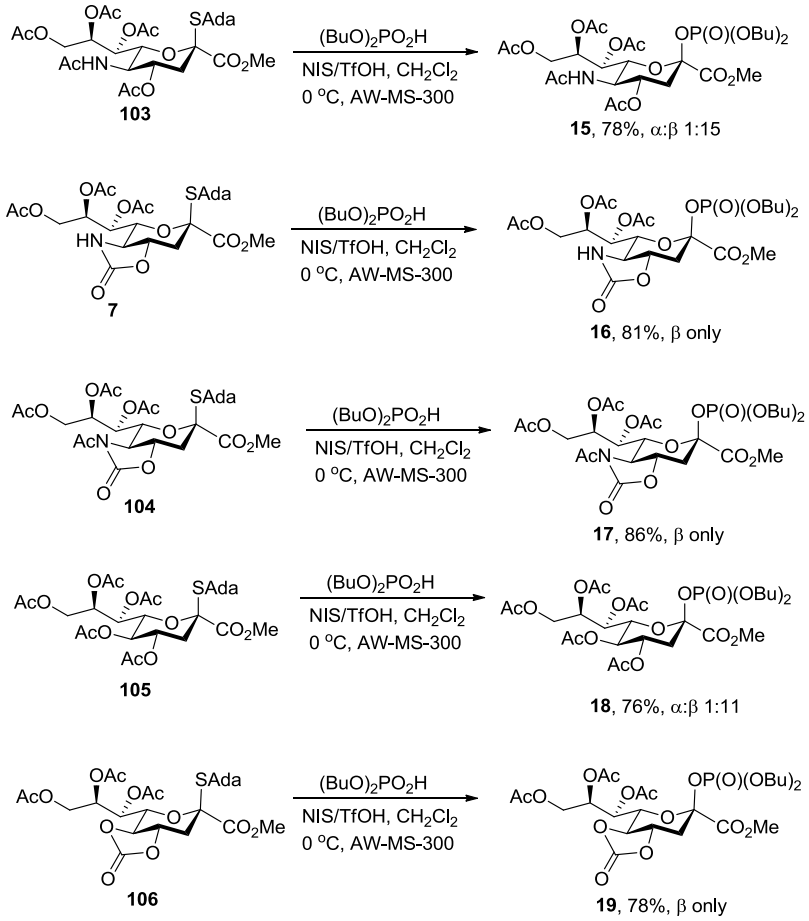


$[\alpha]^{24}_{D}$ = +14.8 (*c* = 0.5, CH_2Cl_2), 1H NMR (500 MHz, $CDCl_3$) δ: 5.76 (m, 1H), 5.36 (m, 1H), 4.64 (d, *J* = 12.5 Hz, 1H), 4.55 (dd, *J* = 10.0, 3.0 Hz, 1H), 4.06 (dd, *J* = 12.0, 8.0 Hz, 1H), 3.78 (s, 3H), 3.71 (t, *J* = 10.5 Hz, 1H), 3.30 (d, *J* = 8.5 Hz, 1H), 2.50 (s, 3H), 2.17 (t, *J* = 12.5 Hz, 1H), 2.11 (s, 3H), 2.09 (s, 3H), 2.03 (s, 3H), 1.55-1.24 (m, 6H), 1.15-1.06 (m, 12H). ^{13}C NMR δ: 172.4, 170.7, 170.5, 169.6, 166.1, 153.9, 103.8, 75.2, 74.4, 73.0, 71.7, 63.0, 61.3, 60.9, 60.4, 59.2, 52.0, 40.6, 40.5, 33.8, 33.5, 24.7, 21.4, 21.3, 21.1, 20.8, 20.7, 16.7. ESIHRMS Calcd. For $C_{28}H_{42}N_2O_{13}Na$ $[M + Na]^+$, 637.2573; found: 637.2575.

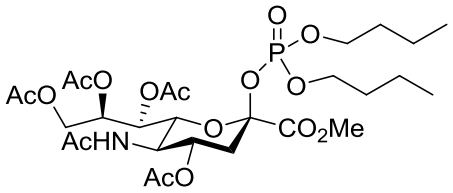
Procedure for radical allylation reaction: To a solution of 5-*N*,4-*O*-oxazolidinone protected adamantyl thiosialoside[3] **7** (25 mg, 0.04 mmol) in 0.75 mL of toluene, was added allyltributyltin (100 µL, 0.32 mmol) followed by a catalytic amount of $(Bu_3Sn)_2$. The solution was degassed, purged with nitrogen and subjected to photolysis (254 nm, Rayonnet® photoreactor, Pyrex®) for 2 days. The reaction mixture was then concentrated and the residue was partitioned between acetonitrile and hexane. The acetonitrile layer was separated and further washed with hexane (2 x 5 mL) and concentrated. The crude residue was dissolved in 0.5 mL of dichloromethane and added acetyl chloride (15 µL, 0.2 mmol) followed by diisopropylethylamine (52 µL, 0.28 mmol) at 0 ^{o}C under nitrogen atmosphere. After warming to room temperature, the reaction mixtue was poured into saturated $NaHCO_3$ solution (2 mL) and was extracted with dichloromethane (2 X 5 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using EtOAc/hexanes (2:3) as eluents to obtain the desired allylated products **8** (6.5 mg, 33% over two steps) as a 1:1 mixture of anomers. The spectral data of both the isomers was in absolute match with the data reported by our group recently.[4]

General protocol for sialophosphate synthesis:

The thiosialoside, dibutyl phosphate (3 eq), pulverized acid washed-300 molecular sieves in dry CH_2Cl_2 were stirred under an argon atmosphere overnight at room temperature. The mixture was cooled to 0 ^{0}C, and NIS (1.05 eq), and triflic acid (0.09 eq) in Et_2O were added. The mixture was stirred for 15 min and was quenched by addition of Hunig's base. The molecular sieves were filtered off and reaction mixture was washed with sat. sodium thiosulfate and brine. The organic layer was dried over sodium sulfate and concentrated under reduced pressure to give crude reaction mixtures which were purified by chromatography over silica gel using the eluents indicated.

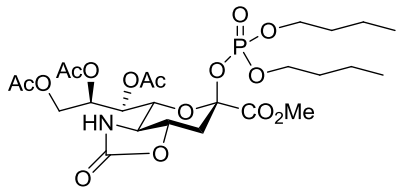


Methyl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-2-(dibutylphosphoryl)-3,5-dideoxy-D-glycero-β-D-galacto-non-2-ulopyranoside)onate (15): This compound was synthesized using the general procedure from thiosialoside **103**[3] (100 mg, 0.156 mmol), dibutyl phosphate (92 uL, 0.463 mmol), AW-MS300 (300 mg), NIS (36 mg, 0.163 mmol) and TfOH (1.2 uL, 0.014 mmol, in 50 uL of Et_2O) in DCM (3 mL). The reaction was complete in 15 min and was quenched with Hunig's base (100 uL). Purification on silica gel using acetone/toluene (1:5) gave phosphate **15** (78 mg, 73%).



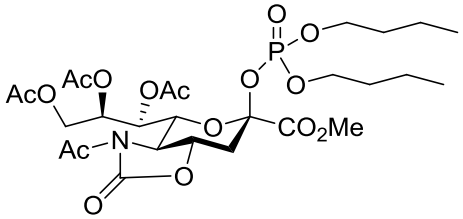
$[\alpha]^{23}{}_{D}$ = - 31 (*c* = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.44-5.42 (m , 1H), 5.37 (d, *J* = 10 Hz, 1H), 5.32-5.24 (m, 2H), 4.57 (dd, *J* = 12, 2.8 Hz, 1H), 4.38 (dd, *J* = 10.4, 2.8, 1H), 4.24 (d. *J* = 8Hz, 1H), 4.20 (t, *J* = 10 Hz, 1H), 4.15-4.01(m, 5 H), 3.83 (s, 3H), 2.63 (dd, *J* = 13.2, 4.8 Hz, 1H), 2.13 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.88 (s, 3H), 1.69-1.60 (m, 4H), 1.45-1.35 (m, 4H), 0.94 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 170.5, 170.4, 170.2, 170.1, 165.9 (C-1, $^3J_{C\text{-}H}$ = 0 Hz), 99.5, 99.4, 73.4, 71.7, 68.4, 68.3, 68.3, 68.3, 68.1, 68.0, 62.4, 53.2, 48.5, 37.3, 37.2, 32.1, 32.1, 32.1, 32.0, 23.1, 20.9, 20.8, 20.8, 20.7, 18.6, 18.6, 13.5. ESIHRMS: *m/z* calcd. for $C_{28}H_{46}NO_{16}PNa$ $(M + Na)^+$ 706.2452, found 706.2454

Methyl (7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-2-(dibutylphosphoryl)-3,5-dideoxy-D-glycero-β-D-galacto-non-2-ulopyranoside)onate (16): This compound was synthesized using the general procedure from thiosialoside **7**[3] (100 mg, 0.171 mmol), dibutyl phosphate (101 uL, 0.514 mmol) AW-MS300 (300 mg), NIS (46 mg, 0.205 mmol) and TfOH (1.3 uL, 0.015 mmol, 0.09 eq in 50 uL of Et_2O) in CH_2Cl_2 (2 mL). The reaction was complete in 15 min and was quenched with Hunig's base (100 uL). Purification by silica gel chromatography using toluene/ EtOAc (3:1) gave the phosphate **16** (86 mg, 81%).



$[\alpha]^{23}$ D = +14 (c = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.36 (brs, 1H), 5.29 (m, 1H), 5.17 (dd, *J* = 8, 2 Hz, 1H), 4.55 (ddd, *J* = 12, 4 Hz, 1H), 4.48 (t, *J* = 2 Hz, 1H), 4.45 (d, *J* = 2 Hz, 1H), 4.35 (dd, *J* = 12.8, 6.4 Hz, 1H), 4.11-4.02 (m, 4H), 3.83 (s, 3H), 3.10 (t, *J* = 11.2 Hz, 1H), 2.82 (dd, *J* = 12.8,4 Hz, 1H), 2.21 (dt, *J* = 12.8, 3.2 Hz, 1H), 2.18 (s, 3H), 2.09 (s, 3H), 2.03 (s, 3H), 1.63 (m, 4H), 1.38 (m,4H), 0.94 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 170.5, 170.0, 165.7 (C-1, $^3J_{C\text{-}H}$ = 0 Hz), 158.9, 99.7, 99.6, 75.6, 74.2, 69.6, 69.0, 68.4, 68.4, 68.4, 68.3, 61.6, 57.7, 53.3, 37.2, 37.1, 32.1, 32.1, 32.0, 20.9, 20.7, 20.6, 18.6, 18.5, 13.5 ESIHRMS: m/z calcd. for $C_{25}H_{40}NO_{15}PNa$ (M + Na)+ 648.2033, found 648.2042.

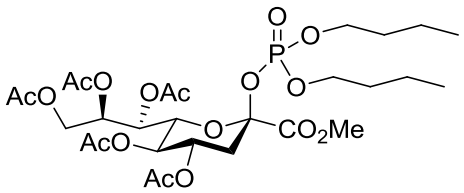
Methyl (5-acetamido-7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-2-(dibutylphosphoryl)-3,5-dideoxy-D-glycero-β-D-galacto-non-2-ulopyranoside)onate (17): This compound was synthesized using the general procedure from thiosialoside **104**[3] (60 mg, 0.096 mmol), dibutyl phosphate (56 uL, 0.28 mmol) AW-MS300 (180 mg), NIS (23 mg, 0.105 mmol) and TfOH (0.7 uL, 0.008 mmol, 0.09 eq in 50 uL of Et_2O) in DCM (2 mL). The reaction was complete in 15 min and was quenched with Hunig's base (50 uL). Purification by silica gel chromatography using EtOAc/Hexanes (1:1) gave the phosphate **17** (55 mg, 86%).



$[\alpha]^{23}{}_D$ = + 43 (*c* = 1, $CHCl_3$).^{1}H NMR (400 MHz, $CDCl_3$): δ 5.52 (q, *J* = 2 Hz, 1H), 5.25 (m, 1H), 4.72 (dd, *J* = 9.6, 2 Hz, 1H), 4.58 (m, 2H), 4.15-4.01 (m, 5H), 3.85 (s, 3H), 3.76 (dd, *J* = 11.2, 9.2 Hz, 1H), 2.89 (dd, *J* = 12.8, 3.2 Hz, 1H), 2.50 (s, 3H), 2.30 (dt, *J* = 12.8, 3.2 Hz, 1H), 2.12 (s, 3H), 2.10 (s, 3H), 2.03 (s, 3H), 1.65 (sext, *J* = 7.2 Hz, 4H), 1.44-1.35 (sext, *J* = 7.2 Hz, 4H), 0.94 (dt, *J* = 7.2, 2.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.1, 170.6, 170.5, 169.7, 165.5 (C-1, $^3J_{C\text{-}H}$ =

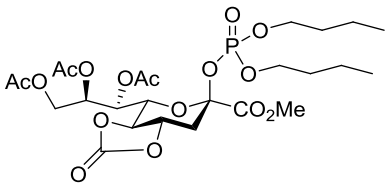
0 Hz) 153.4, 98.8, 98.7, 76.6, 74.0, 72.5, 71.7, 68.5, 68.4, 68.3, 68.3, 62.8, 58.8, 53.4, 36.0, 36.0, 32.1, 32.0, 32.0, 24.6, 20.9, 20.7, 20.7, 18.5, 18.5, 13.5. ESIHRMS: *m/z* calcd. for $C_{27}H_{42}NO_{16}PNa$ $(M + Na)^+$ 690.2139, found 690.2104.

Methyl (4,5,7,8,9-penta-*O*-acetyl-2-(dibutylphosphoryl)-3-deoxy-D-glycero-β-D-galacto-non-2-ulopyranoside)onate (18): This compound was synthesized using the general procedure from thiosialoside **105**[5] (100 mg, 0.155 mmol), dibutyl phosphate (92 uL, 0.467 mmol) AW-MS300 (300 mg), NIS (36 mg, 0.163 mmol) and TfOH (1.2 uL, 0.014 mmol in 50 uL Et_2O) in DCM (3 mL). The reaction was complete in 15 min and was quenched with Hunig's base (100 uL). Purification on silicagel using toluene/EtOAc (1:1) gave phosphate **18** (77mg, 72%).



$[\alpha]^{23}{}_D$ = +63 (*c* = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.43 (dd, *J* = 5.2, 2 Hz, 1H), 5.34 (dt, *J* = 11.2, 4.8 Hz, 1H), 5.29-5.26 (m, 1H), 4.95 (t, *J* = 10 Hz, 1H), 4.51 (dd, *J* = 13.2, 2 Hz, 1H), 4.45 (dd, *J* = 11.2, 2 Hz, 1H), 4.26-4.05 (m, 4H), 3.83 (s, 3H), 2.74 (dd, *J* = 13.2, 6.2 Hz, 1H), 2.10 (s, 3H), 2.07 (s, 4H), 2.02 (s, 3H), 2.02 (s, 4H), 2.0 (s, 3H), 1.71-1.63 (m, 4H), 1.44-1.37 (m, 4H), 0.97 (dt, *J* = 7.2, 3.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 170.0, 170.0, 169.8, 169.8, 165.8 (C-1, $^3J_{C\text{-}H}$ = 0 Hz), 99.2, 99.1, 77.2, 71.6, 70.5, 68.5, 68.4, 68.3, 68.3, 68.2, 67.2, 67.2, 62.2, 53.2, 36.8, 36.7, 3.1, 32.0, 20.8, 20.8, 20.7, 20.7, 20.7, 20.6, 20.6, 18.6, 13.5. ESIHRMS: *m/z* calcd. for $C_{28}H_{45}NO_{17}PNa$ $(M + Na)^+$ 707.2292, found 707.2278.

Methyl (7,8,9-tri-*O*-acetyl-4,5-*O*-carbonyl-2-(dibutylphosphoryl)-3-deoxy-D-glycero-β-D-galacto-non-2-ulopyranoside)onate (19): This compound was synthesized using the general procedure from thiosialoside **106**[5] (58 mg, 0.09 mmol), dibutyl phosphate (59 uL, 0.29 mmol) AW-MS300 (180 mg), NIS (23 mg, 0.1 mmol) and TfOH (0.7 uL, 0.009 mmol in 50 uL Et_2O) in DCM (2 mL). The reaction was complete in 15 min and was quenched with Hunig's base (50 uL). Purification on silicagel using EtOAc/Hexanes (1:1) gave phosphate **19** (48 mg, 78%).



$[\alpha]^{23}_{D}$ = -13 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.47 (dd, *J* = 4.4, 2.8 Hz, 1H), 5.29 (dt, *J* = 4.4, 2.0 Hz, 1H), 4.70-4.65 (m, 2H), 4.40 (dd, *J* = 10, 2.5 Hz, 1H), 4.28 (dd, *J* = 10, 4.8 Hz, 1H), 4.12-4.05 (m, 5H), 3.85 (s, 3H), 2.91 (dd, *J* = 10, 3.2 Hz, 1H), 2.30 (dt, *J* = 10, 2.4 Hz, 1H), 2.14 (s, 3H), 2.09 (s, 3H), 2.04 (s, 3H), 1.70-1.61 (m, 4H), 1.44-1.35 (m, 4H), 0.94 (t, *J* = 6 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.5, 170.1, 169.1, 165.3(C-1, $^3J_{C\text{-}H}$ = 0 Hz), 152.8, 99.07, 99.03, 76.9, 76.5, 73.3, 69.5, 68.59, 68.57, 68.54, 68.4, 61.6, 53.6, 37.48, 37.42, 32.1, 32.09, 32.07, 32.04, 29.6, 20.9, 20.7, 20.5, 18.5, 13.5 ESIHRMS: m/z calcd. for $C_{25}H_{39}NO_{16}PNa$ (M + Na)+ 649.1873, found 649.1859.

In-source fragmentation study of sialophosphates:

The mass spectrometric study was carried out using a Waters LCT Permiere Xe TOF mass spectrometer. The spectra were recorded in positive ion mode with a source temperature of 120 ^{o}C using a desolvation gas flow of 800 L/h. The samples were injected as methanolic solutions (~10 nM). The in-source fragmentation study of the sialophosphates was carried by increasing cone voltages starting from 40V with an incremental change in cone voltage till the onset of fragmentation was observed. For each compound studied 3 mass spectra are reported here. The first spectrum is recorded at a cone voltage of 40V, the second spectrum at the specified cone voltage at which the fragmentation starts and a third spectrum at a cone voltage higher than the fragmentation onset voltage. All peaks indicated on the spectra are for sodiated ions unless otherwise noted.

References:

1. Martichonok, V; Whitesides, G. M. *J. Org. Chem.* **1996**, *61*, 1702-1706.
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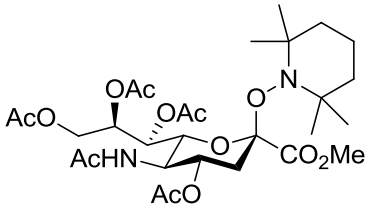
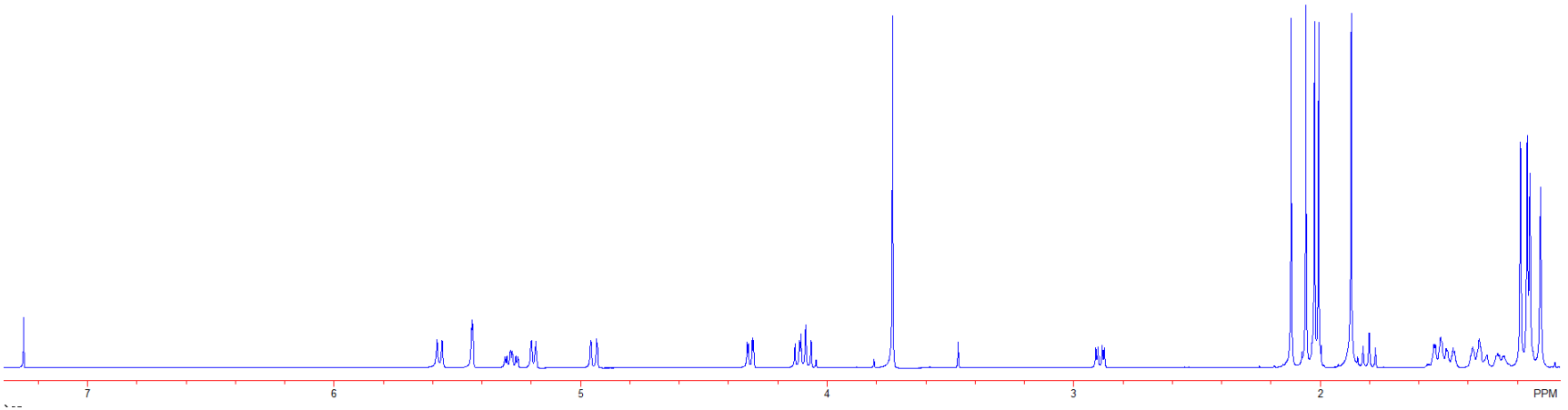
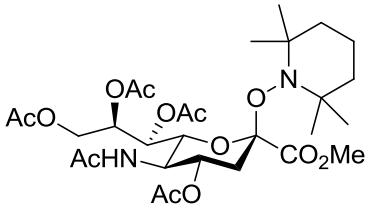
3. Crich, D.; Li, W. *J. Org. Chem.* **2007**, *72*, 7794-7797.
4. Noel, A.; Delpech, B; Crich, D. *Org. Lett.* **2012**, *14*, 1342-1345.
5. Crich, D.; Navuluri, C. *Angew. Chem. Int. Ed.* **2010**, *49*, 3049-3052.

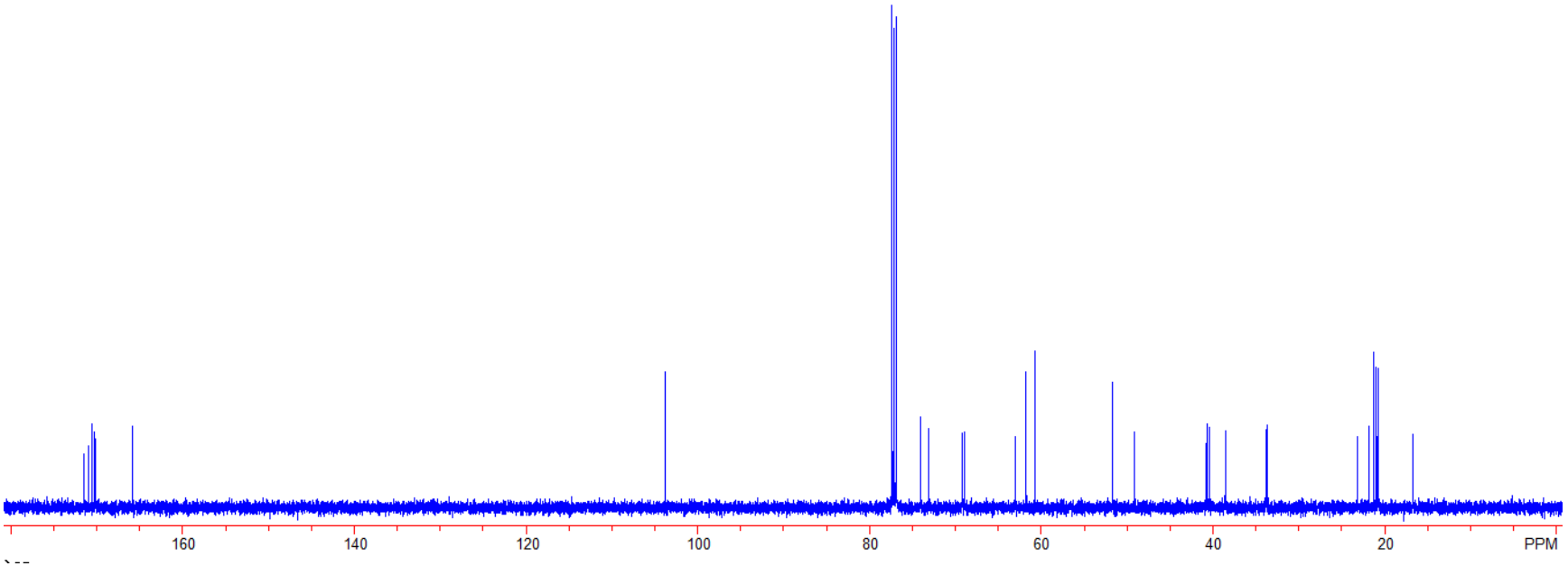
Methyl (1-(1,1,5,5-tetramethylpiperidinyloxy) 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-thio-D-glycero-β-D-galacto-non-2-ulopyranoside)onate ($CDCl_3$, 500 MHz) (2β):



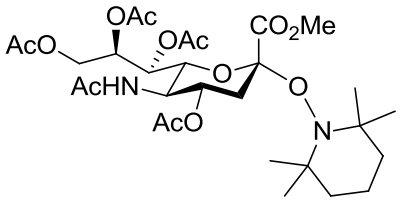


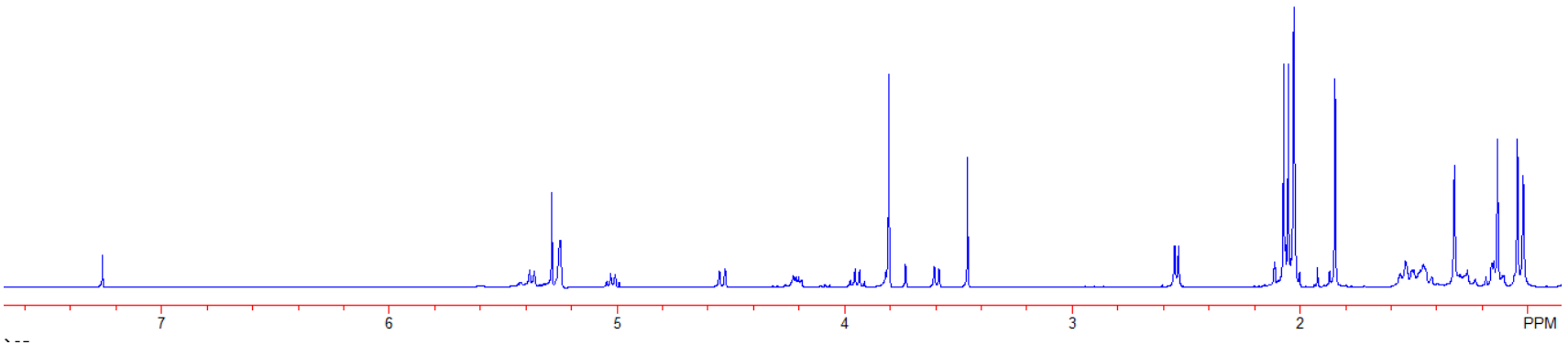
Methyl (1-(1,1,5,5-tetramethylpiperidinyloxy) 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-thio-D-glycero-β-D-galacto-non-2-ulopyranoside)onate ($CDCl_3$, 500 MHz) (2β):



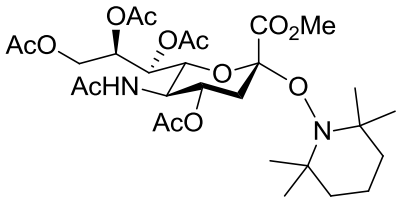


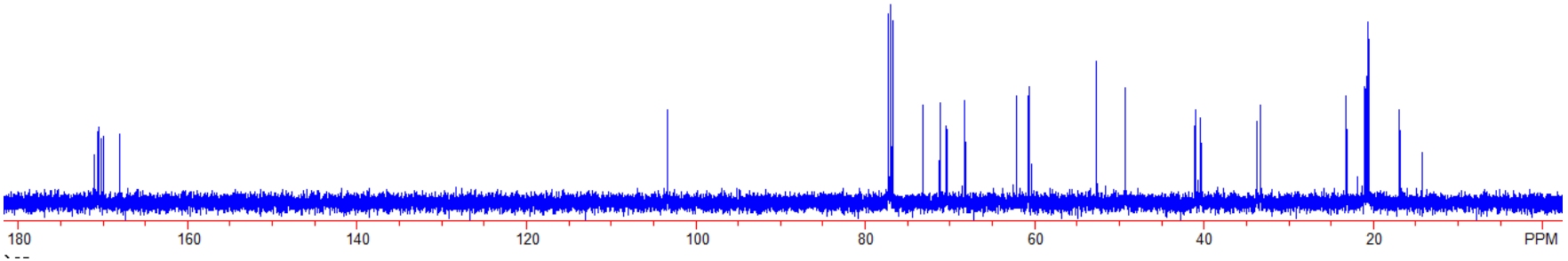
Methyl (1-(1,1,5,5-tetramethylpiperidinyloxy) 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-thio-D-glycero-α-D-galacto-non-2-ulopyranoside)onate ($CDCl_3$, 500 MHz) (2α):



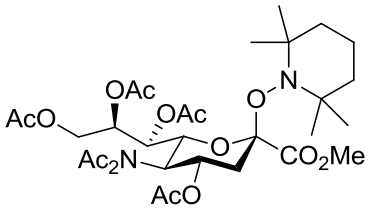


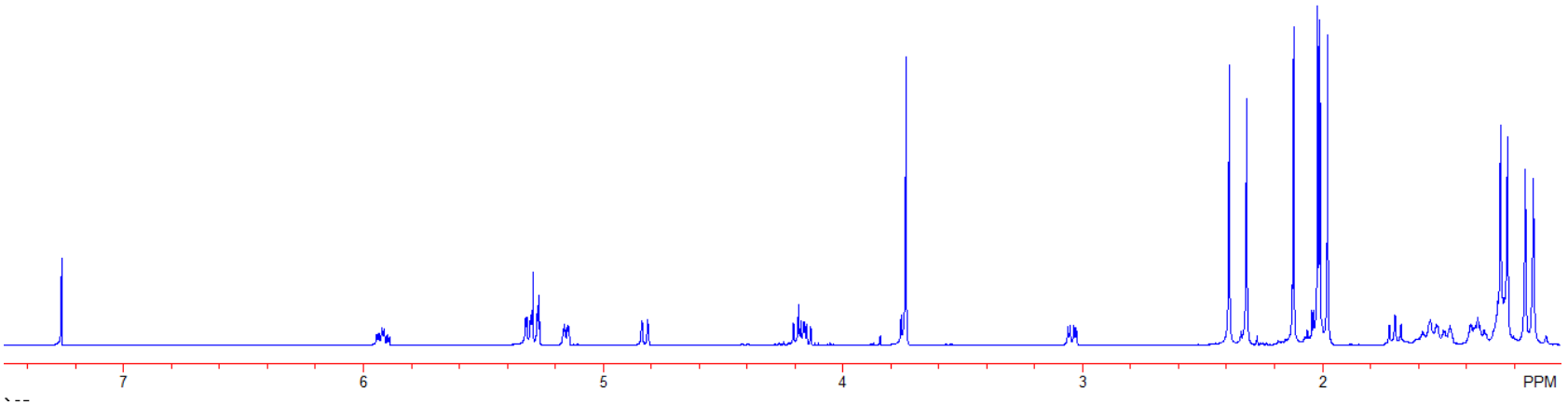
Methyl (1-(1,1,5,5-tetramethylpiperidinyloxy) 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-thio-D-glycero-α-D-galacto-non-2-ulopyranoside)onate ($CDCl_3$, 500 MHz) (2α):



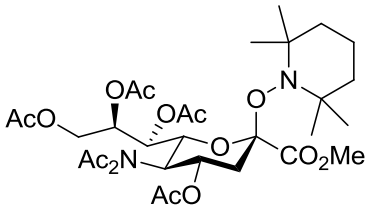


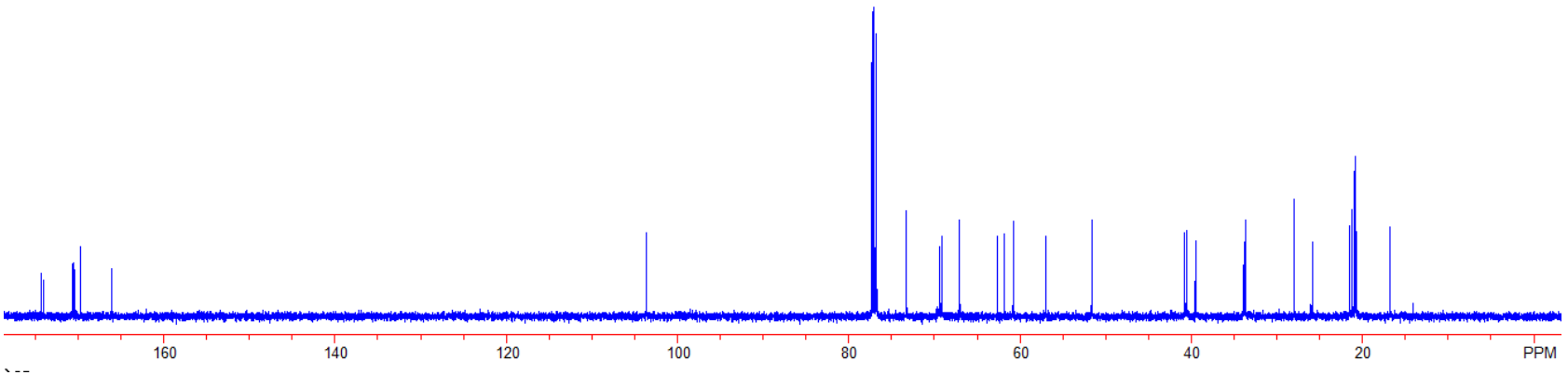
Methyl (1-(1,1,5,5-tetramethylpiperidinyloxy) 5-acetylacetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-thio-D-glycero-β-D-galacto-non-2-ulopyranoside)onate ($CDCl_3$, 500 MHz) (4β):



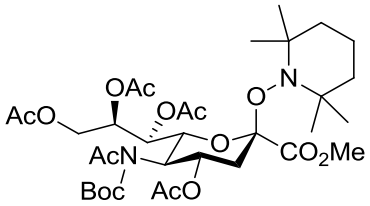


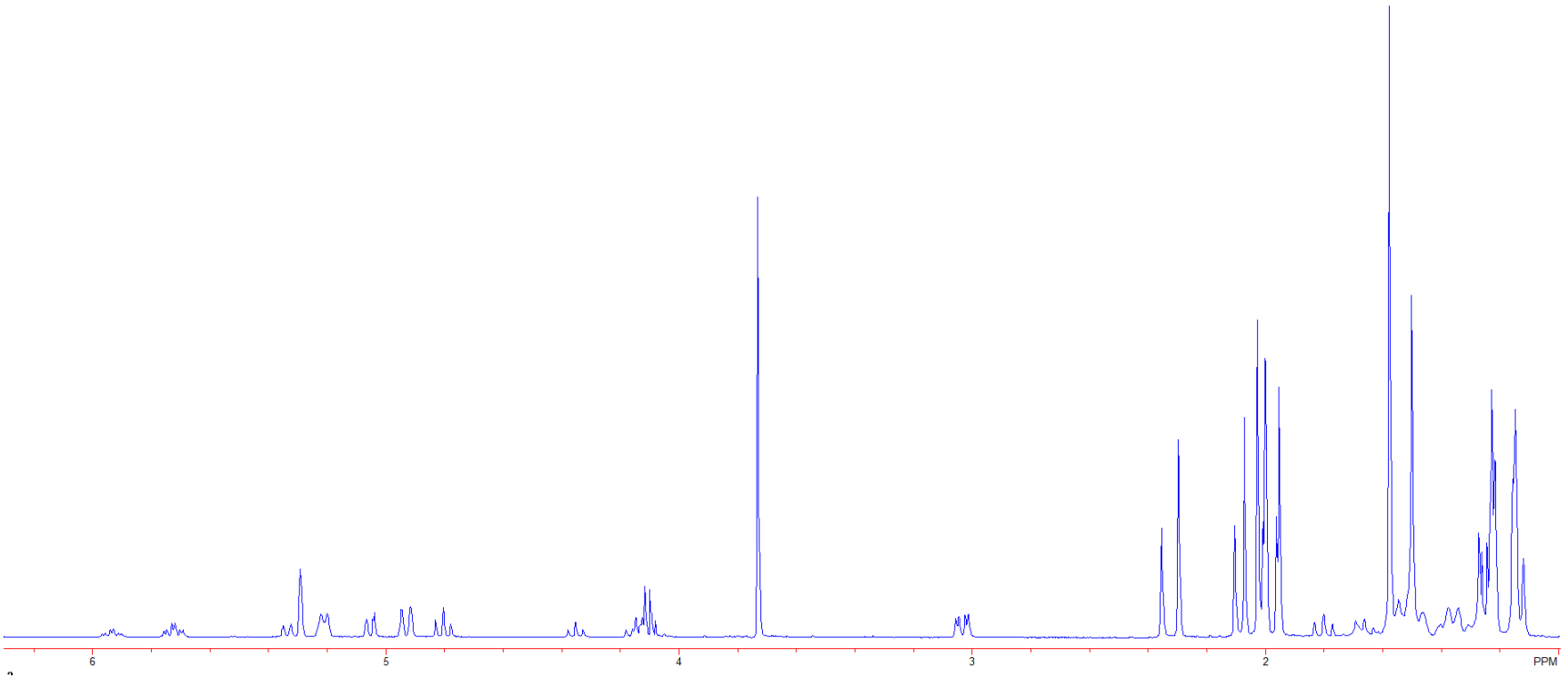
Methyl (1-(1,1,5,5-tetramethylpiperidinyloxy) 5-acetylacetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-thio-D-glycero-β-D-galacto-non-2-ulopyranoside)onate ($CDCl_3$, 500 MHz) (4β):



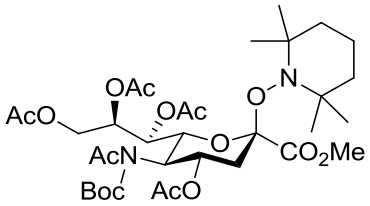


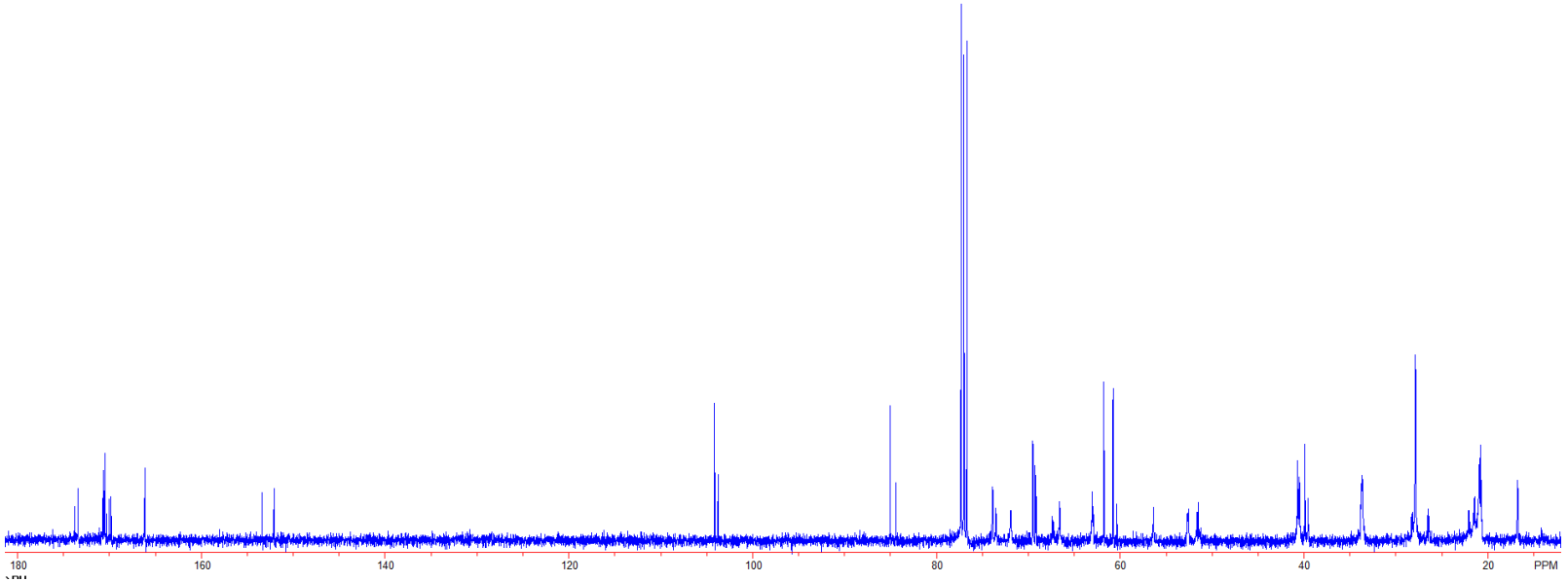
Methyl (1-(1,1,5,5-tetramethylpiperidinyloxy) 5-acetamido-5-*N*-(1,1-dimethylethoxy)carbonyl-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-thio-D-glycero-β-D-galacto-non-2-ulopyranoside)onate ($CDCl_3$, 400 MHz) (101β):



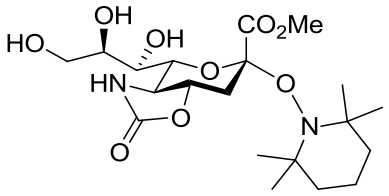


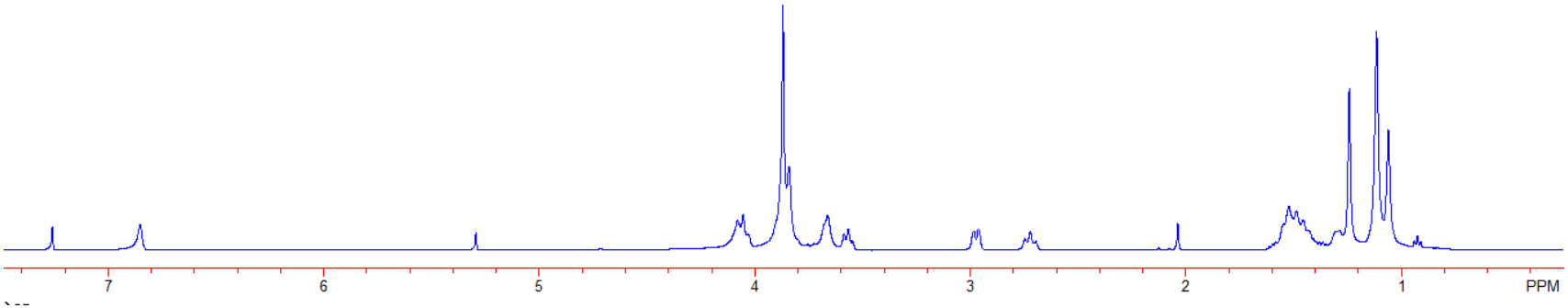
Methyl (1-(1,1,5,5-tetramethylpiperidinyloxy) 5-acetamido-5-*N*-(1,1-dimethylethoxy)carbonyl-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-thio-D-glycero-β-D-galacto-non-2-ulopyranoside)onate ($CDCl_3$, 400 MHz) (101β):



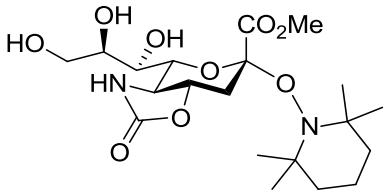


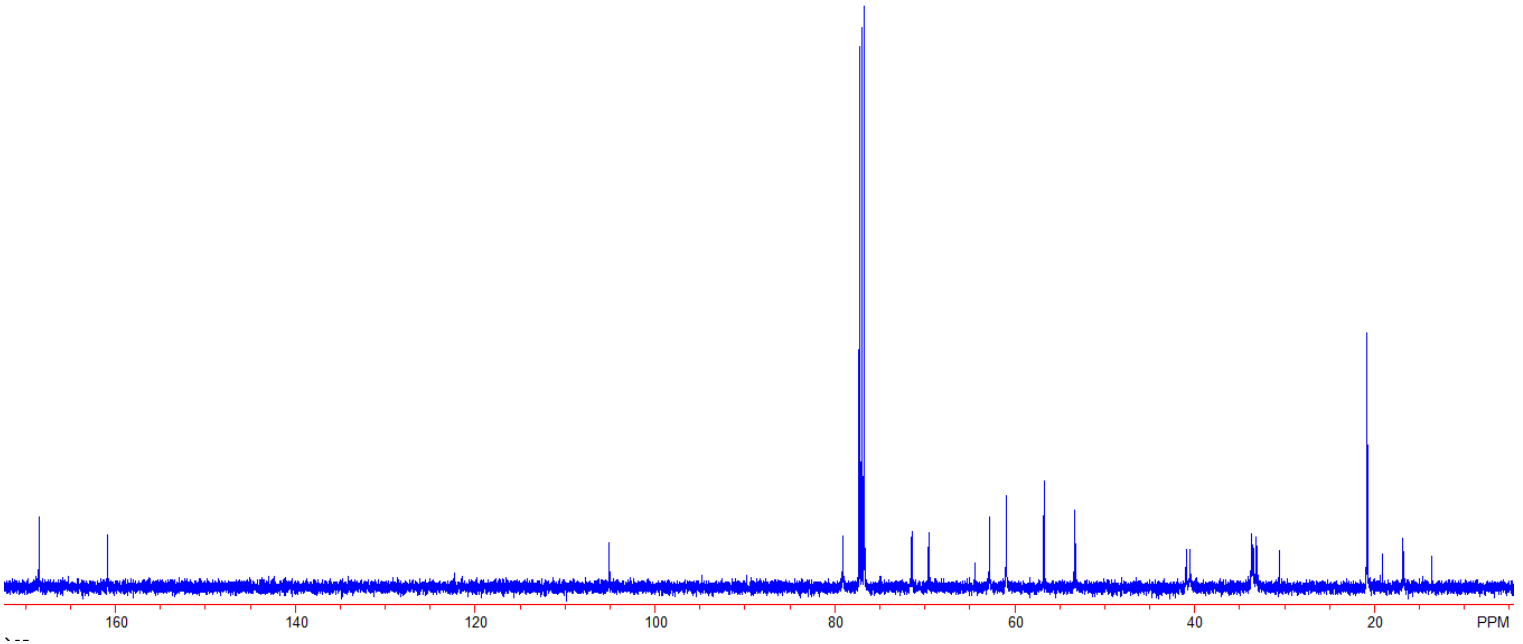
Methyl (1-(1,1,5,5-tetramethylpiperidinyloxy) 5-*N*,4-*O*-carbonyl-3,5-dideoxy-2-thio-D-glycero-α-D-galacto-non-2-ulopyranoside)onate ($CDCl_3$, 500 MHz) (102α):



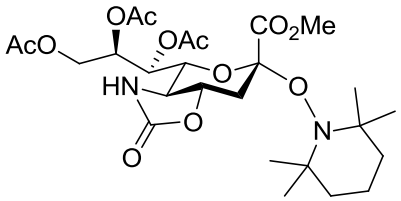


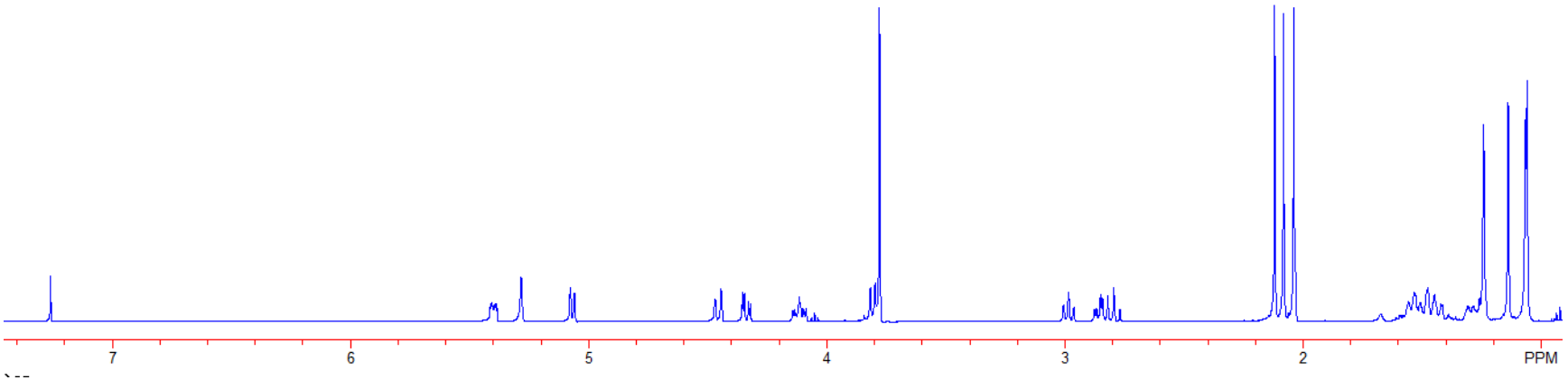
Methyl (1-(1,1,5,5-tetramethylpiperidinyloxy) 5-*N*,4-*O*-carbonyl-3,5-dideoxy-2-thio-D-glycero-α-D-galacto-non-2-ulopyranoside)onate ($CDCl_3$, 500 MHz) (102α):



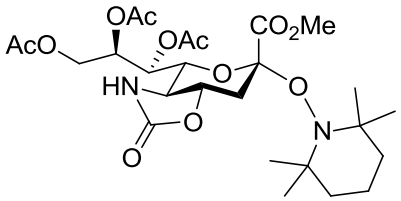


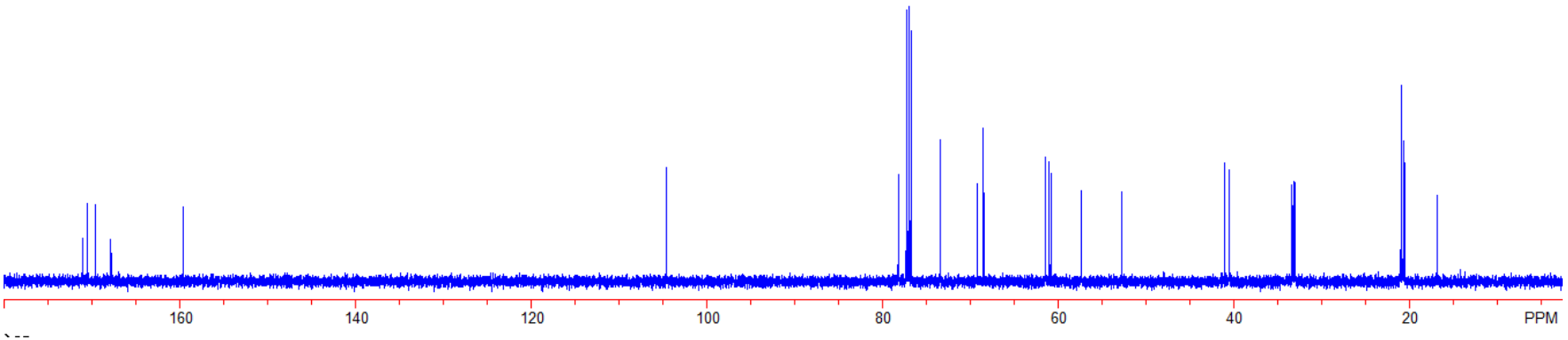
Methyl (1-(1,1,5,5-tetramethylpiperidinyloxy) 7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-2-thio-D-glycero-α-D-galacto-non-2-ulopyranoside)onate ($CDCl_3$, 500 MHz) (5α):



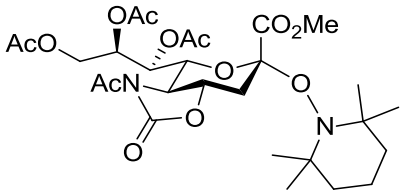


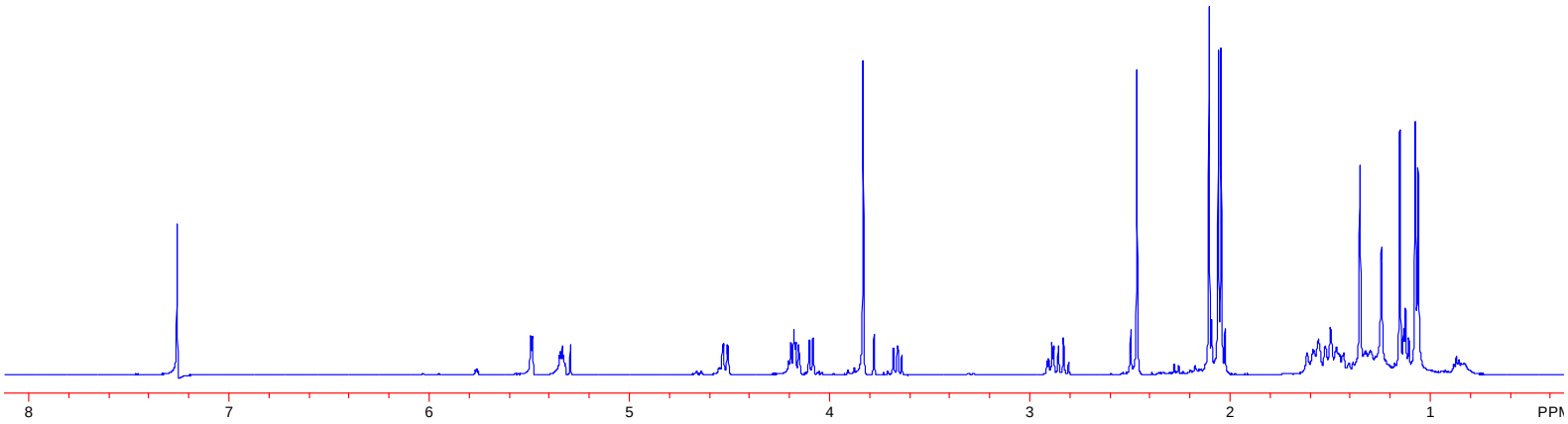
Methyl (1-(1,1,5,5-tetramethylpiperidinyloxy) 7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-2-thio-D-glycero-α-D-galacto-non-2-ulopyranoside)onate ($CDCl_3$, 500 MHz) (5α):



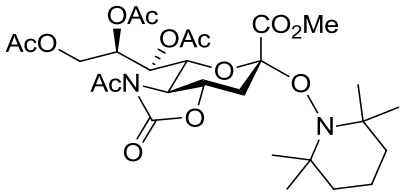


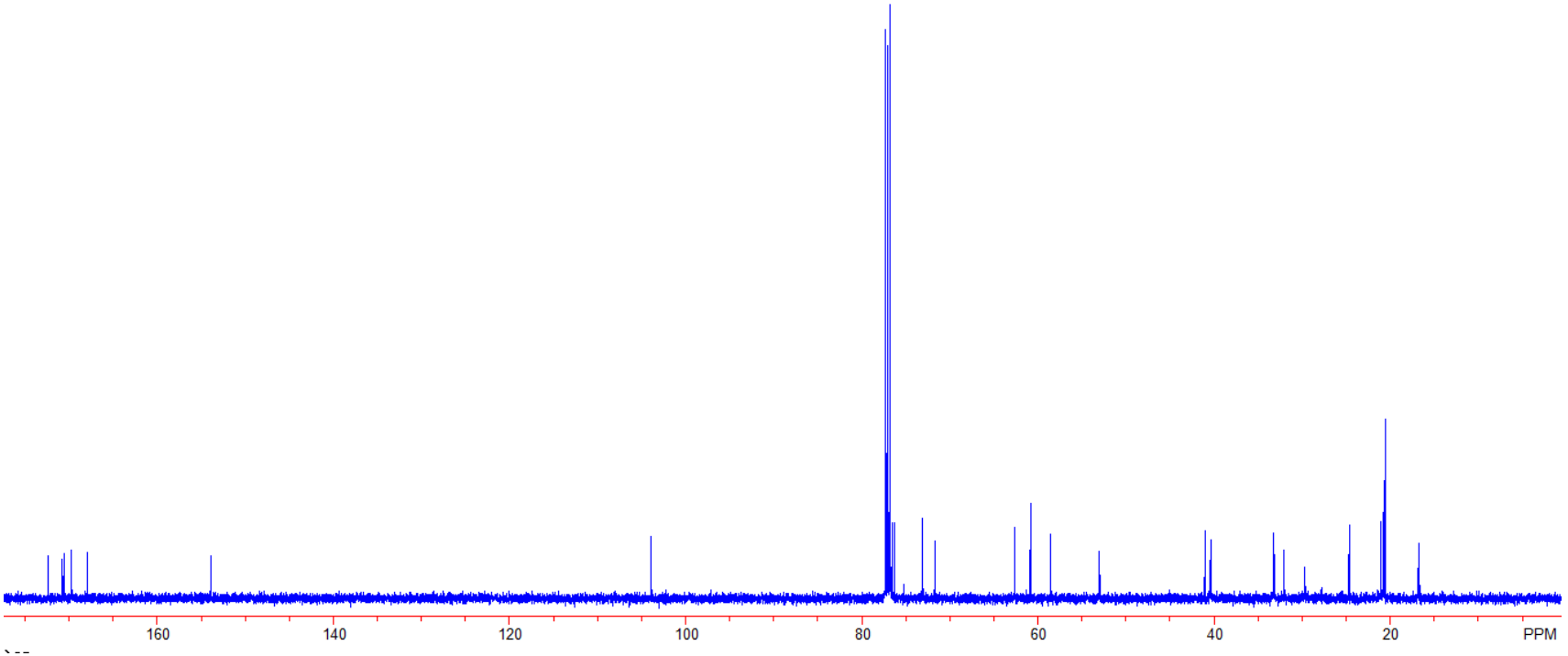
Methyl (1-(1,1,5,5-tetramethylpiperidinyloxy) 5-acetamido-7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-2-thio-D-glycero-α-D-galacto-non-2-ulopyranoside)onate ($CDCl_3$, 500 MHz) (6α):



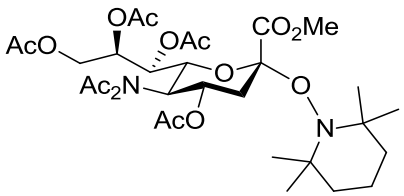


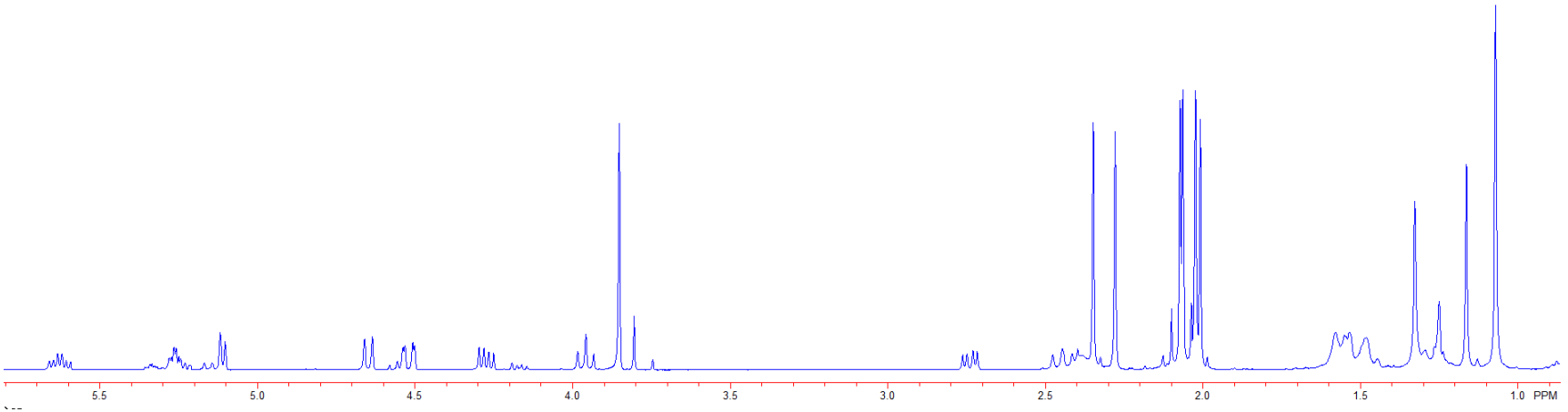
Methyl (1-(1,1,5,5-tetramethylpiperidinyloxy) 5-acetamido-7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-2-thio-D-glycero-α-D-galacto-non-2-ulopyranoside)onate ($CDCl_3$, 500 MHz) (6α):



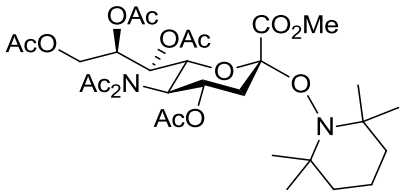


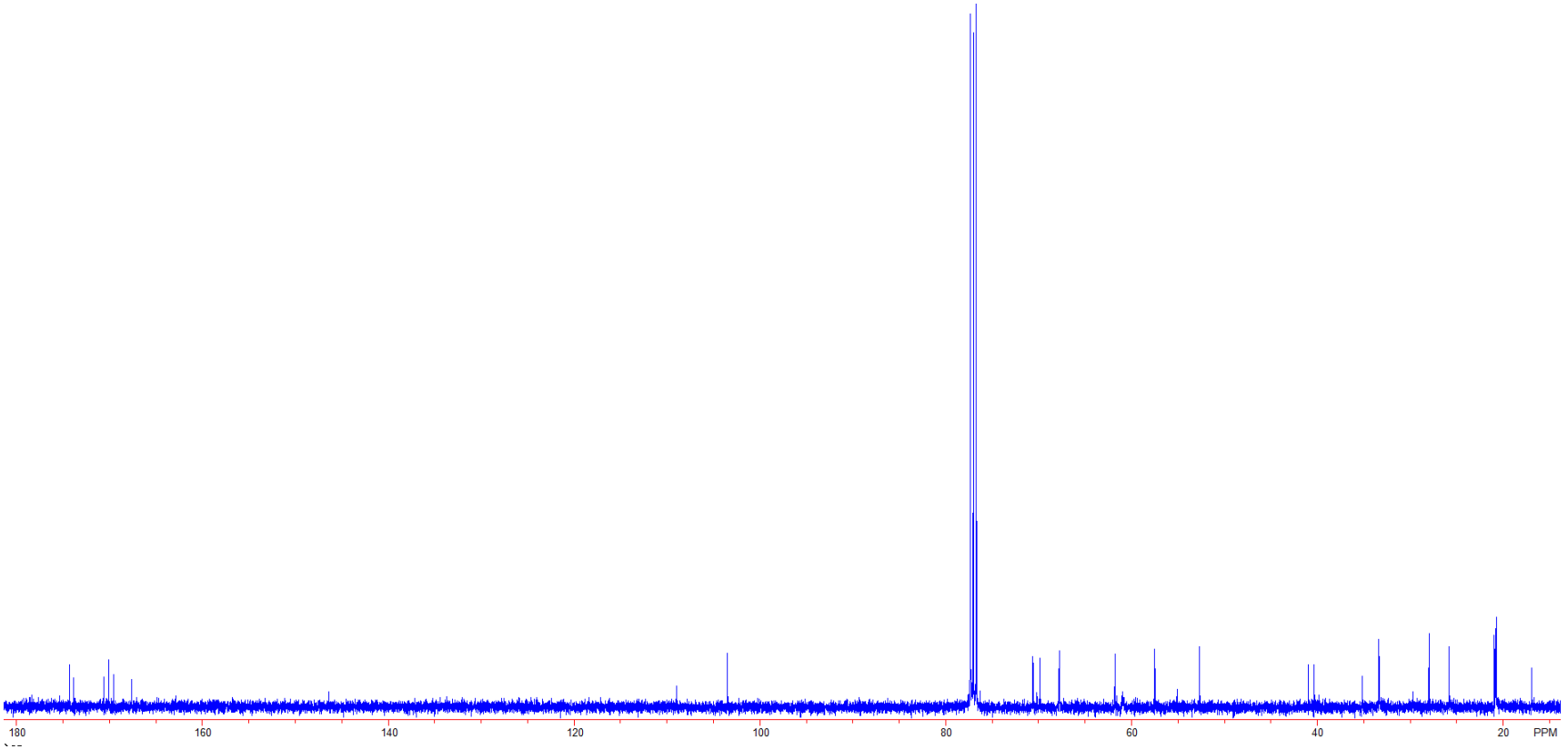
Methyl (1-(1,1,5,5-tetramethylpiperidinyloxy) 5-acetylacetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-thio-D-glycero-β-D-galacto-non-2-ulopyranoside)onate ($CDCl_3$, 400 MHz) (4α):



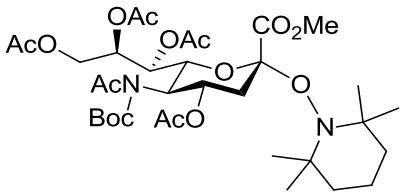


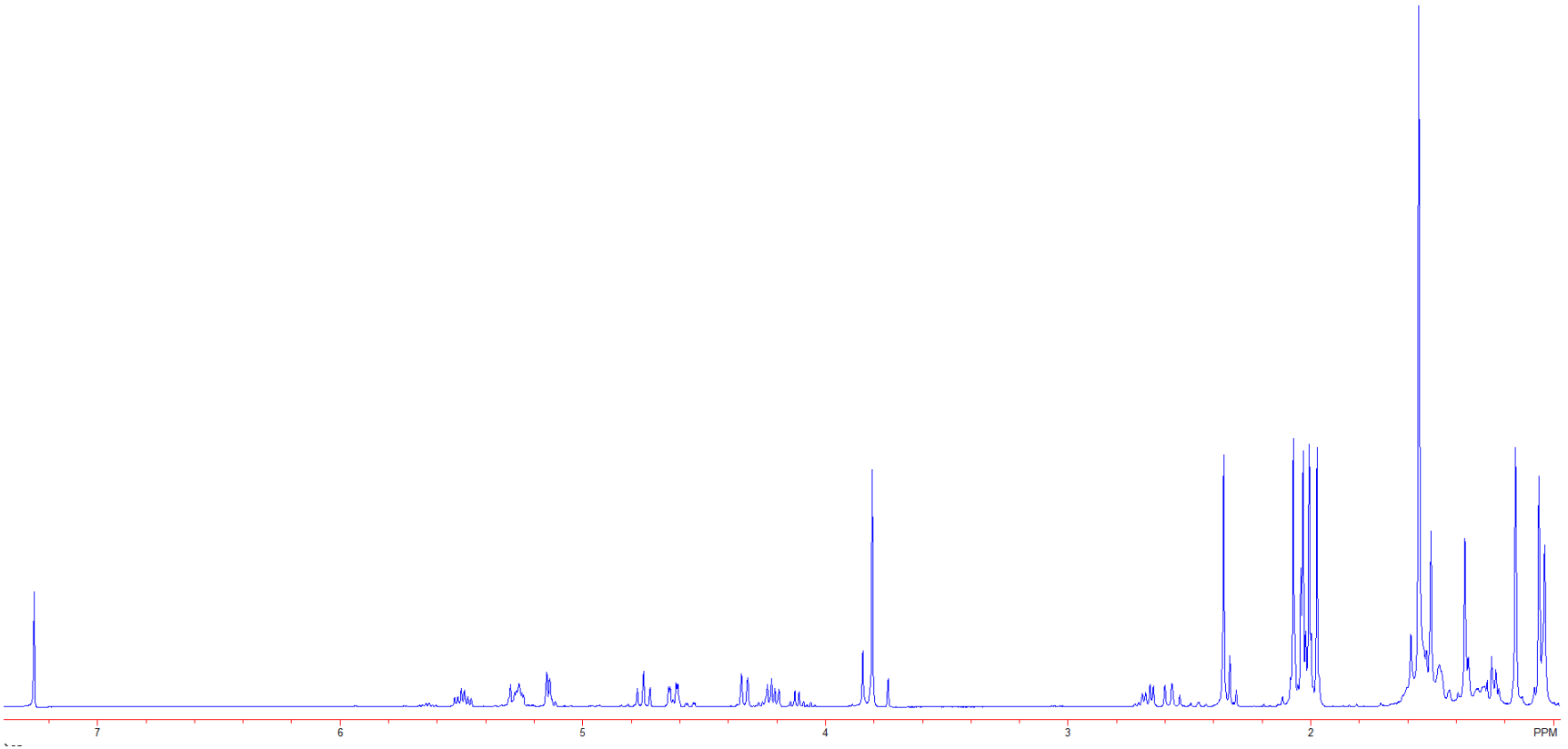
Methyl (1-(1,1,5,5-tetramethylpiperidinyloxy) 5-acetylacetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-thio-D-glycero-β-D-galacto-non-2-ulopyranoside)onate ($CDCl_3$, 400 MHz) (4α):



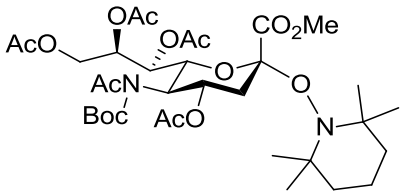


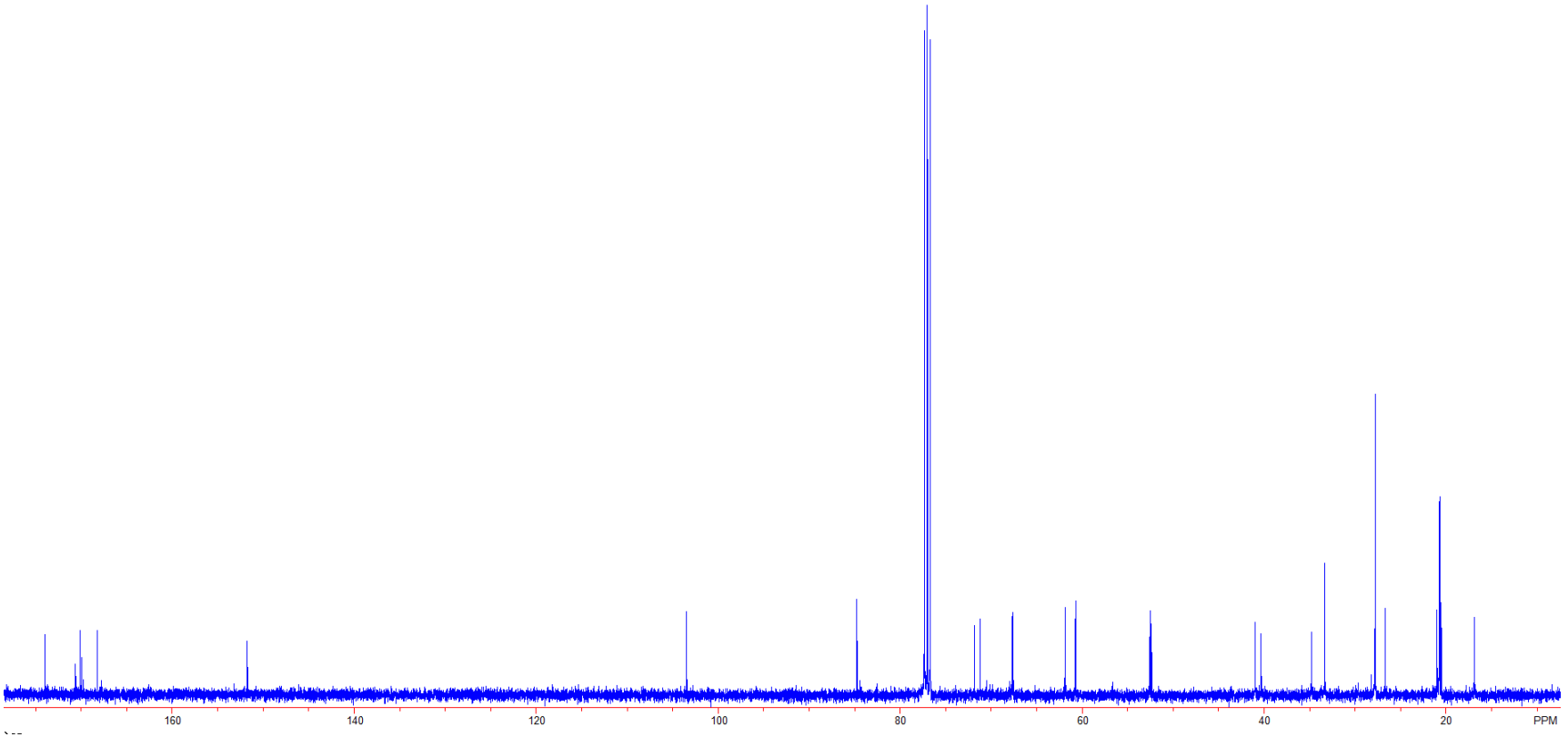
Methyl (1-(1,1,5,5-tetramethylpiperidinyloxy) 5-acetamido-5-*N*-(1,1-dimethylethoxy) carbonyl-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-thio-D-glycero-α-D-galacto-non-2-ulopyranoside)onate ($CDCl_3$, 400 MHz) (101α):



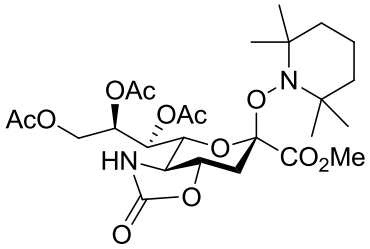


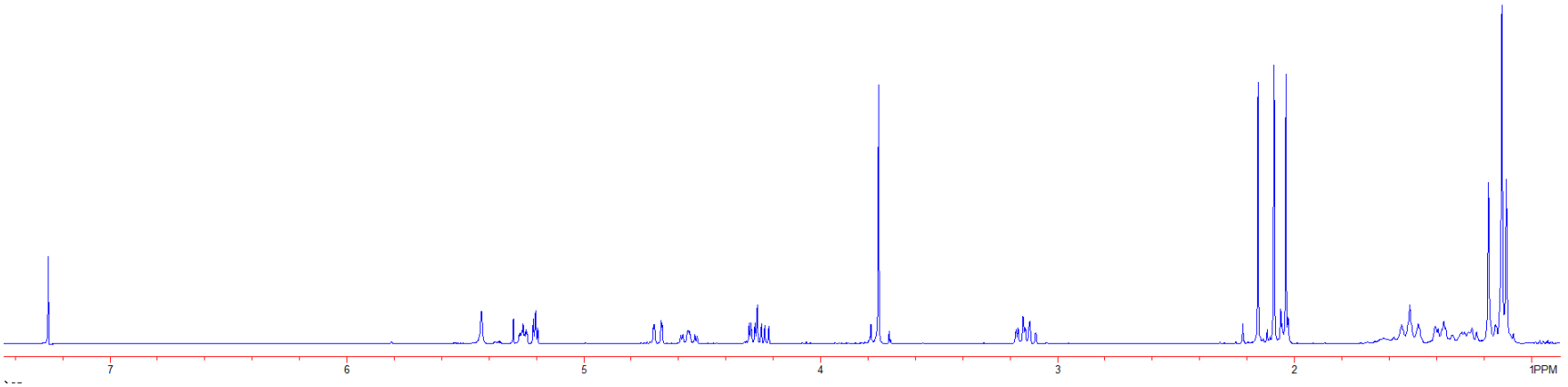
Methyl (1-(1,1,5,5-tetramethylpiperidinyloxy) 5-acetamido-5-*N*-(1,1-dimethylethoxy) carbonyl-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-thio-D-glycero-α-D-galacto-non-2-ulopyranoside)onate ($CDCl_3$, 400 MHz) (101α):



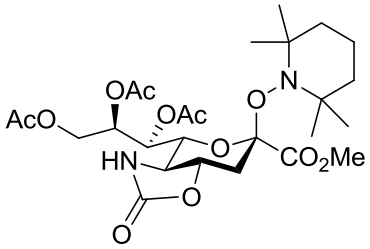


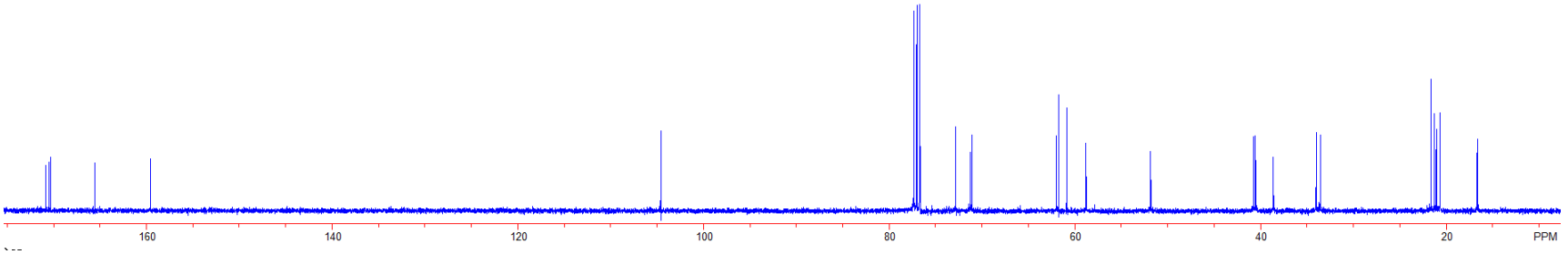
Methyl (1-(1,1,5,5-tetramethylpiperidinyloxy) 7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-2-thio-D-glycero-β-D-galacto-non-2-ulopyranoside)onate ($CDCl_3$, 400 MHz) (5β):



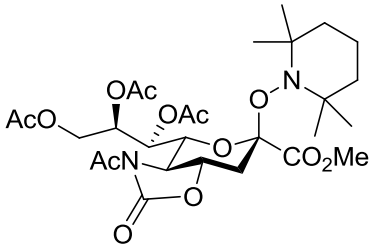


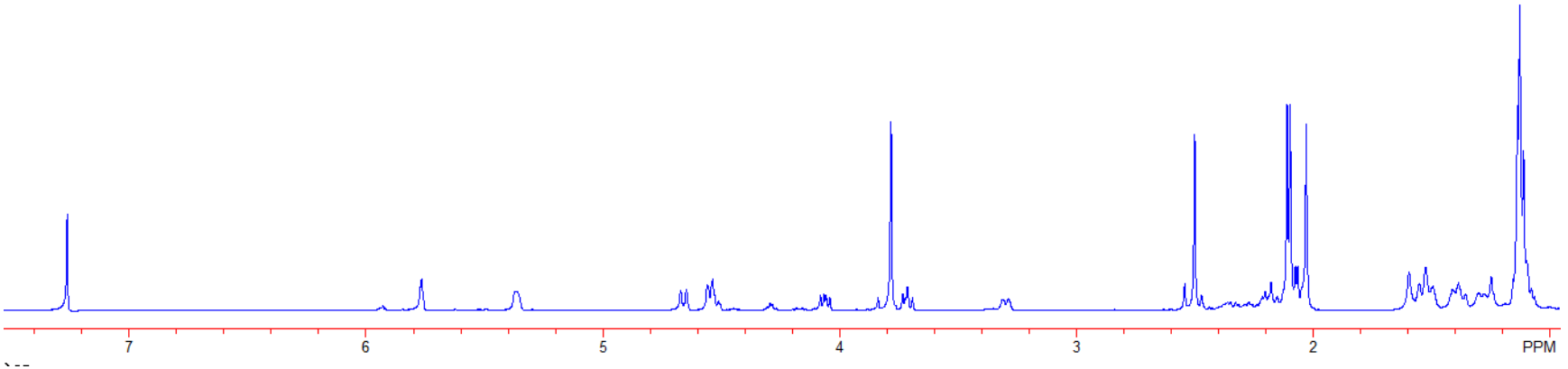
Methyl (1-(1,1,5,5-tetramethylpiperidinyloxy) 7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-2-thio-D-glycero-β-D-galacto-non-2-ulopyranoside)onate ($CDCl_3$, 400 MHz) (5β):



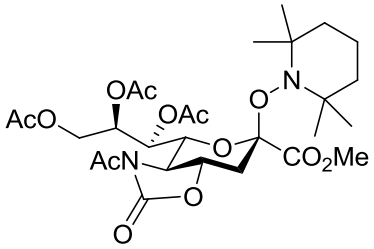


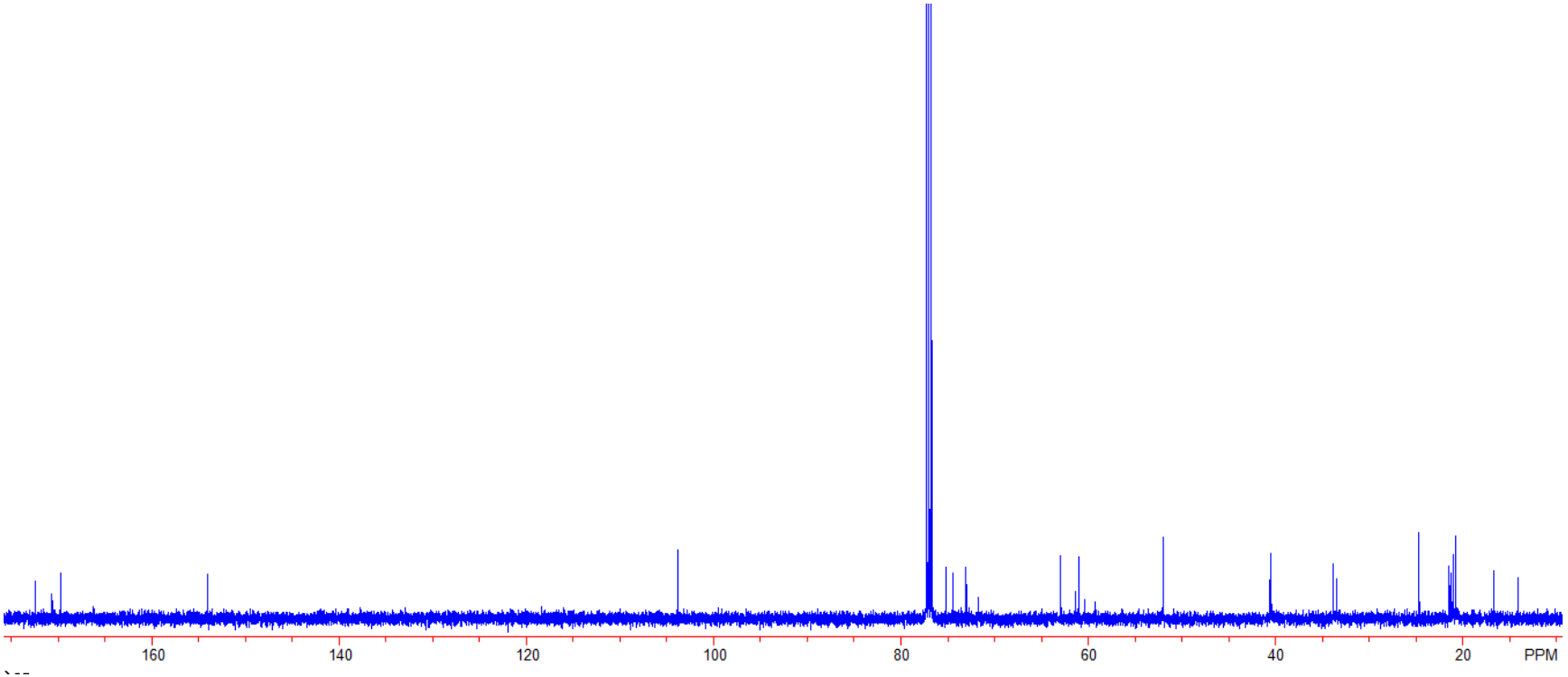
Methyl (1-(1,1,5,5-tetramethylpiperidinyloxy) 5-acetamido-7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-2-thio-D-glycero-β-D-galacto-non-2-ulopyranoside)onate ($CDCl_3$, 500 MHz) (6β):



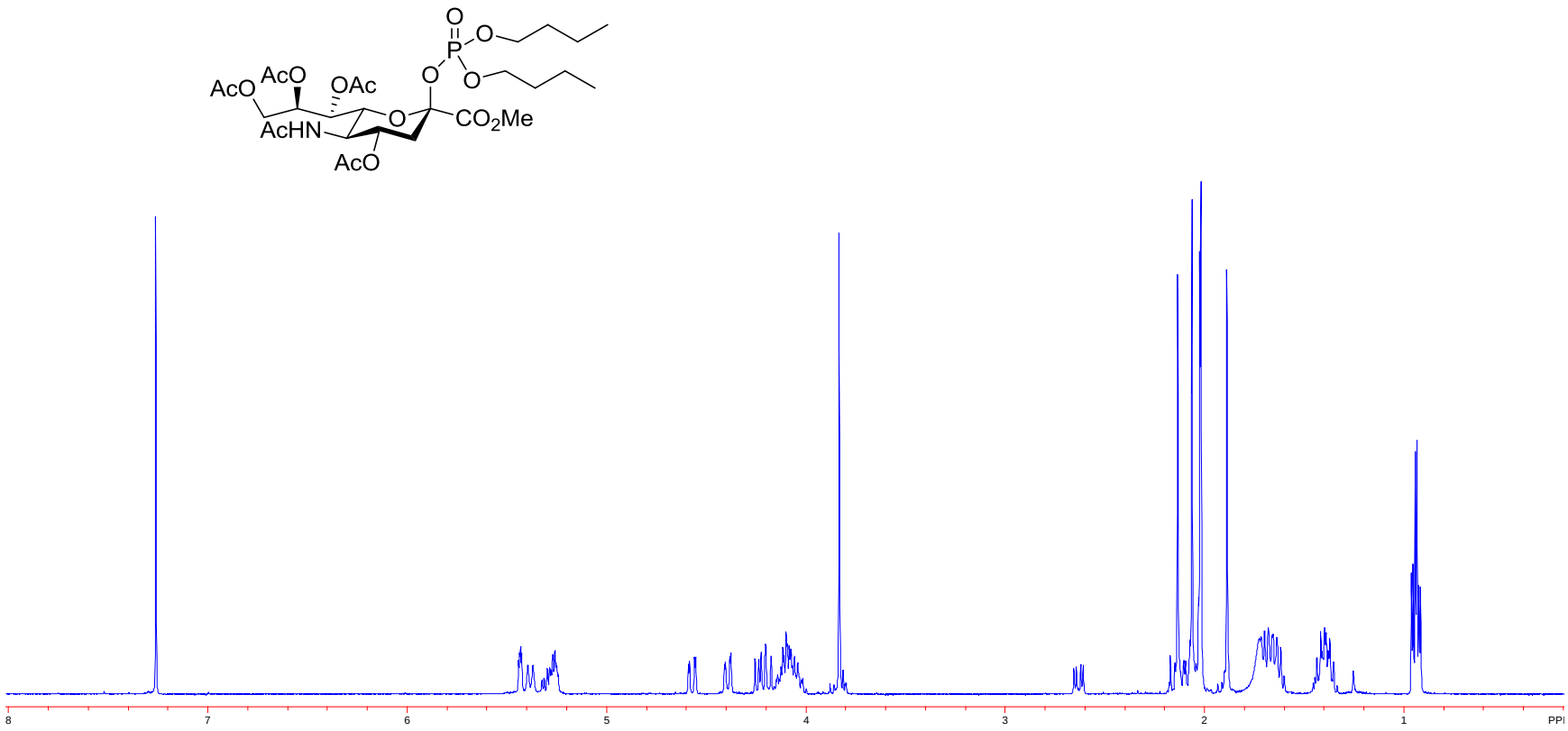


Methyl (1-(1,1,5,5-tetramethylpiperidinyloxy) 5-acetamido-7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-2-thio-D-glycero-β-D-galacto-non-2-ulopyranoside)onate ($CDCl_3$, 500 MHz) (6β):

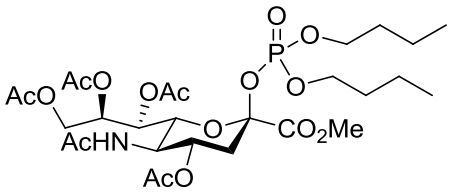




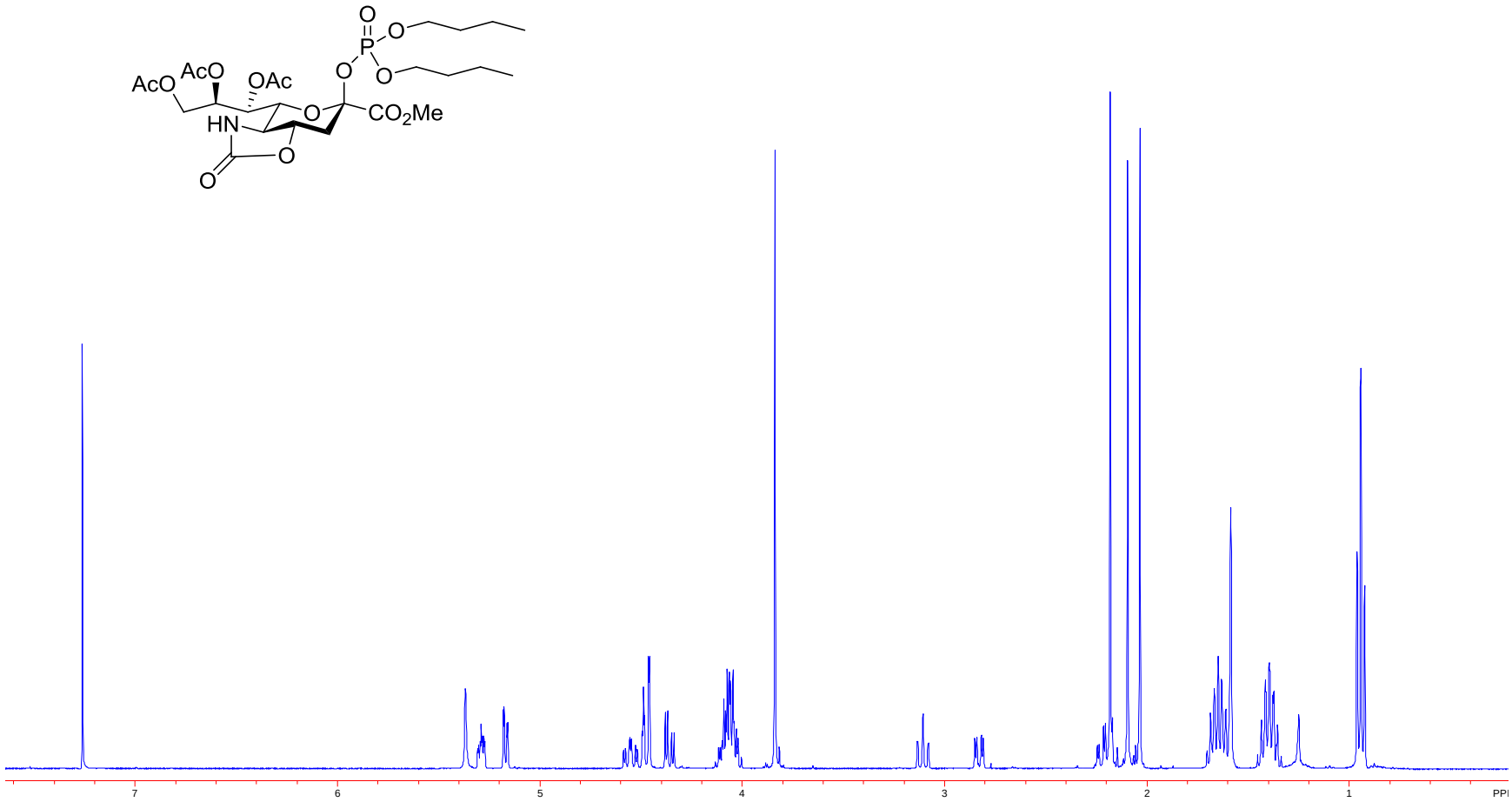
Methyl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-2-(dibutylphosphoryl)-3,5-dideoxy-D-glycero-β-D-galacto-non-2-ulopyranoside)onate (15): ^{1}H NMR (400 MHz, $CDCl_3$)



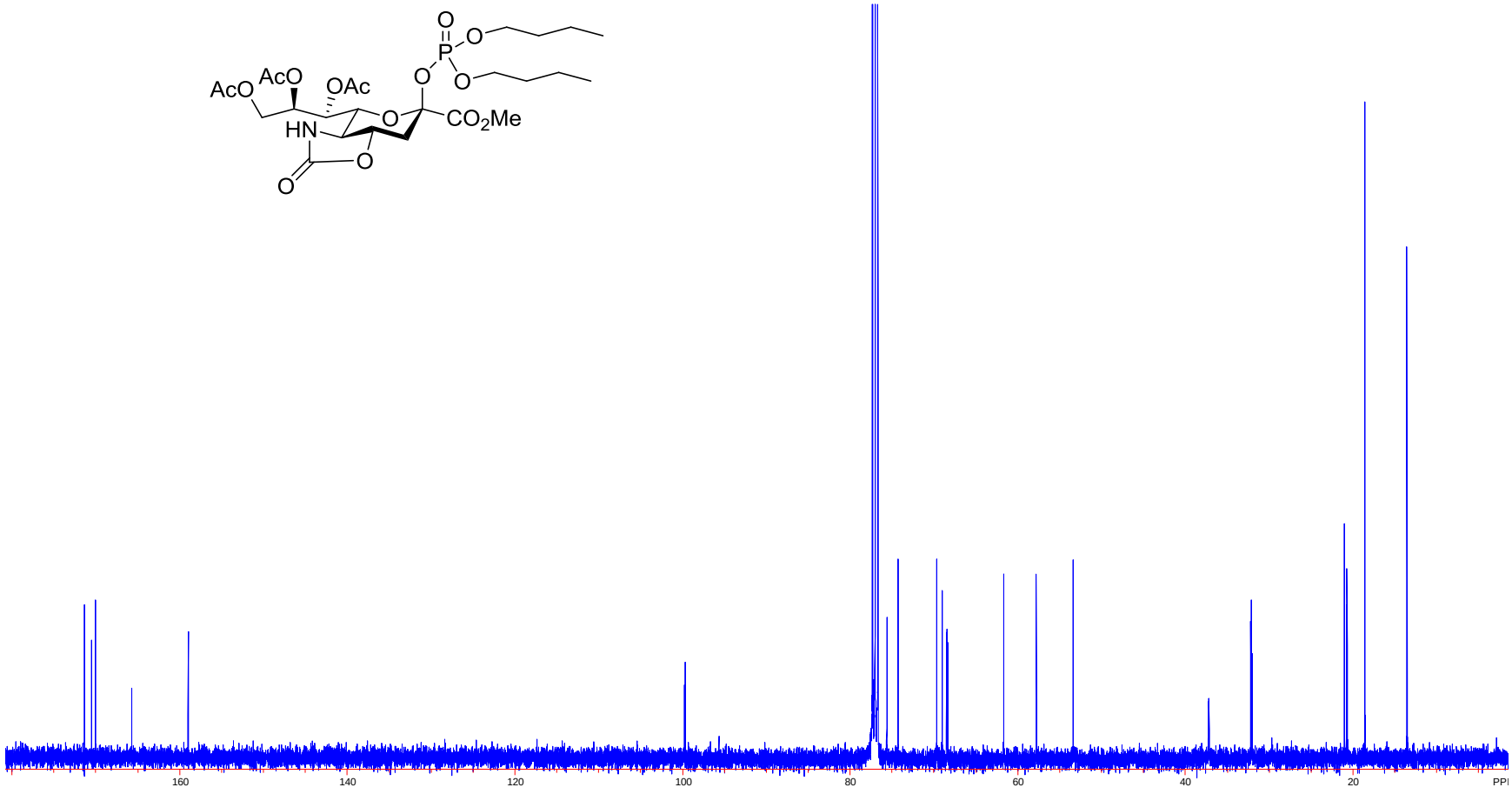
Methyl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-2-(dibutylphosphoryl)-3,5-dideoxy-D-glycero-β-D-galacto-non-2-ulopyranoside)onate (15): ^{13}C NMR (100 MHz, $CDCl_3$)):



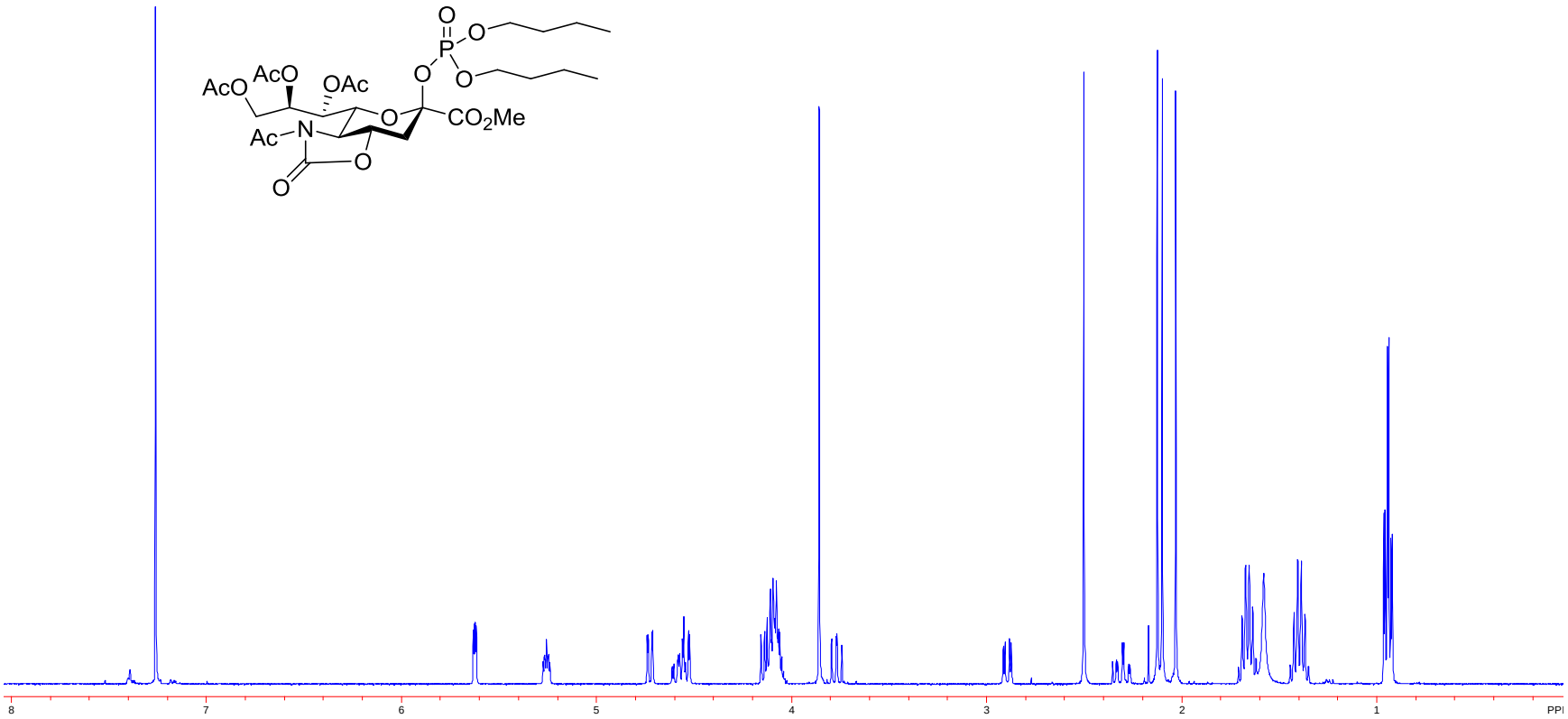
Methyl (7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-2-(dibutylphosphoryl)-3,5-dideoxy-D-glycero-β-D-galacto-non-2-ulopyranoside) onate (16): ^{1}H NMR (400 MHz, $CDCl_3$)



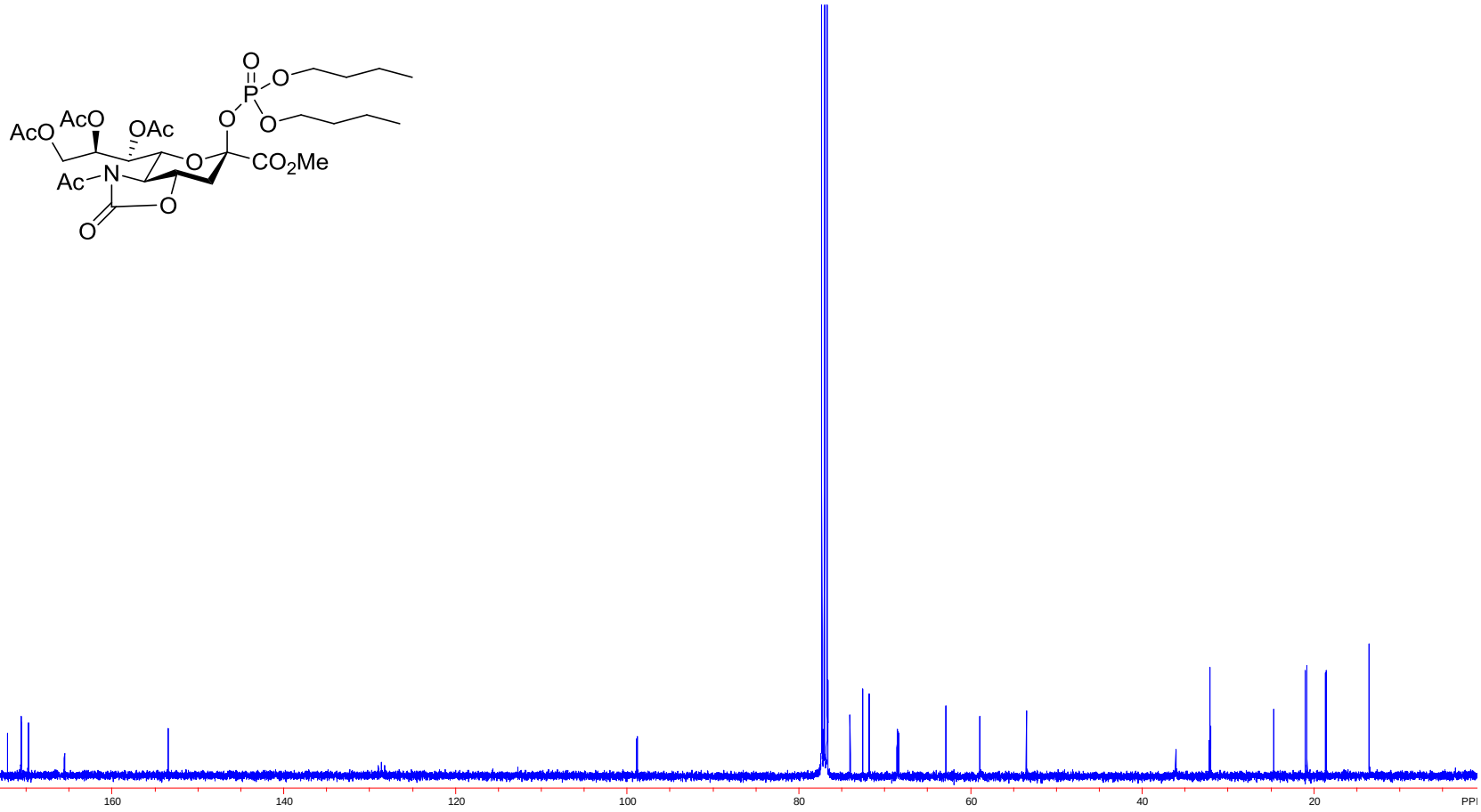
Methyl (7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-2-(dibutylphosphoryl)-3,5-dideoxy-D-glycero-β-D-galacto-non-2-ulopyranoside)onate (16): ^{13}C NMR (100 MHz, $CDCl_3$)



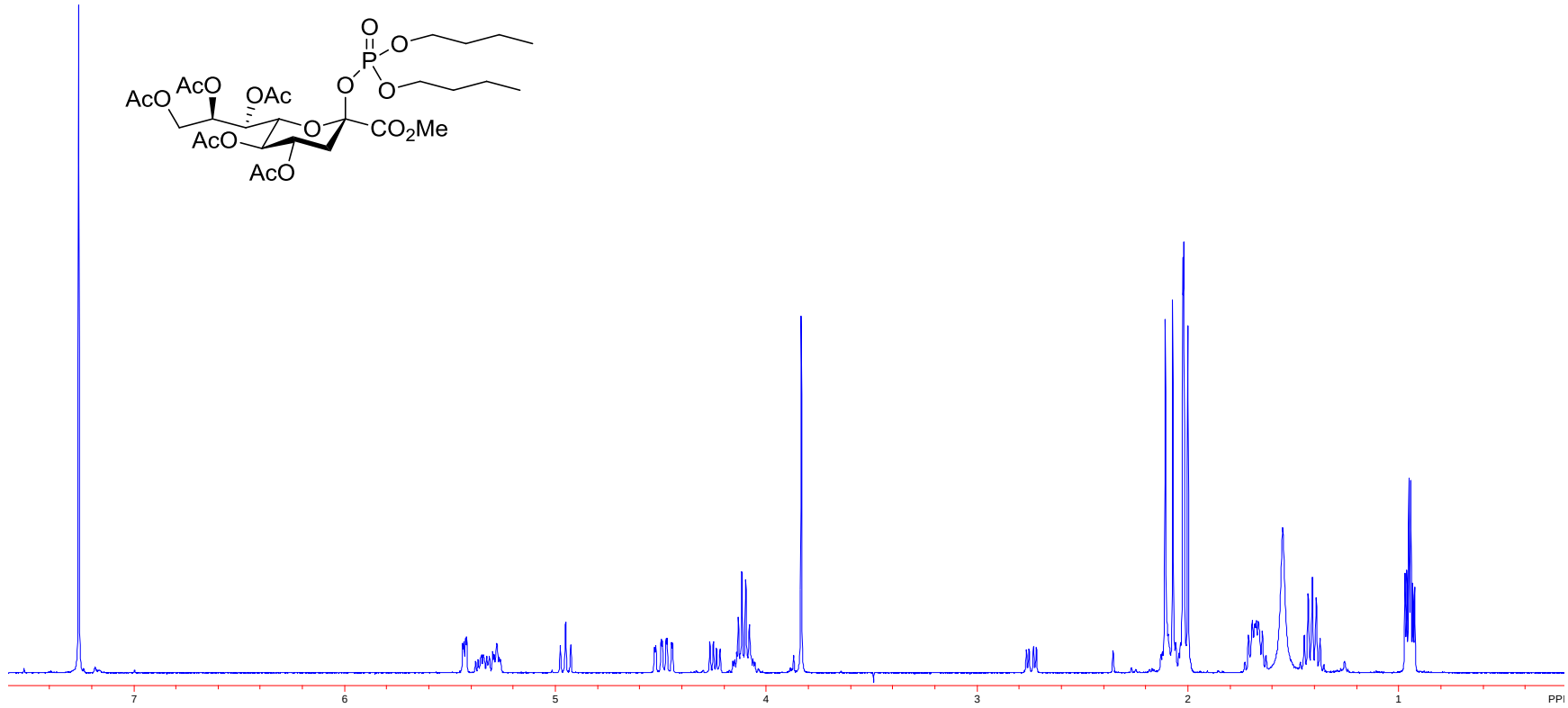
Methyl (5-acetamido-7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-2-(dibutylphosphoryl)-3,5-dideoxy-D-glycero-β-D-galacto-non-2-ulopyranoside)onate (17): ^{1}H NMR (400 MHz, $CDCl_3$)



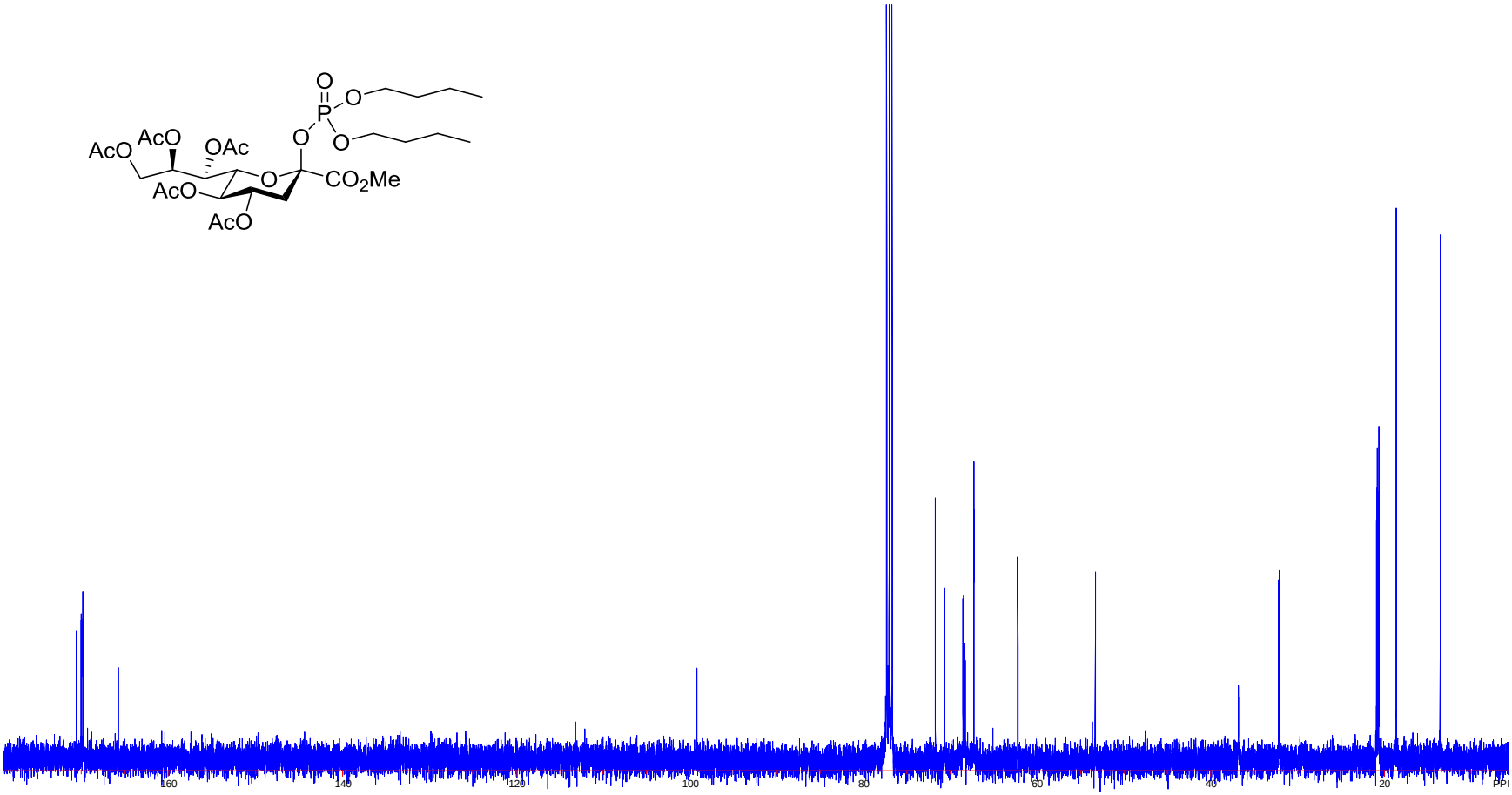
Methyl (5-acetamido-7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-2-(dibutylphosphoryl)-3,5-dideoxy-D-glycero-β-D-galacto-non-2-ulopyranoside)onate (17): ^{13}C NMR (100 MHz, $CDCl_3$)



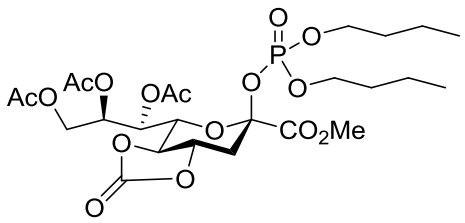
Methyl (4,5,7,8,9-penta-*O*-acetyl-2-(dibutylphosphoryl)-3-deoxy-D-glycero-β-D-galacto-non-2-ulopyranoside)onate (18): ^{1}H NMR (400 MHz, $CDCl_3$)

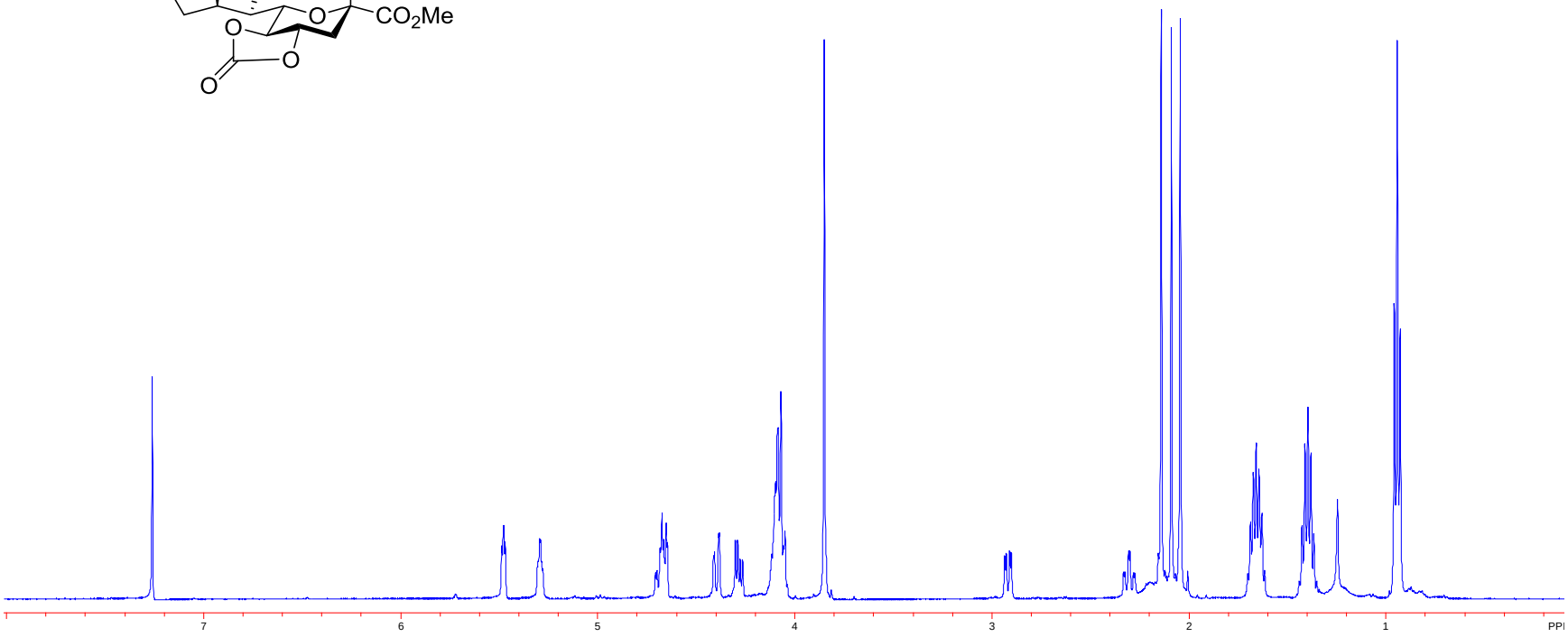


Methyl (4,5,7,8,9-penta-*O*-acetyl-2-(dibutylphosphoryl)-3-deoxy-D-glycero-β-D-galacto-non-2-ulopyranoside)onate (18): ^{13}C NMR (100 MHz, $CDCl_3$)

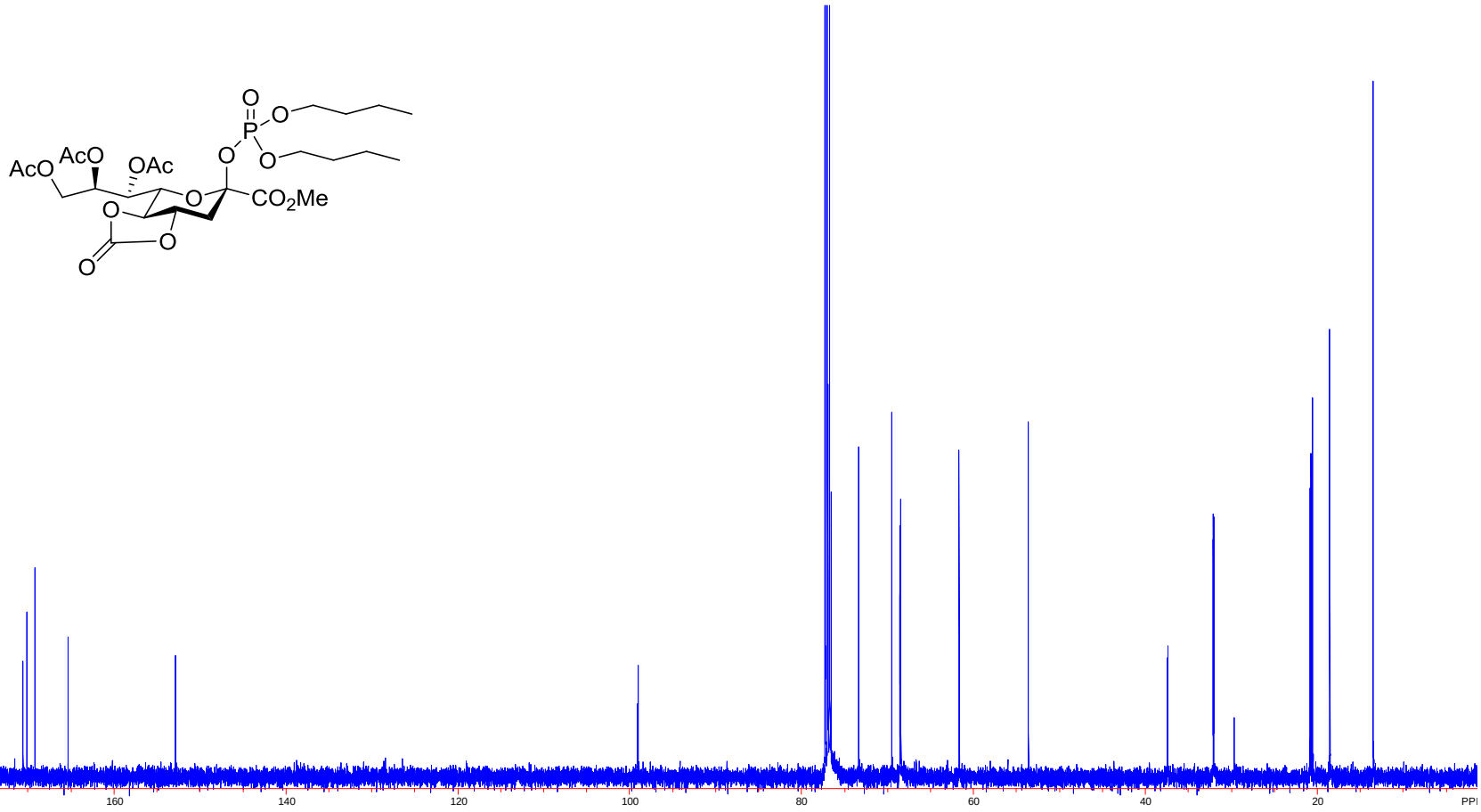


Methyl (7,8,9-tri-*O*-acetyl-4,5-*O*-carbonyl-2-(dibutylphosphoryl)-3-deoxy-D-glycero-β-D-galacto-non-2-ulopyranoside)onate (19): ^{1}H NMR (500 MHz, $CDCl_3$)

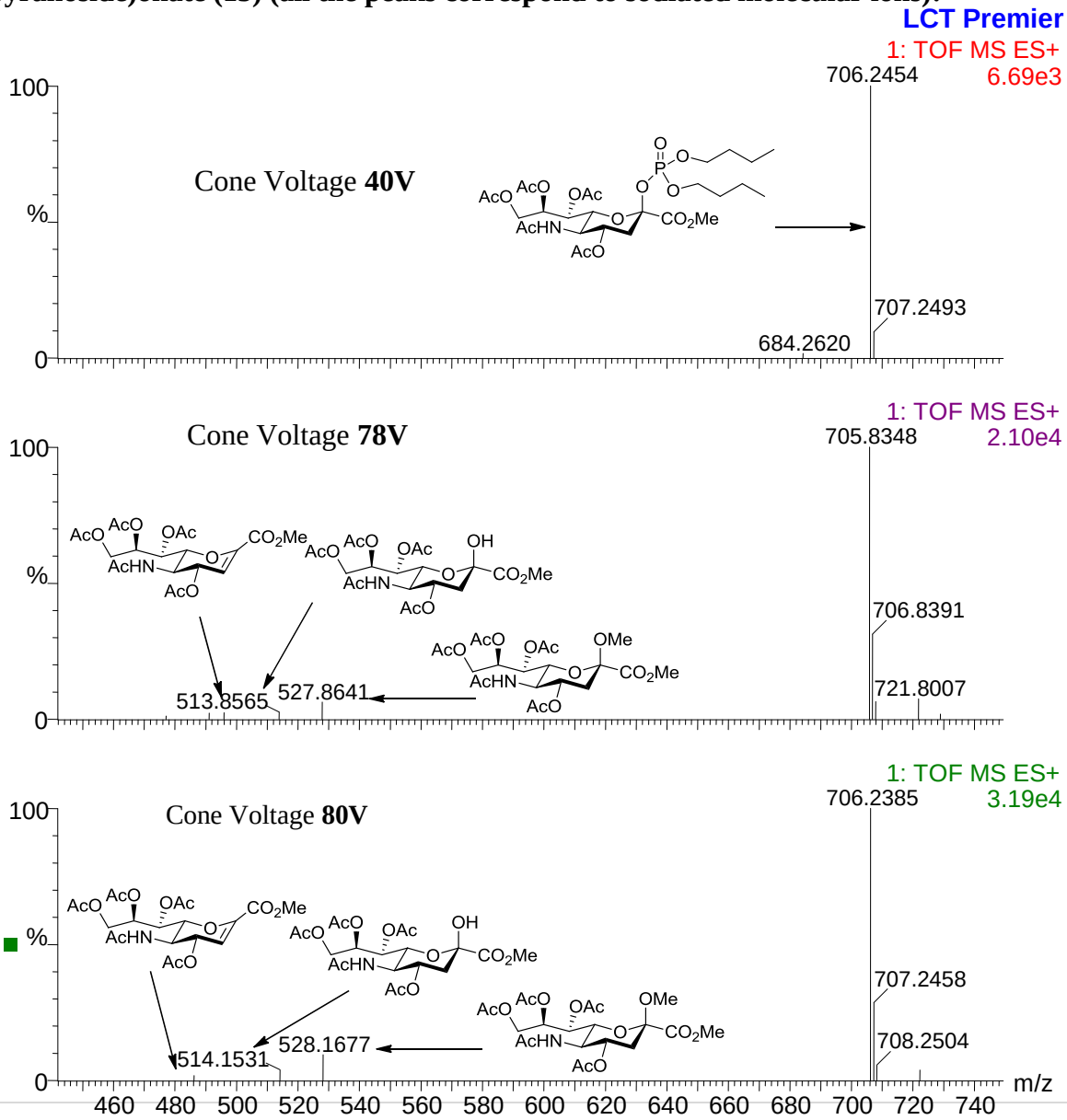




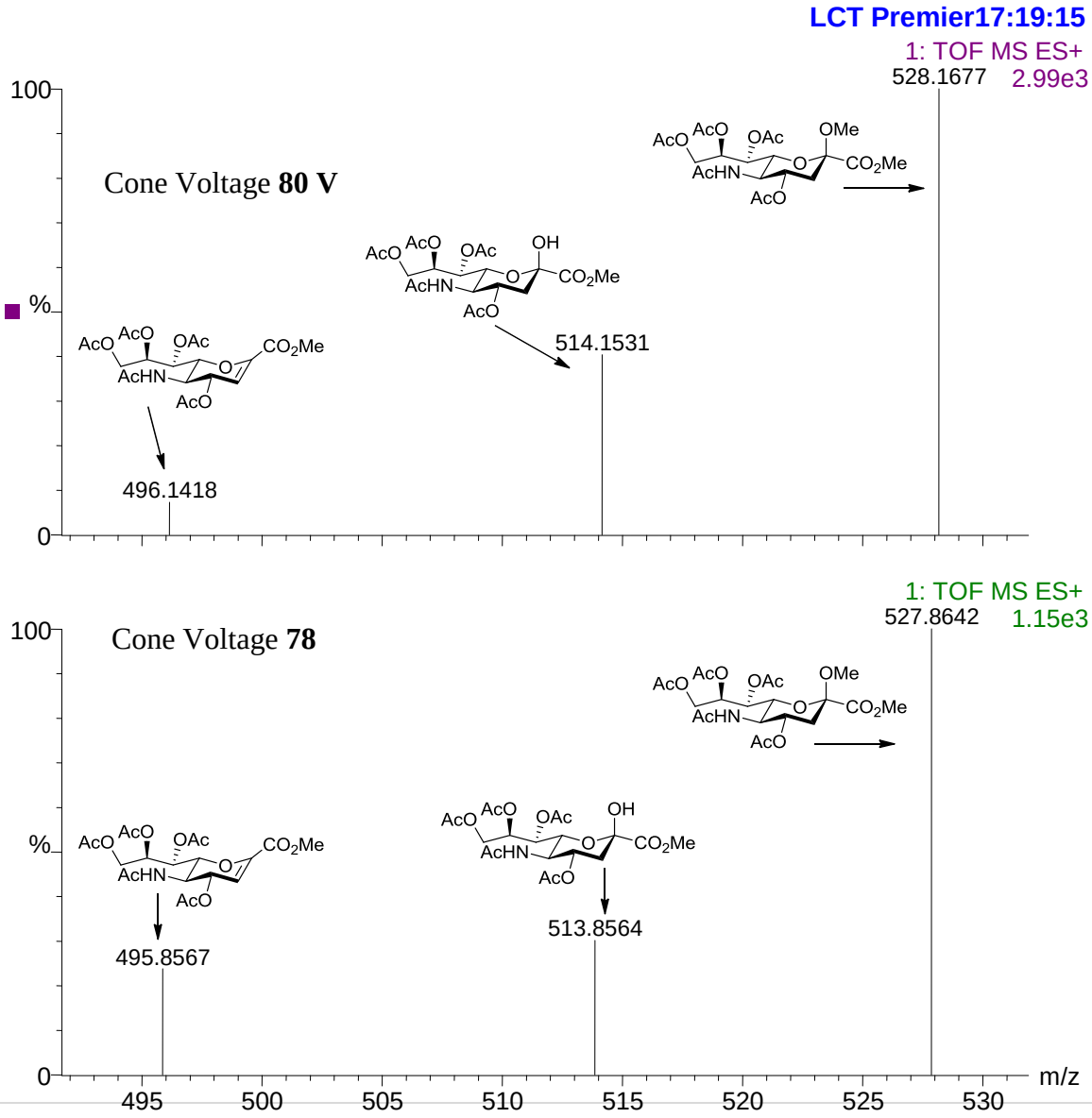
Methyl (7,8,9-tri-*O*-acetyl-4,5-*O*-carbonyl-2-(dibutylphosphoryl)-3-deoxy-D-glycero-β-D-galacto-non-2-ulopyranoside)onate (19): ^{13}C NMR (125 MHz, $CDCl_3$)



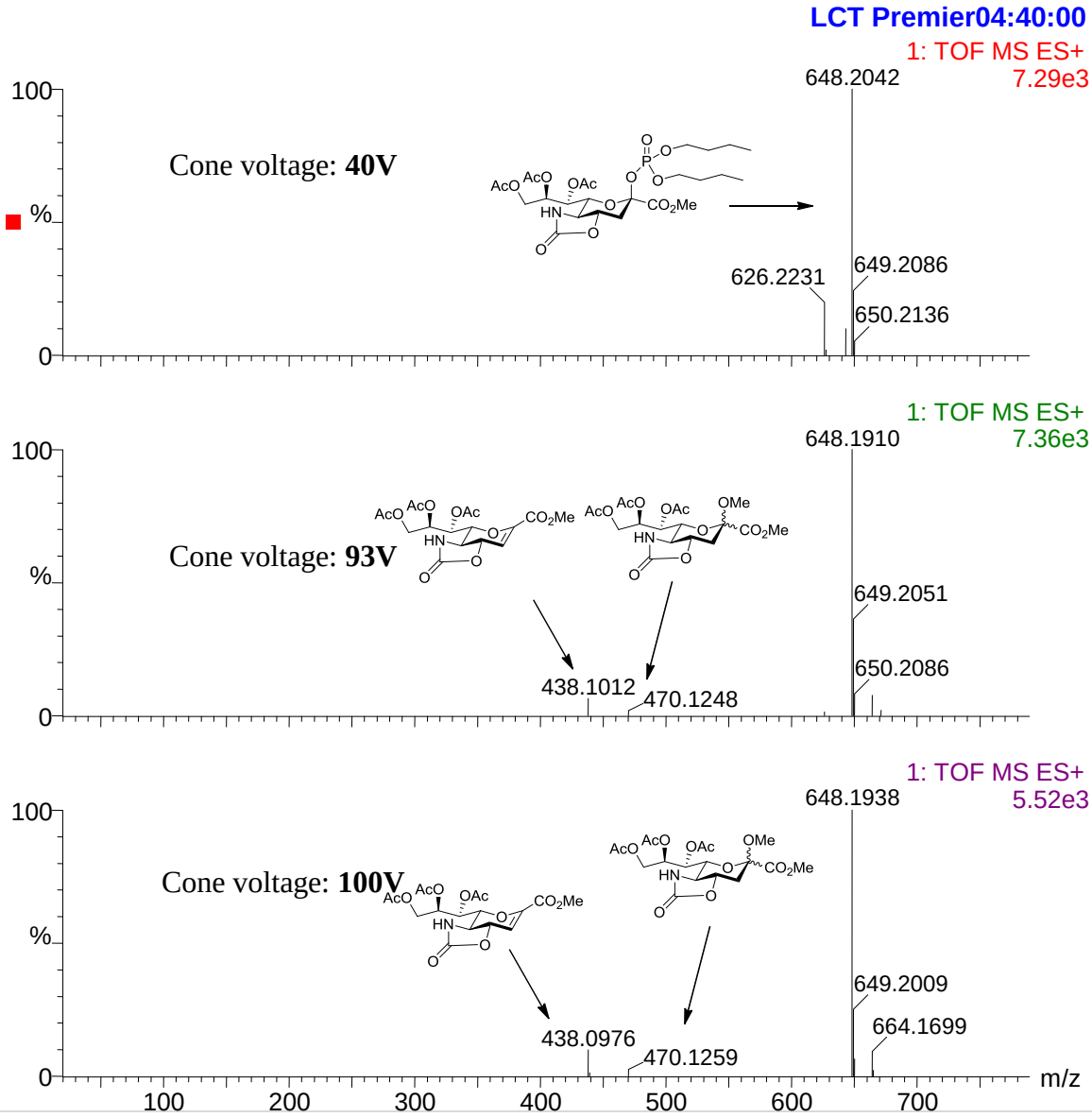
In-source fragmentation of Methyl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-2-(dibutylphosphoryl)-3,5-dideoxy-D-glycero-β-D-galacto-non-2-ulopyranoside)onate (15) (all the peaks correspond to sodiated molecular ions):



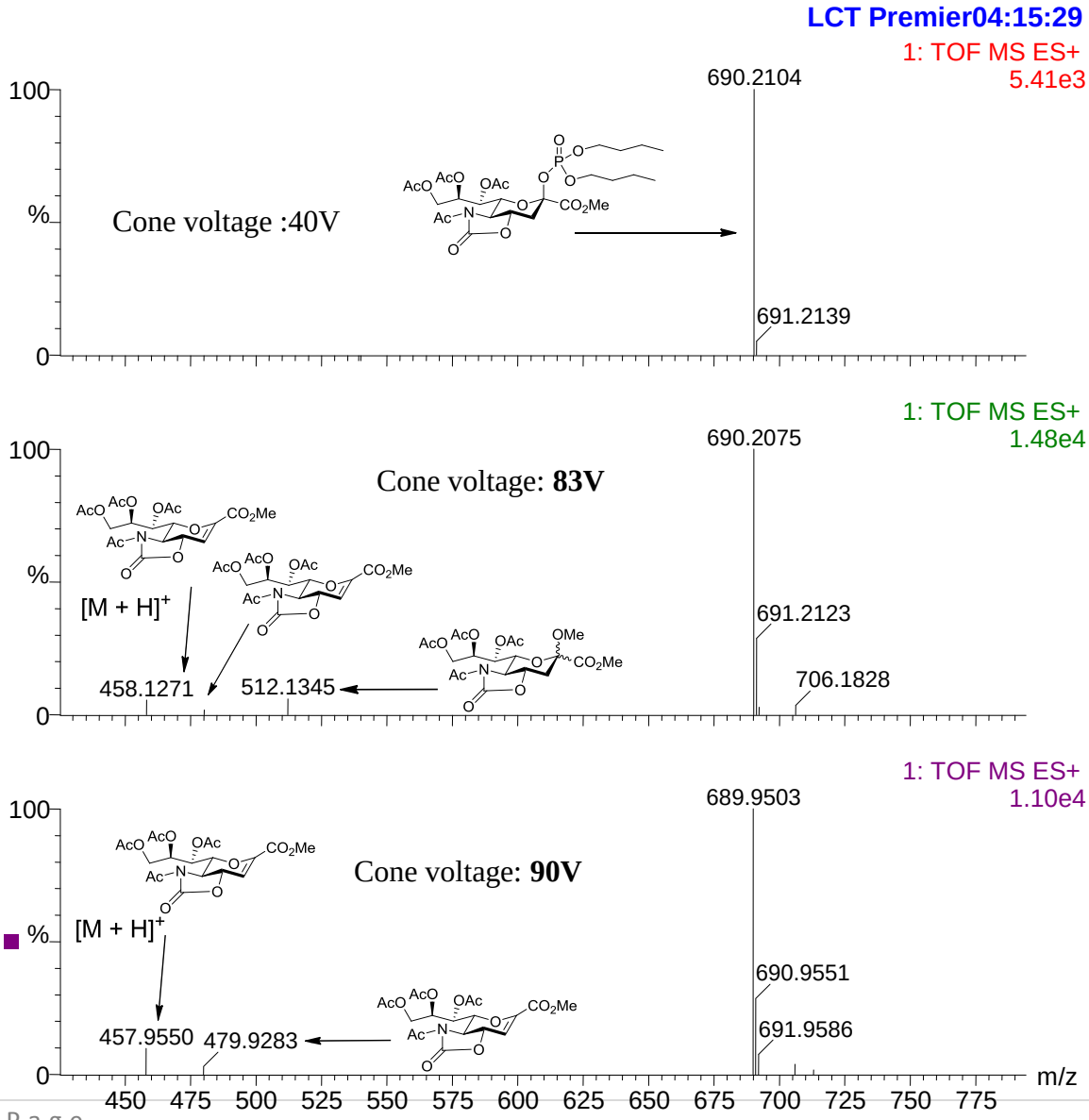
(all the peaks correspond to sodiated molecular ions)



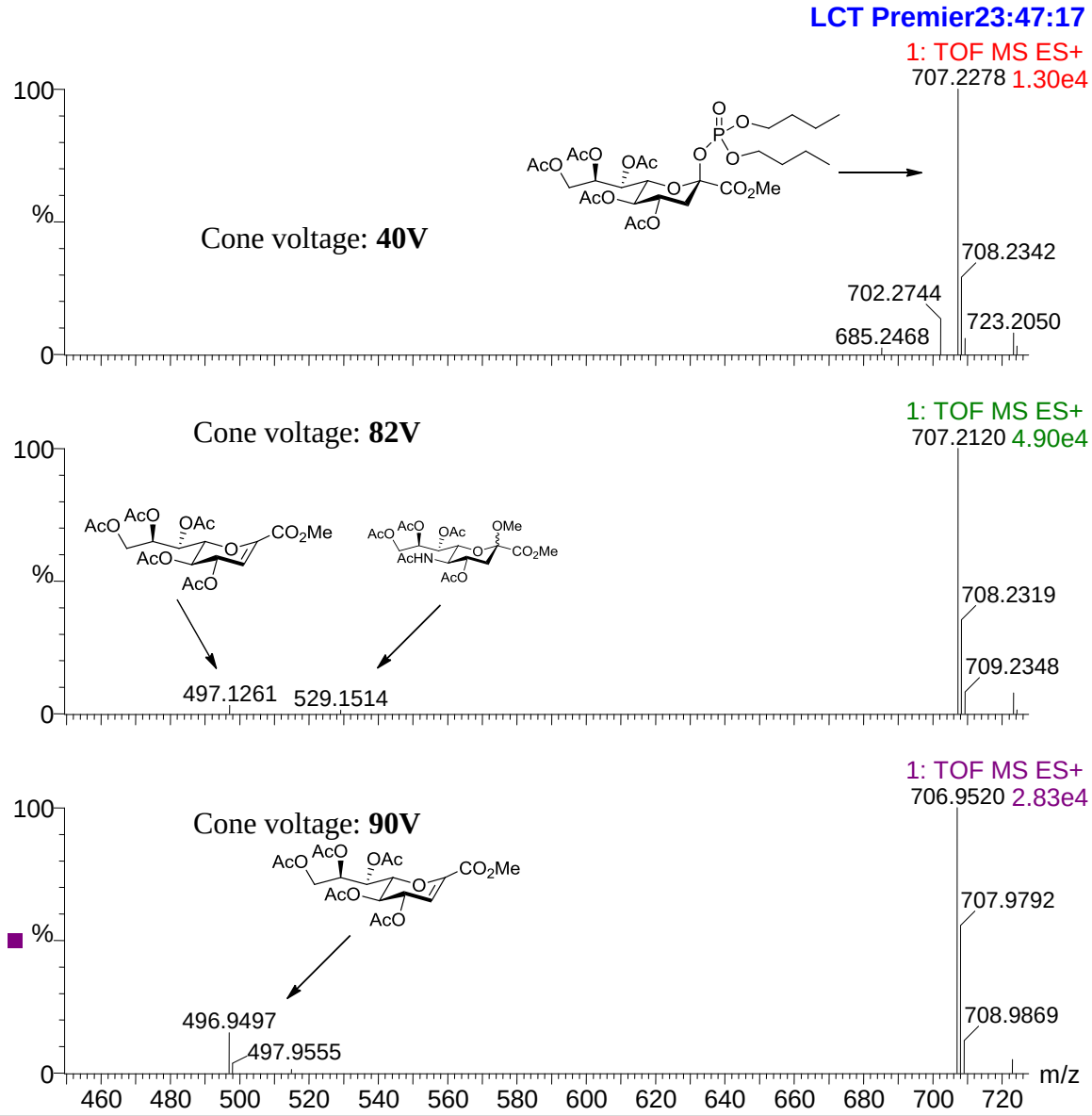
In-source fragmentation of Methyl (7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-2-(dibutylphosphoryl)-3,5-dideoxy-D-glycero-β-D-galacto-non-2-ulopyranoside)onate (16) (all the peaks correspond to sodiated molecular ions):



In-source fragmentation of Methyl (5-acetamido-7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-2-(dibutylphosphoryl)-3,5-dideoxy-D-glycero-β-D-galacto-non-2-ulopyranoside)onate (17) (all the peaks correspond to sodiated molecular ions unless specified):



In-source fragmentation of Methyl (4,5,7,8,9-penta-*O*-acetyl-2-(dibutylphosphoryl)-3-deoxy-D-glycero-β-D-galacto-non-2-ulopyranoside)onate (18) (all the peaks correspond to sodiated molecular ions):



In-source fragmentation of Methyl (7,8,9-tri-*O*-acetyl-4,5-*O*-carbonyl-2-(dibutylphosphoryl)-3-deoxy-D-glycero-β-D-galacto-non-2-ulopyranoside)onate (19): (all the peaks correspond to sodiated molecular ions)