Supporting Information

For

Probing the Influence of Protecting Groups on the Anomeric Equilibrium in Sialic Acid Glycosides with the Persistent Radical Effect

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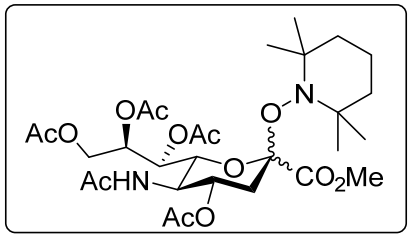
General Experimental. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution unless otherwise stated at 500 or 600 MHz. ESI mass spectra were recorded using a Waters LCT Premiere Xe TOF mass spectrometer. All reagents were purchased from commercial suppliers and were used without further purification and all the reaction solvents were dried over activated molecular sieves prior to use. Chromatographic purifications were carried over silica gel unless otherwise stated. Specific rotations were recorded in CH_2Cl_2 solution at room temperature. The anomeric stereochemistry of the sialosides was assigned based on the $^{3}J_{C1\text{-}H3ax}$ values[1] unless otherwise stated. All deuterated solvents used for the equilibration experiments were purchased from Cambridge Isotope Laboratories.

General protocol 1 : Synthesis of *O*-sialyl hydroxylamines. A solution of sialyl xanthate[2] **8** and nitroxyl radical in anhydrous 1,2-dichloroethane was degassed, purged with argon and photolyzed (254 nm, Rayonnet® photoreactor, Pyrex®). After completion of the reaction, the solution was concentrated under reduced pressure and the residue was purified by column chromatography using the eluents indicated to obtain the *O*-sialyl hydroxylamines as mixtures of anomers.

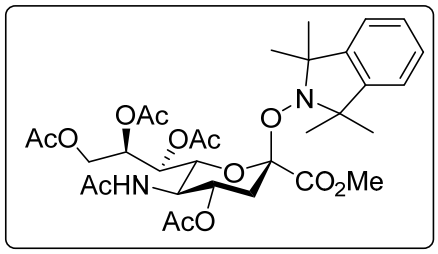
Synthesis of TEMPO sialoside (14).



The mixture of anomers **14** were synthesized following the procedure reported earlier,[3] and purified by neutral alumina column chromatography (eluting with ethylacetae/hexane 1:1) to obtain a separable mixture of anomers the data of which are identical with the earlier report.[3]

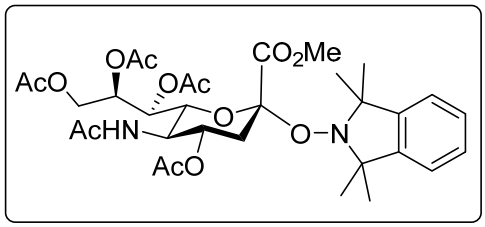
Synthesis of TMIO sialoside (15): This mixture of compounds **15** was synthesized following the general protocol 1 from sialyl xanthate[2] **8** (500 mg, 0.84 mmol), TMIO[4] **11** (1.59 g, 8.4 mmol) and 1,2-dichloroethane (5 mL). The reaction was complete in 2 days, after which the reaction mixture was concentrated and purified by silica gel column chromatography eluting with ethylacetate/hexane (1:3) to obtain the product (402 mg, 72 %) as a separable mixture (α:β, 1:2.2) of diastereomers.

Methyl [2-((1,1,3,3-tetramethylisoindolin-2-yl)oxy) 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-D-glycero-β-D-galacto-non-2-ulopyranosid]onate (15β).



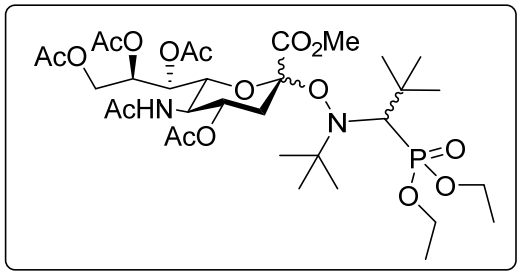
$[\alpha]^{24}_{D}$ = -0.3 (*c* = 0.5, CH_2Cl_2), ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.27 - 7.18 (m, 2 H), 7.06 (dd, *J* = 3.7, 5.1 Hz, 2 H), 5.44 (s, 1 H), 5.35 - 5.20 (m, 3 H), 5.00 (dd, *J* = 1.5, 12.5 Hz, 1 H), 4.43 (dd, *J* = 2.6, 10.6 Hz, 1 H), 4.22 - 4.10 (m, 2 H), 3.65 (s, 3 H), 2.83 (dd, *J* = 4.4, 13.2 Hz, 1 H), 2.14 (s, 3 H), 2.10 (s, 3 H), 2.05 (s, 3 H), 2.03 (s, 3 H), 1.95 (t, *J* = 12.4 Hz, 1 H), 1.88 (s, 3 H), 1.47(s, 3 H), 1.46(s, 3 H), 1.47(s, 3 H), 1.46(s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.4, 171.0, 170.5, 170.2, 170.1, 165.9, 144.1, 143.7, 127.66, 127.60, 121.55, 121.53, 104.6, 74.0, 73.9, 69.64, 69.60, 68.9, 68.5, 63.2, 51.8, 49.1, 38.8, 29.3, 28.8, 26.7, 25.8, 23.21, 21.1, 20.9, 20.71. ESIHRMS Calcd for $C_{32}H_{44}N_2NaO_{13}$ $[M + Na]^+$, 687.2741; found, 687.2756.

Methyl [2-((1,1,3,3-tetramethylisoindolin-2-yl)oxy) 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-D-glycero-α-D-galacto-non-2-ulopyranosid]onate (15α).



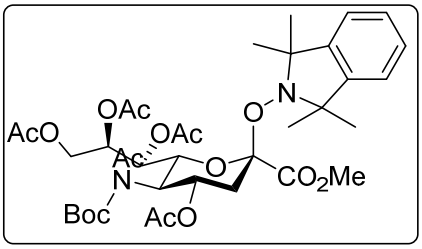
$[\alpha]^{24}_{D}$ = +3.2 (*c* = 0.5, CH_2Cl_2), ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.27 - 7.18 (m, 2 H), 7.12 - 7.03 (m, 2 H), 5.46 - 5.39 (m, 1 H), 5.32 (d, *J* = 7.7 Hz, 1 H), 5.18 - 5.08 (m, 1 H), 4.94 (ddd, *J* = 4.6, 9.7, 12.1 Hz, 1 H), 4.42 (dd, *J* = 2.4, 12.3 Hz, 1 H), 4.20 (dd, *J* = 5.9, 12.5 Hz, 1 H), 4.04 - 3.95 (m, 2 H), 3.86 - 3.76 (m, 3 H), 2.73 (t, *J* = 12.7 Hz, 1 H), 2.52 (dd, *J* = 4.6, 13.0 Hz, 1 H), 2.14 (s, 3 H), 2.09 (s, 3 H), 2.05 (s, 3 H), 2.02 (s, 3 H), 1.89 (s, 3 H), 1.58 (s, 3 H), 1.45 (s, 3 H), 1.38 (s, 3 H), 1.29 (m, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.0, 170.6, 170.19, 170.13, 169.9, 167.6, 144.8, 143.8, 127.5, 127.3, 121.8, 103.1, 76.5, 72.9, 70.5, 69.9, 69.7, 68.7, 67.7, 67.6, 62.1, 52.7, 52.5, 49.5, 34.9, 29.3, 29.1, 26.0. $C_{32}H_{44}N_2NaO_{13}$ $[M + Na]^+$, 687.2741; found, 687.2753.

Methyl ([2-(*N*-tert-butyl-1-diethylphosphono-2,2-dimethylpropylamin-)oxy] 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-D-glycero-α/β-D-galacto-non-2-ulopyranosid)onate (16).



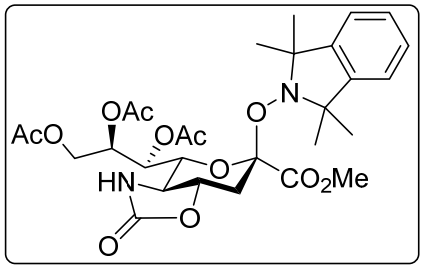
This mixture of compounds **16** was synthesized following the general protocol 1 from sialyl xanthate[2] **8** (100 mg, 0.16 mmol) and **12**[5] (564 mg, 1.92 mmol). The reaction was complete in 2 days, after which the reaction mixture was concentrated and purified by silica gel column chromatography eluting with ethylacetate/hexane (3:2) to obtain the product (52 mg, 45 %) as a inseparable mixture (α:β, 1.5:1) of diastereomers. The anomeric stereochemistry of the diastereomers was determined by comparing the ^{1}H nmr data with **14**. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 5.41 (dd, *J* = 2.4, 5.0 Hz, 1 H), 5.30 - 5.18 (m, 3 H), 5.15 (brs, 1 H), 5.08 (dt, *J* = 6.8, 10.2 Hz, 1 H), 5.05 – 5.00 (m, 1 H), 4.55 (dd, *J* = 2.2, 12.8 Hz, 1 H), 4.41 (dd, *J* = 2.6, 12.5 Hz, 1 H), 4.30 (dd, *J* = 4.8, 12.8 Hz, 1 H), 4.24 (td, *J* = 7.2, 10.6 Hz, 1 H), 4.15 – 3.75 (m, 10 H), 3.81 (s, 3H), 3.79 (s, 3H), 3.62 - 3.59 (m, 2 H), 3.35 (brd, *J* = 4.0 Hz, 1 H), 3.30 (brd, *J* = 3.3 Hz, 1 H), 2.84 (dd, *J* = 4.8, 12.8 Hz, 1 H), 2.76 - 2.68 (m, 2 H), 2.58 (t, *J* = 12.3 Hz, 1 H), 2.07 – 2.04 (m, 18 H), 2.02 (s. 3H), 1.99 (s, 3H), 1.86 (s, 3H), 1.30 - 1.20 (m, 30 H), 1.14 - 1.10 (m, 18 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.08, 171.02, 170.56, 170.53, 170.18, 170.11, 170.0, 169.9, 169.8, 169.7, 167.1, 166.7, 104.9, 103.6, 73.1, 72.5, 70.8, 70.45, 70.41, 70.2, 69.8, 69.3, 67.6, 67.5, 63.5, 63.3, 62.9, 62.8, 62.1, 62.08, 62.02, 61.5, 60.0, 59.0, 58.98, 58.93, 58.8, 52.8, 52.5, 49.0, 48.7, 36.45, 36.41, 35.6, 35.5, 34.3, 34.2, 30.14, 30.10, 30.07, 30.03, 28.4, 28.3, 27.14, 27.11, 23.2, 23.1, 21.09, 21.03, 20.97, 20.94, 20.8, 20.7, 20.6, 20.5, 16.6, 16.58, 16.51, 16.4, 16.2, 16.19, 16.17, 16.14. ESIHRMS Calcd for $C_{33}H_{57}N_2NaO_{16}P$ $[M + Na]^+$, 791.3343; found, 791.3328.

Methyl [2-((1,1,3,3-tetramethylisoindolin-2-yl)oxy)5-acetamido-5-*N*-(1,1-dimethylethoxy) carbonyl-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-D-glycero-β-D-galacto-non-2-ulopyranosid]on ate (27).



To a solution of **15β** (200 mg, 0.30 mmol) in 2 mL of anhydrous THF was added di-*tert*-butyl dicarbonate (90 mg, 0.41 mmol) followed by DMAP (10 mg, 0.08 mmol) at room temperature. After stirring for 10 h at 60 ^{o}C under argon, the reaction mixture was concentrated under reduced pressure and the residue was purified by silica gel column chromatography eluting with ethylacetate/hexane (1:4) to obtain the desired product **27β** (191 mg) in 83 % yield. $[\alpha]^{24}_{D}$ = -22.3 (*c* = 1, CH_2Cl_2), ^{1}H NMR (600 MHz, $CDCl_3$, 22.0 ^{o}C) δ = 7.26 - 7.16 (m, 2 H), 7.10 - 6.92 (m, 2 H), 5.73 (dt, *J* = 4.6, 11.1 Hz, 1 H), 5.35 - 5.23 (m, 2 H), 5.12 (dd, *J* = 2.0, 10.1 Hz, 1 H), 5.06 - 4.96 (m, 1 H), 4.89 (t, *J* = 10.5 Hz, 1 H), 4.38 (s, 1 H), 4.20 (dd, *J* = 8.8, 12.5 Hz, 1 H), 4.15 - 3.99 (m, 1 H), 3.79 (s, 1 H), 3.71 (s, 1 H), 3.65 (s, 2 H), 2.95 (dd, *J* = 4.6, 13.0 Hz, 1 H), 2.46 - 2.29 (m, 3 H), 2.22 - 2.10 (m, 1 H), 2.09 - 1.94 (m, 11 H), 1.60 - 1.42 (m, 16 H), 1.41 - 1.32 (m, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.6, 170.8, 170.49, 170.40, 170.0, 166.1, 152.0, 144.1, 143.8, 127.57, 127.55, 121.5, 121.4, 104.9, 85.0, 74.0, 72.8, 69.62, 69.61, 68.6, 66.6, 63.1, 60.3, 52.3, 51.7, 40.3, 29.5, 28.7, 27.9, 27.8, 27.1, 26.5, 25.8, 21.04, 21.02, 20.9, 20.87, 20.81, 20.7, 14.1. ESIHRMS Calcd for $C_{37}H_{52}N_2NaO_{15}$ $[M + Na]^{+}$, 787.3265; found, 787.3263.

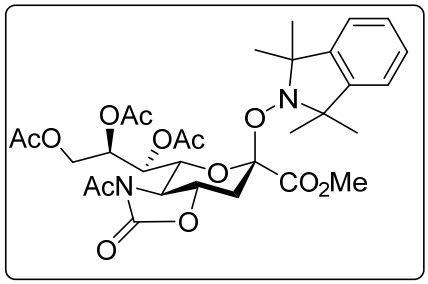
Methyl [2-((1,1,3,3-tetramethylisoindolin-2-yl)oxy)7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-2-D-glycero-β-D-galacto-non-2-ulopyran osid]onate (31β).



To a solution of the compound **27β** (200 mg, 0.26 mmol) in methanol was added a catalytic amount of NaOMe under argon. After stirring for 3 h at room temperature, the reaction mixture was quenched by the addition of Amberlyst 15 ion-exchange resin, filtered and concentrated. The residue was then treated with 2 mL of trifluoroacetic acid for 1 h at room temperature and concentrated under reduced pressure. To a vigorously stirred solution of the concentrate, $NaHCO_3$ (216 mg, 2.6 mmol) in a mixture of acetonitrile (1 mL) and water (2 mL) at 15 ^oC, was added drop-wise, a solution of 4-nitrophenyl chloroformate (104 mg, 0.52 mmol) in acetonitrile (1 mL). After stirring the reaction mixture for 3 h at the same temperature, it was extracted with ethylacetate and the combined extracts were washed with water, brine, dried over Na_2SO_4 and concentrated. The crude residue was immediately dissolved in a 1:1 mixture of acetic anhydride/pyridine (2 mL) and was stirred overnight at room temperature. The solvents were evaporated and the resulting residue was purified by silica gel column chromatography eluting with ethyl acetate/hexane (2:3) to obtain the desired compound **31β** (96 mg) in 61 % yield over 4 steps. $[\alpha]^{24}_D$ = -20.5 (*c* = 1, CH_2Cl_2), ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.29 - 7.18 (m, 2 H), 7.10 - 7.00 (m, 2 H), 5.44 - 5.34 (m, 2 H), 5.26 - 5.20 (m, 1 H), 4.81 - 4.73 (m, 1 H), 4.64 - 4.52 (m, 1 H), 4.41 (dd, *J* = 2.9, 9.9 Hz, 1 H), 4.30 (dd, *J* = 6.6, 12.8 Hz, 1 H), 3.67 (s, 3 H), 3.11 (t, *J* = 10.5 Hz, 1 H), 3.08 - 3.01 (m, 1 H), 2.18 (s, 3 H), 2.10 (s, 3 H), 2.04 (s, 3 H), 1.47 (s, 3 H), 1.40 (s, 3 H), 1.36 (s, 3 H), 1.35 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.9, 170.4, 170.3, 165.6 ($^3J_{C1\text{-}H3ax}$ = 1.6 Hz), 159.3, 143.9, 143.4, 127.69, 127.62, 121.5, 121.4, 105.3, 77.2, 76.9, 76.7,

76.4, 73.8, 71.3, 71.0, 69.6, 68.4, 62.1, 60.0, 58.4, 51.9, 39.0, 29.3, 28.9, 26.3, 25.8, 21.1, 20.7, 20.6. ESIHRMS Calcd for $C_{29}H_{38}N_2NaO_{12}$ $[M + Na]^+$, 629.2322; found, 629.2330.

Methyl [2-((1,1,3,3-tetramethylisoindolin-2-yl)oxy) 5-acetamido-7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-2-D-glycero-β-D-galacto-non-2-ulopyranosid]onate (33β).

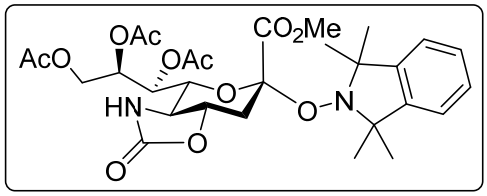


To a solution of the compound **31β** (40 mg, 0.06 mmol) in 1 mL of anhydrous CH_2Cl_2, was added diisopropylethylamine (114 μL, 0.66 mmol) at 0 ^oC, followed by acetyl chloride (21 μL, 0.33 mmol). After the completion of reaction (observed by thin layer chromatography), the reaction mixture was diluted with CH_2Cl_2 (5 mL), poured into cold saturated $NaHCO_3$ solution (5 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 3 mL). The combined organic extracts were washed with water, brine, dried over Na_2SO_4, concentrated under reduced pressure. The residue was purified by silica gel column chromatography eluting with EtOAc/hexane (1:1) to obtain pure **33β** as foam. $[\alpha]^{24}_D$ = -6.4 (*c* = 0.7, CH_2Cl_2), ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.28 - 7.18 (m, 2 H), 7.11 - 7.00 (m, 2 H), 5.62 (s, 1 H), 5.41 (d, *J* = 8.1 Hz, 1 H), 4.81 - 4.68 (m, 2 H), 4.68 - 4.58 (m, 1 H), 4.08 (dd, *J* = 8.4, 12.1 Hz, 1 H), 3.76 - 3.69 (m, 1 H), 3.68 (s, 3 H), 3.08 (dd, *J* = 3.3, 12.1 Hz, 1 H), 2.49 (s, 3 H), 2.23 (t, *J* = 12.7 Hz, 1 H), 2.15 (s, 3 H), 2.13 (s, 2 H), 2.03 (s, 3 H), 1.48 (s, 3 H), 1.43 (s, 3 H), 1.42 (s, 3 H), 1.35 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.4, 171.2, 170.5, 169.6, 165.7, 153.8, 144.0, 143.3, 127.7, 127.6, 121.55, 121.51, 104.3, 76.3, 74.4, 73.9, 72.8, 69.6, 68.8, 63.1, 59.3,

52.0, 37.9, 29.4, 28.9, 26.3, 26.0, 24.7, 21.1, 20.7, 20.6. ESIHRMS Calcd for $C_{31}H_{40}N_2NaO_{13}$ [M + Na]$^+$, 671.2428; found, 671.2400.

General protocol 2: Equilibration of sialosides. A solution of sialyl hydroxylamine (0.05-0.1 M) in deuteriobenzene/deuterio-1,2-dichloroethane/deuterioacetonitrile, in an NMR tube was degassed, sealed under argon and was heated at 90 ^oC. With periodic monitoring, the reaction mixture was heated at the same temperature until it reached equilibrium. The reaction mixture was concentrated under reduced pressure and purified by silica gel column chromatography using ethylacetate/hexane as eluents. Compounds **31α**, **33α** were synthesized using this protocol from corresponding **31β** and **33β** respectively. Compounds **25α**, **30β** and **32β** were also synthesized using this protocol from corresponding **25β**, **30α** and **32α** as reported earlier.[1]

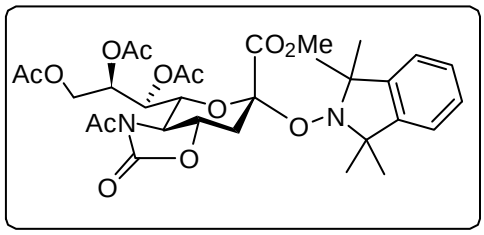
Methyl [2-((1,1,3,3-tetramethylisoindolin-2-yl)oxy)7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-2-D-glycero-α-D-galacto-non-2-ulopyranosid]onate (31α).



$[\alpha]^{24}_D$ = -18.3(*c* = 1, CH_2Cl_2), ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.28 - 7.18 (m, 2 H), 7.11 - 7.02 (m, 2 H), 5.49 (td, *J* = 2.3, 9.7 Hz, 1 H), 5.34 (s, 1 H), 5.15 (d, *J* = 9.9 Hz, 1 H), 4.39 (d, *J* = 2.6 Hz, 2 H), 4.18 (d, *J* = 9.9 Hz, 1 H), 4.06 - 3.96 (m, 1 H), 3.80 (s, 3 H), 3.03 (t, *J* = 10.5 Hz, 1 H), 2.89 - 2.79 (m, 2 H), 2.18 (s, 3 H), 2.13 (s, 3 H), 2.06 (s, 3 H), 1.51 (s, 3 H), 1.46 (s, 3 H), 1.37 (s, 3 H), 1.30 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.1, 170.5, 169.7, 167.3 ($^3J_{C1\text{-}H3ax}$ = 7.0 Hz), 159.4, 144.3, 143.8, 127.5, 127.4, 121.7, 121.5, 104.4, 77.6, 76.7, 73.5, 68.9, 68.8, 68.7, 67.8, 61.4, 60.0, 57.8,

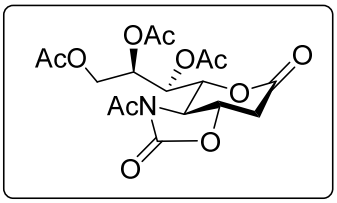
52.9, 34.5, 29.3, 29.2, 26.0, 25.6, 20.9, 20.67, 20.61. ESIHRMS Calcd for $C_{29}H_{38}N_2NaO_{12}$ [M + Na]$^+$, 629.2322; found, 629.2338.

Methyl [2-((1,1,3,3-tetramethylisoindolin-2-yl)oxy) 5-acetamido-7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-2-D-glycero-α-D-galacto-non-2-ulopyranosid]onate (33α).



$[\alpha]^{24}_D$ = -2.1 (*c* = 0.6, CH_2Cl_2), ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.29 - 7.19 (m, 2 H), 7.14 - 7.03 (m, 2 H), 5.61 (d, *J* = 7.0 Hz, 1 H), 5.48 (dt, *J* = 2.9, 6.8 Hz, 1 H), 4.51 (d, *J* = 9.2 Hz, 1 H), 4.47 (dd, *J* = 2.8, 12.3 Hz, 1 H), 4.17 (dd, *J* = 6.6, 12.1 Hz, 1 H), 4.10 - 4.03 (m, 1 H), 3.84 (s, 3 H), 3.72 - 3.66 (m, 1 H), 2.96 (t, *J* = 12.8 Hz, 1 H), 2.83 (dd, *J* = 3.3, 12.1 Hz, 1 H), 2.48 (s, 3 H), 2.14 (s, 3 H), 2.11 (s, 3 H), 2.05 (s, 3 H), 1.55 (s, 3 H), 1.47 (s, 3 H), 1.40 (s, 3 H), 1.31 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.0, 170.6, 170.2, 169.7, 167.6, 153.8, 144.5, 143.6, 127.6, 127.4, 121.7, 121.4, 103.7, 76.1, 75.8, 72.2, 70.3, 68.8, 68.6, 62.7, 60.0, 59.0, 53.0, 33.0, 29.2, 29.1, 25.8, 25.3, 24.6, 21.0, 20.7. ESIHRMS Calcd for $C_{31}H_{40}N_2NaO_{13}$ [M + Na]$^+$, 671.2428; found, 671.2411.

4-Acetamido-6,7,8-tri-*O*-acetyl-4-*N*,3-*O*-carbonyl-2,4-dideoxy-D-glycero-D-galacto-octono-1,5-lactone (34).



A 0.1 M solution of compound **32α** was subjected to equilibration in CD_3CN following the general protocol. After heating for 10 h, the reaction mixture was concentrated and purified to obtain the δ-lactone **34** (1 mg) in 45 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 6.03 (d, *J* = 7.0 Hz, 1 H), 5.39 (dt, *J* = 2.9, 6.2 Hz, 1 H), 5.02 (d, *J* = 9.2 Hz, 1 H), 4.45 - 4.30 (m, 2 H), 4.17 (dd, *J* = 5.7, 12.7 Hz, 1 H), 3.79 (dd, *J* = 9.0, 11.6 Hz, 1 H), 3.31 (dd, *J* = 4.6, 17.1 Hz, 1 H), 2.68 (dd, *J* = 13.0, 17.1 Hz, 1 H), 2.56 - 2.51 (m, 3 H), 2.12 (s, 2 H), 2.11 (s, 2 H), 2.06 (s, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.3, 170.6, 169.6, 164.2, 152.6, 71.8, 71.2, 69.7, 61.7, 60.0, 58.1, 35.1, 29.6, 24.2, 20.9, 20.7, 20.6. ESIHRMS Calcd for $C_{17}H_{21}NNaO_{11}$ $[M + Na]^+$, 438.1012; found, 438.1016.

Crossover of 15 with TEMPO to give 14.

Compound **15** (38.3 mg, 0.06 mmol) and TEMPO (9.4 mg, 0.06 mmol) were dissolved in d_4-1,2-dichloroethan (600 µl) and the mixture was purged with argon, then sealed and heated to 90 ^{o}C. The reaction was monitored by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. After 9 days, no further change was observed. The reaction mixture was concentrated and TEMPO and TMIO were removed by silica gel column chromatography (eluting with chloroform/methanol, 10 : 1) and the residue (31.3 mg) mixture was used to determine the ratio of compounds by ^{1}H and ^{13}C (with inverse gated ^{1}H-decoupling) NMR spectroscopy.

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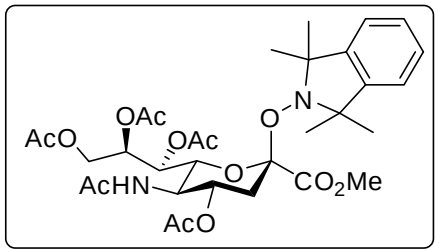
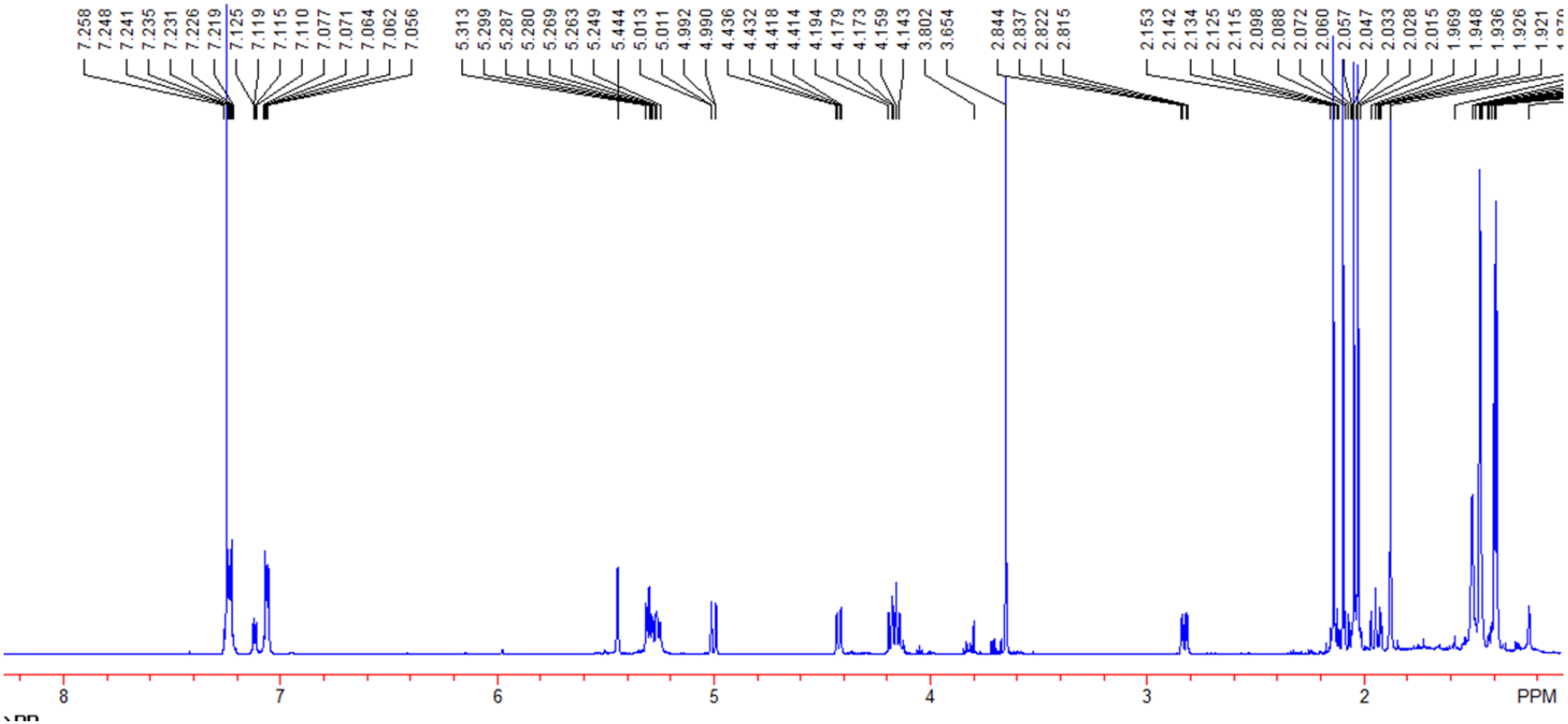
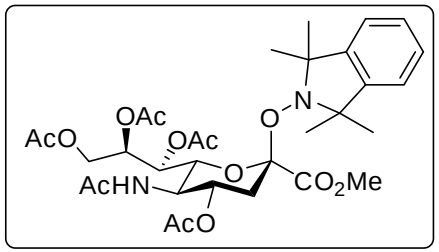
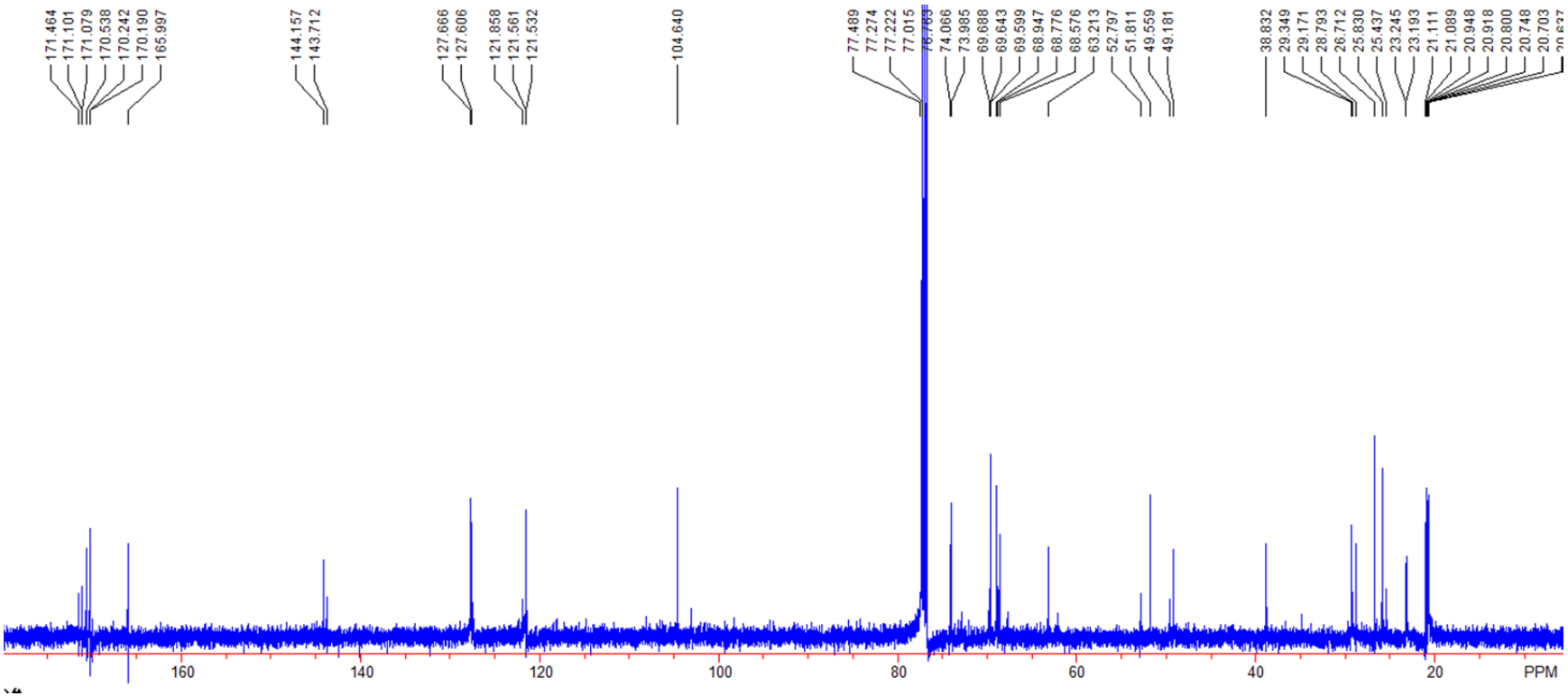
Methyl [2-((1,1,3,3-tetramethylisoindolin-2-yl)oxy) 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-D-glycero-β-D-galacto-non-2-ulopyranosid]onate ^{1}H NMR (600 MHz, $CDCl_3$) (15β)





Methyl [2-((1,1,3,3-tetramethylisoindolin-2-yl)oxy) 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-D-glycero-β-D-galacto-non-2-ulopyranosid]onate ^{13}C NMR (600 MHz, $CDCl_3$) (15β)





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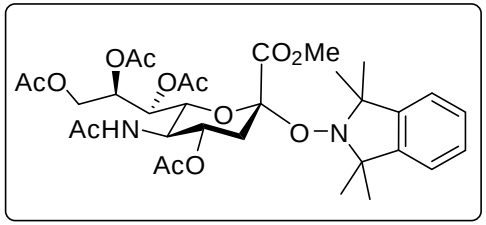
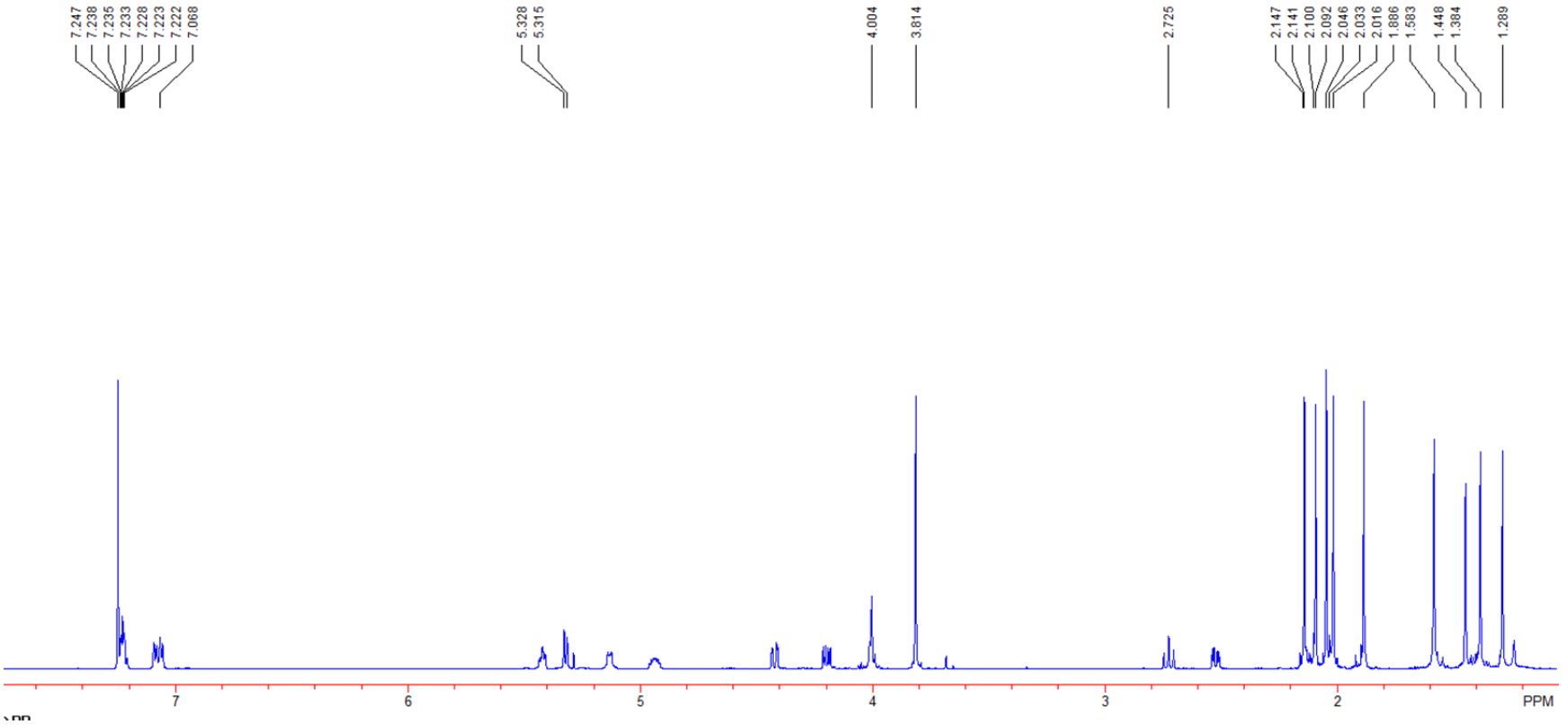
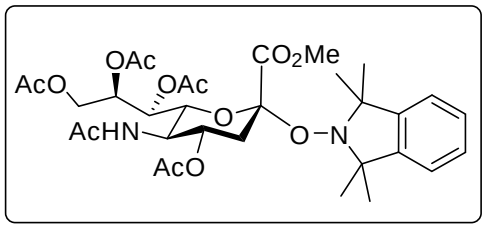
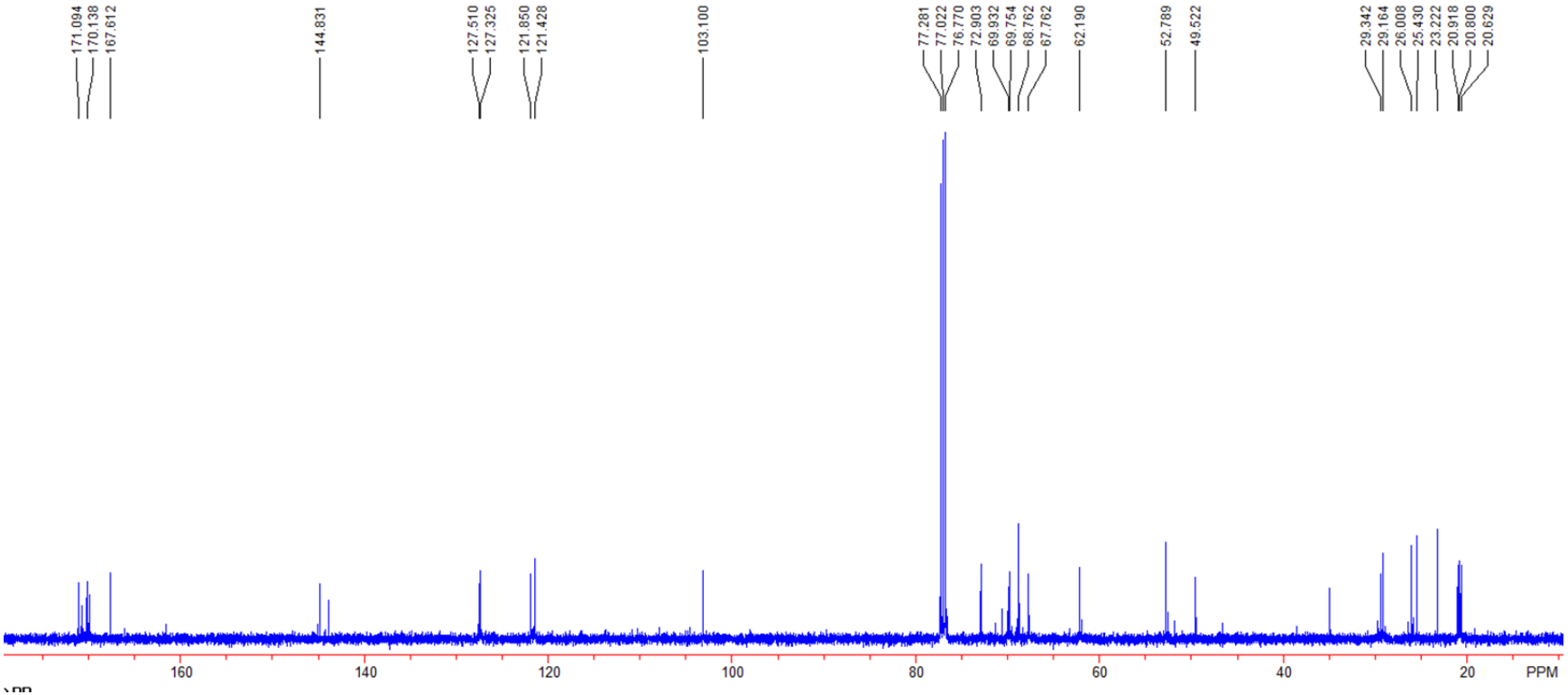


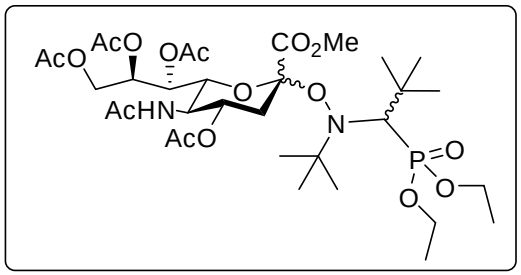


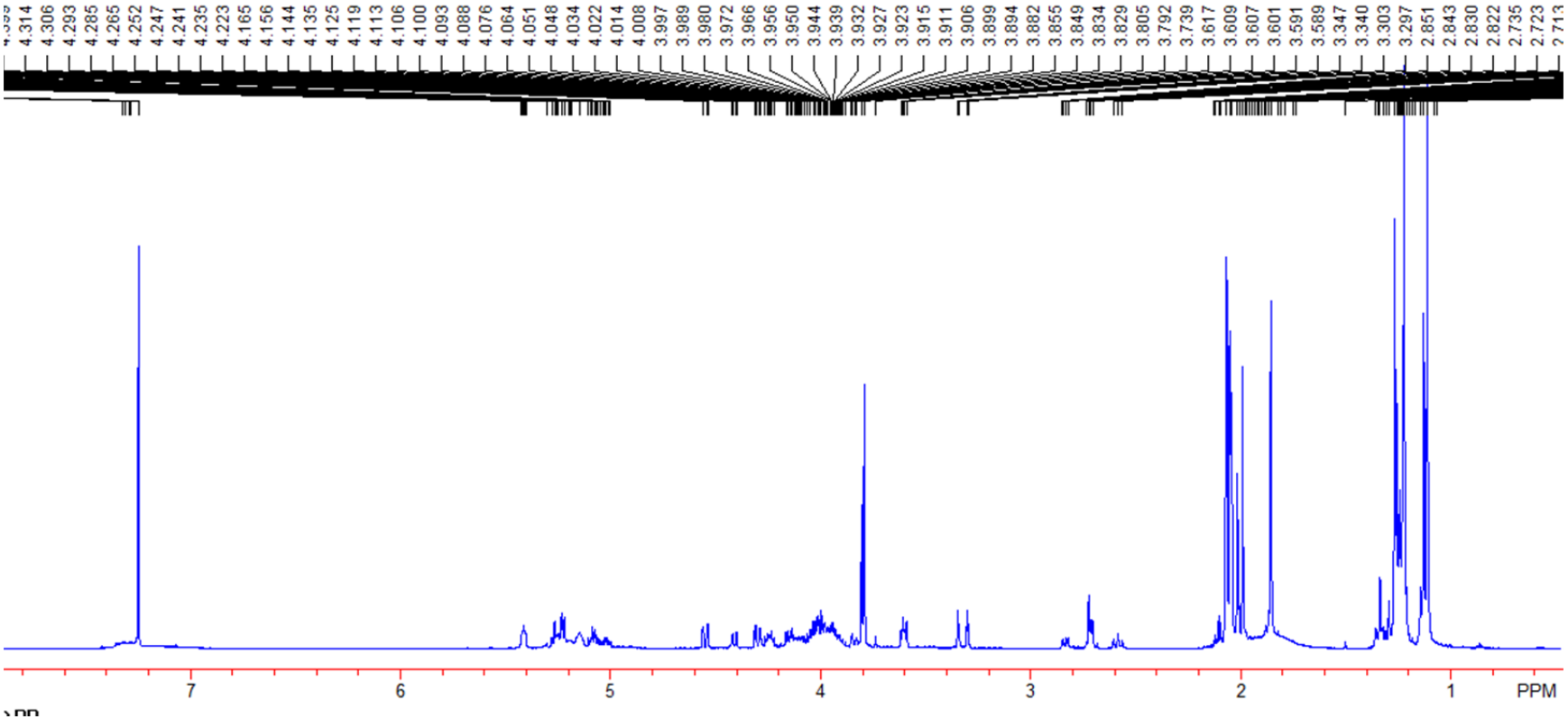
Methyl [2-((1,1,3,3-tetramethylisoindolin-2-yl)oxy) 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-D-glycero-α-D-galacto-non-2-ulopyranosid]onate ^{13}C NMR (150 MHz, $CDCl_3$) (15α)



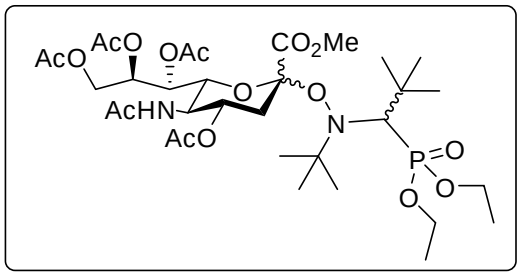


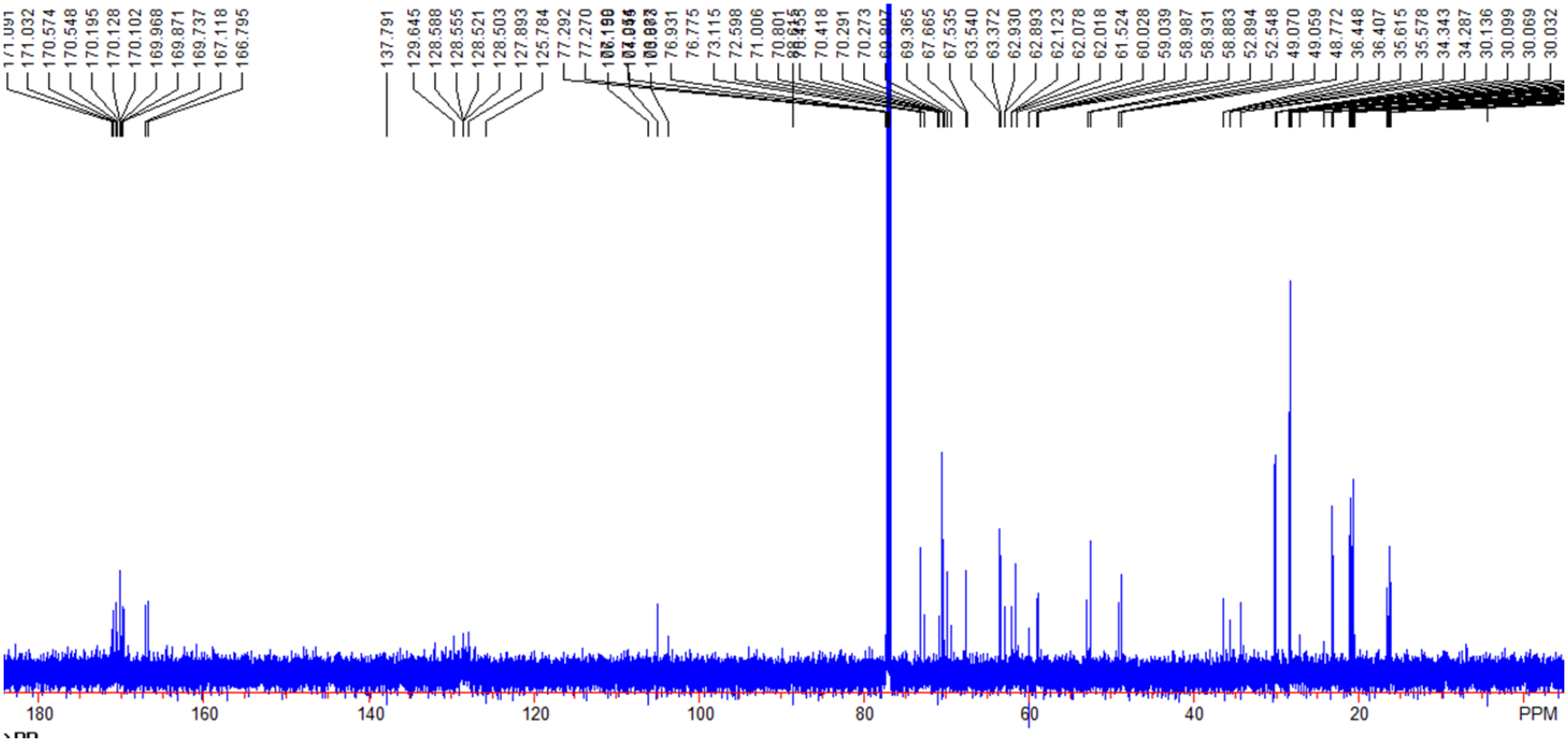
Methyl [2-(*N*-tert-butyl-1-diethylphosphono-2,2-dimethylpropylamin-)oxy] 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-D-glycero-α/β-D-galacto-non-2-ulopyranosid)onate ^{1}H NMR (600 MHz, $CDCl_3$) (16)





Methyl [2-(*N*-tert-butyl-1-diethylphosphono-2,2-dimethylpropylamin-)oxy] 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-D-glycero-α/β-D-galacto-non-2-ulopyranosid)onate ^{13}C NMR (150 MHz, $CDCl_3$) (16)





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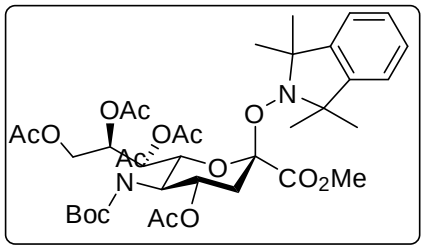

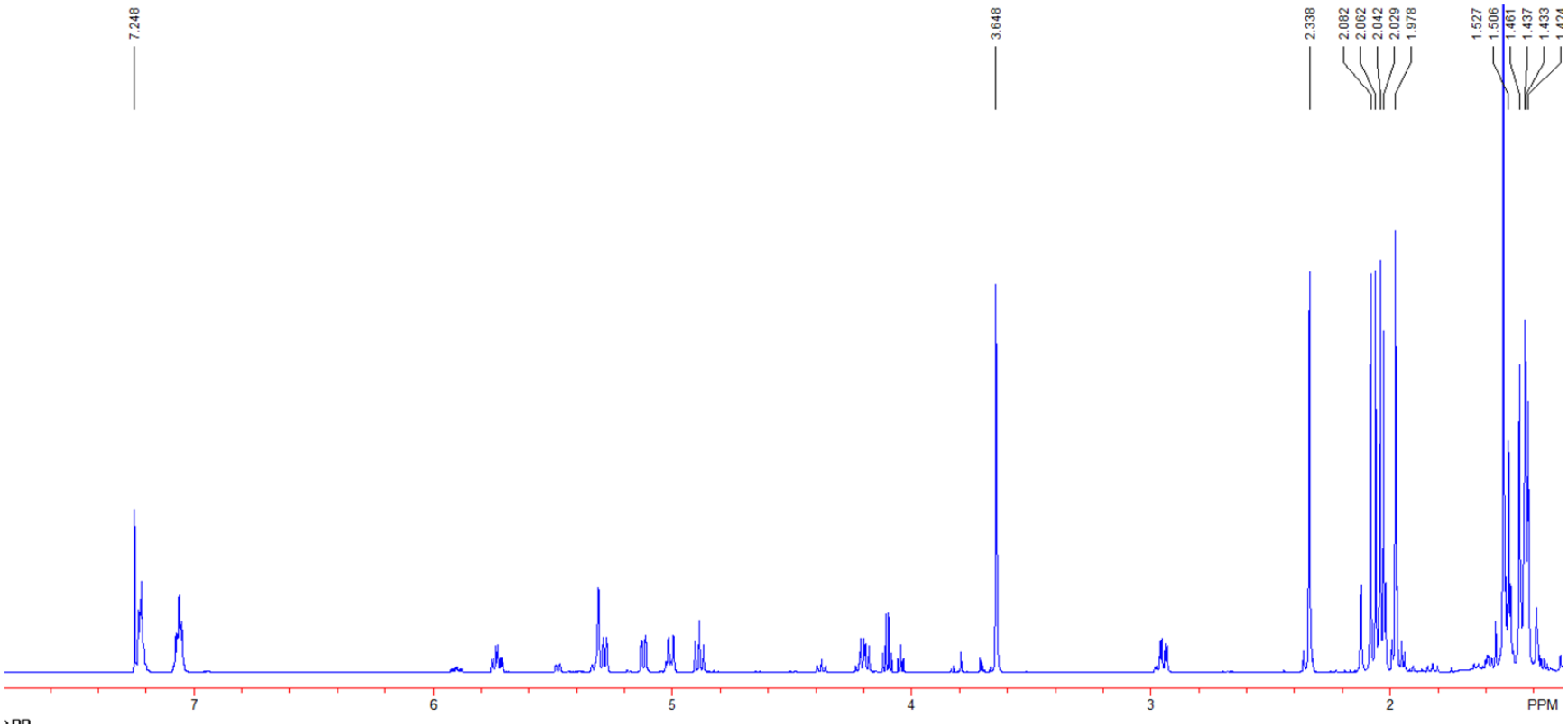

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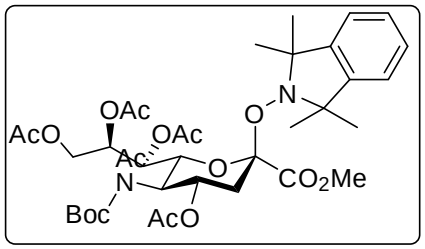
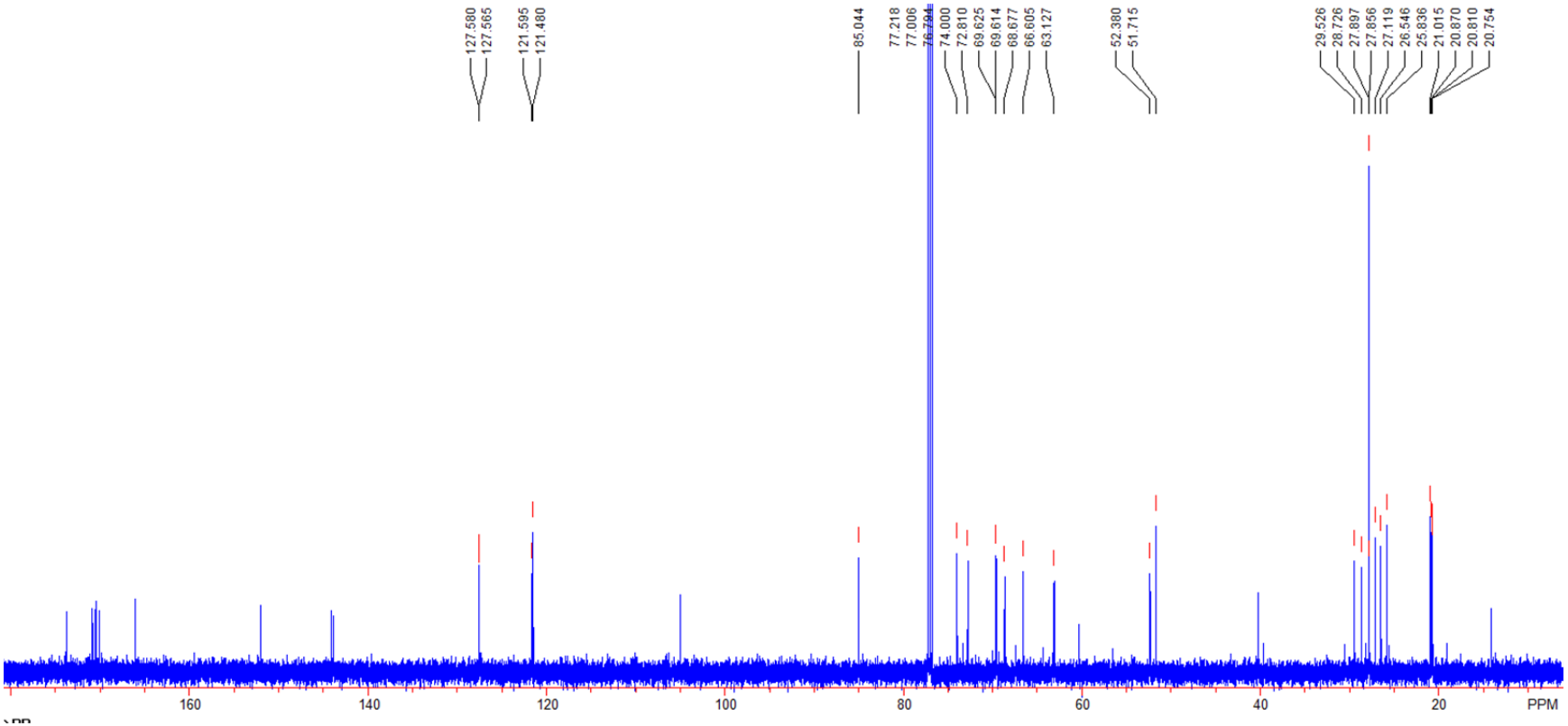
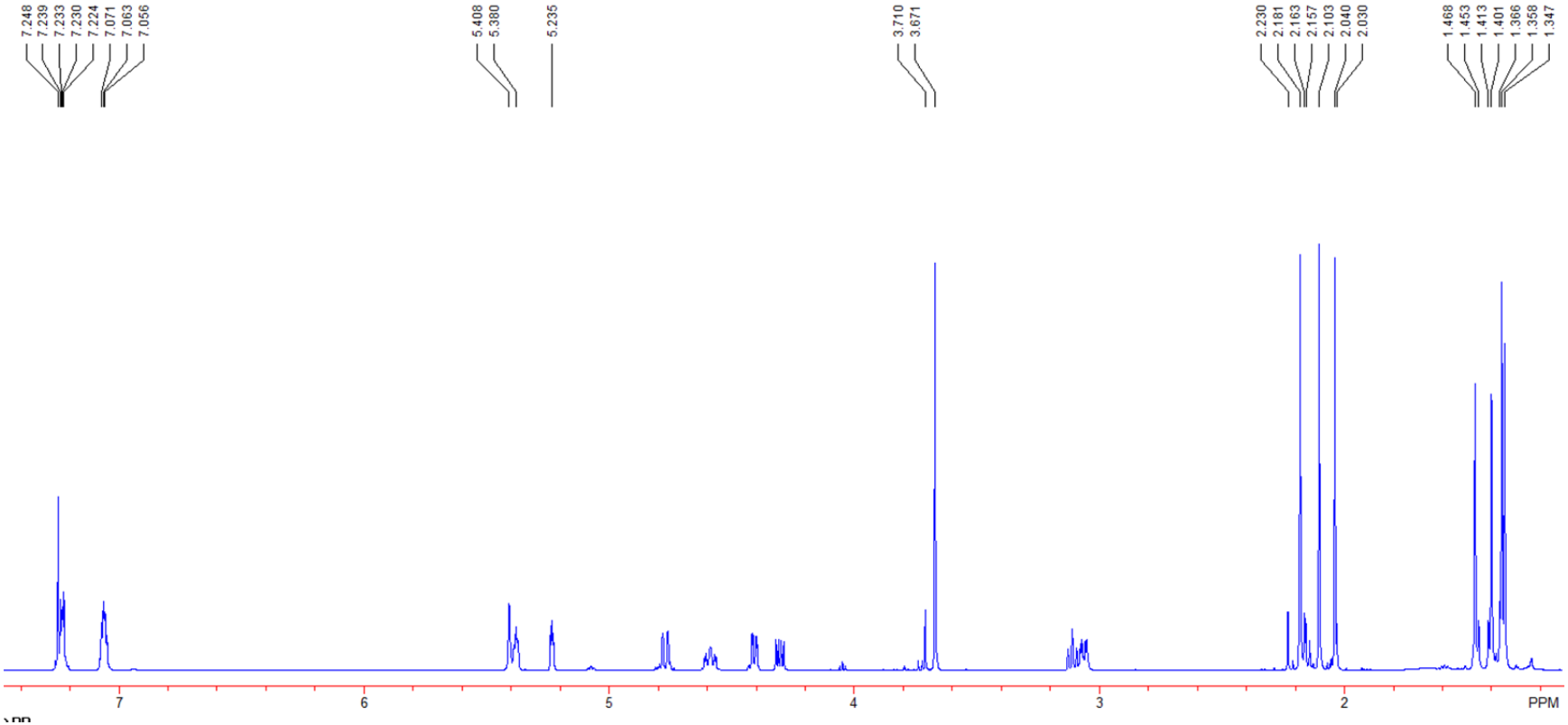




Methyl [2-((1,1,3,3-tetramethylisoindolin-2-yl)oxy) 7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-2-D-glycero-β-D-galacto-non-2-ulopyranosid]onate ^{1}H NMR (600 MHz, $CDCl_3$) (31β)



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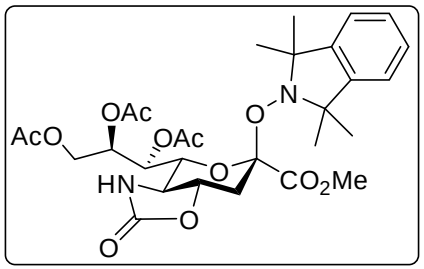
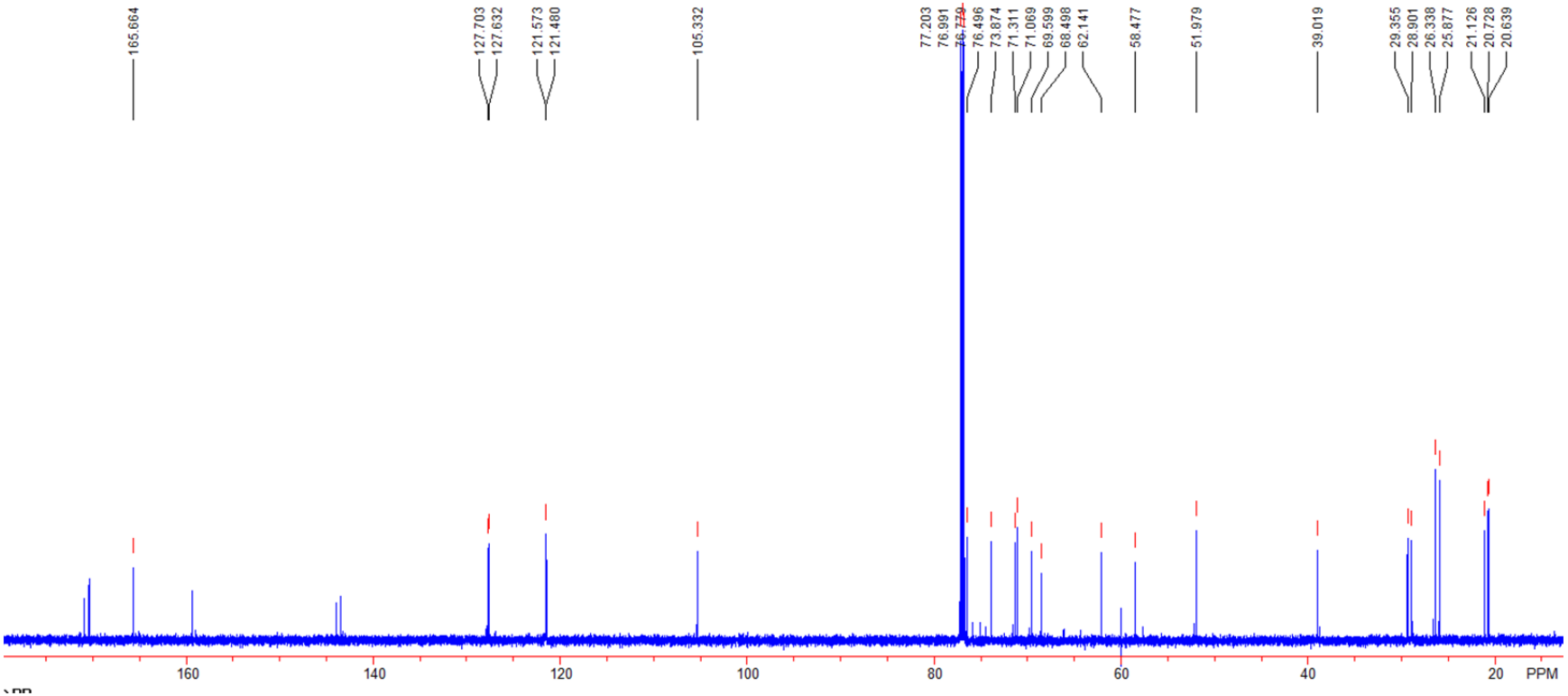
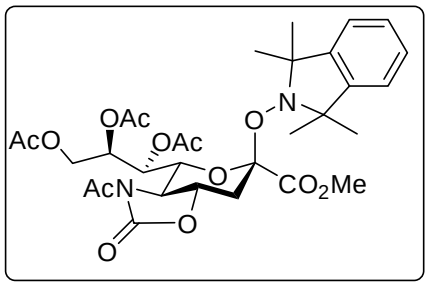
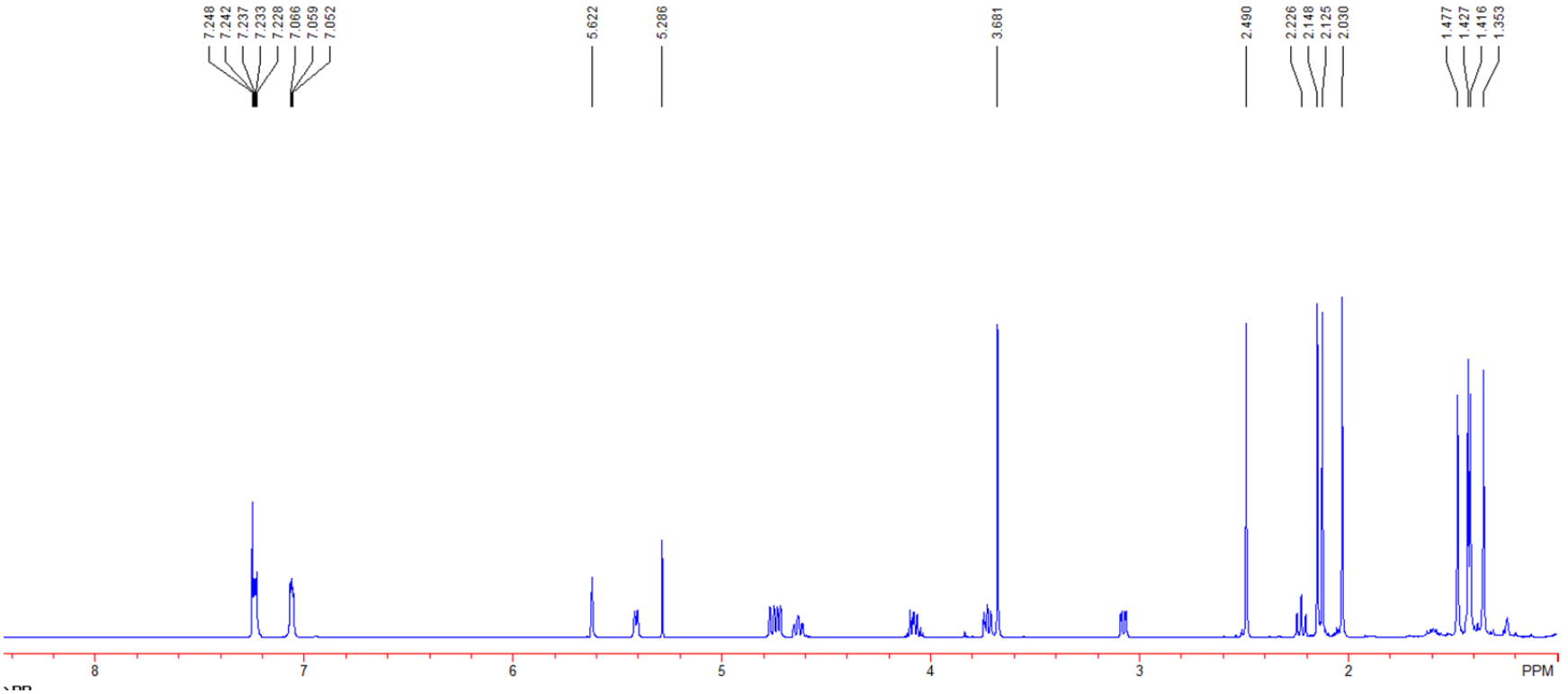




Methyl [2-((1,1,3,3-tetramethylisoindolin-2-yl)oxy) 5-acetamido-7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-2-D-glycero-β-D-galacto-non-2-ulopyranosid]onate ^{1}H NMR (600 MHz, $CDCl_3$) (33β)





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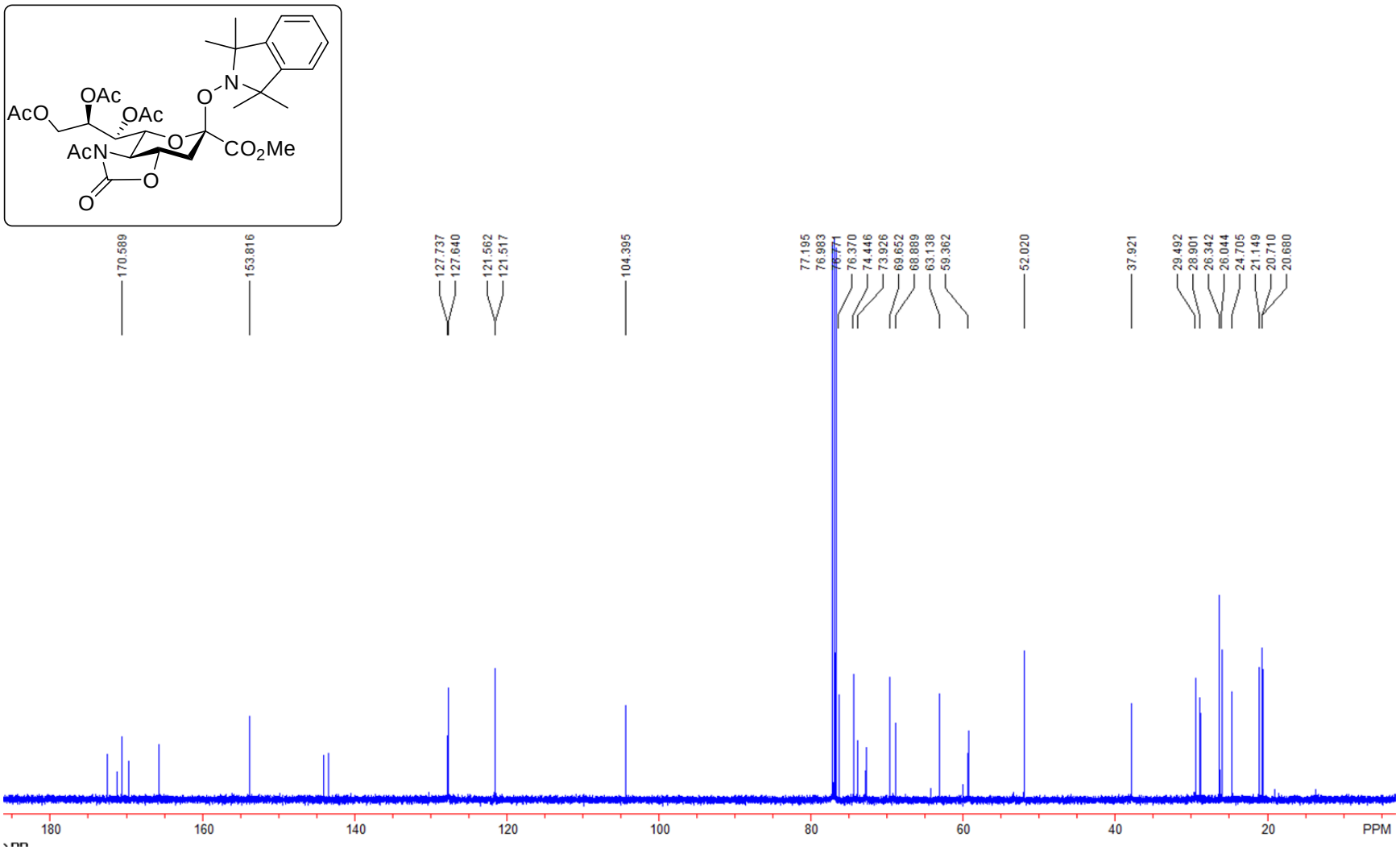

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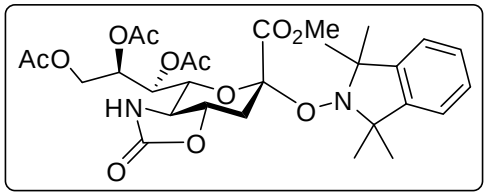

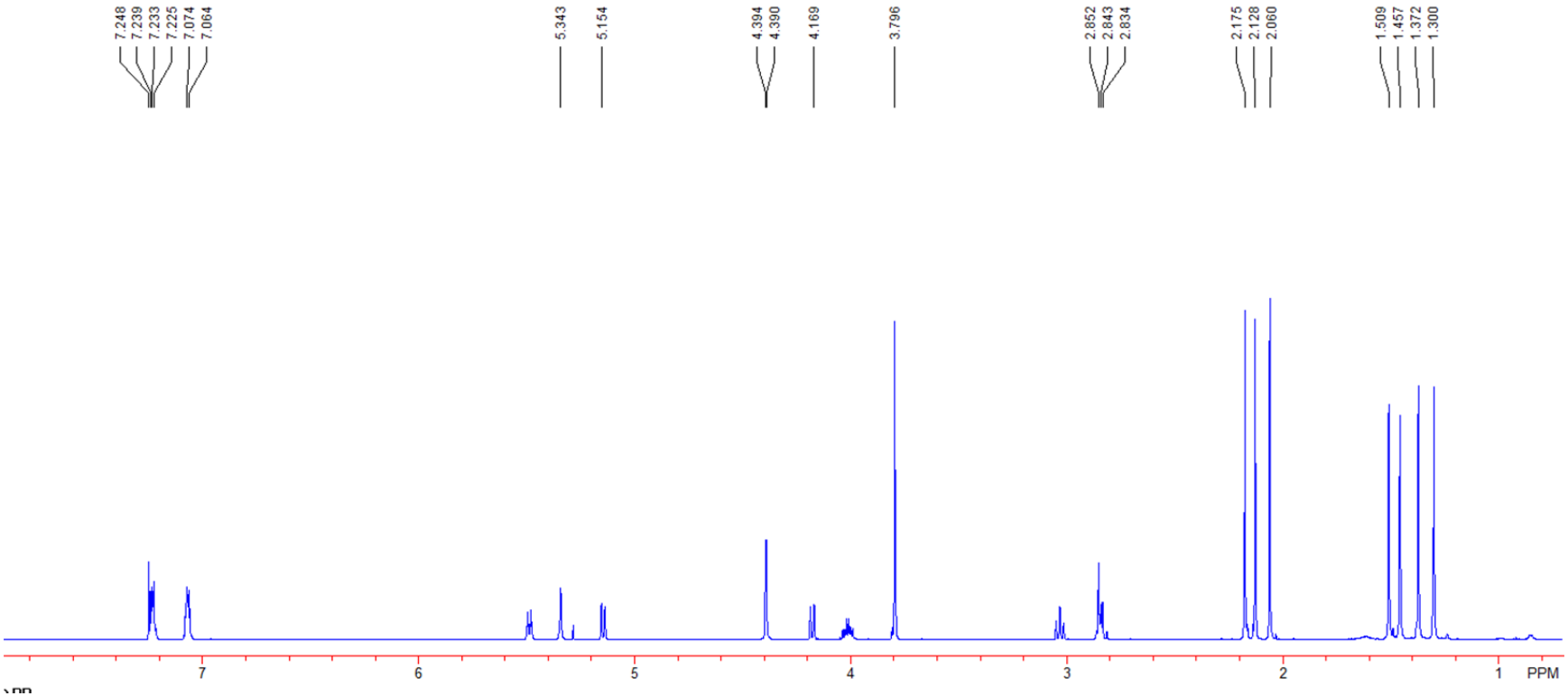

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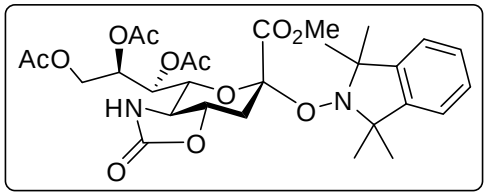
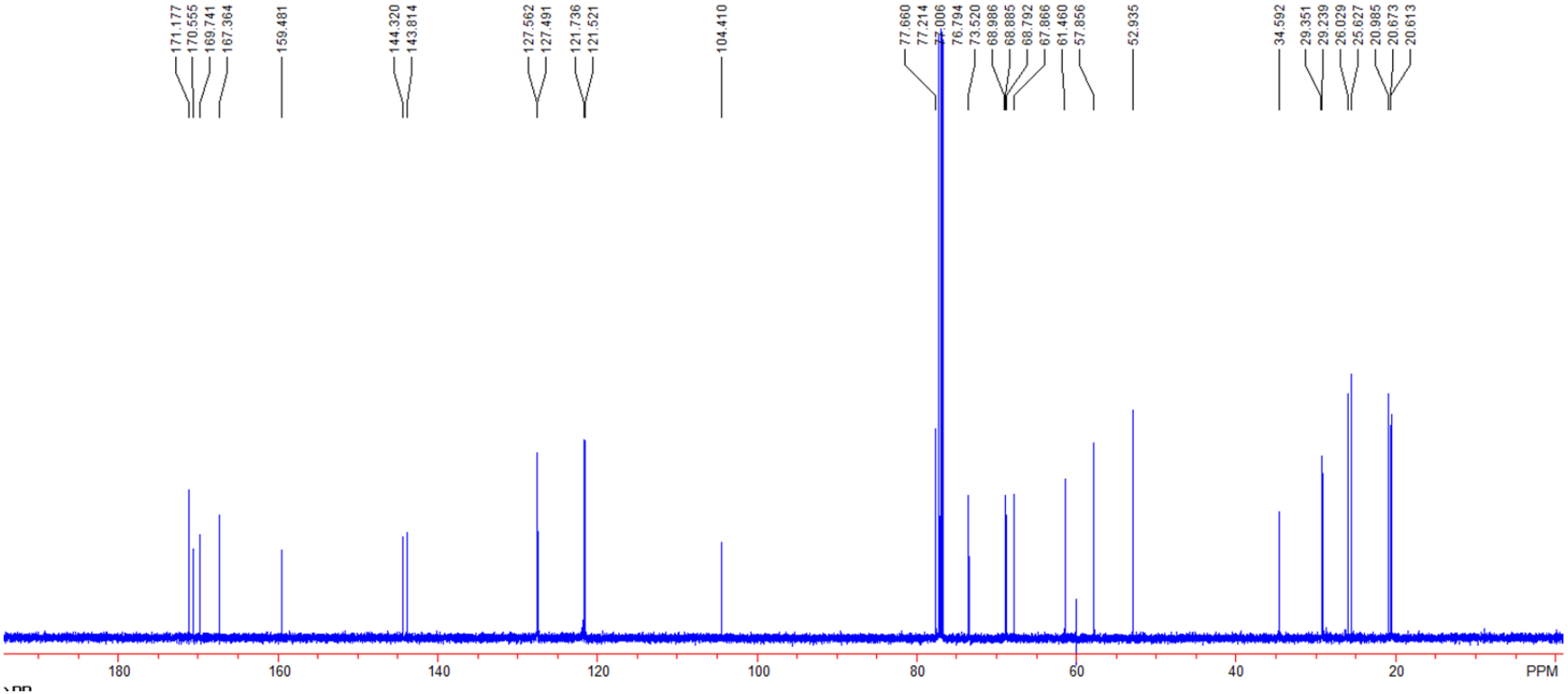
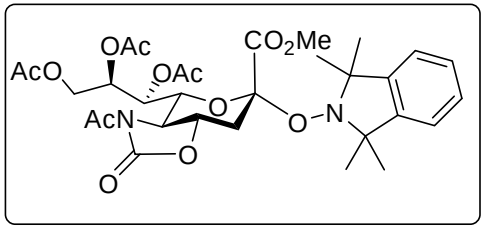
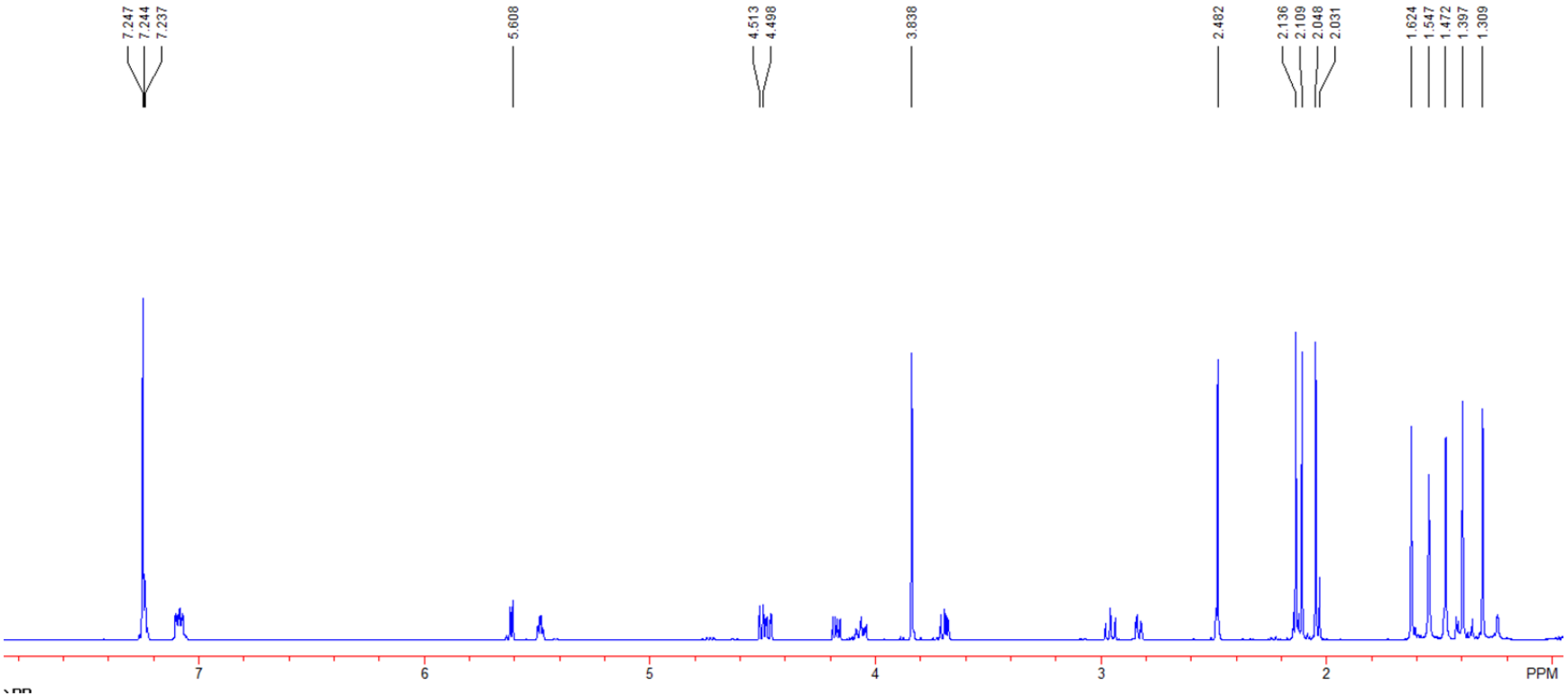




Methyl [2-((1,1,3,3-tetramethylisoindolin-2-yl)oxy) 5-acetamido-7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-2-D-glycero-α-D-galacto-non-2-ulopyranosid]onate ^{1}H NMR (600 MHz, $CDCl_3$) (33α)





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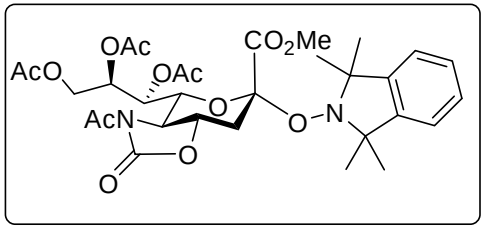
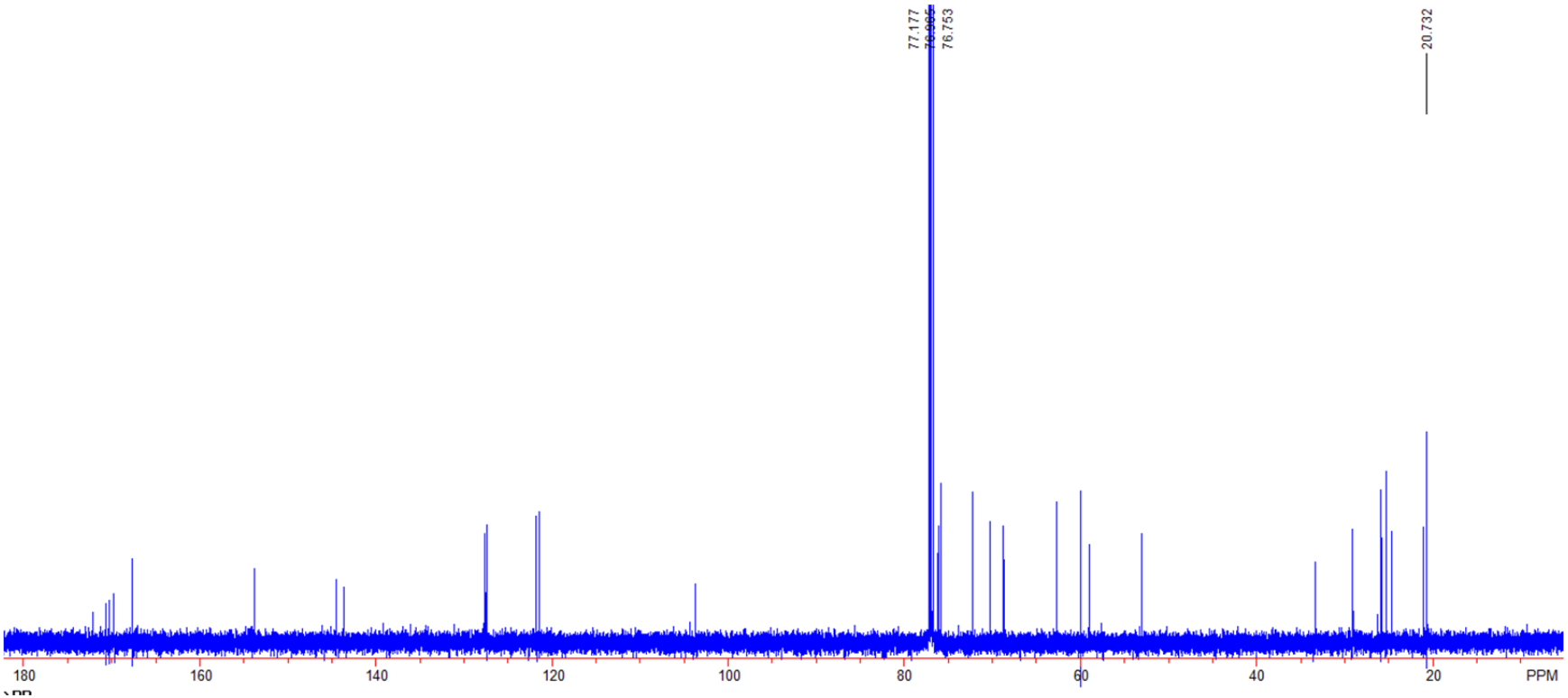
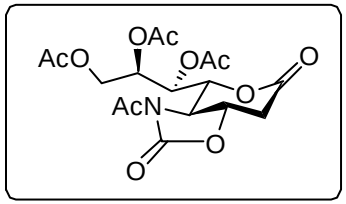
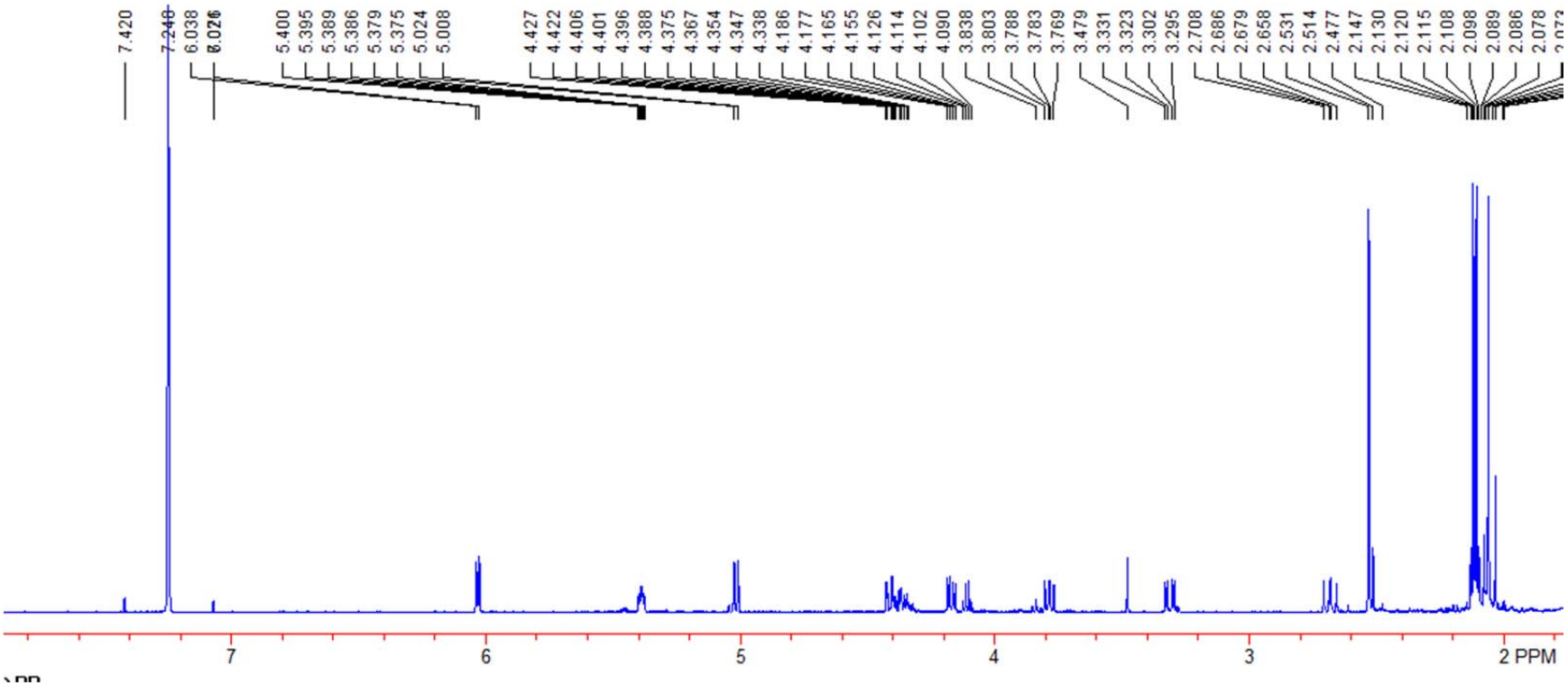




4-Acetamido-6,7,8-tri-*O*-acetyl-4-*N*,3-*O*-carbonyl-2,4-dideoxy-D-glycero-D-galacto-octono-1,5-lactone ^{1}H NMR (600 MHz, $CDCl_3$) (34)





4-Acetamido-6,7,8-tri-*O*-acetyl-4-*N*,3-*O*-carbonyl-2,4-dideoxy-D-glycero-D-galacto-octono-1,5-lactone ^{13}C NMR (150 MHz, $CDCl_3$) (34)