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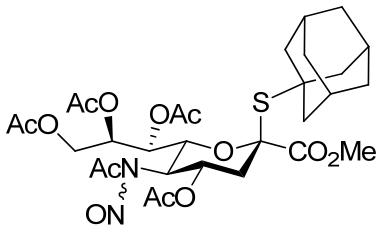
General Experimental: Unless otherwise stated all NMR spectra were recorded in $CDCl_3$ solution. Specific rotations were recorded in $CHCl_3$ solution unless otherwise specified. All reagents and solvents were purchased from commercial suppliers and were used without further purification unless otherwise specified. All reactions were performed in an atmosphere of dry argon. All organic extracts were dried over sodium sulfate and concentrated under aspirator vacuum. Chromatographic purifications were carried out over silica gel. Stereochemical assignments of coupled sialosides were made based on $^3J_{C1\text{-}H3ax}$ coupling constantvalues. The stereochemistry at C5 of deaminated sialosides was determined from the ^3J coupling constants to H5. Compounds numbered **1-40** appear in the manuscript itself, while all subsequent compounds are found only in this supplementary information.

General procedure 1 for nitrosation of sialosides: A stirred solution of sialoside in anhydrous CH_2Cl_2 (0.1 M) was treated with anhydrous pyridine (10 equiv) and was cooled to -10 ^oC. After stirring for 10 min, crushed nitrosyl tetrafluoroborate (4 equiv) was added in one portion to the mixture. The resultant light green solution was stirred at -10 ^oC for 3 h then was diluted with CH_2Cl_2 and washed with cold 1N HCl, followed by cold saturated aqueous $NaHCO_3$. The organic layer was washed with cold brine, dried, and concentrated below 10 ^oC to obtain the nitrosated sialoside which was carried forward without any further purification.

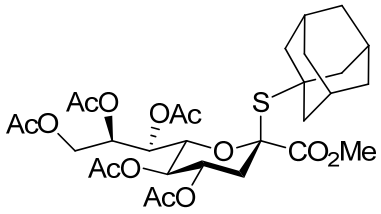
General procedure 2 for deaminations with acetic or thioacetic acid as nucleophile: A solution of the nitrosyl sialoside (0.1 M) and trifluoroethanol (1.5 equiv) in anhydrous CH_2Cl_2 was treated at -10 ^oC with freshly prepared 0.2 N sodium isopropoxide in isopropanol (1.2 equiv). The resulting mixture was stirred for 2 min then was treated with a cold solution of glacial acetic acid (20 equiv) or thioacetic acid (20 equiv) in CH_2Cl_2 (1M). After stirring for 5 min the reaction mixture was warmed to 0 ^oC and was quenched with saturated aqueous $NaHCO_3$. The organic layer was washed with cold brine, dried, concentrated and submitted to flash chromatography to afford the deaminated sialosides.

Methyl (1-adamantanyl 4,7,8,9-penta-*O*-acetyl-3,5-dideoxy-5-(*anti/syn-N-nitrosoacetimido*)-β-D-*glycero*-D-*galacto*-*2*-thiononulopyranosid)onate (7).



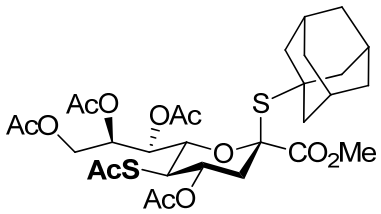
Nitrosation of the thioglycoside **6 (** 0.8 g, 1.2 mmol) was performed using the general procedure **1** using $NOBF_4$ (0.58 g, 5.0 mmol) and pyridine (1 mL, 12 mmol) to afford the title compound **7** as a yellow foam (835 mg) which was carried forward without further purification.

Methyl (1-adamantanyl 4,5,7,8,9-penta-*O*-acetyl-3-deoxy-β-D-*glycero*-D-*galacto*-2-thiononulopyranosid)onate (8).



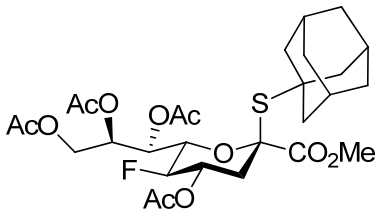
The nitrosyl sialoside **7** (0.15 g, 0.22 mmol) was deaminated using the general procedure **2** with 2,2,2 trifluoroethanol (25 μL, 0.33 mmol), 0.2 N sodium isopropoxide in isopropanol (1.34 mL, 0.26 mmol) and acetic acid (256 μL, 4.4 mmol) to afford **8** after flash chromatography (EtOAc/Hexanes 1/20 to 1/1) as a white foam (84 mg, 58%) with spectral data consistent with those reported in the literature.[1]

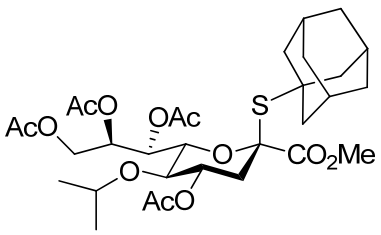
Methyl (1-adamantanyl 4,7,8,9-penta-*O*-acetyl-5-acetylthio-3,5-dideoxy-β-D-*glycero*-D-*galacto*-2-thiononulopyranosid)onate (9).



The nitrosyl sialoside **7** (0.143 g, 0.213 mmol), was deaminated using 2,2,2 trifluoroethanol (23 µL, 0.32 mmol), 0.2 N sodium isopropoxide in isopropanol (1.28 mL, 0.25 mmol) and thioacetic acid (300 µL, 4.26 mmol) to afford **9** after flash chromatography (EtOAc/Hexanes 1/20 to 1/3) as a yellow oil (88 mg, 63%). $[\alpha]^{23}{}_{D} = -41$ (*c* = 0.5, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.69 (brs, 1H), 5.25 (td, *J* = 10.5, 4.8 Hz, 1H), 5.15 (d, *J* = 8.4 Hz, 1H), 5.03 (dd, *J* = 12.6, 1.2 Hz, 1H), 4.64 (dd, *J* = 10.5, 2.4 Hz, 1H), 4.20 (dd, *J* = 12, 8.4 Hz, 1H), 3.82 (s, 3H), 3.56 (t, *J* = 10.5 Hz, 1H, **H_5**), 2.64 (dd, *J* = 13.2, 4.8 Hz, 1H), 2.20 (s, 3H), 2.10 (s, 3H), 2.05 (s, 4H), 1.99 (brs, 9H), 1.94 (s, 3H), 1.87-1.84 (m, 3H), 1.64 (brs, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 192.9, 170.9, 170.4, 170.1, 170.0, 169.6, 85.9, 74.0, 72.6, 70.4, 68.5, 63.3, 52.7, 50.5, 43.8, 43.4, 43.0, 40.6, 35.9, 30.6, 29.8, 21.0, 20.7, 20.7, 20.6.. ESIHRMS: *m/z* calcd. for $C_{30}H_{42}O_{12}S_2Na$ $(M + Na)^+$ 681.2015 found 681.2023.

Methyl (1-adamantanyl 4,7,8,9-penta-O-acetyl-5-fluoro-3,5-dideoxy-β-D-*glycero*-D-*galacto*-2-thiononulopyranosid)onate (10) and Methyl (1-adamantanyl 4,7,8,9-penta-*O*-acetyl-5-*O*-isopropyl-3-deoxy-β-D-*glycero*-D-*galacto*-2-thiononulopyranosid)onate (11)





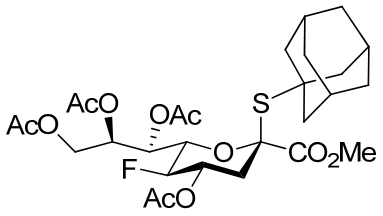
The nitrosyl sialic acid **7** (0.15 g, 0.22 mmol) was deaminated using the general procedure with 2,2,2 trifluoroethanol (25 μL, 0.33 mmol), 0.2 N sodium isopropoxide in isopropanol (1.34 mL, 0.26 mmol) and HF.Pyridine (60 μL, 2.23 mmol) to afford **10** (71 mg, 53%) as a yellow oil along with **11** (21 mg, 15%) a white foam, after flash chromatography (EtOAc/Hexanes 1/20 to 1/1).

10. $[\alpha]^{23}_{D}$ = + 18 (*c* = 1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.62-5.59 (m, 1H), 5.53-5.45 (m, 1H), 5.29-5.27 (m, 1H), 4.75 (dd, *J* = 12.5, 2 Hz, 1H), 4.65 (m, 1H), 4.33-4.29 (dd, *J* = 12.5, 7.5 Hz, 1H), 4.30-4.18 (td, *J* = 50, 9.5Hz, 1H **H_5**), 3.81 (s, 3H), 2.68-2.63 (td, *J* = 13, 4.5Hz, 1H), 2.16 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 2.01-1.99 (m, 6H), 1.86-1.81 (m, 4H), 1.67 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5, 170.4, 169.6, 169.6, 169.6, 88.3, 86.8, 85.5, 71.8, 70.3, 70.1, 69.7, 68.6, 68.4, 62.5, 52.8, 50.6, 43.2, 39.0, 36.0, 29.7, 21.0, 20.9, 20.7, 20.6. ESIHRMS: *m/z* calcd. for $C_{28}H_{39}O_{11}SFNa$ $(M + Na)^+$ 625.2095 found 625.2083.

11. $[\alpha]^{23}_{D}$ = - 7 (*c* = 0.4, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.54 (s, 1H), 5.63 (d, *J* = 2.4 Hz, 2H), 4.81 (d, *J* =12.8, 1H), 4.35 (d, *J* =8.8 Hz, 1H), 2.56 (dd, *J* = 12, 8.8, 1H), 3.79 (s, 3H), 3.66 (m 1H), 3.31 (t, *J* = 8.8 Hz, 1H, **H_5**), 2.53 (dd, *J* = 13.5, 4 Hz, 1H), 2.14 (s, 3H), 2.08 (s, 3H), 2.08 (s, 6H), 2.01-1.97 (br s, 8H), 1.89-1.83 (m, 2H) 1.65 (br s, 6H), 1.10 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.5, 170.4, 170.0, 169.5, 85.4, 73.6, 73.1, 72.6, 72.5, 71.4, 70.6, 62.9, 52.6, 50.1, 43.3, 38.6, 35.9, 29.7, 23.2, 22.2, 21.0, 21.0, 20.9, 20.7. ESIHRMS: *m/z* calcd. for $C_{28}H_{39}O_{11}SFNa$ $(M + Na)^+$ 625.2095 found 625.2083.

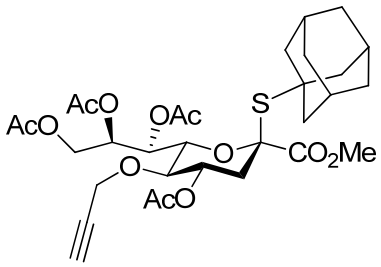
Preparation of sodium 2,2,2 trifluoroethoxide.: Sodium (3 g) was added piecewise carefully to ice cold 2,2,2 trifluoroethanol (300 mL) at 0 ^{o}C. The mixture was warmed to room temperature over 1 h and was stirred until the sodium was completely dissolved. The volatiles were removed under reduced pressure and the resultant solid was dried under high vacuum to afford 2,2,2 trifluoroethoxide (16.5 g, quant) as a free flowing white solid.

Preparation of 10 by deamination using 2,2,2 trifluoroethoxide/18-crown-6.



A stirred solution of 18-crown-6 (130 mg, 0.49 mmol) in anhydrous CH_2Cl_2 (0.5 mL) under was treated with 2,2,2 trifluoroethoxide (54 mg, 0.44 mmol). The mixture was stirred until solids completely dissolved and was then cooled to -10 ^{o}C. The nitrosyl sialoside **7** (0.15 g, 0.22 mmol) in anhydrous CH_2Cl_2 (2.2 mL) at -10 ^{o}C was treated with the cold 2,2,2 trifluoroethoxide/18-crown-6 solution. The mixture was allowed to stir for 2 mins for the reddish color to develop after which 70% HF.Pyridine (60 μL, 2.23 mmol) was added to the reaction mixture via a plastic syringe. The mixture was stirred for 5 min, diluted with CH_2Cl_2 (5 mL) and was quenched by addition of saturated aqueous $NaHCO_3$ (5 mL). The organic layer was washed with brine (5 mL), dried and concentrated to afford a yellow oil that was purified by flash chromatography (EtOAc/Hexanes 1/20 to 1/1) to afford **10** (83 mg, 63%) as a yellow oil.

Methyl (1-adamantanyl 4,7,8,9-penta-*O*-acetyl-5-prop-3-ynyl-3-deoxy-β-D-*glycero*-D-*galacto*-2-thiononulopyranosid)onate (13):

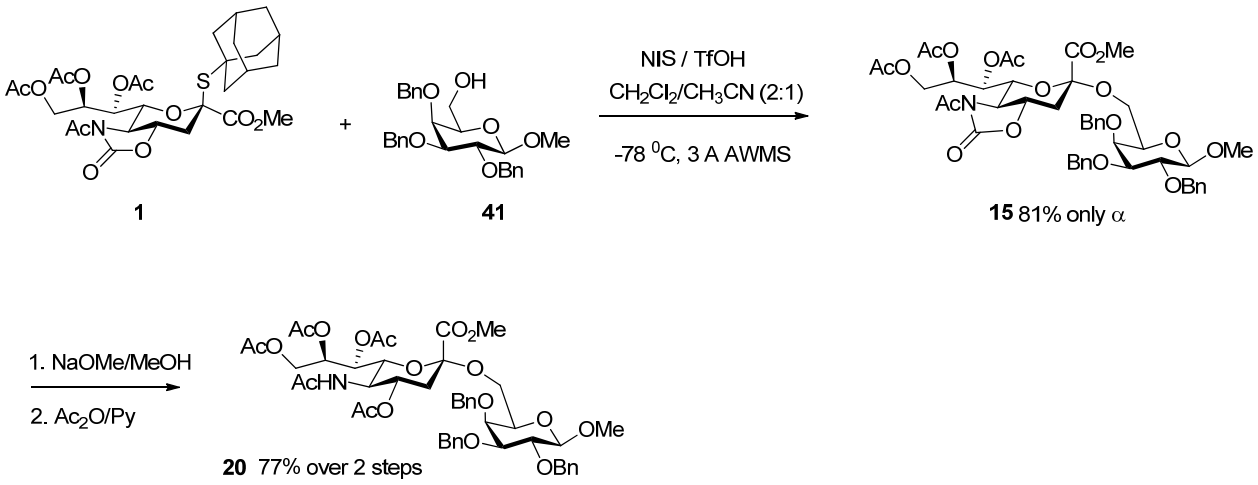


A stirred solution of 18-crown-6 (173 mg, 0.66 mmol) in anhydrous CH_2Cl_2 (1 mL) was treated with 2,2,2 trifluoroethoxide (73 mg, 0.60 mmol) and stirred for 10 min until the solids completely dissolved and was then cooled to -10 ^oC. The nitrosyl sialoside **7** (0.2 g, 0.29 mmol) in anhydrous CH_2Cl_2 (3 mL) at -10 ^oC was treated with the cold 2,2,2 trifluoroethoxide/18-crown-6 solution. The mixture was allowed to stir for 2 minutes for the reddish color to develop at which time propargyl alcohol (3.5 mL, 5.97 mmol) in CH_2Cl_2 (6 mL) was added to the reaction mixture via a plastic syringe, followed immediately by addition of HBF_4 in Et_2O (162 μL, 0.12 mmol). The mixture was stirred for 5 min, diluted with CH_2Cl_2 (5 mL) and was quenched by addition of saturated aqueous $NaHCO_3$ (5 mL). The organic layer was washed with brine (5 mL), dried and concentrated to afford a yellow oil that was purified by flash chromatography (EtOAc/Hexanes 1/20 to 1/1) to afford **13** (125 mg, 66%) as a yellow foam. $[\alpha]^{23}{}_D$ = + 53 (*c* = 1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) 5.58 (t, *J* = 3.2 Hz, 1H), 5.34-5.24 (m, 2H), 4.80 (dd, *J* = 12.4, 2 Hz, 1H), 4.43 (dd, , *J* = 9.6, 3.2 Hz, 1H), 4.30-4.29 (dd, *J* = 15.2, 2.4 Hz, 1H), 4.21- 4.16 (dd, *J* = 15.2, 2.4 Hz, 1H), 3.80 (m, 1H), 3.79 (s, 3H), 3.35 (t, , *J* = 9.6 Hz, 1H **H_5**), 2.59 (dd, , *J* = 13.2, 4.8 Hz, 1H), 2.42 (t, *J* = 2.4 Hz, 1H), 2.14 (s, 3H), 2.07 (s, 3H), 2.04(s, 3H), 2.01 (s, 3H), 2.00-1.95 (m, 7H), 1.85-1.79 (m 3H), 1.64 (br s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.3, 170.1, 169.8, 169.4, 85.4, 79.3, 75.3, 74.6, 72.3, 71.4, 71.3, 70.3, 62.7, 59.2, 52.6, 50.2, 43.3, 38.7, 35.9, 29.7, 21.2, 21.0, 20.8, 20.7. ESIHRMS: *m/z* calcd. for $C_{31}H_{42}O_{12}SNa$ $(M + Na)^+$ 661.2295 found 661.2284.

General procedure 3 for synthesis of disaccharides 20, **21** and **22.**

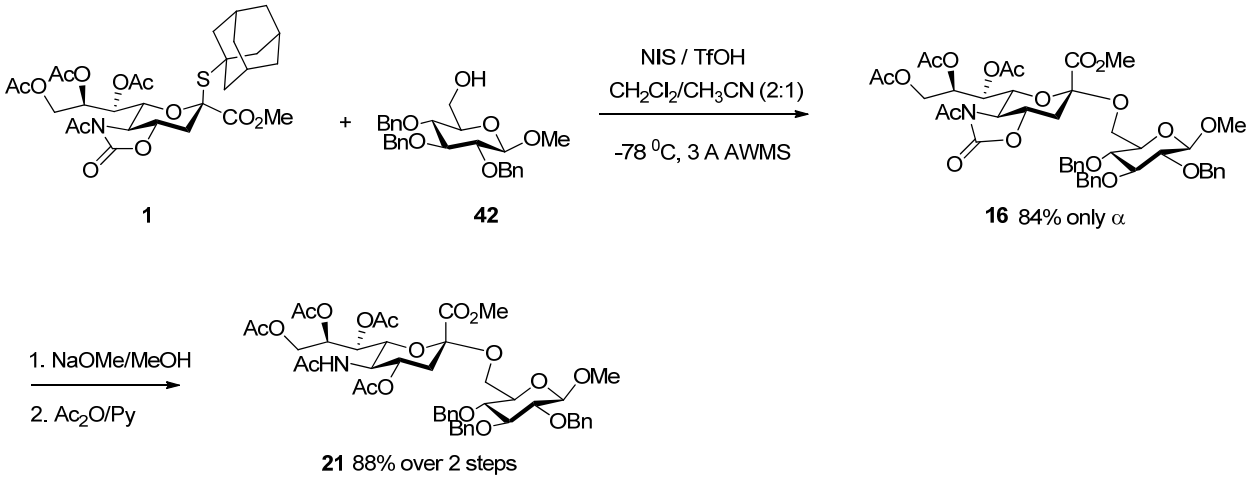
A mixture of the adamantyl thiosialoside (**1**), the acceptor (1.1 equiv), and AW-300 molecular sieves (1 g/mmol) in a mixture of anhydrous CH_2Cl_2 and CH_3CN (2:1, 0.05 M) were stirred overnight at room temperature, then was cooled to -78 ^oC, and was treated with NIS (1.1 equiv) and triflic acid (0.05 equiv). The mixture was stirred for 1.5 h and was quenched by addition of triethylamine (0.2 equiv). The reaction mixture was filtered through a small plug of Celite and was washed with a 20% aqueous solution of sodium thiosulphate, brine, and was concentrated. The residue was purified by flash chromatography to afford the sialosides. To a stirred solution of the so-formed sialoside in anhydrous methanol (0.05M) was added a catalytic quantity of sodium methoxide and the solution was stirred overnight. The reaction mixture was neutralized using Amberlyst 15 resin, was filtered and concentrated to afford the unprotected sialoside, which was dissolved in pyridine and treated with acetic anhydride at 0 ^oC and stirred overnight. The volatiles were removed under reduced pressure and the residue was purified by flash chromatography to afford the pure acetylated sialosides.

Methyl [methyl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-α-D-*glycero*-D-*galacto*-non-2-ulopyranosyl)onate]-(2→6)-2,3,4-tri-*O*-benzyl-β-D-galactopyranoside (20).



Compound **20** was prepared according to general procedure **3** using donor **1 (**0.13 g, 0.21 mmol) and acceptor **(41)** (115 mg, 0.25 mmol) in CH_2Cl_2/CH_3CN (4 mL, 2:1), with NIS (56 mg, 0.25 mmol) and TfOH (2 μL, 0.02 mmol). After chromatographic purification (Hexanes/EtOAc 4/1 – 1/3) pure **15 (**155 mg, 81%) was obtained as a white foam and as a single α-anomer, whose the spectral data matched with the literature data.[2] The sialoside **15** (155 mg, 1.68 mmol) was dissolved in anhydrous methanol (5 mL) and was treated with sodium methoxide (5 mg) and stirred overnight. The reaction mixture was neutralized with Amberlyst 15 resin and was filtered through a small plug of Celite, and concentrated to afford a white solid that was dissolved in pyridine (4 mL). The mixture was cooled to 0 ^oC and was treated with acetic anhydride (4 mL) then stirred overnight at room temperature. The reaction mixture was concentrated under reduced pressure and was purified by chromatography to afford the title compound **20** (121 mg, 77%) as a white foam whose NMR spectra were identical with those reported in the literature.[3]

Methyl [methyl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-α-D-*glycero*-D-*galacto*-non-2-ulopyranosyl)onate]-(2→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (21).



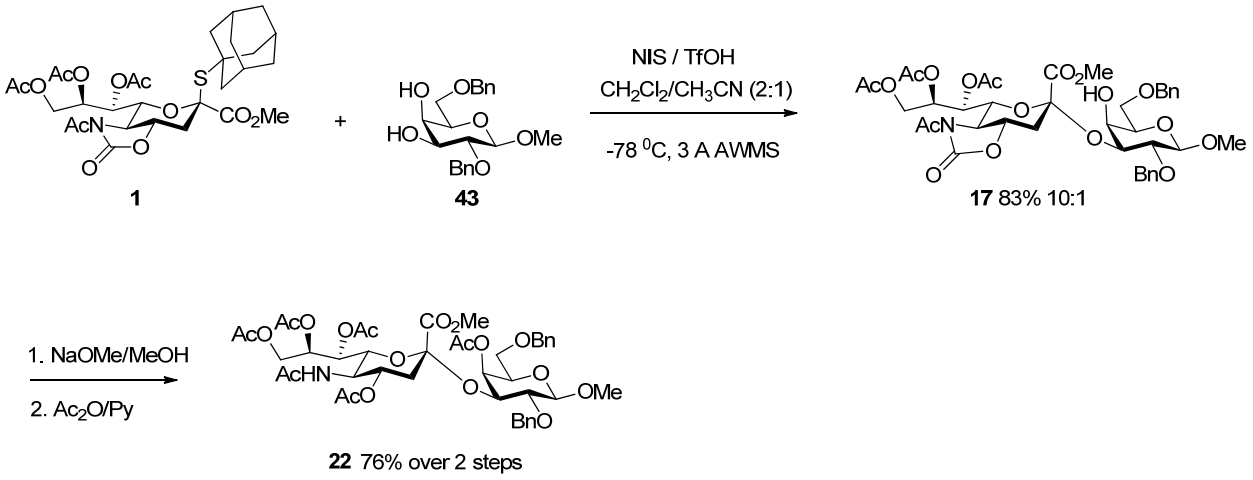
1 **42** **16** 84% only α

21 88% over 2 steps

Compound **21** was prepared according to general procedure **3** using donor **1 (**0.15 g, 0.24 mmol) and acceptor **(42)** (133 mg, 0.28 mmol) in CH_2Cl_2/CH_3CN (4.8 mL, 2:1, with NIS (64 mg, 0.28 mmol) and TfOH (2 μL, 0.02 mmol). Purification by chromatography over silica gel (Hexanes/EtOAc 4/1 – 1/3) was performed to afford pure **16 (**185 mg, 84%) as a white foam and as a single α-anomer, whose spectral data

of which matched with the literature data.[2] The sialoside **16** (185 mg, 0.2 mmol) was dissolved in anhydrous methanol (10 mL) and was treated with sodium methoxide (5 mg) and stirred under overnight. The reaction mixture was neutralized with Amberlyst 15 resin and was filtered through a small plug of Celite, and concentrated to afford a white solid that was dissolved in pyridine (5 mL). The mixture was cooled to 0 ^{o}C and was treated with acetic anhydride (5 mL) and was stirred overnight. The reaction mixture was concentrated under reduced pressure and was purified by chromatography to afford the title compound **21** (165 mg, 88%) as a white foam the NMR spectra of which were identical to the literature data.[2]

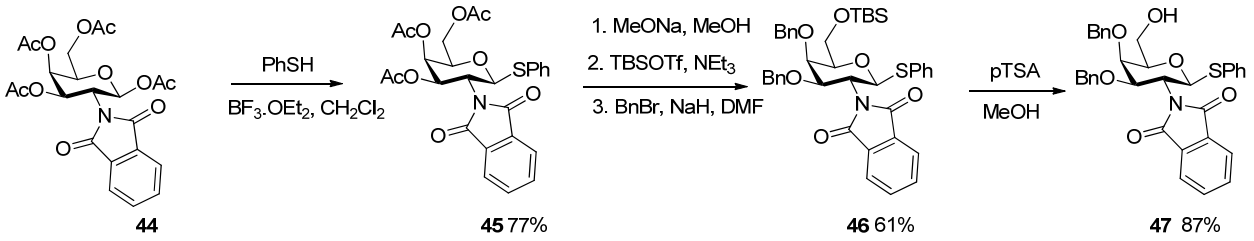
Methyl [methyl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-α-D-*glycero*-D-*galacto*-non-2-ulopyranosyl)onate]-(2→3)-4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranoside (22).



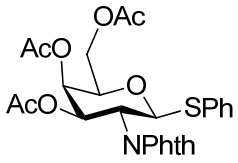
Compound **22** was prepared according to general procedure **3** using donor **1 (**0.5 g, 0.8 mmol) and acceptor **43** (0.36 mg, 0.96 mmol) in CH_2Cl_2/CH_3CN (16 mL, 2:1), with NIS (216 mg, 0.96 mmol) and TfOH (10 μL, 0.08 mmol). Purification by chromatography (Hexanes/EtOAc 4/1 – 1/2) was performed to afford pure **17 (**551 mg, 83%) as a white foam and as a 10:1 α/β mixture, the spectral data of which matched with the literature report for this compound.[2] The sialoside **17** (520 mg, 0.62 mmol) was dissolved in anhydrous methanol (10 mL) and was treated with sodium methoxide (10 mg) and stirred overnight. The reaction mixture was neutralized with Amberlyst 15 resin and was filtered through a small

plug of Celite, concentrated to afford a white solid that was dissolved in pyridine (15 mL). The reaction mixture was cooled to 0 ^{o}C and was treated with acetic anhydride (15 mL) and stirred overnight. The reaction mixture was concentrated under reduced pressure and was purified by chromatography to afford the pure α anomer **22** (422 mg, 76%) as a white foam. $[\alpha]^{23}{}_{D}$ = -18 (*c* = 0.8, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.33-7.32 (m, 4H), 7.29-7.25 (m, 2H), 5.55-5.52 (m, 1H), 5.34 (dd, *J* = 8, 3Hz, 1H), 5.12 (d, *J* = 10.5, 1H), 5.04 (d, *J* = 3.5 Hz, 1H), 4.93-4.88 (dt, *J* = 12, 4.5 Hz, 1H), 4.82 (s, 2H), 4.55 (d, *J* = 12 , 1H), 4.51-4.45 (m, 3H), 4.34 (dd, *J* = 12.5, 2.5 Hz, 1H), 4.16-4.10 (m, 1H), 3.99 (dd, *J* = 12.5, 5 Hz, 1H), 3.84 (s, 3H), 3.81 (s, 1H), 3.72 (dd, *J* = 10.5, 2.5 Hz, 1H), 3.58 (s, 3H), 3.57-3.43 (m, 3H), 2.58 (dd, *J* = 12.5, 5 Hz, 1H), 2.14 (s, 4H), 2.05 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 1.87 (s, 3H), 1.85 (s, 3H) ^{13}C NMR (125 MHz, $CDCl_3$)170.9, 170.6, 170.3, 170.2, 170.1, 170.0, 168.0, 139.6, 138.0, 128.0, 127.6, 127.6, 127.0, 104.5, 97.0, 78.3, 74.5, 73.4, 73.0, 72.2, 71.7, 69.4, 68.5, 68.6, 68.5, 67.0, 62.1, 57.4, 53.0, 49.2, 37.5, 23.2, 21.3, 20.8, 20.8, 20.7, 20.5. ESIHRMS: *m/z* calcd. for $C_{43}H_{55}NO_{19}SNa$ $(M + Na)^{+}$ 912.3266 found 912.3263.

Synthesis of acceptor 47.

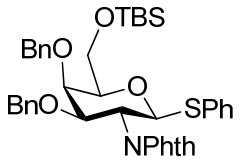


Phenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-thiogalactopyranoside (45).



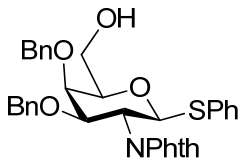
A stirred solution of **44** (1.4 g, 2.9 mmol) in anhydrous CH_2Cl_2 (25 mL) under an argon atmosphere was treated with thiophenol (1.21 mL, 11.7 mmol) and BF_3 etherate (1.45 mL, 11.7 mmol) and was stirred overnight. The reaction mixture was diluted with CH_2Cl_2 (25 mL), and was carefully quenched with saturated aqueous $NaHCO_3$ (50 mL) The organic layer was washed with brine (50 mL), dried and concentrated to give the crude reaction mixture, which was purified by flash chromatography (EtOAc/Hexanes 1/10 to 2/1) to afford the title compound **45** as a yellow oil (1.19 g, 77%). $[\alpha]^{23}_{D} = +41$ (*c* = 1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88-7.84 (m, 2H), 7.77-7.75 (m, 2H), 7.43-7.41(m, 2H), 7.27-7.26 (m, 3H), 5.81 (dd, *J* = 11, 3.5 Hz, 1H), 5.70 (d, *J* = 10.5 Hz, 1H), 5.50 (d, *J* = 3.5 Hz, 1H), 4.63 (t, *J* = 10 Hz, 1H), 4.23 (dd, *J* = 11, 2 Hz, 1H), 4.17-4.10 (m, 2H), 2.17 (s, 3H), 2.04 (s, 3H), 1.83 (s, 3H) ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 170.2, 169.7, 167.9, 167.2, 134.4, 134.3,132.6, 131.7, 131.5, 131.2, 128.8, 128.1, 123.7, 123.6, 84.0, 77.2, 74.5, 68.8, 66.8, 61.6, 50.0, 20.7, 20.6, 20.5. ESIHRMS: *m/z* calcd. for $C_{26}H_{25}NO_9SNa$ $(M + Na)^+$ 550.1148 found 550.1138.

Phenyl 3,4-di-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-2-deoxy-2-phthalimido-β-D-thiogalactopyranoside (46).



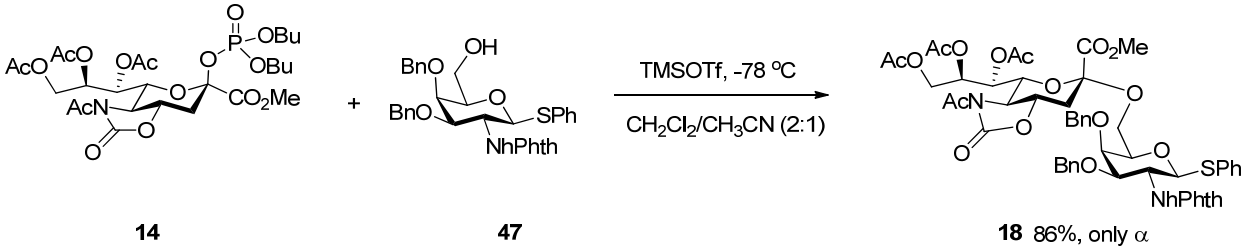
A stirred solution of compound **45** (1.1 g, 2.08 mmol) in anhydrous methanol (30 mL) was treated with sodium methoxide (40 mg) and was stirred overnight. The reaction mixture was neutralized with Amberlyst 15 resin and was concentrated under reduced pressure to give a yellow solid that was dissolved in DMF (15 mL) and was treated with triethylamine (0.44 mL, 3.1 mmol) and TBSOTf (530 µL, 2.3 mmol). After 6 h, the reaction mixture was diluted with EtOAc (20 mL) and was washed with brine (3 x 10 mL). The organic layer was dried and concentrated to afford the silylated thioglycoside as a yellow oil, which was dissolved in DMF (10 mL), cooled to 0 ^{o}C and was treated with benzyl bromide (0.75 mL, 6.2 mmol). The mixture was then treated with sodium hydride (184 mg, 4.59 mmol) portion wise over 1 h. After 3 h, the reaction mixture was quenched with crushed ice and was diluted with EtOAc (20 mL) and was washed with brine (2 x 20 mL). The organic layer was dried and concentrated to afford a yellow oil, purification of which by flash chromatography (EtOAc/Hexanes 1/20 to 1/3) afforded **46** (883 mg, 61%) as a yellow oil. $[\alpha]^{23}{}_{D} =$ + 30 (*c* = 1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81-7.60 (m, 4H), 7.40-7.31 (m, 7H), 7.23-7.18 (m, 3H), 6.98-6.89 (m, 5H), 5.56 (d, *J* = 11 Hz, 1H), 4.66 (t, *J* = 10.5, 1H), 4.59 (d, *J* = 13.5, 2H), 4.53 (d, *J* = 10.5, 1H), 4.28 (d, *J* = 2Hz, 1H), 4.19-4.15 (m, 2H), 3.82 (t, *J* = 10.5, 1H.), 3.75 (t, *J* = 9 Hz, 1H), 3.70-3.68 (m, 1H), 0.92 (s, 9H), 0.08 (s, 3H), 0.05 (s, 3H) NMR (125 MHz, $CDCl_3$) δ 168.4, 167.2, 137.9, 133.8, 133.6, 132.5, 131.9, 131.7, 128.6, 128.4, 128.0, 127.9, 127.7, 127.6, 127.5, 127.4, 127.4, 123.3, 123.1, 83.0, 78.1, 77.9, 73.4, 72.1, 68.8, 67.5, 50.6, 26.0, 18.5, 4.15, 4.98. ESIHRMS: *m/z* calcd. for $C_{40}H_{45}NO_6SSiNa$ $(M + Na)^+$ 718.2635, found718.2628.

Phenyl 3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-thiogalactopyranoside (47).



A stirred solution of **c**ompound **(46)** (0.41 g, 0.58 mmol) in anhydrous methanol (5 mL) was treated with pTSA (25 mg), then stirred overnight before was neutralized with triethylamine. The reaction mixture was concentrated under reduced pressure and was purified by flash chromatography (EtOAc/Hexanes 1/20 to 1/1) to afford **47** (297 mg, 87%) as a yellow oil. $[\alpha]^{23}{}_{D} =$ + 53 (*c* = 1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7..86-7.67 (m, 4H), 7.35 (s, 7H), 7.20-7.18 (m, 3H), 7.09-6.99 (m,5H), 5.56 (dd, *J* = 10.5, 1Hz, 1H), 5.02 (d, *J* = 11.5 , 1Hz, 1H), 4.84 (t, *J* = 10.5 Hz, 1H), 4.63 (d, *J* = 12.5, 2 Hz, 2H), 4.36 (m, 2H), 3.98 (d, *J* = 1Hz, 1H), 3.86 (dd, *J* = 11.5, 7 Hz, 1H), 3.64 (t, *J* = 11.5 Hz, 1H), 3.58 (br s, 1H) 1.68 (br s, 1H), NMR (125 MHz, $CDCl_3$) δ, 168.4, 167.4, 138.1, 137.3, 134.1, 133.9, 133.8, 132.7, 131.8, 131.6, 128.8, 128.4, 128.3, 128.2, 127.9, 127.7, 127.7, 127.5, 84.0, 78.9, 77.6, 74.2, 71.6, 62.2, 51.6. ESIHRMS: *m/z* calcd. for $C_{34}H_{31}NO_6SNa$ $(M + Na)^+$ 604.1770, found 604.1782

Phenyl [methyl (5-acetamido-7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-α(2→6)-3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-thiogalactopyranoside (18).

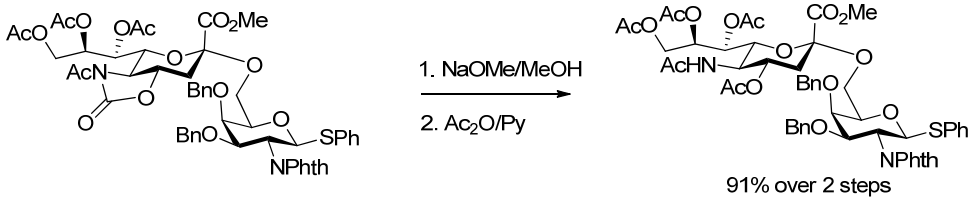


14 **47** **18** 86%, only α

The sialyl phosphate **14**[5] (120 mg, 0.18 mmol), acceptor **47** (114 mg, 0.20 mmol), and AW300 molecular sieves (400 mg) were stirred in a mixture of CH_2Cl_2/CH_3CN (2:1, 4 mL) for 2 h. The mixture was cooled to -78 ^oC and was treated with TMSOTf (32 μL, 0.179 mmol). After 1h the reaction mixture was diluted

with CH_2Cl_2 (5 mL) and was quenched with saturated aqueous $NaHCO_3$ (10 mL). The mixture was warmed to room temperature, filtered through a plug of Celite, and the organic layer was separated and washed with brine (10 mL), dried and concentrated to afford the crude disaccharide, which was purified by flash chromatography (EtOAc/Hexanes 1/20 to 1/1) to afford **18** (163 mg, 86%), a yellow foam, as a single α-anomer. $[\alpha]^{23}{}_D$ = - 18 (*c* = 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.84 (d, *J* = 6.5 Hz, 1H), 7.70-7.65 (m 3H), 7.42-7.40 (m, 2H), 7.37 (d, *J* = 7 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.27 (m 2H), 7.18-7.14 (m, 3H), 7.05-6.96 (m, 4H), 5.58 (dd, *J* = 7.5, 2 Hz, 1H), 5.54 (d, *J* = 11 Hz, 1H), 5.43 (dt, *J* = 7, 2.8 Hz, 1H), 4.98 (d, *J* = 11.5 Hz, 1H), 4.81 (t, *J* = 10.5 Hz, 1H), 4.68 (d, *J* = 11.5 Hz, 1H), 4.60-4.58 (m, 2H), 4.37 (d, *J* = 3Hz, 1H), 4.35 (s, 2H), 4.12-3.98 (m, 4H), 3.81 (t, *J* = 6.5 Hz, 1H), 3.72 (dd, *J* = 11, 9.5 Hz, 1H), 3.67 (s, 3H), 3.60 (dd, *J* = 9.5, 6.5 Hz, 1H), 2.86 (dd, *J* = 12, 3.5 Hz, 1H), 2.49 (s, 3H), 2.13 (s, 4H), 2.08 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 172.0, 170.7, 170.1, 170.0, 168.3, 167.3 (**$^3J_{C\text{-}H}$ = 6.5 Hz**), 150.7, 138.6, 137.4, 133.9, 133.9, 133.0, 131.8, 131.6, 128.6, 120.1, 127.6, 127.5, 127.5, 127.3, 123.5, 123.1, 98.9, 83.8, 77.4, 77.2, 76.9, 75.7, 74.9, 74.1, 71.8, 71.4, 69.3, 63.8, 62.7, 59.0, 53.1, 36.4, 24.7, 21.0, 20.8, 20.7. ESIHRMS: *m/z* calcd. for $C_{53}H_{54}N_2O_{18}SNa$ $(M + Na)^+$ 1061.2290, found 1061.2301.

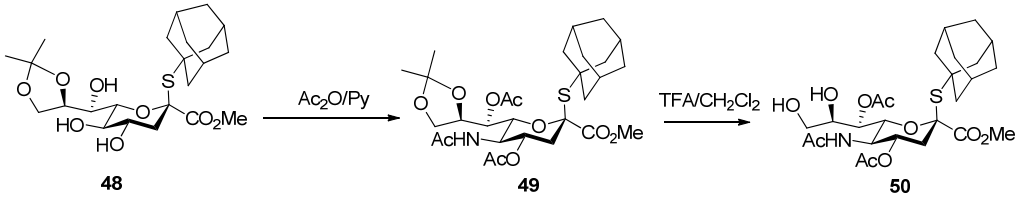
Phenyl [methyl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-α(2→6)-3,4-di-*O*-benzyl-1-thio-2-deoxy-2-phthalimido-β-D-galactopyranoside (23).



A stirred solution of the sialoside **18** (163 mg, 0.182 mmol) in anhydrous methanol (10 mL) was treated with sodium methoxide (10 mg) and was stirred at room temperature overnight. The mixture was neutralized with Amberlyst 15 resin and was filtered through a plug of Celite and concentrated to dryness

to afford a white solid. The crude solid was dissolved in pyridine (10 mL) and was treated with acetic anhydride (10 mL) at 0 °C and stirred overnight. The reaction mixture was concentrated to dryness and was purified by flash chromatography afford the title compound **23** (151 mg, 91%) as a white foam. $[\alpha]^{23}_{D}$ = + 12 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.84 (d, *J* = 6.5 Hz, 1H), 7.71-7.60 (m, 3H), 7.44-7.40 (m, 2H), 7.37 (d, *J* = 7 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.27-7.23 (m, 2H), 7.17 (t, *J* = 3.5 Hz, 2H), 7.05 -6.96 (m, 5H), 5.54 (d, *J* = 10 Hz, 1H), 5.42-5.39 (m, 1H), 5.33 (dd, *J* = 8, 1.5 Hz, 1H), 5.27 (d, *J* = 9.5 Hz, 1H), 4.95 (d, *J* = 11.5 Hz, 1H), 4.95-4.85 (m, 1H), 4.79 (t, *J* = 10.5, 1H), 4.66 (d, *J* = 11.5 Hz, 1H), 4.58 (d, *J* = 12 Hz, 1H), 4.37-4.28 (m, 2H), 4.13 (dd, *J* = 12.5, 5.5, 1H), 4.10-4.05 (m, 3H), 4.00 (dd, *J* = 9.5, 6.5 Hz, 1H), 3.83 (t, *J* = 7Hz, 1H), 3.65 (s, 3H), 3.59 (dd, *J* = 9.5, 7.5 Hz, 1H), 3.47 (br s, 1H), 2.60 (dd, *J* = 12.5, 5 Hz, 1H), 2.13 (s,3H), 2.11 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 1.97 (t, *J* = 12.5 Hz, 1H), 1.88 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.9, 170.7, 170.3, 170.1, 169.8, 168.3, 168.0, 167.4, 138.7, 137.5, 133.7, 133.0, 131.9, 131.7, 129.0, 128.6, 128.2, 128.1, 128.1, 128.0, 127.6, 127.5, 127.3, 127.3, 125.2, 123.5, 123.1, 98.6, 83.9, 76.6, 74.2, 72.6, 71.7, 71.3, 69.0, 68.7, 67.3, 62.8, 62.2, 52.8, 51.5, 50.8, 49.4, 37.8, 23.2, 21.0, 20.8, 20.8, 20.7. ESIHRMS: *m/z* calcd. for $C_{54}H_{58}N_2O_{18}SNa$ $(M + Na)^+$ 1017.3303, found 1017.3313.

Synthesis of acceptor 50.



Methyl (1-adamantanyl 5-acetamido-4,7,-di-*O*-acetyl-8,9-*O*-isopropylidene-dideoxy-β-D-*glycero*-D-*galacto*-2-thiononulopyranosid)onate (49).

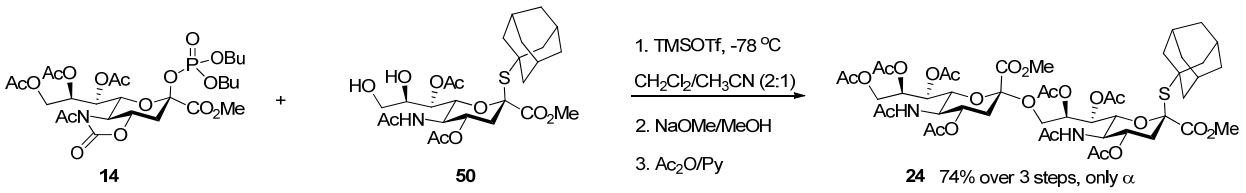
A stirred solution of compound **48**[6] (500 mg, 1.05 mmol) in pyridine (10 mL) at 0 °C under an argon atmosphere was treated with Ac_2O (10 mL). The mixture was warmed to room temperature and was stirred overnight. The volatiles were removed under reduced pressure and the residue was dissolved in

EtOAc (10 mL) and was washed with 1N HCl (10 mL), saturated aqueous $NaHCO_3$ (2 x 5 mL), and brine (5 mL). The organic layer was dried and concentrated to afford the white foam **49** (630 mg, 99%). $[\alpha]^{23}_{D}$ = -23 (*c* = 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.40 (br s, 1H), 5.34-5.29 (m, 2H), 4.42 (d, *J* = 10.4 Hz, 1H), 4.30 (d, *J* = 2.4 Hz, 1H), 4.09 (t, *J* = 9.6 Hz, 1H), 4.02 (t, *J* = 10 Hz, 1H), 3.81 (s, 3H), 2.53 (dd, *J* = 12.8, 4 Hz, 1H), 2.10 (s, 3H), 1.98 (br s, 11H), 1.87 (br s, 6H), 1.64 (br s, 6H), 1.34 (s, 3H), 1.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.8, 170.4, 170.2, 108.5, 86.0, 74.8, 71.8, 69.5, 68.9, 65.6, 52.6, 50.3, 49.8, 43.2, 40.2, 35.9, 35.9, 29.8, 29.8, 26.3, 23.1. ESIHRMS: *m/z* calcd. for $C_{29}H_{43}NO_{10}SNa$ $(M + Na)^+$ 620.2505, found 620.2518.

Methyl (1-adamantanyl 5-acetamido-4,7-di-*O*-acetyl-3,5-dideoxy-β-D-*glycero*-D-*galacto*-2-nonulopyranosid)onate (50).

A stirred solution of the compound **49** (600 mg, 0.1 mmol) in CH_2Cl_2 (10 mL) was treated with TFA (2 mL). The mixture was stirred for 45 min and was concentrated under reduced pressure. The residue was co-evaporated with toluene (3 x 10 mL) and crude acceptor **50** was taken forward to the next step without further purification.

1-Adamantanyl [methyl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-α(2→9)-[methyl (5-acetamido-4,7,8-tri-*O*-acetyl-3,5-dideoxy-β-D-*glycero*-α-D-*galacto*-2-thiononulopyranosyl)onate] (24).

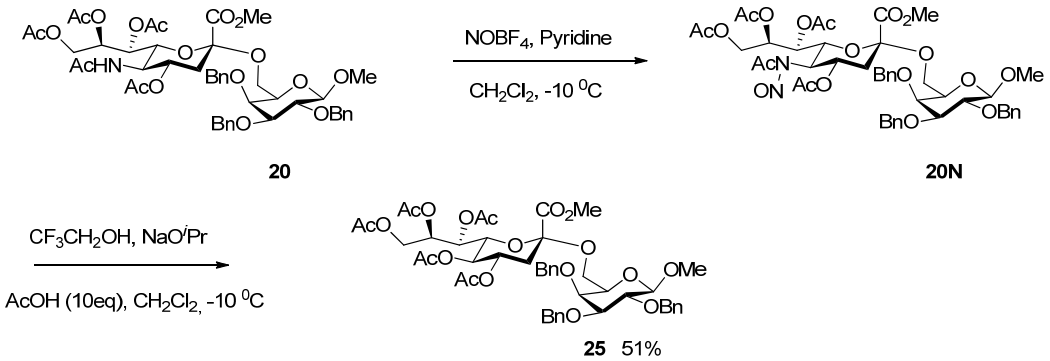


A solution of the sialyl phosphate donor **14**[5] (136 mg, 0.20 mmol), acceptor **50** (147 mg, 0.26 mmol) and AW300 molecular sieves (600 mg) were stirred in a mixture of a mixture of CH_2Cl_2/CH_3CN (2:1, 4.5 mL) for 2 h. The mixture was cooled to -78 °C and was treated with TMSOTf (38 μL, 0.21 mmol) and after 1h

was diluted with CH_2Cl_2 (5 mL) and was quenched with saturated aqueous $NaHCO_3$ (5 mL). The mixture was warmed to room temperature, filtered through a small plug of Celite and the organic layer was separated and washed with brine, dried and concentrated to afford crude **19**. The crude reaction mixture was dissolved in anhydrous methanol (5 mL) and was treated with sodium methoxide (5 mg) and was stirred overnight. The mixture was neutralized with Amberlyst 15 resin, filtered and concentrated to dryness to afford a white foam, which was dissolved in pyridine (5 mL) and was treated with acetic anhydride (5 mL) at 0 ^oC, and stirred overnight. The volatiles were removed under reduced pressure and the residue was purified by flash chromatography to give the desired disialoside **24** (161 mg, 74%) as a white foam. $[\alpha]^{23}{}_D$ = + 28 (*c* = 1, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ: 5.45-5.42 (m, 3H), 5.29-5.19 (m, 3H), 5.09 (d, *J* = 8 Hz, 1H), 4.84-4.79 (m, 1H), 4.50 (d, *J* = 10.5, 1H), 4.25 (d, *J* =11, 2H), 4.10-3.97 (m, 5H), 3.90 (s, 3H), 3.85-3.78 (m, 4H), 2.50 (dd, *J* = 13.5, 5 Hz, 1H), 2.42 (dd, *J* = 12.5, 4.5, 1H), 2.17 (s, 3H), 2.13 (s, 3H), 2.10 (s, 3H), 2.08 (s, 3H), 2.04-1.98 (m, 17H), 1.94 (t, *J* = 12.5 Hz, 1H), 1.87 (m, 9H), 1.69 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.3, 171.1, 170.7, 170.5, 170.4, 170.2, 170.1, 169.9, 169.6, 169.4, 168.3 (**$^3J_{C\text{-}H}$ = 6.5 Hz**), 97.8, 85.7, 74.4, 72.5, 72.0, 69.1, 69.0, 68.8, 67.9, 67.3, 63.6, 62.3, 52.9, 52.4, 50.6, 49.7, 49.4, 39.8, 43.4, 37.8, 35.9, 29.7, 23.2, 23.1, 21.0, 21.0, 20.8, 20.8, 20.7, 20.7, 20.6. ESIHRMS: *m/z* calcd. for $C_{48}H_{68}O_{23}N_2SNa$ $(M + Na)^+$ 1072.3934, found 1072.3940.

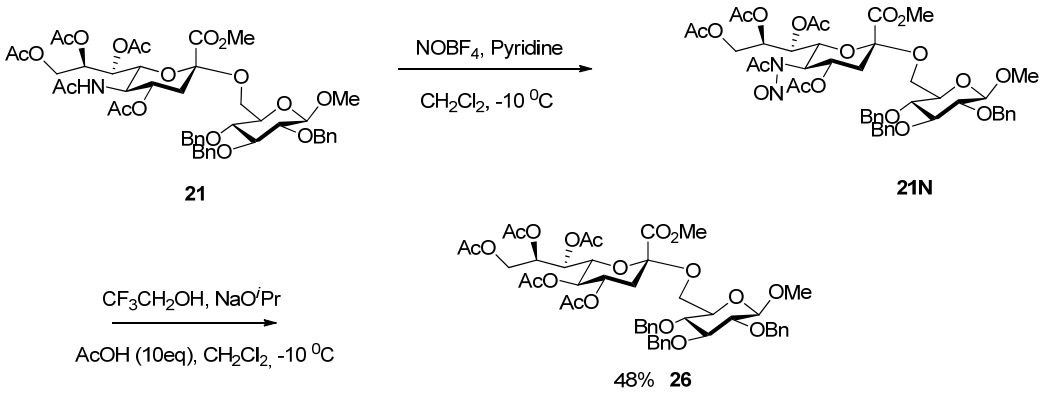
Deamination of disaccharides.

Methyl [methyl (4,5,7,8,9-penta-*O*-acetyl-3-deoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-(2→6)-2,3,4-tri-*O*-benzyl-β-D-galactopyranoside (25).



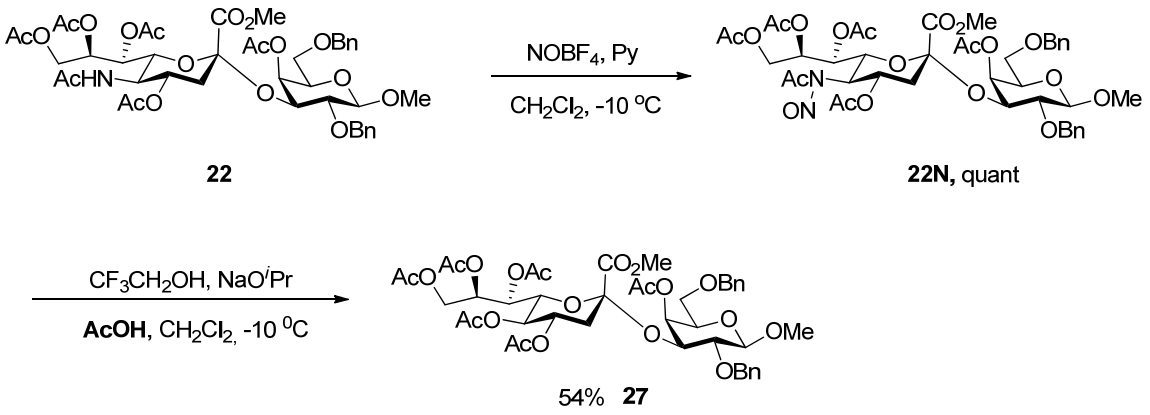
The disaccharide **20** (100 mg, 0.11 mmol) was nitrosated using the general procedure **1** using $NOBF_4$ (50 mg, 0.426 mmol) and pyridine (85 uL, 1.1 mmol) to obtain **20N** (102 mg) as a yellow foam. The deamination of **20N** was carried out using acetic acid as the nucleophile by the general procedure **2** using 2,2,2 trifluoroethanol (12 μL, 0.16 mmol), 0.2 N sodium isopropoxide in isopropanol (0.64 mL, 0.13 mmol) and acetic acid (125 μL, 2.15 mmol) to afford after flash chromatography (EtOAc/Hexanes 1/20 to 1/1) **25** (51 mg, 51%) as a colorless oil whose NMR are identical with those reported in the literature.[1]

Methyl [methyl (4,5,7,8,9-penta-*O*-acetyl-3-deoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-(2→6)-2,3,4-tri-*O*-benzyl-β-D-galactopyranoside (26).



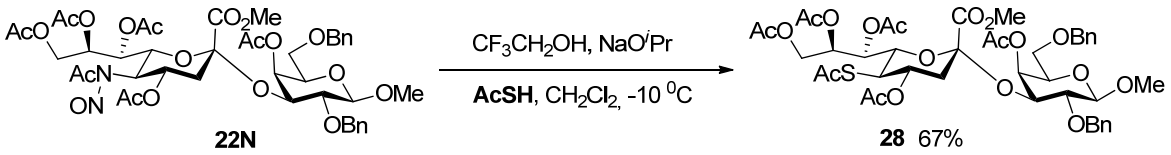
The disaccharide **21** (126 mg, 0.13 mmol) was nitrosated by the general procedure **1** using $NOBF_4$ (63 mg, 0.54 mmol) and pyridine (108 μL, 1.34 mmol) to obtain **21N** (129 mg,) as a yellow foam. The deamination of **21N** was carried out using acetic acid as the nucleophile by the general procedure **2** using 2,2,2 trifluoroethanol (15 μL, 0.20 mmol), 0.2 N sodium isopropoxide in isopropanol (0.8 mL, 0.160 mmol) and acetic acid (152 μL, 2.67 mmol) to afford after flash chromatography (EtOAc/Hexanes 1/20 to 1/1) **26** (60 mg, 48%) as a colorless oil whose NMR spectra are identical with those reported in the literature.[1]

Methyl [methyl (4,5,7,8,9-penta-*O*-acetyl-3-deoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranoside (27).



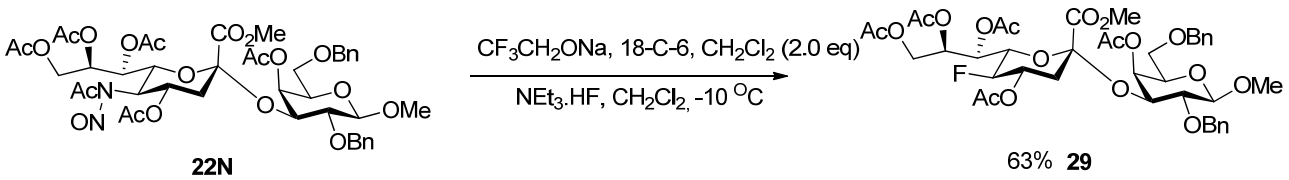
The disaccharide **22** (100 mg, 0.11 mmol) was nitrosated by the general procedure **1** using $NOBF_4$ (52 mg, 0.45 mmol), pyridine (184 μL, 2.24 mmol) to obtain **22N** (103 mg) as a yellow foam. The deamination of **22N** was carried out using acetic acid as the nucleophile by the general procedure **2** using 2,2,2 trifluoroethanol (12 μL, 0.17 mmol), 0.2 N sodium isopropoxide in isopropanol (0.67 mL, 0.134 mmol) and acetic acid (127 μL, 2.24 mmol) to afford after flash chromatography (EtOAc/Hexanes 1/20 to 1/1) **27** (54 mg, 54%) as a colorless oil. $[\alpha]^{23}{}_D = +4$ (*c* = 0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7 Hz, 2H), 7.37-7.32 (m, 6H), 7.30-7.14 (m, 2H), 5.58-5.55 (m, 1H), 5.36 (dd, *J* = 9, 2.5 Hz, 1H), 5.05 (d, *J* = 3 Hz, 1H), 4.98-4.95 (m, 1H), 4.93 (t, *J* = 9.5 Hz, 1H, **H_5**), 4.84-4.78 (m, 2H), 4.55 (d, *J* = 12 Hz, 1H), 4.50-4.46 (m, 3H), 4.28 (dd, *J* = 13, 2.5 Hz, 1H), 4.03 (dd, *J* = 13, 4.5 Hz, 1H), 3.86 (s, 3H), 3.85-3.75 (m, 2H), 3.59 (s, 3H), 3.56-3.52 (m, 1H), 3.48-3.43 (m, 2H), 2.66 (dd, *J* = 13, 4.5 Hz, 1H), 2.15 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H), 1.80 (s, 4H) ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.6, 170.2, 170.1, 170.0, 170.0, 169.8, 167.8, 139.6, 138.0, 128.3, 128.3, 128.0, 127.6, 127.6, 127.0, 127.0, 104.5, 96.9, 78.3, 74.5, 73.4, 73.2, 71.7, 70.9, 69.7, 68.8, 68.5, 67.9, 67.7, 66.3, 61.9, 57.3, 53.1, 37.0, 21.3, 20.8, 20.8, 20.7, 20.7, 20.3. ESIHRMS: *m/z* calcd. for $C_{43}H_{54}O_{20}Na$ $(M + Na)^+$ 913.3106, found 913.3101.

Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-5-acetylthio-3,5-dideoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranoside (28).



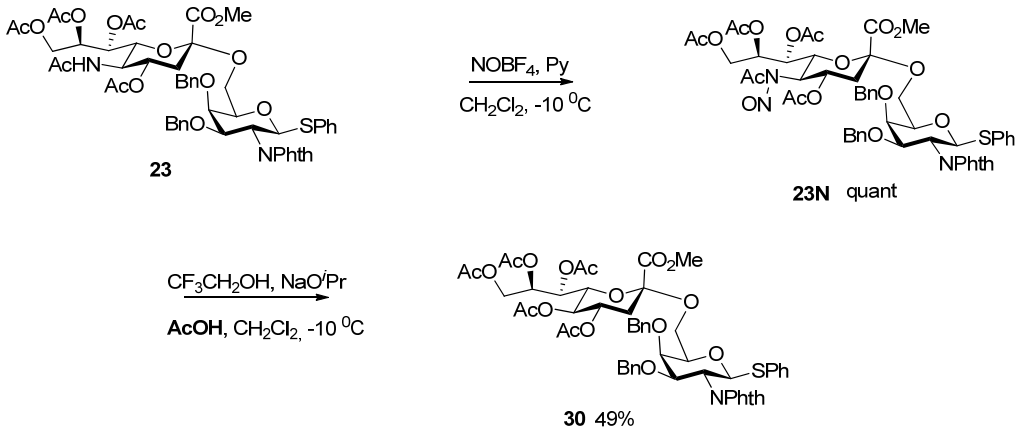
The deamination of **22N** (91 mg, 0.01 mmol), prepared as described under compound **27**, was carried out by the general procedure **2** using 2,2,2 trifluoroethanol (11 µL, 0.15 mmol), 0.2 N sodium isopropoxide in isopropanol (0.59 mL, 0.19 mmol) and thioacetic acid (0.15 mL, 1.98 mmol) to afford after flash chromatography (EtOAc/Hexanes 1/20 to 1/3) **28** (60 mg, 67%) as a colorless oil. $[\alpha]^{23}{}_{D} =$ -18 (*c* = 0.4, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.32 (d, *J* = 4.5, 4H), 7.29-7.25 (m, 2 H), 5.56 (s, 2H), 5.04 (d, *J* = 3 Hz, 1H), 4.94-4.88 (dt, *J* = 12, 4.5 Hz, 1H), 4.84 (s, 2H), 4.54 (d, *J* = 11.5 Hz, 1H), 4.49-4.45 (m, 3H), 4.30 (d, *J* = 13Hz, 1H), 3.97 (d, *J* = 13Hz, 1H), 3.87-3.82 (m, 5H), 3.64 (t, *J* = 12 Hz, 1H **H_5**), 3.59 (s, 3H), 3.55-3.51 (m, 1H), 3.49-3.43 (m, 2H), 2.67 (dd, *J* = 12.5, 4.5 Hz, 1H), 2.30 (s, 3H), 2.13 (s, 3H), 2.07 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H), 1.77 (s, 3H), 1.74 (t, *J* = 12 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.0, 170.7, 170.2, 170.1, 169.7, 169.7, 167.9, 139.7, 138.0, 128.3, 127.6, 127.6, 127.1, 127.0, 104.6, 96.8, 78.3, 77.2, 74.4, 73.4, 72.9, 72.0, 71.7, 69.2, 68.8, 68.5, 68.3, 67.9, 62.0, 57.3, 53.0, 42.7, 38.4, 30.7, 21.3, 20.8, 20.7, 20.7, 20.4. ESIHRMS: *m/z* calcd. for $C_{43}H_{54}O_{19}SNa$ $(M + Na)^+$ 929.2878, found 929.2870.

Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-5-fluoro-3,5-dideoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranoside (29).



A stirred solution of 18-crown-6 (57 mg, 0.22 mmol) in anhydrous CH_2Cl_2 (1 mL) was treated with 2,2,2 trifluoroethoxide (26 mg, 0.44 mmol). The mixture was stirred for 10 min for the solids to completely dissolve and was then cooled to -10 ^oC. The nitrosyl sialoside **22N** (0.1 g, 0.108 mmol), prepared as described in compound **27**, in anhydrous CH_2Cl_2 (2.2 mL) at -10 ^oC was treated with the cold of 2,2,2-trifluoroethoxide/18-crown-6 solution. The mixture was allowed to stir for 2 min for the reddish color to develop after which $HF.NEt_3$ (52 μL, 0.33 mmol) was added to the reaction mixture via a plastic syringe. The mixture was stirred for 5 min, diluted with CH_2Cl_2 (3 mL) and quenched by addition of saturated aqueous $NaHCO_3$ (3 mL). The organic layer was washed with brine (4 mL), dried and concentrated to afford a yellow oil that was purified by flash chromatography (Acetone/Hexanes 1/20 to 1/4) to afford **29** (57 mg, 63%) as a yellow oil. $[\alpha]^{23}{}_D$ = + 11 (*c* = 0.5, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.5 Hz, 2H), 7.33-7.25 (m, 8H), 5.51 (s, 2H), 5.12-5.00 (m, 2H), 4.82 (d, *J* = 12.5 Hz, 1H), 4.77 (*J* = 12.5 Hz, 1H), 4.54 (d, *J* = 11.5 Hz, 1H), 4.48-4.44 (m, 2H), 4.39 (dd, *J* = 10, 3.5 Hz, 1H), 4.34 (dd, *J* = 12.5, 1.5 Hz, 1H), 4.29-4.15 (td, *J* = 49.0, 9.5 Hz, 1H **H_5**), 4.10 (dd, *J* = 12.5, 3.5 Hz, 1H), 3.87 (s, 3H), 3.83-3.74 (m, 2H), 3.59 (s, 3H), 3.55-3.42 (m, 3H), 2.72-2.68 (dd, *J* = 12.5, 4 Hz, 1H), 2.14 (s, 3H), 2. 07 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H), 1.84 (s, 3H), 1.71 (t, *J* = 12.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ170.7, 170.1, 170.0, 169.6, 169.3, 167.6, 139.5, 137.9, 128.3, 128.3, 128.0, 127.9, 127.7, 127.6, 127.2, 127.1, 127.1, 104.6, 97.0, 87.2, 85.7, 78.0, 77.2, 74.4,73.4, 73.3, 71.8, 70.6, 70.4, 69.2, 69.0, 68.8, 68.5, 68.0, 66.9, 61.8, 57.3, 53.2, 36.5, 36.4, 21.2, 20.8, 20.8, 20.7, 20.3. ESIHRMS: *m/z* calcd. for $C_{41}H_{51}FO_{18}Na$ $(M + Na)^+$ 873.2957, found 873.2963.

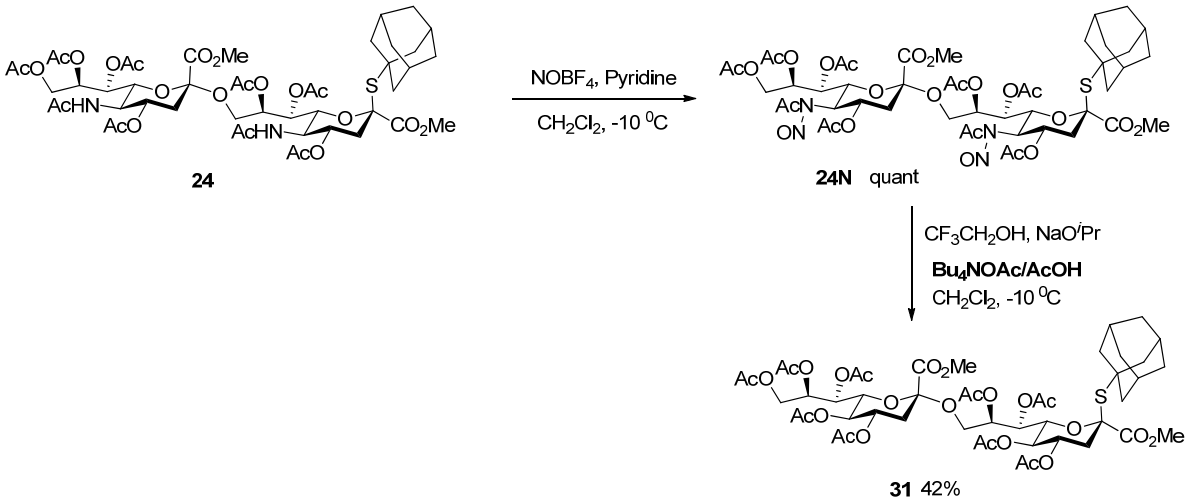
Phenyl [methyl (4,5,7,8,9-penta-*O*-acetyl-3-deoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-(2→6)-3,4-di-*O*-benzyl-1-thio-2-deoxy-2-phthalimido-β-D-galactopyranoside (30).



The disaccharide **23** (160 mg, 0.15 mmol) was nitrosated by the general procedure (**1**) using $NOBF_4$ (71 mg, 0.61 mmol) and pyridine (121 µL, 1.51 mmol) to obtain **23N** (164 mg) as a yellow foam. The deamination of **23N** was carried out using acetic acid as the nucleophile by the general procedure **2** using 2,2,2 trifluoroethanol (16 µL, 0.23 mmol), 0.2 N sodium isopropoxide in isopropanol (0.92 mL, 0.82 mmol) and acetic acid (173 µL, 2.15 mmol) to afford after flash chromatography (EtOAc/Hexanes 1/20 to 1/1) **30** (79 mg, 49%) as a colorless oil. $[\alpha]^{23}{}_D =$ + 21 (*c* = 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.84 (d, *J* = 6.5 Hz, 1H), 7.71-7.60 (m, 3H), 7.44-7.42 (m, 2H), 7.37 (d, *J* = 7 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.27-7.23 (m, 2H), 7.19-7.17 (m, 3H), 7.05 -6.96 (m, 4H), 5.53 (d, *J* = 11 Hz, 1H), 5.48-5.42 (m, 1H), 5.35 (dd, *J* = 9, 2 Hz, 1H), 4.96 (d, *J* = 8 Hz, 1H), 4.94-4.91 (m, 1H), 4.88 (t, *J* = 9.5 Hz, 1H **H_5**), 4.80 (t, *J* = 10.5 Hz, 1H), 4.66 (d, *J* = 11 Hz, 1H), 4.58 (d, *J* = 12.5, 1H), 4.35 (dd, *J* = 11, 3 Hz, 1H), 4.29 (dd, *J* = 13, 2.5 Hz, 2H), 4.18 (d, *J* = 4.5 Hz, 1H), 4.15(dd, *J* = 9.5, 2.5 Hz, 1H), 4.05 (d, *J* = 2 Hz, 1H), 4.00 (dd, *J* = 9.5, 6 Hz, 1H), 3.81 (t, *J* = 7 Hz, 1H), 3.67 (s, 3H), 3.58 (dd, *J* = 9, 7 Hz, 1H), 2.69 (dd, *J* = 13.5, 4.5 Hz, 1H), 2.16 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 2.02 (s, 6H), 1.94 (t, 12.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ170.7, 170.1, 169.9, 169.8, 169.7, 168.3, 167.6, 167.4, 138.6, 137.5, 133.9, 133.8, 133.7, 133.0, 131.9, 131.7, 129.0, 128.6, 128.2, 128.1, 128.1, 127.6, 127.5, 127.5, 127.3, 127.3, 125.2, 123.5, 123.1, 98.4, 83.9, 77.3, 76.9, 74.2, 71.7, 71.3, 71.3, 69.3, 67.9, 67.8, 66.4, 62.9, 62.0, 52.9, 51.5,

37.3, 21.4, 21.0, 20.8, 20.7, 20.7, 20.6, 20.6. ESIHRMS: *m/z* calcd. for $C_{54}H_{57}NO_{19}SNa$, $(M + Na)^+$ 1078.3134, found 1078.3126.

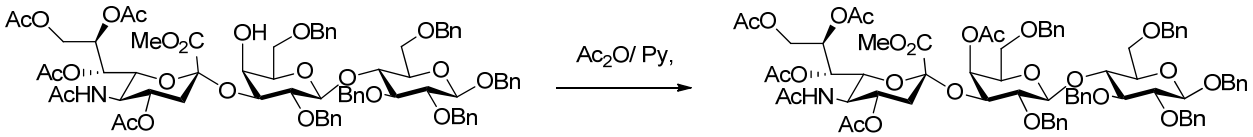
Methyl [methyl (4,5,7,8,9-penta-*O*-acetyl-3,5-dideoxy-α-D-glycero-D-galacto-2-nonulopyranosyl)onate]-α(2→9)-[(1-adamantanyl 4,5,7,8,-tetra-*O*-acetyl-3,5-dideoxy-2-α--D-*glycero*-D-*galacto*-2-thiononulopyranosyl)onate] (31).



The disialoside **24** (150 mg, 0.139 mmol) was nitrosated by the general procedure **1** using $NOBF_4$ (163 mg, 1.39 mmol) and pyridine (450 µL, 5.59 mmol) in anhydrous CH_2Cl_2 (20 mL) to obtain **24N** (158 mg) as a yellow foam. The deamination of **24N** was carried out using acetic acid as the nucleophile by the general procedure **2** using 2,2,2 trifluoroethanol (31 µL, 0.42 mmol), 0.2 N sodium isopropoxide in isopropanol (1.67 mL, 0.34 mmol) and a mixture of tetrabutylammonium acetate (0.86 g, 2.79 mmol), and acetic acid (330 µL, 5.76 mmol) to afford after flash chromatography (EtOAc/Hexanes 1/20 to 1/1) **31** (73 mg, 49%) as a colorless oil. $[\alpha]^{23}{}_D = -21$ (*c* = 1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.44-5.40 (m, 2H), 5.37-5.31 (m, 2H), 5.16 (dd, *J* = 5, 2 Hz, 1H), 4.91-4.86 (m,1H), 4.83 (t, *J* = 10 Hz, 1H **H_5**), 4.79 S(t, 9.5 Hz, 1H **H_5**), 4.67 (dd, *J* = 10, 2.5 Hz, 1H), 4.25 -4.18 (m, 3H), 4.12 (dd, *J* = 12.5, 4.5 Hz, 1H), 3.90 (s, 3H), 3.83 (dd, *J* = 7, 4 Hz, 1H), 3.80 (s, 3H), 2.59 (dd, *J* = 14, 5 Hz,1H), 2.53 (dd. *J* = 12. 4.5 Hz, 1H), 2.18 (s, 3H), 2.17 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.02 (s, 6H), 2.00 (s, 9H), 1.98 (s,

3H), 1.92 (t, *J* = 14 Hz, 1H), 1.86-1.83 (m, 4H), 1.66 (s, 6H) ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.6, 170.5, 170.3, 170.2, 169.9, 169.9, 169.6, 169.5, 169.4, 167.8, 97.8, 85.6, 77.2, 73.4, 71.0, 70.7, 69.2, 69.1, 68.4, 68.4, 67.9, 67.3, 66.6, 63.6, 62.1, 59.2, 52.5, 50.7, 43.3, 39.4, 37.3, 35.9, 29.8, 21.0, 21.0, 20.8, 20.7, 20.7, 20.6, 20.5, 20.5. ESIHRMS: *m/z* calcd. for $C_{48}H_{66}O_{25}SNa$ $(M + Na)^+$ 1097.3512, found 1097.3521.

Benzyl [methyl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-(4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(2→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (33).

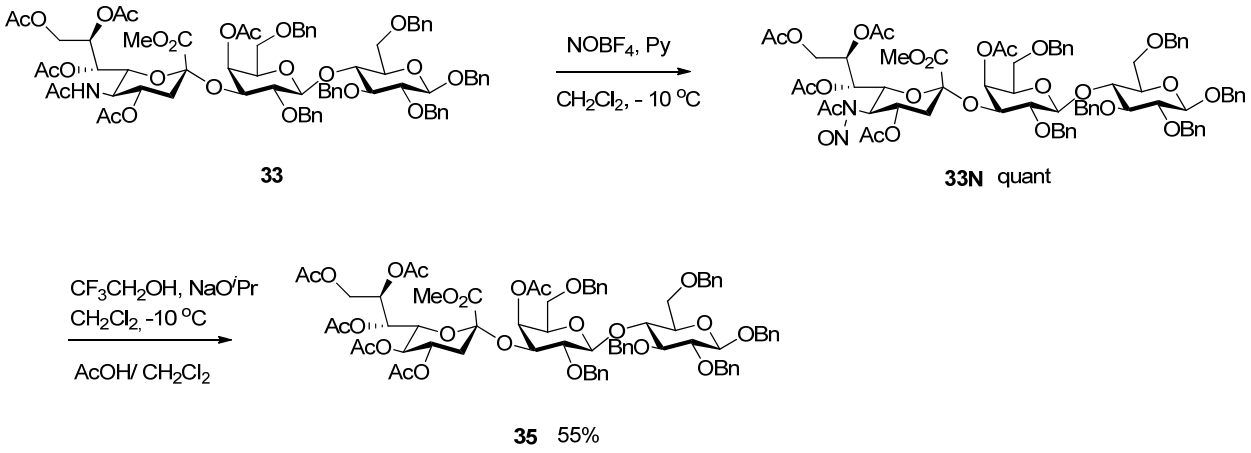


32 **33** quant

A stirred solution of the known GM3 sialoside **32**[7] (110 mg, 0.08 mmol) in anhydrous pyridine (4 mL) was treated with acetic anhydride (4 mL) at 0 °C and the mixture was stirred overnight at room temperature. The volatiles were removed under reduced pressure and the residue was purified by flash chromatography over silica gel to afford **33 (**113 mg, quant) as a white foam. $[\alpha]^{23}_{D}$ = + 32 (*c* = 1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.17 (m, 30 H), 5.63-5.60 (m, 1H), 5.36-5.33 (dd, *J* = 7.5, 2.5 Hz, 1H), 5.11 (d, *J* = 10.5 Hz, 1H), 5.06 (d, *J* = 3 Hz, 1H), 5.06-4.89 (m, 4H), 4.79-4.63 (m, 5H), 4.55-4.49 (m, 2H), 4.46-4.38 (m, 3H), 4.30 (dd, *J* = 12.5, 2.5 Hz, 1H), 4.20 (d, *J* = 11.5 Hz, 1H), 4.13-4.06 (m, 1H), 4.02-3.96 (m, 2H), 3.84 (s, 3H), 3.79-3.62 (m, 5H), 3.57-3.52 (m 1H), 3.48-3.44 (m, 2H), 3.36-3.28 (m 3H), 2.61 (dd, 12.5, 4.5, 1H), 2.10 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.98 (s, 4H), 1.86 (s, 3H), 1.77 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) 170.8, 170.5, 170.3, 169.9, 169.9, 169.9, 167.8, 139.4, 139.2, 138.6, 138.5, 138.1, 137.5, 129.0, 128.4, 128.3, 128.2 (4), 128.1, 128.0, 127.9 (2), 127.8, 127.7, 127.6 (2), 127.5 (2), 127.4 (2), 127.3, 127.2 (2), 127.1 (2), 127.0, 102.3, 102.1, 97.2, 82.8, 81.9, 79.5, 77.2, 76.4, 75.0, 74.9, 74.8, 73.1, 72.8, 72.1, 71.3, 70.9, 69.5, 68.7, 68.6, 68.3, 67.6,67.0, 62.0, 53.1, 49.1,

37.5, 23.1, 21.2, 20.8, 20.7, 20.4. ESIHRMS: *m/z* calcd. for $C_{76}H_{87}NO_{24}Na$ $(M + Na)^+$ 1420.5516, found 1420.5520.

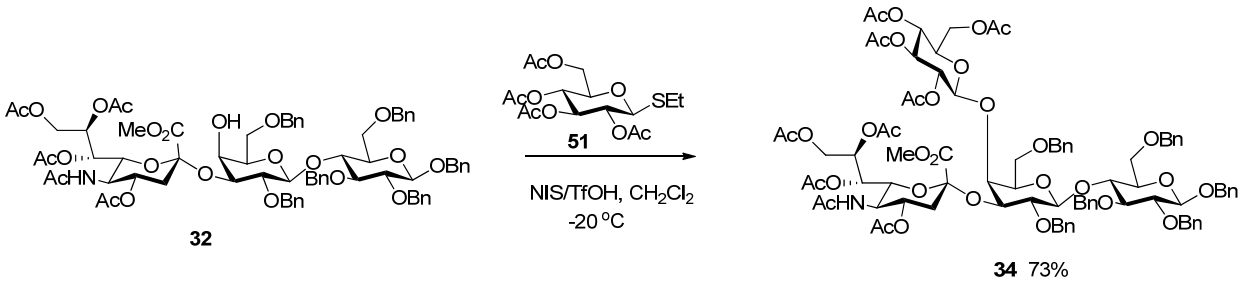
Benzyl [methyl (4,5,7,8,9-penta-*O*-acetyl-3,5-deoxy-α-D-*glycero*-D-*galacto*-2-nulopyranosyl)onate]-(2→3)-(4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(2→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (35).



The trisaccharide **33** (113 mg, 0.08 mmol) was nitrosated by the general procedure **1** using $NOBF_4$ (37 mg, 0.32 mmol) and pyridine (65 µL, 0.8 mmol) to obtain **33N** (115 mg) as a yellow foam. The deamination of **33N** was carried out using acetic acid as the nucleophile by the general procedure **2** using 2,2,2 trifluoroethanol (9 µL, 0.121 mmol), 0.2 N sodium isopropoxide in isopropanol (0.49 mL, 0.096 mmol) and acetic acid (92 µL, 1.61 mmol) to afford after flash chromatography (EtOAc/Hexanes 1/20 to 1/1) **35** (62 mg, 55%) as a colorless oil. $[\alpha]^{23}{}_D =$ + 20 (*c* = 1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.17 (m, 3H), 5.61 (m, 1H), 5.35 (dd, *J* = 8, 2 Hz, 1H), 5.04 (d, *J* = 2.5 Hz, 1H), 4.99-4.83 (m, 6H), 4.75 (t, *J* = 7 Hz, 2H), 4.67 (d, *J* = 10.8 Hz, 1H), 4.61 (d, *J* = 10 Hz, 1H), 4.51 (d, *J* = 10 Hz, 1H) 4.47 (dd, *J* = 8.5, 2.5 Hz, 1H), 4.43 (d, *J* = 7 Hz, 1H), 4.37 (d, *J* = 10.5 Hz, 1H), 4.36 (d, *J* = 10 Hz, 1H), 4.21 (dd, *J* = 10, 2 Hz, 1H), 4.18 (d, *J* = 10 Hz, 1H), 4.01 (dd, *J* = 11, 4 Hz, 1H), 3.95 (t, *J* = 8 Hz, 1H), 3.83 (s, 3H), 3.79 (dd, *J* = 8.5,2 Hz, 1H), 3.74 (m, 1H), 3.65 (t, *J* = 6 Hz, 1H), 3.60 (q, *J* = 5 Hz, 1H), 3.53 (t, *J* = 7.5 Hz, 1H), 3.47-3.43 (m, 3H), 3.32 (m, 1H), 3.26(d, *J* = 6.5 Hz, 1H), 2.64 (dd, 10.5, 4 Hz, 1H), 2.08

(s, 3H), 1.99-1.97 (m, 12H), 1.80 (t, *J* = 10 Hz, 1H), 1.78 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) 170.5, 170.0, 169.9, 169.8, 169.8, 169.7, 169.5, 139.4, 139.2, 138.6, 138.5, 138.1, 137.5, 129.0, 128.4, 128.3, 128.2 (4), 128.1, 128.0, 127.9 (2), 127.8, 127.7, 127.6 (2), 127.5 (2), 127.4 (2), 127.3, 127.2 (2), 127.1 (2), 127.0, 102.3, 102.0, 97.1, 82.8, 81.8, 79.4, 76.4, 75.0, 74.9, 74.7, 73.9, 73.1, 72.7, 71.3, 70.8, 70.8, 69.6, 68.7, 68.5, 67.8, 67.7, 67.6, 67.5, 66.3, 61.9, 53.1, 37.0, 21.2, 20.8, 20.7, 20.7, 20.6, 20.2. ESIHRMS: *m/z* calcd. for $C_{76}H_{86}O_{25}Na$ $(M + Na)^+$ 1421.5356, found 1421.5340. **H-5** δ 4.95 (t, *J* = 9 Hz) found from nOe experiment.

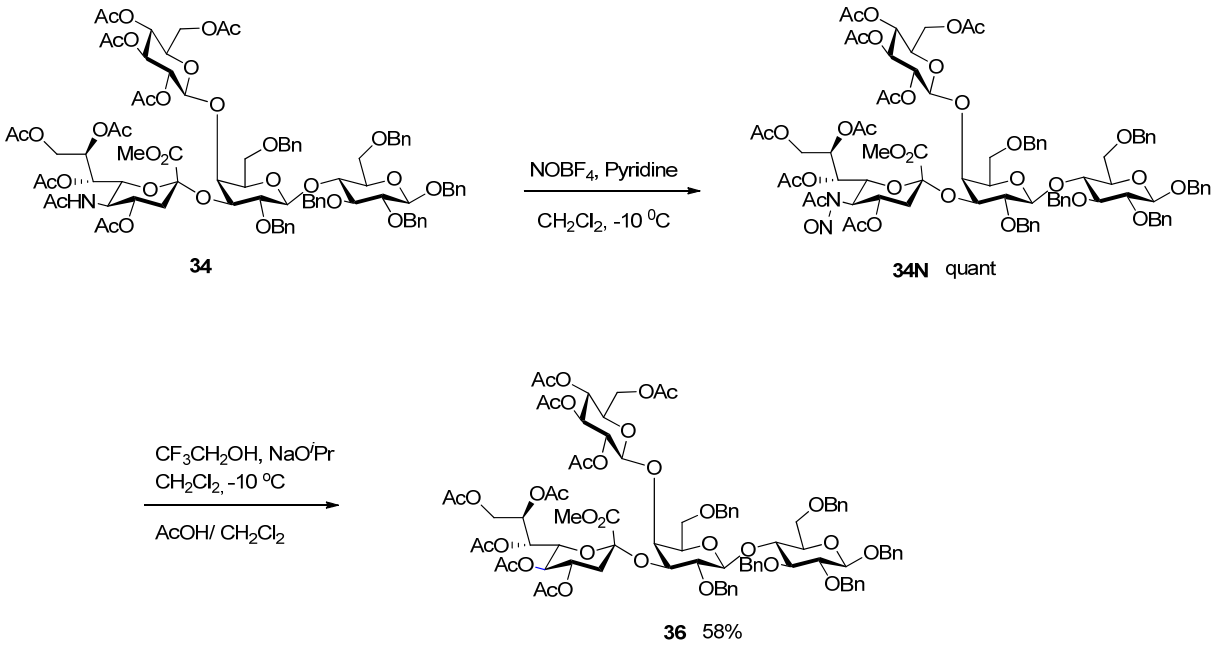
Benzyl [methyl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-2,2',3,6,6'-penta-*O*-benzyl-β-D-lactopyranoside (34).



A solution of the donor **51**[8] (90 mg, 0.22 mmol) and 4 A molecular sieves (600 mg) in anhydrous CH_2Cl_2 (2 mL) was stirred for 4 h. The mixture was cooled to -20 °C and was treated with NIS (61 mg, 0.27 mmol), and TfOH (25 μL, 0.27 mmol). The mixture was stirred for 10 min and the GM3 acceptor **32**[7] (156 mg, 0.11 mmol) in anhydrous CH_2Cl_2 (0.75 mL x 2) was added to the reaction mixture via a syringe over 10 min. The mixture was stirred at -20 °C for 2 h and was quenched by addition of triethylamine (200 μL). The reaction mixture was diluted with CH_2Cl_2 (5 mL) and was filtered through a pad of Celite, and was washed with 20% sodium thiosulphate (4 mL), and brine (5 mL), dried, and concentrated to afford a yellow oil that was purified by flash chromatography (1/5 EtOAc/Hexanes – 4/1 EtOAC/Hexanes) to afford **34** (141 mg**,** 73%) as a colorless oil. $[\alpha]^{23}{}_D$ = + 37 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.5 Hz, 2H), 7.42-7.20 (m, 28 H), 5.28-5.25 (m, 3H), 5.19-5.09 (m, 3H),

5.01 (t, *J* = 9 Hz, 1H), 4.95-4.90 (m, 3H), 4.85-4.77 (m, 4H), 4.66 (s, 1H), 4.64 (s, 1H), 4.53-4.47 (m, 4H), 4.39-4.29 (m, 3H), 4.16-3.95 (m, 7H), 3.90 (m, 1H), 3.87 (s, 3H), 3.84-3.78 (m, 3H), 3.73 (d, *J* = 2.5 Hz, 2H), 3.57 (t, *J* = 9 Hz, 1H), 3.49-3.39 (m, 4H), 2.41 (dd, *J* = 13.5, 5, 1H), 2.16 (s, 4H), 2.12 (s, 3H), 2.04 (s, 3H), 2.00 (s, 6H), 1.90 (s, 6H), 1.92 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) 170.7, 170.7 170.4, 170.3, 170.3, 169.6, 169.5, 169.4, 168.8, 167.8, 139.0, 138.8, 138.6, 138.4, 138.3, 137.6, 129.4, 128.3, 128.2, 128.2, 128.1, 128.1, 128.1, 120.2, 120.2, 127.9, 127.8, 127.6, 127.5, 127.5, 127.4, 127.3, 127.3, 127.3, 102.5, 102.2, 101.5, 99.6, 82.7, 81.7, 78.7, 77.7, 76.0, 75.2, 75.1, 73.2, 73.2, 73.1, 72.6, 72.2, 71.8, 70.9, 70.7, 69.0, 68.7, 68.2, 68.0, 67.8, 66.7, 61.7, 61.6, 53.2, 49.1, 35.6, 23.2, 21.1. ESIHRMS: *m/z* calcd. for $C_{88}H_{103}NO_{32}Na$ $(M + Na)^+$ 1708.6361, found 1708.6348.

Benzyl [methyl (4,5,7,8,9-penta-*O*-acetyl-3,5-dideoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate)-(2→3)-[2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl]-(1→4)-2,2',3,6,6'-penta-*O*-benzyl-β-D-lactopyranoside (36).



The tetrasaccharide **34** (140 mg, 0.083 mmol) was nitrosated by the general procedure **1** using $NOBF_4$ (38 mg, 0.032 mmol) and pyridine (70 μL, 0.83 mmol) to afford the nitrosyl tetrasaccharide **34N** (142 mg) as

a yellow foam. The tetrasaccharide **34N** was deaminated by the general procedure **2** with acetic acid as the nucleophile with 2,2,2 trifluoroethanol (10 μL, 0.12 mmol), 0.2 N sodium isopropoxide in isopropanol (0.5 mL, 0.99 mmol), and acetic acid (95 μL, 1.65 mmol) to afford after purification by normal phase HPLC (Hexanes/EtOAc 80:20 to 30:70) the tetrasaccharide **36** as a colorless oil (81 mg, 58%). $[\alpha]^{23}_{D}$ = + 17 (*c* = 0.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7 Hz, 2H), 7.42-7.20 (m, 6H), 7.34-7.20 (m, 22H), 5.32-5.22 (m, 3H), 5.17 (t, *J* = 10 Hz, 1H) 5.09 (d, *J* = 10 Hz, 1H), 5.01 (t, *J* = 10 Hz, 1H), 4.96-4.90 (m, 3H), 4.85-4.81 (m, 3H), 4.80-4.73 (m, 2H), 4.69-4.64 (m, 2 H), 4.51-4.47 (m, 3H), 4.40-4.37 (m, 3H), 4.16 (dd, *J* = 12.5, 2 Hz, 1H), 4.12-4.08 (m, 2H), 4.03 (t, *J* = 10 Hz, 1H), 3.99-3.94 (m, 2H), 3.92-3.89 (m, 3H), 3.86-3.78 (m, 3H), 3.74 (d, *J* = 1.5 Hz, 2H), 3.58 (t, *J* = 8.5 Hz, 1H), 3.50-3.41 (m, 6H), 2.50 (dd, *J* = 13.5, 5 Hz, 1H), 2.18 (s, 3H), 2.12 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.98 (s, 7H), 1.96 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) 170.6, 170.4, 170.3, 169.9, 169.7, 169.5, 169.5, 169.4, 168.8, 167.5, 139.0, 138.7, 138.6, 138.4, 138.1, 137.6, 129.4, 128.3, 128.2, 128.2, 128.2, 128.2, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.5, 127.4, 127.4, 127.3, 102.5, 102.1, 101.5, 99.6, 82.7, 81.7, 78.6, 77.3, 75.2, 75.2, 75.1, 73.2, 73.2, 73.1, 72.6, 71.8, 71.1, 70.9, 70.8, 69.3, 68.7, 68.2, 68.0, 67.4, 67.3, 66.0, 61.6, 61.4, 53.3, 21.1, 20.8, 20.7, 20.6, 20.6, 20.6, 20.4. ESIHRMS: *m/z* calcd. for $C_{88}H_{102}O_{33}Na$ $(M + Na)^+$ 1709.6201, found 1709.6218.

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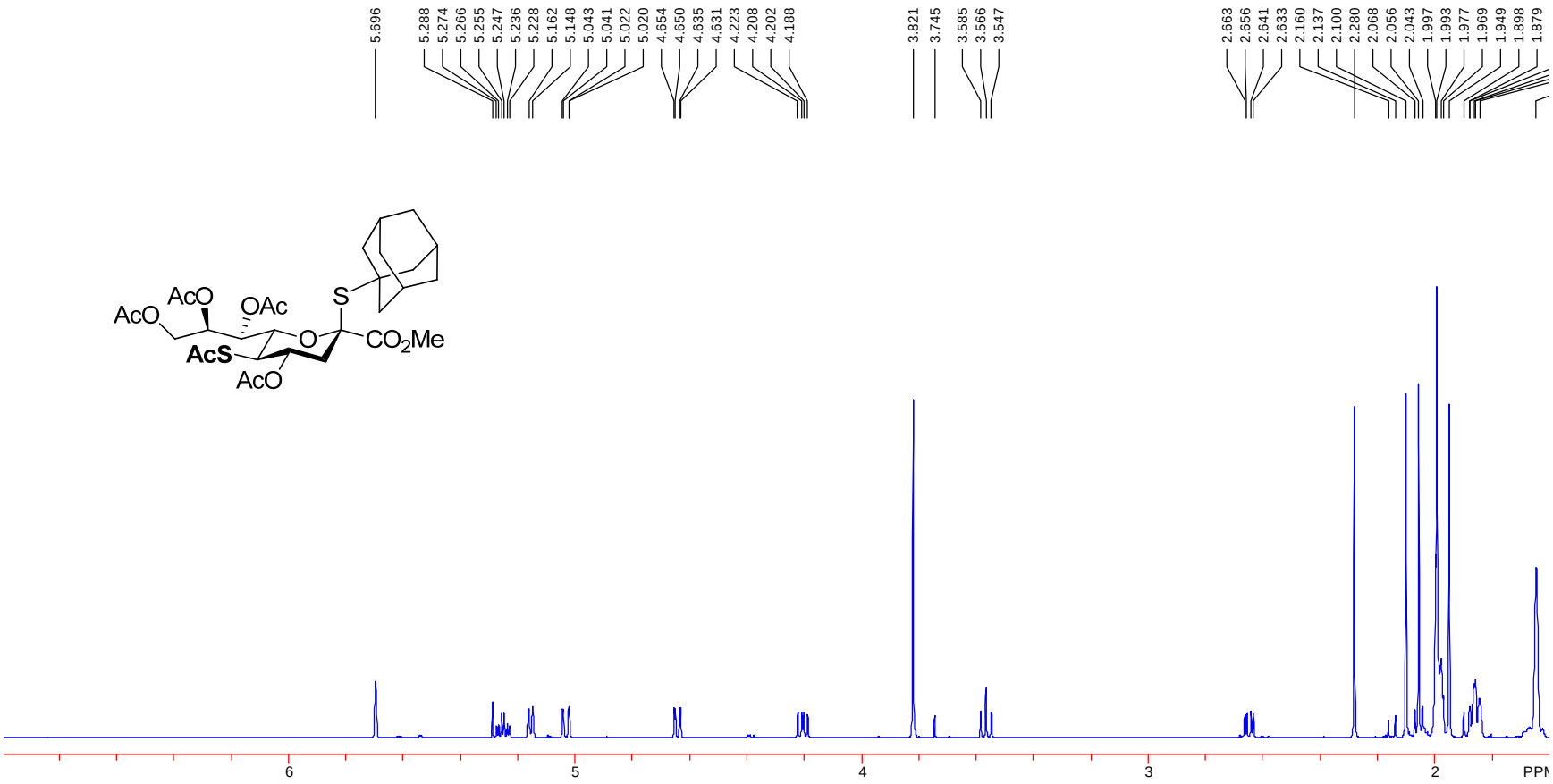
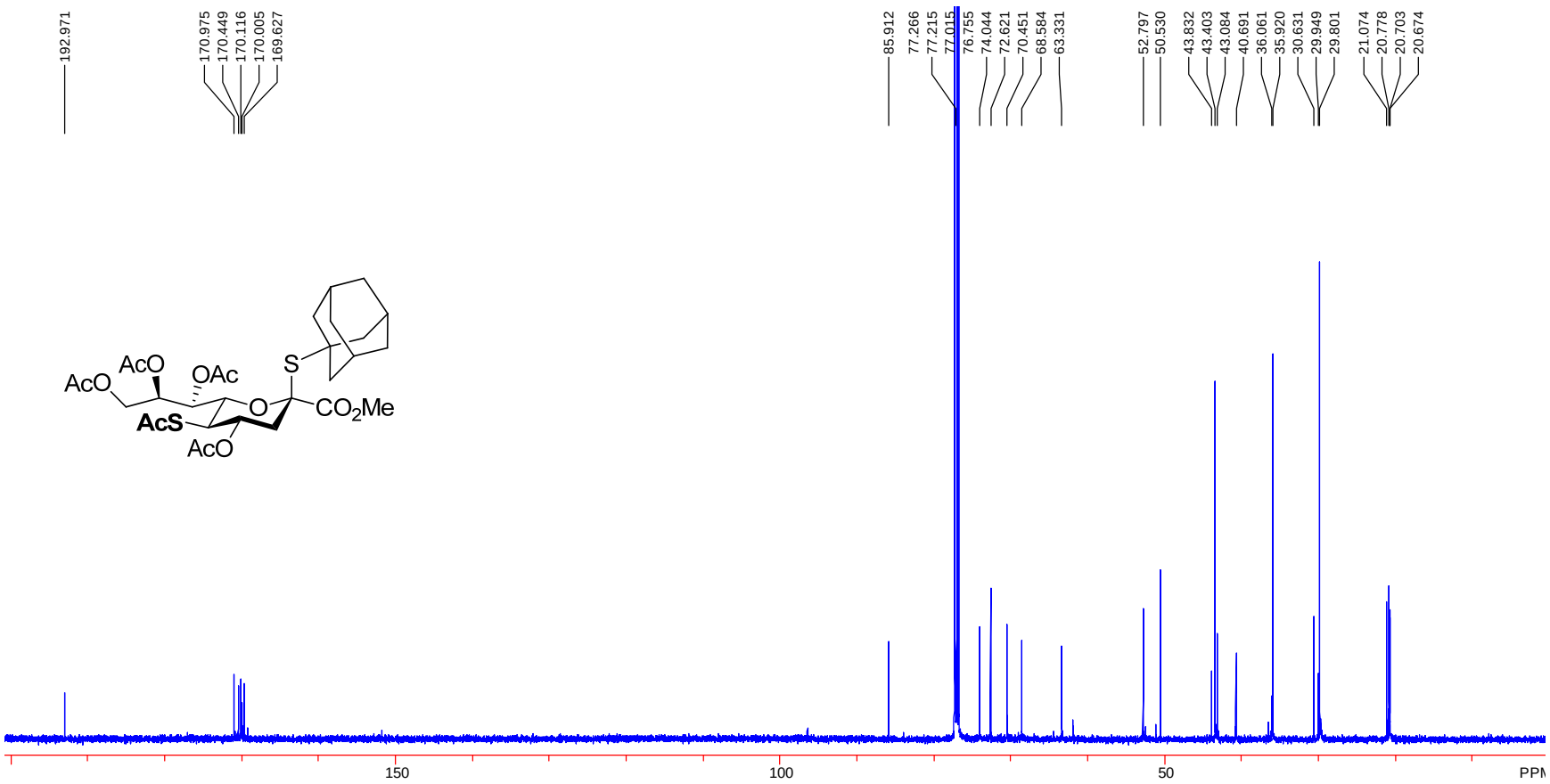
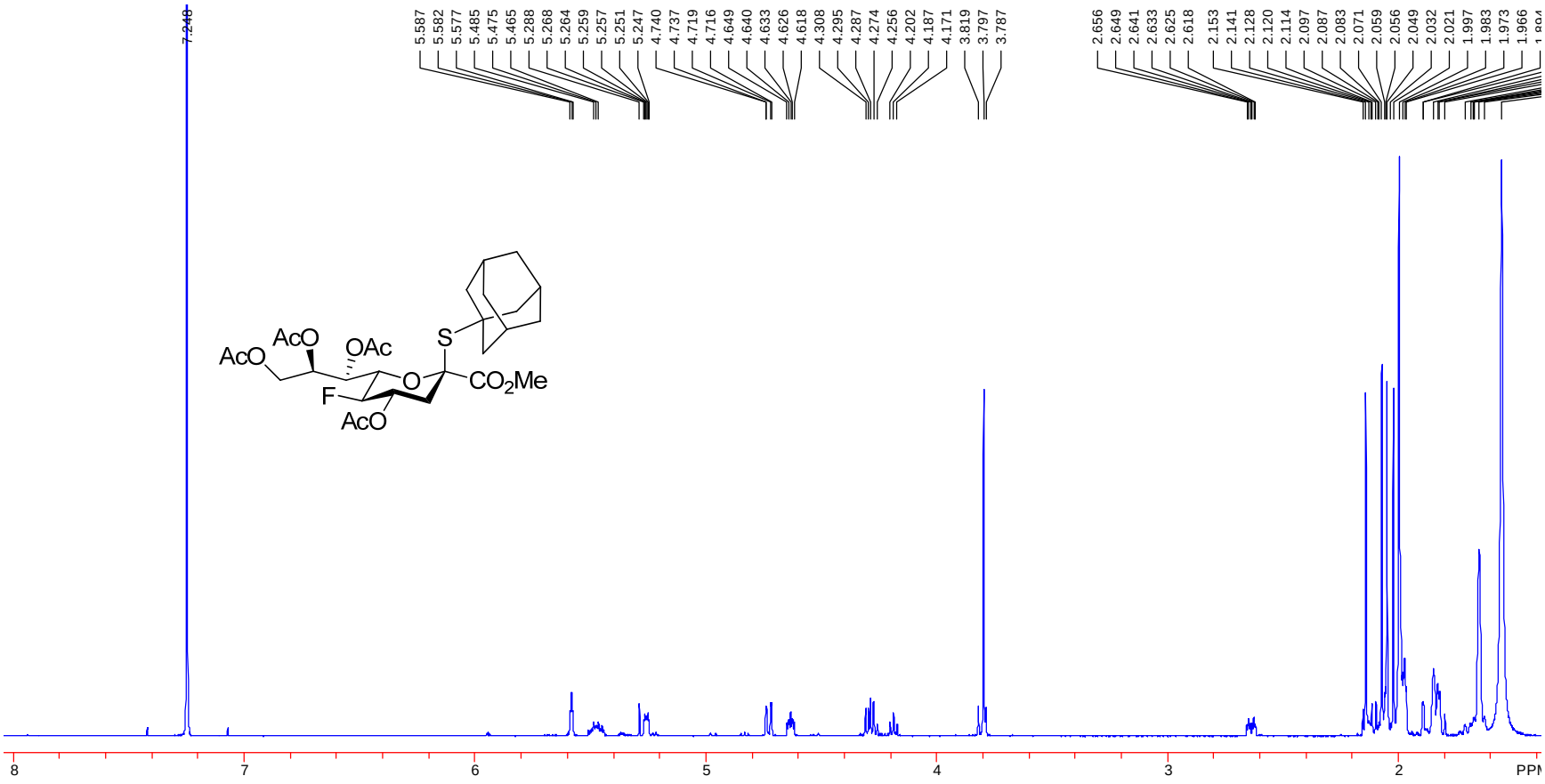
Methyl (1-adamantanyl 4,7,8,9-penta-*O*-acetyl-5-acetylthio-3,5-dideoxy- β-D-*glycero*-D-*galacto*-2-thiononulopyranosid)onate (9) ^{1}H NMR (600 MHz, $CDCl_3$)



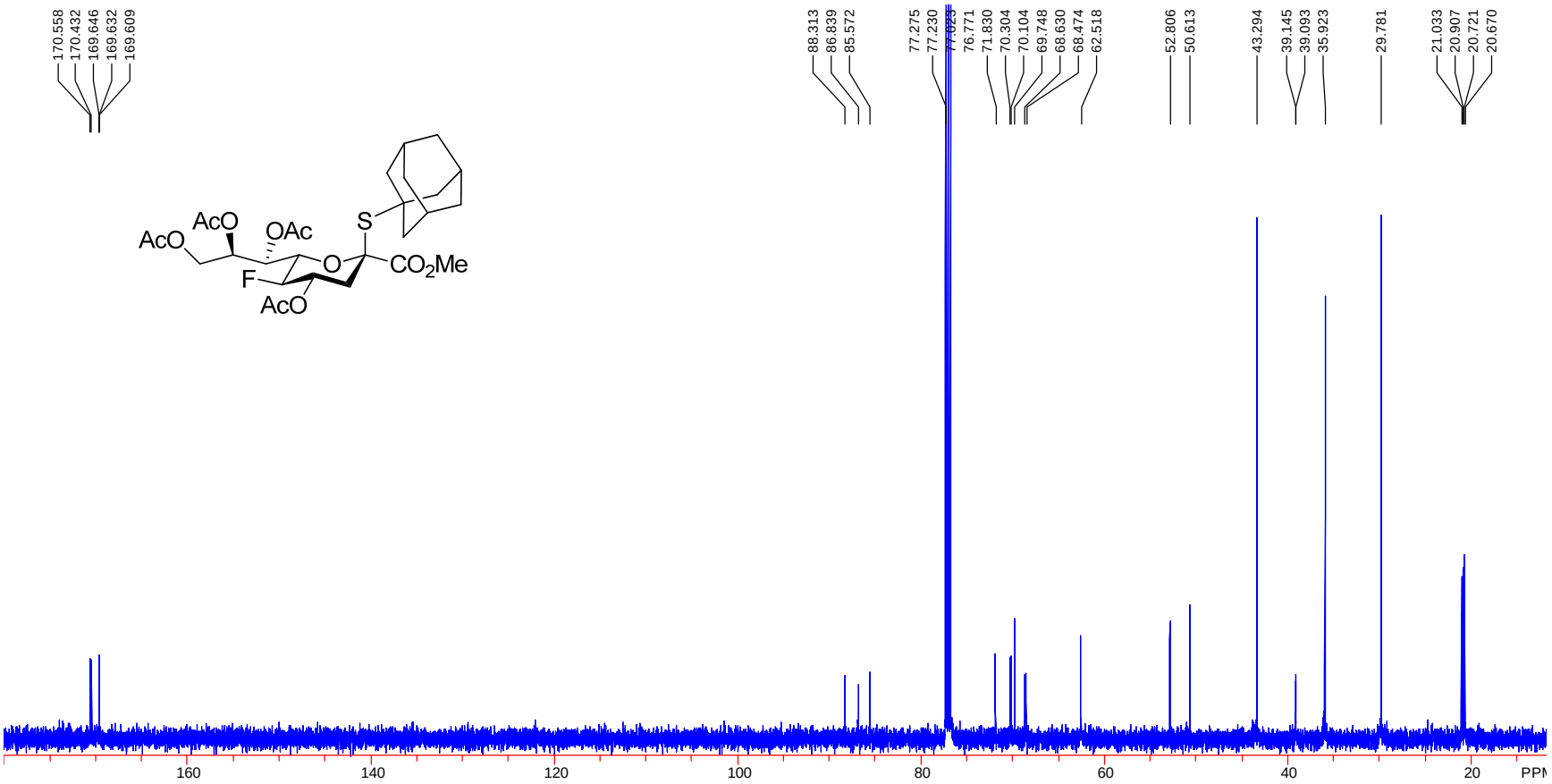
Methyl (1-adamantanyl 4,7,8,9-penta-*O*-acetyl-5-acetylthio-3,5-dideoxy- β-D-*glycero*-D-*galacto*-2-thiononulopyranosid)onate (9) ^{13}C NMR (150 MHz, $CDCl_3$)



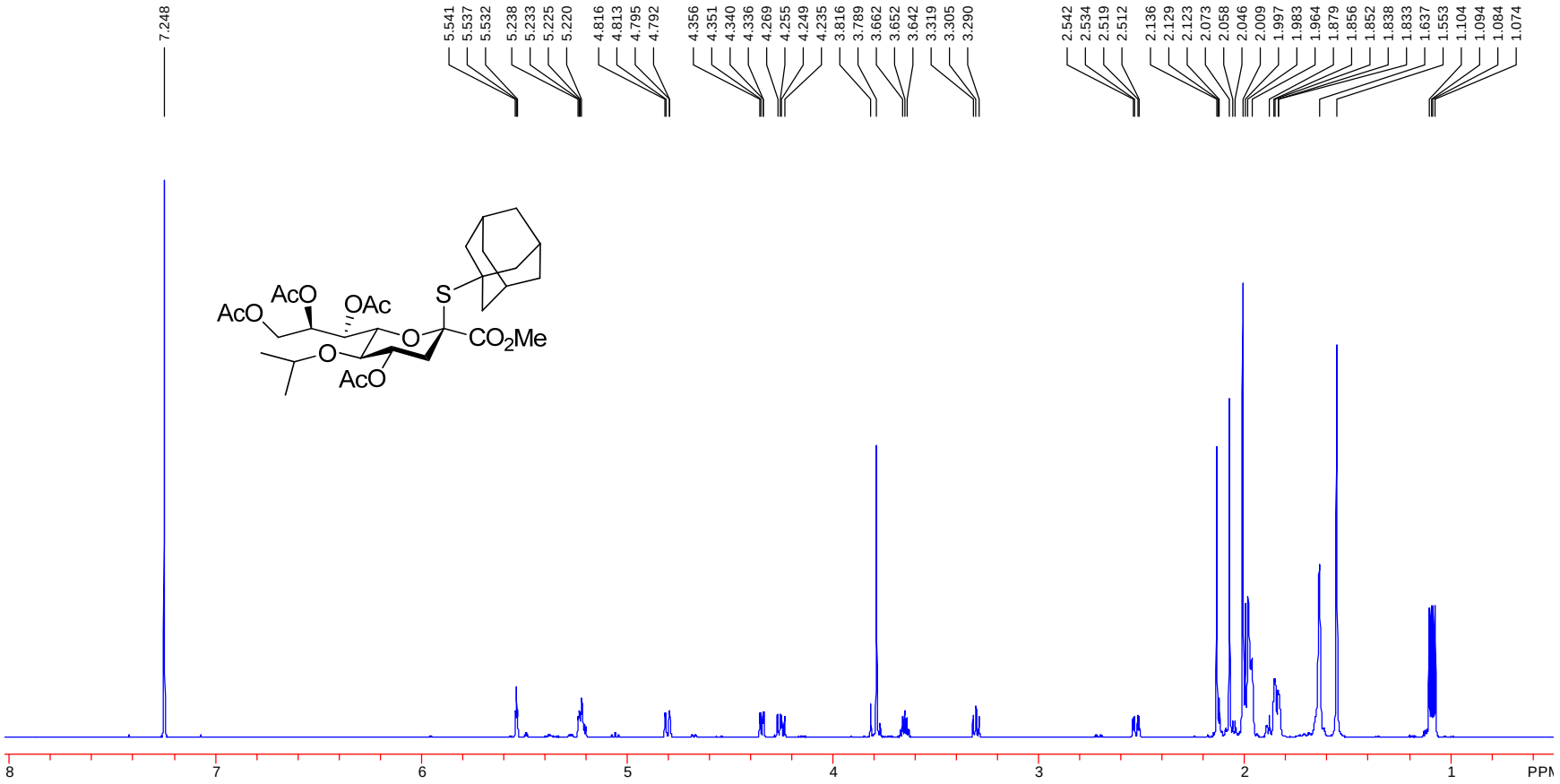
Methyl (1-adamantanyl 4,7,8,9-penta-O-acetyl-5-fluoro-3,5-dideoxy-β-D-*glycero*-D-*galacto*-2-thiononulopyranosid)onate (10) ^{1}H NMR (500 MHz, $CDCl_3$)



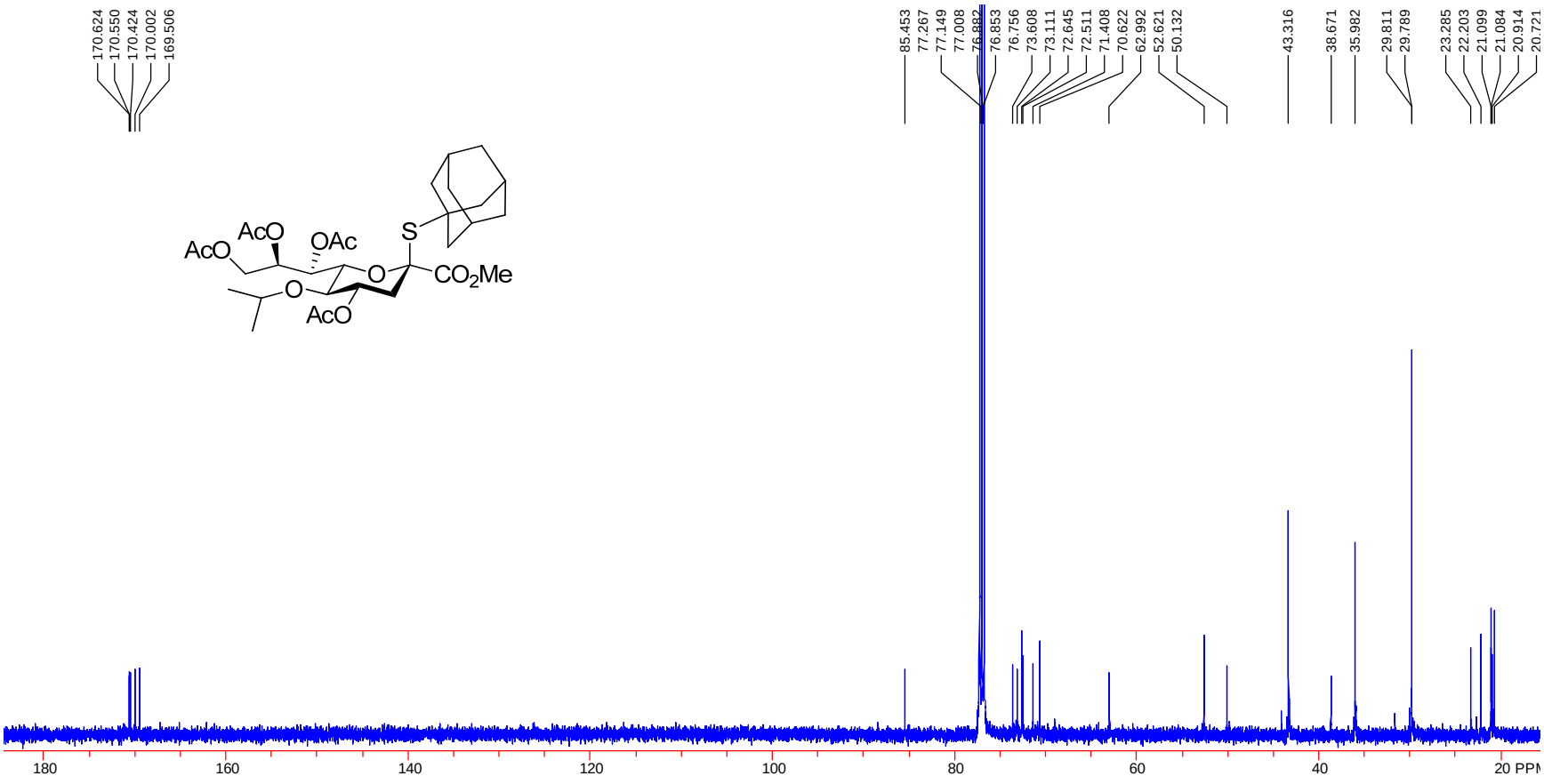
Methyl (1-adamantanyl 4,7,8,9-penta-O-acetyl-5-fluoro-3,5-dideoxy-β-D-*glycero*-D-*galacto*-2-thiononulopyranosid)onate (10) ^{13}C NMR (125 MHz, $CDCl_3$)



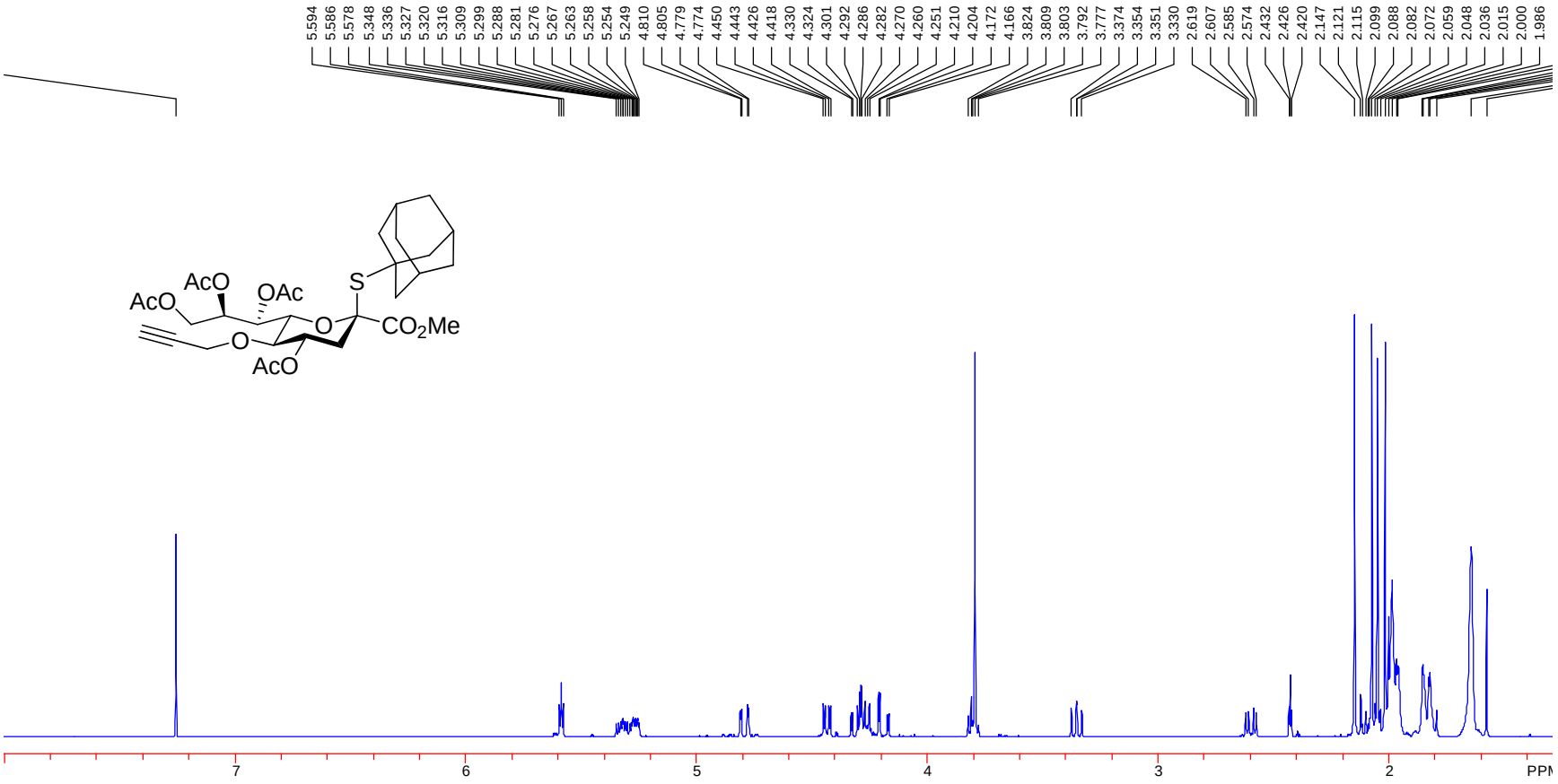
Methyl (1-adamantanyl 4,7,8,9-penta-*O*-acetyl-5-*O*-isopropyl-3-deoxy-β-D-*glycero*-D-*galacto*-2-thiononulopyranosid)onate (11) ^{1}H NMR (500 MHz, $CDCl_3$)



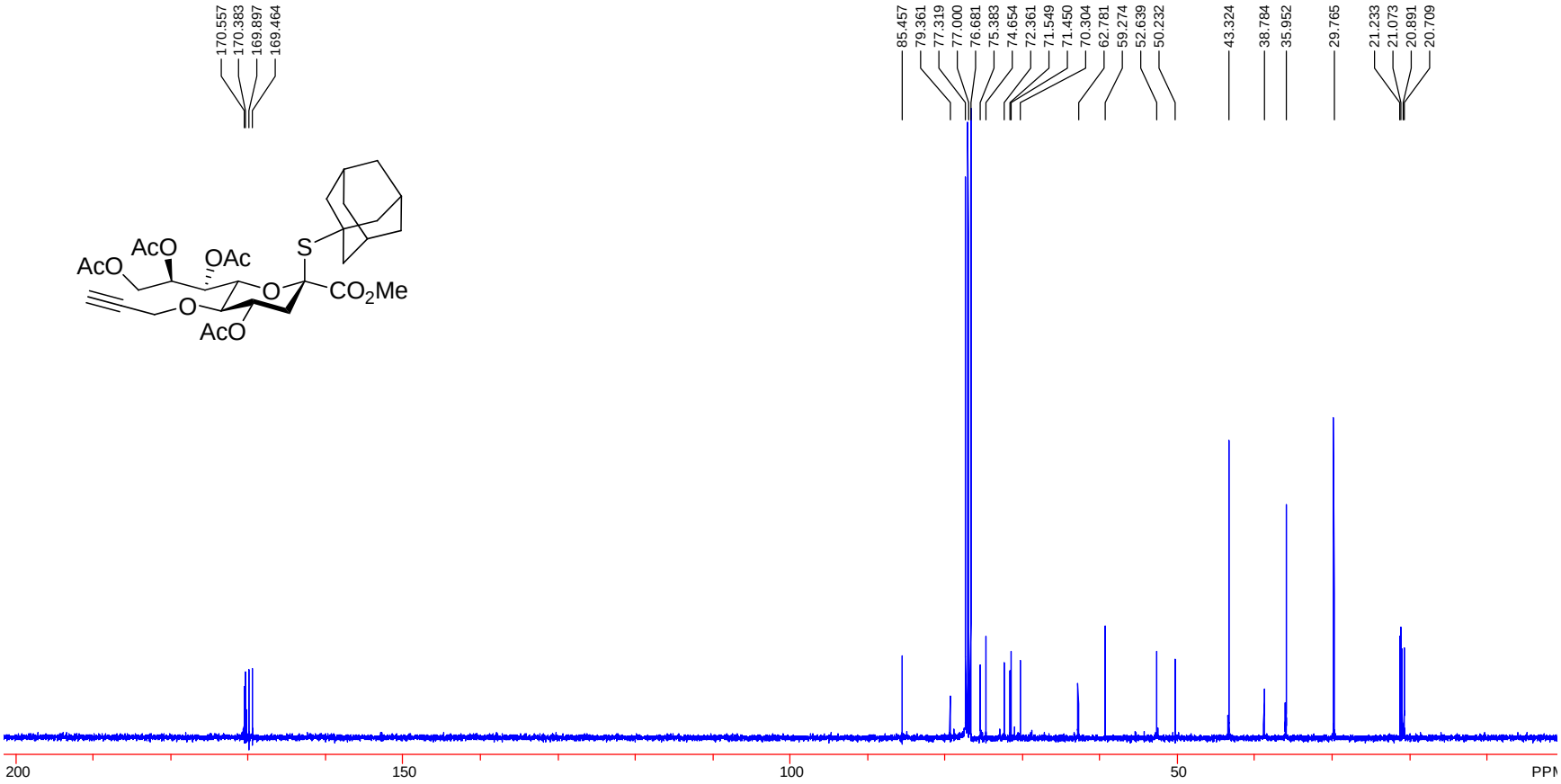
Methyl (1-adamantanyl 4,7,8,9-penta-*O*-acetyl-5-*O*-isopropyl-3-deoxy-β-D-*glycero*-D-*galacto*-2-thiononulopyranosid)onate (11) ^{13}C NMR (100 MHz, $CDCl_3$)



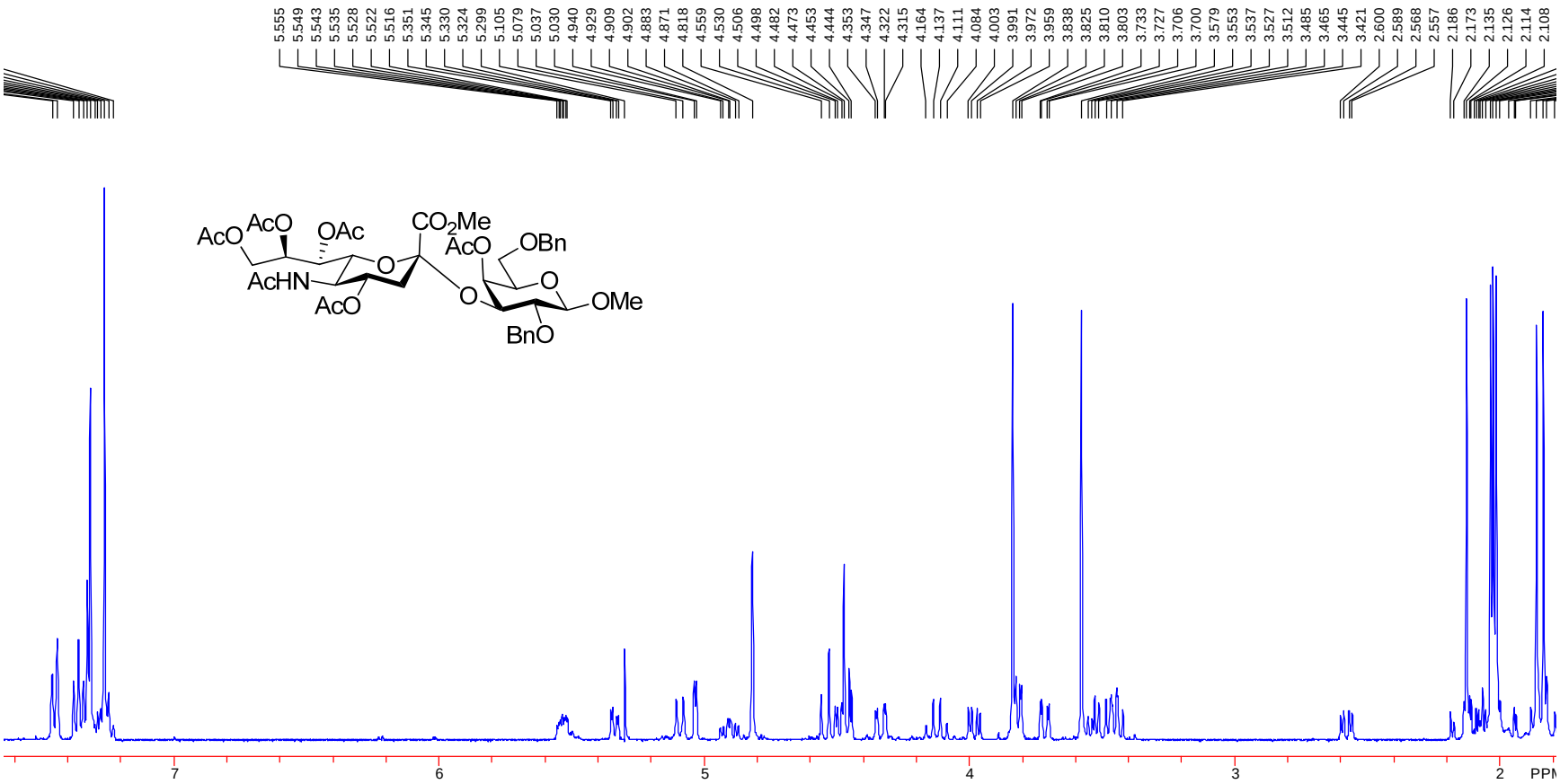
Methyl (1-adamantanyl 4,7,8,9-penta-*O*-acetyl-5-prop-3-ynyl-3-deoxy-β-D-*glycero*-D-*galacto*-2-thiononulopyranosid)onate (13) ^{1}H NMR (400 MHz, $CDCl_3$)



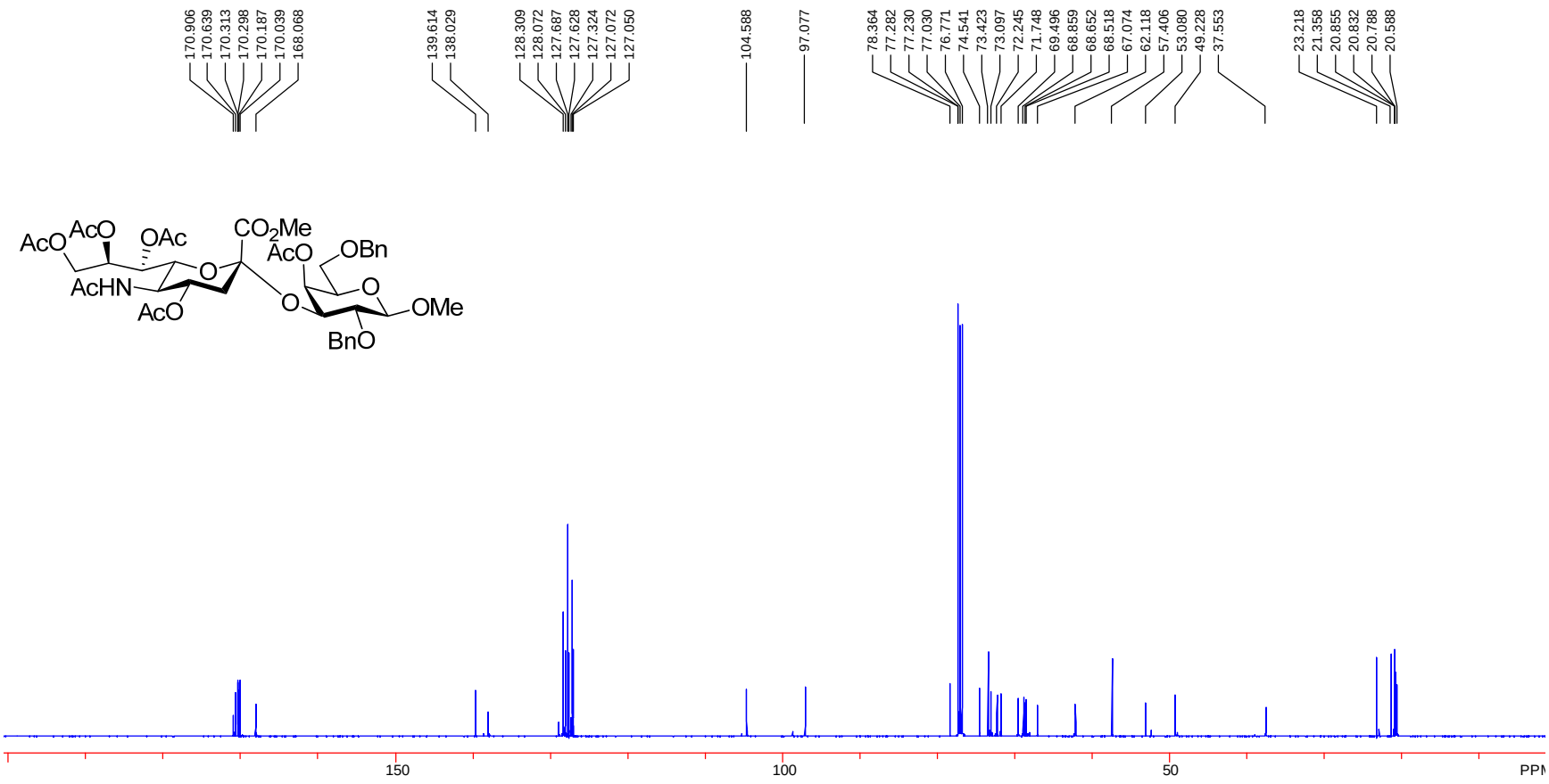
Methyl (1-adamantanyl 4,7,8,9-penta-*O*-acetyl-5-prop-3-ynyl-3-deoxy-β-D-*glycero*-D-*galacto*-2-thiononulopyranosid)onate (13) ^{13}C NMR (100 MHz, $CDCl_3$)



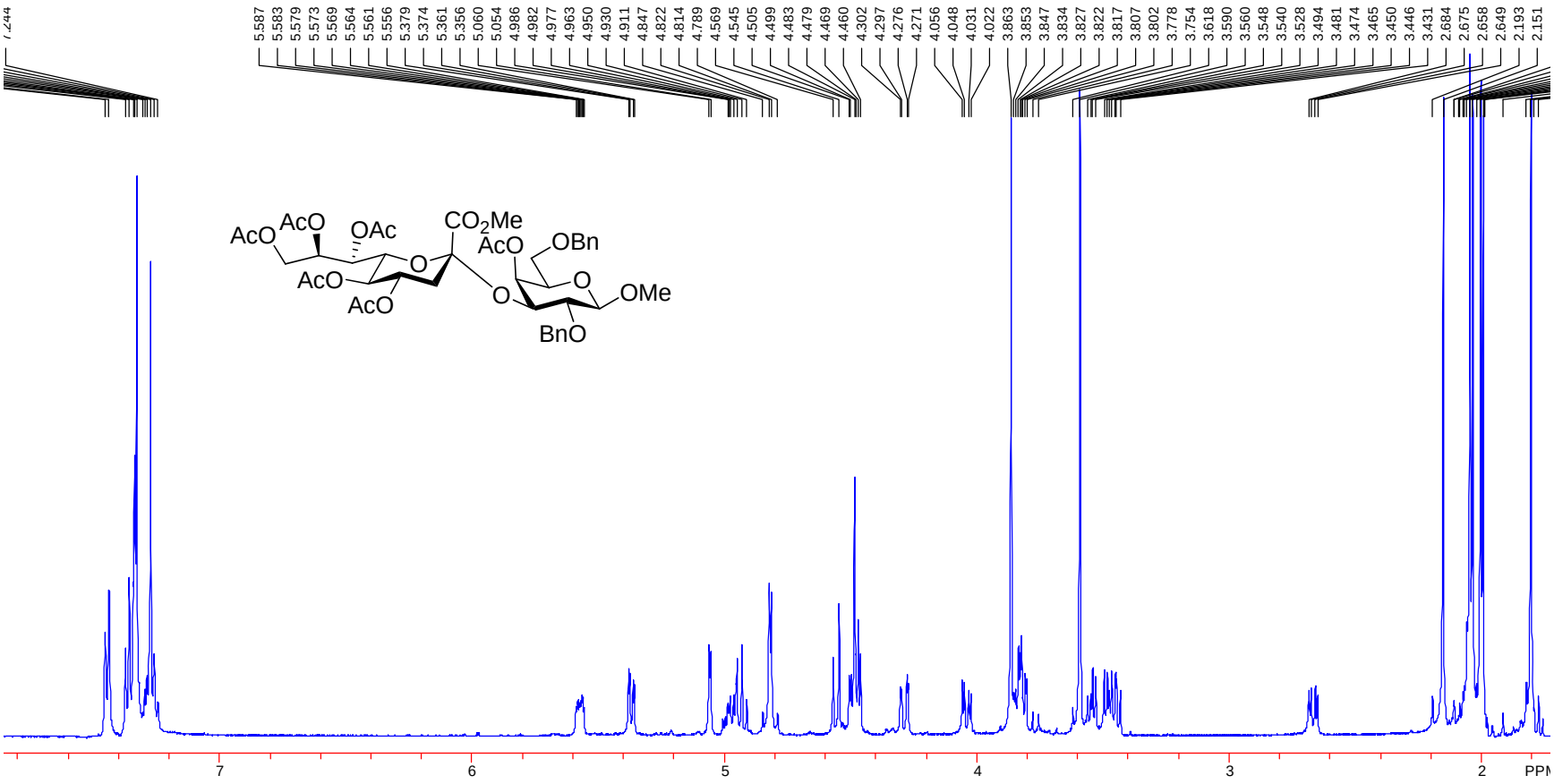
Methyl [methyl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-α-D-*glycero*-D-*galacto*-non-2-ulopyranosyl)onate]-(2→3)-4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranoside (22) ^{1}H NMR (500 MHz, $CDCl_3$)



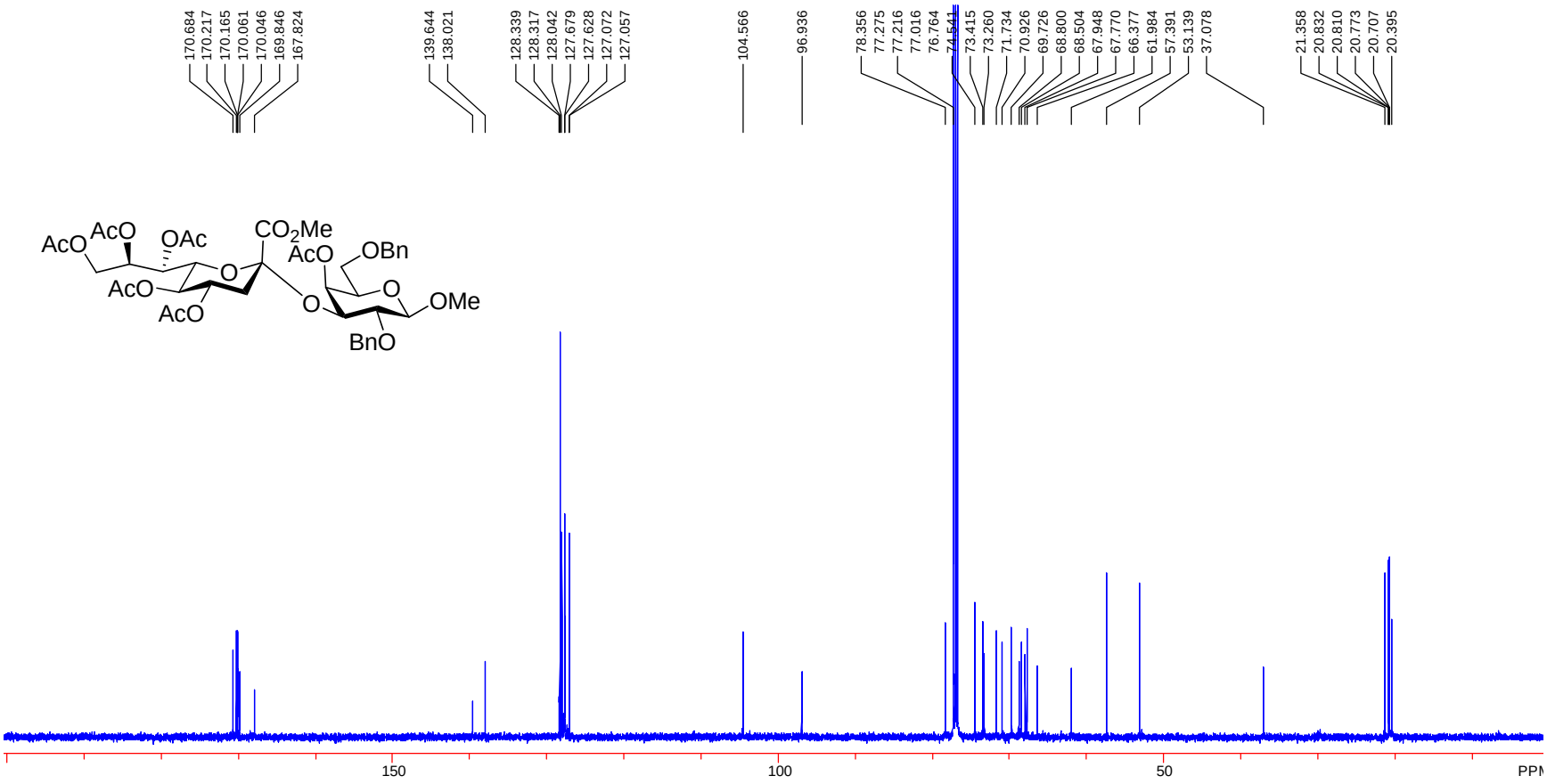
Methyl [methyl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-α-D-*glycero*-D-*galacto*-non-2-ulopyranosyl)onate]-(2→3)-4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranoside (22) ^{13}C NMR (125 MHz, $CDCl_3$)



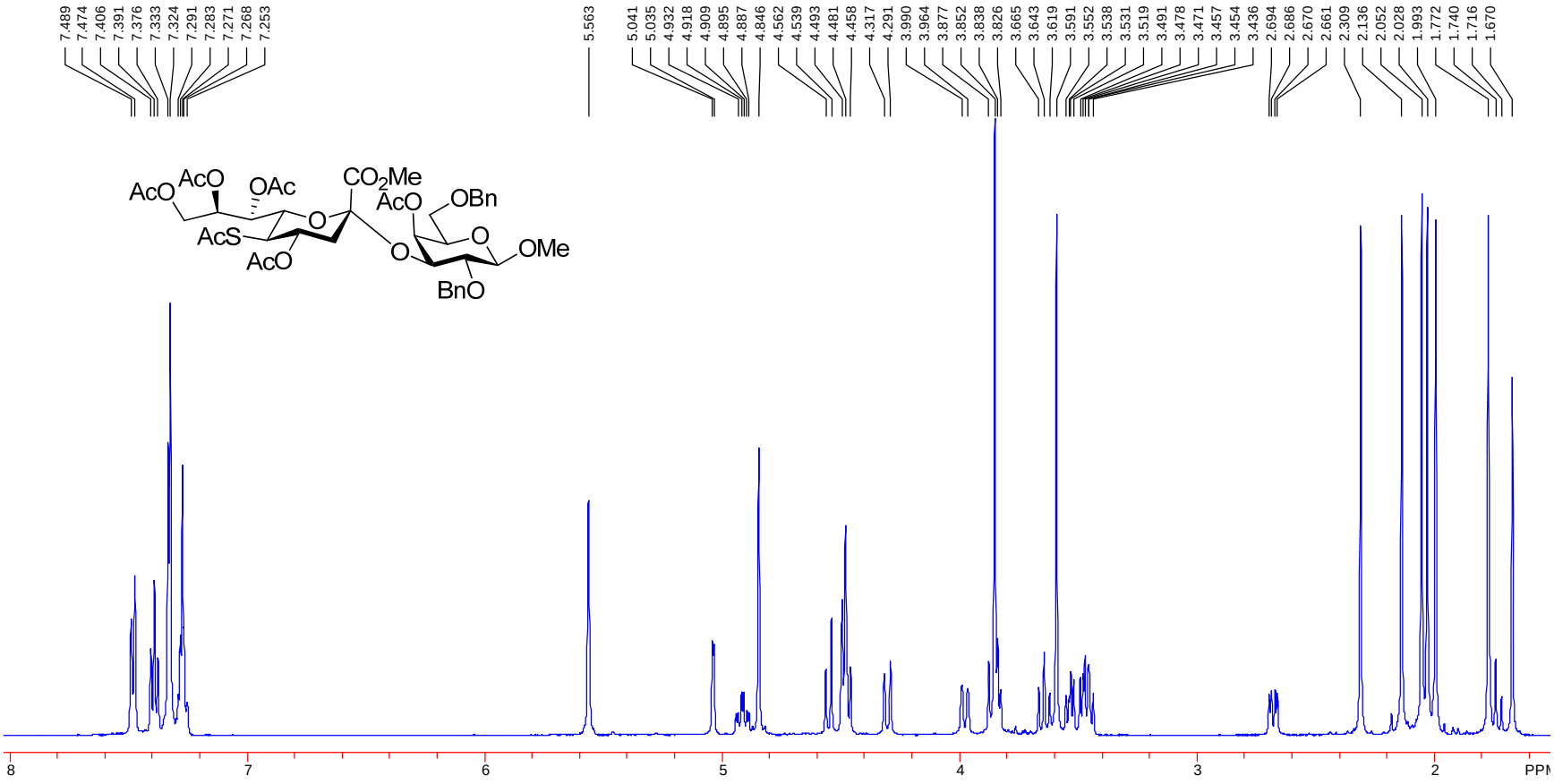
Methyl [methyl (4,5,7,8,9-penta-*O*-acetyl-3-deoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranoside (27) ^{1}H NMR (500 MHz, $CDCl_3$)



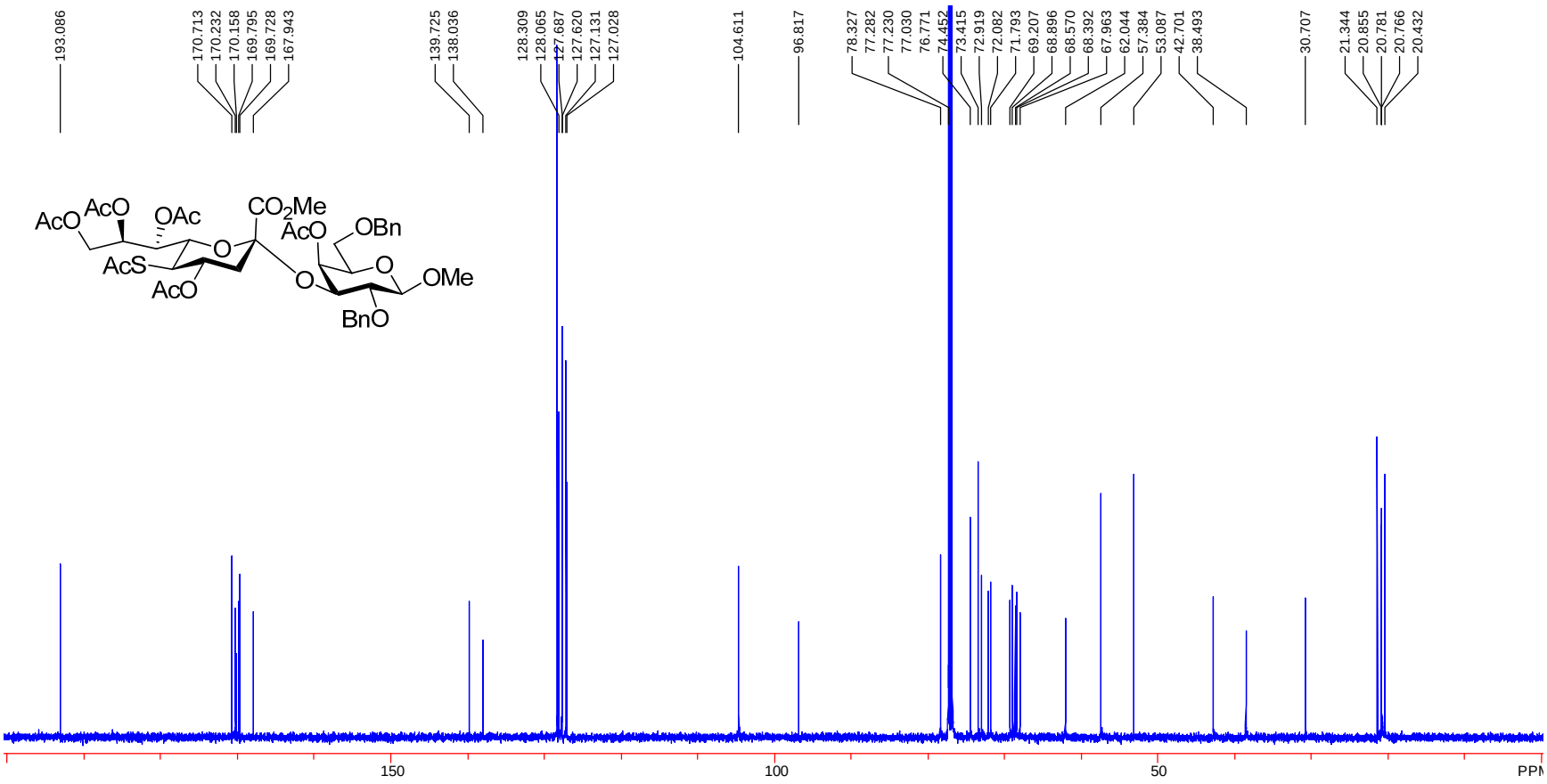
Methyl [methyl (4,5,7,8,9-penta-*O*-acetyl-3-deoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranoside (27) ^{13}C NMR (125 MHz, $CDCl_3$)



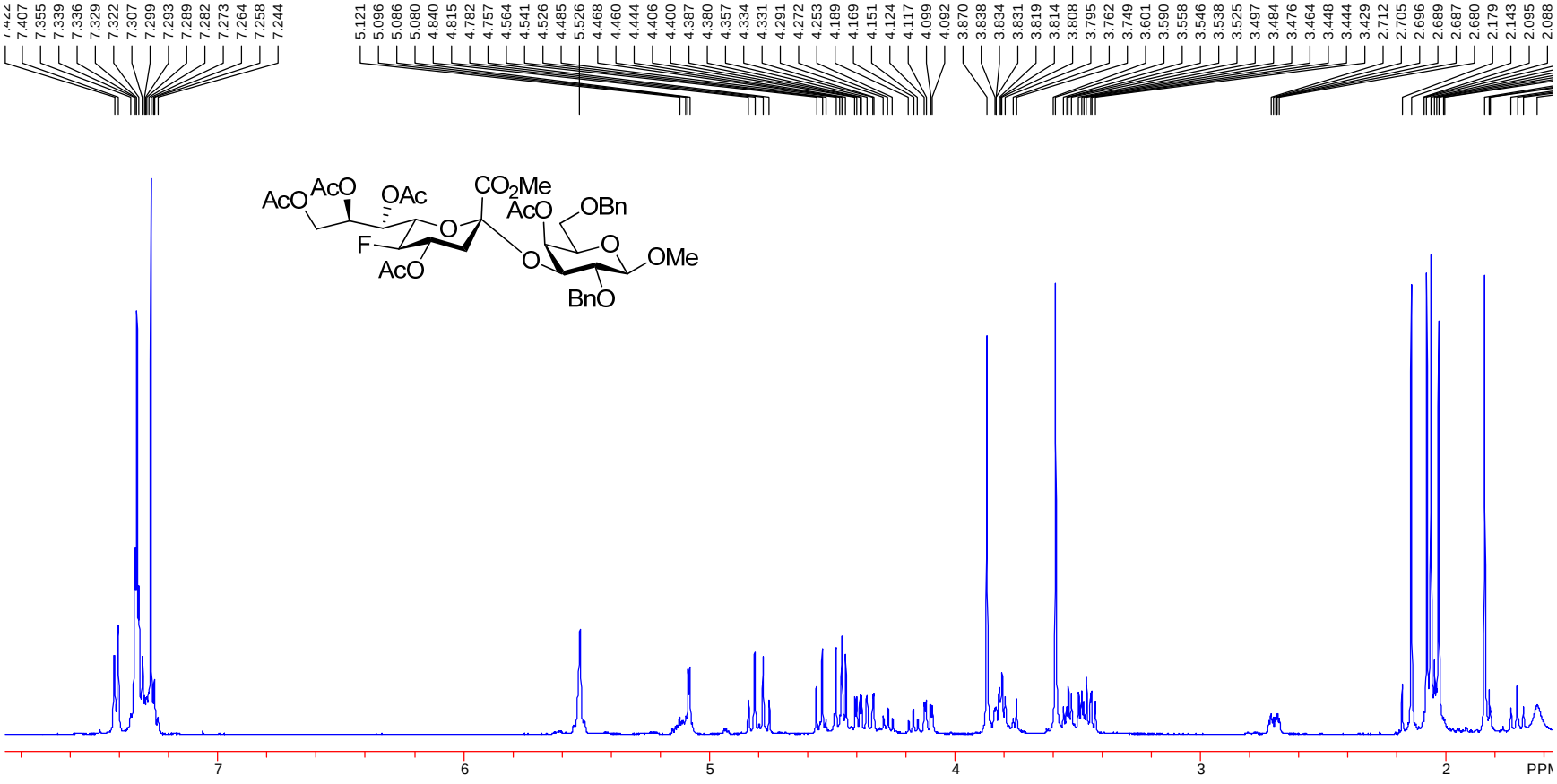
Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-5-acetylthio-3,5-dideoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranoside (28) ^{1}H NMR (500 MHz, $CDCl_3$)



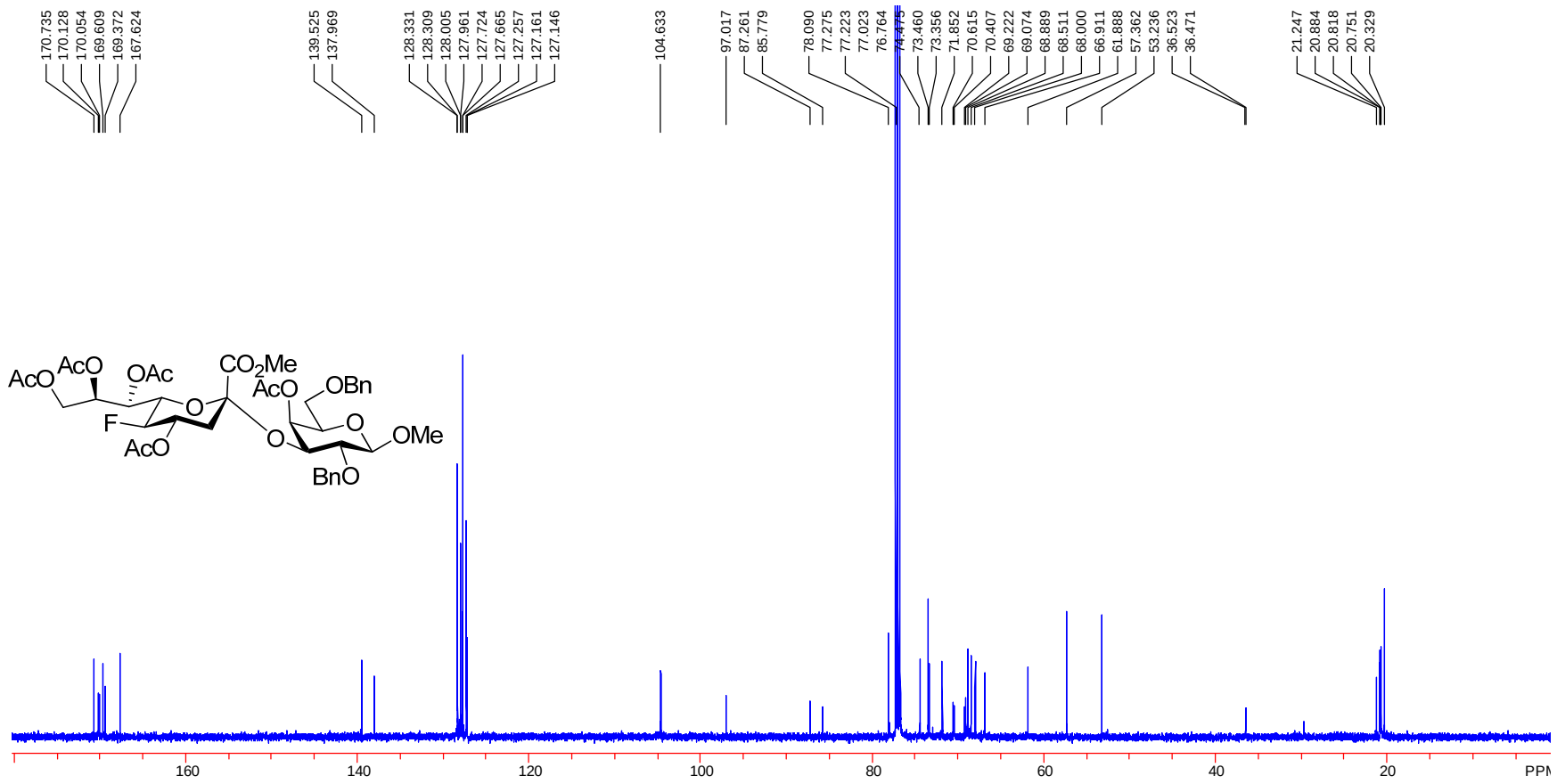
Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-5-acetylthio-3,5-dideoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranoside (28) ^{13}C NMR (125 MHz, $CDCl_3$)



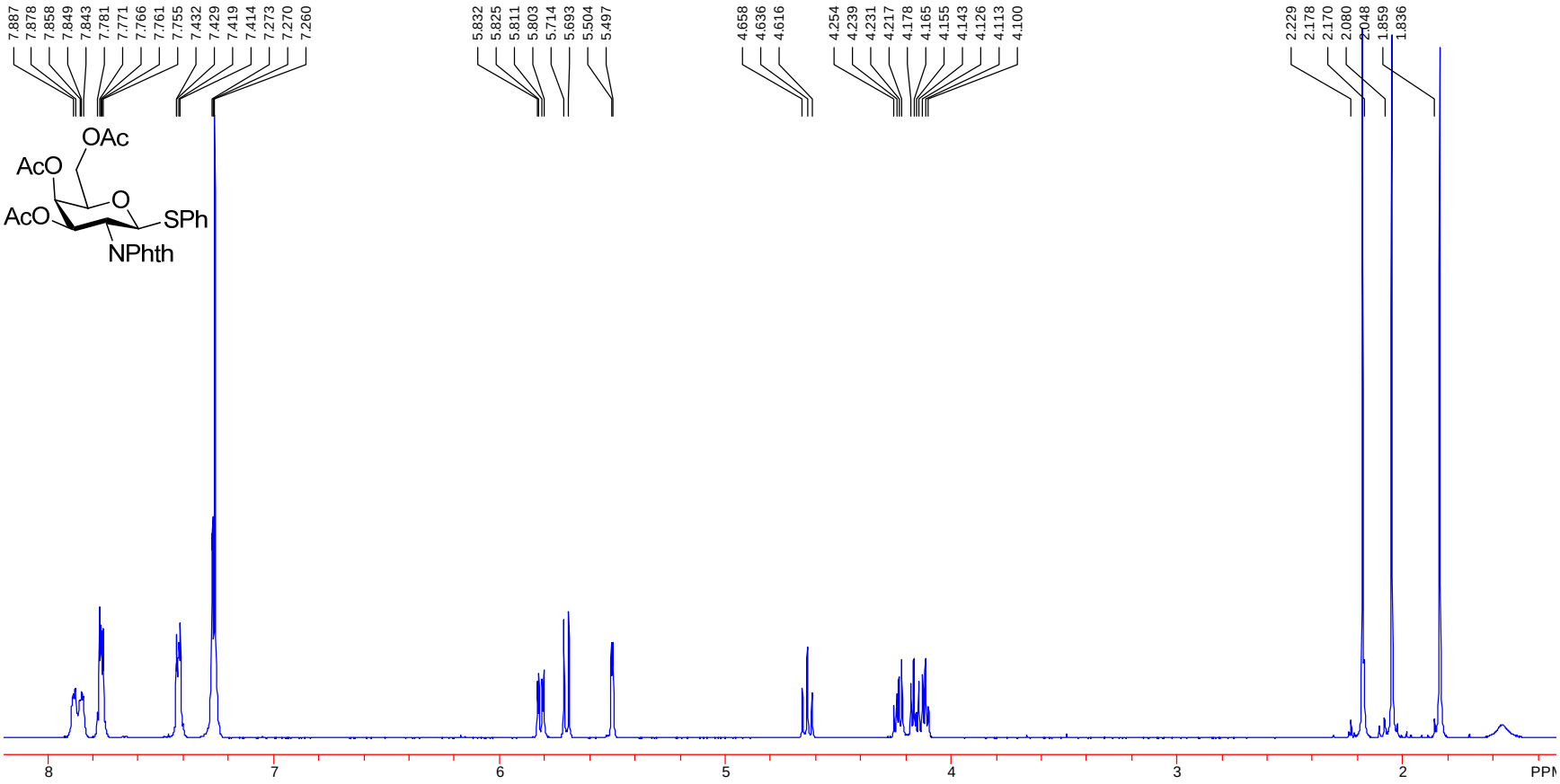
Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-5-fluoro-3,5-dideoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranoside (29) ^{1}H NMR (500 MHz, $CDCl_3$)



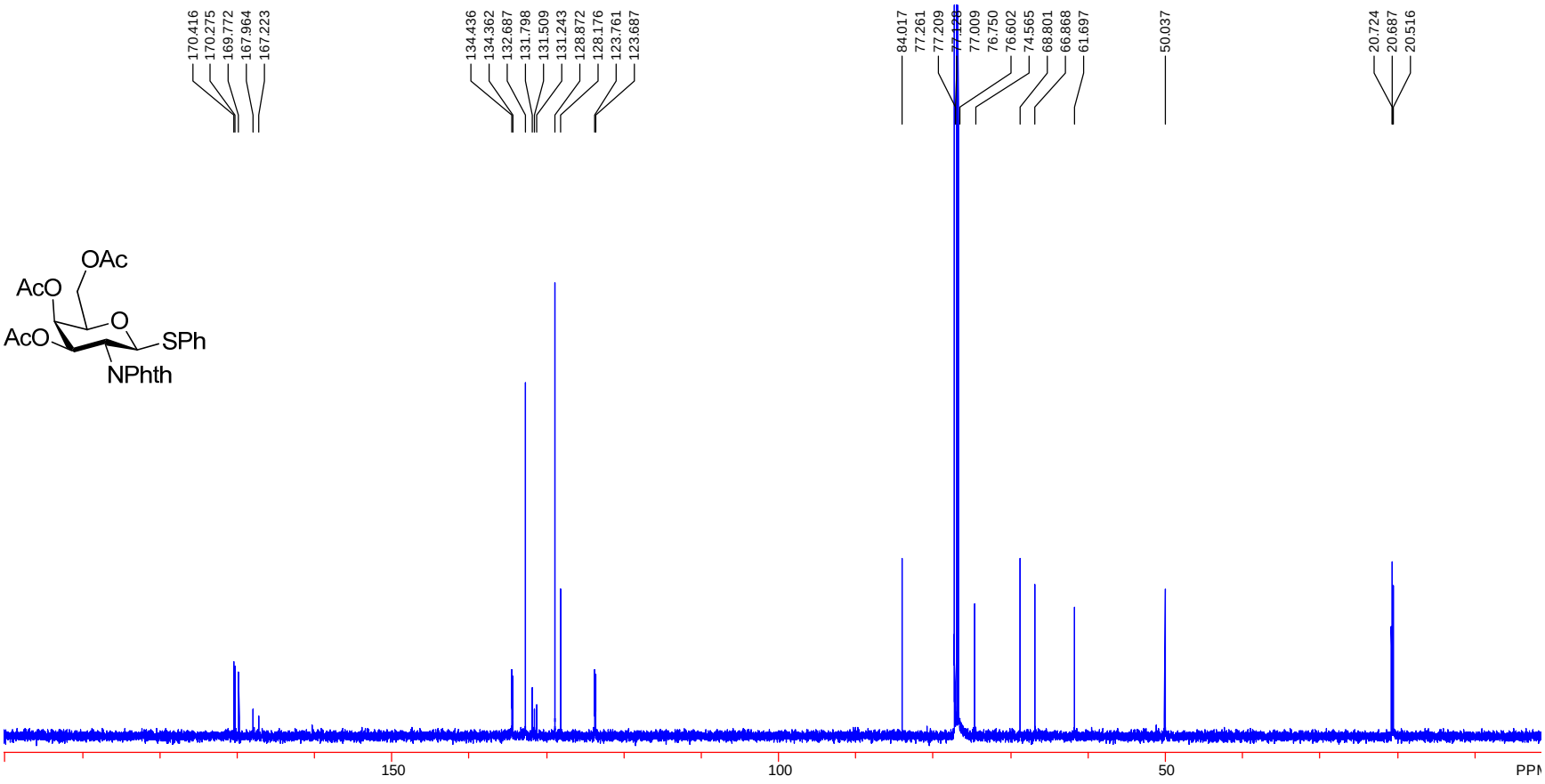
Methyl [methyl (4,7,8,9-tetra-*O*-acetyl-5-fluoro-3,5-dideoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranoside (29) ^{13}C NMR (125 MHz, $CDCl_3$)



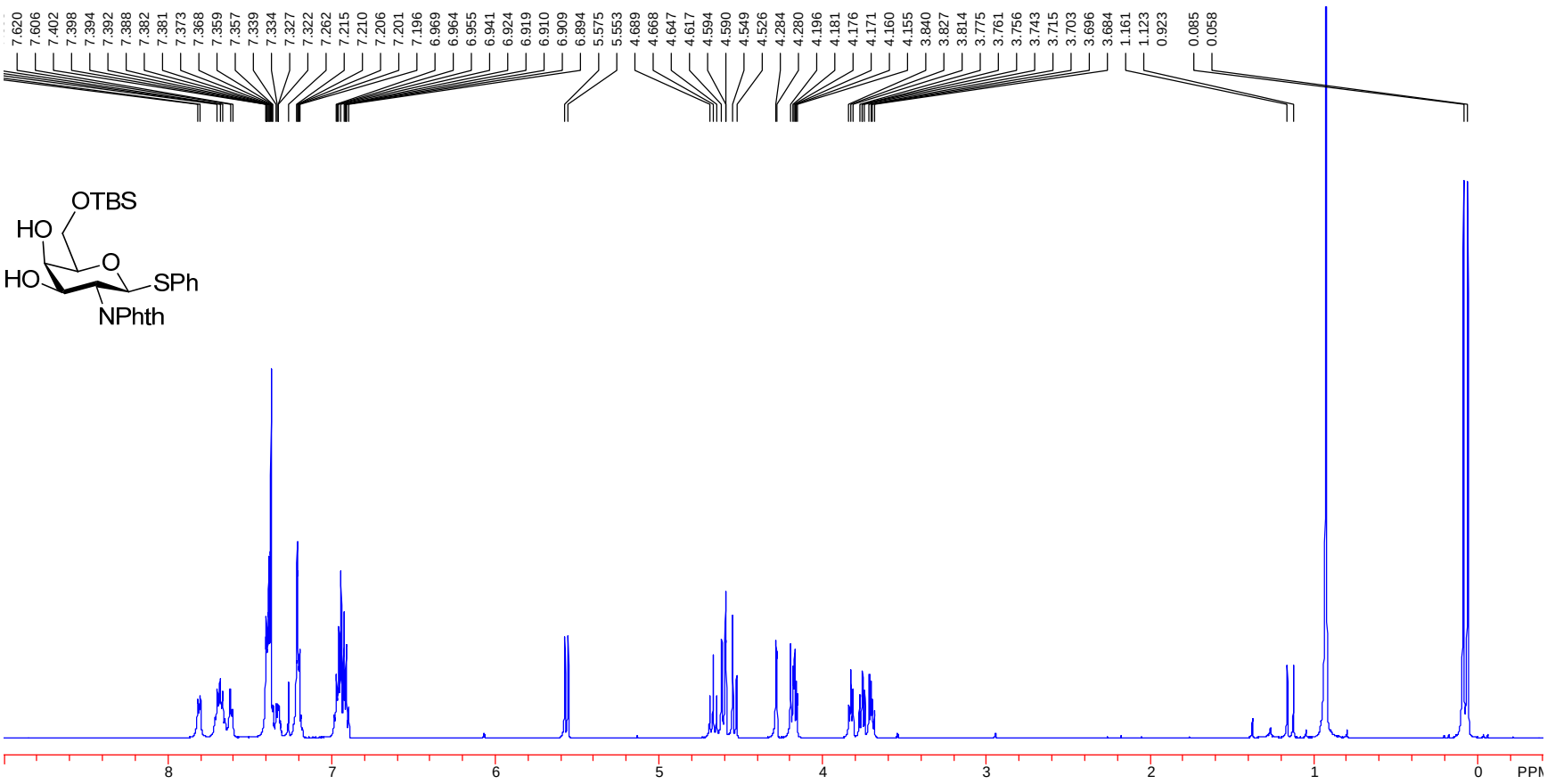
Phenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-thiogalactopyranoside (45) ^{1}H NMR (500 MHz, $CDCl_3$)



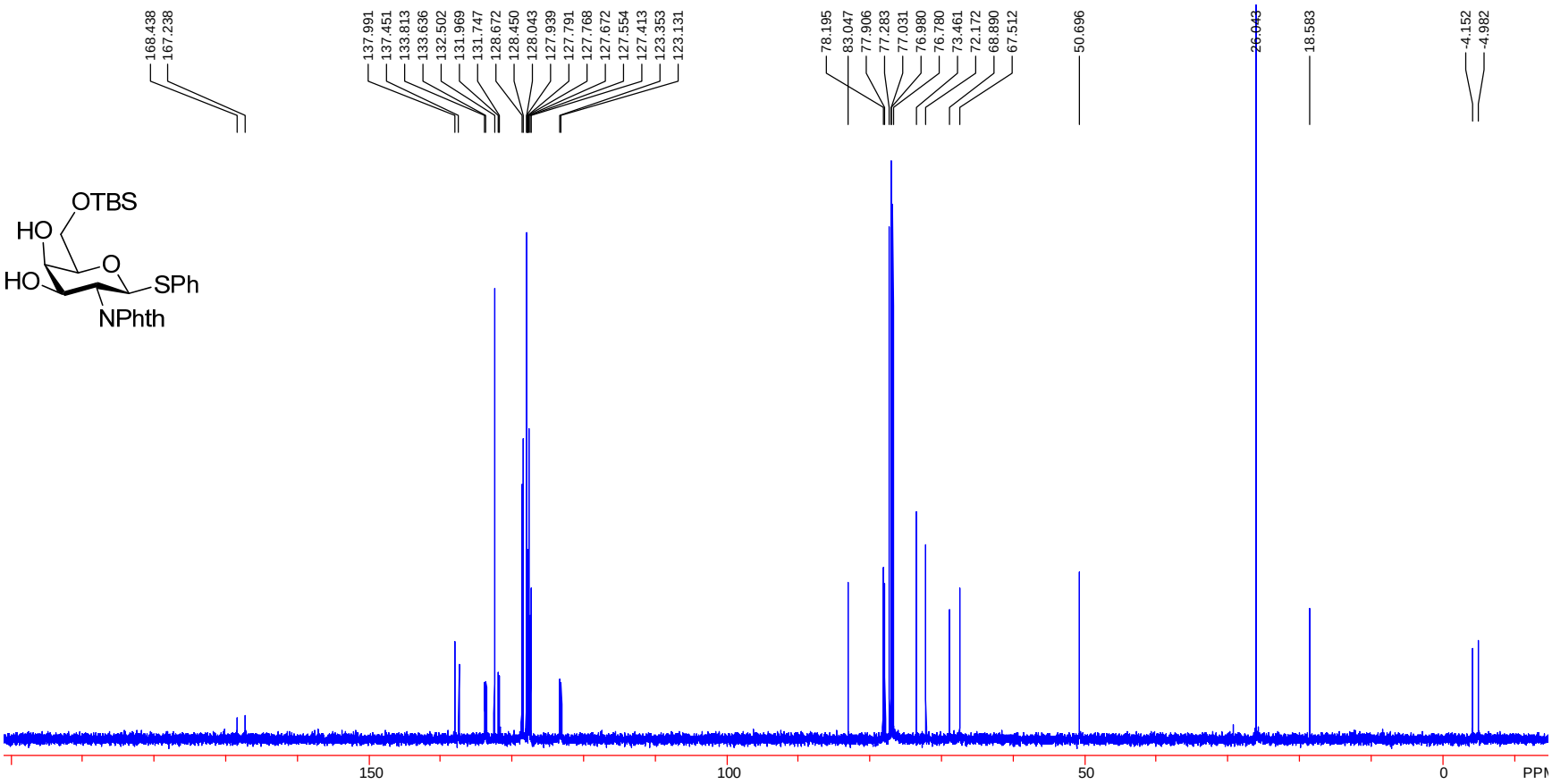
Phenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-thiogalactopyranoside (45) ^{13}C NMR (125 MHz, $CDCl_3$)



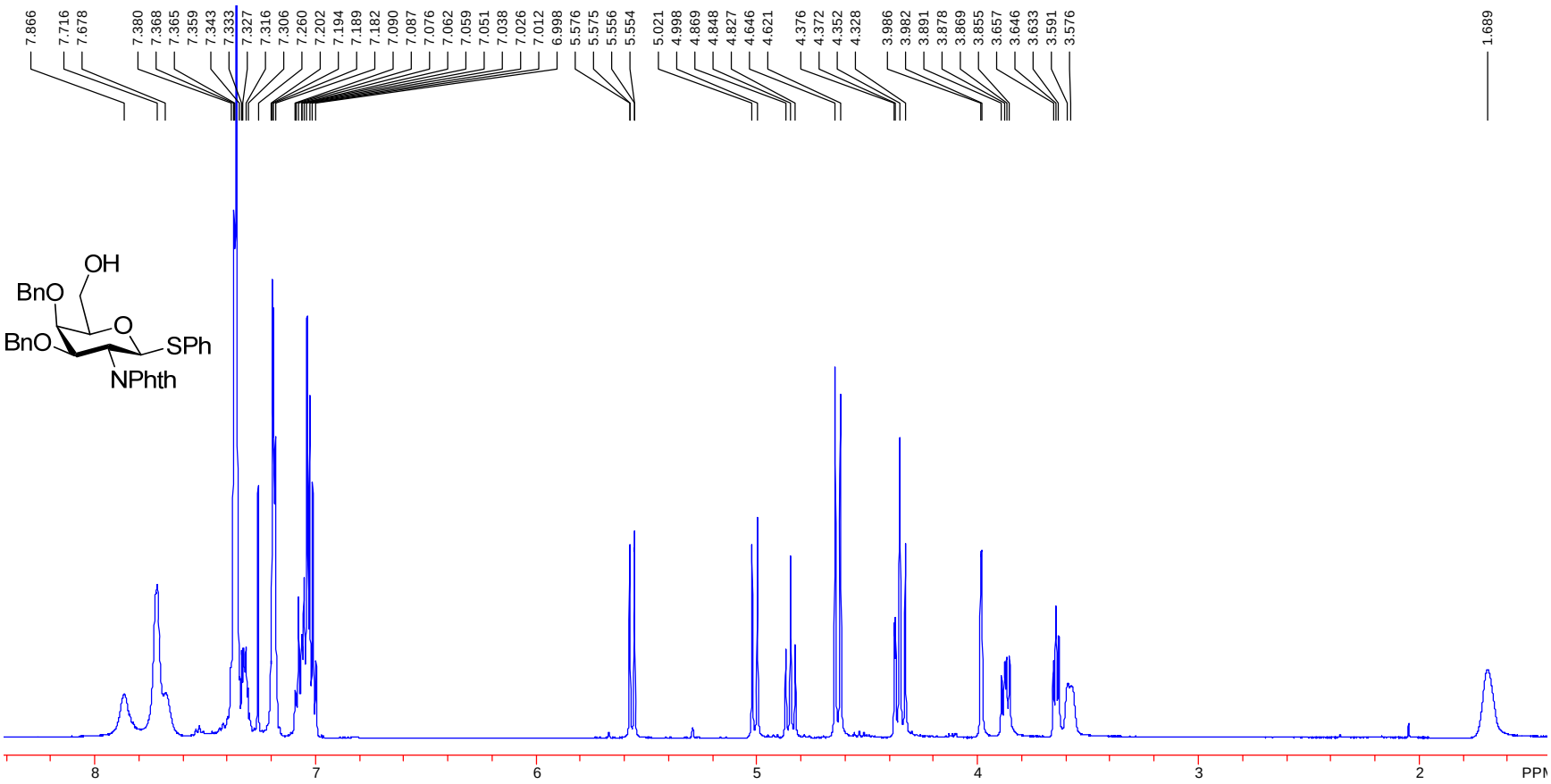
Phenyl 3,4-di-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-2-deoxy-2-phthalimido-β-D-thiogalactopyranoside (46) ^{1}H NMR (500 MHz, $CDCl_3$)



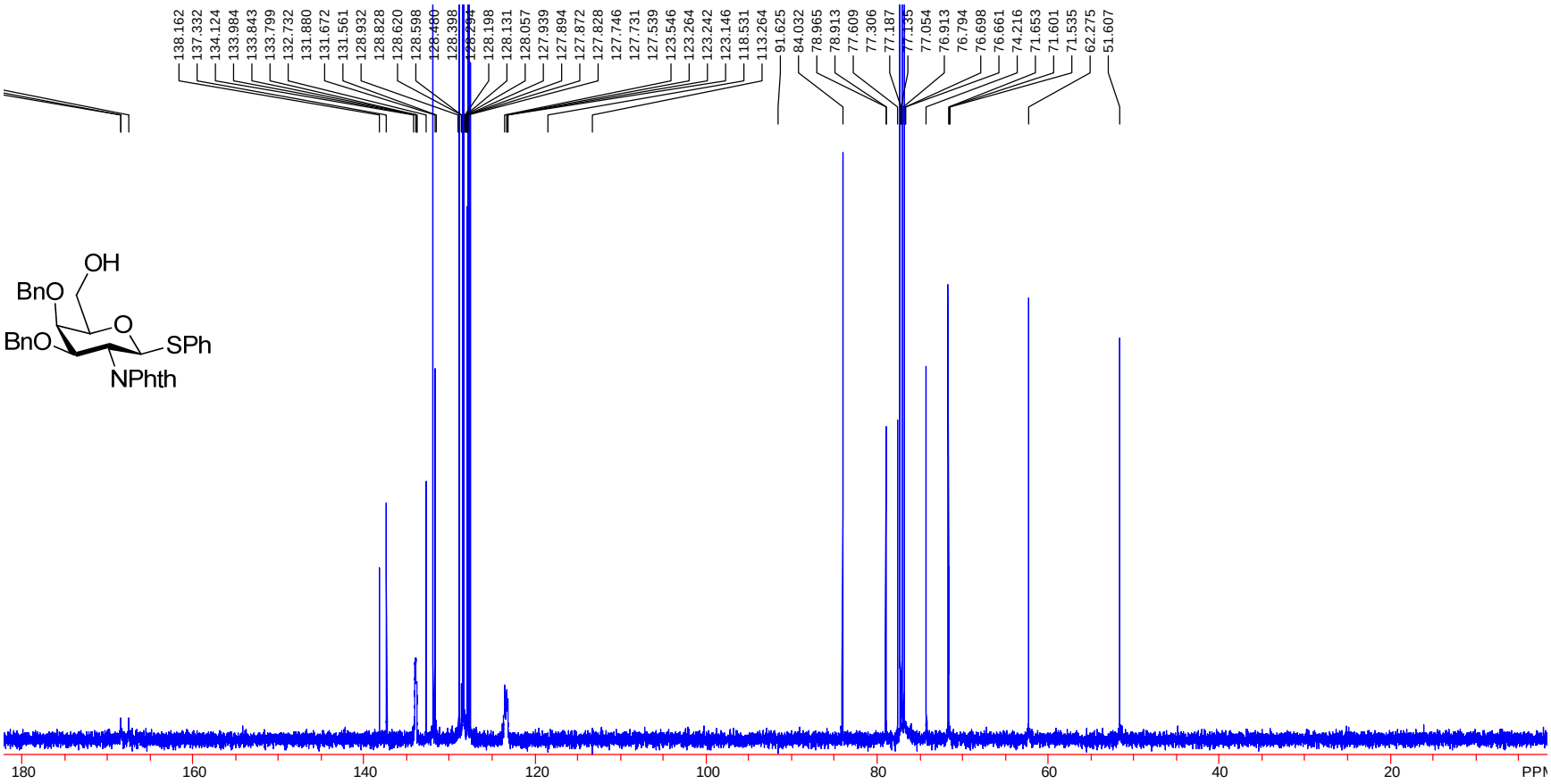
Phenyl 3,4-di-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-2-deoxy-2-phthalimido-β-D-thiogalactopyranoside (46) ^{13}C NMR (125 MHz, $CDCl_3$)



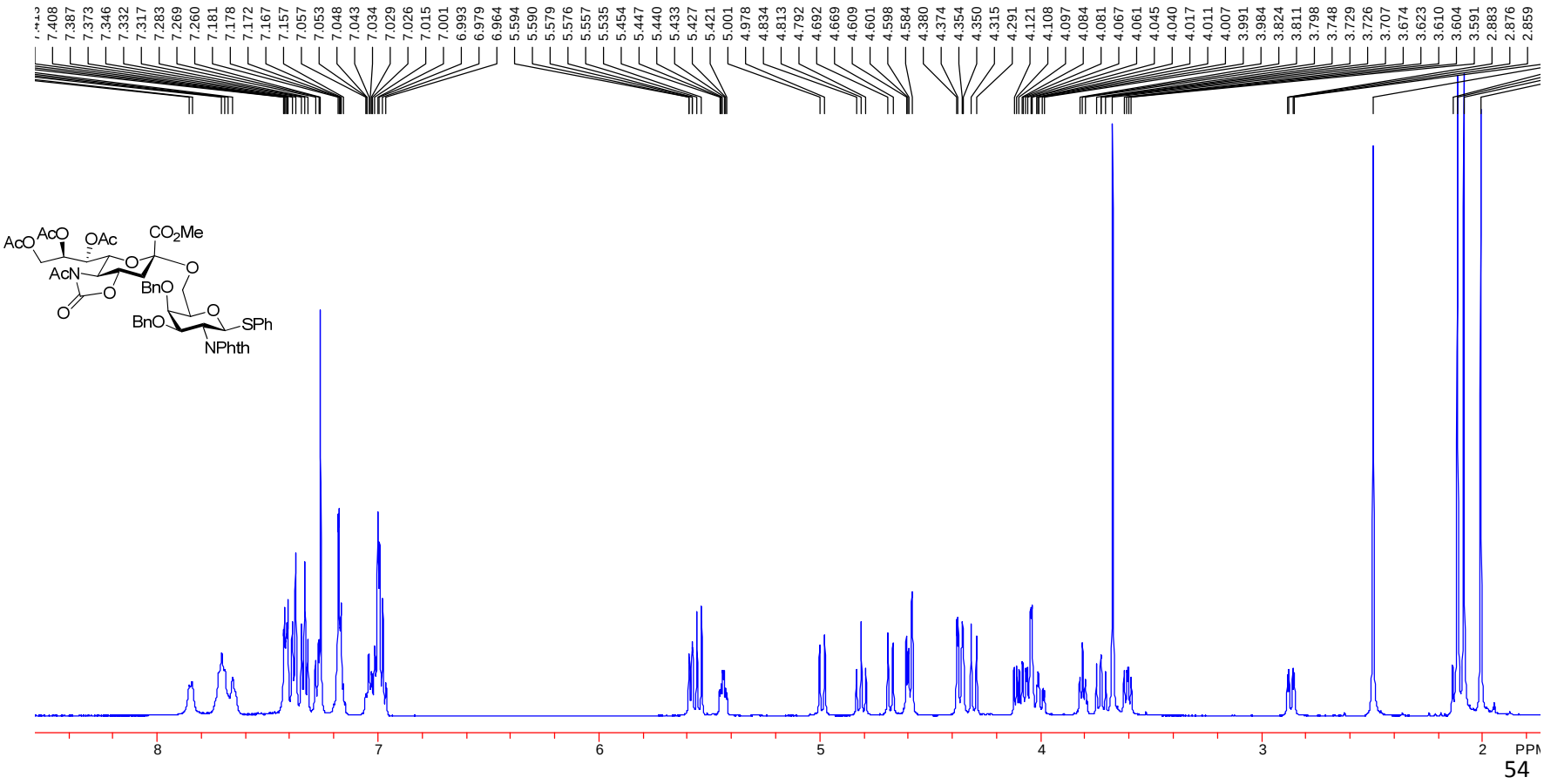
Phenyl 3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-thiogalactopyranoside (47) ^{1}H NMR (500 MHz, $CDCl_3$)



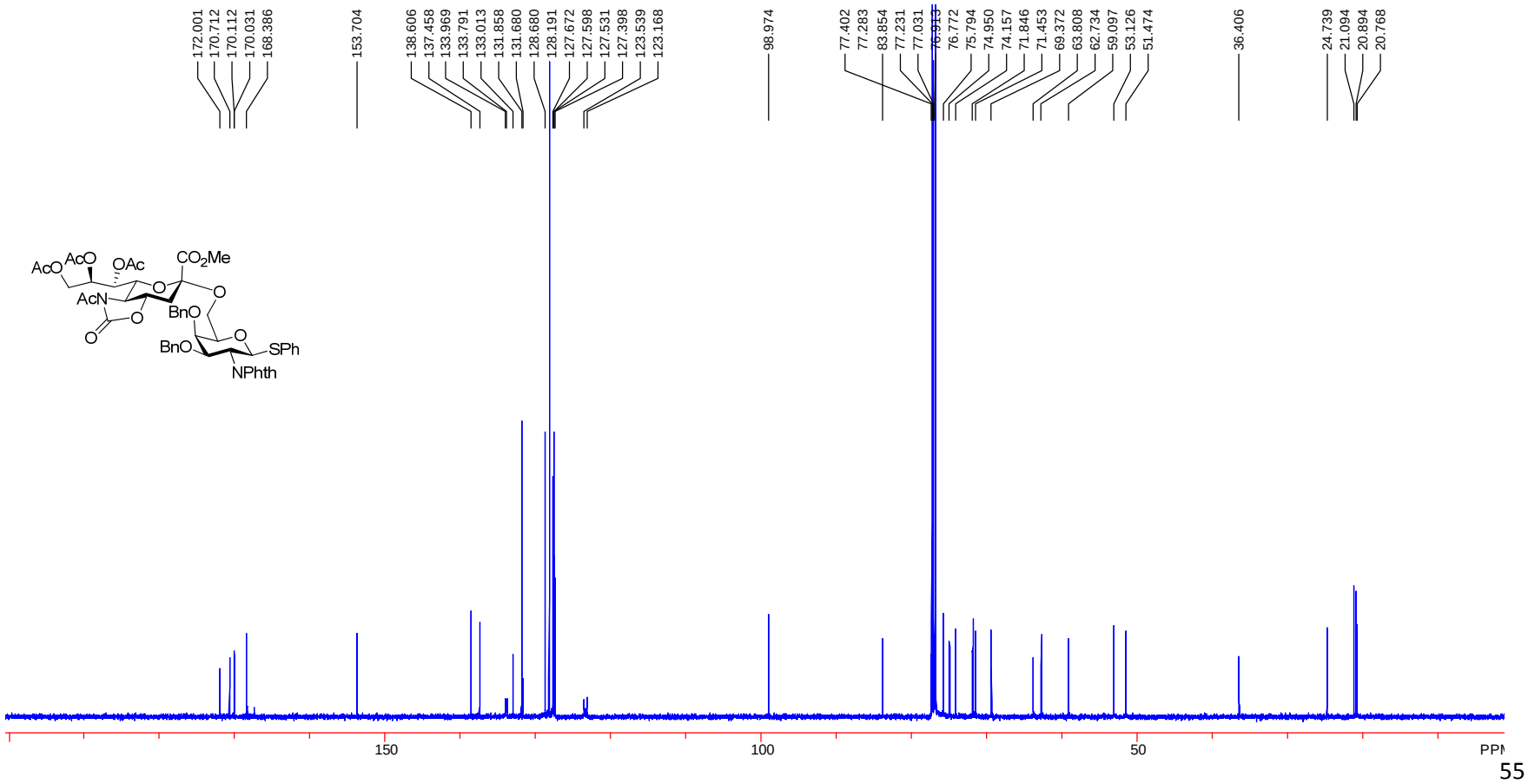
Phenyl 3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-thiogalactopyranoside (47) ^{13}C NMR (125 MHz, $CDCl_3$)



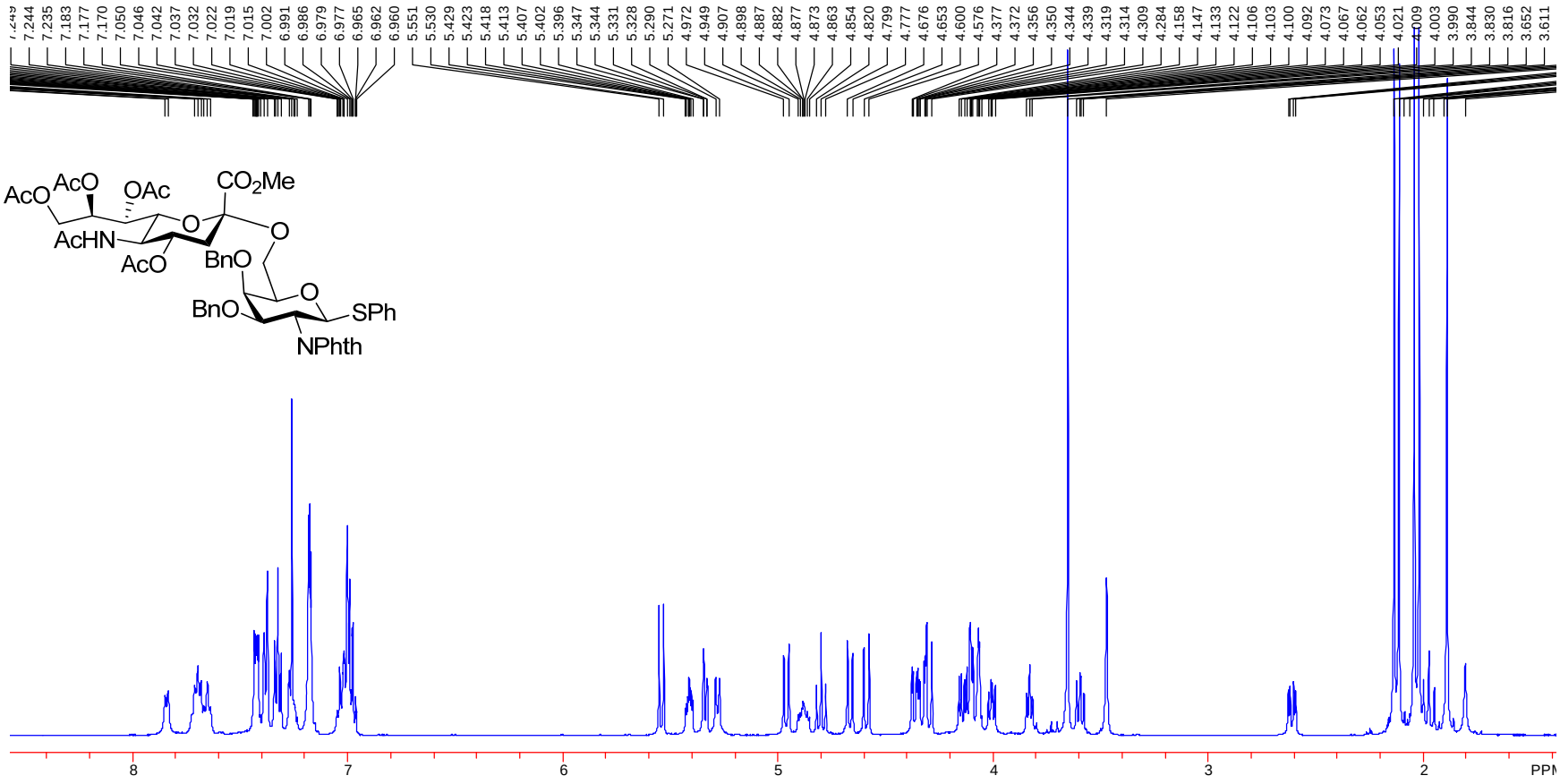
Phenyl [methyl (5-acetamido-7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-α(2→6)-3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-thiogalactopyranoside (18) ^{1}H NMR (500 MHz, $CDCl_3$)



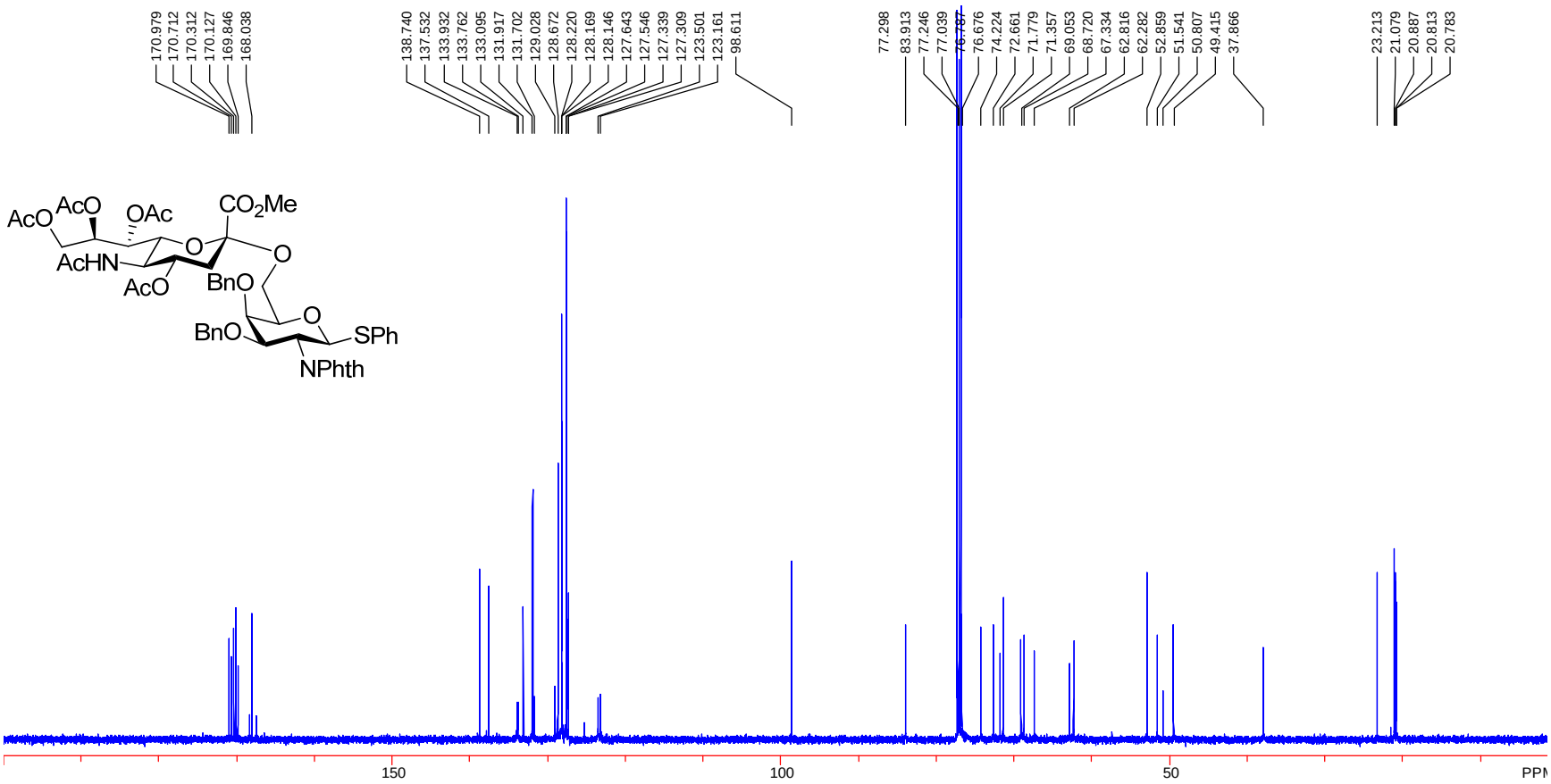
Phenyl [methyl (5-acetamido-7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-α(2→6)-3,4-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-thiogalactopyranoside (18) ^{13}C NMR (125 MHz, $CDCl_3$)



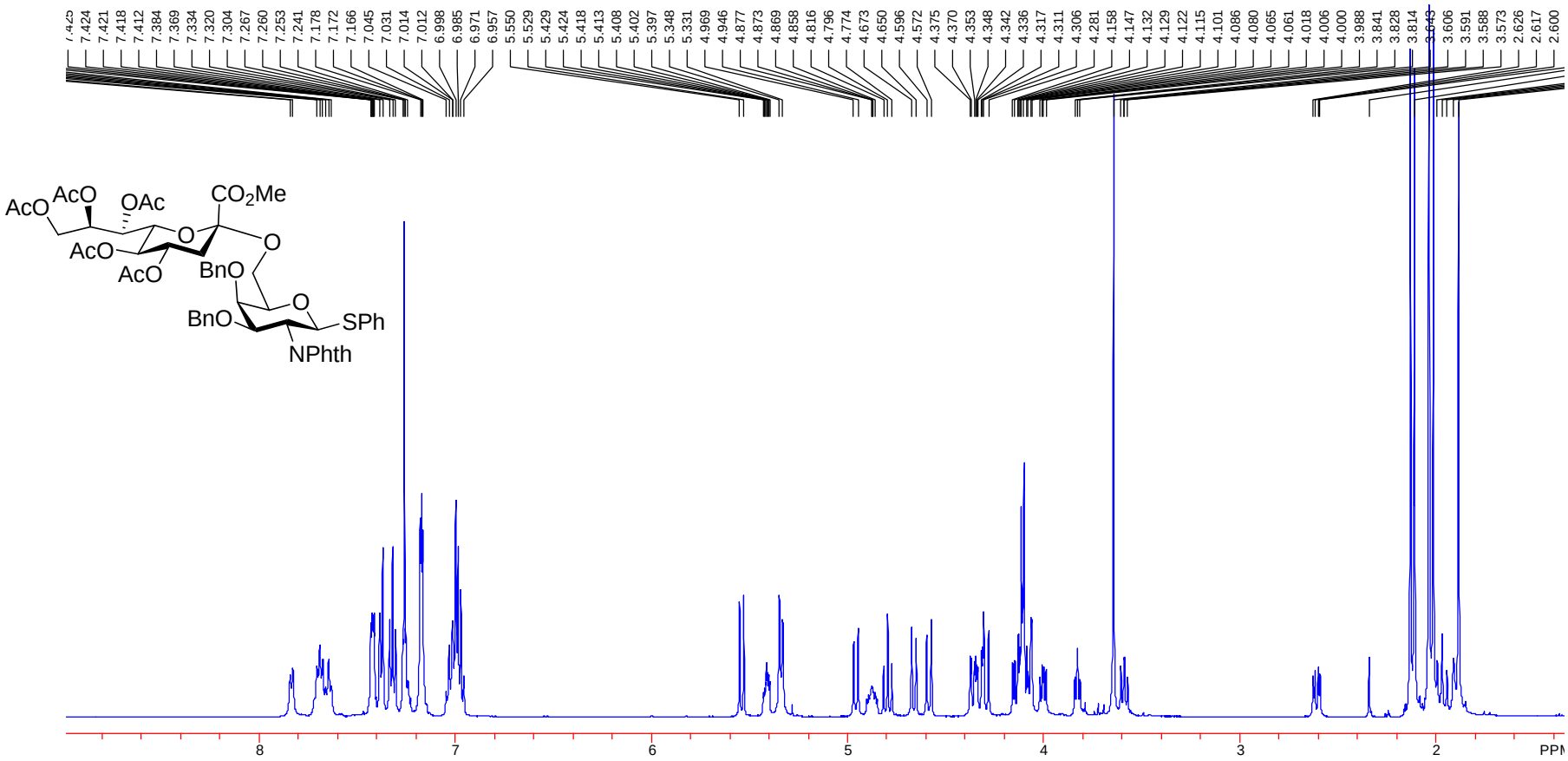
Phenyl [methyl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-α(2→6)-3,4-di-*O*-benzyl-1-thio-2-deoxy-2-phthalimido-β-D-galactopyranoside (23) ^{1}H NMR (500 MHz, $CDCl_3$)



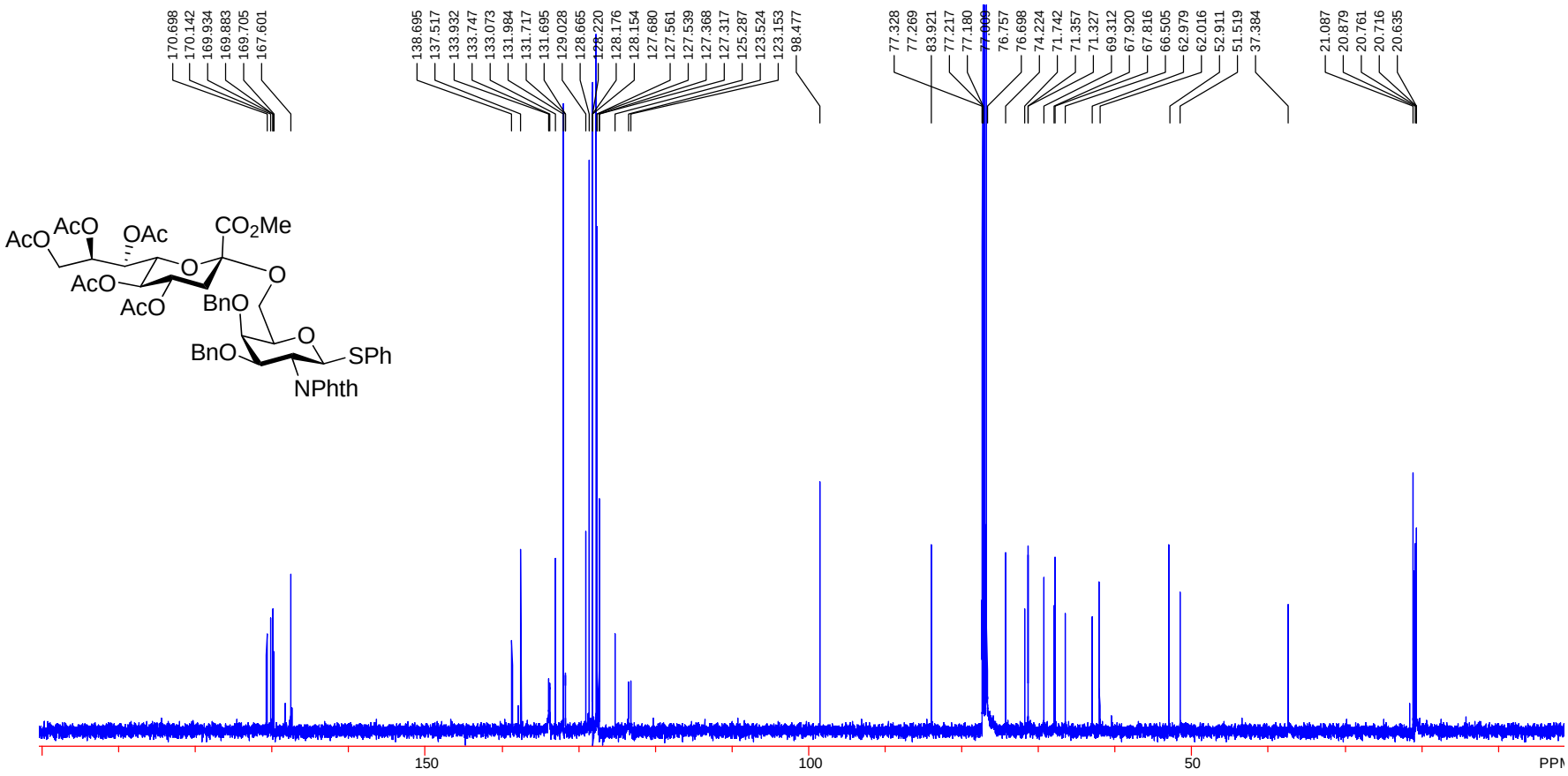
Phenyl [methyl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-α(2→6)-3,4-di-*O*-benzyl-1-thio-2-deoxy-2-phthalimido-β-D-galactopyranoside (23) ^{13}C NMR (125 MHz, $CDCl_3$)



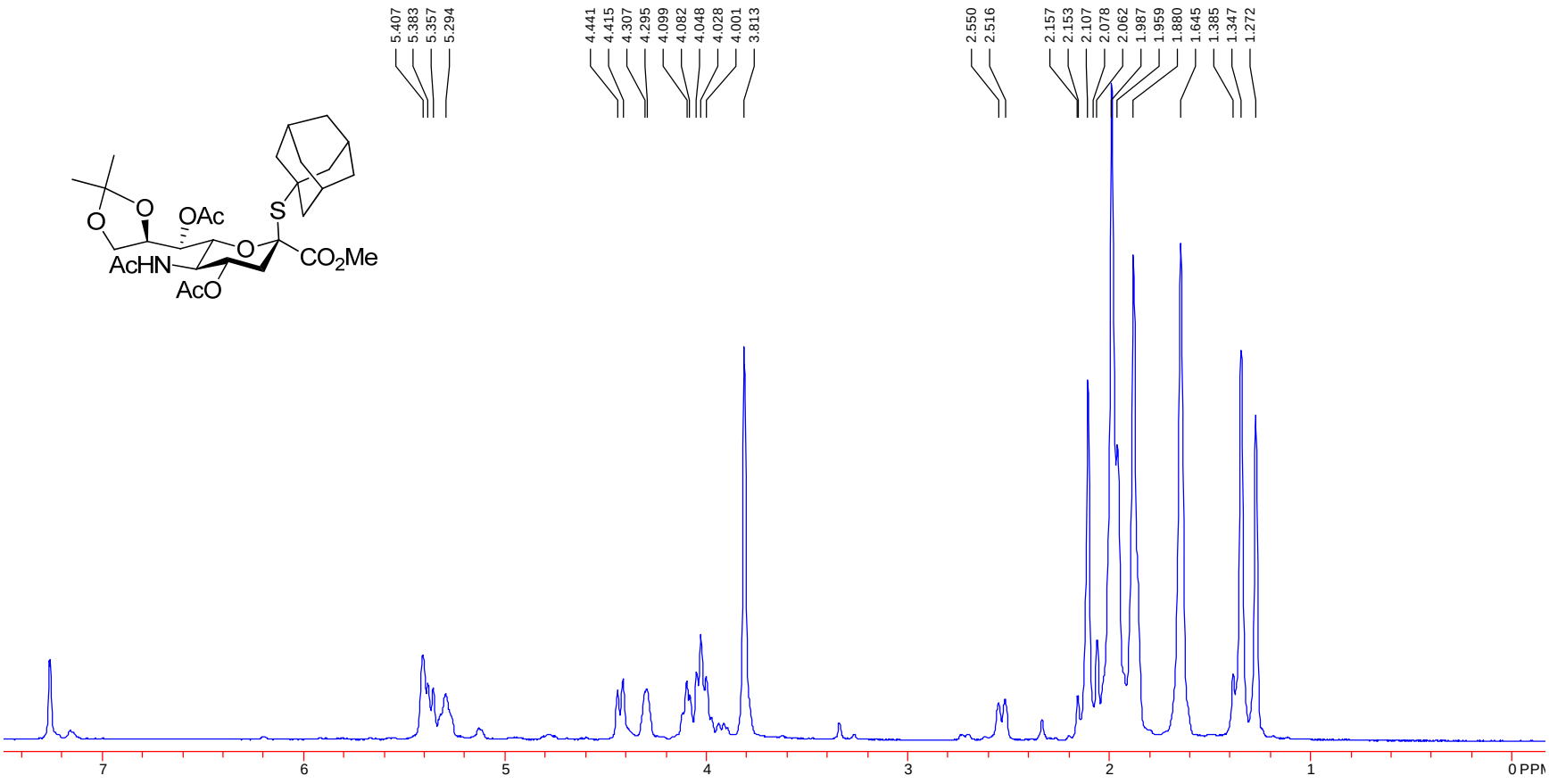
Phenyl [methyl (4,5,7,8,9-penta-*O*-acetyl-3-deoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-(2→6)-3,4-di-*O*-benzyl-1-thio-2-deoxy-2-phthalimido-β-D-galactopyranoside (30) ^{1}H NMR (500 MHz, $CDCl_3$)



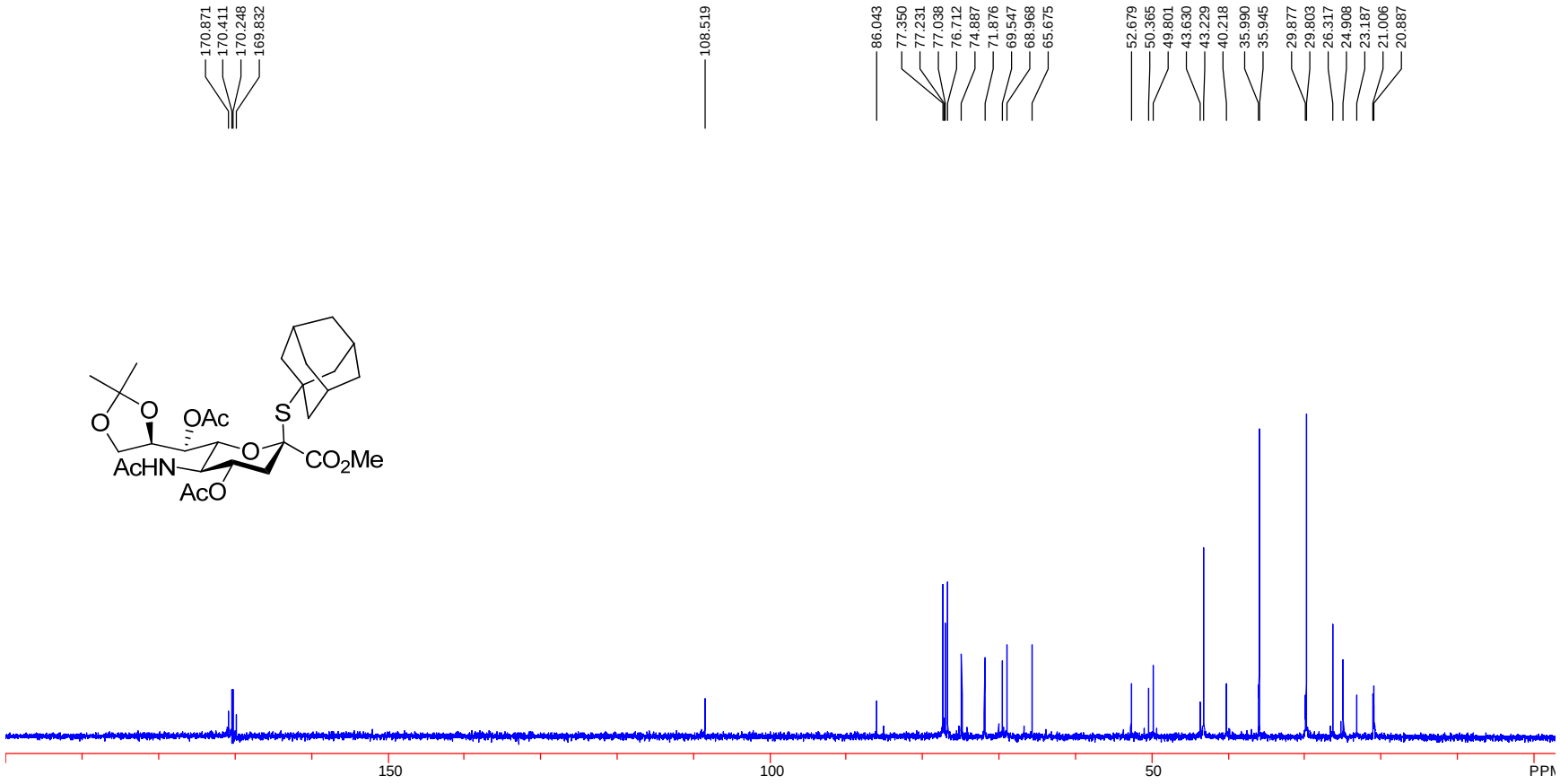
Phenyl [methyl (4,5,7,8,9-penta-*O*-acetyl-3-deoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-(2→6)-3,4-di-*O*-benzyl-1-thio-2-deoxy-2-phthalimido-β-D-galactopyranoside (30) ^{13}C NMR (125 MHz, $CDCl_3$)



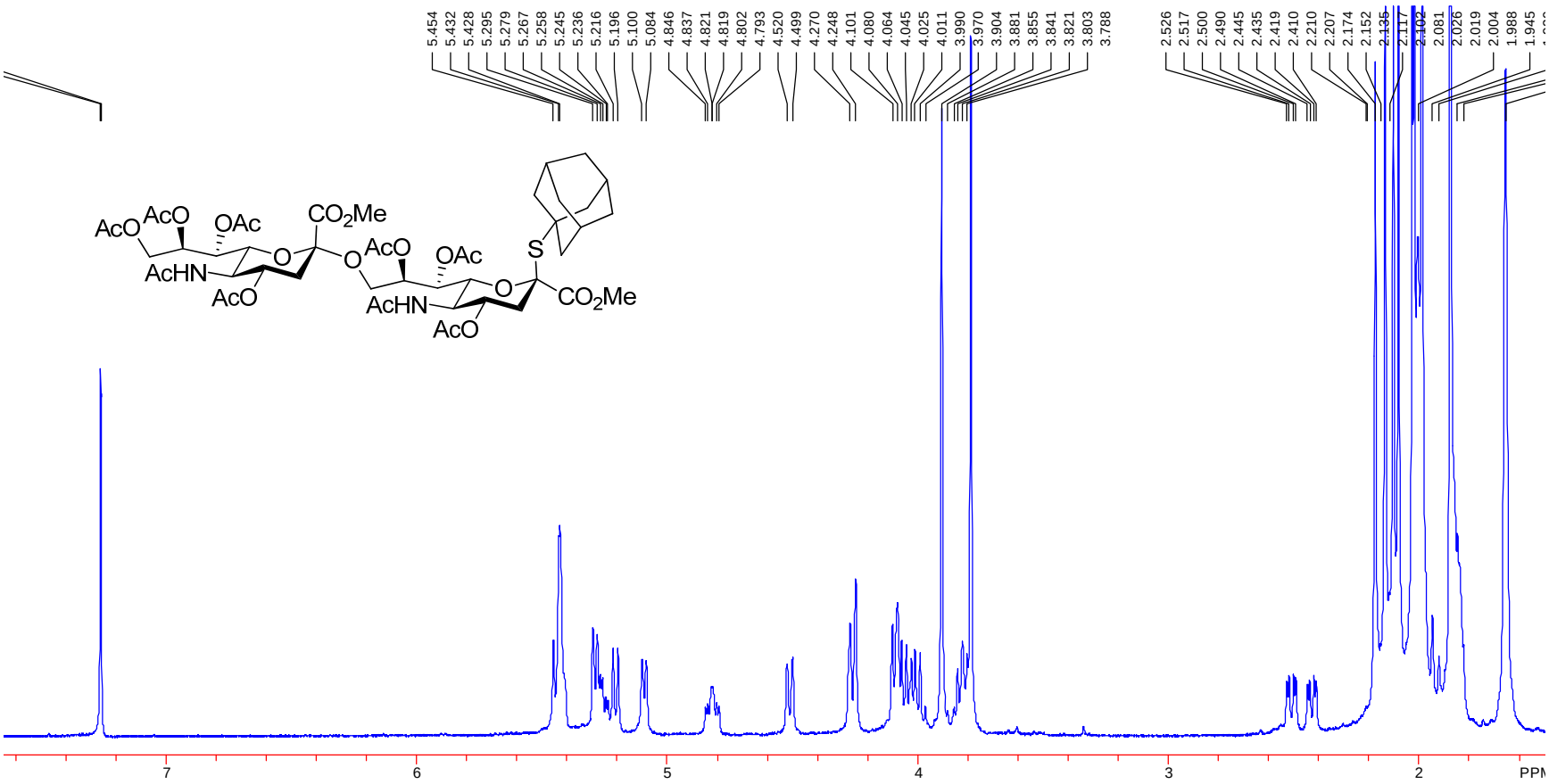
Methyl (1-adamantanyl 5-acetamido-4,7,-di-*O*-acetyl-8,9-*O*-isopropylidene-dideoxy-β-D-*glycero*-D-*galacto*-2-thiononulopyranosid)onate (49) ^{1}H NMR (400 MHz, $CDCl_3$)



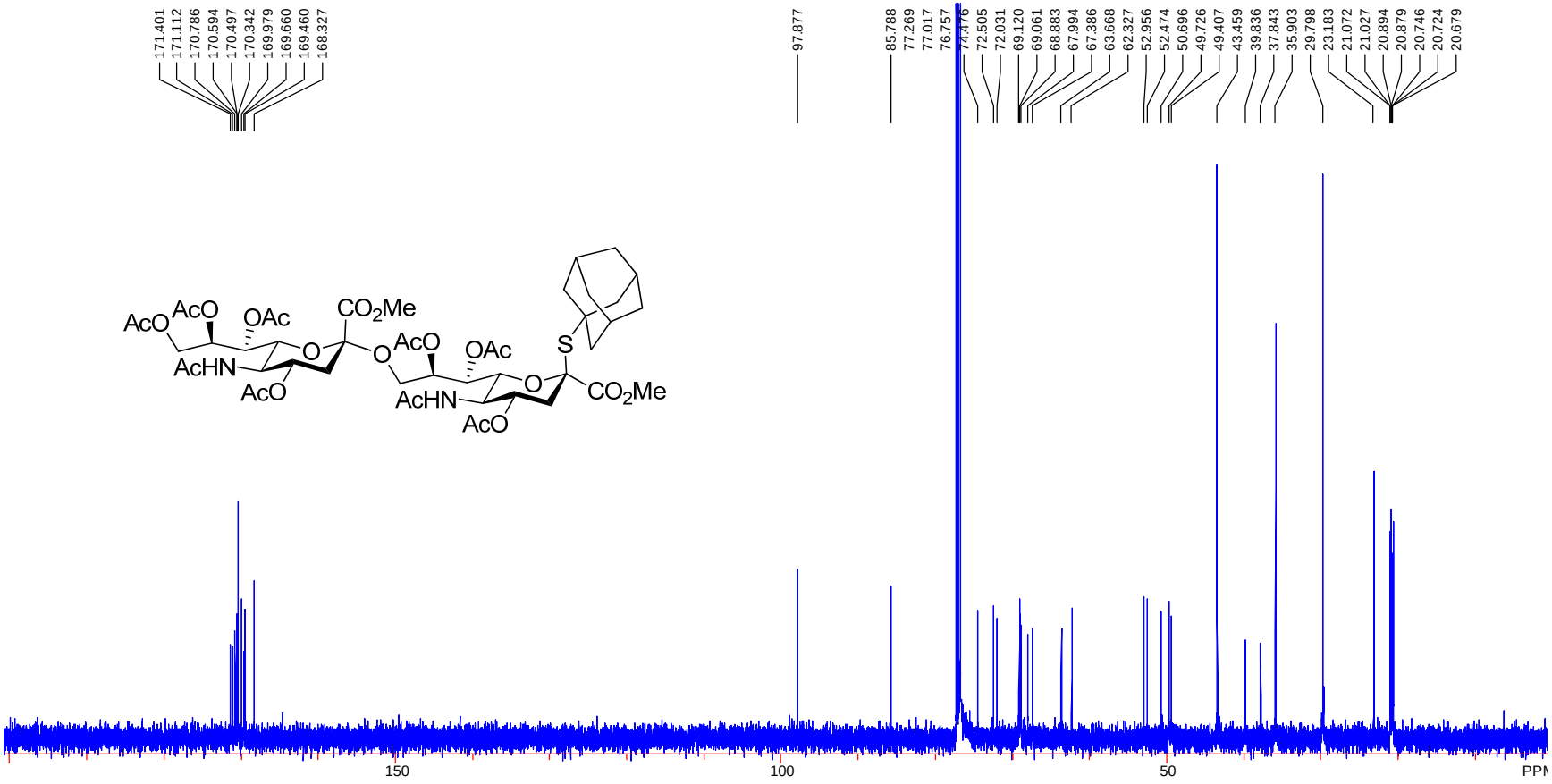
Methyl (1-adamantanyl 5-acetamido-4,7,-di-*O*-acetyl-8,9-*O*-isopropylidene-dideoxy-β-D-*glycero*-D-*galacto*-2-thiononulopyranosid)onate (49) ^{13}C NMR (100 MHz, $CDCl_3$)



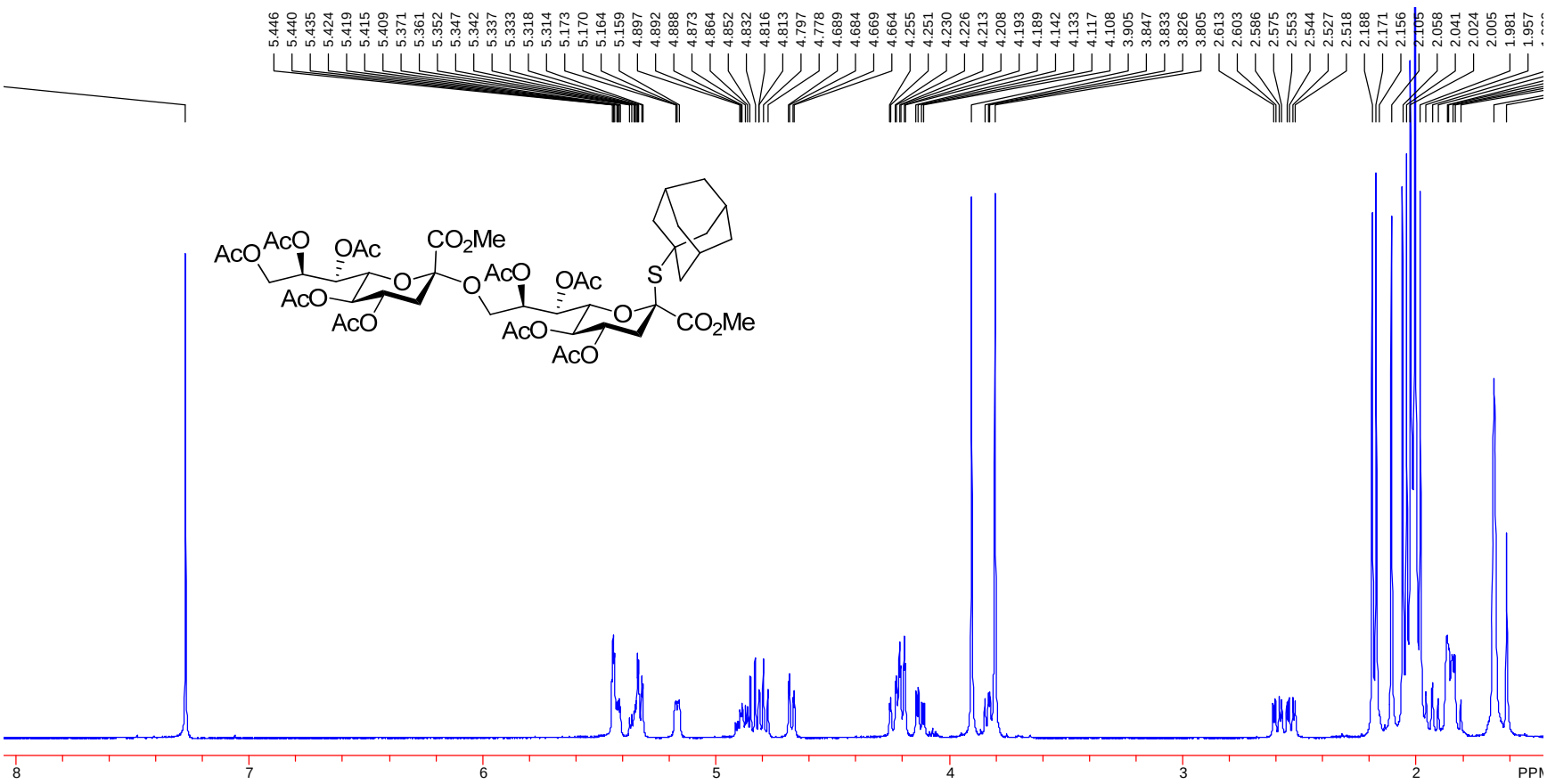
1-Adamantanyl [methyl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-α(2→9)-[methyl (5-acetamido-4,7,8-tri-*O*-acetyl-3,5-dideoxy-β-D-*glycero*-α-D-*galacto*-2-thiononulopyranosyl)onate] (24) ^{1}H NMR (500 MHz, $CDCl_3$)



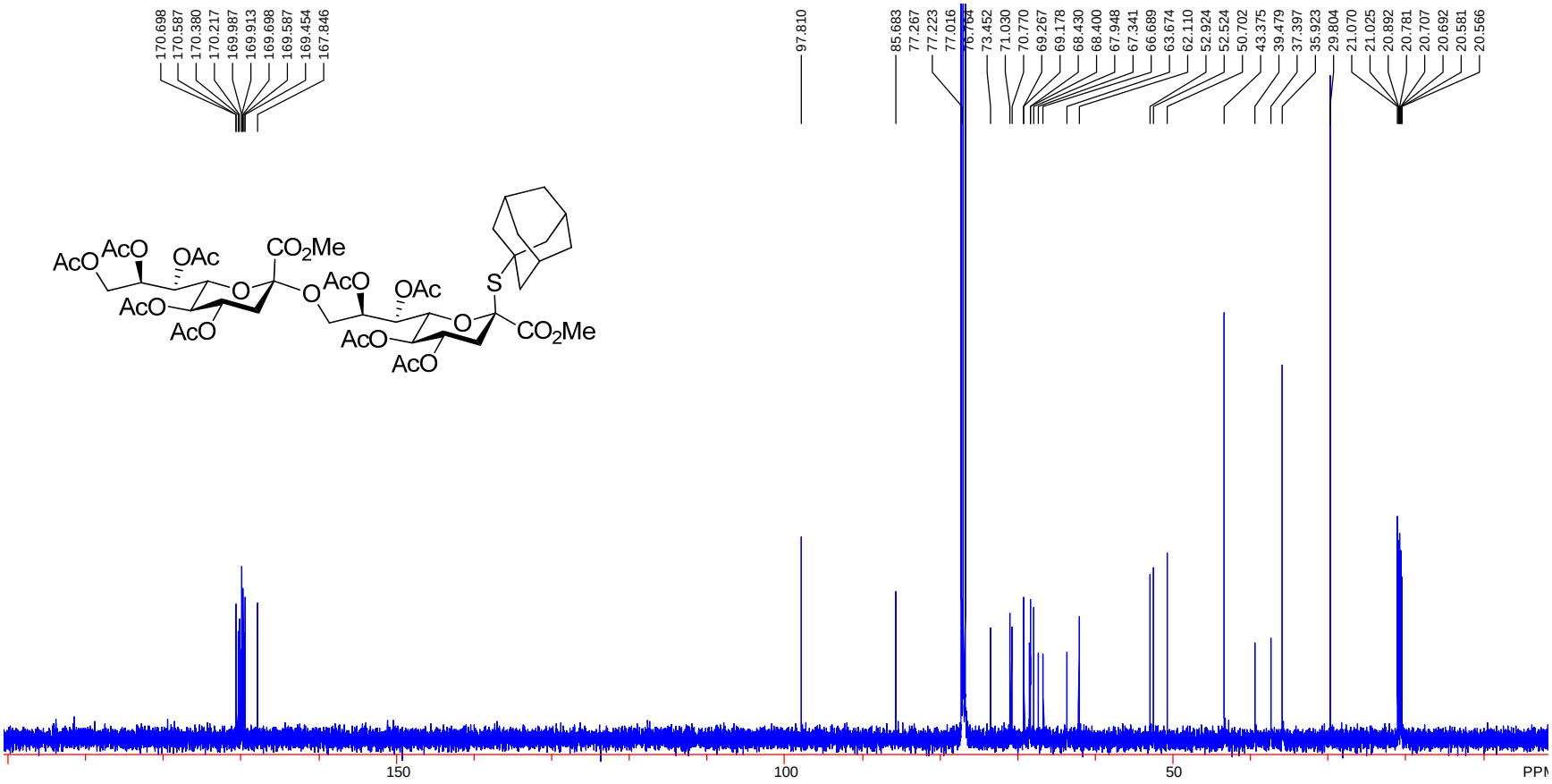
1-Adamantanyl [methyl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-α(2→9)-[methyl (5-acetamido-4,7,8-tri-*O*-acetyl-3,5-dideoxy-β-D-*glycero*-α-D-*galacto*-2-thiononulopyranosyl)onate] (24) ^{13}C NMR (125 MHz, $CDCl_3$)



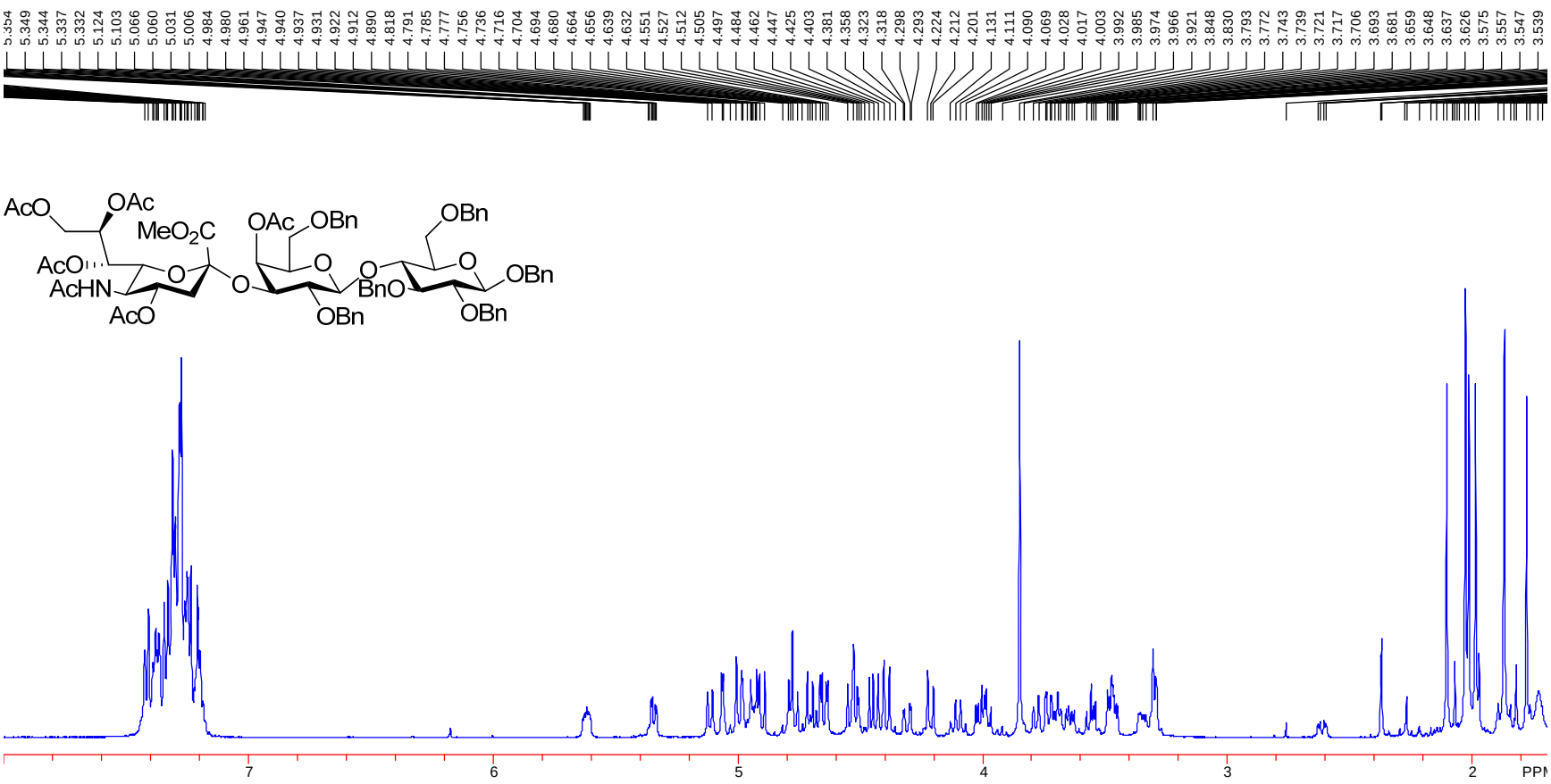
Methyl [methyl (4,5,7,8,9-penta-*O*-acetyl-3,5-dideoxy-α-D-glycero-D-galacto-2-nonulopyranosyl)onate]-α(2→9)-[(1-adamantanyl 4,5,7,8,-tetra-*O*-acetyl-3,5-dideoxy-2-α--D-*glycero*-D-*galacto*-2-thiononulopyranosyl)onate] (31) ^{1}H NMR (500 MHz, $CDCl_3$)



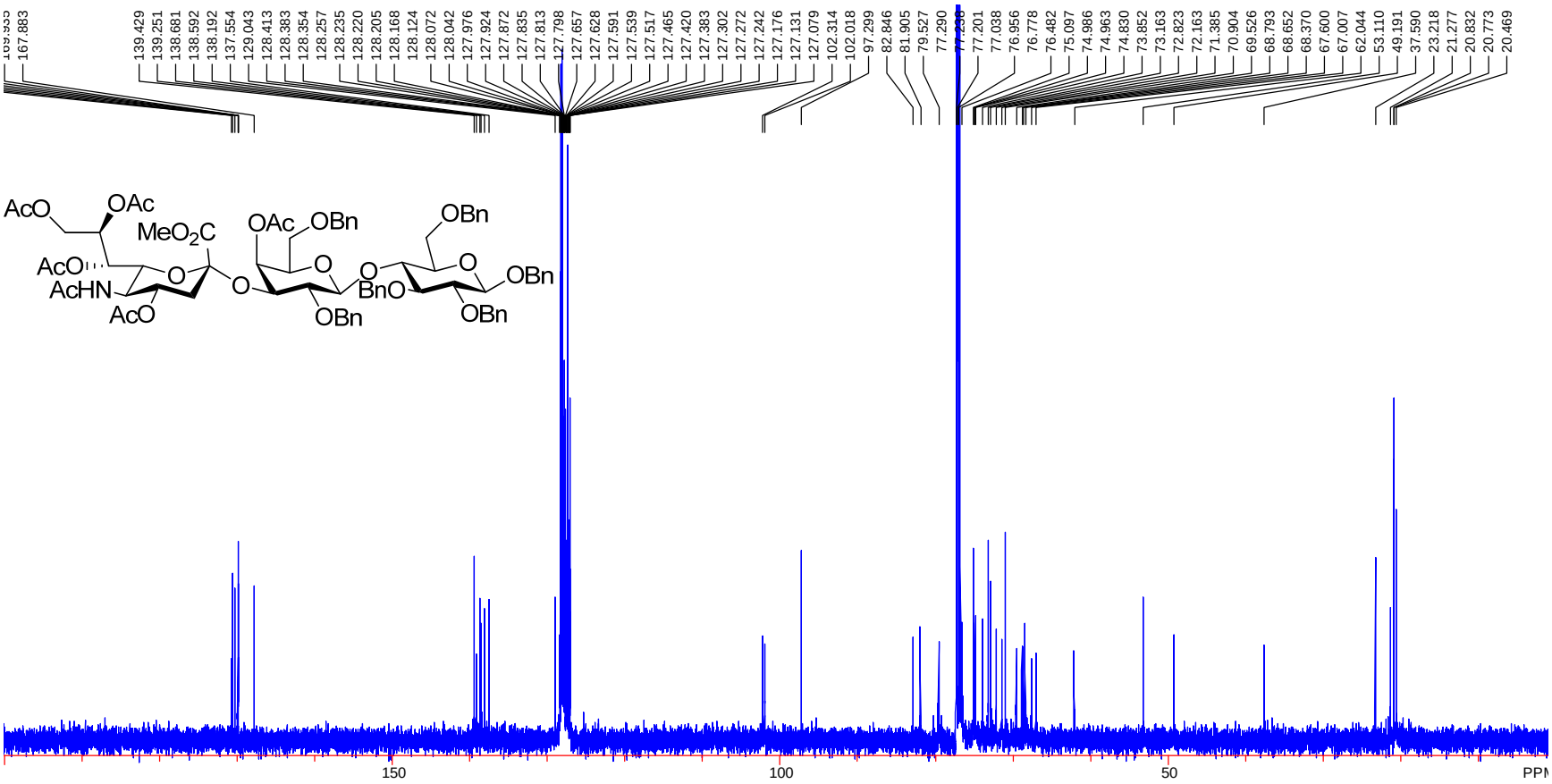
Methyl [methyl (4,5,7,8,9-penta-*O*-acetyl-3,5-dideoxy-α-D-glycero-D-galacto-2-nonulopyranosyl)onate]-α(2→9)-[(1-adamantanyl 4,5,7,8,-tetra-*O*-acetyl-3,5-dideoxy-2-α--D-*glycero*-D-*galacto*-2-thiononulopyranosyl)onate] (31) ^{13}C NMR (125 MHz, $CDCl_3$)



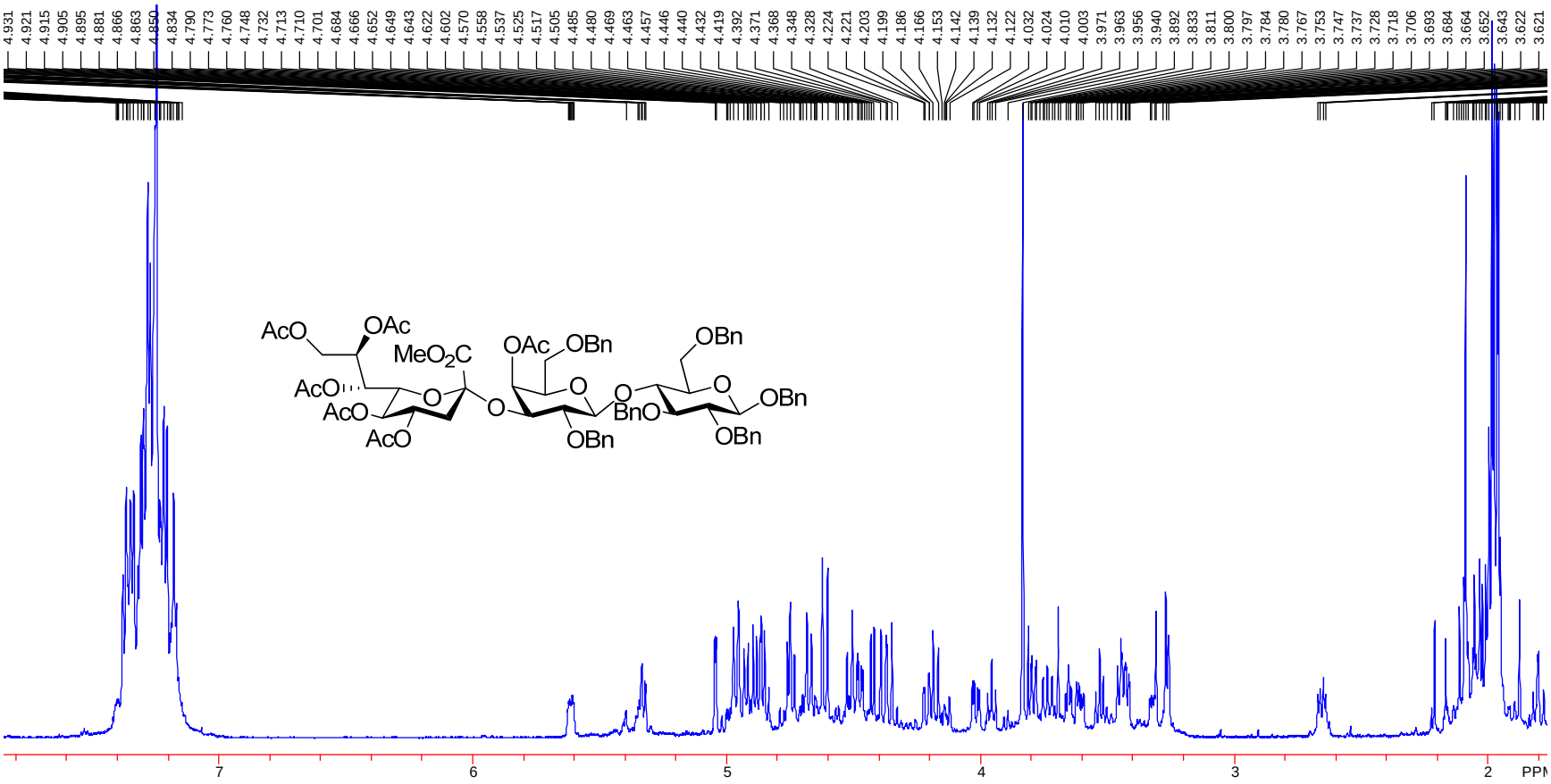
Benzyl [methyl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-(4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(2→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (33) ^{1}H NMR (500 MHz, $CDCl_3$)



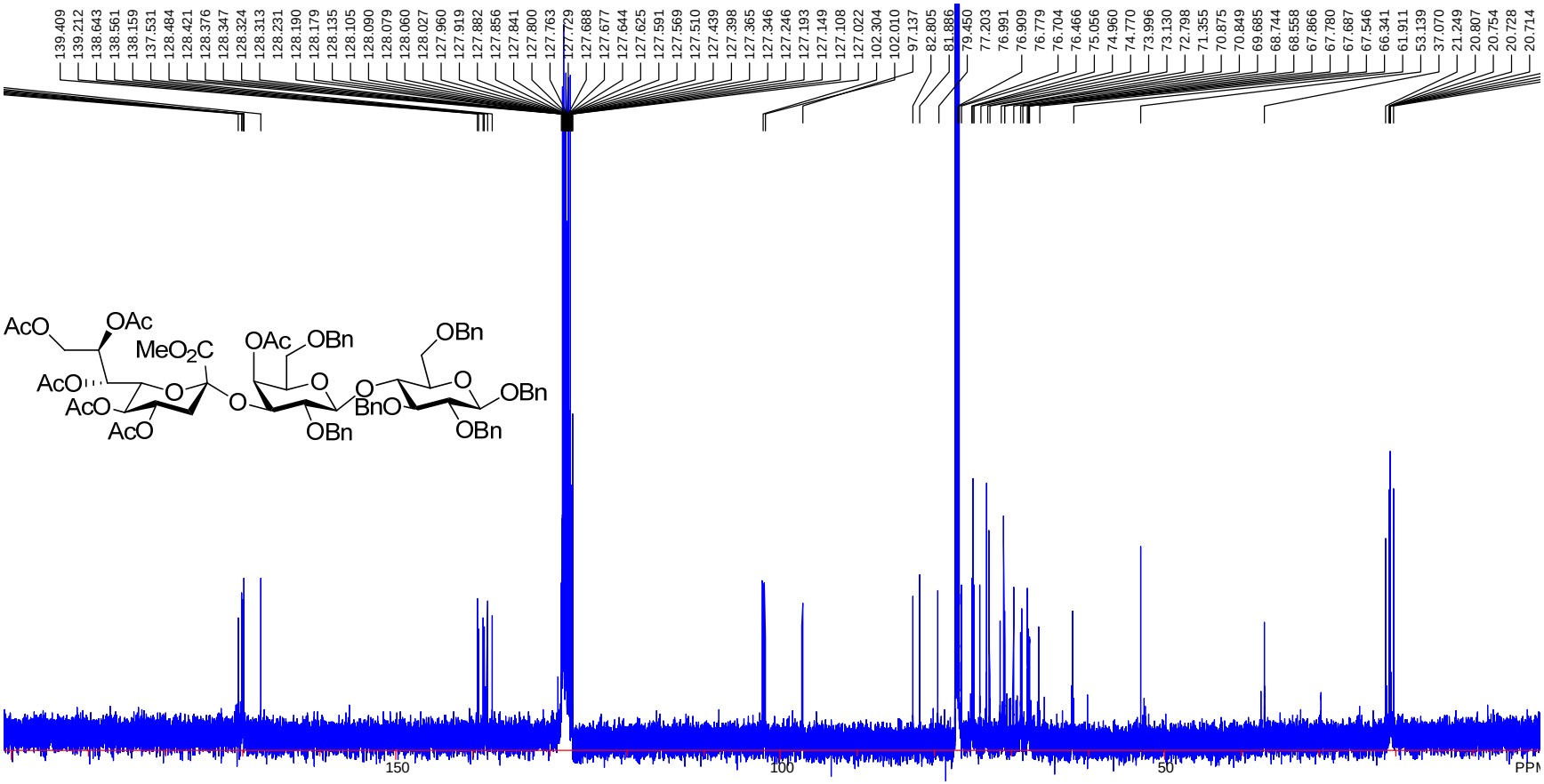
Benzyl [methyl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-(4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(2→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (33) ^{13}C NMR (125 MHz, $CDCl_3$)



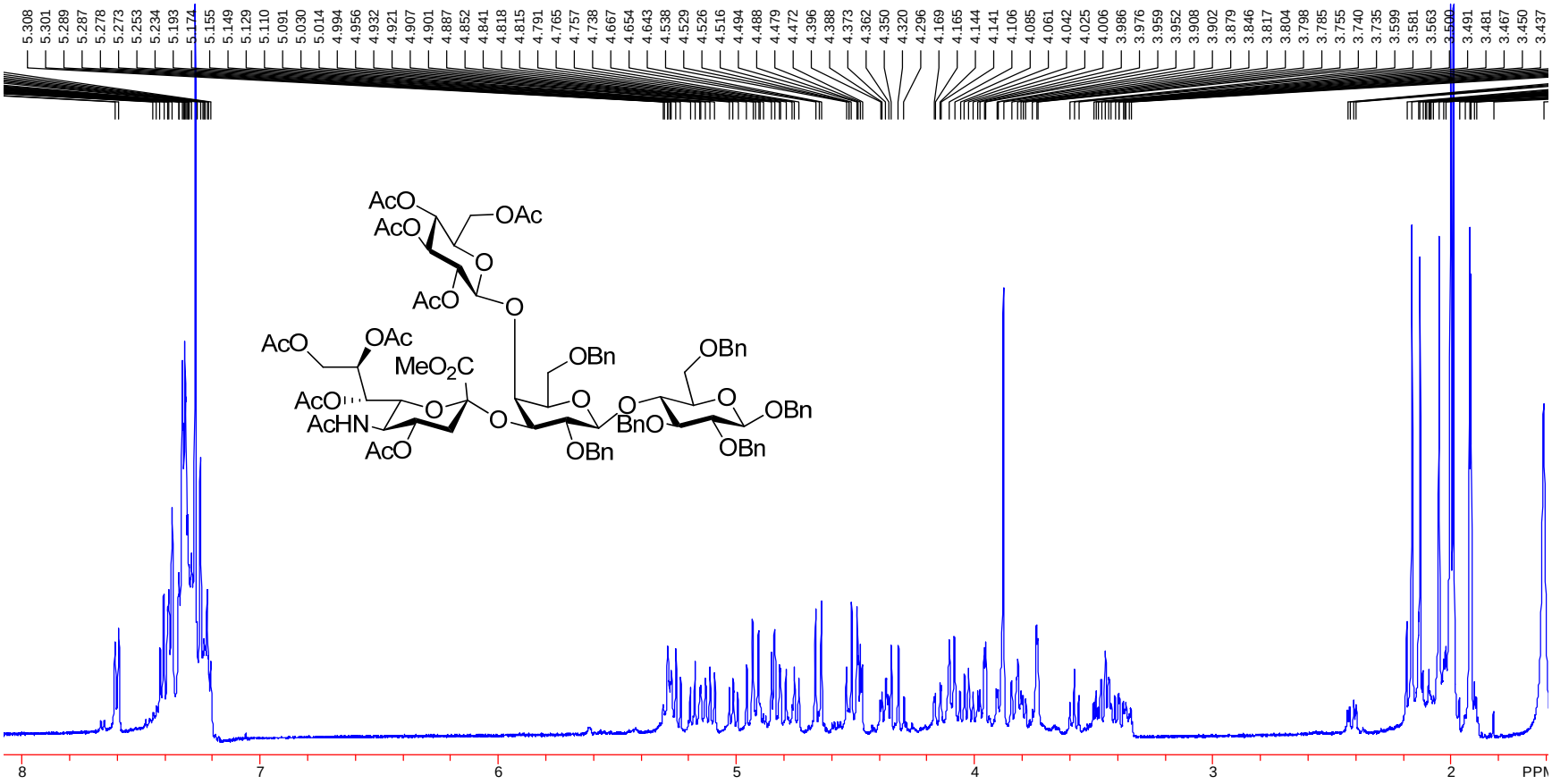
Benzyl [methyl (4,5,7,8,9-penta-*O*-acetyl-3,5-deoxy-α-D-*glycero*-D-*galacto*-2-nulopyranosyl)onate]-(2→3)-(4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(2→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (35) ^{1}H NMR (500 MHz, $CDCl_3$)



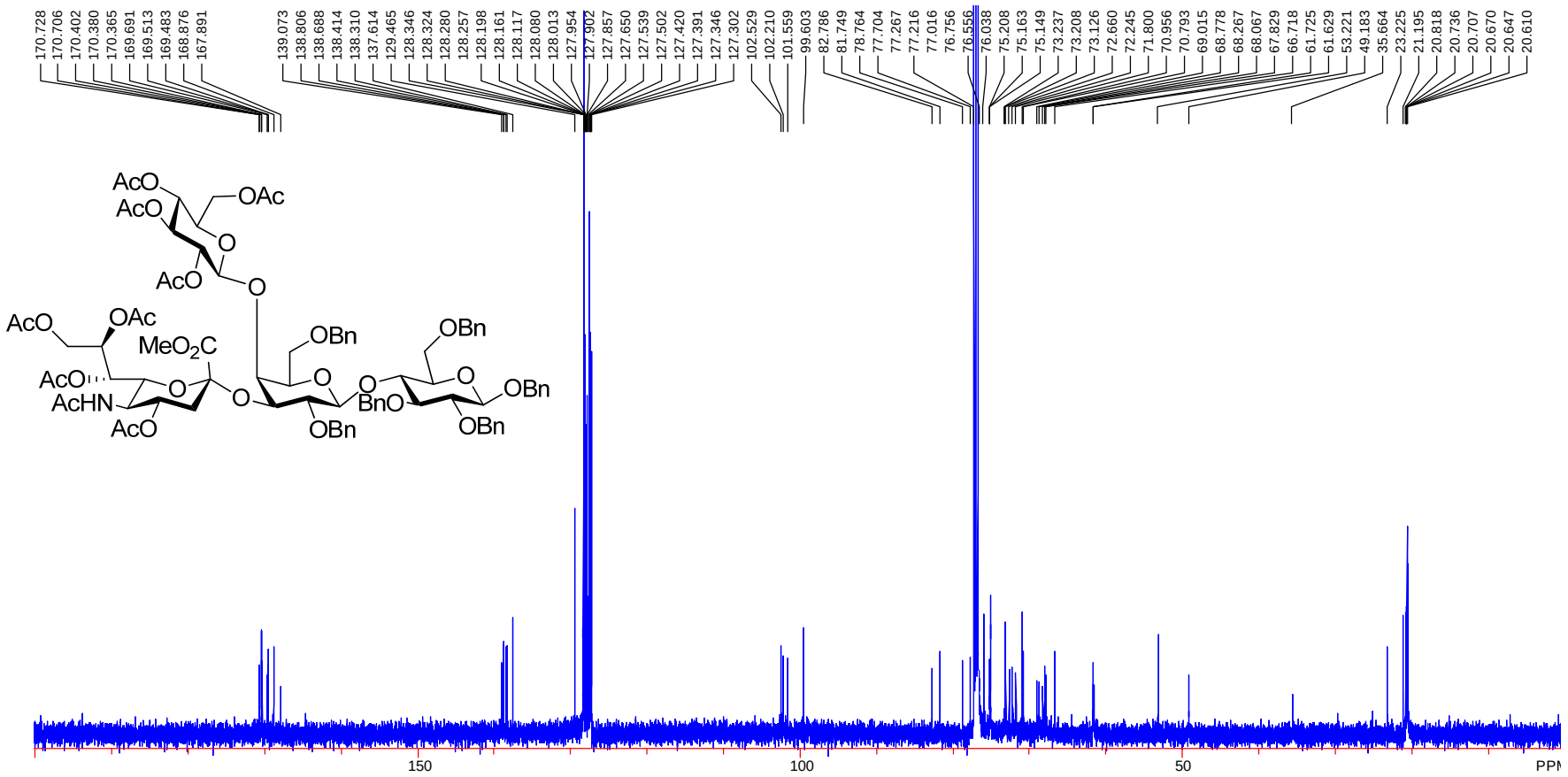
Benzyl [methyl (4,5,7,8,9-penta-*O*-acetyl-3,5-deoxy-α-D-*glycero*-D-*galacto*-2-nulopyranosyl)onate]-(2→3)-(4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(2→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (35) ^{13}C NMR (125 MHz, $CDCl_3$)



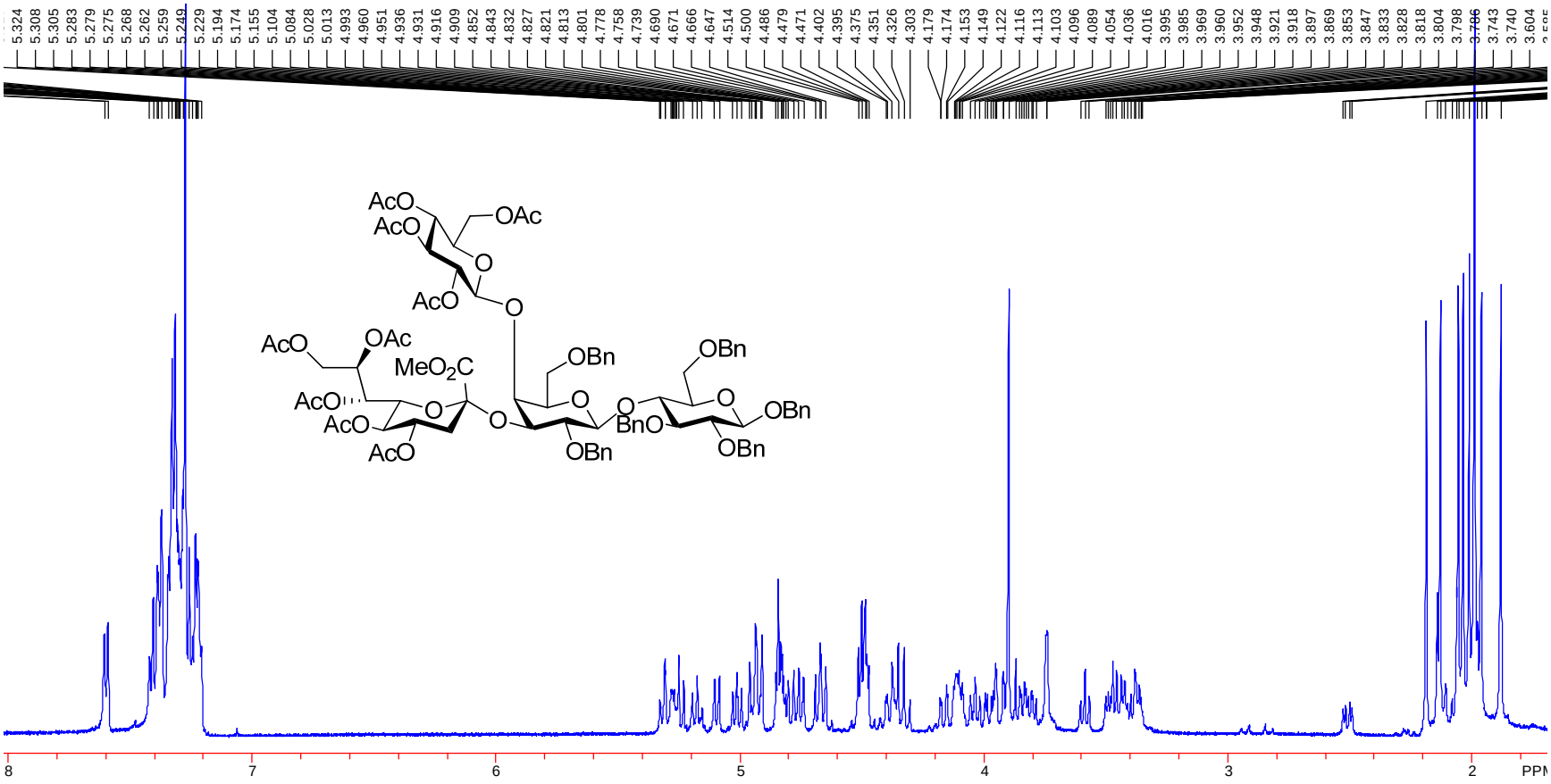
Benzyl [methyl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-2,2',3,6,6'-penta-*O*-benzyl-β-D-lactopyranoside (34) ^{1}H NMR (500 MHz, $CDCl_3$)



Benzyl [methyl (5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-(2→3)-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-2,2',3,6,6'-penta-*O*-benzyl-β-D-lactopyranoside (34) ^{13}C NMR (125 MHz, $CDCl_3$)



Benzyl [methyl (4,5,7,8,9-penta-*O*-acetyl-3,5-dideoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate)-(2→3)-[2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl]-(1→4)-2,2',3,6,6'-penta-*O*-benzyl-β-D-lactopyranoside (36) ^{1}H NMR (500 MHz, $CDCl_3$)



Benzyl [methyl (4,5,7,8,9-penta-*O*-acetyl-3,5-dideoxy-α-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate)-(2→3)-[2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl]-(1→4)-2,2',3,6,6'-penta-*O*-benzyl-β-D-lactopyranoside (36) ^{13}C NMR (125 MHz, $CDCl_3$)