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Regio and Stereo-controlled Synthesis of 6-Deoxy-β-D-*ido*-heptopyranosides Related to *Campylobacter jejuni* HS:4

Saba Homayonia,[a] Pengfei Zhang,[a] Ping Zhang[a] and Chang-Chun Ling[a]*

Department of Chemistry, University of Calgary, 2500 University Drive NW, Calgary

Alberta T2N 1N4, Canada. Email: ccling@ucalgary.ca

Contents

Experimental Section

4-Chlorophenyl 2,3,4-tri-*O*-acetyl-7-*O*-benzyl-6-deoxy-1-thio-α,β-D-*galacto*-heptopyranoside (6)

To a solution of compound **5** (5.1 g, 11.27 mmol) in anhydrous CH_2Cl_2 (60 mL) under an argon atmosphere were added *p*-chlorothiophenol[1] (2.77 g, 19.16 mmol) and boron trifluoride diethyl etherate (2.17 mL, 18.03 mmol) respectively, and the reaction mixture was stirred for 4 hrs at room temperature. The solution was quenched by adding triethylamine followed by acetic anhydride (1.0 mL). After stirring for 1 hr, the solution was evaporated to dryness. The residue was redissolved in EtOAc (170 mL), washed with saturated brine (50 mL), dried over anhydrous Na_2SO_4, filtered, and evaporated. The crude material was then purified by column chromatography on silica gel using a gradient of 20→30 % EtOAc–hexanes as the eluent to afford the product **6** (α/β, 0.11:1) as a syrup (5.81 g, 10.82 mmol, 96% yield). R_f = 0.59 (EtOAc : hexanes, 2 : 3). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.46-7.23 (m, 9H, Ar), 5.31 (dd, *J* = 3.4, 1.0 Hz, 1H, H-4), 5.20 (dd, *J* = 9.9, 9.9 Hz, 1H, H-2), 5.05 (dd, *J* = 9.9, 3.7 Hz, 1H, H-3), 4.66 (d, *J* = 9.9 Hz, 1H, H-1), 4.45 (d, *J* = 12.5 Hz, 1H, PhCH_aH$_b$), 4.41 (d, *J* = 12.5 Hz, 1H, PhCH$_a$$H_b$), 3.91 (ddd, *J* = 9.0, 4.3, 1.1 Hz, 1H, H-5), 3.58-3.43 (m, 2H, H-7a and H-7b), 2.16 (s, 3H, Ac), 2.08 (s, 3H, Ac), 1.97 (s, 3H, Ac), 1.89 (dddd, *J* = 13.8, 9.2, 4.6, 4.6 Hz, 1H, H-6a), 1.74 (dddd, *J* = 14.3, 8.6, 5.7, 4.3 Hz, 1H, H-6b). ^{13}C NMR (101 MHz, $CDCl_3$): δ_C 170.3 (C=O), 169.9 (C=O), 169.5 (C=O), 138.0 (Ar), 134.1 (Ar), 133.6 (Ar), 131.1 (Ar), 129.0 (Ar), 128.9 (Ar), 128.4 (Ar), 128.3 (Ar),

127.7 (Ar), 127.7 (Ar), 127.7 (Ar), 127.4 (Ar), 86.0 (C-1), 73.9 (C-5), 73.0 (Ph*C*H_2), 72.3 (C-3), 69.6 (C-2), 67.5 (C-4), 65.6 (C-7), 31.0 (C-6), 20.8 (Me), 20.6 (Me), 20.5 (Me). HRMS (ESI-QTOF) *m/z* calc'd for $C_{26}H_{29}NClO_8S$ $[M + NH_4]^+$, 554.1610; found, 554.1626.

6-Azidohexyl 2,3,4-tri-*O*-acetyl-7-*O*-benzyl-6-deoxy-β-D-*galacto*-heptopyranoside (8)

A solution of compound **6** (278 mg, 0.52 mmol), the alcohol **7** (372 mg, 2.59 mmol) and molecular sieves (4 Å, crushed, 1 g) in anhydrous CH_2Cl_2 (10.0 mL) was stirred for 1 hr at room temperature. After cooling down the reaction mixture to -40 °C, NIS (175.5 mg, 0.77 mmol) and a catalytic amount of TfOH (15 µL) were added. The mixture was stirred for 1 hr at -40 °C and allowed to warm to room temperature gradually overnight. After TLC showed the disappearance of the starting material, the reaction was quenched by adding triethylamine (0.1 mL). The reaction mixture was filtered to remove molecular sieves and evaporated. The residue was redissolved in EtOAc (30 mL), and washed with a mixture of 10% $NaHCO_3$ (15 mL) and 10% $Na_2S_2O_3$ (15 mL), and saturated brine (20 mL), dried over anhydrous Na_2SO_4, and evaporated. The crude material was then purified by column chromatography on silica gel using a gradient of 15→25% EtOAc–hexanes as the eluent to afford the pure product **8** as a syrup (210 mg, 0.391 mmol, 75% yield). R_f = 0.55 (EtOAc : hexanes 3 : 7). $[\alpha]_D^{20}$: +7.2 (*c* 2.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.38-7.28 (m, 5H, Ar), 5.28 (dd, *J* = 3.5, 1.1 Hz, 1H, H-4), 5.16 (dd, *J* = 10.4, 7.9 Hz, 1H, H-2), 5.02 (dd, *J* = 10.4, 3.4 Hz, 1H, H-3), 4.53 (d, *J* = 12.0 Hz, PhCH_aH_b), 4.44 (d, *J* = 12.0 Hz, 1H, PhCH_aH_b), 4.38 (d, *J* = 7.9 Hz, 1H, H-1), 3.87 (ddd, *J* = 8.7, 4.6, 1.3 Hz, 1H, H-5), 3.79 (ddd,

J = 9.6, 6.2, 6.2 Hz, 1H, OC*H*$_a$H$_b$), 3.61-3.55 (m, 1H, H-7a), 3.50 (ddd, *J* = 9.4, 5.2, 5.2 Hz, 1H, H-7b), 3.38 (ddd, *J* = 9.6, 7.2, 6.3 Hz, 1H, OCH$_a$*H*$_b$), 3.25 (t, *J* = 6.9 Hz, 2H, Hex_NCH$_2$), 2.14 (s, 3H, Ac), 2.07, (s, 3H, Ac), 1.98, (s, 3H, Ac), 1.89-1.80 (m, 1H, H-6a), 1.78-1.69 (m, 1H, H-6b), 1.63-1.51 (m, 4H, 2 × CH$_2$), 1.42-1.32 (m, 4H, 2 × CH$_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 170.5 (C=O), 170.1 (C=O), 169.4 (C=O), 129.5 (Ar), 128.4 (Ar), 127.7 (Ar), 101.2 (C-1), 73.1 (Ph*C*H$_2$), 71.3 (C-3), 69.8 (C-4), 69.7 (OCH$_a$H$_b$), 69.6 (C-2), 69.2 (C-5), 65.5 (C-7), 51.3 (CH$_2$), 30.8 (C-6), 29.3 (CH$_2$), 28.7 (CH$_2$), 26.4 (CH$_2$), 25.4 (CH$_2$), 20.8 (Ac), 20.7 (Ac), 20.6 (Ac). HRMS (ESI-QTOF) *m/z* calc'd for $C_{26}H_{37}N_3O_9$ $[M + NH_4]^+$, 553.2868; found, 553.2882.

4-Chlorophenyl 7-*O*-benzyl-6-deoxy-1-thio-α,β-D-*galacto*-heptopyranoside (9)

To a solution of compound **6** (2.71 g, 5.04 mmol) in anhydrous MeOH (10 mL) was added a solution of NaOMe in anhydrous MeOH (1.5 M, 2.5 mL, 3.4 mmol). After stirring for 0.5 hours, the reaction mixture was neutralized with Amberlite IR-120 (H^+), filtered and evaporated. The crude mixture was purified by column chromatography on silica gel using a gradient of 1→5% MeOH–CH_2Cl_2 as the eluent to afford the desired product **9** (α/β, 0.11:1) as a syrup (1.89 g, 4.59 mmol, 91% yield). R_f = 0.16 (MeOH : CH_2Cl_2, 1 : 9). ^{1}H NMR (600 MHz, $CDCl_3$) for β-anomer: δ_H 7.49 – 7.44 (m, 2H, Ar), 7.35 (m, 2H, Ar), 7.33 – 7.28 (m, 3H, Ar), 7.25 – 7.21 (m, 2H, Ar), 4.49 (d, *J* = 9.6 Hz, 1H, H-1), 4.48 (d, *J* = 12.1 Hz, 1H, PhC*H*$_a$H$_b$), 4.46 (d, *J* = 12.1 Hz, 1H, PhCH$_a$*H*$_b$),3.85 (dd, *J* = 3.4, 3.4 Hz, 1H, H-4), 3.71 (m, 1H, H-5), 3.67 (dd, *J* = 9.3, 9.3 Hz, 1H, H-2), 3.65 – 3.59 (m, 2H, H-4 and H-7a),

3.55 (ddd, *J* = 9.1, 9.1, 3.7 Hz, 1H, H-7b), 3.23 (d, J = 5.0 Hz, 1H, OH-3), 3.08 (d, *J* = 3.8 Hz, 1H, OH-4), 2.97 (s, 1H, OH-2), 2.08 (dddd, *J* = 14.6, 7.8, 5.6, 3.7 Hz, 1H, H-6a), 1.96 (dddd, *J* = 14.6, 8.9, 5.7, 4.4 Hz, 1H, H-6b). ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 137.7 (Ar), 134.0 (Ar), 133.5 (Ar), 131.1 (Ar), 129.0 (Ar), 128.5 (Ar), 127.8 (Ar), 127.6 (Ar), 88.2 (C-1), 75.8 (C-5), 74.9 (C-4), 73.2 (Ph*C*H_2), 70.3 (C-3), 70.1 (C-2), 66.0 (C-7), 31.2 (C-6). HRMS (ESI-QTOF) *m/z* calc'd for $C_{20}H_{23}ClO_5S$ $[M + Na]^+$, 433.0847; found, 433.0866.

4-Chlorophenyl 7-*O*-benzyl-6-deoxy-3,4-*O*-isopropylidene-1-thio-α,β-D-*galacto*-heptopyranoside (10)

To a solution of compound **9** (1.15 g, 2.79 mmol) in anhydrous acetone (15.0 mL) were added 2,2-dimethoxypropane (2.0 mL) and camphorsulfonic acid (20 mg), and the reaction was stirred for 6 hrs at room temperature. Triethylamine (~1 mL) was added, and the solution was evaporated. The residue was redissolved in EtOAc (50 mL), washed with saturated brine (30 mL), dried over anhydrous Na_2SO_4 and evaporated. The crude mixture was purified by column chromatography on silica gel using a gradient of 20→30% EtOAc–hexanes as the eluent to afford the desired product **10** (α/β, 0.06:1) as a syrup (1.142 g, 2.53 mmol, 90% yield). R_f = 0.33 (EtOAc: hexanes, 4:6). ^{1}H NMR (400 MHz, $CDCl_3$) for β-anomer: δ_H 7.51-7.22 (m, 9H, Ar), 4.51 (d, *J* = 11.9 Hz, 1H, PhCH_aH_b), 4.47 (d, *J* = 11.9 Hz, 1H, PhCH_aH_b), 4.45 (d, *J* = 10.2 Hz, 1H, H-1), 4.10 – 4.04 (m, 2H, H-3, H-4), 3.98 (ddd, *J* = 8.7, 4.5, 1.7 Hz, 1H, H-5), 3.70-3.56 (m, 3H, H-7a, H-7b, H-2), 3.60 (dd, *J* = 10.2, 8.7 Hz, 1H, H-2), 2.53, (br s, 1H, OH-2), 2.15 (dddd, *J* = 14.3, 9.4, 9.2, 4.3 Hz, 1H,

H-6a), 2.01 (dddd, *J* = 14.4, 9.4, 9.4, 4.3 Hz, 1H, H-6b), 1.48 (s, 3H, ISP_Me), 1.34 (s, 3H, ISP_Me). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 138.3 (Ar), 134.2 (Ar), 133.7 (Ar), 131.0 (Ar), 129.1 (Ar), 128.4 (Ar), 127.7 (Ar), 127.7 (Ar), 110.0 (ISP_*C*$(CH_3)_2$), 87.8 (C-1), 79.2 (C-4), 75.4 (C-3), 73.2 (C-5), 73.0 (Ph*C*H_2), 71.9 (C-2), 66.1 (C-7), 31.5 (C-6), 28.2 (ISP_Me), 26.3 (ISP_Me). HRMS (ESI-QTOF) *m/z* calc'd for $C_{23}H_{27}ClO_5S$ $[M + Na]^+$, 473.1160; found, 473.1169.

4-Chlorophenyl 2-*O*-acetyl-7-*O*-benzyl-6-deoxy-3,4-*O*-isopropylidene-1-thio-α,β-D-*galacto*-heptopyranoside (11)

Compound **10** (1.1 g, 2.43 mmol) was acetylated in a mixture of Ac_2O (11.0 mL) and anhydrous pyridine (12.0 mL) for 6 hrs at room temperature. The mixture was concentrated under reduced pressure and coevaporated with toluene. The crude mixture was purified by column chromatography on silica gel using a gradient of 15→25% EtOAc–hexanes as the eluent to afford the desired product **11** (α/β, 0.19:1) as a syrup (1.035 g, 2.09 mmol, 86% yield). R_f = 0.35 (EtOAc : hexanes 3 : 7). ^{1}H NMR (400 MHz, $CDCl_3$) for the β-anomer: δ_H 7.45 – 7.26 (m, 7H, Ar), 7.24 – 7.15 (m, 2H, Ar), 5.05 (dd, *J* = 10.2, 7.3 Hz, 1H, H-2), 4.59 (d, *J* = 10.2 Hz, 1H, H-1), 4.49 (d, *J* = 12.1 Hz, 1H, PhC*H*$_a$H$_b$), 4.45 (d, *J* = 12.1 Hz, 1H, PhC*H*$_a$H$_b$), 4.18 (dd, *J* = 7.2, 5.3 Hz, 1H, H-3), 4.10 (dd, *J* = 5.3, 2.1 Hz, 1H, H-4), 3.99 (ddd, *J* = 9.2, 4.4, 2.1 Hz, 1H, H-5), 3.67 – 3.54 (m, 2H, 2 × H-7), 2.20 – 2.11 (m, 4H, Ac + H-6a), 1.99 (dddd, *J* = 14.4, 8.3, 5.7, 4.4 Hz, 1H, H-6b), 1.54 (s, 3H, ISP_Me), 1.32 (s, 3H, ISP_Me). ^{13}C NMR (101 MHz, $CDCl_3$): δ_C 171.5 (C=O), 138.2 (Ar),

133.8 (Ar), 133.2 (Ar), 132.2 (Ar), 131.9 (Ar), 129.5 (Ar), 129.0 (Ar), 128.9 (Ar), 128.4 (Ar), 128.3(Ar), 127.7 (Ar), 127.5 (Ar), 110.3 ($C(Me)_2$), 85.4 (C-1), 77.1 (C-3), 75.5 (C-4), 73.0 (Ph*C*H_2), 72.9 (C-5), 71.5 (C-2), 66.0 (C-7), 31.4 (C-6), 27.7 (ISP_Me), 26.3 (ISP_Me), 21.0 (Ac). HRMS (ESI-QTOF) *m/z* calc'd for $C_{25}H_{29}ClO_6S$ $[M + Na]^+$, 515.1266; found, 515.1267.

6-Azidohexyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (13)

Compound **12** (284 mg, 0.505 mmol) and alcohol **7** (292 mg, 2.04 mmol) were dissolved in anhydrous CH_2Cl_2 (5.0 mL) under argon, 4Å molecule sieves (500 mg) was added. After stirring the mixture for 1 hr, the reaction mixture was cooled down to -78 °C and NIS (225 mg, 0.12 mmol) was added; after 10 min, TfOH (50 µL) was added dropwise. The reaction was continued at -78 °C for 4 hrs, and temperature was allowed to warm up to room temperature gradually. Triethylamine (~0.5 mL) was added, and the mixture was filtered off and concentrated under reduced pressure. The crude mixture was redissolved in EtOAc (30 mL). The organic phase was washed with a mixture of aqueous $NaHCO_3$ (10%, 15 mL) and aqueous $Na_2S_2O_3$ (10%, 15 mL), saturated brine (20 mL), dried over anhydrous Na_2SO_4 and evaporated. The crude mixture was purified by column chromatography on silica gel using a gradient of 15→20% EtOAc–hexanes as the eluent to afford the desired product **13** as a syrup (221 mg, 0.394 mmol, 78% yield). R_f = 0.53 (EtOAc : hexanes 4 : 6). $[\alpha]_D^{20}$: +75.1 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.89-7.82 (m, 2H, Pht), 7.79-7.71 (m, 2H, Pht), 5.78 (dd, *J* = 10.8, 9.1 Hz, 1H, H-3), 5.35 (d, *J* = 8.5 Hz, 1H, H-1), 5.17 (dd, *J* = 10.1, 9.1 Hz, 1H, H-4), 4.33 (dd, *J* = 12.3, 4.6 Hz, 1H, H-6a),

4.31 (dd, *J* = 10.8, 8.8 Hz, 1H, H-2), 4.17 (dd, *J* = 12.3, 2.4 Hz, 1H, H-6b), 3.90 – 3.81 (m, 2H, H-5, OC*H*$_a$H$_b$), 3.43 (ddd, *J* = 9.7, 7.2, 5.8 Hz, 1H, OCH$_a$*H*$_b$), 3.04 (t, *J* = 7.0 Hz, 2H, Hex_NC*H*$_2$), 2.11 (s, 3H, Ac), 2.02 (s, 3H, Ac), 1.86 (s, 3H, Ac), 1.44-1.35 (m, 2H, CH_2), 1.32-1.22 (m, 2H, CH_2), 1.18-1.05 (m, 4H, 2 × CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 170.7 (C=O), 170.1 (C=O), 169.4 (C=O), 167.8 (C=O), 167.4 (C=O), 134.3 (Pht), 123.6 (Pht), 98.2 (C-1), 71.8 (C-5), 70.8 (C-3), 69.8 (OCH$_a$H$_b$), 69.1 (C-4), 62.1 (C-6), 54.7 (C-2), 51.1 (CH_2), 29.1 (CH_2), 28.6 (CH_2), 26.2 (CH_2), 25.4 (CH_2), 20.8 (Ac), 20.6 (Ac), 20.5 (Ac). HRMS (ESI-QTOF) *m/z* calc'd for $C_{26}H_{32}N_4O_{10}$ $[M + Na]^+$, 583.2011; found, 583.2013.

6-Azidohexyl 2-deoxy-2-phthalimido-β-D-glucopyranoside (14)

Compound **13** (280 mg, 0.499 mmol) was transesterified in anhydrous MeOH (4.0 mL), using a solution of guanidine/guanidinium buffer (1 M) in methanol (pH ~10). After stirring for 3 hrs, the reaction mixture was neutralized with acetic acid and concentrated under reduced pressure. The residue was redissolved in EtOAc (20 mL). The organic phase was washed with brine (30 mL), dried over anhydrous Na_2SO_4, and evaporated. The crude mixture was purified by column chromatography on silica gel using 3% MeOH−CH_2Cl_2 as the eluent to afford the desired product **14** as a white solid (213 mg, 0.489 mmol, 98% yield). R_f = 0.29 (MeOH : CH_2Cl_2, 5 : 95). $[\alpha]_D^{20}$: -1.4 (*c* 4.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.81 (dd, *J* = 5.5, 3.0 Hz, 2H, Pht), 7.75 – 7.69 (dd, *J* = 5.5, 3.0 Hz, 2H, Pht), 5.16 (d, *J* = 8.4 Hz, 1H, H-1), 4.28 (dd, *J* = 10.8, 8.8 Hz, 1H, H-3), 4.06 (dd, *J* = 10.8, 8.4 Hz, 1H, H-2), 3.88 (high order m, 2H, H-6a, H-6b), 3.79 (m, 1H, OC*H*$_a$H$_b$), 3.69

(dd, *J* = 9.2, 9.2 Hz, 1H, H-4), 3.45 – 3.34 (m, 2H, H-5, OCH_aH_b), 3.02 (t, *J* = 7.0 Hz, 2H, Hex_NCH_2), 1.45 – 1.29 (m, 2H, CH_2), 1.28 -1.15 (m, 2H, CH_2), 1.15 – 0.99 (m, 4H, 2 × CH_2). ^{13}C NMR (101 MHz, $CDCl_3$): δ_C 168.4 (C=O), 134.1 (Pht), 131.6 (Pht), 123.3 (Pht), 98.4 (C-1), 75.6 (C-5), 71.5 (C-4), 71.2 (C-3), 69.6 (OCH_aH_b), 61.6 (C-6), 56.7 (C-2), 51.1 (NCH_2), 29.0 (CH_2), 28.5 (CH_2), 26.2 (CH_2), 25.3 (CH_2). HRMS (ESI-QTOF) *m/z* calc'd for $C_{20}H_{26}N_4O_7$ $[M + NH_4]^+$, 452.2140; found, 452.2129.

6-Azidohexyl 4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside (15)

To a solution of compound **14** (217 mg, 0.499 mmol) in anhydrous acetonitrile (3.0 mL) were added benzaldehyde dimethyl acetal (0.15 mL, 0.99 mmol), and a catalytic amount of (1S)-(+)-10-camphorsulfonic acid. The reaction was continued at room temperature for 5 hrs and neutralized with triethylamine. The mixture was concentrated under reduced pressure. The crude syrup was redissolved in EtOAc (50 mL). The organic phase was washed with brine (30 mL), dried over anhydrous Na_2SO_4, and evaporated. The crude mixture was purified by column chromatography on silica gel using a gradient of 15→20% EtOAc–hexanes as the eluent to afford the desired product **15** (225 mg, 0.429 mmol, 86% yield). R_f = 0.52 (EtOAc : hexanes, 3 : 7). $[\alpha]_D^{20}$: +12.7 (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.89-7.82 (m, 2H, Pht), 7.78-7.70 (m, 2H, Pht), 7.54-7.46 (m, 2H, Ar), 7.43-7.32 (m, 3H, Ar), 5.57 (s, 1H, PhC*H*), 5.26 (d, *J* = 8.5 Hz, 1H, H-1), 4.63 (high order dd, *J* = 10.4, 8.3 Hz, 1H, H-3), 4.39 (high order dd, *J* = 10.5, 4.2 Hz, 1H, H-6a), 4.24 (dd, *J* = 10.1, 8.6 Hz, 1H, H-2), 3.89-3.79 (m, 2H, H-6b, OCH_aH_b), 3.68-3.56 (m, 2H, H-4, H-5), 3.47-

3.38 (m, 1H, OCH_aH_b), 3.05 (t, *J* = 7.0 Hz, 2H, Hex_NCH_2), 2.58-2.49 (m, 1H, OH-3), 1.52-1.35 (m, 2H, CH_2), 1.31-1.19 (m, 2H, CH_2), 1.18-1.03 (m, 4H, 2 × CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 168.5 (C=O), 168.1 (C=O), 134.2 (Pht), 129.3 (Ar), 128.4 (Ar), 126.3 (Ar), 123.5 (Pht), 123.1 (Pht), 101.9 (Ph<u>*C*</u>H), 98.3 (C-1), 82.3 (C-5), 69.8 (OCH_aH_b), 68.7 (C-6), 68.6 (C-3), 66.2 (C-4), 56.6 (C-2), 29.1 (CH_2), 28.6 (CH_2), 26.2 (CH_2), 25.4 (CH_2). HRMS (ESI-QTOF) *m/z* calc'd for $C_{27}H_{30}N_4O_7$ $[M + Na]^+$, 454.2007; found, 545.2000.

6-Azidohexyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside (16)

To a solution of compound **15** (581 mg, 1.11 mmol) in anhydrous DMF (6.0 mL) under argon atmosphere was added NaH (60% dispersion in mineral oil, 97 mg, 2.44 mmol) at ambient temperature. After stirring for 10 min, benzyl bromide (0.26 mL, 2.22 mmol) was added. After stirring for 1 hr, the reaction mixture was then quenched with a few drops of methanol, diluted with EtOAc (40 mL), and the organic solution was washed with saturated brine (30 mL × 2), dried over anhydrous Na_2SO_4, and evaporated. The crude mixture was purified by column chromatography on silica gel using a gradient of 10→12% EtOAc−hexanes as the eluent to afford the desired product **16** as a syrup (613 mg, 1.0 mmol, 90% yield). R_f = 0.65 (EtOAc : hexanes, 2 : 8). $[\alpha]_D^{20}$: +57.2 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.93-7.66 (m, 4H, Pht), 7.57-7.49 (m, 2H, Ar), 7.44-7.35 (m, 3H, Ar), 7.04- 6.98 (m, 2H, Ar), 6.96-6.85 (m, 3H, Ar), 5.63 (s, 1H, PhC<u>*H*</u>), 5.20 (d, *J* = 8.5 Hz, 1H, H-1), 4.81 (d, *J* = 12.3 Hz, 1H, $PhCH_aH_b$), 4.51 (d, *J* = 12.3 Hz, 1H, $PhCH_aH_b$), 4.49 - 4.39 (m, 2H, H-3, H-6a), 4.22 (dd, *J* = 10.5, 8.5 Hz, 1H, H-2), 3.91-3.76 (m, 3H, H-4, H-6b,

OC*H*$_a$H$_b$), 3.64 (ddd, 1H, *J* = 9.8, 9.8, 4.9 Hz, H-5), 3.39 (ddd, *J* = 9.8, 7.2, 5.7 Hz, 1H, OCH$_a$*H*$_b$), 3.02 (t, *J* = 7.0 Hz, 2H, Hex_NC*H*$_2$), 1.48-1.32 (m, 2H, CH$_2$), 1.30-1.20 (m, 2H, CH$_2$), 1.17-1.03 (m, 4H, 2 × CH$_2$). ^{13}C NMR (100 MHz, CDCl$_3$): δ_C 167.9 (C=O), 167.7 (C=O), 137.9 (Pht), 137.4 (Pht), 133.9 (Pht), 131.6 (Pht), 128.3 (Ar), 128.0 (Ar), 127.3 (Ar), 126.0 (Ar), 123.3 (Pht), 101.3 (Ph*C*H), 98.9 (C-1), 83.1 (C-5), 74.6 (C-3), 74.1 (Ph*C*H$_2$), 69.8 (C-6), 69.6 (OCH$_a$H$_b$), 66.1 (C-4), 55.9 (C-2), 51.1 (CH$_2$), 29.1 (CH$_2$), 28.5 (CH$_2$), 26.1 (CH$_2$), 25.4 (CH$_2$). HRMS (ESI-QTOF) *m/z* calc'd for $C_{34}H_{36}N_4O_7$ [M + Na]$^+$, 635.2476; found, 635.2463.

6-Azidohexyl 3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (17)

To a solution of compound **16** (124 mg, 0.20 mmol) in anhydrous CH_2Cl_2 (5 mL) was added triethylsilane (116 mg, 1.1 mmol) at 0 °C, followed by $BF_3.Et_2O$ (50 µL, 0.4 mmol). After stirring for 4 hours, the reaction was quenched with triethylamine and concentrated under reduced pressure to afford a syrup. The crude mixture was redissolved in EtOAc (30 mL), and the organic solution was washed with brine (30 mL), dried over anhydrous Na_2SO_4, and evaporated. The crude mixture was purified by column chromatography on silica gel using a gradient of 15→20% EtOAc–hexanes as the eluent to afford the desired product **17** as a syrup (94 mg, 0.16 mmol, 76% yield). R_f = 0.69 (EtOAc : hexanes, 3 : 7). $[\alpha]_D^{20}$: +35.3 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.89-7.62 (m, 4H, Pht), 7.42-7.28 (m, 5H, Ar), 7.10-7.02 (m, 2H, Ar), 7.00-6.91 (m, 3H, Ar), 5.13 (d, *J* = 8.3 Hz, 1H, H-1), 4.75 (d, *J* = 12.2 Hz, 1H, PhC*H*$_a$H$_b$), 4.65 (d, *J* = 11.9 Hz, 1H, PhC*H*$_a$H$_b$), 4.59 (d, *J* = 11.9 Hz, 1H, PhCH$_a$*H*$_b$), 4.54 (d, *J* = 12.2 Hz, 1H, PhCH$_a$*H*$_b$), 4.23 (dd,

J = 10.8, 8.3 Hz, 1H, H-3), 4.15 (dd, *J* =10.8, 8.3 Hz, 1H, H-2), 3.87-3.74 (m, 4H, H-4, H-6a, H-6b, OC*H*$_a$H$_b$), 3.65 (ddd, *J* = 9.8, 4.9, 4.9 Hz, 1H, H-5), 3.36 (ddd, *J* = 9.8, 7.3, 5.7 Hz, 1H, OCH$_a$*H*$_b$), 3.01 (t, *J* = 6.9 Hz, 2H, Hex_NC*H*$_2$), 2.94 (d, *J* = 2.6 Hz, 1H, OH-4), 1.47-1.31 (m, 2H, CH$_2$), 1.30-1.18 (m, 2H, CH$_2$), 1.16-1.01 (m, 4H, 2 × CH$_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 168.3 (C=O), 167.6 (C=O), 133.8 (Pht), 128.5 (Ar), 128.1 (Ar), 127.9 (Ar), 127.8 (Ar), 127.7 (Ar), 127.4 (Ar), 123.3 (Pht), 123.1 (Pht), 98.3 (C-1), 78.7 (C-3), 74.5 (C-4), 74.3 (Ph*C*H$_2$), 73.8 (Ph*C*H$_2$), 73.5 (C-5), 70.8 (C-6), 69.3 (OCH$_a$H$_b$), 55.4 (C-2), 51.1 (CH$_2$), 29.4 (CH$_2$), 28.5 (CH$_2$), 26.2 (CH$_2$), 25.4 (CH$_2$). HRMS (ESI-QTOF) *m/z* calc'd for $C_{34}H_{38}N4_5O_7$ [M + NH_4]$^+$, 632.3079; found, 632.3068.

6-Azidohexyl 2-*O*-acetyl-7-*O*-benzyl-6-deoxy-3,4-*O*-isopropylidene-β-D-*galacto*-heptopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (18)

To a solution of glycosyl donor **11** (32 mg, 0.065mmol), glycosyl acceptor **17** (61 mg, 0.099 mmol) in anhydrous CH_2Cl_2 (2 mL), was added crushed molecular sieves (4 Å, 100 mg). After stirring at room temperature for 1 hr, the reaction mixture was cooled down to -50 °C, and NIS (29 mg, 0.131mmol) was added; after another 10 min, TfOH (30 µL) was added. The reaction was stirred at -50 °C for 2 hrs. Triethylamine (~0.5 mL) was added to quench the reaction. The reaction mixture was filtered off and evaporated. The crude mixture was redissolved in EtOAc (30 mL), washed with a mixture of 10% aqueous $Na_2S_2O_3$ (15 mL) and 10% aqueous $NaHCO_3$ (15 mL), saturated brine (20 mL), dried over anhydrous Na_2SO_4, and evaporated. The crude mixture was purified by column

chromatography on silica gel using a gradient of 15→20% EtOAc–hexanes as the eluent to afford recovered acceptor **17** (23 mg, 0.037mmol) and the desired product **18** as a syrup (35 mg, 0.036 mmol, 59% yield based on recovered acceptor). R_f = 0.33 (EtOAc : hexanes, 3 : 7). $[\alpha]_D^{20}$: +24.1 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.87-7.54 (m, 4H, Pht), 7.42-7.26 (m, 10H, Ar), 7.02-6.95 (m, 2H, Ar), 6.89-6.81 (m, 3H, Ar), 5.07 (d, *J* = 8.3 Hz, 1H, GlcN_H-1), 4.94 (dd, *J* = 8.4, 7.3 Hz, 1H, *Galacto*-Hep_H-2), 4.80 (d, *J* = 12.2 Hz, 1H, PhC*H*$_a$H$_b$), 4.76 (d, *J* = 12.2 Hz, 1H, PhC*H*$_a$H$_b$), 4.51 – 4.46 (m, 3H, PhCH$_a$*H*$_b$, PhC*H*$_a$*H*$_b$), 4.43 (d, *J* = 12.2 Hz, 1H, PhCH$_a$*H*$_b$), 4.34 (d, *J* = 8.4 Hz, 1H, *Galacto*-Hep_H-1), 4.20 (dd, *J* = 10.7, 8.2 Hz, 1H, GlcN_H-3), 4.12 (dd, *J* = 10.9, 8.2 Hz, 1H, GlcN_H-2), 3.93 (dd, *J* = 7.2, 2.3 Hz, 1H, *Galacto*-Hep_H-3), 3.91 (dd, *J* = 5.4, 2.3 Hz, 1H, *Galacto*-Hep_H-4), 3.87 (dd, *J* = 8.3, 7.3 Hz, 1H, GlcN_H-4), 3.82-3.73 (m, 4H, *Galacto*-Hep_H-5, GlcN_H-6a, GlcN_H-6b, OC*H*$_a$H$_b$), 3.57 (ddd, *J* = 9.1, 9.0, 4.5 Hz, 1H, *Galacto*-Hep_H-7a), 3.51 (ddd, *J* = 9.9, 3.5, 1.9 Hz, 1H, GlcN_H-5), 3.41 (ddd, *J* = 9.1, 5.1, 5.1 Hz, 1H, *Galacto*-Hep_H-7b), 3.36 (ddd, *J* = 13.2, 7.3, 5.1 Hz, 1H, OCH$_a$*H*$_b$), 3.01 (t, *J* = 6.9 Hz, 2H, Hex_NC*H*$_2$), 2.07 (s, 3H, Ac), 1.94 (dddd, *J* = 13.7, 9.6, 8.9, 4.7 Hz, 1H, *Galacto*-Hep_H-6a), 1.85 (dddd, *J* = 13.9, 9.5, 8.8, 5.4 Hz, 1H, *Galacto*-Hep_H-6b), 1.53 (s, 3H, ISP_CH_3), 1.39 (m, 2H, CH_2), 1.29 (s, 3H, ISP_CH_3), 1.28-1.19 (m, 2H, CH_2), 1.15-1.03 (m, 4H, 2 × CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 138.7 (Pht), 138.5 (Pht), 138.0 (Pht), 133.7 (Pht), 128.4 (Ar), 128.1 (Ar), 128.0 (Ar), 127.9 (Ar), 127.8 (Ar), 127.7 (Ar), 127.6 (Ar), 126.9 (Pht), 100.04 (*Galacto*-Hep_C-1), 98.4(GlcN_C-1), 78.3 (GlcN_C-4), 77.4 (*Galacto*-Hep_C-4), 76.7 (GlcN_C-3), 75.7 (*Galacto*-Hep_C-3), 74.9 (GlcN_C-5), 74.6 (Ph*C*H$_2$), 73.6 (*Galacto*-Hep_C-2), 73.5 (Ph*C*H$_2$), 73.1 (Ph*C*H$_2$), 69.5 (*Galacto*-Hep_C-5), 69.2 (OCH$_a$H$_b$), 67.8 (GlcN_C-6),

66.0 (*Galacto*-Hep_C-7), 55.8 (GlcN_C-2), 51.2 (Ph<u>*C*</u>H_2), 31.2 (*Galacto*-Hep_C-6), 29.1 (CH_2), 28.6 (CH_2), 27.8 (ISP_Me), 26.3 (ISP_Me), 26.2 (CH_2), 25.4 (<u>*C*</u>H_2), 21.0 (*Galacto*-Hep_Ac). HRMS (ESI-QTOF) *m/z* calc'd for $C_{53}H_{62}N_4O_{13}$ $[M + Na]^+$, 985.4206; found, 985.4196.

2,3,4-Tri-*O*-acetyl-7-*O*-benzyl-6-deoxy-D-*galacto*-heptopyranosyl trichloroacetimidate (20).

Crude compound **20**(α/β 0.77:1) was prepared from compound **5** according to our previous procedures.[2] R_f = 0.66 (EtOAc : hexanes, 2:3). Data for the α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$): 8.61 (s, 1H, C=N*H*), 7.41 – 7.28 (m, 5H, Ar), 6.58 (d, *J* = 3.6 Hz, 1H, H-1), 5.55 – 5.34 (m, 3H, H-2, H-3, H-4), 4.56 – 4.40 (m, 3H, H-5 + PhCH_aH_b), 3.65 – 3.47 (m, 2H, H-7a + H-7b), 2.18 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.03 (s, 3H, OAc), 2.00 – 1.71 (m, 2H, H-6a + H-6b). ^{13}C NMR (101 MHz, $CDCl_3$): δ_C 170.4 (C=O), 170.0 (C=O), 169.2 (C=O), 161.1 (*C*=NH), 138.1 (Ar), 138.0 (Ar), 128-127 (Ar), 93.6 (C-1), 73.2 (Ph*C*H_2O), 71.2 (C-3), 69.2 (C-4), 68.0 (C-5), 67.2 (C-2), 65.6 (C-7), 30.6 (C-6), 20.7-20.5 (OAc, × 3). Data for the β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.70 (s, 1H, C=N*H*), 7.41 – 7.28 (m, 5H, Ar), 5.81 (d, *J* = 8.5 Hz, 1H, H-1), 5.55 – 5.34 (m, 2H, H-2, H-4), 5.15 (dd, *J* = 3.6, 10.6 Hz, H-3), 4.56 – 4.40 (m, 2H, PhCH_aH_b), 4.09, (ddd, *J* = 0.9, 4.6, 8.6 Hz, 1H, H-5), 3.65 – 3.47 (m, 2H, H-7a + H-7b), 2.20 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.03 (s, 3H, OAc), 2.00 – 1.71 (m, 2H, H-6a + H-6b). ^{13}C NMR (101 MHz, $CDCl_3$): δ_C 170.3 (OAc), 170.2 (OAc), 170.0 (OAc), 161.1 (*C*=NH), 138.2 (Ar), 128 -127 (Ar), 96.3 (C-1), 73.1 (Ph*C*H_2O), 71.2 (C-5), 70.0 (C-3), 68.3

(C-2), 68.0 (C-4), 65.6 (C-7), 30.8 (C-6), 20.7-20.5 (OAc, × 3). HRMS (ESI-QTOF) *m/z* calc'd for $C_{22}H_{26}Cl_3NO_9$ $[M + Na]^+$, 576.0565; found, 576.0559.

6-Azidohexyl 2,4-di-*O*-acetyl-7-*O*-benzyl-6-deoxy-β-D-*ido*-heptopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (36)

To a solution of compound **35** (38 mg, 0.038 mmol) in anhydrous methanol (1.0 mL) under argon atmosphere was added $PdCl_2$ (4 mg, 0.022 mmol) and the reaction stirred for 24 hrs at ambient temperature. The reaction mixture was filtered off, evaporated and purified by column chromatography on silica gel using 40% EtOAc–hexanes as the eluent to afford the desired product **36** as a syrup (30 mg, 0.031 mmol, 82% yield). R_f = 0.22 (EtOAc : hexanes, 2 : 3). $[\alpha]_D^{20}$: +28.0 (*c* 0.5, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 7.82 (br, 1H, Pht), 7.70 (br, 2H, Pht), 7.66 (br, 1H, Pht), 7.43 – 7.38 (m, 2H, Ar), 7.40 – 7.32 (m, 4H, Ar), 7.30 – 7.26 (m, 4H, Ar), 7.08 – 7.01 (m, 2H, Ar), 6.92 – 6.87 (m, 3H, Ar), 5.08 (d, *J* = 8.7 Hz, GlcN_H-1), 5.07 (d, *J* = ~1 Hz, *ido*-Hep_H-1), 4.93 (d, *J* = 12.1 Hz, 1H, PhC$H_a$$H_b$), 4.83 (dd, *J* = 2.8, 1.1 Hz, 1H, *ido*-Hep_H-2), 4.62 (s, 2H, PhC$H_a$$H_b$), 4.55 (dd, *J* = 1.5, 1.5 Hz, 1H, *ido*-Hep_H-4), 4.49 (d, *J* = 12.1 Hz, 1H, PhC$H_a$$H_b$), 4.42 (d, *J* = 12.1 Hz, 1H, PhC$H_a$$H_b$), 4.39 (d, *J* = 12.1 Hz, 1H, PhC$H_a$$H_b$), 4.27 (dd, *J* = 10.8, 8.6 Hz, 1H, GlcN_H-3), 4.15 (dd, *J* = 8.4, 10.7 Hz, 1H, GlcN_H-2), 4.11 (ddd, *J* = 1.6, 4.3, 9.2 Hz, *ido*-Hep_H-5), 4.06 (ddd, *J* = 2.7, 2.7, 4.2 Hz, 1H, *ido*-Hep_H-3), 4.01 (dd, *J* = 9.9, 8.5 Hz, 1H, GlcN_H-4), 3.81 (ddd, *J* = 6.0, 6.0, 9.9 Hz, OC$H_a$$H_b$), 3.76 (dd, *J* = 2.1, 10.9 Hz, 1H, GlcN_H-6a), 3.73 (dd, *J* = 3.8, 10.9 Hz, GlcN_H-6b), 3.59 (ddd, *J* = 9.9, 3.7, 2.1 Hz, 1H, GlcN_H-5), 3.50 (ddd,

J = 9.0, 9.0, 5.2 Hz, 1H, *ido*-Hep_H-7a), 3.42 – 3.34 (m, 2H, *ido*-Hep_H-7b, OCH_aH_b), 3.28 (d, *J* = 2.6 Hz, *ido*-Hep_OH-3), 3.03 (t, *J* = 7.1 Hz, 2H, CH_2N_3), 2.09 (s, 3H, Ac), 2.03 (s, 3H, Ac), 1.78 (m, 1H, *ido*-Hep_H-6a), 1.66 (m, 1H, *ido*-Hep_H6b), 1.49 – 1.35 (m, 4H, $CH_2CH_2N_3$, $OCH_aH_bCH_2$), 1.31 – 1.20 (m, 4H, $OCH_aH_bCH_2(CH_2)_2$). ^{13}C NMR (151 MHz, $CDCl_3$): δ_C 170.3 (C=O), 170.1 (C=O), 138.9 (Ar), 138.4 (Ar), 138.1 (Ar), 133.9 (Ar), 133.8 (Ar), 128.9 (Ar), 128.4 (Ar), 128.0 (Ar), 127.8 (Ar), 127.8 (Ar), 127.6 (Ar) 127.57 (Ar), 127.0 (Ar), 123.1 (Ar), 123.0 (Ar), 98.4 (GlcN_C-1), 97.3 (*ido*-Hep_H-1), 78.6 (GlcN_C-4), 77.1 (GlcN_C-3), 74.5 (GlcN_C-5), 74.2 ($PhCH_2$), 73. ($PhCH_2$), 73.1 ($PhCH_2$), 70.3 (*ido*-Hep_C-4), 69.6 (*ido*-Hep_C-5)), 69.2 (*ido*-Hep_C-2), 69.19 (OCH_aH_b), 68.7 (GlcN_C-6), 67.3 (*ido*-Hep_C-3), 65.9 (*ido*-Hep_C-3), 55.7 (GlcN_C-2), 51.1 (CH_2N_3), 30.8 (*ido*-Hep_C-6), 29.1 (Hex_CH_2), 28.6 (Hex_CH_2), 26.2 (Hex_CH_2), 25.4 (Hex_CH_2), 21.0 (Ac), 20.7 (Ac). HRMS (ESI-QTOF): *m/z* calc'd for $C_{52}H_{60}N_4O_{14}$ $[M + Na]^+$: 987.3998; found: 987.3999.

6-azidohexyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranoside-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (43)

To a solution of thioglycosyl donor **12** (23.8 mg, 0.042 mmol), glycosyl acceptor **41** (30 mg, 0.028 mmol) in anhydrous acetonitrile (1.0 mL), was added crushed molecular sieves (4 Å, 150 mg). After stirring at room temperature for 2 hrs, the reaction cooled down to -20 °C, and NIS (12.6 mg, 0.056 mmol) was added followed by TfOH (15 µL); the reaction was continued at -20 °C for 1 hr, and gradually warmed up to ambient temperature. Triethylamine (~0.1 mL) was added to quench the reaction. The reaction mixture was

filtered off and evaporated. The mixture was purified by column chromatography on silica gel using 30% EtOAc–hexanes as the eluent. ^{1}H NMR revealed that the major compound was 6-azidohexyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranoside-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (**43**) which is contaminated with other unidentified impurities. Selected ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 5.79 (dd, *J* = 10.7, 9.0 Hz, 1H, H-3'), 5.54 (d, *J* = 8.4 Hz, 1H, H-1'), 5.12 (dd, *J* = 9.1, 10.1 Hz, 1H, H-4'), 4.94 (d, *J* = 8.5 Hz, 1H, H-1), 4.84 (d, *J* = 12.7 Hz, 1H, PhCH_aH$_b$), 4.57 (d, *J* = 11.9 Hz, 1H, PhCH_aH$_b$), 4.54 (d, *J* = 11.9 Hz, 1H, PhCH$_a$$H_b$), 4.49 (d, *J* = 12.7 Hz, 1H, PhCH$_a$$H_b$), 4.34 (dd, J = 10.7, 8.4 Hz, 1H, H-2'), 4.10 (dd, *J* = 8.5, 10.7 Hz, 1H, H-2), 3.94 (dd, *J* = 2.1, 12.2 Hz, 1H, H-6b'), 3.69 (ddd, *J* = 6.0, 6.0, 9.8 Hz, 1H, OCH_aH$_b$),3.59 (dd, *J* = 1.3, 11.1 Hz, 1H, H-6a), 3.49 (dd, *J* = 4.0, 11.1 Hz, 1H, H-6b), 3.47 (ddd, *J* = 2.5, 4.3, 10.0 Hz, 1H, H-5'), 3.36 (ddd, *J* = 1.3, 4.0, 10.1 Hz, 1H, H-5), 3.39 – 3.32 (m, 2H), 2.98 (t, *J* = 6.8 Hz, 2H, CH_2N_3). 2.01 (Ac), 1.98 (Ac), 1.85 (Ac).

4-Chlorophenyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (45)

To a solution of 4-chlorophenyl 3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside **44** (1.031 g, 1.67 mmol) in anhydrous DMF (10.0 mL) under an argon atmosphere was added NaH (60% dispersion in mineral oil, 233 mg, 5.84 mmol) at ambient temperature. After stirring for 15 min, benzyl bromide (0.59 mL, 5.02 mmol) was added. After stirring for 1 hr, the reaction mixture was then quenched with a few drops of acetic acid, diluted by EtOAc (40 mL), and the organic solution was washed with

saturated brine (30 mL × 2), dried over anhydrous Na_2SO_4, and evaporated. The crude mixture was purified by column chromatography on silica gel using 22% EtOAc–hexanes as the eluent to afford the desired product **45** as a syrup (768 mg, 1.087 mmol, 65% yield). R_f = 0.23 (EtOAc : hexanes, 1 : 4). $[\alpha]_D^{20}$: +22.4 (*c* 4.2, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.2 Hz, 1H, Pht), 7.69 (m, 2H, Pht), 7.62 (d, *J* = 7.2 Hz, 1H, Pht), 7.40 – 7.24 (m, 12H, Ar), 7.14 – 7.10 (m, 2H, Ar), 6.99 – 6.96 (m, 2H, Ar), 6.90 – 6.82 (m, 3H, Ar), 5.49 (d, *J* = 10.4 Hz, 1H, H-1), 4.84 (d, *J* = 10.9 Hz, 1H, PhCH_aH$_b$), 4.78 (d, *J* = 12.0 Hz, 1H, PhCH_aH$_b$), 4.66 (d, *J* = 10.8 Hz, 1H, PhCH$_a$$H_b$), 4.63 (d, *J* = 11.9 Hz, 1H, PhCH_aH$_b$), 4.57 (d, *J* = 11.9 Hz, 1H, PhCH$_a$$H_b$), 4.43 (d, *J* = 12.0 Hz, 1H, PhCH$_a$$H_b$), 4.37 (dd, *J* = 10.2, 8.5 Hz, 1H, H-3), 4.21 (dd, *J* = 10.3 Hz, 1H, H-2), 3.82 (dd, *J* = 1.9, 10.8 Hz, H-6a), 3.79 (dd, *J* = 4.4, 10.8 Hz, H-6b), 3.76 (dd, *J* = 8.5, 9.9 Hz, H-4), 3.71 (ddd, *J* = 10.0, 4.3, 2.0 Hz, 1H, H-5). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.0 (C=O), 167.3 (C=O), 138.2 (Ar), 137.9 (Ar), 137.7 (Ar), 134.3 (Ar), 134.2 (Ar), 133.9 (Ar), 133.8 (Ar), 131.6 (Ar), 131.5 (Ar), 130.2 (Ar), 128.9 (Ar), 128.5 (Ar), 128.4 (Ar), 128.1 (Ar), 128.0 (Ar), 127.9 (Ar), 127.7 (Ar), 127.65 (Ar), 127.4 (Ar), 123.5 (Ar), 123.3 (Ar), 82.9 (C-1), 80.2 (C-3), 79.4 (C-4), 79.3 (C-5), 75.0 ($PhCH_2$), 75.0 ($PhCH_2$), 73.4 ($PhCH_2$), 68.8 (C-6), 54.9 (C-2). HRMS (ESI-QTOF): *m/z* calc'd for $C_{41}H_{36}ClNO_6S$ $[M + Na]^+$: 728.1844; found: 728.1842.

3,4,6-Tri-*O*-benzyl-2-deoxy-2-phthalimido-α/β-D-glucopyranosyl trichloroacetimidate (46)

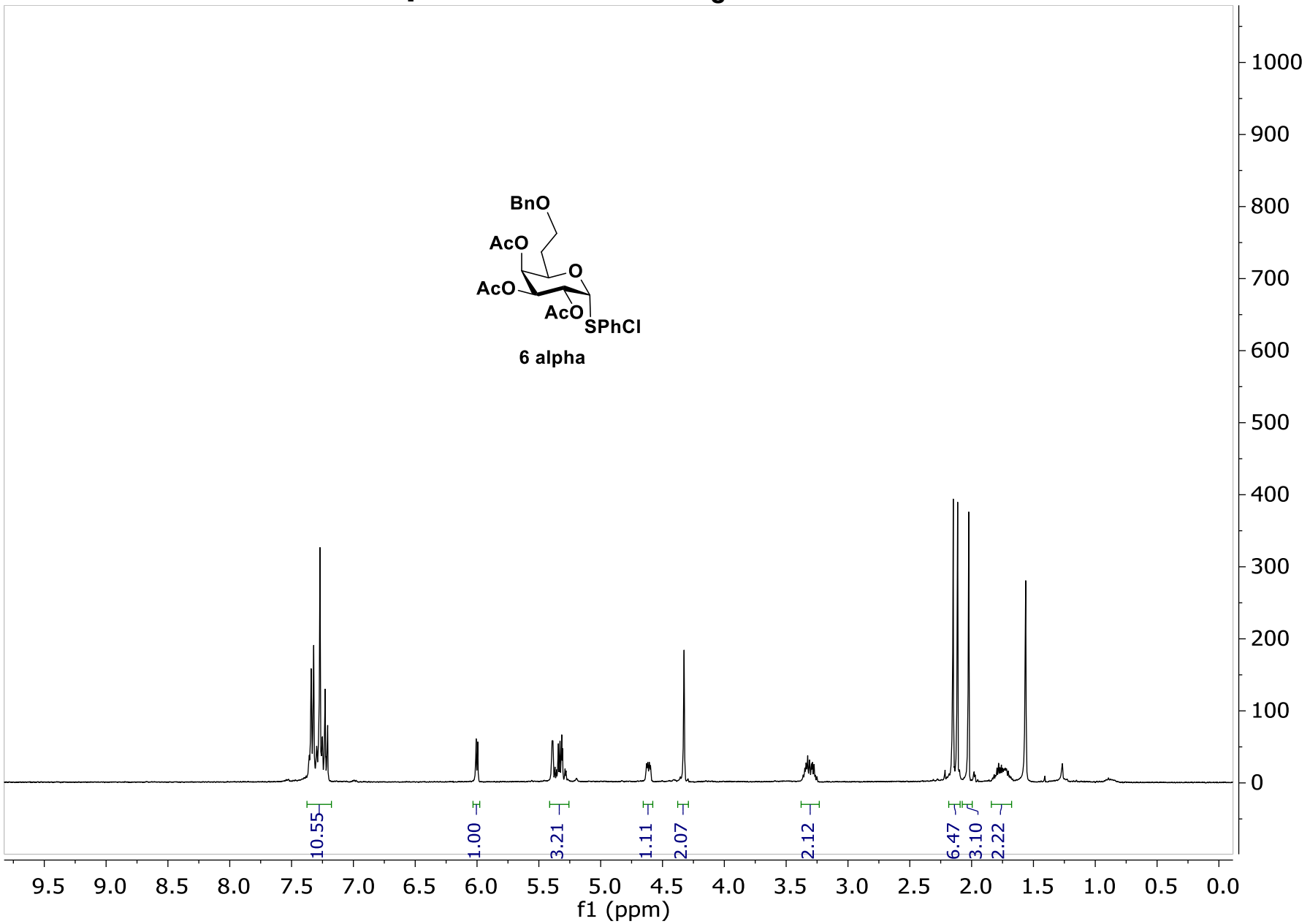
To a solution of 4-chlorophenyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside **45** (1.235 g, 1.748 mmol) in acetone (15.0 mL) and water (2.0 mL) was

added *N*-bromosuccinimide (933 mg, 5.24 mmol) at 0 °C. The ice bath was then removed and the reaction mixture was stirred at room temperature for 1.5 hrs. CH_2Cl_2 (50 mL) was added and the organic solution was washed with saturated aq $Na_2S_2O_3$ solution (30 mL). The aqueous layer was further extracted with CH_2Cl_2 (2 × 70 mL), and the combined organic phases were washed with brine (25 mL), dried over anhydrous Na_2SO_4, filtered off and concentrated. The crude mixture was purified by column chromatography (27→35% EtOAc/hexane) to afford the hemiacetal (740 mg, 73%) as a colorless viscous liquid. To a solution of hemiacetal (208 mg, 0.359 mmol) in anhydrous CH_2Cl_2 (3.0 mL) were added K_2CO_3 (150 mg, 1.085 mmol) and trichloroacetonitrile (0.54 mL, 5.38 mmol). The reaction mixture was stirred at ambient temperature for 3 hrs. The solution was filtered over a bed of celite and concentrated to afford the crude product **46** (α/β 3:97) as a colorless syrup. R_f = 0.66 (EtOAc/hexanes 2:3). The crude product was used directly for the next step without further purification.

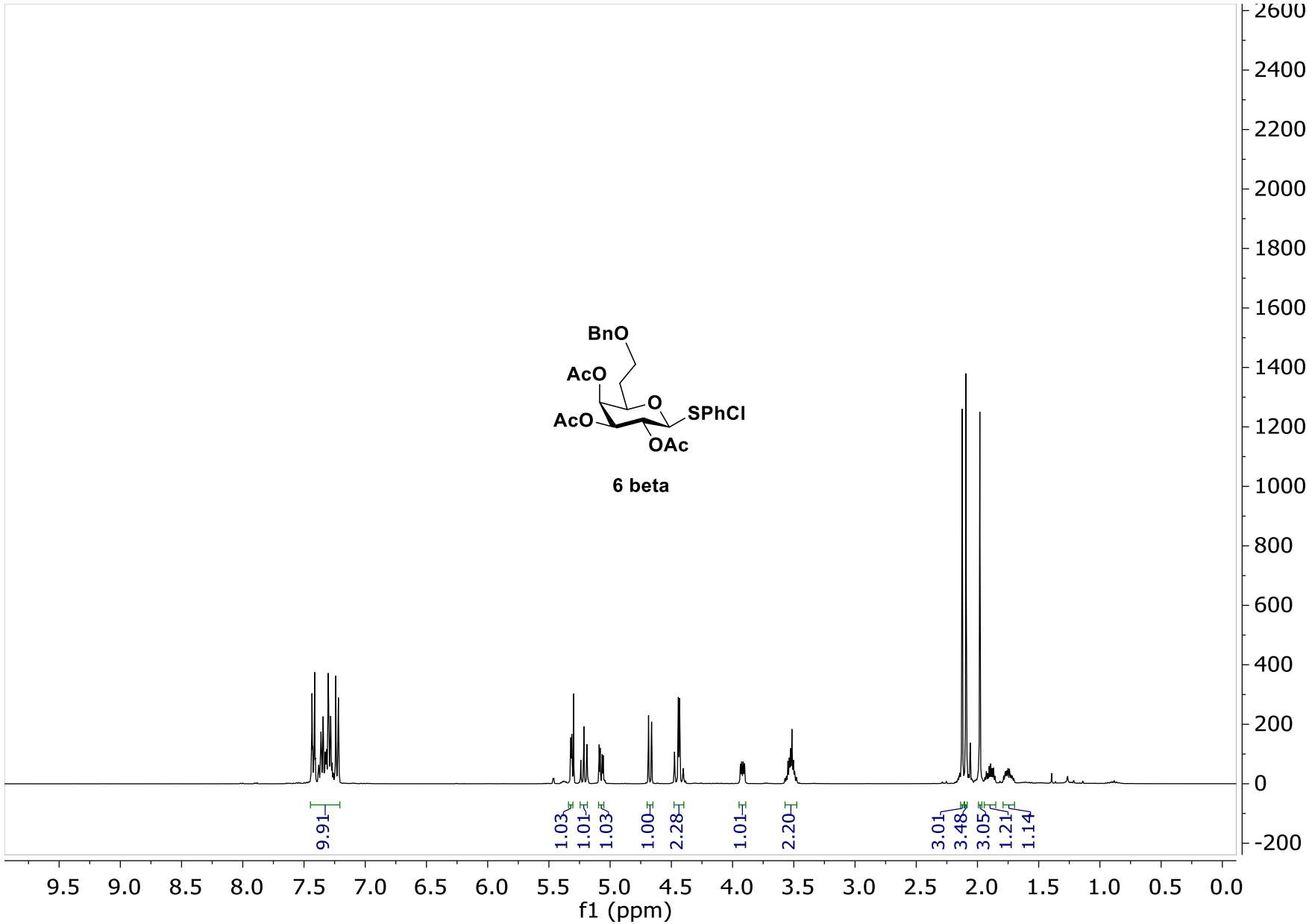
References

1 P. Zhang, K. Ng and C.-C. Ling, *Org Biomol Chem*, 2010, **8**, 128–136.
2 P. Zhang, R. Hevey and C.-C. Ling, *J. Org. Chem.*, 2017, **82**, 9662–9674.

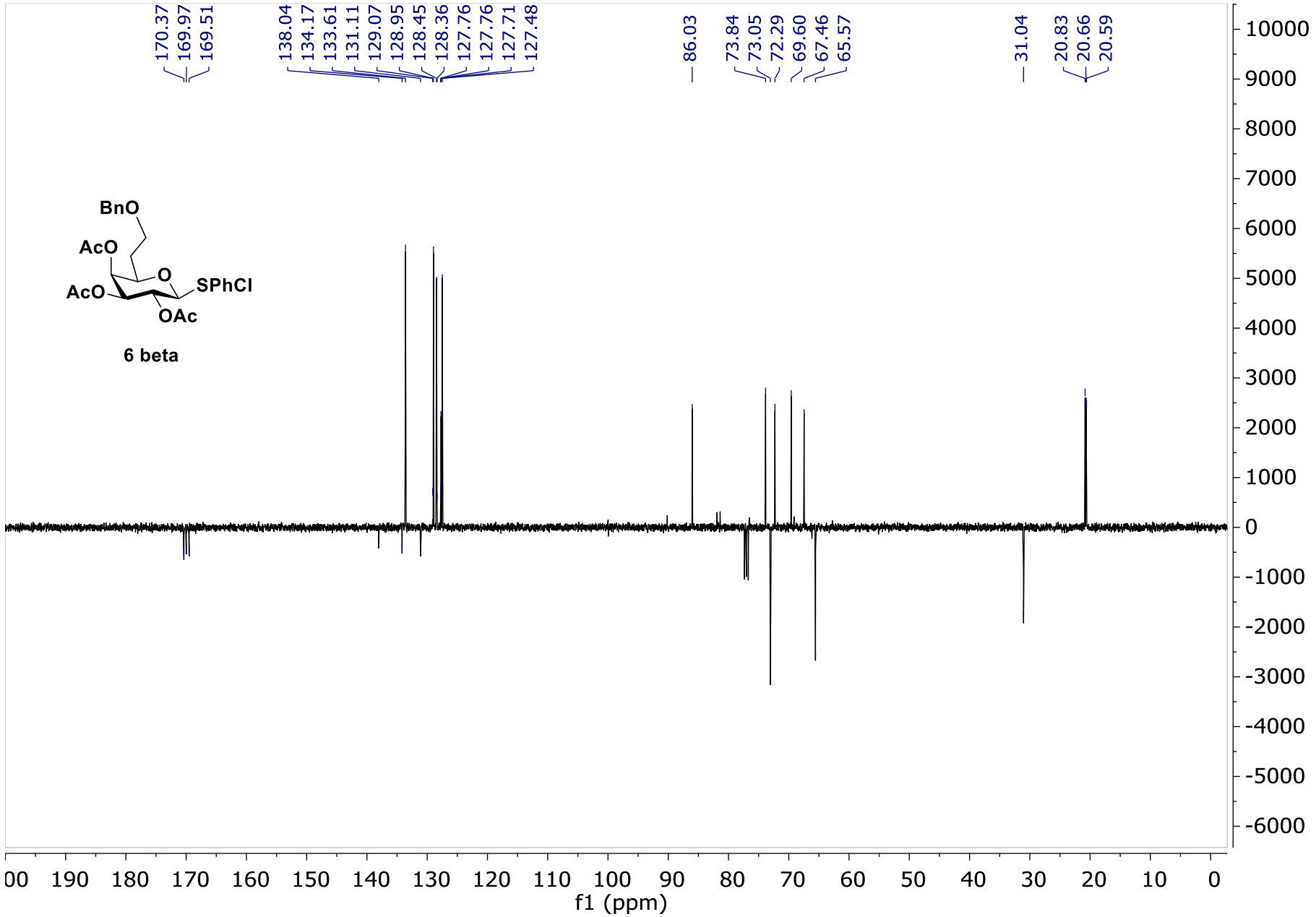
^{1}H NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



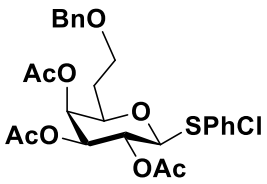
^{1}H NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



^{13}C (DEPT-Q) NMR Spectrum in $CDCl_3$, 100 MHz, 298 K



^{1}H-^{1}H GCOSY NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



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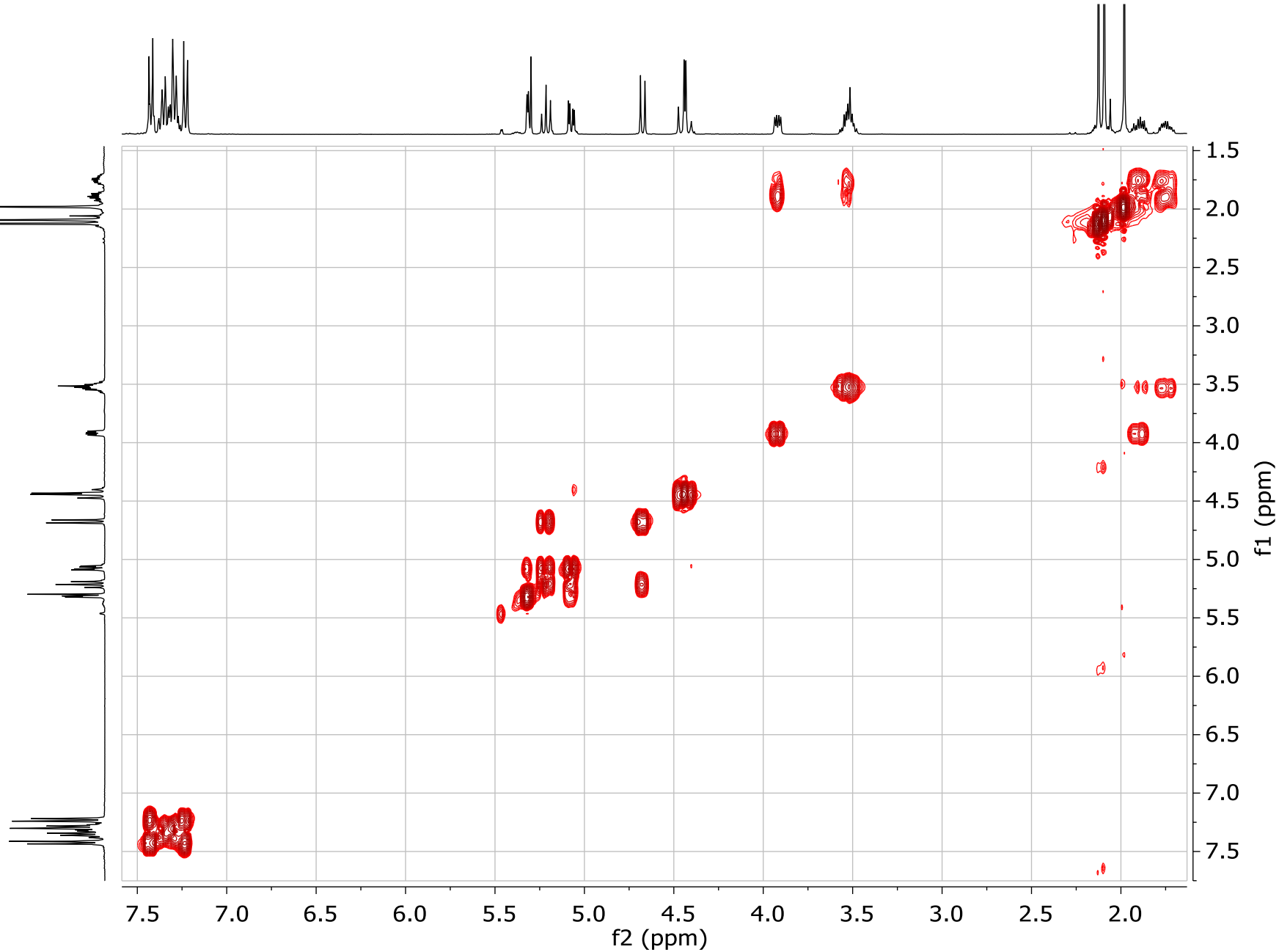

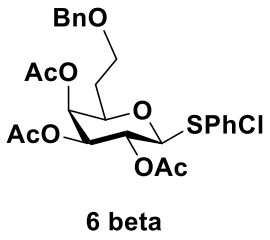

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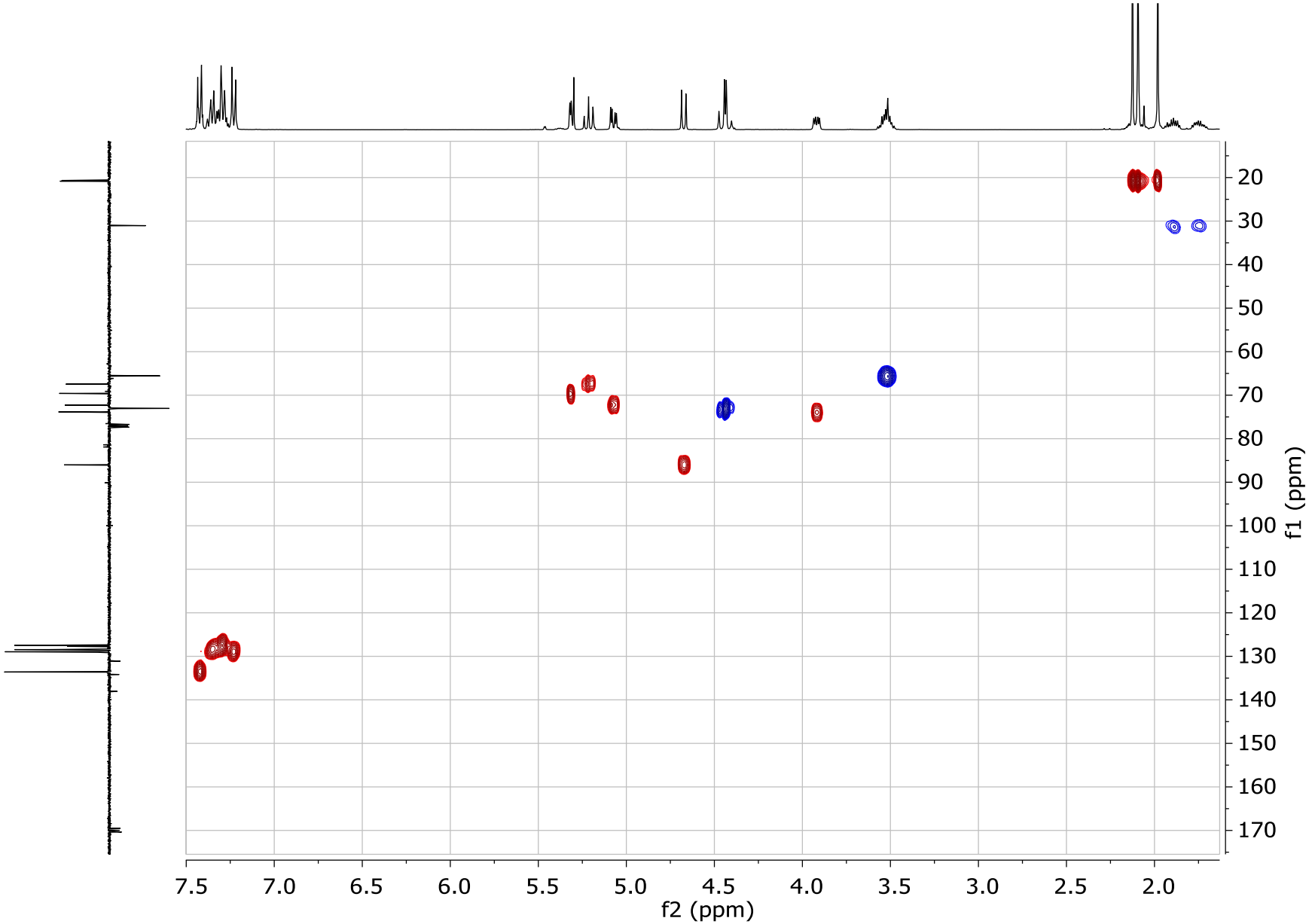
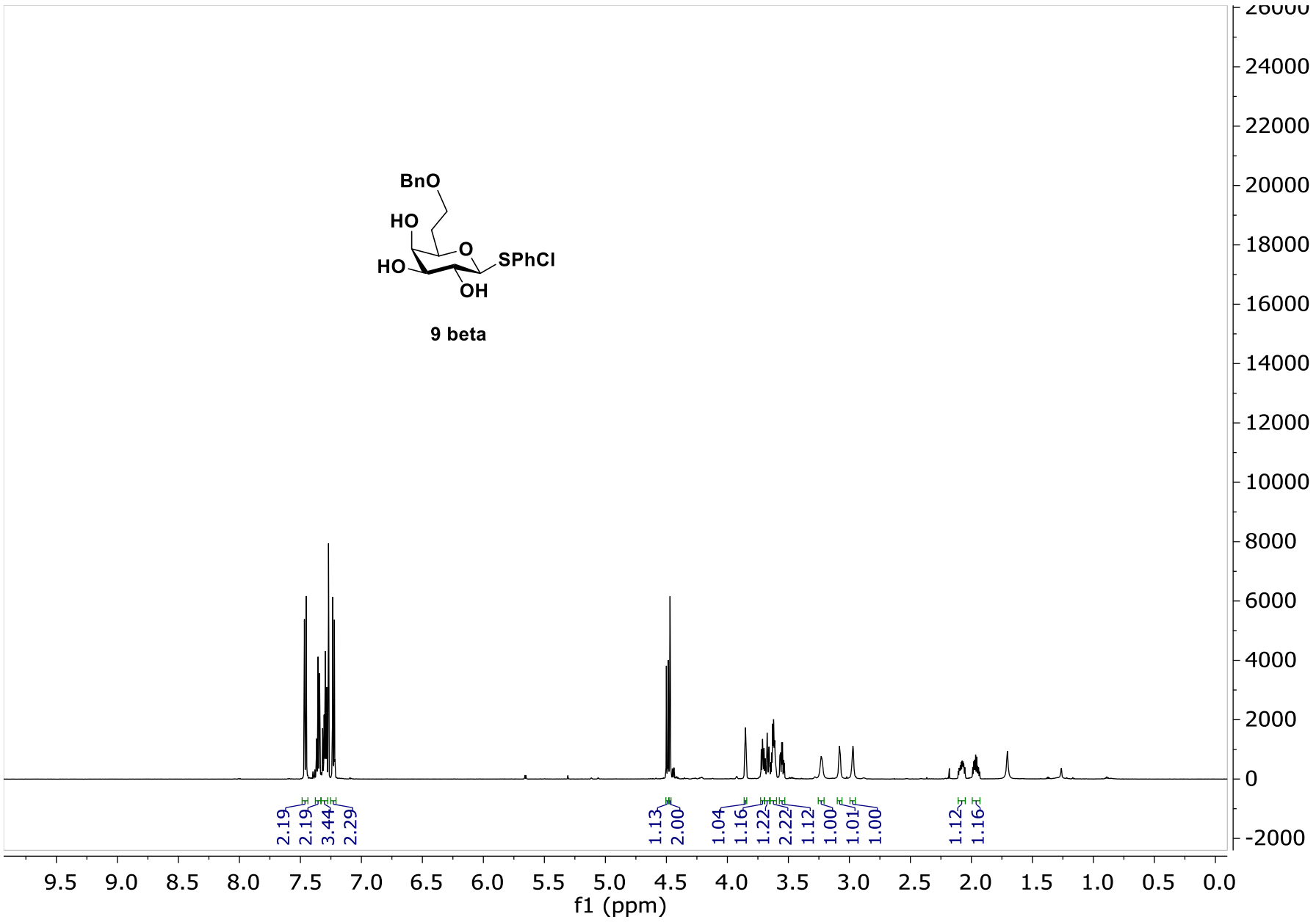
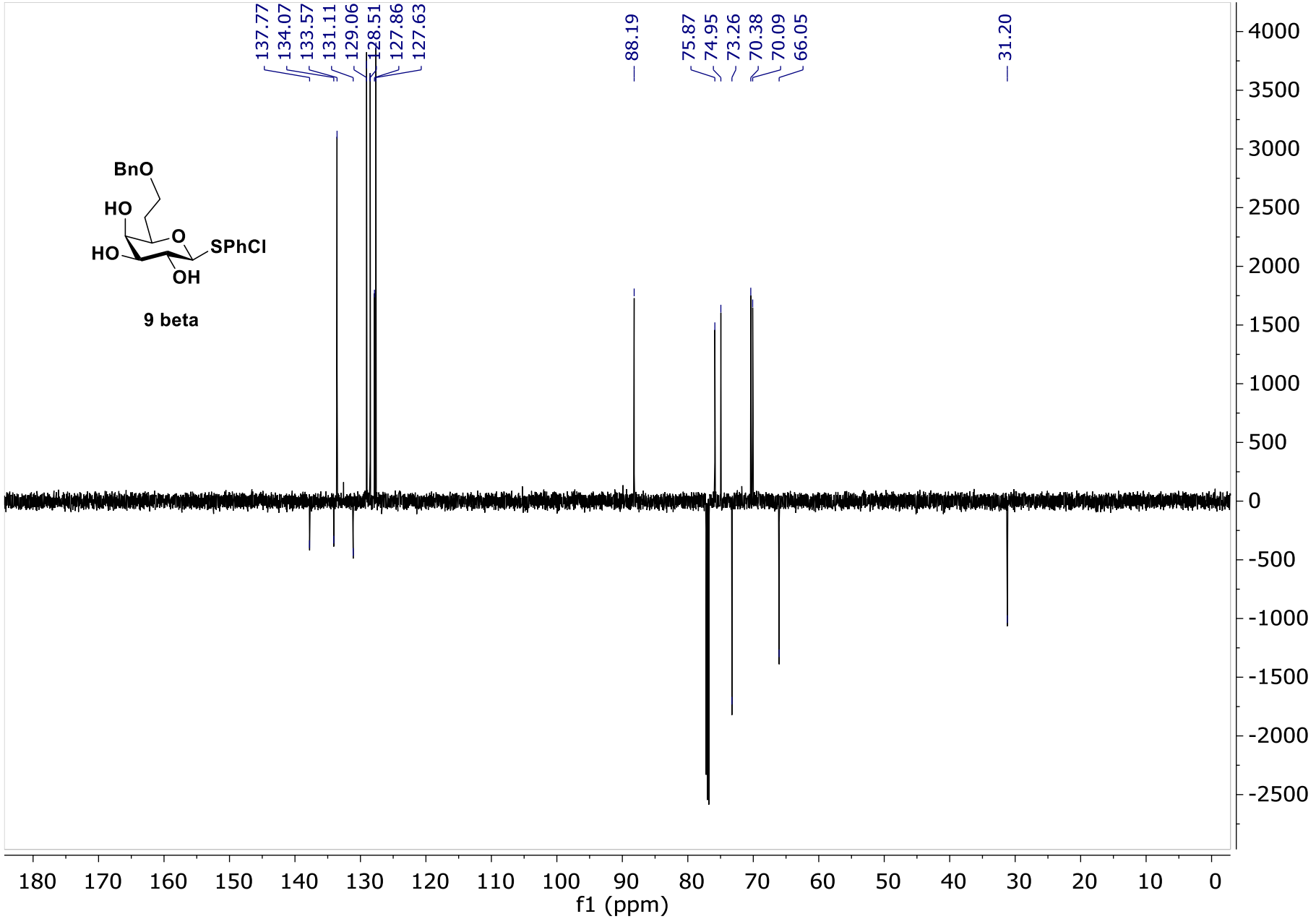
^{1}H-^{13}C GHSQC NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



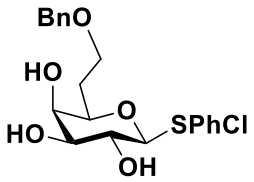
^{1}H NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



^{13}C (DEPT-Q) NMR Spectrum in $CDCl_3$, 100 MHz, 298 K



^{1}H-^{1}H GCOSY NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



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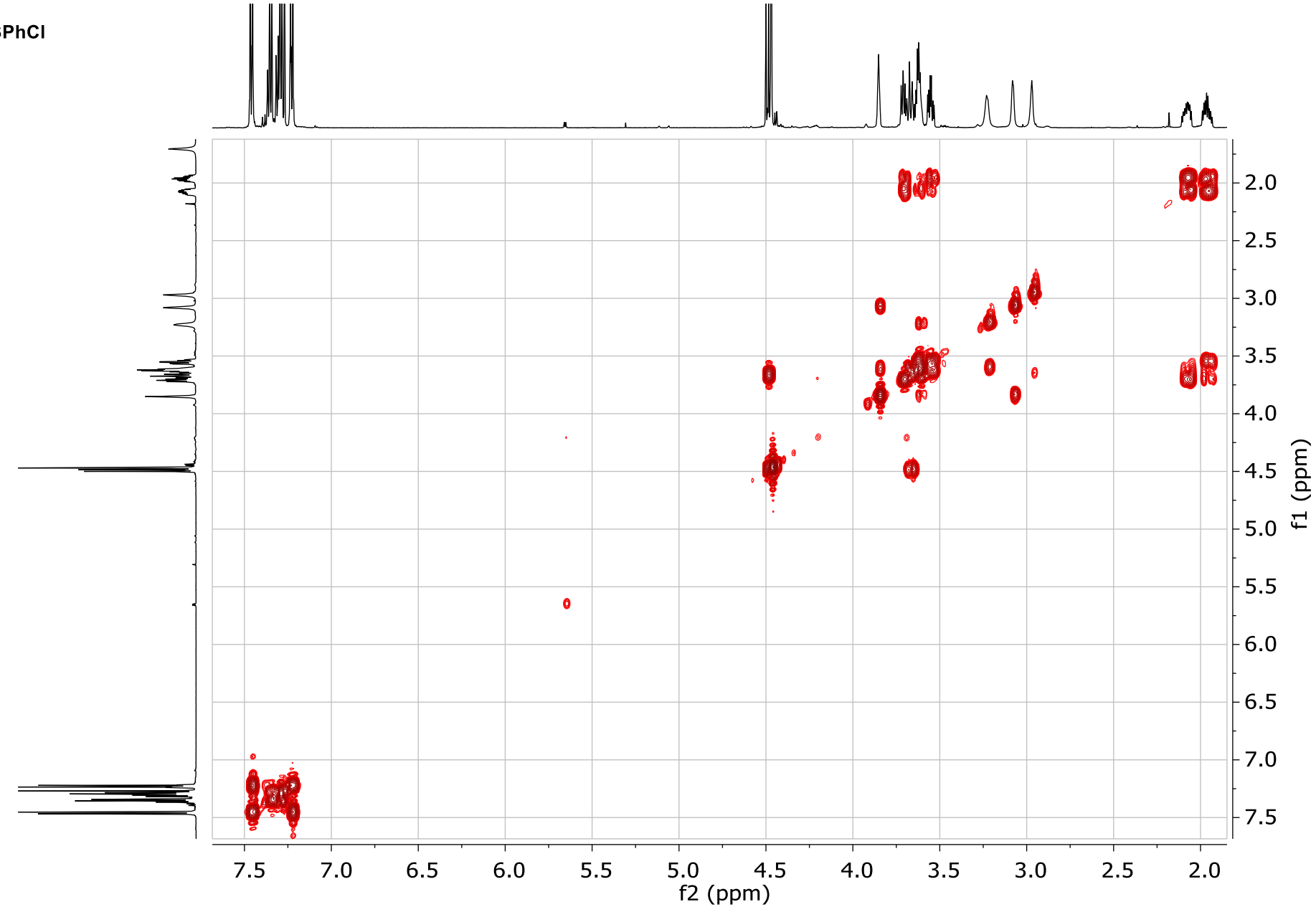

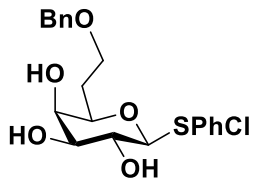

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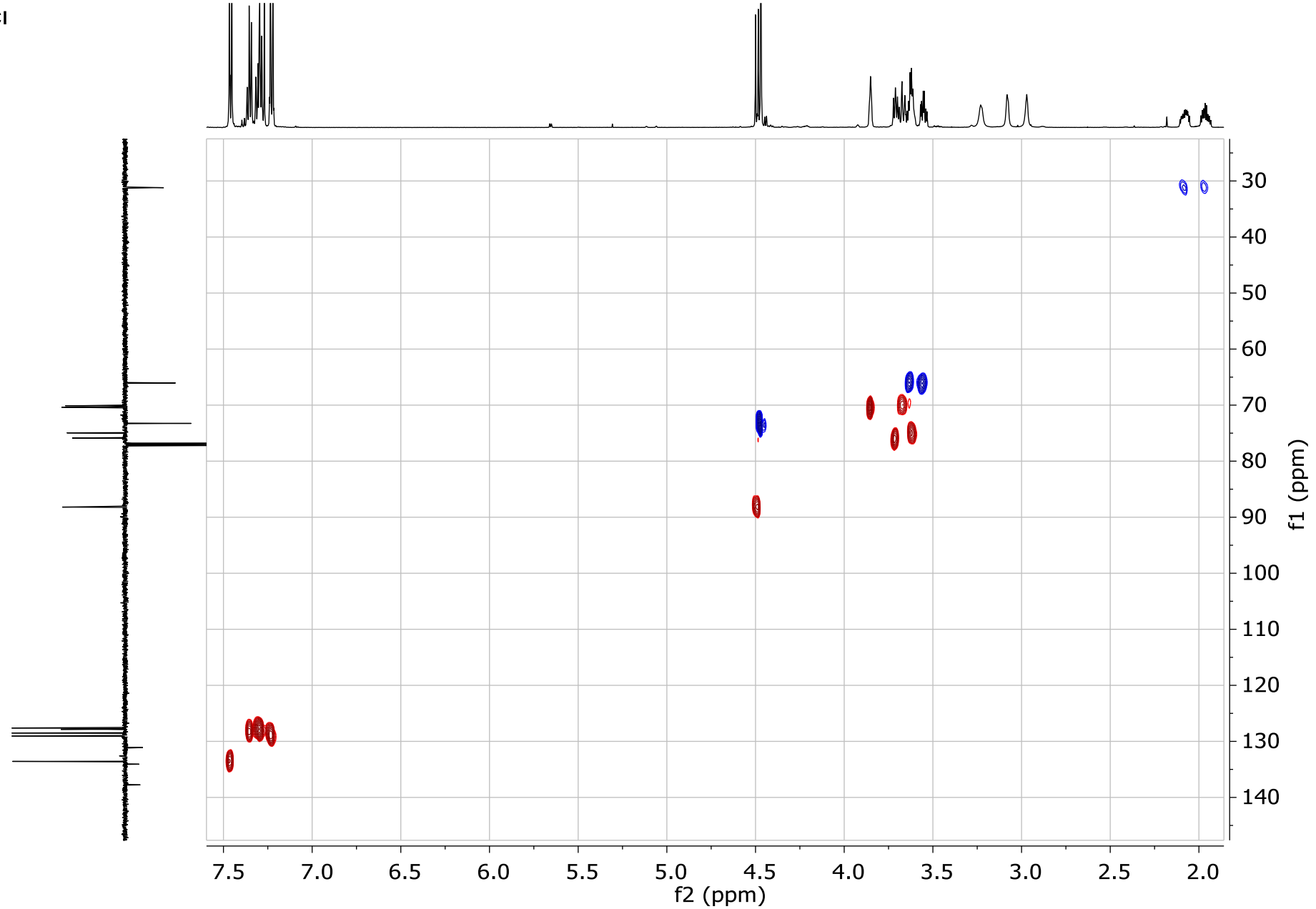
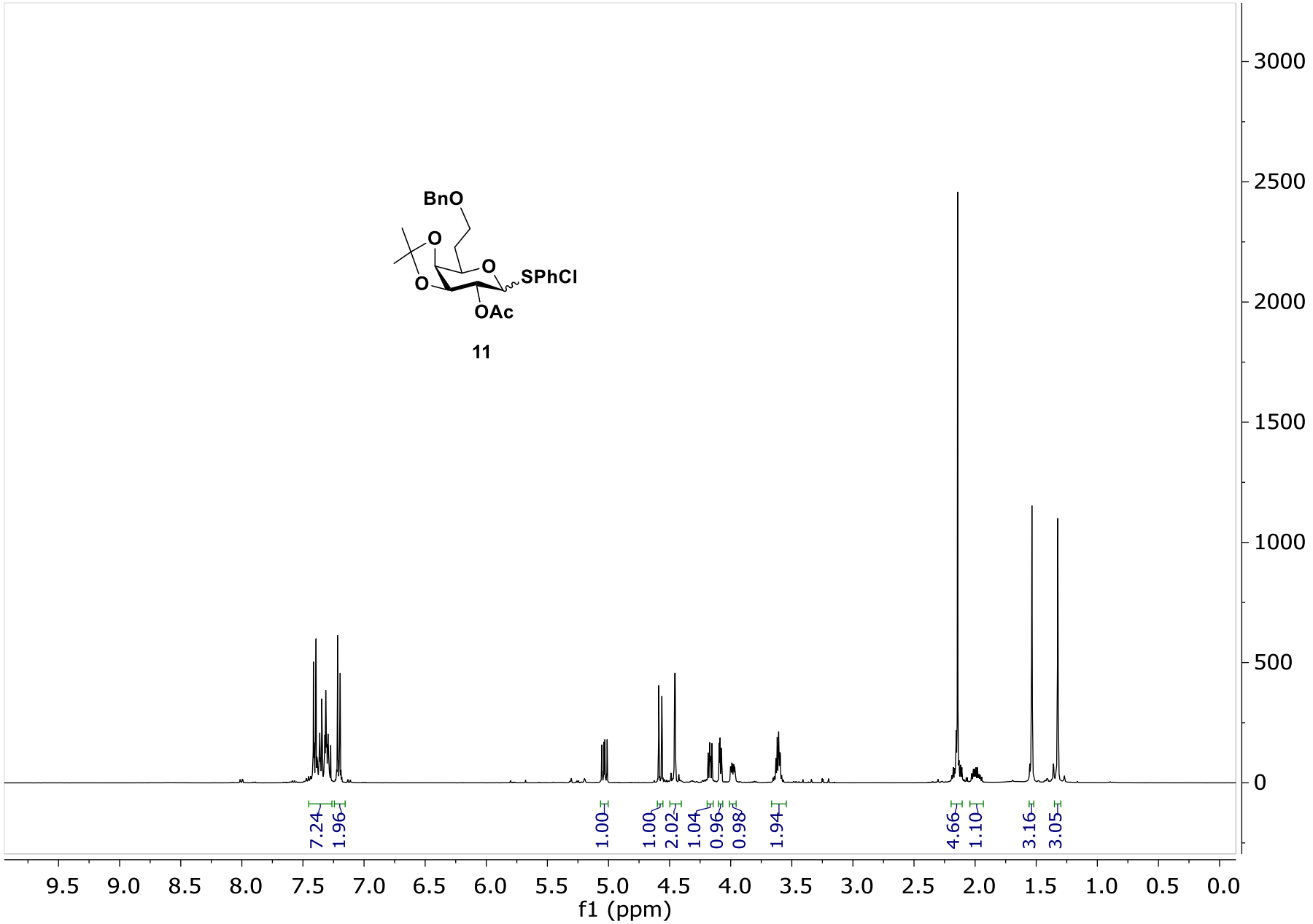
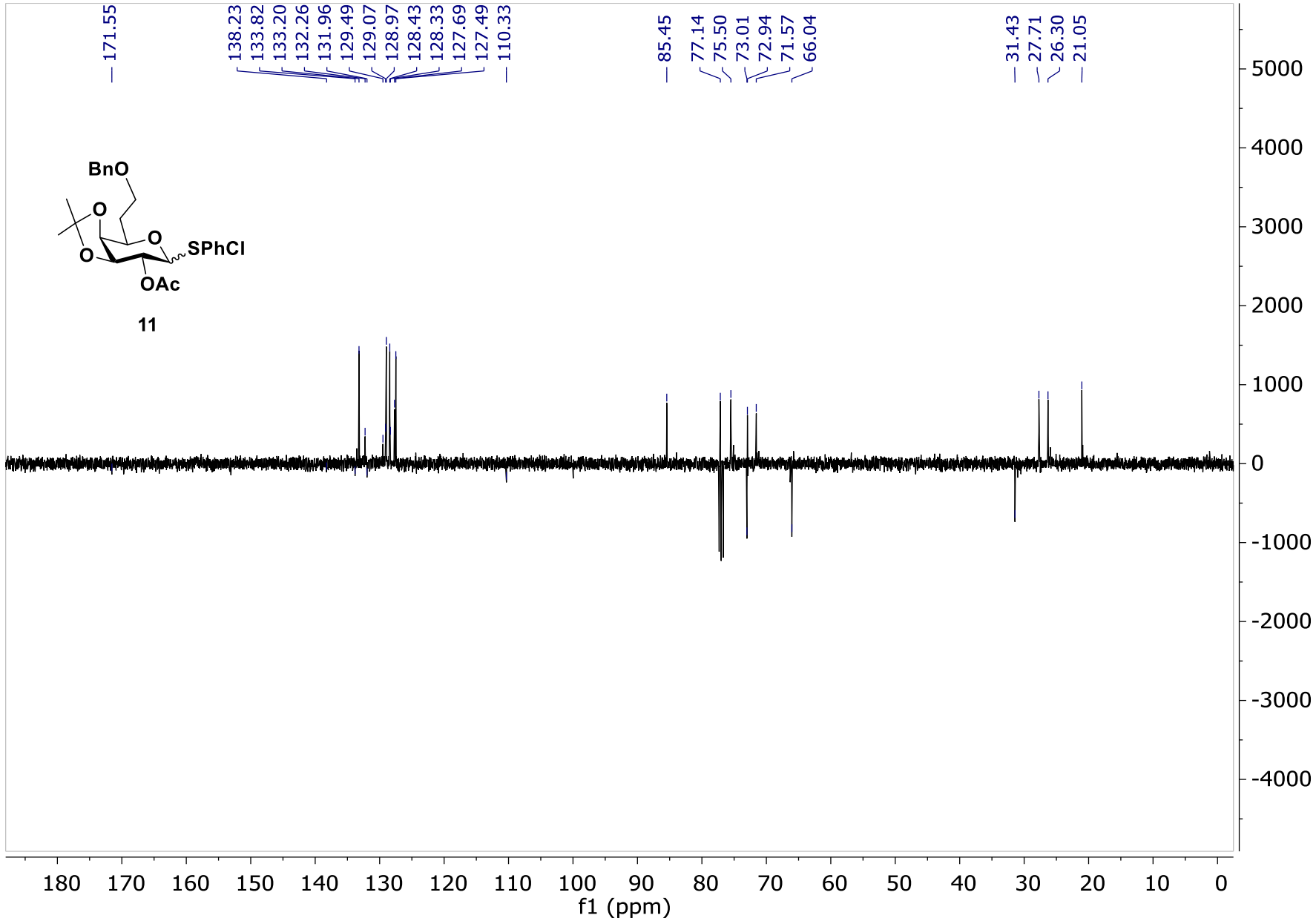
^{1}H-^{13}C GHSQC NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



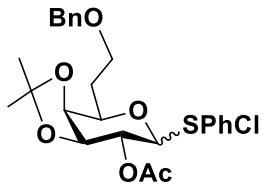
^{1}H NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



^{13}C (DEPT-Q) NMR Spectrum in $CDCl_3$, 100 MHz, 298 K



^{1}H-^{1}H GCOSY NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



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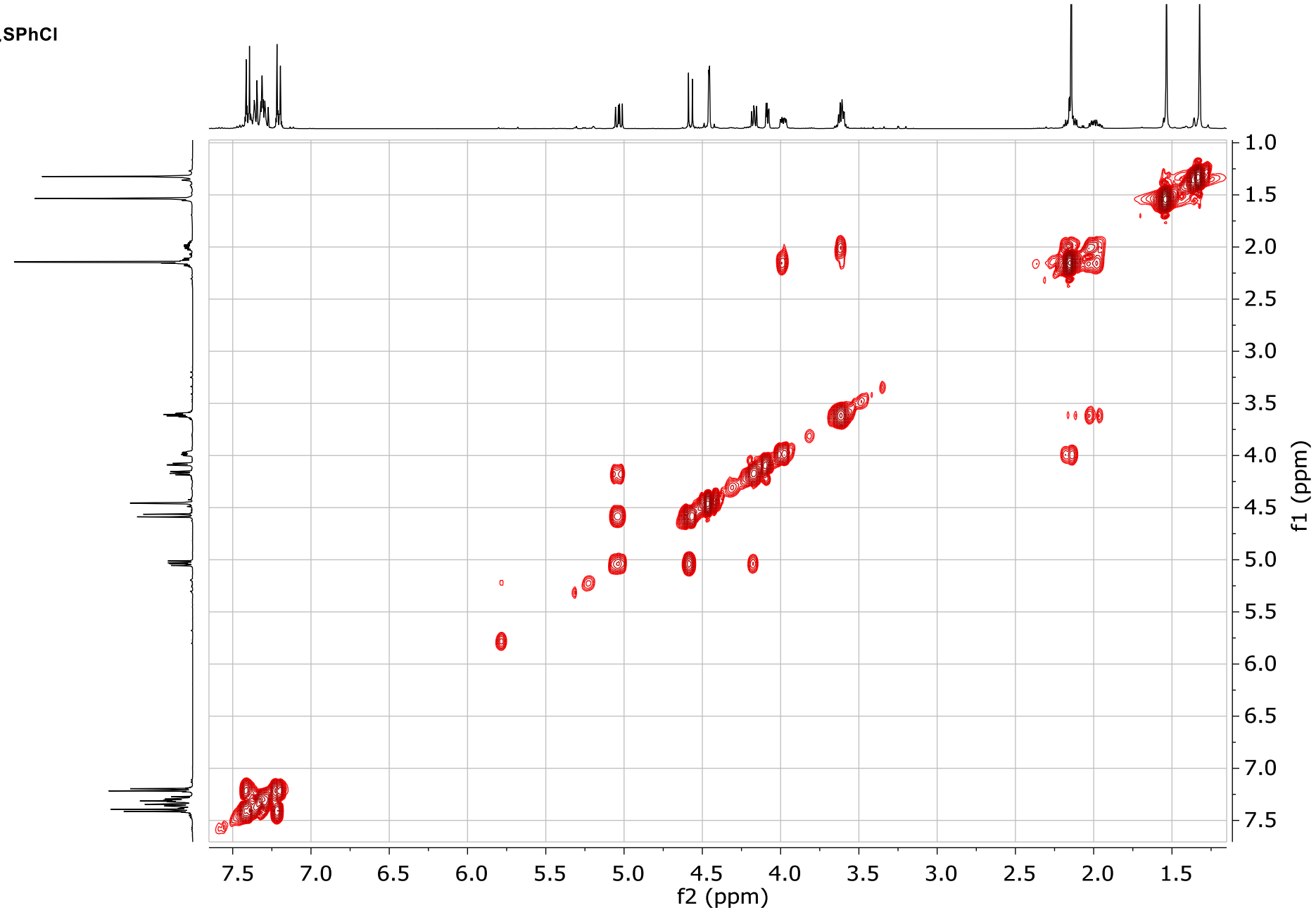

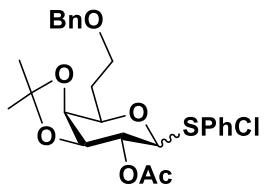

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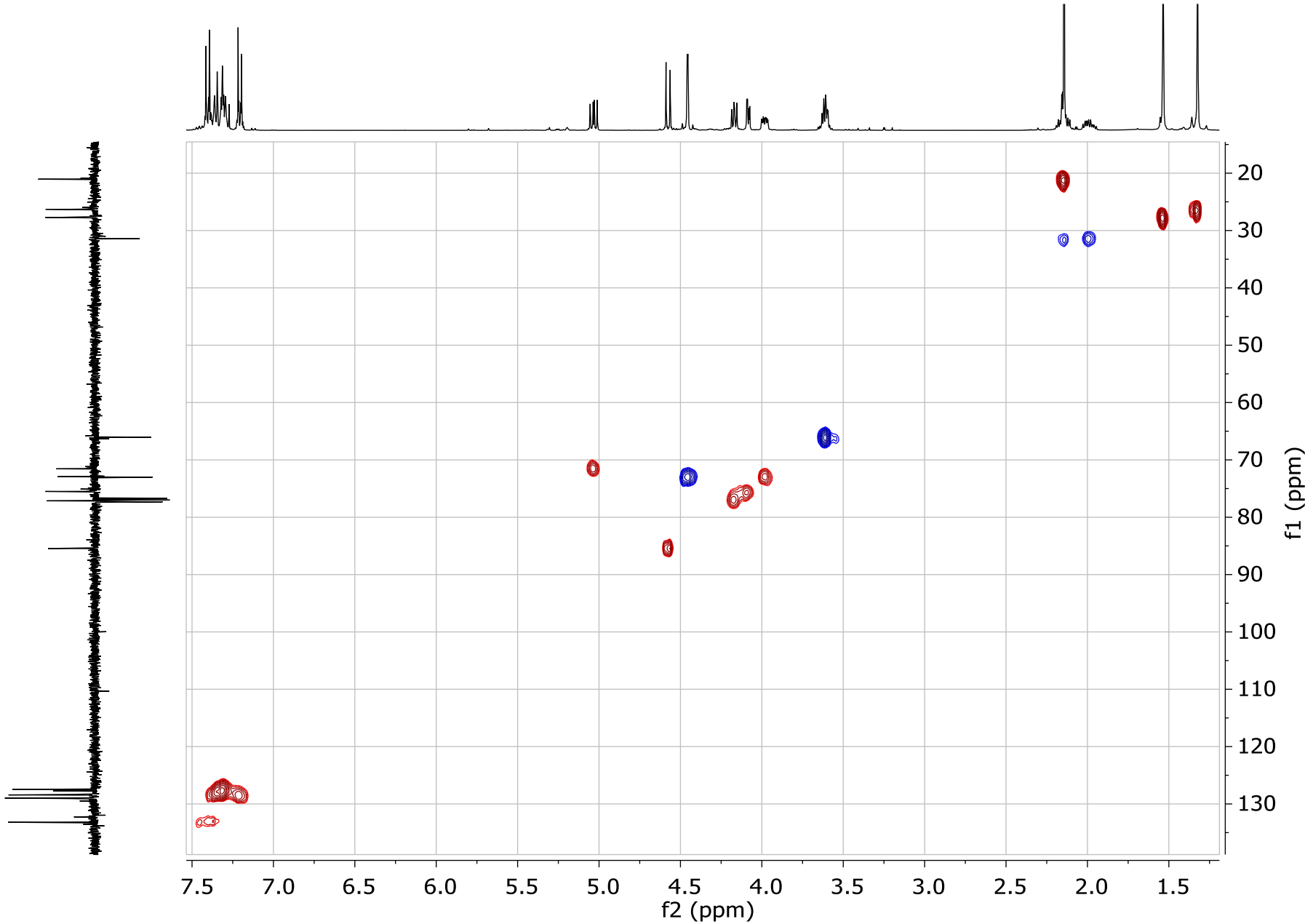
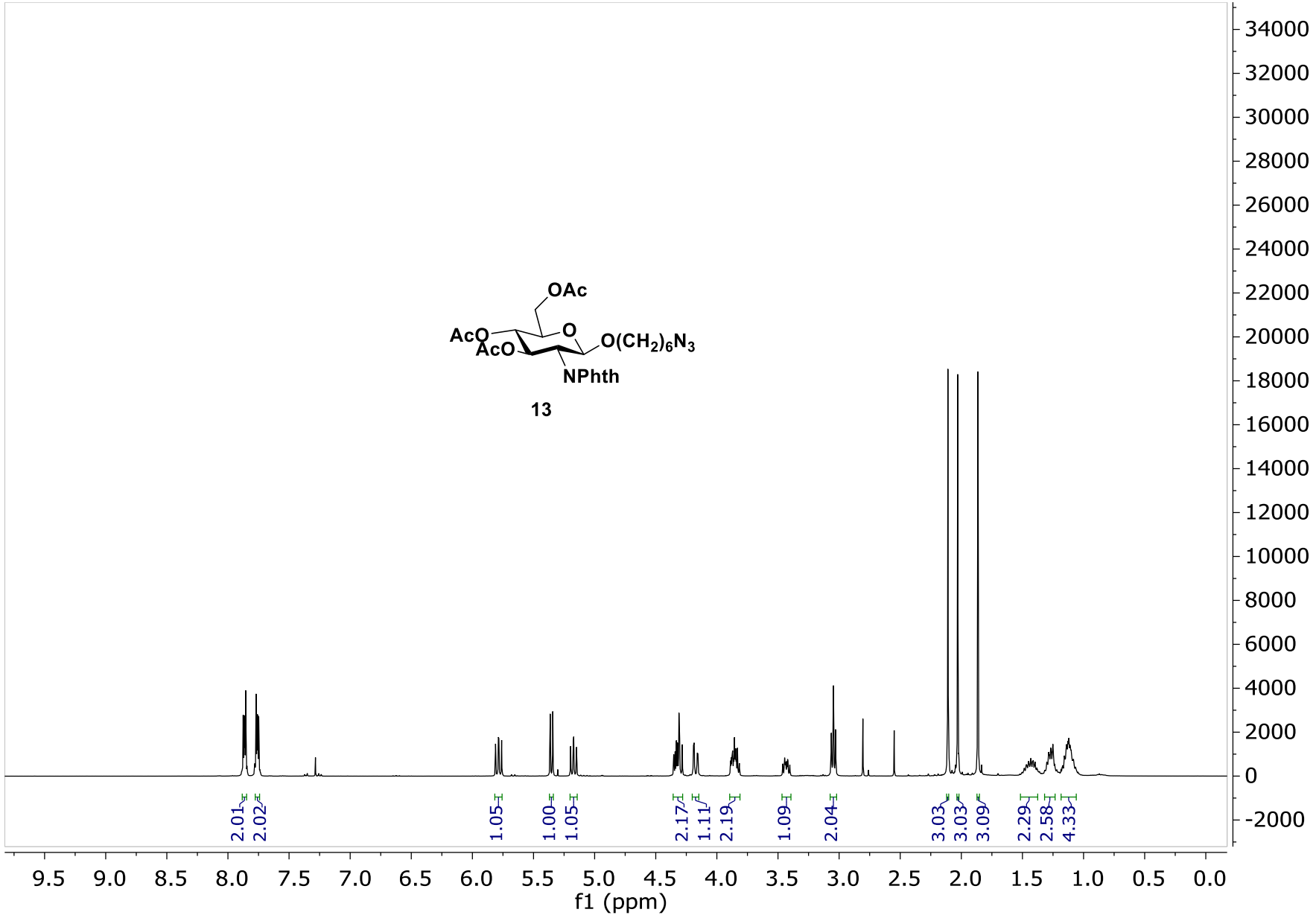
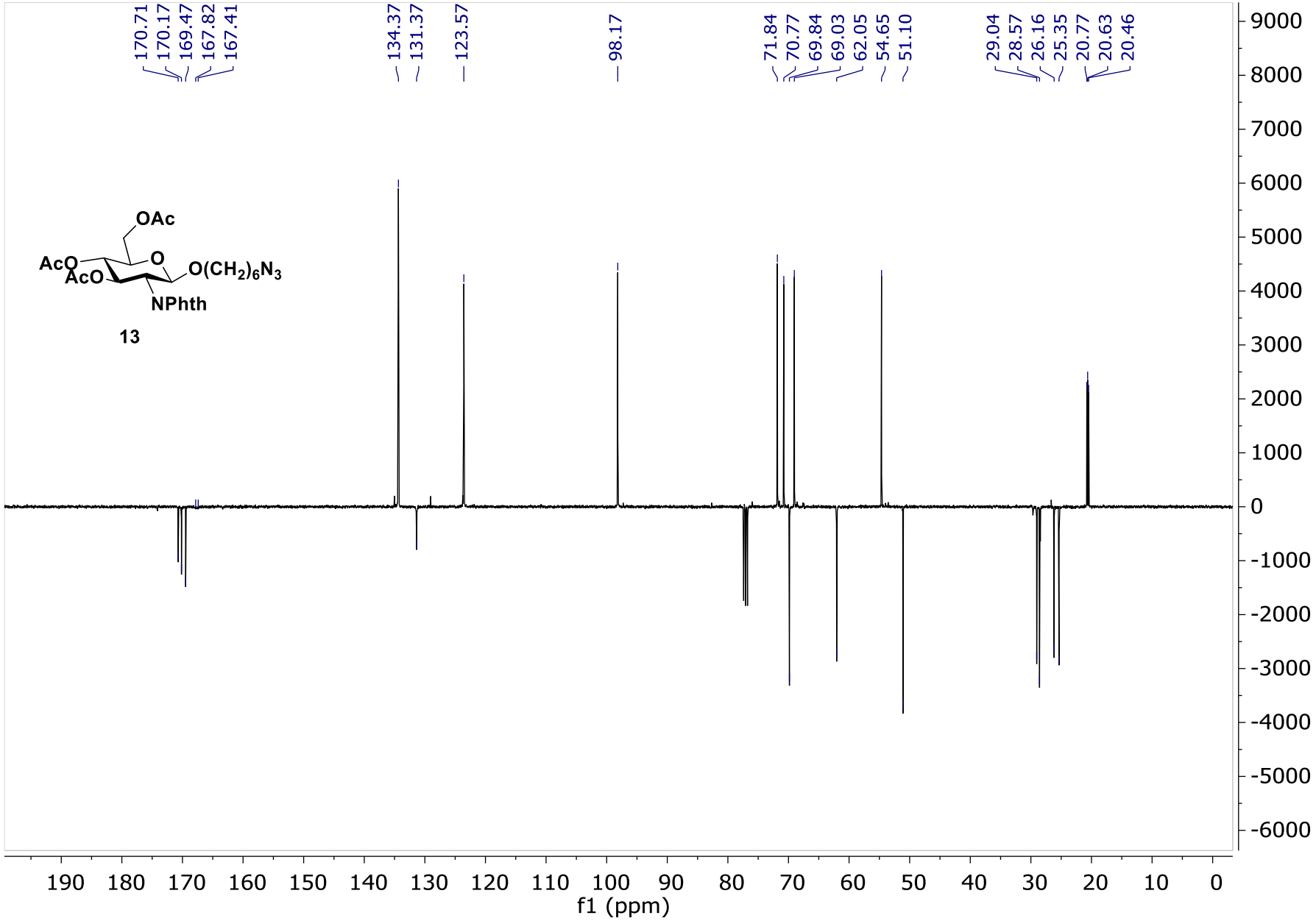
^{1}H-^{13}C GHSQC NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



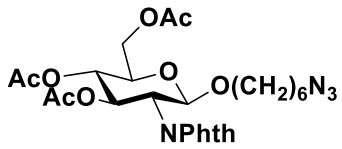
^{1}H NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



^{13}C (DEPT-Q) NMR Spectrum in $CDCl_3$, 100 MHz, 298 K



^{1}H-^{1}H GCOSY NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



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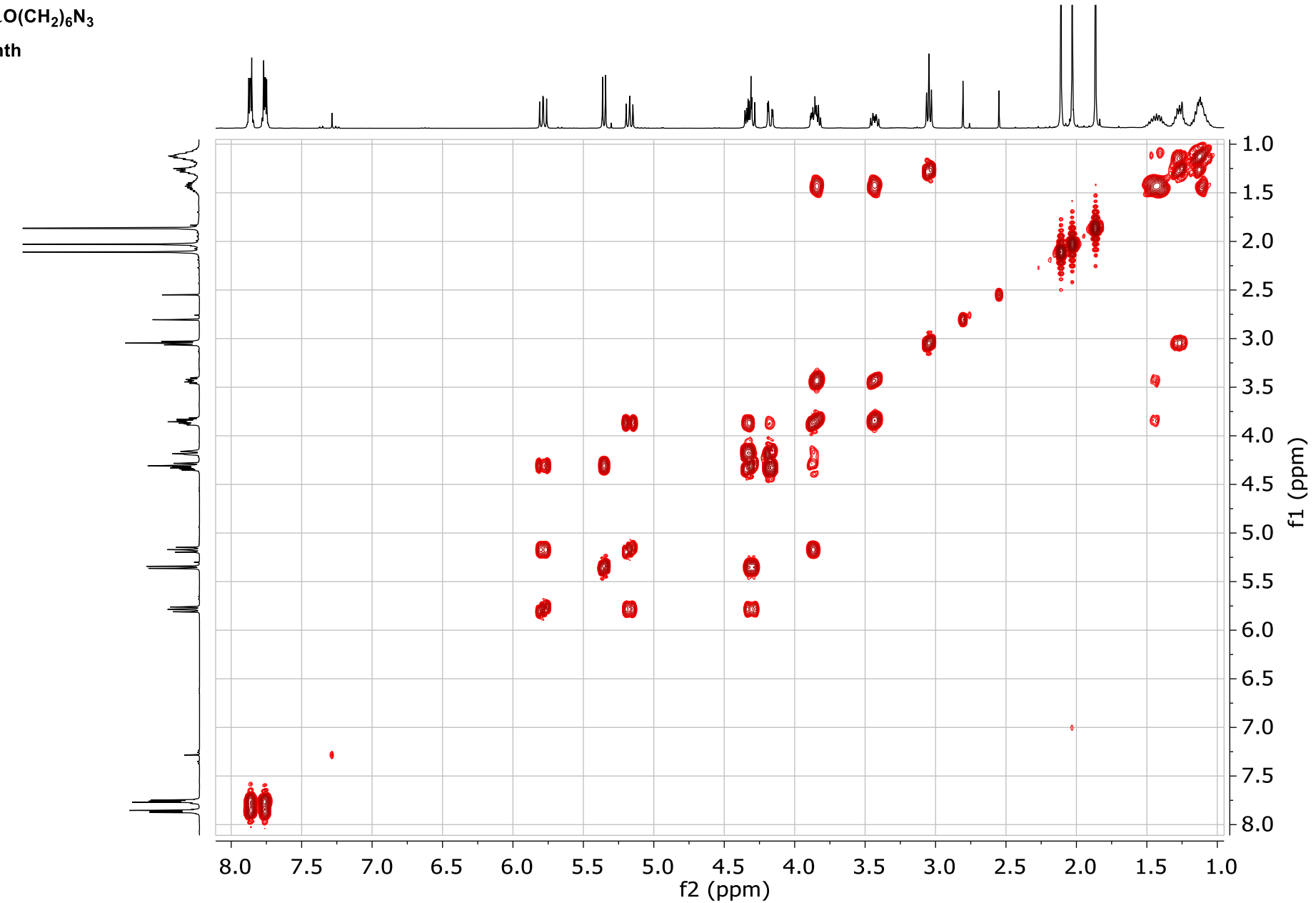
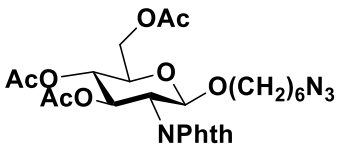


^{1}H-^{13}C GHSQC NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



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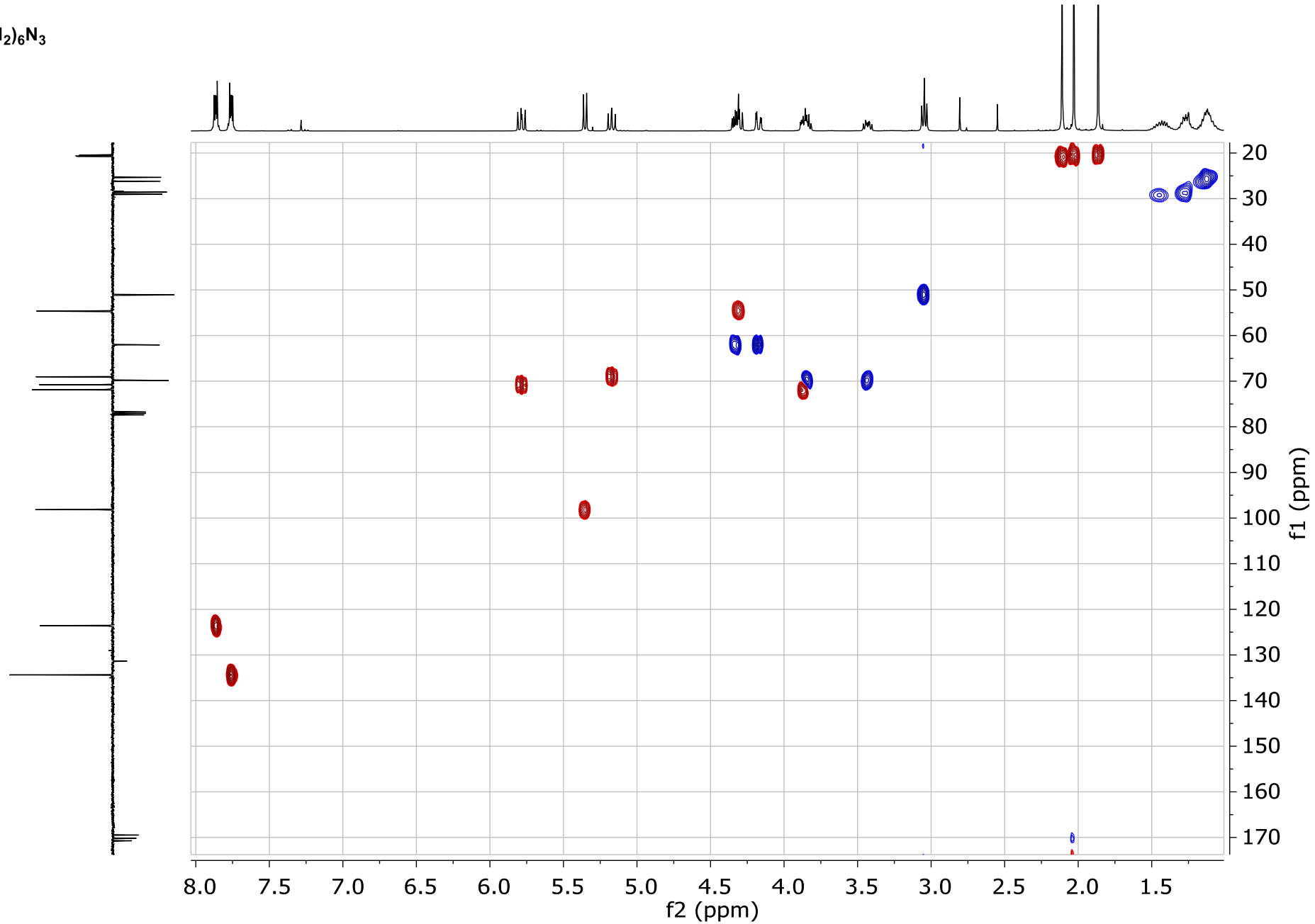
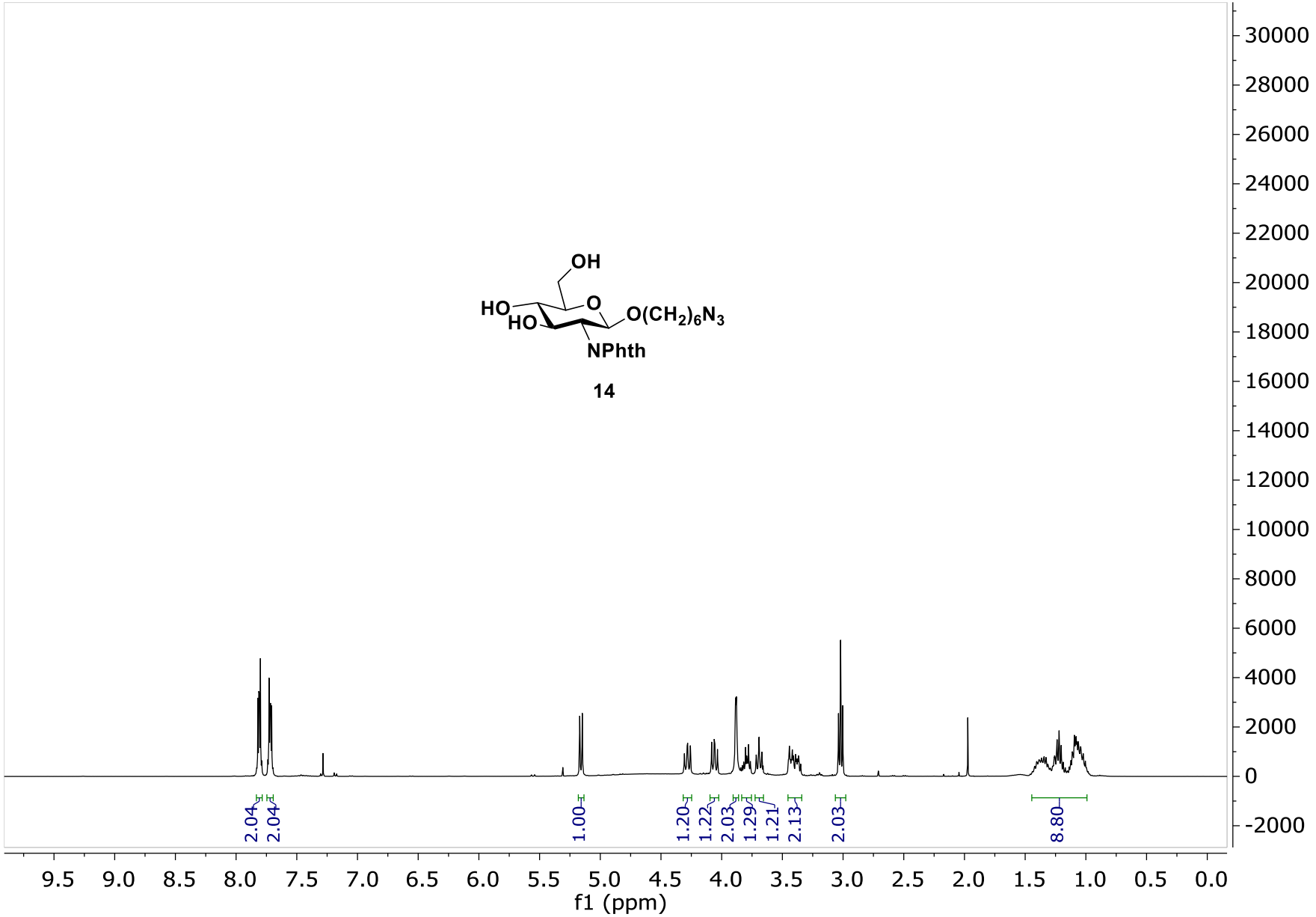
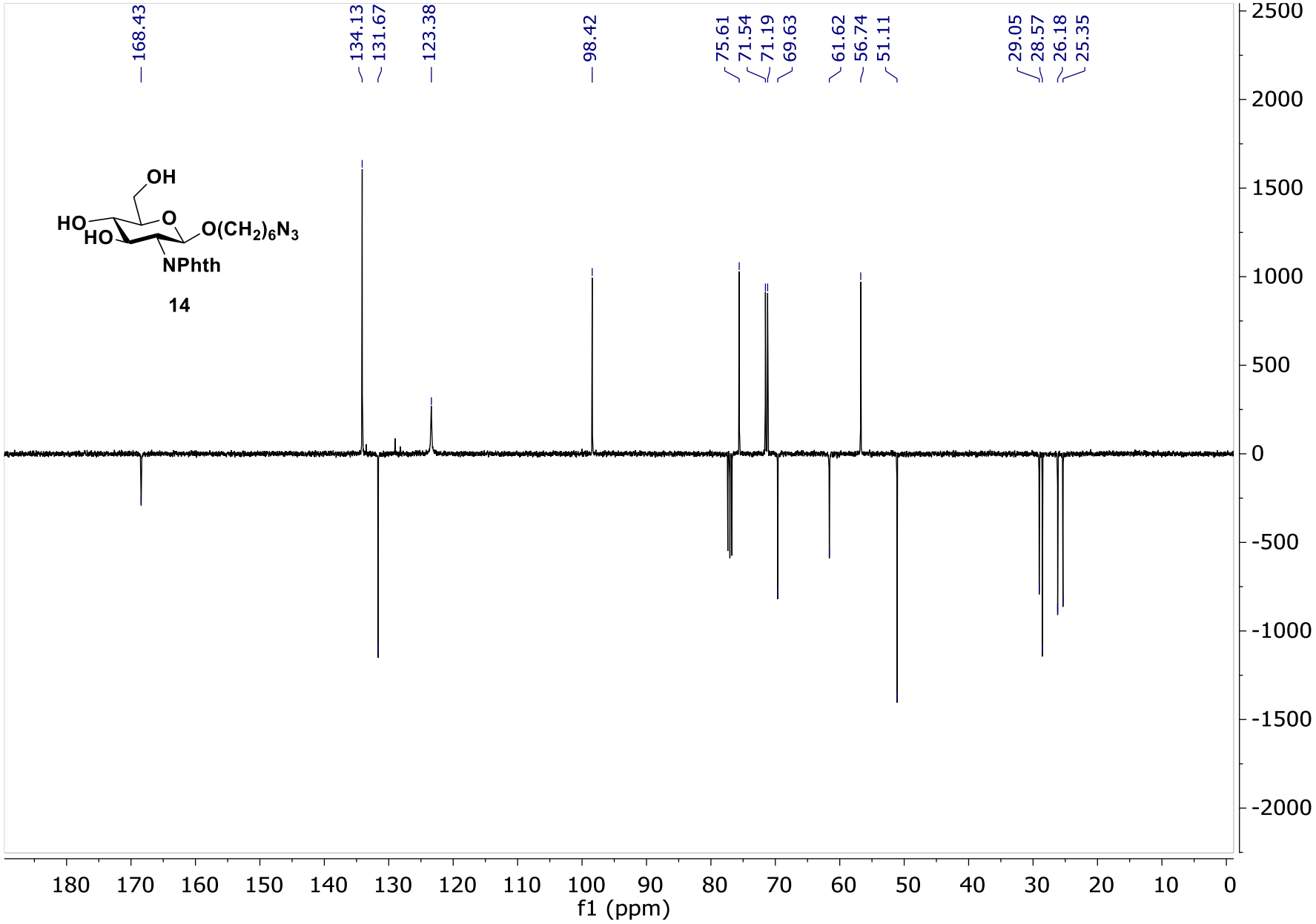


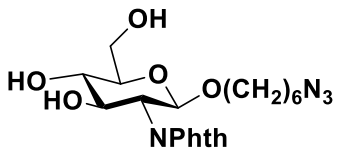
^{1}H NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



^{13}C (DEPT-Q) NMR Spectrum in $CDCl_3$, 100 MHz, 298 K



^{1}H-^{1}H GCOSY NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



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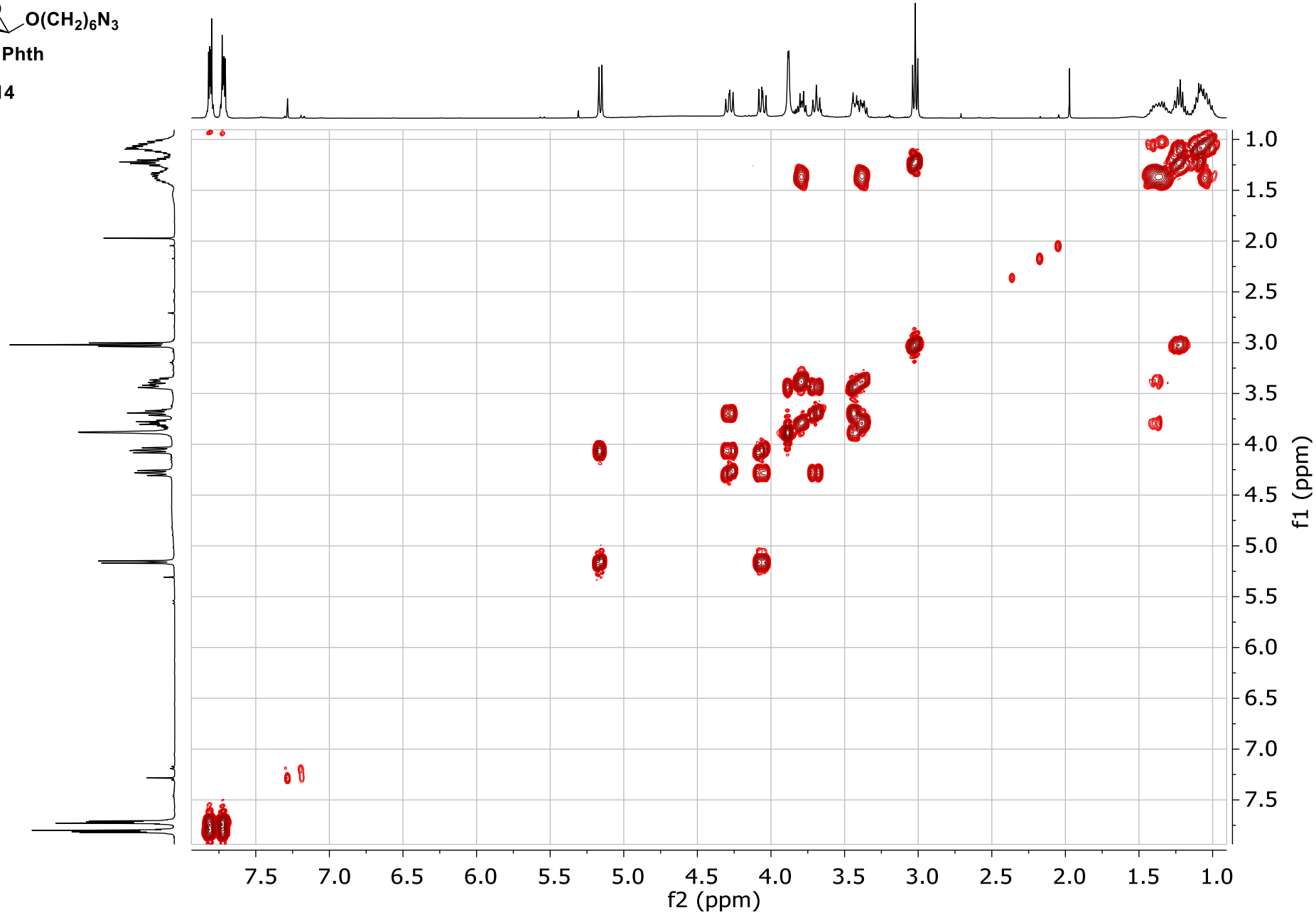
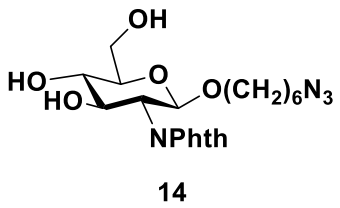


^{1}H-^{13}C GHSQC NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



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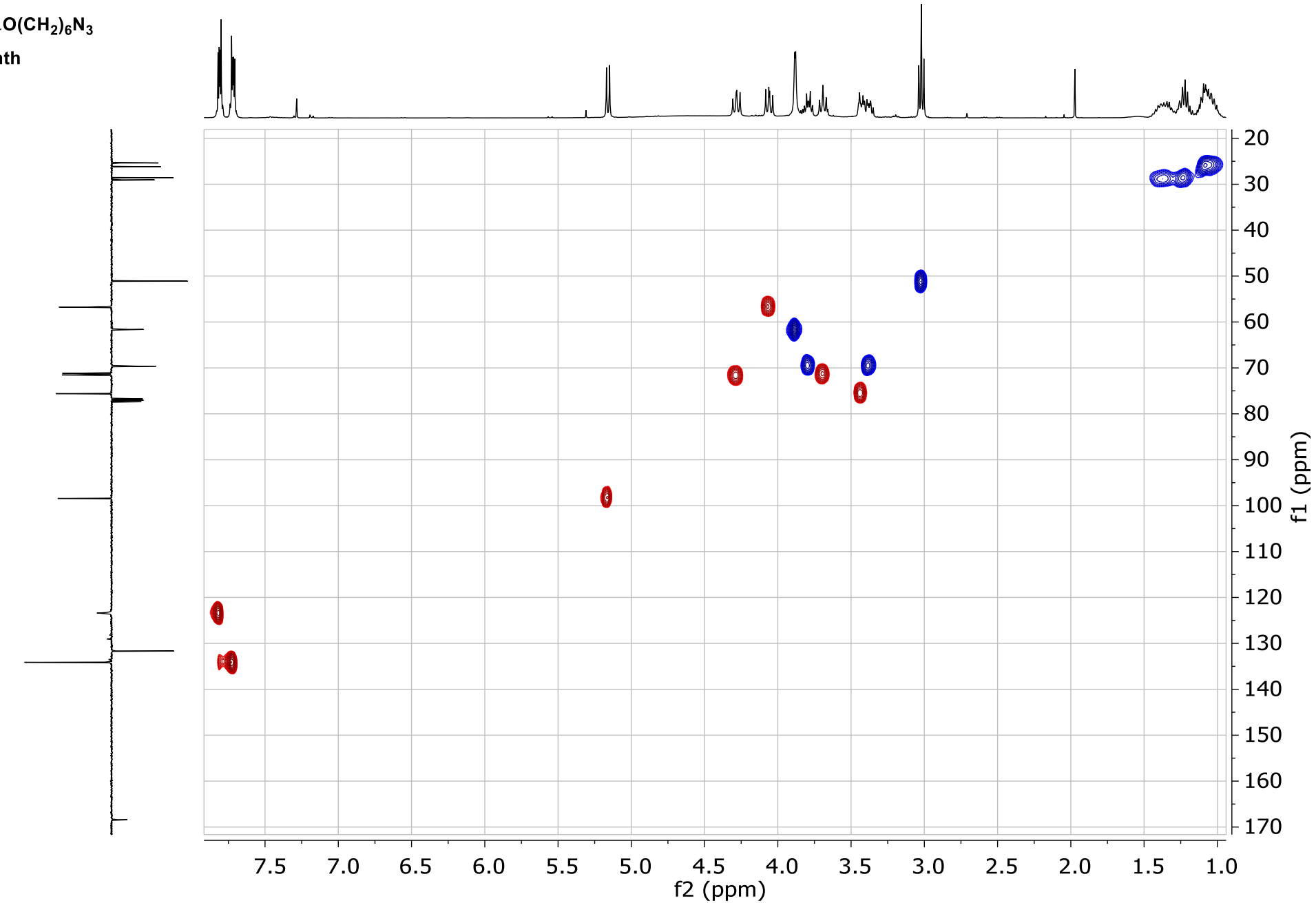
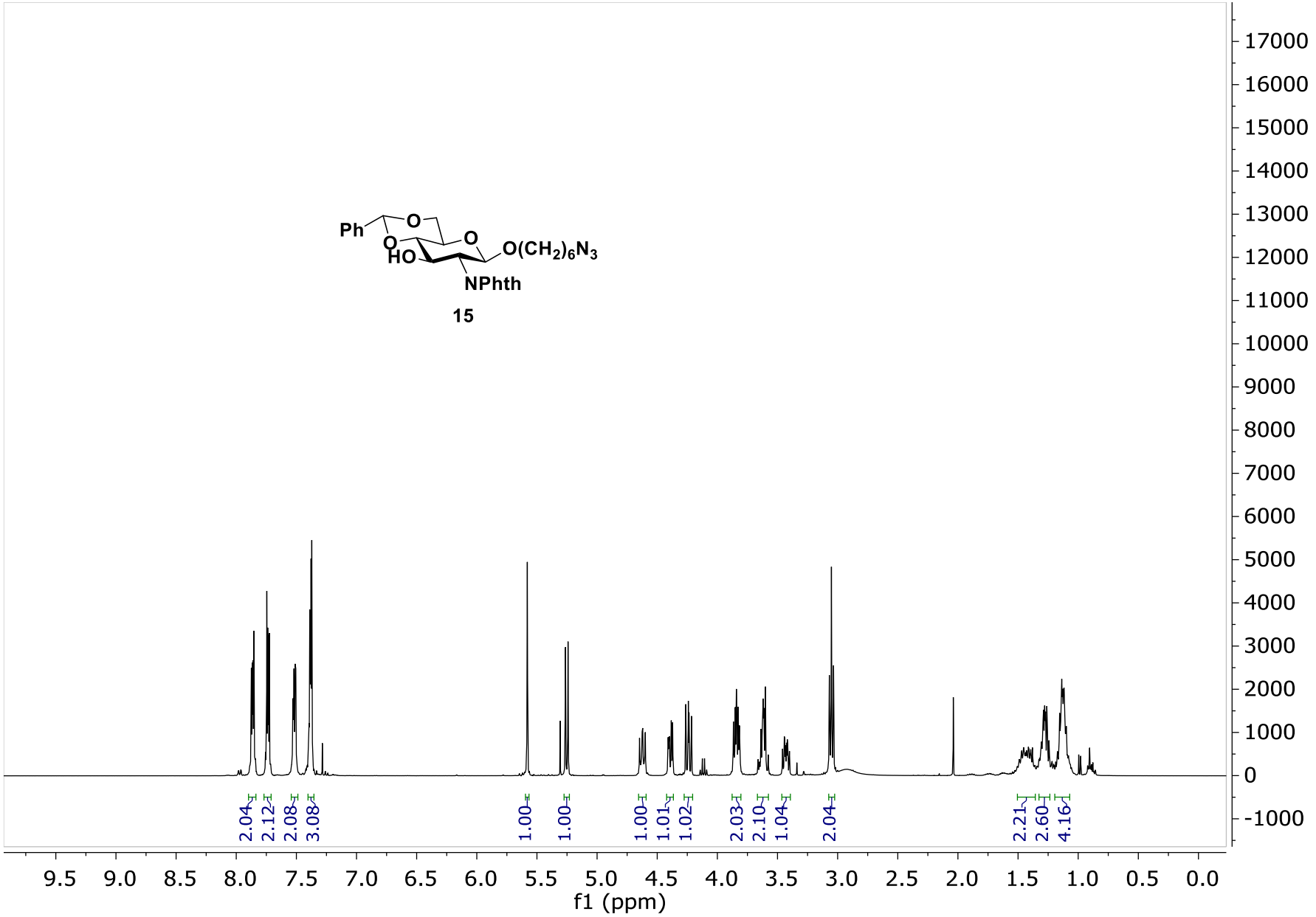
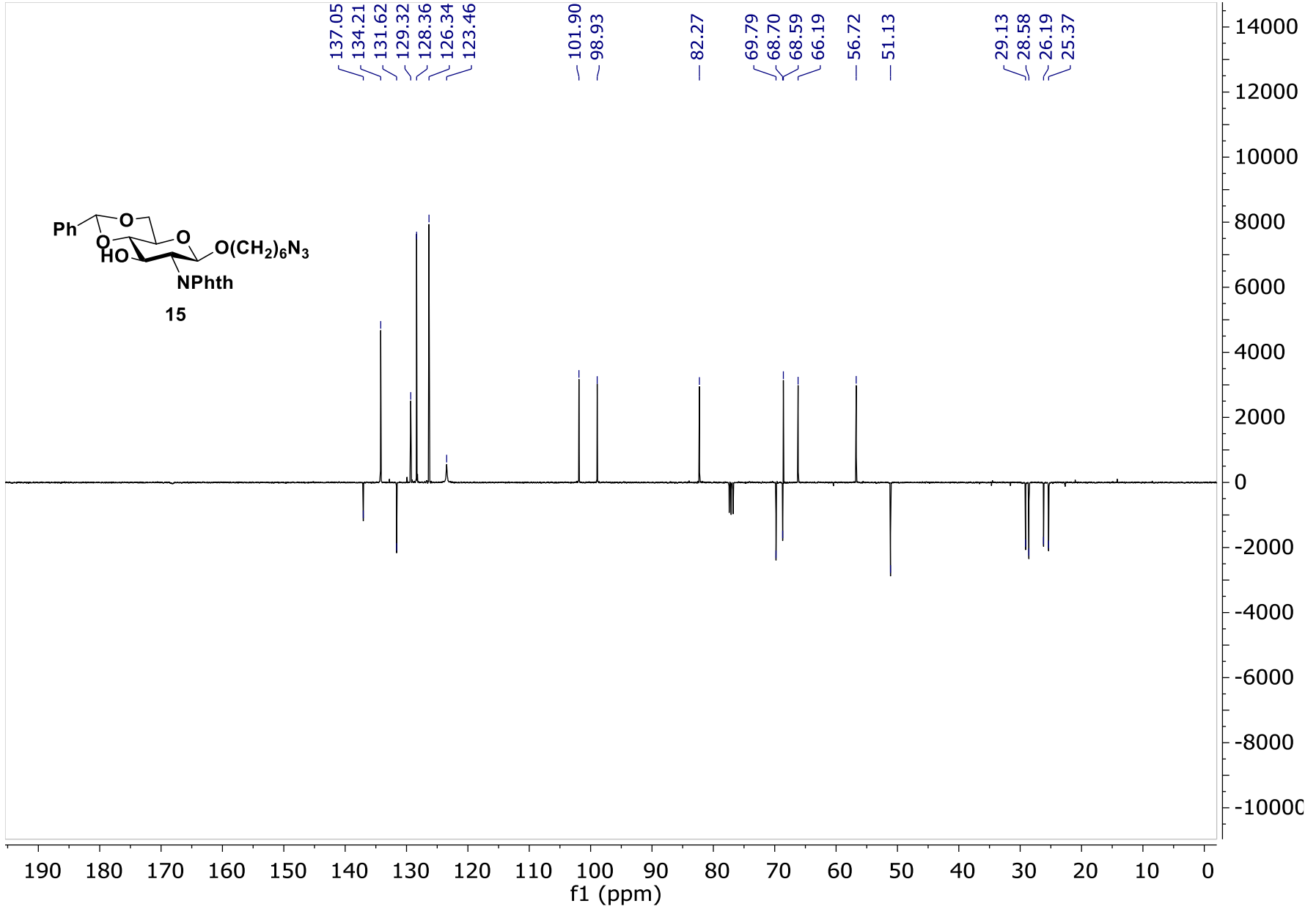
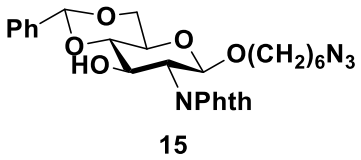


^{1}H NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



^{13}C (DEPT-Q) NMR Spectrum in $CDCl_3$, 100 MHz, 298 K

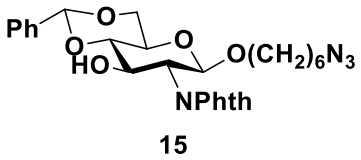




15

^{1}H-^{1}H GCOSY NMR Spectrum in $CDCl_3$, 400 MHz, 298 K

^{1}H-^{13}C GHSQC NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



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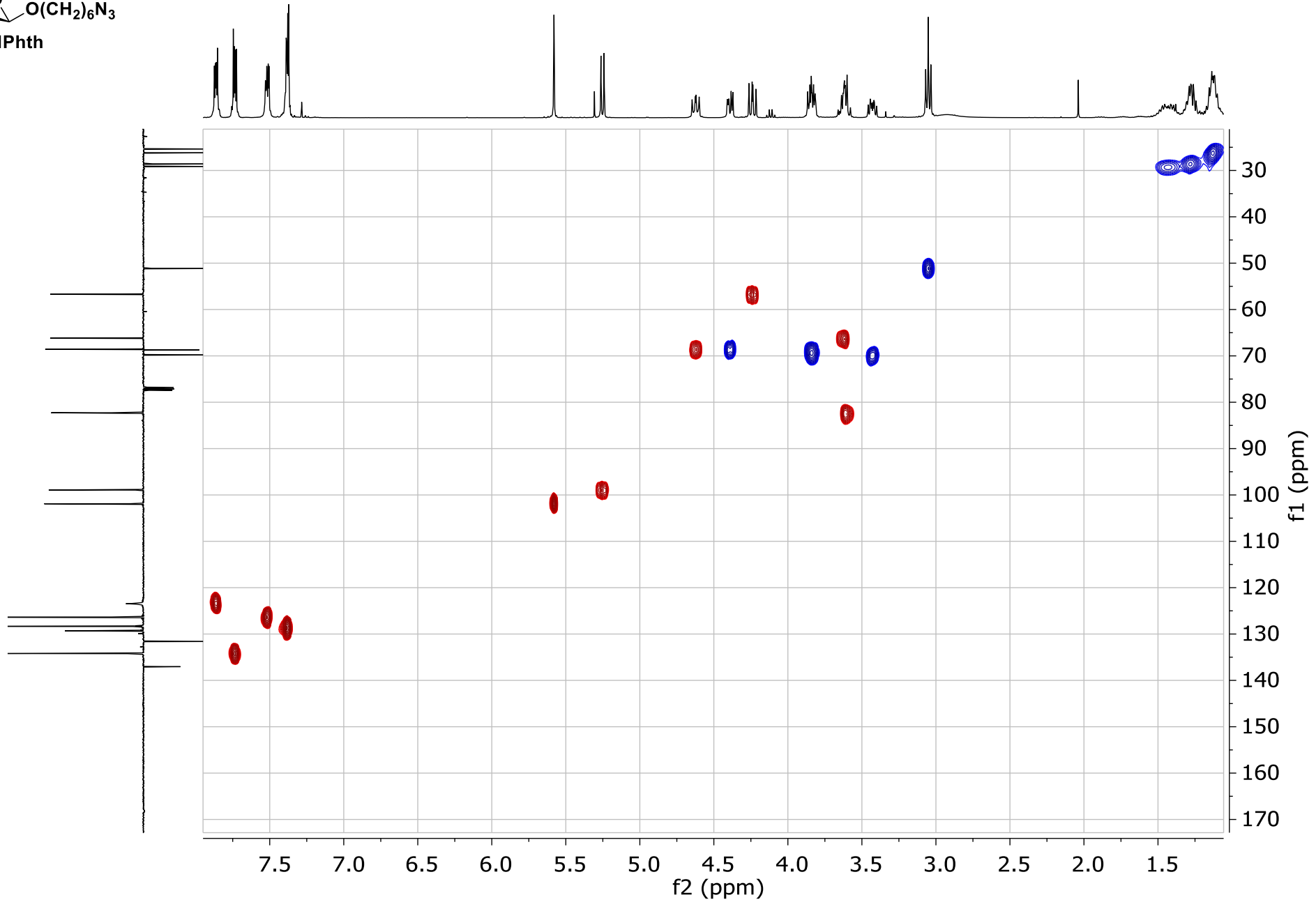
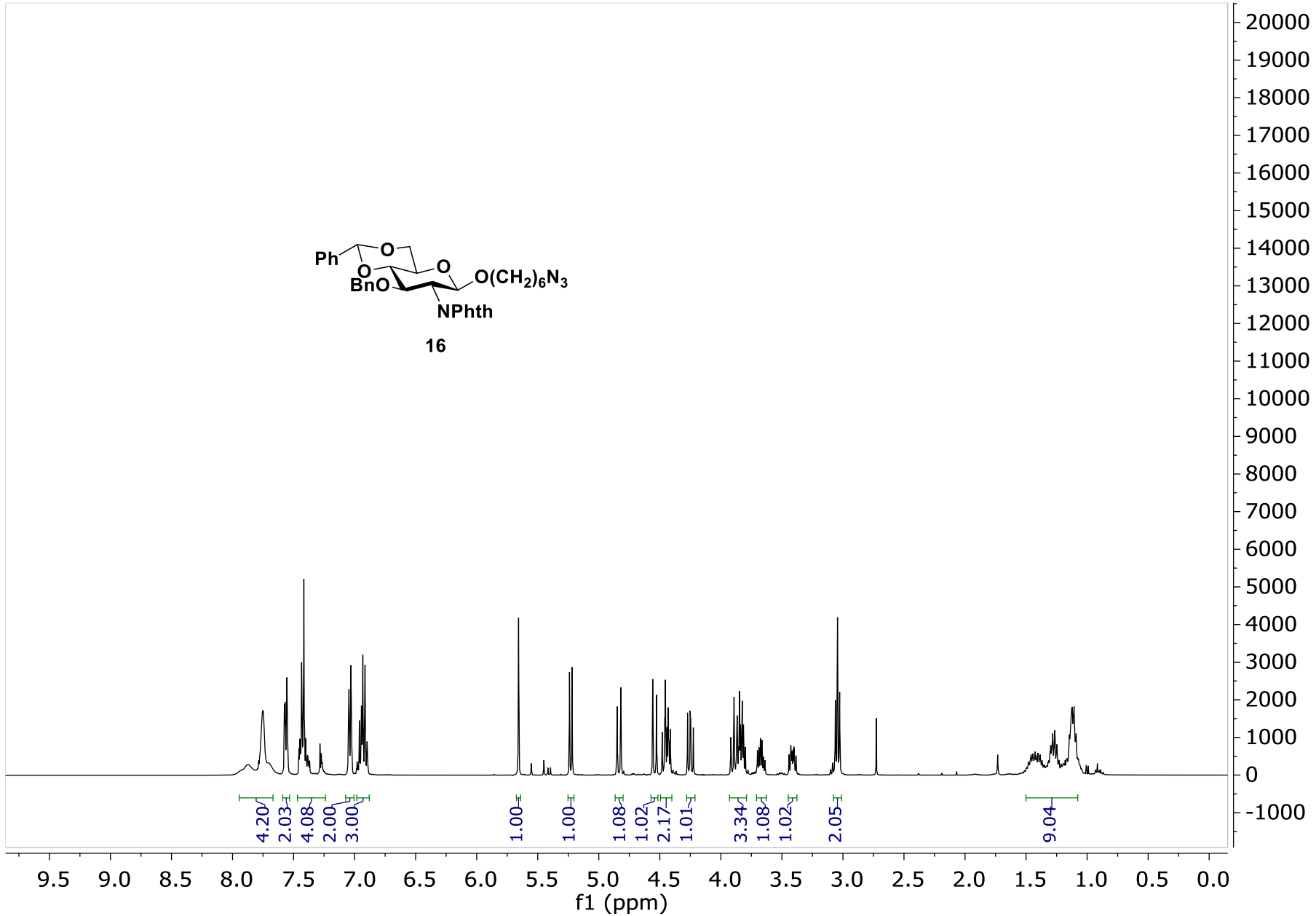
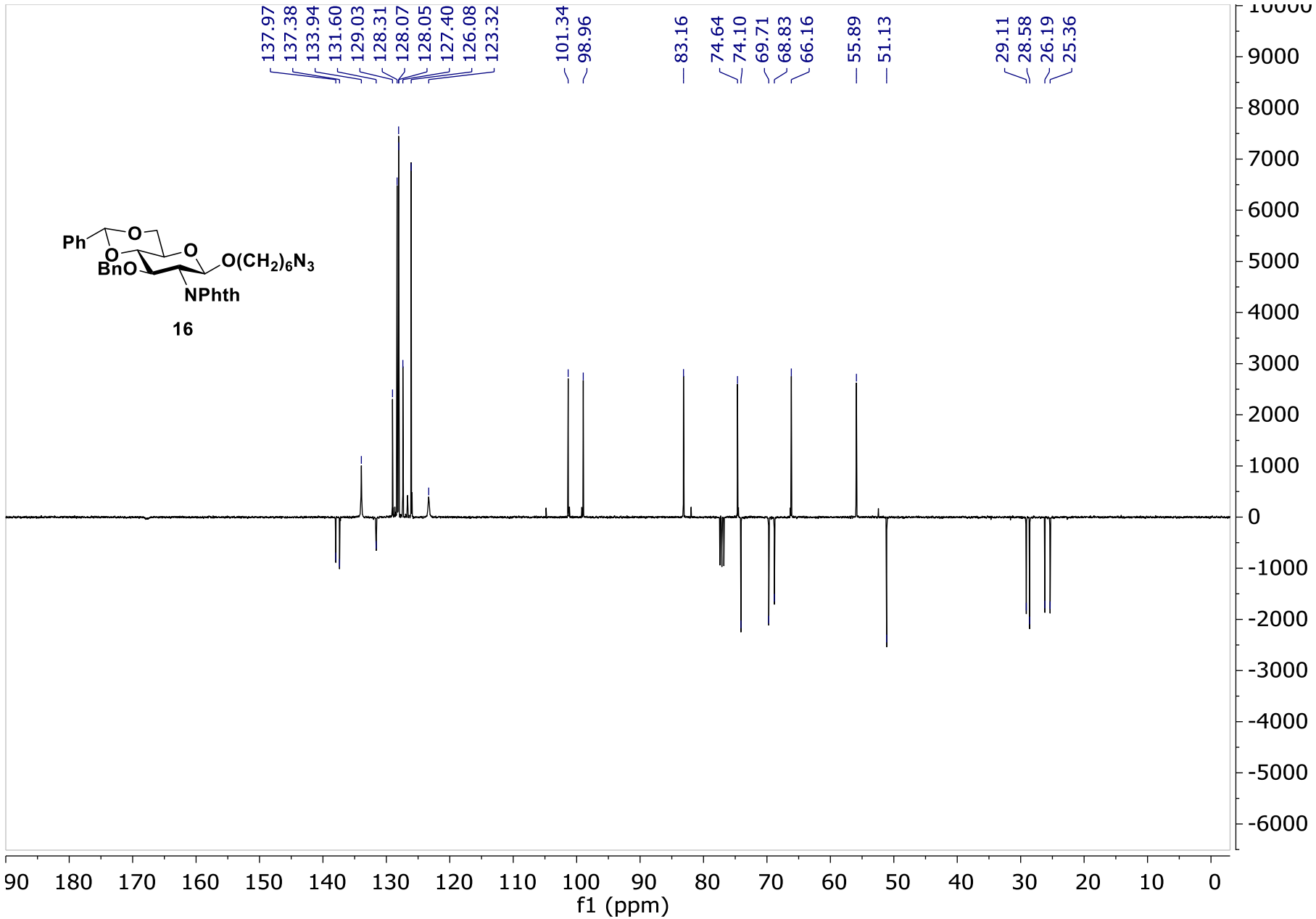
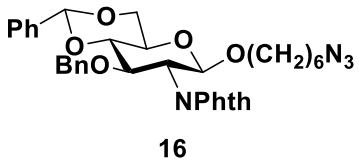


^{1}H NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



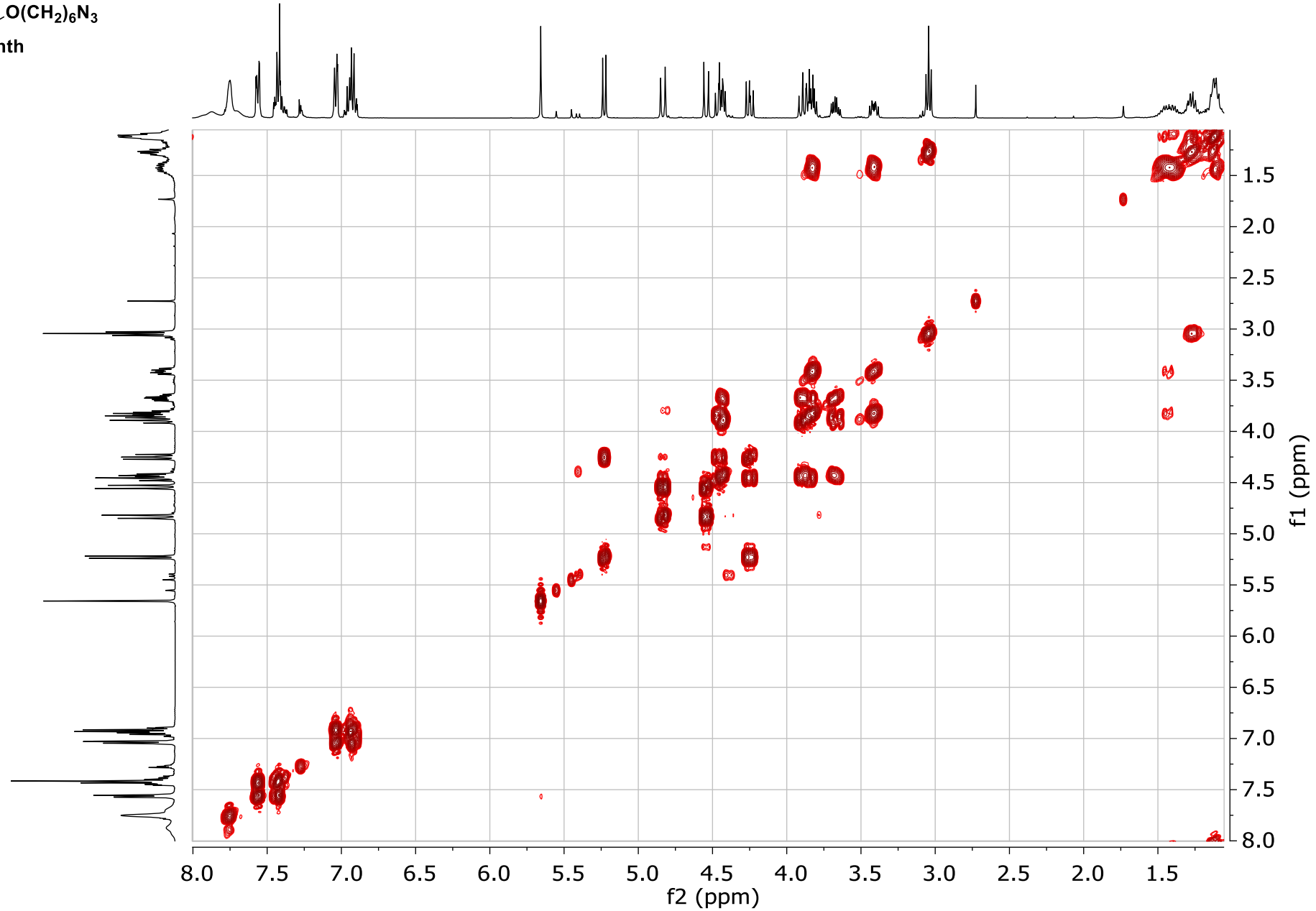
^{13}C (DEPT-Q) NMR Spectrum in $CDCl_3$, 100 MHz, 298 K



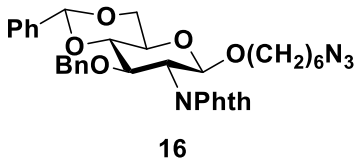


16

^{1}H-^{1}H GCOSY NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



^{1}H-^{13}C GHSQC NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



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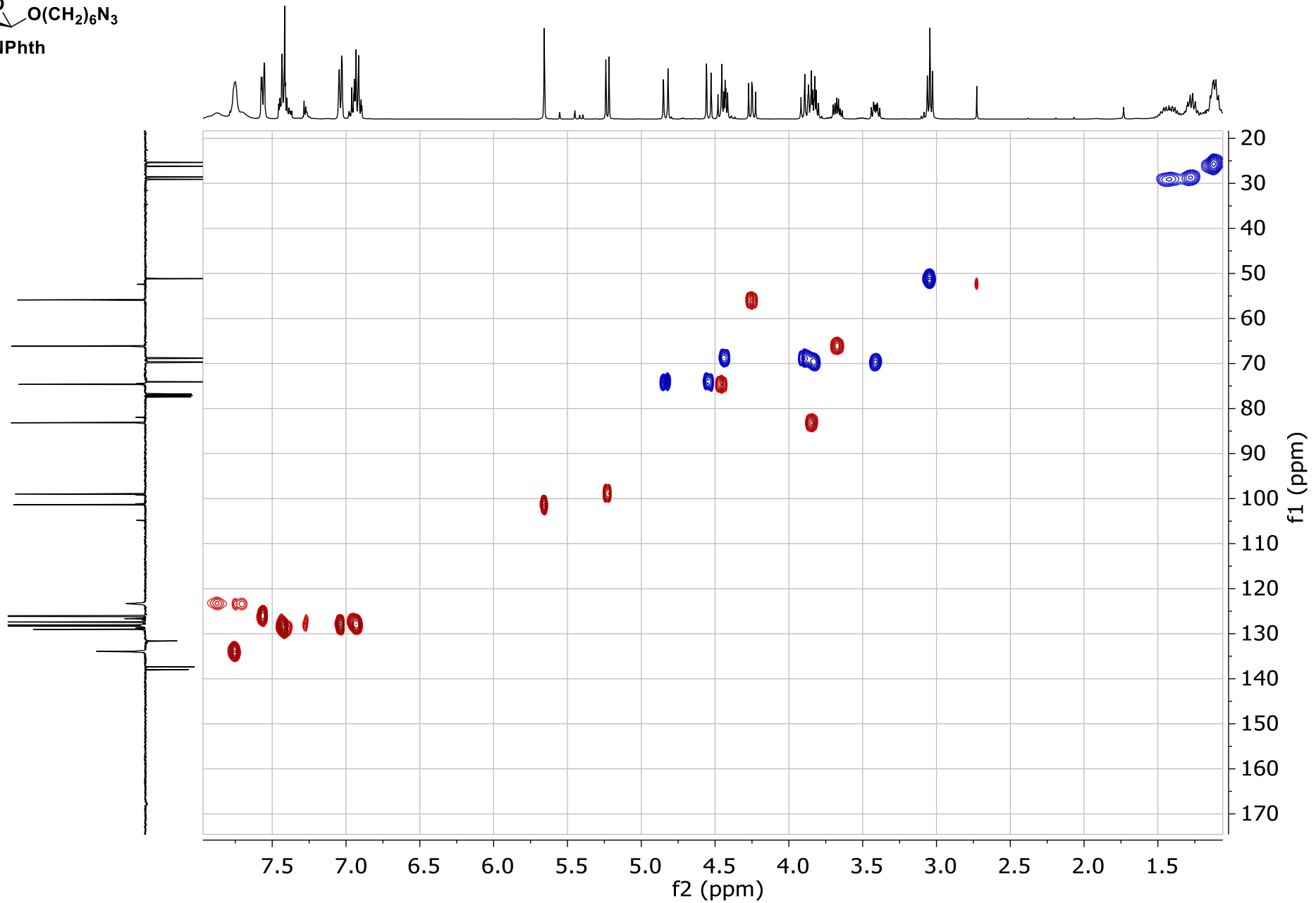
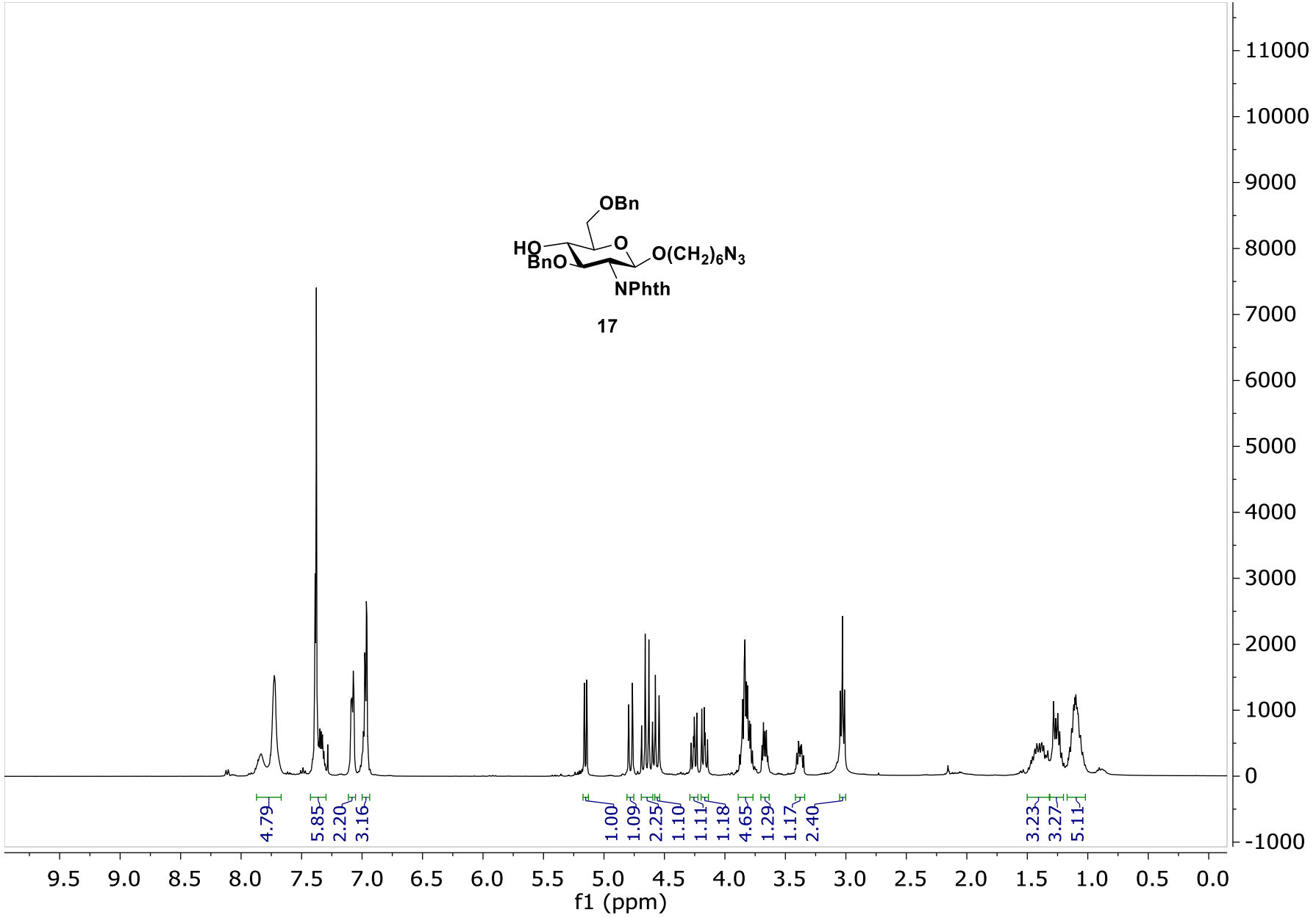
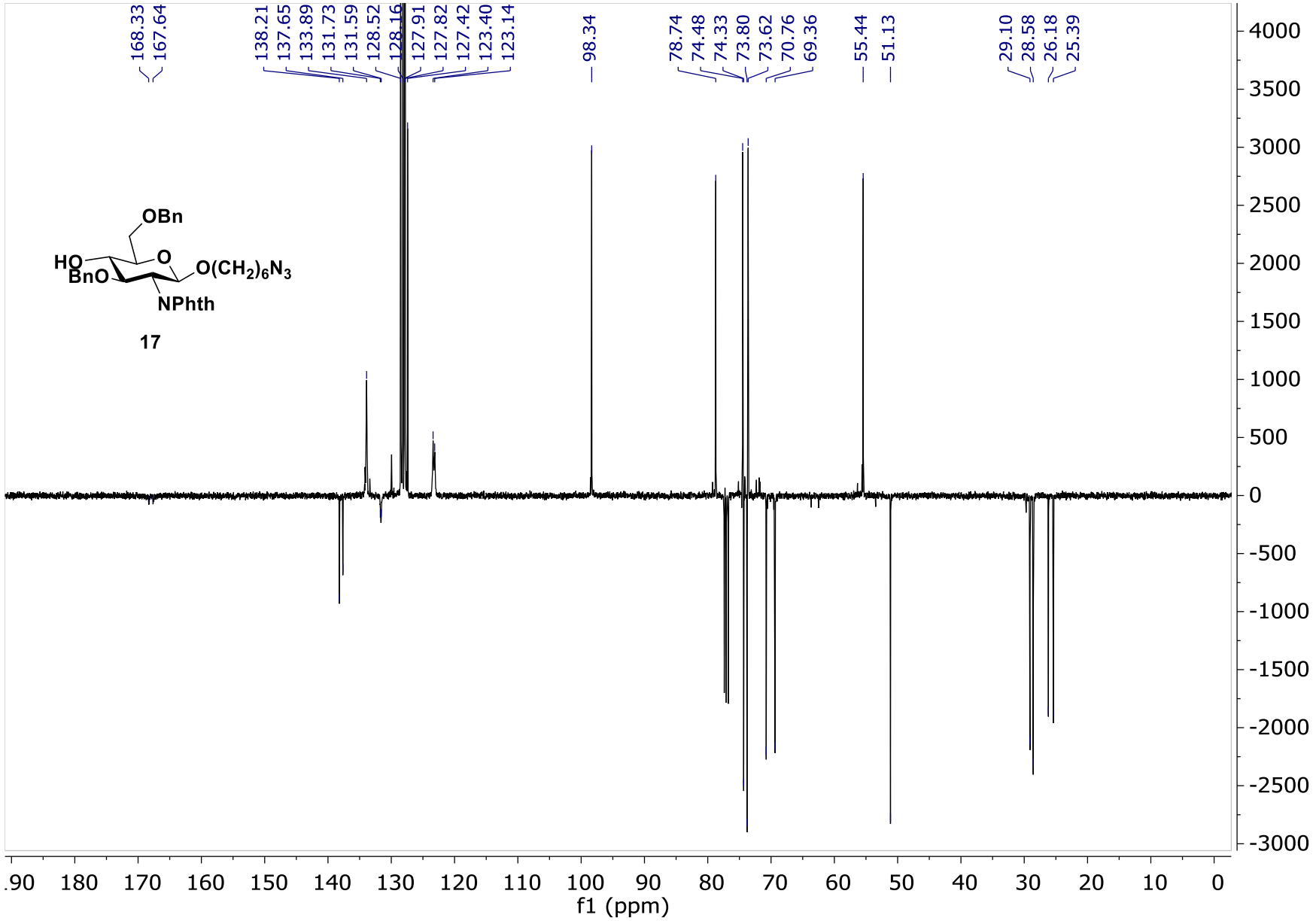
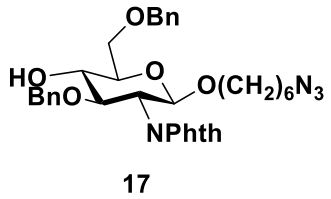


^{1}H NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



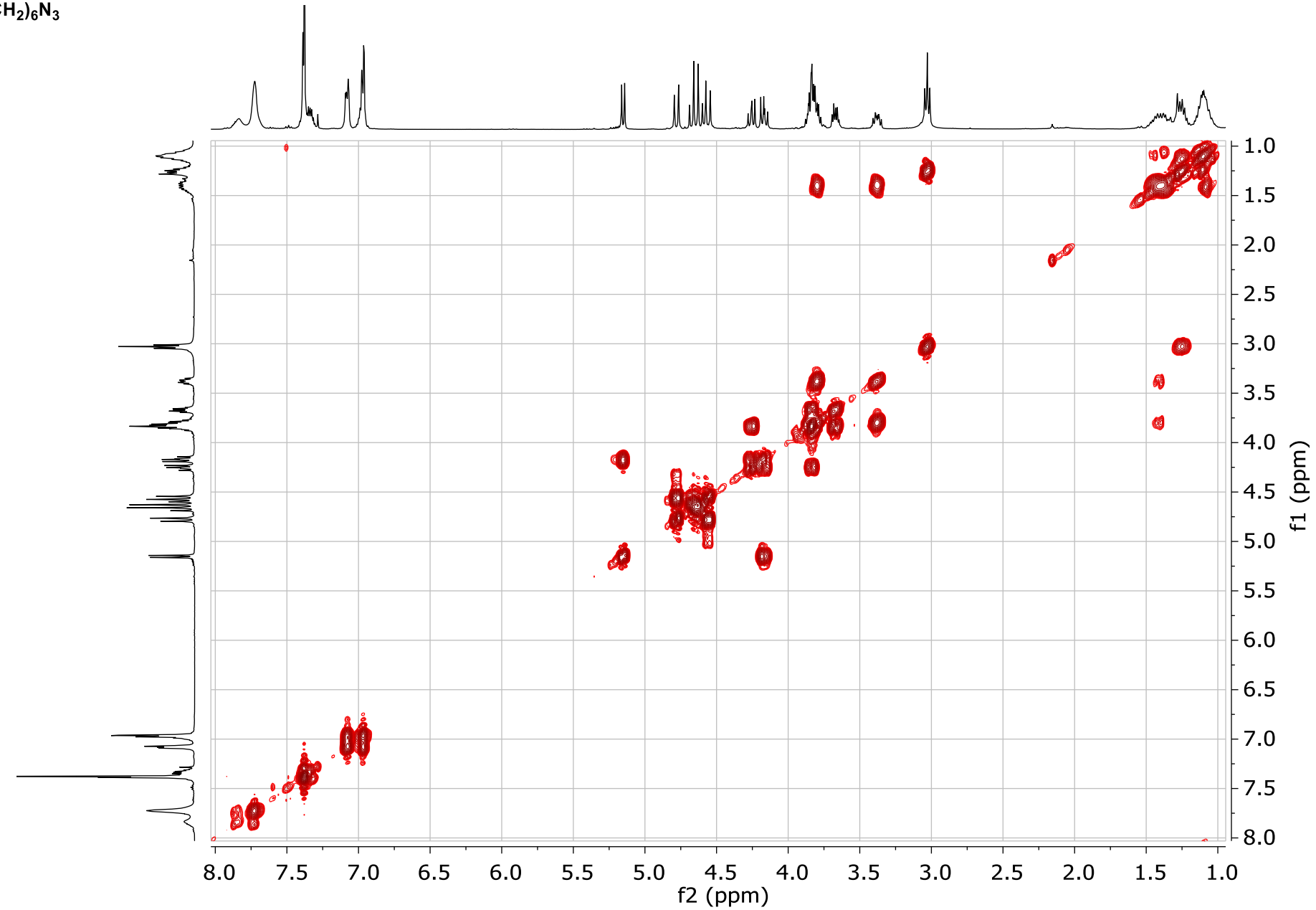
^{13}C (DEPT-Q) NMR Spectrum in $CDCl_3$, 100 MHz, 298 K



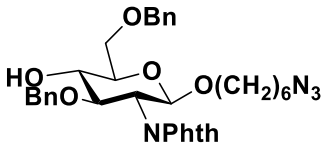


17

^{1}H-^{1}H GCOSY NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



^{1}H-^{13}C GHSQC NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



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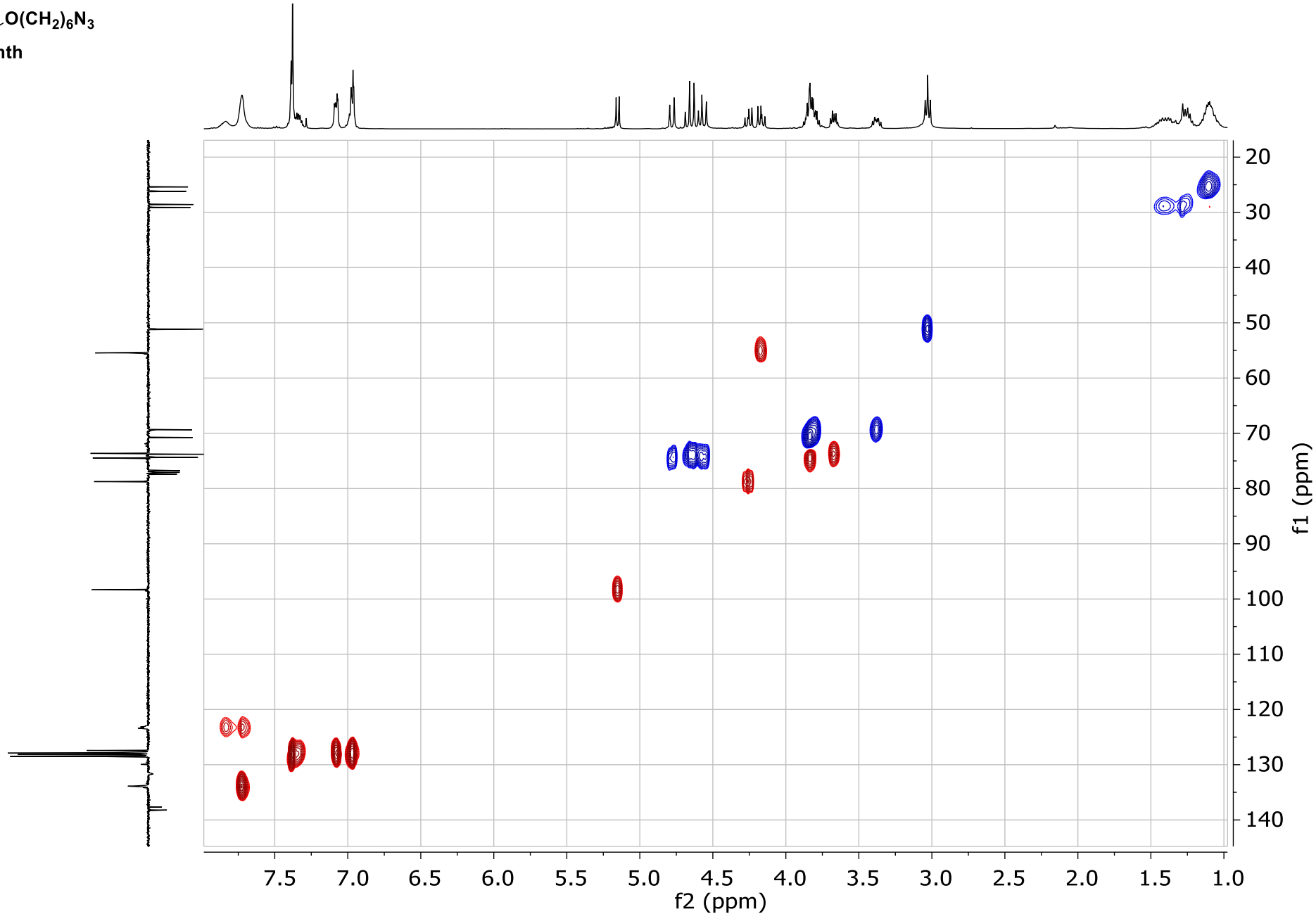
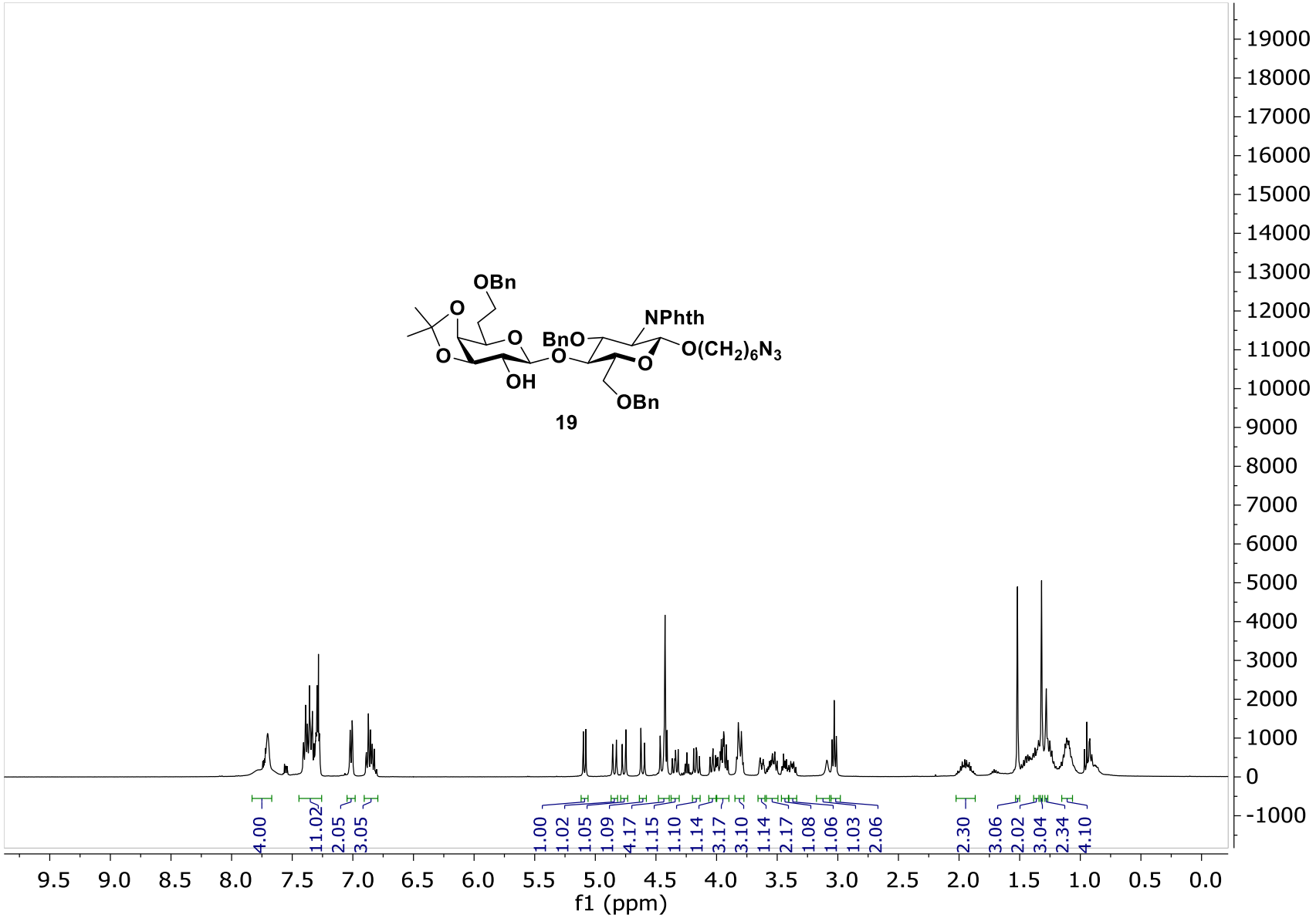
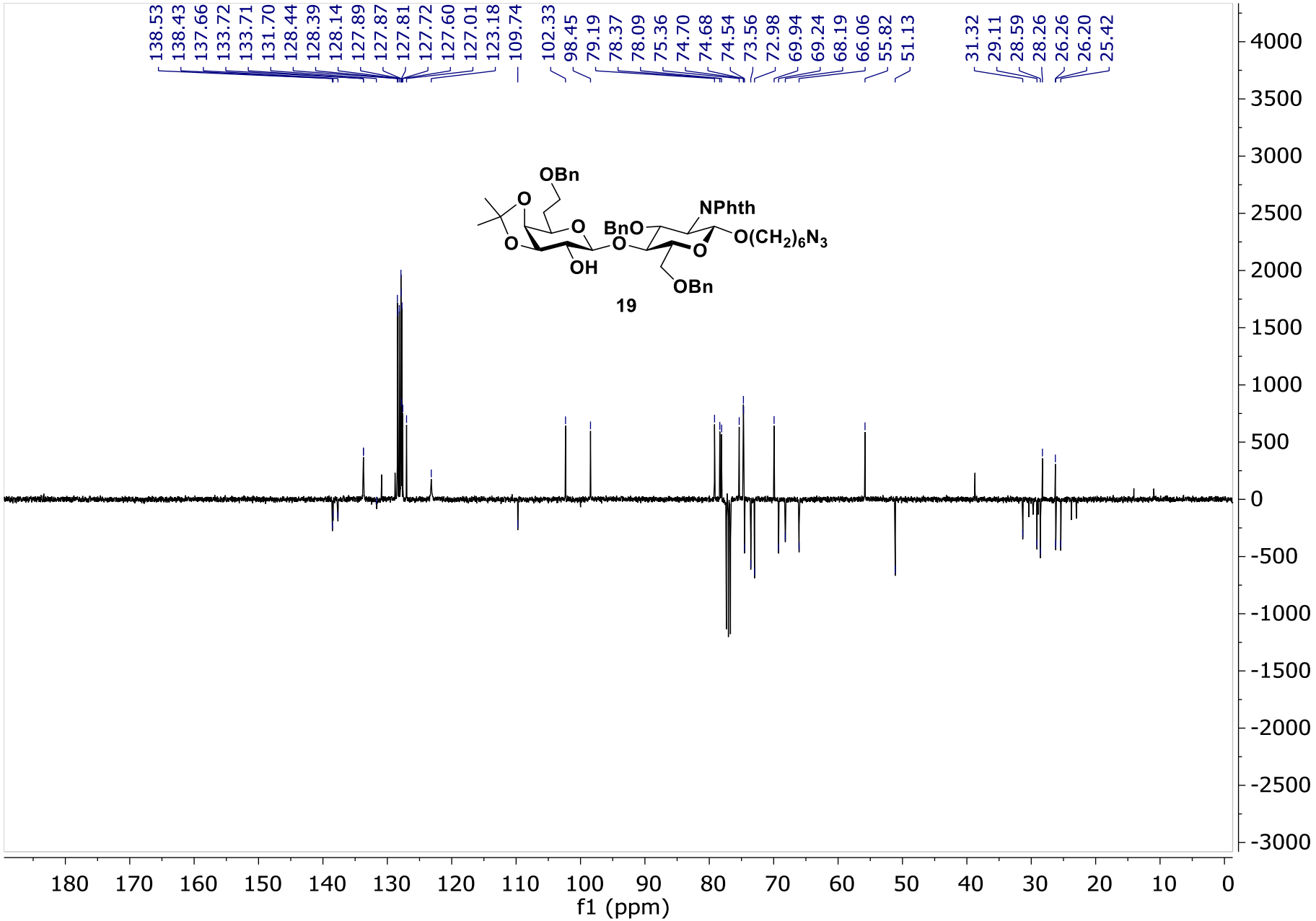


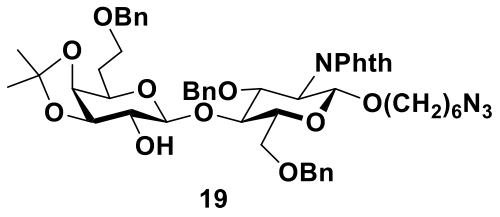
^{1}H NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



^{13}C (DEPT-Q) NMR Spectrum in $CDCl_3$, 100 MHz, 298 K



^{1}H-^{1}H GCOSY NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



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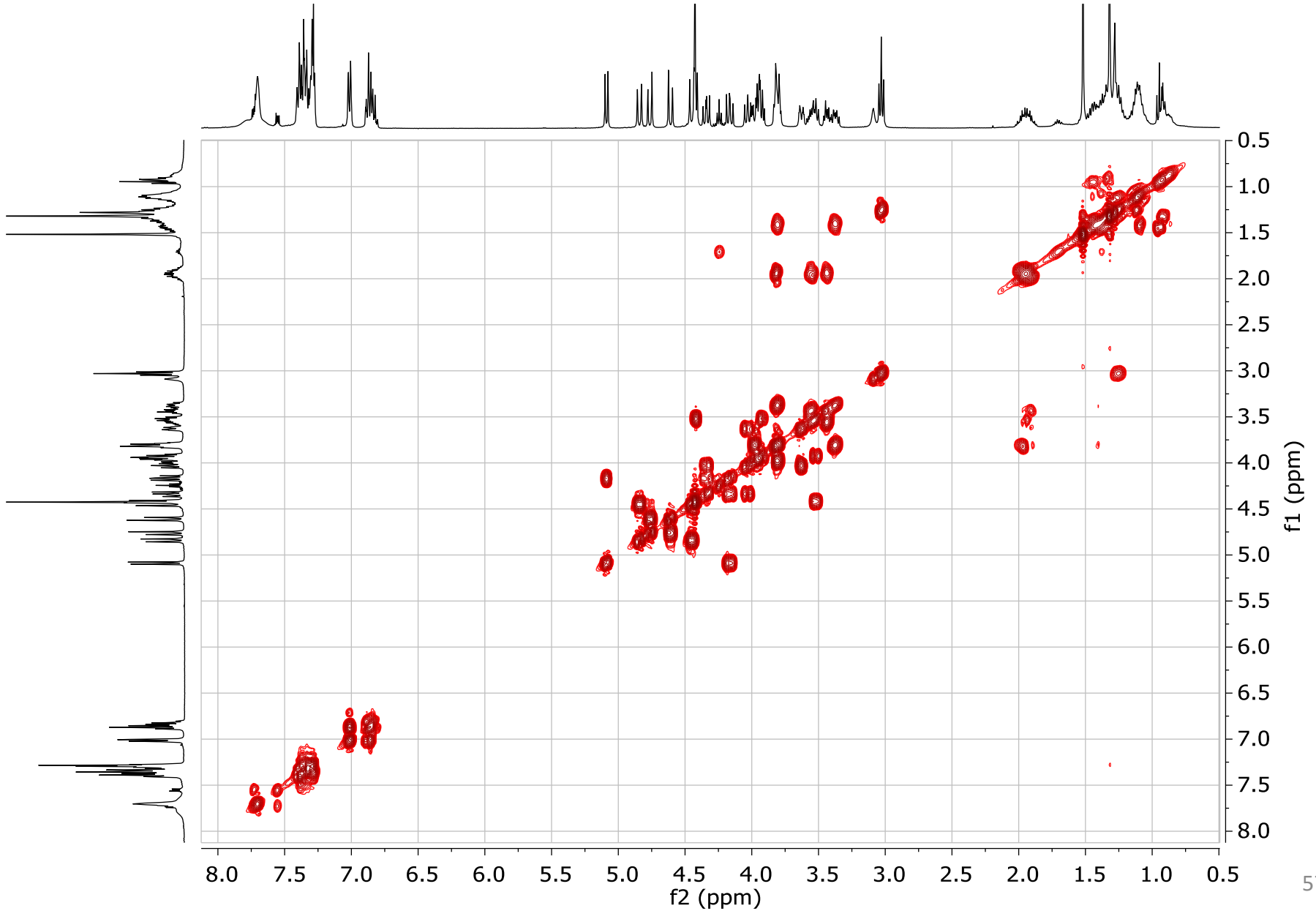
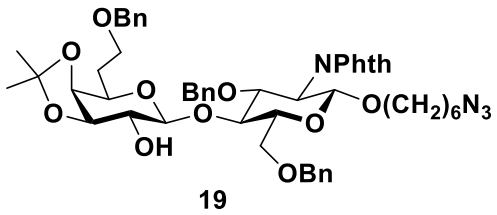


^{1}H-^{13}C GHSQC NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



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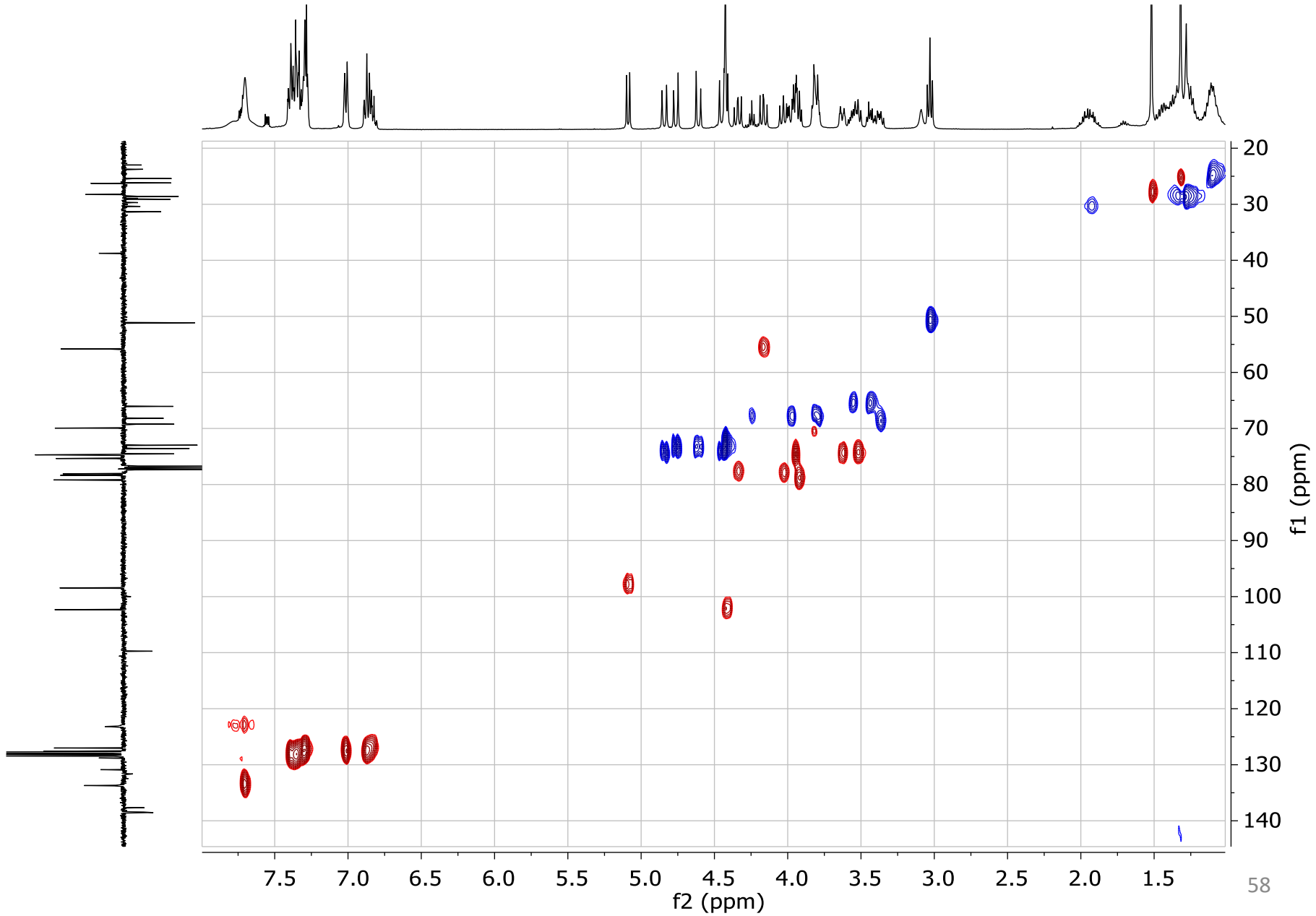
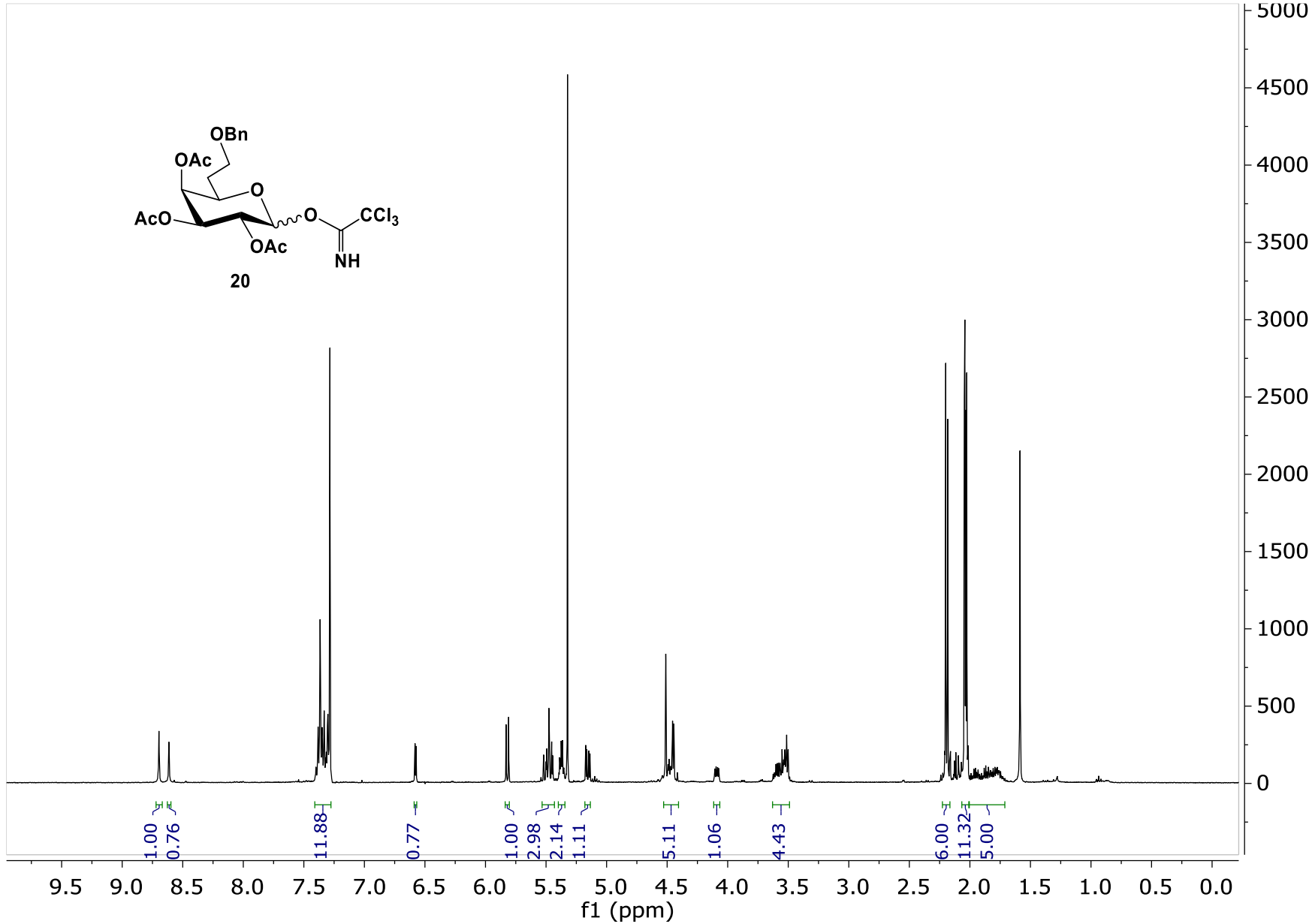
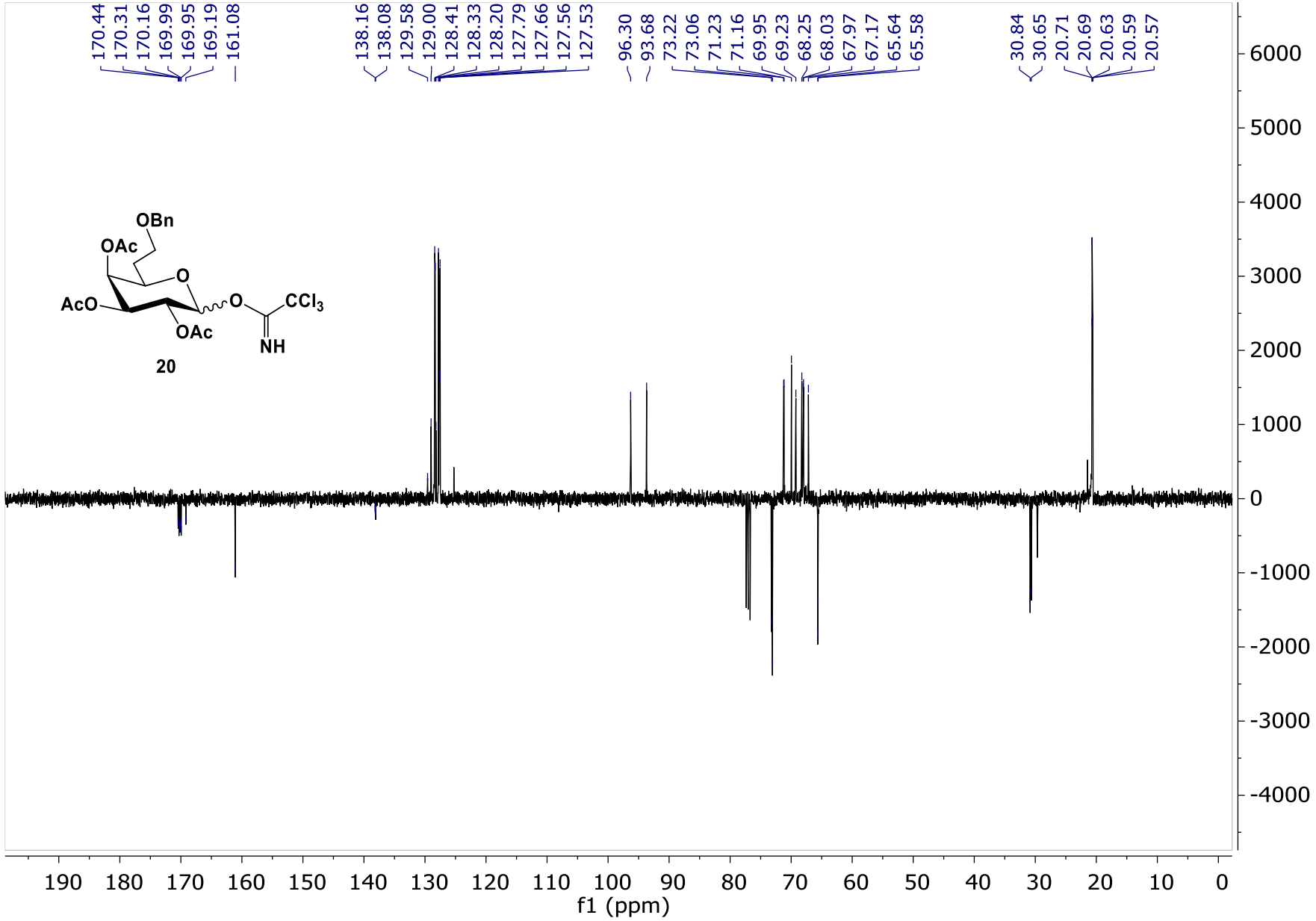
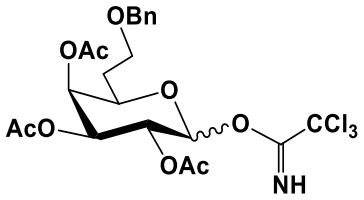


^{1}H NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



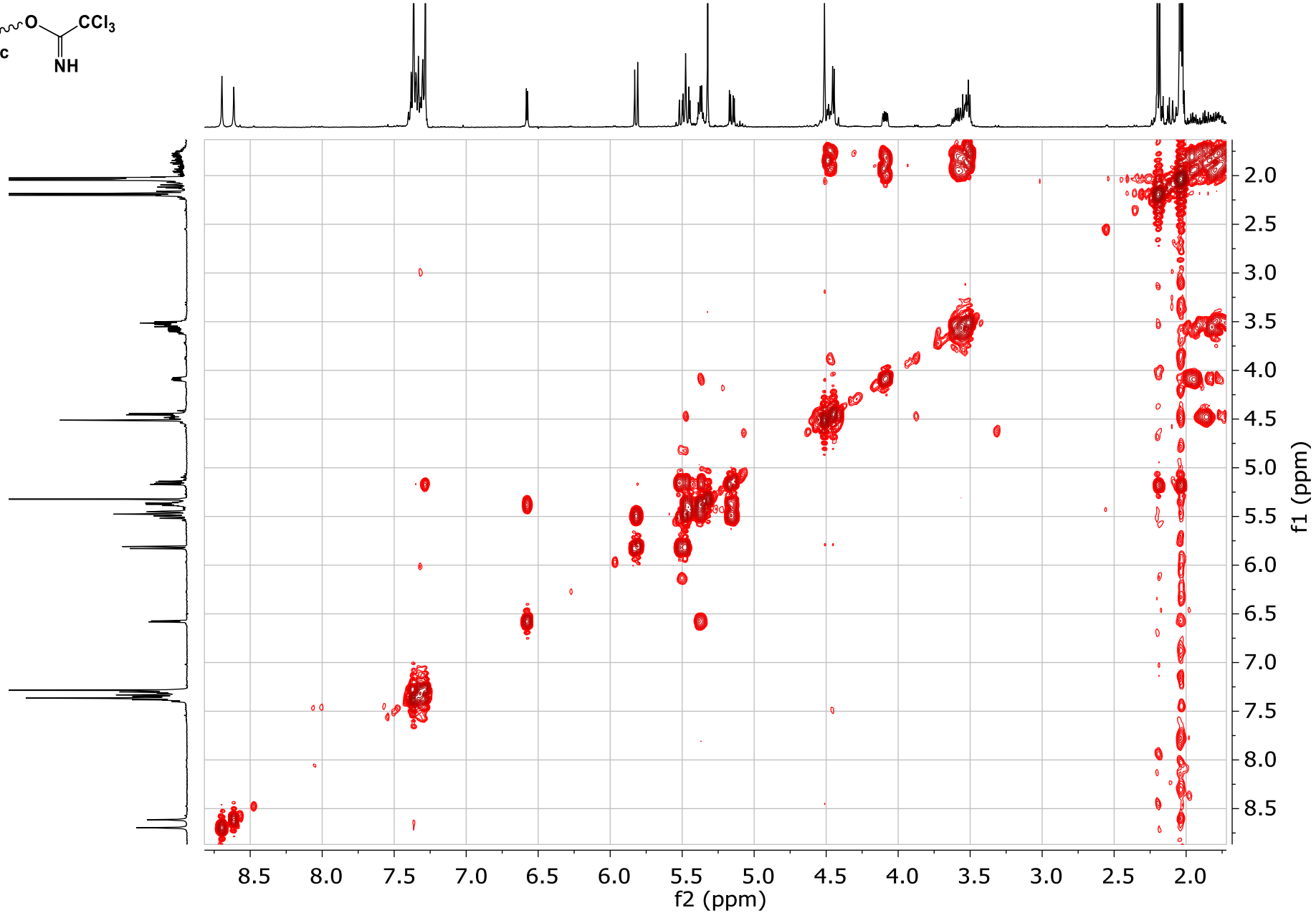
^{13}C (DEPT-Q) NMR Spectrum in $CDCl_3$, 100 MHz, 298 K

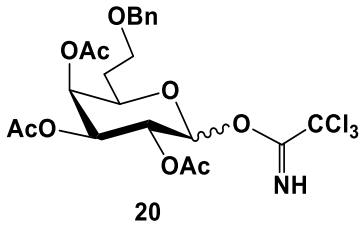




20

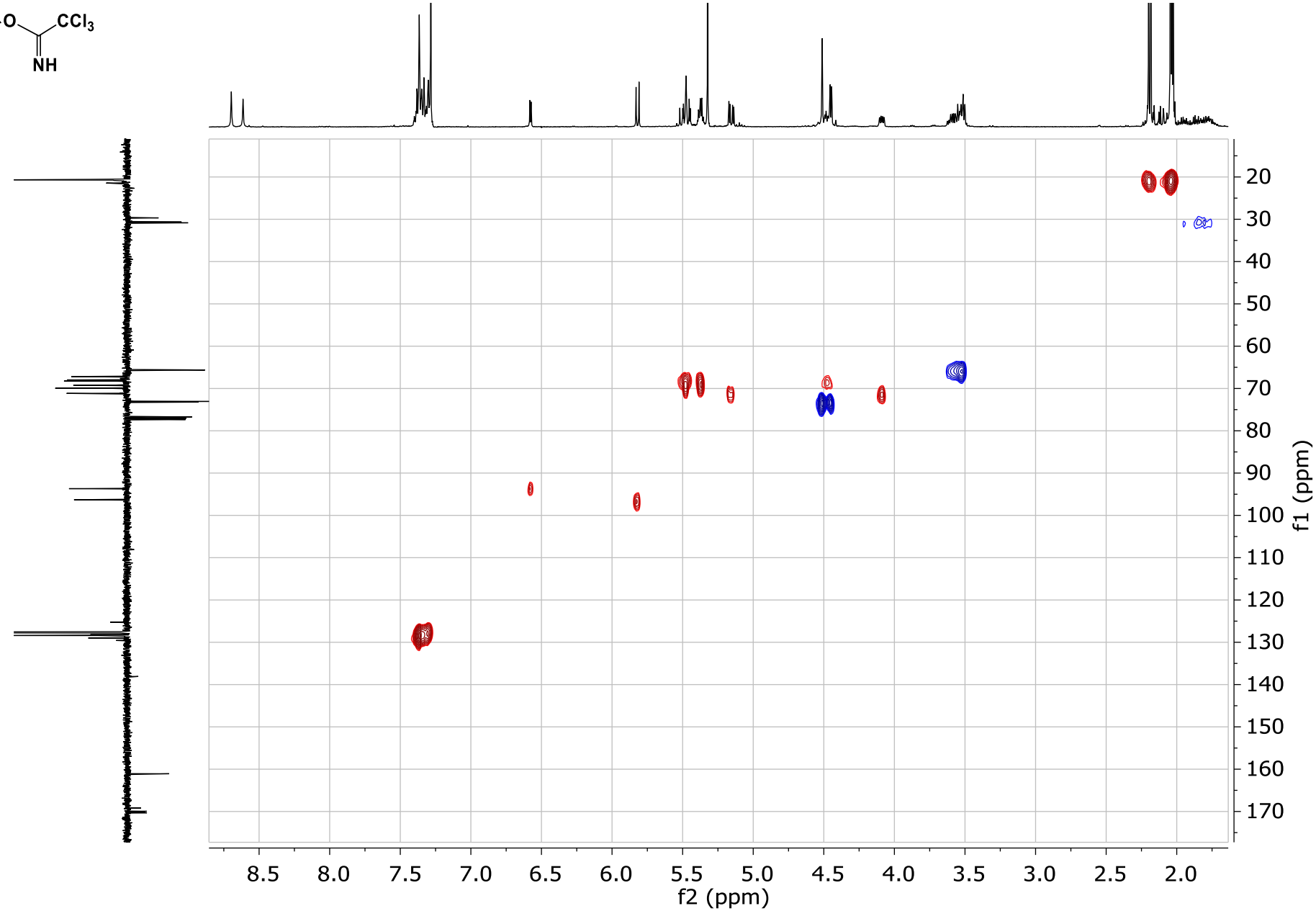
^{1}H-^{1}H GCOSY NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



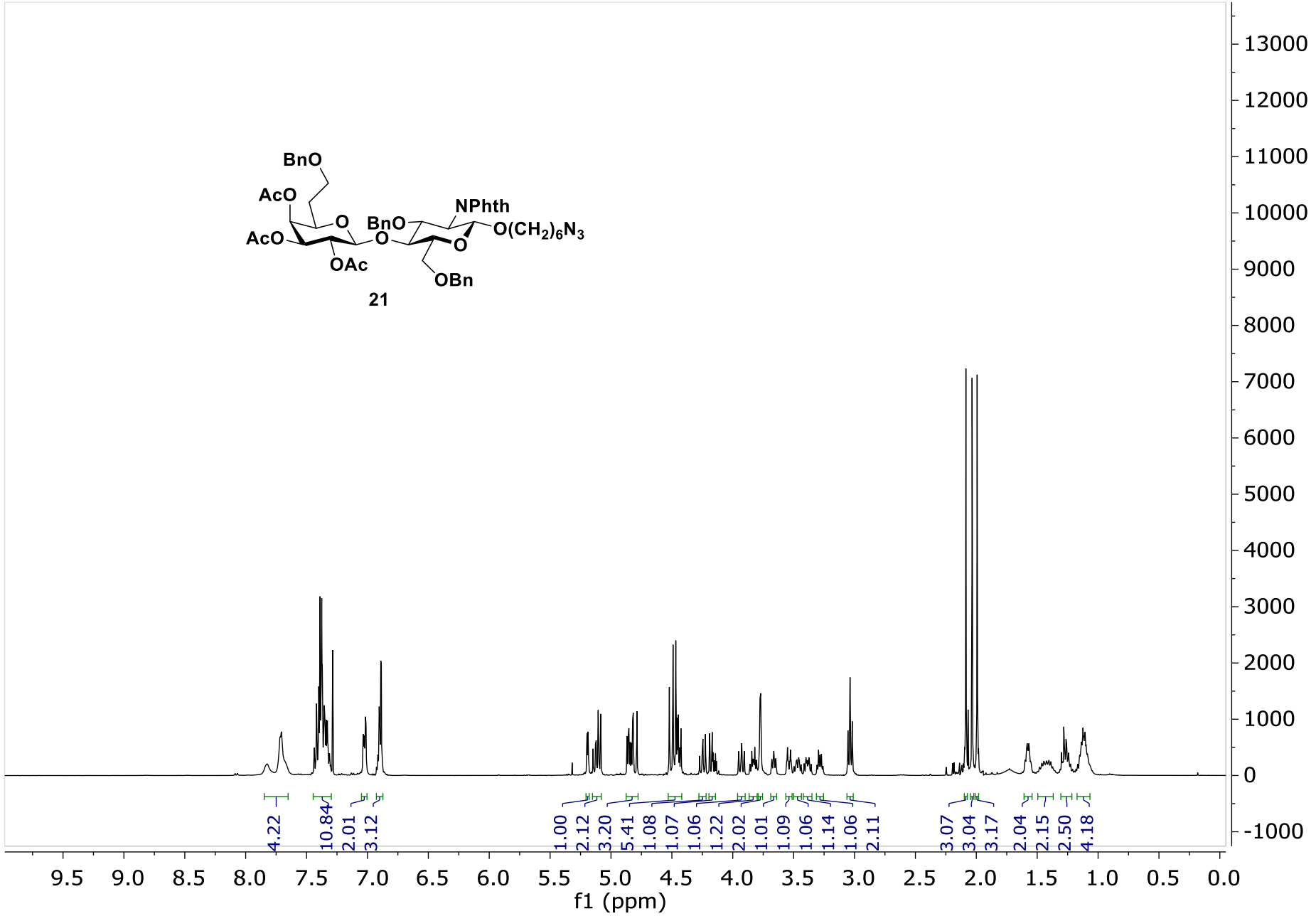


20

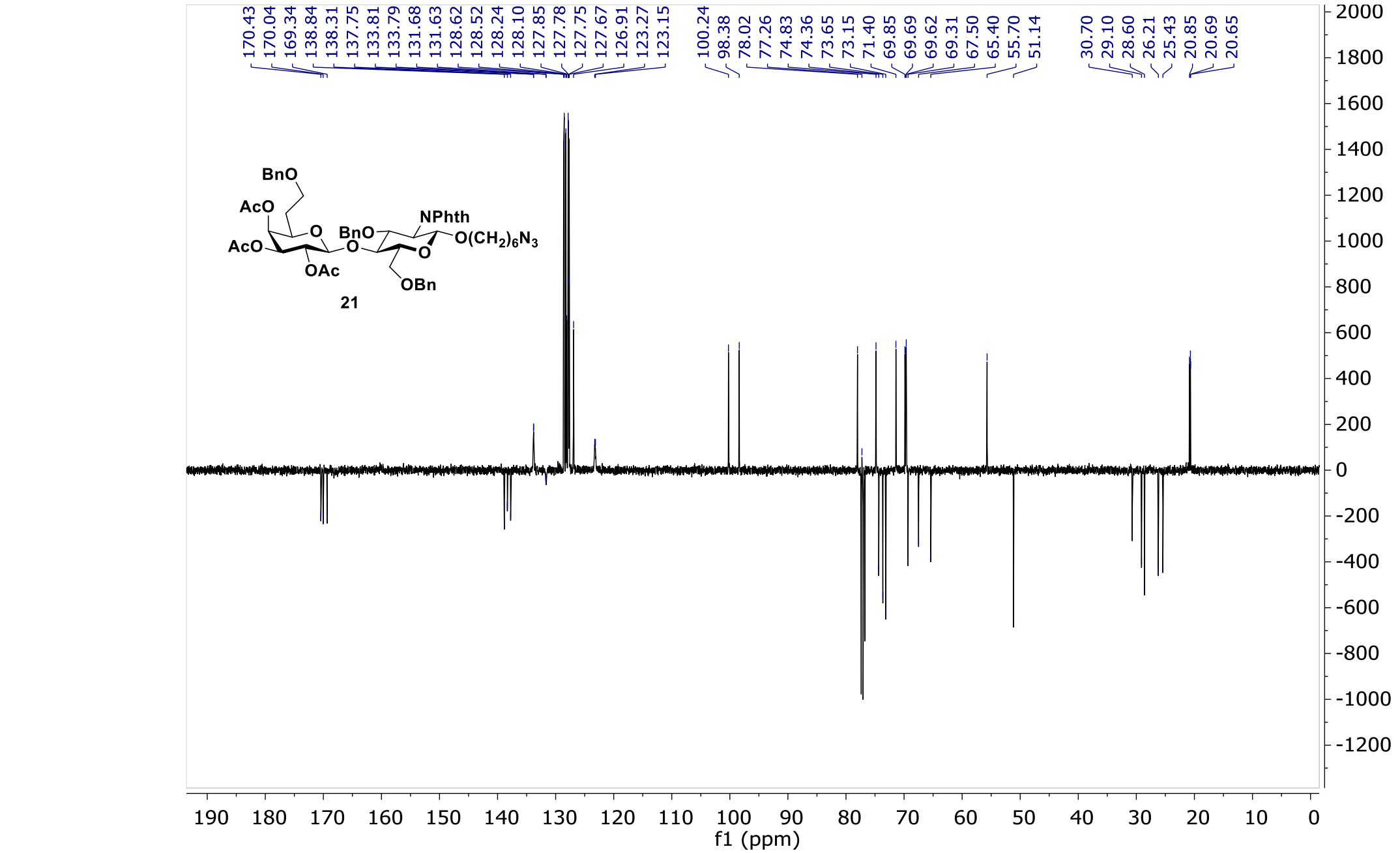
^{1}H-^{13}C GHSQC NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



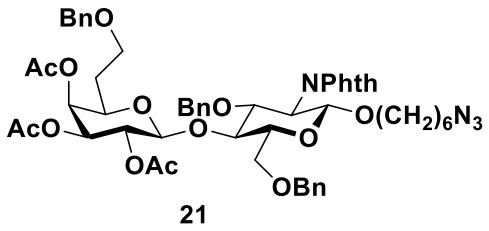
^{1}H NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



^{13}C (DEPT-Q) NMR Spectrum in $CDCl_3$, 100 MHz, 298 K



^{1}H-^{1}H GCOSY NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



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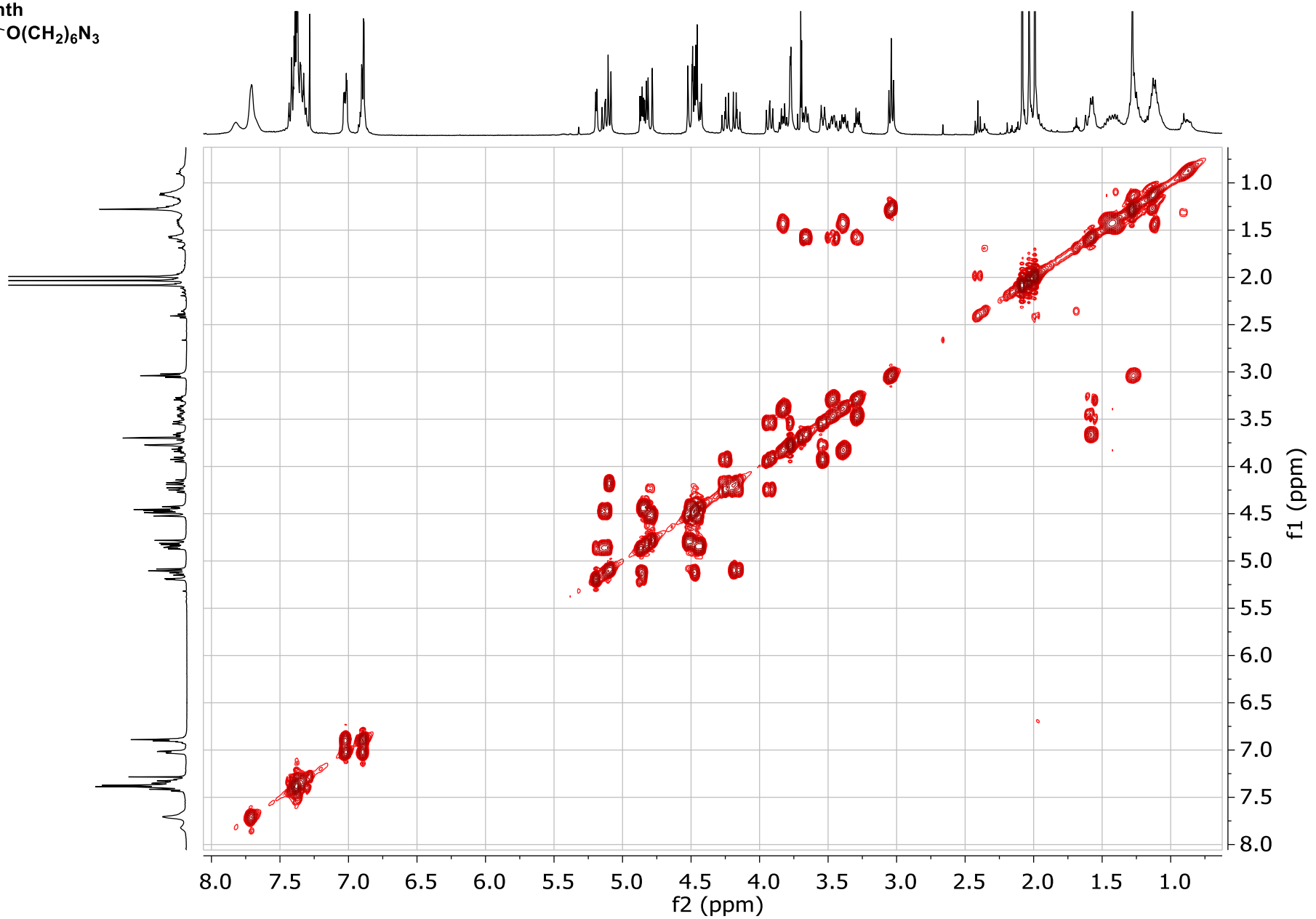
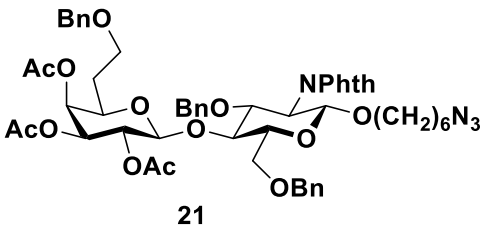


^{1}H-^{13}C GHSQC NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



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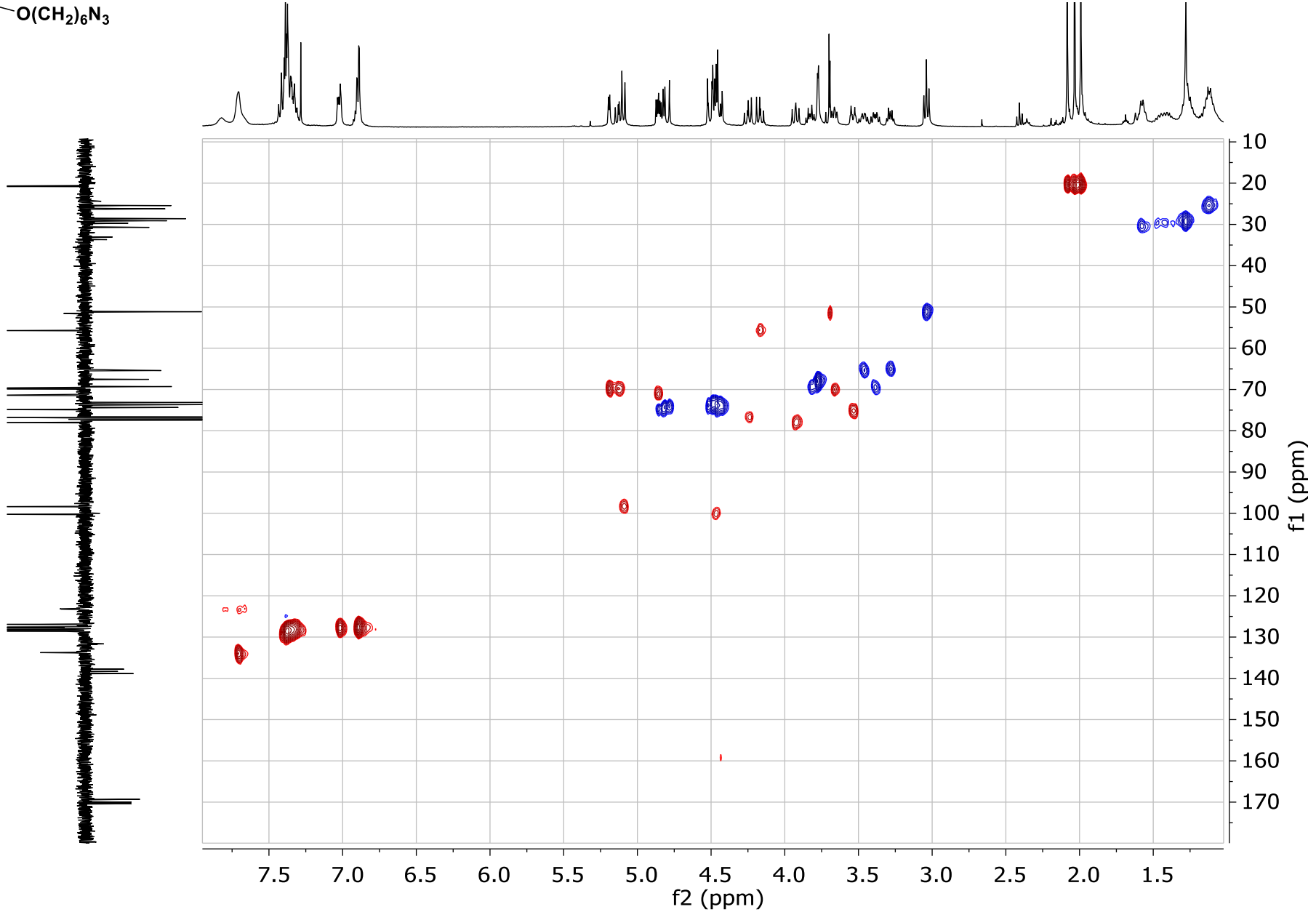
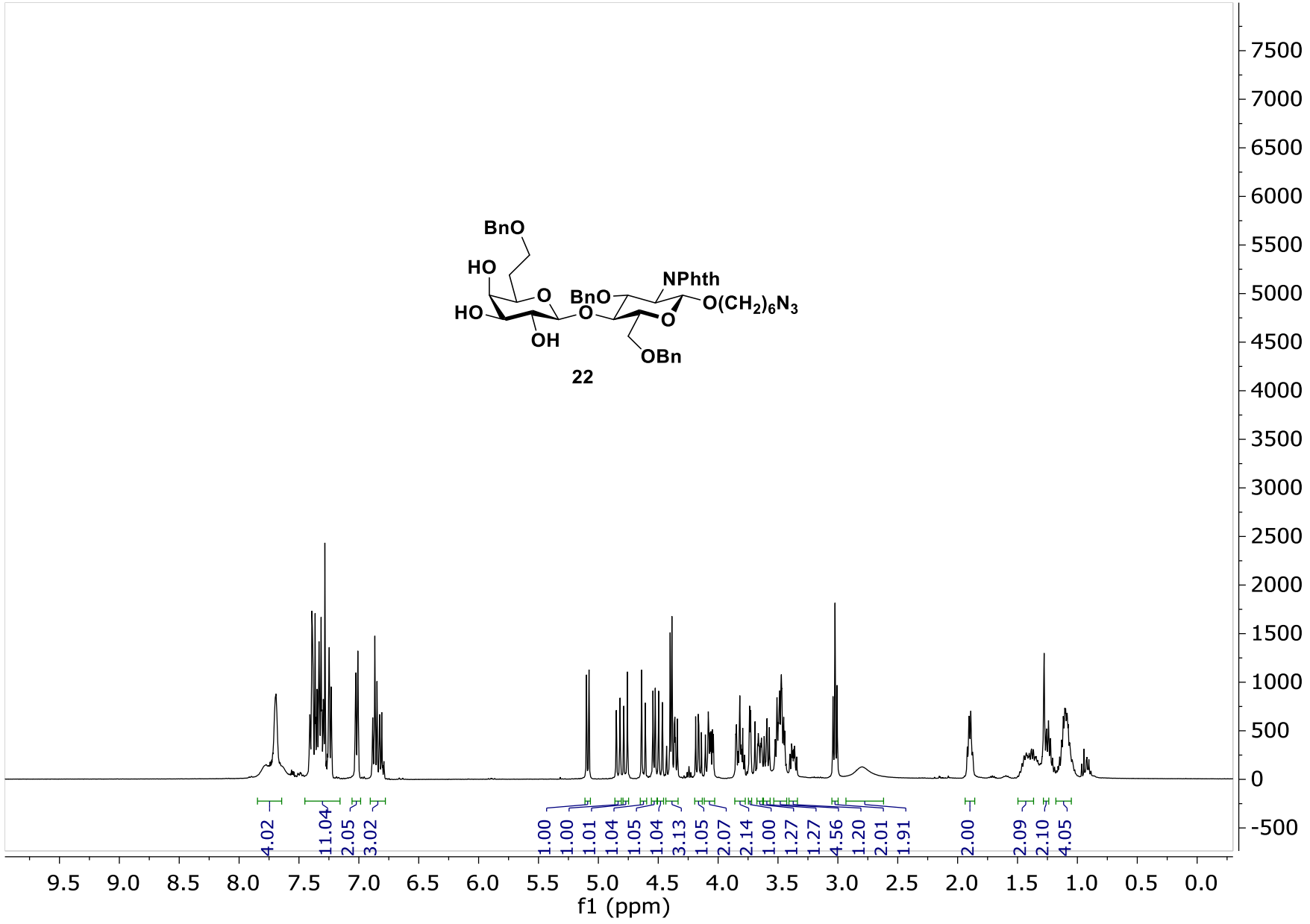
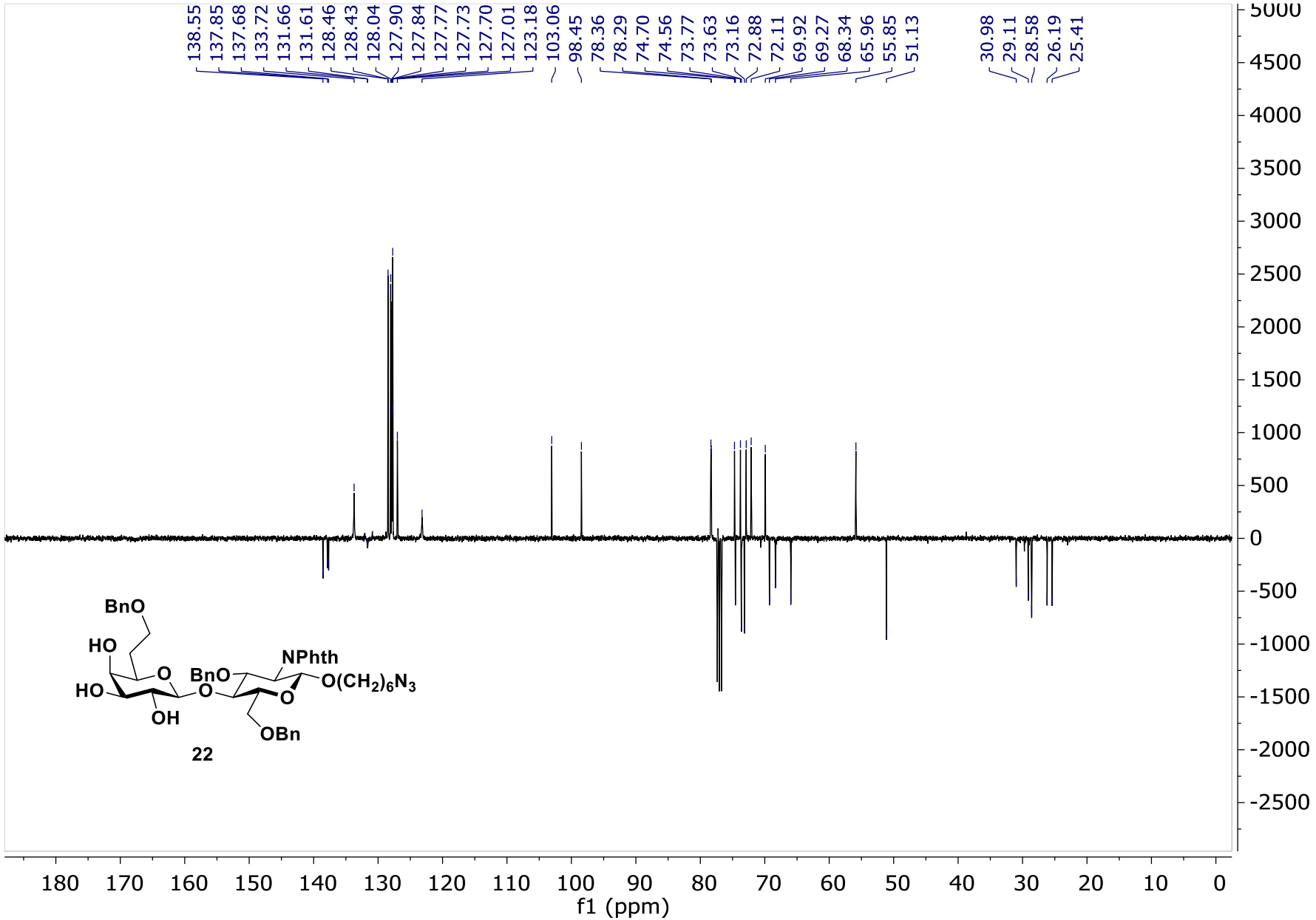


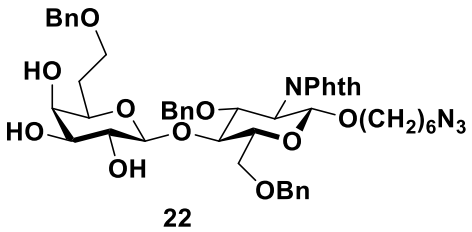
^{1}H NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



^{13}C (DEPT-Q) NMR Spectrum in $CDCl_3$, 100 MHz, 298 K



^{1}H-^{1}H GCOSY NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



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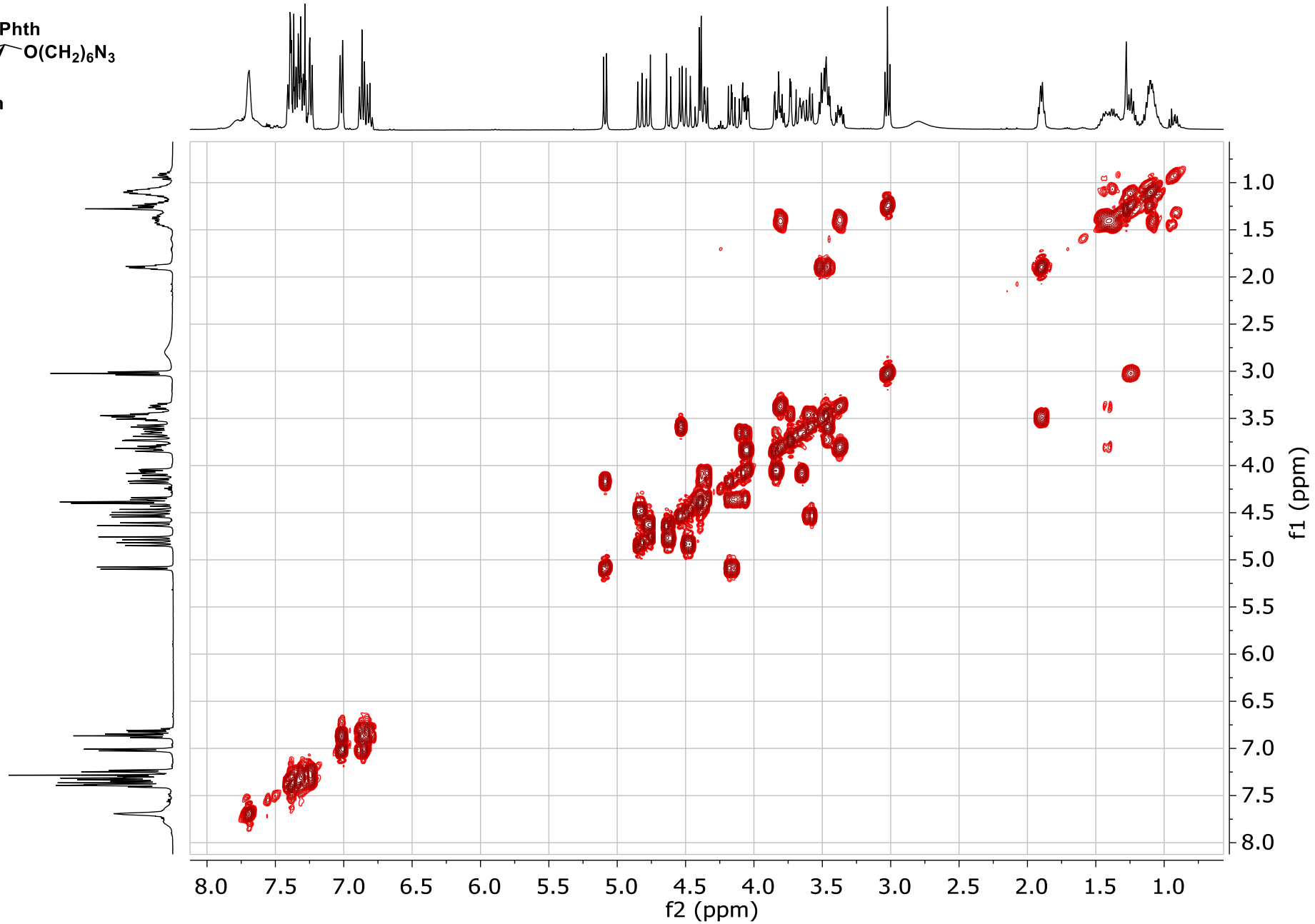
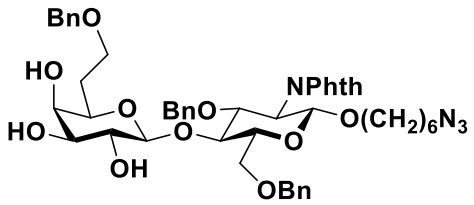


^{1}H-^{13}C GHSQC NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



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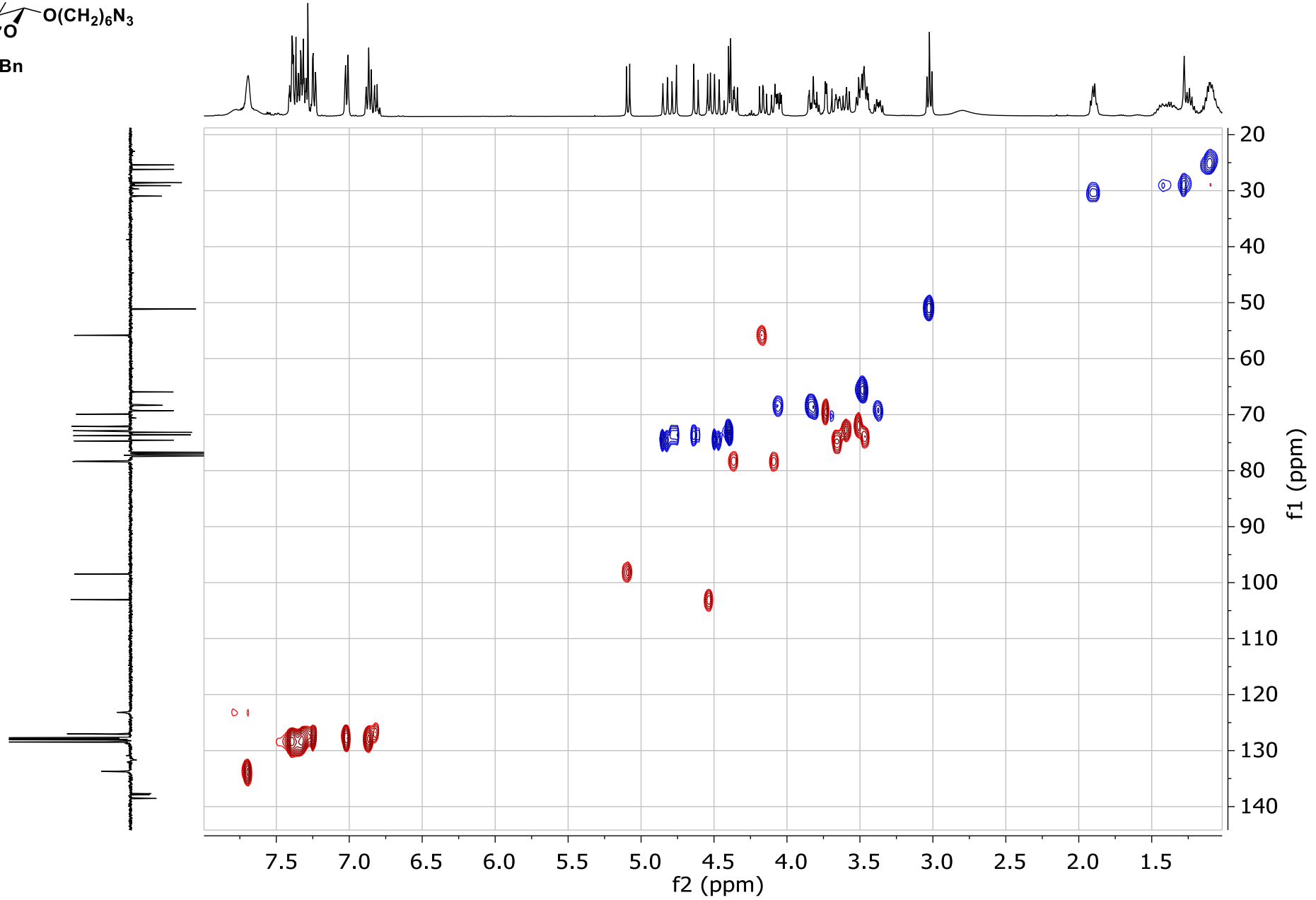
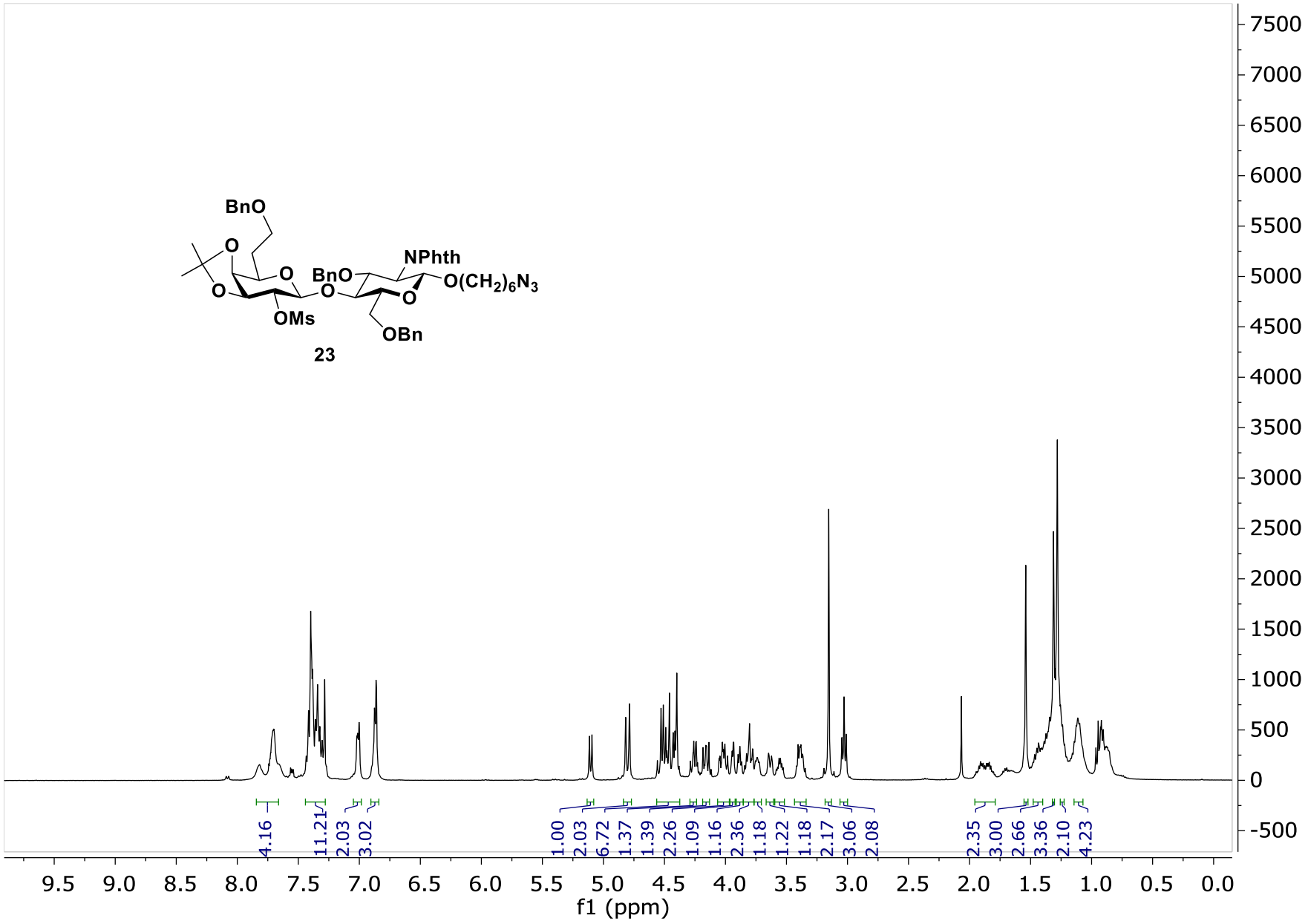
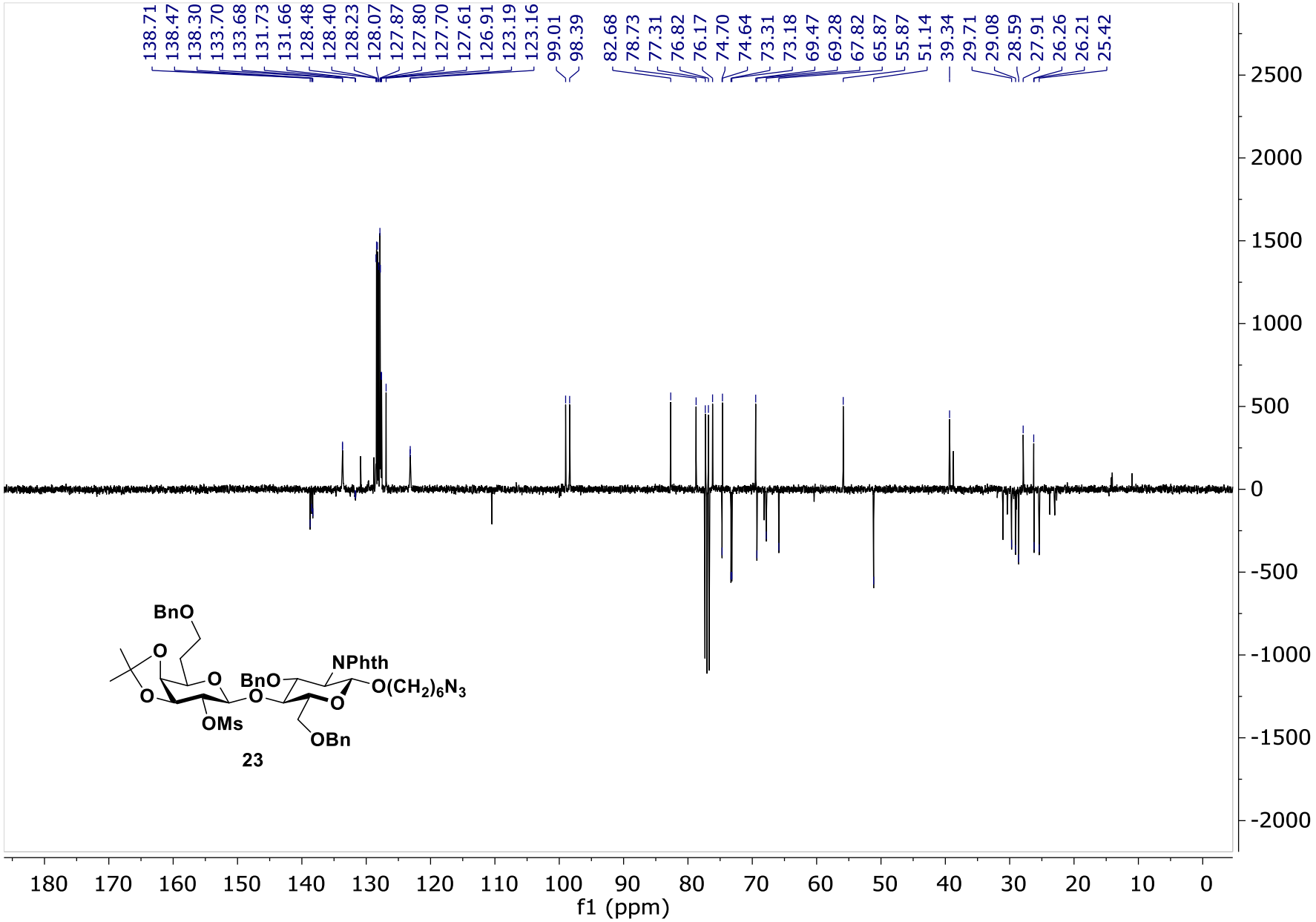
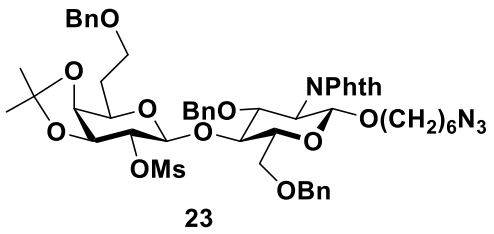


^{1}H NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



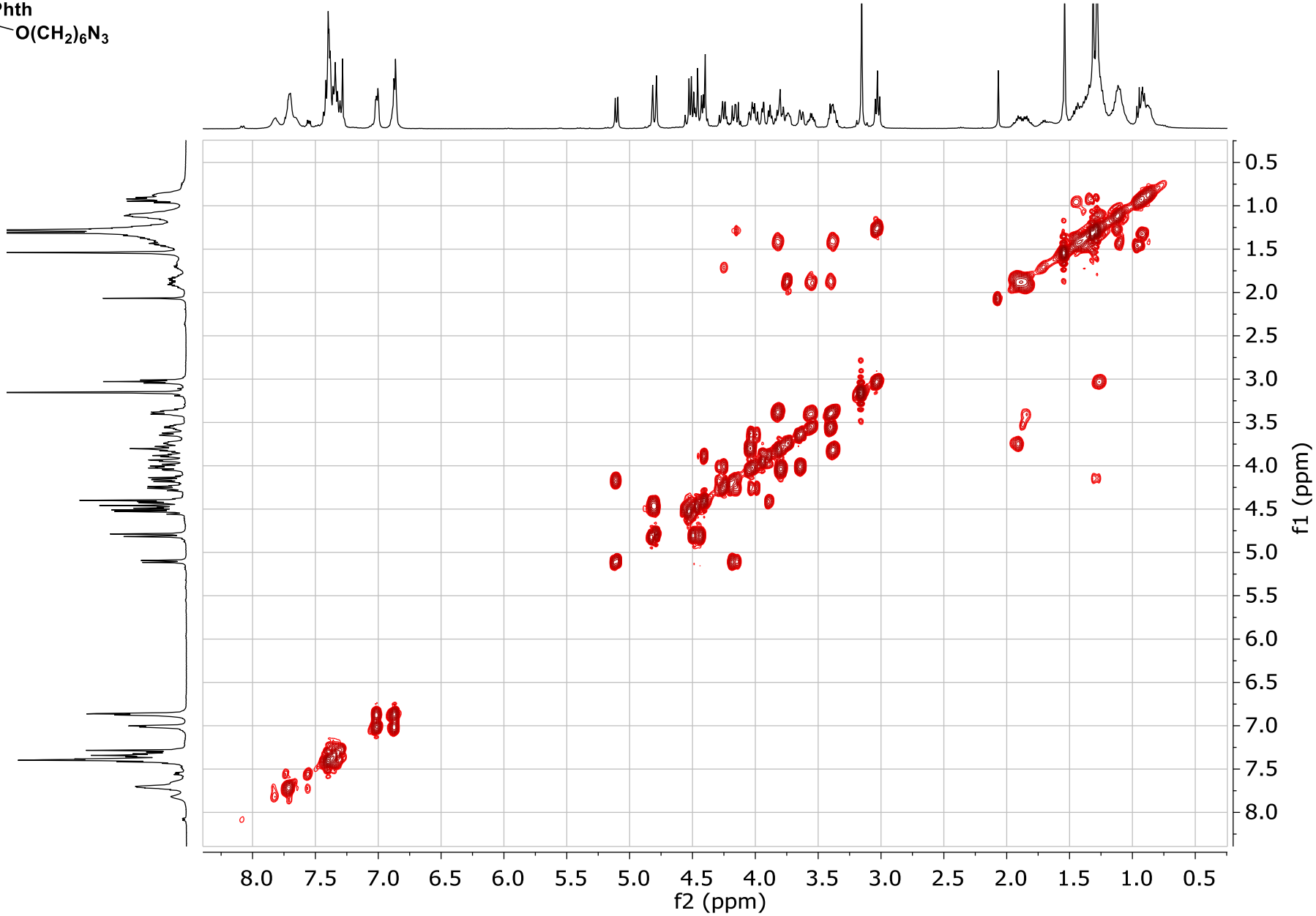
^{13}C (DEPT-Q) NMR Spectrum in $CDCl_3$, 100 MHz, 298 K



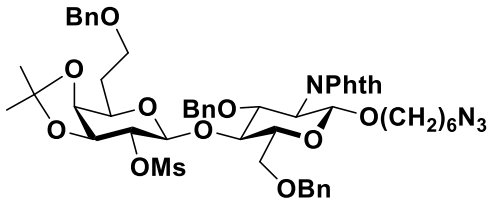


23

^{1}H-^{1}H GCOSY NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



^{1}H-^{13}C GHSQC NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



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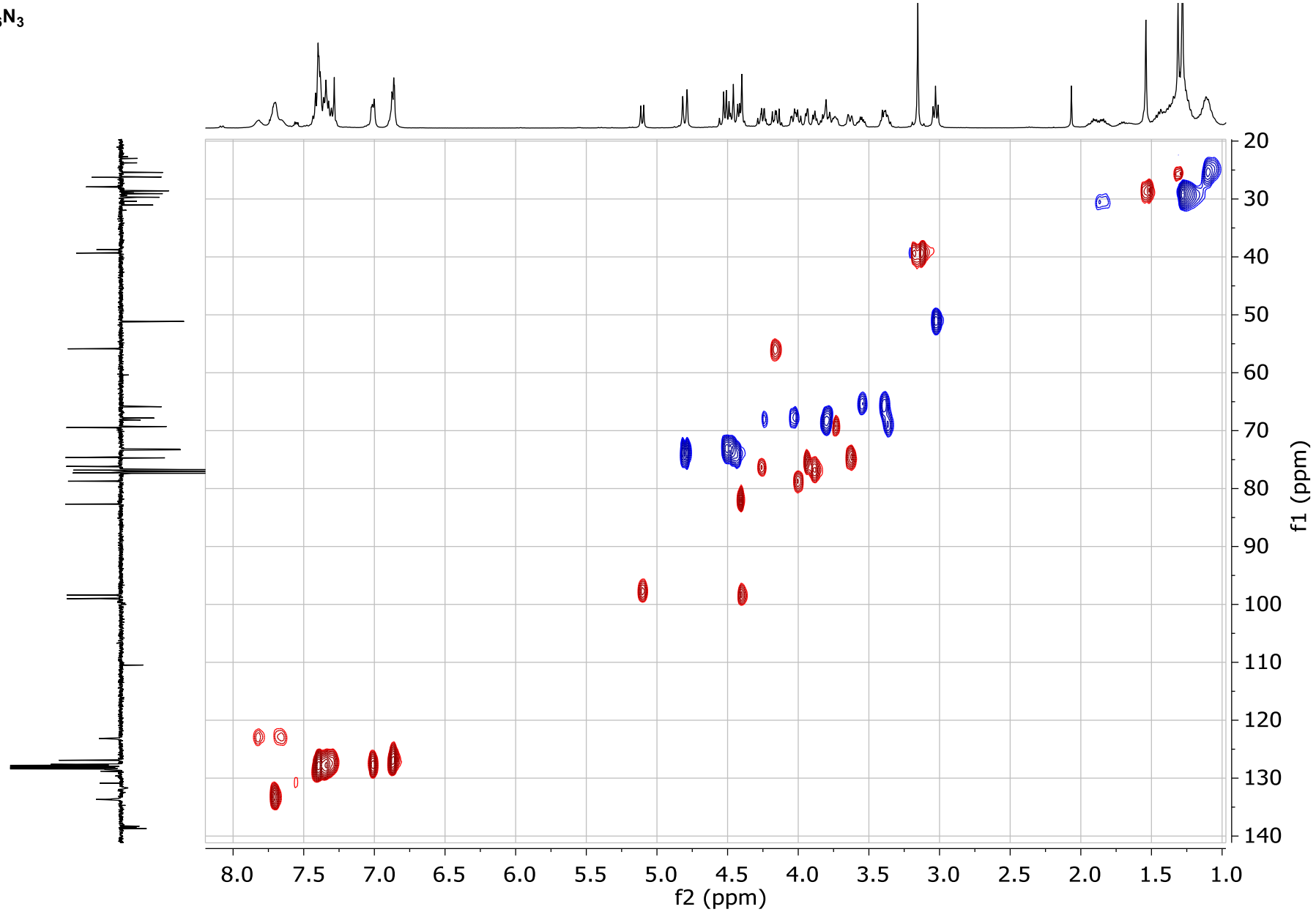
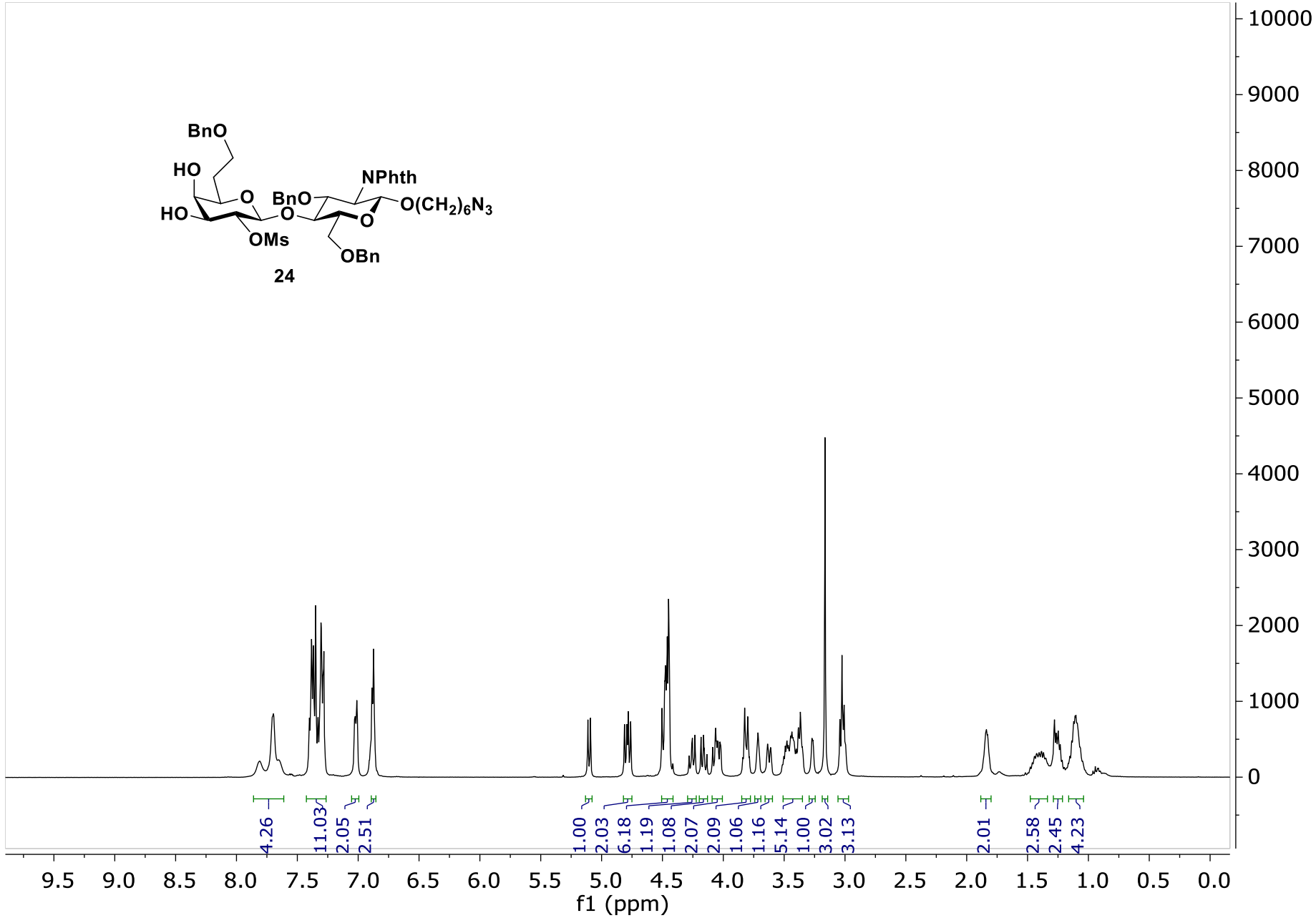
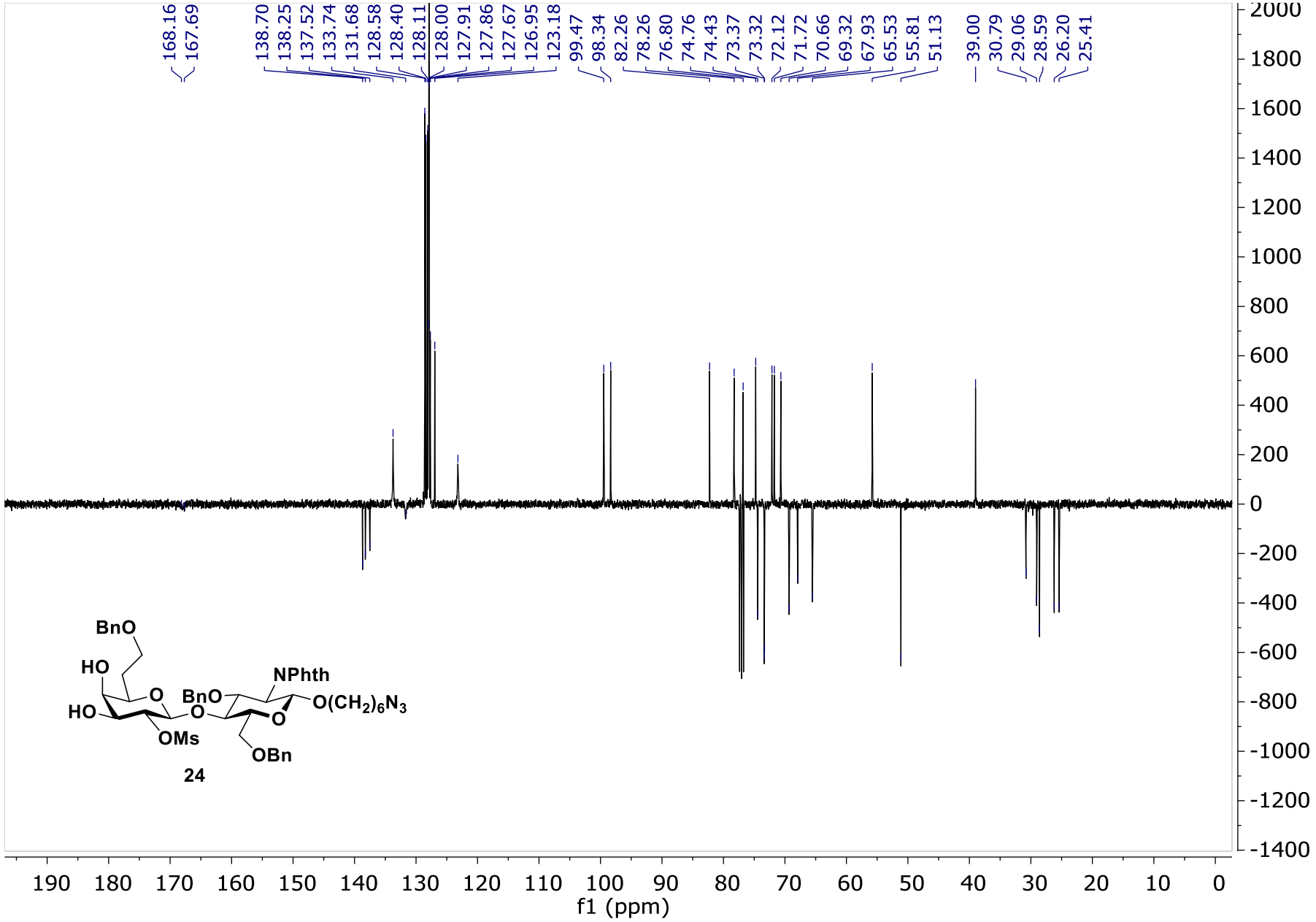


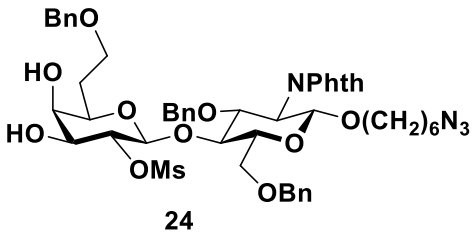
^{1}H NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



^{13}C (DEPT-Q) NMR Spectrum in $CDCl_3$, 100 MHz, 298 K



^{1}H-^{1}H GCOSY NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



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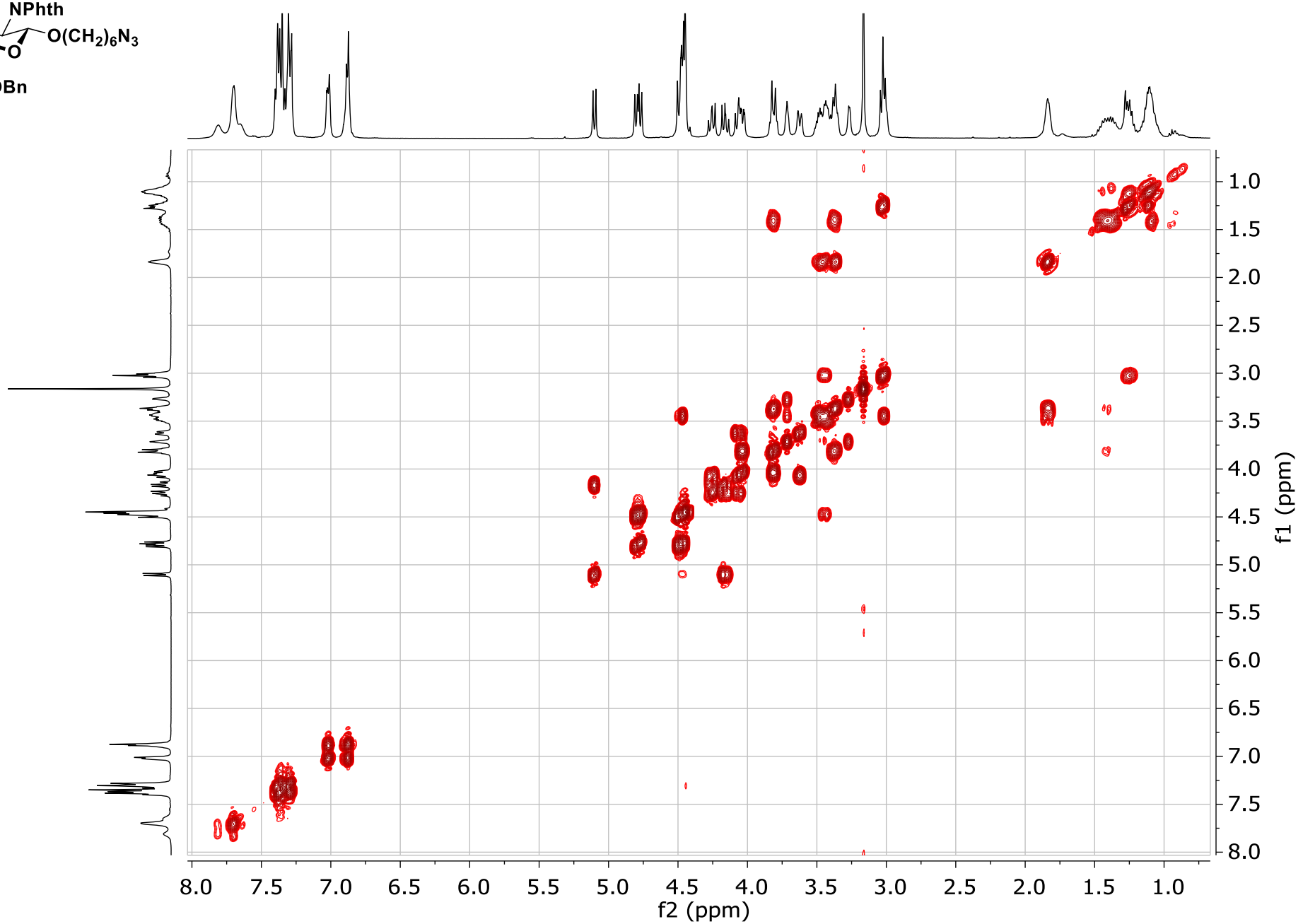
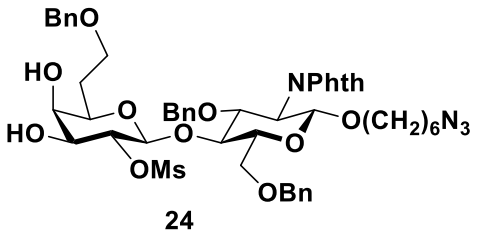


^{1}H-^{13}C GHSQC NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



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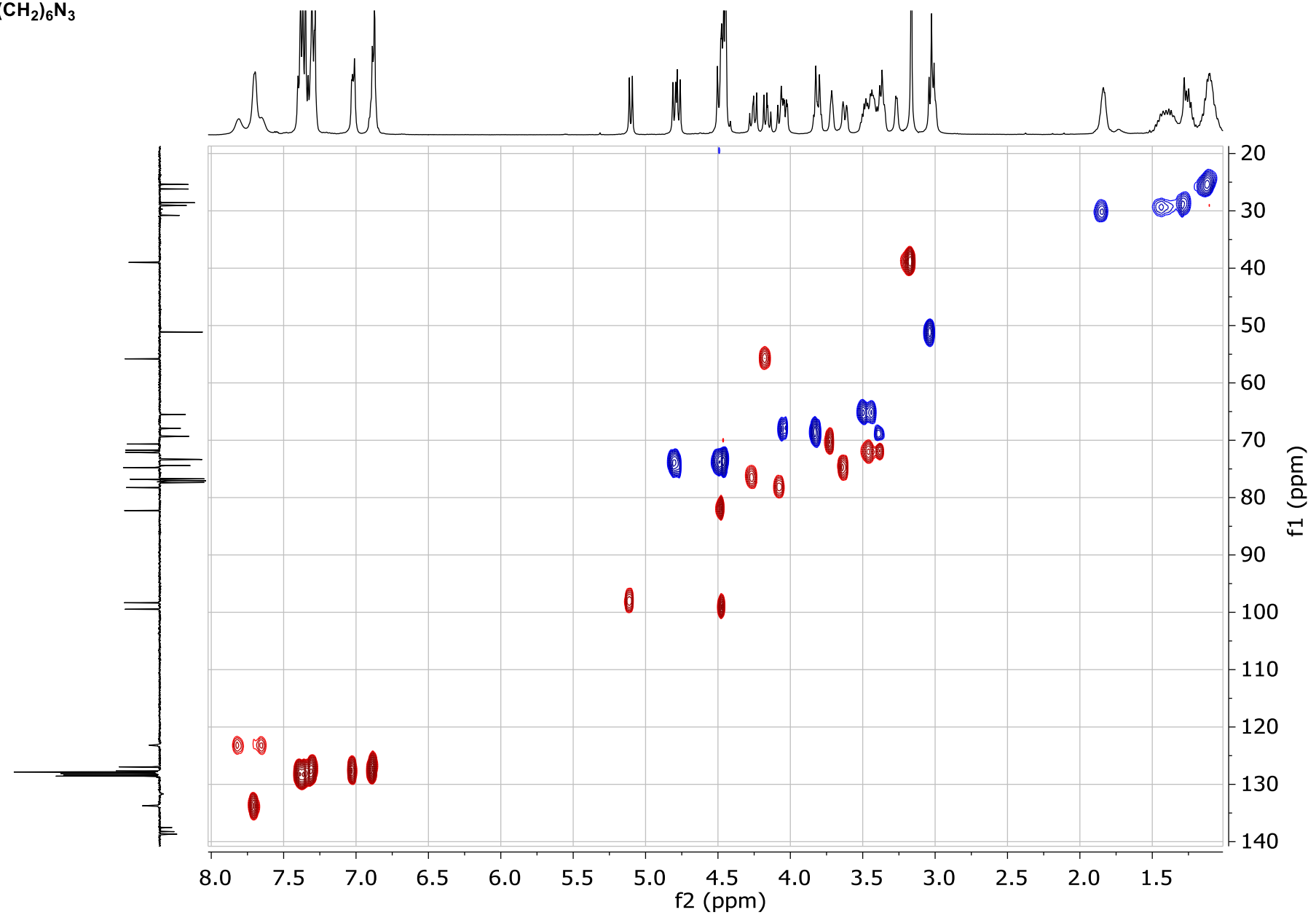
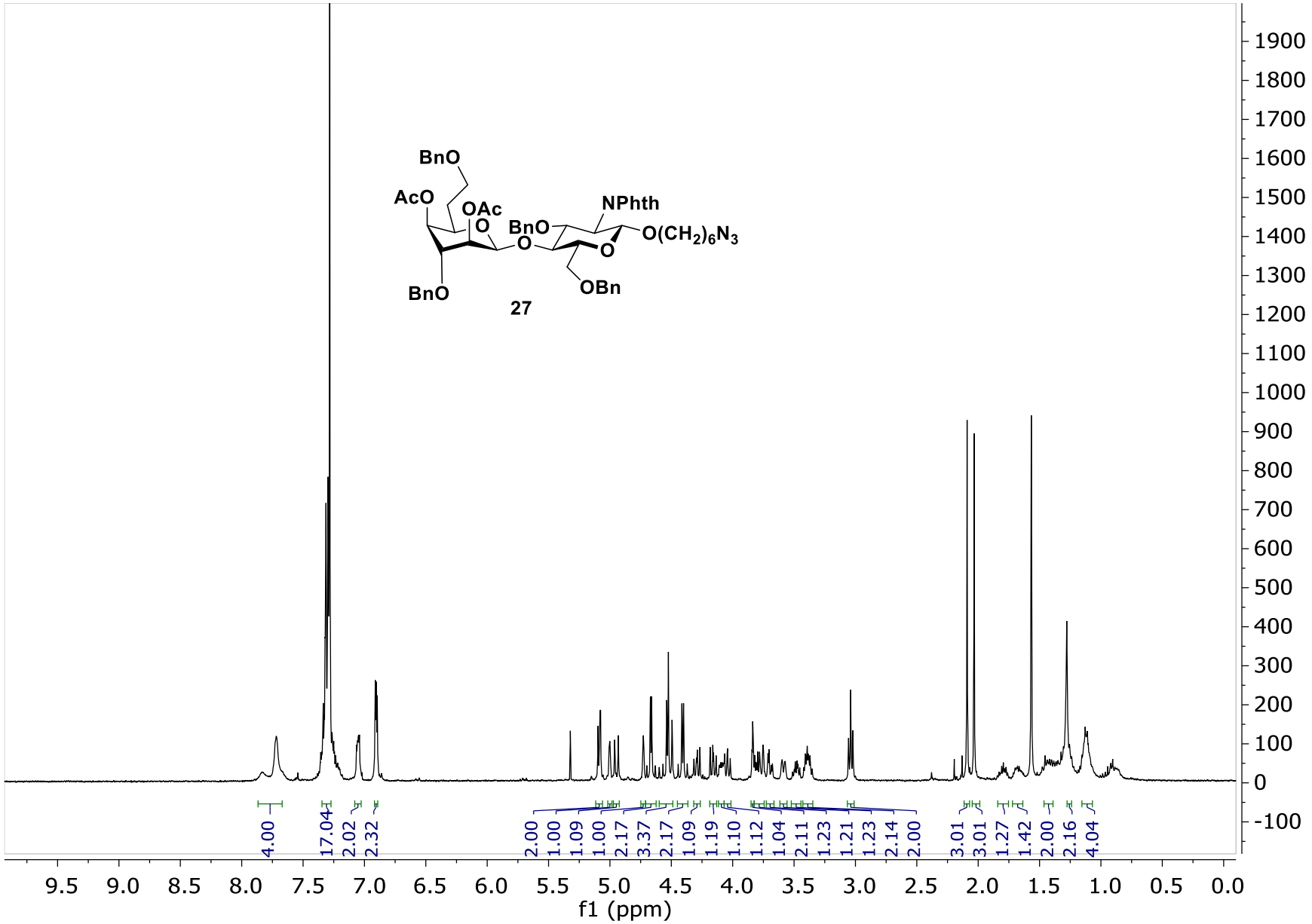
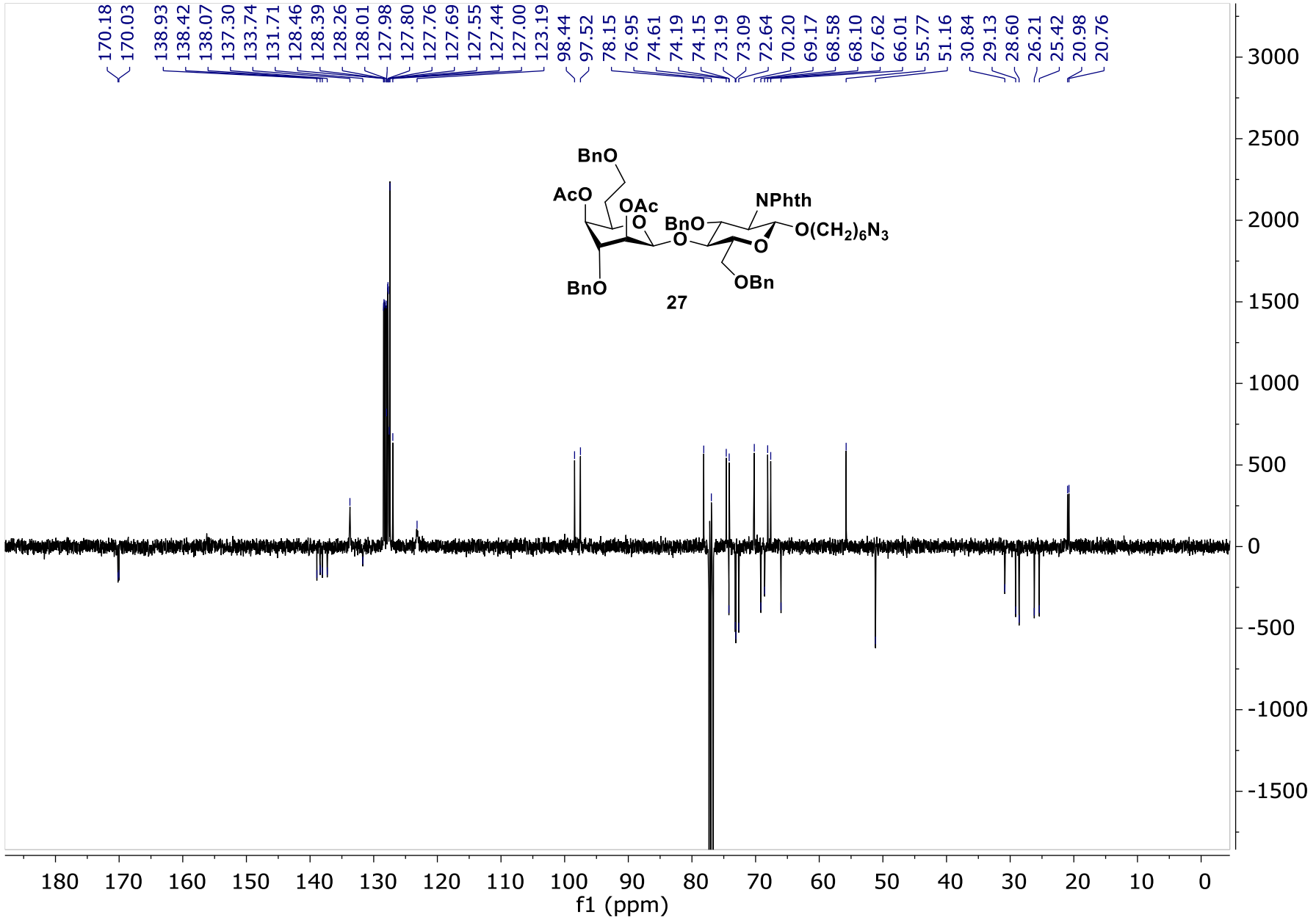


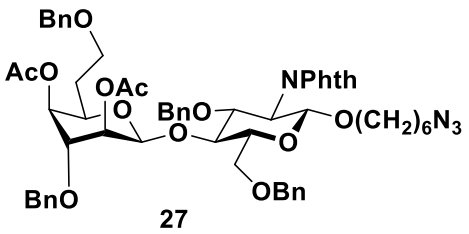
^{1}H NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



^{13}C (DEPT-Q) NMR Spectrum in $CDCl_3$, 100 MHz, 298 K



^{1}H-^{1}H GCOSY NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



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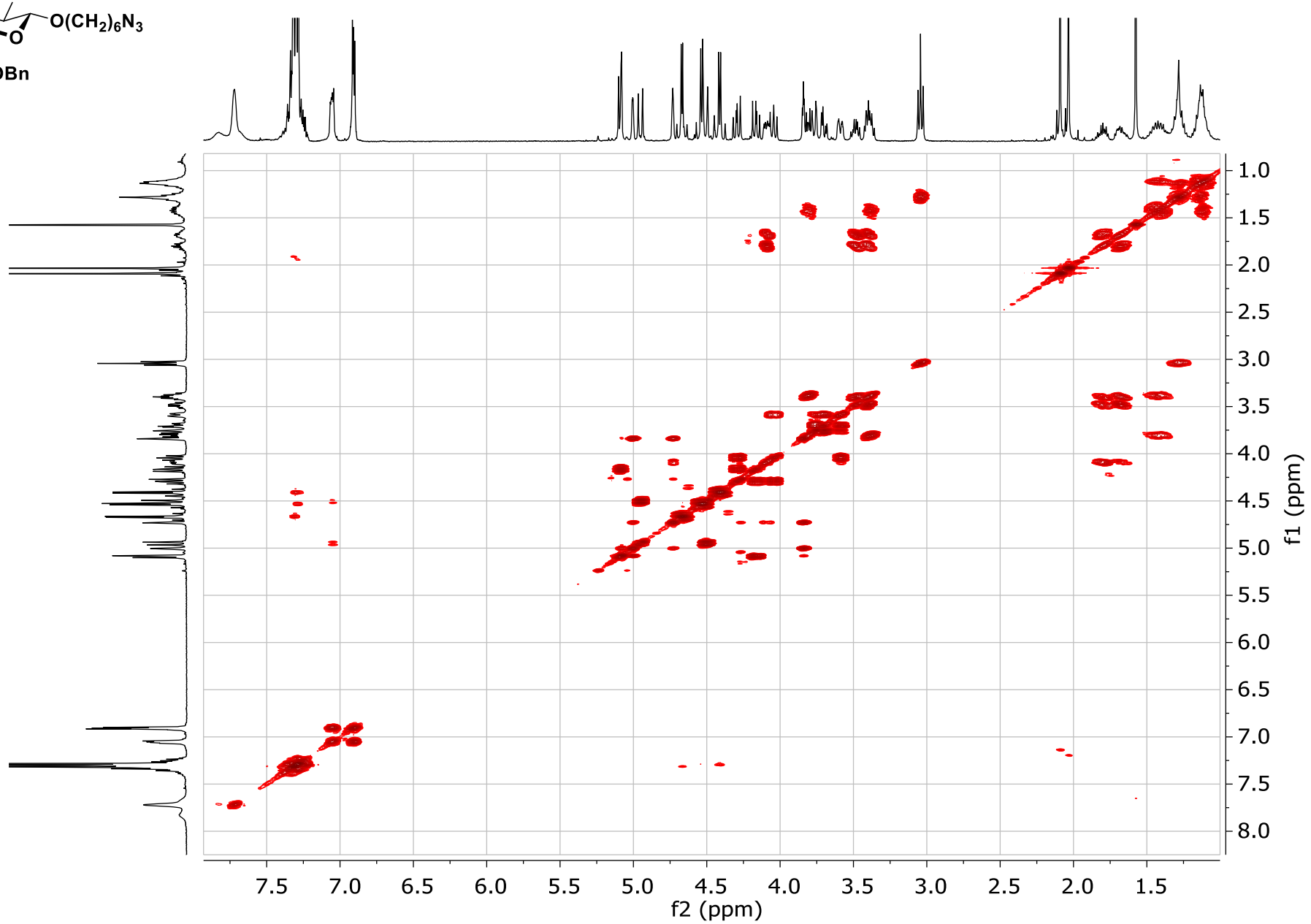
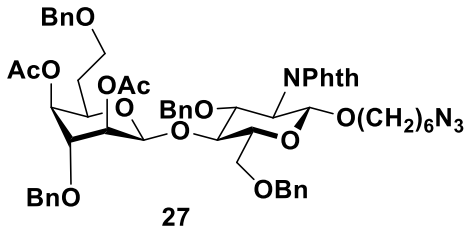


^{1}H-^{13}C GHSQC NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



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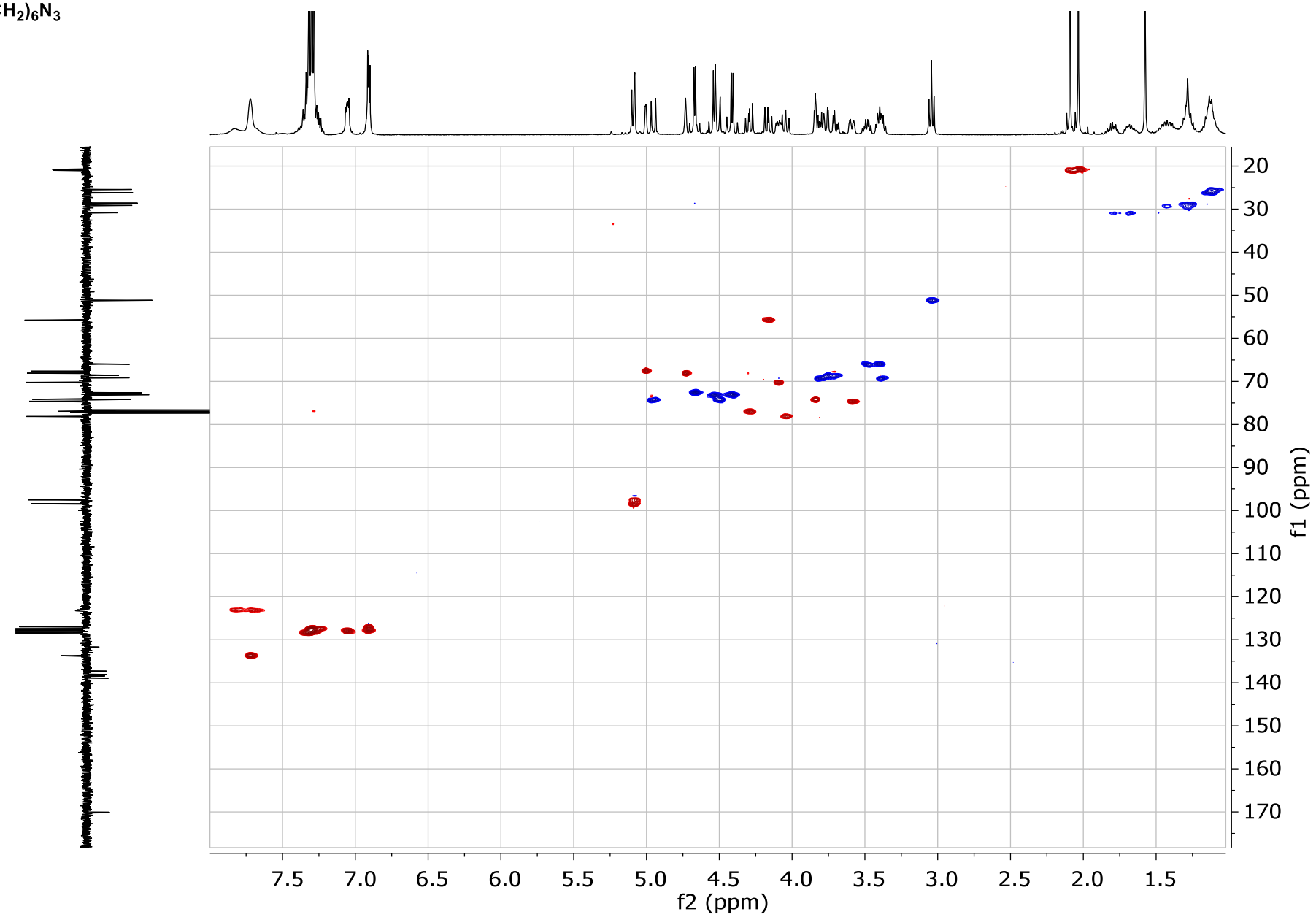
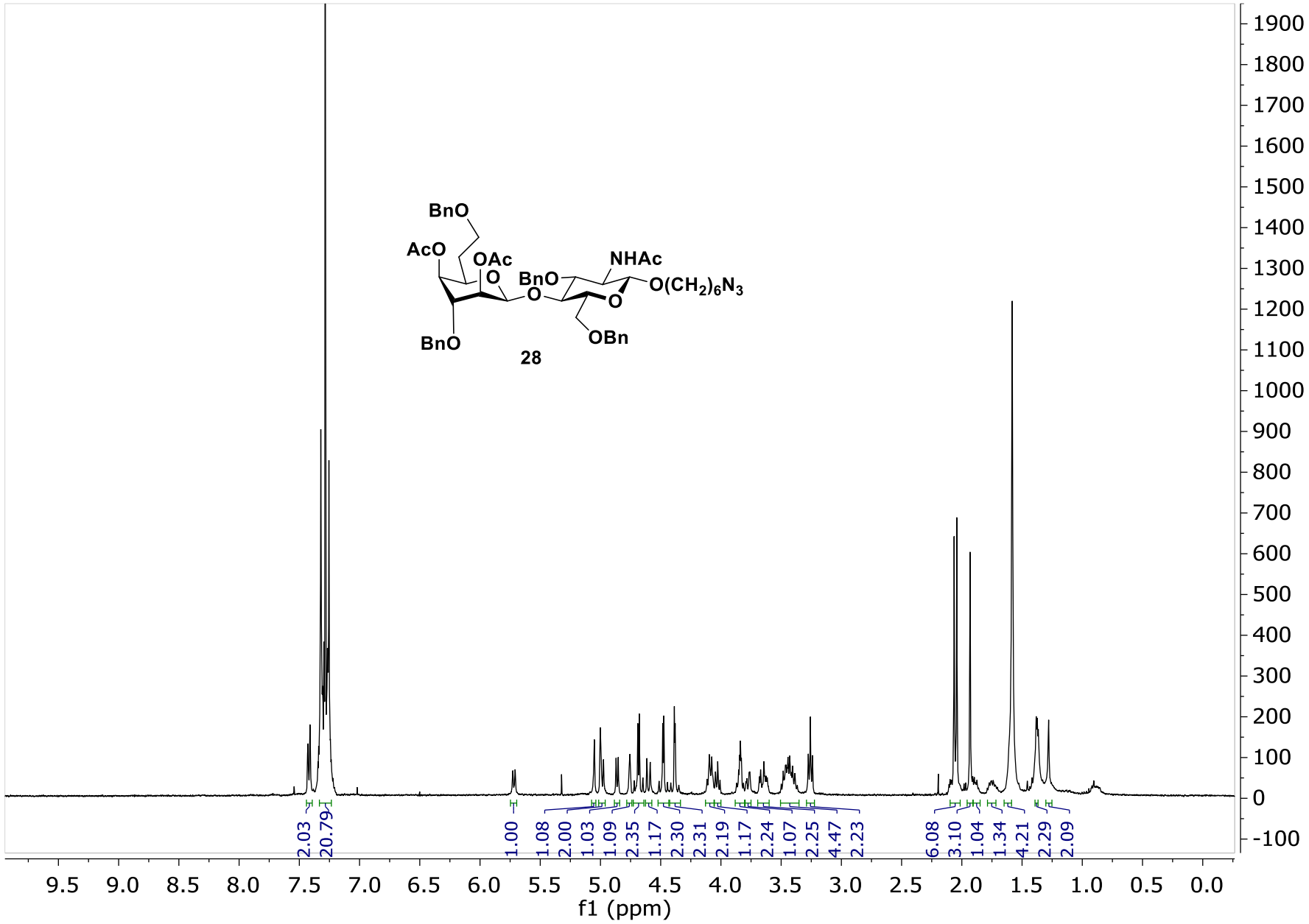
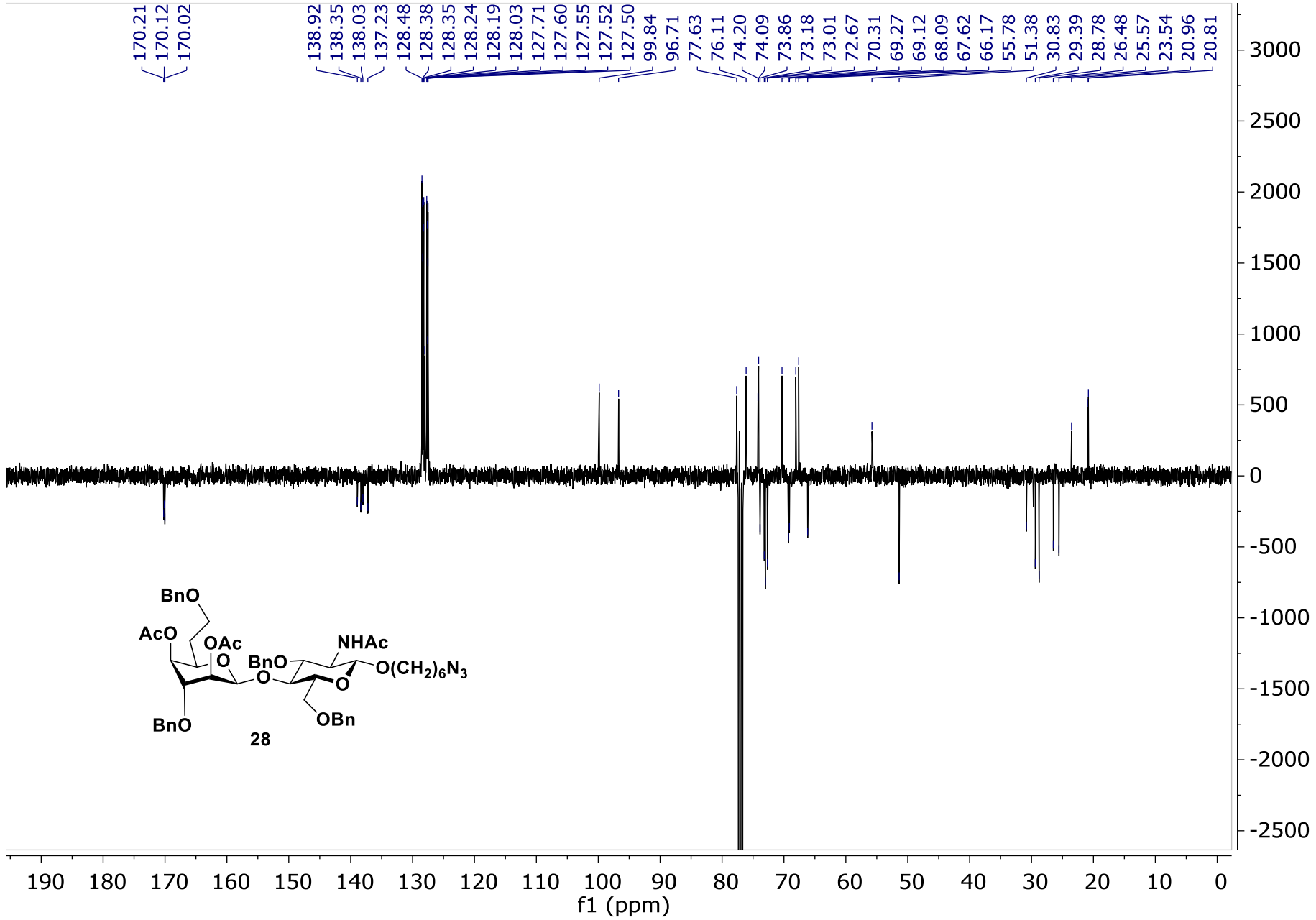
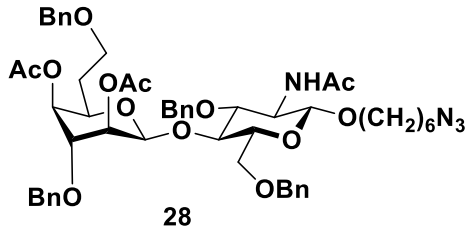


^{1}H NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



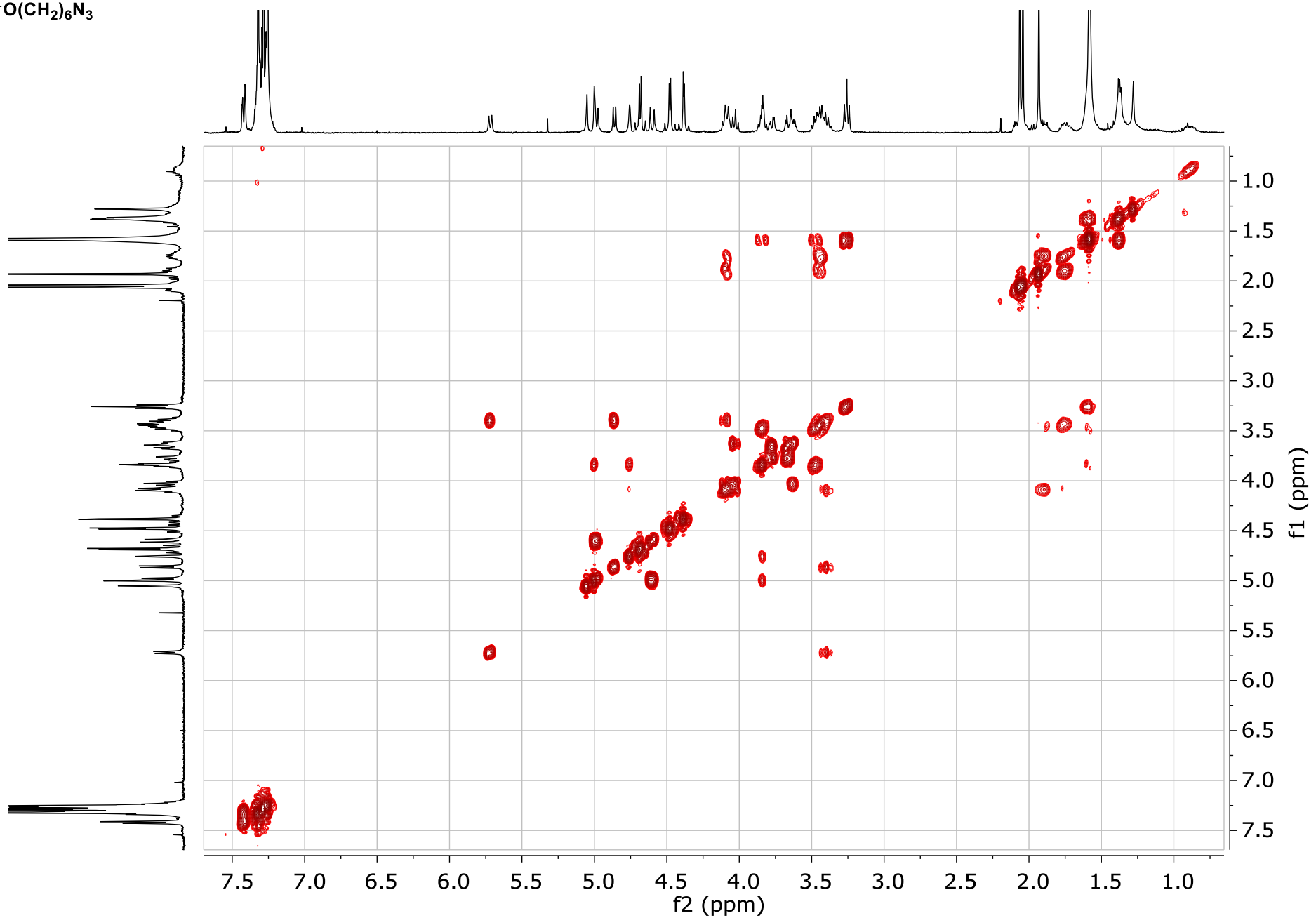
^{13}C (DEPT-Q) NMR Spectrum in $CDCl_3$, 100 MHz, 298 K

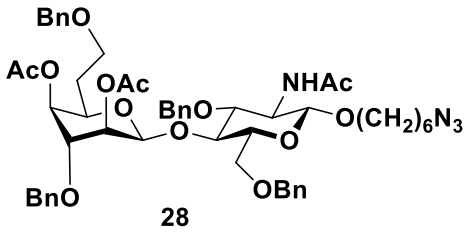




28

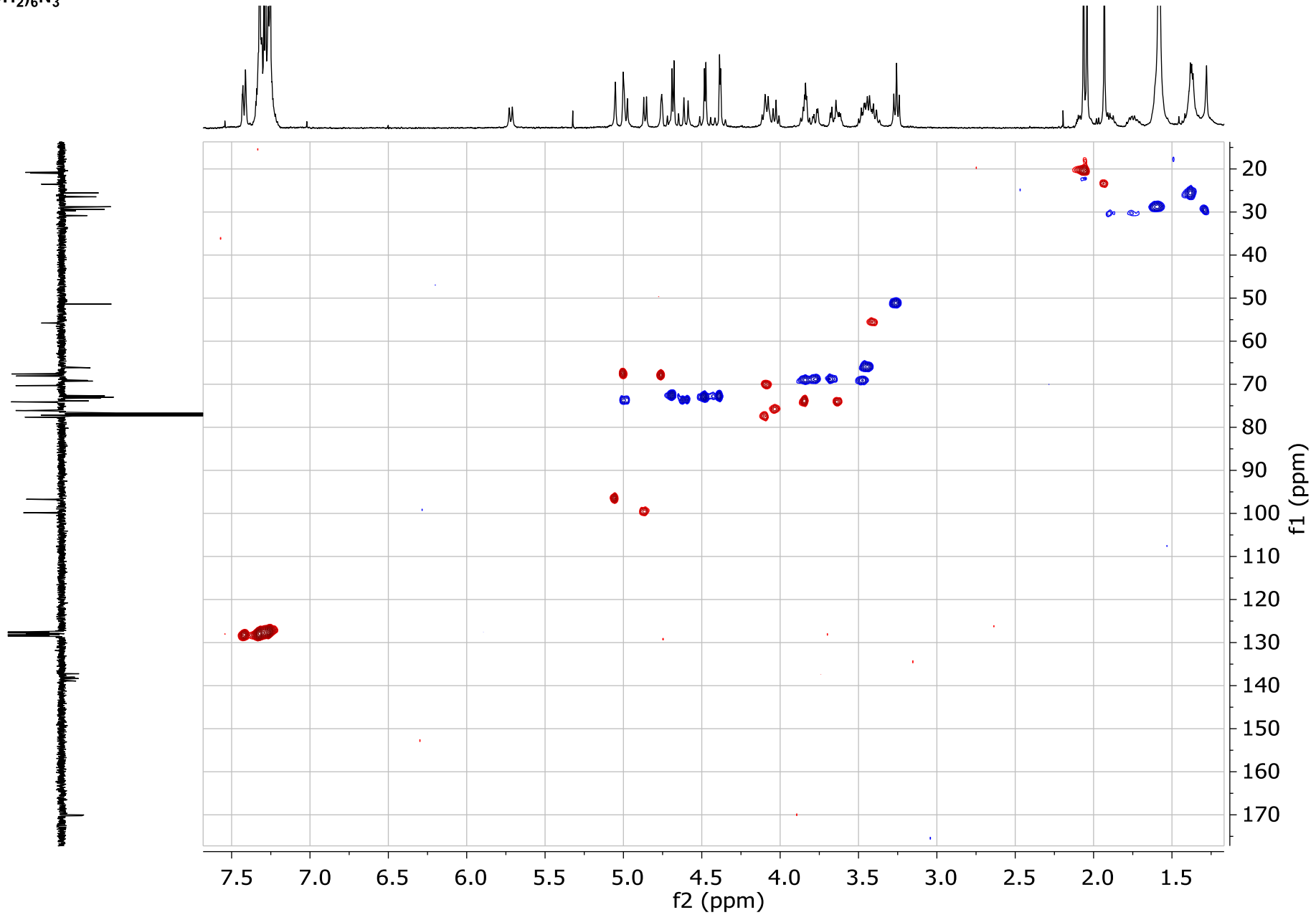
^{1}H-^{1}H GCOSY NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



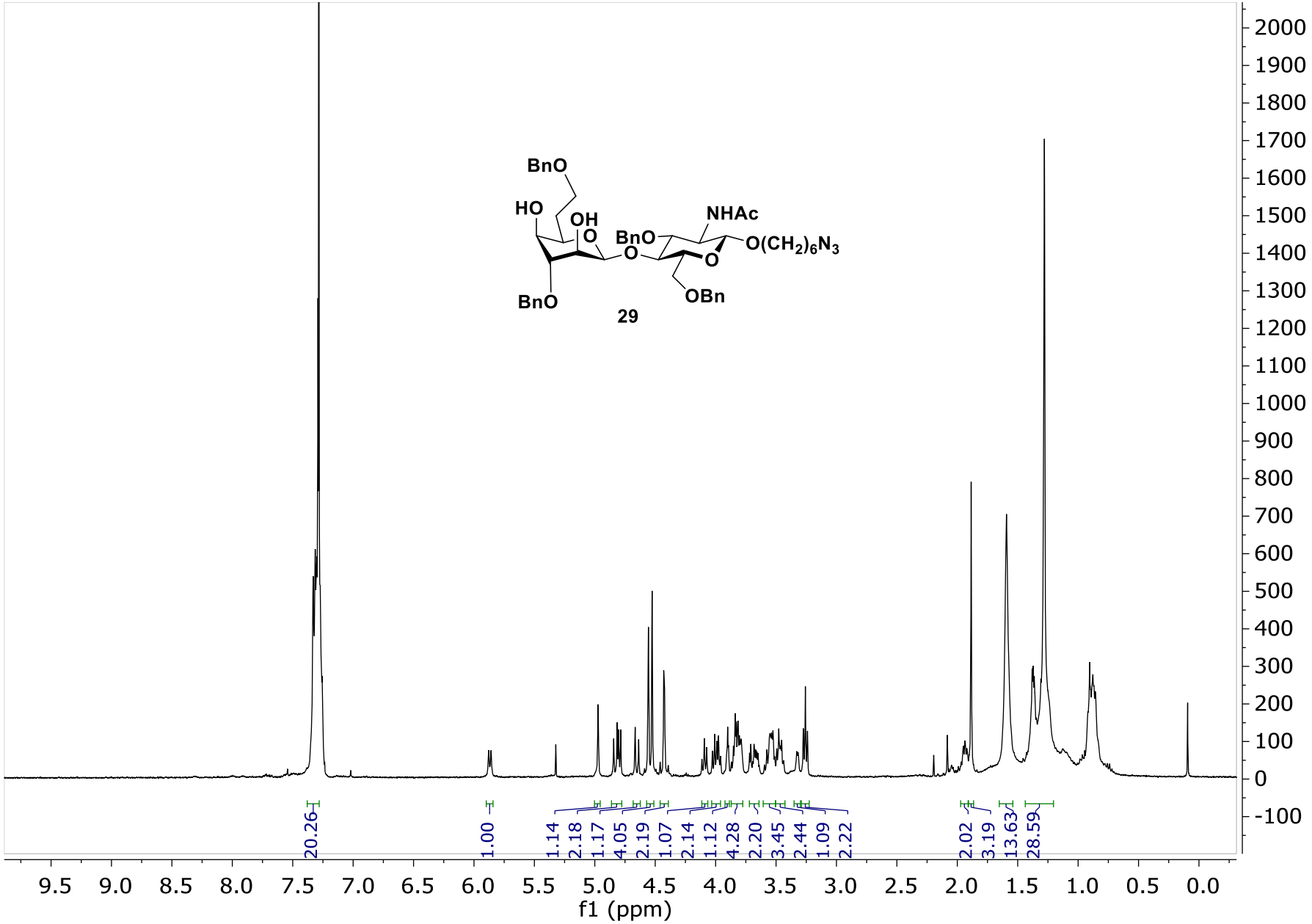


28

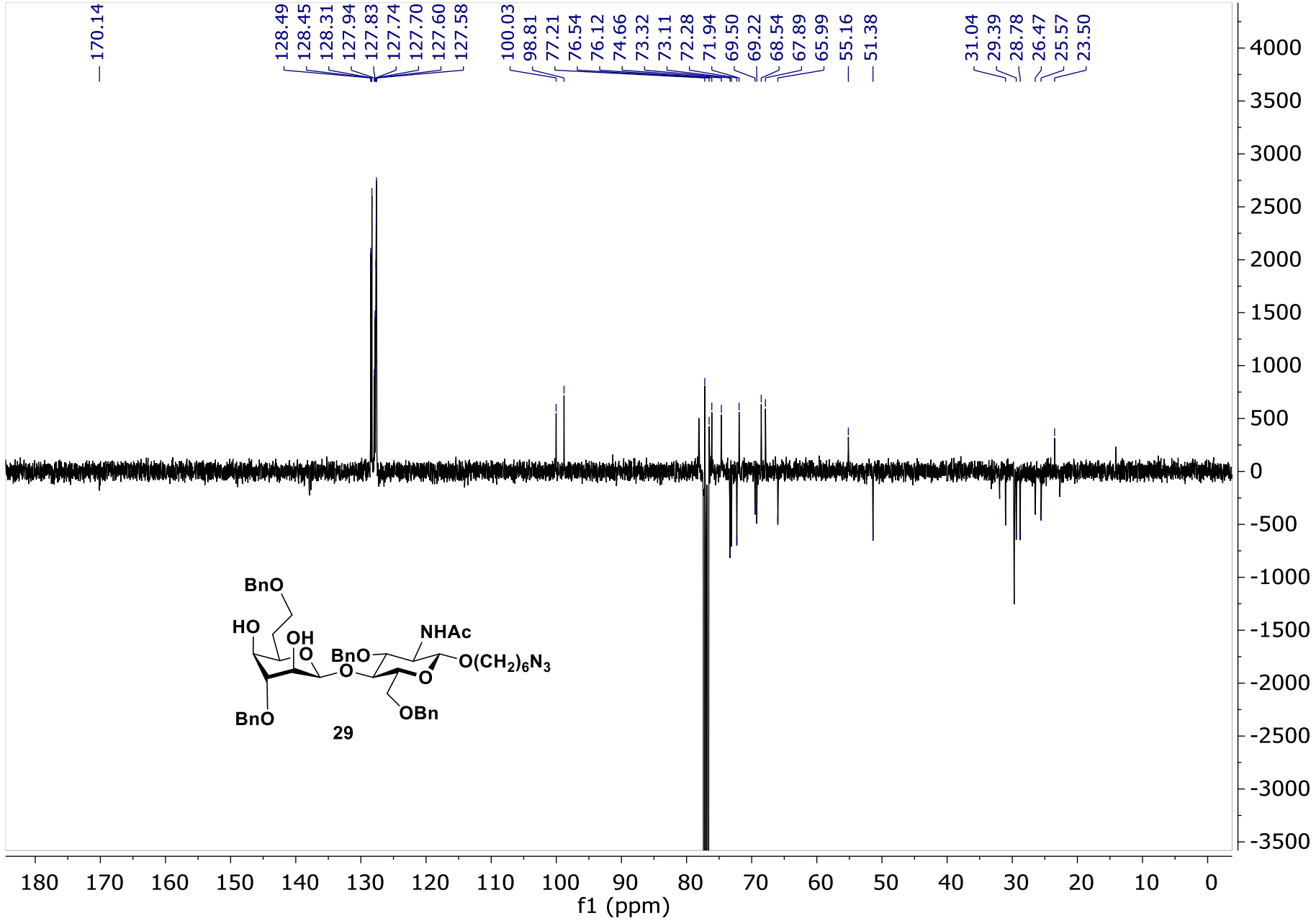
^{1}H-^{13}C GHSQC NMR Spectrum in $CDCl_3$, 400 MHz, 298 K

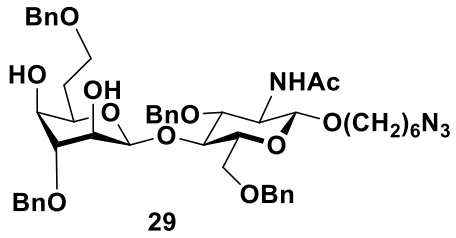


^{1}H NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



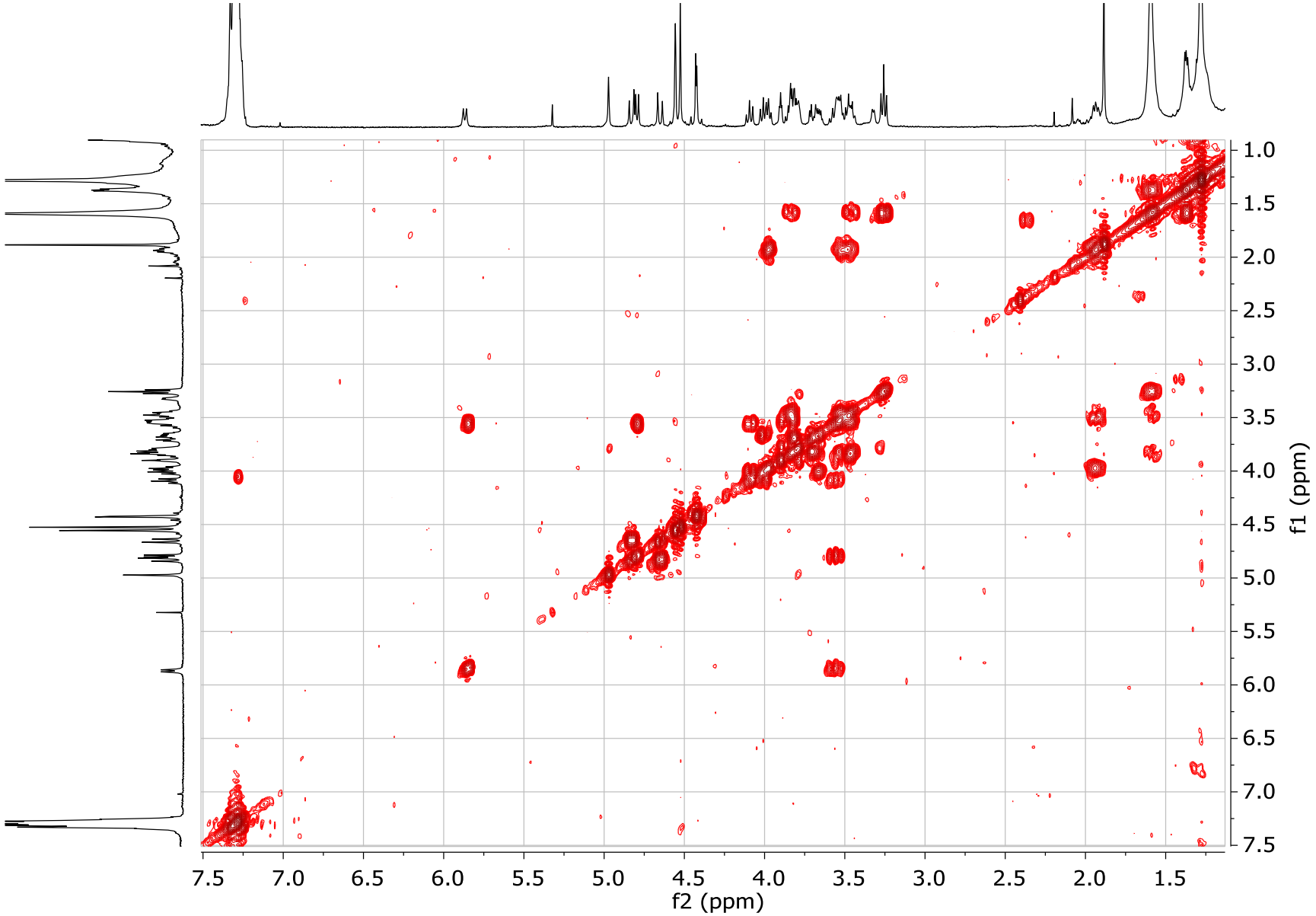
^{13}C (DEPT-Q) NMR Spectrum in $CDCl_3$, 100 MHz, 298 K

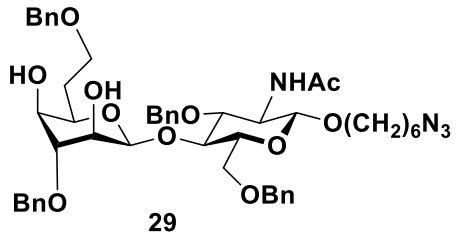




29

^{1}H-^{1}H GCOSY NMR Spectrum in $CDCl_3$, 400 MHz, 298 K





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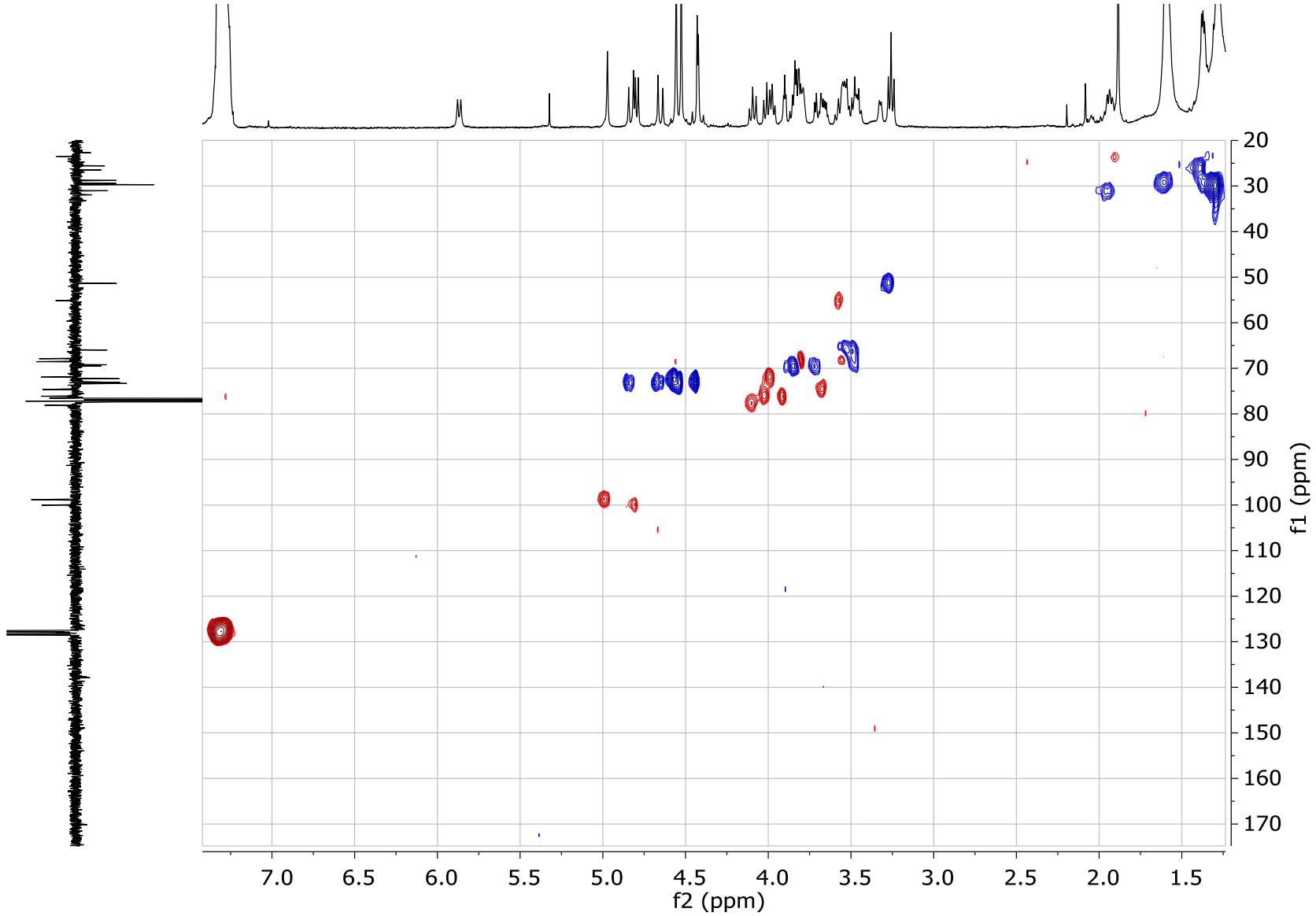
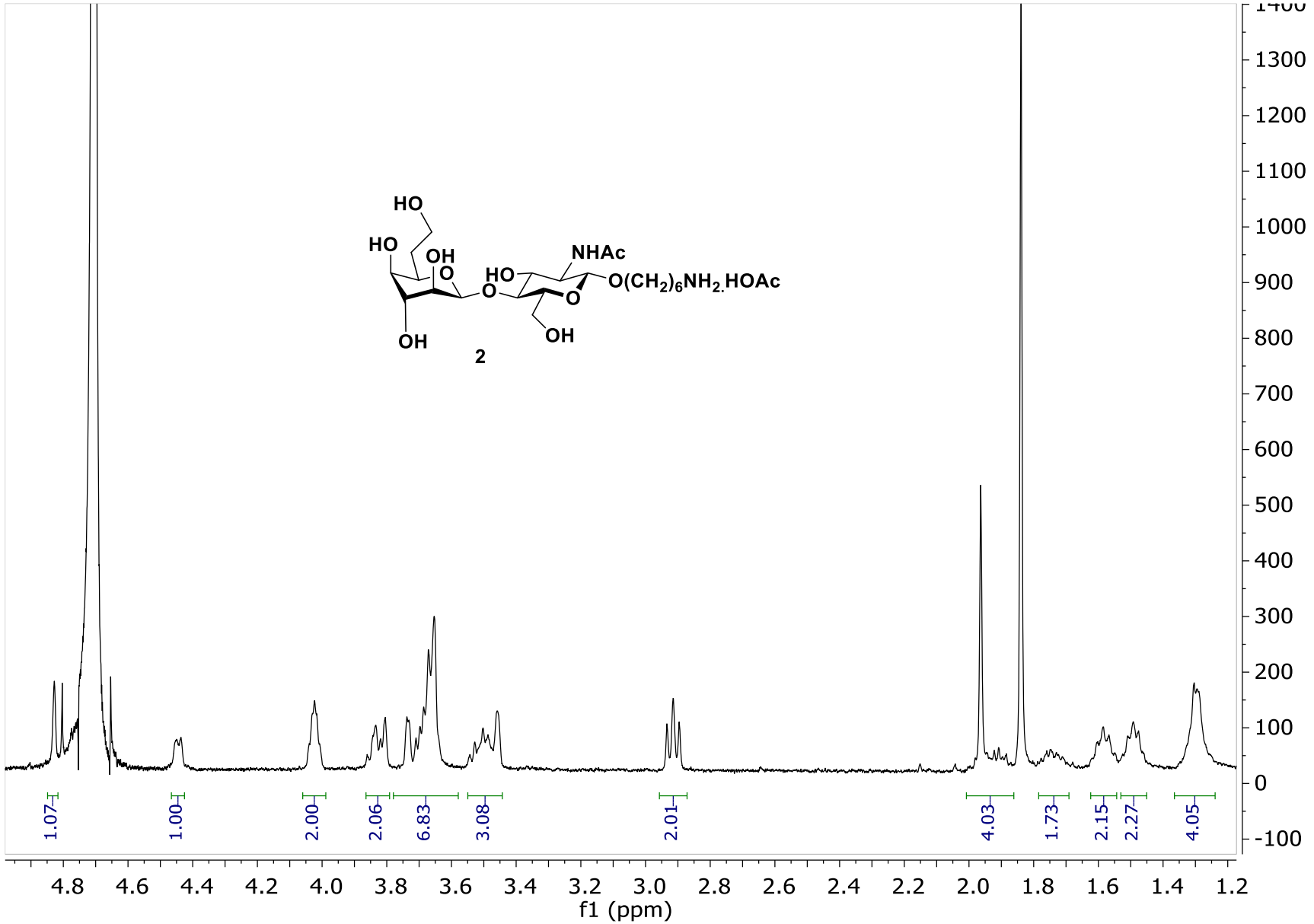
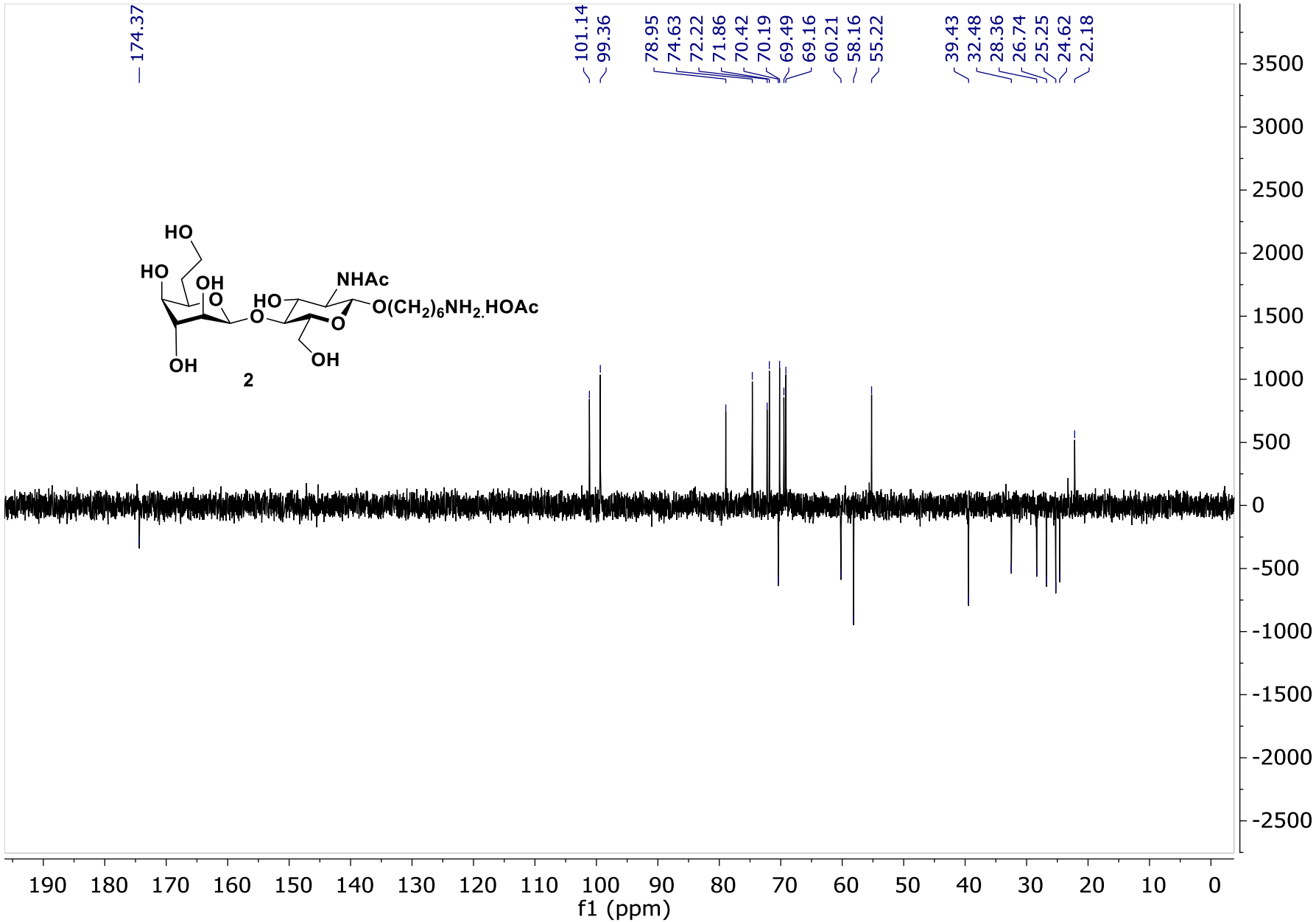
^{1}H-^{13}C GHSQC NMR Spectrum in $CDCl_3$, 400 MHz, 298 K

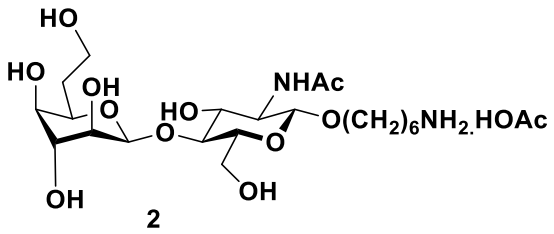


^{1}H NMR Spectrum in D_2O, 400 MHz, 298 K



^{13}C (DEPT-Q) NMR Spectrum in D_2O, 100 MHz, 298 K





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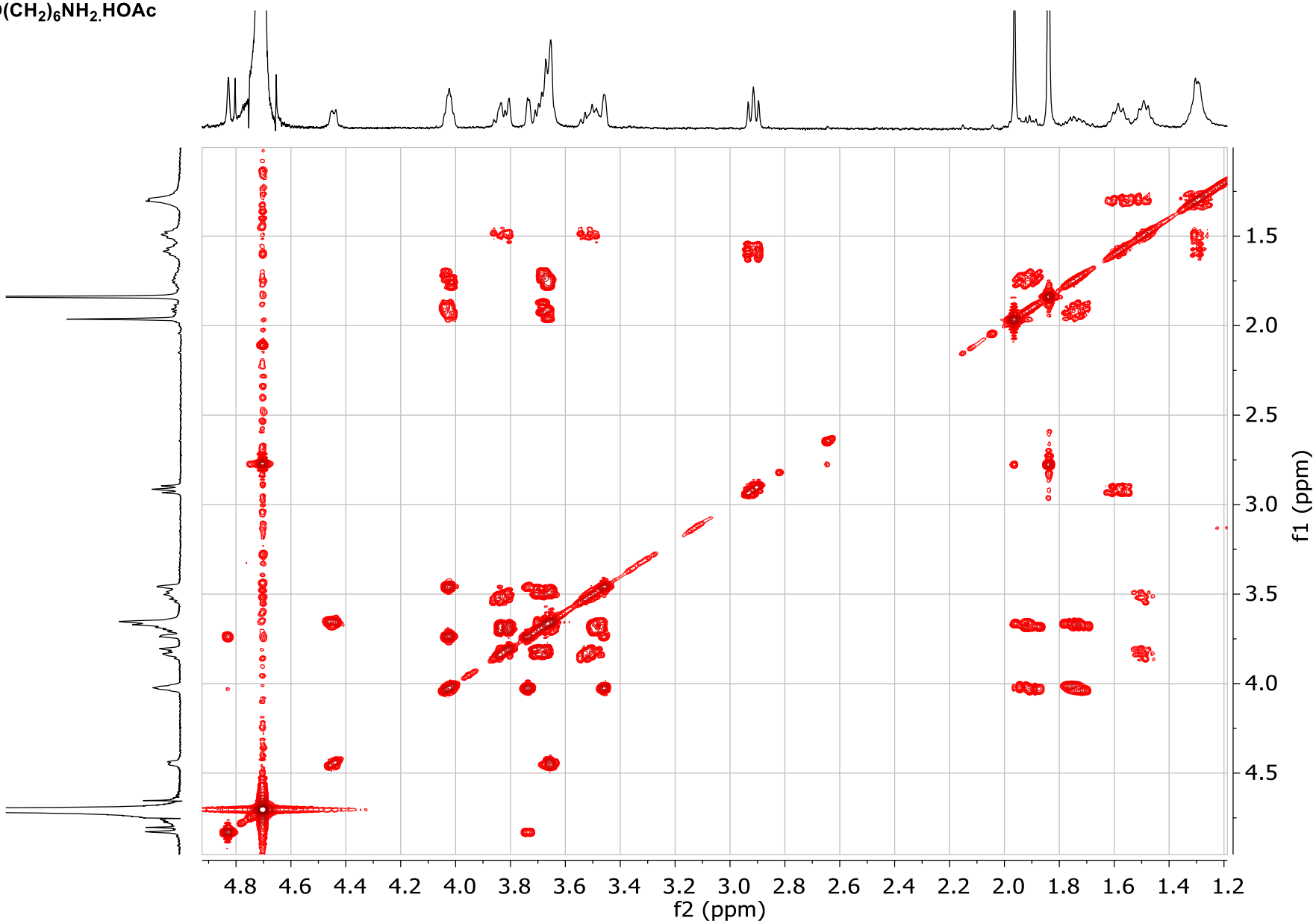
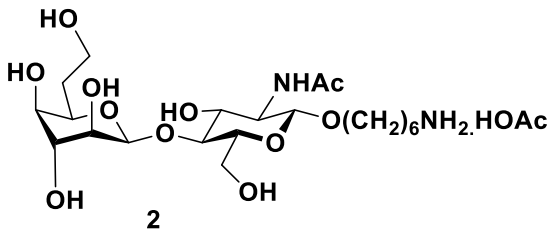
^{1}H-^{1}H GCOSY NMR Spectrum in D_2O, 400 MHz, 298 K



^{1}H-^{13}C GHSQC NMR Spectrum in D_2O, 400 MHz, 298 K



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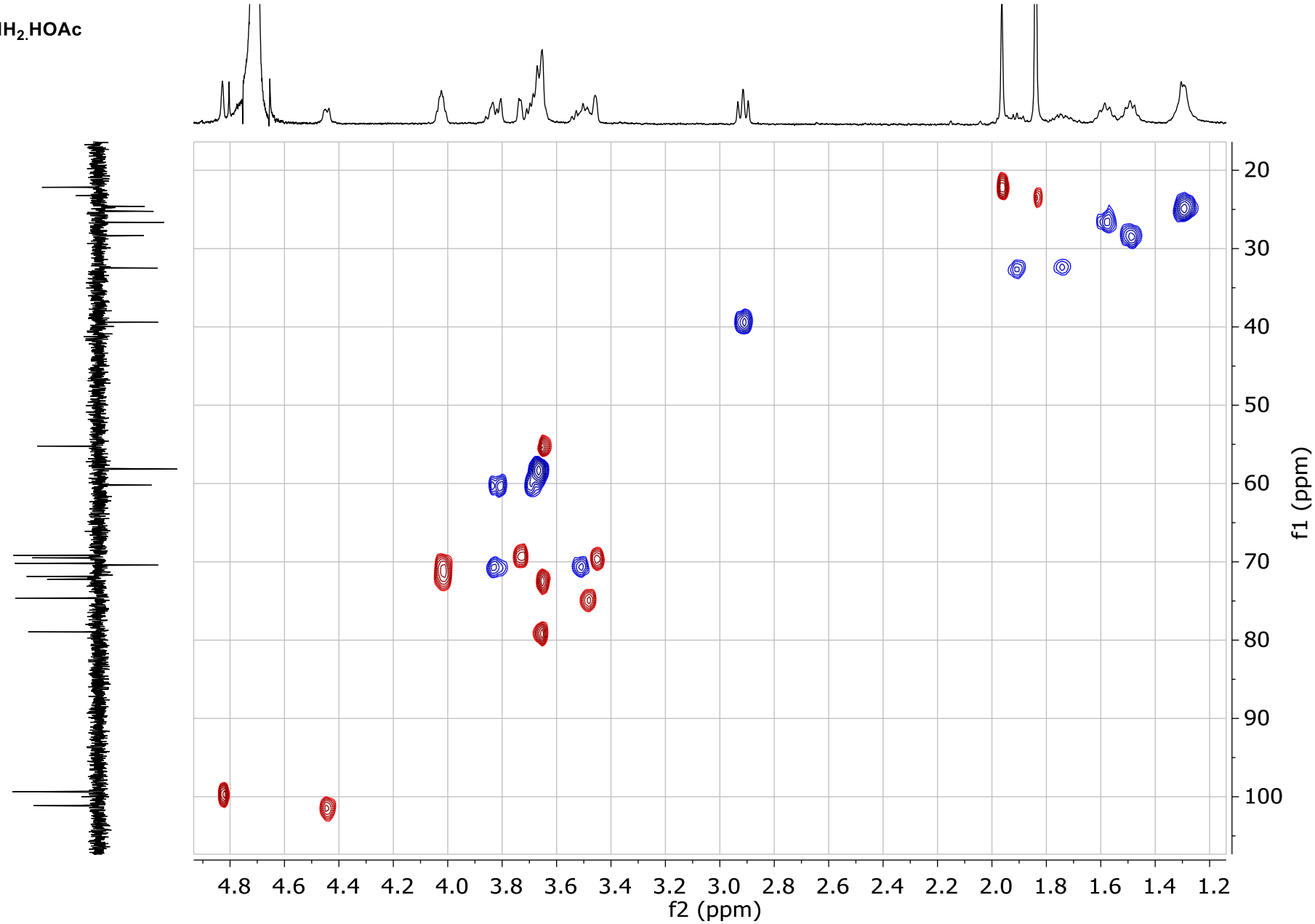
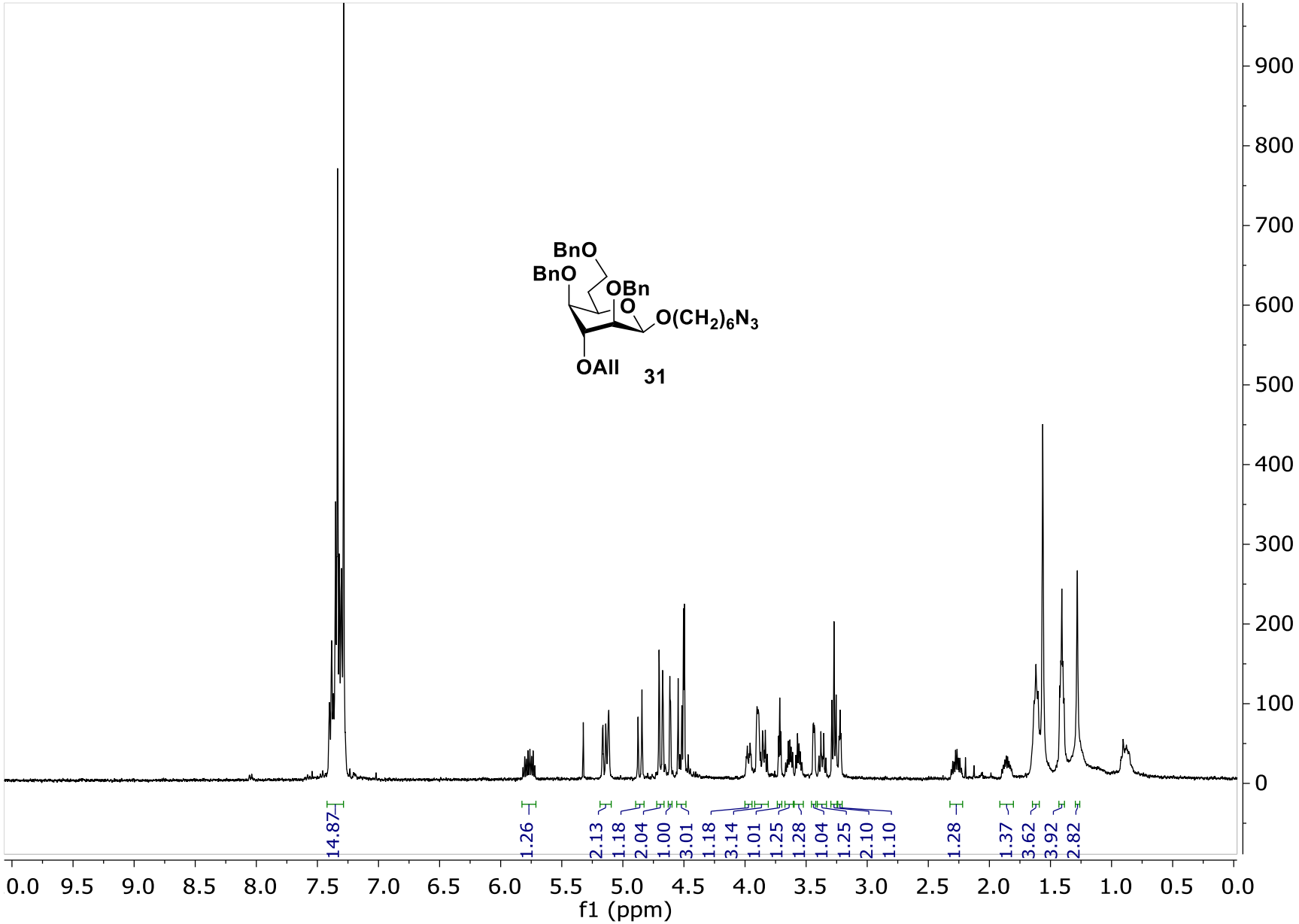
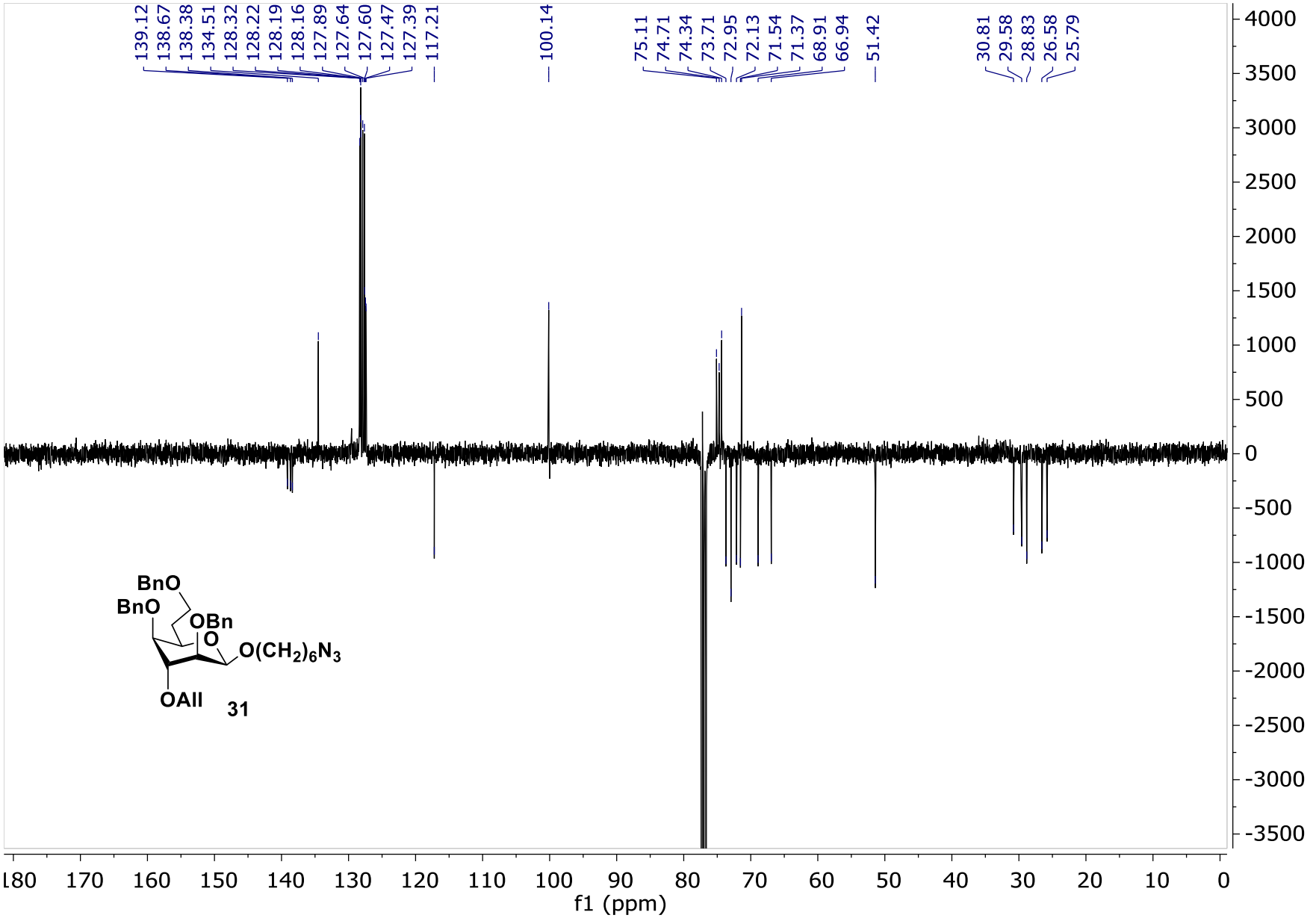
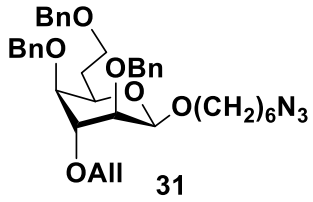


^{1}H NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



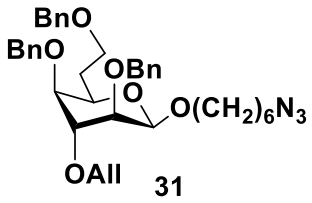
^{13}C (DEPT-Q) NMR Spectrum in $CDCl_3$, 100 MHz, 298 K





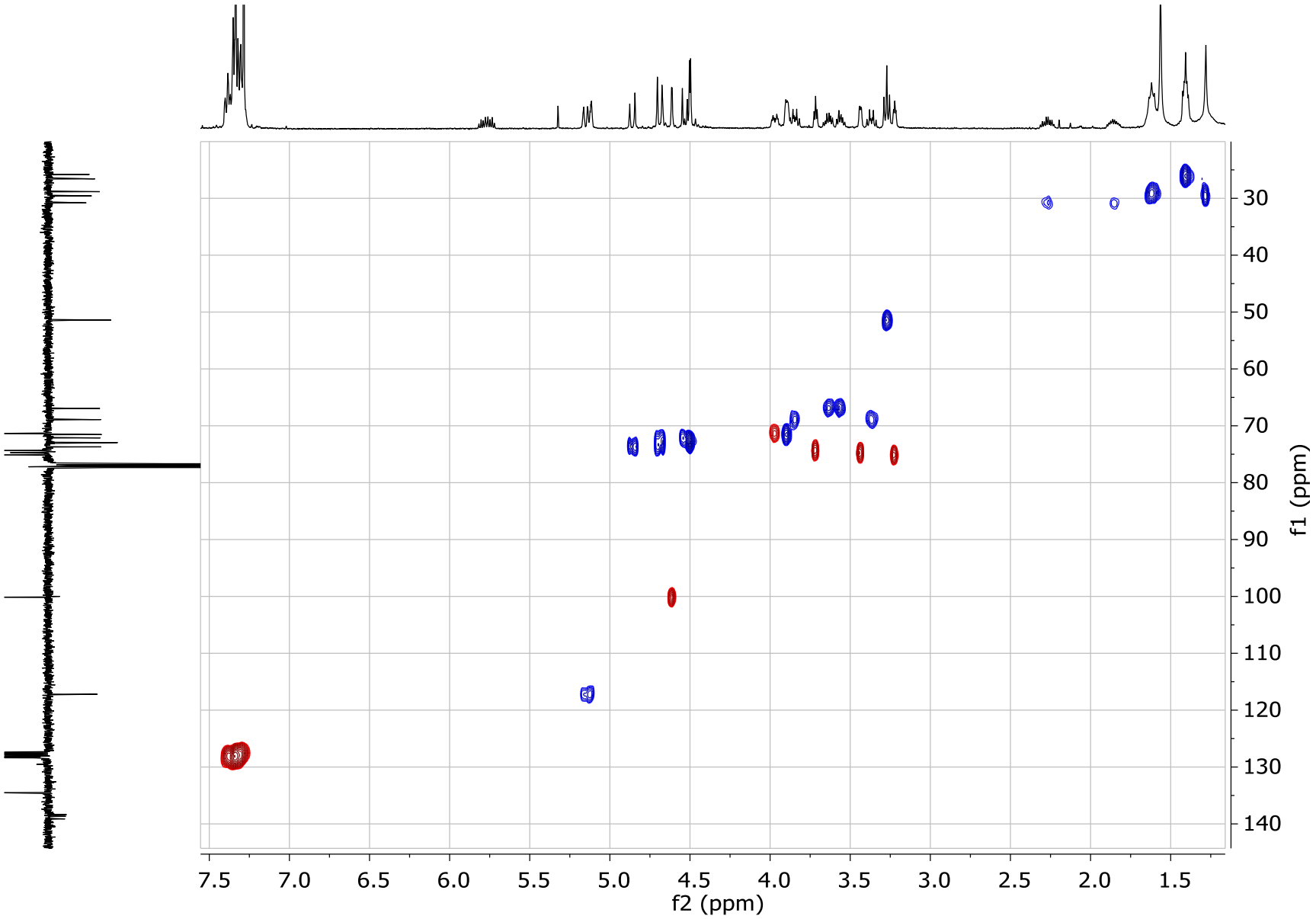
31

^{1}H-^{1}H GCOSY NMR Spectrum in $CDCl_3$, 400 MHz, 298 K

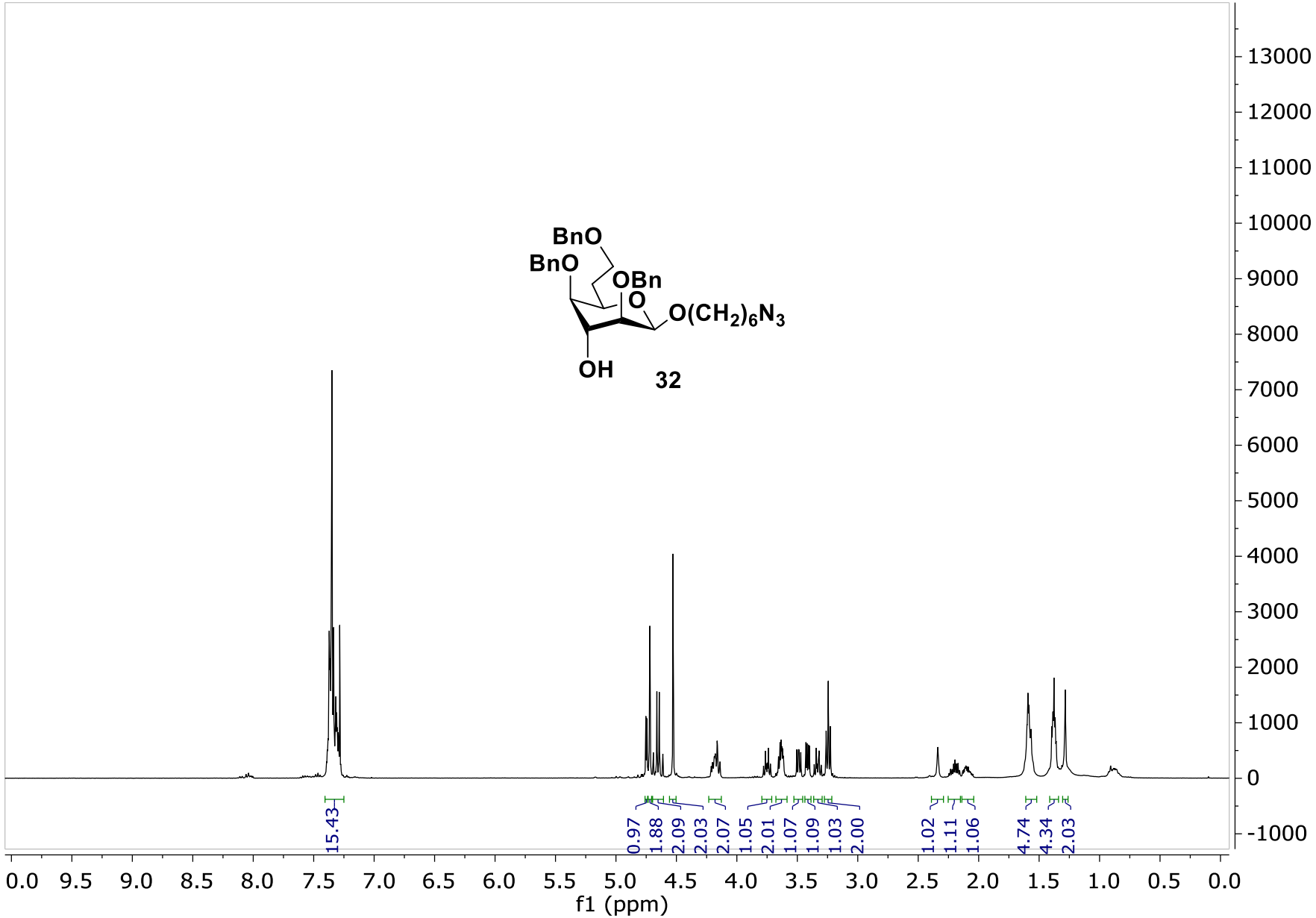


31

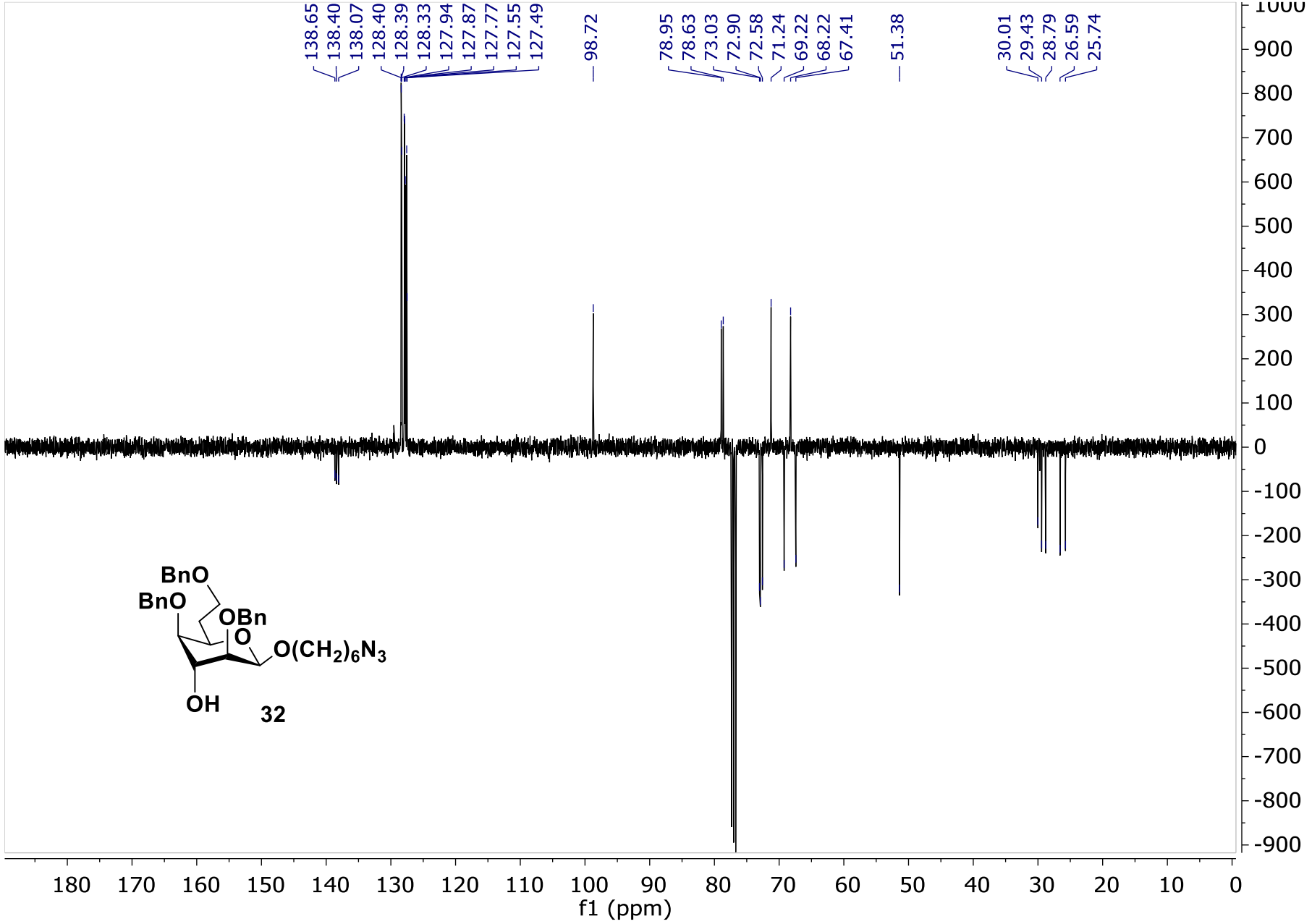
^{1}H-^{13}C GHSQC NMR Spectrum in $CDCl_3$, 400 MHz, 298 K

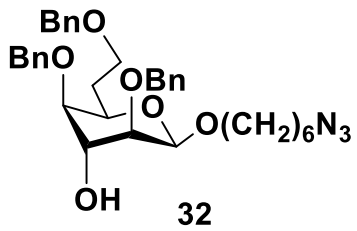


^{1}H NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



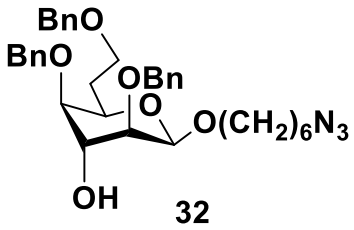
^{13}C (DEPT-Q) NMR Spectrum in $CDCl_3$, 100 MHz, 298 K





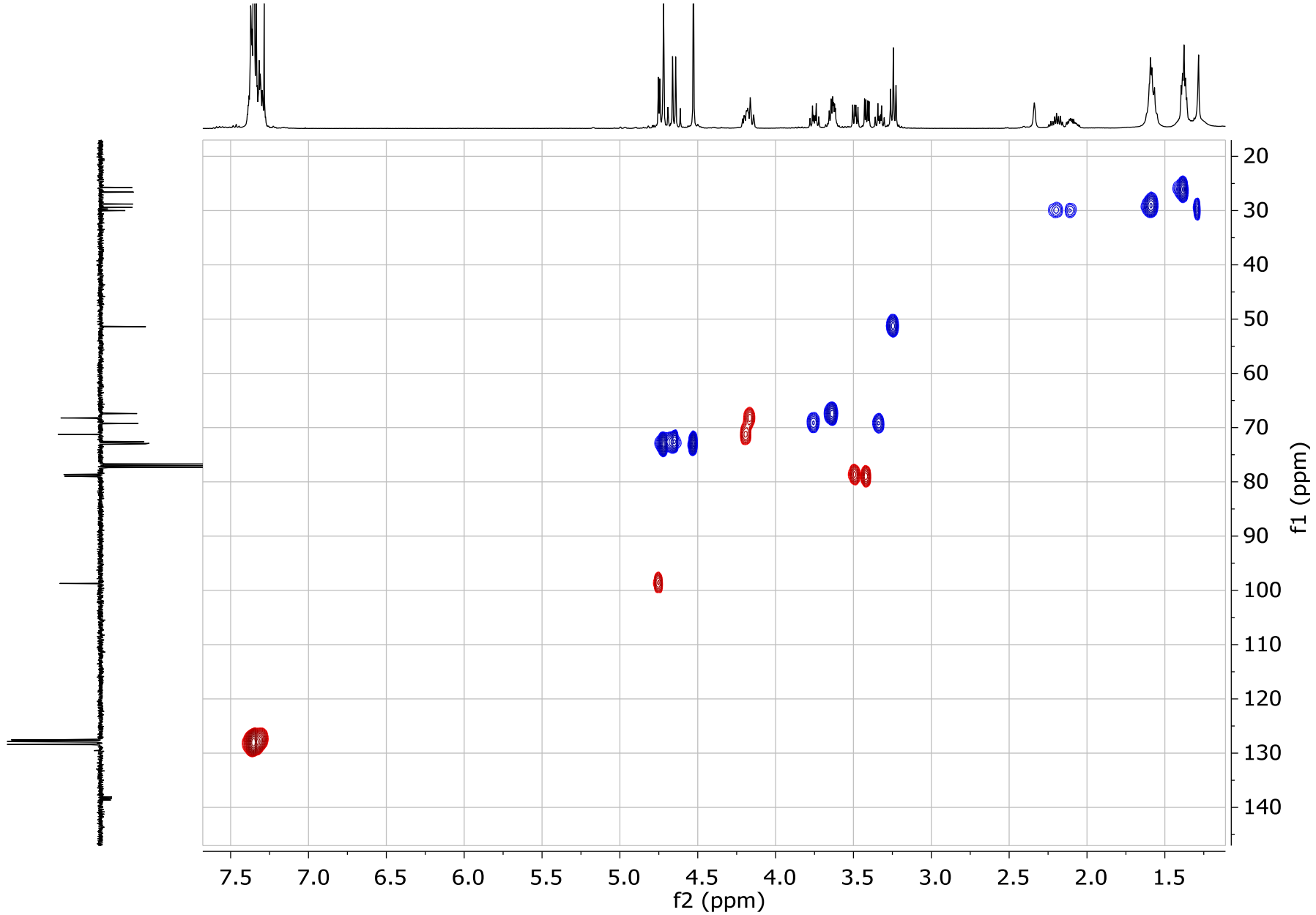
32

^{1}H-^{1}H GCOSY NMR Spectrum in $CDCl_3$, 400 MHz, 298 K

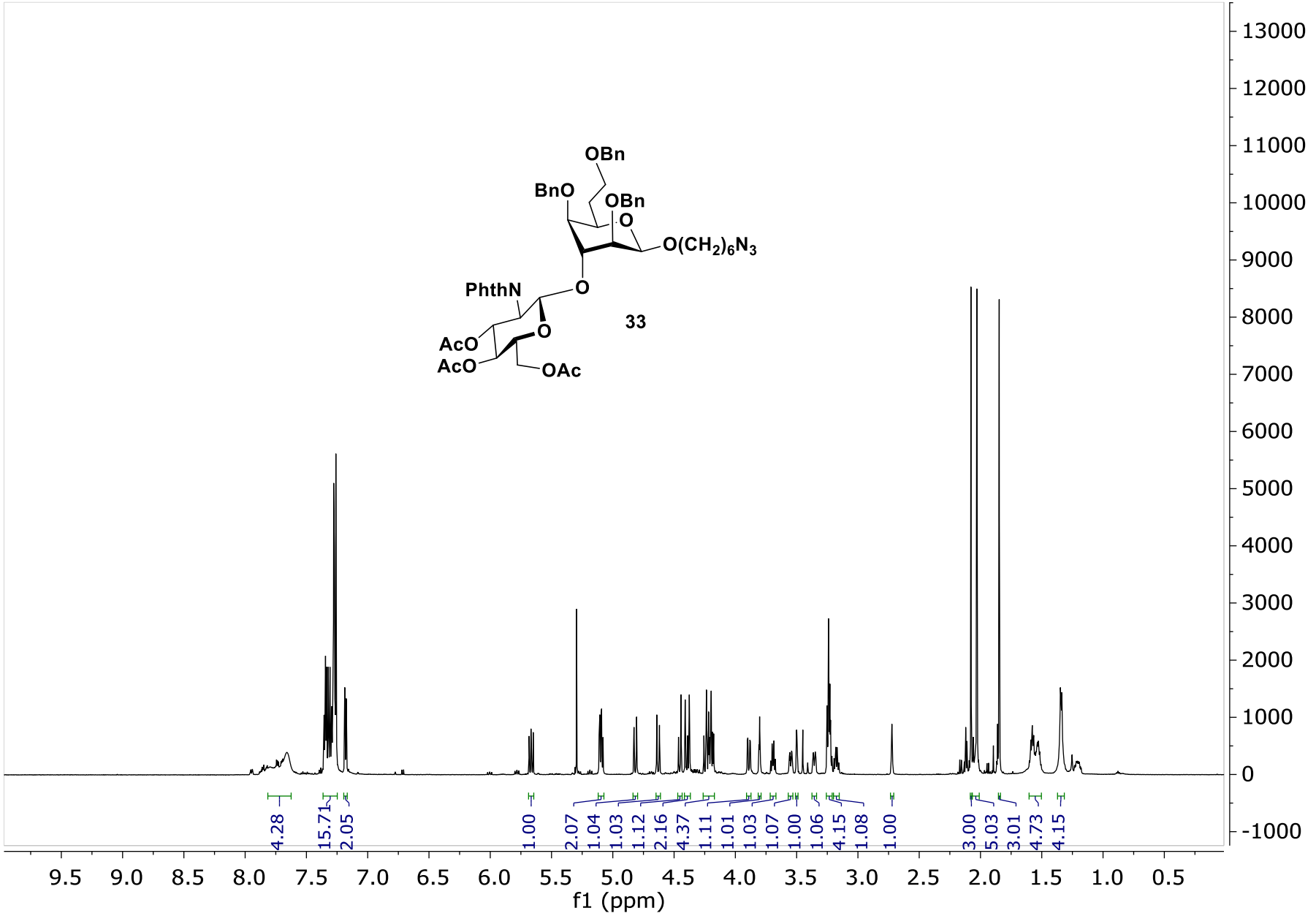


32

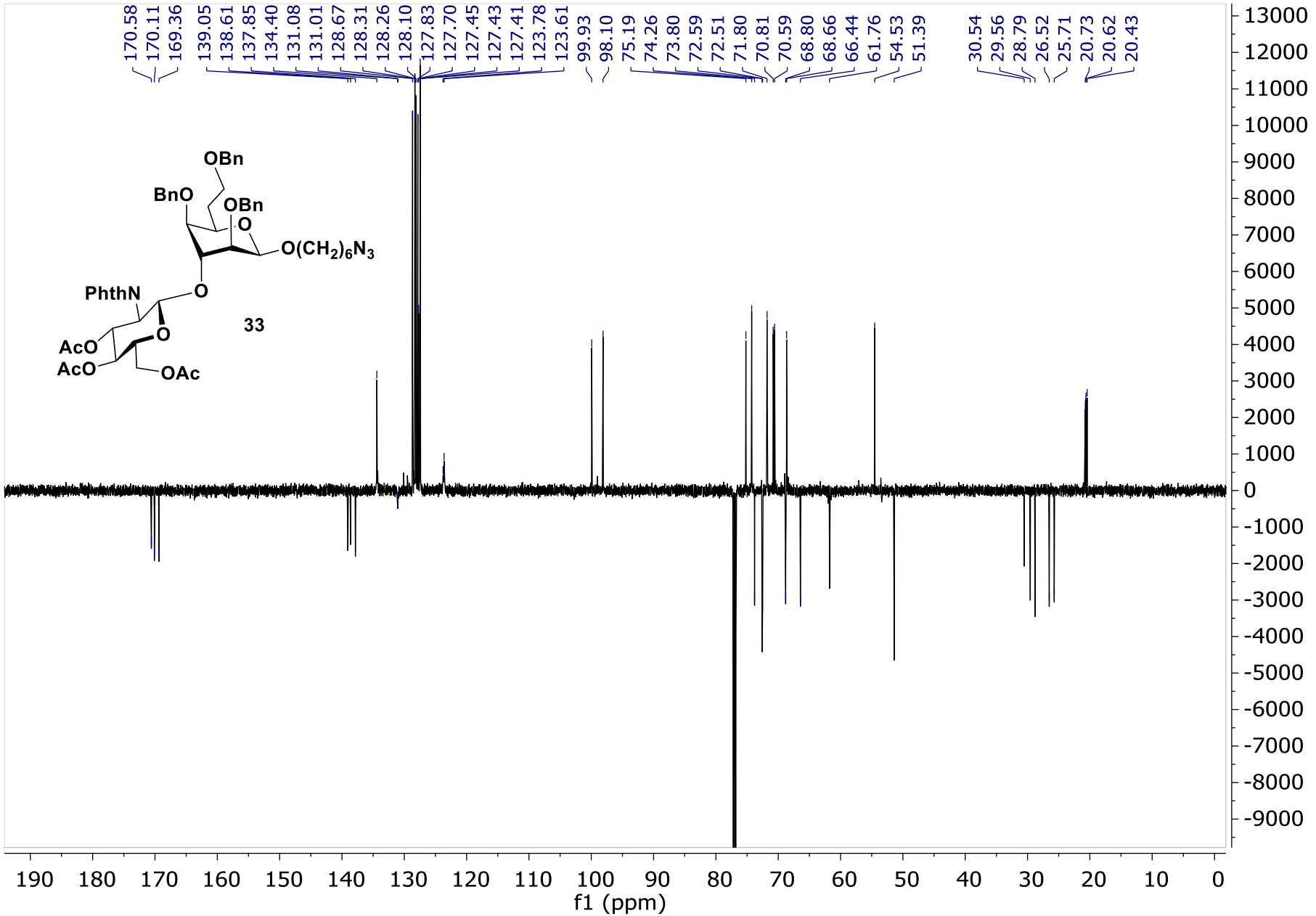
^{1}H-^{13}C GHSQC NMR Spectrum in $CDCl_3$, 400 MHz, 298 K

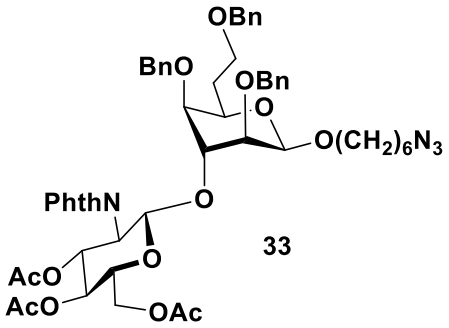


^{1}H NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



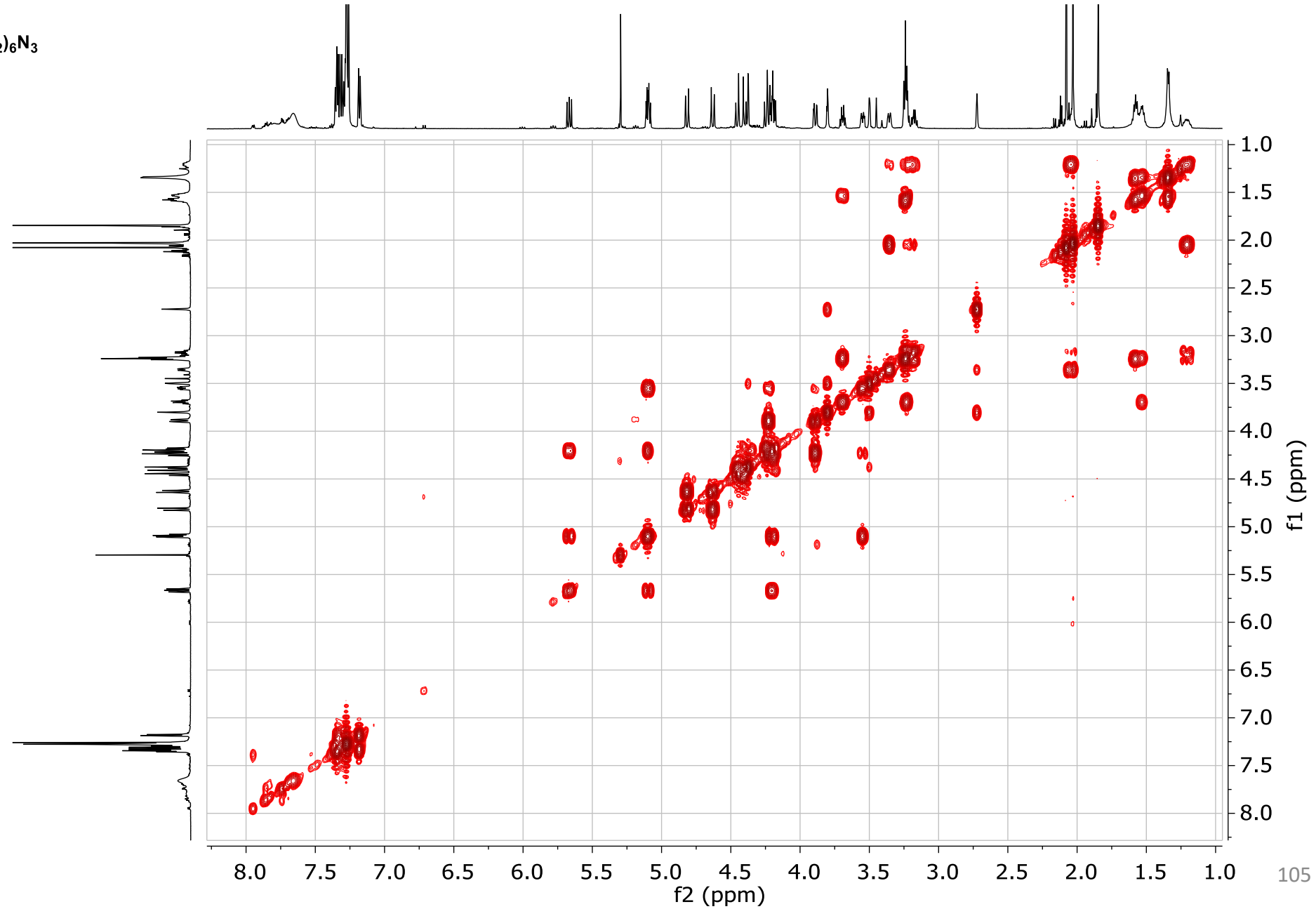
^{13}C (DEPT-Q) NMR Spectrum in $CDCl_3$, 100 MHz, 298 K

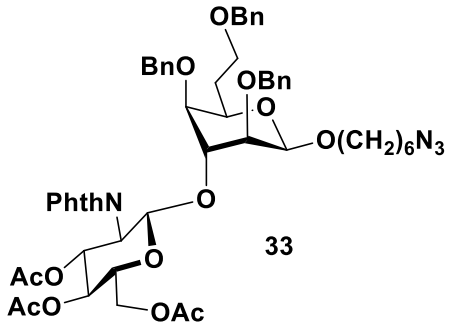




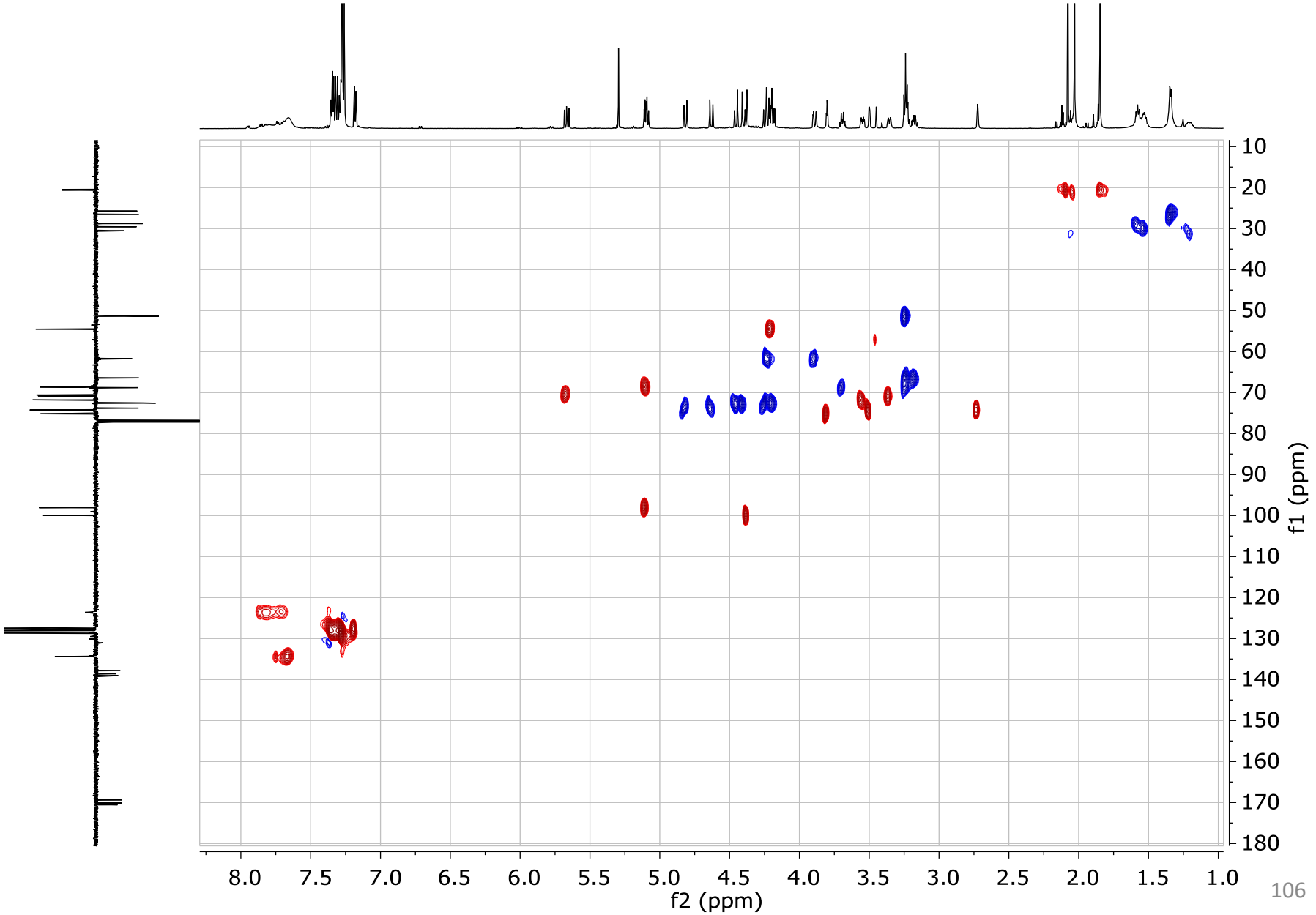
33

^{1}H-^{1}H GCOSY NMR Spectrum in $CDCl_3$, 400 MHz, 298 K

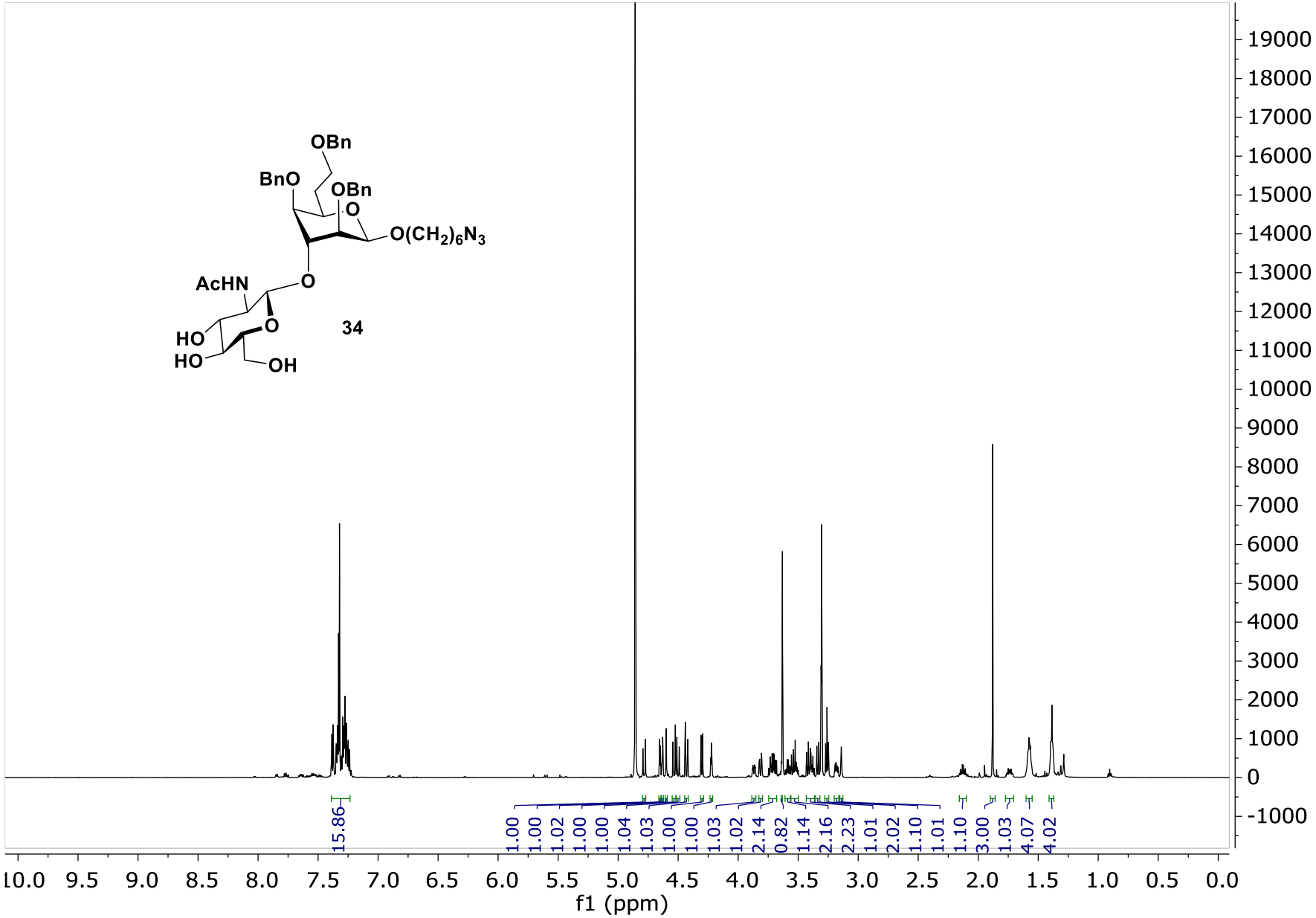




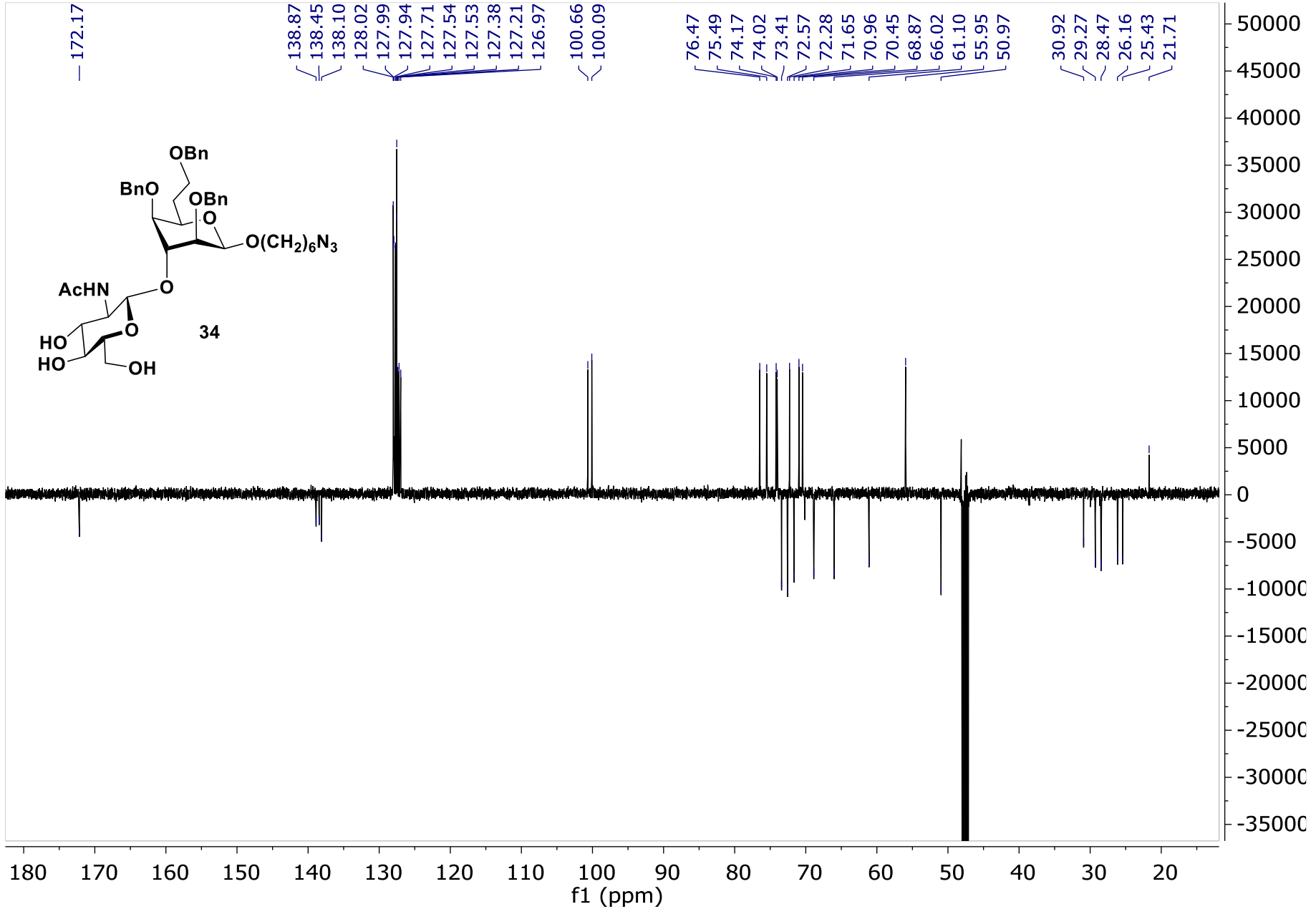
^{1}H-^{13}C GHSQC NMR Spectrum in $CDCl_3$, 400 MHz, 298 K

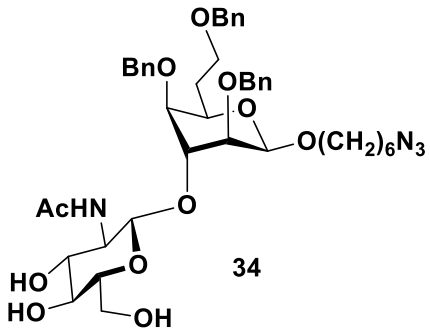


^{1}H NMR Spectrum in CD_3OD, 400 MHz, 298 K



^{13}C (DEPT-Q) NMR Spectrum in CD_3OD, 100 MHz, 298 K





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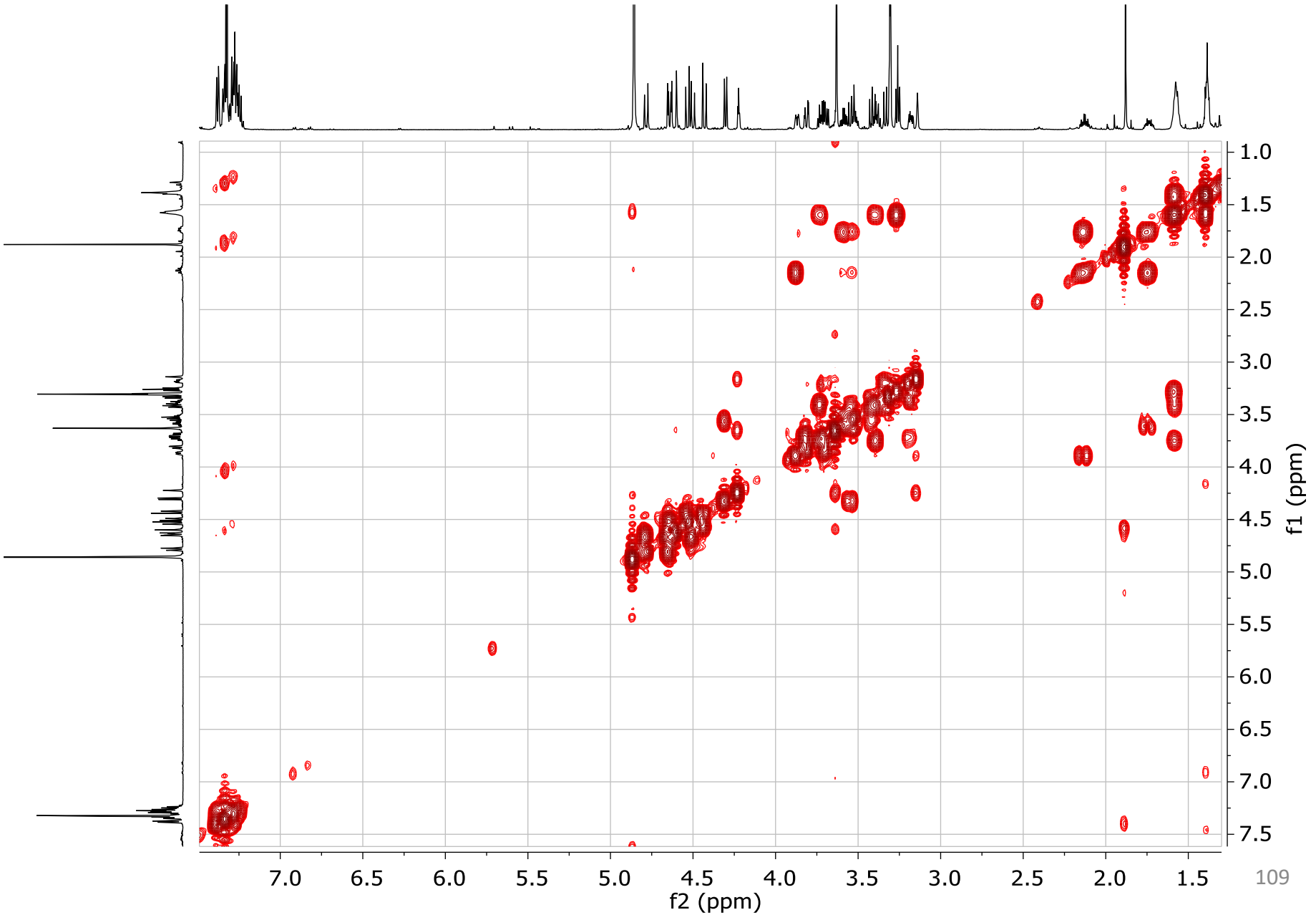
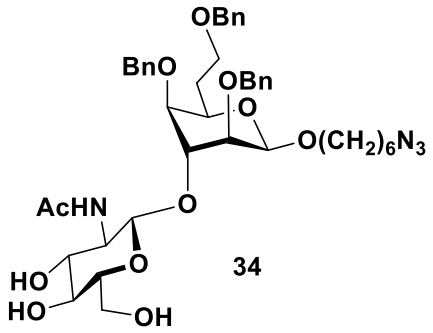
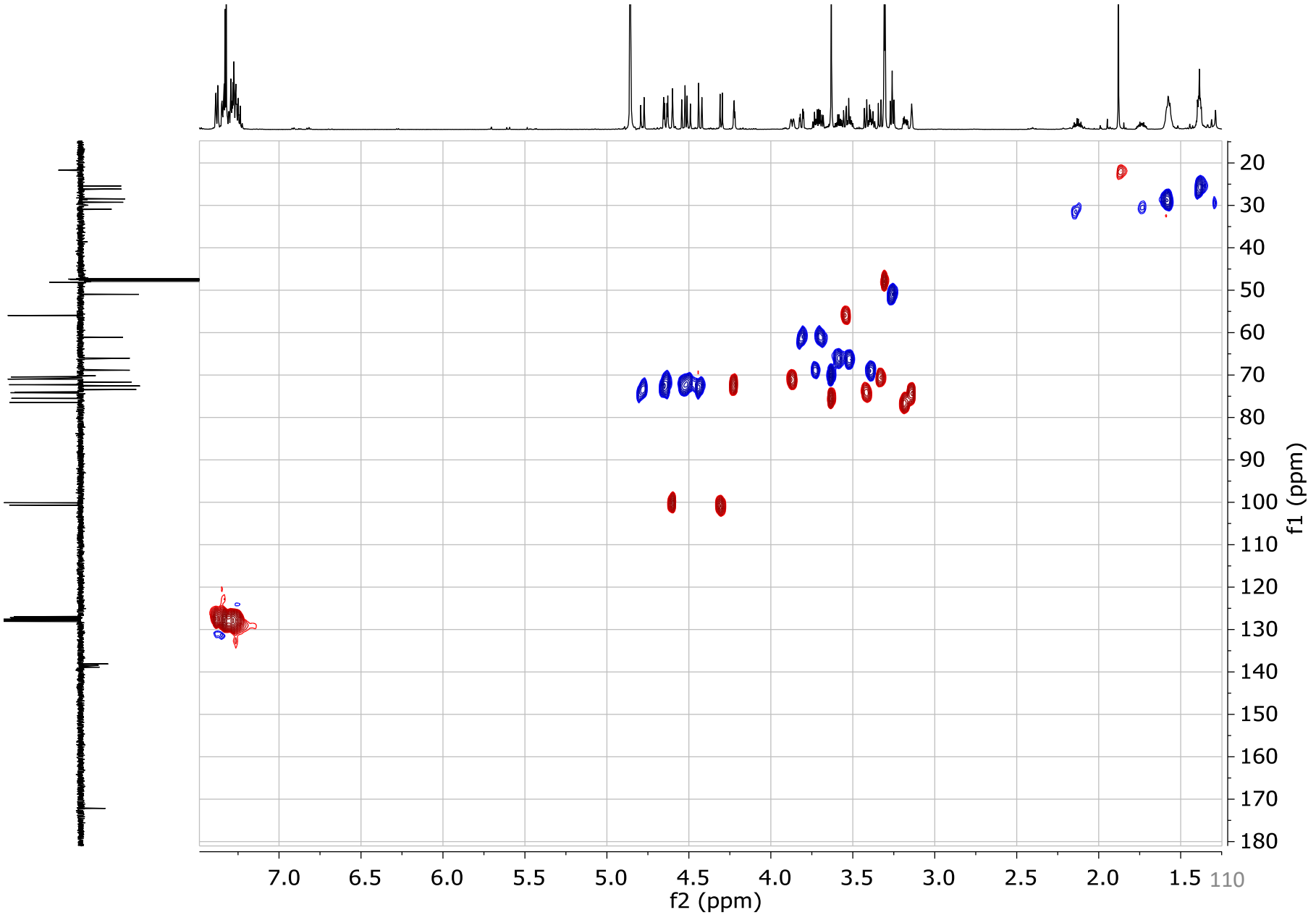
^{1}H-^{1}H GCOSY NMR Spectrum in CD_3OD, 400 MHz, 298 K



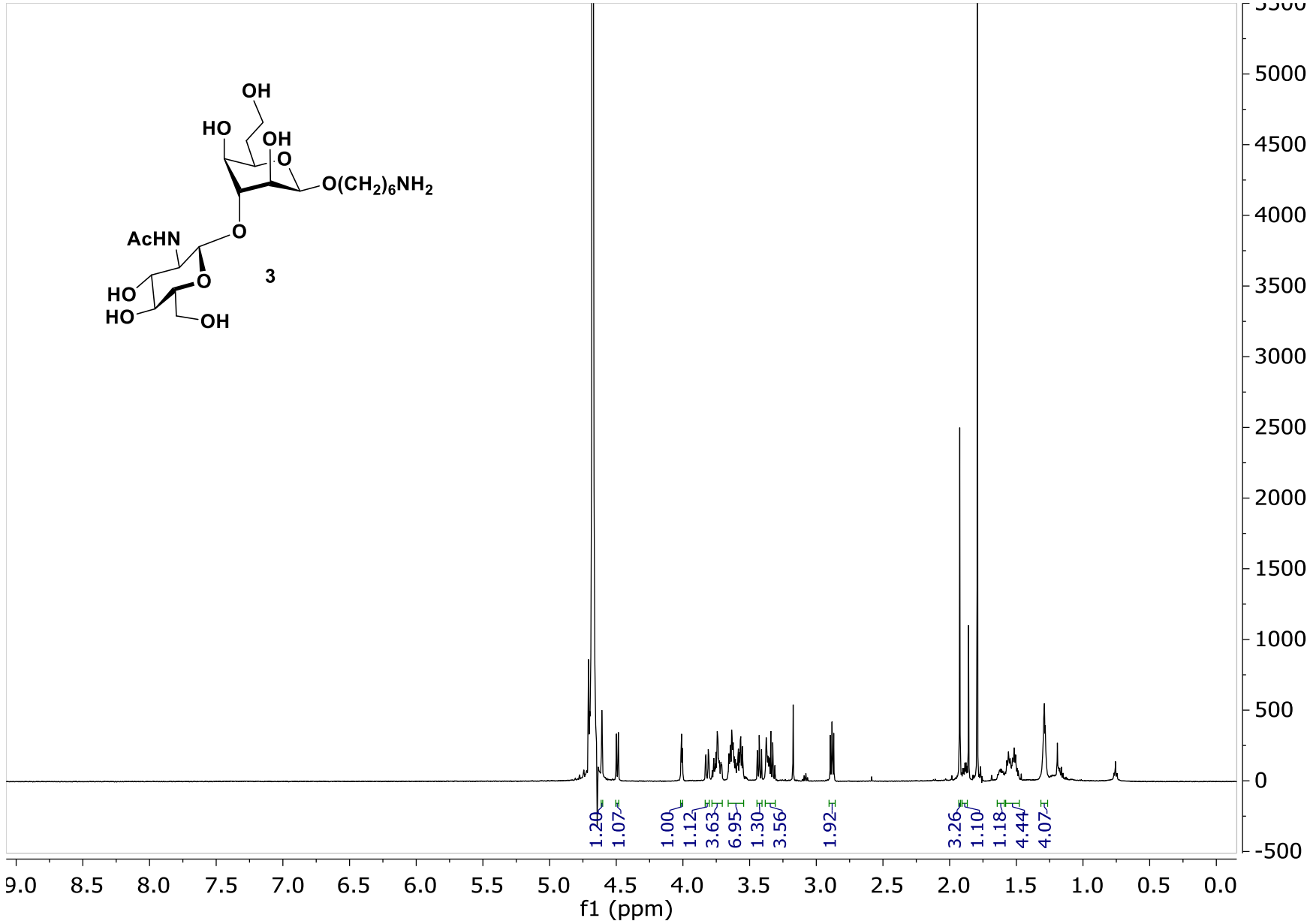


34

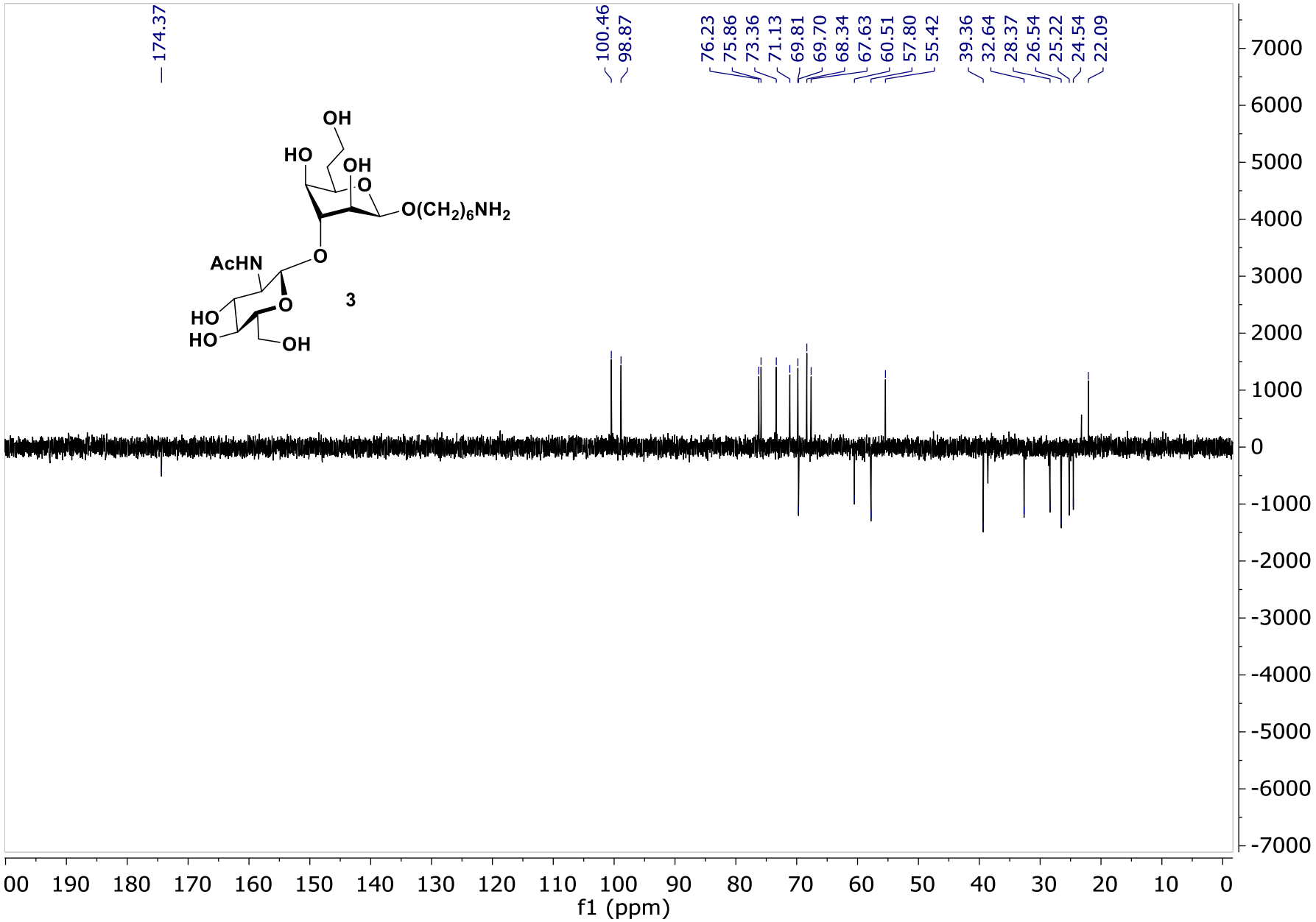
^{1}H-^{13}C GHSQC NMR Spectrum in CD_3OD, 400 MHz, 298 K

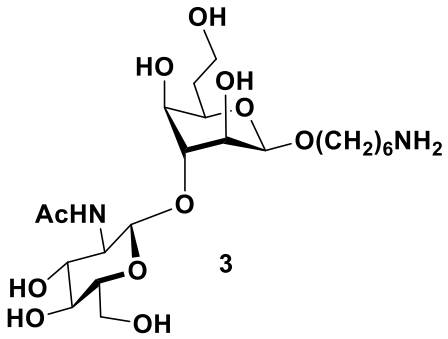


^{1}H NMR Spectrum in D_2O, 400 MHz, 298 K

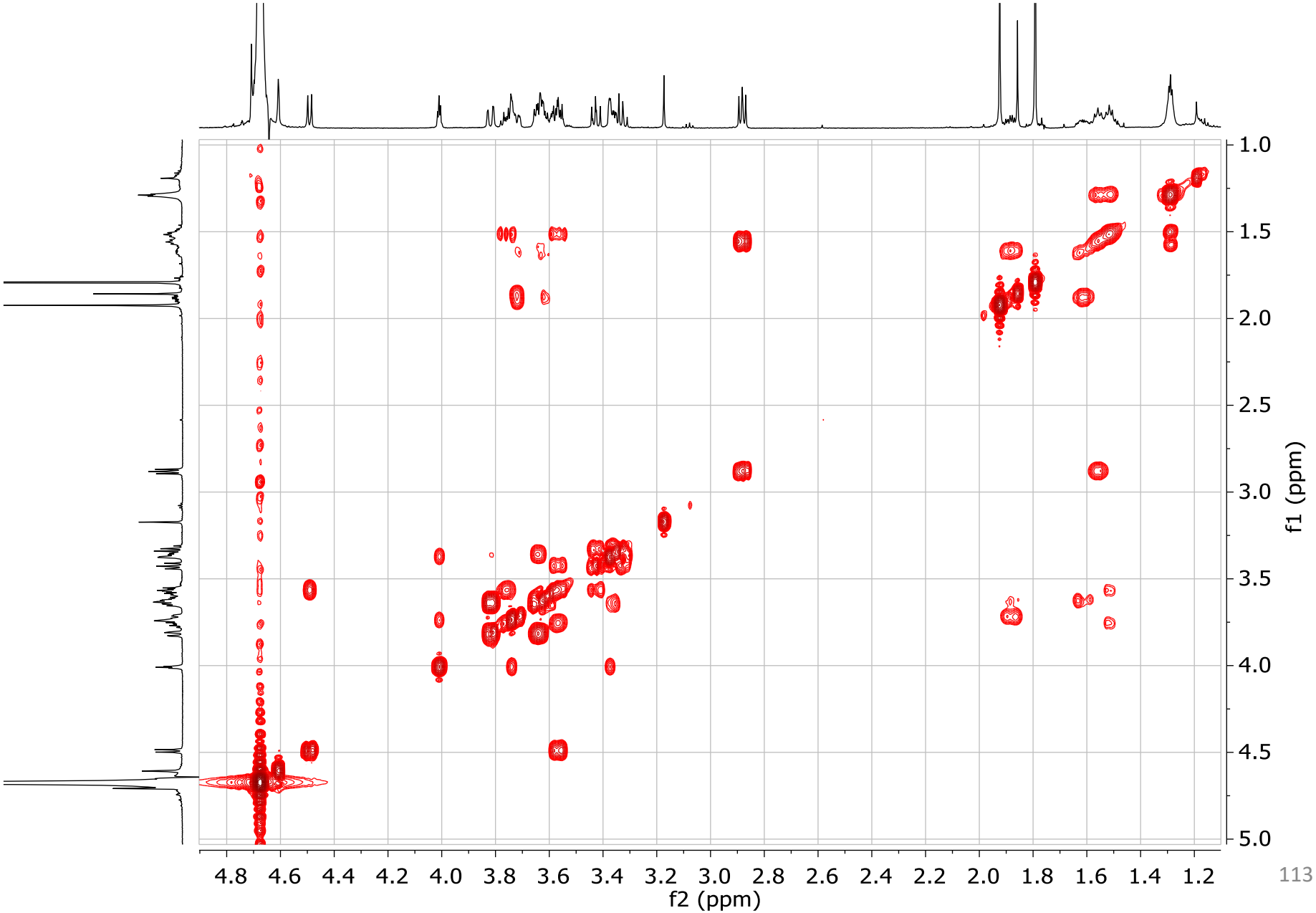


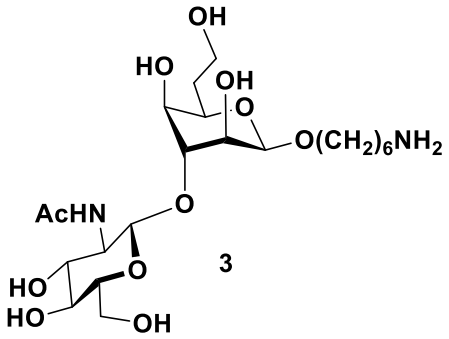
^{13}C (DEPT-Q) NMR Spectrum in D_2O, 100 MHz, 298 K





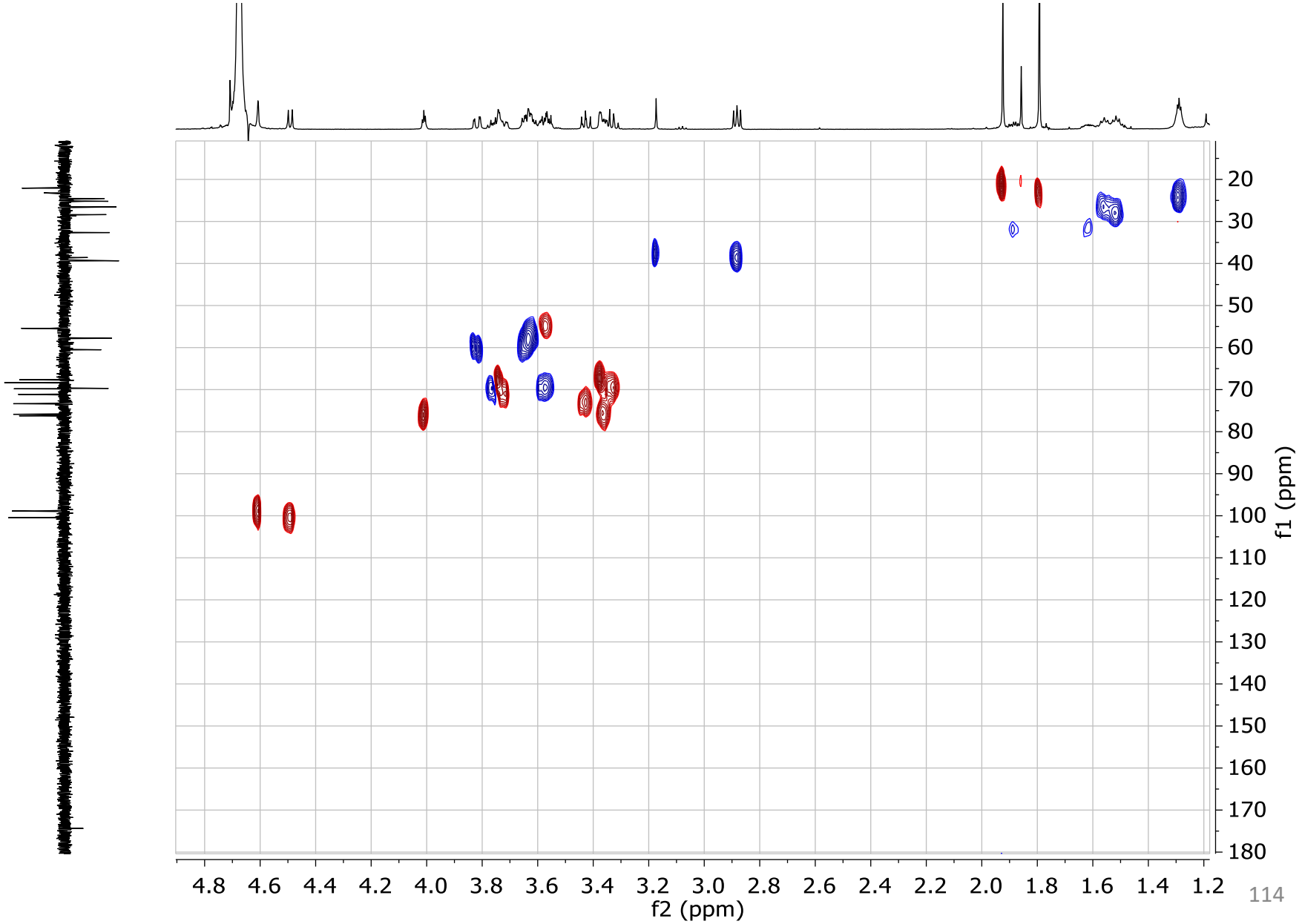
^{1}H-^{1}H GCOSY NMR Spectrum in D_2O, 400 MHz, 298 K



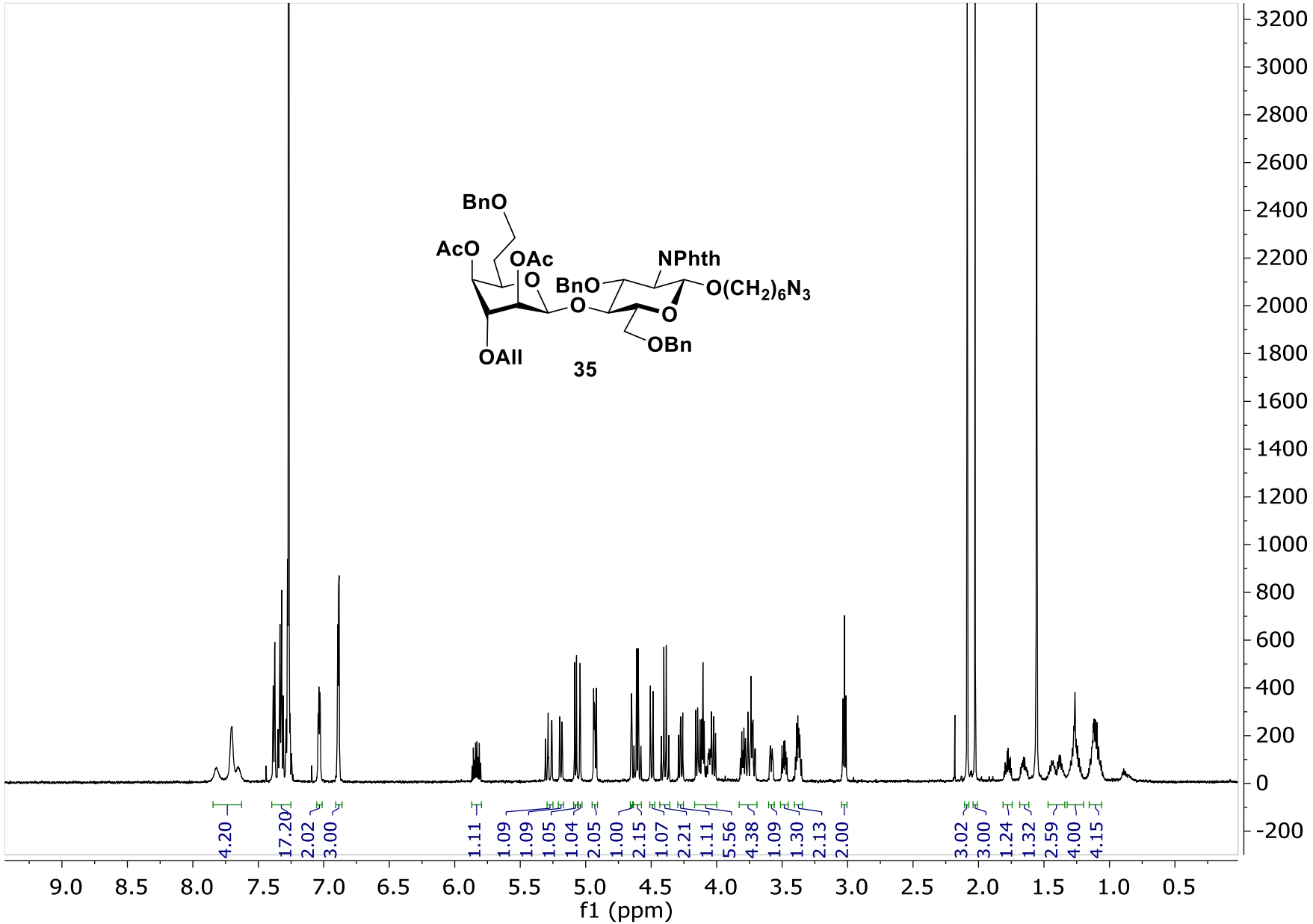


3

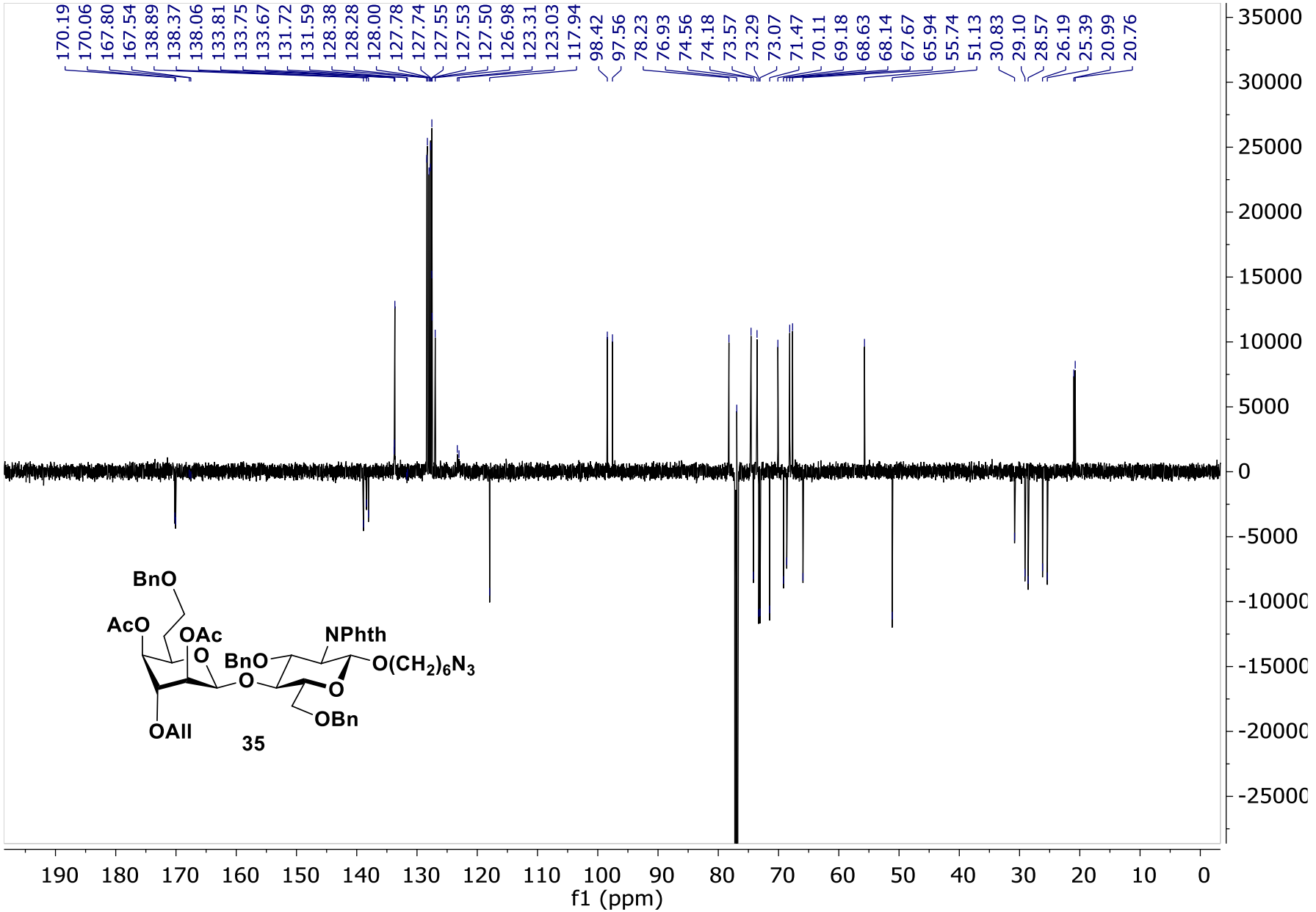
^{1}H-^{13}C GHSQC NMR Spectrum in D_2O, 400 MHz, 298 K

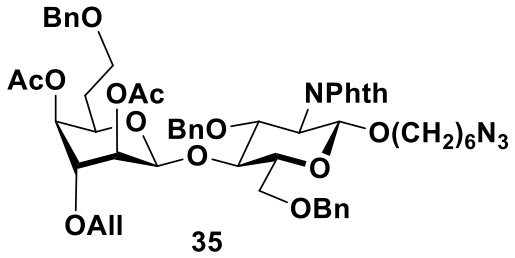


^{1}H NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



^{13}C (DEPT-Q) NMR Spectrum in $CDCl_3$, 100 MHz, 298 K





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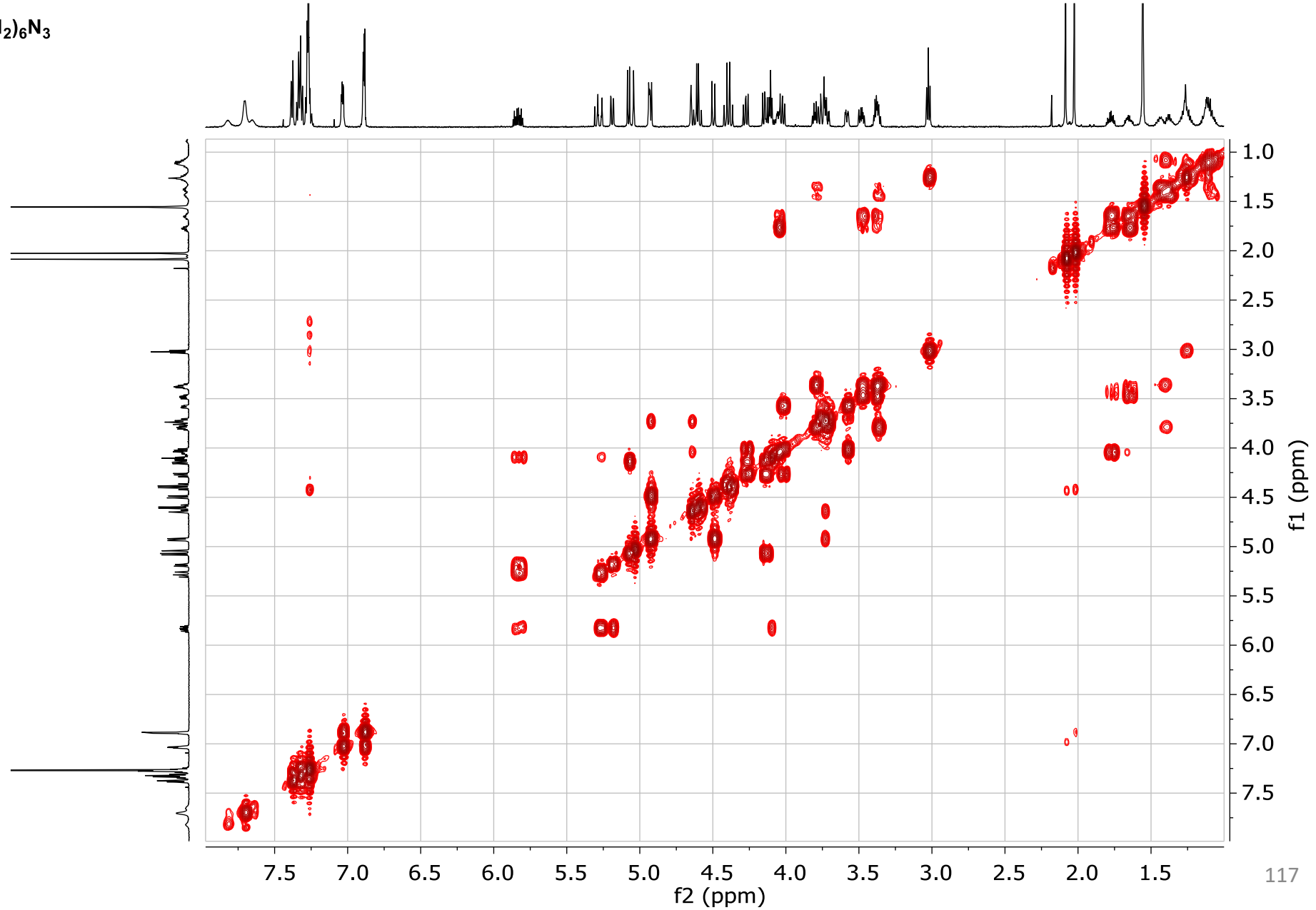
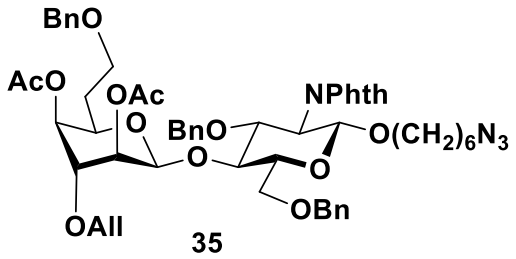
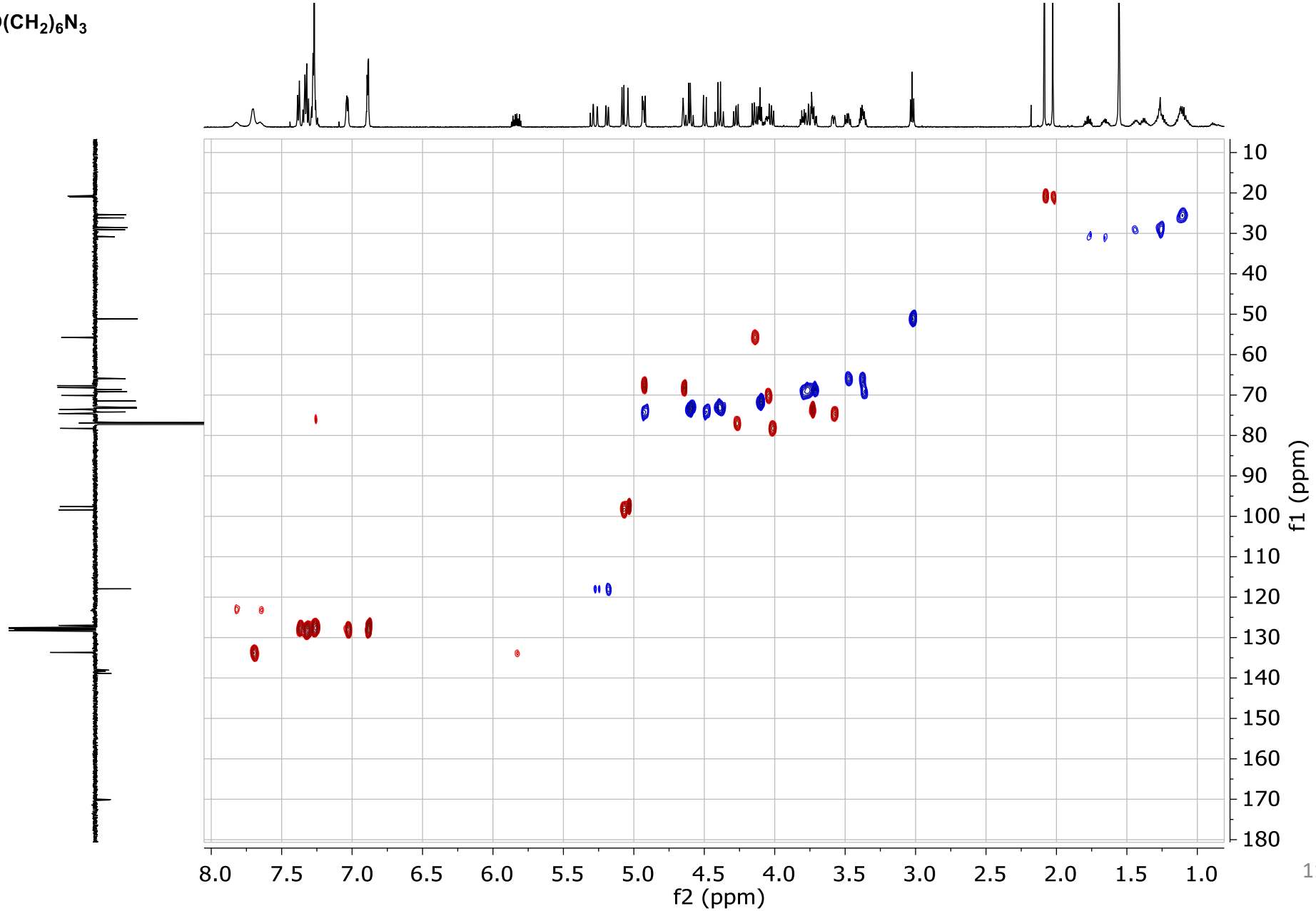
^{1}H-^{1}H GCOSY NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



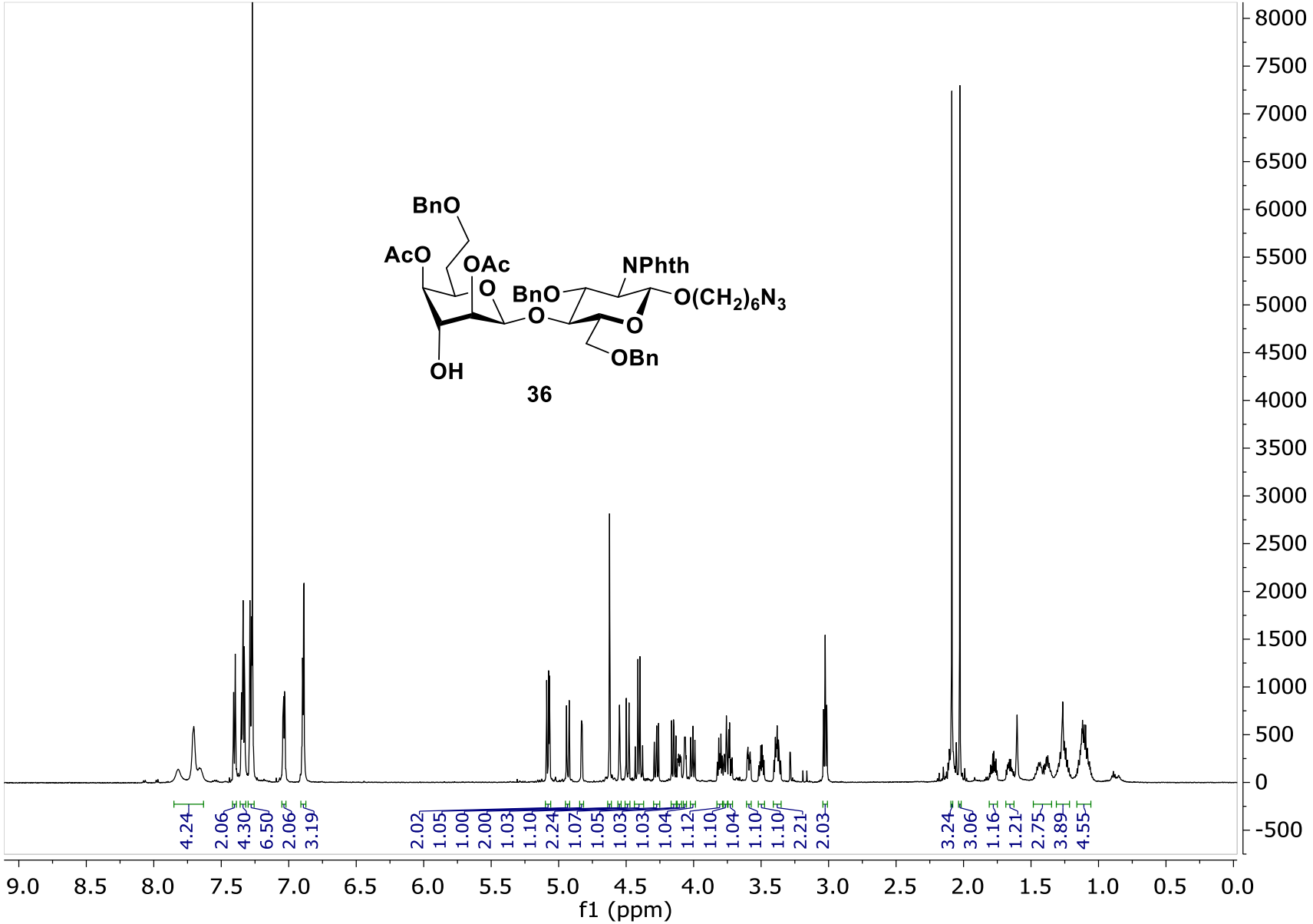


35

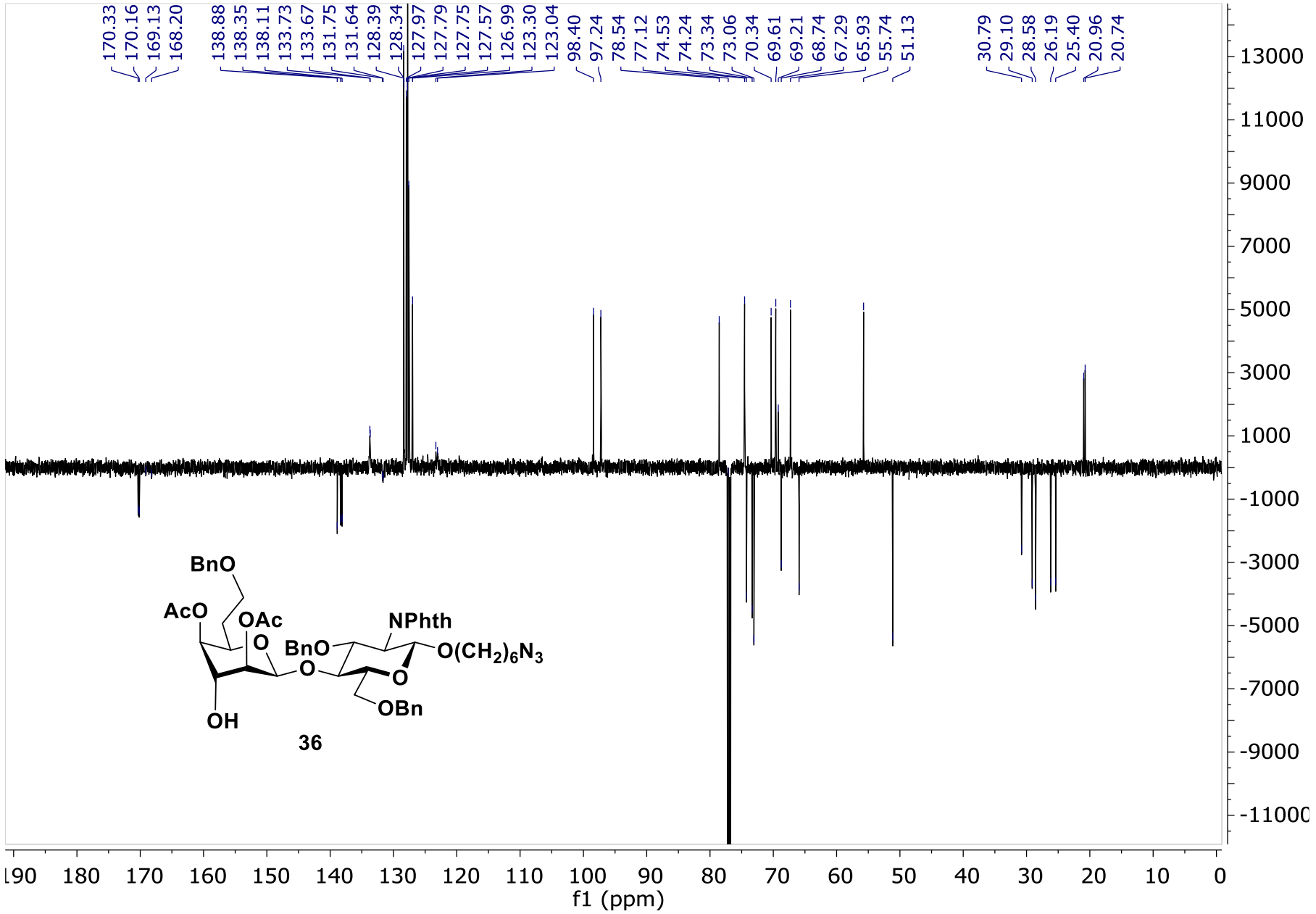
^{1}H-^{13}C GHSQC NMR Spectrum in $CDCl_3$, 400 MHz, 298 K

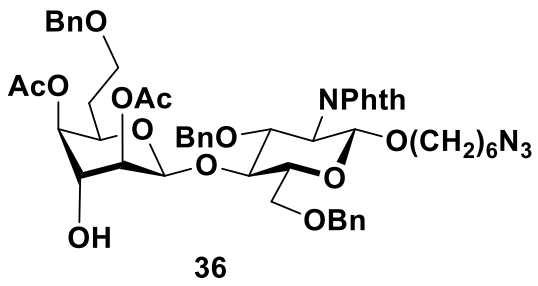


^{1}H NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



^{13}C (DEPT-Q) NMR Spectrum in $CDCl_3$, 100 MHz, 298 K





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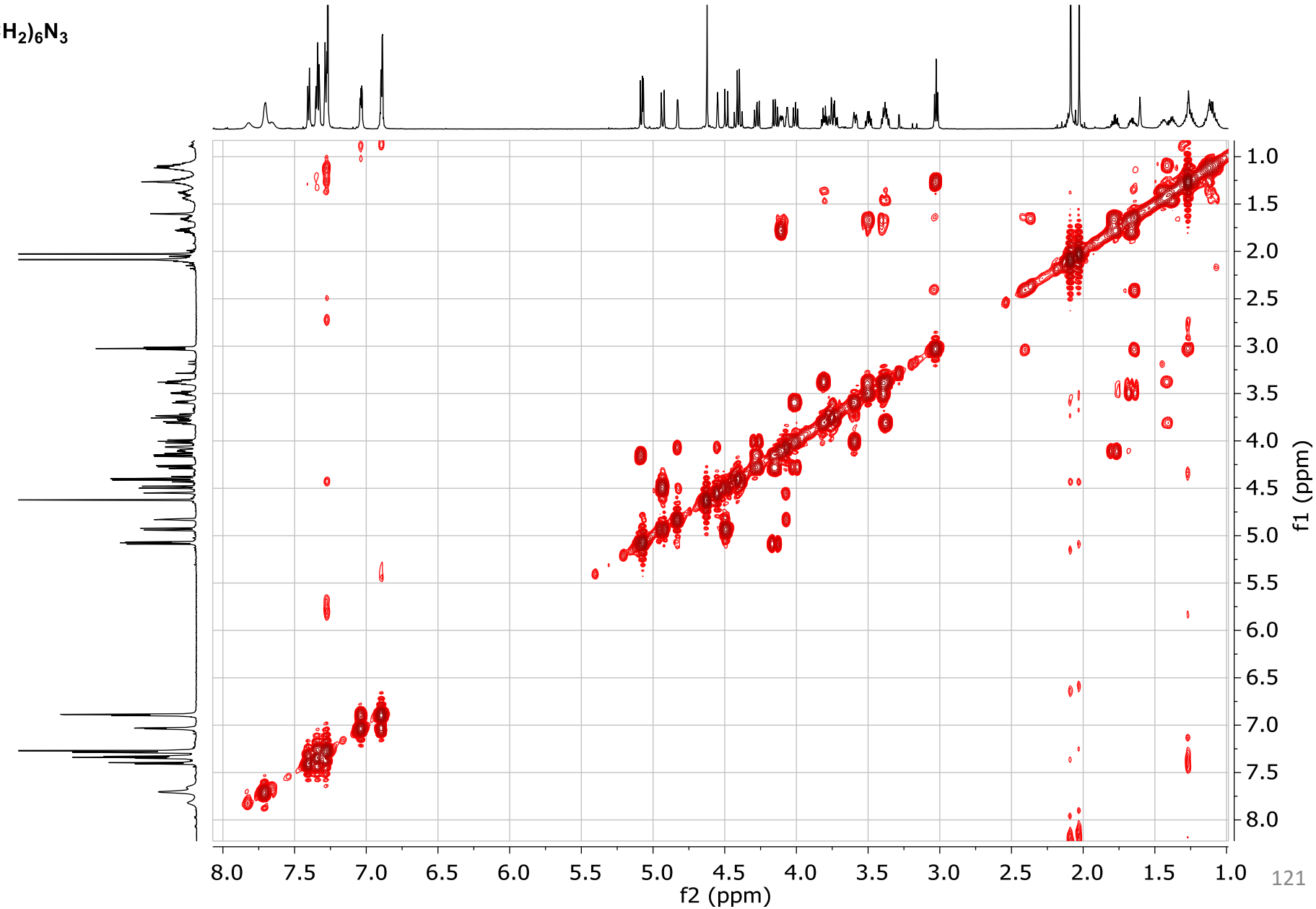
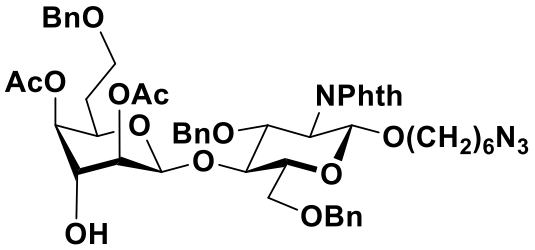
^{1}H-^{1}H GCOSY NMR Spectrum in $CDCl_3$, 400 MHz, 298 K





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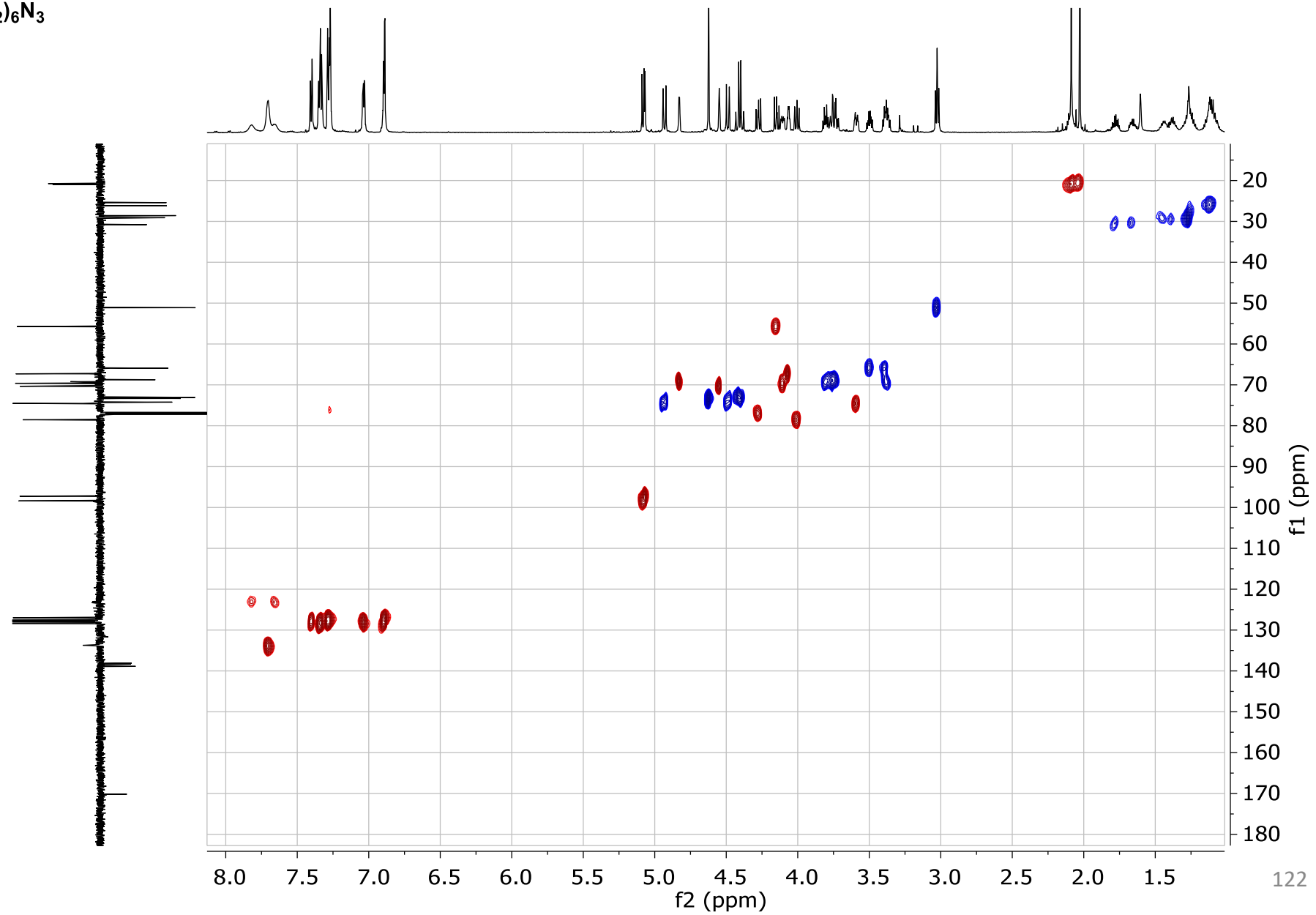
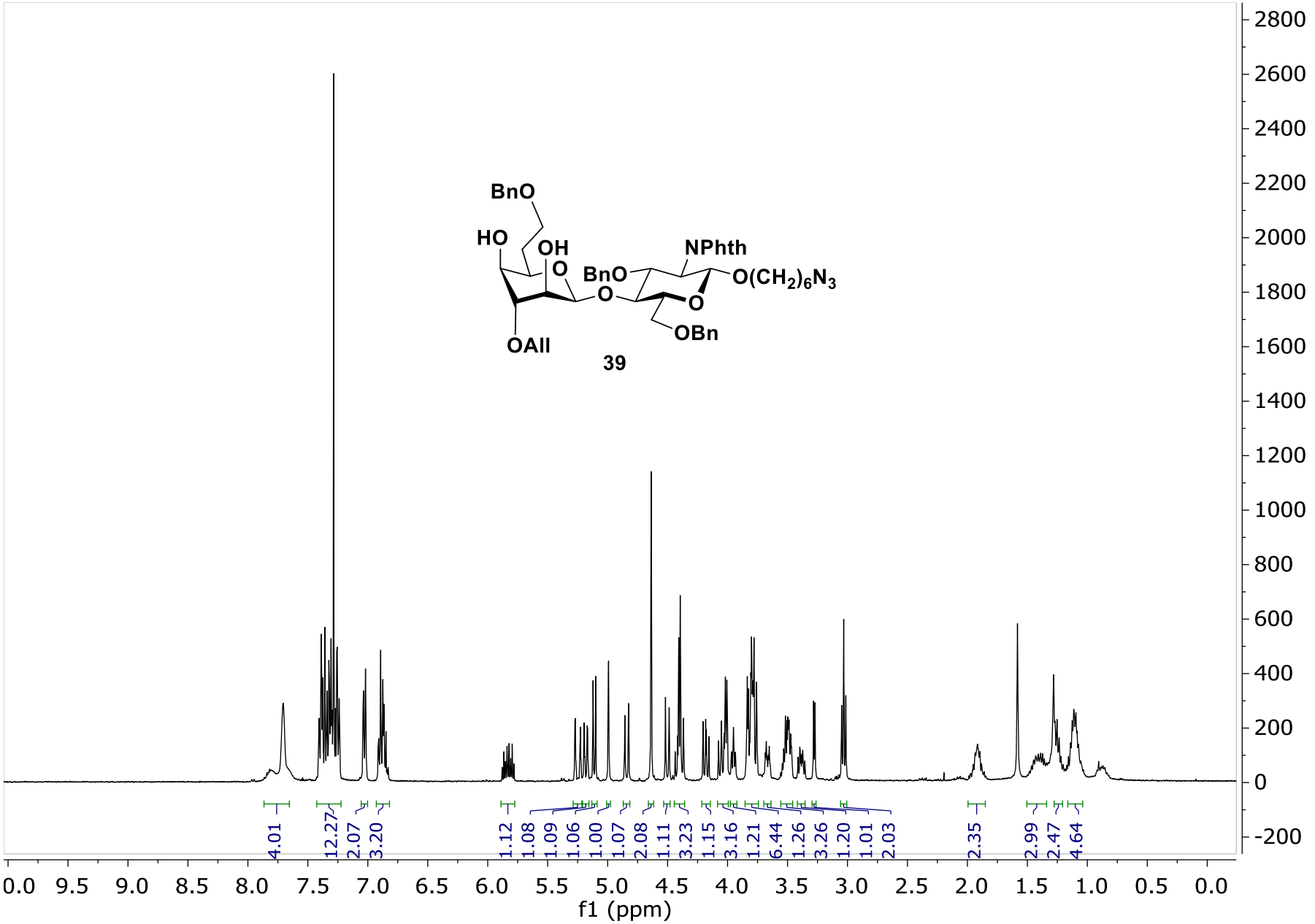
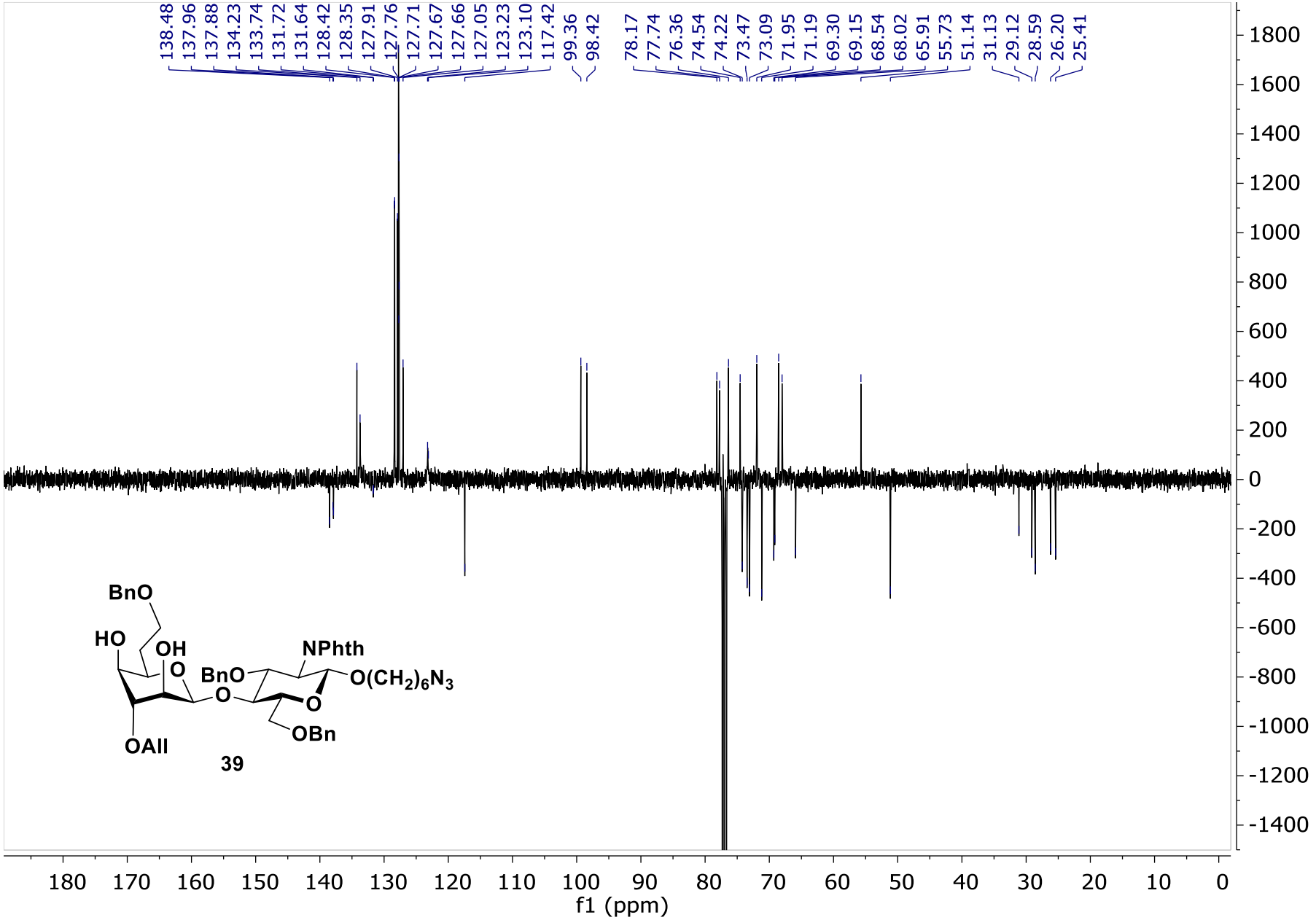
^{1}H-^{13}C GHSQC NMR Spectrum in $CDCl_3$, 400 MHz, 298 K

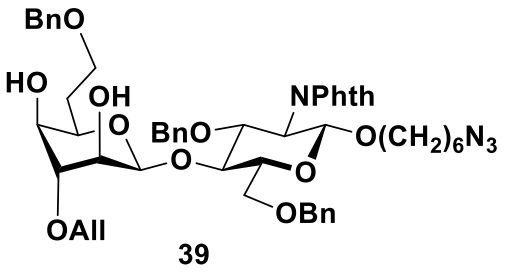


^{1}H NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



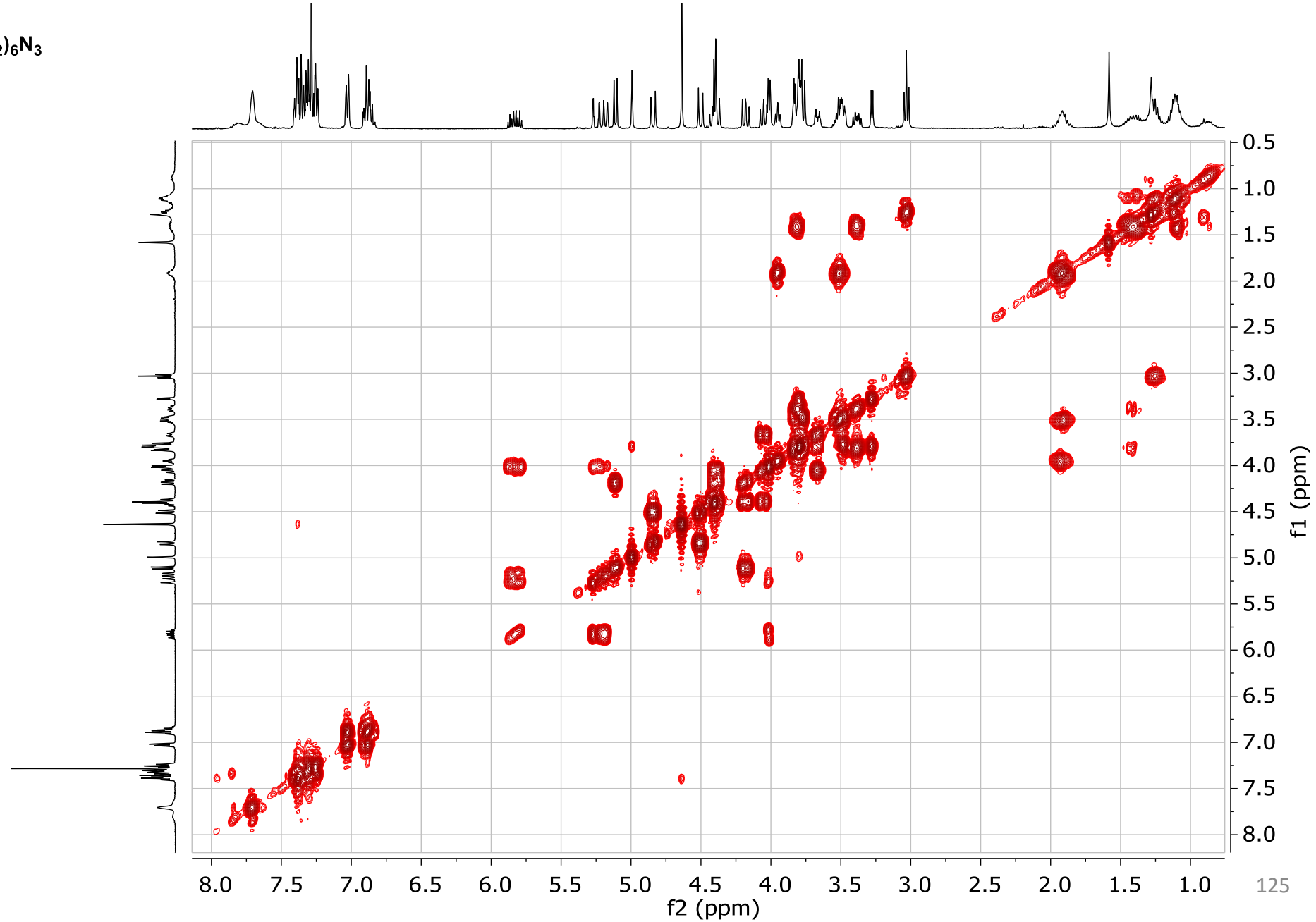
^{13}C (DEPT-Q) NMR Spectrum in $CDCl_3$, 100 MHz, 298 K

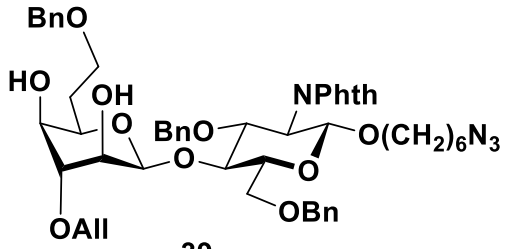




39

^{1}H-^{1}H GCOSY NMR Spectrum in $CDCl_3$, 400 MHz, 298 K





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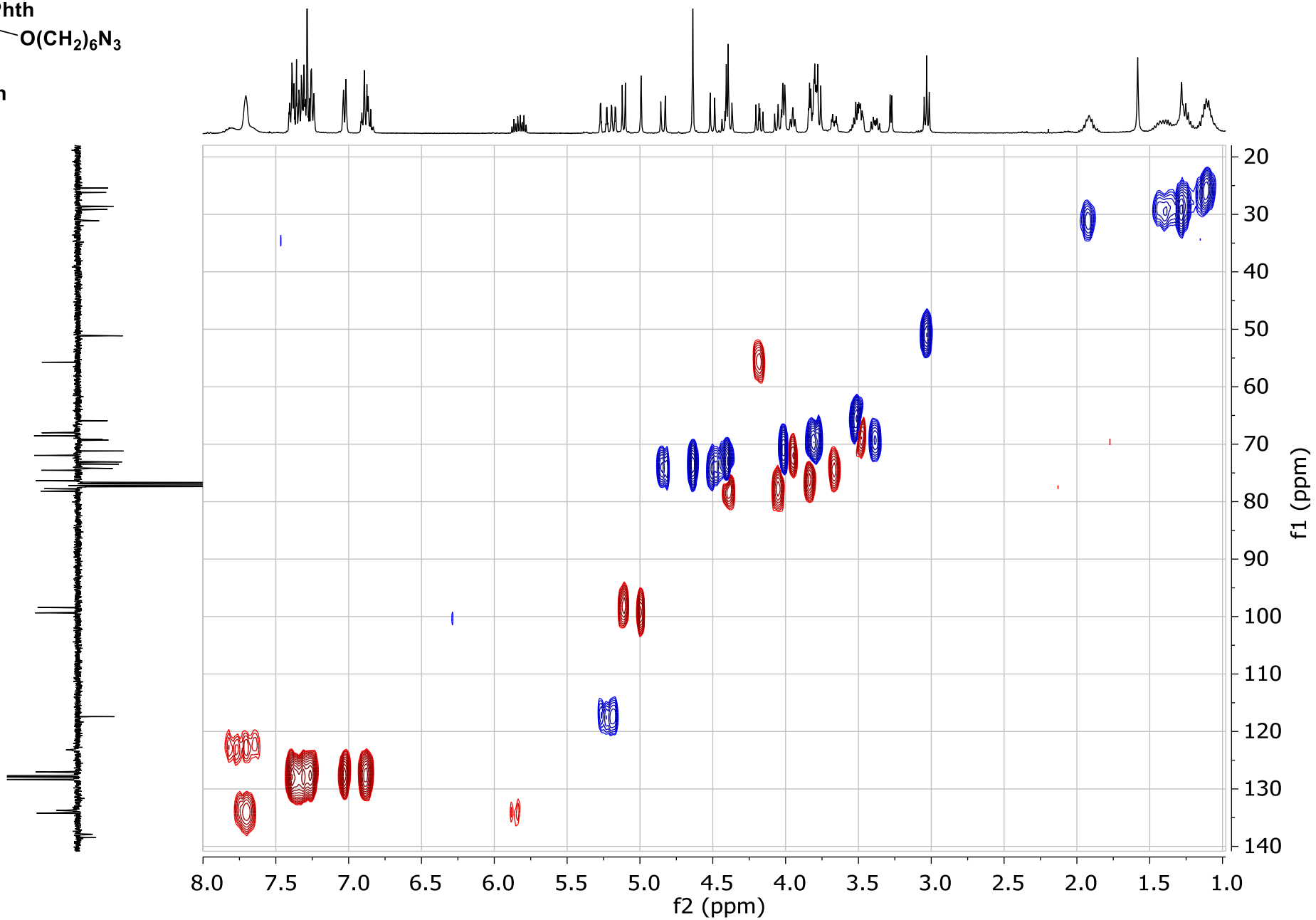
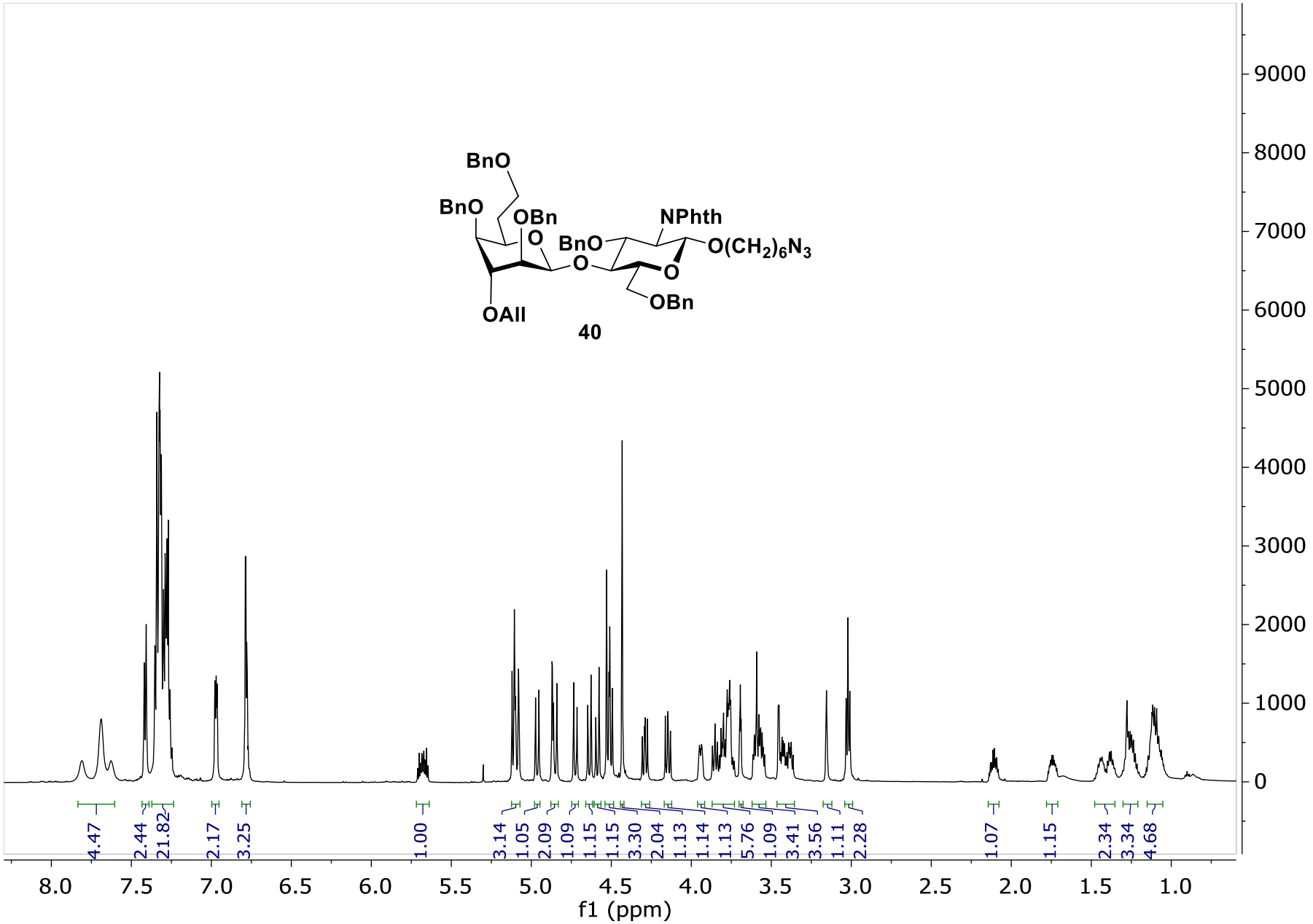
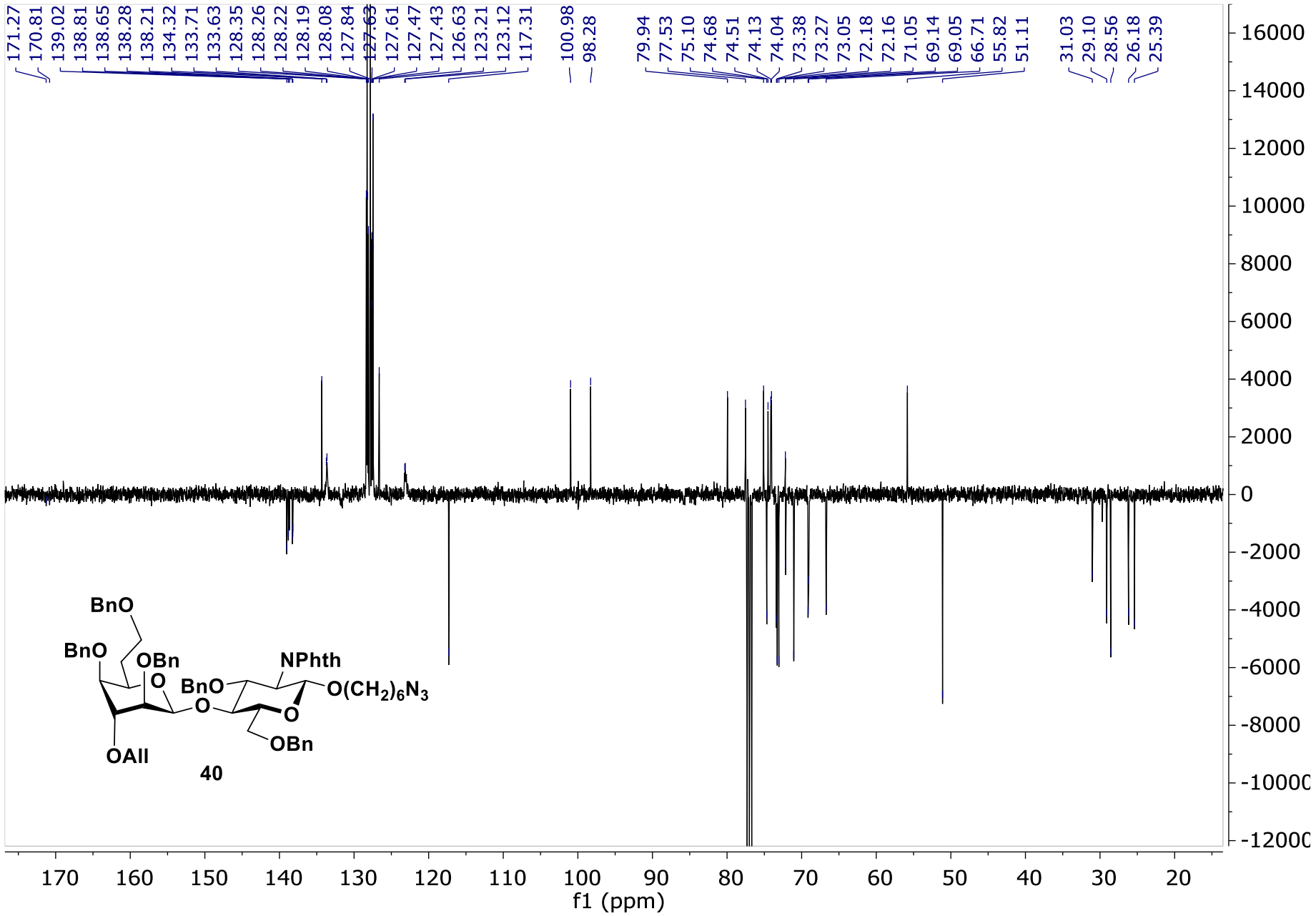
^{1}H-^{13}C GHSQC NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



^{1}H NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



^{13}C (DEPT-Q) NMR Spectrum in $CDCl_3$, 100 MHz, 298 K



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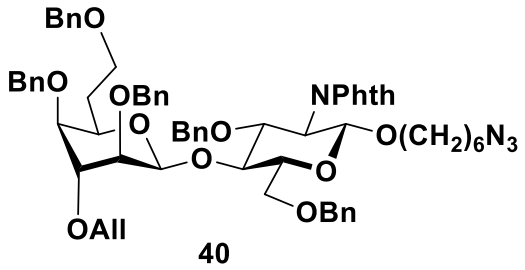

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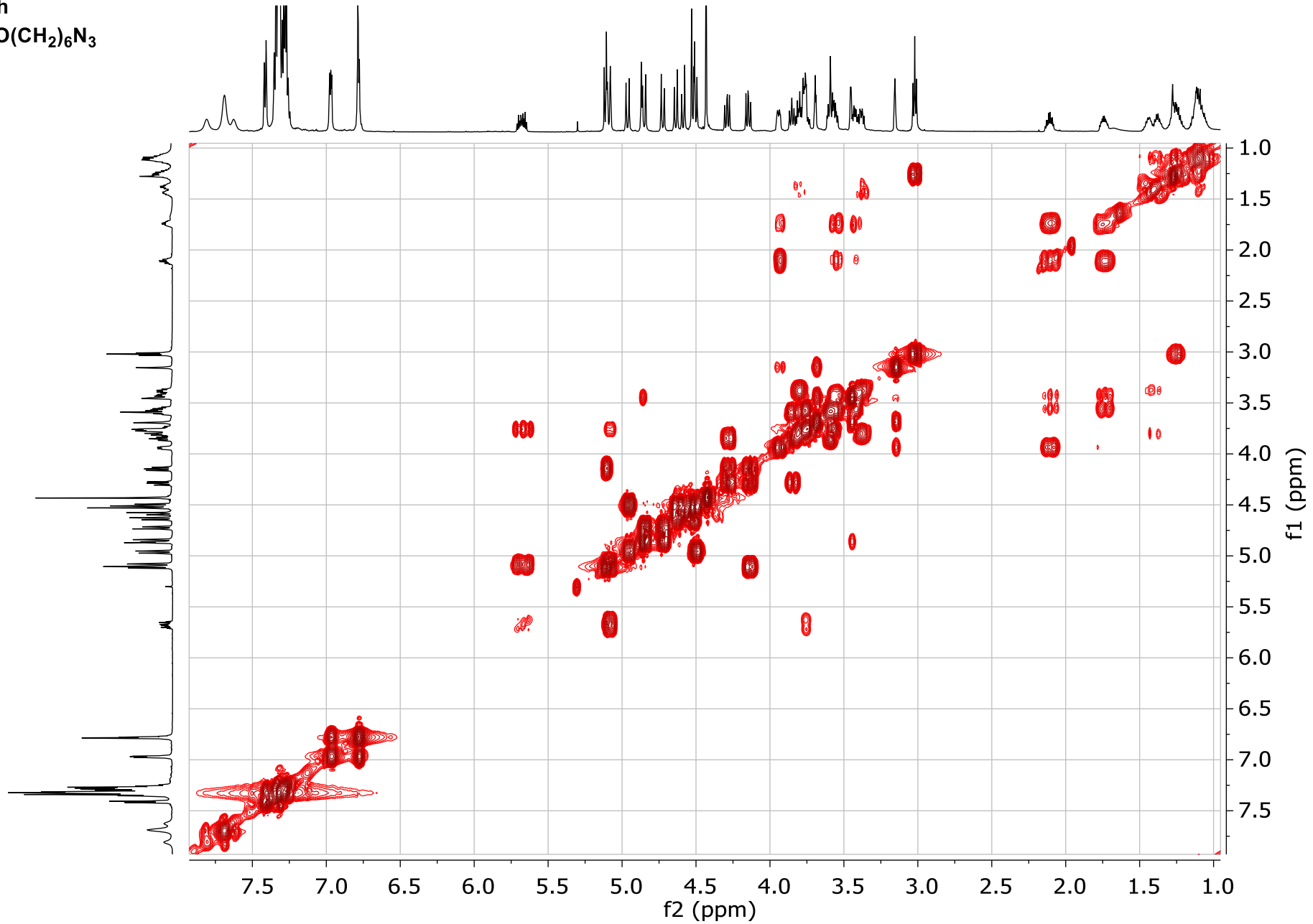
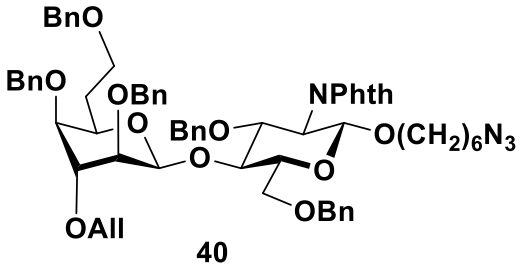
^{1}H-^{1}H GCOSY NMR Spectrum in $CDCl_3$, 400 MHz, 298 K





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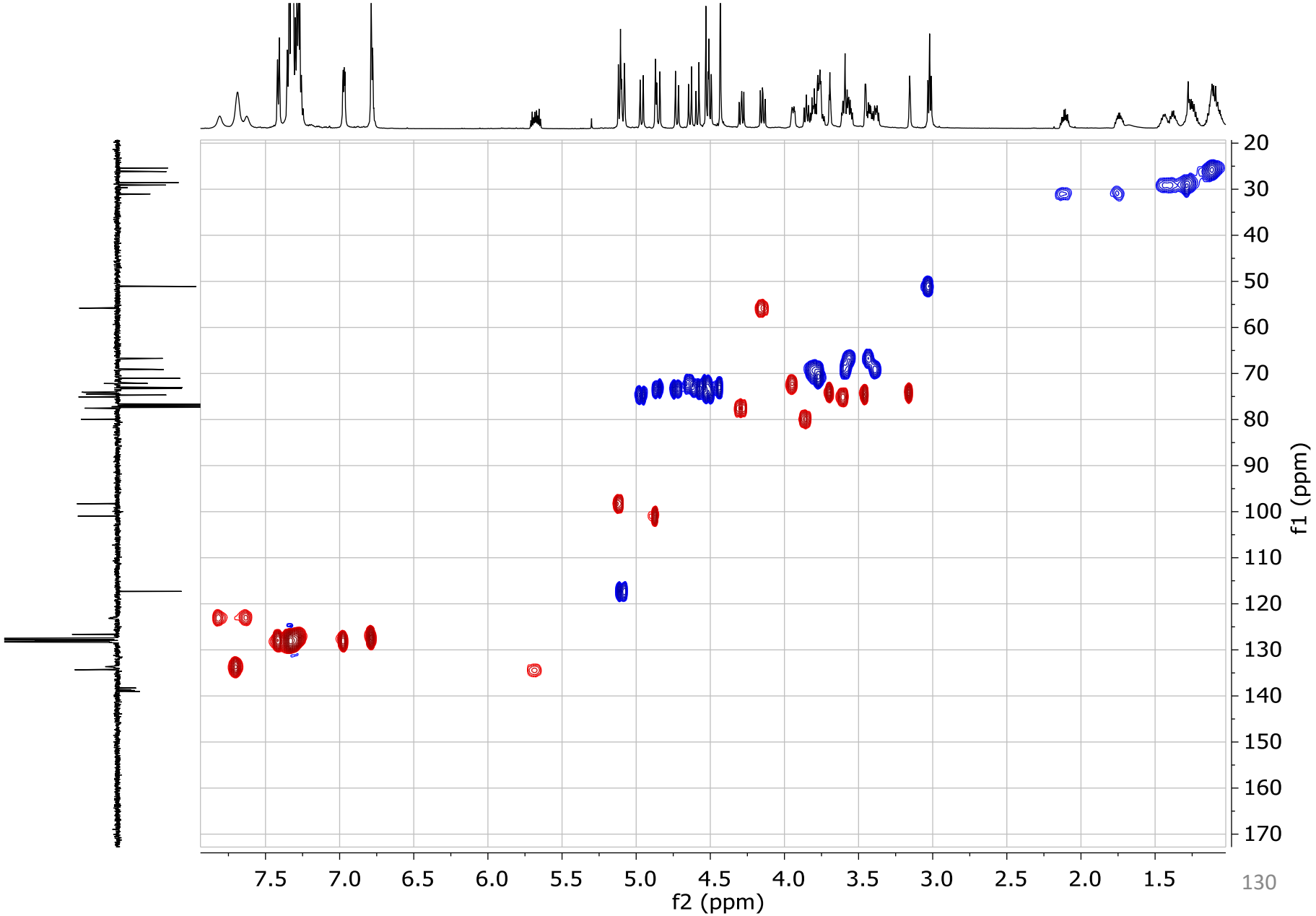
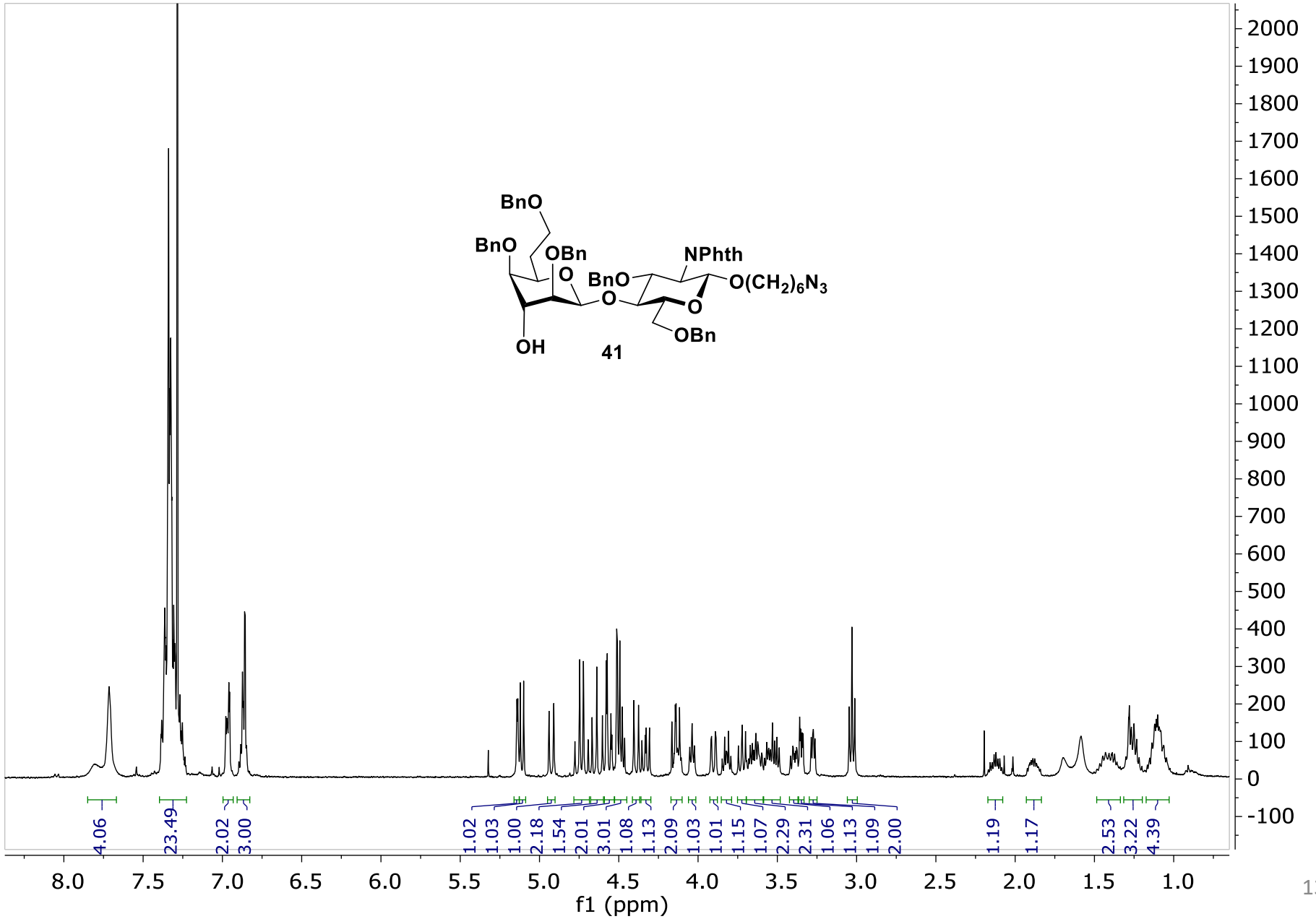
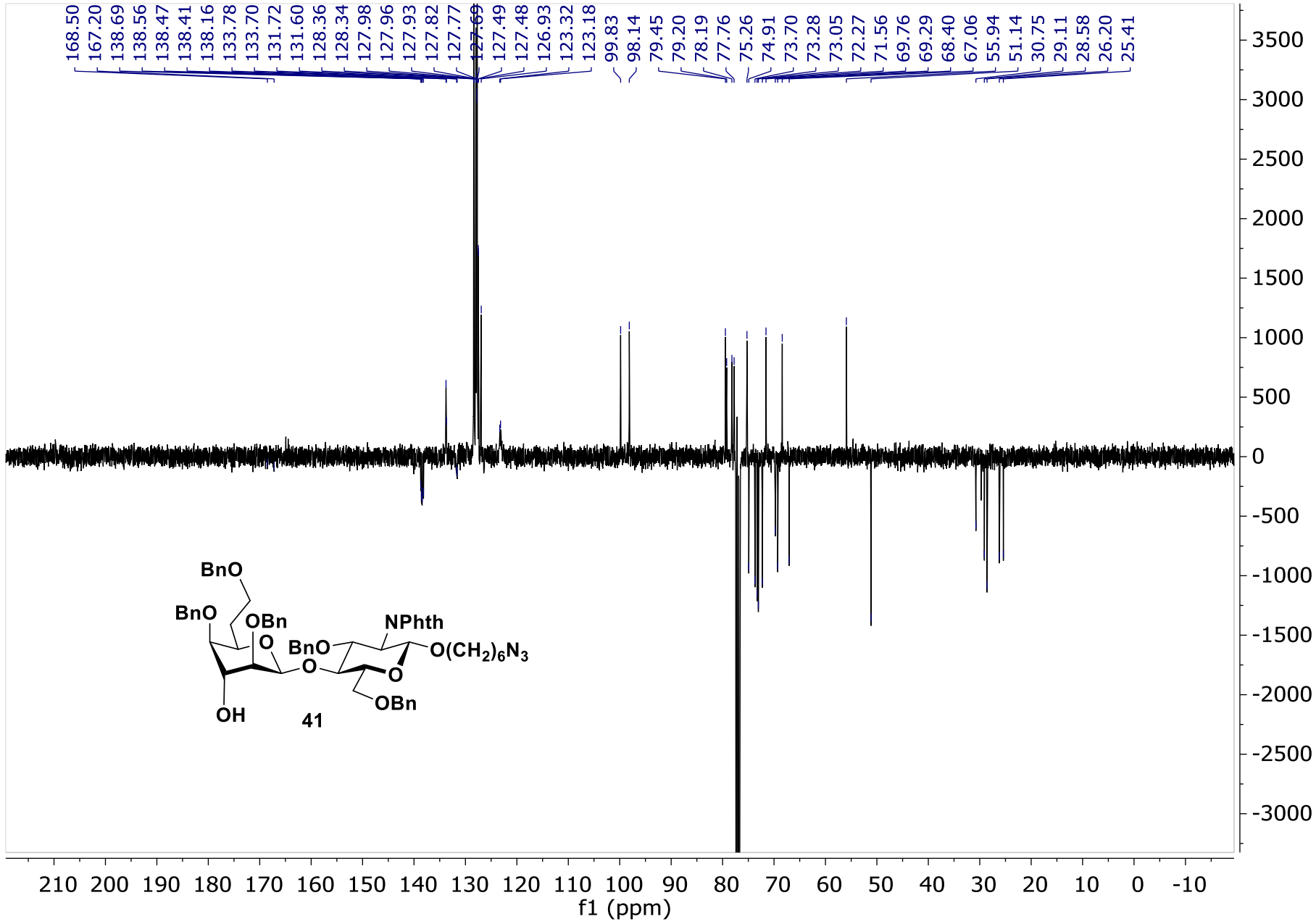
^{1}H-^{13}C GHSQC NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



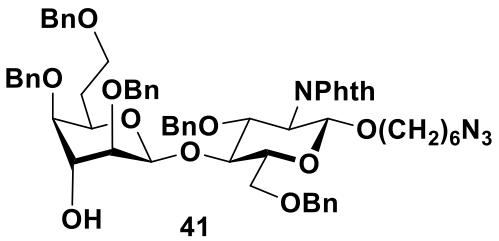
^{1}H NMR Spectrum in $CDCl_3$, 400 MHz, 298 K

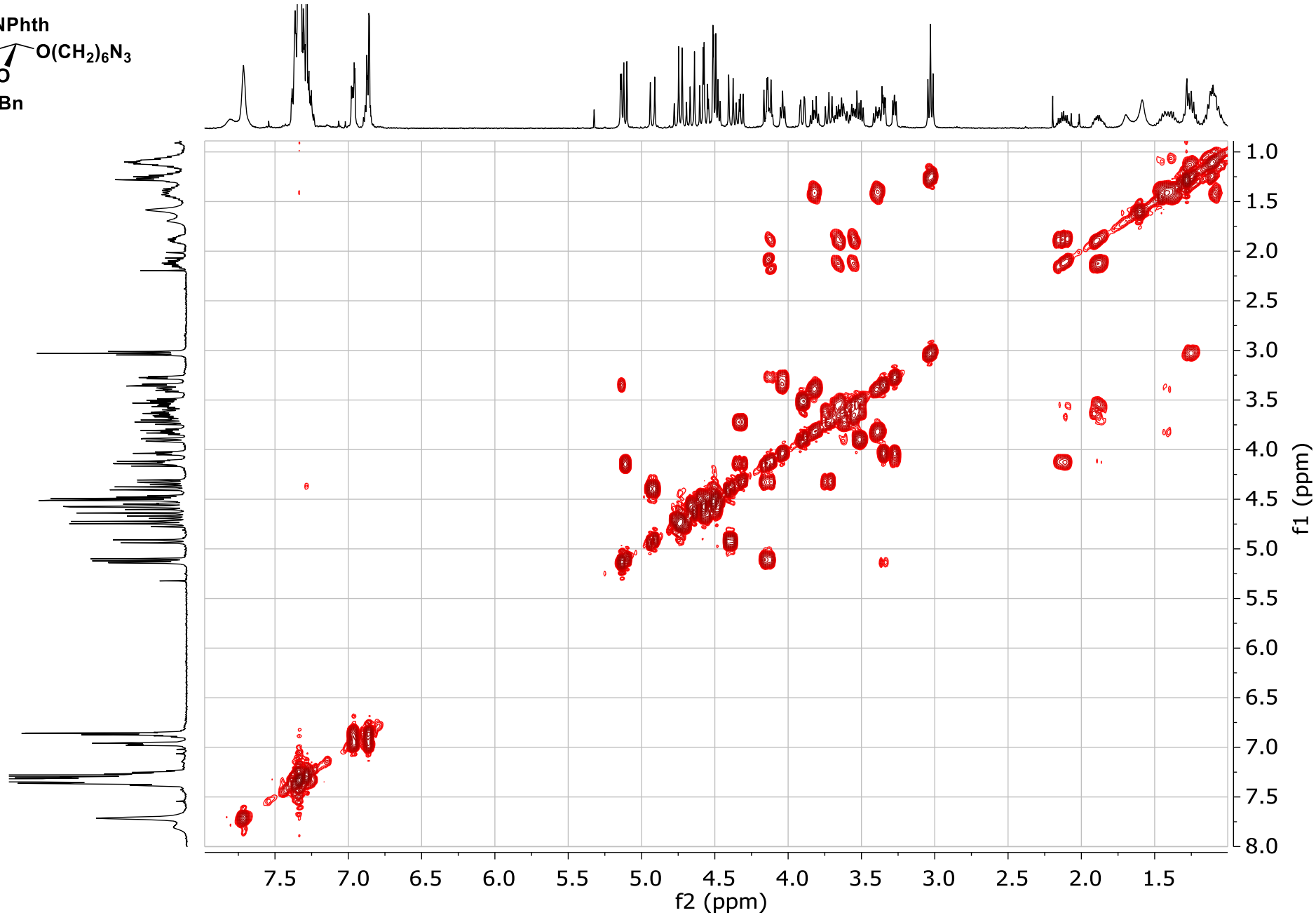


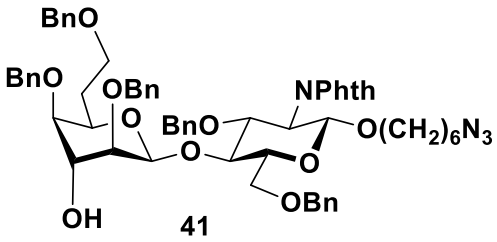
^{13}C (DEPT-Q) NMR Spectrum in $CDCl_3$, 100 MHz, 298 K



^{1}H-^{1}H GCOSY NMR Spectrum in $CDCl_3$, 400 MHz, 298 K







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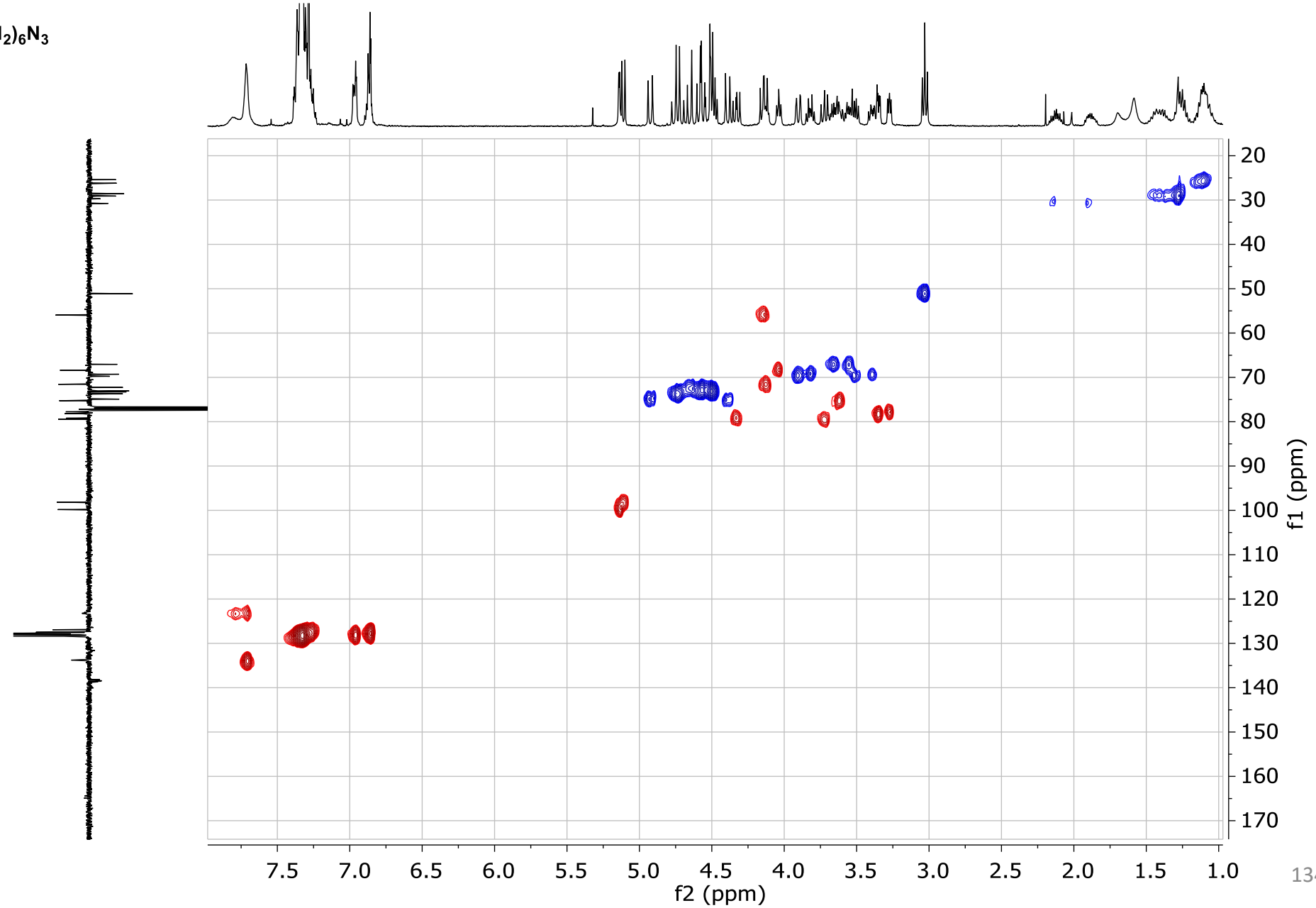
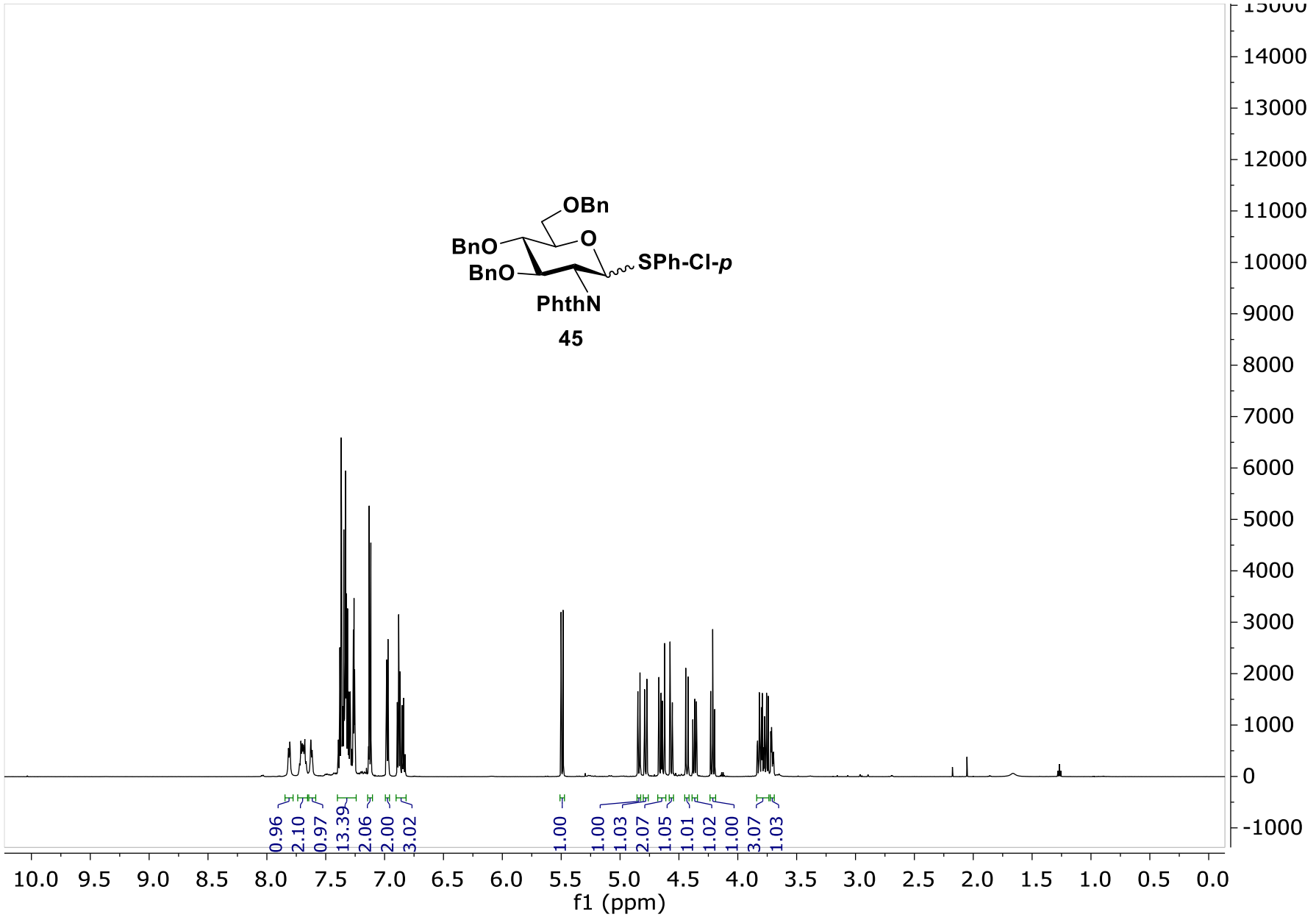
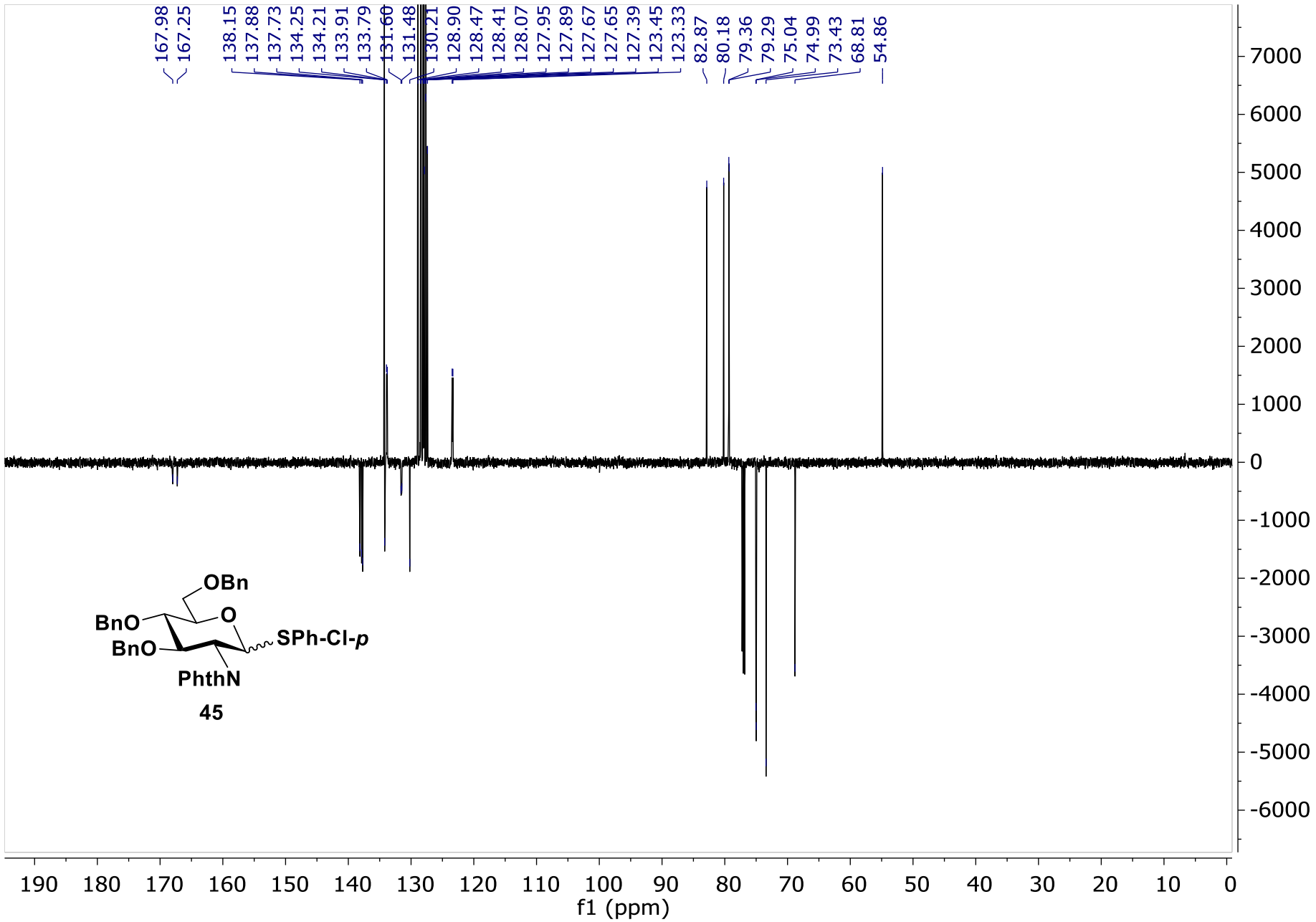
^{1}H-^{13}C GHSQC NMR Spectrum in $CDCl_3$, 400 MHz, 298 K

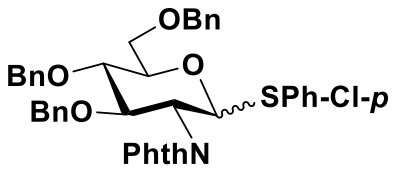


^{1}H NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



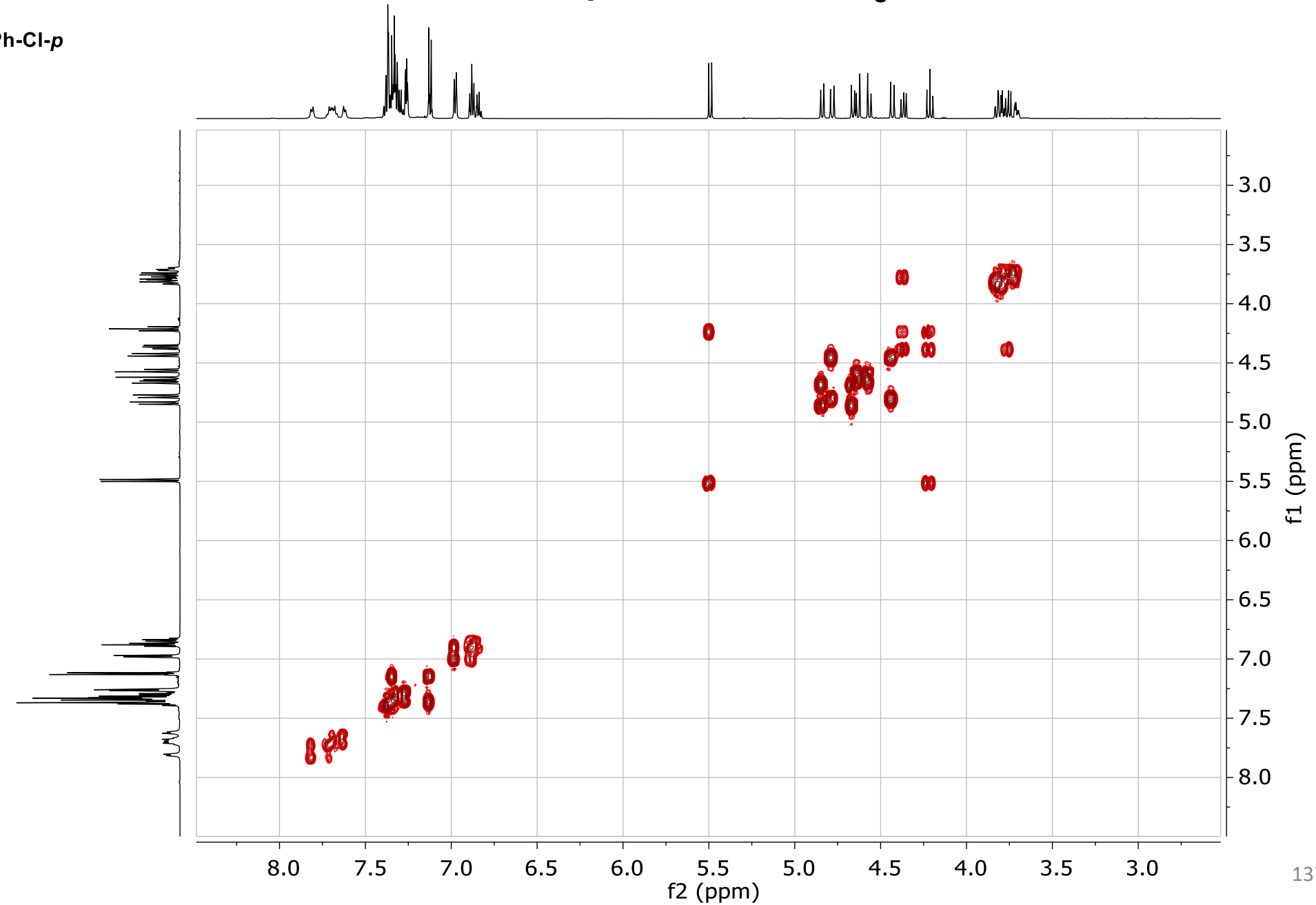
^{13}C (DEPT-Q) NMR Spectrum in $CDCl_3$, 100 MHz, 298 K



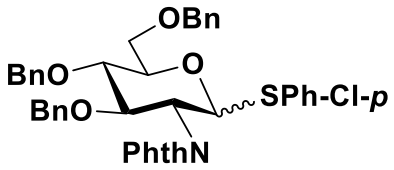


45

^{1}H-^{1}H GCOSY NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



^{1}H-^{13}C GHSQC NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



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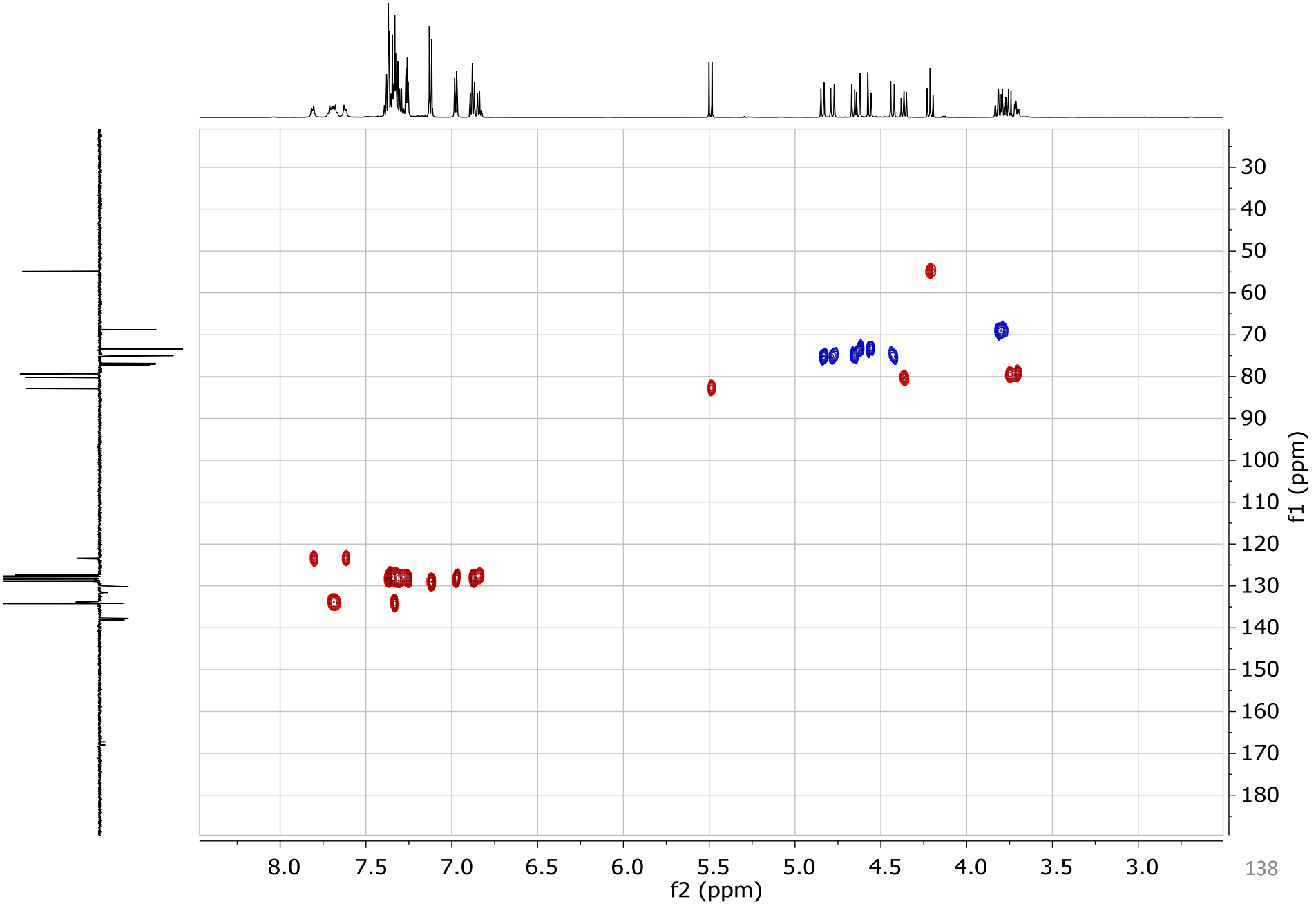
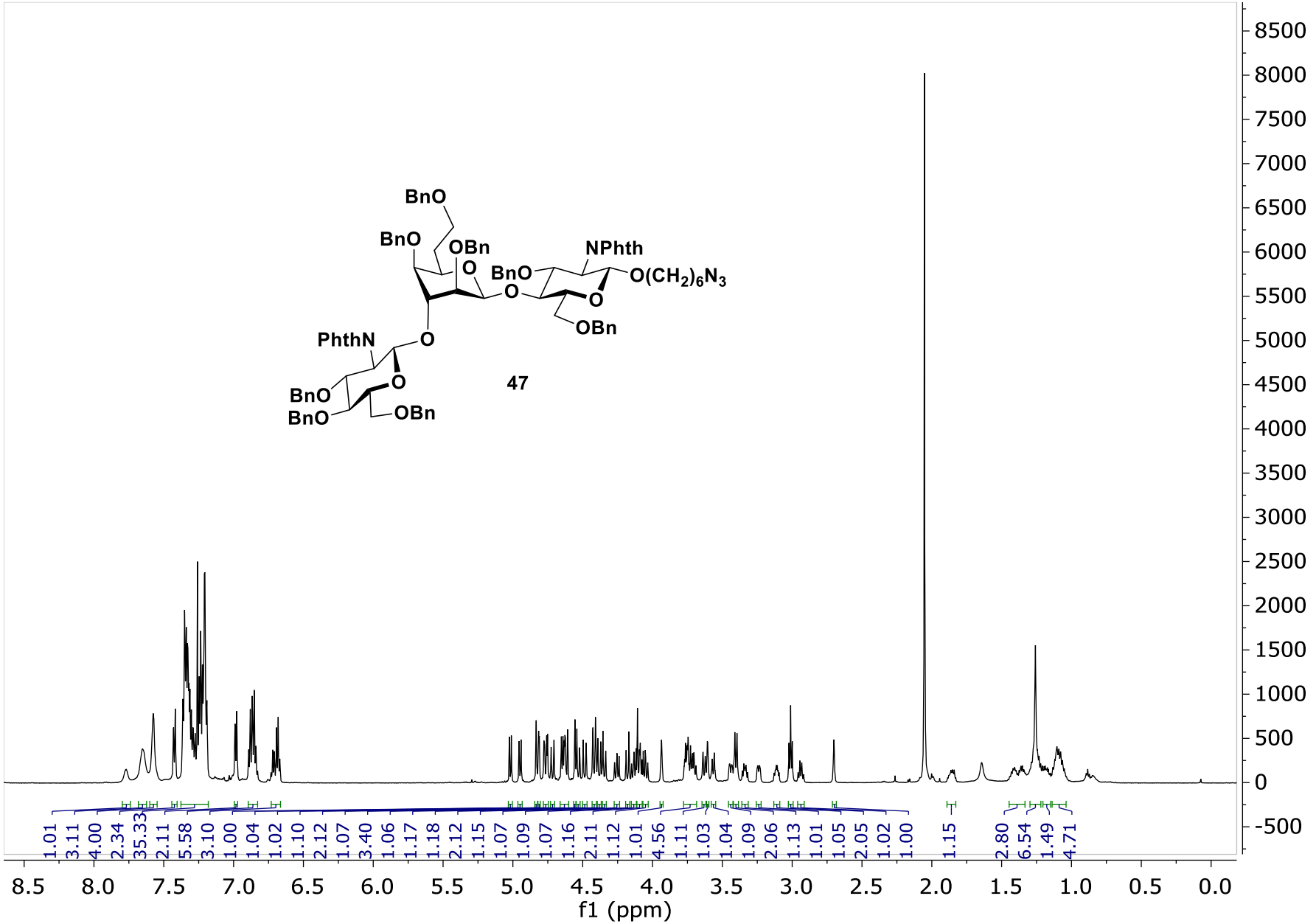
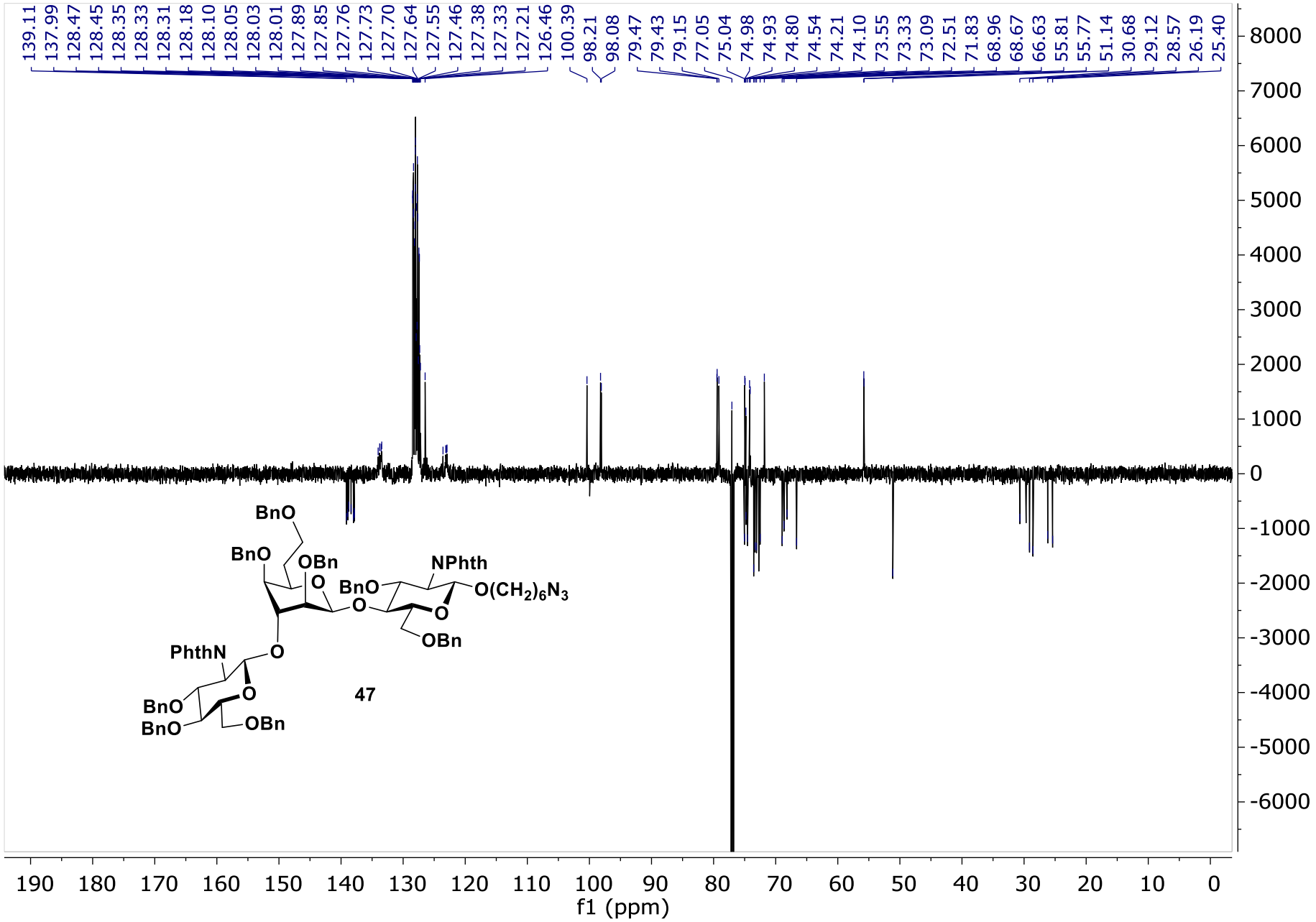


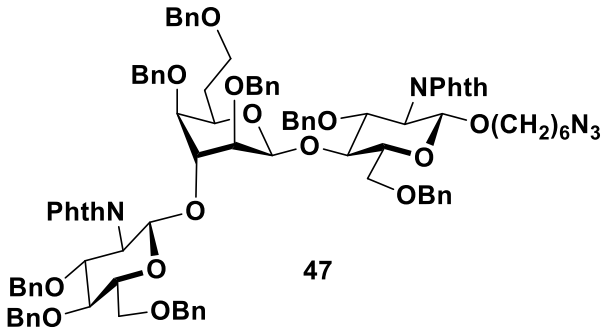
^{1}H NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



^{13}C (DEPT-Q) NMR Spectrum in $CDCl_3$, 100 MHz, 298 K



^{1}H-^{1}H GCOSY NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



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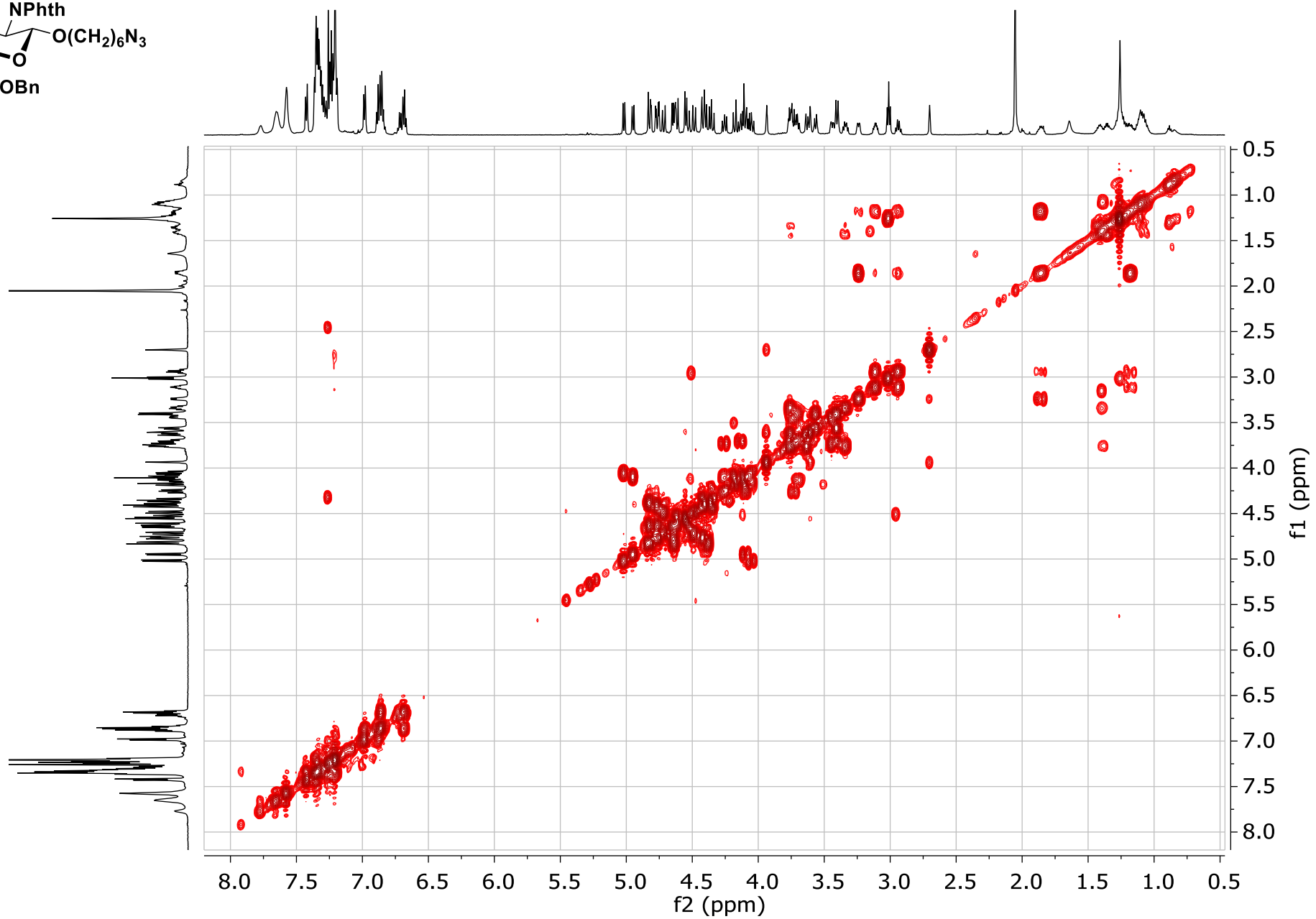
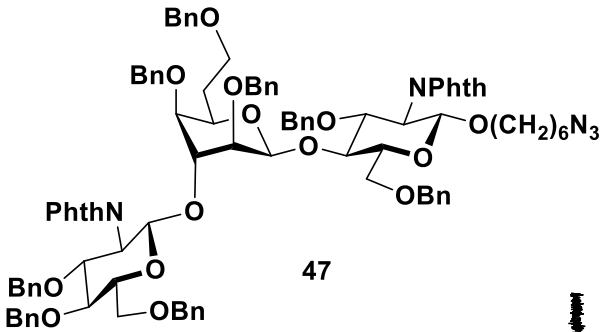


^{1}H-^{13}C GHSQC NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



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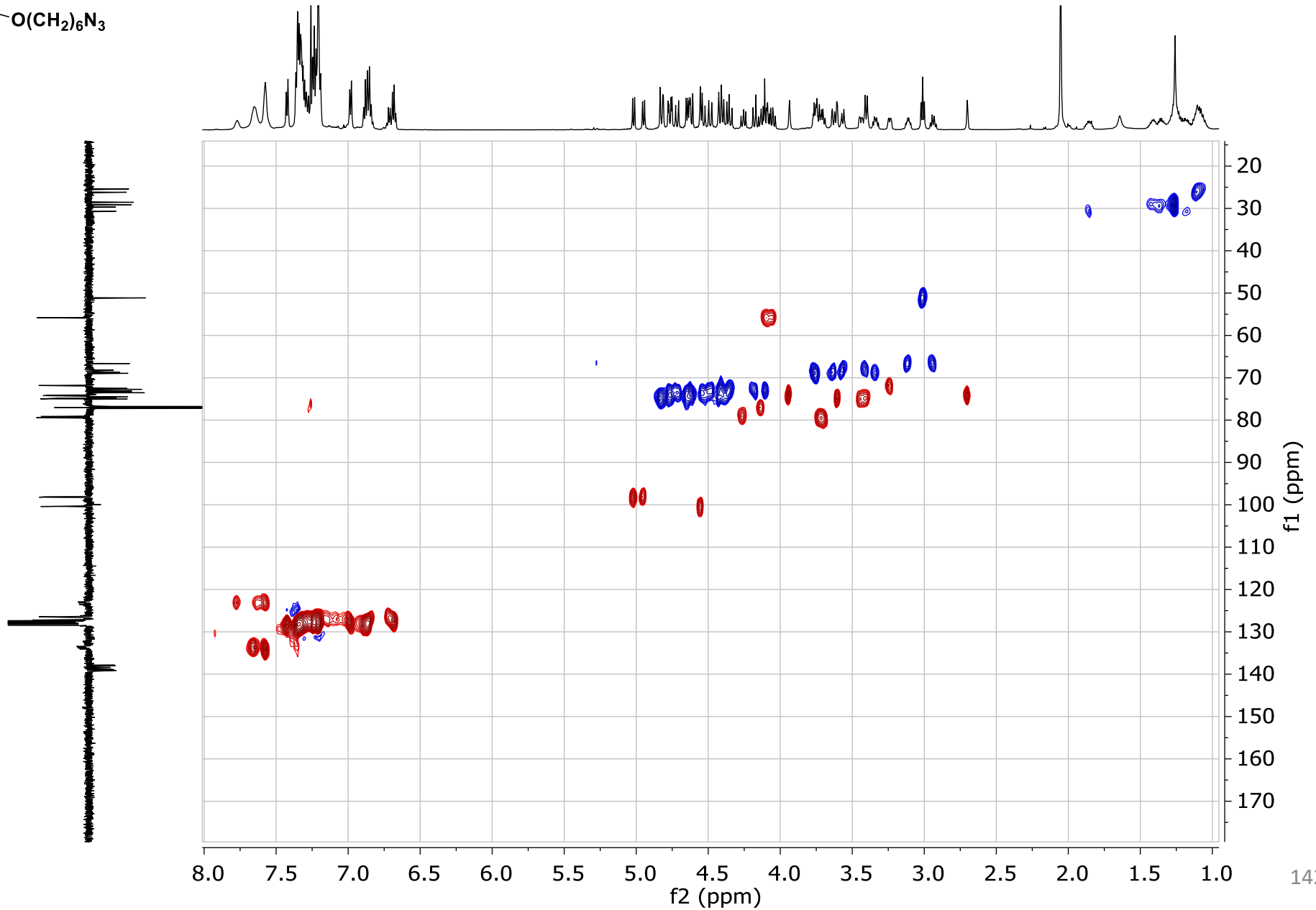
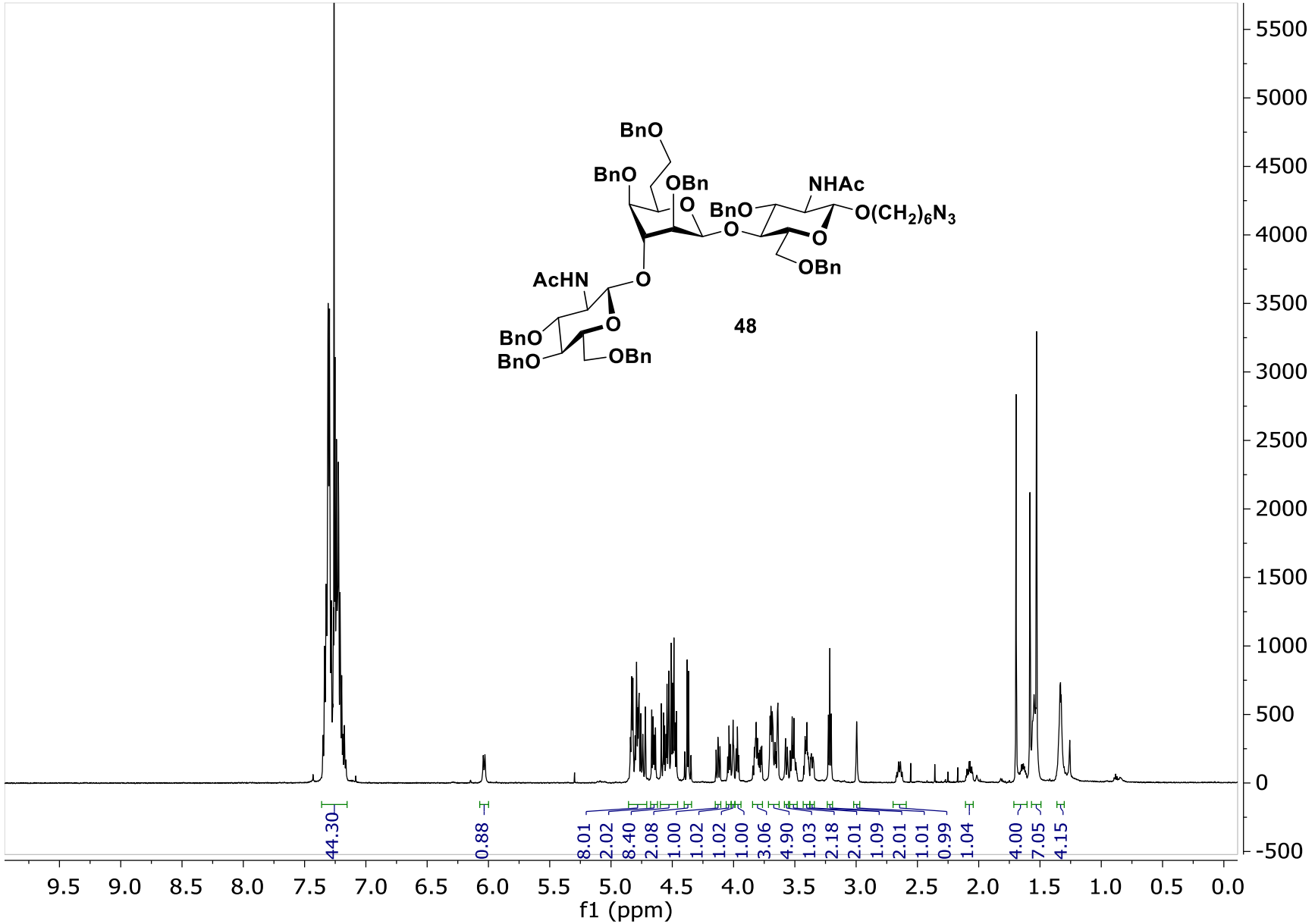
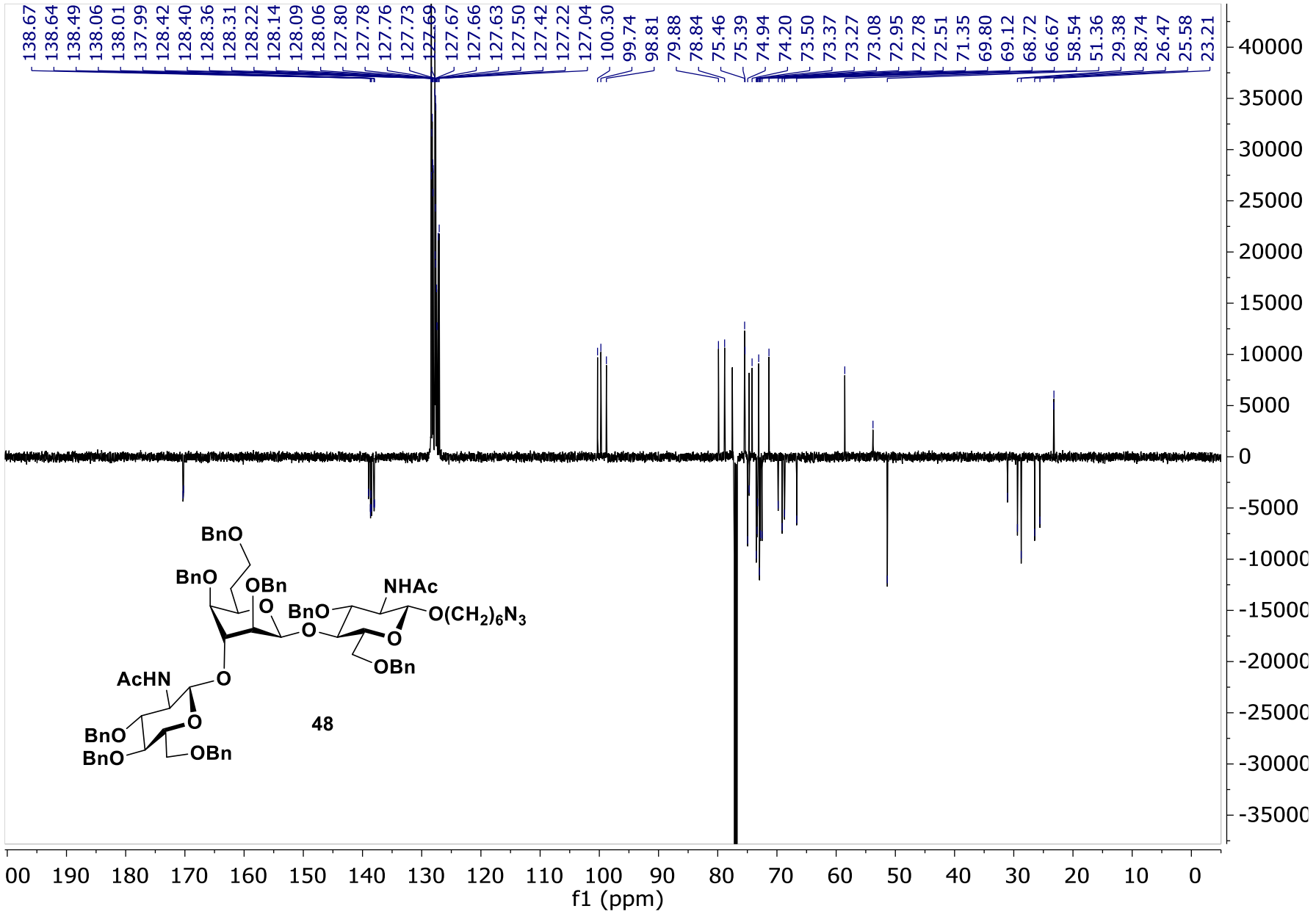
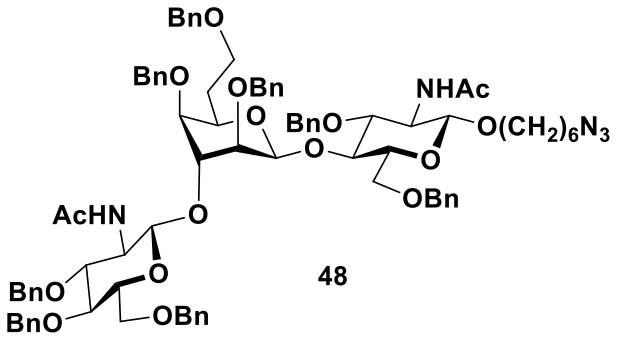


^{13}C (DEPT-Q) NMR Spectrum in $CDCl_3$, 100 MHz, 298 K



^{13}C (DEPT-Q) NMR Spectrum in $CDCl_3$, 100 MHz, 298 K





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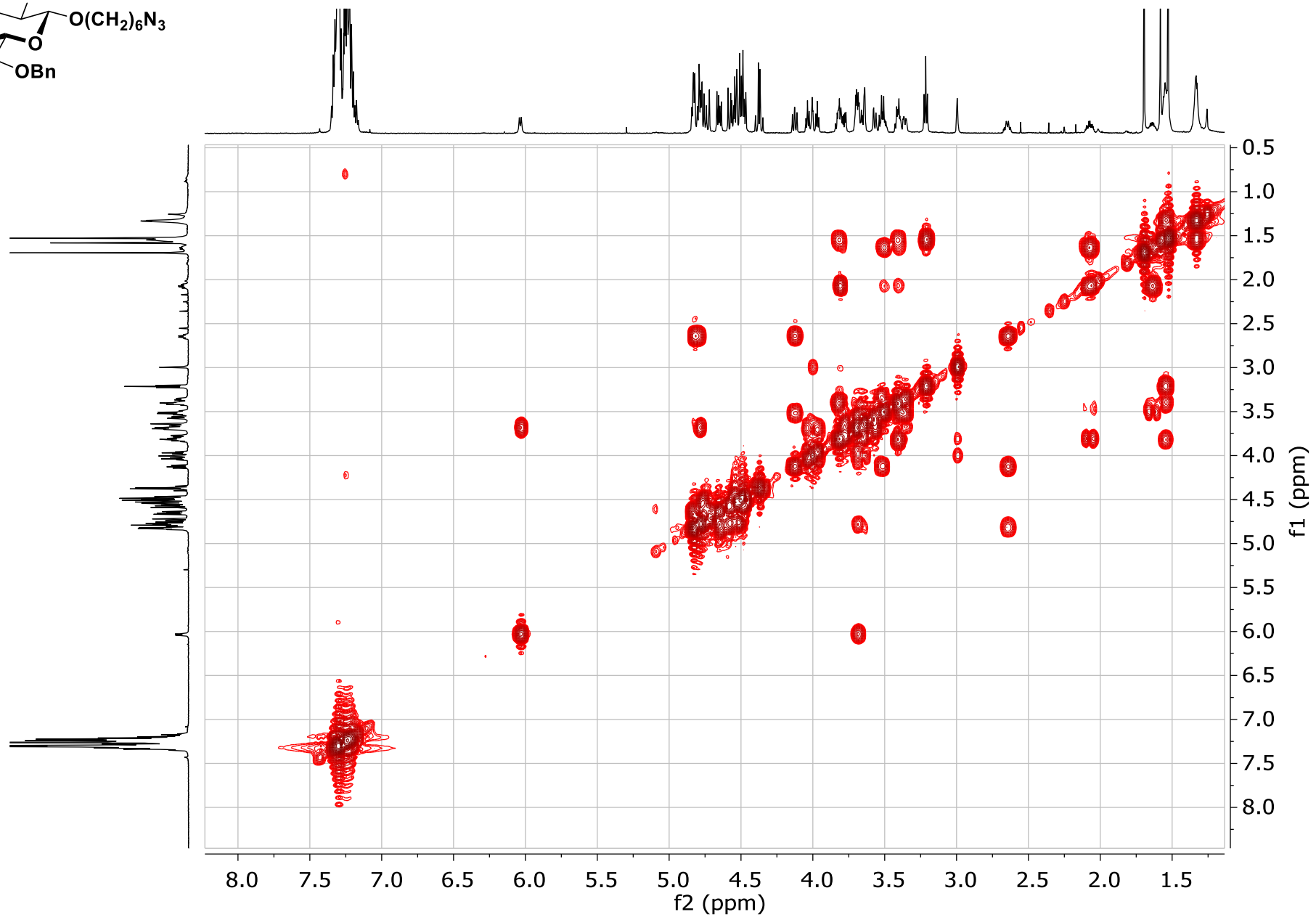
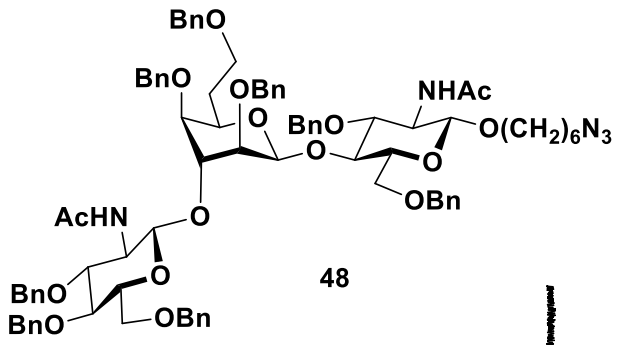
^{1}H-^{1}H GCOSY NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



^{1}H-^{13}C GHSQC NMR Spectrum in $CDCl_3$, 400 MHz, 298 K



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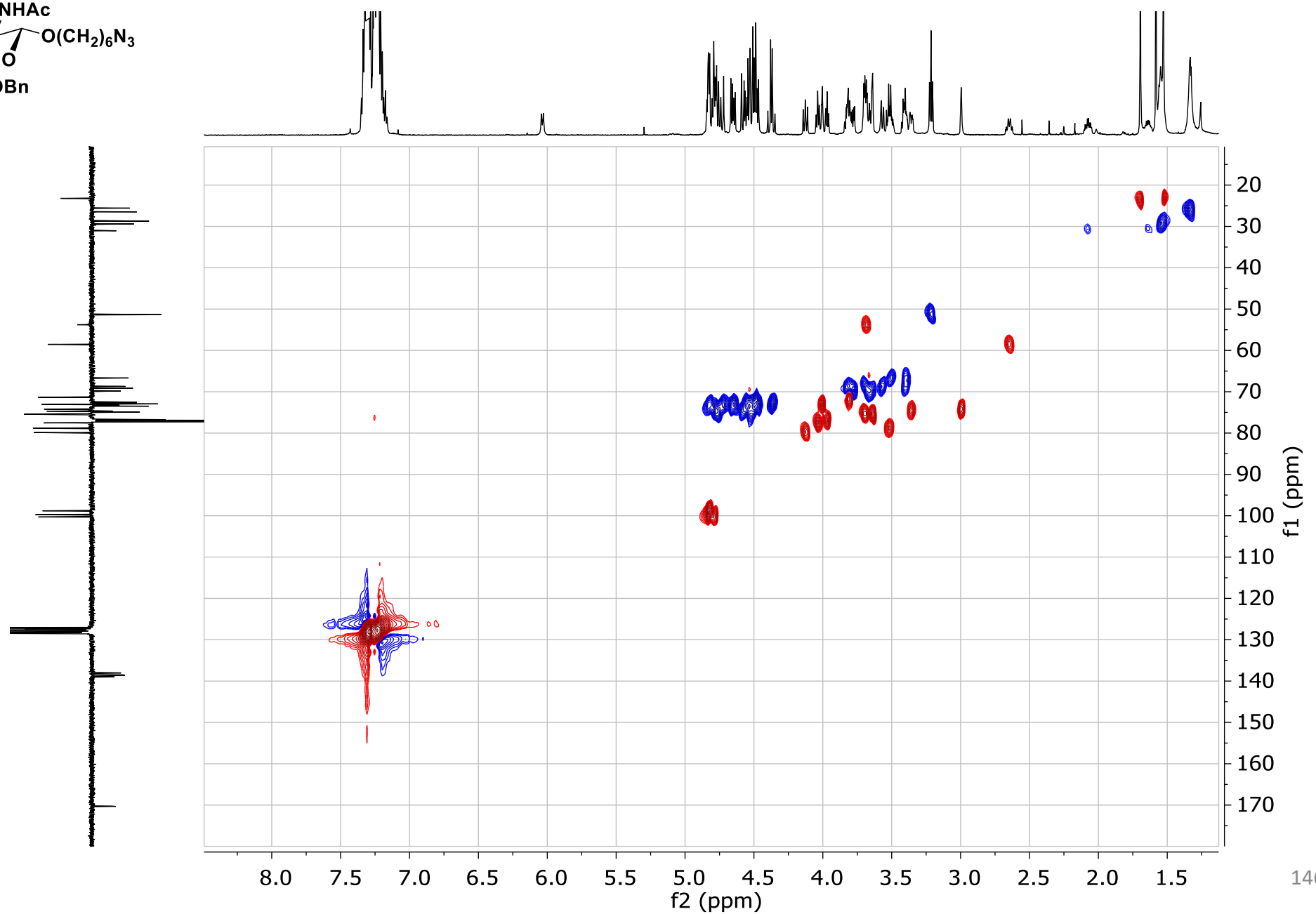
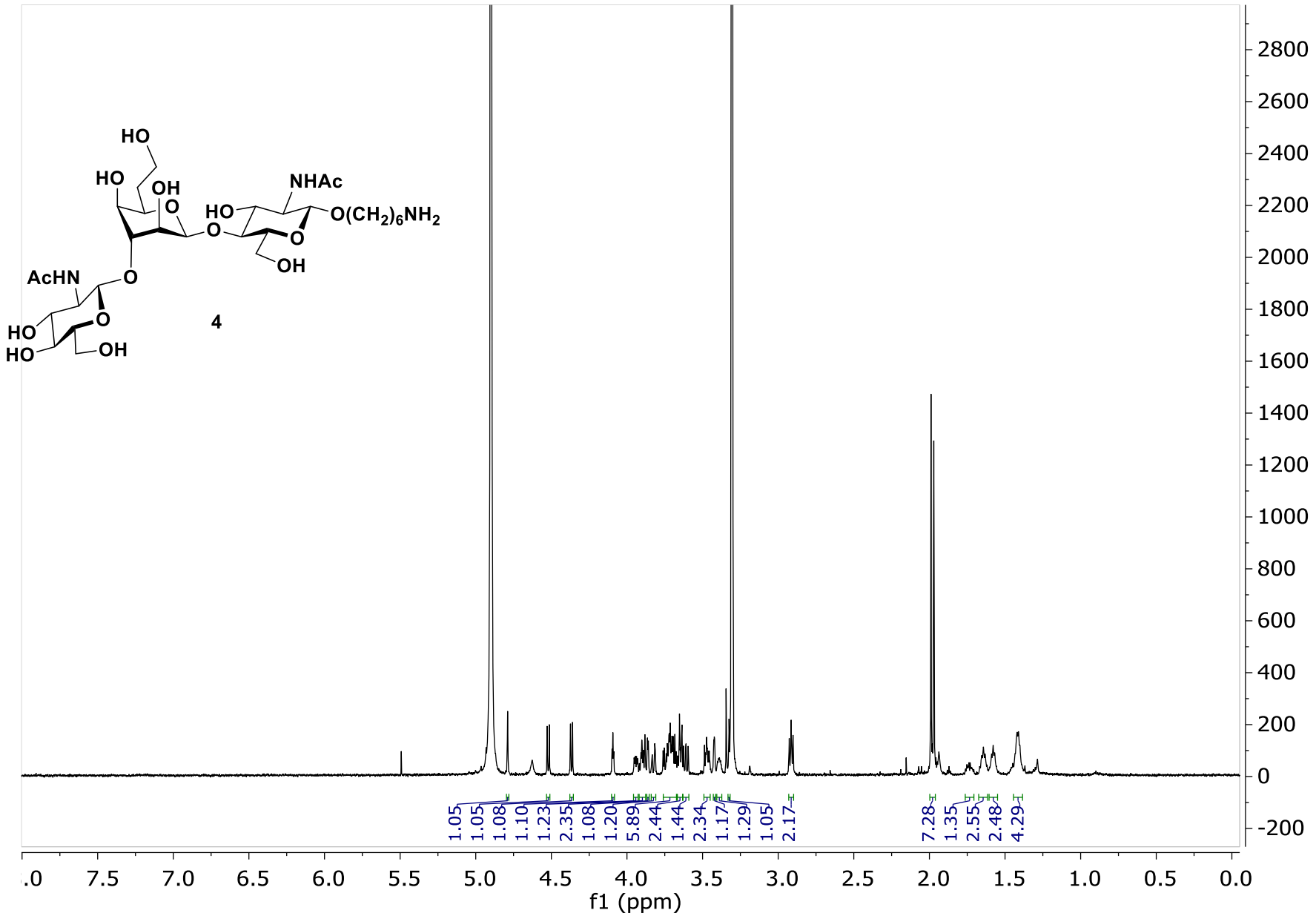
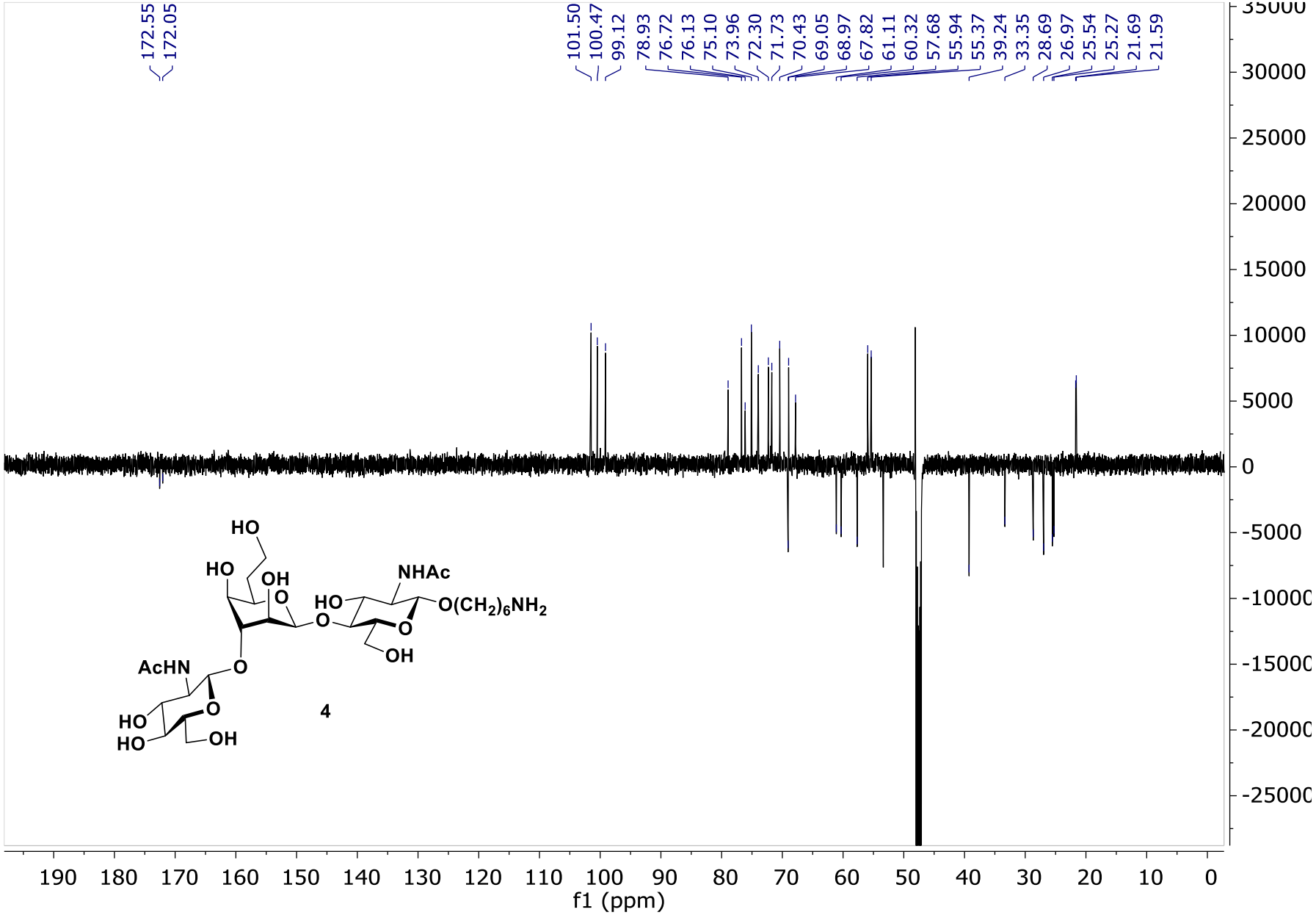


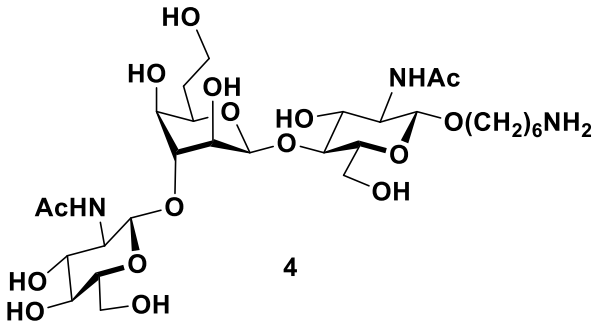
^{1}H NMR Spectrum in D_2O, 400 MHz, 298 K



^{13}C (DEPT-Q) NMR Spectrum in D_2O, 100 MHz, 298 K



^{1}H-^{1}H GCOSY NMR Spectrum in D_2O, 400 MHz, 298 K



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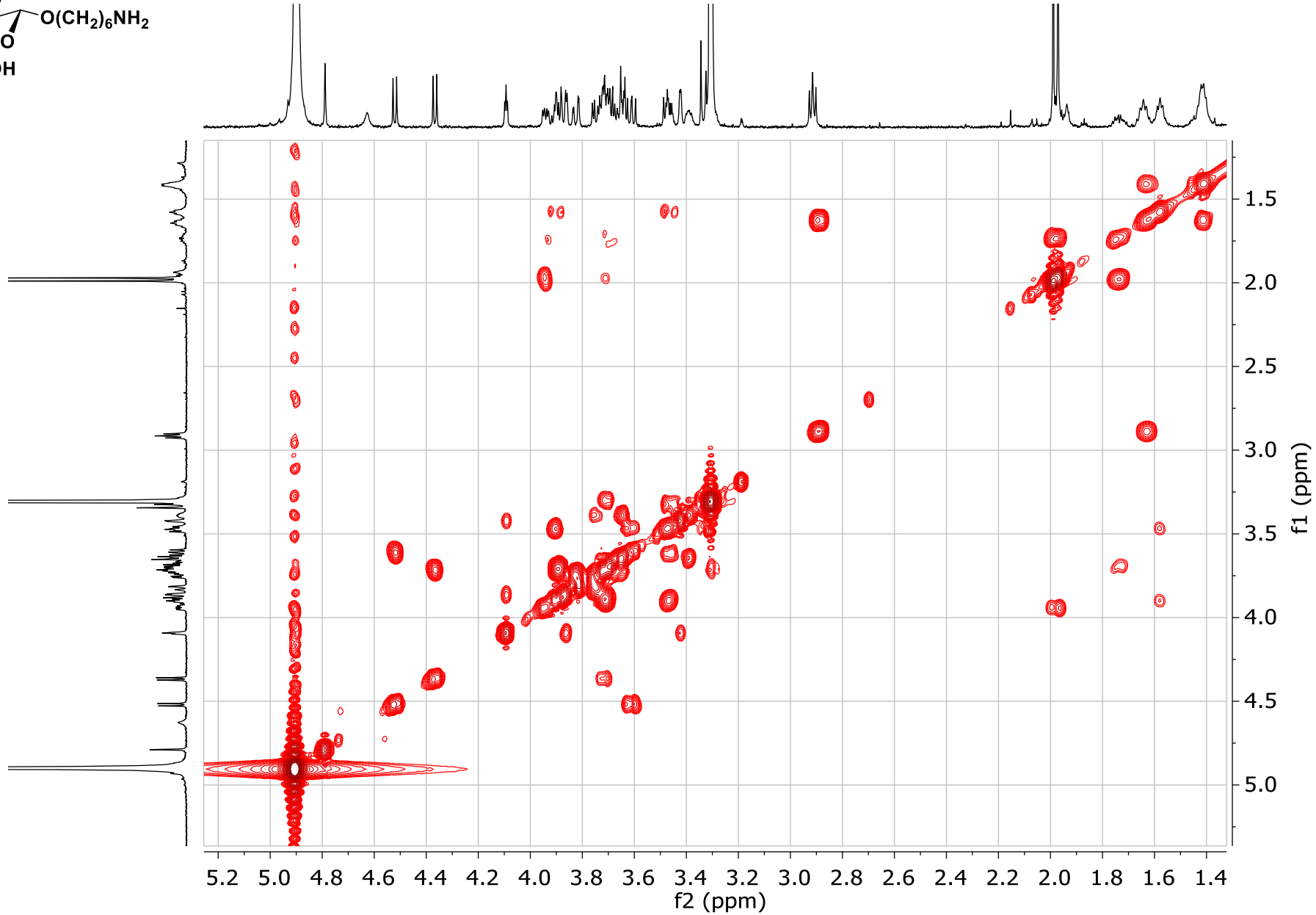
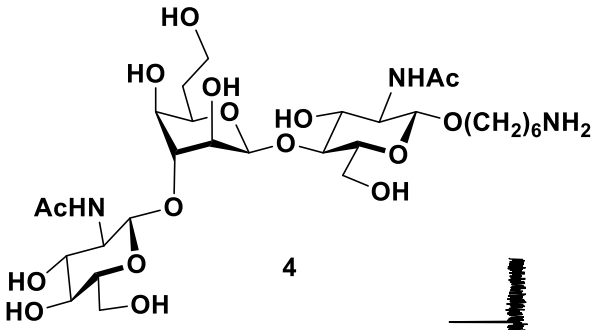


^{1}H-^{13}C GHSQC NMR Spectrum in D_2O, 400 MHz, 298 K



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