Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Synthesis of glycocluster-containing conjugates for a vaccine against cholera

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Supplementary information

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2-[2-(2-Azidoethoxy)ethoxy]ethyl 2,3,4,6-tetra-*O*-2-propyn-1-yl-β-D-glucopyranoside (2):

To a solution of acetate **1** (1.82 g, 3.60 mmol) in MeOH (22 mL) was added 1 M NaOMe in MeOH until the pH was consistently 10. The mixture was stirred at room temperature for 90 min when the reaction was complete. The mixture was diluted with MeOH (≈ 10 mL) and neutralised with Amberlyst IR-120 H+ resin. After filtration over a glass sintered funnel, the resin beads were thoroughly washed with MeOH and DCM and the filtrate was concentrated under vacuum. The crude intermediate (1.23 g, ≈ 3.60 mmol) was dissolved in DMF (60 mL), KOH (2.42 g, 43.2 mmol, 12 equiv, from freshly crushed pellets) was added and the suspension was cooled to 0 °C. Propargyl bromide (80% in toluene, 4.4 mL, 28.8 mmol, 8.0 equiv) was slowly added to the mixture, the temperature was allowed to slowly reach rt and the mixture was stirred for 16 h at room temperature. After addition of H_2O (50 mL), the solution was stirred for 3 h at rt, concentrated under vacuum and coevaporated with H2O. A solution of the crude product in EtOAc (300 mL) was washed with H_2O (100 mL) and brine (100 mL) and the combined aqueous phases were back-washed with EtOAc (100 mL). Chromatography (toluene–acetone 95:5 $\rightarrow$ 9:1) yielded the propargylated derivative **2** (1.26 g, 2.57 mmol, 71%) as a colorless oil. $[\alpha]_D^{23}$ +6.3 (c 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 4.56-4.37 (m, 6H, 3xOC*H*$_2$C≡CH), 4.33 (d, 1H, $J_{1,2}$ = 7.9 Hz, H-1), 4.26-4.17 (m, 2H, OC*H*$_2$C≡CH), 4.00 [m, 1H, CH_2(linker)], 3.84 (dd, 1H, $J_{5,6a}$ = 1.9 Hz, $J_{6a,6b}$ = 10.8 Hz, H-6a), 3.76 (dd, 1H, $J_{5,6b}$ = 5.0 Hz, $J_{6a,6b}$ = 10.8 Hz, H-6b), 3.74 (m, 1H, $CH_{2,linker}$), 3.68-3.65 [m, 8H, CH_2(linker)], 3.55 (t, 1H, $J_{2,3}$ = $J_{3,4}$ = 8.8 Hz, H-3), 3.44 (dd, 1H, $J_{3,4}$ = 8.8 Hz, $J_{4,5}$ = 9.9 Hz, H-4), 3.40-3.38 [m_o, 3H, H-5, CH_2(linker)], 3.36 (dd, 1H, $J_{1,2}$ = 7.9 Hz, $J_{2,3}$ = 9.0 Hz, H-2), 2.49-2.44 (m, 4H, 4xOCH$_2$C≡C*H*); ^{13}C NMR (150 MHz, $CDCl_3$): δ_C 103.17 (C-1), 83.22 (C-3), 81.18 (C-2), 80.04, 80.00, 79.94, 79.51 (4xOCH$_2$*C*≡CH), 75.99 (C-4), 74.66, 74.35, 74.28, 74.23 (4xOCH2C≡CH), 74.02 (C-5), 70.71, 70.57, 70.24, 70.02, 69.03 [5×CH_2(linker)], 68.44 (C-6), 60.20, 59.98, 59.20, 58.63 (4xO*C*H$_2$C≡CH), 50.65 [CH_2(linker)]; HRMS (ESI): *m/z* Found 507.2462; Calc. for $C_{24}H_{35}N_4O_8$ [M + NH_4]$^+$: 507.2455; Anal. Found: C, 58.9; H, 6.2; N, 8.4; Calc. for $C_{24}H_{31}N_3O_8$: C, 58.9; H, 6.4; N, 8.6.

2-[2-(2-(*N*-*tert*-Butyloxycarbonyl)ethoxy)ethoxy]ethyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (4)

Di-*t*-butyl dicarbonate (294 mg, 1.19 mmol, 2.0 equiv) and Pd/C (60 mg) were added to a stirred solution of azide **1** (300 mg, 0.593 mmol) in DCM (4.6 mL) and the stirring under hydrogen (1 atm) at room temperature was continued overnight. The suspension was filtered over Celite and the filtrate was concentrated under vacuum. Chromatography (toluene/acetone 85:15 $\rightarrow$ 8:2) gave the desired Boc-protected amine **4** (320 mg, 0.55 mmol, 93%) as a colorless oil. $[\alpha]_D^{24}$ -17.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 5.21 (t, 1H, $J_{2,3}$ = $J_{3,4}$ = 9.5 Hz, H-3), 5.09 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.9 Hz, H-4), 5.02(s_o, 1H, NH), 5.00 (dd, 1H, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 9.6 Hz, H-2), 4.61 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.26 (dd, 1H, $J_{5,6a}$ = 4.7 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6a), 4.14 (dd, 1H, $J_{5,6b}$ = 2.4 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6b), 3.96 [m, 1H, CH_2(linker)], 3.75 [m, 1H, CH_2(linker)], 3.71 (ddd, 1H, $J_{4,5}$ = 10.0 Hz, $J_{5,6a}$ = 4.7 Hz, $J_{5,6b}$ = 2.3 Hz, H-5), 3.68-3.58 [m, 6H, CH_2(linker)], 3.54 [t, 2H, *J* = 5.1 Hz, CH_2(linker)], 3.32 [q, 2H, *J* = 4.9 Hz, CH_2(linker)], 2.09, 2.05, 2.03, 2.01 (4s, 12 H, OCOC*H*$_3$), 1.45 (s, 9H, C(C*H*$_3$)$_3$); ^{13}C NMR (150 MHz, $CDCl_3$): δ_C 170.66, 170.27, 169.40, 169.35 (4xO*C*OCH$_3$), 155.96 (N*C*OO), 100.82 (C-1), 79.18 (*C*(CH$_3$)$_3$), 72.78 (C-3), 71.77 (C-5), 71.22 (C-2), 70.63, 70.25, 69.04 [5xCH_2(linker)], 68.36 (C-4), 61.91 (C-6), 40.30 [CH_2(linker], 28.39 (C(*C*H$_3$)$_3$), 20.73, 20.65, 20.60, 20.58 (3xOCO*C*H$_3$); HRMS (ESI): *m/z* Found 602.2416; Calc. for $C_{25}H_{41}NO_{14}Na$ [M + Na]$^+$: 602.2425; Anal. Found C, 51.8; H, 7.15; N, 2.4; Calc. for $C_{25}H_{41}NO_{14}$: C, 51.8; H, 7.1; N, 2.4.

(2-(Aminoethylamido)carbonylpentyl 4-(3-deoxy-L-*glycero*-tetronamido)-4,6-dideoxy-α-D-mannopyranoside (7)

Ester **6** (385 mg, 0.979 mmol) was dissolved under Argon in ethylene diamine (8.9 mL) and the solution was stirred at 70 °C overnight. After dilution with H_2O and concentration the crude product was dried

under high vacuum at 50 °C for 3 h. Chromatography (DCM/MeOH/aq NH_4OH 1:0.49:0.01 → 0:98:2) gave the desired amine **7** (404 mg, 0.96 mmol, 98%) as a yellow foam. $[\alpha]_D^{24}$ +21.8 (*c* 1.0, H_2O); ^1H NMR (600 MHz, MeOD): δ_H 4.70 (d, 1H, $J_{1,2}$ = 1.6 Hz, H-1), 4.18 (dd, 1H, *J* = 3.9, 8.1 Hz, H-2'), 3.91 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 10.3 Hz, H-4), 3.83 (dd, 1H, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 10.5 Hz, H-3), 3.80-3.76 (m, 2H, H-2, H-5), 3.75-3.71 (m, 2H, H-4'a, H-4'b), 3.68 (m, 1H, H-1''a), 3.41 (m, 1H, H-1''b), 3.25 (t, 2H, *J* = 6.4 Hz, H-7''), 2.71 (t, 2H, *J* = 6.4 Hz, H-8''), 2.22 (t, 2H, *J* = 7.3 Hz, H-5''), 2.00 (m, 1H, H-3'a), 1.83 (m, 1H, H-3'b), 1.67-1.58 (m, 4H, H-2'', H-4''), 1.44-1.39 (m, 2H, H-3''), 1.17 (d, 3H, $J_{5,6}$ = 6.3 Hz, H-6); ^{13}C NMR (150 MHz, MeOD): δ_C 178.47, 176.90 (*C*O_2CH_3, NH*C*O), 102.12 (C-1), 71.99, 69.06 (2C, C-2, C-5), 71.17 (C-2'), 70.66 (C-3), 68.78 (C-1''), 59.89 (C-4'), 54.89 (C-4), 43.43 (C-7''), 42.51 (C-8''), 38.76 (C-3'), 37.50 (C-5''), 30.72 (C-2''), 27.40 (C-3''), 27.10 (C-4''), 18.78 (C-6); HRMS (ESI): *m/z* Found 422.2494; Calc. for $C_{18}H_{36}N_3O_8$ $[M + H]^+$: 422.2502

(2-(Azidoethylamido)carbonylpentyl β-D-galactopyranoside-(1→4)-glucopyranoside (11)
Ester **9**[50] (5.5 mg, 0.012 mmol) was dissolved under Argon in azido ethan-1-amine **10**[51] (100 μL). The solution was stirred at 100 °C for 44 h, diluted with H_2O and concentrated under vacuum. Chromatography (DCM/MeOH 8:2 → 0:1) gave first the desired azide **11** (3.9 mg, 0.008 mmol, 64%) as a white fluffy solid. ^1H NMR (600 MHz, $CDCl_3$): δ_H 4.45 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1^I), 4.43 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1^{II}), 3.97 (dd, 1H, $J_{5,6a}$ = 2.0 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6^Ia), 3.90 (m_o, 1H, H-4^{II}), 3.89 (m_o, 1H, H-1''a), 3.78 (dd, 1H, $J_{5,6b}$ = 5.0 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6^Ib), 3.76-3.73 (m, 2H, H-6^{II}), 3.71 (m, 1H, H-5^{II}), 3.64 (m_o, 2H, H-3^{II}, H-1''b), 3.62 (m_o, 2H, H-3^I, H-4^I), 3.56 (m, 1H, H-5^I), 3.42-3.40 (m, 2H, H-8''), 3.39-3.37 (m, 2H, H-7''), 3.28 (m, 1H, H-2^I), 2.26 (t, 1H, *J* = 7.4 Hz, H-5''), 1.65-1.59 (m, 4H, H-2'', H-4''), 1.39-1.34 (m, 2H, H-3''); ^{13}C NMR (150 MHz, $CDCl_3$): δ_C 178.09 (NH*C*O), 103.58 (C-1^{II}), 102.68 (C-1^I), 79.03 (C-4^I), 76.01 (C-5^{II}), 75.41 (C-5^I), 75.10 (C-3^I), 73.50 (C-2^I), 73.17 (C-3^{II}), 71.61 (C-2^{II}), 71.01 (C-1''), 69.20 (C-4^{II}), 61.68 (C-6^{II}), 60.74 (C-6^I), 50.73 (C-8''), 39.30 (C-7''), 36.30 (C-5''), 29.04 (C-2''), 25.62 (C-4''), 25.19 (C-4''); HRMS (ESI): *m/z* Found 525.2416; Calc. for $C_{20}H_{37}N_4O_{12}$ $[M + H]^+$: 525.2408.

Acetylated and Boc-protected monosaccharide cluster 16
Propargyl **3** (20 mg, 35.5 μmol) and azide **8** (109 mg, 177 μmol, 5.0 equiv) were allowed to react according to general procedure B. Chromatography (DCM/MeOH) gave the desired product **16** (87 mg, 25.7 μmol, 81%). An analytically pure sample of compound **16** was obtained after acetylation of derivative **17**. $[\alpha]_D^{22}$ +16.7 (*c* 0.43, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ_H 7.78-7.44 (m_o, 12H, NH, H-$5_{triazole}$), 5.27-5.24 (m_o, 4H, H-3), 5.13-5.12 (m_o, 4H, H-2), 5.07-5.04 (m_o, 4H, H-2'), 4.98 (d, 1H, *J* = 12.2 Hz, CH_2-triazole), 4.82-4.77 (m_o, 4H, CH_2-triazole), 4.74-4.73 (m_o, 4H, H-1), 4.65-4.61 (m_o, 4H, CH_2-triazole), 4.59-4.41 (m_o, 8H, H-8a'', H-8b''), 4.37 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1_{Glc}), 4.28-4.22 (m_o, 4H, H-4), 4.18-4.18 (m_o, 8H, H-4'a, H-4'b), 4.06 (m_o, 1H, H-1''a), 3.96-3.89 (m_o, 8H, H-5, H-7a''), 3.80 (m_o, 1H, H-1''b), 3.78-3.60 (m_o, 4H, H-7b''), 3.75-3.37 [m_o, 8H, CH_2(linker)], 3.51 (m_o, 2H, H-$6a_{Glc}$, H-$6b_{Glc}$), 3.45 (m_o, 1H, H-4_{Glc}), 3.44 (m_o, 1H, H-3_{Glc}), 3.32 (m_o, 1H, H-5_{Glc}), 3.29 (t, 1H, $J_{1,2}$ = $J_{2,3}$ = 8.3 Hz, H-2_{Glc}), 3.25-3.22 [m, 2H, CH_2(linker)], 2.30-2.22 (m_o, 8H, H-5''), 2.18-2.14 (m_o, 8H, H-3'a, H-3'b), 2.16, 2.15, 2.09, 2.03, 2.02, 2.00, 1.99 (8s, 48H, CH_{3Ac}), 1.79-1.72 (m, 4H, H-4a''), 1.74-1.66 (m, 4H, H-2a''), 1.61-1.54 (m, 4H, H-4b''), 1.59-1.51 (m, 4H, H-2b''), 1.53-1.46 (m, 4H, H-3a''), 1.43 (s, 9H, CH_{3Boc}), 1.36-1.26 (m, 4H, H-3b''), 1.28-1.26 (m_o, 12H, H-6); ^{13}C NMR (150 MHz, $CDCl_3$): δ_C 174.05, 174.02, 173.95, 173.90 (NH*C*O), 171.08, 171.03, 170.82, 170.41, 170.03, 169.79 (*C*O_2CH_3), 155.94 (NHCOO), 144.65, 144.43, 143.95, 143.81 (C-$4_{triazole}$), 124.59, 124.31, 124.05, 123.81 (C-$5_{triazole}$), 103.47 (C-1_{Glc}), 97.08 (C-1), 84.53 (C-3_{Glc}), 81.42 (C-2_{Glc}), 79.18 (*C*$(CH_3)_3$), 77.20 (C-4_{Glc}), 74.14 (C-5_{Glc}), 71.15, 71.13, 71.11 (C-2'), 70.37, 70.19, 70.07, 68.96 [CH_2(linker)], 69.13, 69.10 (C-2), 68.94, 68.97, 68.94, 68.88 (C-3), 68.49 (C-6_{Glc}), 67.44 (C-5), 66.38, 66.29, 66.26, 66.14 (C-1''), 66.46, 65.23, 65.13, 64.18 (CH_2-triazole), 60.10, 60.08 (C-4'), 50.70, 50.64 (C-4), 50.00, 49.77, 49.75, 49.46 (C-8''), 40.19 [CH_2(linker)], 39.42, 39.36, 39.23 (C-7''), 36.11, 36.09, 36.01, 36.00 (C-5''), 30.76, 30.74 (C-3'), 28.34 (C(CH_3)$_3$), 28.36, 28.34 (C-2''), 25.33, 25.22, 25.21, 25.17 (C-3''), 24.55, 24.43 (C-4''), 20.97, 20.80, 20.78, 20.65 (CH_{3Ac}), 17.79, 17.77, 17.75, 17.74 (C-6); HRMS (ESI):

m/z Found 1513.1954; Calc. for $C_{133}H_{207}N_{21}O_{58}$ $[M + 2H]^{2+}$: 1513.1947; **Anal.** Found C, 52.6; H, 7.0; N, 9.5; Calcd for $C_{133}H_{205}N_{21}O_{58}$: C, 52.8; H, 6.8; N, 9.7.

Boc-protected monosaccharide cluster 17

A solution of the acetylated cluster **16** (77 mg, 25.4 μmol) in MeOH (3.0 mL) was treated following the general procedure C. Preparative HPLC (C18 column, 20% aq ACN for 10 min, 20% → 50% aq ACN in 20 min, 10 ml/min, 10 mg per injection) gave the desired product **17** (47.2 mg, 20.1 μmol, 79%) as a white fluffy solid. $[\alpha]_D^{22}$ +17.0 (*c* 0.87, H_2O); ^{1}H NMR (600 MHz, D_2O): δ_H 8.04, 8.03, 7.99, 7.96 (4s, 4H, H-$5_{triazole}$), 4.97 (d, 1H, *J* = 12.4 Hz, CH_2-triazole), 4.83 (d, 1H, *J* = 12.0 Hz, CH_2-triazole), 4.82 (d, 1H, *J* = 12.4 Hz, CH_2-triazole), 4.79 (m_o, 4H, H-1), 4.73 (d, 1H, *J* = 12.0 Hz, CH_2-triazole), 4.67 (d, 1H, *J* = 12.7 Hz, CH_2-triazole), 4.60 (d, 1H, *J* = 12.7 Hz, CH_2-triazole), 4.57 (d, 1H, *J* = 12.5 Hz, CH_2-triazole), 4.56-4.48 (m_o, 10H, H-1_{Glc}, H-8'', CH_2-triazole), 4.27 (dd_o, 4H, $J_{2',3'a}$ = 3.8 Hz, $J_{2',3'b}$ = 8.7 Hz, H-2'), 4.02 [m, 1H, CH_2(linker)], 3.92-3.88 (m_o, 8H, H-2, H-3), 3.86-3.79 [m_o, 9H, H-4, H-5, CH-$_2$(linker)], 3.74-3.71 (m_o, 9H, H-4', H-6_{Glc}), 4.68-3.59 [m_o, 17H, H-1a'', H-7'', H-3_{Glc}, CH_2(linker)], 3.52-3.50 [m_o, 4H, H-4_{Glc}, H-5_{Glc}, CH_2(linker)], 3.47-3.41 (m_o, 4H, H-1''b), 3.35 (t, 1H, $J_{1,2}$ = $J_{2,3}$ = 8.5 Hz, H-2_{Glc}), 3.19 [t, 2H, *J* = 5.4 Hz, CH_2(linker)], 2.14-2.10 (m_o, 8H, H-5''), 2.04-1.99 (m_o, 4H, H-3'a), 1.86-1.80 (m_o, 4H, H-3'b), 1.55-1.48 (m_o, 8H, H-2''), 1.49-1.42 (m_o, 8H, H-4''), 1.37 (s, 9H, CH_{3Boc}), 1.23-1.18 (m, 8H, H-3''), 1.16-1.14 (m_o, 12H, H-6); ^{13}C NMR (150 MHz, D_2O): δ_C 177.93, 177.61, 177.55 (NH*C*O), 158.72 (NHCOO), 144.74, 144.46 (C-$4_{triazole}$), 125.96, 125.91, 125.79, 125.73 (C-$5_{triazole}$), 103.26 (C-1_{Glc}), 100.40 (C-1), 83.60 (C-3_{Glc}), 81.48 (*C*$(CH_3)_3$), 81.40 (C-2_{Glc}), 77.42 (C-4_{Glc}), 74.02 (C-5_{Glc}), 70.42, 70.31, 70.11 [CH_2(linker)], 70.02, 68.64 (C-2, C-3), 69.79 [CH_2(linker)], 69.59 (C-2'), 68.55 (C-6_{Glc}), 68.26 (C-1''), 67.96 (C-5), 66.15, 65.51, 65.25, 63.95 (CH_2-triazole), 58.45 (C-4'), 53.55 (C-4), 50.20, 50.14 (C-8''), 40.29 [CH_2(linker)], 39.62 (C-7''), 36.62 (C-3'), 36.16 (C-5''), 28.81 (C-2''), 28.36 (C(*C*$H_3)_3$), 26.63 (C-4''), 25.42 (C-3''), 17.49 (C-6); HRMS (ESI): *m/z* Found 2353.2151; Calc. for $C_{101}H_{174}N_{21}O_{42}$ $[M + H]^+$: 2353.2125.

Acetylated and Boc-protected disaccharide cluster 20

Propargyl derivative **3** (17 mg, 30.3 μmol) and azide **14** (150 mg, 152 μmol, 5.0 equiv) were allowed to react according to general procedure B. Chromatography (DCM/MeOH) gave the desired product **20** (128 mg, 28.3 μmol, 89%). An analytically pure sample of compound **20** was obtained after acetylation of derivative **22**. $[\alpha]_D^{23}$ -1.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 7.73, 7.72, 7.70 (4s, 4H, H-$5_{triazole}$), 7.65-7.25 (m_o, 8H, NH), 6.44-6.40 (m_o, 4H, NH), 5.33-5.31 (dd_o, 4H, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 11.1 Hz, H-3^{II}), 5.22-5.20 (m_o, 4H, H-2^{II}), 5.21-5.18 (m_o, 4H, H-3^{I}), 5.11-5.09 (dd_o, 4H, *J* = 4.5, 7.9 Hz, H-2'a^{I}, H-2'a^{II}), 5.07-5.05 (dd_o, 4H, *J* = 4.7, 8.0 Hz, H-2'b^{I}, H-2'b^{II}), 4.99 (d, 1H, *J* = 12.2 Hz, CH_2-triazole), 4.87 (m_o, 4H, H-1^{II}), 4.81-4.76 (m, 3H, CH_2-triazole), 4.75-4.73 (m_o, 4H, H-1^{I}), 4.66-4.60 (m, 4H, CH_2-triazole), 4.57-4.42 (m_o, 8H, H-8''), 4.37 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1_{Glc}), 4.28-4.24 (q, 4H, $J_{4,NH}$ = $J_{3,4}$ = $J_{4,5}$ = 9.8 Hz, H-4^{II}), 4.25-4.17 (m_o, 4H, H-4^{I}), 4.19-4.08 (m_o, 16H, H-$4'^{I}$, H-$4'^{II}$), 4.05 [m, 1H, CH_2(linker)], 3.89-3.88 (m_o, 4H, H-2^{I}), 3.89-3.84 (m_o, 4H, H-5^{I}), 3.84-3.80 (m_o, 4H, H-5^{II}), 3.90-3.65 (m_o, 8H, H-7''), 3.76 [m_o, 1H, CH_2(linker)], 3.74-3.68 (m_o, 4H, H-1''a), 3.72-3.63 [m_o, 4H, CH_2(linker)], 3.59 [t_o, 2H, *J* = 4.5 Hz, CH_2(linker)], 3.54 (m, 2H, H-6_{Glc}), 3.50 [t_o, 2H, *J* = 5.3 Hz, CH-$_2$(linker)], 3.44 (m_o, 1H, H-3_{Glc}), 3.43 (m_o, 1H, H-4_{Glc}), 3.40-3.35 (m, 4H, H-1''b), 3.32 (m, 1H, H-5_{Glc}), 3.28 (t, 1H, $J_{1,2}$ = $J_{2,3}$ = 8.0 Hz, H-2_{Glc}), 3.24-3.22 [m, 2H, CH_2(linker)], 2.27-2.22 (m_o, 8H, H-5''), 2.22, 2.15, 2.12, 2.10, 2.09, 2.08, 2.06, 2.05, 2.04 (9s, 84H, COC*H*$_3$), 2.17-2.12 (m_o, 16H, H-$3'^{I}$, H-$3'^{II}$), 1.80-1.71 (m_o, 4H, H-4''a), 1.75-1.67 (m_o, 4H, H-2''a), 1.63-1.56 (m_o, 4H, H-4''b), 1.61-1.53 (m_o, 4H, H-2''b), 1.51-1.34 (m, 4H, H-3''a), 1.42 (s, 3H, CH_{3Boc}), 1.37-1.25 (m, 4H, H-3''b), 1.26-1.25 (m_o, 12H, H-6^{II}), 1.20-1.18 (d, 12H, H-6^{I}); ^{13}C NMR (150 MHz, $CDCl_3$): δ_C 173.91, 173.89, 173.81, 173.176, 171.66, 171.56, 171.13, 170.87, 170.04, 169.97, 169.89, 169.66 (NH*C*O, O*C*OCH_3), 155.96 (NH*C*OO), 144.83, 144.58, 144.20, 143.92 (C-$4_{triazole}$), 124.41, 123.96, 123.90, 123.68 (C-$5_{triazole}$), 103.50 (C-1_{Glc}), 99.25 (C-1^{II}), 98.35 (C-1^{I}), 84.75 (C-3_{Glc}), 81.66 (C-2_{Glc}), 79.24 (*C*$(CH_3)_3$), 77.48 (C-4_{Glc}), 76.19 (C-2^{I}), 74.23 (C-5_{Glc}), 71.13, 70.85 (C-$2'^{I}$, C-$2'^{II}$), 70.42, 70.21 [CH_2(linker)], 70.13 (C-3^{I}), 70.09 [CH_2(linker)], 69.69 (C-2^{II}), 69.08 (C-5^{II}), 69.00 [CH_2(linker)], 68.55 (C-6_{Glc}), 67.99 (C-3^{II}), 67.54 (C-5^{I}), 66.71, 66.26, 65.46, 64.27 (CH_2-triazole), 66.41, 66.35 (C-1''), 60.09, 59.81 (C-$4'^{I}$, C-$4'^{II}$), 51.69 (C-4^{II}), 51.09, 51.04, 50.98 (C-4^{I}), 49.96, 49.81, 49.51 (C-8''), 40.22 [CH_2(linker)], 39.46, 39.35 (C-7''), 36.14, 36.10, 36.05 (C-5''), 30.72, 30.61 (C-$3'^{I}$, C-$3'^{II}$), 28.53 (C-2''), 28.38 (C(*C*$H_3)_3$), 25.38,

25.27 (C-3''), 24.58, 24.53 (C-4''), 20.98, 20.88, 20.85, 20.82, 20.72 (OCO*C*H$_3$), 17.82 (C-6^{II}), 17.64 (C-6^{I}); HRMS (ESI): *m/z* Found 4517.9312; Calc. for $C_{197}H_{298}N_{25}O_{94}$ $[M + H]^+$: 4517.9307; Anal. Found C, 52.2; H, 6.7; N, 7.5; Calc. for $C_{197}H_{297}N_{25}O_{94}$: C, 52.35; H, 6.6; N, 7.75.

Acetylated and Boc-protected hexaccharide cluster 21

Propargyl derivative **3** (3.8 mg, 6.69 μmol) and azide **15** (83 mg, 33.4 μmol, 5.0 equiv) were allowed to react according to general procedure B. Chromatography (DCM/MeOH) gave the desired, amorphous product **20** (49 mg, 4.67 μmol, 70%). ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 7.75-7.72 (m, 4H, H-5$_{triazole}$), 7.69-7.17(m$_o$, 4H, NH), 6.82-6.40 (m$_o$, 24H, NH), 5.34-5.31 (dd$_o$, 4H, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 11.1 Hz, H-3^{VI}), 5.28-5.21 (m$_o$, 24H, H-2^{VI}, H-3^{I}, H-3^{II}, H-3^{III}, H-3^{IV}, H-3^{V}), 5.11-4.99 (m$_o$, 24H, H-2'), 4.99 (d, 1H, *J* = 12.2 Hz, CH$_2$-triazole), 4.87 (m$_o$, 4H, H-1^{II}), 5.05, 5.02, 4.98, 4.89, 4.72 (m$_o$, 20H, H-1^{I}, H-1^{II}, H-1^{III}, H-1^{IV}, H-1^{V}), 4.95 (s$_o$, 4H, H-1^{VI}), 4.81-4.63 (m, 8H, CH$_2$-triazole), 4.64-4.42 (m$_o$, 8H, H-8''), 4.38 (d, 1H, $J_{1,2}$ = 6.9 Hz, H-1$_{Glc}$), 4.26 (q, 4H, $J_{4,NH}$ = $J_{3,4}$ = $J_{4,5}$ = 10.2 Hz, H-4^{VI}), 4.21-4.10 (m$_o$, 20H, H-4^{I}, H-4^{II}, H-4^{III}, H-4^{IV}, H-4^{V}), 4.19-4.06 (m$_o$, 48H, H-4'^{I}, H-4'^{II}, H-4'^{III}, H-4'^{IV}, H-4'^{V}, H-4'^{VI}), 4.05 [m, 2H, CH$_2$(linker)], 4.10-4.04 (m$_o$, 16H, H-2^{II}, H-2^{III}, H-2^{IV}, H-2^{V}), 3.92 (m$_o$, 4H, H-2^{I}), 3.87-3.83 (m$_o$, 4H, H-5^{VI}), 3.81-3.75 (m$_o$, 20H, H-5^{I}, H-5^{II}, H-5^{III}, H-5^{IV}, H-5^{V}), 3.91-3.66 (m$_o$, 8H, H-7''), 3.72-3.50 [m$_o$, 10H, CH$_2$(linker)], 3.74-3.70 (m$_o$, 4H, H-1''a), 3.56 (m$_o$, 2H, H-6$_{Glc}$), 3.46 (m$_o$, 1H, H-3$_{Glc}$), 3.45 (m$_o$, 1H, H-4$_{Glc}$), 3.40-3.37 (m, 4H, H-1''b), 3.35 (m, 1H, H-5$_{Glc}$), 3.30 (m, 1H, H-2$_{Glc}$), 3.23 [m, 2H, CH$_2$(linker)], 2.28-2.22 (m$_o$, 8H, H-5''), 2.21-2.03 (m, 276H, H-3'^{I}, H-3'^{II}, COC*H$_3$*), 1.80-1.71 (m$_o$, 8H, H-2''a, H-4''a), 1.61-1.59 (m$_o$, 8H, H-2''b, H-4''b), 1.53-1.48 (m, 4H, H-3''a), 1.42 (s, 3H, CH$_{3Boc}$), 1.37-1.32 (m, 4H, H-3''b), 1.25-1.17 (m$_o$, 72H, H-6^{I}, H-6^{II}, H-6^{III}, H-6^{IV}, H-6^{V}, H-6^{VI}); ^{13}C NMR (150 MHz, $CDCl_3$): δ_C 173.91-169.78 (NH*C*O, O*C*OCH$_3$), 155.96 (NH*C*OO), 144.83, 144.50, 144.14, 143.91 (C-4$_{triazole}$), 125.21, 124.37, 123.91, 123.61 (C-5$_{triazole}$), 103.38 (C-1$_{Glc}$), 100.17, 100.13, 99.87, 98.40 (C-1^{I}, C-1^{II}, C-1^{III}, C-1^{IV}, C-1^{V}), 99.25 (C-1^{VI}), 84.78 (C-3$_{Glc}$), 81.65 (C-2$_{Glc}$), 79.25 (*C*(CH$_3$)$_3$), 77.46 (C-4$_{Glc}$), 76.48, 75.45, 75.01, 74.62 (C-2^{I}, C-2^{II}, C-2^{III}, C-2^{IV}, C-2^{V}), 74.22 (C-5$_{Glc}$), 71.12, 71.11, 70.88, 70.84, 70.82, 70.78, 70.75 (C-2'^{I}, C-2'^{II}, C-2'^{III}, C-2'^{IV}, C-2'^{V}, C-2'^{VI}), 70.35, 70.18, 70.14, 70.07, 70.02 [CH$_2$(linker)], 70.40, 70.22, 70.15, 69.80, 69.71, 69.33, 69.30 (C-2^{VI}, C-3^{I}, C-3^{II}, C-3^{III}, C-3^{IV}, C-3^{V}), 67.98 (C-3^{VI}), 69.14, 69.09, 68.98, 68.53 (C-5^{I}, C-5^{II}, C-5^{III}, C-5^{IV}, C-5^{V}), 68.67 (C-6$_{Glc}$), 67.35 (C-5^{VI}), 66.70, 65.41, 64.25 (CH$_2$-triazole), 66.19, 66.04 (C-1''), 60.11, 59.98, 59.94, 59.90, 59.84, 59.78 (C-4'^{I}, C-4'^{II}), 51.69 (C-4^{II}), 52.29, 51.65, 51.54, 51.35, 51.13, 51.02 (C-4^{I}), 50.85 [CH$_2$(linker)], 49.84, 49.50 (C-8''), 40.18 [CH$_2$(linker)], 39.45, 38.83 (C-7''), 36.08, 36.01 (C-5''), 30.71, 30.66, 30.55, 30.51, 30.47 (C-3'^{I}, C-3'^{II}, C-3'^{III}, C-3'^{IV}, C-3'^{V}, C-3'^{VI}), 28.57, 28.45, 28.23 (C-2''), 28.34 (C(*C*H$_3$)$_3$), 25.15 (C-3''), 24.47(C-4''), 20.94-20.53 (OCO*C*H$_3$), 17.88-17.68 (C-6^{I}, C-6^{II}, C-6^{III}, C-6^{IV}, C-6^{V}, C-6^{VI}); HRMS (ESI): *m/z* Found 2631.5535; Calc. for $C_{453}H_{675}N_{43}O_{238}$ $[M + 4H + 2\ NH_3]^{4+}$: 2631.5518.

Boc-protected disaccharide cluster 22

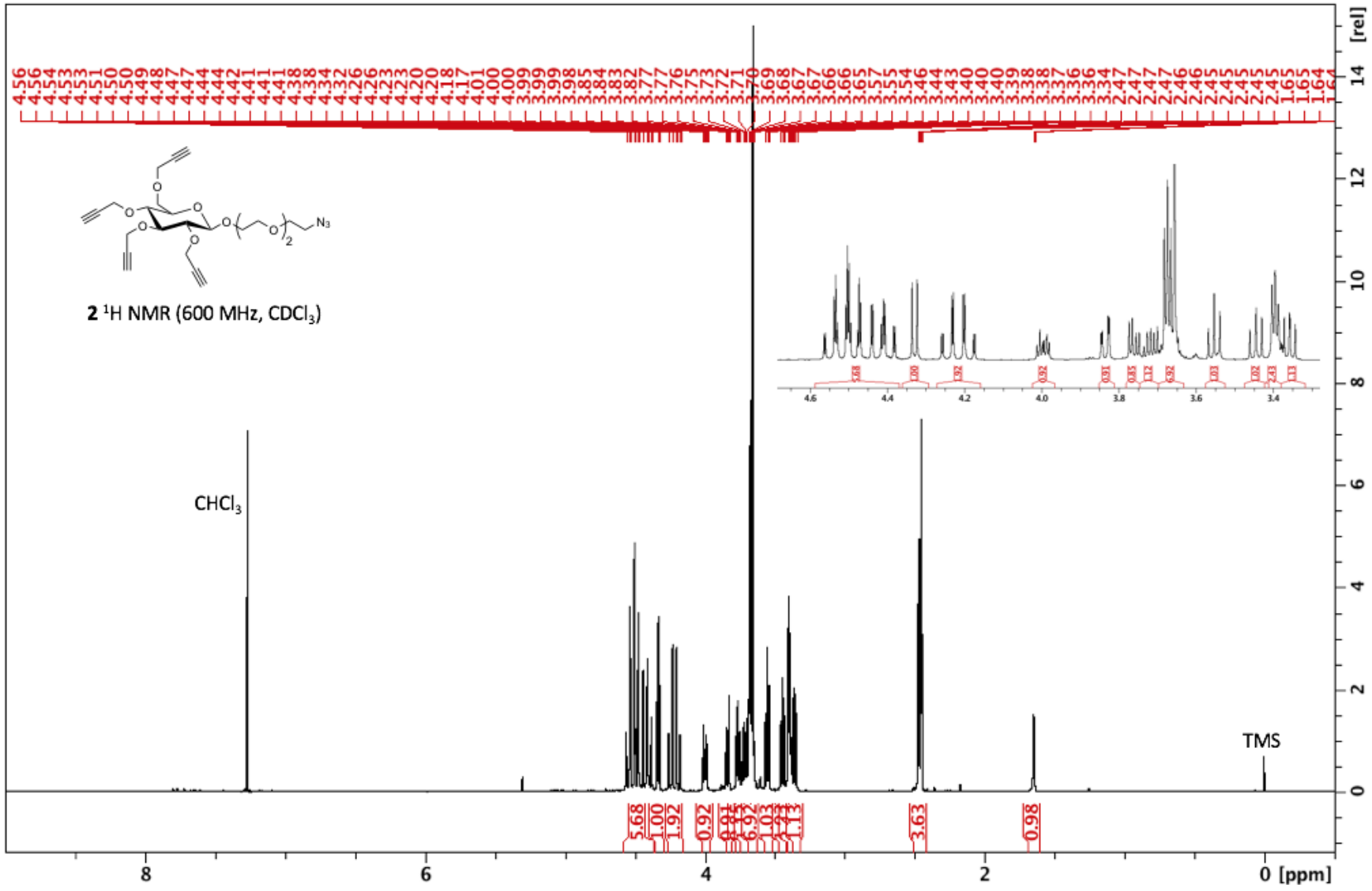
Acetylated cluster **20** (123 mg, 27.2 μmol) in MeOH (2.0 mL) was allowed to react following the general procedure C. Preparative HPLC (C18 column, 20% aq ACN for 10 min, 20% → 50% aq ACN in 20 min, 10 ml/min, 10 mg per injection) gave the desired product **22** (62.7 mg, 18.7 μmol, 67%) as a white fluffy solid. $[\alpha]_D^{20}$ +5.1 (*c* 1.0, H_2O); ^{1}H NMR (600 MHz, D_2O): δ_H 8.04, 8.03, 7.99, 7.95 (4s, 4H, H-5$_{triazole}$), 5.00-4.99 (m$_o$, 4H, H-1^{II}), 4.97 (d, 1H, *J* = 12.3 Hz, CH$_2$-triazole), 4.89-4.87 (m$_o$, 4H, H-1^{I}), 4.84-4.80 (m, 3H, CH$_2$-triazole), 4.72 (d, 1H, *J* = 12.0 Hz, CH$_2$-triazole), 4.67 (d, 1H, *J* = 12.7 Hz, CH$_2$-triazole), 4.61-4.55 (m, 2H, CH$_2$-triazole), 4.54 (d$_o$, 1H, H-1$_{Glc}$), 4.55-4.48 (m$_o$, 8H, H-8''), 4.29-4.26 (m$_o$, 8H, H-2'^{I}, H-2'^{II}), 4.09-4.10 (m$_o$, 4H, H-2^{II}), 4.05-4.01 (m$_o$, 8H, H-3^{I}, H-3^{II}), 4.02 [m, 1H, CH$_2$(linker)], 3.94-3.87 (m$_o$, 16H, H-2^{I}, H-4^{I}, H-4^{II}, H-5^{II}), 3.85-3.81 (m$_o$, 4H, H-5^{I}), 3.81 [m$_o$, 1H, CH$_2$(linker)], 3.74-3.71 (m$_o$, 16H, H-4'^{I}, H-4'^{II}), 3.72 (m, 2H, H-6$_{Glc}$), 3.74-3.60 [m$_o$, 6H, CH$_2$(linker)], 3.68-3.63 (m$_o$, 8H, H-7''), 3.67-3.61 (m$_o$, 4H, H-1''a), 3.61 (m$_o$, 1H, H-3$_{Glc}$), 3.51 (m$_o$, 1H, H-5$_{Glc}$), 3.50 (m$_o$, 1H, H-4$_{Glc}$), 3.53-4.45 [m$_o$, 2H, CH$_2$(linker)], 3.48-3.42 (m, 4H, H-1''b), 3.34 (t, 1H, $J_{1,2}$ = $J_{2,3}$ = 8.5 Hz, H-2$_{Glc}$), 3.18 [t$_o$, 2H, *J* = 5.3 Hz, CH$_2$(linker)], 2.14-2.10 (m$_o$, 8H, H-5''), 2.05-1.99 (m$_o$, 8H, H-3a'^{I}, H-3a'^{II}), 1.89-1.81 (m$_o$, 8H, H-3b'^{I}, H-3b'^{II}), 1.56-1.49 (m$_o$, 8H, H-2''), 1.51-1.43 (m$_o$, 8H, H-4''), 1.37 (s, 3H, CH$_{3Boc}$), 1.25-1.17 (m, 8H, H-3''), 1.17-1.14 (m$_o$, 24H, H-6^{I}, H-6^{II}); ^{13}C NMR (150 MHz, D_2O): δ_C 178.00, 177.95, 177.55, 177.50 (NH*C*O), 158.69 (NH*C*OO), 144.74, 144.46, 144.44 (C-4$_{triazole}$), 125.95, 125.90, 125.78, 125.73 (C-5$_{triazole}$), 103.26 (C-1$_{Glc}$), 102.93 (C-1^{II}), 99.02 (C-1^{I}), 83.59 (C-3$_{Glc}$), 81.46 (*C*(CH$_3$)$_3$), 81.39 (C-2$_{Glc}$), 78.78 (C-2^{I}), 77.40 (C-4$_{Glc}$), 74.02 (C-5$_{Glc}$), 70.42, 70.31,

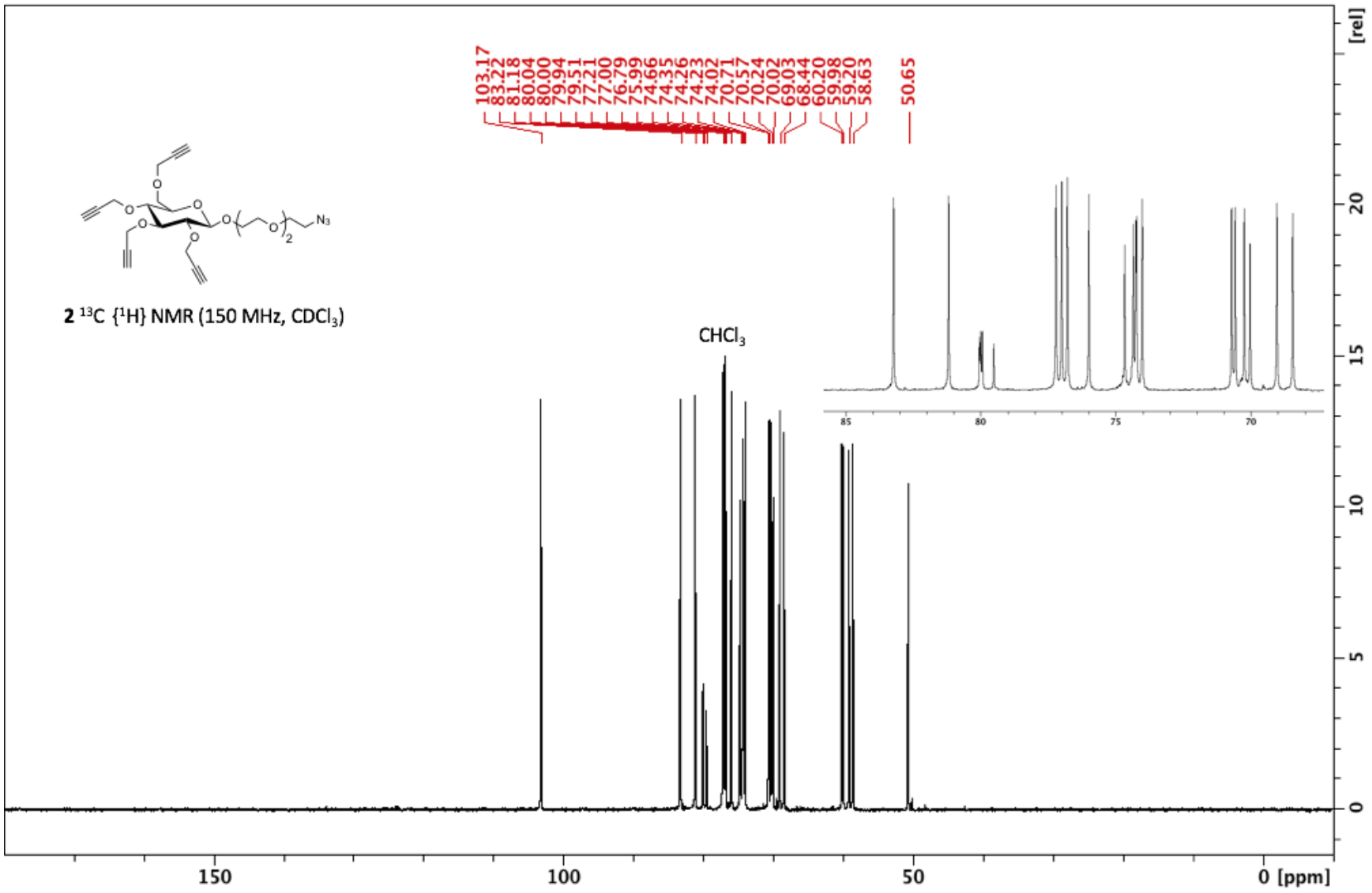
70.13, 70.02, [CH_2(linker)], 69.78 (C-2^{II}), 69.60, 69.59 (C-2'^{I}, C-2'^{II}), 68.64 (C-5^{II}), 68.55 (C-6$_{Glc}$), 68.49, 68.46, 66.44 (C-1''), 68.35 (C-3^{I}, C-3^{II}), 68.22 (C-5^{I}), 66.15, 65.49, 65.25, 63.96(CH_2-triazole), 58.46 (C-4'^{I}, C-4'^{II}), 53.70, 53.39 (C-4^{I}, C-4^{II}), 50.20, 50.15, 50.13, 50.11 (C-8''), 40.30 [CH_2(linker)], 39.64, 39.61, 39.59 (C-7''), 36.64, 36.60 (C-3'^{I}, C-3'^{II}), 36.17 (C-5''), 28.8 (C-2''), 28.38 (C(CH_3)$_3$), 25.63 (C-4''), 25.45, 25.42 (C-3''), 17.82 (C-6^{I}, C-6^{II}); HRMS (ESI): *m/z* Fund 3341.6335; Calc. for $C_{141}H_{242}N_{25}O_{66}$ $[M + H]^+$: 3341.6349.

Boc-protected hexasaccharide cluster 25

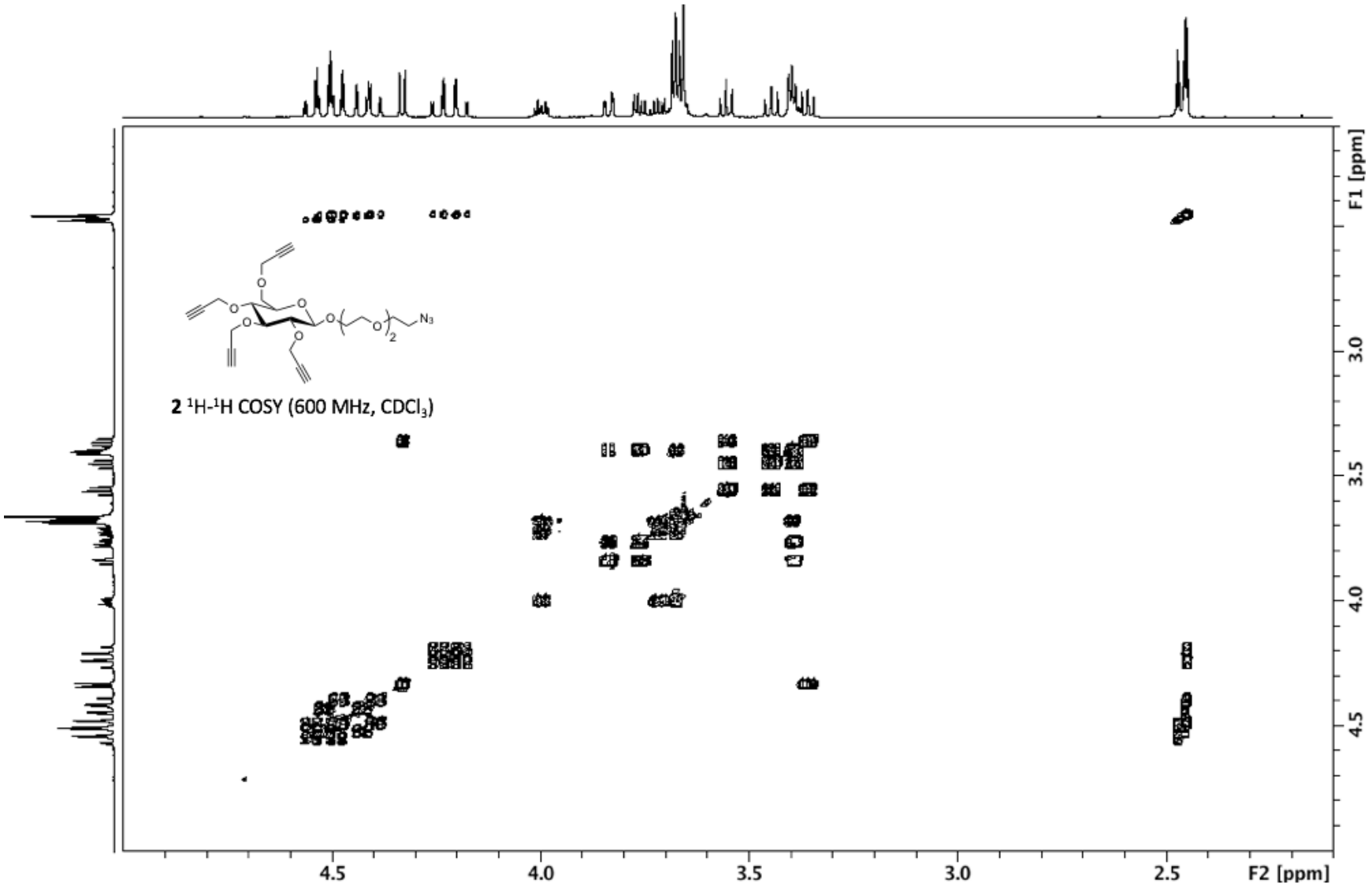
Acetylated cluster **21** (49 mg, 4.67 μmol) in MeOH (1.0 mL) was allowed to react following the general procedure C. Preparative HPLC (C18 column, 20% aq ACN for 10 min, 5% → 250% aq ACN in 20 min, 10 ml/min, 10 mg per injection) gave the desired product **25** (15.9 mg, 2.18 μmol, 47%) as a white fluffy solid. $[\alpha]_D^{20}$ +1.2 (*c* 1.0, H_2O); ^{1}H NMR (600 MHz, D_2O): δ_H 8.03, 8.02, 7.98, 7.95 (4s, 4H, H-5$_{triazole}$), 5.16, 5.15, 5.12 (3s, 16H, H-1^{II}, H-1^{III}, H-1^{IV}, H-1^{V}), 5.03 (s, 4H, H-1^{VI}), 4.96 (d, 1H, *J* = 12.0 Hz, CH_2-triazole), 4.85 (m$_o$, 4H, H-1^{I}), 4.72-4.56 (m, 7H, CH_2-triazole), 4.54 (m$_o$, 1H, H-1$_{Glc}$), 4.53-4.46 (m$_o$, 8H, H-8''), 4.29-4.27 (m$_o$, 24H, H-2'^{I}, H-2'^{II}, H-2'^{III}, H-2'^{IV}, H-2'^{V}, H-2'^{VI}), 4.18-4.14 (m$_o$, 16H, H-2^{II}, H-2^{III}, H-2^{IV}, H-2^{V}), 4.16-4.12, 4.04-4.01 (2m$_o$, 16H, H-3^{II}, H-3^{III}, H-3^{IV}, H-3^{V}), 4.10 (s$_o$, 4H, H-2^{VI}), 4.05-4.02 [m$_o$, 9H, H-3^{VI}, H-4^{I}, CH_2(linker)], 4.14, 3.94-3.87 (2m$_o$, 20H, H-4^{II}, H-4^{III}, H-4^{IV}, H-4^{V}, H-4^{VI}), 3.93 (m$_o$, 9H, H-3^{I}), 3.92 (m$_o$, 4H, H-2^{I}), 4.94-3.87 (m$_o$, 20H, H-5^{II}, H-5^{III}, H-5^{IV}, H-5^{V}, H-5^{VI}), 3.85-3.80 (m$_o$, 4H, H-5^{I}), 3.80 [m$_o$, 1H, CH_2(linker)], 3.74-3.72 (m$_o$, 48H, H-4'^{I}, H-4'^{II}, H-4'^{III}, H-4'^{IV}, H-4'^{V}, H-4'^{VI}), 3.72-3.50 [m$_o$, 8H, CH_2(linker)], 3.66-3.61 (m$_o$, 12H, H-1''a, H-7''), 3.60 (m$_o$, 1H, H-3$_{Glc}$), 3.50 (m$_o$, 1H, H-5$_{Glc}$), 3.49 (m$_o$, 1H, H-4$_{Glc}$), 3.50-3.44 (m, 4H, H-1''b), 3.33 (t, 1H, $J_{1,2}$ = $J_{2,3}$ = 8.5 Hz, H-2$_{Glc}$), 3.17 [t$_o$, 2H, *J* = 5.1 Hz, CH_2(linker)], 2.14-2.09 (m$_o$, 8H, H-5''), 2.05-2.00 (m$_o$, 24H, H-3a'^{I}, H-3a'^{II}, H-3a'^{III}, H-3a'^{IV}, H-3a'^{V}, H-3a'^{VI}), 1.87-1.81 (m$_o$, 24H, H-3b'^{I}, H-3b'^{II}, H-3b'^{III}, H-3b'^{IV}, H-3b'^{V}, H-3b'^{VI}), 1.56-1.48 (m$_o$, 8H, H-2''), 1.50-1.44 (m$_o$, 8H, H-4''), 1.37 (s, 3H, CH_{3Boc}), 1.23-1.18 (m, 8H, H-3''), 1.17-1.14 (m$_o$, 72H, H-6^{I}, H-6^{II}, H-6^{III}, H-6^{IV}, H-6^{V}, H-6^{VI}); ^{13}C NMR (150 MHz, D_2O): δ_C 178.04, 177.97, 177.54, 177.49 (NH*C*O), 158.66 (NH*C*OO), 144.73, 144.44 (C-4$_{triazole}$), 125.93, 125.88, 125.76, 125.71 (C-5$_{triazole}$), 103.23 (C-1$_{Glc}$), 102.78 (C-1^{VI}), 101.46, 101.36 (C-1^{II}, C-1^{III}, C-1^{IV}, C-1^{V}), 99.08 (C-1^{I}), 83.53 (C-3$_{Glc}$), 81.36 (C-2$_{Glc}$), 78.31 (C-2^{I}), 77.93, 77.82, 77.74 (C-2^{II}, C-2^{III}, C-2^{IV}, C-2^{V}), 77.37 (C-4$_{Glc}$), 74.00 (C-5$_{Glc}$), 70.42, 70.31, 70.12 [CH_2(linker)], 69.73 (C-2^{VI}), 69.59 (C-2'^{I}, C-2'^{II}, C-2'^{III}, C-2'^{IV}, C-2'^{V}, C-2'^{VI}), 68.89, 68.67 (C-5^{II}, C-5^{III}, C-5^{IV}, C-5^{V}, C-5^{VI}), 68.48 (C-1''), 68.37, 68.12, 68.04 (C-3^{I}, C-3^{II}, C-3^{III}, C-3^{IV}, C-3^{V}, C-3^{VI}), 68.23 (C-5^{I}), 66.12, 65.47, 65.24, 63.95 (CH_2-triazole), 58.46 (C-4'^{I}, C-4'^{II}), 53.73, 53.57, 53.36 (C-4^{I}, C-4^{II}, C-4^{III}, C-4^{IV}, C-4^{V}, C-4^{VI}), 50.21, 50.14 (C-8''), 40.32 [CH_2(linker)], 39.70 (C-7''), 36.64, 36.60 (C-3'^{I}, C-3'^{II}, C-3'^{III}, C-3'^{IV}, C-3'^{V}, C-3'^{VI}), 36.16 (C-5''), 28.82 (C-2''), 28.40 (C(CH_3)$_3$), 25.63 (C-4''), 25.46 (C-3''), 17.58, 17.49 (C-6^{I}, C-6^{II}, C-6^{III}, C-6^{IV}, C-6^{V}, C-6^{VI}); HRMS (ESI): *m/z* Found 7295.3243; Calc. for $C_{301}H_{514}N_{41}O_{162}$ $[M + H]^+$: 7295.3146.

Propargyl intermediate **2**

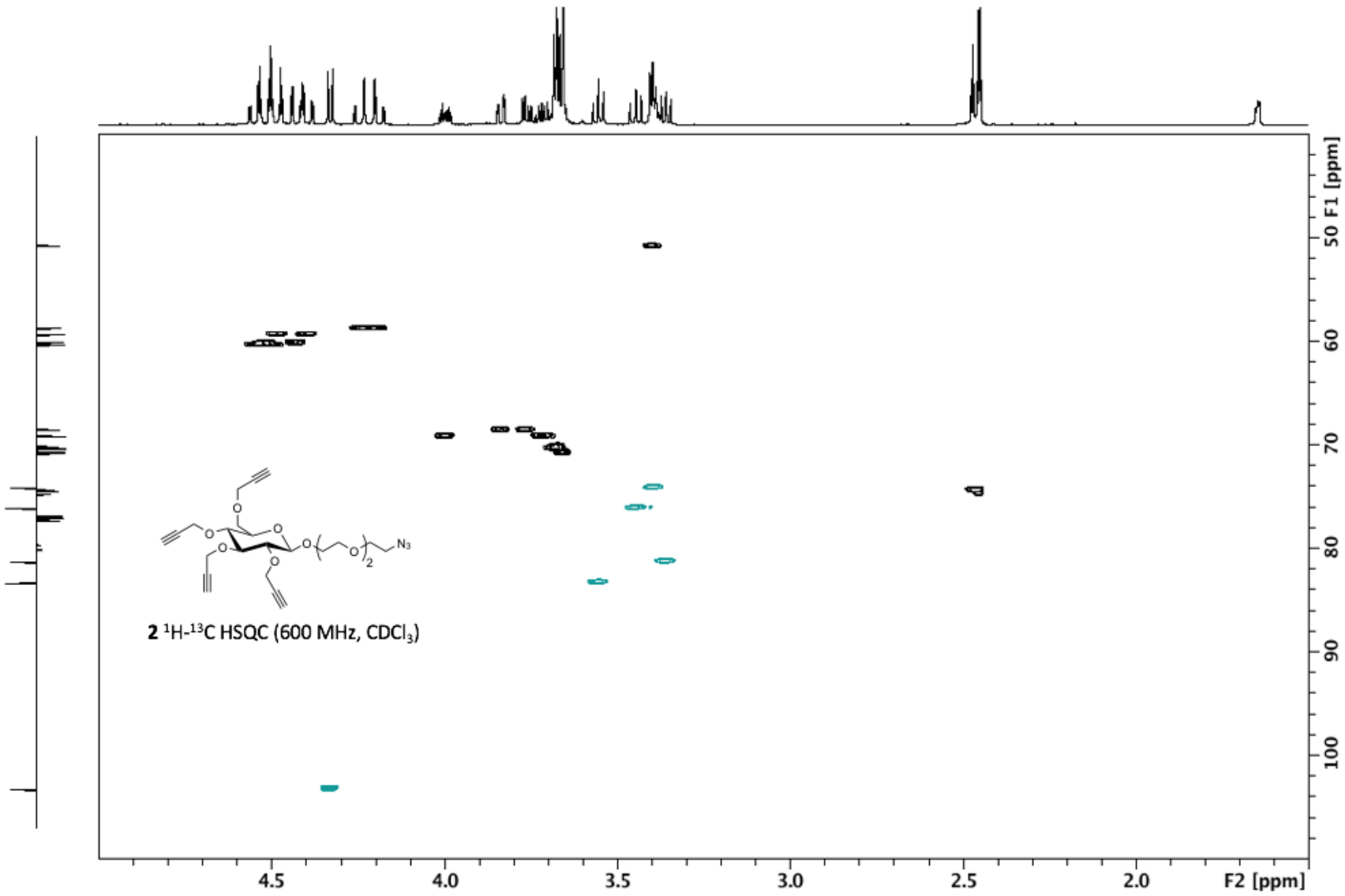




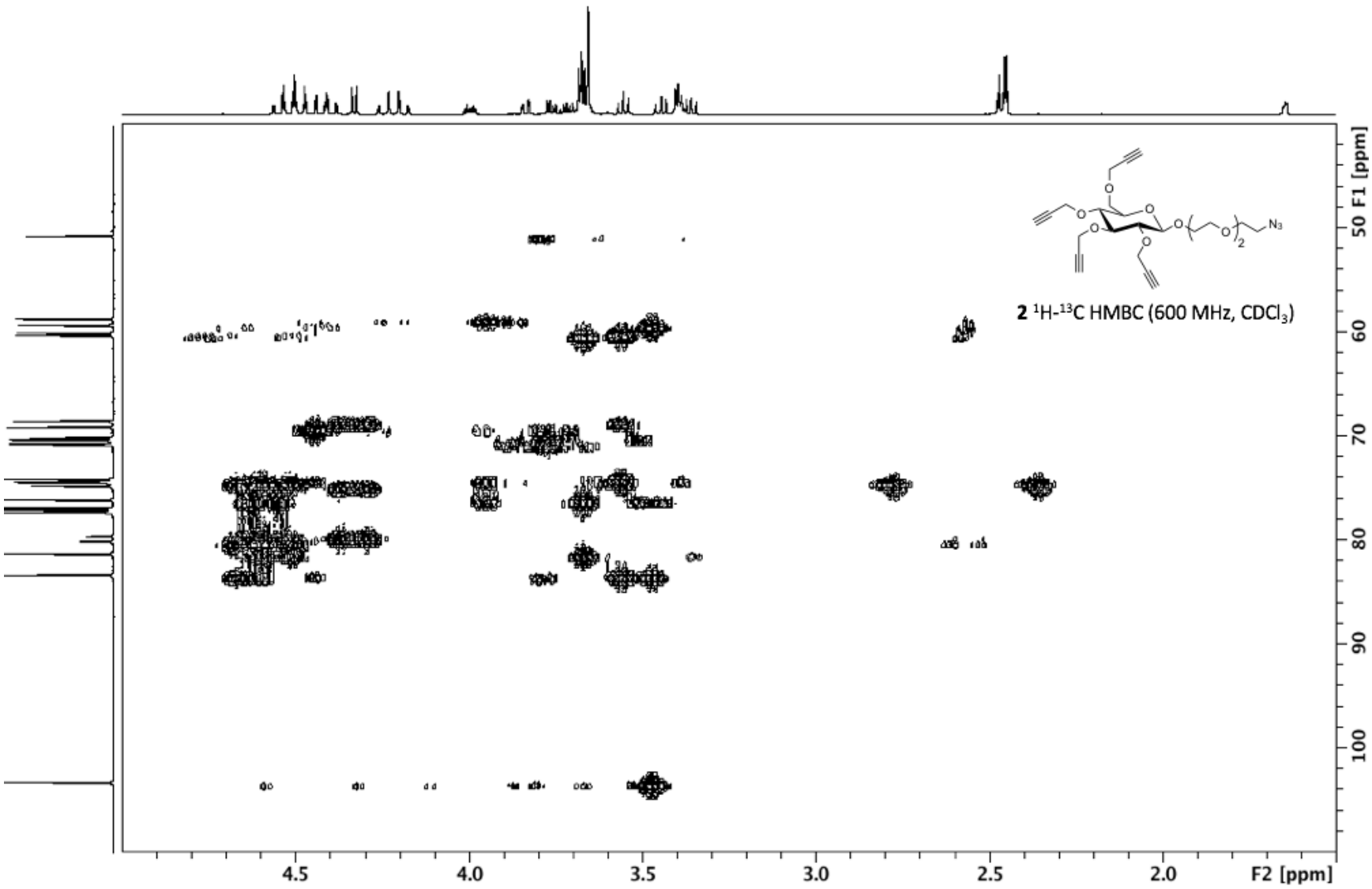
2 ^{13}C $\{^{1}H\}$ NMR (150 MHz, $CDCl_3$)



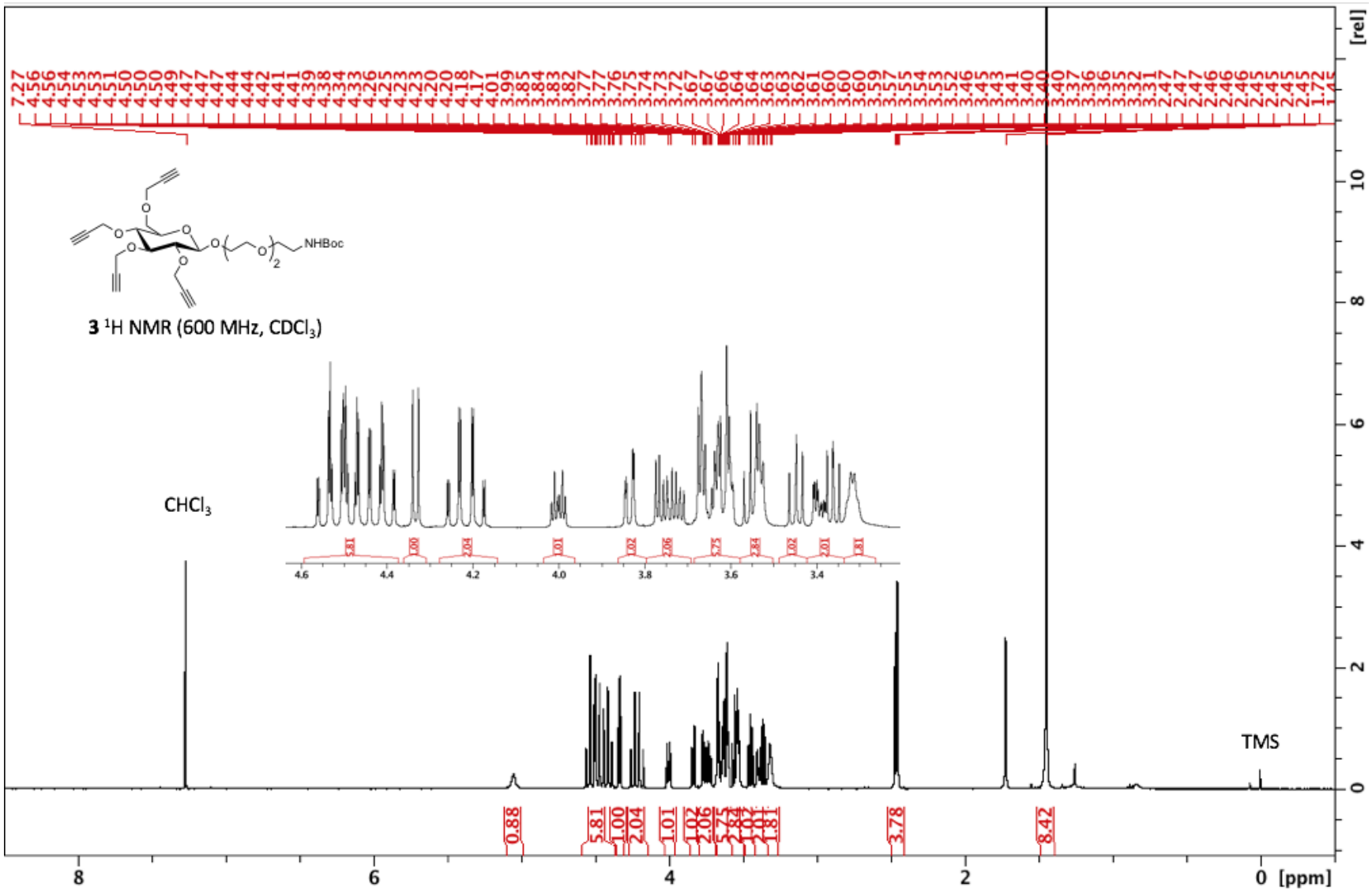
2 ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$)

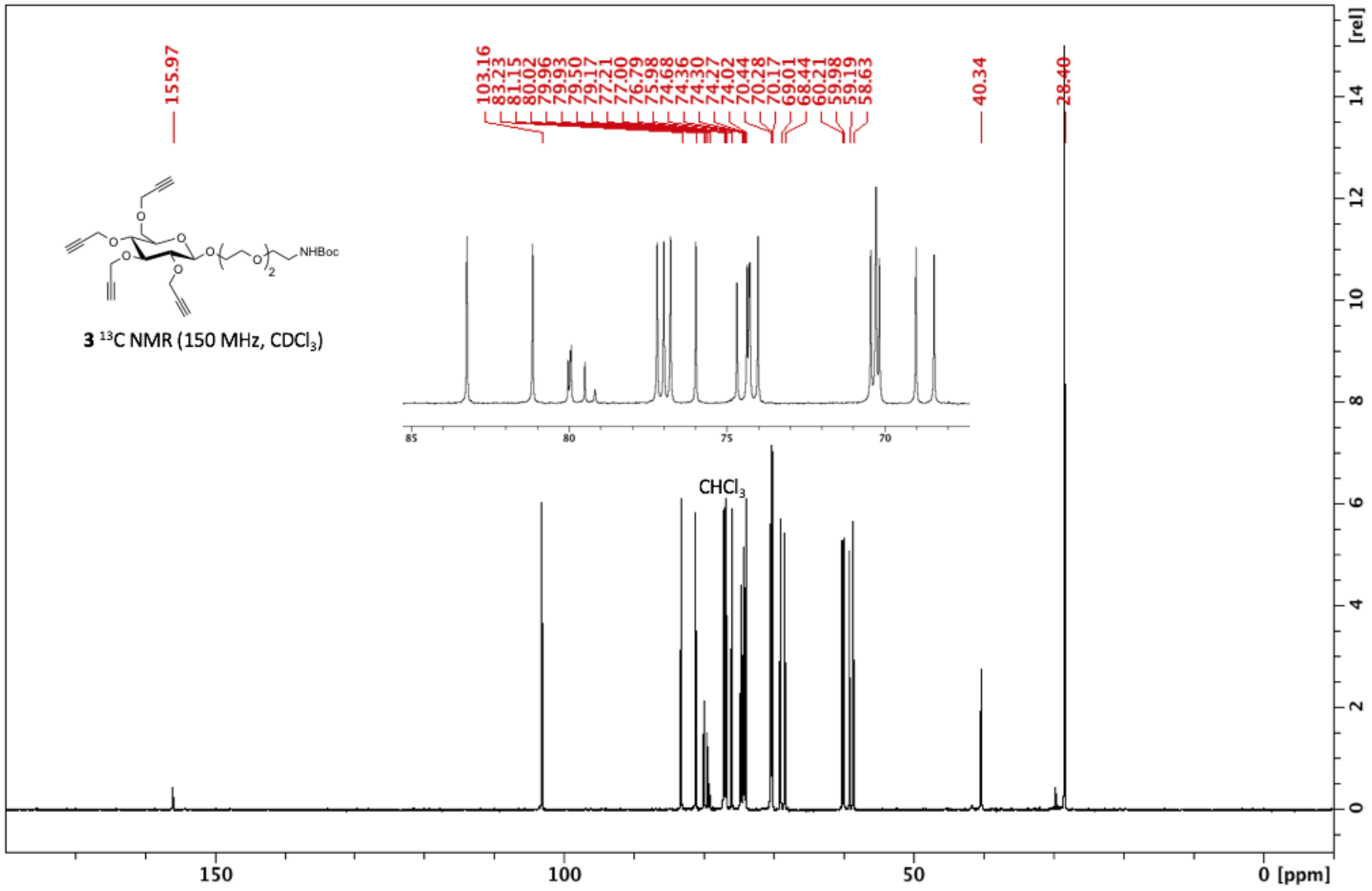


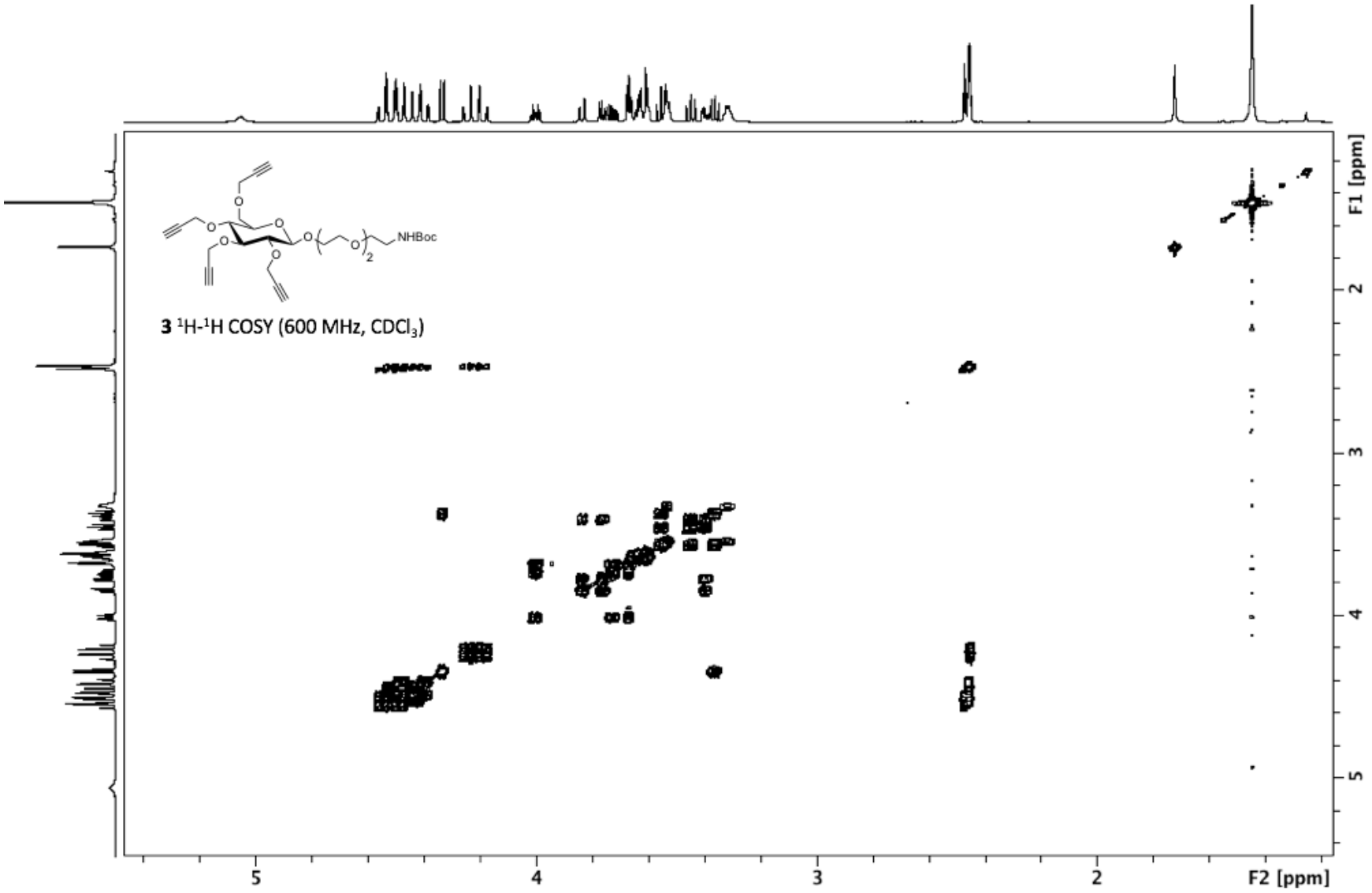
2 ^{1}H-^{13}C HSQC (600 MHz, $CDCl_3$)

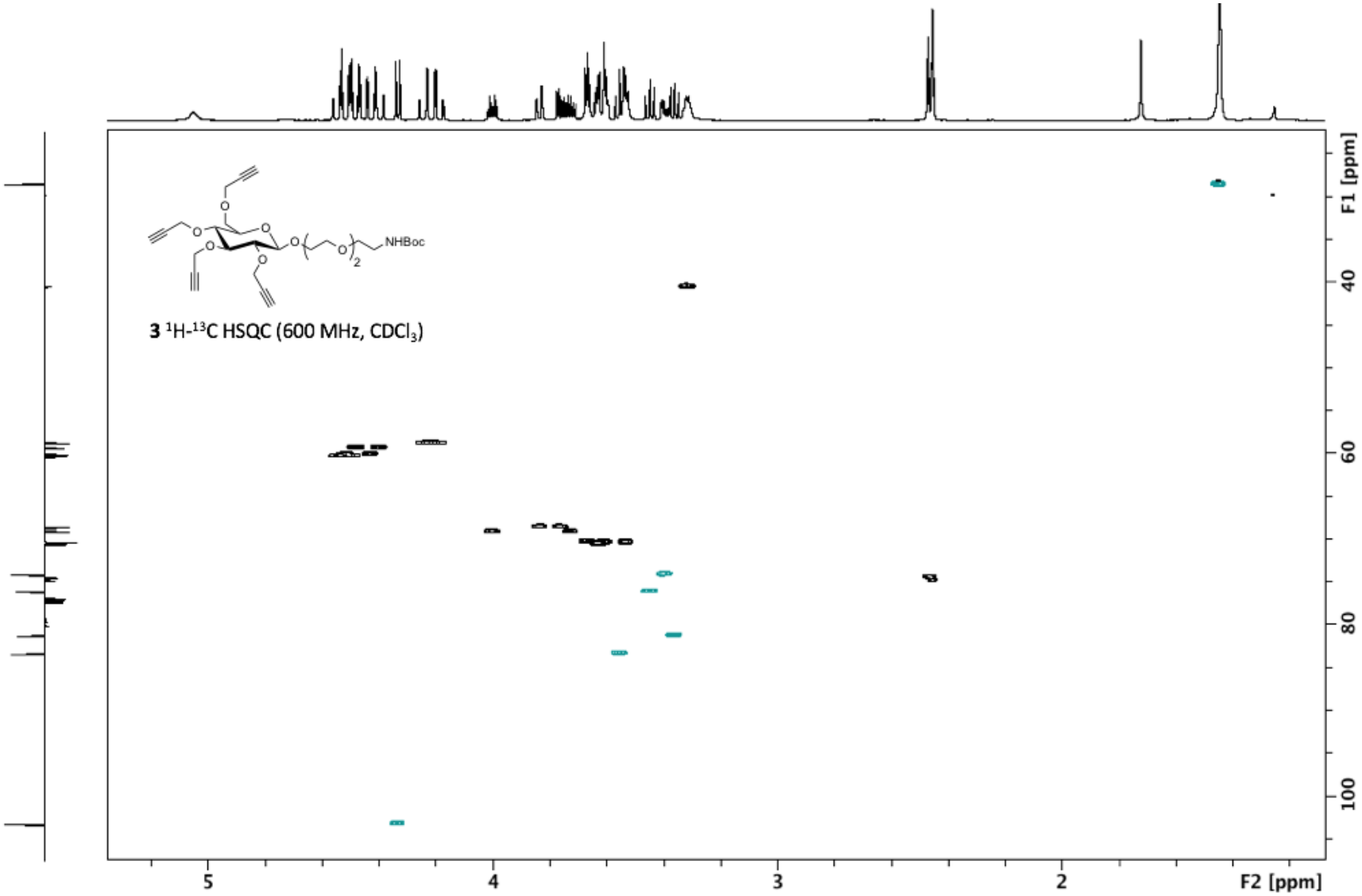

2 ^{1}H-^{13}C HMBC (600 MHz, $CDCl_3$)
F2 [ppm]
F1 [ppm]
4.5
4.0
3.5
3.0
2.5
2.0
50
60
70
80
90
100

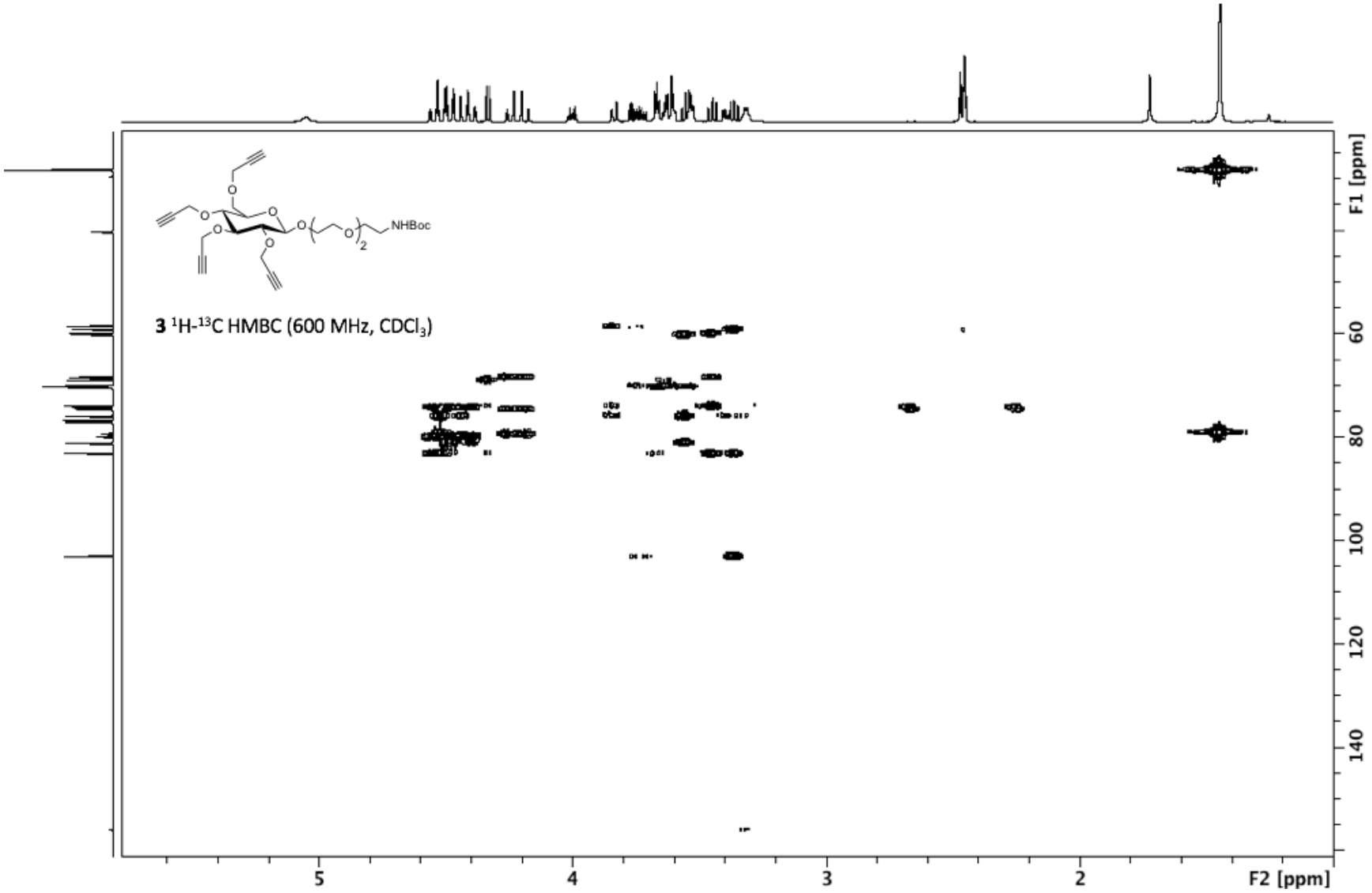
Boc-protected compound **3**



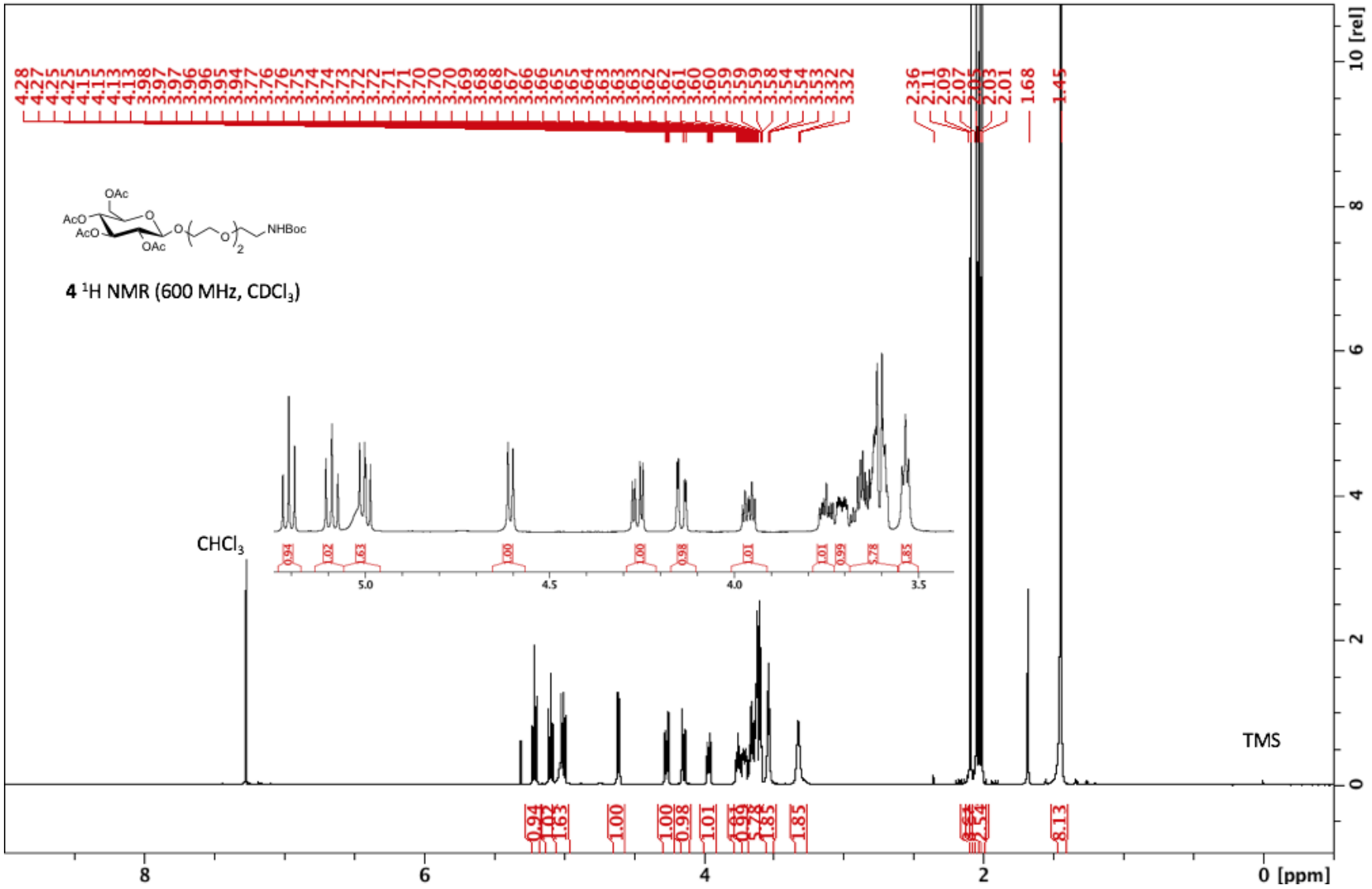

155.97
103.16
83.23
81.15
80.02
79.96
79.93
79.50
79.17
77.21
77.00
76.79
75.98
74.68
74.36
74.30
74.27
74.02
70.44
70.28
70.17
69.01
68.44
60.21
59.98
59.19
58.63
40.34
28.40
NHBoc
3 13C NMR (150 MHz, CDCl3)
CHCl3
[rel]
150
100
50
0 [ppm]

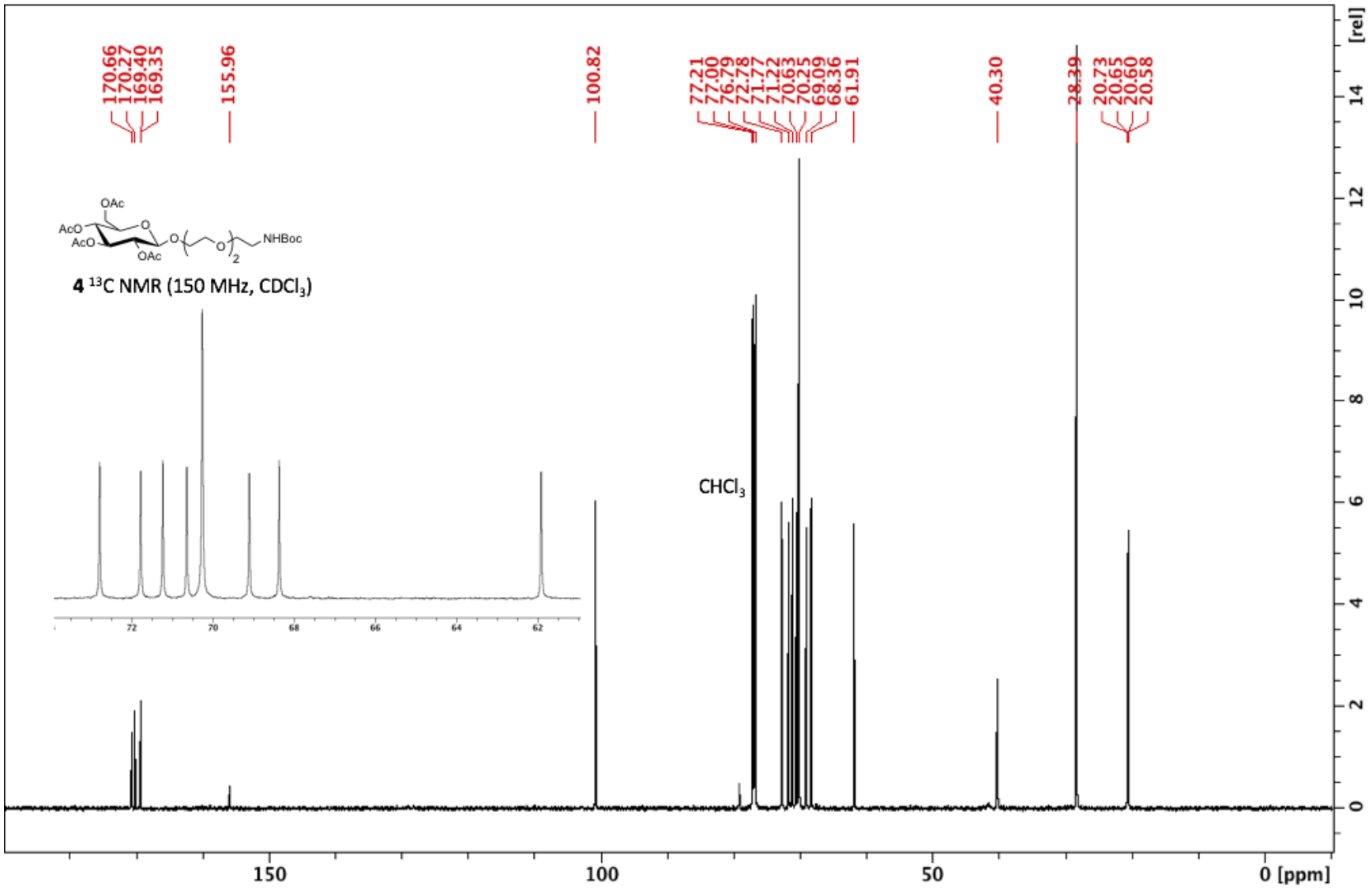

NHBoc
2
3 ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$)
F1 [ppm]
F2 [ppm]
2
3
4
5
5
4
3
2

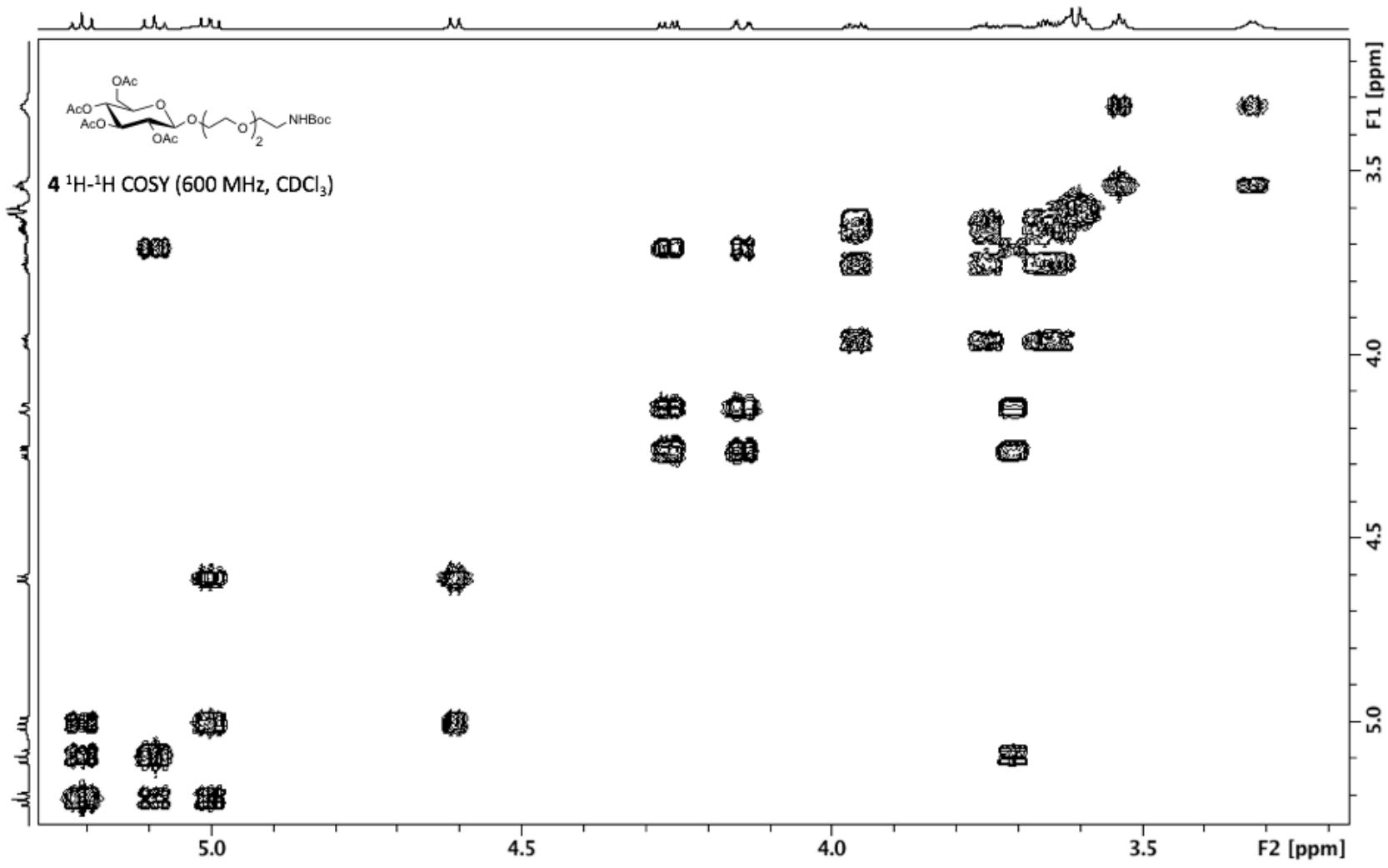

NHBoc
2
3 ^{1}H-^{13}C HSQC (600 MHz, $CDCl_3$)
F1 [ppm]
40
60
80
100
5
4
3
2
F2 [ppm]

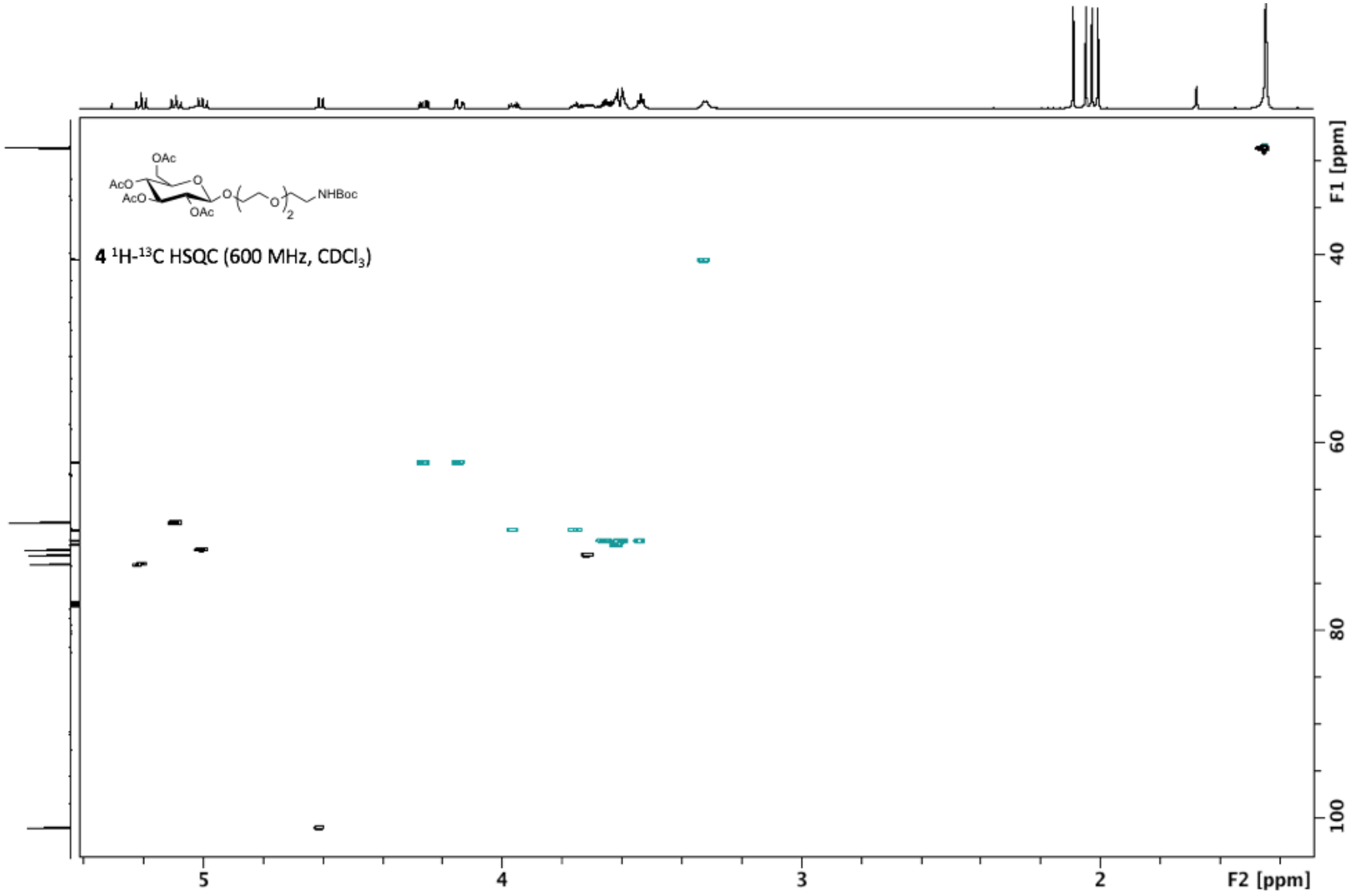

NHBoc
2
3 ^{1}H-^{13}C HMBC (600 MHz, $CDCl_3$)
F1 [ppm]
60
80
100
120
140
5
4
3
2
F2 [ppm]

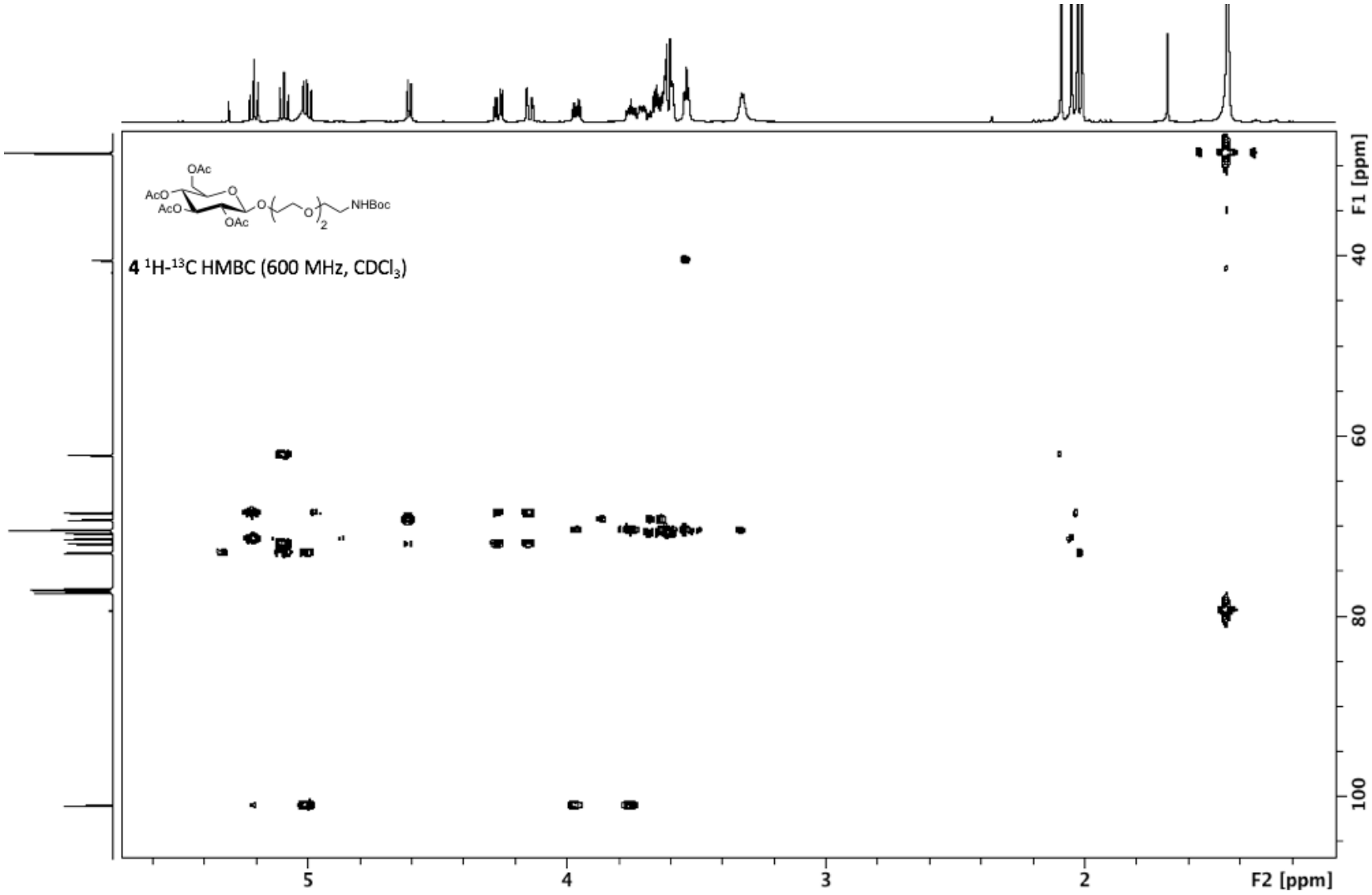
Acetate **4**


4.28 4.27 4.25 4.25 4.15 4.13 4.13 3.98 3.97 3.97 3.96 3.96 3.95 3.94 3.77 3.76 3.75 3.74 3.74 3.73 3.72 3.72 3.71 3.71 3.70 3.70 3.70 3.69 3.68 3.67 3.66 3.65 3.65 3.64 3.63 3.63 3.62 3.62 3.61 3.60 3.60 3.59 3.59 3.59 3.58 3.54 3.54 3.53 3.32 3.32
2.36 2.11 2.09 2.07 2.05 2.03 2.01 1.68 1.45
OAc
AcO
AcO
OAc
O
O
O
2
NHBoc
4 ^{1}H NMR (600 MHz, $CDCl_3$)
$CHCl_3$
TMS
0.94 1.02 1.63 1.00 1.00 0.98 1.01 0.99 5.78 1.85 1.85 8.13
10 [rel]
0 [ppm]

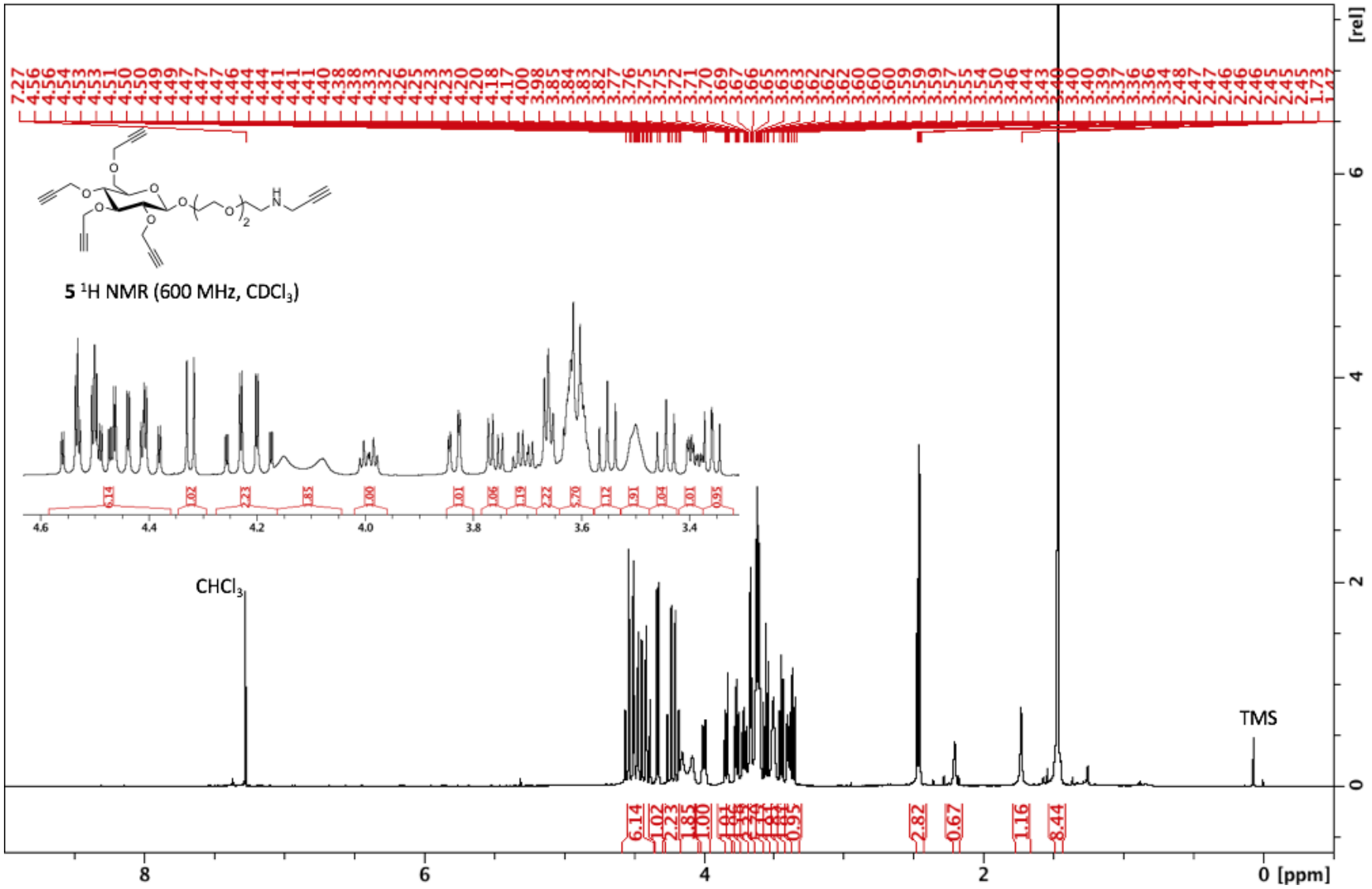

170.66
170.27
169.40
169.35
155.96
100.82
77.21
77.00
76.79
72.78
71.77
71.22
70.63
70.25
69.09
68.36
61.91
40.30
28.39
20.73
20.65
20.60
20.58
OAc
AcO
AcO
OAc
O
O
O
2
NHBoc
4 13C NMR (150 MHz, CDCl3)
CHCl3
72
70
68
66
64
62
150
100
50
0 [ppm]
[rel]
0
2
4
6
8
10
12
14

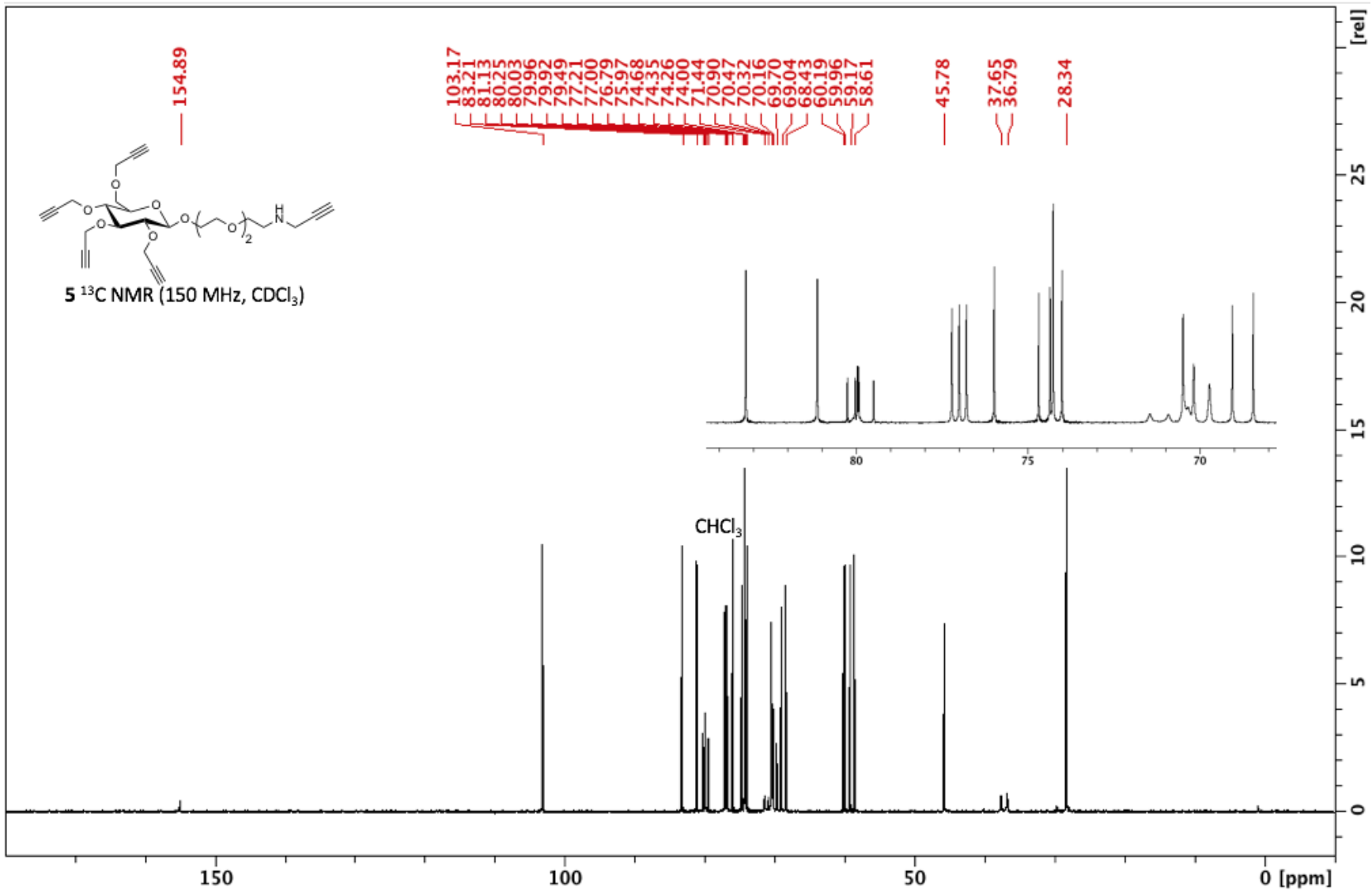

4 ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$)
OAc
AcO
AcO
OAc
O
O
O
2
NHBoc
F1 [ppm]
3.5
4.0
4.5
5.0
5.0
4.5
4.0
3.5
F2 [ppm]

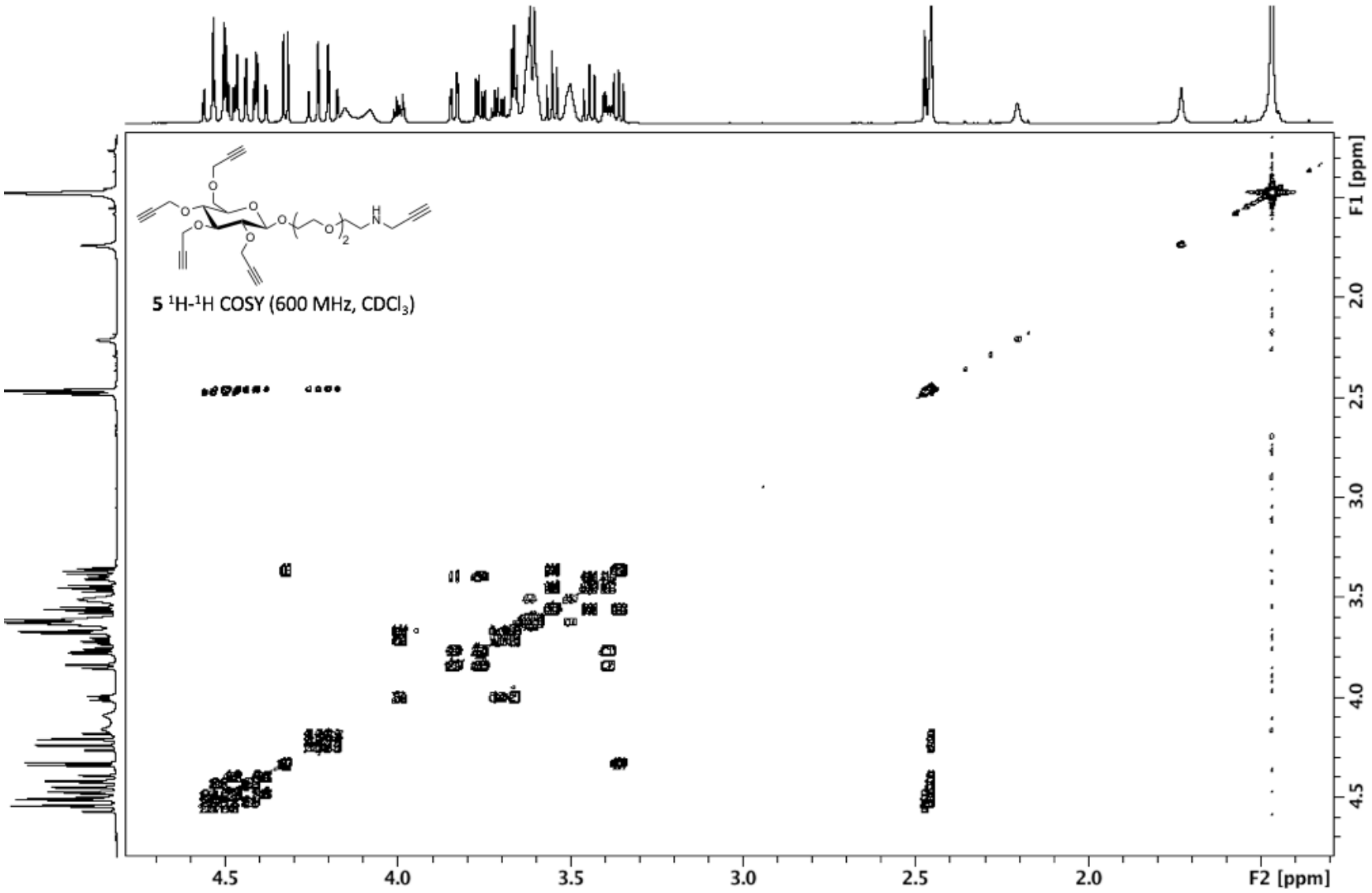

OAc
AcO
AcO
OAc
O
O
O
2
NHBoc
4 ^{1}H-^{13}C HSQC (600 MHz, $CDCl_3$)
F1 [ppm]
40
60
80
100
5
4
3
2
F2 [ppm]

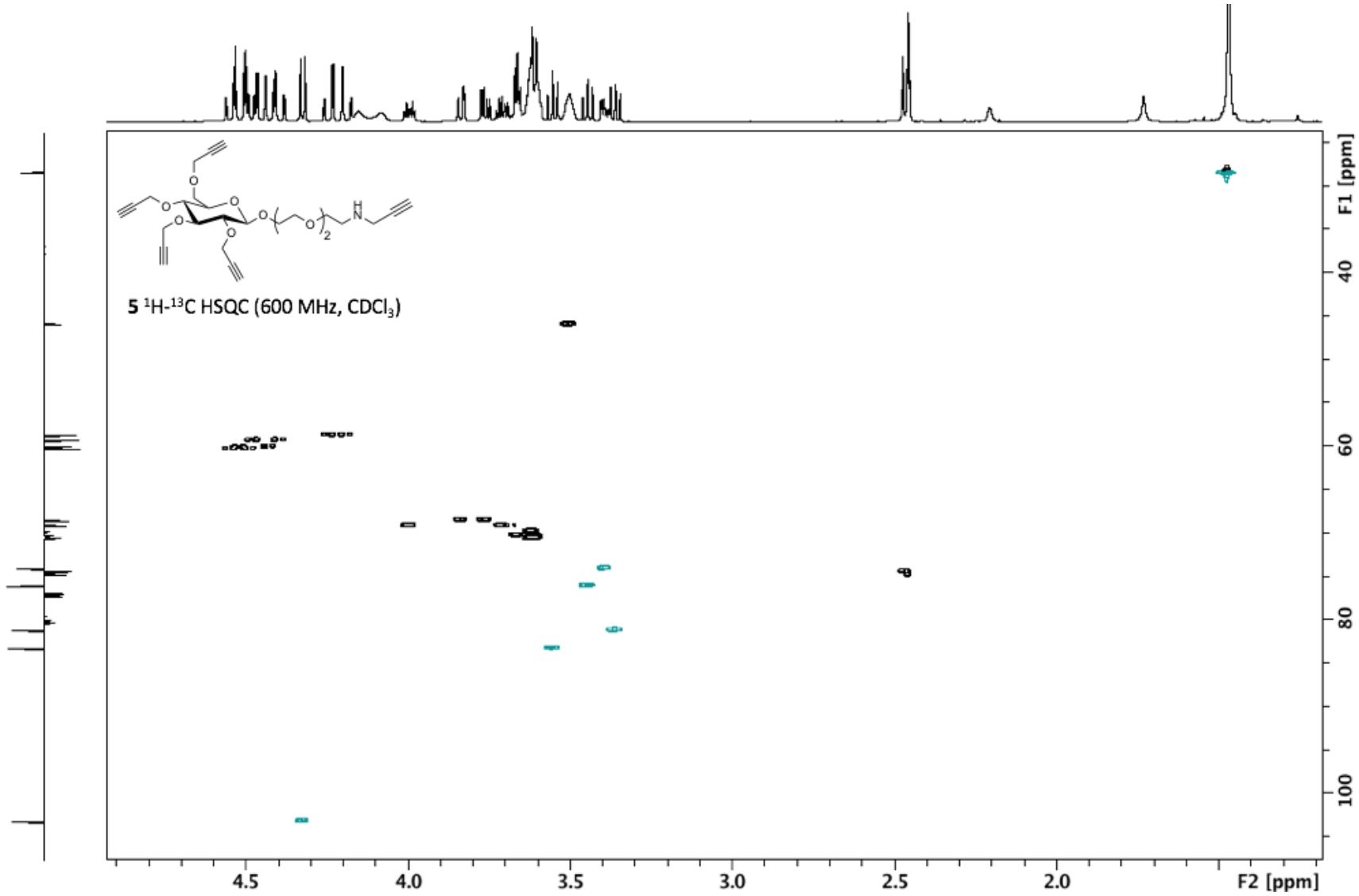

OAc
AcO
AcO
OAc
O
O
O
2
NHBoc
4 ¹H-¹³C HMBC (600 MHz, CDCl₃)
F1 [ppm]
40
60
80
100
5
4
3
2
F2 [ppm]

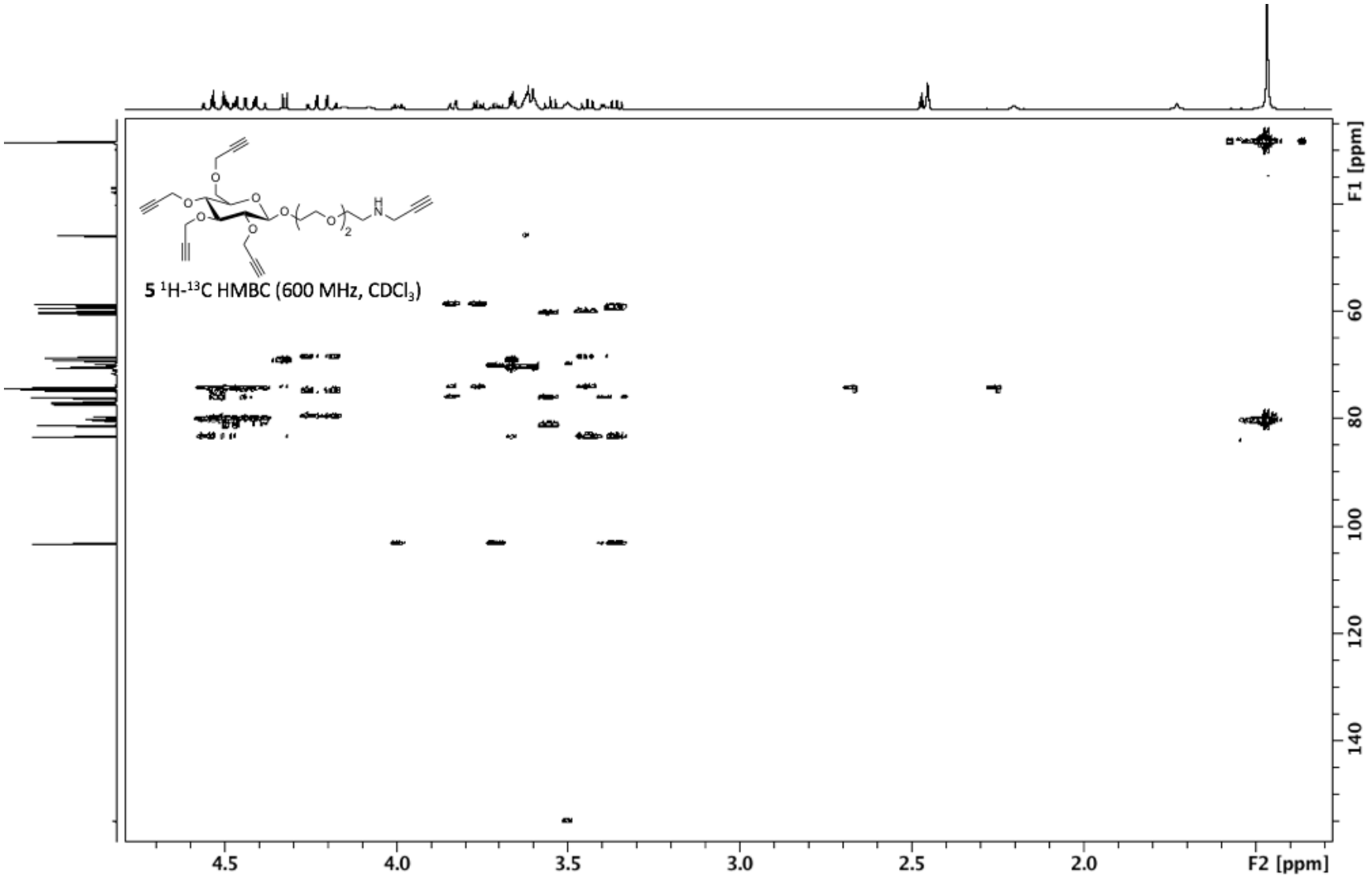
N-propargylated derivative **5**



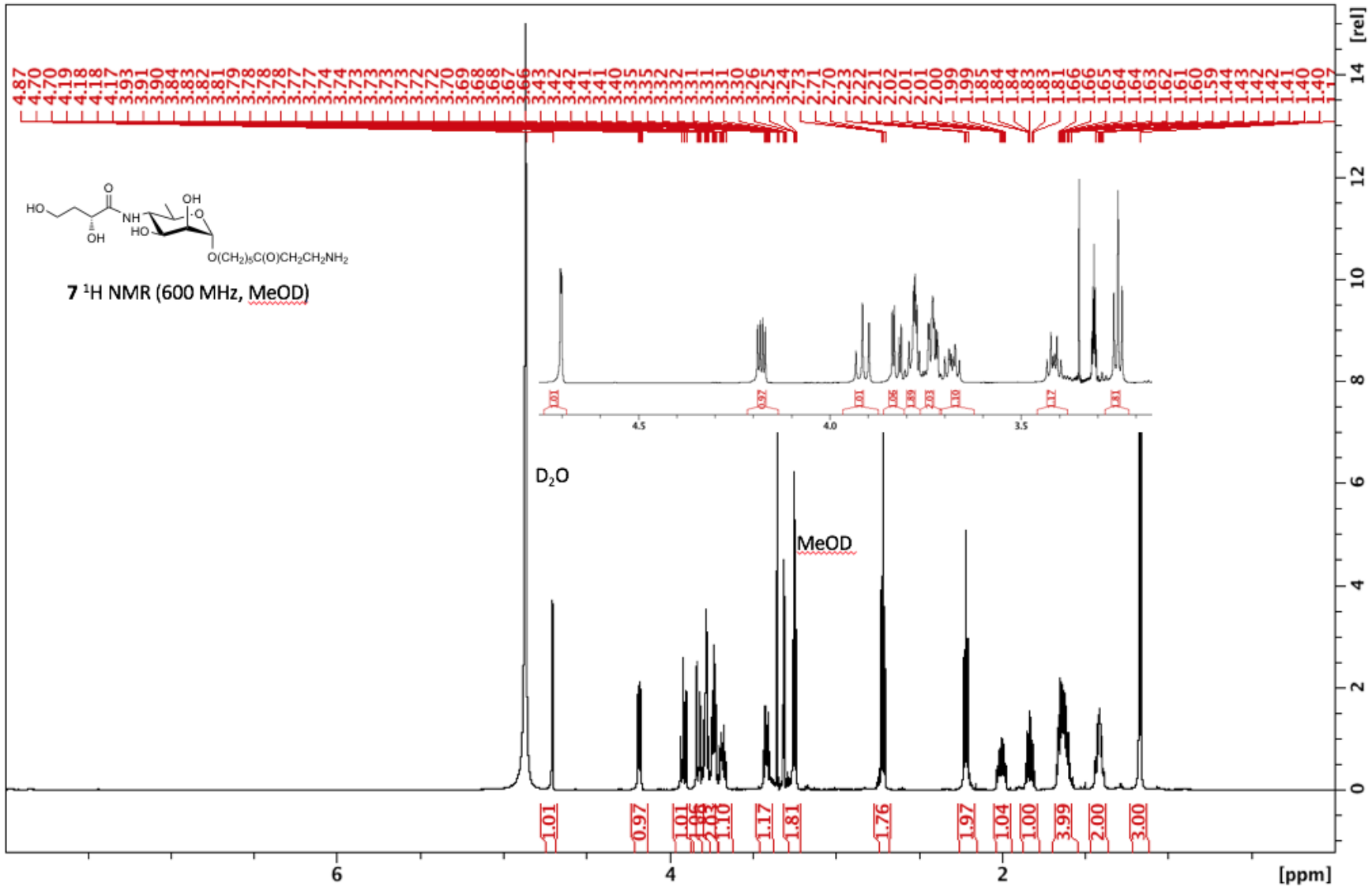

154.89
103.17
83.21
81.13
80.25
80.03
79.96
79.92
79.49
77.21
77.00
76.79
75.97
74.68
74.35
74.26
74.00
71.44
70.90
70.47
70.32
70.16
69.70
69.04
68.43
60.19
59.96
59.17
58.61
45.78
37.65
36.79
28.34
5 13C NMR (150 MHz, CDCl3)
CHCl3
150
100
50
0 [ppm]
[rel]

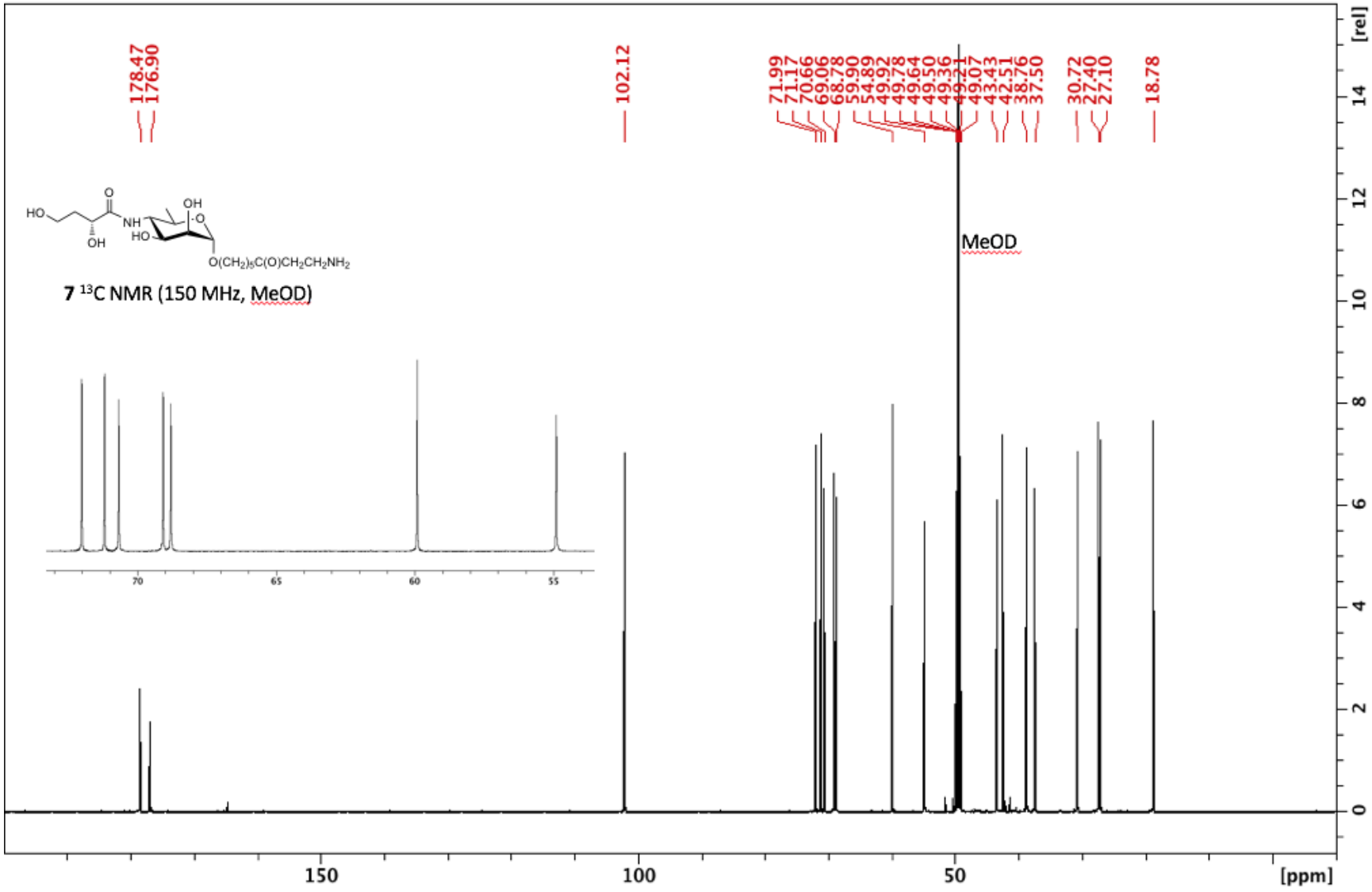

5 ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$)
F1 [ppm]
F2 [ppm]
4.5
4.0
3.5
3.0
2.5
2.0

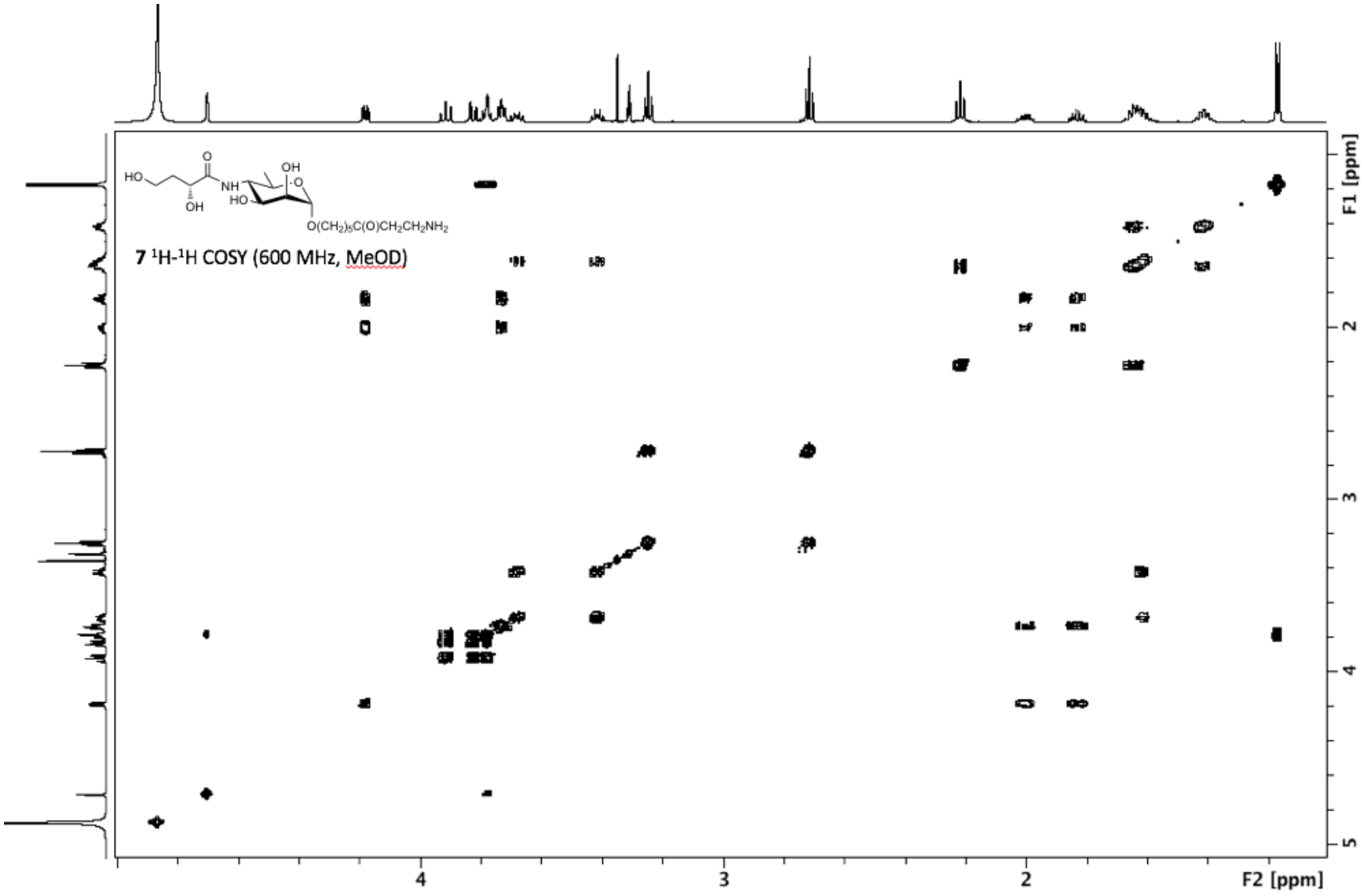

5 ^{1}H-^{13}C HSQC (600 MHz, $CDCl_3$)
F1 [ppm]
40
60
80
100
4.5
4.0
3.5
3.0
2.5
2.0
F2 [ppm]

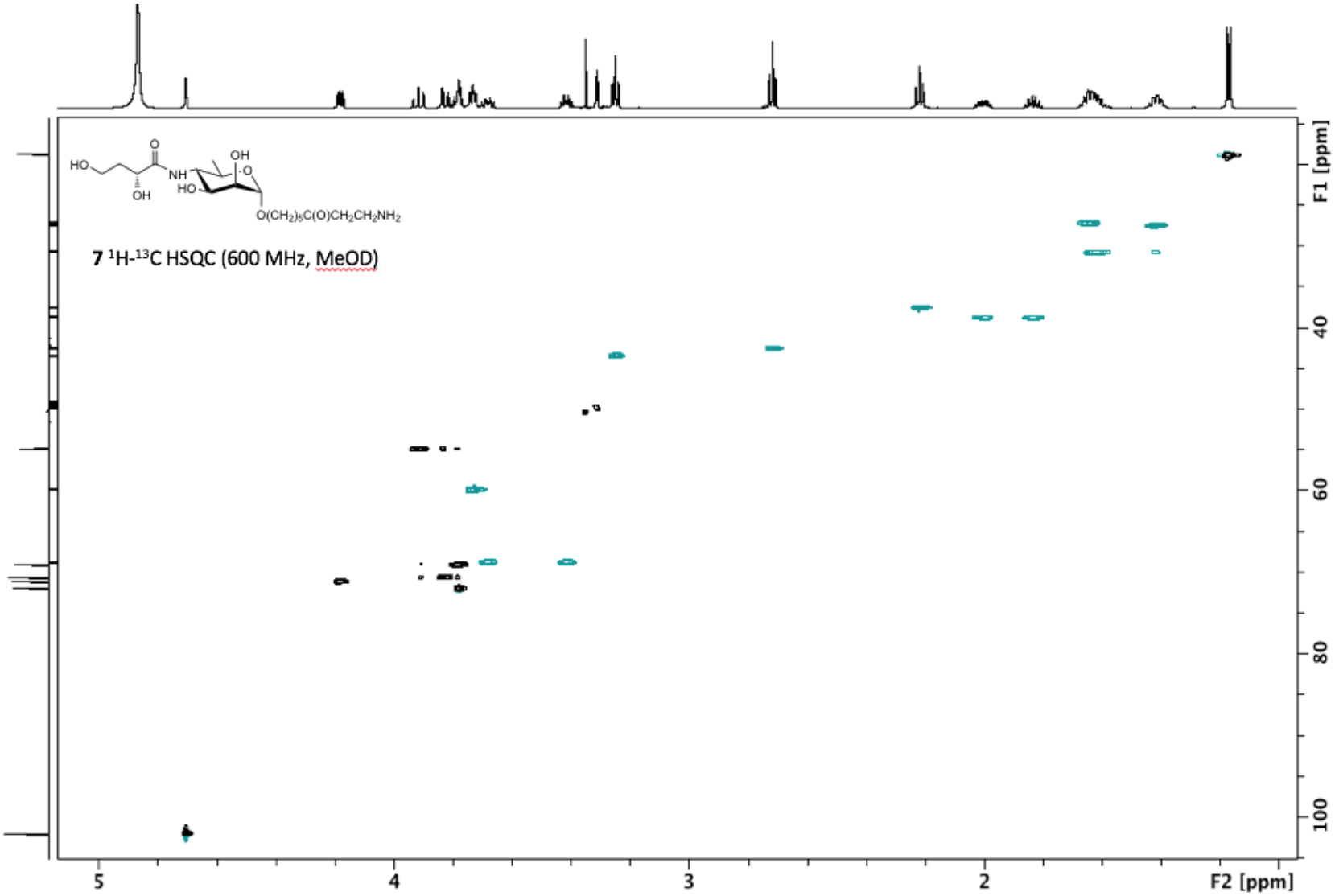

5 ^{1}H-^{13}C HMBC (600 MHz, $CDCl_3$)
F1 [ppm]
60
80
100
120
140
4.5
4.0
3.5
3.0
2.5
2.0
F2 [ppm]

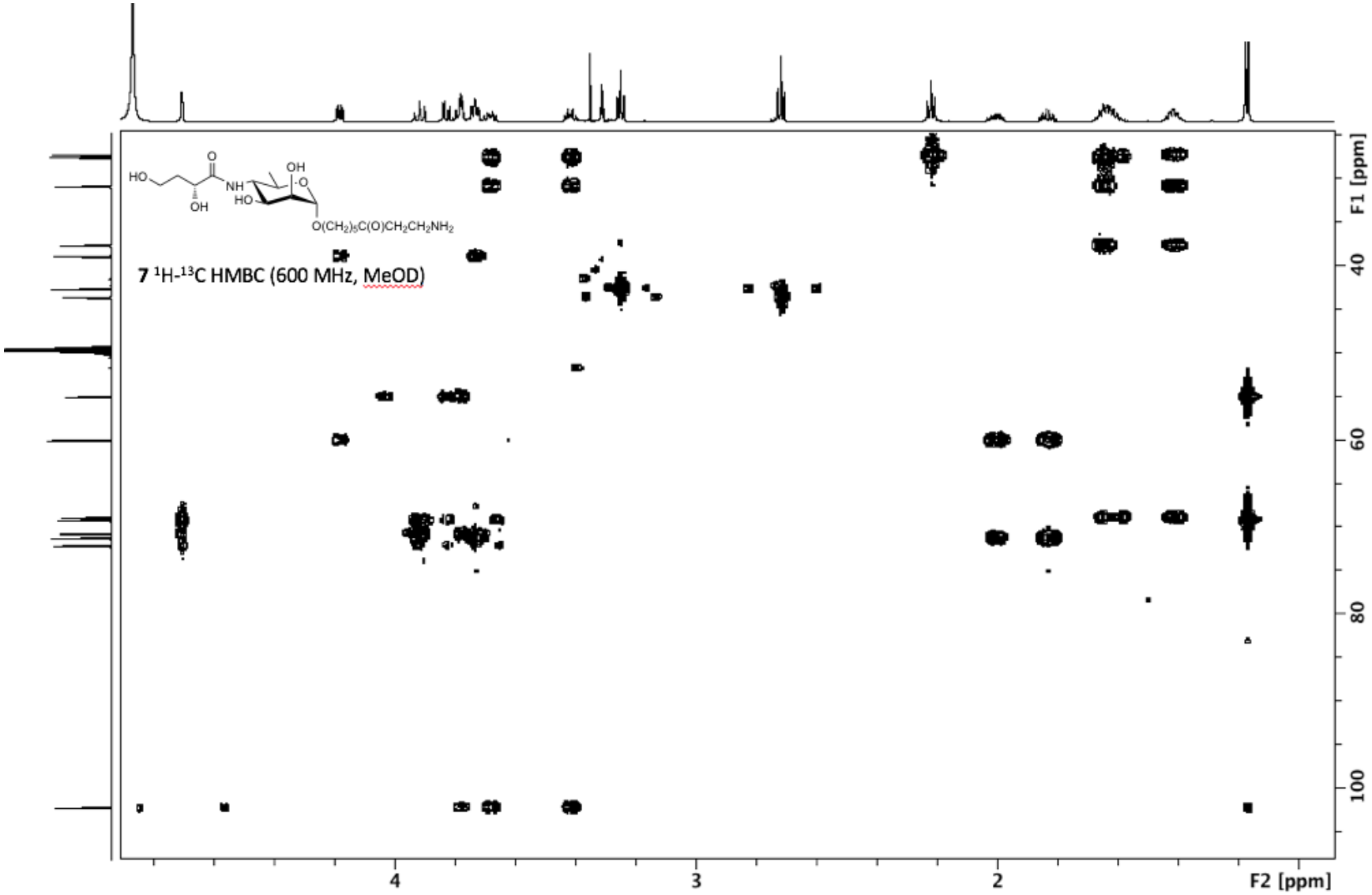
Amine **7**



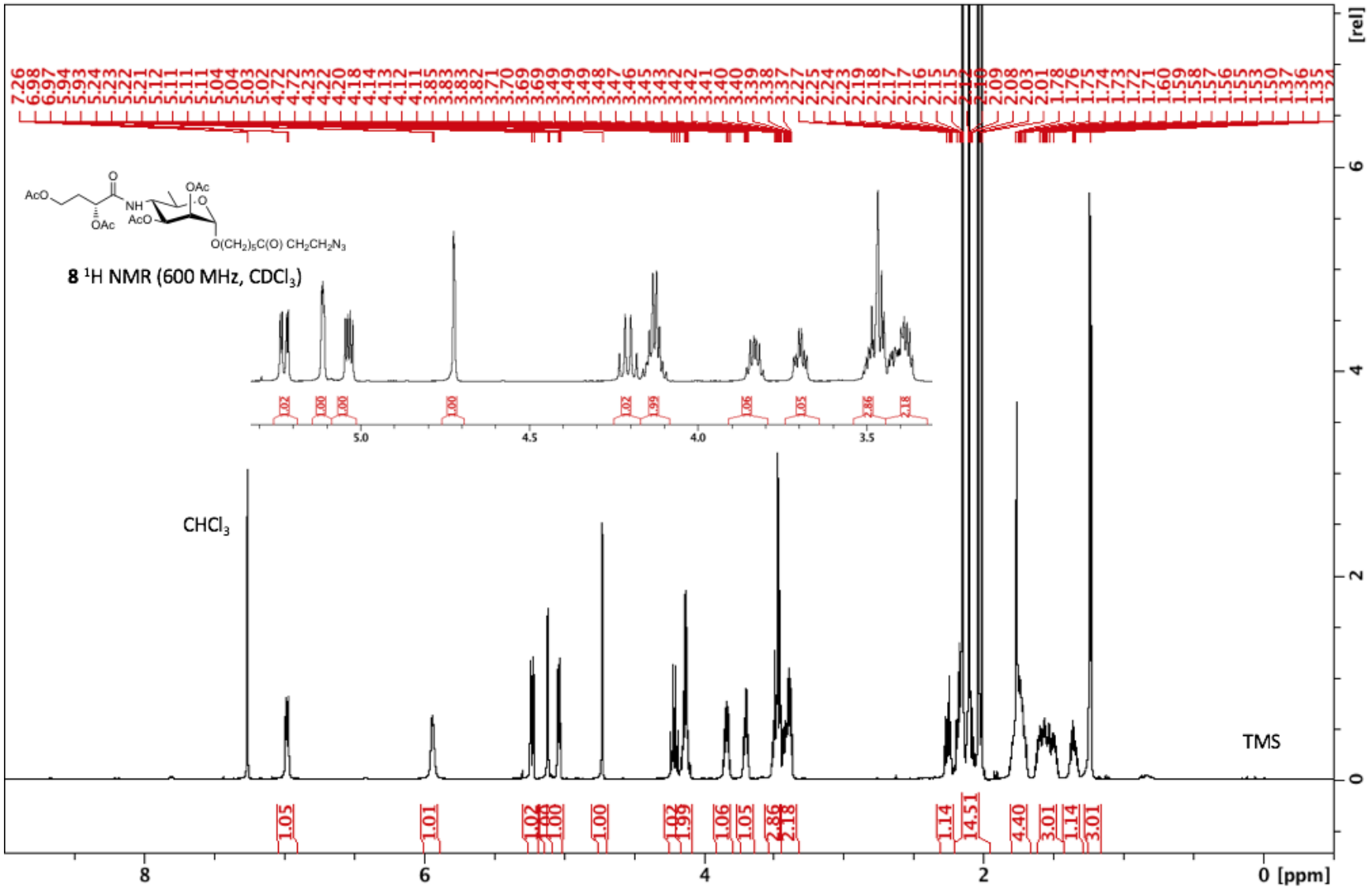

178.47
176.90
102.12
71.99
71.17
70.66
69.06
68.78
59.90
54.89
49.92
49.78
49.64
49.50
49.36
49.21
49.07
43.43
42.51
38.76
37.50
30.72
27.40
27.10
18.78
MeOD
HO
OH
NH
HO
OH
O
O(CH2)5C(O)CH2CH2NH2
7 13C NMR (150 MHz, MeOD)
70
65
60
55
150
100
50
[ppm]
[rel]
0
2
4
6
8
10
12
14

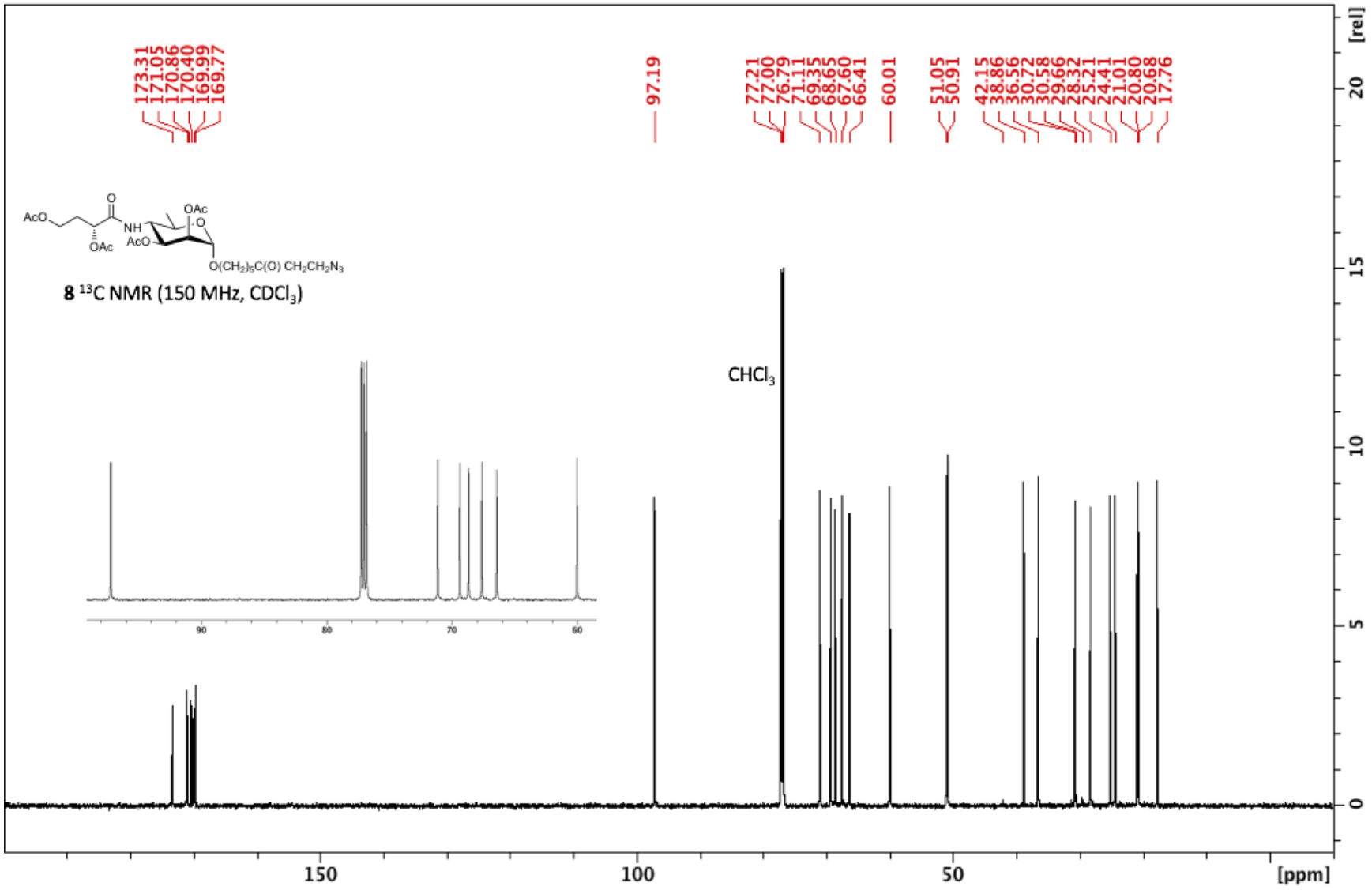

7 ^{1}H-^{1}H COSY (600 MHz, MeOD)
HO
O
NH
OH
HO
OH
O
O(CH2)5C(O)CH2CH2NH2
F1 [ppm]
F2 [ppm]
2
3
4
5

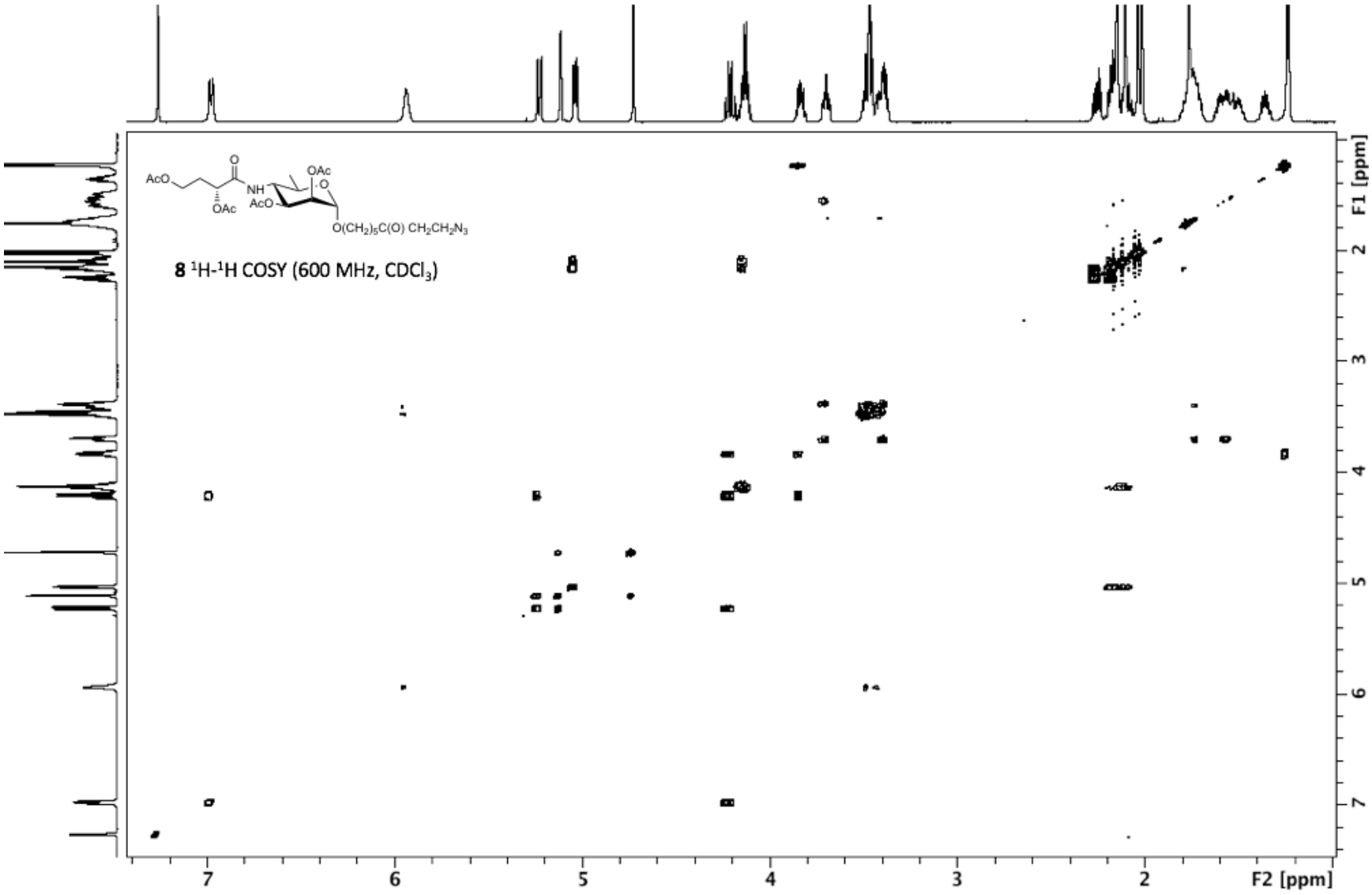

7 ^{1}H-^{13}C HSQC (600 MHz, MeOD)
F1 [ppm]
F2 [ppm]
40
60
80
100
5
4
3
2

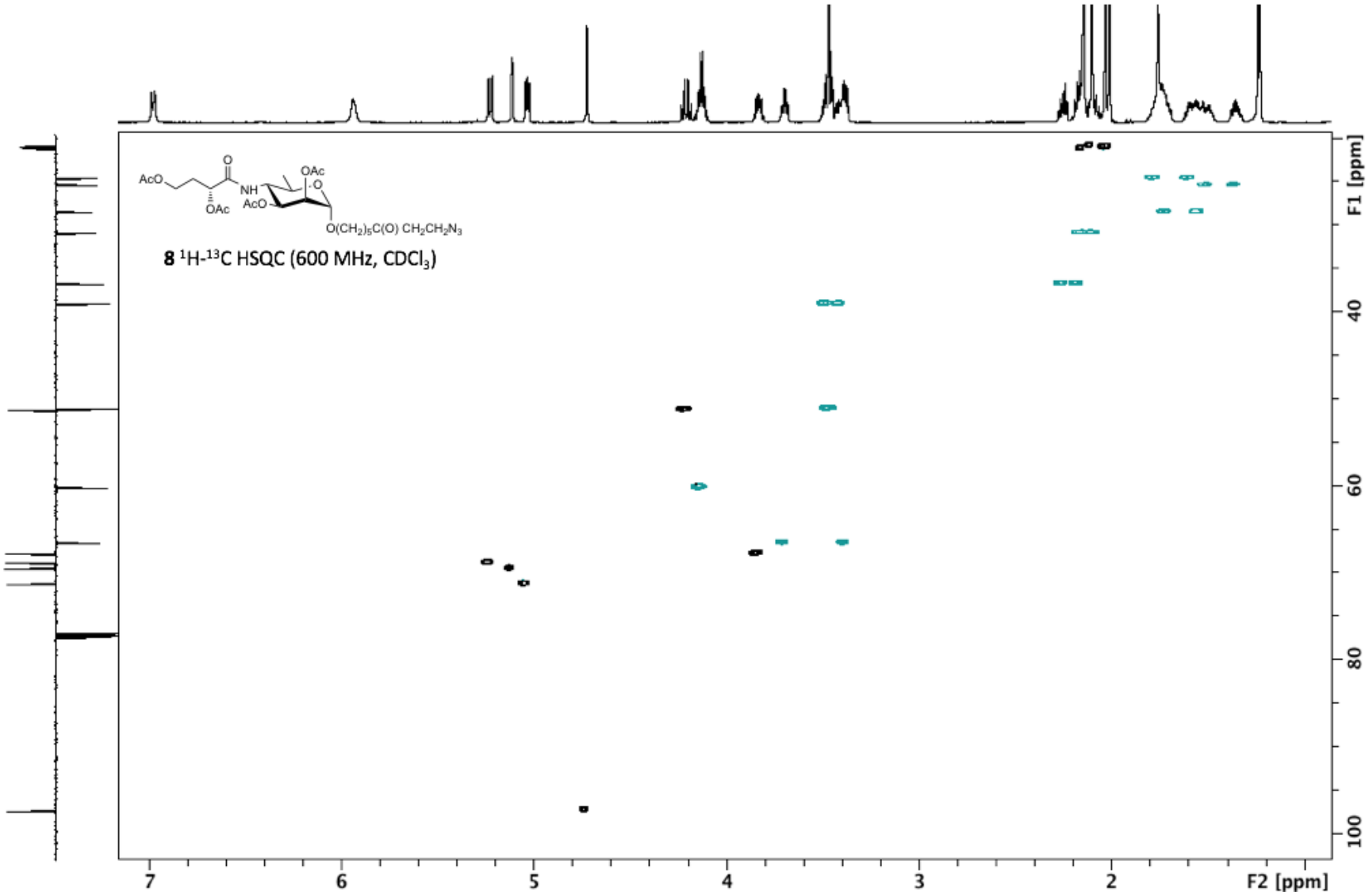

7 ^{1}H-^{13}C HMBC (600 MHz, MeOD)
F1 [ppm]
F2 [ppm]
40
60
80
100
4
3
2

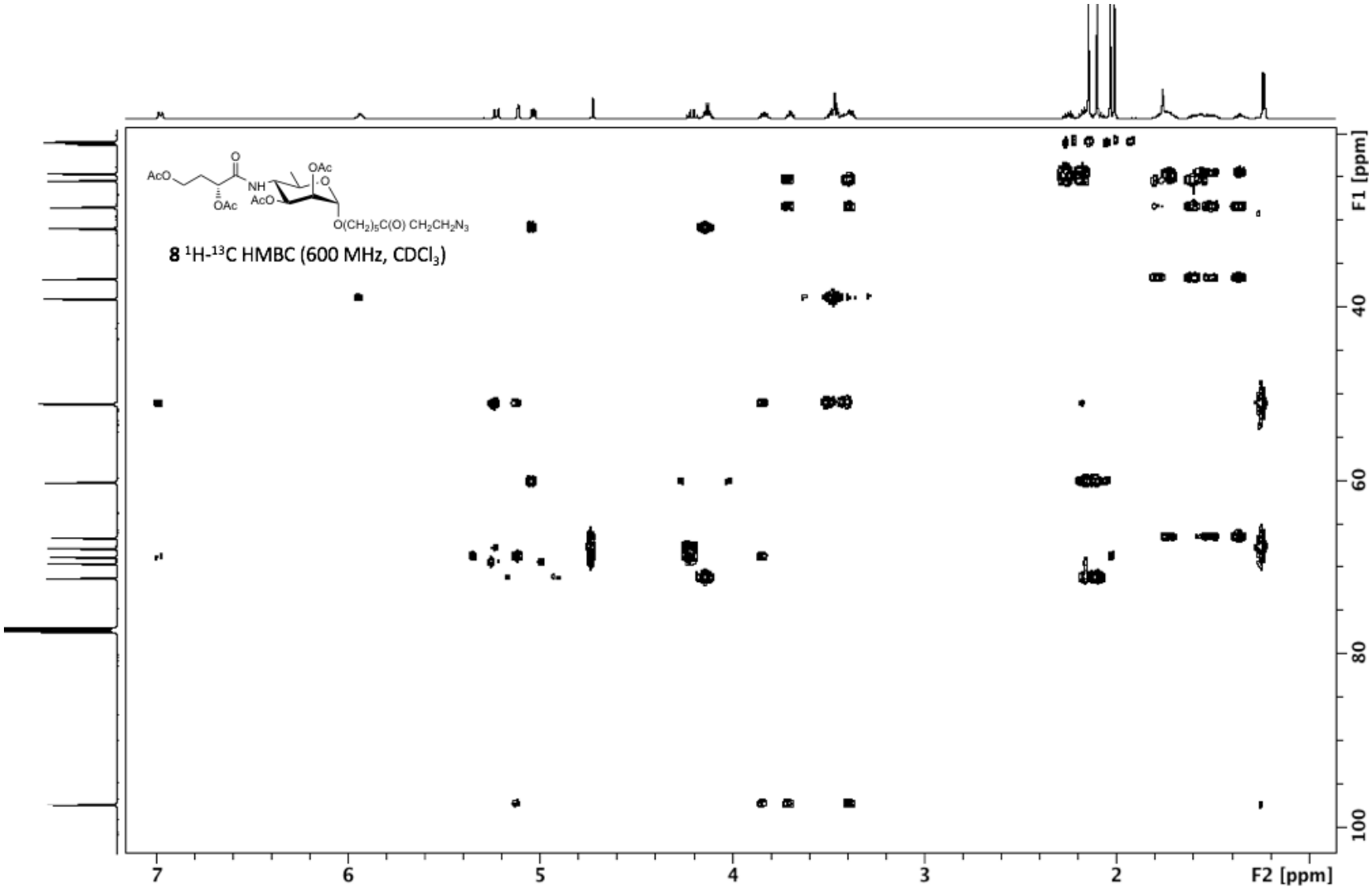
Azide **8**



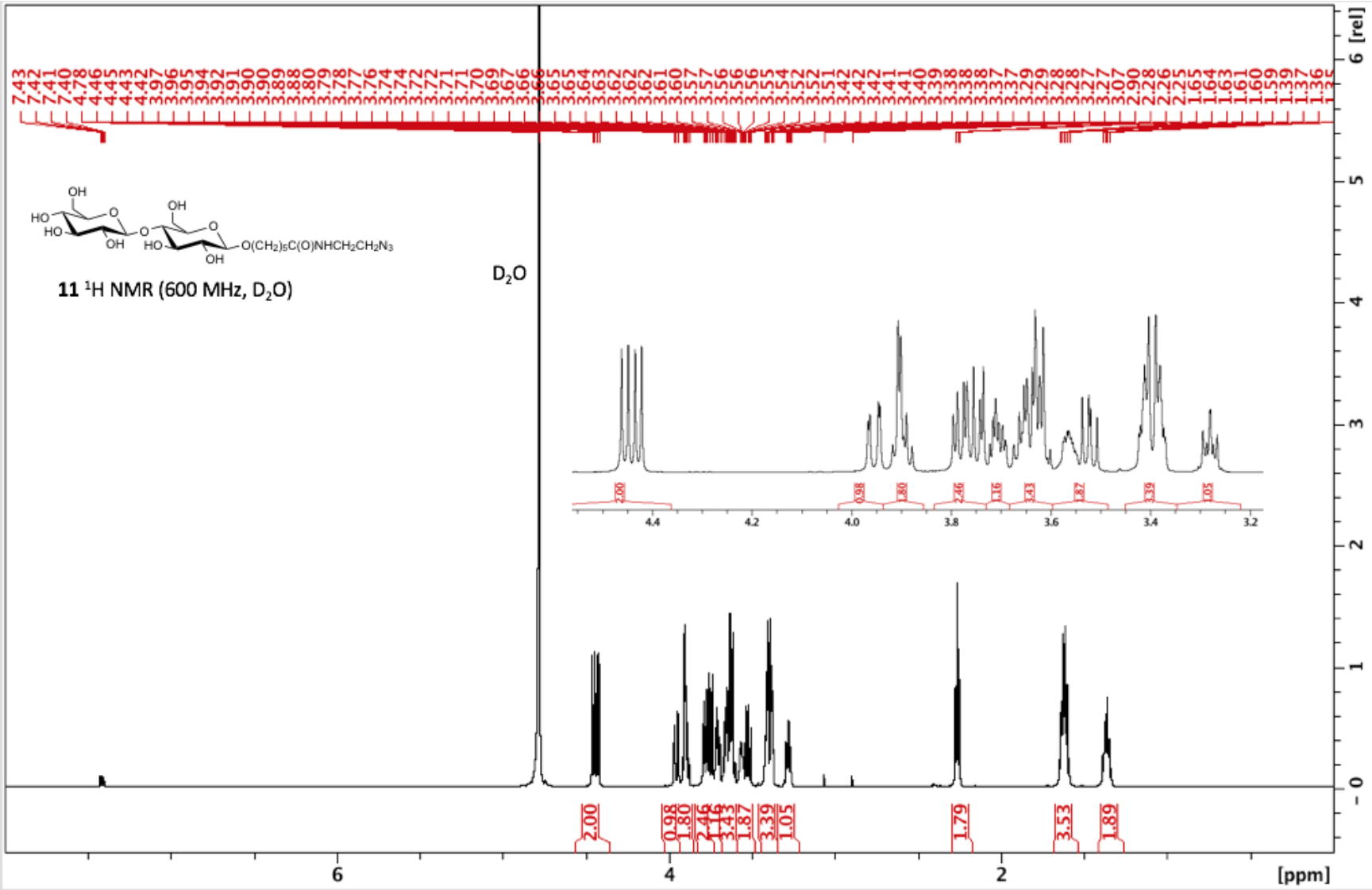

173.31
171.05
170.86
170.40
169.99
169.77
97.19
77.21
77.00
76.79
71.11
69.35
68.65
67.60
66.41
60.01
51.05
50.91
42.15
38.86
36.56
30.72
30.58
29.66
28.32
25.21
24.41
21.01
20.80
20.68
17.76
AcO
OAc
NH
AcO
OAc
O
O(CH2)5C(O) CH2CH2N3
8 13C NMR (150 MHz, CDCl3)
CHCl3
[rel]
[ppm]
150
100
50
0
5
10
15
20
90
80
70
60

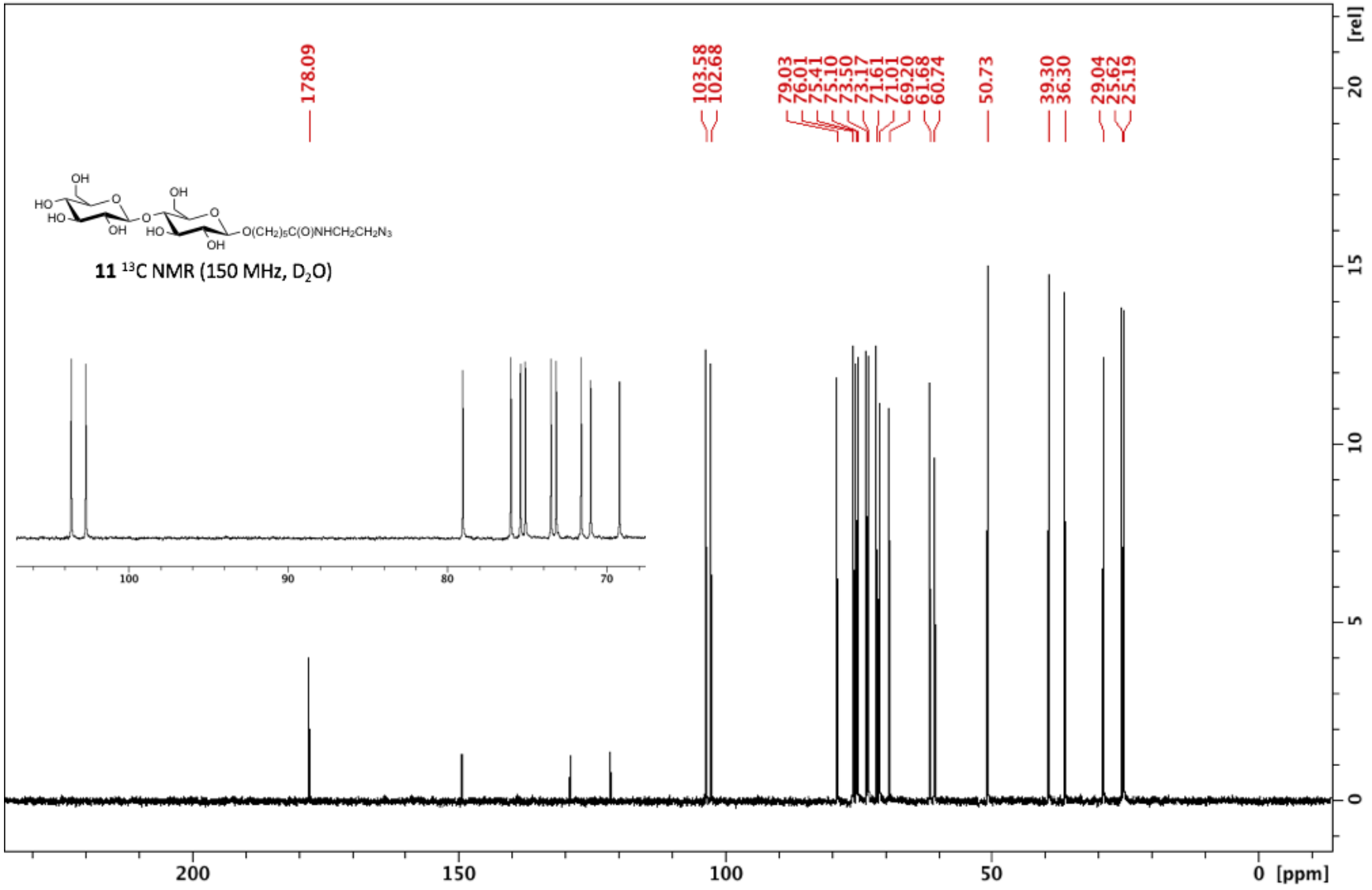

8 ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$)
AcO
OAc
NH
AcO
OAc
O
O(CH2)5C(O) CH2CH2N3
F1 [ppm]
F2 [ppm]
7
6
5
4
3
2

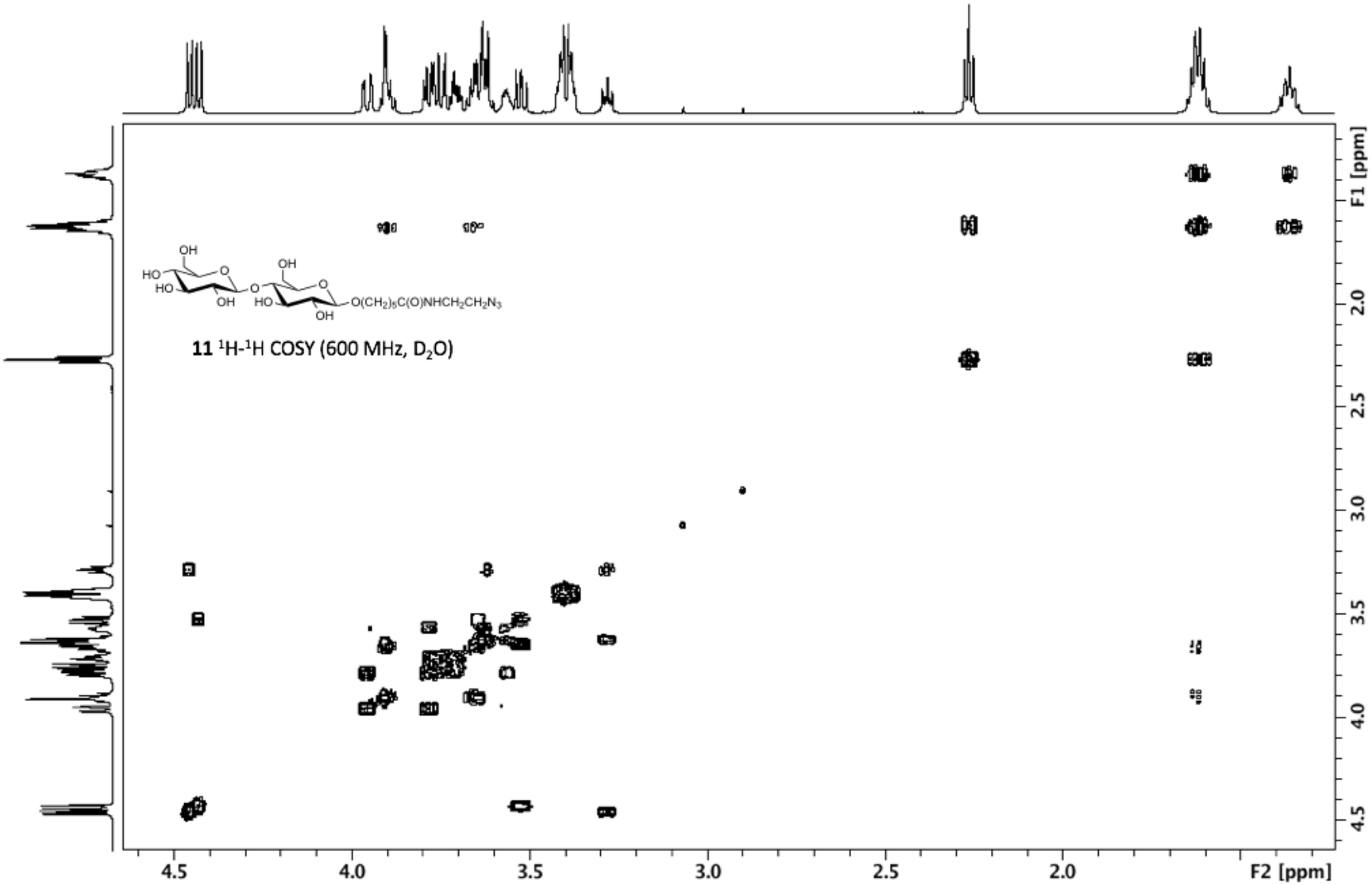

8 ^{1}H-^{13}C HSQC (600 MHz, $CDCl_3$)
AcO
OAc
NH
AcO
OAc
O
OAc
O
$O(CH_2)_5C(O)\ CH_2CH_2N_3$
F1 [ppm]
40
60
80
100
7
6
5
4
3
2
F2 [ppm]

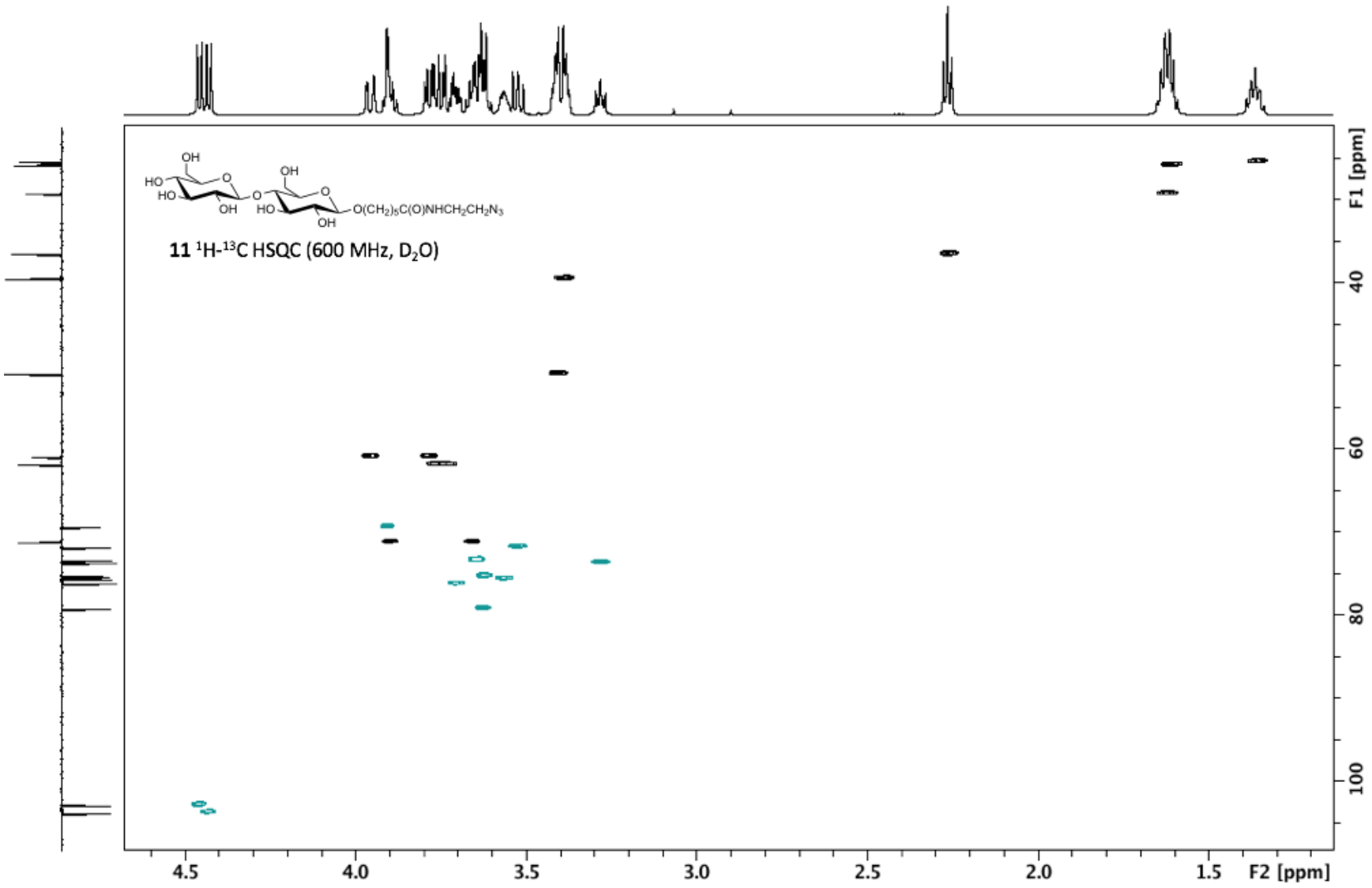

8 ^{1}H-^{13}C HMBC (600 MHz, $CDCl_3$)
F1 [ppm]
F2 [ppm]
7
6
5
4
3
2
40
60
80
100

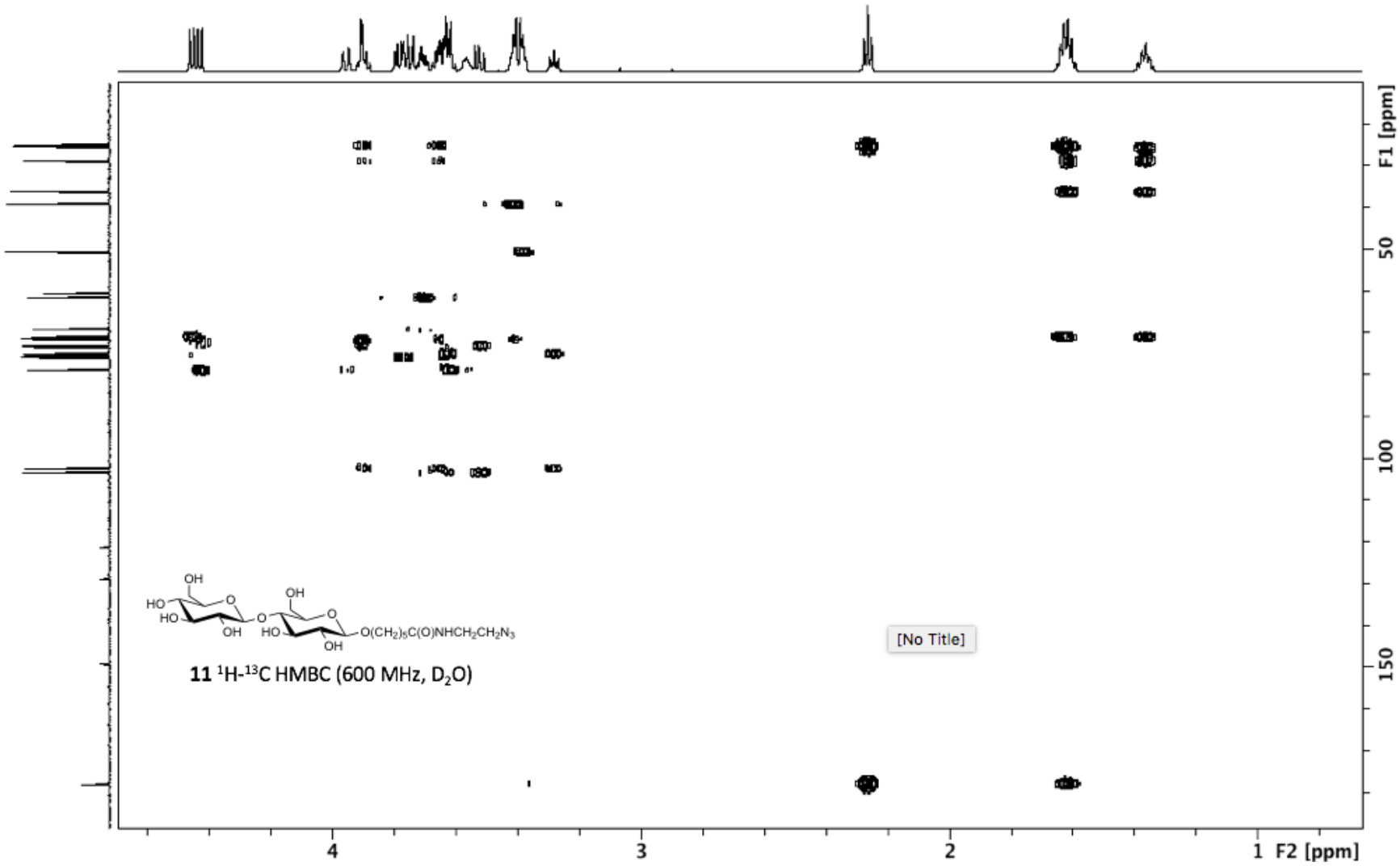
Lactose derivative **11**




178.09
103.58
102.68
79.03
76.01
75.41
75.10
73.50
73.17
71.61
71.01
69.20
61.68
60.74
50.73
39.30
36.30
29.04
25.62
25.19
[rel]
20
15
10
5
0
200
150
100
50
0 [ppm]
100
90
80
70
11 13C NMR (150 MHz, D2O)

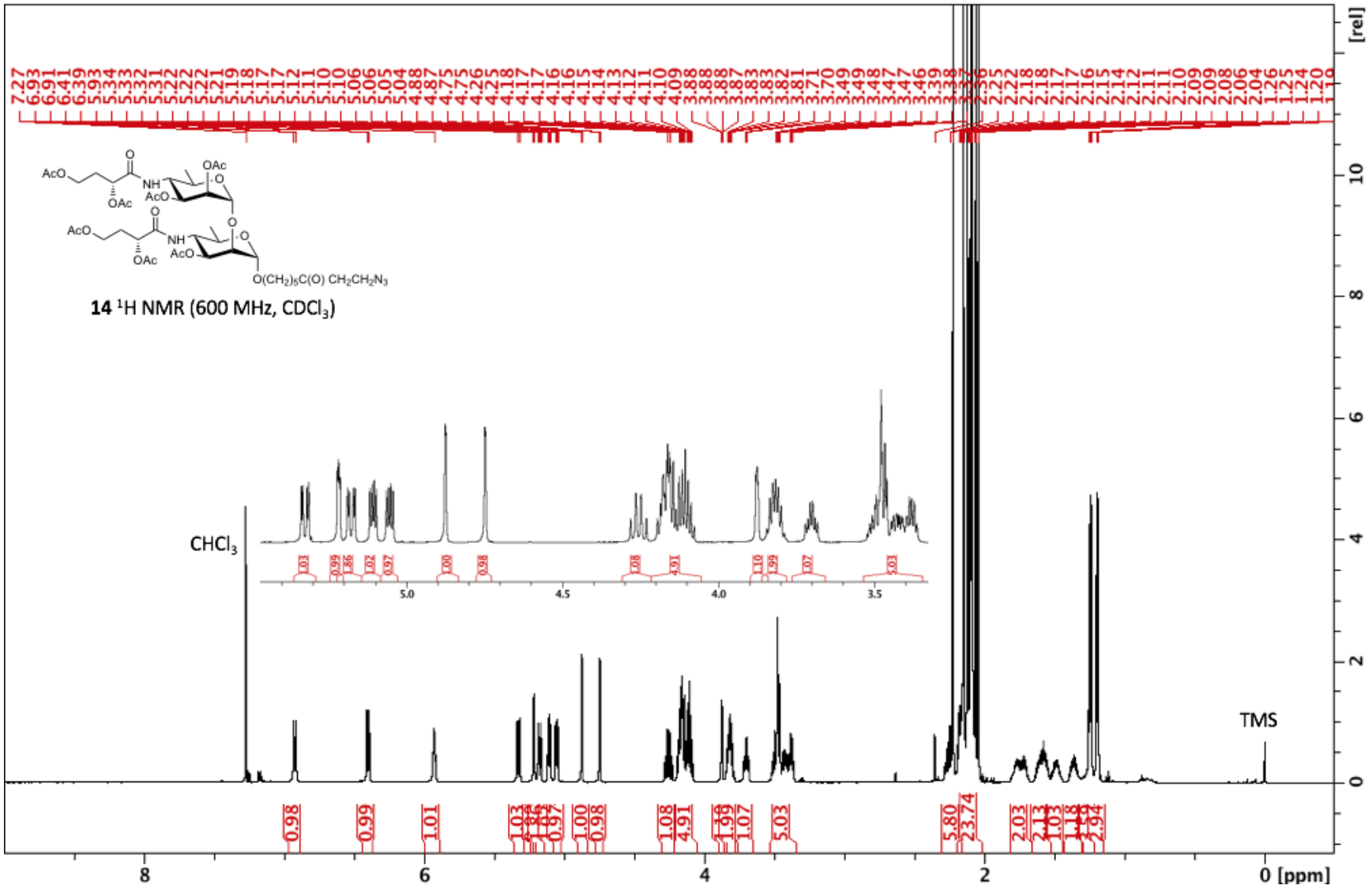

OH
HO
HO
O
OH
O
OH
HO
O
OH
O(CH2)5C(O)NHCH2CH2N3
11 1H-1H COSY (600 MHz, D2O)
F1 [ppm]
2.0
2.5
3.0
3.5
4.0
4.5
4.5
4.0
3.5
3.0
2.5
2.0
F2 [ppm]

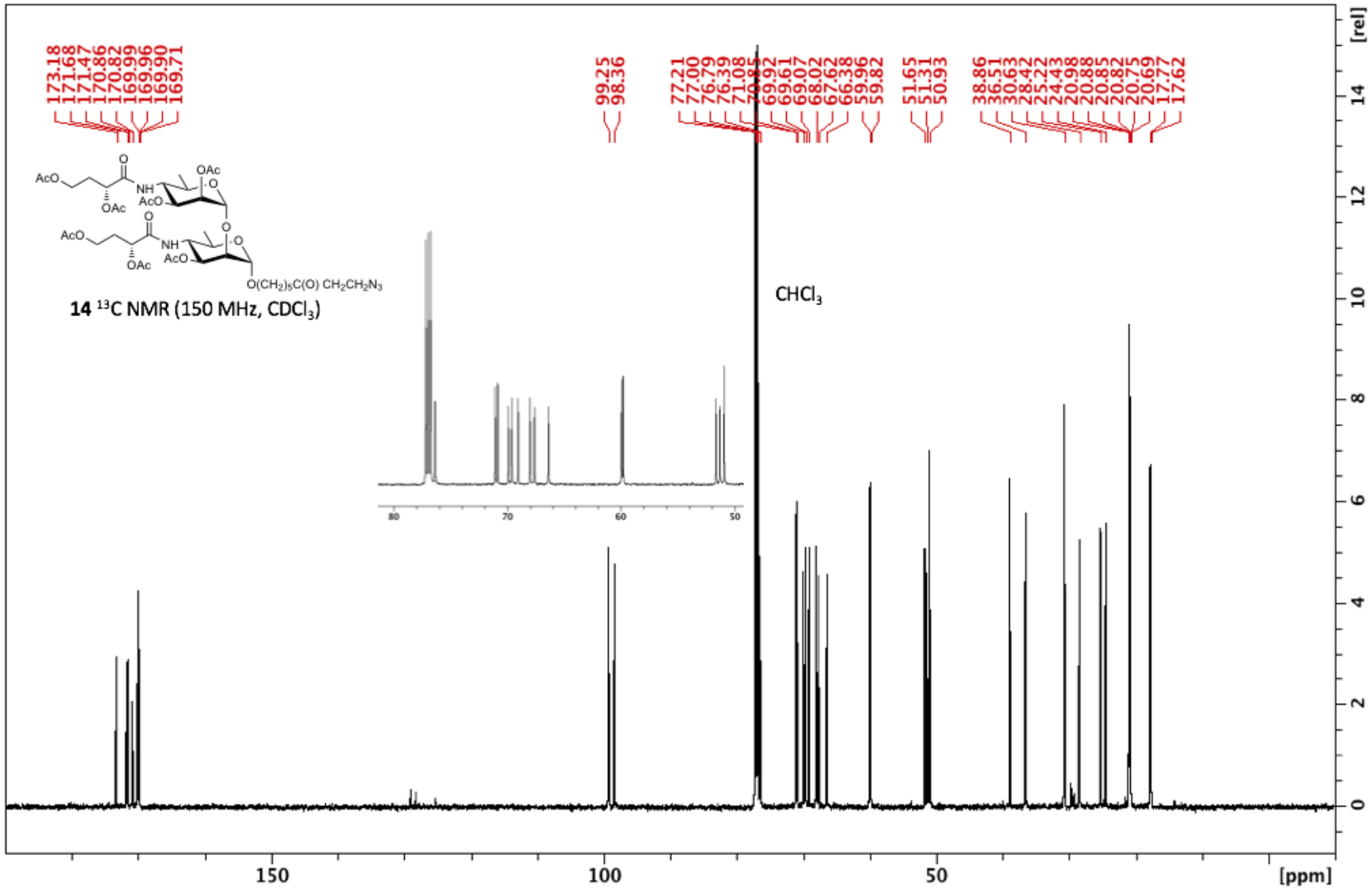

11 ^{1}H-^{13}C HSQC (600 MHz, D_2O)
F1 [ppm]
F2 [ppm]
4.5
4.0
3.5
3.0
2.5
2.0
1.5
40
60
80
100

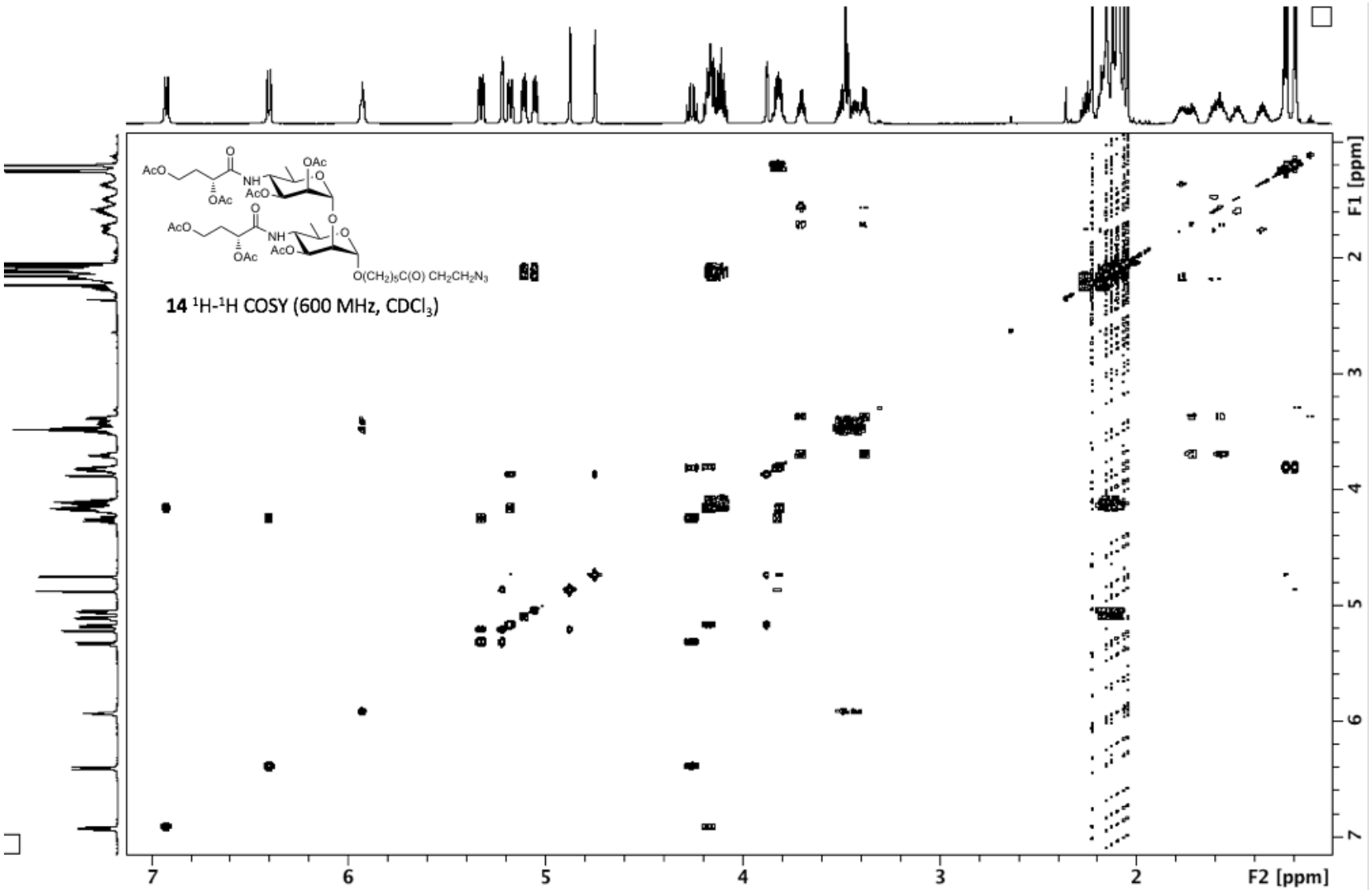


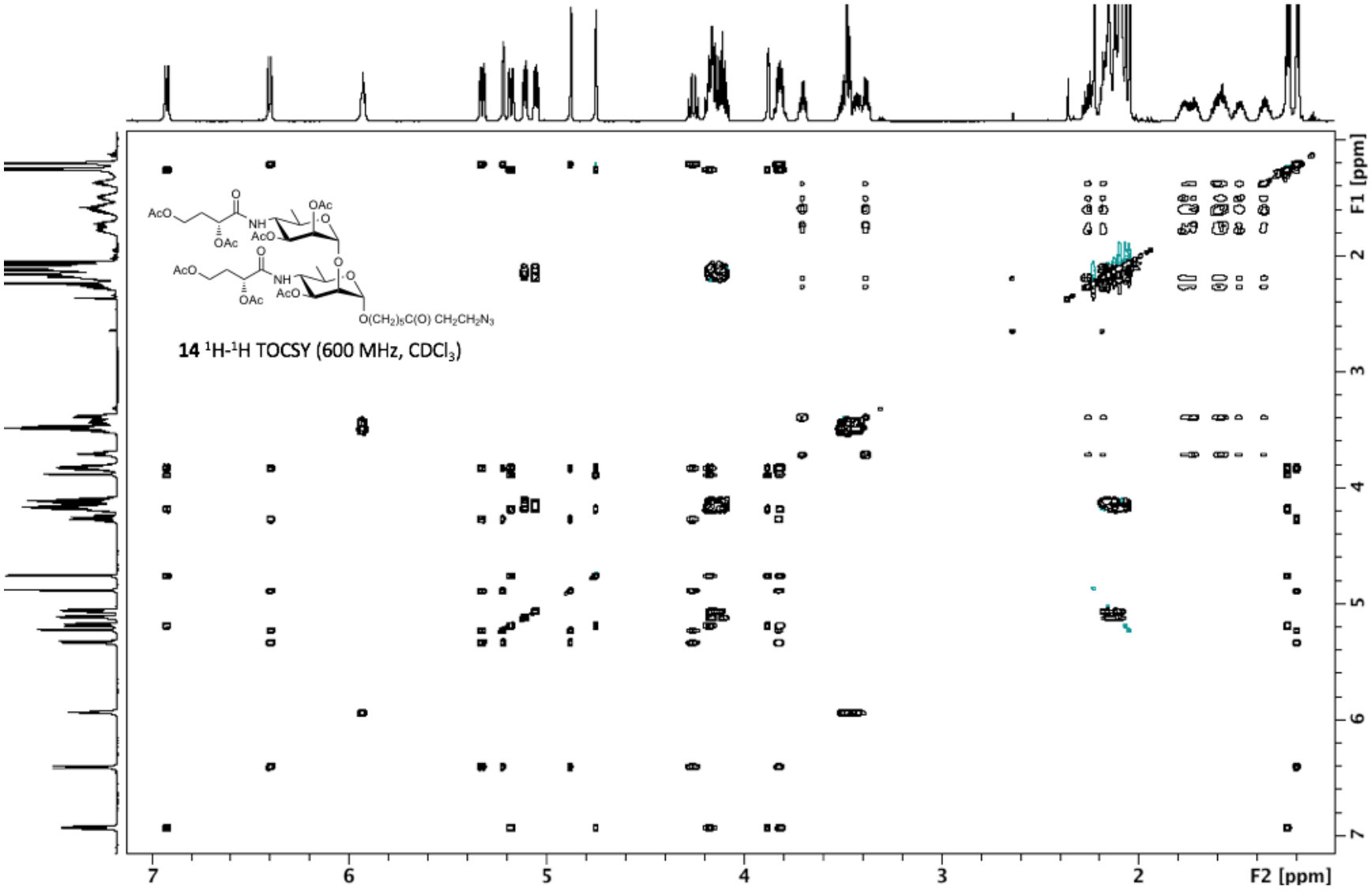
11 ^{1}H-^{13}C HMBC (600 MHz, D_2O)

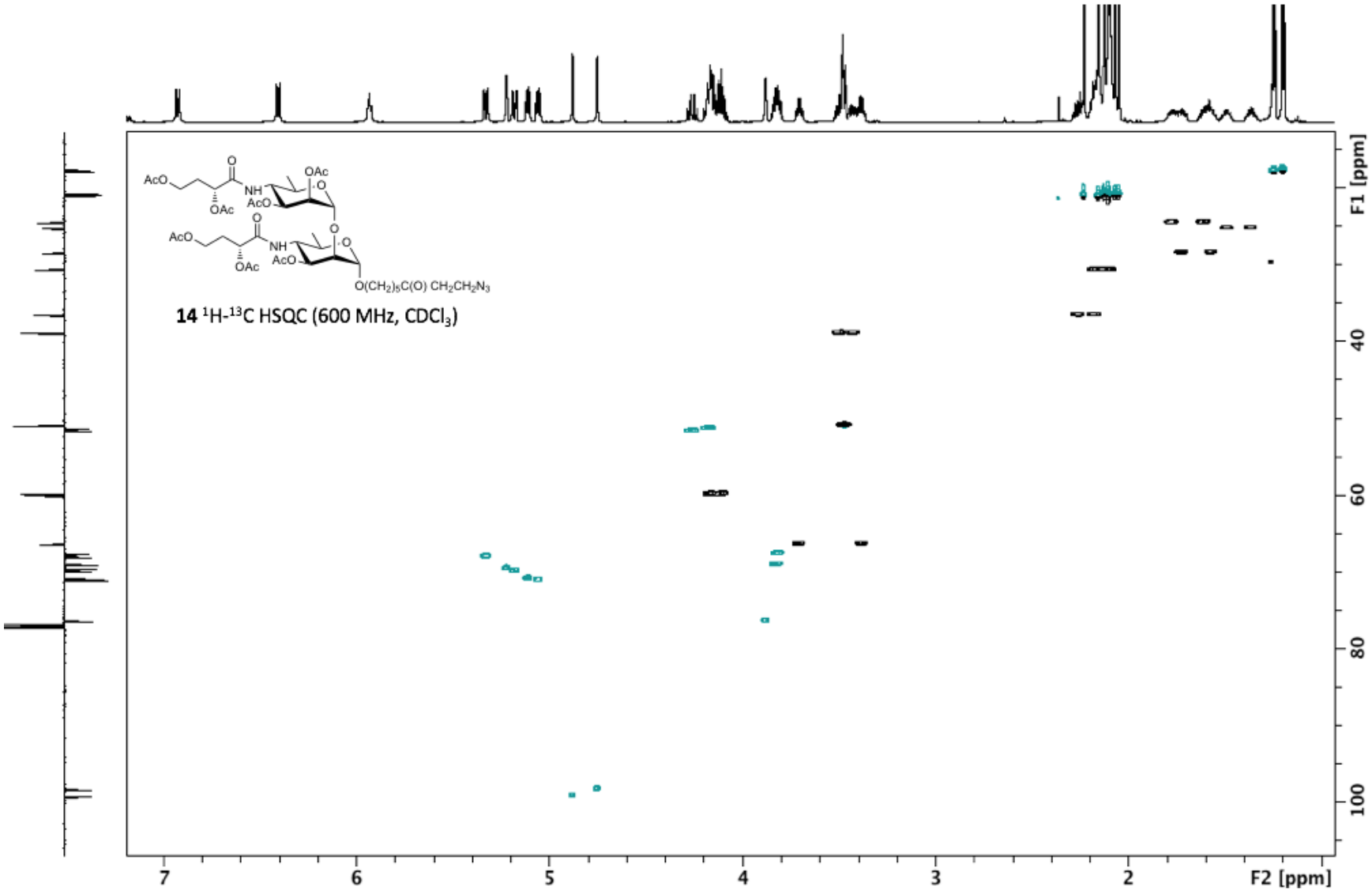
Disaccharide derivative **14**

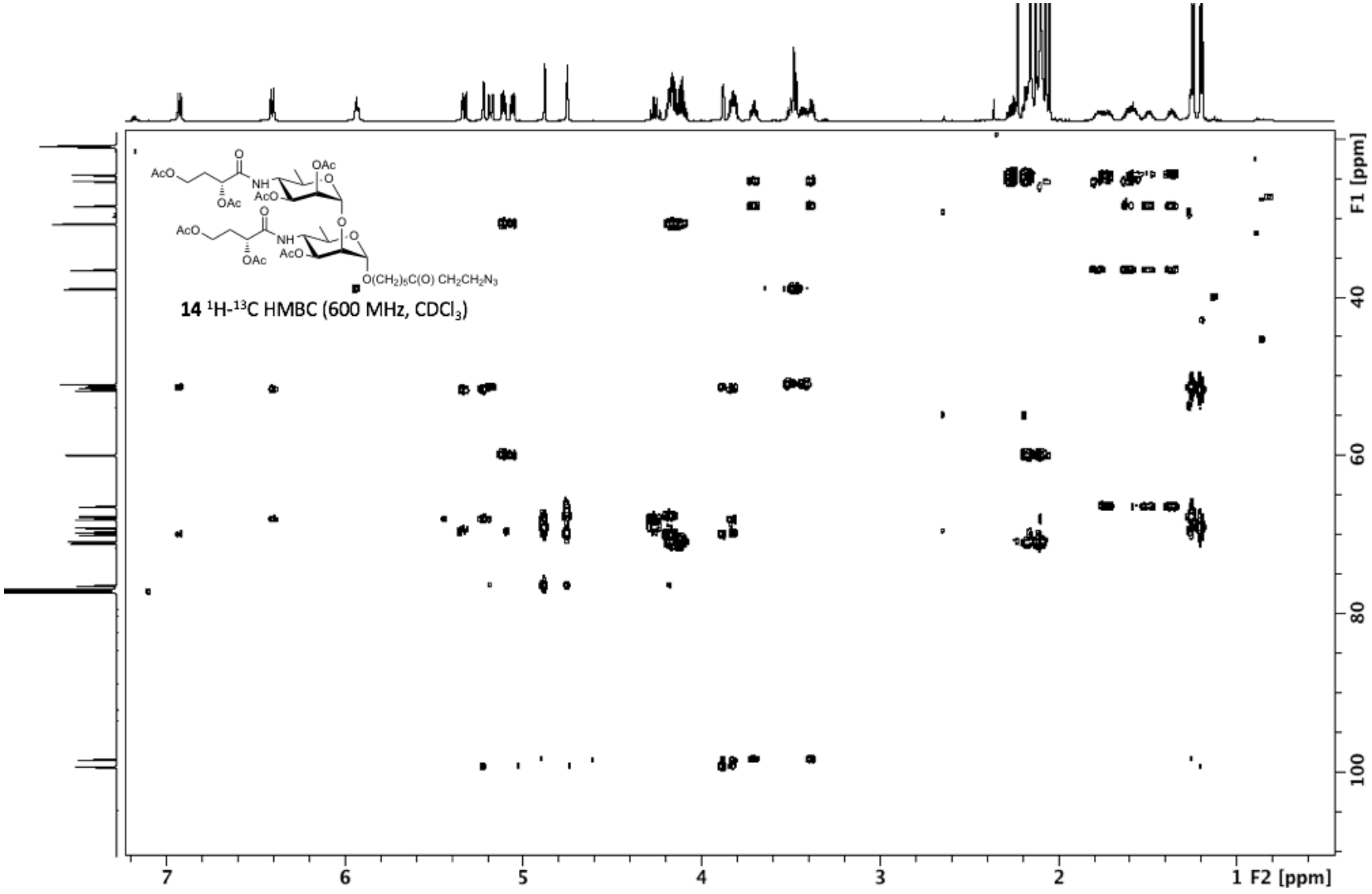



173.18
171.68
171.47
170.86
170.82
169.99
169.96
169.90
169.71
99.25
98.36
77.21
77.00
76.79
76.39
71.08
70.85
69.92
69.61
69.07
68.02
67.62
66.38
59.96
59.82
51.65
51.31
50.93
38.86
36.51
30.63
28.42
25.22
24.43
20.98
20.88
20.85
20.82
20.75
20.69
17.77
17.62
CHCl3
14 13C NMR (150 MHz, CDCl3)
[rel]
[ppm]
150
100
50

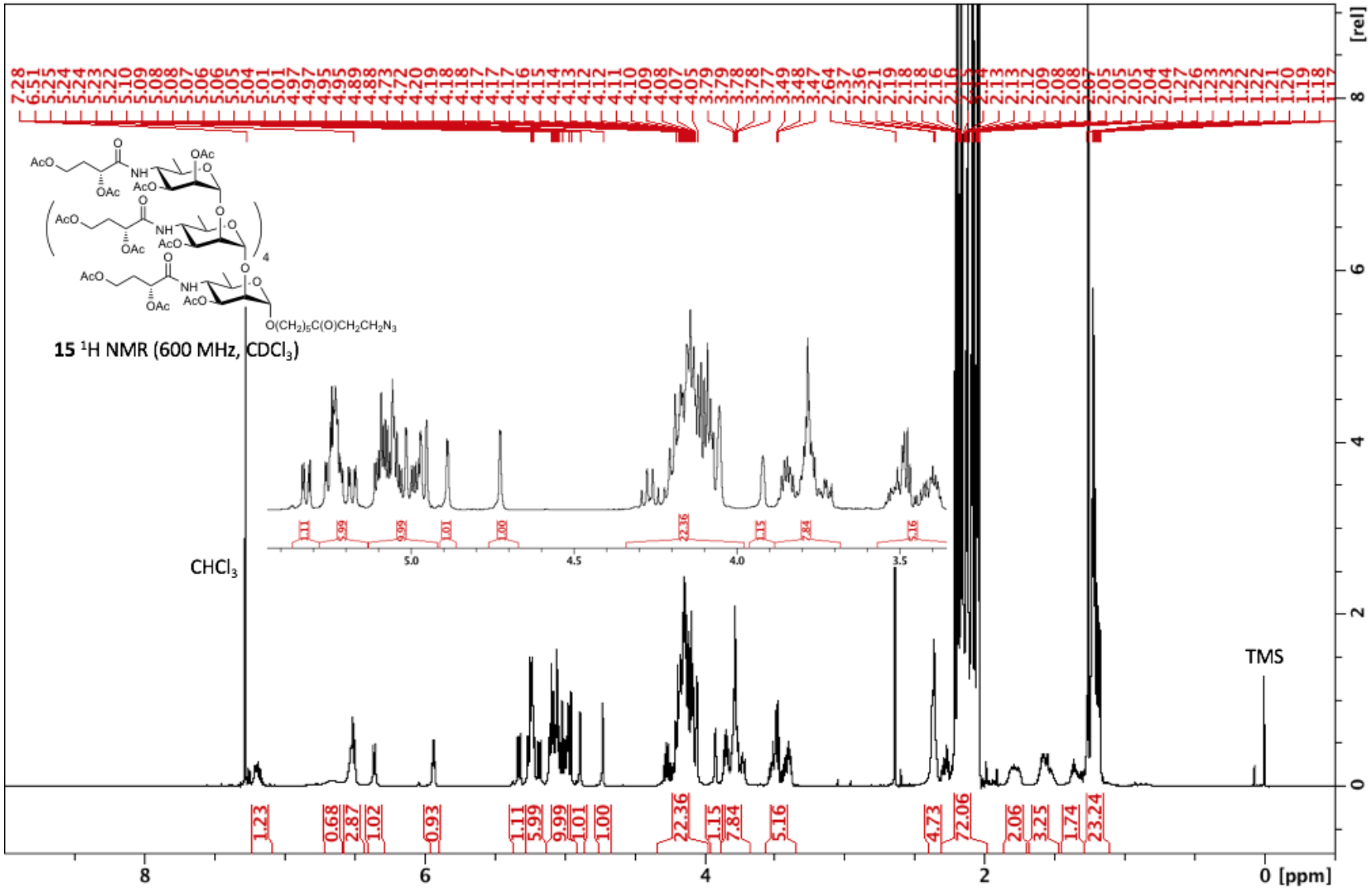

14 ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$)
F1 [ppm]
F2 [ppm]
1
2
3
4
5
6
7

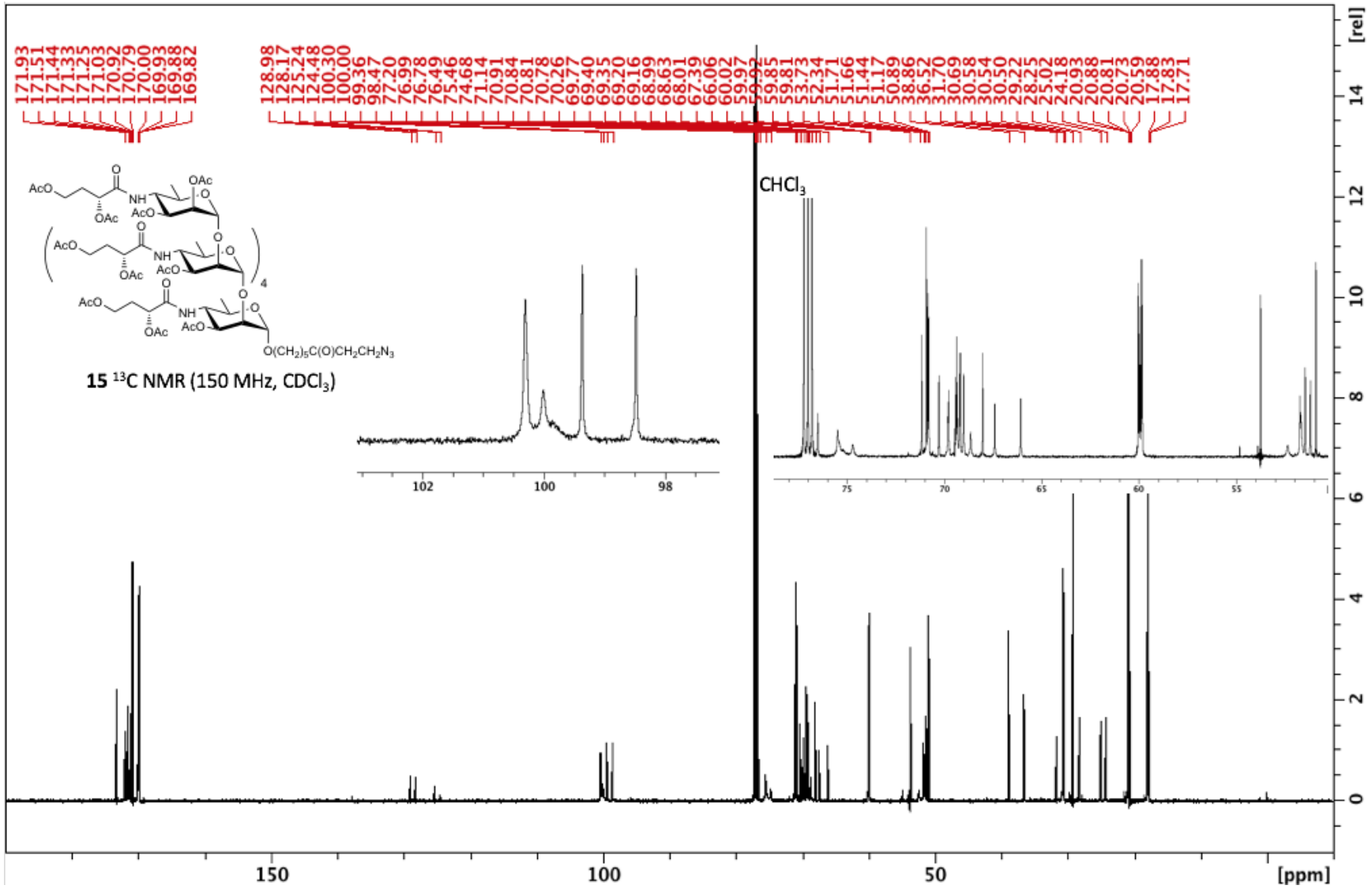

14 ^{1}H-^{1}H TOCSY (600 MHz, $CDCl_3$)
F1 [ppm]
F2 [ppm]
1
2
3
4
5
6
7

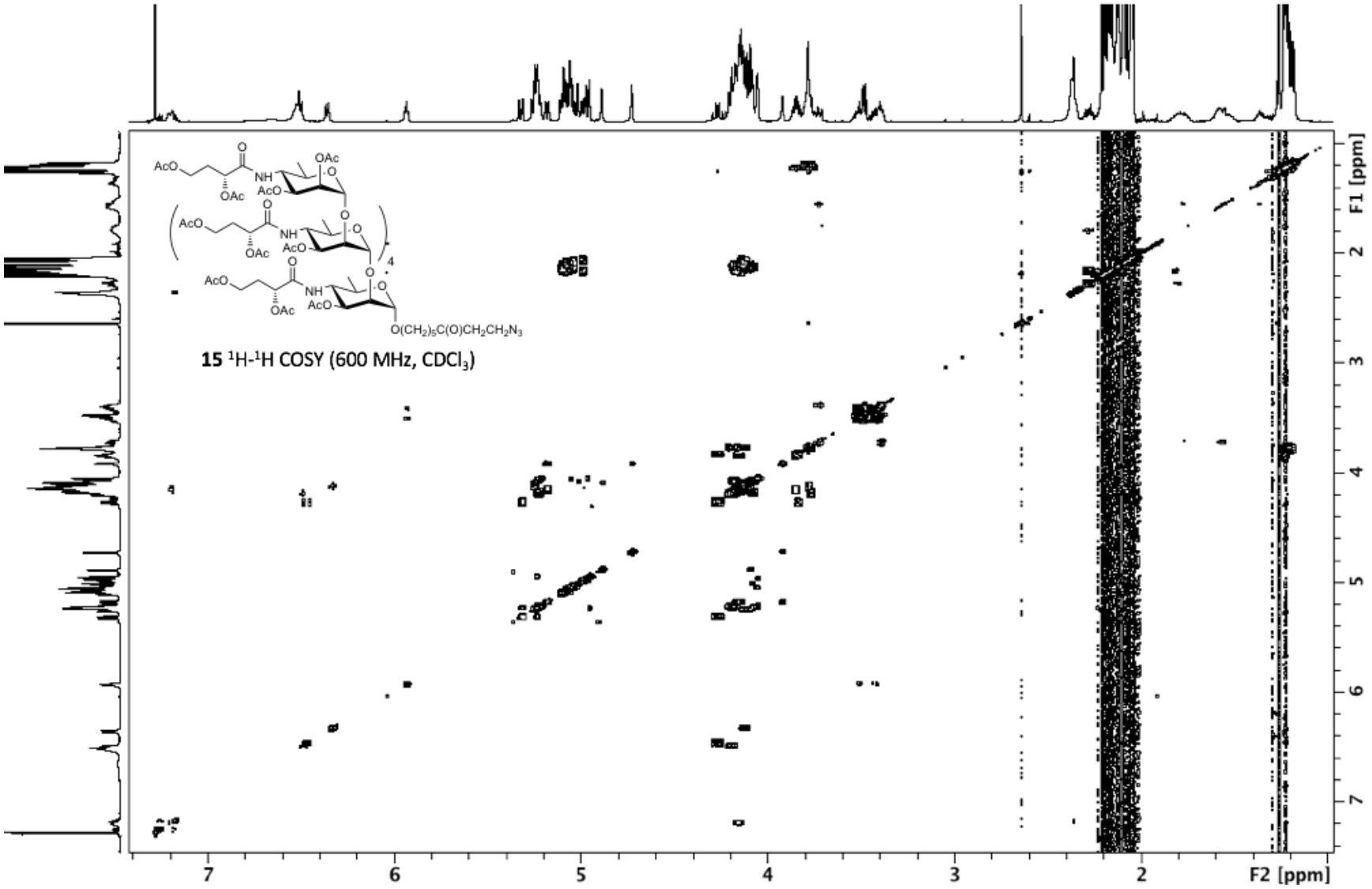

AcO
OAc
NH
AcO
OAc
O
O
O(CH2)5C(O) CH2CH2N3
14 1H-13C HSQC (600 MHz, CDCl3)
F1 [ppm]
40
60
80
100
7
6
5
4
3
2
F2 [ppm]

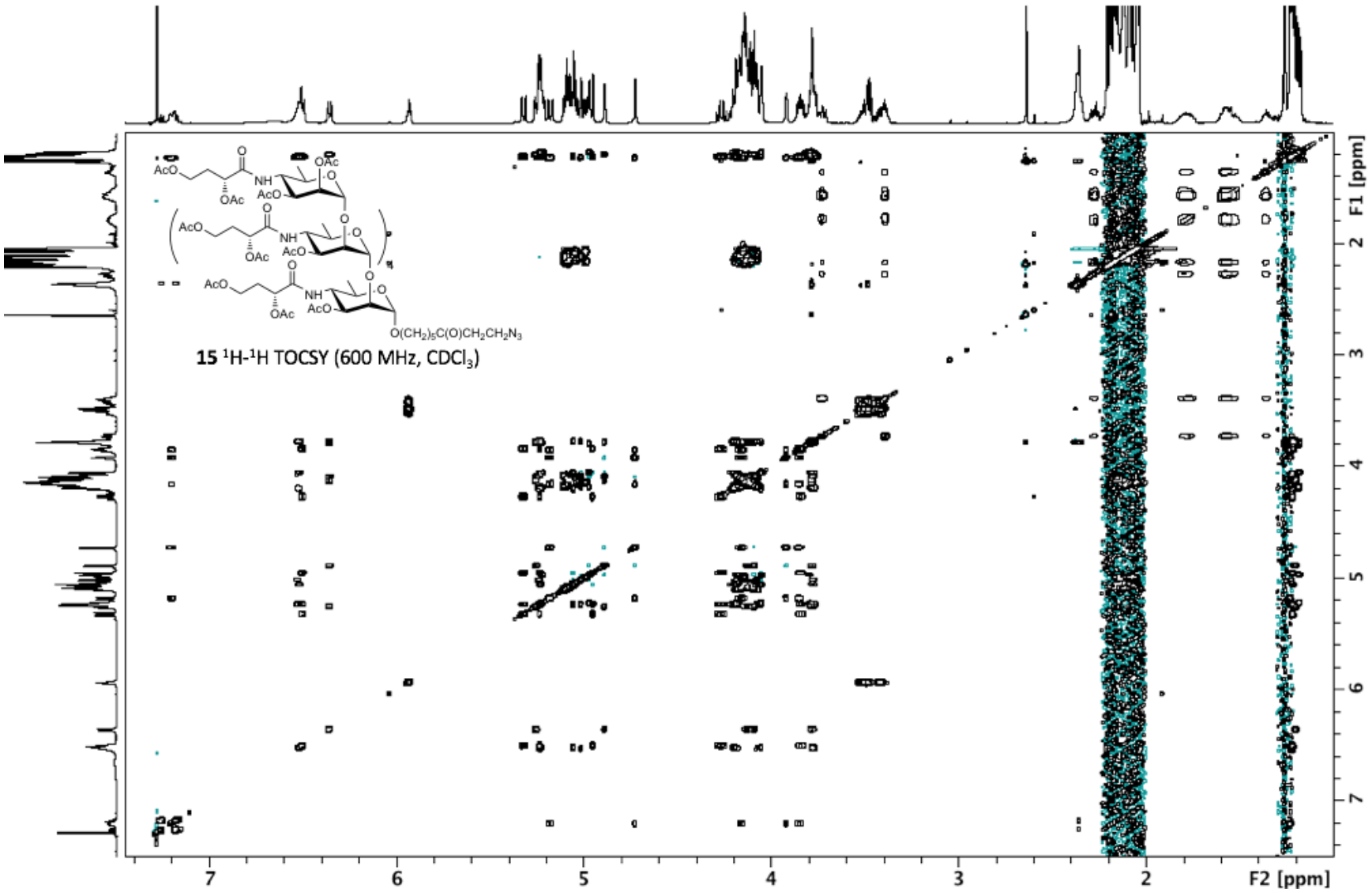

AcO
OAc
NH
AcO
OAc
O
O
O(CH2)5C(O) CH2CH2N3
14 1H-13C HMBC (600 MHz, CDCl3)
F1 [ppm]
40
60
80
100
7
6
5
4
3
2
1 F2 [ppm]

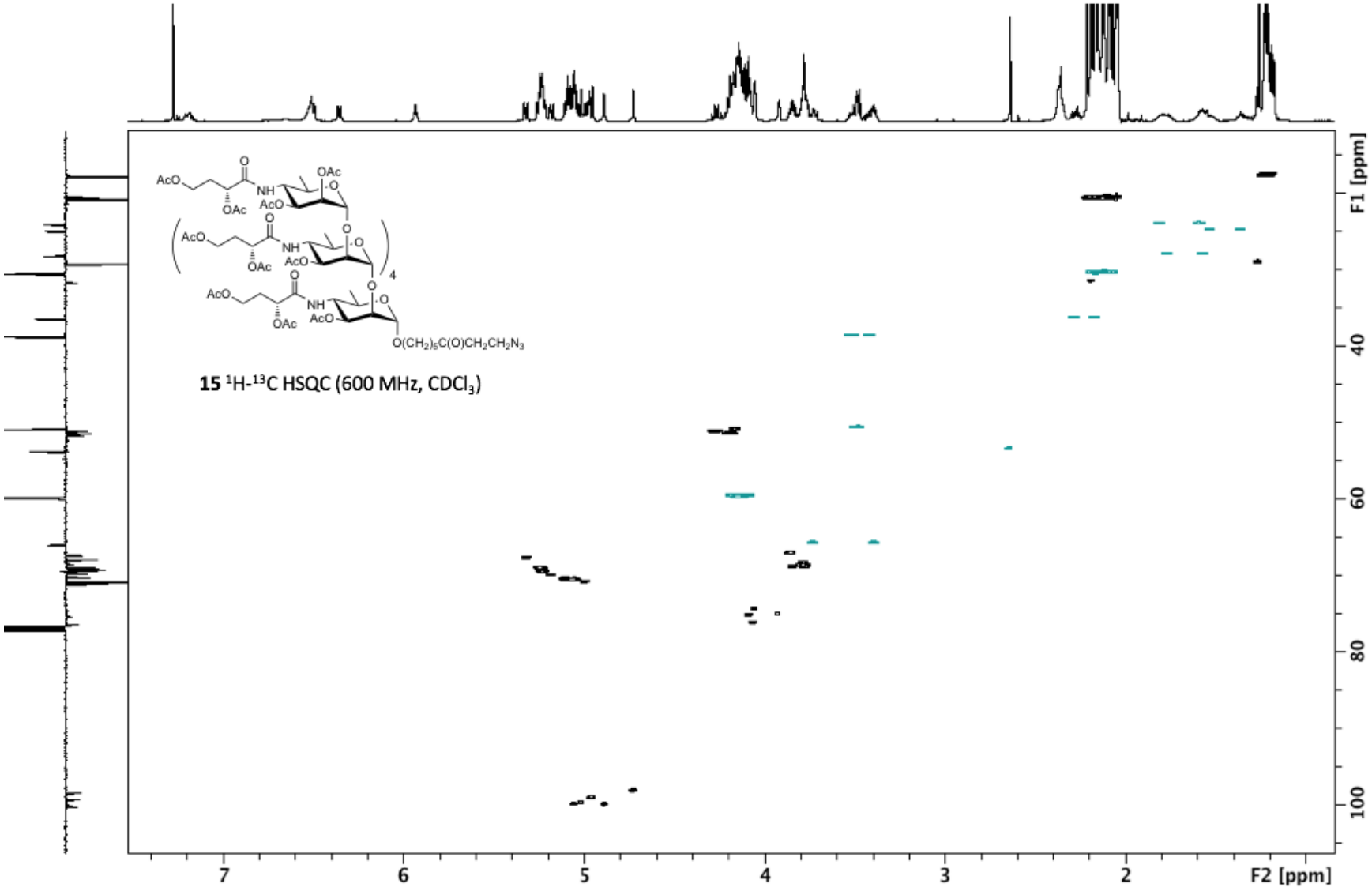
Hexasaccharide derivative **15**

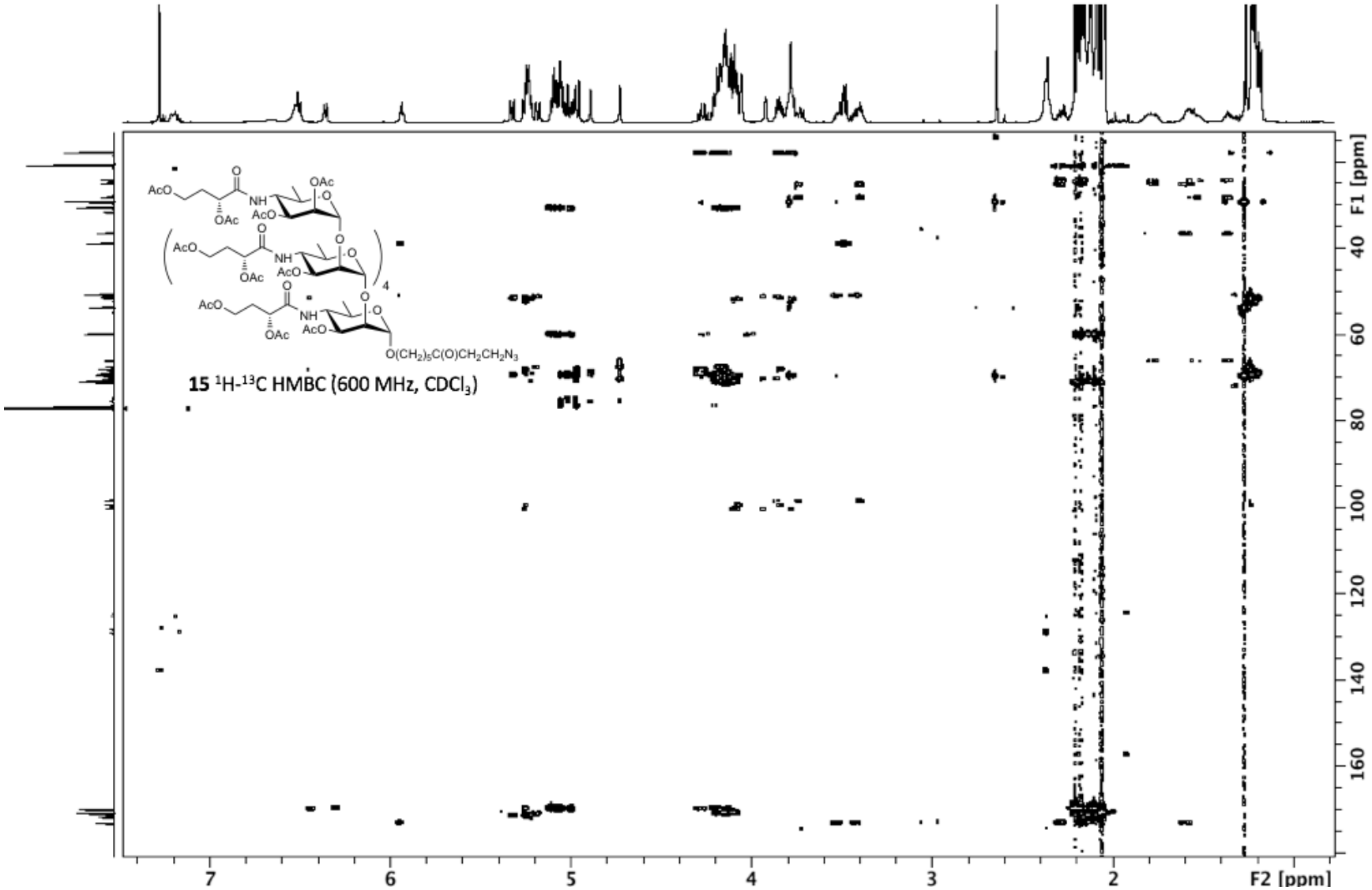



171.93
171.51
171.44
171.33
171.25
171.03
170.92
170.79
170.00
169.93
169.88
169.82
128.98
128.17
125.24
124.48
100.30
100.00
99.36
98.47
77.20
76.99
76.78
76.49
75.46
74.68
71.14
70.91
70.84
70.81
70.78
70.26
69.77
69.40
69.35
69.20
69.16
68.99
68.63
68.01
67.39
66.06
60.02
59.97
59.92
59.85
59.81
53.73
52.34
51.71
51.66
51.44
51.17
50.89
38.86
36.52
31.70
30.69
30.58
30.54
30.50
29.22
28.25
25.02
24.18
20.93
20.88
20.81
20.73
20.59
17.88
17.83
17.71
CHCl3
15 13C NMR (150 MHz, CDCl3)
[rel]
[ppm]

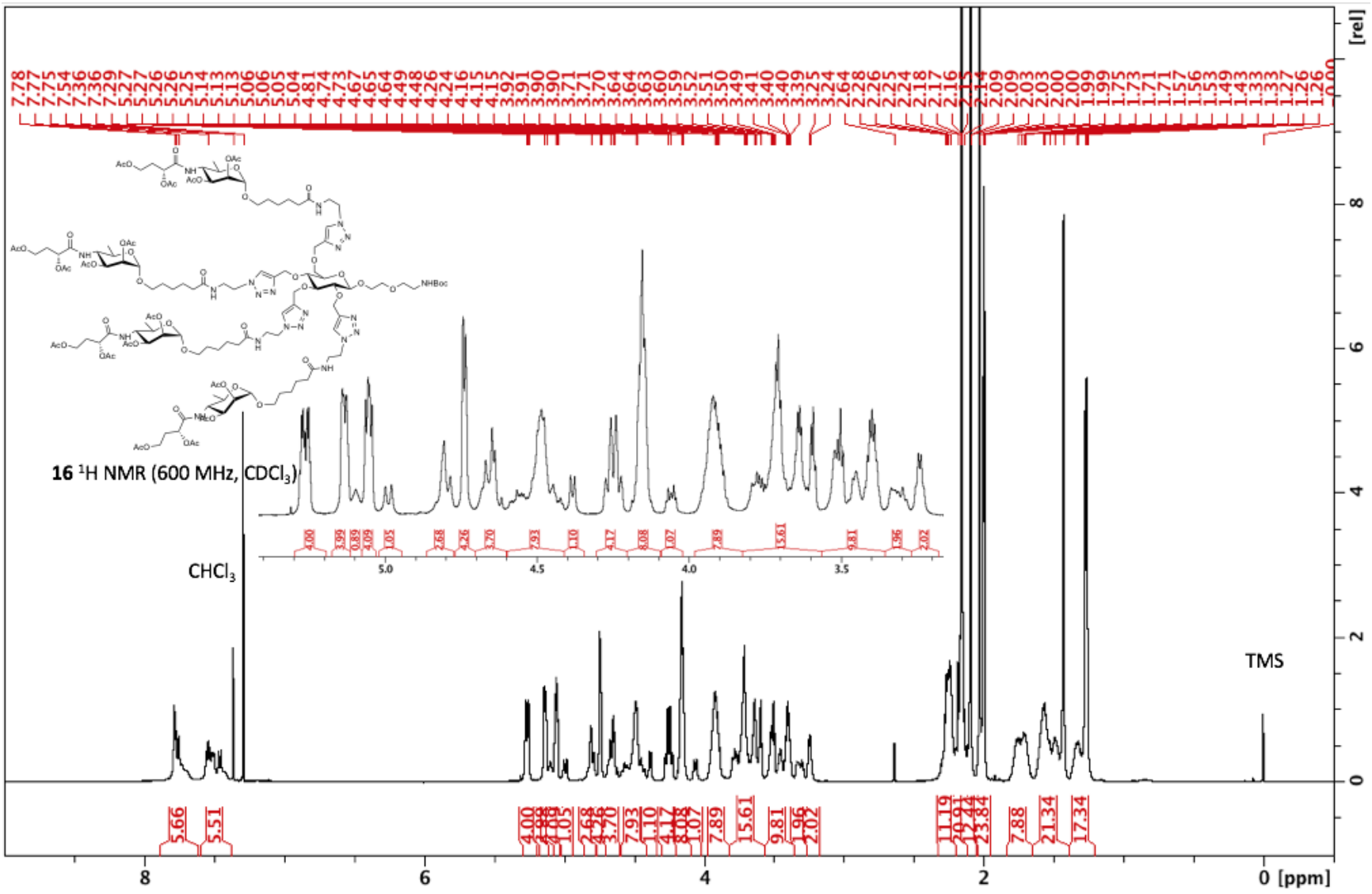

15 ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$)
F1 [ppm]
F2 [ppm]
1
2
3
4
5
6
7

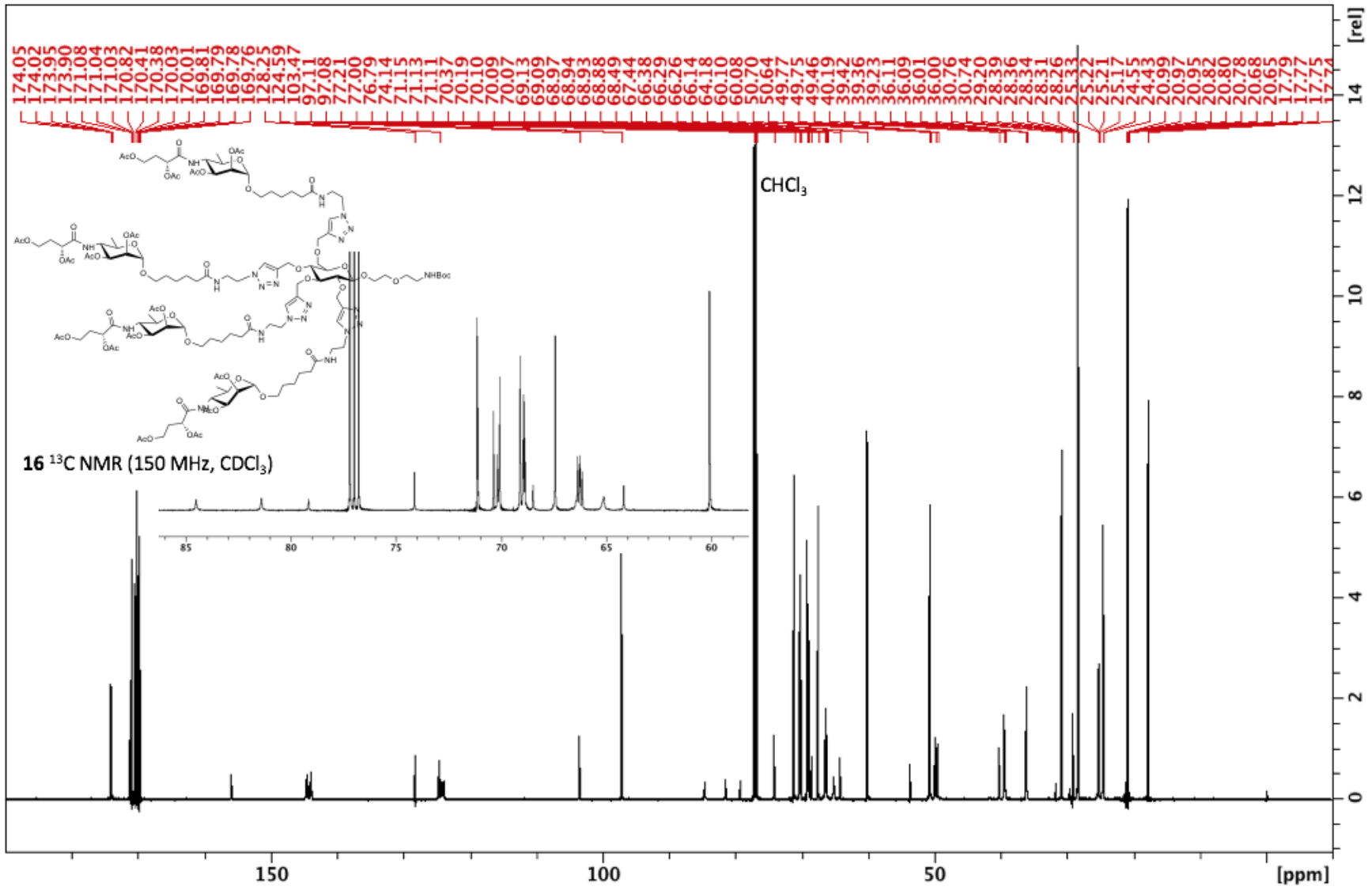

15 ^{1}H-^{1}H TOCSY (600 MHz, $CDCl_3$)
F1 [ppm]
F2 [ppm]
1
2
3
4
5
6
7

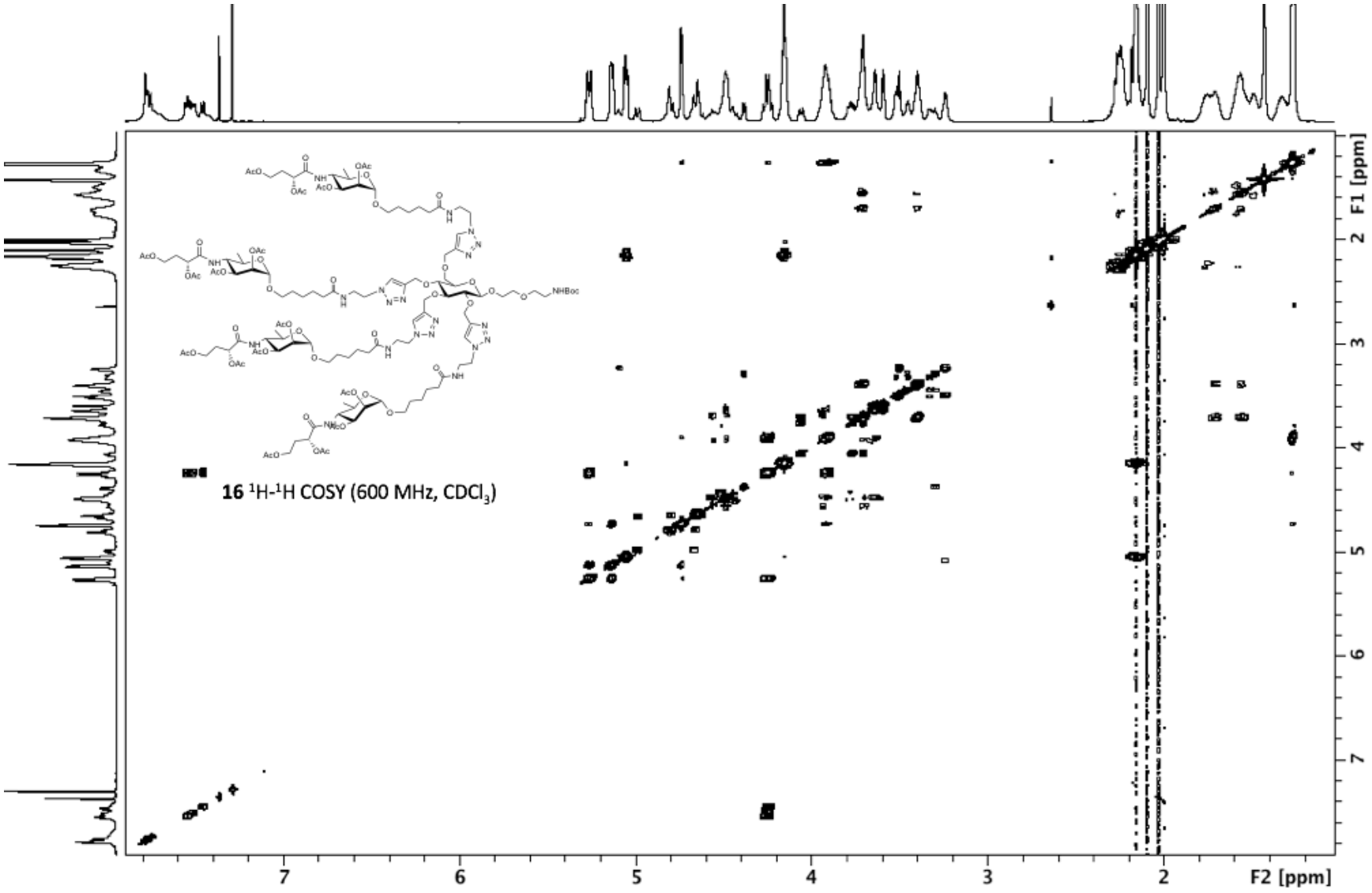

AcO
OAc
NH
AcO
OAc
4
O(CH2)5C(O)CH2CH2N3
15 1H-13C HSQC (600 MHz, CDCl3)
F1 [ppm]
40
60
80
100
7
6
5
4
3
2
F2 [ppm]

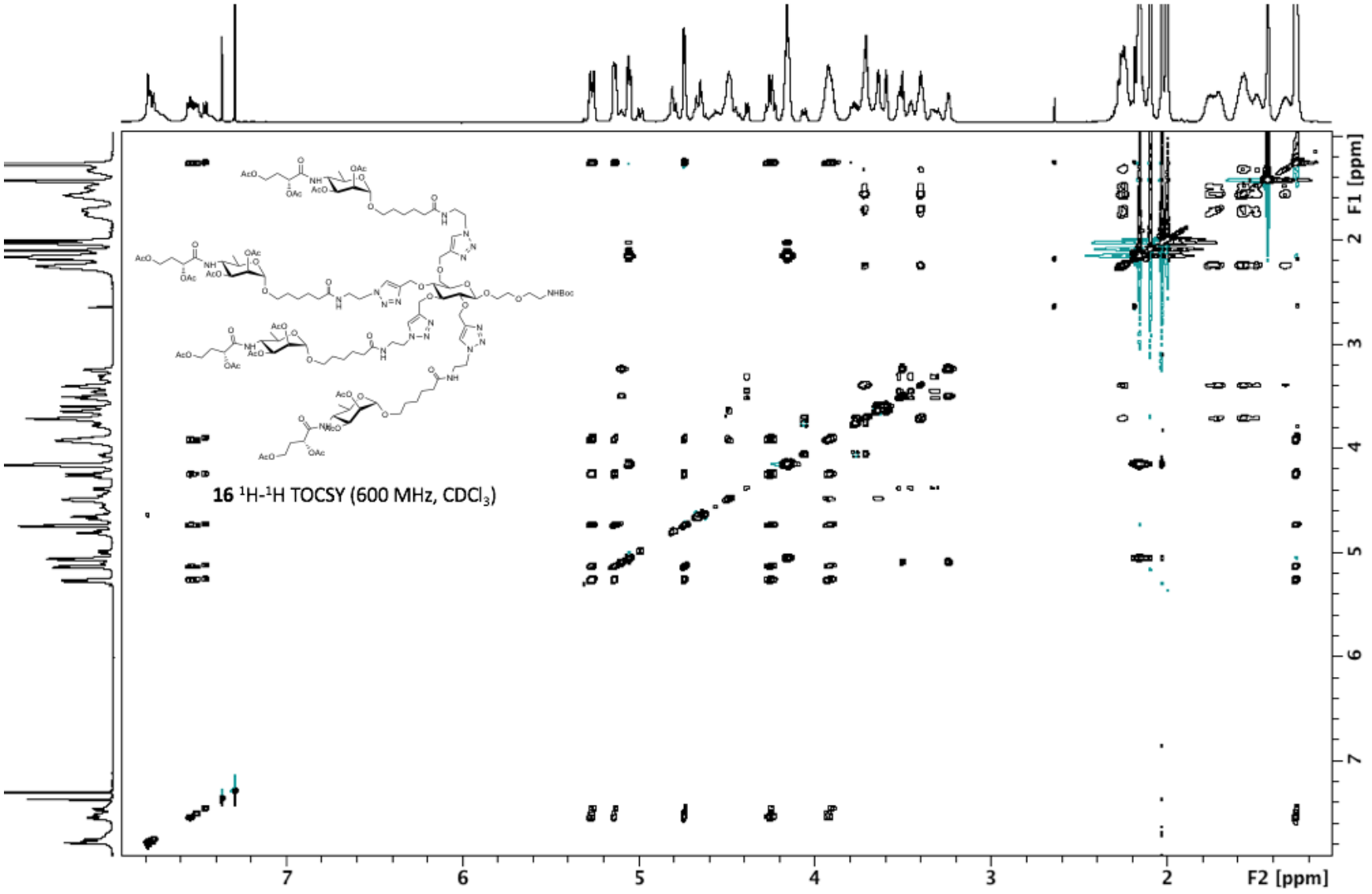

15 ^{1}H-^{13}C HMBC (600 MHz, $CDCl_3$)
F1 [ppm]
F2 [ppm]
7
6
5
4
3
2
40
60
80
100
120
140
160

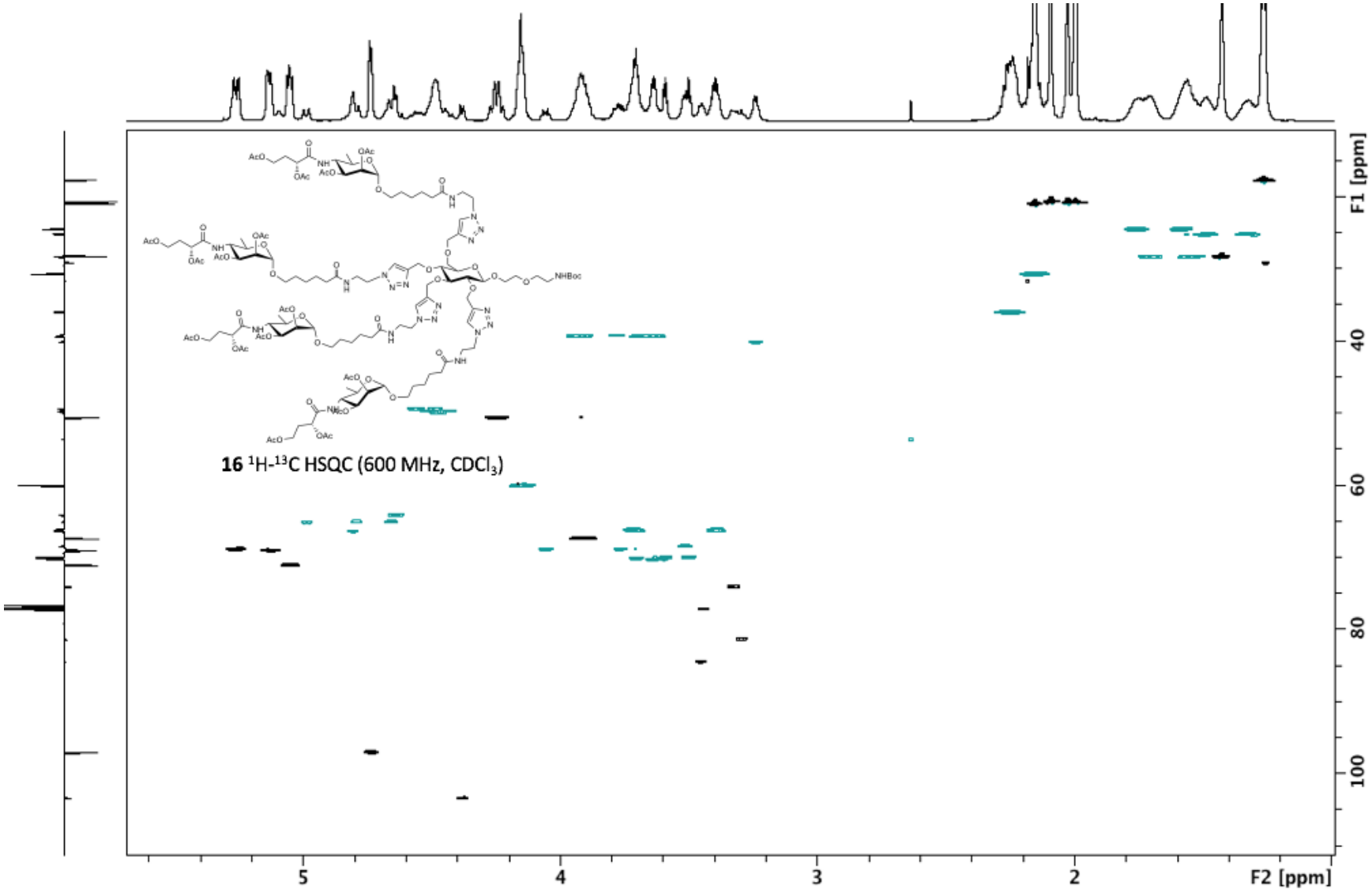
Boc-protected, acetylated monosaccharide cluster **16**

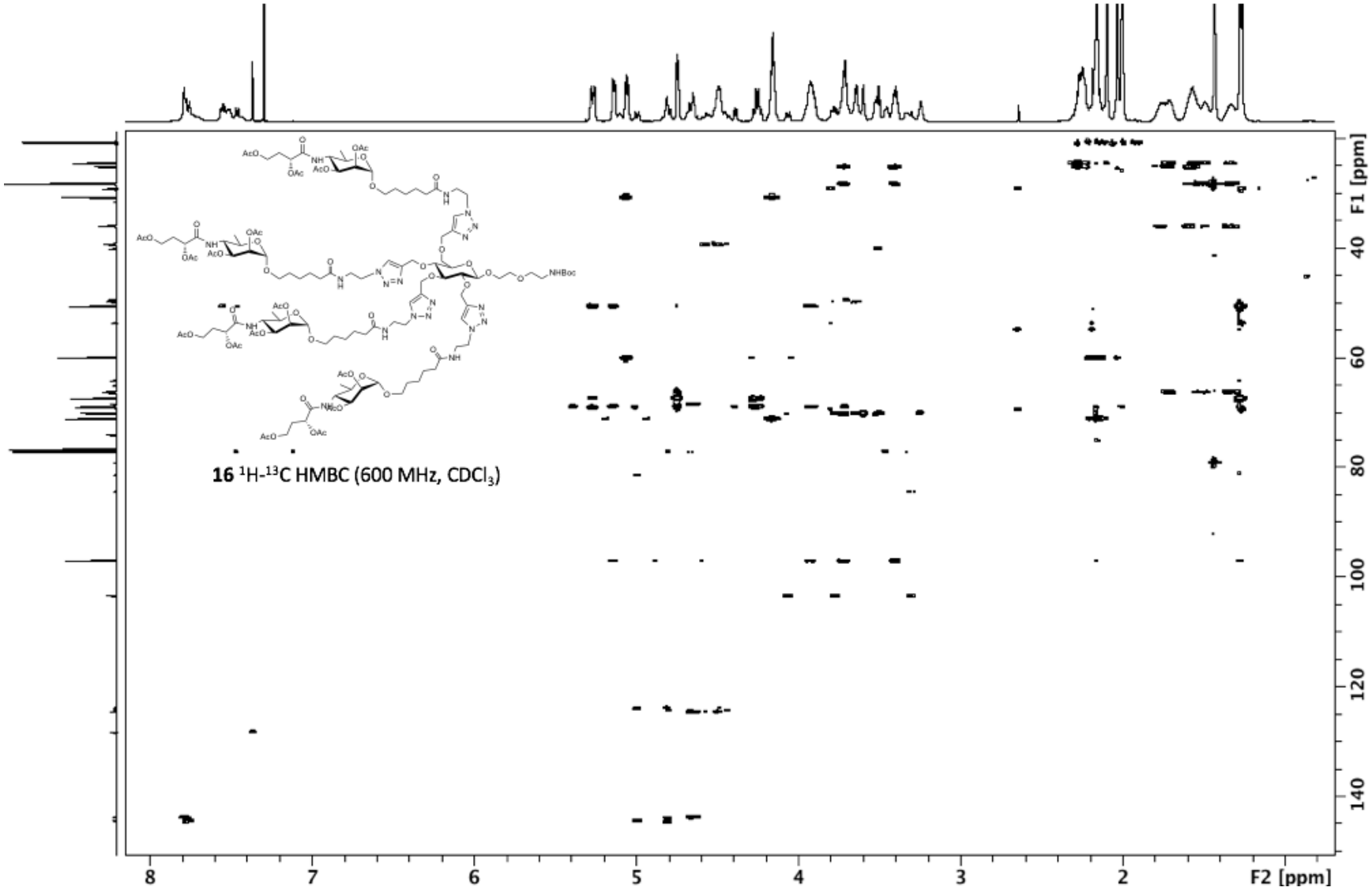



174.05
174.02
173.95
173.90
171.08
171.04
171.03
170.82
170.41
170.38
170.03
170.01
169.81
169.79
169.78
169.76
128.25
124.59
103.47
97.11
97.08
77.21
77.00
76.79
74.14
71.15
71.13
71.11
70.37
70.19
70.10
70.09
70.07
69.13
69.09
68.97
68.94
68.93
68.88
68.49
67.44
66.38
66.29
66.26
66.14
64.18
60.10
60.08
50.70
50.64
49.77
49.75
49.46
40.19
39.42
39.36
39.23
36.11
36.09
36.01
36.00
30.76
30.74
29.20
28.39
28.36
28.34
28.31
28.26
25.33
25.22
25.21
25.17
24.55
24.43
20.99
20.97
20.95
20.82
20.80
20.78
20.65
17.79
17.77
17.75
17.74
CHCl3
16 13C NMR (150 MHz, CDCl3)
[rel]
[ppm]


16 ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$)
F1 [ppm]
F2 [ppm]
7
6
5
4
3
2

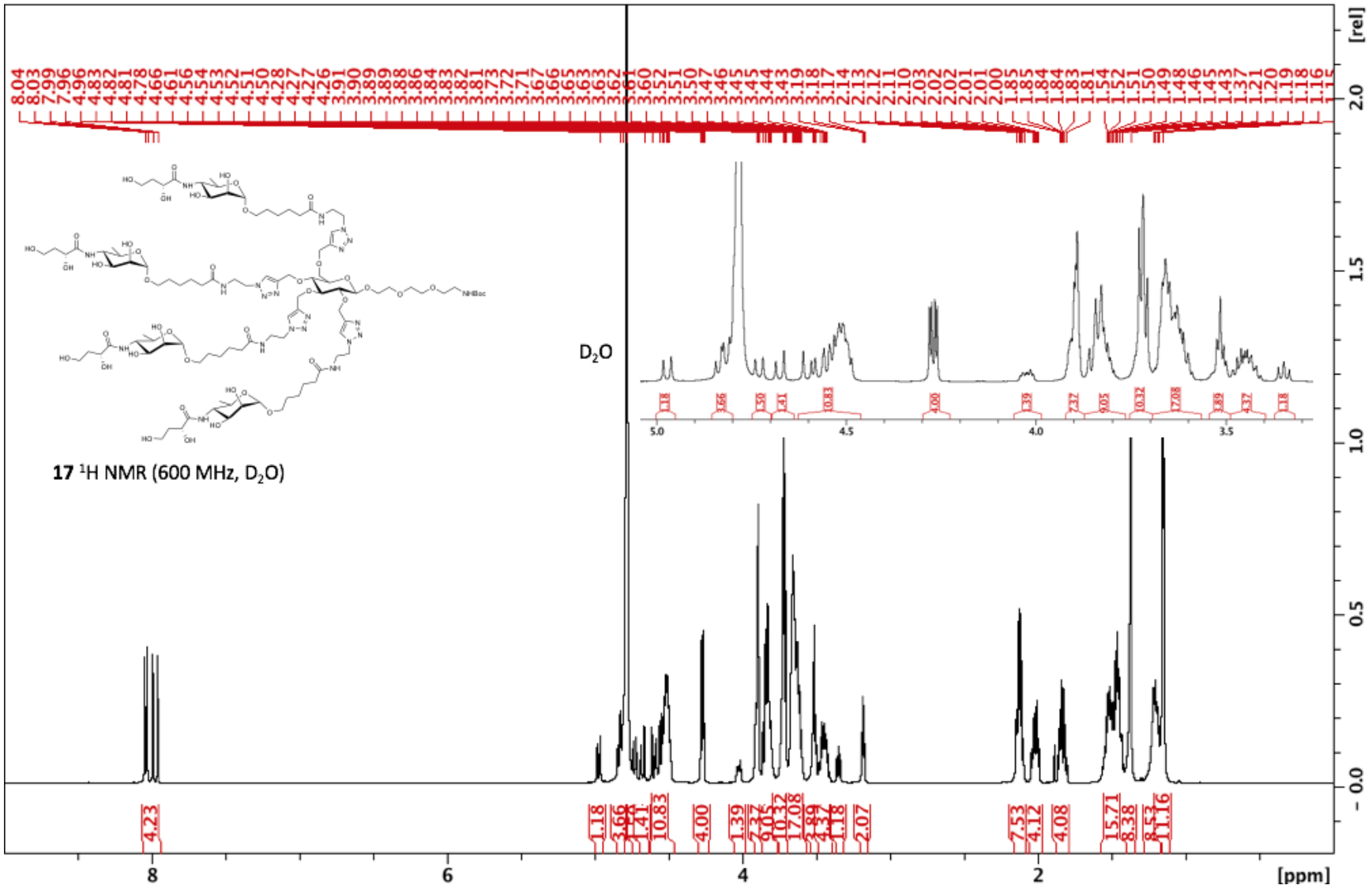

16 ^{1}H-^{1}H TOCSY (600 MHz, $CDCl_3$)
F1 [ppm]
F2 [ppm]
2
3
4
5
6
7

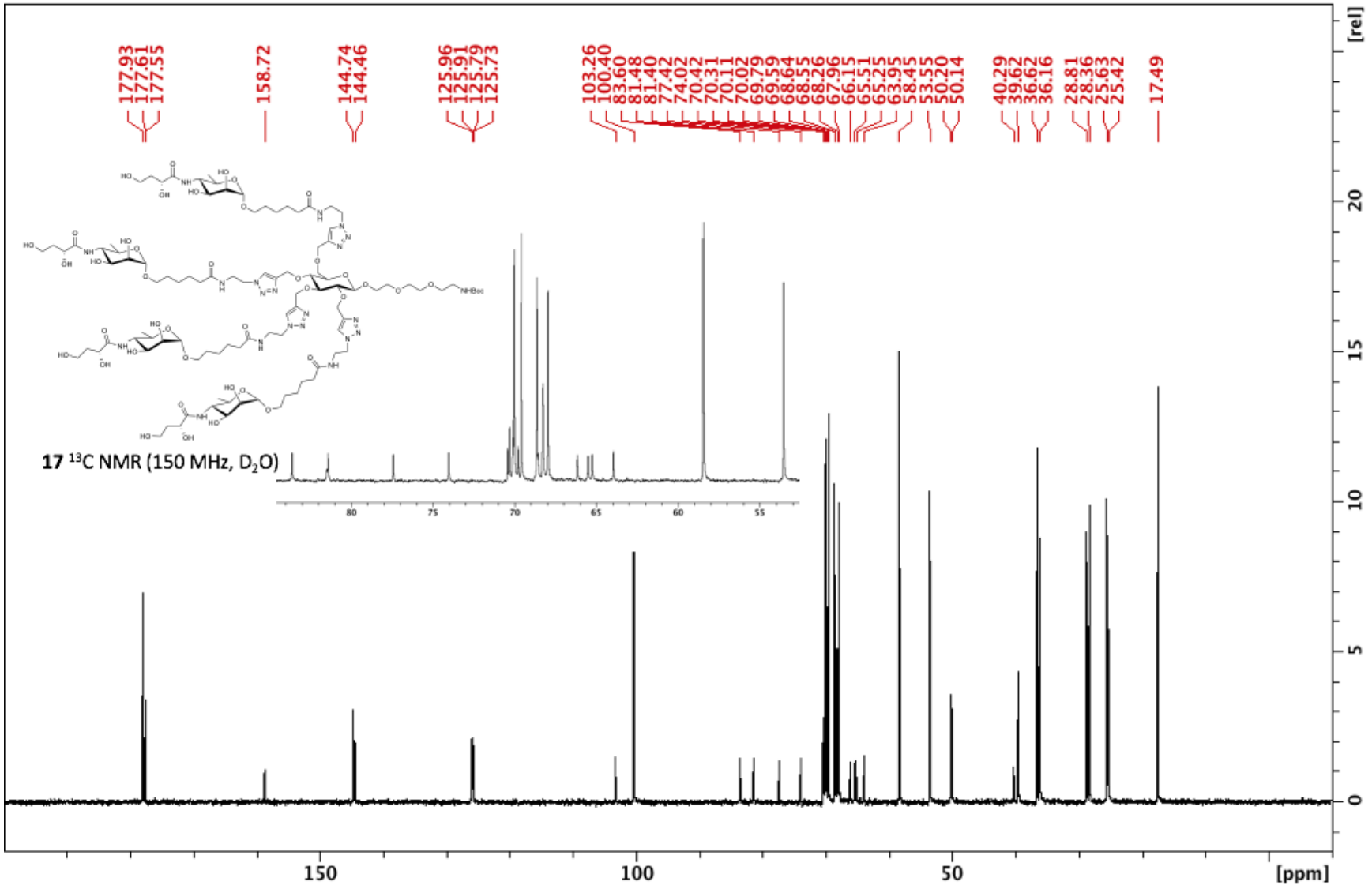

16 ^{1}H-^{13}C HSQC (600 MHz, $CDCl_3$)
F1 [ppm]
F2 [ppm]
5
4
3
2
40
60
80
100

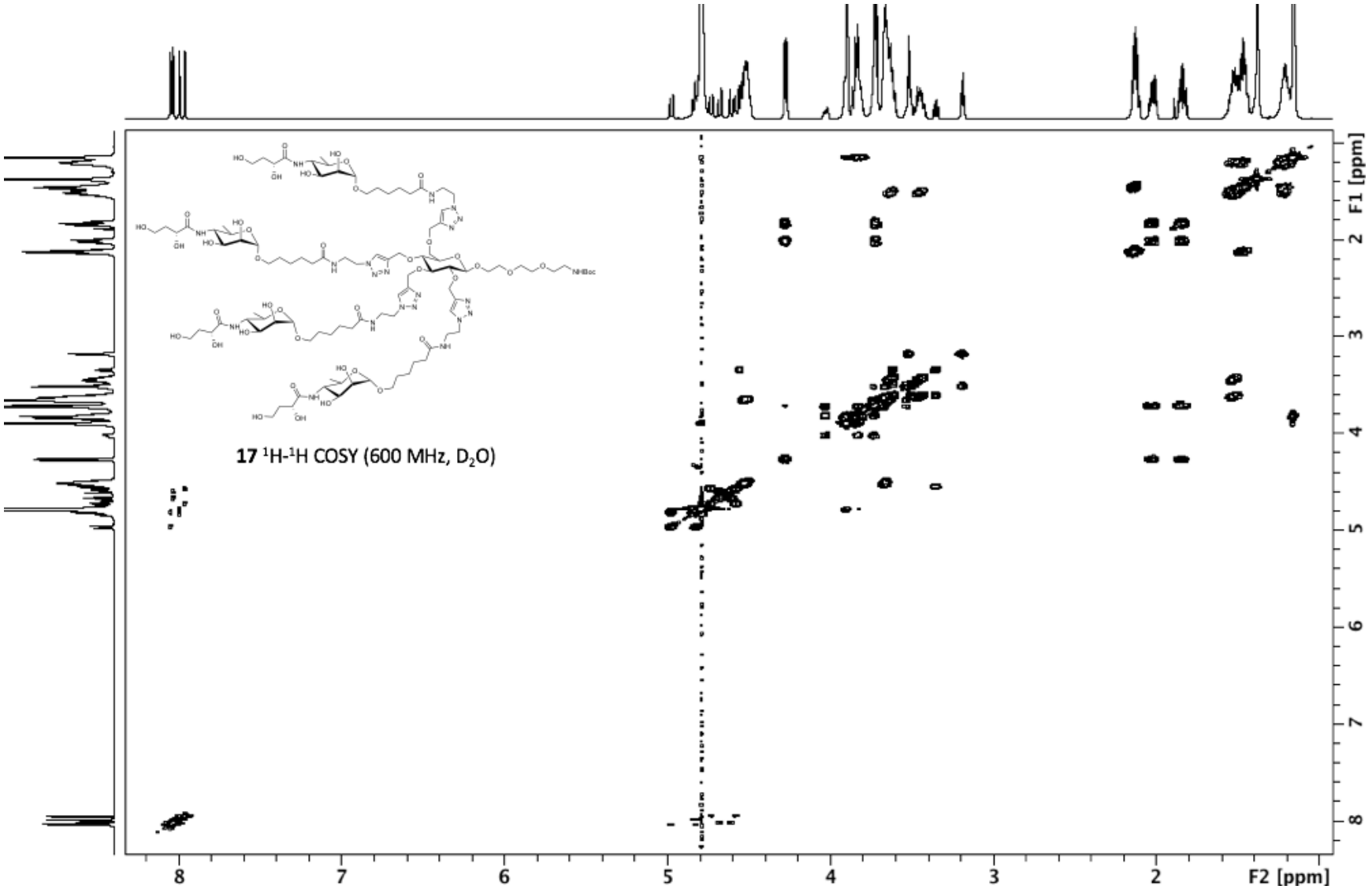


16 ^{1}H-^{13}C HMBC (600 MHz, $CDCl_3$)

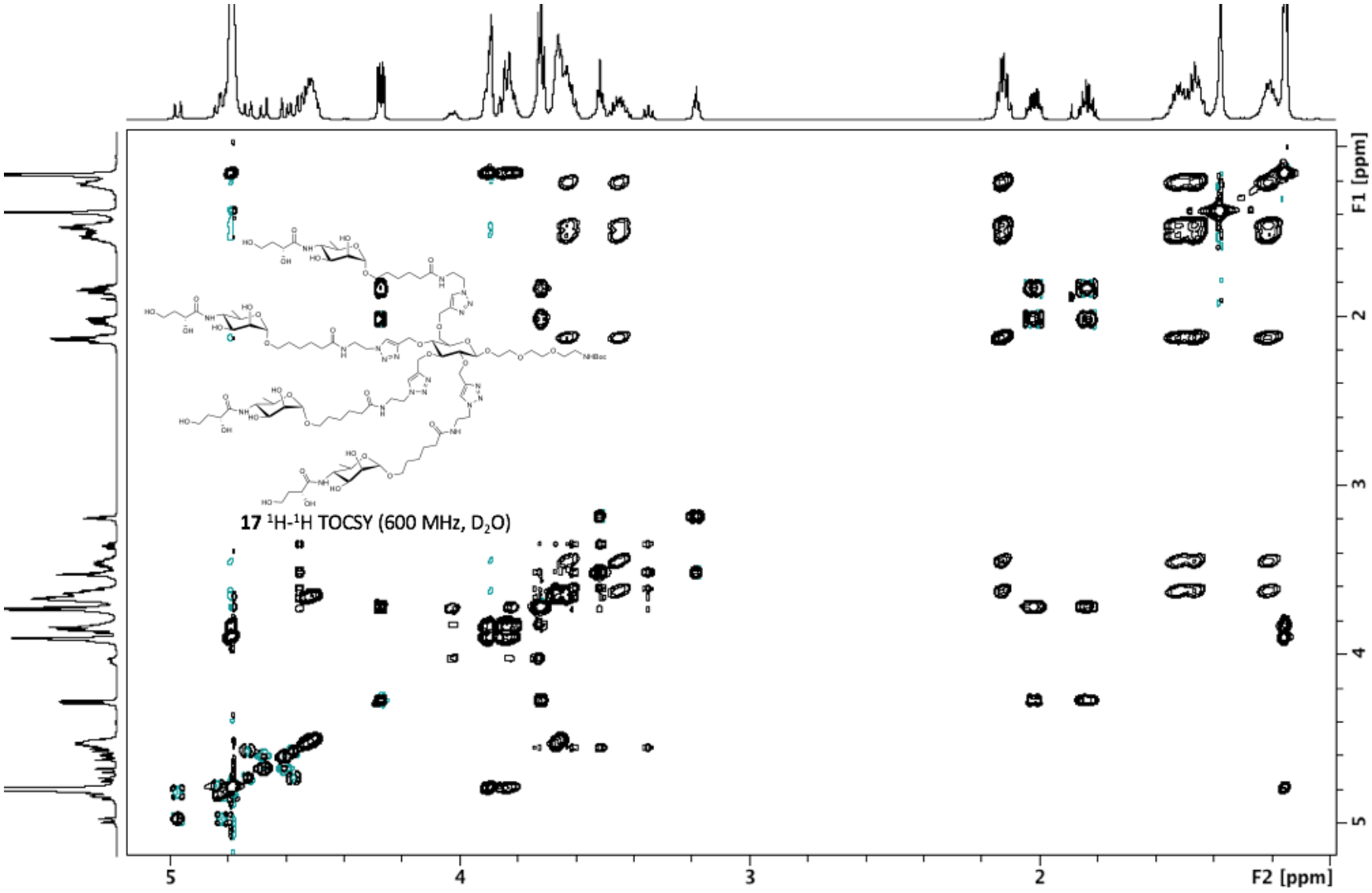
Boc-protected monosaccharide **17**

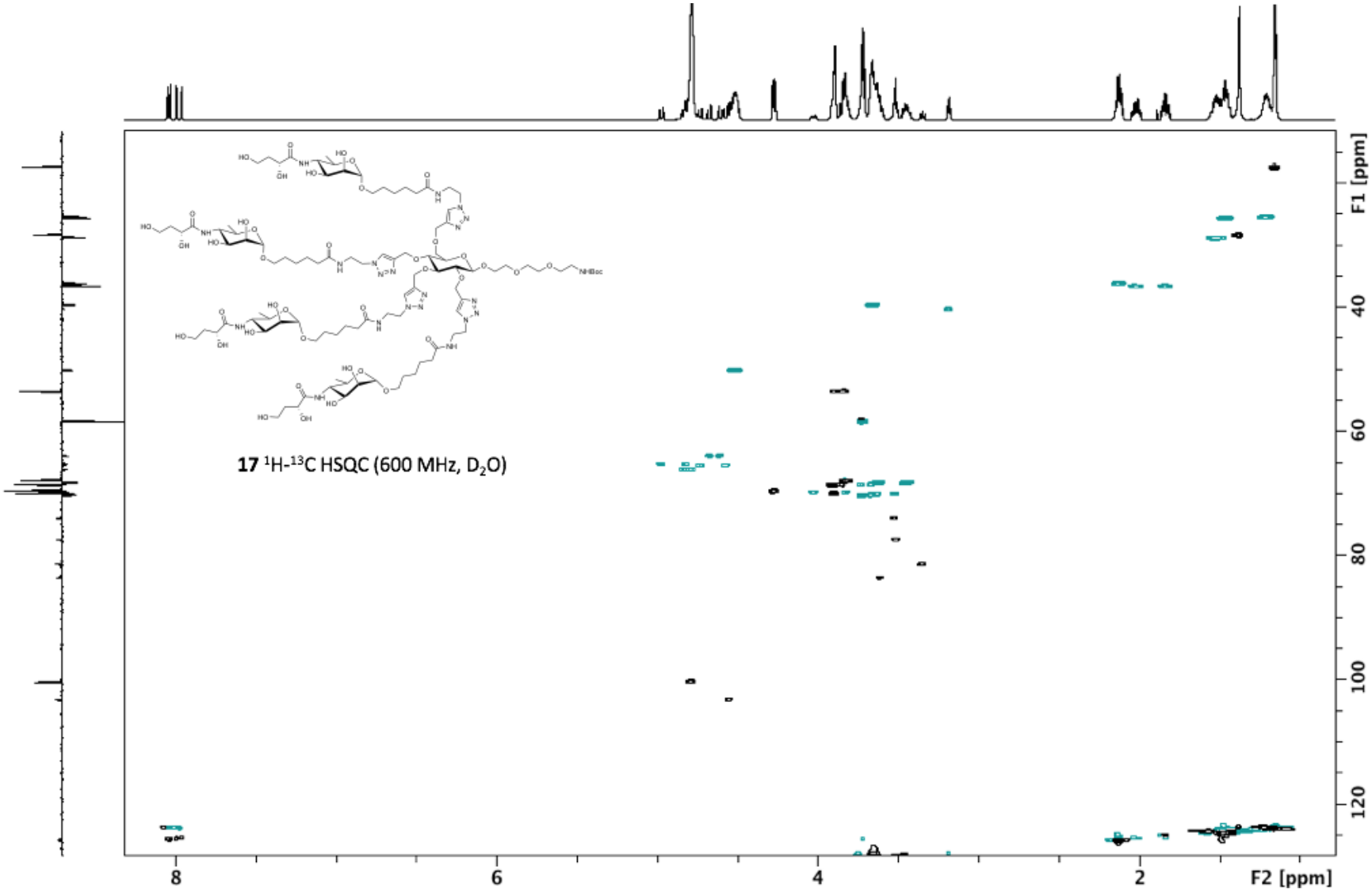


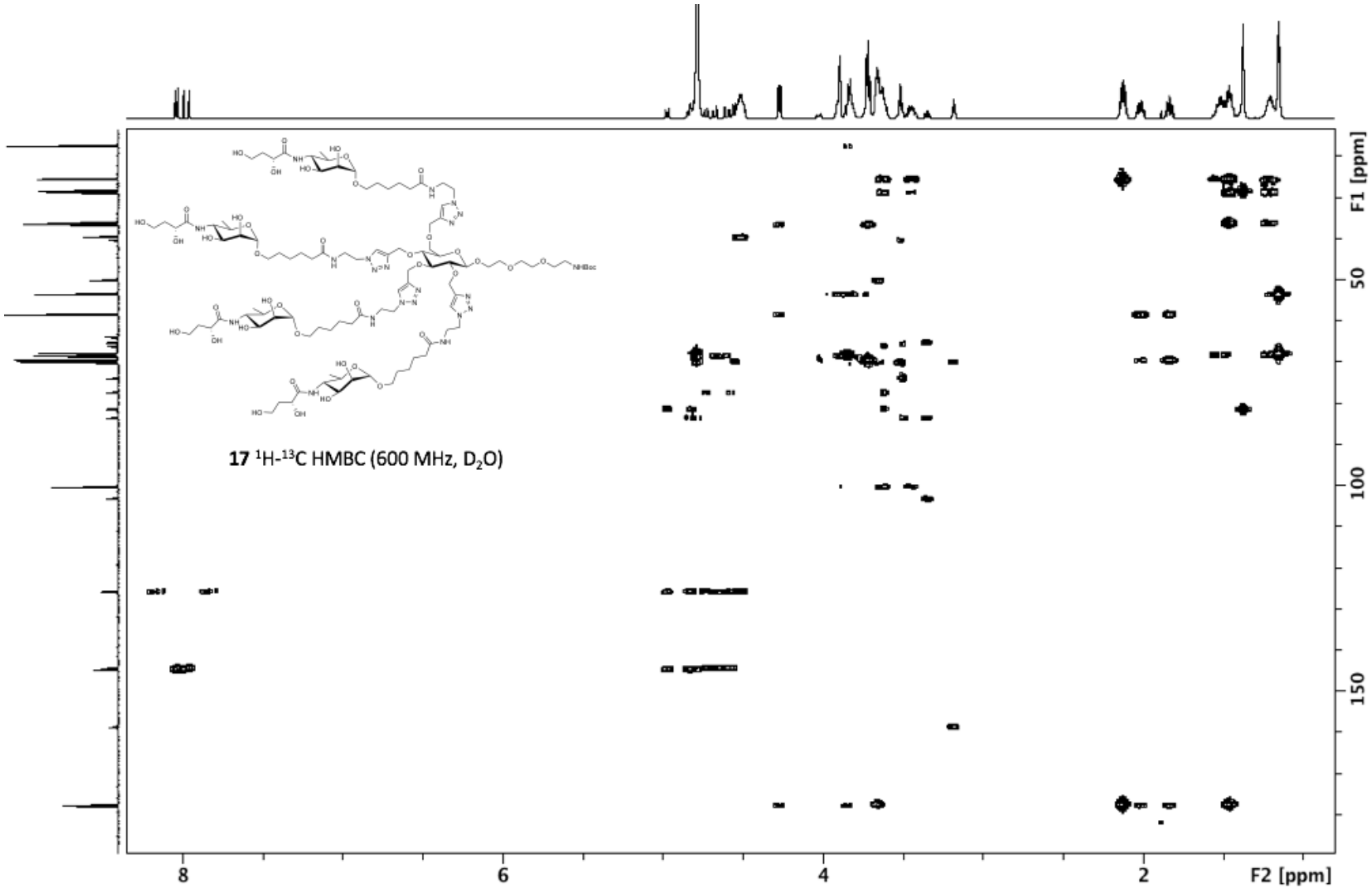

177.93
177.61
177.55
158.72
144.74
144.46
125.96
125.91
125.79
125.73
103.26
100.40
83.60
81.48
81.40
77.42
74.02
70.42
70.31
70.11
70.02
69.79
69.59
68.64
68.55
68.26
67.96
66.15
65.51
65.25
63.95
58.45
53.55
50.20
50.14
40.29
39.62
36.62
36.16
28.81
28.36
25.63
25.42
17.49
[rel]
0
5
10
15
20
150
100
50
[ppm]
17 13C NMR (150 MHz, D2O)
80
75
70
65
60
55



17 ^{1}H-^{1}H COSY (600 MHz, D_2O)

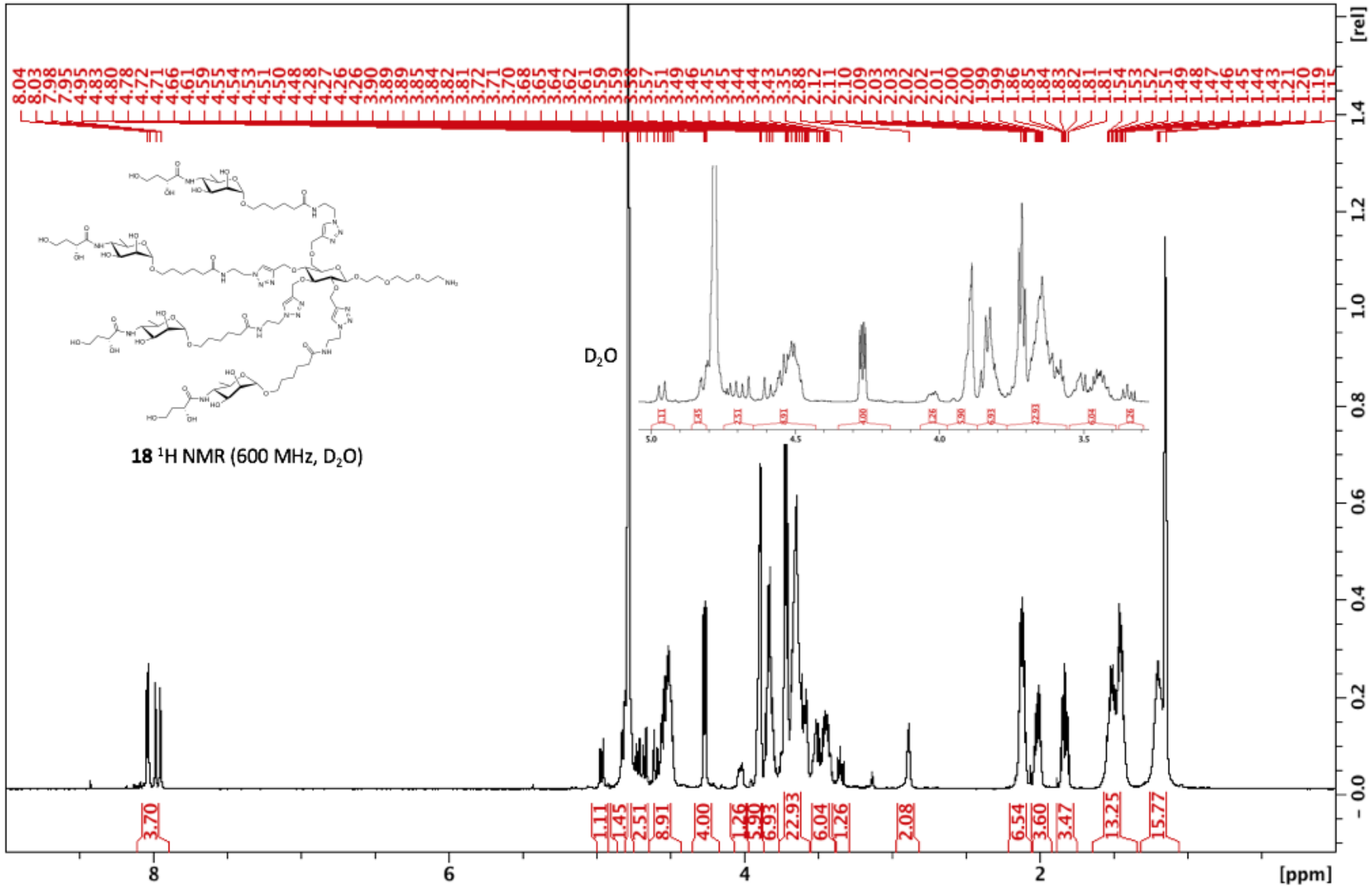

17 ^{1}H-^{1}H TOCSY (600 MHz, D_2O)
F1 [ppm]
F2 [ppm]
5
4
3
2
2
3
4
5

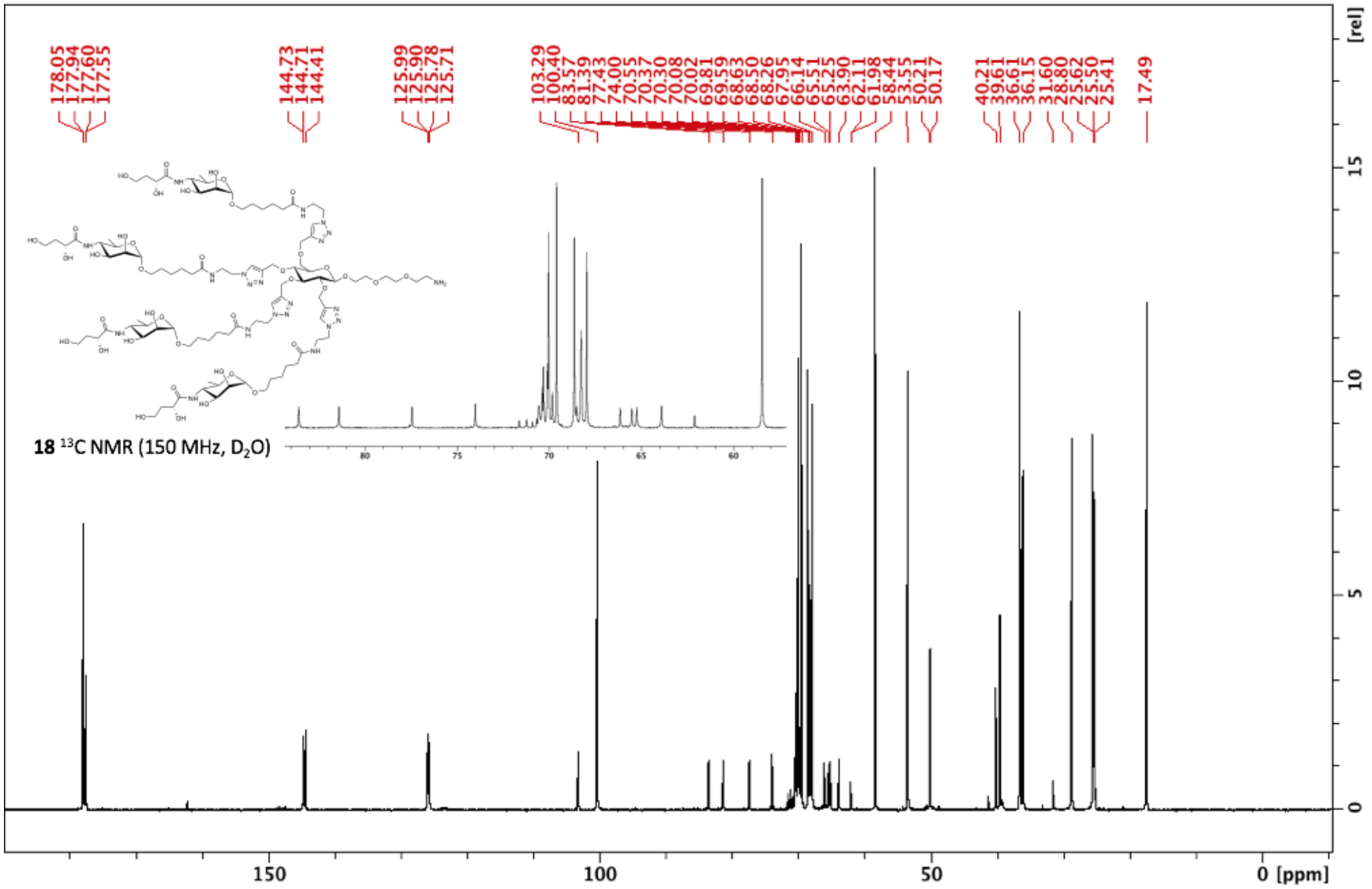

17 ^{1}H-^{13}C HSQC (600 MHz, D_2O)
F1 [ppm]
F2 [ppm]
8
6
4
2
40
60
80
100
120

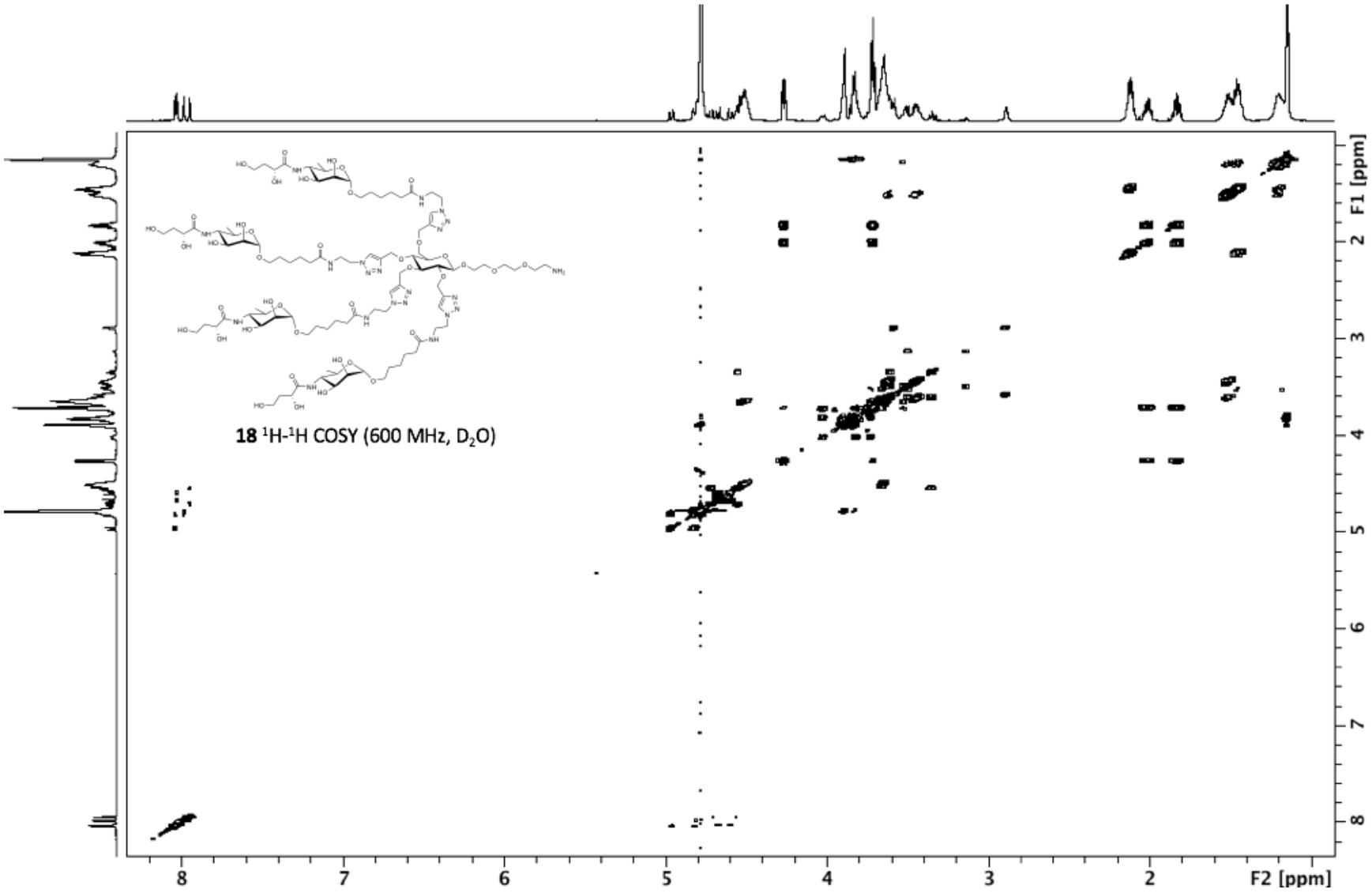


17 ^{1}H-^{13}C HMBC (600 MHz, D_2O)

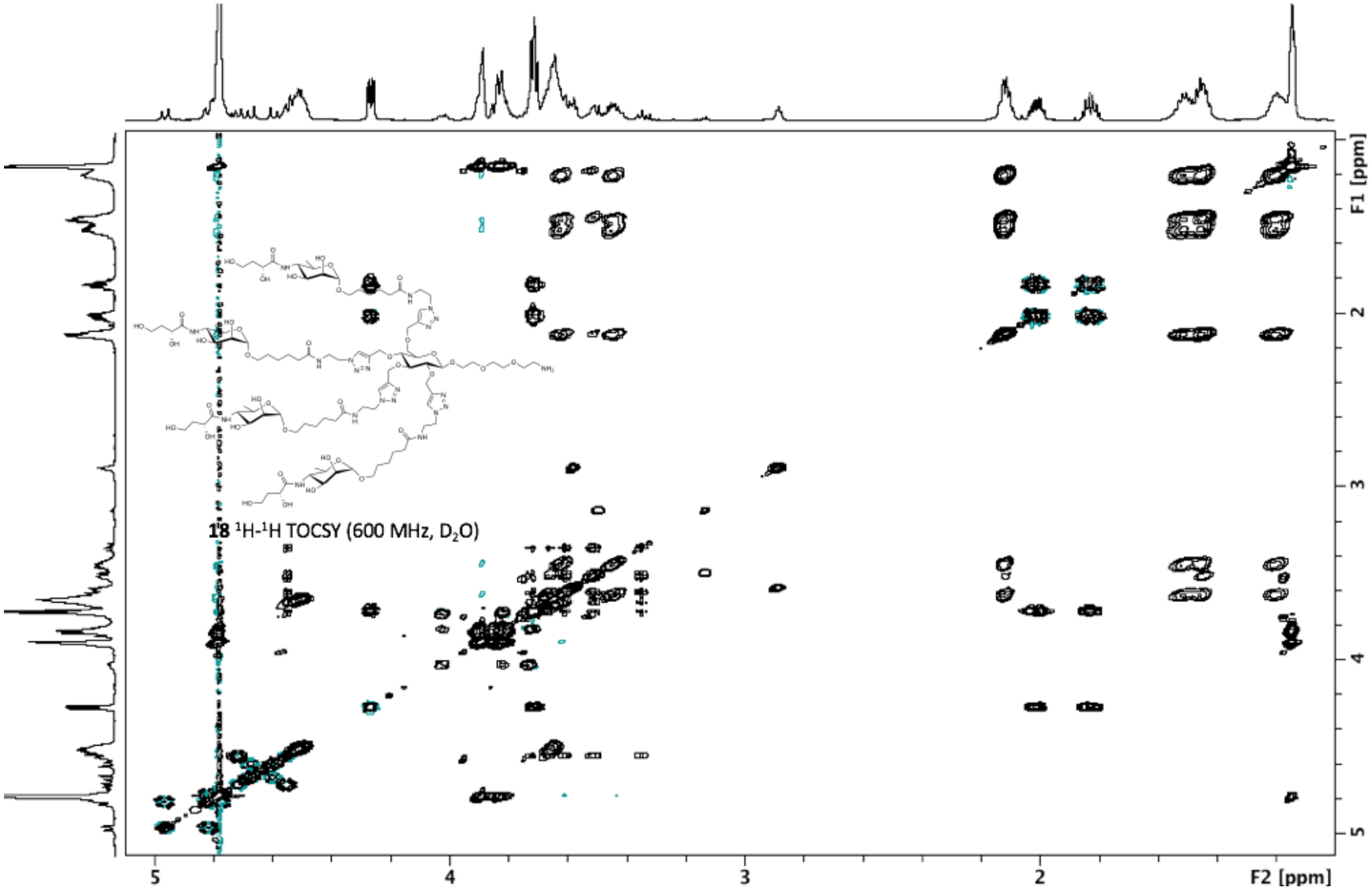
Amine monosaccharide cluster**18**

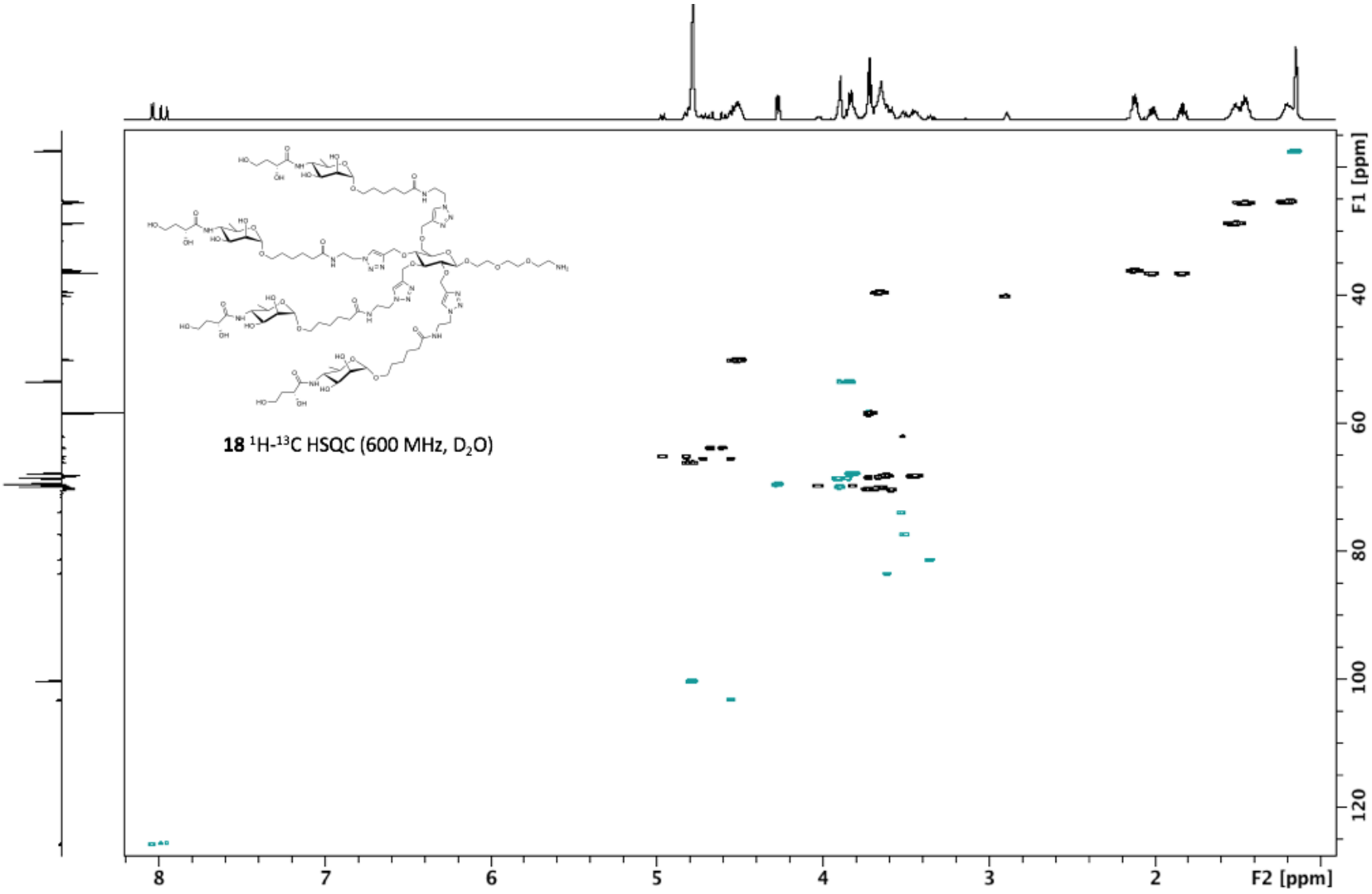


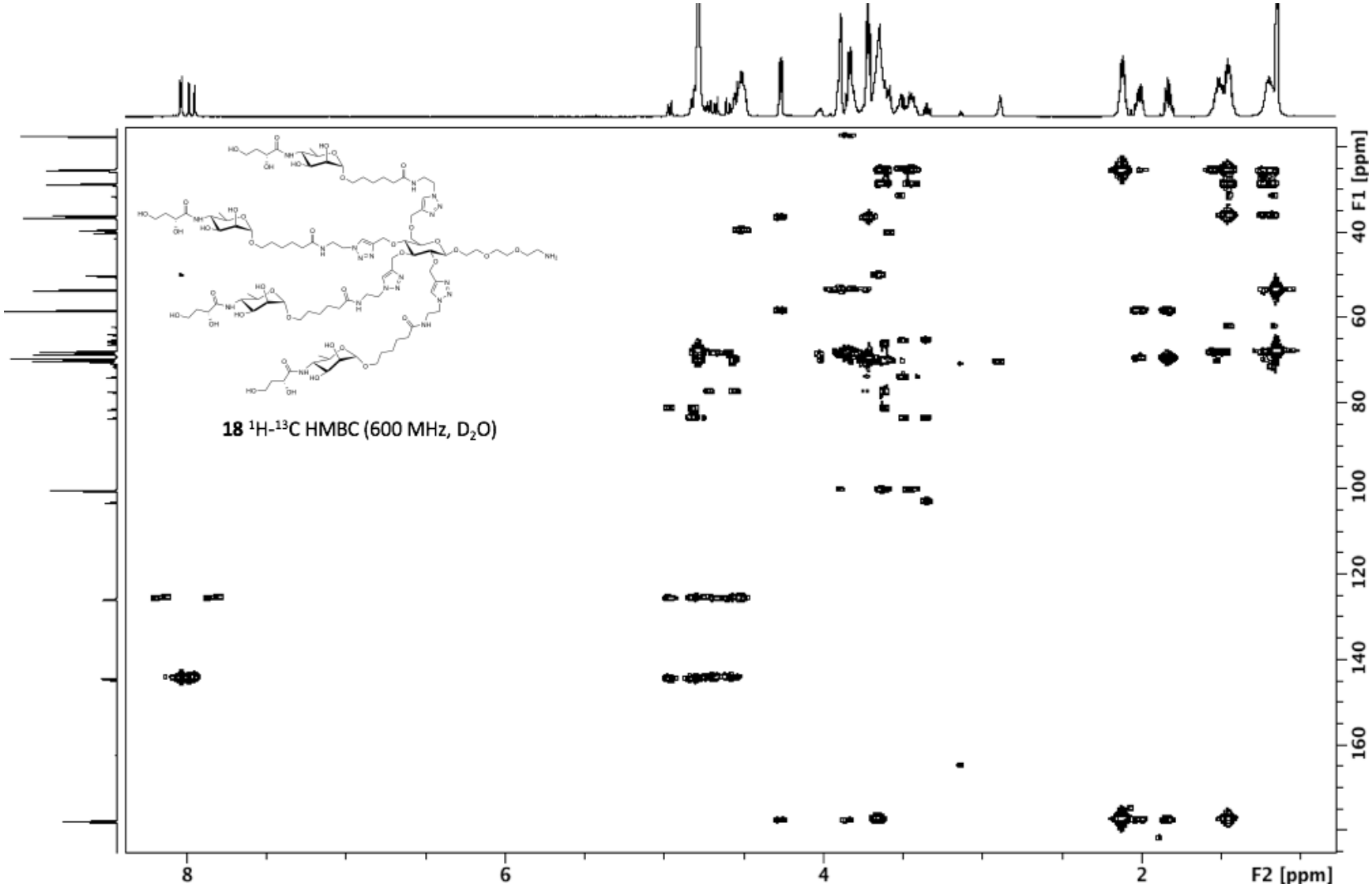

178.05
177.94
177.60
177.55
144.73
144.71
144.41
125.99
125.90
125.78
125.71
103.29
100.40
83.57
81.39
77.43
74.00
70.55
70.37
70.30
70.08
70.02
69.81
69.59
68.63
68.50
68.26
67.95
66.14
65.51
65.25
63.90
62.11
61.98
58.44
53.55
50.21
50.17
40.21
39.61
36.61
36.15
31.60
28.80
25.62
25.50
25.41
17.49
[rel]
0
5
10
15
150
100
50
0 [ppm]
18 13C NMR (150 MHz, D2O)



18 ^{1}H-^{1}H COSY (600 MHz, D_2O)

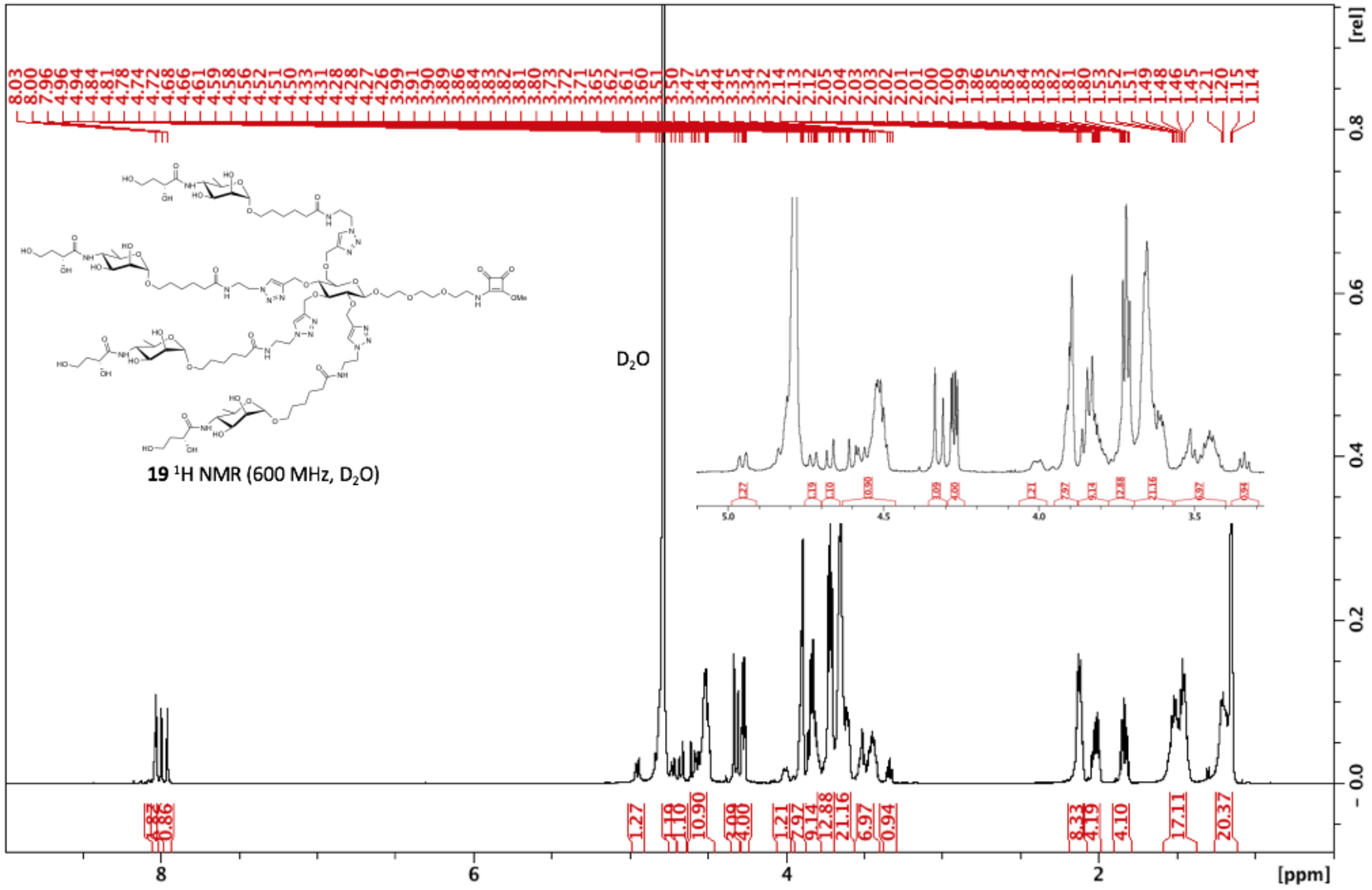

18 ^{1}H-^{1}H TOCSY (600 MHz, D_2O)
F1 [ppm]
F2 [ppm]
5
4
3
2
2
3
4
5

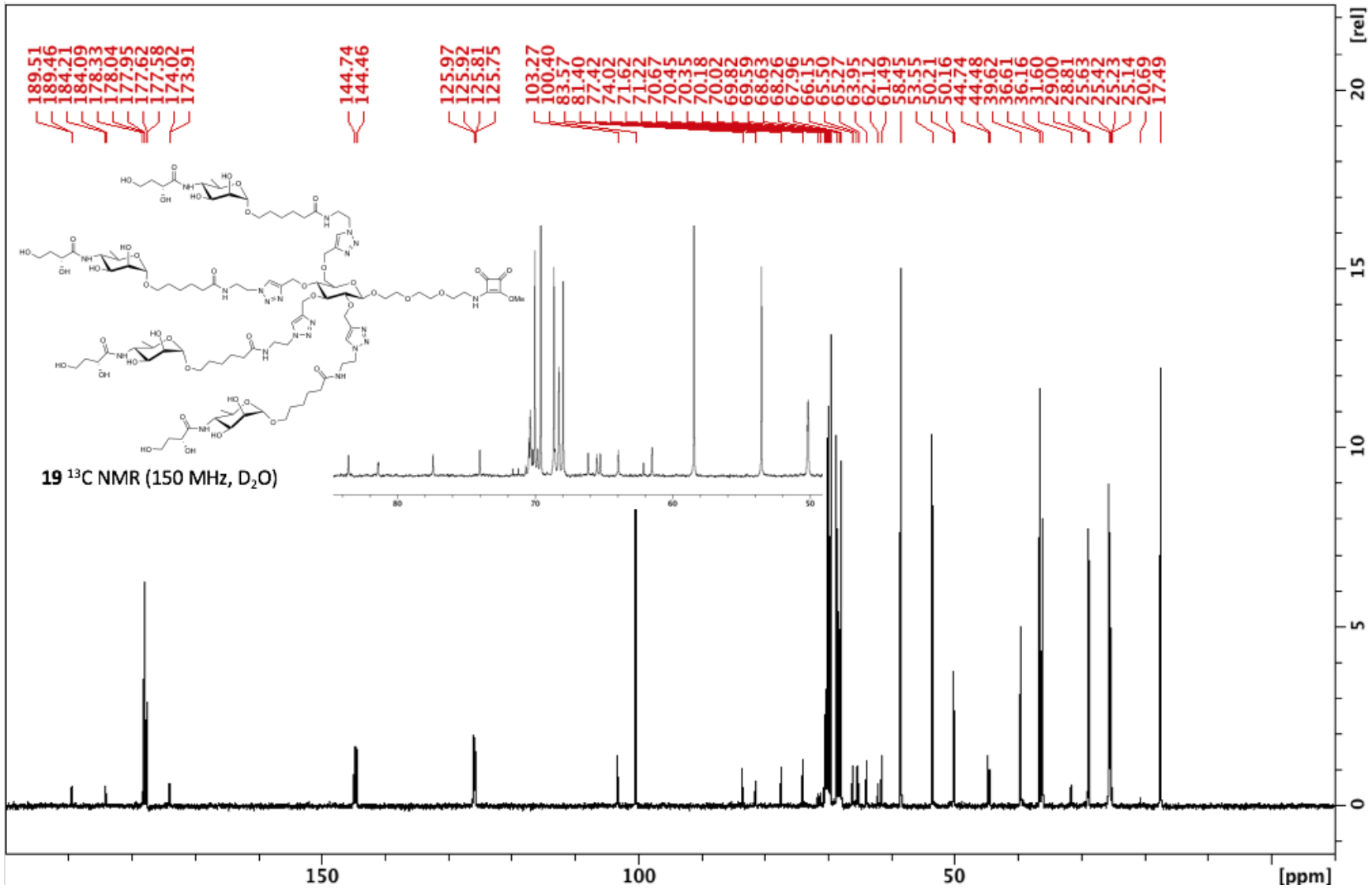

18 ^{1}H-^{13}C HSQC (600 MHz, D_2O)
F1 [ppm]
40
60
80
100
120
8
7
6
5
4
3
2
F2 [ppm]



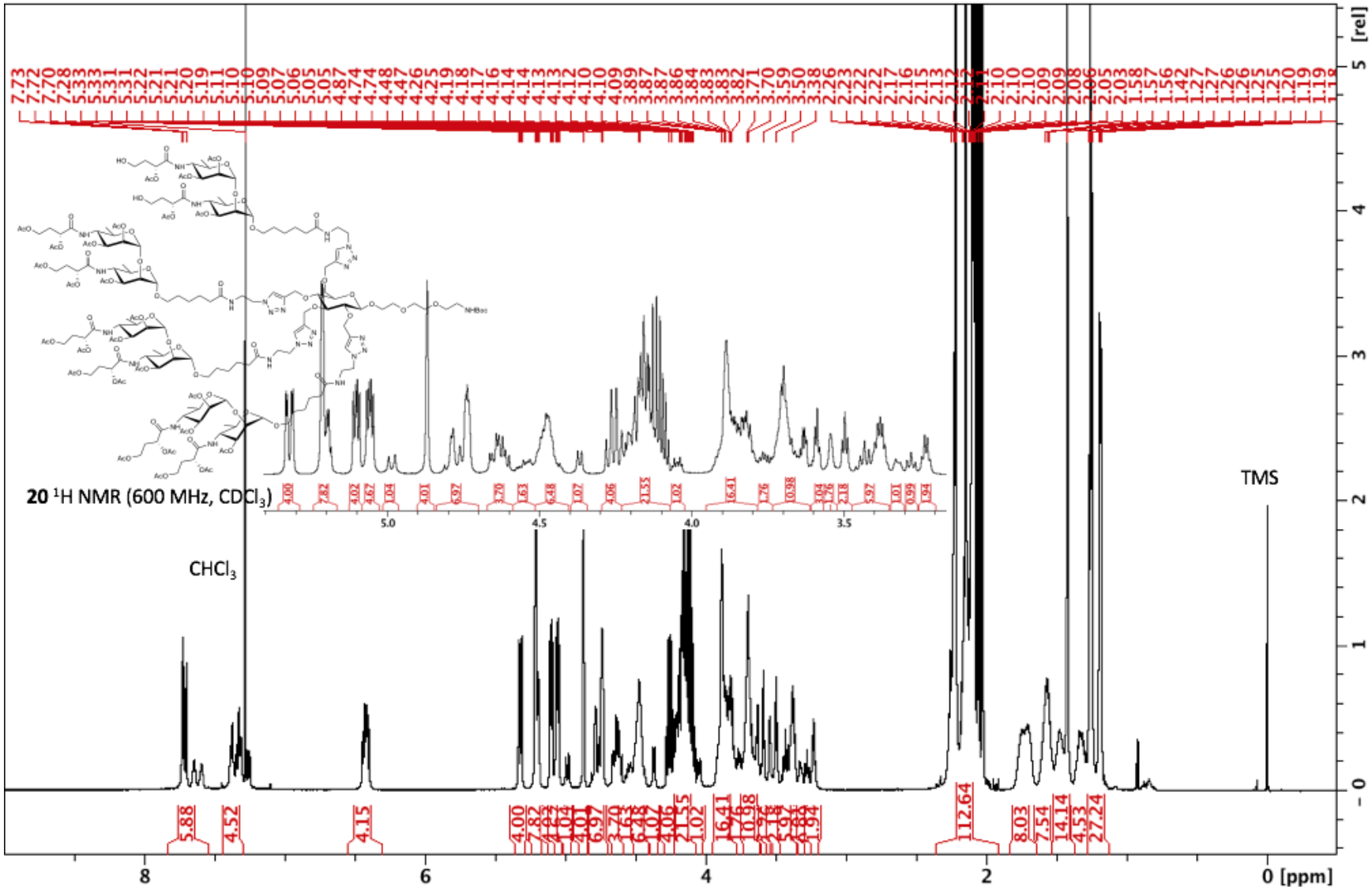
18 ^{1}H-^{13}C HMBC (600 MHz, D_2O)

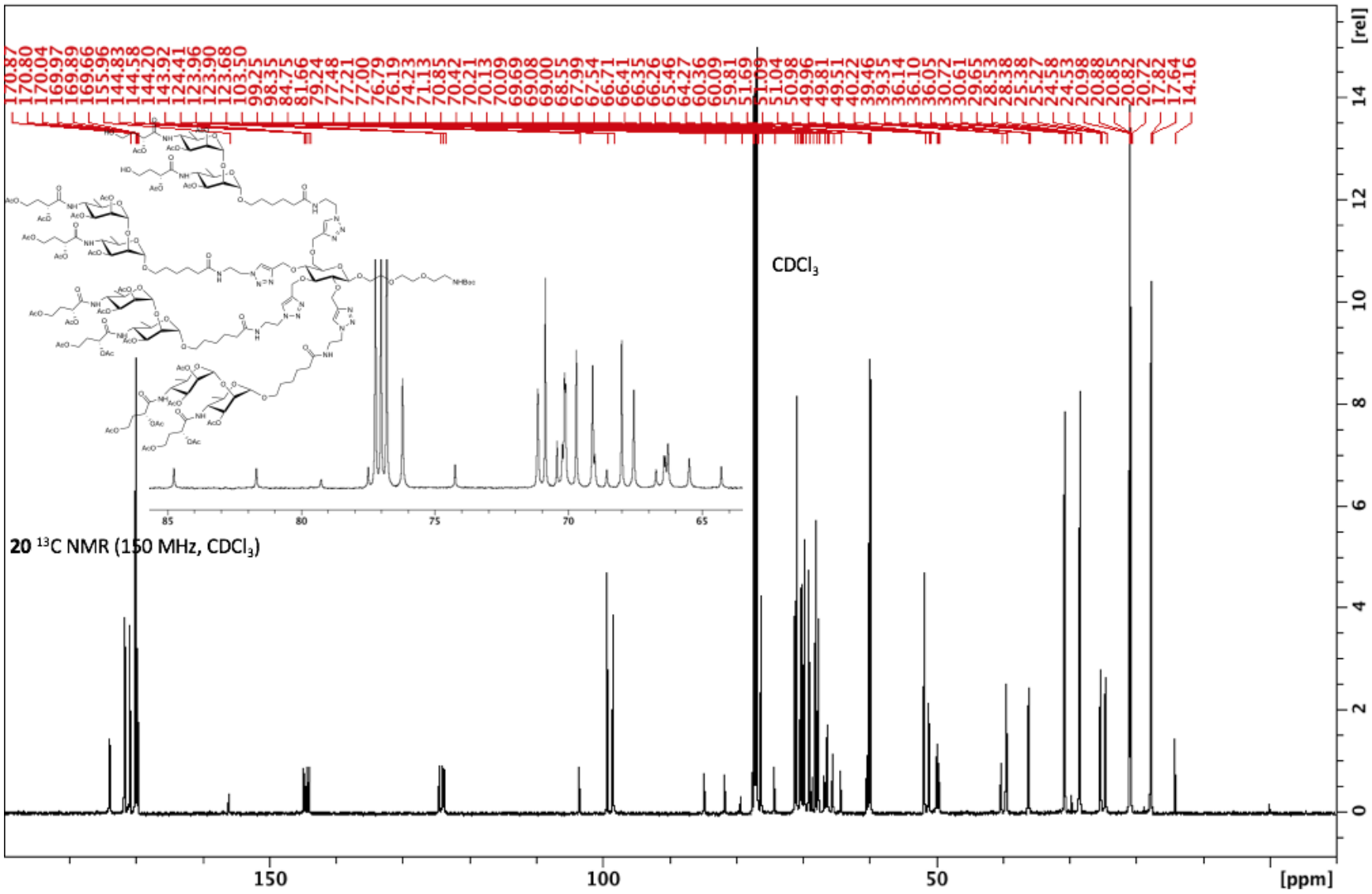
Squarate monosaccharide cluster **19**

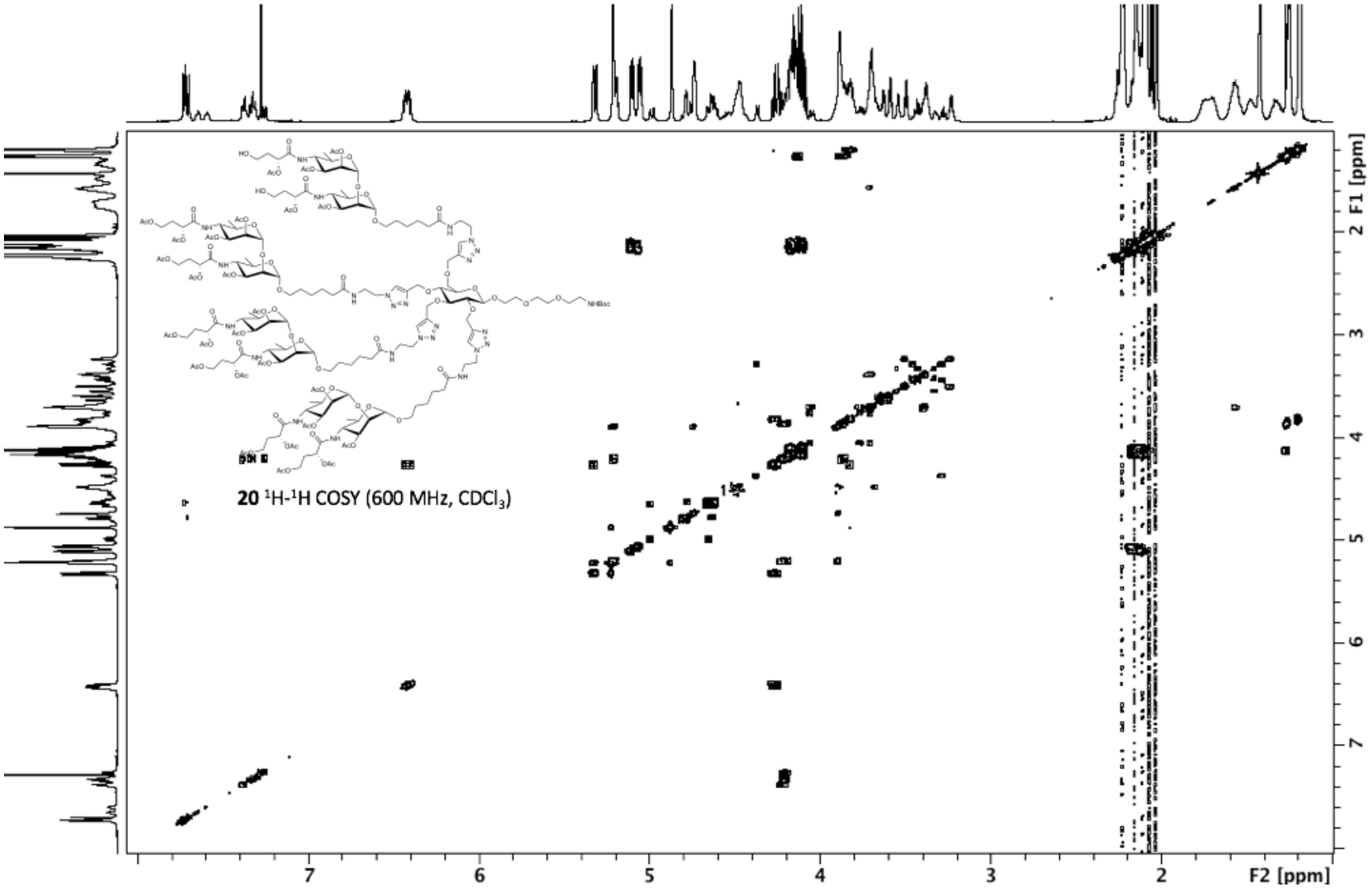


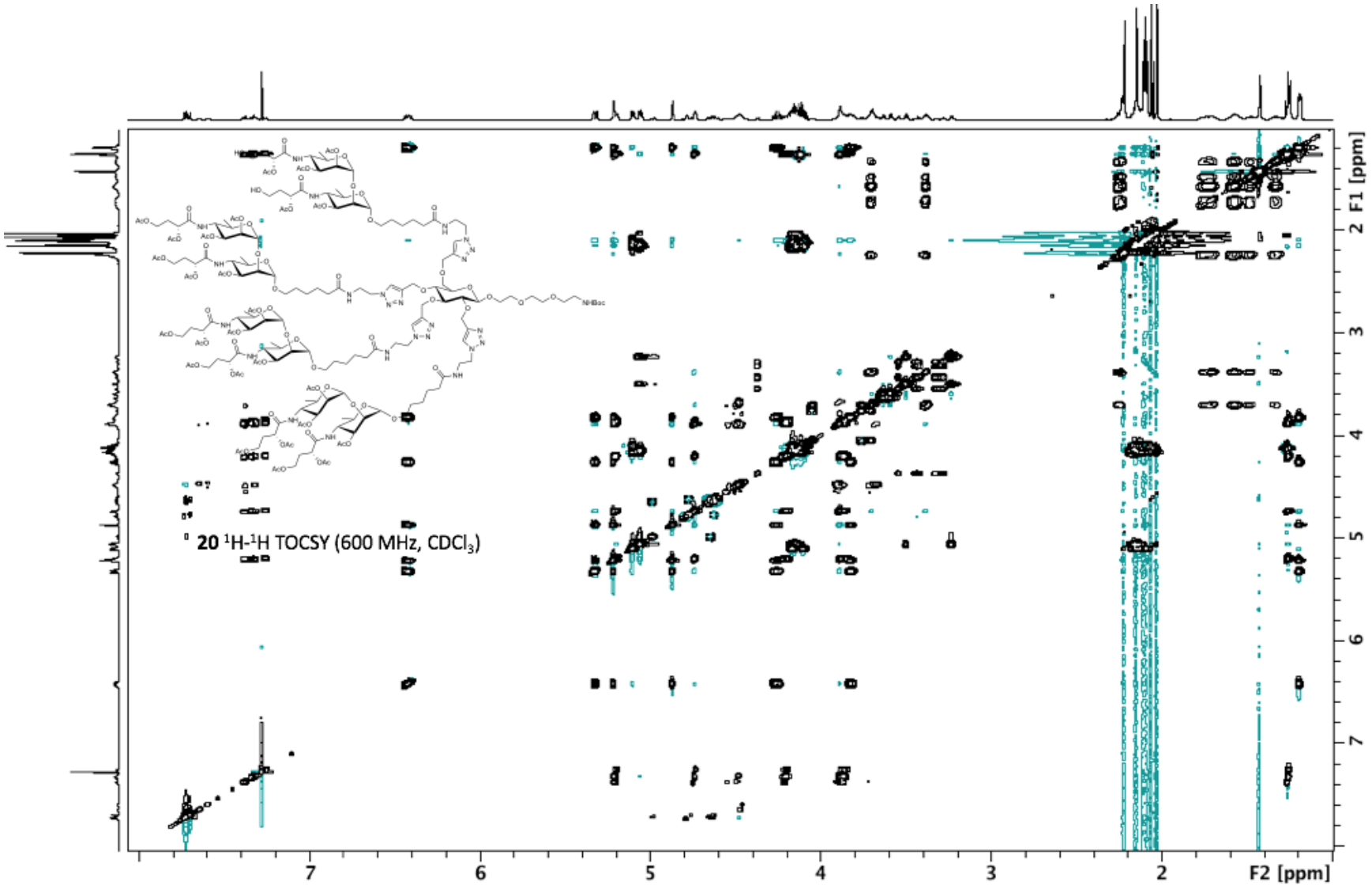

189.51
189.46
184.21
184.09
178.33
178.04
177.95
177.62
177.58
174.02
173.91
144.74
144.46
125.97
125.92
125.81
125.75
103.27
100.40
83.57
81.40
77.42
74.02
71.62
71.22
70.67
70.45
70.35
70.18
70.02
69.82
69.59
68.63
68.26
67.96
66.15
65.50
65.27
63.95
62.12
61.49
58.45
53.55
50.21
50.16
44.74
44.48
39.62
36.61
36.16
31.60
29.00
28.81
25.63
25.42
25.23
25.14
20.69
17.49
[rel]
20
15
10
5
0
150
100
50
[ppm]
19 13C NMR (150 MHz, D2O)

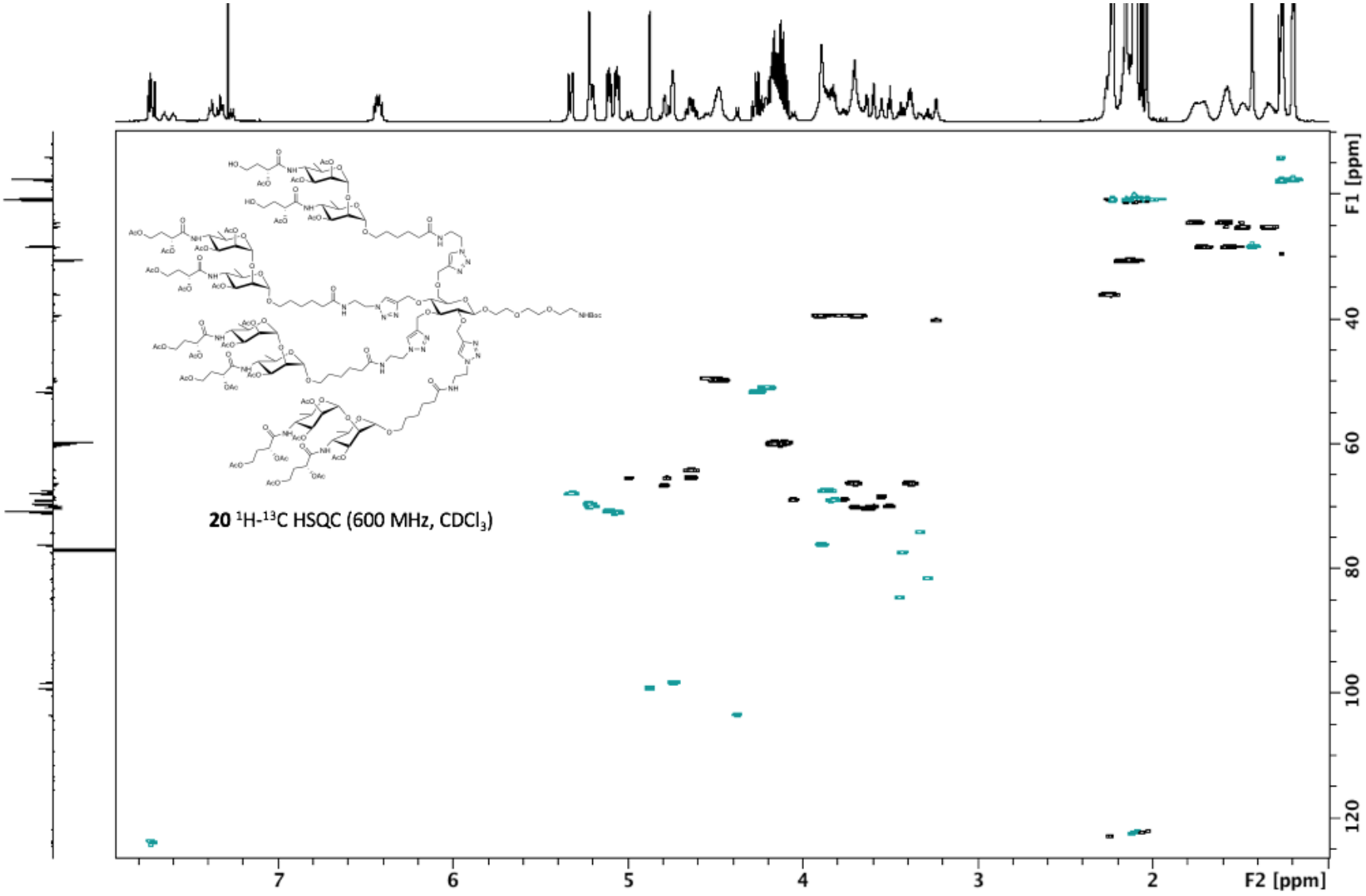
Acetylated, Boc-protected disaccharide cluster **20**

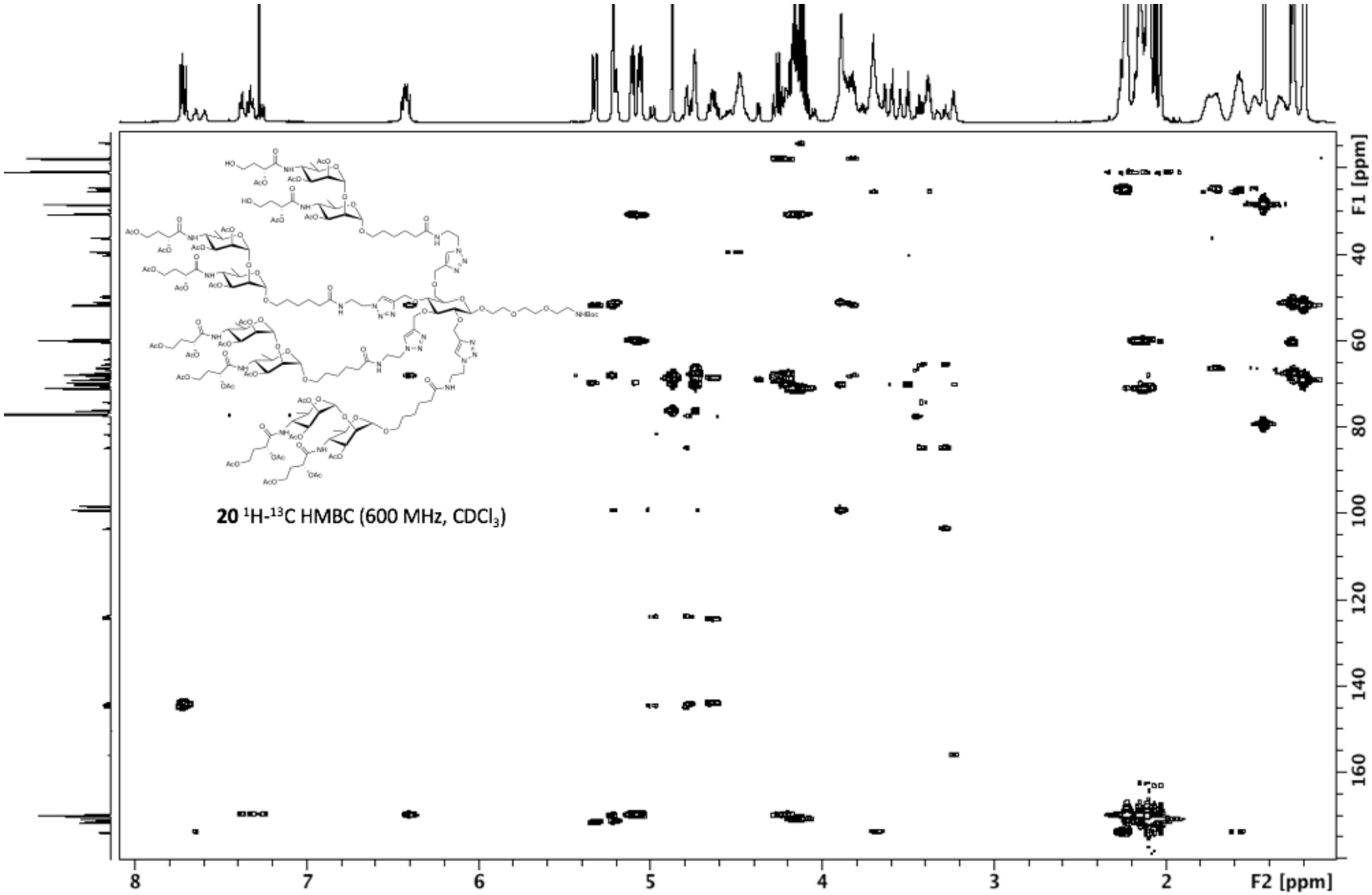



170.87
170.80
170.04
169.97
169.89
169.66
155.96
144.83
144.58
144.20
143.92
124.41
123.96
123.90
123.68
103.50
99.25
98.35
84.75
81.66
79.24
77.48
77.21
77.00
76.79
76.19
74.23
71.13
70.85
70.42
70.21
70.13
70.09
69.69
69.08
69.00
68.55
67.99
67.54
66.71
66.41
66.35
66.26
65.46
64.27
60.36
60.09
59.81
51.69
51.09
51.04
50.98
49.96
49.81
49.51
40.22
39.46
39.35
36.14
36.10
36.05
30.72
30.61
29.65
28.53
28.38
25.38
25.27
24.58
24.53
20.98
20.88
20.85
20.82
20.72
17.82
17.64
14.16
CDCl3
85
80
75
70
65
20 13C NMR (150 MHz, CDCl3)
150
100
50
[ppm]
0
2
4
6
8
10
12
14
[rel]

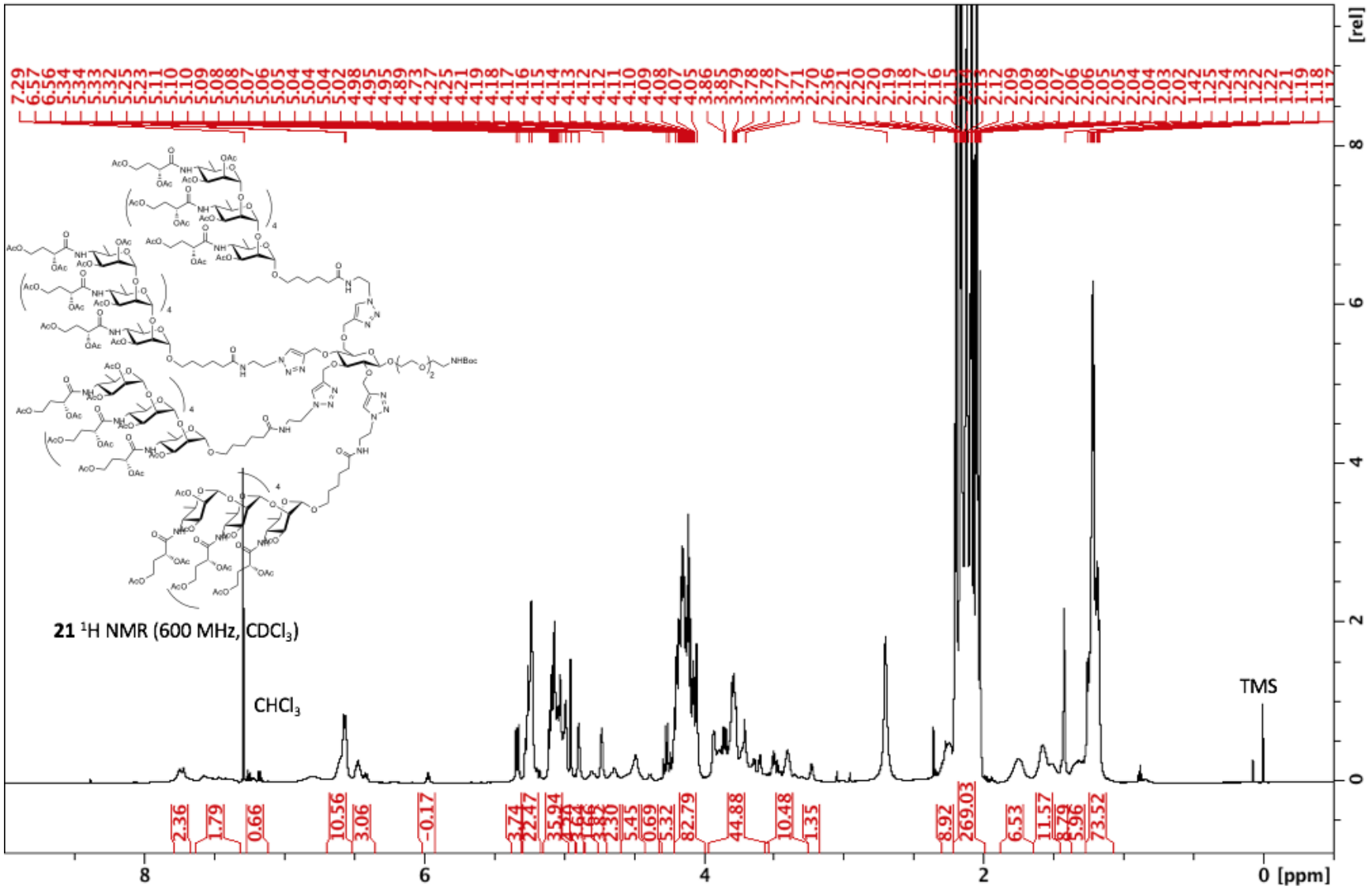

20 ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$)
F2 [ppm]
F1 [ppm]

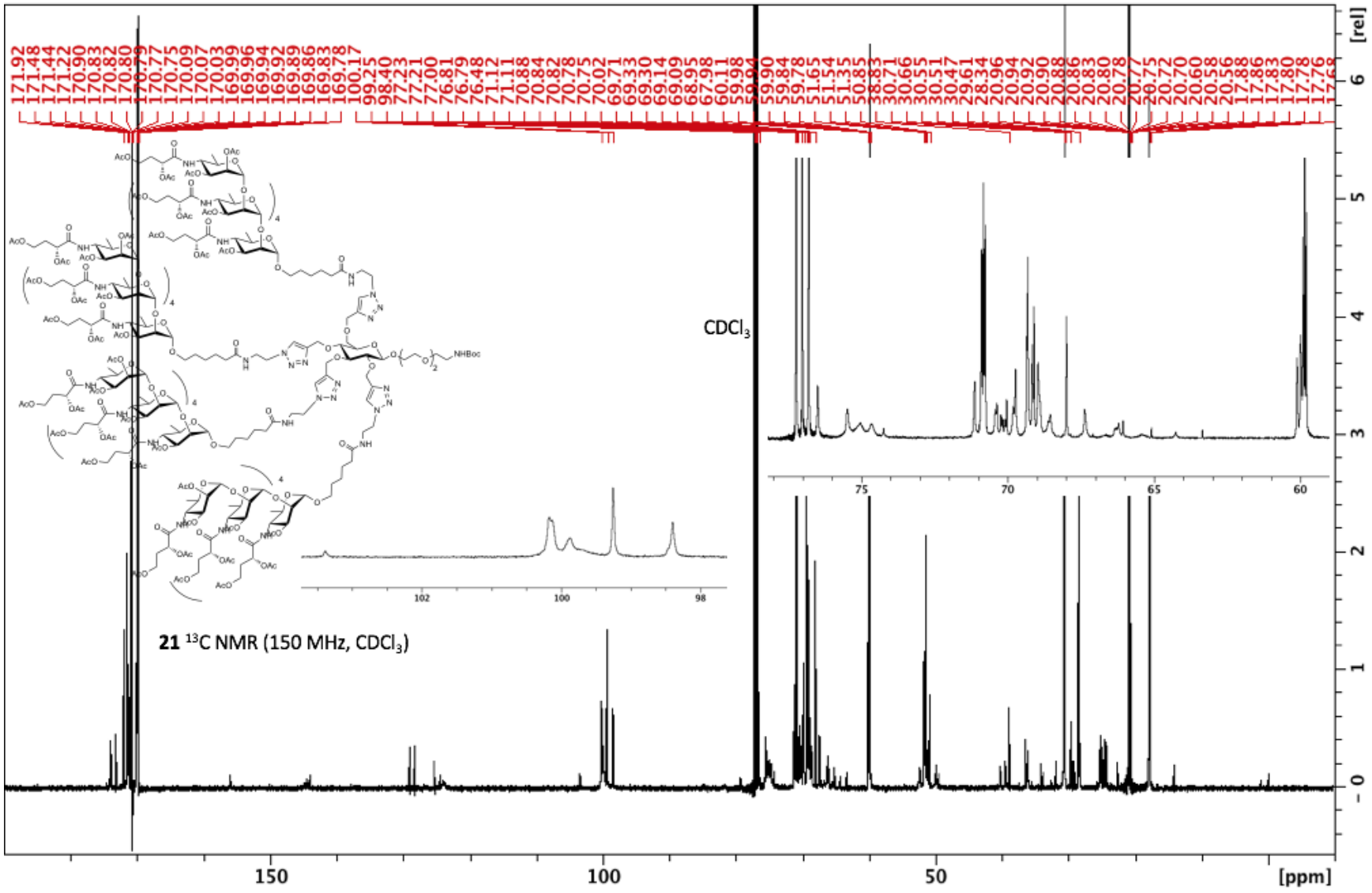

20 ^{1}H-^{1}H TOCSY (600 MHz, $CDCl_3$)
F1 [ppm]
F2 [ppm]
2
3
4
5
6
7

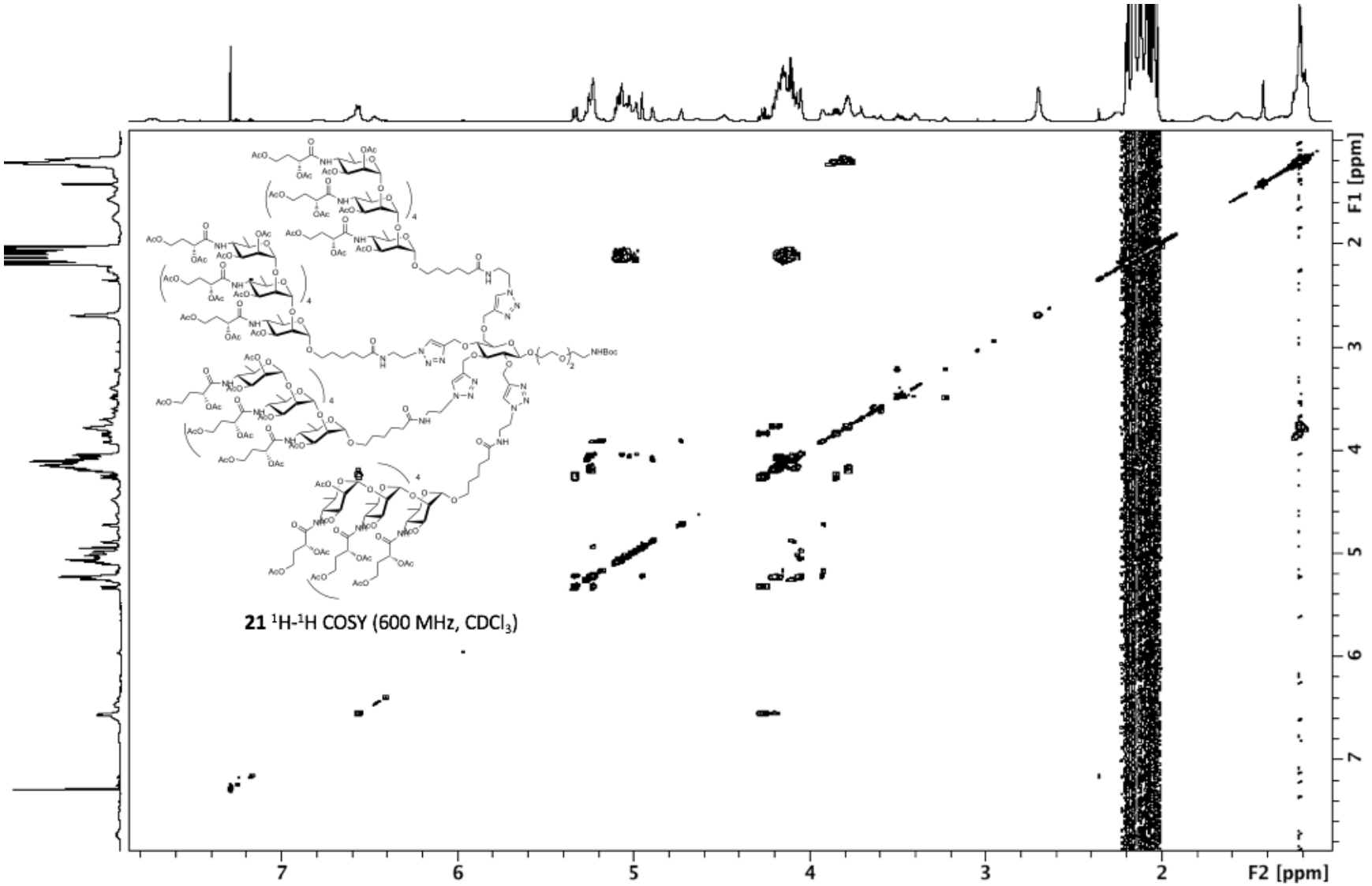

20 ^{1}H-^{13}C HSQC (600 MHz, $CDCl_3$)
F1 [ppm]
F2 [ppm]
7
6
5
4
3
2
40
60
80
100
120


20 ^{1}H-^{13}C HMBC (600 MHz, $CDCl_3$)
F1 [ppm]
F2 [ppm]
8
7
6
5
4
3
2
40
60
80
100
120
140
160

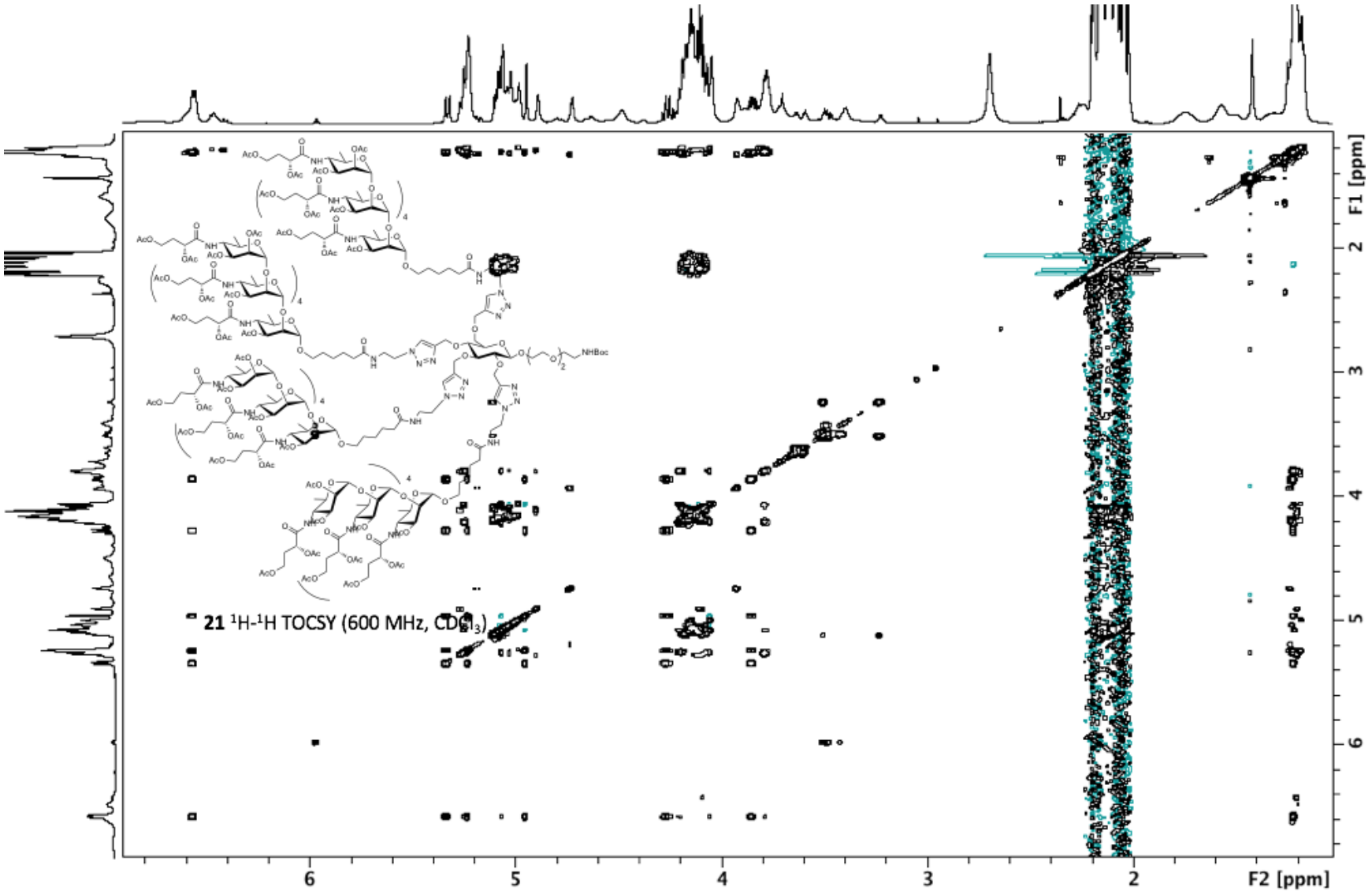
Acetylated, Boc-protected hexasaccharide cluster **21**

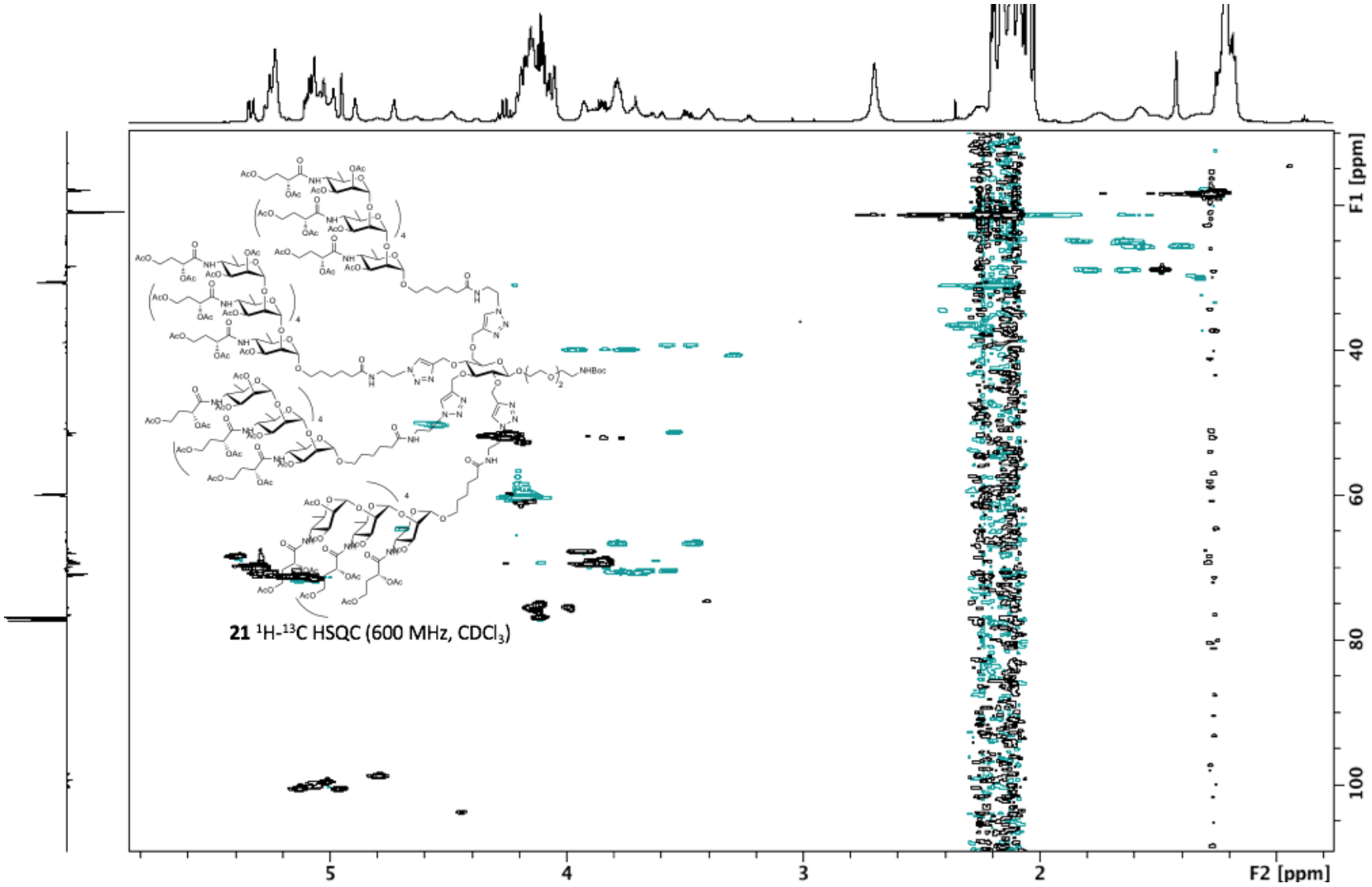


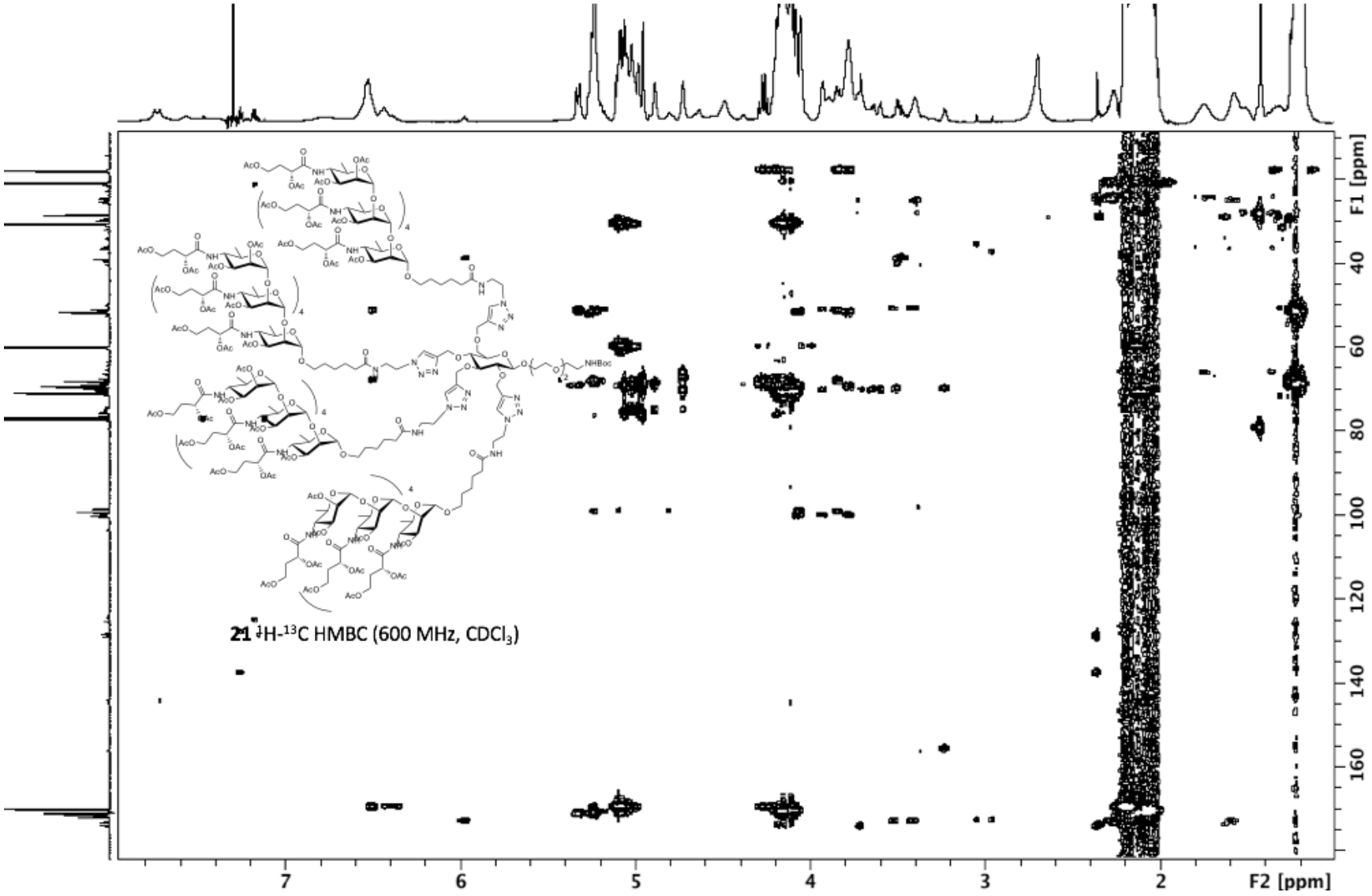

171.92
171.48
171.44
171.22
170.90
170.83
170.82
170.80
170.79
170.77
170.75
170.09
170.07
170.03
169.99
169.96
169.94
169.92
169.89
169.86
169.83
169.78
100.17
99.25
98.40
77.23
77.21
77.00
76.81
76.79
76.48
71.12
71.11
70.88
70.84
70.82
70.78
70.75
70.02
69.71
69.33
69.30
69.14
69.09
68.95
67.98
60.11
59.98
59.94
59.90
59.84
59.78
51.65
51.54
51.35
50.85
38.83
30.71
30.66
30.55
30.51
30.47
29.61
28.34
20.96
20.94
20.92
20.90
20.88
20.83
20.80
20.78
20.77
20.75
20.72
20.70
20.60
20.58
20.56
17.88
17.86
17.83
17.80
17.78
17.76
17.68
CDCl3
21 13C NMR (150 MHz, CDCl3)
[rel]
[ppm]



21 ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$)

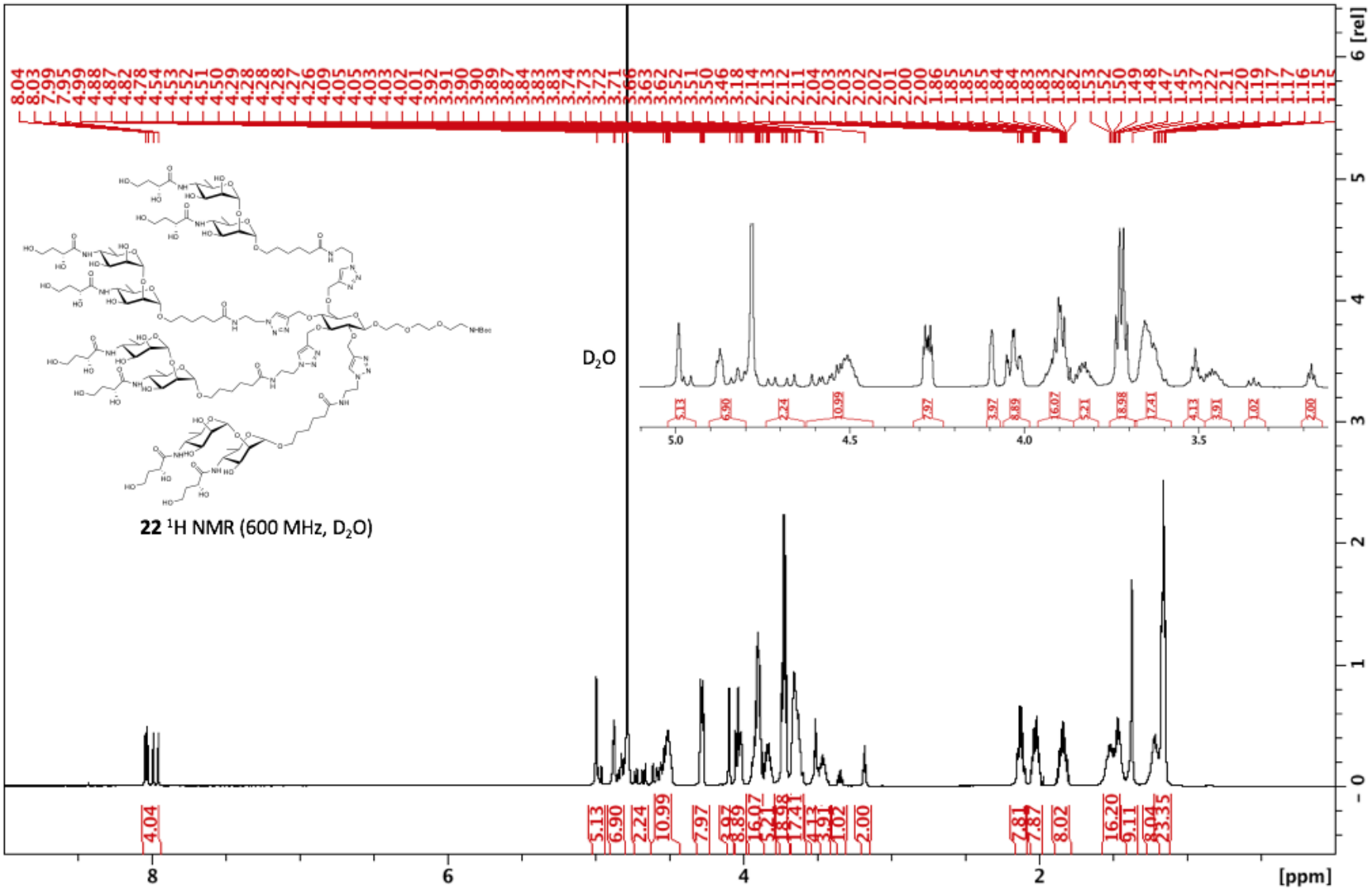

21 ^{1}H-^{1}H TOCSY (600 MHz, $CDCl_3$)
F1 [ppm]
F2 [ppm]
2
3
4
5
6

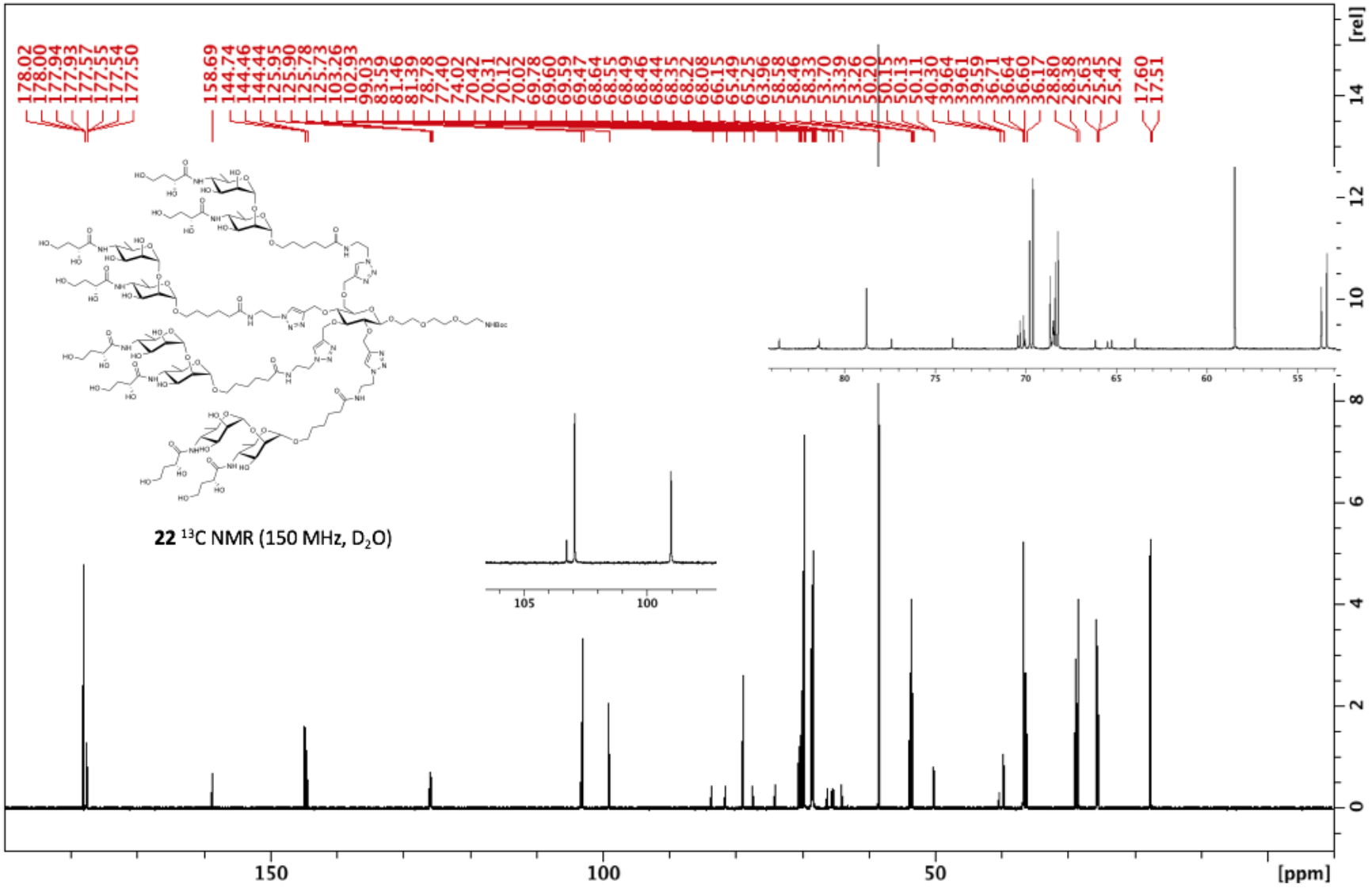

F1 [ppm]
40
60
80
100
5
4
3
2
F2 [ppm]
21 ^{1}H-^{13}C HSQC (600 MHz, $CDCl_3$)

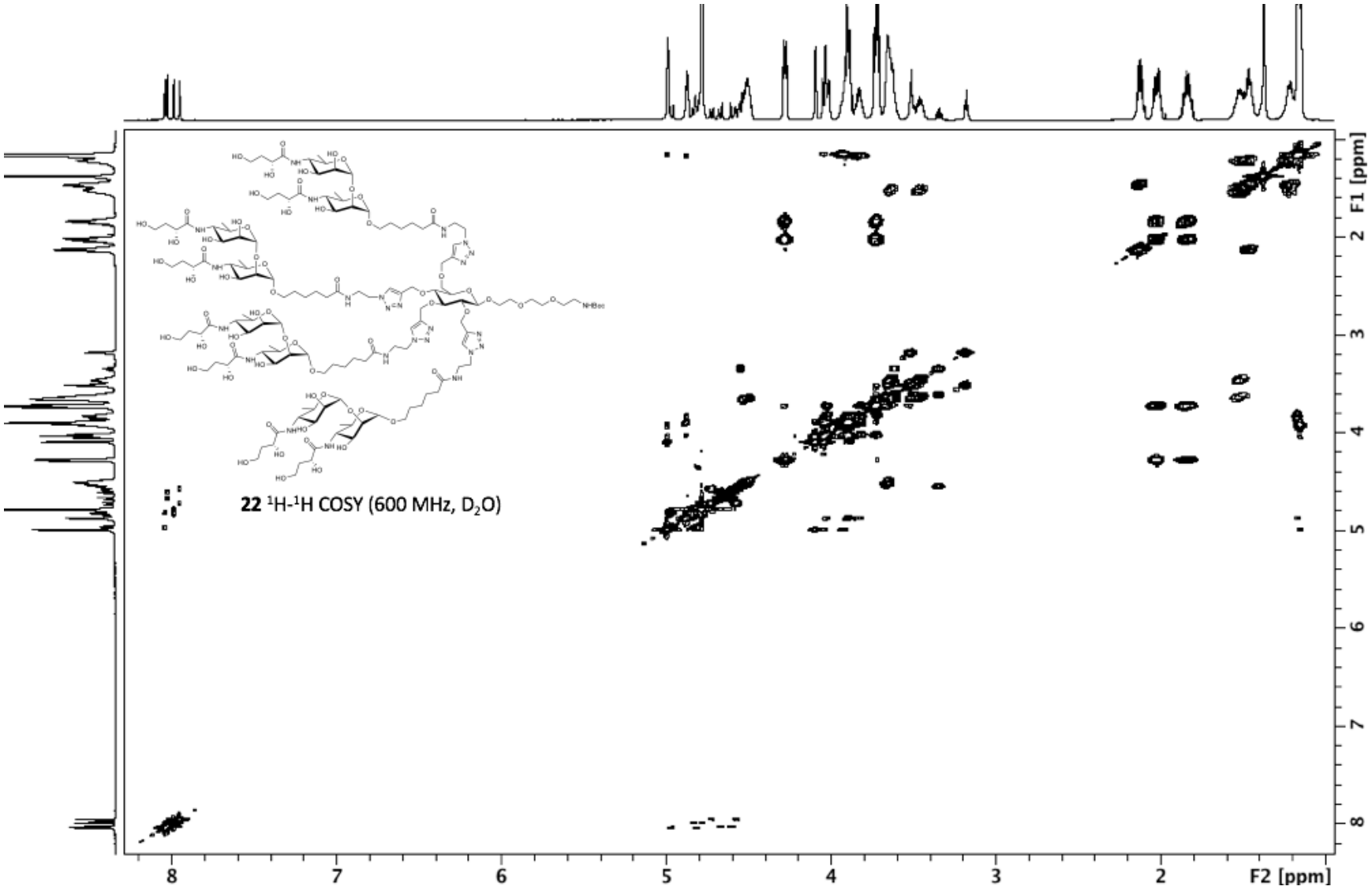


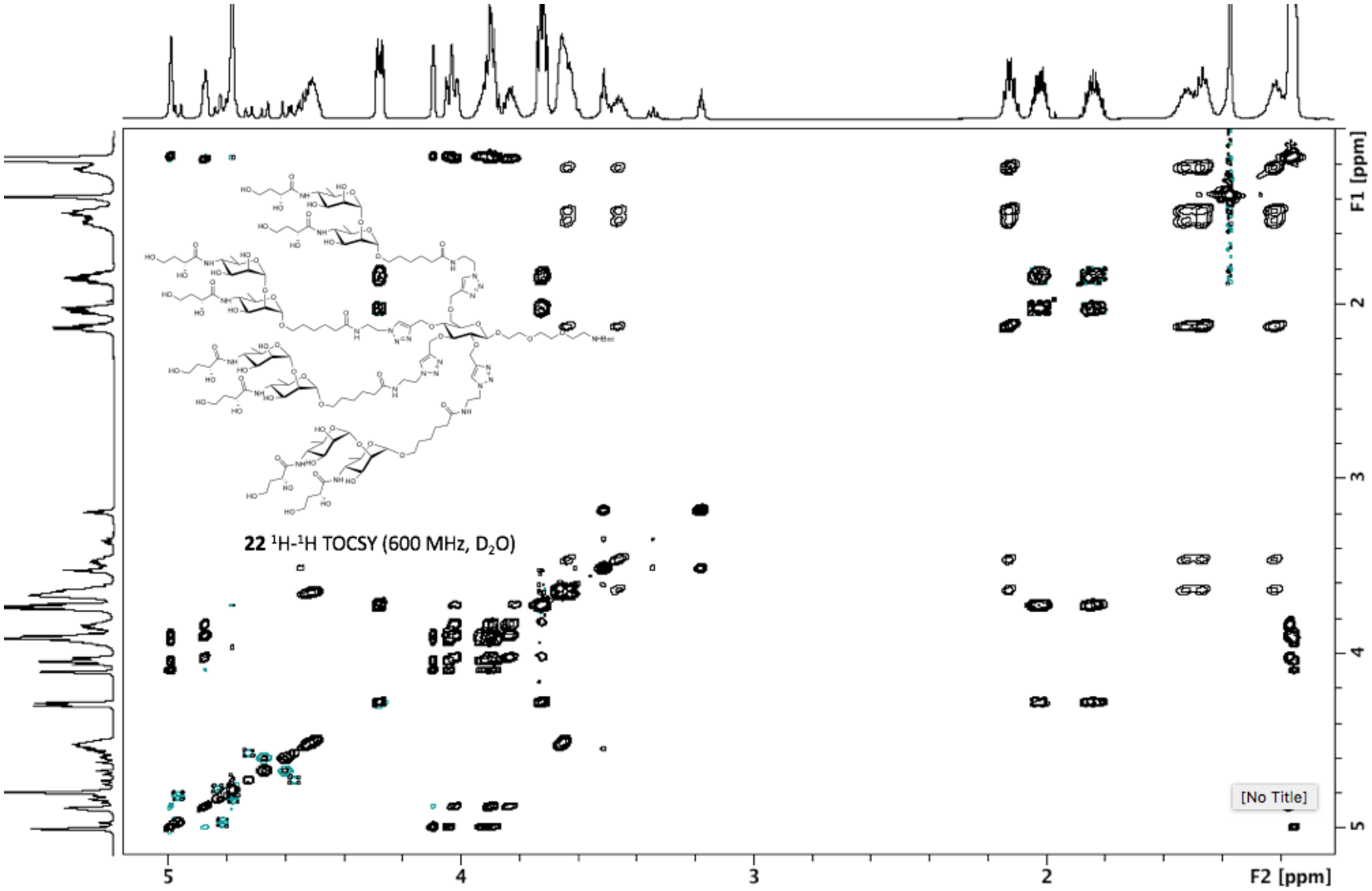
21 ^{1}H-^{13}C HMBC (600 MHz, $CDCl_3$)

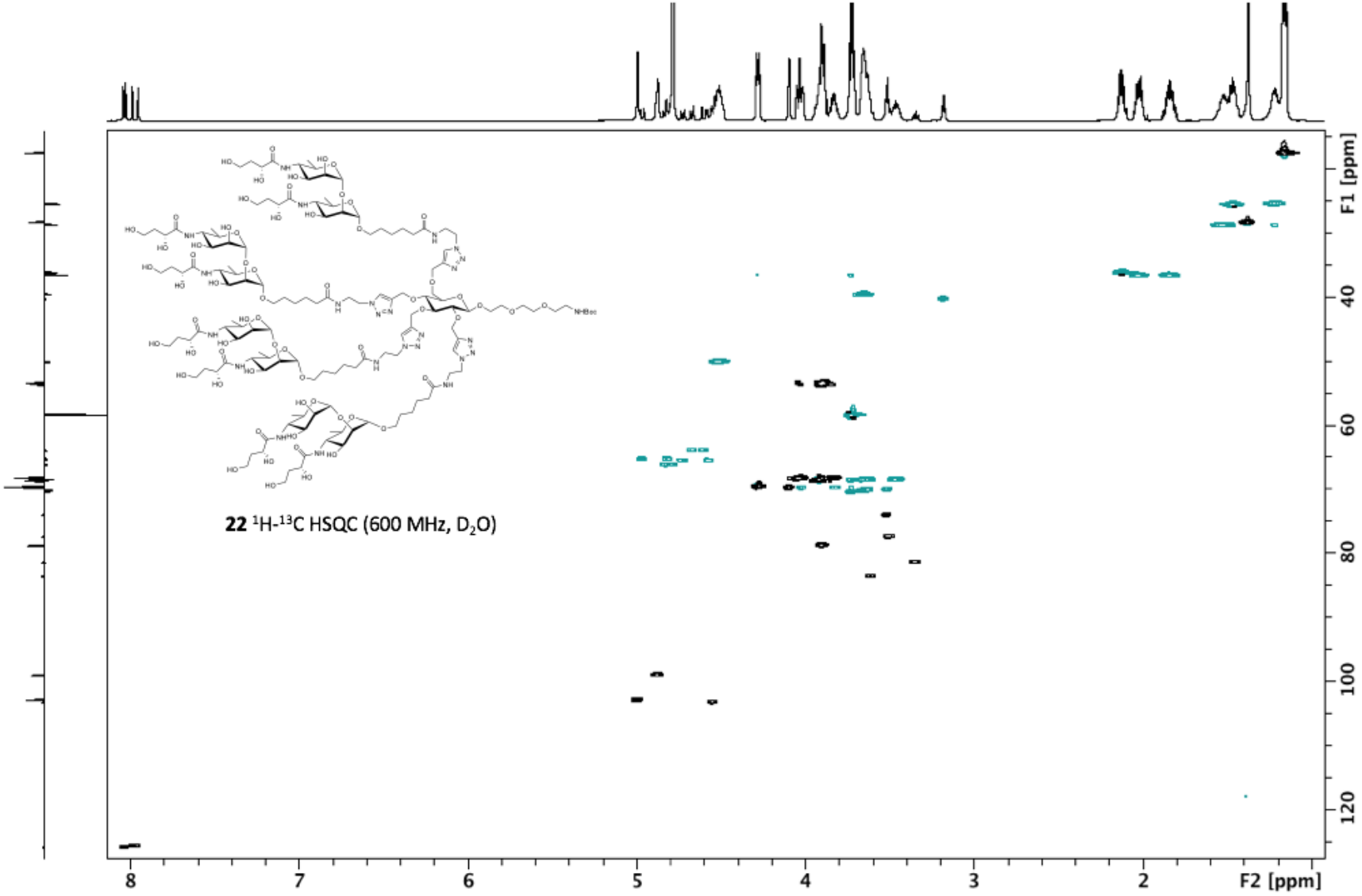
Boc-protected disaccharide cluster **22**

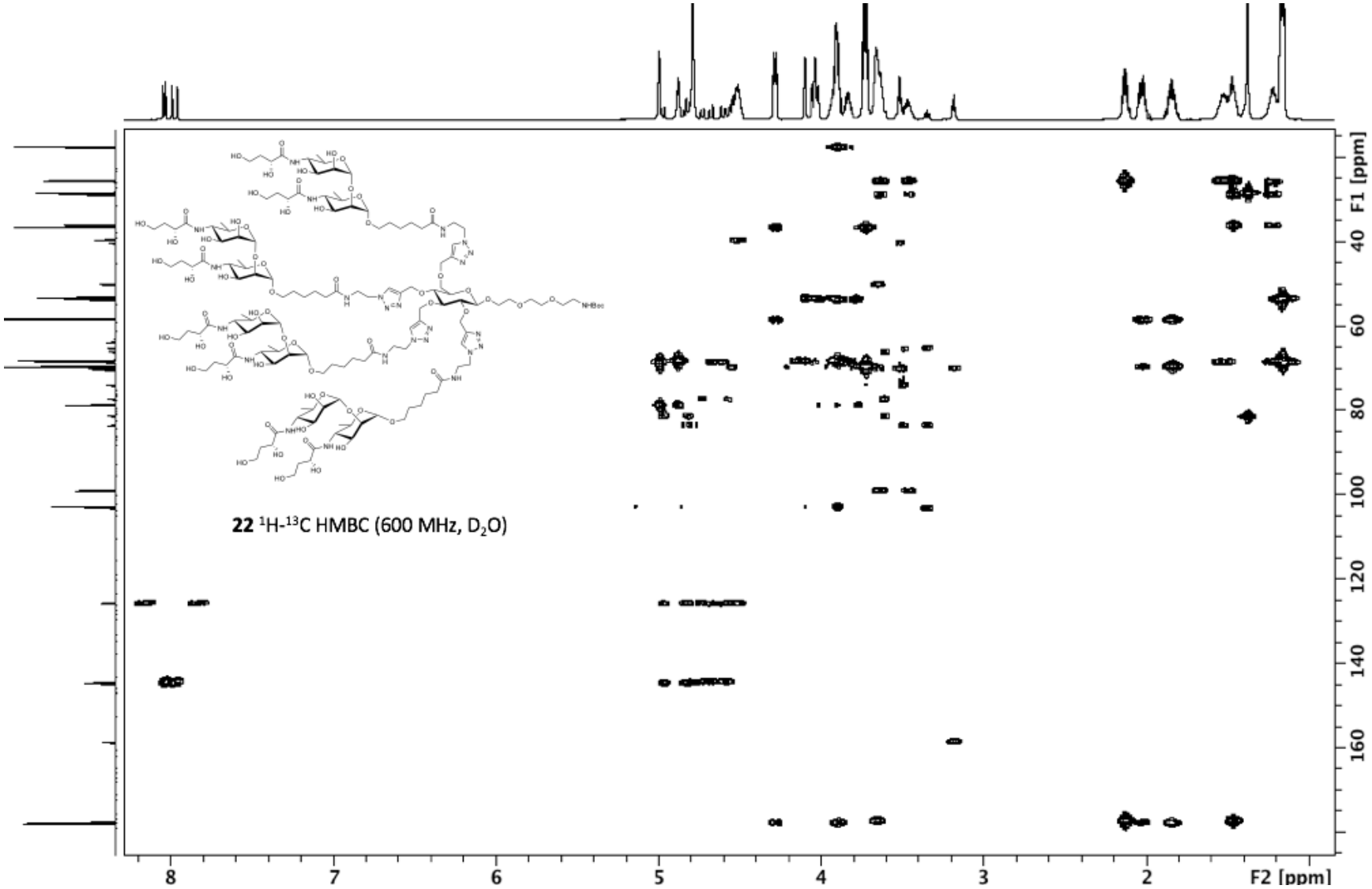



178.02
178.00
177.94
177.93
177.57
177.55
177.54
177.50
158.69
144.74
144.46
144.44
125.90
125.78
125.73
103.26
102.93
99.03
83.59
81.46
81.39
78.78
77.40
74.02
70.42
70.31
70.12
70.02
69.78
69.60
69.59
69.47
68.64
68.55
68.49
68.46
68.44
68.35
68.22
68.08
66.15
65.49
65.25
63.96
58.58
58.46
58.33
53.70
53.39
53.26
50.20
50.15
50.13
50.11
40.30
39.64
39.61
39.59
36.71
36.64
36.60
36.17
28.80
28.38
25.63
25.45
25.42
17.60
17.51
22 13C NMR (150 MHz, D2O)
[rel]
[ppm]

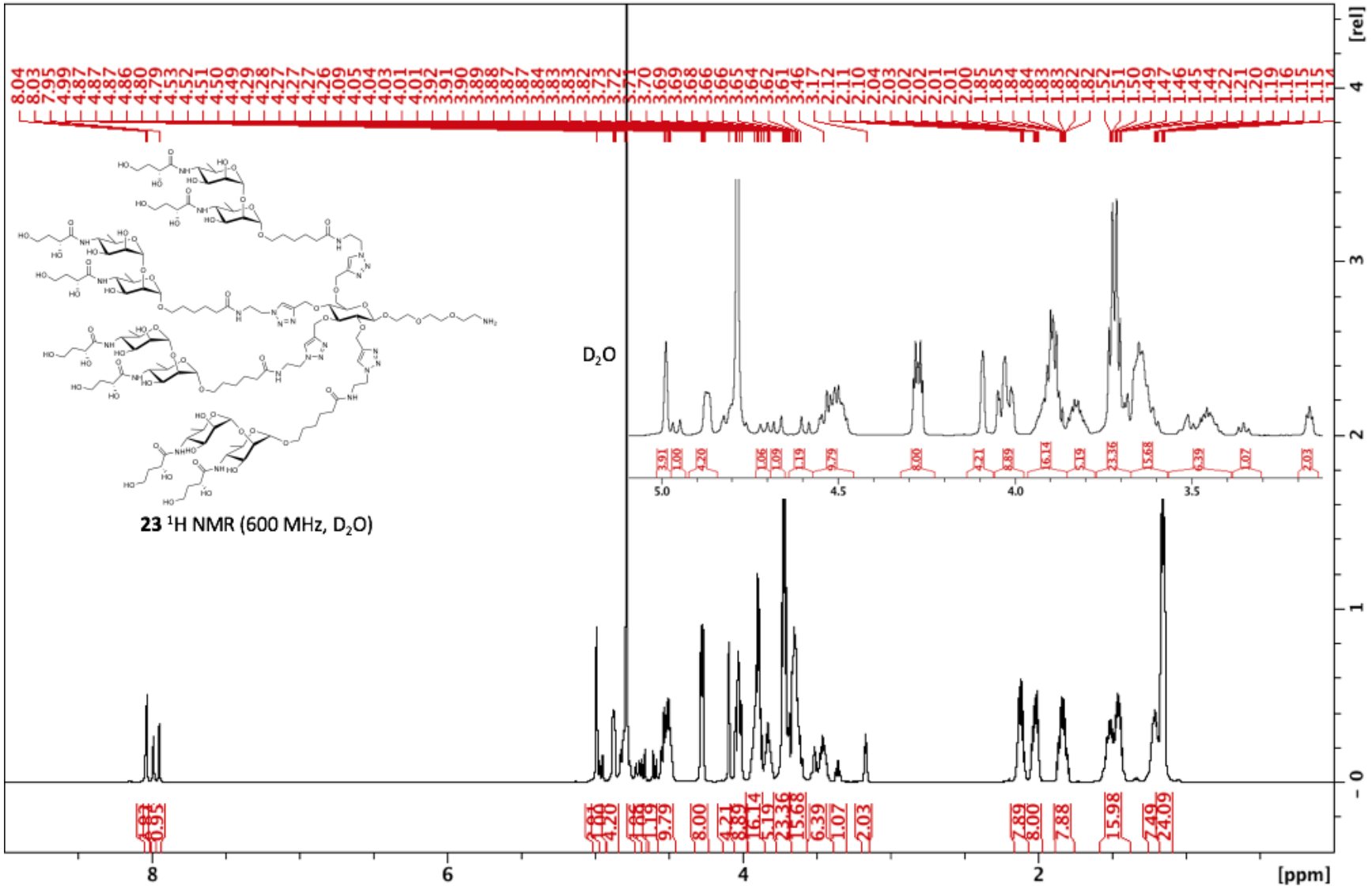

22 ^{1}H-^{1}H COSY (600 MHz, D_2O)
F1 [ppm]
F2 [ppm]
8
7
6
5
4
3
2

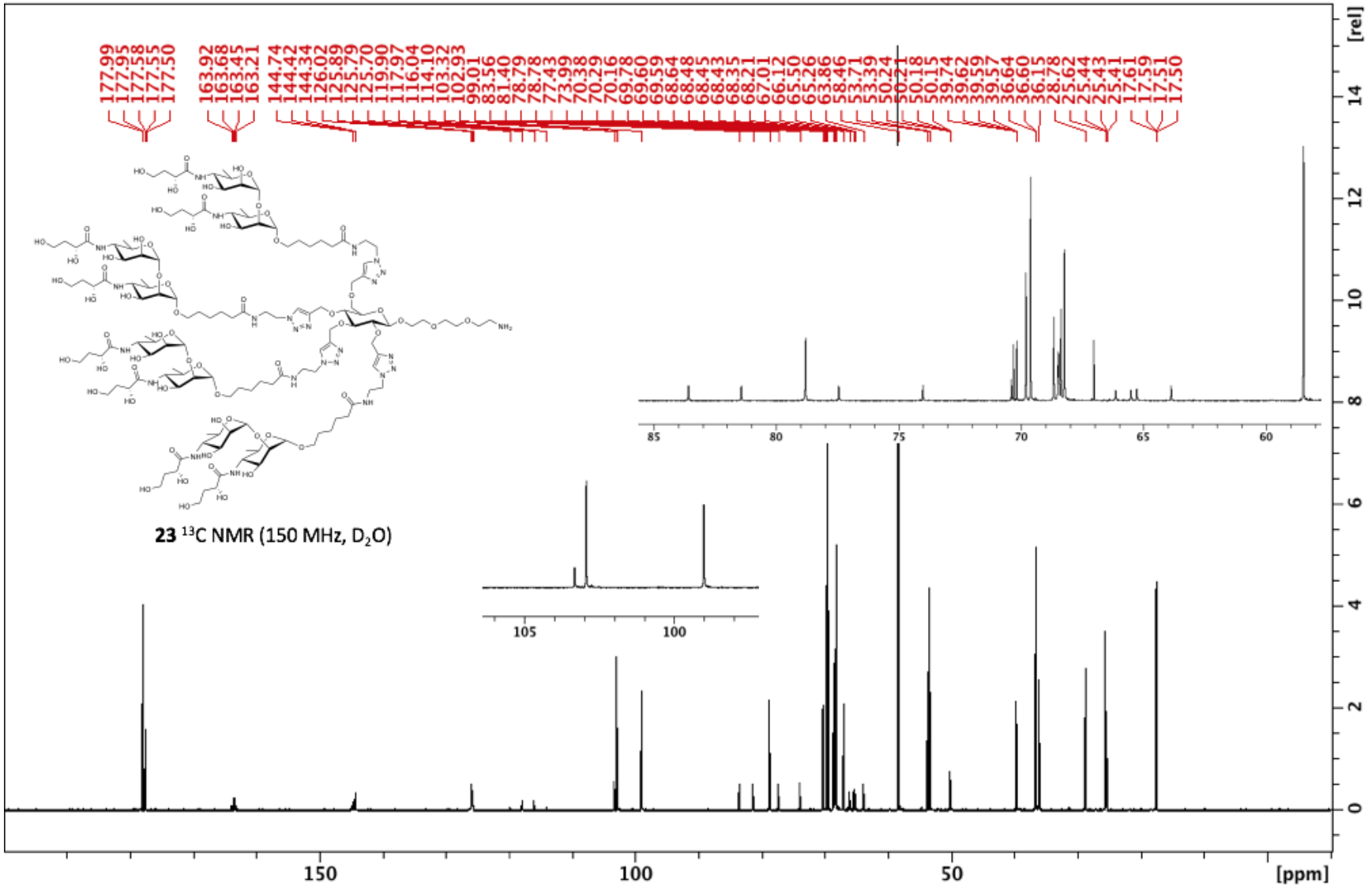

22 ^{1}H-^{1}H TOCSY (600 MHz, D_2O)
F1 [ppm]
F2 [ppm]
5
4
3
2
[No Title]

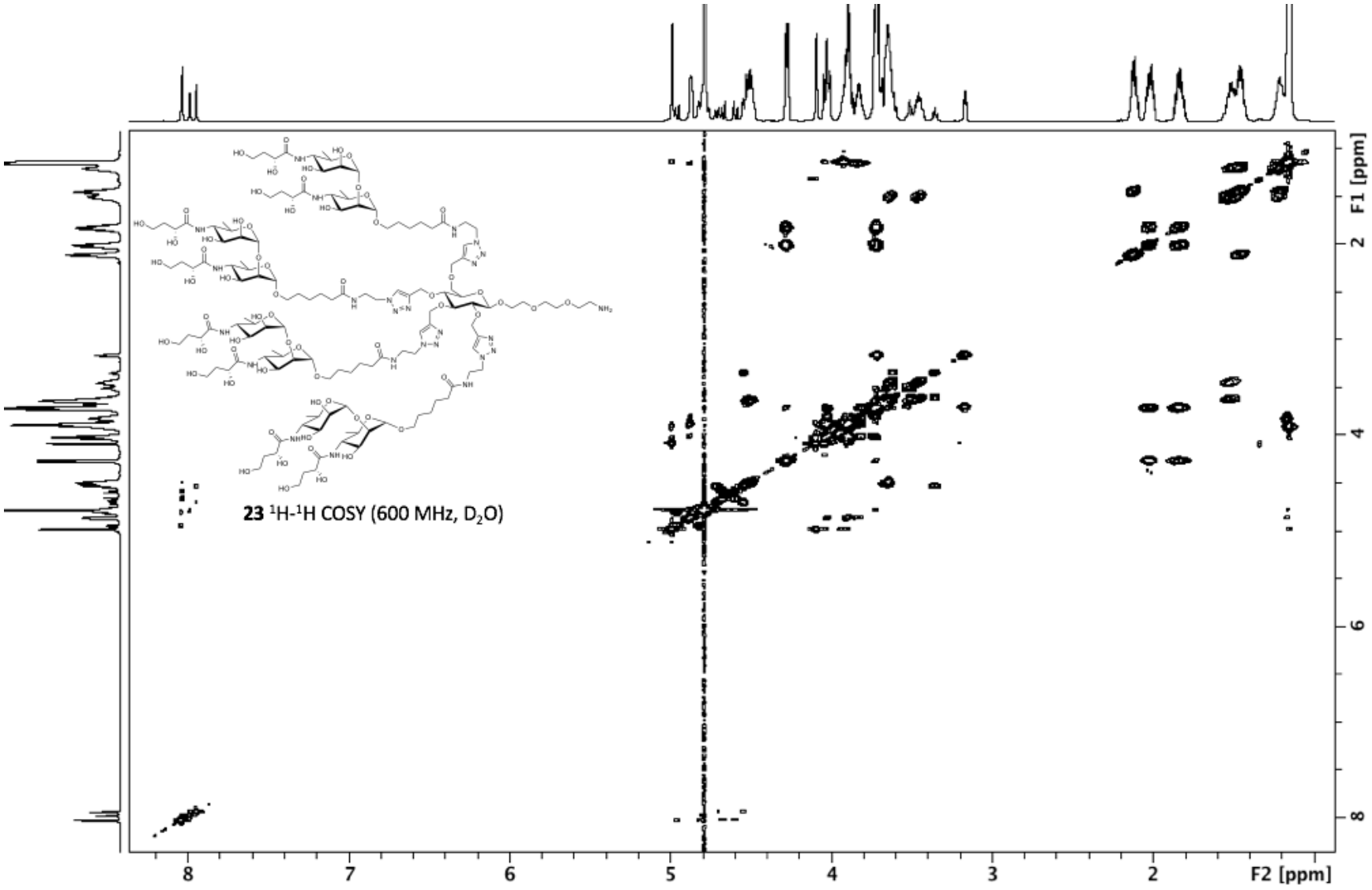

22 ^{1}H-^{13}C HSQC (600 MHz, D_2O)
F1 [ppm]
40
60
80
100
120
8
7
6
5
4
3
2
F2 [ppm]


22 ^{1}H-^{13}C HMBC (600 MHz, D_2O)
F1 [ppm]
F2 [ppm]
8
7
6
5
4
3
2
40
60
80
100
120
140
160

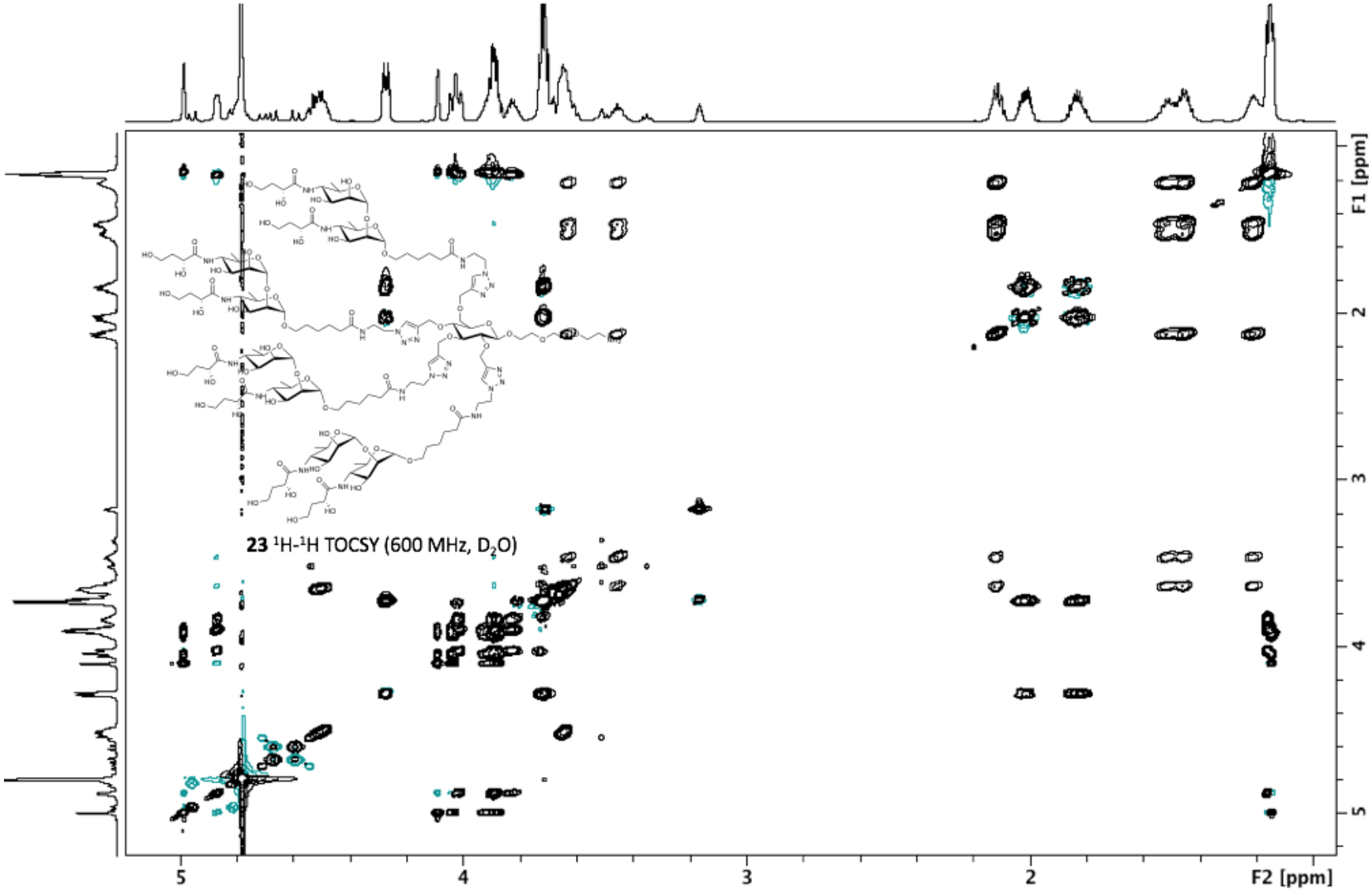
Amine disaccharide cluster **23**

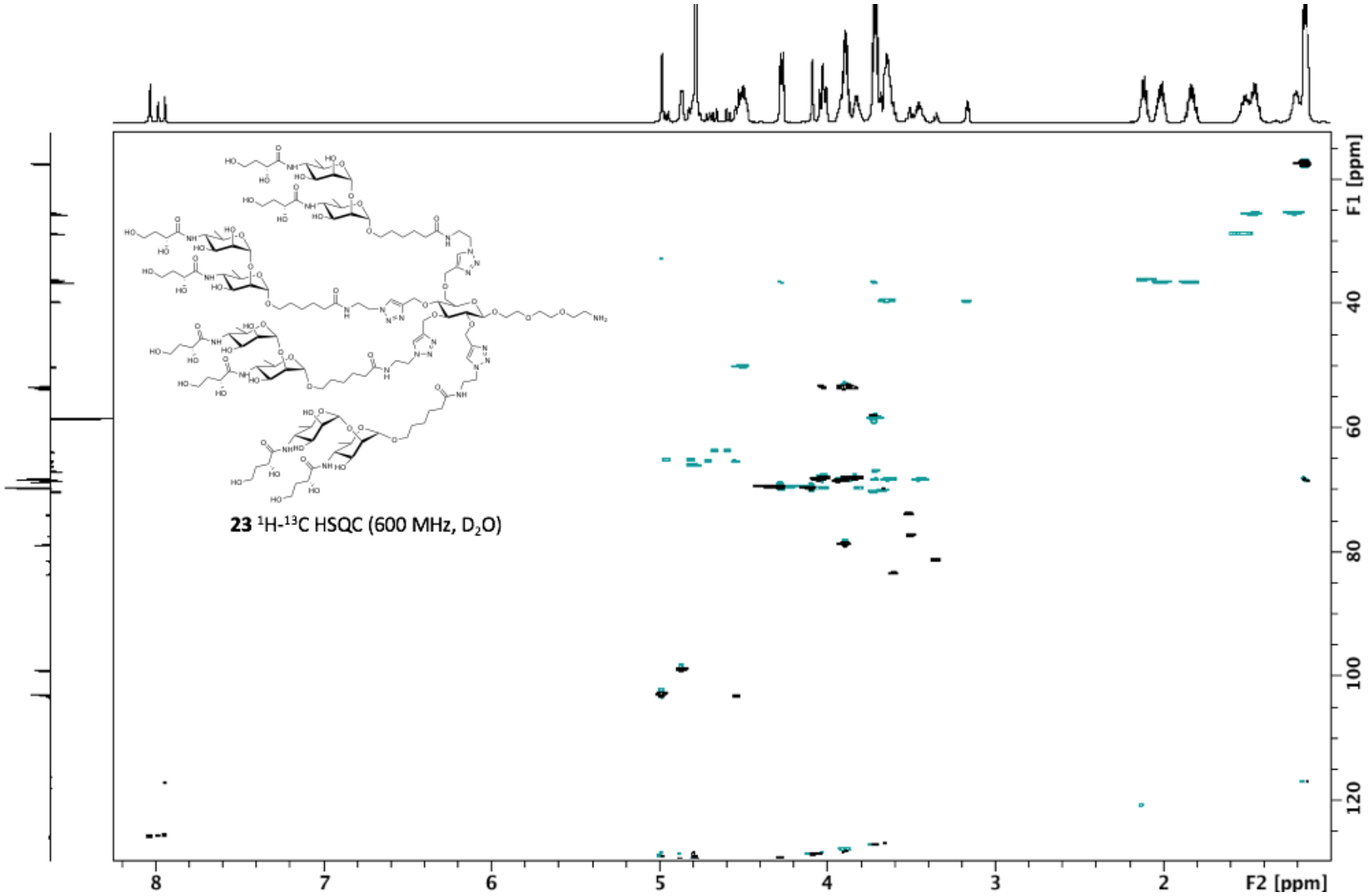



177.99
177.95
177.58
177.55
177.50
163.92
163.68
163.45
163.21
144.74
144.42
144.34
126.02
125.89
125.79
125.70
119.90
117.97
116.04
114.10
103.32
102.93
99.01
83.56
81.40
78.79
78.78
77.43
73.99
70.38
70.29
70.16
69.78
69.60
69.59
68.64
68.48
68.45
68.43
68.35
68.21
67.01
66.12
65.50
65.26
63.86
58.46
53.71
53.39
50.24
50.21
50.18
50.15
39.74
39.62
39.59
39.57
36.64
36.60
36.15
28.78
25.62
25.44
25.43
25.41
17.61
17.59
17.51
17.50
23 13C NMR (150 MHz, D2O)
[rel]
[ppm]

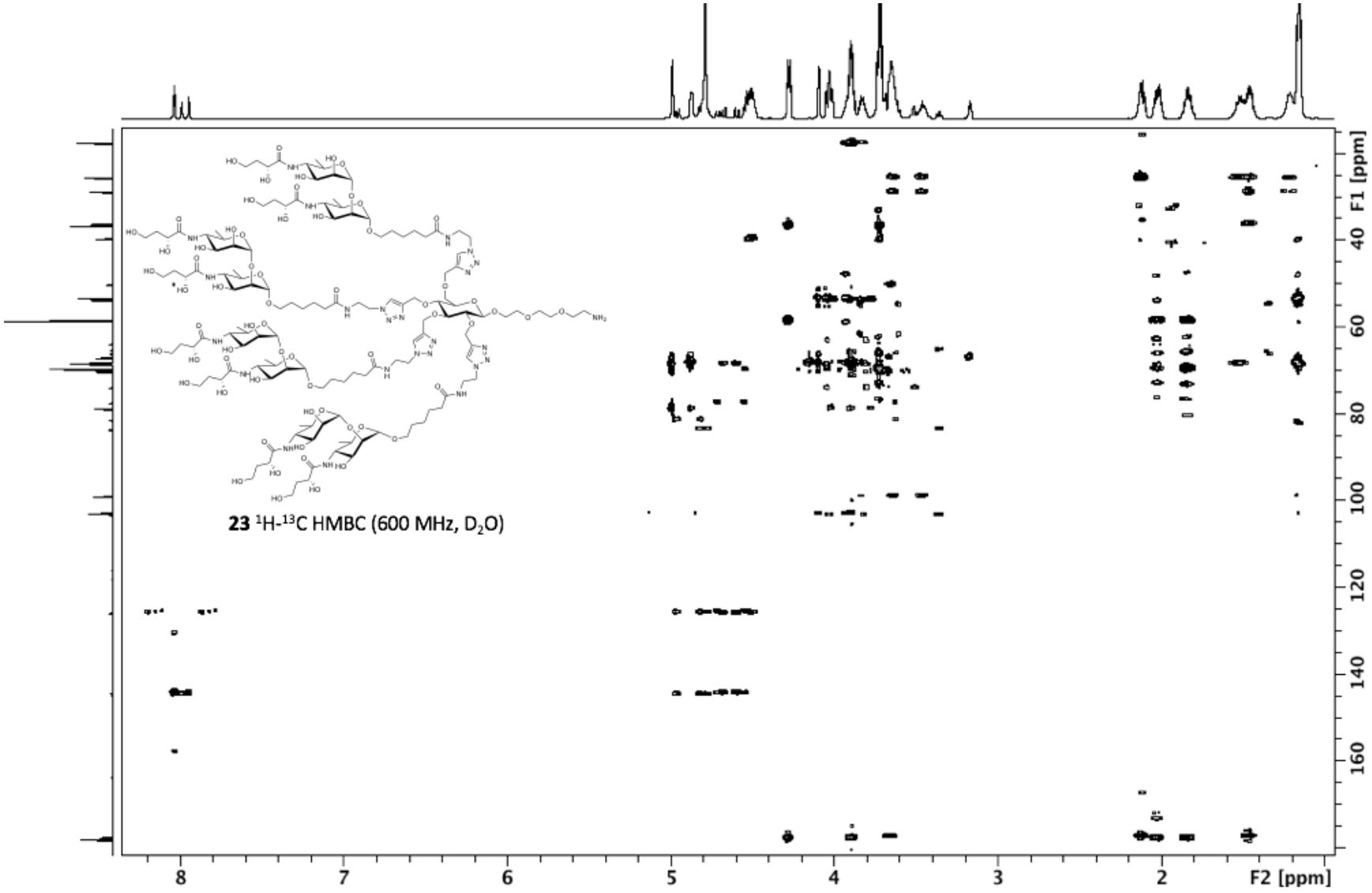


23 ^{1}H-^{1}H COSY (600 MHz, D_2O)


23 ^{1}H-^{1}H TOCSY (600 MHz, D_2O)
F1 [ppm]
F2 [ppm]
5
4
3
2
2
3
4
5

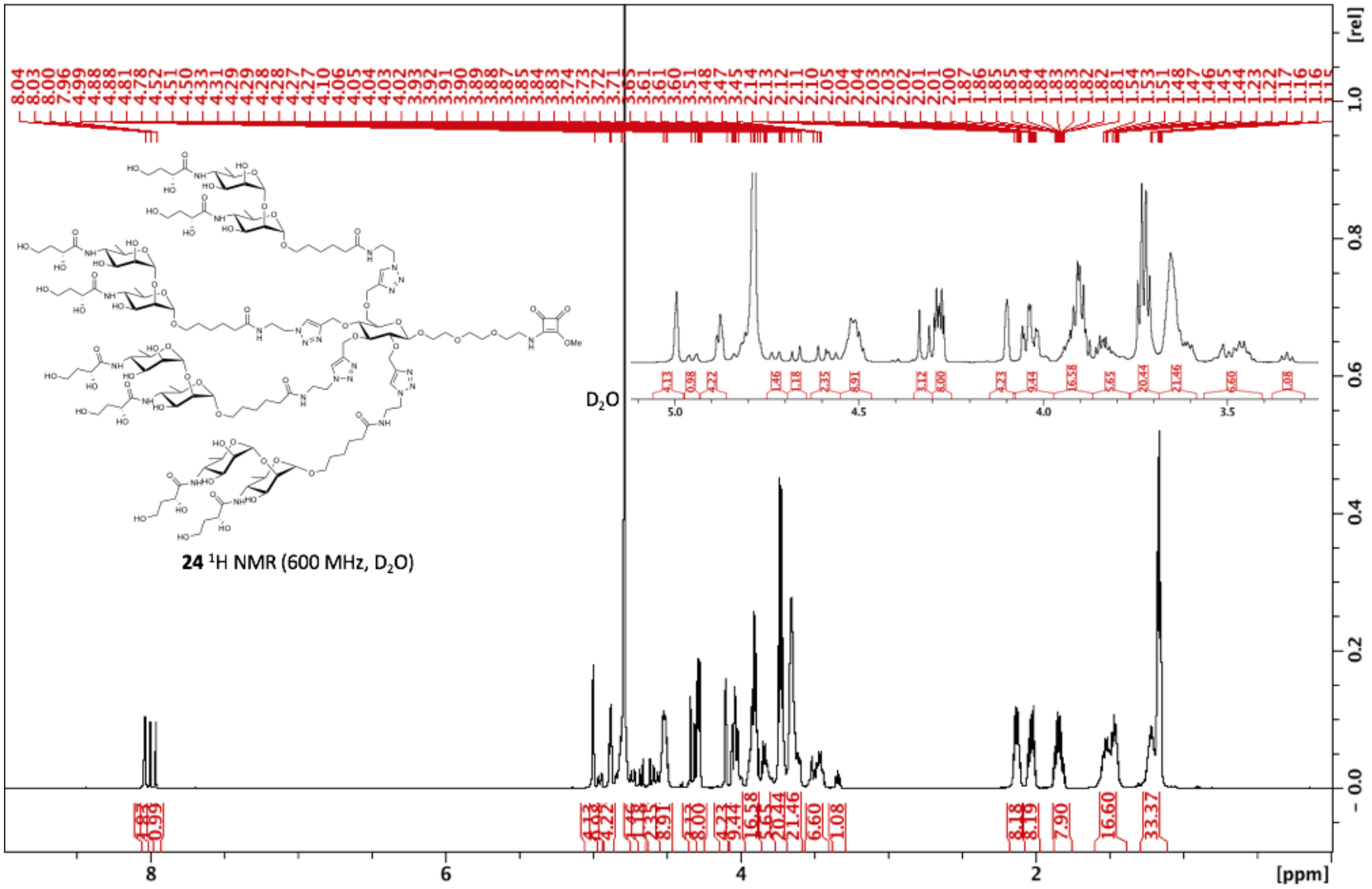


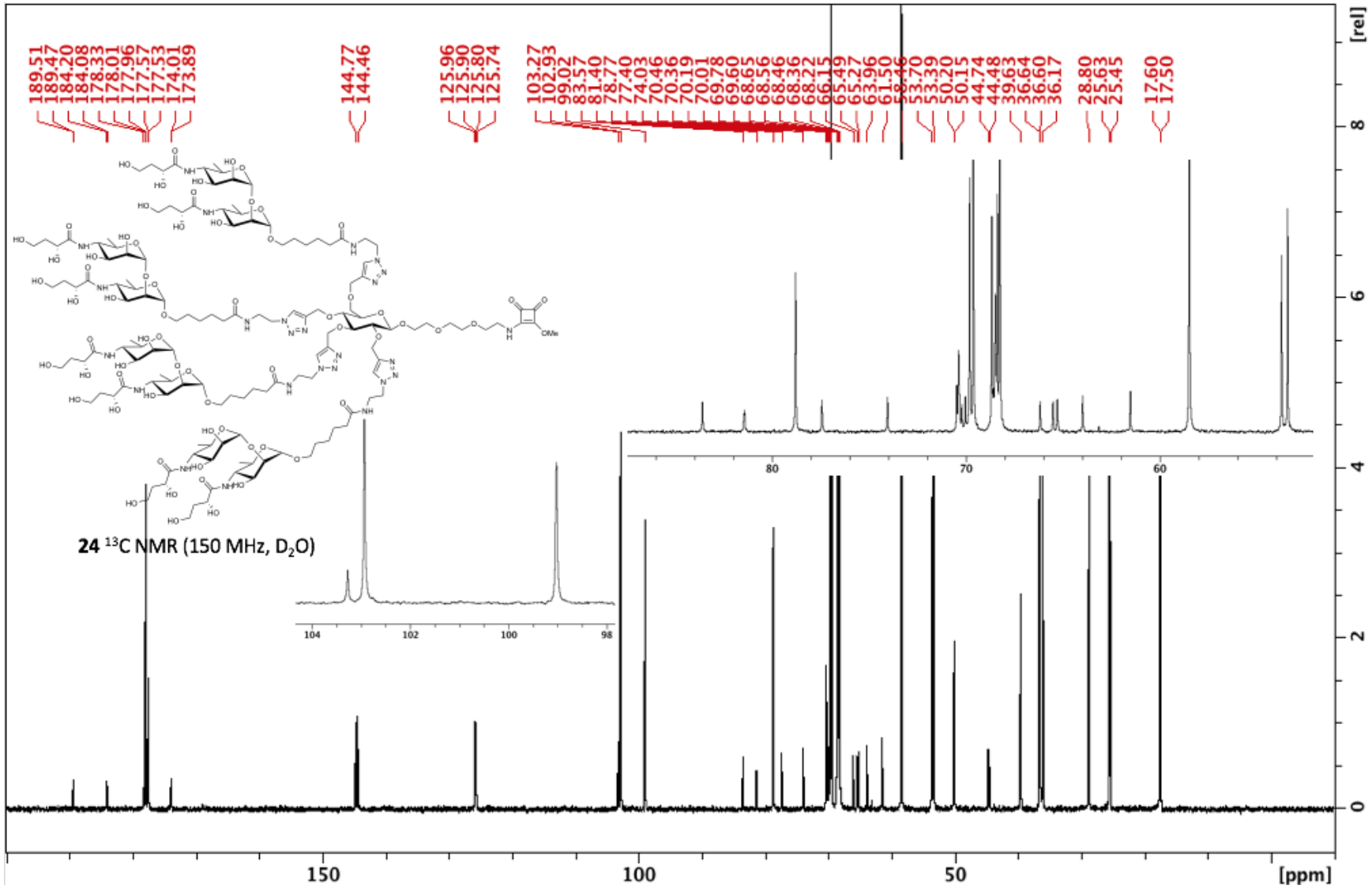
23 ^{1}H-^{13}C HSQC (600 MHz, D_2O)



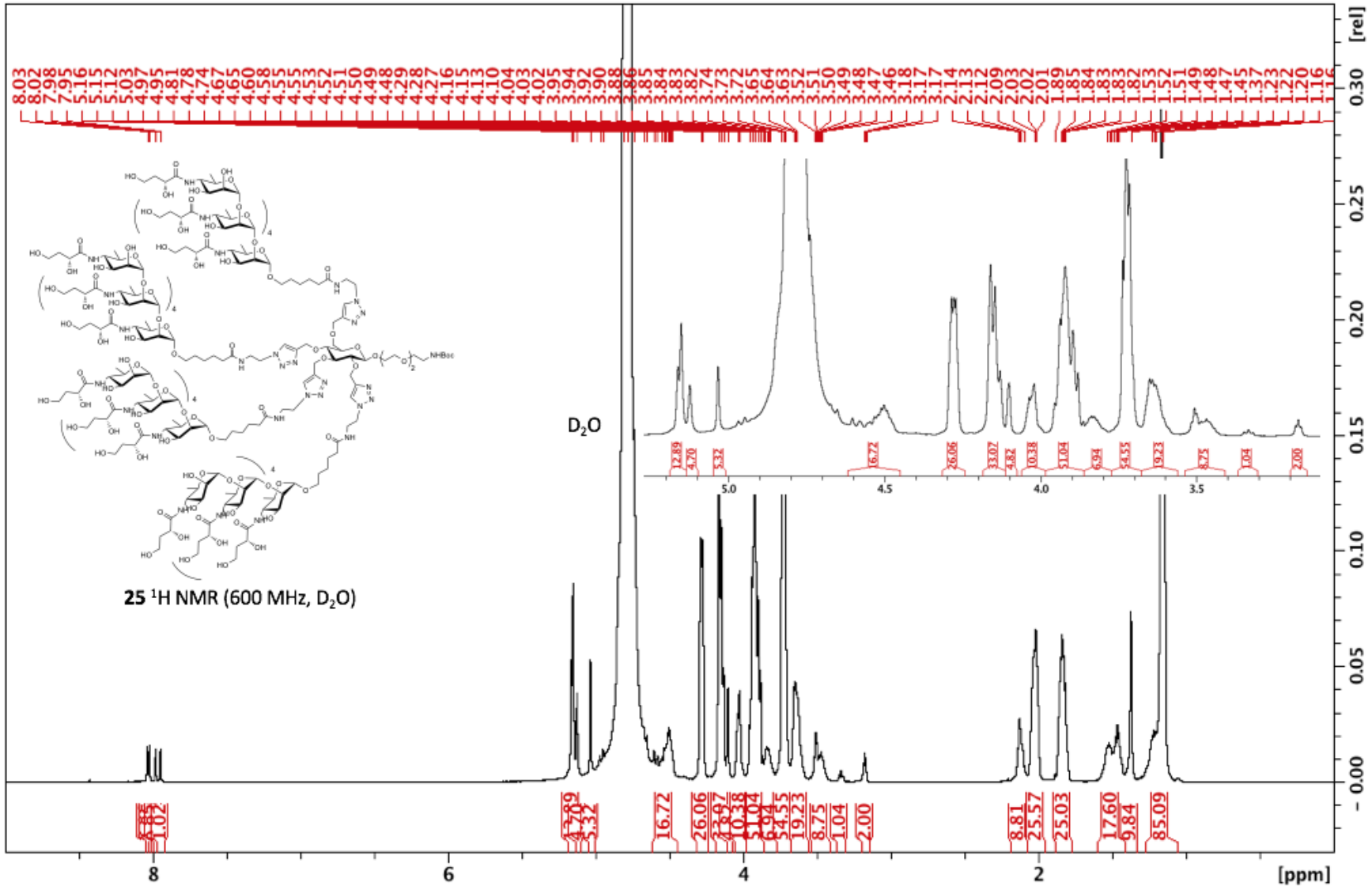
23 ^{1}H-^{13}C HMBC (600 MHz, D_2O)

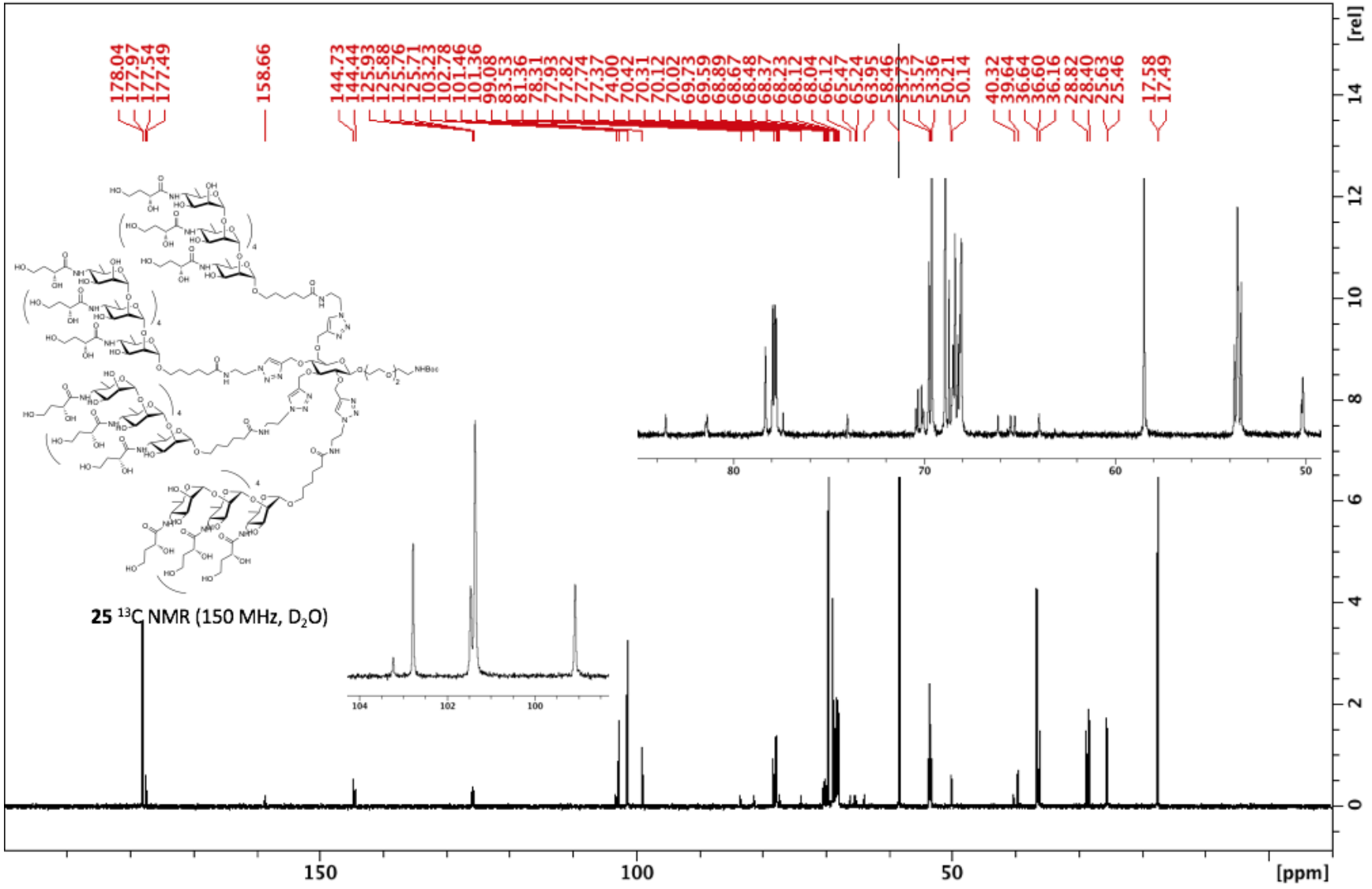
Squarate disaccharide cluster **24**



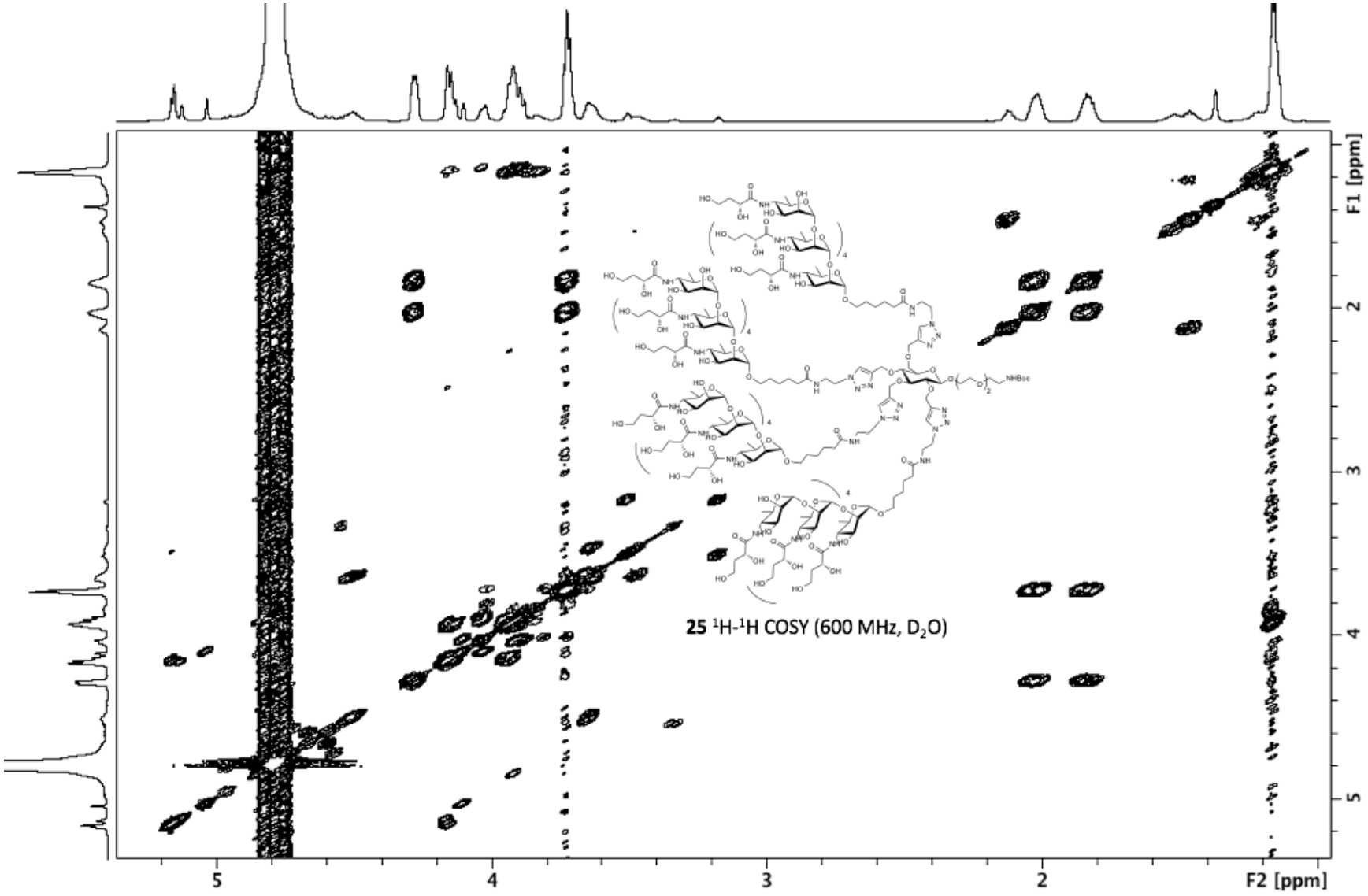

189.51
189.47
184.20
184.08
178.33
178.01
177.96
177.57
177.53
174.01
173.89
144.77
144.46
125.96
125.90
125.80
125.74
103.27
102.93
99.02
83.57
81.40
78.77
77.40
74.03
70.46
70.36
70.19
70.01
69.78
69.60
68.65
68.56
68.46
68.36
68.22
66.15
65.49
65.27
63.96
61.50
58.46
53.70
53.39
50.20
50.15
44.74
44.48
39.63
36.64
36.60
36.17
28.80
25.63
25.45
17.60
17.50
24 13C NMR (150 MHz, D2O)
[rel]
[ppm]

Boc-protected hexasaccharide cluster **25**

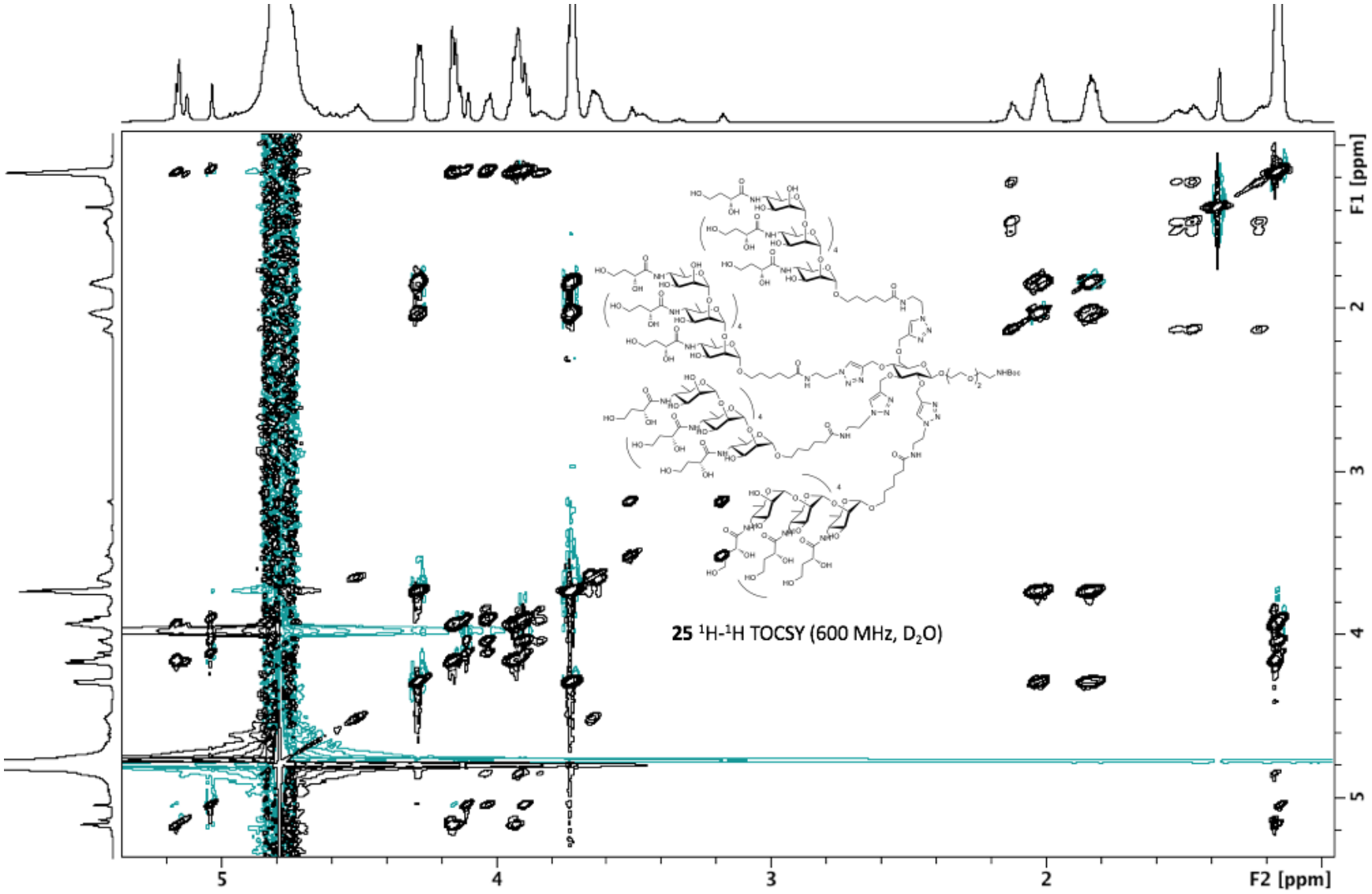




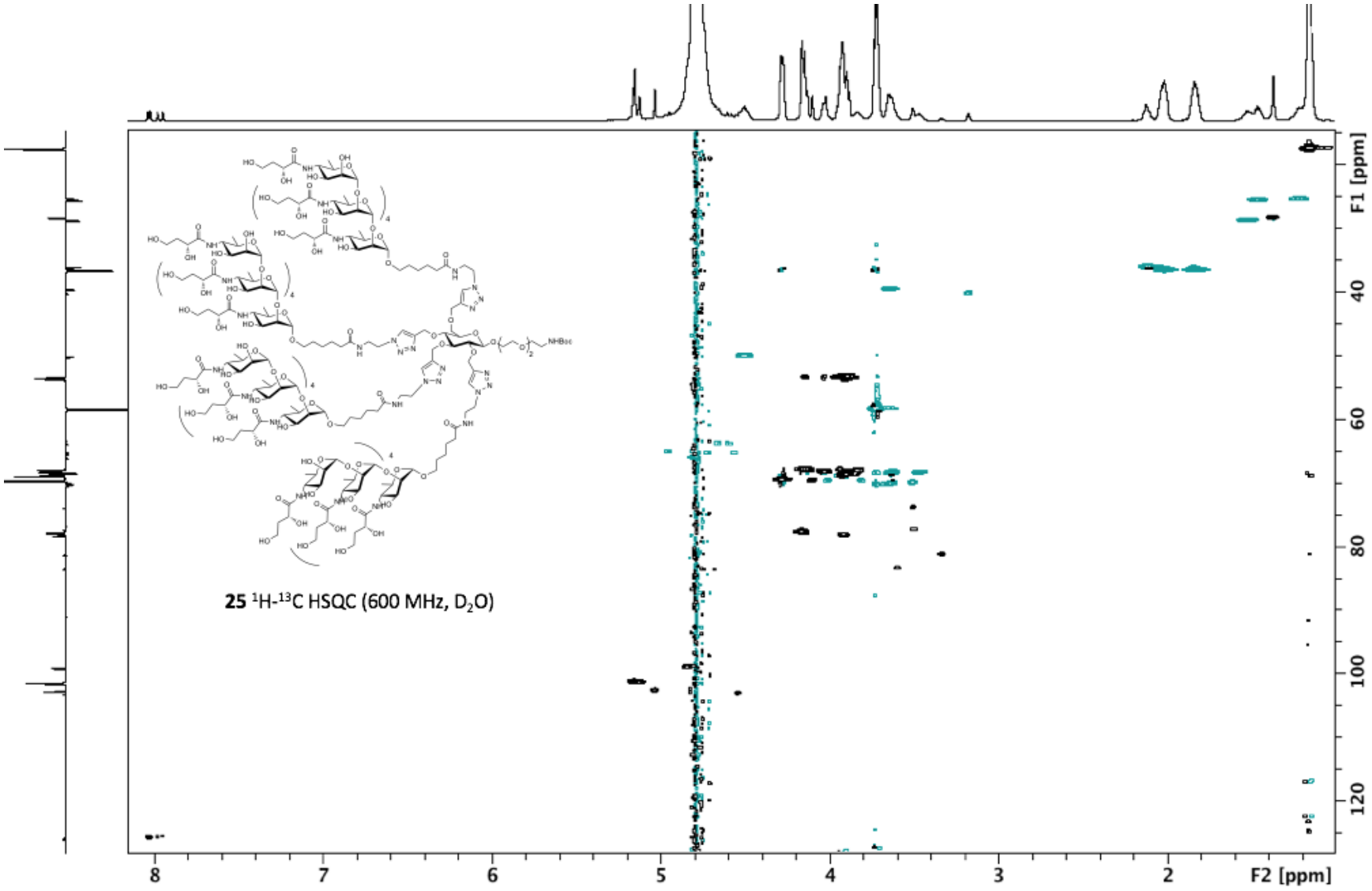
25 ^{13}C NMR (150 MHz, D_2O)



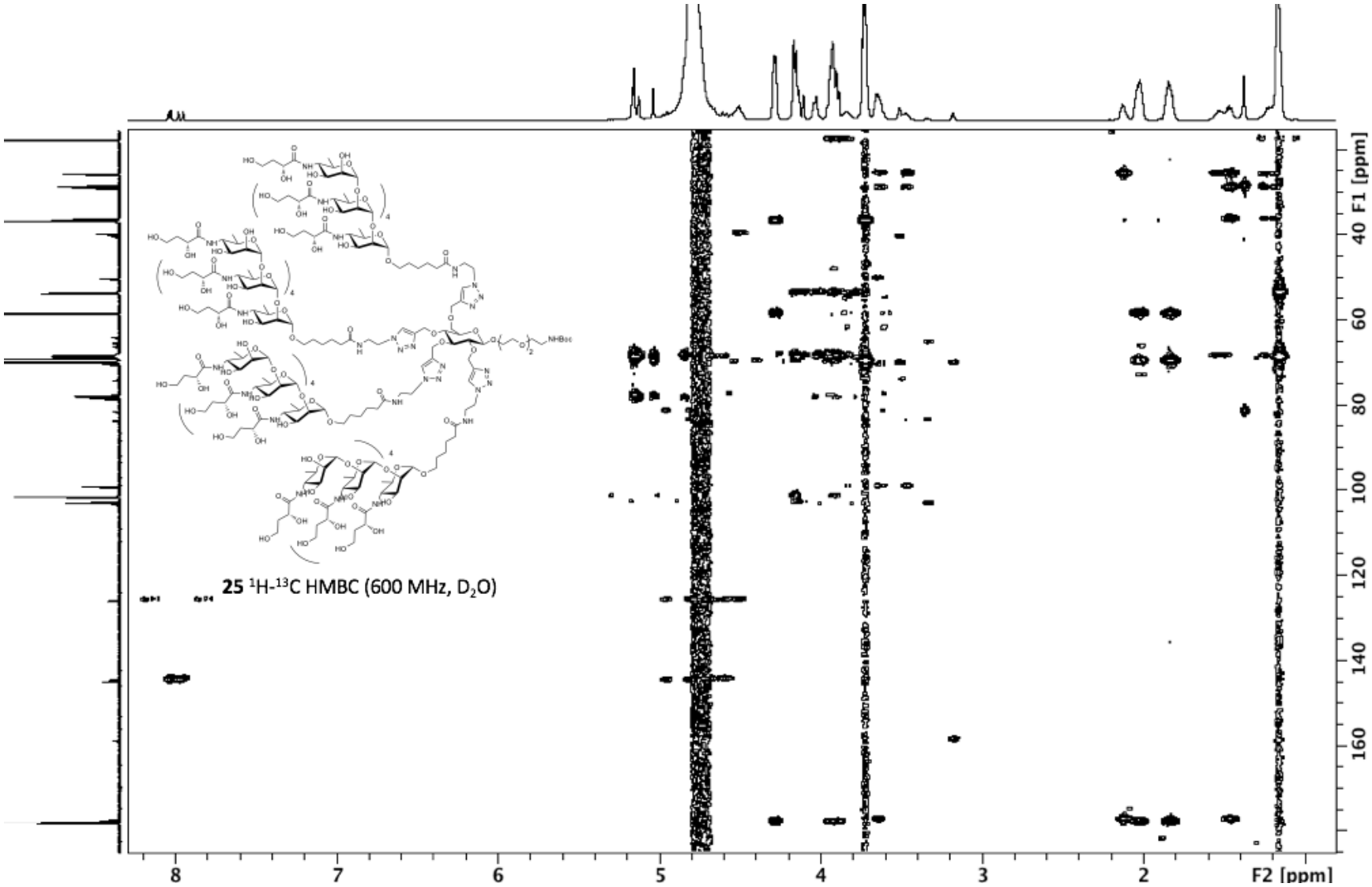
25 ^{1}H-^{1}H COSY (600 MHz, D_2O)



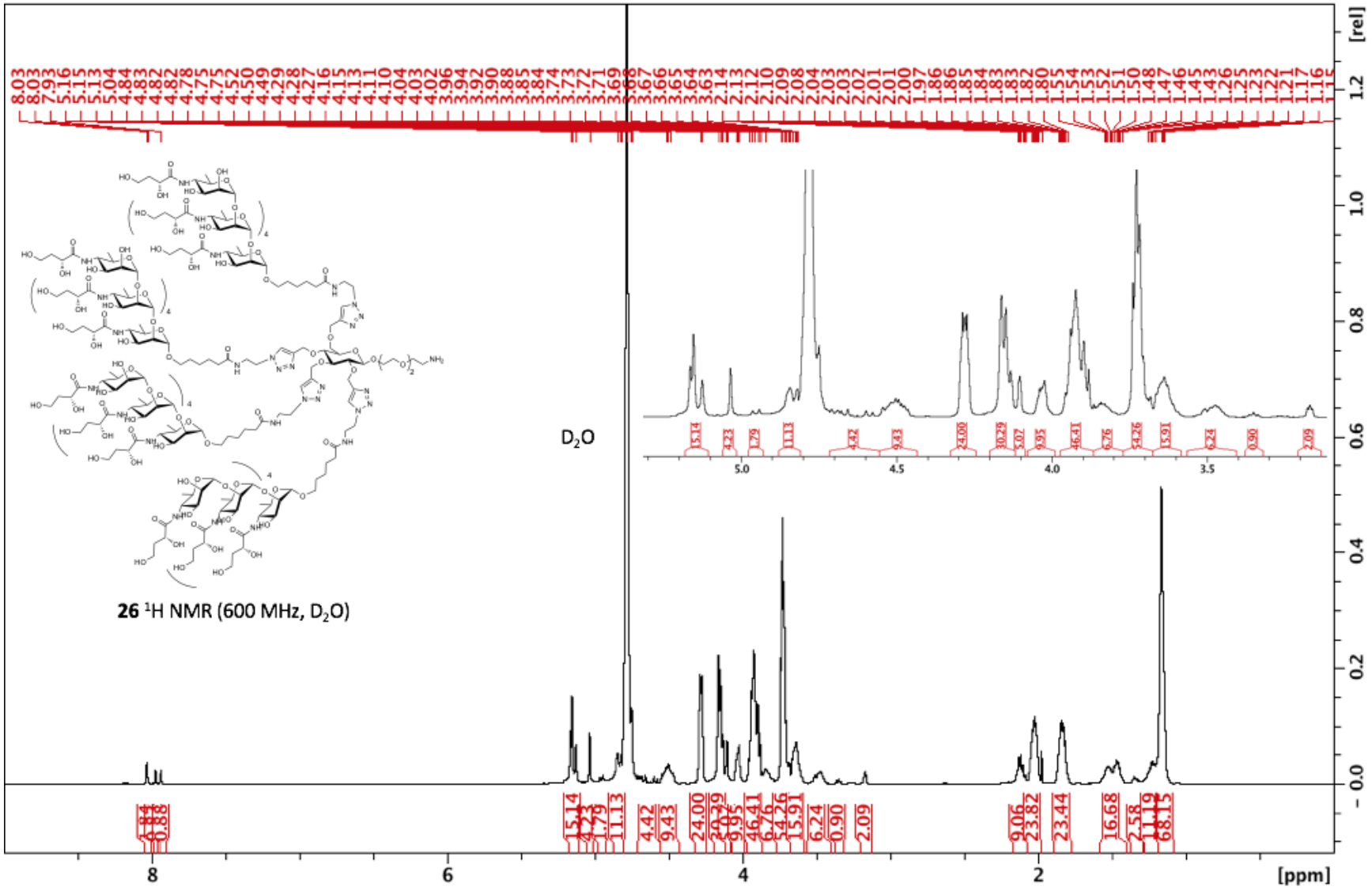
25 ^{1}H-^{1}H TOCSY (600 MHz, D_2O)

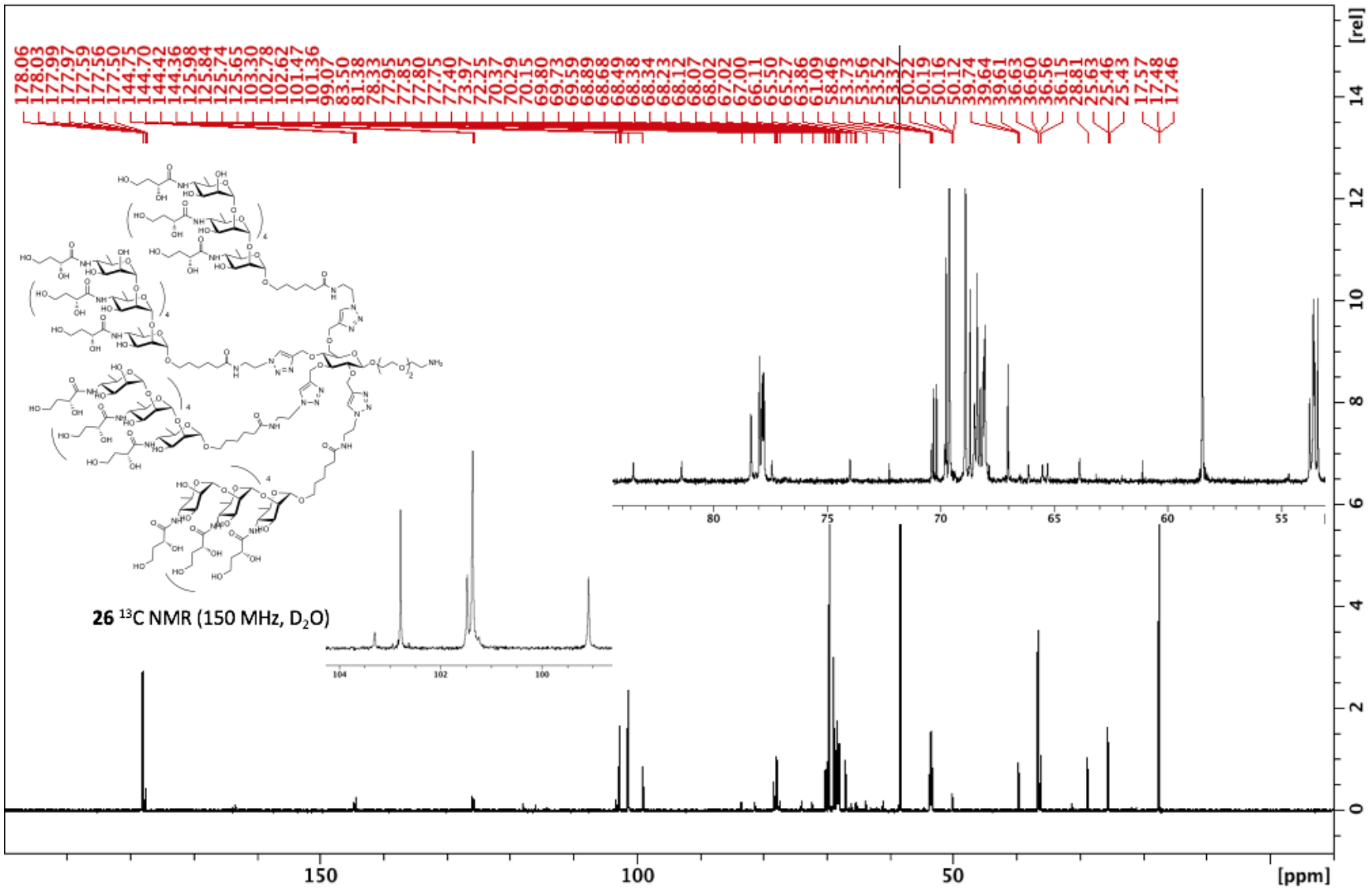


25 ^{1}H-^{13}C HSQC (600 MHz, D_2O)

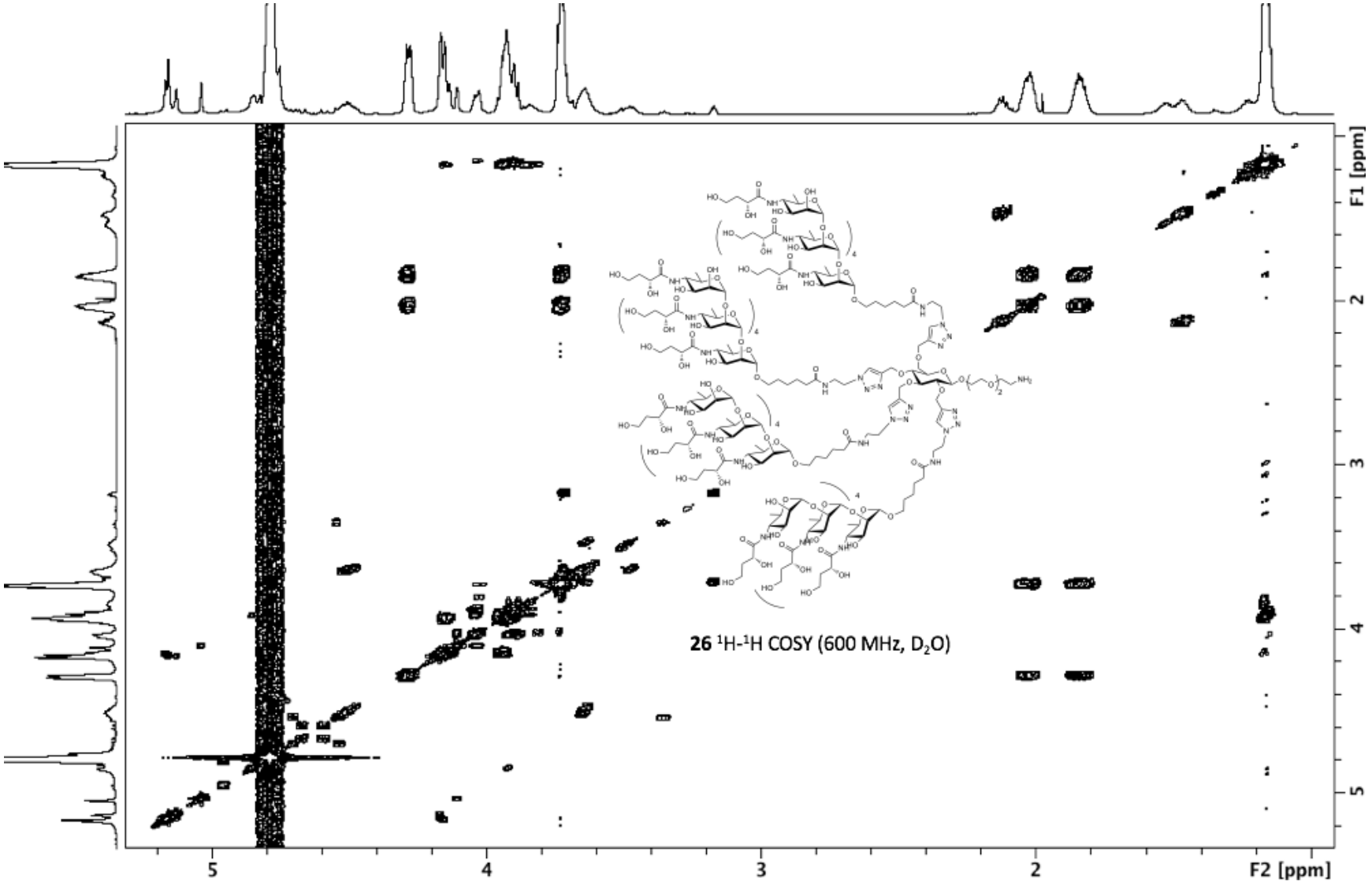

25 ^{1}H-^{13}C HMBC (600 MHz, D_2O)
F1 [ppm]
F2 [ppm]
8
7
6
5
4
3
2
40
60
80
100
120
140
160

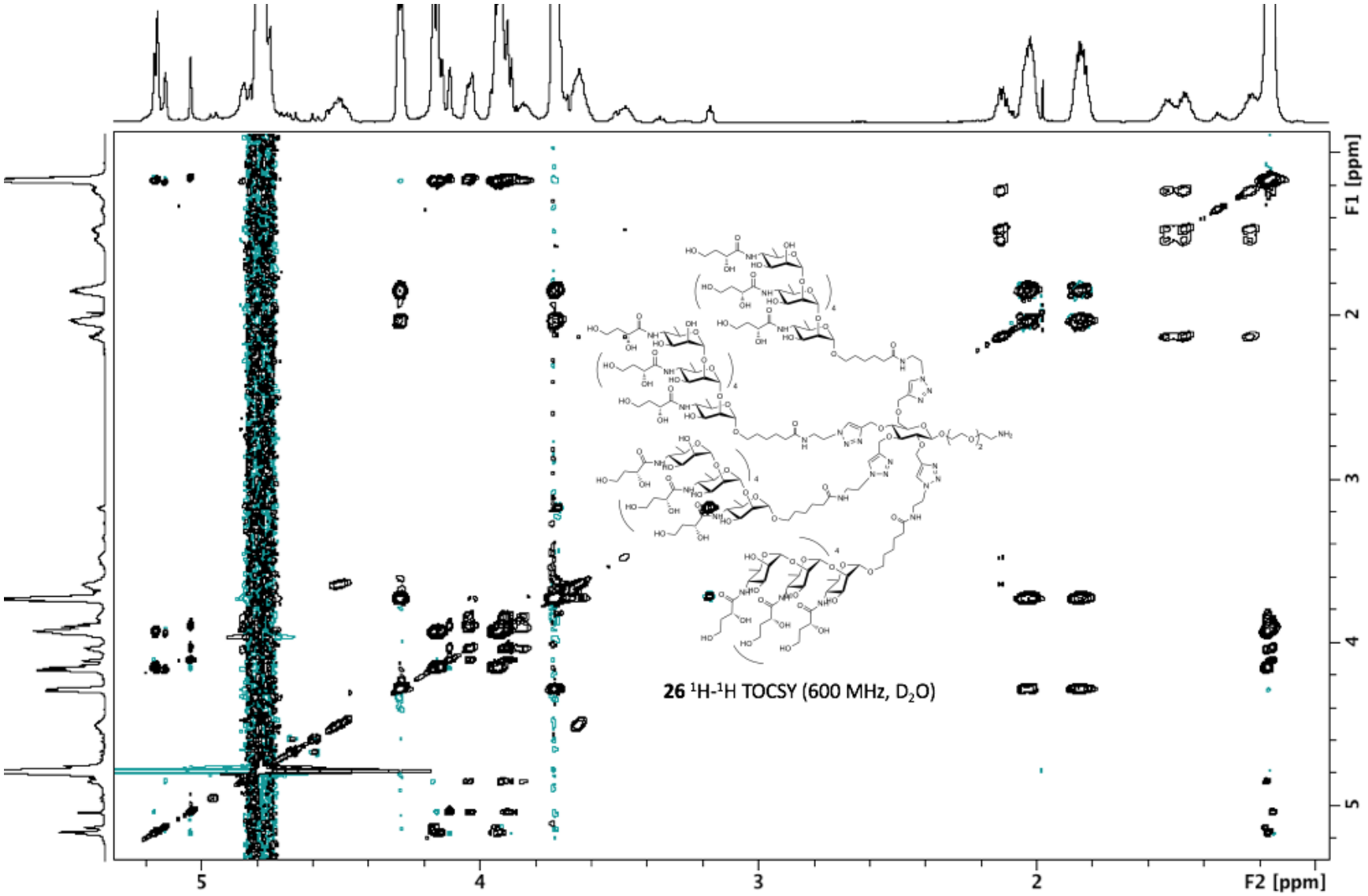
Amine hexasaccharide cluster **26**

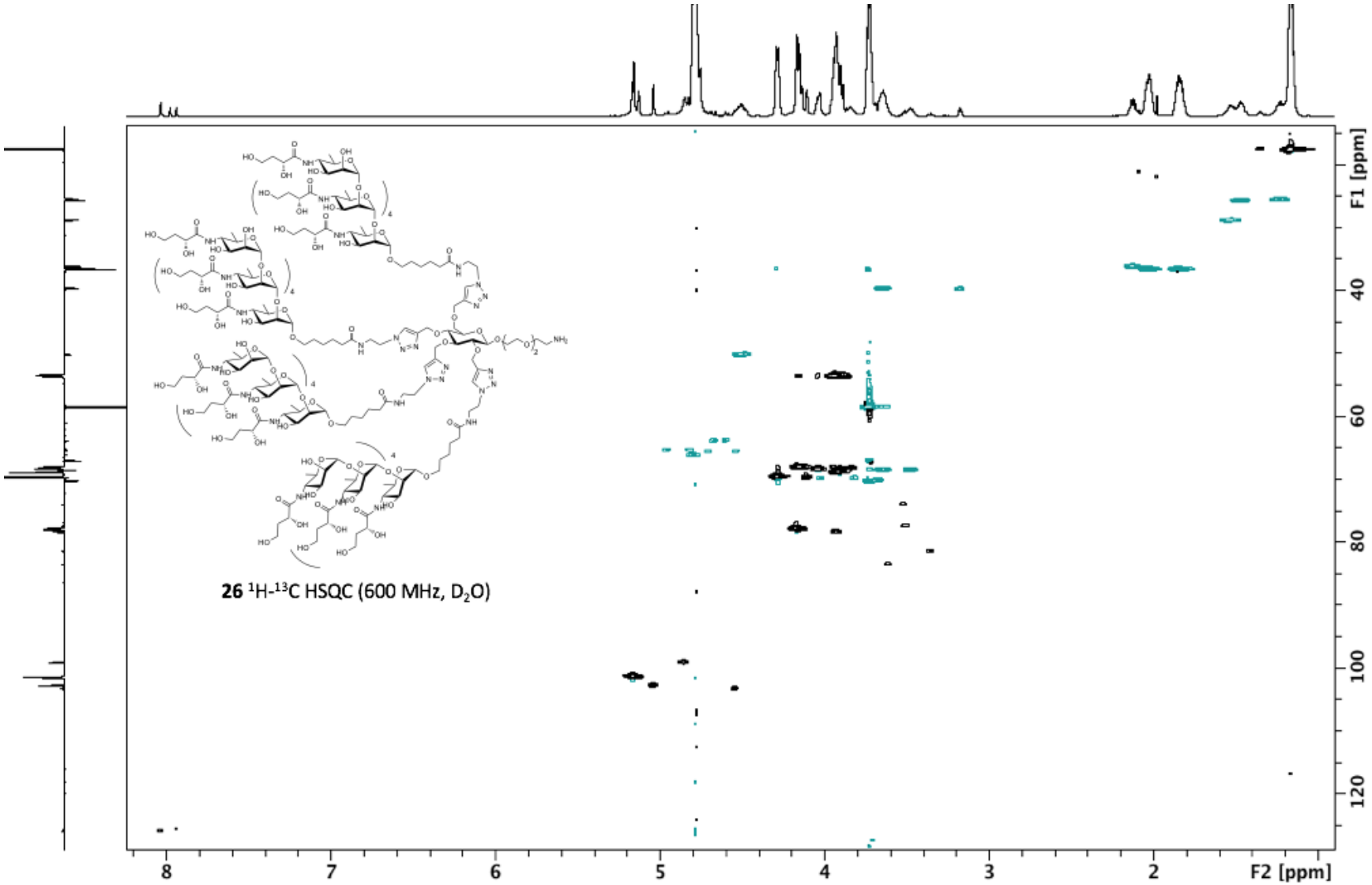




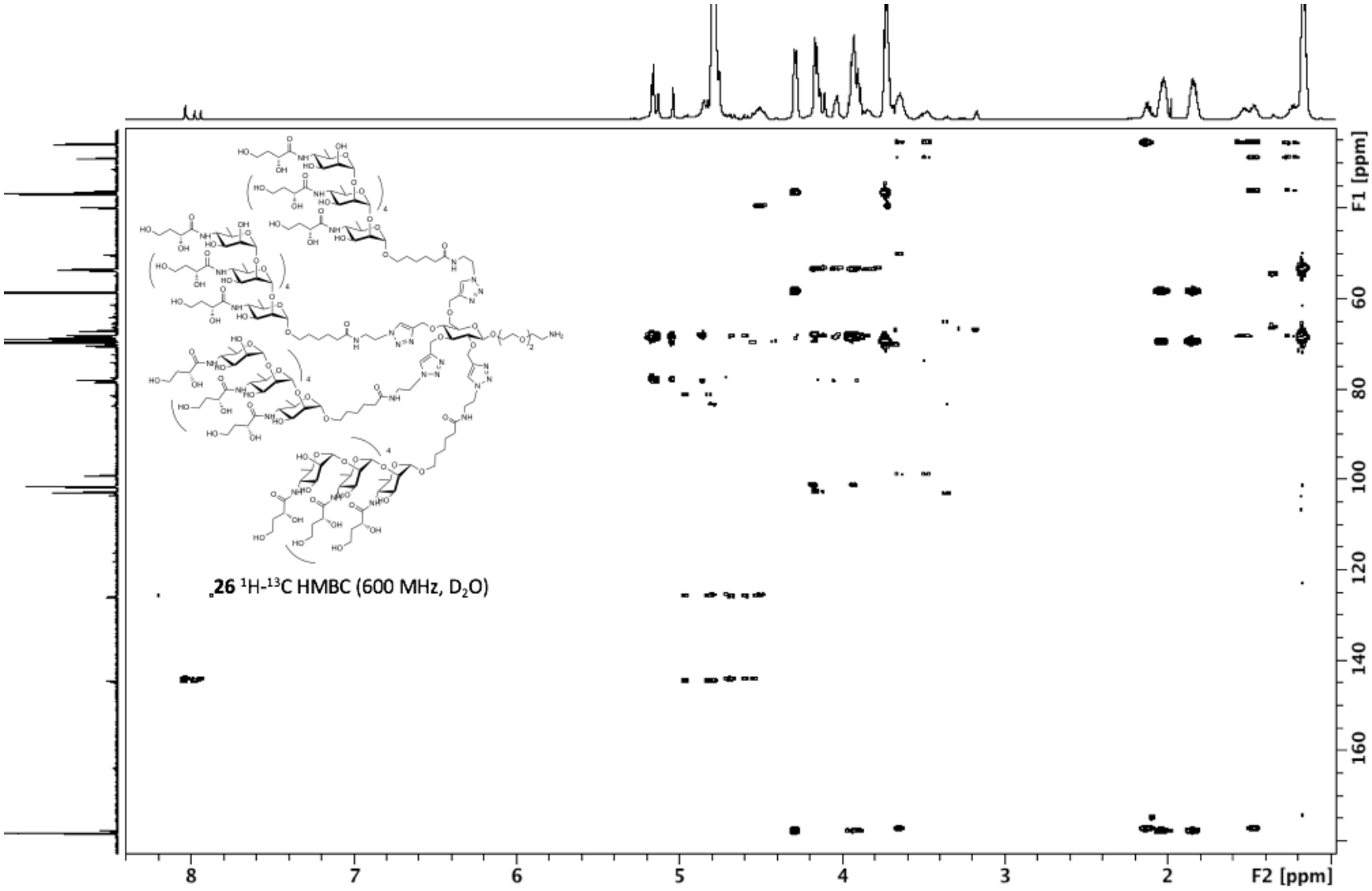
26 ^{13}C NMR (150 MHz, D_2O)


F1 [ppm]
F2 [ppm]
5
4
3
2
26 ^{1}H-^{1}H COSY (600 MHz, D_2O)


F1 [ppm]
F2 [ppm]
5
4
3
2
26 ^{1}H-^{1}H TOCSY (600 MHz, D_2O)

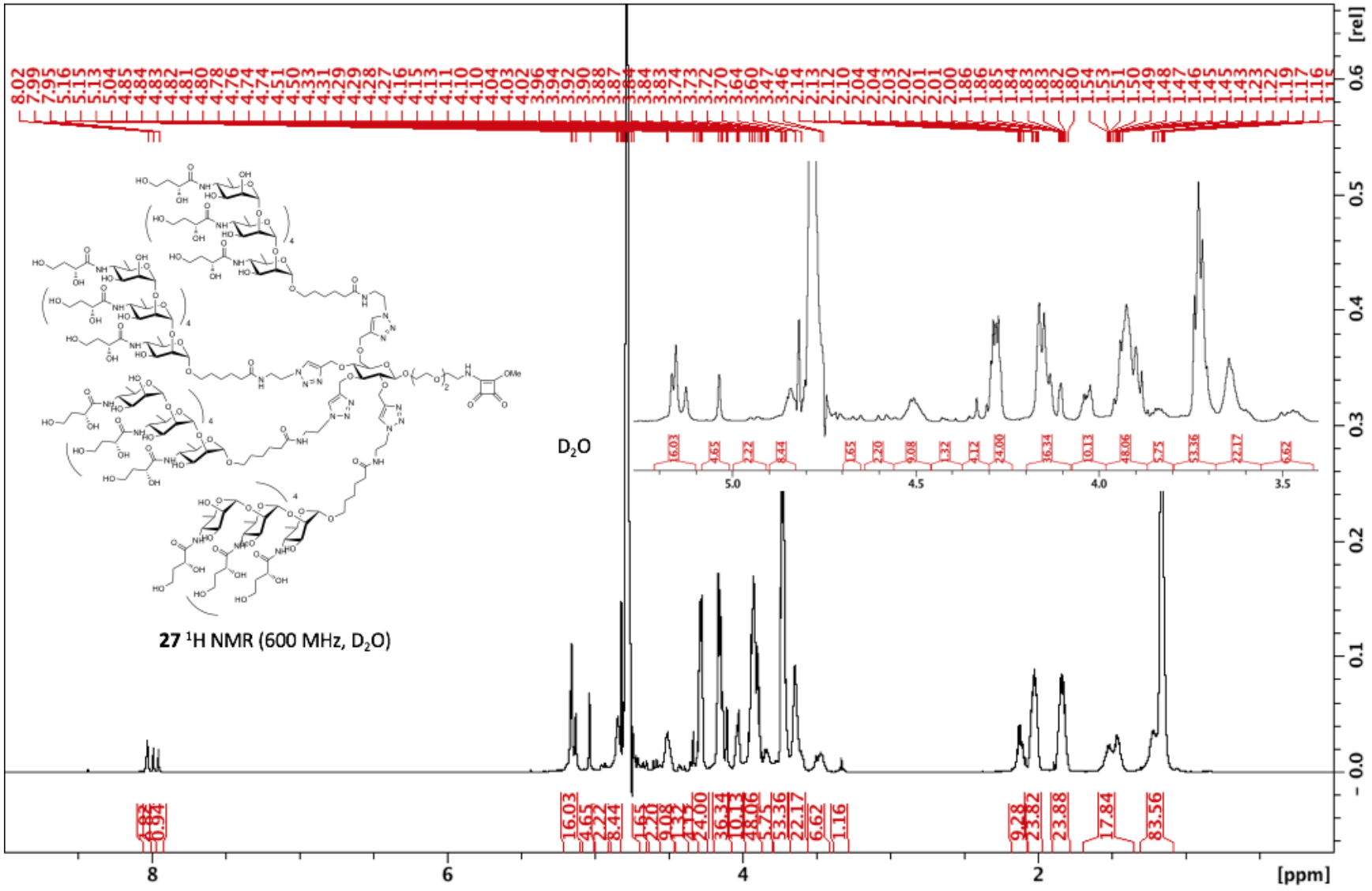


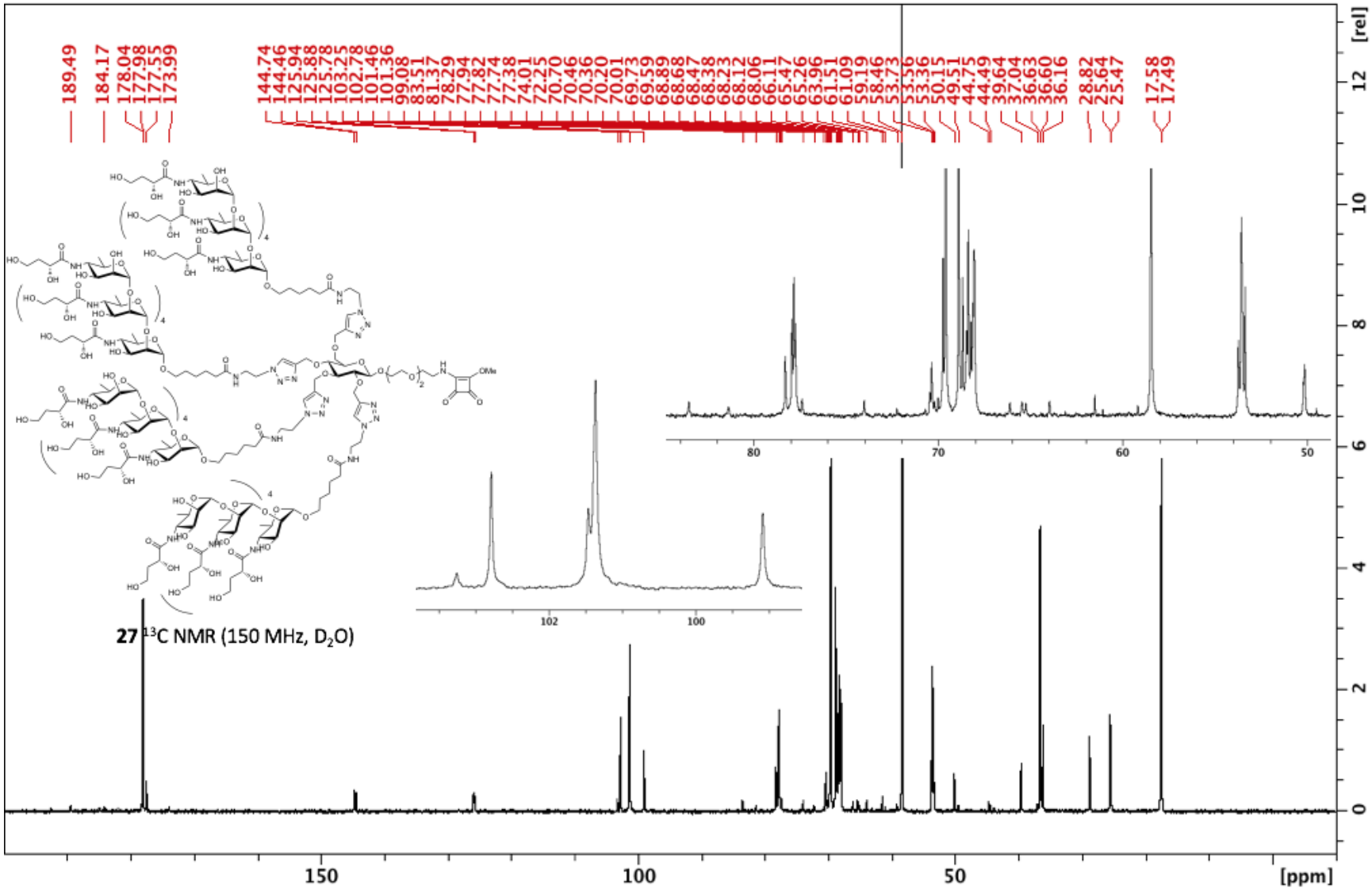
26 ^{1}H-^{13}C HSQC (600 MHz, D_2O)



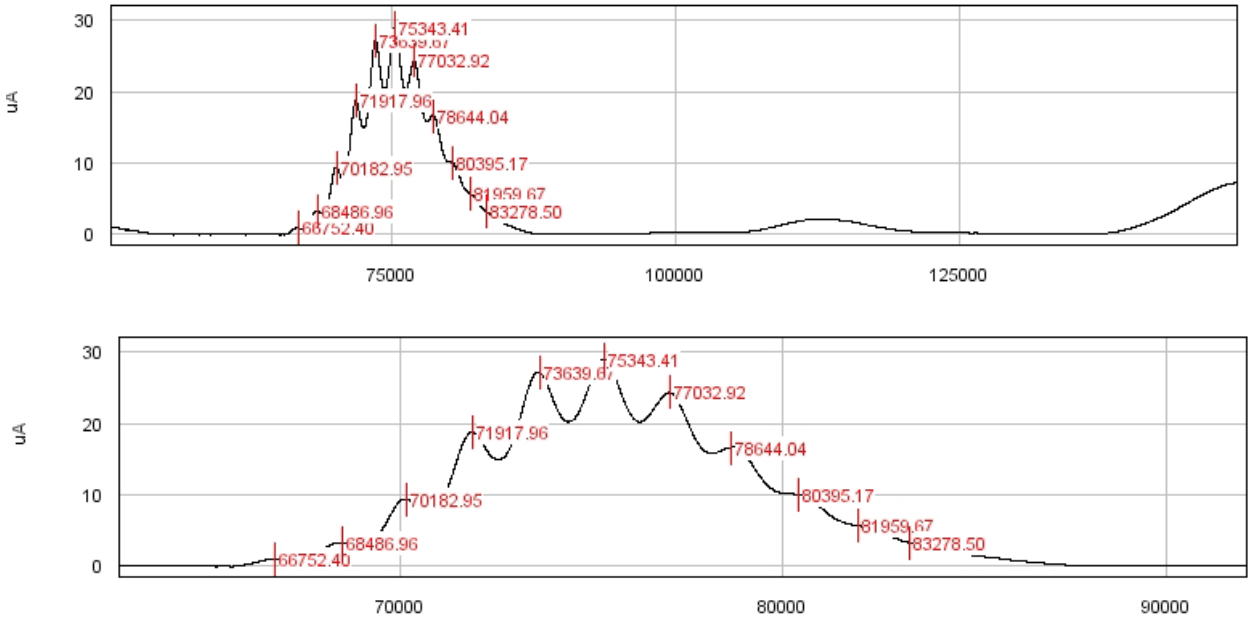
26 ^{1}H-^{13}C HMBC (600 MHz, D_2O)

Squarate hexasaccharide cluster **27**

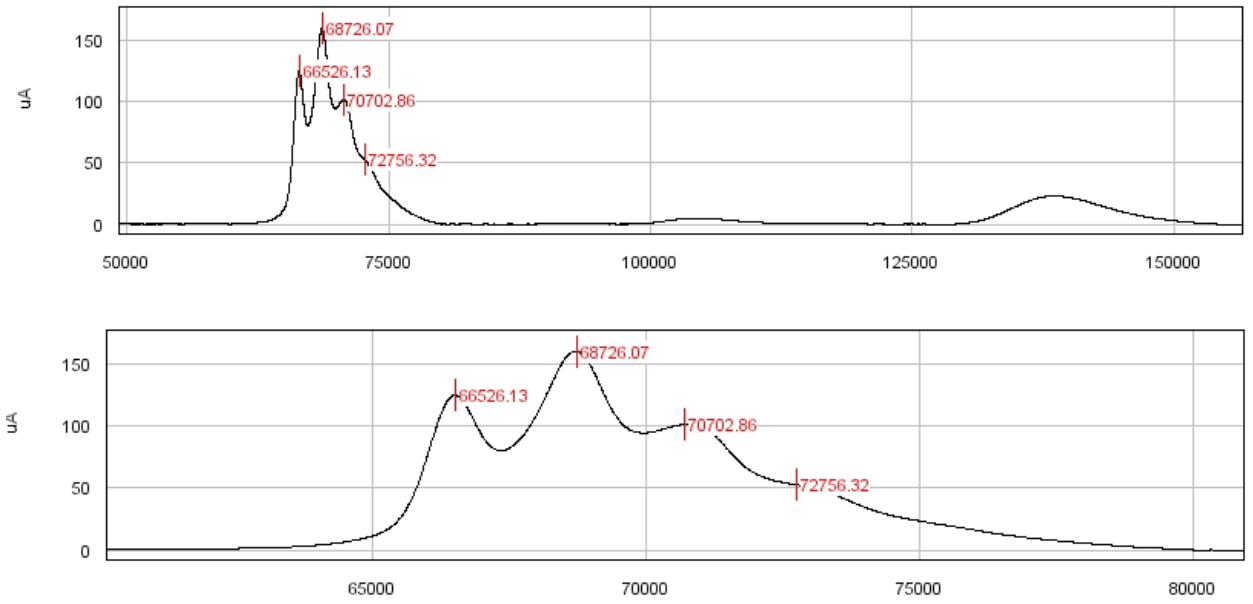



189.49
184.17
178.04
177.98
177.55
173.99
144.74
144.46
125.94
125.88
125.78
103.25
102.78
101.46
101.36
99.08
83.51
81.37
78.29
77.94
77.82
77.74
77.38
74.01
72.25
70.70
70.46
70.36
70.20
70.01
69.73
69.59
68.89
68.68
68.47
68.38
68.23
68.12
68.06
66.11
65.47
65.26
63.96
61.51
61.09
59.19
58.46
53.73
53.56
53.36
50.15
49.51
44.75
44.49
39.64
37.04
36.63
36.60
36.16
28.82
25.64
25.47
17.58
17.49
27 13C NMR (150 MHz, D2O)
[rel]
[ppm]

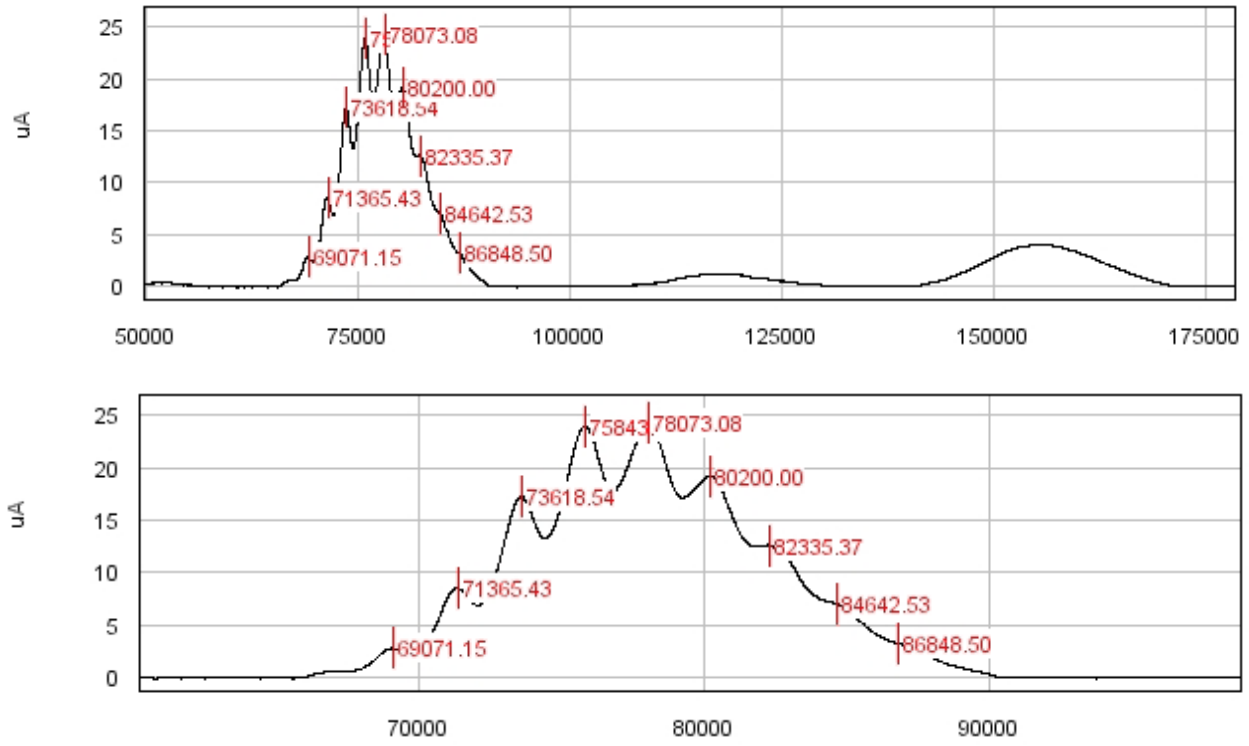
Glycoconjugate **28**



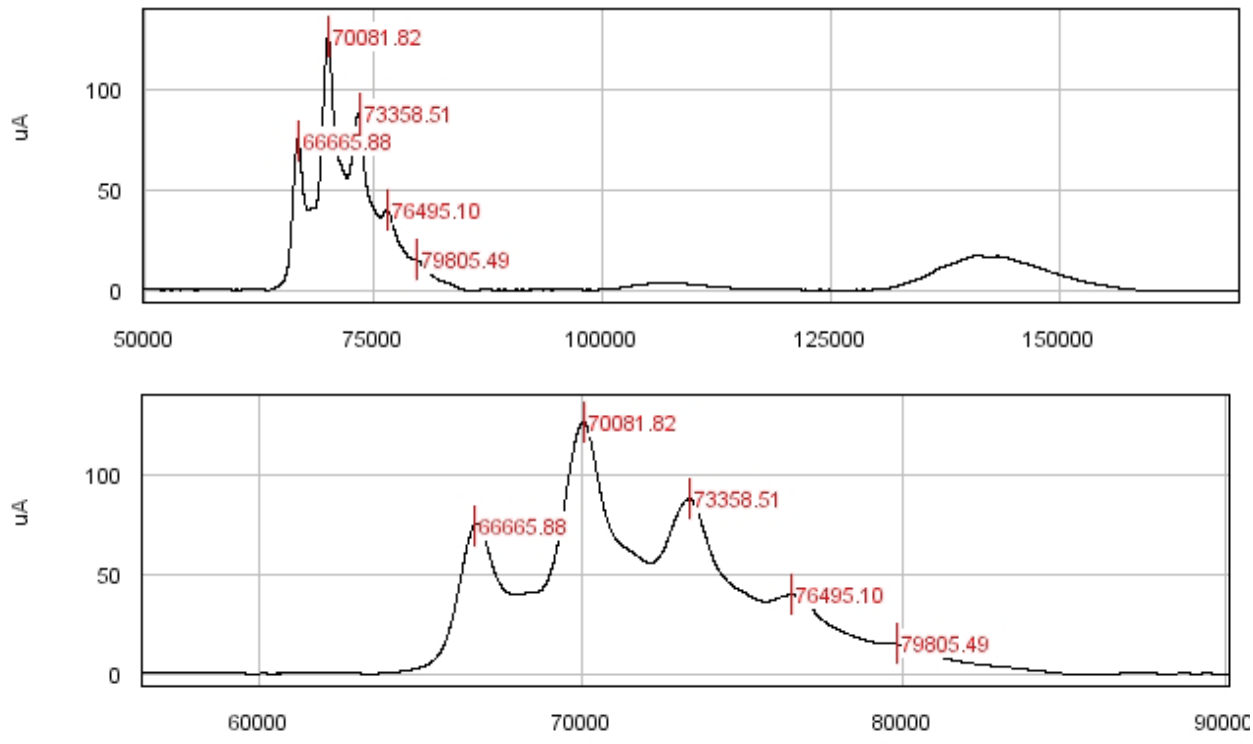
Glycoconjugate **29**



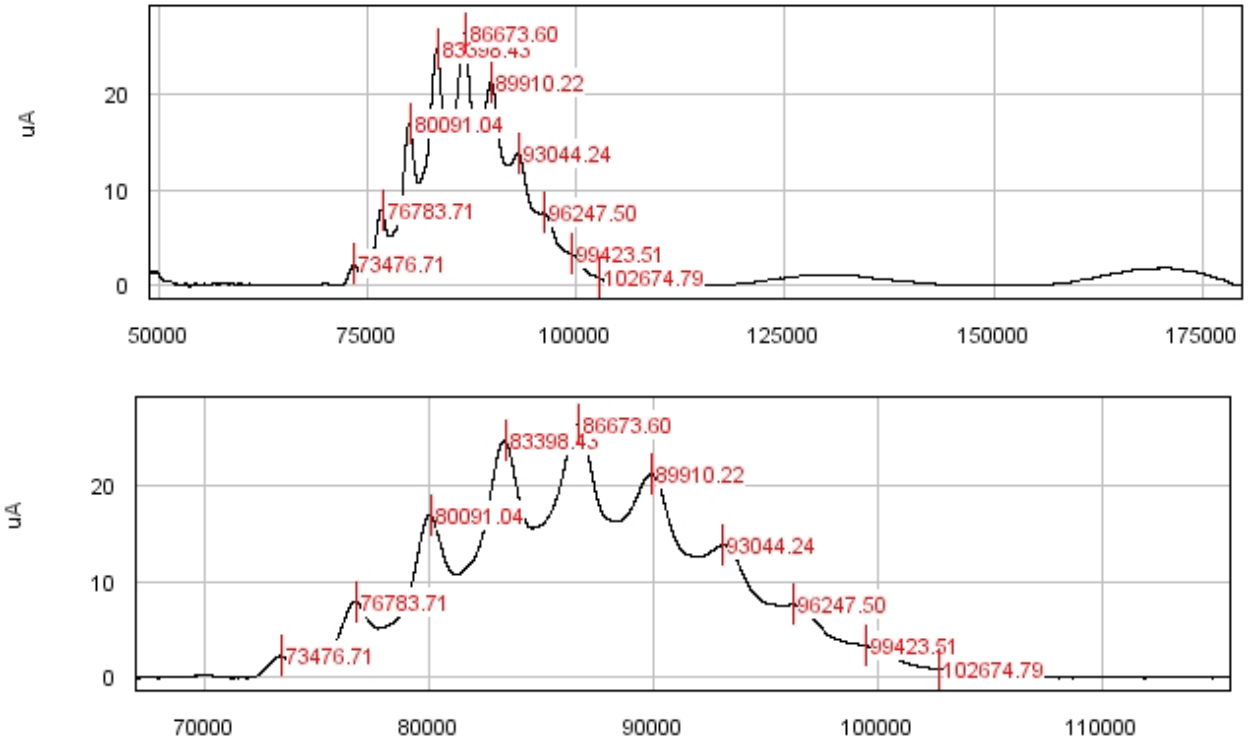
Glycoconjugate **30**



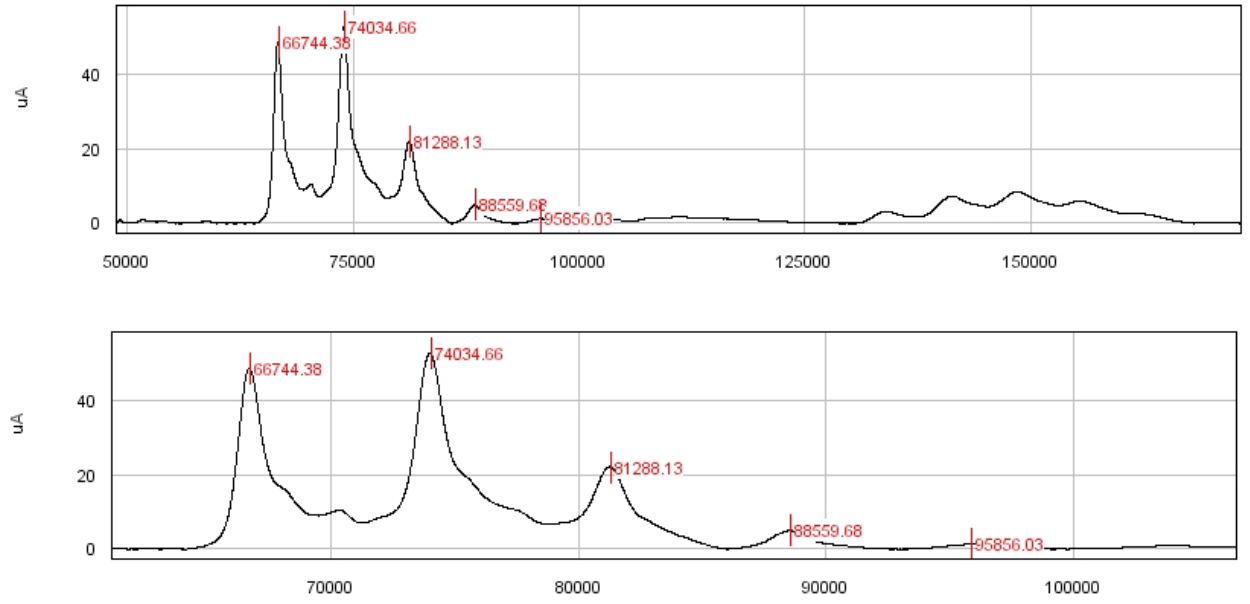
Glycoconjugate **31**



Glycoconjugate **32**



Glycoconjugate **33**



Glycoconjugate **34**