Supporting Information

for

Selectively charged and zwitterionic analogues of the smallest immunogenic structure of Streptococcus pneumoniae type 14

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Contents

Experimental procedures and characterization data of 10-23.

General procedure A for the de-*O*-isopropylidenation of 11-12 and 14-15:

The appropriate protected sugar (1 mmol) was dissolved in 70% aq AcOH (13 mL) and heated to 40 °C while stirring until TLC analysis (TLC, EtOAc or 9:1 $CHCl_3$-MeOH, 3-5 h) revealed the complete disappearance of the starting material and formation of a more retained product. The solution was then cooled to room temperature and coevaporated with toluene (4×20 mL) under diminished pressure. The crude product was purified by flash chromatography on silica gel.

General procedure B for the regioselective protection with *tert*-butyldimethylsilyl chloride (TBDMSCl) at C-6 of 16-19:

A solution of the approproate diol (**16-19**) (1 eq) in dry pyridine (7.0 mL) treated with TBDMSCl (2 eq) and the solution was left to react at room temeperature until TLC analysis (TLC, 1:1 hexane- EtOAc or EtOAc) showed complete disappearance of the starting material (2-4 h) and formation of a slower moving product. The reaction was diluted with $CHCl_3$, washed with satd aq $NaHCO_3$ and then brine. The organic phase was dried, filtered and concentrated under diminished pressure. The crude product was purified by flash chromatography on silica gel.

Methyl 2-acetamido-2-deoxy-4,6-*O*-isopropylidene-β-D-glucopyranoside (10).

A solution of known **8** [1] (5.37 g, 22.8 mmol) in dry DMF (83 mL) was cooled at 0 °C and treated with freshly distilled 2-methoxypropene (6.6 mL, 68.4 mmol, 3 eq) and camphorsulfonic acid (CSA, 530 mg, 2.28 mmol, 0.1 eq). The reaction mixture was stirred at room temperature until TLC analysis (8:2 $CHCl_3$-MeOH, 4 h) revealed the complete disappearance of the starting material. Et_3N (3 mL) was added, stirring was pursued for 30 min and concentrated under diminished pressure. Purification of the crude product by flash chromatography on silica gel (8:2 $CHCl_3$-MeOH) gave pure **10** (5.71 g, 91%) as a white foam, R_f 0.47 (8:2 $CHCl_3$-MeOH). Physic-chemical properties and NMR data were in agreement with those reported in the literature [2].

3-azidopropyl 2-acetamido-2-deoxy-4,6-*O*-isopropylidene-β-D-glucopyranoside (13).

A solution of known **9** [3] (2.96 g, 9.73 mmol) in dry DMF (33 mL) was cooled at 0 °C and treated with freshly distilled 2-methoxypropene (2.8mL, 29.2 mmol, 3 eq) and camphorsulfonic acid (CSA, 226 mg, .973 mmol, 0.1 eq). The reaction mixture was stirred at room temperature until TLC analysis (8:2 $CHCl_3$-MeOH, 2 h) revealed the complete disappearance of the starting material. Et_3N (3 mL) was added, stirring was pursued for 30 min and concentrated under diminished pressure. Purification of the crude product by flash chromatography on silica gel (EtOAc + 0.1% Et_3N) gave pure **13** (2.95 g, 88%) as a white foam, R_f 0.37 (9:1 $CHCl_3$-MeOH), $[\alpha]_D$ -46.5 (*c* 1.11 in $CHCl_3$), ^{1}H NMR (250.13 MHz, CD_3CN): δ 6.61 (d,1H, $J_{2,NH}$ 9.2 Hz, N*H*), 4.40 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1), 3.84-3.68 (m, 4H, H-6a, H-6b, CH_2O, OH-3), 3.63 (dd, 1H, $J_{2,3}$ 8.7 Hz, $J_{3,4}$ 9.5 Hz, H-3), 3.57-3.40 (m, 3H, H-2, H-4, CH_2O), 3.34 (t, 2H, J_{vic} 6.7 Hz, CH_2N_3), 3.18 (dt, 1H, $J_{4,5}$ 9.8 Hz, $J_{5,6a}$ $J_{5,6b}$ = 5.6 Hz, H-5), 1.90 (s, 3H, *Me*CO), 1.76 (m, 2H, CH_2), 1.46, 1.34 (2s, each 3H, CMe_2); ^{13}C NMR (62.9 MHz, CD_3CN): δ 171.6 (*C*=O), 102.6 (C-1), 100.2 (*C*Me_2), 74.8 (C-4), 73.1 (C-3), 68.1 (C-5), 67.1 (*C*H_2*O*), 62.6 (C-6), 57.6 (C-2), 48.8 (*C*H_2N_3), 29.6 (*C*H_2), 29.4, 19.4 (CMe_2), 23.3 (*Me*CO). Anal. Found: C, 48.84; H, 7.05; N, 16.29. Cal for $C_{14}H_{24}N_4O_6$ (344.37): C, 48.83; H, 7.03; N, 16.27.

Methyl 2-acetamido-3-*O*-benzoyl-2-*deoxy*-β-D-glucopyranoside (16)

A solution of known **10** [2] (520 mg, 1.89 mmol) in dry pyridine (6 mL) was cooled to 0°C, treated with BzCl (580 µL, 5.08 mmol, 2.7 eq) and stirred at 0°C until TLC analysis (EtOAc, 2.5 h) revealed the complete disappearance of the starting material and the formation of a faster moving product UV visible (R_f 0.56). The mixture was poured into icy water, stirred for 30 min and extracted with $CHCl_3$ (3×50 mL). The combined extracts were collected, washed with 1M HCl (10 mL) then satd aq $NaHCO_3$ (10 mL), dried and concentrated under diminished pressure. Purification of the crude product by flash chromatography on silica gel (25:75 hexane-EtOAc + 0.1% Et_3N) gave pure methyl 2-acetamido-3-*O*-benzoyl-2-deoxy-4,6-*O*-isopropylidene-β-D-glucopyranoside (**11**) (631 mg, 88%) as a white foam, R_f 0.23 (25:75 hexane-EtOAc), $[\alpha]_D$ -27.5 (c 1.1 in $CHCl_3$); ^{1}H NMR (250.13 MHz, CD_3CN): δ 7.98 (m, 2H, Ar-*H*), 7.63 (m, 1H, Ar-*H*), 7.48 (m, 2H, Ar-*H*), 6.56 (d, 1H, $J_{2,NH}$ 9.7 Hz, N*H*), 5.27 (dd, 1H, $J_{2,3}$ 10.2 Hz, $J_{3,4}$ 9.4 Hz, H-3), 4.56 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1), 4.01 (dd, 1H, H-2), 3.96 (dd, 1H, $J_{4,5}$ 9.7 Hz, H-4), 3.95-3.79 (m, 2H, H-6a, H-6b), 3.42 (m, 1H, H-5), 3.42 (s, 3H, OMe), 1.70 (s, 3H, *Me*CO), 1.44-1.27 (2s, each 3H, CMe_2); ^{13}C NMR (62.9 MHz, CD_3CN): δ 170.8

(CONH), 166.8 (PhCO), 134.3-129.5 (Ar-CH), 130.8 (Ar-C), 103.3 (C-1), 100.4 (*C*Me$_2$), 74.1 (C-3), 72.7 (C-4), 67.9 (C-5) , 62.6 (C-6), 57.3 (OMe), 55.2 (C-2), 29.3, 19.4 (C*Me$_2$*) 23.0 (MeCO). Anal. Found: C, 60.18; H, 6.67; N, 3.72. Calc for $C_{19}H_{25}NO_7$ (379.41): C, 60.15; H, 6.64; N, 3.69.

Hydrolysis of **11** (202 mg, 0.533 mmol) performed according to the general procedure A. The crude product was purified by flash chromatography (EtOAc + 0.1% Et$_3$N) to give pure the known diol **16** (174 mg, 96%) as a white solid, R_f 0.22 (9:1 $CHCl_3$-MeOH). Physic-chemical properties and NMR data were in agreement with those reported in the literature [4].

Methyl 2-acetamido-3-*O*-benzyl-2-*deoxy*-β-D-glucopyranoside (17)

Compound **10** (6.30 g, 22.9 mmol) was dissolved in THF-H_2O (99.5:0.5, 150 mL). Powdered KOH (5.10 g, 91.2 mmol, 4 eq) and 18-crown-6 (150 mg, 0.57 mmol, 0.025 eq) were added, and the resulting mixture was vigorously stirred at room temperature for 30 min at 0°C. Benzyl bromide (5.24 ml, 45.62 mmol, 2 eq) was added, and the reacting mixture was stirred at room temperature until TLC analysis (EtOAc, 4 h) revealed the complete disappearance of the starting material and the formation of a major faster-moving product (R_f 0.41). MeOH (2 mL) was added, the mixture was stirred for an additional 10 min, solvents were evaporated under diminished pressure and the residue was portioned between CH_2Cl_2 (40 mL) and H_2O (40 mL). The aqueous phase was extracted with CH_2Cl_2 (3×40 mL) and the collected organic layers were dried, filtered and concentrated under diminished pressure. Purification of the crude product by flash chromatography on silica gel (4:6 hexane-EtOAc + 0.1% Et$_3$N) gave pure methyl 2-acetamido-3-*O*-benzyl-2-deoxy-4,6-*O*-isopropylidene-β-D-glucopyranoside (**12**) (6.53 g, 78%) as a white solid, R_f 0.41 (EtOAc), $[\alpha]_D$ +22.6 (*c* 1.1 in $CHCl_3$), mp 172-174 °C (from EtOAc-hexane), ^{1}H NMR (250.13 MHz, CD_3CN): δ 7.39-7.22 (m, 5H, Ar-*H*), 6.63 (d, 1H, $J_{2,NH}$ 8.2 Hz, N*H*), 4.73, 4.56 (AB system, 2H, $J_{A,B}$ 11.7 Hz, C*H*$_2$Ph), 4.35 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1), 3.85 (dd, 1H, $J_{6a,6b}$ 10.2 Hz, $J_{5,6b}$ 5.6, H-6b), 3.76 (dd, 1H, $J_{5,6a}$=$J_{5,6b}$ 5.6 Hz, H-6a), 3.75 (m, 2H, H-2, H-4), 3.49 (dd, 1H, $J_{2,3}$ 8.9 Hz, $J_{3,4}$ 10 Hz, H-3), 3.37 (s, 3H, O*Me*), 3.22 (dt, 1H, $J_{4,5}$ 10.9 Hz, H-5), 1.85 (s, 3H, *Me*CON), 1.49, 1.37 (2s, each 3H, C*Me$_2$*); ^{13}C NMR (62.9 MHz, CD_3CN): δ 170.9 (C=O), 139.9 (Ar-C), 129.1, 128.6, 128.3 (Ar-CH), 103.7 (C-1), 100.1 (*C*Me$_2$), 80.0 (C-3), 75.3 (C-4), 74.2 (*C*H$_2$Ph), 67.7 (C-5), 62.7 (C-6), 57.1 (O*Me*), 55.5 (C-2), 29.5, 19.5 (C*Me$_2$*), 23.3

(*Me*CON). Anal. Found: C, 62.41; H, 7.43; N, 3.80. Calc for $C_{19}H_{27}NO_6$ (365.43): C, 62.45; H, 7.45; N, 3.83.

Hydrolysis of **12** (3.97 g, 10.86 mmol) performed according to the general procedure A. The crude product was purified by flash chromatography (EtOAc + 0.1% Et_3N) to give pure the known diol **17** (3.39 g, 96%) as a white solid, R_f 0.18 (9:1 $CHCl_3$- MeOH), mp 205-209 °C (from EtOAc), $[\alpha]_D$ -25.9 (*c* 1.1 in $CHCl_3$), Lit [5] $[\alpha]_D$ -26.6 (*c* 0.74 in CH_3OH). NMR data were in agreement with those reported in the literature [5].

3-Azidopropyl 2-acetamido-3-*O*-benzoyl-2-deoxy-β-D-glucopyranoside (18)

A solution of **13** (412 mg, 1.20 mmol) in dry pyridine (4.5 mL) was cooled to 0°C, treated with BzCl (0.43 mL, 3.71 mmol, 3.1 eq) and stirred at 0°C until TLC analysis (EtOAc, 2.5 h) revealed the complete disappearance of the starting material and the formation of a faster moving product UV visible (R_f 0.62). The mixture was poured into icy water, stirred for 15 min and extracted with $CHCl_3$ (3×10 mL). The combined extracts were collected, washed with 1M HCl (5 mL) then satd aq $NaHCO_3$ (5 mL), dried and concentrated under diminished pressure. The crude residue (520 mg, 97%) was constituted (NMR) exclusively by a 3-azidopropyl 2-acetamido-3-*O*-benzoyl-2-deoxy-4,6-*O*-isopropylidene-β-D-glucopyranoside (**14**) as a white foam, R_f 0.27 (1:1 hexane-EtOAc), ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 170.4 (Me*C*O), 167.0 (Ph*C*O), 133.4, 129.7, 128.4 (Ar-*C*H), 129.0 (Ar-*C*), 102.0 (C-1), 99.6 (*C*Me_2), 73.3 (C-3), 71.7 (C-4), 66.7 (C-5), 66.0 (*C*H_2O), 61.8 (C-6), 53.6 (C-2), 47.7 (*C*H_2N_3), 28.7 (*C*H_2), 28.6, 18.7 (*Me*$_2$C), 23.0 (*Me*CON). Hydrolysis of crude **14** (493 mg, 1.10 mmol) performed according to the general procedure A. The crude product was purified by flash chromatography (EtOAc + 0.1% Et_3N) to give pure the diol **18** (413 mg, 89% calculated from **13**) as a white foam, R_f 0.29 (EtOAc), $[\alpha]_D$ -3.54 (*c* 1.0 in MeOH); ^1H NMR (250.13 MHz, CD_3CN): δ 8.01 (m, 2H, Ar-*H*), 7.61 (m, 1H, Ar-*H*), 7.48 (m, 2H, Ar-*H*), 6.98 (d, 1H, $J_{2,NH}$ 8.5 Hz, N*H*), 5.23 (dd, 1H, $J_{2,3}$ 9.4 Hz, H-3), 4.62 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1), 4.38 (bt, 1H, OH-6), 3.96 (dd, 1H, H-2), 3.90-3.51 (m, 6H, H-4, H-6a, H-6b, OH-4, C*H*$_2$O), 3.45 (ddd, 1H, $J_{4,5}$ 10.3 Hz, $J_{5,6a}$ 2.6 Hz, $J_{5,6b}$ 6.8 Hz, H-5), 4.38 (bt, 1H, OH-6), 3.35 (t, 2H, J_{vic} 6.8 Hz, C*H*$_2$N$_3$), 1.79 (m, 2H, C*H*$_2$), 1.70 (s, 3H, *Me*CO); ^{13}C NMR (62.9 MHz, CD_3CN): δ 171.3 (Me*C*O), 167.2 (Ph*C*O), 134.1, 130.4, 129.4 (Ar*C*H), 130.9 (Ar-*C*), 101.6 (C-1), 77.5 (C-3), 77.0 (C-5), 69.5 (C-4), 66.9 (*C*H_2*O*), 62.3 (C-6), 54.7 (C-2),

48.8 (*C*H_2N_3), 29.5 (*C*H_2), 23.0 (*Me*CON). Anal. Found: C, 52.97; H, 5.95; N, 13.75. Calc for $C_{18}H_{24}N_4O_7$ (408.41): C, 52.94; H, 5.92; N, 13.72.

3-Azidopropyl 2-acetamido-3-*O*-benzyl-2-deoxy-β-D-glucopyranoside (19)

Compound **13** (300 mg, 0.87 mmol) was dissolved in THF-H_2O (99.5:0.5, 6.0 mL). Powdered KOH (195 mg, 3.49 mmol, 4 eq) and 18-crown-6 (5.75 mg, 0.022 mmol, 0.025 eq) were added, and the resulting mixture was vigorously stirred at room temperature for 30 min at 0°C. Benzyl bromide (0.21 ml, 1.74 mmol, 2 eq) was added, and the reacting mixture was stirred at room temperature until TLC analysis (EtOAc, 4 h) revealed the complete disappearance of the starting material and the formation of a major faster-moving product (R_f 0.57). MeOH (1 mL) was added, the mixture was stirred for an additional 10 min, solvents were evaporated under diminished pressure and the residue was portioned between CH_2Cl_2 (20 mL) and H_2O (20 mL). The aqueous phase was extracted with CH_2Cl_2 (4×20 mL) and the collected organic layers were dried, filtered and concentrated under diminished pressure. The crude residue (359 mg, 95%) was constituted (NMR) exclusively by a 3-azidopropyl 2-acetamido-3-*O*-benzyl-2-deoxy-4,6-*O*-isopropylidene-β-D-glucopyranoside (**15**) as a white solid, R_f 0.23 (1:1 hexane-EtOAc), δ ^{13}C NMR (62.9 MHz, CD_3CN): δ 170.7 (*C*=O), 140.1 (Ar-*C*), 129.1-128.3 (Ar-*C*H), 102.9 (C-1), 100.1 (*C*Me_2), 79.9 (C-3), 75.3 (C-4), 74.2 (*C*H_2Ph), 67.8 (C-5), 67.0 (*C*H_2*O*), 62.8 (C-6), 55.7 (C-2), 48.7 (*C*H_2N_3), 29.5 (*C*H_2), 29.3, 19.5 (*Me*$_2$*C*), 23.3 (*Me*CO).

Hydrolysis of crude **15** (359 mg, 0.826 mmol) performed according to the general procedure A. The crude product was purified by flash chromatography (EtOAc + 0.1% Et_3N) to give pure the diol **19** (313 mg, 91% calculated from **13**) as a white solid, R_f 0.15 (EtOAc), mp 156-158 °C (from EtOAc), $[\alpha]_D$ +1.68 (*c* 0.95 in MeOH), ^{1}H NMR (250.13 MHz, CD_3CN): δ 7.34-7.28 (m, 5H, Ar-*H*), 6.60 (d, 1H, $J_{2,NH}$ 9.1 Hz, N*H*), 4.79, 4.63 (AB system, 2H, $J_{A,B}$ 11.3 Hz, C*H*$_2$Ph), 4.40 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1), 3.84 (dt, 1H, J_{vic} 5.8 Hz, J_{gem} 10.2 Hz, C*H*$_2$O), 3.75-3.60 (m, 4H, H-2, H-6a, H-6b, OH-4), 3.53 (dt, 1H, J_{vic} 6.3 Hz, J_{gem} 10.2 Hz, C*H*$_2$O), 3.45 (m, 2H, H-3, H-4), 3.28 (ddd, 1H, $J_{4,5}$ 9.3 Hz, $J_{5,6a}$ 3.0 Hz, $J_{5,6b}$ 5.5 Hz, H-5), 3.35 (t, 2H, J_{vic} 6.8 Hz, C*H*$_2$N$_3$), 3.00 (bt, 1H, OH-6), 1.84 (s, 3H, *Me*CO), 1.77 (m, 2H, C*H*$_2$); ^{13}C NMR (62.9 MHz, CD_3CN): δ 170.9 (*C*=O), 140.1 (Ar-*C*), 129.1, 128.8, 128.3 (Ar-*C*H), 102.2 (C-1), 83.4 (C-3), 77.0 (C-5), 74.9 (*C*H_2Ph), 71.9 (C-4), 66.7 (*C*H_2*O*), 62.7 (C-6), 55.5 (C-2), 48.8 (*C*H_2N_3), 29.6 (*C*H_2), 23.3 (*Me*CON). Anal.

Found: C, 54.85; H, 6.67; N, 14.24. Calc for $C_{18}H_{26}N_4O_6$ (394.43): C, 54.81; H, 6.64; N, 14.20.

Methyl 2-acetamido-3-*O*-benzoyl-6-*O*-*tert*-butyldimethylsilyl-2-deoxy-β-D-glucopyranoside (20)

Silylation of **16** (159 mg, 0.468 mmol) performed according to the general procedure B. The crude product was purified by flash chromatography (35:65 hexane-EtOAc + 0.1 % Et_3N) to give pure the acceptor **20** (172 mg, 81%) as a white solid, R_f 0.70 (9:1 $CHCl_3$-MeOH), mp 165-172 °C (from EtOAc-hexane), $[\alpha]_D$ -18.8 (*c* 1.0 in $CHCl_3$), ^{1}H NMR (250.13 MHz, CD_3CN): δ 8.00 (m, 2H, Ar-*H*), 7.61 (m, 1H, Ar-*H*), 7.49 (m, 2H, Ar-*H*), 6.58 (d, 1H, $J_{2,NH}$ 9.6 Hz, N*H*), 5.17 (dd, 1H, $J_{2,3}$ 10.6 Hz, $J_{3,4}$ 9.0 Hz, H-3), 4.48 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1), 3.94 (dd, 1H, $J_{5,6b}$ 2.5 Hz, $J_{6a,6b}$ 11.3 Hz, H-6b), 3.90 (dd, 1H, $J_{5,6a}$ 4.7 Hz, H-6a), 3.89 (m, 1H, H-2), 3.82 (d, 1H, $J_{4,OH}$ 5.2 Hz, OH-4), 3.70 (ddd, 1H, $J_{4,5}$ 9.7 Hz, H- 4), 3.43 (ds, 3H, OMe), 3.42 (ddd, 1H, H-5), 1.67 (s, 3H, *Me*CO), 0.92 (s, 9H, SiC*Me*$_3$), 0.11, 0.10 (2s, each 3H, *Me*$_2$Si); ^{13}C NMR (62.9 MHz, CD_3CN): δ 170.8 (Me*C*O), 167.2 (Ph*C*O), 134.1, 130.4, 129.4 (Ar-*C*H), 131.1 (Ar-*C*), 102.5 (C-1), 77.8 (C-3), 77.1 (C-5), 69.4 (C-4), 63.5 (C-6), 56.9 (OMe), 54.6 (C-2), 26.2 (C*Me*$_2$), 23.0 (*Me*CO), 19.0 (Si*C*Me$_3$), -5.02, -5.12 (*Me*$_2$Si). Anal. Found: C, 58.28; H, 7.81; N, 3.12. Calc for $C_{22}H_{35}NO_7Si$ (453.61): C, 58.25; H, 7.78; N, 3.09.

Methyl 2-acetamido-3-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-2-deoxy-β-D-glucopyranoside (21)

Silylation of **17** (3.38 g, 10.4 mmol) performed according to the general procedure B. The crude product was purified by flash chromatography (1:9 hexane- EtOAc + 0.1 % Et_3N) to give pure the acceptor **21** (4.24 g, 93%) as a white solid, R_f 0.52 (EtOAc), $[\alpha]_D$ +1.01 (*c* 1.0 in $CHCl_3$); ^{1}H NMR (250.13 MHz, CD_3CN): δ 7.35-7.20 (m, 5H, Ar-*H*), 6.69 (d, 1H, $J_{2,NH}$ 9.4 Hz, N*H*), 4.79, 4.62 (AB system, J_{AB} 11.3 Hz, CH_2Ph), 4.28 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1), 3.91 (dd, 1H, $J_{6a,6b}$ 11.3 Hz, $J_{5,6b}$ 2.6 Hz, H-6b), 3.79-3.63 (m, 1H, H-2, H-6a, OH-4), 3.50-3.40 (m, 2H, H-3, H-4), 3.38 (s, 3H, O*Me*), 3.22 (ddd, 1H, $J_{4,5}$ 9.4 Hz, $J_{5,6a}$ 4.6 Hz, H-5), 1.83 (s, 3H, CH_3CON), 0.90 (s, 9H, C*Me*$_3$), 0.088, 0.086 (2s, each 3H, *Me*$_2$Si); ^{13}C NMR (62.9 MHz, CD_3CN): δ 171.0 (C=O), 140.2 (Ar-C), 129.1, 128.7, 128.3 (*Ar*-CH), 102.9 (C-1), 83.7 (C-3), 77.1 (C-5), 74.9 (*C*H_2Ph), 71.6 (C-4), 63.8 (C-6), 56.7 (O*Me*), 55.3 (C-2), 26.2 (C*Me*$_3$), 23.4 (*Me*CON), 18.9 (SiC*Me*$_3$), -5.06, -5.13

(*Me*$_2$Si). Anal. Found: C, 60.14; H, 8.45; N, 3.22. Calc for $C_{22}H_{37}NO_6Si$ (439.62): C, 60.11; H, 8.48; N, 3.19.

3-Azidopropyl 2-acetamido-3-*O*-benzoyl-6-*O*-*tert*-butyldimethylsilyl-2-deoxy-β-D-glucopyranoside (22)

Silylation of **18** (1.54 g, 3.77 mmol) performed according to the general procedure B. The crude product was purified by flash chromatography (1:1 hexane-EtOAc + 0.1 % Et_3N) to give the acceptor pure **22** (1.80 g, 91%) as a white foam, R_f 0.76 (EtOAc), $[\alpha]_D$ -11.2 (*c* 1.0 in $CHCl_3$), ^{1}H NMR (250.13 MHz, CD_3CN): δ 8.03-7.98 (m, 2H, Ar-*H*), 7.65-7.58 (m, 1H, Ar-*H*), 7.52-7.45 (m, 2H, Ar-*H*), 6.73 (d, 1H, $J_{2,NH}$ 9.6 Hz, N*H*), 5.19 (dd, 1H, $J_{2,3}$ 10.6 Hz, $J_{3,4}$ 9.0 Hz, H-3), 4.57 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1), 3.98-3.78 (m, 5H, H-2, H-6a, H-6b, OH, C*H*$_2$O), 3.69 (bt, 1H, $J_{4,5}$ 9.5 Hz, H-4), 3.43 (ddd, 1H, $J_{5,6a}$ 2.4 Hz, $J_{5,6b}$ 4.3 Hz, H-5), 3.57 (dt, 1H, J_{vic} 6.2 Hz, J_{gem} 10.2 Hz, C*H*$_2$O), 3.35 (t, 2H, J_{vic} 6.8 Hz, C*H*$_2$N$_3$), 1.79 (m, 2H, C*H*$_2$), 1.69 (s, 3H, *Me*CO), 0.92 (s, 9H, C*Me*$_3$), 0.10, 0.09 (2s, each 3H, *Me*$_2$Si); ^{13}C NMR (62.9 MHz, CD_3CN): δ 171.0 (Me*C*O), 167.2 (Ph*C*O), 134.1 130.4,129.4 (Ar*C*H), 131.0 (Ar-*C*), 101.6 (C-1), 77.6 (C-3), 77.1 (C-5), 69.4 (C-4), 66.9 (*C*H$_2$O), 63.5 (C-6), 54.7 (C-2), 48.8 (*C*H$_2$N$_3$), 29.5 (*C*H$_2$), 26.2 (C*Me*$_3$), 23.0 (*Me*CON), 18.9 (*C*Me$_3$), -5.02, -5.09 (*Me*$_2$Si). Anal. Found: C, 55.19; H, 7.36; N, 10.76. Calc for $C_{24}H_{38}N_4O_7Si$ (522.67): C, 55.15; H, 7.33; N, 10.72.

3-Azidopropyl 2-acetamido-3-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-2-deoxy-β-D-glucopyranoside (23)

Silylation of **19** (925 mg, 2.34 mmol) performed according to the general procedure B. The crude product was purified by flash chromatography (1:1 hexane- EtOAc + 0.1 % Et_3N) to give pure the acceptor **23** (1.14 g, 96%) as a white foam, R_f 0.25 (1:1 hexane-EtOAc), $[\alpha]_D$ +11.2 (*c* 1.3 in $CHCl_3$), ^{1}H NMR (250.13 MHz, CD_3CN): δ 7.34-7.24 (m, 5H, Ar-*H*), 6.73 (m, 1H, N*H*), 4.80, 4.64 (AB system, 2H, $J_{A,B}$ 11.3 Hz, C*H*$_2$Ph), 4.37 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1), 3.90 (dd, 1H, $J_{6a,6b}$ 11.0 Hz, $J_{5,6b}$ 4.1 Hz, H-6b), 3.85-3.63 (m, 4H, H-2, H-6a, OH-4, C*H*$_2$O), 3.54-3.45 (m, 3H, H-3, H-4, C*H*$_2$O), 3.33 (t, 2H, J_{vic} 6.8 Hz, C*H*$_2$N$_3$), 3.26 (ddd, 1H, $J_{4,5}$ 9.4 Hz, $J_{5,6a}$ 5.3 Hz, H-5), 1.86 (s, 3H, *Me*CO), 1.76 (m, 2H, C*H*$_2$), 0.91 (s, 9H, SiC*Me*$_3$), 0.093 (s, 6H, *Me*$_2$Si); ^{13}C NMR (62.9 MHz, CD_3CN): δ 170.9 (*C*O), 140.0 (Ar-*C*), 129.1, 128.7, 128.3 (Ar-*C*H), 102.1 (C-1), 83.6 (C-3), 77.1 (C-5), 71.6 (C-4), 66.6 (*C*H$_2$O), 63.8 (C-6), 55.4 (C-2), 48.8 (*C*H$_2$N$_3$), 29.6 (*C*H$_2$), 26.2 (C*Me*$_3$), 23.4

(*Me*CON), 18.9 (*C*Me$_3$), -5.03, -5.09 (*Me*$_2$Si). Anal. Found: C, 56.71; H, 7.96; N, 11.05. Calc for $C_{24}H_{40}N_4O_6Si$ (508.69): C, 56.67; H, 7.93; N, 11.01.

Experimental procedures and characterization data of 25-28

4-*O*-[Benzyl 2-*O*-benzyl-3,4-*O*-isopropylidene-β-D-galactopyranosyl uronate]-2,3:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose dimethyl acetal (25)

A solution of **24** [6] (700 mg, 1.17 mmol) in acetone (117 mL) was treated with 5% aq. $NaHCO_3$ (58.45 mL), KBr (278.3, 2.34 mmol, 2 eq) and TEMPO (255.8, 1.64 mmol, 1.4 eq) and the mixture was stirred at 0°C. After 10 min 13% aq. NaOCl (4.9 mL) was added and the mixture was stirred at room temperature until the starting material was completely reacted (15 min, TLC, EtOAc). The reaction mixture was repeatedly co-evaporated with toluene (5×30 mL) under diminished pressure. A solution of the crude product in dry DMF (30.7 mL) KF (680 mg, 11.6 mmol, 10 eq) was added, after 10 min at 0°C was treated with BnBr (497 µL, 5.85 mmol, 5 eq) and the reaction was stirred overnight at room temperature. The suspension was concentrated and the residue was portioned between CH_2Cl_2 (35 mL) and H_2O (35 mL). The reaction was concentrated under diminished pressure and the residue was portioned between CH_2Cl_2 (30 mL) and satd aq NaCl (30 mL). The aqueous phase was extracted with CH_2Cl_2 (3×50 mL) and the collected organic layers were dried over $MgSO_4$, filtered and concentrated under diminished pressure. Purification of the crude product by flash chromatography on silica gel (7:3 hexane-EtOAc) gave pure **25** (763.5 mg, 93%) as a colorless syrup, R_f 0.22 (7:3 hexane-EtOAc), $[\alpha]_D$ -12.0 (*c* 1.16 in $CHCl_3$), ^{1}H NMR (250.13 MHz, CD_3CN): δ 7.39-7.27 (m, 10H, Ar-*H*), 5.28, 5.13 (AB system, 2H, $J_{A,B}$ 12.6 Hz, COOC*H*$_2$Ph), 4.79, 4.69 (AB system, 2H, $J_{A,B}$ 12.0 Hz, OC*H*$_2$Ph), 4.68 (d, 1H, $J_{1',2'}$ 8.1 Hz, H-1'), 4.52 (m, 2H, H-5', H-2), 4.44 (dd, 1H, $J_{3',4'}$ 5.5 Hz, $J_{4',5'}$ 2.4 Hz, H-4'), 4.35 (d, 1H, $J_{1,2}$ 6.0 Hz, H-1), 4.23 (m, 1H, H-5), 4.20 (dd, 1H, $J_{2',3'}$ 7.1 Hz, H-3'), 4.13 (dd, 1H, $J_{2,3}$ 7.0 Hz, $J_{3,4}$ 1.2 Hz, H-3), 4.05 (dd, 1H, $J_{5,6b}$ 5.9 Hz, $J_{6a,6b}$ 8.7 Hz, H-6b), 3.94 (dd, 1H, $J_{5,6a}$ 6.4 Hz, H-6a), 3.82 (dd, 1H, $J_{4,5}$ 6.1 Hz, H-4), 3.34, 3.33 (2s, each 3H, O*Me*), 3.31 (dd, 1H, H-2'), 1.39, 1.30 (2s, each 3H, C*Me*$_2$), 1.27, 1.34 (2s, each 6H, 2×C*Me*$_2$); ^{13}C NMR (62.9 MHz, CD_3CN): δ 167.7 (C-6'), 139.4, 136.9 (2×Ar-*C*), 129.4-128.4 (Ar-*C*H), 110.9, 110.6, 109.2 (3×*C*Me$_2$), 106.1 (C-1), 103.1 (C-1'), 80.6 (C-2'), 79.6 (C-3'), 78.3 (C-3), 77.8 (C-4), 77.5 (C-5), 76.4 (C-2), 75.1 (C-4'), 74.2 (O*C*H$_2$Ph), 72.5 (C-5'), 67.1 (COO*C*H$_2$Ph),

66.5 (C-6), 55.8, 54.5 (2×O*Me*), 28.0, 27.7, 27.3, 26.9, 26.4, 25.5 (3×*Me*$_2$C). Anal Found: C, 63.26; H, 7.19. Calc for $C_{37}H_{50}O_{13}$ (702.79): C, 63.23; H, 7.17.

4-*O*-[Benzyl 2-*O*-benzyl-3,4-di-*O*-acetyl-β-D-galactopyranosyl uronate]-1,2,3,6-tetra-*O*-acetyl-α,β-D-glucopyranoside (26)

A solution of protected disaccharide **25** (810.4 mg, 1.153 mmol) in 80% aq AcOH (4 mL) was stirred at 80 °C until the starting material was completely reacted (TLC, 9:1 $CHCl_3$-MeOH, 4 h) with formation of a slower moving product. The solution was concentrated under diminished pressure by co-evaporation with toluene (4×30 mL), a mixture of 1:2 Ac_2O-Py was added, the solution was stirred overnight at room temperature and was concentrated under diminished pressure by co-evaporation with toluene (4×35 mL). Flash chromatographic purification on silica gel, eluting with 6:4 hexane- EtOAc, afforded pure **26** (808 mg, 89%) as an 1:1 α/β anomeric mixture, as established on the basis of the integration of the H-1 signals (^{1}H NMR), a white foam, R_f 0.76 (6:4 hexane-EtOAc), ^{1}H NMR (250.13 MHz, CD_3CN) of **α-26**: δ 6.18 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1); **β-26**: δ 5.81 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1); cluster of signals for both anomers: δ 7.44-7.21 (m, 10H, Ar-*H*), 5.53 (m, 1H, H-4'), 5.40 (m, 1H, H-3), 5.12, 5.07 (AB system, 2H, $J_{A,B}$ 12.1 Hz, COOC*H*$_2$Ph), 4.92 (m, 2H, H-2, H-3'), 4.73, 4.71, 4.58, 4.56 (2×AB systems, each 2H, $J_{A,B}$ 11.2, $J_{A,B}$ 11.5 Hz, C*H*$_2$Ph), 4.52-4.45 (m, 2H, H-1', H-5'), 4.40-4.31 (m, 2H, H-6a, H-6b), 4.12-3.95 (m, 2H, H-5, H-4), 3.46 (m, 1H, H-2'), 2.18, 2.12, 2.09, 2.06, 2.02 (5s, each 3H, 5×*Me*CO), 2.00, 1.98 (2s, each 6H, 4×*Me*CO), 1.89 (m, 9H, 3×*Me*CO); ^{13}C NMR (62.9 MHz, CD_3CN): of **α-26**: δ 89.5 (C-1); **β-26**: δ 92.2 (C-1); cluster of signals for both anomers: δ 171.4-170.0 (C=O), 167.9 (C-6'), 139.0, 138.9, 136.4 (Ar-*C*), 129.5-128.7 (Ar-*C*H), 103.4, 103.2 (C-1'), 77.4, 77.3 (C-2'), 76.6, 76.4 (C-4), 75.9 (*C*H$_2$Ph), 74.4, 71.8 (C-5), 72.9 (C-5'), 72.6 (C-3'), 72.5, 69.9 (C-3), 71.0, 70.2 (C-2), 69.5 (C-4'), 67.9 (COO*C*H$_2$Ph), 62.5, 62.2 (C-6), 21.1-20.5 (*Me*CO).

4-*O*-[Benzyl 2-*O*-benzyl-3,4-di-*O*-acetyl-β-D-galactopyranosyl uronate]-2,3,6-tri-*O*-acetyl-α,β-D-glucopyranose (27)

A solution of **26** in dry DMF (804.5 mg, 1.02 mmol) was treated with NH_2NH_2·AcOH (110.6 mg, 1.23 mmol, 1.2 eq) and the mixture was stirred at 60°C until the starting material was completely disappeared (TLC, 2:8 hexane-EtOAc, 30 min). The reaction was concentrated under diminished pressure and the residue was portioned between

CH_2Cl_2 (30 mL) and satd aq NaCl (30 mL). The aqueous phase was extracted with CH_2Cl_2 (3×50 mL) and the collected organic layers were dried over $MgSO_4$, filtered and concentrated under diminished pressure. Purification of the crude product by flash chromatography on silica gel (7:3 hexane-EtOAc) gave pure **27** (602 mg, 79%) as an 7:3 α/β anomeric mixture, as established on the basis of the integration of the C1 signals (^{13}C NMR), as a white foam, R_f 0.22 (1:1 hexane-EtOAc); ^1H NMR (250.13 MHz, CD_3CN): of **α-27**: δ 5.42 (dd, 1H, $J_{2,3}$ 9.3 Hz, $J_{3,4}$ 10.4 Hz, H-3), 5.23 (m, 1H, H-1), 3.44 (d, 1H, $J_{2',3'}$ 10.0 Hz, H-2'), 2.08, 2.02, 1.98, 1.86, 1.85 (5s, each 3H, 5×*Me*CO); **β-27**: δ 3.42 (d, 1H, $J_{2',3'}$ 9.9 Hz, H-2'), 2.06, 2.01, 1.99, 1.97, 1.87 (5s, each 3H, 5×*Me*CO); cluster of signals for both anomers: δ 7.37-7.24 (m, 10H, Ar-*H*), 5.47 (d, 1H, $J_{4',5'}$ 1.6 Hz, $J_{3',4'}$ 3.7 Hz, H-4'), 5.16, 5.08 (AB system, 2H, $J_{A,B}$ 12.1 Hz, COOCH_2Ph), 5.00 (d, 1H, H-3'), 4.78-4.68 (m, 3H, β-H-1, β-H-3, α,β-H-2), 4.73, 4.55 (AB system, 2H, $J_{A,B}$ 11.5, CH_2Ph), 4.48 (d, 1H, H-5'), 4.46 (m, 1H, H-1'), 4.38-4.11 (m, 3H, H-5, H-6a, H-6b), 3.92-3.79 (m, 1H, H-4); ^{13}C NMR (62.9 MHz, CD_3CN): of **α-27**: δ 103.4 (C-1'), 90.4 (C-1), 77.4 (C-4), 69.2 (C-5), 72.0, (C-2), 70.0 (C-3); **β-27**: δ 103.3 (C-1'), 95.2 (C-1), 77.1 (C-4), 73.6, 73.4, 73.0 (C-2, C-3, C-4); cluster of signals for both anomers: δ 171.5-170.6 (*C*=O), 167.1 (C-6'), 139.0, 136.4 (Ar-*C*), 129.5-128.7 (Ar-*C*H), 77.3 (C-2'), 75.9 (*C*H_2Ph), 72.9 (C-5'), 72.6 (C-3'), 69.6 (C-4'), 67.9 (COO*C*H_2Ph), 62.9 (C-6), 21.1-20.6 (*Me*CO).

4-*O*-[Benzyl 2-*O*-benzyl-3,4-di-*O*-acetyl-β-D-galactopyranosyl uronate]-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl trichloroacetimidate (28)

A solution of **27** (350 mg, 0.469 mmol) in dry CH_2Cl_2 (2.20 mL) was cooled at 0 °C and a large excess of CCl_3CN (282 mL, 2.81 mmol, 6 eq) and a catalytic amount of DBU (0.054 eq) were added. The reaction mixture was stirred at room temperature until TLC analysis (1:1 hexane-EtOAc, 30 min) showed the disappearance of the starting product and then was concentrated under diminished pressure. Purification of the crude by flash chromatography on silica gel (6:4 hexane-EtOAc) gave pure the donor **28** (380 mg, 91%) as a white foam, R_f 0.25 (6:4 hexane-EtOAc), $[\alpha]_D$ +59.6 (*c* 1.14 in $CHCl_3$), ^1H NMR (250.13 MHz, $CDCl_3$): δ 8.63 (s, 1H, NH), 7.34-7.15 (m, 10H, Ar-*H*), 6.46 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 5.58 (dd, 1H, $J_{4',5'}$ 1.4 Hz, $J_{3',4'}$ 3.5 Hz, H-4'), 5.60 (dd, 1H, $J_{2,3}$ 10.3 Hz, $J_{3,4}$ 9.1 Hz, H-3), 5.13, 5.04 (AB system, 2H, $J_{A,B}$ 11.9 Hz, COOCH_2Ph), 5.04 (dd, 1H, H-2), 4.92 (dd, 1H, $J_{2',3'}$ 10.2 Hz, H-3'), 4.67, 4.57 (AB system, 2H, $J_{A,B}$ 11.6, CH_2Ph),

4.40 (dd, 1H, $J_{6a,6b}$ 12.3 Hz, $J_{5,6b}$ 1.9 Hz, H-6b), 4.39 (dd, 1H, $J_{1',2'}$ 7.6 Hz, H-1'), 4.19 (d, 1H, H-5'), 4.13 (dd, 1H, H-6a), 4.07 (ddd, 1H, $J_{4,5}$ 10.1 Hz, $J_{5,6a}$ 3.7 Hz, H-5), 3.54 (dd, 1H, H-2'), 2.14, 1.99, 1.98, 1.85, 1.82 (5s, each 3H, 5×*Me*CO); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 170.7, 170.0, 169.9, 169.8, 169.5 (5×*C*=O), 165.4 (C-6'), 160.7 (*C*=NH), 137.7, 134.7 (2×Ar-*C*), 128.9-127-5 (Ar-*C*H), 102.5 (C-1'), 92.9 (C-1), 90.7 (*C*Cl_3), 76.4 (C-2'), 75.3 (*C*H_2Ph), 75.1 (C-4), 72.1 (C-5'), 71.9 (C-3'), 71.3 (C-5), 69.8, (C-2), 68.9 (C-3), 68.4 (C-4'), 67.3 (COO*C*H_2Ph, 61.0 (C-6), 20.8-20.2 (5×*Me*CO). Anal. Found: C, 51.25; H, 4.78; N, 1.59. Calc for $C_{38}H_{42}Cl_3NO_{17}$ (891.10): C, 51.22; H, 4.75; N, 1.57.

Experimental procedures and characterization data of 31-40

General procedure A for the 4-*O*-glycosylation. A mixture of the appropriate acceptors **20-23** (1.0 eq), excess of opportune donors **39,30** (1.5 eq) and activated AW-300 MS (800 mg) in dry CH_2Cl_2 (17 mL), was stirred for 30 min at room temperature. The suspension was then cooled to -30 °C and a solution of TMSOTf (0.5 eq) in dry CH_2Cl_2 was added. The reaction mixture was allowed to slowly attain room temperature with stirring until the appropriate acceptor was disappeared (17-24 h, TLC) and the formation of a higher major UV visible spot. Et_3N (0.5 mL) was added and after 30 min the mixture was filtered through a short pad of Celite, diluted with CH_2Cl_2 and concentrated under diminished pressure. Purification of crude product by flash chromatography on silica gel afforded pure the disaccharide **31-35**.

Methyl 4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-2-acetamido-3-*O*-benzoyl-6-*O*-*t*-butyldimethylsilyl-2-*deoxy*-β-D-glucopyranoside (31).

A solution of acceptor **20** (161 mg, 0.355 mmol, 1 eq) and donor **29** (262 mg, 0.532 mmol, 1.5 eq) in dry CH_2Cl_2 (5.5 mL) was treatment with TMSOTf (32 μL, 0.177 mmol, 0.5 eq) in dry CH_2Cl_2 (0.5 mL) in accordance with the general procedure A. The reaction was stirred until the acceptor was disappeared (12 h, TLC,). Purification of the crude product by flash chromatography on silica gel (3:7 hexane-EtOAc + 0.1% Et_3N) gave pure disaccharide **31** (173 mg, 62%) as a white foam, R_f 0.23 (3:7 hexane-EtOAc), $[\alpha]_D$ -11.95 (*c* 0.94 in $CHCl_3$), ^{1}H NMR (250.13 MHz, CD_3CN-$CDCl_3$): δ 8.01-7.98 (m, 2H, Ar-*H*), 7.61-7.54 (m, 1H, Ar-*H*), 7.49-7.41 (m, 2H, Ar-*H*), 6.48 (d, 1H, $J_{2,NH}$ 9.5 Hz, N*H*), 5.24 (dd, 1H, $J_{2,3}$ 10.5 Hz, $J_{3,4}$ 9.2 Hz, H-3), 5.11 (dd, 1H, $J_{3',4'}$ 3.1 Hz, $J_{4',5'}$ 1.1 Hz, H-4'), 4.86 (dd, 1H, $J_{2',3'}$ 10.3 Hz, H-3'), 4.82 (dd, 1H, $J_{1',2'}$ 7.3 Hz, H-2'), 4.67 (d,

1H, H-1'), 4.47 (d, 1H, $J_{1,2}$ 8.5, H-1), 4.10-3.98 (m, 2H, H-4, H-6b), 3.95-3.83 (m, 2H, H-2, H-6a), 3.69 (dt, 1H, $J_{5',6'a}$=$J_{5',6'b}$ 6.5 Hz, H-5'), 3.52 (dd, 1H, $J_{6'a,6'b}$ 11.2 Hz, H-6'b), 3.44 (m, 1H, H-5), 3.42 (s, 3H, OMe), 3.37 (dd, 1H, H-6'a), 2.01, 1.94, 1.86, 1.86 (4s, each 3H, 4×*Me*COO), 1.72 (s, 3H, *Me*CON), 0.94 (s, 9H, *Me*$_3$C), 0.13, 0.12 (2s, each 3H, *Me*$_2$Si); ^{13}C NMR (62.9 MHz, CD_3CN-$CDCl_3$): δ 170.7-170.2 (*C*=O), 166.5 (Ph*C*O), 133.9, 130.3, 129.2 (Ar-*C*H), 131.2 (Ar-*C*), 102.3 (C-1), 100.7 (C-1'), 75.8 (C-5), 75.5 (C-4), 74.4 (C-3), 71.5 (C-3'), 71.3 (C-5'), 69.9 (C-2'), 67.8 (C-4'), 61.9 (C-6), 61.5 (C-6'), 56.8 (O*Me*), 54.5 (C-2), 26.2 (*Me*$_3$C), 23.3 (*MeC*ON), 21.1-20.7 (4×*MeC*OO), 18.8 (Me$_3$*C*), -4.86, -5.09 (*Me*$_2$Si). Anal. Found: C, 55.18; H, 6.86; N, 1.82. Calc for $C_{36}H_{53}NO_{16}Si$ (783.90): C, 55.16; H, 6.82; N, 1.79.

Methyl 4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-2-acetamido-3-*O*-benzyl-6-*O*-*t*-butyldimethylsilyl-2-*deoxy*-β-D-glucopyranoside (32).

A solution of acceptor **21** (773 mg, 1.76 mmol, 1 eq) and donor **29** (1.26 g, 2.56 mmol, 1.5 eq) in dry CH_2Cl_2 (28 mL) was treatment with AW-300 MS (1.45 g) and TMSOTf (154 μL, 0.852 mmol, 0.5 eq) in dry CH_2Cl_2 (1.0 mL) in accordance with the general procedure A. The reaction was stirred until the acceptor was disappeared (12 h, TLC, 3:7 hexane-EtOAc). Purification of the crude product by flash chromatography on silica gel (3:7 hexane-EtOAc) gave pure disaccharide **32** (542 mg, 40%) as a white foam, R_f 0.38 (3:7 esano-EtOAc), $[\alpha]_D$ -8.75 (*c* 1.12 in $CHCl_3$), ^{1}H NMR (250.13 MHz, CD_3CN): δ 7.38-7.26 (m, 5H, Ar-*H*), 6.55 (d, 1H, $J_{2,NH}$ 9.3 Hz, N*H*), 5.32 (dd, 1H, $J_{4',5'}$ 0.8 Hz, $J_{3',4'}$ 3.3 Hz, H-4'), 5.09 (dd, 1H, $J_{1',2'}$ 7.5 Hz, $J_{2',3'}$ 10.4 Hz, H-2'), 5.01 (dd, 1H, H-3'), 4.86, 4.57 (AB system, 2H, $J_{A,B}$ 10.7 Hz, CH_2Ph), 4.85 (d, 1H, H-1'), 4.28 (d, 1H, $J_{1,2}$ 8.2 Hz, H-1), 4.03-3.85 (m, 6H, H-5', H-6'a, H-6'b, H-4, H-6a, H-6b), 3.69 (ddd, 1H, $J_{2,3}$ 8.7 Hz, H-2), 3.50 (dd, 1H, $J_{3,4}$ 10.1 Hz, H-3), 3.37 (s, 3H, O*Me*), 2.09, 2.04, 1.93, 1.91 (4s, each 3H, 4×*Me*COO), 1.84 (s, 3H, *Me*CON), 0.93 (s, 9H, *Me*$_3$C), 0.12 (s, 6H, *Me*$_2$Si); ^{13}C NMR (62.9 MHz, CD_3CN): δ 171.2-170.5 (5×C=O), 140.1 (Ar-*C*), 128.9-128.3 (Ar-*C*H), 102.8 (C-1), 100.7 (C-1'), 80.8 (C-3), 76.3 (C-4), 76.2 (C-5), 73.9 (CH_2Ph), 71.7 (C-5'), 71.7 (C-3'), 70.3 (C-2'), 68.3 (C-4'), 62.8 (C-6), 62.3 (C-6'), 56.6 (O*Me*), 26.3 (*Me*$_3$C), 23.3 (*Me*CON), 21.0-20.1 (4×*Me*COO), 18.9 (Me$_3$*C*), -4.80, -5.07 (Me$_2$Si). Anal. Found: C, 56.14; H, 7.18; N, 1.80. Calc for $C_{36}H_{55}NO_{15}Si$ (769.91): C, 56.16; H, 7.20; N, 1.82.

3-Azidopropyl 4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-2-acetamido-3-*O*-benzoyl-6-*O*-*t*-butyldimethylsilyl-2-*deoxy*-β-D-glucopyranoside (33).

A solution of acceptor **22** (215 mg, 0.41 mmol, 1 eq) and donor **29** (306 mg, 0.62 mmol, 1.5 eq) in dry CH_2Cl_2 (5.5 mL) was treatment with AW-300 MS (350 mg) and TMSOTf (38 μL, 0.21 mmol, 0.5 eq) in dry CH_2Cl_2 (0.5 mL) in accordance with the general procedure A. The reaction was stirred until the acceptor was disappeared (16 h, TLC, 1:1 hexane-EtOAc). Purification of the crude product by chromatography on silica (first 65:35 hexane-EtOAc + 0.1% Et_3N then 1:1 hexane-EtOAc + 0.1% Et_3N) gave pure disaccharide **33** (165 mg, 47%) as a white foam, R_f 0.27 (1:1 toluene-EtOAc), $[\alpha]_D$ -3.28 (*c* 0.97 in $CHCl_3$), ^{1}H NMR (250.13 MHz, CD_3CN): δ 8.02-7.95 (m, 2H, Ar-*H*), 7.62-7.56 (m, 1H, Ar-*H*), 7.50-7.42 (m, 2H, Ar-*H*), 6.52 (d, 1H, $J_{2,NH}$ 9.3 Hz, N*H*), 5.25 (dd, 1H, $J_{2,3}$ 10.5 Hz, $J_{3,4}$ 9.6 Hz, H-3), 5.11 (dd, 1H, $J_{3',4'}$ 3.1 Hz, $J_{4',5'}$ 1.0 Hz, H-4'), 4.90 (dd, 1H, $J_{2',3'}$ 10.3 Hz, H-3'), 4.82 (dd, 1H, $J_{1',2'}$ 7.5 Hz, H-2'), 4.69 (d, 1H, H-1'), 4.57 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1), 4.00 (t, 1H, $J_{4,5}$ 9.6 Hz, H-4), 3.92-3.79 (m, 4H, H-2, H-6a, H-6b, H-6'b), 3.90 (m, 1H, CH_2O), 3.71 (dt, 1H, $J_{5',6'a}$=$J_{5',6'b}$ 6.6 Hz, H-5'), 3.59-3.43 (m, 2H, H-5, H-6'a), 3.52 (dt, 1H, J_{vic} 6.7 Hz, J_{gem} 11.0 Hz, CH_2O), 3.35 (t, 2H, J_{vic} 6.7 Hz, CH_2N_3), 2.00, 1.93, 1.86, 1.85 (4s, each 3H, 4×*Me*COO), 1.79 (m, 2H, CH_2), 1.72 (s, 3H, *Me*CON), 0.94 (s, 9H, *Me*$_3$C), 0.14, 0.12 (2s, each 3H, *Me*$_2$Si); ^{13}CNMR (62.9 MHz, CD_3CN): δ 171.0-170.2 (5×*C*=O), 166.6 (Ph*C*O), 133.9, 130.4, 129.3 (Ar-*C*H), 131.3 (Ar-*C*), 101.5 (C-1), 100.8 (C-1'), 76.0 (C-5), 75.5 (C-4), 74.4 (C-3), 71.5 (C-3'), 71.4 (C-5'), 70.0 (C-2'), 67.9 (C-4'), 66.8 (*C*H_2O), 62.0 (C-6), 61.6 (C-6'), 54.7 (C-2), 48.8 (*C*H_2N_3), 29.5 (*C*H_2), 26.2 (*Me*$_3$C), 23.0 (*MeC*ON), 20.9-20.5 (4×*Me*COO), 18.8 (Me$_3$*C*), -4.86, -5.07 (*Me*$_2$Si). Anal. Found: C, 53.54; H, 6.65; N, 6.60. Calc for $C_{38}H_{56}N_4O_{16}Si$ (852.96): C, 53.51; H, 6.62; N, 6.57.

3-Azidopropyl 4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-2-acetamido-3-*O*-benzyl-6-*O*-*t*-butyldimethylsilyl-2-*deoxy*-β-D-glucopyranoside (34).

A solution of acceptor **23** (412 mg, 0.81 mmol, 1 eq) and donor **29** (599 mg, 1.22 mmol, 1.5 eq) in dry CH_2Cl_2 (12.5 mL) was treatment with AW-300 MS (621 mg) and TMSOTf (73 μL, 0.405 mmol, 0.5 eq) in accordance with the general procedure A. The reaction was stirred until the acceptor was disappeared (4 h, TLC, 7:3 CH_2Cl_2-EtOAc). Purification of the crude product by chromatography on silica (1:1 hexane-EtOAc +

0.1% Et_3N) gave pure disaccharide **34** (489 mg, 72%) as a white foam, R_f 0.16 (1:1 toluene-EtOAc), $[\alpha]_D$ -10.63 (*c* 1.05 in $CHCl_3$), ^1H NMR (250.13 MHz, CD_3CN): δ_H 7.38-7.24 (m, 5H, Ar-*H*), 6.51 (d, 1H, $J_{2,NH}$ 9.2 Hz, N*H*), 5.32 (dd, 1H, $J_{3',4'}$ 3.3 Hz, $J_{4',5'}$ 0.9 Hz, H-4'), 4.09 (dd, 1H, $J_{1',2'}$ 7.5 Hz, $J_{2',3'}$ 10.4 Hz, H-2'), 5.00 (dd, 1H, H-3'), 4.86-4.56 (AB system, 2H, $J_{A,B}$ 10.7 Hz, CH_2Ph), 4.85 (d, 1H, H-1'), 4.37 (d, 1H, $J_{1,2}$ 8.2 Hz, H-1), 4.04 (dd, 1H, $J_{5',6'b}$ 4.8 Hz, $J_{6'a,6'b}$ 12.5 Hz, H-6'b), 3.98 (dd, 1H, $J_{3,4}$ 10.2 Hz, $J_{4,5}$ 9.4 Hz, H-4), 3.94-3.83 (m, 4H, H-6a, H-6b, H-5', H-6'a), 3.80 (dt, 1H, J_{vic} 5.8 Hz, J_{gem} 10.2 Hz, CH_2O), 3.67 (ddd, 1H, $J_{2,3}$ 10.1 Hz, H-2), 3.52 (dt, 1H, J_{vic} 6.2 Hz, J_{gem} 10.2 Hz, CH_2O), 3.50 (dd, 1H, H-3), 3.34 (t, 2H, J_{vic} 6.8 Hz, CH_2N_3), 3.28 (dt, 1H, $J_{5,6a}$=$J_{5,6'b}$ 2.2 Hz, H-5), 1.95, 1.94, 1.92, 1.91 (4s, each 3H, 4×*Me*COO), 1.85 (s, 3H, *Me*CON), 1.79 (m, 2H, CH_2), 0.93(s, 9H, *Me*$_3$C), 0.12 (s, each 3H, *Me*$_2$Si); ^{13}C NMR (62.9 MHz, CD_3CN): δ 171.1, 170.9, 170.7, 170.6, 170.4 (5×*C*=O), 140.1 (Ar-*C*), 128.9, 128.2 (Ar-*C*H), 102.0 (C-1), 100.7 (C-1'), 80.6 (C-3), 76.3 (C-5), 76.2 (C-4), 73.8 (*C*H_2Ph), 71.7 (C-3'), 71.6 (C-5'), 70.3 (C-2'), 68.3 (C-4'), 66.6 (*C*H_2O), 62.3 (C-6'), 62.2 (C-6), 55.0 (C-2), 48.8 (*C*H_2N_3), 29.6 (*C*H_2), 26.3 (*Me*$_3$C), 23.3 (*MeC*ON), 21.0-20.8 (4×*Me*COO), 18.9 (Me$_3$*C*), -4.82, -5.08 (*Me*$_2$Si). Anal. Found: C, 54.44; H, 7.01; N, 6.72. Calc for $C_{38}H_{56}N_4O_{15}Si$ (838.98): C, 54.40; H, 6.97; N, 6.68.

Methyl 4-*O*-(2,3,4-tetra-*O*-acetyl-6-azido-6-*deoxy*-β-D-galactopyranosyl)-2-acetamido-3-*O*-benzyl-6-*O*-*t*-butyldimethyl-silyl-2-*deoxy*-β-D-glucopyranoside (35).

A solution of acceptor **21** (193 mg, 0.44 mmol, 1 eq) and donor **30** (315 mg, 0.66 mmol, 1.5 eq) in dry CH_2Cl_2 (7.5 mL) was treatment with AW-300 MS (380 mg) and TMSOTf (40 μL, 0.22 mmol, 0.5 eq) in dry CH_2Cl_2 (0.5 mL) in accordance with the general procedure A. The reaction was stirred until the acceptor was disappeared (12 h, TLC, 4:6 CH_2Cl_2-EtOAc). Purification of the crude product by chromatography on silica (7:3 AcOEt-CH_2Cl_2) gave pure disaccharide **35** (189 mg, 57%) as a white foam, R_f 0.39 (6:4 CH_2Cl_2-EtOAc), $[\alpha]_D$ -26.4 (*c* 1.0 in $CHCl_3$), ^1H NMR (250.13 MHz, CD_3CN): δ 7.37-7.31 (m, 5H, Ar-*H*), 6.70 (d, 1H, $J_{2,NH}$ 9.3 Hz, N*H*), 5.29 (dd, 1H, $J_{3',4'}$ 3.3 Hz, $J_{4',5'}$ 1.1 Hz, H-4'), 5.09 (dd, 1H, $J_{2',3'}$ 10.4 Hz, $J_{1',2'}$ 7.6 Hz, H-4'), 5.01 (dd, 1H, H-4'), 4.91, 4.58 (AB system, 2H, $J_{A,B}$ 10.9 Hz, CH_2Ph), 4.86 (d, 1H, H-1'), 4.29 (d, 1H, $J_{1,2}$ 8.1 Hz, H-1), 3.95 (dd, 1H, $J_{3,4}$ 10.0 Hz, $J_{4,5}$ 8.6 Hz, H-4), 3.64 (ddd, $J_{2,3}$ 8.4 Hz, 1H, H-2), 3.92-3.84 (m, 3H, H-5, H-6a, H-6b), 3.83 (m, 1H, H-5'), 3.48 (dd, 1H, H-3), 3.37 (s, 3H, O*Me*), 3.30 (dd, 1H, $J_{6'a,6'b}$ 12.3 Hz, $J_{5',6'b}$ 5.2 Hz, H-6'b), 3.09 (dd, 1H, $J_{5',6'a}$ 4.7 Hz, H-6'a), 2.09,

2.04, 1.92, (3s, each 3H, 3×*Me*COO), 1.85 (s, 3H, *Me*CON), 0.94 (s, 9H, *Me*$_3$C), 0.12, 0.11 (2s, each 3H, *Me*$_2$Si); ^{13}C NMR (62.9 MHz, CD_3CN): δ 171.2-170.5 (4×C=O), 140.1 (Ar-*C*), 128.9-128.2 (Ar-CH), 102.8 (C-1), 100.5 (C-1'), 80.8 (C-3), 76.2 (C-4), 76.1 (C-5), 74.6 (CH_2Ph), 73.1 (C-5'), 71.6 (C-3'), 70.3 (C-2'), 68.8 (C-4'), 62.1 (C-6), 56.6 (O*Me*), 55.1 (C-2), 50.9 (C-6'), 26.2 (*Me*$_3$C), 23.3 (*Me*CON), 21.0-20.7 (3×*Me*COO), 18.8 (*Me*$_3$C), -4.87, -5.12 (*Me*$_2$Si). Anal. Found: C, 54.27; H, 6.99; N, 7.49. Calc for $C_{34}H_{54}N_4O_{13}Si$ (752.89): C, 54.24; H, 6.96; N, 7.44.

General procedure B for the preparation of lactosamine acceptor 36-40.

A solution of appropriate protected disaccharide **31-35** (1 mmol) in 70% aq AcOH (58 mL) was stirred at 70 °C until the TLC analysis revealed the complete reaction of the starting material with formation of slower moving products. The solution was then cooled to room temperature and repeatedly co-evaporated with toluene (4×30 mL) under diminished pressure. Purification of the crude residue by flash chromatography on silica gel affording the lactosamine acceptors pure **36-40**.

Methyl 4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-2-acetamido-3-*O*-benzoyl-2-*deoxy*-β-D-glucopyranoside (36).

Selective hydrolysis of **31** (220 mg, 0.28 mmol) was performed according to the general procedure B. The reaction was stopped after 1 h (TLC, EtOAc) and the crude product was purified by flash chromatography (95:5 CH_3Cl-MeOH) to give acceptor pure **36** (156 mg, 83%) as a white foam, R_f 0.23 (95:5 $CHCl_3$-MeOH), $[\alpha]_D$ -8.13 (*c* 1.0 in $CHCl_3$), ^{1}H NMR (250.13 MHz, CD_3CN-$CDCl_3$): δ 8.03-7.96 (m, 2H, Ar-*H*), 7.61-7.54 (m, 1H, Ar-*H*), 7.48-7.40 (m, 2H, Ar-*H*), 6.64 (d,1H, $J_{2,NH}$ 9.5 Hz, N*H*), 5.26 (dd, 1H, $J_{2,3}$ 10.6 Hz, $J_{3,4}$ 9.1 Hz, H-3), 5.10 (dd, 1H, $J_{3',4'}$ 3.3 Hz, $J_{4',5'}$ 1.2 Hz, H-4'), 4.93 (dd, 1H, $J_{2',3'}$ 10.3 Hz, H-3'), 4.85 (dd, 1H, $J_{1',2'}$ 7.6 Hz, H-2'), 4.66 (d, 1H, H-1'), 4.51 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1), 4.02-3.90 (m, 2H, H-4, H-2), 3.82 (dd, 1H, $J_{6'a,6'b}$ 12.1 Hz, $J_{5',6'b}$ 2.0 Hz, H-6'b), 3.71-3.63 (m, 2H, H-6'a, H-6b), 3.51-3.40 (m, 3H, H-5', H-5, OH-6), 3.44 (s, 3H, OMe), 3.31 (dd, 1H, $J_{6a,6b}$ 11.0 Hz, $J_{5,6a}$ 6.0 Hz, H-6a), 2.02, 1.91, 1.88, 1.86 (4s, each 3H, *Me*COO), 1.72 (s, 3H, *Me*CON); ^{13}C NMR (62.9 MHz, CD_3CN-$CDCl_3$): δ 170.8-170.2 (5×*MeC*O), 166.4 (Ph*C*O), 133.8, 130.2, 129.1 (Ar-*C*H), 130.9 (Ar-*C*), 102.2 (C-1), 101.1 (C-1'), 76.2 (C-4), 75.7 (C-5), 74.6 (C-3), 71.3 (C-3'), 70.9 (C- 5'), 69.8 (C-2'), 67.5 (C-4'), 61.0 (C-6), 60.7 (C-6'), 56.0 (*Me*O), 54.5 (C-2), 23.1 (*MeC*ON), 20.9, 20.7,

20.6, 20.5 (4×*Me*COO). Anal. Found: C, 53.83; H, 5.89; N, 2.12. Calc for $C_{30}H_{39}NO_{16}$ (669.63): C, 53.81; H, 5.87; N, 2.09.

Methyl 4-O-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-2-acetamido-3-*O*-benzyl-2-*deoxy*-β-D-glucopyranoside (37).

Selective hydrolysis of **32** (525 mg, 0.68 mmoli) was performed according to the general procedure B. The reaction was stopped after 2 h (TLC, EtOAc) and the crude product was purified by flash chromatography (95:5 CH_3Cl-MeOH) to give acceptor pure **37** (371 mg, 83%) as a white foam, R_f 0.22 (3:7 hexane-EtOAc), $[\alpha]_D$ -6.13 (*c* 1.06 in $CHCl_3$), ^{1}H NMR (250.13 MHz, CD_3CN): δ 7.37-7.21 (m, 5H, Ar-*H*), 6.59 (d, 1H, $J_{2,NH}$ 9.3 Hz, N*H*), 5.30 (dd, 1H, $J_{3',4'}$ 3.1 Hz, $J_{4',5'}$ 0.9 Hz, H-4'), 5.13-5.01 (m, 2H, H-2', H-3'), 4.86, 4.56 (AB system, 2H, $J_{A,B}$ 10.8 Hz, CH_2Ph), 4.80 (d, 1H, $J_{1',2'}$ 7.9 Hz, H-1'), 4.32 (d, 1H, $J_{1,2}$ 8.2 Hz, H-1), 4.02-3.83 (m, 4H, H-5', H-6'a, H-6'b, H-4), 3.81-3.62 (m, 3H, H-2, H-6a, H-6b), 3.53 (dd, 1H, $J_{2,3}$ 8.7 Hz, $J_{3,4}$ 10.1 Hz, H-3), 3.40 (s, 3H, OMe), 3.30 (ddd, 1H, $J_{4,5}$ 9.5 Hz, $J_{5,6a}$ 2.3 Hz, $J_{5,6a}$ 4.3 Hz, H-5), 3.10 (bt, 1H, OH-6), 2.09, 2.04, 1.91, 1.89 (4s, each 3H, 4×*Me*COO), 1.84 (s, 3H, *Me*CON); ^{13}C NMR (62.9 MHz, CD_3CN): δ 171.0, 170.9, 170.8, 170.7, 170.4 (5×C=O), 139.9 (Ar-*C*), 128.9-128.1 (Ar-*C*H), 102.8 (C-1), 101.0 (C-1'), 80.9 (C-3), 77.1 (C-4), 76.2 (C-5), 73.9 (*C*H_2Ph), 71.6 (C-3'), 71.3 (C-5'), 70.3 (C-2'), 68.1 (C-4'), 61.9 (C-6'), 61.1 (C-6), 56.8 (O*Me*), 54.9 (C-2), 23.3 (*Me*CON), 20.9-20.8 (4×*Me*COO). Anal. Found: C, 54.99; H, 6.34; N, 2.18. Calc for: $C_{30}H_{41}NO_{15}$ (655.65): C, 54.96; H, 6.30; N, 2.14.

3-Azidopropyl 4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-2-acetamido-3-*O*-benzoyl-2-*deoxy*-β-D-glucopyranoside (38).

Selective hydrolysis of **33** (290 mg, 0.34 mmol) was performed according to the general procedure B. The reaction was stopped after 2 h (TLC, EtOAc) and the crude product was purified by flash chromatography (1:9 hexane-EtOAc) to give acceptor pure **38** (242 mg, 96%) as a white foam, R_f 0.34 (EtOAc), $[\alpha]_D$ -15.58 (*c* 1.2 in $CHCl_3$), ^{1}H NMR (250.13 MHz, CD_3CN): δ 8.04-8.00 (m, 2H, Ar-*H*), 7.62-7.54 (m, 1H, Ar-*H*), 7.51-7.42 (m, 2H, Ar-*H*), 6.58 (d,1H, $J_{2,NH}$ 9.5 Hz, N*H*), 5.27 (dd, 1H, $J_{2,3}$ 10.6 Hz, $J_{3,4}$ 9.2 Hz, H-3), 5.10 (dd, 1H, $J_{3',4'}$ 3.4 Hz, $J_{4',5'}$ 1.2 Hz, H-4'), 4.95 (dd, 1H, $J_{2',3'}$ 10.4 Hz, H-3'), 4.84 (dd, 1H, $J_{1',2'}$ 7.7 Hz, H-2'), 4.64 (d, 1H, H-1'), 4.60 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1), 3.96 (dd, 1H, $J_{4,5}$ 9.8 Hz, H-4), 3.89 (m, 1H, H-2), 3.84 (m, 1H, CH_2O), 3.78 (m, 1H, H-6'b), 3.69

(m, 1H, H-6'a), 3.69 (m, 1H, H-5'), 3.57 (dt, 1H, J_{vic} 6.3 Hz, J_{gem} 10.3 Hz, CH_2O), 3.46 (ddd, 1H, $J_{6a,6b}$ 11.1 Hz, $J_{5,6b}$ 7.4 Hz, H-6b), 3.44 (m, 1H, H-5), 3.28 (m, 1H, H-6a), 3.36 (t, 2H, J_{vic} 6.8 Hz, CH_2N$_3$), 3.10 (bt, 1H, $J_{OH,6a}$=$J_{OH,6b}$ 5.0 Hz, OH-6), 2.02, 1.91, 1.89, 1.86 (4s, each 3H, 4×*Me*COO), 1.78 (m, 2H, CH_2), 1.71 (s, 3H, *Me*CON); ^{13}C NMR (62.9 MHz, CD$_3$CN): δ 171.0-170.5 (5×*C*=O), 166.6 (Ph*C*O), 134.1, 130.4, 129.4 (Ar-*C*H), 131.2 (Ar-*C*), 101.5 (C-1), 101.3 (C-1'), 76.5 (C-4), 76.0 (C-5), 74.7 (C-3), 71.5 (C-3'), 71.1 (C-5'), 70.0 (C-2'), 67.8 (C-4'), 67.0 (*C*H$_2$O), 61.2 (C-6), 60.9 (C-6'), 54.8 (C-2), 48.8 (*C*H$_2$N$_3$), 29.5 (*C*H$_2$), 23.0 (*Me*CON), 20.9-20.6 (4×*Me*COO). Anal. Found: C, 52.06; H, 5.76; N, 7.62. Calc for C$_{32}$H$_{42}$N$_4$O$_{16}$ (738.70): C, 52.03; H, 5.73; N, 7.58.

3-Azidopropyl 4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-2-acetamido-3-*O*-benzyl-2-*deoxy*-β-D-glucopyranosyde (39).

Selective hydrolysis of **34** (135 mg, 0.161 mmol) was performed according to the general procedure B. The reaction was stopped after 1.5 h (TLC, EtOAc) and the crude product was purified by flash chromatography (1:9 hexane-EtOAc) to give acceptor pure **39** (94 mg, 81%) as a white foam, R_f 0.28 (EtOAc), [α]$_D$ -9.9 (*c* 1.10 in CHCl$_3$), ^{1}H NMR (250.13 MHz, CD$_3$CN): δ 7.36-7.25 (m, 5H, Ar-*H*), 6.60 (d,1H, $J_{2,NH}$ 9.3 Hz, N*H*), 5.30 (dd, 1H, $J_{3',4'}$ 3.1 Hz, $J_{4',5'}$ 0.9 Hz, H-4'), 5.12-5.03 (m, 2H, H-2', H-3'), 4.86, 4.57 (AB system, 2H, $J_{A,B}$ 10.8 Hz, *CH*$_2$Ph), 4.81 (d, 1H, $J_{1',2'}$ 7.9 Hz, H-1'), 4.40 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1), 4.01 (M, 1H, CH_2O), 3.98 (m, 1H, H-5'), 3.91-380 (m, 3H, H-4, H-6'a, H-6'b), 3.79-3.65 (m, 2H, H-6a, H-6b), 3.71 (m, 1H, $J_{2,3}$ 8.7 Hz, H-2), 3.53 (dd, 1H, $J_{3,4}$ 10.2 Hz, H-3), 3.52 (dt, 1H, J_{vic} 6.4 Hz, J_{gem} 10.2 Hz, CH_2O), 3.34 (t, 2H, J_{vic} 6.7 Hz, CH_2N$_3$), 3.30 (ddd, 1H, $J_{4,5}$ 9.5 Hz, $J_{5,6a}$ 2.3 Hz, $J_{5,6b}$ 4.4 Hz, H-5), 2.09, 2.04, 1.91, 1.89 (4s, each 3H, 4×*Me*COO), 1.84 (s, 3H, *Me*CON), 1.77 (m, 2H, CH_2); ^{13}C NMR (62.9 MHz, CD$_3$CN): δ 171.1-170.5 (5×*C*=O), 140.O (Ar-*C*), 128.9-128.2 (Ar-*C*H), 102.0 (C-1), 101.1 (C-1'), 80.9 (C-3), 77.2 (C-4), 76.5 (C-5), 74.0 (*C*H$_2$Ph), 71.6 (C-3'), 71.4 (C-5'), 70.3 (C-2'), 68.2 (C-4'), 66.8 (*C*H$_2$O), 62.0 (C-6'), 61.2 (C-6), 55.1 (C-2), 48.8 (*C*H$_2$N$_3$), 29.6 (*C*H$_2$), 23.3 (*Me*CON), 21.0-20.8 (4×*Me*CO). Anal. Found: C, 52.06; H, 6.15; N, 7.76. Calc for C$_{32}$H$_{44}$N$_4$O$_{15}$ (724.28): C, 52.03; H, 6.12; N, 7.73.

Methyl 4-*O*-(2,3,4-tetra-*O*-acetyl-6-azido-6-*deoxy*-β-D-galactopyranosyl)-2-acetamido-3-*O*-benzyl-2-*deoxy*-β-D-glucopyranoside (40).

Selective hydrolysis of **35** (158 mg, 0.21 mmol) was performed according to the general procedure B. The reaction was stopped after 1 h (TLC, EtOAc) and the crude product was purified by flash chromatography (1:9 hexane-EtOAc) to give acceptor pure **40** (123 mg, 92%) as a white foam, R_f 0.27 (95:5 EtOAc-MeOH), $[\alpha]_D$ -14.5 (*c* 1.0 in $CHCl_3$), ^{1}H NMR (250.13 MHz, CD_3CN): δ 7.36-7.30 (m, 5H, Ar-*H*), 6.73 (d, 1H, $J_{2,NH}$ 9.3 Hz, NH), 5.28 (dd, 1H, $J_{3',4'}$ 3.0 Hz, $J_{4',5'}$ 1.1 Hz, H-4'), 5.12-5.02 (m, 2H, H-2', H-3'), 4.90, 4.57 (AB system, 2H, $J_{A,B}$ 10.9 Hz, CH_2Ph), 4.81 (d, 1H, $J_{1',2'}$ 7.9 Hz, H-1'), 4.30 (d, 1H, $J_{1,2}$ 8.2 Hz, H-1), 3.86 (dd, 1H, $J_{3,4}$ 10.1 Hz, $J_{4,5}$ 8.9 Hz, H-4), 3.84 (m, 1H, H-5'), 3.80 (dd, 1H, $J_{6a,6b}$ 12.2 Hz, $J_{5,6b}$ 2.2 Hz, H-6b), 3.67 (dd, 1H, $J_{5,6a}$ 8.8 Hz, H-6a), 3.65 (m, 1H, H-2), 3.50 (dd, 1H, $J_{2,3}$ 8.6 Hz, H-3), 3.31 (ddd, 1H, H-5), 3.28 (dd, 1H, $J_{6'a,6'b}$ 12.8 Hz, $J_{5',6'b}$ 7.4 Hz, H-6'b), 3.12 (dd, 1H, $J_{5',6'a}$ 5.5 Hz, H-6'a), 3.39 (s, 3H, O*Me*), 2.10, 2.04, 1.92 (3s, each 3H, 3×*Me*COO), 1.84 (s, 3H, *Me*CON); ^{13}C NMR (62.9 MHz, CD_3CN): δ 171.3, 171.2, 170.9, 170.7 (4×C=O), 140.1 (Ar-*C*), 129.0-128.2 (Ar-CH), 102.9 (C-1), 100.8 (C-1'), 81.1 (C-3), 77.1 (C-4), 76.3 (C-5), 74.5 (CH_2Ph), 72.6 (C-3'), 72.5 (C-5'), 70.4 (C-2'), 68.8 (C-4'), 61.1 (C-6), 56.9 (O*Me*), 55.2 (C-2), 50.8 (C-6'), 23.3 (*Me*CON), 21.0-20.8 (3×*Me*COO). Anal. Found: C, 52.75; H, 6.08; N, 8.82. Calc for $C_{28}H_{38}N_4O_{13}$ (638.63): C, 52.71; H, 6.05; N, 8.79.

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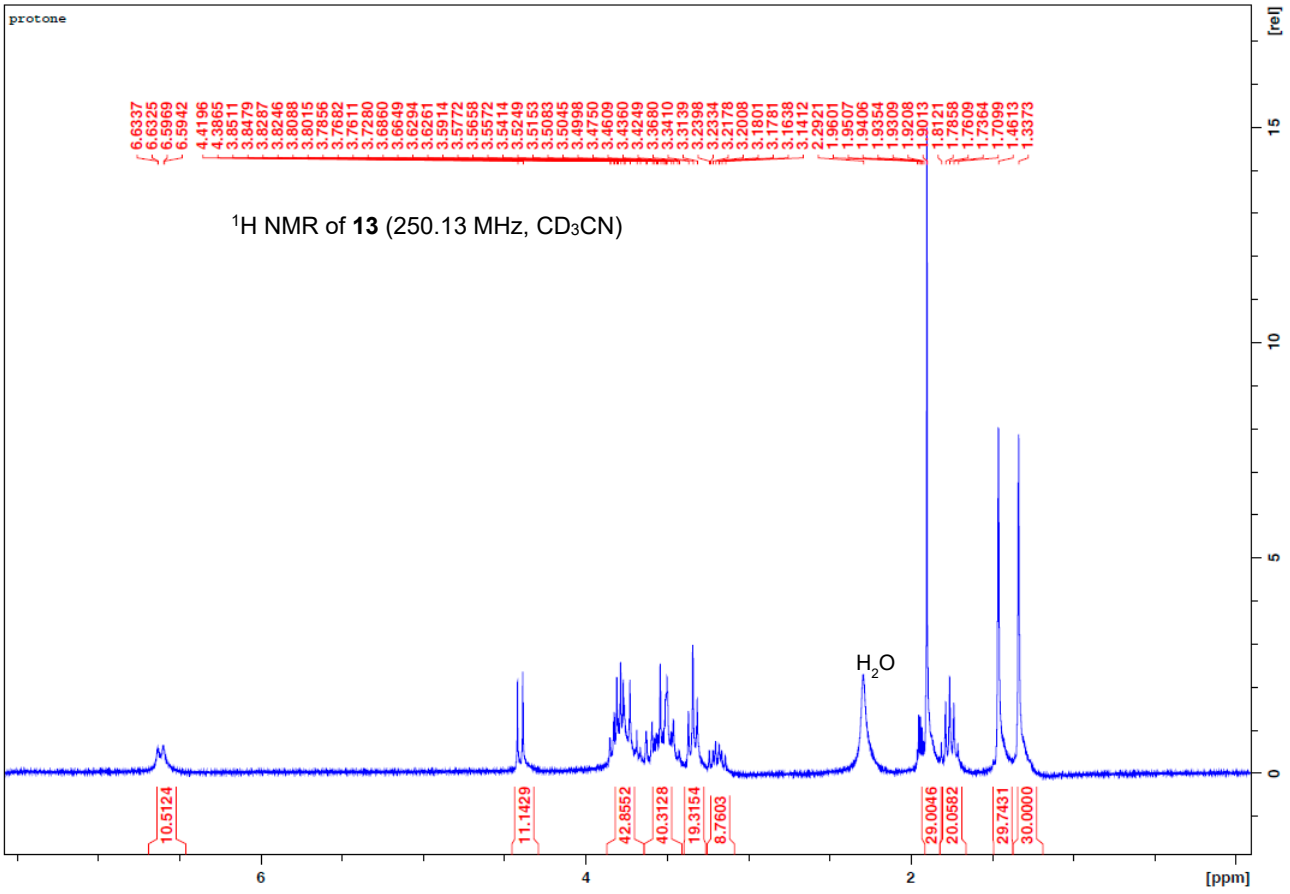
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3.8088
3.8015
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3.7611
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3.5914
3.5772
3.5658
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3.5414
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3.4609
3.4360
3.4249
3.3680
3.3410
3.3139
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3.2334
3.2178
3.2008
3.1801
3.1781
3.1638
3.1412
2.2921
1.9601
1.9507
1.9406
1.9354
1.9309
1.9208
1.9013
1.8121
1.7858
1.7609
1.7364
1.7099
1.4613
1.3373
^{1}H NMR of **13** (250.13 MHz, CD_3CN)
H_2O
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11.1429
42.8552
40.3128
19.3154
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20.0582
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30.0000
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2
[ppm]
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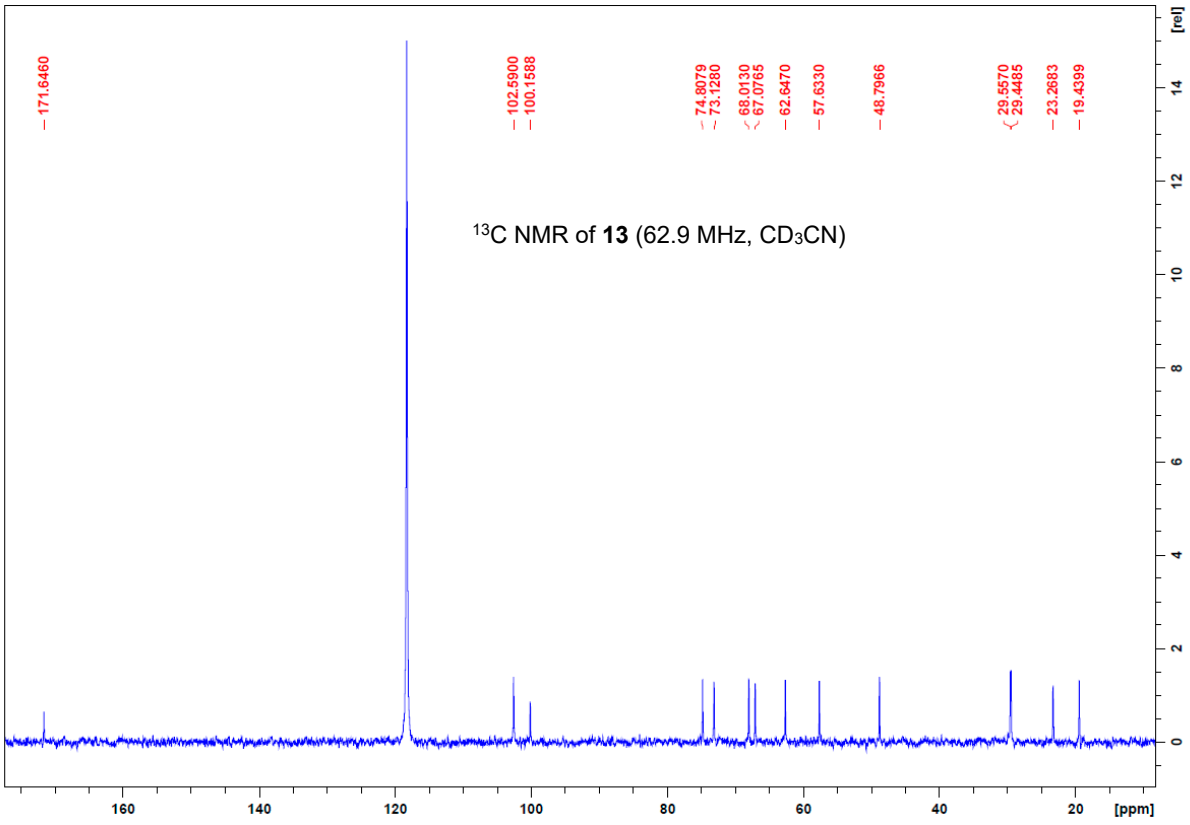
15
10
5
0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73.1280
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67.0765
62.6470
57.6330
48.7966
29.5570
29.4485
23.2683
19.4399
^{13}C NMR of **13** (62.9 MHz, CD_3CN)
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140
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100
80
60
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20
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6
4
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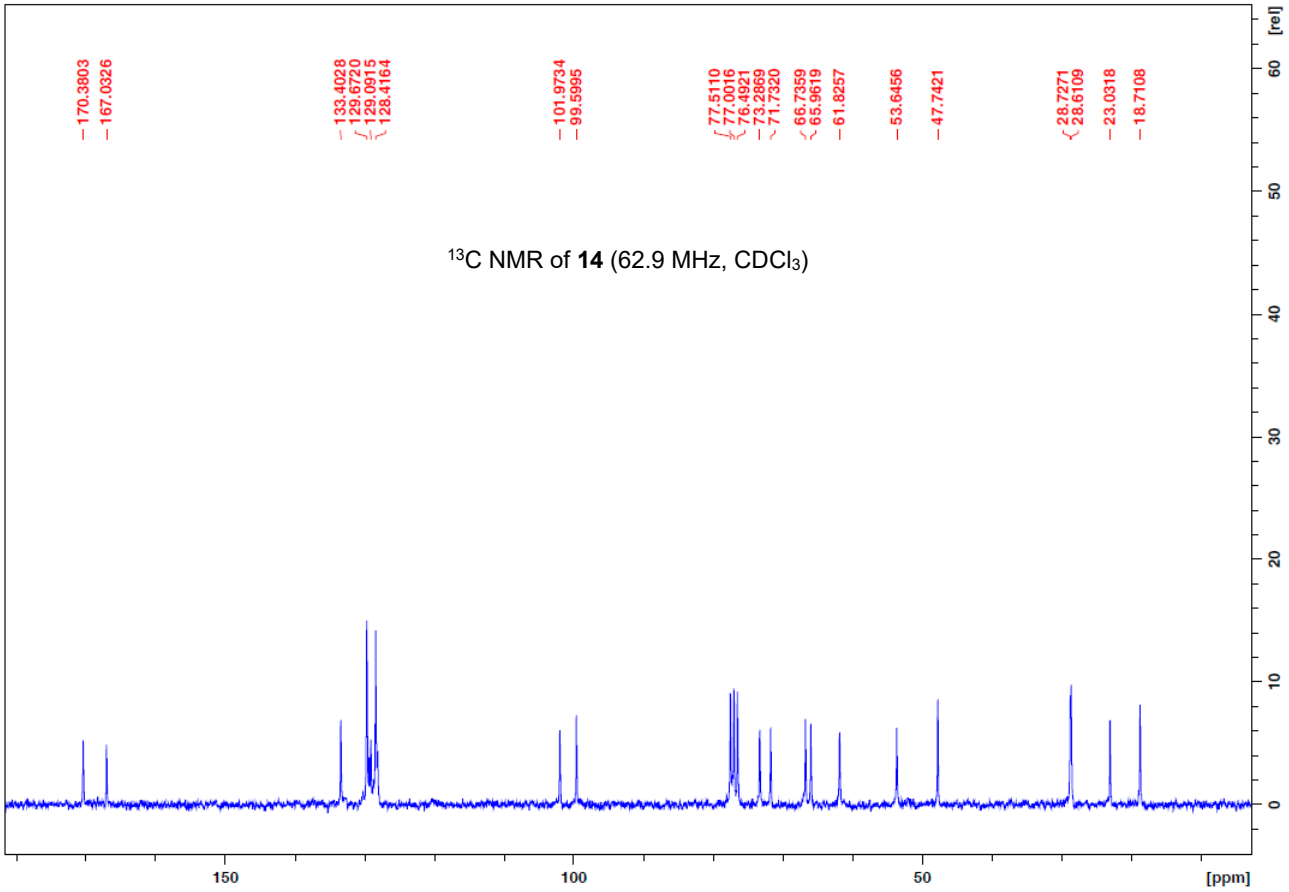
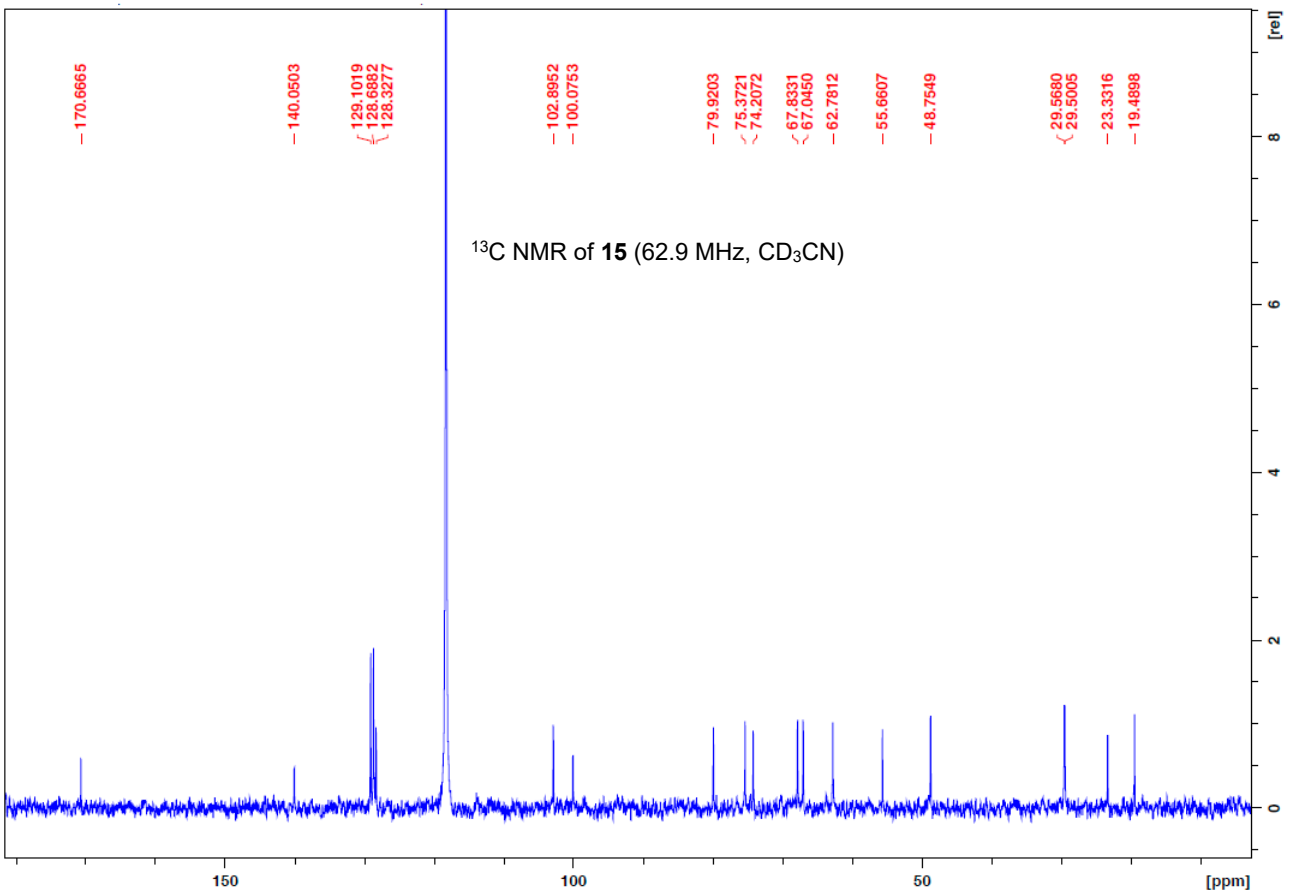
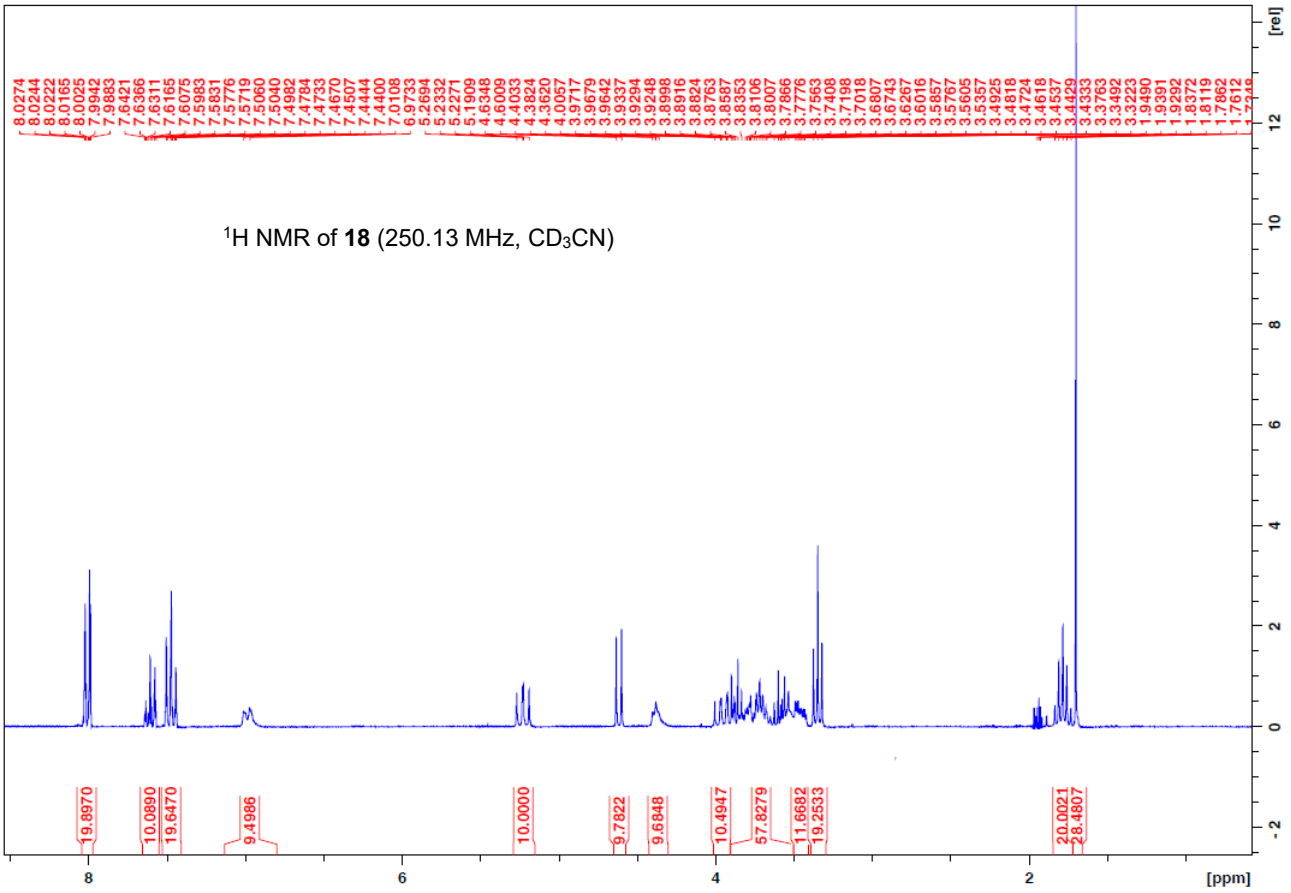


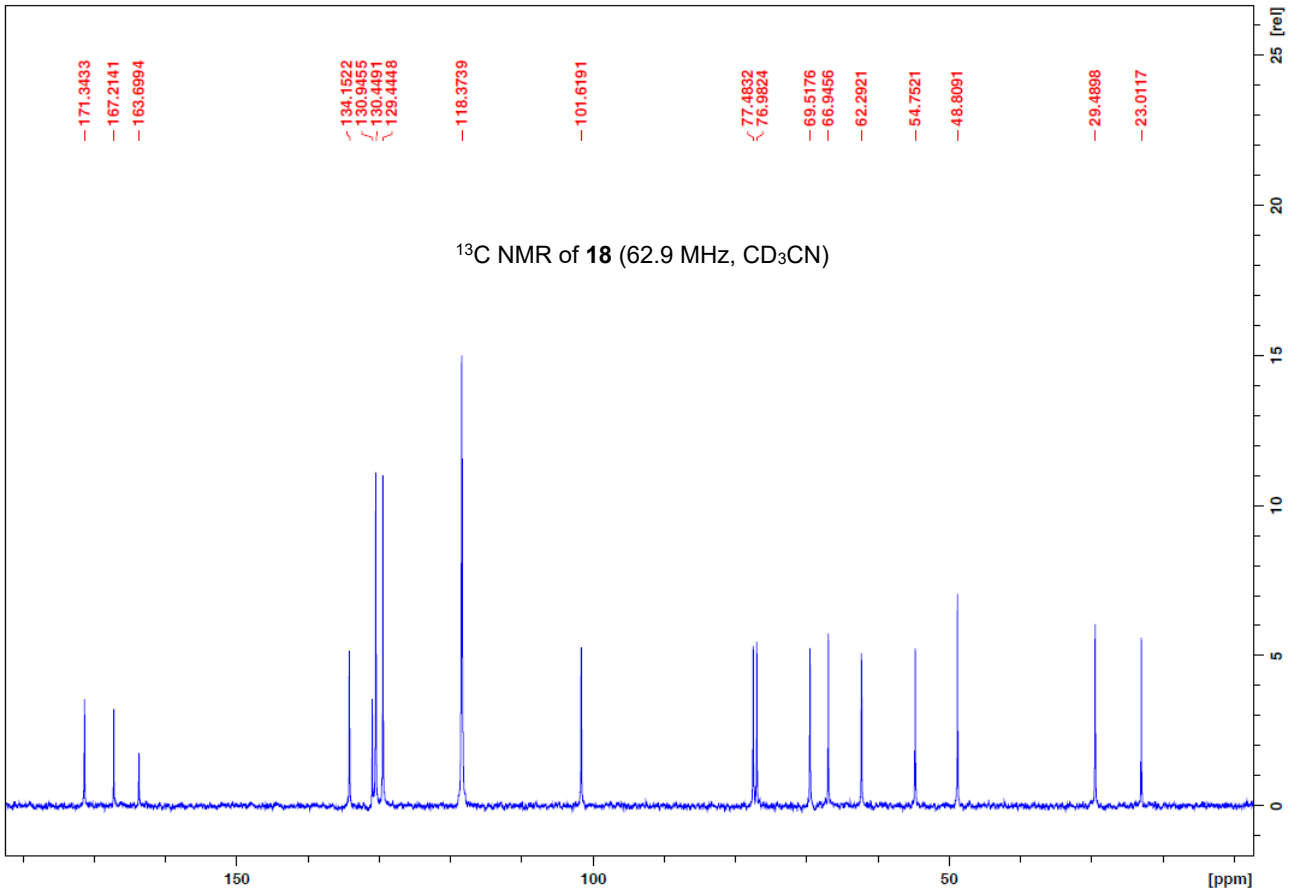
^{13}C NMR of **14** (62.9 MHz, $CDCl_3$)



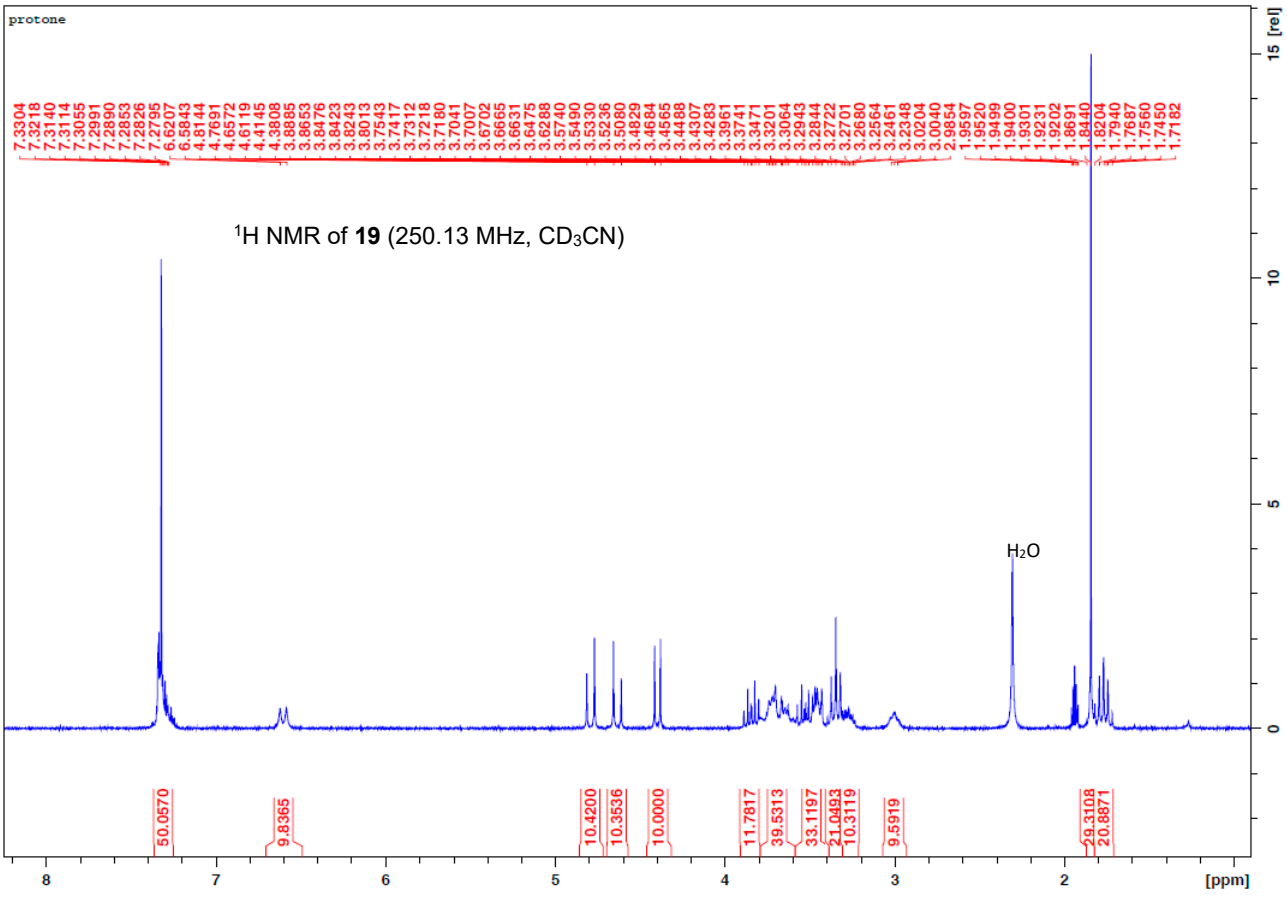
^{13}C NMR of **15** (62.9 MHz, CD_3CN)



^{1}H NMR of **18** (250.13 MHz, CD_3CN)



^{13}C NMR of **18** (62.9 MHz, CD_3CN)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6.6207
6.5843
4.8144
4.7691
4.6572
4.6119
4.4145
4.3808
3.8885
3.8653
3.8476
3.8423
3.8243
3.8013
3.7543
3.7417
3.7312
3.7218
3.7180
3.7041
3.7007
3.6702
3.6665
3.6631
3.6475
3.6288
3.5740
3.5490
3.5330
3.5236
3.5080
3.4829
3.4684
3.4565
3.4488
3.4307
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3.3741
3.3471
3.3201
3.3064
3.2943
3.2844
3.2722
3.2701
3.2680
3.2564
3.2461
3.2348
3.0204
3.0040
2.9854
1.9597
1.9520
1.9499
1.9400
1.9301
1.9231
1.9202
1.8691
1.8440
1.8204
1.7940
1.7687
1.7560
1.7450
1.7182
^{1}H NMR of **19** (250.13 MHz, CD_3CN)
H_2O
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9.8365
10.4200
10.3536
10.0000
11.7817
39.5313
33.1197
21.0493
10.3119
9.5919
29.3108
20.8871
8
7
6
5
4
3
2
[ppm]
15 [rel]
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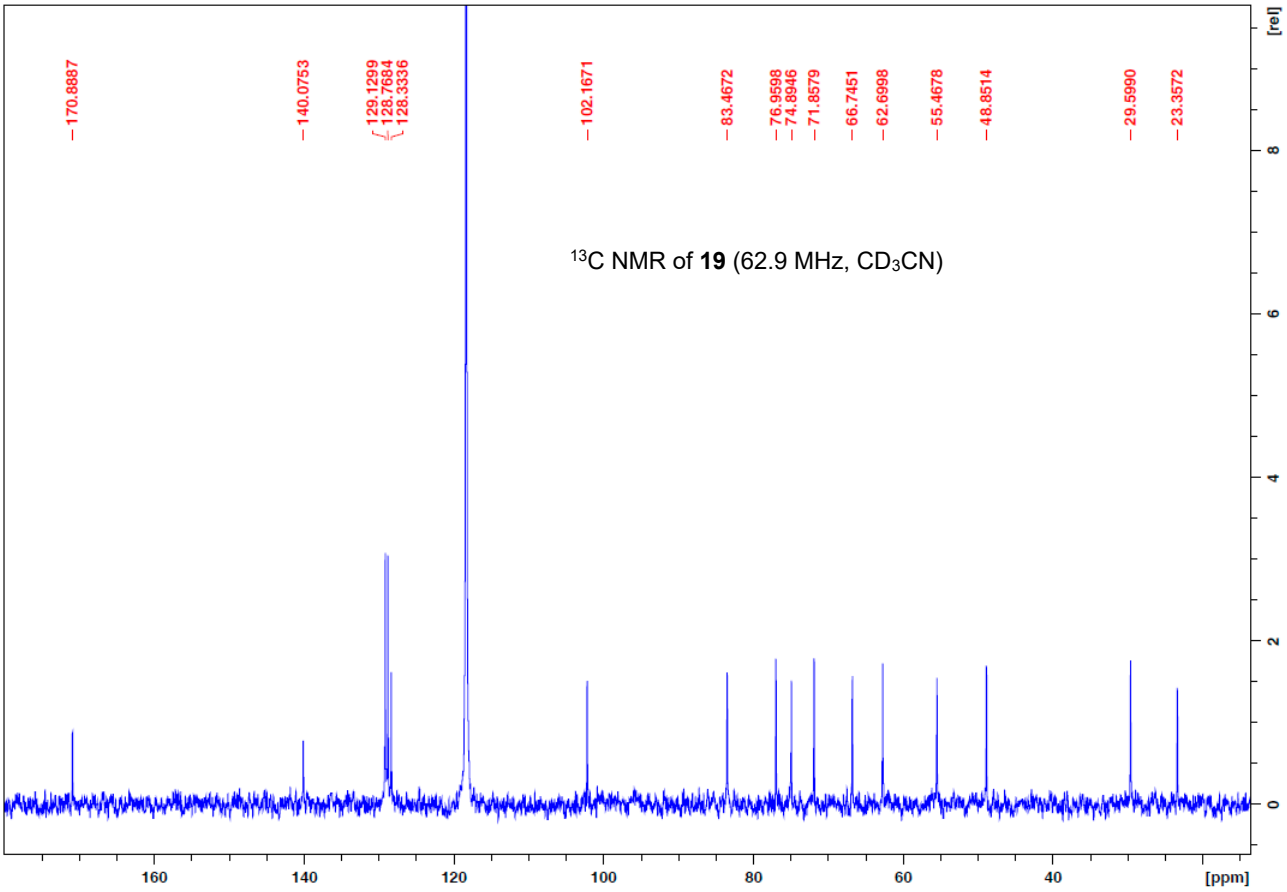
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128.3336
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83.4672
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74.8946
71.8579
66.7451
62.6998
55.4678
48.8514
29.5990
23.3572
^{13}C NMR of **19** (62.9 MHz, CD_3CN)
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100
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[ppm]
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8
6
4
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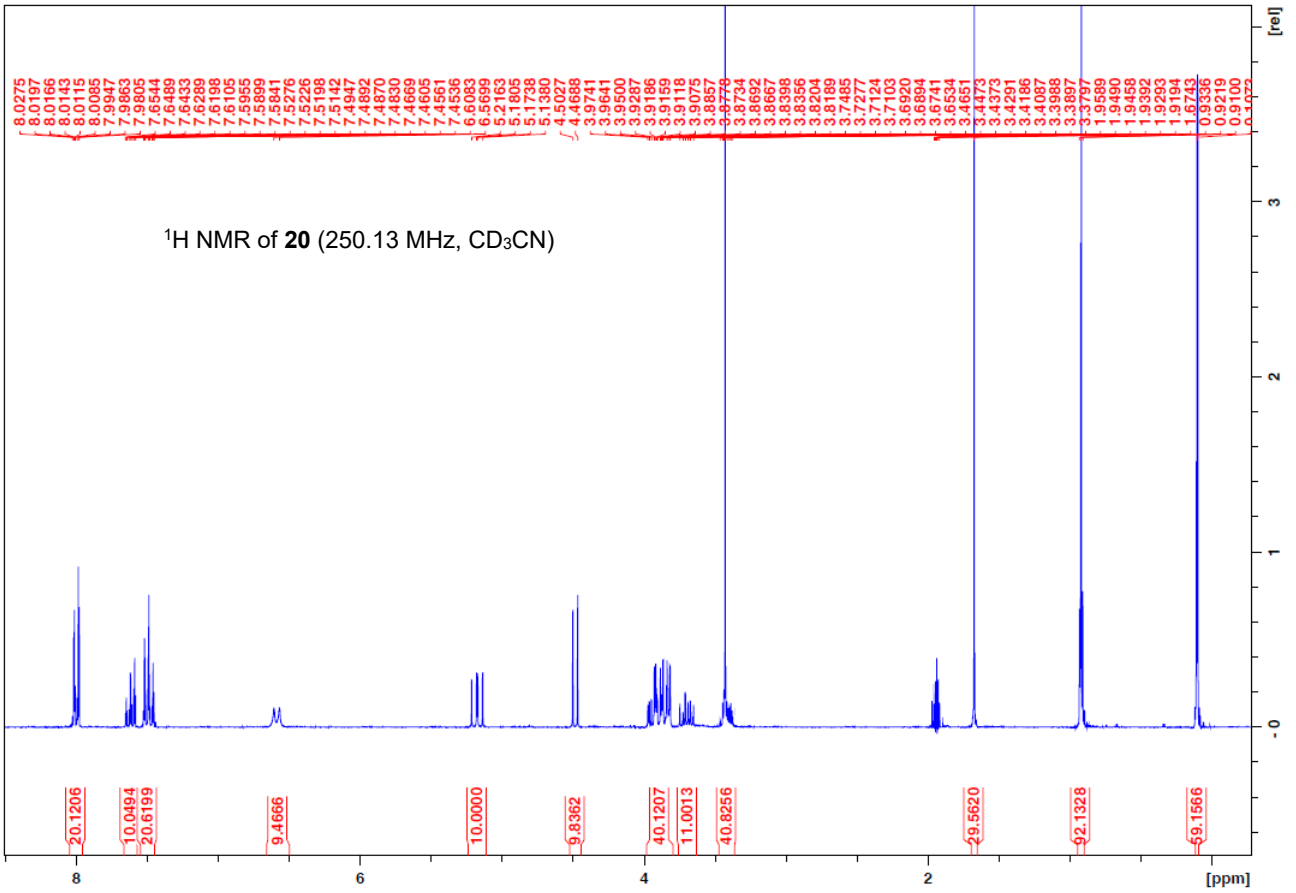
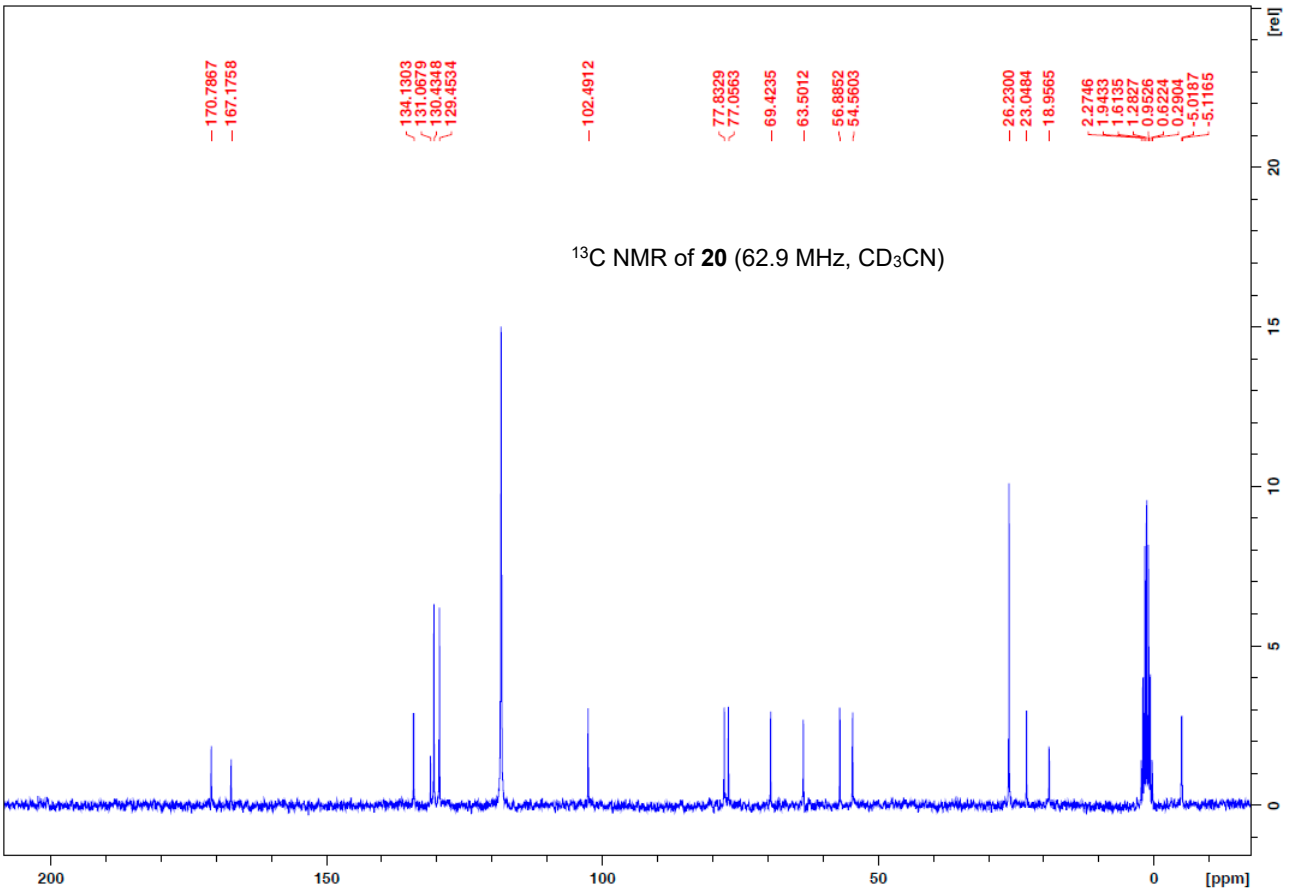
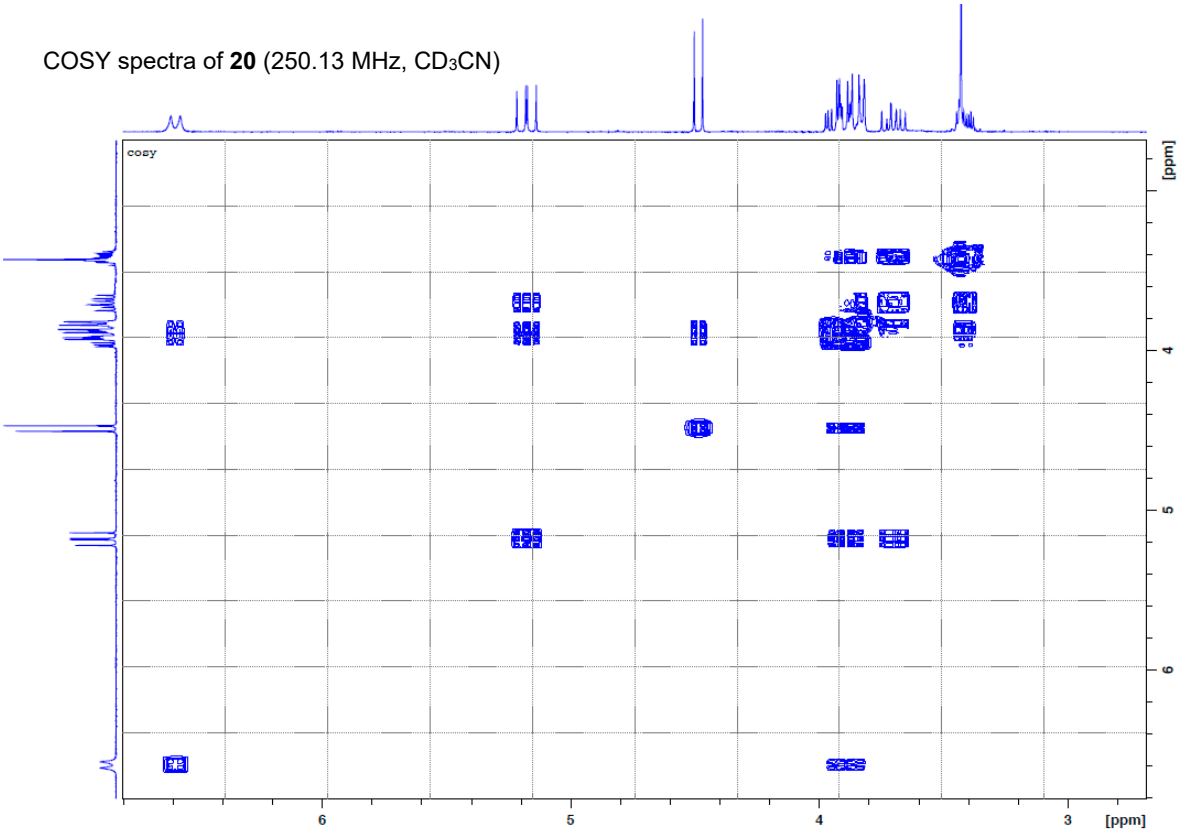


^{1}H NMR of **20** (250.13 MHz, CD_3CN)

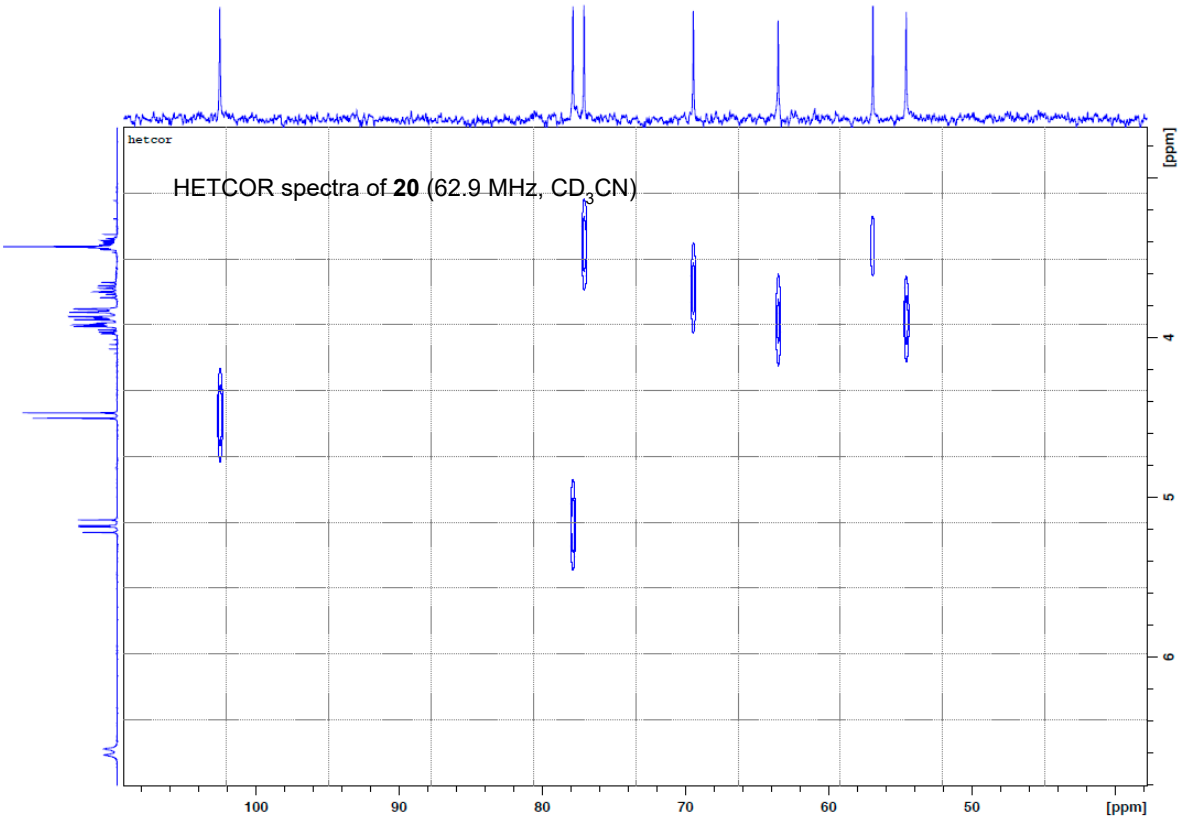


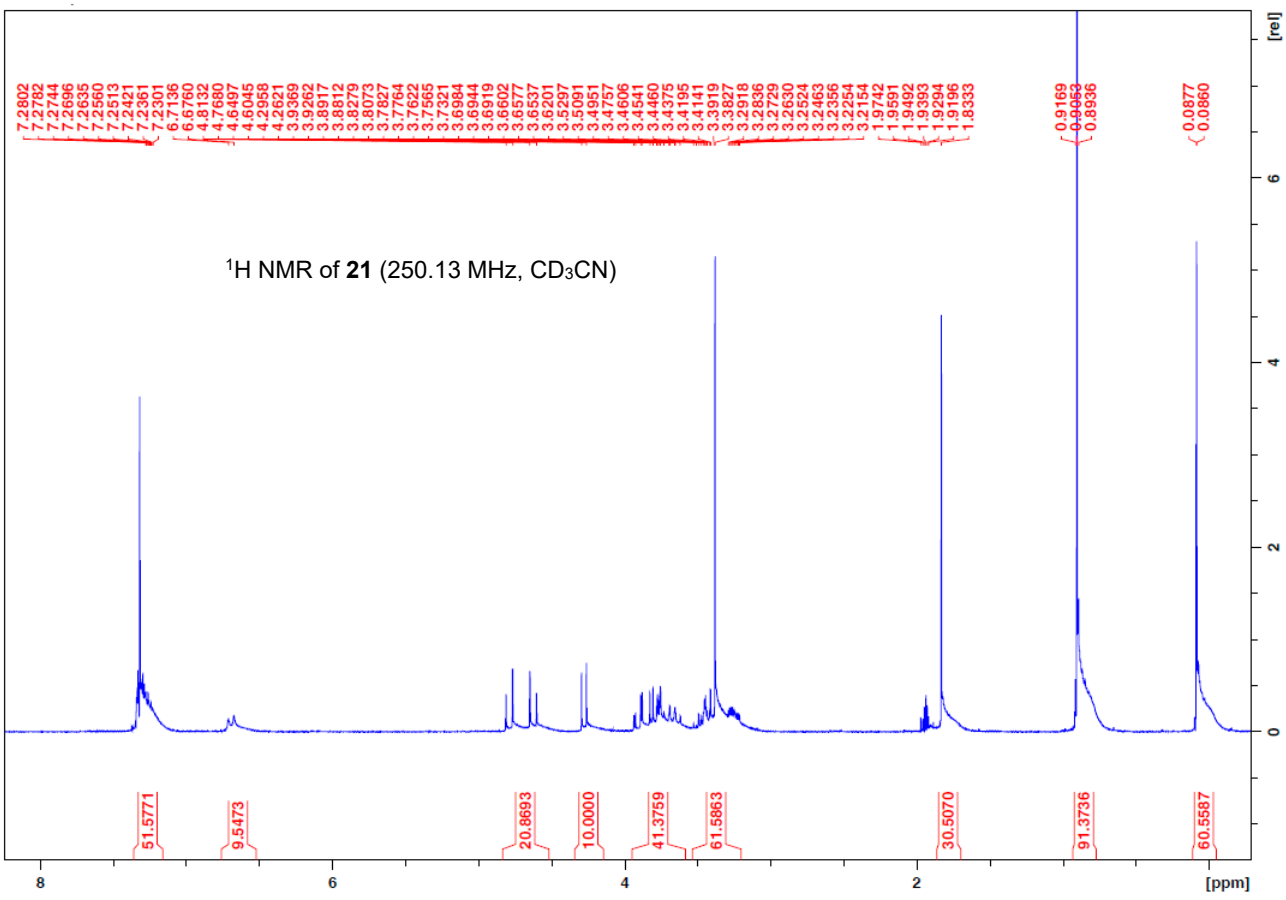
^{13}C NMR of **20** (62.9 MHz, CD_3CN)

COSY spectra of **20** (250.13 MHz, CD_3CN)



HETCOR spectra of **20** (62.9 MHz, CD_3CN)




^{1}H NMR of **21** (250.13 MHz, CD_3CN)
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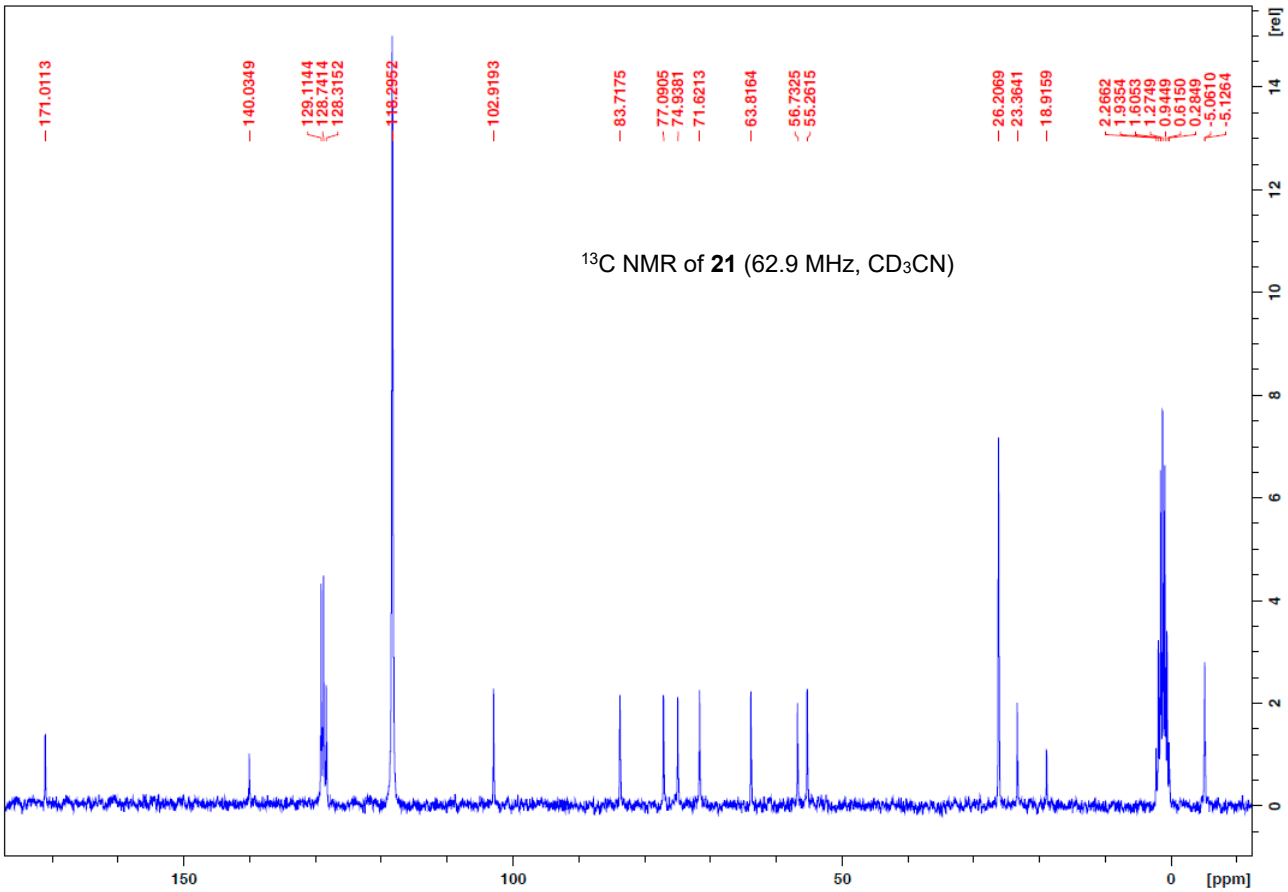
[ppm]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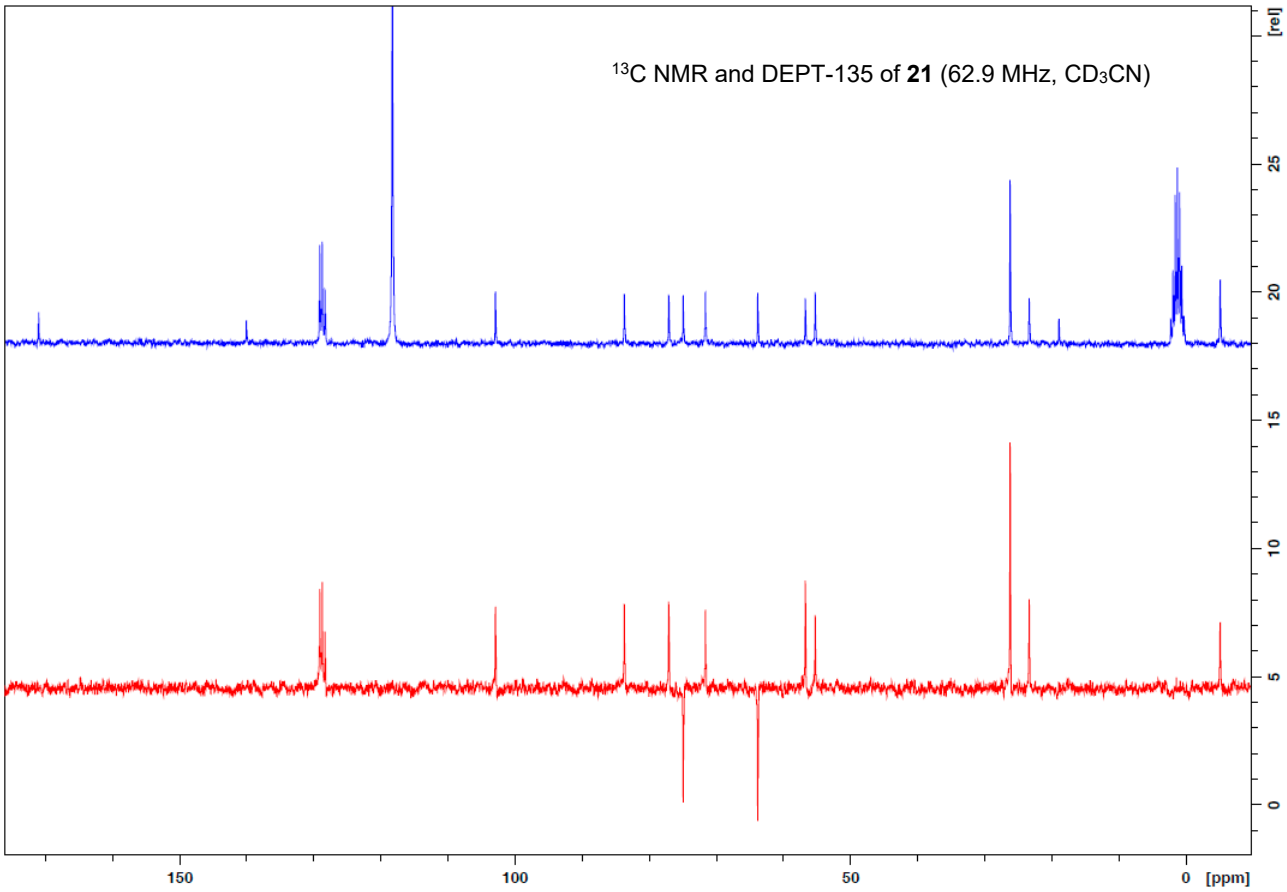
[ppm]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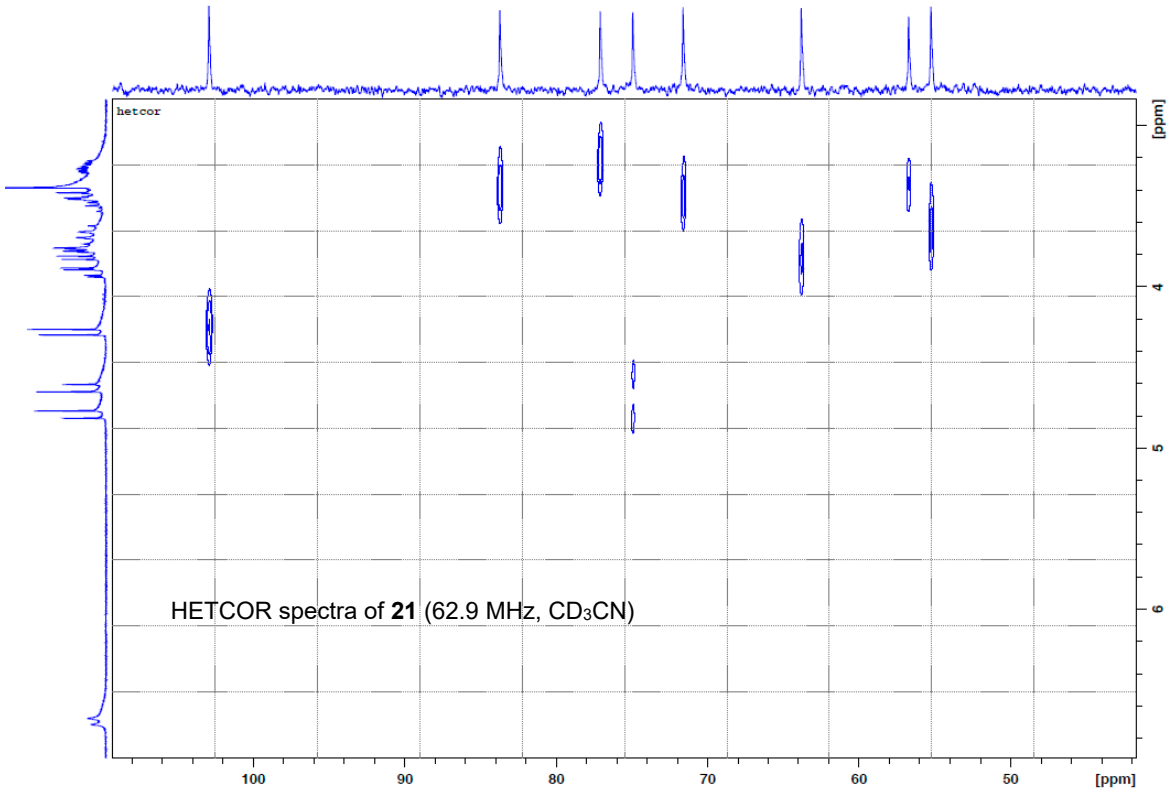
[ppm]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HETCOR spectra of **21** (62.9 MHz, CD_3CN)
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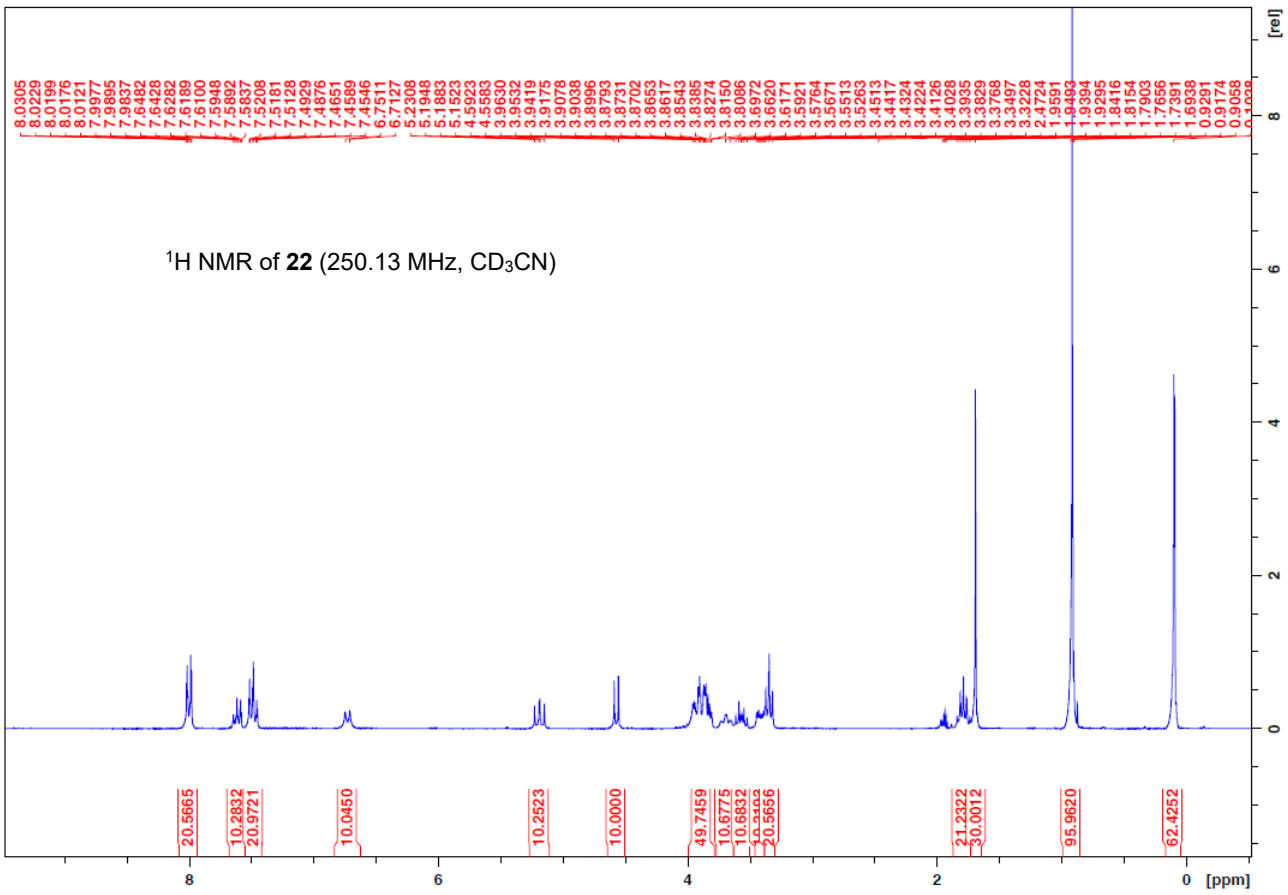
70
60
50
[ppm]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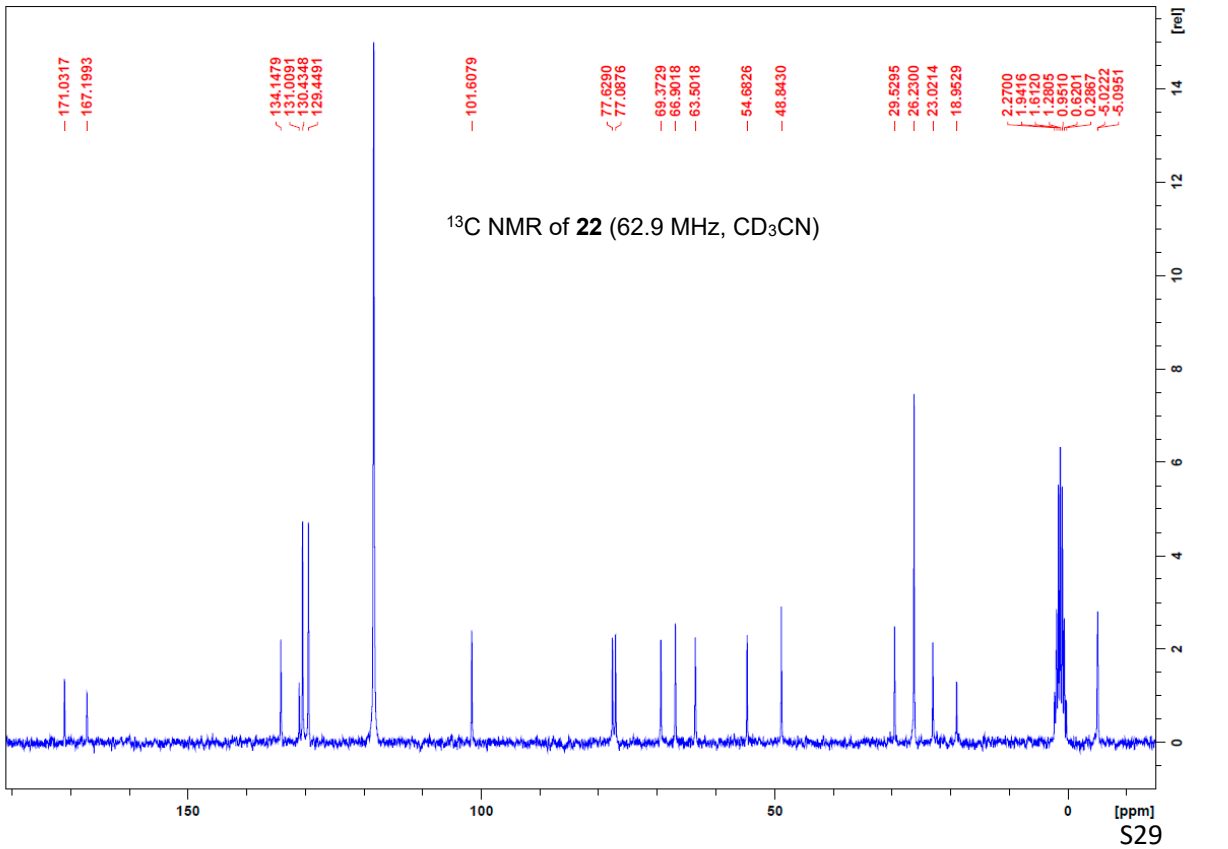
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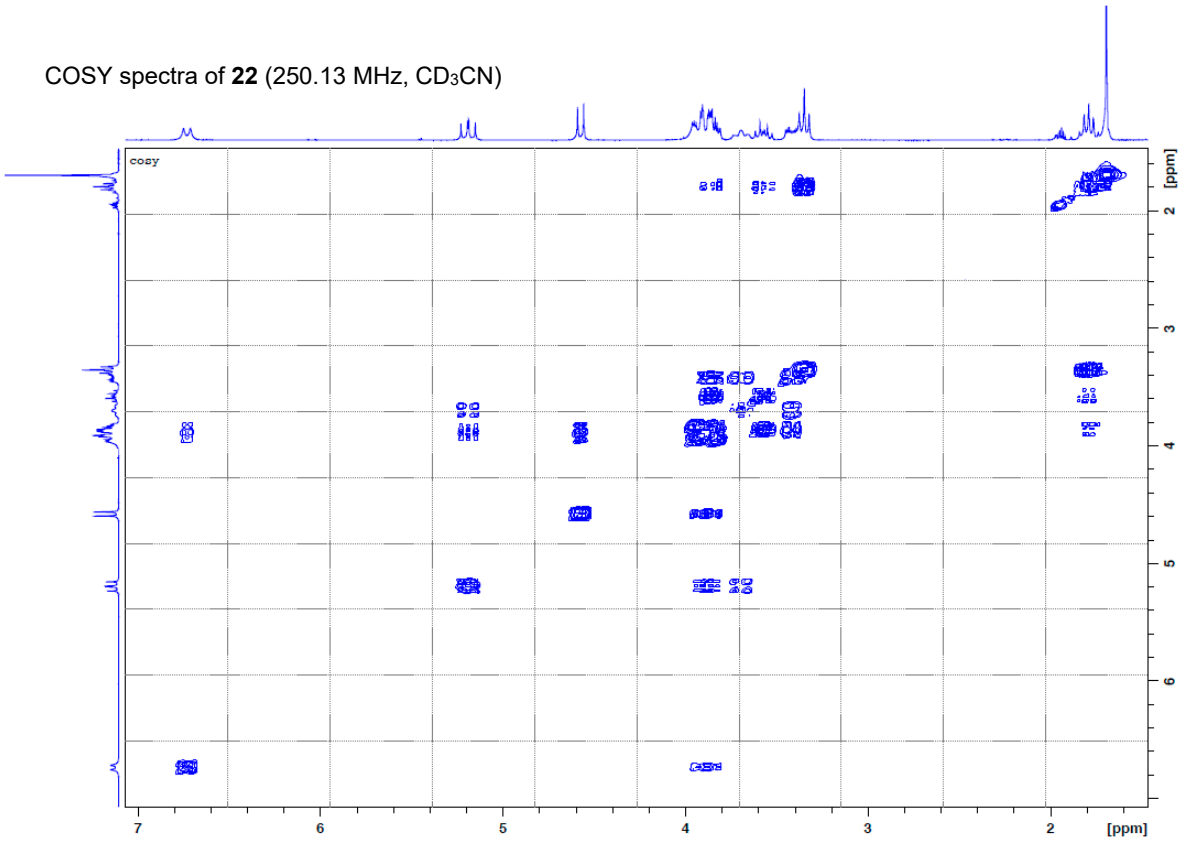
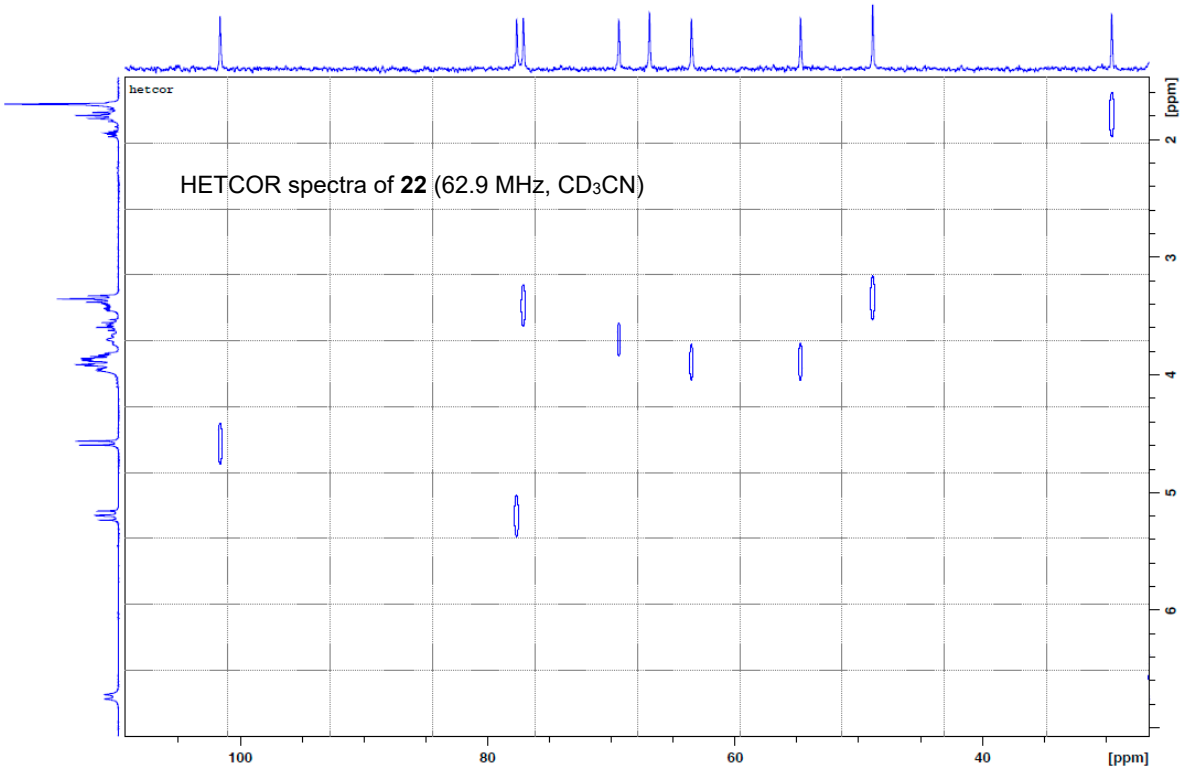
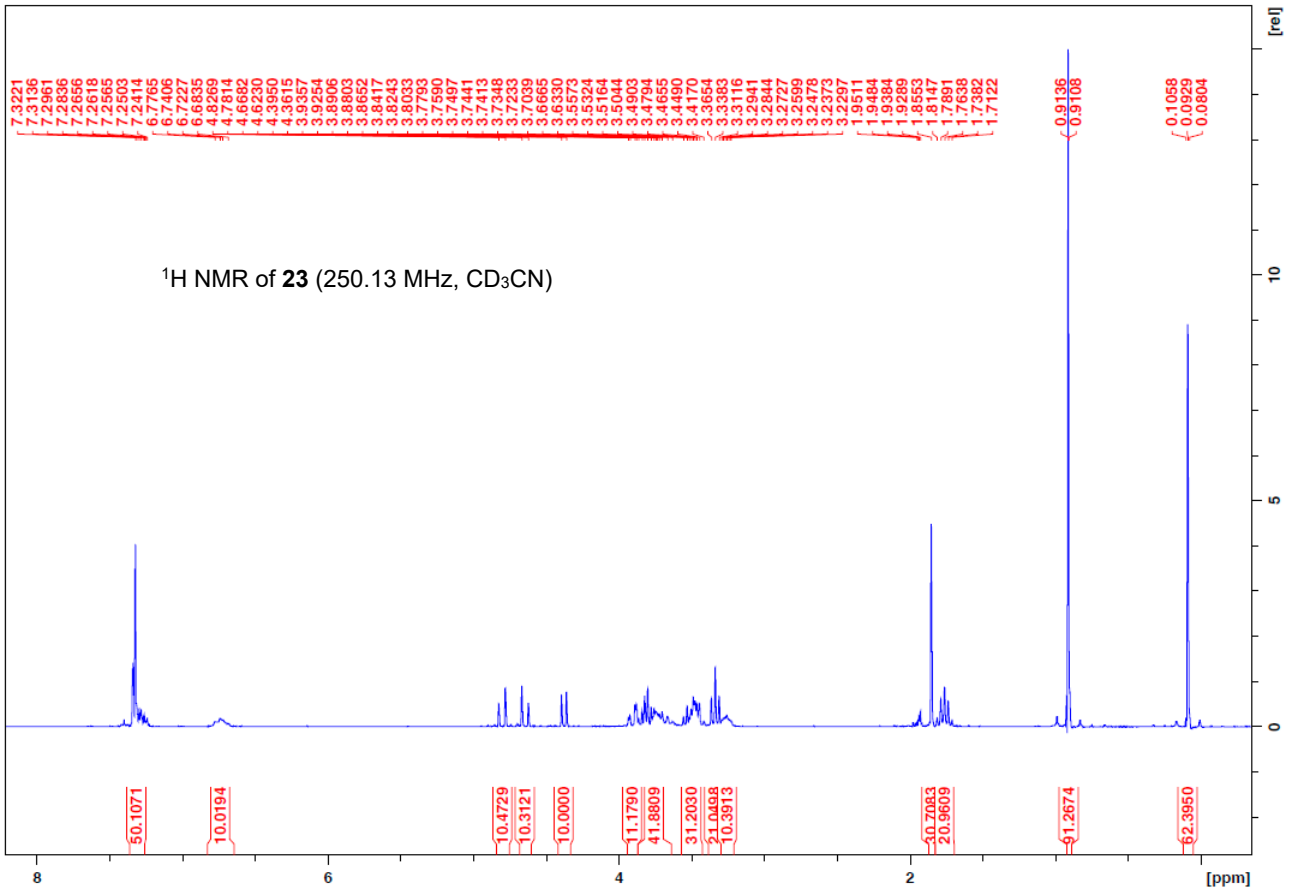
[ppm]

COSY spectra of **22** (250.13 MHz, CD_3CN)



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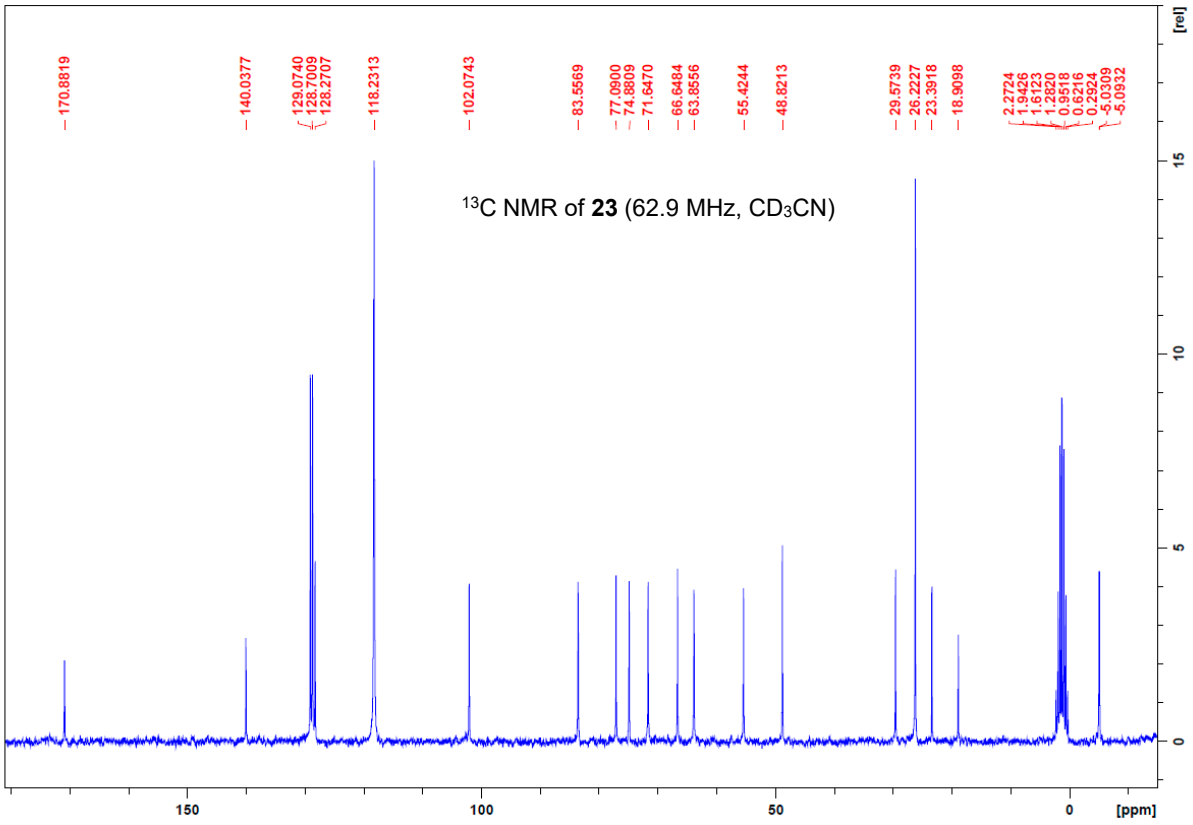
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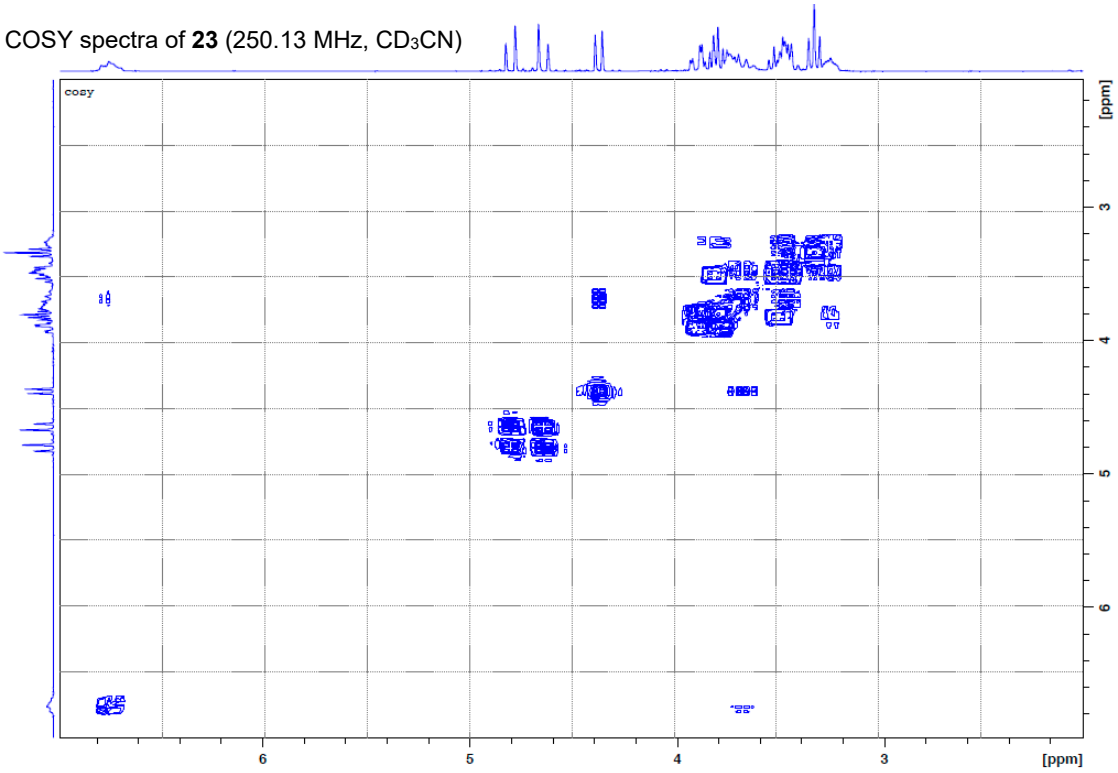
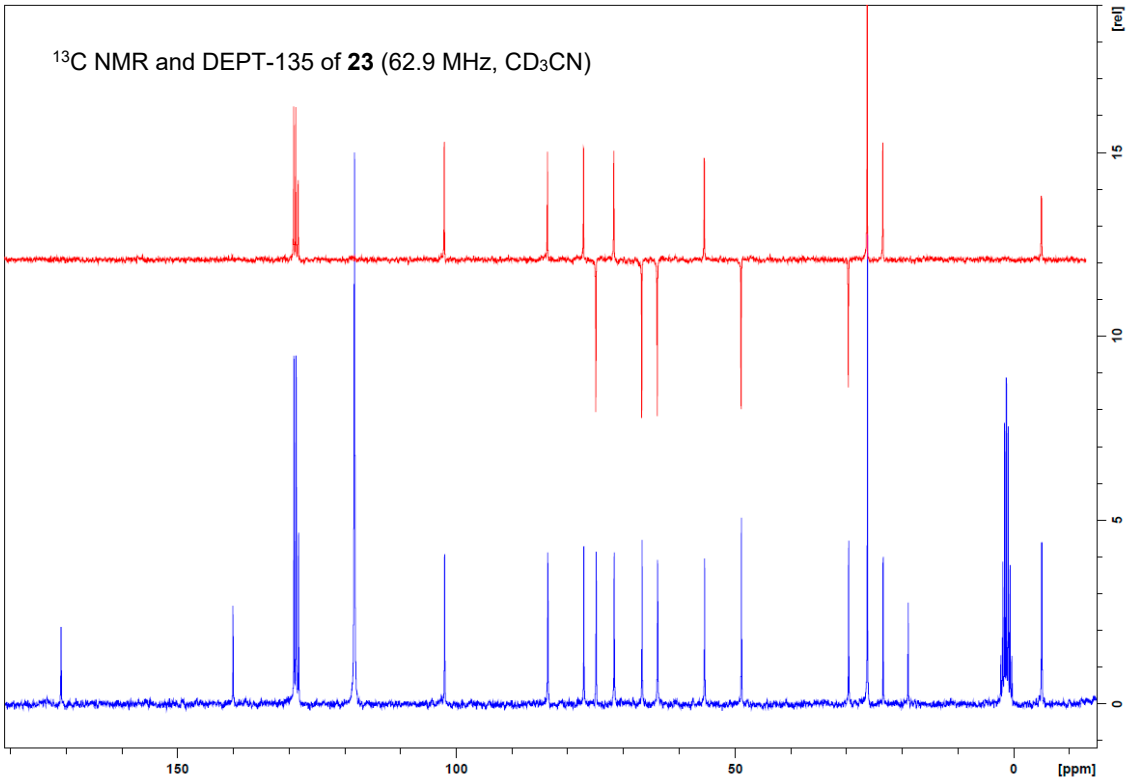
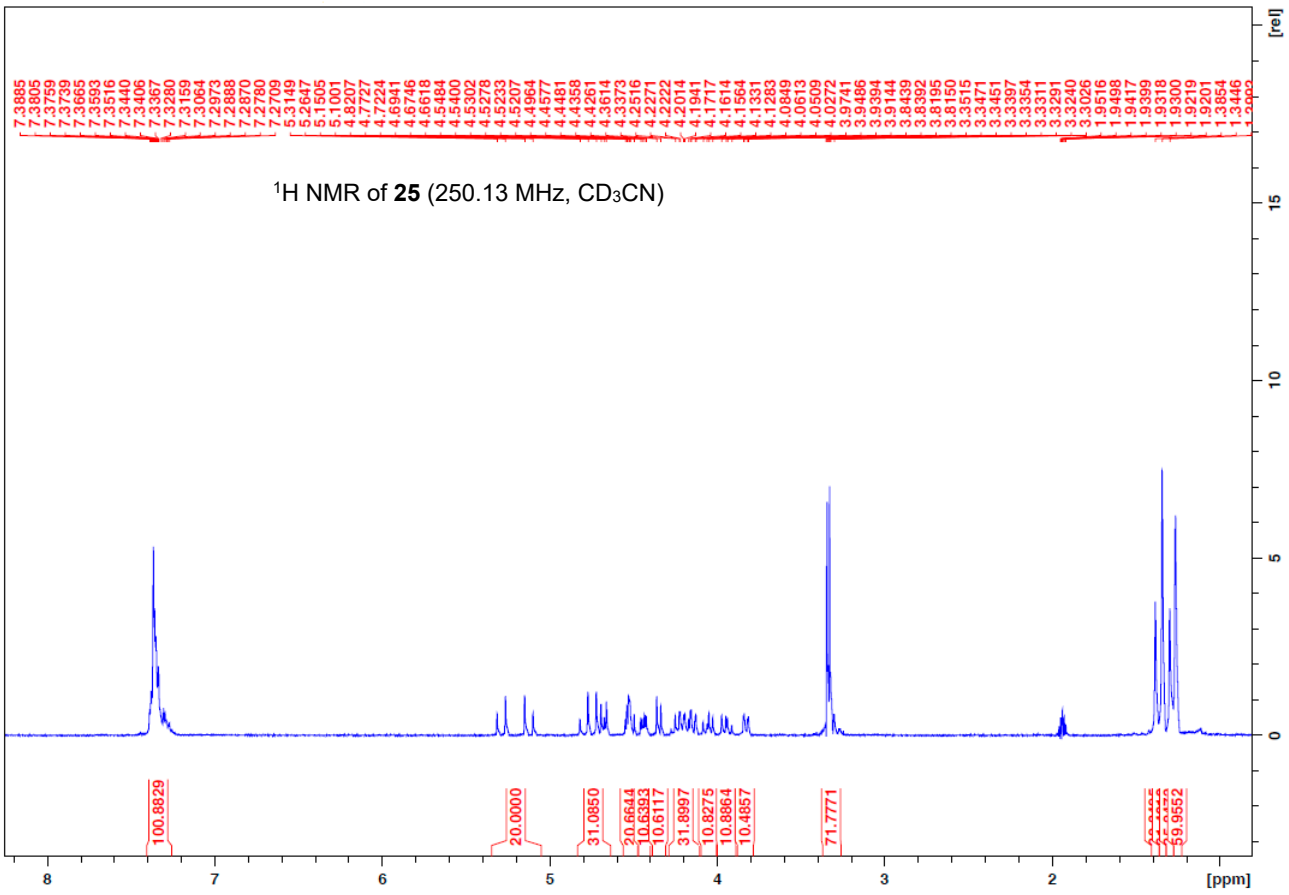
[ppm]

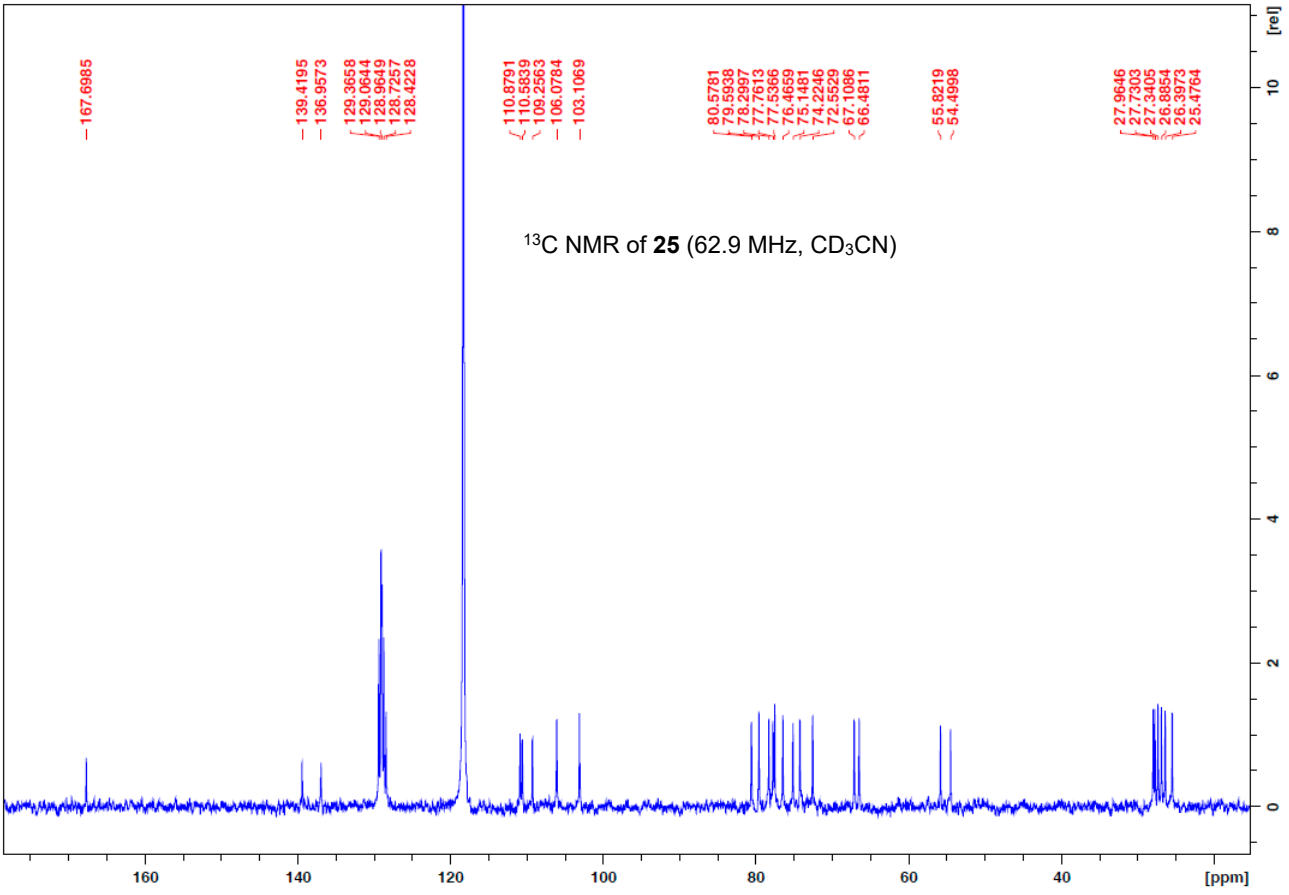
COSY spectra of **23** (250.13 MHz, CD_3CN)



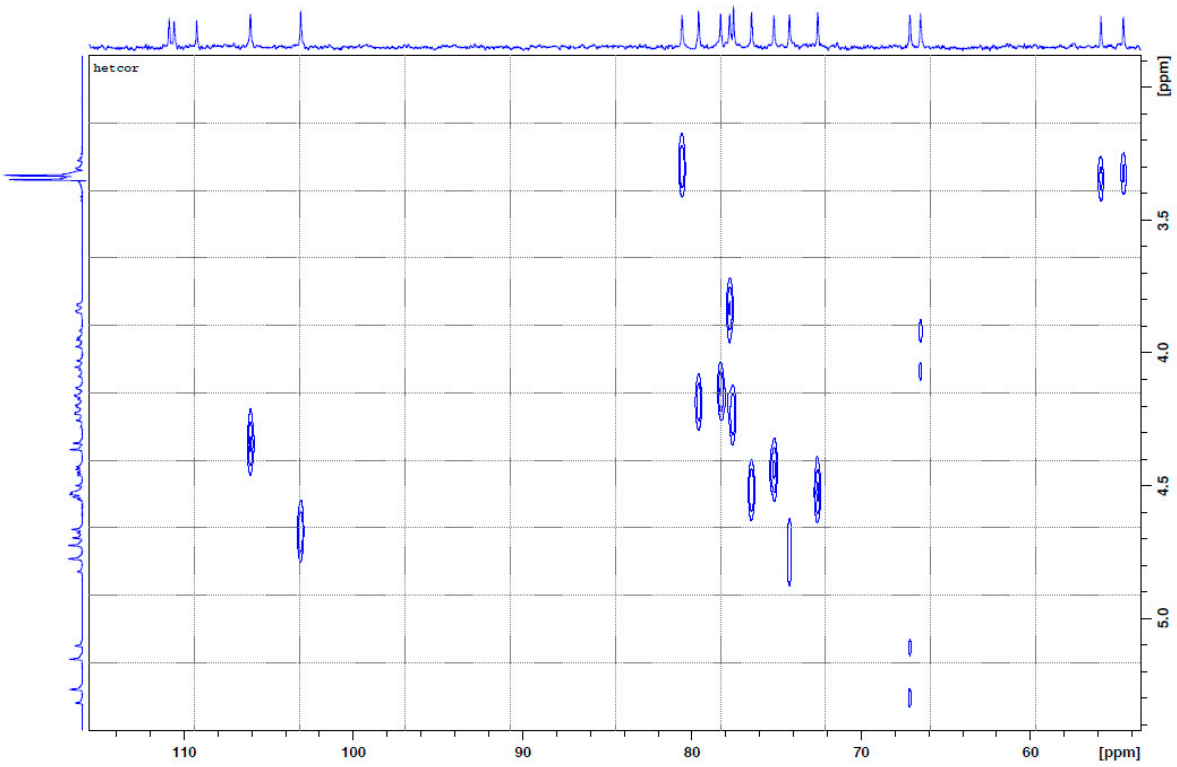
^{13}C NMR and DEPT-135 of **23** (62.9 MHz, CD_3CN)



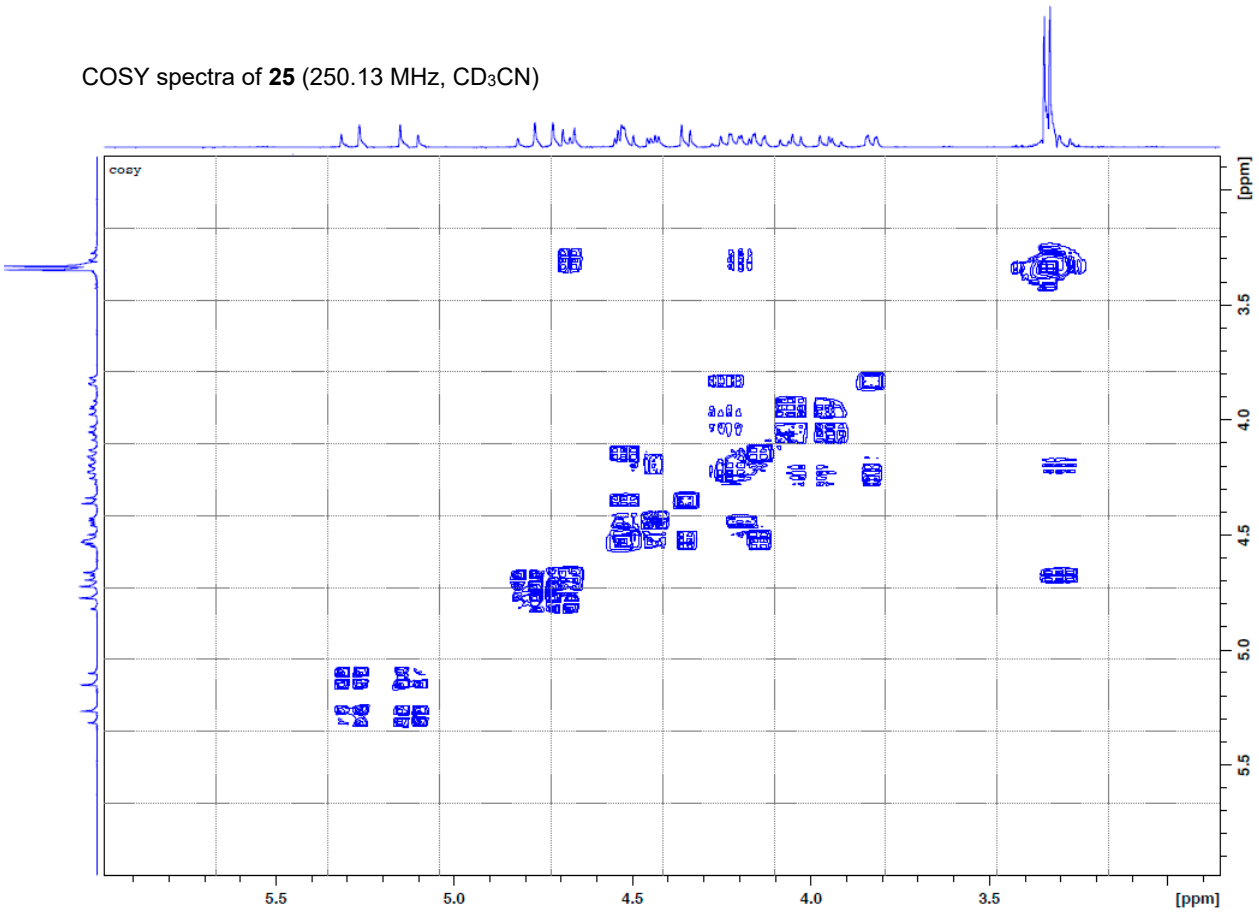

^{1}H NMR of **25** (250.13 MHz, CD_3CN)
[rel]
[ppm]

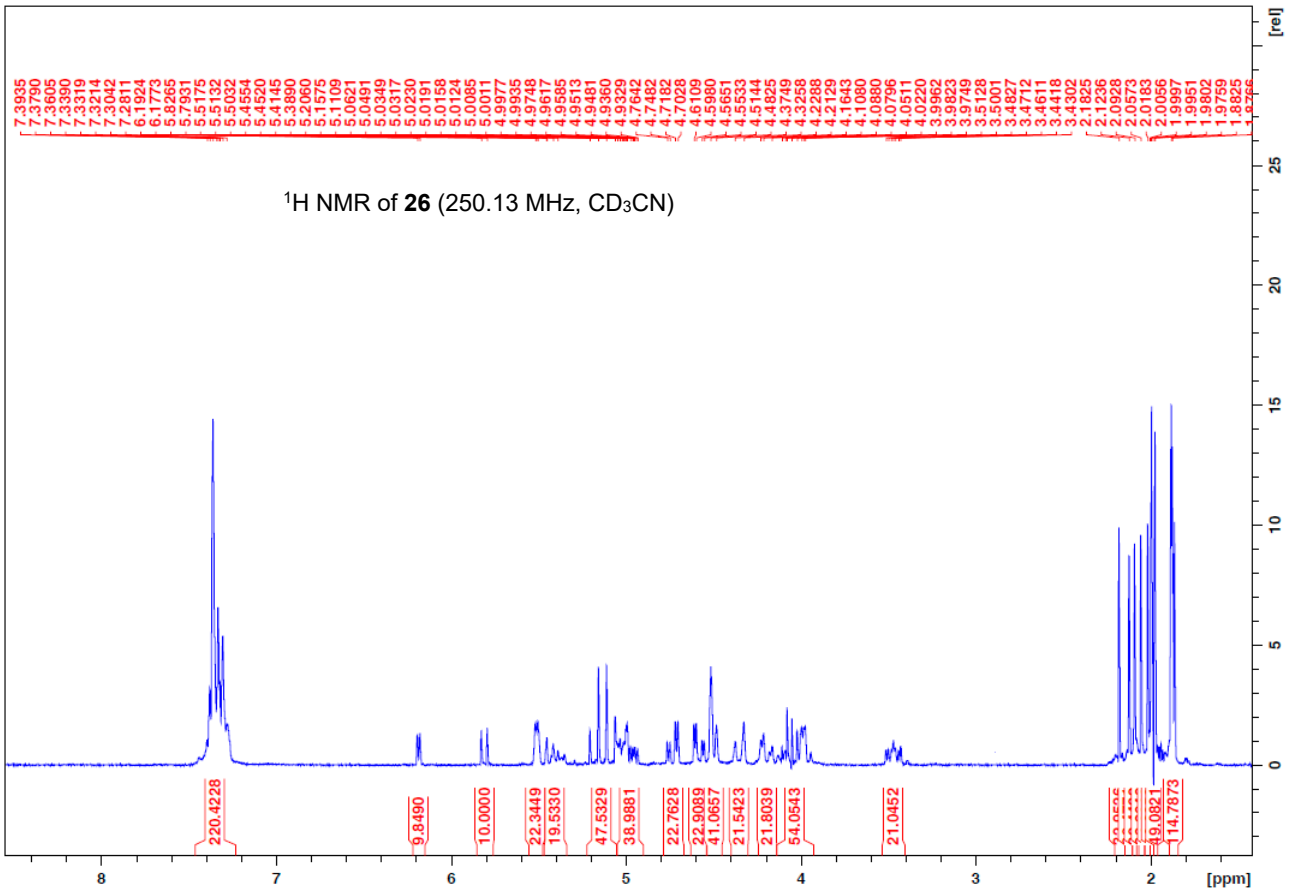

^{13}C NMR of **25** (62.9 MHz, CD_3CN)
[rel]
[ppm]

HETCOR spectra of **25** (62.9 MHz, CD_3CN)

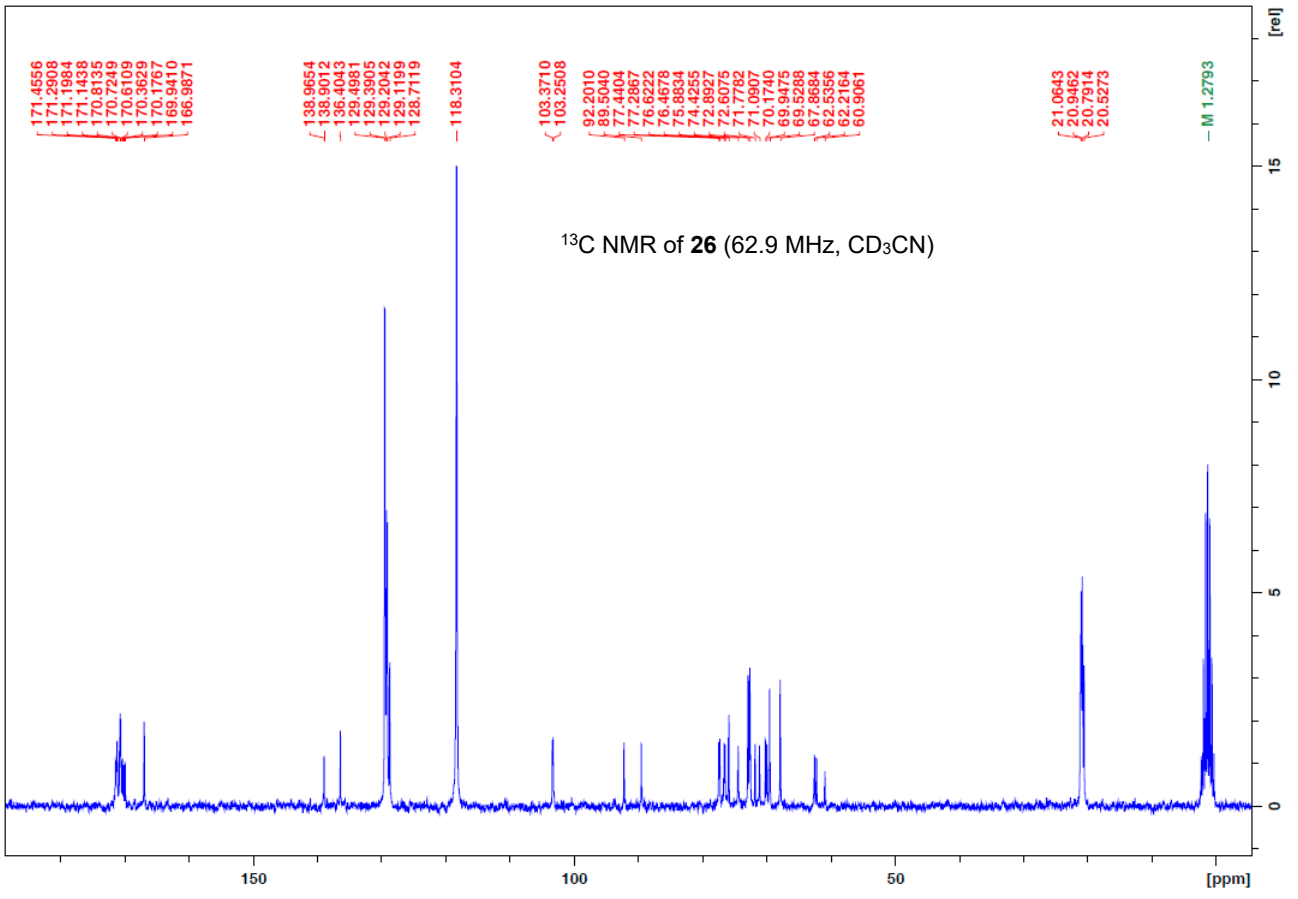


COSY spectra of **25** (250.13 MHz, CD_3CN)



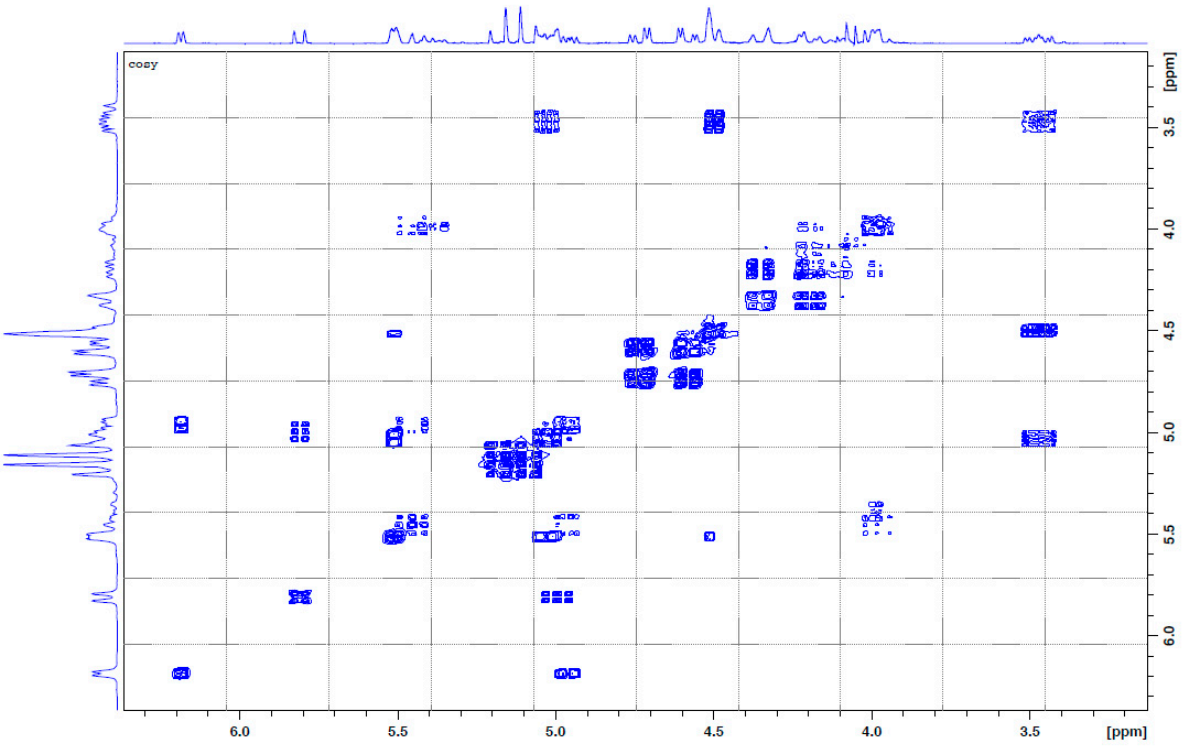


^{1}H NMR of **26** (250.13 MHz, CD_3CN)

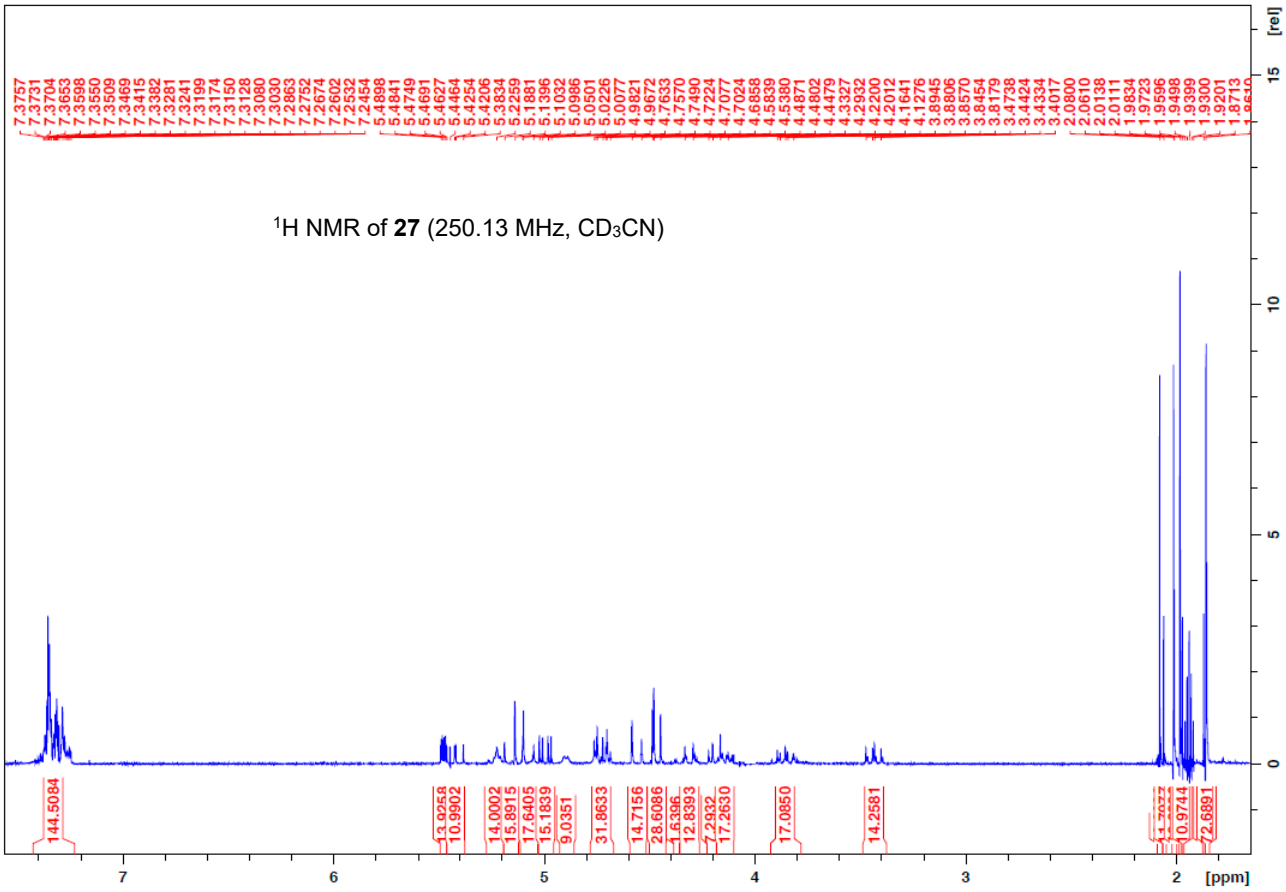


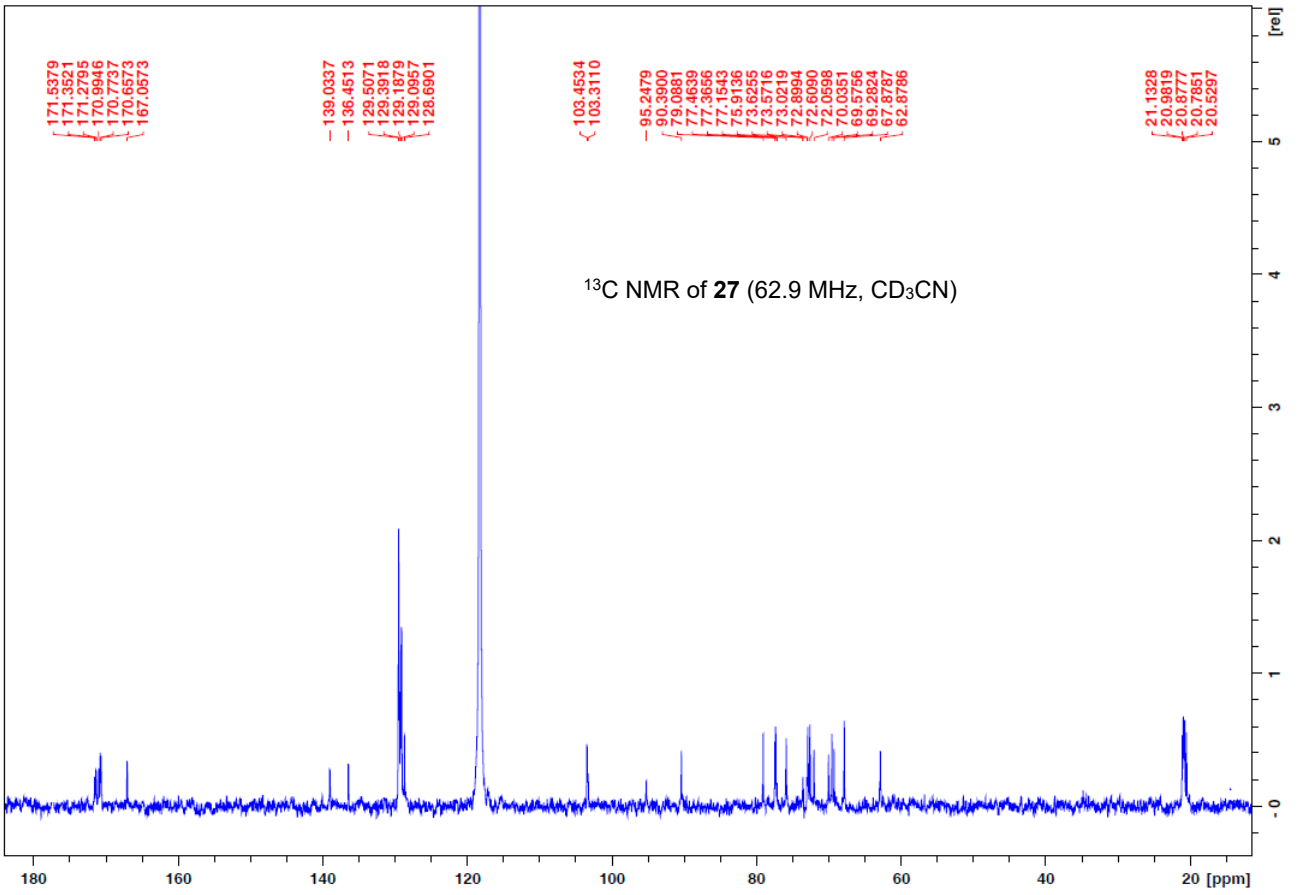
^{13}C NMR of **26** (62.9 MHz, CD_3CN)

COSY spectra of **26** (250.13 MHz, CD_3CN)

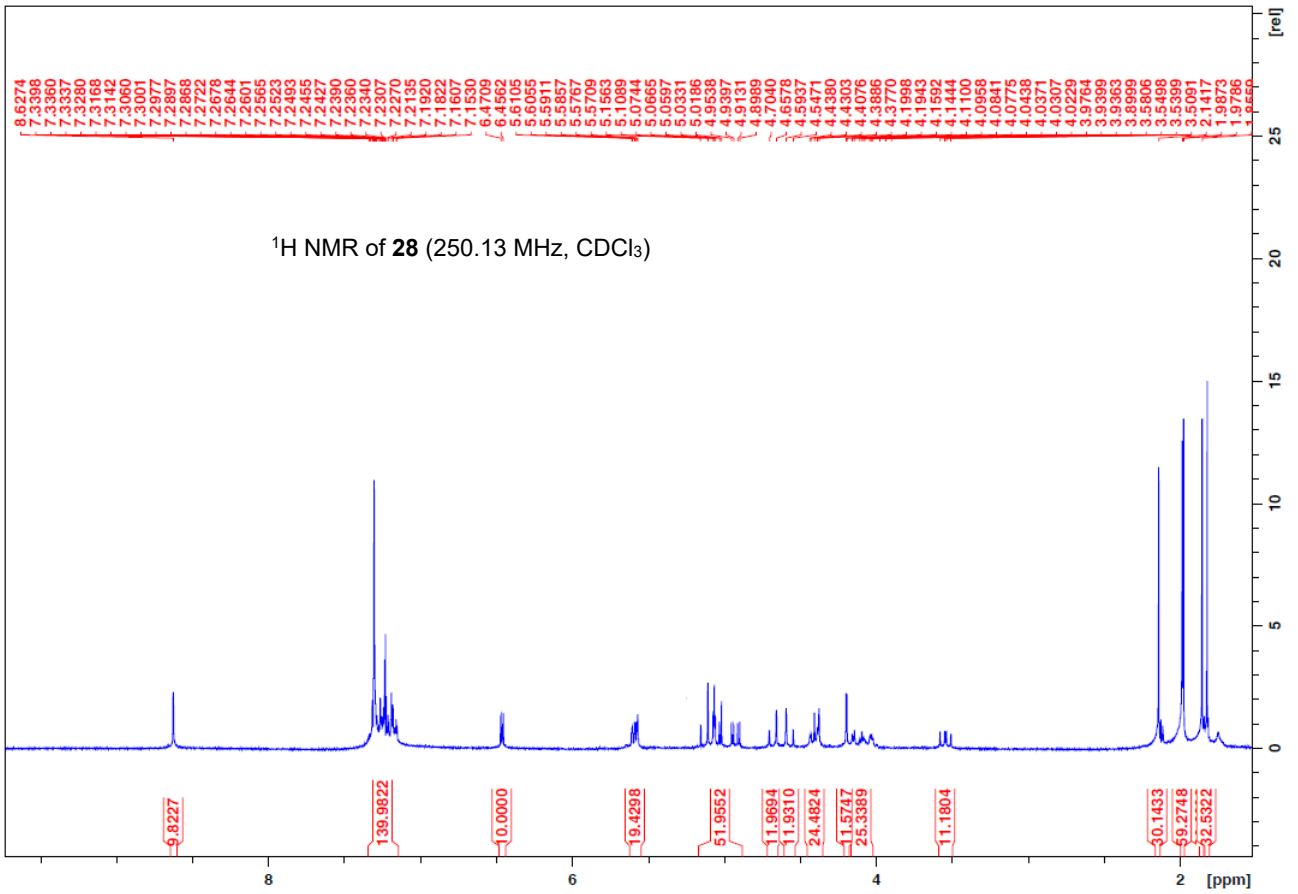


^1H NMR of **27** (250.13 MHz, CD_3CN)

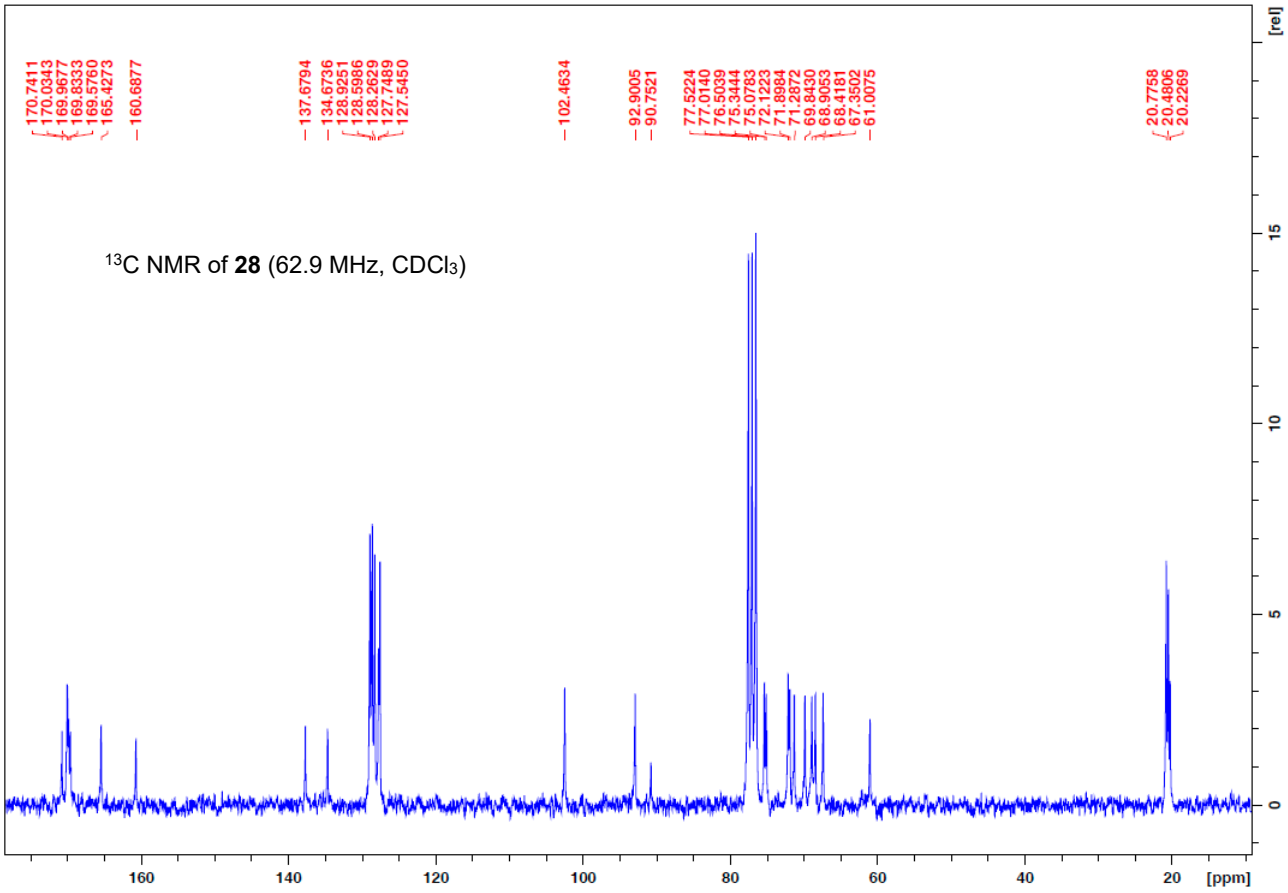




^{13}C NMR of **27** (62.9 MHz, CD_3CN)

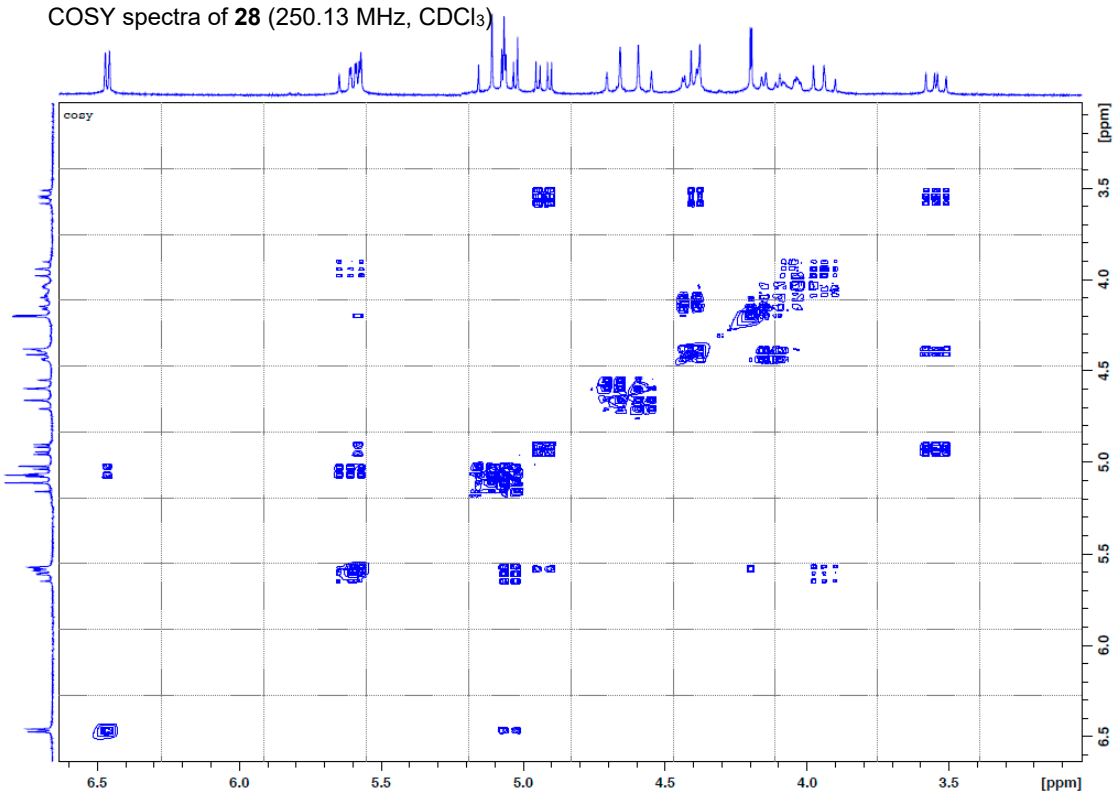


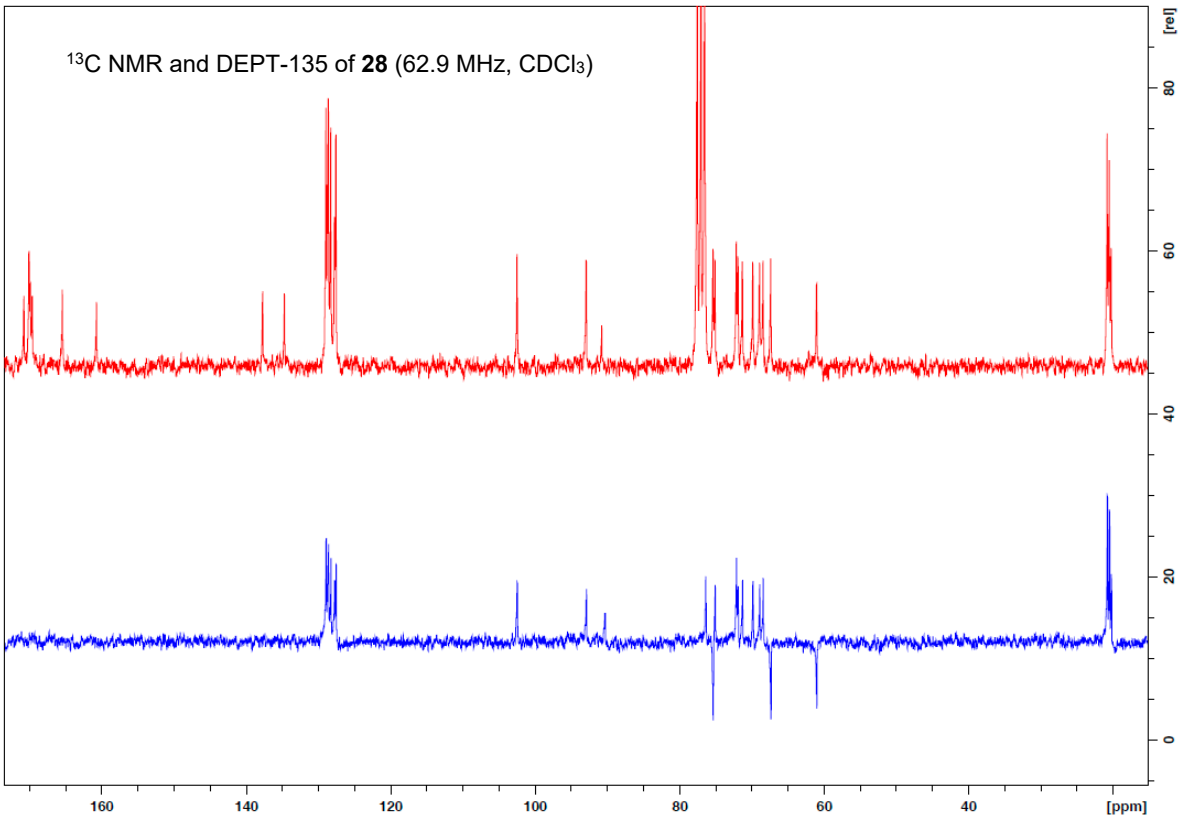
^{1}H NMR of **28** (250.13 MHz, $CDCl_3$)

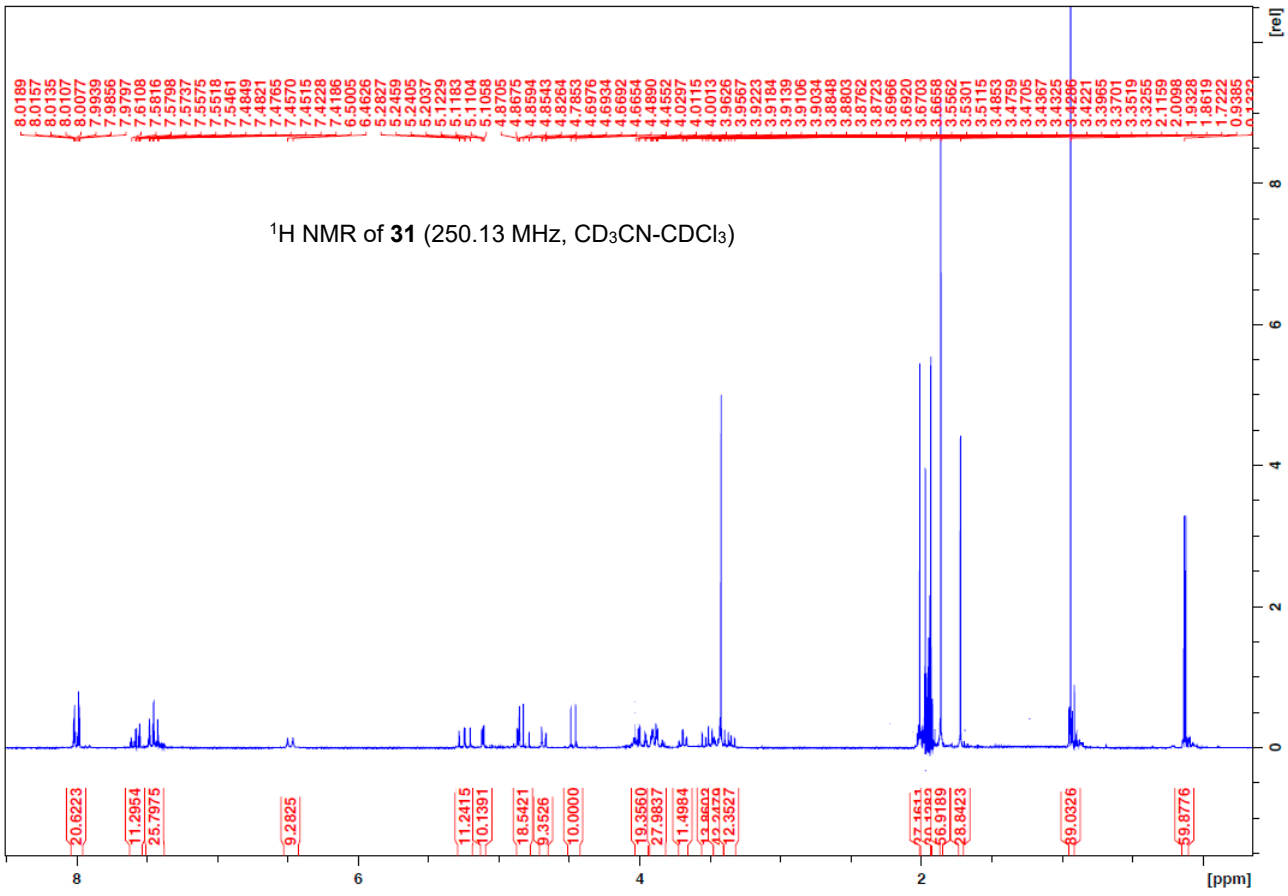


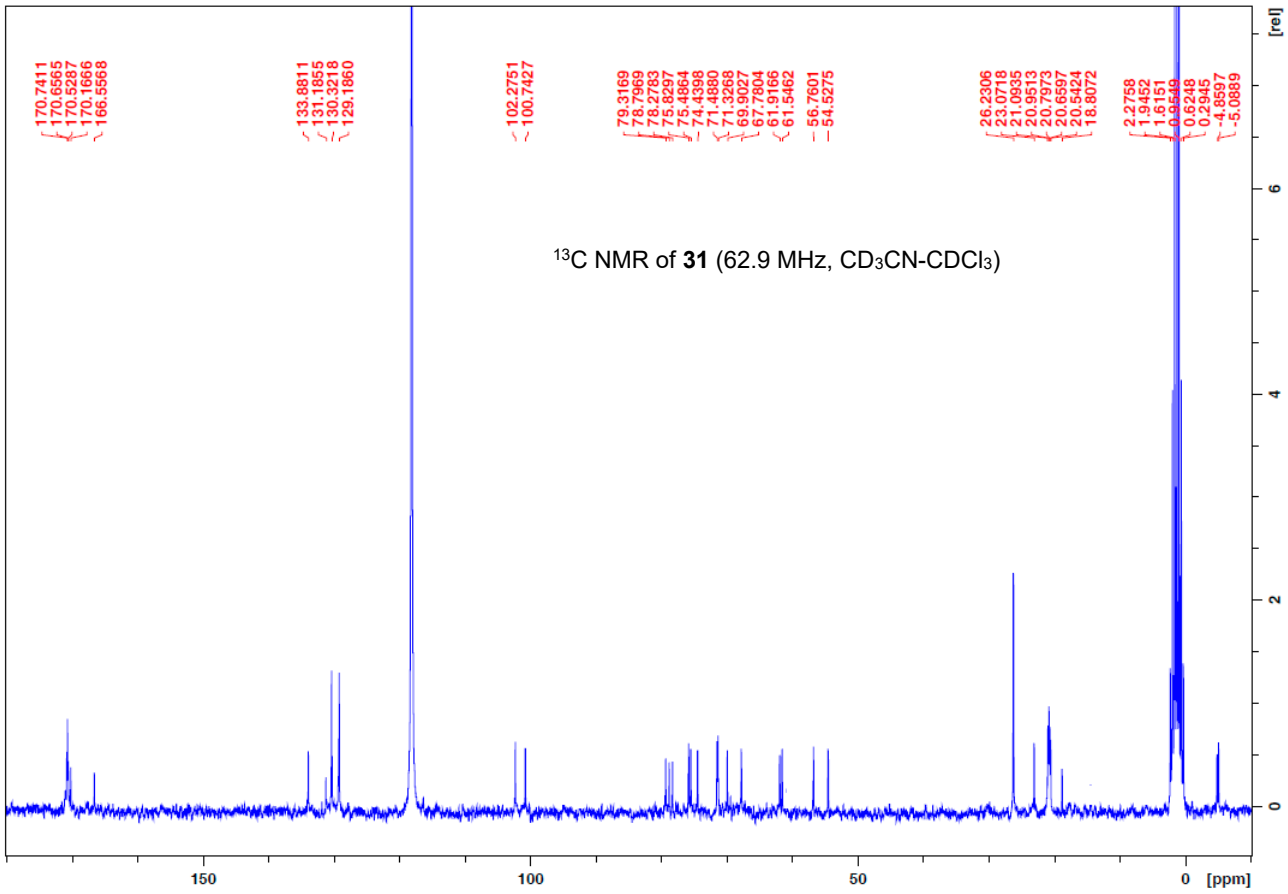
^{13}C NMR of **28** (62.9 MHz, $CDCl_3$)

COSY spectra of **28** (250.13 MHz, $CDCl_3$)

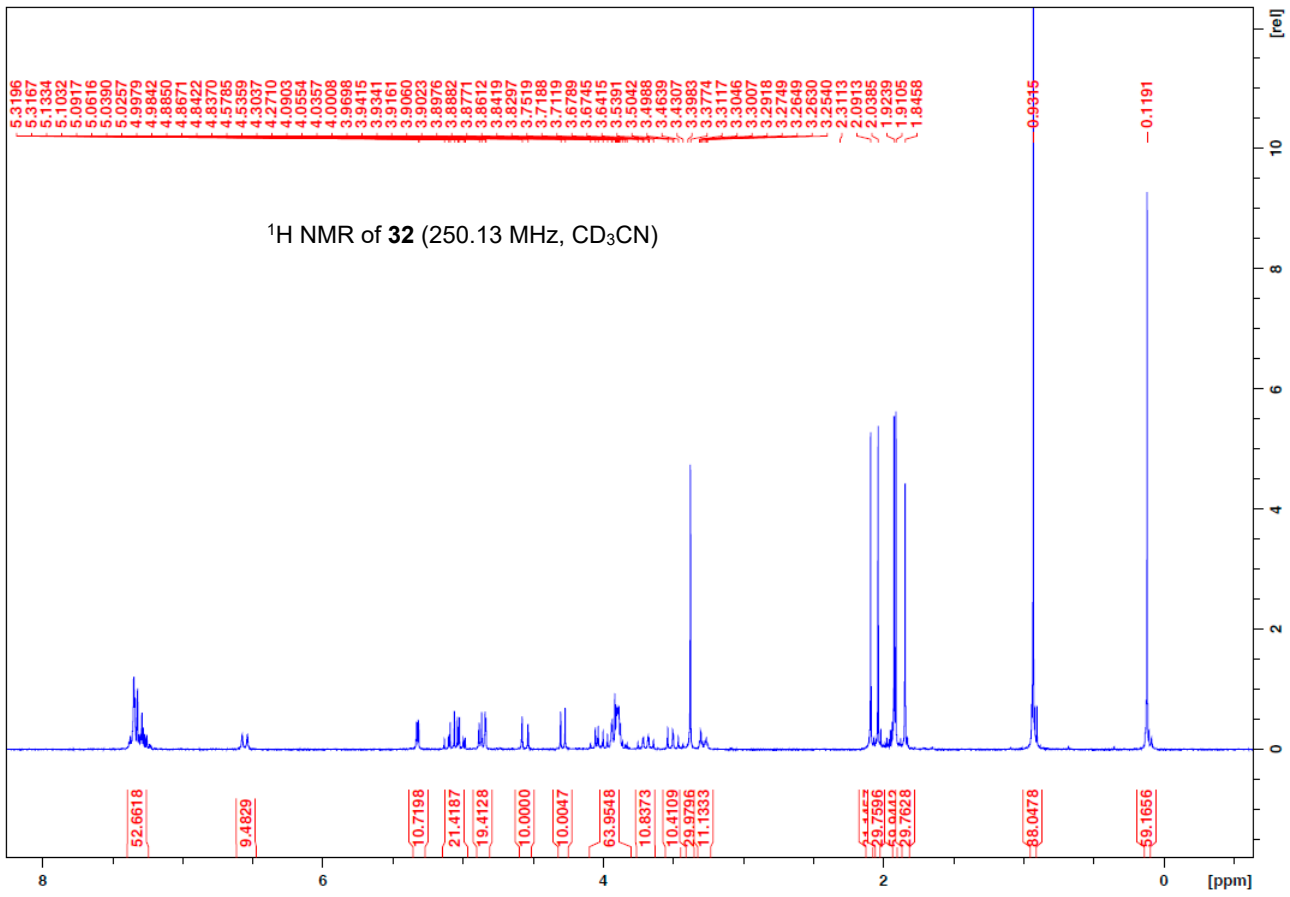



^{13}C NMR and DEPT-135 of **28** (62.9 MHz, $CDCl_3$)
[rel]
80
60
40
20
0
160
140
120
100
80
60
40
[ppm]

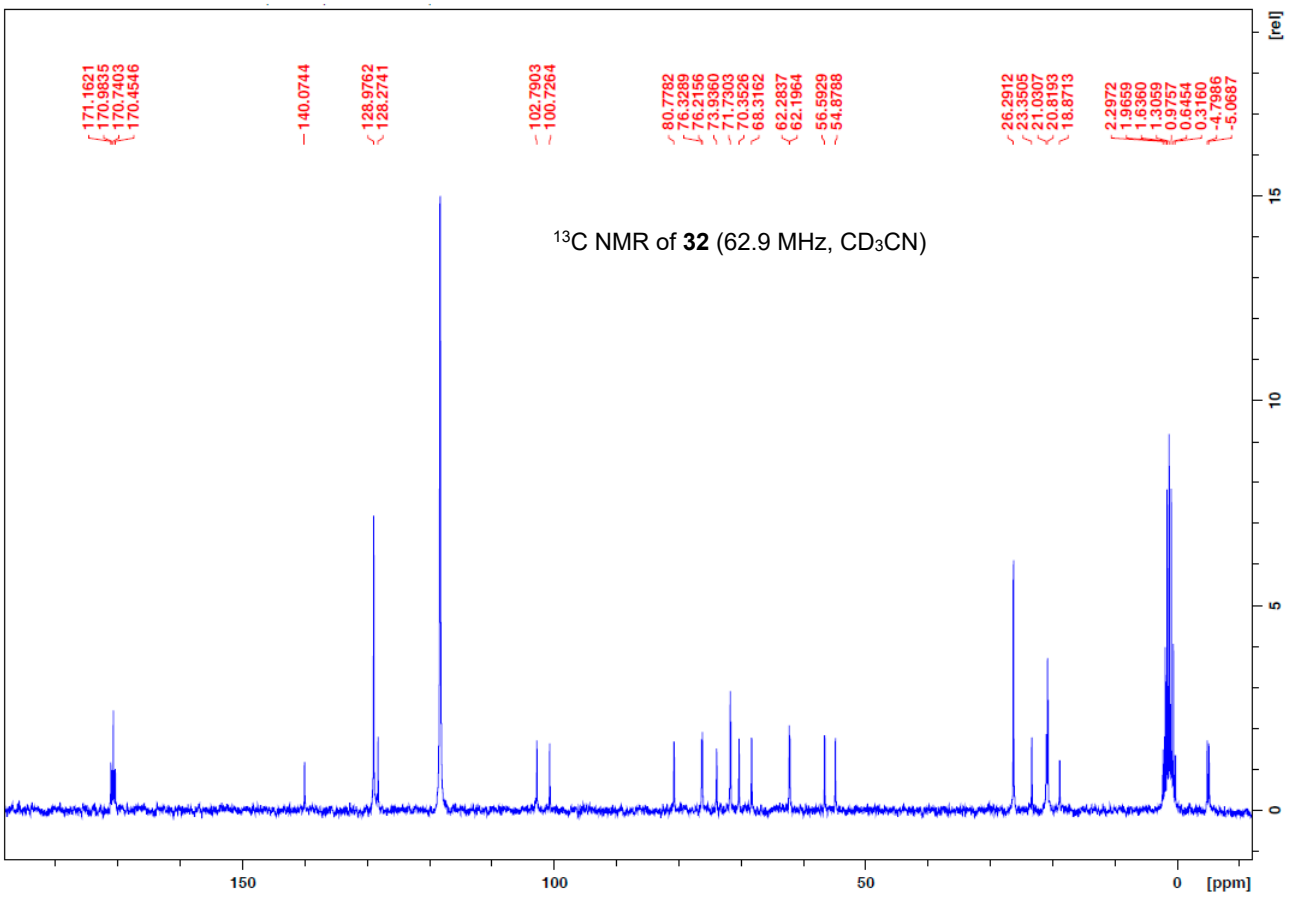

^{1}H NMR of **31** (250.13 MHz, CD_3CN-$CDCl_3$)
[rel]
8
6
4
2
0
20.6223
11.2954
25.7975
9.2825
11.2415
10.1391
18.5421
9.3526
10.0000
19.3560
27.9837
11.4984
12.3527
28.8423
89.0326
59.8776
8
6
4
2
[ppm]



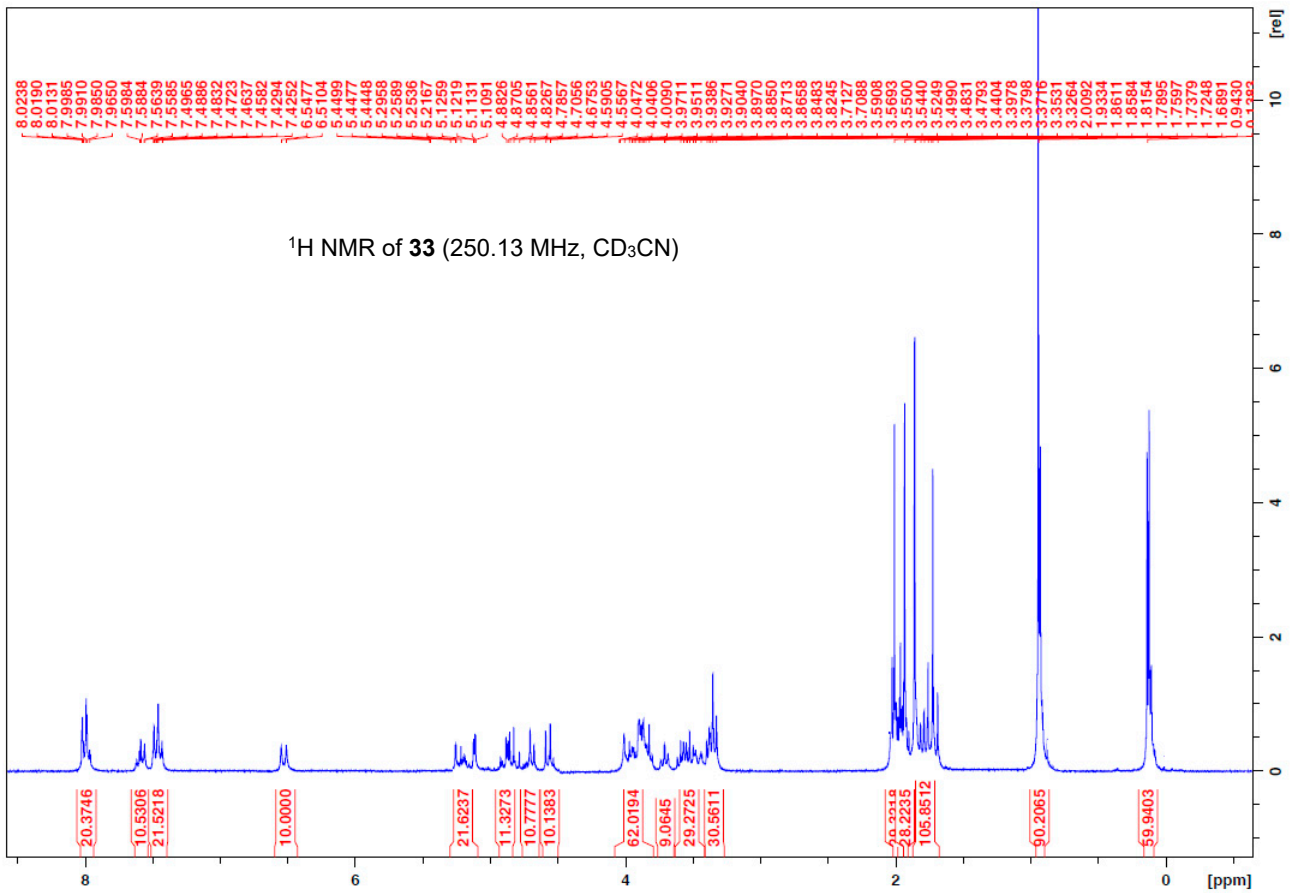
^{13}C NMR of **31** (62.9 MHz, CD_3CN-$CDCl_3$)



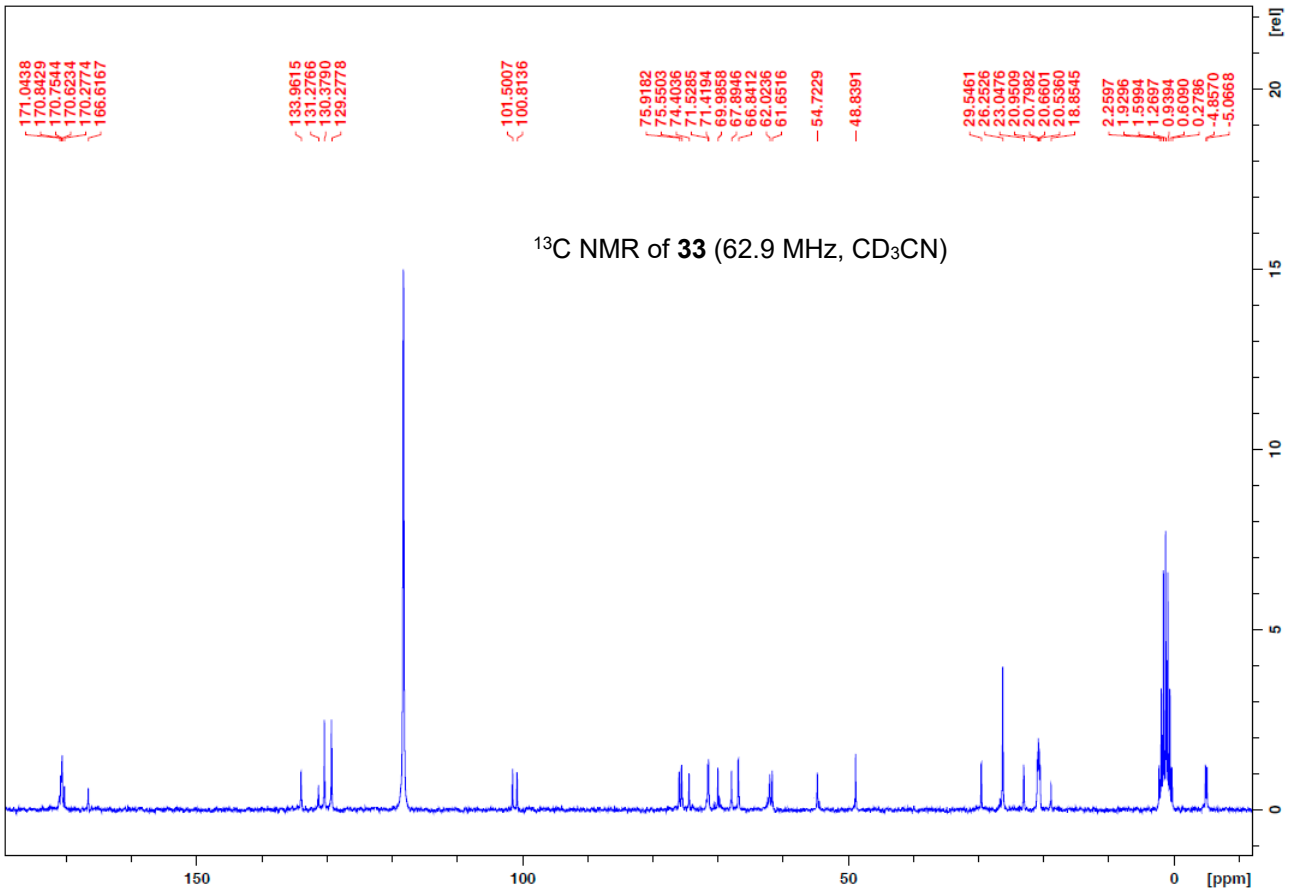
^{1}H NMR of **32** (250.13 MHz, CD_3CN)



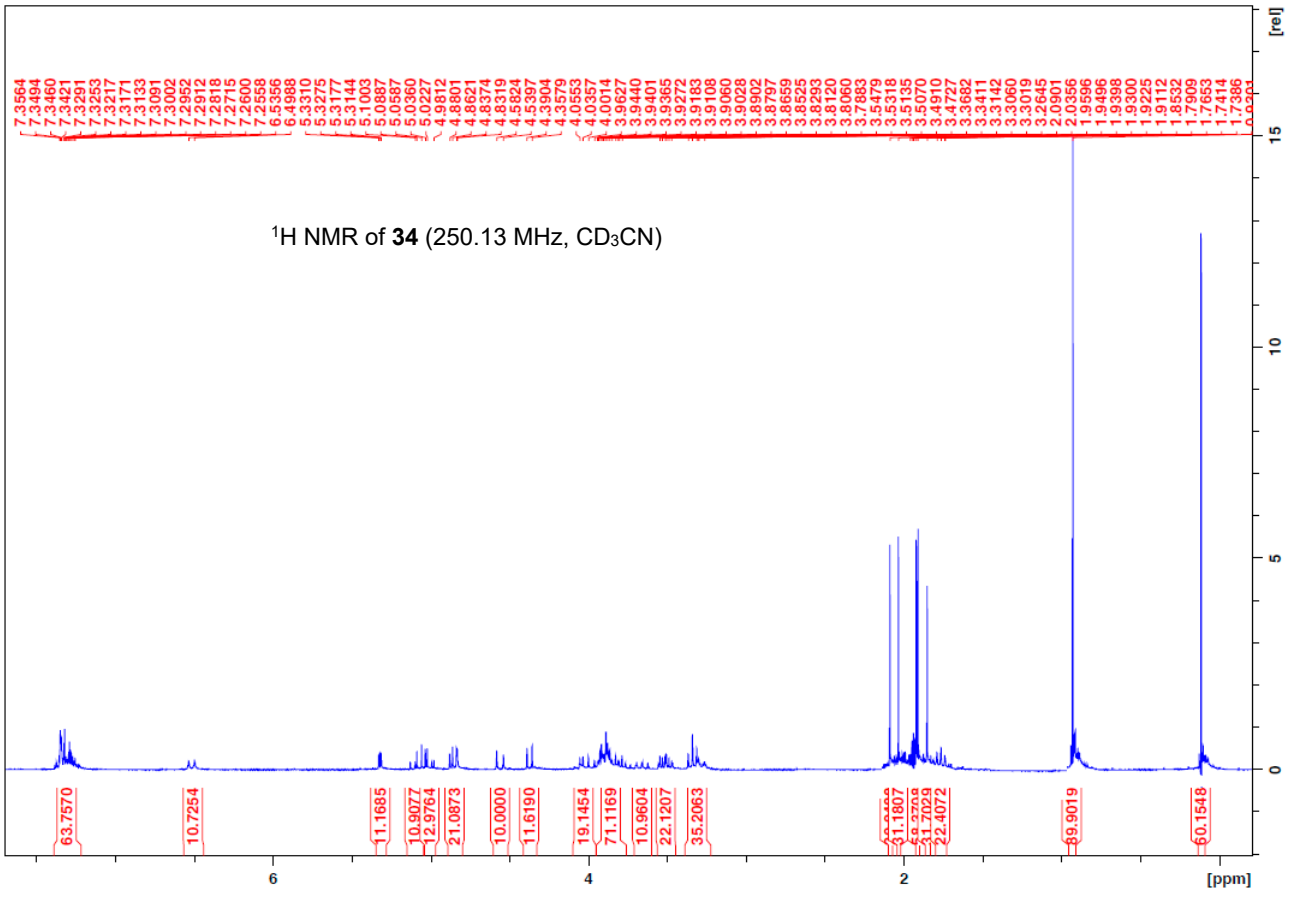
^{13}C NMR of **32** (62.9 MHz, CD_3CN)



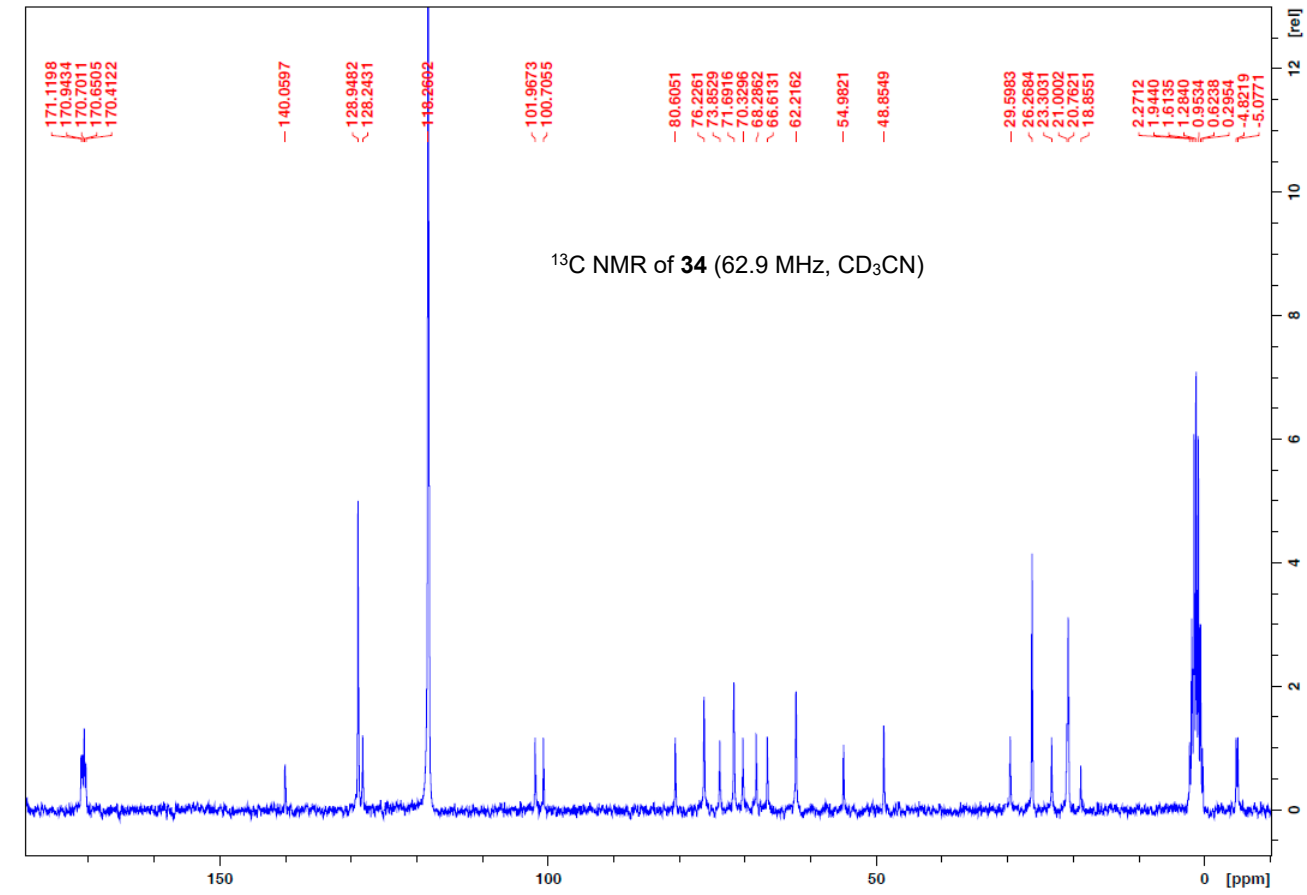
^{1}H NMR of **33** (250.13 MHz, CD_3CN)



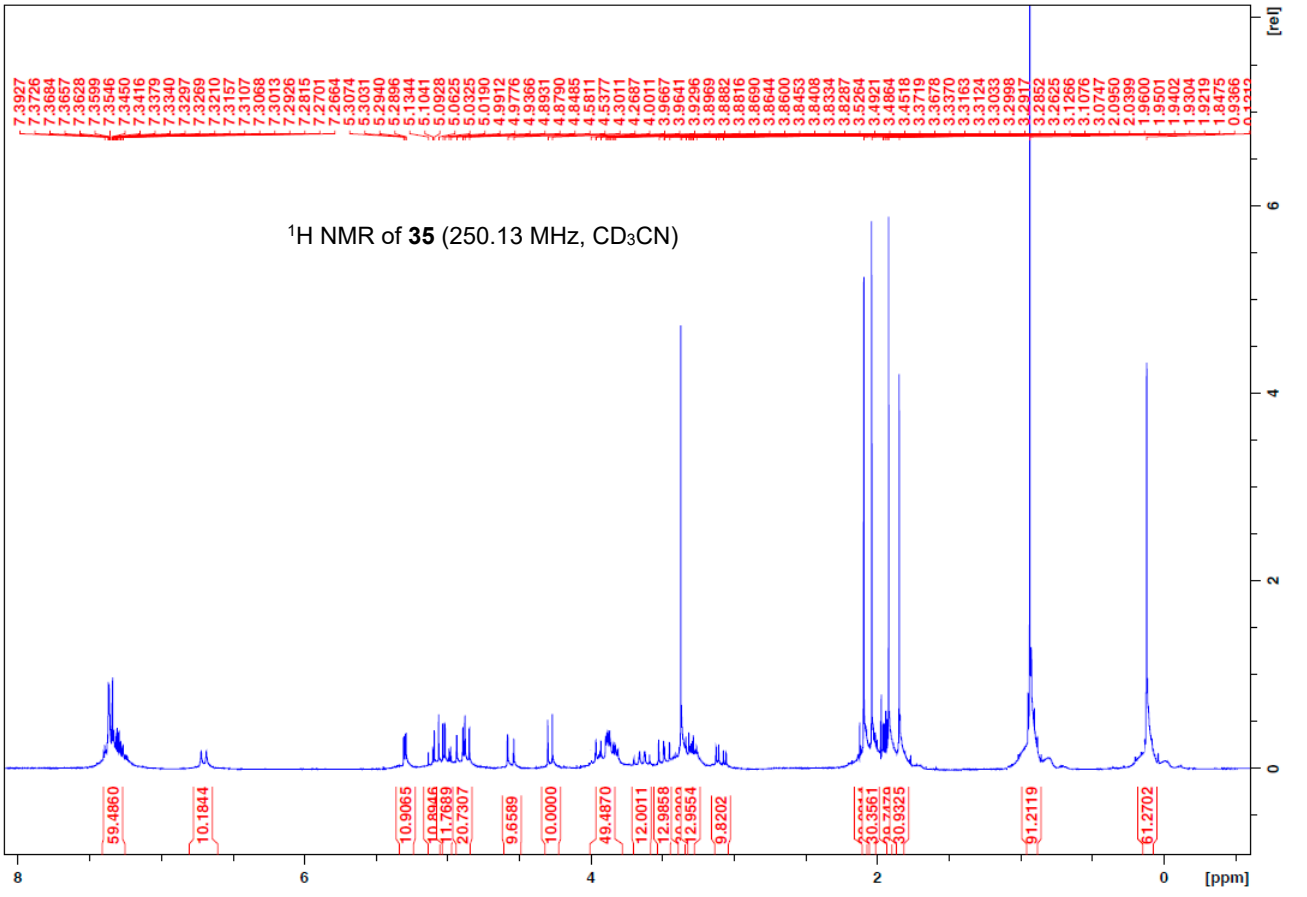
^{13}C NMR of **33** (62.9 MHz, CD_3CN)



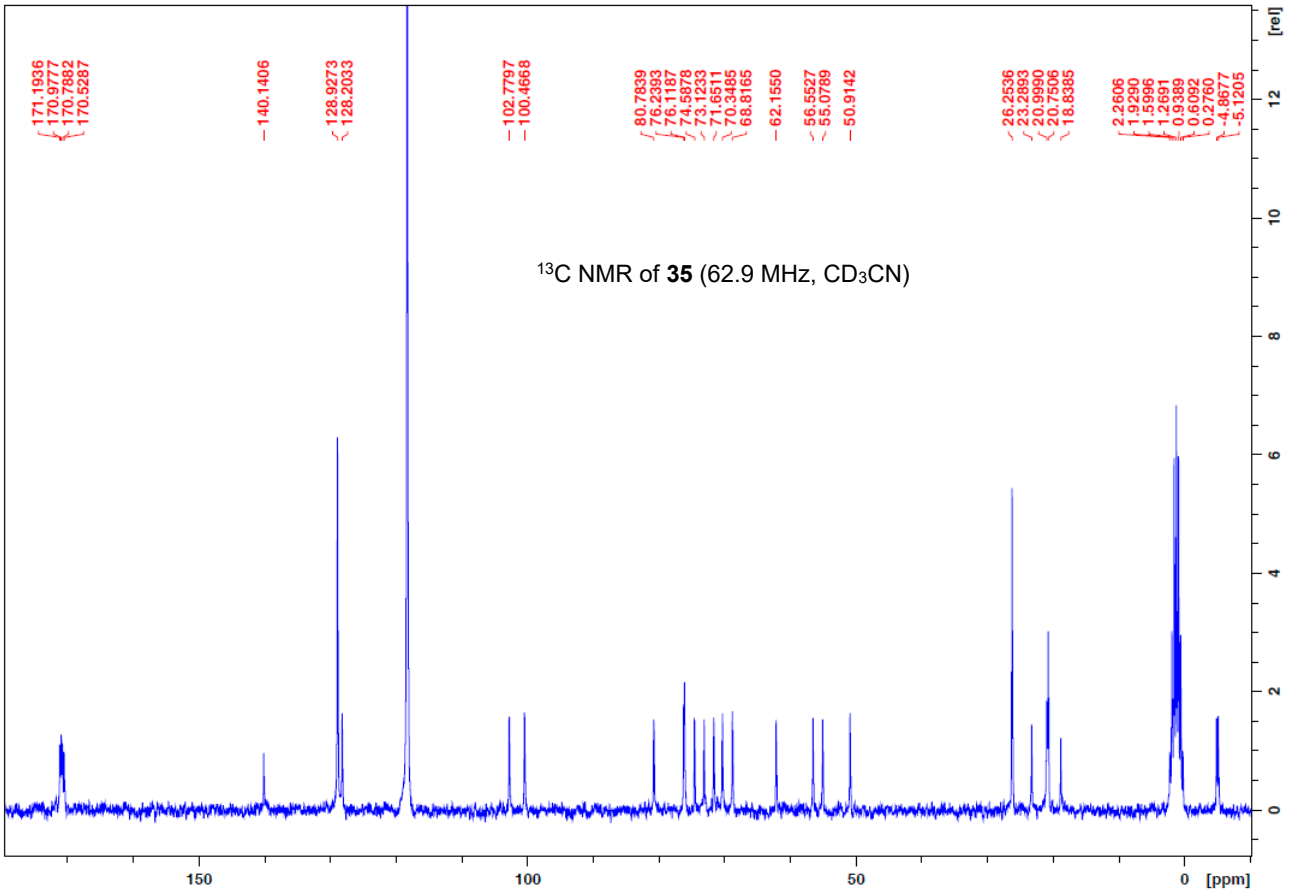
^{1}H NMR of **34** (250.13 MHz, CD_3CN)



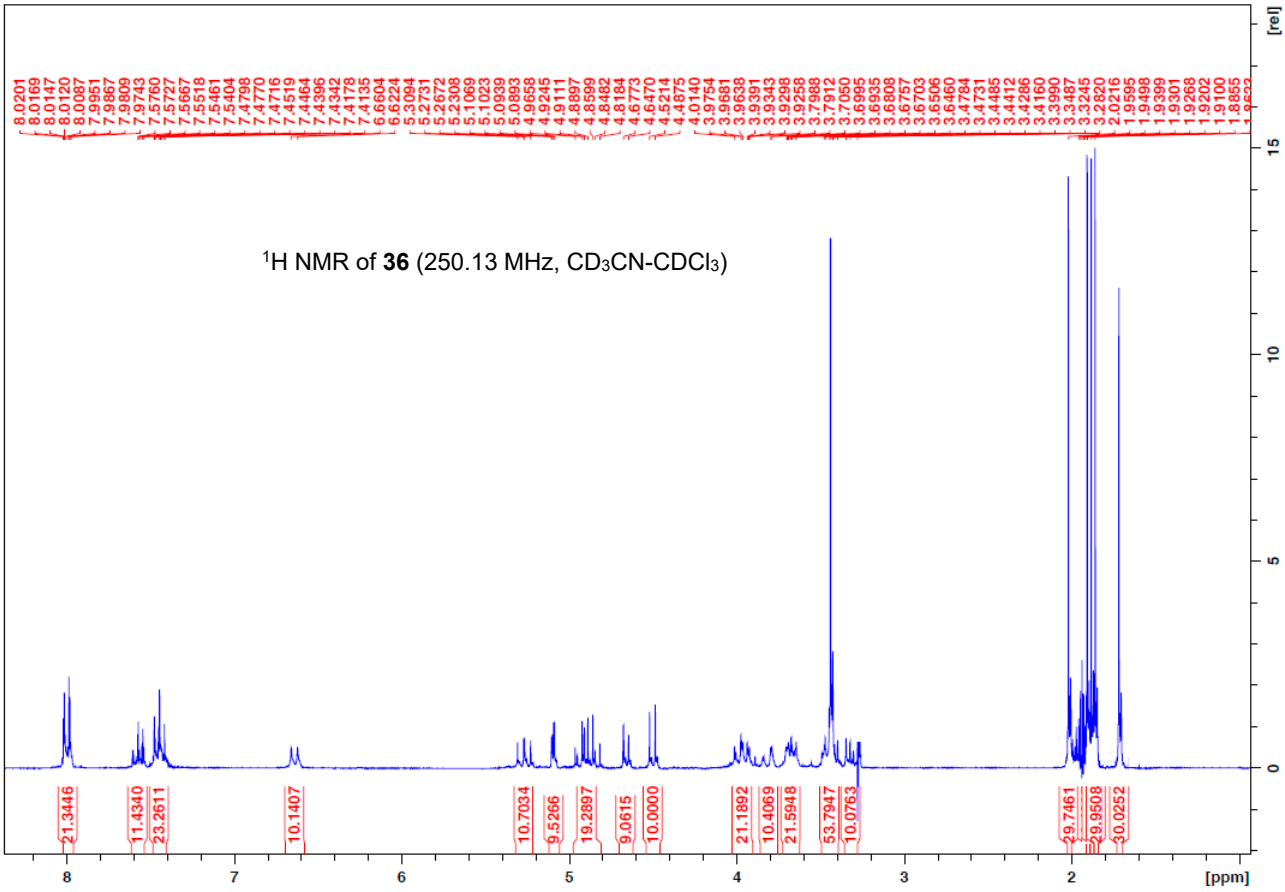
^{13}C NMR of **34** (62.9 MHz, CD_3CN)



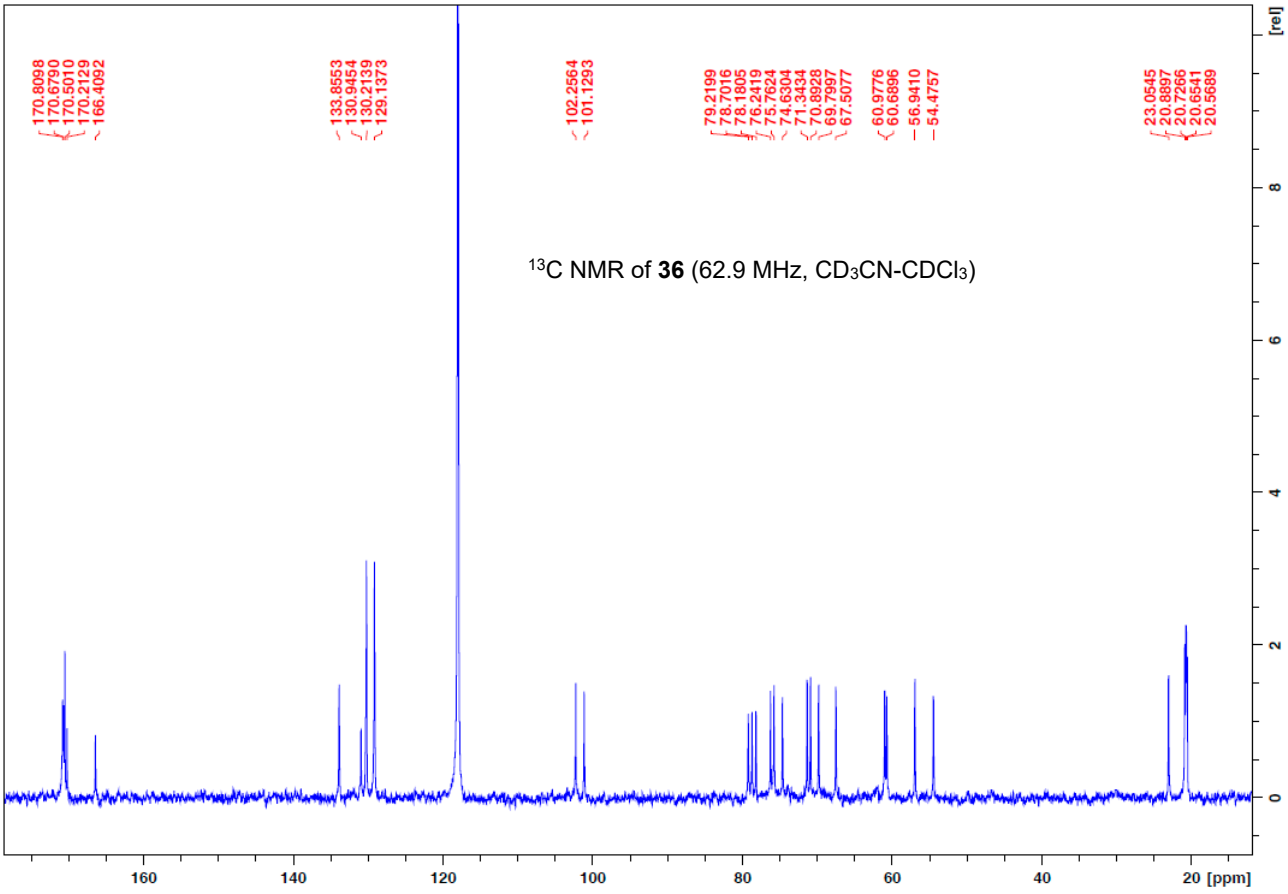
^{1}H NMR of **35** (250.13 MHz, CD_3CN)



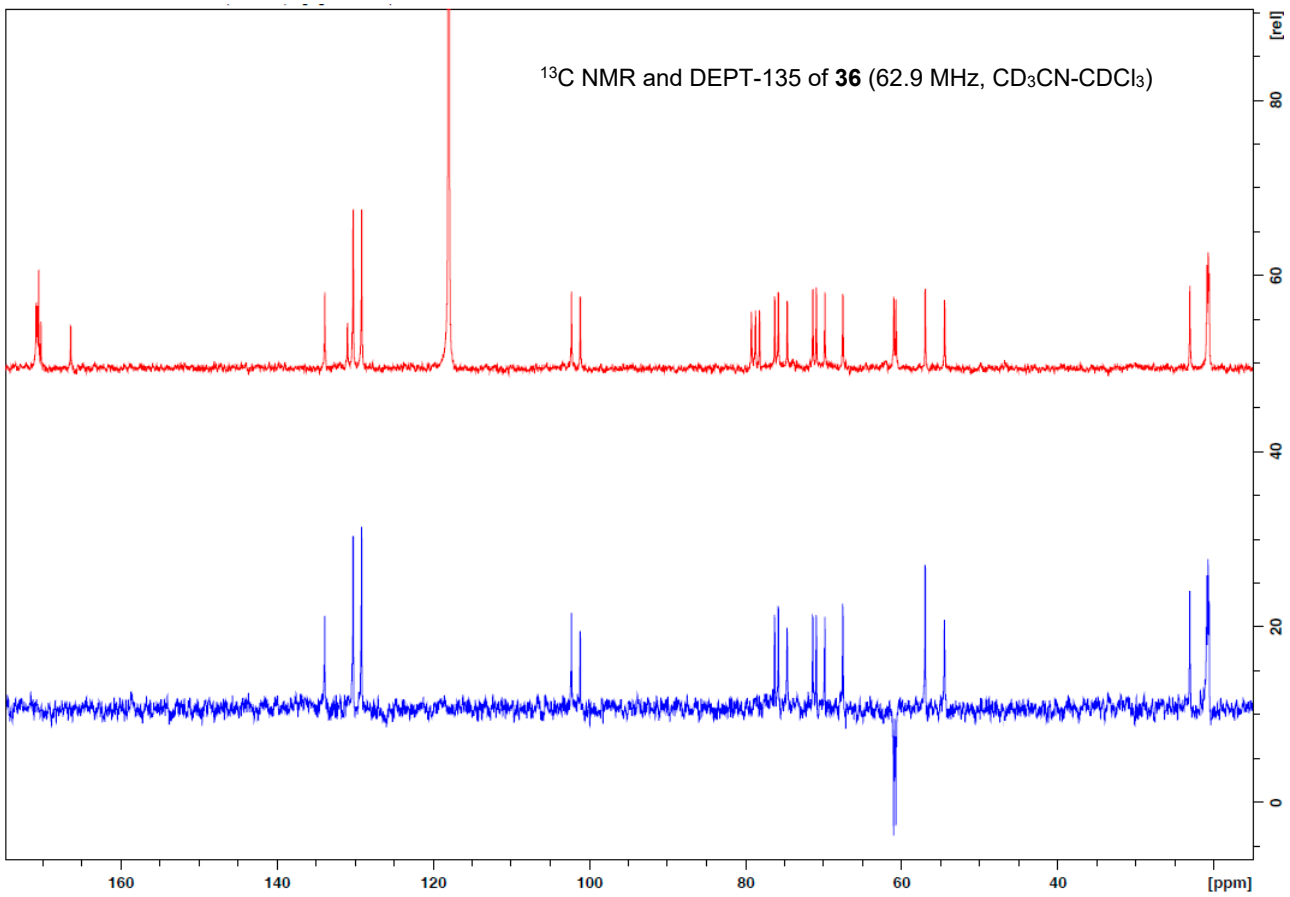
^{13}C NMR of **35** (62.9 MHz, CD_3CN)



^{1}H NMR of **36** (250.13 MHz, CD_3CN-$CDCl_3$)

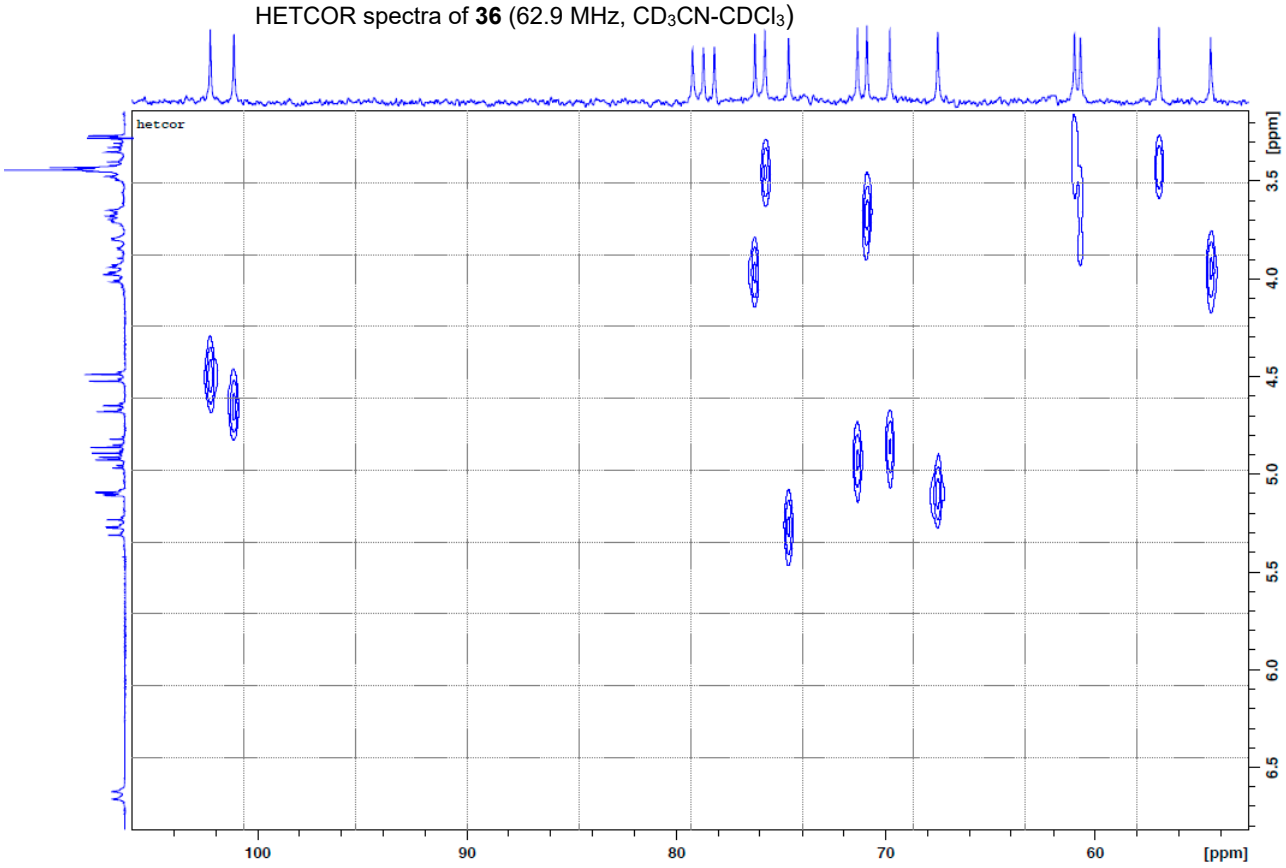


^{13}C NMR of **36** (62.9 MHz, CD_3CN-$CDCl_3$)

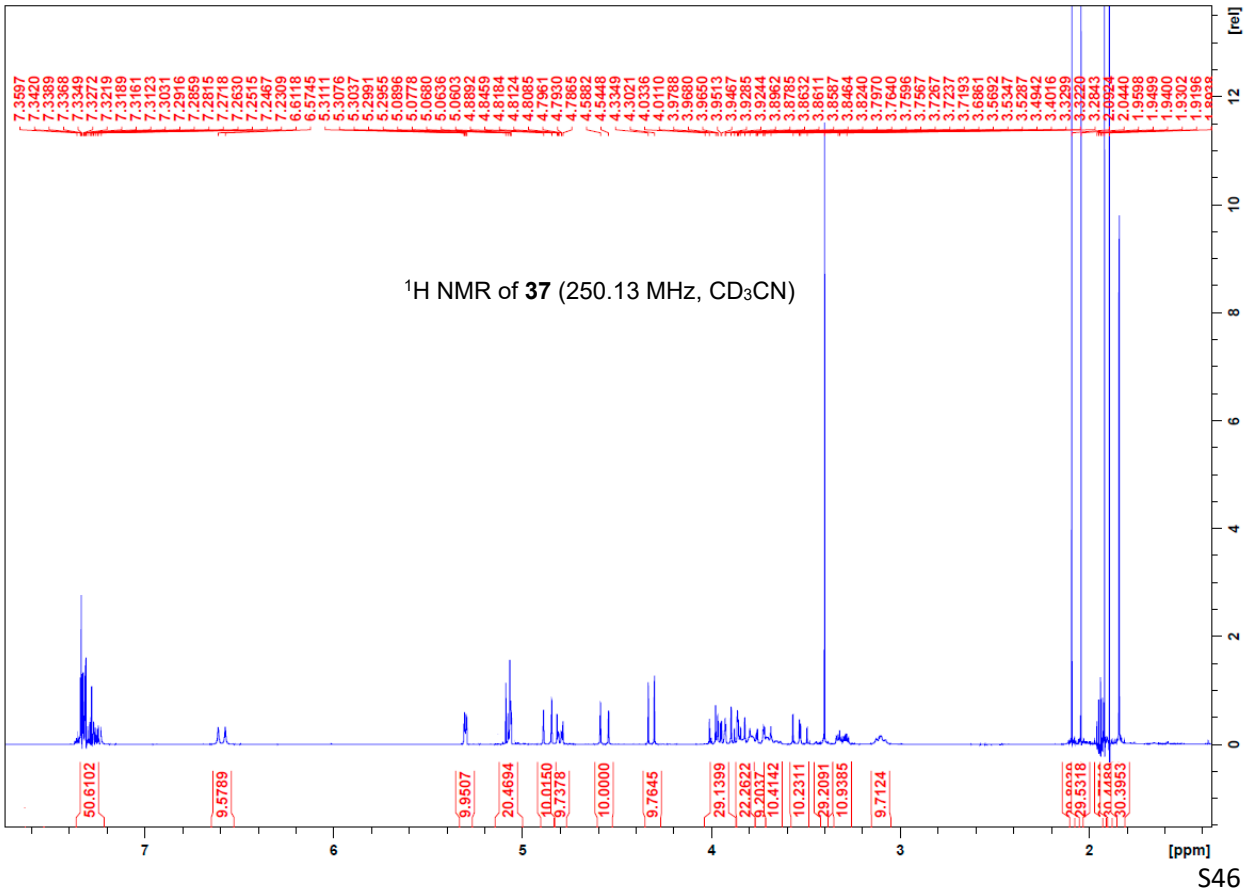


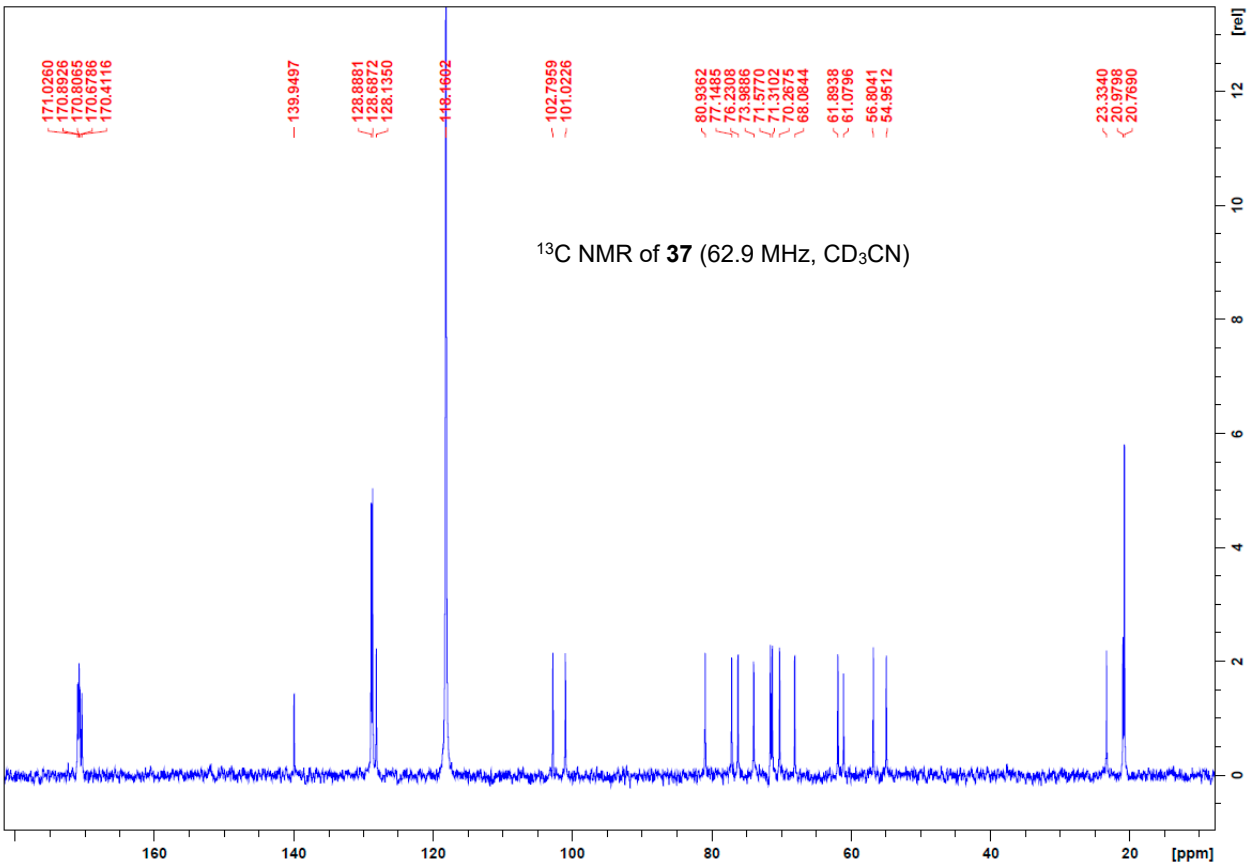
^{13}C NMR and DEPT-135 of **36** (62.9 MHz, CD_3CN-$CDCl_3$)

HETCOR spectra of **36** (62.9 MHz, CD_3CN-$CDCl_3$)

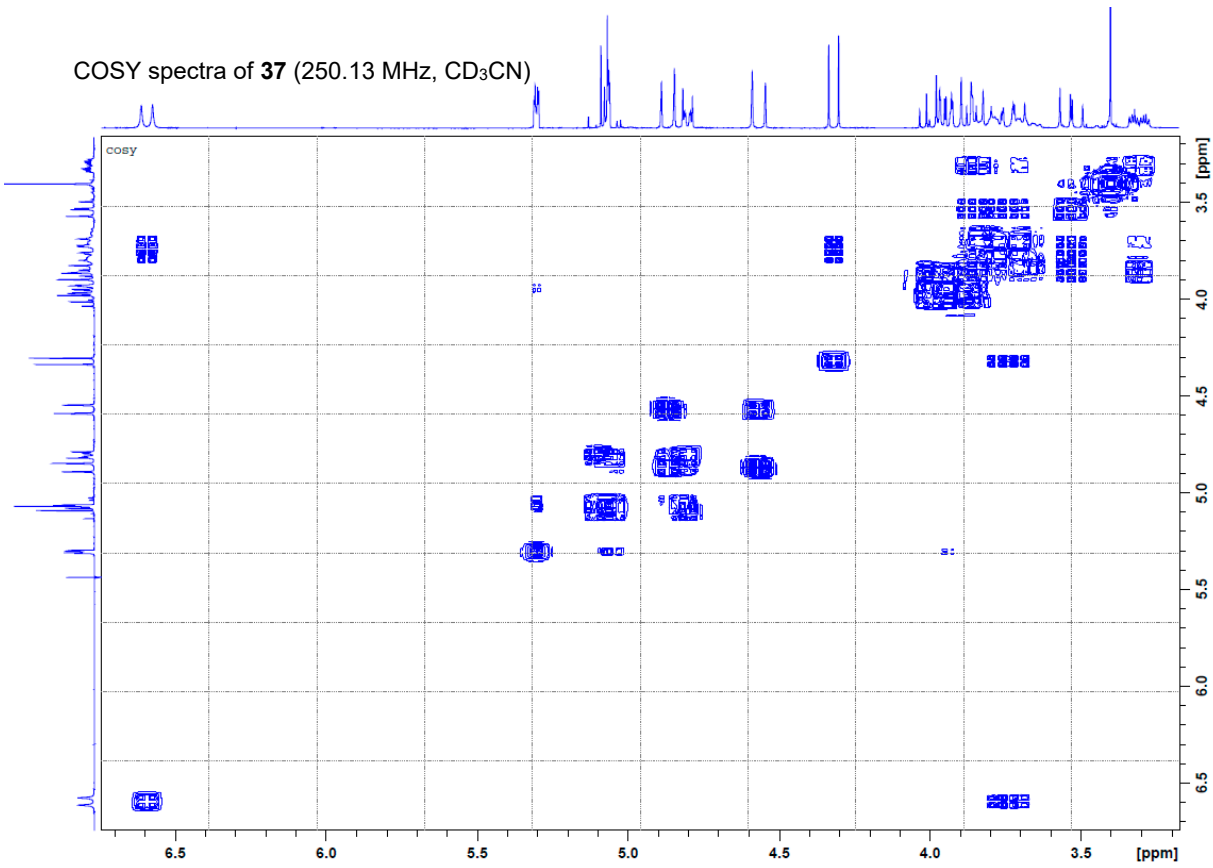


^1H NMR of **37** (250.13 MHz, CD_3CN)

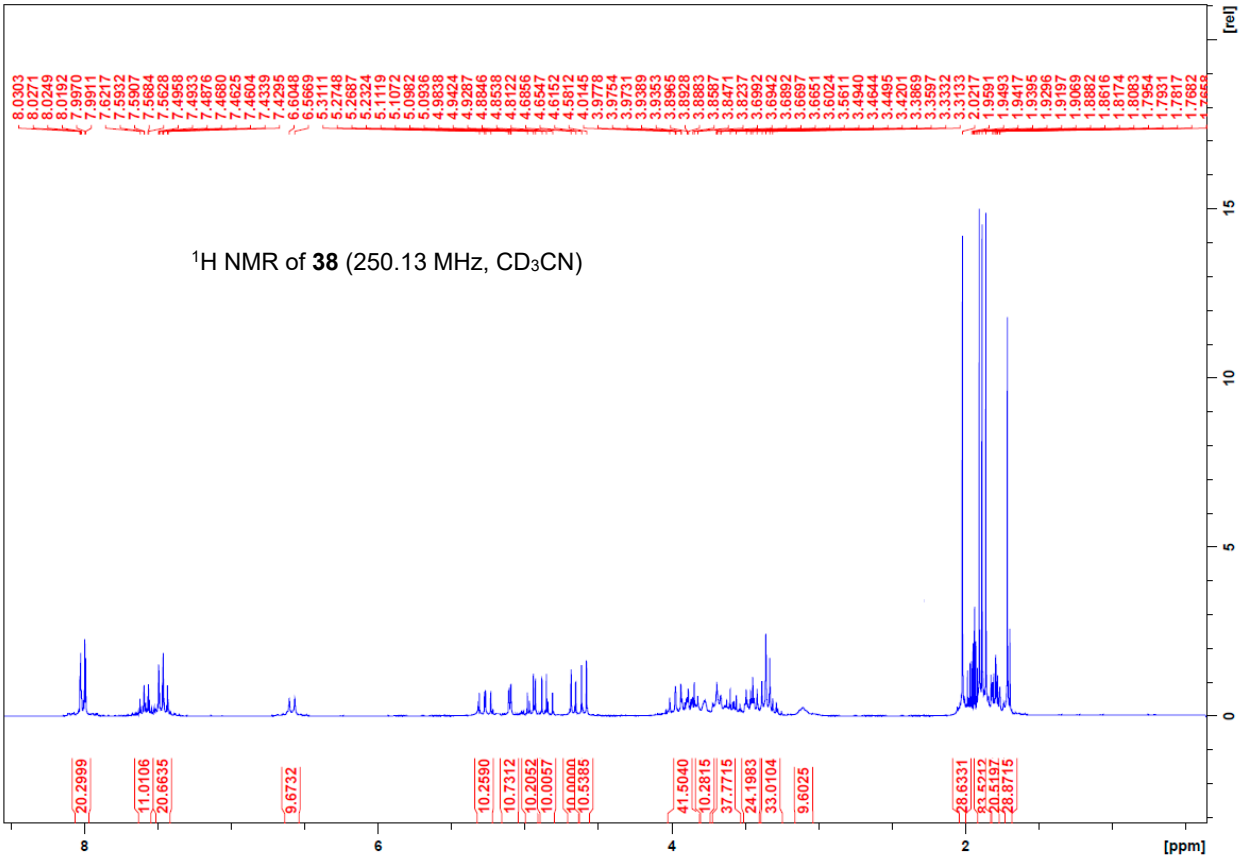


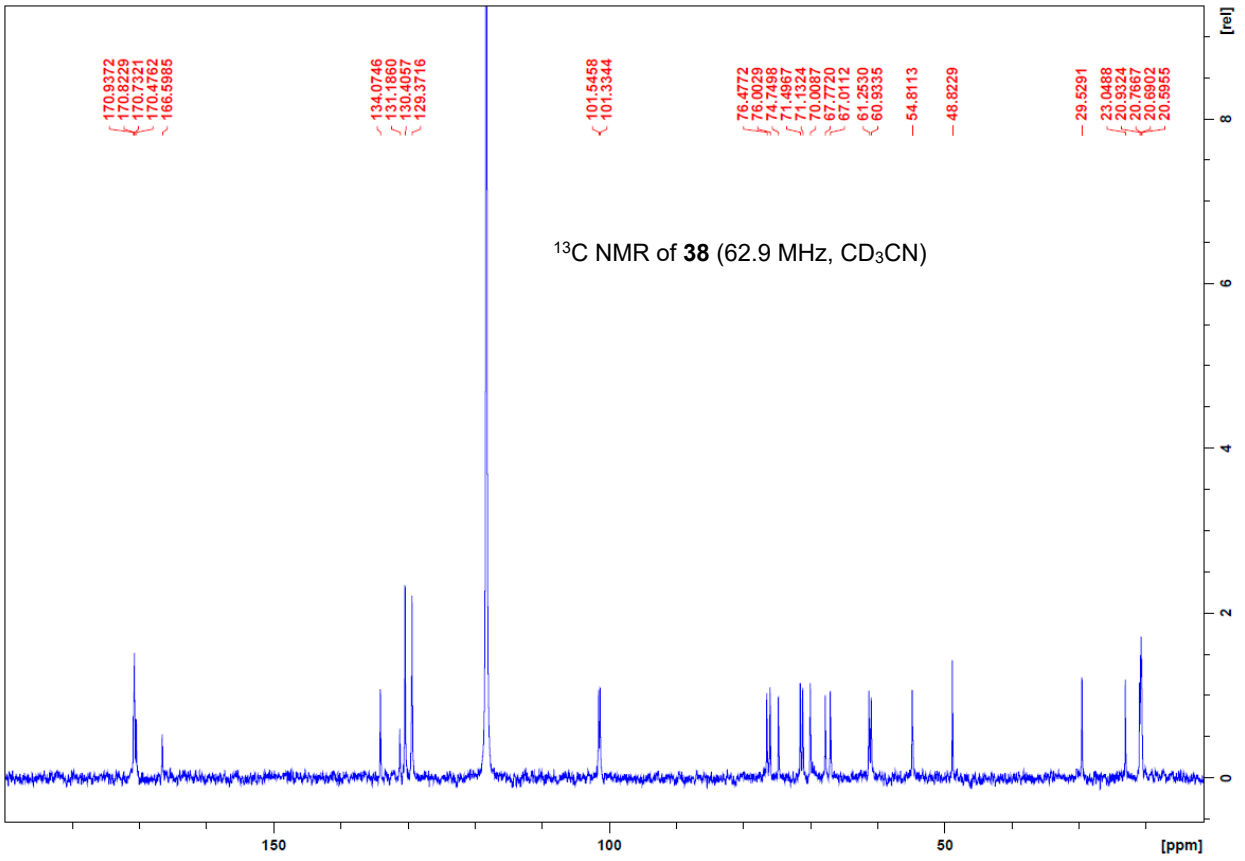


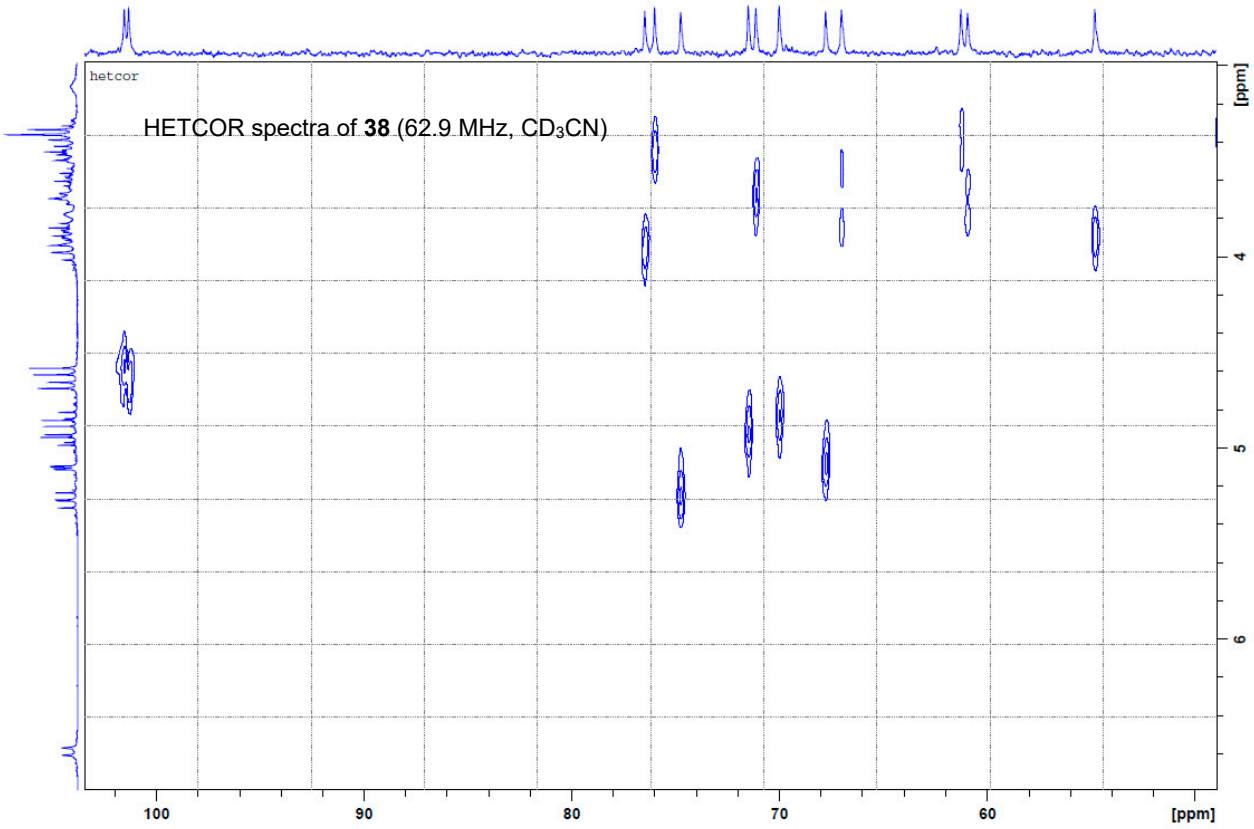
^{13}C NMR of **37** (62.9 MHz, CD_3CN)

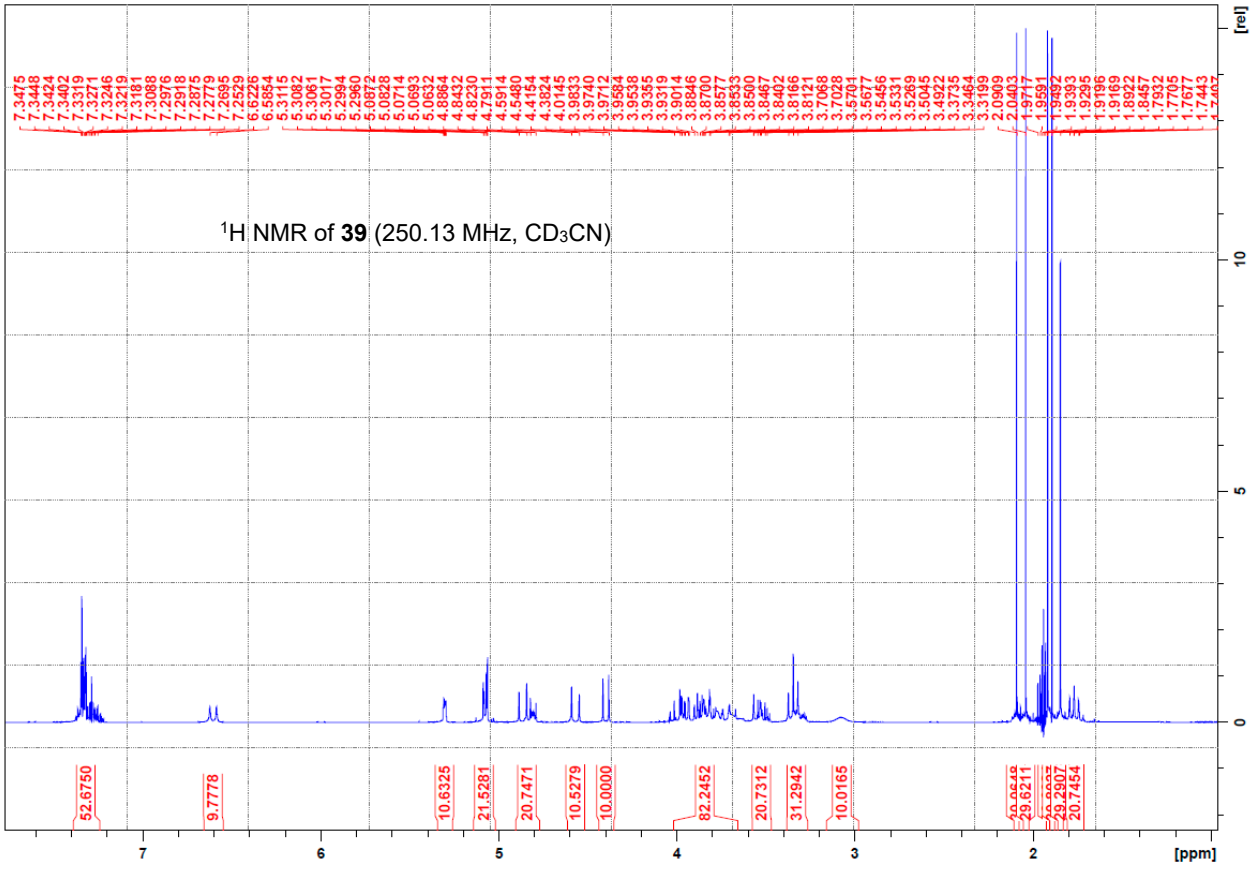


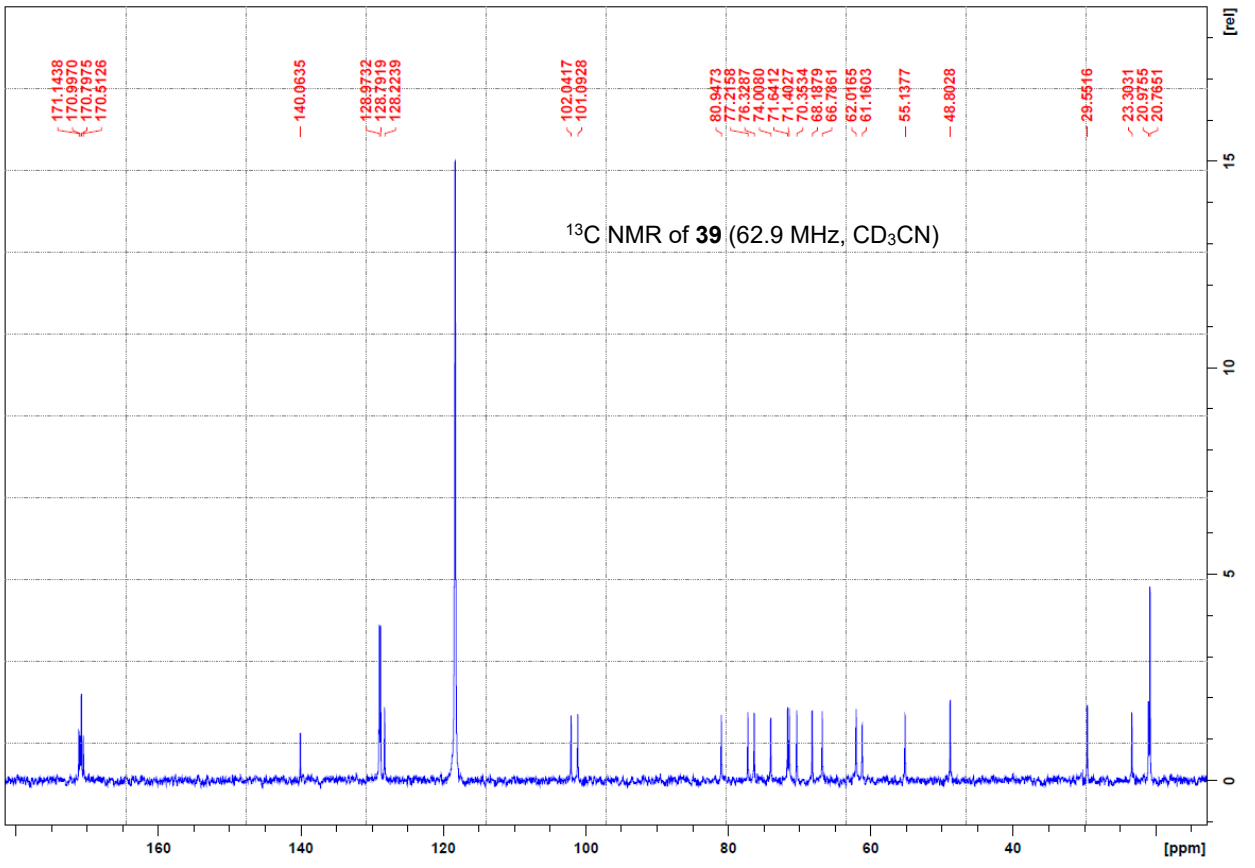
COSY spectra of **37** (250.13 MHz, CD_3CN)


^{1}H NMR of **38** (250.13 MHz, CD_3CN)
[rel]
[ppm]

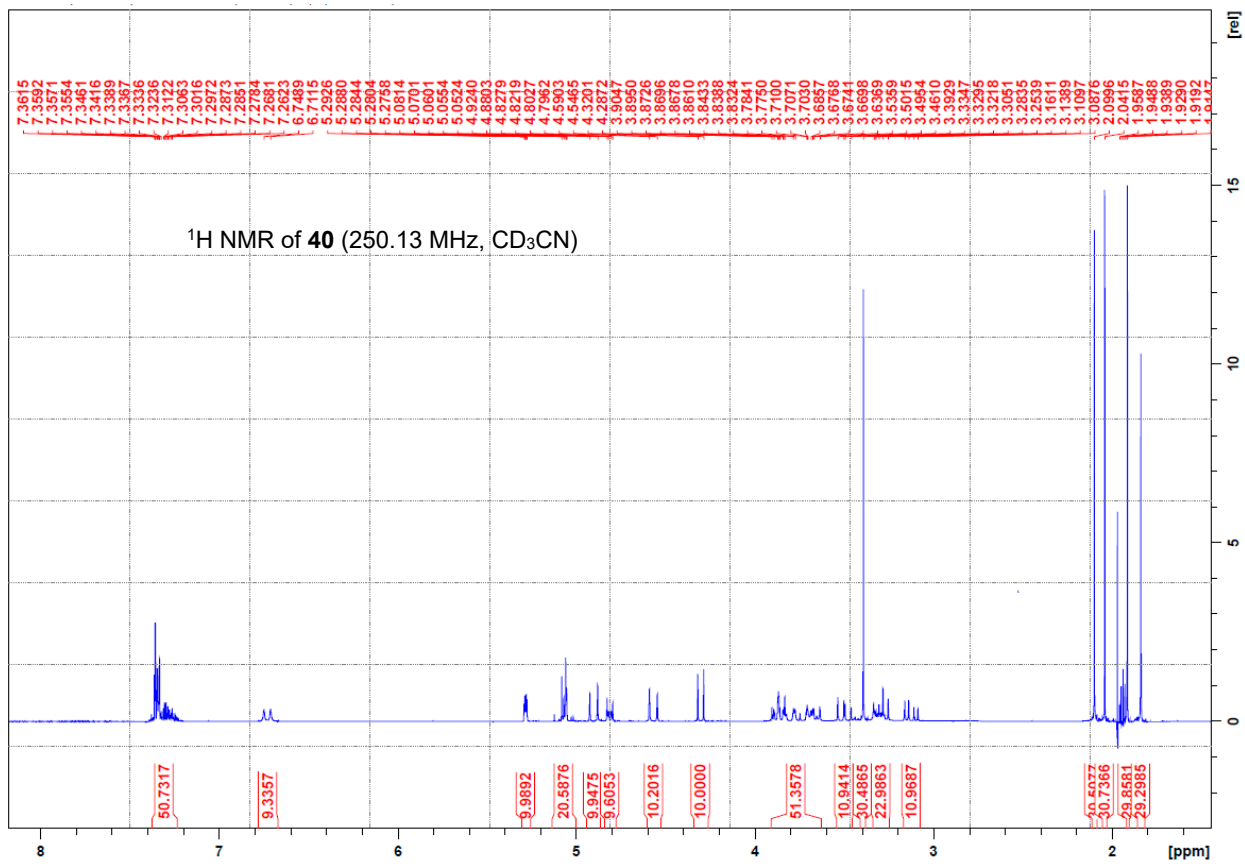

^{13}C NMR of **38** (62.9 MHz, CD_3CN)
[rel]
[ppm]


hetcor
HETCOR spectra of 38 (62.9 MHz, CD3CN)
100
90
80
70
60
[ppm]

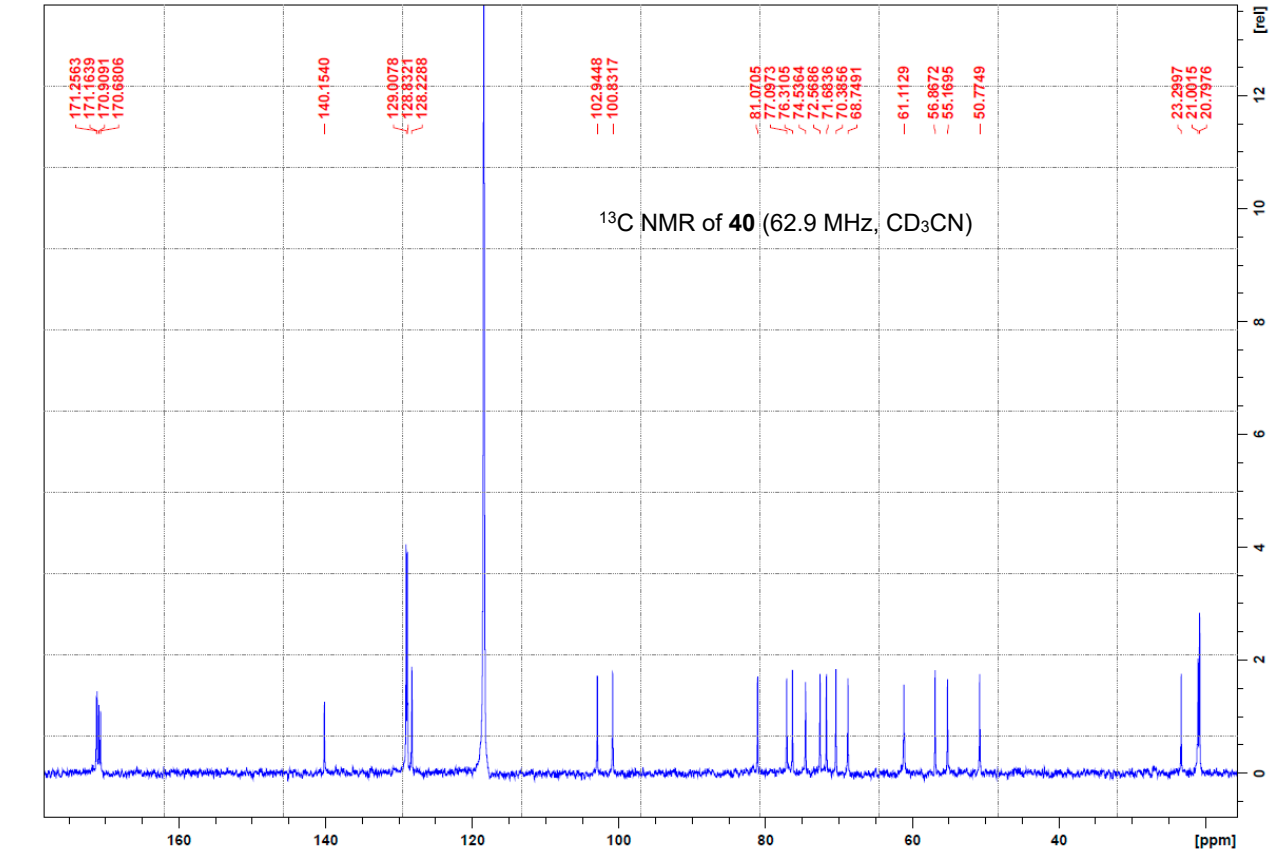

1H NMR of 39 (250.13 MHz, CD3CN)
[rel]
[ppm]



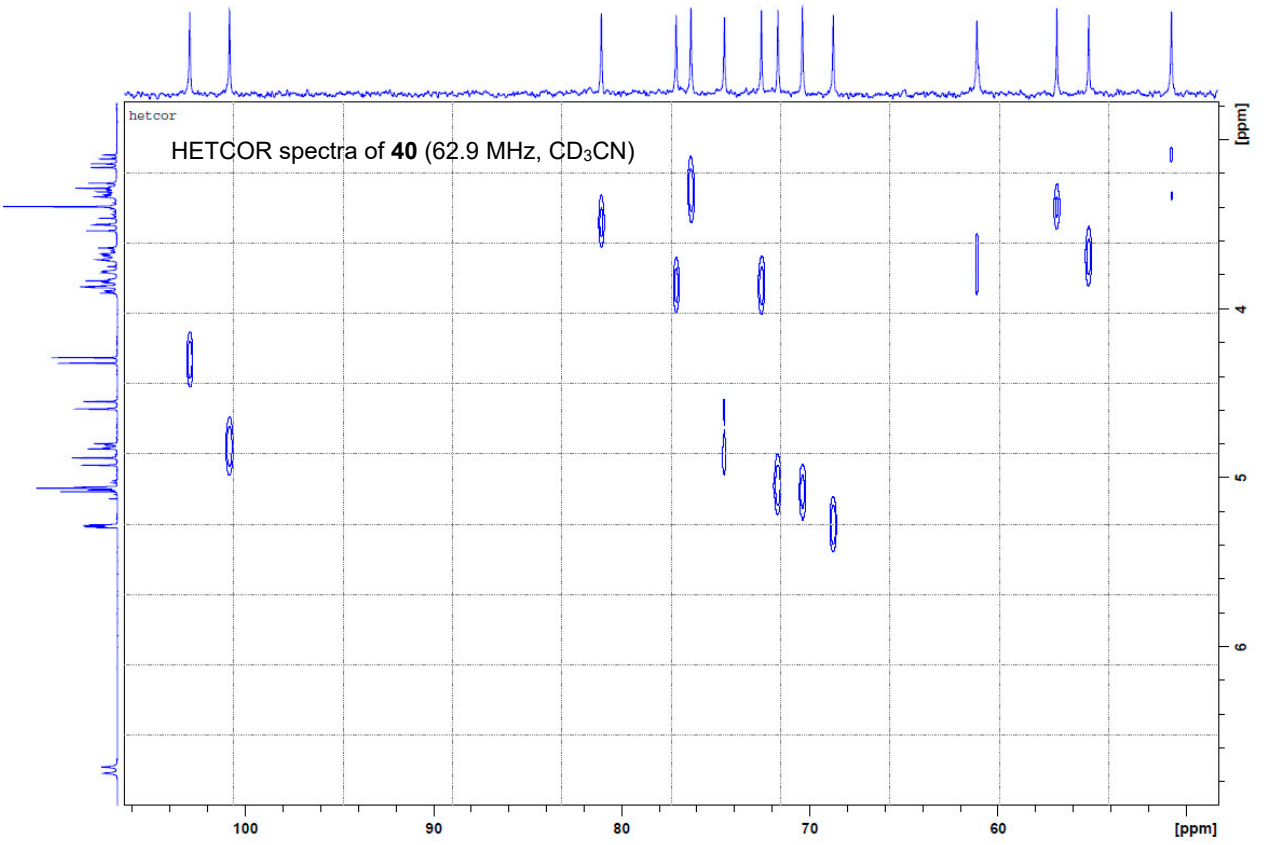
^{13}C NMR of **39** (62.9 MHz, CD_3CN)



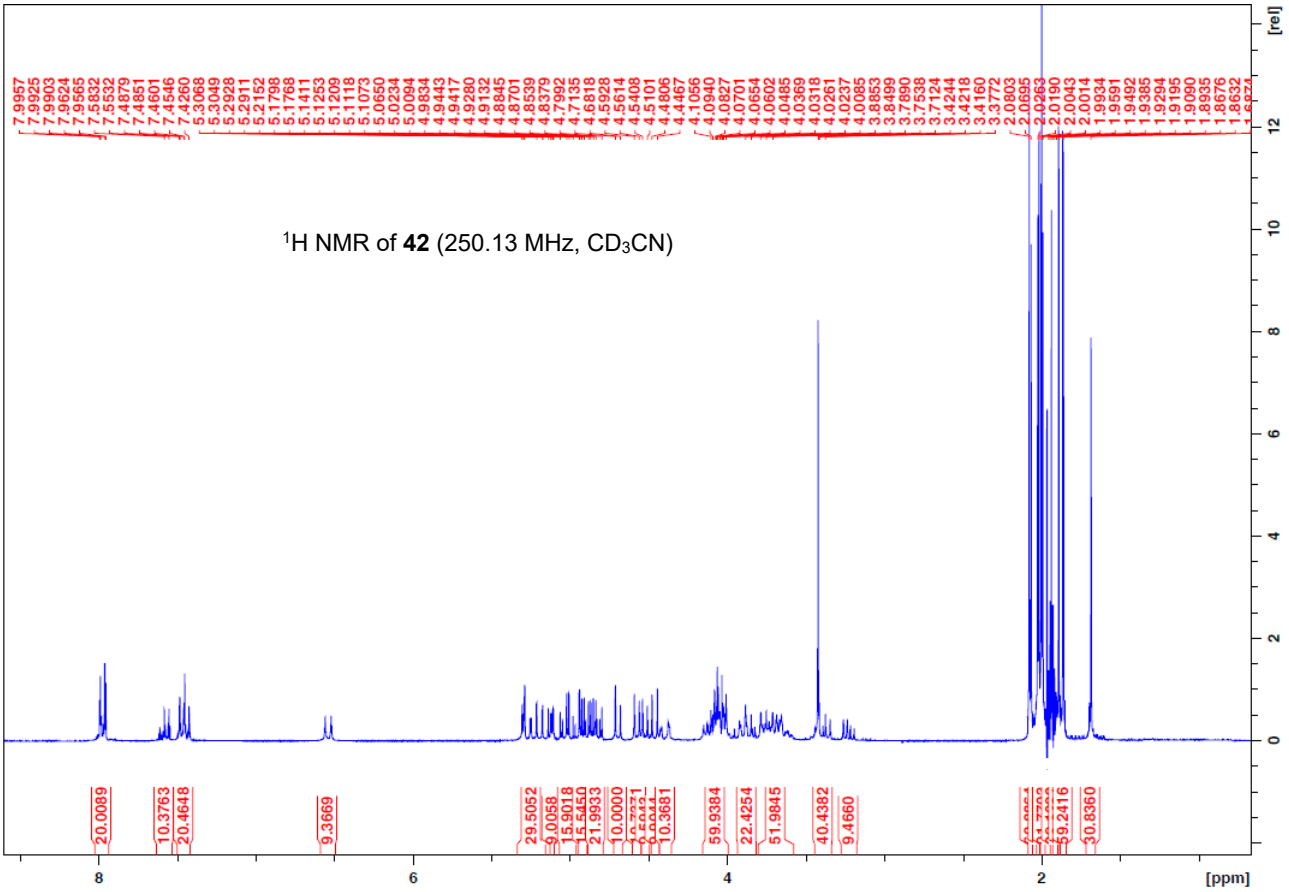
^{1}H NMR of **40** (250.13 MHz, CD_3CN)

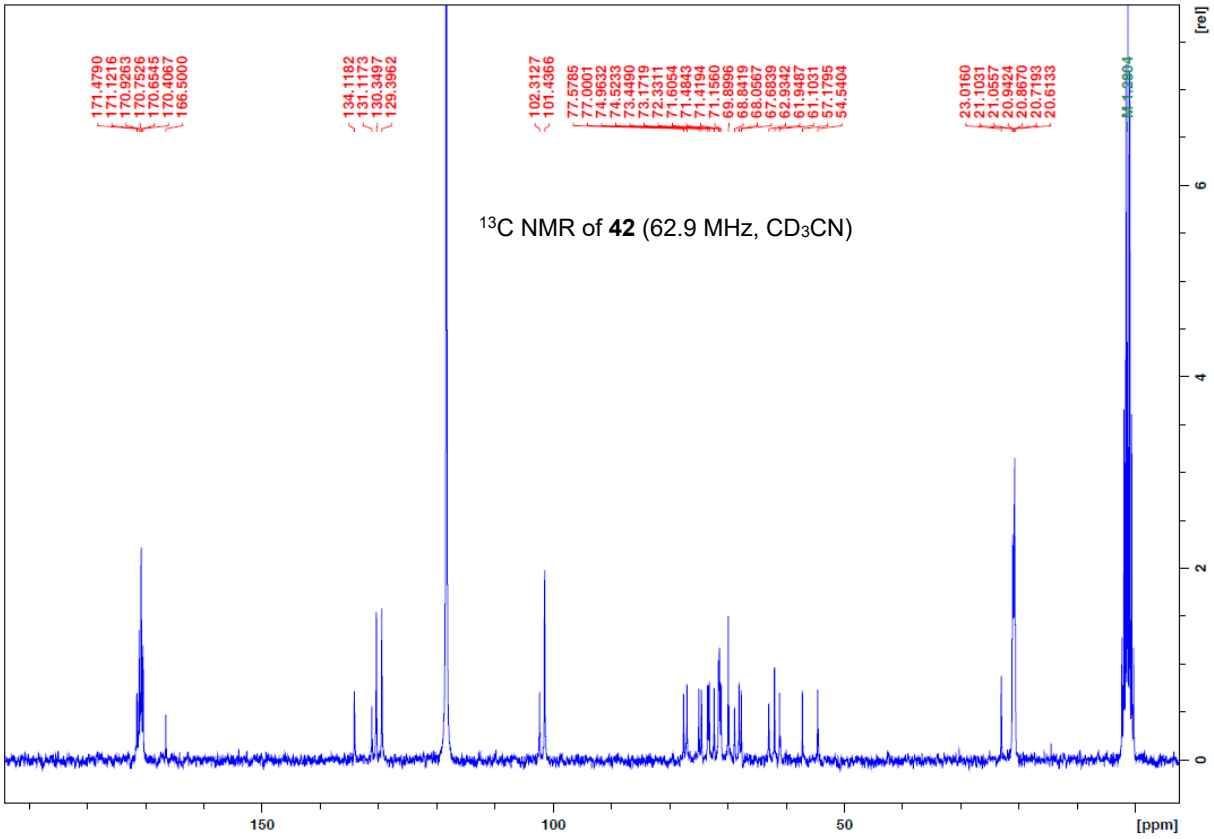


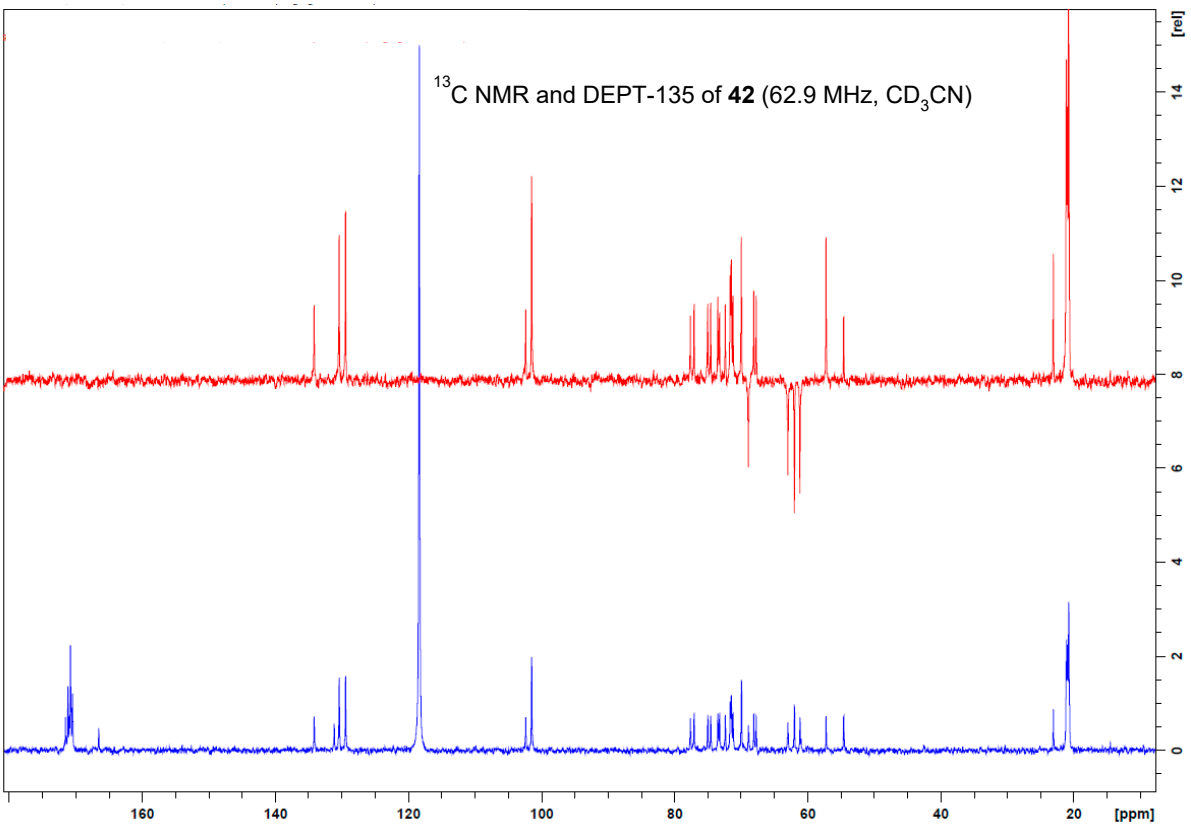
^{13}C NMR of **40** (62.9 MHz, CD_3CN)

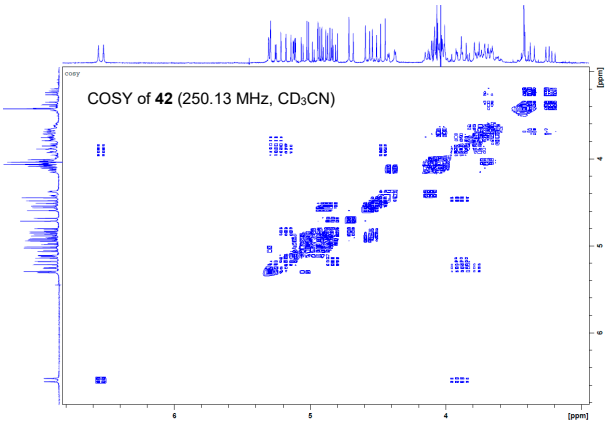


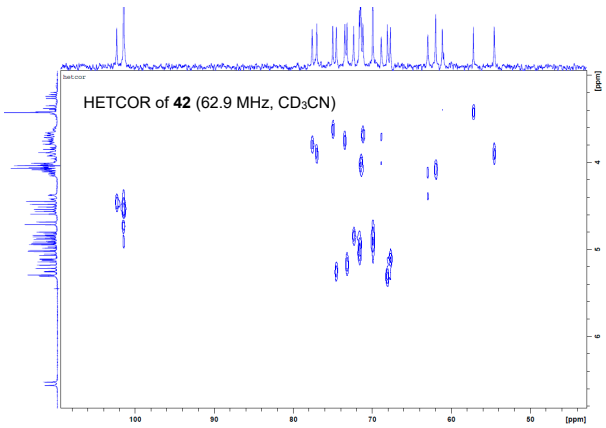
HETCOR spectra of **40** (62.9 MHz, CD_3CN)

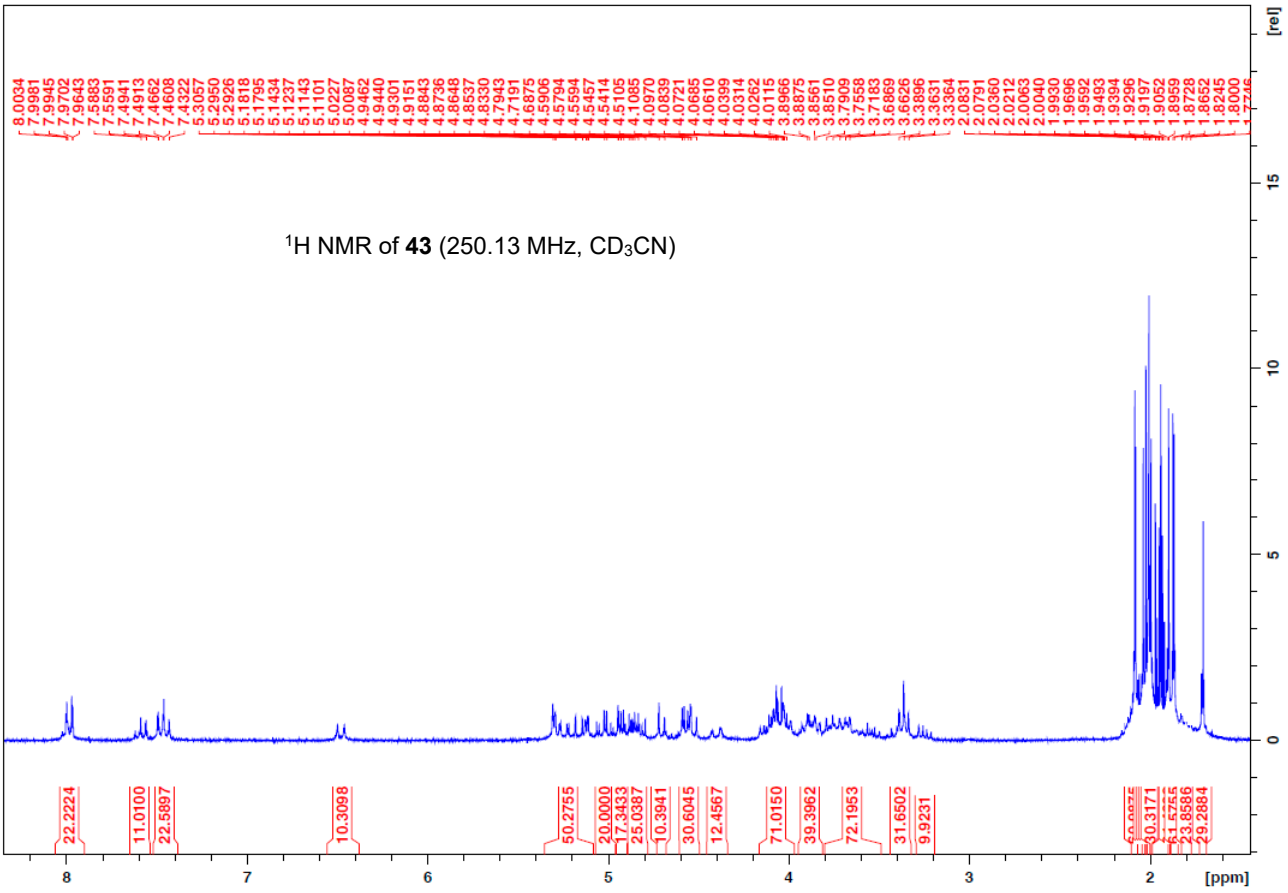

^{1}H NMR of **42** (250.13 MHz, CD_3CN)
[rel]
[ppm]

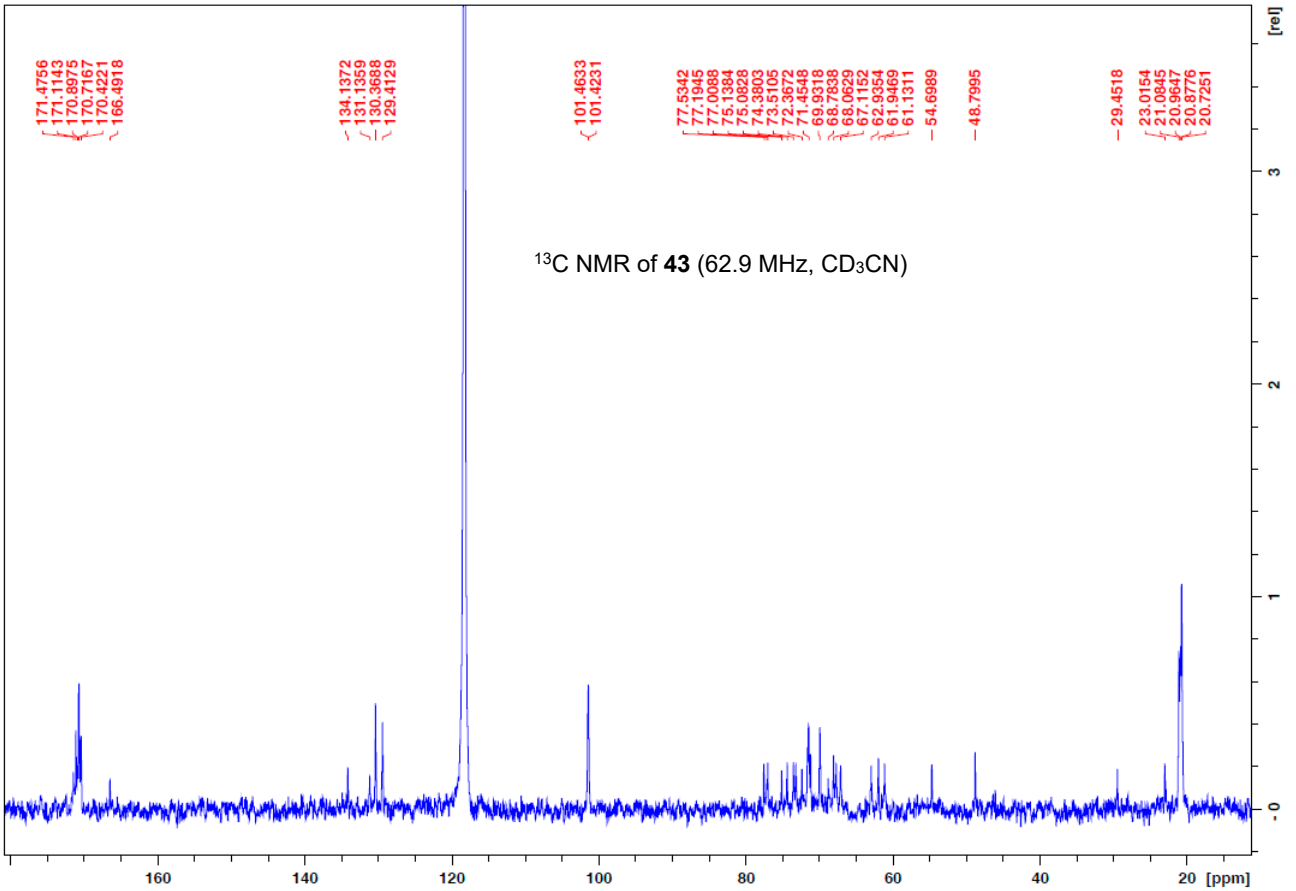

^{13}C NMR of **42** (62.9 MHz, CD_3CN)
[rel]
[ppm]


^{13}C NMR and DEPT-135 of **42** (62.9 MHz, CD_3CN)
[rel]
14
12
10
8
6
4
2
0
160
140
120
100
80
60
40
20
[ppm]

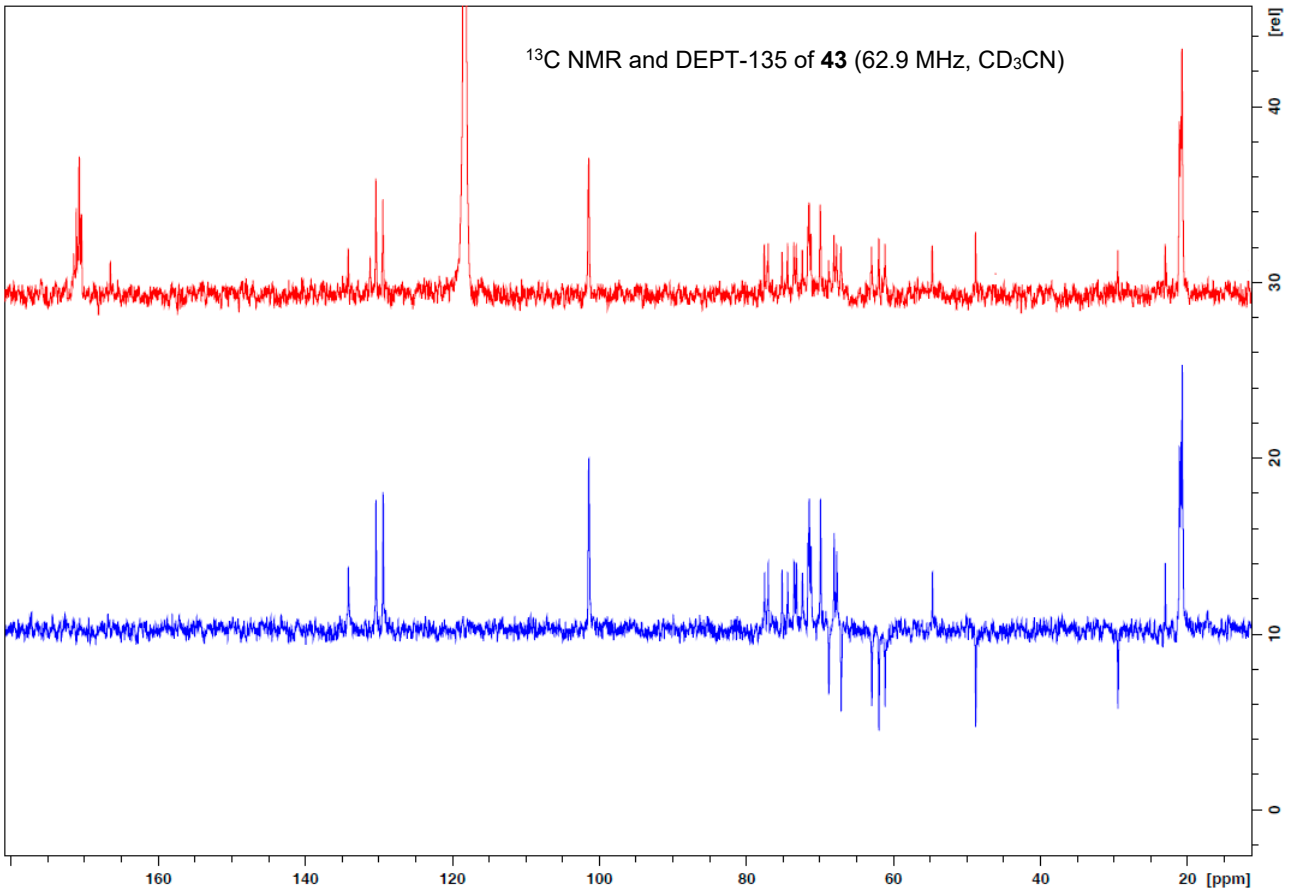

COSY of **42** (250.13 MHz, CD_3CN)
[ppm]
6
5
4
[ppm]


HETCOR of **42** (62.9 MHz, CD_3CN)
[ppm]
100
90
80
70
60
50
[ppm]

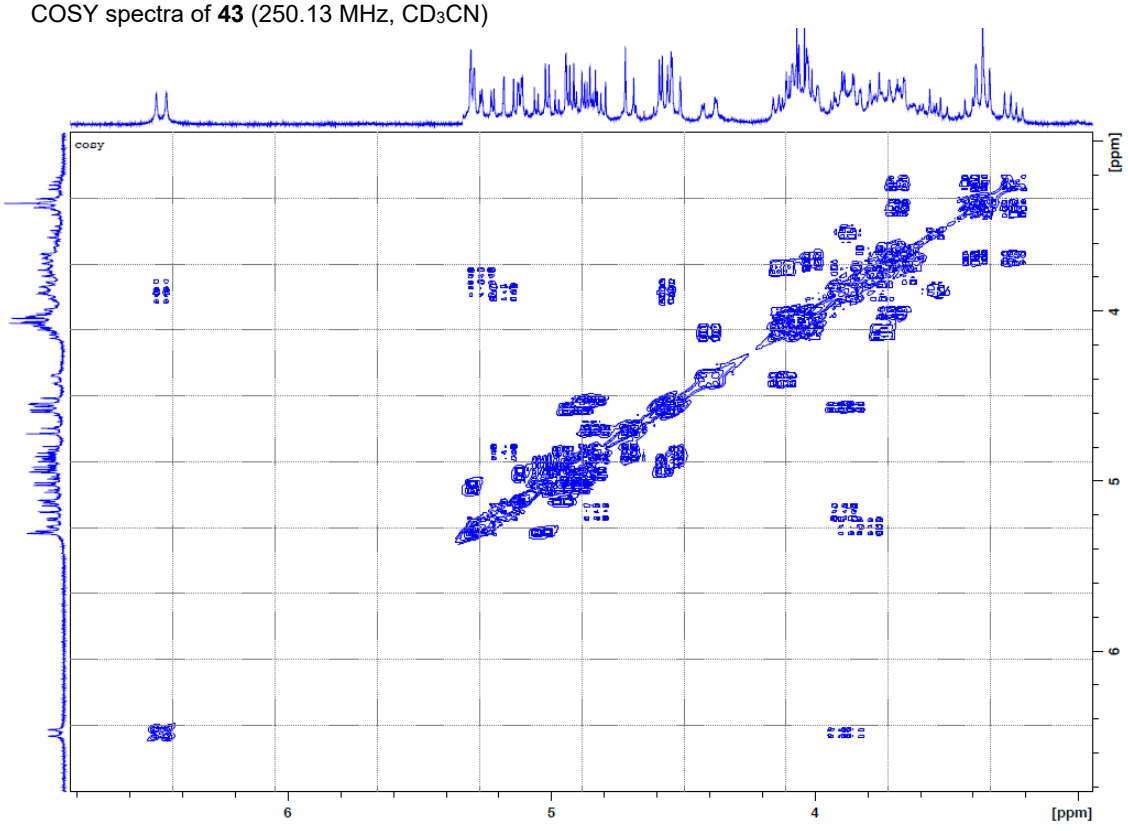

^{1}H NMR of **43** (250.13 MHz, CD_3CN)
[rel]
[ppm]

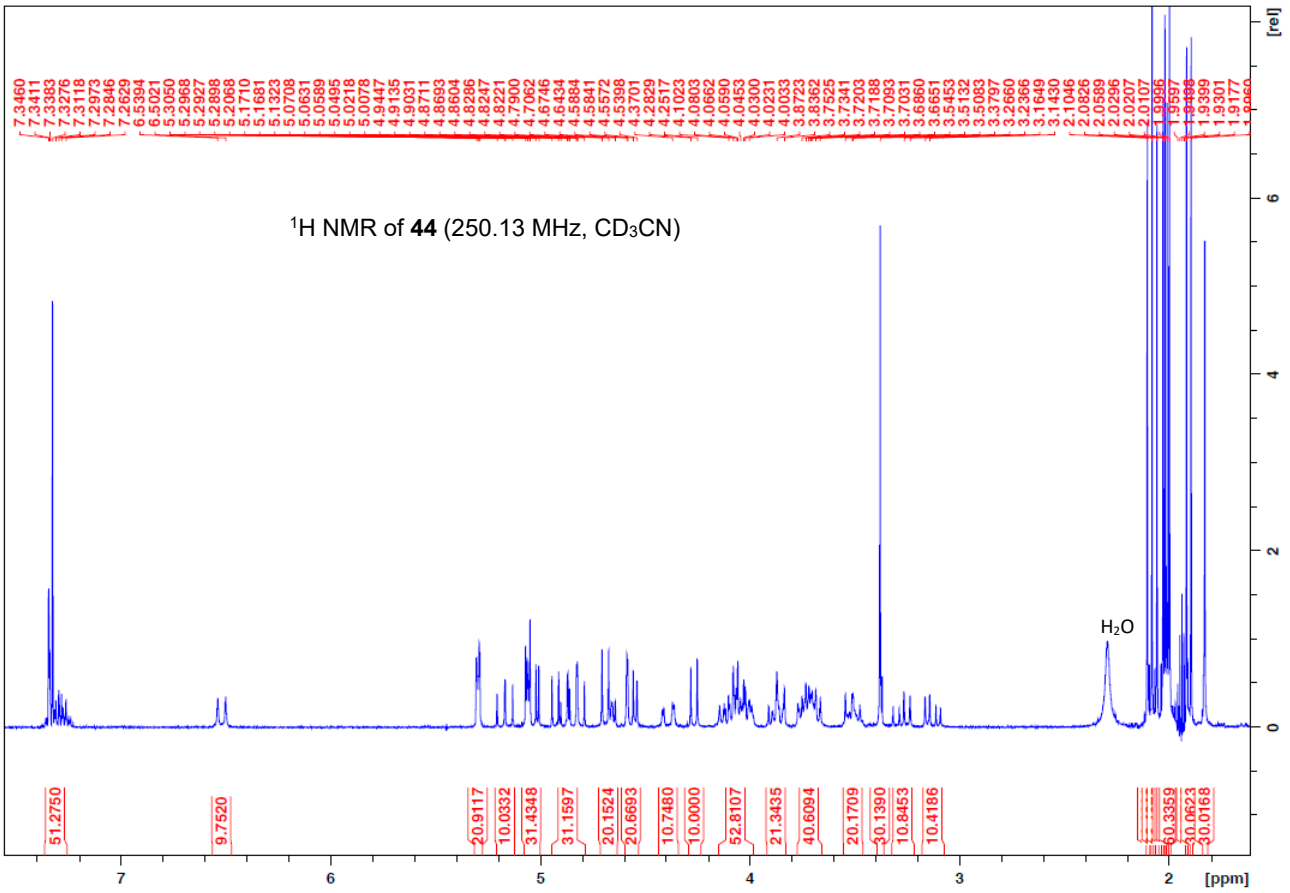

^{13}C NMR of **43** (62.9 MHz, CD_3CN)
[rel]
[ppm]

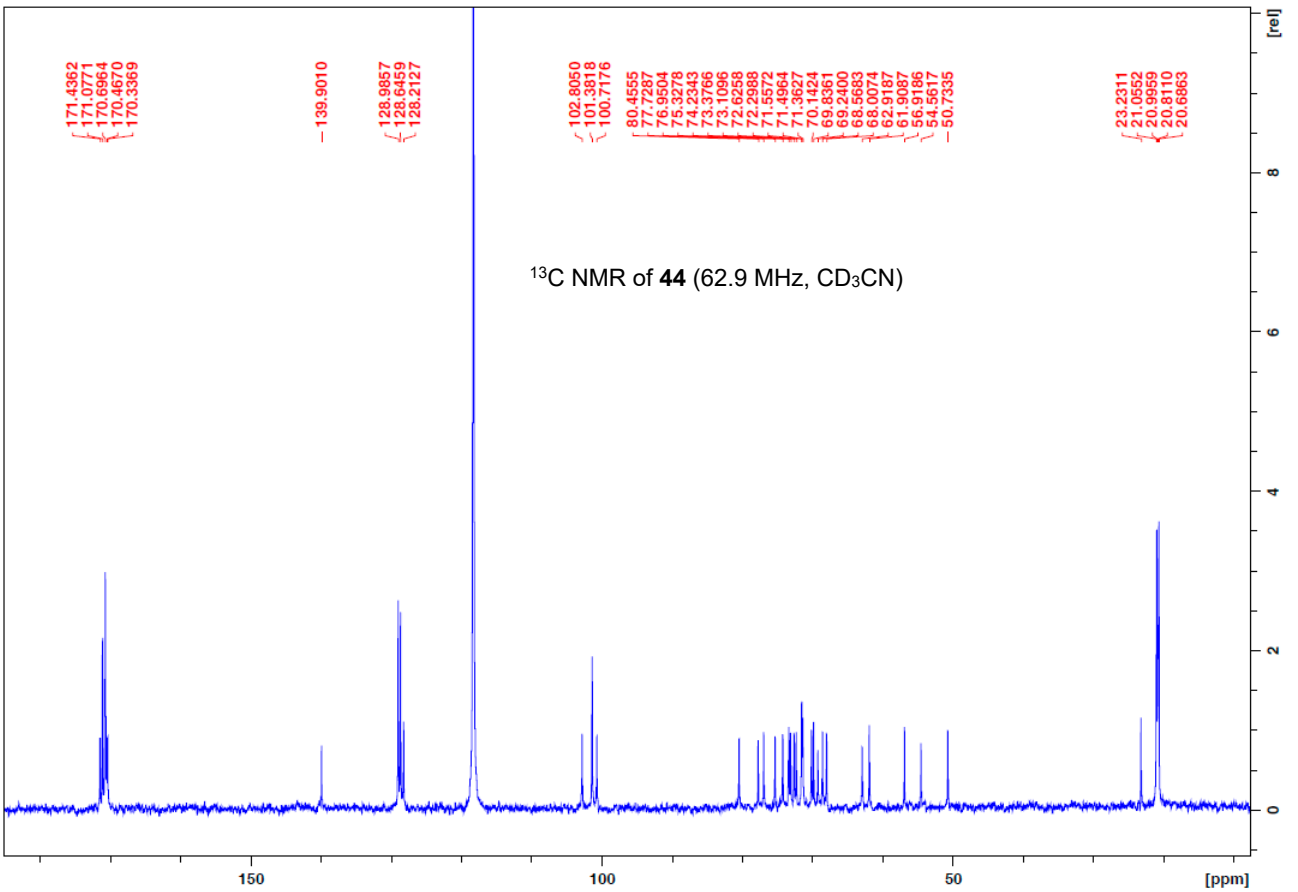
^{13}C NMR and DEPT-135 of **43** (62.9 MHz, CD_3CN)

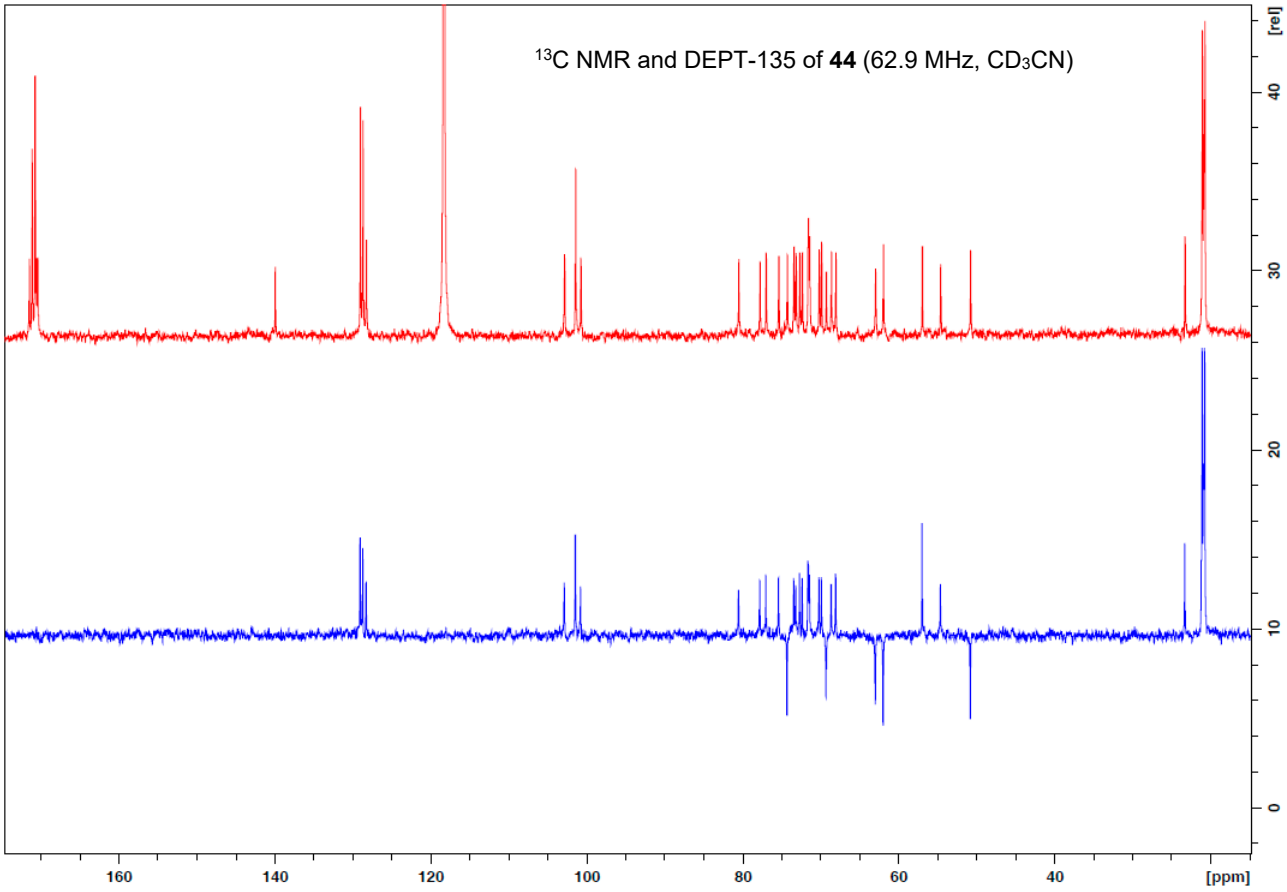


COSY spectra of **43** (250.13 MHz, CD_3CN)

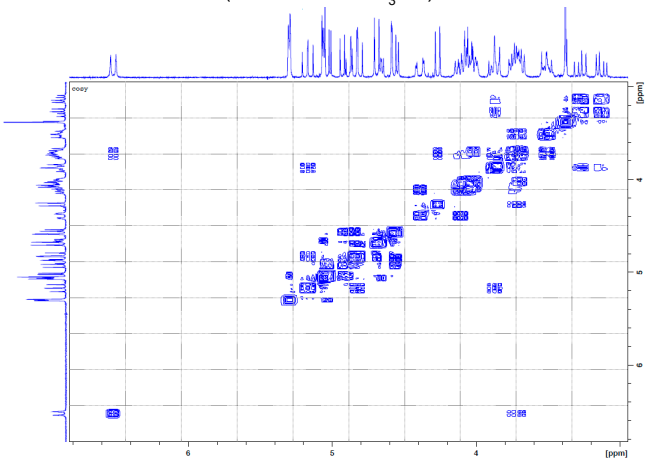



^{1}H NMR of **44** (250.13 MHz, CD_3CN)
H_2O
[rel]
[ppm]

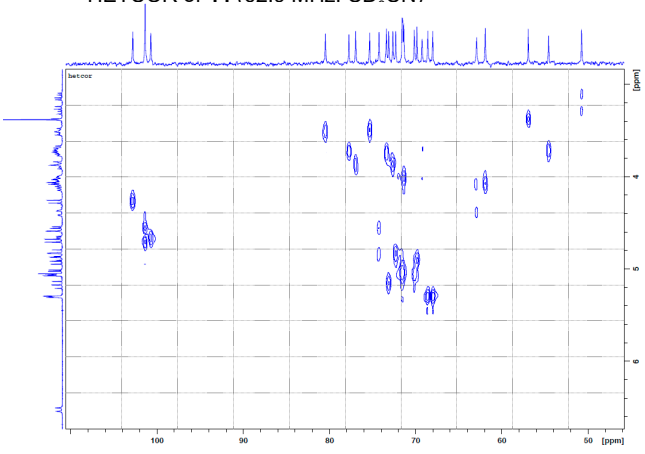

^{13}C NMR of **44** (62.9 MHz, CD_3CN)
[rel]
[ppm]

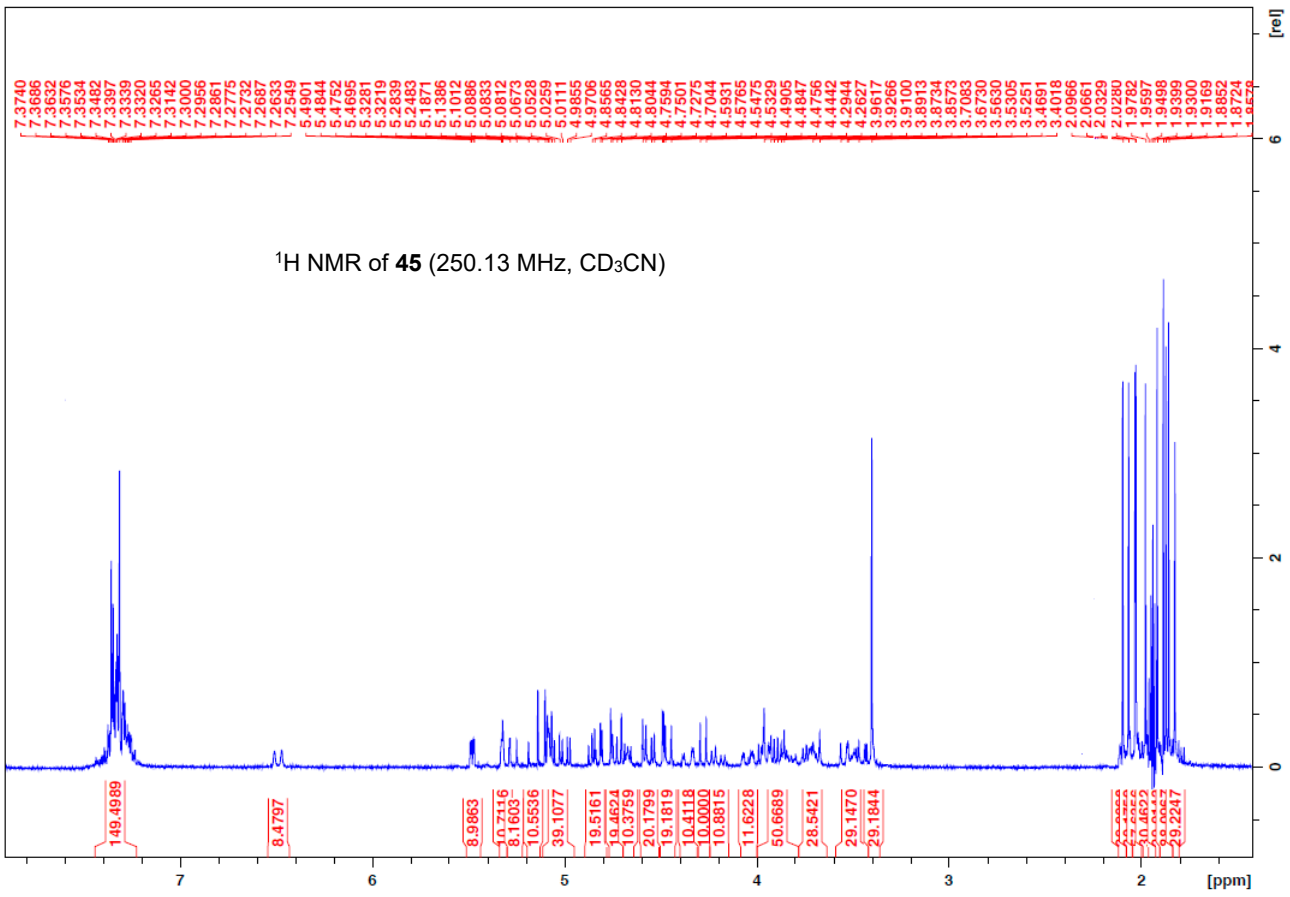


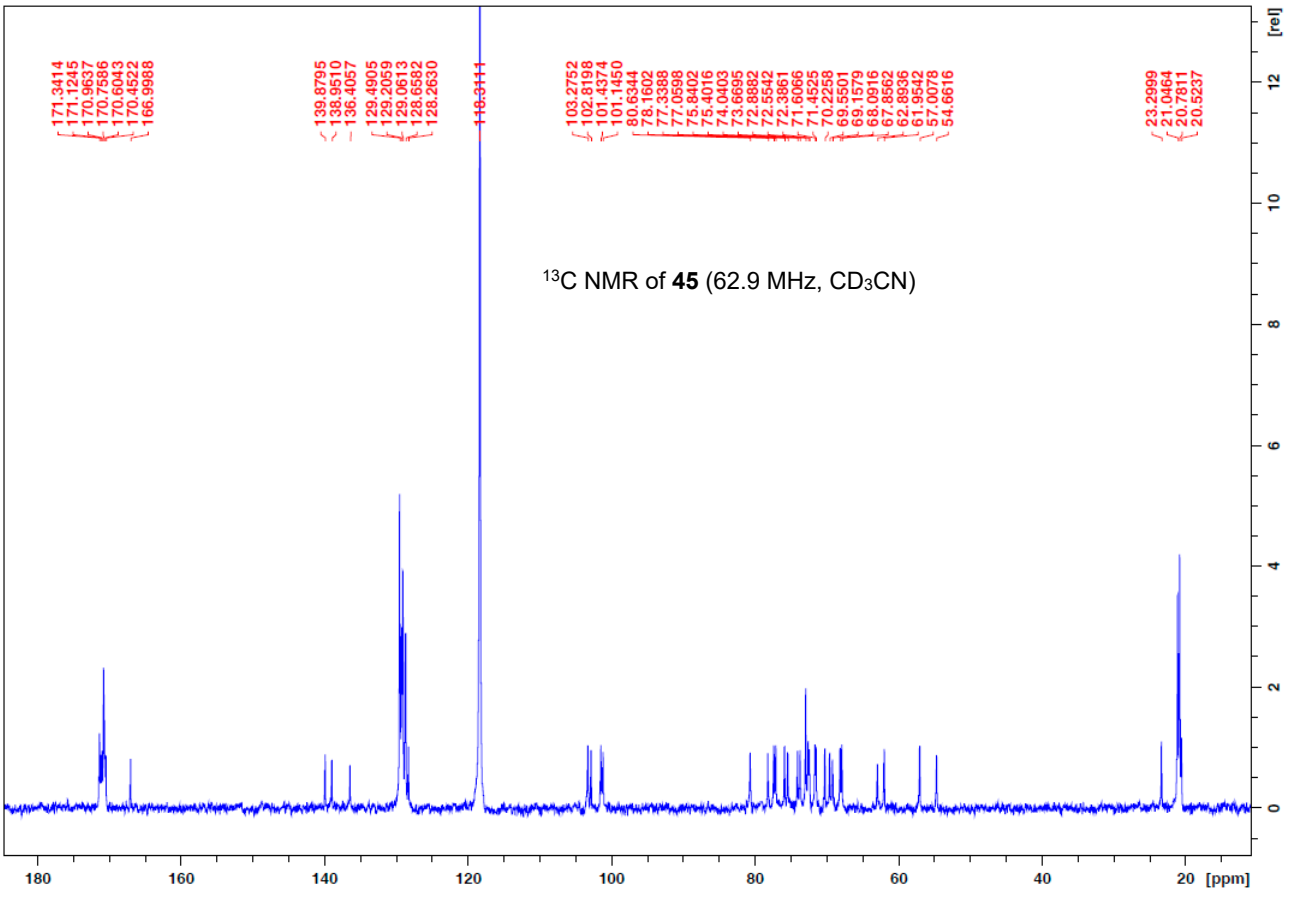
COSY of **44** (250.13 MHz, CD_3CN)

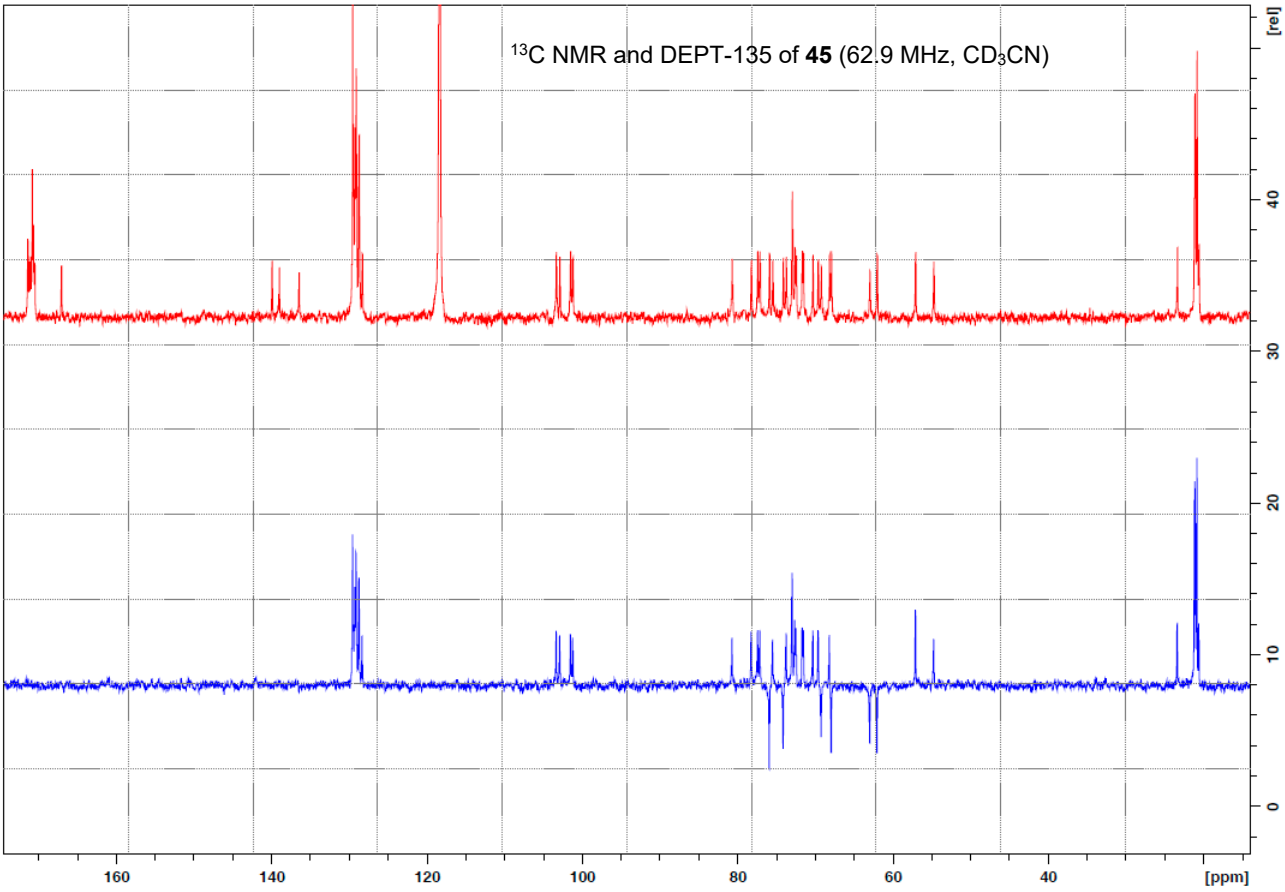


HETCOR of **44** (62.9 MHz, CD_3CN)

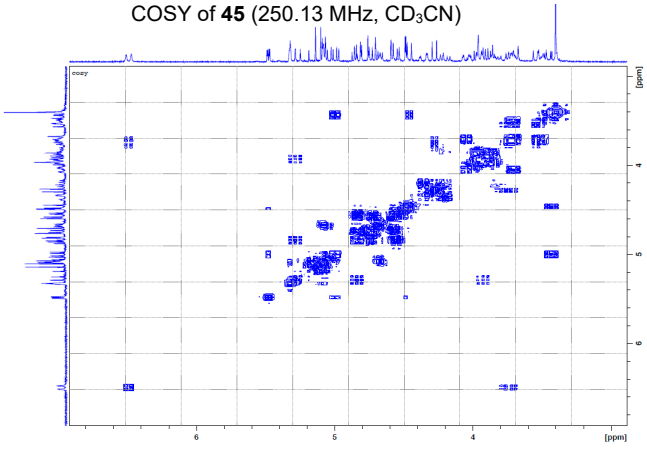



^{1}H NMR of **45** (250.13 MHz, CD_3CN)
[rel]
[ppm]

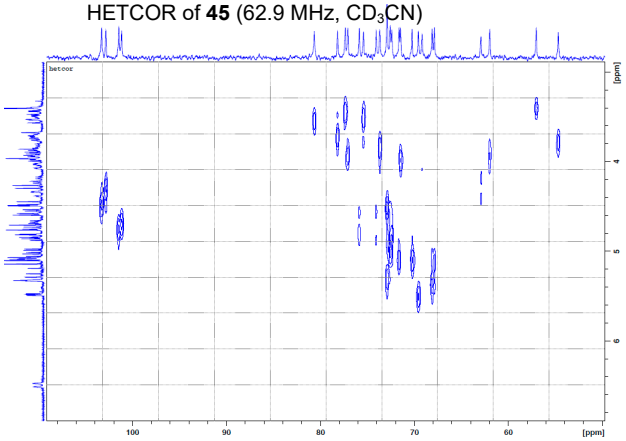

^{13}C NMR of **45** (62.9 MHz, CD_3CN)
[rel]
[ppm]

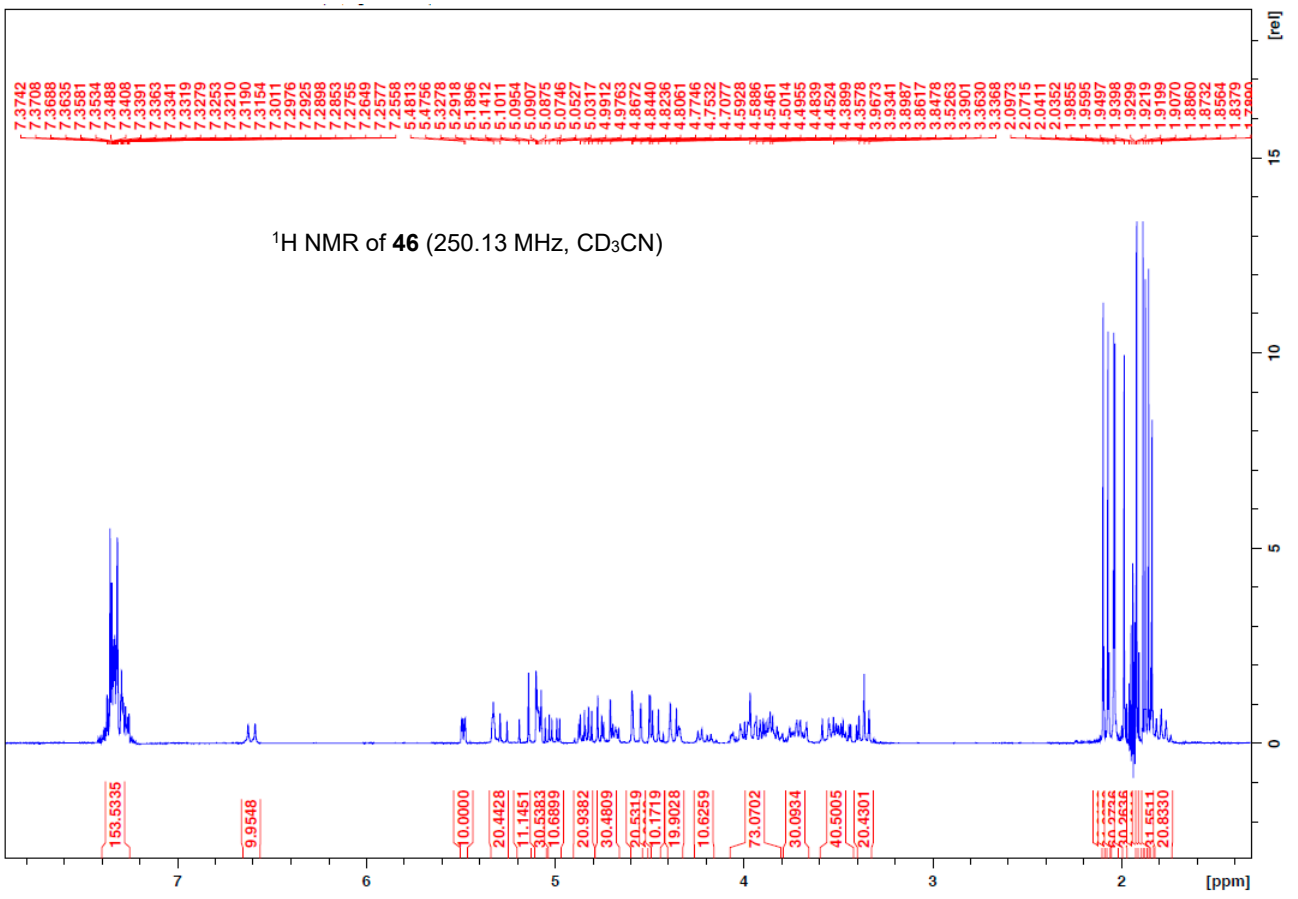


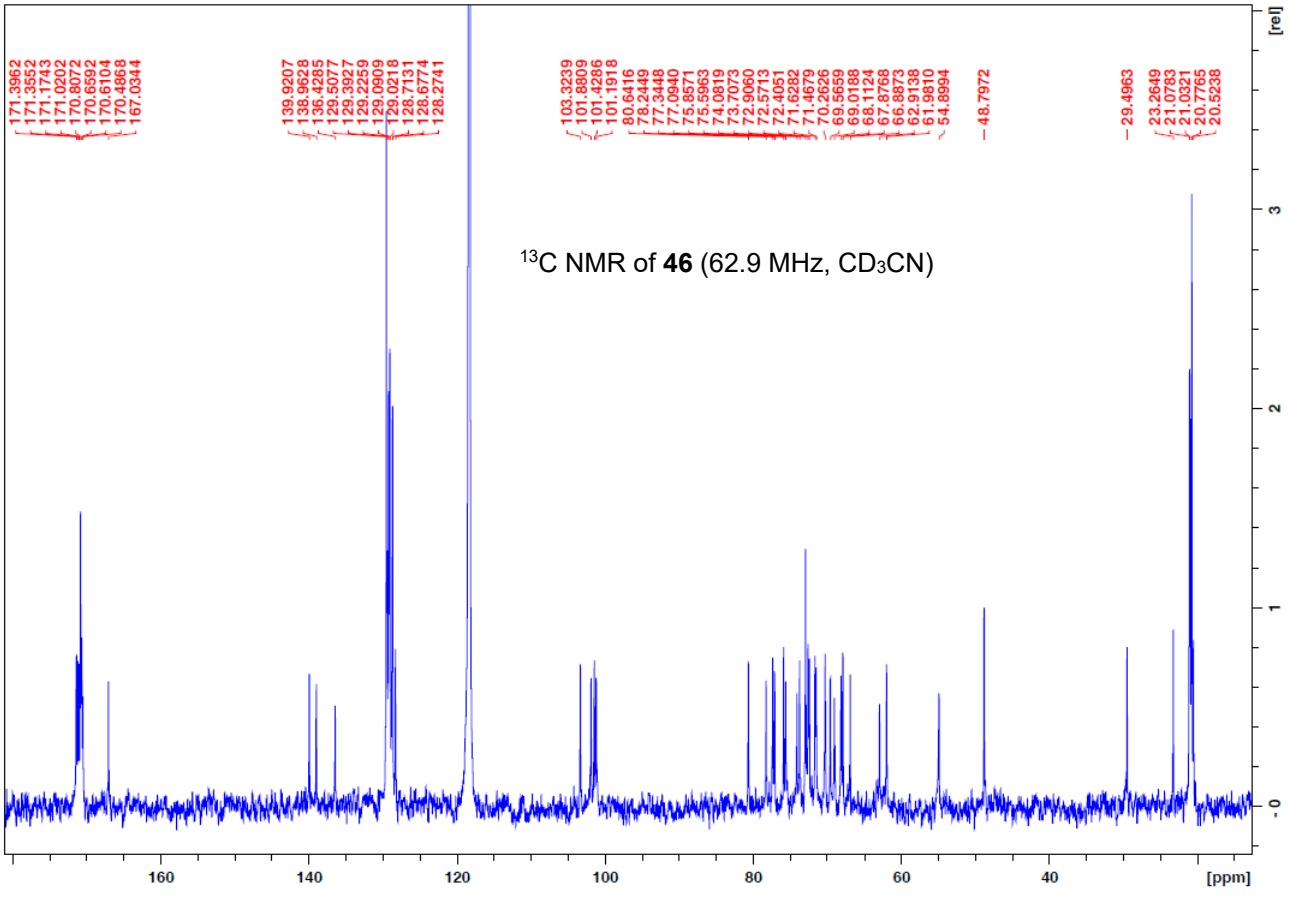
COSY of **45** (250.13 MHz, CD_3CN)

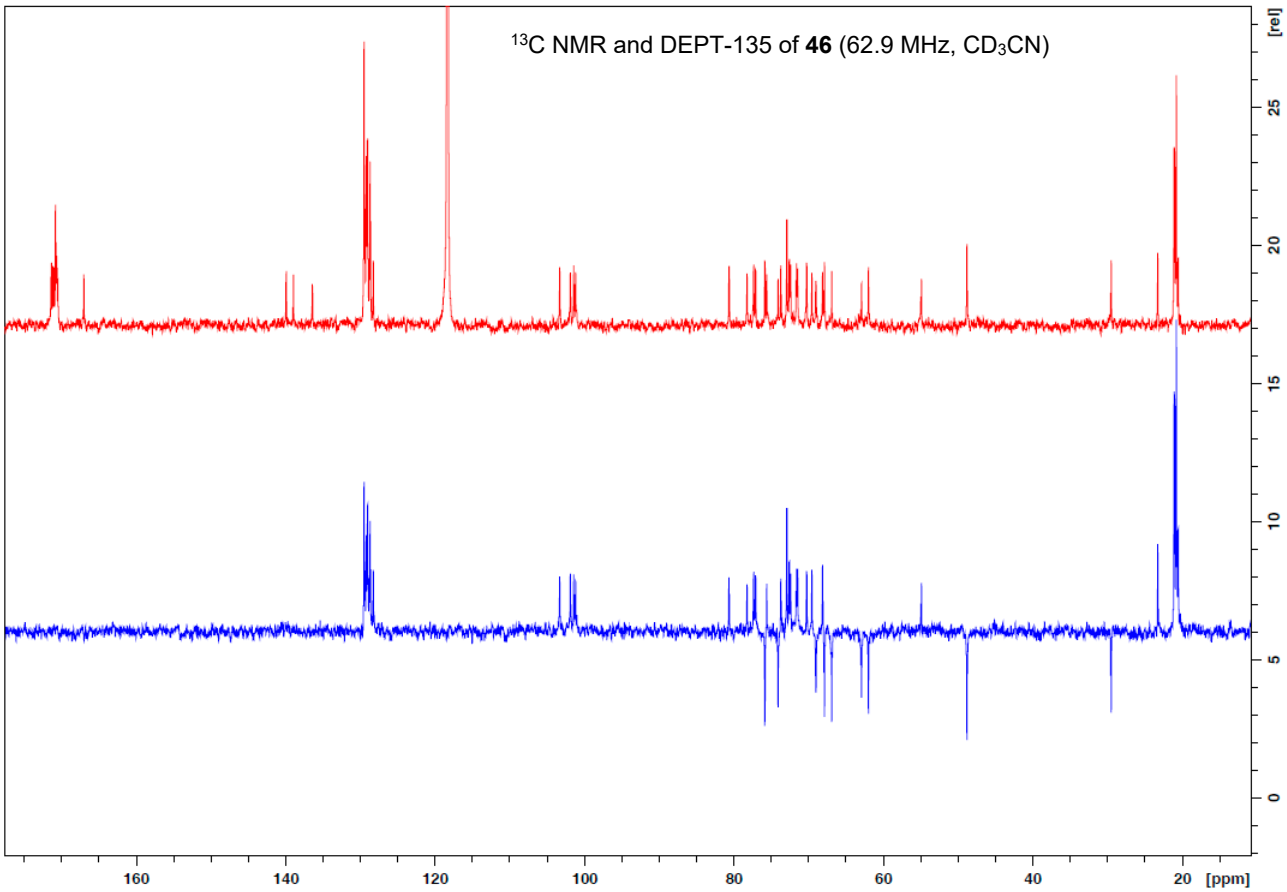


HETCOR of **45** (62.9 MHz, CD_3CN)

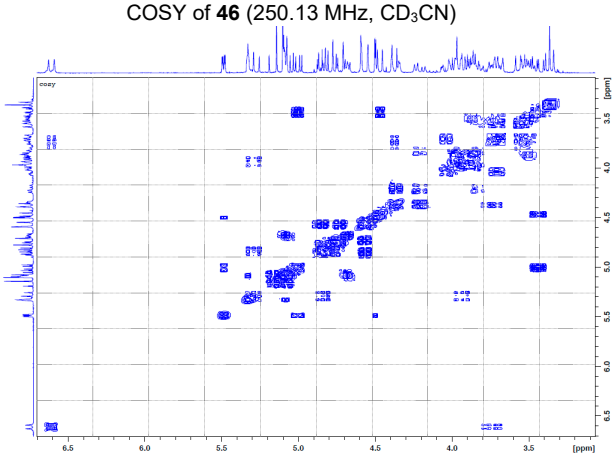



^{1}H NMR of **46** (250.13 MHz, CD_3CN)
[rel]
[ppm]

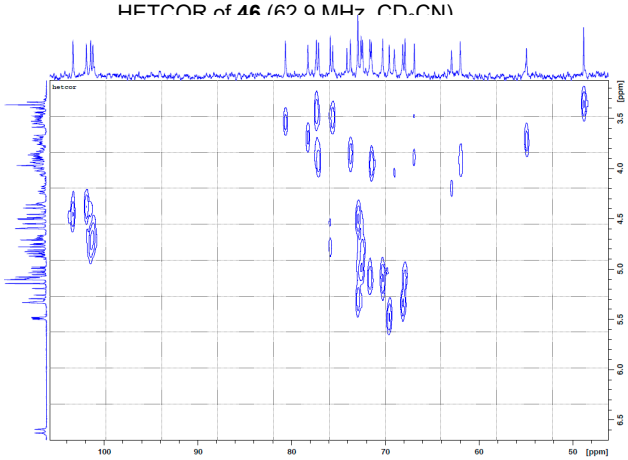

^{13}C NMR of **46** (62.9 MHz, CD_3CN)
[rel]
[ppm]

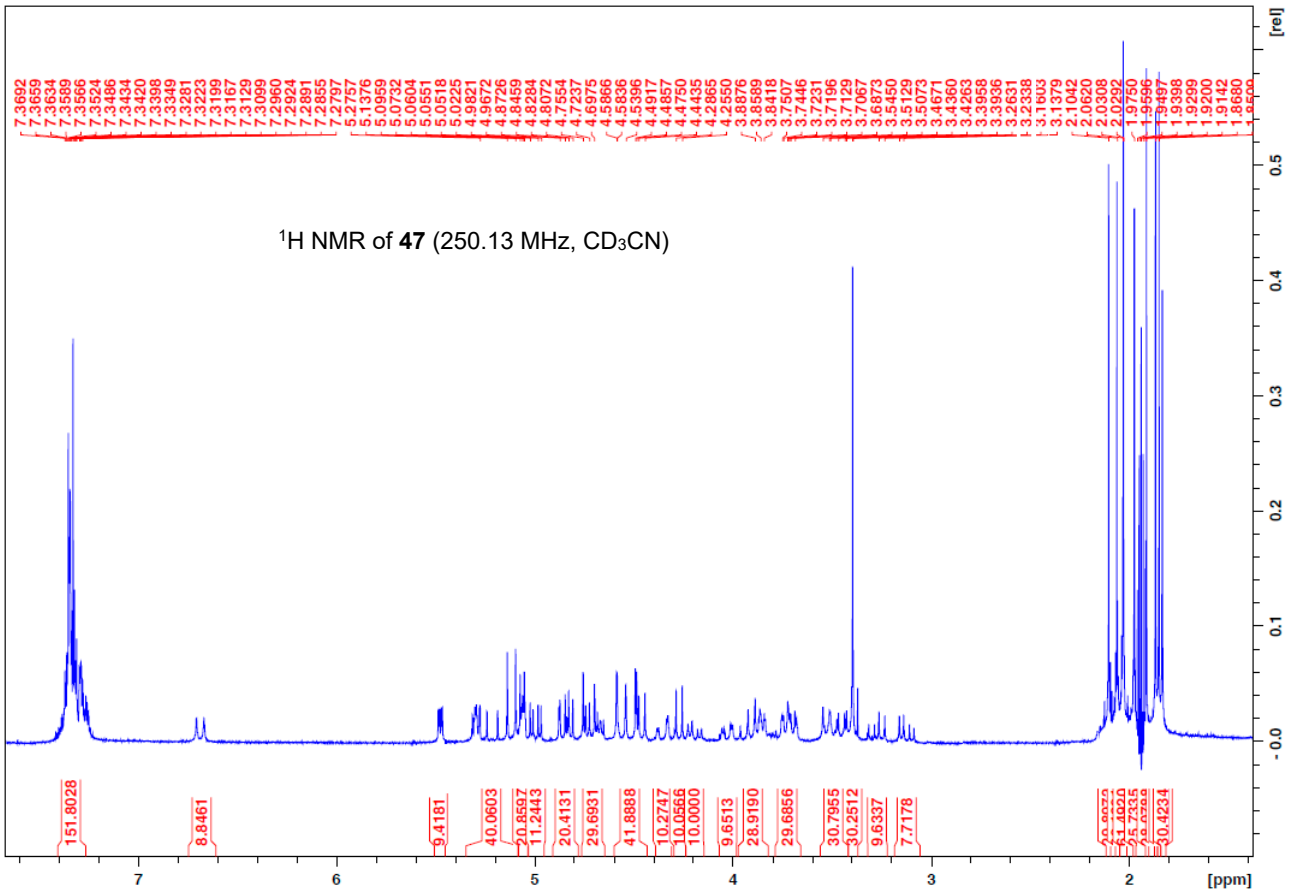


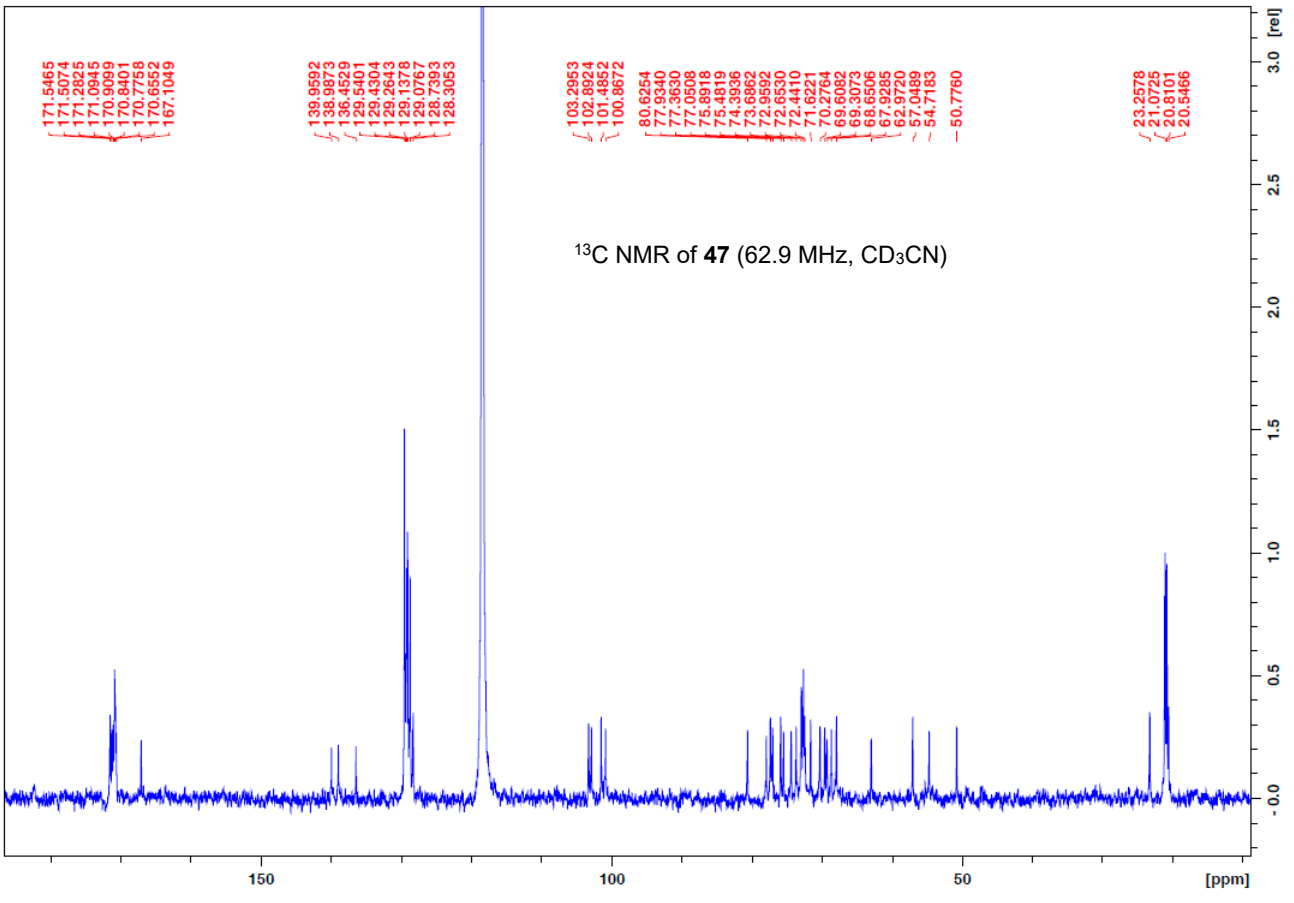
COSY of **46** (250.13 MHz, CD_3CN)

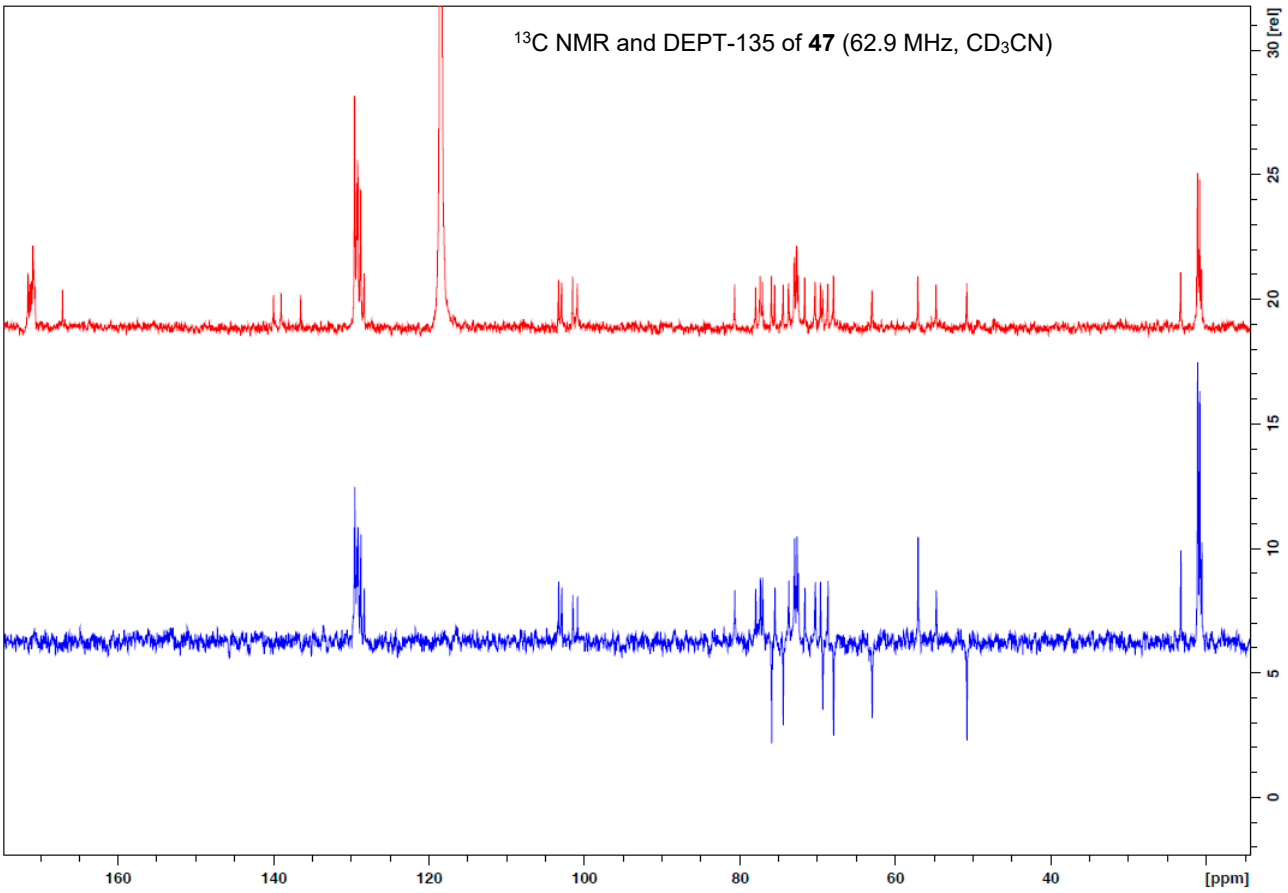


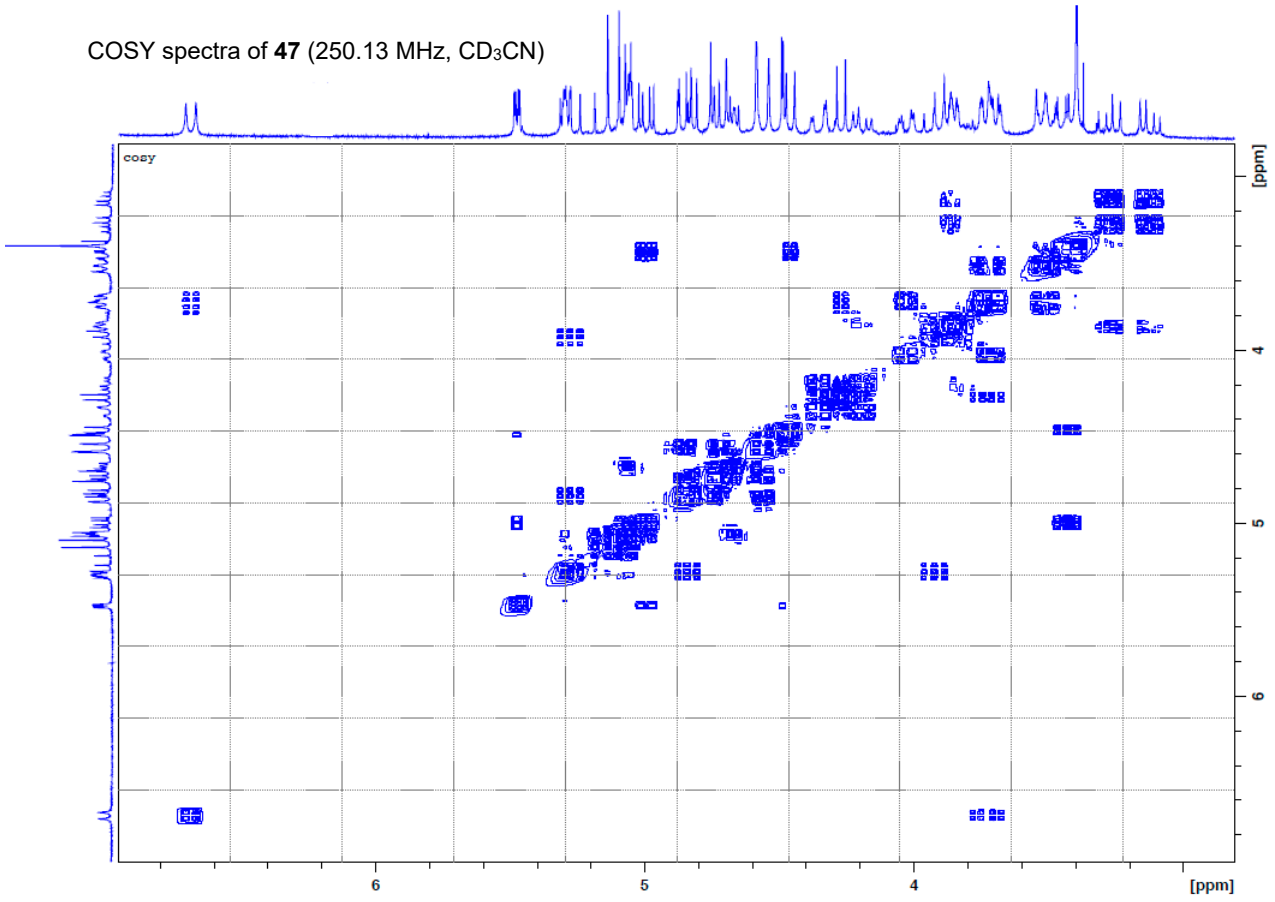
HETCOR of **46** (62.9 MHz, CD_3CN)

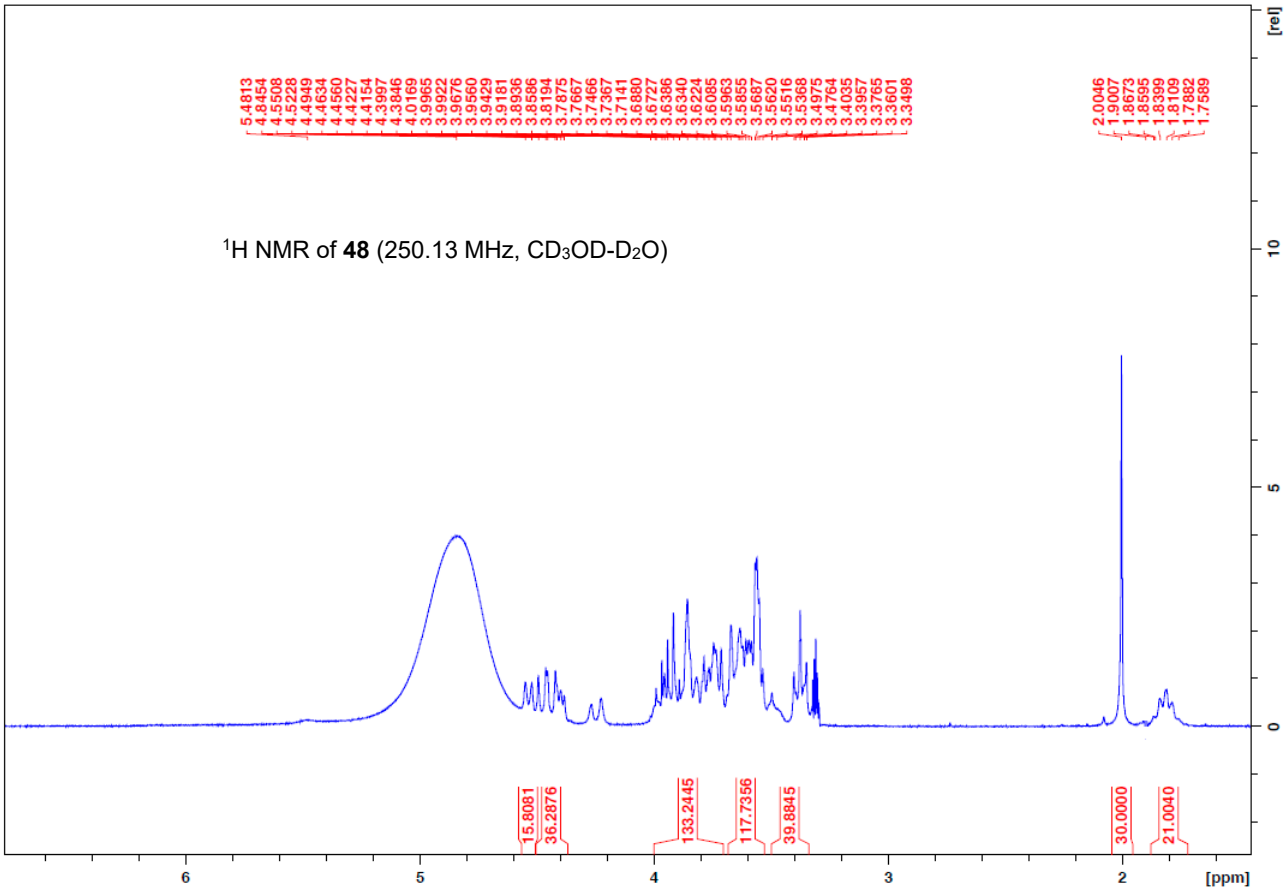



^{1}H NMR of **47** (250.13 MHz, CD_3CN)
[rel]
[ppm]

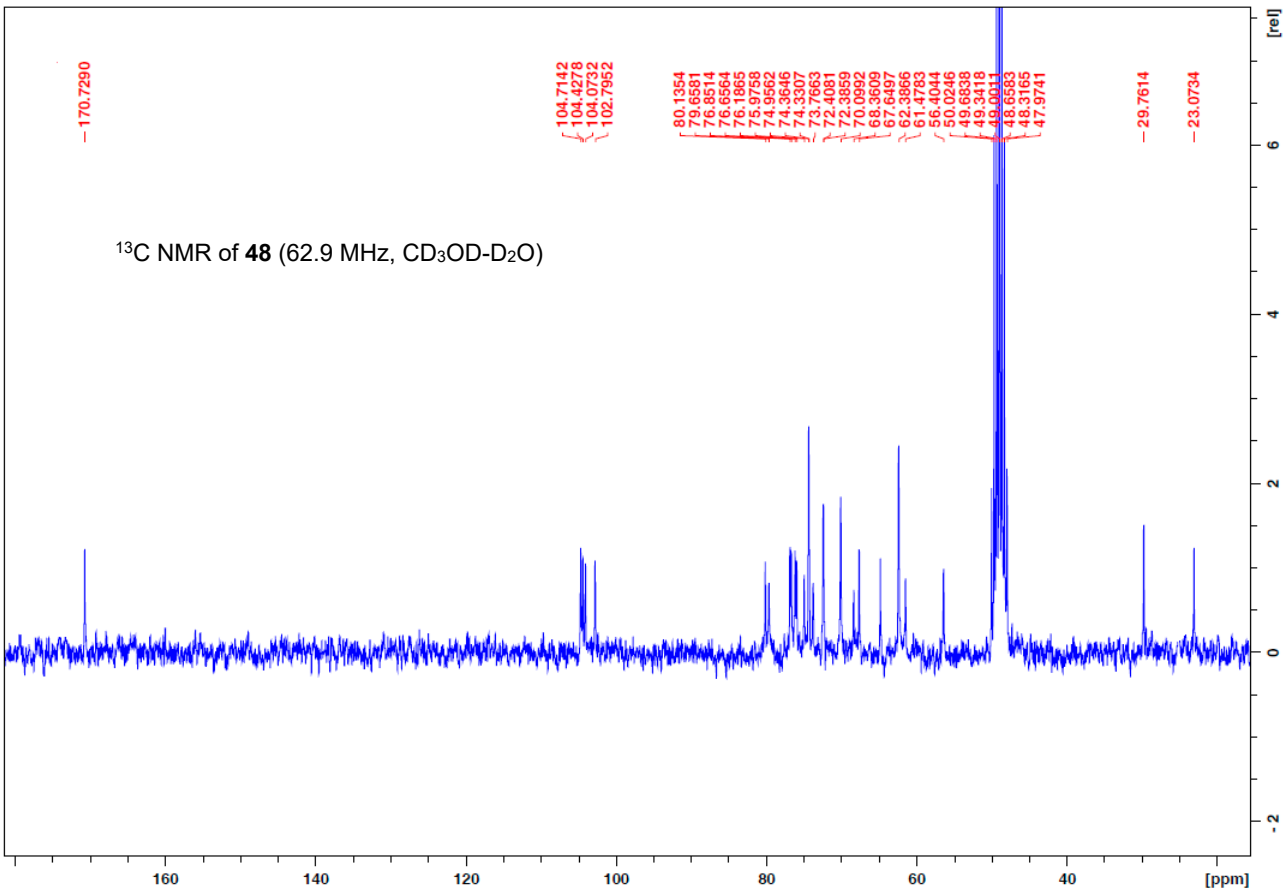

^{13}C NMR of **47** (62.9 MHz, CD_3CN)
[rel]
[ppm]


^{13}C NMR and DEPT-135 of **47** (62.9 MHz, CD_3CN)
30 [rel]
25
20
15
10
5
0
160
140
120
100
80
60
40
[ppm]

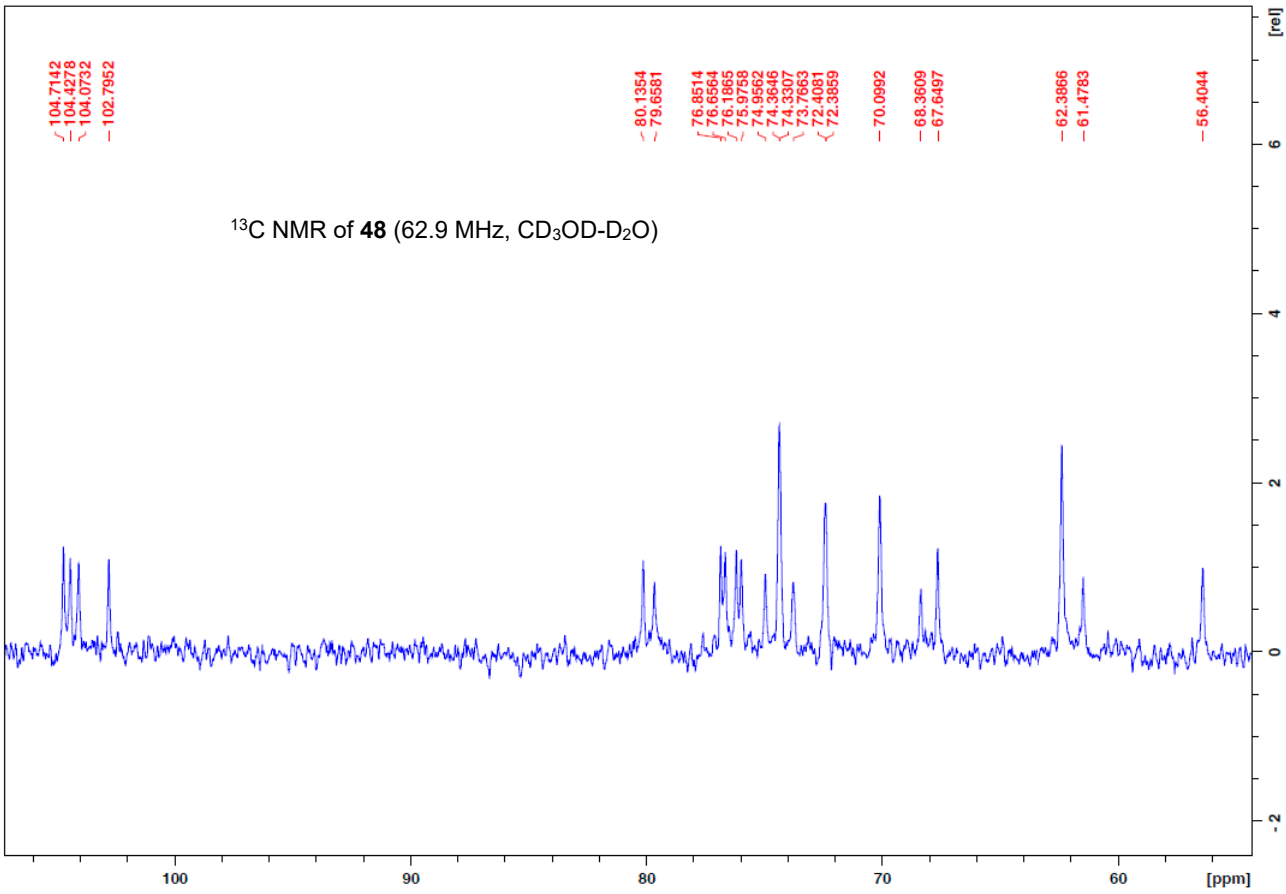

COSY spectra of **47** (250.13 MHz, CD_3CN)
cosy
[ppm]
4
5
6
6
5
4
[ppm]



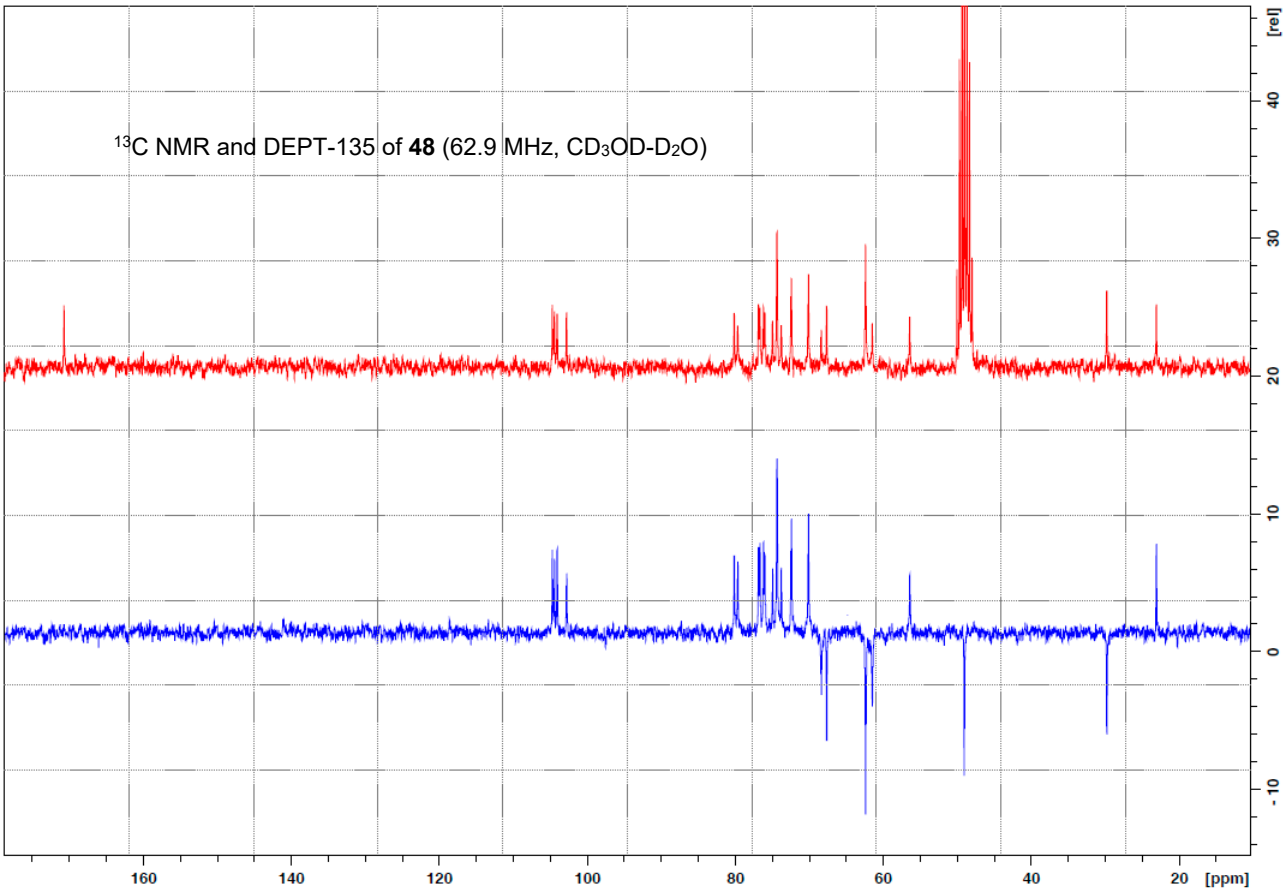
^{1}H NMR of **48** (250.13 MHz, CD_3OD-D_2O)



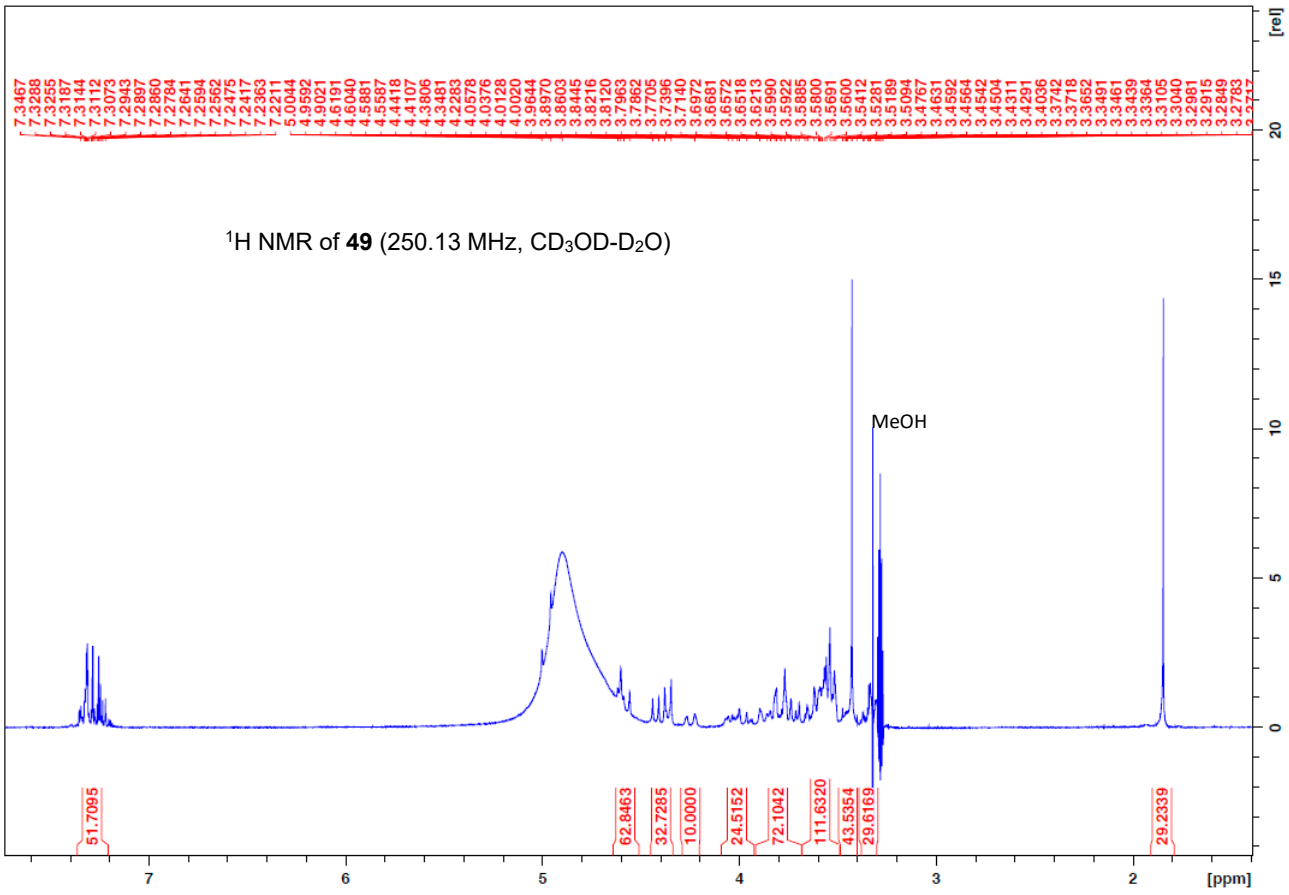
^{13}C NMR of **48** (62.9 MHz, CD_3OD-D_2O)

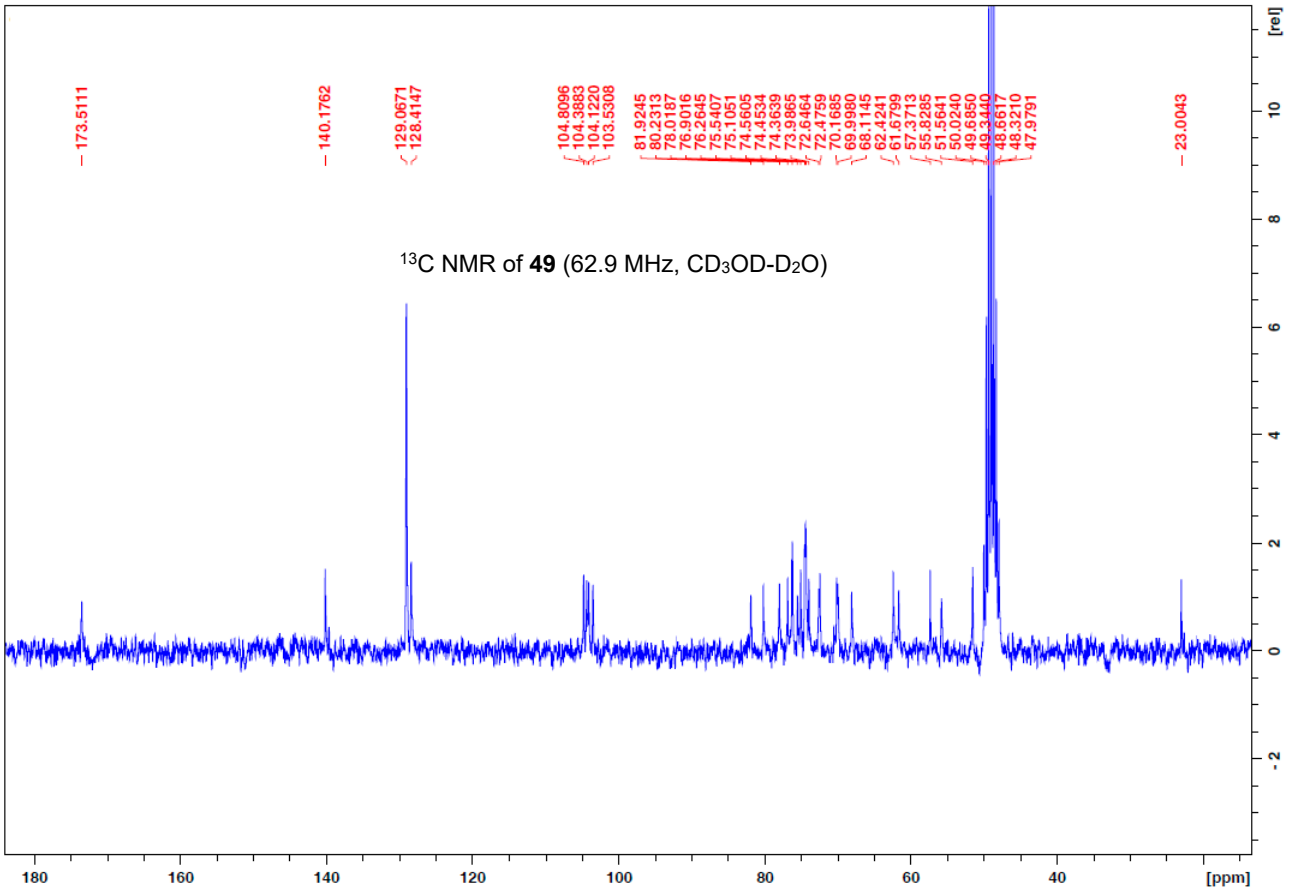


^{13}C NMR of **48** (62.9 MHz, CD_3OD-D_2O)

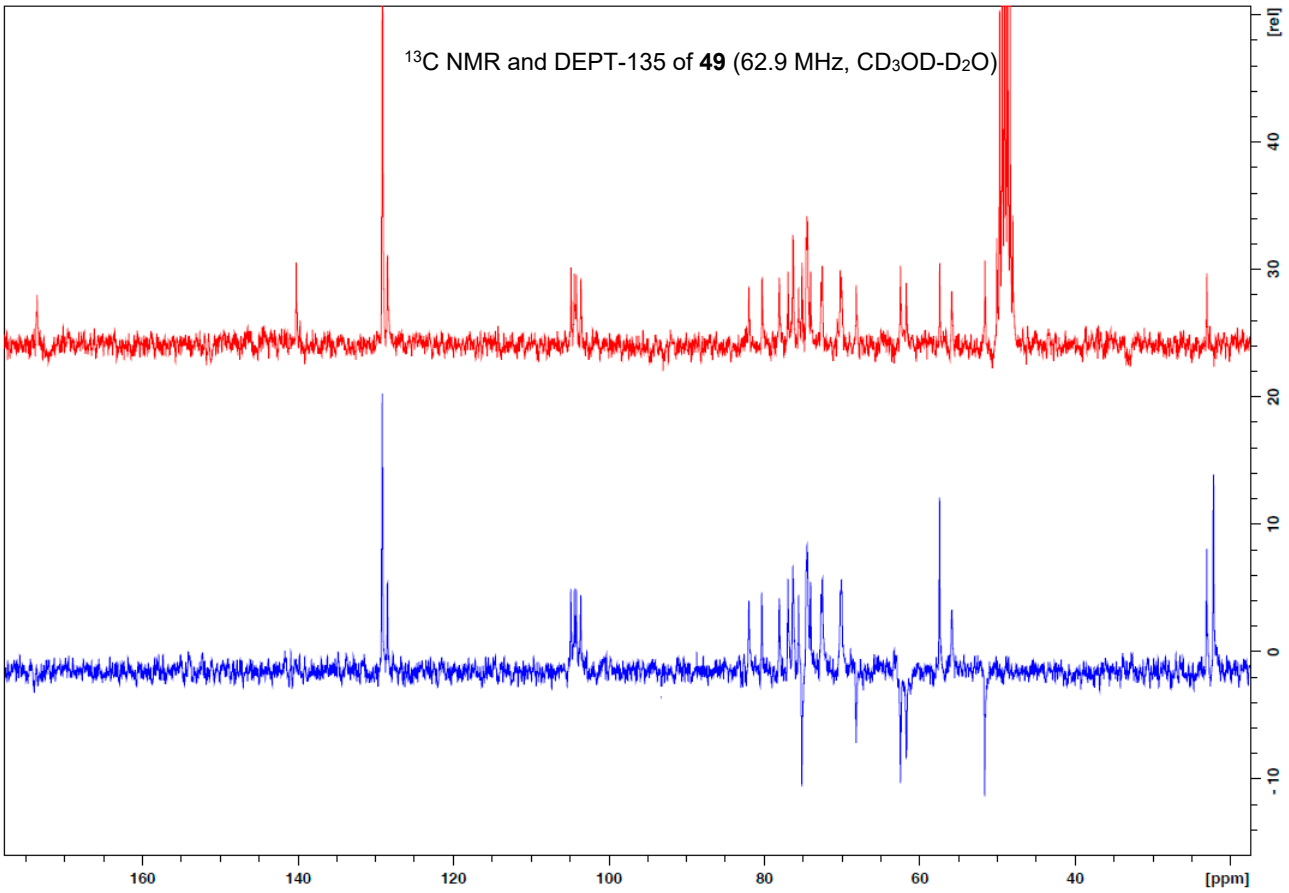


^{13}C NMR and DEPT-135 of **48** (62.9 MHz, CD_3OD-D_2O)

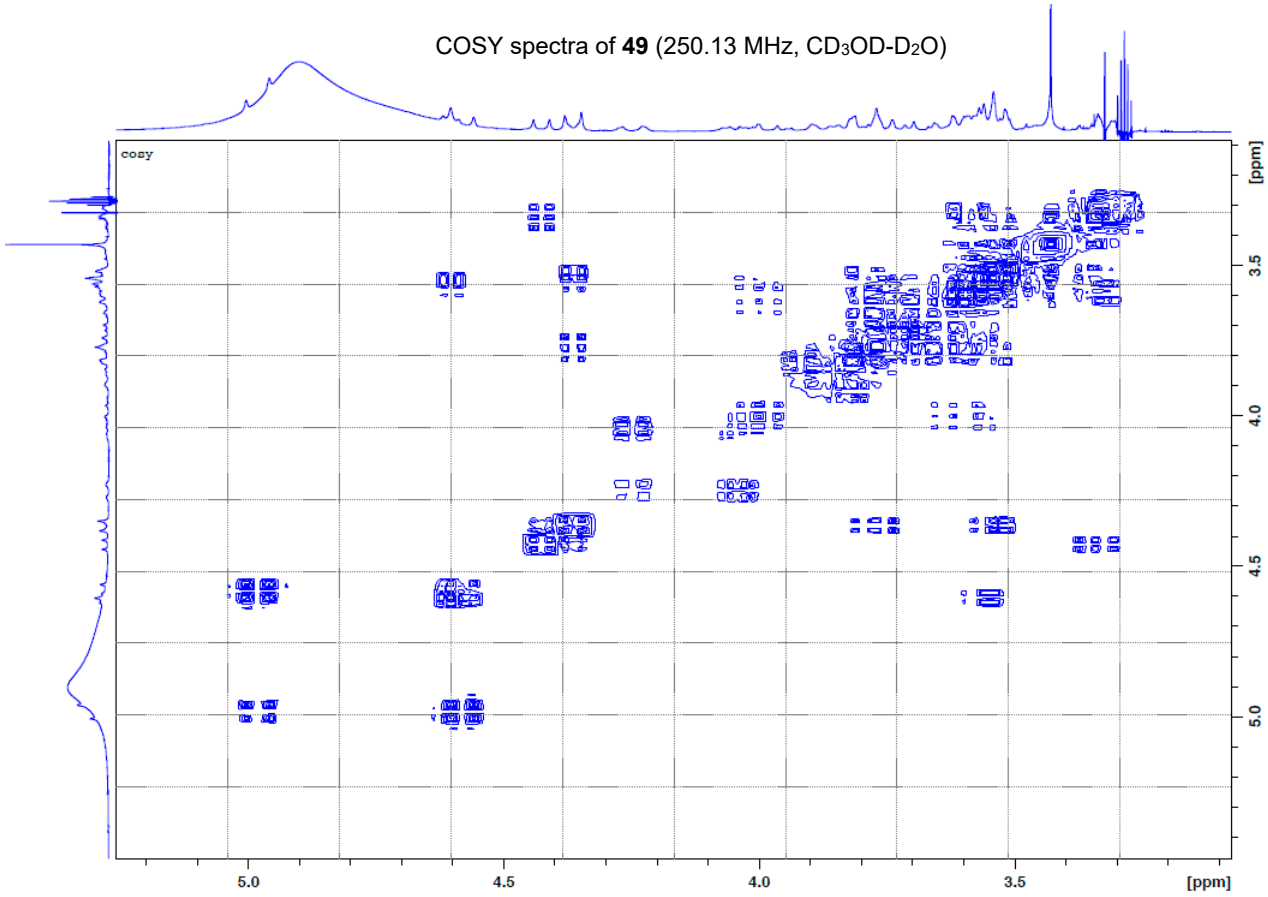

^{1}H NMR of **49** (250.13 MHz, CD_3OD-D_2O)
MeOH
[rel]
[ppm]

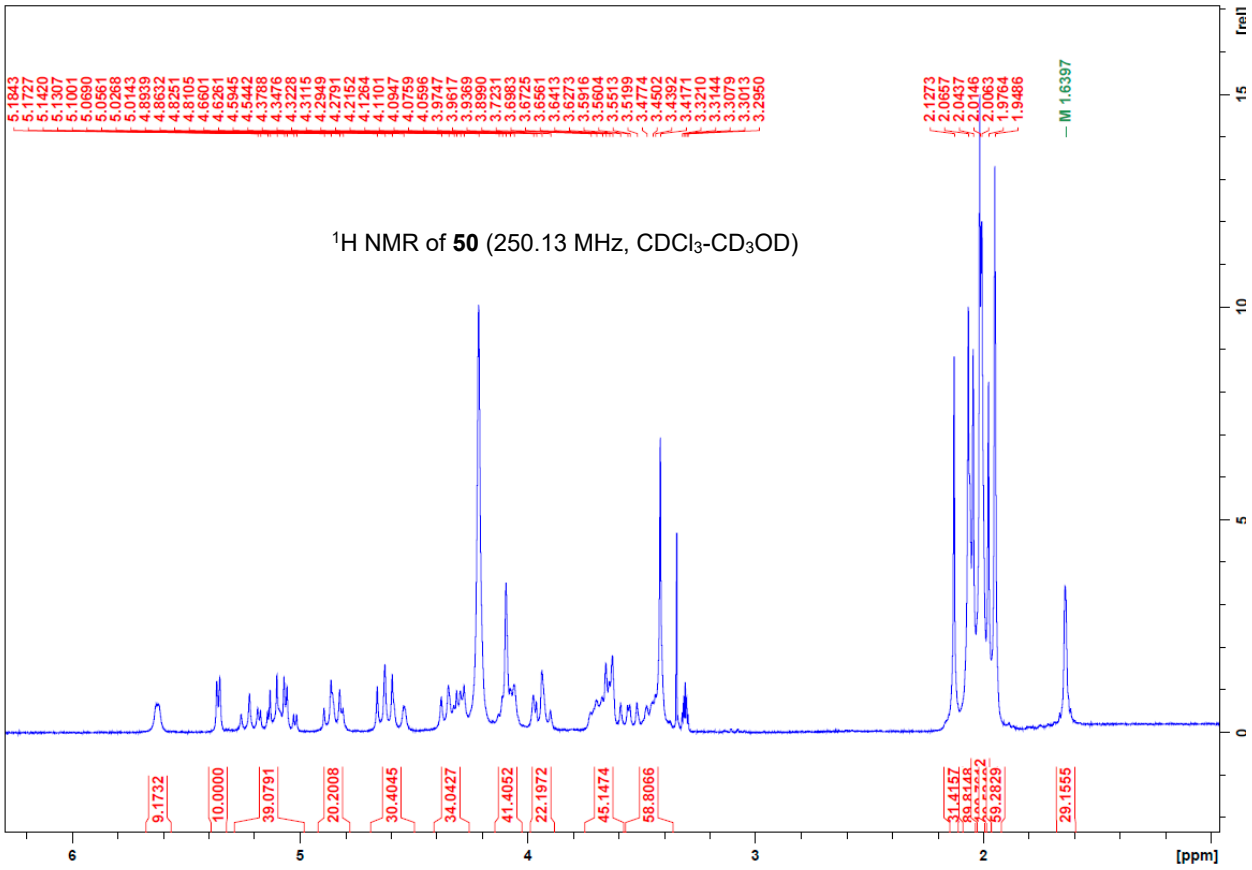

^{13}C NMR of **49** (62.9 MHz, CD_3OD-D_2O)
[rel]
[ppm]

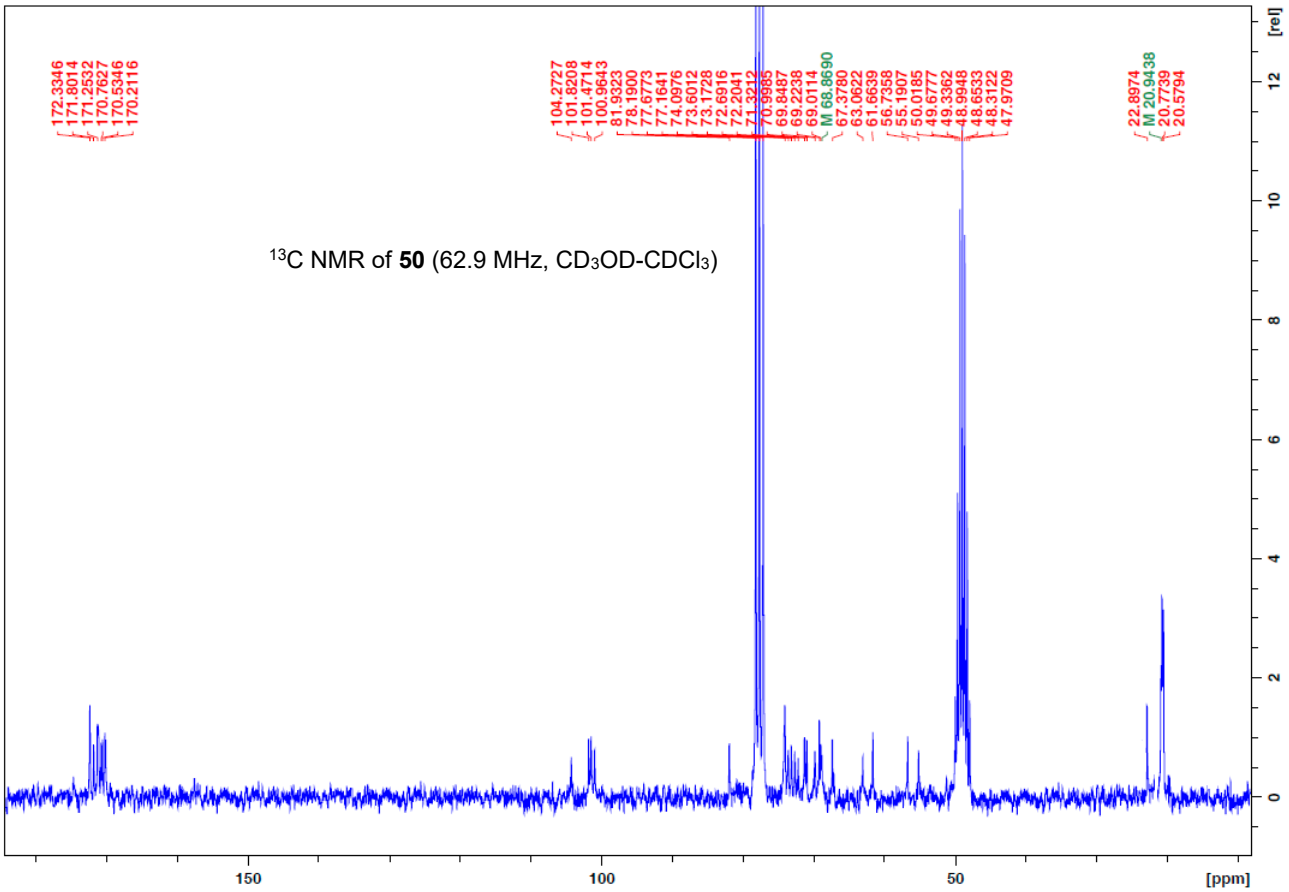
^{13}C NMR and DEPT-135 of **49** (62.9 MHz, CD_3OD-D_2O)



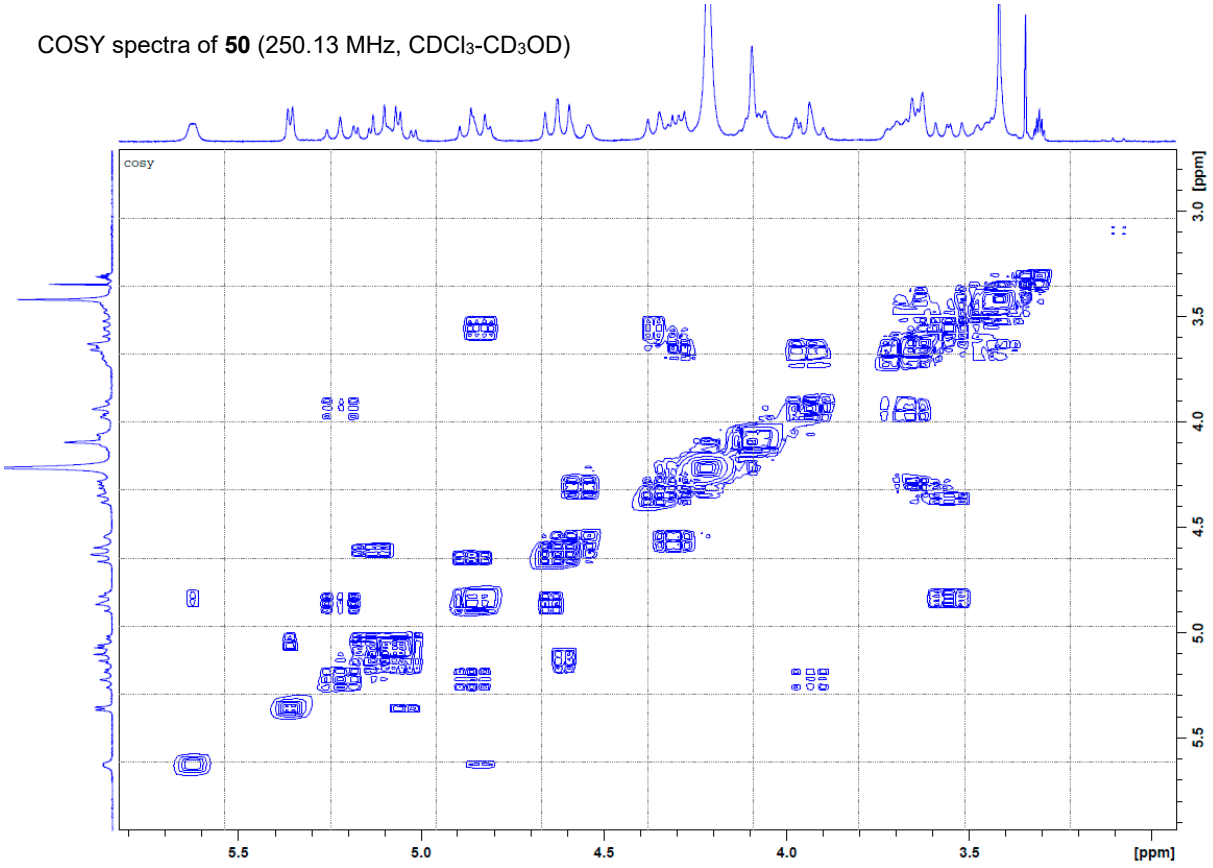
COSY spectra of **49** (250.13 MHz, CD_3OD-D_2O)



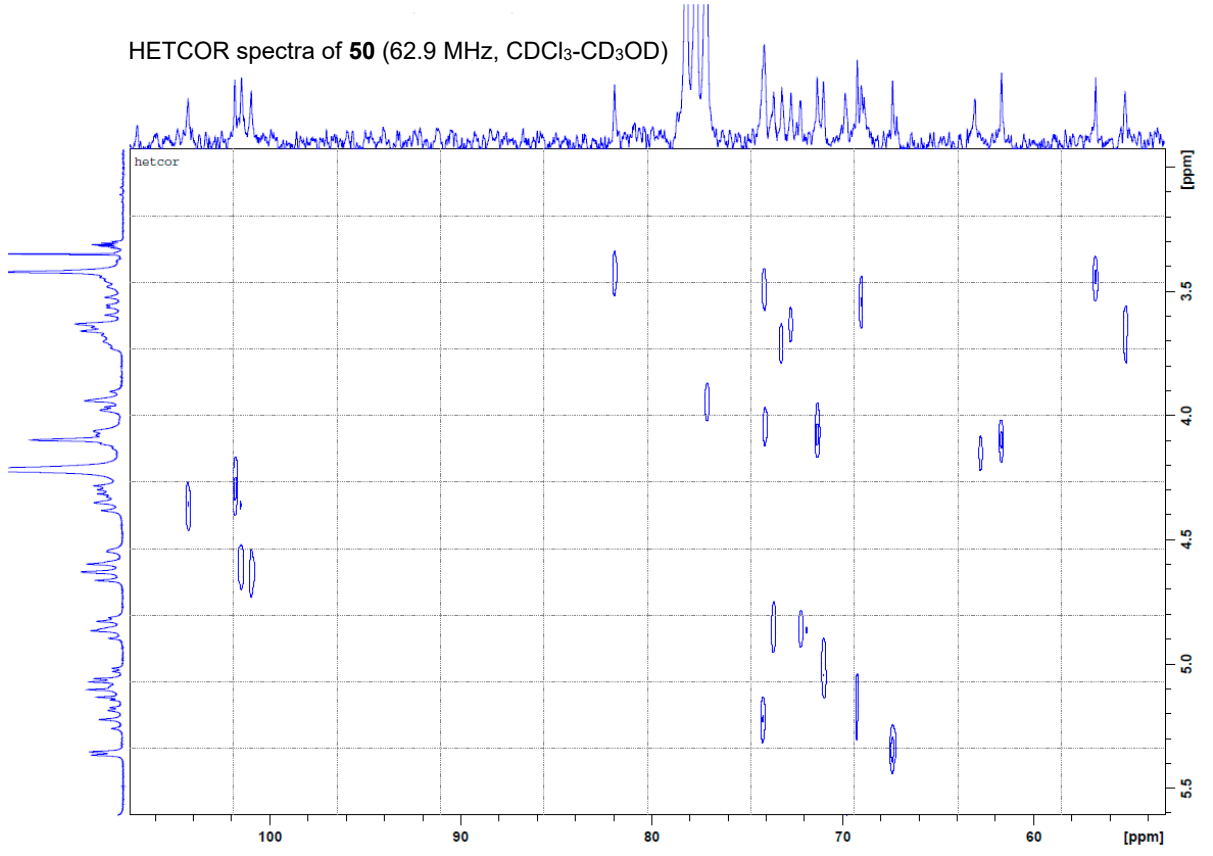

^{1}H NMR of **50** (250.13 MHz, $CDCl_3$-CD_3OD)
[rel]
[ppm]

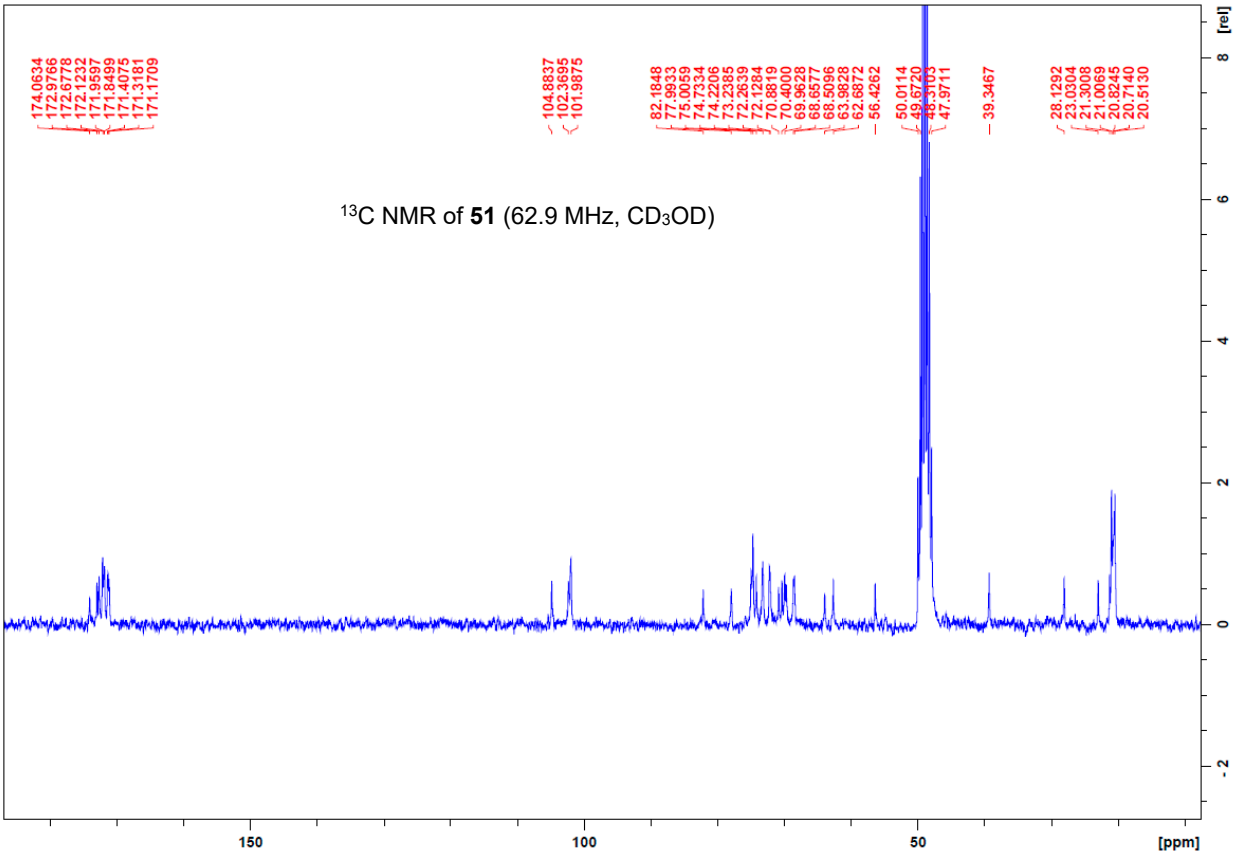

^{13}C NMR of **50** (62.9 MHz, CD_3OD-$CDCl_3$)
[rel]
[ppm]

COSY spectra of **50** (250.13 MHz, $CDCl_3$-CD_3OD)

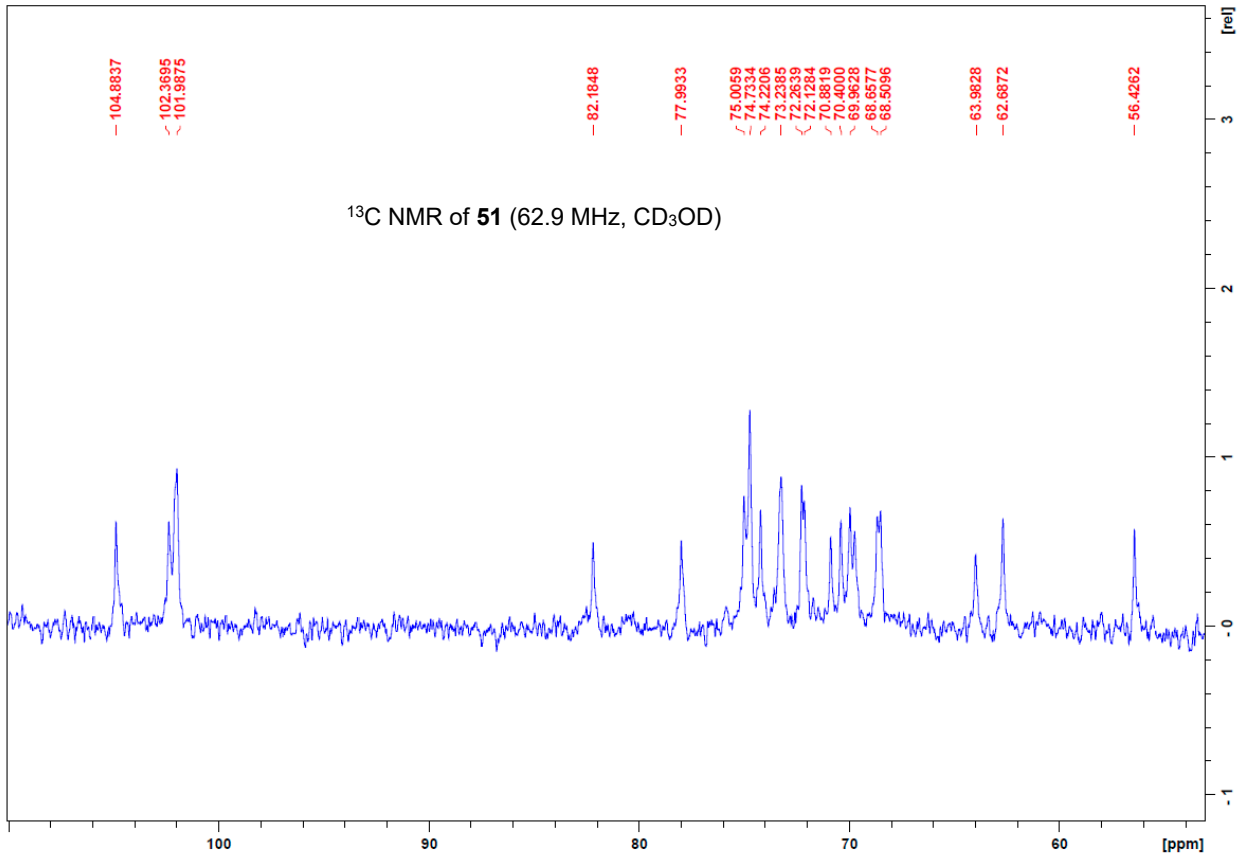


HETCOR spectra of **50** (62.9 MHz, $CDCl_3$-CD_3OD)



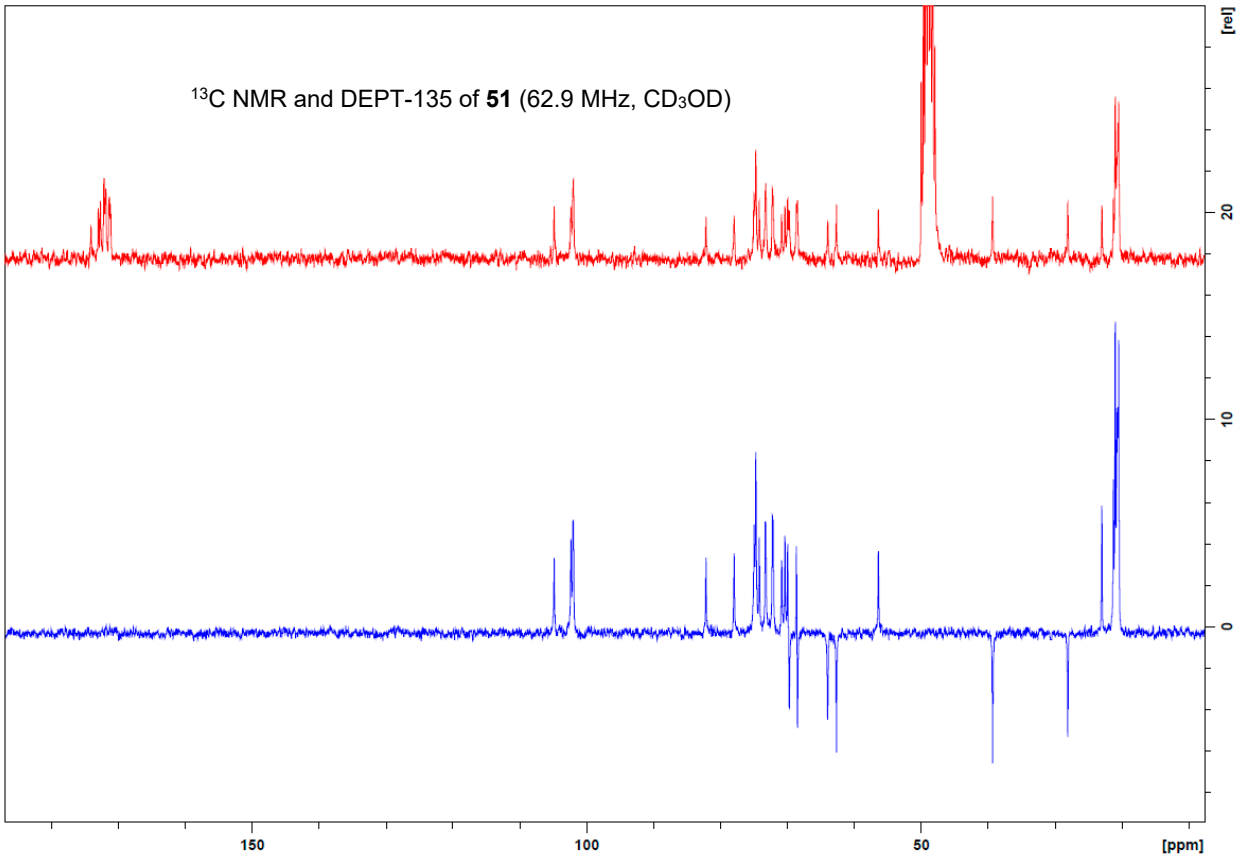


^{13}C NMR of **51** (62.9 MHz, CD_3OD)

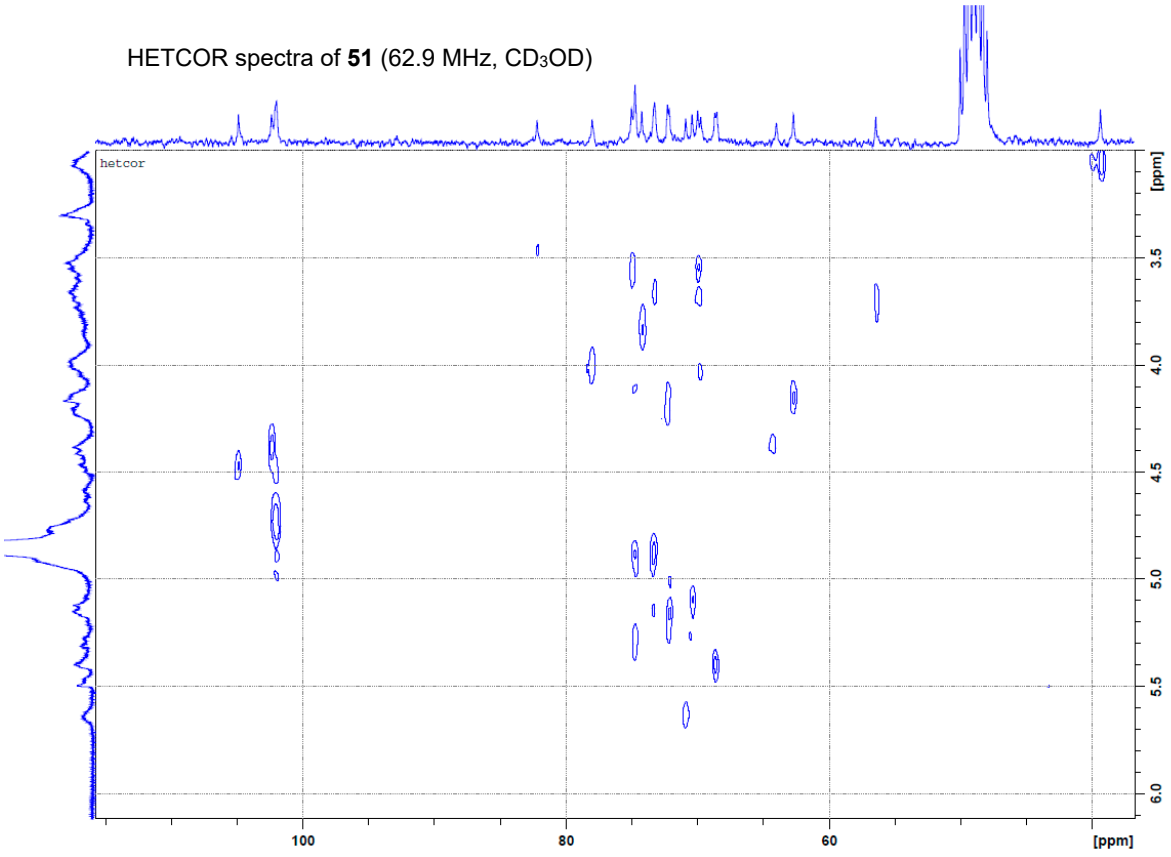


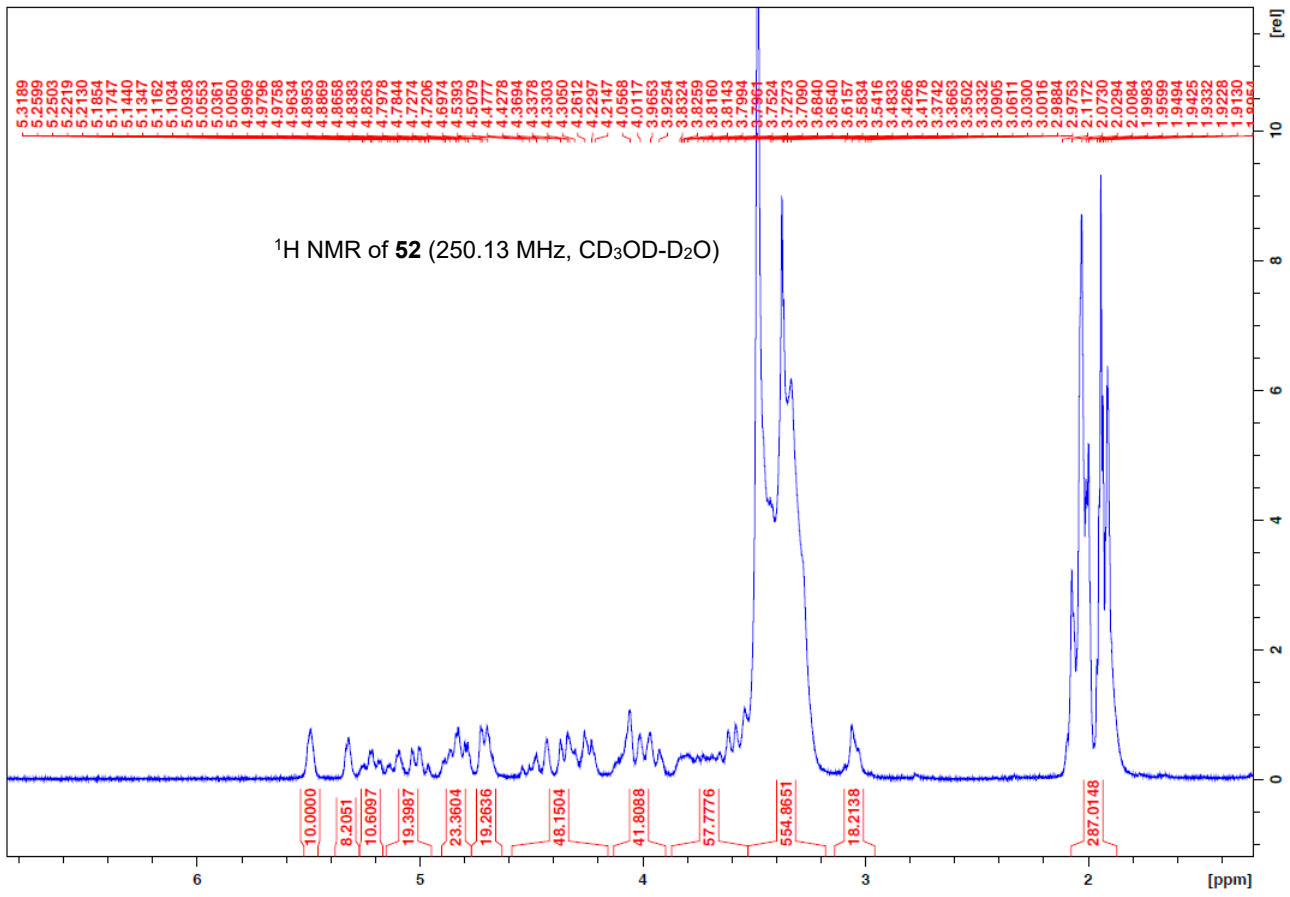
^{13}C NMR of **51** (62.9 MHz, CD_3OD)

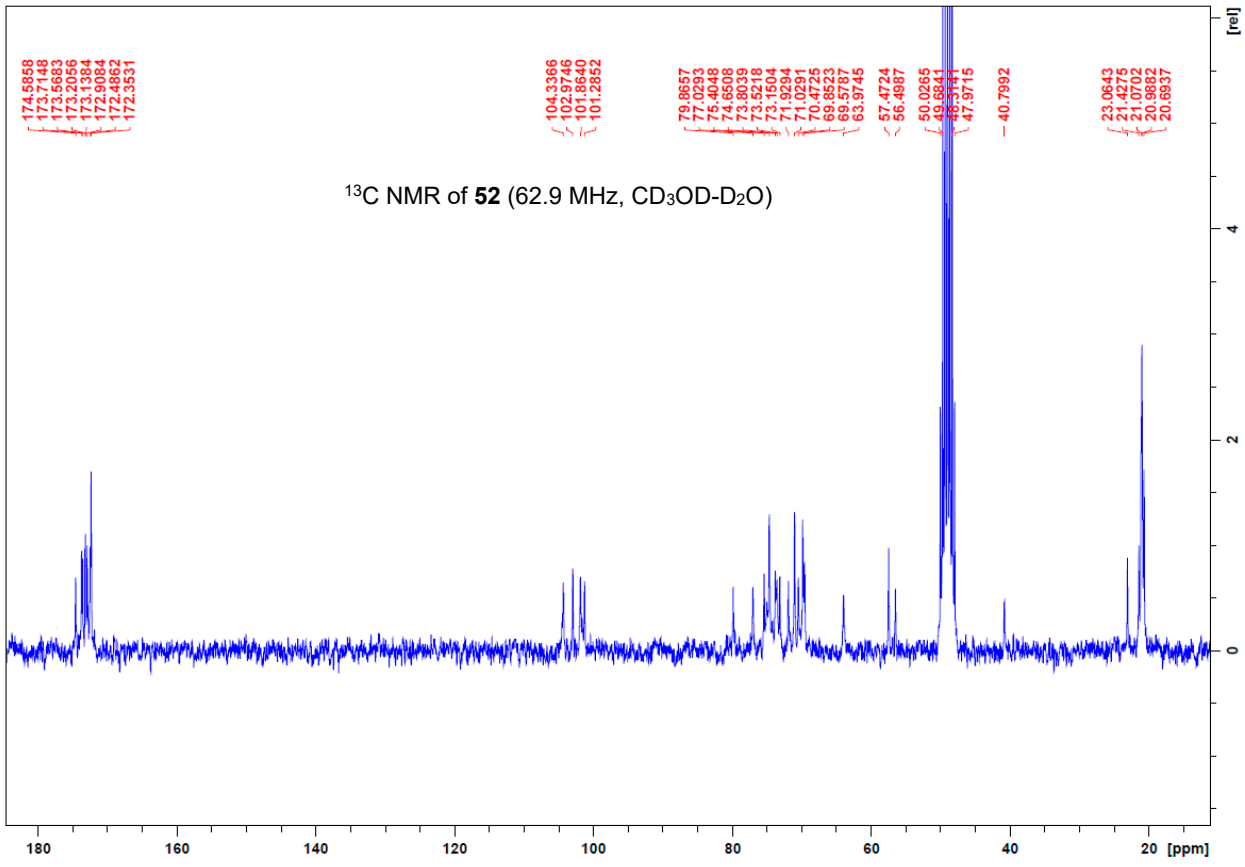
^{13}C NMR and DEPT-135 of **51** (62.9 MHz, CD_3OD)



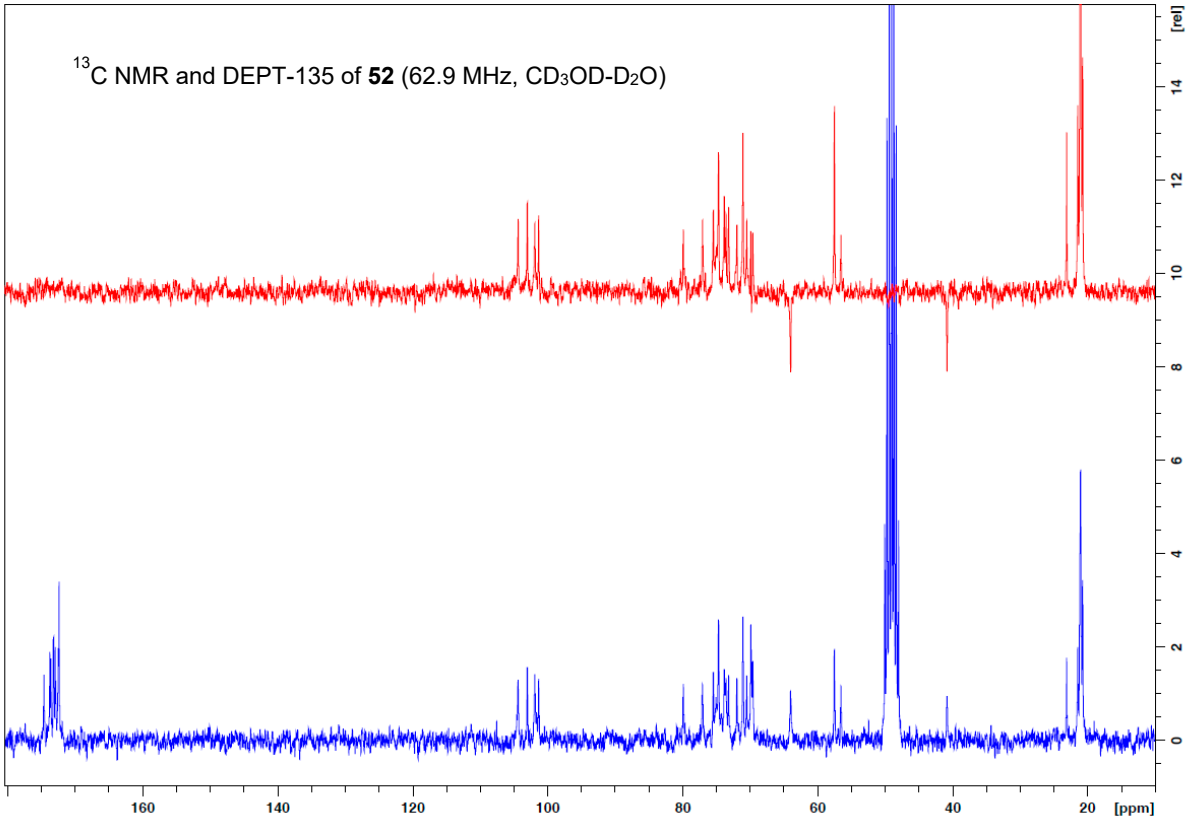
HETCOR spectra of **51** (62.9 MHz, CD_3OD)



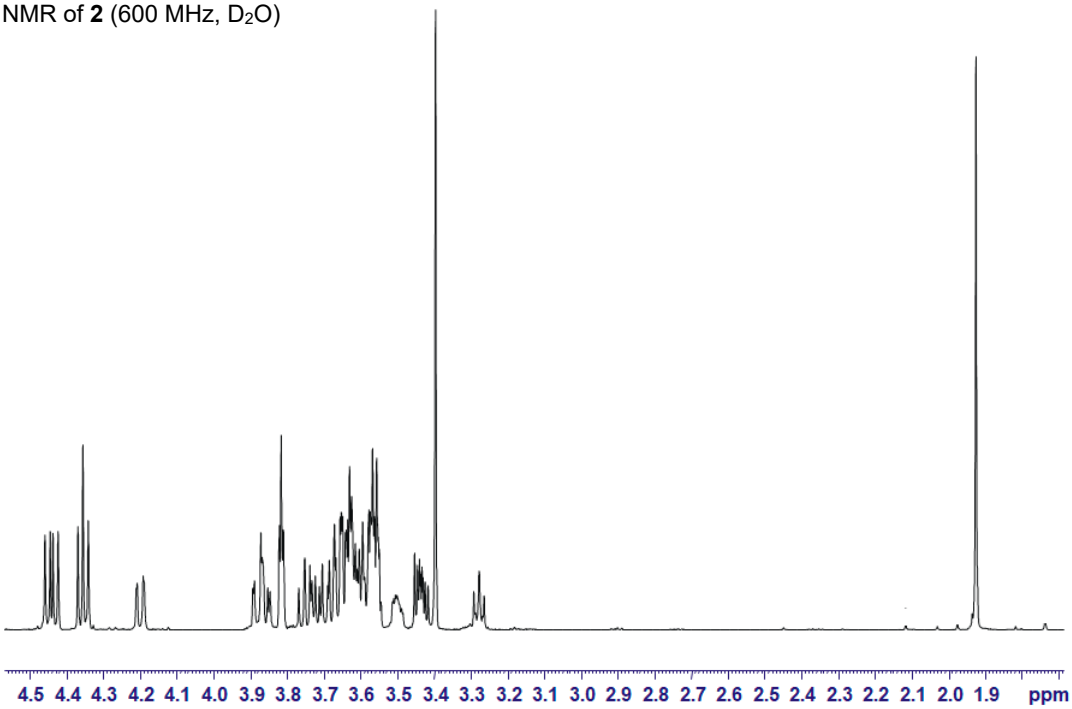

^{1}H NMR of **52** (250.13 MHz, CD_3OD-D_2O)
[rel]
[ppm]


^{13}C NMR of **52** (62.9 MHz, CD_3OD-D_2O)
[rel]
[ppm]

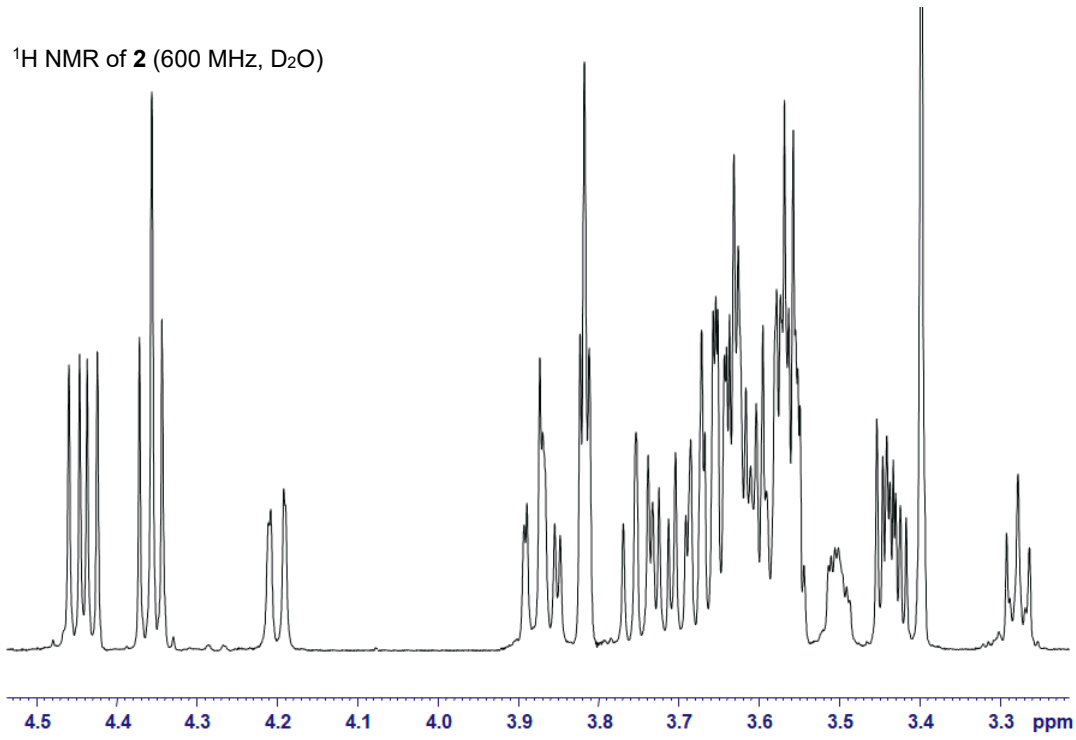
^{13}C NMR and DEPT-135 of **52** (62.9 MHz, CD_3OD-D_2O)



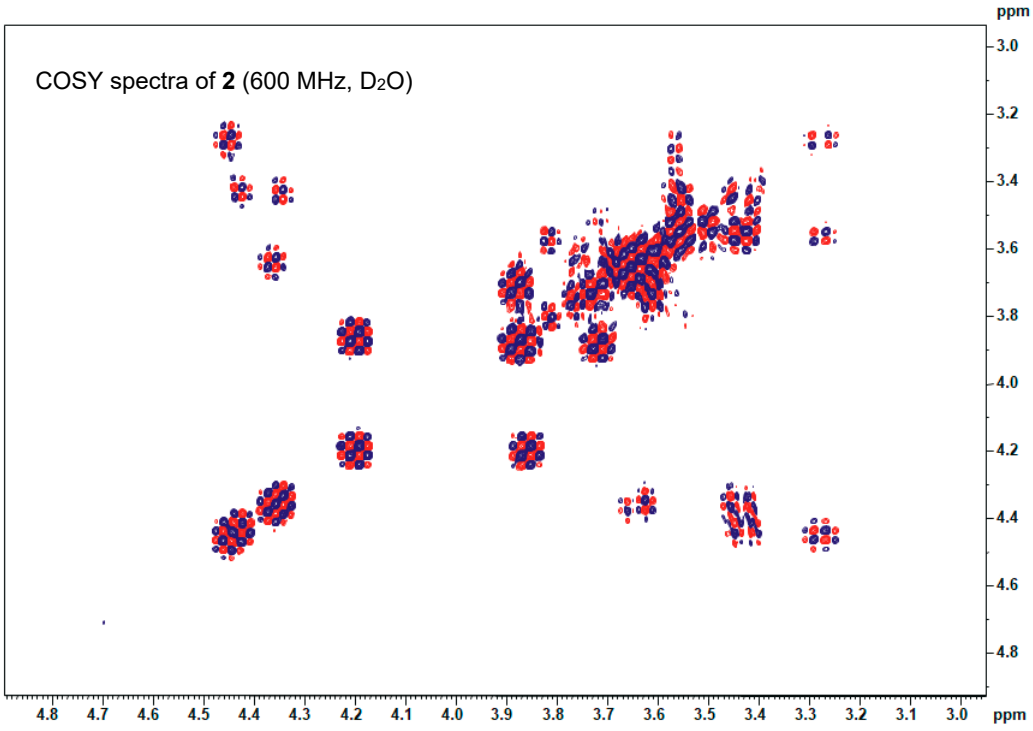
^{1}H NMR of **2** (600 MHz, D_2O)

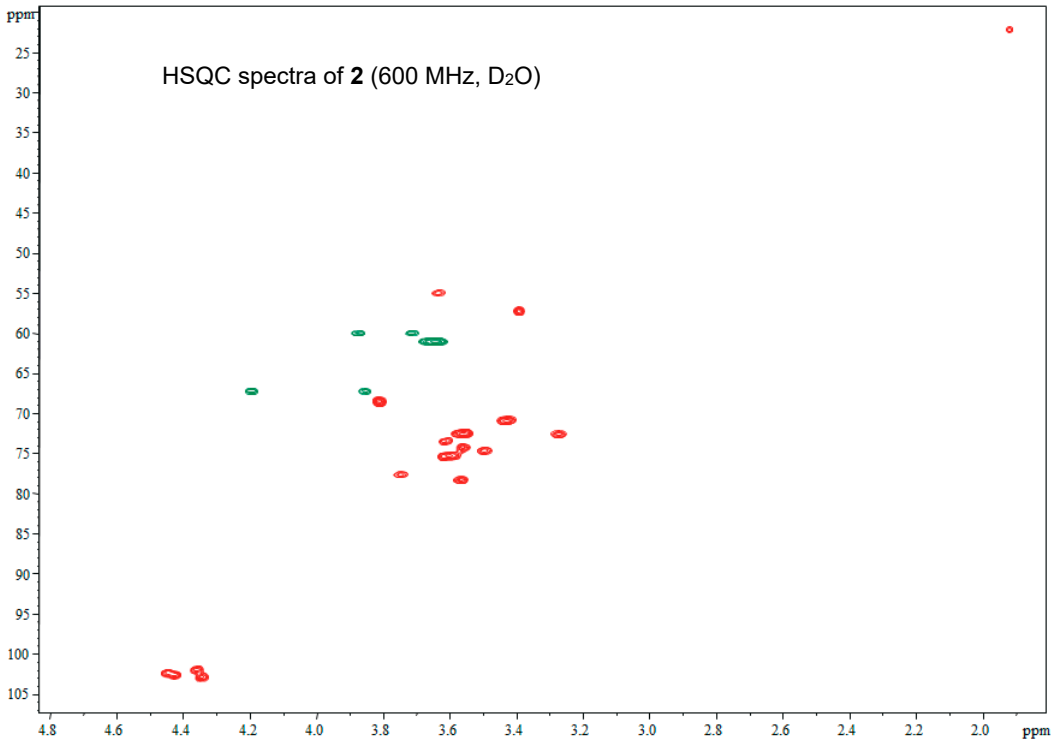


^{1}H NMR of **2** (600 MHz, D_2O)

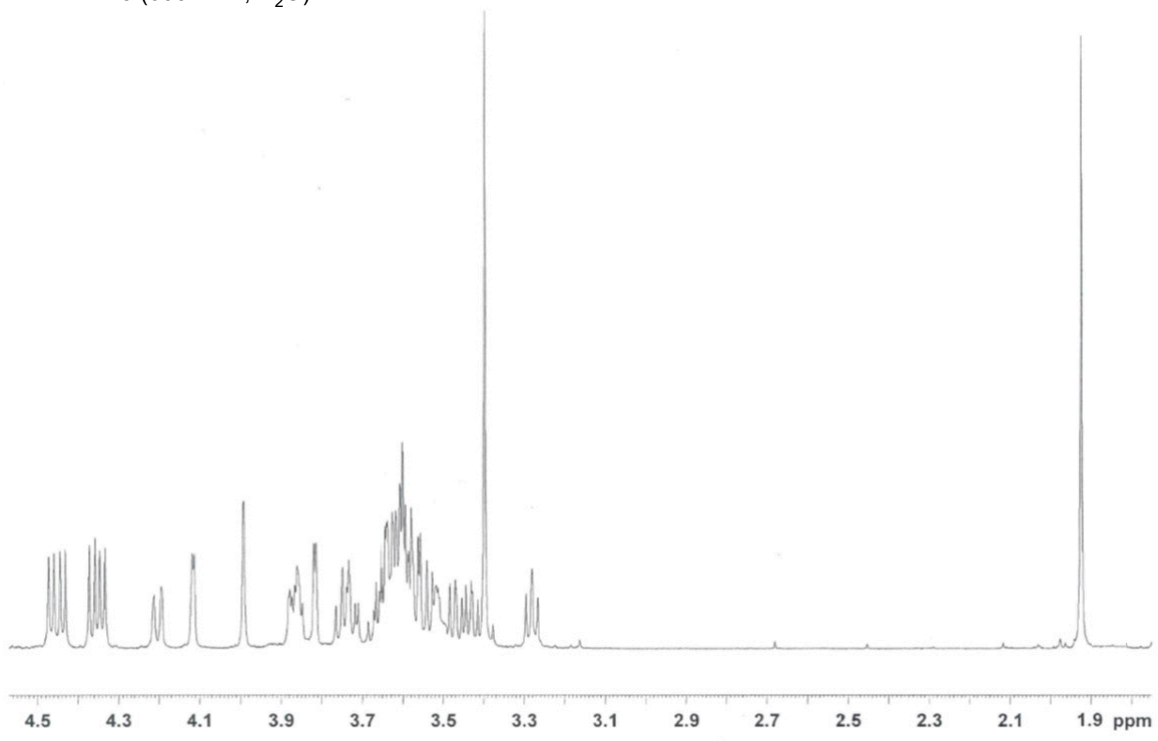


COSY spectra of **2** (600 MHz, D_2O)

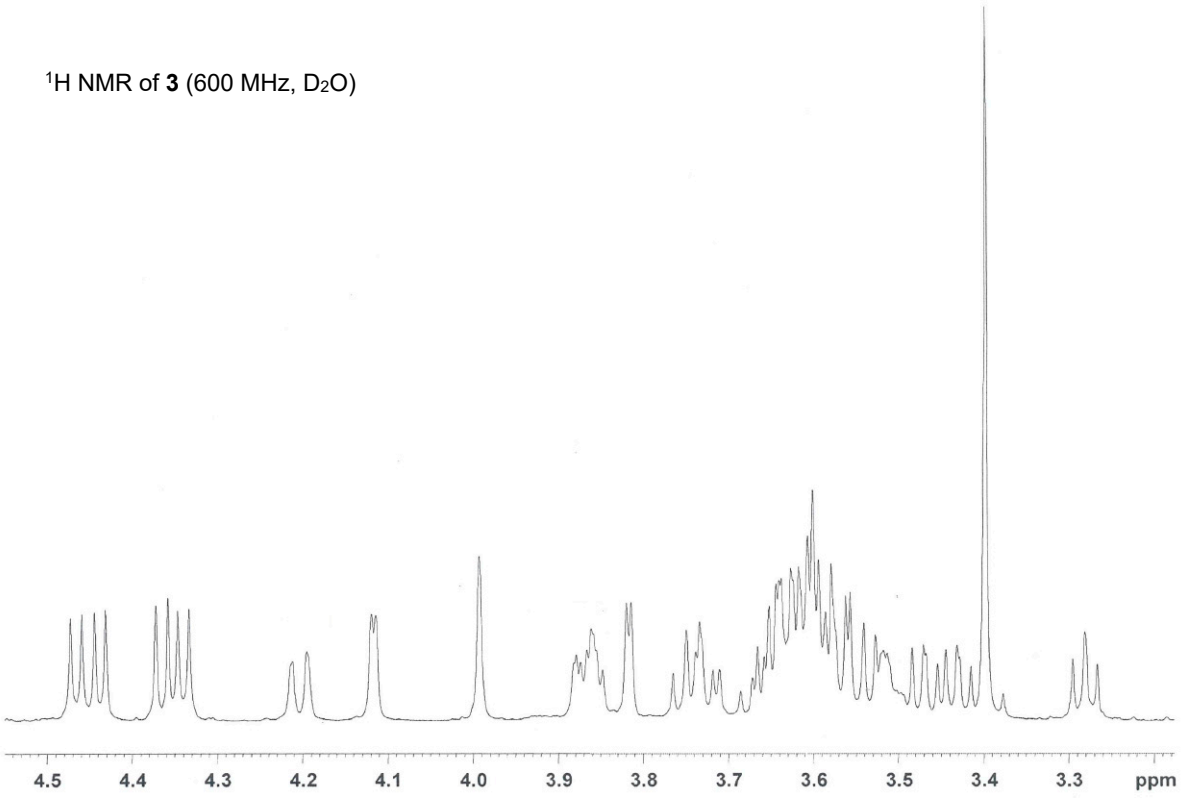




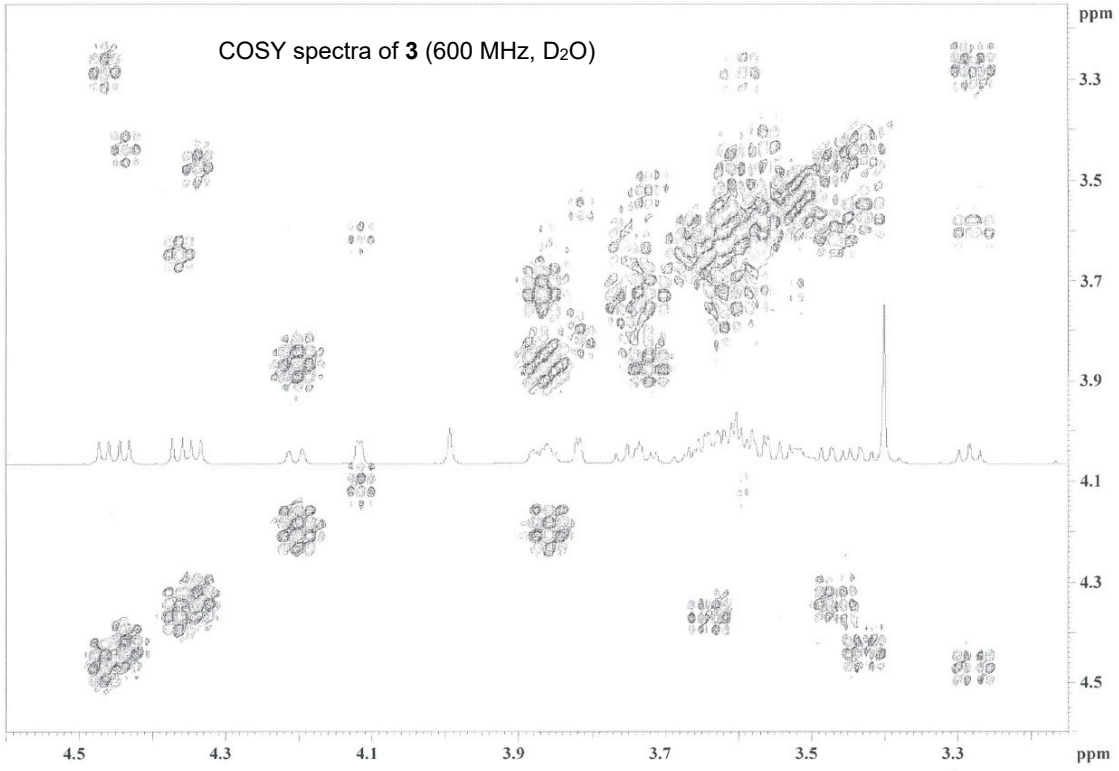
^{1}H NMR of **3** (600 MHz, D_2O)



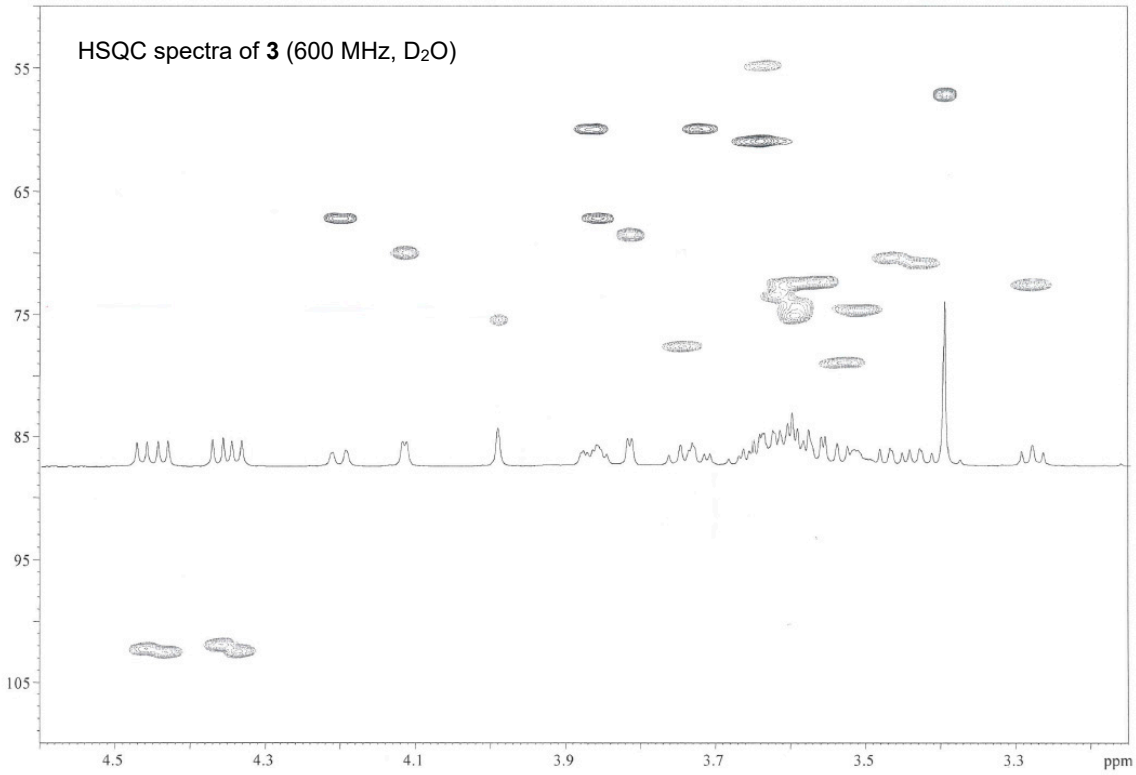
^{1}H NMR of **3** (600 MHz, D_2O)



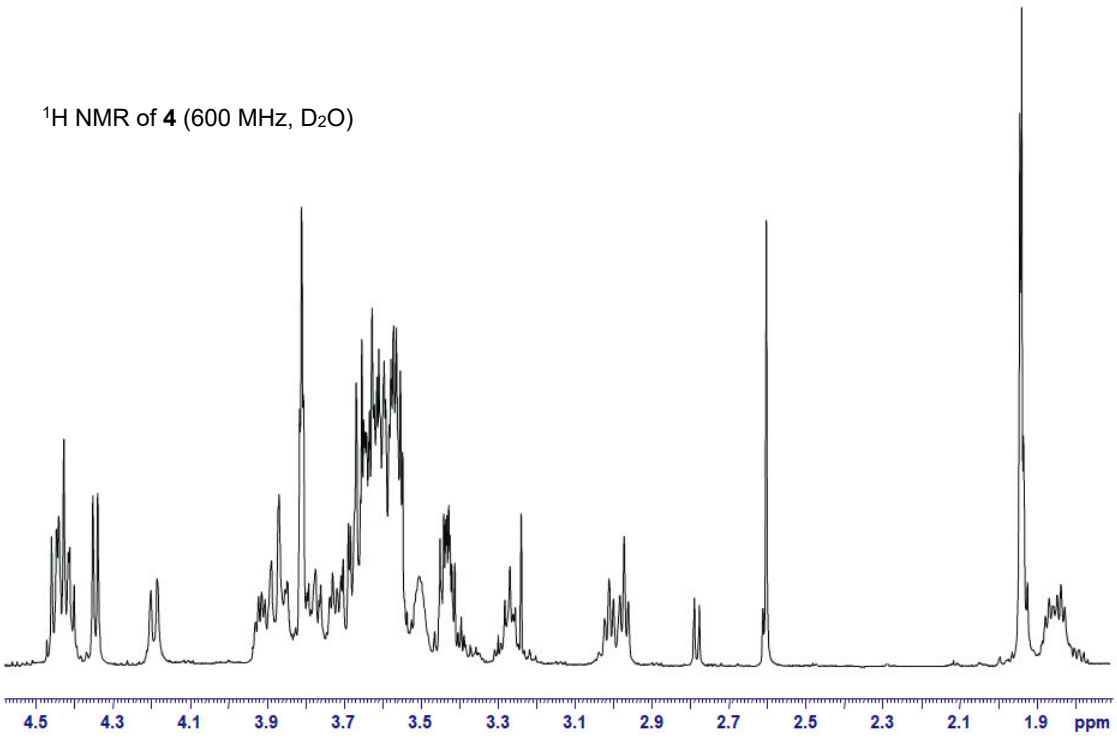
COSY spectra of **3** (600 MHz, D_2O)



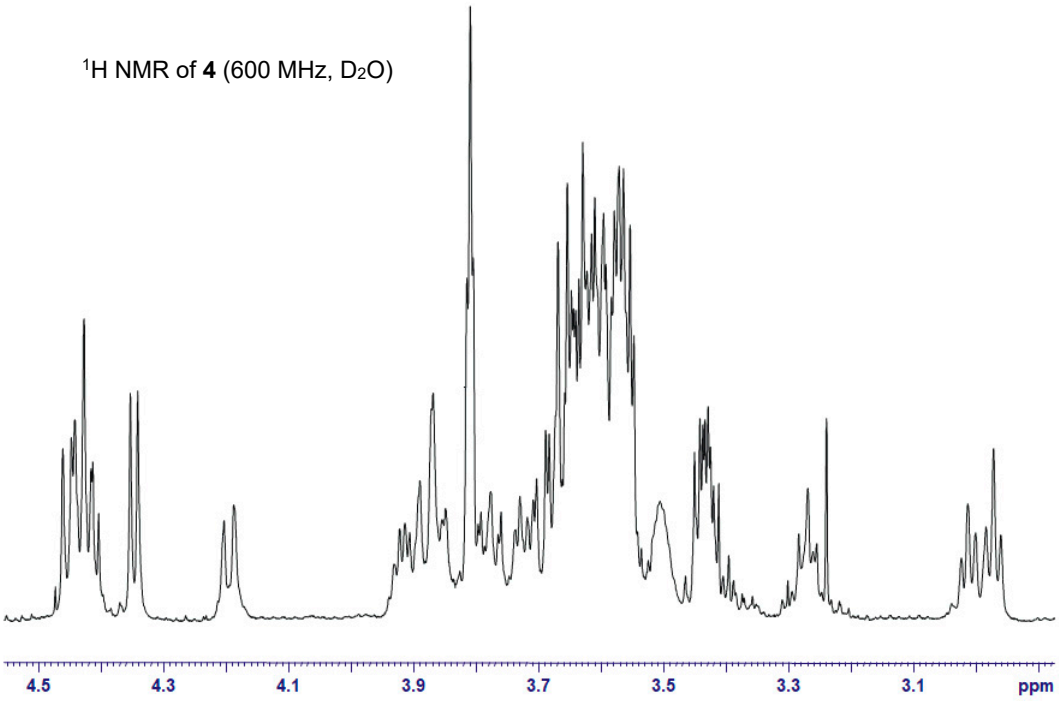
HSQC spectra of **3** (600 MHz, D_2O)



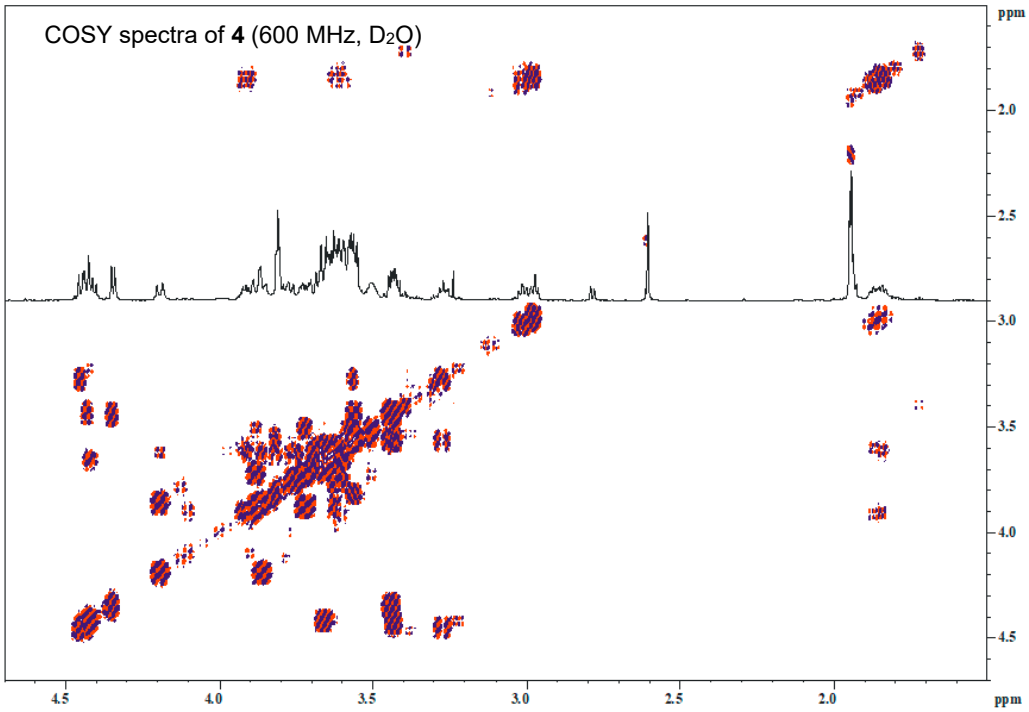
^1H NMR of **4** (600 MHz, D_2O)



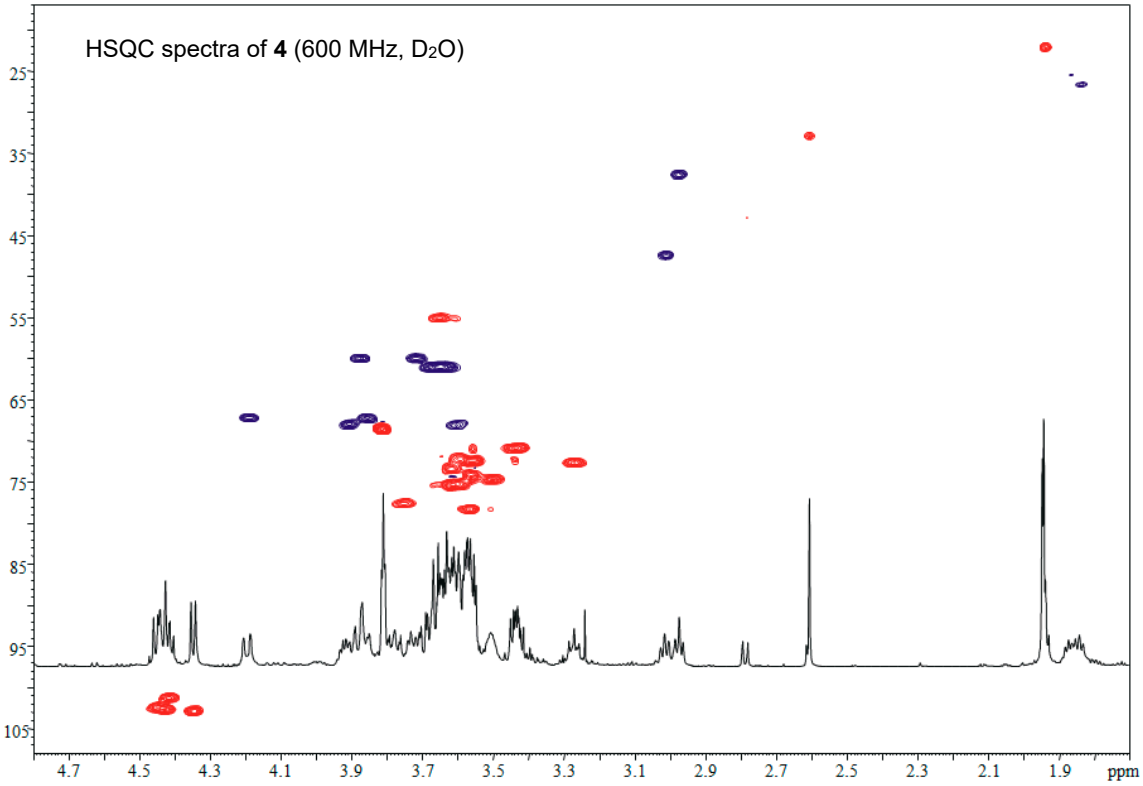
^{1}H NMR of **4** (600 MHz, D_2O)



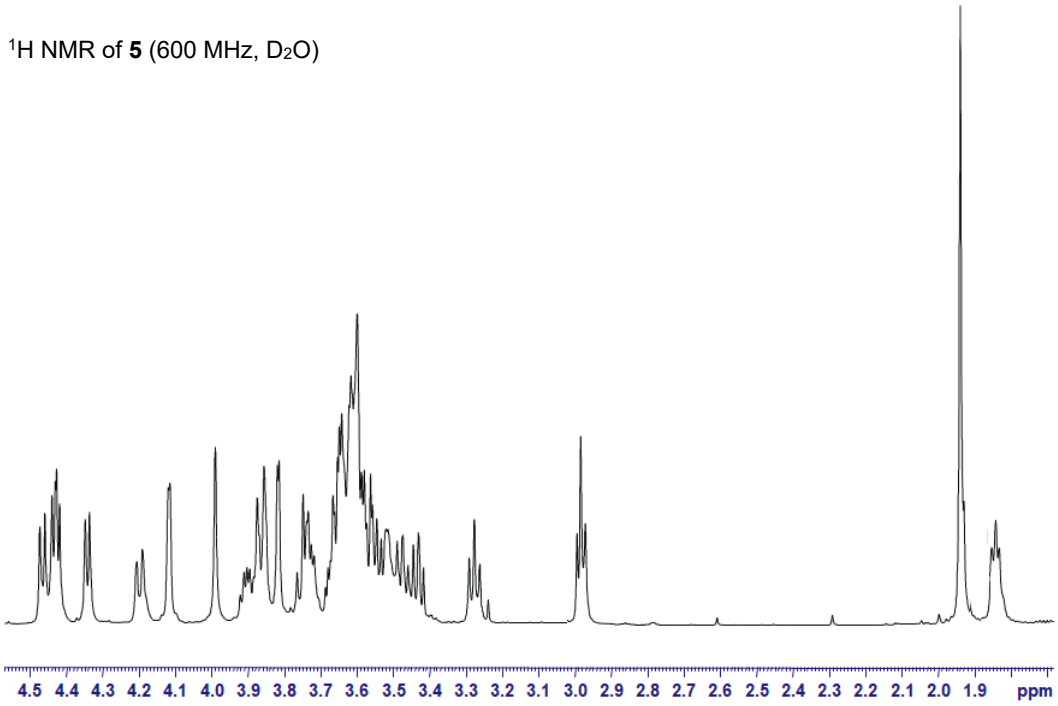
COSY spectra of **4** (600 MHz, D_2O)



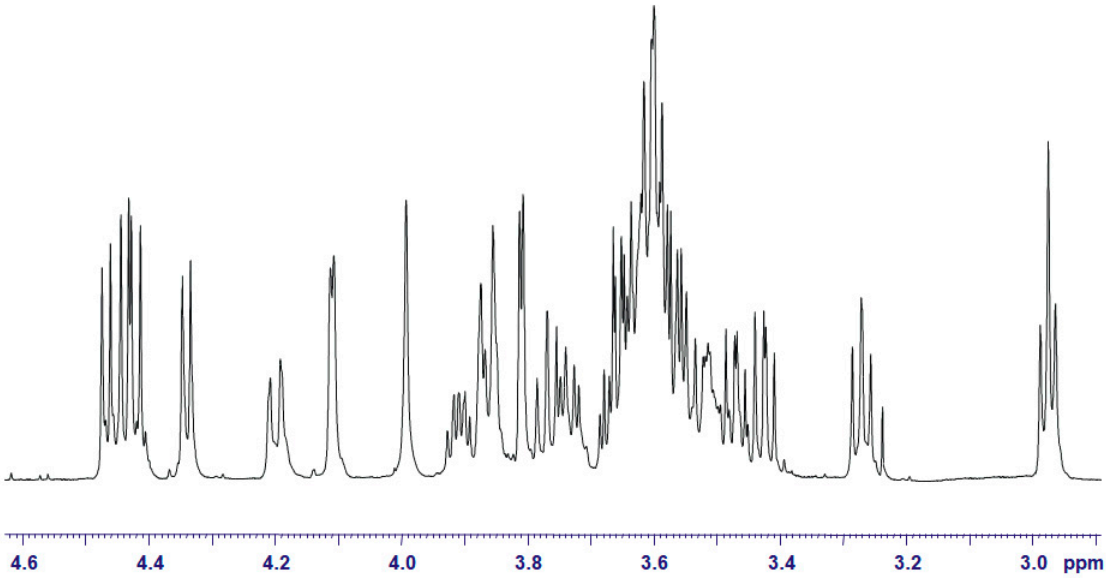
HSQC spectra of **4** (600 MHz, D_2O)



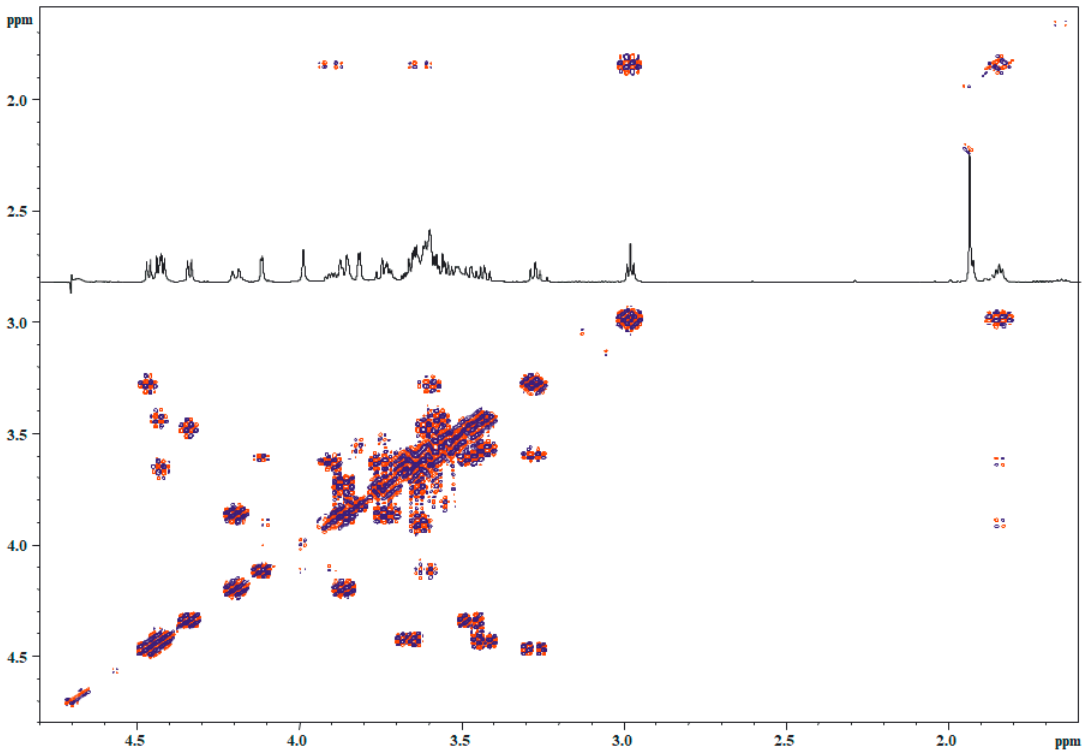
^1H NMR of **5** (600 MHz, D_2O)



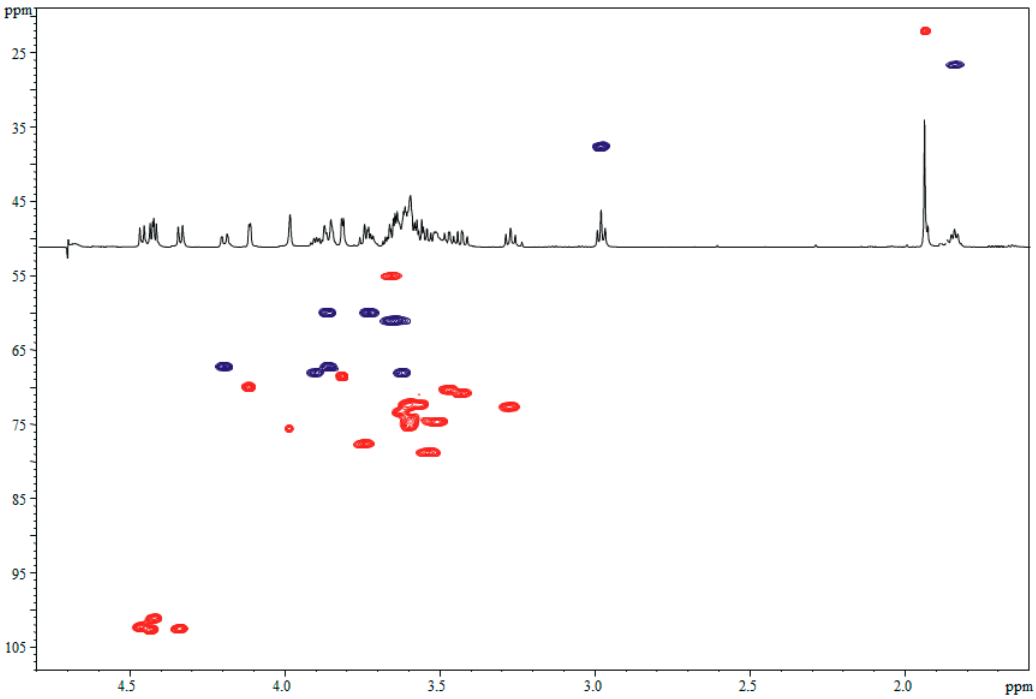
^{1}H NMR of **5** (600 MHz, D_2O)



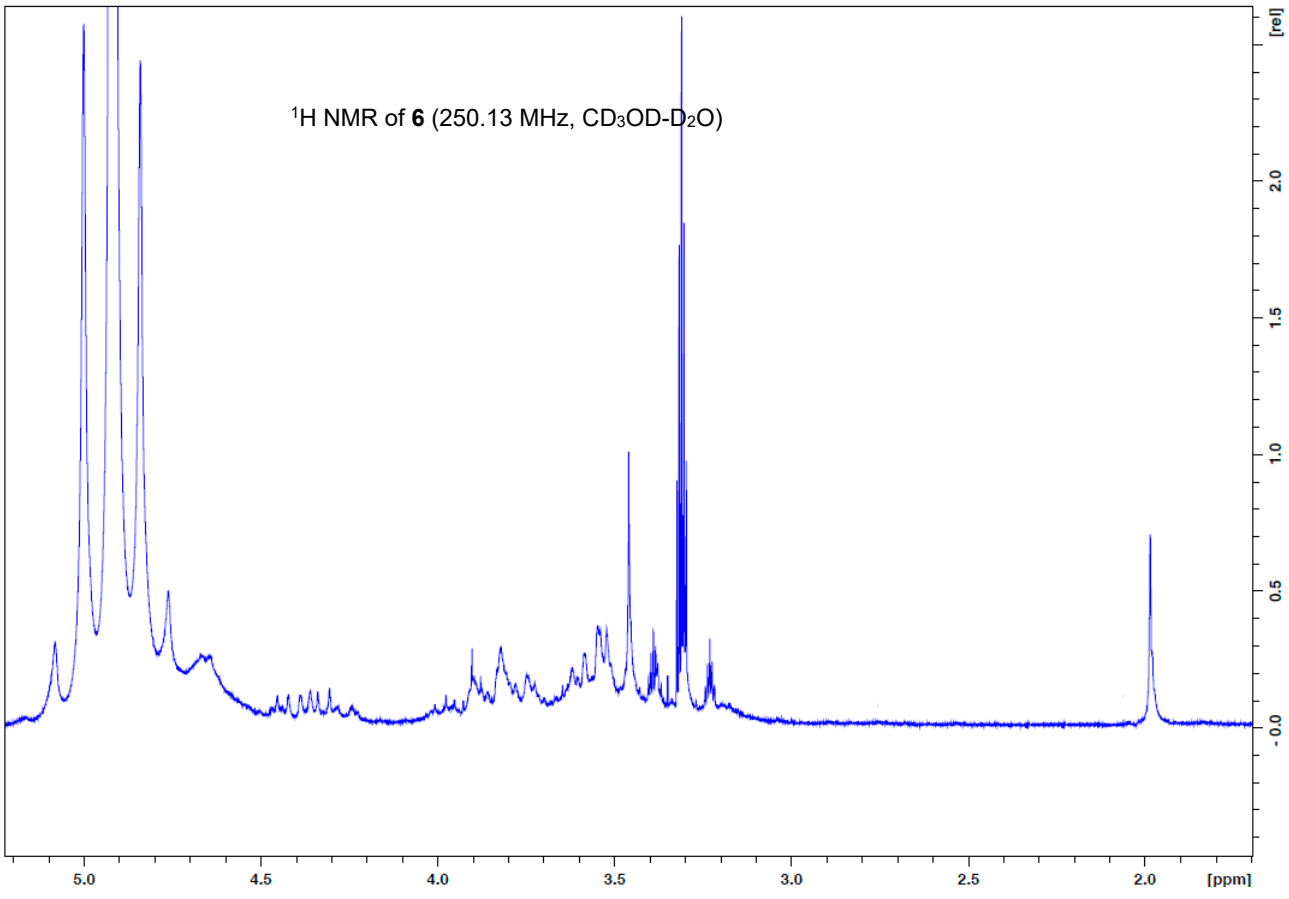
COSY spectra of **5** (600 MHz, D2O)



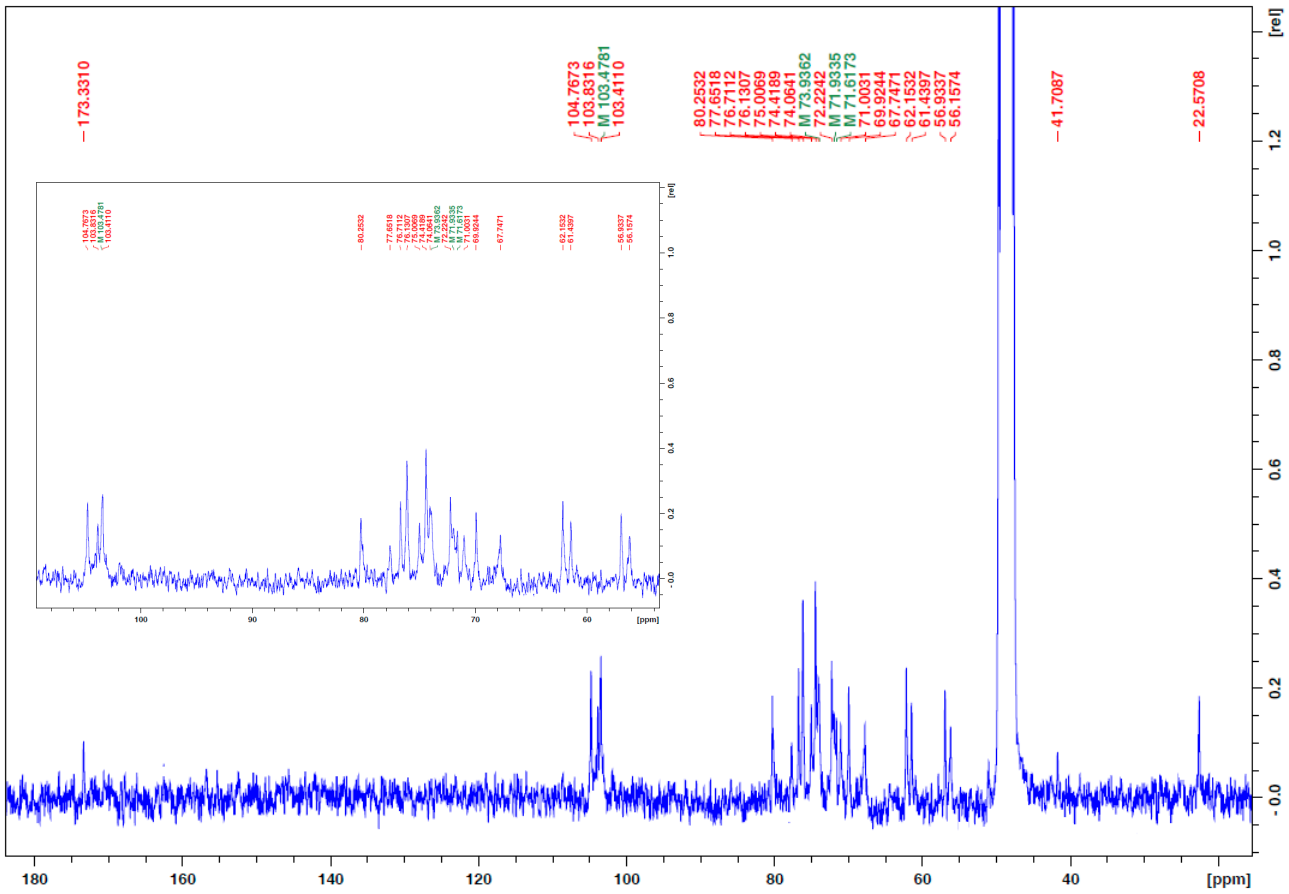
HSQC spectra of **5** (600 MHz, D_2O)



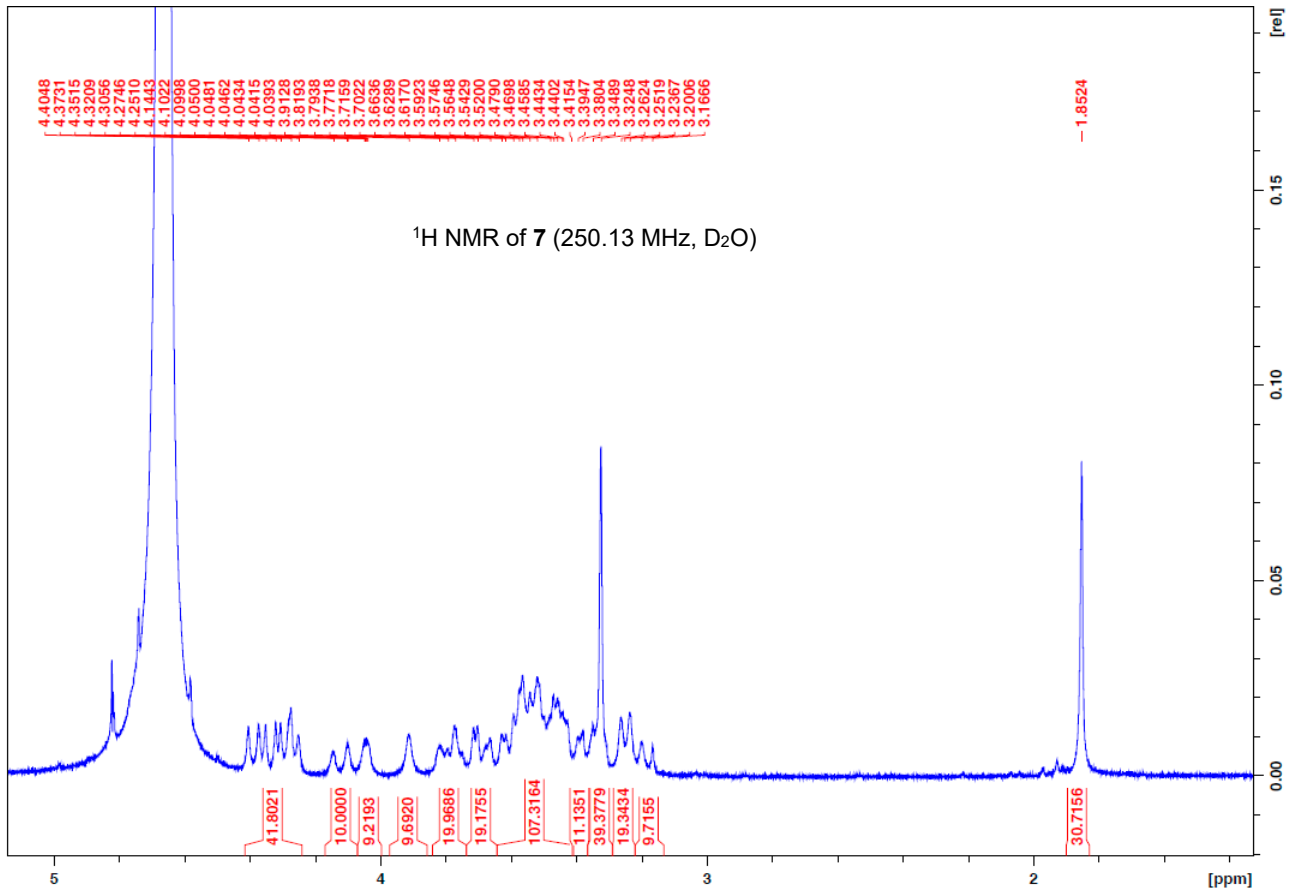
^{1}H NMR of **6** (250.13 MHz, CD_3OD-D_2O)

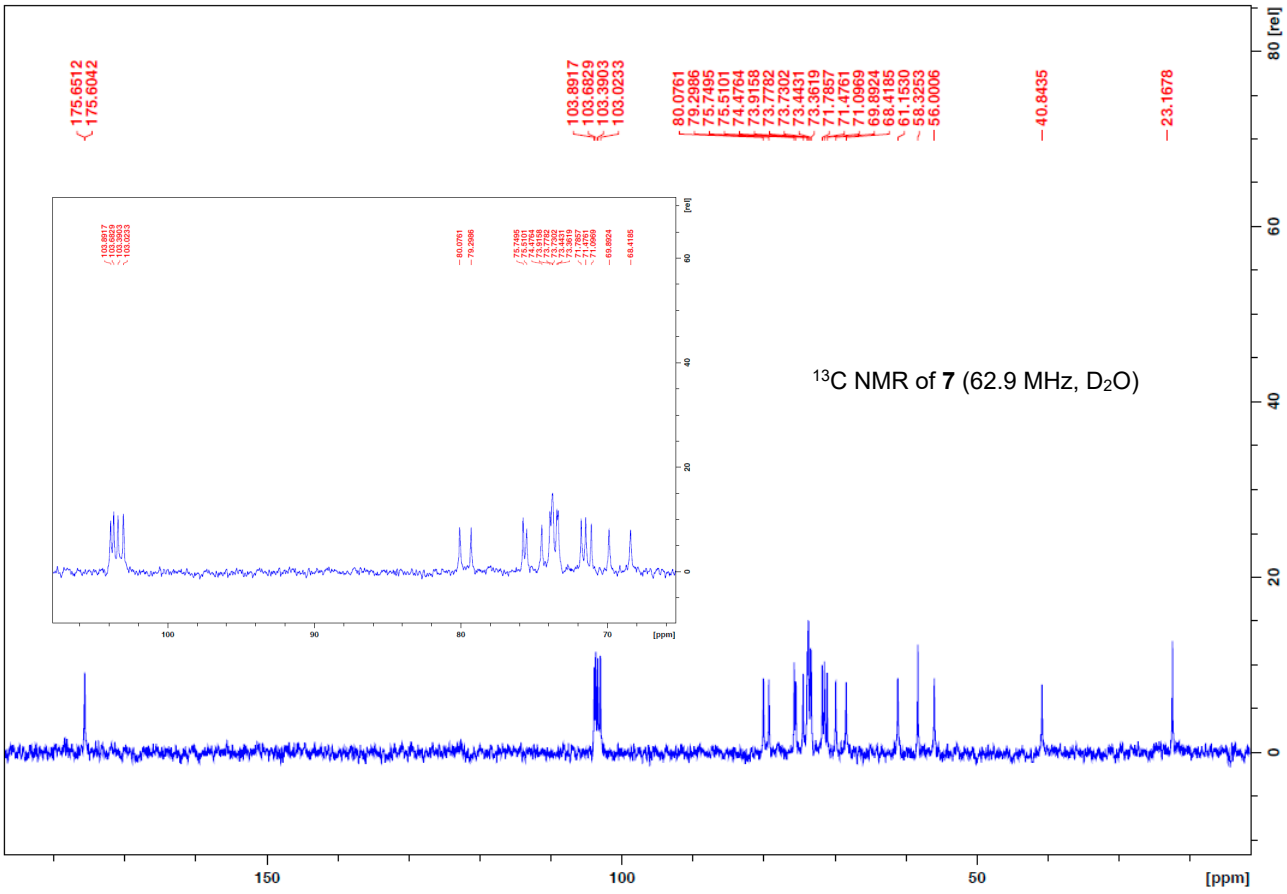


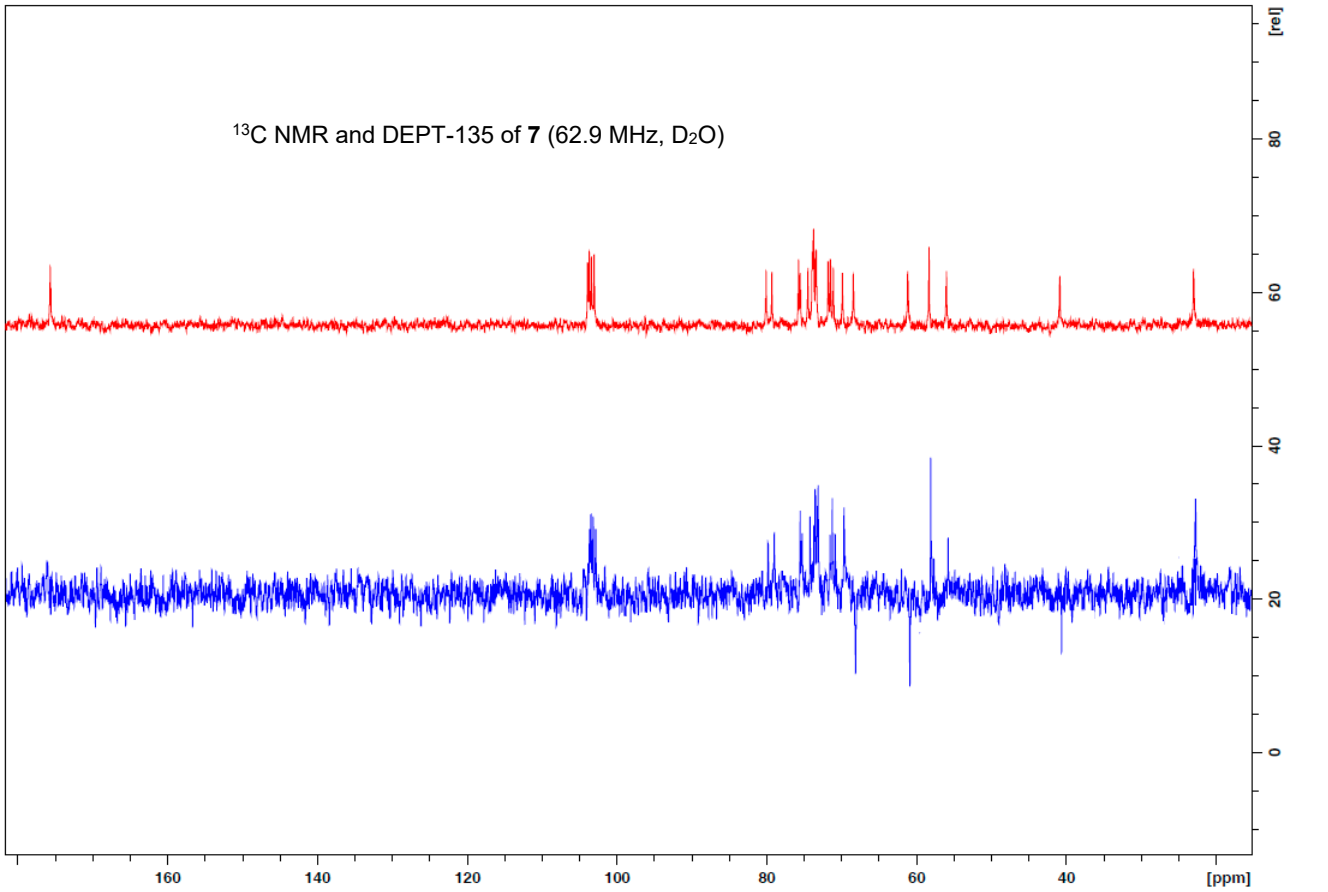
^{13}C NMR of **6** (62.9 MHz, CD_3OD-D_2O)



^{1}H NMR of **7** (250.13 MHz, D_2O)




175.6512
175.6042
103.8917
103.6829
103.3903
103.0233
80.0761
79.2986
75.7495
75.5101
74.4764
73.9158
73.7782
73.7302
73.4431
73.3619
71.7857
71.4761
71.0969
69.8924
68.4185
61.1530
58.3253
56.0006
40.8435
23.1678
[rel]
[ppm]
^{13}C NMR of **7** (62.9 MHz, D_2O)


^{13}C NMR and DEPT-135 of **7** (62.9 MHz, D_2O)
[rel]
[ppm]