Electronic Supplementary Information

Conformational modulation of peptides using β-amino benzenesulfonic acid (^{S}Ant)

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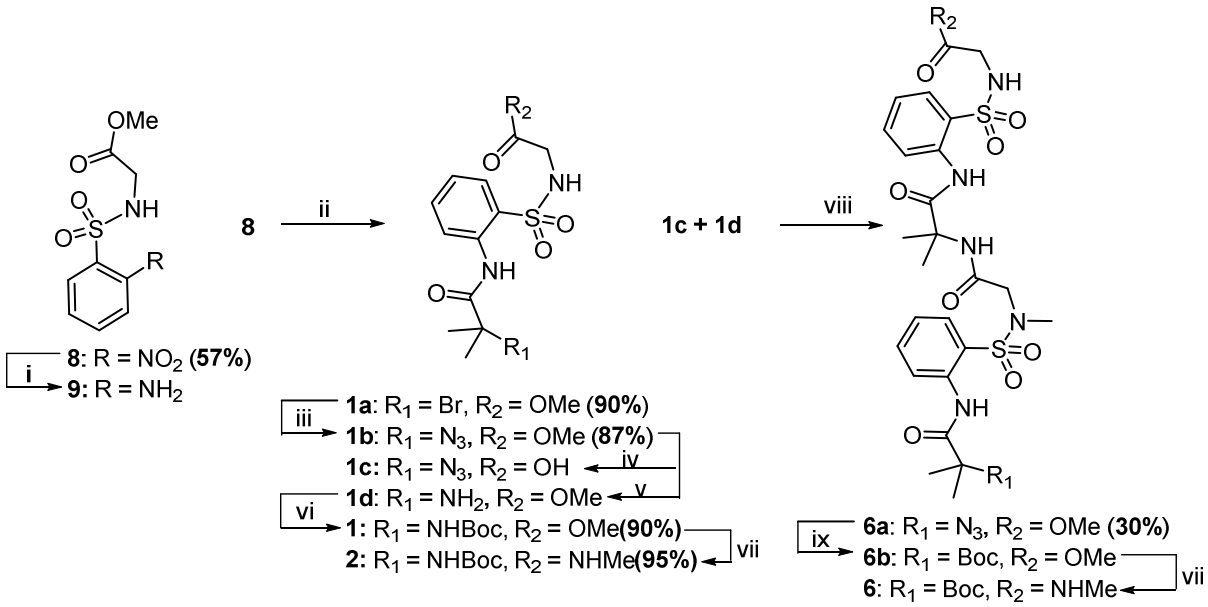
General Methods.

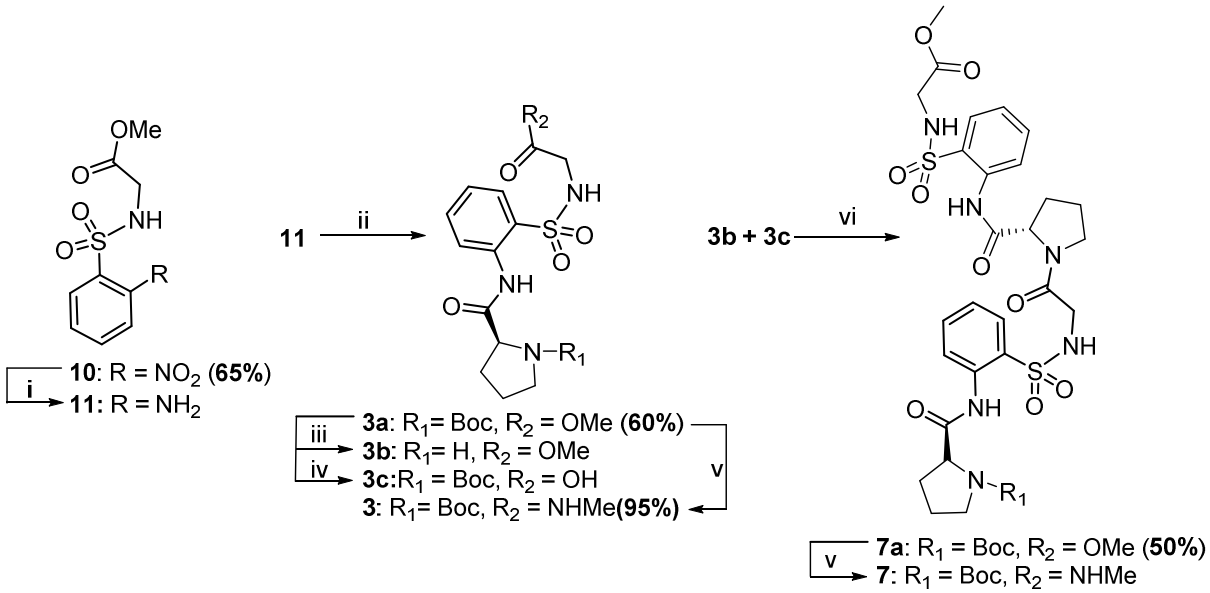
Unless otherwise stated, all chemicals and reagents were obtained commercially. Dry solvents were prepared by the standard procedures. Analytical thin layer chromatography was done on pre-coated silica gel plates (Kieselgel $60F_{254}$, Merck). Column chromatographic purifications were done with 100-200 mesh silica gel. NMR spectra were recorded in $CDCl_3$ on AV 200 MHz, AV 400 MHz or AV 500 MHz spectrometers. All chemical shifts are reported in δ ppm downfield to TMS and peak multiplicities are referred to as singlet (s), doublet (d), quartet (q), broad singlet (bs), and multiplet (m). The titration studies were done in $CDCl_3$. IR spectra were recorded in $CHCl_3$ using Shimadzu FTIR-8400 spectrophotometer. Melting points were determined on a Buchi melting point B-540 instrument. HRMS data were recorded on a Thermo Scientific Q-Exactive, Accela 1250 pump.

Scheme 1:



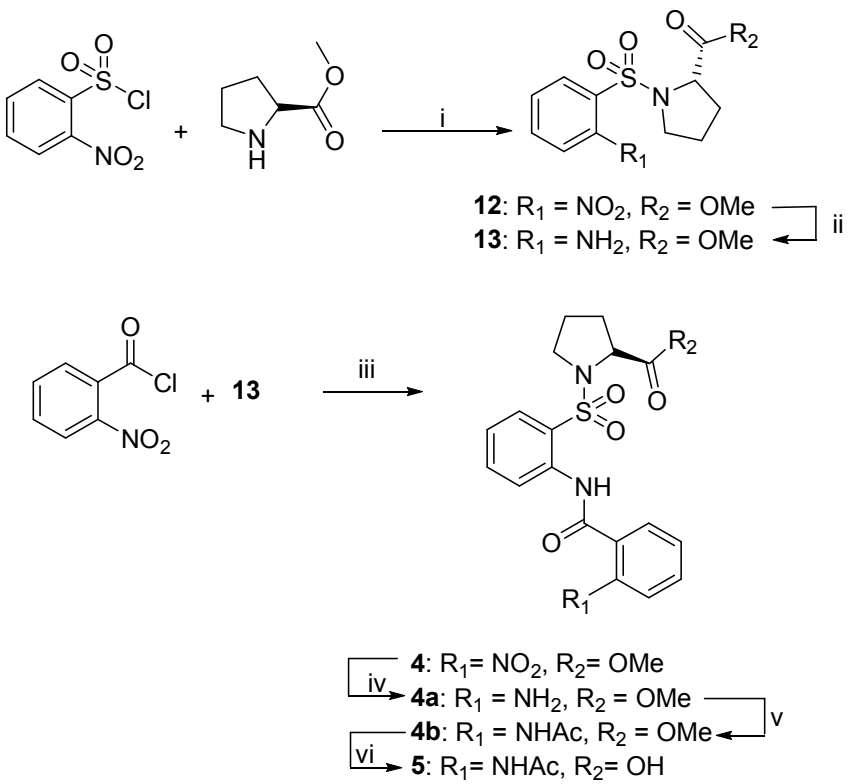
Reagents and conditions: (i) Pd/C, MeOH, H_2, 60 psi, 12h; (ii) 2-bromo-2-methyl isopropyl bromide, DIPEA, DCM, rt, 8 h; (iii) NaN_3, DMF, 80^0C, 12h; (iv) $LiOH.H_2O$, MeOH, rt, 12h; (v) Pd/C, MeOH, 60 psi, 5h; (vi) $(Boc)_2O$, Et_3N, rt, 12h; (vii) methanolic CH_3NH_2, MeOH, 12h; (viii) HBTU, DIPEA, CH_3CN, rt, 72 h; (ix) Pd/C, DIPEA, $(Boc)_2O$, MeOH, H_2, 60 psi, 48 h.

Scheme 2:



Reagents and conditions: (i) Pd/C, MeOH, H_2, 60 psi, 12h; (ii) Boc-Pro-OH, ethyl chloroformate, Et_3N, THF, 80 °C, 48 h; (iii) TFA, DCM (1:1); (iv) $LiOH.H_2O$, MeOH; (v) methanolic CH_3NH_2, MeOH, 12h; (vi) EDC.HCl, HOBt, Et_3N, DCM, rt, 12 h;

Scheme 3:



Reagents and conditions: (i) Et_3N, DCM, rt, 5h; (ii) Pd/C, MeOH, 60 psi, 6h; (iii) Et_3N, DCM, 8h; (iv) Pd/C, MeOH, 60 psi, 6h; (v) Py, Ac_2O, DCM, 6h; (vi) $LiOH.H_2O$, MeOH, rt, 5h.

Synthetic Procedures:

Reduction of nitro 8, 10, 12 and 4 & azido compounds 1c, 6a and 4 to amines 9, 11, 13 & 1d, 6b and 4a, respectively:

General procedure:

To the solutions of nitro compounds **8**, **10**, **12** and **4** & azido compounds **1c**, **6a** and **14** (0.5 g, 1.59 mmol) in methanol (15 mL), 10% Pd/C (0.06 g) was added. Then, the reaction mixture was subjected to hydrogenation in a parr shaker at 60 psi for 12 h. Later, the catalyst was filtered through celite and the solvent was removed under reduced pressure to get the products **9**, **11**, **13** & **1d**, **6b** and **4a**, which were carried forward to the next reaction without any purification. The amines obtained from the azido compounds were subjected to Boc protection *insitu*, wherever necessary, by adding $(Boc)_2O$ and Et_3N to the reaction mixture.

C-terminus amidation of esters 1, 6b, 3a, 7a to amides 2, 6, 3 and 7, respectively:

The compounds **1**, **6b**, **3a** and **7a** were dissolved in MeOH (2 mL) followed by addition of methanolic methyl amine solution (2 mL) at 0 ^{o}C. The reaction was monitored by TLC and after completion, the solvent was stripped off. The crude products were purified by column chromatography which yielded the amide products **2, 6, 3,** and **7**, respectively.

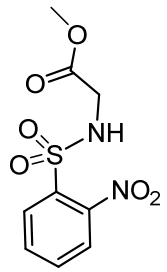
Hydrolysis of esters 1b, 3b and 4b to acids 1c, 3c and 5, respectively:

To the solutions of esters **1b**, **3b** and **4b** (10 mmol, 1 equiv) in methanol, $LiOH{\cdot}H_2O$ (40 mmol, 4 equiv) was added in water (12 mL) at 0 °C and the reaction mixture was stirred for 12 h. After the complete consumption of the starting material, the solvent was evaporated under reduced pressure and the residue was treated with sat. $KHSO_4$ solution and was followed by extraction with DCM (2 X 25 mL). The corresponding acid derivatives **1c**, **3c** and **5**, respectively, obtained after evaporation of the solvent were taken for the next reaction without any purification.

Boc deprotection of 3a to 3b:

The solution of **3a** (3 mmol) was subjected to deprotection using DCM/TFA (1:1, 5 mL) at 0°C. After completion of the reaction (~2 h), the solvent was stripped off. The amine **3b**, obtained after evaporation of the solvent was used for the next step without any purification**.**

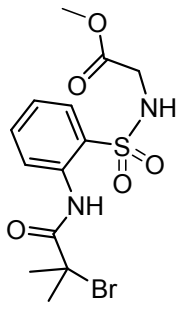
Methyl ((2-nitrophenyl)sulfonyl)glycinate 8:



8

To a solution of glycine methyl ester hydrochloride in dry DCM (10 mL), Et_3N (0.57 mL, 4 mmol) was added and stirred at 0 ^oC for 15 min. Then 2-nitrobenzenesulfonylchloride (0.3 g, 1.3 mmol) was added to the reaction mixture. The reaction mixture was allowed to attain room temperature and was further stirred for 12 h. Later, the reaction mixture was washed sequentially with sat. $NaHCO_3$, dil. HCl and brine solutions. The organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to get the crude product which on purification by column chromatography (eluent: pet ether/ethyl acetate: 60:40, R*f*: 0.5) yielded **8** (0.18 g, 50%); mp: 108-110 ^oC; IR ($CHCl_3$) ν (cm^{-1}): 3685, 3617, 3363, 3019, 2400, 1749, 1543, 1440, 161, 1218, 1171, 1046, 771, 668, 588; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.11-8.08 (m, 1H), 7.95-7.92 (m, 1H), 7.76-7.74 (m, 2H), 6.08-6.05 (t, *J* = 5.1 Hz, 1H), 4.03-4.01 (d, *J* = 5.8 Hz, 2H), 3.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169, 133.7, 132.9, 130.5, 125.6, 52.5, 44.7; HRMS: $C_9H_{10}O_6N_2NaS$, Calcd: 297.0152 Found: 297.0149.

Methyl ((2-(2-bromo-2-methylpropanamido)phenyl)sulfonyl)glycinate 1a:

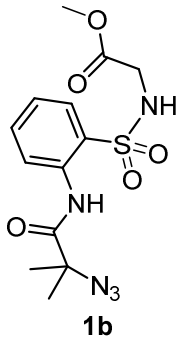


1a

To a solution of amine **9** (0.17g, 0.7 mmol) in dry DCM at 0 ^oC, 2-bromo-2-methylpropanoyl bromide (0.09 mL, 0.7 mmol) was added followed by the addition of Et_3N (0.12 mL, 0.8 mmol) and the reaction mixture was stirred for 12 h after attaining room temperature. Later, the reaction mixture was washed sequentially with sat. $NaHCO_3$ and brine solutions. The organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to get the crude product which on purification by column chromatography (eluent: pet ether/ethyl acetate: 70:30, R*f*: 0.5) yielded **1a** (0.26 g, 97%); IR ($CHCl_3$) ν (cm^{-1}): 3331, 3022, 1745, 1700, 1586, 1528, 1438, 1332, 1218, 1154, 1113, 850, 771, 497; ^1H NMR (400 MHz,

$CDCl_3$) δ: 9.98 (s, 1H), 8.37-8.35 (d, *J* = 8.3 Hz, 1H), 7.95-7.93 (d, *J* = 8 Hz, 1H), 7.67-7.63 (t, *J* = 7.8 Hz, 1H), 7.31-7.29 (d, *J* = 6.3 Hz, 1H), 5.55-5.52 (t, *J* = 5.3 Hz, 1H), 4.18-4.13(q, ethyl acetate), 3.81-3.8 (d, *J* = 5.5 Hz, 2H), 3.63 (s, 3H), 2.11 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.1, 168.5, 135.6, 134.3, 129.4, 126.8, 124.3, 123.2, 60.5, 60.4, 52.7, 43.8, 31.5, 21, 14.1; HRMS: $C_{13}H_{17}O_5N_2BrNaS$, Calcd: 416.9913 Found: 416.9909.

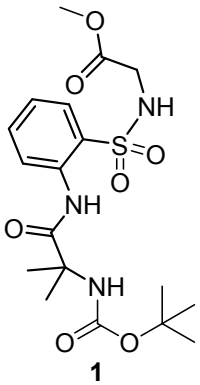
Methyl ((2-(2-azido-2-methylpropanamido)phenyl)sulfonyl)glycinate 1b:



1b

A solution of compound **1a** (0.36g, 0.9 mmol) and NaN_3 (0.18g, 2.9 mmol) in dry DMF was heated at 80 ^oC for 8h. Later, the reaction mixture was dissolved in ethyl acetate and washed with water and brine solutions sequentially to remove DMF. The organic layer was then dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to get the crude product which on purification by column chromatography (eluent: pet ether/ethyl acetate: 70:30, R*f*: 0.5) yielded **1b** (0.29 g, 89%); IR ($CHCl_3$) ν (cm^{-1}): 3330, 3020, 2119, 1749, 1697, 1584, 1523, 1439, 1344, 1217, 1127, 771, 668, 460; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.02 (s, 1H), 8.41-8.39 (d, *J* = 8 Hz, 1H), 7.94-7.92 (dd, *J* = 7.8 Hz, *J* = 1.5 Hz, 1H), 7.64-7.60 (t, *J* = 7 Hz, 1H), 7.30-7.25 (m, 1H), 5.5 (s, 1H), 3.8 (s, 2H), 3.63 (s, 3H), 1.68 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171, 168.7, 135.4, 134.3, 129.4, 127.1, 124.2, 123, 64.7, 52.7, 43.7, 24.3; HRMS: $C_{13}H_{17}O_5N_5NaS$, Calcd: 378.0843 Found: 378.0842.

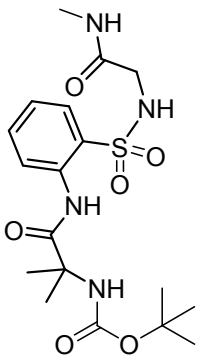
Methyl-((2-(2-((tert-butoxycarbonyl)amino)-2-methylpropanamido)phenyl)sulfonyl) glycinate 1:



1

Compound **1** was isolated as a white solid; mp: 110-113 ^oC; IR ($CHCl_3$) ν (cm^{-1}): 3356, 3020, 2400, 1698, 1583, 1514, 1439, 1336, 1218, 1128, 929, 771, 666, 476; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.64 (s, 1H), 8.04-8.02 (d, *J* = 7.9 Hz, 1H), 7.86-7.85 (dd, *J* = 7.9 Hz, *J* = 1.2 Hz, 1H), 7.58-7.55 (t, *J* = 7.9 Hz, 1H), 7.22-7.19 (t, *J* = 7.9 Hz, 1H), 7.22-7.19 (t, *J* = 7.9 Hz, 1H), 6.93 (bs, 1H), 4.97 (s, 1H), 3.71-3.7 (d, *J* = 6.1 Hz, 2H), 3.47 (s, 3H), 1.6 (s, 6H), 1.5 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 172.8, 168.4, 156.1, 135.3, 133.4, 128.9, 124.1, 81.6, 57.7, 52.3, 44.1, 28.5, 25.5; HRMS: $C_{18}H_{27}O_7N_3NaS$, Calcd: 452.1462 Found: 452.1458

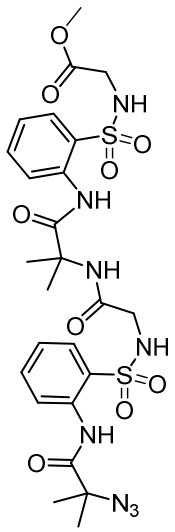
tert-butyl-(2-methyl-1-((2-(N-(2-(methylamino)-2-oxoethyl)sulfamoyl)phenyl)amino)-1-oxo propan-2-yl)carbamate 2:



2

Compound **2** was isolated quantitatively according to the general method mentioned earlier (eluent: pet ether/ethyl acetate: 30:70, R*f*: 0.4); mp: 143-146 ^{o}C; IR ($CHCl_3$) ν (cm^{-1}): 3683, 3620, 3439, 3376, 3217, 3020, 2400, 1682, 1582, 1503, 1337, 1217, 1159, 771, 669, 505; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.28 (s, 1H), 7.83-7.81 (dd, *J* = 9 Hz, 1H), 7.54-7.50 (t, *J* = 8.2 Hz, 1H), 7.23-7.19 (t, *J* = 8 Hz, 1H), 6.99-6.96 (t, *J* = 6.2 Hz, 1H), 6.37 (bs, 1H), 5.14 (bs, 1H), 3.47-3.45 (d, *J* = 6.5 Hz, 2H), 2.58-2.57 (d, *J* = 4.8 Hz, 3H), 1.53 (s, 6H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.2, 168.2, 156.2, 134.8, 133.8, 129.7, 129.2, 125.1, 81.5, 57.3, 45.5, 28.3, 25.4; HRMS: $C_{18}H_{28}O_6N_4NaS$, Calcd: 451.1622 Found: 451.1617.

Methyl-((2-(2-(2-((2-(2-azido-2-methylpropanamido)phenyl)sulfonamido)acetamido)-2-methylpropanamido)phenyl)sulfonyl)glycinate 6a:

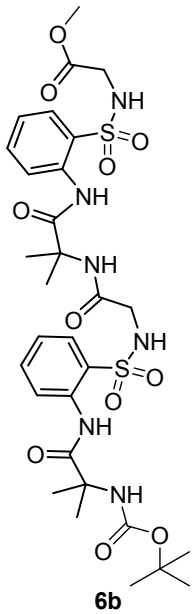


6a

The acid **1c** (0.07 g, 0.2 mmol) was coupled with the amine **1b** (0.07 g, 0.2 mmol) using HBTU (0.1 g, 0.2 mmol), Et_3N (0.05 mL, 0.3 mmol) and HOBt (0.006 g, 0.04 mmol) in dry CH_3CN at 0 °C, the reaction mixture was allowed to attain room temperature and stirred for 72h. Later, the solvent in the reaction mixture was stripped off under reduced pressure; the residue obtained was dissolved in ethyl acetate and washed sequentially with sat. $NaHCO_3$, brine and sat. $KHSO_4$ solutions. Then, the organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to get the crude product which on purification by column chromatography (eluent: pet ether/ethyl acetate: 20:80, R*f*: 0.4) yielded **6a** (0.06 g, 40%); mp: 101-103 ^{o}C ; IR ($CHCl_3$) ν (cm^{-1}): 3683, 3618, 3363, 3019, 2400, 2119, 1745, 1696, 1583, 1520, 1438, 1335, 1217, 1156, 928, 770, 668; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.99 (s, 1H), 9.30 (s, 1H), 8.37-8.35 (d, *J* = 8.2 Hz, 1H), 8-7.98 (d, *J* = 8.2 Hz, 1H), 7.88-7.86 (d, *J* = 7.7 Hz, 1H), 7.72-7.7 (d, *J* = 7.7 Hz, 1H), 7.57-7.53 (t, *J* = 7.5 Hz, 1H), 7.51-7.47 (t, *J* = 7.5 Hz, 1H), 7.22-7.19 (t, *J* = 7.7 Hz, 1H), 7.14-7.11 (t, *J* = 7.7 Hz, 3.72 (s, 2H), 3.59 (s, 2H), 3.42 (s, 3H), 1.57 (s, 6H), 1.5 (s, 6H); ^{13}C NMR

(100 MHz, $CDCl_3$) δ: 171.5, 171.3, 170.6, 168.4, 165.7, 135.5, 134.5, 133.7, 129.5, 128.8, 128.5, 127.1, 124.7, 124.6, 124.2, 123.2, 64.7, 60.3, 58.3, 52.4, 46.5, 44, 38.5, 25.1, 24.4; HRMS: $C_{25}H_{33}O_9N_8S$, Calcd: 653.1806 Found: 653.1804; $C_{25}H_{33}O_9N_8NaS$, Calcd: 675.1626 Found: 675.1613.

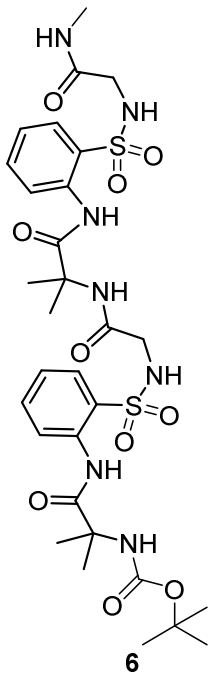
Methyl-((2-(2-(2-((2-(2-((tert-butoxycarbonyl)amino)-2-methylpropanamido)phenyl) sulfonamido)acetamido)-2-methylpropanamido)phenyl)sulfonyl)glycinate 6b:



6b

The Boc protected compound **6b** (0.15 g, 50%) was isolated as a white solid using the general method mentioned earlier; mp: 101-103 ^oC IR ($CHCl_3$) ν (cm^{-1}): 3364, 3019, 2400, 1695, 1583, 1522, 1438, 1335, 1217, 1045, 929, 771, 669, 479; ^1H NMR (500 MHz, $CDCl_3$) δ: 10.1 (s, 1H), 9.56 (s, 1H), 8.67-8.66 (d, *J* = 8.2 Hz, 1H), 8.09-8.07 (d, *J* = 7.9 Hz, 1H), 7.83-7.81 (dd, *J* = 7.9 Hz, *J* = 1.5 Hz, 1H), 7.58-7.54 (m, 2H), 7.22-7.19 (m, 2H), 7.13-7.1 (m, 1H), 7.02-6.99 (m, 1H), 3.72-3.71 (m, 2H), 3.47-3.46 (m, 2H), 3.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.7, 169.1, 168.6, 154.6, 150.5, 138, 135.2, 133.5, 129, 128.9, 124.6, 124.1, 86, 58.1, 52.2, 49.7, 44.1, 28.2, 27.6, 25.3, 25.1; HRMS: $C_{30}H_{43}O_{11}N_6S_2$, Calcd: 727.2426 Found: 727.2430.

tert-butyl-(2-methyl-1-((2-(N-(2-((2-methyl-1-((2-(N-(2-(methylamino)-2-xoethyl)sulfamoyl) phenyl)amino)-1-oxopropan-2-yl)amino)-2-oxoethyl)sulfamoyl)phenyl)amino)-1-oxopropan -2-yl)carbamate 4c:

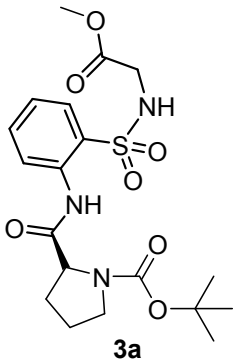


6

Compound **6** was isolated as a white solid using the general method mentioned earlier (eluent: pet ether/ethyl acetate: 30:70, R*f*: 0.4) quantitatively; mp: 168-171 ^oC; IR ($CHCl_3$) ν (cm^{-1}): 3685, 3624, 3373, 3019, 2400, 1668, 1582, 1519, 1424, 1336, 1218, 1045, 929, 771, 668, 626; ^1H NMR (500 MHz, $CDCl_3$) δ: 9.39 (s, 1H), 9.17 (s, 1H), 7.93-7.91 (d, *J* = 7.9 Hz, 2H), 7.86-7.84 (dd, *J* = 7.9 Hz, J = 1.2 Hz, 1H), 7.66-7.62 (t, *J* = 8.5 Hz, 1H), 7.6-7.56 (t, *J* =8.2 Hz, 1H), 7.34-7.31(t, *J* = 7.3 Hz, 1H), 7.25-7.24 (d, *J* = 7 Hz, 2H), 7.07 (bs, 1H), 6.87-6.84 (t, *J* = 6.4 Hz, 1H), 6.48 (bs, 1H), 5.08 (bs, 1H), 3.64-3.63 (d, *J* = 6.1 Hz, 2H), 3.46-3.45 (d, *J* = 6.7 Hz, 2H),

2.68-2.67 (d, *J* = 4.8 Hz, 3H), 1.61 (s, 6H), 1.54 (s, 6H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.1, 172, 170.8, 168.2, 156.4, 134.6, 134.2, 133.9, 129.8, 129.6, 129, 125.8, 124.9, 81.8, 57.9, 57.6, 46.1, 45.4, 28.5, 26.1, 25.5, 25; HRMS: $C_{30}H_{44}O_{10}N_7S_2$, Calcd: 726.2586 Found: 727.2590. $C_{30}H_{44}O_{10}N_7S_2$, Calcd: 748.2405 Found: 748.2397.

tert-butyl-2-((2-(N-(2-methoxy-2-oxoethyl)sulfamoyl)phenyl)carbamoyl)pyrrolidine-1-carboxylate 3a:

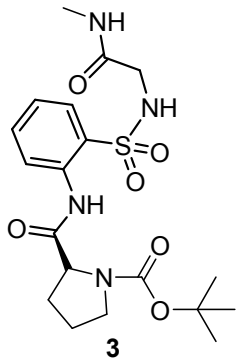


3a

To a two necked round-bottom flask containing Boc-Pro-OH (0.21 g, 0.98 mmol) in THF, dry Et_3N (0.12 mL, 1.22 mmol) and ethyl chloroformate (0.09 mL, 0.98 mmol) were added drop wise at 0 °C followed by the addition of amine **11** (0.2 g, 0.81 mmol). The reaction mixture was stirred at 0 °C for 1 h and then refluxed for 48 h. Later, the reaction mixture was cooled to room temperature and filtered. The solvent was evaporated to get the crude product, which was taken into DCM (30 mL) and washed with sat. $NaHCO_3$, brine and sat. $KHSO_4$ solutions. The organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to get the crude product which was further purified by column chromatography (eluent: pet ether/ethyl acetate: 30:70, R*f*: 0.5) to furnish **3a** (0.21 g, 60%) as a sticky substance; $[\alpha]^{26}_D$: -110° (*c* 1, $CHCl_3$); IR ($CHCl_3$) ν (cm^{-1}) 3684, 3621, 3344, 3213, 3020, 1742, 1673, 1583, 1519, 1476, 1440, 1392, 1295, 1217, 1157, 1130, 1044, 928, 770, 668, 491; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.47 (s, 1H), 8.11-8.09 (d, *J* = 7.6 Hz, 1H), 7.84-7.82 (dd, *J* = 7.9 Hz, 1.5 Hz, 1H), 7.55-7.52 (t, *J* = 7Hz, 1H), 7.21-7.17 (t, *J* = 7.2 Hz, 1H), 7.08 (bs, 1H), 4.36-4.34 (dd, *J* = 8.5 Hz, 3Hz, 1H), 3.76-3.71 (dd, *J* = 17.7 Hz, 5.8 Hz, 1H), 3.66-3.61 (dd, *J* = 6.4 Hz, 18 Hz, 1H), 3.55-3.51 (m, 1H), 3.42 (s, 3H), 2.3 (bs, 1H), 2.25-2.19 (m, 1H), 1.96-1.91 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.9, 168.4, 156.6, 134.8, 133.4, 129.0, 128.9, 124.4, 124.1, 81.8, 62.0, 52.2, 47.5, 43.8, 30.3, 28.4, 28.2, 24.3; HRMS: $C_{19}H_{28}O_7N_3S$, Calcd: 442.1642 Found: 442.1644; $C_{19}H_{27}O_7N_3SNa$, Calcd: 464.1462 Found: 464.1465.

tert-butyl-2-((2-(N-(2-(methylamino)-2-oxoethyl)sulfamoyl)phenyl) carbamoyl)pyrrolidine-1-carboxylate 3:

Compound **3** was isolated as a white solid using the general method mentioned earlier (eluent: pet. ether/ethyl acetate: 40:60, R*f*: 0.4) in 95% yield; mp: 130-132 °C; $[\alpha]^{26}_D$: -42° (*c* 1, $CHCl_3$); IR ($CHCl_3$) ν (cm^{-1}): 3683, 3618, 3438, 3356, 3192, 3018, 2888, 2400, 1670, 1583, 1523, 1475,

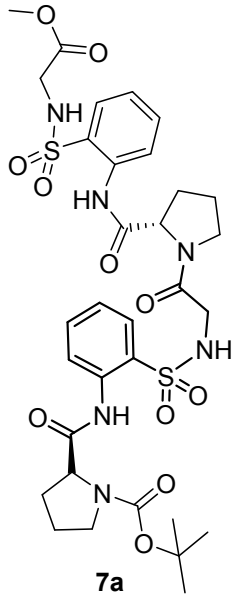


3

1420, 1394, 1336, 1218, 1158, 927, 847, 771, 590; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.26 (s, 1H), 8.03-7.99 (d, *J* = 8.1 Hz, 1H), 7.92-7.87 (dd, *J* = 7.9 Hz, 1.5 Hz, 1H), 7.64-7.56 (m, 1H), 7.33-7.24 (m, 2H), 7.2-7.14 (m, 1H), 6.52-6.49 (m, 1H), 4.3-4.24 (m, 1H), 3.63-3.42 (m, 4H), 2.67-2.64 (d, *J* = 4.8 Hz, 3H), 2.33-2.23 (m, 2H), 2.14-1.89 (m, 2H), 1.47 (s, 9H), ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.3, 168.1, 156.1, 134.2, 133.8, 129.3, 125.3, 125.0, 81.4, 61.9, 47.5, 45.4, 30.4, 28.4, 25.9, 24.5; HRMS: $C_{19}H_{29}O_6N_4S$, Calcd: 441.1802 Found: 441.1794; $C_{19}H_{28}O_6N_4SNa$, Calcd: 463.1622 Found: 463.1613.

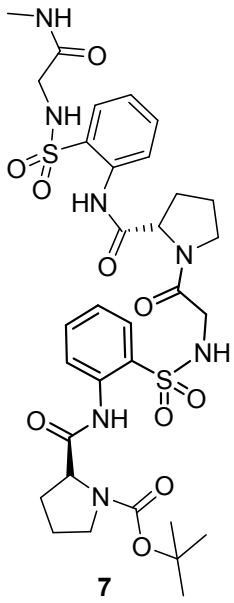
tert-butyl-2-((2-(N-(2-(2-((2-(N-(2-methoxy-2-oxoethyl)sulfamoyl)phenyl)-carbamoyl) pyrrolidin-1-yl)-2-oxoethyl)sulfamoyl)phenyl)carbamoyl) pyrrolidine-1-carboxylate 7a:

The acid **3c** (0.09 g, 0.22 mmol) was coupled with the amine **3b** (0.07 g, 0.22 mmol) in the presence of EDC. HCl (0.05 g, 0.27 mmol), Et_3N (0.09 mL, 0.68 mmol) and HOBt (0.006 g, 0.04 mmol) using dry DCM as solvent at 0 °C. The reaction mixture was allowed to attain room temperature and stirred for 12 h. Later, the reaction mixture was washed with sat. $NaHCO_3$, water, sat $KHSO_4$ and brine solutions. The organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to get the crude product which on purification by column chromatography (eluent: pet ether/ethyl acetate: 40:60, R*f*: 0.4) yielded **16a** (0.08 g, 50%) as a white solid; mp: 150-153 °C; $[\alpha]^{26}_{D}$: -90° (*c* 1, $CHCl_3$); IR ($CHCl_3$) ν (cm^{-1}): 3344, 3017, 1690, 1584, 1525, 1438, 1387, 1332, 1218, 1156, 1126, 847, 770, 480. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.75 (s, 1H), 9.36 (s, 1H), 8.27 (d, *J* = 7.7 Hz, 1H), 8.16-8.14 (d, *J* = 8 Hz, 1H), 7.91-7.89 (d, *J* = 7.5 Hz, 1H), 7.82-7.8 (d, *J* = 7.7 Hz, iH), 7.59-7.5 (m, 2H), 7.24-7.16 (m, 2H), 7.01 (bs, 1H), 6.75 (bs, 1H), 4.44-4.4 (m, 2H), 4.15-4.09 (q, ethyl acetate), 3.93-3.82 (m, 1H), 3.77-3.75 (m, 2H), 3.67-3.53 (m, 2H), 3.46 (s, 2H), 3.39-3.36 (m, 1H), 2.3-1.92 (m, 8H), 1.53 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.3, 169.1, 168.5, 156.5, 135.6, 134.8, 133.8, 133.5, 129.1, 129, 128.6, 124.1, 123.7, 81.4, 62.1, 61.9, 60.3, 52.3, 47.6, 46.5, 44.5, 44, 30.4, 28.7, 28.5, 24.8, 24.3; HRMS: $C_{32}H_{43}O_{11}N_6S_2$, Calcd: 751.2426 Found: 751.2418; $C_{32}H_{42}O_{11}N_6S_2Na$, Calcd: 773.2245 Found: 773.2234.



7a

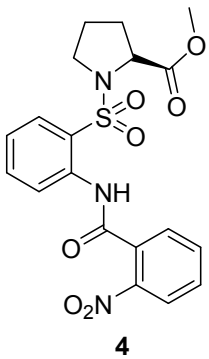
tert-butyl-2-((2-(N-(2-(2-((2-(N-(2-(methylamino)-2-oxoethyl)sulfamoyl)phenyl) carbamoyl)pyrrolidin-1-yl)-2-oxoethyl)sulfamoyl)phenyl)carbamoyl)pyrrolidine-1-carboxylate 7:



7

The compound **7** was isolated as a white solid following the general method mentioned earlier in 90% yield; mp: 160-162 °C; $[\alpha]^{26}_{D}$: -92.3° (*c* 0.26, $CHCl_3$); IR ($CHCl_3$) ν (cm^{-1}): 3684, 3618, 3019, 2400, 1666, 1584, 1523, 1475, 1423, 1334, 1215, 1045, 928, 770, 669, 490; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.45 (s, 1H), 9.41 (s, 1H), 8.22-8.2 (d, *J* = 8.2 Hz, 1H), 8.11-8.09 (d, *J* = 7.9 Hz, 1H), 7.94-7.92 (d, *J* = 7.3 Hz, 1H), 7.88-7.86 (d, *J* = 7.3 Hz, 1H), 7.62-7.59 (t, *J* = 7.6 Hz, 1H), 7.58-7.55 (t, *J* = 8.2 Hz, 1H), 7.25-7.21 (m, 2H), 7.01 (bs, 2H), 6.73 (bs, 1H), 4.33-4.32 (dd, *J* = 8.9 Hz, 2.7 Hz, 1H), 4.28-4.27 (d, *J* = 5.2 Hz, 1H), 3.92-3.88 (dd, *J* = 16.9 Hz, 3.2 Hz, 1H), 3.73-3.69 (m, 1H), 3.56-3.42 (m, 5H), 3.31-3.28 (m, 1H), 2.69-2.68 (d, *J* = 4.9 Hz, 3H), 2.3-2.29 (m, 1H), 2.25-2.22 (m, 2H), 2.1-1.93 (m, 5H), 1.53 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.2, 169.3, 168.5, 168.3, 157.1, 135.1, 134.6, 134.2, 130.0, 129.1, 128.7, 126.6, 124.9, 124.4, 124.2, 123.4, 82.1, 62.1, 47.7, 46.6, 45.3, 44.3, 30.5, 29.1, 28.6, 26.6, 24.7, 24.3; HRMS: $C_{32}H_{44}O_{10}N_7S_2$, Calcd: 750.2586 Found: 751.2578; $C_{32}H_{43}O_{10}N_7S_2Na$, Calcd: 772.2405 Found: 772.2386.

Methyl ((2-(2-nitrobenzamido)phenyl)sulfonyl)prolinate 4:

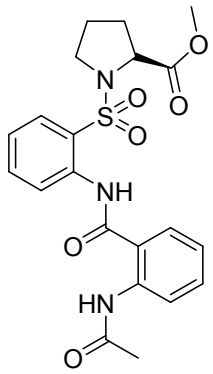


4

To a solution of amine **13** (0.2 g, 0.7 mmol) in DCM (10 mL), pyridine (0.08 mL, 1.05 mmol) was added followed by the addition of 2-nitro benzoyl chloride (0.19 g, 1.05 mmol) drop wise at 0 °C. The reaction mixture was allowed to attain room temperature and stirred for 5 h. Later, the reaction mixture was diluted with DCM and washed with CuSO4 solution, water, sat. $NaHCO_3$ solutions. The organic layer was dried over Na_2SO_4 and evaporated under reduced pressure. The residue obtained was purified by column chromatography (eluent: pet ether/ethyl acetate: 60:40, R*f*: 0.5) yielding **4** (0.277 g, 90%); mp: 143-146 °C; $[\alpha]^{26}_{D}$: -164° (*c* 1, $CHCl_3$); IR ($CHCl_3$) ν (cm^{-1}): 3323, 3022, 2400, 1743, 1690, 1586, 1531, 1437, 1348, 1218, 1157, 1077, 1020, 857, 771, 499; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 10.08 (s, 1H), 8.69-8.65 (d, *J* = 8.2 Hz, 1H), 8.16-8.12

(d, *J* = 7.3 Hz, 1H), 7.99-7.94 (dd, *J* = 7.9 Hz, 1.5 Hz, 1H), 7.78-7.59 (m, 4H), 7.34-7.26 (m, 1H), 4.45-4.38 (dd, *J* = 8.8 Hz, 4.2 Hz, 1H), 3.44 (s, 3H), 3.33-3.21 (m, 2H), 2.29-2.14 (m, 1H), 2.06-1.83 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 172.4, 164.8, 146.5, 136.3, 134.7, 133.8, 132.9, 130.5, 130, 128.6, 125.7, 124.4, 124.3, 123.4, 59.2, 52.4, 48.7, 30.8, 24.7; HRMS: $C_{19}H_{20}O_7N_3S$, Calcd: 434.1016 Found: 434.1016.

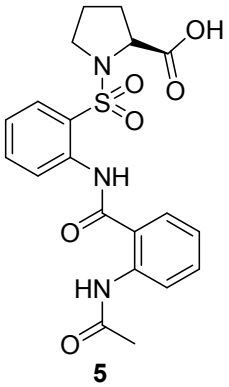
Methyl ((2-(2-acetamidobenzamido)phenyl)sulfonyl)prolinate 4a:



4a

Compound **4a** was obtained as white solid using the general method mentioned earlier. mp: 113-115 °C; $[\alpha]^{26}_D$: -62° (*c* 1, $CHCl_3$); IR ($CHCl_3$) ν (cm^{-1}): 3785, 3682, 3620, 3343, 3018, 2400, 1748, 1686, 1663, 1583, 1522, 1429, 1336, 1294, 1218, 1045, 928, 668; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 11.13 (s, 1H), 8.69-8.67 (d, *J* = 8.2 Hz, 1H), 8.57-8.55 (dd, *J* = 8.5 Hz, 1 Hz, 1H), 7.95-7.94 (dd, *J* = 8.2 Hz, 1.5 Hz, 1H), 7.79-7.78 (dd, *J* = 7.9 Hz, 1.2 Hz, 1H), 7.68-7.64 (t, *J* = 8.6 Hz, 1H), 7.56-7.52 (t, *J* = 8.5 Hz, 1H), 7.31-7.28 (t, *J* = 8.2 Hz, 1H), 7.19-7.15 (t, *J* = 8.2 Hz, 1H), 4.54-4.32 (dd, *J* = 8.5 Hz, 3.3 Hz, 1H), 3.46 (s, 3H), 3.44-3.35 (m, 2H), 2.23 (s, 3H), 2.18-2.08 (m, 1H), 2.04-1.92 (m, 2H), 1.91-1.82 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.8, 168.9, 167.4, 140.5, 136.2, 134.3, 133.4, 129.8, 126.9, 124.3, 123, 121.5, 119.5, 59.9, 52.3, 48.5, 30.9, 25.3, 24.5; HRMS: $C_{21}H_{24}O_6N_3S$, Calcd: 446.138 Found: 446.138; $C_{24}H_{22}O_6N_4BrS$, Calcd: 468.12 Found: 468.1199.

((2-(2-acetamidobenzamido)phenyl)sulfonyl)proline 5:



5

Compound **5** was obtained as a brown solid using the general method mentioned earlier. mp: 169-172 °C; $[\alpha]^{26}_D$: -92° (*c* 1, $CHCl_3$); IR ($CHCl_3$) ν (cm^{-1}): 3684, 3619, 3353, 3020, 2400, 1734, 1664, 1583, 1523, 1471, 1430, 1331, 1296, 1217, 1045, 928, 770, 667, 626, 607; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.42 (s, 1H), 10.25 (s, 1H), 8.48-8.46 (d, *J* = 8 Hz, 1H), 8.19-8.17 (dd, *J* = 8 Hz, 1H), 7.96-7.94 (d, *J* = 9 Hz, 1H), 7.74-7.72 (d, *J* = 7.7 Hz, 1H), 7.68-7.64 (t, *J* = 7.5 Hz, 1H), 7.55-7.51 (t, *J* = 7.5 Hz, 1H), 7.3-7.23 (m, 4H), 4.47-4.44 (dd, *J* = 3 Hz, J = 8.7 Hz, 1H), 3.46-3.36 (m, 2H), 3.3-3.25 (m, 1H), 2.21 (s, 3H), 2.17-2.04 (m, 2H), 1.94-1.88 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.8, 171.3, 167, 138.1, 136, 134.2, 132.6, 129.8, 127.1, 126.7, 124.6, 124.2, 124, 123, 60, 47.9, 30.9, 24.9, 24.6; HRMS: $C_{20}H_{22}O_6N_3S$, Calcd: 432.1224 Found: 432.1224.

Crystal data: Data for the compounds **1**, **2**, **3**, **4** and **5** were collected on SMART APEX-II CCD using Mo-Kα radiation (λ = 0.7107 Å) to a maximum θ range of 25.00°. Crystal to detector distance 5.00 cm, 512 x 512 pixels / frame, Oscillation / frame -0.5º, maximum detector swing angle = –30.0º, beam center = (260.2, 252.5), in plane spot width = 1.24, SAINT integration with different exposure time per frame and SADABS correction applied. All the structures were solved by direct methods using SHELXTL. All the data were corrected for Lorentzian, polarisation and absorption effects. SHELX-97 (ShelxTL) was used for structure solution and full matrix least squares refinement on F^2. Hydrogen atoms were included in the refinement as per the riding model. The refinements were carried out using SHELXL-97.

Crystal data for 1:

Single crystals of **1** were grown by slow evaporation of its solution in ethyl acetate and DCM. Colorless cube like crystal of approximate size 0.31 x 0.12 x 0.07 mm^3, was used for data collection. Multi-run data acquisition. Total scans = 4, total frames = 1271, Oscillation / frame -0.3º, exposure / frame = 15.0 sec / frame, θ range = 2.23 to 25.00°, completeness to θ of 25.00 º is 99.9 %. $C_{18}H_{27}N_3O_7S$, *MW* = 429.49, Crystals belong to Triclinic, space group P-1, *a* = 10.0269(3), *b* = 11.0127(3), *c* = 19.1212(5) Å, V = 2072.5(1) $Å^3$, *Z* = 4, D_c = 1.376 g/cc, (Mo–K_α) = 0.201 mm^{-1}, 30705 reflections measured, 7277 unique [I>2σ(I)], R1 = 0.036, wR2 = 0.0829, Largest diff. peak and hole 0.576 and -0.519 e.$Å^{-3}$. Two molecules with different conformations were present in the unit cell of **1**. One of the molecules showed intra-residual C6 H-bonding while the other molecule revealed inter-residual C11 H-bonding. The two molecules are shown in Fig. 1.

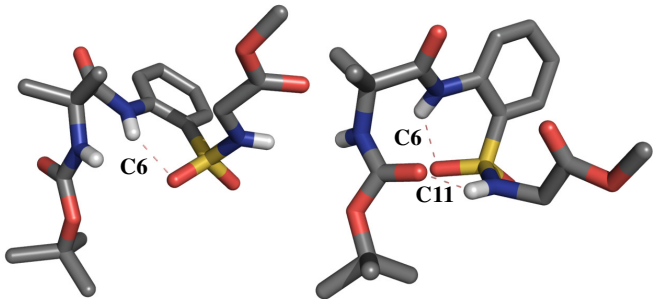


Fig. 1: Crystal structures of peptide **1** with only C6 H-bonding (left) and with C6 and C11 H-bonding (right) present in the unit cell of **1**.

Crystal data for 2:

Single crystals of **2** were grown by slow evaporation of the solution in ethyl acetate. Colorless needle like crystal of approximate size 0.42 x 0.25 x 0.12 mm^3, was used for data collection. Multi-run data acquisition. Total scans = 4, total frames = 1271, Oscillation / frame -0.3º, exposure / frame = 15.0 sec / frame, θ range = 2.23 to 25.00°, completeness to θ of 25.00 º is 100%. $C_{18}H_{28}N_4O_6S$, *MW* = 428.5, Crystals belong to Monoclinic, space group P21/c, *a* = 15.5747(6), *b* = 9.4947(3), *c* = 15.4473(6) Å, V = 2141.33(14) $Å^3$, *Z* = 4, D_c = 1.329 g/cc, (Mo–K_α) = 0.192 mm^{-1}, 16008 reflections measured, 3775 unique [I>2σ(I)], R1 = 0.0532, wR2 = 0.1145, Largest diff. peak and hole 0.286 and -0.347 e.$Å^{-3}$.

Crystal data for 3:

Single crystals of **3** were grown by slow evaporation of its solution in DCM and pet. ether. Colorless needle like crystal of approximate size 0.32 x 0.09 x 0.07 mm^3, was used for data collection. Multi-run data acquisition. Total scans = 4, total frames = 1559, exposure / frame = 10.0 sec / frame, θ range = 2.53 to 25.00°, completeness to θ of 25.00 º is 99.9 %. $C_{19}H_{28}N_4O_6S$, *MW* = 440.51, crystals belong to orthorhombic, space group $P2_12_12_1$, *a* = 9.2146(8) Å, *b* = 14.611(1) Å, *c* = 16.096(1) Å, V = 2166.9(3) $Å^3$, *Z* = 4, D_c = 1.35 g/cc, (Mo–K_α) = 0.192 mm^{-1}, 9609 reflections measured, 3803 unique, [I>2σ(I)] R1 = 0.0376, wR2 = 0.0809, largest diff. peak and hole 0.389 and -0.425 e.$Å^{-3}$.

Crystal data for 4:

Single crystals of **4** were grown by slow evaporation of the solution in chloroform. Colorless plate like crystal of approximate size 0.42 x 0.31 x 0.08 mm^3, was used for data collection. Multi-run data acquisition. Total scans = 4, total frames = 1559, exposure / frame = 10.0 sec / frame, θ range = 1.90 to 25.00°, completeness to θ of 25.00 º is 99.9 %. $C_{19}H_{19}N_3O_7S$, *MW* = 433.43, crystals belong to monoclinic, space group $P2_1$, *a* = 7.5913(1) Å, *b* = 12.3192 (2) Å, *c* = 11.3409 (2) Å, V = 1004.34(3) $Å^3$, *Z* = 4, D_c = 1.433 g/cc, (Mo–K_α) = 0.209 mm^{-1}, 14526 reflections measured, 3527 unique, [I>2σ(I)] R1 = 0.0344, wR2 = 0.0857, largest diff. peak and hole 0.137 and -0.189 e.$Å^{-3}$.

Crystal data for 5:

Single crystals of **5** were grown by slow evaporation of the solution in acetone. Colorless needle like crystal of approximate size 0.43 x 0.19 x 0.1 mm^3, was used for data collection. Multi-run

data acquisition. Total scans = 4, total frames = 1559, exposure / frame = 10.0 sec / frame, θ range = 2.20 to 25.00°, completeness to θ of 25.00 ° is 99.9 %. $C_{20}H_{21}N_3O_6S$, *MW* = 431.46, crystals belong to monoclinic, space group $P2_1$, *a* = 10.3772(5) Å, *b* = 10.9443(5) Å, *c* = 17.4395(7) Å, V = 1979.93(15) $Å^3$, *Z* = 4, D_c = 1.447 g/cc, (Mo–K_α) = 0.208 mm^{-1}, 14978 reflections measured, 6559 unique, [I>2σ(I)] R1 = 0.0388, wR2 = 0.1001, largest diff. peak and hole 0.244 and -0.274 e.$Å^{-3}$. It was observed that in the crystal lattice of **5**, there existed two molecules with slightly different conformation at C-terminus. The overlaid structure of **5** is shown in Fig. 2.

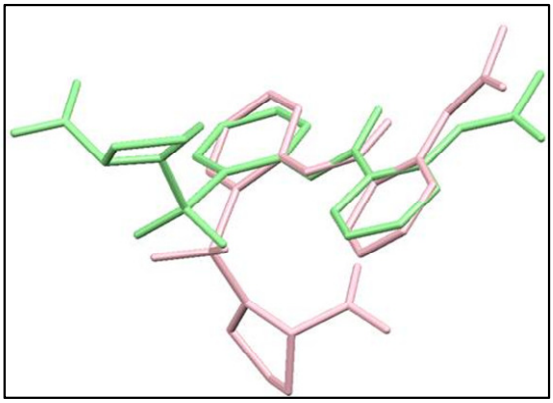
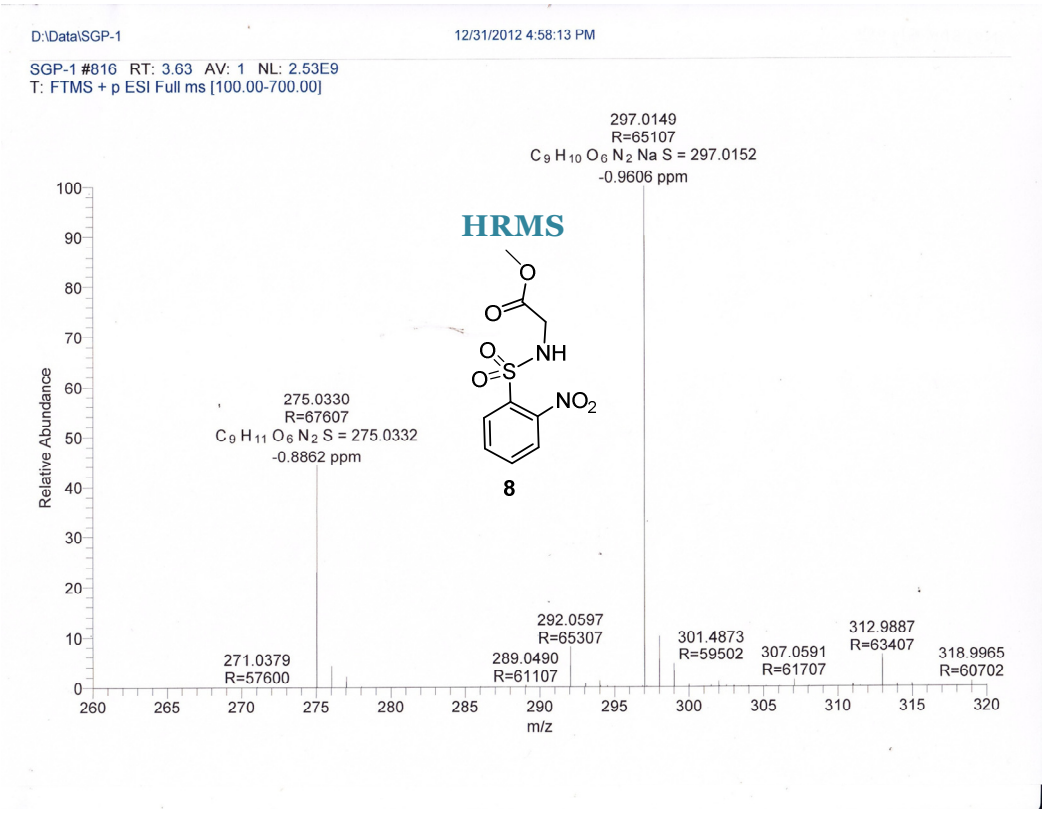


Fig. 2: Overlaid structure of the two conformers present in crystal lattice of **5**.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HRMS
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8
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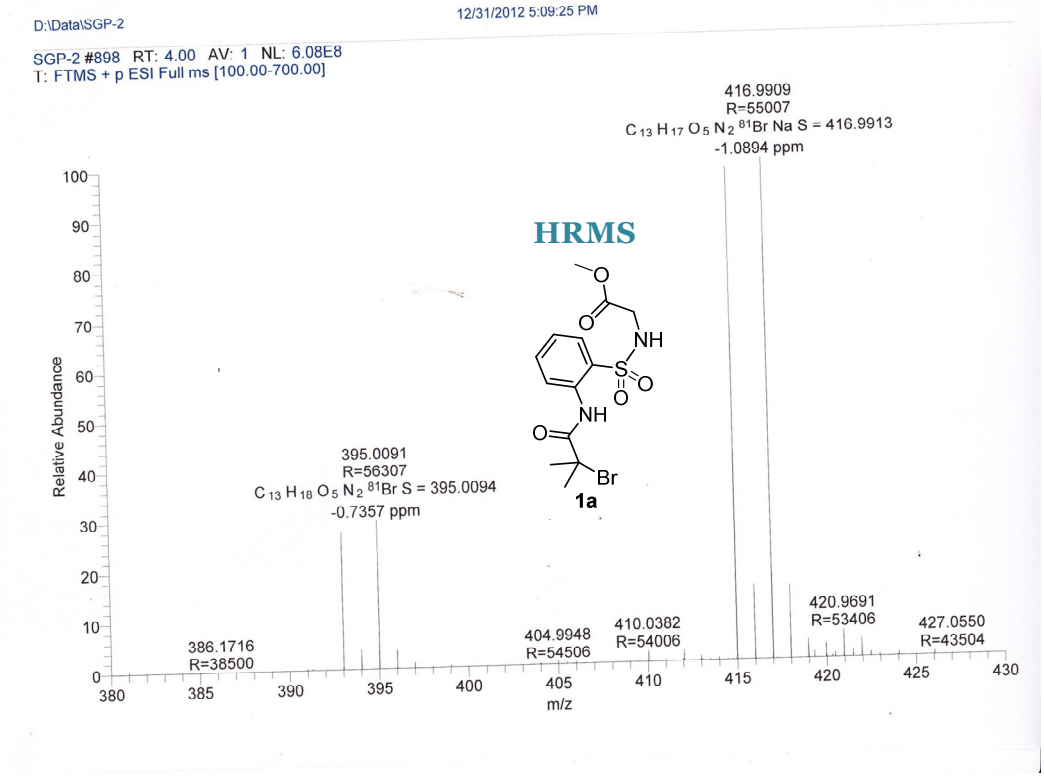
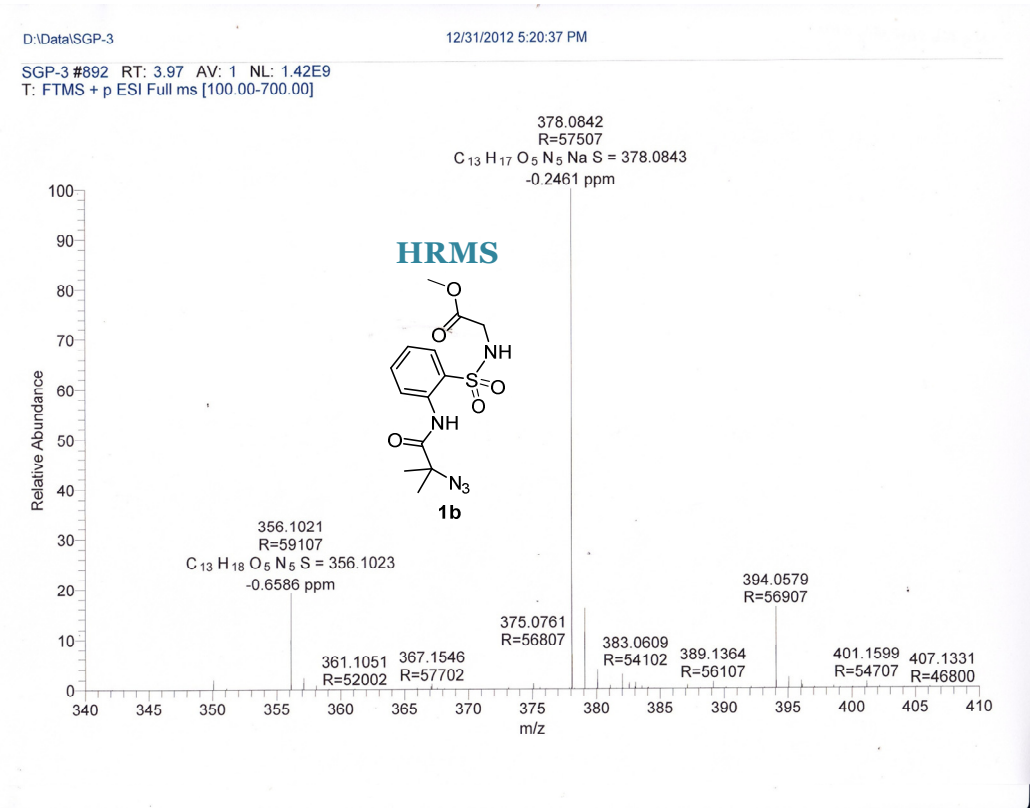
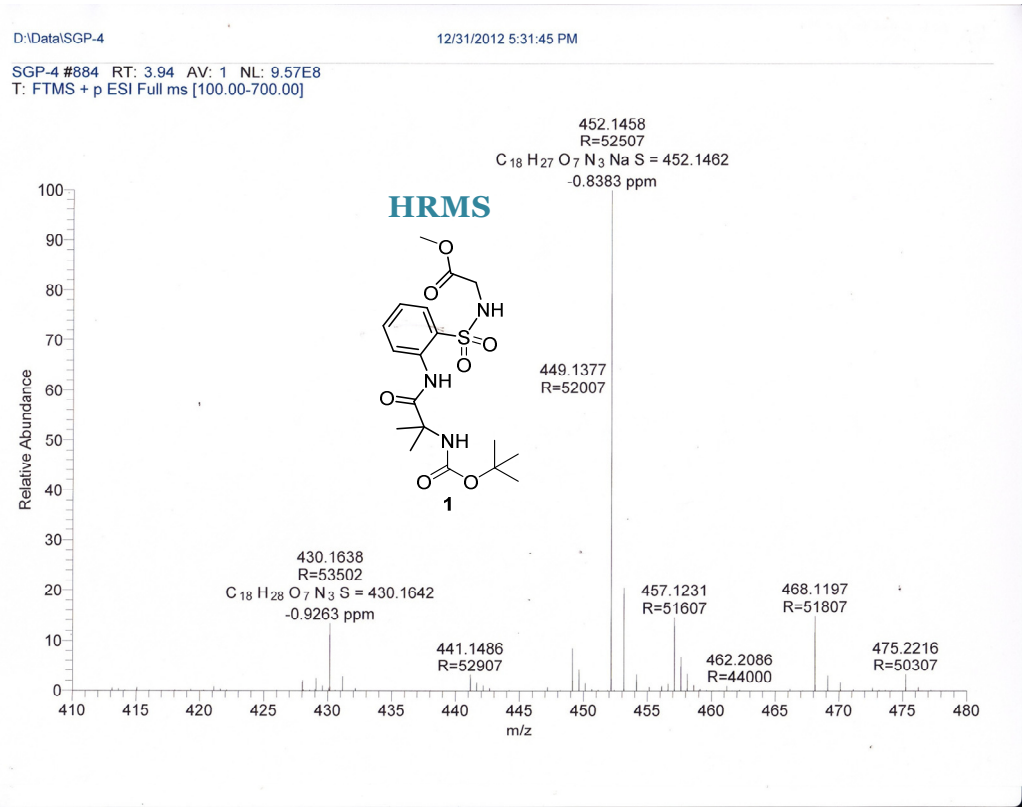
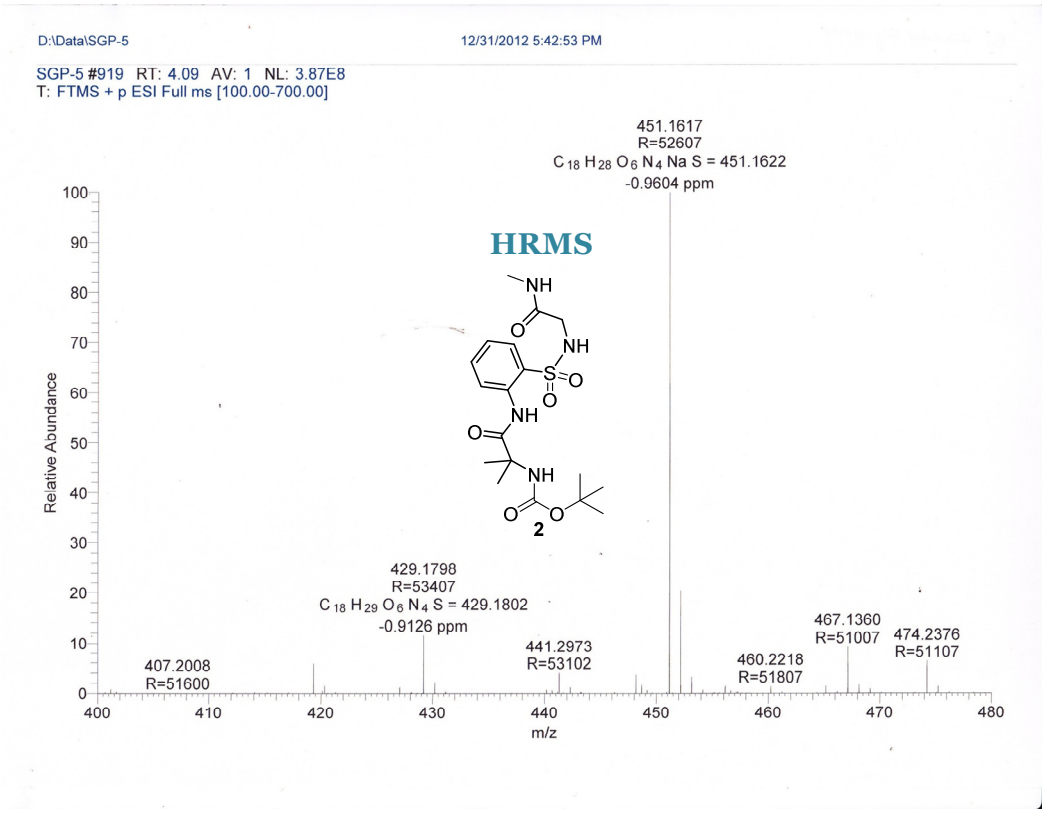
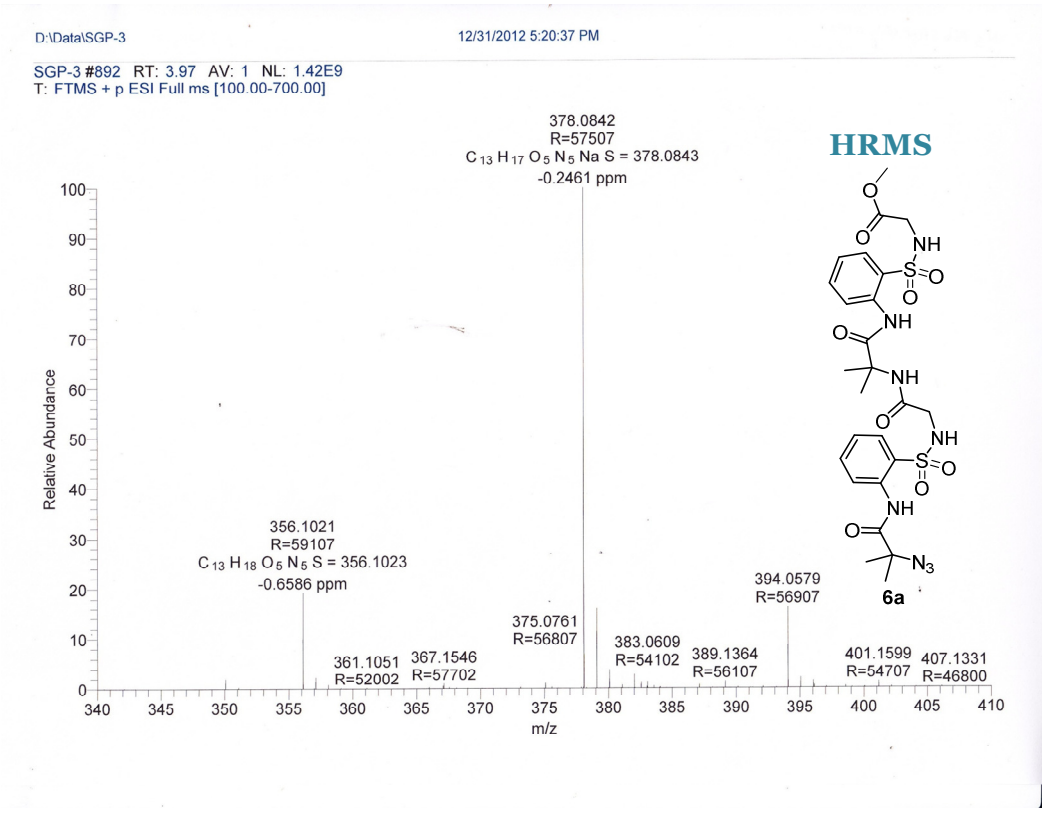
318.9965
R=60702
Relative Abundance
m/z

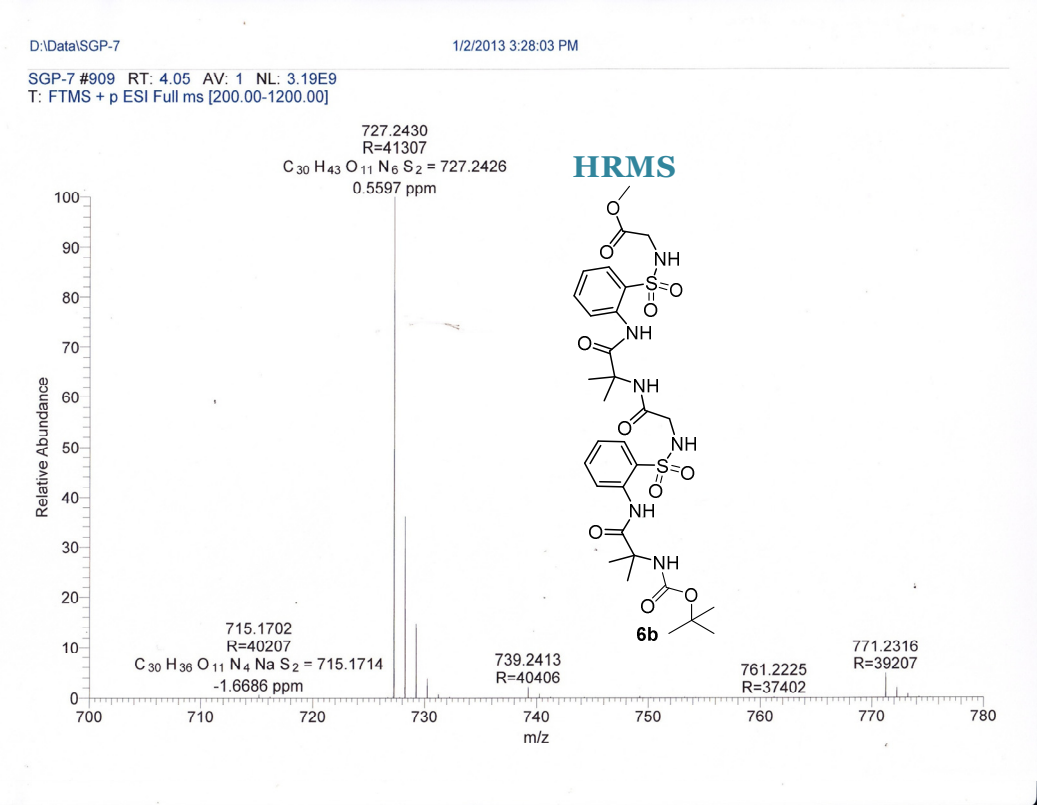

D:\Data\SGP-2
12/31/2012 5:09:25 PM
SGP-2 #898 RT: 4.00 AV: 1 NL: 6.08E8
T: FTMS + p ESI Full ms [100.00-700.00]
416.9909
R=55007
C13 H17 O5 N2 81Br Na S = 416.9913
-1.0894 ppm
HRMS
395.0091
R=56307
C13 H18 O5 N2 81Br S = 395.0094
-0.7357 ppm
1a
386.1716
R=38500
404.9948
R=54506
410.0382
R=54006
420.9691
R=53406
427.0550
R=43504
Relative Abundance
m/z

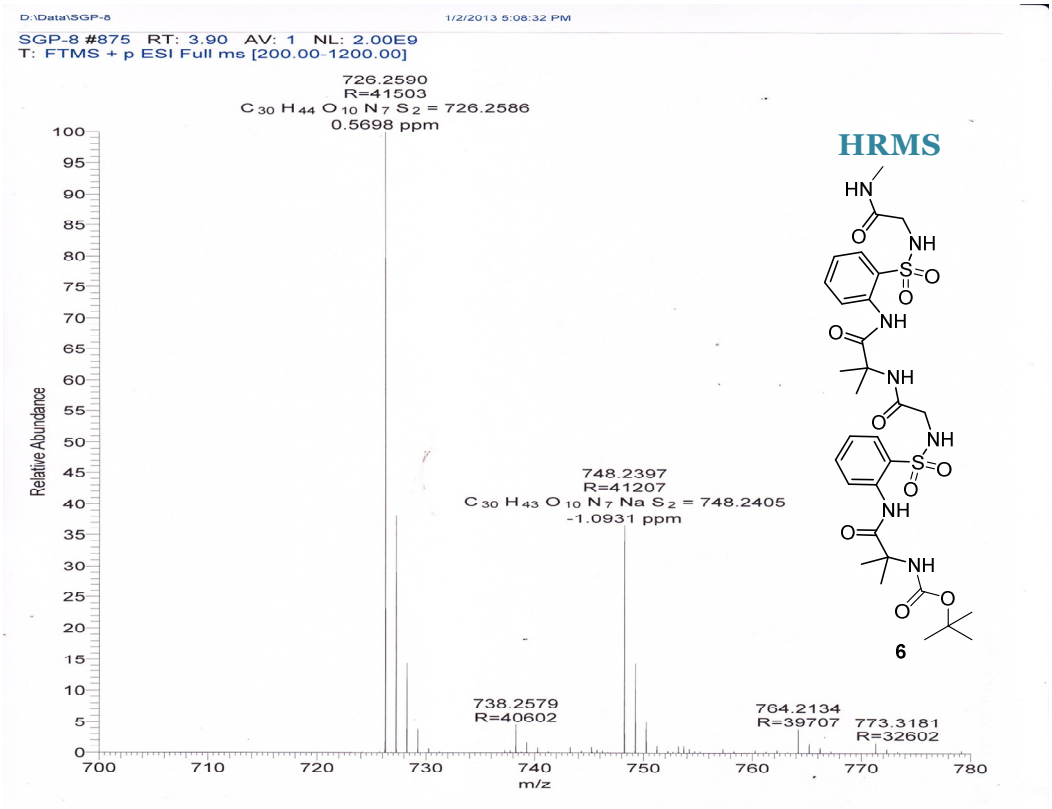

D:\Data\SGP-3
12/31/2012 5:20:37 PM
SGP-3 #892 RT: 3.97 AV: 1 NL: 1.42E9
T: FTMS + p ESI Full ms [100.00-700.00]
378.0842
R=57507
C13 H17 O5 N5 Na S = 378.0843
-0.2461 ppm
HRMS
1b
356.1021
R=59107
C13 H18 O5 N6 S = 356.1023
-0.6586 ppm
361.1051
R=52002
367.1546
R=57702
375.0761
R=56807
383.0609
R=54102
389.1364
R=56107
394.0579
R=56907
401.1599
R=54707
407.1331
R=46800
Relative Abundance
m/z

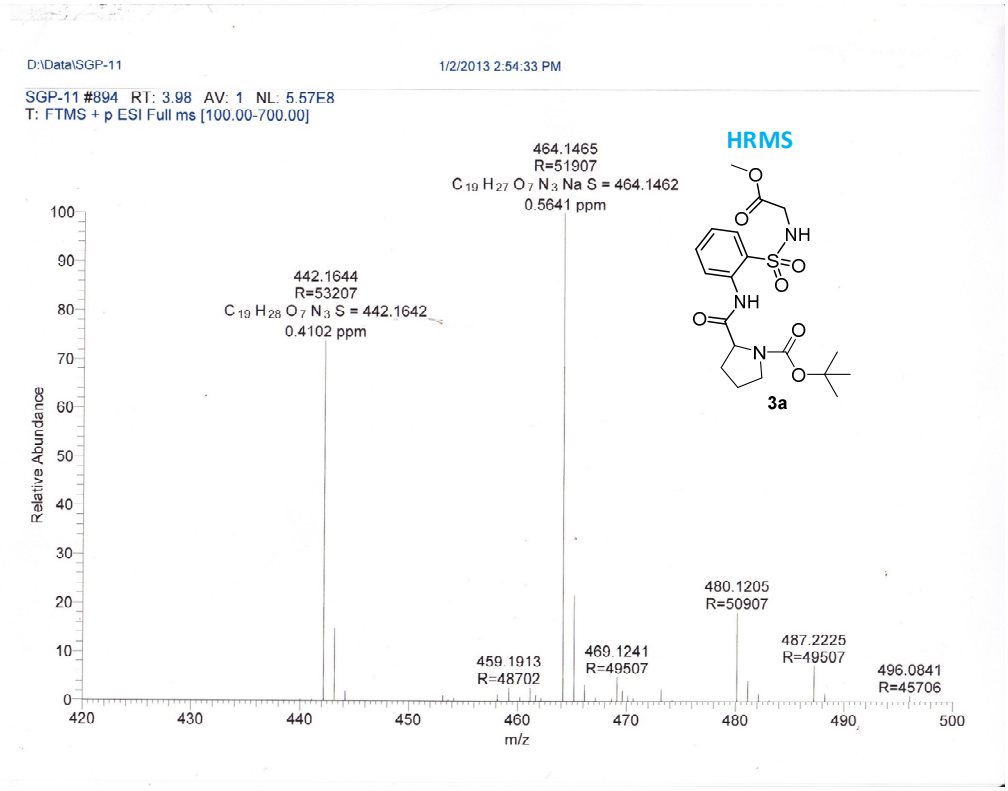

D:\Data\SGP-4
12/31/2012 5:31:45 PM
SGP-4 #884 RT: 3.94 AV: 1 NL: 9.57E8
T: FTMS + p ESI Full ms [100.00-700.00]
452.1458
R=52507
C18 H27 O7 N3 Na S = 452.1462
-0.8383 ppm
HRMS
1
449.1377
R=52007
430.1638
R=53502
C18 H28 O7 N3 S = 430.1642
-0.9263 ppm
441.1486
R=52907
457.1231
R=51607
462.2086
R=44000
468.1197
R=51807
475.2216
R=50307
Relative Abundance
m/z

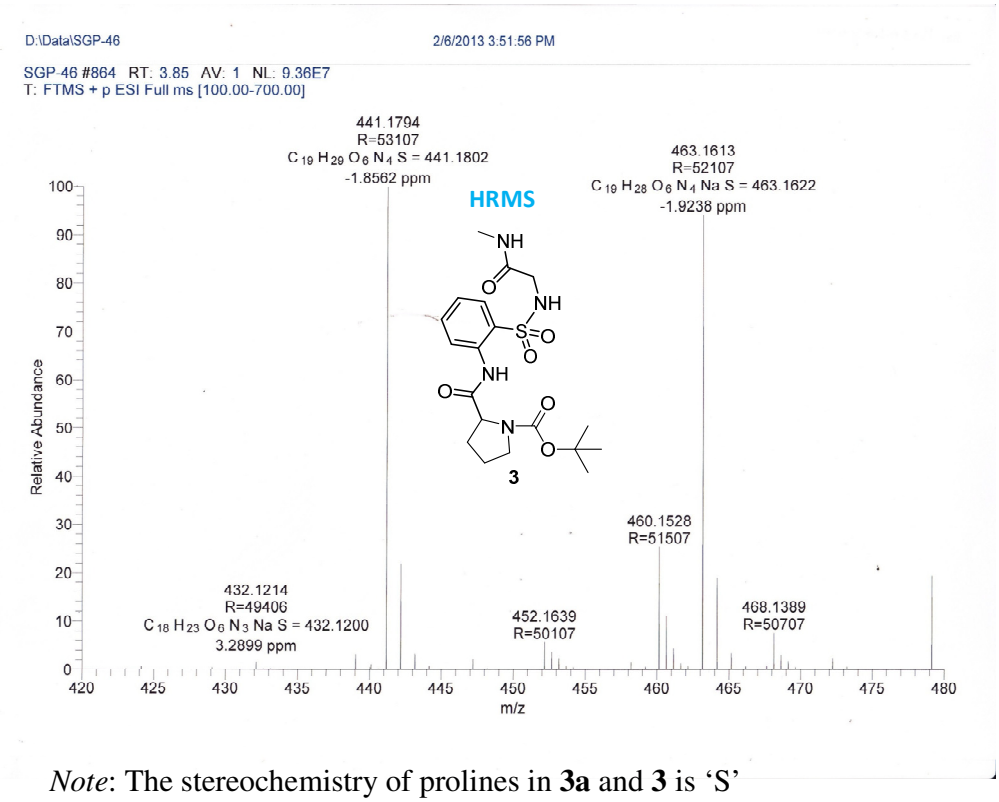

D:\Data\SGP-5
12/31/2012 5:42:53 PM
SGP-5 #919 RT: 4.09 AV: 1 NL: 3.87E8
T: FTMS + p ESI Full ms [100.00-700.00]
451.1617
R=52607
C 18 H 28 O 6 N 4 Na S = 451.1622
-0.9604 ppm
HRMS
2
429.1798
R=53407
C 18 H 29 O 6 N 4 S = 429.1802
-0.9126 ppm
407.2008
R=51600
441.2973
R=53102
460.2218
R=51807
467.1360
R=51007
474.2376
R=51107
Relative Abundance
m/z


D:\Data\SGP-3
12/31/2012 5:20:37 PM
SGP-3 #892 RT: 3.97 AV: 1 NL: 1.42E9
T: FTMS + p ESI Full ms [100.00-700.00]
378.0842
R=57507
C 13 H 17 O 5 N 5 Na S = 378.0843
-0.2461 ppm
HRMS
6a
356.1021
R=59107
C 13 H 18 O 5 N 5 S = 356.1023
-0.6586 ppm
361.1051
R=52002
367.1546
R=57702
375.0761
R=56807
383.0609
R=54102
389.1364
R=56107
394.0579
R=56907
401.1599
R=54707
407.1331
R=46800
Relative Abundance
m/z

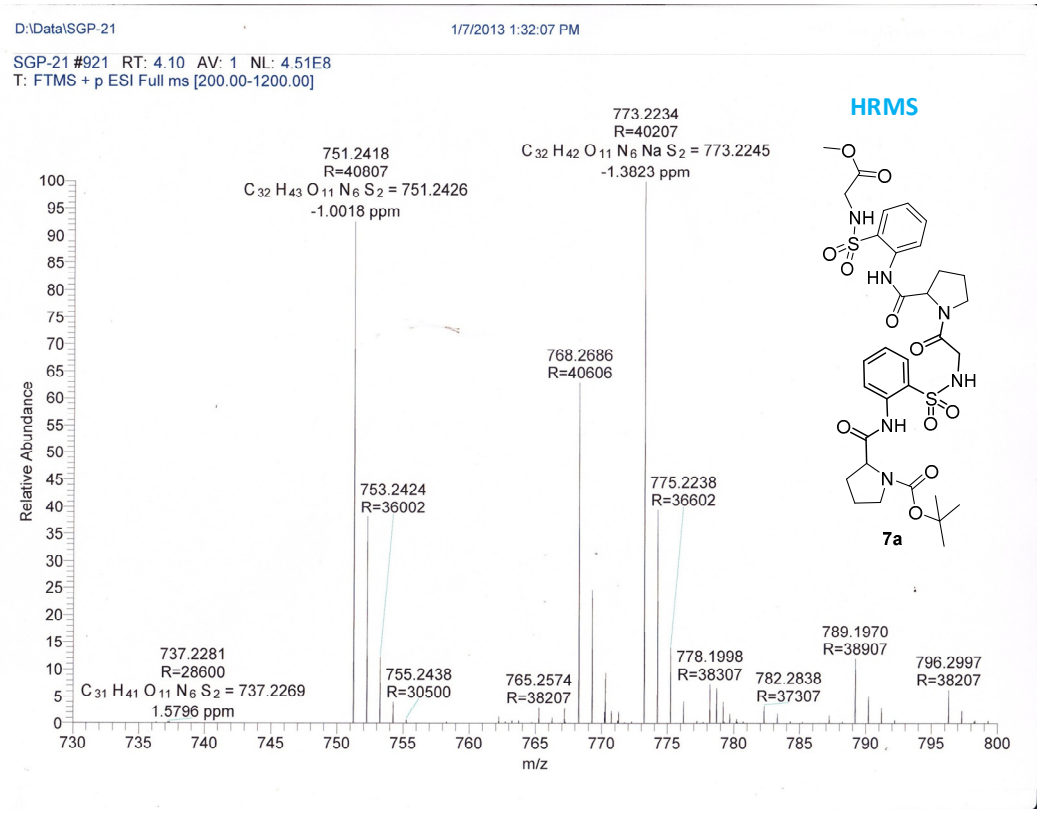

D:\Data\SGP-7
1/2/2013 3:28:03 PM
SGP-7 #909 RT: 4.05 AV: 1 NL: 3.19E9
T: FTMS + p ESI Full ms [200.00-1200.00]
727.2430
R=41307
C30 H43 O11 N6 S2 = 727.2426
0.5597 ppm
HRMS
715.1702
R=40207
C30 H36 O11 N4 Na S2 = 715.1714
-1.6686 ppm
739.2413
R=40406
761.2225
R=37402
771.2316
R=39207
6b
Relative Abundance
m/z


D:\Data\SGP-8
1/2/2013 5:08:32 PM
SGP-8 #875 RT: 3.90 AV: 1 NL: 2.00E9
T: FTMS + p ESI Full ms [200.00-1200.00]
726.2590
R=41503
C30 H44 O10 N7 S2 = 726.2586
0.5698 ppm
HRMS
748.2397
R=41207
C30 H43 O10 N7 Na S2 = 748.2405
-1.0931 ppm
738.2579
R=40602
764.2134
R=39707
773.3181
R=32602
6
Relative Abundance
m/z

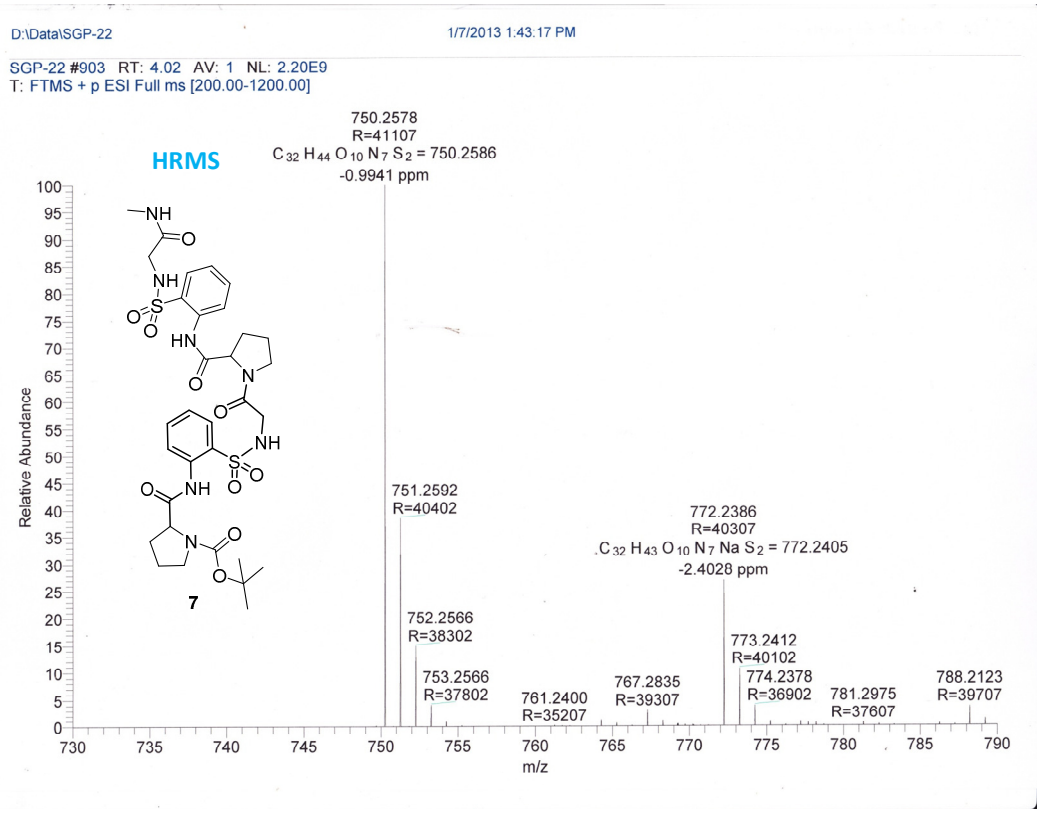


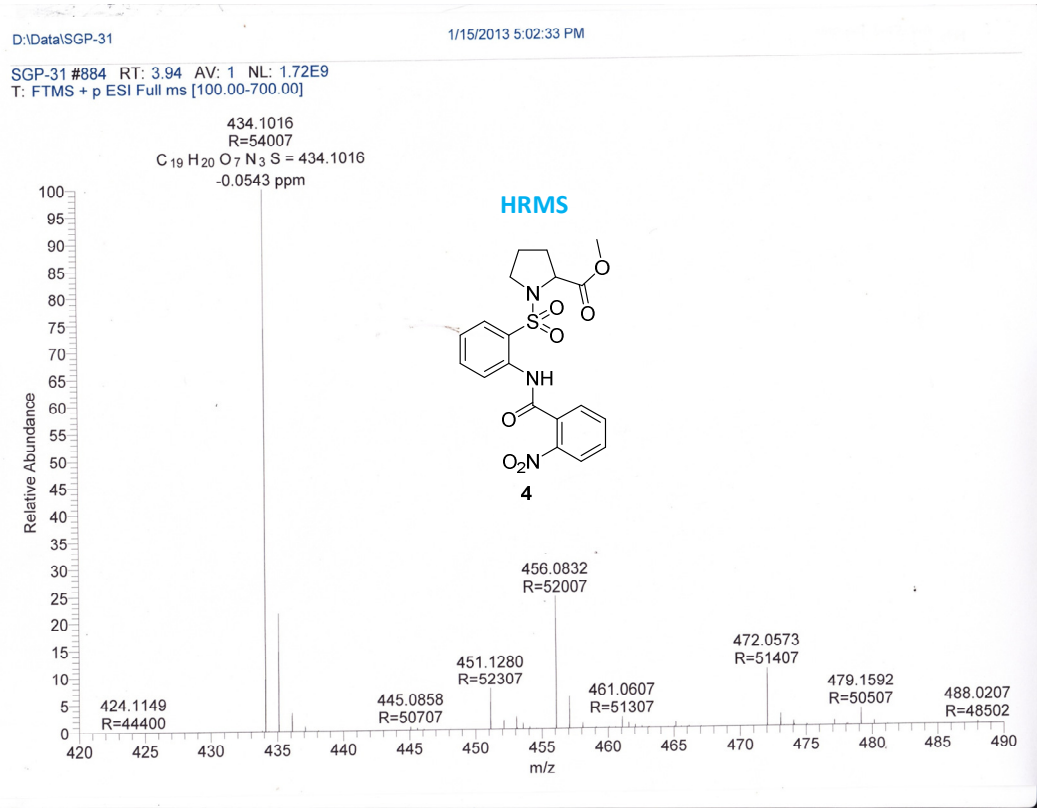


Note: The stereochemistry of prolines in **3a** and **3** is 'S'

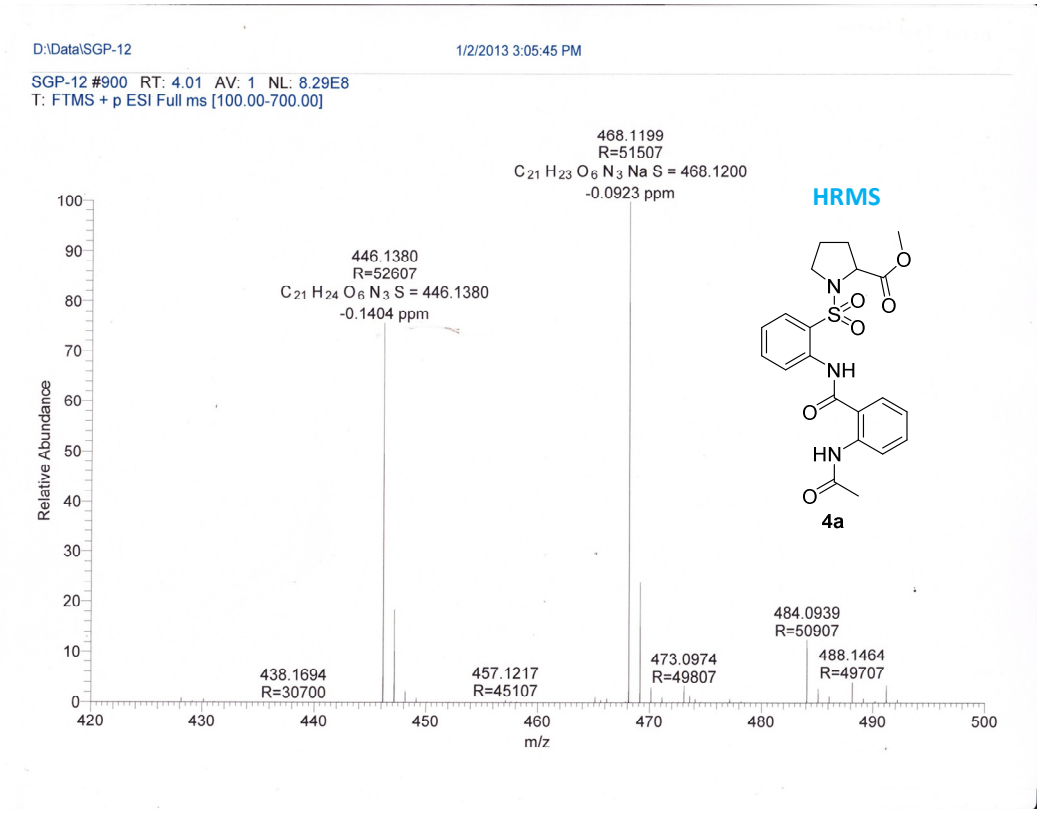


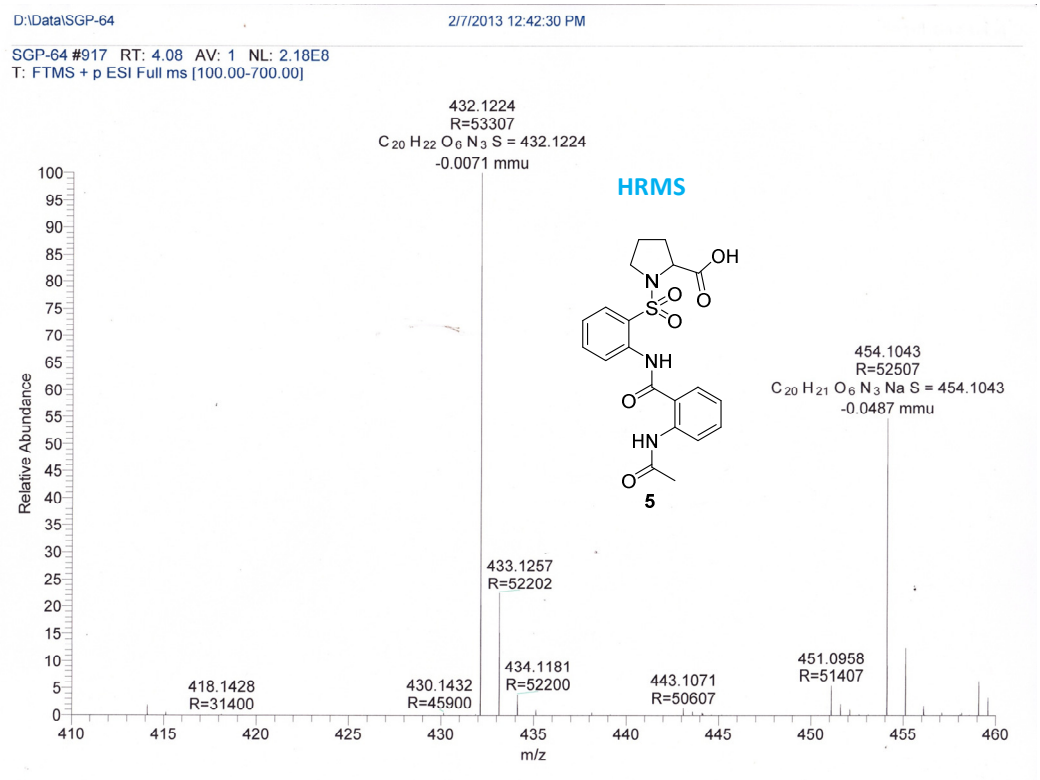
Note: The stereochemistry of prolines in **7** is 'S'



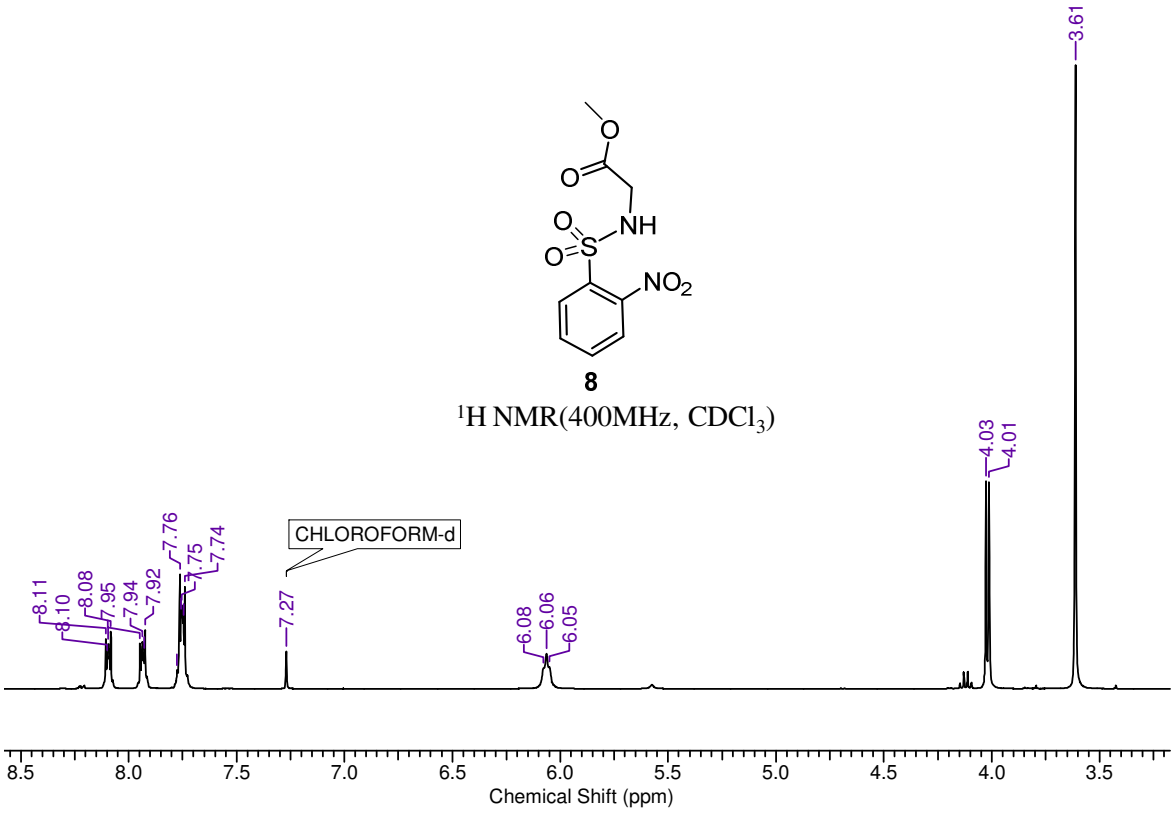


Note: The stereochemistry of prolines in **4** and **7**



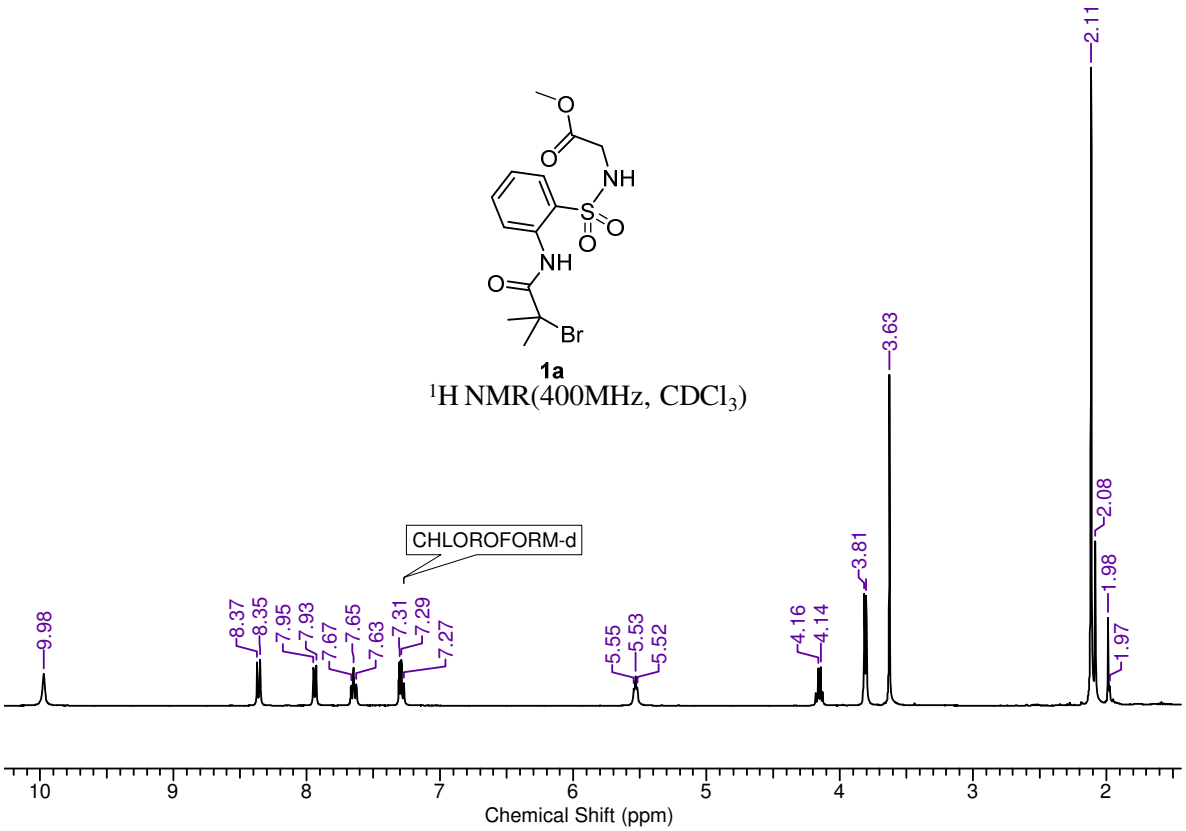


Note: The stereochemistry of prolines in **4a** and **5** is 'S'



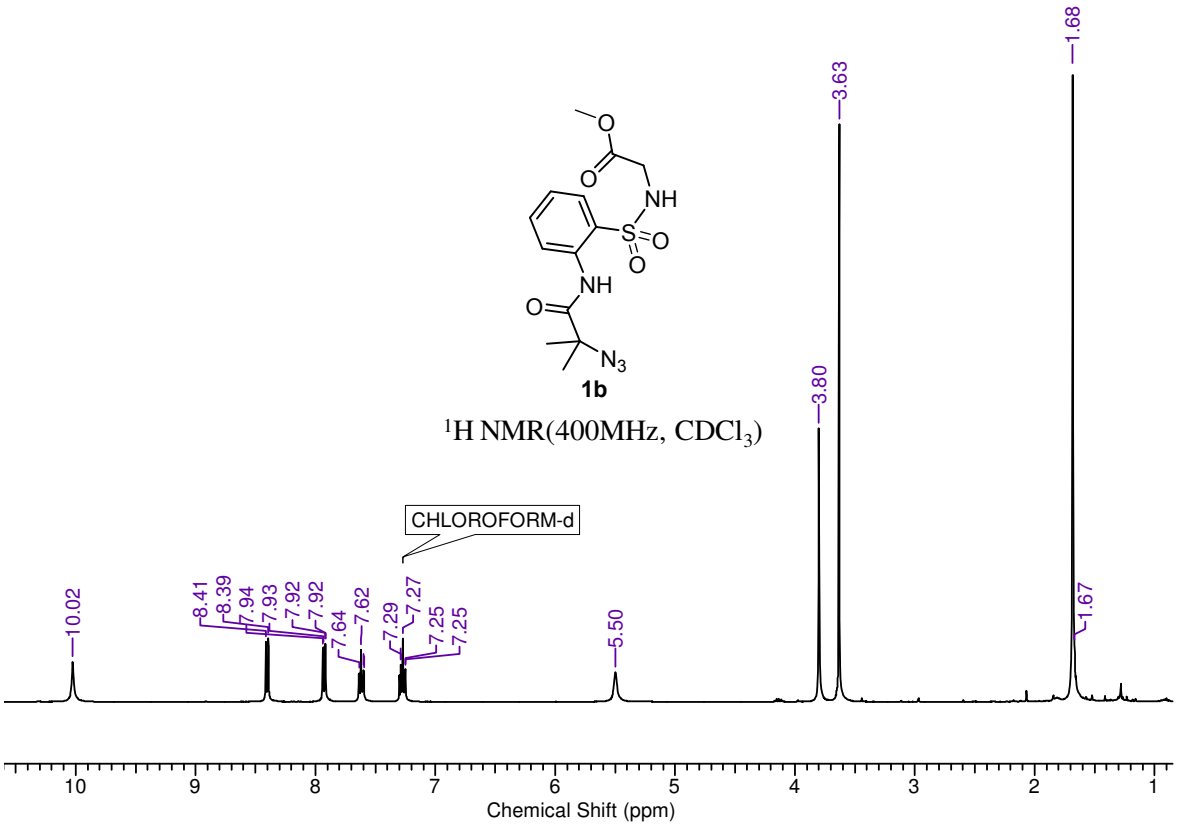
8

^{1}H NMR(400MHz, $CDCl_3$)



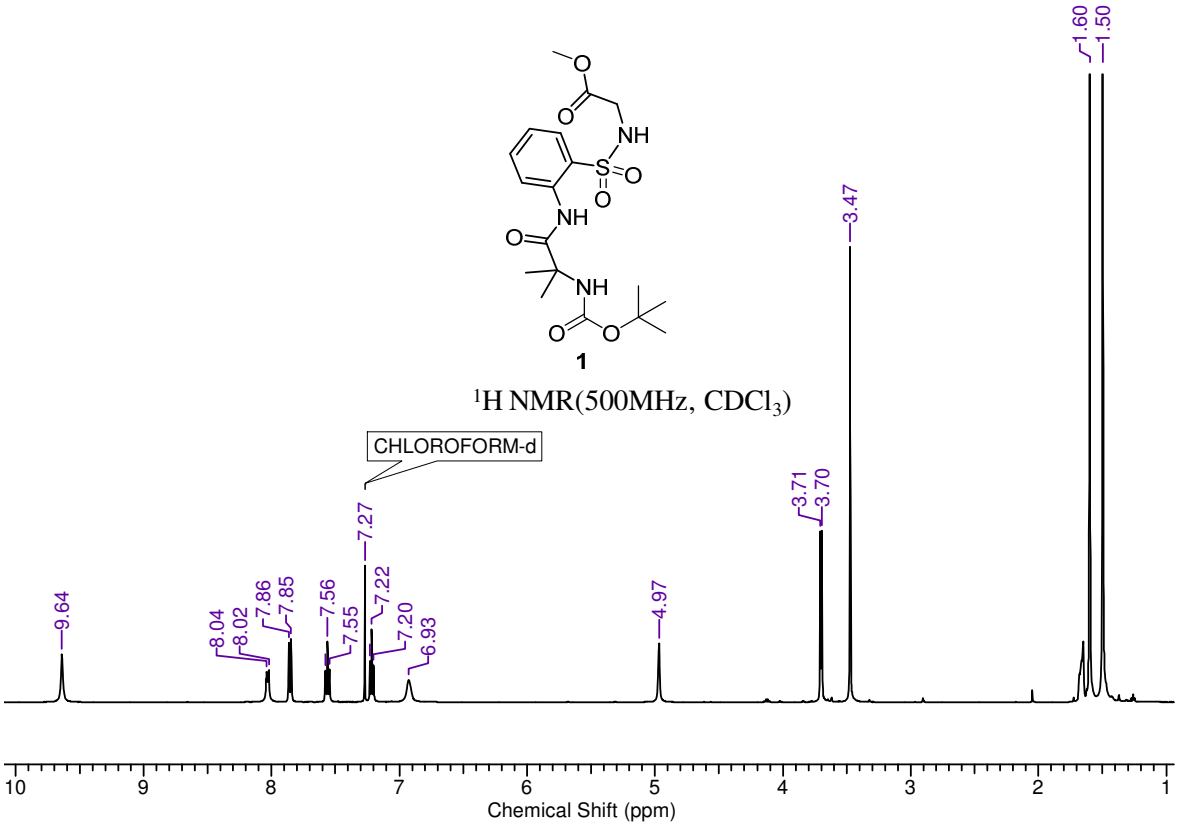
1a

^{1}H NMR(400MHz, $CDCl_3$)



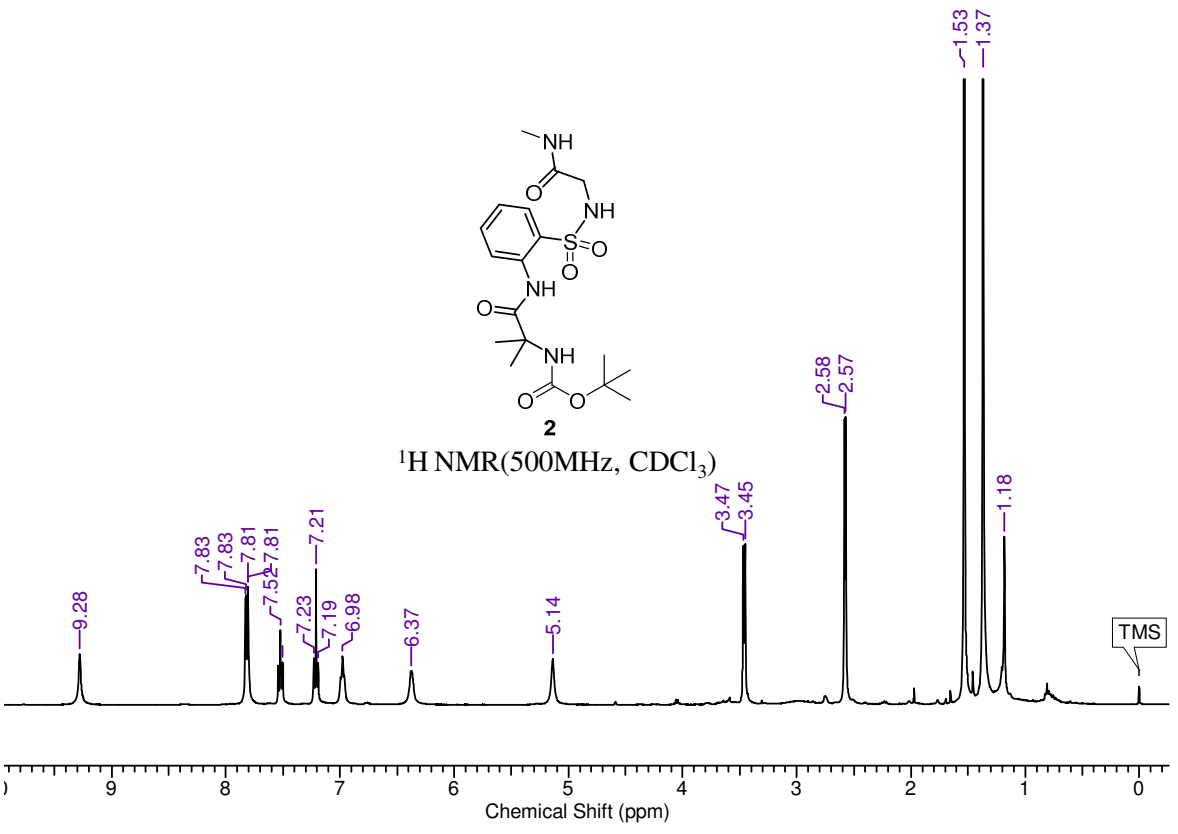
1b

^{1}H NMR(400MHz, $CDCl_3$)



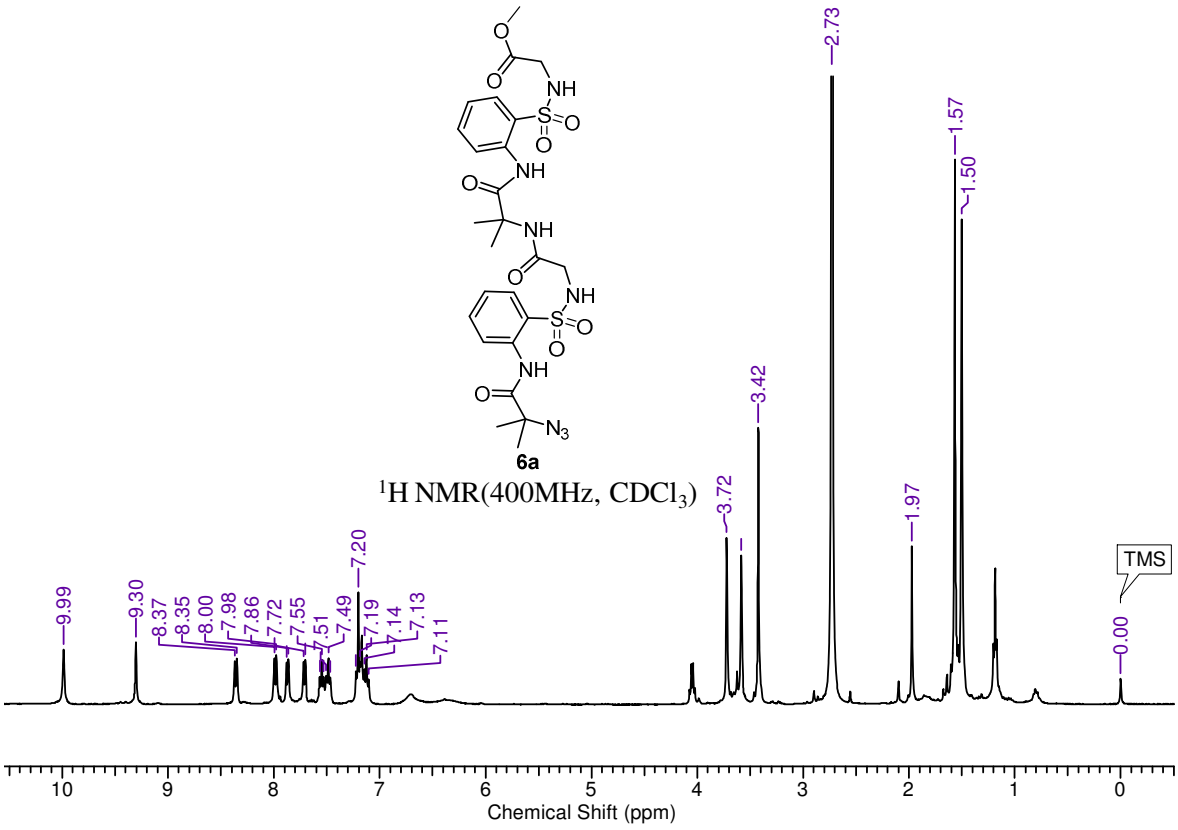
1

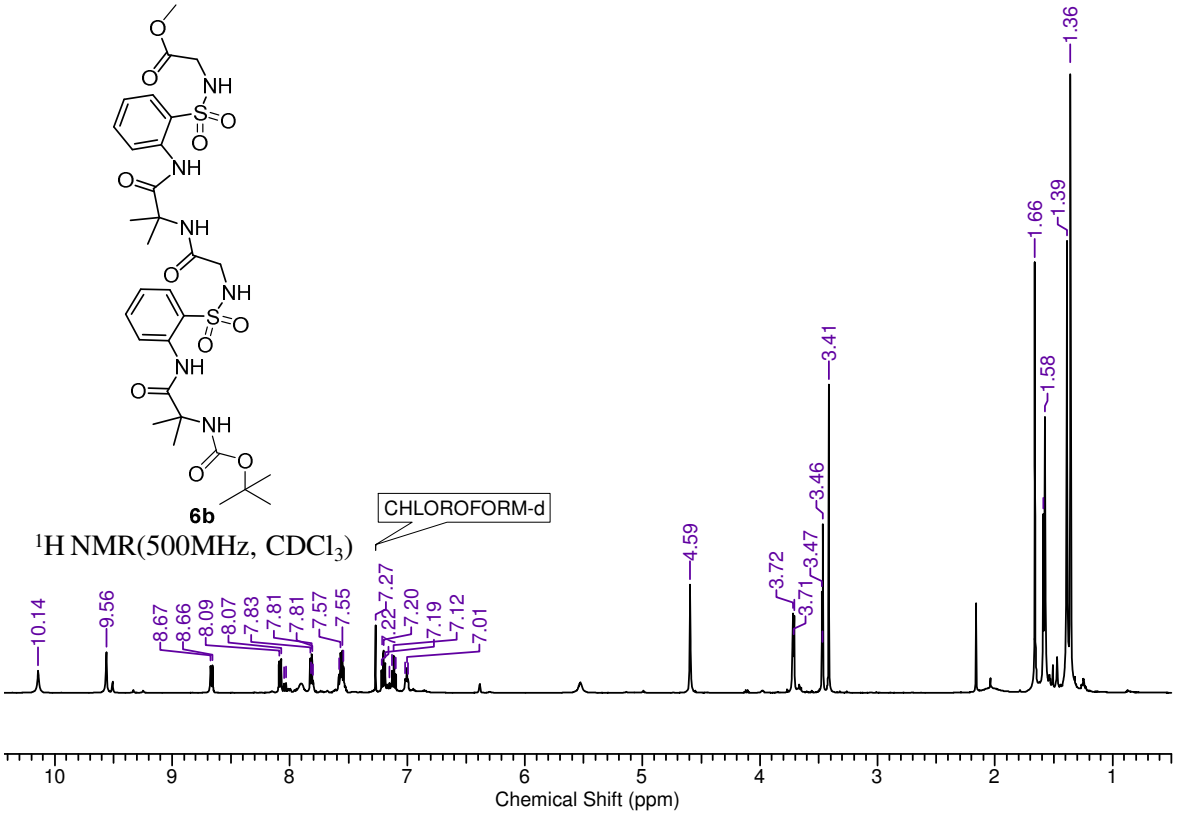
^{1}H NMR(500MHz, $CDCl_3$)

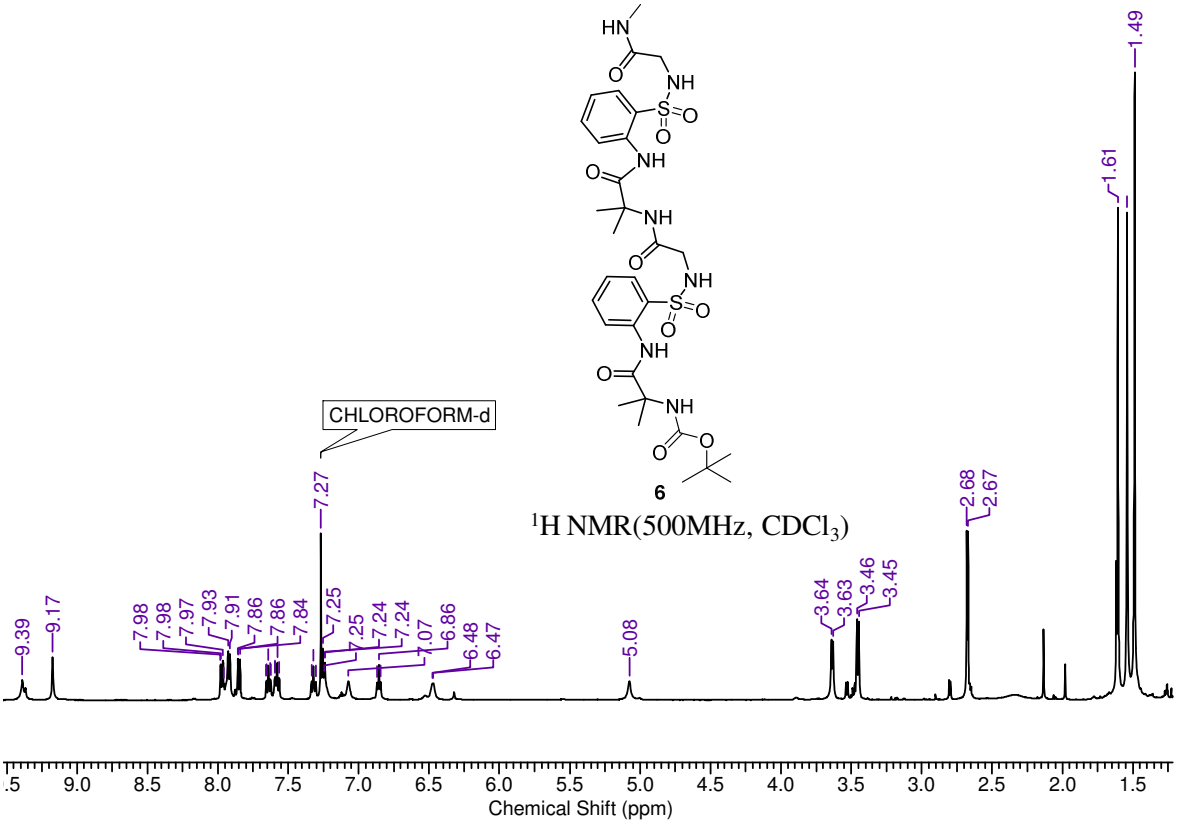


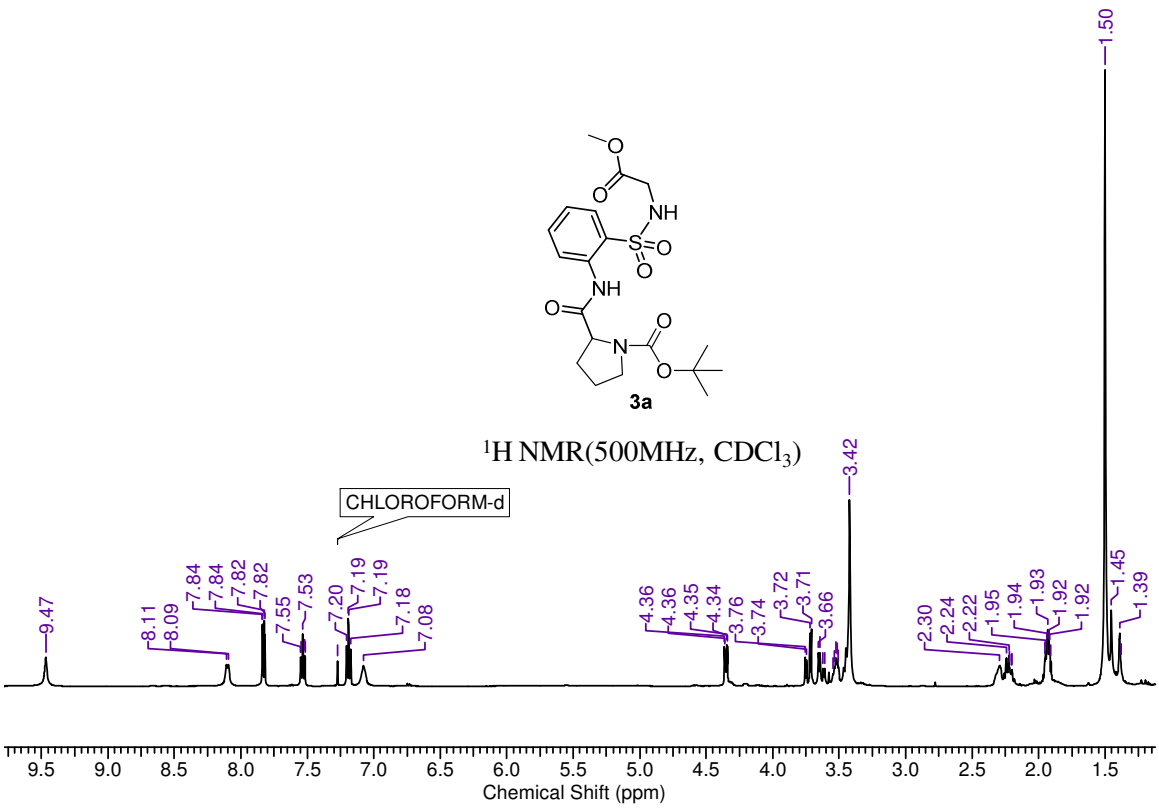
2

^{1}H NMR(500MHz, $CDCl_3$)

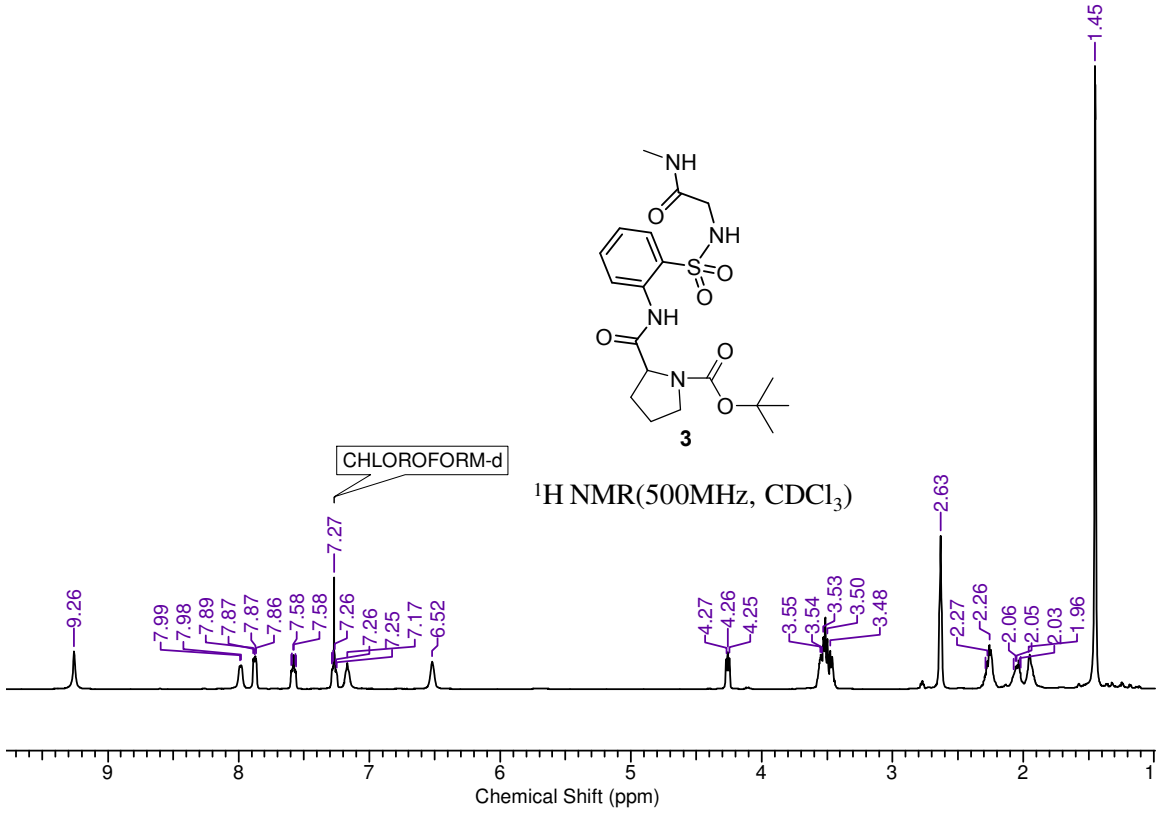

6a
^{1}H NMR(400MHz, $CDCl_3$)
9.99
9.30
8.37
8.35
8.00
7.98
7.86
7.72
7.55
7.51
7.49
7.20
7.19
7.14
7.13
7.11
3.72
3.42
2.73
1.97
1.57
1.50
TMS
0.00
Chemical Shift (ppm)

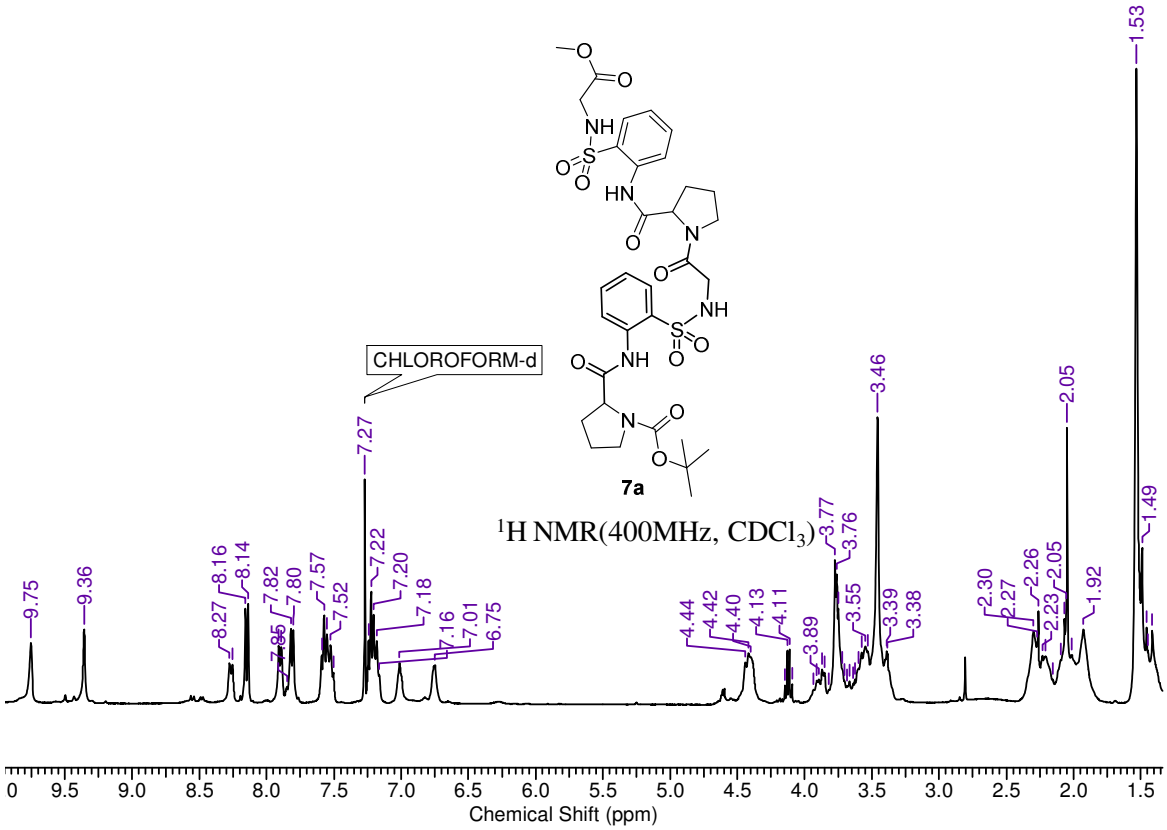

6b
^{1}H NMR(500MHz, $CDCl_3$)
CHLOROFORM-d
10.14
9.56
8.67
8.66
8.09
8.07
7.83
7.81
7.81
7.57
7.55
7.27
7.22
7.20
7.19
7.12
7.01
4.59
3.72
3.71
3.47
3.46
3.41
1.66
1.58
1.39
1.36
Chemical Shift (ppm)



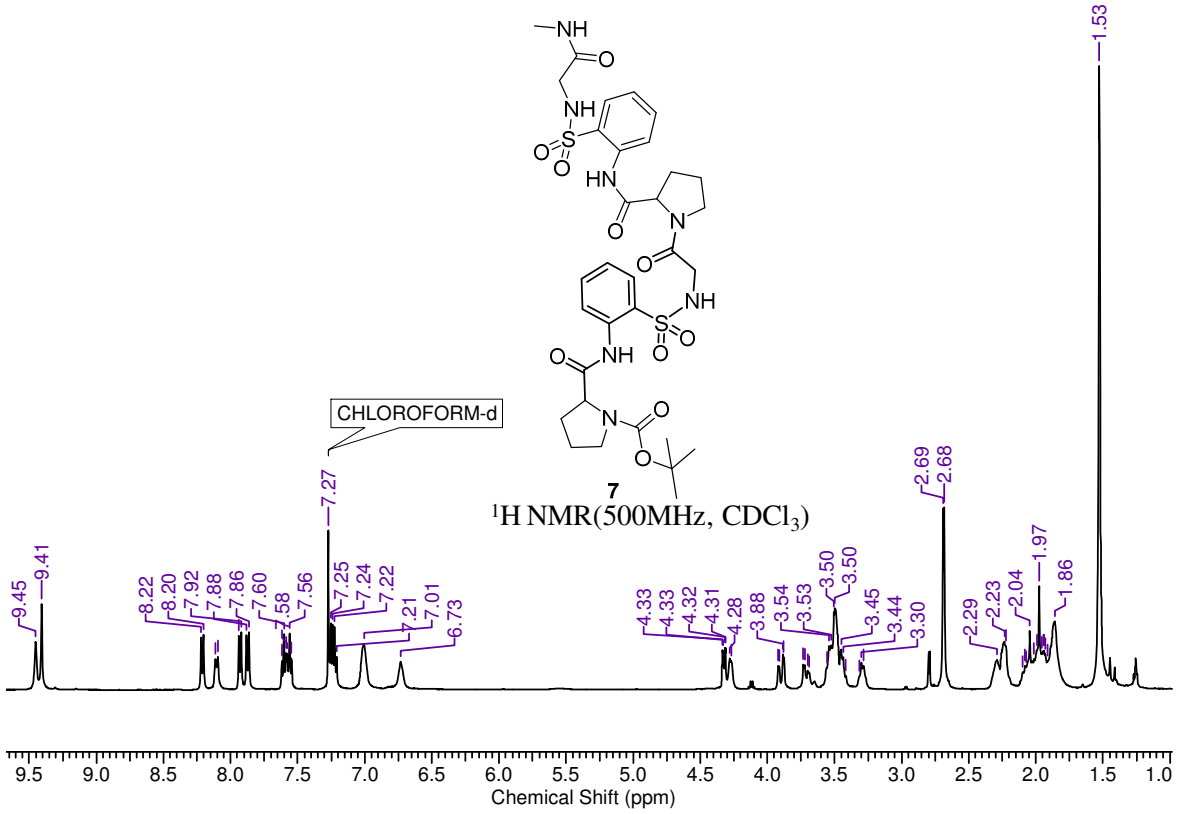


Note: The stereochemistry of prolines in **3a** is 'S'



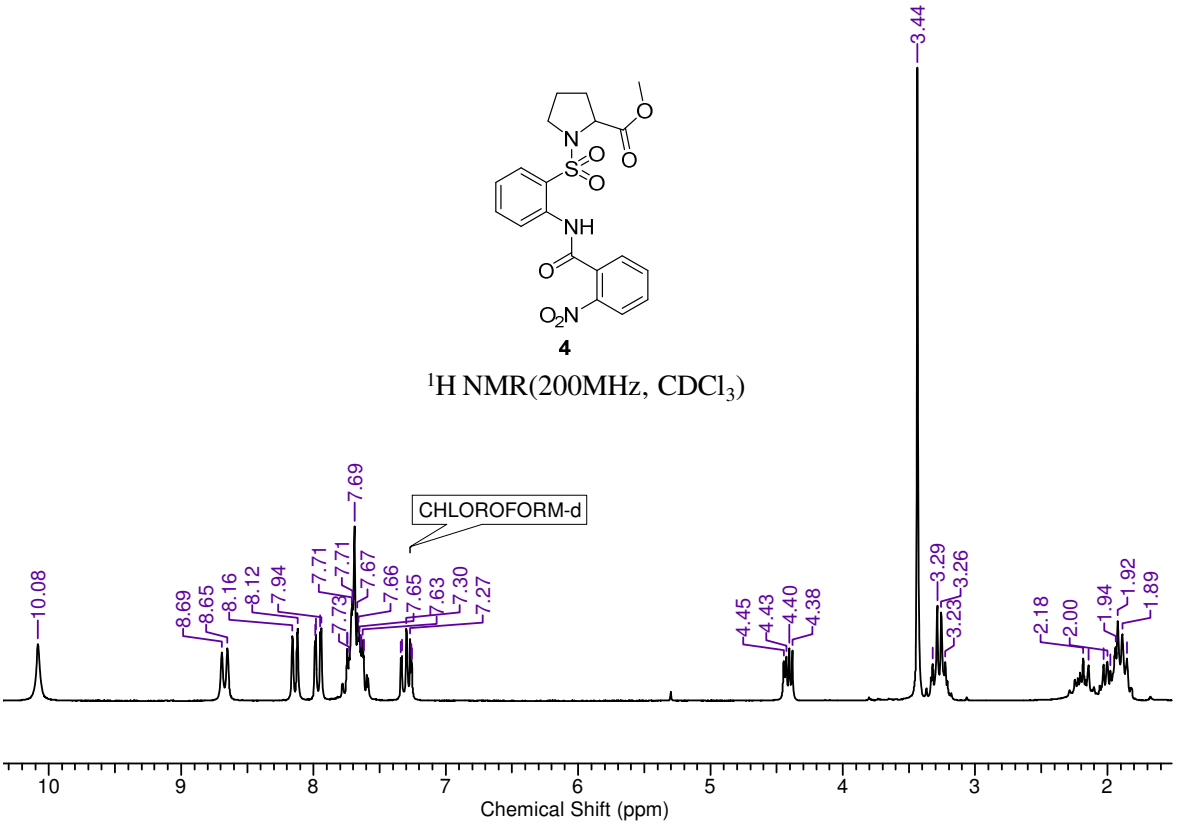


Note: The stereochemistry of prolines in **7a** and **3** is 'S'



7

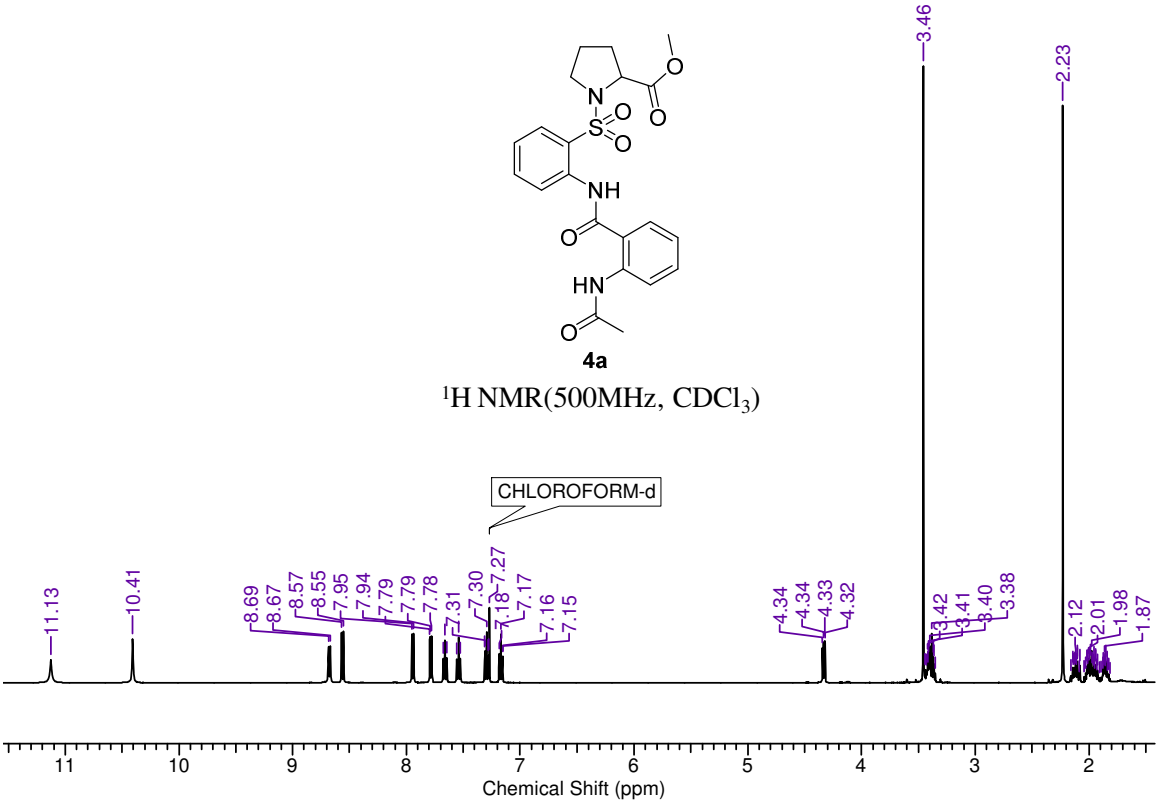
^{1}H NMR(500MHz, $CDCl_3$)



4

^{1}H NMR(200MHz, $CDCl_3$)

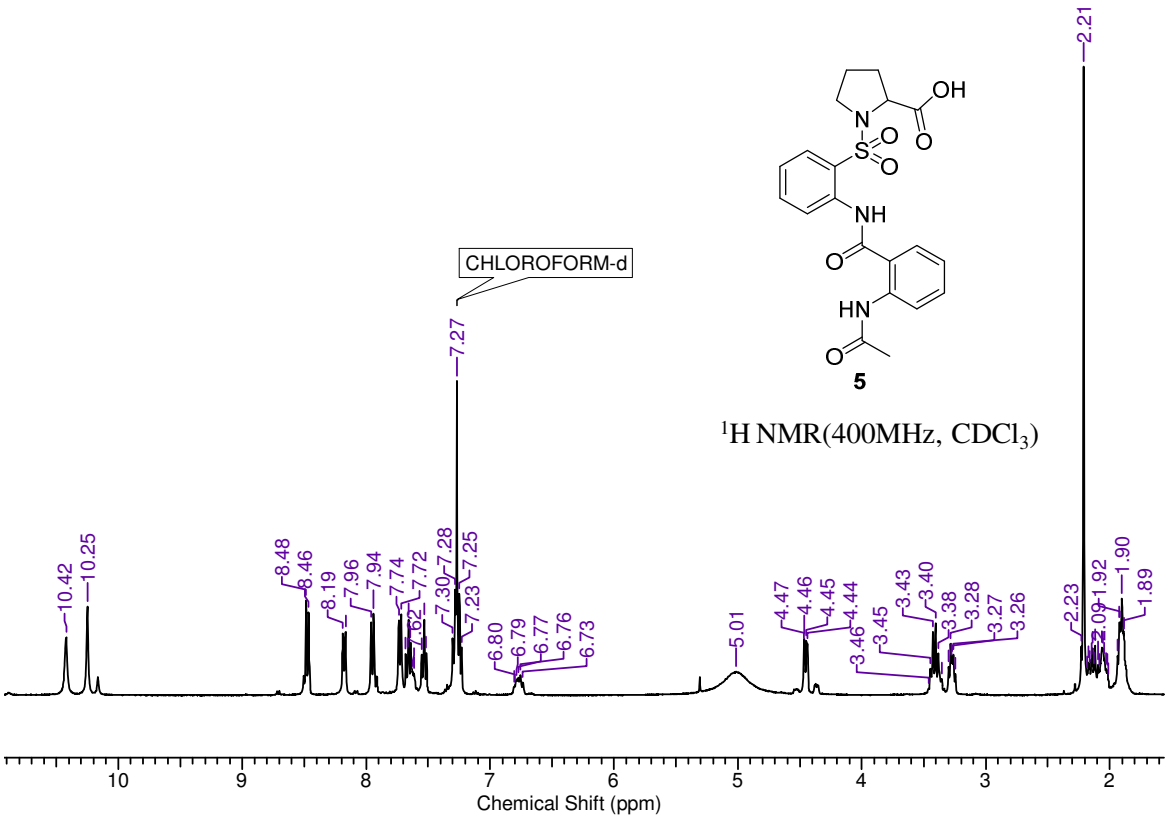
Note: The stereochemistry of prolines in **7** and **4** is 'S'



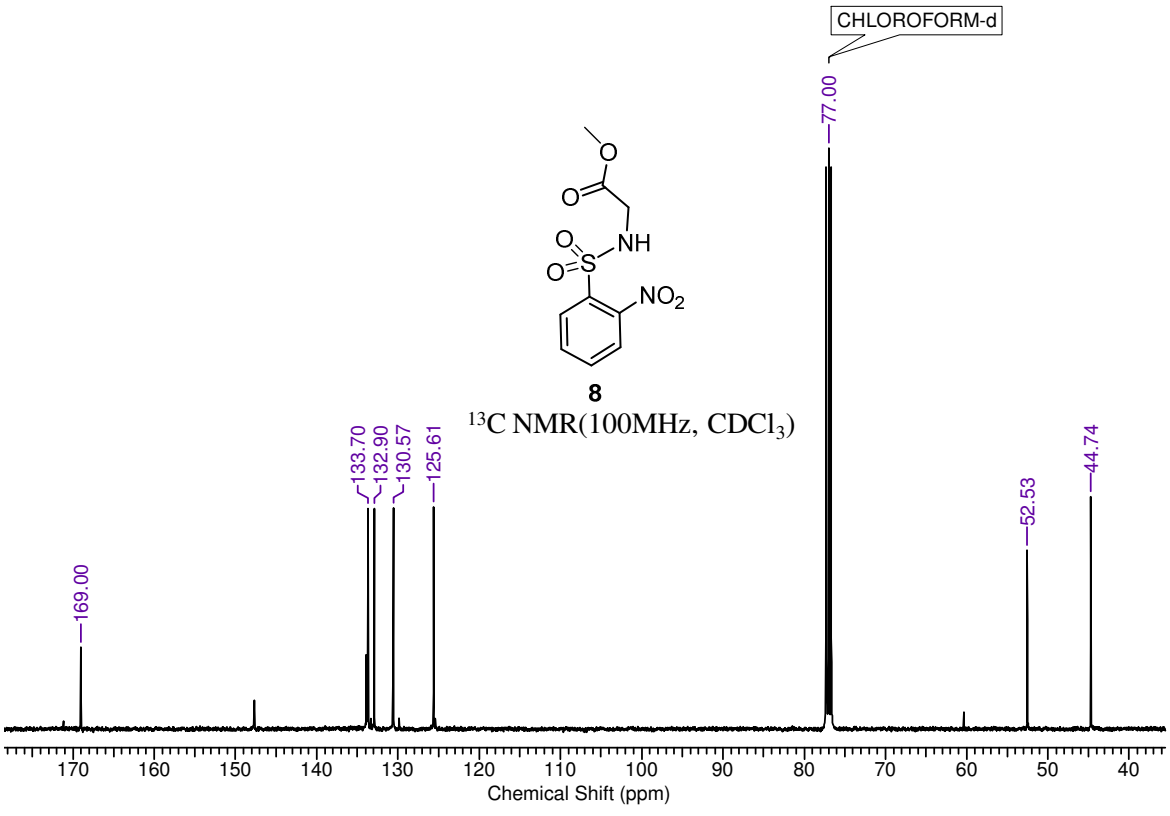
4a

^{1}H NMR(500MHz, $CDCl_3$)

Note: The stereochemistry of prolines in **4a** is 'S'

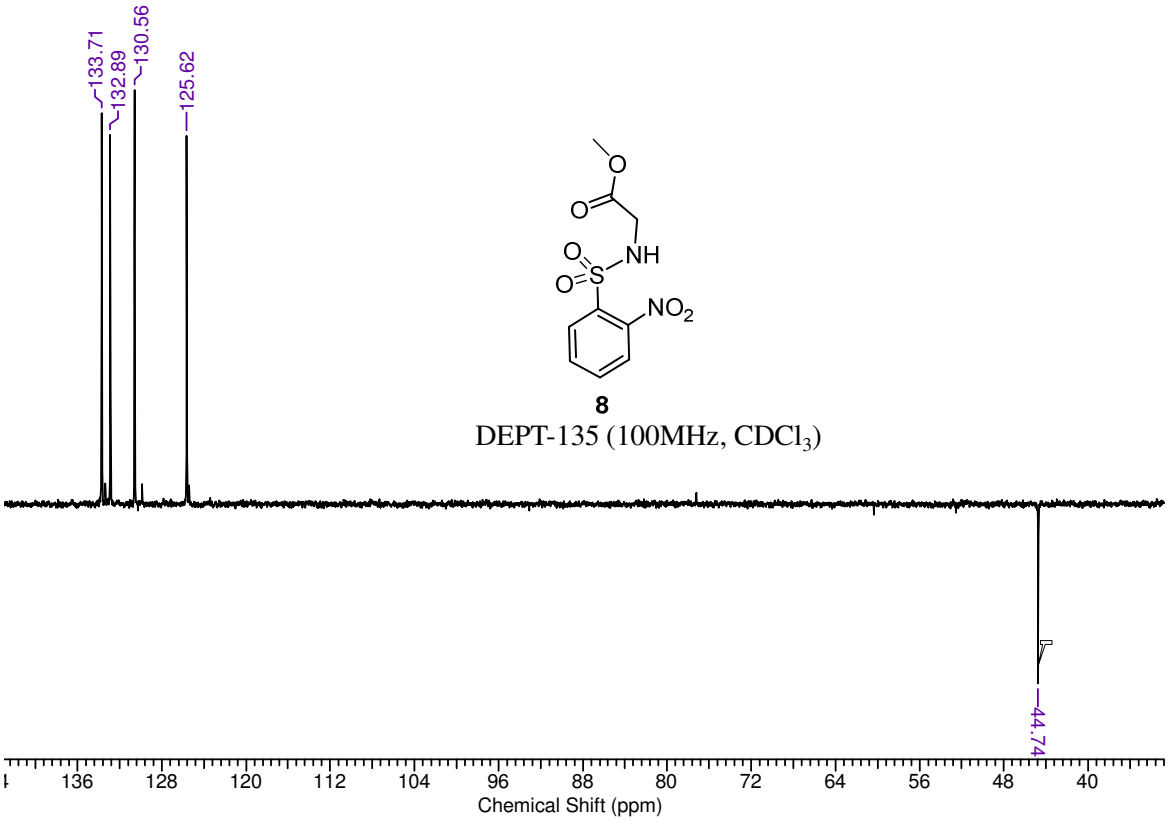


^{1}H NMR(400MHz, $CDCl_3$)



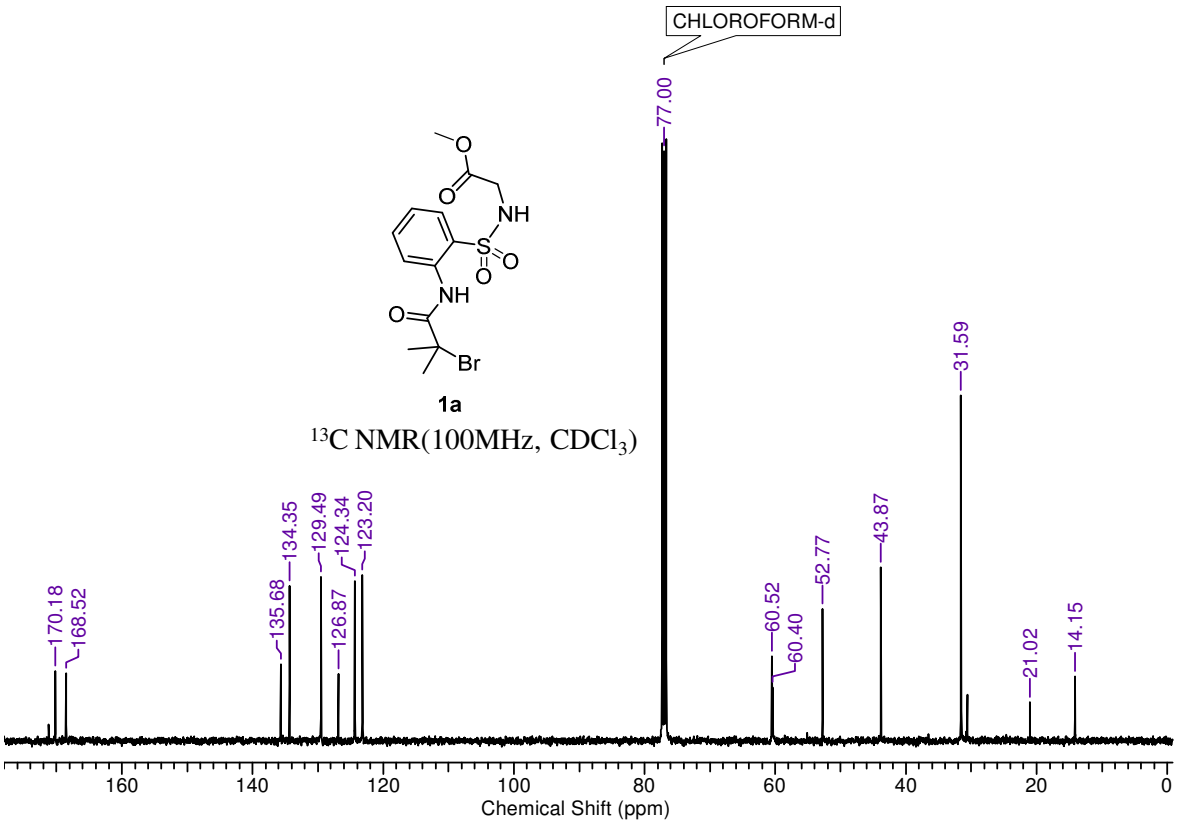
^{13}C NMR(100MHz, $CDCl_3$)

Note: The stereochemistry of prolines in **5** is 'S'



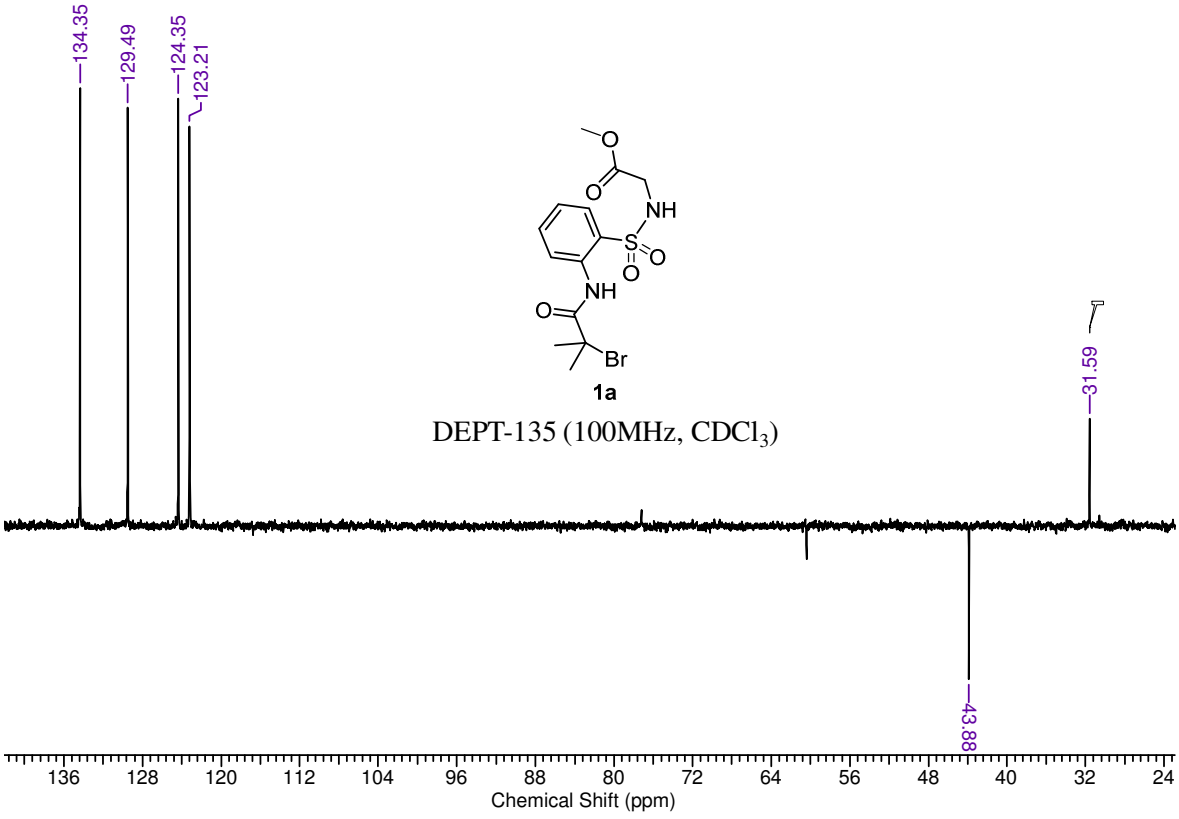
8

DEPT-135 (100MHz, $CDCl_3$)



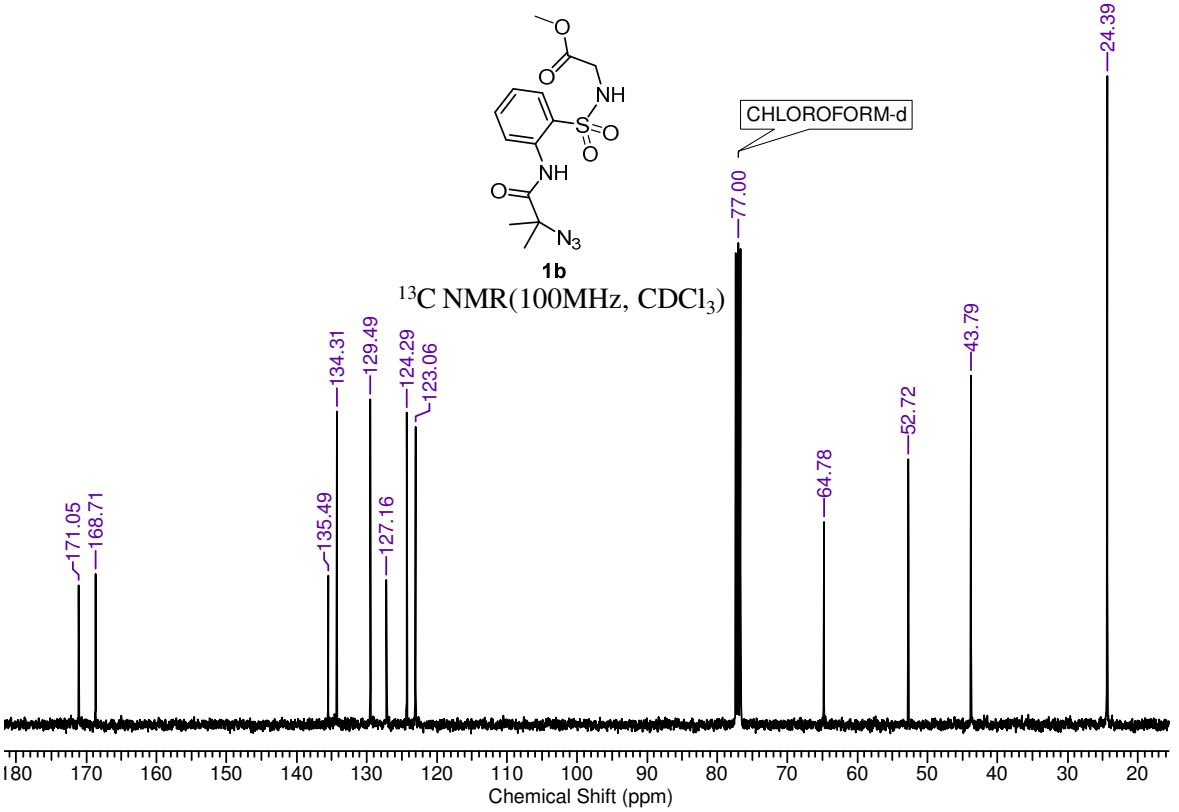
1a

^{13}C NMR(100MHz, $CDCl_3$)



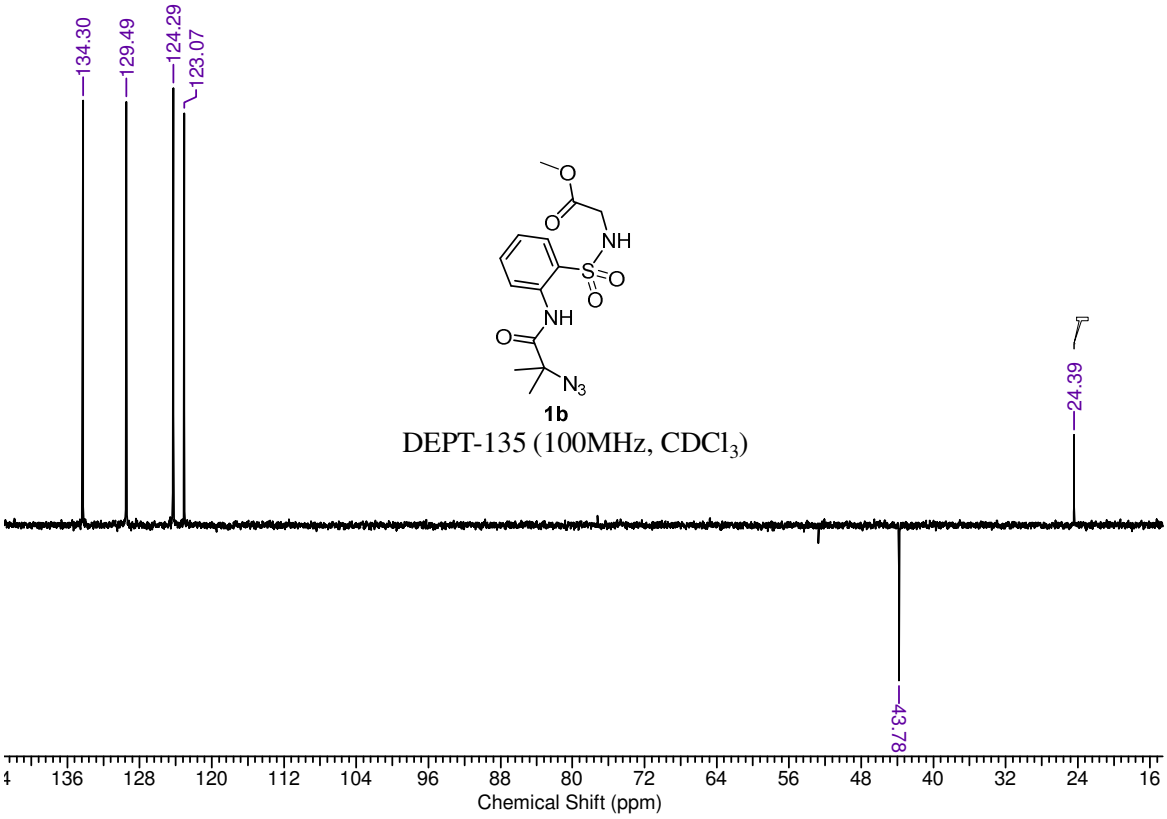
1a

DEPT-135 (100MHz, $CDCl_3$)



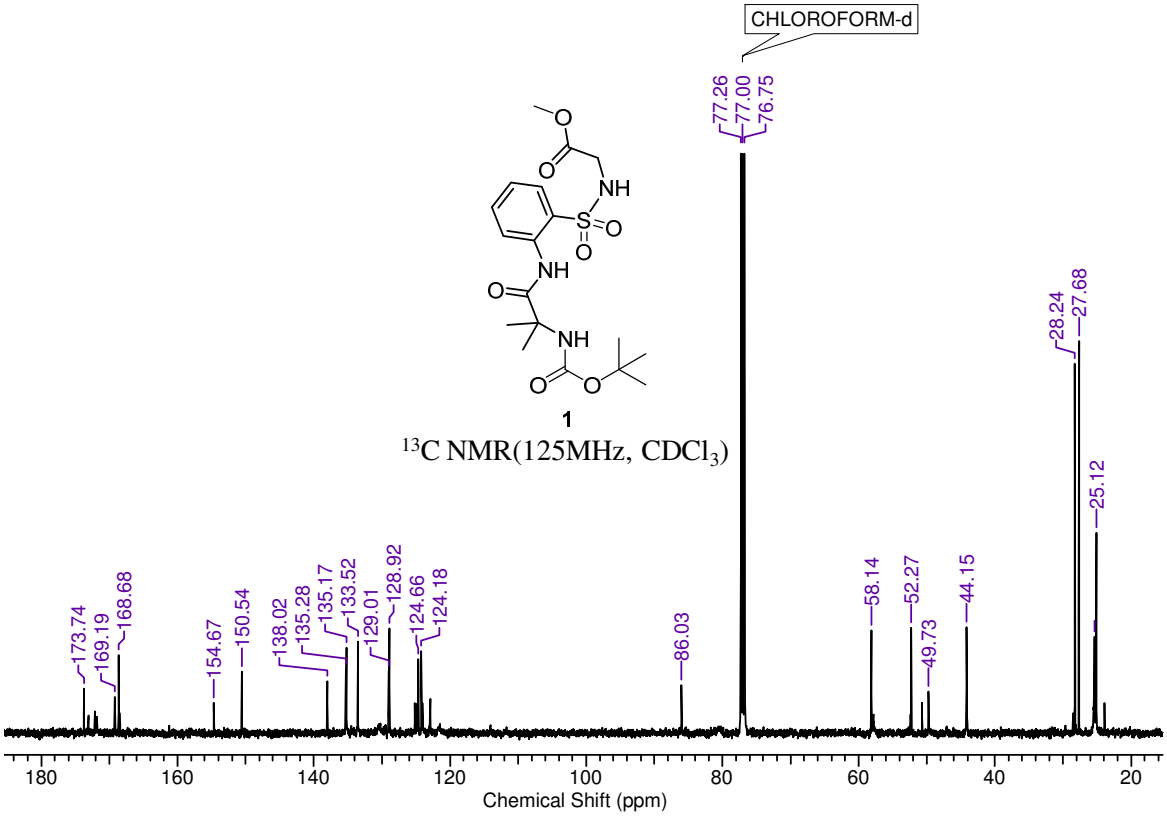
1b

^{13}C NMR(100MHz, $CDCl_3$)



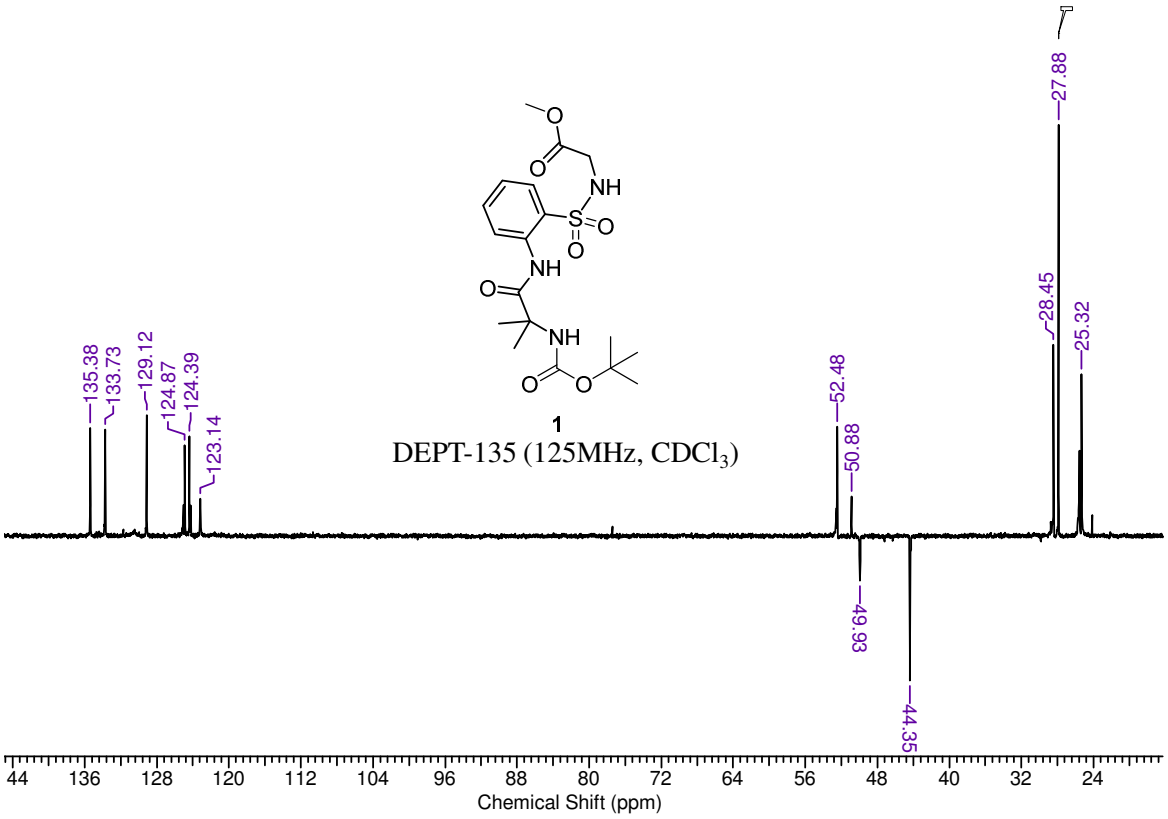
1b

DEPT-135 (100MHz, $CDCl_3$)



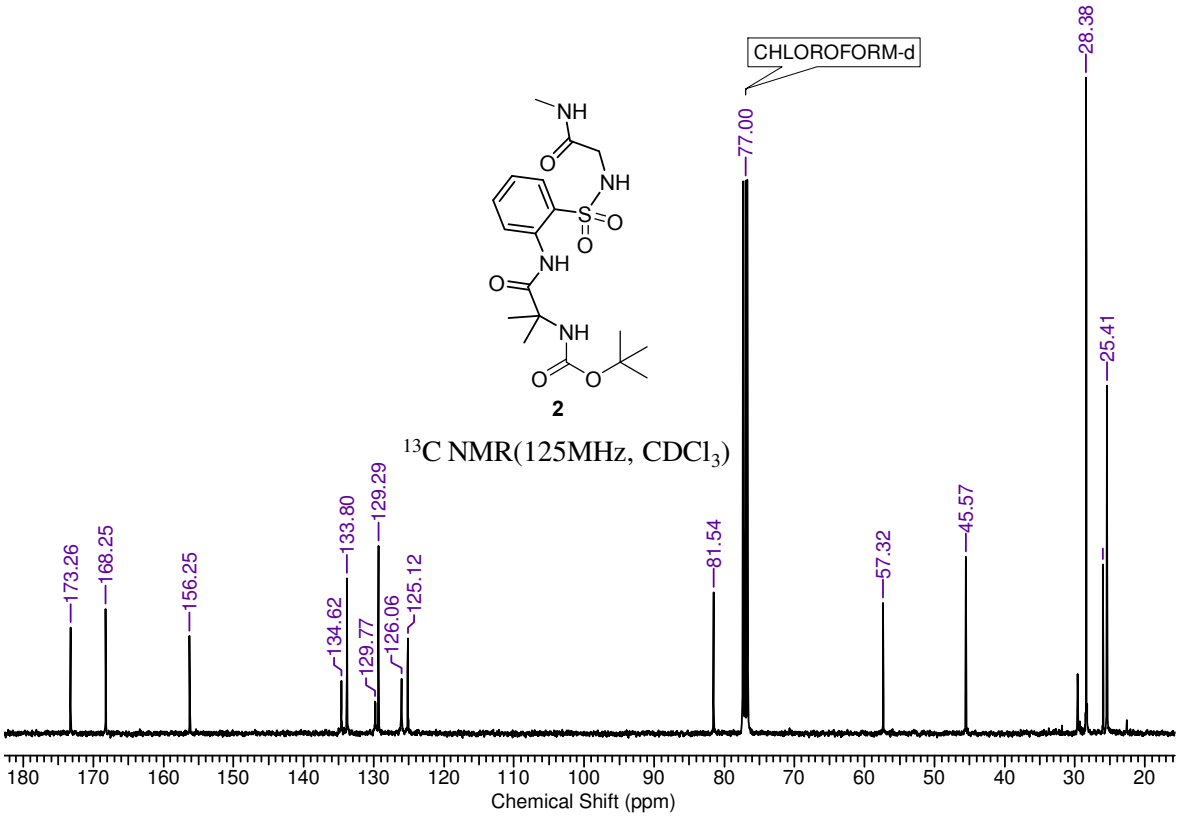
1

^{13}C NMR(125MHz, $CDCl_3$)



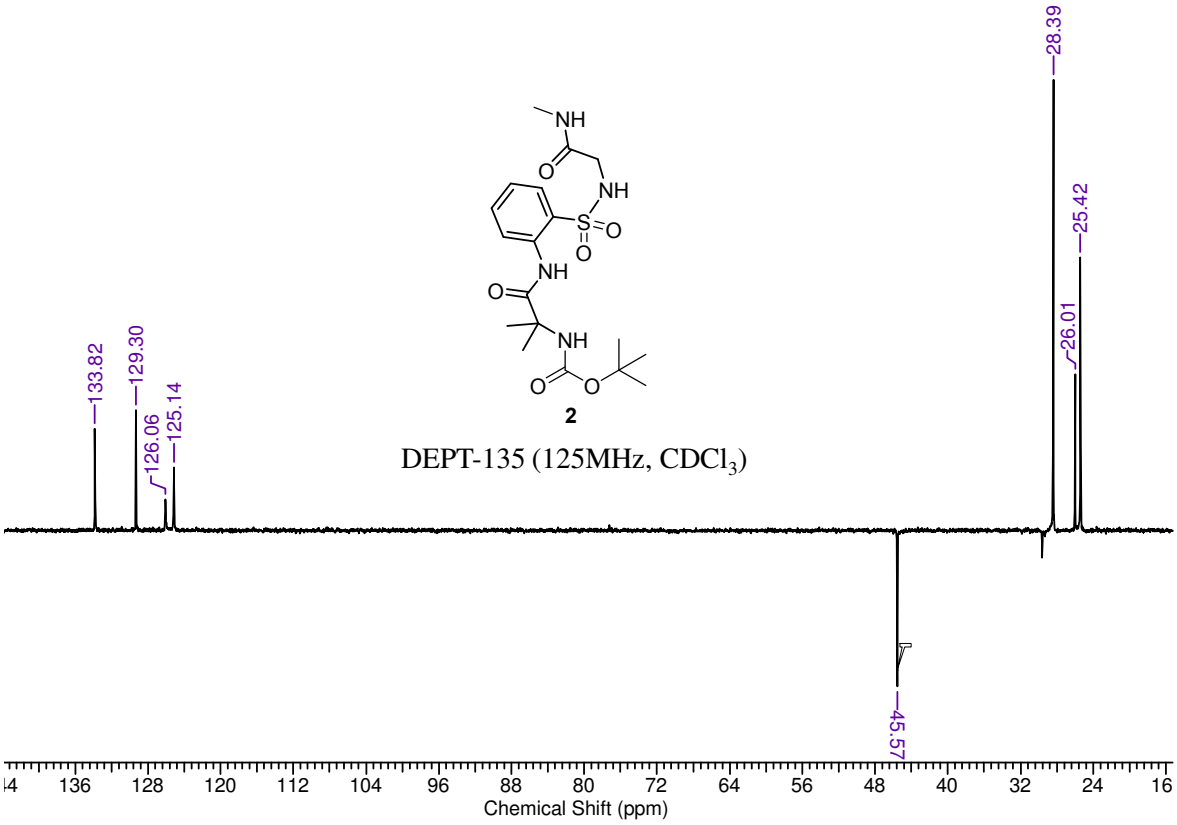
1

DEPT-135 (125MHz, $CDCl_3$)



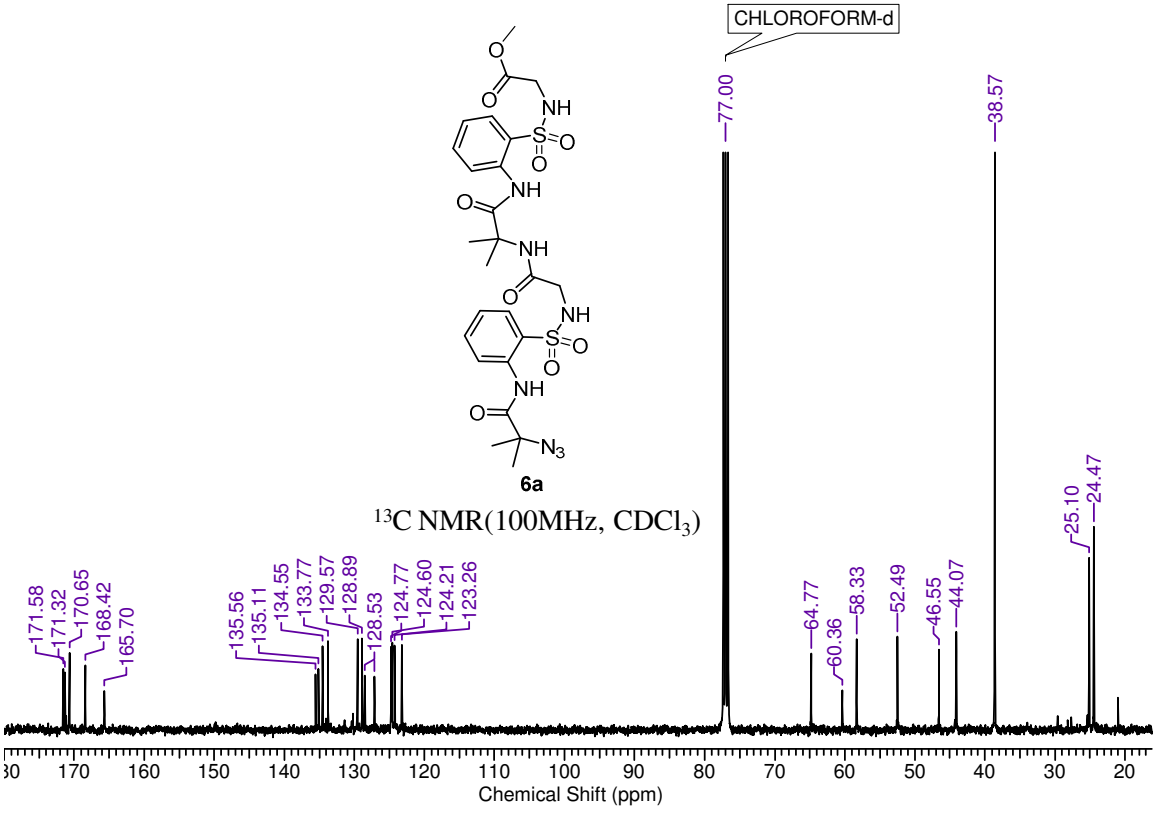
2

^{13}C NMR(125MHz, $CDCl_3$)



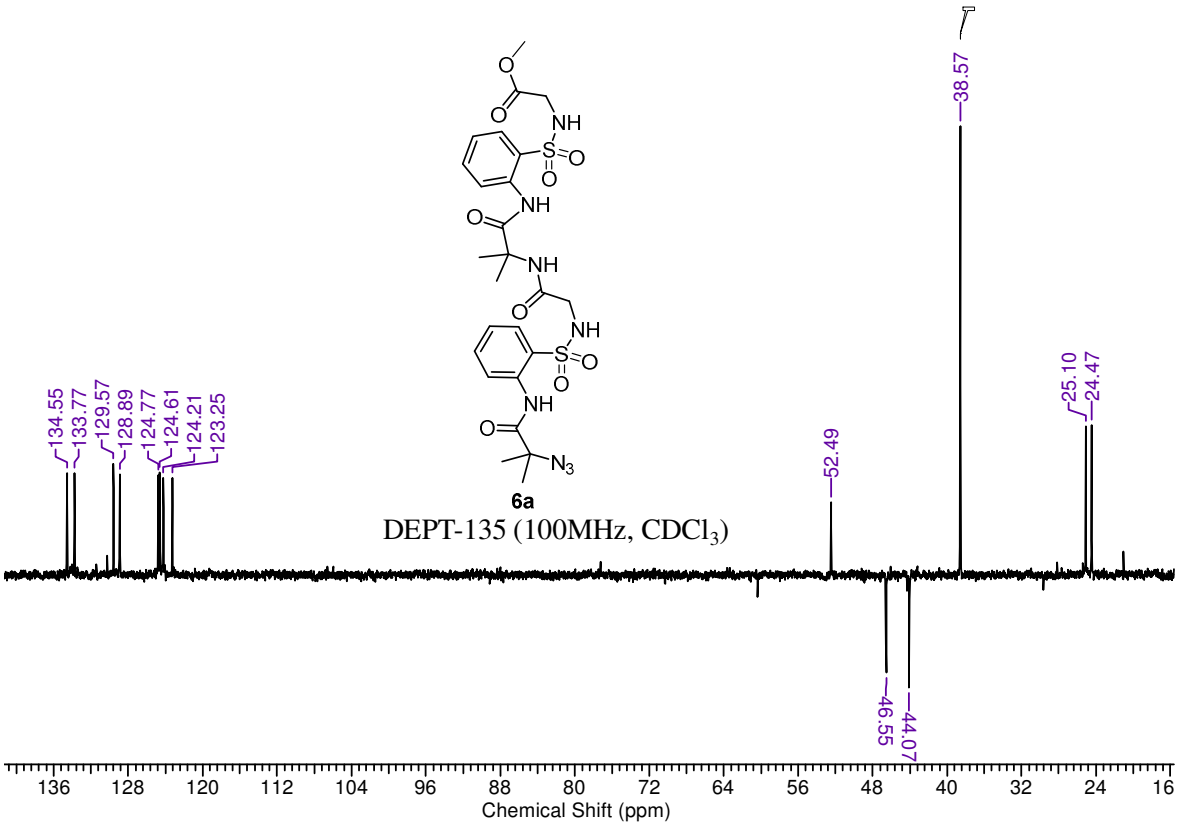
2

DEPT-135 (125MHz, $CDCl_3$)



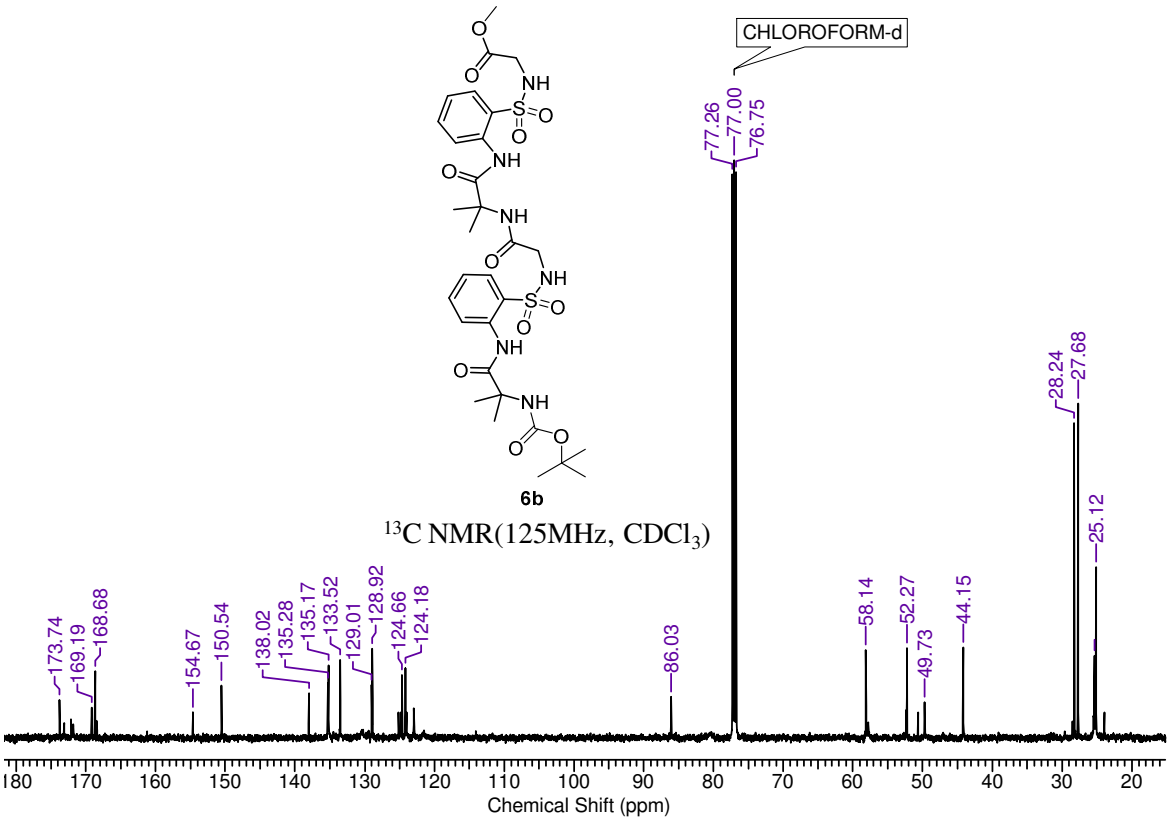
6a

^{13}C NMR(100MHz, $CDCl_3$)



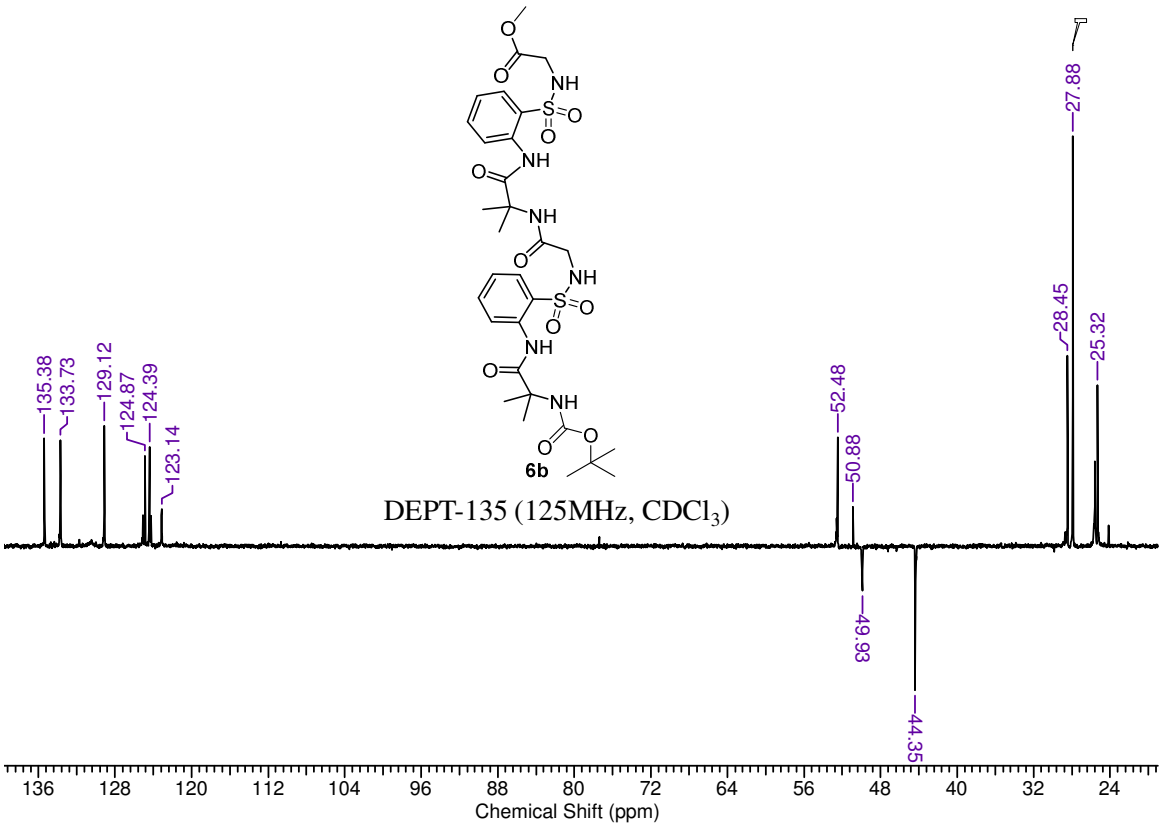
6a

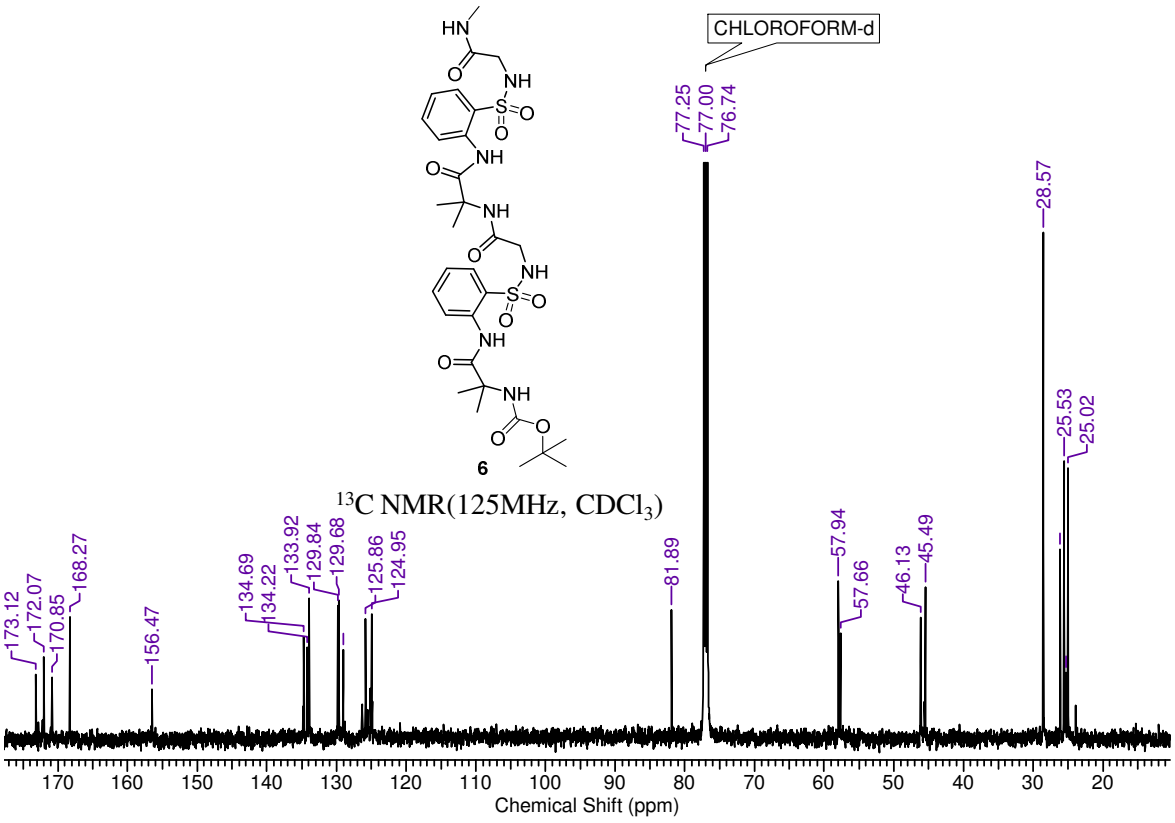
DEPT-135 (100MHz, $CDCl_3$)

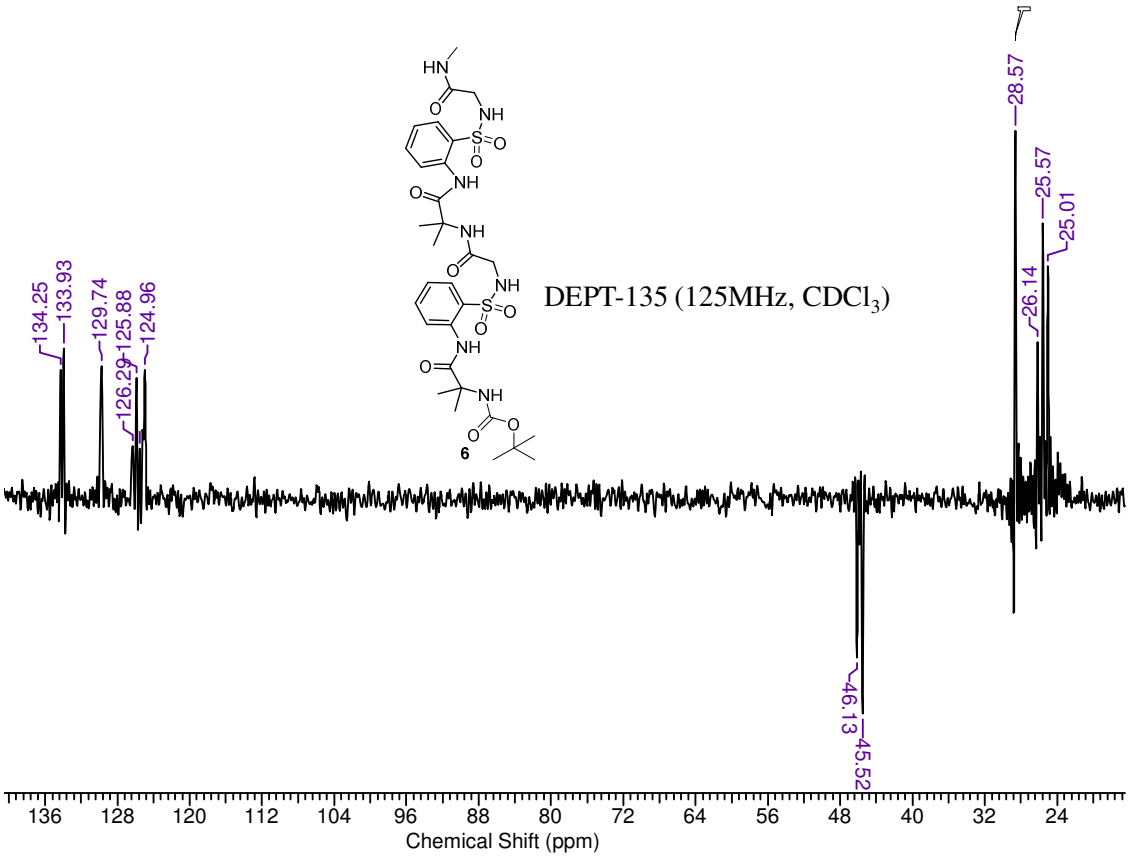


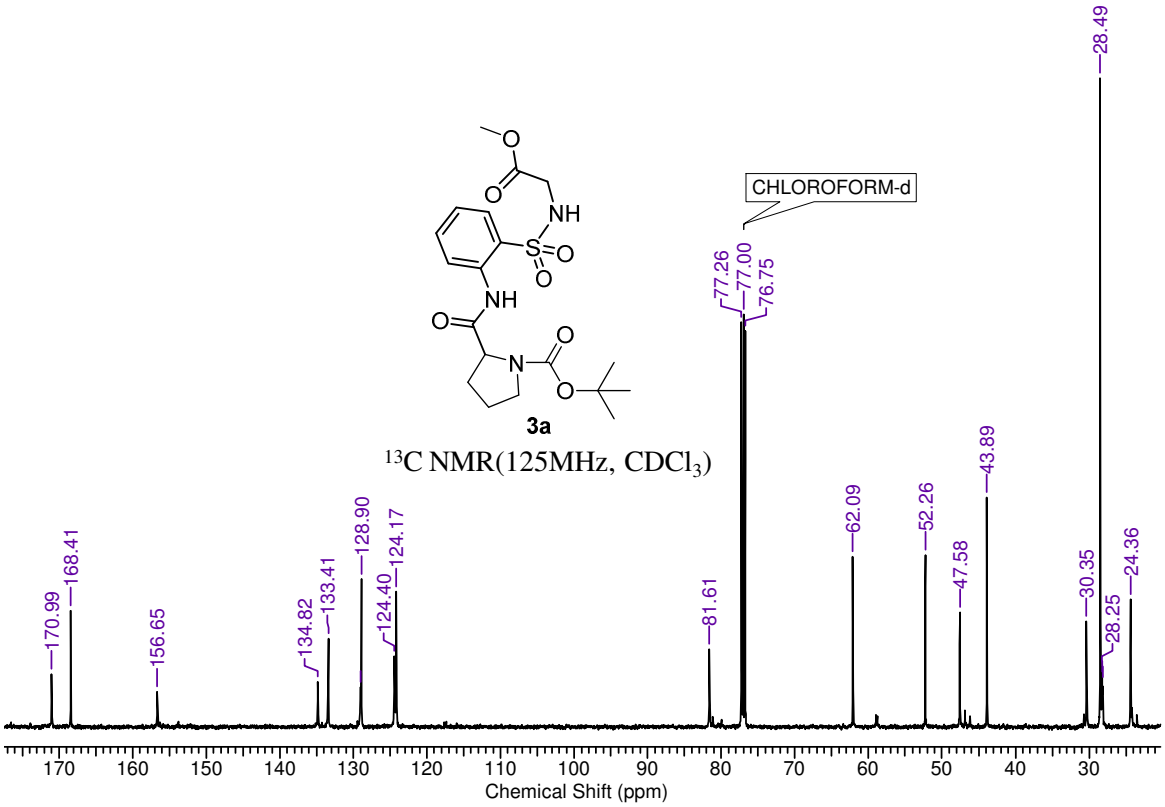
6b

^{13}C NMR(125MHz, $CDCl_3$)


6b
DEPT-135 (125MHz, CDCl3)
135.38
133.73
129.12
124.87
124.39
123.14
52.48
50.88
49.93
44.35
28.45
27.88
25.32
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
Chemical Shift (ppm)

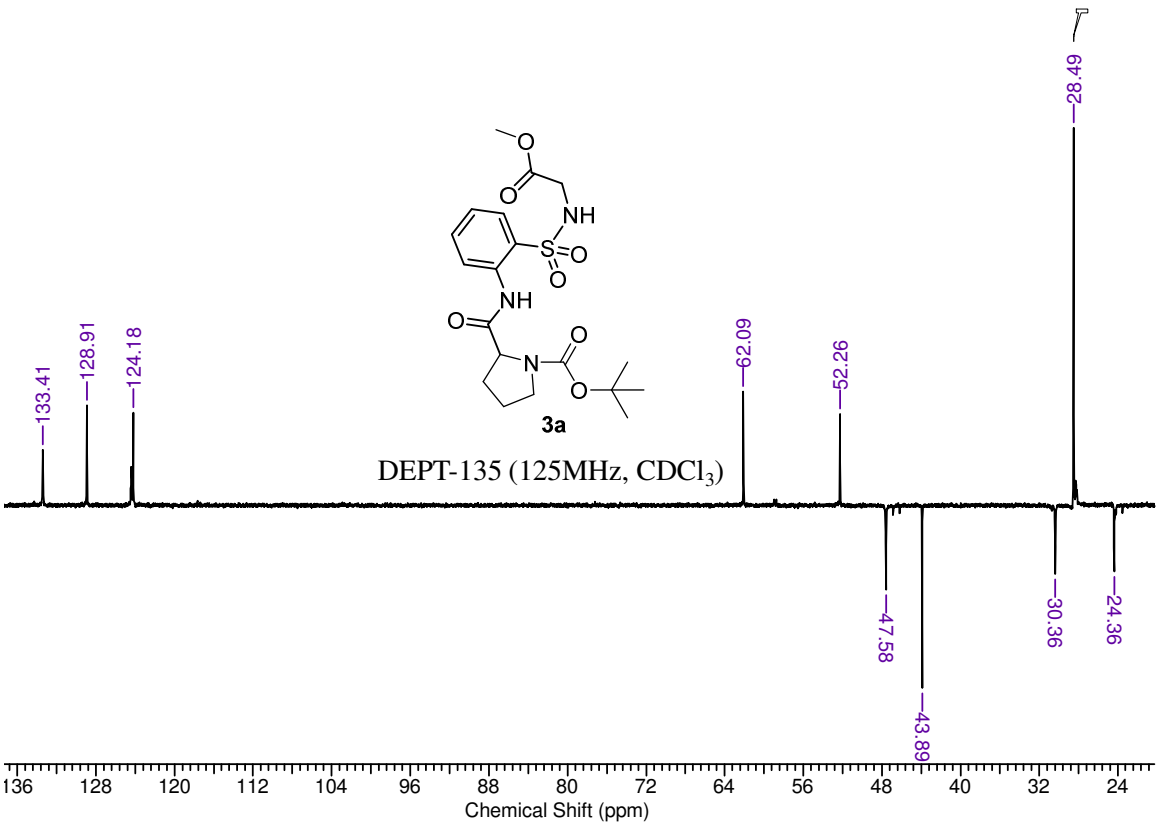

CHLOROFORM-d
77.25
77.00
76.74
28.57
25.53
25.02
173.12
172.07
170.85
168.27
156.47
134.69
134.22
133.92
129.84
129.68
125.86
124.95
81.89
57.94
57.66
46.13
45.49
6
^{13}C NMR(125MHz, CDCl$_3$)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
Chemical Shift (ppm)


28.57
25.57
25.01
26.14
134.25
133.93
129.74
126.29
125.88
124.96
46.13
45.52
6
DEPT-135 (125MHz, CDCl$_3$)
136 128 120 112 104 96 88 80 72 64 56 48 40 32 24
Chemical Shift (ppm)



3a

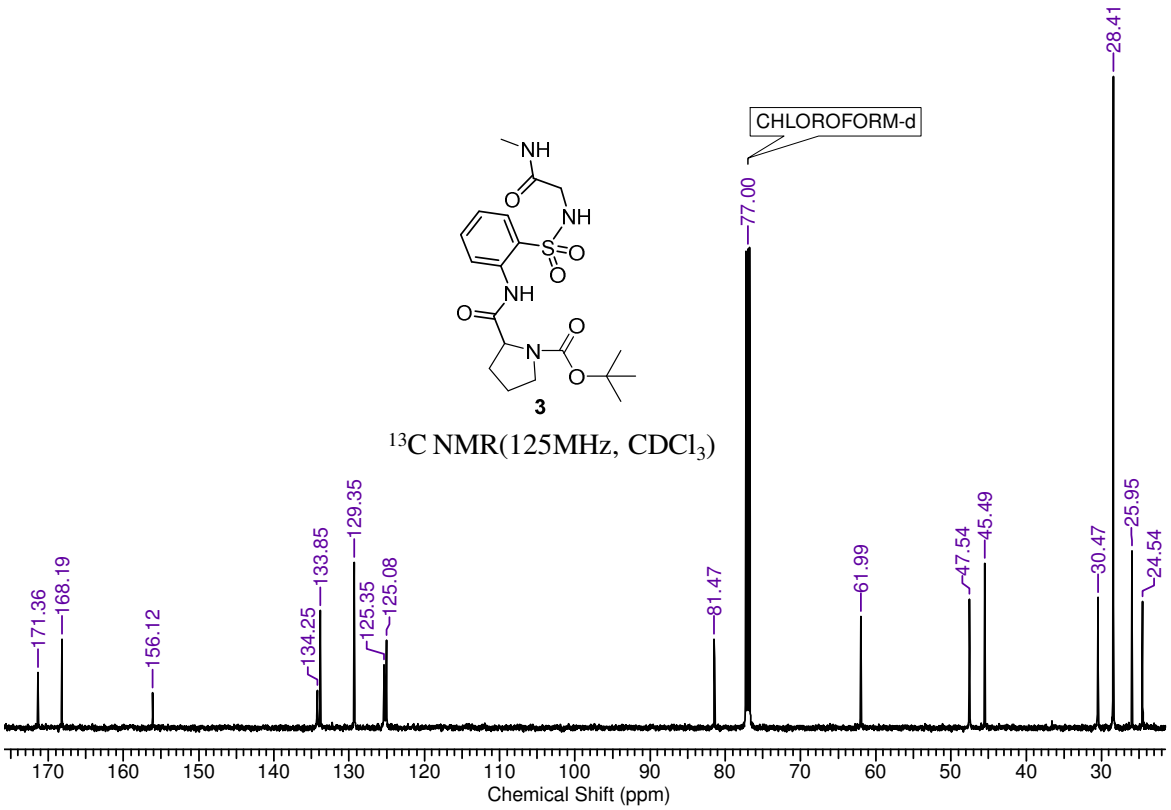
^{13}C NMR(125MHz, $CDCl_3$)



3a

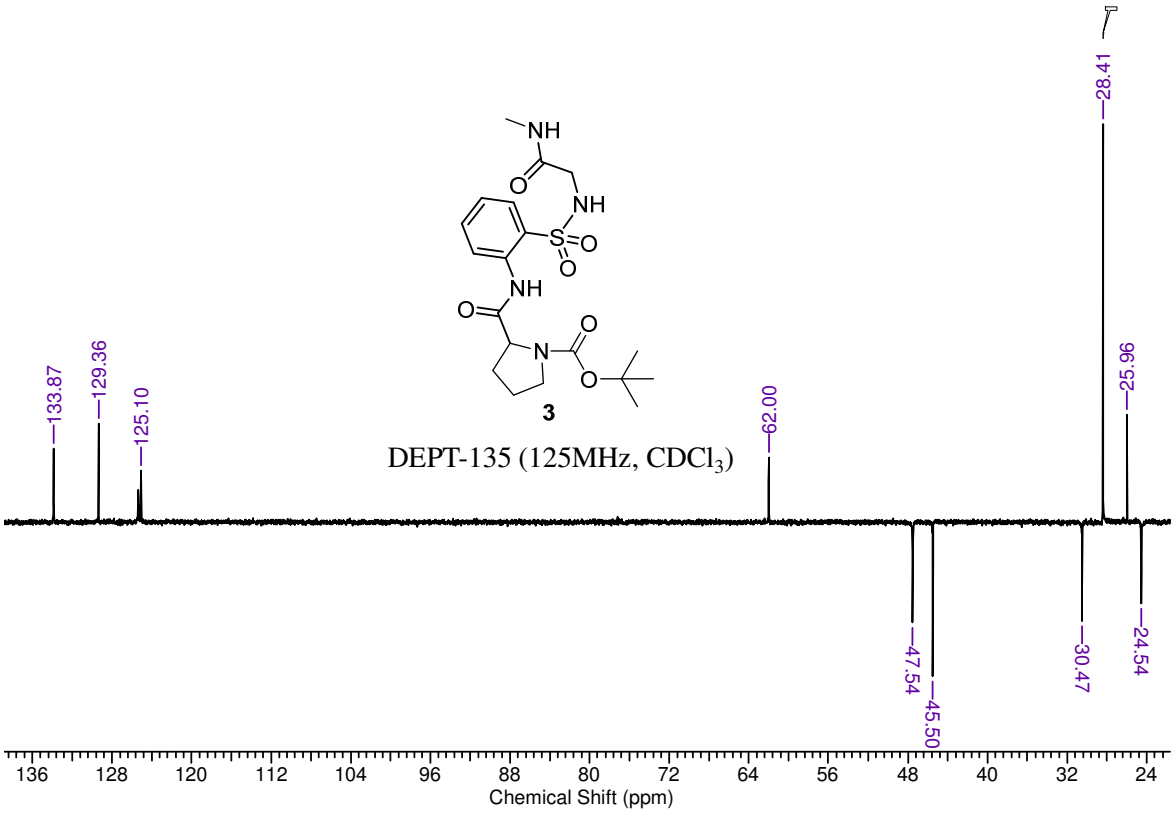
DEPT-135 (125MHz, $CDCl_3$)

Note: The stereochemistry of prolines in **3a** is 'S'



3

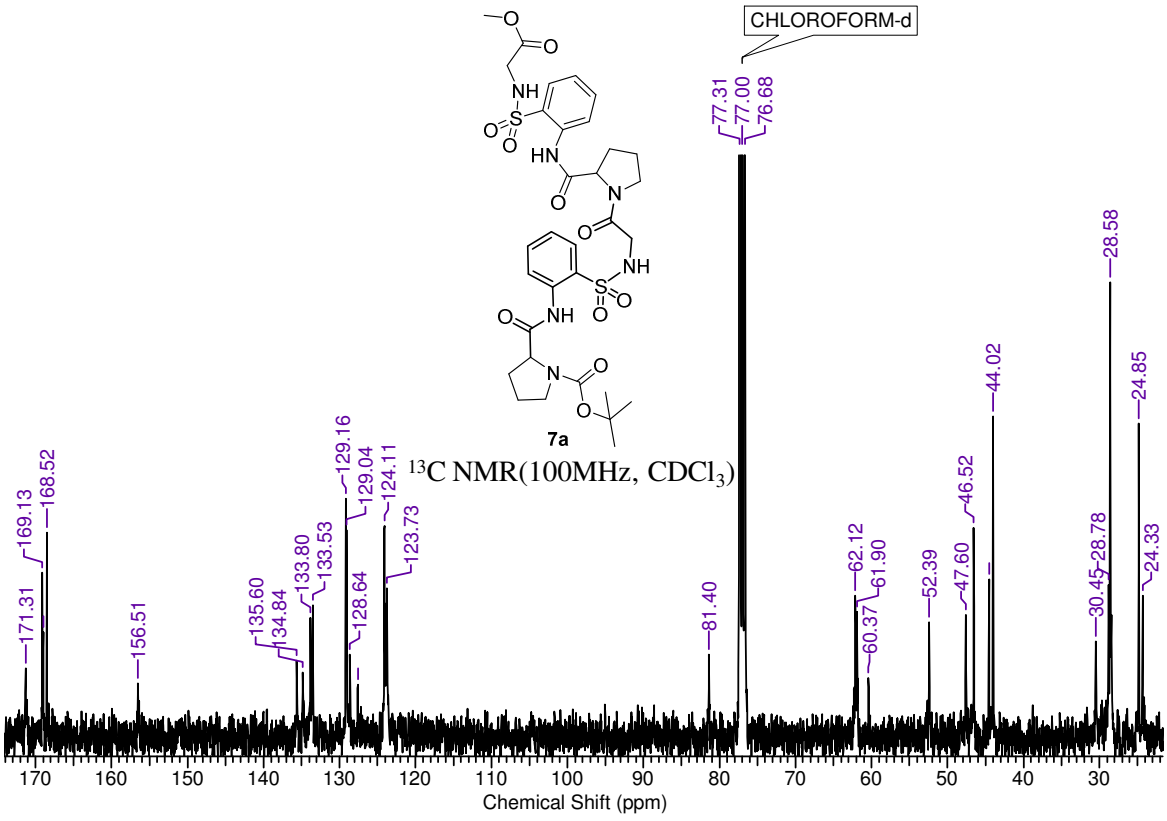
^{13}C NMR(125MHz, $CDCl_3$)

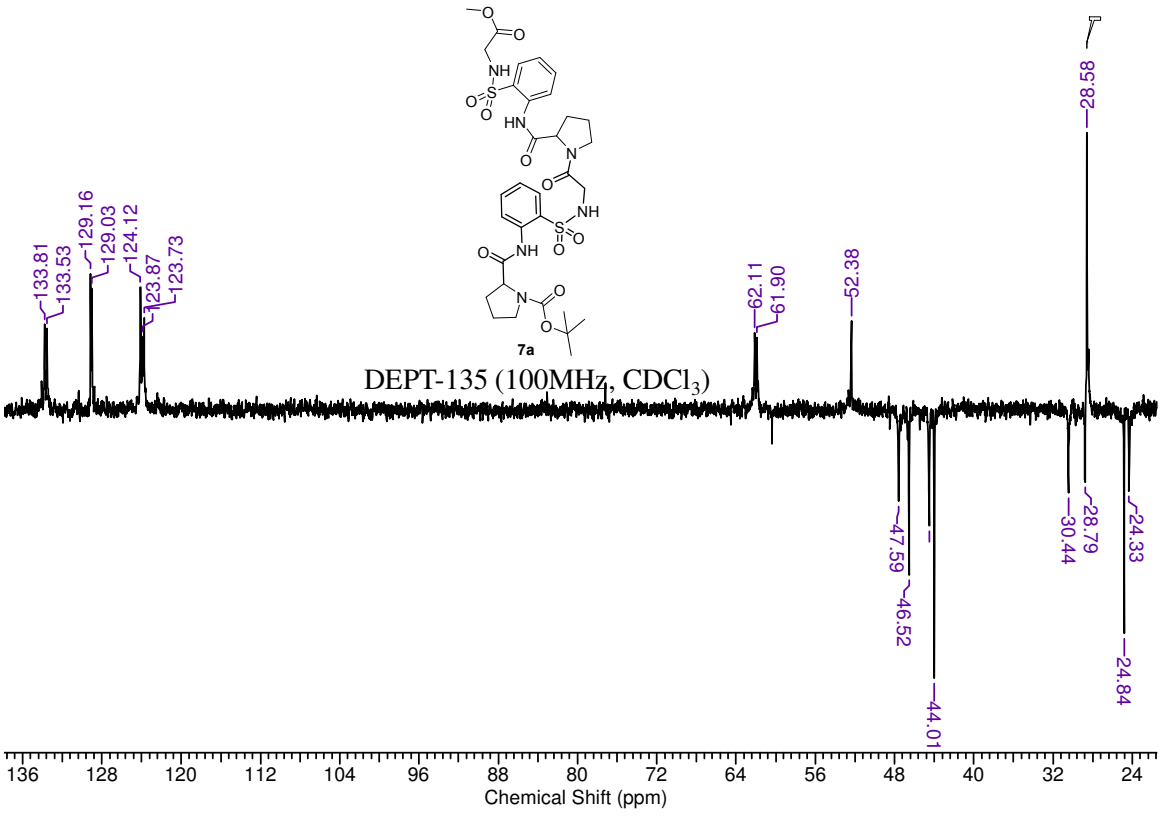


3

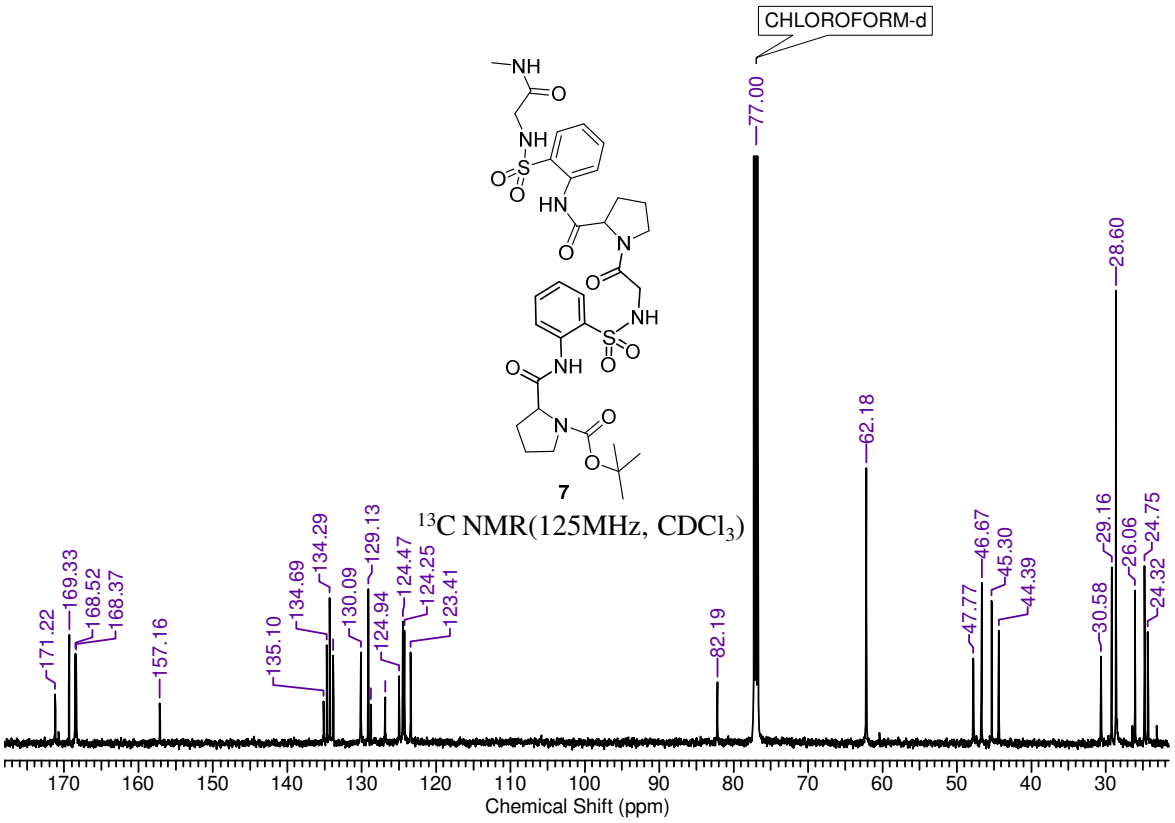
DEPT-135 (125MHz, $CDCl_3$)

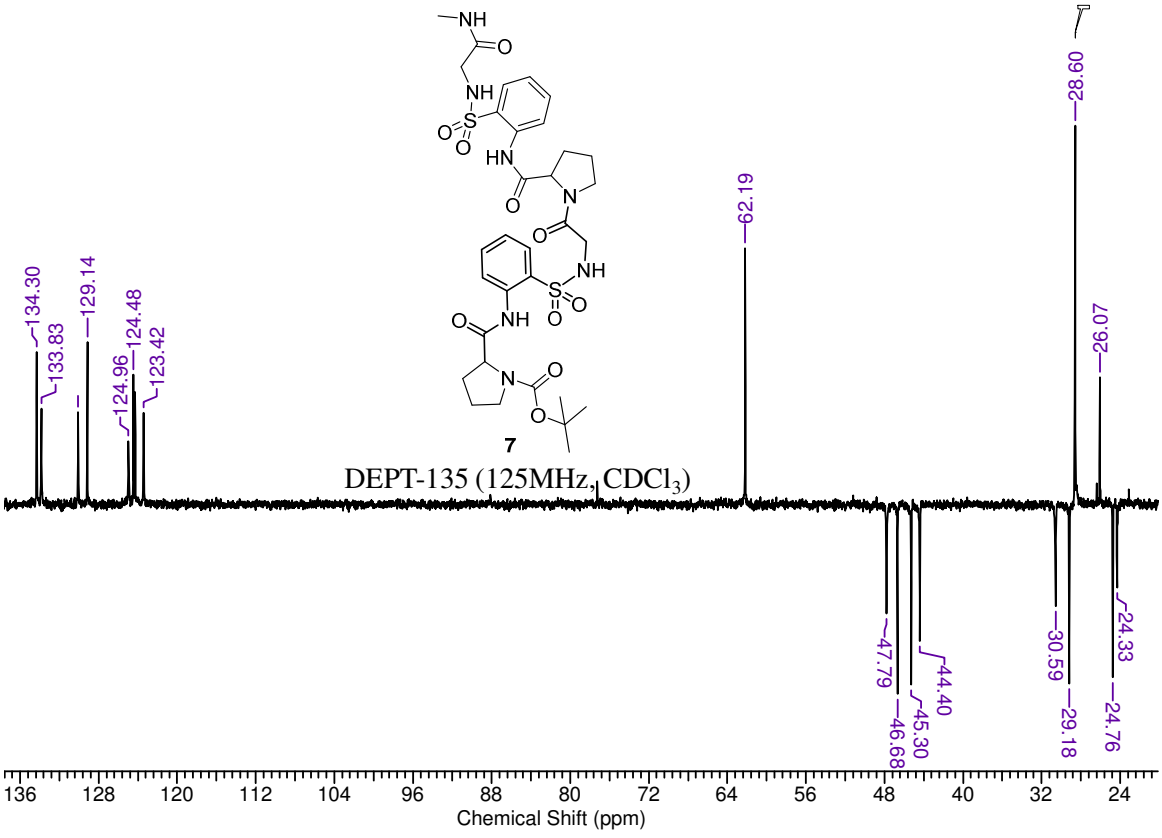
Note: The stereochemistry of prolines in **3** is 'S'



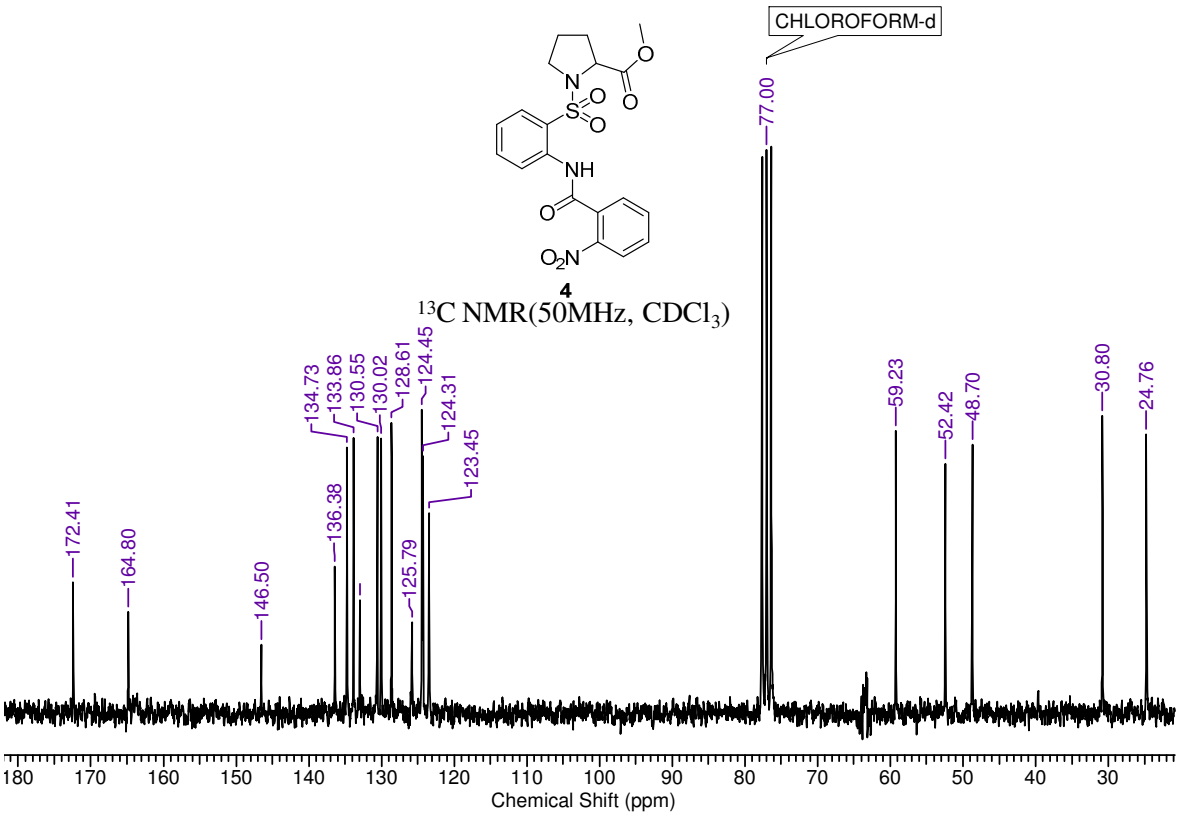


Note: The stereochemistry of prolines in **7a** is 'S'



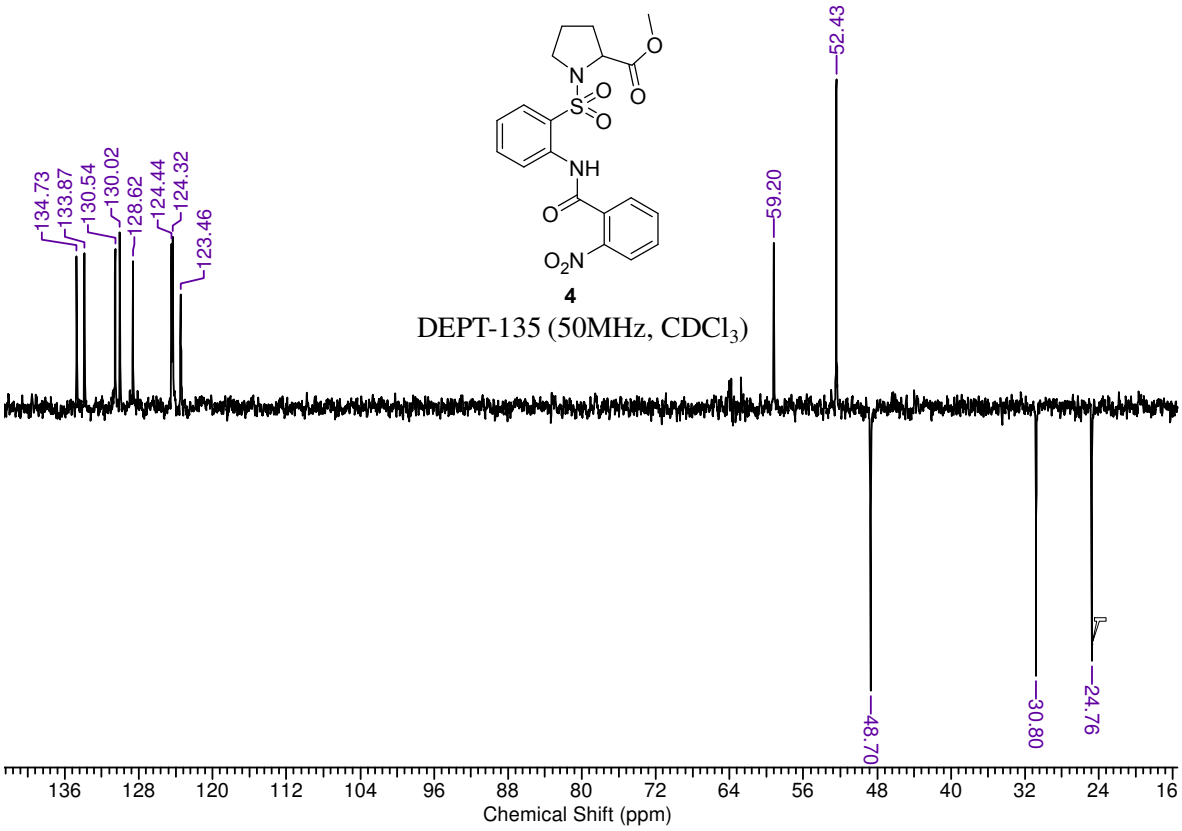


Note: The stereochemistry of prolines in **7** is 'S'



4

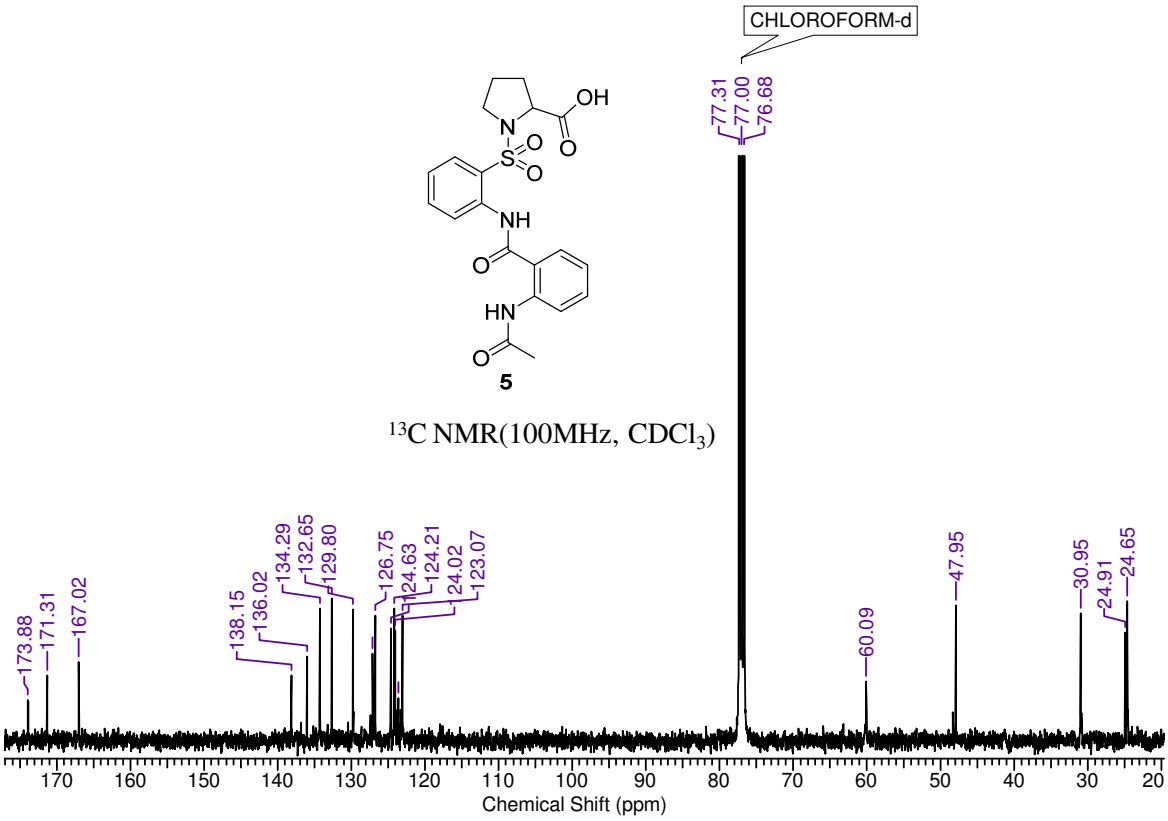
^{13}C NMR(50MHz, $CDCl_3$)



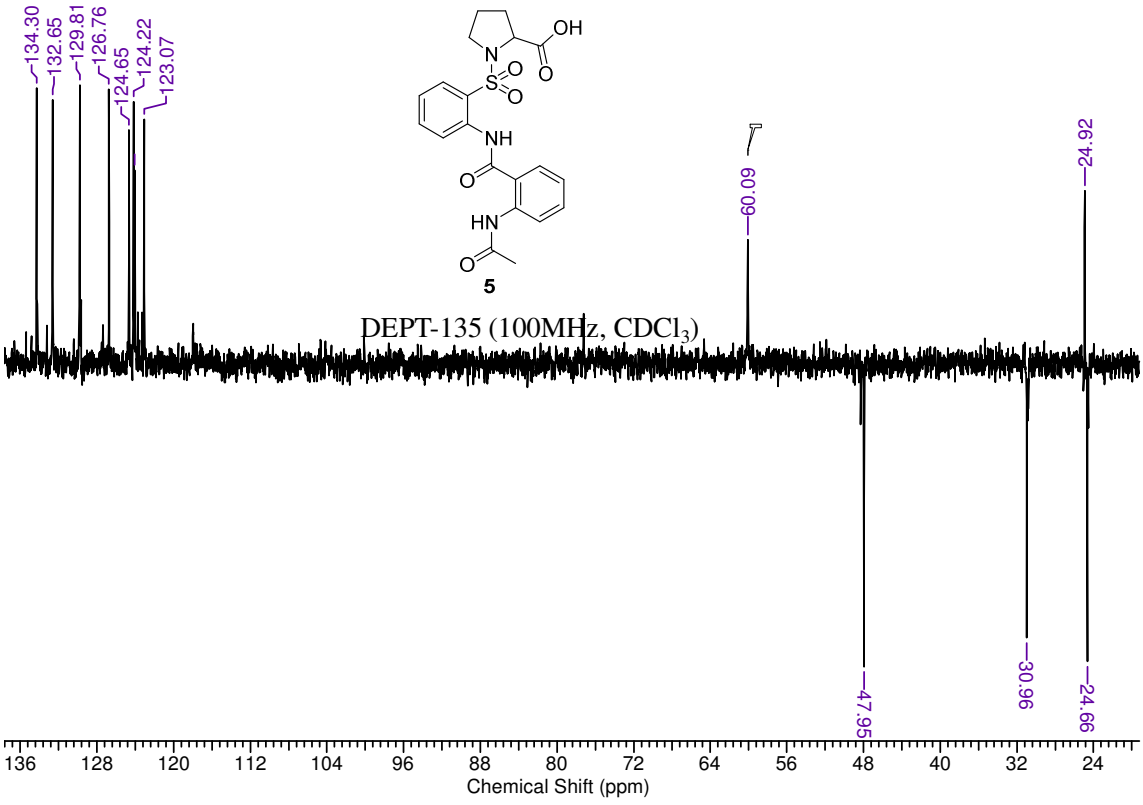
4

DEPT-135 (50MHz, $CDCl_3$)

Note: The stereochemistry of prolines in **4** is 'S'

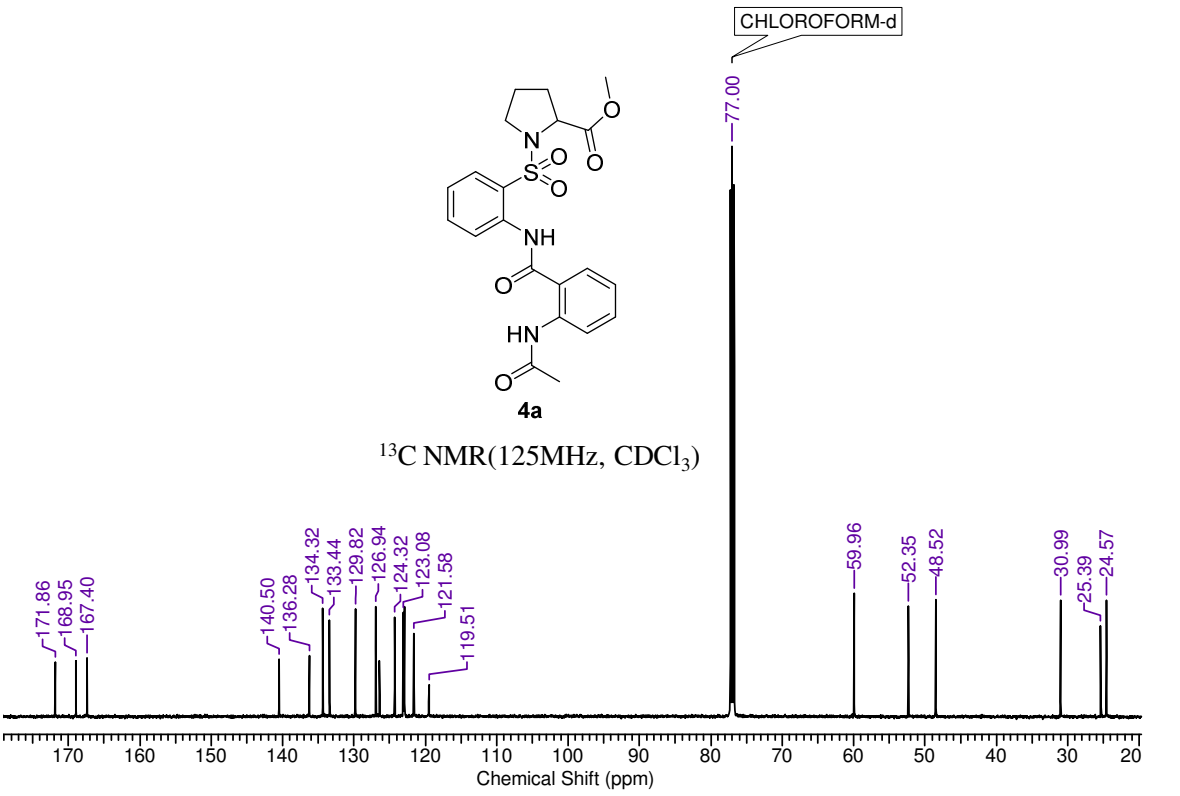


^{13}C NMR(100MHz, $CDCl_3$)



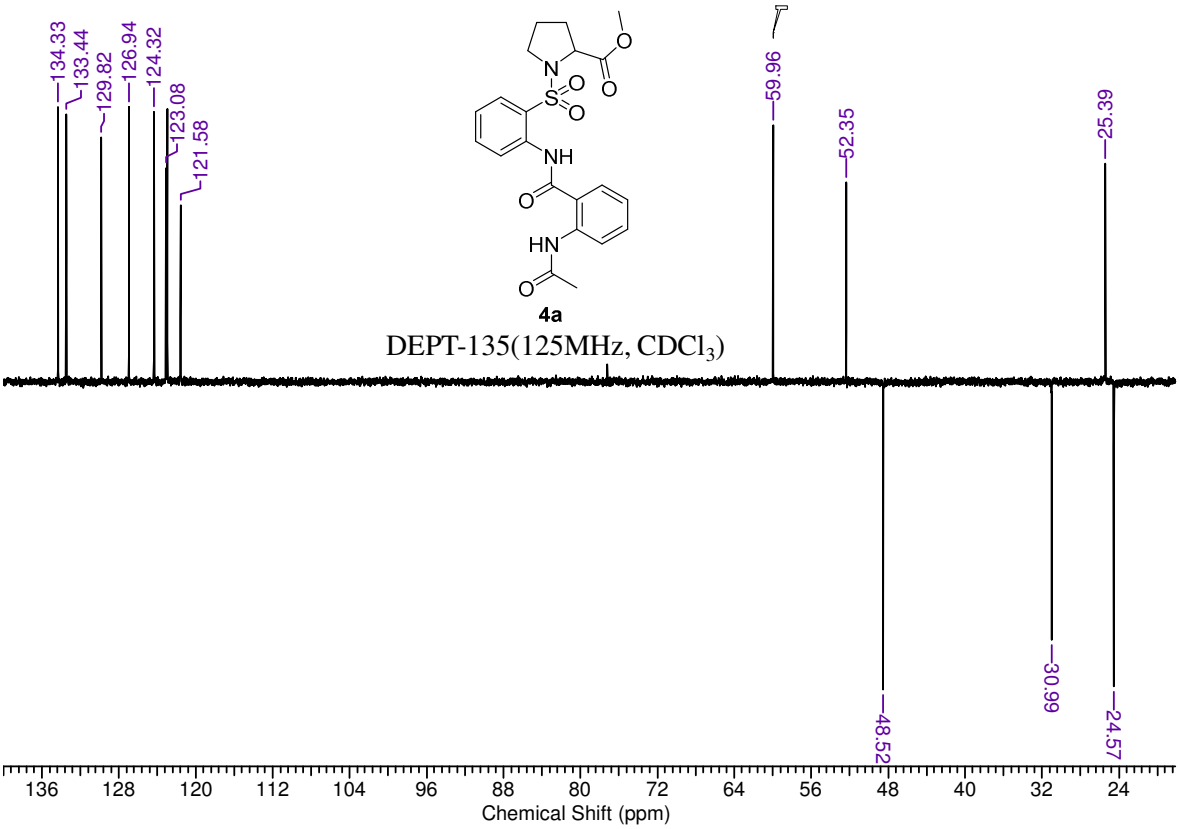
DEPT-135 (100MHz, $CDCl_3$)

Note: The stereochemistry of prolines in **5** is 'S'



4a

^{13}C NMR(125MHz, $CDCl_3$)



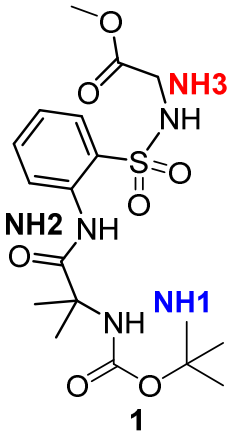
4a

DEPT-135(125MHz, $CDCl_3$)

Note: The stereochemistry of prolines in **4a** is 'S'

Table S1. Titration study of 1 in $CDCl_3$ (20 mmol) with DMSO-d_6 (volume of DMSO-d_6 added at each addition = 5 µl)

Volume of DMSO-d6 added (in µL)	Chemical Shift (in ppm)		
	δNH1	δNH2	δNH3
0	4.95	9.64	6.93
5	5.1	9.63	6.94
10	5.22	9.61	6.96
15	5.35	9.59	6.98
20	5.52	9.56	7
25	5.61	9.55	7.01
30	5.69	9.53	7.01
35	5.76	9.51	7.02
40	5.81	9.51	7.02
45	5.87	9.49	7.01
50	5.93	9.47	6.98



1

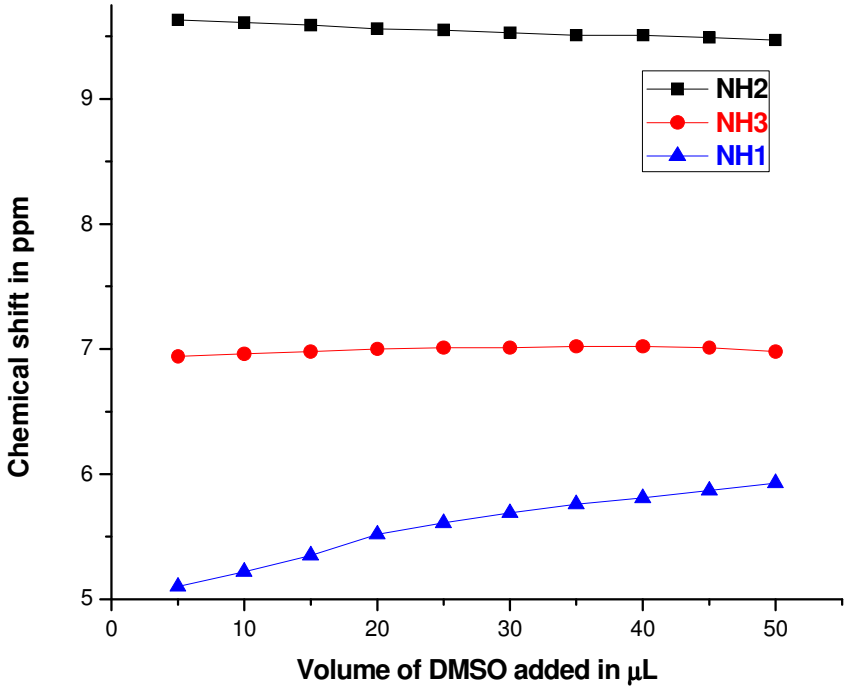
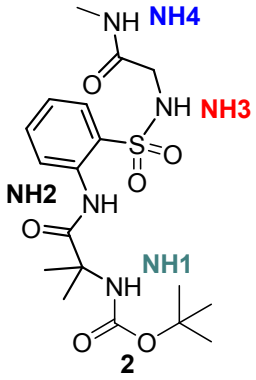


Table S2. Titration study of 2 in $CDCl_3$ (20 mmol) with DMSO-d_6 (volume of DMSO-d_6 added at each addition = 5 µl)

Volume of DMSO-d_6 added (in µL)	Chemical Shift (in ppm)			
	δNH1	δNH2	δNH3	δNH4
0	5.06	9.35	7.04	6.41
5	5.21	9.35	7.04	6.41
10	5.41	9.34	7.06	6.42
15	5.52	9.33	7.06	6.43
20	5.64	9.33	7.07	6.44
25	5.7	9.32	7.07	6.44
30	5.77	9.31	7.08	6.44
35	5.83	9.31	7.08	6.45
40	5.92	9.3	7.08	6.46
45	5.96	9.3	7.08	6.46
50	6.02	9.3	7.08	6.47



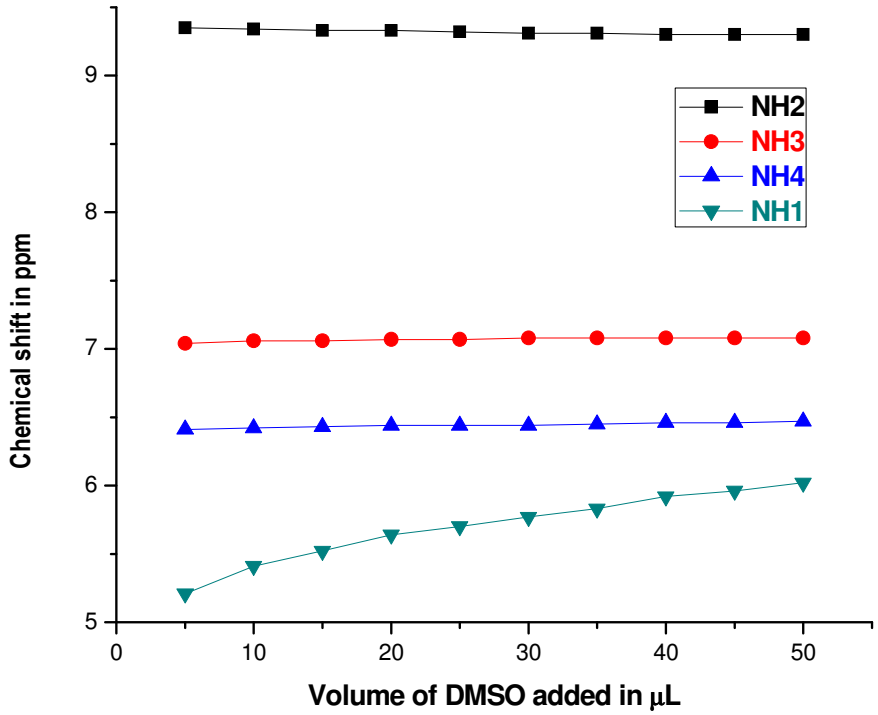
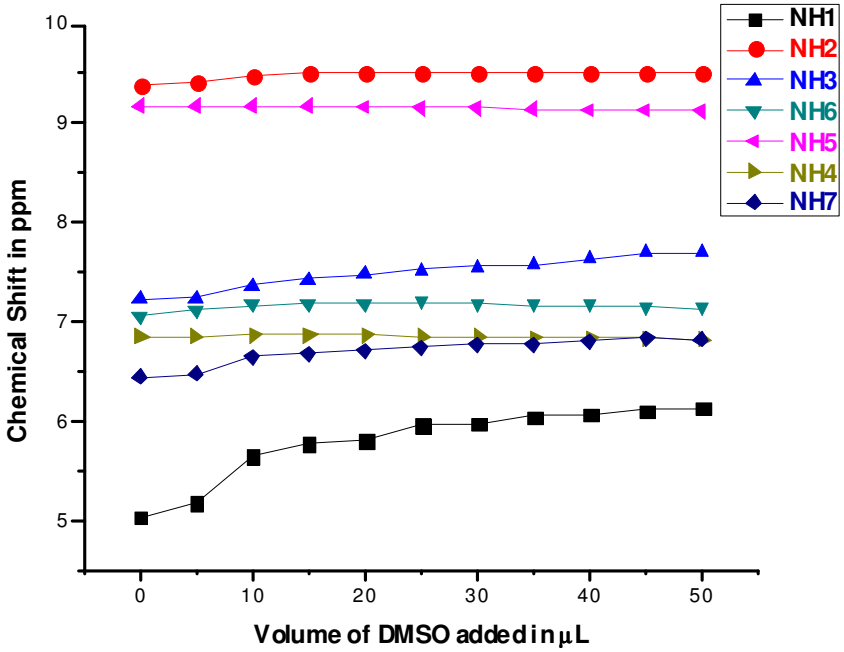
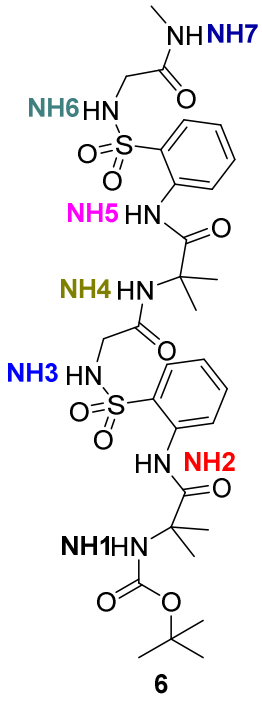


Table S3. Titration study of 6 in $CDCl_3$ (20 mmol) with DMSO-d_6 (volume of DMSO-d_6 added at each addition = 5 µl)

Volume of DMSO- d_6 added in µL	Chemical Shift in ppm						
	δNH1	δNH2	δNH3	δNH4	δNH5	δNH6	δNH7
0	5.04	9.39	7.24	7.06	9.18	6.86	6.45
5	5.18	9.41	7.25	7.13	9.18	6.86	6.48
10	5.65	9.49	7.37	7.17	9.18	6.87	6.65
15	5.77	9.5	7.43	7.19	9.18	6.87	6.69
20	5.81	9.5	7.47	7.19	9.17	6.87	6.72
25	5.96	9.51	7.53	7.2	9.16	6.86	6.75
30	5.98	9.51	7.56	7.18	9.16	6.86	6.77
35	6.05	9.52	7.58	7.17	9.15	6.85	6.78
40	6.07	9.51	7.63	7.17	9.14	6.84	6.8
45	6.11	9.51	7.69	7.15	9.14	6.84	6.84

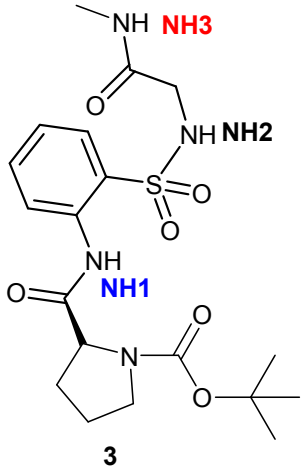




6

Table S4. Titration study of 3 in $CDCl_3$ (20 mmol) with DMSO-d_6 (volume of DMSO-d_6 added at each addition = 5 µl)

Volume of DMSO-d_6 added (in µL)	Chemical Shift (in ppm)		
	δNH1	δNH2	δNH3
5	9.26	7.17	6.5
10	9.26	7.17	6.51
15	9.26	7.17	6.51
20	9.27	7.17	6.51
25	9.27	7.18	6.52
30	9.27	7.18	6.53
35	9.28	7.18	6.54
40	9.28	7.18	6.54
45	9.28	7.18	6.55
50	9.29	7.19	6.56



3

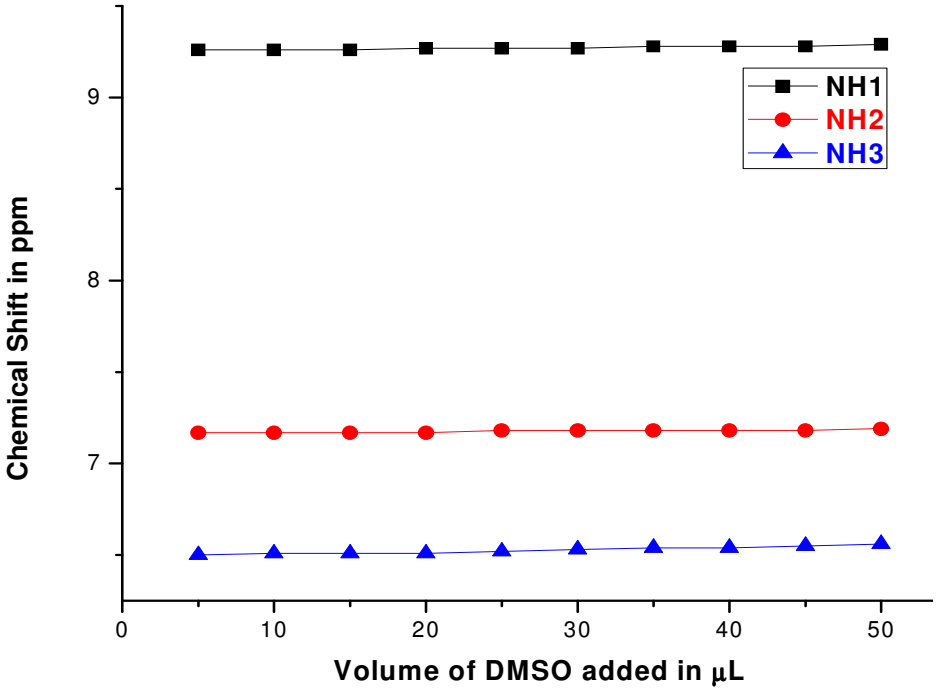
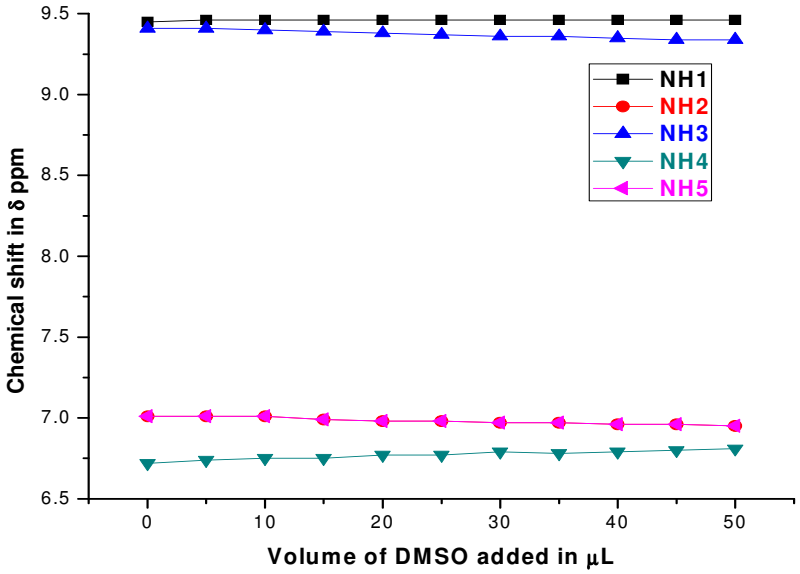


Table S5. Titration study of 7 in $CDCl_3$ (20 mmol) with DMSO-d_6 (volume of DMSO-d_6 added at each addition = 5 µl)

Volume of DMSO-d_6 added (in µL)	Chemical Shift (in ppm)				
	δNH1	δNH2	δNH3	δNH4	δNH5
5	9.45	7.01	9.41	6.72	7.01
10	9.46	7.01	9.41	6.74	7.01
15	9.46	7.01	9.4	6.75	7.01
20	9.46	6.99	9.39	6.75	6.99
25	9.46	6.98	9.38	6.77	6.98
30	9.46	6.98	9.37	6.77	6.98
35	9.46	6.97	9.36	6.79	6.97
40	9.46	6.97	9.36	6.78	6.97
45	9.46	6.96	9.35	6.79	6.96
50	9.46	6.96	9.34	6.8	6.96



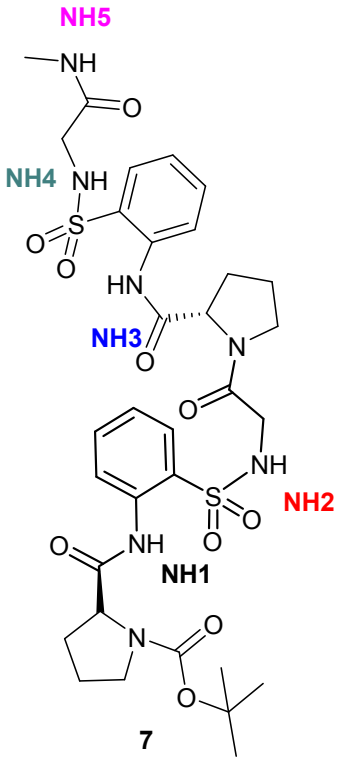
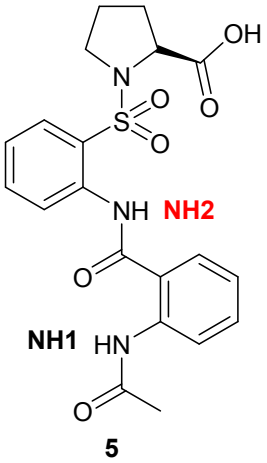


Table S6. Titration study of 5 in $CDCl_3$ (20 mmol) with DMSO-d_6 (volume of DMSO-d_6 added at each addition = 5 µl)

Volume of DMSO-d_6 added (in µL)	Chemical Shift (in ppm)	
	δNH1	δNH2
5	10.9	10.42
10	10.94	10.44
15	10.96	10.44
20	10.97	10.43
25	10.97	10.42
30	10.96	10.41
35	10.95	10.4
40	10.94	10.38
45	10.92	10.36
50	10.91	10.35



5

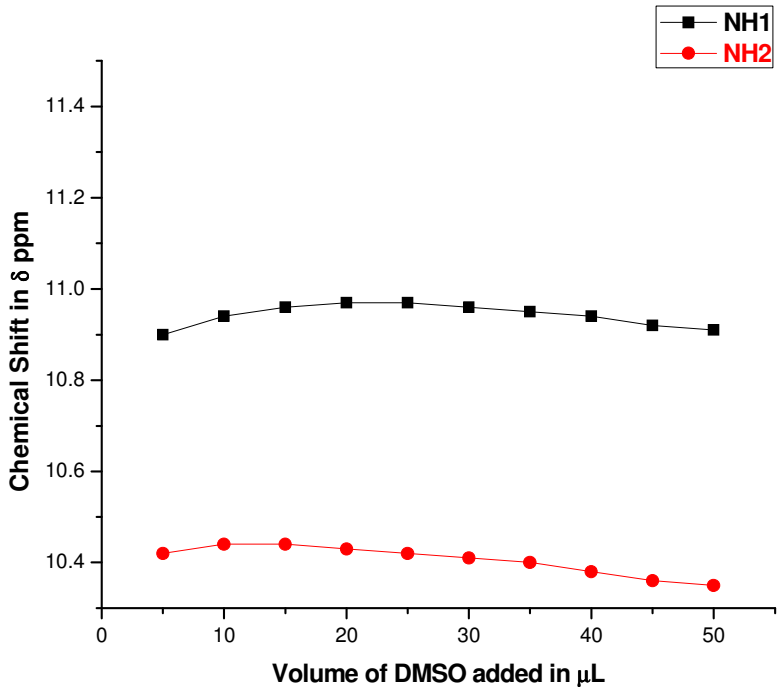
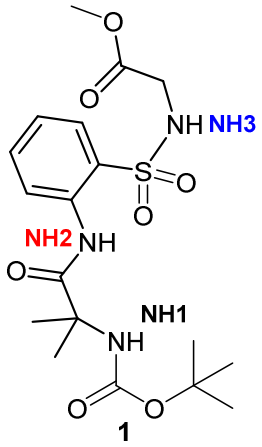


Table S7. Variable temperature study of 1 (20 mmol, 400 MHz, $CDCl_3$).

Temperature (in °K)	Chemical shift in ppm		
	δNH1	δNH2	δNH3
268	5.06	9.64	7.01
273	4.99	9.64	7
278	4.97	9.64	6.98
283	4.97	9.64	6.97
288	4.96	9.64	6.96
293	4.95	9.64	6.94
298	4.95	9.64	6.92
303	4.94	9.64	6.9
308	4.94	9.65	6.88
313	4.93	9.65	6.85
318	4.93	9.65	6.82
323	4.92	9.65	6.81



1

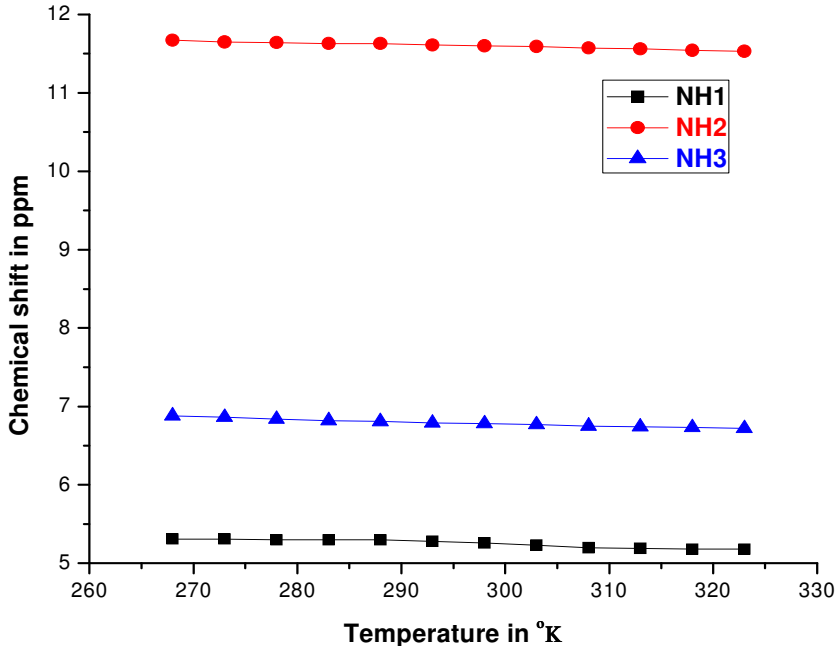
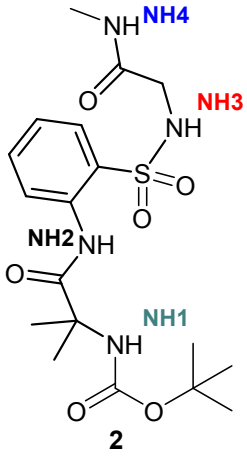


Table S8. Variable temperature study of 2 (20 mmol, 400 MHz, $CDCl_3$).

Temperature (in °K)	Chemical Shift (in ppm)			
	δNH1	δNH2	δNH3	δNH4
268	5.1	9.33	7.14	6.48
273	5.09	9.34	7.13	6.48
278	5.09	9.34	7.11	6.47
283	5.08	9.34	7.09	6.45
288	5.07	9.35	7.07	6.43
293	5.06	9.35	7.05	6.42
293	5.06	9.35	7.03	6.4
303	5.05	9.36	7	6.39
308	5.04	9.36	6.99	6.38
313	5.03	9.37	6.96	6.36
318	5.03	9.37	6.95	6.35
323	5.02	9.38	6.92	6.34



2

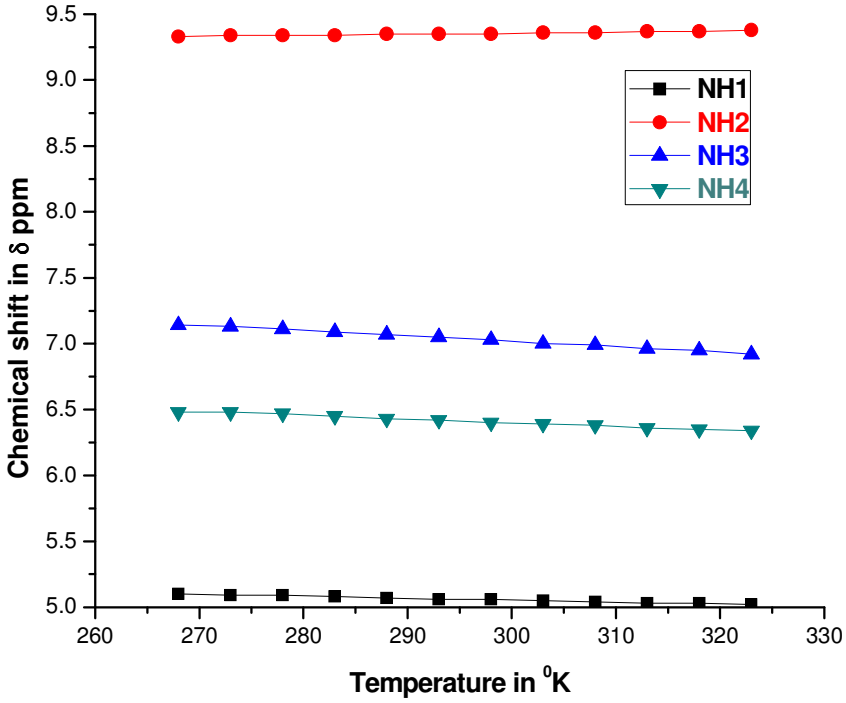
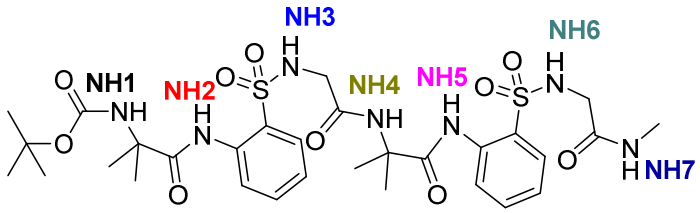


Table S9. Variable temperature study of 6 (10 mmol, 400 MHz, $CDCl_3$).



6

Temperature (in °K)	Chemical Shift in ppm						
	δNH1	δNH2	δNH3	δNH4	δNH5	δNH6	δNH7
268	5.11	9.4	7.27	7.13	9.2	6.92	6.62
273	5.1	9.4	7.27	7.13	9.19	6.91	6.6
278	5.1	9.4	7.26	7.12	9.19	6.9	6.58
283	5.09	9.4	7.26	7.11	9.19	6.89	6.56
288	5.09	9.4	7.26	7.1	9.19	6.88	6.53
293	5.08	9.4	7.26	7.09	9.18	6.86	6.5
298	5.08	9.4	7.25	7.08	9.18	6.85	6.48
303	5.07	9.4	7.21	7.08	9.18	6.83	6.46
308	5.07	9.4	7.19	7.06	9.18	6.82	6.43
313	5.06	9.4	7.17	7.05	9.18	6.8	6.41

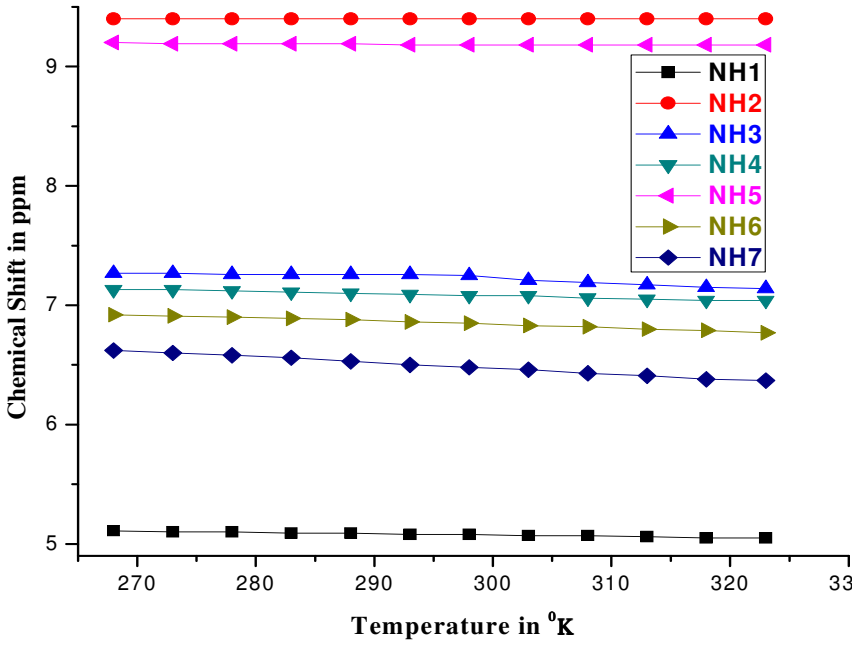
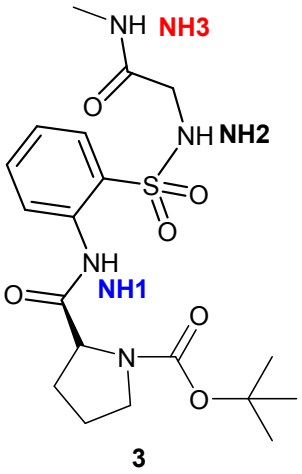
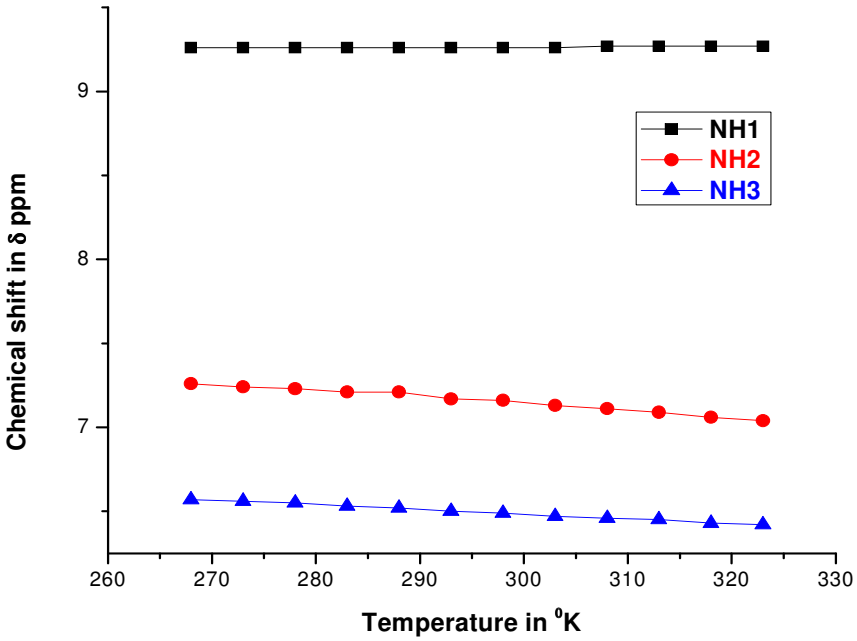


Table S10. Variable temperature of 3 in $CDCl_3$ (20 mmol) with DMSO-d_6 (volume of DMSO-d_6 added at each addition = 5 µl)

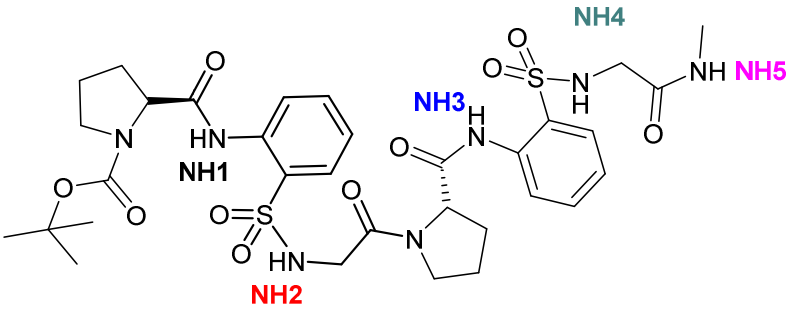
Temperature (in °K)	Chemical shift in ppm		
	δNH1	δNH2	δNH3
268	9.26	7.26	6.57
273	9.26	7.24	6.56
278	9.26	7.23	6.55
283	9.26	7.21	6.53
288	9.26	7.21	6.52
293	9.26	7.17	6.5
298	9.26	7.16	6.49
303	9.26	7.13	6.47
308	9.27	7.11	6.46
313	9.27	7.09	6.45
318	9.27	7.06	6.43
323	9.27	7.04	6.42



3



Variable temperature of 7 in $CDCl_3$ (20 mmol) with DMSO-d_6 (volume of DMSO-d_6 added at each addition = 5 µl)



7

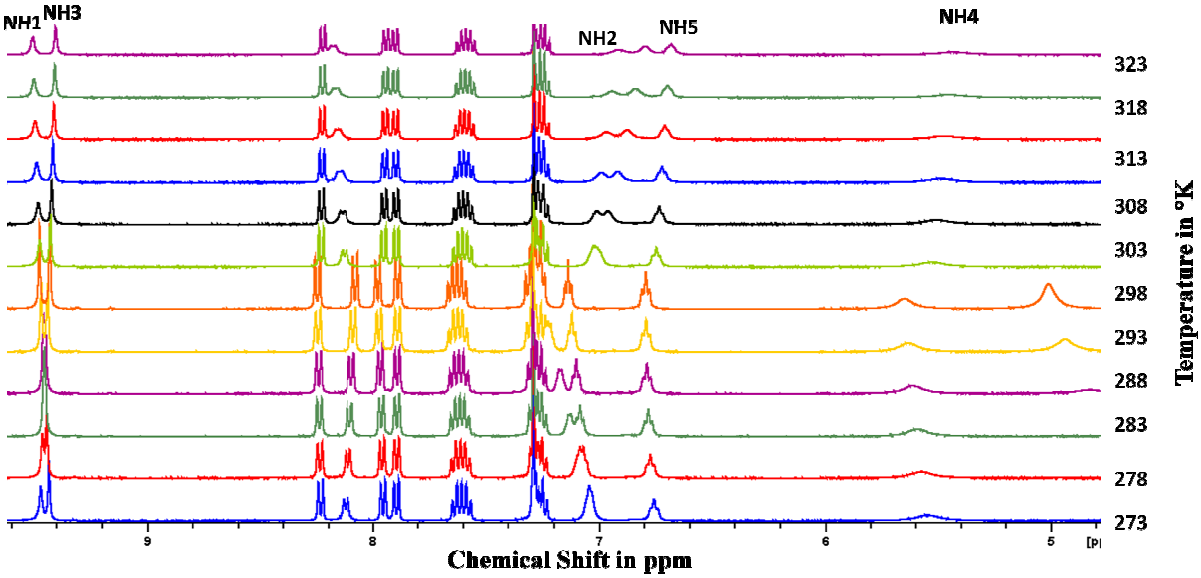
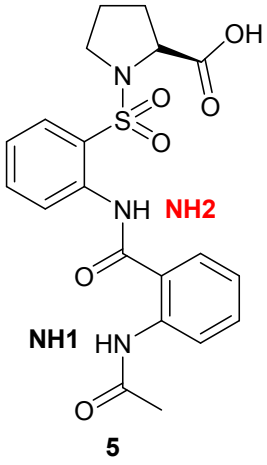


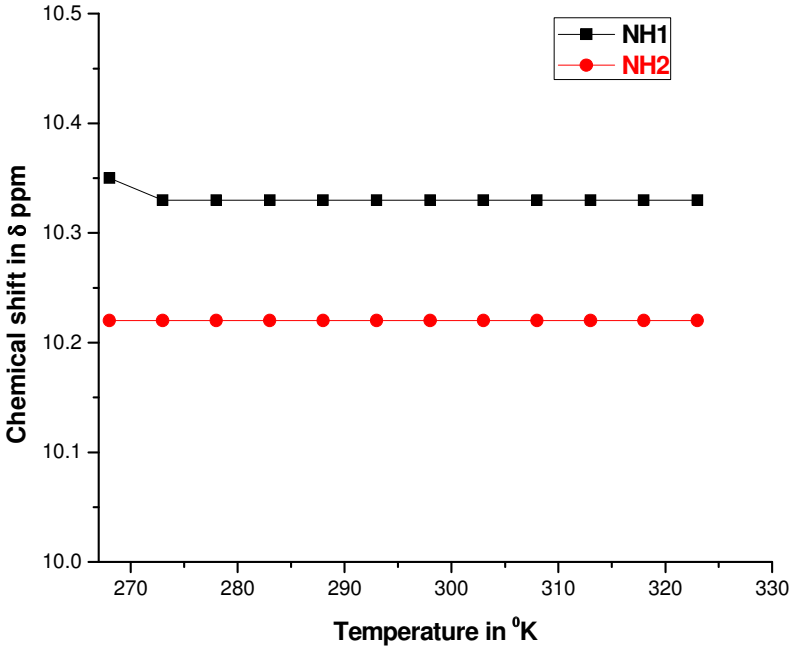
Fig. 3: Stacked plot for variable temperature study of **7**.

Table S11. Variable temperature of 5 in $CDCl_3$ (20 mmol) with DMSO-d_6 (volume of DMSO-d_6 added at each addition = 5 µl)

Temperature in °K	Chemical Shift (in ppm)	
	δNH1	δNH2
268	10.35	10.22
273	10.33	10.22
278	10.33	10.22
283	10.33	10.22
288	10.33	10.22
293	10.33	10.22
298	10.33	10.22
303	10.33	10.22
308	10.33	10.22
313	10.33	10.22
318	10.33	10.22
323	10.33	10.22



5



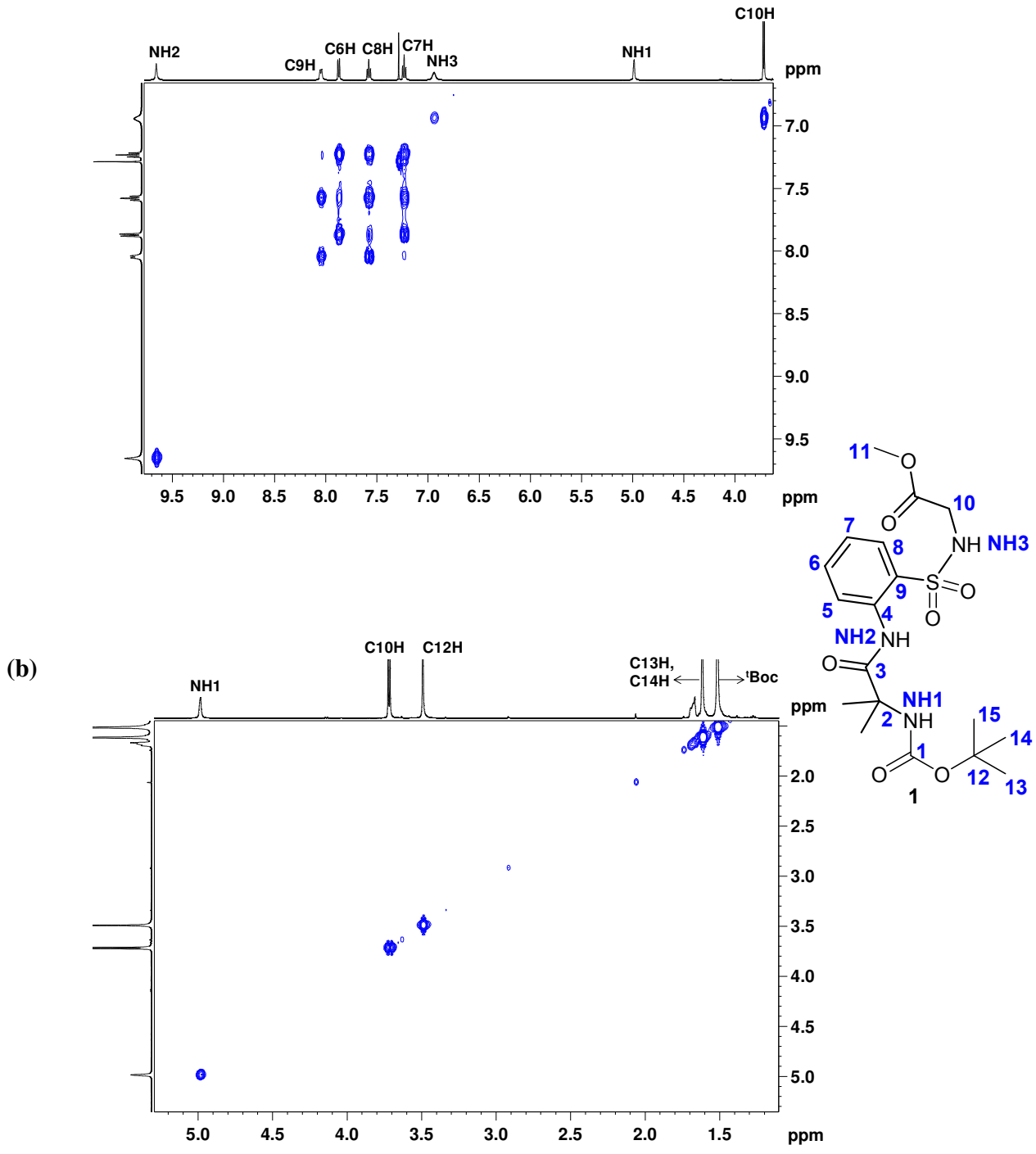


Fig. 4: Partial COSY spectra of **1** (400MHz, $CDCl_3$): aromatic (a) and aliphatic (b) regions.

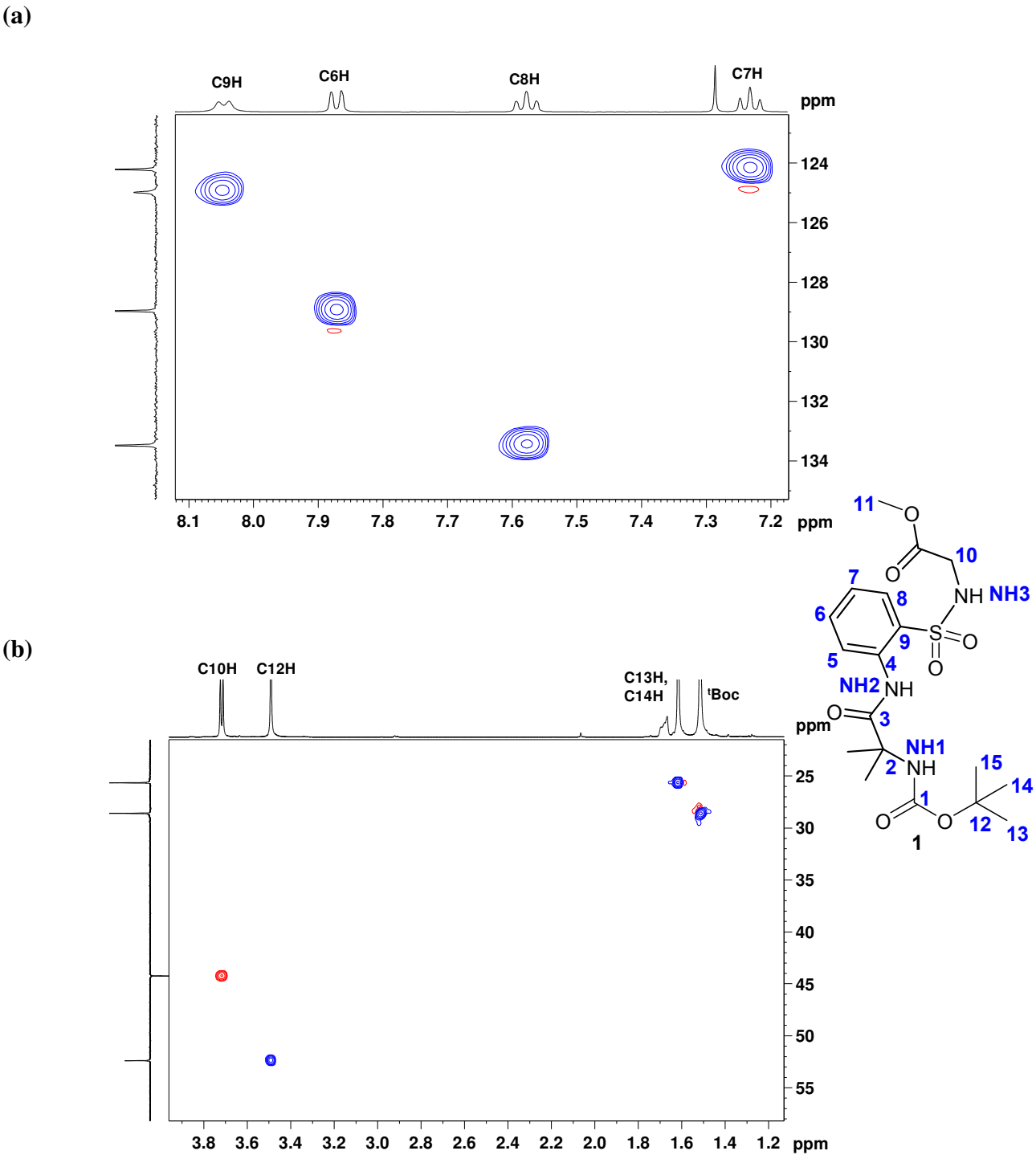


Fig. 5: Partial HSQC spectra of **1** (400MHz, $CDCl_3$): aromatic (a) and aliphatic (b) regions.

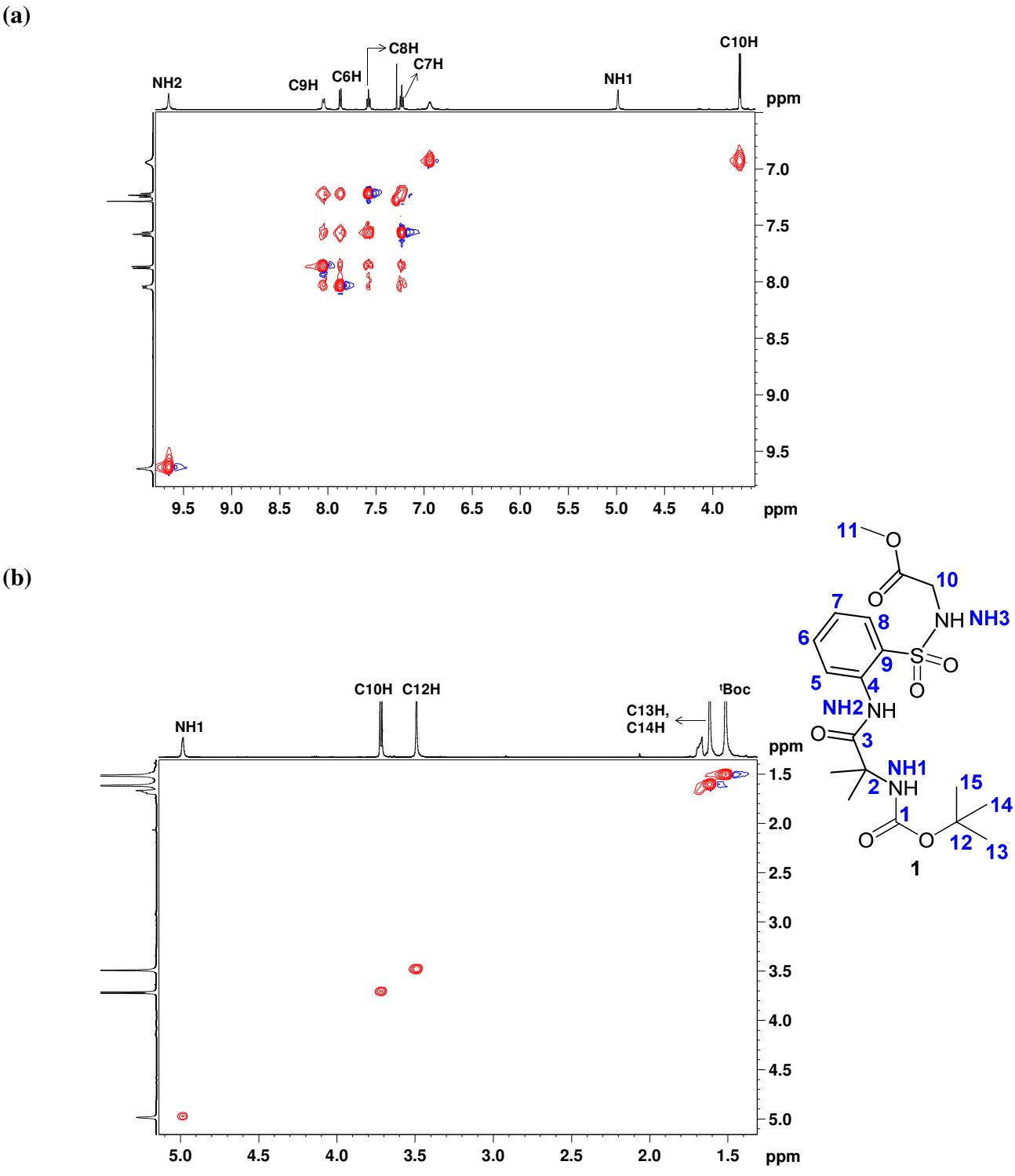


Fig. 6: Partial TOCSY spectra of **1** (400MHz, $CDCl_3$): aromatic (a) and aliphatic (b) regions.

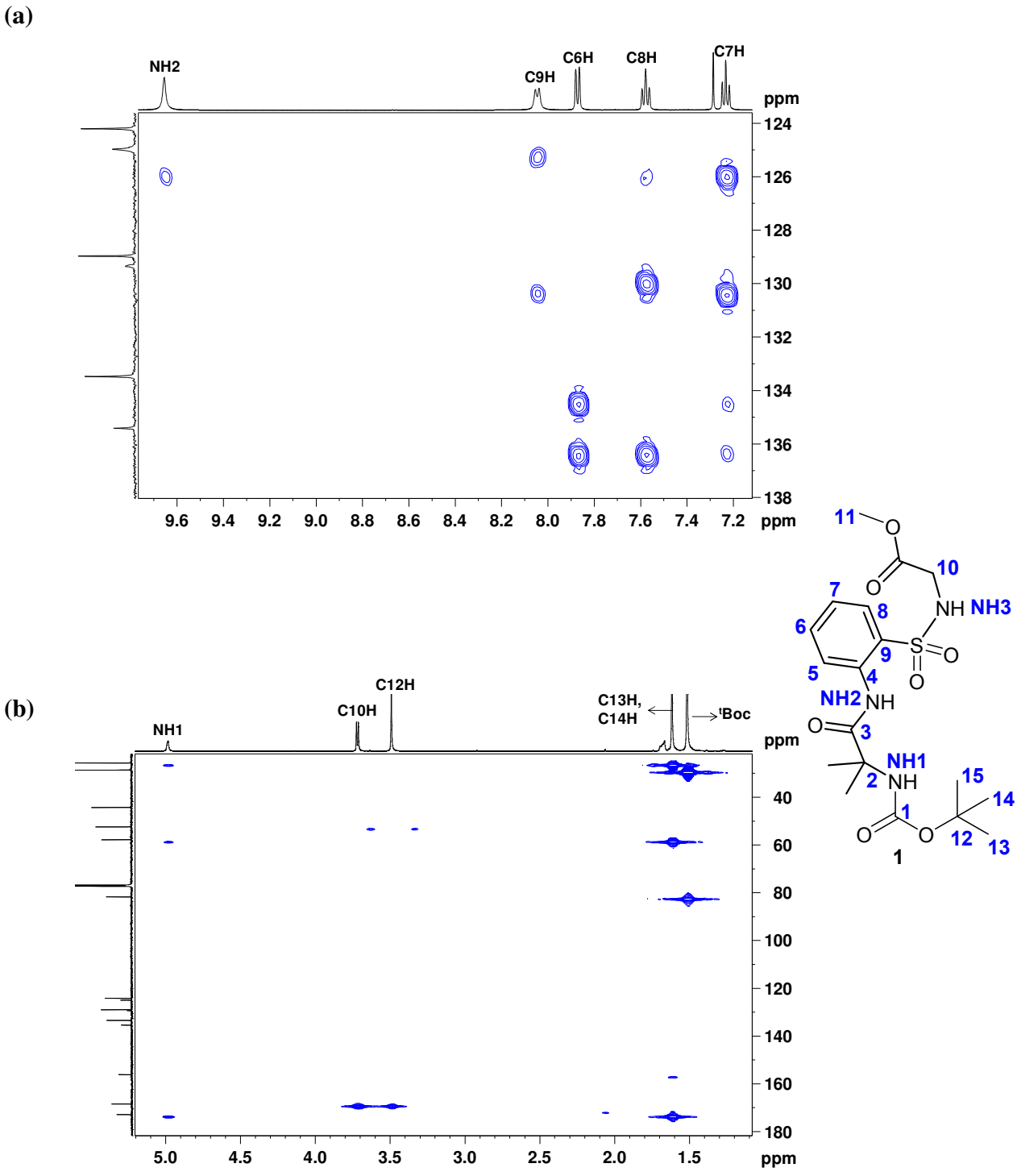


Fig. 7: Partial HMBC spectra of **1** (400MHz, $CDCl_3$): aromatic (a) and aliphatic (b) regions.

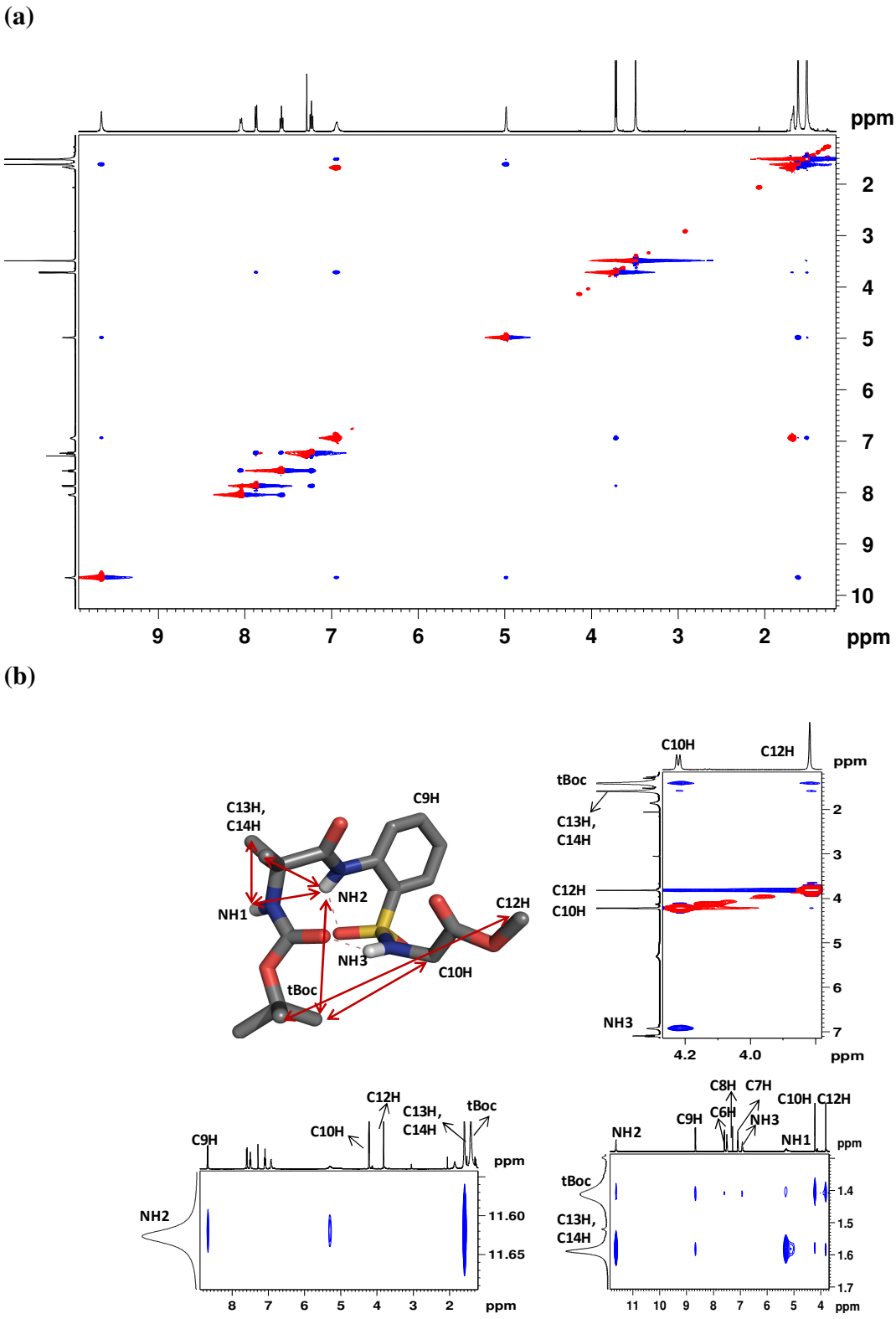


Fig. 8: (a) Full 2D NOESY spectrum of **1** (400MHz, $CDCl_3$) and (b) selected 2D excerpts of **1**.

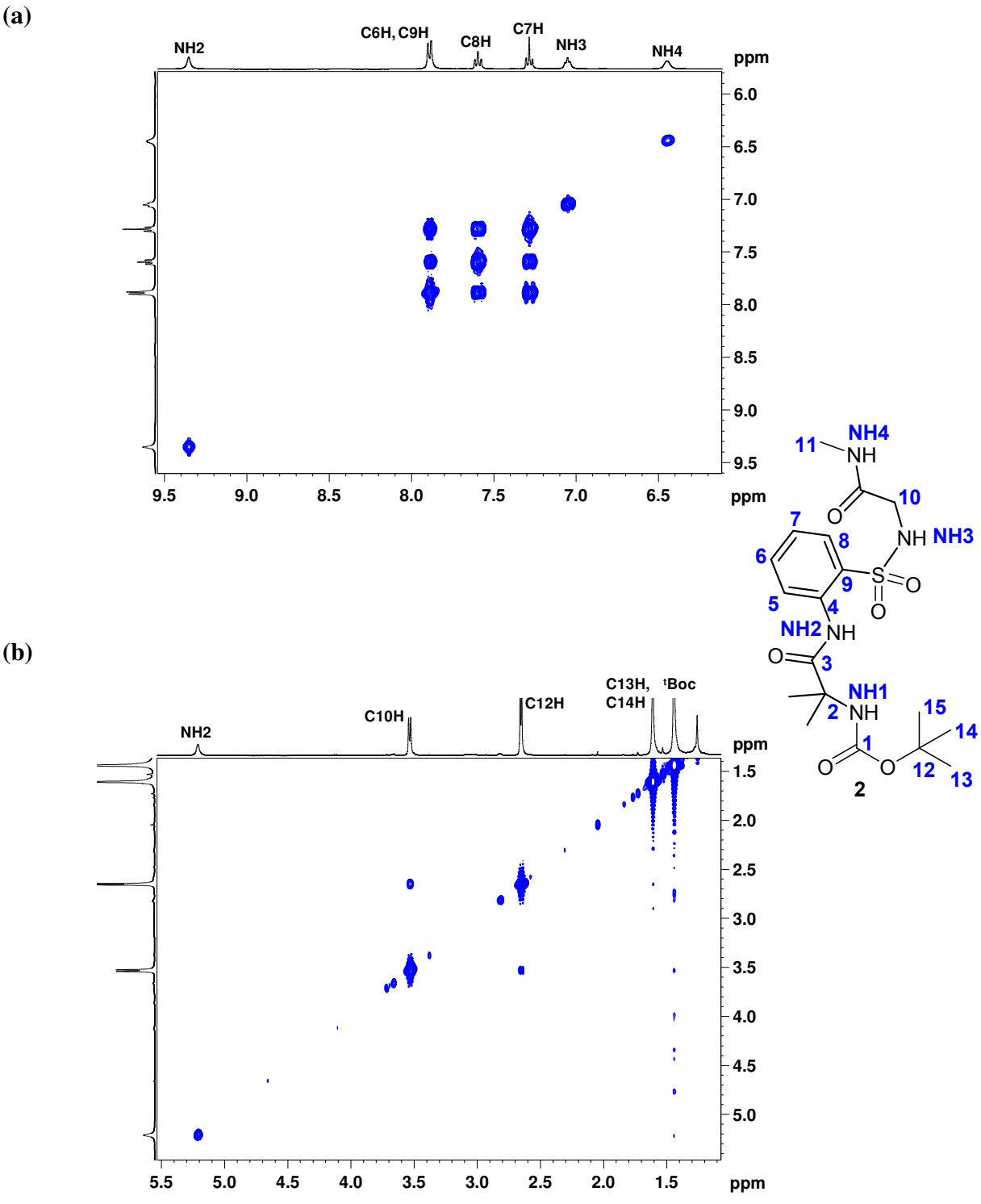


Fig. 9: Partial COSY spectra of **2** (400MHz, $CDCl_3$): aromatic (a) and aliphatic (b) regions.

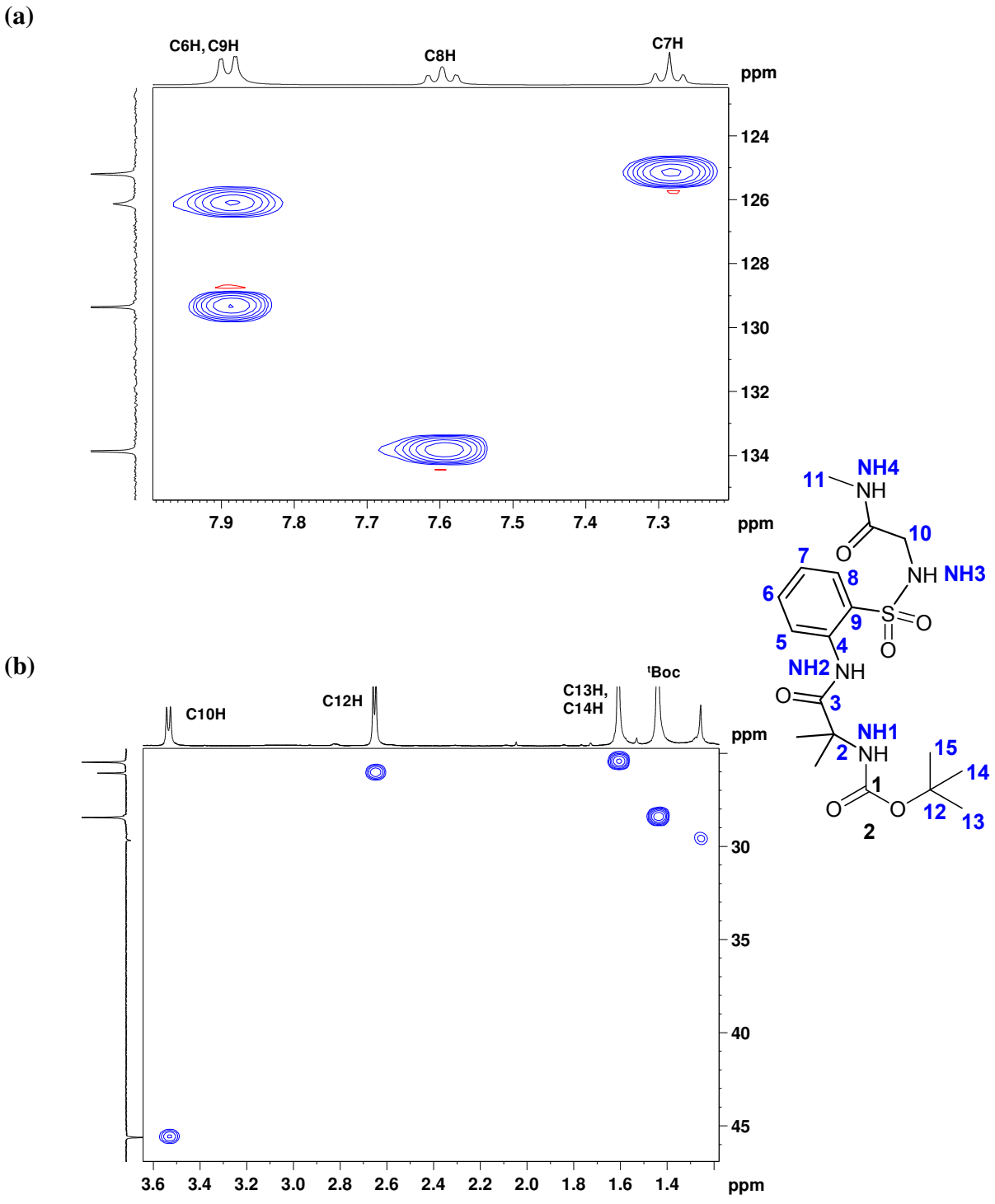


Fig. 10: Partial HSQC spectra of **2** (400MHz, $CDCl_3$): aromatic (a) and aliphatic (b) regions.

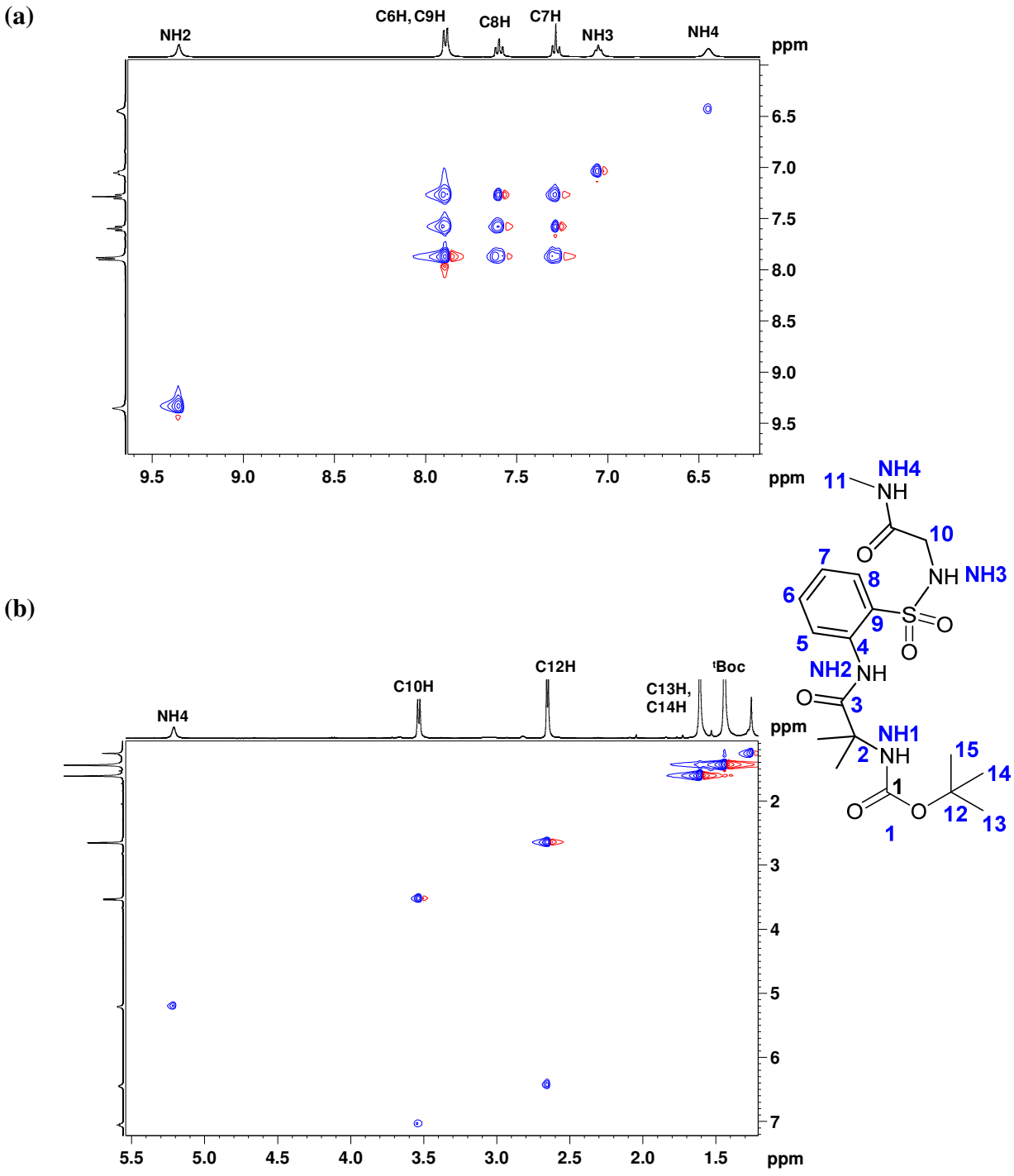


Fig. 11: Partial TOCSY spectra of **2** (400MHz, $CDCl_3$): aromatic (a) and aliphatic (b) regions.

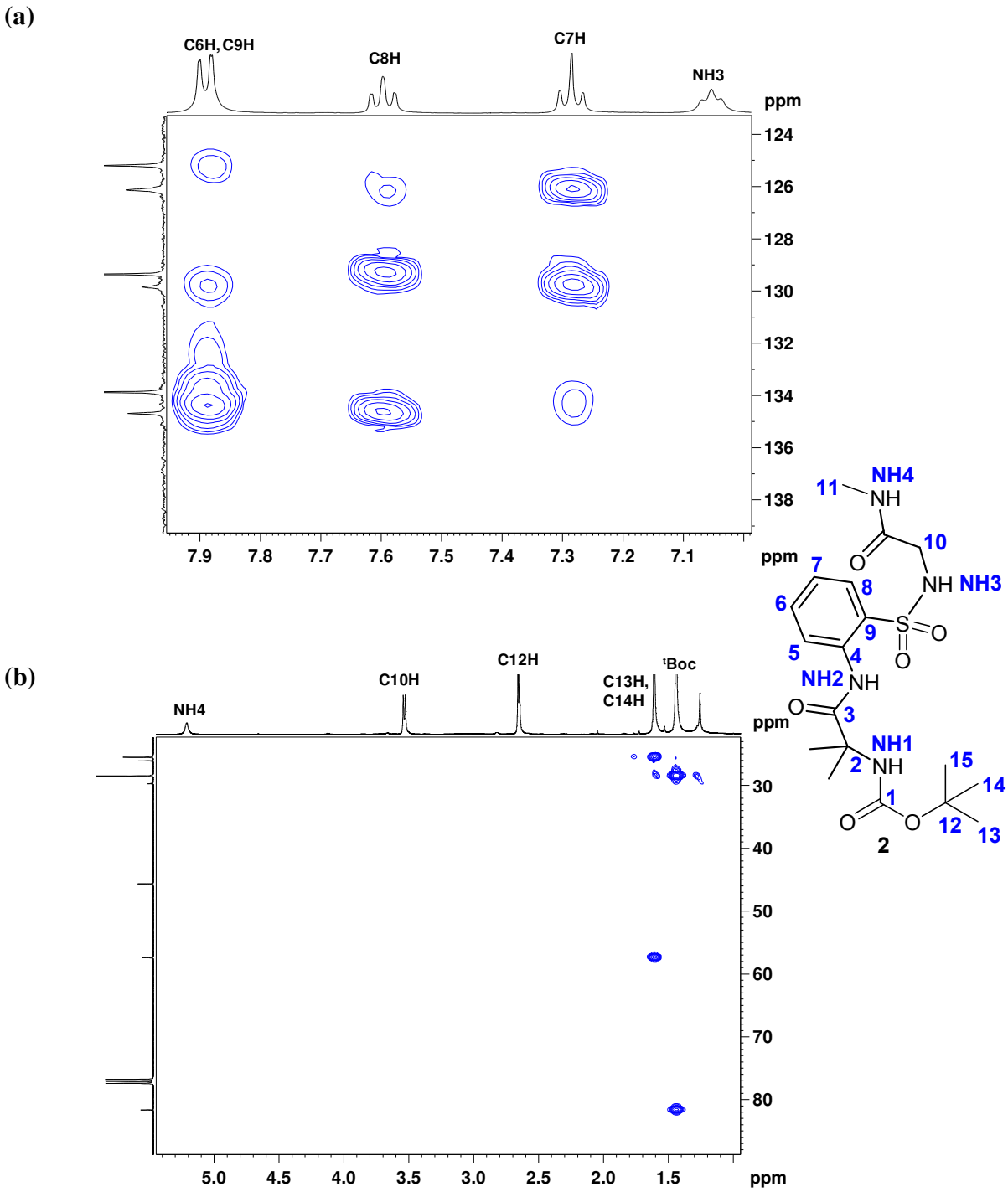


Fig. 12: Partial HMBC spectra of **2** (400MHz, $CDCl_3$): aromatic (a) and aliphatic (b) regions.

(a)

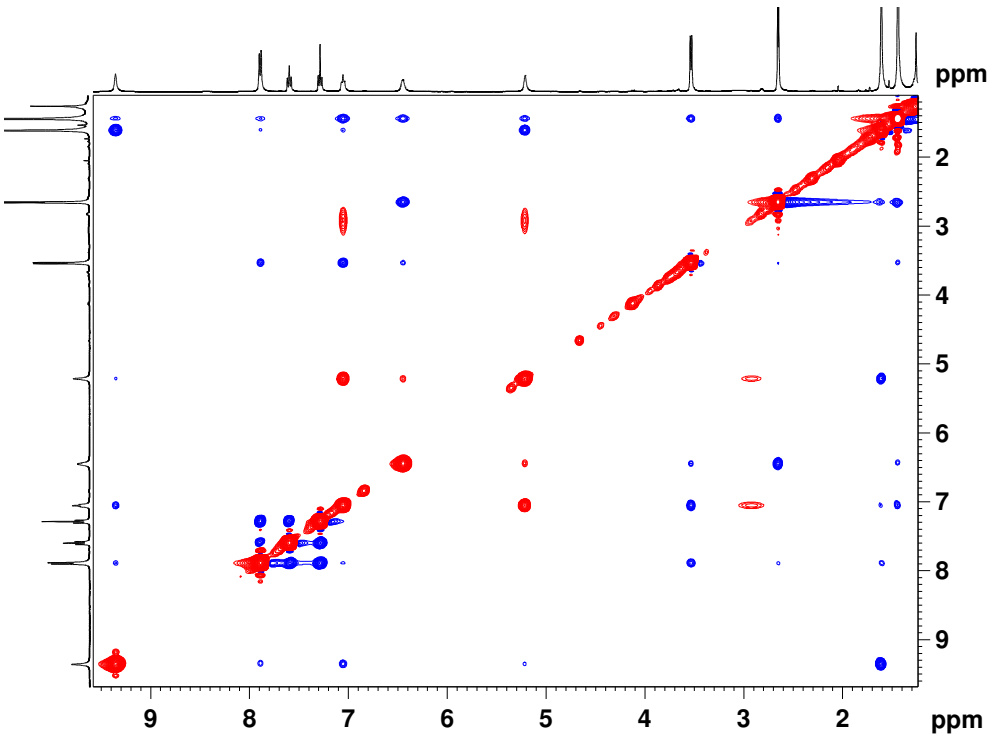


Fig. 13: (a) Full 2D NOESY spectrum of **2** (400MHz, $CDCl_3$).

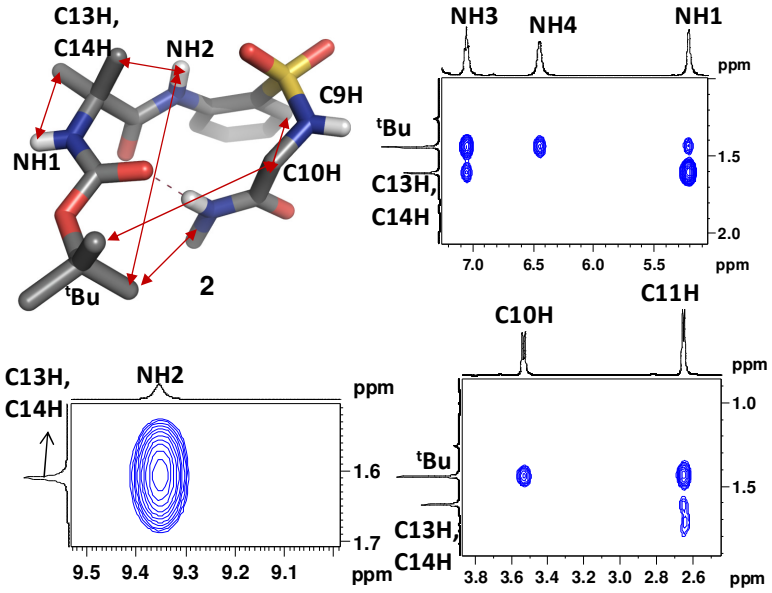


Fig. 13: (a) Full 2D NOESY spectrum of **2** (400MHz, $CDCl_3$) and (b) selected 2D excerpts of **2**.

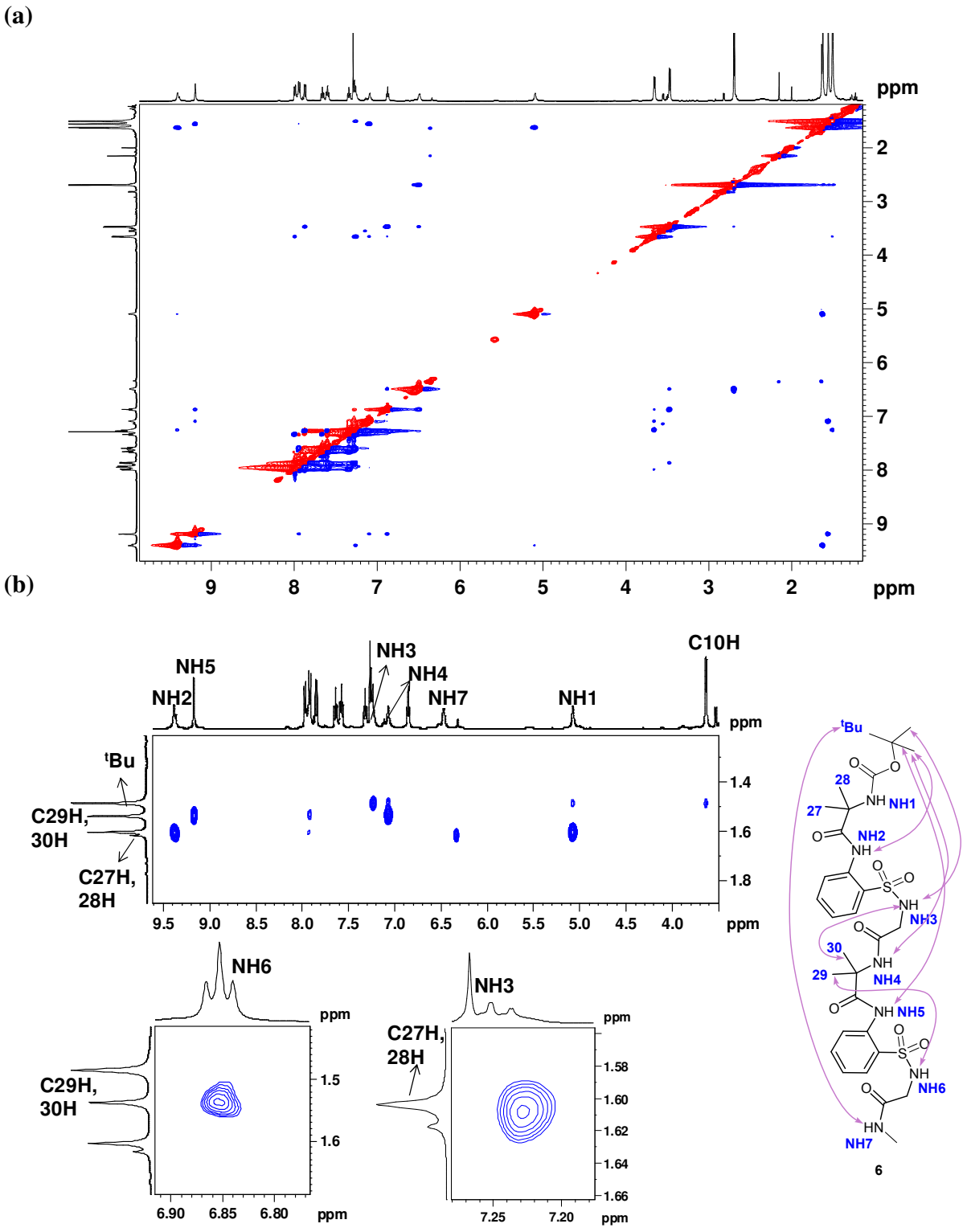


Fig. 14: (a) Full 2D NOESY spectrum of **6** (400MHz, $CDCl_3$). (b) Selected 2D excerpts of **6**.

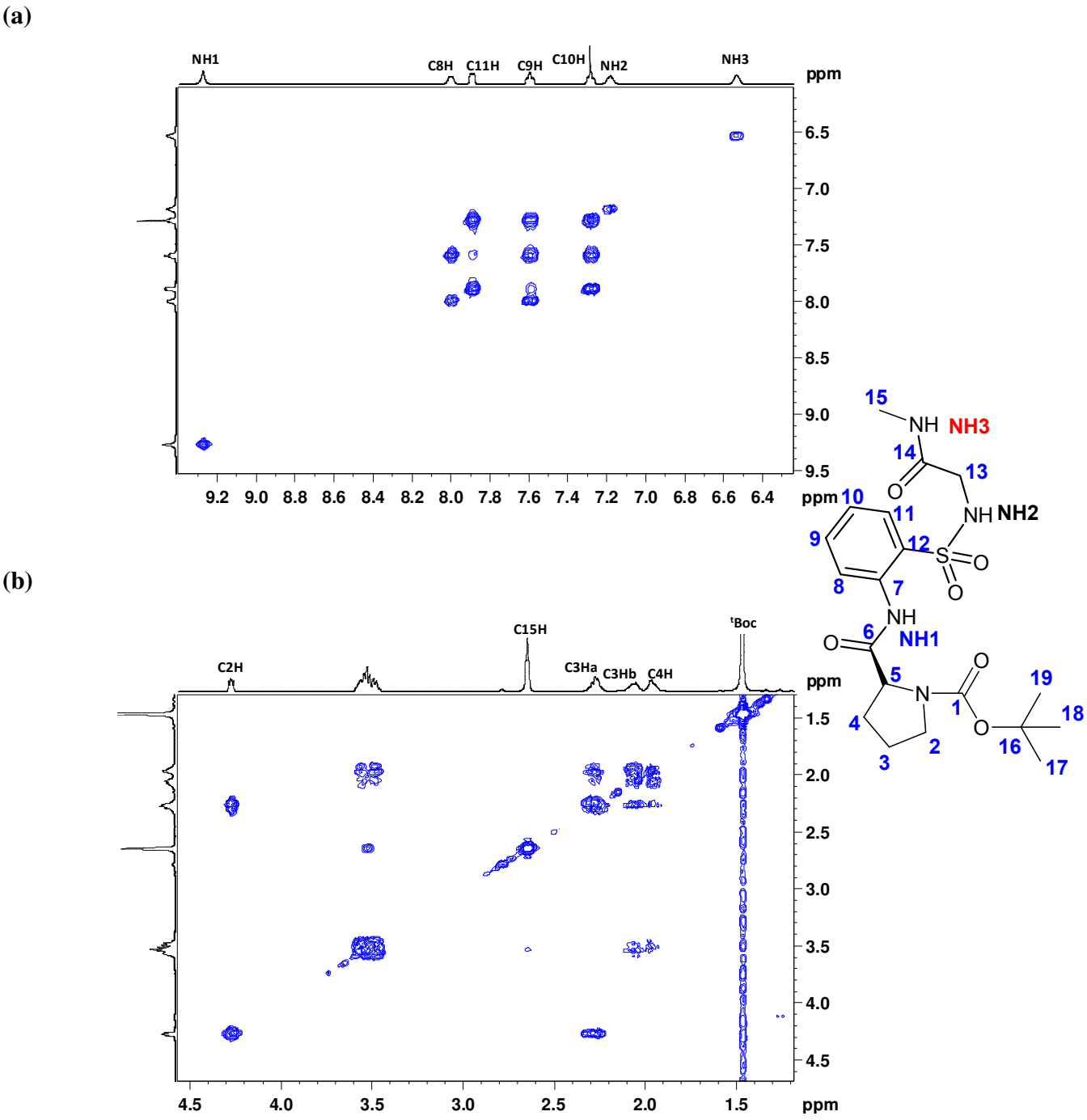


Fig. 15: Partial COSY spectra of **3** (400MHz, $CDCl_3$): aromatic (a) and aliphatic (b) regions.

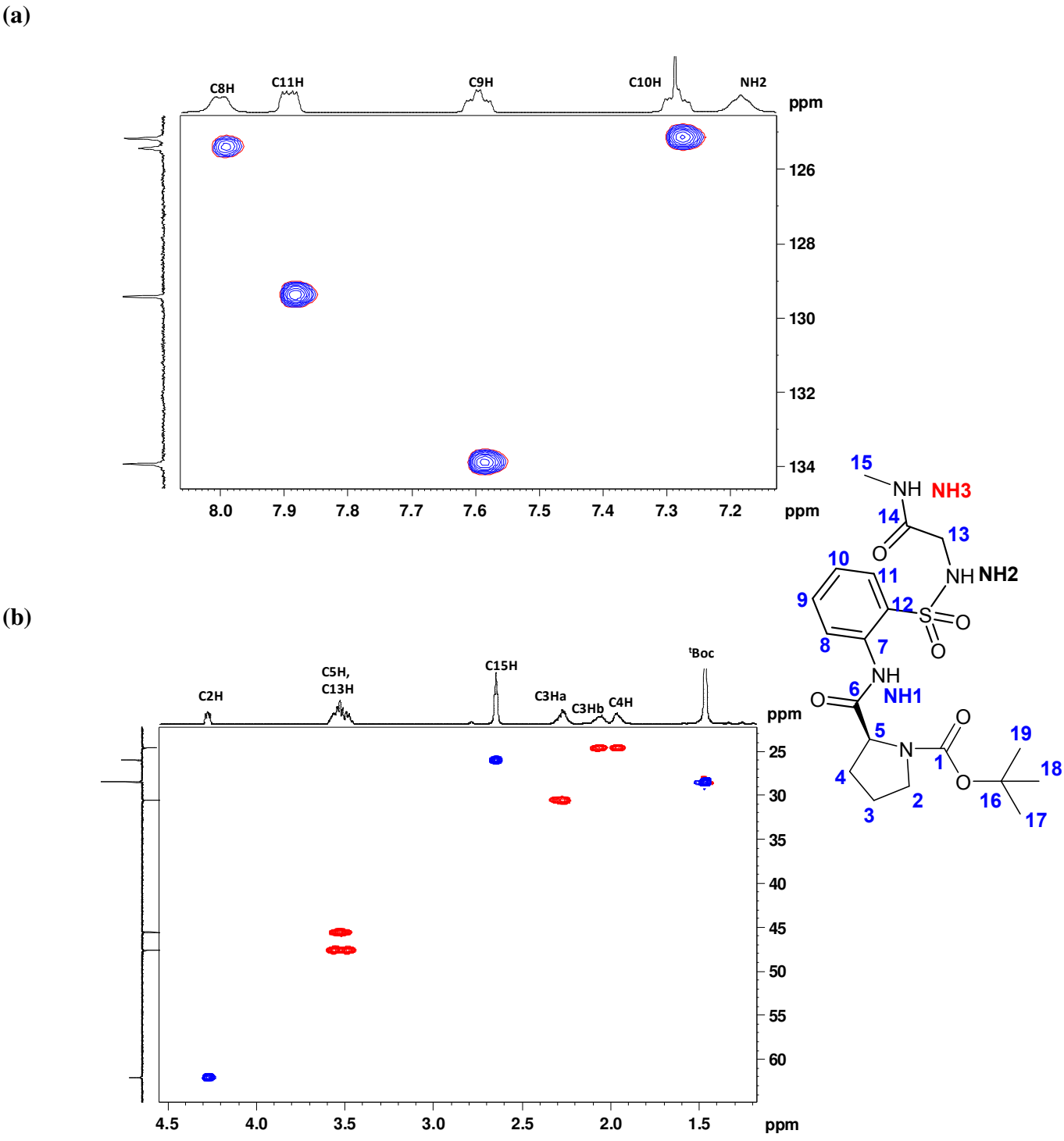


Fig. 16: Partial HSQC spectra of **3** (400MHz, $CDCl_3$): aromatic (a) and aliphatic (b) regions.

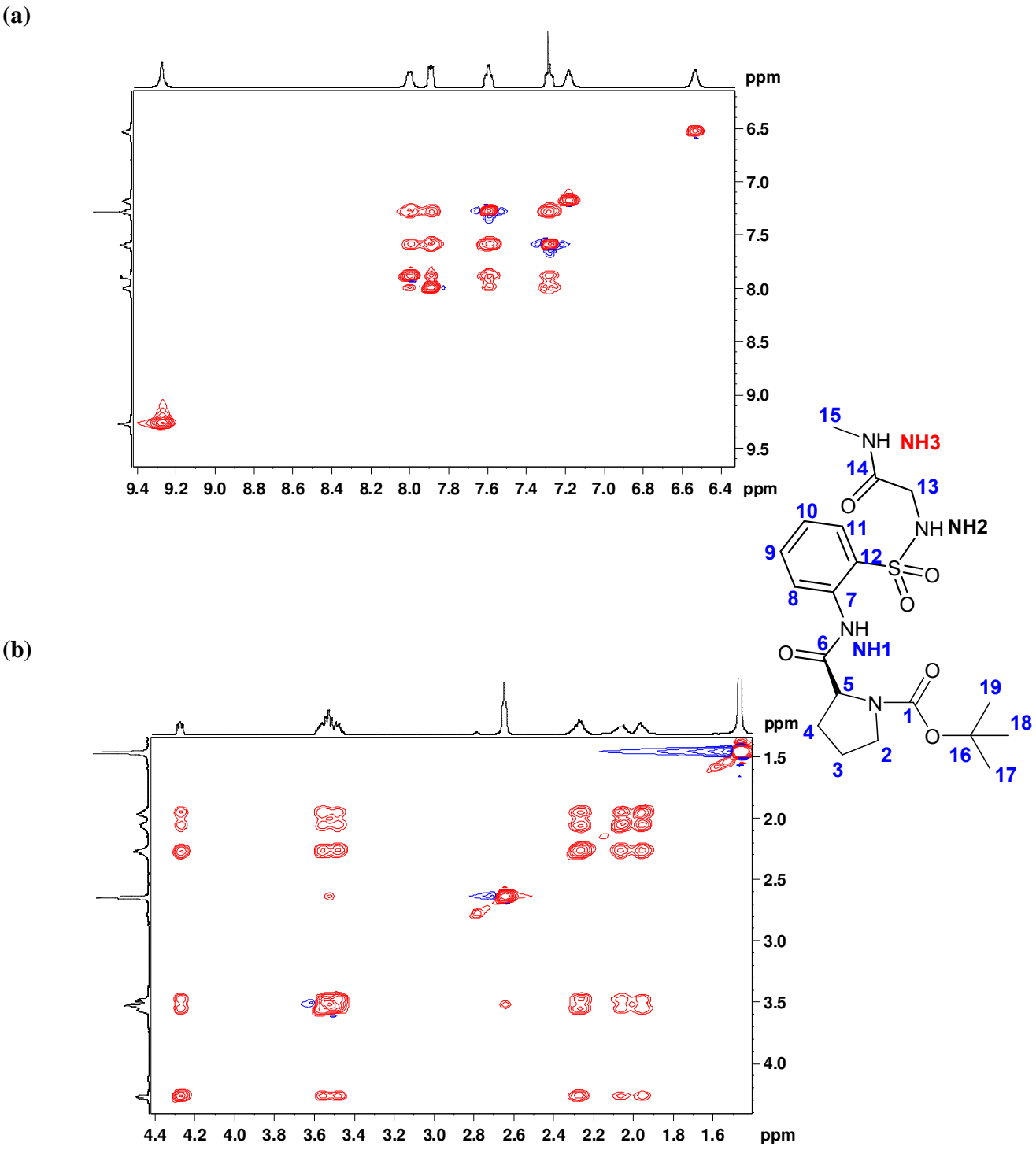


Fig. 17: Partial TOCSY spectra of **3** (400MHz, $CDCl_3$): aromatic (a) and aliphatic (b) regions.

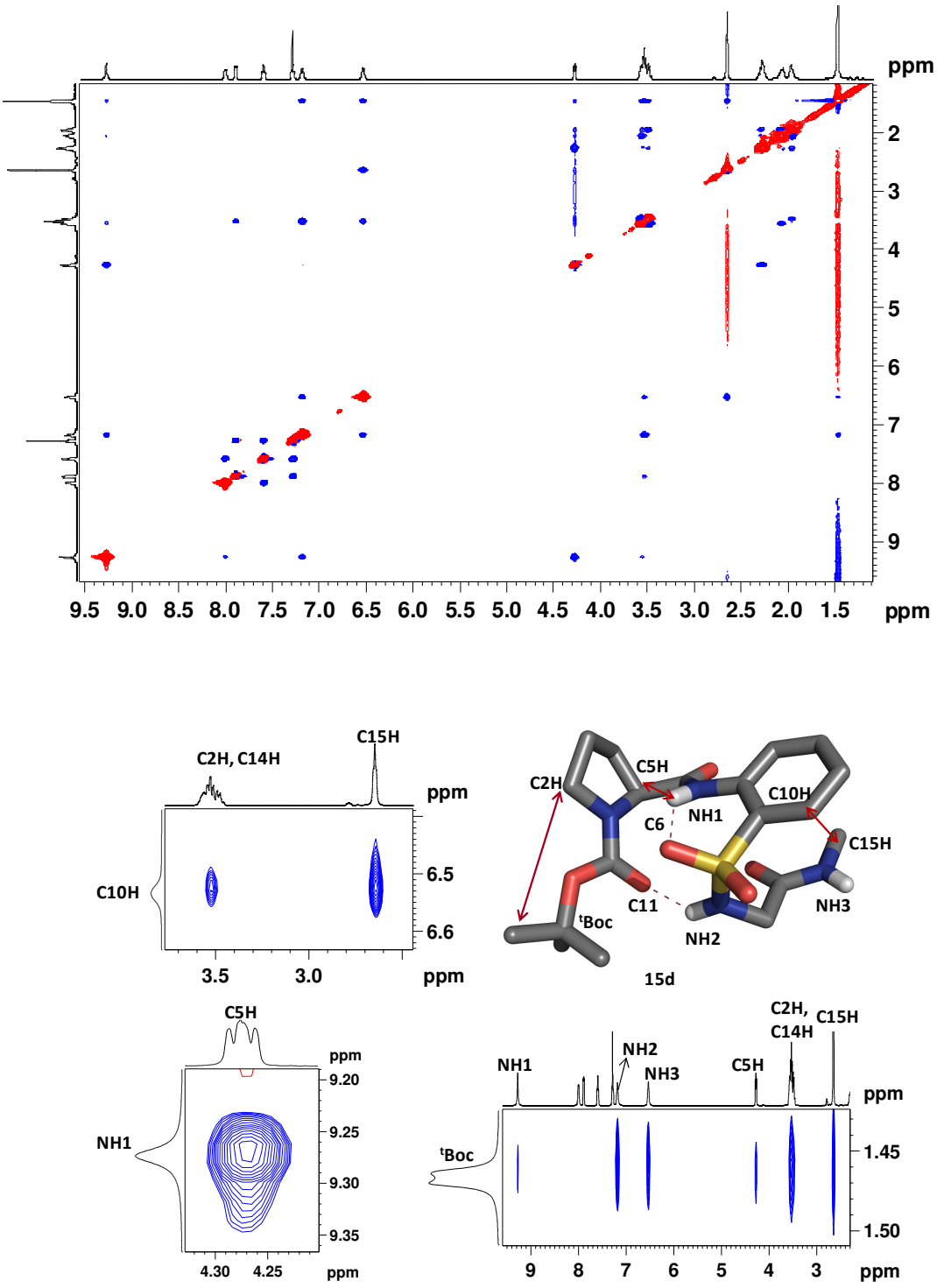


Fig. 18: (a) Full 2D NOESY spectrum of **3** (400MHz, $CDCl_3$). (b) Selected 2D excerpts of **3**.

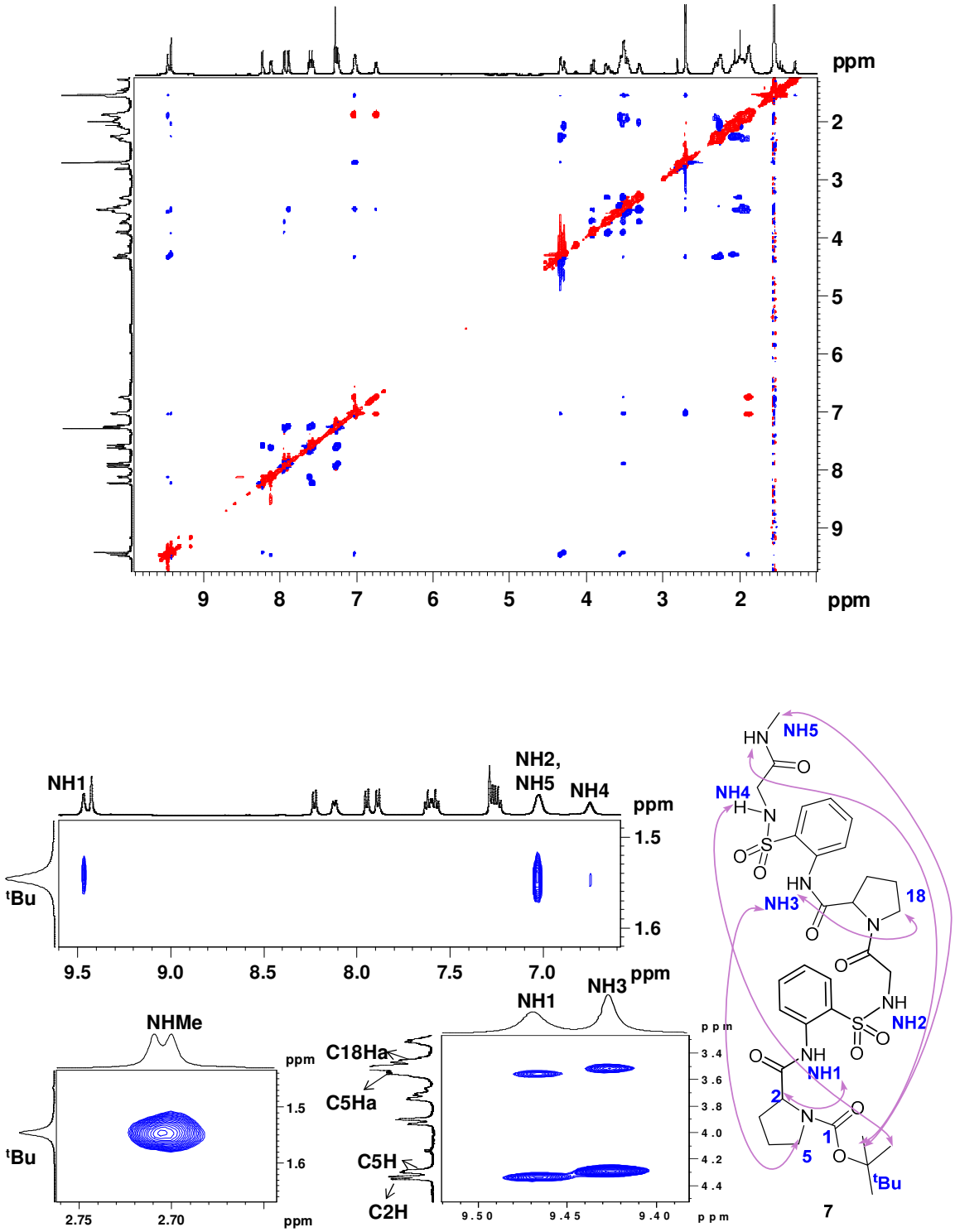


Fig. 19: (a) Full 2D NOESY spectrum of **7** (400MHz, $CDCl_3$). (b) Selected 2D excerpts of **7**. *Note*: The stereochemistry of prolines in **7** is 'S'

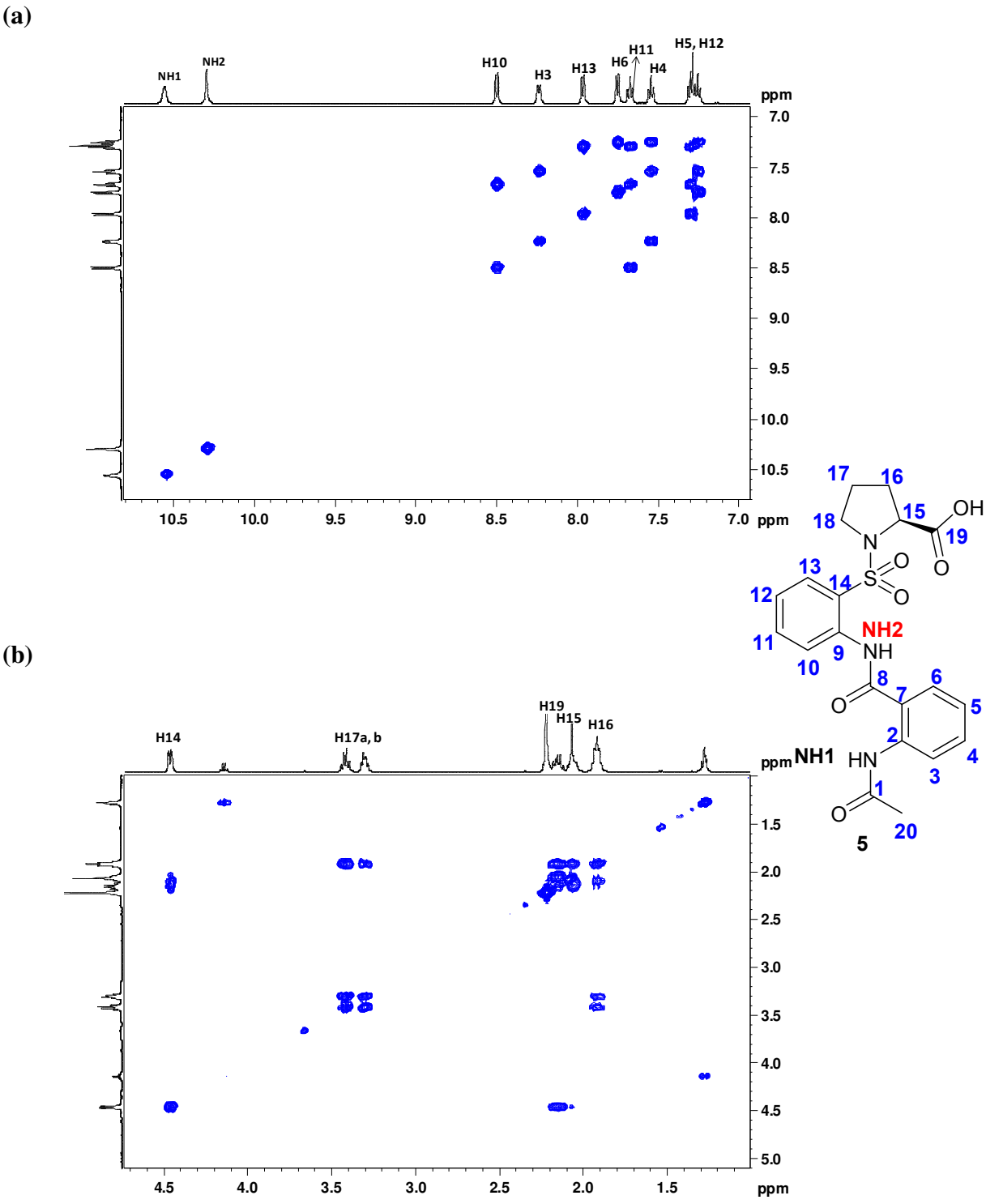


Fig. 20: Partial COSY spectra of **5** (400MHz, $CDCl_3$): aromatic (a) and aliphatic (b) regions.

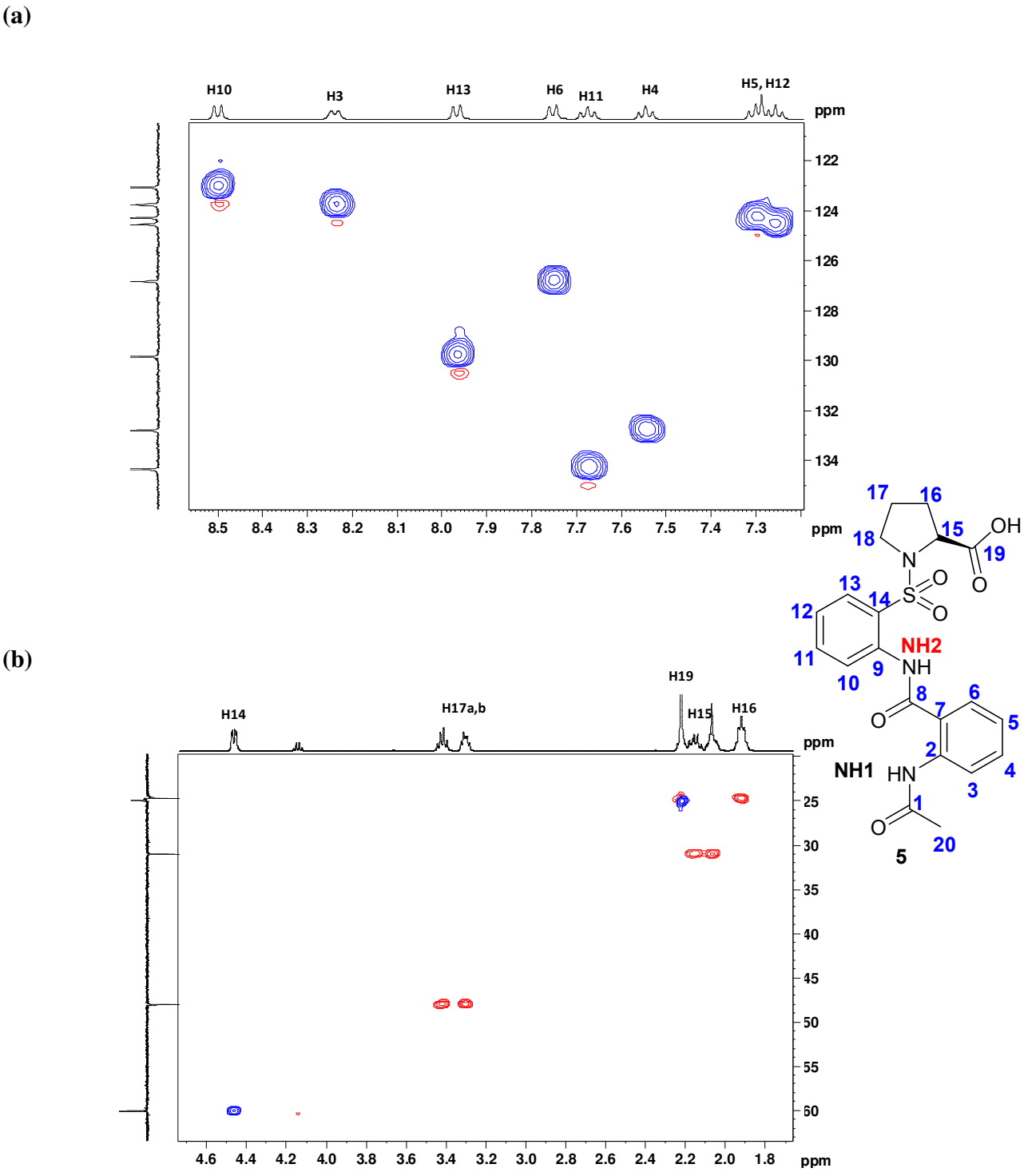


Fig. 21: Partial HSQC spectra of **5** (400MHz, $CDCl_3$): aromatic (a) and aliphatic (b) regions.

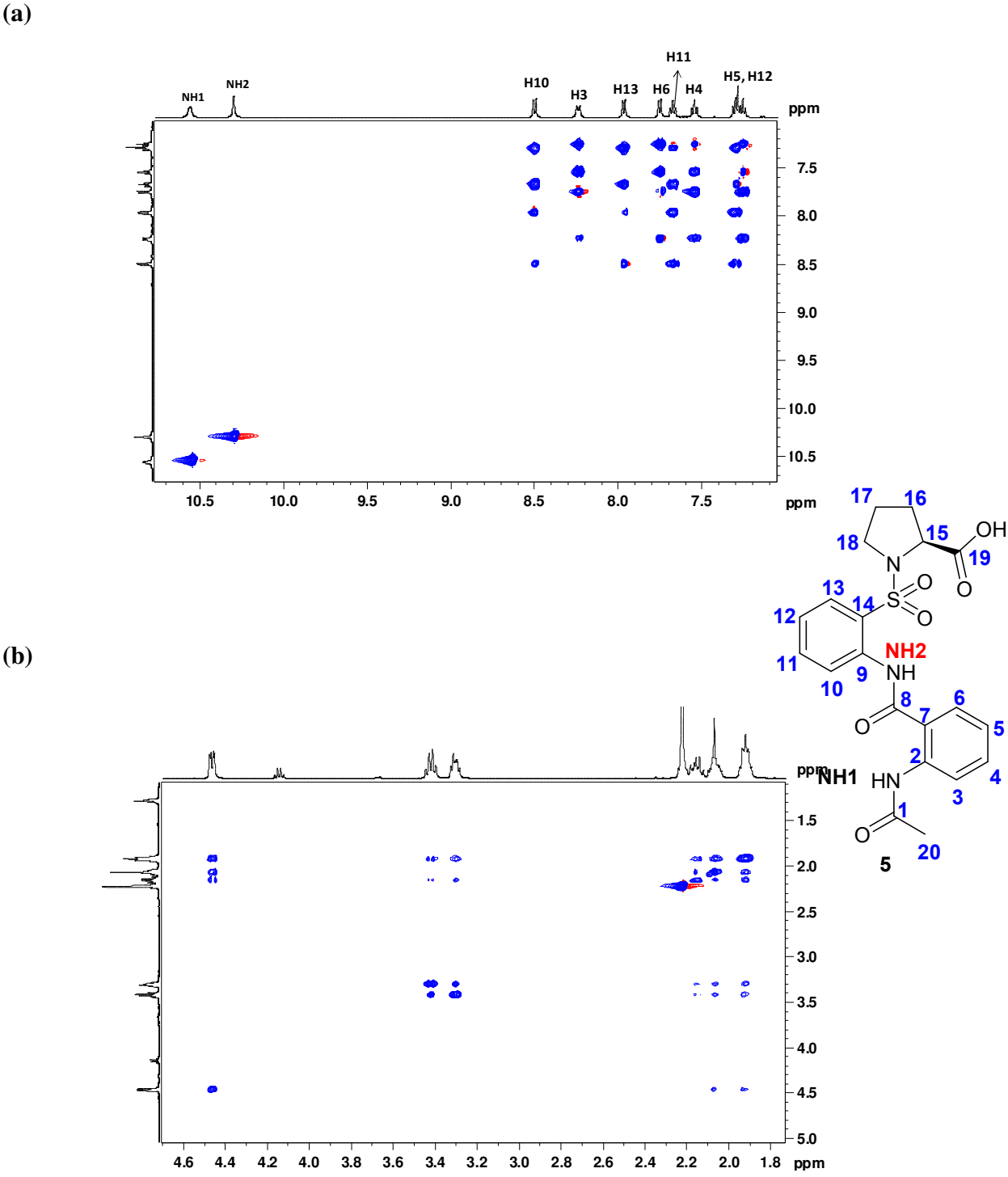


Fig. 22: Partial TOCSY spectra of **5** (400MHz, $CDCl_3$): aromatic (a) and aliphatic (b) regions.

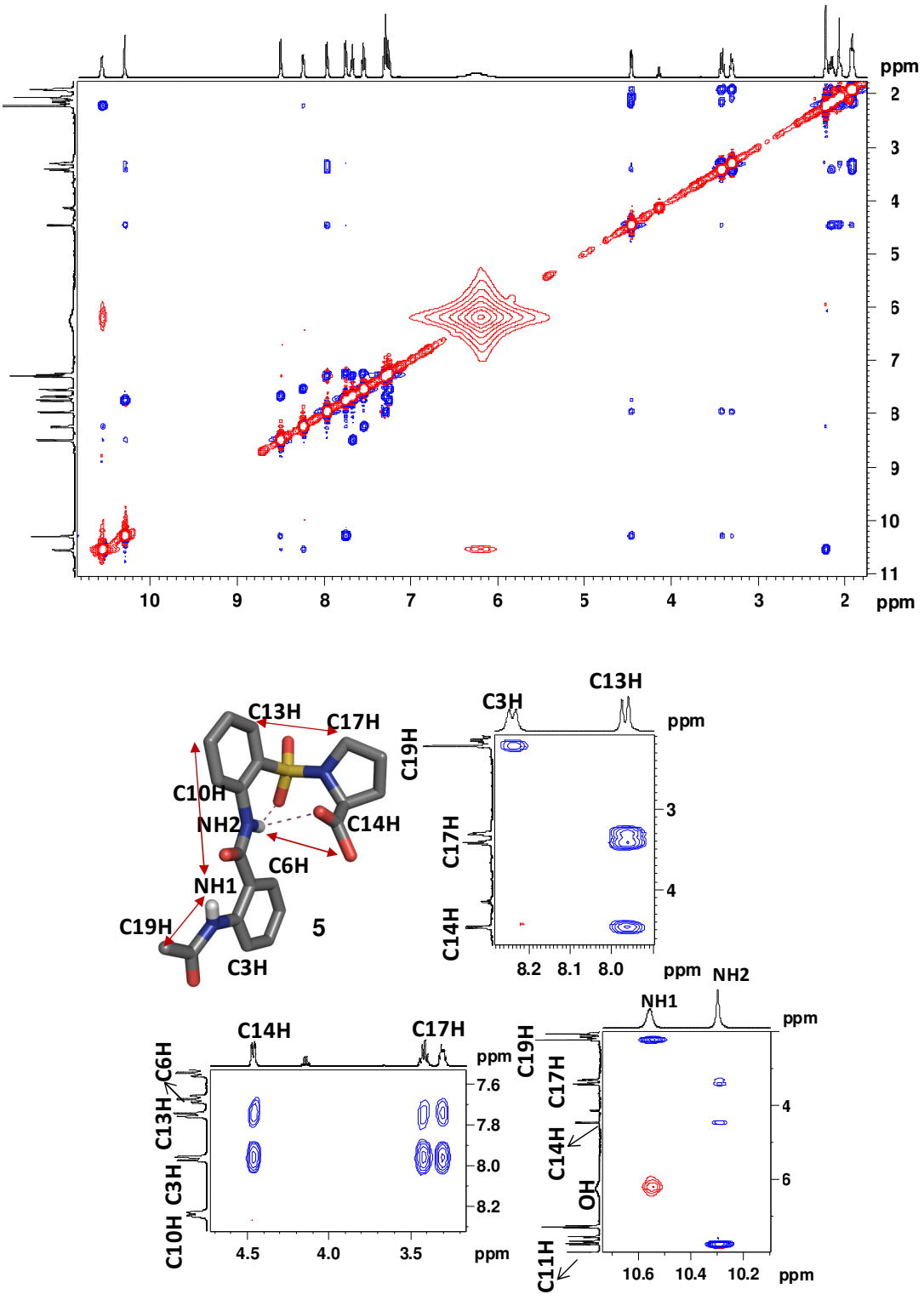


Fig. 23: (a) Full 2D NOESY spectrum of **5** (400MHz, $CDCl_3$). (b) Selected 2D excerpts of **5**.

Molecular Dynamics

Compound 1

(F2)	(F1)	Upper bound	Lower bound	Between
8.0303	7.5553	2.684	2.196	5/6H
7.5636	7.212	2.718592	2.224303	6/7H
9.6396	6.9224	3.363521	2.751972	NH3/NH2
9.637	4.9697	3.314141	2.71157	NH1/NH2
9.6396	1.6036	2.784664	2.278361	NH2/17/18
9.6423	1.5017	3.9166	3.204491	NH2/BOC
8.0303	1.5983	3.985347	3.260738	5/17/18H
7.856	3.7011	3.323854	2.719517	8/10H
6.9307	1.499	2.910141	2.381024	BOC/NH3
6.928	3.7011	2.828308	2.31407	NH3/10
4.9727	1.499	3.426222	2.803272	NH1/BOC
4.9727	1.5983	2.511948	2.055231	NH1/17/18
3.704	1.4963	3.52523	2.884279	10/BOC
3.476	1.5017	3.650256	2.986573	OMe/BOC
3.476	1.609	4.493942	3.676861	OMe/17/18

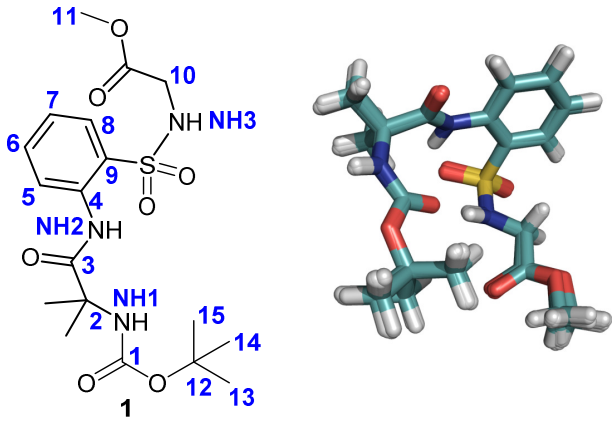


Fig. 24: Molecular structure of compound **1**(left) and 20 minimum energy structures overlaid with the crystal of **1**(right).

Compound 2

(F2) [ppm]	(F1) [ppm]	Upper bound	Lower bound	Between
7.6326	7.0607	2.684	2.196	8/7H
7.4791	7.0537	2.6683	2.183154	7/6H
8.574	7.4652	2.579017	2.110105	5/6H
11.6424	1.5585	2.816481	2.304394	NH2/19/18
5.4568	1.5585	2.686452	2.198006	NH1/BOC
8.567	1.3842	5.720153	4.680125	BOC/5
7.6395	1.4051	4.913939	4.020496	BOC/8
7.6395	4.0063	3.293398	2.694599	11/NH3
6.5726	4.0272	3.422157	2.799947	11/NH4
6.6981	2.8138	2.738348	2.240467	NH4/NHMe

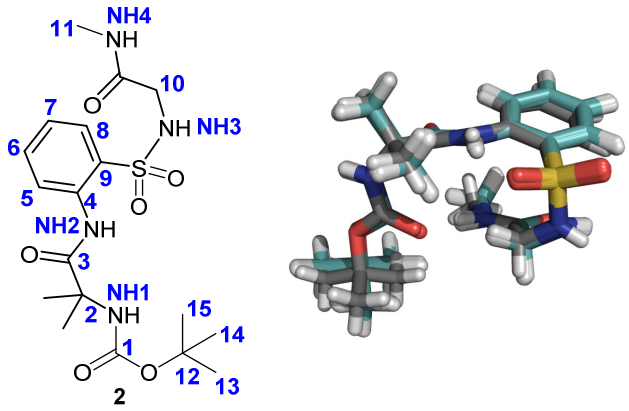


Fig. 25: Molecular structure of compound **2** (left) and 20 minimum energy structures overlaid with the crystal of **2**(right).

Compound 3

(F2) [ppm]	(F1) [ppm]	Upper bound	Lower bound	Between
7.9978	7.5825	2.684	2.196	H11/H12
7.5964	7.2688	2.696757	2.206438	H11/H10
9.2712	7.9885	4.392856	3.594155	NH1/H12
9.2758	7.1673	3.154809	2.581207	NH1/NH2
9.2712	6.5305	5.45429	4.462601	NH1/NH3
9.2758	4.2697	2.616967	2.141155	NH1/2H
9.2712	3.5315	3.694086	3.022434	NH1/13H/5A/B
9.2758	2.2488	4.523345	3.700918	NH1/3A/B

9.2712	2.0458	4.251398	3.478416	NH1/4A/B
9.2712	1.4644	5.022962	4.109696	NH1/BOC
7.1857	1.4644	3.310548	2.70863	BOC/NH2
6.5351	1.4644	3.460344	2.83119	BOC/NH1
4.2697	1.4552	4.556337	3.727912	BOC/2H
3.5269	1.4552	3.212379	2.62831	BOC/13H
2.6502	1.4552	3.514687	2.875653	BOC/NHMe
7.9978	2.258	4.412825	3.610493	H12/3A/B
7.9978	2.6364	5.38997	4.409975	H12/NHMe
7.887	3.513	3.434231	2.809825	9H/13H
7.9978	4.2605	6.37174	5.213241	2H/12H
7.8824	6.5213	5.827683	4.768104	9H/NH3
7.1811	6.5213	3.147128	2.574923	NH3/NH2
7.1811	4.2605	4.401099	3.6009	NH2/2H
7.1719	3.5222	2.71477	2.221176	NH2/13H
7.5964	2.6364	5.901956	4.828873	NHMe/11H
7.2872	2.6364	5.997773	4.907269	NHMe/10H
6.5398	2.6364	2.814807	2.303024	NHMe/NH3
6.5305	3.5222	3.250352	2.659379	13H/NH3
6.5305	4.2697	5.336982	4.366622	NH3/2H
3.5315	2.6364	4.324653	3.538353	NHMe/13H

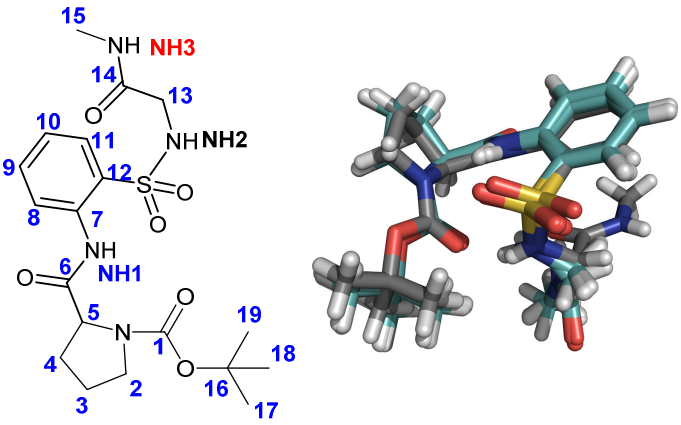


Fig. 26: Molecular structure of compound **3** (left) and 20 minimum energy structures overlaid with the crystal of **3** (right). *Note*: The stereochemistry of prolines in **3** is 'S'

Compound 6

(F2) [ppm]	(F1) [ppm]	Upper bound	Lower bound	Between
7.8977	7.2742	2.684	2.196	8/7H
7.6061	7.2742	2.865283	2.344323	6/7H
9.351	7.8827	4.147947	3.393775	NH2/5
9.351	7.0429	3.636337	2.975185	NH3/NH2
9.351	5.2074	4.142322	3.389173	NH2/NH1
9.3611	1.6017	2.823851	2.310424	NH2/17/18
7.8877	1.5967	4.414694	3.612022	5/17/18H
7.8877	2.6376	5.674307	4.642615	NHMe/8
7.8927	3.5227	3.607189	2.951336	8/10H
7.0529	1.4408	3.567655	2.918991	NH3/BOC
7.0479	1.6017	4.233911	3.464109	NH3/17/18
7.0529	3.5277	3.216966	2.632063	NH3/10
6.4444	1.4408	3.90891	3.198199	NH4/BOC
6.4494	2.6477	3.05275	2.497704	NH4/NHMe
6.4444	3.5277	3.876314	3.171529	NH4/10
5.2124	1.4307	4.554215	3.726176	NH1/BOC
5.2174	1.6017	3.139259	2.568485	NH1/17/18
3.5328	1.4357	3.866436	3.163448	10/BOC
2.6528	1.4307	3.692889	3.021455	NHMe/BOC
2.6528	1.6117	4.658031	3.811116	NHMe/17/18

Compound 7

(F2) [ppm]	(F1) [ppm]	Upper Bound	Lower Bound	Between
8.6312	7.5378	2.684	2.196	7/8H
8.5011	7.6619	2.629874	2.151715	13/14
11.0247	8.643	4.607795	3.770014	NH1/7
11.0247	8.4952	5.772299	4.72279	NH1/14H
11.0247	2.2131	2.906552	2.378088	NHMe/NH1
10.4396	3.3123	4.195369	3.432575	NH2/18A
10.4337	3.4541	4.360875	3.567988	NH2/18B
10.4337	4.4943	4.052497	3.315679	NH2/15
10.4396	7.8097	2.458587	2.011571	NH2/4
10.4337	8.4893	4.512979	3.692437	NH2/14
8.643	2.2131	4.835988	3.956717	CH3/7
7.9929	2.6622	5.035036	4.119575	NHMe/11
7.9929	3.3064	3.807805	3.115477	11/18A
7.9929	3.4423	3.784294	3.09624	11/18B
7.9929	4.4884	3.582876	2.931444	11/15H
7.9929	6.7341	4.253833	3.480409	11/NH3
6.74	1.9176	4.278895	3.500914	NH3/22
6.74	2.6681	2.862852	2.342334	NH3/NHMe
6.7341	3.5546	3.986484	3.261669	NH3/23A
6.7341	4.5356	3.343321	2.735445	NH3/20
4.5534	1.9176	2.725229	2.229733	20/22
4.5534	2.3431	3.296262	2.696942	20/21
4.4943	2.1244	2.738926	2.240939	15/17A
4.4943	3.3241	2.918458	2.38783	15/18A/23
4.4943	3.5546	2.761679	2.259556	15/18B
3.5605	1.9117	3.00602	2.459471	23/22
3.4423	1.9057	3.284064	2.686962	18/17A/17B
3.3123	1.888	2.624196	2.147069	22/23
3.4423	2.154	3.045297	2.491606	16/18
3.3123	2.148	3.18383	2.604952	16/18B
2.6681	1.9117	4.318525	3.533338	NHMe/22
2.349	1.8939	2.270122	1.857372	22/21