Electronic Supplementary Information

Reversal of H-bonding Direction by N- Sulfonation: A Case Study With a Synthetic Reverse-Turn Peptide Motif*

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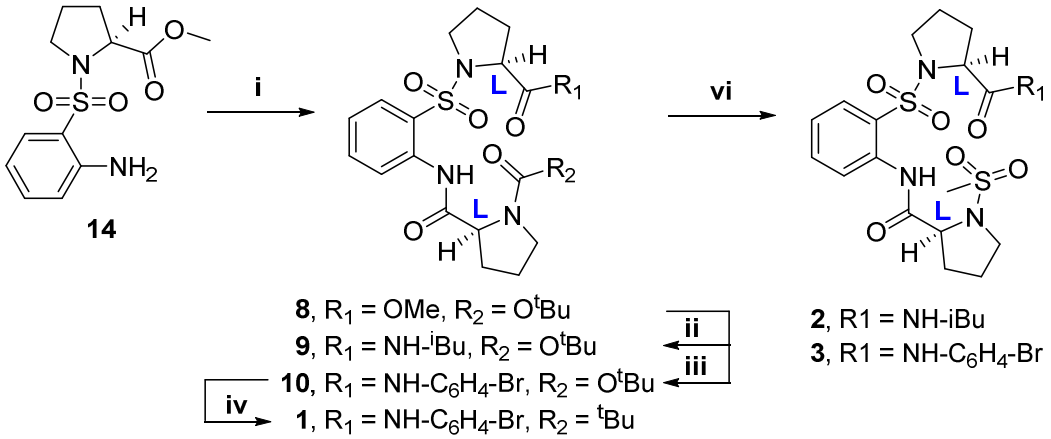
General Methods.

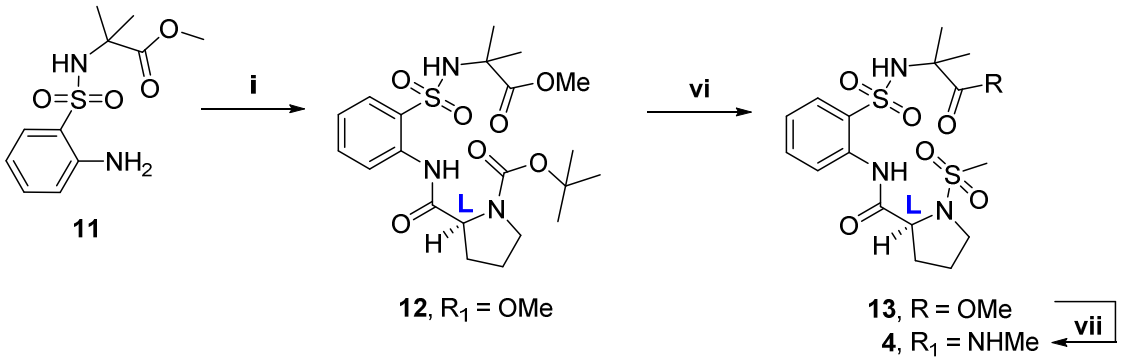
Unless otherwise stated, all the chemicals and reagents were obtained commercially. Dry solvents were prepared by the standard procedures. Analytical Thin Layer Chromatography was done on pre-coated silica gel plates (Kieselgel $60F_{254}$, Merck). Unless otherwise stated Column Chromatographic purifications were done with 100-200 or 240-400 Mesh Silica gel. NMR spectra were recorded in $CDCl_3$ on AV 200 MHz, AV 400 MHz, JEOL 400MHz or AV 500 MHz spectrometers. All chemical shifts are reported in δ ppm downfield to TMS and peak multiplicities as singlet (s), doublet (d), quartet (q), broad singlet (bs), and multiplet (m) etc. The titration studies were done in $CDCl_3$. Elemental analyses were performed on an Elmentar-Vario-EL (Heraeus Company Ltd., Germany). IR spectra were recorded in $CHCl_3$ using Shimadzu FTIR-8400 spectrophotometer. Melting points were determined on a Buchi Melting Point B-540. MALDI-TOF/TOF mass spectra were obtained from ABSCIEX TOF/TOFTM 5800 mass Spectrometer.

Synthetic Schemes

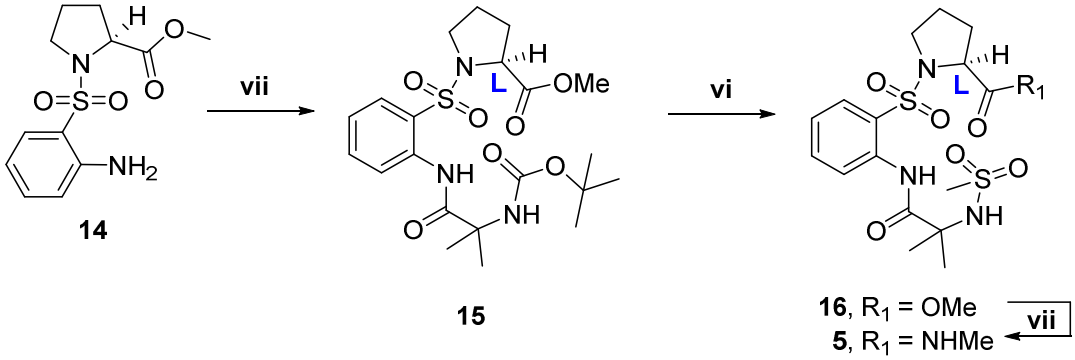
Scheme:1



Scheme:2

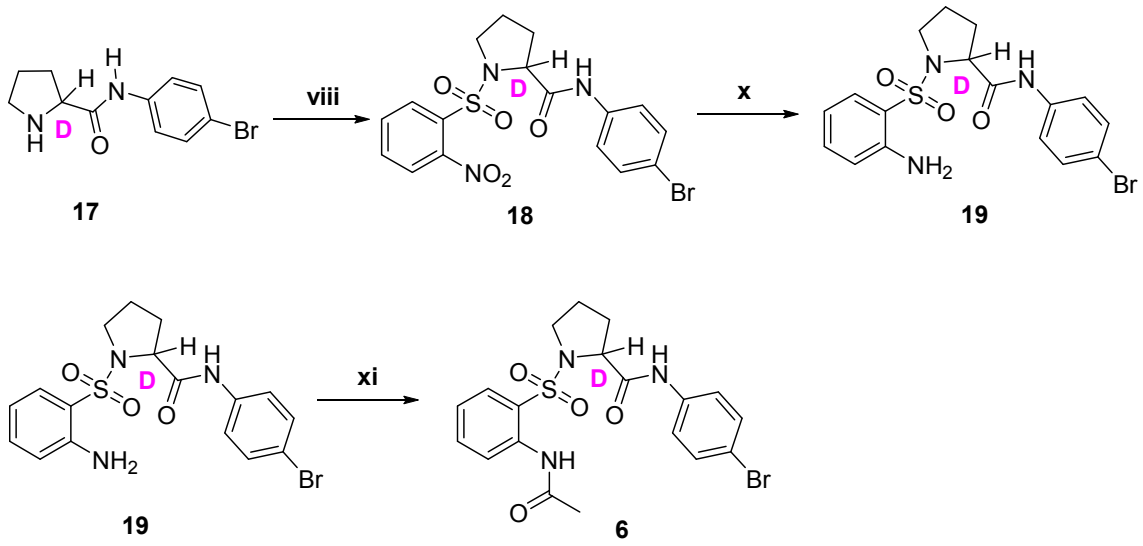


Scheme:3

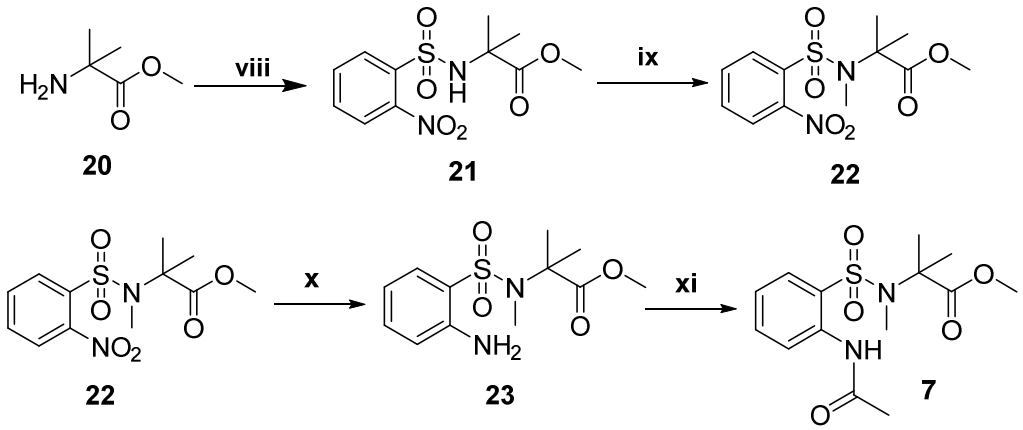


Reagents and Conditions: (i) Boc-^{L}Pro-OH, Ethylchloroformate, Et_3N, THF, 70^{o}C, 48h; (ii) (a) $LiOH.H_2O$, MeOH, H_2O, RT, 3h (b) HBTU, Et_3N, $^{i}BuNH_2$, RT, 12h; (iii) (a) ii(a) (b) HBTU, Et_3N, 4-Br-C_6H_4-NH_2, DCM, RT, 12h; (iv) (a) TFA, DCM, RT, 3h, (b) PivCl, Et_3N, DCM, RT, 12h; (v) (vi) Mes-Cl, Et_3N, DCM, RT, 12h; (vii) CH_3NH_2, MeOH, 3h.

Scheme:4



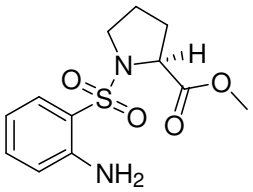
Scheme:5



Reagents and Conditions: (viii) 2-nitro benzene sulfonyl chloride, Et_3N, DCM, rt, 3h; (ix) Ag_2O, CH_3I, DMF, rt, 12h; (x) Zn, $HCOONH_4$, MeOH, rt, 3h; (xi) CH_3COCl, Et_3N, DCM, rt, 12h.

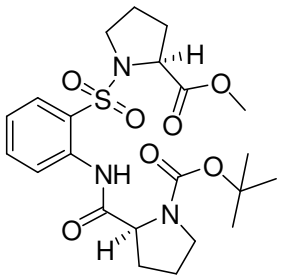
Experimental Procedures

Methyl ((2-aminophenyl)sulfonyl)-L-prolinate 14



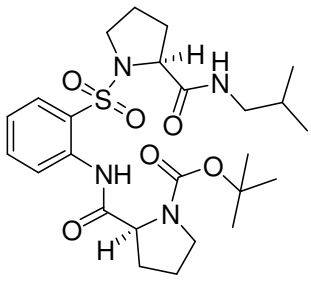
Compond **14** was prepared following the reported procedure[1]

Tert-butyl(S)-2-((2-(((S)-2-(methoxycarbonyl)pyrrolidin-1-yl)sulfonyl)phenyl)carbamoyl)pyrrolidine-1-carboxylate 8



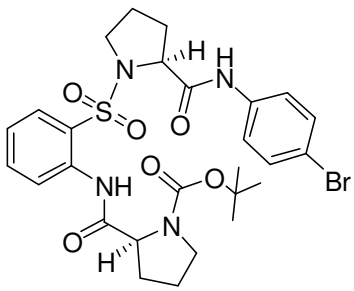
To a solution of Boc-^{L}Pro-OH (2g, 9.302mmols) in THF (50mL), Et_3N (2.6mL, 1.88g, 18.605mmol) was added followed by the addition of Ethylchloroformate (1.1mL, 1.288g, 11.944mmol). After 30 minutes, compound **14** in THF (20mL) was added and heated to reflux for 48 hours. The reaction mixture was evaporated under reduced pressure and the residue in DCM (10mL) was washed with saturated solutions of sodium bicarbonate (7mL) followed by potassium bisulphate (7mL) and water (7mL). The washings were extracted with DCM (7mLx3), dried with anhydrous Na_2SO_4 and evaporated under reduced pressure to obtain the crude residue which was purified by column chromatography, (40:60 pet ether/ethyl acetate, R_f: 0.5) to afford **8** as a viscous liquid (3.18g, 71%). $[\alpha]^{26}_{D}$: -232.87° (*c* = 1, $CHCl_3$); IR ($CHCl_3$, ν (cm^{-1}): 3309, 3018, 2401, 1746, 1694, 1584, 1531, 1436, 1247; ^{1}H NMR ($CDCl_3$/200MHz): δ ppm 10.12-9.99 (d, *J*=25.52Hz, 1H), 8.55-8.66 (t, *J*=10.3, 1H), 7.86 (s, 1H), 7.52-7.59 (t, *J*=8.14Hz, 1H), 7.15-7.22 (t, *J*=7.58Hz, 1H), 4.36-4.51 (m, 2H), 3.63 (s, 3H), 3.33-3.49 (m, 4H), 1.37-1.46 (d, *J*=17.05Hz, 9H); ^{13}C NMR ($CDCl_3$, 50MHz): δ ppm 172.1, 136.6, 134.2, 129.5, 125.2, 123.5, 80.2, 60.9, 59.9, 52.4, 48.2, 47.1, 30.8, 28.2, 24.5; MALDI-TOF-MS: 504.1741 $(M+Na)^+$, 520.1484 $(M+K)^+$; Elemental Analysis calculated for $C_{22}H_{31}N_3O_7S$: C, 54.87; H, 6.49; N, 8.73; Found: C, 59.22; H, 6.01; N, 8.99.

Tert-butyl(S)-2-((2-(((S)-2-(isobutylcarbamoyl)pyrrolidin-1-yl)sulfonyl)phenyl)carbamoyl)pyrrolidine-1-carboxylate 9



Compound **8** (0.5g, 1.038mmol) was subjected to ester hydrolysis using LiOH. H_2O (0.25g, 10.382mmol) in methanol (5mL) and water (5mL) to obtain the free acid. To a solution of free acid in DCM (10mL), isobutylamine (0.21mL, 0.152g, 2.076mmols), was added followed by HBTU (0.814g, 2.076mmols), and Et_3N (0.43mL, 0.315g, 3.114mmols). After 12 hours, the reaction mixture was diluted with DCM (5mL) and the organic layer was washed with saturated solutions of sodium bicarbonate (5mL), potassium bisulphate (5mL) and water (5mL) sequentially. The organic layer was dried over anhydrous Na_2SO_4 solution and evaporated under reduced pressure to get crude product which was purified by column chromatography, (30:70 pet. ether/ethyl acetate, R_f: 0.5) to afford **9** as a white solid (0.476g, 88%). mp: 70-74^{o}C; $[\alpha]^{26}_D$: -230.44° (*c* = 0.1, $CHCl_3$); IR ($CHCl_3$, ν (cm^{-1}): 3317, 3018, 2932, 2400, 1689, 1583, 1528, 1398, 1216; ^{1}H NMR ($CDCl_3$/200MHz): δ ppm 10.16-10.28 (d, *J*=24.23, 1H), 8.6-8.75 (d, *J*=26.65, 1H), 7.78-7.82 (s, *J*=7.83Hz, 1H), 7.56-7.64 (t, *J*=7.75Hz, 1H), 7.18-7.25 (t, *J*=7.58Hz, 1H), 6.77-6.83 (m, *J*=5.12Hz, 1H), 4.36 (s, 1H), 4.15-4.19 (m, 1H), 3.49-3.57 (m, 3H), 2.96-3.20 (m, 3H), 2.16-2.18 (m, 2H), 1.66-2.03 (m, 6H), 1.42 (s, 9H), 0.89-0.93 (d, *J*=6.69Hz, 1H); ^{13}C NMR ($CDCl_3$, 50MHz): δ ppm 171.8, 170.5, 134.7, 129.5, 123.9, 80.5, 62.6, 49.2, 46.8, 38.5, 30.3, 28.4, 24.3, 19.9; MALDI-TOF-MS: 545.2320 $(M+Na)^+$, 561.2062 $(M+K)^+$; Elemental Analysis calculated for $C_{25}H_{38}N_4O_6S$: C, 57.45; H, 7.33; N, 10.72; Found: C, 54.22; H, 7.01; N, 10.59.

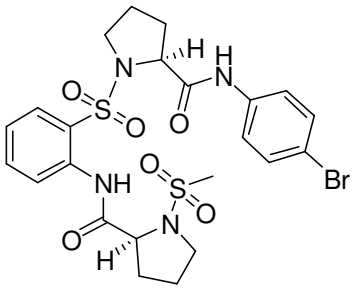
Tert-butyl(S)-2-((2-(((S)-2-((4-bromophenyl)carbamoyl)pyrrolidin-1-yl)sulfonyl)phenyl)carbamoyl)pyrrolidine-1-carboxylate 10



Compound **10** was synthesized following the procedure for **9** using 4-Br aniline as amine. Purified by column chromatography, (35:65 pet. ether/ethyl acetate, R_f: 0.5) colourless viscous liquid (93%). $[\alpha]^{27}_D$: -239.31° (*c* = 0.1, $CHCl_3$); IR ($CHCl_3$, ν (cm^{-1}): 3425, 3020, 2400, 1682, 1583, 1530, 1370, 1215; ^{1}H NMR ($CDCl_3$/400MHz): 10.22 (s, 1H), 8.81 (s, 1H), 8.50-8.54 (d, *J*=8.46, 1H), 7.82-7.87 (dd, *J*=8.08, *J*=1.26, 1H), 7.50-7.58 (t, *J*=7.96, 1H), 7.38 (s, 4H), 7.18-7.25 (t, *J*=7.64, 1H), 4.29-4.46 (m, 2H), 3.18-3.80

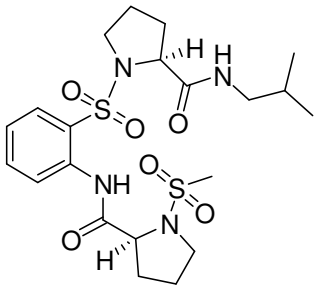
(m, 5H); 2.1-2.32 (m, 3H), 1.79-2.04 (m, 4H), 1.44 (s, 9H); ^{13}C NMR ($CDCl_3$,50MHz): δ ppm 171.3, 169.2, 136.5, 136.2, 134.6, 131.6, 129.5, 124.0, 116.9, 80.7, 62.3, 49.5, 47.3, 31.2, 30.5, 28.3, 24.3; MALDI-TOF-MS: 620.7892 $(M)^+$, 643.1767 $(M+Na)^+$, 659.1454 $(M+K)^+$; Elemental Analysis calculated for $C_{27}H_{33}BrN_4O_6S$: C, 52.18; H, 5.35; N, 9.01; Found: C, 54.33; H, 5.97; N, 8.84.

(S)-*N*-(4-bromophenyl)-1-((2-((S)-1-(methylsulfonyl)pyrrolidine-2-carboxamido)phenyl)sulfonyl)pyrrolidine-2-carboxamide 3



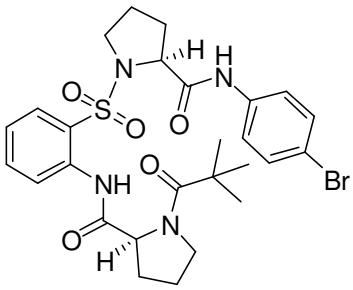
Compound **10** (0.5, 0.8052mmol) was subjected to ^{t}Boc deprotection using TFA (2mL) in DCM (2mL). The reaction mixture was evaporated and the residue was neutralized with $NaHCO_3$ solution, followed by extraction using DCM (2mL) and evaporation to yield the free amine. To a solution of free amine in DCM (5mL), Et_3N (0.34mL, 0.244g, 2.415mmols) was added followed by the addition of Mesyl chloride (0.07mL, 0.11g, 0.9662mmols). After 12 hours, reaction mixture was diluted with DCM (2mL) and the organic layer was washed with saturated sodium bicarbonate (2mL), potassium bisulphate (2mL) and water (2mL) sequentially. The organic layer was dried over anhydrous Na_2SO_4 solution and evaporated under reduced pressure to get crude product which was purified by column chromatography, (35:65 pet. ether/ethyl acetate, R_f: 0.5) to afford **3** as a white crystalline solid (0.46, 97%). mp: 190-192^{o}C; $[\alpha]^{27}_D$: -248.81° (*c* = 0.1, $CHCl_3$); IR ($CHCl_3$, ν (cm^{-1}): 3352, 3019, 2400, 1692, 1589, 1534, 1341, 1200; ^{1}H NMR ($CDCl_3$/400MHz): δ ppm 10.57 (s, 1H), 8.63-8.65 (d, *J*=7.78, 1H), 8.37 (s, 1H), 7.92-7.95 (d, *J*=9.29, 1H), 7.51-7.55 (m, 1H), 7.35-7.37 (d, *J*=8.78, 2H), 7.26-7.29 (d, *J*=8.78, 2H), 7.20-7.24 (m, 1H), 4.26-4.30 (m, 2H), 3.86-3.91 (m, 1H), 3.77-3.81 (m, 1H), 3.52-3.59 (m, 1H), 3.40-3.46 (m, 1H), 2.96-2.98 (s, 3H), 2.28-2.40 (m, 2H), 1.89-2.18 (m, 7H), 1.72-1.86 (m, 2H); ^{13}C NMR ($CDCl_3$, 100MHz): δ ppm 170.0, 169.1, 136.4, 136.2, 135.3, 131.5, 130.6, 124.0, 121.8, 121.0, 117.0, 63.4, 63.0, 50.1, 48.8, 34.3, 31.8, 31.1, 24.8, 24.7; MALDI-TOF-MS: 621.0372 $(M+Na)^+$, 637.0112 $(M+K)^+$; Elemental Analysis calculated for $C_{23}H_{27}BrN_4O_6S_2$: C, 46.08; H, 4.54; N, 9.35; Found: C, 46.64; H, 4.76; N, 9.23.

(S)-*N*-isobutyl-1-((2-((S)-1-(methylsulfonyl)pyrrolidine-2-carboxamido)phenyl)sulfonyl)pyrrolidine-2-carboxamide 2



Compound **2** was synthesized from compound **9**, following the synthetic procedure for compound **3**. Purified by column chromatography, (30:70 pet. ether/ethyl acetate, R_f: 0.5) to afford **2** as a white crystalline solid (98%). mp: 143-148°C; $[\alpha]^{27}_D$: -169.19° (*c* = 0.1, $CHCl_3$); IR ($CHCl_3$, ν (cm^{-1}): 3336, 3020, 2400, 1699, 1589, 1521, 1427, 1338, 1217; ^{1}H NMR ($CDCl_3$/200MHz): δ ppm 10.47 (s, 1H), 8.69-8.73 (d, *J*=8.46Hz, 1H), 7.88-7.93 (dd, *J*=7.96Hz, *J*=1.52Hz, 1H), 7.55-7.64 (t, *J*=8.54Hz, 1H), 7.19-7.27 (t, *J*=8.40Hz, 1H), 6.72-6.78 (t, *J*=5.75Hz, 1H), 4.25-4.35 (m, 1H), 4.09-4.15 (m, *J*=8.08Hz, *J*=3.16Hz, 1H), 3.68-3.81 (m, 1H), 3.38-3.55 (m, 2H), 3.07-3.18 (m, 4H), 2.96 (s, 2H), 2.68-2.98 (m, 2H), 2.23-2.25 (m, 3H), 1.93-2.16 (m, 4H), 1.76-1.93 (m, 2H), 1.56-1.73 (m, 1H), 1.16-1.45 (m, 6H); ^{13}C NMR ($CDCl_3$, 50MHz): δ ppm 170.5, 170.2, 136.5, 135.1, 130.5, 124.0, 123.4, 121.2, 63.3, 62.6, 49.7, 48.5, 46.6, 45.5, 34.8, 31.7, 31.0, 28.2, 24.8, 24.5, 19.9, 8.4; MALDI-TOF-MS: 501.2457 $(M+H)^+$, 523.2364 $(M+Na)^+$, 539.2071 $(M+K)^+$; Elemental Analysis calculated for $C_{21}H_{32}N_4O_6S_2$: C, 50.38; H, 6.44; N, 11.19; Found: C, 50.14; H, 6.85; N, 11.46

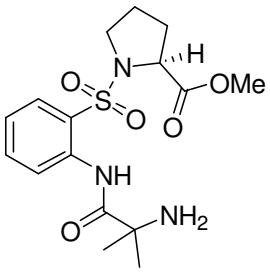
(S)-*N*-(4-bromophenyl)-1-((2-((S)-1-pivaloylpyrrolidine-2-carboxamido)phenyl)sulfonyl)pyrrolidine-2-carboxamide 1



Compound **1** was synthesized from **10,** following the procedure for **3**, using pivaloyl chloride as acylating agent. Purified by column chromatography, (30:70 ethyl acetate/pet. ether, R_f: 0.5) white crystalline solid (93%). mp: 200-202°C; $[\alpha]^{25}_D$: -223.95° (*c* = 0.1, $CHCl_3$); IR ($CHCl_3$, ν (cm^{-1}): 3331, 3020, 2400, 1696, 1598, 1522, 1435, 1338, 1215; ^{1}H NMR ($CDCl_3$/500MHz): δ ppm 10.04 (s, 1H), 8.97 (s, 1H), 8.37-8.38 (d, *J*=7.93Hz, 1H), 7.84-7.86 (d, *J*=6.71Hz, 1H), 7.47-7.50 (t, *J*=7.32Hz, 1H), 7.34-7.40 (m, 4H), 7.17-7.20 (t, *J*=7.32Hz, 1H), 4.54-4.56 (m, 1H), 4.44-4.46 (m, 1H), 3.83-3.86 (t, *J*=7.32Hz, 2H), 3.71-3.76 (m, 1H), 3.54-3.59 (m, 1H), 2.14-2.24 (m, 3H), 2.07-2.11 (m, 1H), 1.96-2.03 (m, 2H), 1.83-1.93 (m, 1H), 1.78-1.83 (m, 1H), 1.28 (s, 9H); ^{13}C

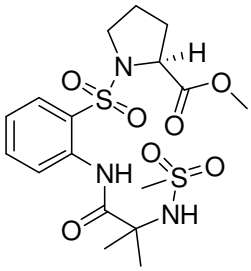
NMR ($CDCl_3$, 125 MHz): δ ppm 178.0, 171.3, 169.1, 136.7, 134.6, 131.6, 129.9, 124.0, 122.7, 121.8, 116.9, 64.1, 61.7, 49.6, 48.7, 38.9, 30.6, 28.5, 27.2, 26.0, 24.2; MALDI-TOF-MS: 606.0644 $(M+H)^+$, 629.0980 $(M+Na)^+$, 645.0698 $(M+K)^+$; Elemental Analysis calculated for $C_{27}H_{33}BrN_4O_5S$: C, 53.55; H, 5.49; N, 9.25; Found: C, 55.25; H, 5.92; N, 9.44.

Methyl ((2-(2-amino-2-methylpropanamido)phenyl)sulfonyl)-L-prolinate 15



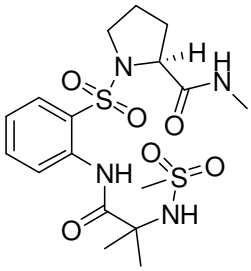
Compound **15** was synthesized following reported procedure.[2]

Methyl((2-(2-methyl-2-(methylsulfonamido)propanamido)phenyl)sulfonyl)-L-prolinate 16



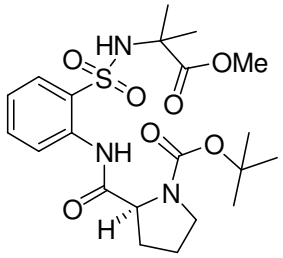
Compound **16** was synthesized from **15**, following the procedure for **3**. Purified by column chromatography, (40:60 pet. ether/ethyl acetate, R_f: 0.5), colorless high viscous liquid (95%). $[\alpha]^{26}_D$: -100.61° (*c* = 0.1, $CHCl_3$); IR ($CHCl_3$, ν (cm^{-1}): 3334, 3020, 2400, 1738, 1698, 1586, 1531, 1435, 1328, 1215; ^1H NMR ($CDCl_3$/400MHz): 10.27 (s, 1H), 8.57-8.62 (d, *J*=8.34, 1H), 7.55-7.64 (dd, *J*=8.59Hz, *J*=1.39Hz, 1H), 7.19-7.23 (d, *J*=1.39Hz, 1H), 5.8 (s, 1H), 4.33-4.99 (m, 1H), 3.68 (s, 3H), 3.45-3.55 (m, 1H), 3.29-3.41 (m, 1H), 3.11 (s, 3H), 1.82-2.21 (m, 5H), 1.70-1.73 (d, *J*=5.81Hz, 6H); ^{13}C NMR ($CDCl_3$, 50MHz): δ ppm 173.0, 172.6, 136.7, 134.5, 129.6, 124.8, 123.8, 122.1, 60.5, 60.0, 52.7, 48.7, 44.0, 30.9, 26.0, 25.6, 24.5; MALDI-TOF-MS: 448.2263 $(M+H)^+$, 470.1576 $(M+Na)^+$, 486.1205 $(M+K)^+$; Elemental Analysis calculated for $C_{17}H_{25}N_3O_7S_2$: C, 45.63; H, 5.63; N, 9.39; Found: C, 45.26; H, 5.34; N, 9.57.

(S)-*N*-methyl-1-((2-(2-methyl-2-(methylsulfonamido)propanamido)phenyl)sulfonyl)pyrrolidine-2-carboxamide 5



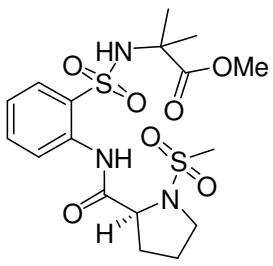
Compound **16** (0.2g, 0.4479mmol) was amidated using saturated methylamide solution in methanol (5mL). The reaction mixture was evaporated and the residue was purified by column chromatography (05:95 methanol/dichloromethane, R_f: 0.5) afforded **5** as a white crystalline solid (1.85, 92%), mp: 165-168^oC; $[\alpha]^{27}_D$: -110.17° (*c* = 0.1, $CHCl_3$); IR ($CHCl_3$, ν (cm^{-1}): 3335, 3019, 2400, 1664, 1585, 1533, 1326, 1216; ^1H NMR ($CDCl_3$/400MHz): δ ppm 10.31 (s, 1H), 8.58-8.60 (d, *J*=8.31Hz, 1H), 7.86-7.89 (dd, *J*=8.07Hz, *J*=1.47Hz, 1H), 7.59-7.63 (t, *J*=8.68Hz, 1H), 7.21-7.26 (t, *J*=8.19Hz, 1H), 6.71 (s, 1H), 5.88 (s, 1H), 4.09-4.12 (dd, *J*=8.80Hz, *J*=3.67Hz, 1H), 3.65-3.71 (m, 1H), 3.34-3.40 (m, 1H), 3.12 (s, 3H), 2.67-2.68 (d, *J*=4.89Hz, 1H), 2.05-2.12 (m, 1H), 1.95-2.03 (m, 1H), 1.77-1.88 (m, 3H), 1.69-1.72 (d, *J*=12.47Hz, 6H); ^{13}C NMR ($CDCl_3$, 100MHz): δ ppm 173.0, 171.6, 137.0, 135.0, 130.2, 124.0, 122.1, 62.2, 60.4, 49.3, 44.1, 31.2, 26.2, 26.1, 25.6, 24.4; MALDI-TOF-MS: 447.1573 $(M+H)^+$, 469.1438 $(M+Na)^+$, 485.1076 $(M+K)^+$; Elemental Analysis calculated for $C_{17}H_{26}N_4O_6S_2$: C, 45.73; H, 5.87; N, 12.55; Found: C, 45.49; H, 5.65; N, 12.16.

Tert-butyl(S)-2-((2-(N-(1-methoxy-2-methyl-1-oxopropan-2-yl)sulfamoyl)phenyl)carbamoyl)pyrrolidine-1-carboxylate 12



Compond **12** was prepared following the reported procedure[3]

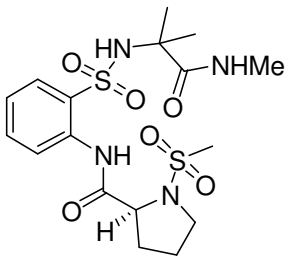
Methyl(S)-2-methyl-2-((2-(1-(methylsulfonyl)pyrrolidine-2-carboxamido)phenyl)sulfonamido)propanoate 13



Compound **13** was synthesized from compound **12**, following the synthetic procedure for **1**. Purified by column chromatography, (30:70 pet. ether/ethyl acetate, R_f: 0.5), white solid (95%), mp: 72-74^oC; $[\alpha]^{27}_D$: -40.94° (*c* = 0.1, $CHCl_3$); IR ($CHCl_3$, ν (cm^{-1}): 3332, 3020, 2400, 1732, 1620, 1522, 1436, 1216; ^1H NMR

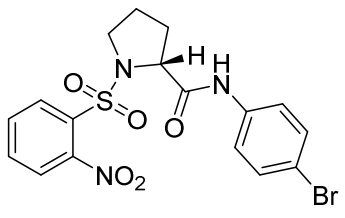
($CDCl_3$/200MHz): δ ppm 10.09 (s, 1H), 8.24-8.28 (d, *J*=8.08Hz, 1H), 7.80-7.84 (d, *J*=7.96Hz,1H), 7.48-7.55 (t, *J*=7.39Hz, 1H), 7.15-7.22 (t, *J*=7.64Hz, 1H), 6.56 (s, 1H), 4.34-4.40 (m, 1H), 4.02-4.13 (m, 1H), 3.42-3.69 (m, 3H) 3.37 (s, 3H), 3.08 (s, 3H), 2.21-2.39 (m, 3H), 1.31-1.42 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ ppm 173.2, 170.6, 156.8, 134.3, 132.7, 131.5, 128.2, 124.0, 81.4, 61.9, 59.9, 58.0, 52.1, 47.4, 30.2, 28.3, 25.5, 25.2, 23.9; MALDI-TOF-MS: 448.1569 $(M+H)^+$, 470.1021 $(M+Na)^+$, 486.0770 $(M+K)^+$; Elemental Analysis calculated for $C_{17}H_{25}N_3O_7S_2$: C, 45.63; H, 5.63; N, 9.39; Found: C, 45.42; H, 5.26; N, 9.72.

(S)-*N*-(2-(*N*-(2-methyl-1-(methylamino)-1-oxopropan-2-yl)sulfamoyl)phenyl)-1-(methylsulfonyl)pyrrolidine-2-carboxamide 4



Compound **4** was prepared, from compound **13**, following the procedure for **5**. Purified by column chromatography, (05:95 methanol/dichloromethane, R_f: 0.5) to furnish **4** as a white crystalline solid (96%). mp: 178-179°C; $[\alpha]^{26}_D$: -25.16° (*c* = 0.1, $CHCl_3$); IR ($CHCl_3$, ν (cm^{-1}): 3341, 3020, 2401, 1652, 1585, 1469, 1438, 1343, 1216; ^{1}H NMR ($CDCl_3$/400MHz): δ ppm 10.03 (s, 1H), 8.26-8.28 (d, *J*=8.28Hz, 1H), 7.90-7.93 (dd, *J*=7.78Hz, *J*=1.25Hz,1H), 7.56-7.60 (m, 1H), 7.28-7.24 (t, *J*=7.65Hz, 1H), 6.56 (s, 1H), 7.45 (s, 1H), 4.29-4.33 (t, *J*=6.52Hz, 1H), 3.7-3.75 (m, 1H), 3.40-3.46 (m, 1H), 3.05 (s, 3H), 2.66-2.68 (d, *J*=4.77Hz, 3H), 2.37-2.42 (m, 2H), 2.02-2.09 (m, 2H), 1.29-1.32 (d, *J*=12.55Hz, 6H); ^{13}C NMR ($CDCl_3$, 100MHz): δ ppm 173.9, 169.8, 134.3, 133.8, 130.7, 129.4, 124.7, 123.2, 62.8, 60.2, 50.0, 53.0, 35.0, 31.6, 26.5, 25.0; MALDI-TOF-MS: 447.1363 $(M+H)^+$, 469.1172 $(M+Na)^+$, 485.0930 $(M+K)^+$; Elemental Analysis calculated for $C_{17}H_{26}N_4O_6S_2$: C, 45.73; H, 5.87; N, 12.55; Found: C, 45.48; H, 5.59; N, 12.17.

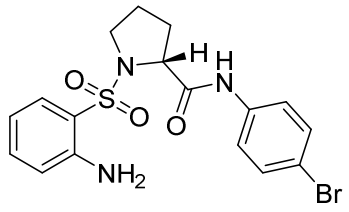
(R)-N-(4-bromophenyl)-1-(2-nitrophenylsulfonyl)pyrrolidine-2-carboxamide 18



To a solution of compound H-^{D}Pro *p*-Br anilide (1.35g, 5.016moles) in DCM (20mL), Et_3N (2mL, 1.5g, 15moles) was added, followed by 2-nitrobenzene sulfonyl chloride (0.926g, 4.18moles) and 25% wt. of DMAP (0.030g). After 12 hours, the reaction mixture was diluted with DCM (5mL) and the organic layer was washed with saturated solutions

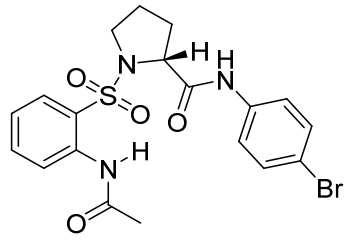
of sodium bicarbonate (10mL), potassium bisulphate (10mL), water (10mL) and saturated NaCl solution (10mL). The organic layer was dried over anhydrous Na_2SO_4 solution and evaporated under reduced pressure to obtain the crude product which was purified by column chromatography, (50:50 pet. ether/ethyl acetate, R_f: 0.5) to afford **18** as a white solid (1.8g, 94%). mp: 68-72°C; $[\alpha]^{28}_D$: +127° (*c* = 0.1, $CHCl_3$); IR ($CHCl_3$, ν (cm^{-1}): 3356, 3019, 2400, 1691, 1653, 1591, 1546, 1370, 1215; ^{1}H NMR ($CDCl_3$/200MHz): 8.52 (s, 1H), 8.03-8.12 (m, 1H), 7.66-7.75 (m, 2H), 7.59-7.64 (m, 1H), 7.30-7.40 (m, 4H), 4.52-4.55 (m, 1H), 3.62-3.71 (m, 2H), 2.34-2.46 (m, 1H), 2.11-2.26 (m, 1H), 1.92-2.07 (m, 2H); ^{13}C NMR ($CDCl_3$,50MHz): δ ppm 168.8, 148.1, 136.2, 134.5, 132.0, 131.8, 131.3, 130.5, 124.2, 121.2, 117.1, 62.6, 49.6, 30.8, 24.5; MALDI-TOF-MS: 454.0768 $(M+H)^+$, 476.0637 $(M+Na)^+$, 492.0313 $(M+K)^+$; Elemental analysis calculated for $C_{17}H_{16}BrN_3O_5S$: C, 44.94; H, 3.55; N, 9.25; Found: C, 44.28; H, 4.02; N, 8.66.

(R)-1-(2-aminophenylsulfonyl)-N-(4-bromophenyl)pyrrolidine-2-carboxamide 19



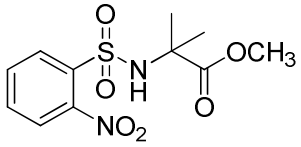
To a solution of compound **18** (2g, 4.402moles) in MeOH (10mL), anhydrous $HCOONH_4$ (2.77, 44.02moles) and activated Zn (2.87, 44.02moles), pre-treated with HCl and thoroughly washed with water and ether prior to use) were added and stirred at room temperature for 3 hours. The reaction mixture was then filtered through celite and the filtrate was evaporated under reduced pressure. The residue obtained was dissolved in DCM (10mL) and purified by column chromatography, (65:35 pet. ether/ethyl acetate, R_f: 0.5) to afford **19** as a colorless viscous liquid (1.7, 96%). mp: 60-63°C; $[\alpha]^{27}_D$: +129° (*c* = 0.1, $CHCl_3$); IR ($CHCl_3$, ν (cm^{-1}): 3486, 3384, 3019, 2400, 1687, 1590, 1519, 1341, 1306, 1215; ^{1}H NMR ($CDCl_3$/200MHz): δ ppm 8.845 (s, 1H), 7.67-7.72 (m, 1H), 7.43-7.45 (m, 4H), 7.29-7.49 (m, 1H), 6.72-6.85 (m, 2H), 5.15 (s, 2H) 4.42-4.47 (m, 1H), 3.48-3.55 (m, 2H), 2.29-2.37 (m, 1H), 1.73-2.01 (m, 3H); ^{13}C NMR ($CDCl_3$, 50MHz): δ ppm 169.4, 146.2, 136.4, 135.1, 131.7, 130.3, 121.3, 118.2, 118.0, 117.0, 62.1, 49.6, 30.4, 24.5; MALDI-TOF-MS: 424.0486 $(M+H)^+$, 446.0358 $(M+Na)^+$, 462.0073 $(M+K)^+$; Elemental analysis calculated for $C_{17}H_{18}BrN_3O_3S$: C, 48.12; H, 4.28; N, 9.90; Found: C, 47.75; H, 4.52; N, 9.68.

(R)-1-(2-acetamidophenylsulfonyl)-N-(4-bromophenyl)pyrrolidine-2-carboxamide 6



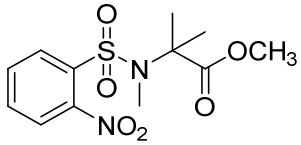
To a solution of compound **19** (0.4g, 9.427moles) in DCM (10mL), Et_3N (0.4mL, 2.86g, 28.28moles) was added followed by acetyl chloride (0.11mL, 0.1739g, 14.28moles). After 3 hours, the reaction mixture was diluted with DCM (5mL) and the organic layer was washed with saturated solutions of sodium bicarbonate (5mL), potassium bisulphate (5mL), water (5mL) and NaCl (5mL). The organic layer was dried over anhydrous Na_2SO_4 solution and evaporated under reduced pressure to obtain the crude product which was purified by column chromatography, (30:70 pet. ether/ethyl acetate, R_f: 0.5) to afford **6** as a white crystalline solid (0.37, 81%). mp: 202-205^oC; $[\alpha]^{28}_D$: +132.9° (*c* = 0.1, $CHCl_3$); IR ($CHCl_3$, ν (cm^{-1}): 3390, 3019, 2400, 1698, 1588, 1427, 1338, 1217; ^1H NMR ($CDCl_3$/200MHz): δ ppm 9.54 (s, 1H), 8. 54 (s, 1H), 8.51 (s, 1H), 7.84-7.89 (m, 1H), 7.59-7.67 (m, 1H), 7.4-7.49 (m, 4H), 7.21-7.28 (m, 1H), 4.24-4.34 (m, 1H), 3.52-3.61 (m, 1H), 3.22-3.35 (m, 1H), 2.21 (s, 3H) 1.75-2.00 (m, 4H); ^{13}C NMR ($CDCl_3$, 50MHz): δ ppm 168.8, 137.0, 136.2, 135.1, 131.9, 129.9, 124.7, 124.4, 123.3, 123.2, 121.4, 117.3, 62.5, 49.9, 30.5, 25.0, 24.5; MALDI-TOF-MS: 446.1022 $(M+H)^+$, 488.0991 , 504.0633 $(M+K)^+$; Elemental analysis calculated for $C_{19}H_{20}BrN_3O_4S$: C, 48.93; H, 4.32; N, 9.01; Found: C, 48.35; H, 4.56; N, 8.86

Methyl 2-methyl-2-(2-nitrophenylsulfonamido)propanoate 21



Compound **21** was synthesized following the reported procedure.[1]

Methyl 2-methyl-2-((N-methyl-2-nitrophenyl)sulfonamido)propanoate 22

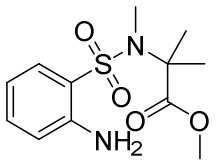


To a solution of compound **21** (0.5g, 1.656 moles) in DMF (5mL), Ag_2O (0.7676g, 3.3112moles) was added followed by methyl iodide (0.2mL, 0.470g, 3.3112moles). After 3 hours, the reaction mixture was diluted with ethyl acetate (5mL) and the organic layer was washed with water (5mL) and brine (5mL). The organic layer was dried over anhydrous Na_2SO_4 solution and evaporated under reduced pressure

to obtain the crude product which was purified by column chromatography, (30:70 pet. ether/ethyl acetate, R_f: 0.5) to afford **22** as a white crystalline solid (0.42, 80%). mp: 101-103°C; IR ($CHCl_3$, ν (cm^{-1}): 3404, 3021, 2400, 1740, 1546, 1437, 1372, 1216; ^{1}H NMR ($CDCl_3$/200MHz): 8.19-8.24 (m, 1H), 7.63-7.73 (m, 3H), 3.72 (s, 3H), 2.93 (s, 3H), 1.56 (s, 6H); ^{13}C NMR ($CDCl_3$, 50MHz): δ ppm 170.4, 147.7, 133.5, 132.3, 131.4, 130.7, 123.8, 64.7, 51.5, 30.6, 27.8; MALDI-TOF-MS: 317.1046 $(M+H)^+$, 339.1021 $(M+Na)^+$, 355.0847 $(M+K)^+$; Elemental analysis calculated for $C_{12}H_{16}N_2O_6S$: C, 45.56; H, 5.10; N, 8.86; Found: C, 46.29; H, 4.92; N, 8.96.

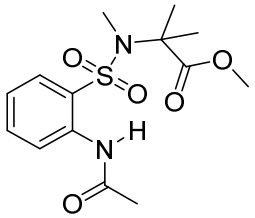
Methyl 2-((2-amino-N-methylphenyl)sulfonamido)-2-methylpropanoate 23

Compound **23** was synthesized following the procedure for **19**

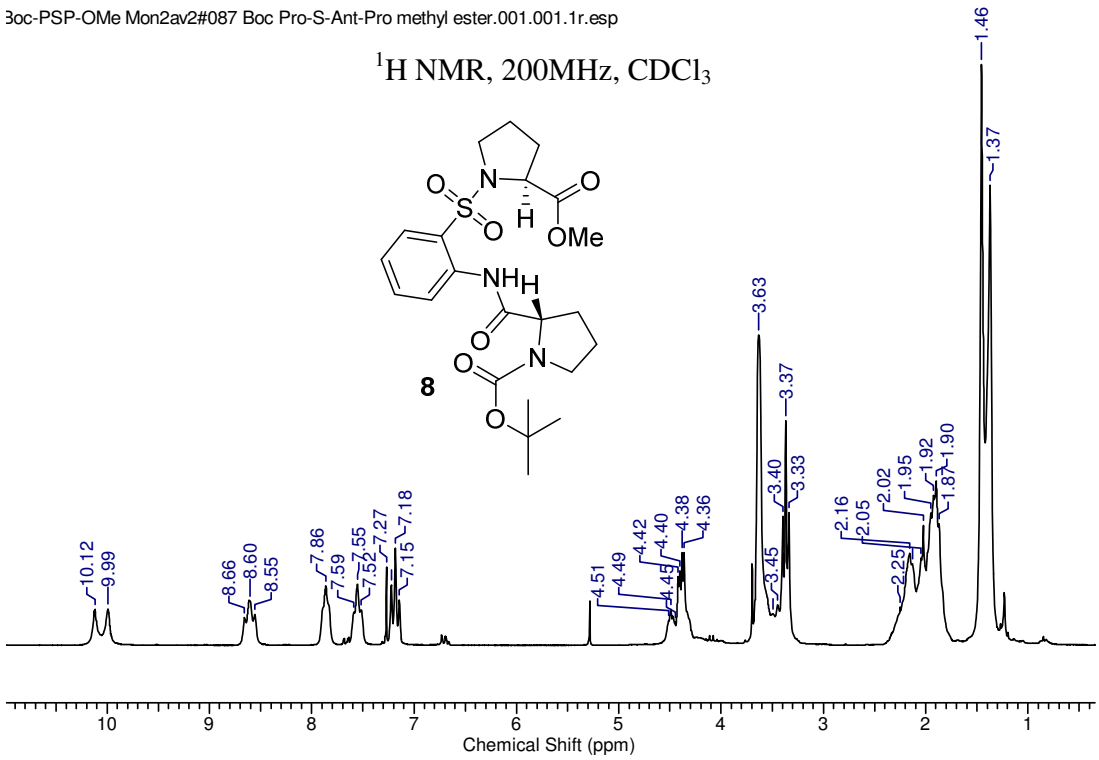


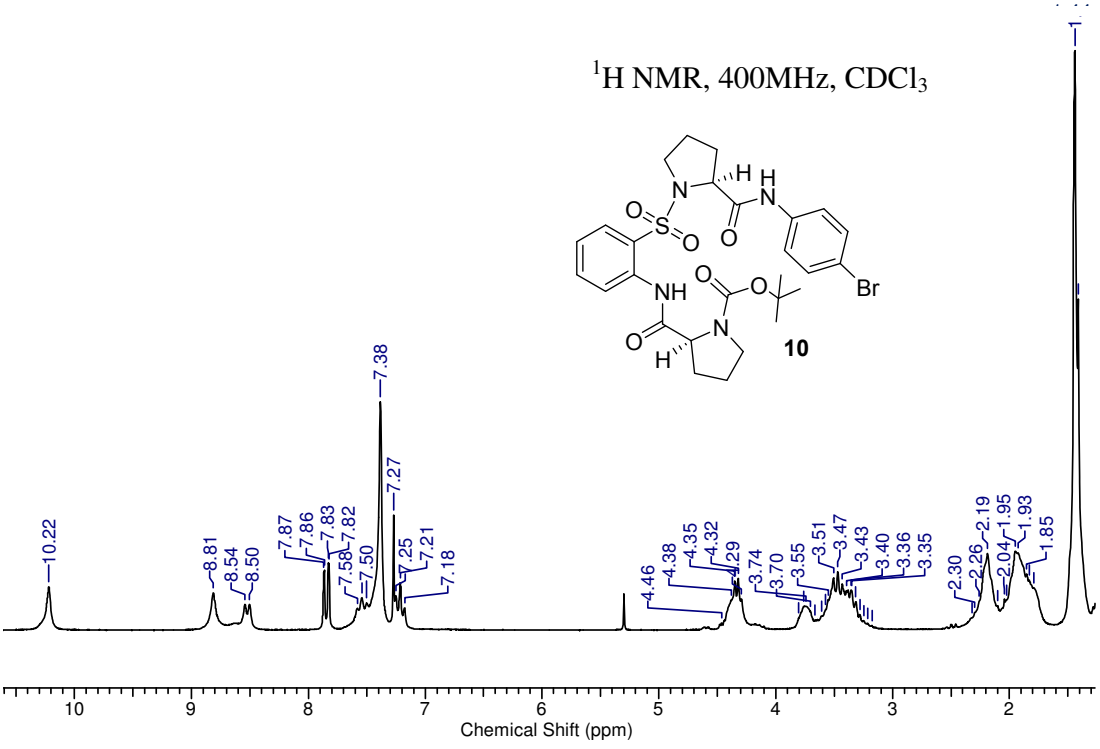
Purified by column chromatography, (70:30 pet. ether/ethyl acetate, R_f: 0.5), white crystalline solid (97%). mp: 114-116°C; IR ($CHCl_3$, ν (cm^{-1}): 3486, 3380, 3235, 3020, 2400, 1735, 1637, 1485, 1454, 1216; ^{1}H NMR ($CDCl_3$/200MHz): δ ppm 7.73-7.77 (m, 1H), 7.25-7.33 (m, 1H), 6.65-6.74 (m, 2H), 5.30 (s, 2H), 3.82 (s, 3H), 2.63 (s, 3H) 1.56 (s, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ ppm 157.7, 146.4, 134.5, 131.2, 118.1, 117.4, 116.3, 62.3, 52.7, 30.2, 24.1; LC-MS: 308.86 $(M+Na)^+$; Elemental analysis calculated for $C_{12}H_{18}N_2O_4S$: C, 50.33; H, 6.34; N, 9.78; Found: C, 49.87; H, 5.95; N, 9.92.

Methyl 2-((2-acetamido-N-methylphenyl)sulfonamido)-2-methylpropanoate 7



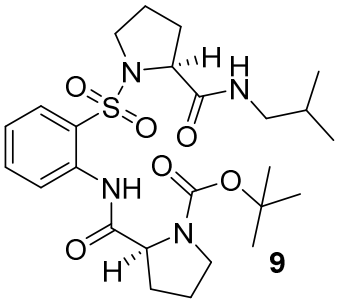
Compound **7** was prepared following the procedure for **6,** using acetyl chloride was used as the acetylating agent. Purified by column chromatography, (70:30 pet. ether/ethyl acetate, R_f: 0.5) to furnish **7** as a white solid (96%), crystallized from methanol. mp: 92-94°C; IR ($CHCl_3$, ν (cm^{-1}): 3334, 3019, 2401, 1737, 1699, 1583, 1529, 1468, 1436, 1322, 1216; ^{1}H NMR ($CDCl_3$/200MHz): δ ppm 9.55 (s, 1H), 8.56-8.61 (d, *J*=8.34Hz, 1H), 7.95-7.99 (dd, *J*=8.02Hz, *J*=1.45Hz, 1H), 7.52-7.61 (m, 1H), 7.13-7.21 (m, 1H), 3.83 (s, 3H), 2.62 (s, 3H), 2.33 (s, 3H), 1.56 (s, 6H); ^{13}C NMR ($CDCl_3$, 50MHz): δ ppm 175.6, 169.6, 137.3, 134.5, 130.8, 124.6, 122.9, 62.9, 53.0, 30.5, 24.8, 24.1; LC-MS: 339.06 $(M+Na)^+$; Elemental analysis calculated for $C_{14}H_{20}N_2O_5S$: C, 51.21; H, 6.14; N, 8.53; Found: C, 50.83; H, 5.82; N, 8.26.


Boc-PSP-OMe Mon2av2#087 Boc Pro-S-Ant-Pro methyl ester.001.001.1r.esp
1H NMR, 200MHz, CDCl3
8
Chemical Shift (ppm)


1H NMR, 400MHz, CDCl3
10
Chemical Shift (ppm)

Boc-PSP-NHiBu Tue4av2#043 Boc pro S-Ant Pro isobutylamide.001.001.1r.esp

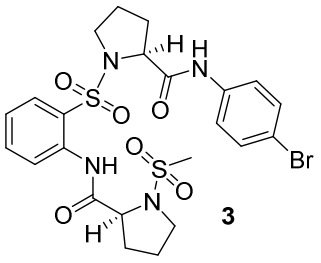
^{1}H NMR, 200MHz, $CDCl_3$



9

un4av400#004 MPSPNHB.001.001.1r.esp

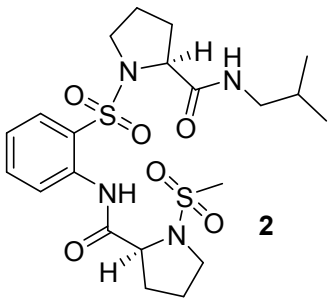
^{1}H NMR, 400MHz, $CDCl_3$



3

Mes-PSP-NHiBu Thu4av2#068 Mesyl Pro S-Ant Pro isobutylamide.001.001.1r.esp

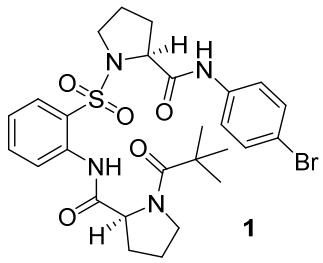
^{1}H NMR, 200MHz, $CDCl_3$



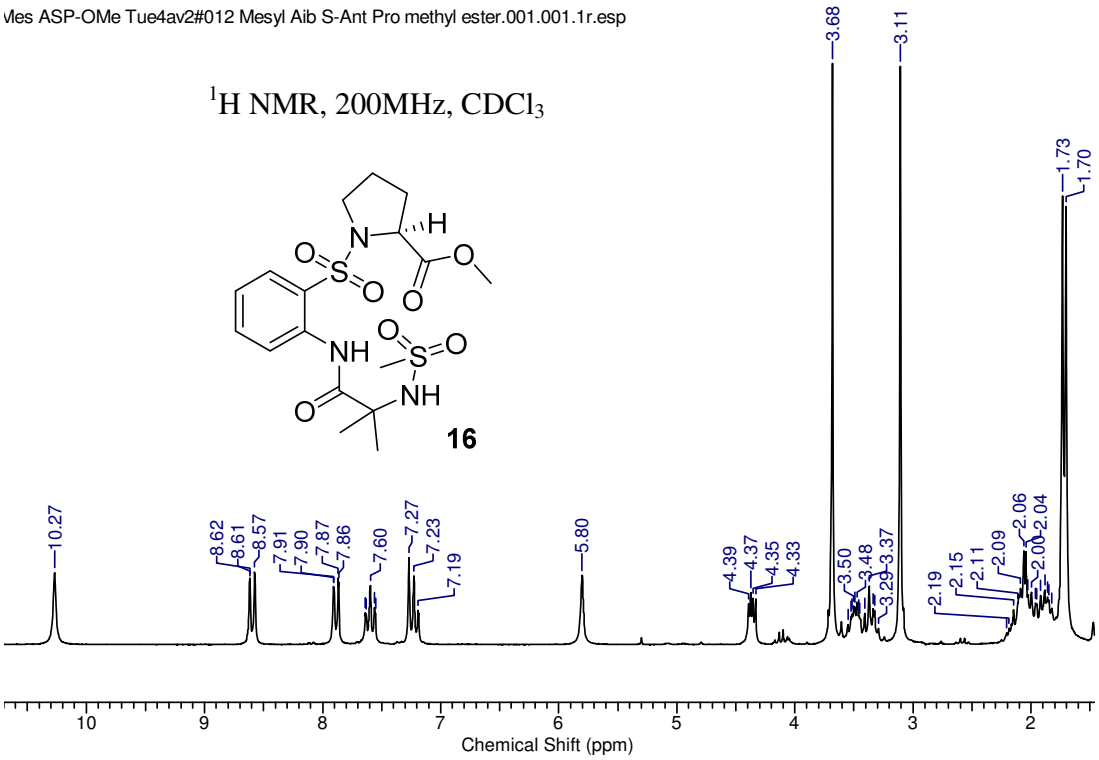
2

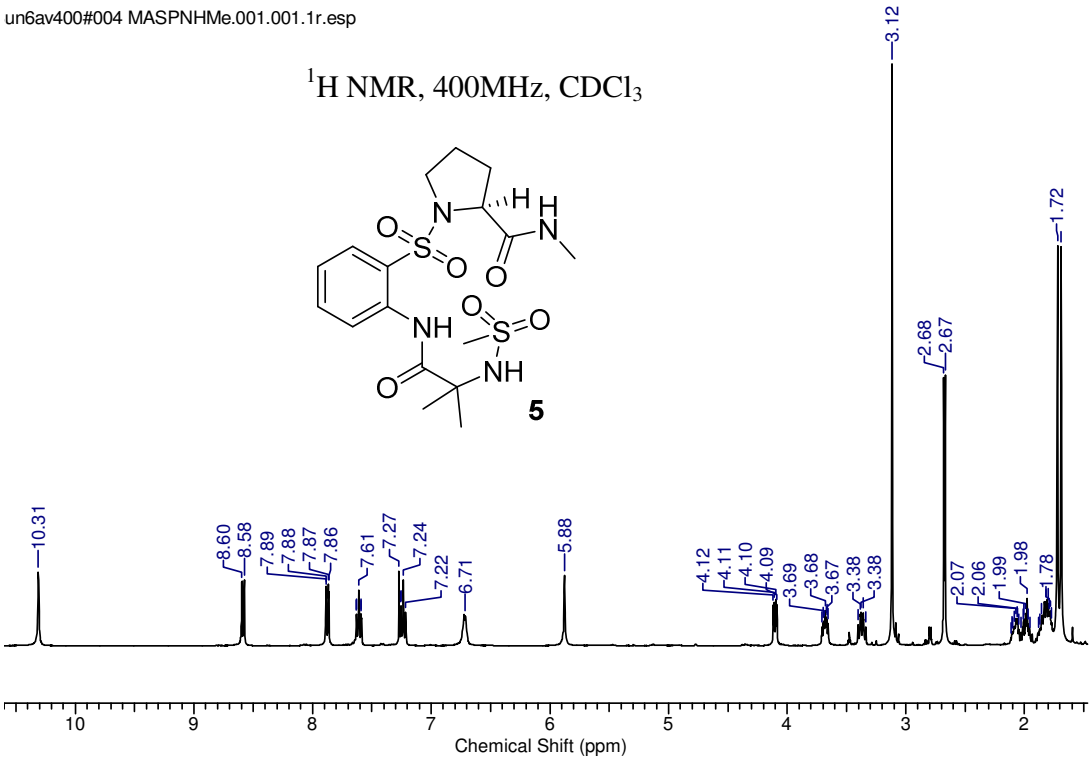
ri3av500#004.001.001.1r.esp

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



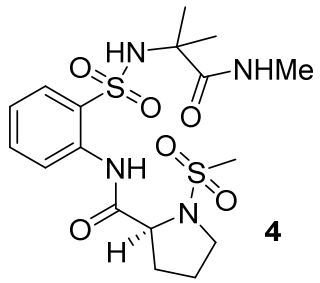
1


Mes ASP-OMe Tue4av2#012 Mesyl Aib S-Ant Pro methyl ester.001.001.1r.esp
1H NMR, 200MHz, CDCl3
16
Chemical Shift (ppm)


un6av400#004 MASPNHMe.001.001.1r.esp
1H NMR, 400MHz, CDCl3
5
Chemical Shift (ppm)

Sat5av400#007 MPSANHMe.001.001.1r.esp

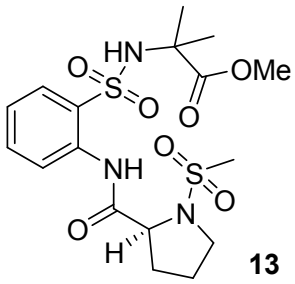
^{1}H NMR, 400MHz, $CDCl_3$



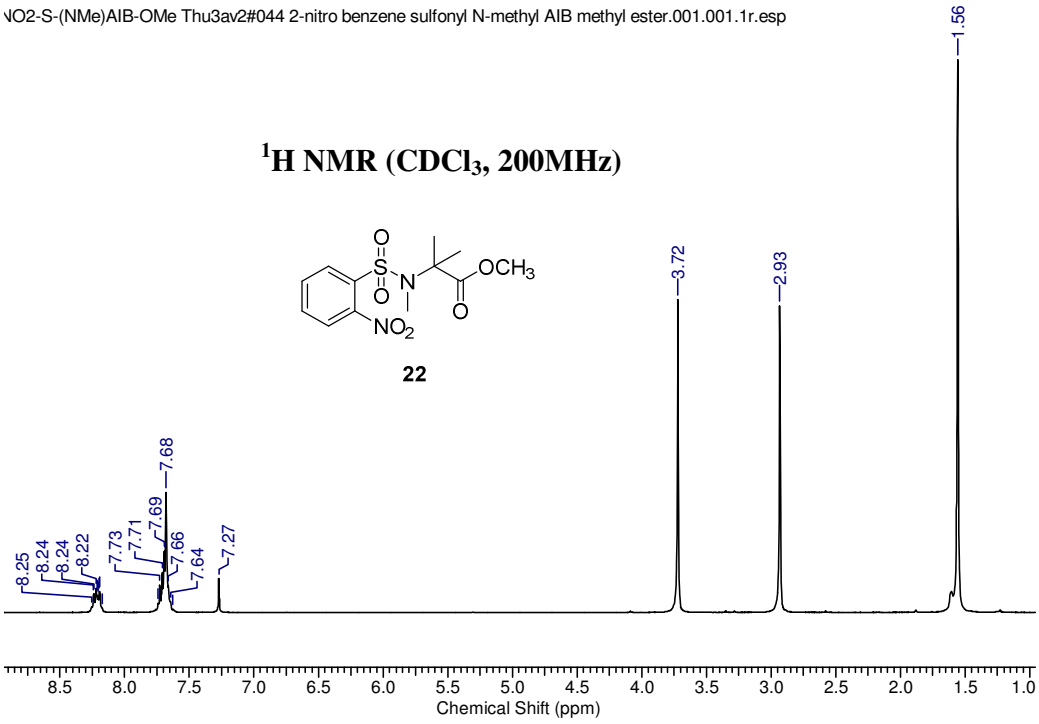
4

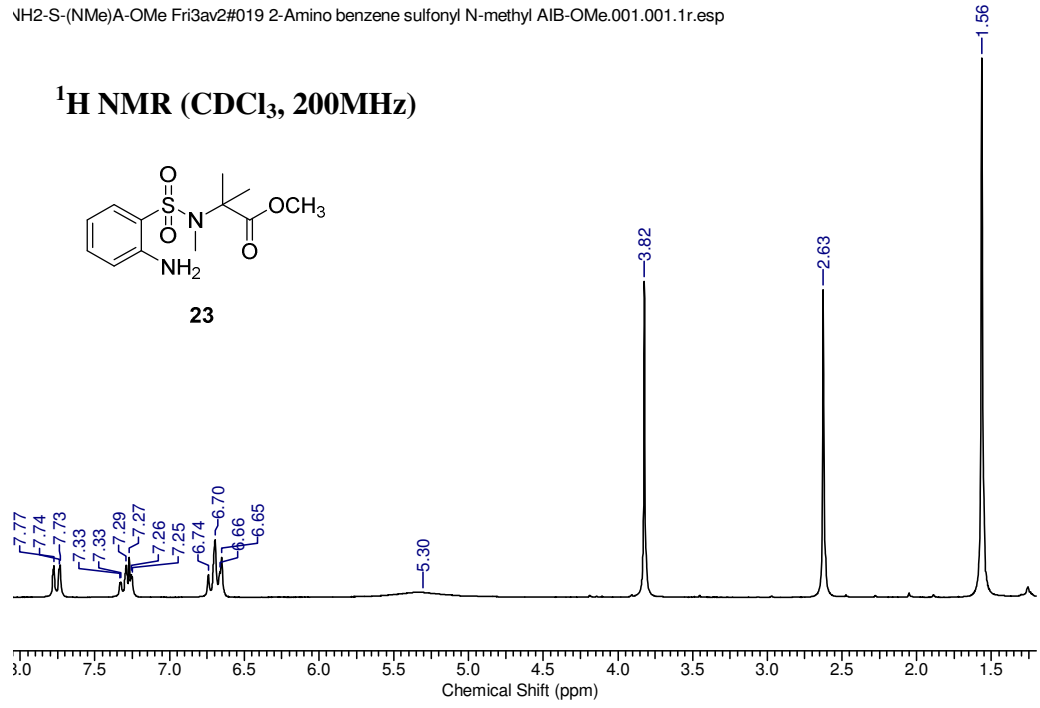
IPSA-OMe Fri5av2#067 Mesyl Pro S-Ant Aib methylester.001.001.1r.esp

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



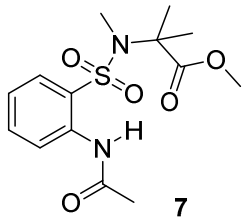
13


NO2-S-(NMe)AIB-OMe Thu3av2#044 2-nitro benzene sulfonyl N-methyl AIB methyl ester.001.001.1r.esp
1H NMR (CDCl3, 200MHz)
22
Chemical Shift (ppm)


NH2-S-(NMe)A-OMe Fri3av2#019 2-Amino benzene sulfonyl N-methyl AIB-OMe.001.001.1r.esp
1H NMR (CDCl3, 200MHz)
23
Chemical Shift (ppm)

SNMeAOMe Mon4av2#067 Acetyl Sulfo Ant N-methyl AIB-OMe..good.001.001.1r.esp

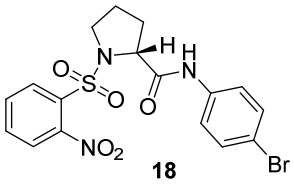
^{1}H NMR ($CDCl_3$, 200MHz)



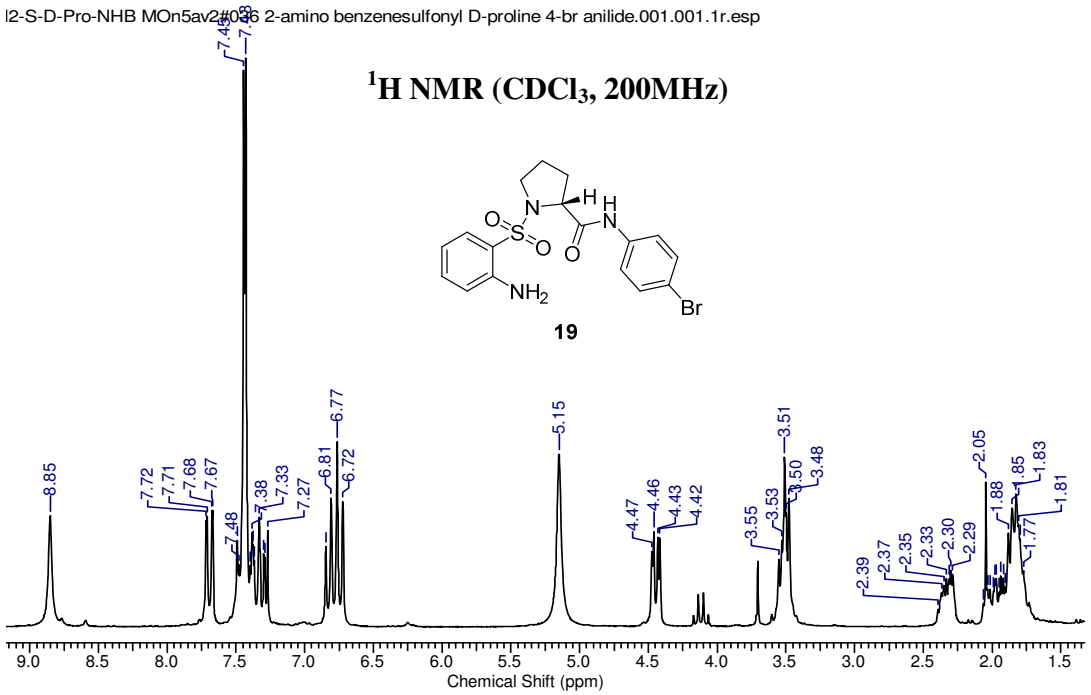
7

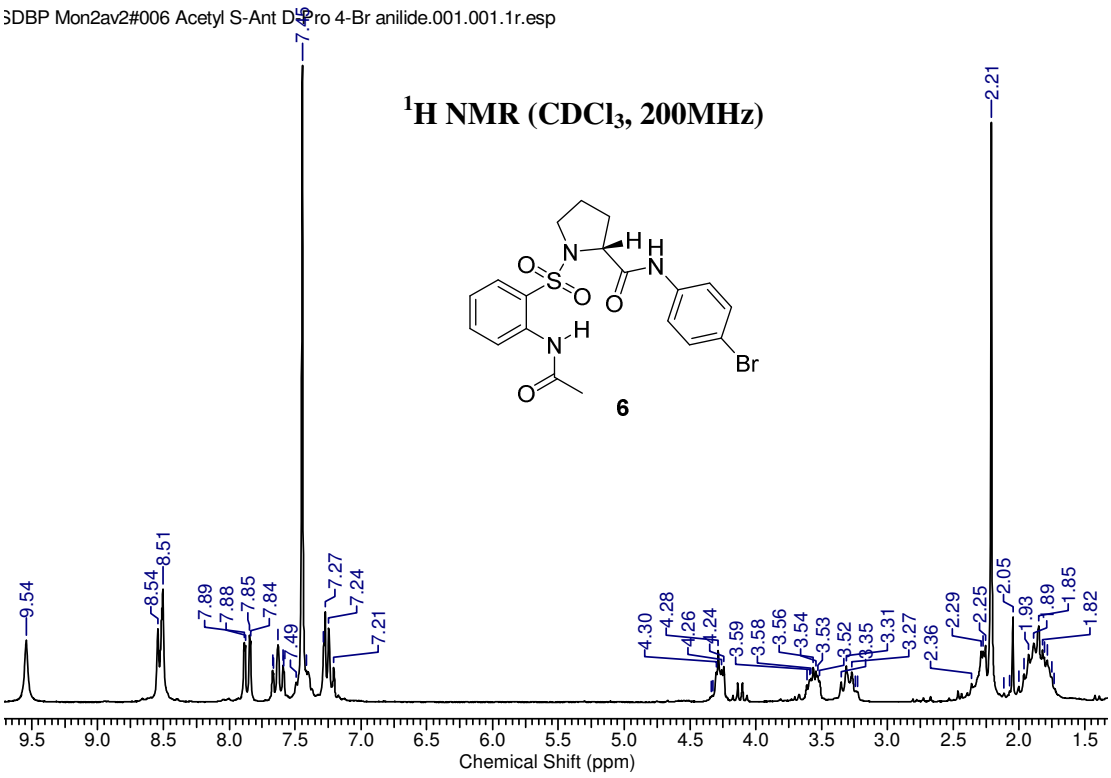
NO2-S-D-Pro-NHB MOn5av2#014 2-nitro benzenesulfonyl D-Pro 4-Br anilide.001.001.1r.esp

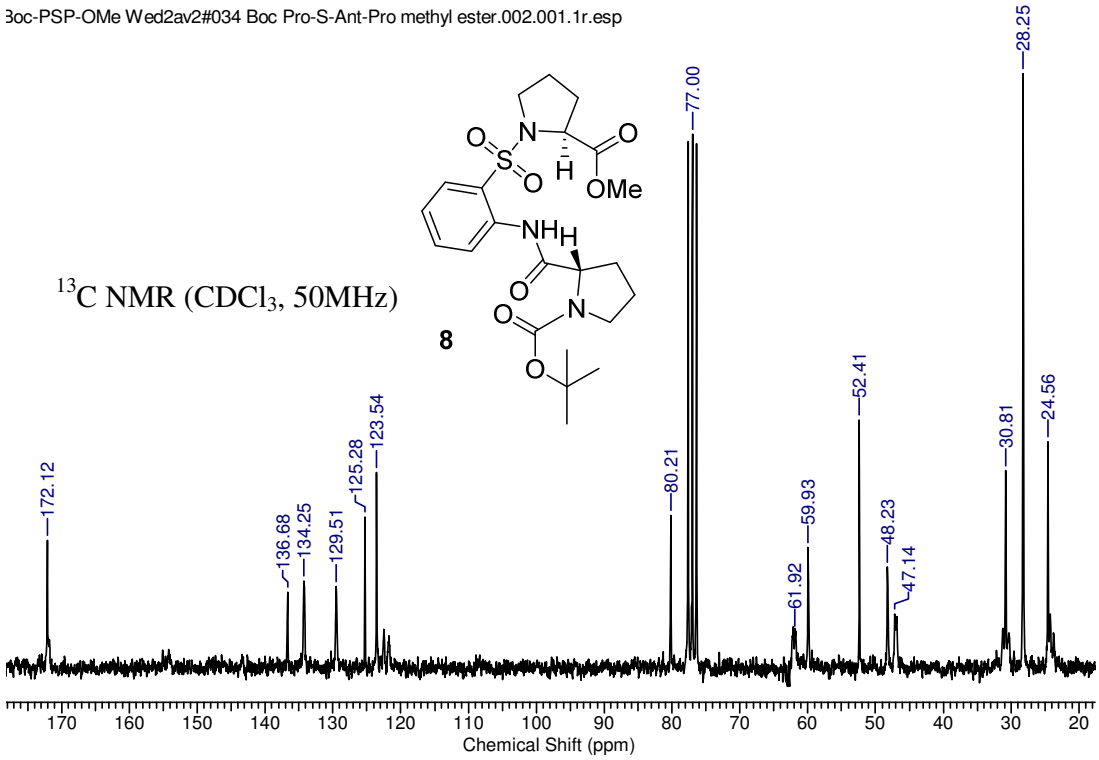
^{1}H NMR ($CDCl_3$, 200MHz)

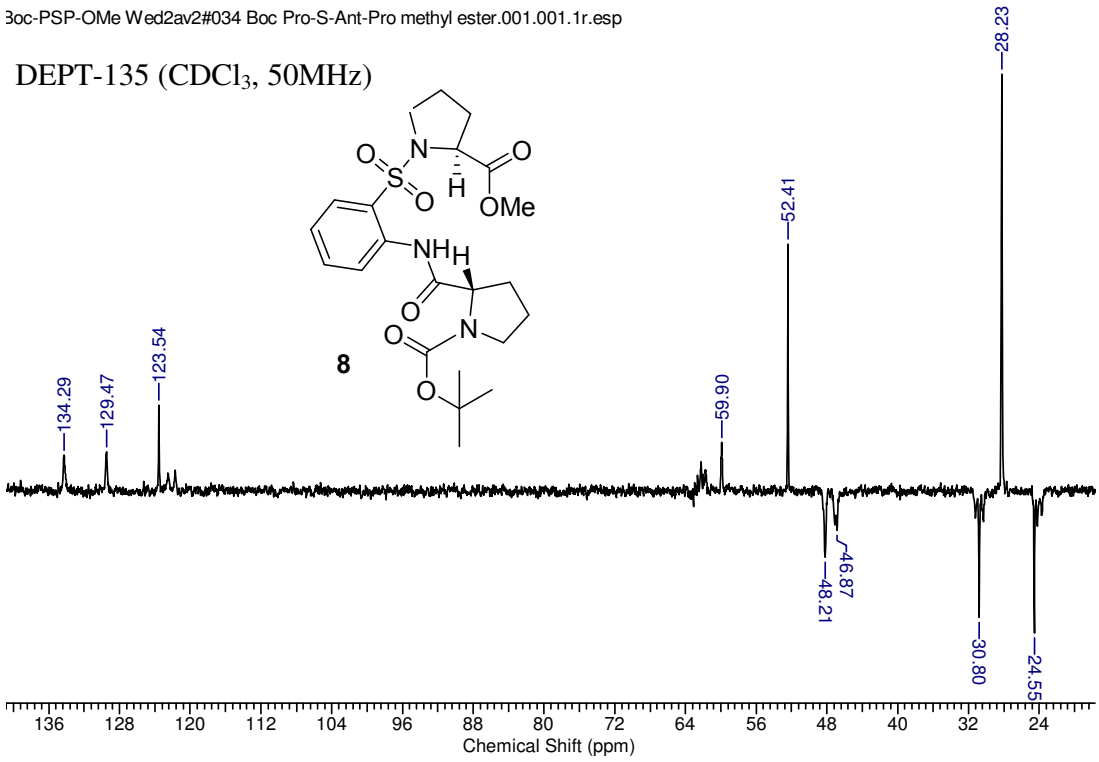


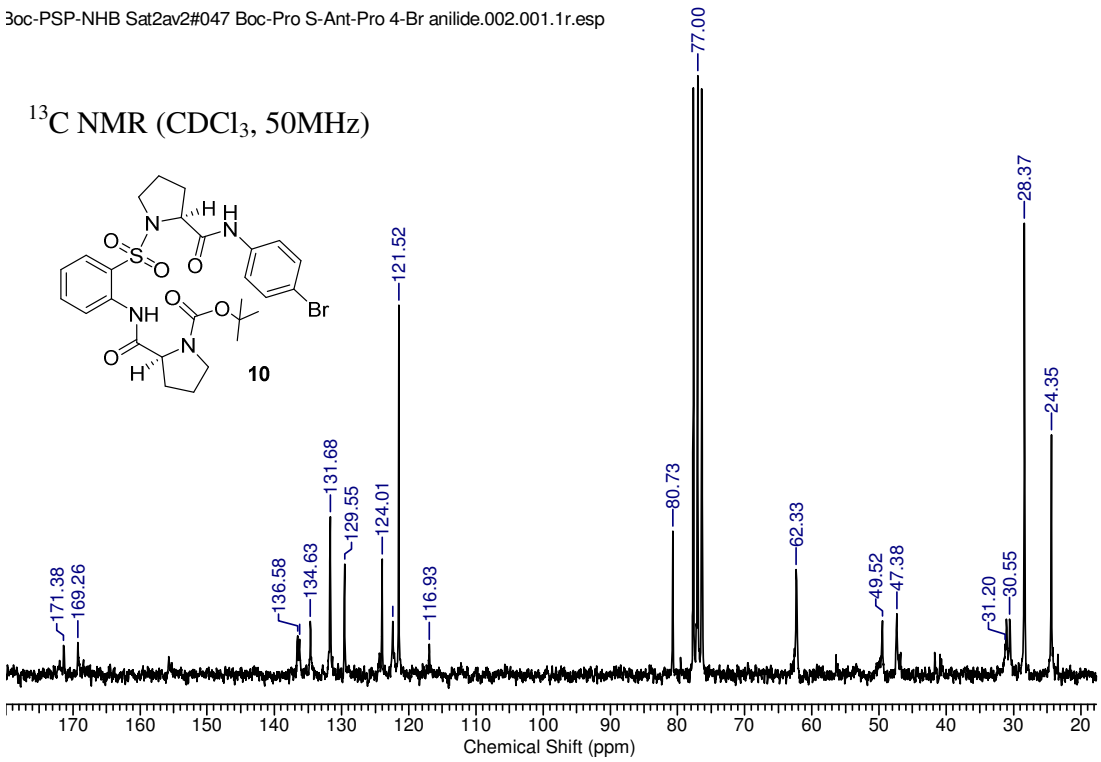
18

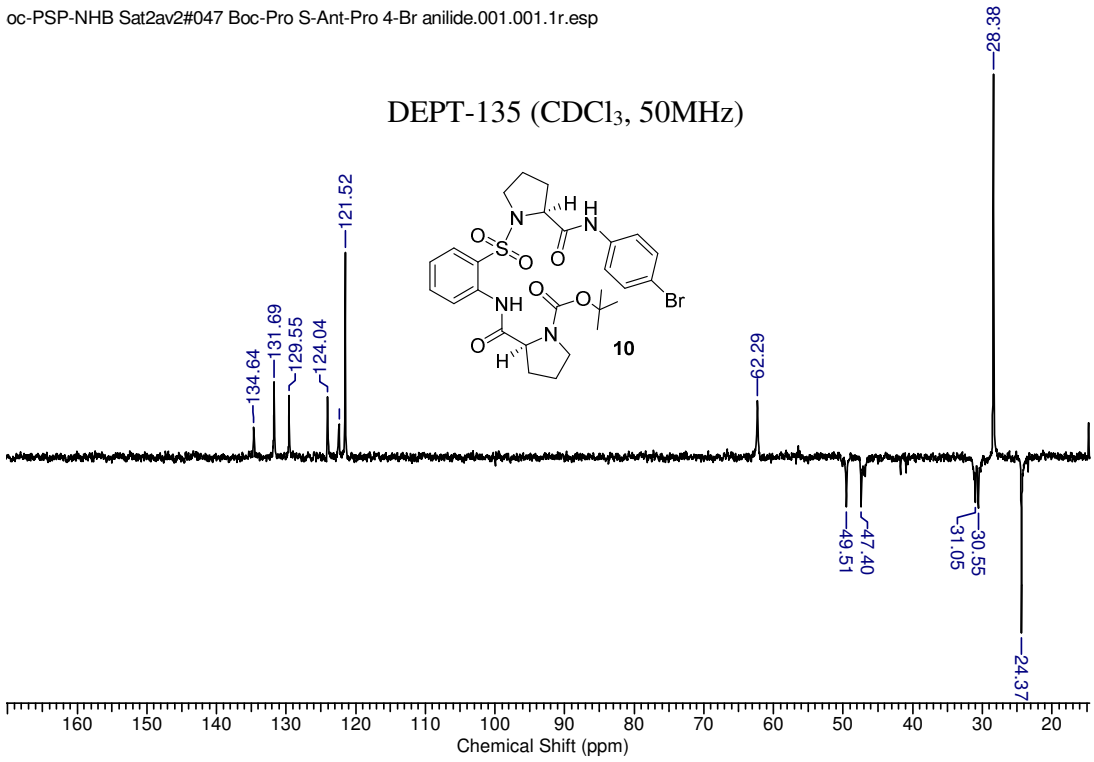

l2-S-D-Pro-NHB MOn5av2#036 2-amino benzenesulfonyl D-proline 4-br anilide.001.001.1r.esp
1H NMR (CDCl3, 200MHz)
19
Chemical Shift (ppm)

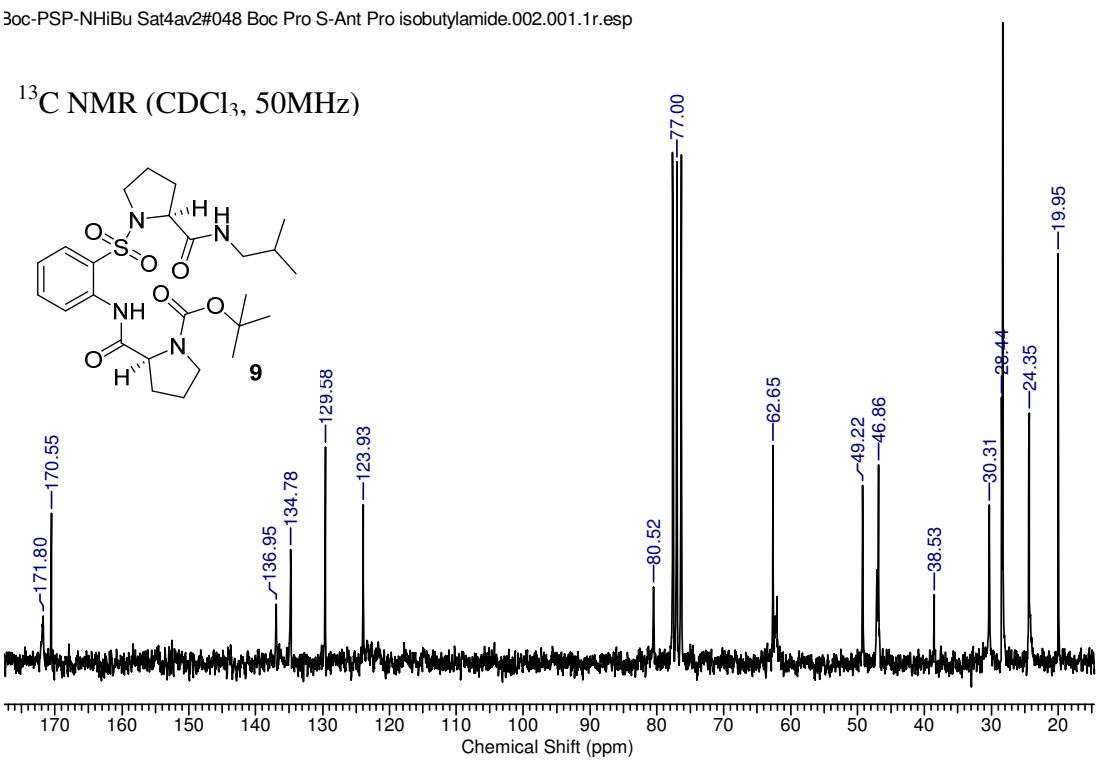

SDBP Mon2av2#006 Acetyl S-Ant D-Pro 4-Br anilide.001.001.1r.esp
1H NMR (CDCl3, 200MHz)
6
Chemical Shift (ppm)

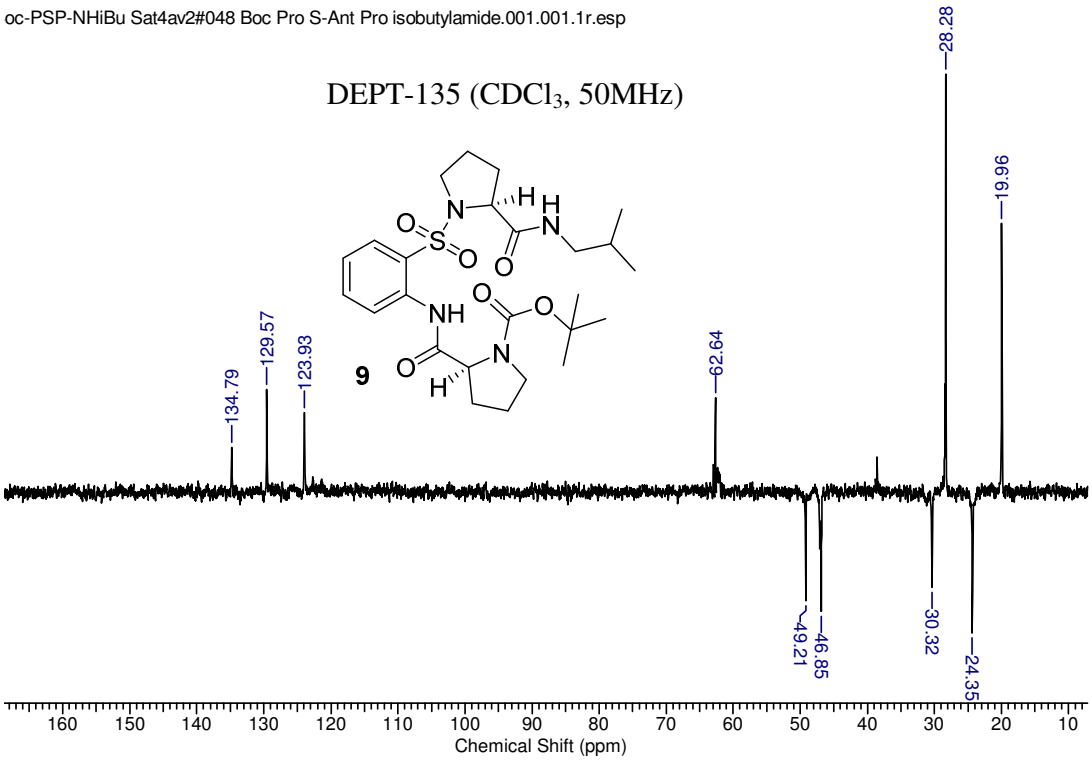

Boc-PSP-OMe Wed2av2#034 Boc Pro-S-Ant-Pro methyl ester.002.001.1r.esp
13C NMR (CDCl3, 50MHz)
8
172.12
136.68
134.25
129.51
125.28
123.54
80.21
77.00
61.92
59.93
52.41
48.23
47.14
30.81
28.25
24.56
Chemical Shift (ppm)


Boc-PSP-OMe Wed2av2#034 Boc Pro-S-Ant-Pro methyl ester.001.001.1r.esp
DEPT-135 (CDCl3, 50MHz)
8
134.29
129.47
123.54
59.90
52.41
48.21
46.87
30.80
28.23
24.55
Chemical Shift (ppm)


3oc-PSP-NHB Sat2av2#047 Boc-Pro S-Ant-Pro 4-Br anilide.002.001.1r.esp
13C NMR (CDCl3, 50MHz)
10
171.38
169.26
136.58
134.63
131.68
129.55
124.01
121.52
116.93
80.73
77.00
62.33
49.52
47.38
31.20
30.55
28.37
24.35
Chemical Shift (ppm)

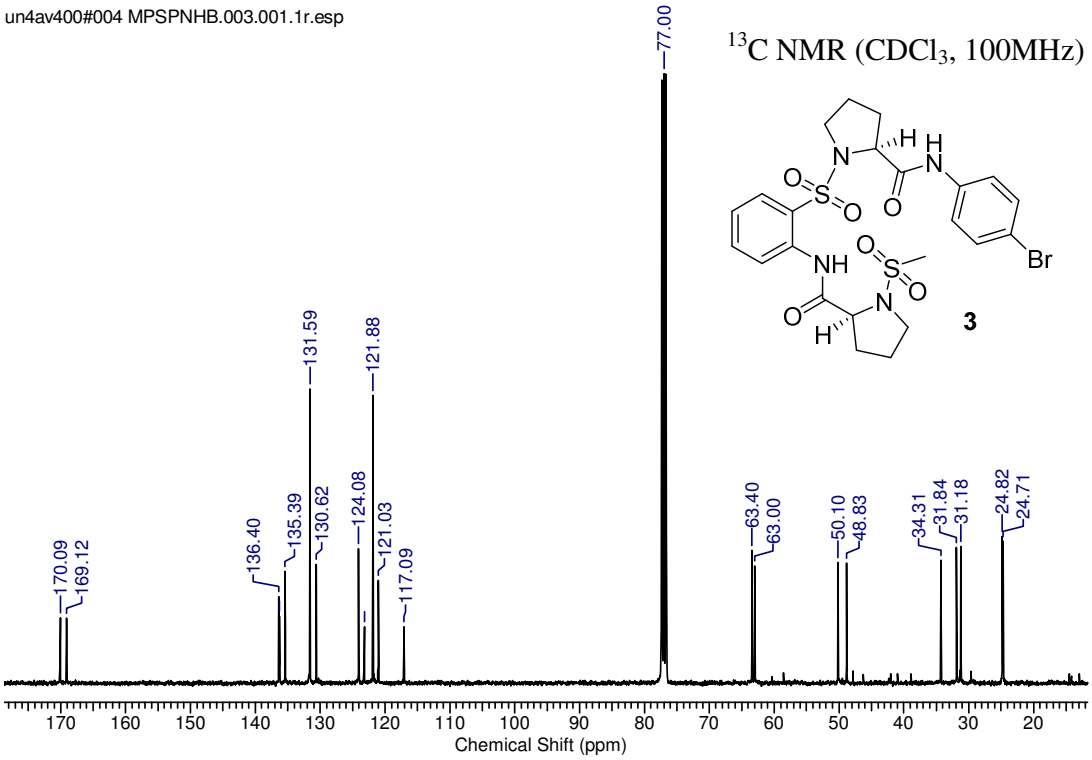

oc-PSP-NHB Sat2av2#047 Boc-Pro S-Ant-Pro 4-Br anilide.001.001.1r.esp
DEPT-135 (CDCl3, 50MHz)
10
134.64
131.69
129.55
124.04
121.52
62.29
49.51
47.40
31.05
30.55
28.38
24.37
Chemical Shift (ppm)


3oc-PSP-NHiBu Sat4av2#048 Boc Pro S-Ant Pro isobutylamide.002.001.1r.esp
13C NMR (CDCl3, 50MHz)
9
171.80
170.55
136.95
134.78
129.58
123.93
80.52
77.00
62.65
49.22
46.86
38.53
30.31
28.44
24.35
19.95
Chemical Shift (ppm)


oc-PSP-NHiBu Sat4av2#048 Boc Pro S-Ant Pro isobutylamide.001.001.1r.esp
DEPT-135 (CDCl3, 50MHz)
9
134.79
129.57
123.93
62.64
49.21
46.85
30.32
28.28
24.35
19.96
Chemical Shift (ppm)

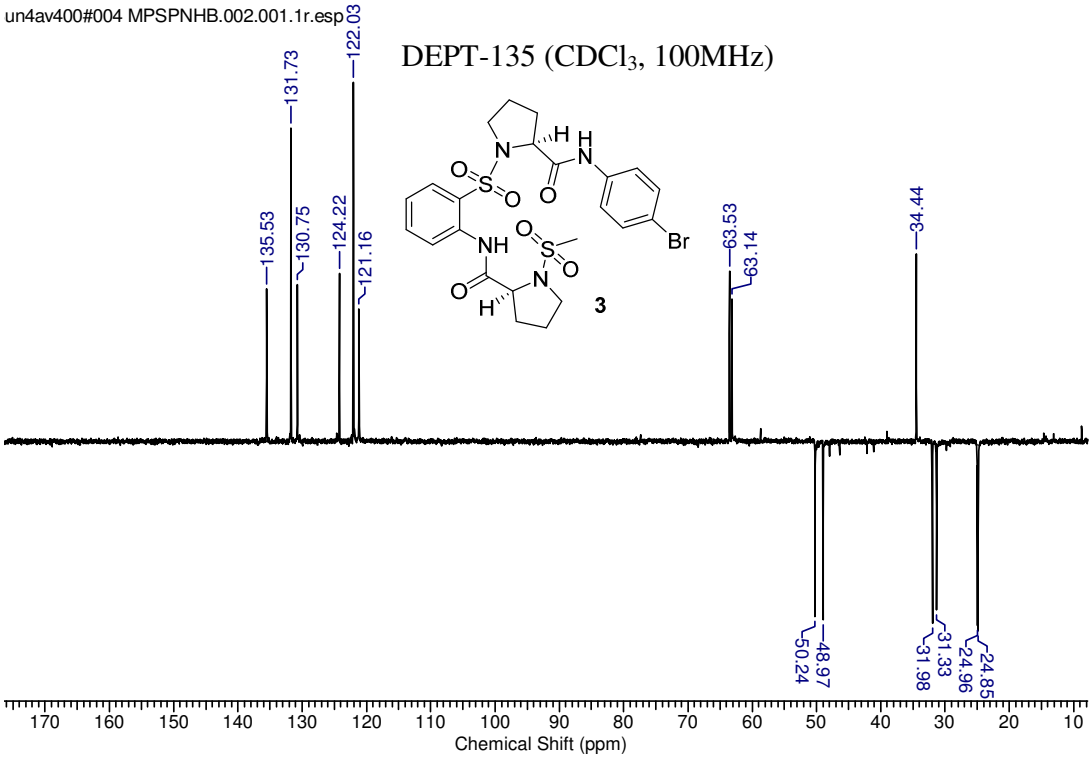
un4av400#004 MPSPNHB.003.001.1r.esp

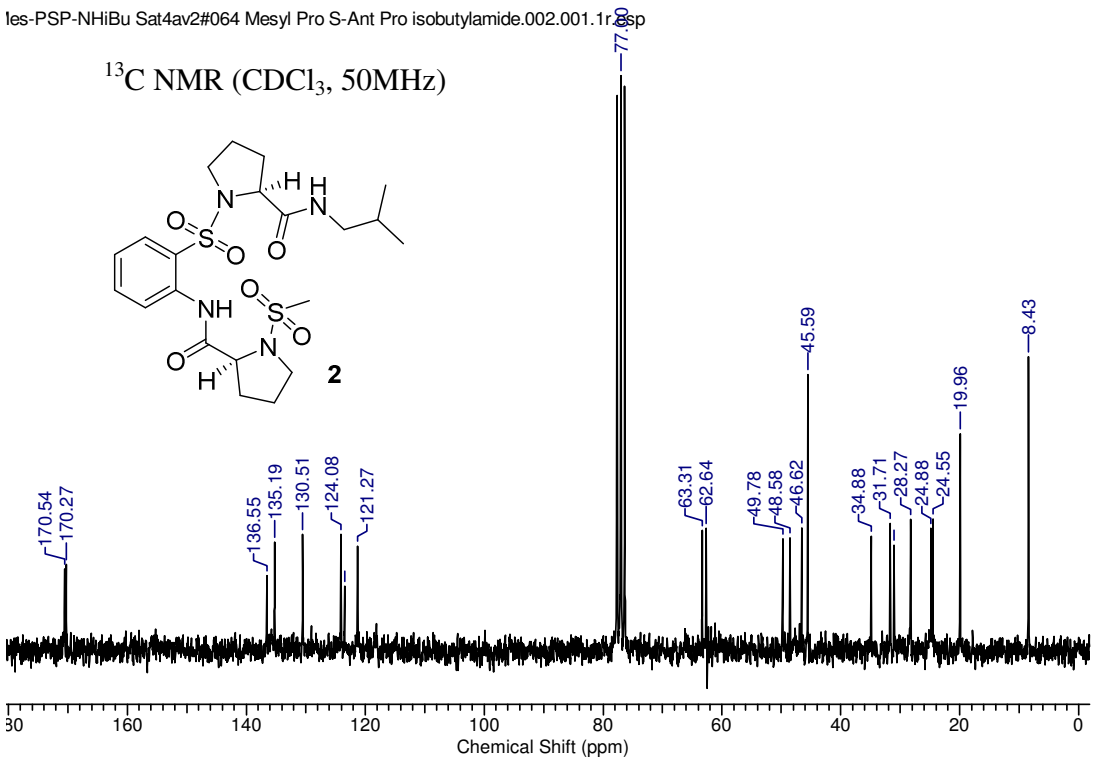
^{13}C NMR ($CDCl_3$, 100MHz)

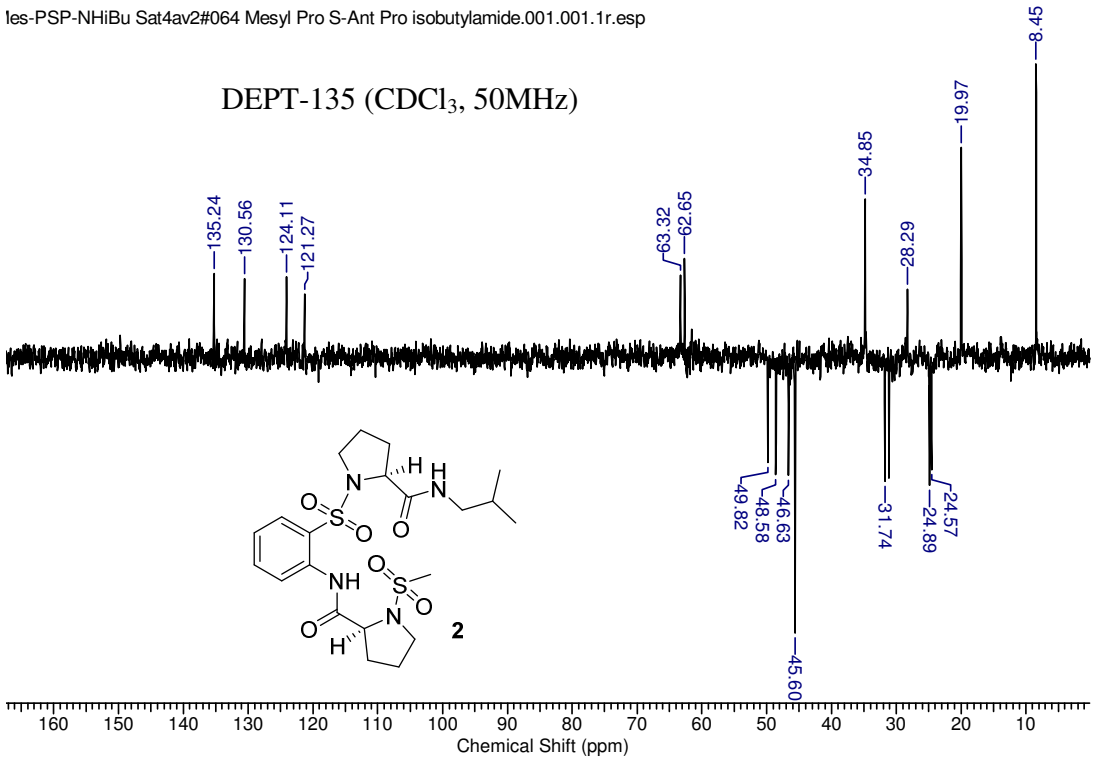


un4av400#004 MPSPNHB.002.001.1r.esp

DEPT-135 ($CDCl_3$, 100MHz)

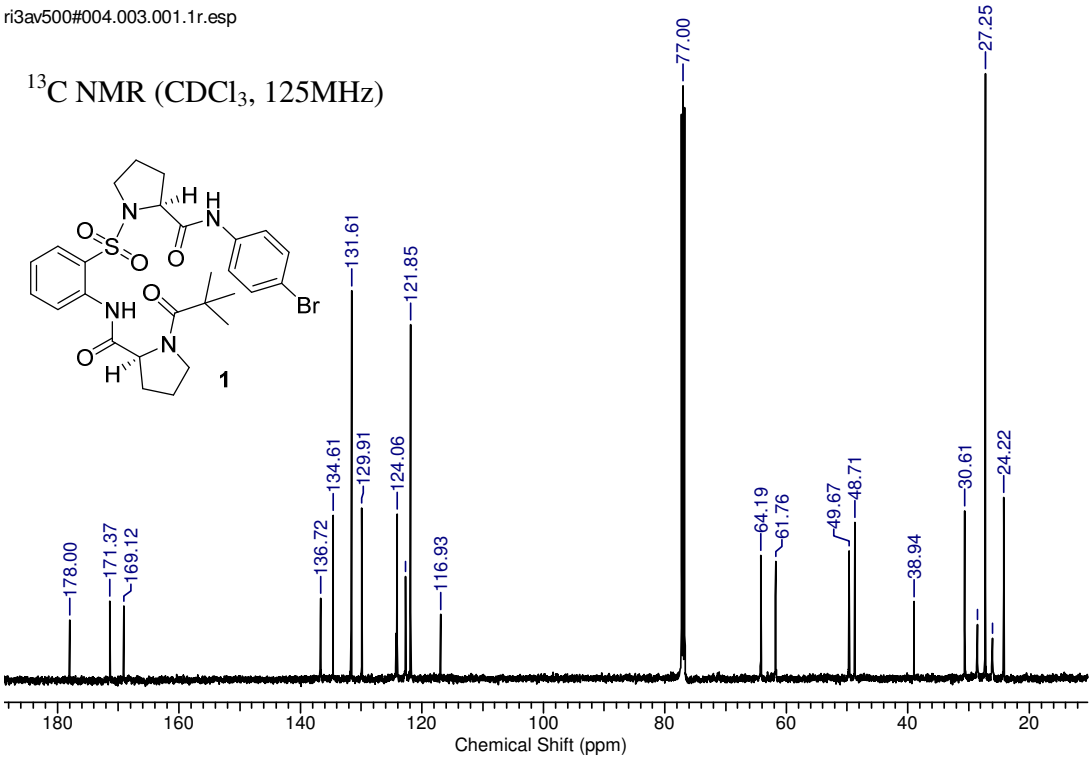



les-PSP-NHiBu Sat4av2#064 Mesyl Pro S-Ant Pro isobutylamide.002.001.1r.esp
13C NMR (CDCl3, 50MHz)
2
170.54
170.27
136.55
135.19
130.51
124.08
121.27
77.00
63.31
62.64
49.78
48.58
46.62
45.59
34.88
31.71
28.27
24.88
24.55
19.96
8.43
Chemical Shift (ppm)


les-PSP-NHiBu Sat4av2#064 Mesyl Pro S-Ant Pro isobutylamide.001.001.1r.esp
DEPT-135 (CDCl3, 50MHz)
2
135.24
130.56
124.11
121.27
63.32
62.65
49.82
48.58
46.63
45.60
34.85
31.74
28.29
24.89
24.57
19.97
8.45
Chemical Shift (ppm)

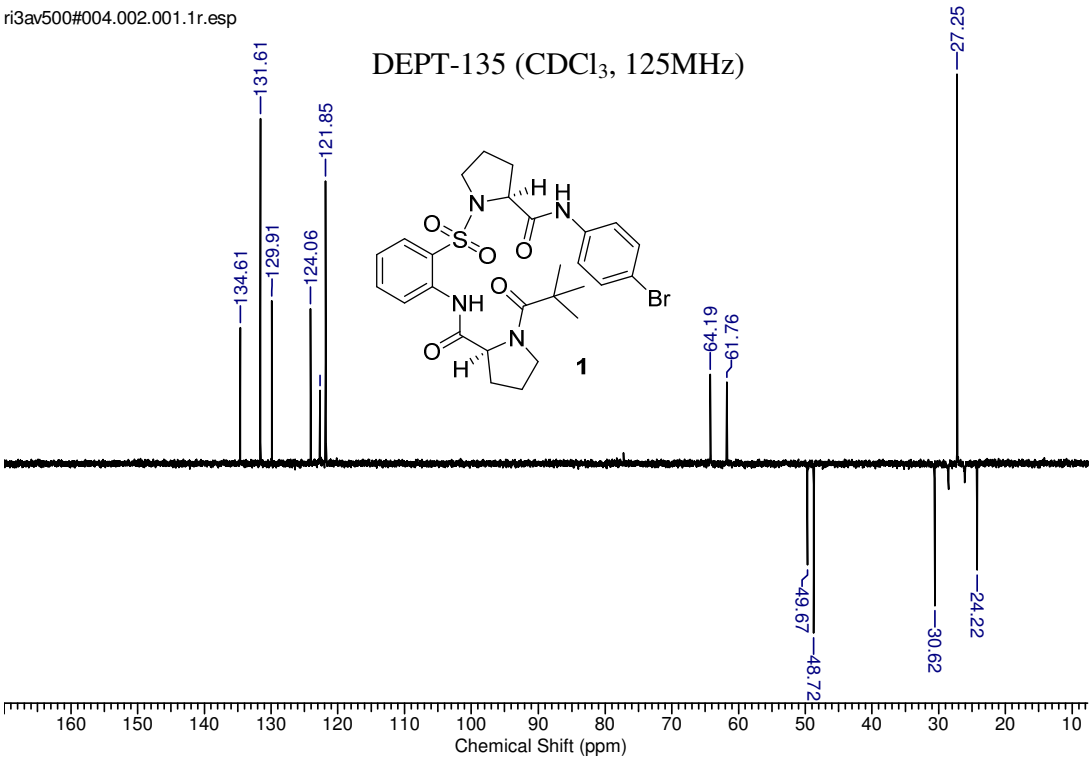
ri3av500#004.003.001.1r.esp

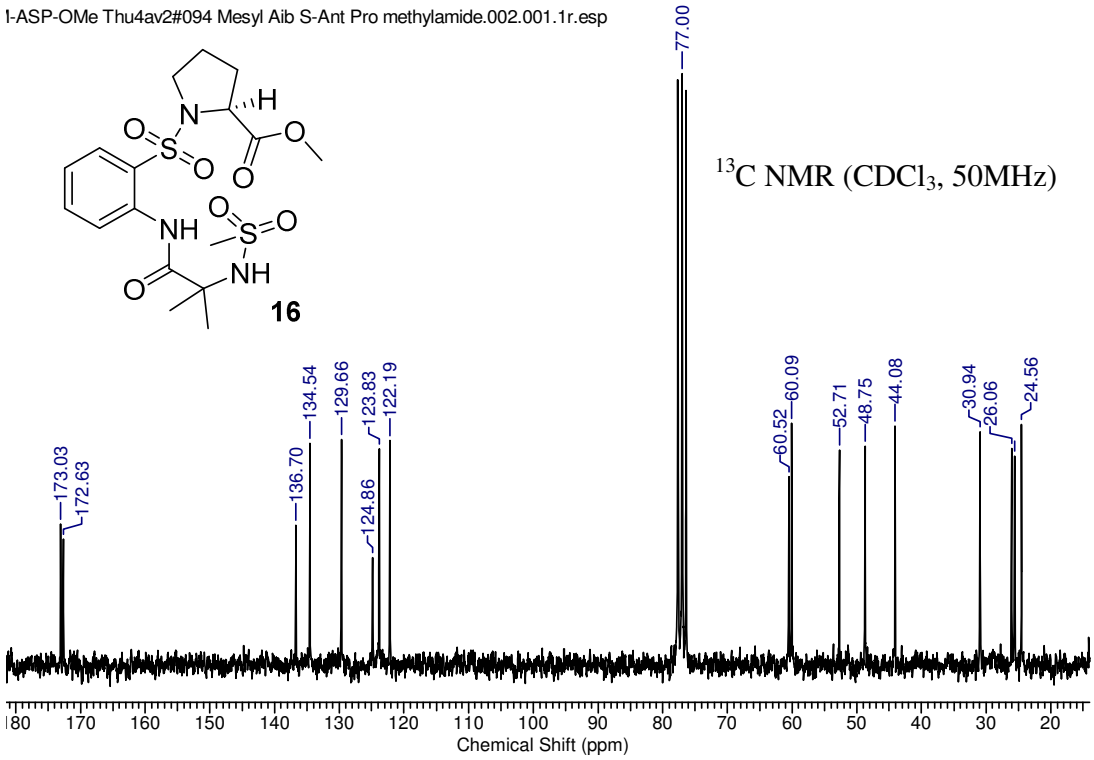
^{13}C NMR ($CDCl_3$, 125MHz)



ri3av500#004.002.001.1r.esp

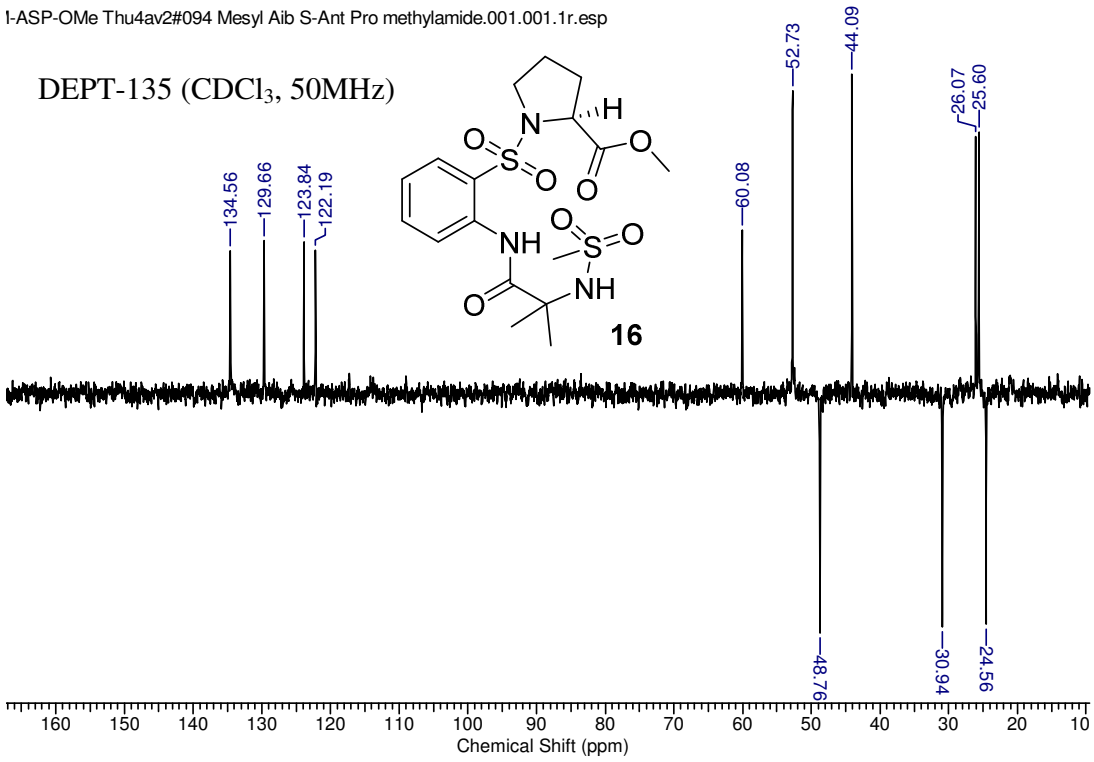
DEPT-135 ($CDCl_3$, 125MHz)





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

16

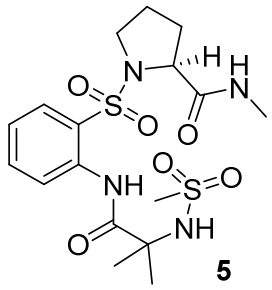


DEPT-135 ($CDCl_3$, 50MHz)

16

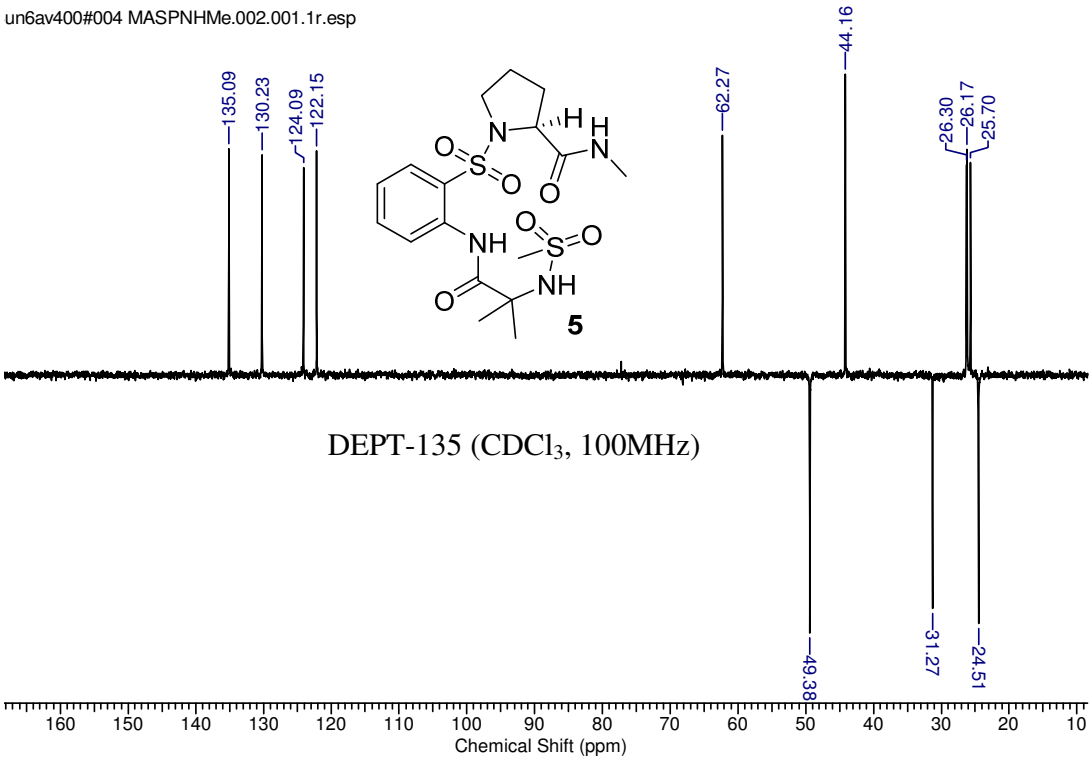
un6av400#004 MASPNHMe.003.001.1r.esp

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



5

un6av400#004 MASPNHMe.002.001.1r.esp

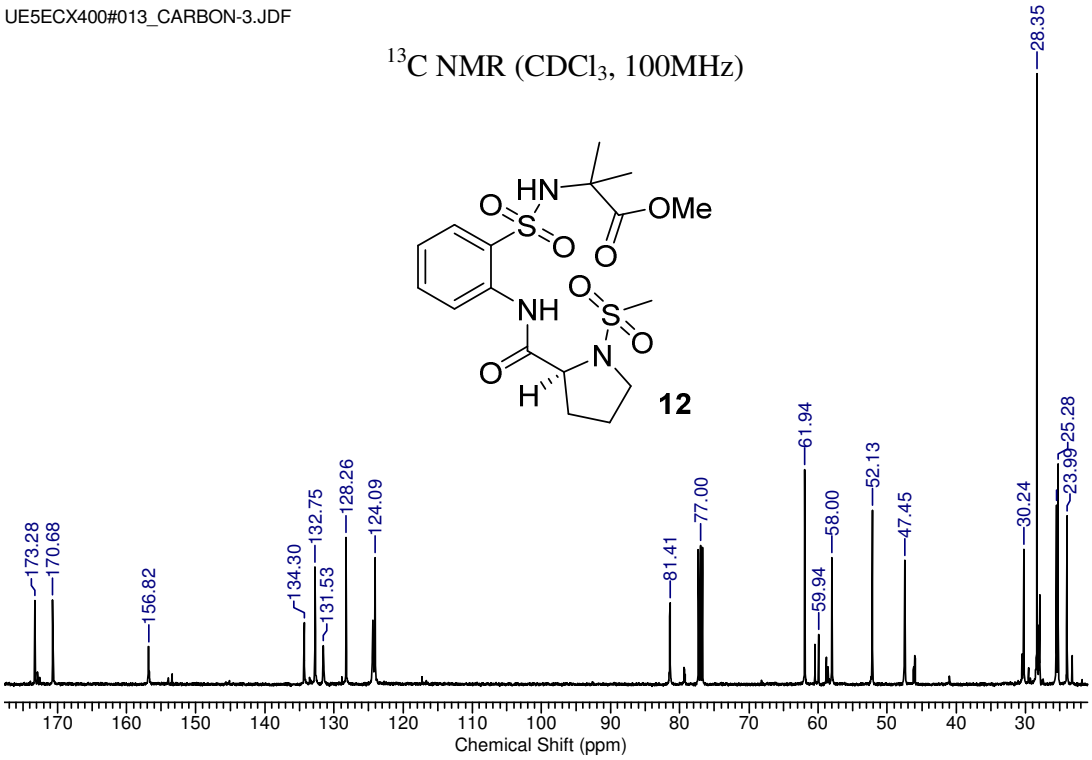


5

DEPT-135 ($CDCl_3$, 100MHz)

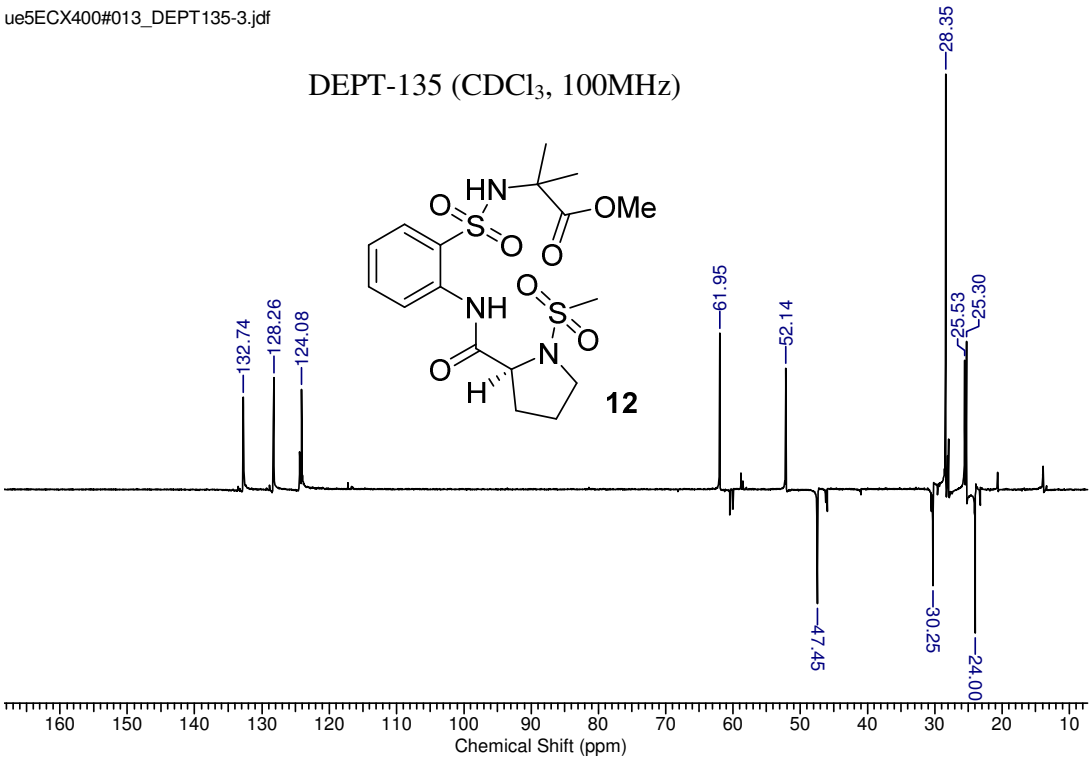
UE5ECX400#013_CARBON-3.JDF

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



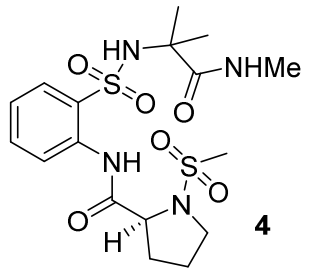
ue5ECX400#013_DEPT135-3.jdf

DEPT-135 ($CDCl_3$, 100MHz)



at5av400#007 MPSANHMe.003.001.1r.esp

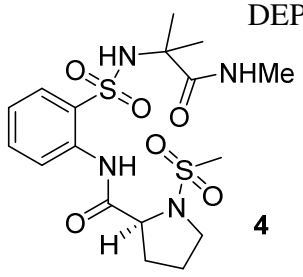
^{13}C NMR ($CDCl_3$, 100MHz)



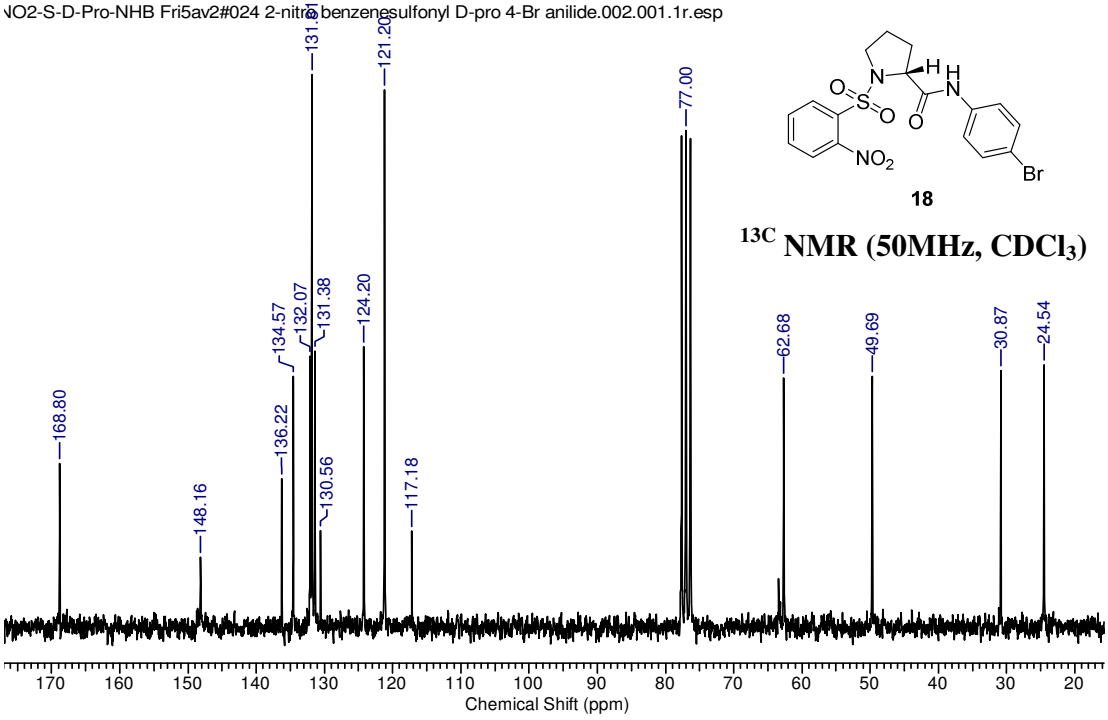
4

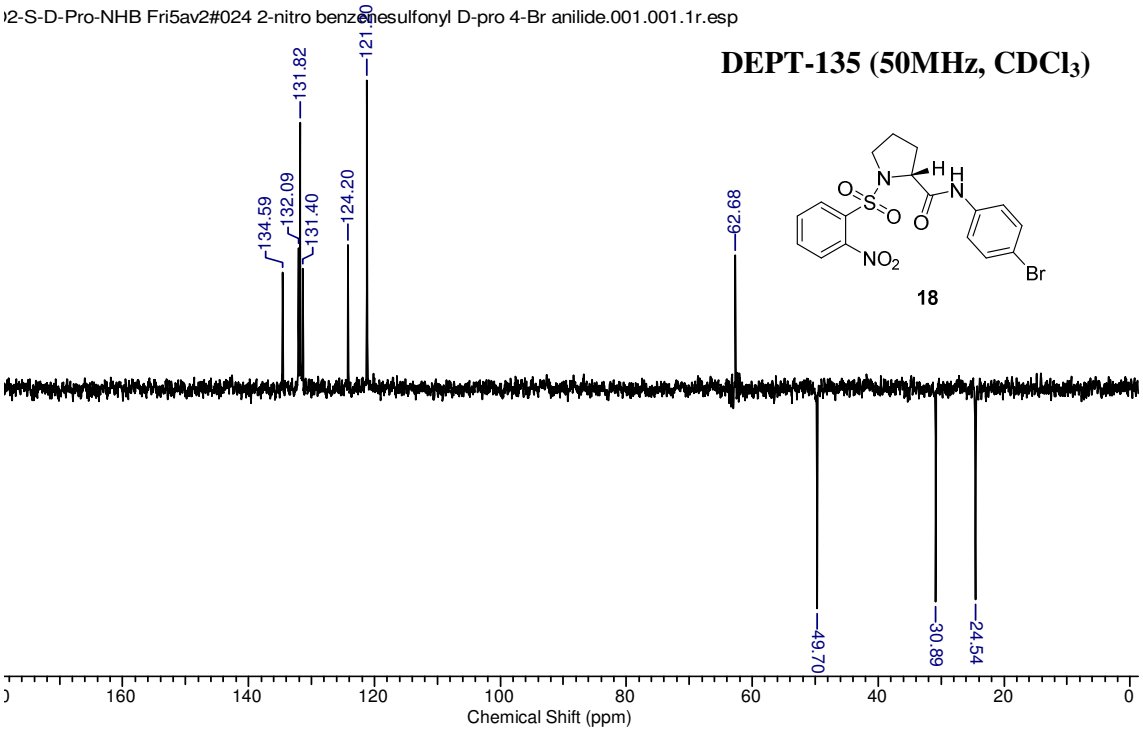
at5av400#007 MPSANHMe.002.001.1r.esp

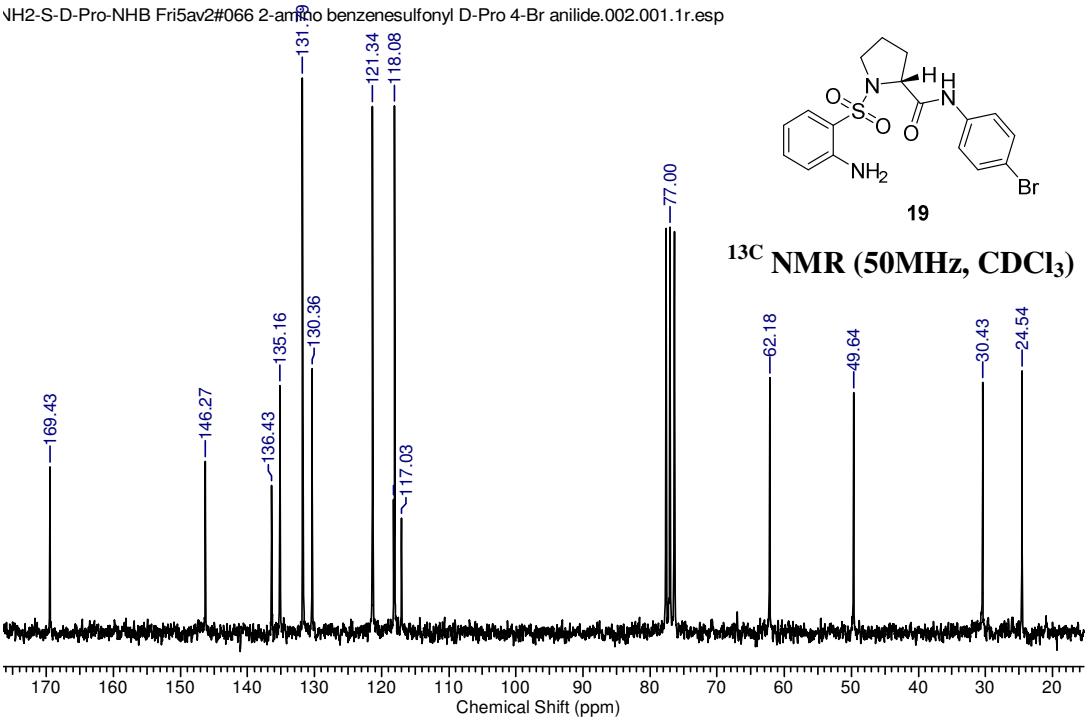
DEPT-135 ($CDCl_3$, 100MHz)



4

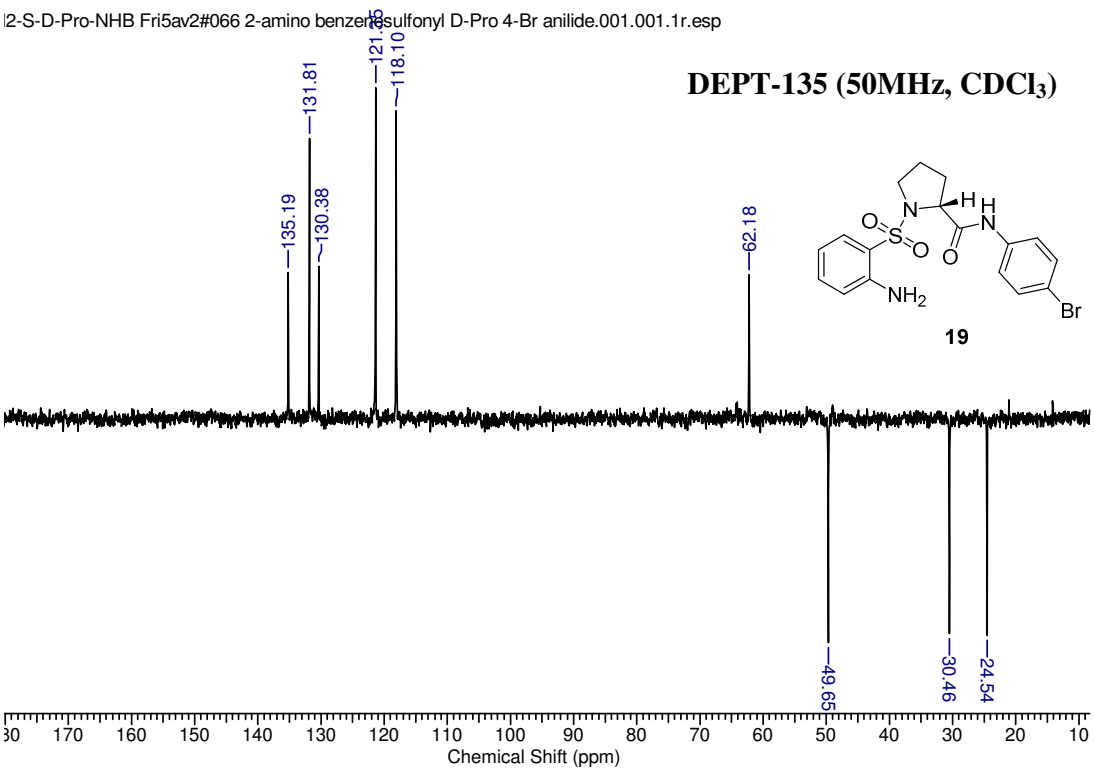

NO2-S-D-Pro-NHB Fri5av2#024 2-nitro benzenesulfonyl D-pro 4-Br anilide.002.001.1r.esp
131.82
121.20
77.00
134.57
132.07
131.38
124.20
62.68
49.69
30.87
24.54
168.80
136.22
130.56
148.16
117.18
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
Chemical Shift (ppm)
18
13C NMR (50MHz, CDCl3)


2-S-D-Pro-NHB Fri5av2#024 2-nitro benzenesulfonyl D-pro 4-Br anilide.001.001.1r.esp
131.82
121.20
134.59
132.09
131.40
124.20
62.68
49.70
30.89
24.54
160 140 120 100 80 60 40 20 0
Chemical Shift (ppm)
DEPT-135 (50MHz, CDCl3)
18



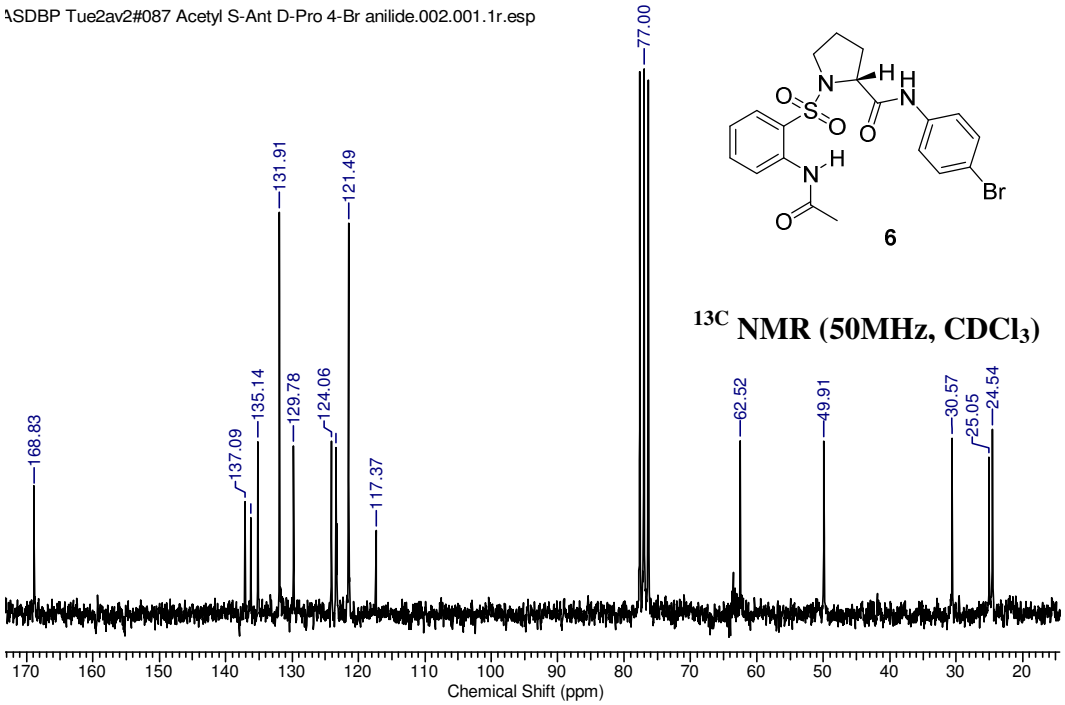
19

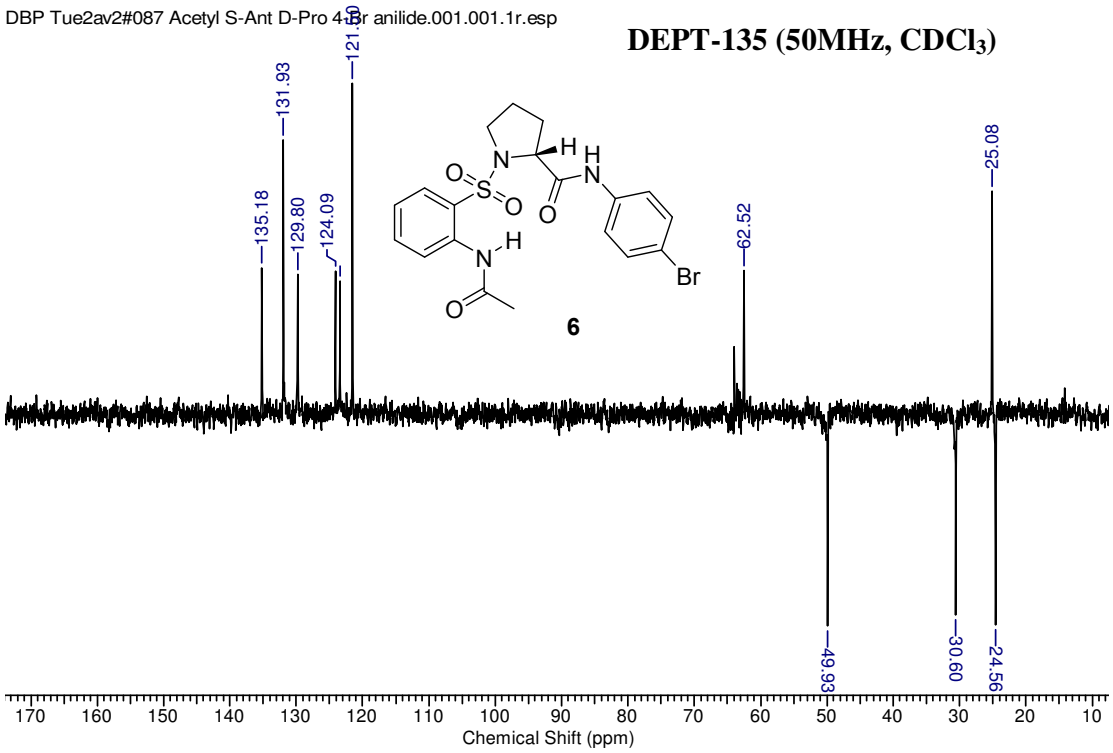
^{13C} NMR (50MHz, $CDCl_3$)

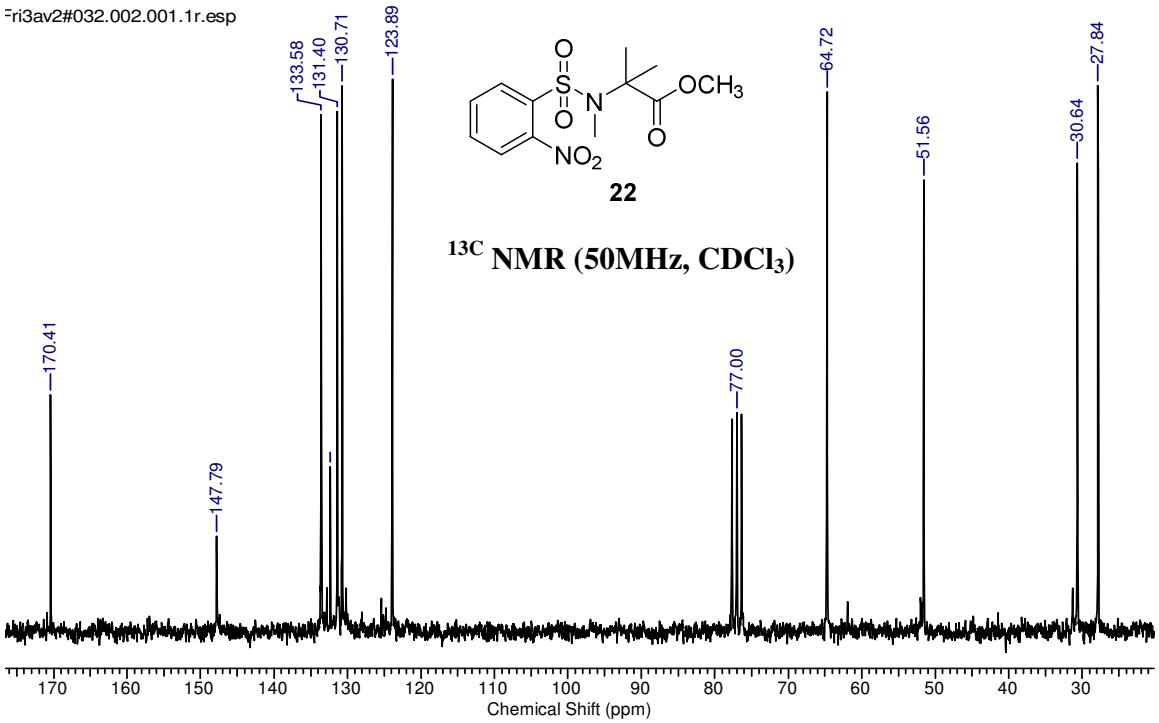


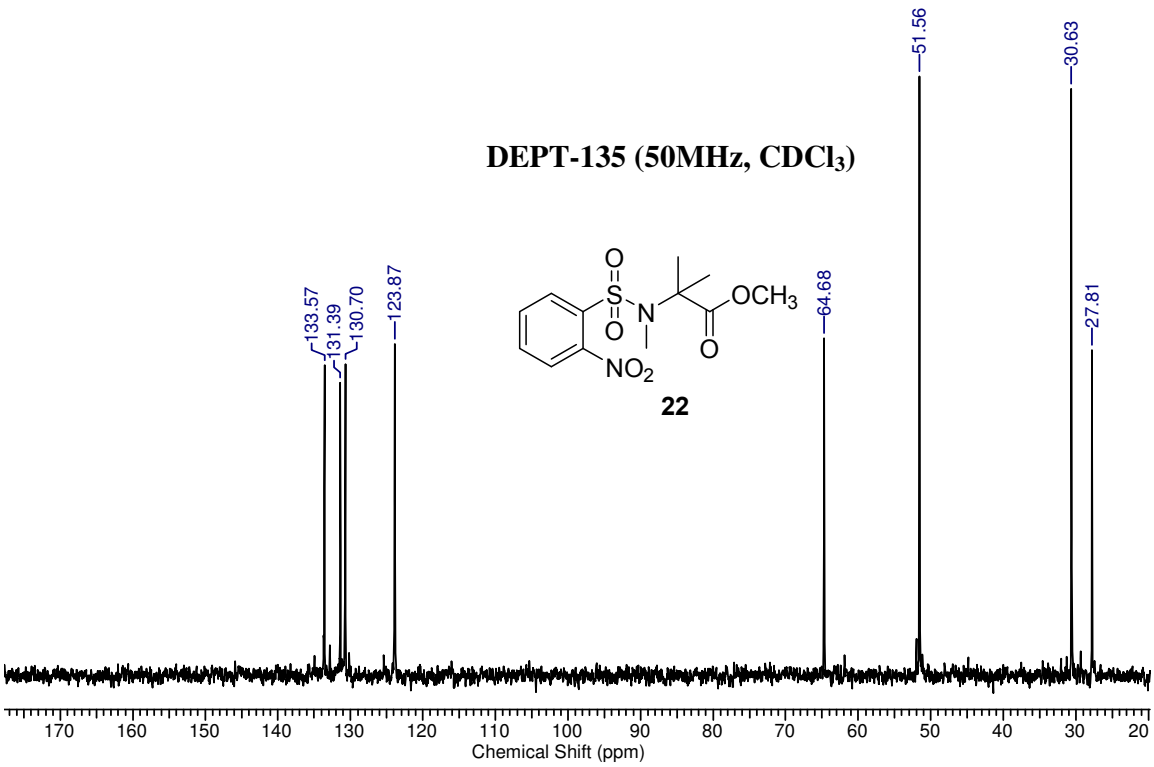
19

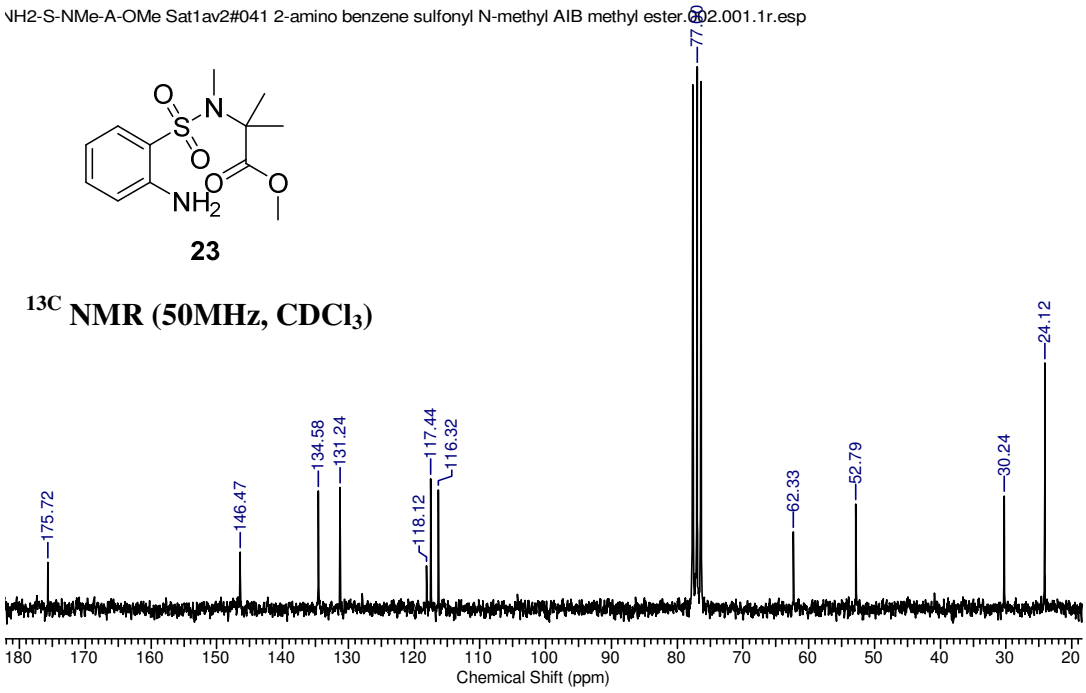
DEPT-135 (50MHz, $CDCl_3$)


ASDBP Tue2av2#087 Acetyl S-Ant D-Pro 4-Br anilide.002.001.1r.esp
77.00
131.91
121.49
135.14
129.78
124.06
168.83
137.09
117.37
62.52
49.91
30.57
25.05
24.54
Chemical Shift (ppm)
6
13C NMR (50MHz, CDCl3)


DBP Tue2av2#087 Acetyl S-Ant D-Pro 4-Br anilide.001.001.1r.esp
DEPT-135 (50MHz, CDCl3)
131.93
121.80
135.18
129.80
124.09
62.52
25.08
49.93
30.60
24.56
Chemical Shift (ppm)
6


Fri3av2#032.002.001.1r.esp
133.58
131.40
130.71
123.89
64.72
51.56
30.64
27.84
170.41
147.79
77.00
22
13C NMR (50MHz, CDCl3)
Chemical Shift (ppm)

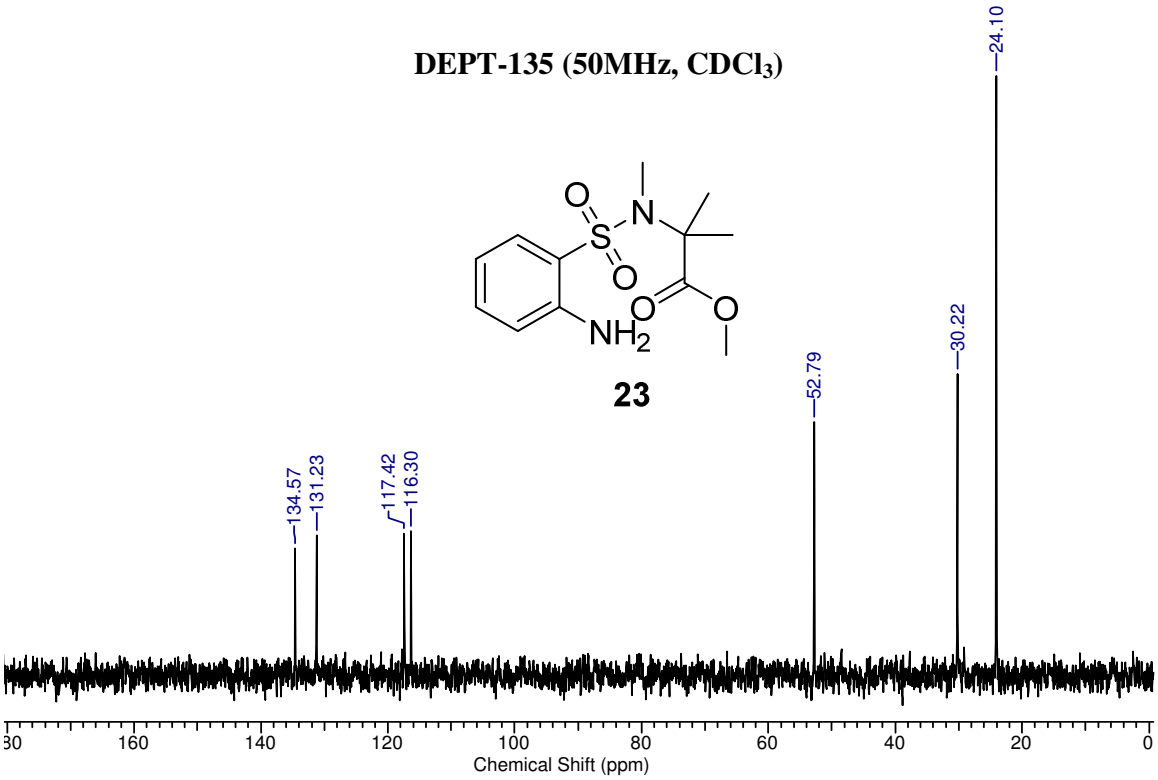

51.56
30.63
DEPT-135 (50MHz, CDCl3)
133.57
131.39
130.70
123.87
64.68
27.81
22
Chemical Shift (ppm)



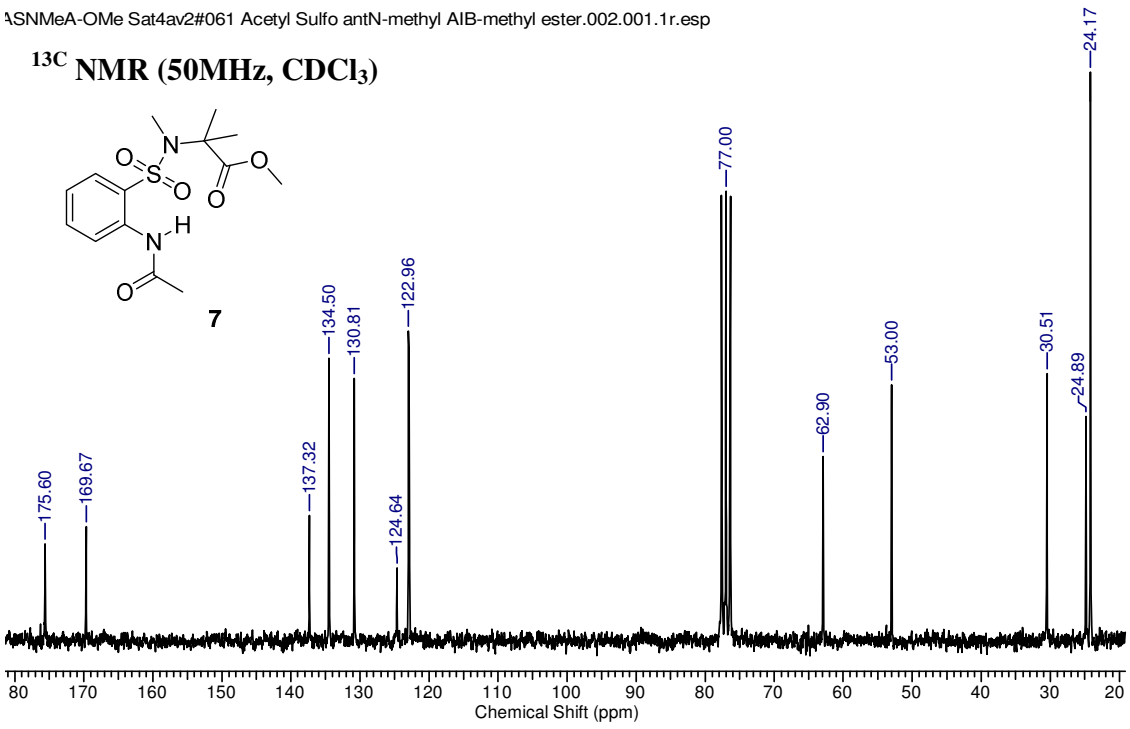
23

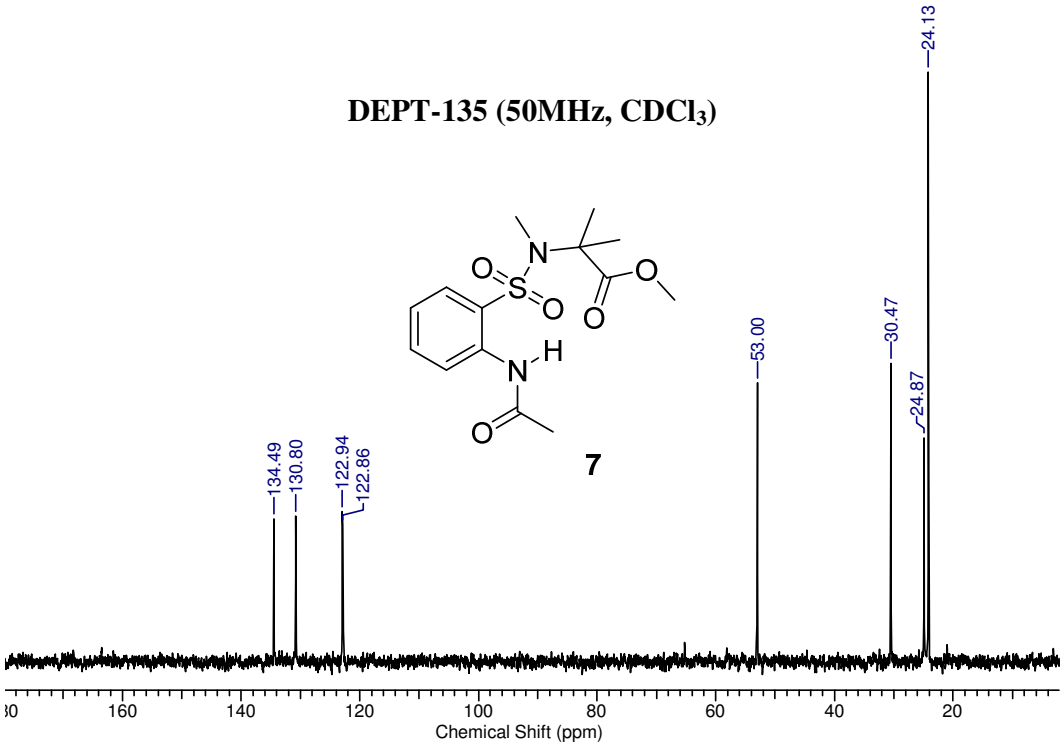
^{13C} NMR (50MHz, $CDCl_3$)

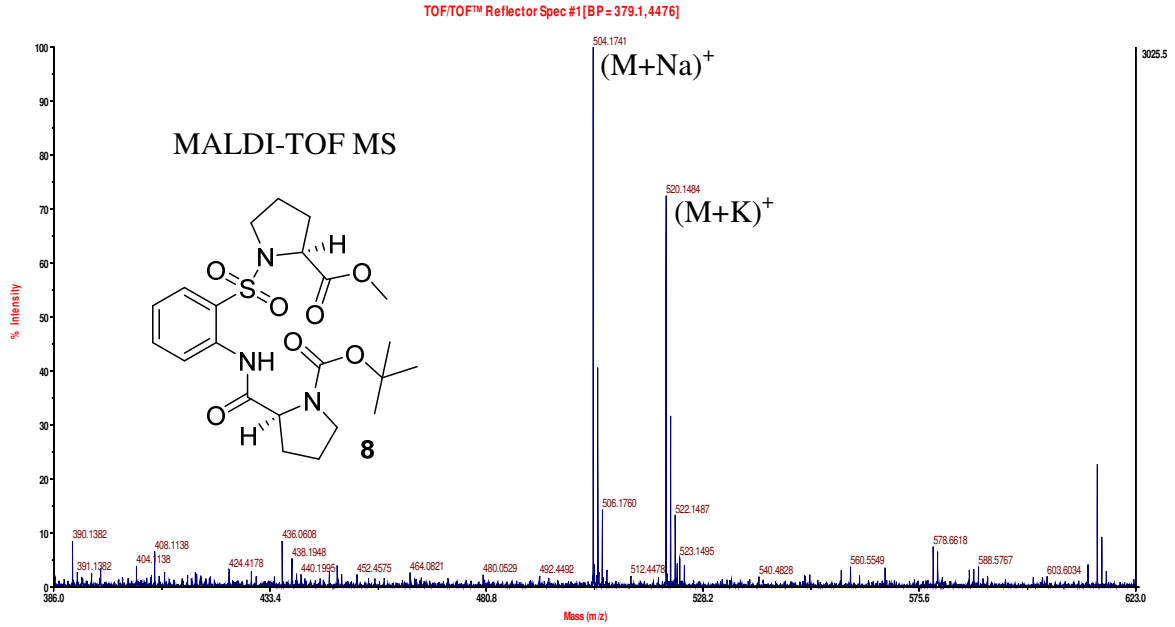
DEPT-135 (50MHz, $CDCl_3$)

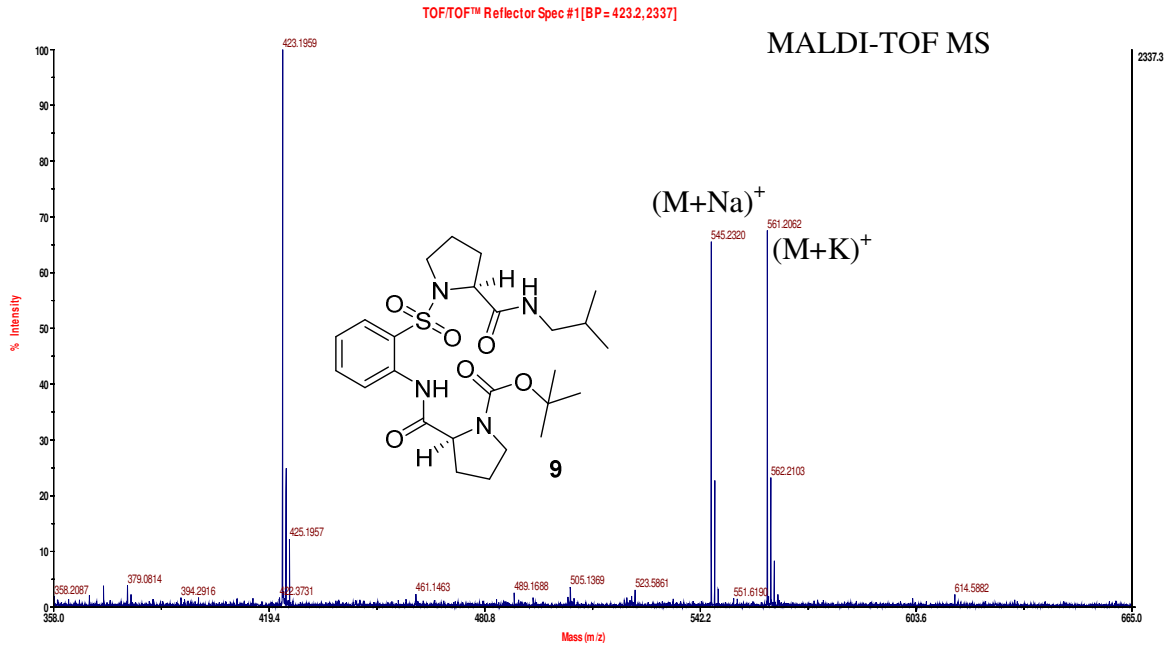


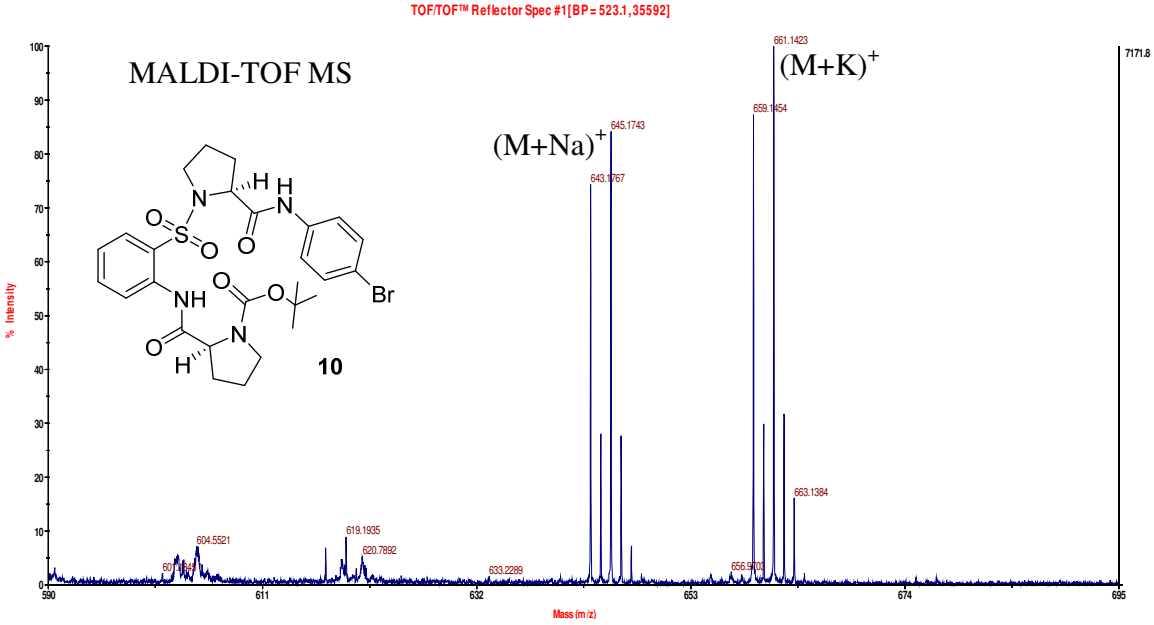
23

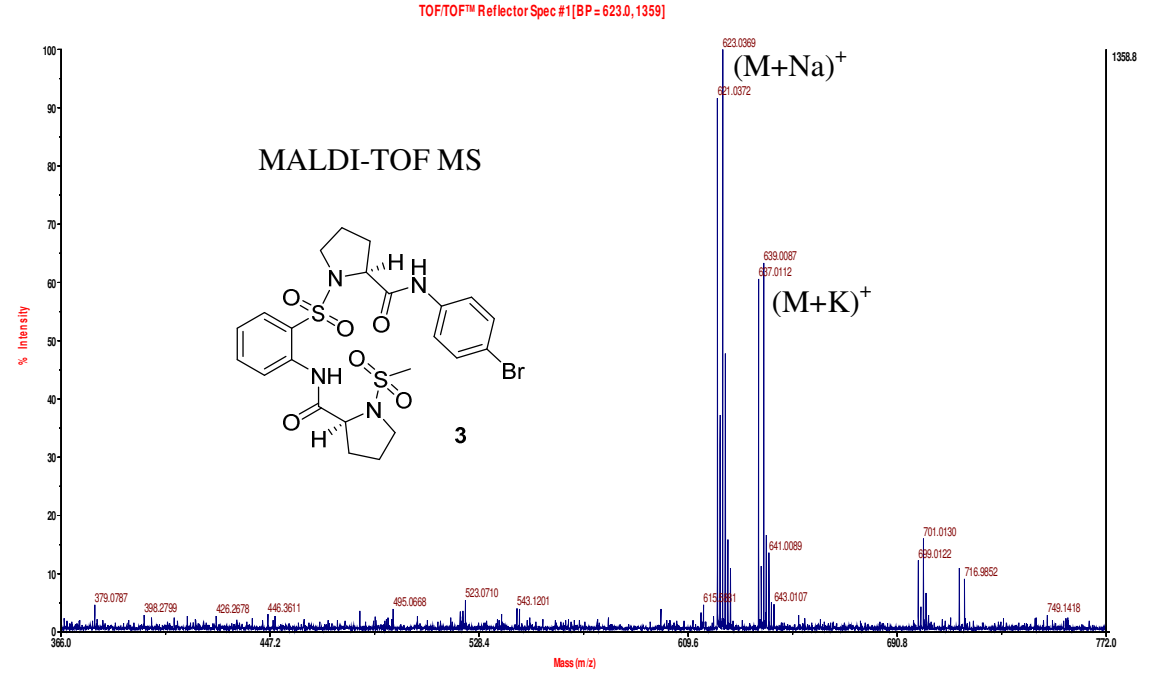

ASNMeA-OMe Sat4av2#061 Acetyl Sulfo antN-methyl AIB-methyl ester.002.001.1r.esp
13C NMR (50MHz, CDCl3)
7
175.60
169.67
137.32
134.50
130.81
124.64
122.96
77.00
62.90
53.00
30.51
24.89
24.17
Chemical Shift (ppm)

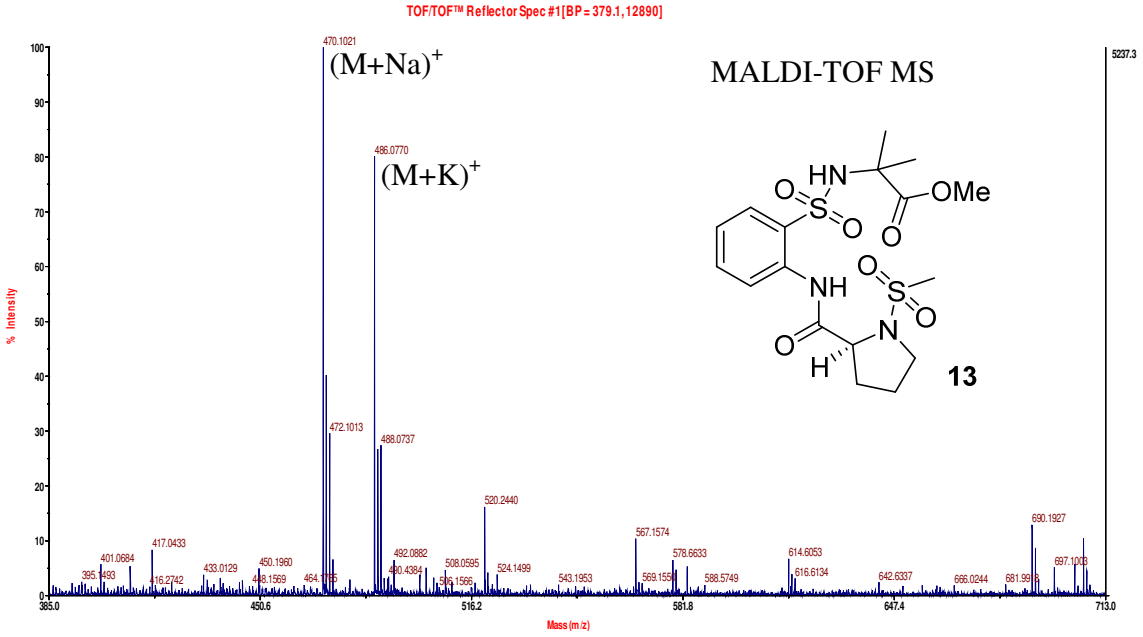

DEPT-135 (50MHz, CDCl3)
7
134.49
130.80
122.94
122.86
53.00
30.47
24.87
24.13
Chemical Shift (ppm)

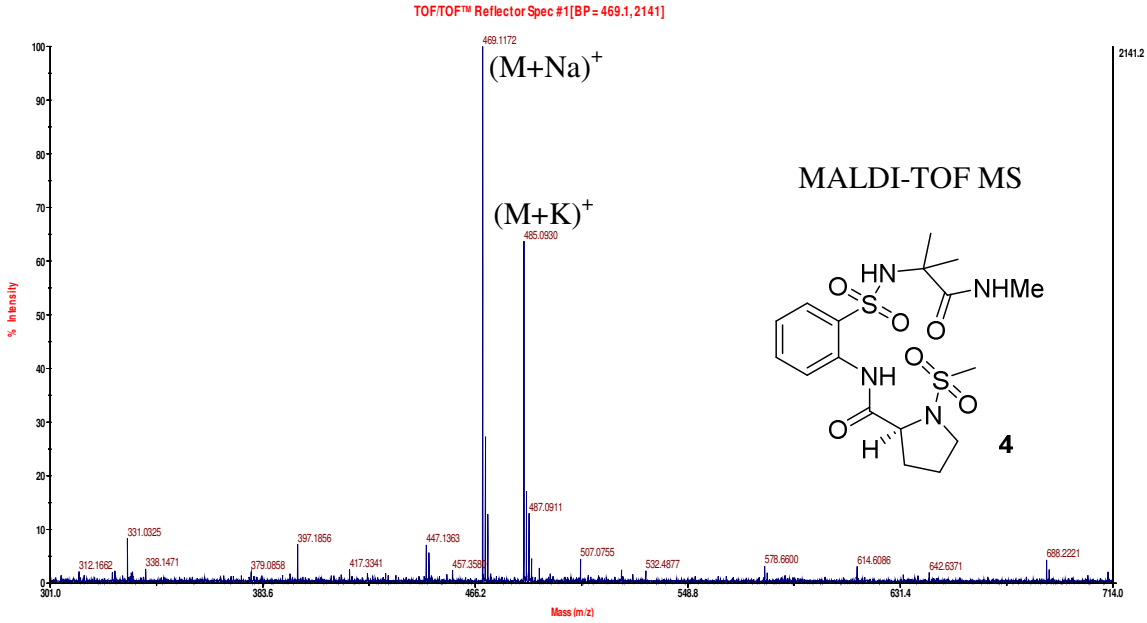

TOF/TOF™ Reflector Spec #1 [BP = 379.1, 4476]
MALDI-TOF MS
(M+Na)+
(M+K)+
504.1741
520.1484
506.1760
522.1487
523.1495
8
% Intensity
Mass (m/z)

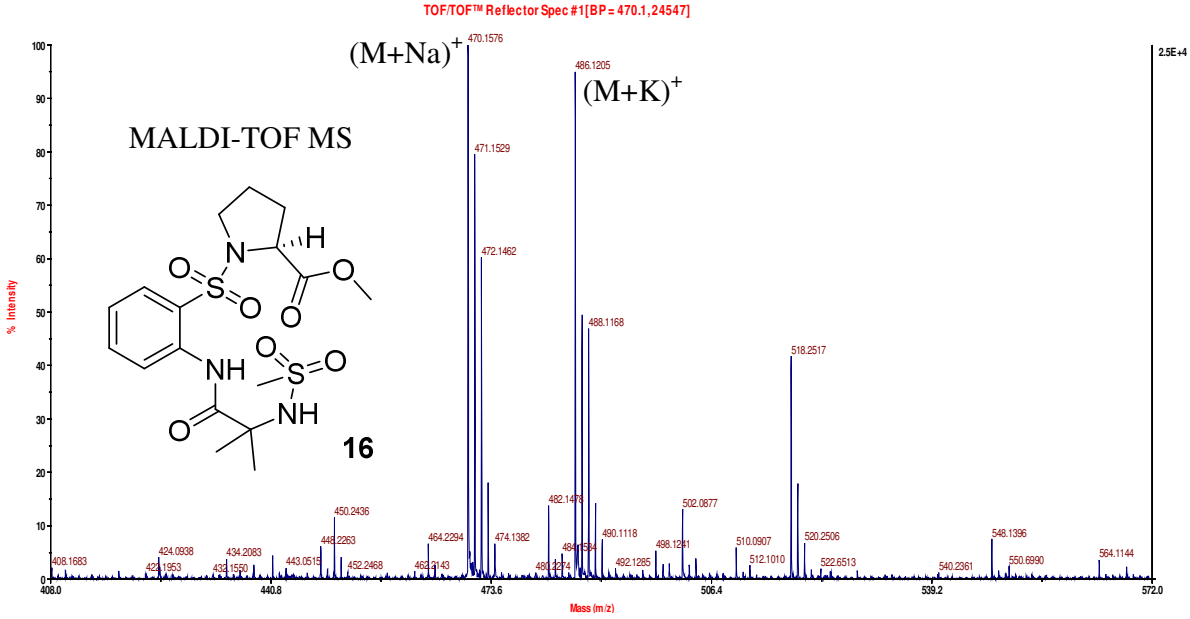

TOF/TOF™ Reflector Spec #1 [BP = 423.2, 2337]
MALDI-TOF MS
(M+Na)+
(M+K)+
423.1959
545.2320
561.2062
562.2103
425.1957
9
% Intensity
Mass (m/z)

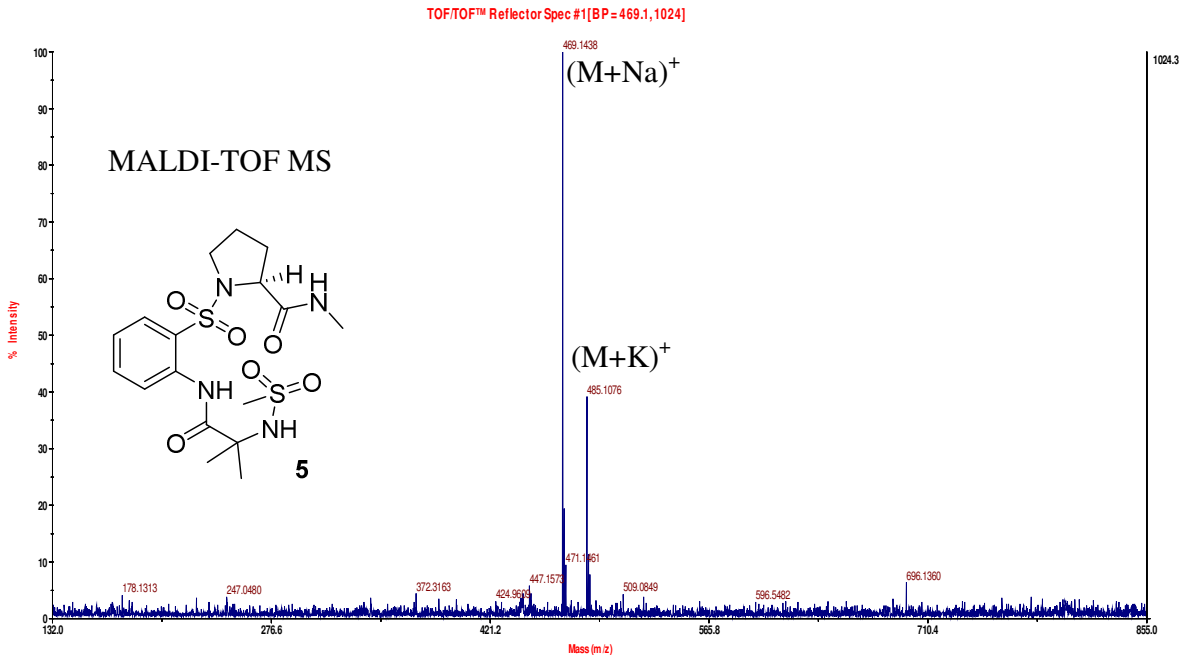

TOF/TOF™ Reflector Spec #1[BP = 523.1, 35592]
MALDI-TOF MS
(M+Na)+
(M+K)+
661.1423
645.1743
643.1767
659.1454
663.1384
619.1935
604.5521
620.7892
633.2289
656.9705
7171.8
% Intensity
Mass (m/z)
10

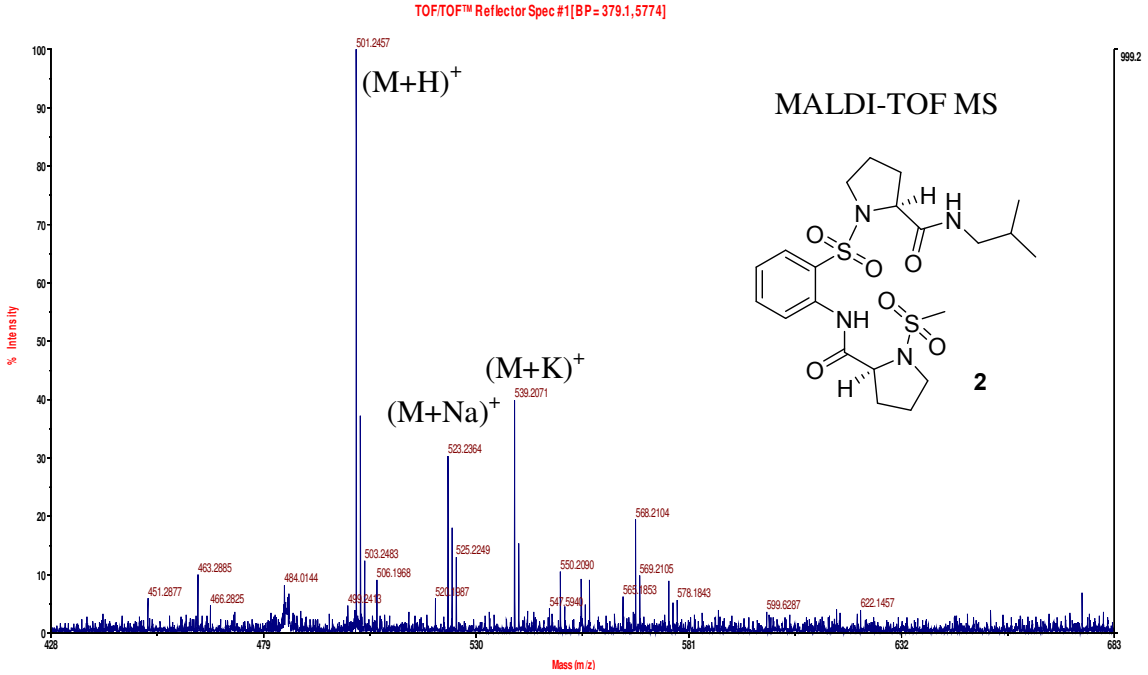

TOF/TOF™ Reflector Spec #1[BP = 623.0, 1359]
MALDI-TOF MS
(M+Na)+
(M+K)+
623.0369
621.0372
639.0087
637.0112
641.0089
643.0107
701.0130
699.0122
716.9852
749.1418
379.0787
398.2799
426.2678
446.3611
495.0668
523.0710
543.1201
1358.8
% Intensity
Mass (m/z)
3

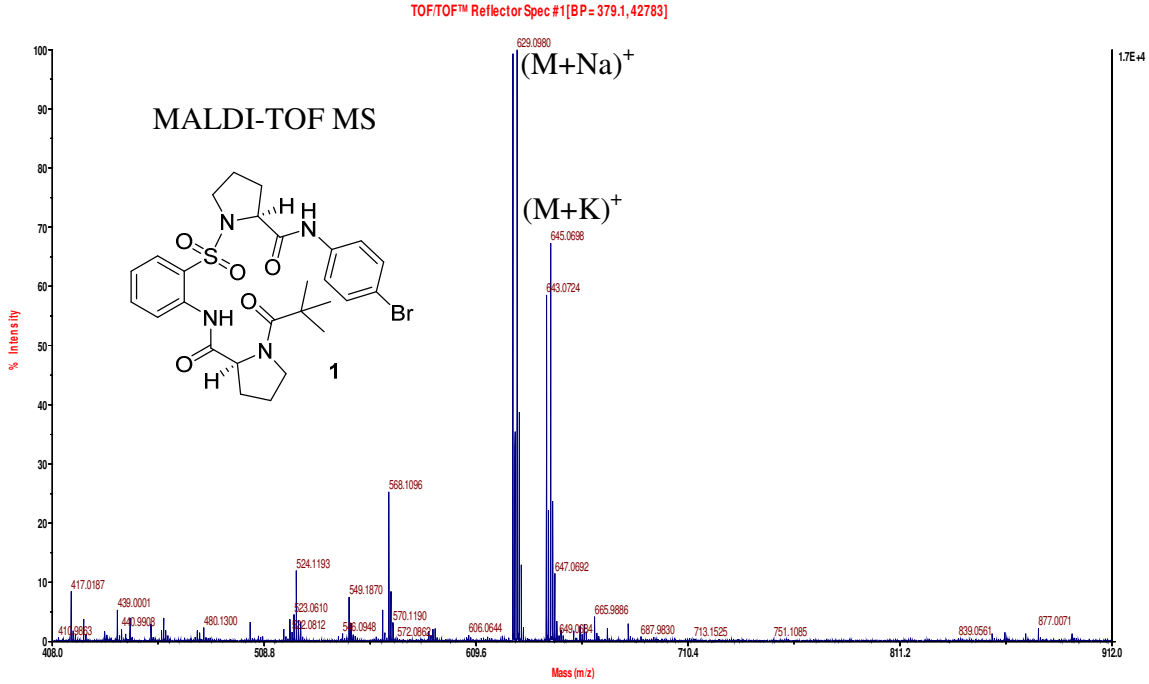

TOF/TOF™ Reflector Spec #1[BP = 379.1, 12890]
(M+Na)+
(M+K)+
MALDI-TOF MS
13
% Intensity
Mass (m/z)

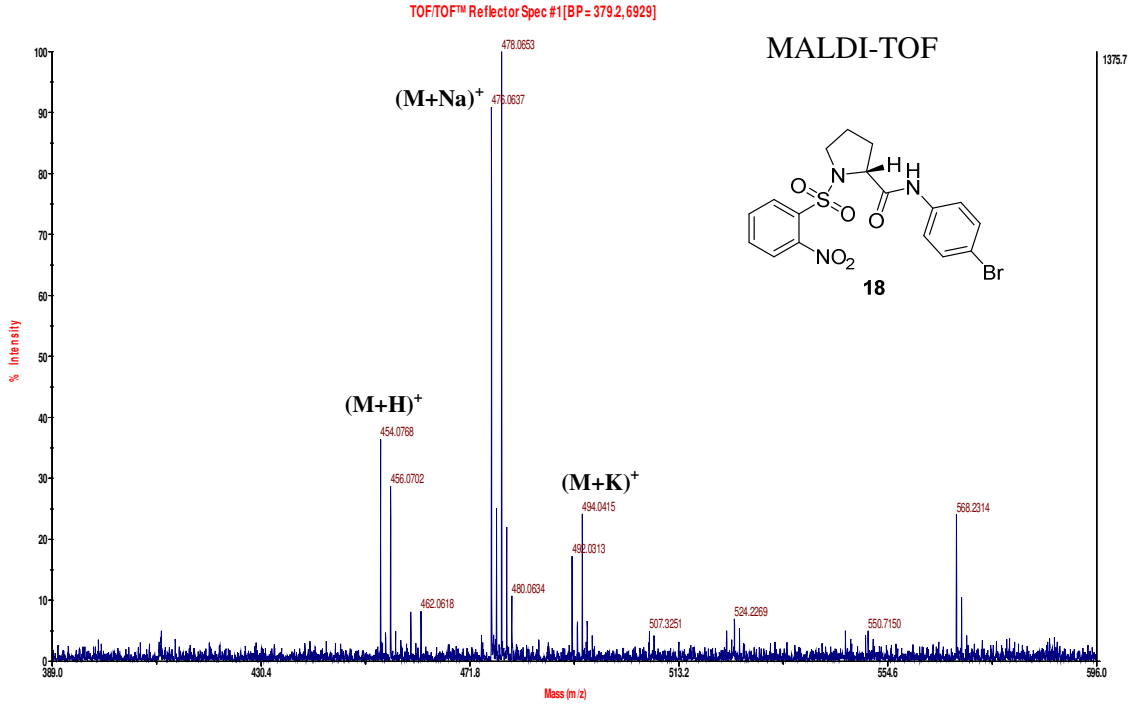

TOF/TOF™ Reflector Spec #1[BP = 469.1, 2141]
(M+Na)+
(M+K)+
MALDI-TOF MS
4
% Intensity
Mass (m/z)

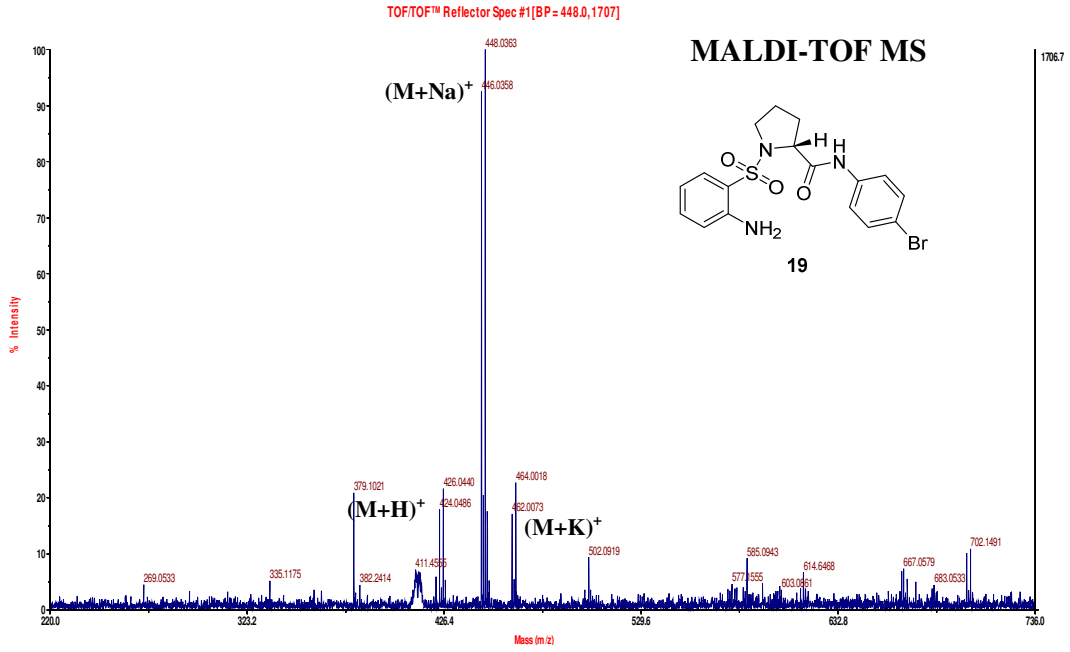

TOF/TOF™ Reflector Spec #1[BP = 470.1, 24547]
(M+Na)+
(M+K)+
MALDI-TOF MS
16
% Intensity
Mass (m/z)
2.5E+4

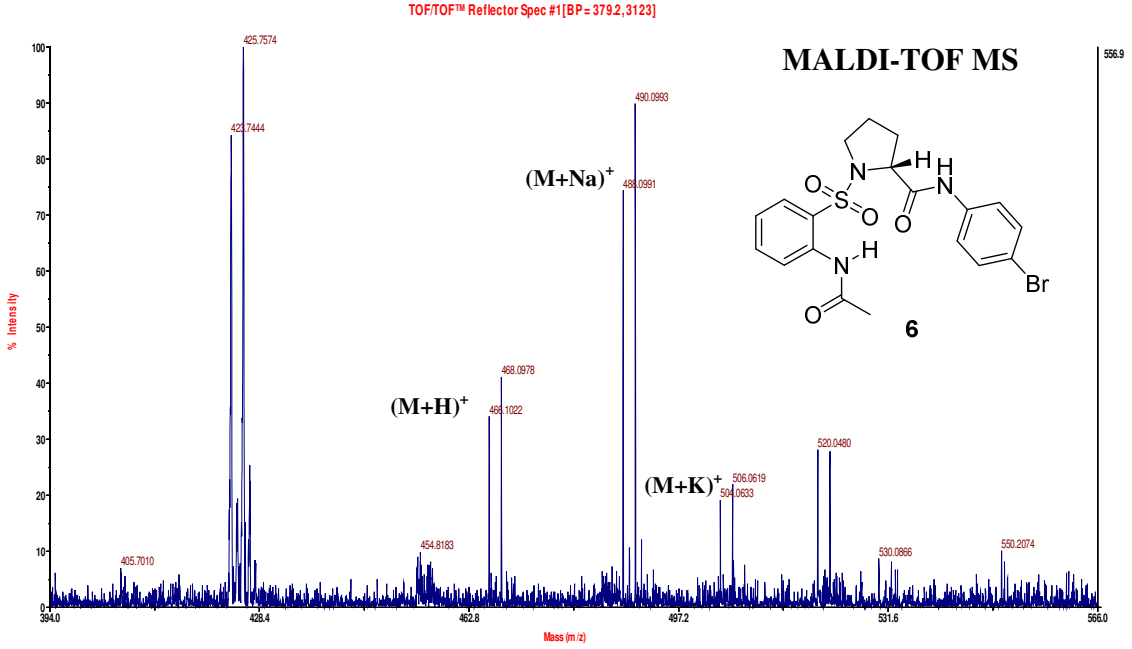

TOF/TOF™ Reflector Spec #1[BP = 469.1, 1024]
(M+Na)+
(M+K)+
MALDI-TOF MS
5
% Intensity
Mass (m/z)
1024.3

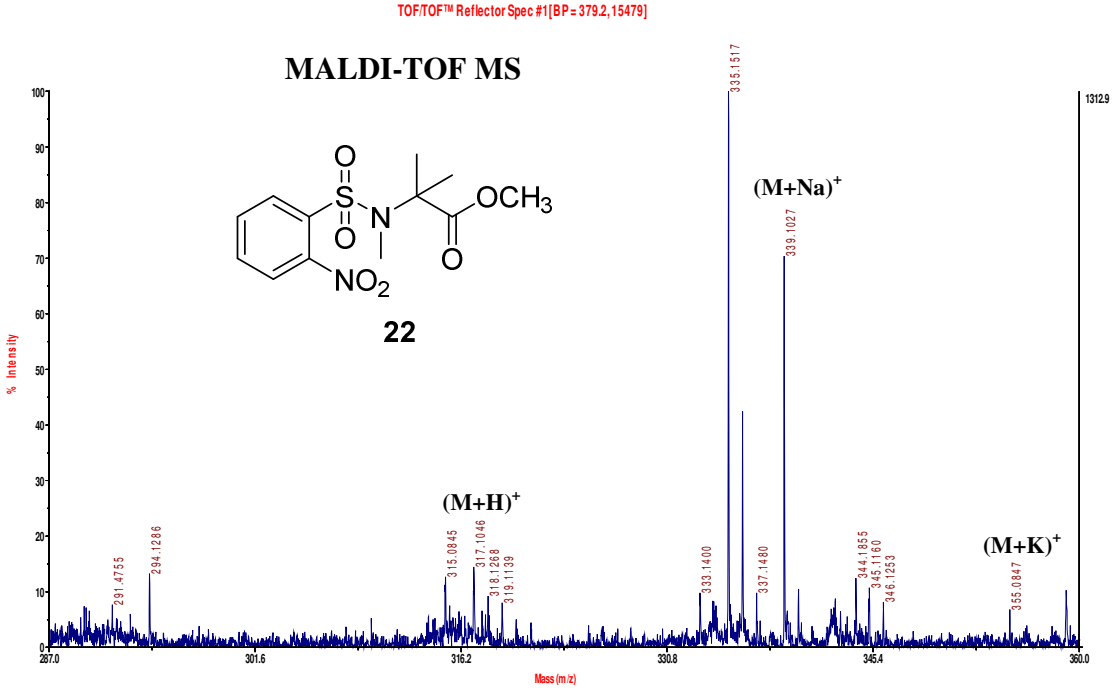

TOF/TOF™ Reflector Spec #1[BP = 379.1, 5774]
MALDI-TOF MS
(M+H)+
(M+Na)+
(M+K)+
2
% Intensity
Mass (m/z)

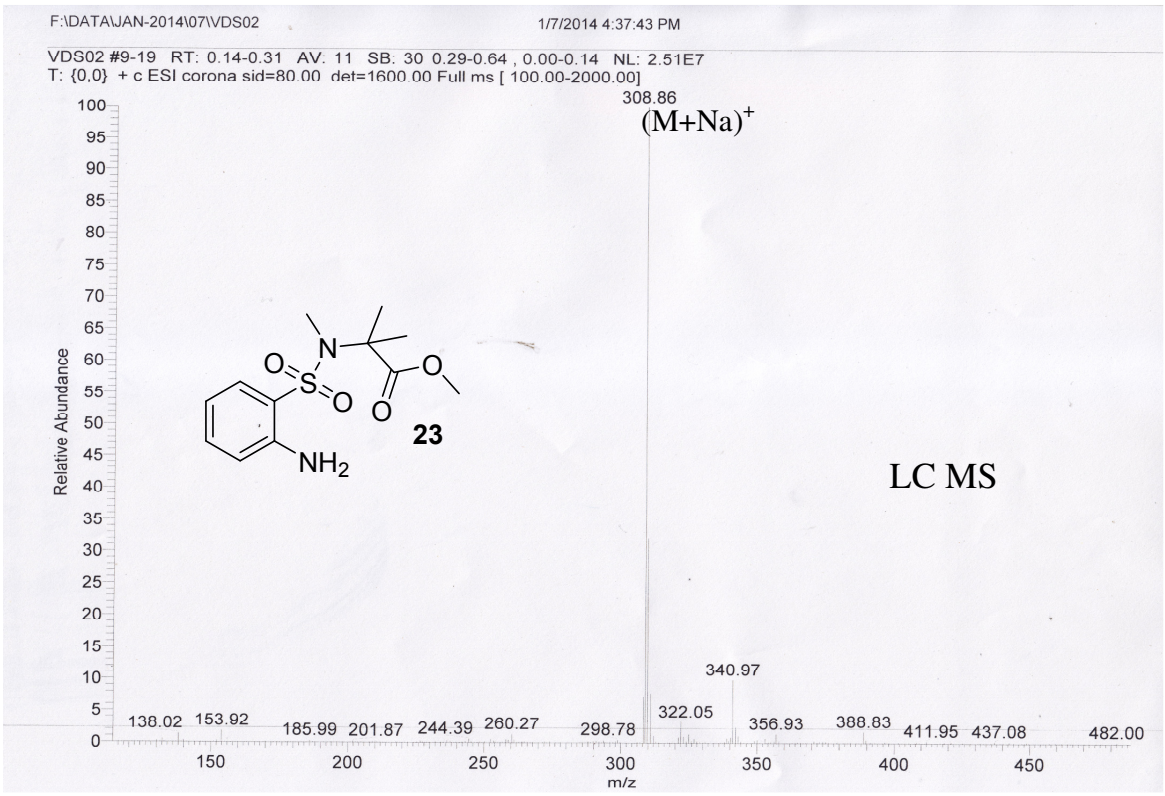

TOF/TOF™ Reflector Spec #1[BP = 379.1, 42783]
MALDI-TOF MS
(M+Na)+
(M+K)+
1
% Intensity
Mass (m/z)

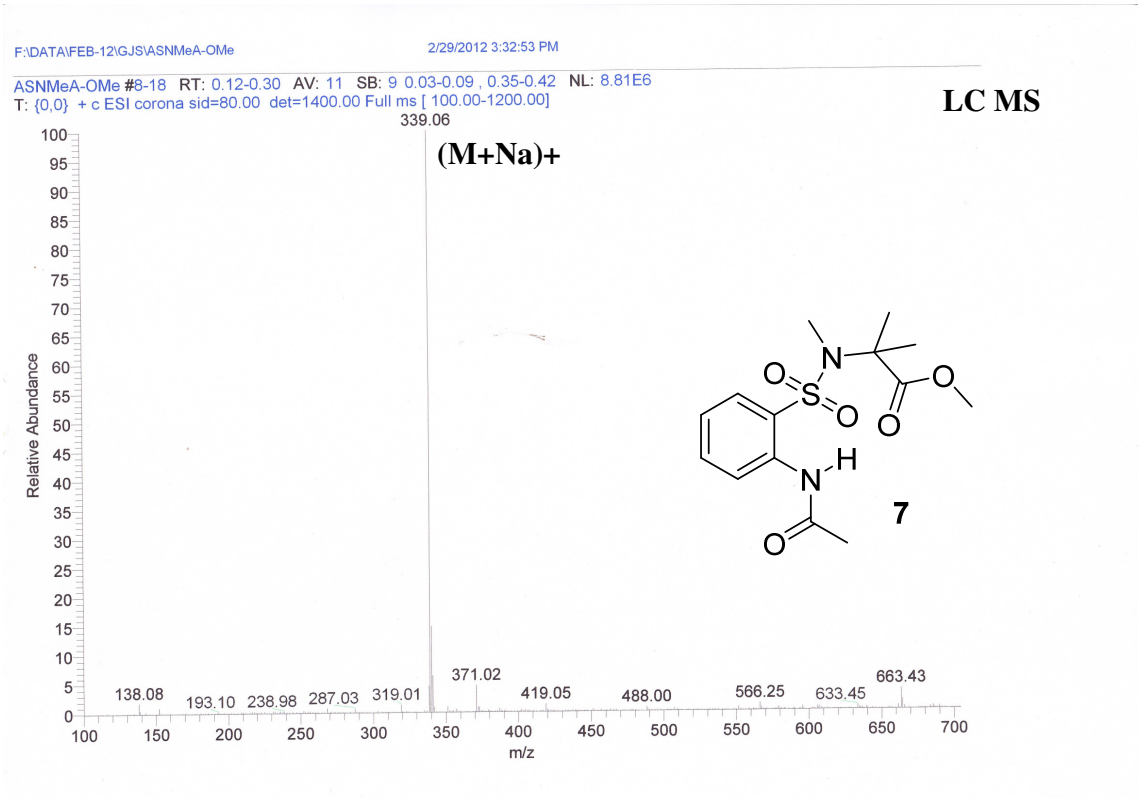

TOF/TOF™ Reflector Spec #1[BP = 379.2, 6929]
MALDI-TOF
(M+Na)+
(M+H)+
(M+K)+
18
% Intensity
Mass (m/z)


TOF/TOF™ Reflector Spec #1[BP = 448.0, 1707]
MALDI-TOF MS
(M+Na)+
(M+H)+
(M+K)+
19
% Intensity
Mass (m/z)


TOF/TOF™ Reflector Spec #1[BP = 379.2, 3123]
MALDI-TOF MS
(M+Na)+
(M+H)+
(M+K)+
6
% Intensity
Mass (m/z)


TOF/TOF™ Reflector Spec #1[BP = 379.2, 15479]
MALDI-TOF MS
(M+Na)+
(M+H)+
(M+K)+
22
% Intensity
Mass (m/z)


F:\DATA\JAN-2014\07\VDS02
1/7/2014 4:37:43 PM
VDS02 #9-19 RT: 0.14-0.31 AV: 11 SB: 30 0.29-0.64 , 0.00-0.14 NL: 2.51E7
T: {0,0} + c ESI corona sid=80.00 det=1600.00 Full ms [100.00-2000.00]
308.86
(M+Na)+
Relative Abundance
m/z
340.97
322.05
138.02
153.92
185.99
201.87
244.39
260.27
298.78
356.93
388.83
411.95
437.08
482.00
23
LC MS


F:\DATA\FEB-12\GJS\ASNMeA-OMe
2/29/2012 3:32:53 PM
ASNMeA-OMe #8-18 RT: 0.12-0.30 AV: 11 SB: 9 0.03-0.09 , 0.35-0.42 NL: 8.81E6
T: {0,0} + c ESI corona sid=80.00 det=1400.00 Full ms [100.00-1200.00]
339.06
(M+Na)+
LC MS
Relative Abundance
m/z
371.02
663.43
138.08
193.10
238.98
287.03
319.01
419.05
488.00
566.25
633.45
7

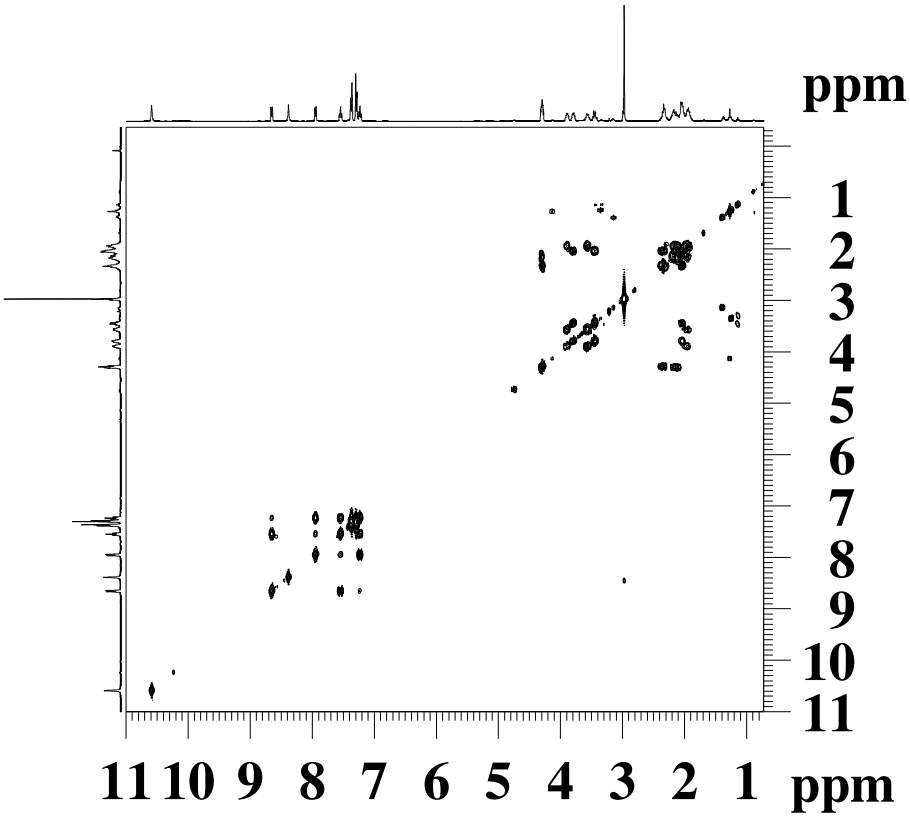


Figure 1: COSY Spectrum of **3** (500MHz, $CDCl_3$).

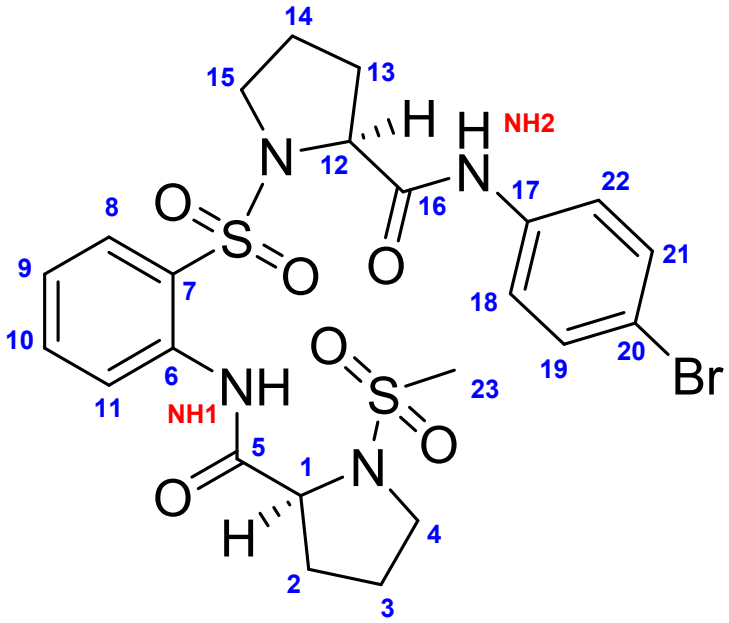


Figure 2: Molecular Structure of compound **3.**

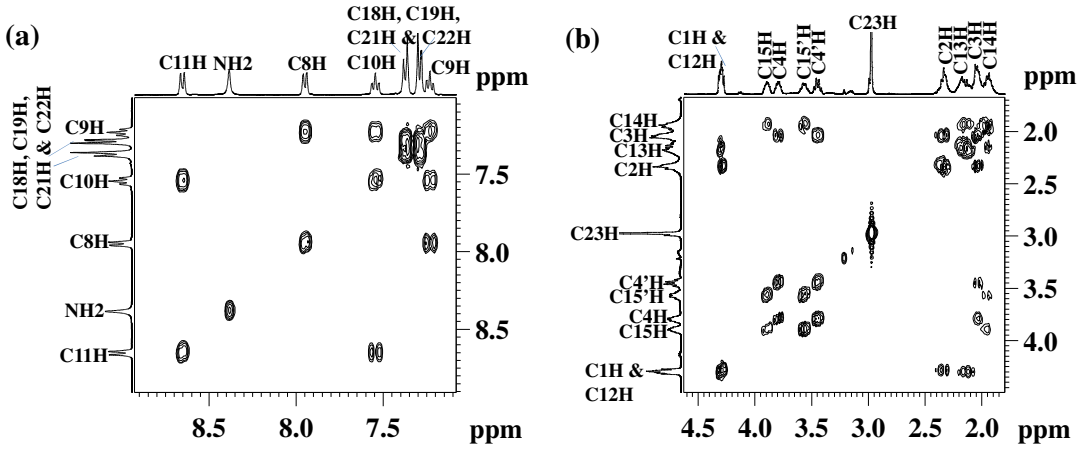


Figure 3: Partial COSY Spectrum of **3** (500MHz, $CDCl_3$); (a) aromatic and (b) aliphatic regions.

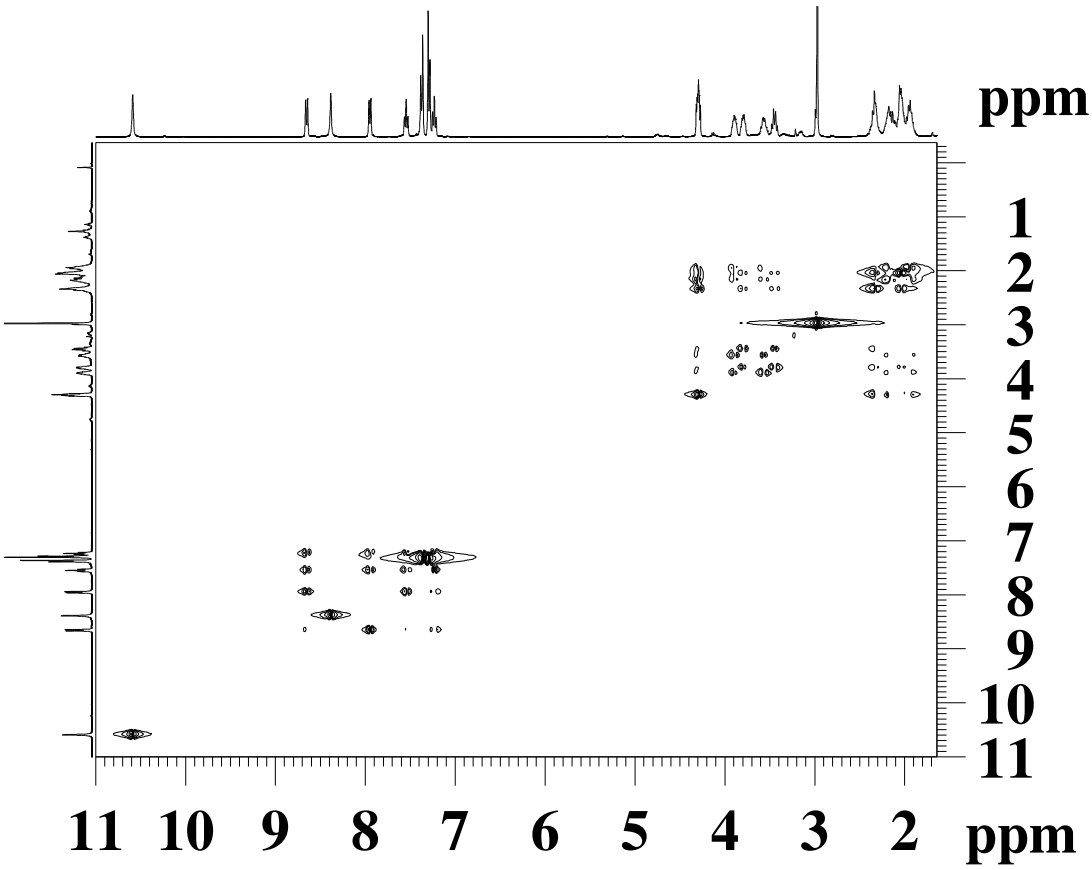


Figure 4: TOCSY Spectrum of **3** (500MHz, $CDCl_3$).

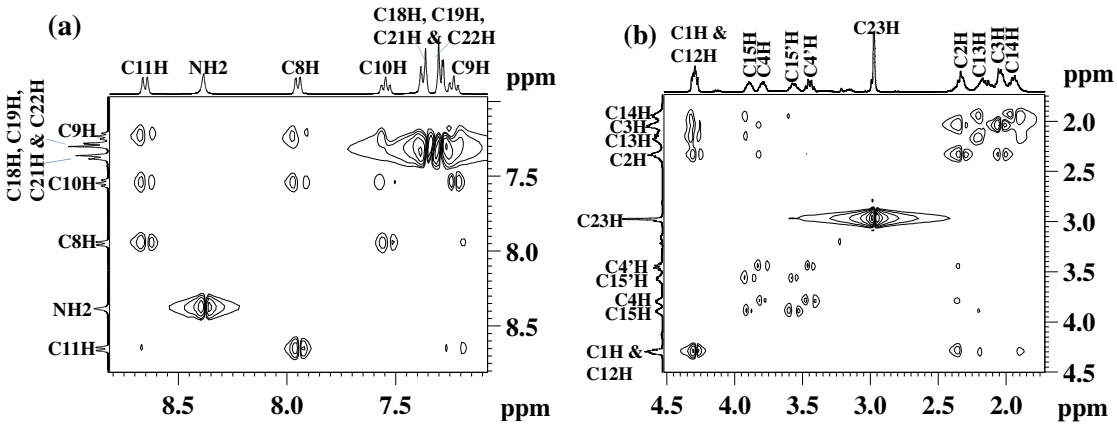


Figure 5: Partial TOCSY Spectrum of **3** (500MHz, $CDCl_3$); (a) aromatic and (b) aliphatic regions.

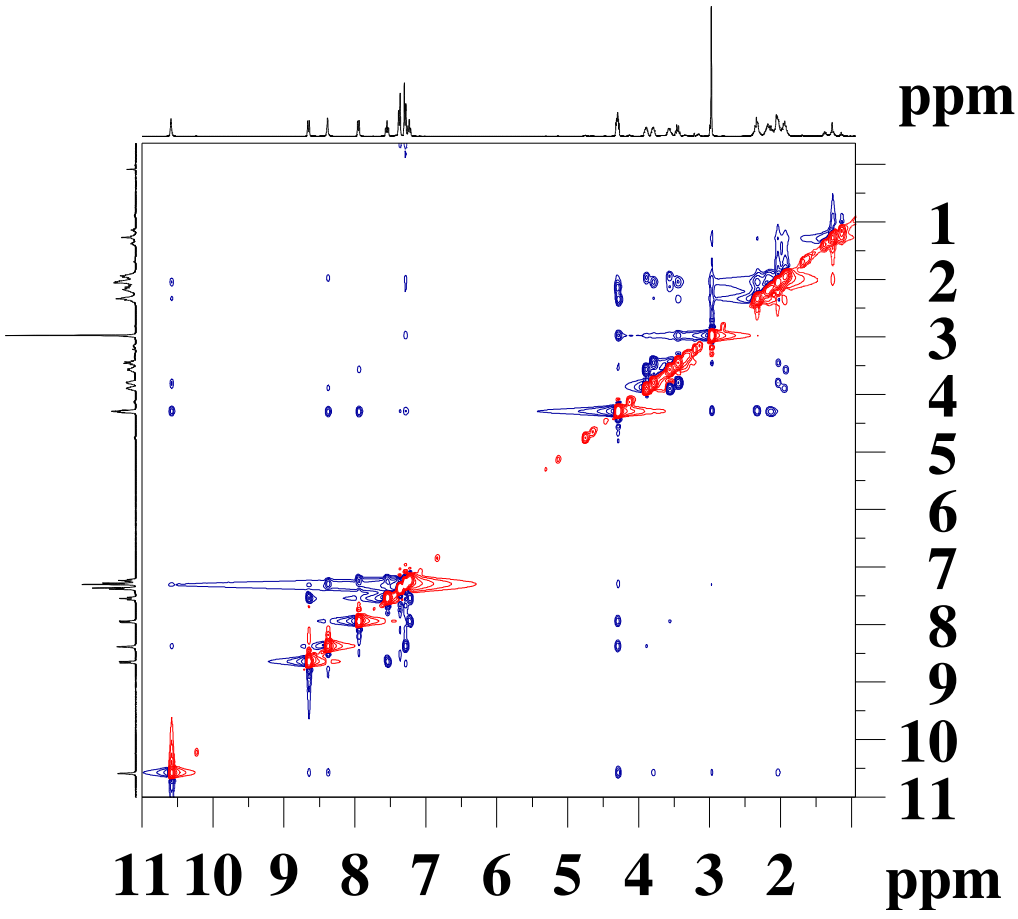


Figure 6: NOESY Spectrum of **3** (500MHz, $CDCl_3$).

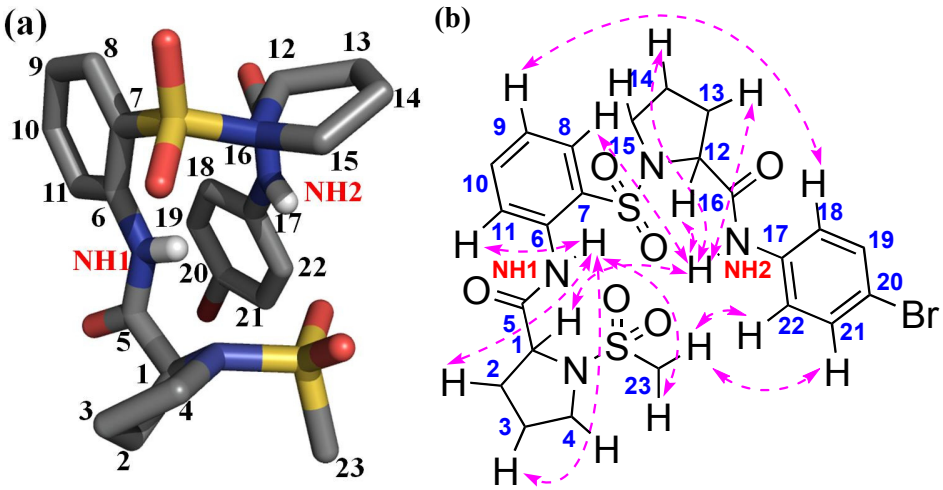


Figure 7: Pymol rendered crystal structures of **3**; (a) with numbering and (b) with NOE interactions.

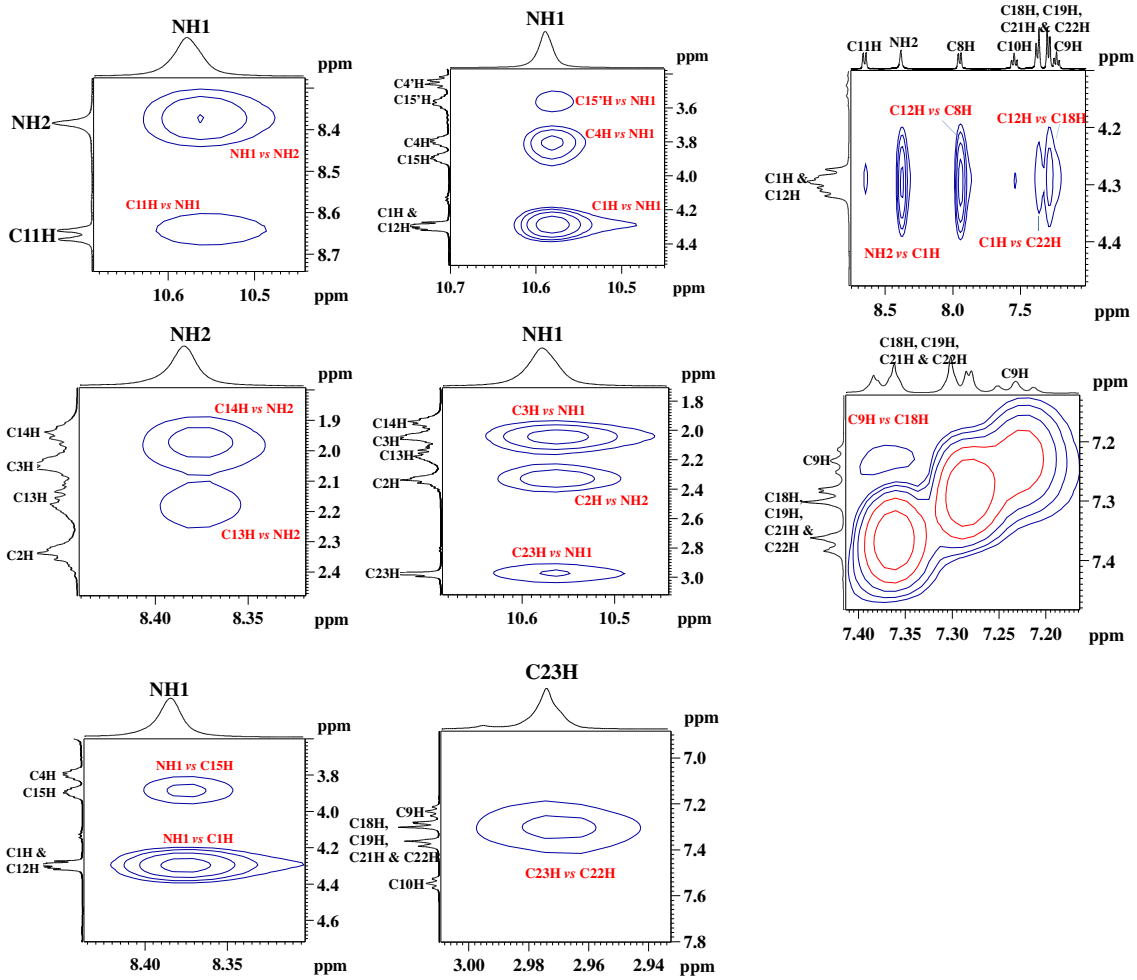


Figure 8: Partial 2D NOESY Extracts of **3** (500MHz, $CDCl_3$).

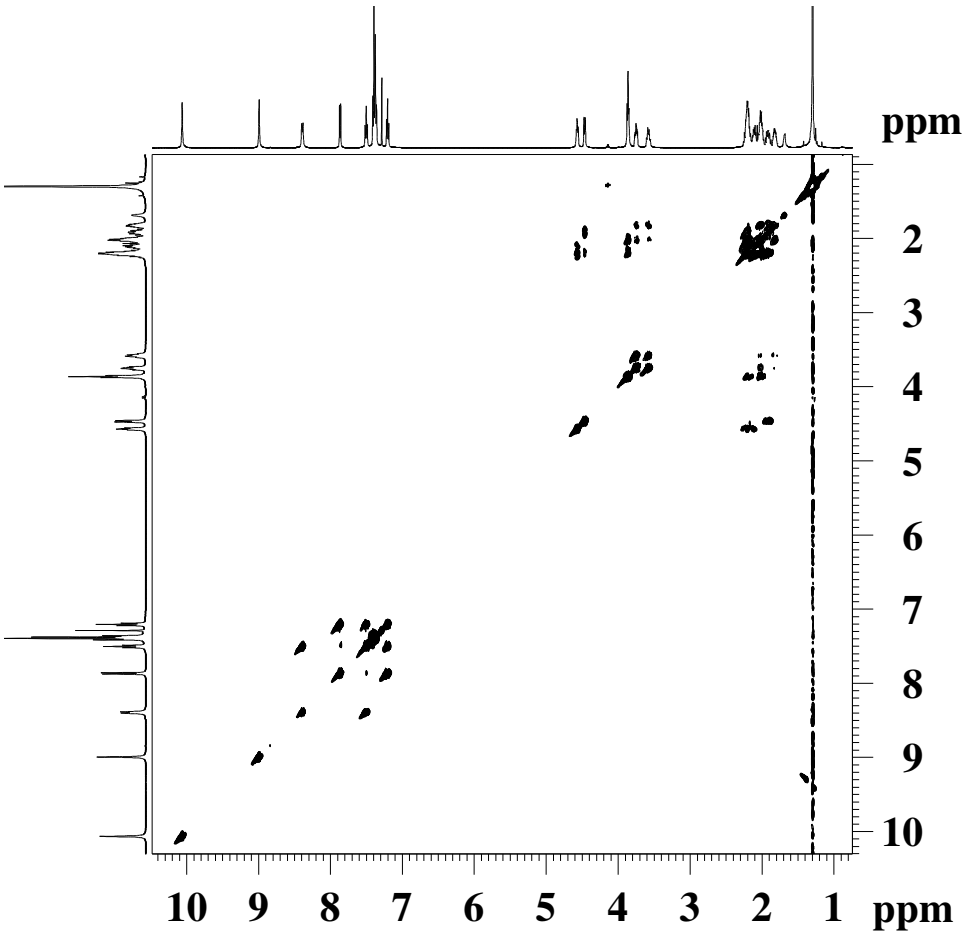


Figure 9: COSY Spectrum of **1** (500MHz, $CDCl_3$).

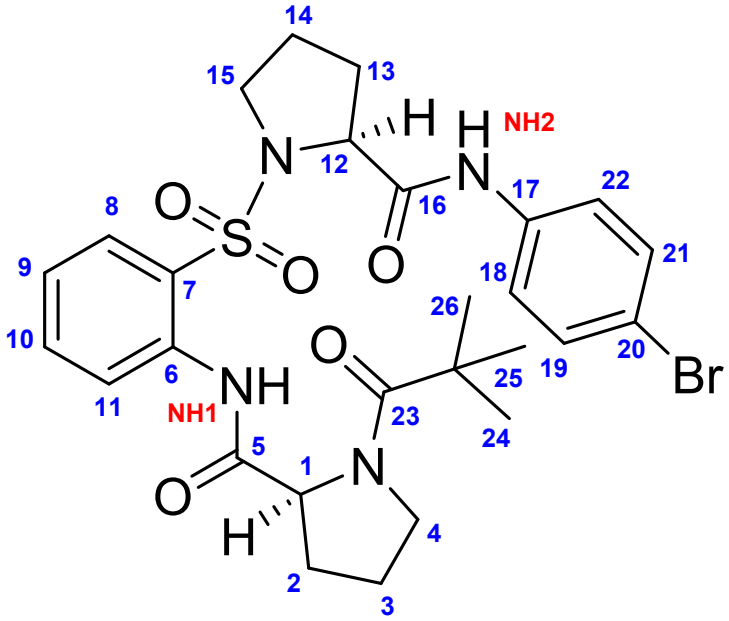


Figure 10: Molecular Structure of compound **1.**

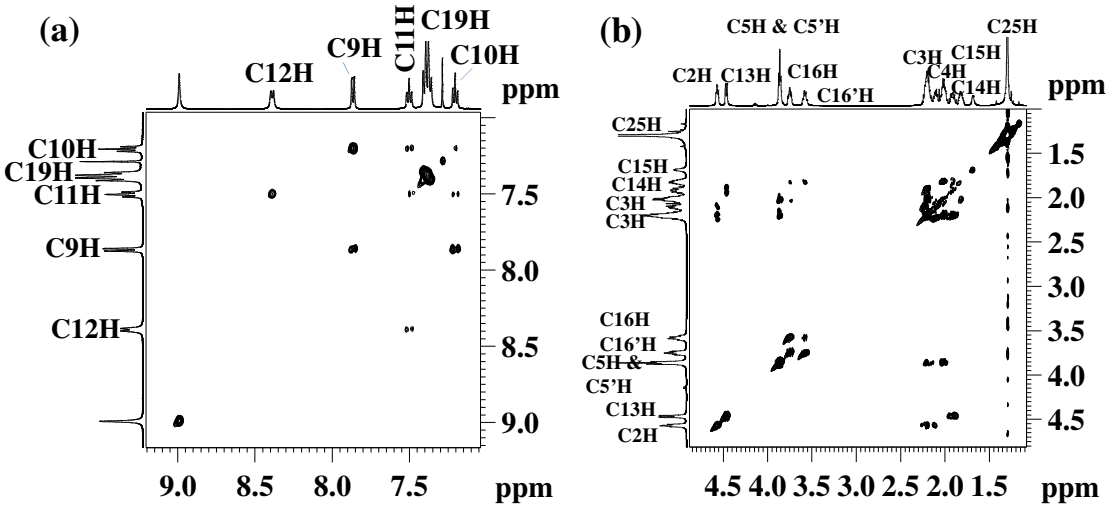


Figure 11: Partial COSY Spectrum of **1** (500MHz, $CDCl_3$); (a) aromatic and (b) aliphatic regions.

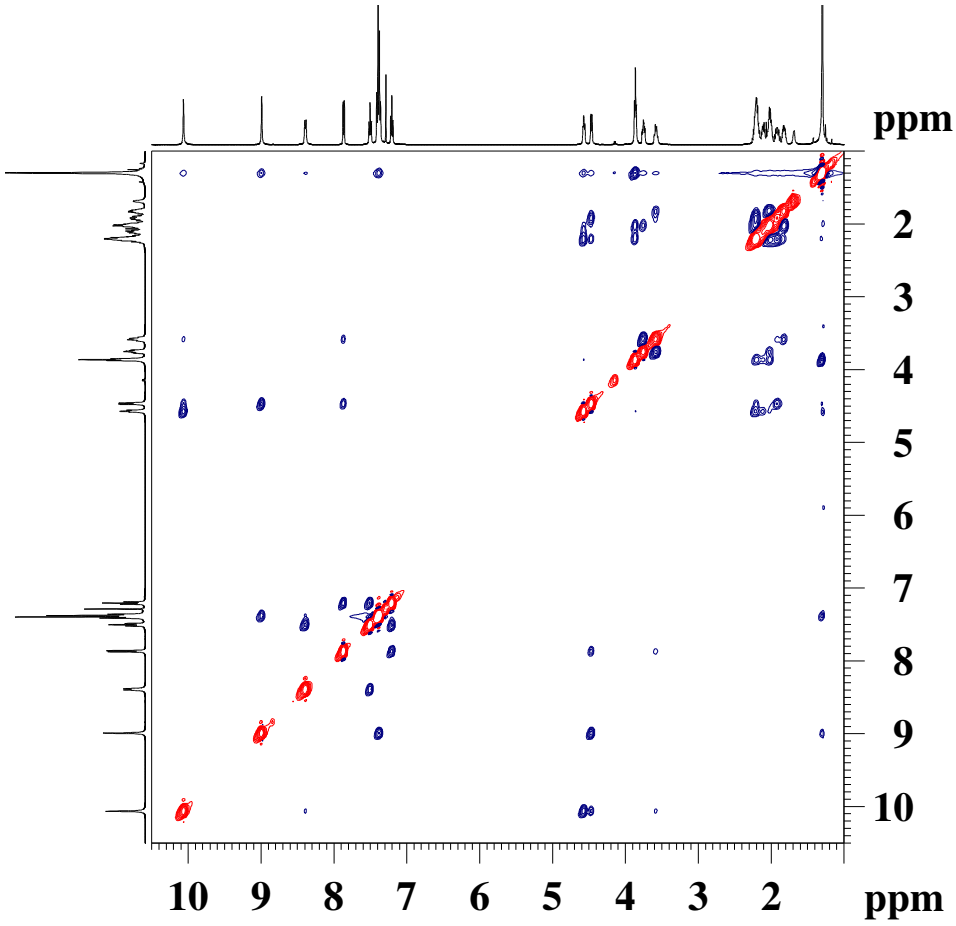


Figure 12: NOESY Spectrum of **1** (500MHz, $CDCl_3$).

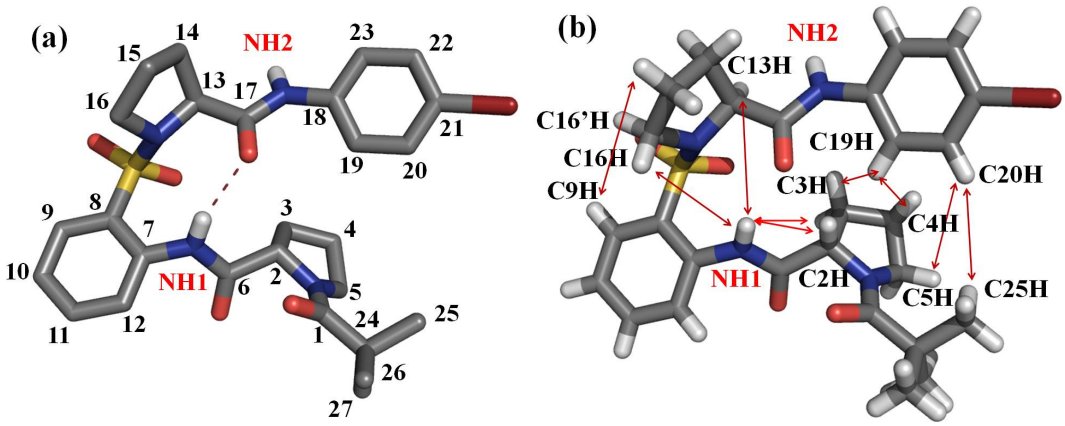


Figure 13: Pymol rendered crystal structures of **1**; (a) with numbering and (b) with NOE interactions.

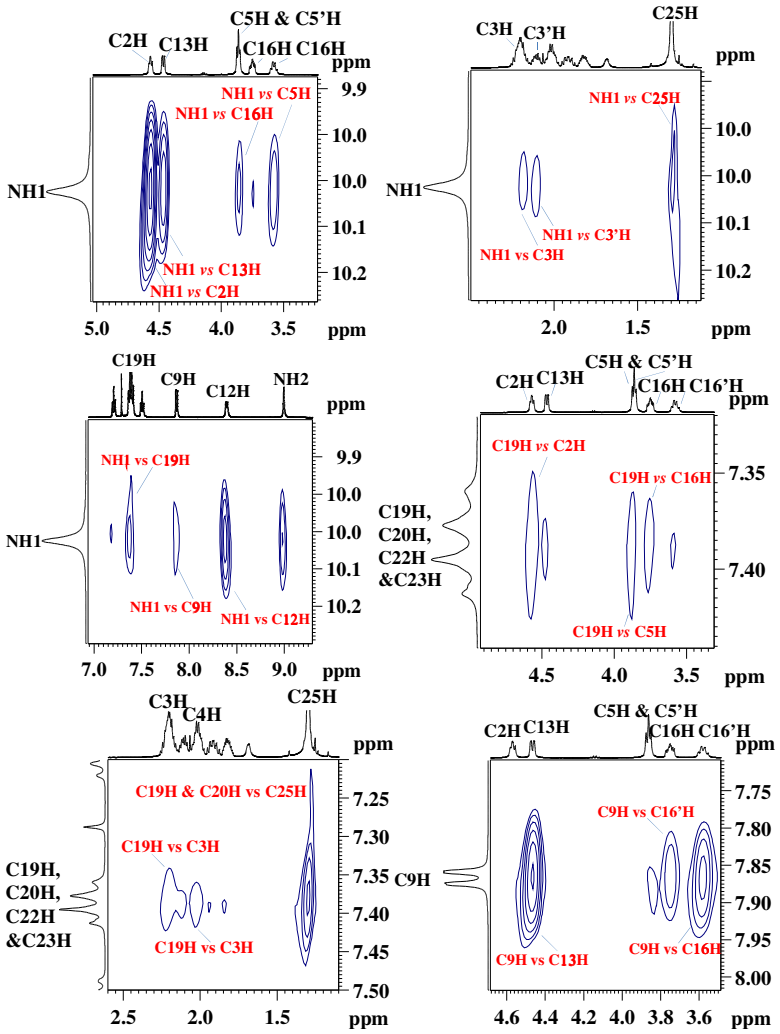


Figure 14: Partial 2D NOESY Extracts of **1** (500MHz, $CDCl_3$).

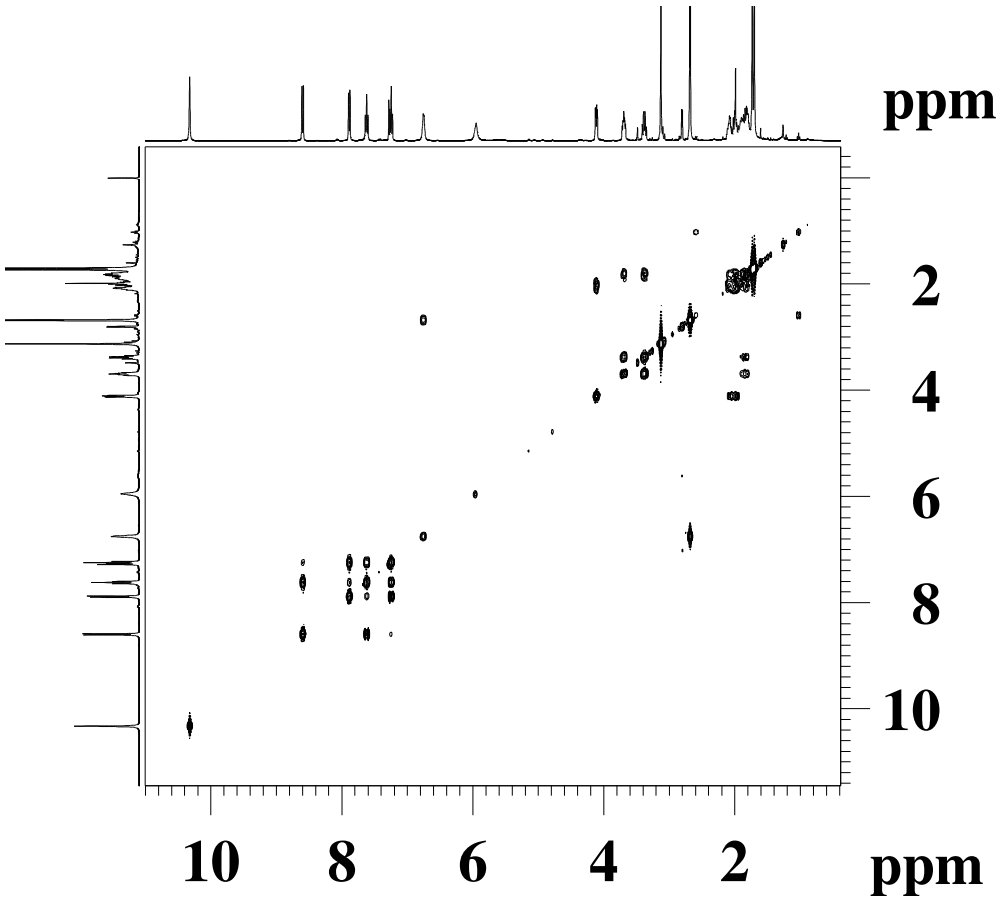


Figure 15: COSY Spectrum of **5** (500MHz, $CDCl_3$).

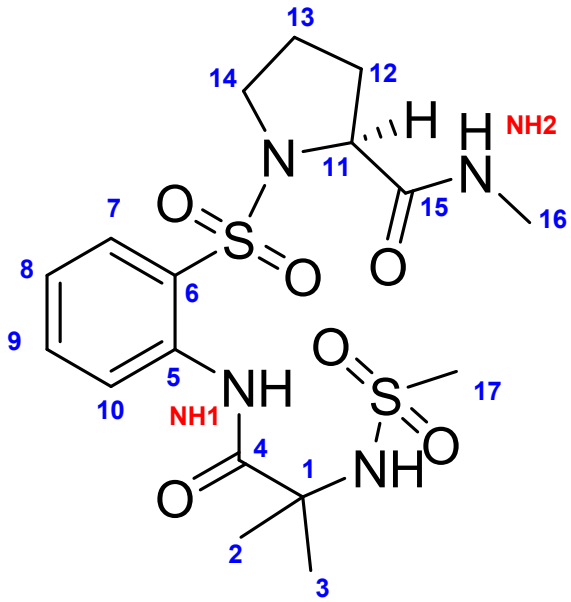


Figure 16: Molecular Structure of compound **5.**

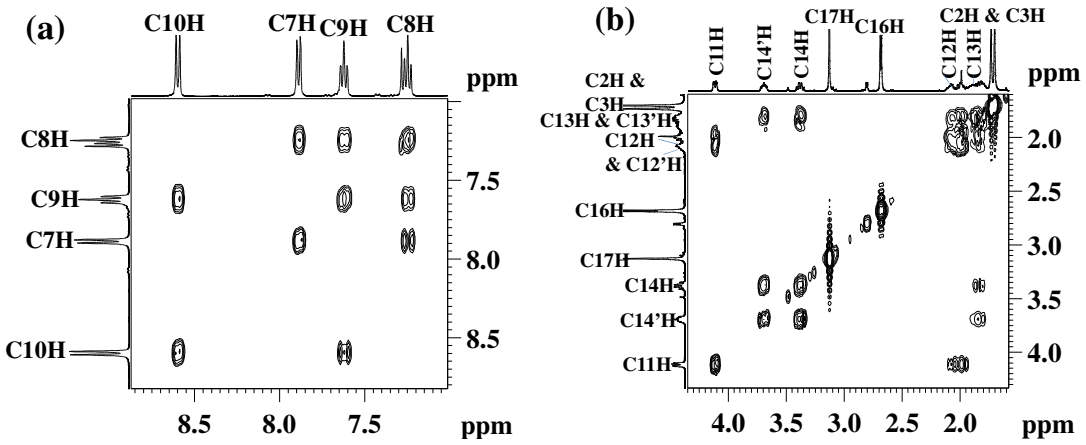


Figure 17: Partial COSY Spectrum of **5** (500MHz, $CDCl_3$); (a) aromatic and (b) aliphatic regions.

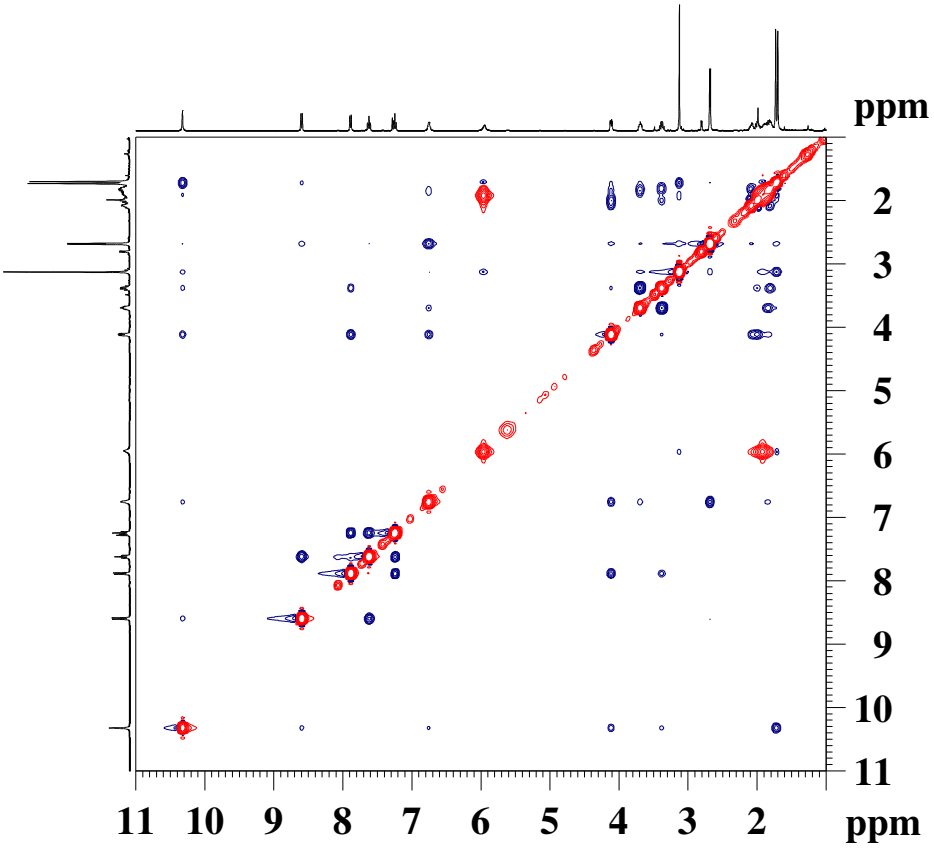


Figure 18: NOESY Spectrum of **5** (500MHz, $CDCl_3$).

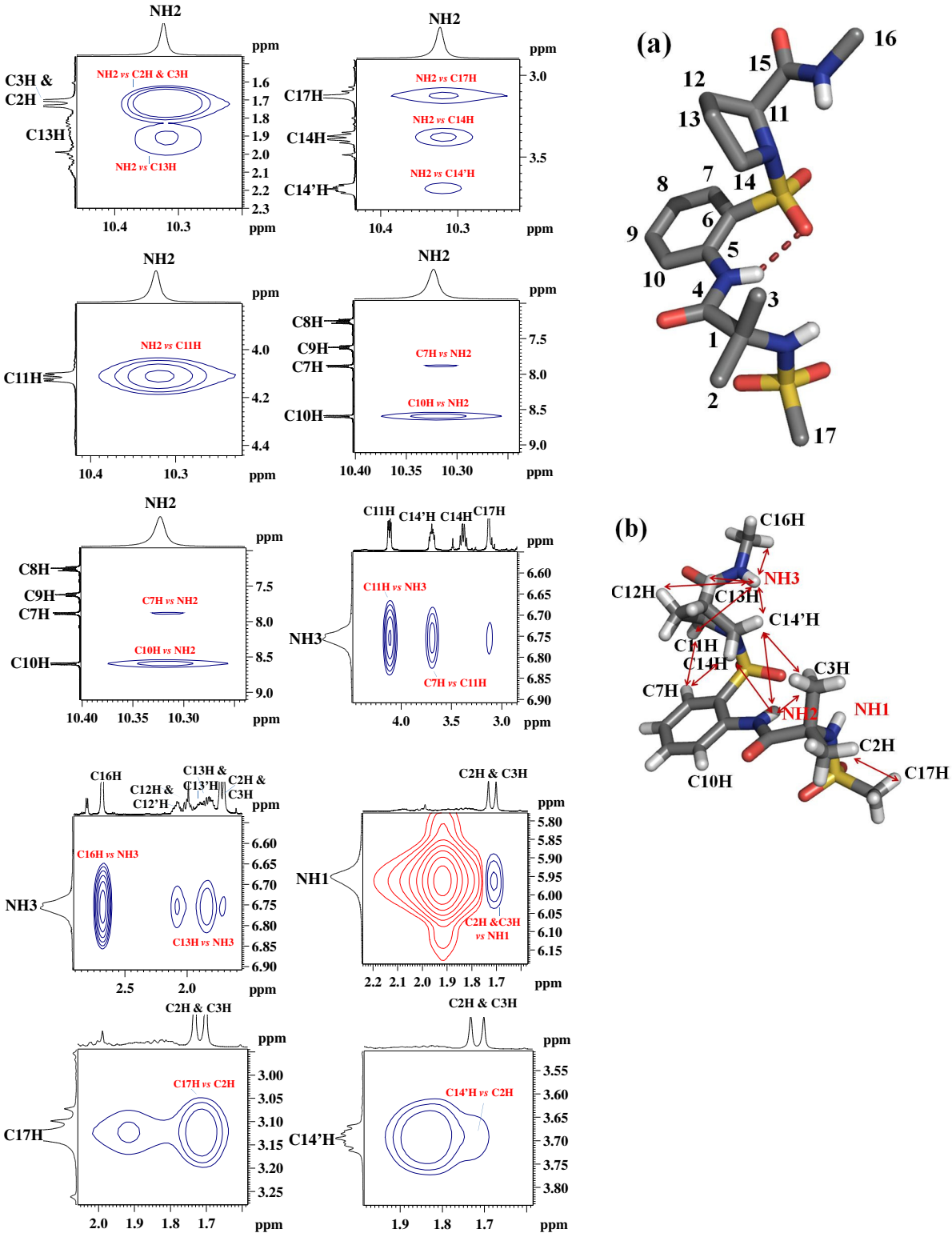


Figure 19: Partial 2D NOESY Extracts of **5** (500MHz, $CDCl_3$). Pymol rendered crystal structures of **5**; (a) with numbering and (b) with NOE interactions.

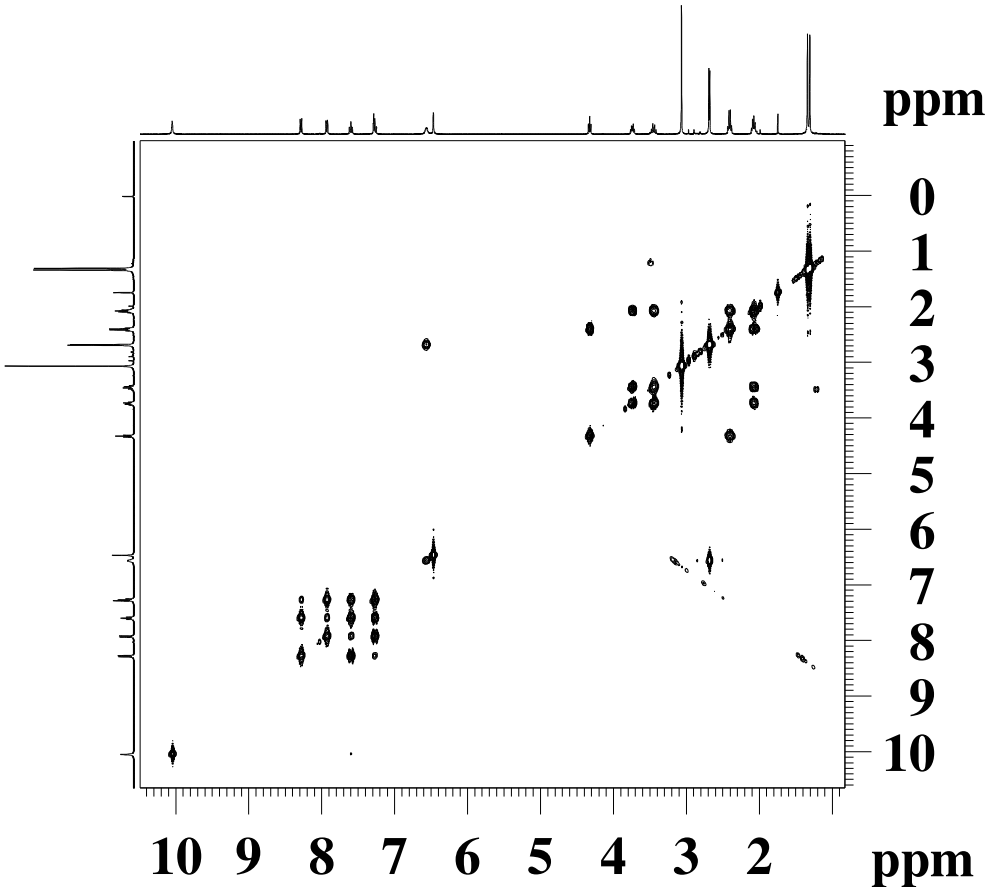


Figure 20: COSY Spectrum of **4** (500MHz, $CDCl_3$).

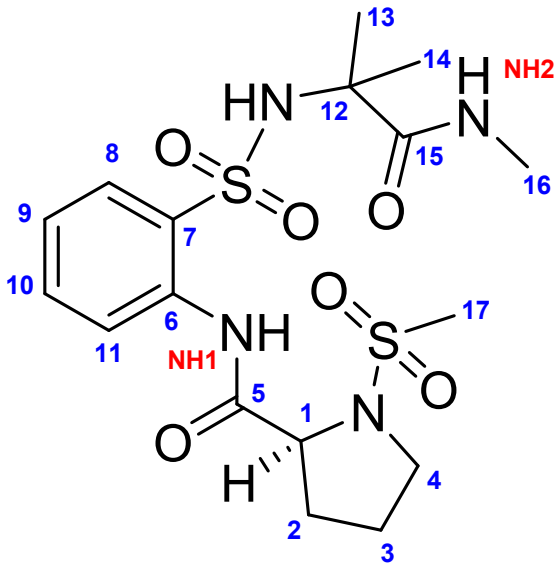


Figure 21: Molecular Structure of compound **4.**

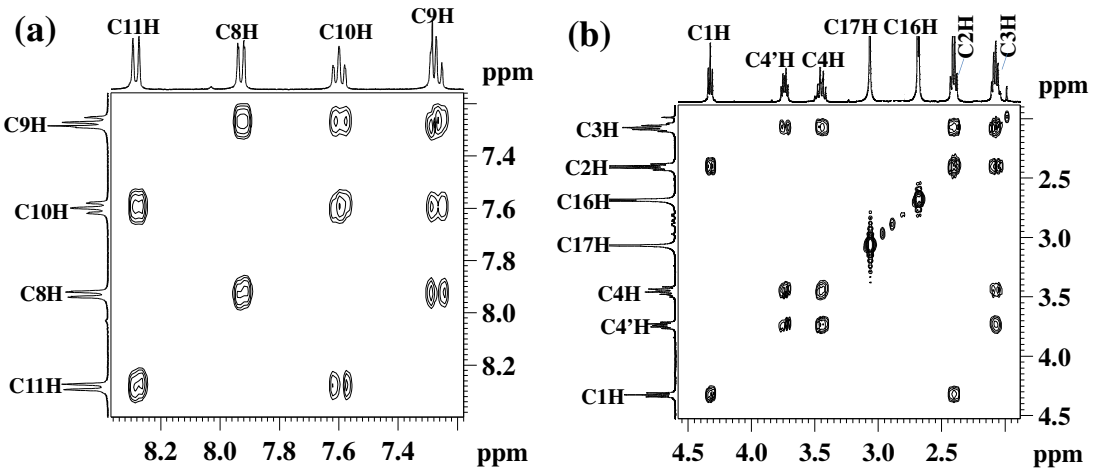


Figure 22: Partial COSY Spectrum of **4** (500MHz, $CDCl_3$); (a) aromatic and (b) aliphatic regions.

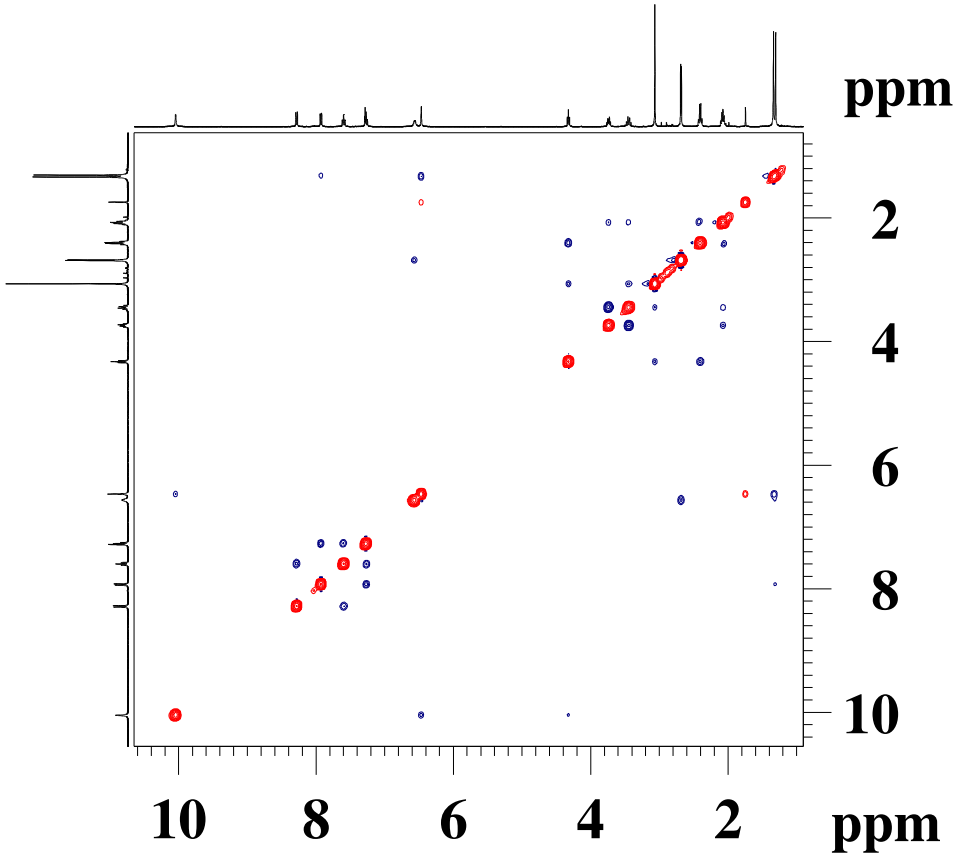


Figure 23: NOESY Spectrum of **4** (500MHz, $CDCl_3$).

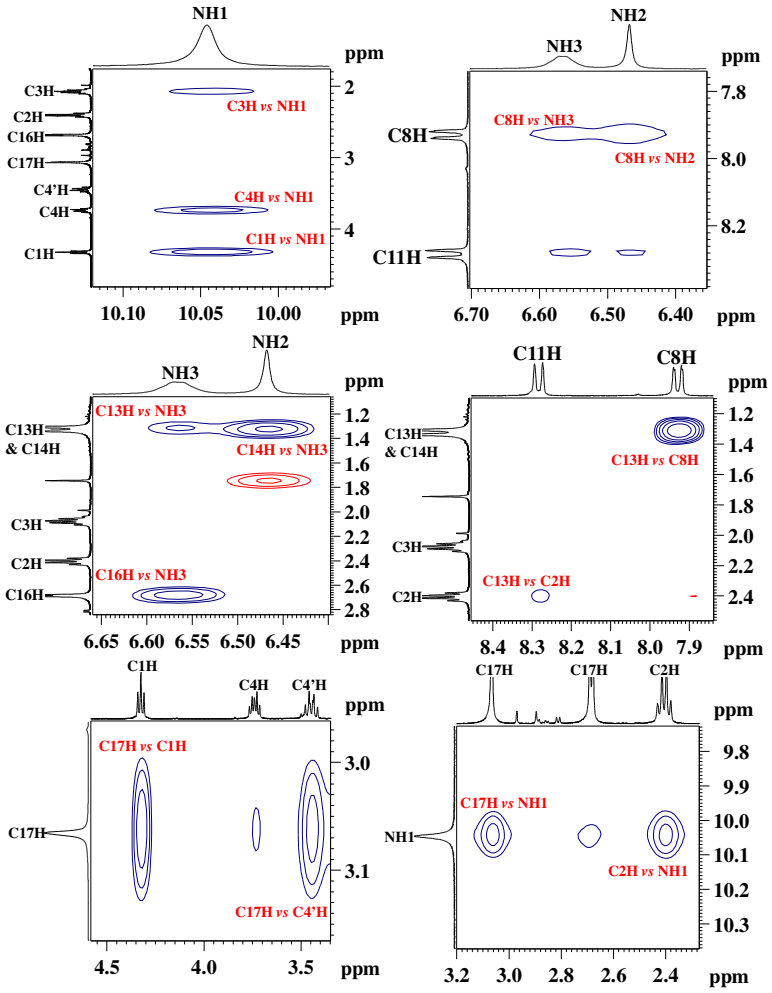


Figure 24: Partial 2D NOESY Extracts of **4** (500MHz, $CDCl_3$).

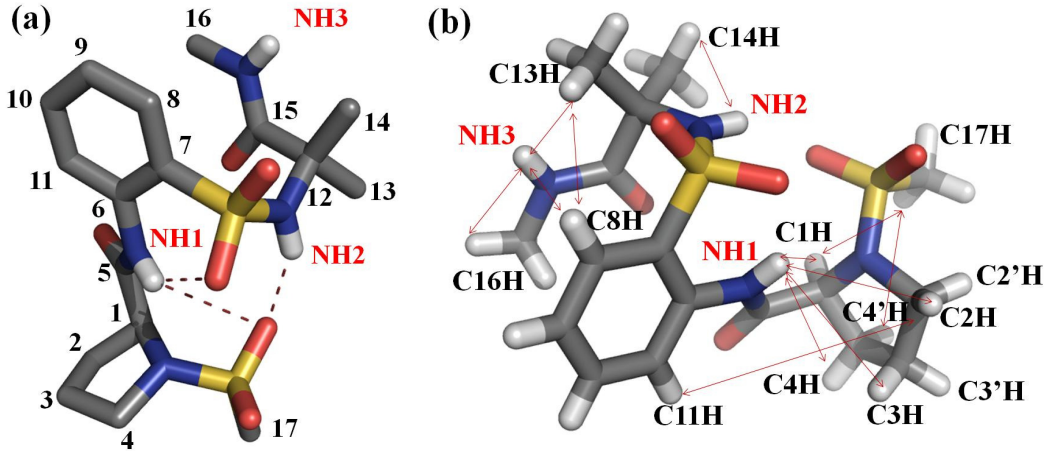
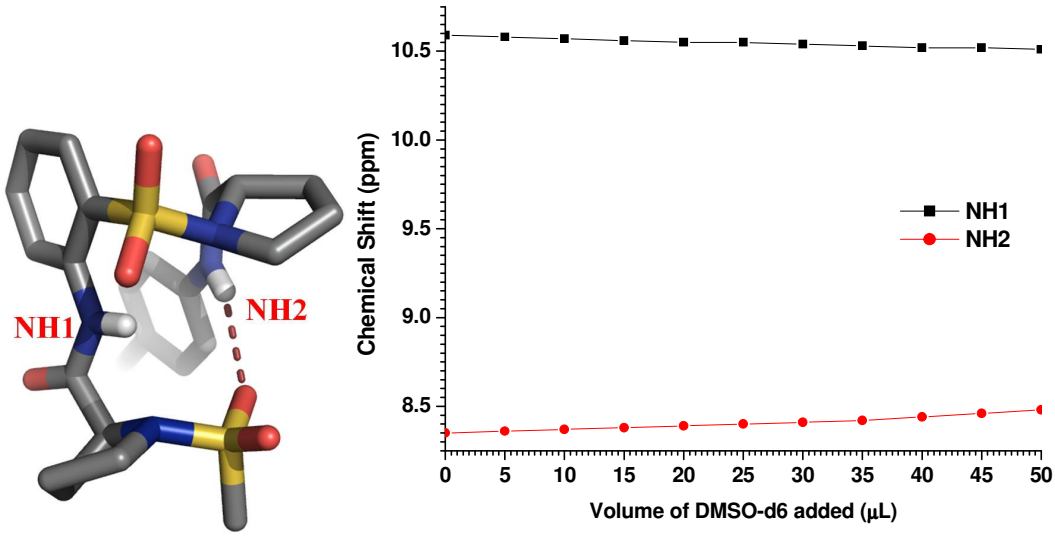


Figure 25: Pymol rendered crystal structures of **4**; (a) with numbering and (b) with NOE interactions.

Table S1. DMSO-*d6* titration plots of compound 3 (5 mmol, 400 MHz, $CDCl_3$).

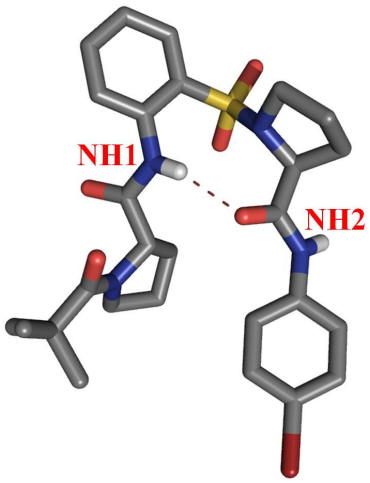


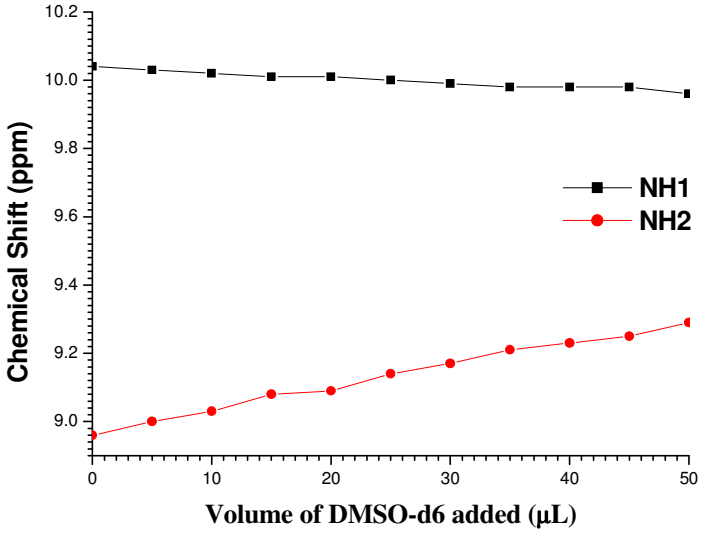
Volume of DMSO-d6 added (µL)	Chemical shift in (ppm)	
	NH1	NH2
0	10.59	8.35
5	10.58	8.36
10	10.57	8.37
15	10.56	8.38
20	10.55	8.39
25	10.55	8.40
30	10.54	8.41
35	10.53	8.42
40	10.52	8.44
45	10.52	8.46
50	10.51	8.48

Major Inferences:-

(a) δNH1 = 0.08 ppm
(b) δNH2 = 0.13ppm

Table S2. DMSO-*d6* titration plots of compound 1 (5 mmol, 400 MHz, $CDCl_3$).



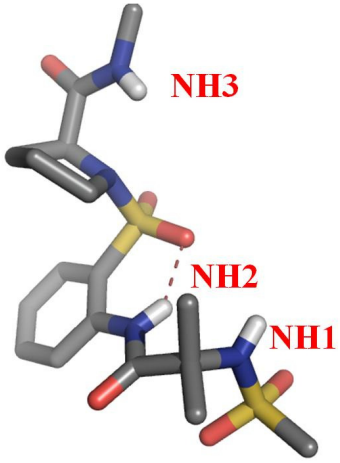


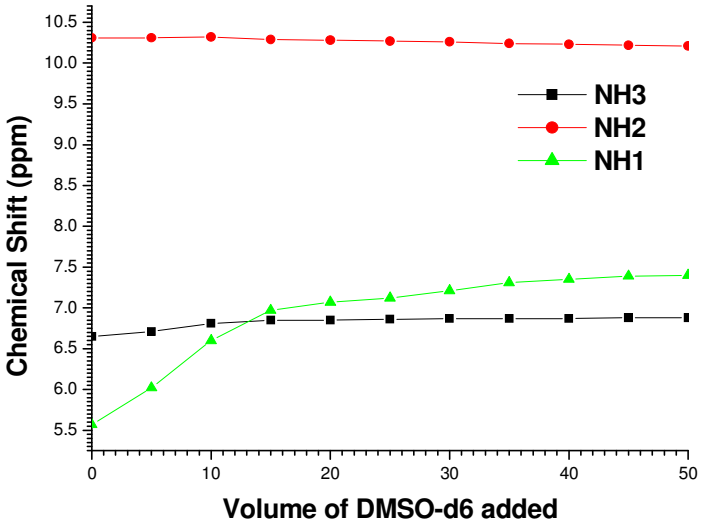
Volume of DMSO-d6 added (µL)	Chemical shift in (ppm)	
	NH1	NH2
0	10.04	8.96
5	10.03	9.00
10	10.02	9.03
15	10.01	9.08
20	10.01	9.09
25	10.0	9.14
30	9.99	9.17
35	9.98	9.21
40	9.98	9.23
45	9.98	9.25
50	9.96	9.29

Major Inferences:-

(a) δNH1 = 0.08 ppm
(b) δNH2 = 0.33ppm

Table S3. DMSO-*d6* titration plots of compound 5 (5 mmol, 400 MHz, $CDCl_3$).



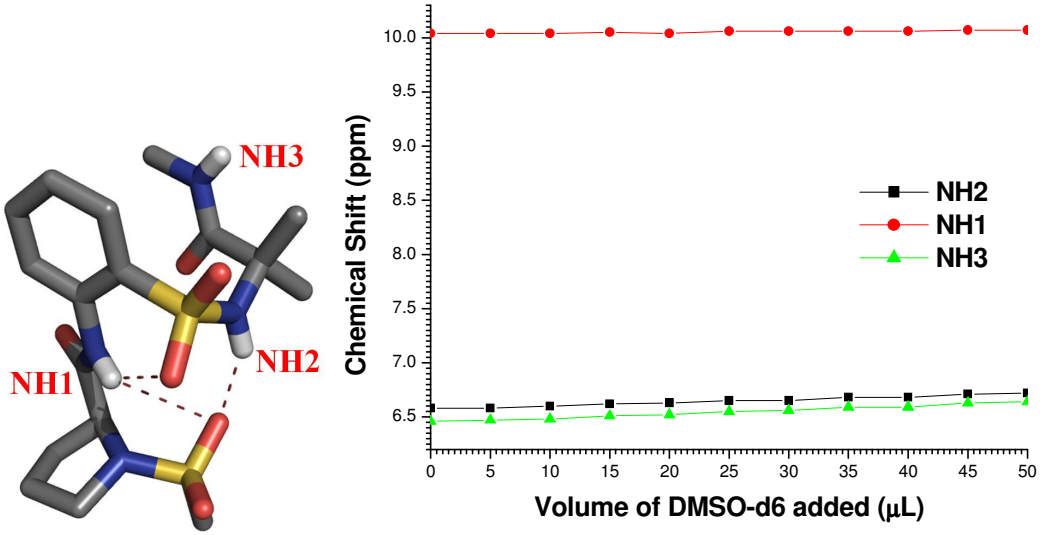


Volume of DMSO-d6 added (µL)	Chemical shift in (ppm)		
	NH3	NH2	NH1
0	6.65	10.31	5.57
5	6.71	10.31	6.02
10	6.81	10.32	6.60
15	6.85	10.29	6.97
20	6.85	10.28	7.07
25	6.86	10.27	7.12
30	6.87	10.26	7.21
35	6.87	10.24	7.31
40	6.87	10.23	7.35
45	6.88	10.22	7.39
50	6.88	10.21	7.40

Major Inferences:-

(a) δNH1 = 0.83 ppm
(b) δNH2 = 0.10ppm
(c) δNH3 = 0.23ppm

Table S4. DMSO-*d6* titration plots of compound 4 (5 mmol, 400 MHz, $CDCl_3$).

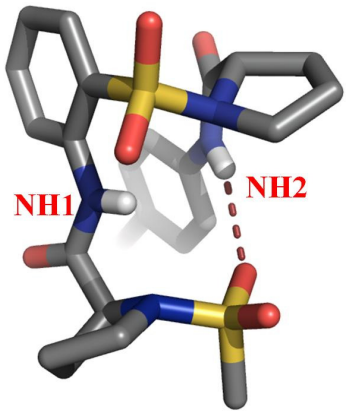


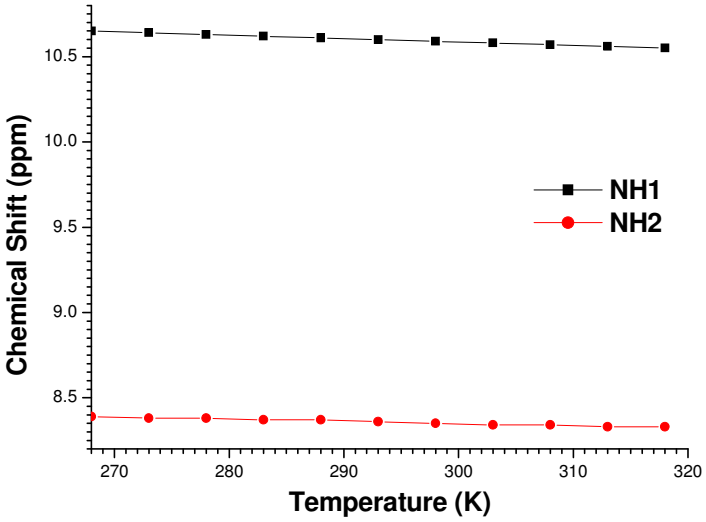
Volume of DMSO-d6 added (µL)	Chemical shift in (ppm)		
	NH2	NH1	NH3
0	6.58	10.04	6.46
5	6.58	10.04	6.47
10	6.60	10.04	6.48
15	6.62	10.05	6.51
20	6.63	10.04	6.52
25	6.65	10.06	6.55
30	6.65	10.06	6.56
35	6.68	10.06	6.59
40	6.68	10.06	6.59
45	6.71	10.07	6.63
50	6.72	10.07	6.64

Major Inferences:-

(a) δNH1 = 0.03 ppm
(b) δNH2 = 0.14ppm
(c) δNH3 = 0.18ppm

Table S5. Temperature Variation Study of Compound 3 (5 mmol, 400 MHz, $CDCl_3$).



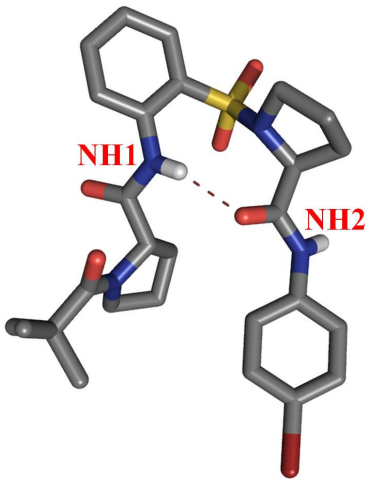


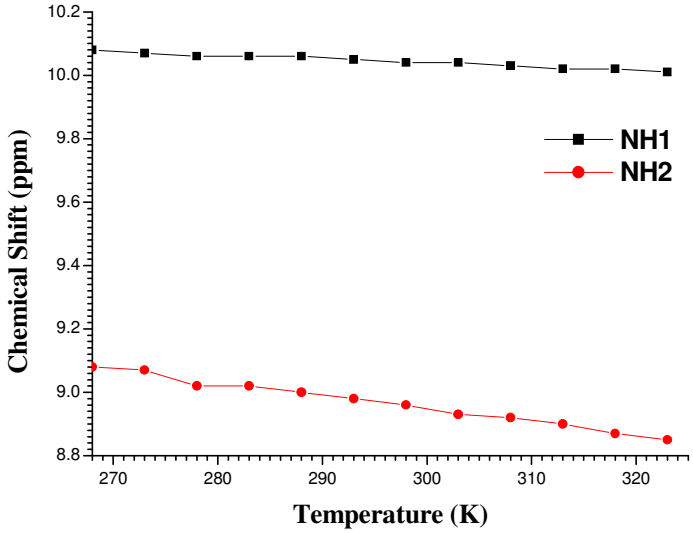
Temperature (K)	Chemical shift in (ppm)	
	NH1	NH2
268	10.65	8.39
273	10.64	8.38
278	10.63	8.38
283	10.62	8.37
288	10.61	8.37
293	10.60	8.36
298	10.59	8.35
303	10.58	8.34
308	10.57	8.34
313	10.56	8.33
318	10.55	8.33
323	10.54	8.32

Major Inferences upon varying the temperature from 268-323K:-

(a) δNH1 = 0.11ppm; $\Delta\delta/\Delta T$ = -2 ppbK^{-1}
(b) δNH2 = 0.07ppm; $\Delta\delta/\Delta T$ = -1.27 ppbK^{-1}

Table S6. Temperature Variation Study of Compound 1 (5 mmol, 400 MHz, $CDCl_3$).



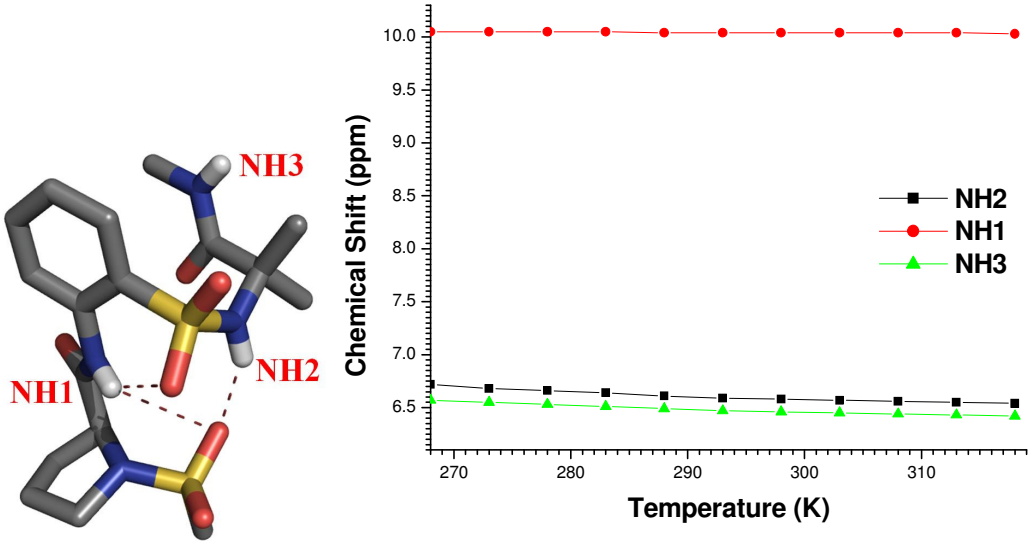


Temperature (K)	Chemical shift in (ppm)	
	NH1	NH2
268	10.08	9.08
273	10.07	9.07
278	10.06	9.02
283	10.06	9.02
288	10.06	9.00
293	10.05	8.98
298	10.04	8.96
303	10.04	8.93
308	10.03	8.92
313	10.02	8.90
318	10.02	8.87
323	10.01	8.85

Major Inferences upon varying the temperature from 268-323K:-

(a) δNH1 = 0.07 ppm; $\Delta\delta/\Delta T$ = -1.27 ppbK^{-1}
(b) δNH2 = 0.23 ppm; $\Delta\delta/\Delta T$ = -4.18 ppbK^{-1}

Table S7. Temperature Variation Study of Compound 4 (5 mmol, 400 MHz, $CDCl_3$).

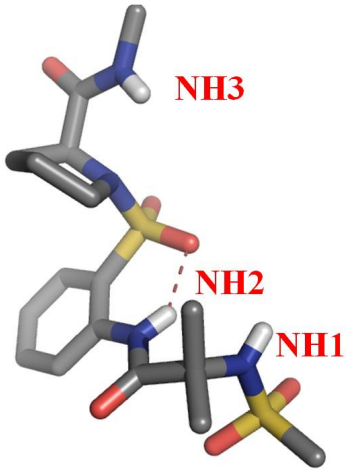


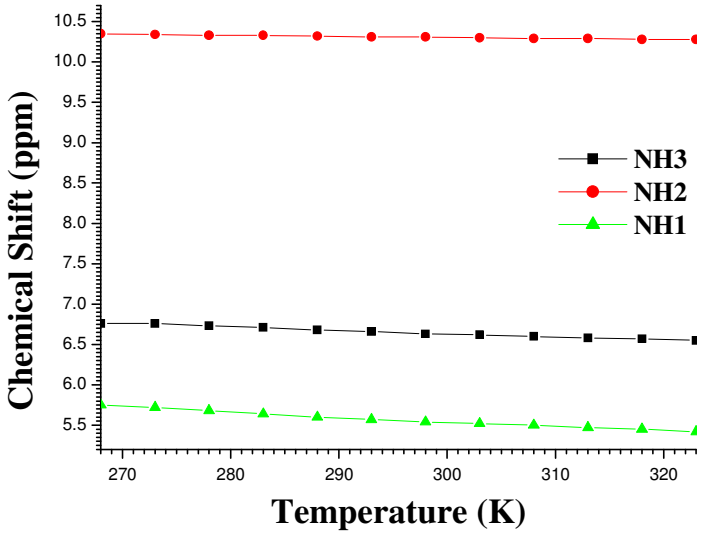
Temperature (K)	Chemical shift in (ppm)		
	NH2	NH1	NH3
268	6.72	10.05	6.57
273	6.68	10.05	6.55
278	6.66	10.05	6.53
283	6.64	10.05	6.51
288	6.61	10.04	6.49
293	6.59	10.04	6.47
298	6.58	10.04	6.46
303	6.57	10.04	6.45
308	6.56	10.04	6.44
313	6.55	10.04	6.43
318	6.54	10.03	6.42
323	6.53	10.03	6.40

Major Inferences upon varying the temperature from 268-323K:-

(a) δNH1 = 0.02 ppm; $\Delta\delta/\Delta T$ = -0.36 ppbK^{-1}
(b) δNH2 = 0.19 ppm; $\Delta\delta/\Delta T$ = -3.45 ppbK^{-1}
(c) δNH3 = 0.17 ppm; $\Delta\delta/\Delta T$ = -3.09 ppbK^{-1}

Table S8. Temperature Variation Study of Compound 5 (5 mmol, 400 MHz, $CDCl_3$).





Temperature (K)	Chemical shift in (ppm)		
	NH3	NH2	NH1
268	6.76	10.35	5.75
273	6.76	10.34	5.72
278	6.73	10.33	5.68
283	6.71	10.33	5.64
288	6.68	10.32	5.60
293	6.66	10.31	5.57
298	6.63	10.31	5.54
303	6.62	10.30	5.52
308	6.60	10.29	5.50
313	6.58	10.29	5.47
318	6.57	10.28	5.45
323	6.55	10.28	5.42

Major Inferences upon varying the temperature from 268-323K:-

(a) δNH1 = 0.33 ppm; $\Delta\delta/\Delta T$ = -6 ppbK^{-1}
(b) δNH2 = 0.07 ppm; $\Delta\delta/\Delta T$ = -1.27 ppbK^{-1}
(c) δNH3 = 0.21 ppm; $\Delta\delta/\Delta T$ = -3.82 ppbK^{-1}

Crystal Data[4]

Compound 1: Single crystals of **1** were grown by slow evaporation of the solution mixture of ethyl acetate and pet. ether. Colorless block crystal of size 0.49 x 0.42 x 0.31 mm^3, was used for data collection, Temperature = 296(2) K, Wave length = 0.71073 Å Quadrant data acquisition, F(000) = 1256, θ range = 1.76° to 28.29°, completeness to θ is 100 %, Goodness-of-fit on F2 = 1.067, $C_{27}H_{33}BrN_4O_5S$, M = 605.54. Crystals belong to Orthorhombic, space group P212121, a = 6.7186(2) , b = 15.8096(5), c = 26.5176(7) Å, α = β = γ = 90°, V = 2816.66(14) $Å^3$, Z = 4, Dc = 1.428 g/cc, μ (Mo–Kα) = 1.577 mm-1, 6952 total reflections, 4854 unique reflections, R value 0.0698, wR2 = 0.1124.

Compound 2: Single crystals of **2** were grown by slow evaporation of the solution mixture of ethylacetate and pet.ether. Colorless needle crystal of size 0.64 x 0.19 x 0.13 mm^3, was used for data collection, Temperature = 297(2)K, Wave length = 0.71073 Å Quadrant data acquisition, Total scans = 4, F(000) = 1064, θ range = 2.19° to 25.49°, completeness to θ of 24.99 ° is 100 %, Goodness-of-fit on F2 = 1.018, $C_{21}H_{32}N_4O_6S_2$, M = 500.63. Crystals belong to Monoclinic, space group C2, a = 18.6244(11), b = 8.4267(4), c = 16.0611(8) Å, α = 90, β = 93.118(5), γ = 90, 2516.9(2) Å3, Z = 4, Dc = 1.321 g/cc, μ (Mo–Ka) = 0.254 mm-1, 4429 total reflections, 4052 unique [I>2s(I)], R value 0.0430, wR2 = 0.1171.

Compound 3: Single crystals of **3** were grown by slow evaporation of the solution mixture of ethylacetate and pet.ether. Colorless needle crystal of size 0.65 x 0.33 x 0.29 mm^3, was used for data collection, Temperature = 296(2)K, Wave length = 0.71073 Å Quadrant data acquisition, F(000) = 616, θ range = 2.36° to 30.42°, completeness to θ is 95 %, Goodness-of-fit on F2 = 0.993, $C_{23}H_{27}BrN_4O_6S_2$, M = 599.53. Crystals belong to Monoclinic, space group P21, a = 8.1060(12) , b = 10.5928(16), c = 14.983(2) Å, α = 90, β = 96.273(8), γ = 90, V = 1278.8(3) $Å^3$, Z = 2, Dc = 1.557 g/cc, μ (Mo–Kα) = 1.817 mm-1, 7389 total reflections, 5331 unique reflections, R value 0.0355, wR2 = 0.0875.

Compound 4: Single crystals of **4** were grown by slow evaporation of the solution mixture of ethylacetate and pet.ether. Colorless block crystal of size 0.50 x 0.45 x 0.35 mm^3, was used for data collection, Temperature = 296(2)K, Wave length = 0.71073 Å

Quadrant data acquisition, F(000) = 944, θ range = 2.53 ° to 28.10°, completeness to θ is 100 %, Goodness-of-fit on F2 = 1.082, $C_{17}H_{26}N_4O_6S_2$, M = 446.54. Crystals belong to Orthorhombic, space group P212121, a = 9.5896(2), b = 14.7665(3), c = 14.7848(3) Å, α = β = γ = 90°, V = 2093.60(19) $Å^3$, Z = 4, Dc = 1.417 g/cc, μ (Mo–Kα) = 0.296 mm-1, 2902 total reflections, 2703 unique reflections, R value 0.0346, wR2 = 0.0908.

Compound 5: Single crystals of **5** were grown by slow evaporation of the solution mixture of ethylacetate and pet.ether. Colorless plate crystal of size 0.47 x 0.31 x 0.05 mm^3, was used for data collection, Temperature = 297(2)K, Wave length = 0.71073 Å Quadrant data acquisition, F(000) = 472, θ range = 1.65° to 30°, completeness to θ is 87 %, Goodness-of-fit on F2 = 1.027, $C_{17}H_{26}N_4O_6S_2$, M = 446.54. Crystals belong to Monoclinic, space group P21, a = 7.7425(4), b = 10.0108(6), c = 13.8284(8) Å, α = 90, β = 102.033(3), γ = 90, V = 1048.27(10) $Å^3$, Z = 2, Dc = 1.415 g/cc, μ (Mo–Kα) = 0.296 mm-1, 5303 total reflections, 4805 unique reflections, R value 0.0317, wR2 = 0.0819.

Compound 6: Single crystals of **6** were grown by slow evaporation of the solution mixture of Dichloromethane and methanol. Colorless needle type crystal of approximate size 0.45 x 0.23 x 0.19 mm^3, was used for data collection, Temperature = 296(2) K, Wave length = 0.71073 Å, Quadrant data acquisition, Total scans = 4, F(000) = 952, θ range = 2.56° to 28.31°, Goodness-of-fit on F^2 = 0.988, $C_{19}H_{20}BrN_3O_4S$, M = 466.35. Crystals belong to Orthorhombic, space group P212121, a = 9.2942(10) Å, b = 13.9119(13) Å, c = 15.3096(17) Å, α = β = γ = 90°, V = 1979.5 (4) $Å^3$, Z = 4, Dc = 1.565 g/cc, μ (Mo–Kα) = 0.71073 mm-1, total reflections = 4865, 3065 unique reflections, R value 0.0432, wR_2 = 0.0926.

Compound 7: Single crystals of **7** were grown by slow evaporation of the solution of methanol. Colorless block crystal of approximate size 0.66 x 0.27 x 0.14 mm^3, was used for data collection, Temperature = 297(2) K, Wave length = 0.227 Å, Quadrant data acquisition, F(000) = 348, θ range = 2.69 to 28°, completeness to θ of 28° is 99.3 %, Goodness-of-fit on F^2 = 1.059, $C_{14}H_{20}N_2O_5S$, M = 328.38. Crystals belong to Triclinic, space group P1, a = 7.1146(3) Å, b = 8.0387(3) Å, c = 15.0865(6) Å, α = 90.323(2), β = 100.054(2), γ = 109.252(2) , V = 800.21(6) $Å^3$, Z = 2, Dc = 1.363 g/cc, μ (Mo–Kα) =

0.227 mm-1, 3852 reflections collected, 3360 unique [I>2σ(I)], R value 0.0386, wR_2 = 0.1169.

Table S9: Torsion angle parameters

Comp. No	Torsion angle Parameters								
	Xaa		^{S}Ant			*Yaa*		CSNC dihedral angle	
	φ	ψ	φ	θ	ψ	φ	ψ	ω1	ω2
1	-67.00	146.81	-127.75	8.19	-66.93	-112.56	168.11	155.17	-
2	-86.86	-31.16	-178.38	-1.01	-71.75	-104.28	-19.44	-68.72	66.55
3	-118.80	11.82	167.80	1.25	-69.47	-95.56	-34.47	-58.74	58.78
4	-107.89	6.11	-145.57	-0.51	69.16	-73.91	120.54	-74.22	61.71
5	-67.21	-45.70	166.28	-9.41	-91.78	-116.43	-10.20	-88.43	-74.75
6	-	-	-158.56	-0.69	61.57	86.66	-163.12	-163.29	-
7	-	-	148.56	6.17	-68.56	-72.75	147.82	155.86	-

Table S10: Intra-molecular hydrogen-bonding parameters

Comp. No	Torsion angle Parameters							
	Type of H-bonding	Atoms involved	Distances (Å)		Angles (degree)			Torsion (degree)
			(NH···O)	(N···O)	(NH···O)	(AO···H)	(AO···N)	(AO···NH)
1	C-9	N(2)H(2N)···O(5)	2.216	3.041	160.84	114.46	113.15	76.90
	C-6	N(2)H(2N)···O(3)	2.994	2.964	79.74	75.47	79.78	103.21
2	C-14	N(4)H(4N)···O(6)	2.478	3.110	134.09	120.93	131.40	163.29
	C-6	N(2)H(2N)···O(2)	2.231	2.844	137.57	88.61	83.87	-62.85
3	C-14	N(4)H(4N)···O(6)	2.436	3.226	152.87	137.40	140.69	-121.60
	C-6	N(2)H(2N)···O(2)	2.303	2.891	125.67	84.68	82.00	-78.19
4	C-11	N(3)H(3N)···O(6)	2.292	3.070	150.62	126.63	126.62	-92.91
	C-6	N(2)H(2N)···O(2)S2	2.221	2.855	137.22	93.60	83.66	-23.93
	C-7	N(2)H(2N)···O(2)S1	3.030	3.462	116.87	79.84	87.19	-127.91
5	C-6	N(1)H(1N)···O(2)	2.072	2.717	141.32	102.17	92.23	-13.38
6	C-9	N(1)H(1N)···O(4)	2.21	3.025	158.06	120.18	125.96	-161.98
	C-6	N(1)H(1N)···O(2)	2.67	3.095	77.34	77.07	79.90	-87.28
7	C-9	N(2)H(2N)···O(5)	2.132	2.929	158.17	119.51	122.51	71.03
	C-6	N(2)H(2N)···O(3)	2.741	3.061	104.41	79.62	79.75	89.06

A = S (sulphur) or C (carbon)

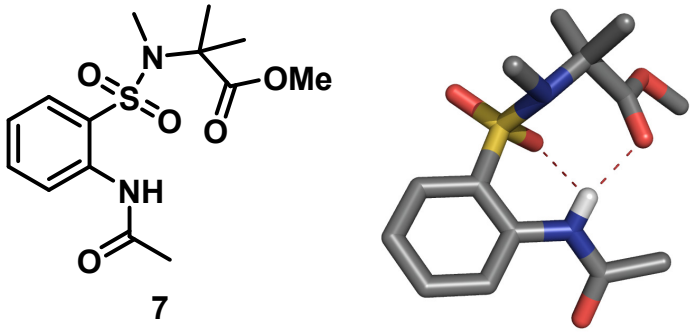
Table S11: Inter-molecular interactions

Co. No	Type of interactions	Atoms involved	Distances (Å)		Angles (degree)	Torsion (degree)
			(DH···A)	(D···A)	(DH···A)	(AO···DH)
1	CH···O	C(5)H(5A)···O(1)	2.664	3.369	129.82	62.02

	CH···O	C(13)H(13)···O(2)	2.648	3.260	120.73	-139.55
	NH···O	N(4)H(4)···O(2)	1.952	2.810	174.33	-162.45
	CH···O	C(16)H(16A)···O(3)	2.542	3.231	127.90	88.84
2	CH···O	C(2)H(2B)···O(4)	2.505	3.269	136.18	133.73
	CH···O	C(21)H(21B)···O(4)	2.702	3.280	119.18	159.62
	CH···O	C(13)H(13B)···O(1)	2.499	3.457	169.53	-143.68
	CH···O	C(10)H(10)···O(2)	2.416	3.300	159.73	-54.28
	CH···O	C(9)H(9)···O(3)	2.622	3.324	132.80	-170.90
3	CH···O	C(24)H(224C)···O(1)	2.302	3.212	158.00	-98.14
	CH···O	C(24)H(24A)···O(5)	2.660	3.614	172.91	-148.73
	CH···O	C(1)H(1A)···O(5)	2.606	3.499	151.67	24.10
	CH···O	C(10)H(10)···O(3)	2.476	3.332	153.26	67.01
	Br···O	Br(1)···O(3)	-	3.236	-	-179.31
	CH···O	C(14)H(14B)···O(4)	2.710	3.514	140.70	-171.54
4	CH···O	C(17)H(17A)···O(1)	2.577	3.495	159.90	29.57
	CH···O	C(17)H(17B)···O(3)	2.367	3.302	164.56	60.17
	CH···O	C(4)H(4B)···O(2)	2.645	3.435	138.78	9.59
	CH···O	C(10)H(10)···O(2)	2.713	3.487	141.27	-14.88
	NH···O	N(4)H(4N)···O(4)	2.173	2.903	140.31	98.60
	CH···O	C(16)H(16B)···O(4)	2.608	3.200	120.17	-140.46
5	CH···O	C(17)H(17C)···O(1)	2.604	3.395	139.86	32.14
	CH···O	C(14)H(14B)···O(5)	2.520	3.242	131.20	-58.02
	CH···O	C(13)H(13B)···O(5)	2.651	3.315	126.00	168.55
	CH···O	C(3)H(3C)···O(6)	2.526	3.318	139.94	-79.83
	NH···O	N(4)H(4N)···O(4)	2.065	2.954	169.76	175.71
	CH···O	C(7)H(7)···O(2)	2.549	3.390	148.78	88.90
	CH···O	C(14)H(14)···O(3)	2.523	3.390	148.78	88.90
6	CH···O	C(19)H(19A)···O(3)	2.538	3.435	155.67	127.96
	CH···O	C(9)H(9A)···O(1)	2.581	3.268	127.89	179.04
	CH···O	C(8)H(8)···O(1)	2.518	3.163	119.92	97.74
	NH···O	N(3)H(3N)···O(1)	2.189	3.010	159.45	-114.93
	CH···O	C(5)H(5)···O(2)	2.599	3.460	154.04	116.74
	CH···O	C(14)H(14)···O(3)	2.588	3.292	132.81	39.70
7	CH···O	C(6)H(6)···O(1)	2.479	3.259	138.71	-139.21
	CH···O	C(11)H(11C)···O(2)	2.611	3.526	159.22	-143.15
	CH···O	C(13)H(13C)···O(2)	2.612	3.517	168.29	23.96
	CH···O	C(8)H(8C)···O(1)	2.709	3.635	159.92	167.22
	CH···O	C(5)H(5)···O(2)	2.599	3.460	154.04	116.74

A = S (sulphur) or C (carbon)
D = N (nitrogen) or C (carbon)

Crystal Structure of 7



7

References

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(2) A. Roy, A. S. Kotmale, R. L. Gawade, V. G. Puranik, P. R. Rajamohanan, G. J. Sanjayan, *RSC Adv.* 2014, **4**, 13018-13025

(3) V. V. E. Ramesh, S. S. Kale, A. S. Kotmale, R. L. Gawade, V. G. Puranik, P. R. Rajamohanan and G. J. Sanjayan, *Org. Lett.*, 2013, **15**, 1504–1507.

(4) Crystal structure was solved by direct method and refined by full matrix least squares on *F*2 for all data using SHELXTL software (SHELX-97)[5]. The hydrogen atom of hydroxy group was located on the difference map and refined isotropically. Other hydrogen atoms were refined in the riding mode. Crystallographic data of **1-7** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1027031-1027037 respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

(5) G. M. Sheldrick, SHELX-97 program for crystal structure solution and refinement, University of Gottingen, Germany, 1997.