

Palladium-Catalysed Aminosulfonylation of Aryl-, Alkenyl- and Heteroaryl Halides: Scope of the Three-Component Synthesis of *N*-Aminosulfonamides

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Electronic Supporting Information

Experimental

General considerations

Chemicals were purchased from Sigma Aldrich, Alfa Aesar, TCI UK or Acros and used without further purification with the exception of DABCO which was sublimed (50 °C, 1 mbar) prior to use. Anhydrous (where stated), HPLC grade solvents were purchased from Sigma Aldrich, Fisher Scientific or Rathburn and used directly without further purification with the exception of 1,4-dioxane which was distilled from calcium hydride onto 4 Å molecular sieves which had been activated by heating under vacuum (0.1 mbar) at >200 °C for 12 hrs. 'Petrol' refers to the fraction of light petroleum ether boiling in the range 40-60 °C. Cesium carbonate was dried prior to use in a vacuum drying pistol (120 °C, 10 mbar) for 18 hrs.

Reactions were performed with continuous magnetic stirring, under an atmosphere of nitrogen, unless otherwise stated, using standard Schlenk techniques and all glassware was dried in an oven (>200 °C, overnight) and allowed to cool under a flow of nitrogen (passed through a Drierite[®] filled tube) prior to use. Flash column chromatography was performed using Apollo scientific silica gel 60 (particle size 0.040-0.063 nm) with the indicated eluents. Thin Layer Chromatography (TLC) analysis was carried out on Merck Kieselgel 60 PF254 pre-coated aluminium backed sheets and visualised either by UV fluorescence (254 nm) and/or by staining with potassium permanganate (KMnO₄).

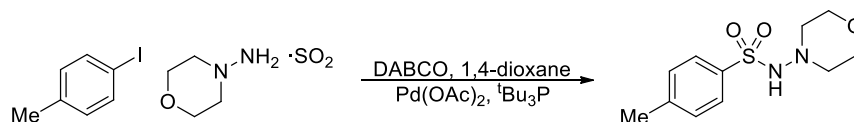
NMR spectra were recorded at ambient temperature on either Brüker DPX200 (200 MHz), DPX400 (400 MHz) or AVC500 (500 MHz) spectrometers. Chemical shifts (δ) are reported in parts per million (ppm) and referenced relative to the residual solvent peak(s) (as specified). Coupling constants (*J*) are given in Hertz (Hz) and rounded to the nearest 0.1 Hz. Assignments were made on the basis of chemical shifts, coupling constants, COSY, HSQC and comparison with spectra of related compounds. Signal multiplicities are denoted as: s, singlet; d, doublet; t, triplet; q, quartet; quin., quintet; m, multiplet; br., broad; app., apparent.

Melting points were measured using a Leica Gallen III hot-stage microscope. Low resolution mass spectra were recorded on a Fisons Platform spectrometer (ESI). High resolution mass spectra were measured by the internal service at the University of Oxford using a Bruker Daltonics microTOF spectrometer. *m/z* ratio values are reported in Daltons; high resolution values are calculated to four decimal places from the molecular formula, all found within a tolerance of 5 ppm. Infrared spectra were determined neat using a Bruker Tensor 27 FT spectrometer with an internal range of 600-4000 cm⁻¹.

Data for compounds not included below can be found in our earlier Communicaiton.¹

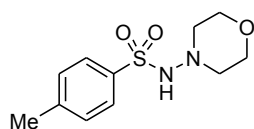
N-Aminosulfonamides

General procedure for the formation of *N*-morpholinosulfonamides using 4-aminomorpholine-sulfur dioxide complex, **8, exemplified by the preparation of 4-methyl-*N*-morpholinobenzenesulfonamide, **4a****



A glass reaction tube was charged with 4-iodotoluene (50 mg, 0.23 mmol), 4-aminomorpholine-sulfur dioxide complex **8** (57 mg, 0.34 mmol), 1,4-diazabicyclo[2.2.2]octane (DABCO) (28 mg, 0.25 mmol), palladium(II) acetate (5 mg, 23 μmol) and tri-*tert*-butylphosphonium tetrafluoroborate (13 mg, 46 μmol) and sealed under N₂. 1,4-Dioxane (1.6 mL) was added and the tube heated at 70 °C with stirring for 16 hrs. After cooling, the reaction mixture was filtered through Celite. The Celite pad was washed sequentially with CH₂Cl₂ (10 mL) and Et₂O (5 mL) and the combined organic extracts concentrated *in vacuo*. Purification by flash column chromatography (50–100% Et₂O in petrol) afforded the *N*-aminosulfonamide **4a** as colourless crystals (54 mg, 92%). Data for all compounds made by this method is either previously reported in our communication¹ or reported below, made by the DABSO method.

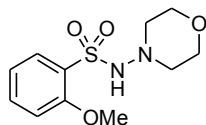
General procedure (A) for the formation of *N*-aminosulfonamides using DABCO·(SO₂)₂ complex, **1 (0.6 equivalents), and DABCO (0.5 equivalents), exemplified by the preparation of 4-methyl-*N*-morpholinobenzenesulfonamide, **4a****



A glass reaction tube was charged with 4-iodotoluene (50 mg, 0.23 mmol), 4-aminomorpholine (33 μl, 0.34 mmol), DABCO·(SO₂)₂ complex **1** (33 mg, 0.14 mmol), 1,4-diazabicyclo[2.2.2]octane (13 mg, 0.11 mmol), palladium(II) acetate (5 mg, 23 μmol) and tri-*tert*-butylphosphonium tetrafluoroborate (13 mg, 46 μmol) and sealed under N₂. 1,4-Dioxane (1.6 mL) was added and the tube heated at 70 °C for 16 hrs. After cooling, the reaction mixture was filtered through Celite. The Celite pad was washed sequentially with CH₂Cl₂ (10 mL) and Et₂O (5 mL) and the combined organic extracts concentrated *in vacuo*. Purification by flash column chromatography (50–100% Et₂O in petrol) afforded the *N*-

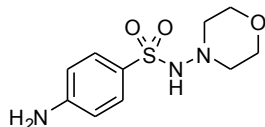
aminosulfonamide 4a as colourless crystals (54 mg, 92%). Data previously reported in communication.¹

General procedure (B) for the formation of *N*-aminosulfonamides using DABCO·(SO₂)₂ complex, **1 (1.1 equivalents), exemplified by the preparation of 2-methoxy-*N*-morpholinobenzenesulfonamide (Table 2, Entry 7)**



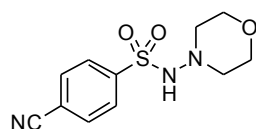
A glass reaction tube was charged with 2-iodoanisole (50 mg, 0.21 mmol), 4-aminomorpholine (31 µl, 0.32 mmol), DABCO·(SO₂)₂ complex **1** (57 mg, 0.24 mmol), palladium(II) acetate (5 mg, 21 µmol) and tri-*tert*-butylphosphonium tetrafluoroborate (12 mg, 42 µmol) and sealed under N₂. 1,4-Dioxane (1.6 mL) was added and the tube heated at 70 °C for 16 hrs. After cooling, the reaction mixture was filtered through Celite. The Celite pad was washed sequentially with CH₂Cl₂ (10 mL) and Et₂O (5 mL) and the combined organic extracts concentrated *in vacuo*. Purification by flash column chromatography (50–100% Et₂O in petrol) afforded the *N*-aminosulfonamide as colourless crystals (44 mg, 76%). Data previously reported in communication.¹

4-Amino-*N*-morpholinobenzenesulfonamide (Table 2, Entry 9)



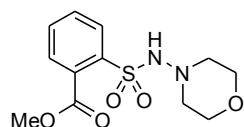
The general procedure A was followed with the use of 4-iodoaniline (50 mg, 0.23 mmol). Flash column chromatography (100% Et₂O) afforded the *N*-aminosulfonamide as colourless crystals (52 mg, 88%); mp 159-160 °C (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.73 (2H, d, *J* 8.6, Ar-*H*), 6.69 (2H, d, *J* 8.6, Ar-*H*), 5.17 (1H, s, NH), 4.16 (2H, br. s, NH₂), 3.62 (4H, t, *J* 4.6, (NCH₂CH₂O)₂), 2.63 (4H, t, *J* 4.6, (NCH₂CH₂O)₂); ¹³C NMR (125 MHz, CDCl₃) δ 150.8, 130.3, 126.6, 113.8, 66.7, 56.8; IR ν_{max} (neat)/cm⁻¹ 3478, 3374, 3148, 1632, 1594, 1501, 1314 (SO₂), 1143 (SO₂), 1099; LRMS (ESI) *m/z* 280 (35%, [M+Na]⁺), 537 (100%, [2M+Na]⁺); HRMS (ESI) found *m/z* 280.0718 [M+Na]⁺, C₂₁H₂₂N₂O₃SNa requires *m/z* 280.0726.

4-Cyano-*N*-morpholinobenzenesulfonamide (Table 2, Entry 11)



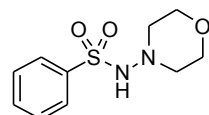
The general procedure B was followed with the use of 4-iodobenzonitrile (50 mg, 0.22 mmol). Flash column chromatography (50–100% Et₂O in petrol) afforded the *N*-aminosulfonamide as colourless crystals (25 mg, 43%); mp 185–186 °C (CH₂Cl₂); ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.24 (1H, s, NH), 8.08 (2H, d, *J* 8.4, Ar-*H*), 8.01 (2H, d, *J* 8.4, Ar-*H*), 3.45 (4H, t, *J* 4.4, (NCH₂CH₂O)₂), 2.50 – 2.47 (4H, m, (NCH₂CH₂O)₂); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 142.9, 132.6, 128.7, 117.2, 116.9, 66.5, 56.9; IR ν_{max} (neat)/cm⁻¹ 3194, 2960, 2923, 2853, 2233 (CN), 1459, 1338 (SO₂), 1264, 1165 (SO₂), 1110, 1090; LRMS (ESI) *m/z* 266 (100%, [M-H]⁻); HRMS (ESI) found *m/z* 266.0610 [M-H]⁻, C₁₁H₁₂N₃O₃S requires 266.0605.

Methyl 2-(*N*-morpholinosulfamoyl)benzoate (Table 2, Entry 13)



The general procedure B was followed with the use of 2-iodomethylbenzoate (50 mg, 0.19 mmol). Flash column chromatography (25–50% EtOAc in petrol) afforded the *N*-aminosulfonamide as a yellow oil (20 mg, 39%). ¹H NMR (500 MHz, CDCl₃) δ 8.22 – 8.20 (1H, m, Ar-*H*), 7.78 – 7.76 (1H, m, Ar-*H*), 7.69 – 7.66 (2H, m, Ar-*H*), 6.77 (1H, s, NH), 3.99 (3H, s, Me), 3.58 (4H, t, *J* 4.5, (NCH₂CH₂O)₂), 2.68 (4H, t, *J* 4.5, (NCH₂CH₂O)₂); ¹³C NMR (125 MHz, CDCl₃) δ 168.3, 137.7, 132.8, 131.6, 131.2, 131.1, 130.1, 66.5, 56.4, 53.5; IR ν_{max} (neat)/cm⁻¹ 3240, 2961, 2855, 1723 (CO), 1436, 1340 (SO₂), 1297, 1263, 1171 (SO₂), 1112, 1061; LRMS (ESI) *m/z* 323 (90%, [M+Na]⁺), 623 (100%, [2M+Na]⁺); HRMS (ESI) found *m/z* 323.0678 [M+Na]⁺, C₁₂H₁₆N₂O₅SNa requires *m/z* 323.0672.

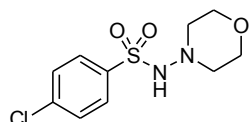
N-Morpholinobenzenesulfonamide (Table 2, Entry 15)



The general procedure B was followed with the use of iodobenzene (50 mg, 0.25 mmol). Flash column chromatography (50–100% Et₂O in hexane) afforded the *N*-aminosulfonamide as colourless crystals (46 mg, 77%); mp 121–122 °C (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ

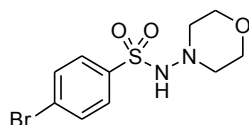
8.00 – 7.97 (2H, m, Ar-*H*), 7.64 – 7.60 (1H, m, Ar-*H*), 7.56 – 7.52 (2H, m, Ar-*H*), 5.43 (1H, s, *NH*), 3.61 (4H, t, *J* 4.5, (NCH₂CH₂O)₂), 2.62 (4H, t, *J* 4.5, (NCH₂CH₂O)₂); ¹³C NMR (125 MHz, CDCl₃) δ 138.6, 133.2, 128.8, 128.1, 66.6, 56.8; IR ν_{max} (neat)/cm⁻¹ 3213, 2963, 2858, 1448, 1362, 1327 (SO₂), 1264, 1164 (SO₂), 1110; LRMS (ESI) *m/z* 265 (60%, [M+Na]⁺), 507 (100%, [2M+Na]⁺); HRMS (ESI) found *m/z* 265.0618 [M+Na]⁺, C₁₀H₁₄N₂O₃SNa requires *m/z* 265.0617.

4-Chloro-*N*-morpholinobenzenesulfonamide (Table 2, Entry 17)



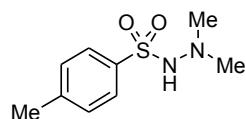
The general procedure B was followed with the use of 1-chloro-4-iodobenzene (50 mg, 0.21 mmol). Flash column chromatography (50–75% Et₂O in petrol) afforded the *N*-aminosulfonamide **XX** as colourless crystals (49 mg, 84%); mp 174–175 °C (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.92 (2H, d, *J* 8.6, Ar-*H*), 7.51 (2H, d, *J* 8.6, Ar-*H*), 5.58 (1H, s, *NH*), 3.62 (4H, t, *J* 4.6, (NCH₂CH₂O)₂), 2.65 (4H, t, *J* 4.6, (NCH₂CH₂O)₂); ¹³C NMR (100 MHz, CDCl₃) δ 139.8, 137.1, 129.6, 129.2, 66.6, 56.8; IR ν_{max} (neat)/cm⁻¹ 3190, 2975, 2856, 1336 (SO₂), 1164 (SO₂), 1111; LRMS (ESI) *m/z* 277, 279 (20%, 10%, [M+H]⁺), 299, 301 (70%, 40%, [M+Na]⁺), 331 (30%, [M+Na+MeOH]⁺), 577 (100%, [2M+Na]⁺); HRMS (ESI) found *m/z* 299.0228, 301.0198 [M+Na]⁺, C₁₀H₁₃ClN₂O₃SNa requires *m/z* 299.0228, 301.0198.

4-Bromo-*N*-morpholinobenzenesulfonamide (Table 2, Entry 18)



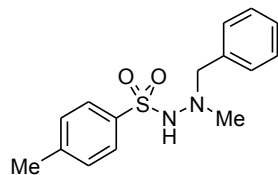
The general procedure B was followed with the use of 1-bromo-4-iodobenzene (65 mg, 0.23 mmol). Flash column chromatography (50–75% Et₂O in petrol) afforded the *N*-aminosulfonamide as colourless crystals (57 mg, 77%); mp 170–171 °C (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.84 (2H, d, *J* 8.6, Ar-*H*), 7.67 (2H, d, *J* 8.6, Ar-*H*), 5.60 (1H, s, *NH*), 3.63 (4H, t, *J* 4.6, (NCH₂CH₂O)₂), 2.65 (4H, t, *J* 4.6, (NCH₂CH₂O)₂); ¹³C NMR (100 MHz, CDCl₃) δ 137.6, 132.2, 129.7, 128.3, 66.6, 56.8; IR ν_{max} (neat)/cm⁻¹ 3195, 2970, 2858, 1338 (SO₂), 1165 (SO₂), 1112; LRMS (ESI) *m/z* 321, 323 (20%, [M+H]⁺), 342, 344 (45%, [M+Na]⁺), 663, 665, 667 (80%, 100%, 90%, [2M+Na]⁺); HRMS (ESI) found *m/z* 342.9729, 344.9706 [M+Na]⁺, C₁₀H₁₃BrN₂O₃SNa requires *m/z* 342.9722, 344.9702.

***N'*,*N'*,4-Trimethylbenzenesulfonohydrazide (Table 3, Entry 4)**



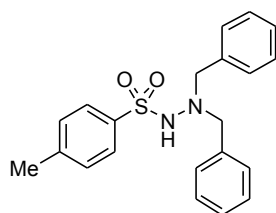
The general procedure A was followed with the use of 1,1-dimethylhydrazine (21 mg, 0.34 mmol). Flash column chromatography (25–50% Et₂O in petrol) afforded the *N*-aminosulfonamide as colourless crystals (32 mg, 65%); mp 76–77 °C (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.84 (2H, d, *J* 8.1, Ar-*H*), 7.32 (2H, d, *J* 8.1, Ar-*H*), 5.14 (1H, br. s, *NH*), 2.45 (3H, s, Ar-*Me*), 2.40 (6H, s, *NMe*₂); ¹³C NMR (100 MHz, CDCl₃) δ 143.8, 135.8, 129.5, 128.2, 48.5, 21.6; IR ν_{max} (neat)/cm⁻¹ 3258, 2919, 1596, 1458, 1394, 1325 (SO₂), 1156 (SO₂), 1092, 1036; LRMS (ESI) *m/z* 237 (70%, [M+Na]⁺), 269 (30%, [M+Na+MeOH]⁺), 451 (100%, [2M+Na]⁺); HRMS (ESI) found *m/z* 237.0670 [M+Na]⁺, C₉H₁₄N₂O₂SNa requires *m/z* 237.0668.

***N'*-Benzyl-*N'*,4-dimethylbenzenesulfonohydrazide (Table 3, Entry 5)**



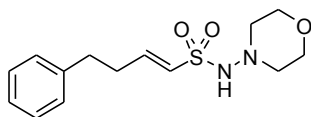
The general procedure A was followed with the use of 1-benzyl-1-methylhydrazine (47 mg, 0.34 mmol). Flash column chromatography (11:8:1 petrol:Et₂O:Et₃N) afforded the *N*-aminosulfonamide as yellow crystals (53 mg, 80%); mp 84–85 °C (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.83 (2H, d, *J* 8.2, Ar-*H*), 7.29 – 7.25 (5H, m, Ar-*H*), 7.16 – 7.14 (2H, m, Ar-*H*), 5.51 (1H, s, *NH*), 3.71 (2H, s, NCH₂Ph), 2.43 (3H, s, Ar-*Me*), 2.32 (3H, s, NHN*Me*); ¹³C NMR (100 MHz, CDCl₃) δ 143.7, 135.7, 135.2, 129.6, 129.4, 128.3, 128.2, 127.7, 64.5, 44.8, 21.6; IR ν_{max} (neat)/cm⁻¹ 3236, 1597, 1493, 1452, 1399, 1328 (SO₂), 1162 (SO₂), 1091; LRMS (ESI) *m/z* 291 (20%, [M+H]⁺), 313 (80%, [M+Na]⁺), 603 (100%, [2M+Na]⁺); HRMS (ESI) found *m/z* 313.0972 [M+Na]⁺, C₁₅H₁₈N₂O₂SNa requires *m/z* 313.0981.

***N',N'*-Dibenzyl-4-methylbenzenesulfonohydrazide (Table 3, Entry 6)**



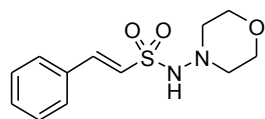
The general procedure A was followed with the use of 4-iodotoluene (350 mg, 1.61 mmol), 1,1-dibenzylhydrazine (511 mg, 2.41 mmol), DABCO-(SO₂)₂ complex (231 mg, 0.96 mmol), DABCO (90 mg, 0.80 mmol), palladium(II) acetate (36 mg, 0.16 mmol), tri-*tert*-butylphosphonium tetrafluoroborate (93 mg, 0.32 mmol) and 1,4-dioxane (11 mL). Flash column chromatography (13:6:1 petrol:Et₂O:Et₃N) afforded the *N*-aminosulfonamide **XX** as pale yellow crystals (499 mg, 85%); mp 123-124 °C (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.72 (2H, d, *J* 8.3, Ar-*H*), 7.28 – 7.26 (6H, m, Ar-*H*), 7.19 – 7.16 (6H, m, Ar-*H*), 5.53 (1H, s, NH), 3.73 (4H, s, N(CH₂Ph)₂), 2.41 (3H, s, Me); ¹³C NMR (100 MHz, CDCl₃) δ 143.6, 135.4, 134.9, 129.8, 129.4, 128.4, 128.2, 127.6, 59.7, 21.6; IR ν_{max} (neat)/cm⁻¹ 3203, 1738, 1598, 1427, 1325 (SO₂), 1157 (SO₂), 1091; LRMS (ESI) *m/z* 367 (80%, [M+H]⁺), 389 (60%, [M+Na]⁺), 755 (100%, [2M+Na]⁺); HRMS (ESI) found *m/z* 389.1280 [M+Na]⁺, C₂₁H₂₂N₂O₂SNa requires *m/z* 389.1294.

(*E*)-*N*-Morpholino-4-phenylbut-1-ene-1-sulfonamide (Table 4, Entry 1)



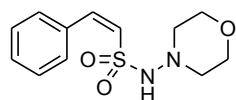
The general procedure B was followed with the use of (*E*)-(4-iodobut-3-enyl)benzene² (50 mg, 0.19 mmol). Flash column chromatography (25–75% Et₂O in petrol) afforded the *N*-aminosulfonamide as colourless crystals (35 mg, 60%); mp 95-97 °C (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.27 (2H, m, Ar-*H*), 7.24 – 7.17 (3H, m, Ar-*H*), 6.92 (1H, dt, *J* 15.2, 6.7, CH₂CHCH), 6.26 (1H, dt, *J* 15.2, 1.5, CH₂CHCH), 5.13 (1H, br. s, NH), 3.67 (4H, t, *J* 4.6, (NCH₂CH₂O)₂), 2.84 (2H, t, *J* 7.4, CCH₂CH₂CH), 2.72 (4H, t, *J* 4.6, (NCH₂CH₂O)₂), 2.67 – 2.59 (2H, m, CCH₂CH₂CH); ¹³C NMR (100 MHz, CDCl₃) δ 146.7, 139.9, 128.6, 128.3, 127.2, 126.4, 66.6, 57.2, 33.7, 32.6; IR ν_{max} (neat)/cm⁻¹ 3210, 3060, 2960, 2856, 2284, 1960, 1714, 1632, 1496, 1361 (SO₂), 1278, 1149 (SO₂), 1072, 1011; LRMS (ESI) *m/z* 297 (20%, [M+H]⁺), 319 (80%, [M+Na]⁺), 615 (100%, [2M+Na]⁺), 911 (10%, [3M+Na]⁺); HRMS (ESI) found *m/z* 319.1091 [M+Na]⁺, C₁₄H₂₀N₂O₃SNa requires *m/z* 319.1087.

(E)-N-Morpholino-2-phenylethanesulfonamide (Table 4, Entry 3)



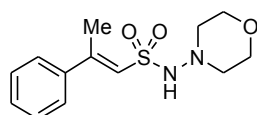
The general procedure B was followed with the use of (*E*)-(2-iodovinyl)benzene³ (50 mg, 0.22 mmol). Flash column chromatography (25–75% Et₂O in petrol) afforded the *N*-aminosulfonamide as colourless crystals (31 mg, 53%); mp 159–161 °C (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.62 (1H, d, *J* 15.5, CHCHSO₂), 7.56 – 7.40 (5H, m, Ar-*H*), 6.81 (1H, d, *J* 15.5, CHCHSO₂), 5.31 (1H, br. s, NH), 3.73 (4H, t, *J* 4.6, (NCH₂CH₂O)₂), 2.88 (4H, t, *J* 4.6, (NCH₂CH₂O)₂); ¹³C NMR (100 MHz, CDCl₃) δ 143.7, 132.5, 131.1, 129.2, 128.3, 123.5, 66.6, 57.4; IR ν_{max} (neat)/cm⁻¹ 3175, 2851, 1457, 1370, 1327 (SO₂), 1263, 1137 (SO₂), 1108; LRMS (ESI) *m/z* 269 (15%, [M+H]⁺), 291 (55%, [M+Na]⁺), 323 (15%, [M+Na+MeOH]⁺), 559 (100%, [2M+Na]⁺), 827 (20%, [3M+Na]⁺); HRMS (ESI) found *m/z* 291.0772 [M+Na]⁺, C₉H₁₄N₂O₂SNa requires *m/z* 291.0774.

(Z)-N-Morpholino-2-phenylethanesulfonamide (Table 4, Entry 4)



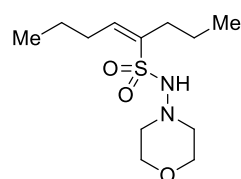
The general procedure B was followed with the use of (*Z*)-(2-iodovinyl)benzene³ (>20:1, *Z*:*E*) (50 mg, 0.22 mmol). Flash column chromatography (25–75% Et₂O in petrol) afforded an inseparable mixture (3.5:1, *Z*:*E*) of *Z* *N*-aminosulfonamide and *E* *N*-aminosulfonamide as a yellow oil (30 mg, 51%); ¹H NMR (400 MHz, CDCl₃) δ 7.77 – 7.72 (2H, m, Ar-*H*, *Z*), 7.62 (0.3H, d, *J* 15.5, CHCHSO₂, *E*), 7.54 – 7.33 (4.5H, m, Ar-*H*, *Z* and *E*), 7.09 (1H, d, *J* 12.2, CHCHSO₂, *Z*), 6.81 (0.3H, d, *J* 15.5, CHCHSO₂, *E*), 6.48 (1H, d, *J* 12.2, CHCHSO₂, *Z*), 5.51 (0.3H, s, NH, *E*), 5.48 (1H, s, NH, *Z*), 3.75 – 3.65 (5.2H, m, (NCH₂CH₂O)₂, *Z* and *E*), 2.87 (1.2H, t, *J* 4.6, (NCH₂CH₂O)₂, *E*), 2.78 (4H, t, *J* 4.5, (NCH₂CH₂O)₂, *Z*); ¹³C NMR (100 MHz, CDCl₃) δ 143.7 (*E*), 141.3 (*Z*), 132.5 (*E*), 131.1 (*E*), 130.4 (*Z*), 130.1 (*Z*), 129.2 (*E*), 128.3 (*E* and *Z*) (2H), 126.9 (*Z*), 123.5 (*E* and *Z*) (2H), 66.6 (*E*), 66.5 (*Z*), 57.4 (*E*), 57.1 (*Z*); LRMS (ESI) *m/z* 269 (15%, [M+H]⁺), 291 (55%, [M+Na]⁺), 323 (15%, [M+Na+MeOH]⁺), 559 (100%, [2M+Na]⁺), 827 (20%, [3M+Na]⁺); HRMS (ESI) found *m/z* 291.0772 [M+Na]⁺, C₉H₁₄N₂O₂SNa requires *m/z* 291.0774.

(E)-N-Morpholino-2-phenylprop-1-ene-1-sulfonamide (Table 4, Entry 6)



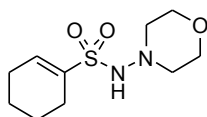
The general procedure B was followed with the use of (*E*)-(1-iodoprop-1-en-2-yl)benzene³ (50 mg, 0.20 mmol). Flash column chromatography (25–75% Et₂O in petrol) afforded the *N*-aminosulfonamide as colourless crystals (50 mg, 86%); mp 117–118 °C (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.46 – 7.40 (5H, m, Ar-*H*), 6.54 (1H, d, *J* 1.2, *CH*), 5.43 (1H, s, *NH*), 3.75 (4H, t, *J* 4.5, (NCH₂CH₂O)₂), 2.89 (4H, t, *J* 4.5, (NCH₂CH₂O)₂), 2.59 (3H, d, *J* 1.2, *Me*); ¹³C NMR (100 MHz, CDCl₃) δ 154.0, 140.3, 129.8, 128.8, 126.3, 124.1, 66.7, 57.3, 17.9; IR ν_{max} (neat)/cm⁻¹ 3226, 2830, 1608, 1309 (SO₂), 1263, 1140 (SO₂), 1106; LRMS (ESI) *m/z* 283 (10%, [M+H]⁺), 305 (15%, [M+Na]⁺), 587 (100%, [2M+Na]⁺), 869 (30%, [3M+Na]⁺); HRMS (ESI) found *m/z* 305.0928 [M+Na]⁺, C₁₃H₁₈N₂O₃SNa requires *m/z* 305.0930.

(Z)-N-Morpholinooct-4-ene-4-sulfonamide (Table 4, Entry 7)



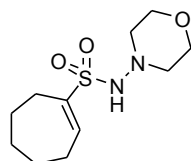
The general procedure B was followed with the use of (*Z*)-4-iodooct-4-ene⁴ (50 mg, 0.21 mmol). Flash column chromatography (25–75% Et₂O in petrol) afforded the *N*-aminosulfonamide as colourless crystals (33 mg, 57%); mp 73–75 °C (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 6.78 (1H, t, *J* 7.6, *CH*), 5.09 (1H, br. s, *NH*), 3.70 (4H, t, *J* 4.5, (NCH₂CH₂O)₂), 2.81 (4H, t, *J* 4.5 (NCH₂CH₂O)₂), 2.34 (2H, app. t, *J* 8.0, CHCCH₂), 2.21 (2H, app. q, *J* 7.4, CH₂CHCCH₂), 1.67 – 1.46 (4H, m, 2 x CH₂), 1.00 – 0.94 (6H, m, 2 x *Me*); ¹³C NMR (100 MHz, CDCl₃) δ 144.2, 137.7, 66.7, 57.3, 30.5, 29.0, 22.8, 21.8, 14.1, 13.8; IR ν_{max} (neat)/cm⁻¹ 3205, 2957, 2872, 1455, 1323 (SO₂), 1279, 1170, 1138 (SO₂), 1108, 1074; LRMS (ESI) *m/z* 277 (25%, [M+H]⁺), 299 (85%, [M+Na]⁺), 331 (20%, [M+Na+MeOH]⁺), 575 (100%, [2M+Na]⁺), 851 (15%, [3M+Na]⁺); HRMS (ESI) found *m/z* 299.1400 [M+Na]⁺, C₁₂H₂₄N₂O₃SNa requires *m/z* 299.1400.

***N*-Morpholinocyclohex-1-ene-1-sulfonamide (Table 4, Entry 8)**



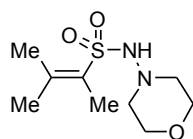
The general procedure B was followed with the use of 1-iodocyclohex-1-ene³ (50 mg, 0.24 mmol). Flash column chromatography (25–75% Et₂O in petrol) afforded the *N*-aminosulfonamide as colourless crystals (47 mg, 79%); mp 120–122 °C (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 6.98 – 6.94 (1H, m, CH), 5.13 (1H, br. s, NH), 3.72 (4H, t, *J* 4.6, (NCH₂CH₂O)₂), 2.82 (4H, t, *J* 4.6, (NCH₂CH₂O)₂), 2.40 – 2.34 (2H, m, CH₂), 2.32 – 2.25 (2H, m, CH₂), 1.76 – 1.69 (2H, m, CH₂), 1.67 – 1.60 (2H, m, CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 140.2, 136.5, 66.6, 57.3, 25.5, 23.7, 22.1, 20.9; IR ν_{max} (neat)/cm⁻¹ 3196, 1438, 1319 (SO₂), 1263, 1143 (SO₂), 1108, 1052; LRMS (ESI) *m/z* 247 (10%, [M+H]⁺), 269 (85%, [M+Na]⁺), 301 (25%, [M+Na+MeOH]⁺), 515 (100%, [2M+Na]⁺), 761 (10%, [3M+Na]⁺); HRMS (ESI) found *m/z* 269.0930 [M+Na]⁺, C₁₀H₁₈N₂O₃SNa requires *m/z* 269.0930.

***N*-Morpholinocyclohept-1-ene-1-sulfonamide (Table 4, Entry 9)**



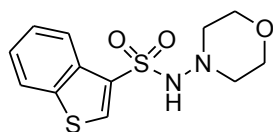
The general procedure B was followed with the use of 1-iodocyclohept-1-ene² (50 mg, 0.23 mmol). Flash column chromatography (25–75% Et₂O in petrol) afforded the *N*-aminosulfonamide as colourless crystals (52 mg, 89%); mp 109–110 °C (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.16 (1H, t, *J* 6.5, CH), 5.09 (1H, br. s, NH), 3.73 (4H, t, *J* 4.6, (NCH₂CH₂O)₂), 2.84 (4H, t, *J* 4.6, (NCH₂CH₂O)₂), 2.58 – 2.54 (2H, m, CH₂), 2.40 – 2.34 (2H, m, CH₂), 1.83 – 1.77 (2H, m, CH₂), 1.66 – 1.56 (4H, m, 2 x CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 144.8, 141.3, 66.6, 57.6, 31.4, 28.6, 28.0, 26.5, 25.5; IR ν_{max} (neat)/cm⁻¹ 3168, 2919, 2849, 1645, 1455, 1299 (SO₂), 1157, 1140 (SO₂), 1114; LRMS (ESI) *m/z* 261 (15%, [M+H]⁺), 283 (45%, [M+Na]⁺), 543 (100%, [2M+Na]⁺), 803 (25%, [3M+Na]⁺); HRMS (ESI) found *m/z* 283.1088 [M+Na]⁺, C₁₁H₂₀N₂O₃SNa requires *m/z* 283.1087.

3-Methyl-*N*-morpholinobut-2-ene-2-sulfonamide (Table 4, Entry 10)



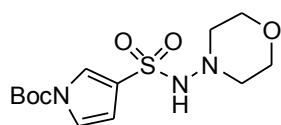
The general procedure B was followed with the use of 2-iodo-3-methylbut-2-ene⁵ (50 mg, 0.26 mmol). Flash column chromatography (25–75% Et₂O in petrol) afforded the *N*-aminosulfonamide as colourless crystals (43 mg, 72%); mp 132–133 °C (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 5.26 (1H, br. s, NH), 3.71 (4H, t, *J* 4.6, (NCH₂CH₂O)₂), 2.81 (4H, t, *J* 4.6, (NCH₂CH₂O)₂), 2.25 (3H, app. d, *J* 2.7, MeCSO₂), 2.07 (3H, app. t, *J* 1.0, MeCCSO₂), 1.92 (3H, app. d, *J* 0.8, MeCCSO₂); ¹³C NMR (100 MHz, CDCl₃) δ 147.4, 128.8, 66.8, 57.0, 24.3, 22.8, 16.6; IR ν_{max} (neat)/cm⁻¹ 3174, 2960, 2920, 2863, 1653, 1457, 1319 (SO₂), 1260, 1151 (SO₂), 1106; LRMS (ESI) *m/z* 235 (5%, [M+H]⁺), 257 (80%, [M+Na]⁺), 289 (30%, [M+Na+MeOH]⁺), 491 (100%, [2M+Na]⁺); HRMS (ESI) found *m/z* 257.0932 [M+Na]⁺, C₉H₁₈N₂O₃Na requires *m/z* 257.0930.

N-(Morpholin-4-yl)-1-benzothiophene-3-sulfonamide (Table 5, Entry 2)



The general procedure B was followed with the use of 3-iodo-1-benzothiophene⁵ (62 mg, 0.24 mmol). Flash chromatography (25—100% Et₂O in petrol) afforded the *N*-aminosulfonamide as a white solid (53 mg, 73%); mp 142–144 °C (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 8.38 (1H, s, C=CHS), 8.37–8.32 (1H, m, Ar-*H*), 7.95–7.88 (1H, m, Ar-*H*), 7.57–7.44 (2H, m, 2 × Ar-*H*), 5.68 (1H, s, NH), 3.55 (4H, app t, *J* 4.5, N(CH₂CH₂)₂O), 2.60 (4H, app t, *J* 4.5, N(CH₂CH₂)₂O); ¹³C NMR (100 MHz, CDCl₃) δ 140.1, 136.2, 133.8, 132.3, 125.8, 125.7, 123.8, 122.9, 66.5, 56.9; IR ν_{max} (neat)/cm⁻¹ 3242, 2963, 2857, 2361, 1336 (SO₂), 1158 (SO₂); LRMS (ESI⁺) *m/z* 619 (100%, [2M + Na]⁺) 321 (69%, [M + Na]⁺); HRMS (ESI⁺) found *m/z* 321.0335 [M + Na]⁺, C₁₂H₁₄N₂NaO₃S₂⁺ requires *m/z* 321.0344.

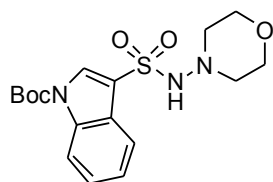
tert-Butyl 3-(morpholin-4-ylsulfamoyl)-1*H*-pyrrole-1-carboxylate (Table 5, Entry 3)



The general procedure B was followed with the use of *tert*-butyl 3-iodo-pyrrole-1-carboxylate⁶ (70 mg, 0.24 mmol). Flash chromatography (25—100% Et₂O in petrol) afforded

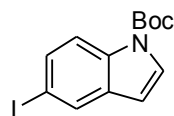
the *N*-aminosulfonamide as a white solid (16 mg, 20%); mp 130-132 °C (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.84-7.81 (1H, m, C=CHN), 7.30-7.28 (1H, m, CH=CHN), 6.55 (1H, dd, *J* 3.5, 2.0, CH=CHN), 5.47 (1H, s, NH), 3.68 (4H, app t, *J* 4.5, N(CH₂CH₂)₂O), 2.75 (4H, app t, *J* 4.5, N(CH₂CH₂)₂O), 1.63 (9H, s, Me); ¹³C NMR (100 MHz, CDCl₃) δ 147.5, 125.3, 124.2, 121.5, 110.5, 86.0, 66.6, 57.0, 27.9; IR ν_{max} (neat)/cm⁻¹ 3227, 2979, 2925, 2857, 1755 (CO), 1334 (SO₂), 1154 (SO₂); LRMS (ESI⁺) *m/z* 686 (100%, [2M + Na]⁺); HRMS (ESI⁺) found *m/z* 354.1094 [M + Na]⁺, C₁₃H₂₁N₃NaO₅S⁺ requires *m/z* 354.1095.

***tert*-Butyl 3-(morpholin-4-ylsulfamoyl)-1*H*-indole-1-carboxylate (Table 5, Entry 4)**



The general procedure B was followed with the use of *tert*-butyl 3-iodo-1*H*-indole-1-carboxylate⁷ (92 mg, 0.24 mmol). Flash chromatography (25—100% Et₂O in petrol) afforded the *N*-aminosulfonamide as a white solid (44 mg, 48%); mp 149-153 °C (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 8.24 (1H, s, C=CHN) overlapping 8.23 (1H, app d, *J* 9.5, Ar-*H*), 8.02-7.95 (1H, m, Ar-*H*), 7.48-7.35 (2H, m, 2 × Ar-*H*), 5.71 (1H, s, NH), 3.60 (4H, app t, *J* 4.5, N(CH₂CH₂)₂O), 2.69 (4H, app t, *J* 4.5, N(CH₂CH₂)₂O), 1.70 (9H, s, Me); ¹³C NMR (100 MHz, CDCl₃) δ 148.5, 135.5, 131.3, 126.0, 125.1, 124.2, 120.7, 118.7, 115.5, 85.8, 66.5, 57.0, 28.1; IR ν_{max} (neat)/cm⁻¹ 3161, 2976, 2957, 2360, 1748 (CO), 1341 (SO₂), 1146 (SO₂); LRMS (ESI⁺) *m/z* 785 (100%, [2M + Na]⁺), 404 (48%, [M + Na]⁺), 382 (18%, [M + H]⁺); HRMS (ESI⁺) found *m/z* 404.1244 [M + Na]⁺, C₁₇H₂₃N₃NaO₅S⁺ requires *m/z* 404.1251.

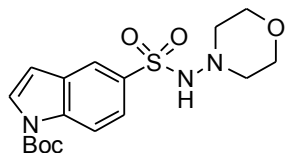
***tert*-Butyl 5-iodo-1*H*-indole-1-carboxylate**



Di-*tert*-butyldicarbonate (1.55 g, 7.11 mmol), NEt₃ (2.7 mL, 19.4 mmol) and 4-dimethylaminopyridine (79 mg, 0.65 mmol) were added to a solution of 5-iodoindole (1.57 g, 6.46 mmol) in CH₂Cl₂ (30 mL). The reaction mixture was stirred at rt for 1 h and then washed twice with sodium metabisulphite (5% aq solution), dried over MgSO₄, filtered and concentrated *in vacuo*. Flash chromatography (5% ethyl acetate in petrol) afforded the titled *iodide* as a light orange solid (1.41 g, 63%); mp 45-46 °C (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.93 (1H, d, *J* 8.5, Ar*H*) overlapping 7.90 (1H, d, *J* 2.0, Ar*H*), 7.59 (1H, dd, *J* 8.5,

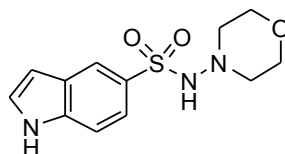
2.0, ArH) overlapping 7.56 (1H, d, J 3.5, CH=CHN), 6.49 (1H, d, J 3.5, CH=CHN), 1.68 (9H, s, $3 \times$ Me); ^{13}C NMR (100 MHz, CDCl_3) δ 149.4, 134.5, 132.9, 132.6, 129.7, 126.7, 117.0, 106.2, 86.7, 84.1, 28.2; IR ν_{max} (neat)/ cm^{-1} 3115, 2979, 2933, 1731 (CO); m/z (FI^+) $\text{C}_{13}\text{H}_{14}\text{INO}_2^+$ ($[\text{M}]^+$) requires 343.0096; found 343.0092.

***tert*-Butyl 5-(morpholin-4-ylsulfamoyl)-1*H*-indole-1-carboxylate (Table 5, Entry 5)**



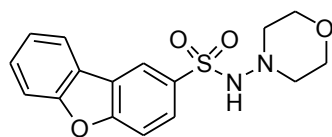
The general procedure B was followed with the use of *tert*-butyl 5-iodo-1*H*-indole-1-carboxylate (82 mg, 0.24 mmol). Flash chromatography (25—100% Et_2O in petrol) afforded the *N*-aminosulfonamide as an off-white solid (75 mg, 81%); mp 167-170 °C (CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3) δ 8.30 (1H, app d, J 9.0, Ar-*H*), 8.23 (1H, app d, J 1.5, Ar-*H*), 7.90 (1H, app dd, J 9.0, 1.5, Ar-*H*), 7.72 (1H, d, J 3.5, CH=CHN), 6.69 (1H, d, J 3.5, CH=CHN), 5.56 (1H, s, NH), 3.58 (4H, app t, J 4.5, $\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}$), 2.61 (4H, app t, J 4.5, $\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}$), 1.69 (9H, s, Me); ^{13}C NMR (100 MHz, CDCl_3) δ 149.1, 137.5, 132.6, 130.2, 128.1, 123.6, 122.0, 115.4, 107.5, 84.8, 66.6, 56.7, 28.1; IR ν_{max} (neat)/ cm^{-1} 3211, 2977, 2858, 1740 (CO), 1335 (SO_2), 1156 (SO_2); LRMS (ESI^-) m/z 380 (100%, $[\text{M} - \text{H}]^-$); HRMS (ESI^+) found m/z 404.1245 $[\text{M} + \text{Na}]^+$, $\text{C}_{17}\text{H}_{23}\text{N}_3\text{NaO}_5\text{S}^+$ requires m/z 404.1251.

1*H*-indole-5-sulfonamide, *N*-4-morpholinyl (Table 5, Entry 6)



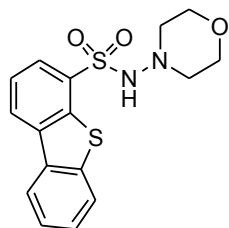
The general procedure B was followed with the use of 5-iodo-1*H*-indole (58 mg, 0.24 mmol). Flash chromatography (25—100% Et_2O in petrol) afforded the *N*-aminosulfonamide as a white solid (50 mg, 74%); mp 143-145 °C (CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3) δ 8.48 (1H, br. s, N(indole)*H*), 8.33 (1H, app br. d, J 1.0, Ar-*H*), 7.79 (1H, app dd, J 8.5, 1.0, Ar-*H*), 7.49 (1H, app d, J 8.5, Ar-*H*), 7.37 (1H, app t, J 3.0, CH=CHN), 6.71 (1H, app dt, J 3.0, 1.0, CH=CHN), 5.25 (1H, br. s, NH), 3.59 (4H, app t, J 4.5, $\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}$), 2.59 (4H, app t, J 4.5, $\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}$); ^{13}C NMR (100 MHz, CDCl_3) δ 138.0, 129.3, 127.3, 126.7, 122.4, 121.2, 111.5, 104.0, 66.6, 56.7; IR ν_{max} (neat)/ cm^{-1} 3356, 3224, 2858, 1326 (SO_2), 1151 (SO_2); LRMS (ESI^-) m/z 280 (100%, $[\text{M} - \text{H}]^-$); HRMS (ESI^+) found m/z 304.0725 $[\text{M} + \text{Na}]^+$, $\text{C}_{12}\text{H}_{15}\text{N}_3\text{NaO}_3\text{S}^+$ requires m/z 304.0726.

***N*-(Morpholin-4-yl)dibenzo[*b,d*]furan-2-sulfonamide (Table 5, Entry 7)**



The general procedure B was followed with the use of 3-iododibenzofuran (71 mg, 0.24 mmol). Flash chromatography (25—100% Et₂O in petrol) afforded the *N*-aminosulfonamide as a white solid (71 mg, 89%); mp 197-199 °C (decomp.) (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 8.63 (1H, app d, *J* 2.0, Ar-*H*), 8.10 (1H, app dd, *J* 8.5, 2.0, Ar-*H*), 8.05-8.00 (1H, m, Ar-*H*), 7.69 (1H, app d, *J* 8.5, Ar-*H*), 7.67-7.62 (1H, m, Ar-*H*), 7.57 (1H, app td, *J* 7.5, 1.5, Ar-*H*), 7.44 (1H, app t, *J* 7.5, Ar-*H*), 5.50 (1H, s, NH), 3.60 (4H, app t, *J* 4.5, N(CH₂CH₂)₂O), 2.65 (4H, app t, *J* 4.5, N(CH₂CH₂)₂O); ¹³C NMR (100 MHz, CDCl₃) δ 158.4, 157.0, 133.1, 128.6, 127.2, 124.8, 123.8, 123.1, 121.7, 121.2, 112.10, 112.08, 66.6, 56.8; IR ν_{max} (neat)/cm⁻¹ 3196, 2962, 2917, 2859, 1324 (SO₂), 1159 (SO₂); LRMS (ESI⁺) *m/z* 687 (100%, [2M + Na]⁺), 355 (77%, [M + Na]⁺); HRMS (ESI⁺) found *m/z* 355.0707 [M + Na]⁺, C₁₆H₁₆N₂NaO₄S⁺ requires *m/z* 355.0723.

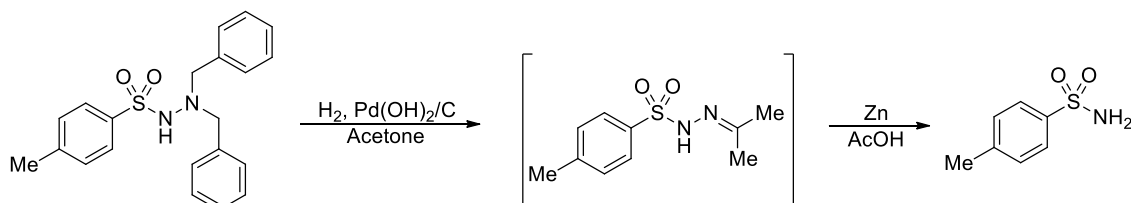
***N*-(Morpholin-4-yl)dibenzo[*b,d*]thiophene-4-sulfonamide (Table 5, Entry 8)**



The general procedure B was followed with the use of 4-iododibenzothiophene (74 mg, 0.24 mmol). Flash chromatography (25—100% Et₂O in petrol) afforded the *N*-aminosulfonamide **XX** as a white solid (77 mg, 92%); mp 169-172 °C (CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 8.40 (1H, app dd, *J* 8.0, 1.0, Ar-*H*), 8.23-8.19 (1H, m, Ar-*H*), 8.17 (1H, app dd, *J* 7.5, 1.0, Ar-*H*), 7.95-7.91 (1H, m, Ar-*H*), 7.64 (1H, app t, *J* 7.5, Ar-*H*), 7.60-7.51 (2H, m, Ar-*H*), 5.70 (1H, s, NH), 3.51 (4H, app t, *J* 4.5, N(CH₂CH₂)₂O), 2.54 (4H, app t, *J* 4.5, N(CH₂CH₂)₂O); ¹³C NMR (125 MHz, CDCl₃) δ 140.1, 137.6(4), 137.6(0), 134.0, 132.3, 128.7, 127.9, 126.0, 125.0, 124.3, 122.7, 121.8, 66.5, 56.7; IR ν_{max} (neat)/cm⁻¹ 3218, 2964, 2922, 2858, 1335 (SO₂), 1142 (SO₂); LRMS (ESI⁻) *m/z* 347 (100%, [M - H]⁻); HRMS (ESI⁺) found *m/z* 371.0490 [M + Na]⁺, C₁₆H₁₆N₂NaO₃S₂⁺ requires *m/z* 371.0495.

N-N Bond Cleavage

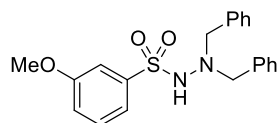
General procedure (C) for the formation of unsubstituted sulfonamides from the corresponding dibenzyl-*N*-aminosulfonamide, exemplified by the preparation of tosylamine



A glass reaction tube was charged with recrystallised *N*',*N*'-dibenzyl-4-methylbenzenesulfonohydrazide **4b** (293 mg, 0.80 mmol) and Pearlman's catalyst ($\text{Pd}(\text{OH})_2$ on carbon, 20 wt% Pd, ~60% moisture, 140 mg, 0.08 mmol). Acetone (2 mL) was added and the reaction mixture degassed with N_2 . The tube was flushed with H_2 gas and left stirring under a balloon of H_2 atmosphere for 16 hrs. The reaction flask was purged with N_2 , the suspension filtered through Celite and the Celite pad washed with CH_2Cl_2 (5 mL). The filtrate was concentrated *in vacuo* affording *tosyl hydrazone 9* (180 mg, 100%) as analytically pure white crystals; ^1H NMR (400 MHz, CDCl_3) δ 7.85 (2H, d, J 8.0, Ar-*H*), 7.31 (2H, d, J 8.0, Ar-*H*), 2.43 (3H, s, Ar-*Me*), 1.94 (3H, s, NC*Me*), 1.80 (3H, s, NC*Me*); ^{13}C NMR (100 MHz, CDCl_3) δ 156.2, 144.0, 135.4, 129.5, 128.0, 25.3, 21.6, 16.8; IR ν_{max} (neat)/ cm^{-1} 3225, 1655, 1597, 1389, 1330 (SO_2), 1158 (SO_2), 1086; LRMS (ESI) m/z 227 (65%, $[\text{M}+\text{H}]^+$), 249 (95%, $[\text{M}+\text{Na}]^+$), 281 (40%, $[\text{M}+\text{Na}+\text{MeOH}]^+$), 475 (100%, $[\text{2M}+\text{Na}]^+$); HRMS (ESI) found m/z 249.0668 $[\text{M}+\text{Na}]^+$, $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_2\text{SNa}$ requires m/z 249.0668.

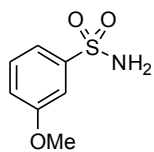
The *N-N* bond cleavage was carried out in accordance with a similar literature procedure.⁸ The crude sulfonyl hydrazone (180 mg, 0.80 mmol) was dissolved in acetic acid (5 mL) and zinc dust (1.31 g, 25 mmol) added under N_2 . The resulting suspension was stirred at 25 °C for 1 hr. CH_2Cl_2 (10 mL) was added to the reaction mixture, sonicated for 1 min and filtered through Celite, the zinc residue being washed with further CH_2Cl_2 (5 mL). The organic solution was washed with water (10 mL) and brine (10 mL), dried over MgSO_4 , filtered and concentrated *in vacuo* affording analytically pure tosyl amine **10a** (114 mg, 83%); ^1H NMR (400 MHz, CDCl_3) δ 7.82 (2H, d, J 8.3, Ar-*H*), 7.31 (2H, d, J 8.3, Ar-*H*), 4.95 (2H, br. s, NH_2), 2.44 (3H, s, *Me*); ^{13}C NMR (100 MHz, CDCl_3) δ 143.6, 139.0, 129.7, 126.4, 21.5; LRMS (ESI) m/z 194 (100%, $[\text{M}+\text{Na}]^+$), 226 (80%, $[\text{M}+\text{Na}+\text{MeOH}]^+$). Data was consistent with a commercially available sample.

N,N'-Dibenzyl-3-methoxybenzenesulfonohydrazide (Scheme 4)



The general procedure B was followed with the use of 3-iodoanisole (350 mg, 1.50 mmol) and 1,1-dibenzylhydrazine (476 mg, 2.24 mmol). Flash column chromatography (11:8:1 petrol:Et₂O:Et₃N) afforded the *N*-aminosulfonamide as a pale yellow oil (450 mg, 79%); ¹H NMR (400 MHz, CDCl₃) δ 7.48 (1H, d, *J* 7.7, Ar-*H*), 7.34 – 7.25 (8H, m, Ar-*H*), 7.20 – 7.18 (4H, m, Ar-*H*), 7.04 (1H, dd, *J* 8.2, 2.1, Ar-*H*), 5.59 (1H, s, NH), 3.80 (3H, s, OMe), 3.75 (4H, s, N(CH₂Ph)₂); ¹³C NMR (100 MHz, CDCl₃) δ 159.5, 139.5, 134.9, 129.7, 129.6, 128.4, 127.7, 120.6, 119.7, 112.4, 59.9, 55.4; IR ν_{max} (neat)/cm⁻¹ 1598, 1478, 1315 (SO₂), 1240, 1150 (SO₂), 1022; LRMS (ESI) *m/z* 405 (15%, [M+Na]⁺), 787 (100%, [2M+Na]⁺); HRMS (ESI) found *m/z* 405.1227 [M+Na]⁺, C₂₁H₂₂N₂O₃SNa requires *m/z* 405.1243.

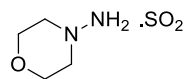
3-Methoxybenzenesulfonamide (10b, Scheme 4)



The general procedure C was followed using re-crystallised *N,N'*-dibenzyl-3-methoxybenzenesulfonohydrazide (120 mg, 0.31 mmol) to first afford the *hydrazone* as a white solid; ¹H NMR (200 MHz, CDCl₃) δ 7.57 – 7.38 (3H, m, Ar-*H*), 7.16 – 7.10 (1H, m, Ar-*H*), 3.87 (3H, s, OMe), 1.96 (3H, s, NCM₂), 1.80 (3H, s, NCM₂); LRMS (ESI) *m/z* 210 (100%, [M+Na]⁺). Zinc in acetic acid reduction afforded unsubstituted sulfonamide **10b** as colourless crystals (46 mg, 80%); ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.48 (1H, t, *J* 7.9, Ar-*H*), 7.41 – 7.35 (4H, m, Ar-*H* incl. NH₂), 7.16 (1H, dd, *J* 8.2, 2.4, Ar-*H*), 3.82 (3H, s, OMe); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 159.2, 145.4, 130.1, 117.6 (2C), 110.8, 55.5; LRMS (ESI) *m/z* 186 (100%, [M-H]⁻). HRMS (ESI) *m/z* 210.0192 [M+Na]⁺, C₇H₉NO₃SNa requires 210.0195. Data consistent with literature.⁹

Sulfur dioxide complexes

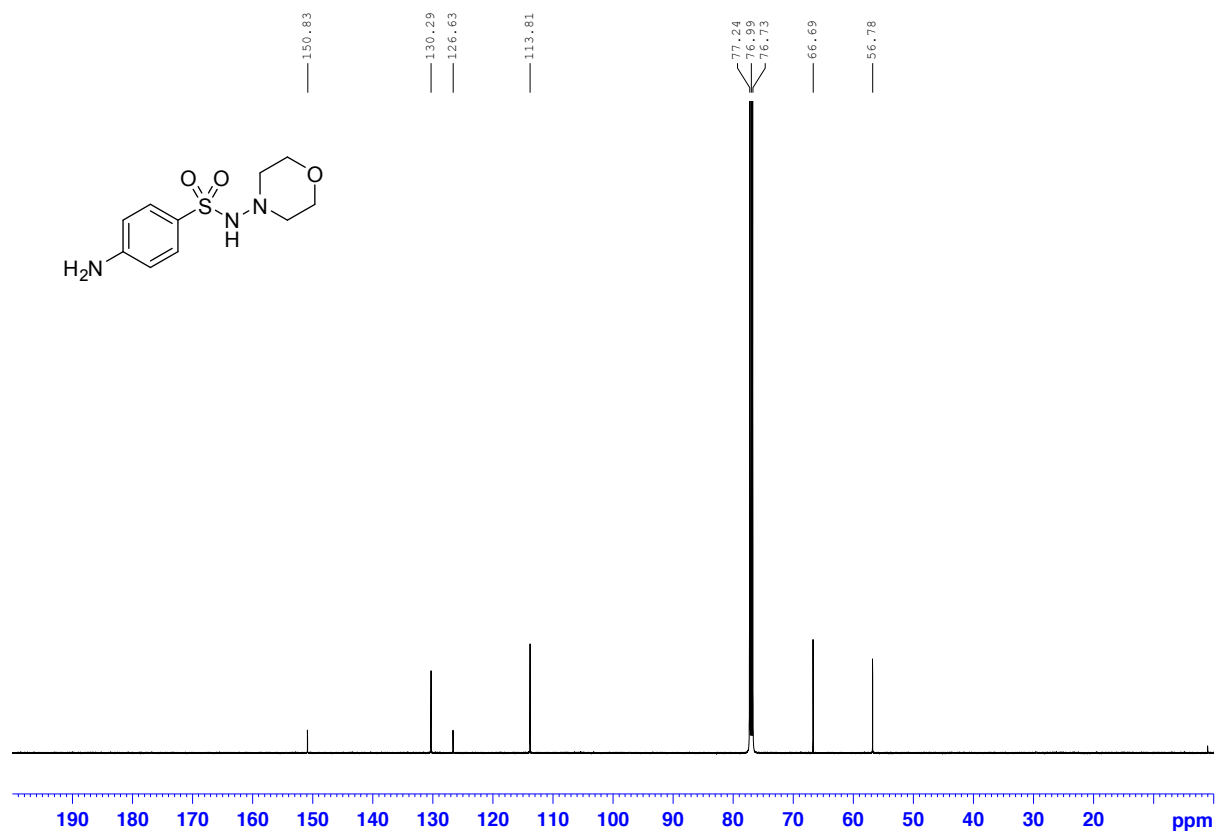
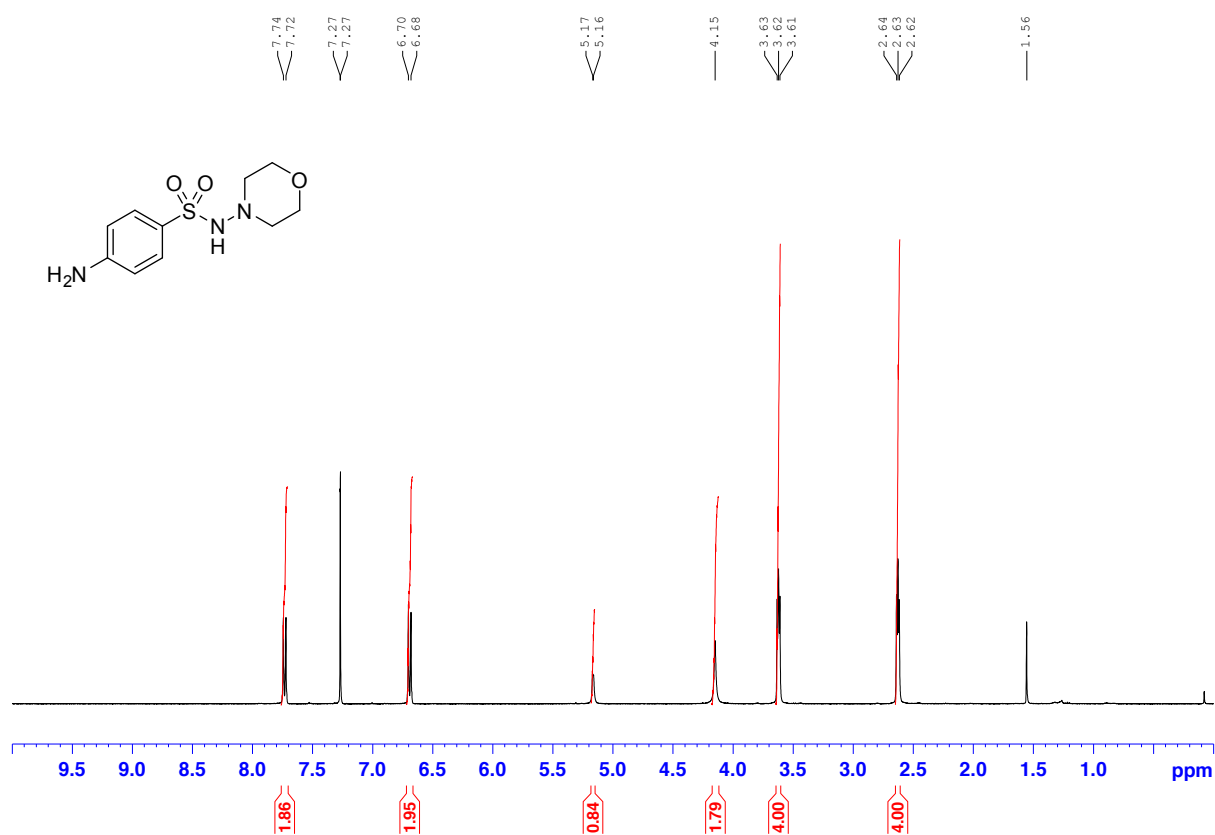
4-Aminomorpholine-sulfur dioxide complex, **8**

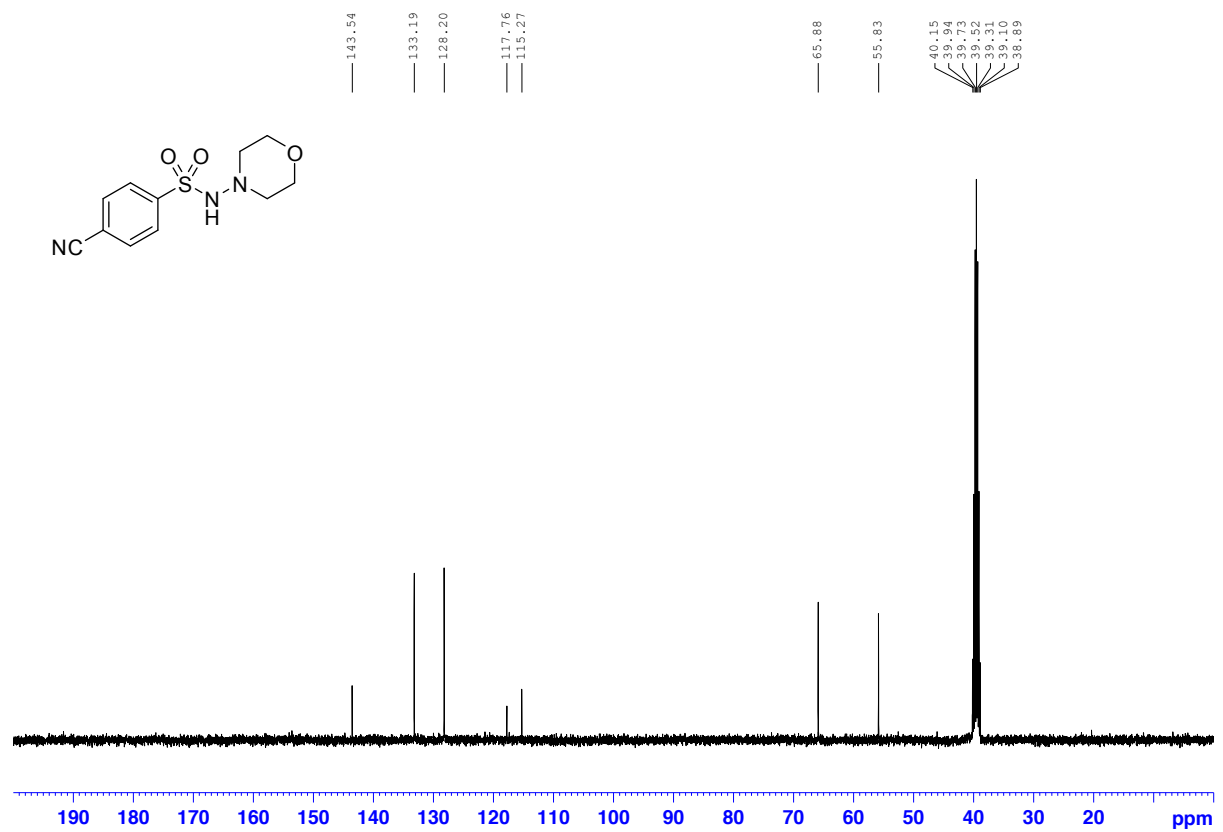
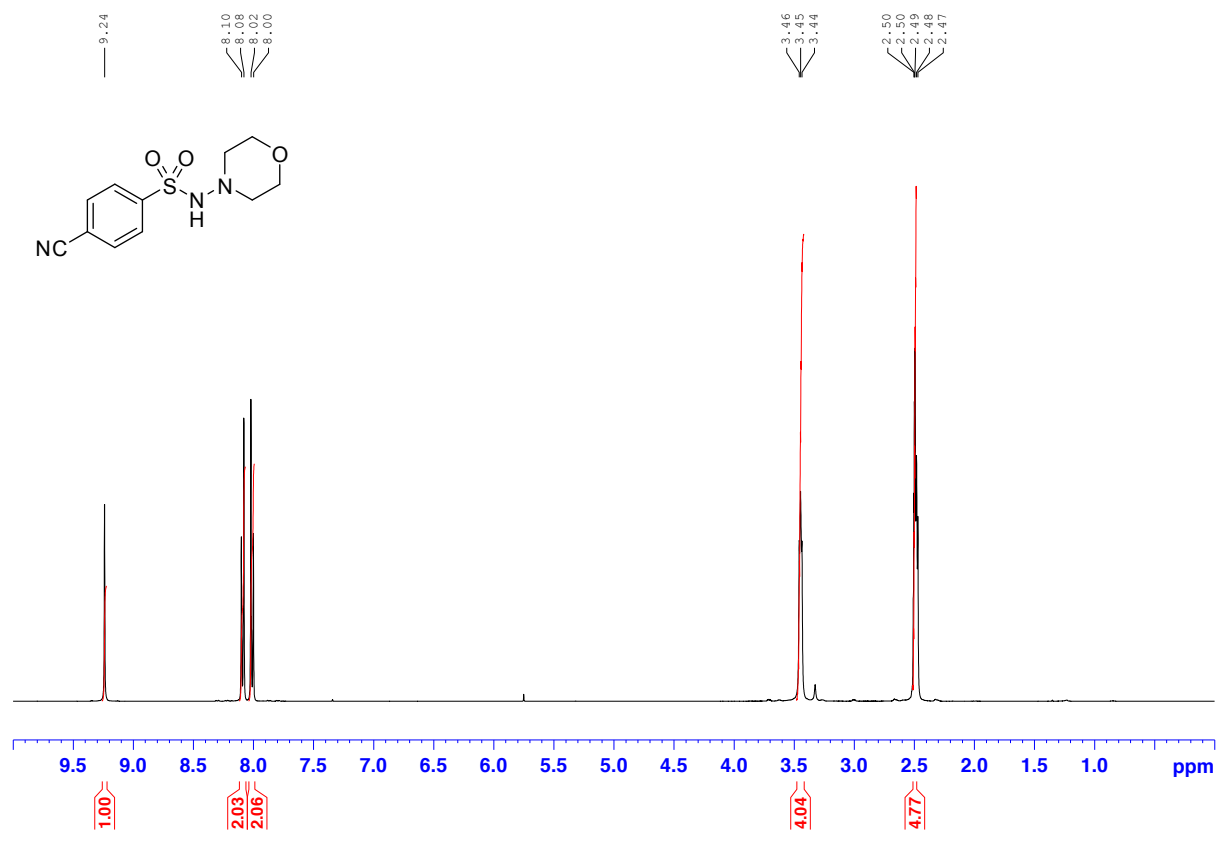


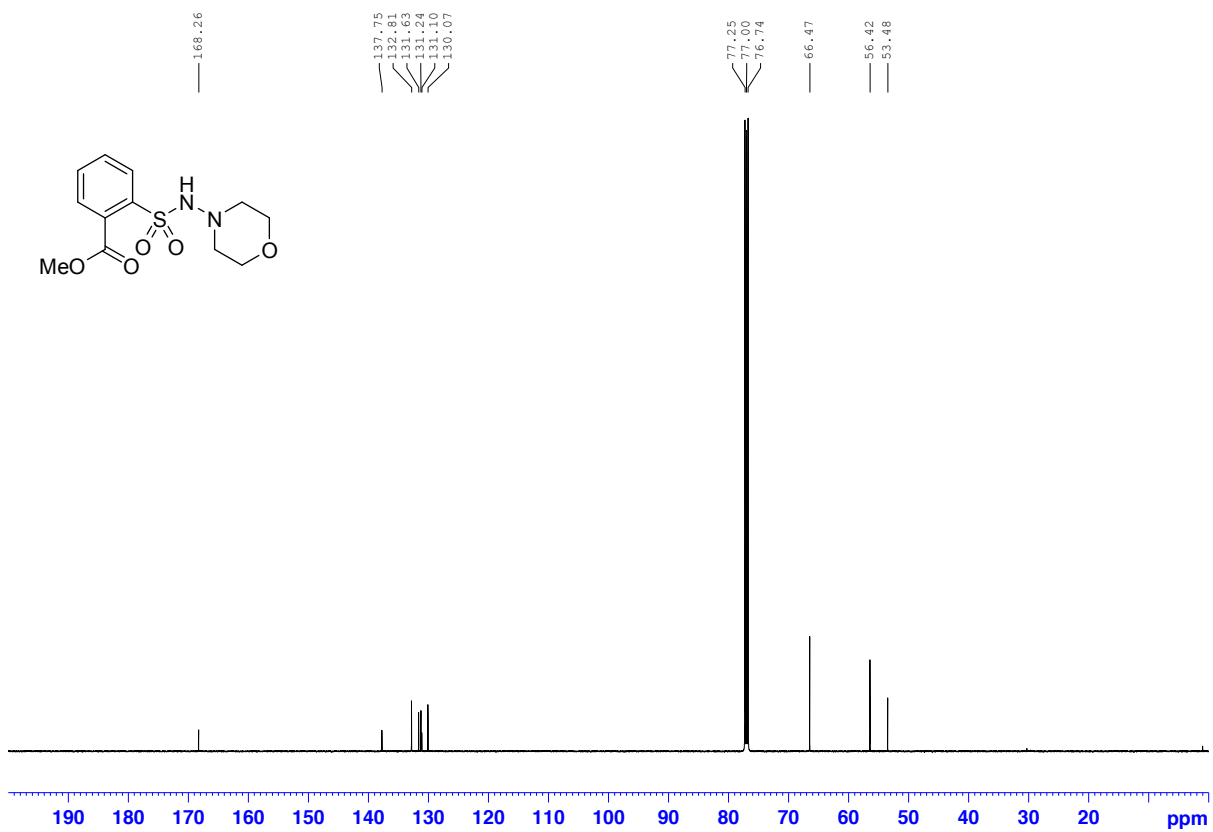
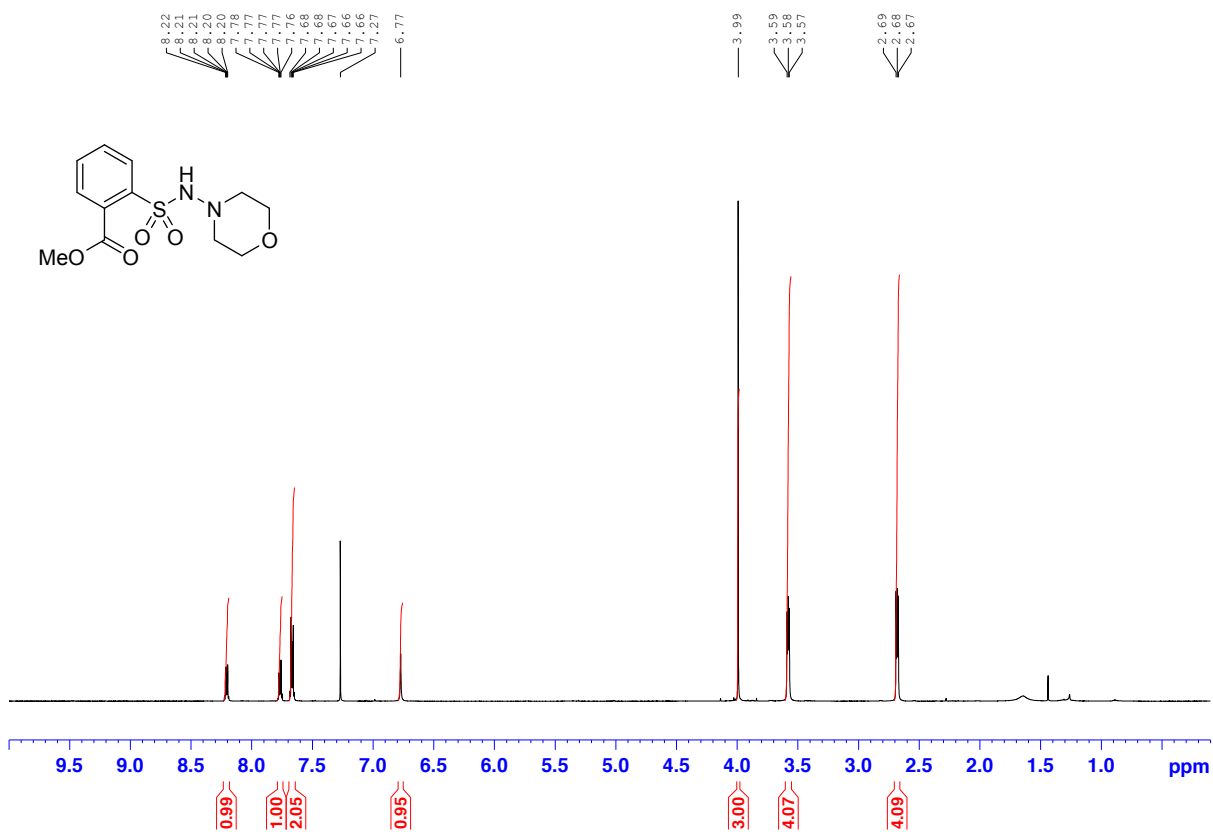
The general procedure as described for DABSO in our communication¹ was followed with the use of distilled 4-aminomorpholine (1.00 mL, 10.4 mmol) affording *complex 8* as a white powder (1.65 g, 96%). Elemental analysis found 29.01% C, 6.15% H, 16.82% N, 19.08% S; C₄H₁₀N₂O₃S requires 28.91% C, 6.06% H, 16.86% N, 19.29% S; ¹H NMR (400 MHz, MeOD-d₄) δ 3.80 (4H, br. s, (NCH₂CH₂O)₂), 2.99 (4H, br. s, (NCH₂CH₂O)₂); ¹³C NMR (100 MHz, MeOD-d₄) δ 66.5, 56.0; IR ν_{max} (neat)/cm⁻¹ 2869, 2600 (br.), 2173, 1630, 1595, 1468, 1299 (SO₂), 1200, 1104 (SO₂). DSC analysis for both this complex and DABSO are attached. For this complex the first ‘event’ occurs around 95 °C (melting) but for DABSO this occurs around 220 °C (decomposition).

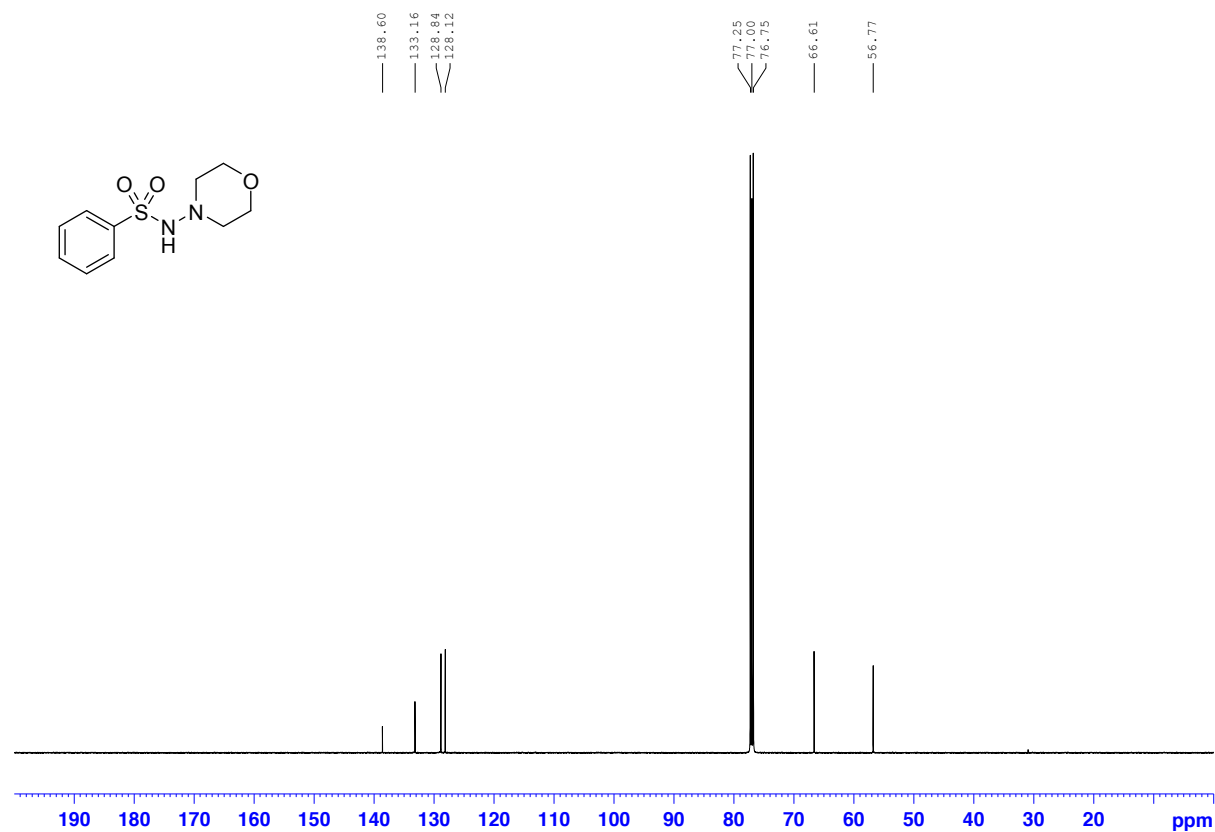
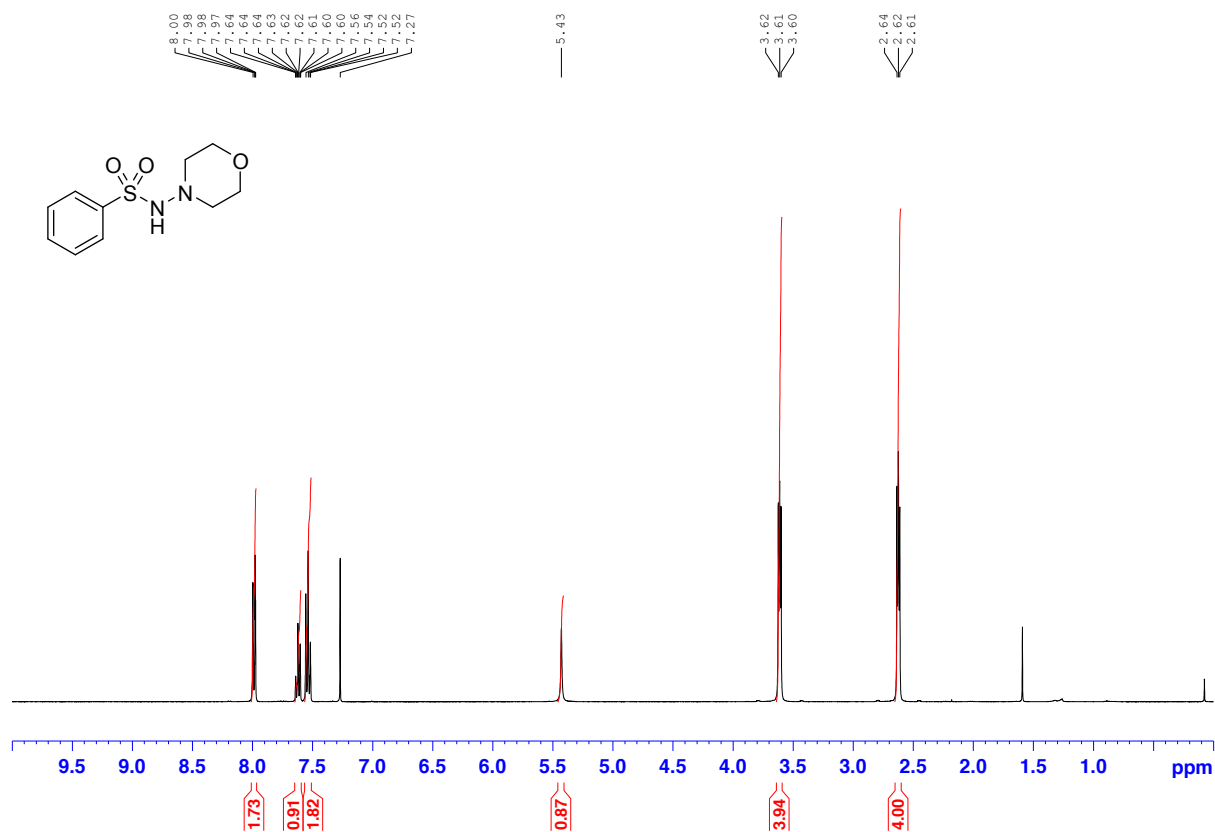
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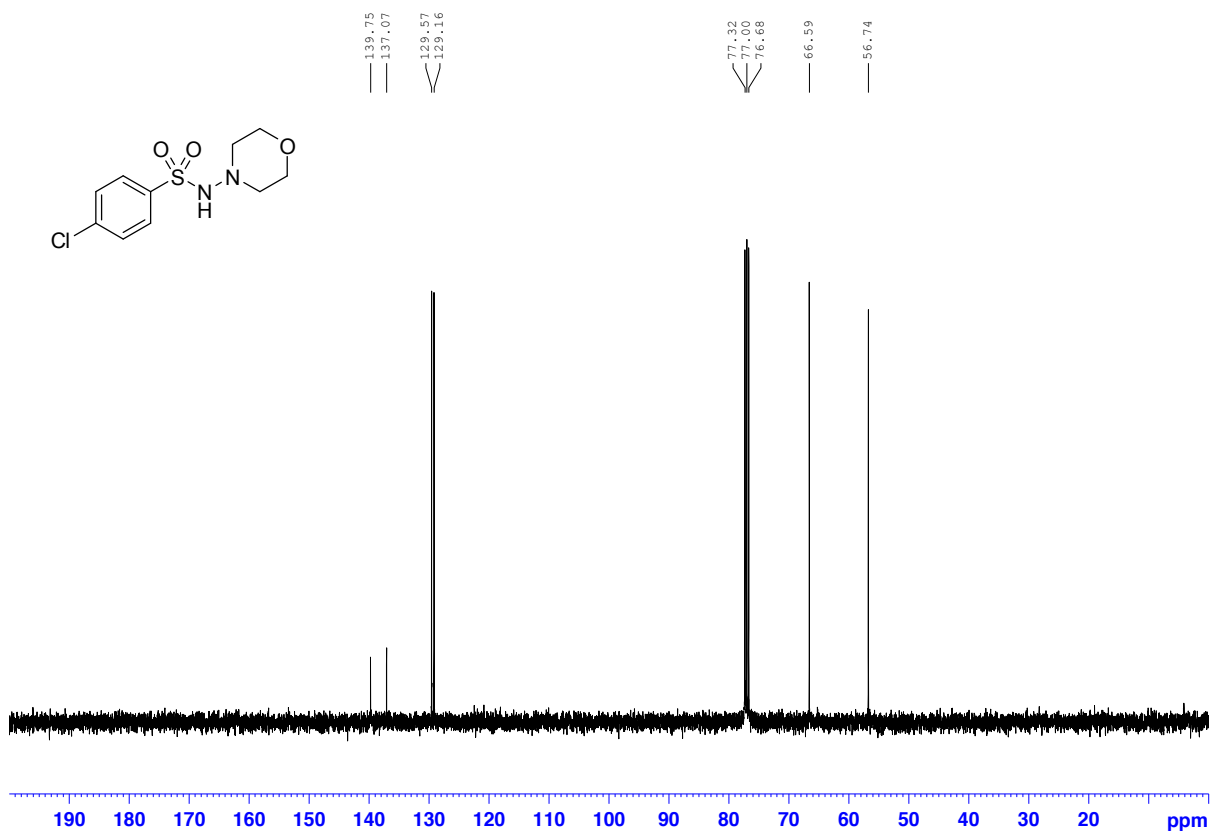
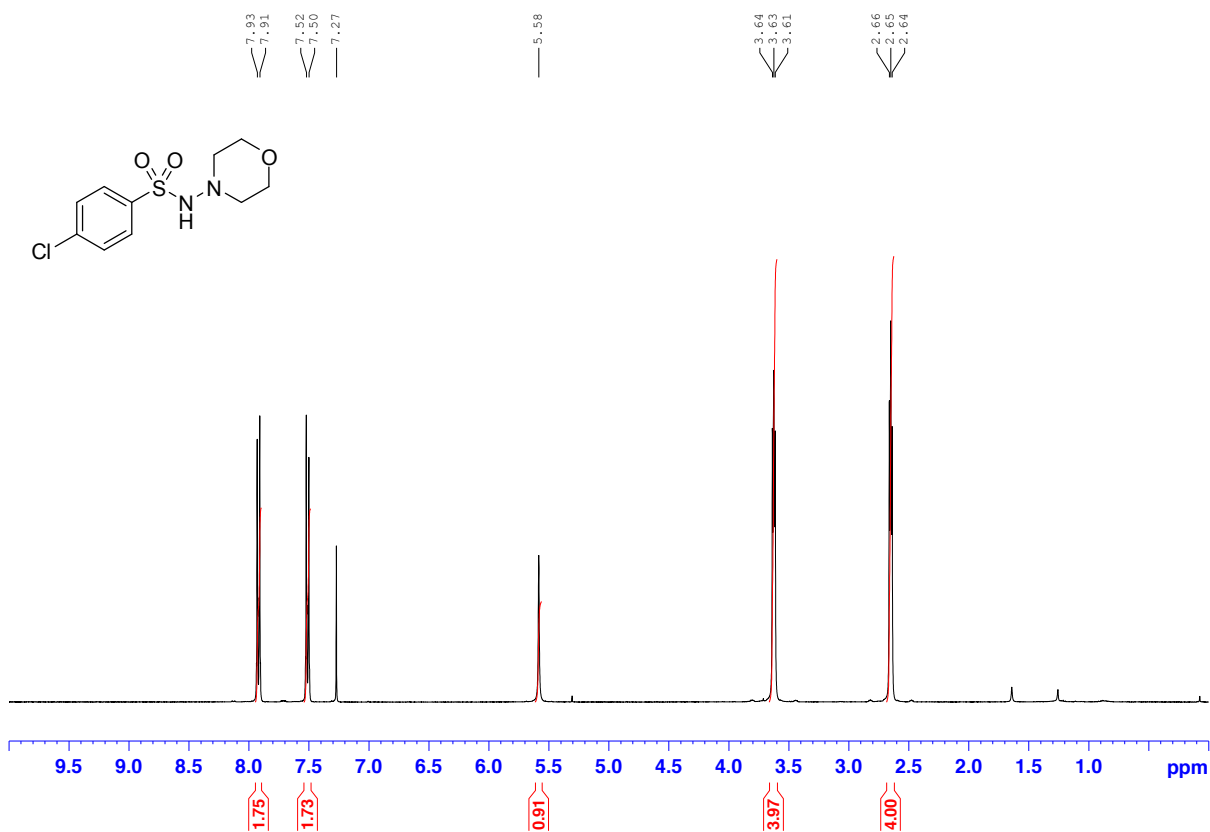
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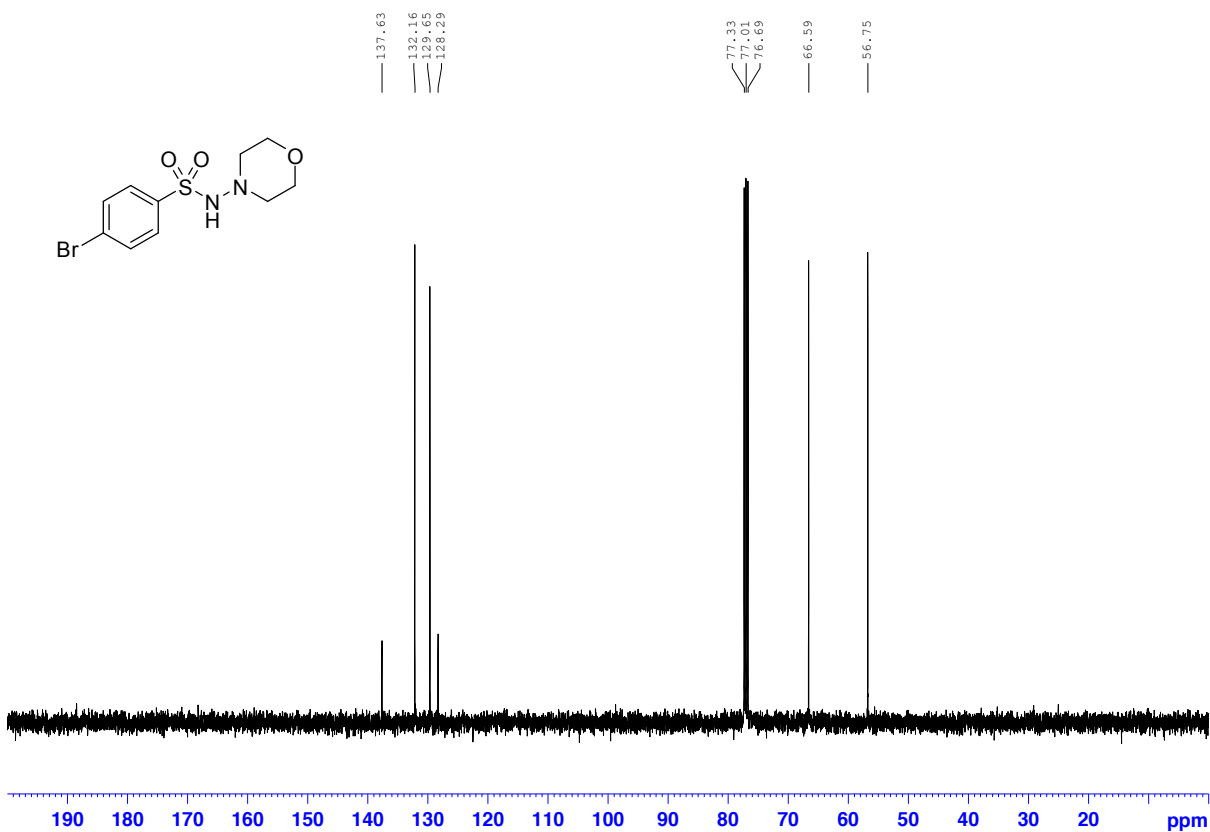
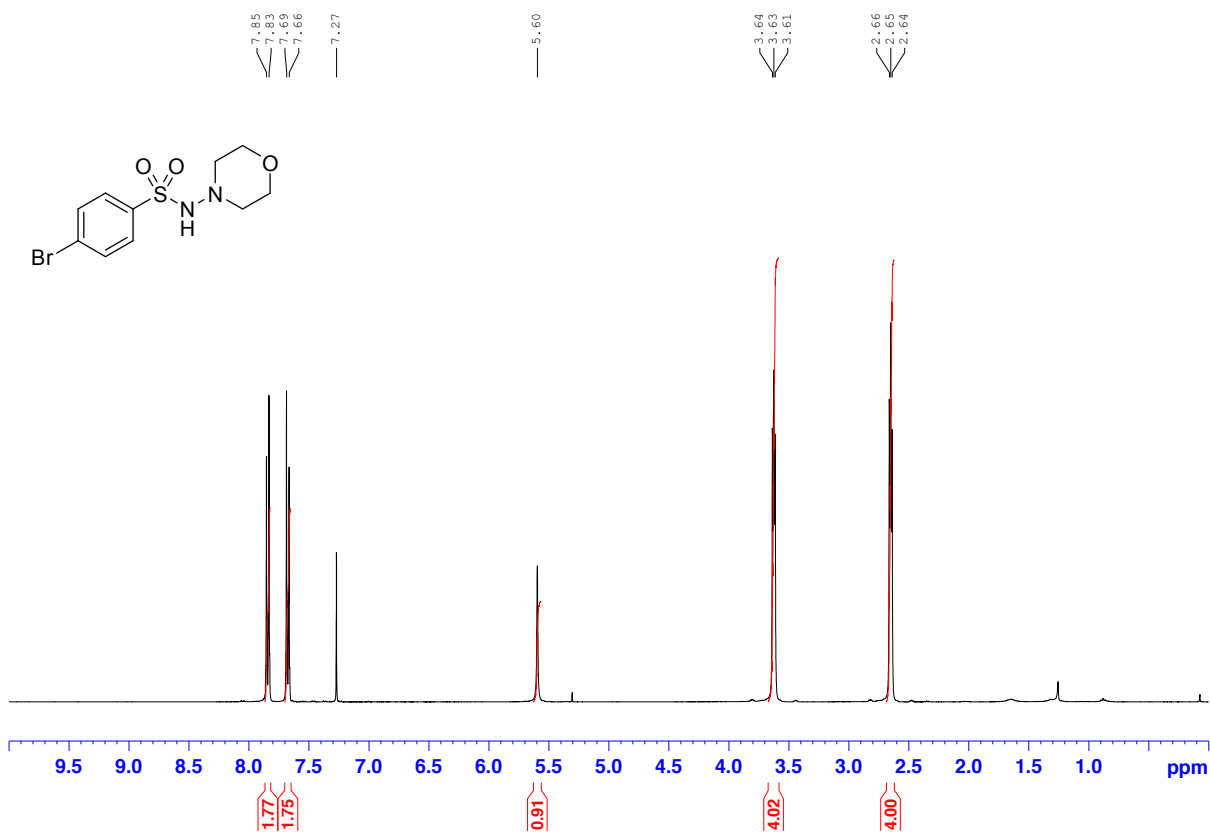


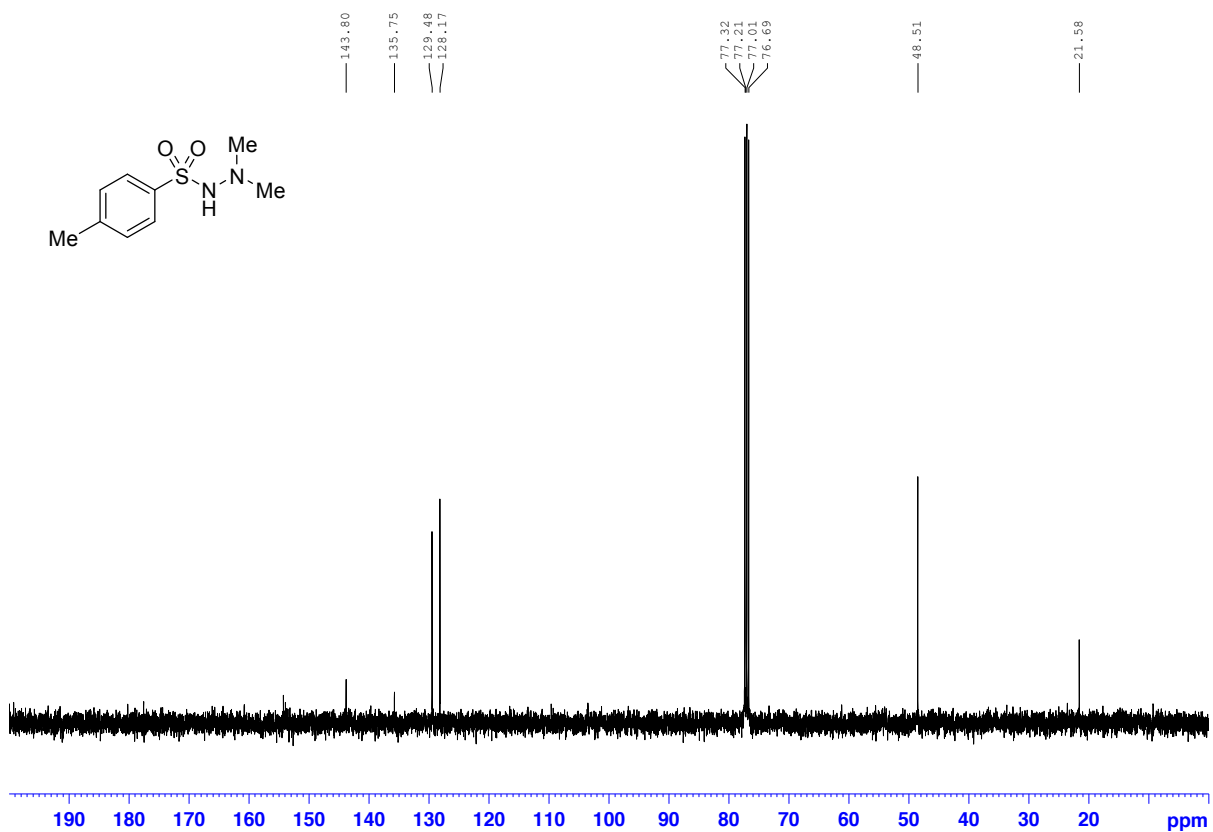
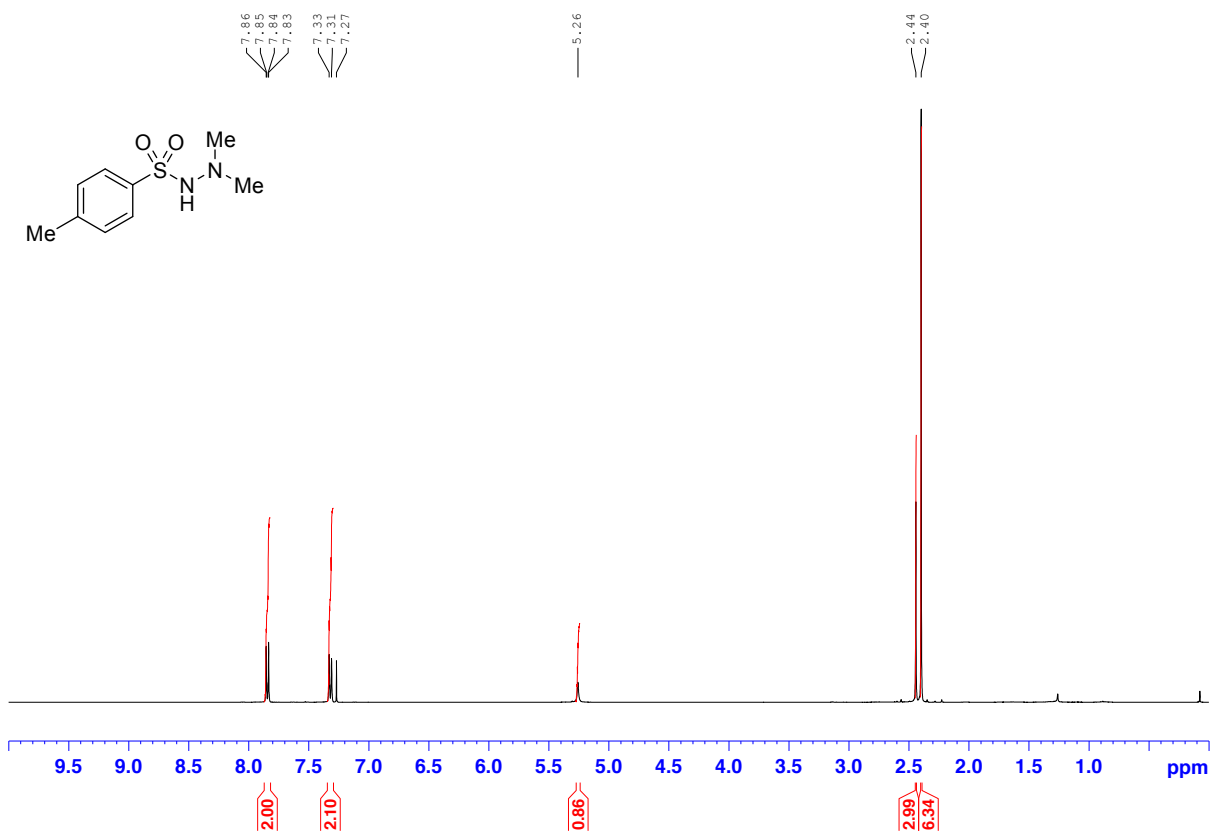


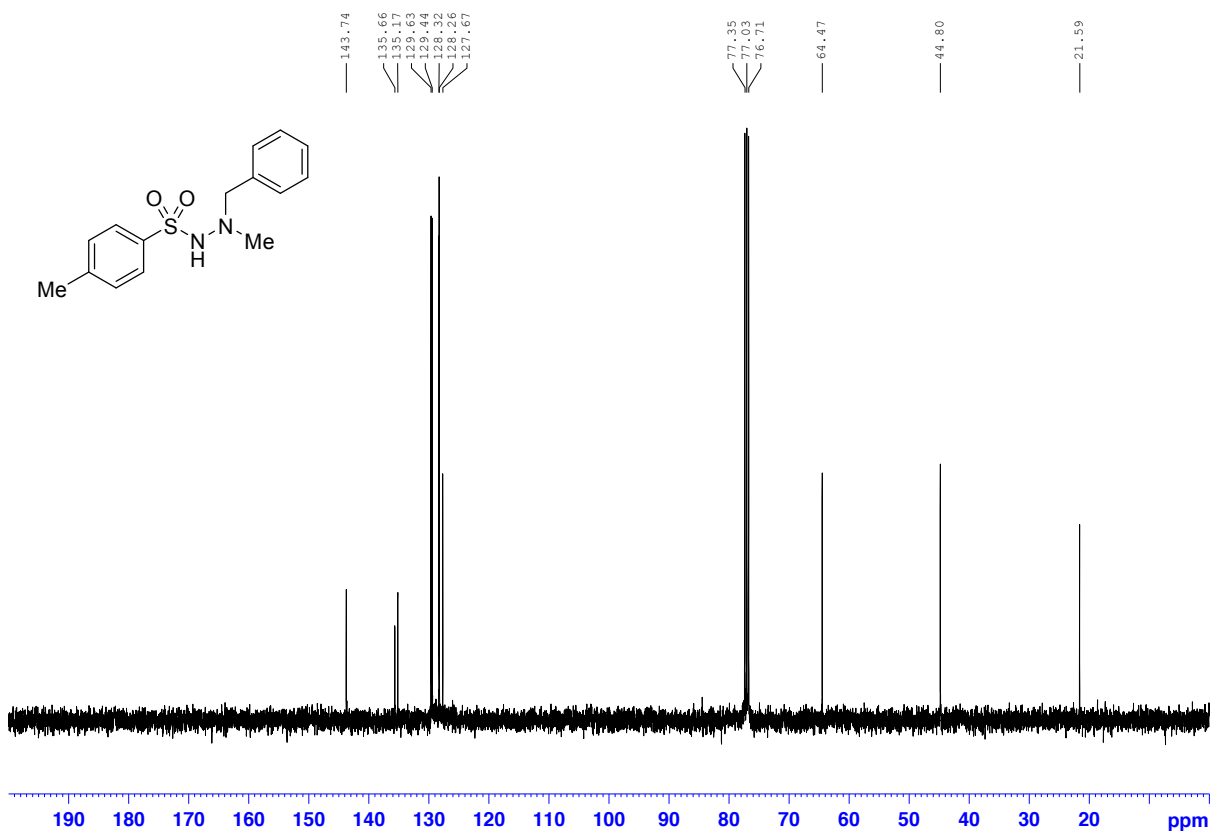
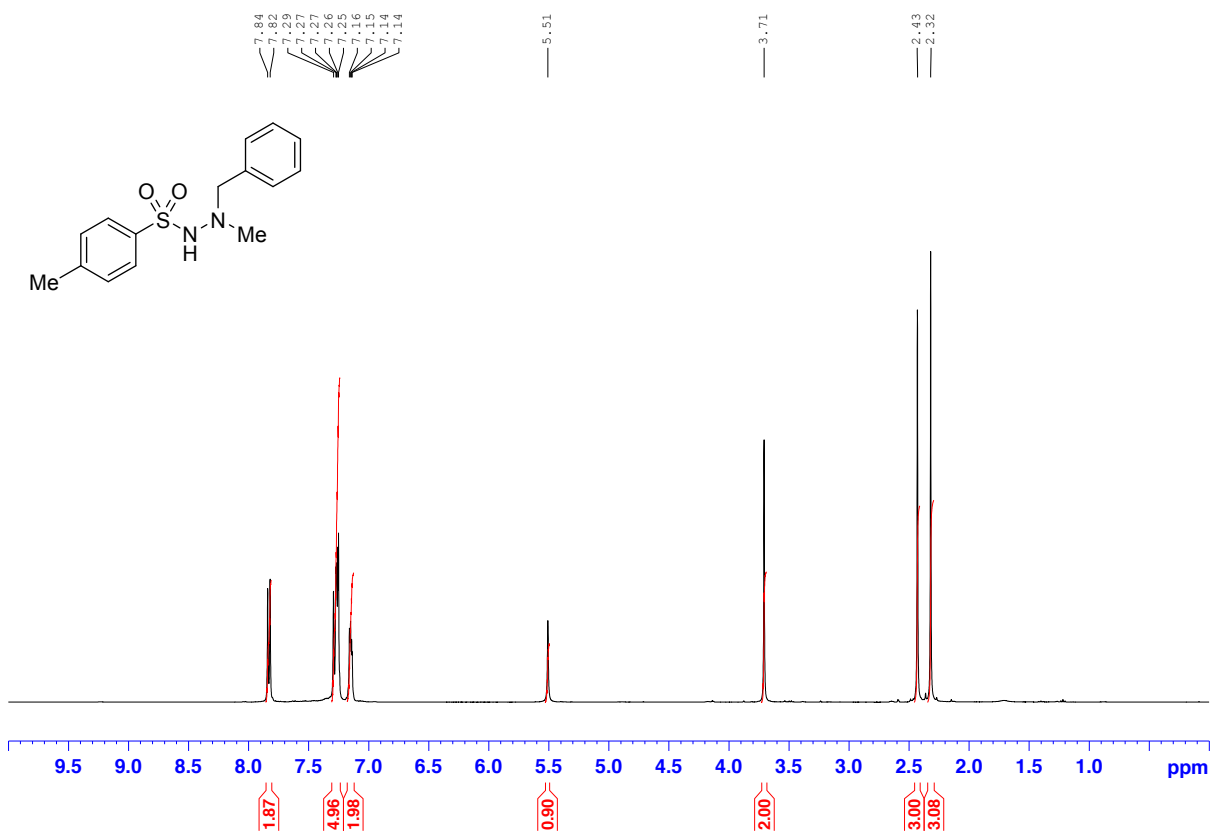


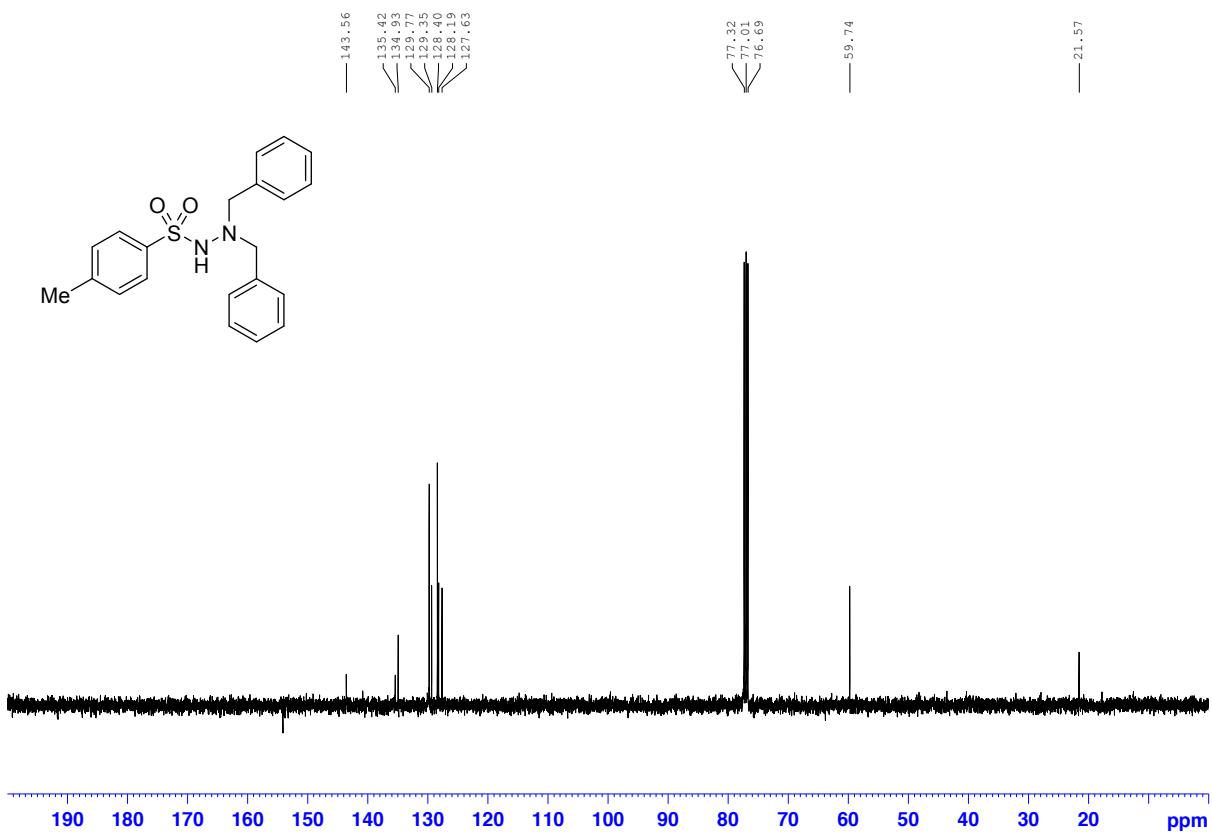
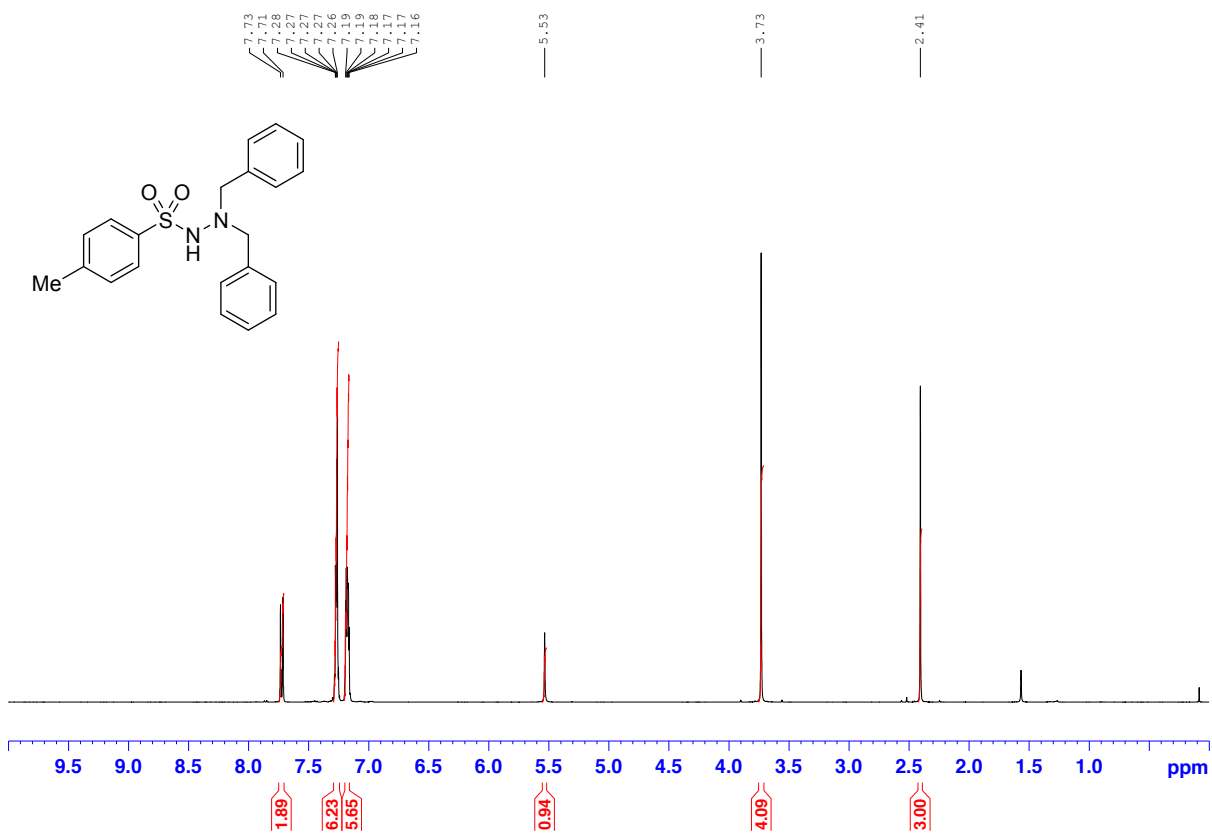


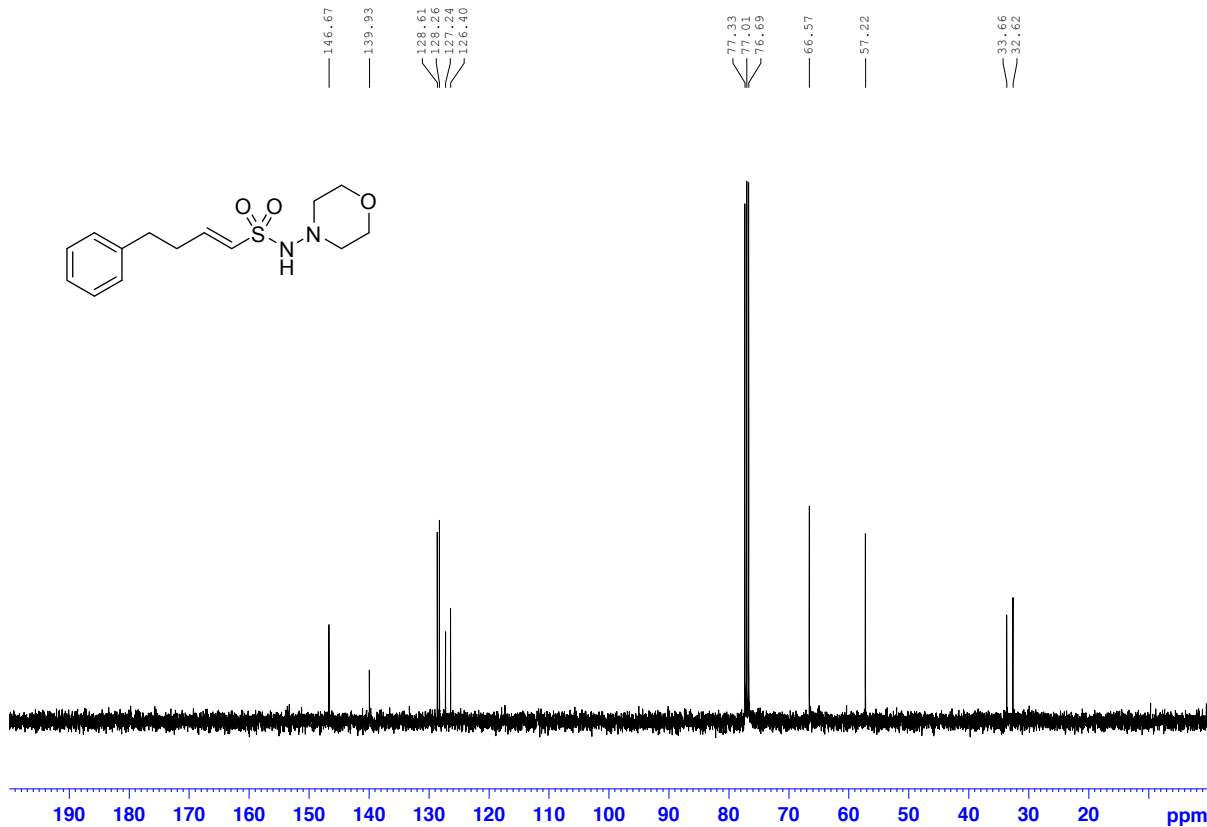
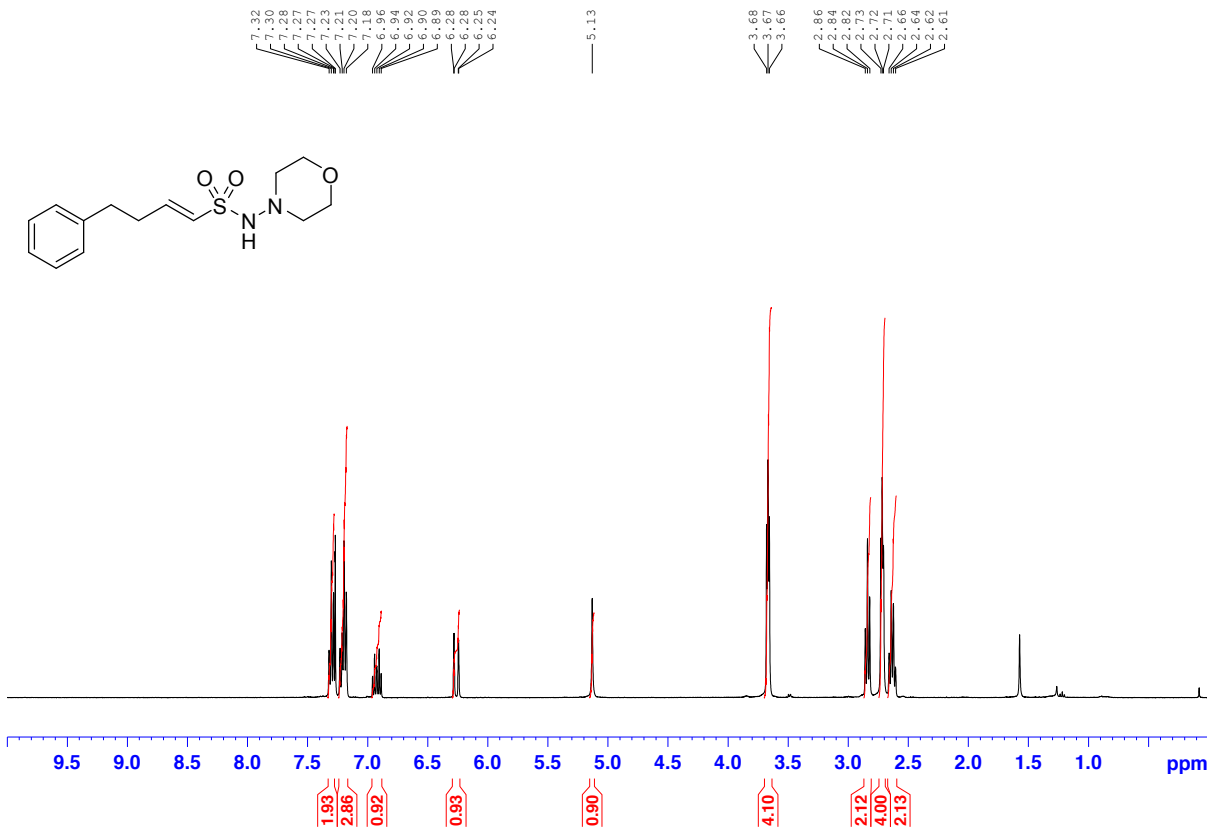


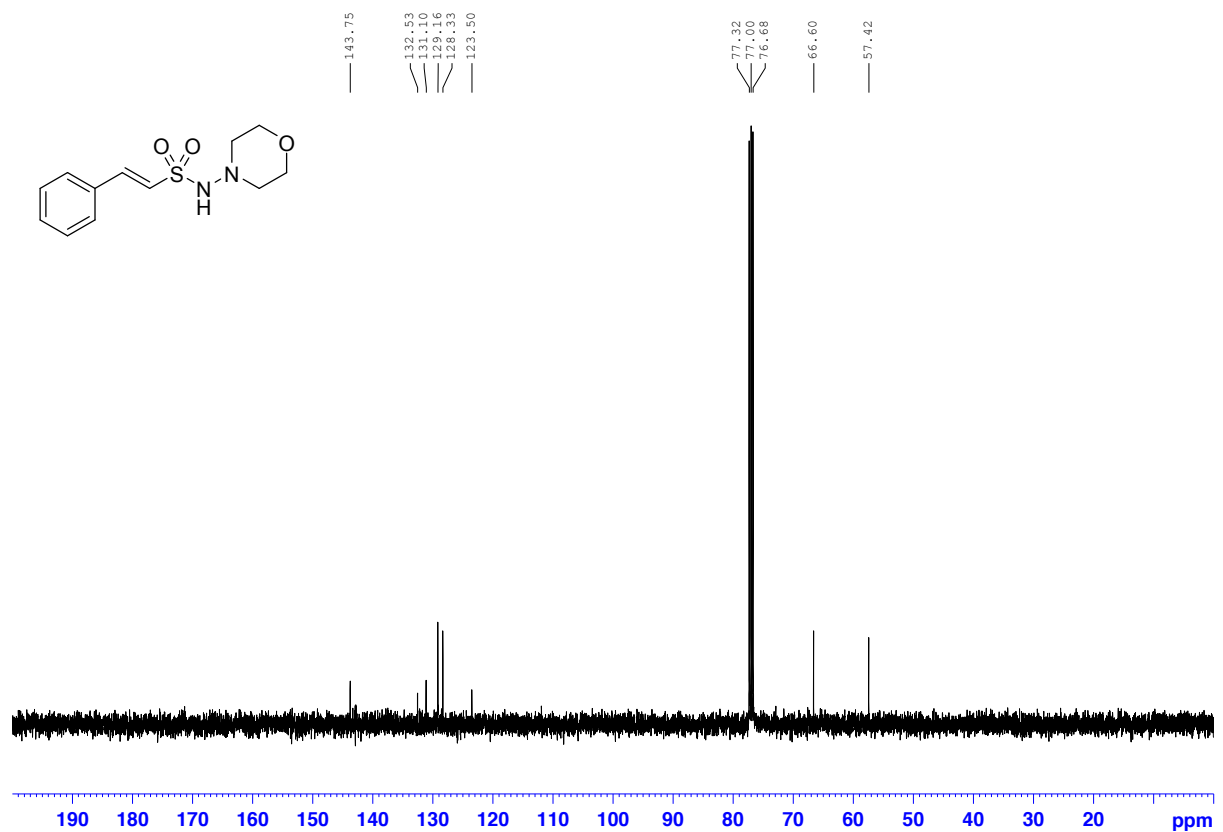
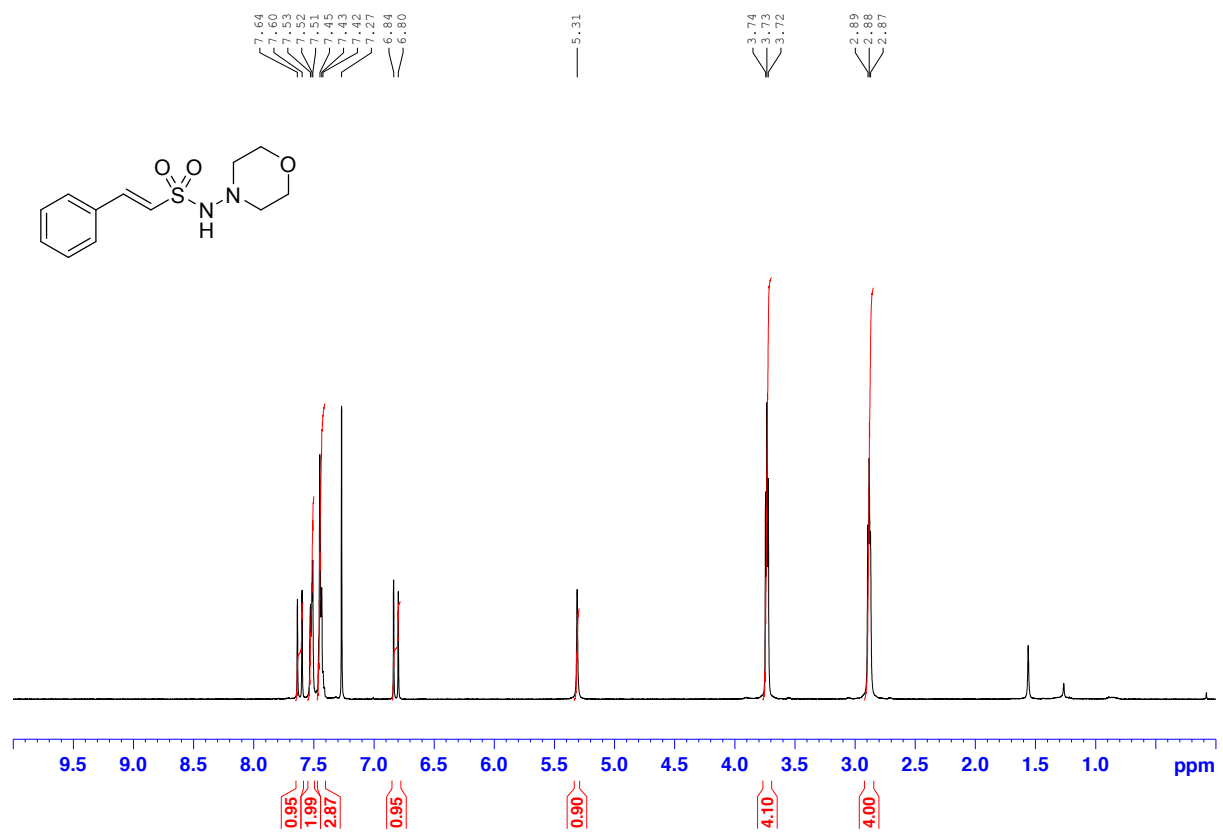


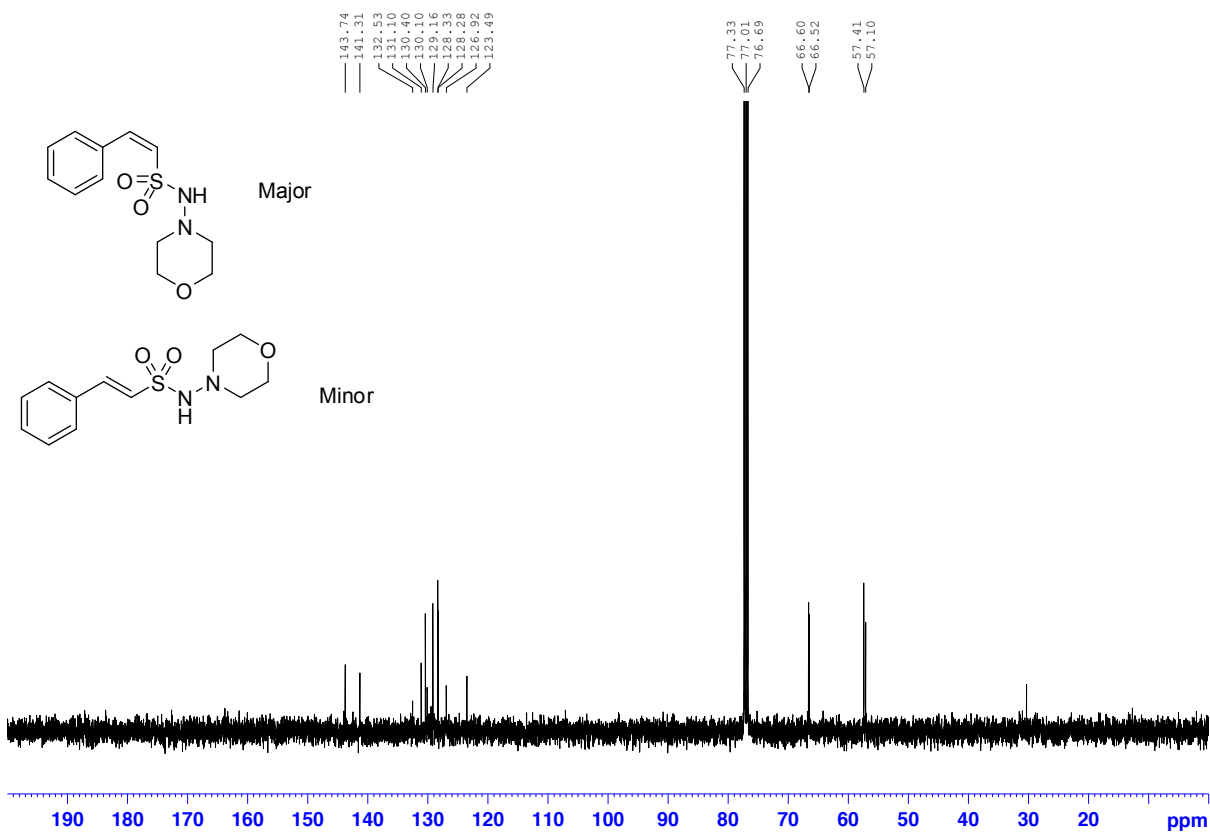
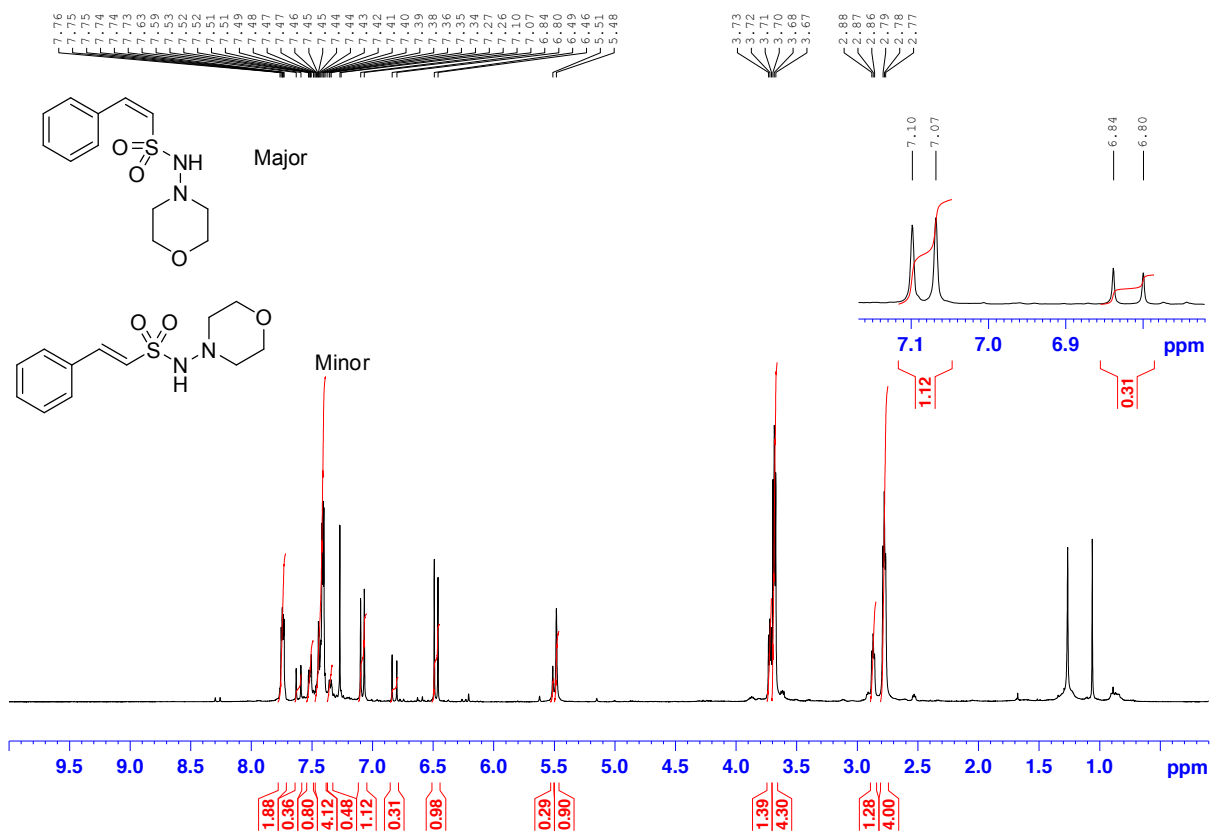


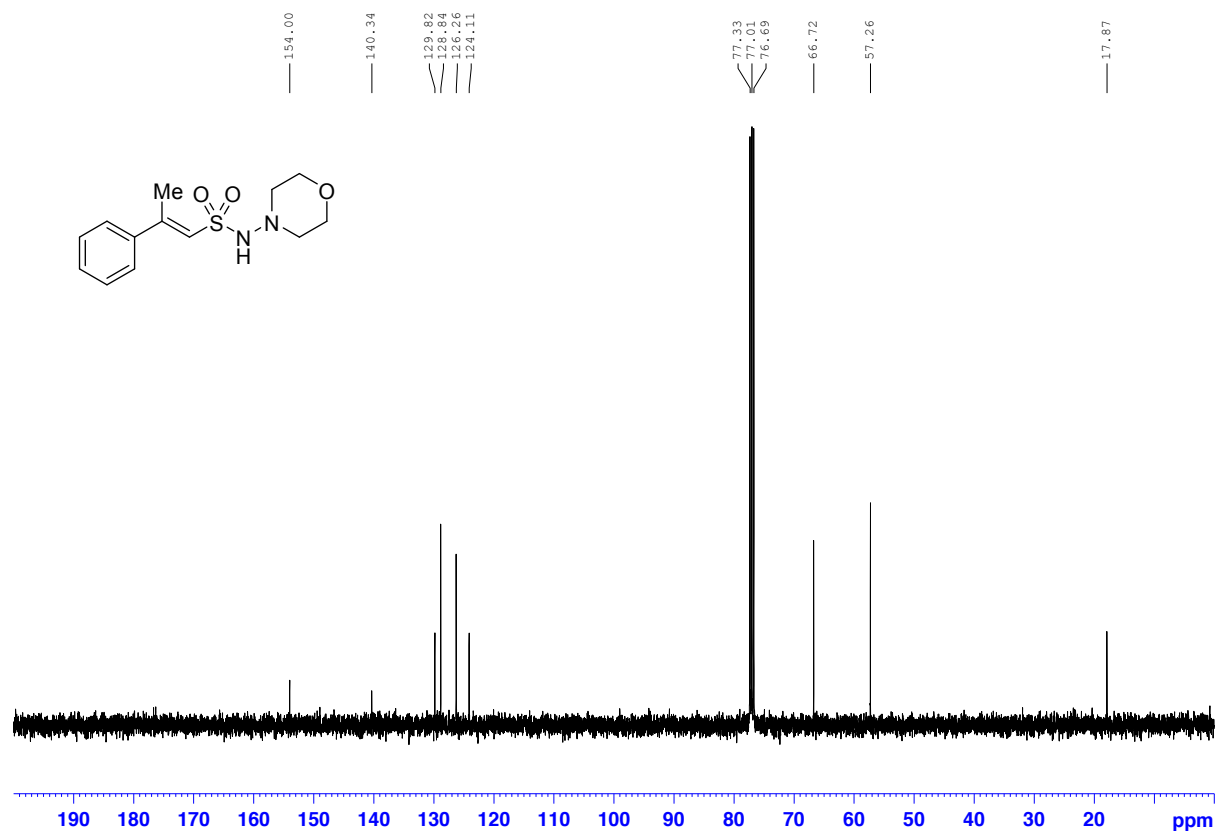
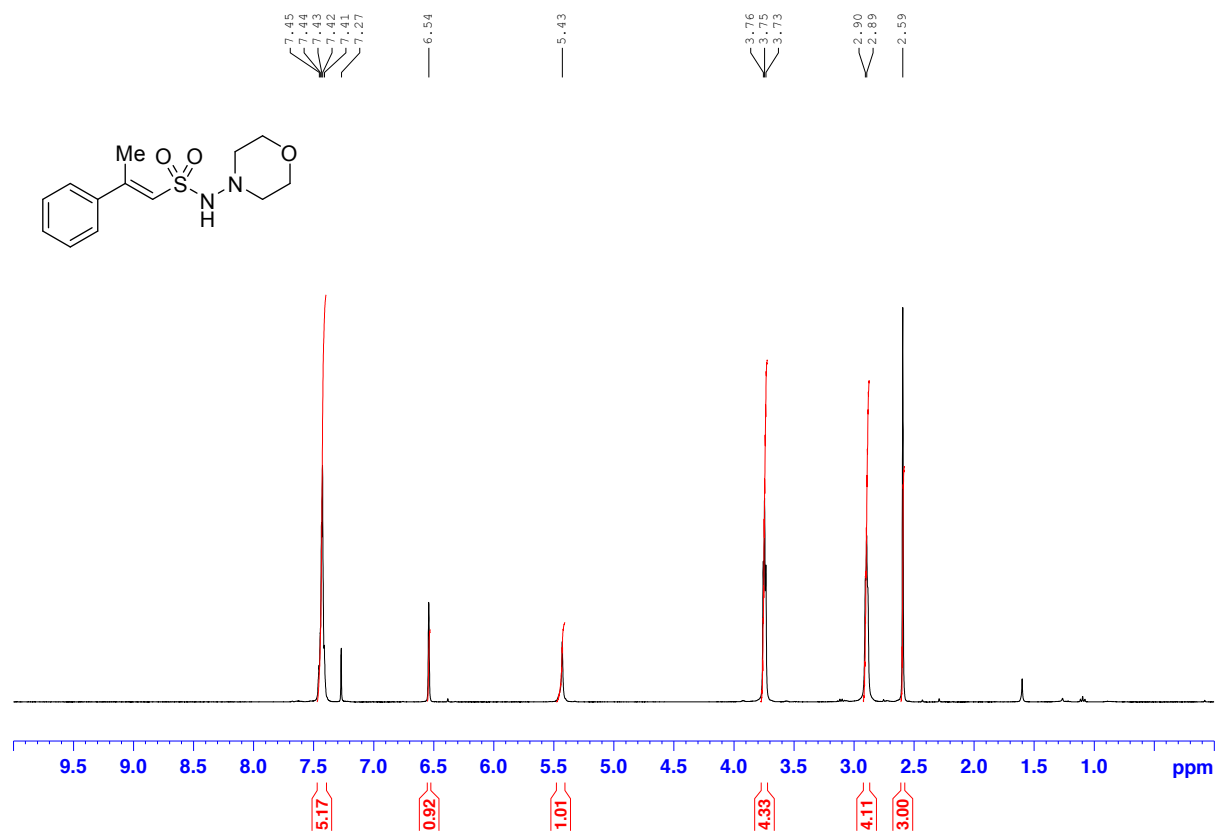


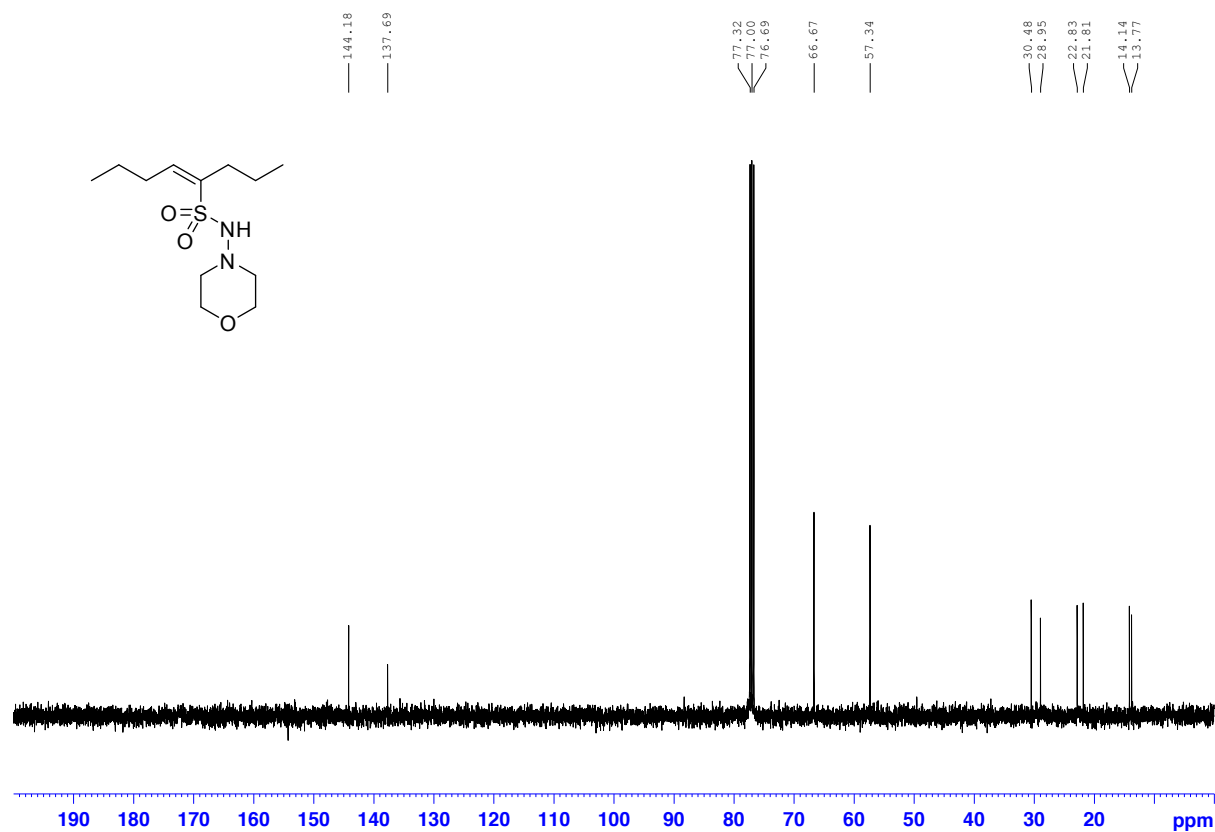
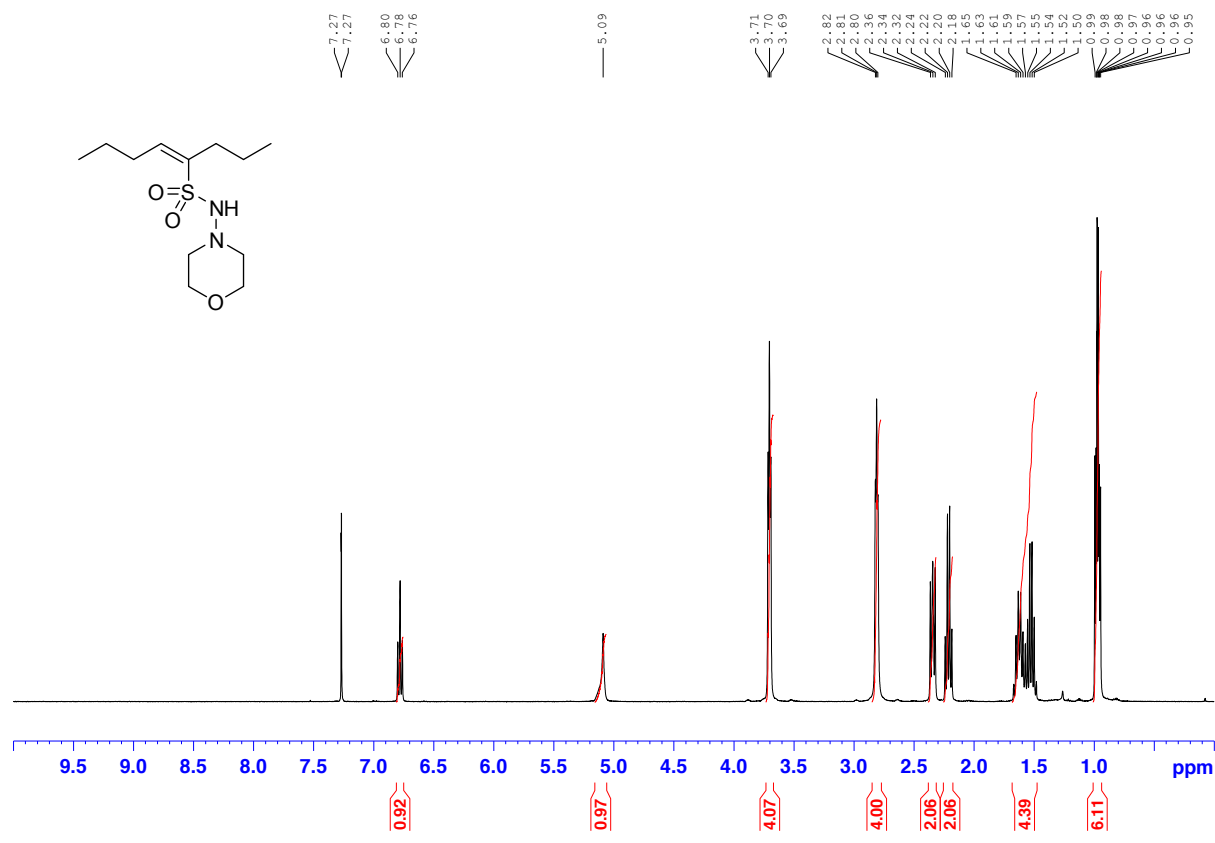


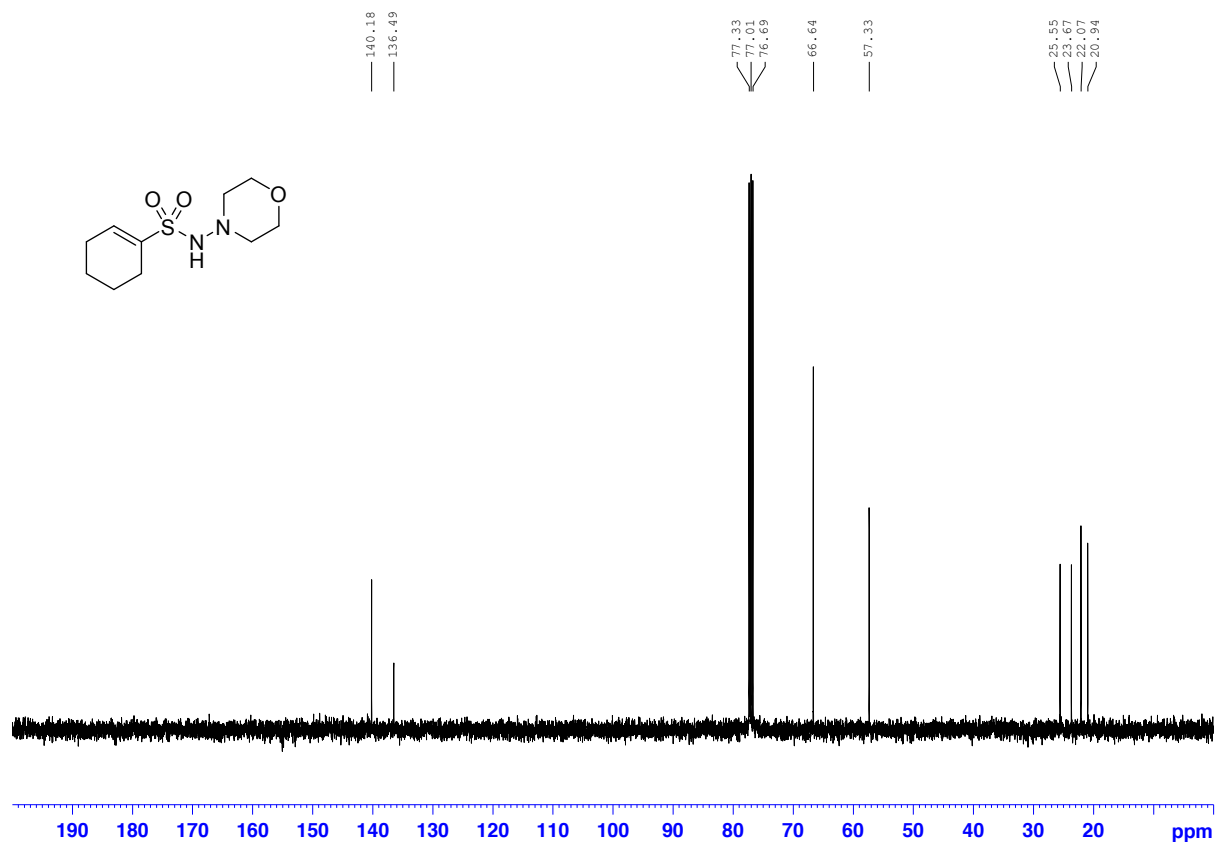
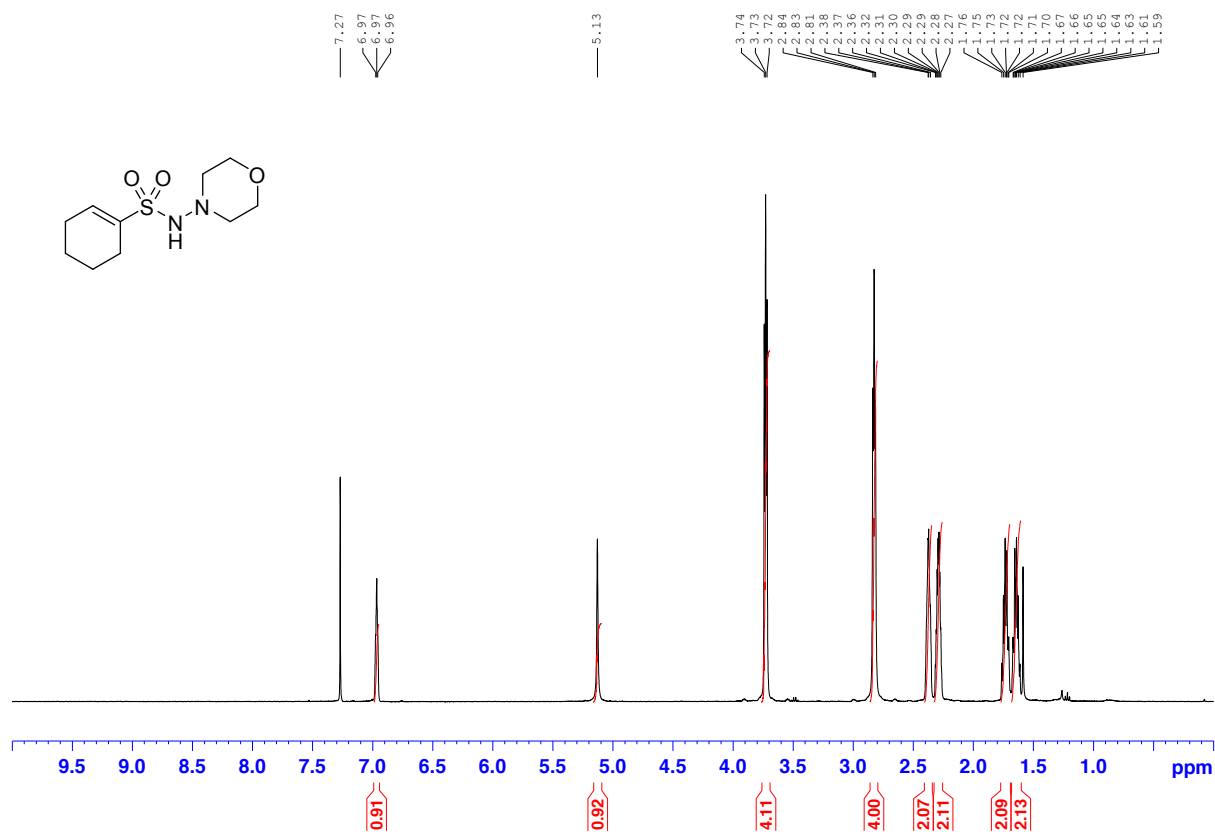


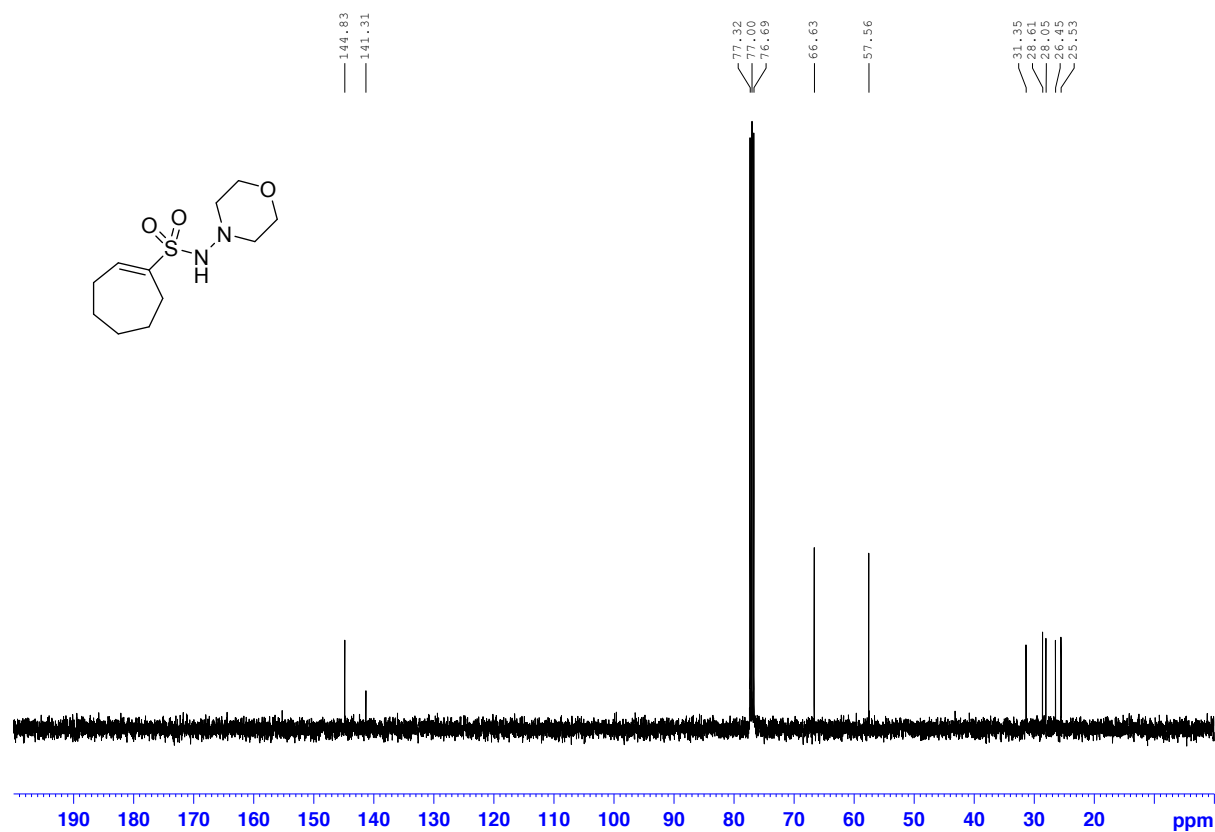
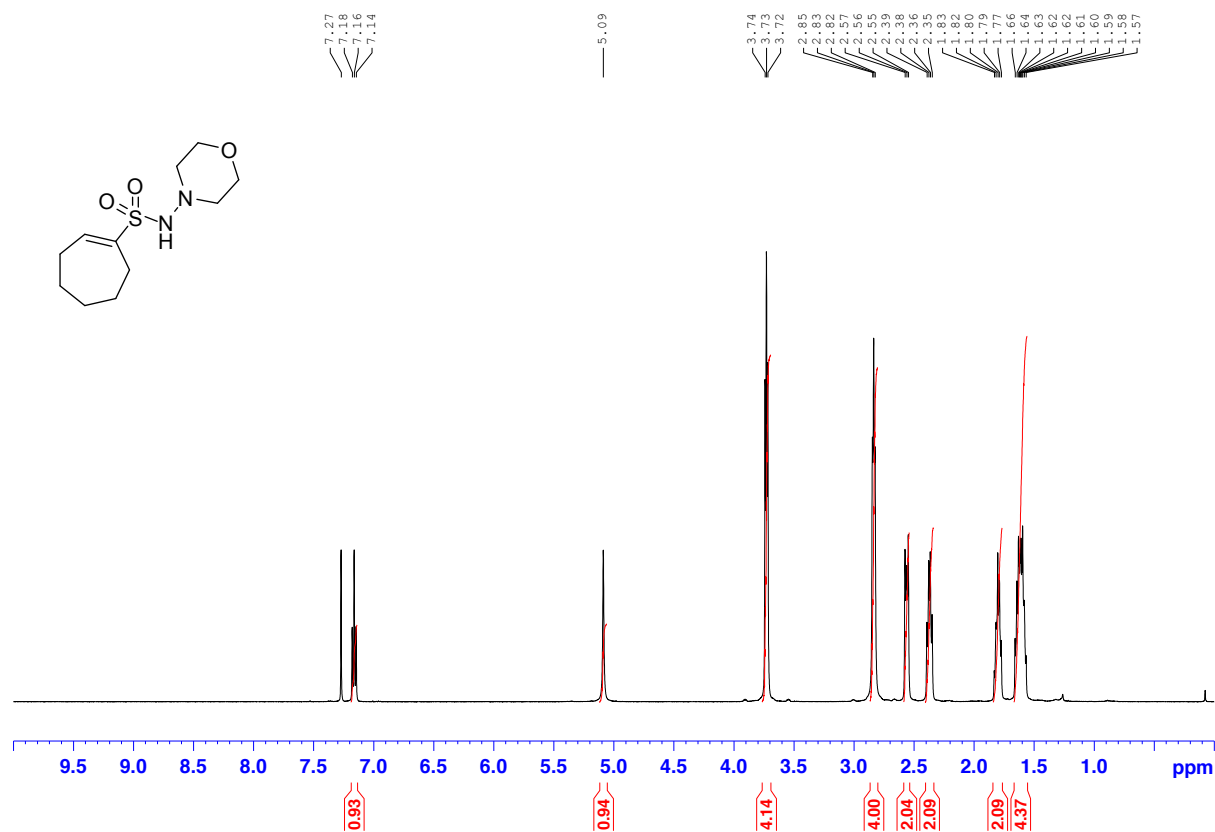


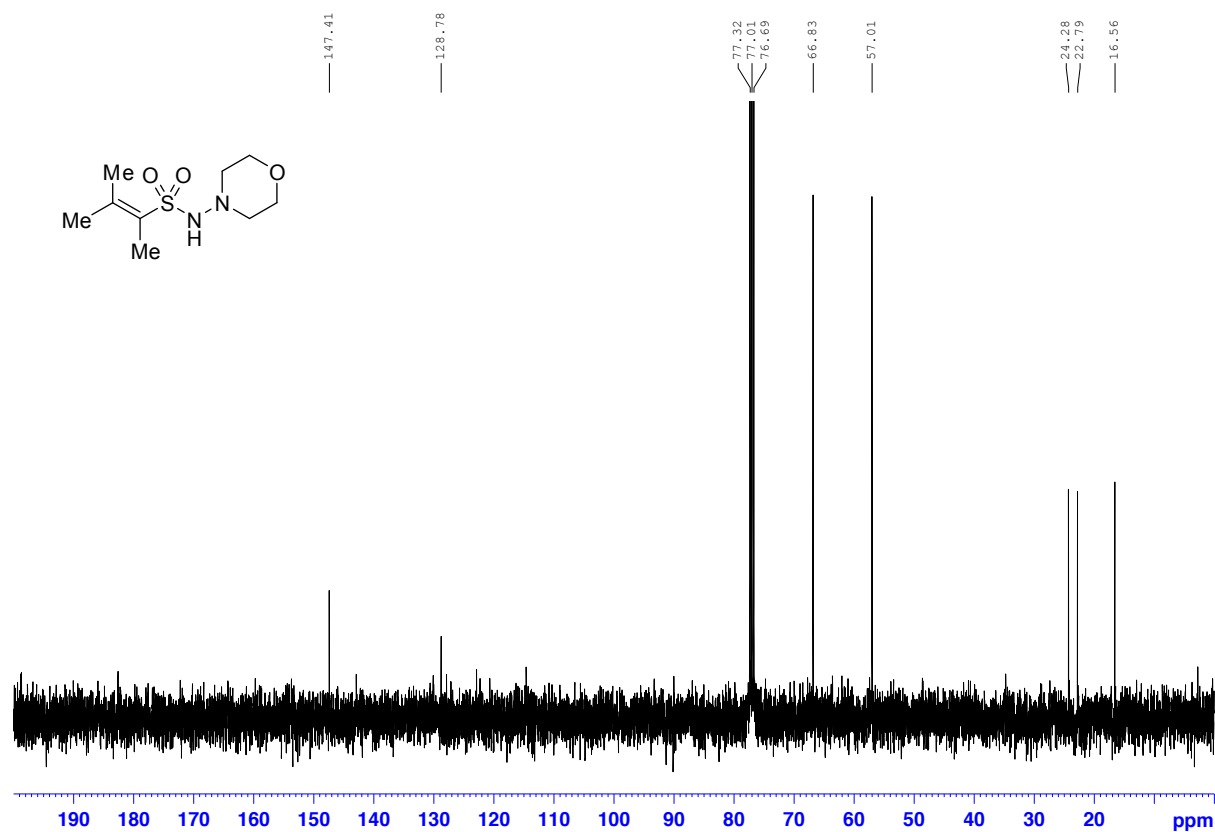
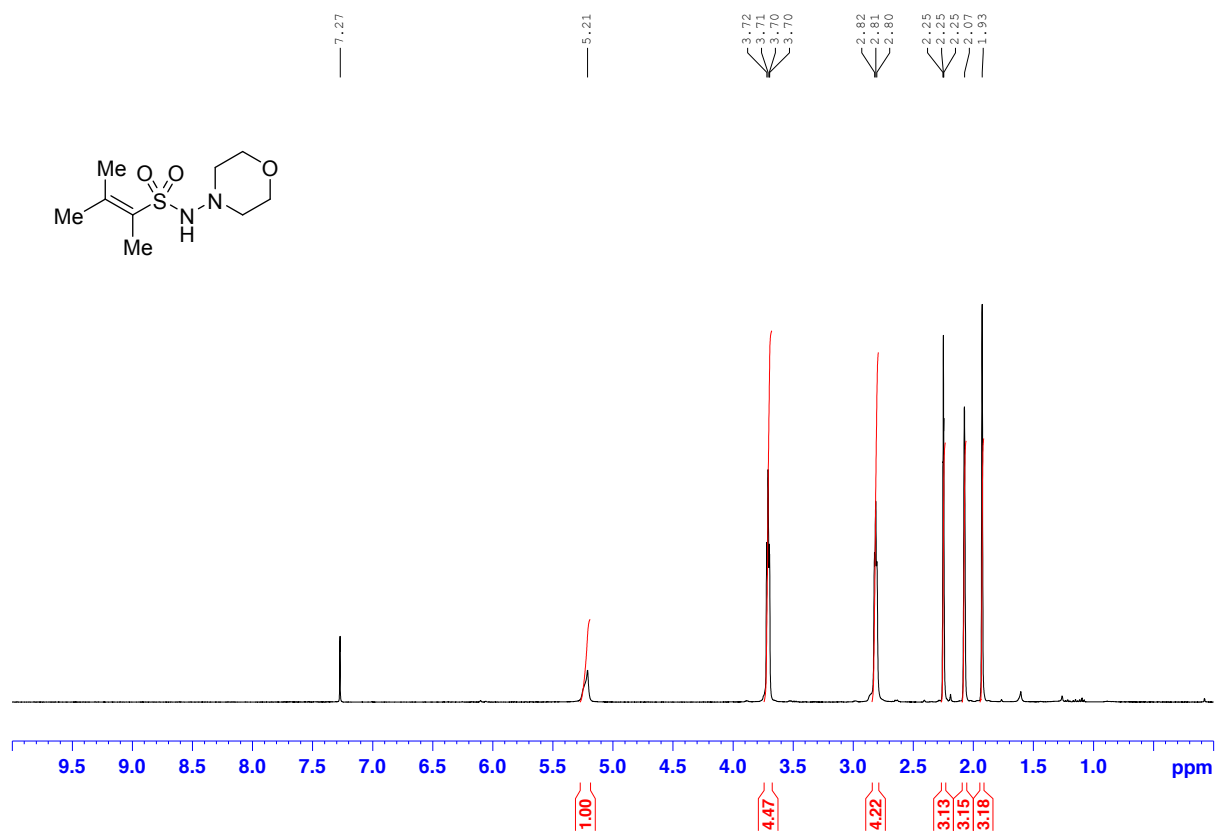


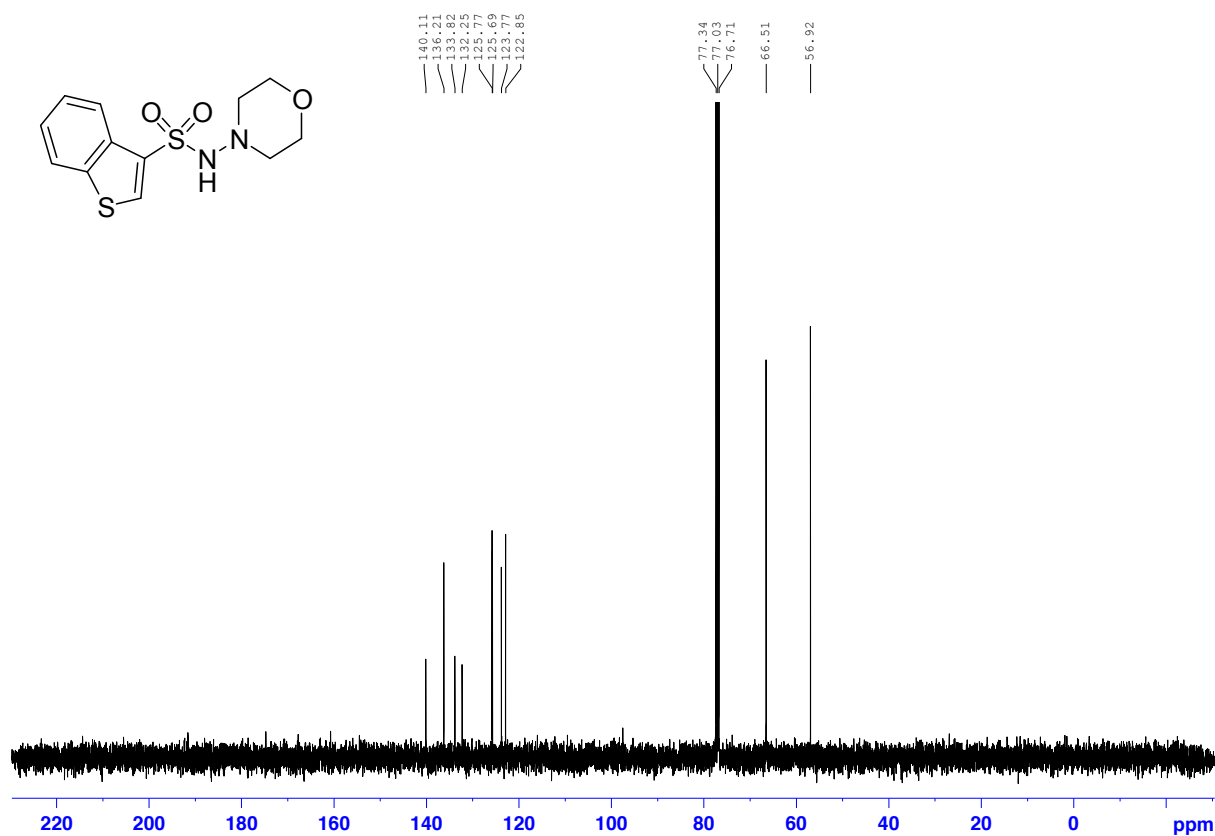
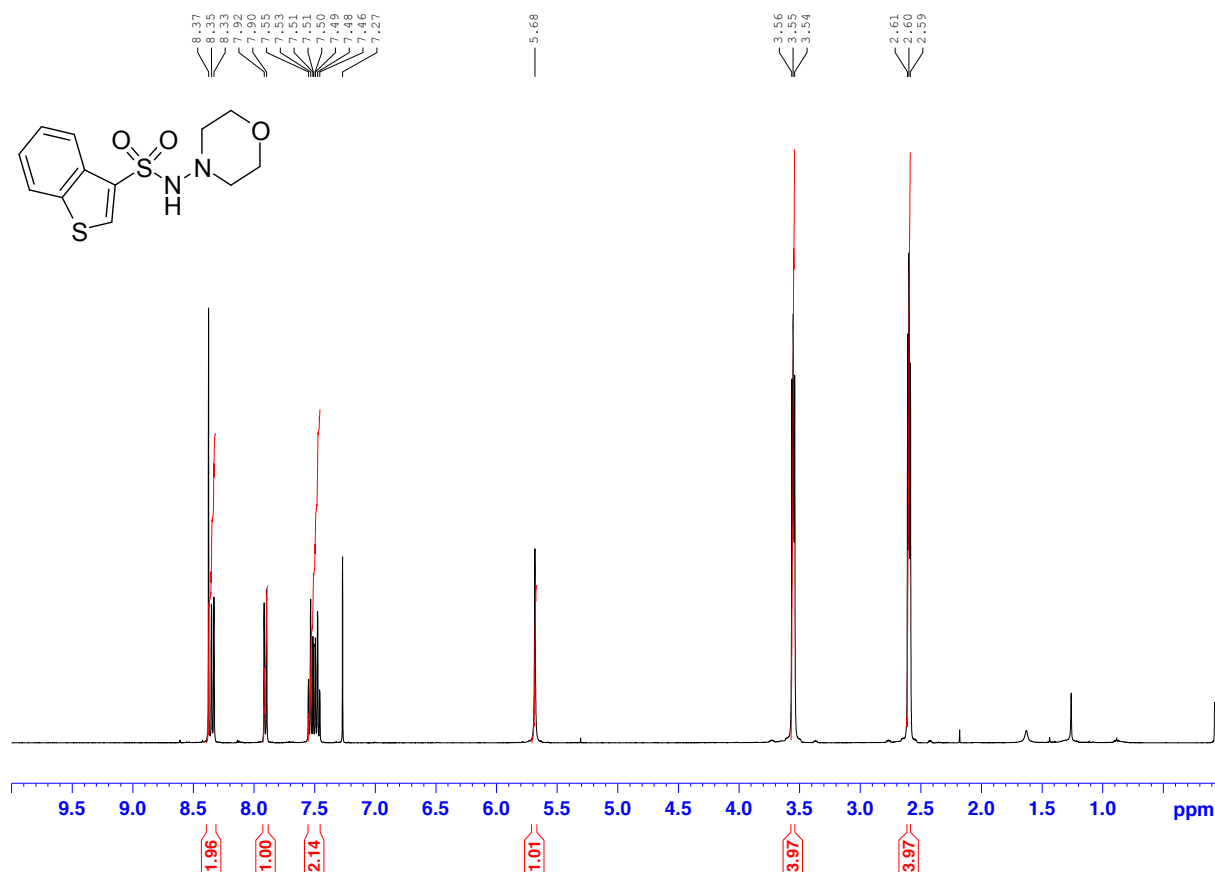


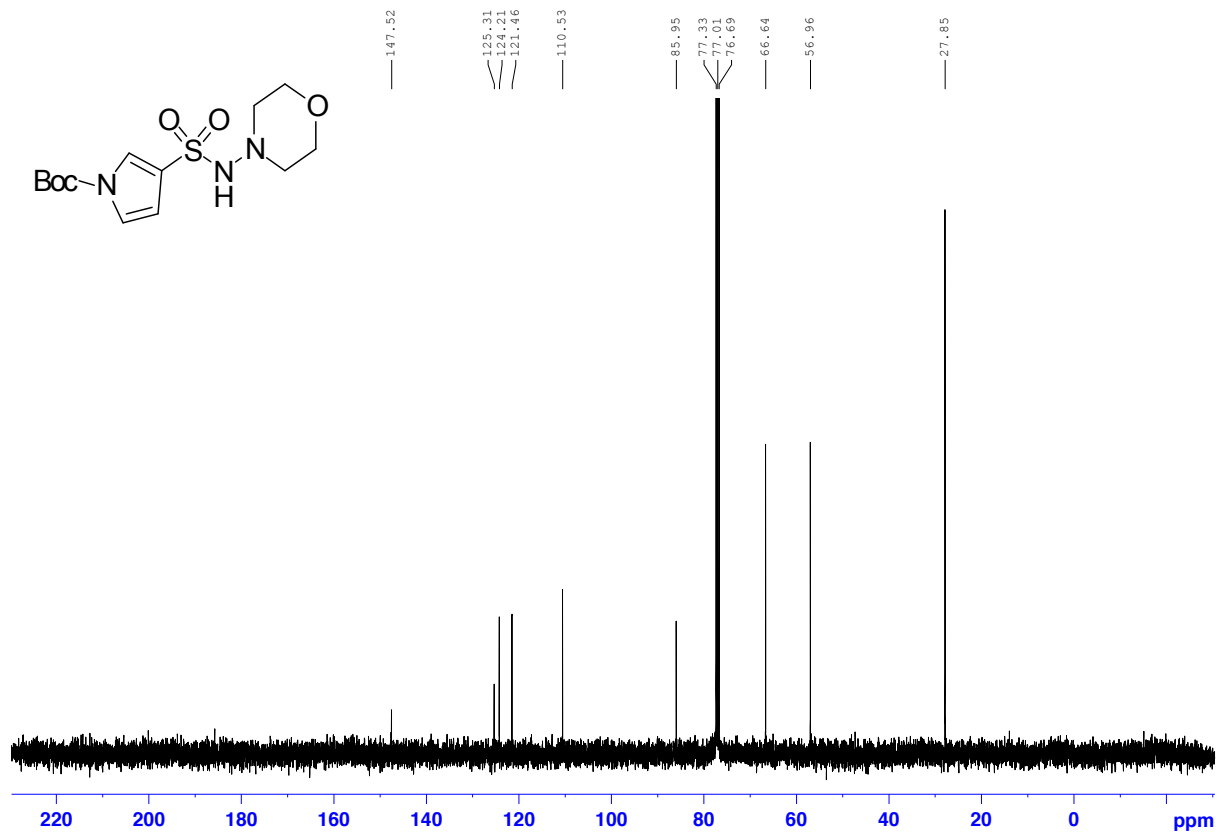
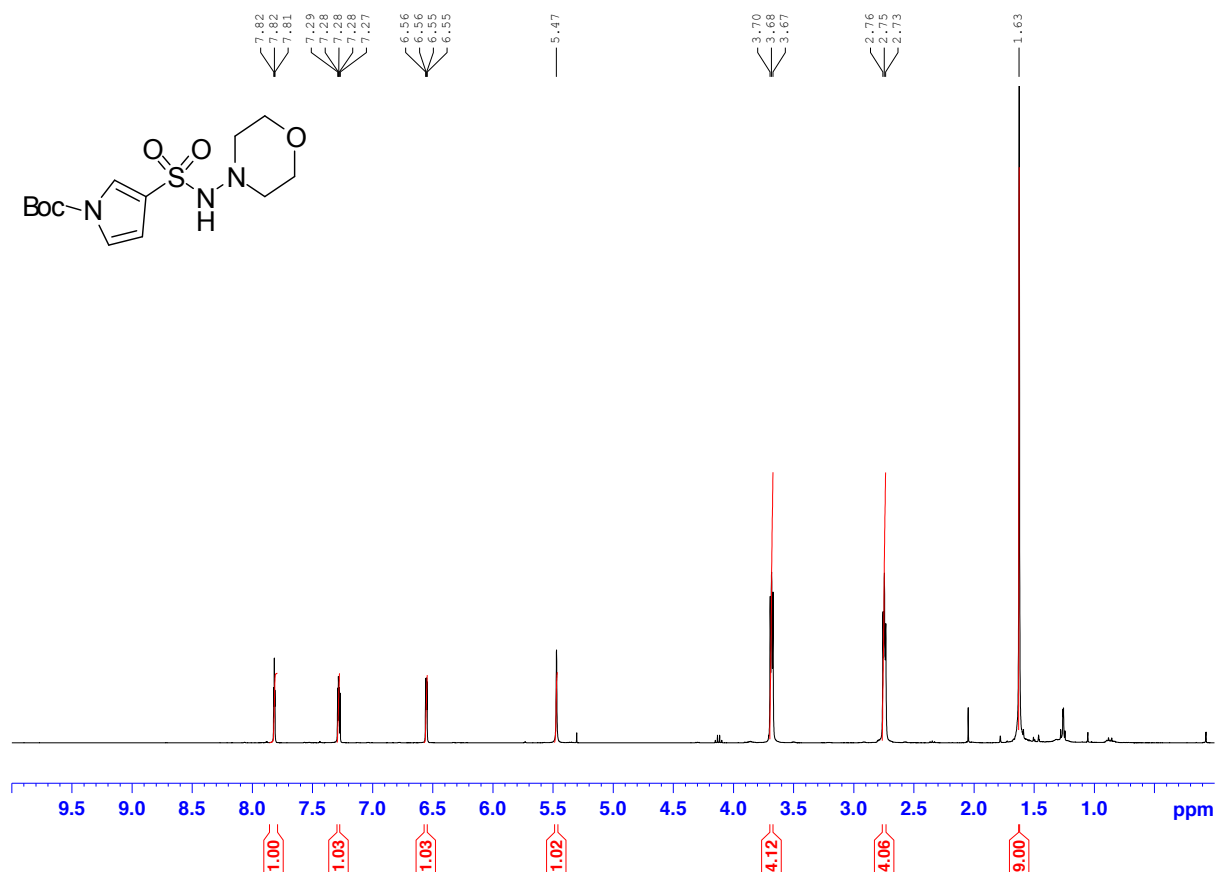


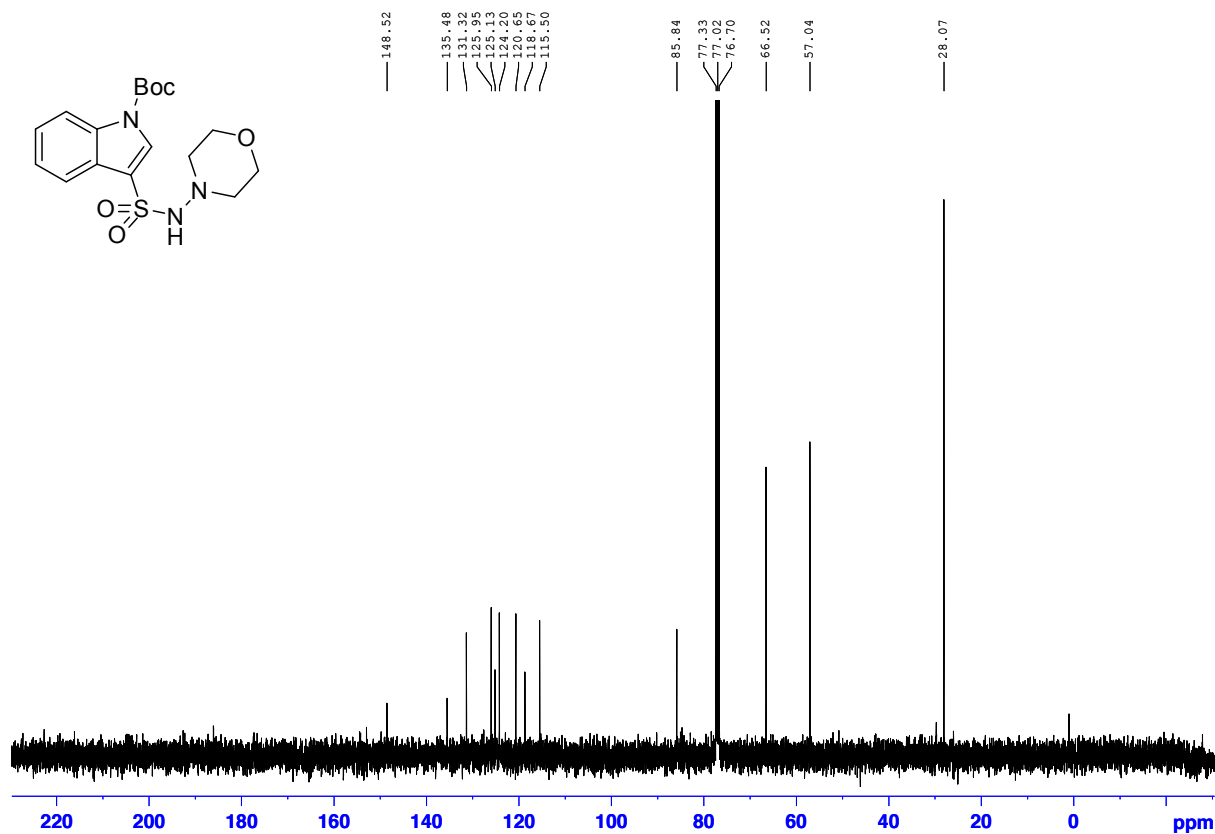
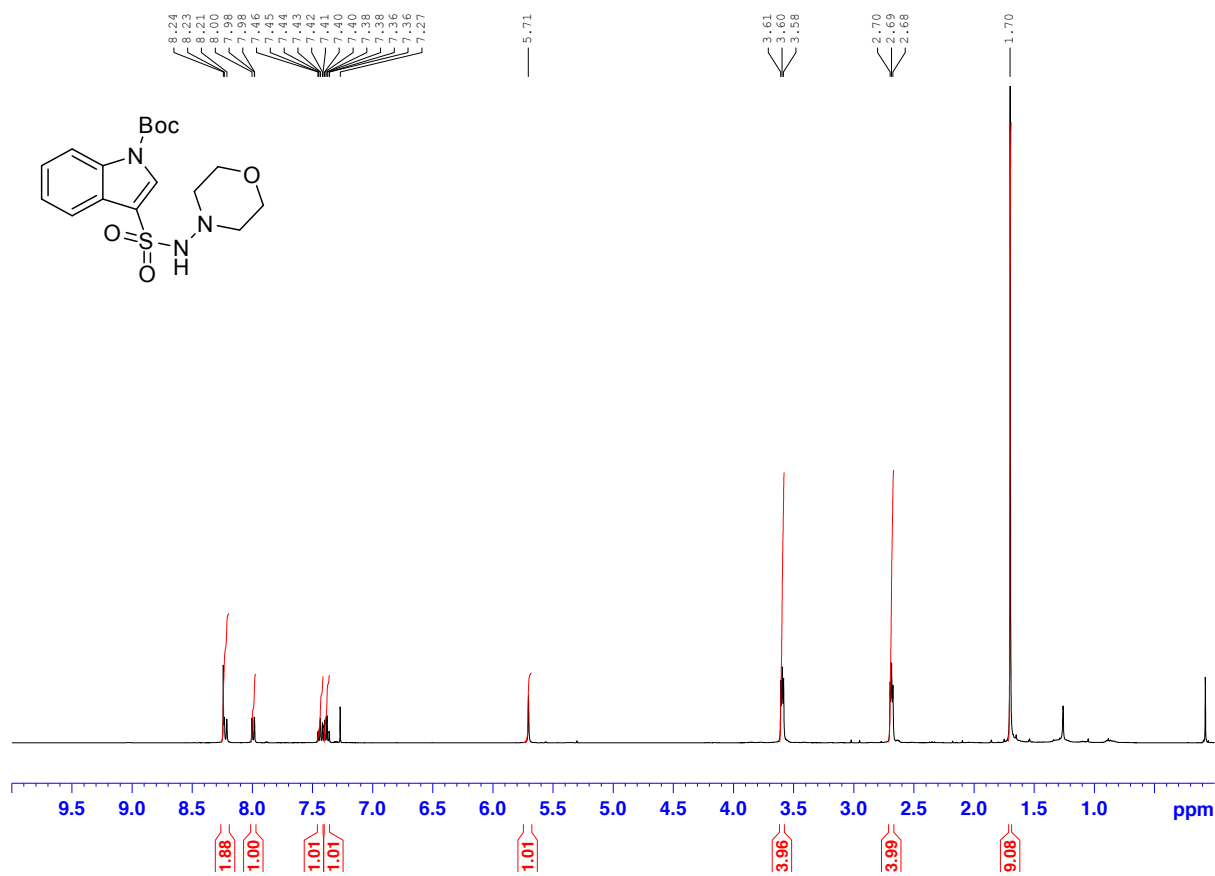


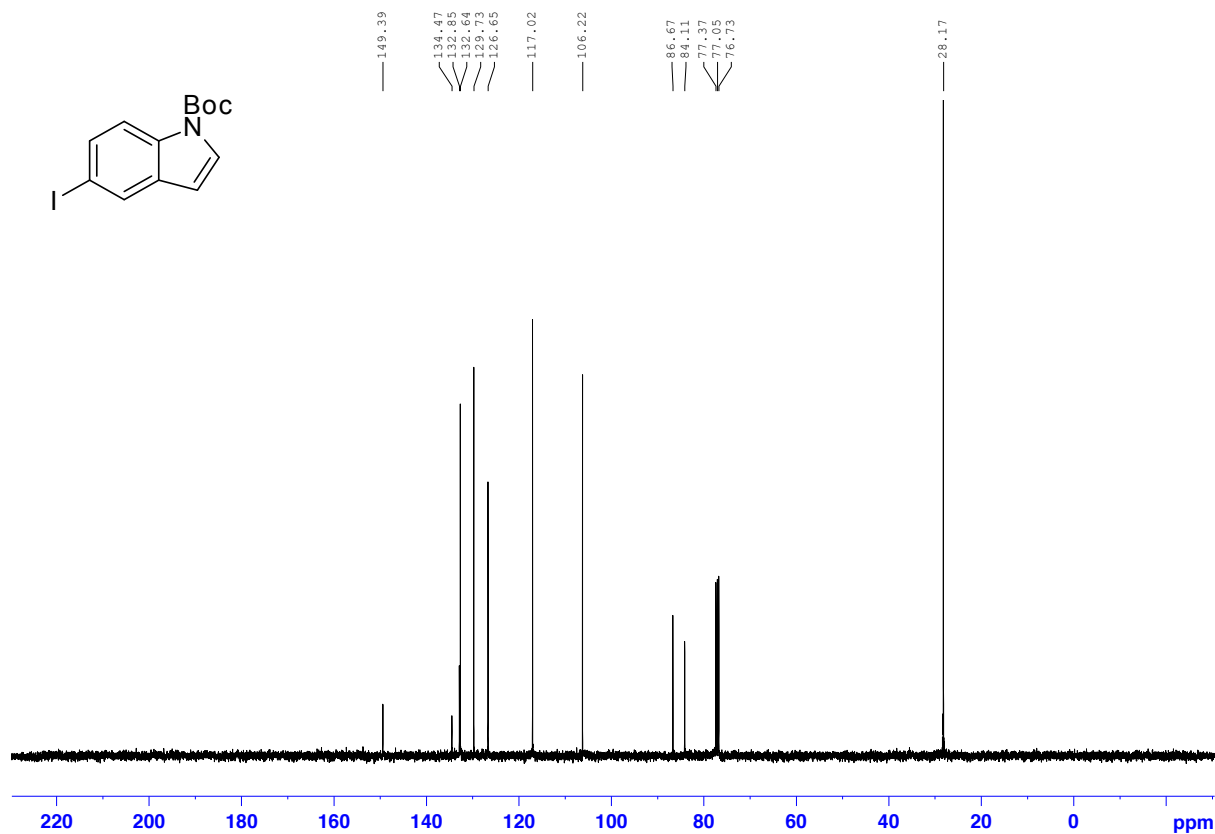
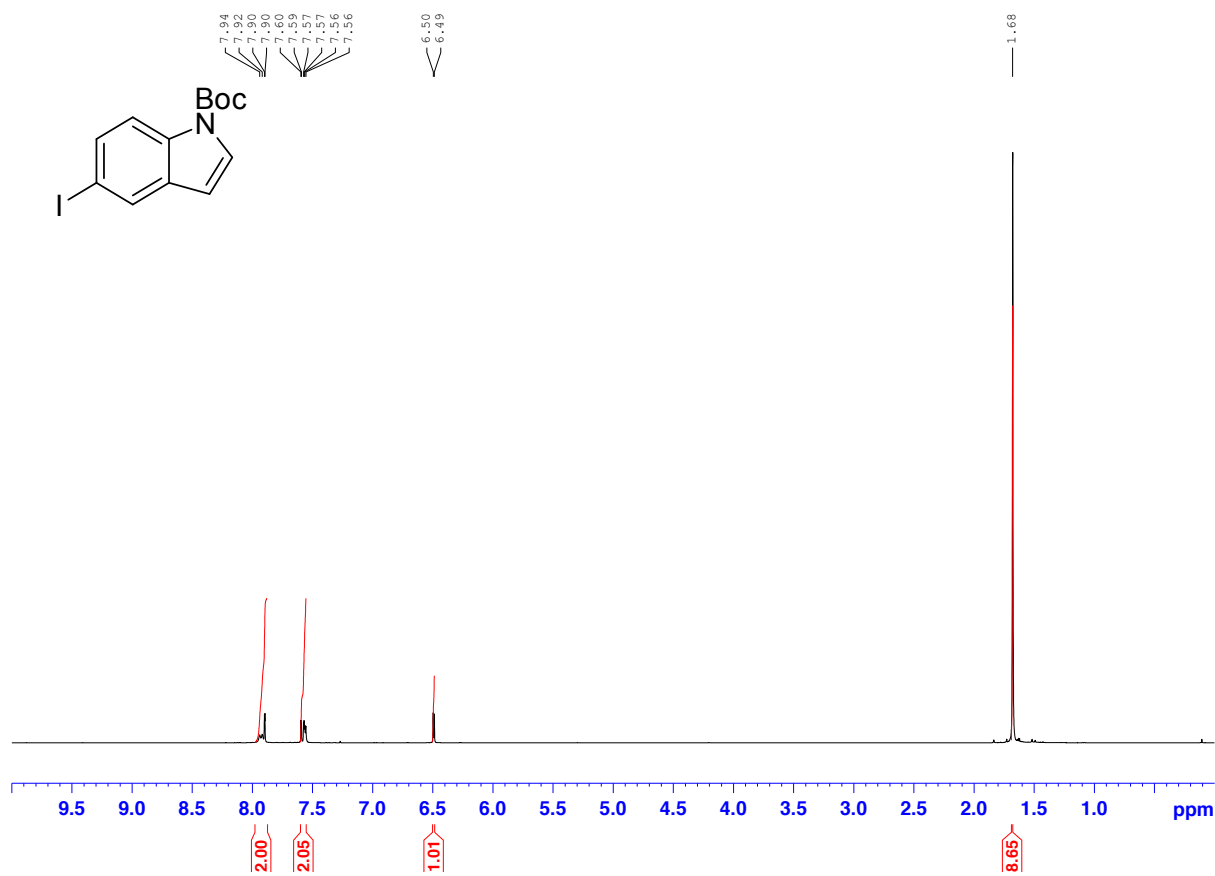


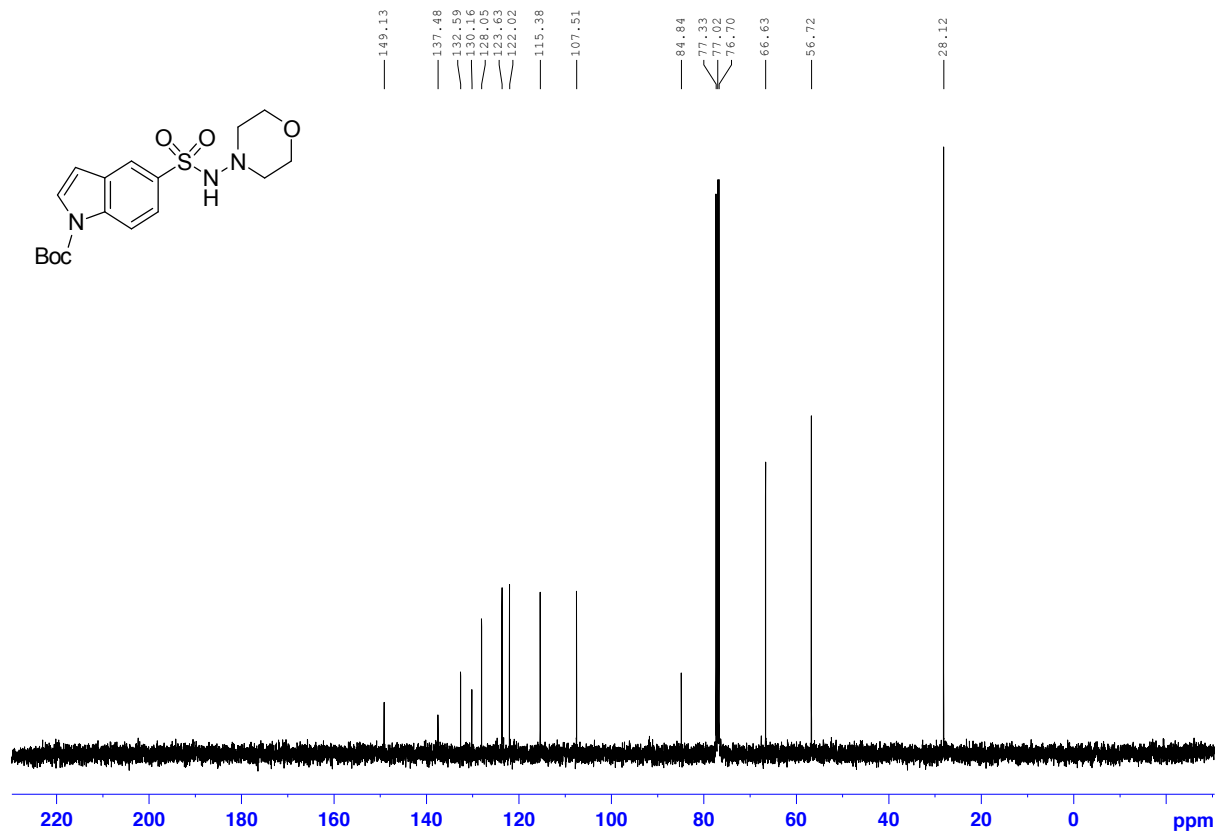
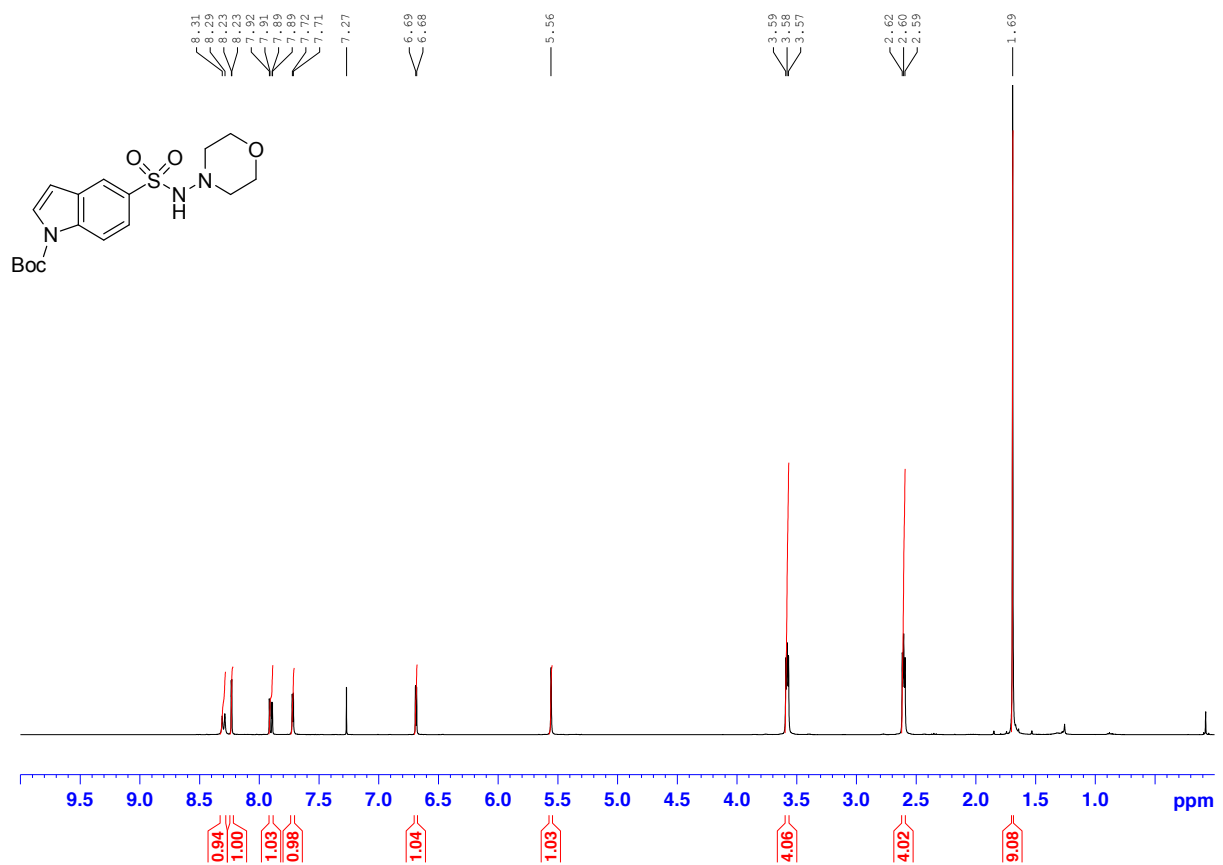


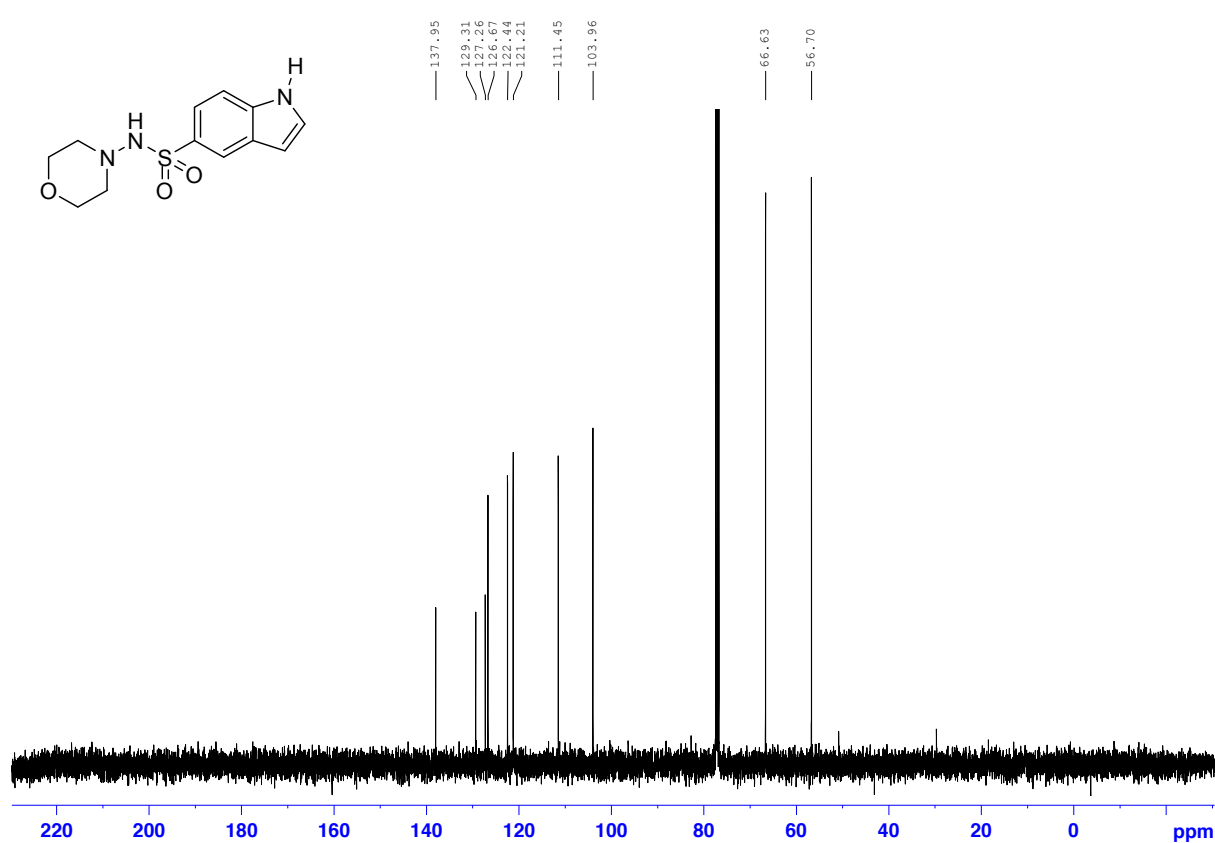
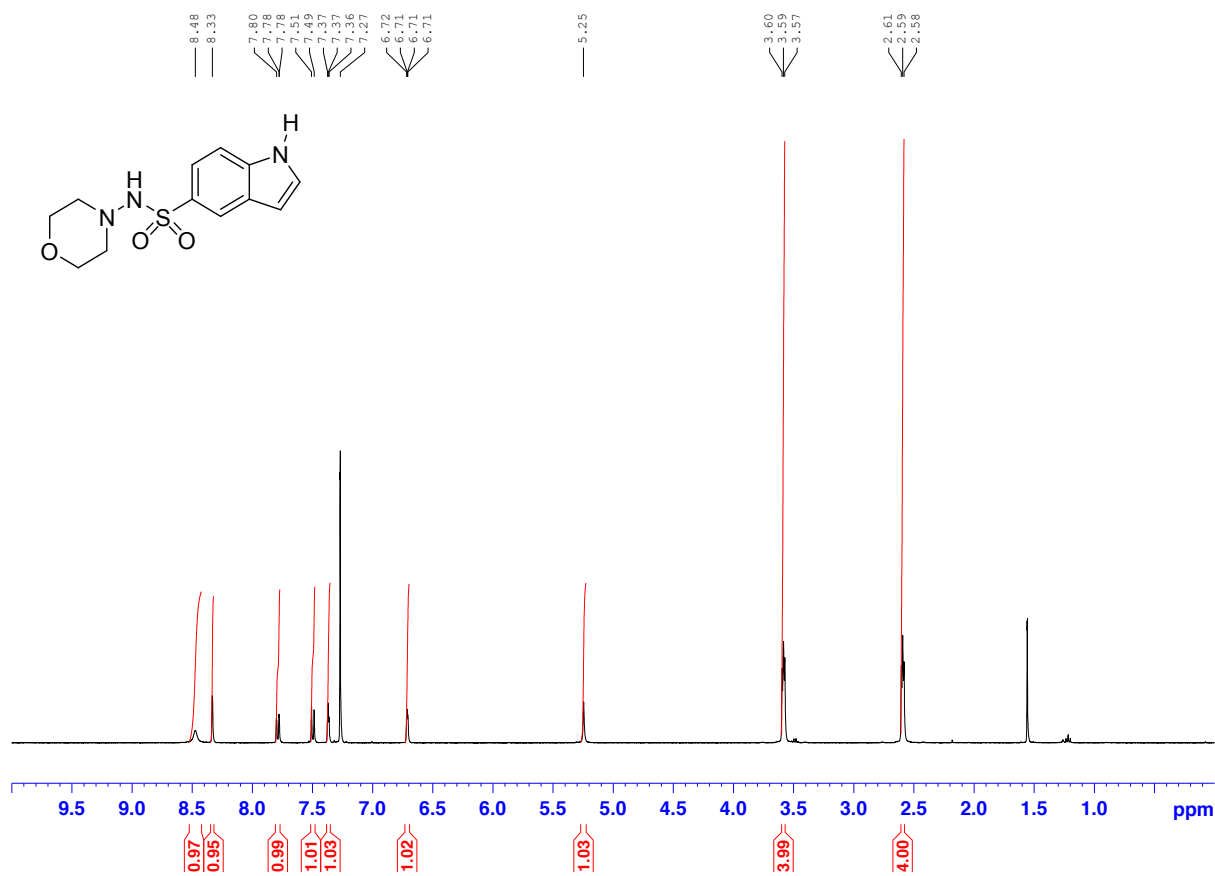


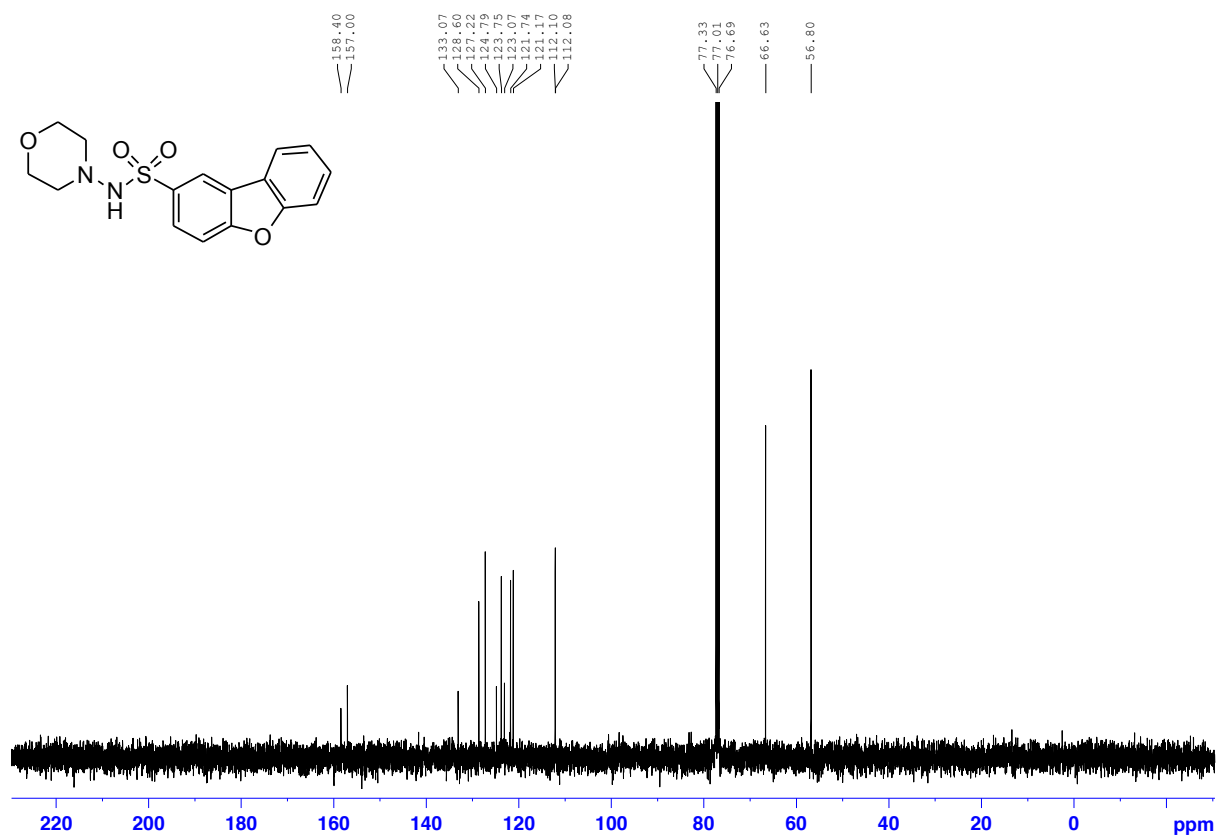
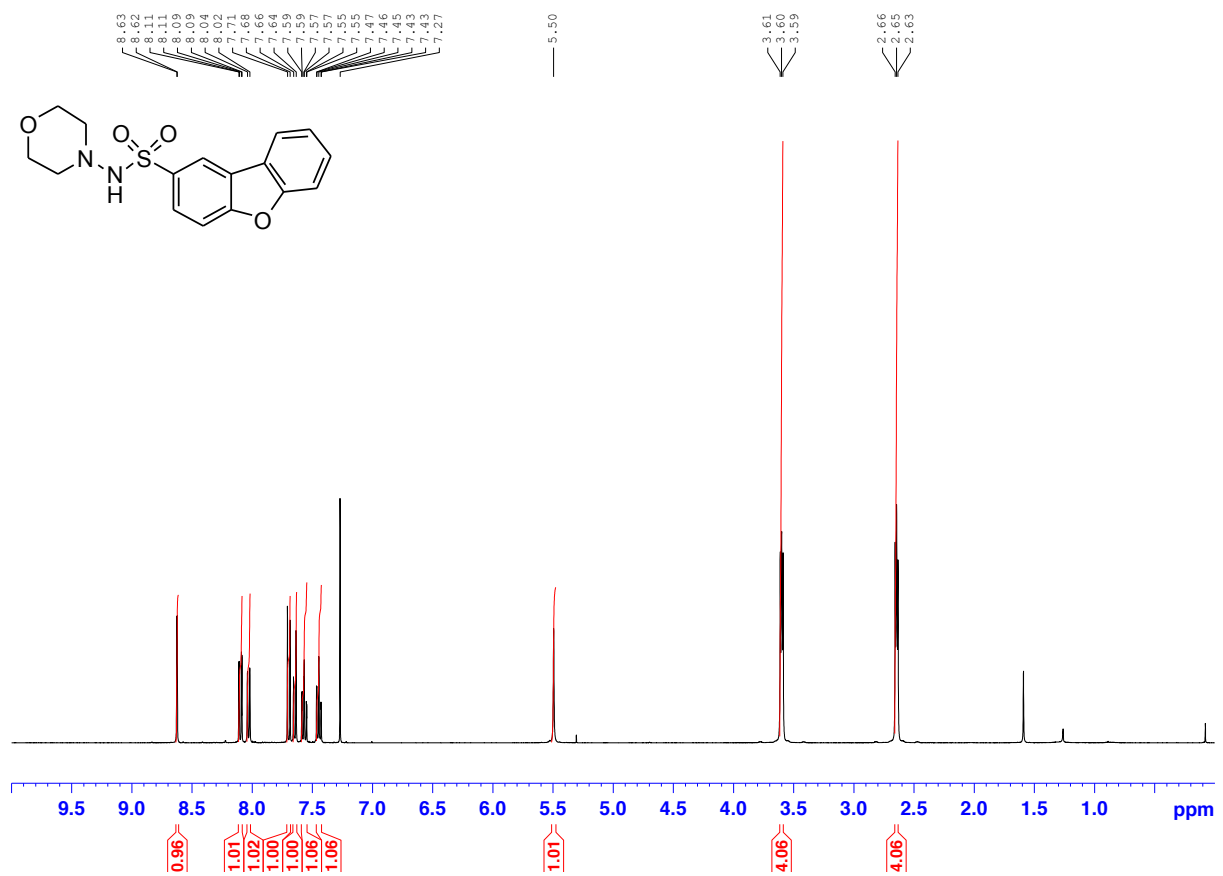


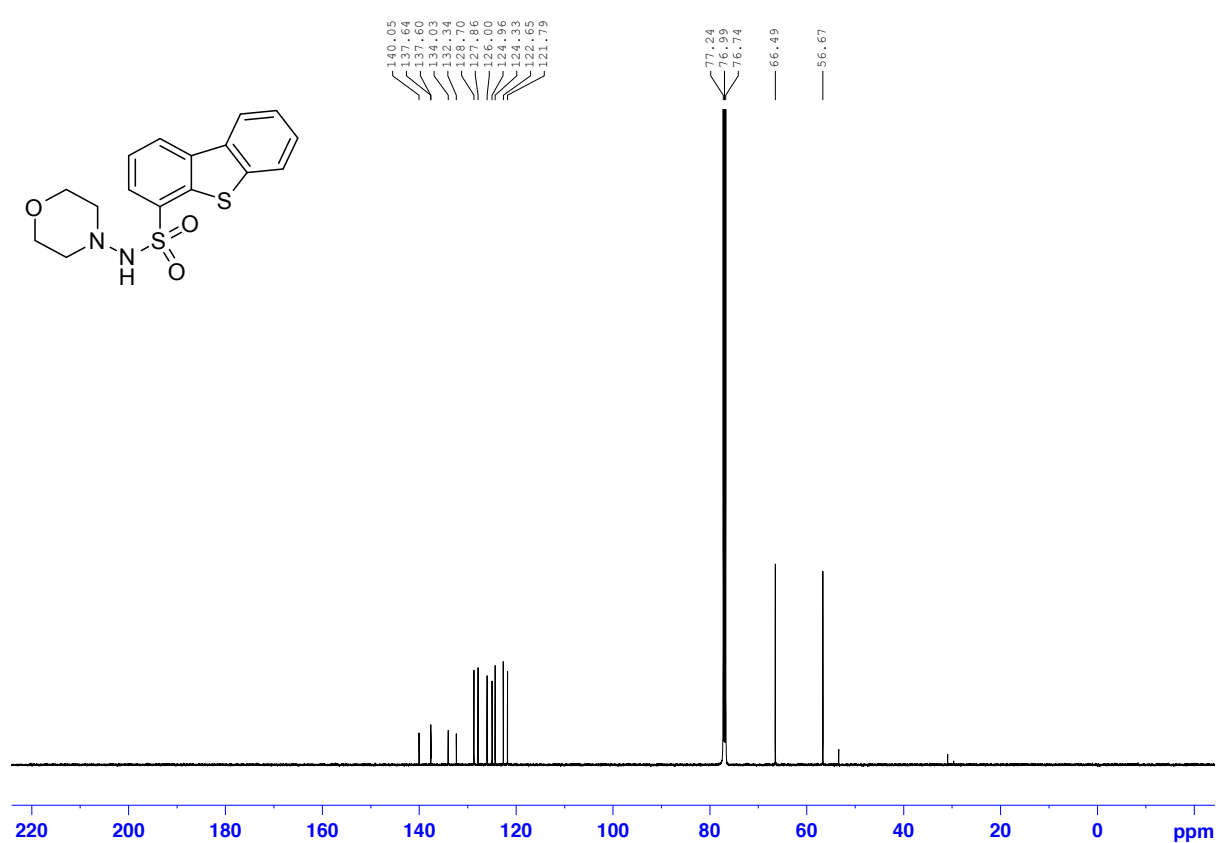
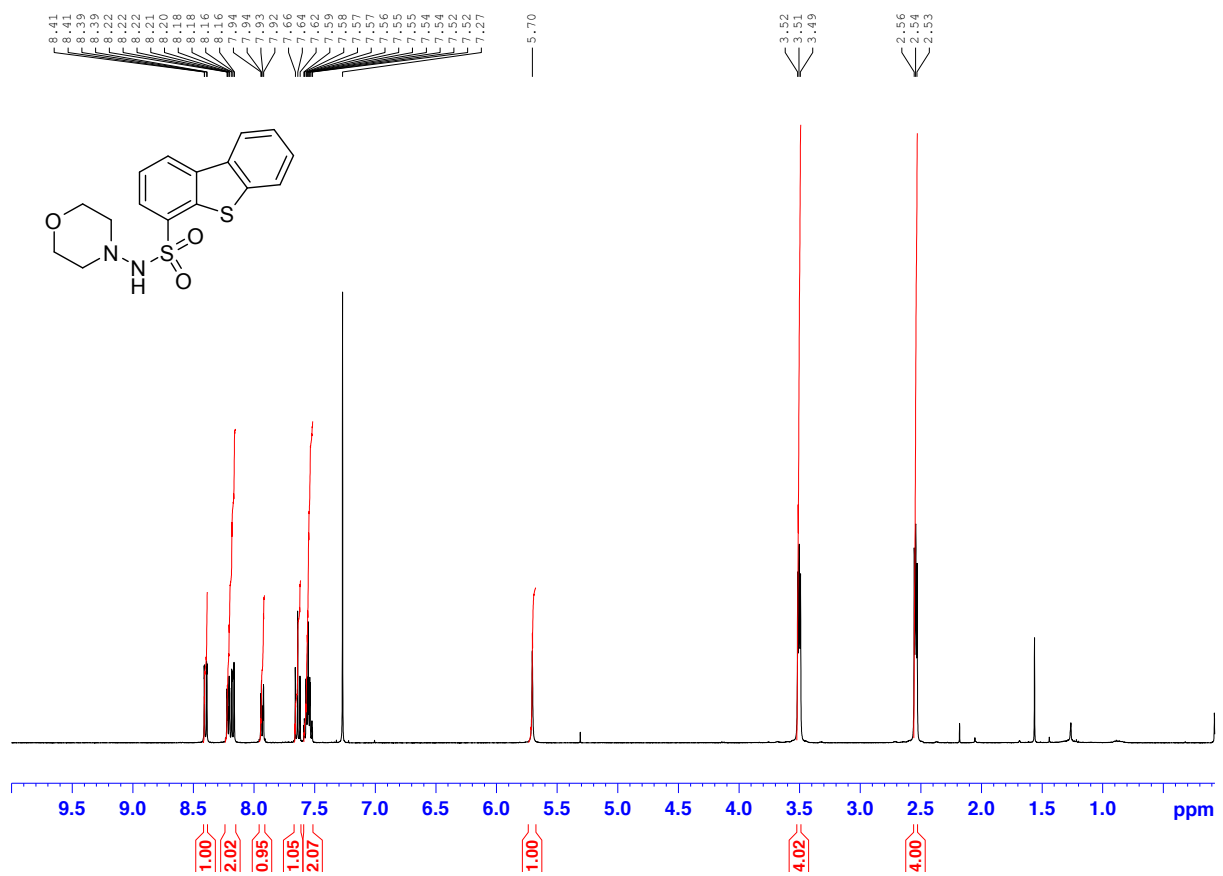


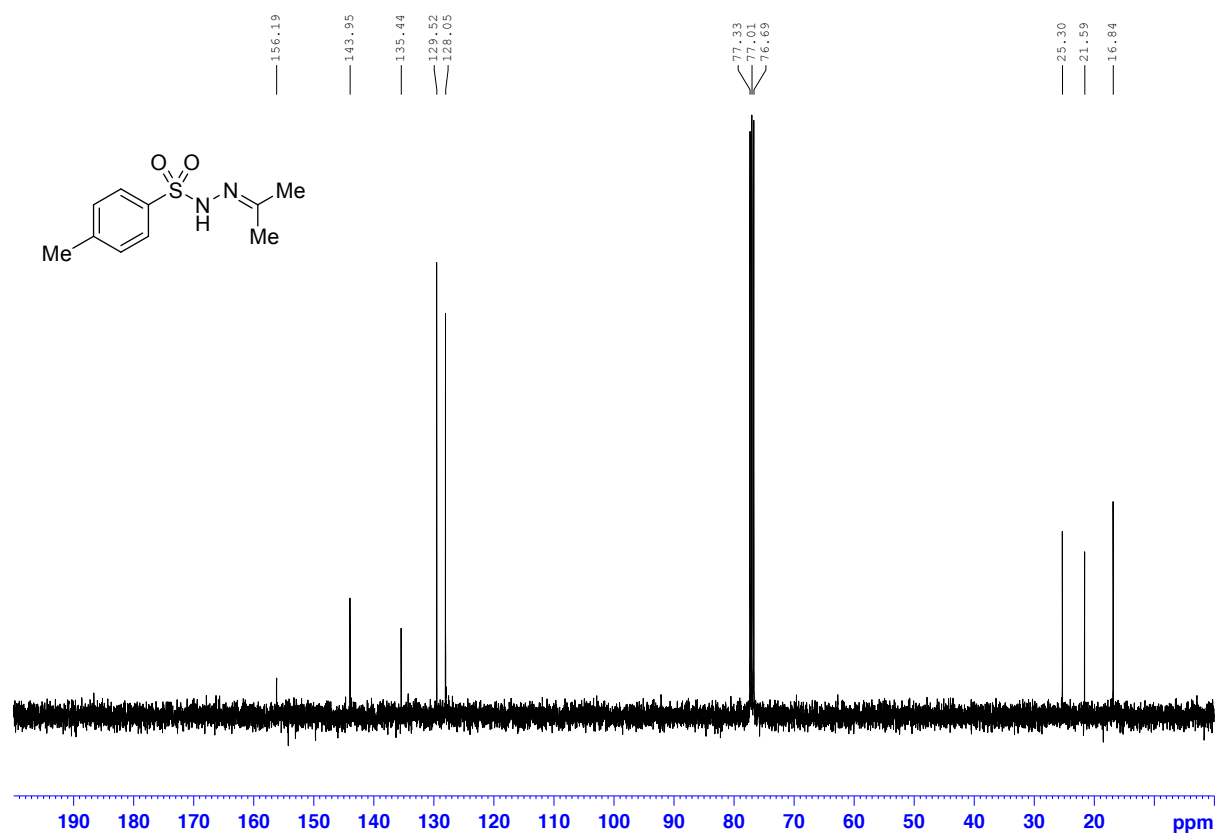
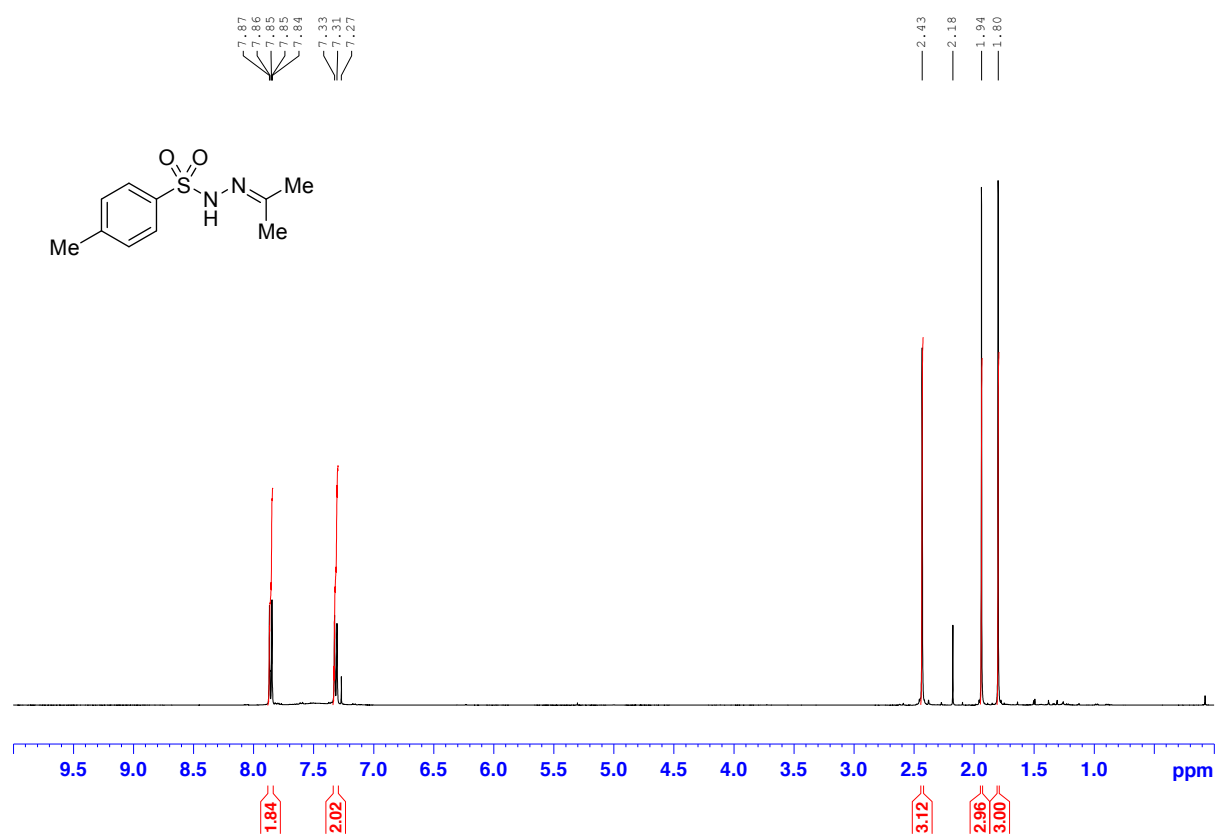


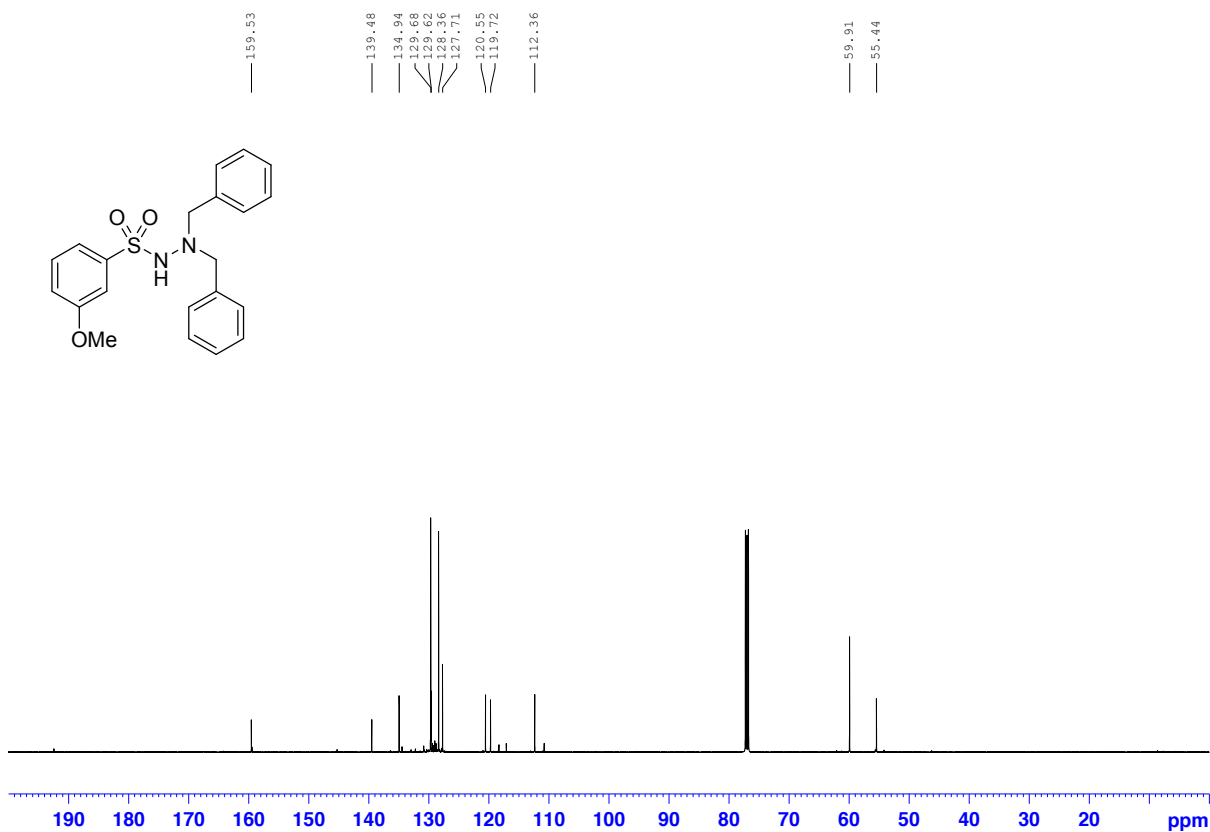
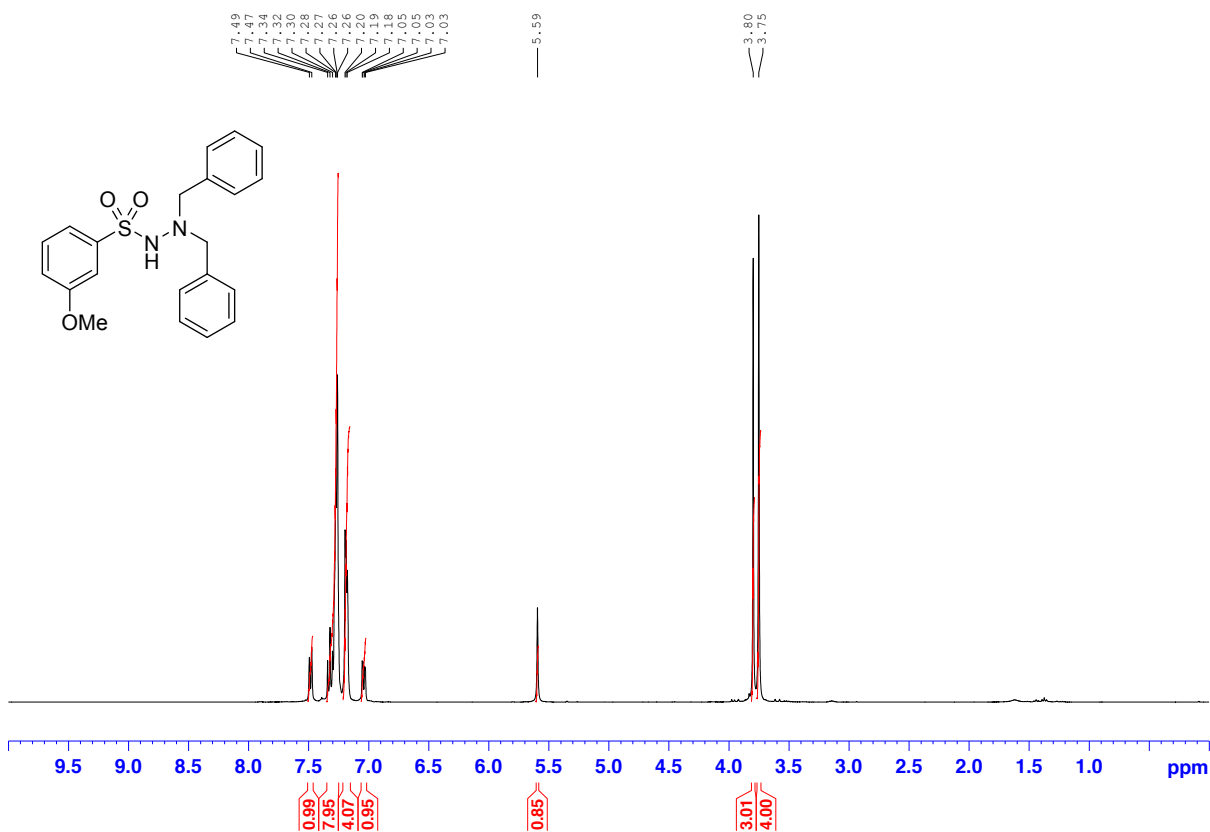


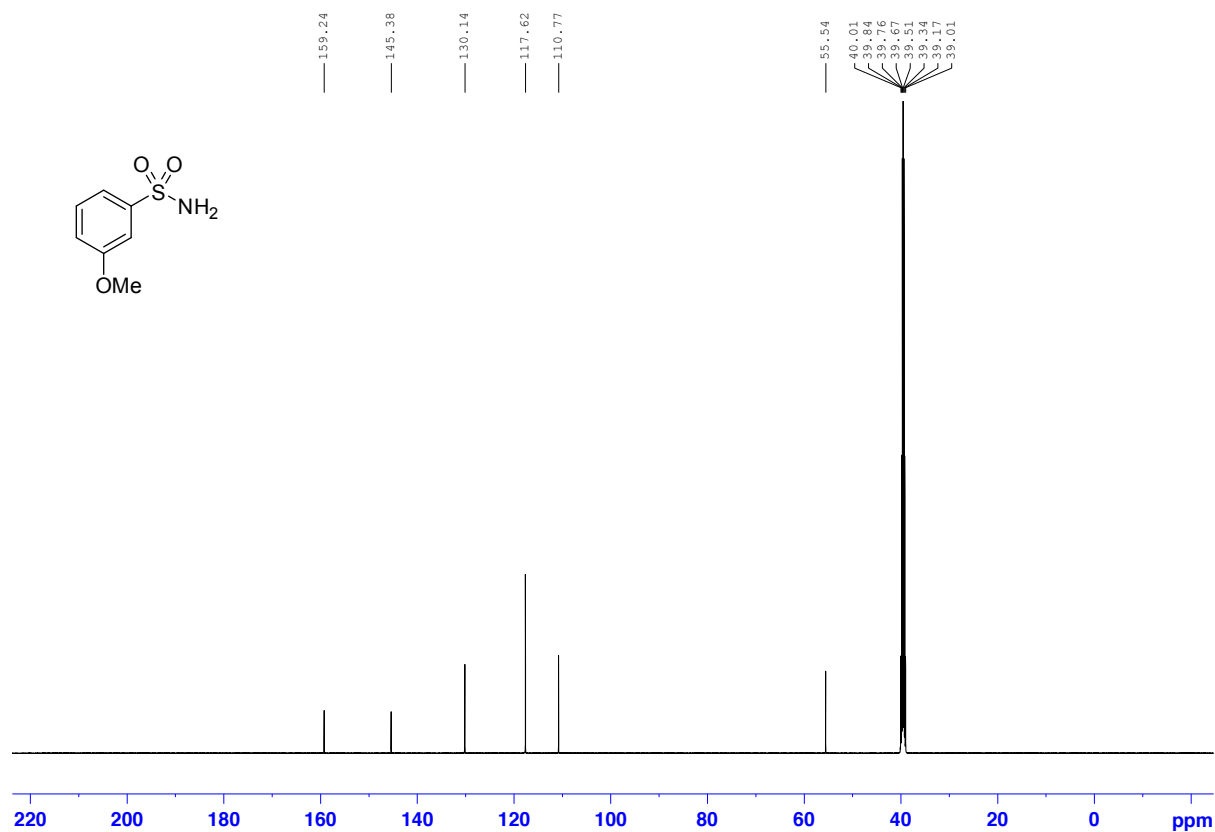
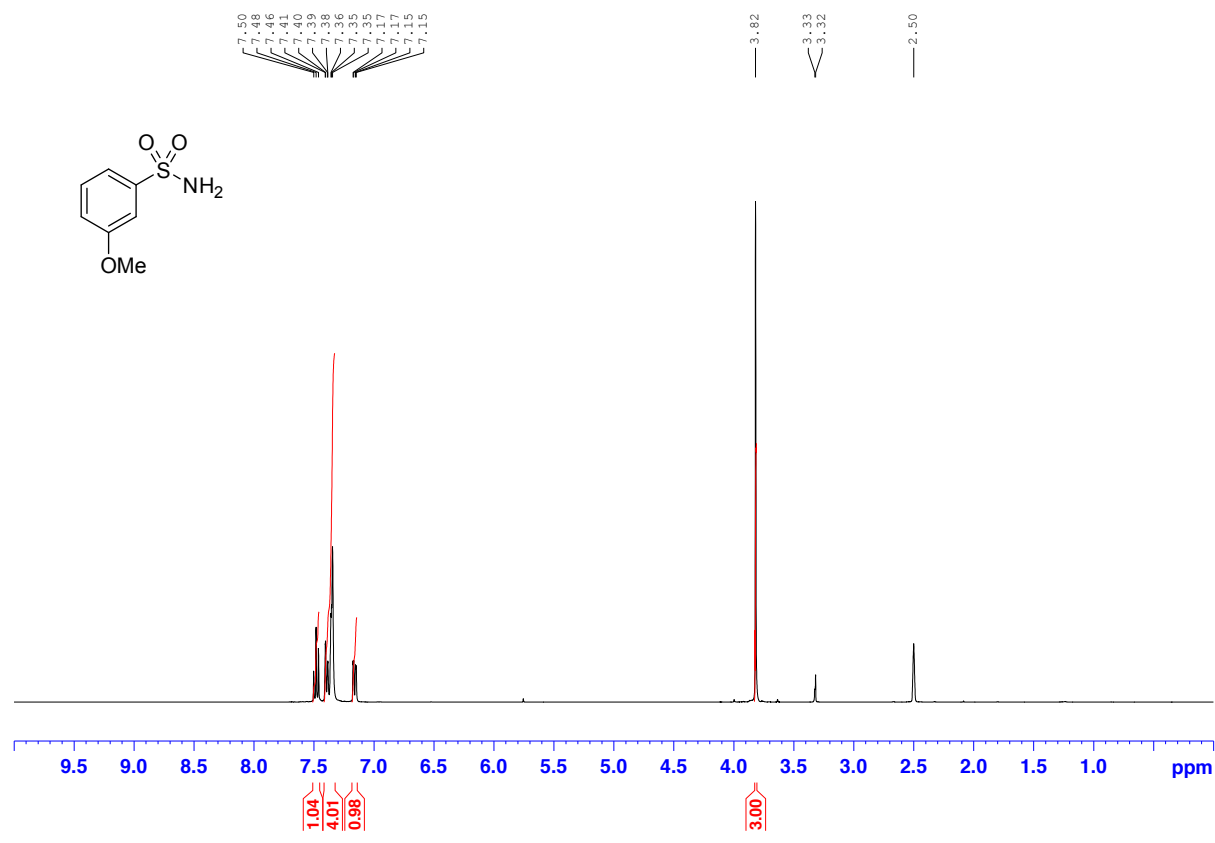


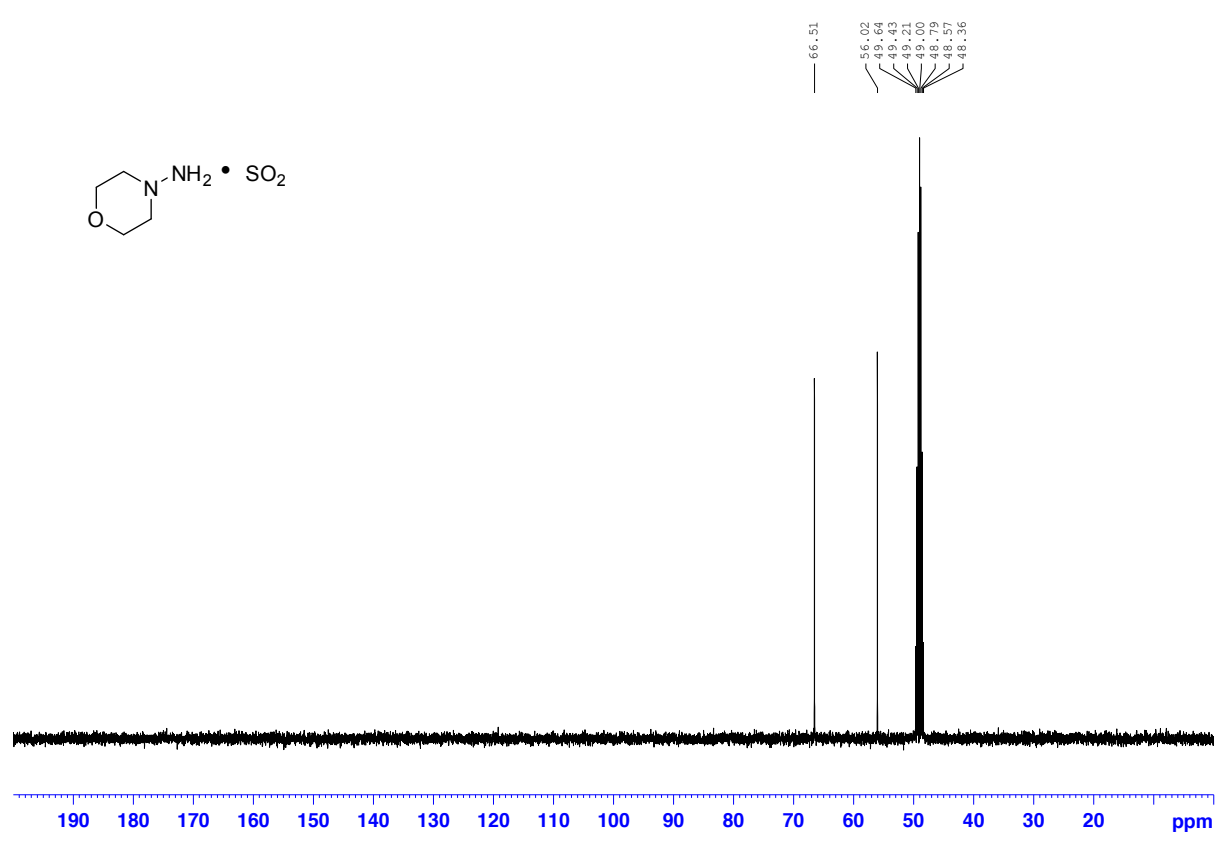
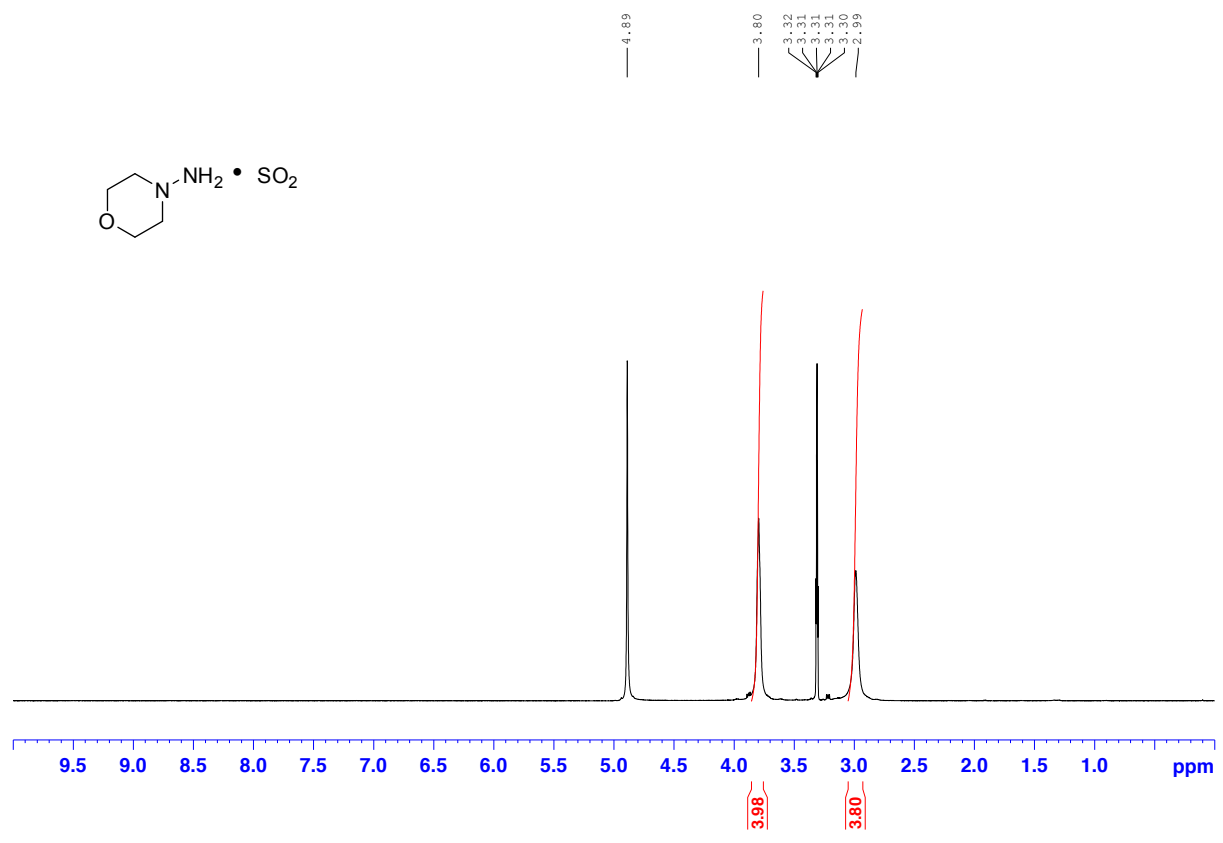






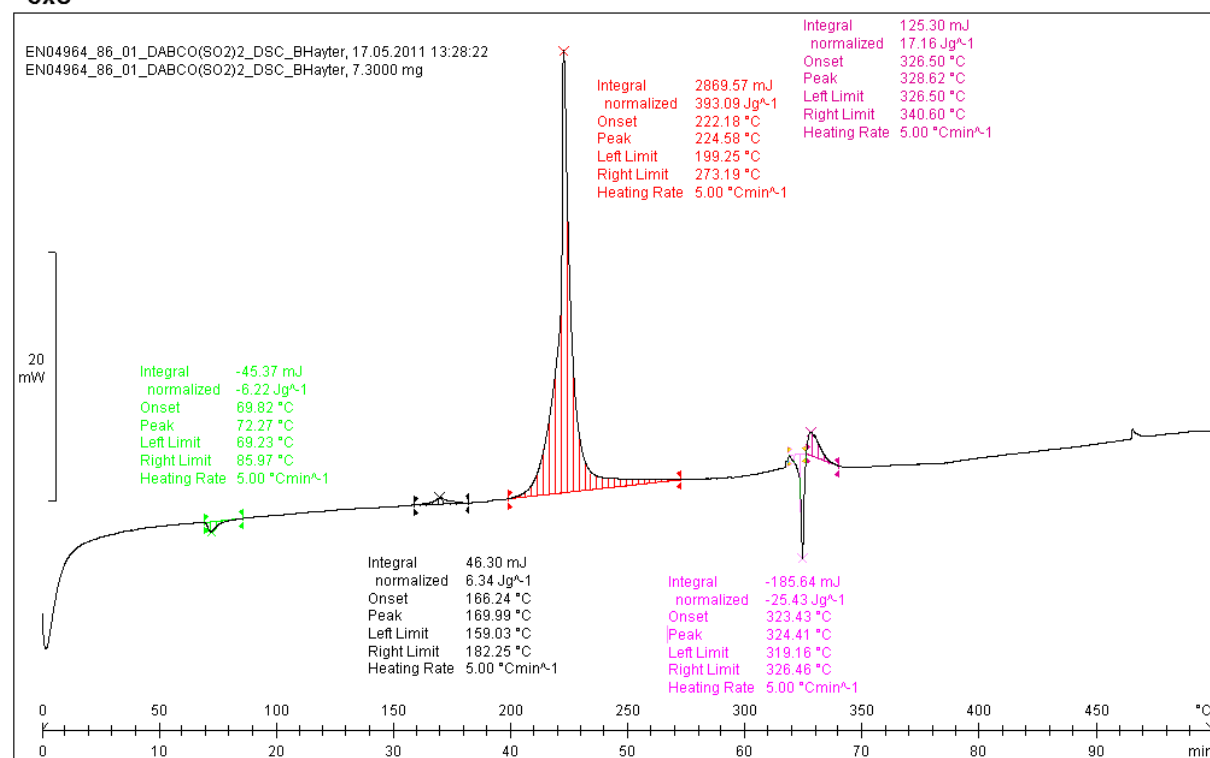






DABCO-(SO₂)₂ DSC

^exo



4-Aminomorpholine sulfur dioxide complex DSC

^exo

