Supporting Information

Palladium-Catalyzed Annulation of N-alkoxy benzsulfonamides with Arynes by C–H Functionalization: Access to Dibenzosultams

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1. General

Instrumentation

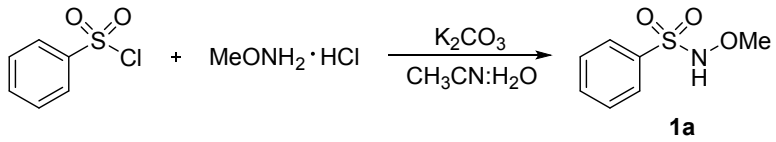
All the reactions were carried out under an Ar atmosphere using standard Schlenk techniques. Glassware was dried in an oven (150 ºC) and heated under reduced pressure before use. Reaction progress was monitored by thin layer chromatography (TLC) using Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm). The silica gel (size 200-300 mesh) used for the column chromatography was purchased from Qingdao Haiyang Chemistry Plant (China). NMR spectra were recorded on a Bruker Avance 400 spectrometers using $CDCl_3$ and DMSO-d_6 as a solvent. Chemical shifts (δ) are reported in ppm, using TMS as an internal standard. Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant *J* (Hz) and integration. Melting points were uncorrected. High resolution mass spectrometry (HRMS) was recorded using electron-spray ionization (ESI) technique. The GC yields were determined by GC analysis on an Agilent 6890N Gas Chromatography with 1,3,5-trimethoxybenzene as an internal standard.

Chemicals

Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification. Molecular sieves (4 Å) were dried at 120 ºC for 24 h prior to use. All solvents were dried by employing a solvent purification system MB SPS-800, degassed and stored over molecular sieves under a nitrogen atmosphere. CsF was vacuum dried at 100 ºC for 12 h. *N*-alkoxy benzsulfonamides **1a–1r**[1] and **1a-*d*$_5$**[2] were prepared according to the reported procedure. Aryne precursors **2a-e** were prepared according to literature procedures.[3]

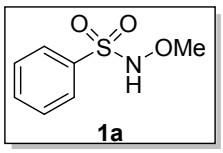
2. Experimental Procedures and Spectroscopic Data for the New Compounds

2.1 A Typical Procedure for Synthesis of *N*-Methoxy Benzsulfonamide 1a[1]



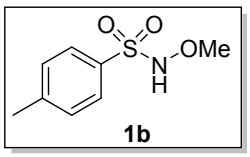
1a

To a 150 mL round bottom flask equipped with a large magnetic stir bar, benzenesulfonyl chloride (883 mg, 5 mmol, 1.0 equiv) dissolved in acetonitrile (30 mL) and O-methylhydroxylamine hydrochloride (501 mg, 6 mmol, 1.2 equiv) dissolved in water (30 mL), K_2CO_3 (898 mg, 6.5 mmol, 1.3equiv). The reaction was stirred at room temperature overnight. The mixture was extracted with CH_2Cl_2 (3×30 mL), the organic layer was dried with sodium sulfate. Solvent was removed under reduced pressure and the crude product **1a** was further purified through flash column chromatography.



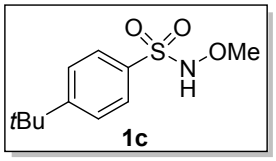
1a

***N*-methoxy benzsulfonamide (1a).** Isolated in 88% yield (822.8 mg, 4.40 mmol) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.92 (d, J = 7.6 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.7 Hz, 2H), 7.39 (s, 1H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, rt): δ 136.6, 133.9, 129.2, 128.5, 65.1.



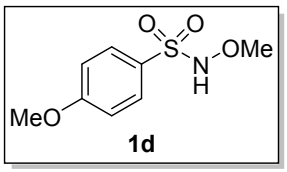
1b

***N*-methoxy-4-methylbenzsulfonamide (1b).** Isolated in 92% yield (924.6 mg, 4.60 mmol) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.80 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.23 (s, 1H), 3.77 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, rt): δ 145.0, 133.7, 129.8, 128.6, 65.1, 21.8.



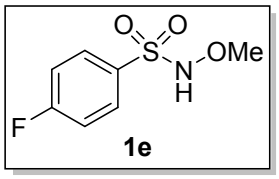
1c

4-(*tert*-butyl)-*N*-methoxy benzsulfonamide (1c). Isolated in 94% yield (1142.1 mg, 4.70 mmol) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.85 (d, J = 8.5 Hz, 2H), 7.55 (d, J = 8.6 Hz, 2H), 7.30 (s, 1H), 3.78 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, rt): δ 157.9, 133.6, 128.5, 126.2, 65.1, 35.4, 31.1.



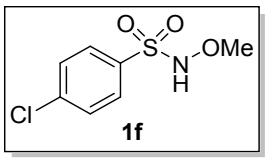
1d

4-methoxy-*N*-methoxy benzsulfonamide (1d). Isolated in 93% yield (1009.1 mg, 4.65 mmol) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.83 (d, J = 8.9 Hz, 2H), 7.29 (s, 1H), 6.98 (d, J = 8.9 Hz, 2H), 3.85 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, rt): δ 163.9, 130.8, 128.0, 114.4, 65.0, 55.8.



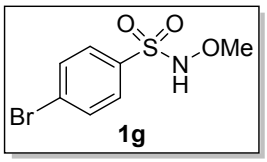
1e

4-fluoro-*N*-methoxy benzsulfonamide (1e). Isolated in 88% yield (902.0 mg, 4.40 mmol) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.97-7.94 (m, 2H), 7.27-7.21 (m, 3H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, rt): δ 167.3, 164.8, 132.6, 132.6, 131.6, 131.5, 116.7, 116.4, 65.3.



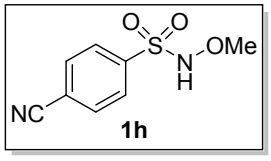
1f

4-chloro-*N*-methoxy benzsulfonamide (1f). Isolated in 93% yield (1207.7 mg, 4.65 mmol) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.86 (d, J = 8.6 Hz, 2H), 7.52 (d, J = 8.6 Hz, 2H), 7.23 (d, J = 3.3 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, rt): δ 140.7, 135.1, 130.1, 129.6, 65.3.



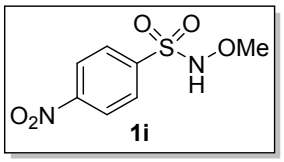
1g

4-bromo-*N*-methoxy benzsulfonamide (1g). Isolated in 85% yield (1126.3 mg, 4.25 mmol) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.78 (d, J = 8.6 Hz, 2H), 7.69 (d, J = 8.6 Hz, 2H), 7.20 (s, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, rt): δ 135.6, 132.6, 130.1, 129.3, 65.3.



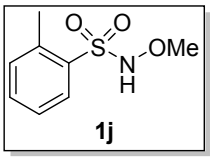
1h

4-cyano-*N*-methoxy benzsulfonamide (1h). Isolated in 78% yield (826.8 mg, 3.90 mmol) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.05 (d, J = 7.8 Hz, 2H), 7.85 (d, J = 7.9 Hz, 2H), 7.29 (s, 1H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, rt): δ 140.8, 133.0, 129.3, 117.6, 117.3, 65.6.



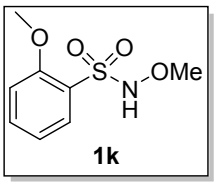
1i

***N*-methoxy-4-nitrobenzsulfonamide (1i).** Isolated in 78% yield (904.8 mg, 3.90 mmol) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 10.91 (s, 1H), 8.45 (d, J = 8.8 Hz, 2H), 8.10 (d, J = 8.8 Hz, 2H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, rt): δ 150.3, 142.6, 129.6, 124.4, 64.7.



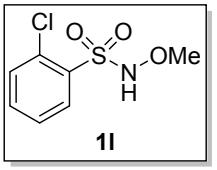
1j

***N*-methoxy-2-methylbenzsulfonamide (1j).** Isolated in 93% yield (934.7 mg, 4.65 mmol) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.92 (d, J = 7.8 Hz, 1H), 7.44-7.40 (m, 2H), 7.28 - 7.24 (m, 2H), 3.58 (s, 3H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, rt): δ 138.6, 134.9, 133.9, 132.7, 131.0, 126.4, 64.8, 20.7.



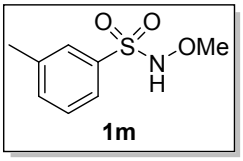
1k

***N*-methoxy-2-methoxybenzsulfonamide (1k).** Isolated in 86% yield (933.1 mg, 4.30 mmol) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.97-7.94 (m, 1H), 7.84 (s, 1H), 7.64-7.56 (m, 1H), 7.11 (t, J = 7.6 Hz, 1H), 7.05 (d, J = 8.4 Hz, 1H), 3.98 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, rt): δ 156.2, 135.7, 131.9, 124.4, 121.1, 112.3, 65.0, 56.7.



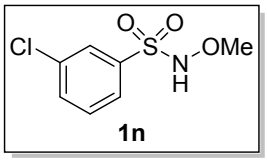
1l

2-chloro-*N*-methoxy benzsulfonamide (1l). Isolated in 84% yield (928.2 mg, 4.20 mmol) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.16-8.14 (m, 1H), 7.88 (s, 1H), 7.61- 7.52 (m, 2H), 7.50-7.45 (m, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, rt): δ 135.0, 134.3, 133.3, 131.7, 131.6, 127.6, 65.3.



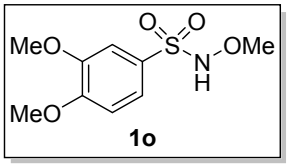
1m

***N*-methoxy-3-methylbenzsulfonamide (1m).** Isolated in 96% yield (964.8 mg, 4.80 mmol) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.73-7.72 (m, 2H), 7.43-7.41 (m, 2H), 7.15 (s, 1H), 3.79 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, rt): δ 139.5, 136.4, 134.8, 129.1, 128.9, 125.8, 65.2, 21.5.



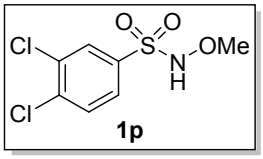
1n

3-chloro-*N*-methoxy benzsulfonamide (1n). Isolated in 86% yield (950.3 mg, 4.30 mmol) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.88 (t, J = 1.9 Hz, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.60 (d, J = 8.1 Hz, 1H), 7.51-7.45 (m, 2H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, rt): δ 138.2, 135.2, 134.0, 130.4, 128.5, 126.6, 65.2.



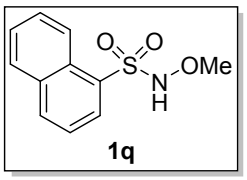
1o

3,4-dimethoxy-*N*-methoxy benzsulfonamide (1o). Isolated in 91% yield (1123.9 mg, 4.55 mmol) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.55-7.53 (m, 1H), 7.35 (s, 1H), 7.28 (s, 1H), 6.95 (d, J = 8.5 Hz, 1H), 3.92 (s, 3H), 3.89 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, rt): δ 153.7, 149.2, 128.1, 123.0, 110.8, 110.7, 65.1, 56.4, 56.3.



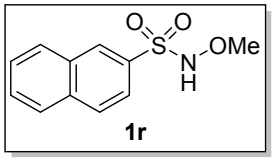
1p

3,4-dichloro-*N*-methoxy benzsulfonamide (1p). Isolated in 81% yield (1032.8 mg, 4.05 mmol) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.01 (d, J = 2.1 Hz, 1H), 7.76-7.73 (m, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.18 (s, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, rt): δ 139.1, 136.3, 134.0, 131.3, 130.6, 127.6, 65.5.



1q

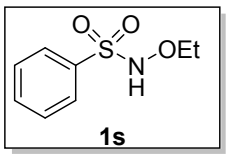
***N*-methoxy naphthalene-1-sulfonamide (1q).** Isolated in 86% yield (1019.1 mg, 4.30 mmol) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.64 (d, J = 8.6 Hz, 1H), 8.37 (d, J = 7.3 Hz, 1H), 8.15 (d, J = 8.2 Hz, 1H), 7.97 (d, J = 8.1 Hz, 1H), 7.70 (t, J = 7.7 Hz, 1H), 7.61 (q, J = 8.1 Hz, 2H), 7.36 (s, 1H), 3.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, rt): δ 135.7, 134.3, 132.3, 131.5, 129.4, 128.9, 128.7, 127.2, 124.4, 124.2, 65.2.



1r

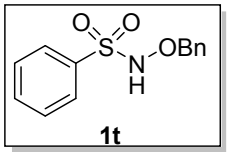
***N*-methoxy naphthalene-2-sulfonamide (1r).** Isolated in 91% yield (1078.4 mg, 4.55 mmol) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.52 (s, 1H), 7.98 (d, J = 8.7 Hz, 2H), 7.92-7.87 (m,

2H), 7.69-7.60 (m, 2H), 7.29 (s, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, rt): δ 135.5, 133.4, 132.1, 130.7, 129.5, 129.5, 129.5, 128.1, 127.8, 123.1, 65.3.



1s

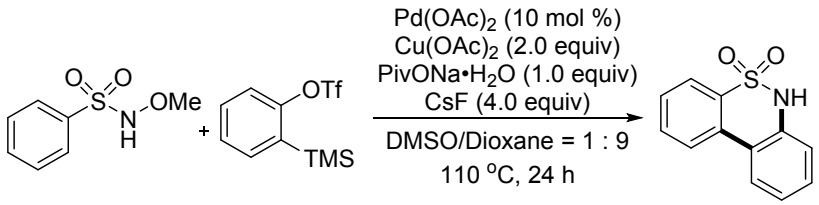
***N*-ethoxy benzsulfonamide (1s).** Isolated in 94% yield (944.7 mg, 4.70 mmol) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.97-7.92 (m, 2H), 7.69–7.63 (m, 1H), 7.56 (t, J = 7.7 Hz, 2H), 6.92 (s, 1H), 4.05 (q, J = 7.0, 2H), 1.21 (t, J = 7.0, 3H);^{13}C NMR (100 MHz, $CDCl_3$, rt): δ 136.7, 133.8, 129.1, 128.5, 73.0, 13.6.



1t

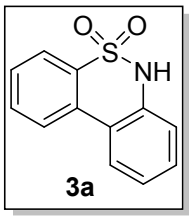
***N*-benzoxy benzsulfonamide (1t).** Isolated in 88% yield (1157.2 mg, 4.33 mmol) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$, rt): δ 7.95 (d, J = 7.6 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.55 (t, J = 7.7 Hz, 2H), 7.35 (s, 5H), 6.90 (s, 1H), 4.99 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, rt) : δ 136.7, 135.2, 133.9, 129.4, 129.1, 128.8, 128.5, 79.5.

2.2 A Typical Procedure for Palladium-Catalyzed Annulation of *N*-Methoxy Benzsulfonamide 1a with Benzyne Precursor 2a.

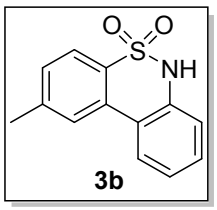


1a **2a** **3a**

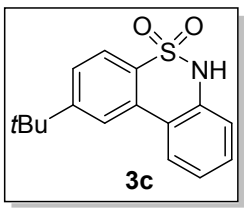
A flame-dried 25 mL Schlenk with a magnetic stir bar was charged with $Pd(OAc)_2$ (4.49 mg, 0.02 mmol, 10 mmol %), $Cu(OAc)_2$ (72.86 mg, 0.4 mmol), *N*-methoxybenzsulfonamide **1a** (37.40 mg, 0.2 mmol) , CsF (121.52 mg, 0.8 mmol) and PivONa·H_2O (28.43 mg, 0.2 mmol) in a mixed solvents of dioxane (2.7 mL) and DMSO (0.3 mL) under argon. To this solution were added 2-(trimethylsilyl)phenyl triflate (**2a**) (119.2 mg, 0.4 mmol) via a syringe. The reaction mixture was heated to 110 ºC for 24 h, then cooled to ambient temperature, quenched with water, and extracted with diethyl ether (20 mL × 3). The combined extracts were washed with brine and dried over anhydrous sodium sulfate. The volatiles were removed under reduced pressure to give crude products, which were purified by silica gel column chromatography (eluent: CH_2Cl_2). Further purification with recrystallization gave **3a** (37.9 mg, 0.164 mmol, 82%) as a white solid.



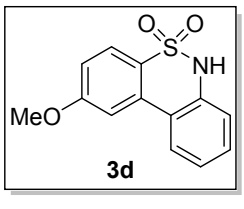
6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (3a).[4] Isolated in 82% yield (37.9 mg, 0.164 mmol) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6, rt): δ 11.39 (br.s, 1H), 8.26-8.20 (m, 2H), 7.94 (d, J = 7.8 Hz, 1H), 7.81 (t, J = 7.7 Hz, 1H), 7.67 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.22 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, rt): δ 136.5, 134.4, 132.6, 131.7, 130.4, 128.5, 125.6, 125.4, 123.9, 121.4, 121.1, 119.6. HRMS (ESI): *m/z* calcd for $C_{12}H_9NO_2S$: $[M+Na]^+$ 254.0245. Found: 254.0241.



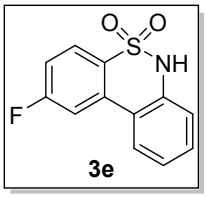
2-methyl-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (3b).[4] Isolated in 83% yield (40.7 mg, 0.166 mmol) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6, rt): δ 11.31 (br.s, 1H), 8.22 (d, J = 8.0 Hz, 1H), 8.09 (s, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.48 (t, J = 8.2 Hz, 2H), 7.31 (t, J = 7.7 Hz, 1H), 7.22 (d, J = 8.0 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, rt): δ 142.8, 136.7, 132.0, 131.7, 130.2, 129.1, 125.7, 125.3, 123.7, 121.4, 121.1, 119.5, 21.3. HRMS (ESI): *m/z* calcd for $C_{13}H_{11}NO_2S$: $[M+Na]^+$ 268.0403. Found: 268.0393.



2-(*tert*-butyl)-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (3c). Isolated in 86% yield (49.4 mg, 0.172 mmol) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6, rt): δ 11.29 (br.s, 1H), 8.30 (d, J = 8.0 Hz, 1H), 8.14 (s, 1H), 7.86 (d, J = 8.2 Hz, 1H), 7.70 (d, J = 8.3 Hz, 1H), 7.46 (t, J = 7.7 Hz, 1H), 7.30 (t, J = 7.7 Hz, 1H), 7.20 (d, J = 8.0 Hz, 1H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6, rt): δ 155.5, 136.7, 132.0, 131.5, 130.2, 125.6, 125.5, 123.8, 122.1, 121.7, 121.1, 119.5, 35.2, 30.8. HRMS (ESI): *m/z* calcd for $C_{16}H_{17}NO_2S$ $[M+Na]^+$ 310.0872. Found: 310.0858.

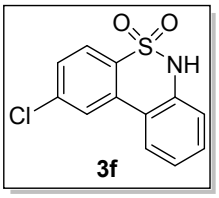


2-methoxy-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (3d).[5] Isolated in 89% yield (46.5 mg, 0.178 mmol) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6, rt): δ 11.29 (br.s, 1H), 8.25 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 8.7 Hz, 1H), 7.68 (s, 1H), 7.47 (t, J = 7.7 Hz, 1H), 7.28 (t, J = 7.7 Hz, 1H), 7.23-7.17 (m, 2H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, rt): δ 162.2, 137.0, 133.9, 130.5, 127.3, 125.8, 123.7, 123.4, 121.3, 119.5, 114.8, 109.8, 55.9. HRMS (ESI): *m/z* calcd for $C_{13}H_{11}NO_3S$ $[M+Na]^+$ 284.0352. Found: 284.0349.



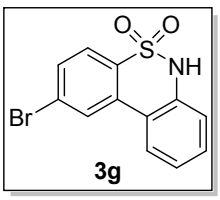
3e

2-fluoro-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (3e).[6] Isolated in 72% yield (35.9 mg, 0.144 mmol) as a faint yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6, rt): δ 11.50 (br.s, 1H), 8.23 (d, J = 7.8 Hz, 1H), 8.16-8.12 (m, 1H), 8.03-8.00 (m, 1H), 7.51 (t, J = 7.4 Hz, 2H), 7.30 (t, J = 7.6 Hz, 1H), 7.23 (d, J = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, rt): δ 165.4, 162.9, 136.8, 135.0, 134.9, 131.1, 130.9, 130.9, 125.9, 124.5, 124.4, 123.9, 120.7, 120.7, 119.6, 116.0, 115.8, 112.5, 112.3; ^{19}F NMR (564 MHz, DMSO-d_6, rt): δ –105.5. HRMS (ESI): *m/z* calcd for $C_{12}H_8FNO_2S$ $[M+Na]^+$ 272.0152. Found: 272.0148.



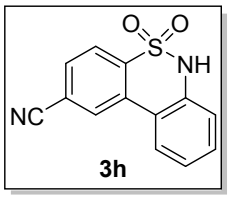
3f

2-chloro-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (3f). Isolated in 66% yield (35.0 mg, 0.132 mmol) as a faint yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6, rt): δ 11.56 (br.s, 1H), 8.36 (s, 1H), 8.28 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.51 (t, J = 7.7 Hz, 1H), 7.30 (t, J = 7.7 Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, rt): δ 137.6, 136.9, 133.8, 133.0, 131.1, 128.5, 125.9, 125.4, 124.0, 123.3, 120.5, 119.7. HRMS (ESI): *m/z* calcd for $C_{12}H_8ClNO_2S$ $[M+Na]^+$ 287.9856. Found: 287.9852.

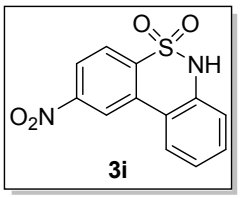


3g

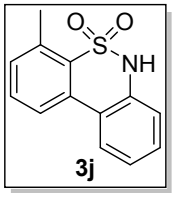
2-bromo-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (3g). Isolated in 59% yield (36.5 mg, 0.118 mmol) as a faint yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6, rt): δ 11.57 (br.s, 1H), 8.49 (s, 1H), 8.29 (d, J = 8.0 Hz, 1H), 7.87 (t, J = 8.6 Hz, 2H), 7.51 (t, J = 7.6 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.22 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, rt): δ 136.8, 133.9, 133.4, 131.4, 131.1, 128.3, 126.5, 125.9, 124.0, 123.3, 120.4, 119.7. HRMS (ESI): *m/z* calcd for $C_{12}H_8BrNO_2S$ $[M+Na]^+$ 331.9351. Found: 331.9344.



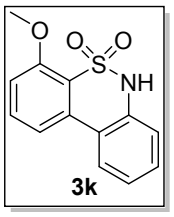
6*H*-dibenzo[c,e][1,2]thiazine-2-carbonitrile 5,5-dioxide (3h). Isolated in 58% yield (29.7 mg, 0.116 mmol) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6, rt): δ 11.77 (br.s, 1H), 8.83 (s, 1H), 8.35 (d, J = 7.9 Hz, 1H), 8.11 (s, 2H), 7.55 (t, J = 7.6 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.25 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, rt): δ 137.2, 136.6, 132.8, 131.8, 131.5, 130.2, 126.0, 124.3, 122.4, 120.3, 119.9, 117.7, 115.4. HRMS (ESI): *m/z* calcd for $C_{13}H_8N_2O_2S$ $[M+Na]^+$ 279.0199. Found: 279.0197.



2-nitro-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (3i).[4] Isolated in 53% yield (29.3 mg, 0.106 mmol) as a faint yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6, rt): δ 11.85 (br.s, 1H), 8.99-8.92 (m, 1H), 8.44-8.38 (m, 2H), 8.20 (d, J = 8.6 Hz, 1H), 7.57 (t, J = 7.5 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.27 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, rt): δ 149.9, 138.3, 136.7, 133.4, 131.7, 126.1, 124.4, 123.4, 123.2, 120.9, 120.5, 119.9. HRMS (ESI): *m/z* calcd for $C_{12}H_8N_2O_4S$ $[M+Na]^+$ 299.0097. Found: 299.0087.

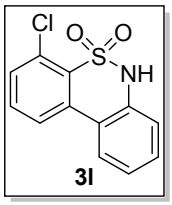


4-methyl-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (3j). Isolated in 85% yield (41.7 mg, 0.170 mmol) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6, rt): δ 11.31 (br.s, 1H), 8.12 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 8.1 Hz, 1H), 7.65 (t, J = 7.7 Hz, 1H), 7.47-7.44 (m, 2H), 7.27 (t, J = 7.7 Hz, 1H), 7.17 (d, J = 8.0 Hz, 1H), 2.68 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, rt): δ 136.0, 134.0, 133.7, 132.7, 132.0, 131.5, 130.2, 125.9, 124.0, 123.8, 122.0, 119.4, 20.1. HRMS (ESI): *m/z* calcd for $C_{13}H_{11}NO_2S$ $[M+Na]^+$ 268.0403. Found: 268.0396.

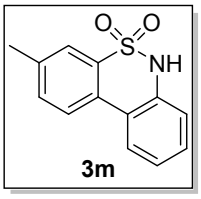


4-methoxy-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (3k). Isolated in 89% yield (46.5 mg, 0.178 mmol) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6, rt): δ 11.13 (br.s, 1H), 8.08 (d, J = 8.0 Hz,

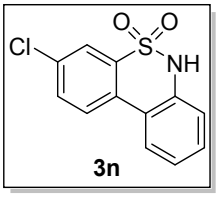
1H), 7.75-7.67 (m, 2H), 7.44 (t, J = 7.6 Hz, 1H), 7.28-7.22 (m, 2H), 7.15 (d, J = 8.0 Hz, 1H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, rt): δ 155.4, 136.3, 133.8, 133.2, 130.3, 125.8, 124.0, 123.7, 121.3, 119.3, 117.2, 111.9, 56.5. HRMS (ESI): *m/z* calcd for $C_{13}H_{11}NO_3S$ $[M+Na]^+$ 284.0352. Found: 284.0344.



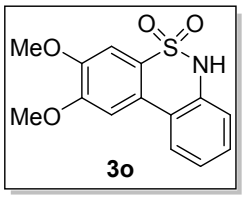
4-chloro-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (3l). Isolated in 56% yield (29.7 mg, 0.112 mmol) as a faint yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6, rt): δ 11.50 (br.s, 1H), 8.19 (d, J = 7.3 Hz, 1H), 8.14 (d, J = 7.7 Hz, 1H), 7.77-7.66 (m, 2H), 7.49 (t, J = 8.2 Hz, 1H), 7.31 (t, J = 7.2 Hz, 1H), 7.21 (d, J = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, rt): δ 135.8, 134.8, 133.0, 132.9, 130.9, 130.5, 128.0, 126.1, 125.1, 124.4, 121.6, 119.9. HRMS (ESI): *m/z* calcd for $C_{12}H_8ClNO_2S$ $[M+Na]^+$ 287.9856. Found: 287.9849.



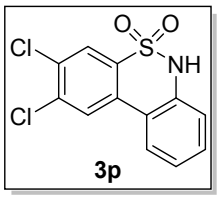
3-methyl-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (3m).[4] Isolated in 91% yield (44.6 mg, 0.182 mmol) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6, rt): δ 11.33 (br.s, 1H), 8.16 (d, J = 8.0 Hz, 1H), 8.12 (d, J = 8.1 Hz, 1H), 7.76 (s, 1H), 7.61 (d, J = 8.2 Hz, 1H), 7.44 (t, J = 7.7 Hz, 1H), 7.27 (t, J = 7.7 Hz, 1H), 7.20 (d, J = 8.0 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, rt): δ 138.7, 136.3, 134.3, 133.3, 129.9, 129.1, 125.5, 125.1, 123.8, 121.5, 121.0, 119.6, 20.7. HRMS (ESI): *m/z* calcd for $C_{13}H_{11}NO_2S$ $[M+Na]^+$ 268.0403. Found: 268.0393.



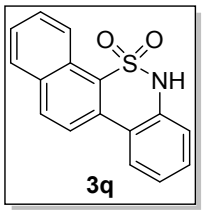
3-chloro-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (3n). Isolated in 60% yield (31.8 mg, 0.120 mmol) as a faint yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6, rt): δ 11.62 (br.s, 1H), 8.29 (d, J = 8.7 Hz, 1H), 8.22 (d, J = 8.0 Hz, 1H), 7.96 (s, 1H), 7.88 (d, J = 8.6 Hz, 1H), 7.50 (t, J = 7.7 Hz, 1H), 7.32 (t, J = 7.7 Hz, 1H), 7.22 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, rt): δ 136.3, 135.6, 133.1, 132.6, 130.8, 130.7, 128.0, 125.6, 124.2, 120.9, 119.9. HRMS (ESI): *m/z* calcd for $C_{12}H_8ClNO_2S$ $[M+Na]^+$ 287.9856. Found: 287.9845.



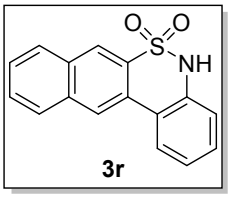
2,3-dimethoxy-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (3o). Isolated in 69% yield (40.2 mg, 0.138 mmol) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6, rt): δ 11.24 (br.s, 1H), 8.22 (d, J = 8.0 Hz, 1H), 7.65 (s, 1H), 7.41 (t, J = 7.7 Hz, 1H), 7.35 (s, 1H), 7.27 (t, J = 7.6 Hz, 1H), 7.17 (d, J = 8.0 Hz, 1H), 3.98 (s, 3H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, rt): δ 152.0, 149.0, 136.2, 129.4, 126.9, 125.5, 125.2, 123.6, 121.5, 119.4, 107.9, 103.4, 56.2, 56.1. HRMS (ESI): *m/z* calcd for $C_{14}H_{13}NO_4S$ $[M+Na]^+$ 314.0457. Found: 314.0444.



2,3-dichloro-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (3p). Isolated in 53% yield (31.7 mg, 0.106 mmol) as a faint yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6, rt): δ 11.74 (br.s, 1H), 8.55 (s, 1H), 8.27 (d, J = 7.6 Hz, 1H), 8.15 (s, 1H), 7.52 (t, J = 7.1 Hz, 1H), 7.31 (t, J = 7.1 Hz, 1H), 7.23 (d, J = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, rt): δ 136.7, 136.0, 134.0, 132.2, 131.4, 131.3, 127.9, 126.0, 124.3, 123.2, 120.1, 120.0. HRMS (ESI): *m/z* calcd for $C_{12}H_7Cl_2NO_2S$ $[M+Na]^+$ 321.9468. Found: 321.9465.

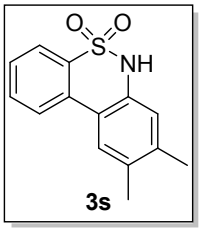


6*H*-benzo[c]naphtho[2,1-e][1,2]thiazine 5,5-dioxide (3q). Isolated in 79% yield (44.4 mg, 0.158 mmol) as a orange solid. ^{1}H NMR (400 MHz, DMSO-d_6, rt): δ 11.72 (br.s, 1H), 8.97 (d, J = 8.7 Hz, 1H), 8.31-8.27 (m, 3H), 8.12 (d, J = 8.1 Hz, 1H), 7.80-7.68 (m, 2H), 7.53 (t, J = 7.7 Hz, 1H), 7.38-7.25 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, rt): δ 136.5, 132.9, 132.3, 131.6, 130.7, 129.6, 128.8, 128.6, 127.3, 126.3 (× 2), 123.9 (× 2), 122.8, 121.7, 119.3. HRMS (ESI): *m/z* calcd for $C_{16}H_{11}NO_2S$ $[M+Na]^+$ 304.0403. Found: 304.0400.

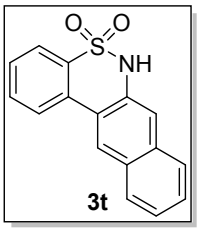


5*H*-benzo[c]naphtho[2,3-e][1,2]thiazine 6,6-dioxide (3r).[7] Isolated in 93% yield (52.3 mg, 0.186 mmol) as a faint yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6, rt): δ 11.27 (br.s, 1H), 8.82 (s, 1H),

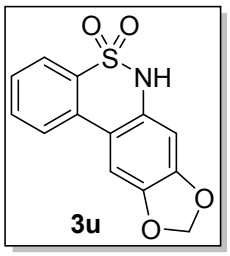
8.64 (s, 1H), 8.35 (d, J = 7.8 Hz, 1H), 8.25 (d, J = 8.0 Hz, 1H), 8.16 (d, J = 8.1 Hz, 1H), 7.75-7.66 (m, 2H), 7.48 (t, J = 7.4 Hz, 1H), 7.35 (t, J = 7.4 Hz, 1H), 7.25 (d, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, rt): δ 136.6, 134.1, 133.4, 131.0, 130.2, 128.8, 128.5, 128.3, 127.7, 125.5, 125.2, 124.2, 122.4, 121.5, 120.2. HRMS (ESI): *m/z* calcd for $C_{16}H_{11}NO_2S$ $[M+Na]^+$ 304.0403. Found: 304.0402.



8,9-dimethyl-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (3s). Isolated in 89% yield (46.1 mg, 0.178 mmol) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6, rt): δ 11.12 (br.s, 1H), 8.17 (d, J = 8.1 Hz, 1H), 7.96-7.89 (m, 2H), 7.75 (t, J = 7.7 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 6.99 (s, 1H), 2.28 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, rt): δ 139.3, 134.3 (× 2), 132.4, 132.3, 132.0, 127.9, 125.8, 125.1, 121.2, 120.5, 119.2, 19.4, 18.9. HRMS (ESI): *m/z* calcd for $C_{14}H_{13}NO_2S$ $[M+Na]^+$ 282.0559. Found: 282.0556.

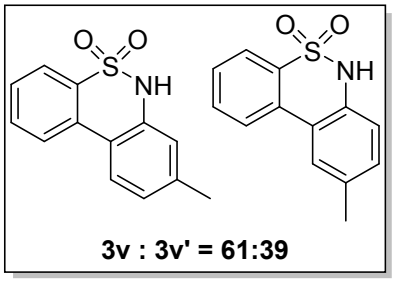


6*H*-benzo[e]naphtho[2,3-c][1,2]thiazine 5,5-dioxide (3t). Isolated in 68% yield (38.2 mg, 0.136 mmol) as a yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6, rt): δ 11.47 (br.s, 1H), 8.87 (s, 1H), 8.43 (d, J = 8.0 Hz, 1H), 8.06 (d, J = 8.1 Hz, 1H), 7.98 (d, J = 7.8 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.87 (t, J = 7.8 Hz, 1H), 7.70 (t, J = 7.6 Hz, 1H), 7.66 (s, 1H), 7.58 (t, J = 7.5 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, rt): δ 135.6, 134.3, 133.5, 132.8, 131.9, 129.9, 128.8, 128.6, 127.7, 126.7, 126.3, 125.7, 125.5, 122.1, 121.4, 116.1. HRMS (ESI): *m/z* calcd for $C_{16}H_{11}NO_2S$ $[M+Na]^+$ 304.0403. Found: 304.0401.



6*H*-[1,3]dioxolo[4',5':4,5]benzo[1,2-c]benzo[e][1,2]thiazine 5,5-dioxide (3u). Isolated in 75% yield (41.3 mg, 0.150 mmol) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6, rt): δ 11.11 (br.s, 1H), 8.12 (d, J = 8.1 Hz, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.78-7.73 (m, 2H), 7.58 (t, J = 7.5 Hz, 1H), 6.76 (s, 1H), 6.12 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, rt): δ 148.9, 144.7, 133.3, 132.4, 132.0,

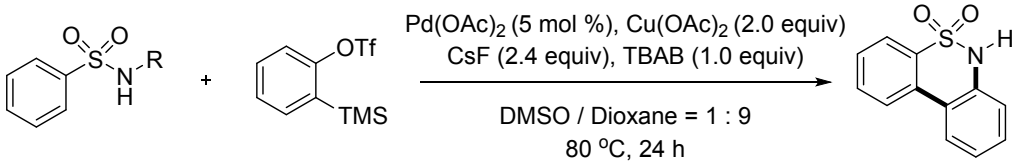
131.8, 127.6, 125.3, 121.1, 115.3, 104.5, 101.9, 100.7. HRMS (ESI): *m/z* calcd for $C_{13}H_9NO_4S$ $[M+Na]^+$ 298.0144. Found:298.0140.



8-methyl-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide/9-methyl-6H-dibenzo[c,e] [1,2] thiazine 5,5-dioxide[5] **(3v/3v').** Isolated in 71% yield (34.8 mg, 0.142 mmol) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6, rt): δ 11.25 (br.s, 2H), 8.24-8.18 (m, 2H), 8.08 (d, J = 8.1 Hz, 1H), 8.02 (d, J = 1.9 Hz, 1H), 7.93-7.90 (m, 1H), 7.82-7.76 (m, 2H), 7.68-7.61 (m, 2H), 7.30-7.27 (m, 1H), 7.13-7.10 (m, 2H), 7.01 (s, 1H), 2.39 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, rt): δ 142.4, 138.4, 136.5, 136.0, 135.9, 135.1, 134.4, 134.3, 133.7, 133.7, 133.0, 130.3, 129.9, 127.4, 127.3, 127.1, 126.8, 123.4，123.1, 123.0, 121.7, 121.6, 120.8, 22.8, 22.5. HRMS (ESI): *m/z* calcd for $C_{13}H_{11}NO_2S$ $[M+Na]^+$ 268.0403. Found: 268.0400.

3. Optimization of the reaction conditions

3.1 Screening directing groups [a]

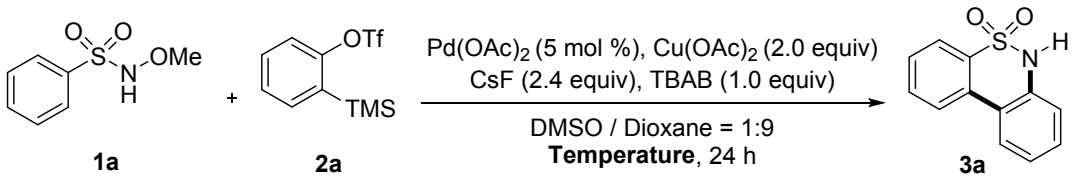


1 **2a** **3**

Entry[a]	Directing group (*N*-R)	Yield (%)[b]
1	***N*-OMe**	**8(5)**[c]
2	*N*-Ph	0
3	*N*-CH_2Ph	0
4	*N*-^{n}Pr	0
5	*N*-Ac	0

[a] The reaction was carried out using **1** (0.2 mmol), **2a** (2.0 equiv), $Pd(OAc)_2$ (5.0 mol%), $Cu(OAc)_2$ (2.0 equiv), TBAB (1.0 equiv) and CsF (2.4 equiv) and 4 Å molecular sieves (100 mg) in DMSO/dioxane = 1:9 (3 mL) as solvent at 80 °C for 24 h. [b] Yields were determined by GC using 1,3,5-trimethoxybenzene as an internal standard, based on N-methoxy benzsulfonamide **1**. [c] Isolated yields are shown in parentheses.

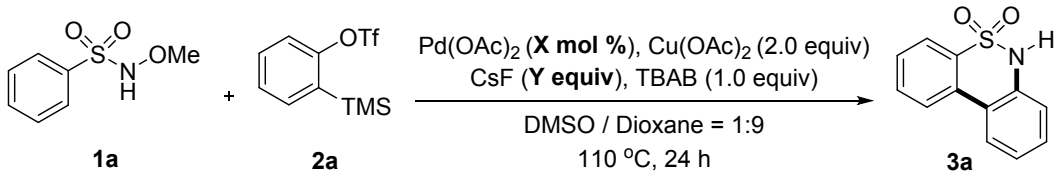
3.2 Screening reaction temperature [a]



Entry	Temperature (°C)	Yield (%)[b]
1	80	8(5)[c]
2	90	10
3	100	14
4	**110**	**26**
5	120	21
6	130	18
7	140	13

[a] The reaction was carried out using **1a** (0.2 mmol), **2a** (2.0 equiv), $Pd(OAc)_2$ (5.0 mol%), $Cu(OAc)_2$ (2.0 equiv), TBAB (1.0 equiv) and CsF (2.4 equiv) and 4 Å molecular sieves (100 mg) in DMSO/dioxane = 1:9 (3 mL) as solvent for 24 h. [b] Yields were determined by GC using 1,3,5-trimethoxybenzene as an internal standard, based on N-methoxy benzsulfonamide **1a**. [c] Isolated yields are shown in parentheses.

3.3 Screening the amount of Pd catalyst and CsF[a]

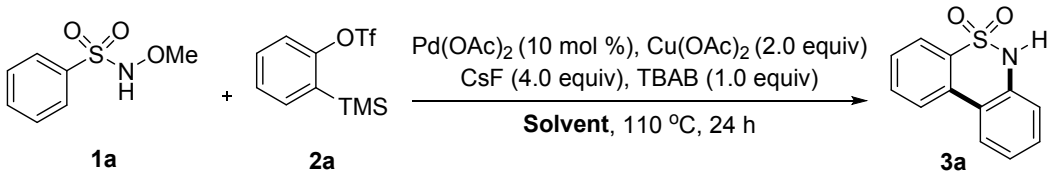


1a **2a** **3a**

Entry	$Pd(OAc)_2$ (X mol %)	CsF (Y equiv)	Yield (%)[b]
1	5	2.4	26
2	5	3.0	27
3	**5**	**4.0**	**44**
4	5	5.0	42
5	5	0	0
6	3	4.0	32
7	**10**	**4.0**	**51**
8	15	4.0	49
9	20	4.0	50
10	0	4.0	0

[a] The reaction was carried out using **1a** (0.2 mmol), **2a** (2.0 equiv), $Pd(OAc)_2$ (X mol%), $Cu(OAc)_2$ (2.0 equiv), TBAB (1.0 equiv) and CsF (Y equiv) and 4 Å molecular sieves (100 mg) in DMSO/dioxane = 1:9 (3 mL) as solvent at 110 °C for 24 h. [b] Yields were determined by GC using 1,3,5-trimethoxybenzene as an internal standard, based on N-methoxy benzsulfonamide **1a**.

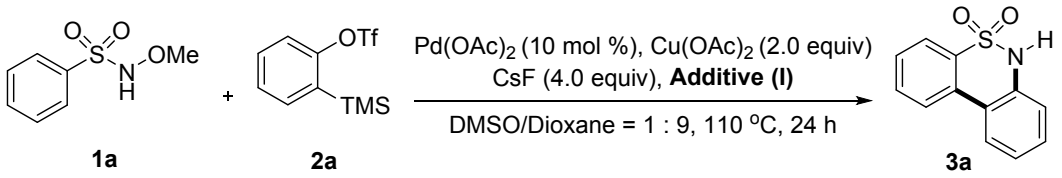
3.4 Screening solvents[a]



Entry	Solvent	Yield (%)[b]
1	DMSO/Dioxane = 1:9	51
2	CF_3CH_2OH	0
3	Toluene	18
4	CH_3CN	6
5	DMF	6
6	Dioxane	31
7	DMSO	0
8	DMF/CH_3CN = 1:1	0
9	DMSO/Dioxane = 1:5	42
10	DMSO/Dioxane = 1:2	38
11	DMSO/Dioxane = 1:1	17
12	DMSO/Dioxane = 2:1	9

[a] The reaction was carried out using **1a** (0.2 mmol), **2a** (2.0 equiv), $Pd(OAc)_2$ (10 mol%), $Cu(OAc)_2$ (2.0 equiv), TBAB (1.0 equiv) and CsF (4.0 equiv) and 4 Å molecular sieves (100 mg) at 110 °C for 24 h. [b] Yields were determined by GC using 1,3,5-trimethoxybenzene as an internal standard, based on N-methoxy benzsulfonamide **1a**.

3.5 Screening additive(I) [a]

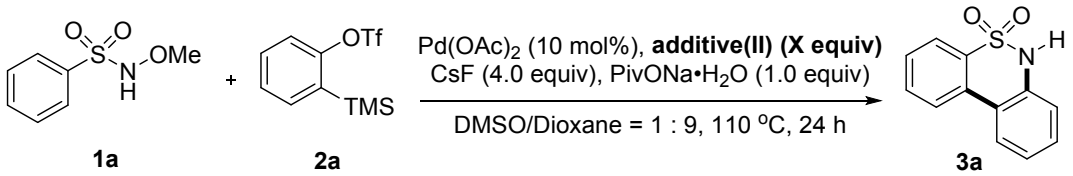


1a **2a** **3a**

Entry	Additive I	Additive I (X equiv)	Yield (%)[b]
1	TBAB	1	51
2	TBAC	1	16
3	TBAI	1	0
4	18-crown-6	1	39
5	TBAB+18-crown-6	1	32
6	$(BnO)_2PO_2H$	1	0
7	Adm-1-COOH	1	0
8	PivOH	1	27
9	**PivONa·H_2O**	**1**	**89**
10	$NaPF_6$	1	12
11	K_2HPO_4	1	11
12	K_3PO_4	1	21
13	KH_2PO_4	1	27
14	$K_2S_2O_8$	1	22
15	PivONa·H_2O	0.3	62
16	PivONa·H_2O	0.6	73
17	PivONa·H_2O	1.5	35
18	PivONa·H_2O	2	19
19	-	0	0

[a] The reaction was carried out using **1a** (0.2 mmol), **2a** (2.0 equiv), $Pd(OAc)_2$ (10 mol%), $Cu(OAc)_2$ (2.0 equiv), additive(I) and CsF (4.0 equiv) and 4 Å molecular sieves (100 mg) in DMSO/dioxane = 1:9 (3 mL) as solvent at 110 °C for 24 h. [b] Yields were determined by GC using 1,3,5-trimethoxybenzene as an internal standard, based on N-methoxy benzsulfonamide **1a**.

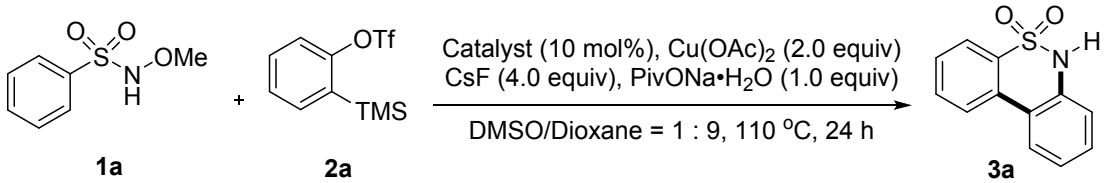
3.6 Screening additive(II) [a]



Entry	Additive II	Additive II（X equiv）	Yield (%)[b]
1	Ditertbutyl peroxide	2	0
2	AgOAc	2	7
3	$Cu(OAc)_2·H_2O$	2	49
4	BQ	2	0
5	Ag_2O	2	0
6	MnO_2	2	6
7	$PhI(OAc)_2$	2	0
8	O_2	2	0
9	$Cu(CF_3SO_3)_2$	2	12
10	$Co(OAc)_2$	2	5
11	$Mn(OAc)_2$	2	4
12	CsOAc	2	0
13	KOAc	2	8
14	NaOAc	2	0
15	$Fe(OAc)_2$	2	0
16	-	0	0
17	$Cu(OAc)_2$ (0.5 equiv)	0.5	56
18	$Cu(OAc)_2$ (1.0 equiv)	1	68
19	**$Cu(OAc)_2$ (2.0 equiv)**	**2**	**89**
20	$Cu(OAc)_2$ (3.0 equiv)	3	79
21	$Cu(OAc)_2$ (4.0 equiv)	4	72

[a] The reaction was carried out using **1a** (0.2 mmol), **2a** (2.0 equiv), $Pd(OAc)_2$ (10 mol%), additive(II), $PivONa·H_2O$ (1.0 equiv) and CsF (4.0 equiv) and 4 Å molecular sieves (100 mg) in DMSO/dioxane = 1:9 (3 mL) as solvent at 110 °C for 24 h. [b] Yields were determined by GC using 1,3,5-trimethoxybenzene as an internal standard, based on N-methoxy benzsulfonamide **1a**.

3.7 Screening catalyst [a]



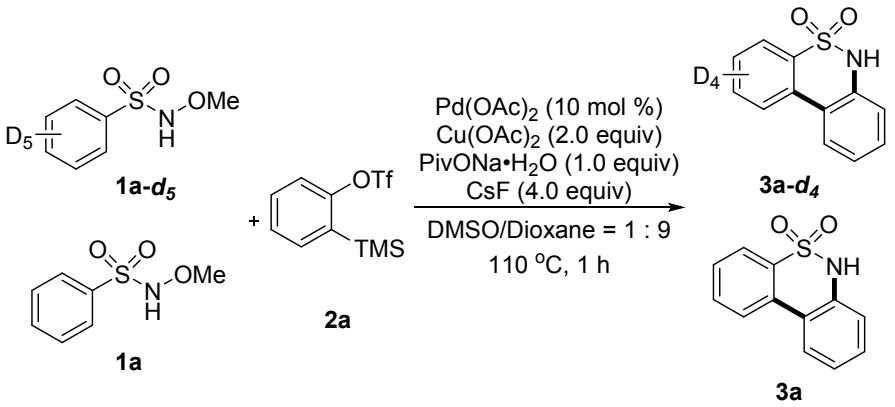
1a **2a** **3a**

Entry[a]	Catalyst	Ligand (30 mol %)	Yield (%)[b]
1	$Pd(PPh_3)_4$	-	34
2	$PdCl_2(dppf)$	-	60
3	$PdCl_2(PPh_3)_2$	-	27
4	$Pd(dba)_2$	-	35
5	$PdCl_2(PhCN)_2$	-	45
6	$PdCl_2(PCy_3)_2$	-	21
7	$Pd(TFA)_2$	-	34
8	$[Cp^*RhCl_2]_2$	-	0
9	$[RuCl_2(pcymene)]_2$	-	0
10	**$Pd(OAc)_2$**	**-**	**89**
11	$Pd(OAc)_2$	PPh_3	62
12	$Pd(OAc)_2$	PCy_3	79
13	$Pd(OAc)_2$	Dppb	55
14	$Pd(OAc)_2$	Dppf	34
15	$Pd(OAc)_2$	Xanphos	20
16	$Pd(OAc)_2$	Dppp	53

[a] The reaction was carried out using **1a** (0.2 mmol), **2a** (2.0 equiv), catalyst (10 mol%), $Cu(OAc)_2$ (2.0 equiv), $PivONa{\cdot}H_2O$ (1.0 equiv) and CsF (4.0 equiv) and 4 Å molecular sieves (100 mg) in DMSO/dioxane = 1:9 (3 mL) as solvent at 110 °C for 24 h. [b] Yields were determined by GC using 1,3,5-trimethoxybenzene as an internal standard, based on N-methoxy benzsulfonamide **1a**.

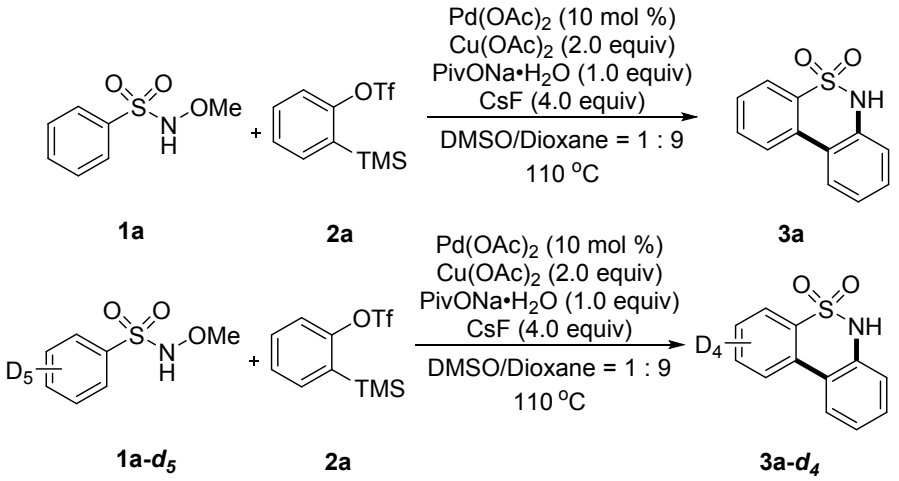
4. Kinetic Isotope Effect (KIE) Experiments

Intermolecular Competitive Reaction



A flame-dried 25 mL Schlenk with a magnetic stir bar was charged with $Pd(OAc)_2$ (4.49 mg, 0.02 mmol, 10 mmol %), $Cu(OAc)_2$ (72.86 mg, 0.4 mmol), *N*-methoxybenzsulfonamide **1a** (18.7mg, 0.1 mmol), *N*-methoxy-2,3,4,5,6-pentadeueriobenzsulfonamide**1a-*d*$_5$** (19.2 mg, 0.1 mmol), CsF (121.52 mg, 0.8 mmol) and $PivONa{\cdot}H_2O$ (28.43 mg, 0.2 mmol) in a mixed solvents of dioxane (2.7 mL) and DMSO (0.3 mL) under argon. To this solution were added 2-(trimethylsilyl)phenyl triflate (**2a**) (119.2 mg, 0.4 mmol) via a syringe. The reaction mixture was heated to 110 ºC for 1 h, then cooled to ambient temperature, quenched with water, and extracted with diethyl ether (20 mL × 3). The combined extracts were washed with brine and dried over anhydrous sodium sulfate. The volatiles were removed under reduced pressure to give crude products, which were purified by column chromatography (eluent: CH_2Cl_2). The products **3a** and **3a-*d*$_4$** were obtained in 13% combined yield. The ratio of **3a**/**3a-*d*$_4$** was determined to be 80/20 by ^{1}H NMR analysis.

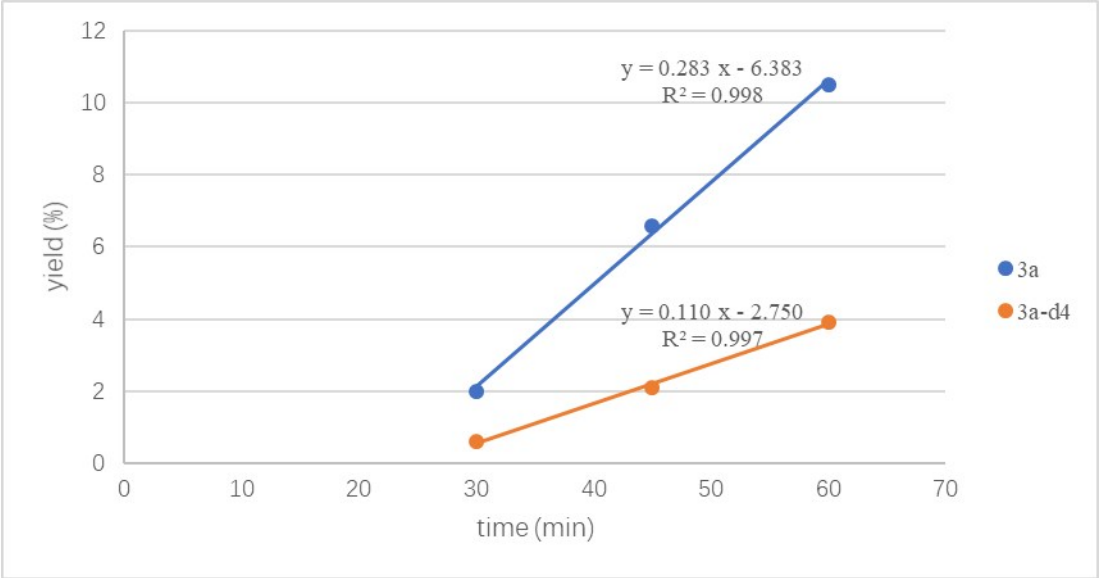
KIE for Two Parallel Reactions



A flame-dried 25 mL Schlenk with a magnetic stir bar was charged with $Pd(OAc)_2$ (4.49 mg, 0.02 mmol, 10 mmol %), $Cu(OAc)_2$ (72.86 mg, 0.4 mmol), *N*-methoxybenzsulfonamide **1a** (37.40 mg, 0.2 mmol), CsF (121.52 mg, 0.8 mmol) and $PivONa \cdot H_2O$ (28.43 mg, 0.2 mmol) in a mixed solvents of dioxane (2.7 mL) and DMSO (0.3 mL) under argon. To this solution were added 2-(trimethylsilyl)phenyl triflate (**2a**) (119.2 mg, 0.4 mmol) via a syringe. The reaction mixture was stirred at 110 ºC. The initial reaction rate of **3a** was obtained by plotting the product GC yield along the reaction time.

A flame-dried 25 mL Schlenk with a magnetic stir bar was charged with $Pd(OAc)_2$ (4.49 mg, 0.02 mmol, 10 mmol %), $Cu(OAc)_2$ (72.86 mg, 0.4 mmol), *N*-methoxy-2,3,4,5,6-pentadeuerio-benzsulfonamide **1a-*d*$_5$** (38.40 mg, 0.2 mmol), CsF (121.52 mg, 0.8 mmol) and $PivONa \cdot H_2O$ (28.43 mg, 0.2 mmol) in a mixed solvents of dioxane (2.7 mL) and DMSO (0.3 mL) under argon. To this solution were added 2-(trimethylsilyl)phenyl triflate (**2a**) (119.2 mg, 0.4 mmol) via a syringe. The reaction mixture was stirred at 110 ºC. The initial reaction rate of **3a-*d*$_4$** was obtained by plotting the product GC yield along the reaction time.

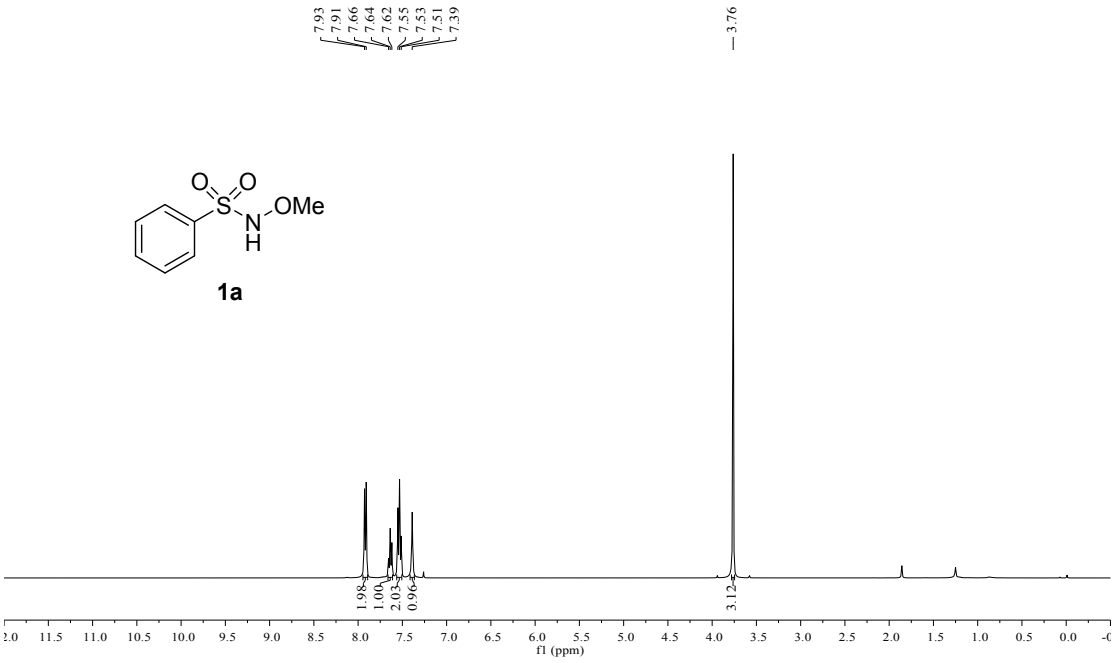
Time (min)	GC Yield (%)	
	3a	**3a-d_4**
30	2.0	0.6
45	6.6	2.1
60	10.5	3.9



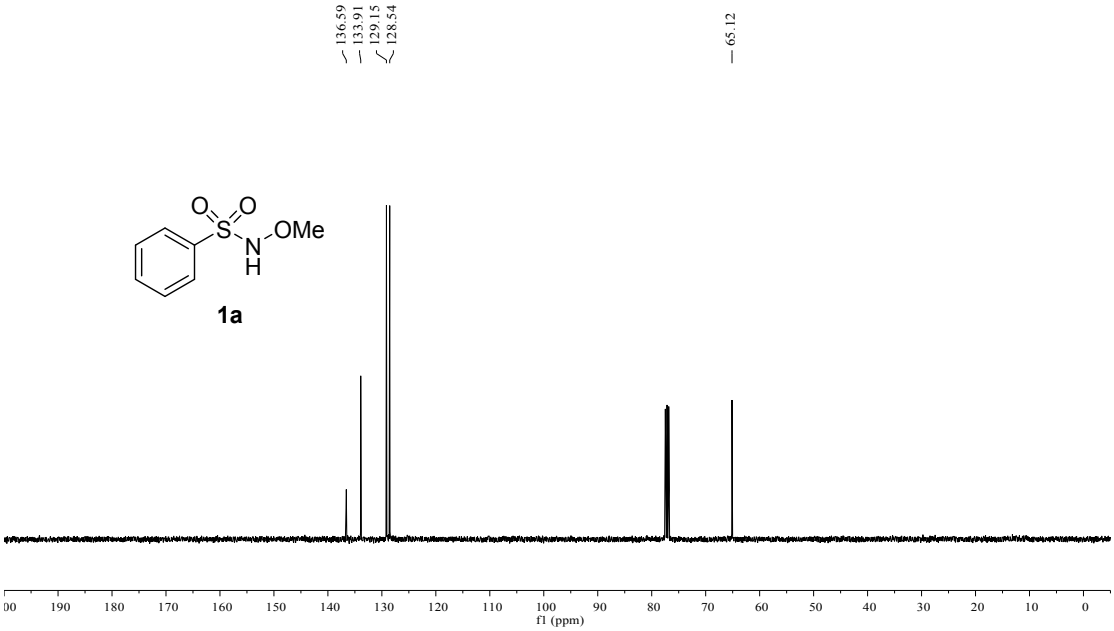
According to the above data, the ratios of initial rate constants were calculated as follows.

$$k_H/k_D = 0.283/0.110 = 2.6$$

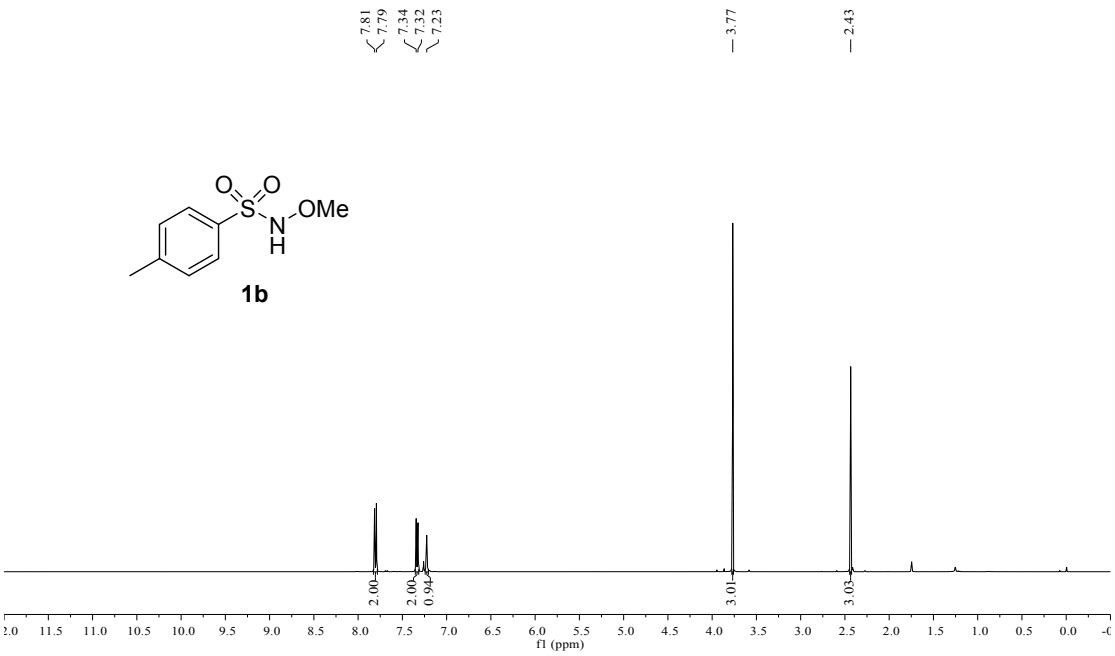
5. ***Copies of ^{1}H NMR and ^{13}C NMR Charts for N-alkoxy benzsulfonamids***



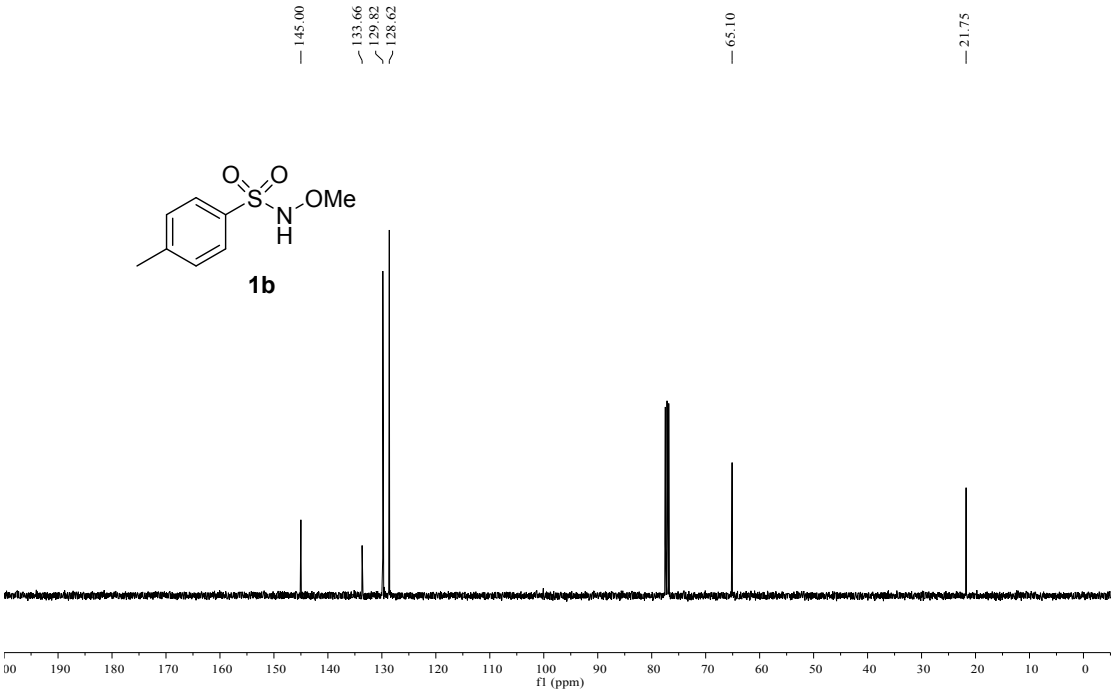
^{1}H NMR of *N*-methoxy benzsulfonamide (**1a**)



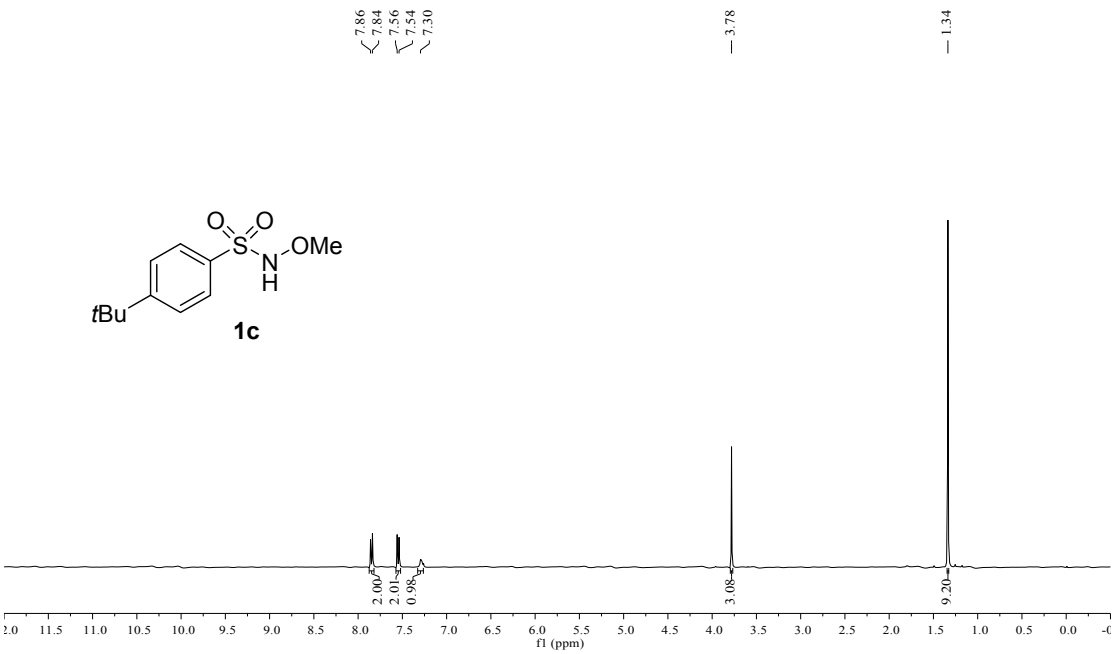
^{13}C NMR of *N*-methoxy benzsulfonamide (**1a**)



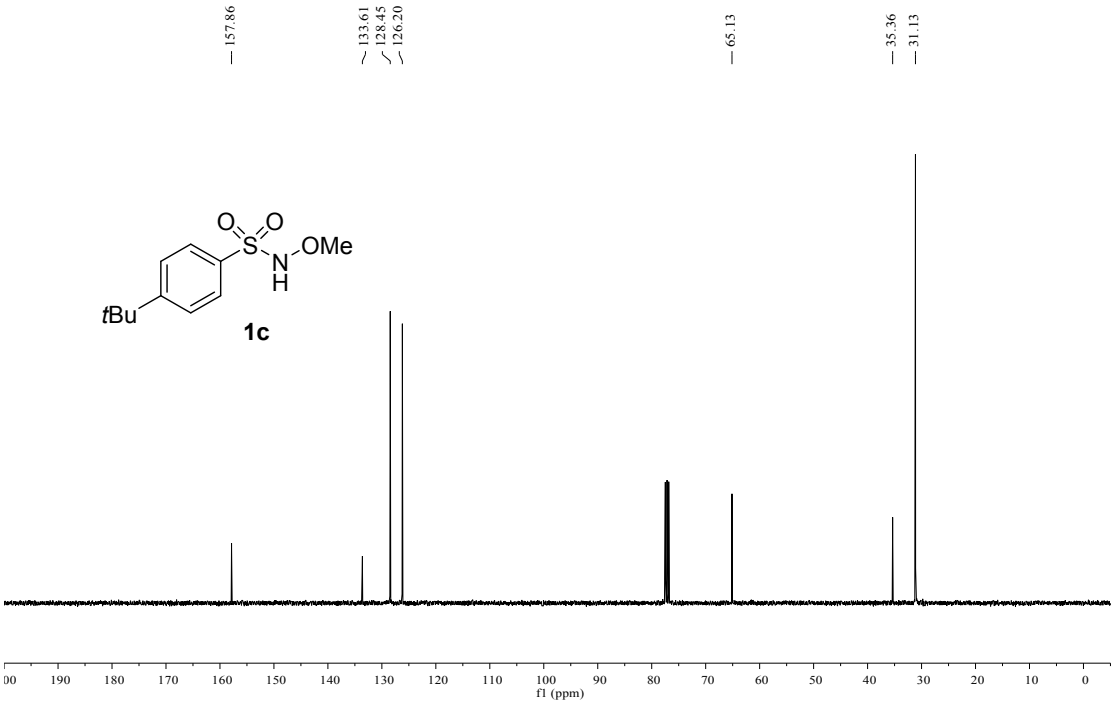
^{1}H NMR of *N*-methoxy-4-methylbenzsulfonamide (**1b**)



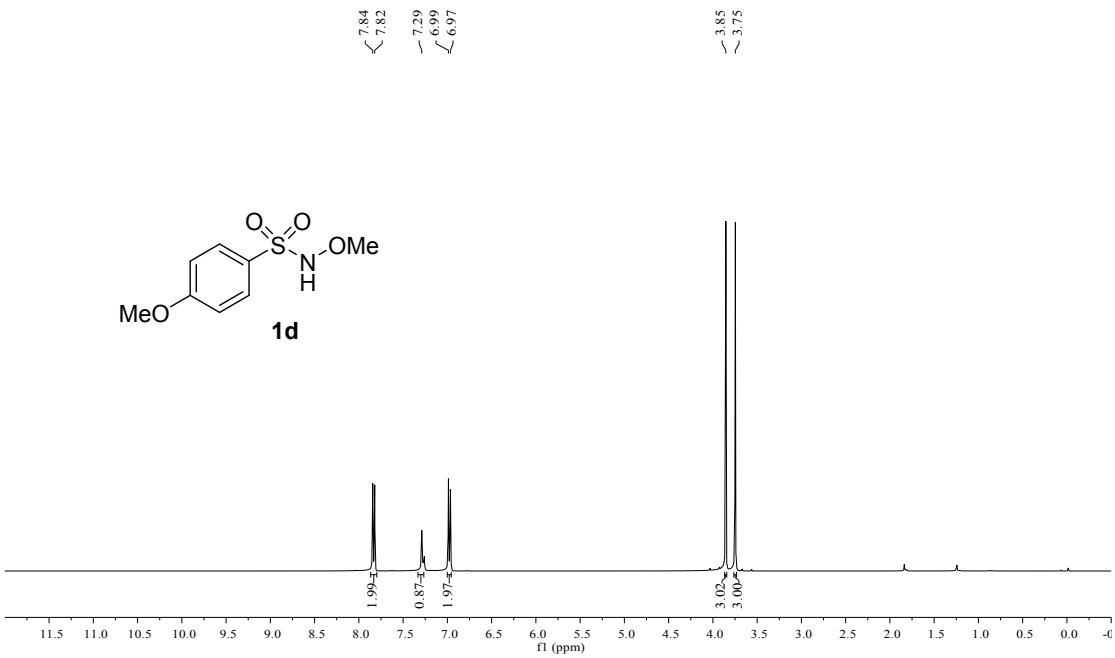
^{13}C NMR of *N*-methoxy-4-methylbenzsulfonamide (**1b**)



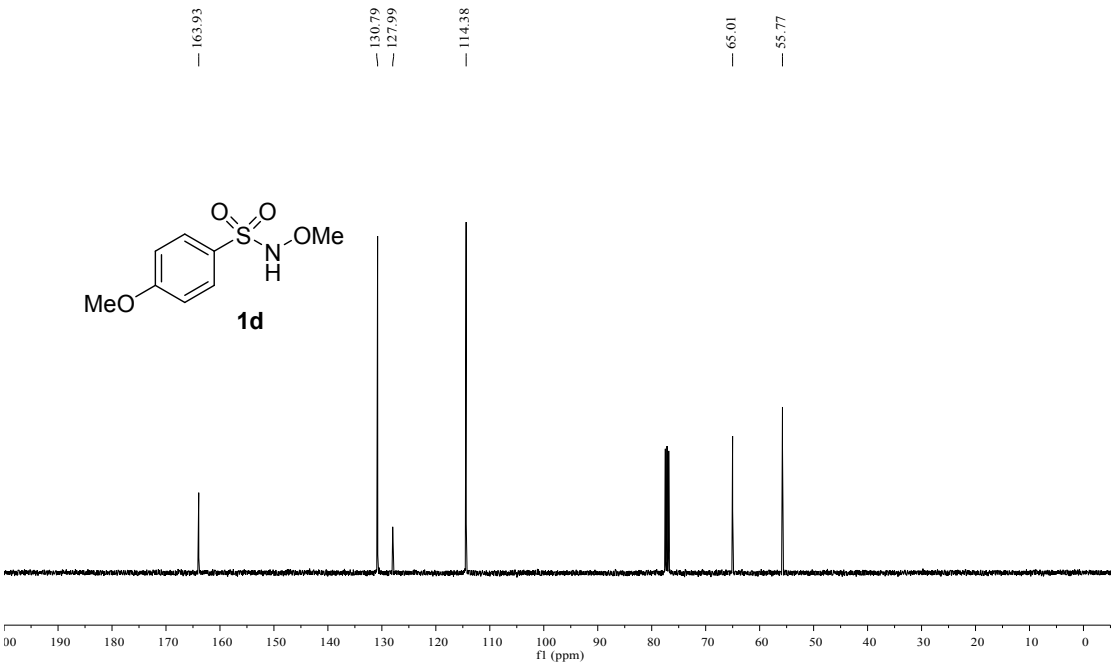
^{1}H NMR of 4-(*tert*-butyl)-*N*-methoxy benzsulfonamide (**1c**)



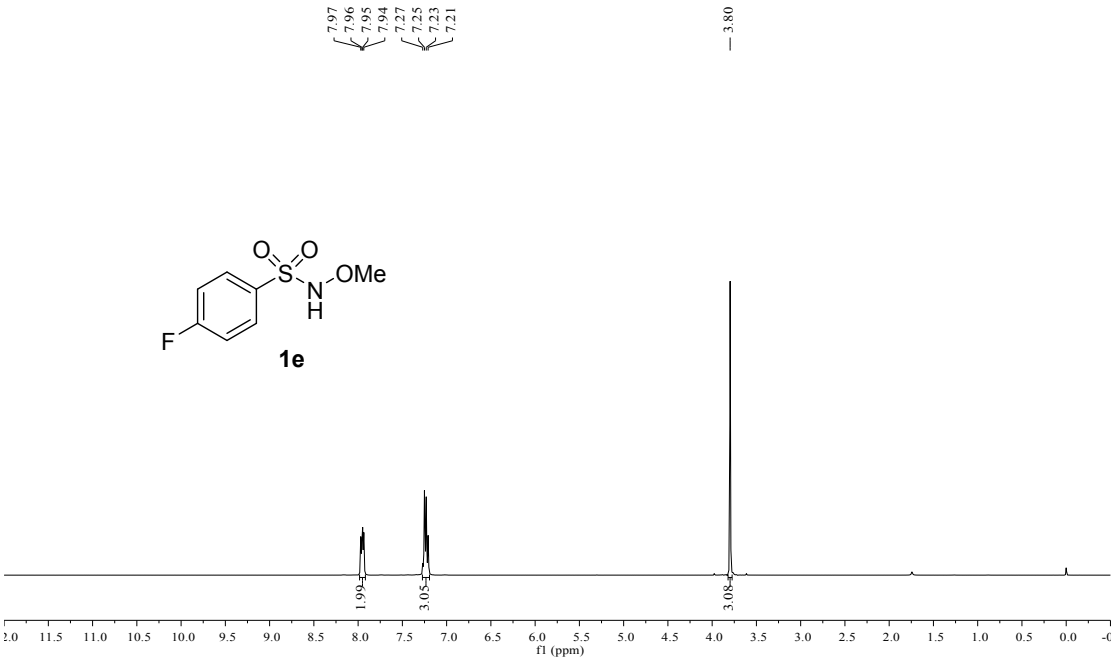
^{13}C NMR of 4-(*tert*-butyl)-*N*-methoxy benzsulfonamide (**1c**)



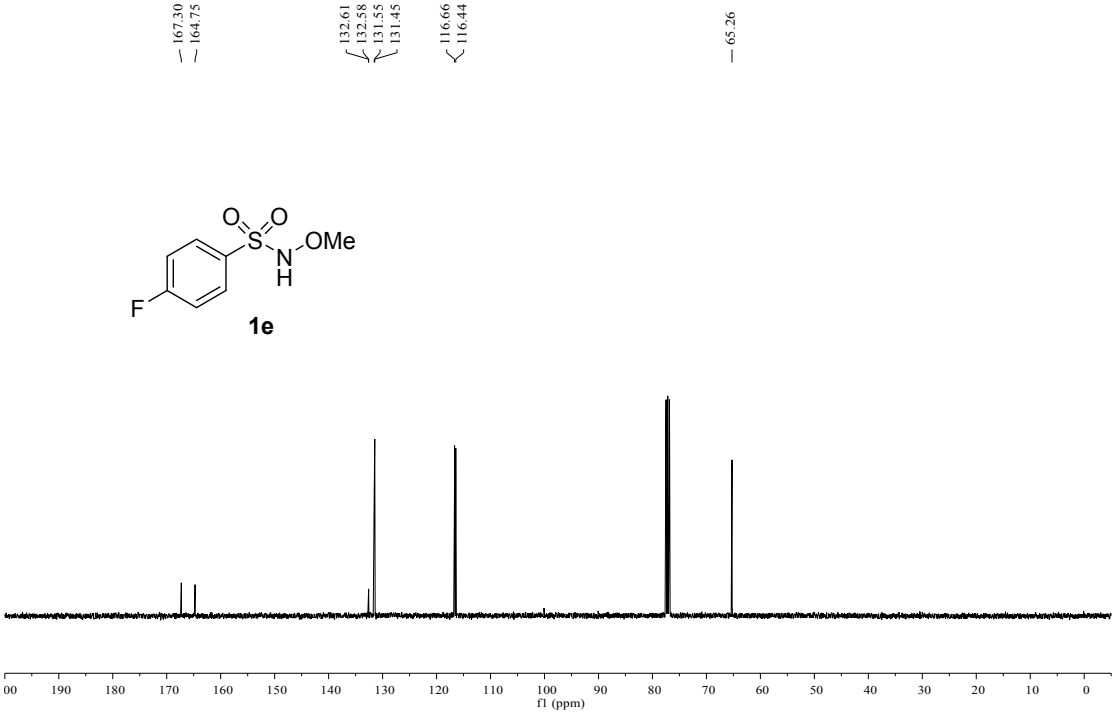
^{1}H NMR of 4-methoxy-*N*-methoxy benzsulfonamide (**1d**)



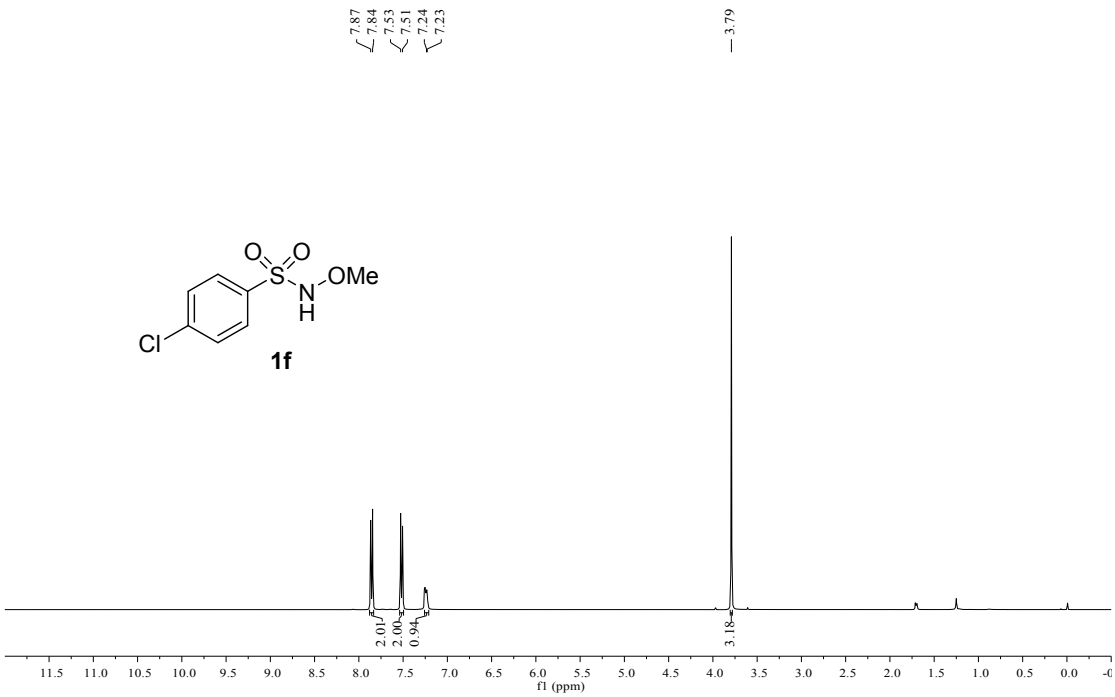
^{13}C NMR of 4-methoxy-*N*-methoxy benzsulfonamide (**1d**)



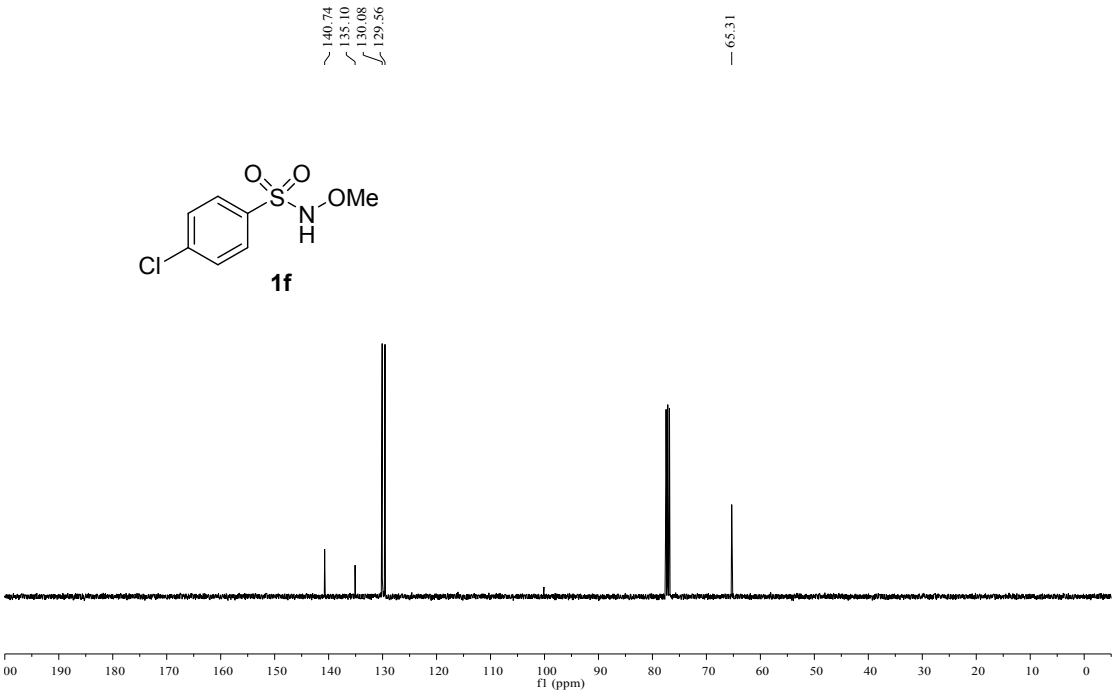
^{1}H NMR of 4-fluoro-*N*-methoxy benzsulfonamide (**1e**)



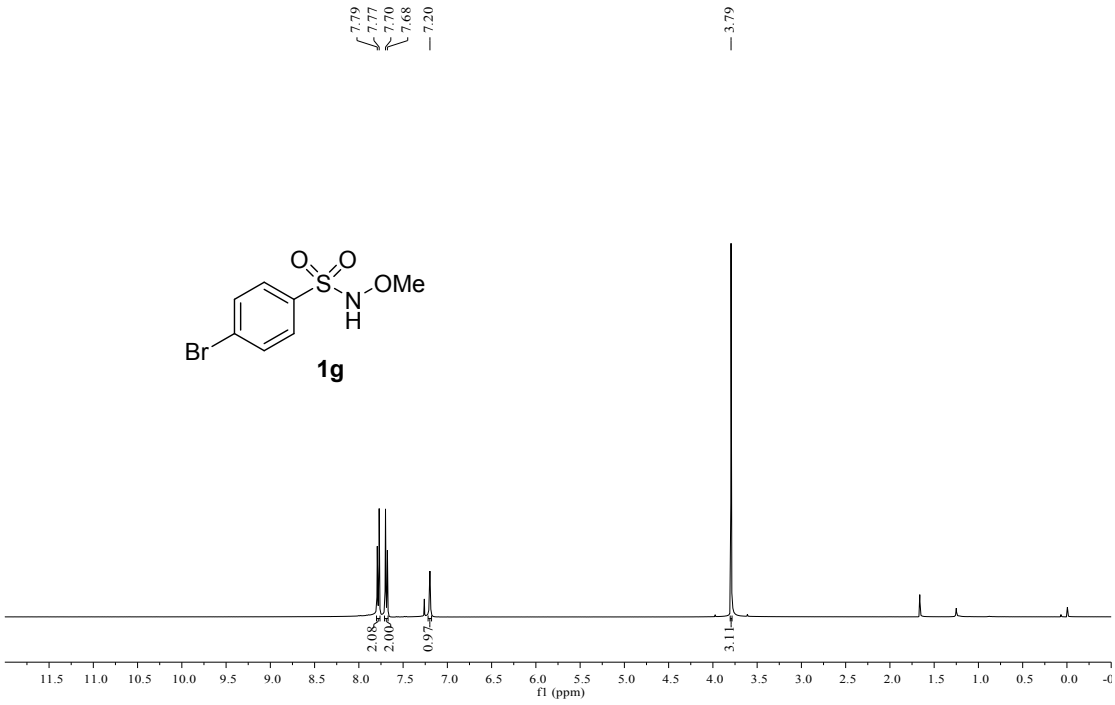
^{13}C NMR of 4-fluoro-*N*-methoxy benzsulfonamide (**1e**)



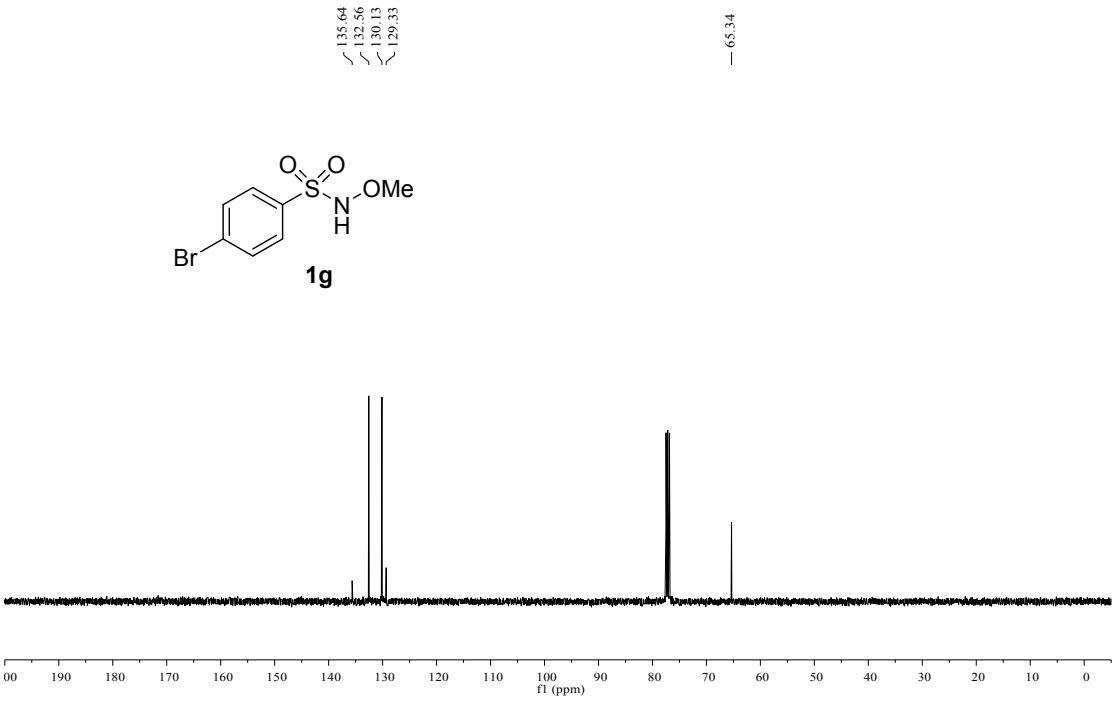
^{1}H NMR of 4-chloro-*N*-methoxy benzsulfonamide (**1f**)



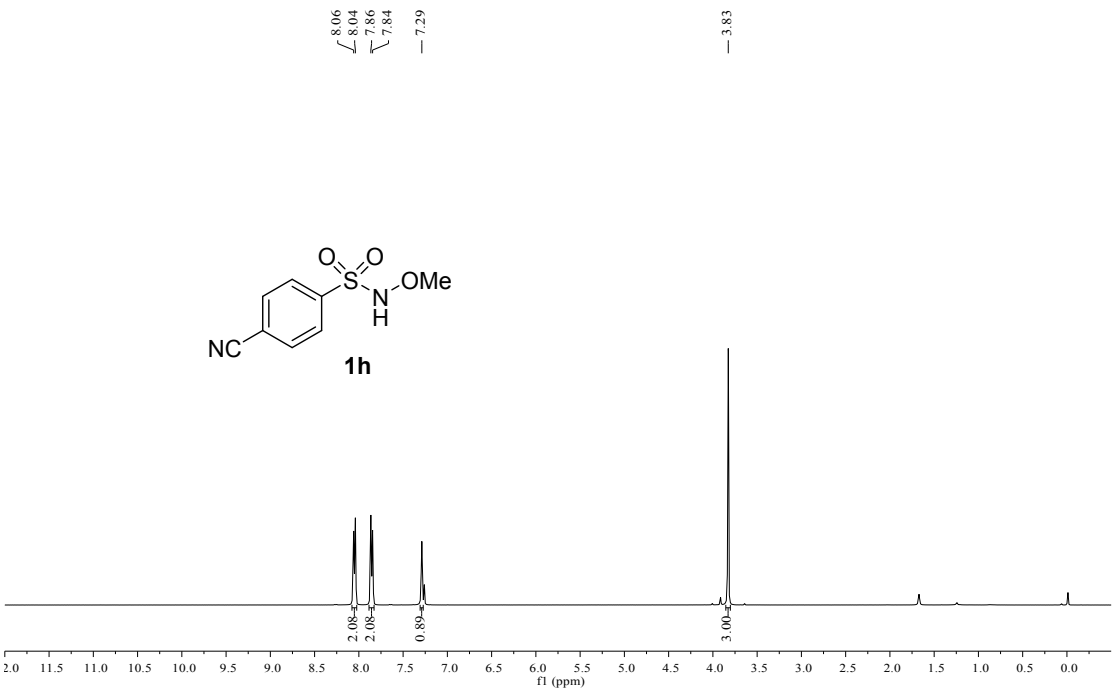
^{13}C NMR of 4-chloro-*N*-methoxy benzsulfonamide (**1f**)



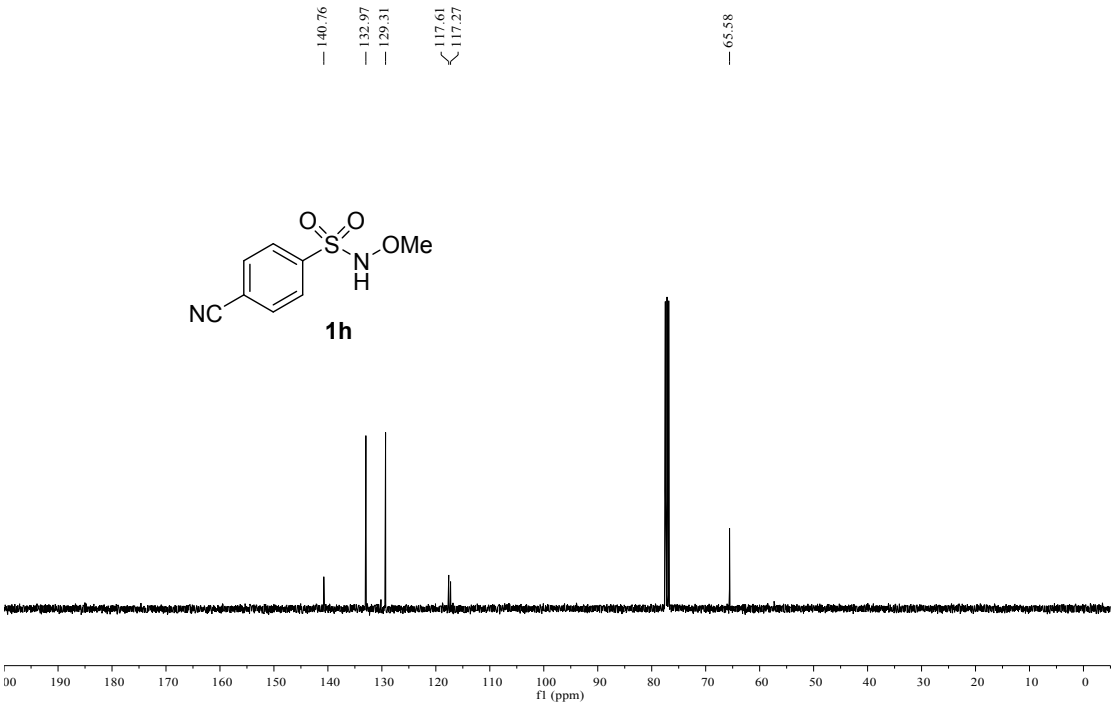
^{1}H NMR of 4-bromo-*N*-methoxy benzsulfonamide (**1g**)



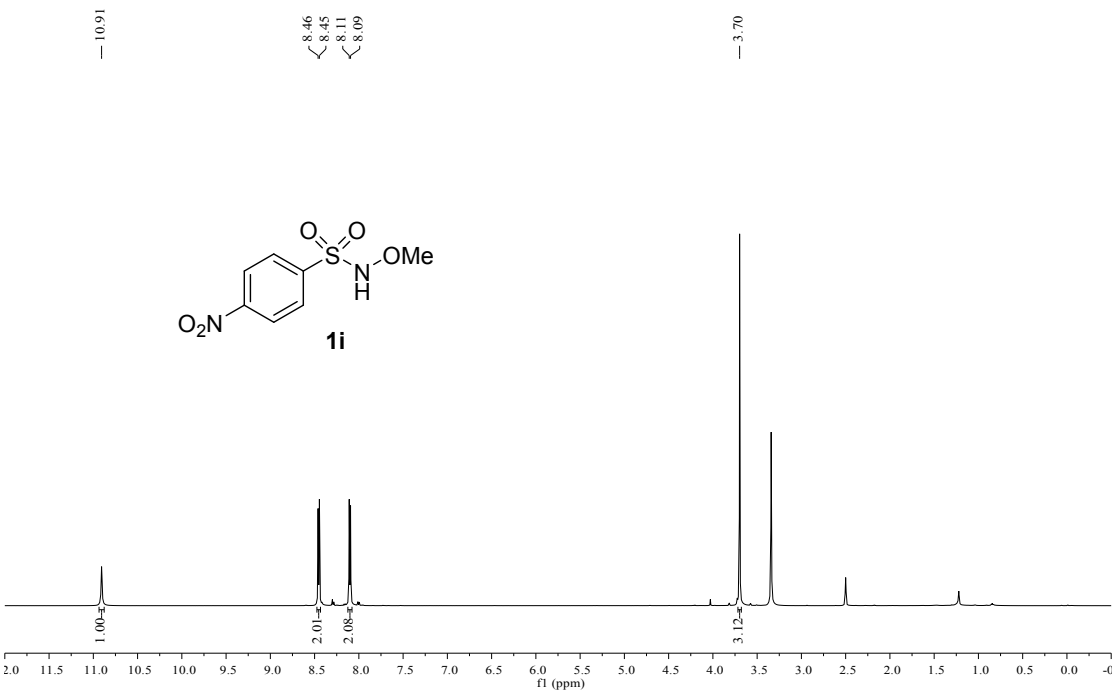
^{13}C NMR of 4-bromo-*N*-methoxy benzsulfonamide (**1g**)



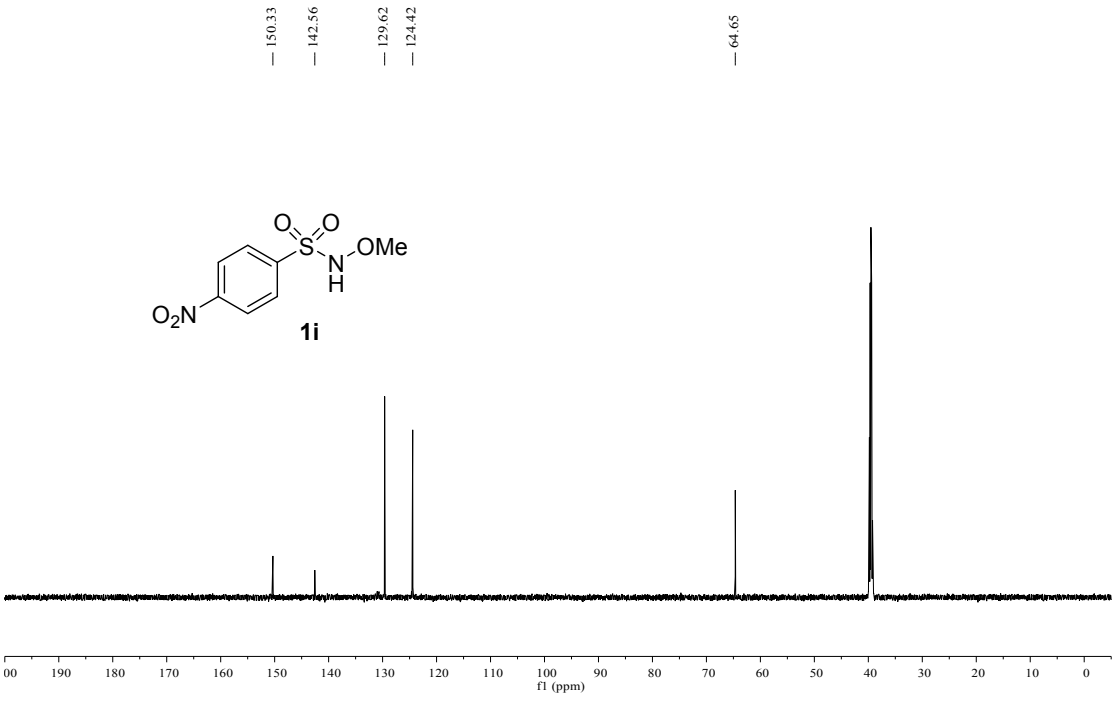
^{1}H NMR of 4-cyano-*N*-methoxy benzsulfonamide (**1h**)



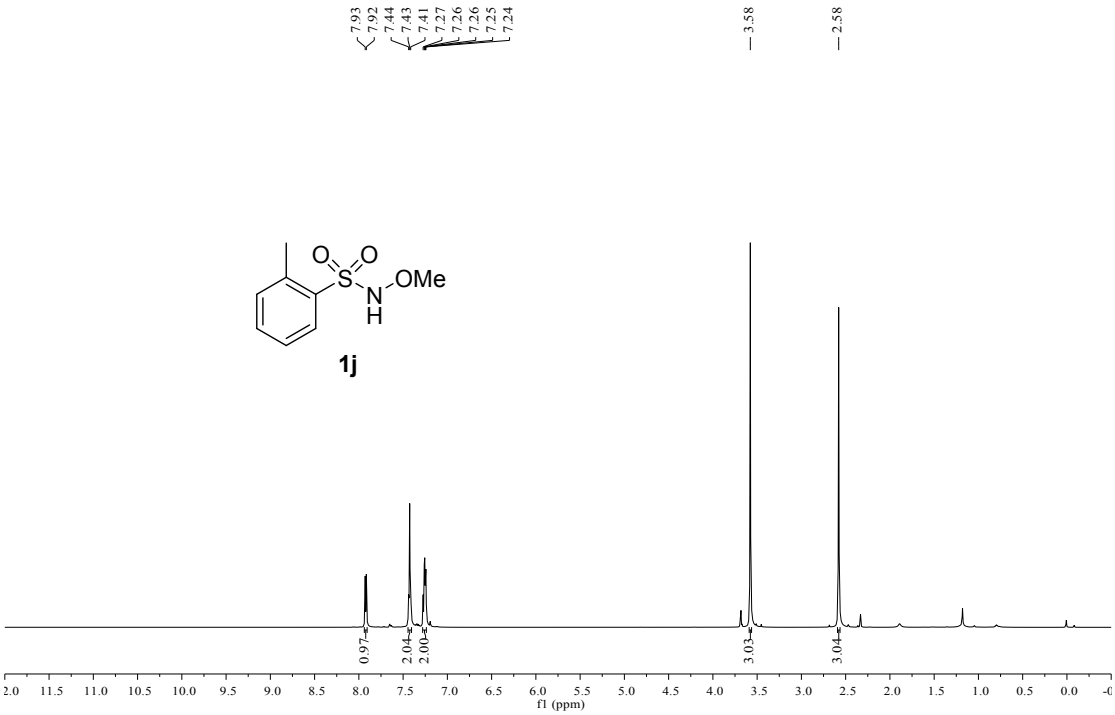
^{13}C NMR of 4-cyano-*N*-methoxy benzsulfonamide (**1h**)



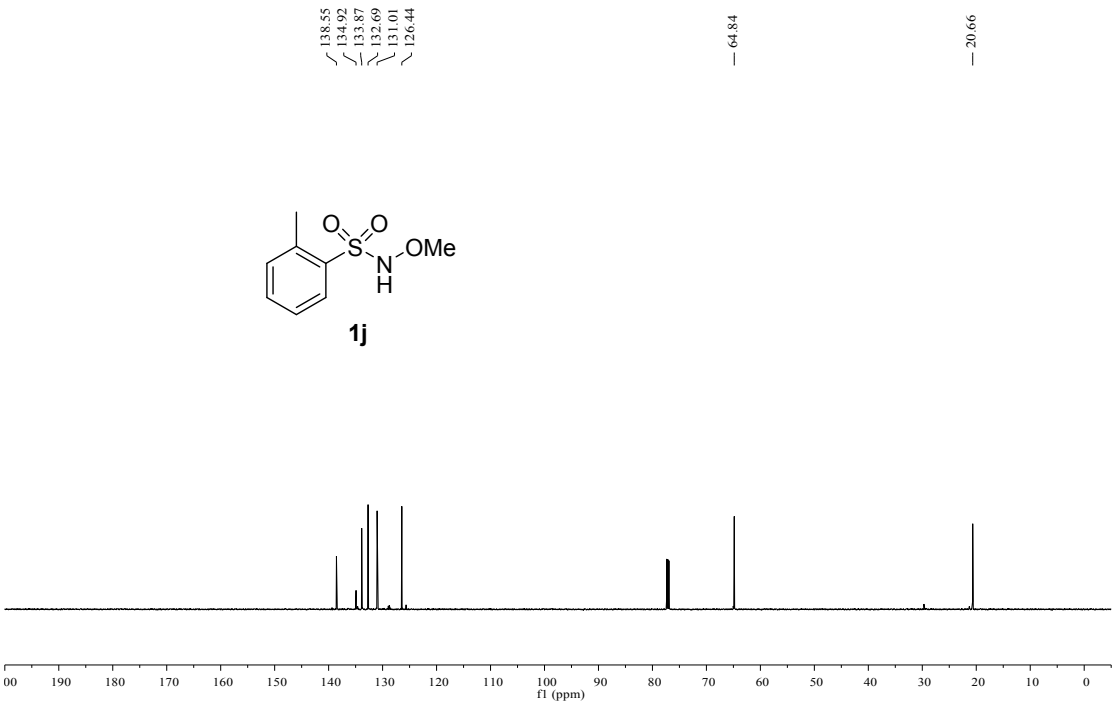
^{1}H NMR of *N*-methoxy-4-nitrobenzsulfonamide **(1i)**



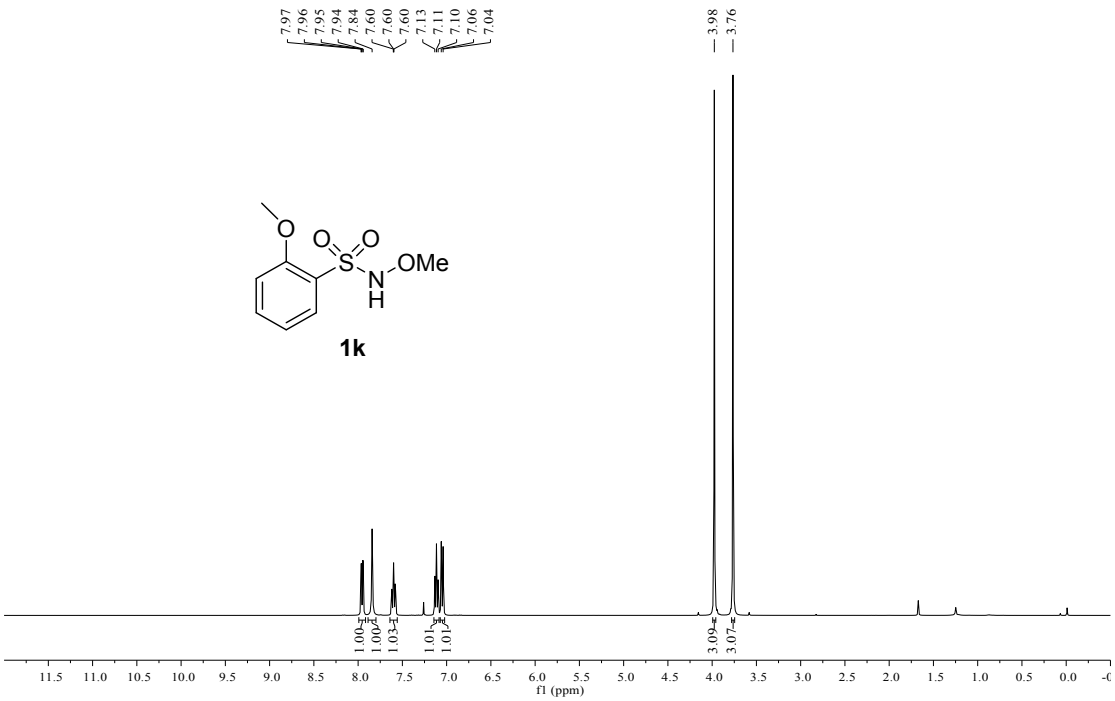
^{13}C NMR of *N*-methoxy-4-nitrobenzsulfonamide (**1i**)



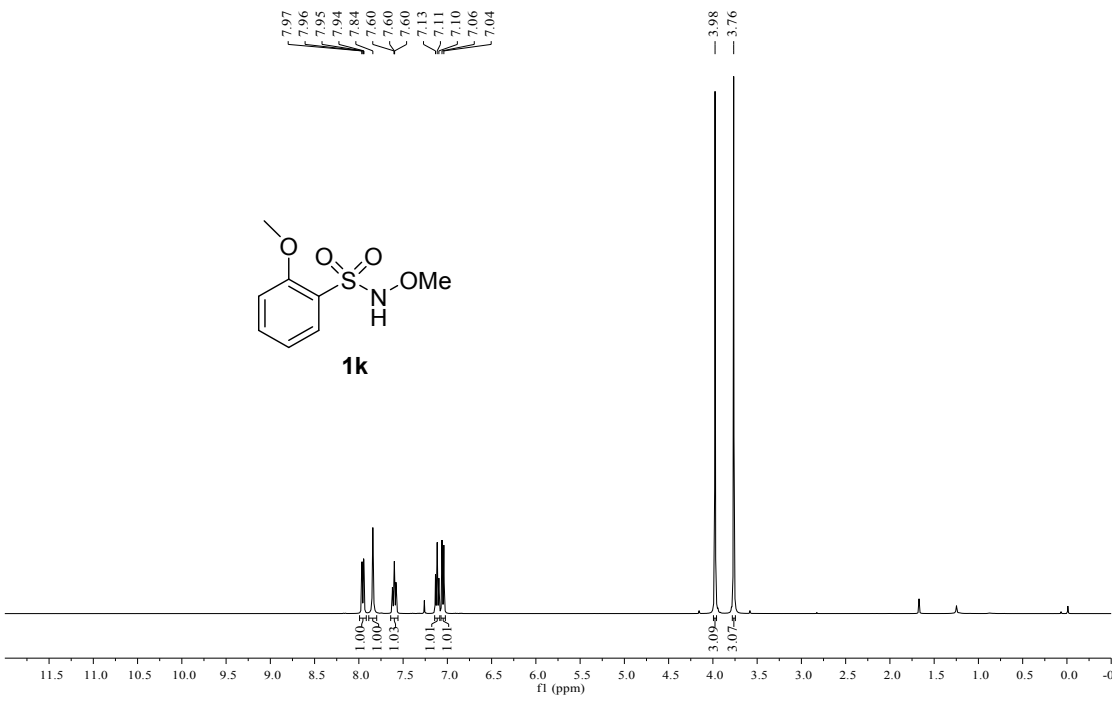
^{1}H NMR of *N*-methoxy-2-methylbenzsulfonamide (**1j**)



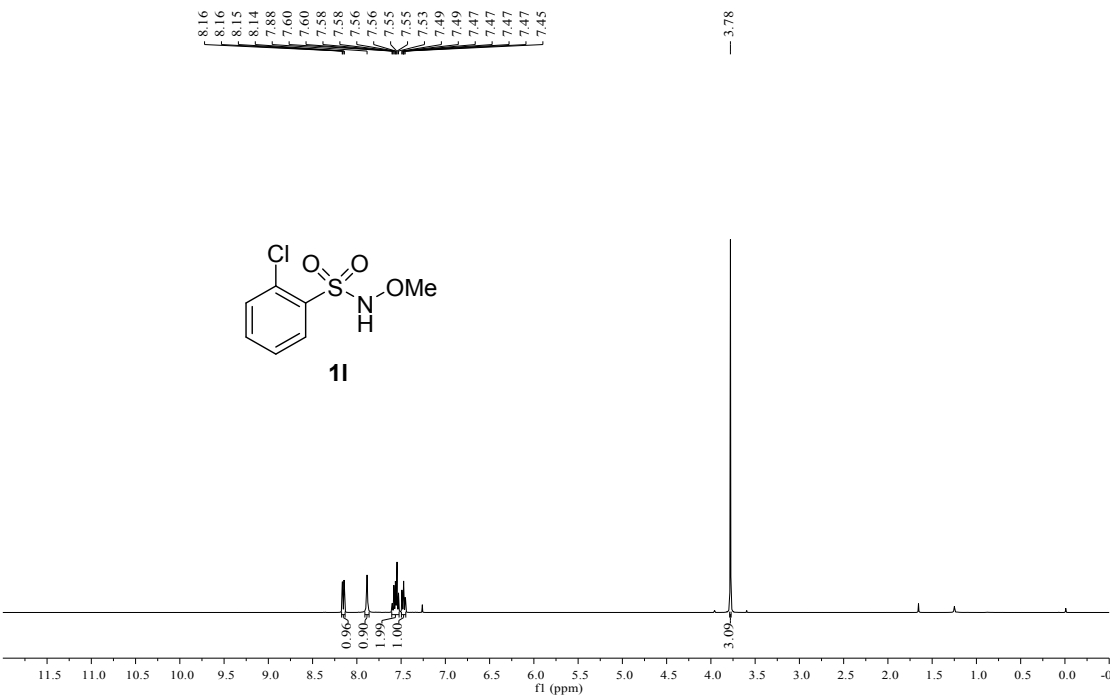
^{13}C NMR of *N*-methoxy-2-methylbenzsulfonamide (**1j**)



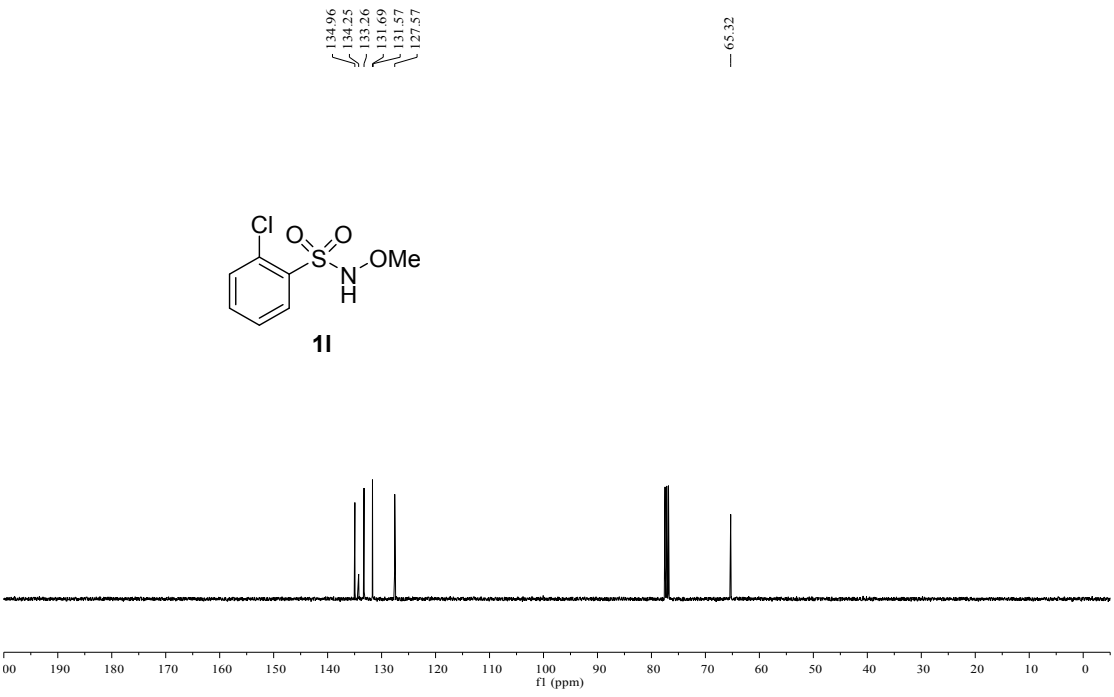
^{1}H NMR of *N*-methoxy-2-methoxybenzsulfonamide (**1k**)



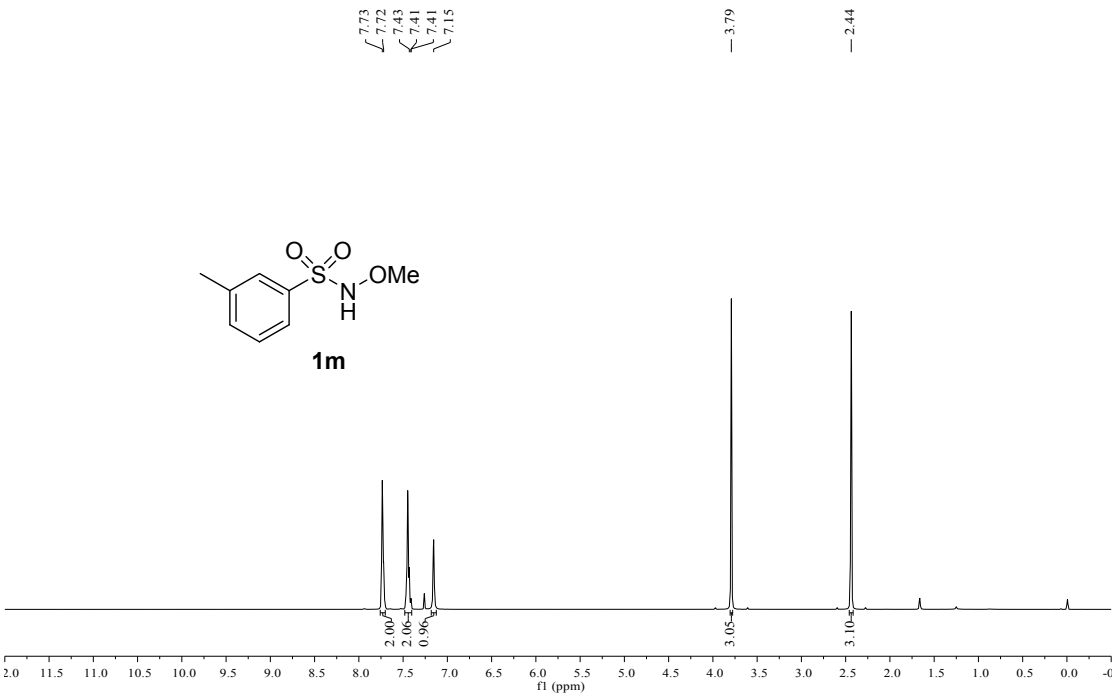
^{13}C NMR of *N*-methoxy-2-methoxybenzsulfonamide (**1k**)



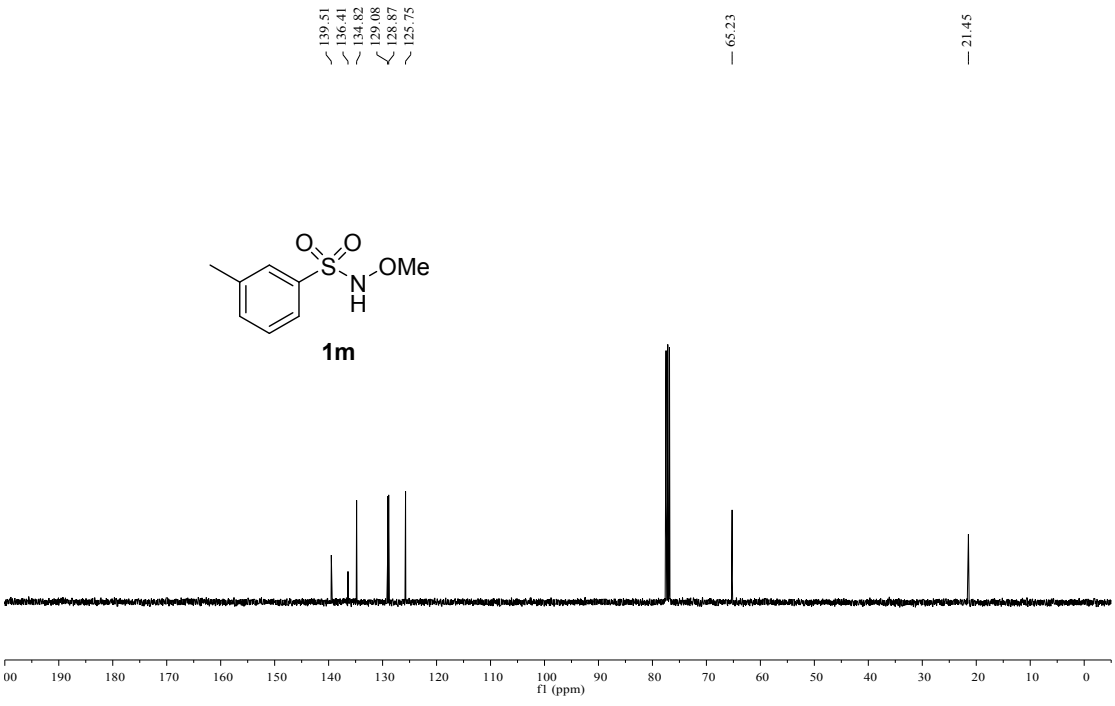
^{1}H NMR of 2-chloro-*N*-methoxy benzsulfonamide (**1l**)



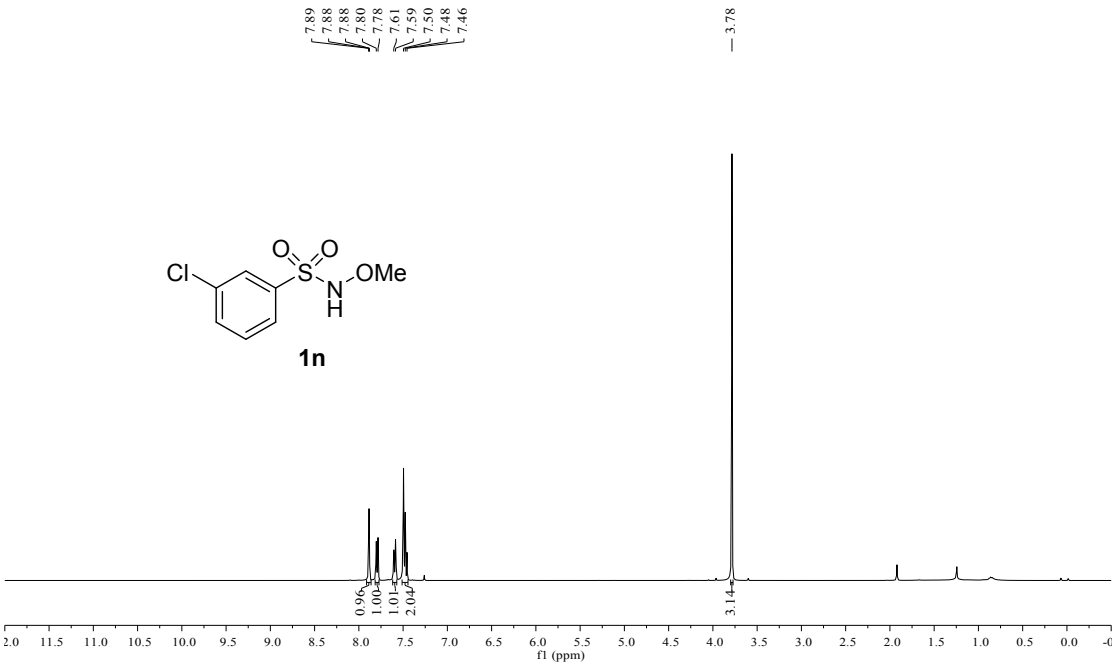
^{13}C NMR of 2-chloro-*N*-methoxy benzsulfonamide (**1l**)



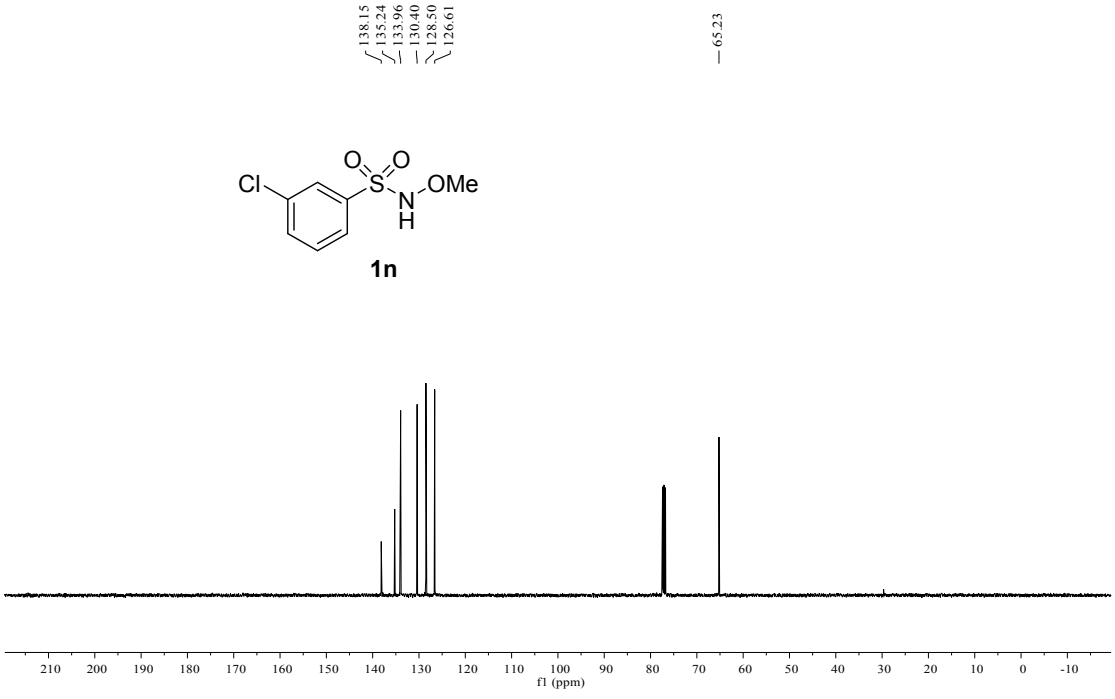
^{1}H NMR of *N*-methoxy-3-methylbenzsulfonamide (**1m**)



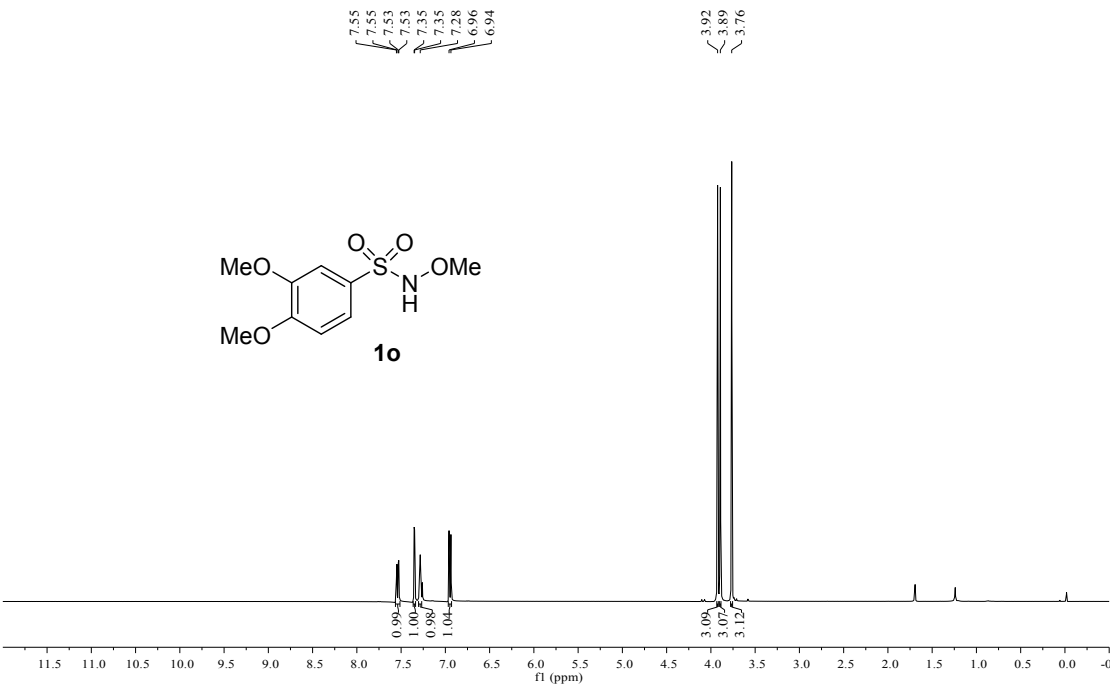
^{13}C NMR of *N*-methoxy-3-methylbenzsulfonamide (**1m**)



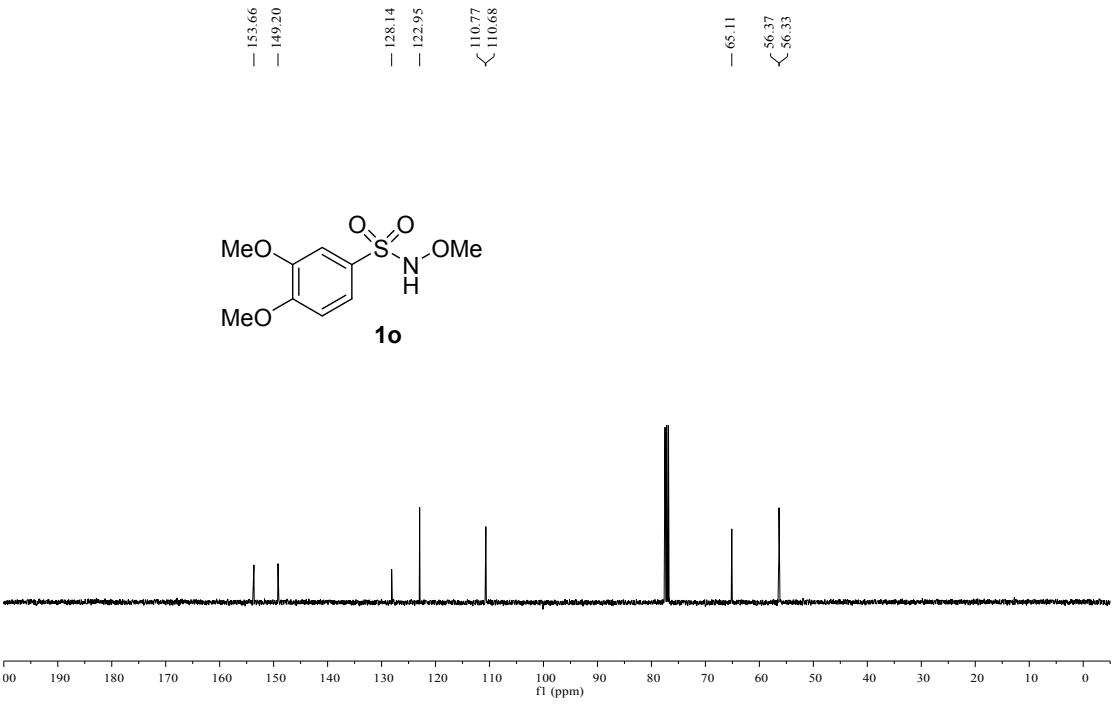
^{1}H NMR of 3-chloro-*N*-methoxy benzsulfonamide (**1n**)



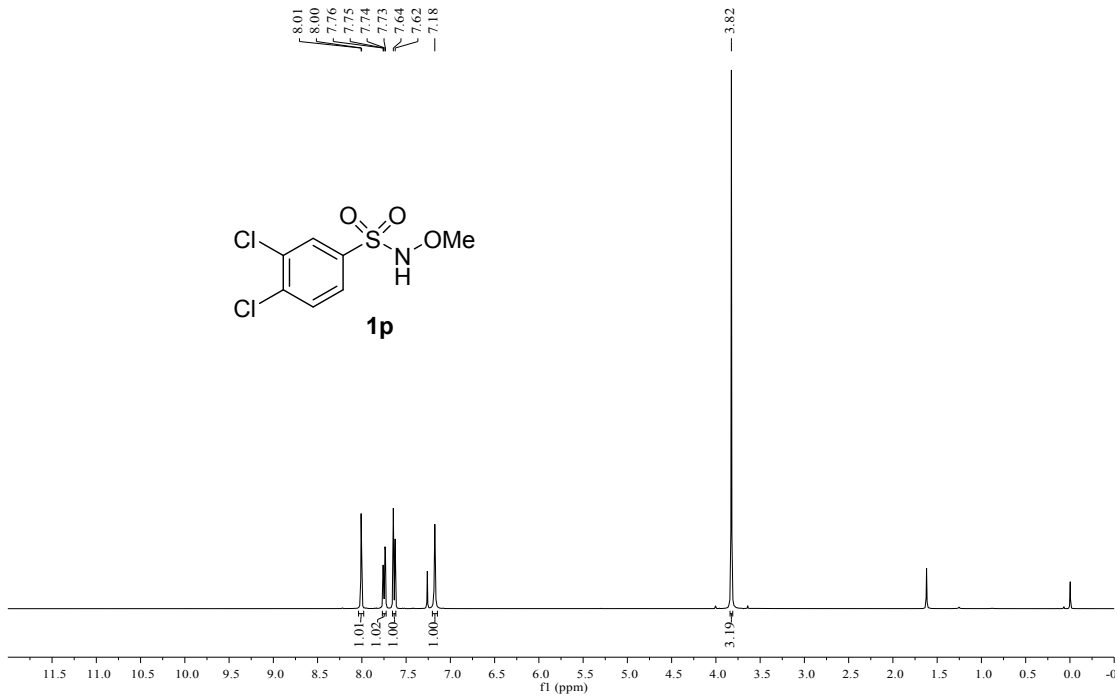
^{13}C NMR of 3-chloro-*N*-methoxy benzsulfonamide (**1n**)



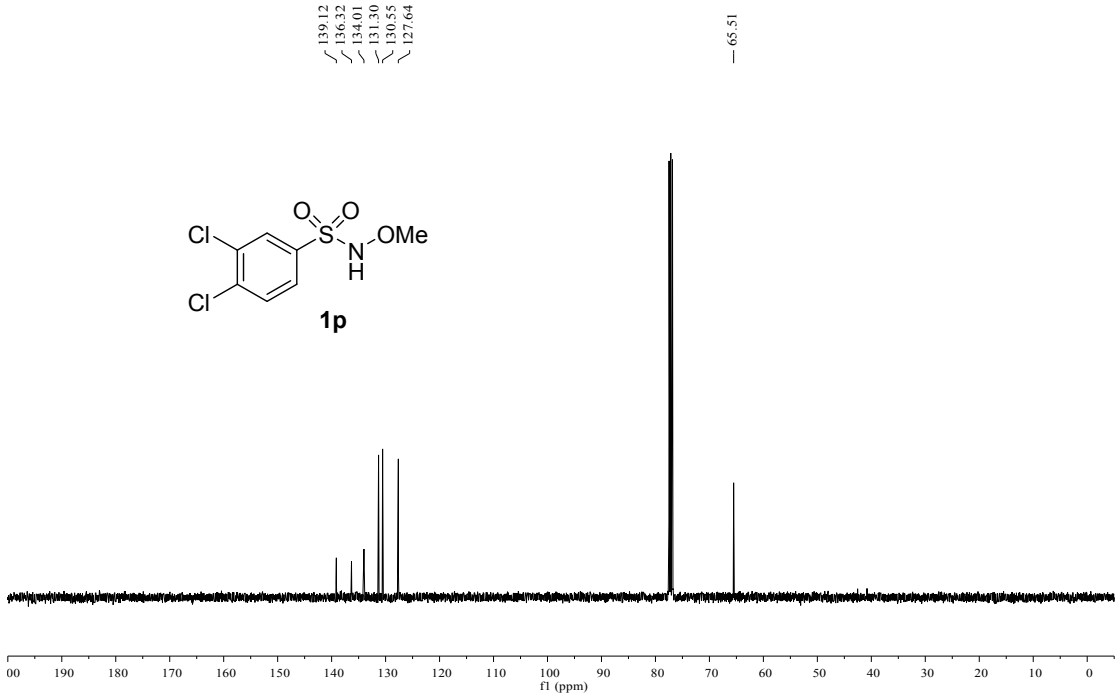
^{1}H NMR of 3,4-dimethoxy-*N*-methoxy benzsulfonamide (**1o**)



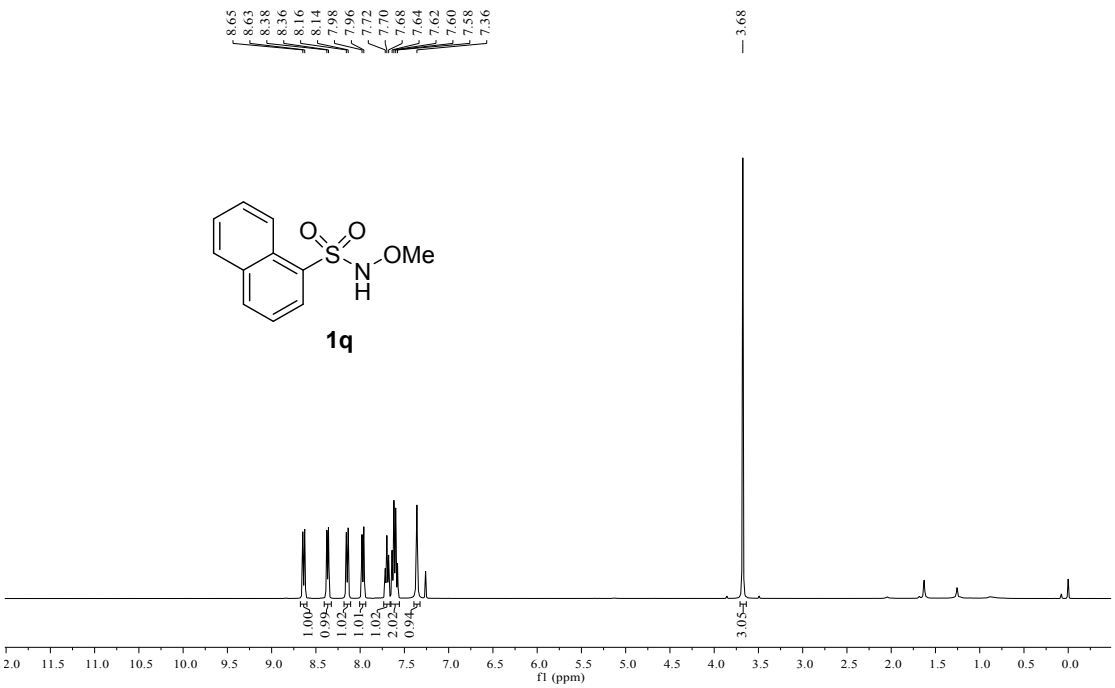
^{13}C NMR of 3,4-dimethoxy-*N*-methoxy benzsulfonamide (**1o**)



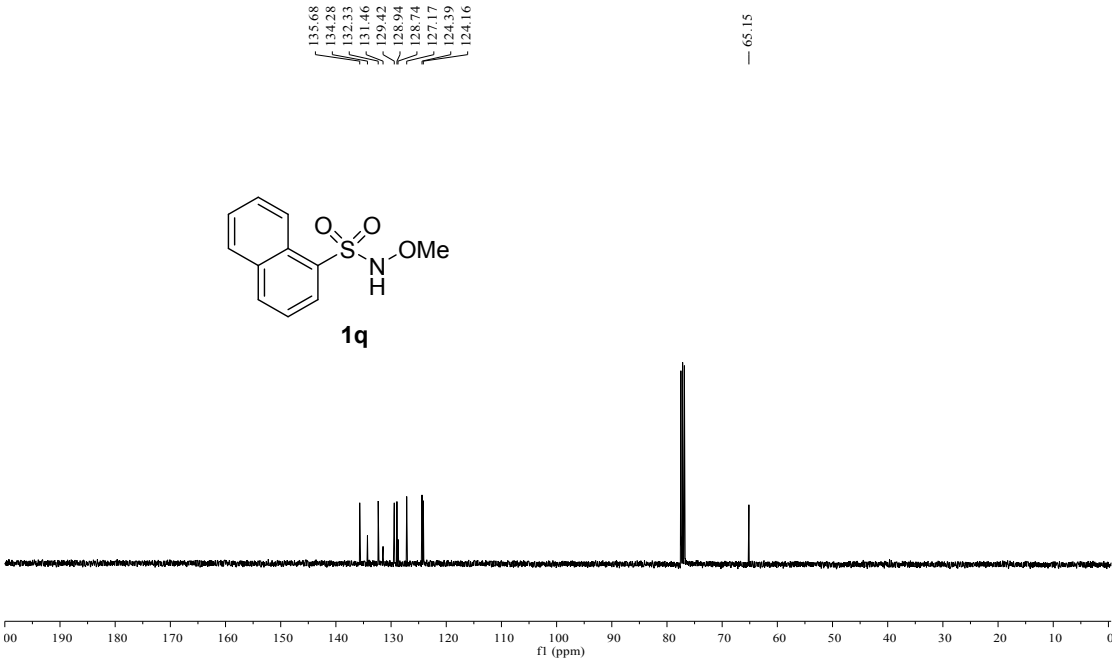
^{1}H NMR of 3,4-dichloro-*N*-methoxy benzsulfonamide (**1p**)



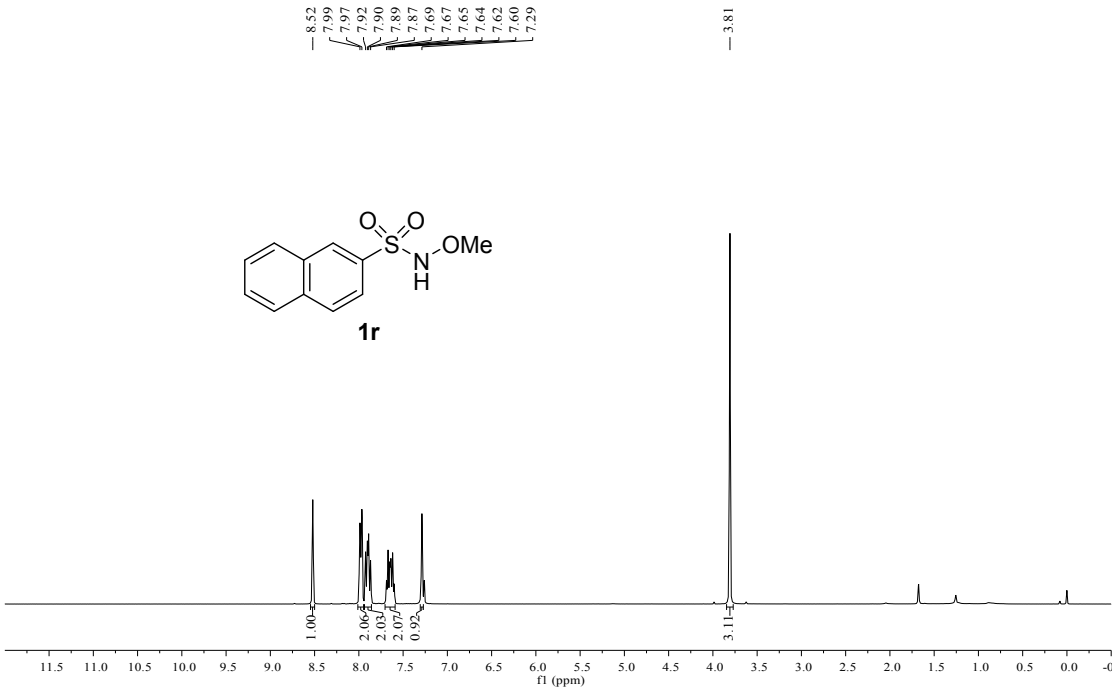
^{13}C NMR of 3,4-dichloro-*N*-methoxy benzsulfonamide (**1p**)



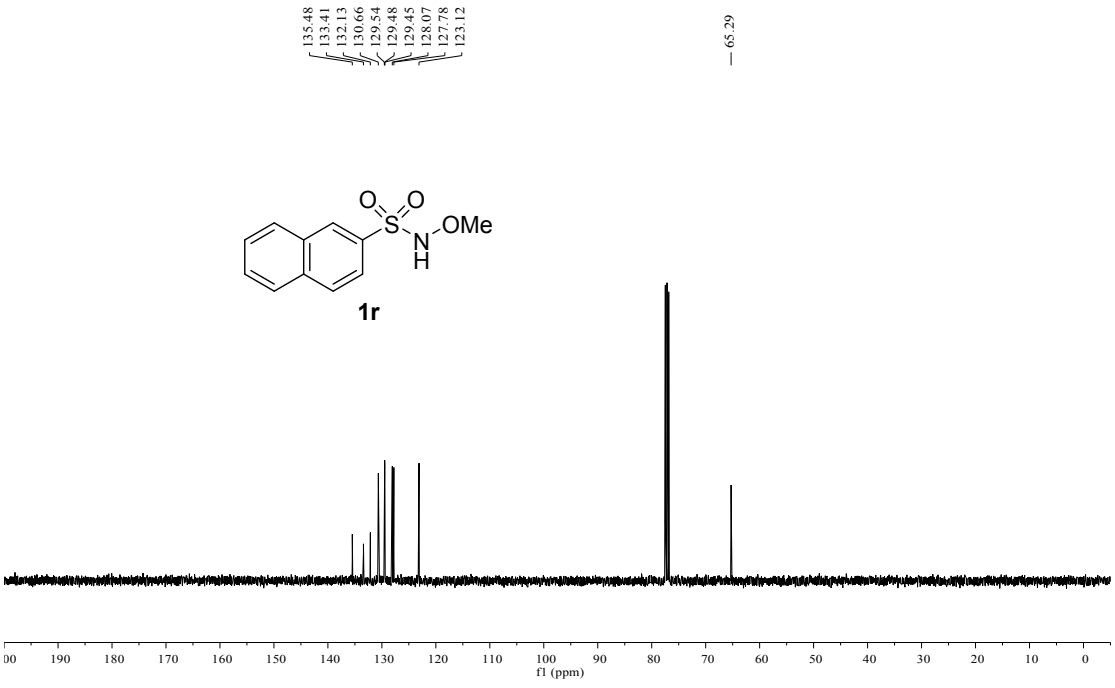
^{1}H NMR of *N*-methoxy naphthalene-1-sulfonamide (**1q**)



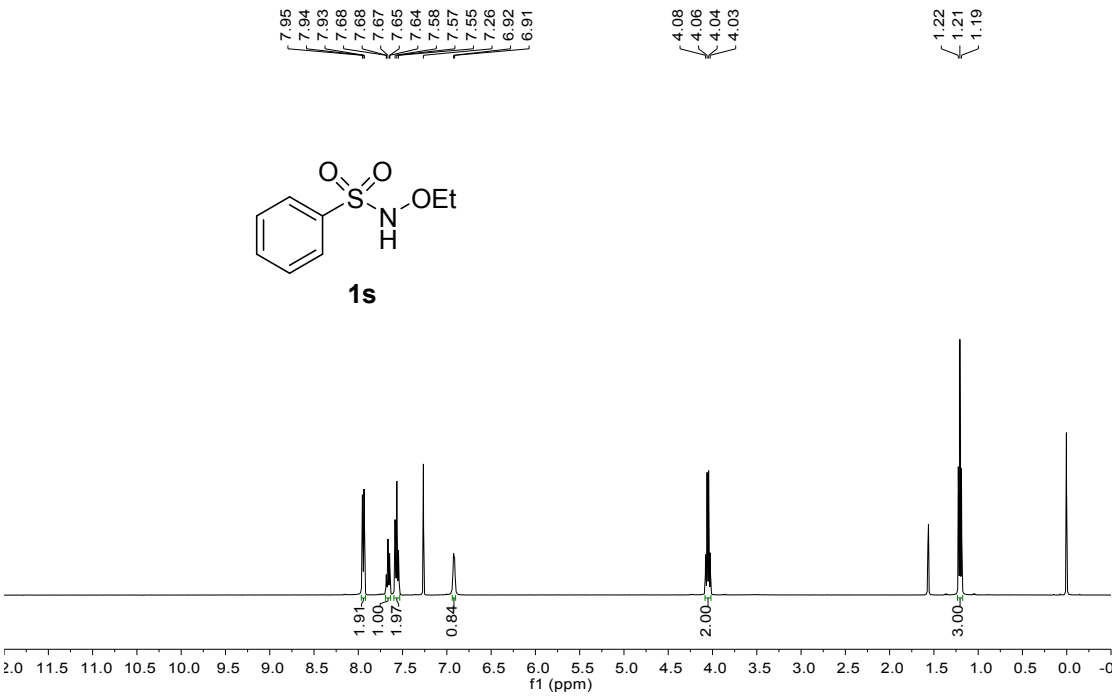
^{13}C NMR of *N*-methoxynaphthalene-1-sulfonamide (**1q**)



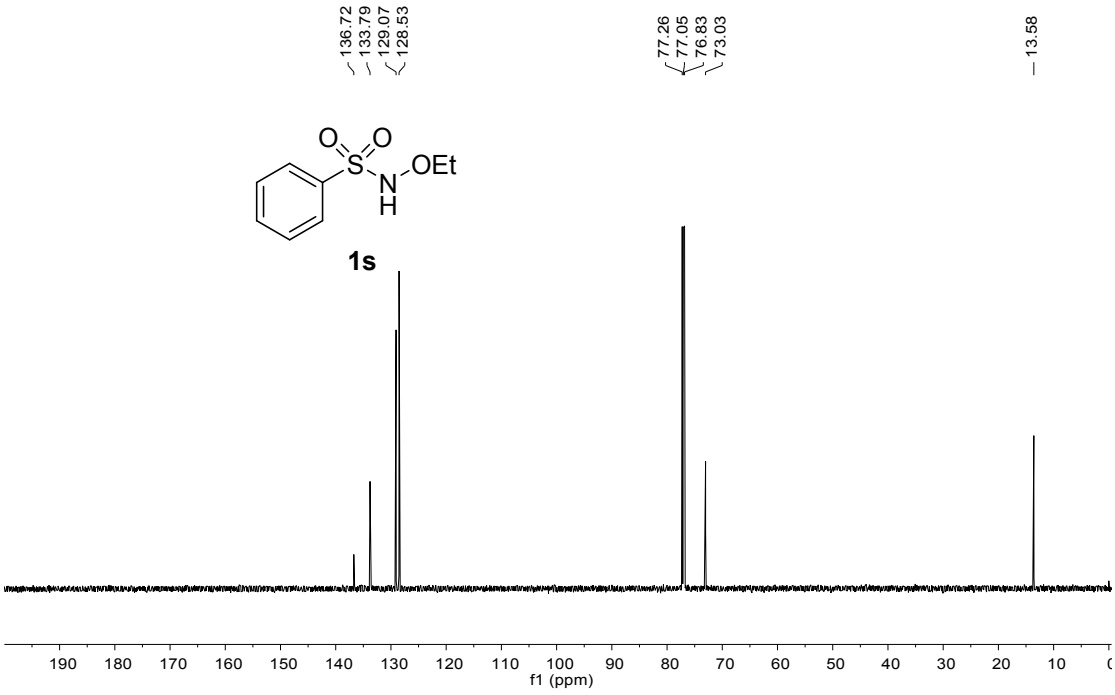
^{1}H NMR of *N*-methoxy naphthalene-2-sulfonamide (**1r**)



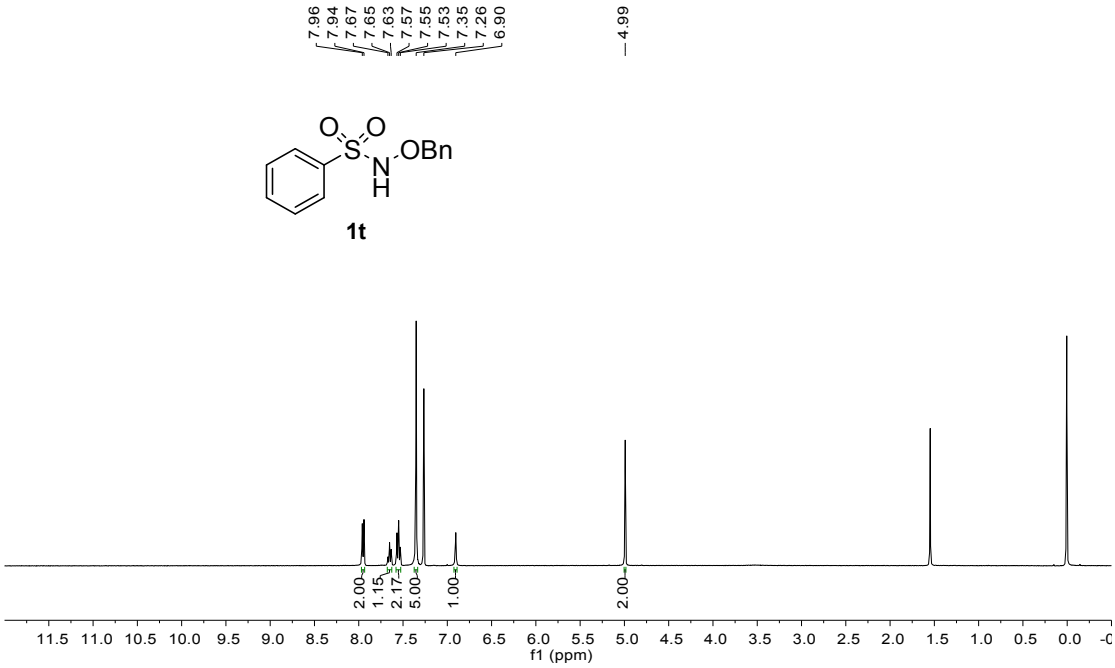
^{13}C NMR of *N*-methoxy naphthalene-2-sulfonamide (**1r**)



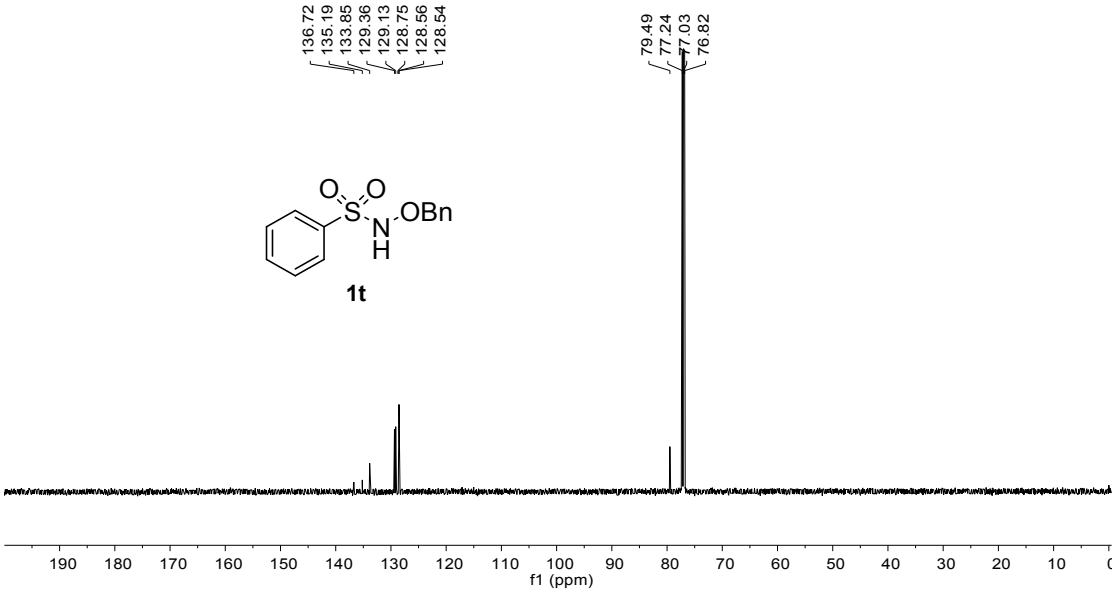
^{1}H NMR of *N*-ethoxy benzenesulfonamide (**1s**)



^{13}C NMR of *N*-ethoxy benzenesulfonamide (**1s**)

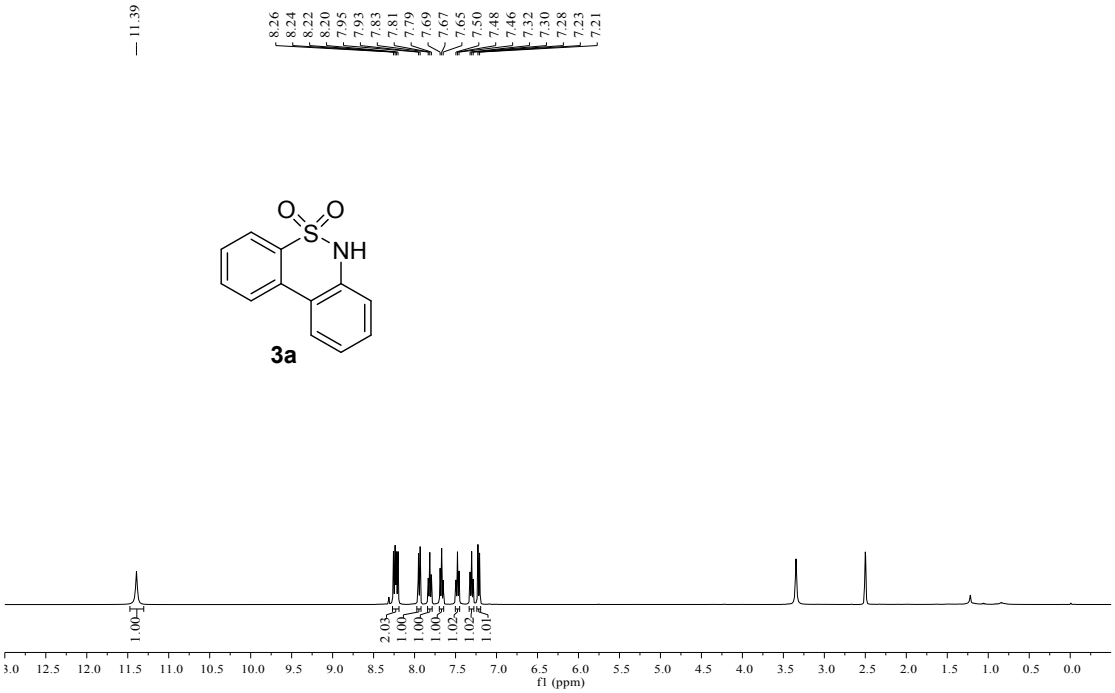


^{1}H NMR of *N*-benzyloxy benzenesulfonamide (**1t**)

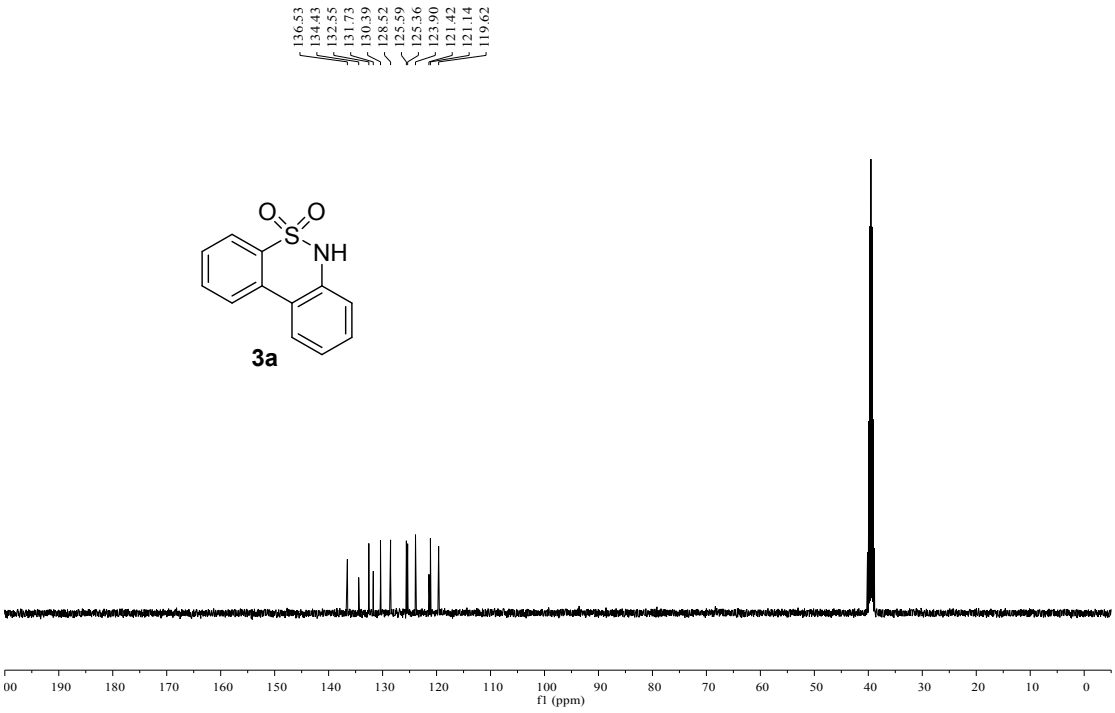


^{13}C NMR of *N*-benzyloxy benzenesulfonamide (**1t**)

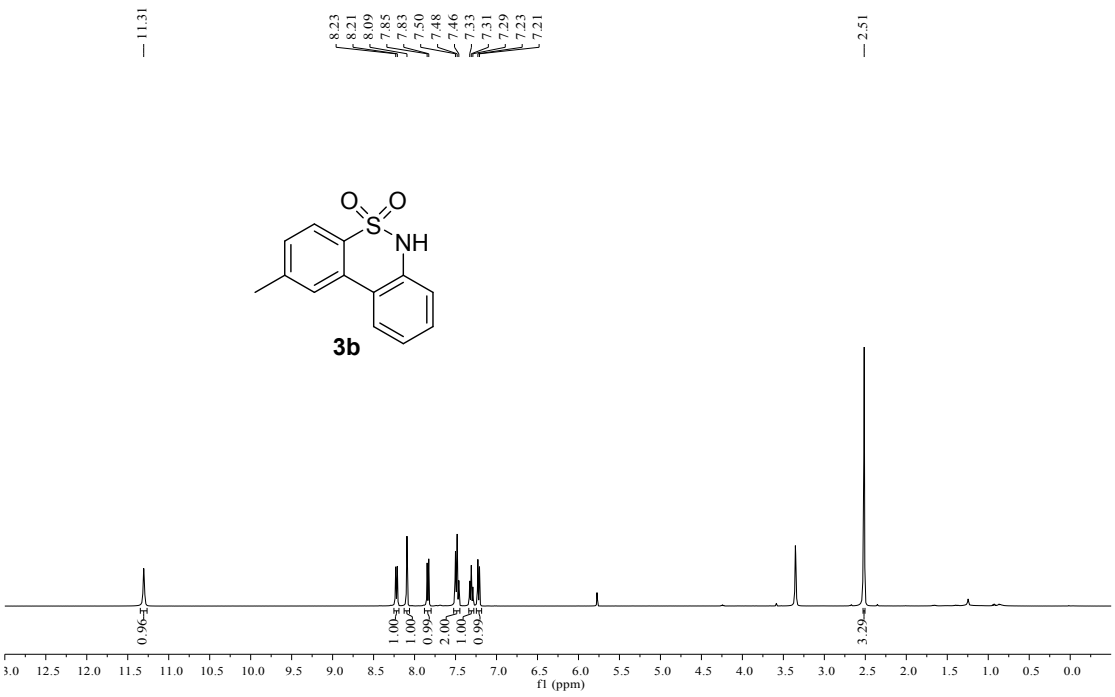
6. Copies of ^{1}H NMR and ^{13}C NMR Charts for products



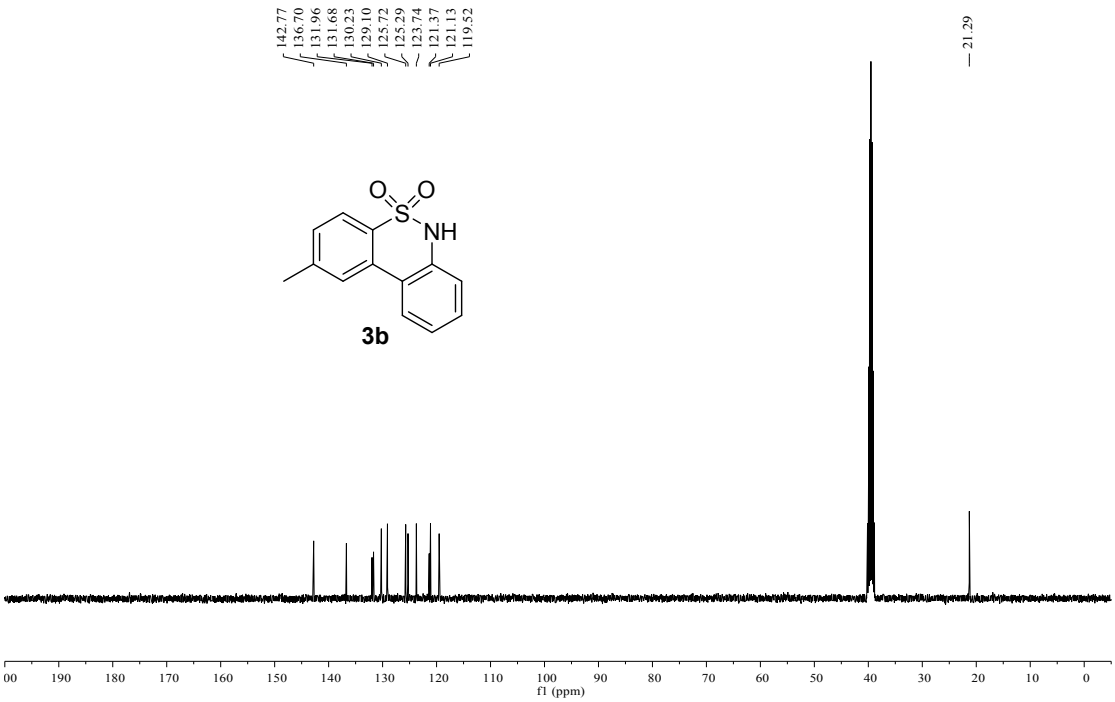
^{1}H NMR of 6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3a**)



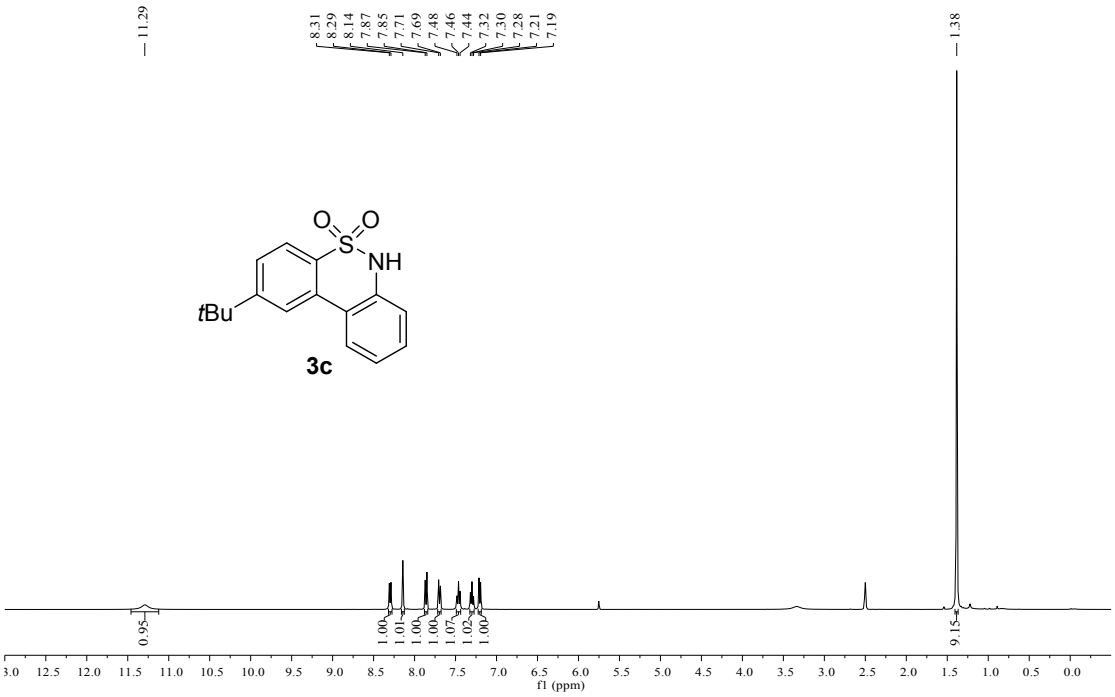
^{13}C NMR of 6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3a**)



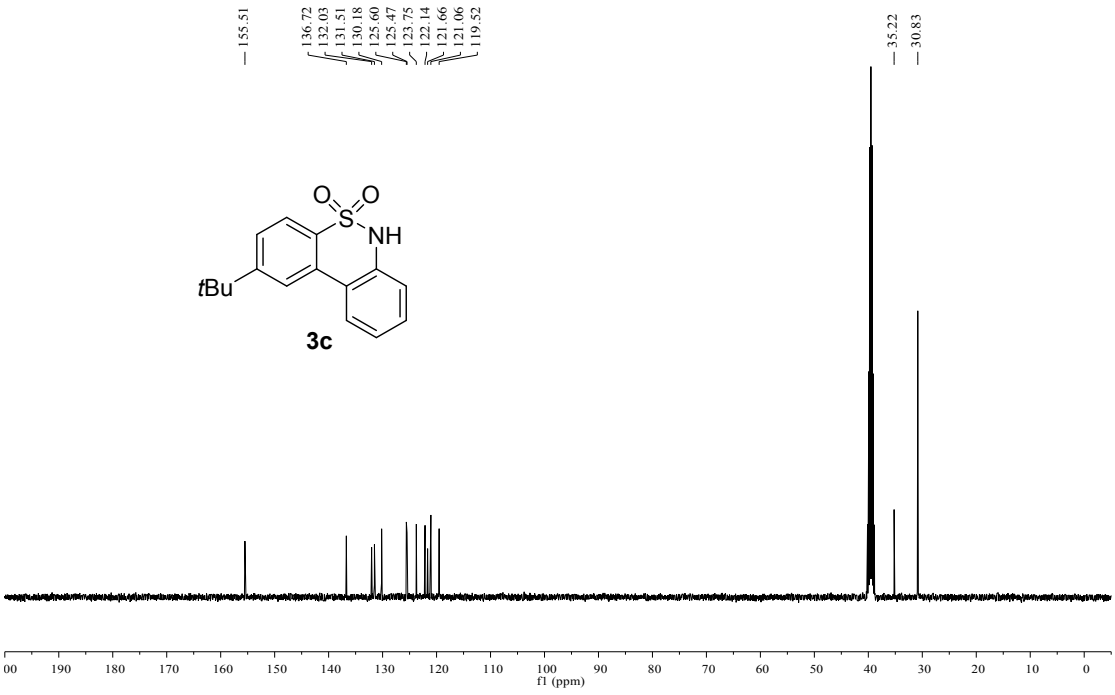
^{1}H NMR of 2-methyl-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3b**)



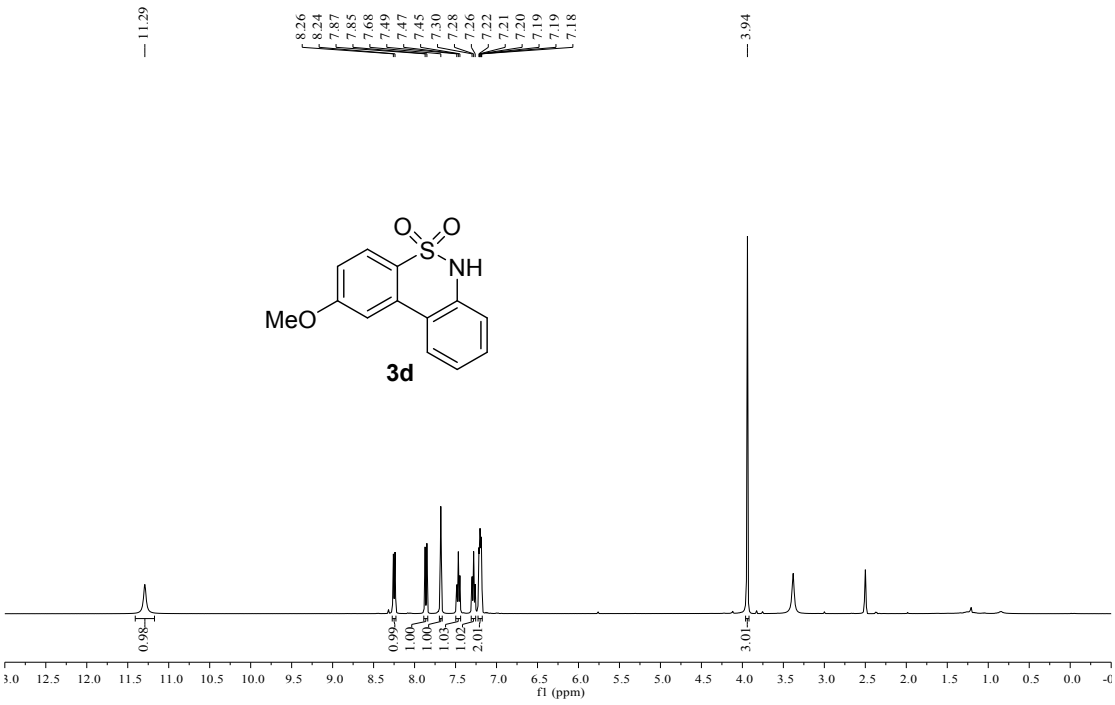
^{13}C NMR of 2-methyl-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3b**)



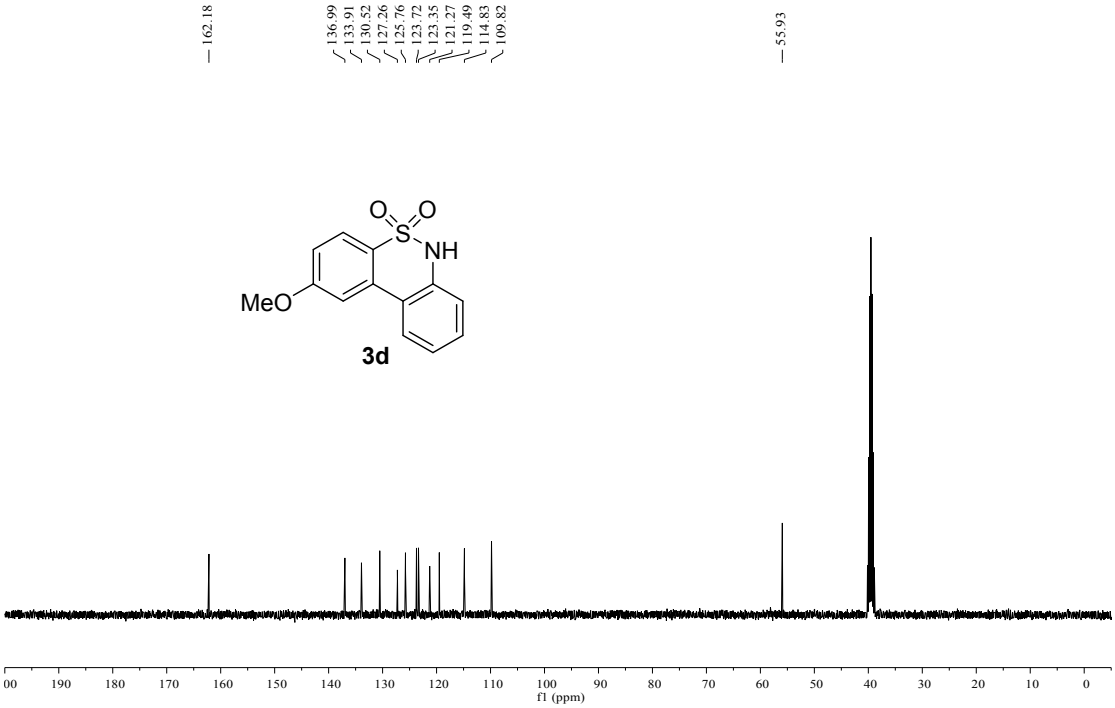
^{1}H NMR of 2-(*tert*-butyl)-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3c**)



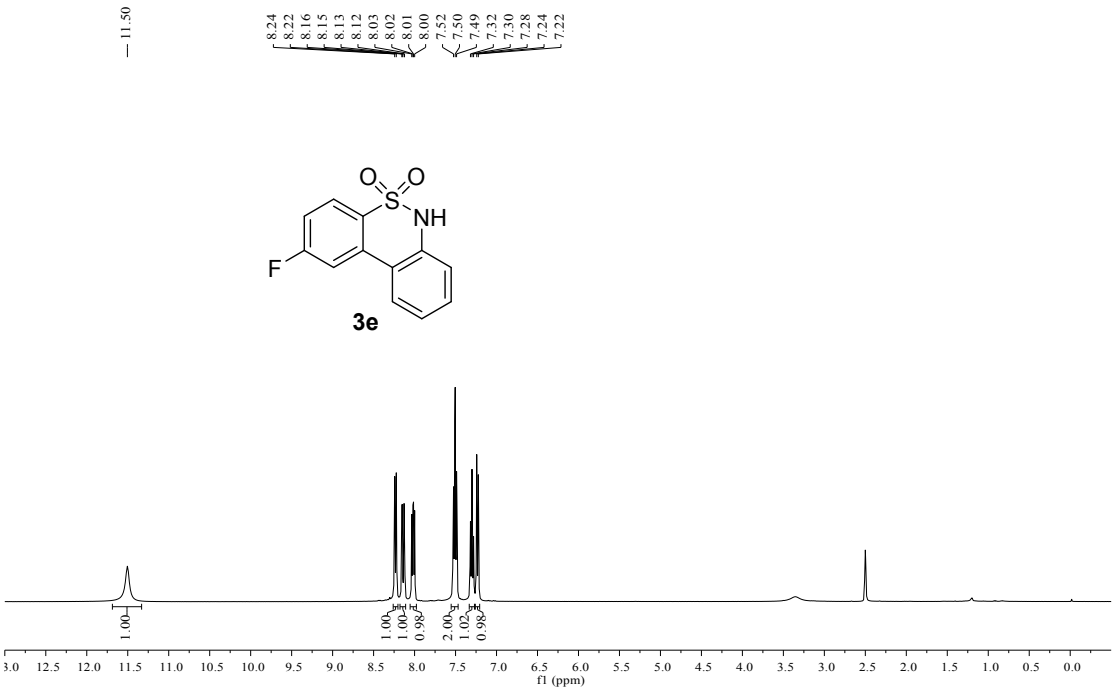
^{13}C NMR of 2-(*tert*-butyl)-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3c**)



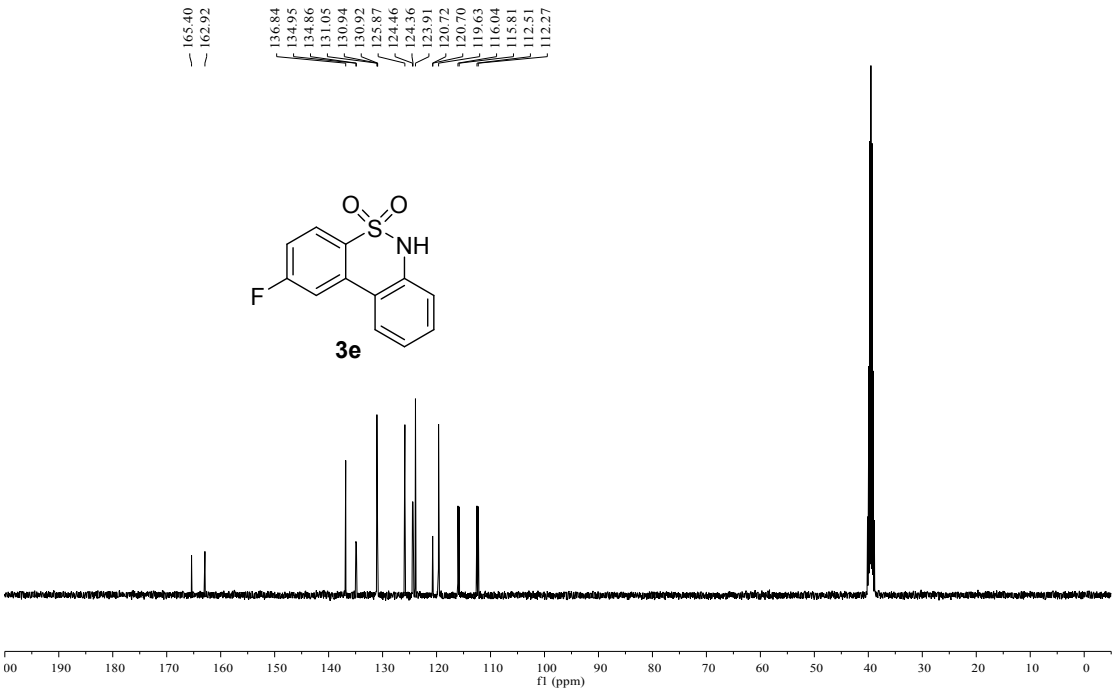
^{1}H NMR of 2-methoxy-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3d**)



^{13}C NMR of 2-methoxy-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3d**)

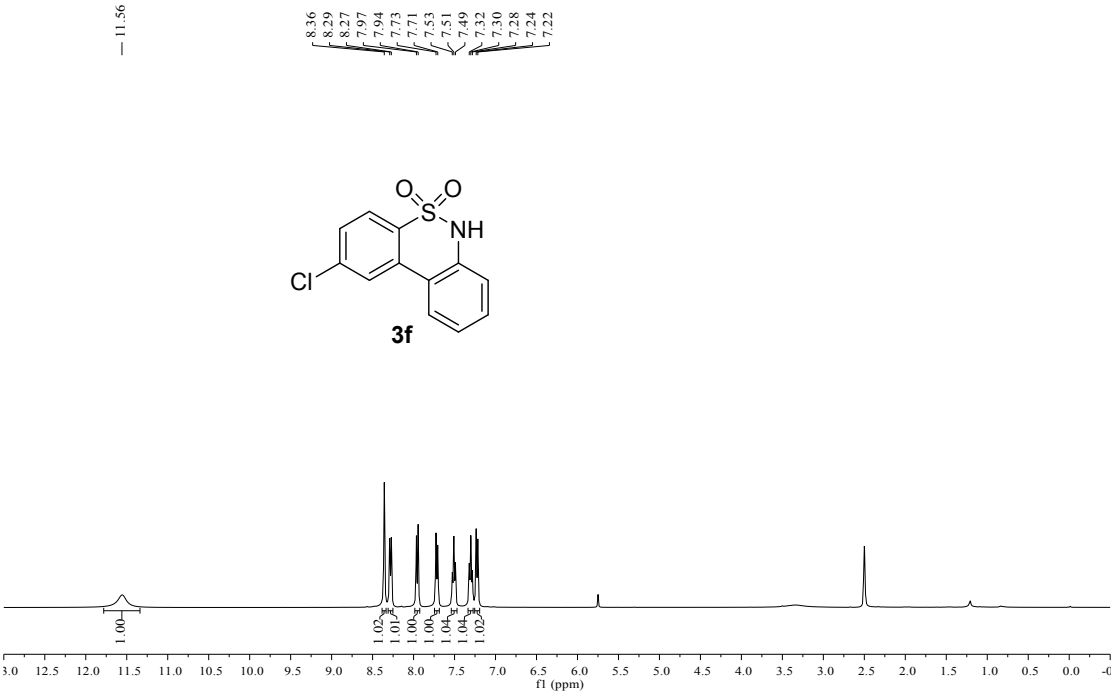


^{1}H NMR of 2-fluoro-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3e**)

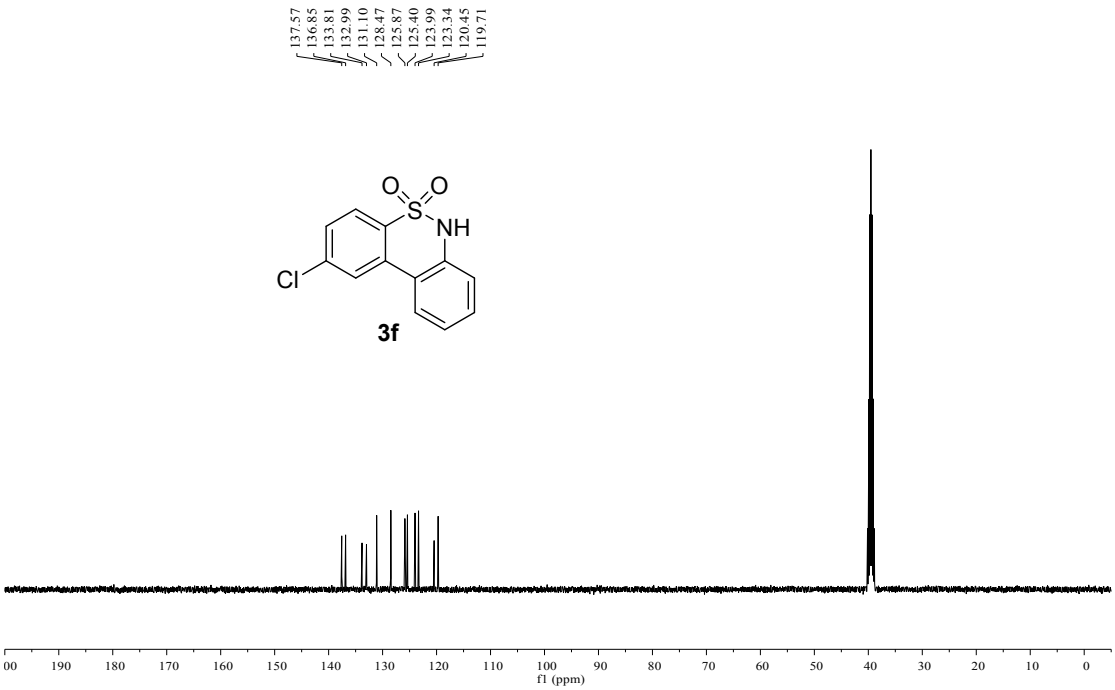


^{13}C NMR of 2-fluoro-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3e**)

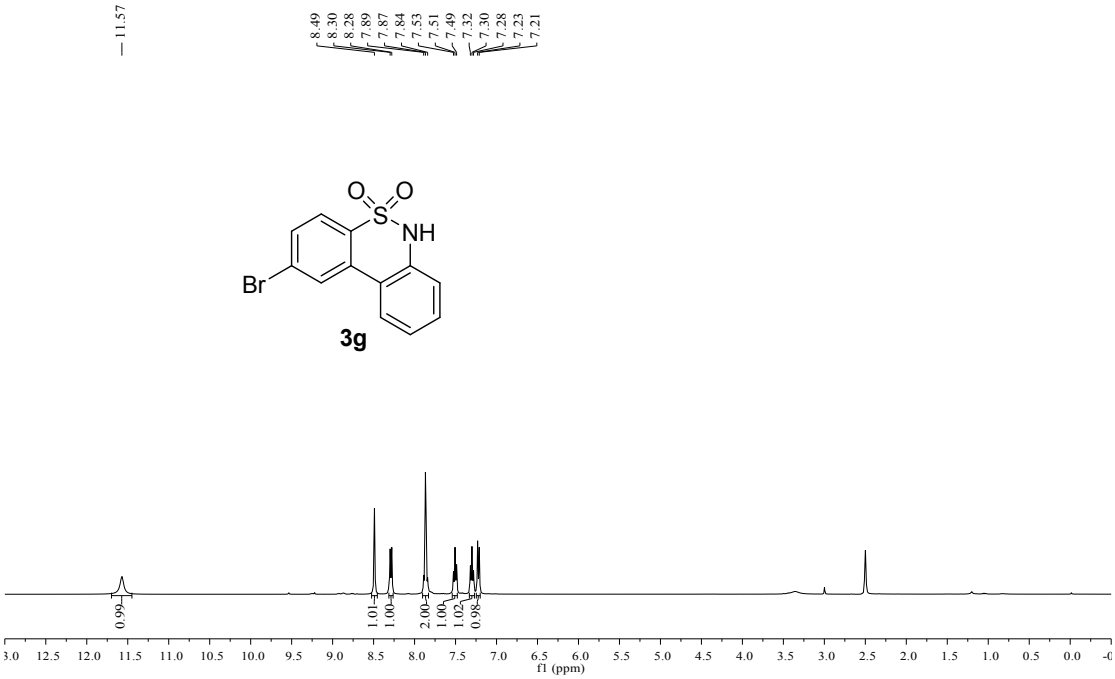
^{19}F NMR of 2-fluoro-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3e**)



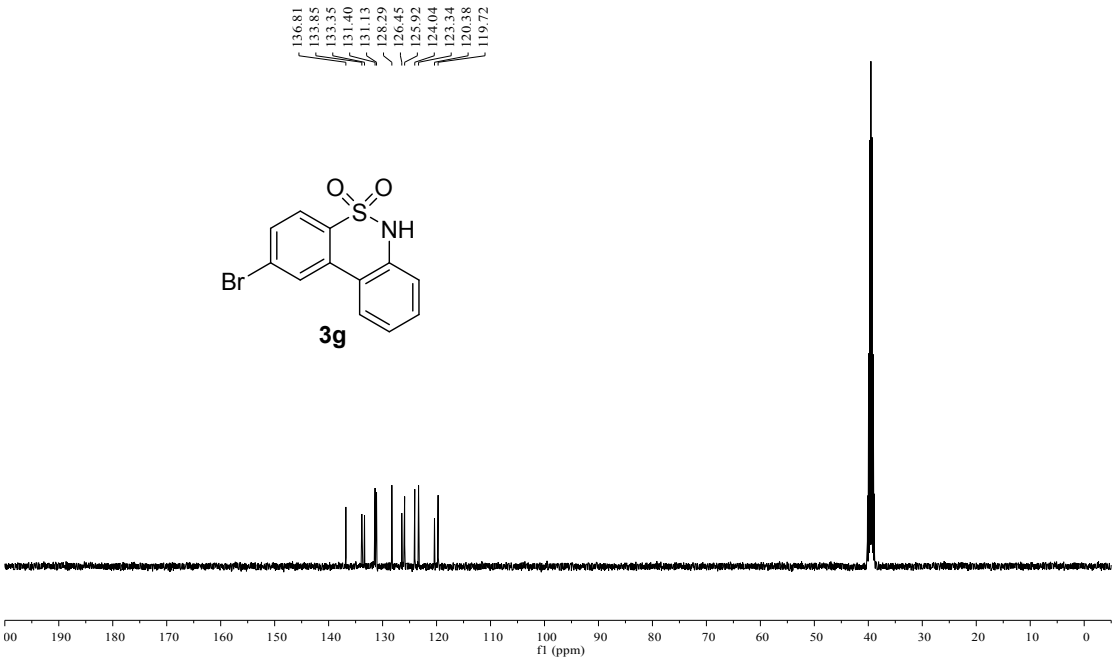
^{1}H NMR of 2-chloro-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3f**)



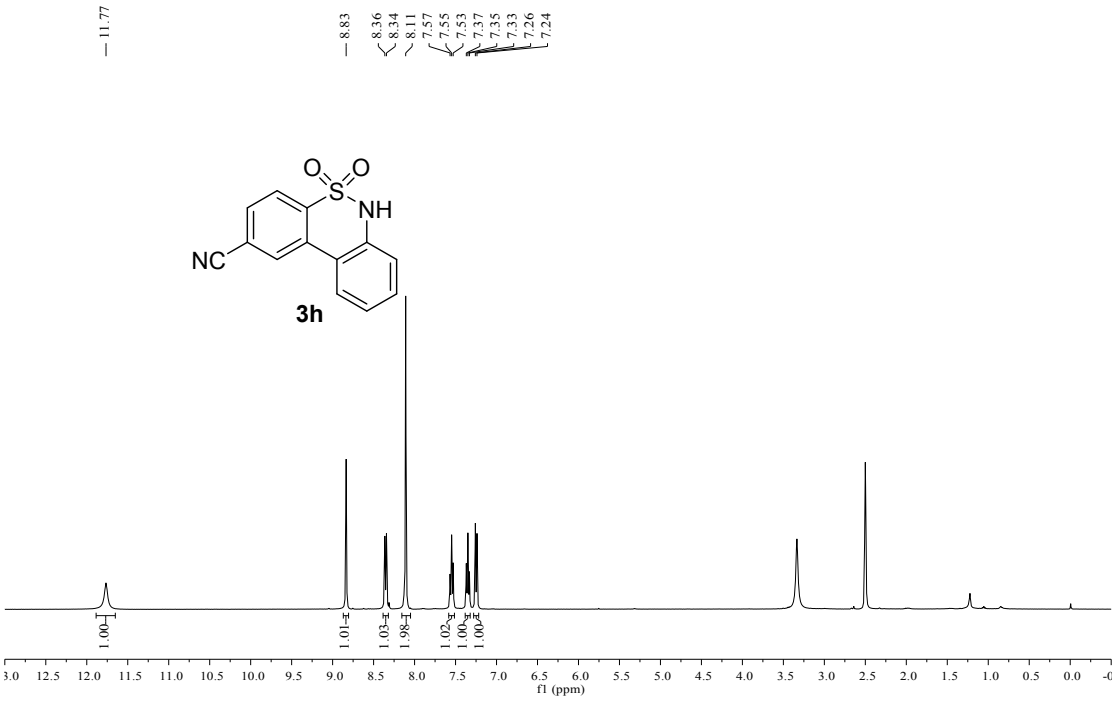
^{13}C NMR of 2-chloro-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3f**)



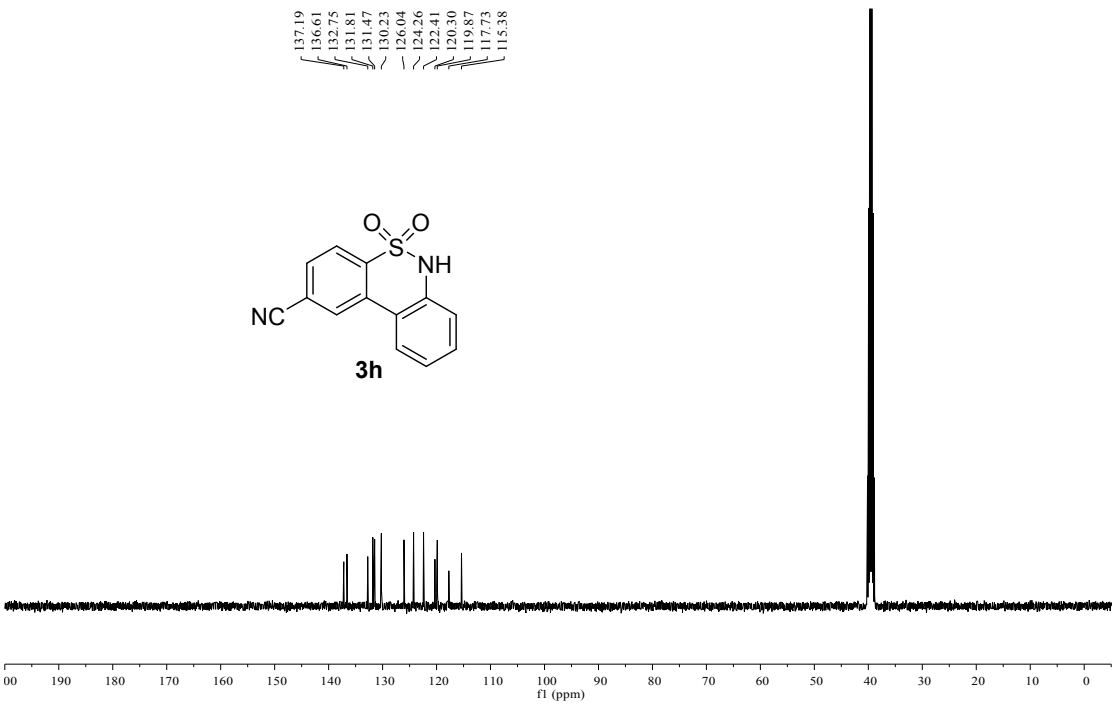
^{1}H NMR of 2-bromo-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3g**)



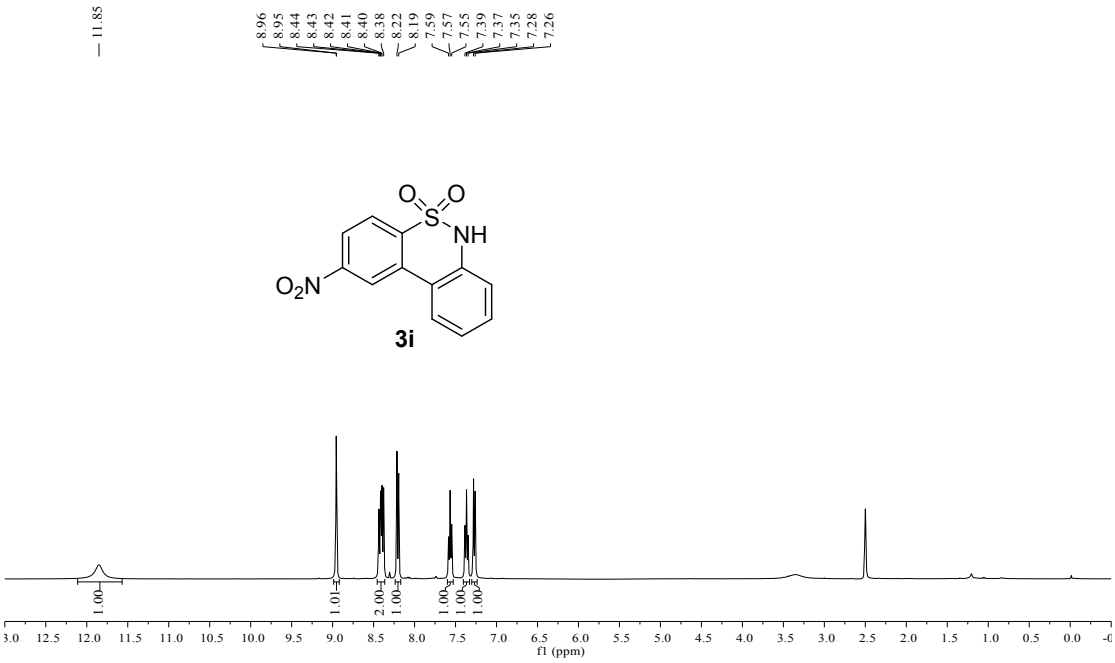
^{13}C NMR of 2-bromo-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3g**)



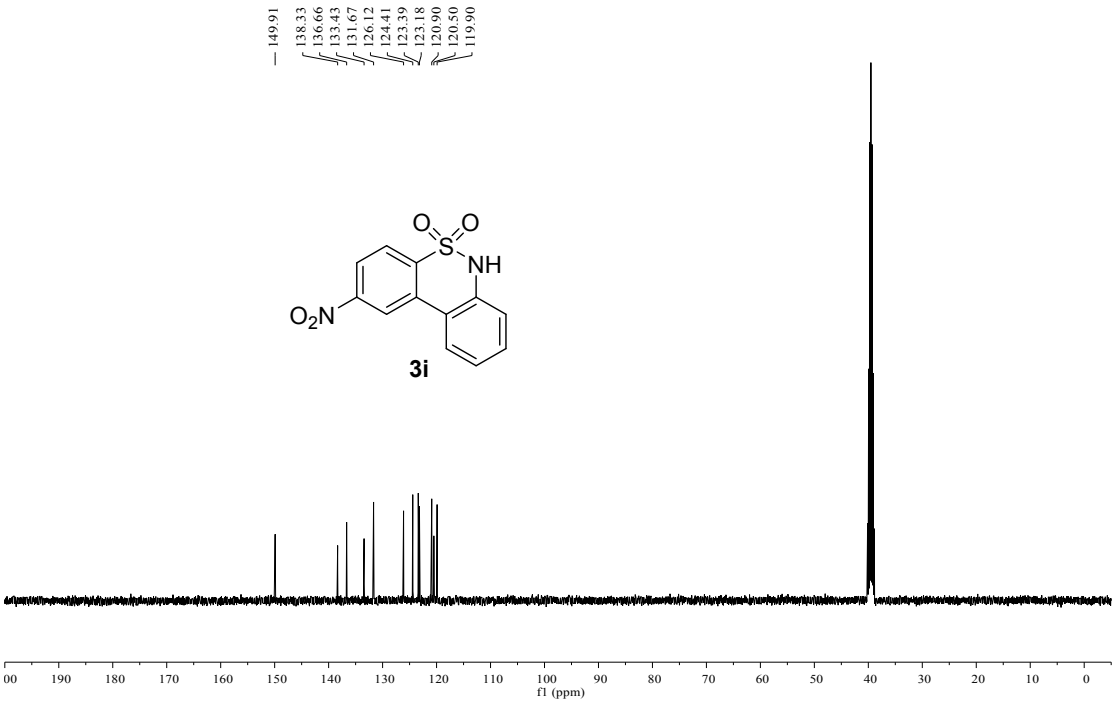
^{1}H NMR of 6*H*-dibenzo[c,e][1,2]thiazine-2-carbonitrile 5,5-dioxide (**3h**)



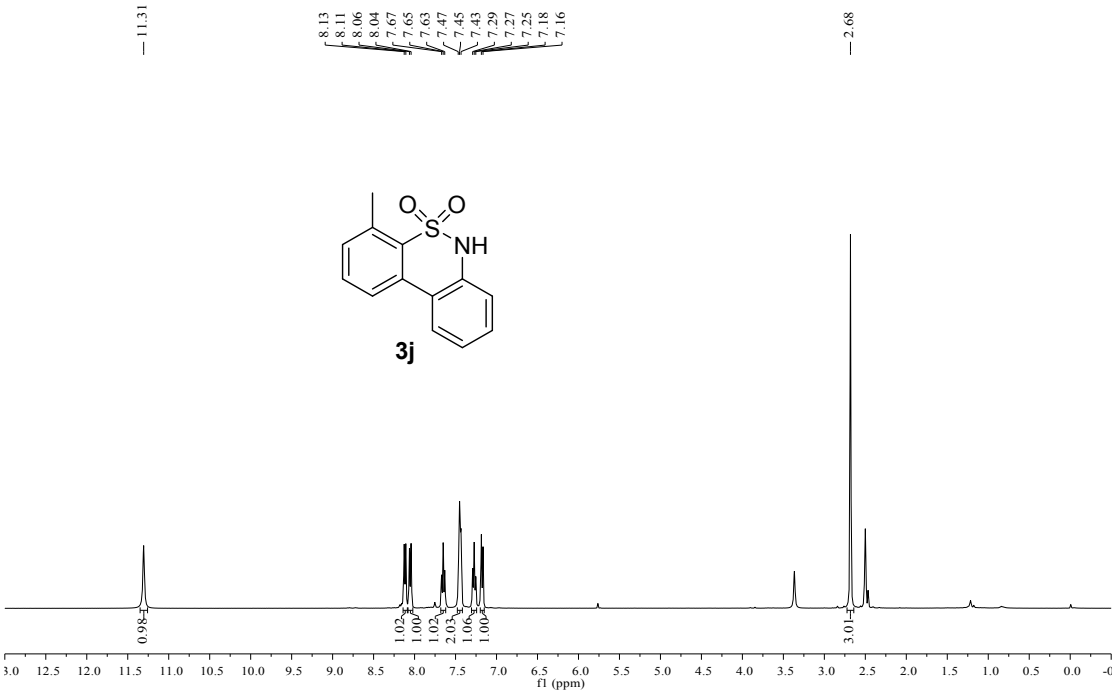
^{13}C NMR of 6*H*-dibenzo[c,e][1,2]thiazine-2-carbonitrile 5,5-dioxide (**3h**)



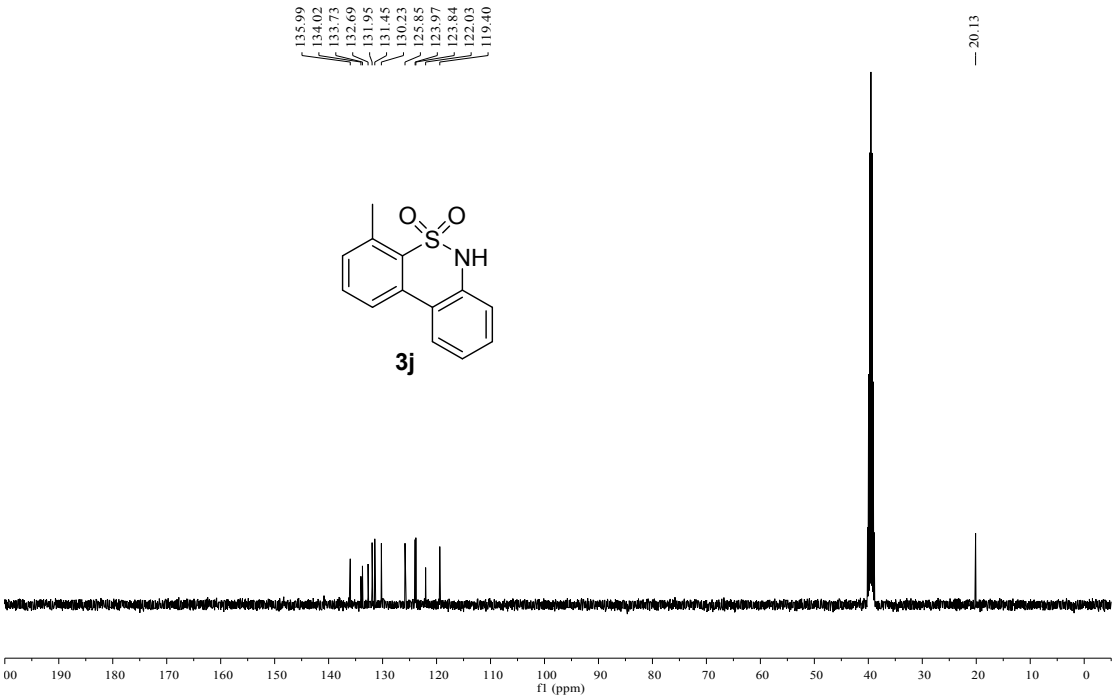
^{1}H NMR of 2-nitro-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3i**)



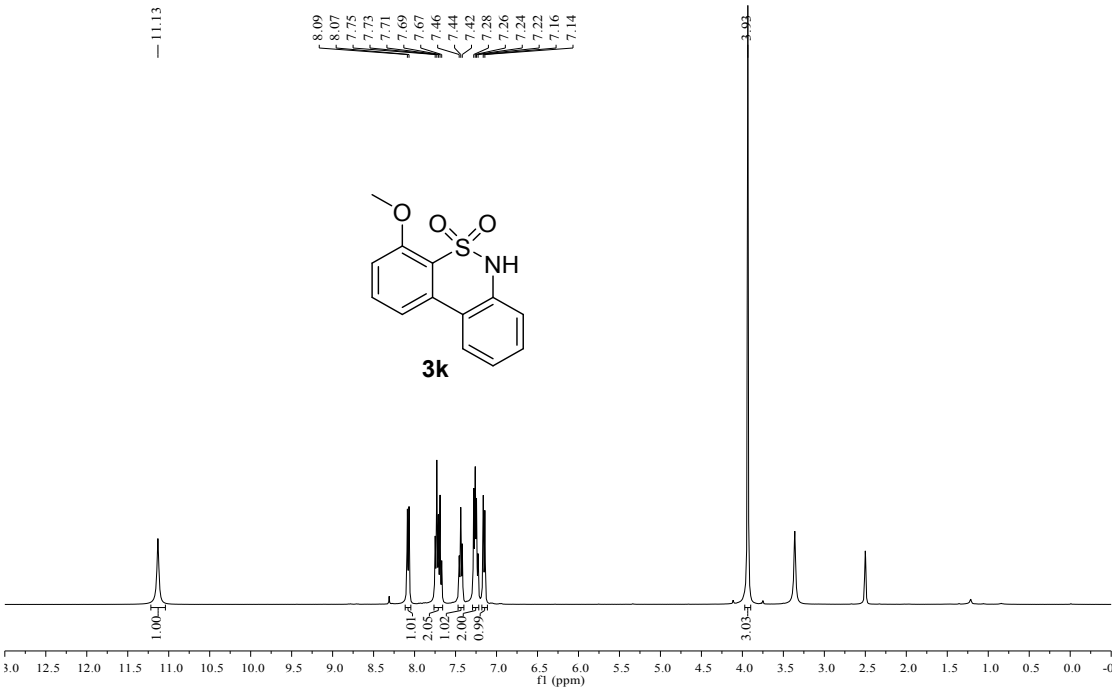
^{13}C NMR of 2-nitro-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3i**)



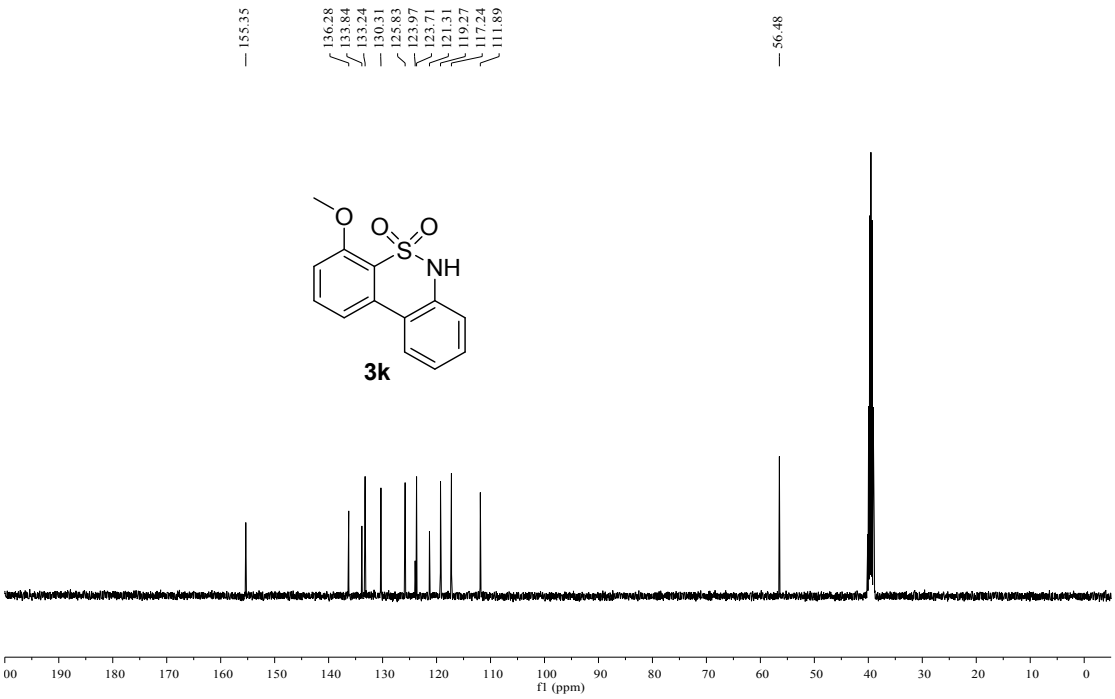
^{1}H NMR of 4-methyl-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3j**)



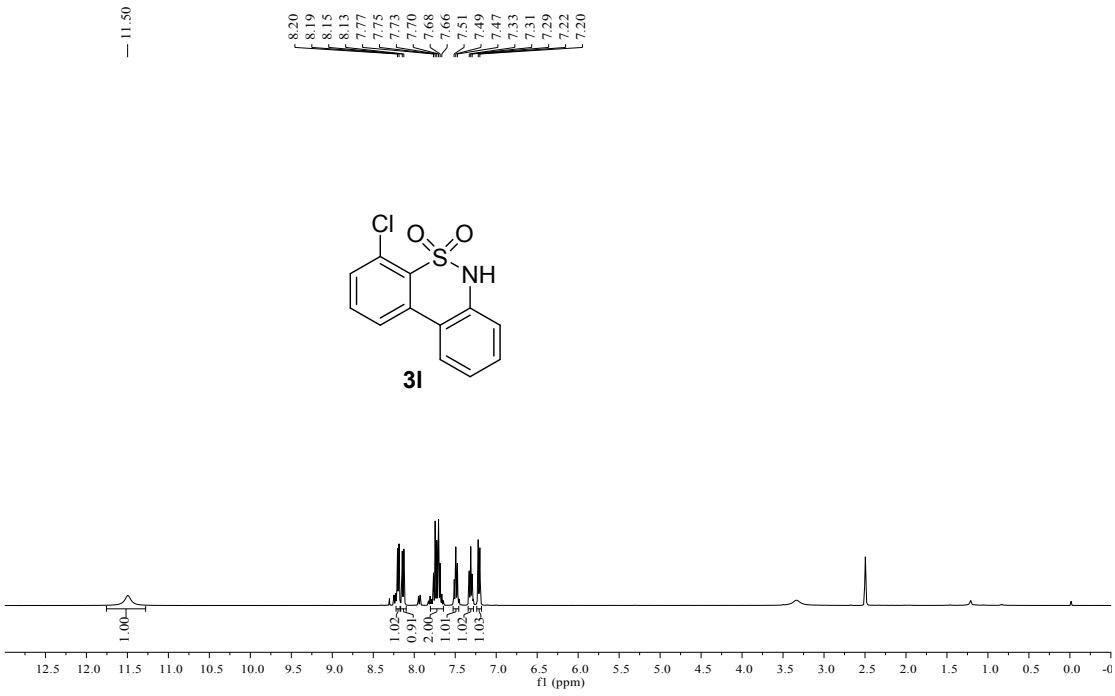
^{13}C NMR of 4-methyl-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3j**)



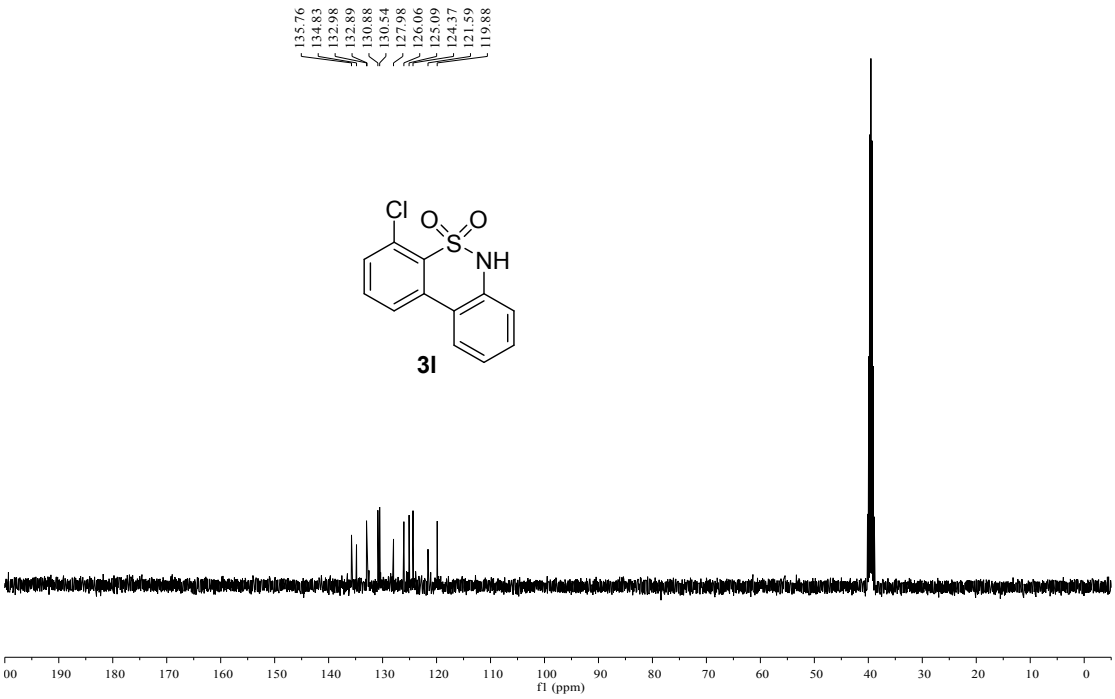
^{1}H NMR of 4-methoxy-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3k**)



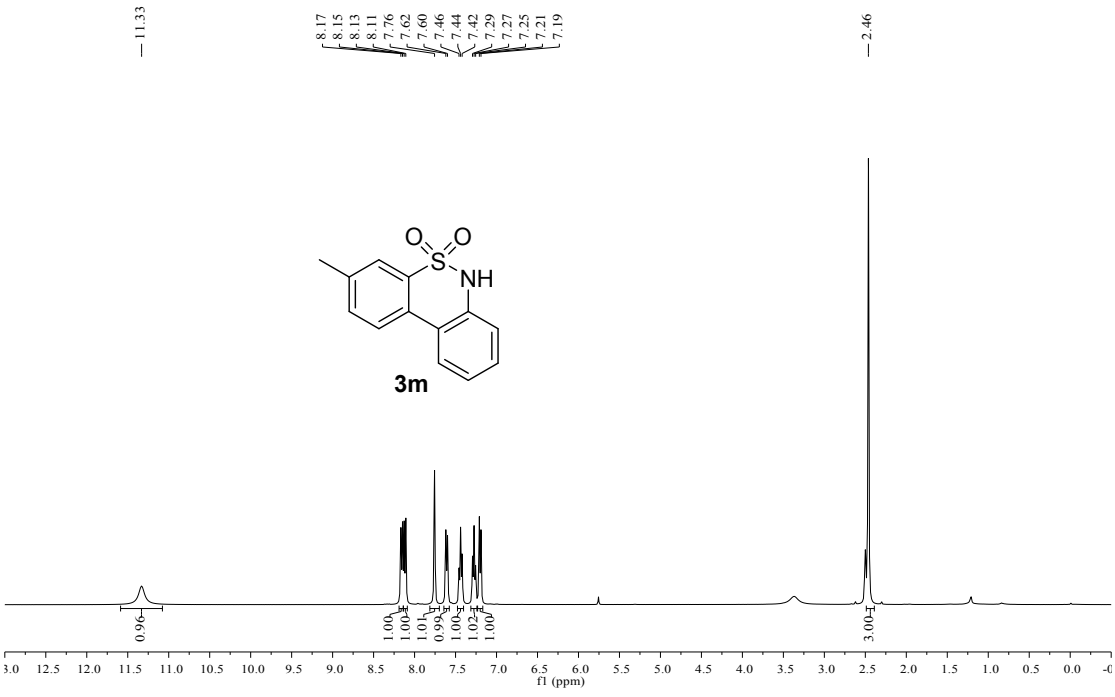
^{13}C NMR of 4-methoxy-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3k**)



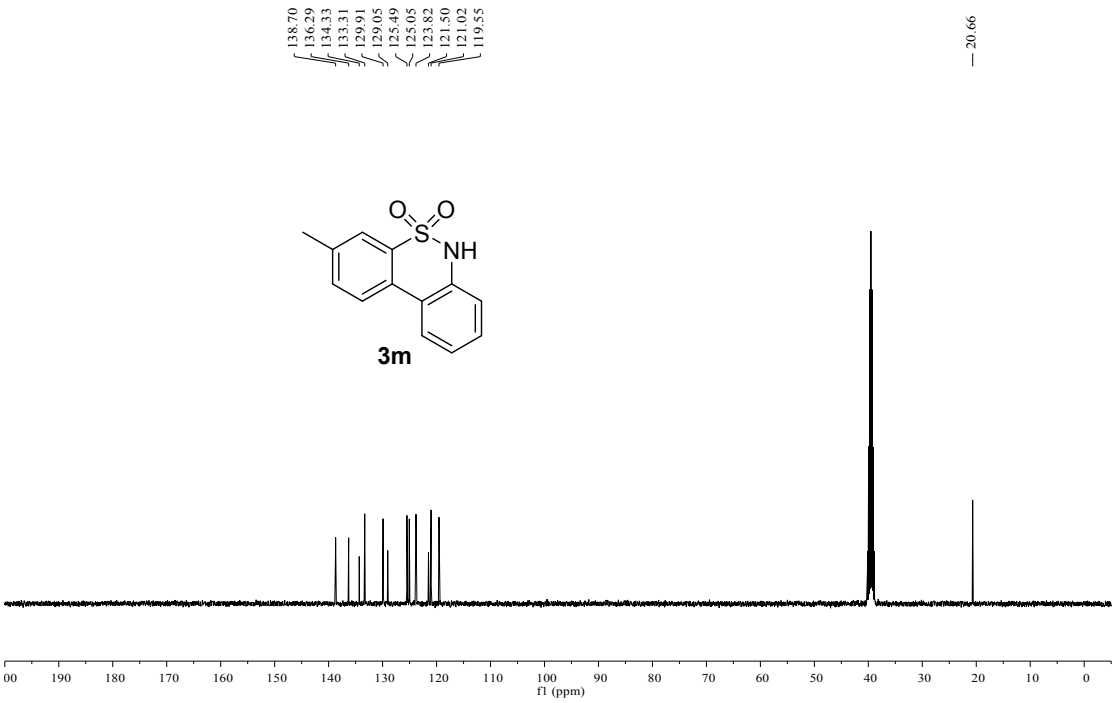
^{1}H NMR of 4-chloro-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3l**)



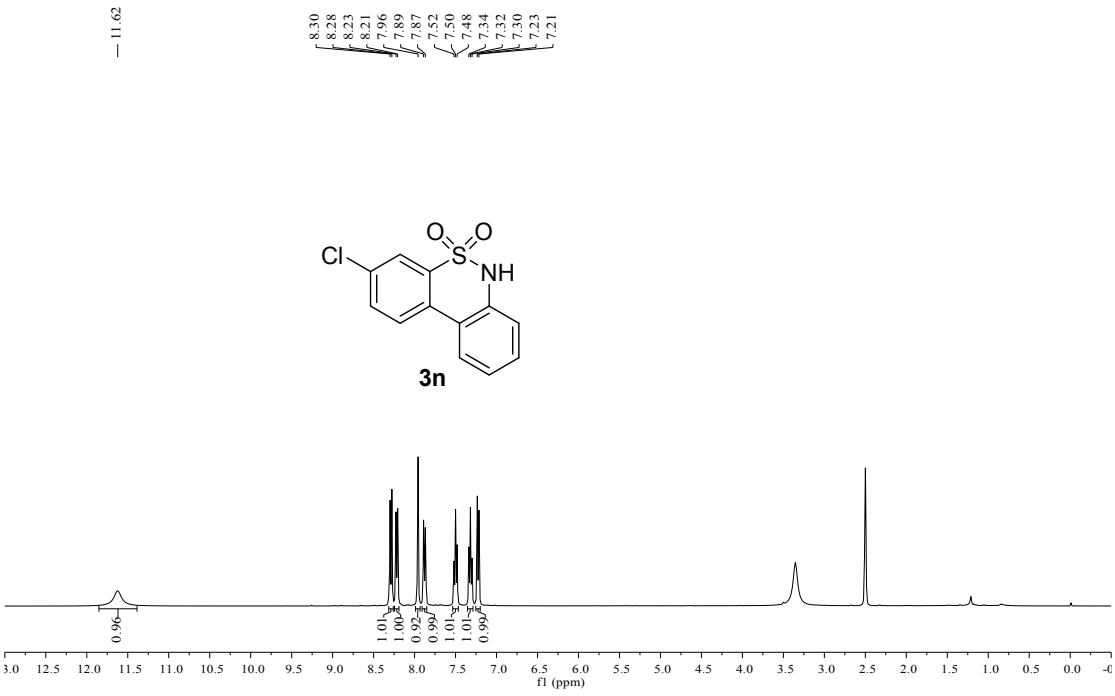
^{13}C NMR of 4-chloro-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3l**)



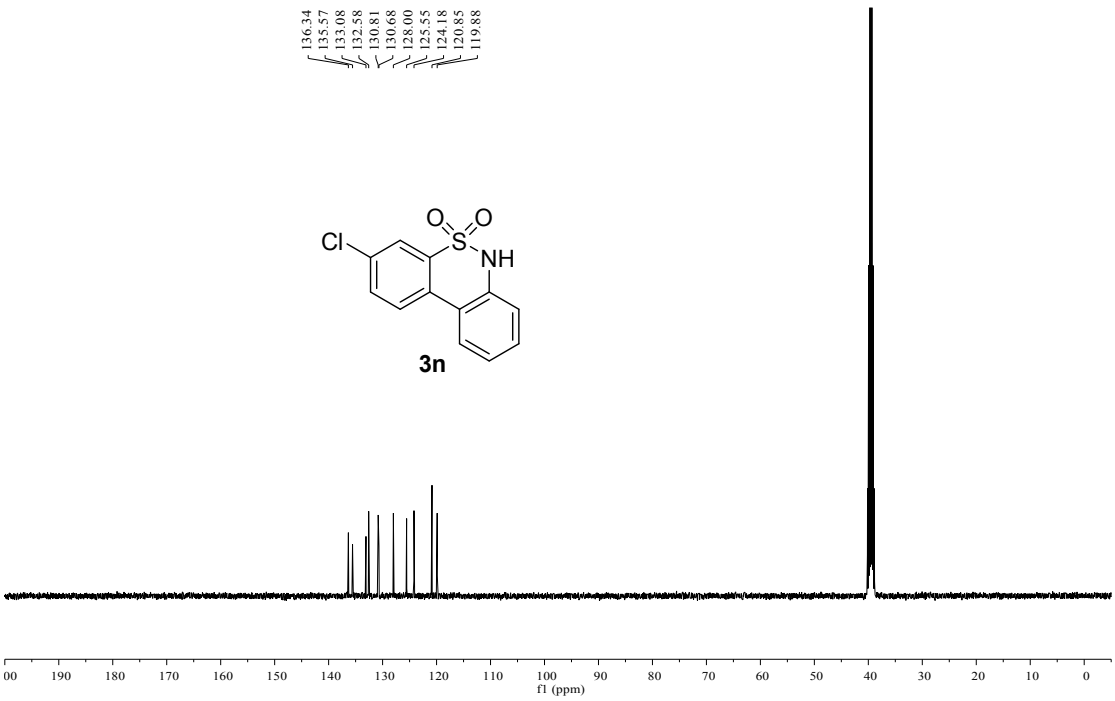
^{1}H NMR of 3-methyl-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3m**)



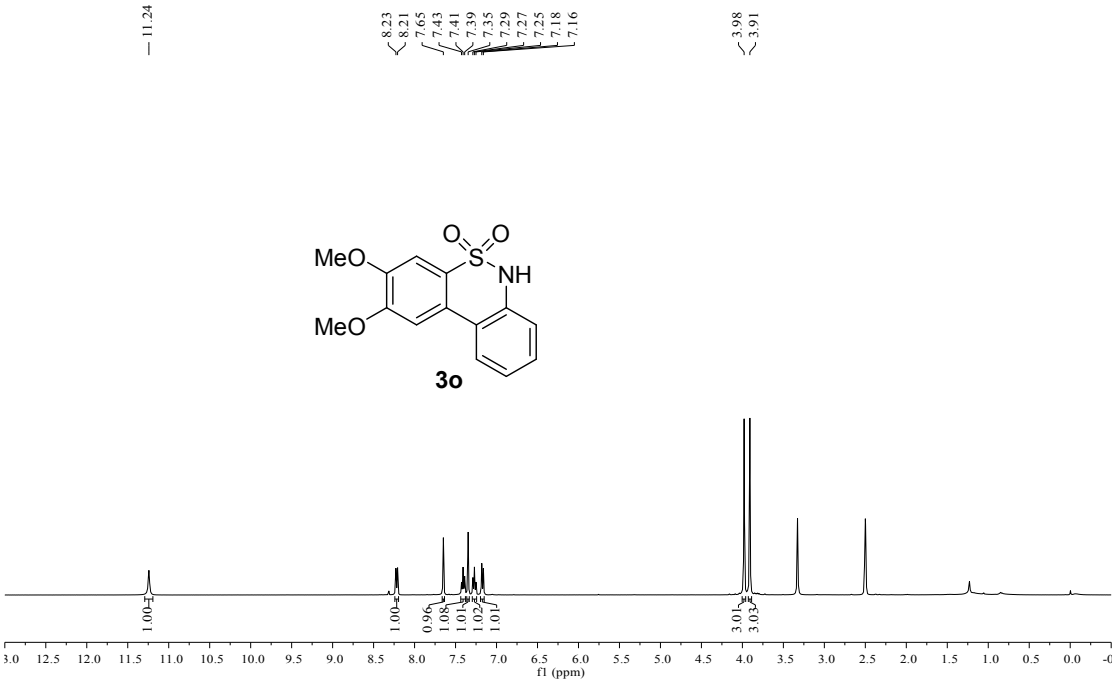
^{13}C NMR of 3-methyl-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3m**)



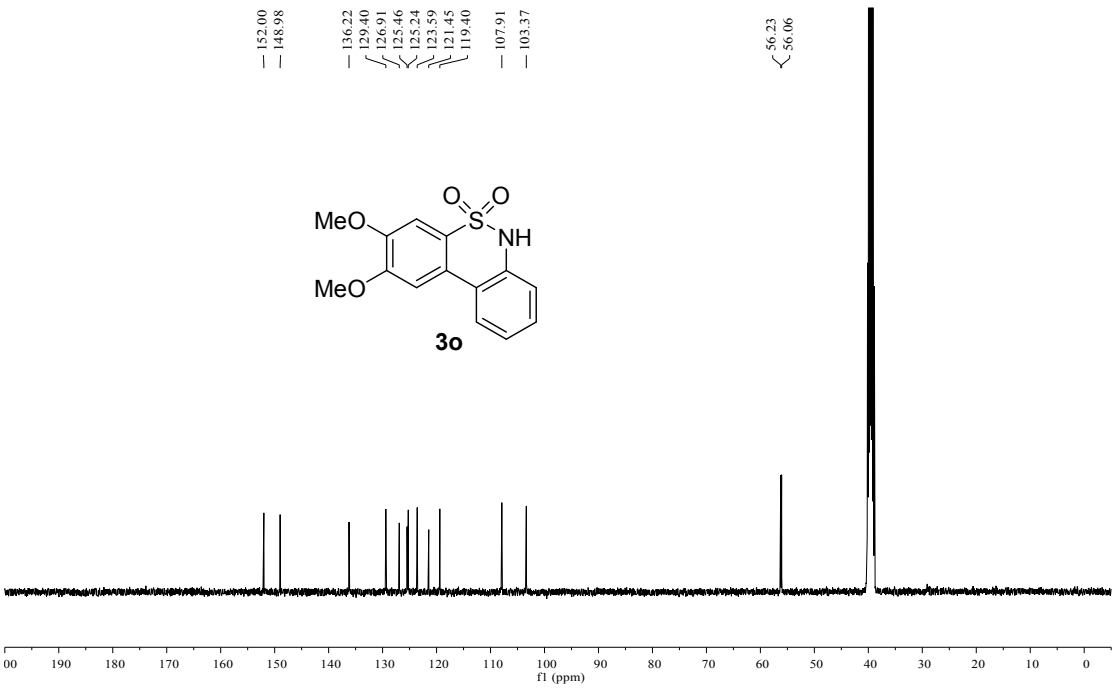
^{1}H NMR of 3-chloro-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3n**)



^{13}C NMR of 3-chloro-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3n**)

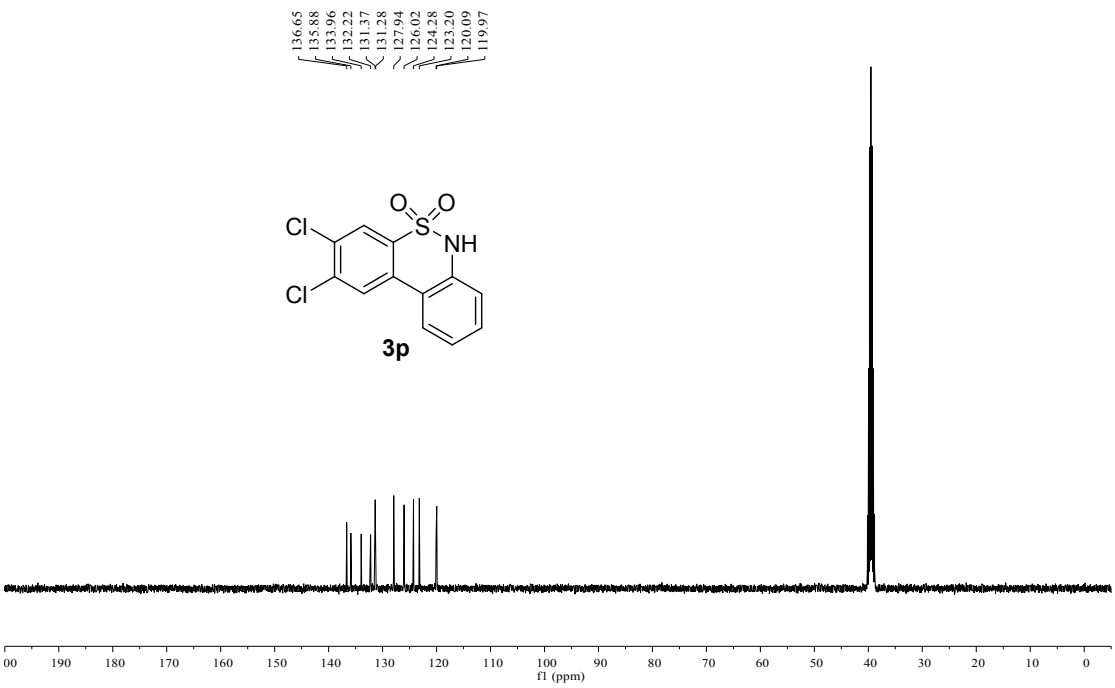


^{1}H NMR of 2,3-dimethoxy-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3o**)

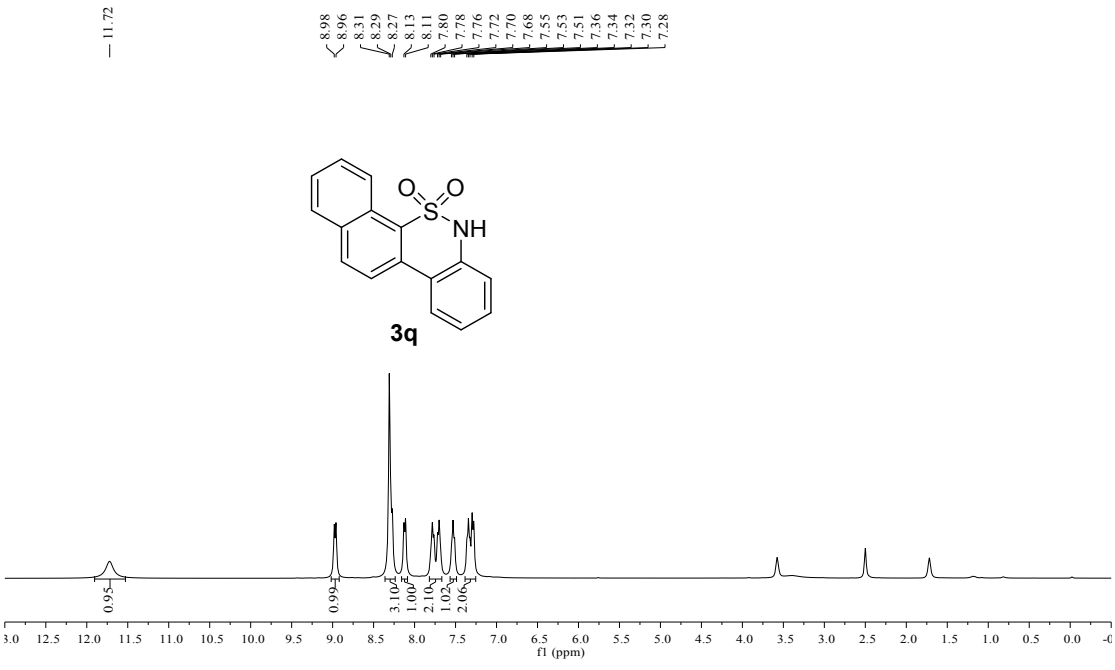


^{13}C NMR of 2,3-dimethoxy-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3o**)

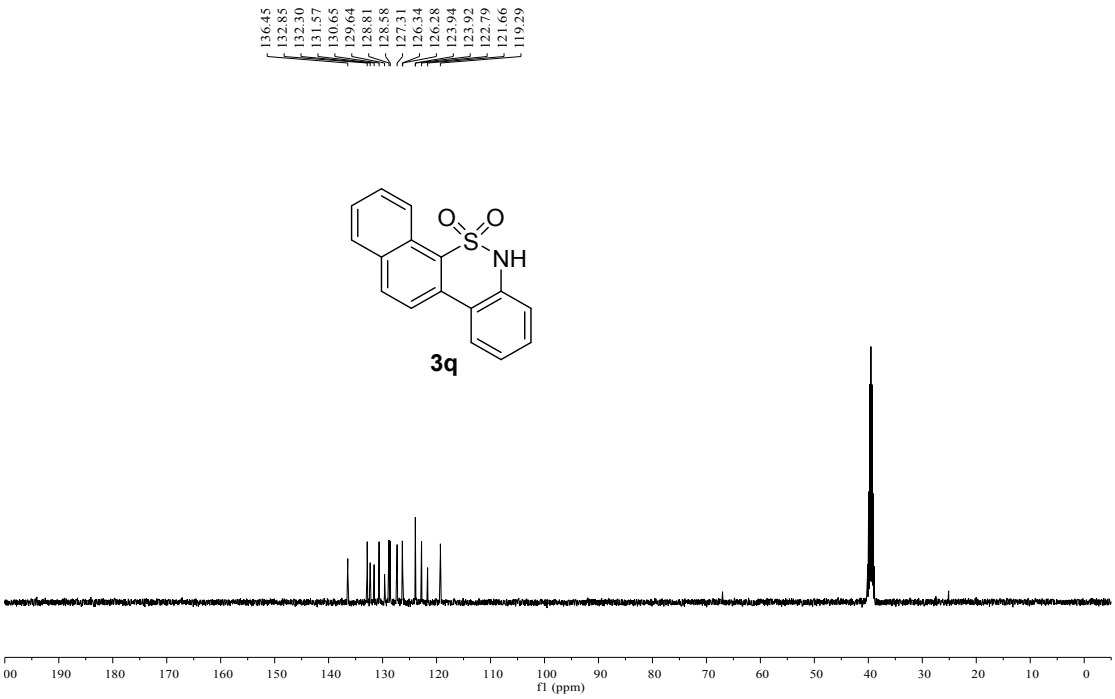
^{1}H NMR of 2,3-dichloro-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3p**)



^{13}C NMR of 2,3-dichloro-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3p**)

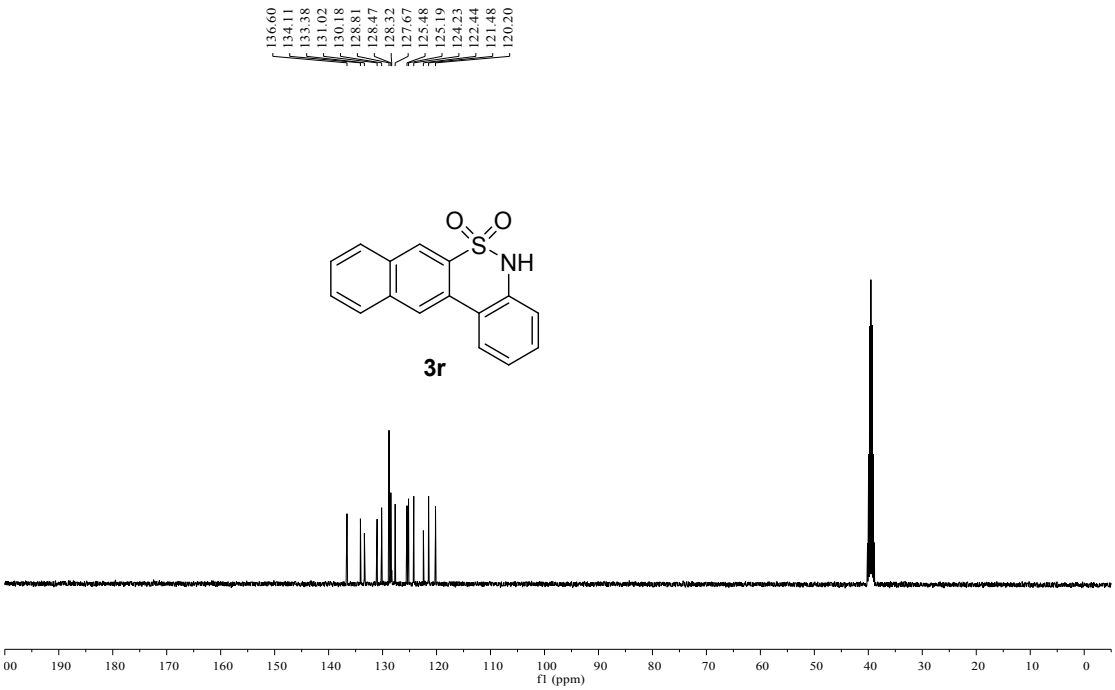


^{1}H NMR of 6*H*-benzo[c]naphtho[2,1-e][1,2]thiazine 5,5-dioxide (**3q**)

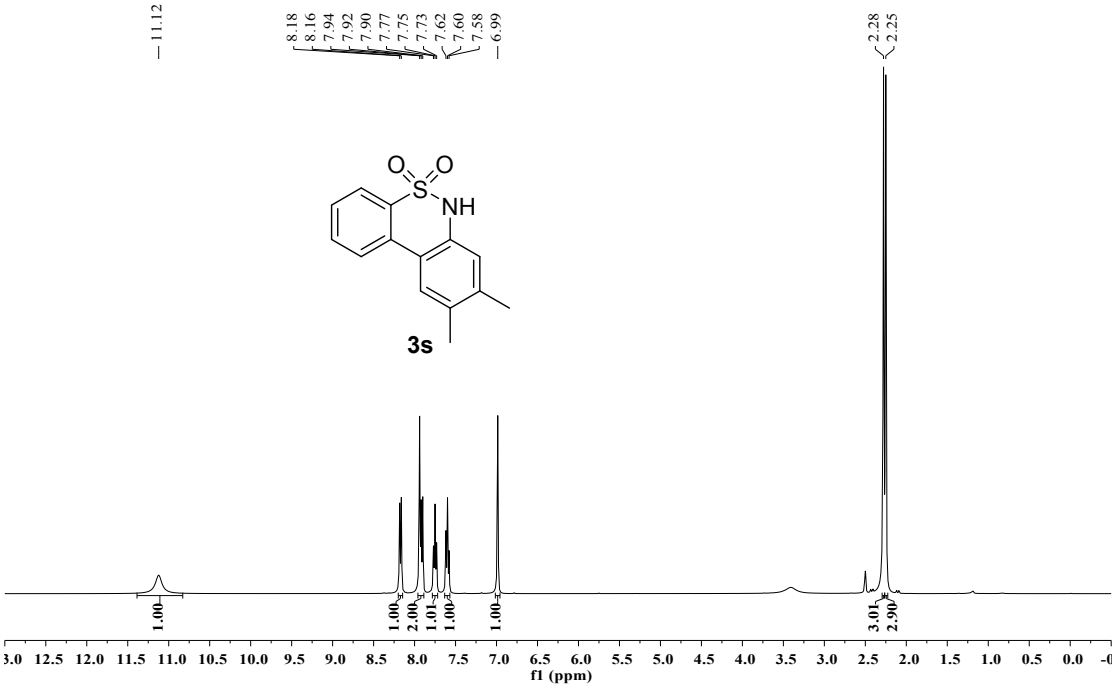


^{13}C NMR of 6*H*-benzo[c]naphtho[2,1-e][1,2]thiazine 5,5-dioxide (**3q**)

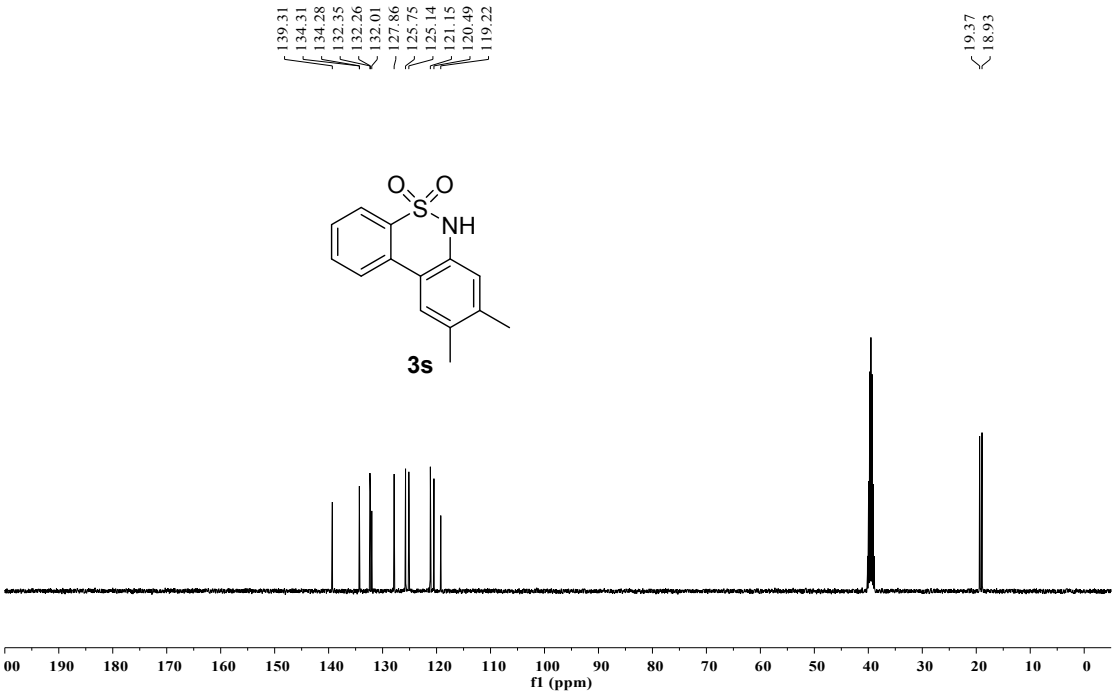
^{1}H NMR of 5*H*-benzo[c]naphtho[2,3-e][1,2]thiazine 6,6-dioxide (**3r**)



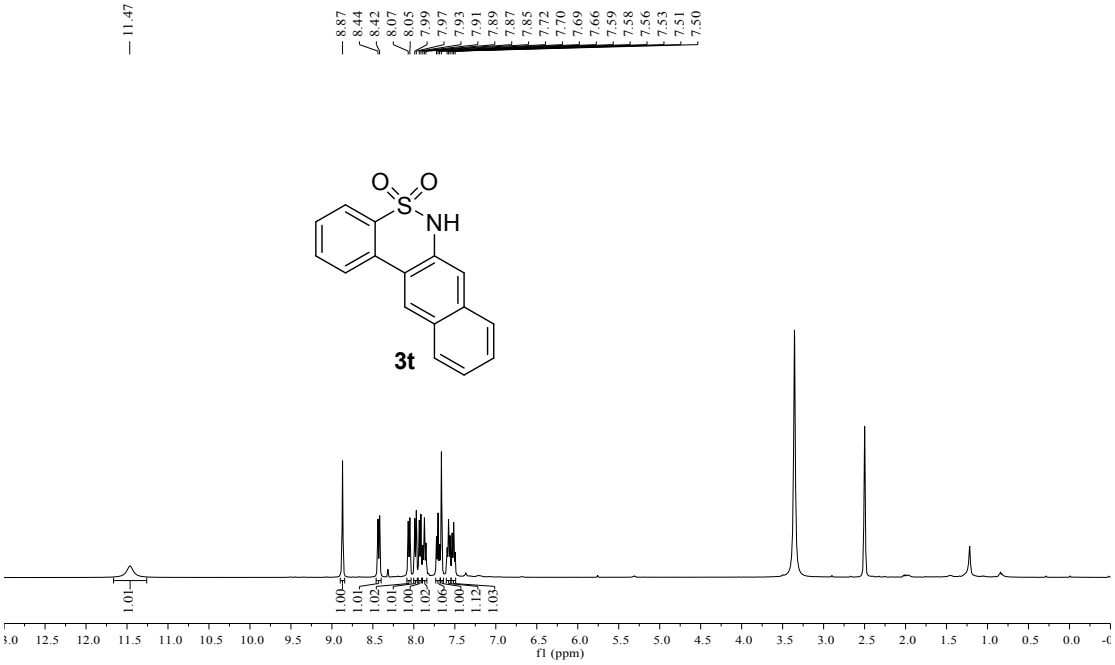
^{13}C NMR of 5*H*-benzo[c]naphtho[2,3-e][1,2]thiazine 6,6-dioxide (**3r**)



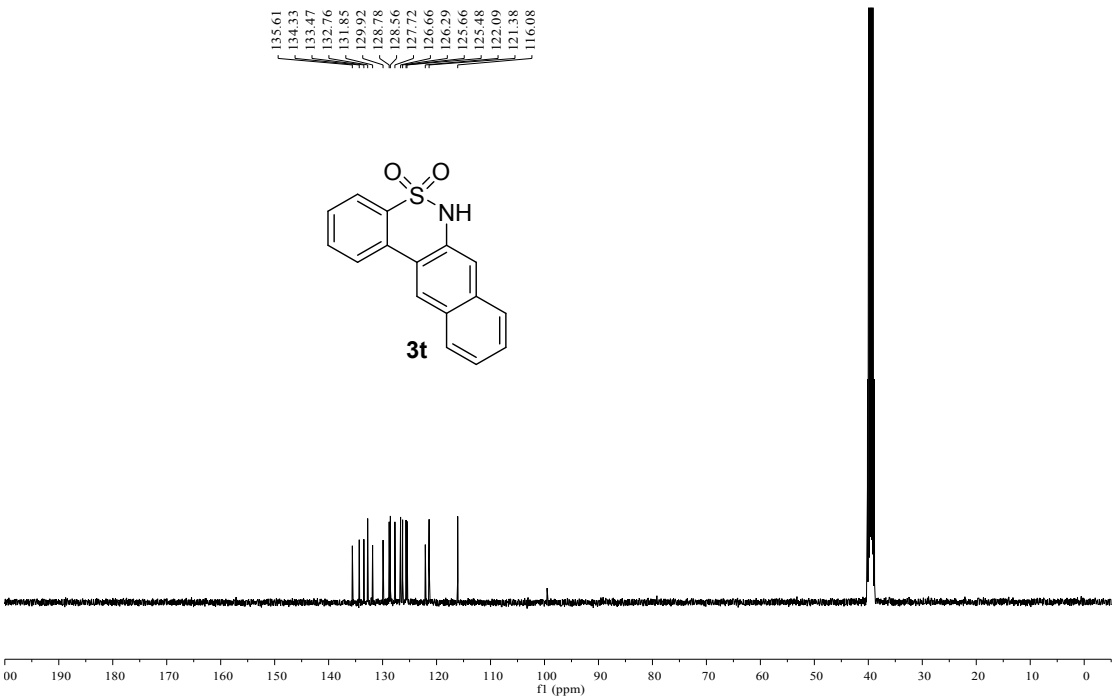
^{1}H NMR of 8,9-dimethyl-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3s**)



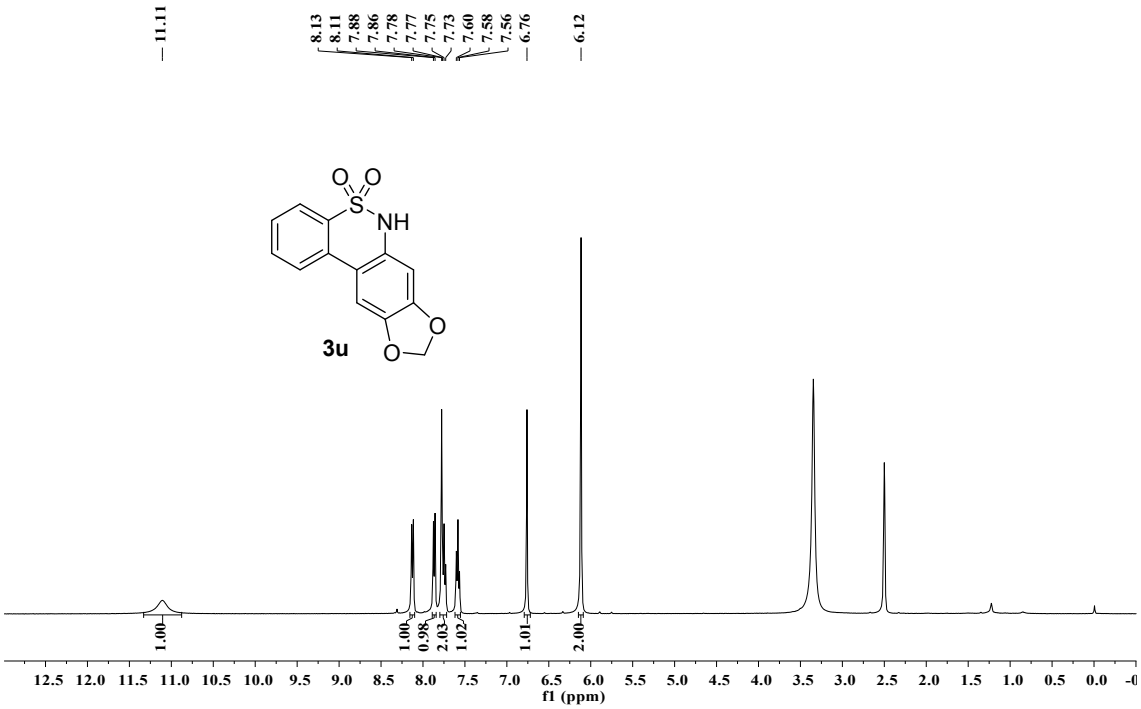
^{13}C NMR of 8,9-dimethyl-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3s**)



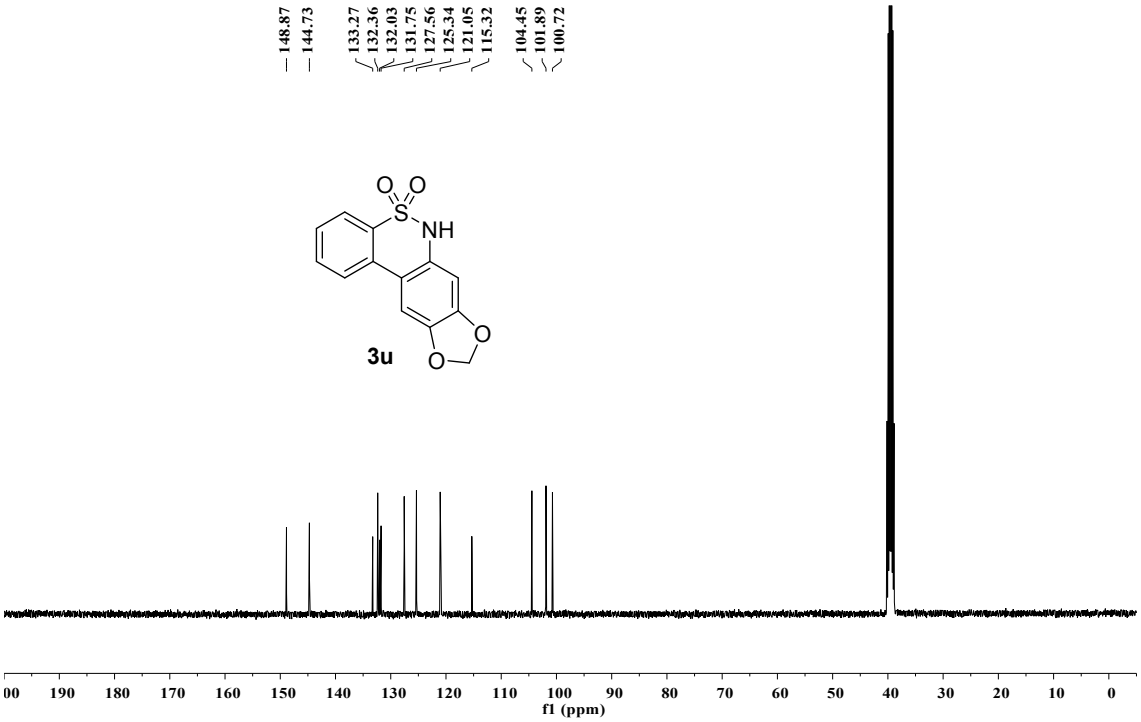
^{1}H NMR of 6*H*-benzo[e]naphtho[2,3-c][1,2]thiazine 5,5-dioxide (**3t**)



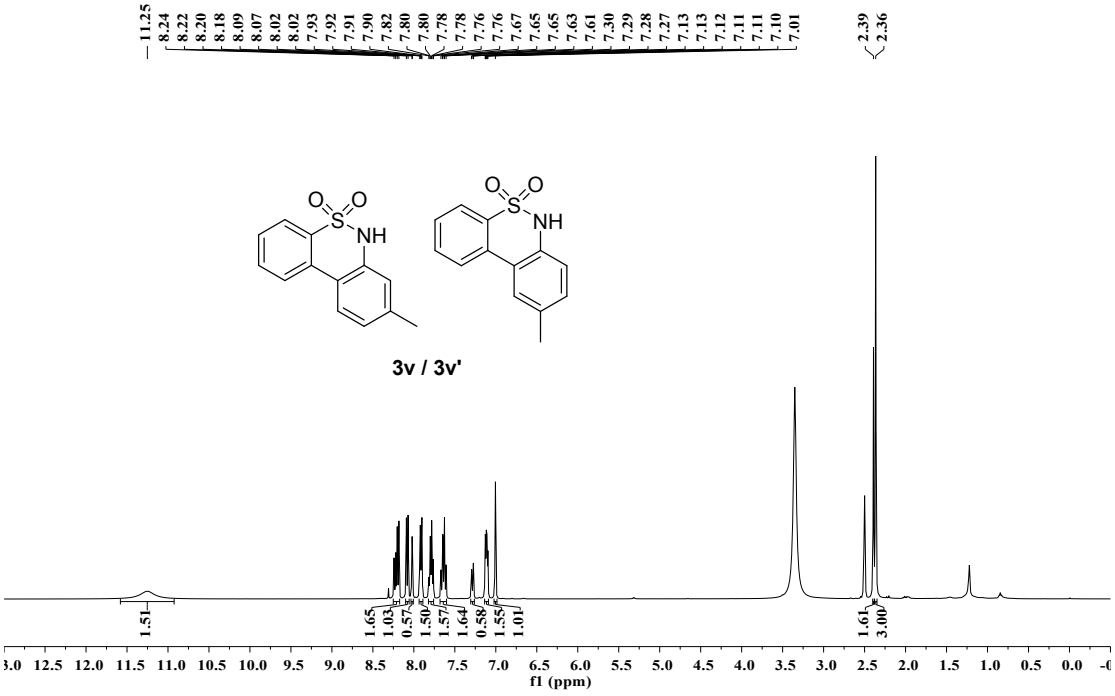
^{13}C NMR of 6*H*-benzo[e]naphtho[2,3-c][1,2]thiazine 5,5-dioxide (**3t**)



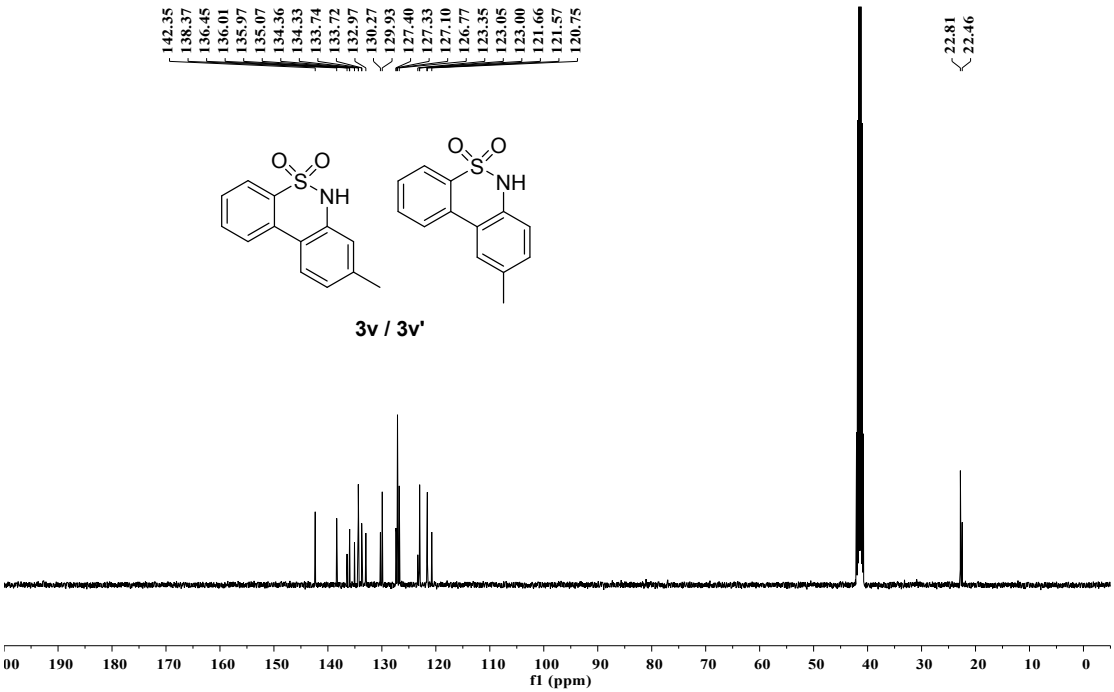
^{1}H NMR of 6*H*-[1,3]dioxolo[4',5':4,5]benzo[1,2-c]benzo[e][1,2]thiazine 5,5-dioxide (**3u**)



^{13}C NMR of 6*H*-[1,3]dioxolo[4',5':4,5]benzo[1,2-c]benzo[e][1,2]thiazine 5,5-dioxide (**3u**)

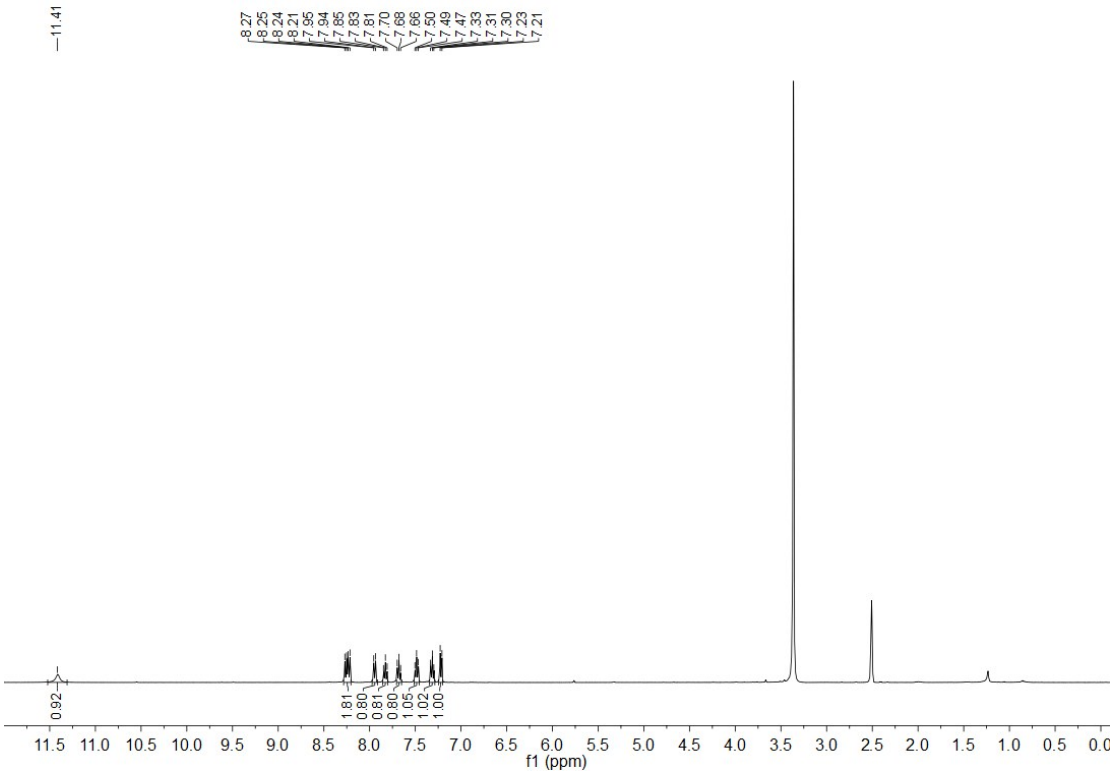


^{1}H NMR of 8-methyl-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide and 9-methyl-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3v/3v'**)



^{13}C NMR of 8-methyl-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide and 9-methyl-6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide (**3v/3v')**

7. NMR spectra for KIE studies



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