Electronic Supplementary Information (ESI)

Regioselective and oxidant-free sulfinylation of indoles and pyrroles with sulfinamides

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2. General Information

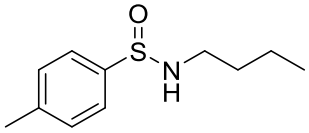
Common reagents and materials were purchased from commercial sources and were used without further purification. TLC plates were visualized by exposure to ultra violet light (UV). IR spectra were recorded by using an Electrothemal Nicolet 380 spectrometer. High-resolution mass spectra (HRMS) were recorded by using an Electrothemal LTQ-Orbitrap mass spectrometer. Melting points were measured by using a Gongyi X-5 microscopy digital melting point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were obtained by using a Bruker Avance III 400 MHz or a JNM-ECZ400S/L1 400 MHz NMR spectrometer. Chemical shifts for protons are reported in parts per million (δ scale) and are referenced to residual protium in the NMR solvents [$CDCl_3$: δ 7.26, DMSO-d_6: δ 2.50]. Chemical shifts for carbon resonances are reported in parts per million (δ scale) and are referenced to the carbon resonances of the solvent ($CDCl_3$: δ 77.0, DMSO-d_6: δ 39.43). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), integration, and coupling constant in Hertz (Hz).

3. General Procedures for the Preparation of Sulfinamides 1

3.1 General procedure for the preparation of sulfinamides 1a–1c and 1e–1g [1]

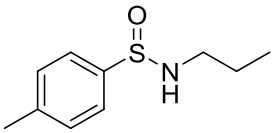
To a three-necked round bottomed flask was added sodium arylsulfinate (2 mmol, 1 equiv.) in anhydrous toluene (5 mL) under argon atmosphere. After cooling the solution to 0 °C oxalyl chloride (2.2 mmol, 1.1 equiv.) was added dropwise. The reaction mixture was heated to room temperature during 1 h to generate sulfinyl chloride *in situ*. A second round bottomed flask was charged with the corresponding amine (2.4 mmol, 1.2 equiv.) and trimethylamine (3.0 mmol, 1.5 equiv.) in anhydrous toluene (6 mL). To this flask, the *in situ* generated sulfinyl chloride was added dropwise at 0 °C. The reaction mixture was stirred for 1 h at room temperature and then poured in H_2O (5 mL) and extracted with EtOAc (5 mL) three times. The combined organic layers were dried over anhydrous Na_2SO_4 and concerntrated in vacuo. The crude product was purified by flash chromatography on silica gel (100–200 mesh). The product was identified by NMR and HRMS spectra.

***N*-butyl-*4*-methylbenzenesulfinamide (1a)**



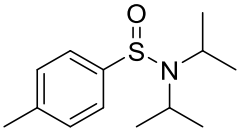
White solid, 311.0 mg, 73% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (d, *J* = 7.9 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 4.18 (s, 1H), 3.13–3.05 (m, 1H), 2.84–2.76 (m, 1H), 2.40 (s, 3H), 1.51–1.44 (m, 2H), 1.35–1.25 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.1, 140.9, 129.3, 125.8, 40.6, 32.4, 21.2, 19.8, 13.5; HRMS (ESI) m/z: Calcd for $C_{11}H_{17}NaNOS$ $[M+Na]^+$: 234.0923. Found: 234.0919.

4-Methyl-*N*-propylbenzenesulfinamide (1b)



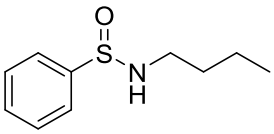
White solid, 275.8 mg, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 4.32 (s, 1H), 3.04–2.96 (m, 1H), 2.76–2.68 (m, 1H), 2.35 (s, 3H), 1.51–1.42 (m, 2H), 0.83 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.1, 140.8, 129.2, 125.7, 42.6, 23.6, 21.1, 11.1; HRMS (ESI) m/z: Calcd for $C_{10}H_{15}NaNOS$ $[M+Na]^+$: 220.0767. Found: 220.0769.

***N,N*-diisopropyl-4-methylbenzenesulfinamide (1c)**



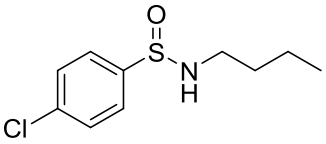
White solid, 258.1 mg, 54% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 3.57–3.47 (m, 2H), 2.36 (s, 3H), 1.37 (d, *J* = 6.8 Hz, 6H), 1.08 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.4, 140.2, 129.2, 126.4, 46.3, 23.7, 23.6, 21.1; HRMS (ESI) m/z: Calcd for $C_{13}H_{21}NaNOS$ $[M+Na]^+$: 262.1236. Found: 262.1231.

***N*-butylbenzenesulfinamide (1e)**



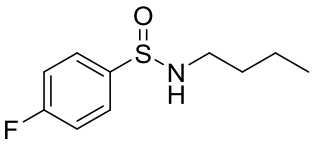
Yellow liquid, 279.7 mg, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71–7.69 (m, 2H), 7.51–7.44 (m, 3H), 4.07 (s, 1H), 3.15–3.07 (m, 1H), 2.85–2.77 (m, 1H), 1.51–1.44 (m, 2H), 1.35–1.24 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.2, 130.6, 128.6, 125.8, 40.7, 32.4, 19.8, 13.5; HRMS (ESI) m/z: Calcd for $C_{10}H_{15}NaNOS$ $[M+Na]^+$: 220.0767. Found: 220.0762.

***N*-butyl-4-chlorobenzenesulfinamide (1f)**



Yellow liquid, 300.3 mg, 65% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64–7.62 (m, 2H), 7.48–7.46 (m, 2H), 4.07–4.06 (m, 1H), 3.14–3.06 (m, 1H), 2.82–2.74 (m, 1H), 1.52–1.44 (m, 2H), 1.35–1.24 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.8, 137.1, 128.9, 127.4, 40.7, 32.4, 19.8, 13.5; HRMS (ESI) m/z: Calcd for $C_{10}H_{14}ClNaN0S$ $[M+Na]^+$: 254.0377. Found: 254.0380.

***N*-butyl-4-fluorobenzenesulfinamide (1g)**

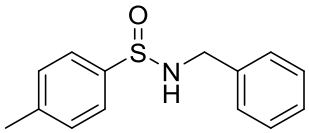


Yellow liquid, 236.5 mg, 55% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67–7.64 (m, 2H), 7.17–7.12 (m, 3H), 4.28 (s, 1H), 3.10–3.02 (m, 1H), 2.79–2.71 (m, 1H), 1.49–1.41 (m, 2H), 1.32–1.23 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.2 (d, $J_{C\text{-}F}$ = 250.9 Hz), 139.8 (d, $J_{C\text{-}F}$ = 2.8 Hz), 128.2 (d, $J_{C\text{-}F}$ = 8.9 Hz), 115.8 (d, $J_{C\text{-}F}$ = 22.3 Hz), 40.5, 32.4, 19.8, 13.5; HRMS (ESI) m/z: Calcd for $C_{10}H_{14}FNaNOS$ $[M+Na]^+$: 238.0672. Found: 238.0675.

3.2 General procedure for the preparation of sulfinamide 1d [2]

To a solution of *p*-toluensulfonyl chloride (190 mg, 1 mmol, 1 equiv) and triethylamine (1.4 mL, 10 mmol, 10 equiv.) in CH_2Cl_2 (3.0 mL) solution at 0 °C under argon atmosphere, was added a solution of triphenylphosphine (262 mg, 1 mmol, 1equiv.) and benzylic amine (109 µl, 1 mmol, 1 equiv.) in CH_2Cl_2 (3.0 mL) solution over a period of 1 h. After addition, TLC showed all of the sulfonyl chloride was consumed. The reaction mixture was concentrated by rotavap. The crude product was purified by flash chromatography on silica gel (100–200 mesh) to give the desired sulfinamide.

***N*-benzyl-4-methylbenzenesulfinamide (1d)**

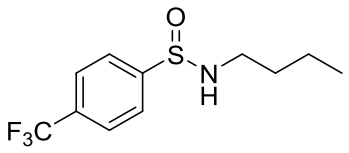


White solid, 303.8 mg, 62% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (d, *J* = 8.0 Hz, 2H), 7.31–7.24 (m, 7H), 4.44 (s, 1H), 4.22 (dd, *J* = 13.5, 5.1 Hz, 1H), 3.88 (dd, *J* = 13.5, 7.2 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.2, 140.7, 137.7, 129.5, 128.5, 128.2, 127.5, 125.9, 44.4, 21.2; HRMS (ESI) m/z: Calcd for $C_{14}H_{15}NaNOS$ $[M+Na]^+$: 268.0767. Found: 268.0771.

3.3 General procedure for the preparation of sulfinamide 1h-1j [1]

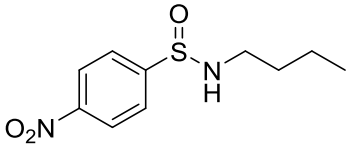
To a solution of sulfonyl chloride (2 mmol, 1.0 equiv.) and triethylamine (4 mmol, 2.0 equiv.) in anhydrous CH_2Cl_2 (6 mL) at 0 °C under argon atmosphere, was added a solution of butan-1-amine (2 mmol, 1.0 equiv.) and triphenylphosphine (2 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (6 mL) over a period of 12 min. The reaction mixture was stirred for 18 h. The reaction mixture was concentrated by rotavap. The crude product was purified by flash chromatography on silica gel (100–200 mesh) to give the desired sulfinamide.

***N*-butyl-4-(trifluoromethyl)benzenesulfinamide (1h)**



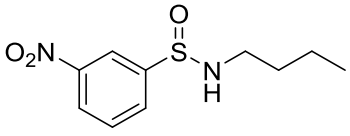
White solid, 296.8 mg, 56% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 4.28–4.19 (m, 1H), 3.18–3.04 (m, 1H), 2.79–2.70 (m, 1H), 1.51–1.44 (m, 2H), 1.36–1.26 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.4, 132.8 (q, $J_{C\text{-}F}$ = 32.8 Hz), 126.7, 125.8 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.6 (q, $J_{C\text{-}F}$ = 272.6 Hz), 40.9, 32.4, 19.9, 13.6; HRMS (ESI) m/z: Calcd for $C_{11}H_{14}F_3NaNOS$ $[M+Na]^+$: 288.0640. Found: 288.0648.

***N*-butyl-4-nitrobenzenesulfinamide (1i)**



Yellow solid, 246.8 mg, 51% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.35–8.32 (m, 2H), 7.91–7.87 (m, 2H), 4.35–4.32 (m, 1H), 3.17–3.08 (m, 1H), 2.76–2.68 (m, 1H), 1.52–1.44 (m, 2H), 1.36–1.26 (m, 2H), 0.85 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.2, 149.4, 127.4, 123.9, 40.9, 32.4, 19.9, 13.6; HRMS (ESI) m/z: Calcd for $C_{10}H_{14}NaN_2O_3S$ $[M+Na]^+$: 265.0617. Found: 265.0623.

***N*-butyl-3-nitrobenzenesulfinamide (1j)**



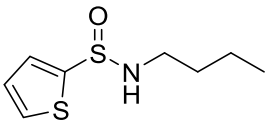
Yellow solid, 174.2 mg, 36% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.53 (t, *J* = 2.0 Hz, 1H), 8.32 (ddd, *J* = 8.2, 2.2, 1.1 Hz, 1H), 8.03 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.70 (t, *J* = 7.9 Hz, 1H), 4.51–4.38 (m, 1H), 3.15–3.07 (m, 1H), 2.77–2.69 (m, 1H), 1.52–1.45 (m, 2H), 1.36–1.25 (m, 2H), 0.84 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:

148.4, 147.1, 132.1, 129.9, 125.5, 121.5, 40.8, 32.4, 19.8, 13.5; HRMS (ESI) m/z: Calcd for $C_{10}H_{14}NaN_2O_3S$ $[M+Na]^+$: 265.0617. Found: 265.0619.

3.4 General procedure for the preparation of sulfinamide 1k [1]

To a solution of thiophene-2-sulfonyl chloride (2 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (6 mL) at 0 °C under argon atmosphere, was added a solution of butan-1-amine (2 mmol, 1.0 equiv.), triphenylphosphine (2 mmol, 1.0 equiv.) and triethylamine (2 mmol, 2.0 equiv.) in anhydrous CH_2Cl_2 (6 mL) over a period of 12 min. The reaction mixture was stirred for 18 h. The reaction mixture was concentrated by rotavap. The crude product was purified by flash chromatography on silica gel (100–200 mesh) to give the desired sulfinamide.

***N*-butylthiophene-2-sulfinamide (1k)**



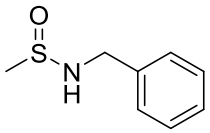
Yellow liquid, 263.9 mg, 65% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (d, *J* = 4.9 Hz, 1H), 7.37 (d, *J* = 3.5 Hz, 1H), 7.09 (t, *J* = 4.2 Hz, 1H), 4.43–4.41 (m, 1H), 3.21–3.13 (m, 1H), 3.03–2.94 (m, 1H), 1.56–1.49 (m, 2H), 1.38–1.29 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.2, 131.0, 129.7, 127.7, 41.0, 32.5, 19.8, 13.5; HRMS (ESI) m/z: Calcd for $C_8H_{13}NaNOS_2$ $[M+Na]^+$: 226.0331. Found: 226.0333.

3.5 General procedure for the preparation of sulfinamide 1l [3]

The dimethyl disulfide (10 mmol, 1.0 equiv.) and acetic acid (20 mmol, 2.0 equiv.) were mixed and cooled to -20 °C. Sulfuryl chloride (31 mmol, 3.1 equiv.) was added dropwise with stirring over a period of 30 min. The reaction mixture was then stirred for 3 h at -20 °C and then allowed to warm to room temperature over a period of about 2 h. Evolution of SO_2 and HCl was observed during this time. The mixture was warmed to 35 °C for 1 h. The resulting acetyl chloride was evaporated under reduced pressure, providing the desired product methanesulfinic chloride as a liquid which was used without further purification.

The crude product methanesulfinic chloride in CH_2Cl_2 (7 mL) was added dropwise to a solution of benzylamine (40 mmol, 2.0 equiv.) in CH_2Cl_2 (40 mL) at -78 °C. The mixture was stirred for 3 h at room temperature. The solution was filtered and the filtrate was washed with water and then dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (100–200 mesh) to afford the desired sulfinamide.

***N*-benzylmethanesulfinamide (1l)**

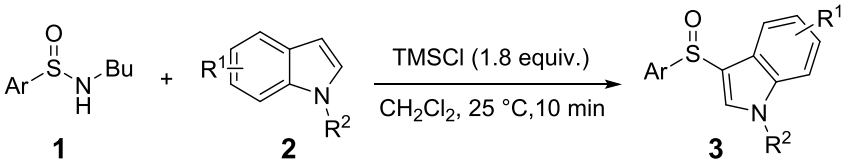


Yellow liquid, 2.54g, 75% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31–7.24 (m, 5H), 4.43–4.40 (m, 1H), 4.28–4.17 (m, 2H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.9, 128.6, 128.0, 127.6, 45.8, 41.6; HRMS (ESI) m/z: Calcd for $C_8H_{11}NaNOS$ $[M+Na]^+$: 192.0454. Found: 192.0459.

4. Experimental Procedure of Sulfoxides

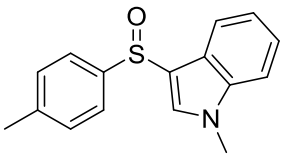
4.1 Experimental Procedure of Sulfoxides 3a-3ag

The mixture of an arylsulfiniamide (0.2 mmol, 1 equiv.), an indole (0.24 mmol, 1.2 equiv.) and TMSCl (0.36 mmol, 1.8 equiv.) in CH_2Cl_2 (1.0 mL) was stirred at 25 °C for 10 min, then water (5 mL) and dichloromethane (10 mL) were added. The two layers were separated, and the aqueous phase was extracted with dichloromethane (3 × 10 mL). The combined organic extracts were washed by brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (100–200 mesh) to afford the desired sulfoxide.



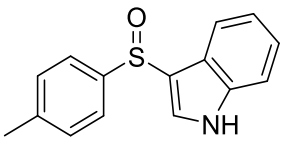
1 **2** **3**

1-Methyl-3-(*p*-tolylsulfinyl)-1*H*-indole (3a)



White solid, m.p. = 138–139 °C; 44.7 mg, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H),7.34–7.24 (m, 4H), 7.12–7.08 (m, 1H), 3.79 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.9, 140.3, 137.6, 132.5, 129.5, 124.8, 124.3, 123.2, 121.3, 119.8, 116.5, 110.0, 33.2, 21.2; FTIR (film): 3458, 3051, 2921, 1515, 1458, 1173, 1033, 1013, 810, 765, 742, 621 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{16}H_{15}NaNOS$ $[M+Na]^+$: 292.0767. Found: 292.0765.

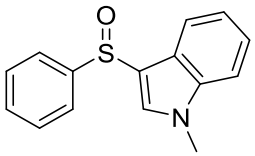
3-(*p*-Tolylsulfinyl)-1*H*-indole (3b)



White solid, m.p. = 120–122 °C; 45.4 mg, 89% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.49 (s, 1H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 1H), 7.16 (d, *J* = 2.3 Hz, 1H),

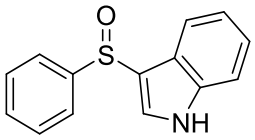
7.10 (t, *J* = 7.6 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.5, 139.8, 137.1, 130.0, 129.6, 124.9, 123.4, 123.3, 121.3, 119.1, 115.8, 112.5, 21.2; FTIR (film): 3166, 2978, 2920, 2852, 1491, 1426, 1081, 1021, 1002, 809, 763, 743 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{15}H_{13}NaNOS$ $[M+Na]^+$: 278.0610. Found:278.0611.

1-Methyl-3-(phenylsulfinyl)-1*H*-indole (3c)



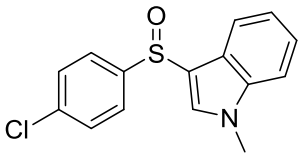
White solid, m.p. = 126–128 °C; 45.9 mg, 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (d, *J* = 6.9 Hz, 2H), 7.50–7.41 (m, 5H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.1, 137.6, 132.8, 130.0, 128.7, 124.8, 124.2, 123.2, 121.3, 119.7, 116.2, 110.0, 33.2; FTIR (film): 3452, 3053, 2922, 2850, 2359, 1516, 1473, 1458, 1033, 997, 742, 695 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{15}H_{13}NaNOS$ $[M+Na]^+$: 278.0610. Found: 278.0613.

3-(Phenylsulfinyl)-1*H*-indole (3d)



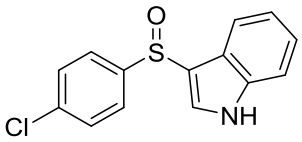
White solid, m.p. = 126–128 °C; 45.3 mg, 94% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ:11.97 (s, 1H), 8.13 (d, *J* = 2.7 Hz, 1H), 7.66 (d, *J* = 7.4 Hz, 2H), 7.56–7.42 (m, 4H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 144.8, 136.9, 130.7, 129.8, 128.8, 124.3, 123.1, 122.7, 120.5, 118.9, 116.2, 112.6; FTIR (film): 3164, 2918, 2851, 1455, 1424, 1243, 1016, 993, 742 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{14}H_{11}NaNOS$ $[M+Na]^+$: 264.0454. Found: 264.0451.

3-((4-Chlorophenyl)sulfinyl)-1-methyl-1*H*-indole (3e)



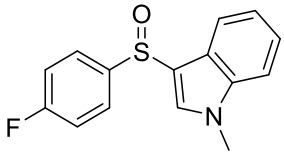
White solid, m.p. = 144–146 °C; 48.0 mg, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66 (d, *J* = 8.3 Hz, 2H), 7.55 (s, 1H), 7.47–7.42 (m, 3H), 7.36 (d, *J* = 8.3 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.9, 137.7, 136.1, 132.9, 129.0, 126.2, 124.0, 123.4, 121.5, 119.6, 115.7, 110.2, 33.3; FTIR (film): 3455, 3052, 2924, 1515, 1471, 1457, 1085, 1031, 1008, 975, 821, 765, 738 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{15}H_{12}NaClNOS$ $[M+Na]^+$: 312.0220. Found: 312.0218.

3-((4-Chlorophenyl)sulfinyl)-1*H*-indole (3f)



White solid, m.p. = 128–130 °C; 50.1 mg, 91% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.42 (s, 1H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.43 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 1H), 724–7.22 (m, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.7, 137.1, 136.4, 130.3, 129.2, 126.3, 123.6, 123.1, 121.6, 119.0, 115.3, 112.6; FTIR (film): 3159, 2923, 2849, 1473, 1424, 1004, 742 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{14}H_{10}NaClNOS$ $[M+Na]^+$: 298.0064. Found: 298.0068.

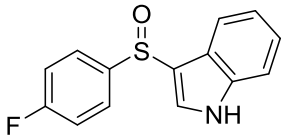
3-((4-Fluorophenyl)sulfinyl)-1-methyl-1*H*-indole (3g)



White solid, m.p. = 130–132 °C; 45.9 mg, 84% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (dd, *J* = 8.7, 5.1 Hz, 2H), 7.51 (s, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.14 (t, *J* = 8.6 Hz, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.7 (d, $J_{C\text{-}F}$ = 250.7 Hz), 139.8 (d, $J_{C\text{-}F}$ = 2.9 Hz), 137.8, 132.8, 127.1 (d, $J_{C\text{-}F}$ = 8.8 Hz), 124.1, 123.4, 121.5, 119.7, 116.2, 116.1 (d, $J_{C\text{-}F}$ = 22.6 Hz,

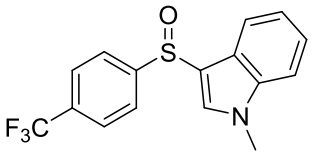
1C), 110.1, 33.3; FTIR (film): 3438, 3093, 2924, 1586, 1516, 1488, 1458, 1247, 1221, 1031, 1011, 833, 765, 742 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{15}H_{12}NaFNOS$ $[M+Na]^+$: 296.0516. Found: 296.0513.

3-((4-Fluorophenyl)sulfinyl)-1*H*-indole (3h)



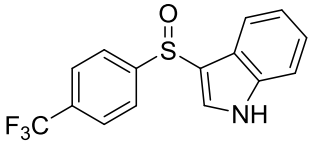
Pale yellow oil, 48.2 mg, 93% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.72 (s, 1H), 7.66 (dd, *J* = 8.7, 5.1 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.26–7.23 (m, 2H), 7.19–7.11 (m, 5H), 7.02 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.8 (d, $J_{C\text{-}F}$ = 250.8 Hz), 138.5, 137.2, 130.4, 127.1 (d, $J_{C\text{-}F}$ = 8.8 Hz), 123.5, 123.1, 121.5, 118.9, 116.2 (d, $J_{C\text{-}F}$ = 22.6 Hz), 115.2, 112.6; FTIR (film): 3398, 2062, 2924, 1587, 1487, 1223, 1140, 1010, 823, 744 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{14}H_{10}NaFNOS$ $[M+Na]^+$: 282.0359. Found: 282.0362.

1-Methyl-3-((4-(trifluoromethyl)phenyl)sulfinyl)-1*H*-indole (3i)



White solid, m.p. = 149–151 °C; 54.3 mg, 84% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.58 (s, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.3 Hz, 1H), 7.30–7.25 (m, 1H), 7.11–7.07 (m, 1H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.0, 137.8, 133.3, 131.9 (q, $J_{C\text{-}F}$ = 32.7 Hz), 125.8, (q, $J_{C\text{-}F}$ = 3.7 Hz),125.3, 124.1, 123.63, 123.58 (q, $J_{C\text{-}F}$ = 271.0 Hz), 121.8, 119.7, 115.5, 110.3, 33.5; FTIR (film): 2924, 2358, 1518, 1398, 1322, 1168, 1060, 1034, 745 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{16}H_{12}NaF_3NOS$ $[M+Na]^+$: 346.0484. Found: 346.0490.

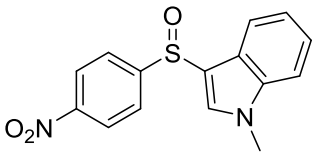
3-((4-(Trifluoromethyl)phenyl)sulfinyl)-1*H*-indole (3j)



White solid, m.p. = 127–129 °C; 55.6 mg, 90% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.08 (s, 1H), 8.24 (d, *J* = 2.9 Hz, 1H), 7.89–7.84 (m, 4H), 7.49 (d, *J* = 8.2 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.16 (t, *J* = 7.2 Hz, 1H); 6.97

(t, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 150.1, 137.1, 131.5, 130.0 (q, J_{C-F} = 32.1 Hz), 125.9, (q, J_{C-F} = 3.9 Hz), 125.4, 123. 8 (q, J_{C-F} = 271.5 Hz), 123.0, 120.9, 118.7, 115.2, 112.8; FTIR (film): 3165, 2981, 2359, 1605, 1321, 1125, 1059, 1006, 747 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{15}H_{10}NaF_3NOS$ [M+Na]$^+$: 332.0327. Found: 332.0332.

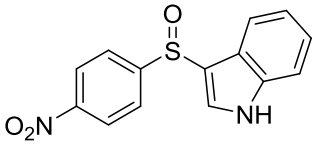
1-Methyl-3-((4-nitrophenyl)sulfinyl)-1*H*-indole (3k)



0.72 mmol of TMSCl was used.

Yellow solid, m.p. = 144–146 °C; 51.6 mg, 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.28 (d, *J* = 8.8 Hz, 2H), 7.86 (d, *J* = 8.8 Hz, 2H), 7.64 (s, 1H), 7.35–7.24 (m, 3H), 7.07 (t, *J* = 7.5 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.2, 148.7, 137.8, 133.6, 125.9, 123.9, 123.8, 121.9, 119.5, 114.7, 110.4, 33.5; FTIR (film): 3094, 2926, 2359, 1517, 1343, 1041, 852, 747 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{15}H_{12}NaN_2O_3S$ [M+Na]$^+$: 323.0461. Found: 323.0465.

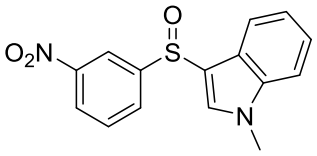
3-((4-Nitrophenyl)sulfinyl)-1*H*-indole (3l)



0.72 mmol of TMSCl was used.

Yellow solid, m.p. = 149–151 °C; 51.5 mg, 90% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.12 (s, 1H), 8.33 (d, *J* = 8.4 Hz, 2H), 8.27 (d, *J* = 2.8 Hz, 1H), 7.89 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H); 7.16 (t, *J* = 7.6 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 152.6, 148.3, 137.1, 131.8, 125.9, 124.0, 123.0, 122.9, 121.0, 118.7, 114.8, 112.9; FTIR (film): 3413, 2358, 1524, 1345, 1025, 1005, 749 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{14}H_{10}NaN_2O_3S$ [M+Na]$^+$: 309.0304. Found: 309.0308.

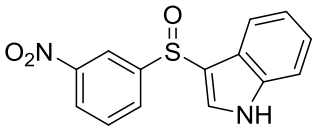
1-Methyl-3-((3-nitrophenyl)sulfinyl)-1*H*-indole (3m)



0.72 mmol of TMSCl was used.

Pale yellow oil, 50.4 mg, 84% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.48 (t, *J* = 2.0 Hz, 1H), 7.26–7.23 (m, 1H), 8.09 (d, *J* = 7.8 Hz, 1H), 7.68–7.65 (m, 2H), 7.35 (d, *J* = 8.7 Hz, 2H), 7.26 (t, *J* = 8.1 Hz, 1H), 7.07 (t, *J* = 8.0 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.4, 147.6, 137.9, 133.6, 130.6, 129.9, 124.7, 123.8, 123.7, 121.9, 120.1, 119.5, 114.8, 110.5, 33.5; FTIR (film): 3091, 2927, 1526, 1457, 1348, 1037, 731 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{15}H_{12}NaN_2O_3S$ $[M+Na]^+$: 323.0461. Found: 323.0468.

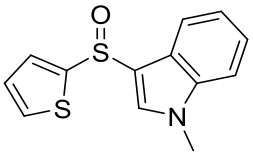
3-((3-Nitrophenyl)sulfinyl)-1*H*-indole (3n)



0.72 mmol of TMSCl was used.

Pale yellow oil, 48.6 mg, 85% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.10 (s, 1H), 8.49 (t, *J* = 2.0 Hz, 1H), 8.31 (ddd, *J* = 8.2, 2.4, 1.0 Hz, 1H), 8.26 (s, 1H), 7.98 (dt, *J* = 7.9, 1.3 Hz, 1H), 7.78 (t, *J* = 8.0 Hz, 1H); 7.49 (d, *J* = 8.1 Hz, 1H), 7.22–7.14 (m, 2H), 6.99–6.95 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 148.1, 147.7, 137.0, 131.9, 130.8, 130.7, 124.8, 123.0, 122.9, 121.0, 119.0, 118.7, 114.9, 112.8; FTIR (film): 3414, 2925, 1717, 1351, 1275, 1051, 1025, 1006, 749 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{14}H_{10}NaN_2O_3S$ $[M+Na]^+$: 309.0304. Found: 309.0310.

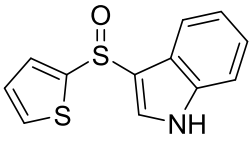
1-Methyl-3-(thiophen-2-ylsulfinyl)-1*H*-indole (3o)



0.72 mmol of TMSCl was used.

Pale yellow oil, 44.4 mg, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (d, *J* = 9.8 Hz, 2H), 7.55 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.52 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 1H), 7.30 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.15 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.09 (dd, *J* = 5.0, 3.7 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.6, 137.8, 131.5, 130.8, 129.5, 127.3, 124.2, 123.4, 121.4, 119.9, 116.6, 110.2, 33.4; FTIR (film): 3096, 2922, 2236, 1516, 1483, 1335, 1036, 907, 729 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{13}H_{11}NaNOS_2$ $[M+Na]^+$: 284.0174. Found: 284.0172.

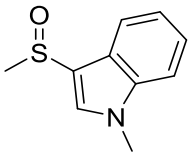
3-(Thiophen-2-ylsulfinyl)-1*H*-indole (3p)



0.72 mmol of TMSCl was used.

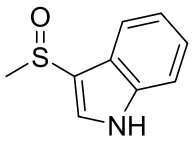
Pale yellow oil, 42.5 mg, 86% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.00 (s, 1H), 8.07 (t, *J* = 3.2 Hz, 1H), 7.85–7.84 (m, 1H), 7.53–7.45 (m, 3H), 7.23–7.04 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 148.2, 137.0, 131.1, 129.5, 128.8, 127.6, 123.0, 122.8, 120.6, 119.1, 116.7, 112.6; FTIR (film): 3177, 2923, 2851, 2362, 1659, 1422, 1244, 1008, 744 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{12}H_9NaNOS_2$ $[M+Na]^+$: 270.0018. Found: 227.0021.

1-Methyl-3-(methylsulfinyl)-1*H*-indole (3q)



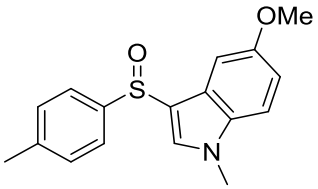
Pale yellow oil, 20.0 mg, 52% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.92 (s, 1H), 7.88 (d, *J* = 8.3 Hz, 1H), 7.57 (d, *J* = 8.3 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 7.5, 1.0 Hz, 1H), 3.83 (s, 3H), 2.95 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 137.3, 130.8, 123.9, 122.7, 120.7, 119.2, 115.9, 111.0, 40.5, 32.9; FTIR (film): 3401, 2360, 1562, 1519, 1264, 1023, 1000, 746 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{10}H_{11}NaNOS$ $[M+Na]^+$: 216.0454. Found: 216.0457.

3-(Methylsulfinyl)-1*H*-indole (3r)



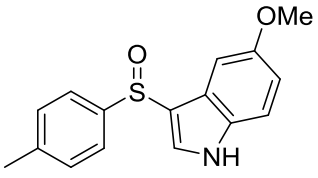
Pale yellow oil, 21.1 mg, 59% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.85 (s, 1H), 7.90 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 7.5, 1H), 2.96 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 136.8, 127.1, 123.6, 122.6, 120.4, 119.0, 116.9, 112.6, 40.3; FTIR (film): 3419, 2359, 1652, 1023, 1003, 751 cm^{-1}; HRMS (ESI) m/z: Calcd for C_9H_9NaNOS [M+Na]$^+$: 202.0297. Found: 202.0302.

5-Methoxy-1-methyl-3-(*p*-tolylsulfinyl)-1*H*-indole (3s)



White solid, m.p. = 147–149 °C; 52.1 mg, 87% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (d, *J* = 8.2 Hz, 2H), 7.42 (s, 1H), 7.29 (d, *J* = 7.7 Hz, 2H), 7.20 (d, *J* = 8.9 Hz, 1H), 6.89 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.85 (d, *J* = 2.3 Hz, 1H), 3.77 (s, 3H), 3.68 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.0, 140.7, 140.2, 132.8, 132.7, 129.4, 125.0, 124.9, 115.8, 113.7, 110.8, 101.0, 55.4, 33.4, 21.2; FTIR (film): 3457, 3094, 2921, 1513, 1491, 1462, 1371, 1061, 1034, 1014, 976, 809, 790, 635 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{17}H_{17}NaNO_2S$ [M+Na]$^+$: 322.0872. Found: 322.0869.

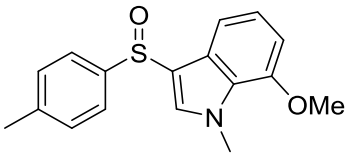
5-Methoxy-3-(*p*-tolylsulfinyl)-1*H*-indole (3t)



Yellow solid, m.p. = 120–122 °C; 53.0 mg, 93% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.64 (s, 1H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 3.0 Hz, 1H), 7.08 (d, *J* = 8.8 Hz, 1H), 6.74–6.70 (m, 2H), 3.55 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.8, 140.5, 139.8, 131.9, 130.2, 129.6, 124.9, 124.1, 115.5, 113.7, 113.2, 100.4, 55.3, 21.2; FTIR (film): 3156, 2926, 2830, 1585, 1487, 1466, 1438, 1294, 1208,

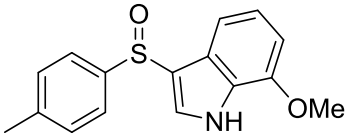
1172, 1022, 1001, 808, 631 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{16}H_{15}NaNO_2S$ $[M+Na]^+$: 308.0716. Found: 308.0714.

7-Methoxy-1-methyl-3-(*p*-tolylsulfinyl)-1*H*-indole (3u)



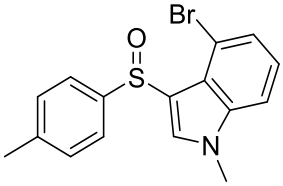
Pale yellow oil, 49.1 mg, 82% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (d, *J* = 8.2 Hz, 2H), 7.32 (s, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.03 (dd, *J* = 8.1, 0.8 Hz, 1H), 6.94 (t, *J* = 7.9 Hz, 1H), 6.62 (d, *J* = 7.7 Hz, 1H), 4.05 (s, 3H), 3.88 (s, 3H),2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.9, 141.0, 140.2, 133.2, 129.5, 127.4, 126.8, 124.9, 122.0, 116.3, 112.2, 103.8, 55.3, 37.2, 21.2; FTIR (film): 3424, 3099, 2922, 2850, 1578, 1493, 1415, 1370, 1322, 1260, 1171, 1103, 1036, 1013, 810, 779, 732 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{17}H_{17}NaNO_2S$ $[M+Na]^+$: 322.0872. Found: 322.0875.

7-Methoxy-3-(*p*-tolylsulfinyl)-1*H*-indole (3v)



Yellow solid, m.p. = 120–123 °C; 49.6 mg, 87% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.03 (s, 1H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 2.9 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.00–6.91 (m, 3H), 6.59 (d, *J* = 7.5 Hz, 1H), 3.81 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.4, 140.6, 140.3, 129.5, 128.7, 127.5, 125.0, 124.9, 121.9, 117.6, 111.9, 103.1, 55.2, 21.2; FTIR (film): 3110, 2920, 2850, 1581, 1493, 1424, 1255, 1099, 1002, 780, 731 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{16}H_{15}NaNO_2S$ $[M+Na]^+$: 308.0716. Found: 308.0714.

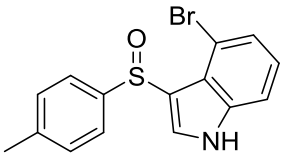
4-Bromo-1-methyl-3-(*p*-tolylsulfinyl)-1*H*-indole (3w)



Pale yellow oil, 21.6 mg, 31% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (d, *J* = 7.7 Hz, 2H), 7.38–7.36 (m, 2H), 7.30–7.25 (m, 3H), 7.18 (t, *J* = 7.7Hz, 1H), 3.77 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.5,

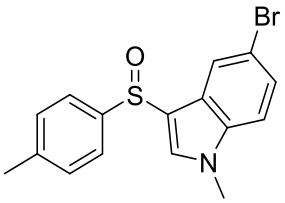
140.9, 138.3, 132.1, 129.5, 125.6, 125.3, 125.1, 123.7, 119.0, 113.1, 109.3, 33.6, 21.3; FTIR (film): 3455, 3105, 2921, 1556, 1508, 1434, 1417, 1332, 1290, 1197, 1033, 1014, 963, 809, 772, 732 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{16}H_{14}NaBrNOS$ $[M+Na]^+$: 369.9872. Found: 369.9875.

4-Bromo-3-(*p*-tolylsulfinyl)-1*H*-indole (3x)



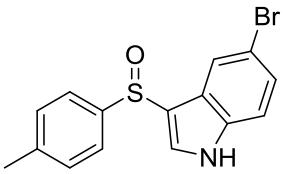
Pale yellow oil, 28.0 mg, 42% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.93 (s, 1H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.30–7.26 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.01 (d, *J* = 1.0 Hz, 1H), 6.98 (t, *J* = 7.9 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.3, 140.8, 137.8, 129.7, 128.9, 125.8, 125.2, 124.7, 123.9, 118.3, 112.3, 111.8, 21.3; FTIR (film): 2924, 2853, 2366, 1616, 1490, 1178, 1123, 1008, 683 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{15}H_{12}NaBrNOS$ $[M+Na]^+$: 355.9715. Found: 355.9711.

5-Bromo-1-methyl-3-(*p*-tolylsulfinyl)-1*H*-indole (3y)



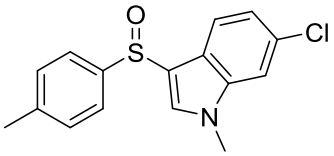
White solid, m.p. = 142–144 °C; 43.7 mg, 63% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65 (s, 1H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.44 (s, 1H), 7.34–7.29 (m, 3H), 7.18 (d, *J* = 8.5 Hz, 1H), 3.78 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.6, 140.5, 136.3, 133.1, 129.6, 126.2, 125.8, 124.6, 122.2, 116.4, 114.7, 111.5, 33.4, 21.2; FTIR (film): 3444, 2922, 1619, 1513, 1486, 1448, 1219, 1132, 1031, 1014, 809 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{16}H_{14}NaBrNOS$ $[M+Na]^+$: 369.9872. Found: 369.9869.

5-Bromo-3-(*p*-tolylsulfinyl)-1*H*-indole (3z)



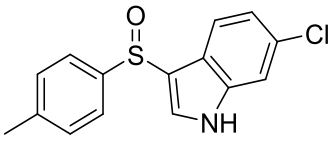
Yellow solid, m.p. = 125–127 °C; 60.0 mg, 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.08 (s, 1H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 1.5 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 2.9 Hz, 1H), 7.15 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.03 (d, *J* = 8.7 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.0, 139.1, 135.8, 130.7, 129.9, 126.3, 124.9, 124.7, 121.5, 115.4, 114.6, 114.1, 21.3; FTIR (film): 3145, 2920, 2870, 1492, 1453, 1412, 1295, 1112, 1080, 1021, 1002, 885, 806, 732 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{15}H_{12}NaBrNOS$ $[M+Na]^+$: 355.9715. Found: 355.9713.

6-Chloro-1-methyl-3-(*p*-tolylsulfinyl)-1*H*-indole (3aa)



Yellow solid, m.p. = 134–136 °C; 36.7 mg, 60% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (d, *J* = 8.1 Hz, 2H), 7.49 (s, 1H), 7.37 (d, *J* = 8.6 Hz, 1H), 7.33 (d, *J* = 1.5 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.06 (dd, *J* = 8.6, 1.6 Hz, 1H), 3.78 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.7, 140.5, 138.1, 133.0, 129.5, 129.3, 124.7, 122.7, 121.9, 120.7, 117.2, 110.1, 33.3, 21.2; FTIR (film): 3484, 3101, 2922, 1608, 1514, 1491, 1460, 1331, 1174, 1080, 1070, 1035, 1014, 829, 807, 648 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{16}H_{14}NaClNOS$ $[M+Na]^+$: 326.0377. Found: 326.0379.

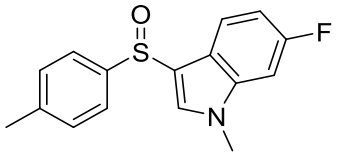
6-Chloro-3-(*p*-tolylsulfinyl)-1*H*-indole (3ab)



Yellow solid, m.p. = 119–121 °C; 41.1 mg, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.28 (s, 1H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.30–7.26 (m, 3H), 7.24 (d, *J* = 8.6 Hz, 1H), 7.18 (d, *J* = 1.0 Hz, 1H), 6.97 (dd, *J* = 8.6, 1.4 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.9, 139.7, 137.4, 130.0, 129.8, 129.5, 124.8, 122.2, 121.9, 120.0,

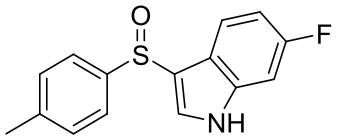
116.9, 112.4, 21.3; FTIR (film): 3151, 3103, 2923, 1666, 1615, 1492, 1443, 1403, 1270, 1081, 1021, 1006, 908, 806, 785 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{15}H_{12}NaClNOS$ $[M+Na]^+$: 312.0220. Found: 312.0222.

6-Fluoro-1-methyl-3-(*p*-tolylsulfinyl)-1*H*-indole (3ac)



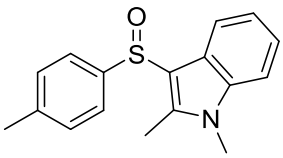
White solid, m.p. = 143–145 °C; 40.2 mg, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 (d, *J* = 8.1 Hz, 2H), 7.49 (s, 1H), 7.38 (dd, *J* = 8.8, 5.2 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.01 (dd, *J* = 9.3, 2.0 Hz, 1H), 6.85 (dt, *J* = 9.3, 2.1 Hz, 1H), 3.78 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.3 (d, $J_{C\text{-}F}$ = 241.0 Hz), 140.8, 140.5, 138.0 (d, $J_{C\text{-}F}$ = 11.9 Hz), 132.9, 129.6, 124.8, 121.0 (d, $J_{C\text{-}F}$ = 10.1 Hz), 120.6, 117.1 (d, $J_{C\text{-}F}$ = 3.0 Hz), 110.2 (d, $J_{C\text{-}F}$ = 24.7 Hz), 96.7 (d, $J_{C\text{-}F}$ = 26.5 Hz), 33.4, 21.2; FTIR (film): 3440, 3102, 2923, 2853, 1622, 1583, 1516, 1491, 1462, 1335, 1244, 1098, 1033, 1014, 897, 828, 808, 689 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{16}H_{14}NaFNOS$ $[M+Na]^+$: 310.0672. Found: 310.0675.

6-Fluoro-3-(*p*-tolylsulfinyl)-1*H*-indole (3ad)



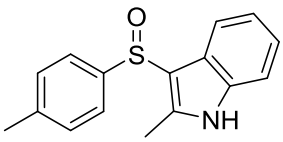
Yellow solid, m.p. = 102–104 °C; 45.9 mg, 84% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.78 (s, 1H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.24–7.21 (m, 2H), 6.85 (dd, *J* = 9.3, 1.9 Hz, 1H), 6.73 (dt, *J* = 9.3, 2.1 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.2 (d, $J_{C\text{-}F}$ = 240.5 Hz), 140.8, 139.5, 137.4 (d, $J_{C\text{-}F}$ = 12.5 Hz), 130.3 (d, $J_{C\text{-}F}$ = 2.5 Hz), 129.8, 124.8, 120.0 (d, $J_{C\text{-}F}$ = 10.0 Hz), 119.7, 116.2, 110.3 (d, $J_{C\text{-}F}$ = 24.7 Hz), 98.9 (d, $J_{C\text{-}F}$ = 26.2 Hz), 21.3; FTIR (film): 3128, 3091, 3060, 2920, 1626, 1592, 1513, 1448, 1417, 1340, 1240, 1145, 1022, 1002, 950, 805, 615 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{15}H_{12}NaFNOS$ $[M+Na]^+$: 296.0516. Found: 296.0514.

1,2-Dimethyl-3-(*p*-tolylsulfinyl)-1*H*-indole (3ae)



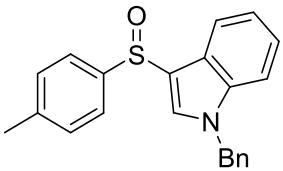
White solid, m.p. = 128–130 °C; 48.1 mg, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (d, *J* = 8.2 Hz, 2H), 7.30–7.23 (m, 4H), 7.16 (t, *J* = 7.7 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 3.68 (s, 3H), 2.68 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.3, 141.1, 139.6, 137.1, 129.4, 124.7, 123.9, 122.3, 121.1, 119.3, 112.6, 109.3, 29.6, 21.1, 10.9; FTIR (film): 3049, 2918, 1526, 1474, 1399, 1037, 1015, 760, 740 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{17}H_{17}NaNOS$ $[M+Na]^+$: 306.0923. Found: 306.0925.

2-Methyl-3-(*p*-tolylsulfinyl)-1*H*-indole (3af)



Yellow solid, m.p. = 120–122 °C; 47.4 mg, 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.99 (s, 1H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 7.5 Hz, 2H), 7.19 (t, *J* = 7.7 Hz, 2H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 2.40 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.3, 140.1, 140.0, 135.8, 129.6, 124.8, 124.3, 122.5, 121.0, 118.9, 111.7, 111.4, 21.2, 11.6; FTIR (film): 3178, 3103, 2924, 1618, 1490, 1451, 1409, 1289, 1082, 1003, 923, 808, 743 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{16}H_{15}NaNOS$ $[M+Na]^+$: 292.0767. Found: 292.0763.

1-Benzyl-3-(*p*-tolylsulfinyl)-1*H*-indole (3ag)

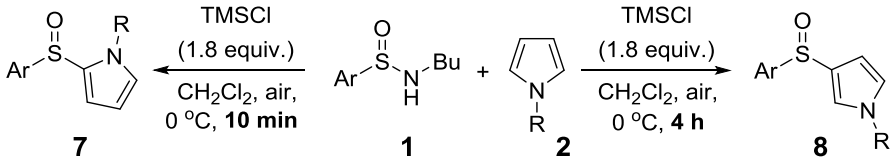


White solid, m.p. = 140–142 °C; 48.3 mg, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (d, *J* = 7.9 Hz, 2H), 7.59 (s, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.35–7.29 (m, 6H), 7.21 (t, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 7.2 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 5.31 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.8, 140.3, 137.3, 135.6, 131.9, 129.5, 128.9, 128.0, 126.9, 124.8, 124.4, 123.3, 121.4, 120.0, 117.2, 110.5, 50.5, 21.2; FTIR (film): 3456, 3031,

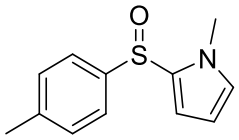
2922, 1510, 1455, 1386, 1162, 1080, 1034, 1014, 810, 761, 742, 732, 697 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{22}H_{19}NaNOS$ $[M+Na]^+$: 368.1080. Found: 368.1084.

4.2 Experimental Procedure of Sulfoxides 7a-7g and 8a-8g

The mixture of an arylsulfiniamide (0.2 mmol, 1 equiv.), a pyrrole (0.24 mmol, 1.2 equiv.) and TMSCl (0.36 mmol, 1.8 equiv.) in CH_2Cl_2 (1.0 mL) was stirred at 0 °C for 10 min (for **7**) or 4 h (for **8**), then water (5 mL) and dichloromethane (10 mL) were added. The two layers were separated, and the aqueous phase was extracted with dichloromethane (3 × 10 mL). The combined organic extracts were washed by brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (100–200 mesh) to afford the desired sulfoxide.

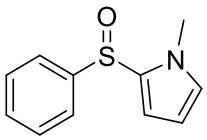


1-Methyl-2-(*p*-tolylsulfinyl)-1*H*-pyrrole (7a)



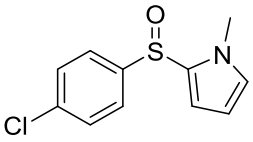
White solid, m.p. = 47–49 °C; 33.3 mg, 76% yield; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.43 (d, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 6.74 (s, 1H), 6.53–6.52 (m, 1H), 6.12 (s, 1H), 3.56 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.5, 139.6, 129.6, 128.8, 124.8, 117.1, 108.0, 34.6, 21.2; FTIR (film): 2949, 2359, 2342, 1739, 1372, 1274, 1238, 1045, 764, 668 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{12}H_{13}NaNOS$ $[M+Na]^+$: 242.0610. Found: 242.0611.

1-Methyl-2-(phenylsulfinyl)-1*H*-pyrrole (7b)



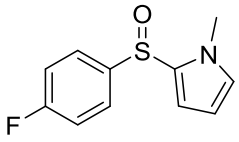
Yellow solid, m.p. = 57–59 °C; 22.1 mg, 54% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55–7.53 (m, 2H), 7.49–7.42 (m, 3H), 6.74 (s, 1H), 6.55 (dd, *J* = 3.7, 1.4 Hz, 1H), 6.13–6.11 (m, 1H), 3.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.0, 130.1, 129.4, 129.0, 128.9, 124.8, 117.4, 108.1, 34.6; FTIR (film): 3102, 2926, 1442, 1291, 1082, 1035, 731 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{11}H_{11}NaNOS$ $[M+Na]^+$: 228.0454. Found: 228.0457.

2-((4-Chlorophenyl)sulfinyl)-1-methyl-1*H*-pyrrole (7c)



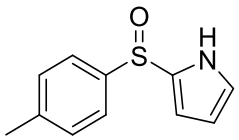
Pale yellow oil, 33.9 mg, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49–7.43 (m, 4H), 6.75 (s, 1H), 6.55 (dd, *J* = 3.8, 1.6 Hz, 1H), 6.13–6.12 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.7, 136.4, 129.3, 129.1, 128.9, 126.3, 117.6, 108.2, 34.6; FTIR (film): 3101, 2925, 1471, 1290, 1088, 1037, 1009, 823, 737 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{11}H_{10}NaClNOS$ $[M+Na]^+$: 262.0064. Found: 262.0061.

2-((4-Fluorophenyl)sulfinyl)-1-methyl-1*H*-pyrrole (7d)



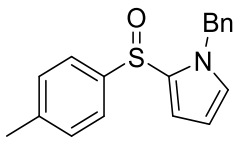
Pale yellow oil, 20.1 mg, 45% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (dd, *J* = 8.6, 5.1 Hz, 2H), 7.18 (t, *J* = 8.6 Hz, 2H), 6.76 (s, 1H), 6.52 (dd, *J* = 3.7, 1.4 Hz, 1H), 6.13–6.12 (m, 1H), 3.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.8 (d, $J_{C\text{-}F}$ = 250.8 Hz), 138.5 (d, $J_{C\text{-}F}$ = 3.0 Hz), 129.3, 129.2, 127.1 (d, $J_{C\text{-}F}$ = 8.7 Hz), 117.4, 116.2 (d, $J_{C\text{-}F}$ = 22.6 Hz), 108.2, 34.6; FTIR (film): 3099, 2925, 1588, 1488, 1290, 1222, 1037, 835, 732 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{11}H_{10}NaFNOS$ $[M+Na]^+$: 246.0359. Found: 246.0363.

2-(*p*-Tolylsulfinyl)-1*H*-pyrrole (7e)



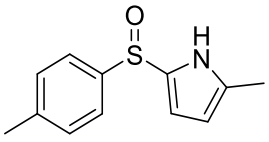
White solid, m.p. = 100–102 °C; 28.3 mg, 69% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.75 (s, 1H), 7.53 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 6.92 (s, 1H), 6.54 (s, 1H), 6.18 (d, *J* = 2.0 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.0, 140.0, 129.7, 129.3, 124.9, 124.4, 114.3, 109.0, 21.3; FTIR (film): 3178, 3049, 2936, 2854, 1492, 1081, 1022, 1009, 808, 738 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{11}H_{11}NaNOS$ $[M+Na]^+$: 228.0454. Found: 228.0457.

1-Benzyl-2-(*p*-tolylsulfinyl)-1*H*-pyrrole (7f)



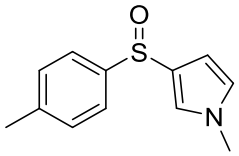
Pale yellow oil, 33.6 mg, 57% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39 (d, *J* = 8.2 Hz, 2H), 7.24–7.18 (m, 5H), 6.97–6.94 (m, 2H), 6.74–6.73 (m, 1H), 6.51 (dd, *J* = 2.8, 1.7 Hz, 1H), 6.17 (dd, *J* = 3.7, 2.9 Hz, 1H), 5.29 (d, *J* = 15.5 Hz, 1H), 5.12 (d, *J* = 15.5 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.5, 139.8, 136.6, 131.0, 129.5, 128.5, 127.6, 127.5, 127.3, 124.7, 116.4, 108.8, 50.9, 21.2; FTIR (film): 3031, 2923, 1454, 1287, 1080, 1038, 810, 728 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{18}H_{17}NaNOS$ $[M+Na]^+$: 318.0923. Found: 318.0927.

2-Methyl-5-(*p*-tolylsulfinyl)-1*H*-pyrrole (7g)



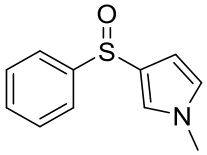
Pale yellow oil, 28.1 mg, 64% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.46 (s, 1H), 7.50 (d, *J* = 7.9 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 6.48–6.46 (m, 1H), 5.80 (t, *J* = 3.0 Hz, 1H), 2.39 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.7, 140.1, 136.0, 129.6, 126.8, 124.9, 116.0, 107.1, 21.3, 12.9; FTIR (film): 3177, 2924, 2359, 1566, 1274, 1148, 1024, 764 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{12}H_{13}NaNOS$ $[M+Na]^+$: 242.0610. Found: 242.0617.

1-Methyl-3-(*p*-tolylsulfinyl)-1*H*-pyrrole (8a)



White solid, m.p. = 84–86 °C; 32.0 mg, 73% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.98 (s, 1H), 6.61 (d, *J* = 2.3 Hz, 1H), 6.18 (dd, *J* = 2.6, 1.7 Hz, 1H), 3.66 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.8, 140.2, 129.3, 126.8, 124.4, 124.2, 123.8, 107.3, 36.4, 21.1; FTIR (film): 3452, 3105, 2922, 1673, 1516,1493, 1420, 1121, 1080, 1034, 1013, 810, 706, 635 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{12}H_{13}NaNOS$ $[M+Na]^+$: 242.0610. Found: 242.0607.

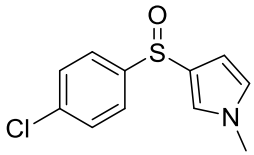
1-Methyl-3-(phenylsulfinyl)-1*H*-pyrrole (8b)



The reaction was performed for 5 h.

White solid, m.p. = 82–84 °C; 30.0 mg, 73% yield; H NMR (400 MHz, $CDCl_3$) δ: 7.64 (d, *J* = 6.8 Hz, 2H), 7.48–7.40 (m, 3H), 6.97 (m, 2H), 6.58 (t, *J* = 2.3 Hz, 1H), 6.14 (dd, *J* = 2.6, 1.6 Hz, 1H), 3.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.0, 130.0, 128.7, 126.6, 124.5, 124.5, 124.0, 107.6, 36.5; FTIR (film): 3445, 3108, 2920, 1670, 1515, 1442, 1419, 1304, 1121, 1081, 1032, 996, 750, 691, 632 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{11}H_{11}NaNOS$ $[M+Na]^+$: 228.0454. Found: 228.0452.

3-((4-Chlorophenyl)sulfinyl)-1-methyl-1*H*-pyrrole (8c)

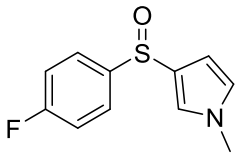


The reaction was performed for 5 h.

Yellow solid, m.p. = 64–66 °C; 32.0 mg, 67% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 6.98 (s, 1H), 6.58 (t, *J* = 2.4 Hz, 1H), 6.11 (t, *J* = 2.2 Hz, 1H), 3.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.7, 136.0, 128.9, 126.1, 125.9, 124.7, 124.2, 107.4, 36.5; FTIR (film): 3457, 3109, 2923,

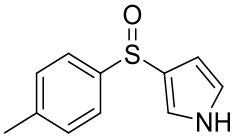
2235, 1515, 1472, 1419, 1120, 1077, 1034, 1009, 907, 820, 793, 738, 726, 632 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{11}H_{10}NaClNOS$ $[M+Na]^+$: 262.0064. Found: 262.0062.

3-((4-Fluorophenyl)sulfinyl)-1-methyl-1*H*-pyrrole (8d)



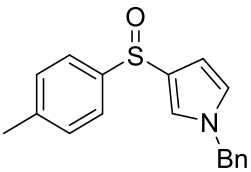
Pale yellow oil, 30.0 mg, 67% yield; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.64–7.60 (m, 2H), 7.17–7.12 (m, 2H), 6.97 (s, 1H), 6.59 (t, *J* = 2.4 Hz, 1H), 6.12–6.11 (m, 1H), 3.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.7 (d, J_{C-F} = 250.1 Hz), 140.7 (d, J_{C-F} = 3.1 Hz), 126.7 (d, J_{C-F} = 8.7 Hz), 126.5, 124.5, 124.1, 115.9 (d, J_{C-F} = 22.6 Hz), 107.4, 36.5; FTIR (film): 3443, 3109, 2922, 1673, 1558, 1516, 1489, 1420, 1220, 1152, 1121, 1080, 1032, 1010, 835, 812, 635 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{11}H_{10}NaFNOS$ $[M+Na]^+$: 246.0359. Found: 262.0362.

3-(*p*-Tolylsulfinyl)-1*H*-pyrrole (8e)



White solid, m.p. = 150–152 °C; 25.4 mg, 62% yield; ^1H NMR (400 MHz, $CDCl_3$) δ: 10.06 (s, 1H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 1.1 Hz, 1H), 6.69 (d, *J* = 1.7 Hz, 1H), 6.16 (s, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.3, 140.6, 129.5, 124.7, 121.8, 121.8, 120.5, 106.6, 21.3; FTIR (film): 3189, 3050, 2922, 2850, 1491, 1082, 1042, 1021, 1008, 808, 636 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{11}H_{11}NaNOS$ $[M+Na]^+$: 228.0454. Found: 228.0456.

1-Benzyl-3-(*p*-tolylsulfinyl)-1*H*-pyrrole (8f)

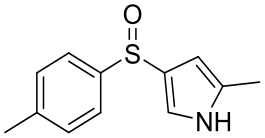


The reaction was performed for 5 h.

White solid, m.p. = 103–105 °C; 36.0 mg, 61% yield; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.56 (d, *J* = 8.1 Hz, 2H), 7.38–7.32 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.15–7.13 (m, 2H), 7.08 (t, *J* = 1.8 Hz, 1H), 6.67 (t, *J* = 2.5 Hz, 1H),

6.19 (dd, *J* = 2.8, 1.8 Hz, 1H), 5.03 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.9, 140.3, 136.1, 129.4, 128.8, 128.0, 127.2, 127.1, 124.5, 123.8, 123.3, 107.5, 53.7, 21.2; FTIR (film): 3449, 3106, 3031, 2922, 1505, 1454, 1397, 1114, 1080, 1031, 1014, 907, 809, 708, 634 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{18}H_{17}NaNOS$ $[M+Na]^+$: 318.0923. Found: 318.0920.

2-Methyl-4-(*p*-tolylsulfinyl)-1*H*-pyrrole (8g)



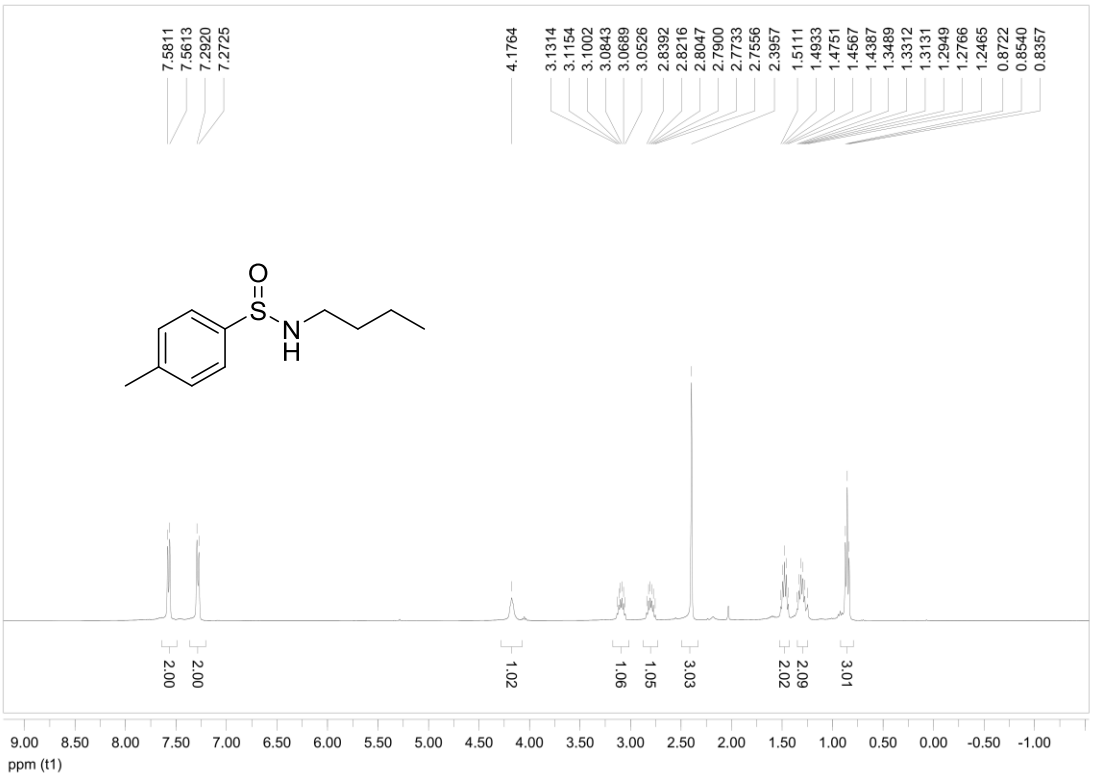
0.72 mmol of TMSCl was used for 12 h.

Pale yellow oil, 31.1 mg, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.13 (s, 1H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 2H), 6.45–6.43 (m, 1H), 5.89–5.87 (m, 1H), 2.38 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.3, 140.1, 133.6, 129.5, 124.6, 118.3, 106.6, 103.6, 21.3, 11.0; FTIR (film): 3187, 3101, 2959, 2857, 1492, 1205, 1082, 1005, 808, 729 cm^{-1}; HRMS (ESI) m/z: Calcd for $C_{12}H_{13}NaNOS$ $[M+Na]^+$: 242.0610. Found: 242.0615.

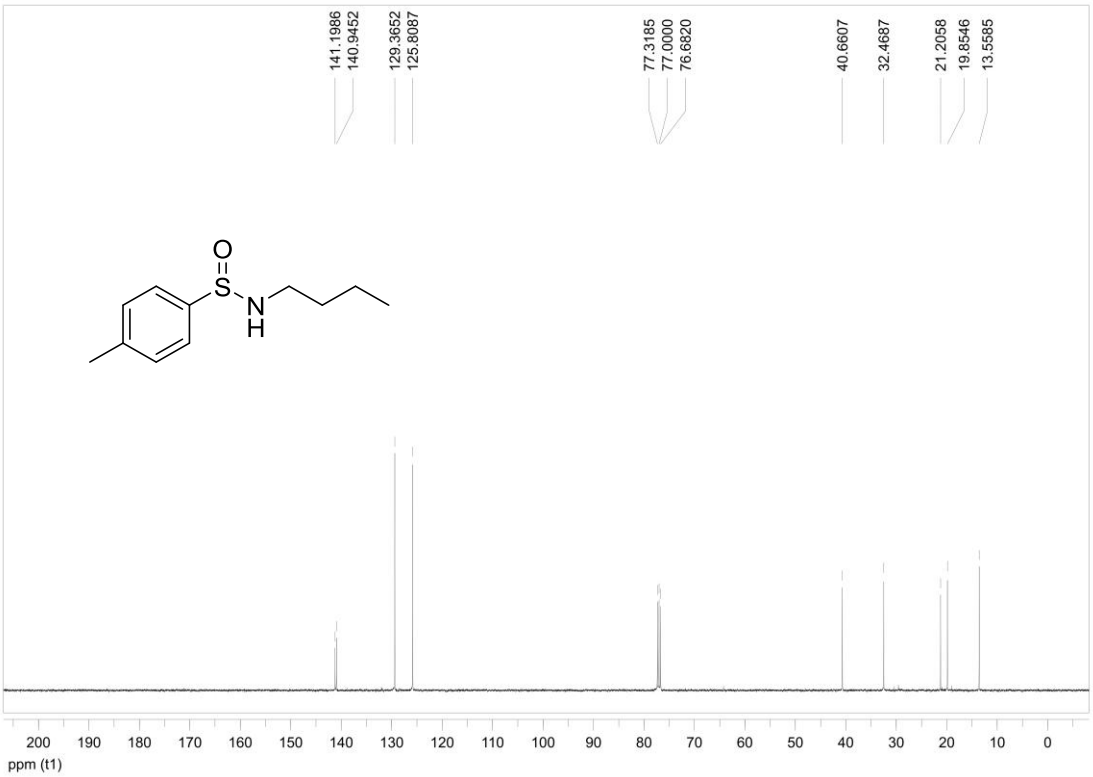
5. NMR Spectra of Sulfinamides and Sulfoxides

Sulfinamide **1a**

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

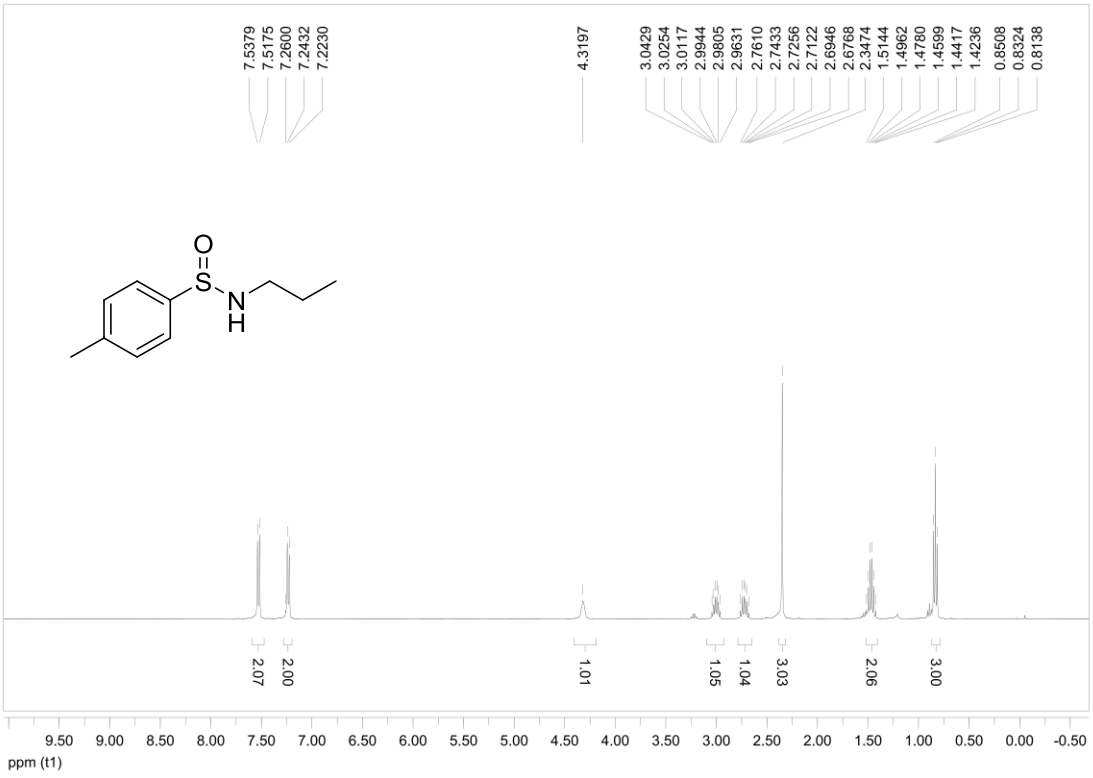


^{13}C NMR (100 MHz, $CDCl_3$)

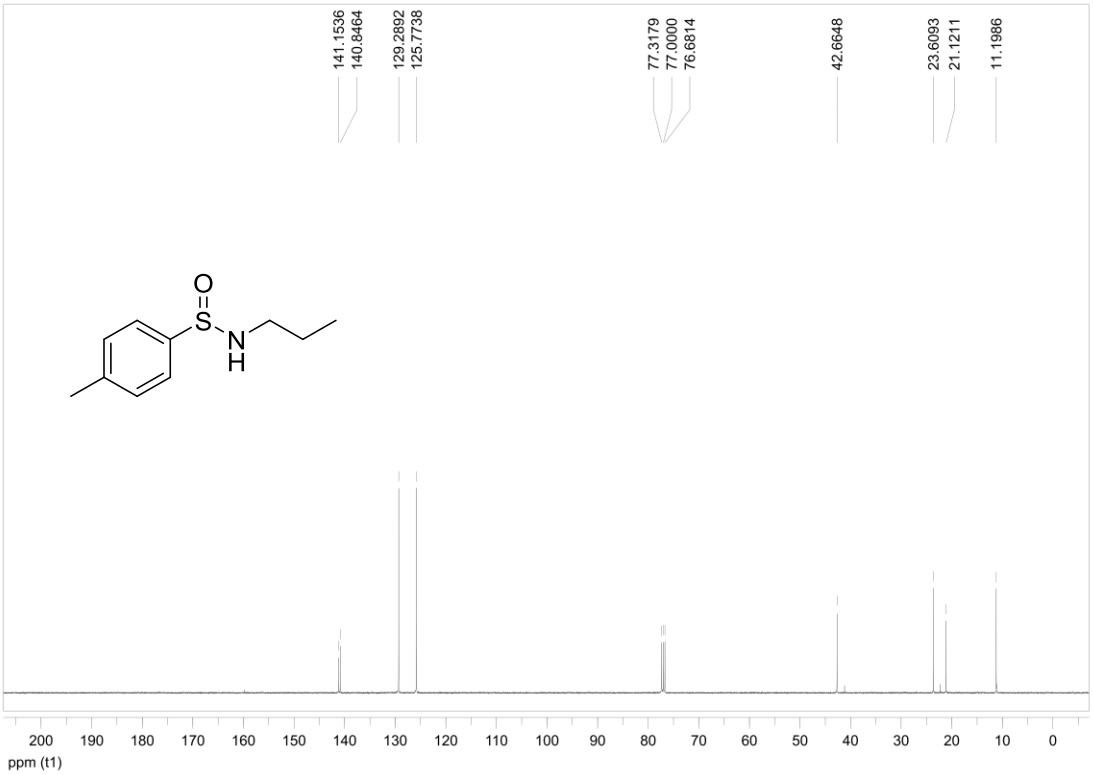


Sulfinamide **1b**

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

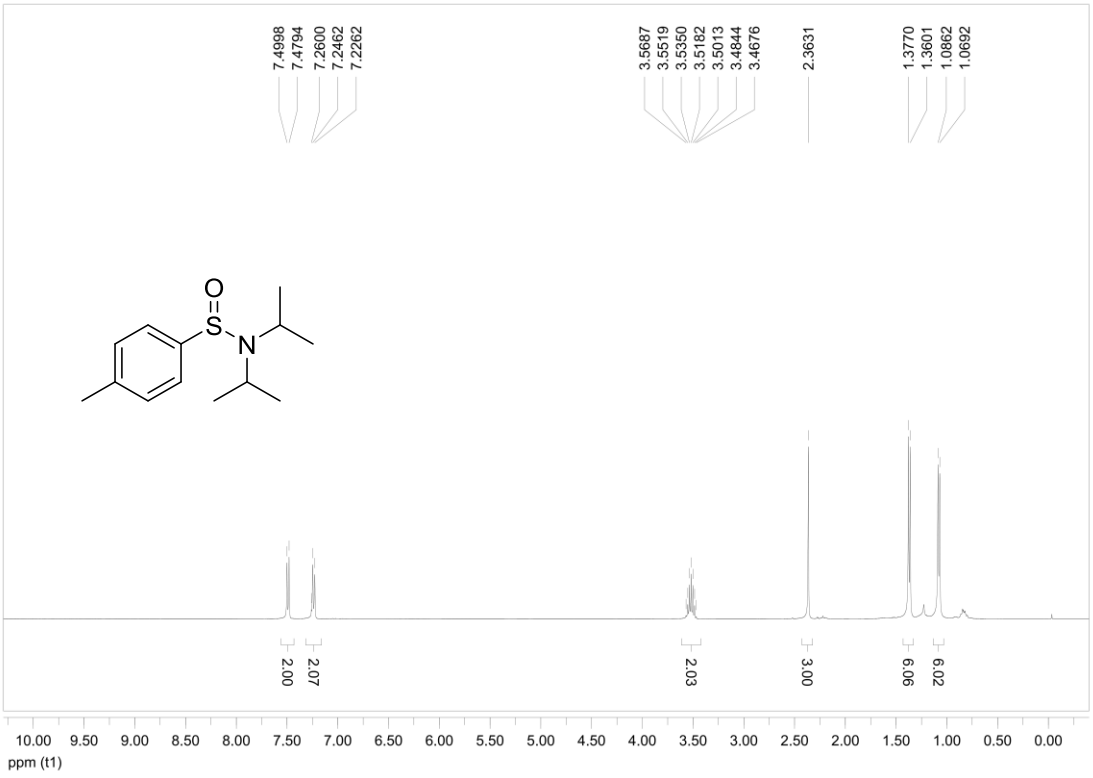


^{13}C NMR (100 MHz, $CDCl_3$)

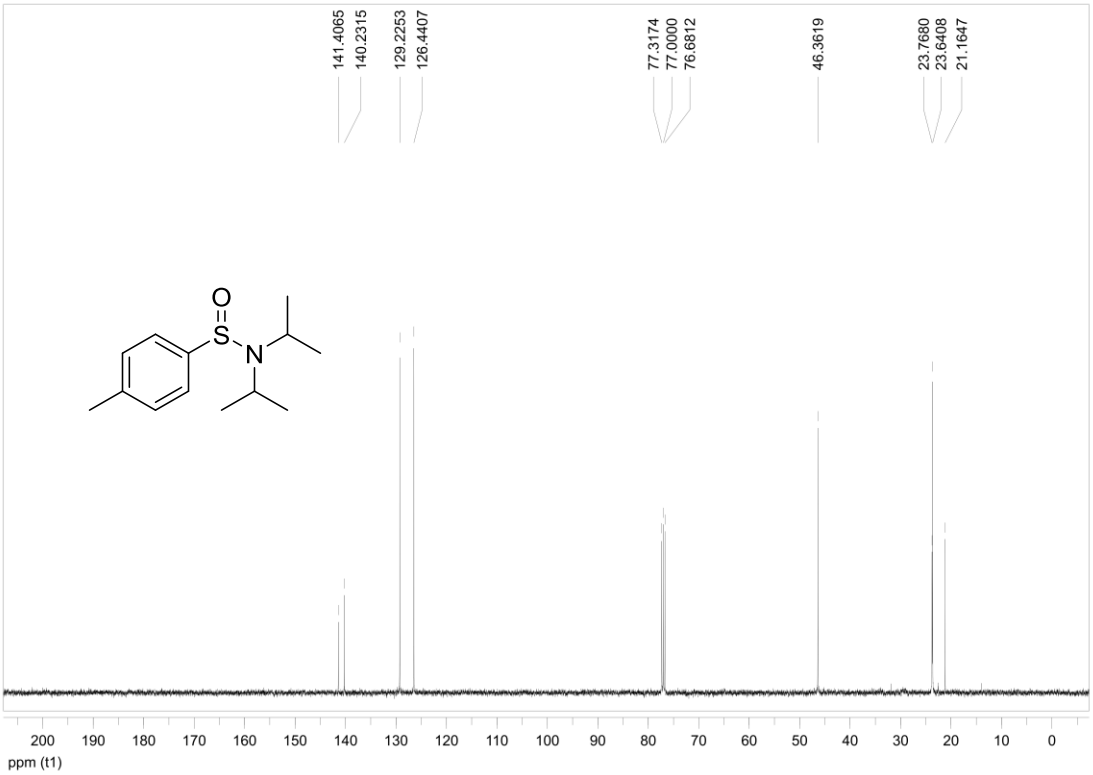


Sulfinamide **1c**

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



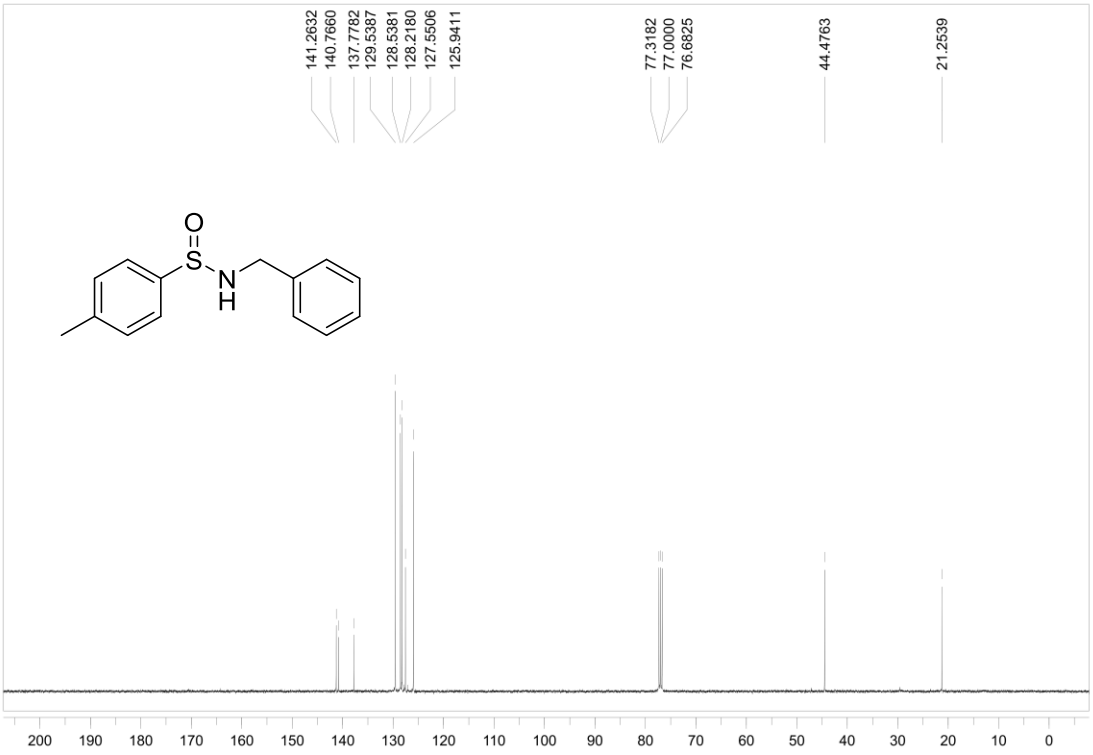
^{13}C NMR (100 MHz, $CDCl_3$)



Sulfinamide **1d**

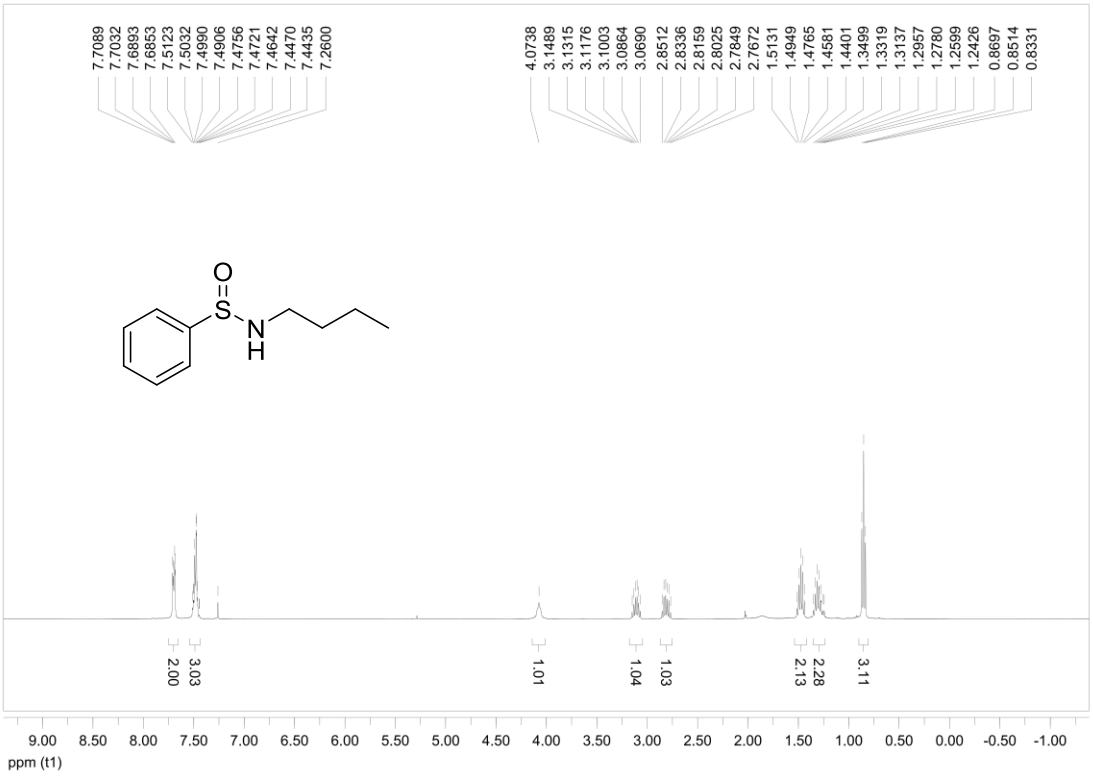
^{1}H NMR (400 MHz, $CDCl_3$)

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

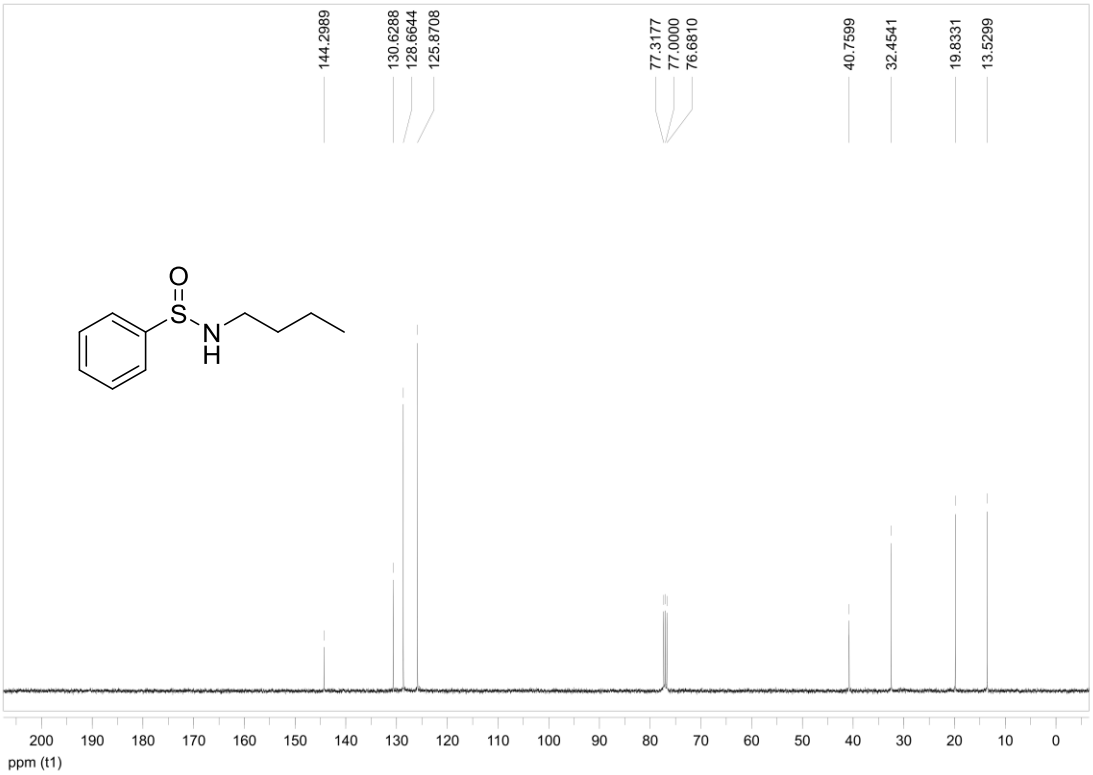


Sulfinamide **1e**

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

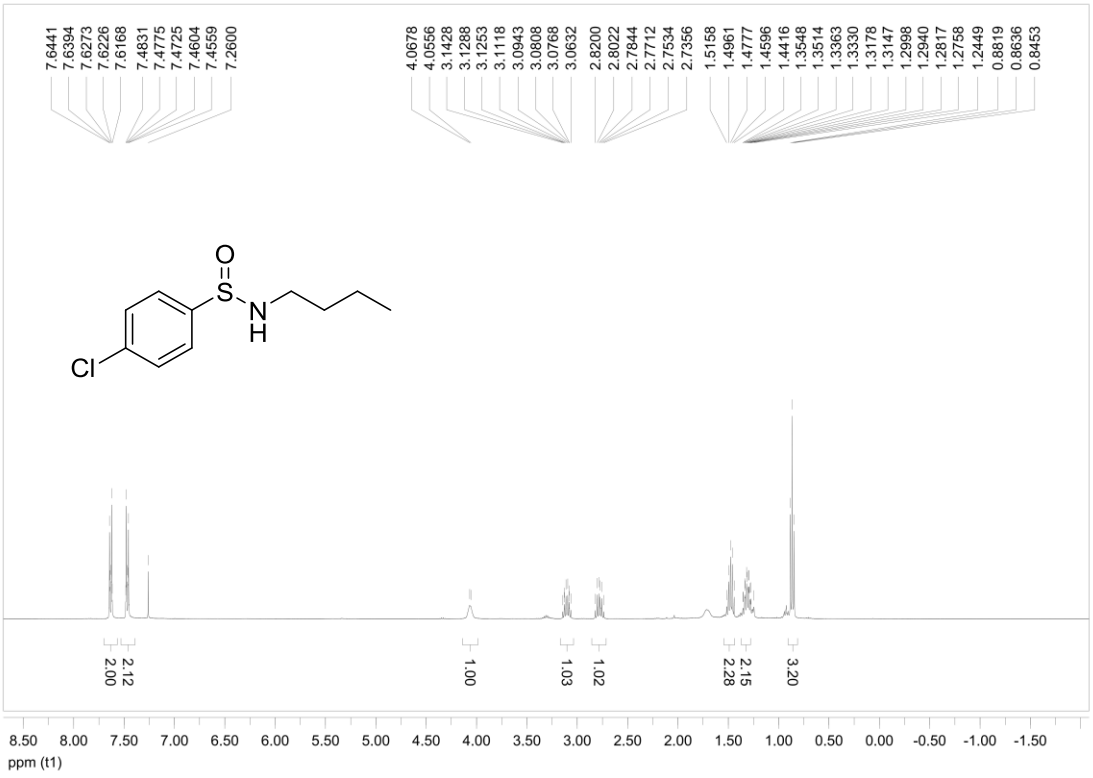


^{13}C NMR (100 MHz, $CDCl_3$)

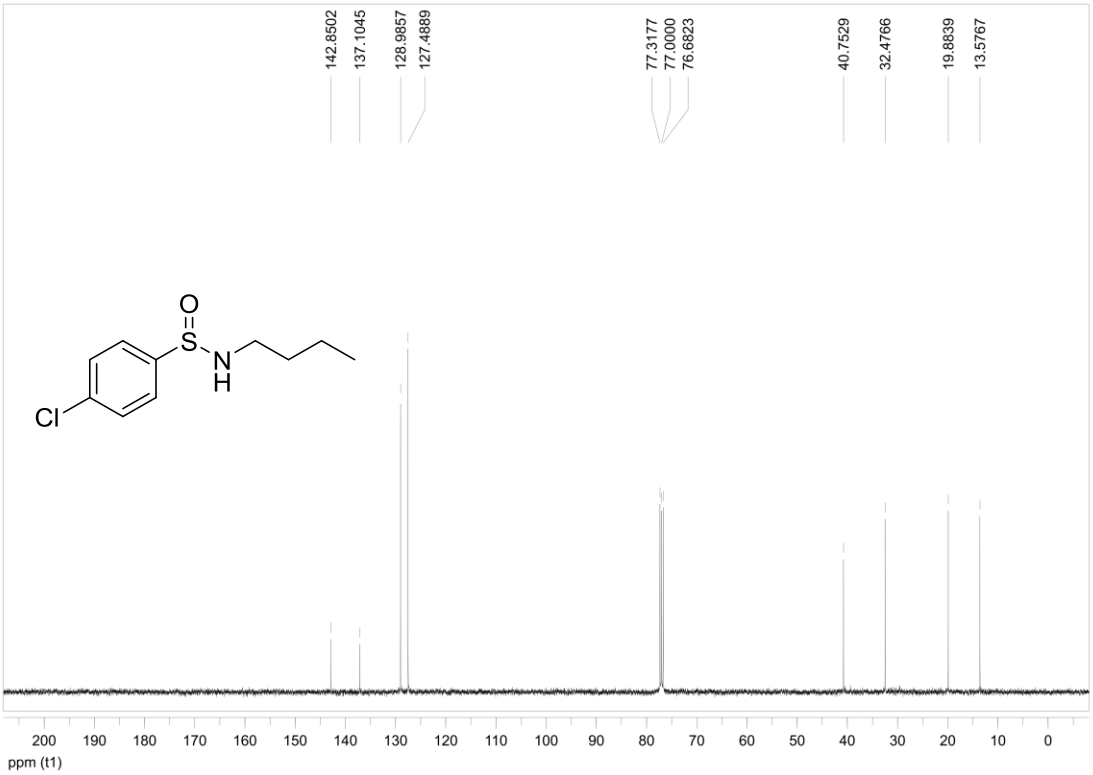


Sulfinamide **1f**

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

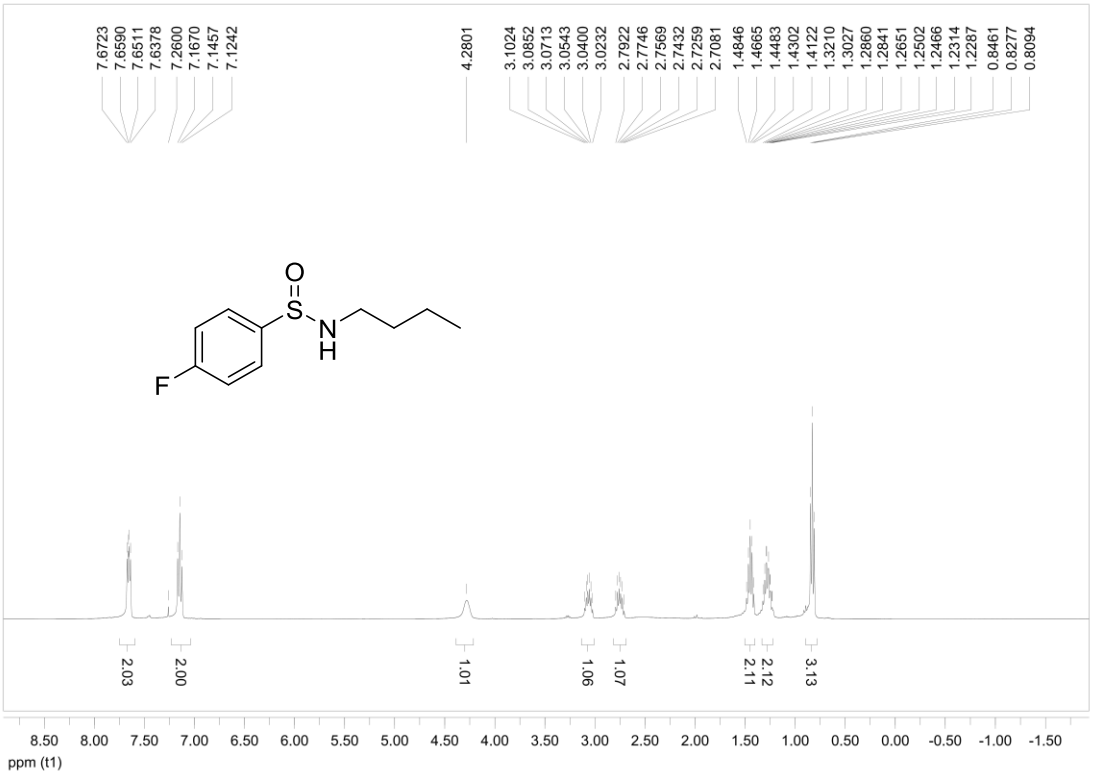


^{13}C NMR (100 MHz, $CDCl_3$)

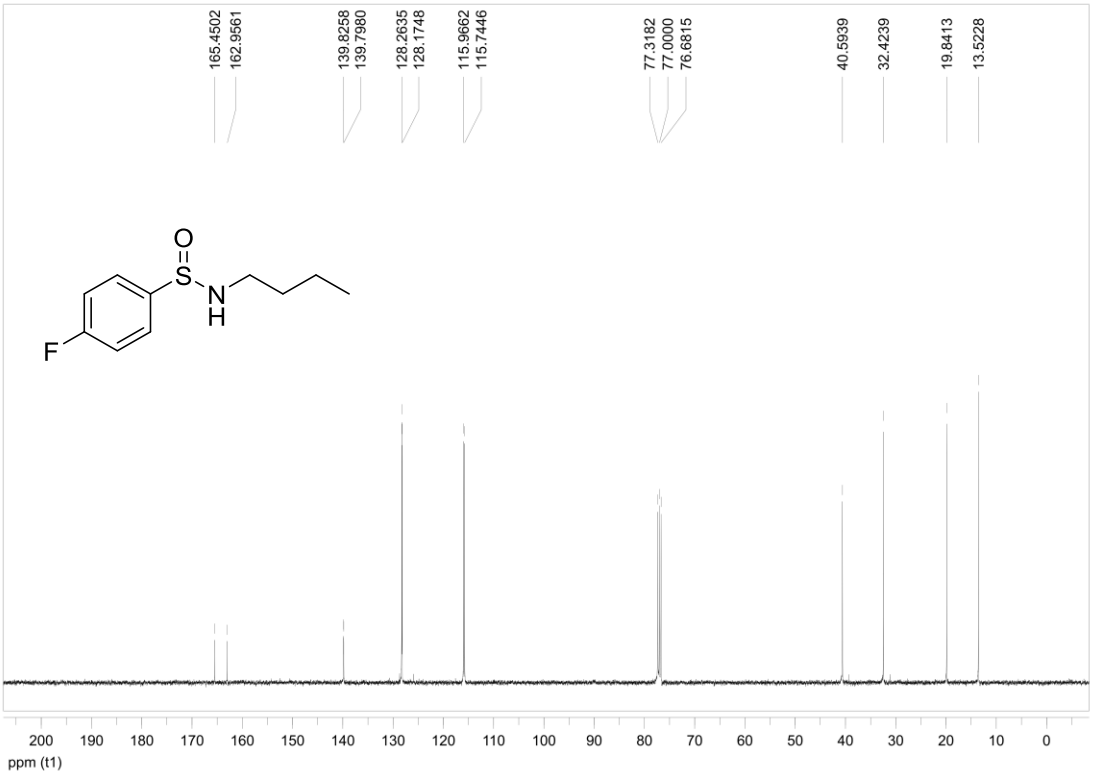


Sulfinamide **1g**

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

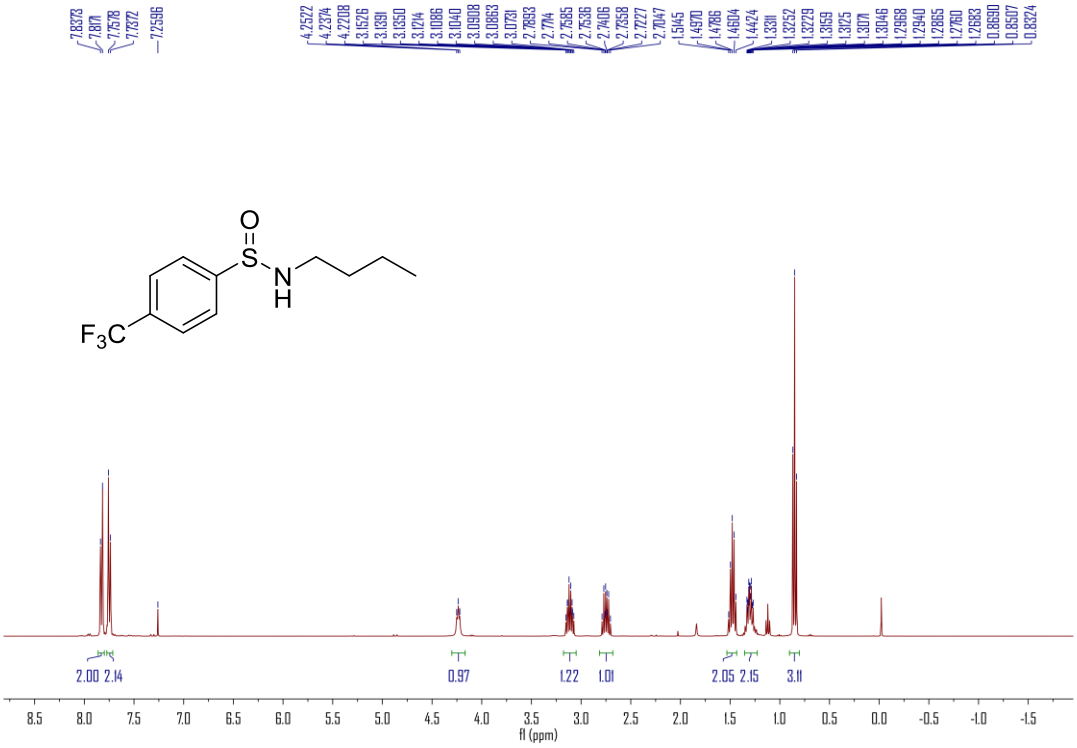


^{13}C NMR (100 MHz, $CDCl_3$)

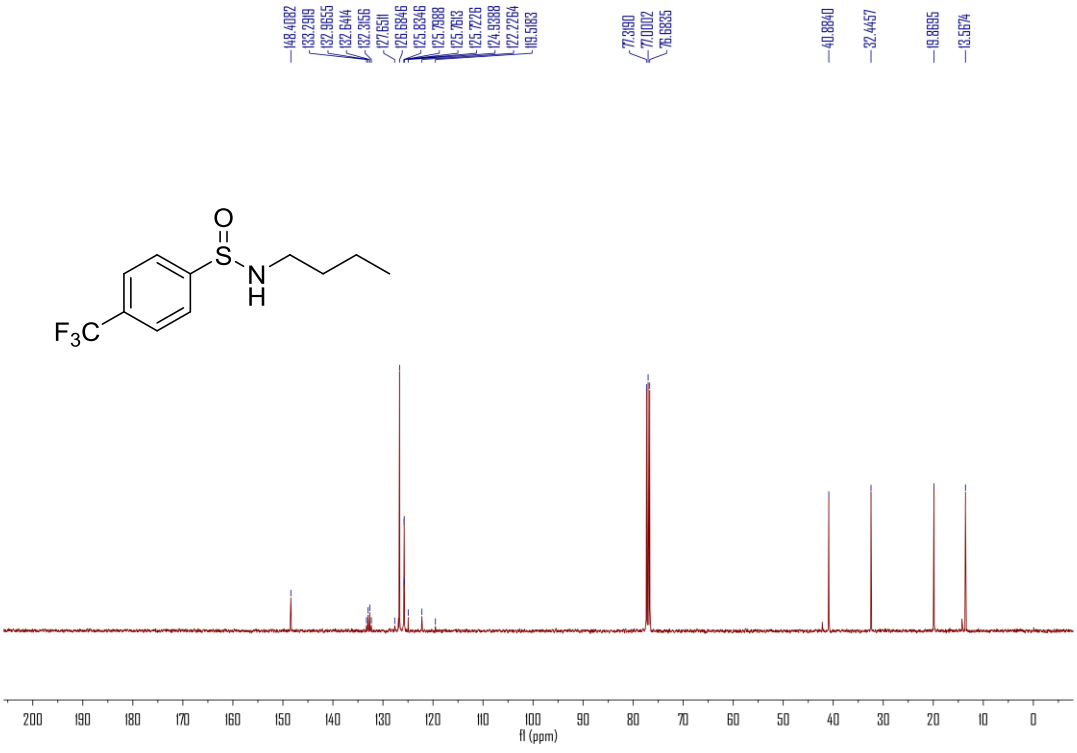


Sulfinamide **1h**

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

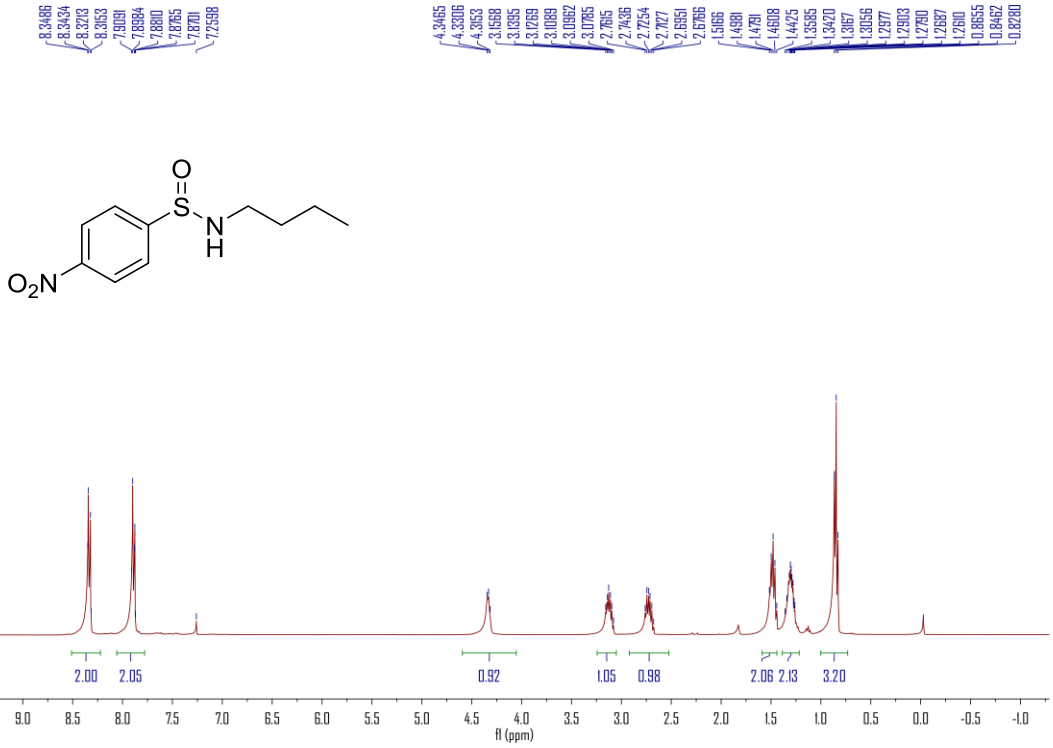


^{13}C NMR (100 MHz, $CDCl_3$)

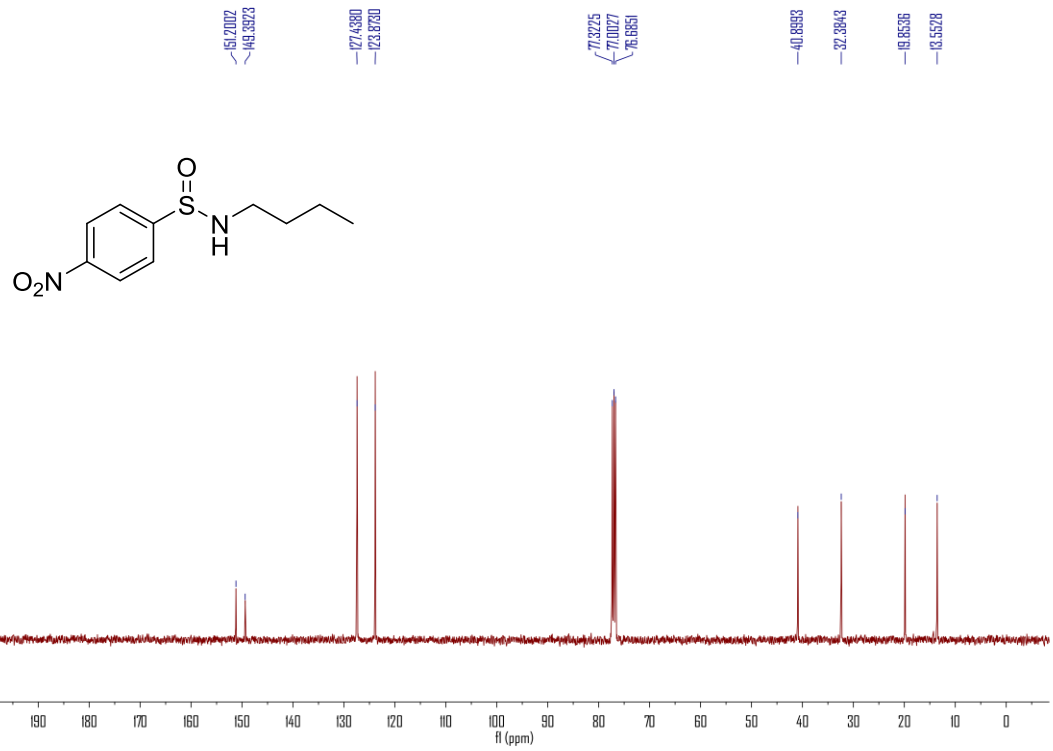


Sulfinamide **1i**

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

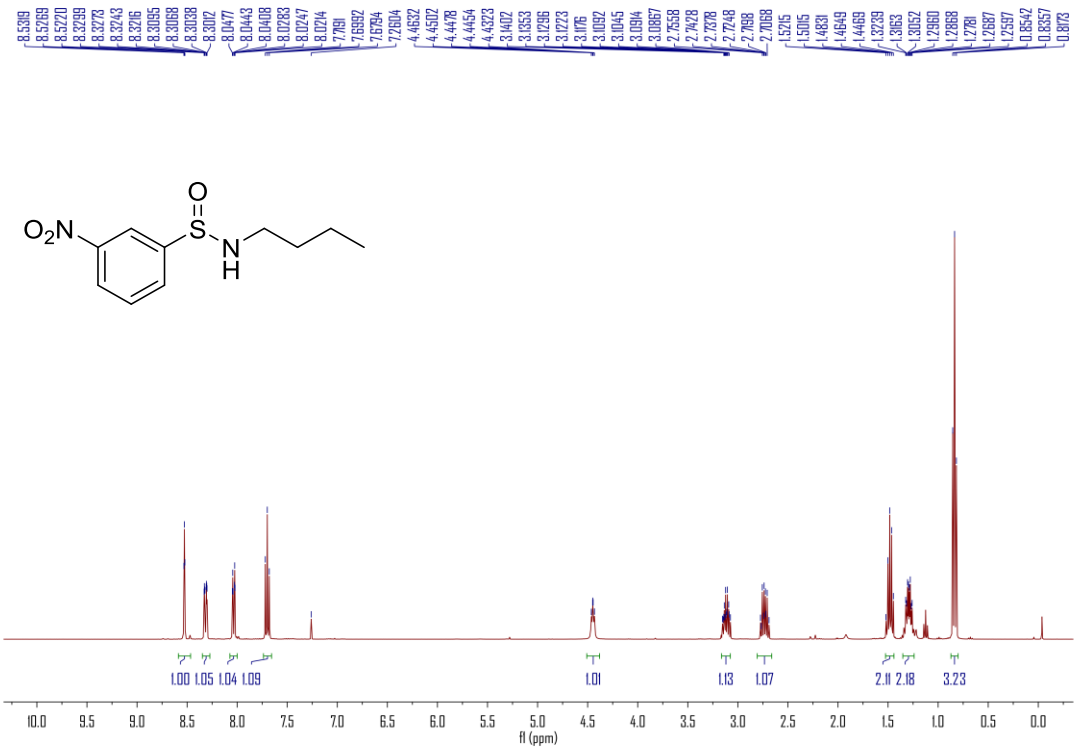


^{13}C NMR (100 MHz, $CDCl_3$)

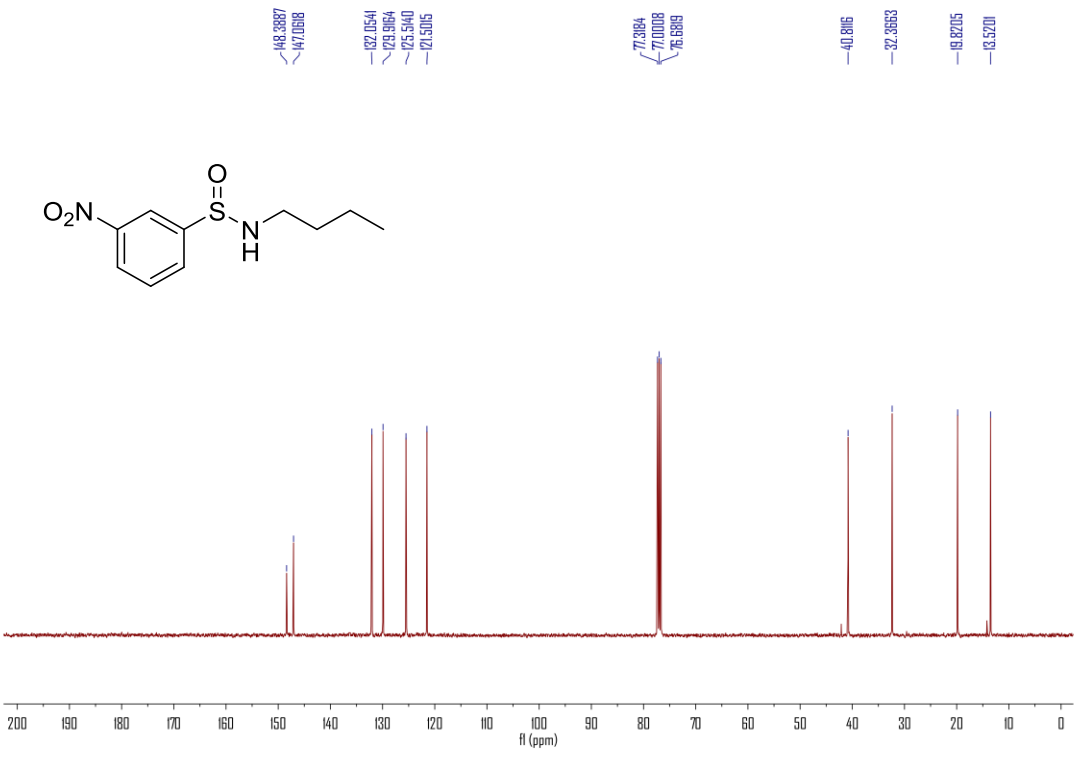


Sulfinamide **1j**

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

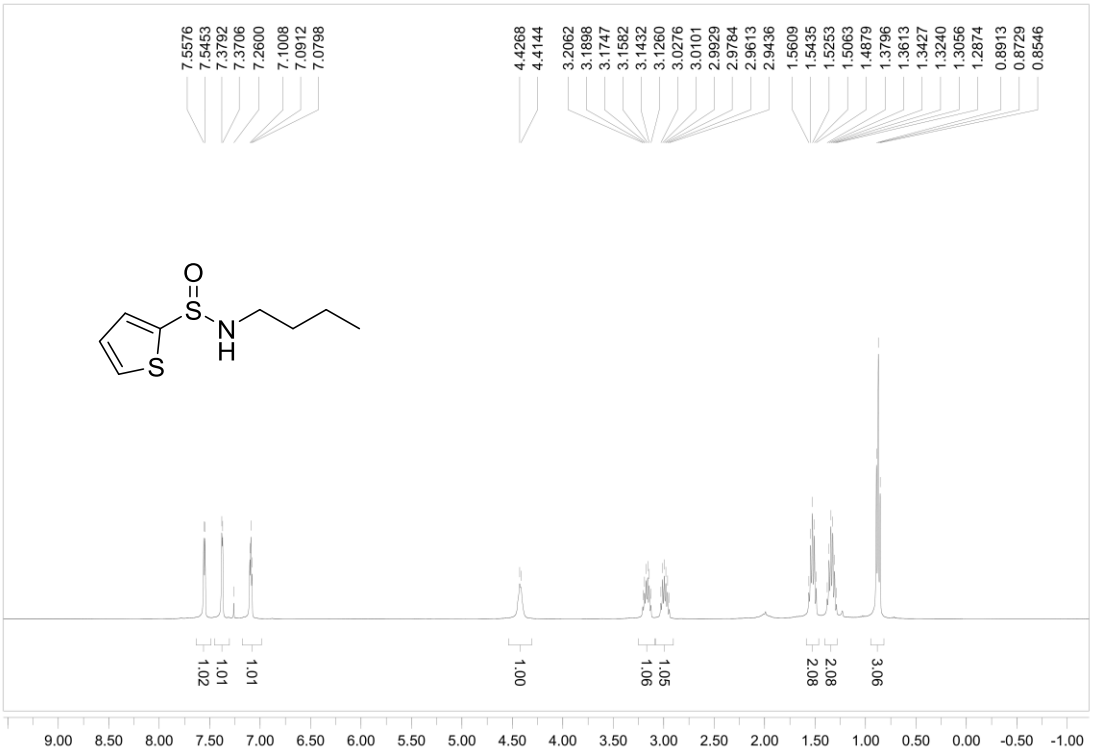


^{13}C NMR (100 MHz, $CDCl_3$)

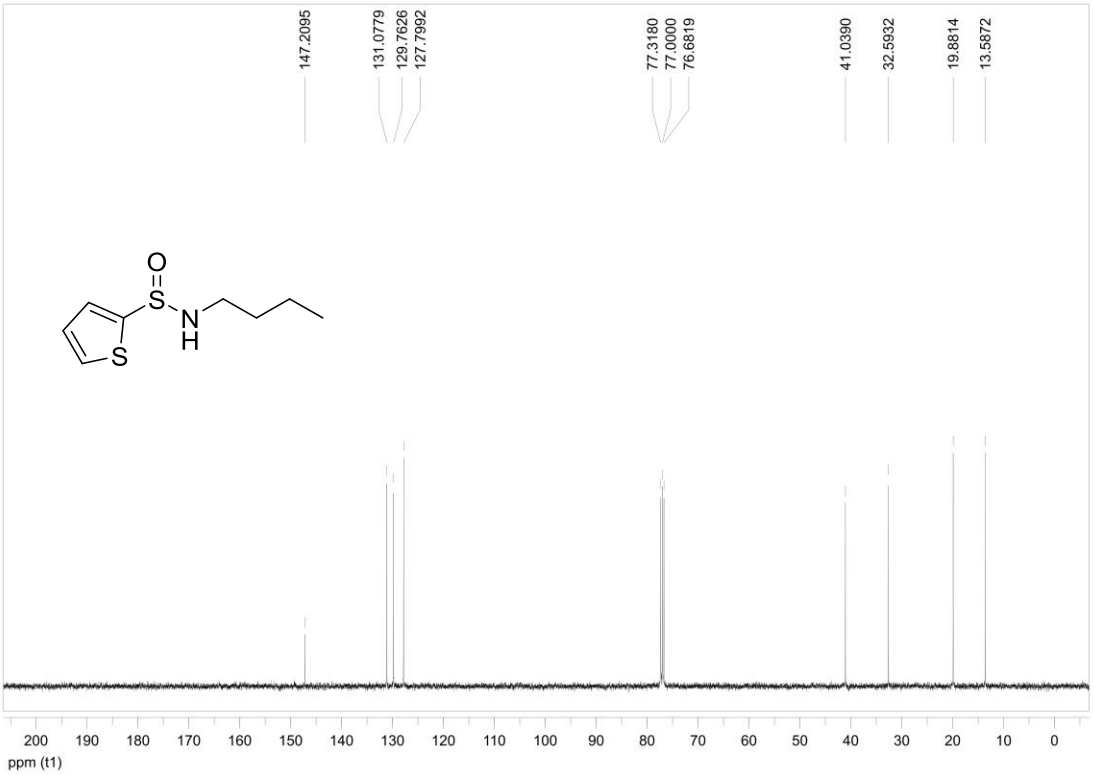


Sulfinamide **1k**

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

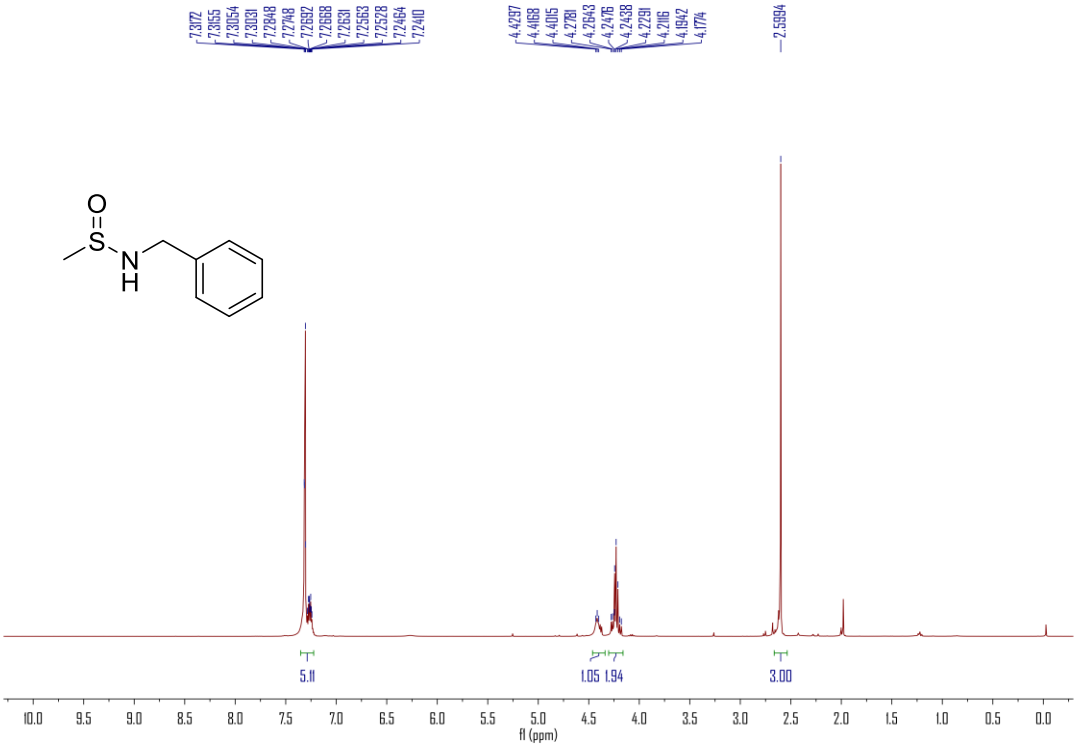


^{13}C NMR (100 MHz, $CDCl_3$)

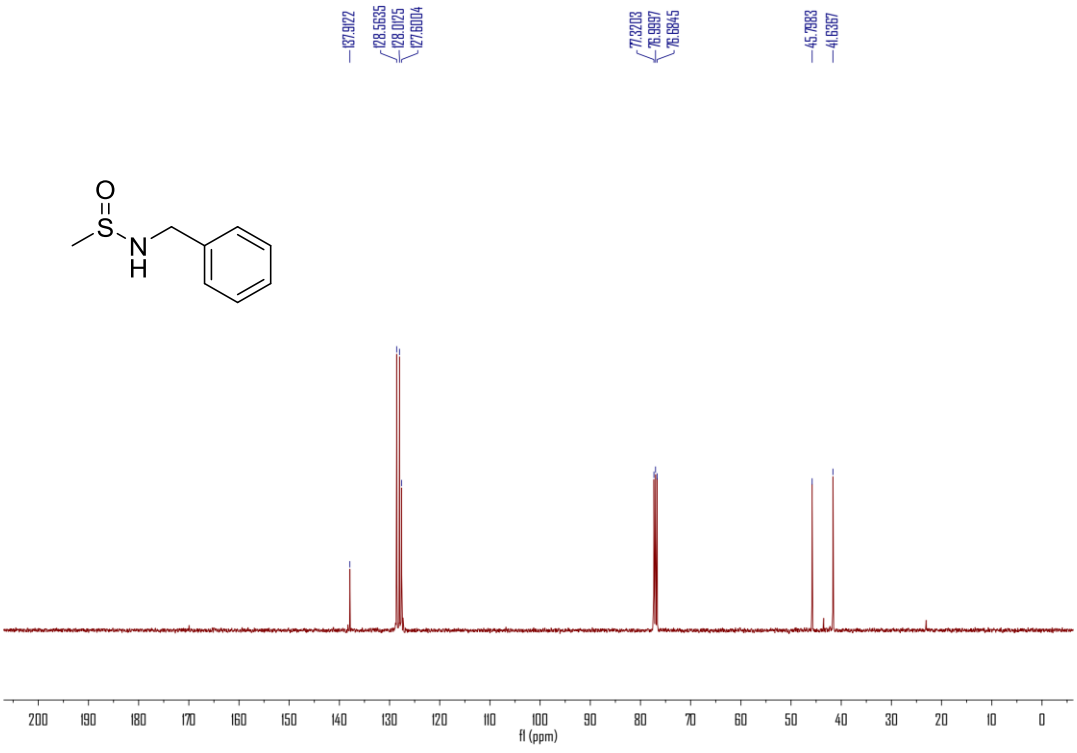


Sulfinamide **1l**

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

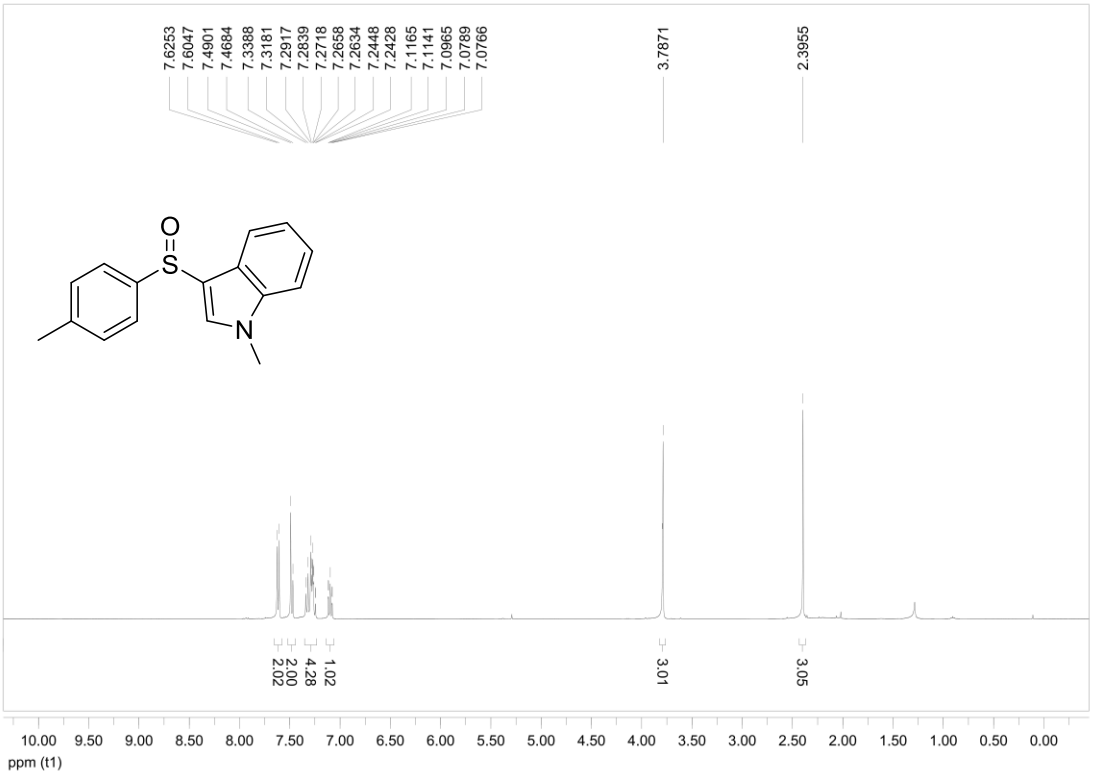


^{13}C NMR (100 MHz, $CDCl_3$)

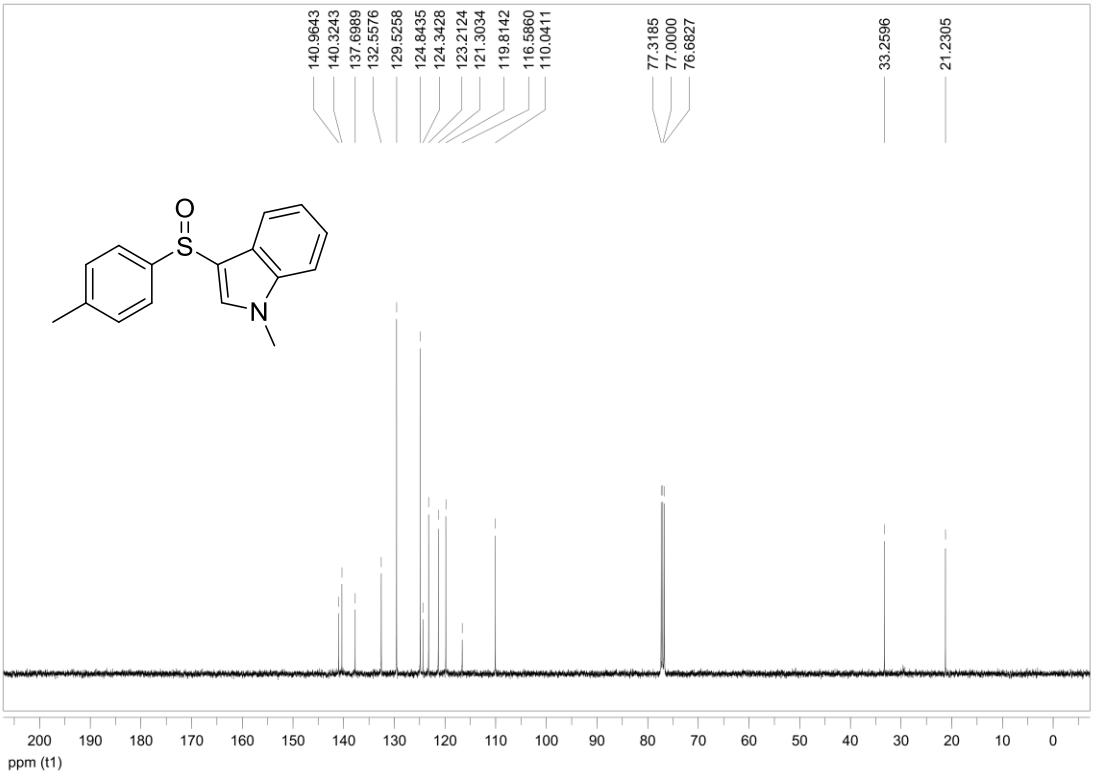


Sulfoxide **3a**

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

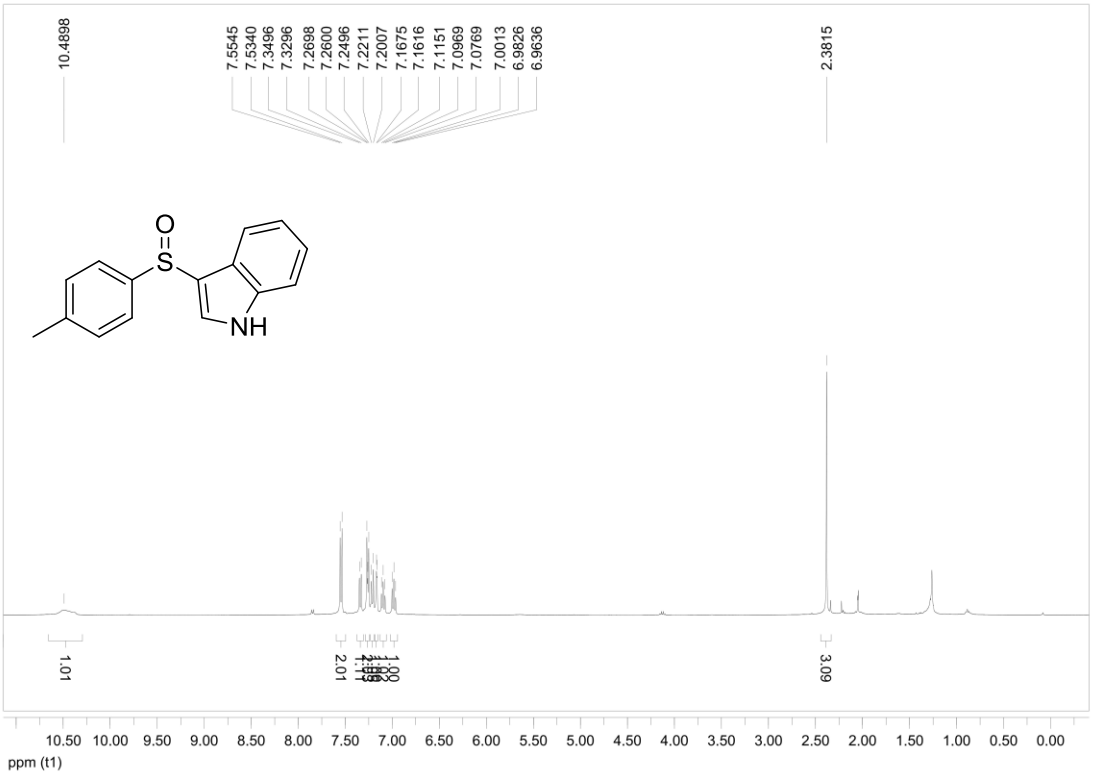


^{13}C NMR (100 MHz, $CDCl_3$)

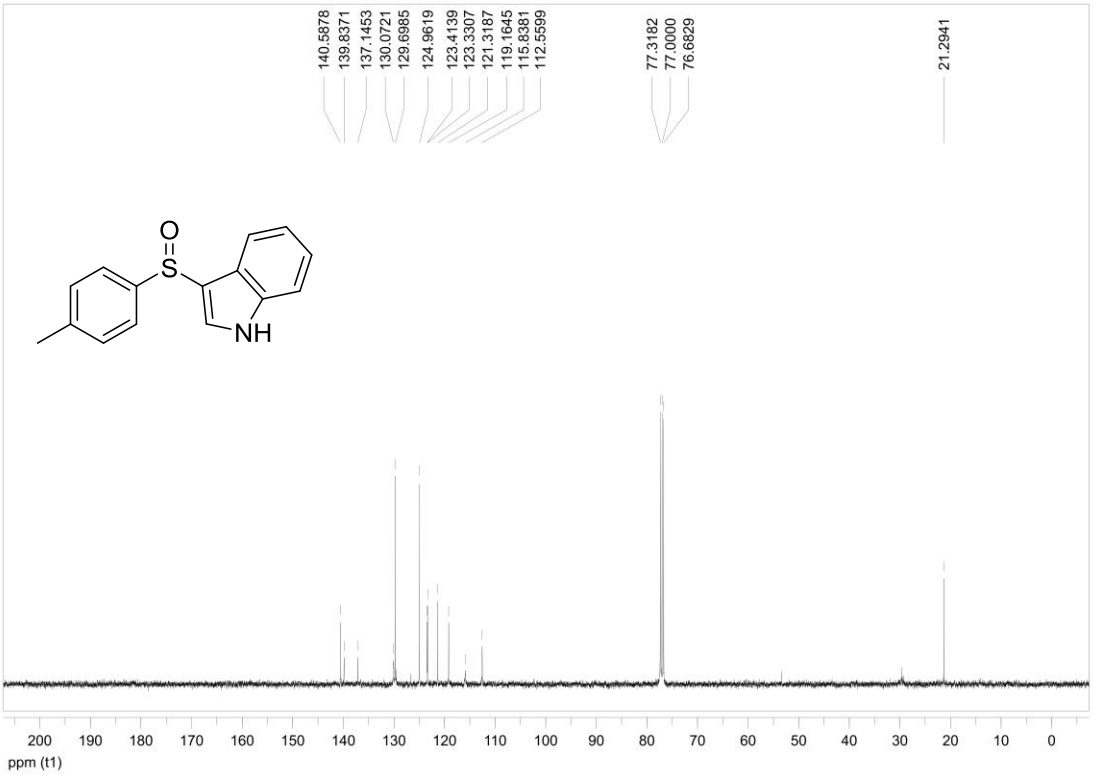


Sulfoxide **3b**

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

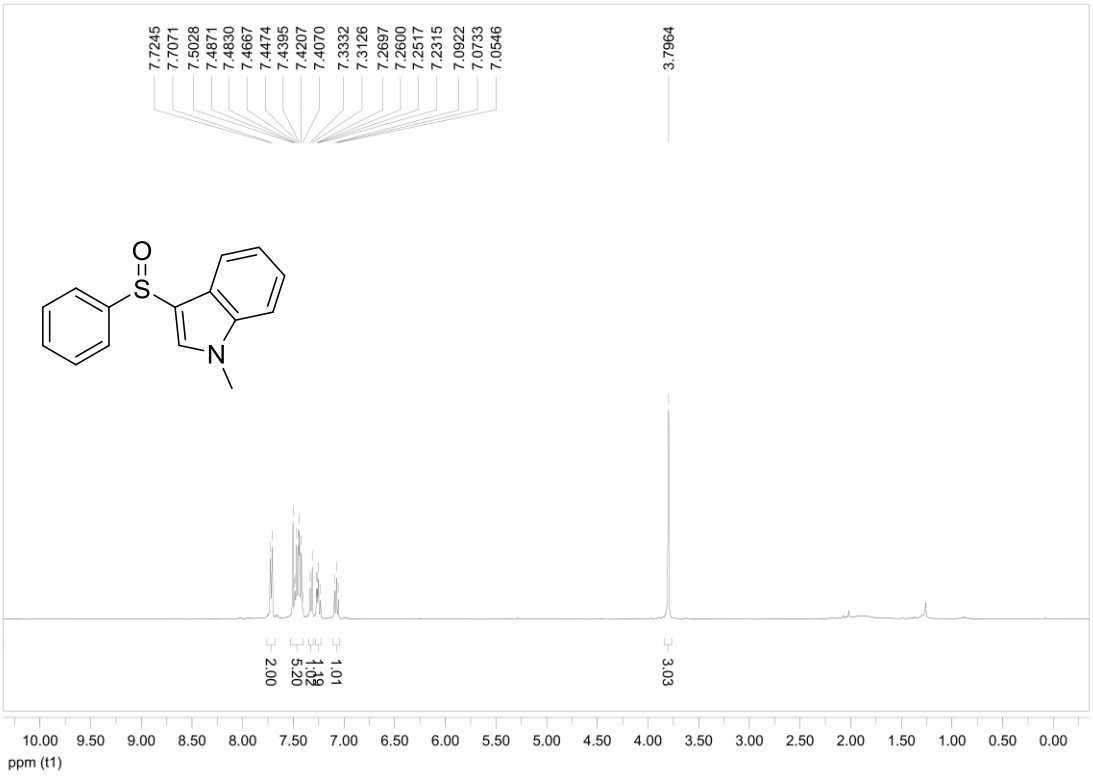


^{13}C NMR (100 MHz, $CDCl_3$)

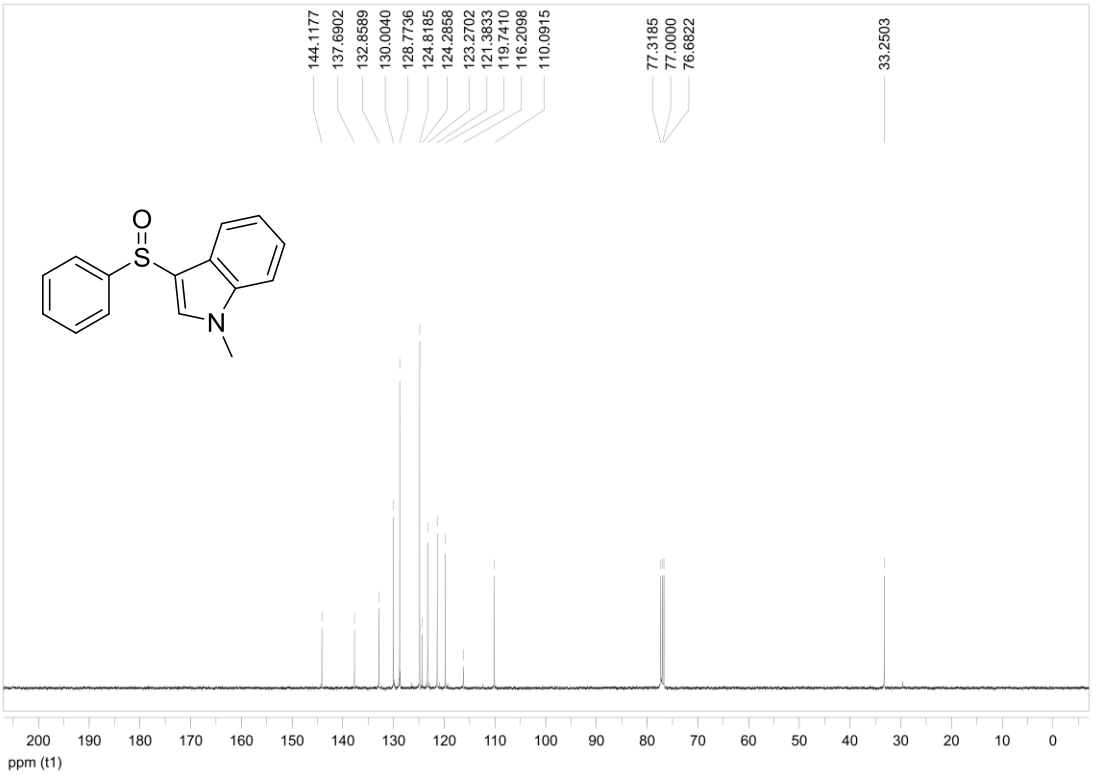


Sulfoxide **3c**

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

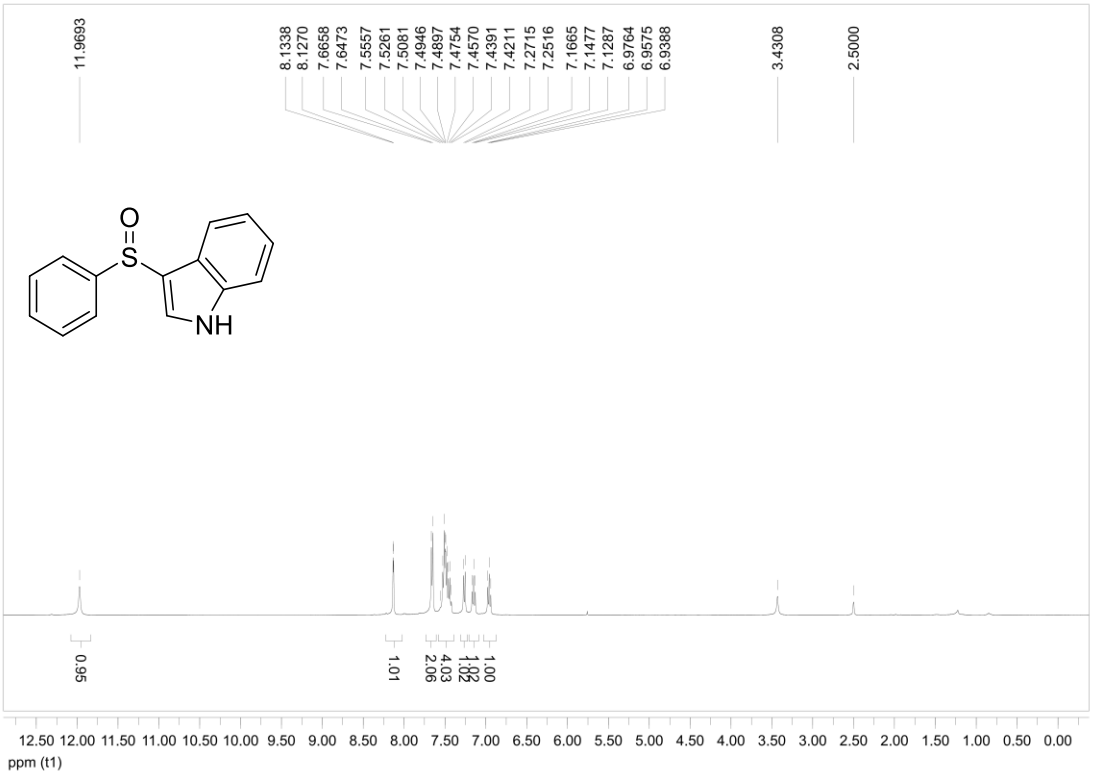


^{13}C NMR (100 MHz, $CDCl_3$)

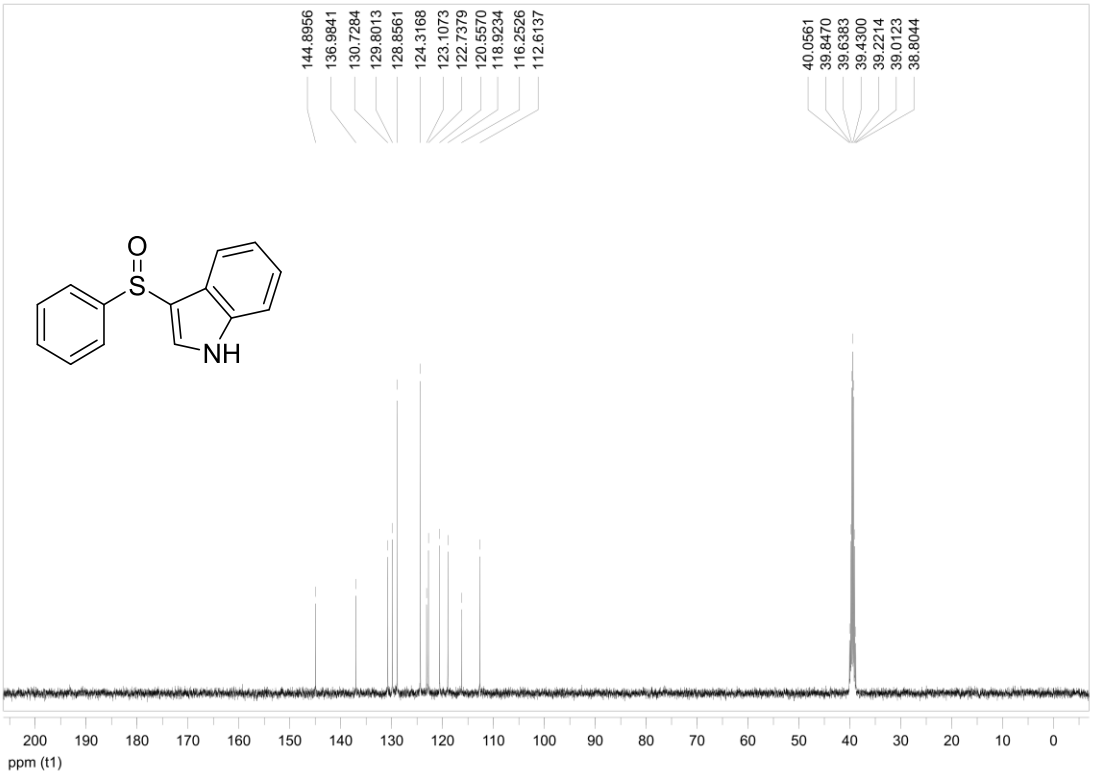


Sulfoxide **3d**

^{1}H NMR (400 MHz, DMSO-d_6)

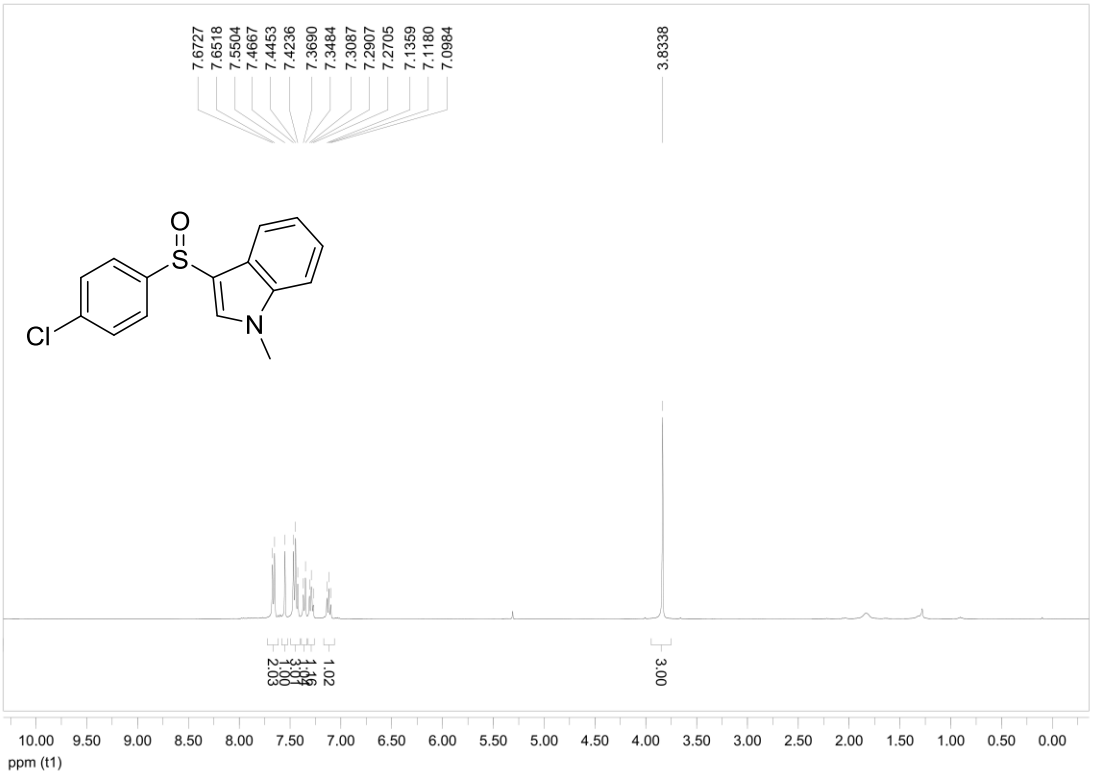


^{13}C NMR (100 MHz, DMSO-d_6)

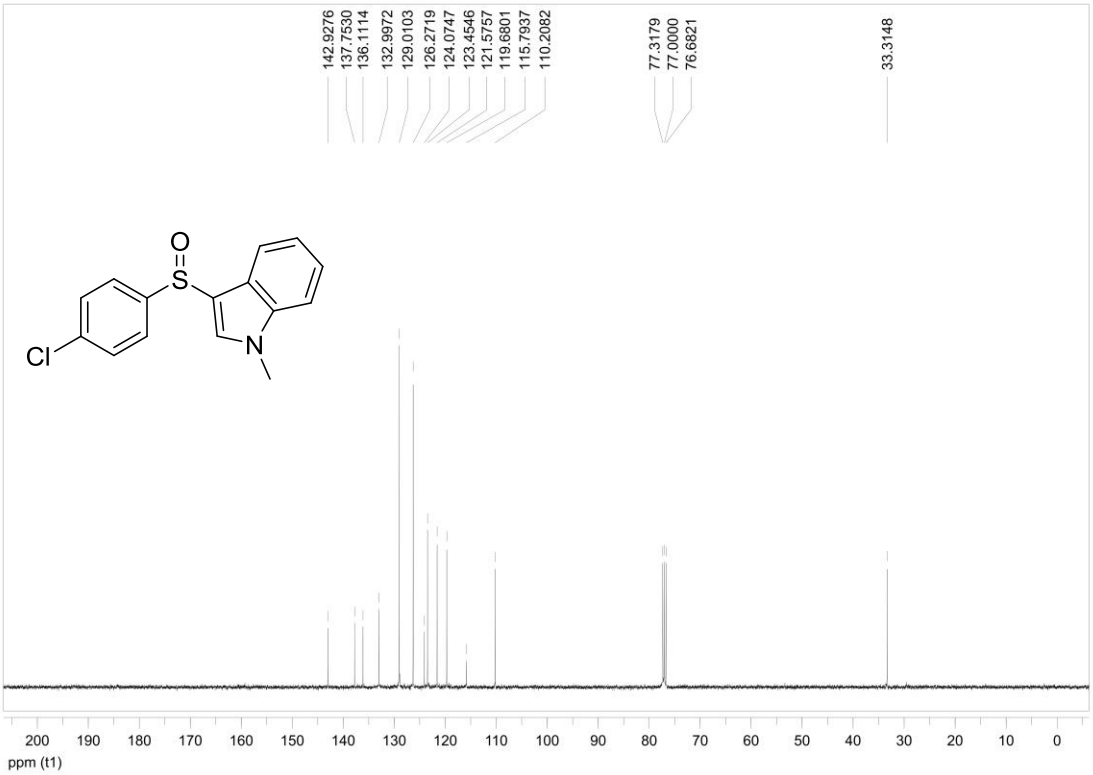


Sulfoxide **3e**

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

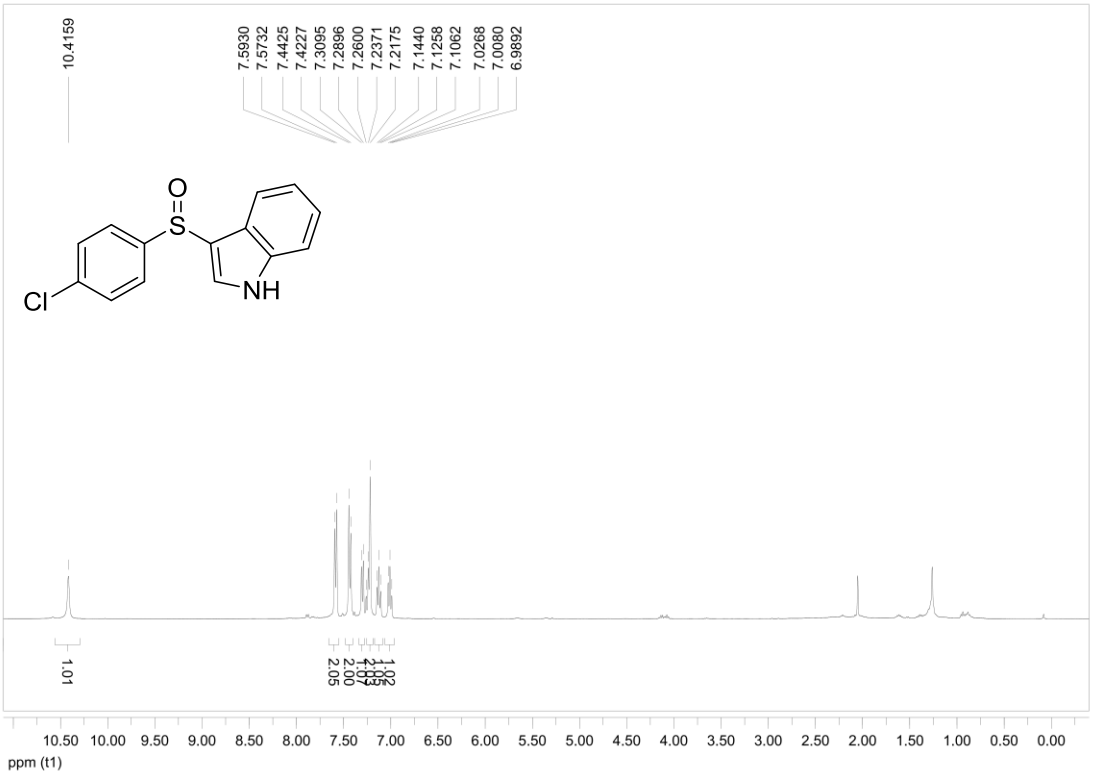


^{13}C NMR (100 MHz, $CDCl_3$)

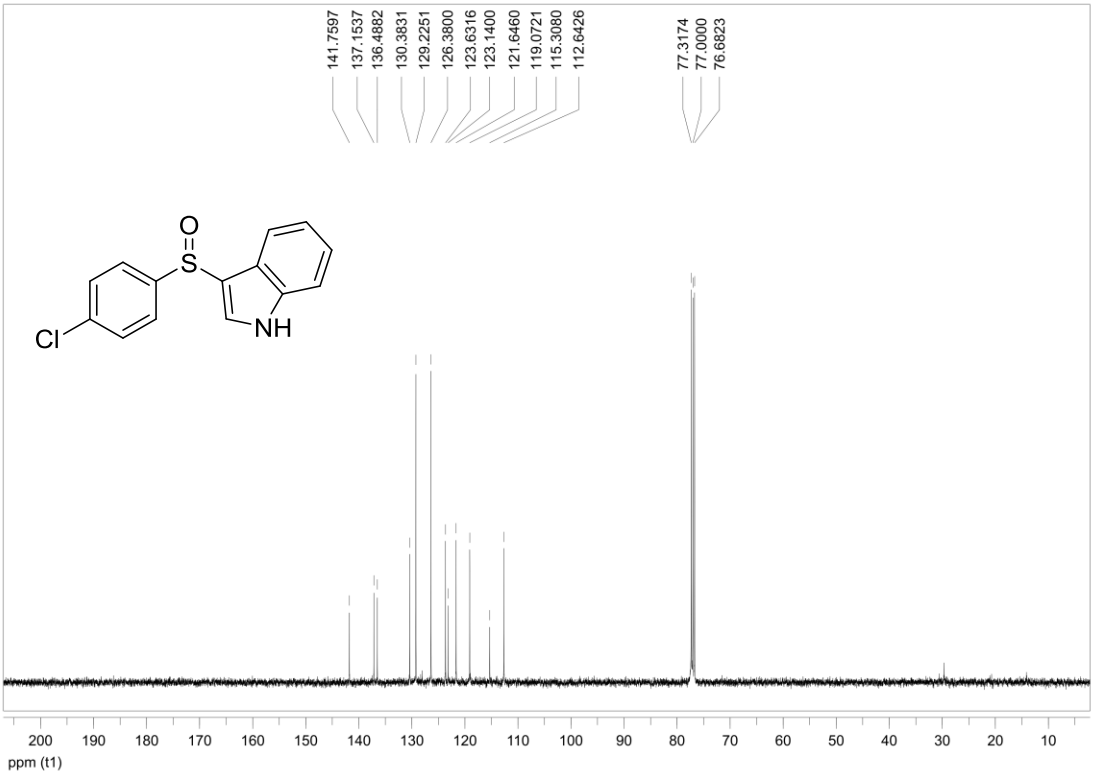


Sulfoxide **3f**

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

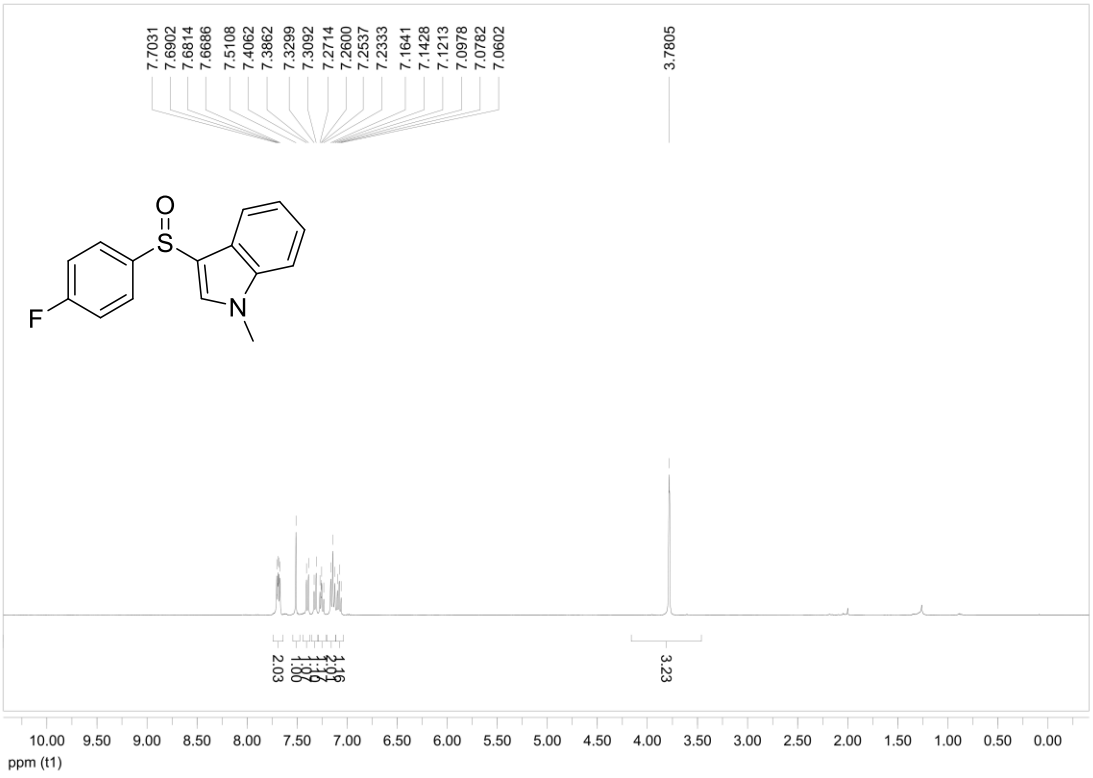


^{13}C NMR (100 MHz, $CDCl_3$)

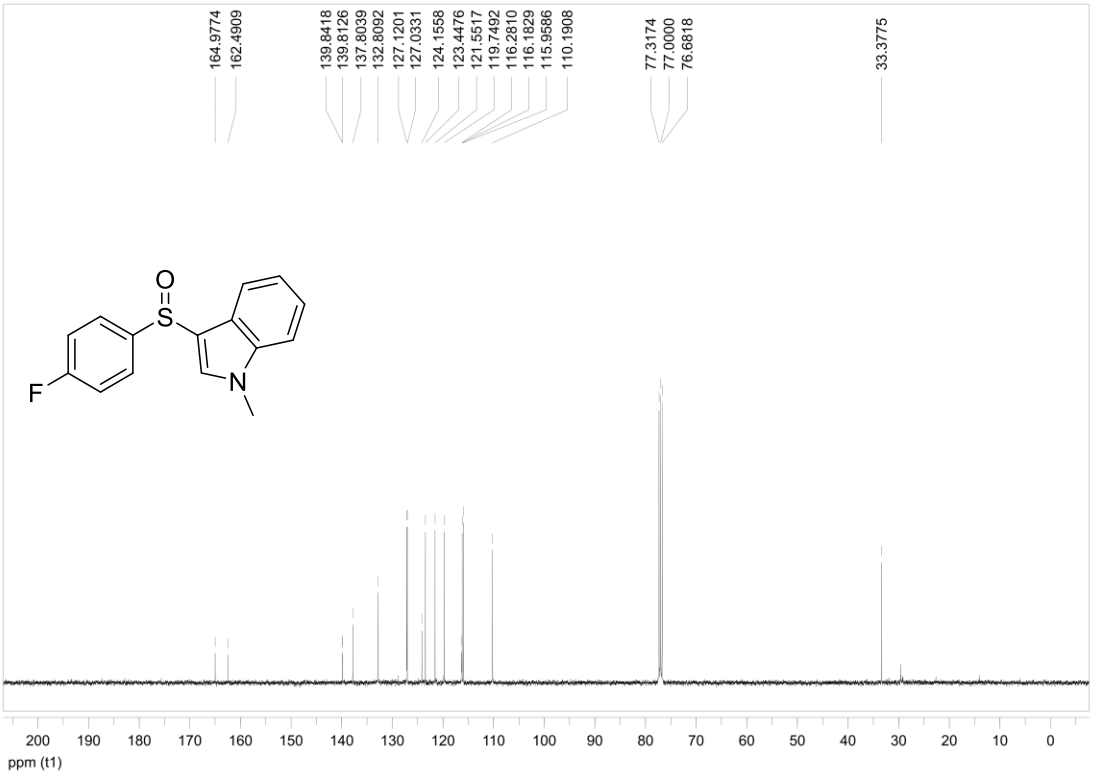


Sulfoxide **3g**

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

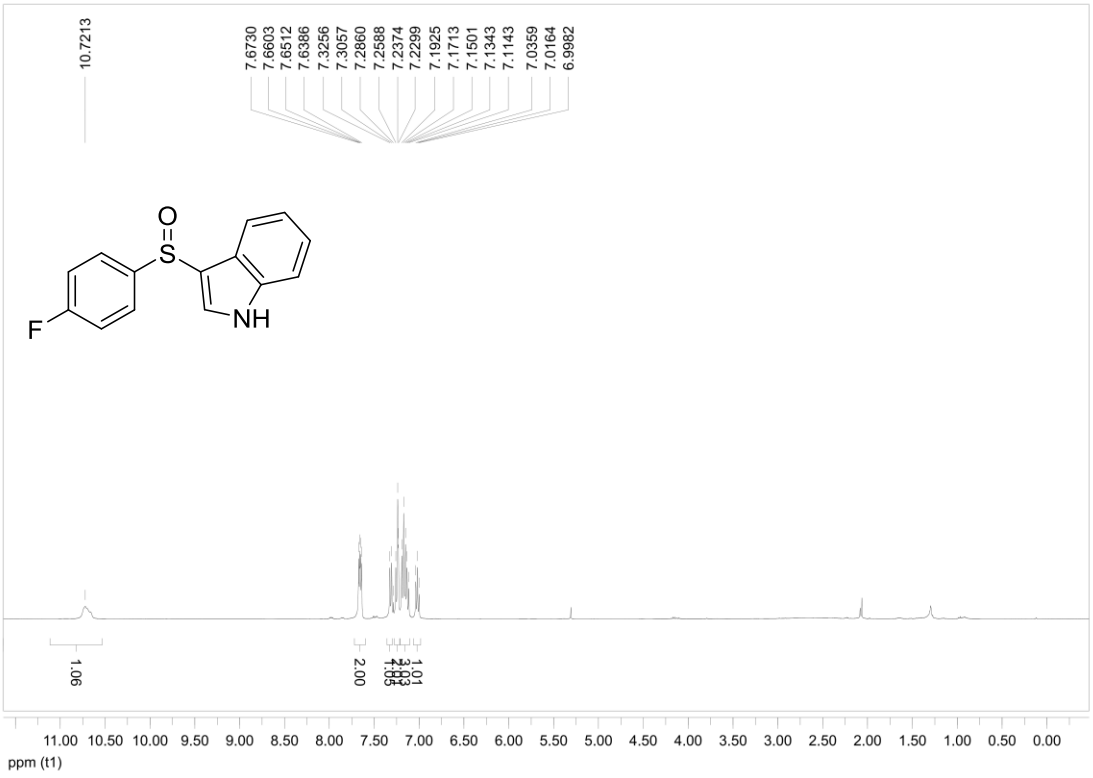


^{13}C NMR (100 MHz, $CDCl_3$)

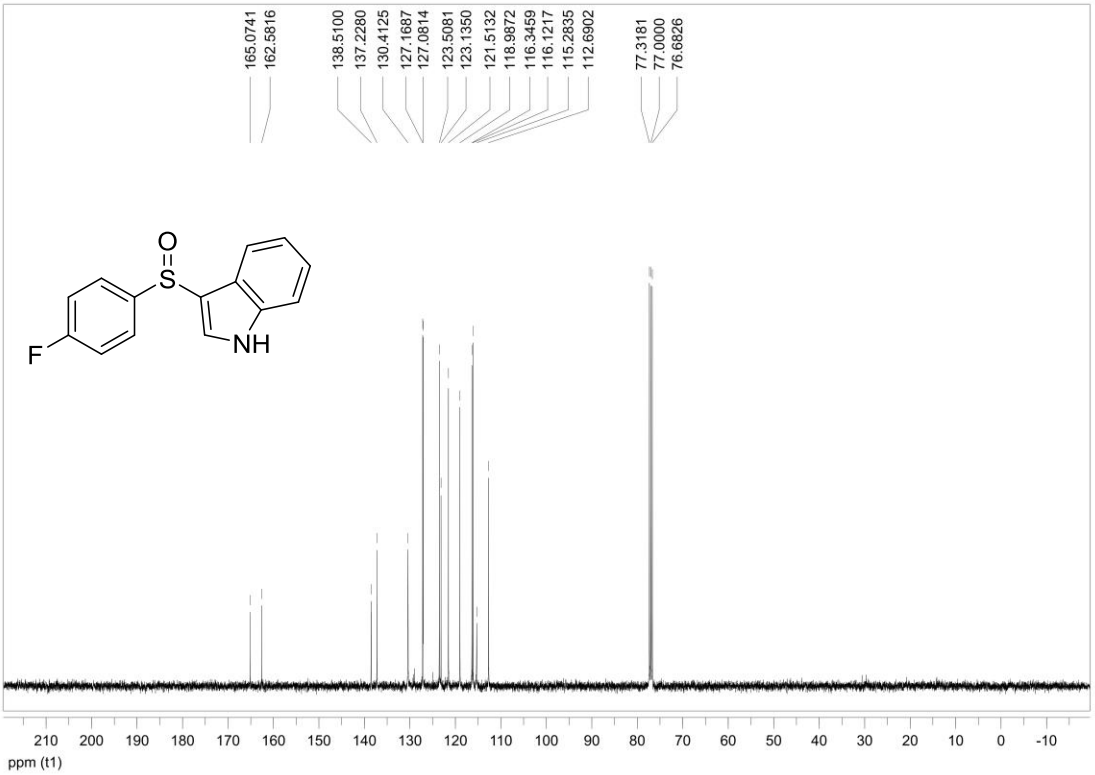


Sulfoxide **3h**

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

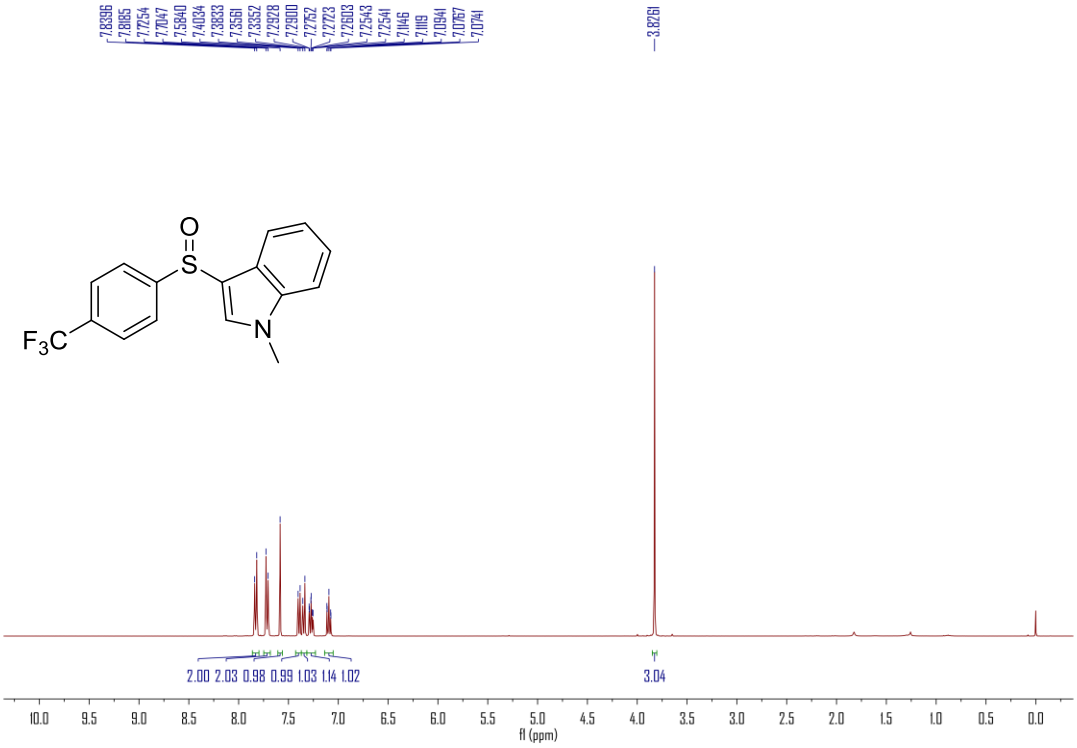


^{13}C NMR (100 MHz, $CDCl_3$)

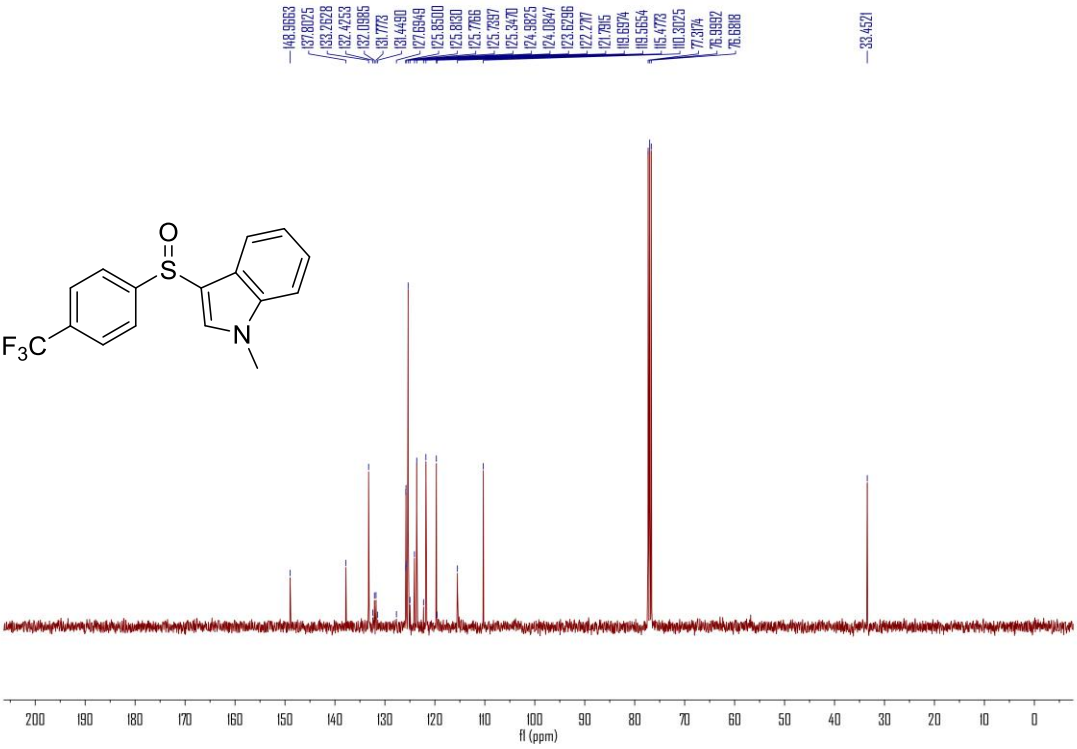


Sulfoxide **3i**

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

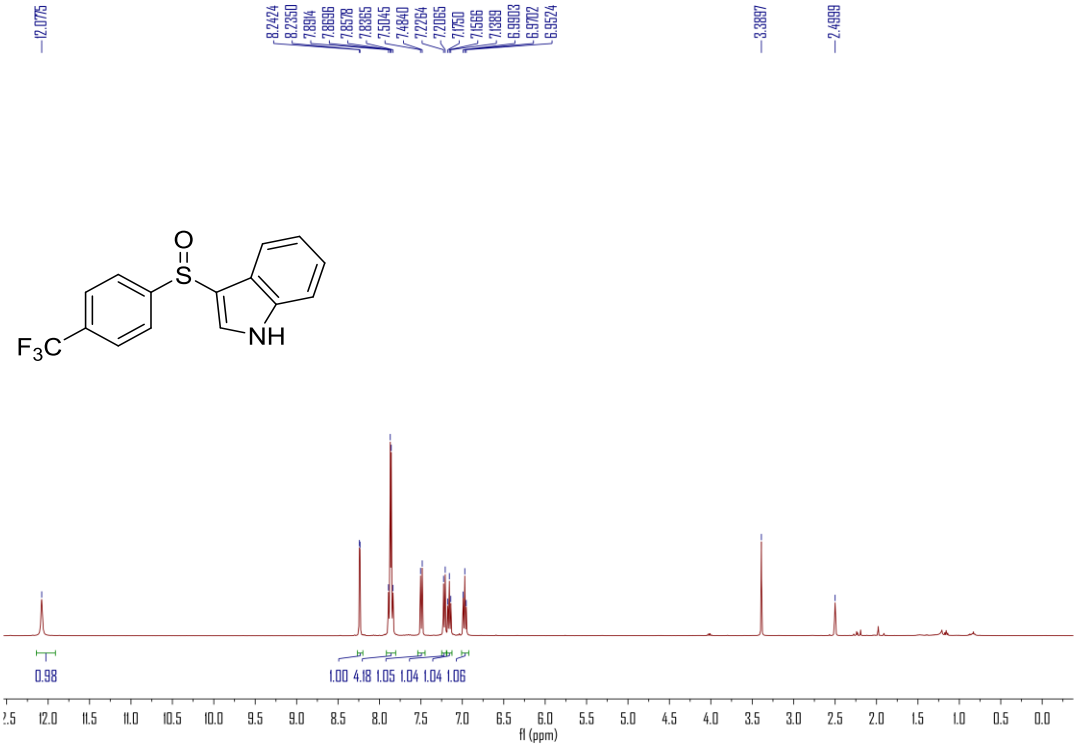


^{13}C NMR (100 MHz, $CDCl_3$)

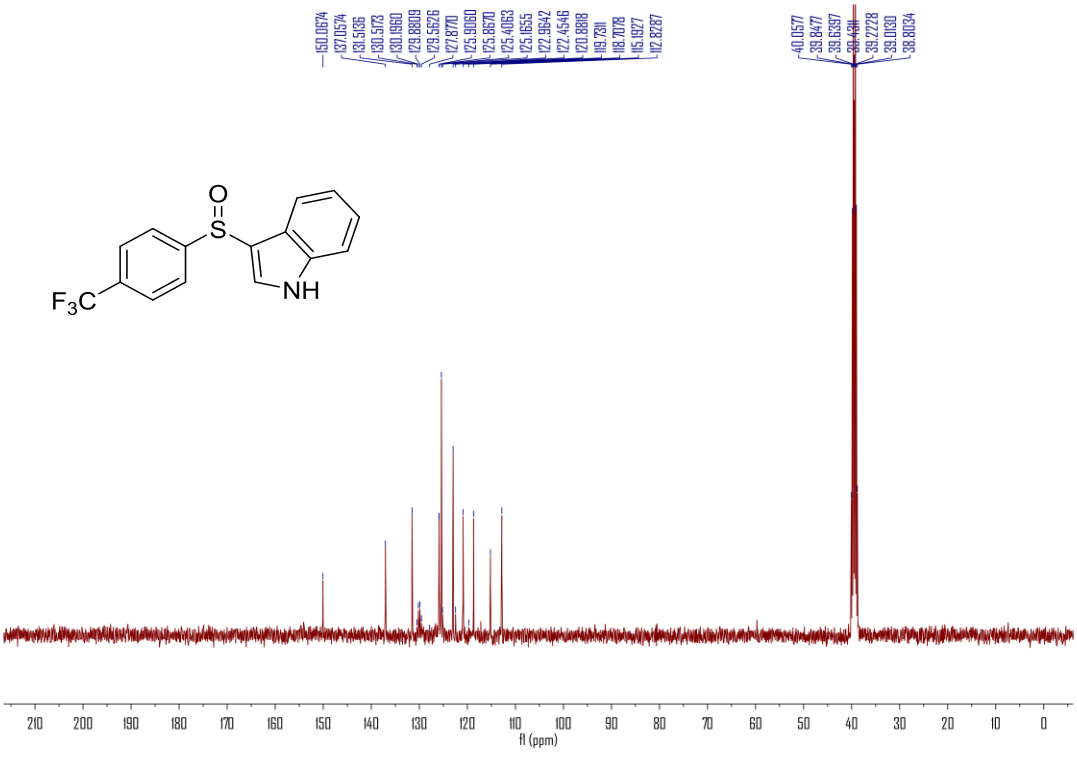


Sulfoxide **3j**

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

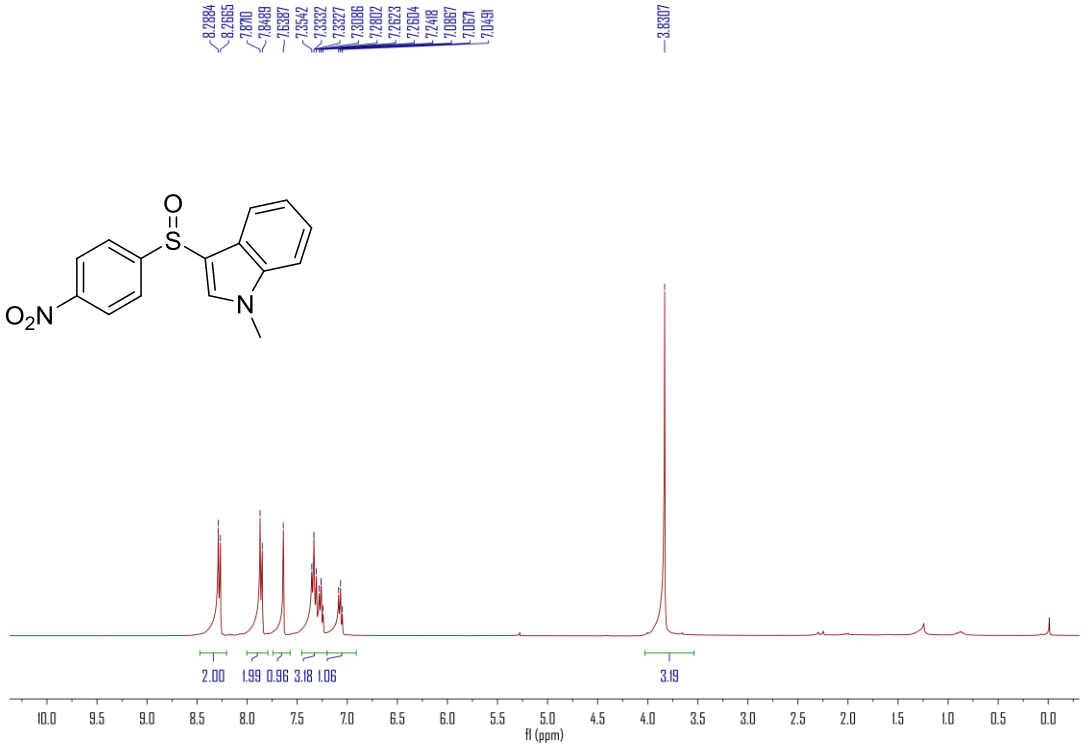


^{13}C NMR (100 MHz, $CDCl_3$)

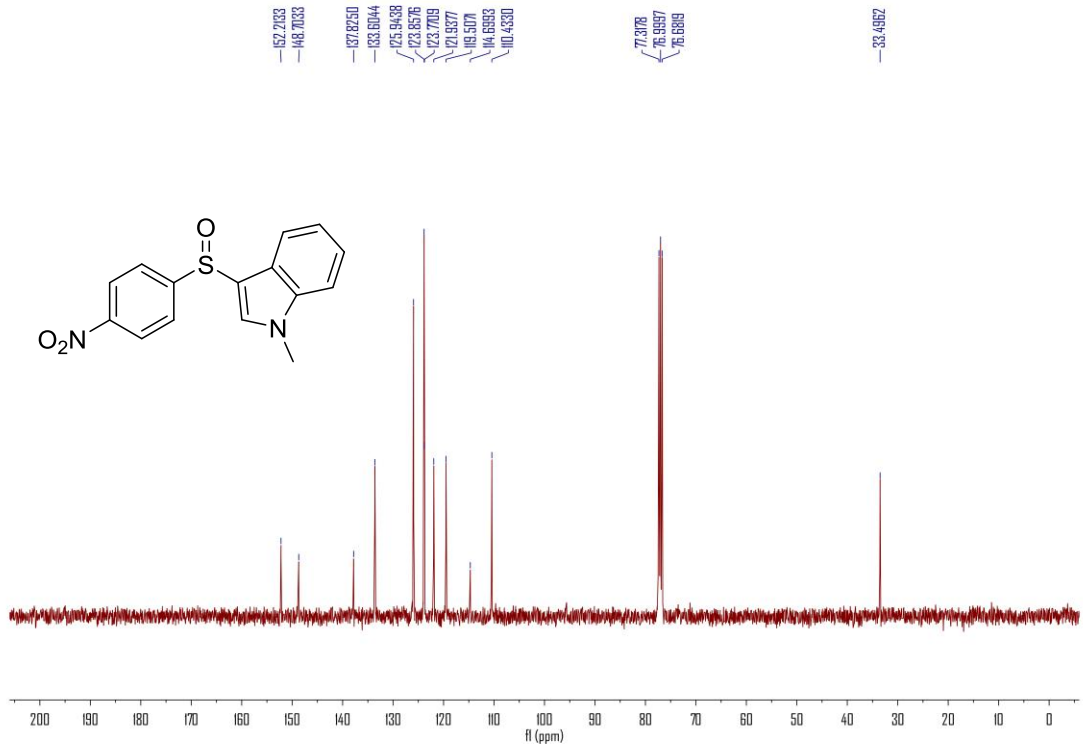


Sulfoxide **3k**

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

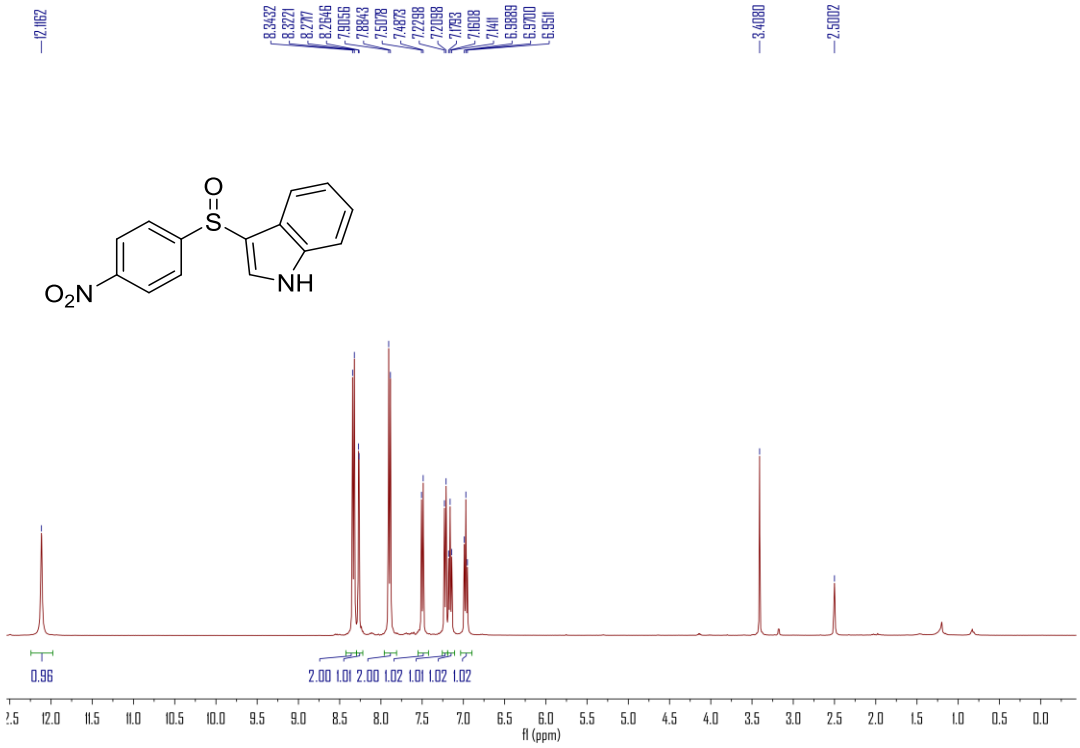


^{13}C NMR (100 MHz, $CDCl_3$)

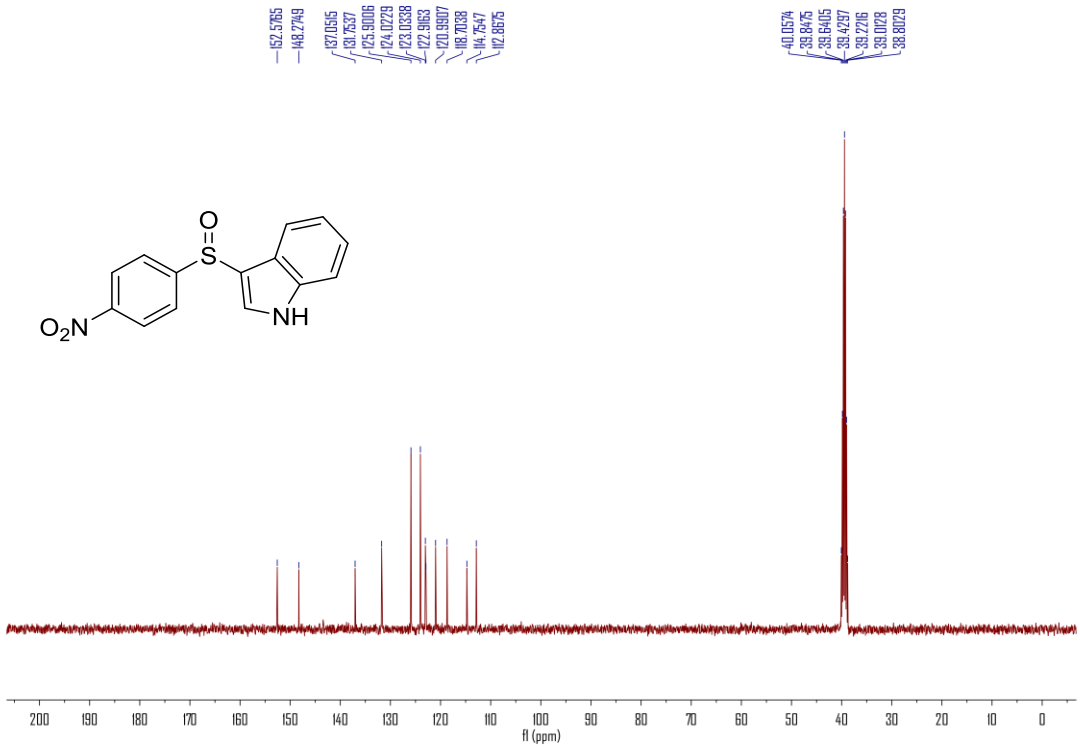


Sulfoxide **3l**

^{1}H NMR (400 MHz, DMSO-d_6)

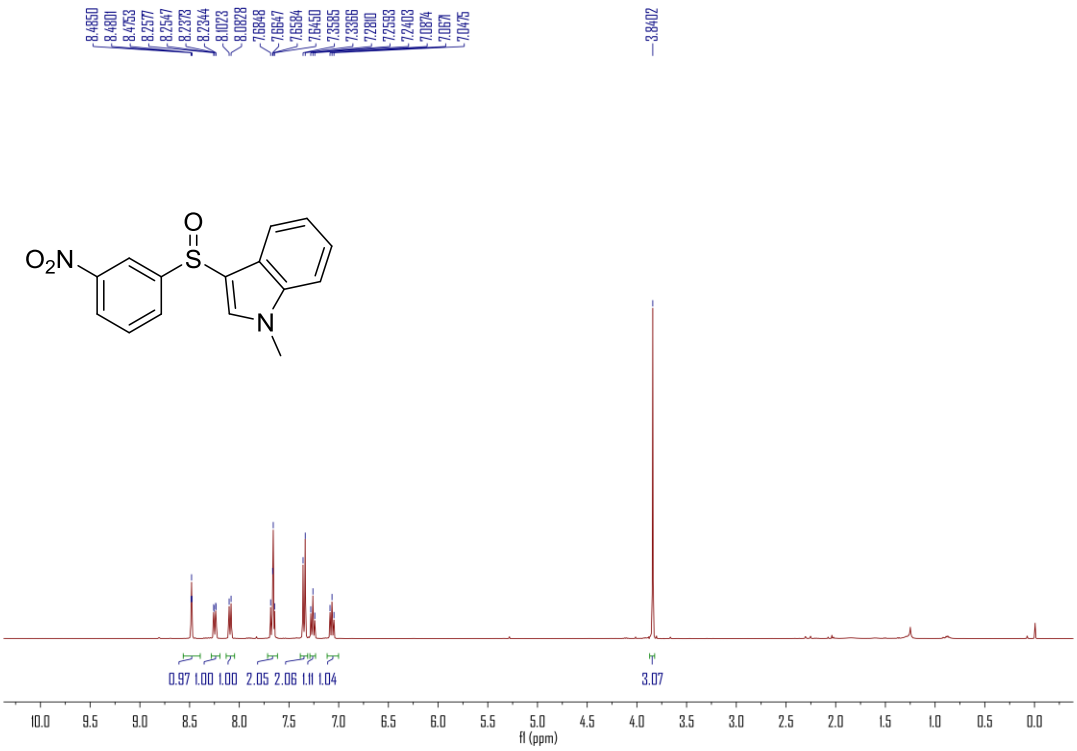


^{13}C NMR (100 MHz, $CDCl_3$)

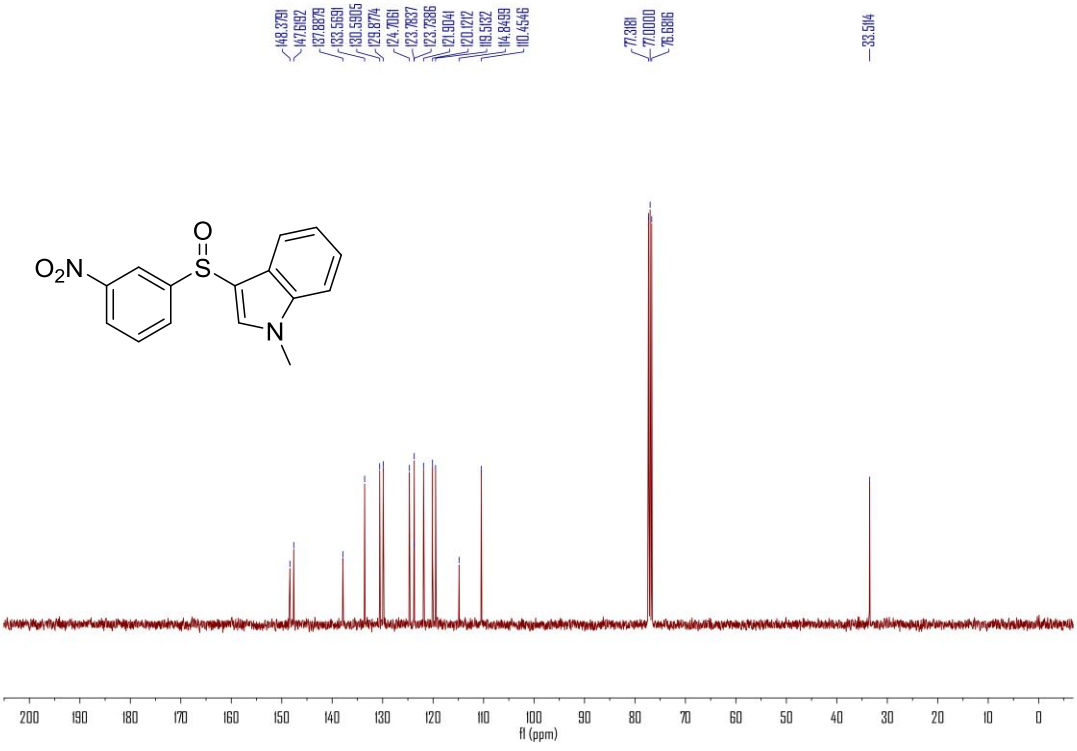


Sulfoxide **3m**

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

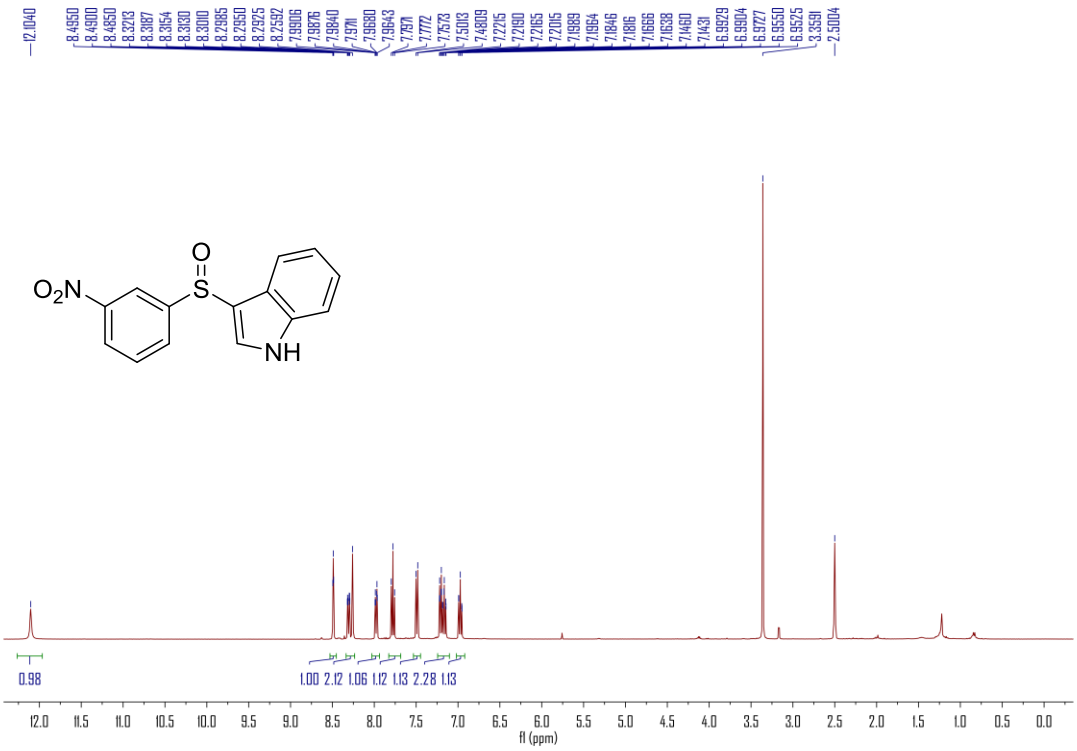


^{13}C NMR (100 MHz, $CDCl_3$)

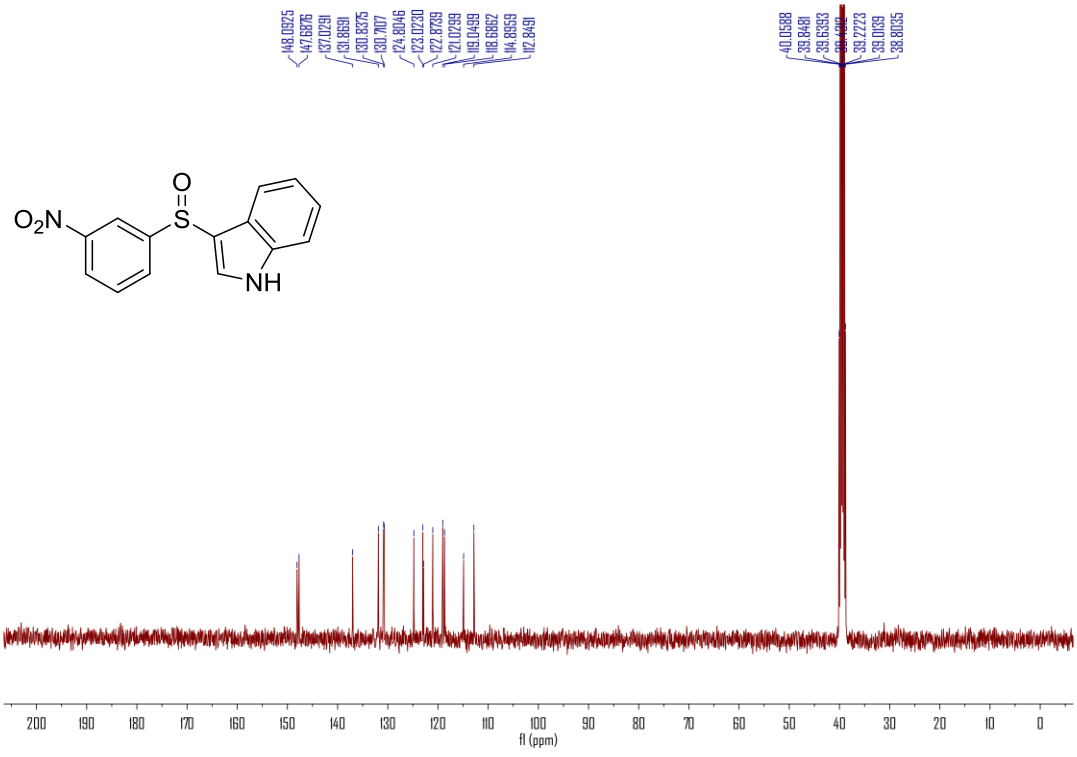


Sulfoxide **3n**

^{1}H NMR (400 MHz, DMSO-d_6)

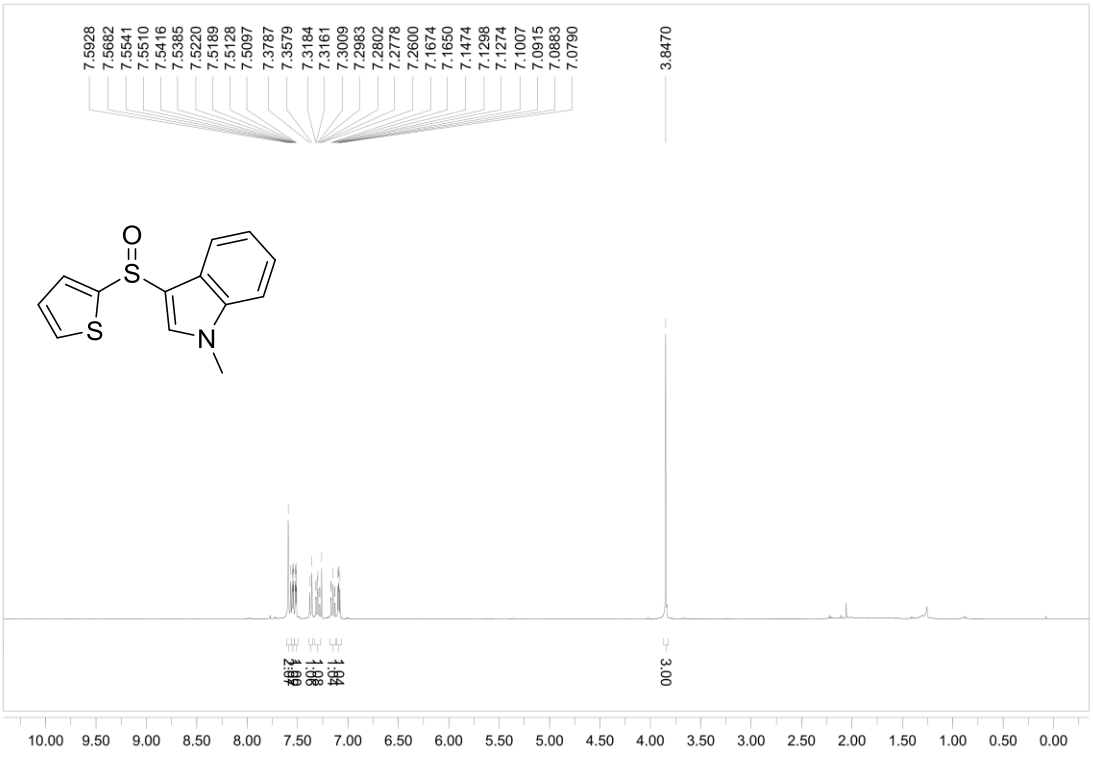


^{13}C NMR (100 MHz, $CDCl_3$)

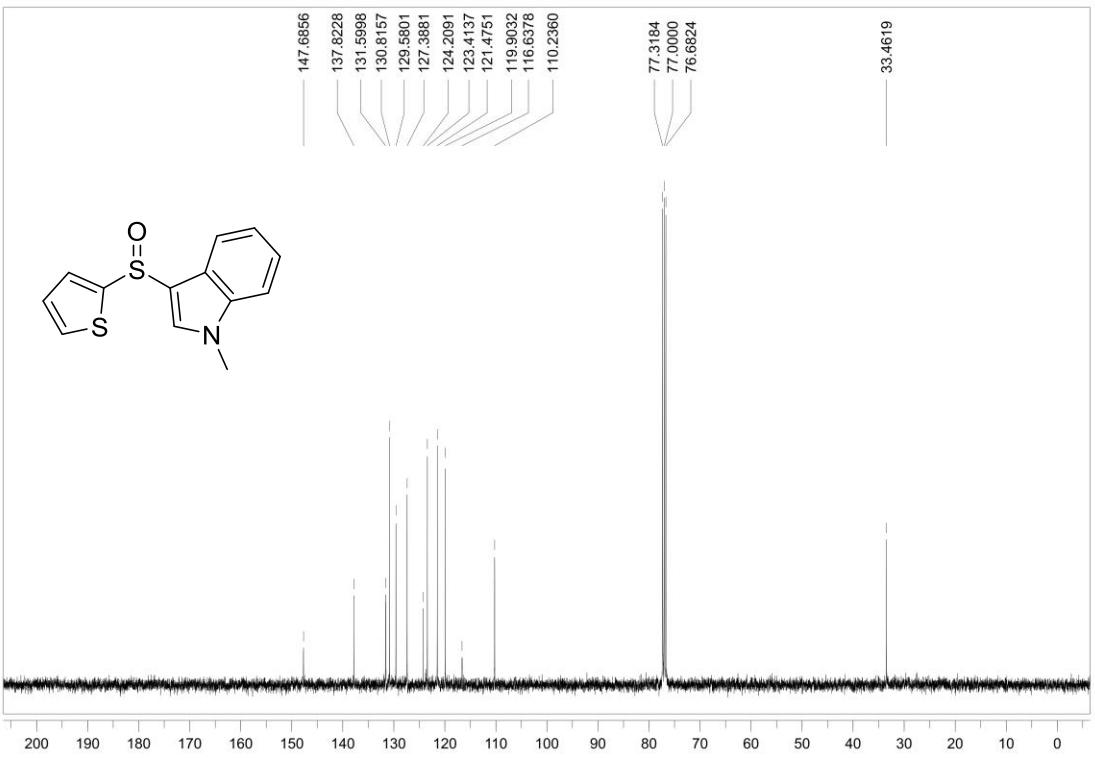


Sulfoxide **3o**

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



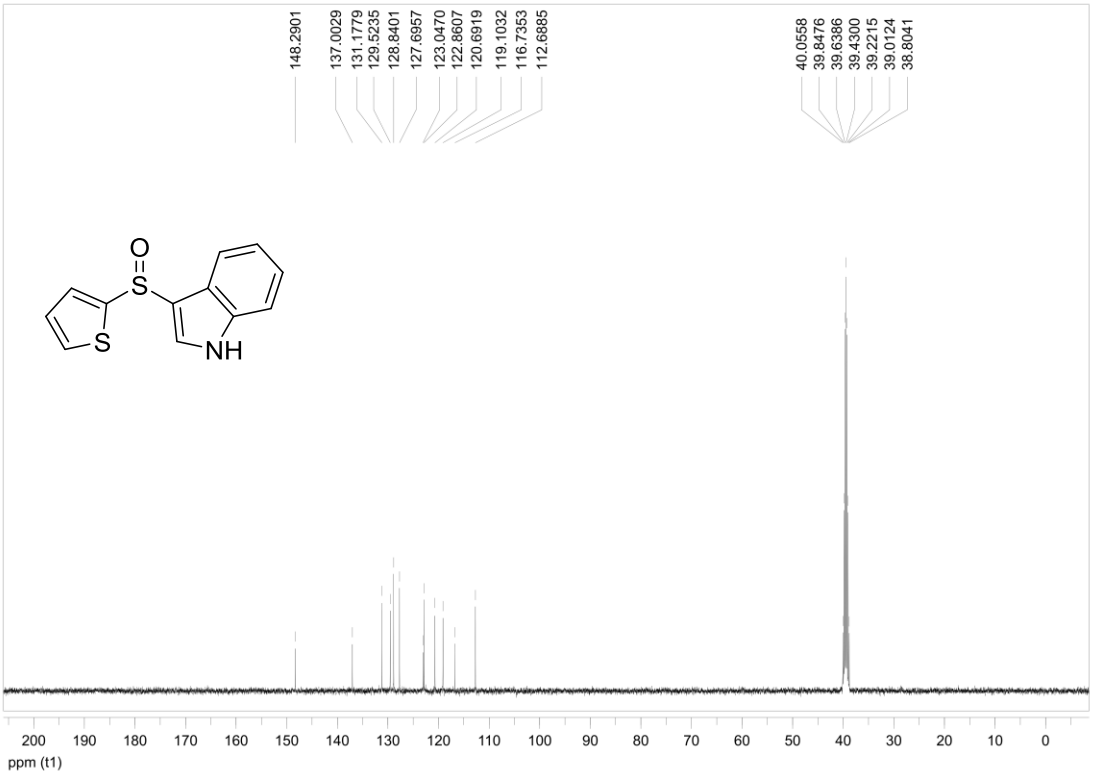
^{13}C NMR (100 MHz, $CDCl_3$)



Sulfoxide **3p**

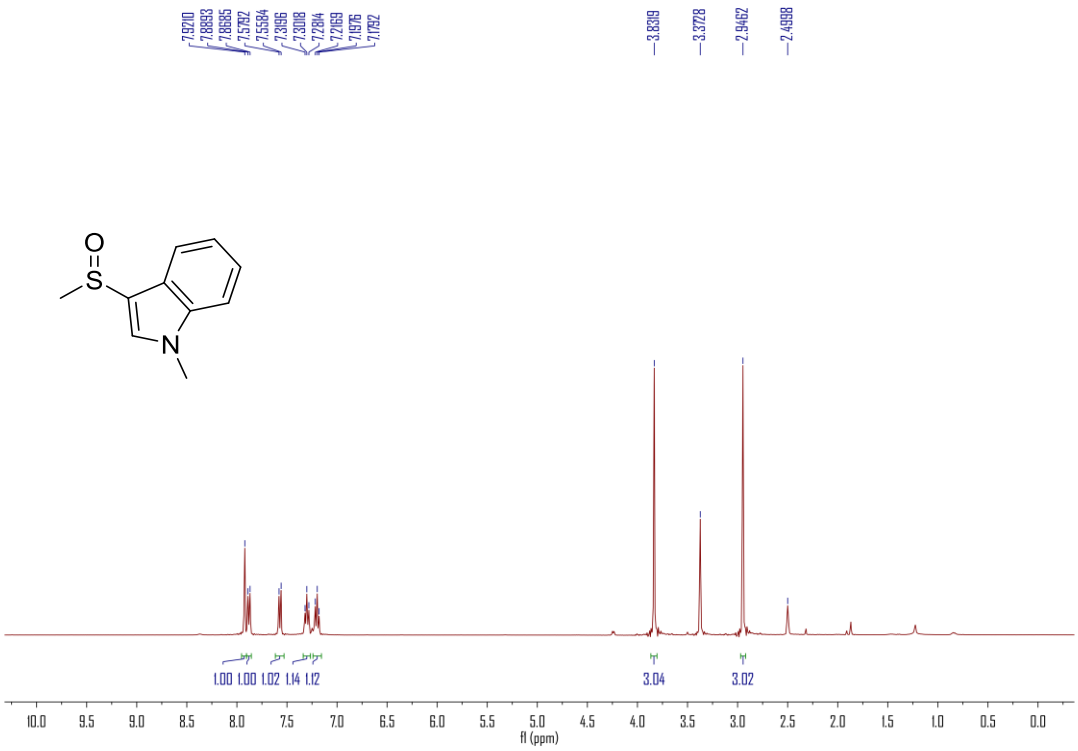
^{1}H NMR (400 MHz, DMSO-d_6)

^{13}C NMR (100 MHz, DMSO-d_6)

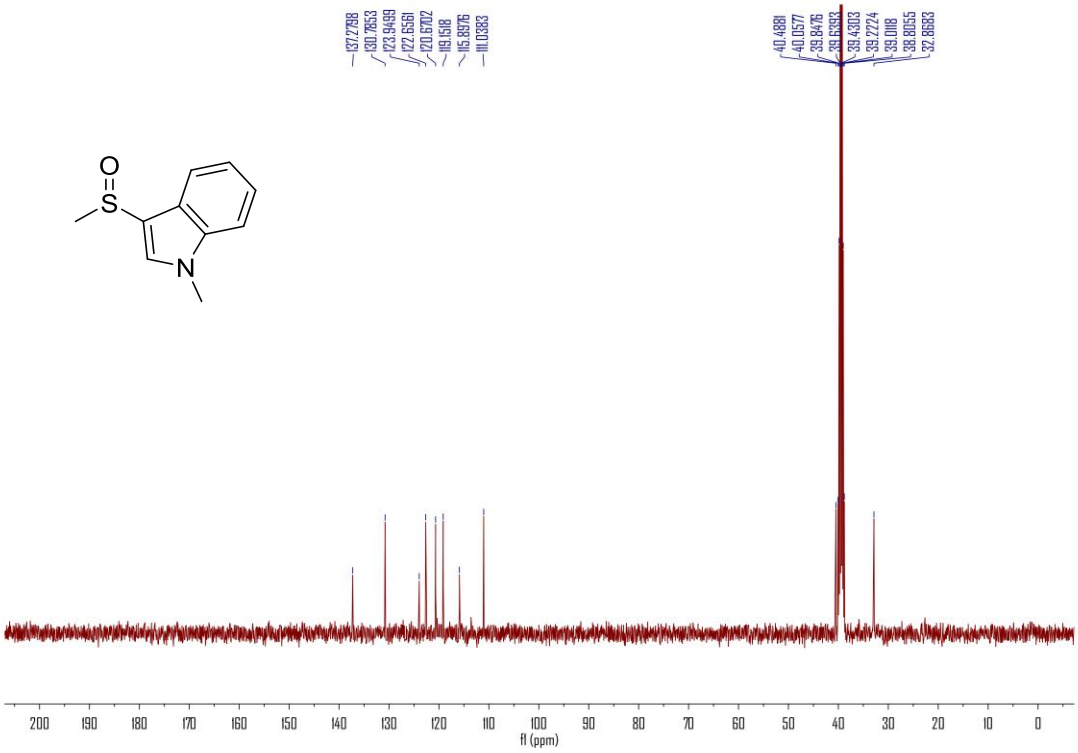


Sulfoxide **3q**

^{1}H NMR (400 MHz, DMSO-d_6)

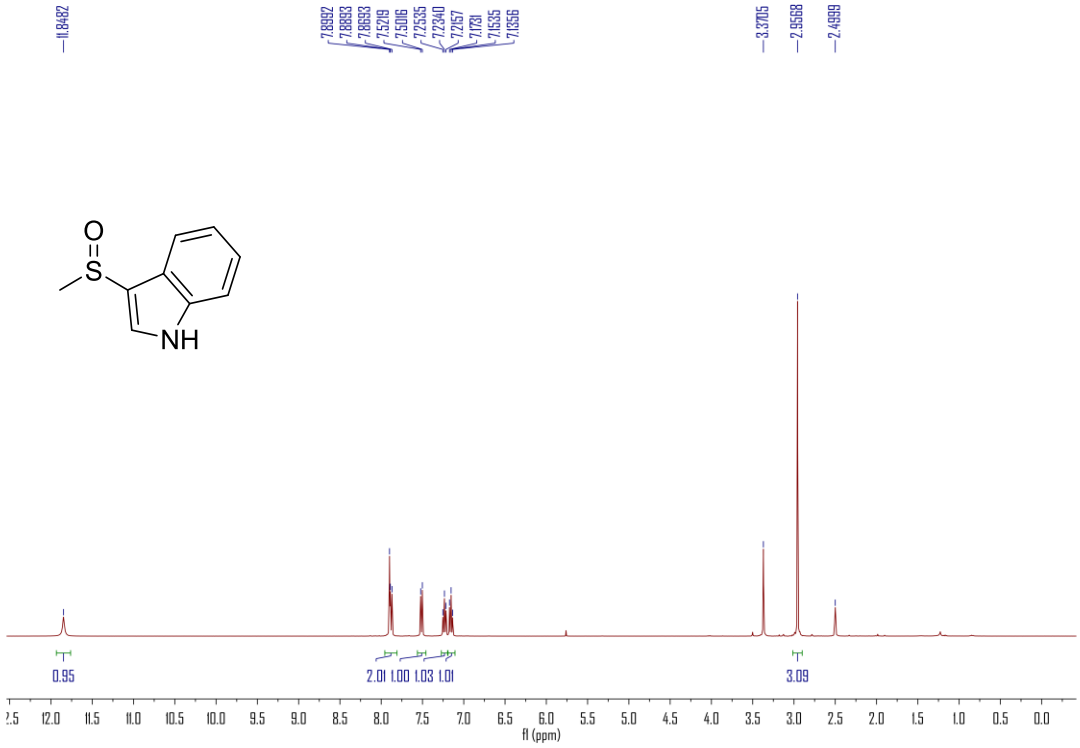


^{13}C NMR (100 MHz, DMSO-d_6)

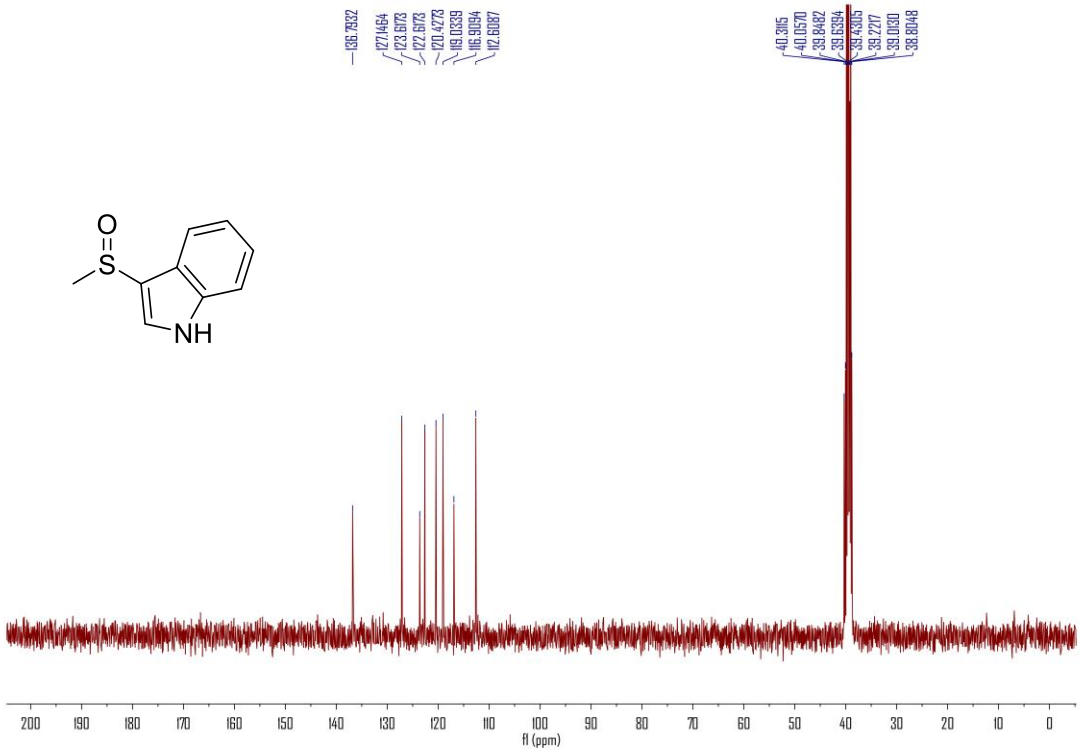


Sulfoxide **3r**

^{1}H NMR (400 MHz, DMSO-d_6)

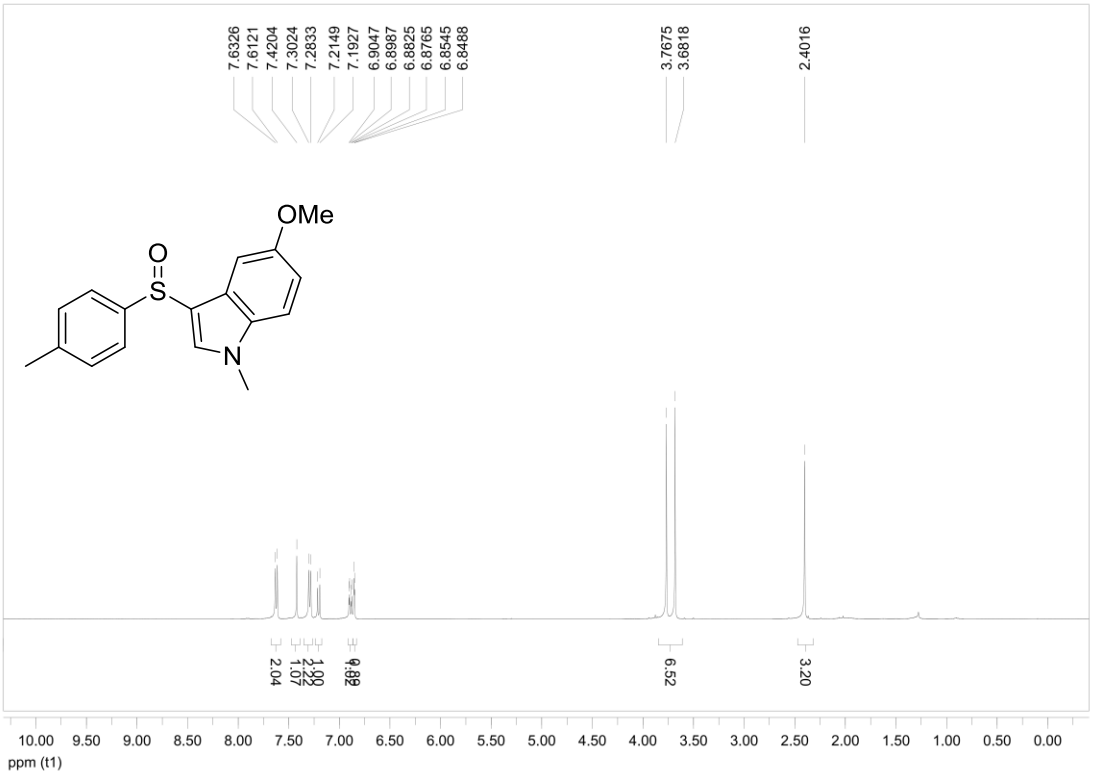


^{13}C NMR (100 MHz, DMSO-d_6)

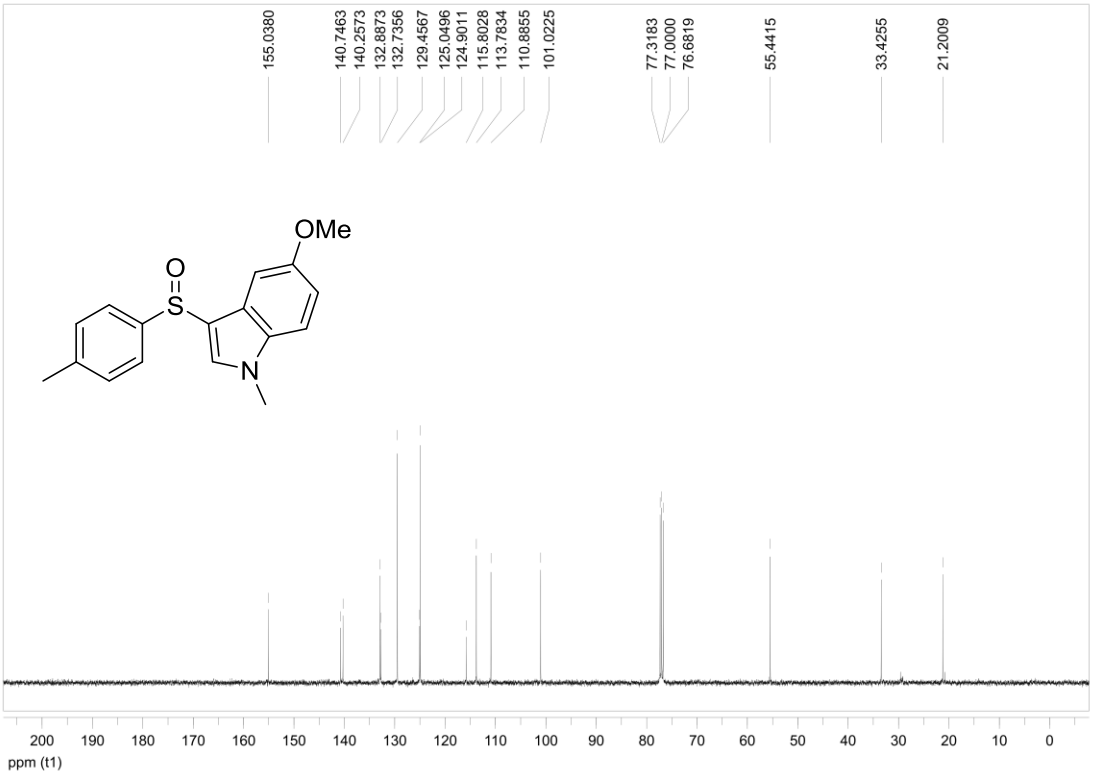


Sulfoxide **3s**

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

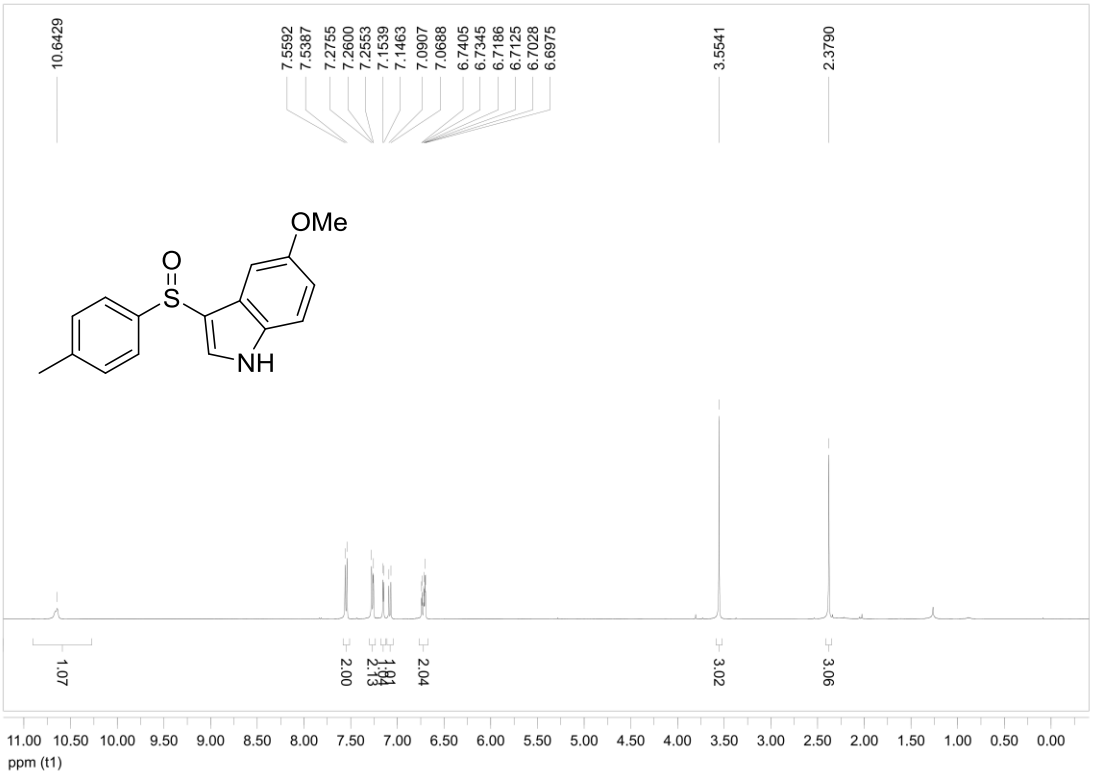


^{13}C NMR (100 MHz, $CDCl_3$)

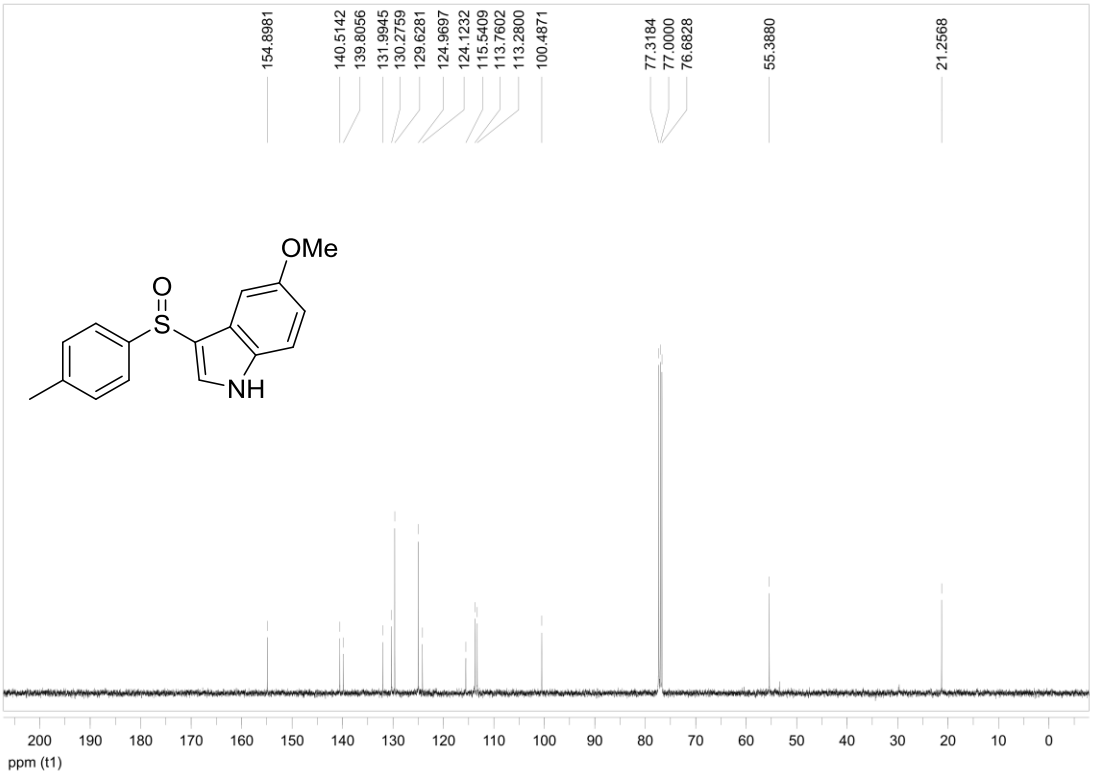


Sulfoxide **3t**

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

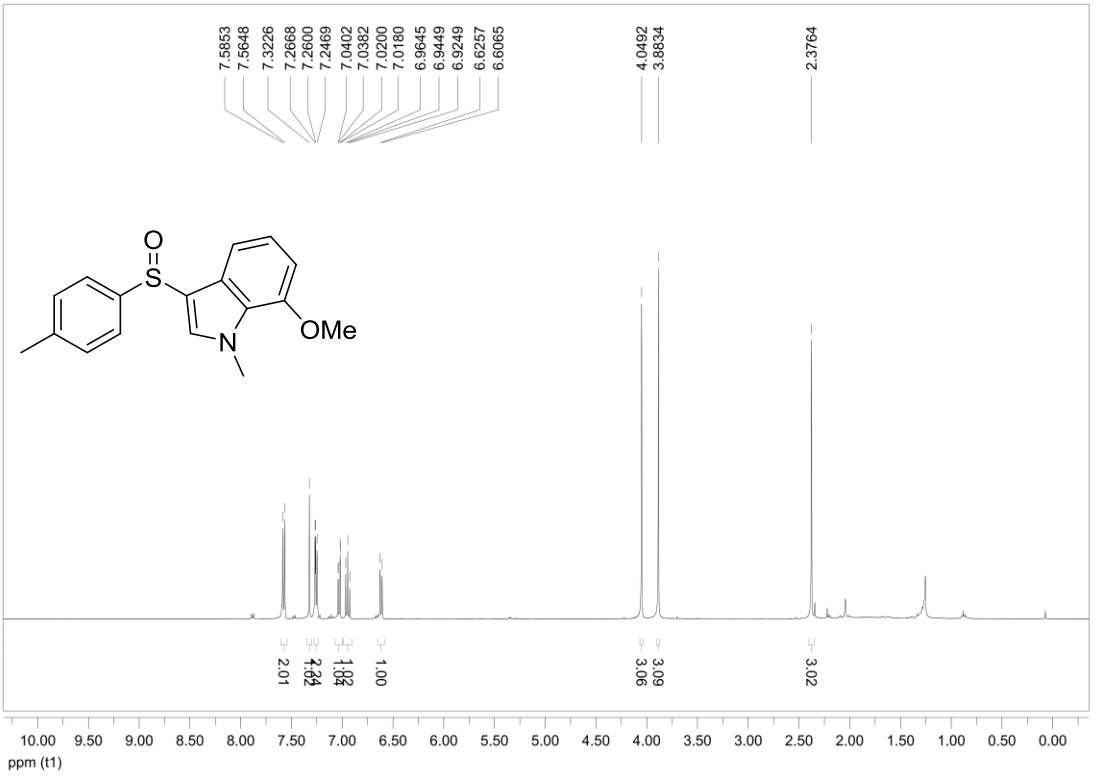


^{13}C NMR (100 MHz, $CDCl_3$)

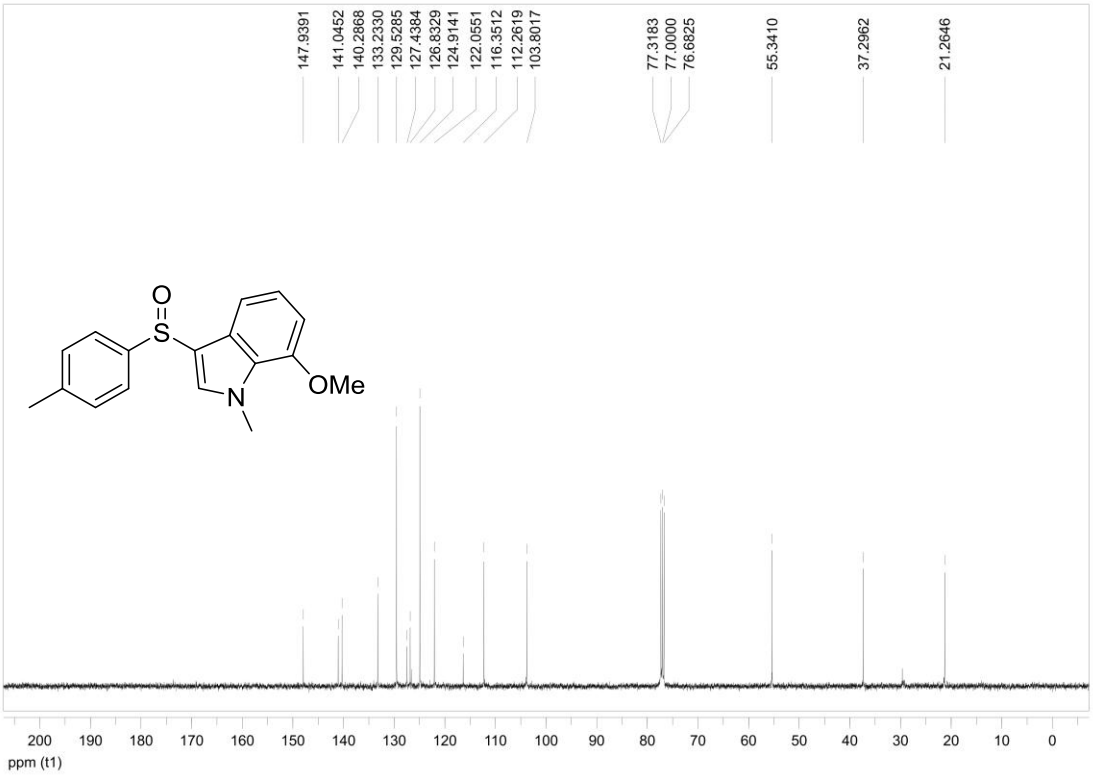


Sulfoxide **3u**

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

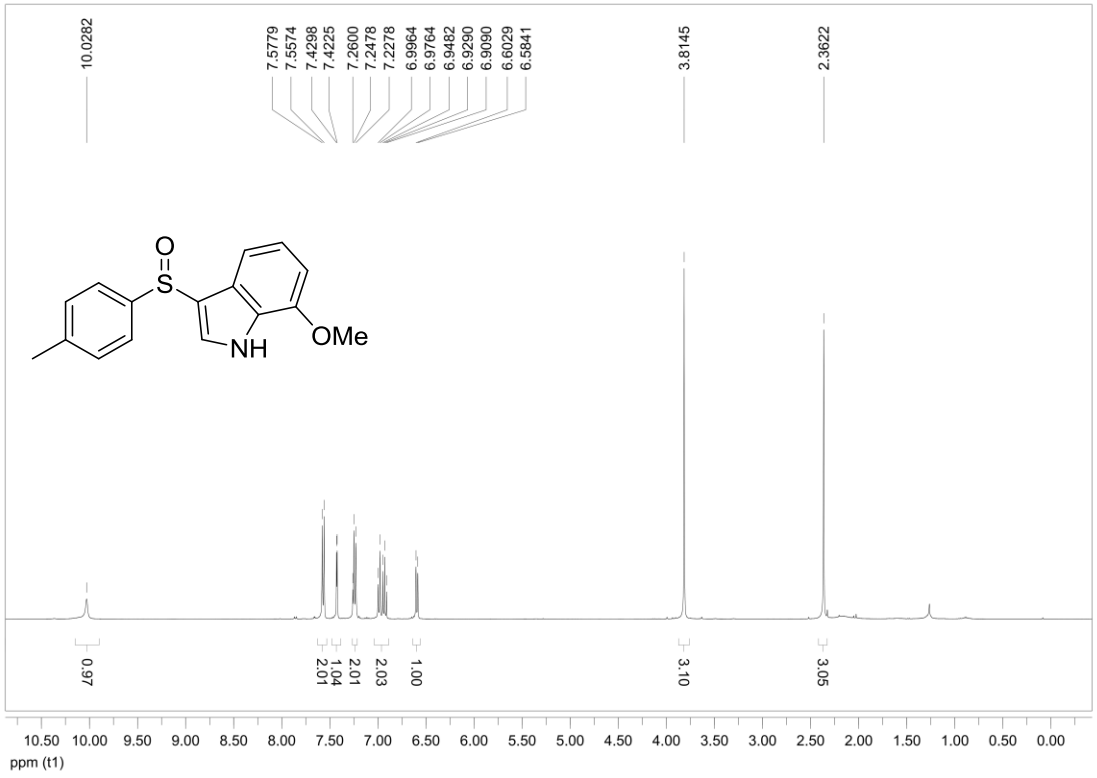


^{13}C NMR (100 MHz, $CDCl_3$)

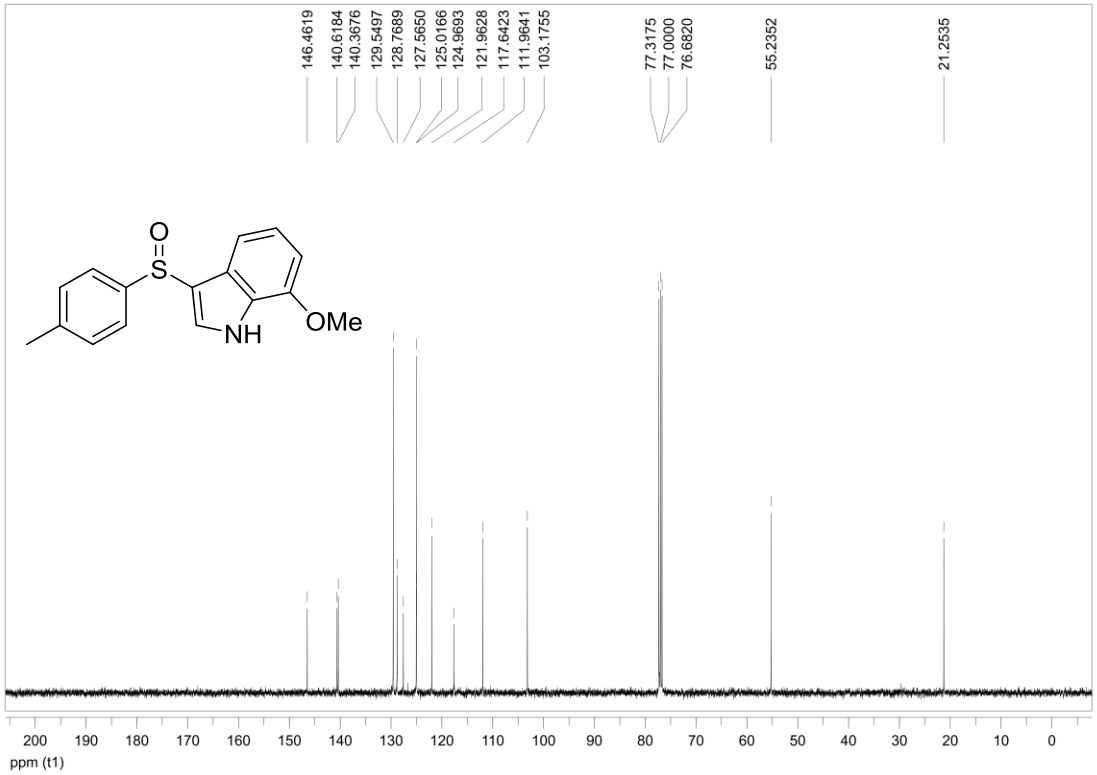


Sulfoxide **3v**

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

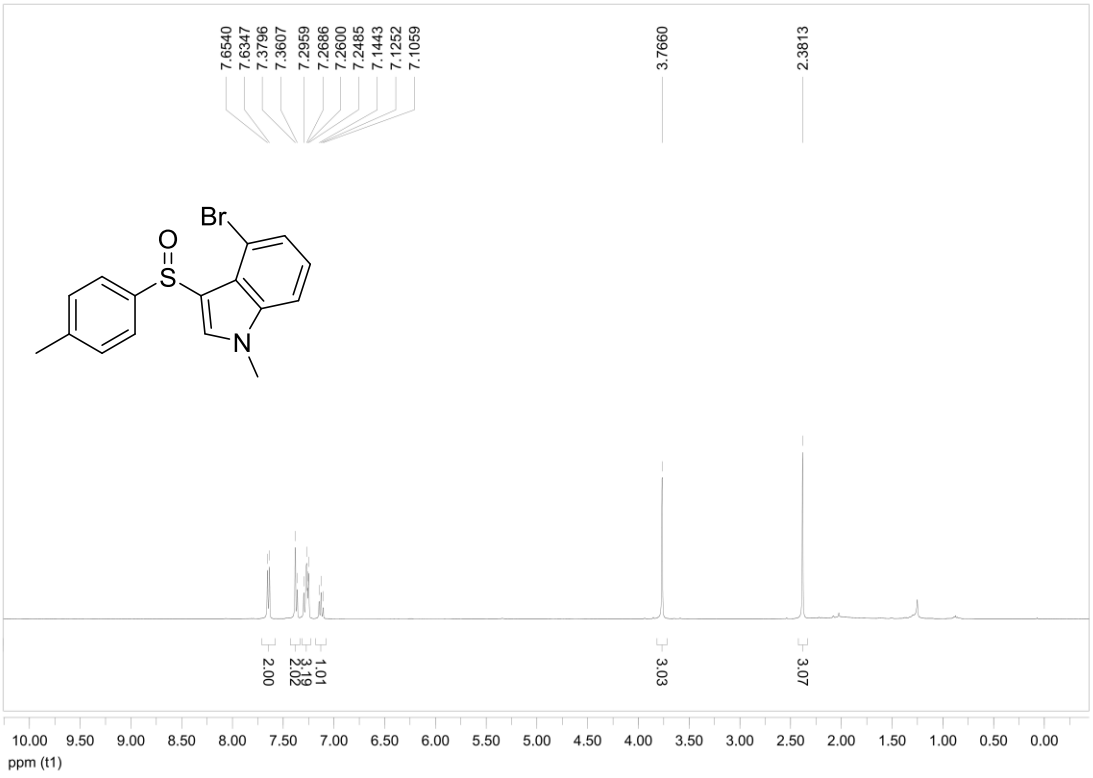


^{13}C NMR (100 MHz, $CDCl_3$)

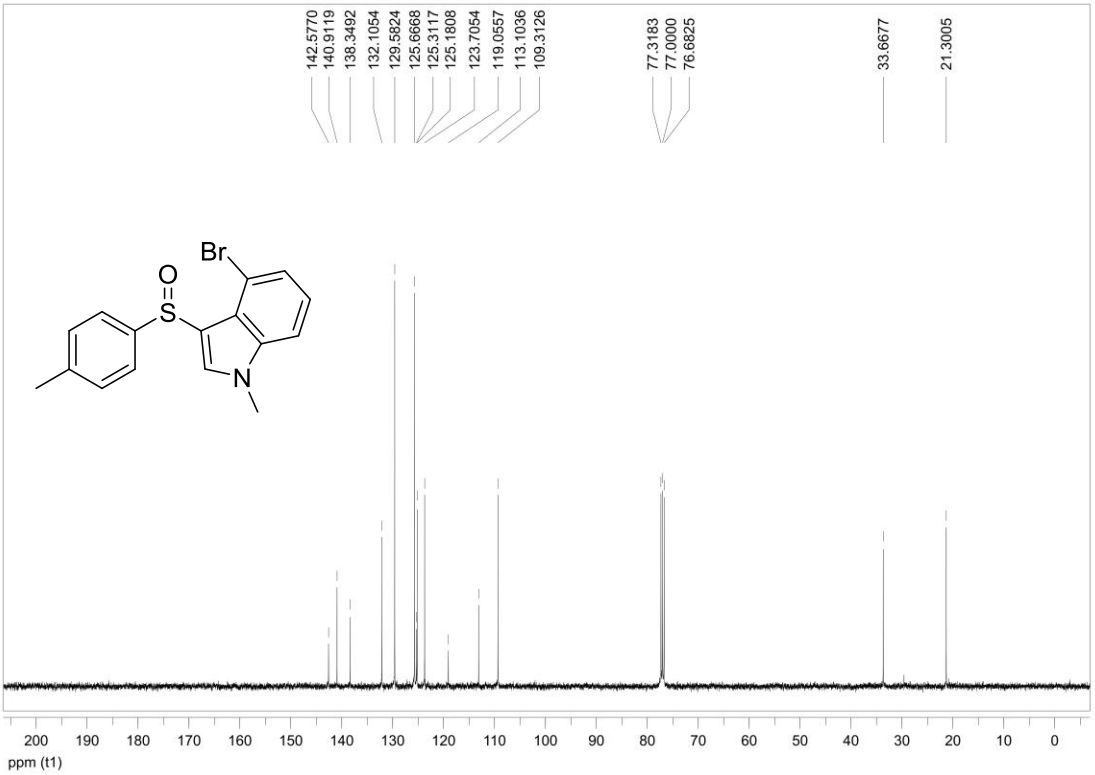


Sulfoxide **3w**

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

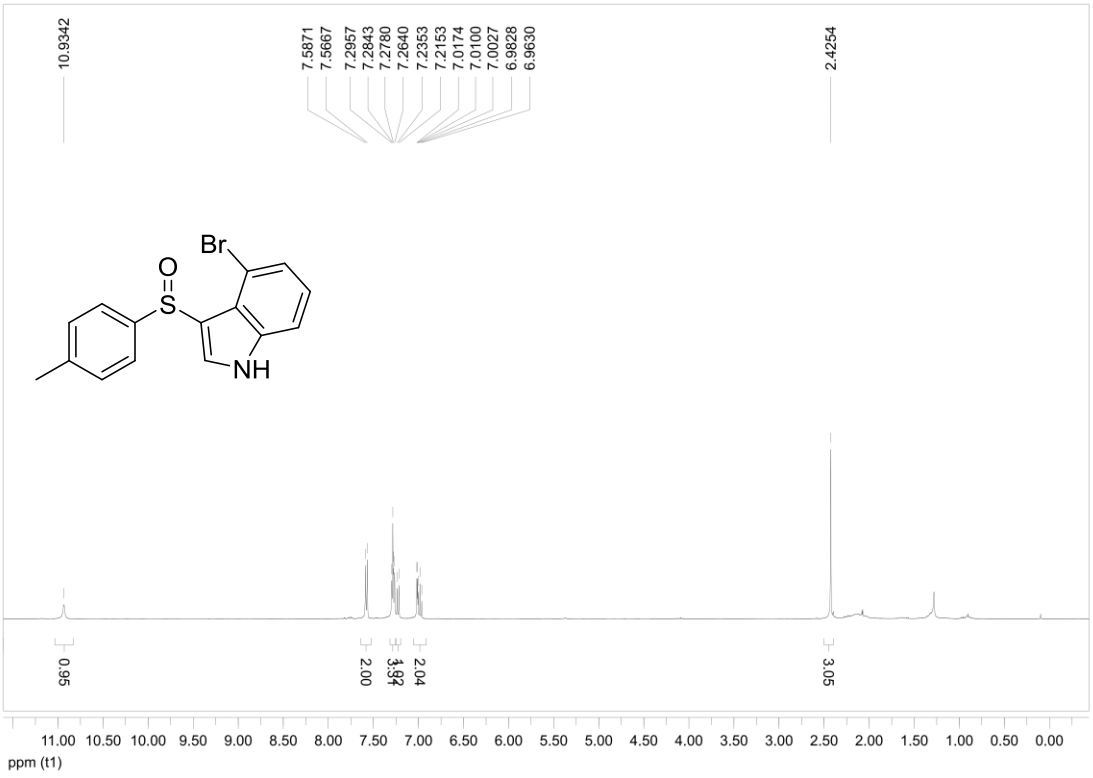


^{13}C NMR (100 MHz, $CDCl_3$)

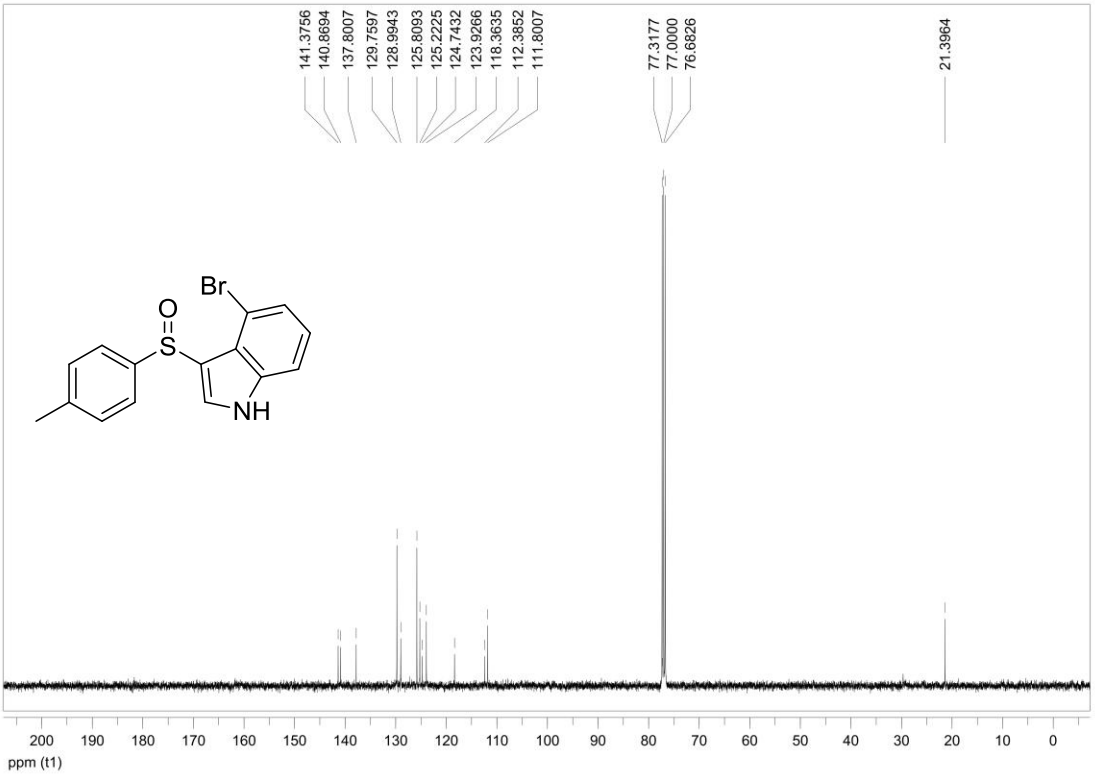


Sulfoxide **3x**

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

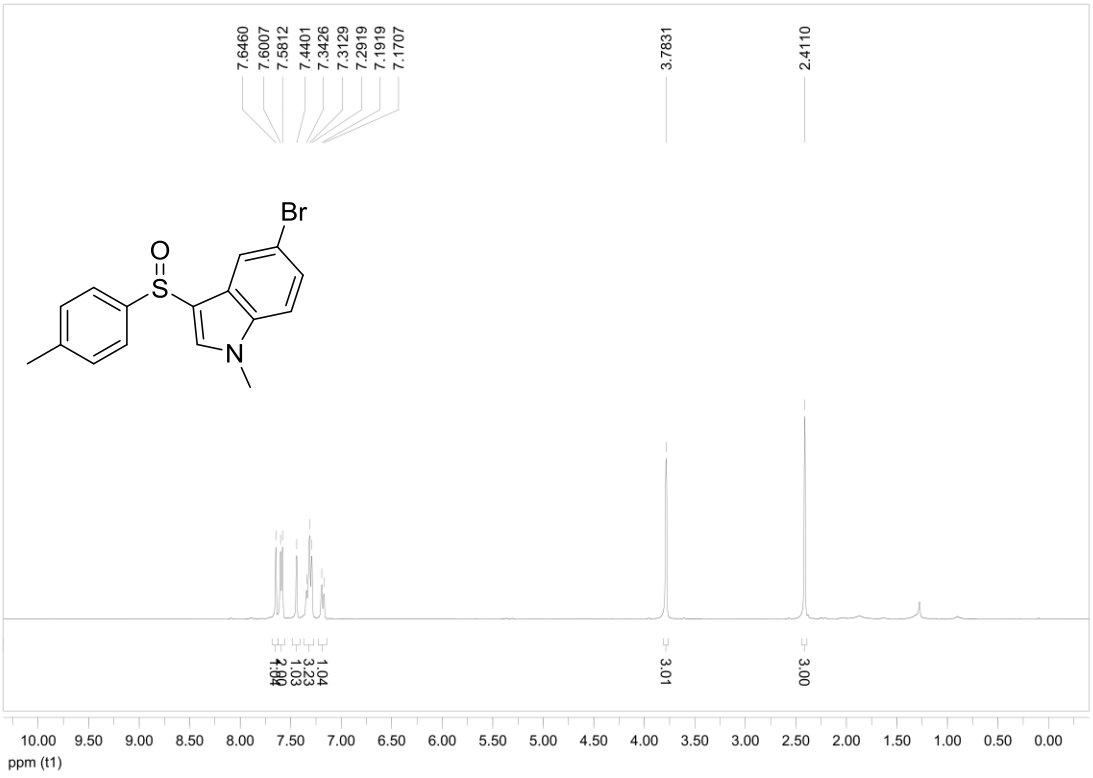


^{13}C NMR (100 MHz, $CDCl_3$)

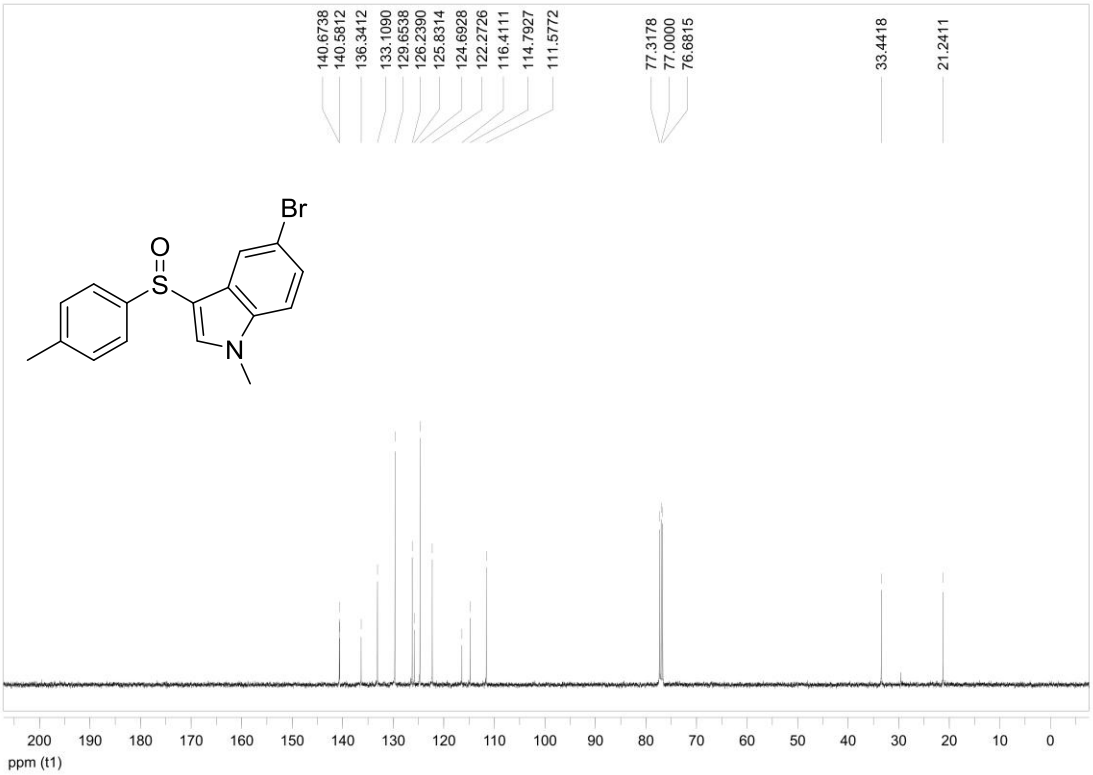


Sulfoxide **3y**

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

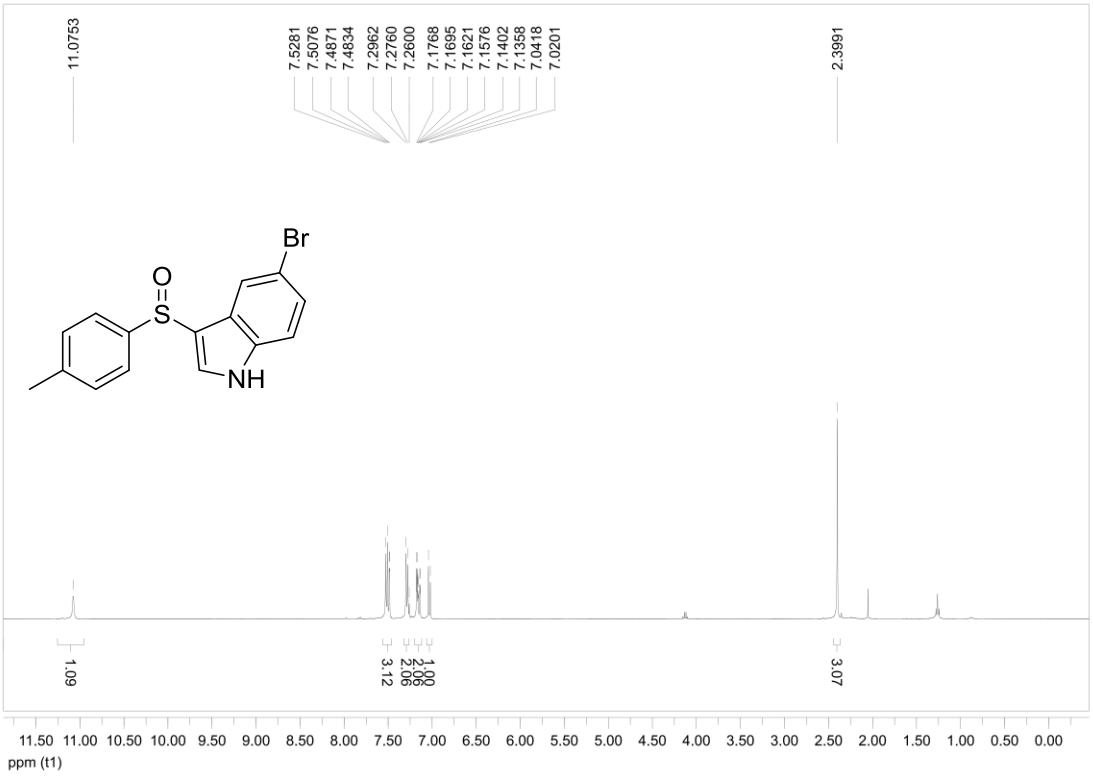


^{13}C NMR (100 MHz, $CDCl_3$)

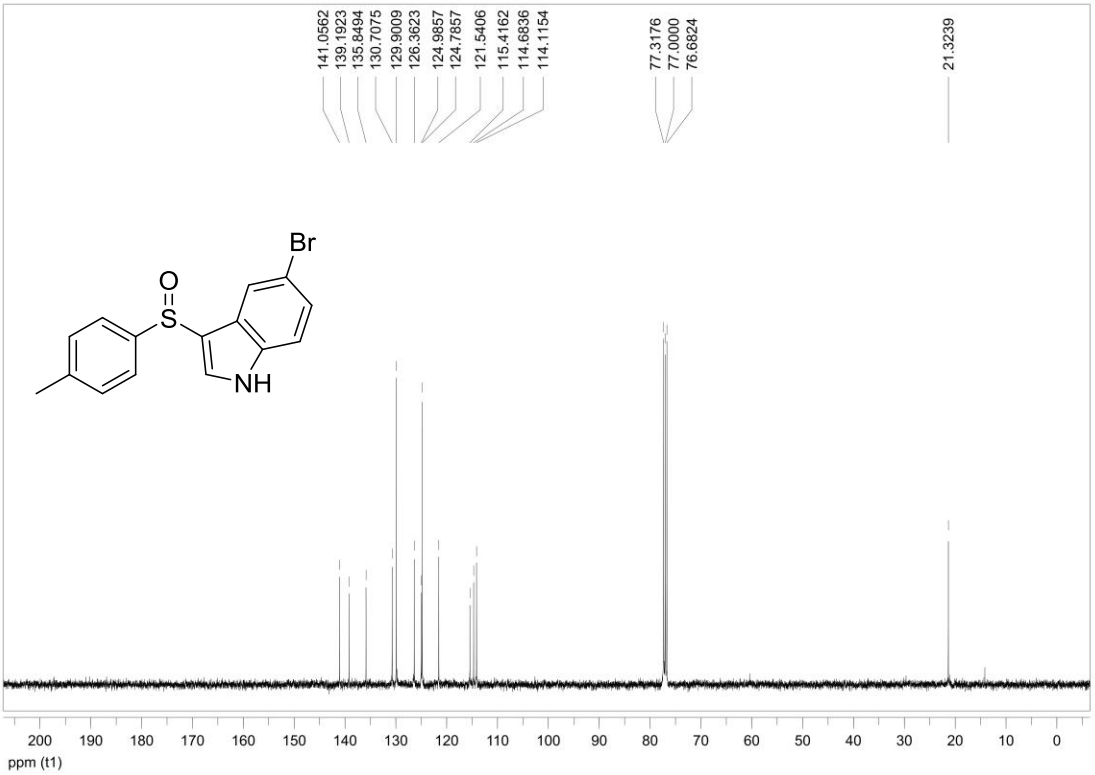


Sulfoxide **3z**

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

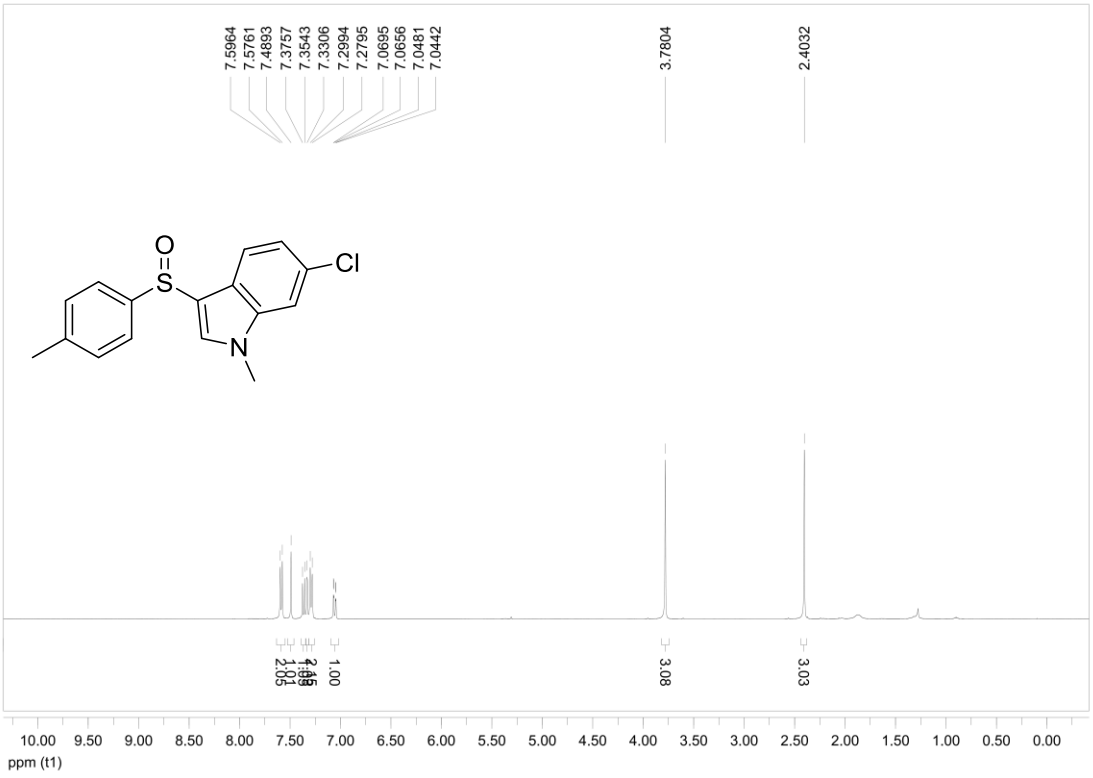


^{13}C NMR (100 MHz, $CDCl_3$)

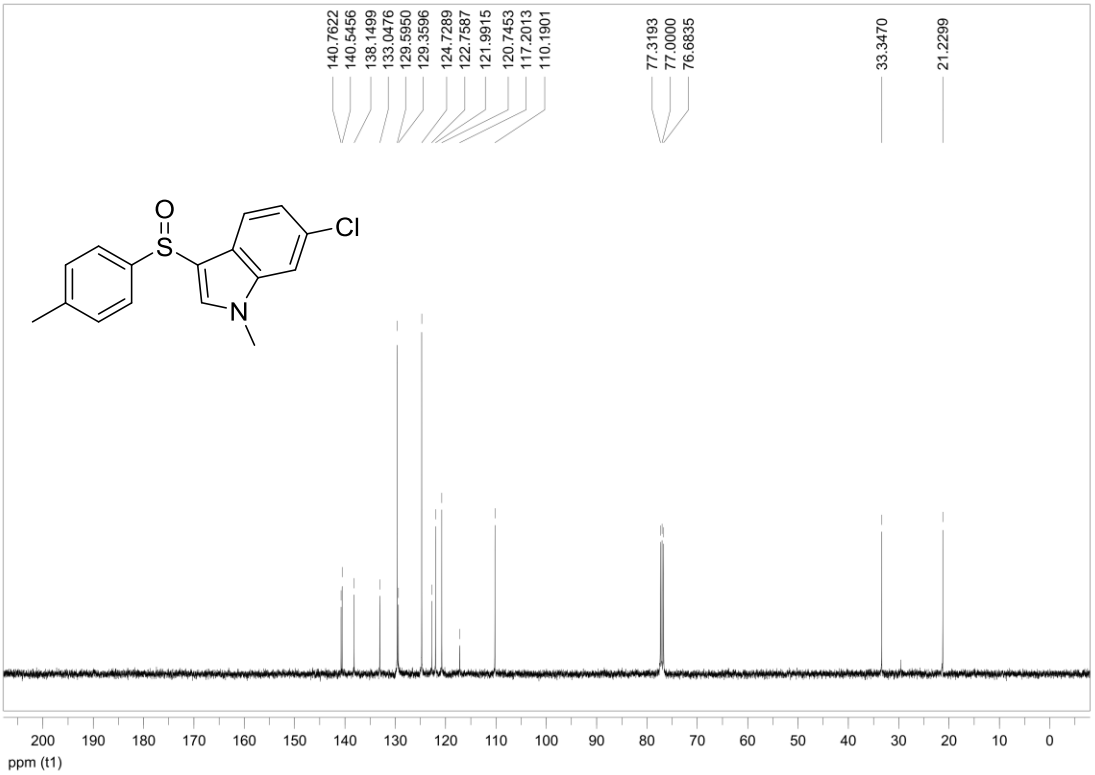


Sulfoxide **3aa**

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

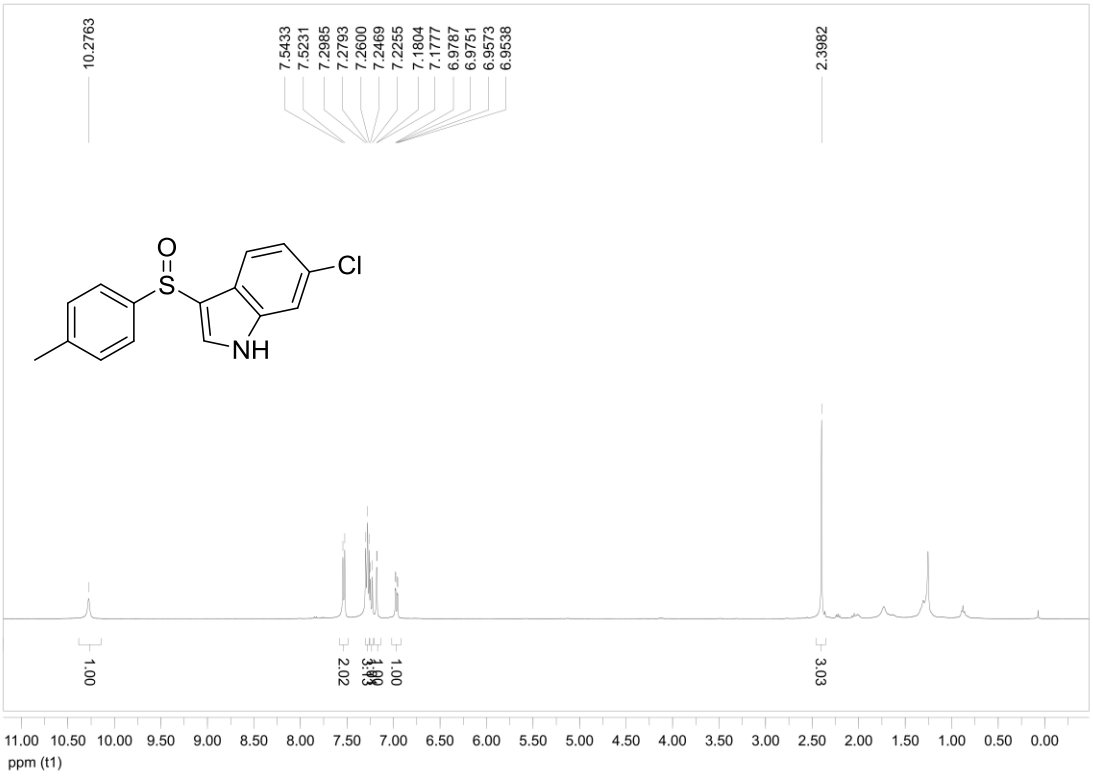


^{13}C NMR (100 MHz, $CDCl_3$)

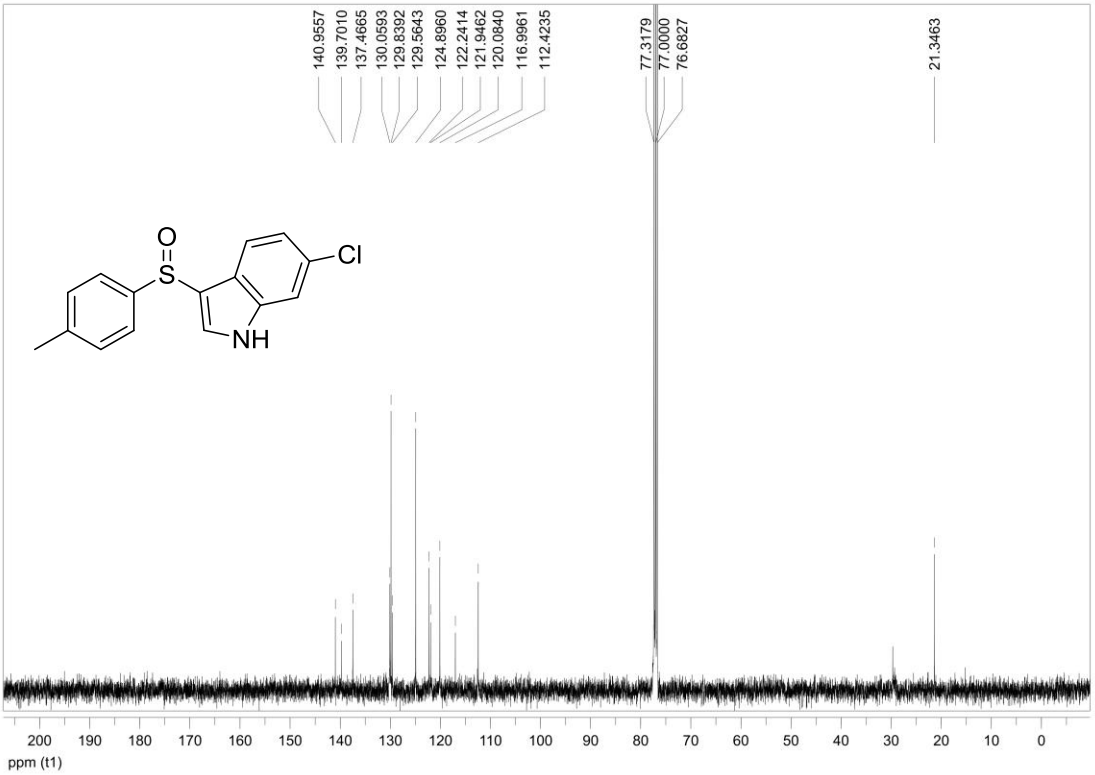


Sulfoxide **3ab**

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

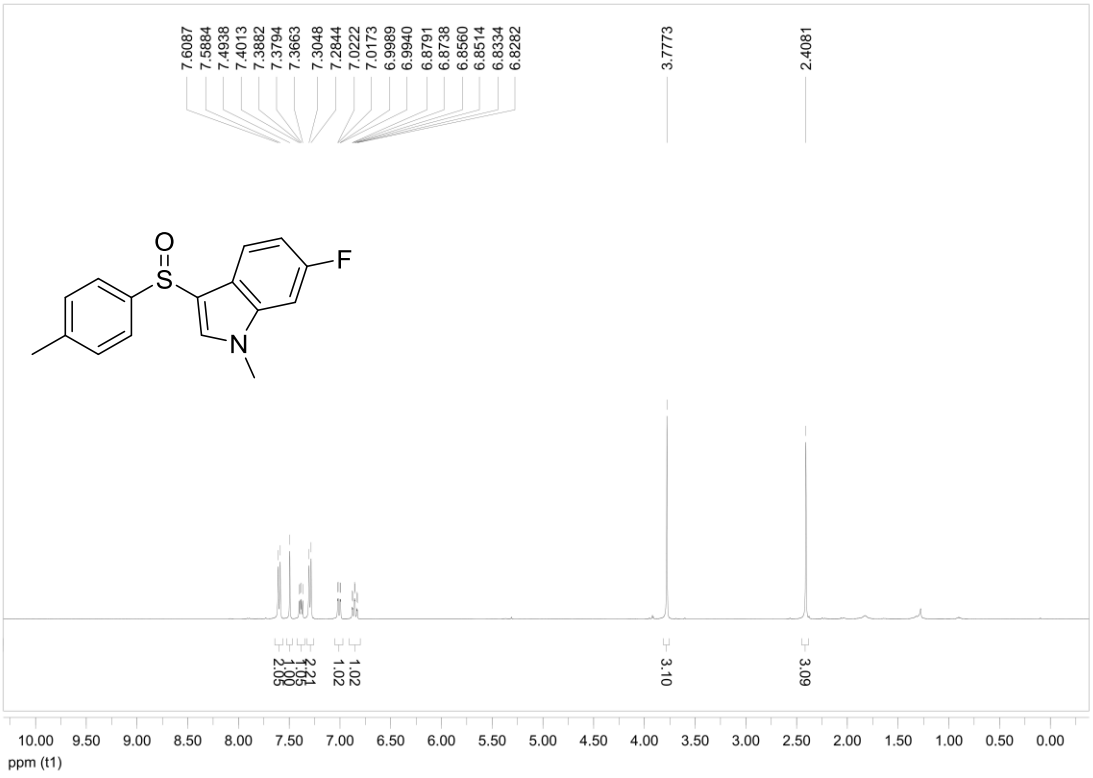


^{13}C NMR (100 MHz, $CDCl_3$)

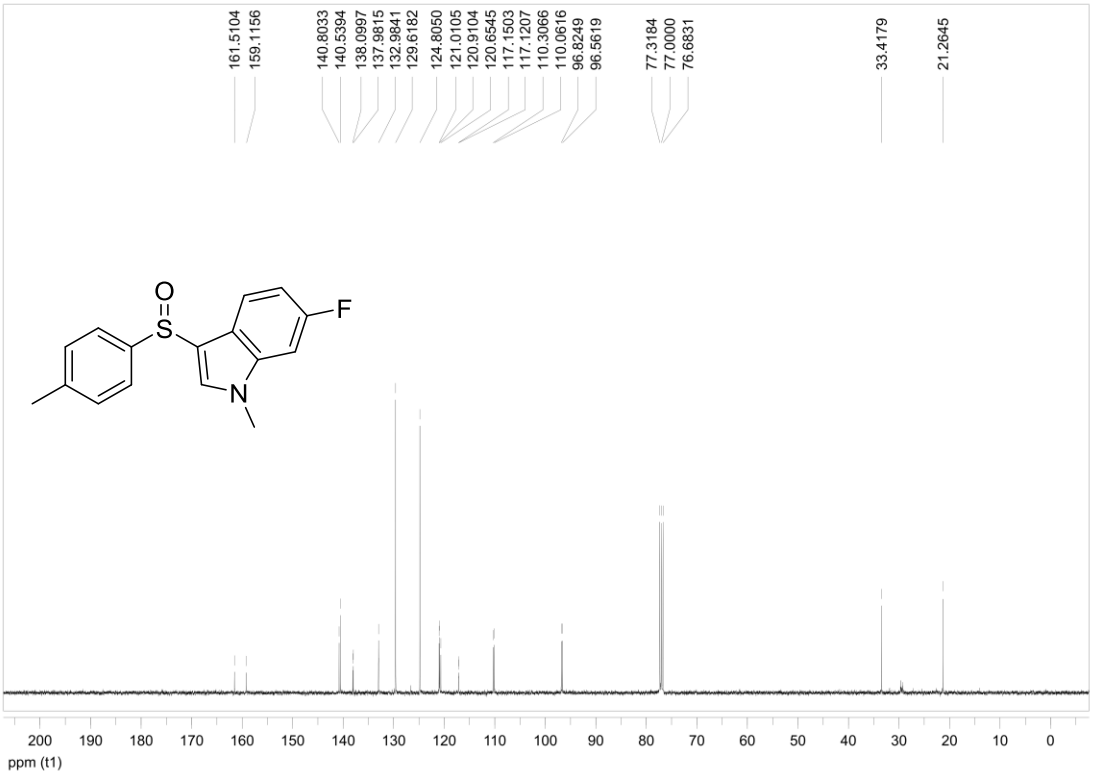


Sulfoxide **3ac**

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

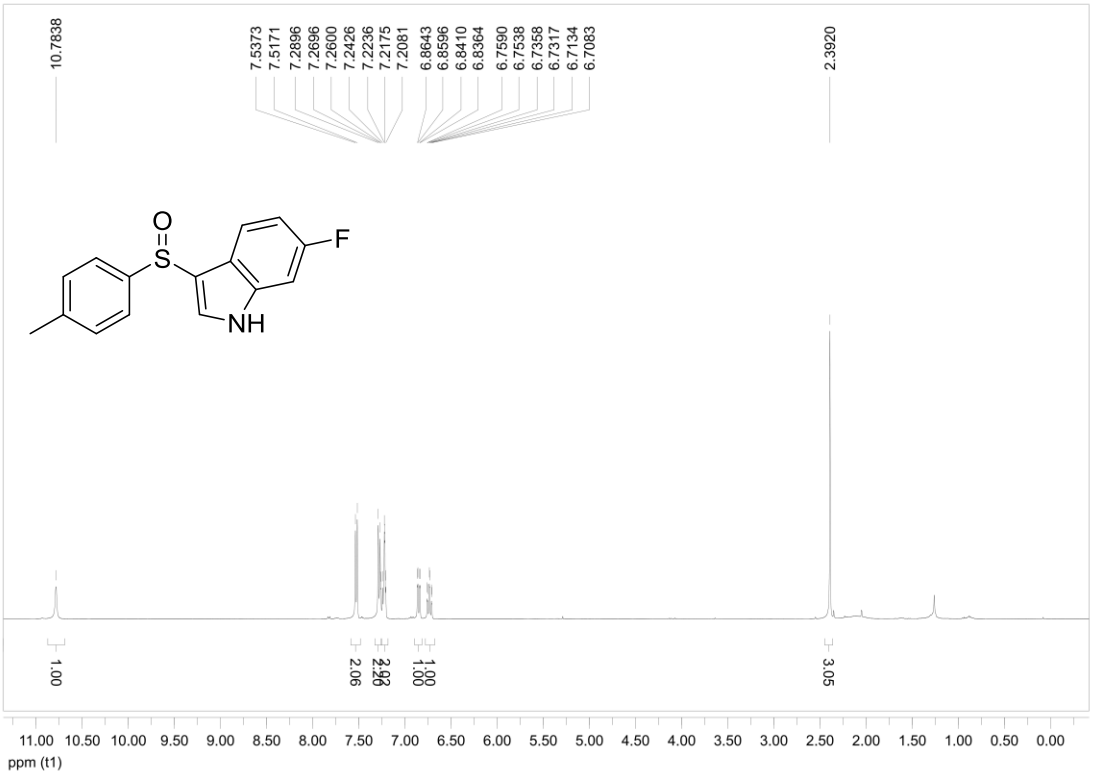


^{13}C NMR (100 MHz, $CDCl_3$)

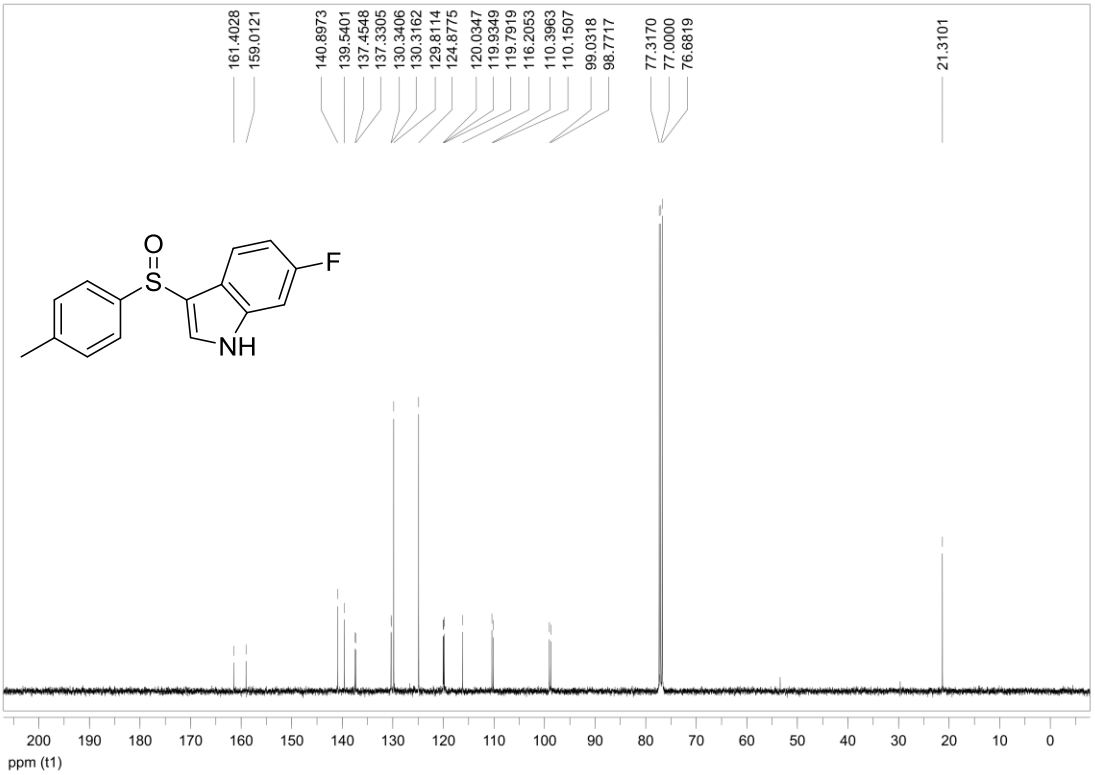


Sulfoxide **3ad**

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

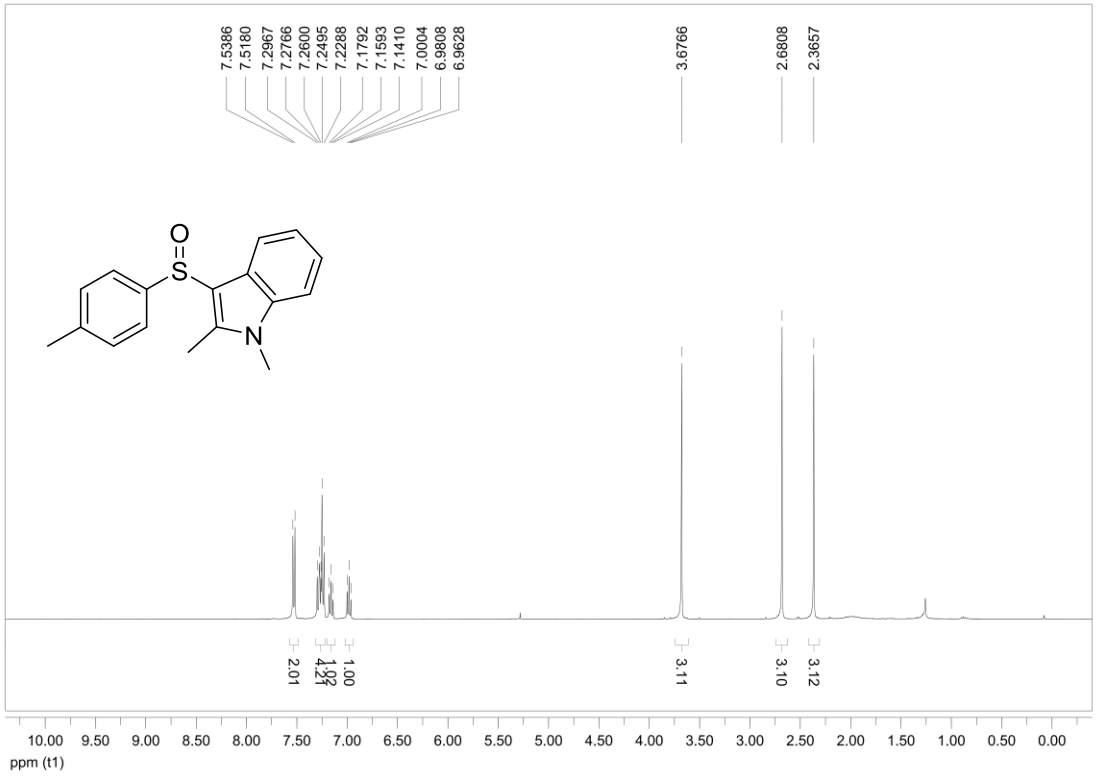


^{13}C NMR (100 MHz, $CDCl_3$)

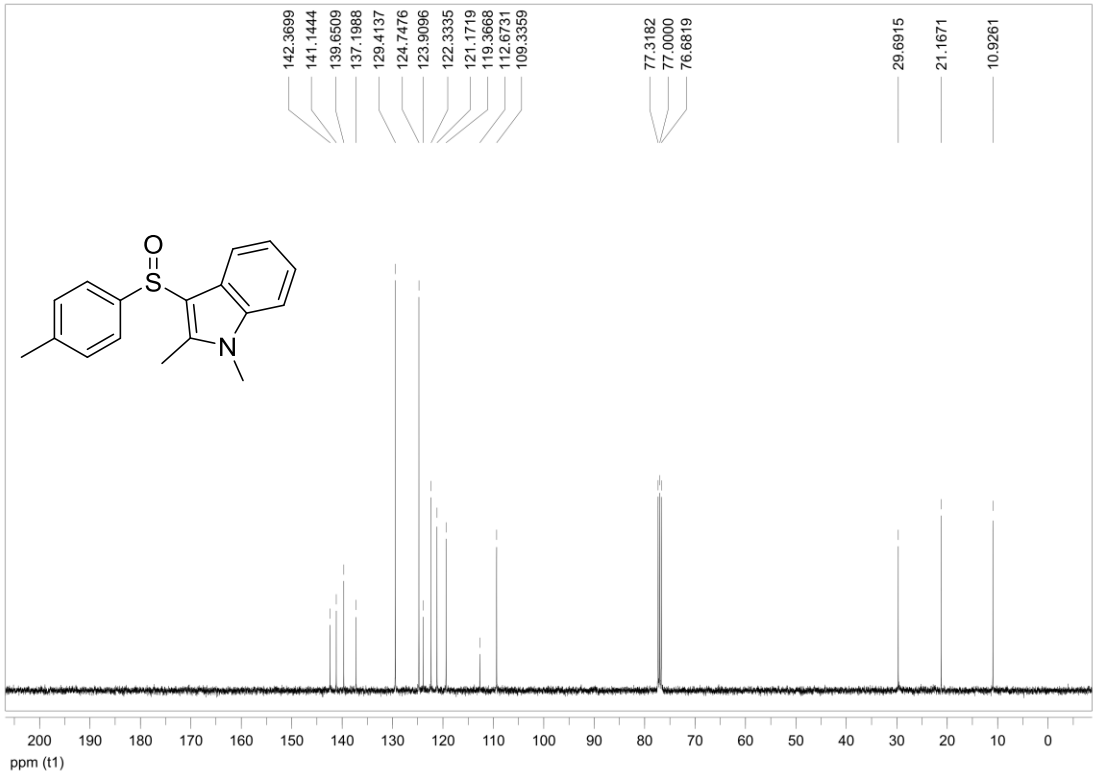


Sulfoxide **3ae**

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

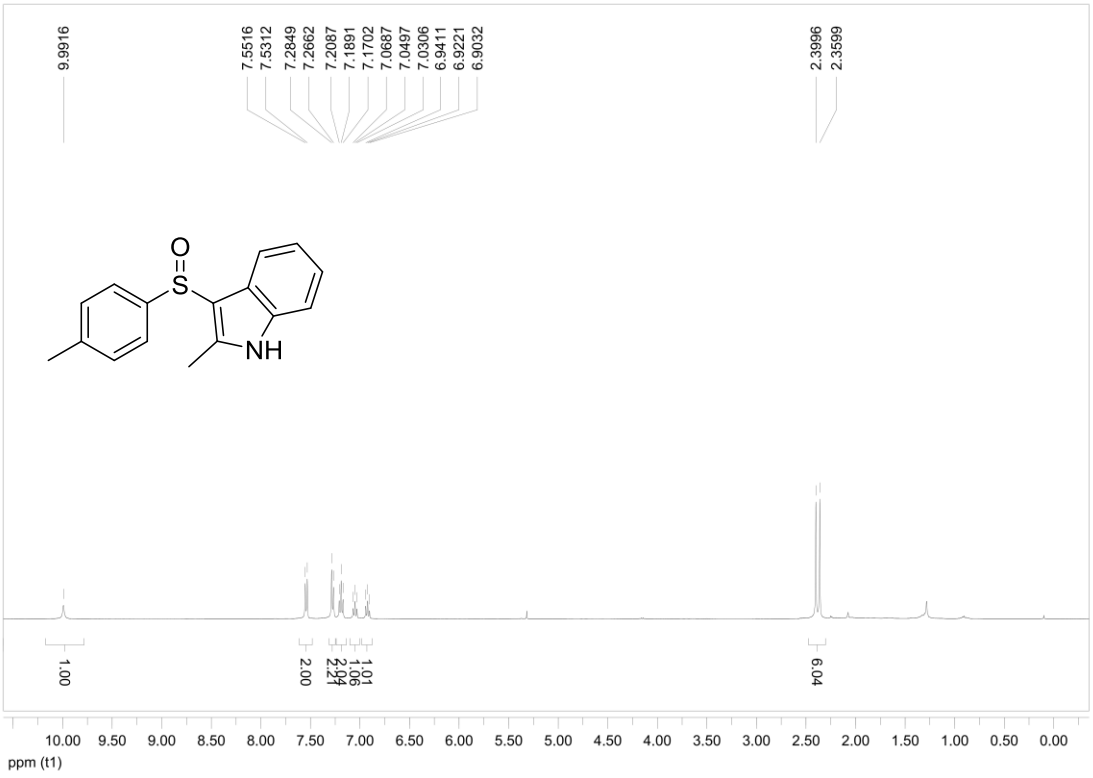


^{13}C NMR (100 MHz, $CDCl_3$)

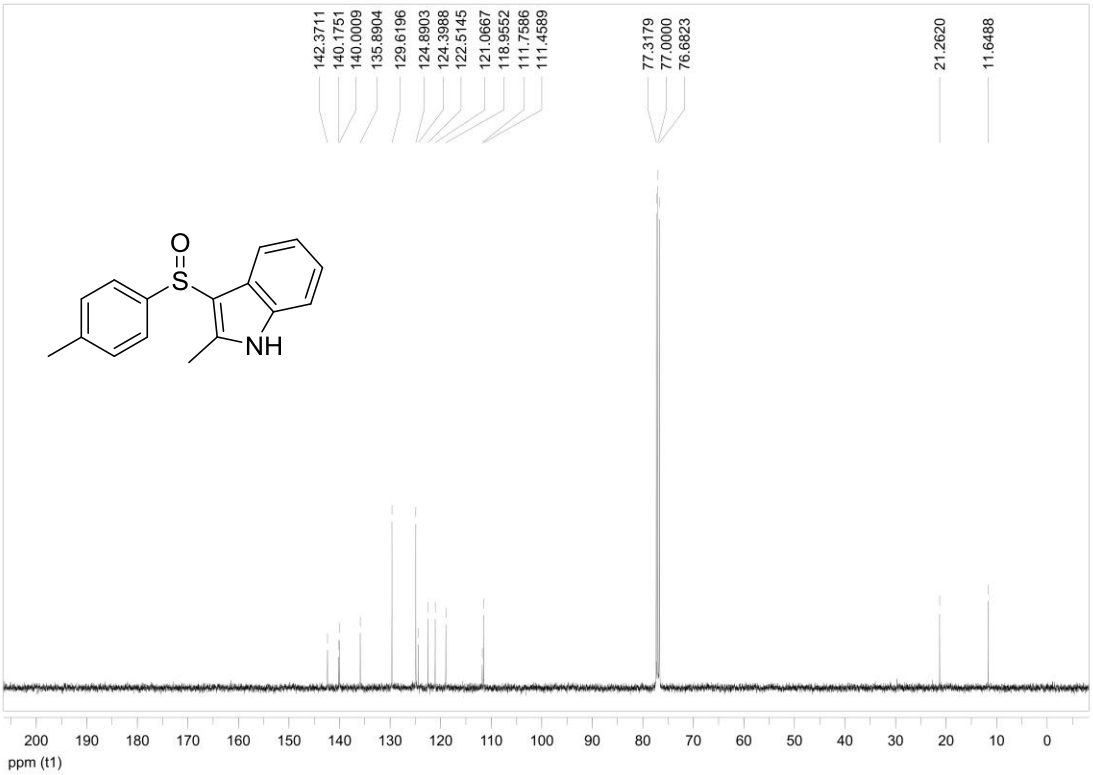


Sulfoxide **3af**

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

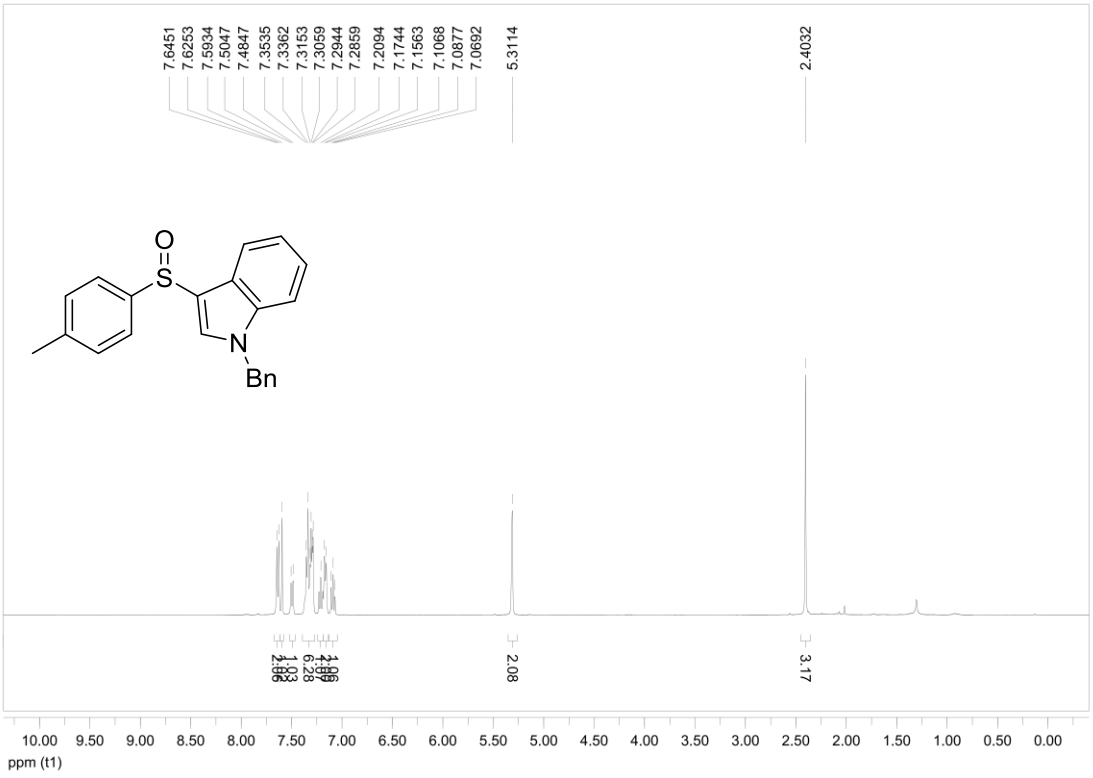


^{13}C NMR (100 MHz, $CDCl_3$)

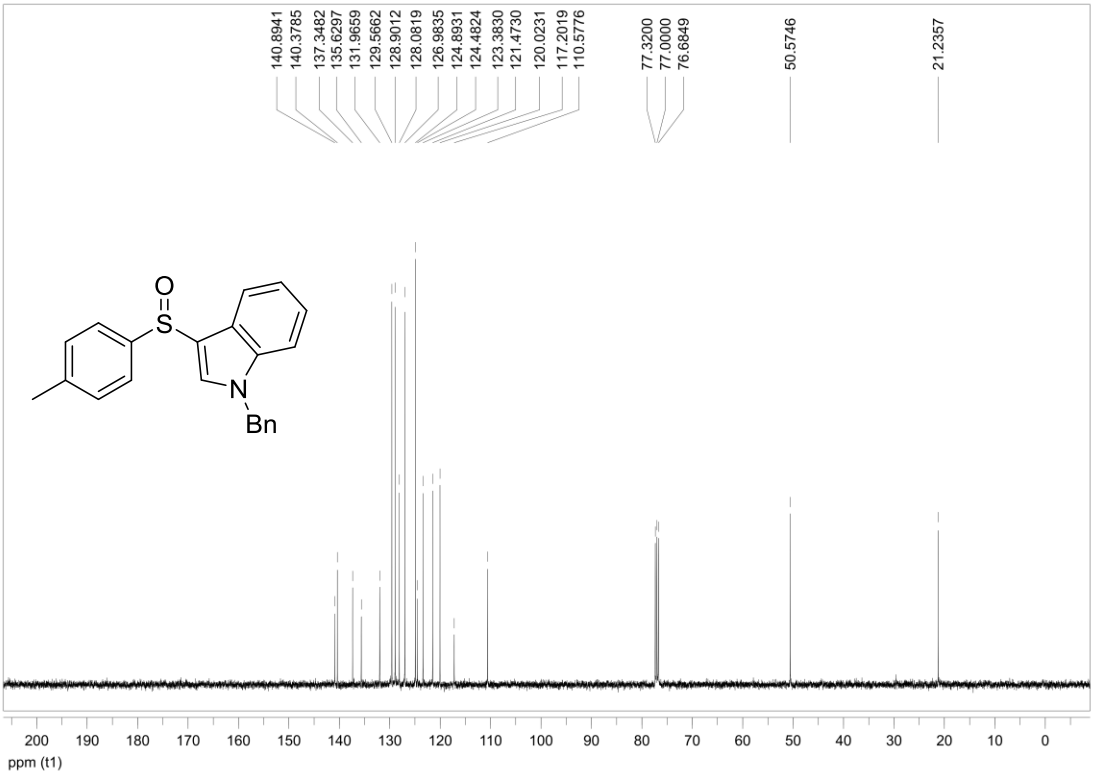


Sulfoxide **3ag**

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

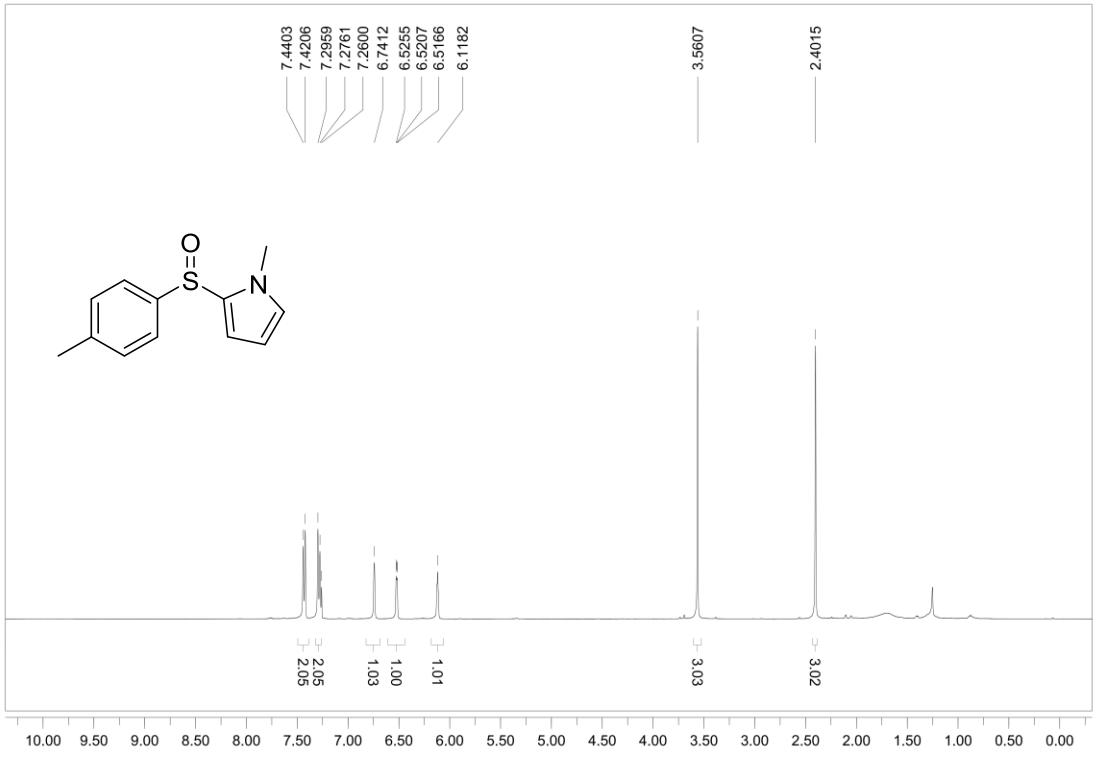


^{13}C NMR (100 MHz, $CDCl_3$)

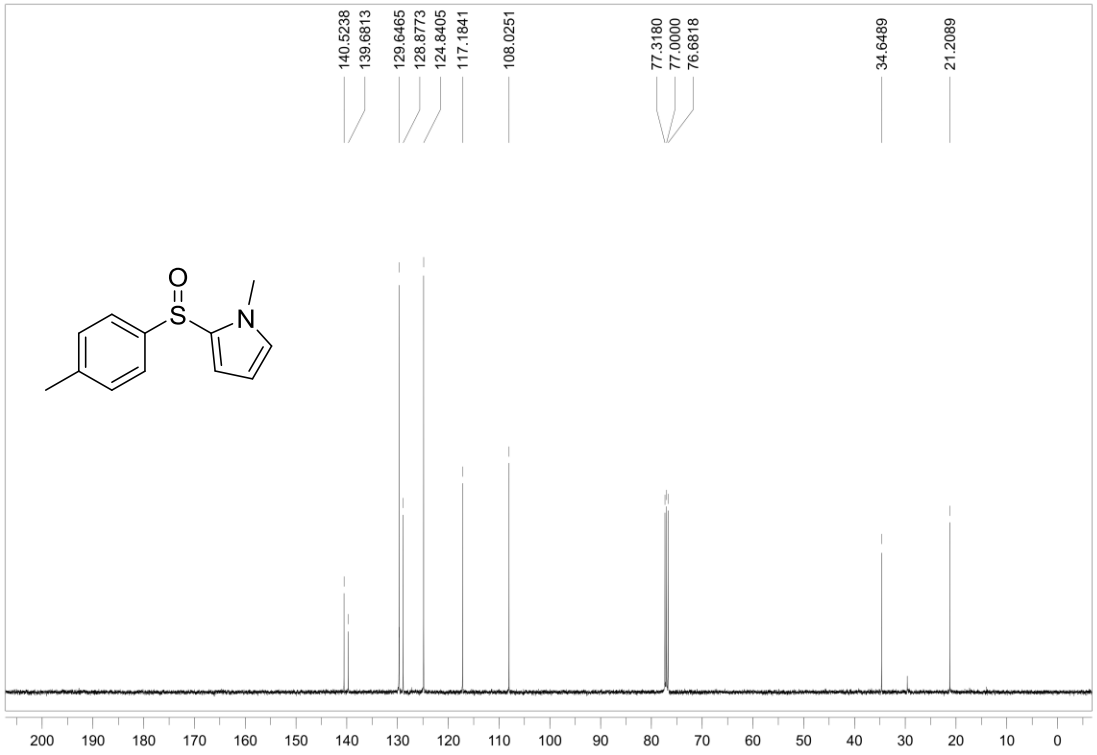


Sulfoxide **7a**

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

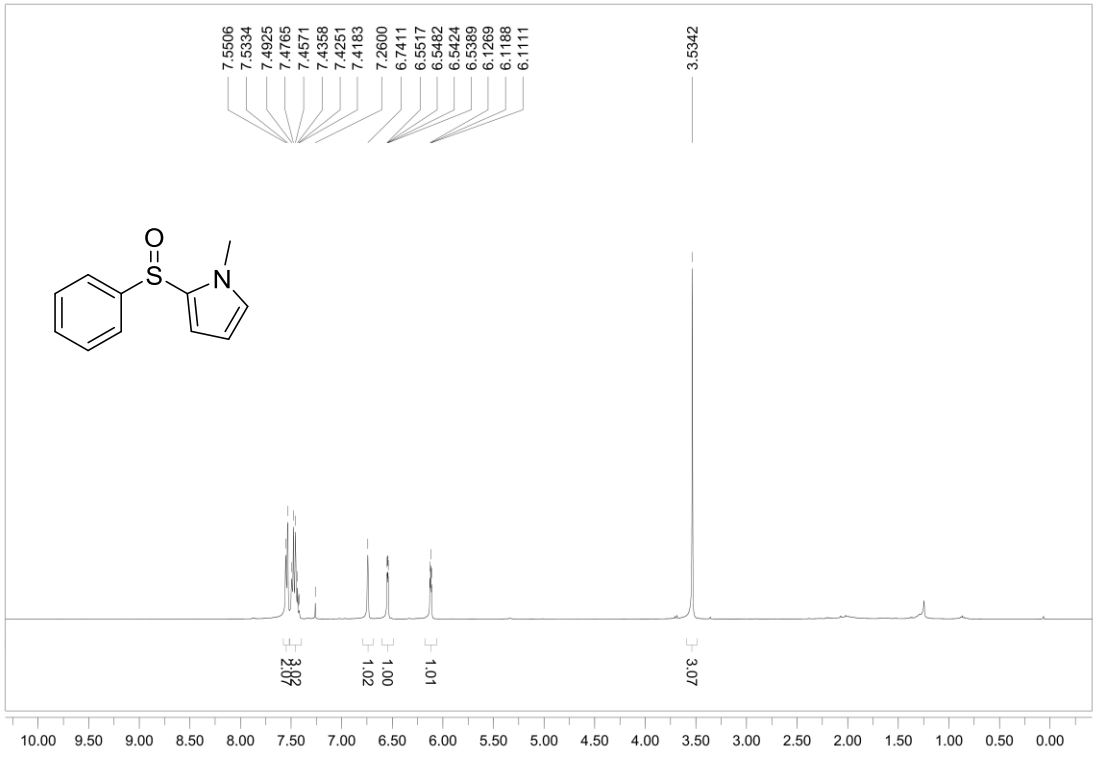


^{13}C NMR (100 MHz, $CDCl_3$)

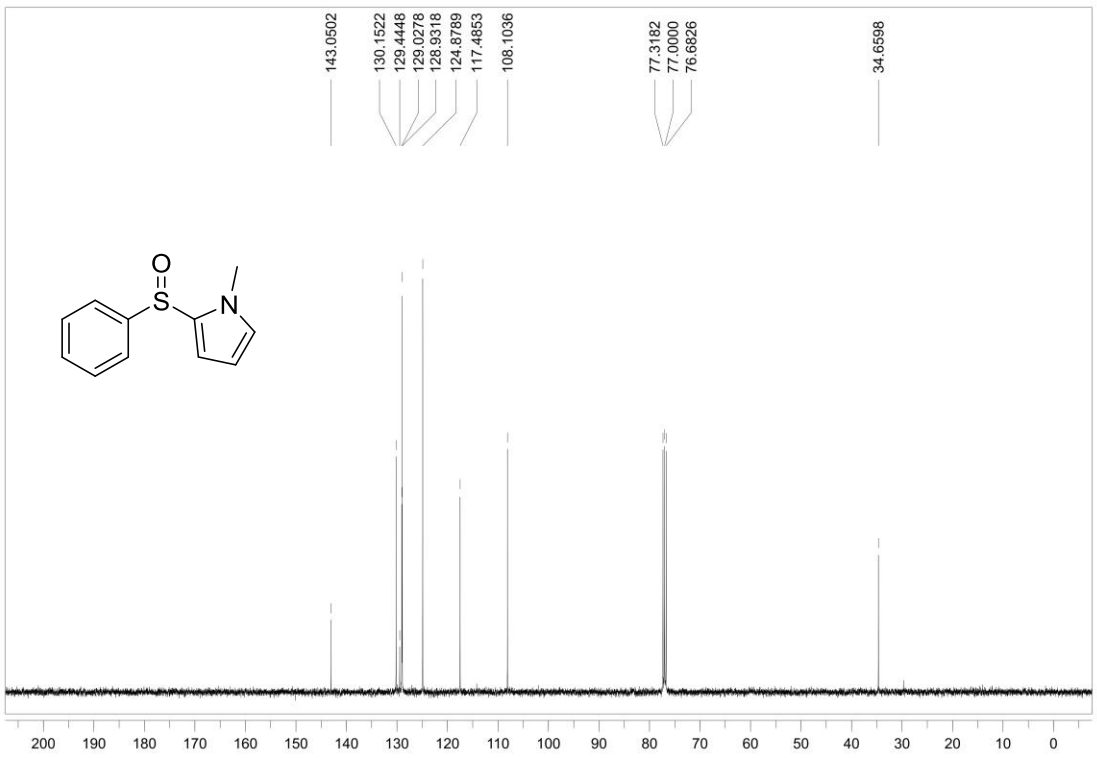


Sulfoxide **7b**

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

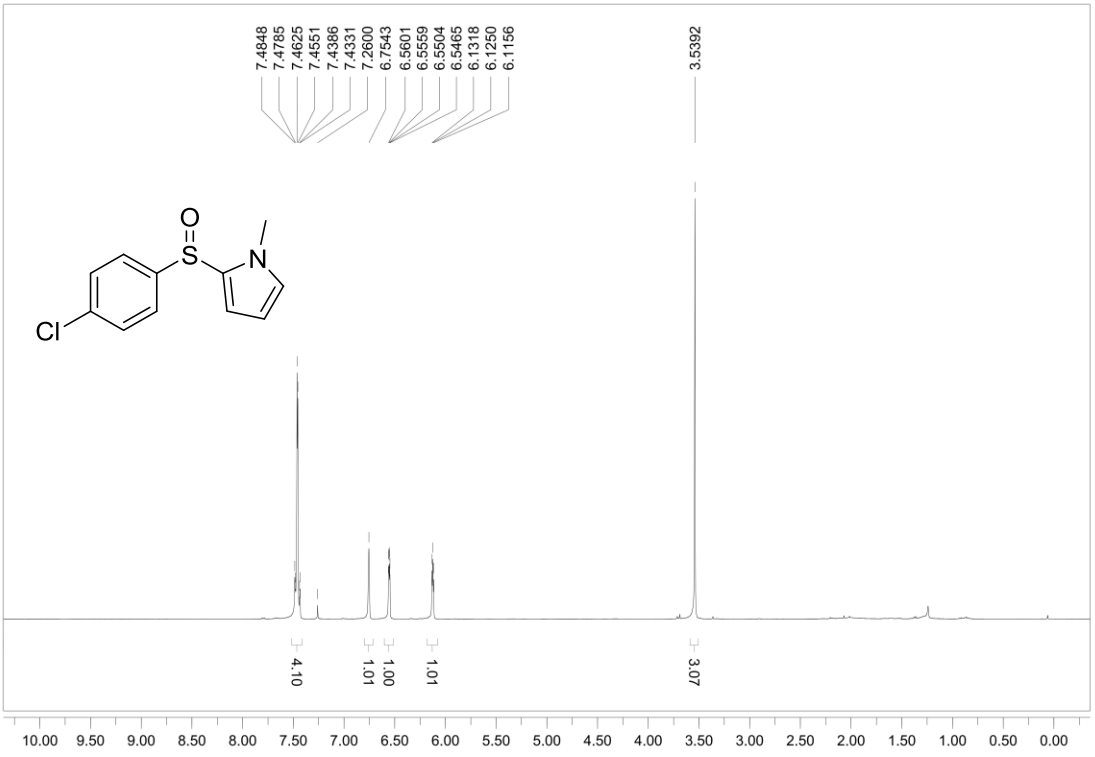


^{13}C NMR (100 MHz, $CDCl_3$)

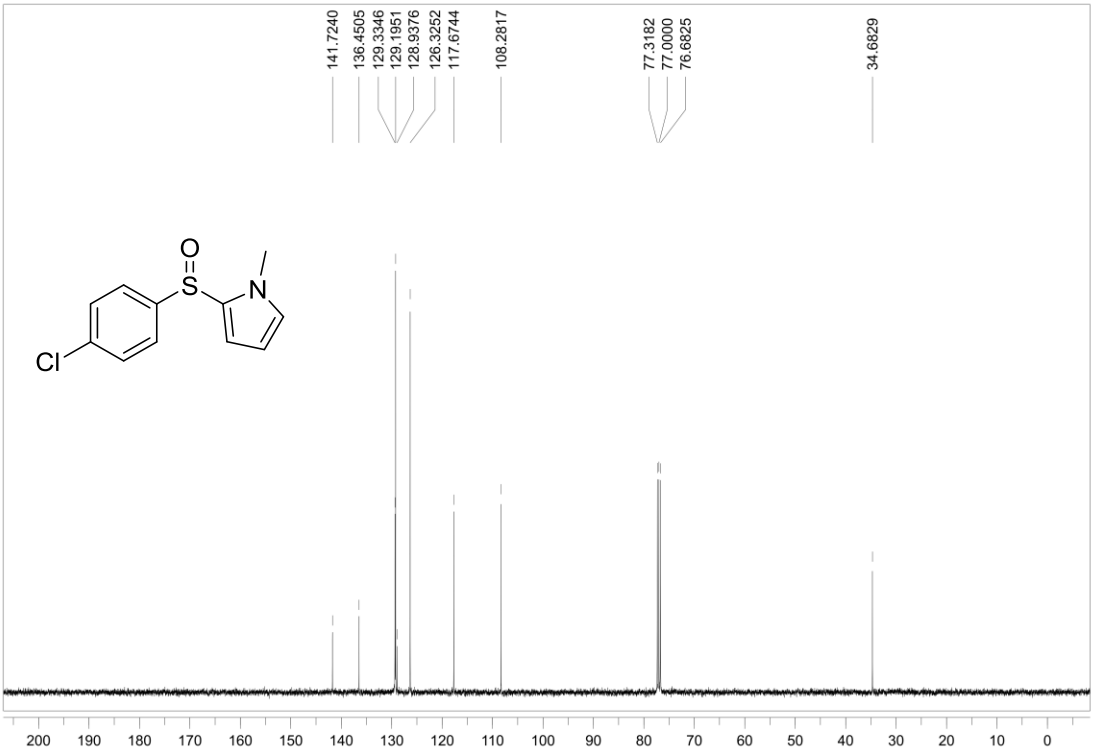


Sulfoxide **7c**

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

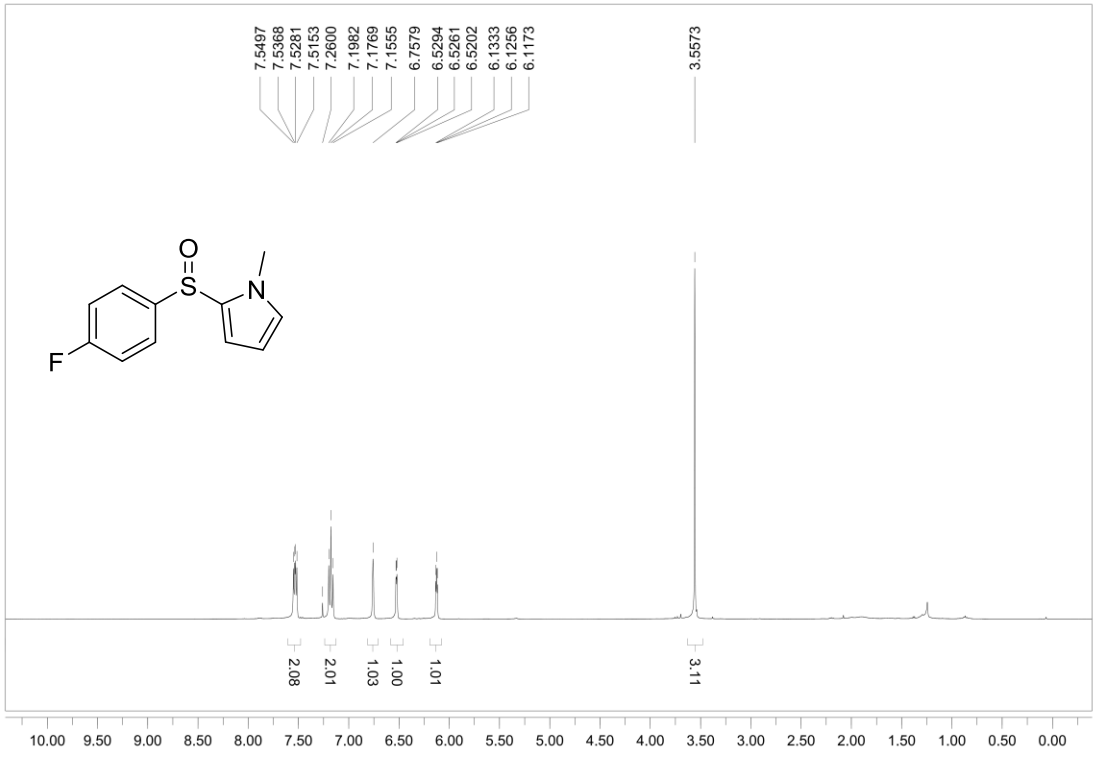


^{13}C NMR (100 MHz, $CDCl_3$)

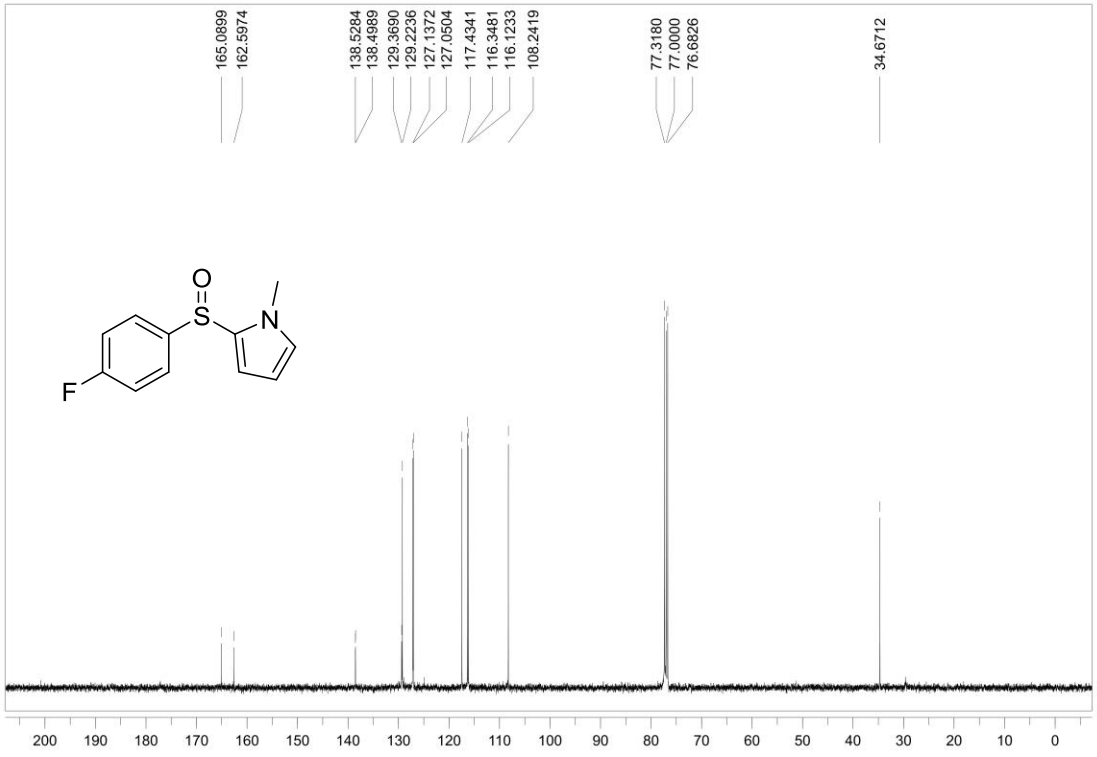


Sulfoxide **7d**

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

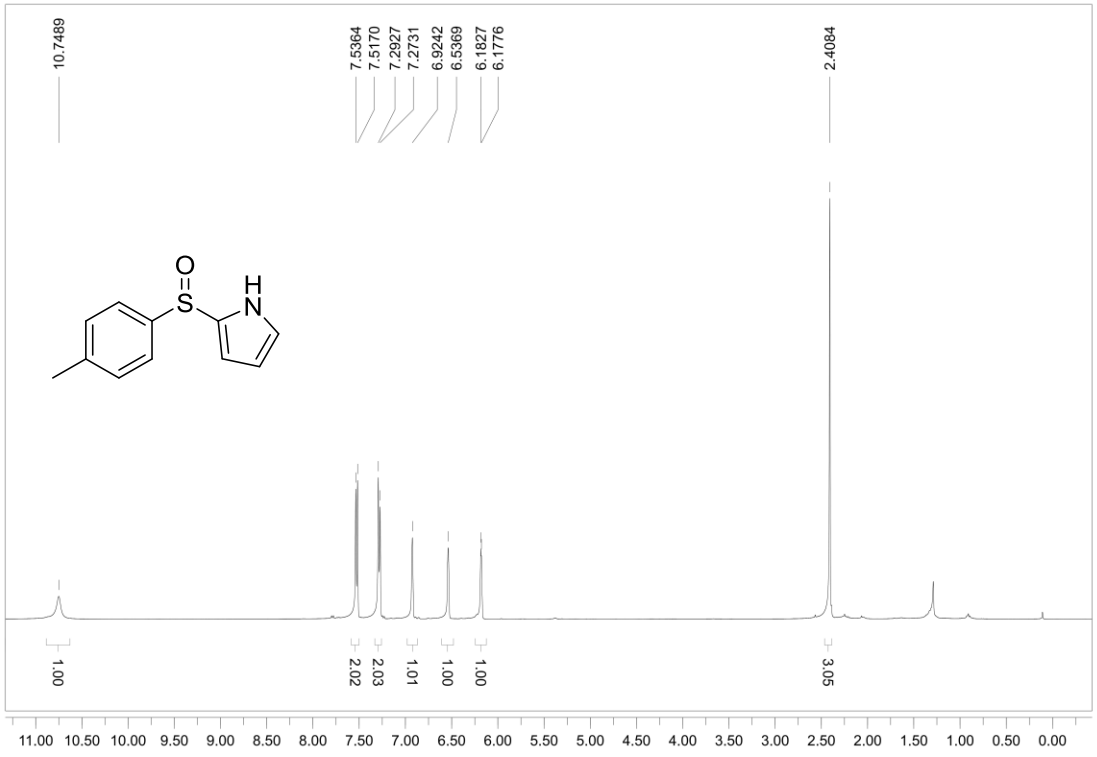


^{13}C NMR (100 MHz, $CDCl_3$)

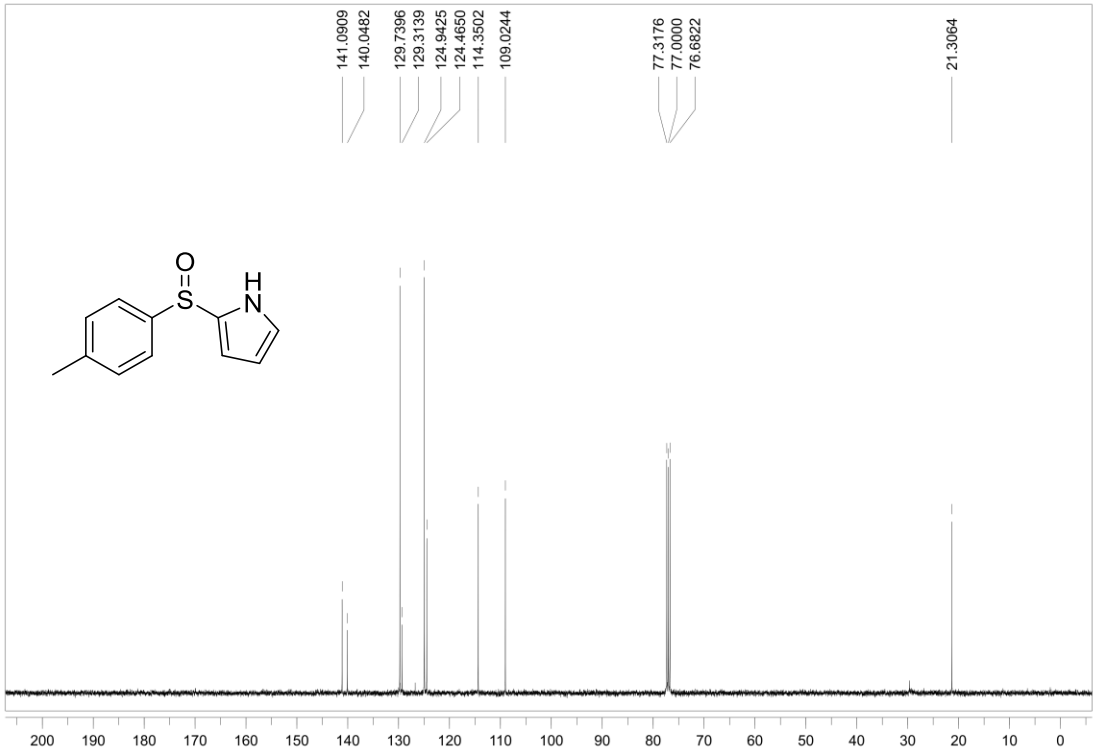


Sulfoxide **7e**

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

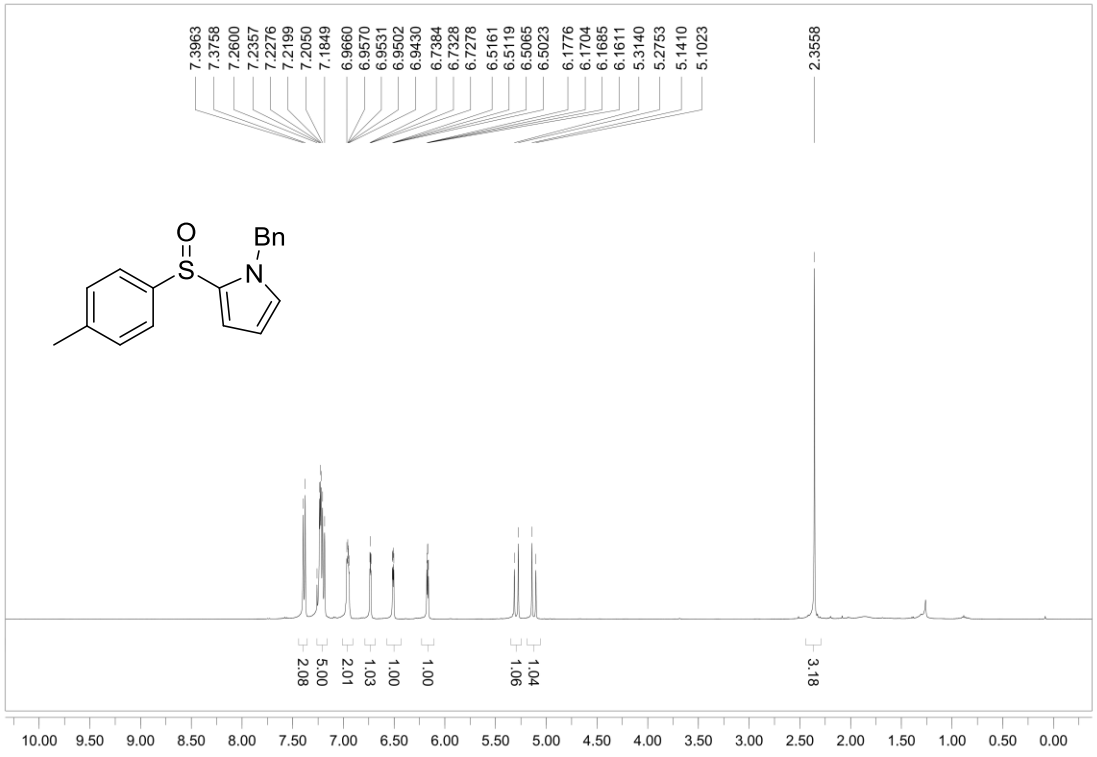


^{13}C NMR (100 MHz, $CDCl_3$)

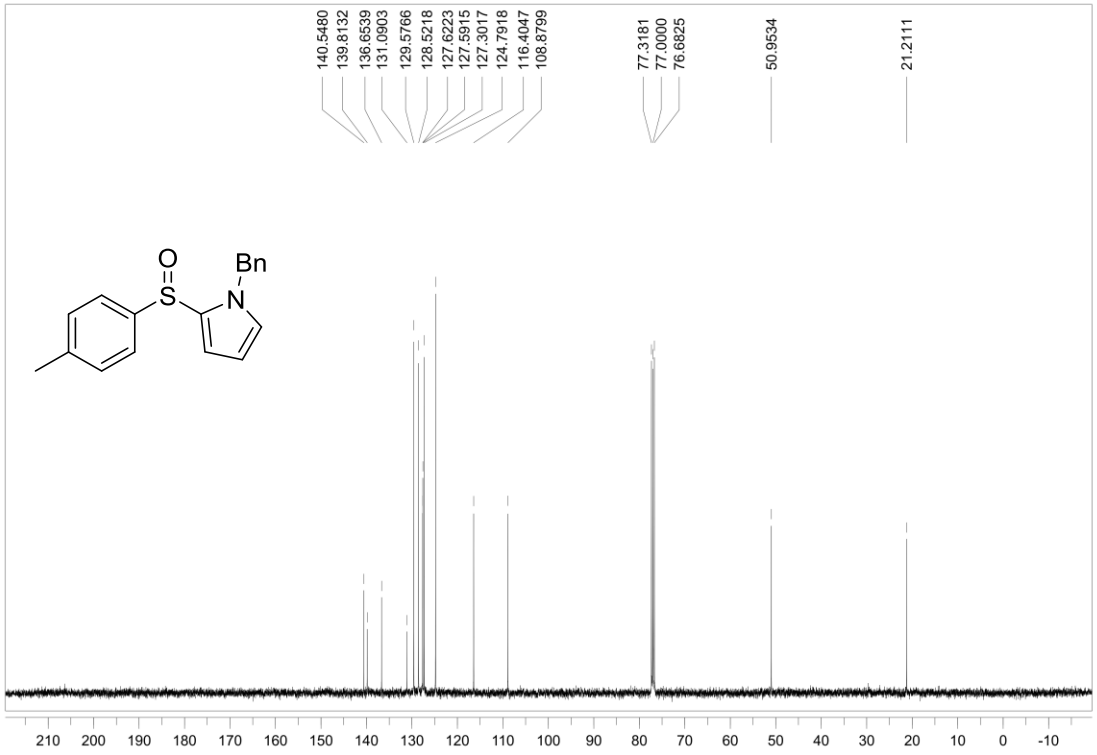


Sulfoxide **7f**

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

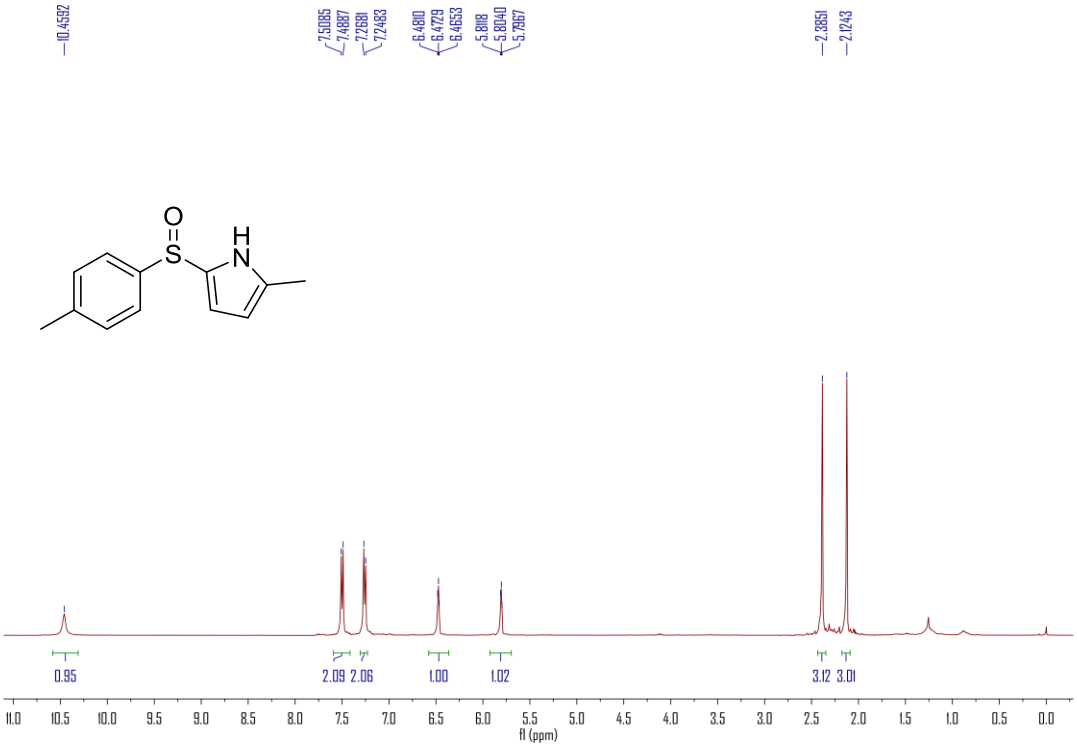


^{13}C NMR (100 MHz, $CDCl_3$)

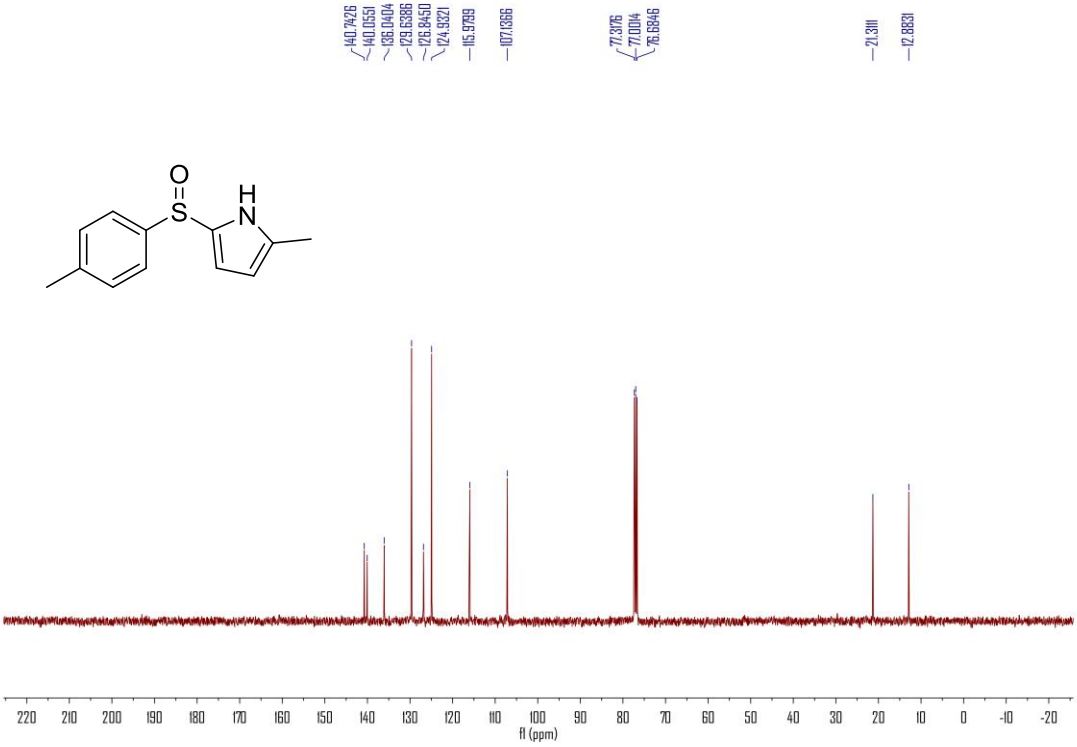


Sulfoxide **7g**

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

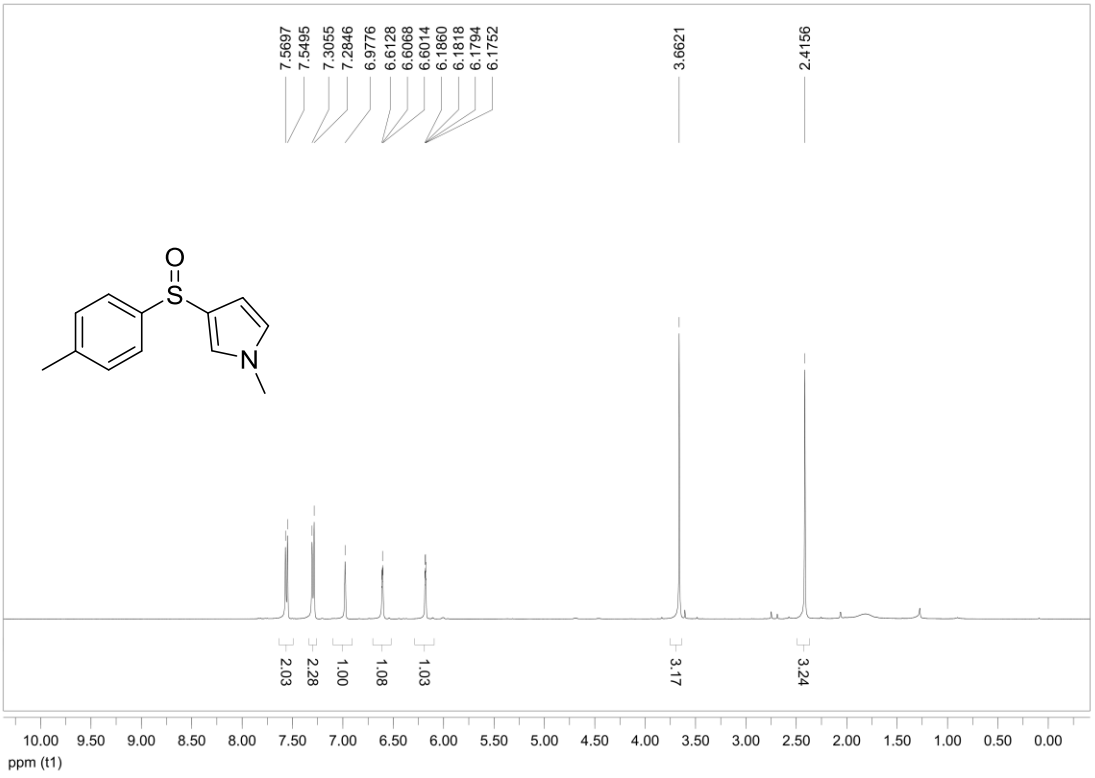


^{13}C NMR (100 MHz, $CDCl_3$)

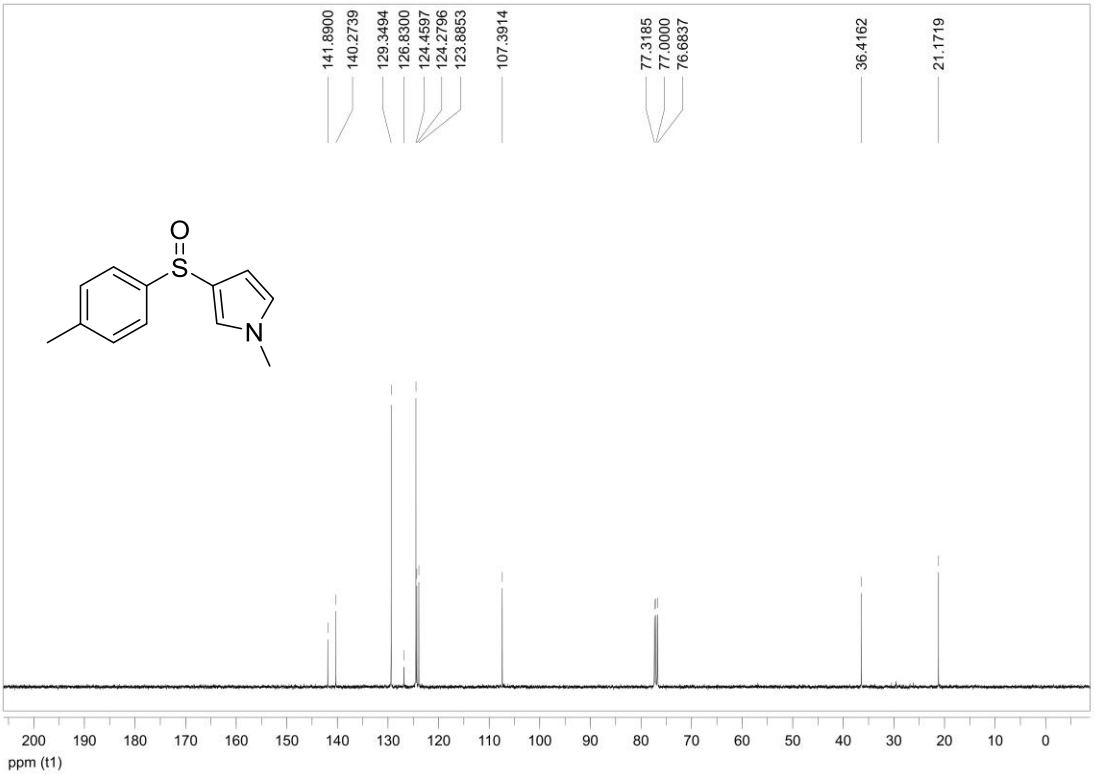


Sulfoxide **8a**

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

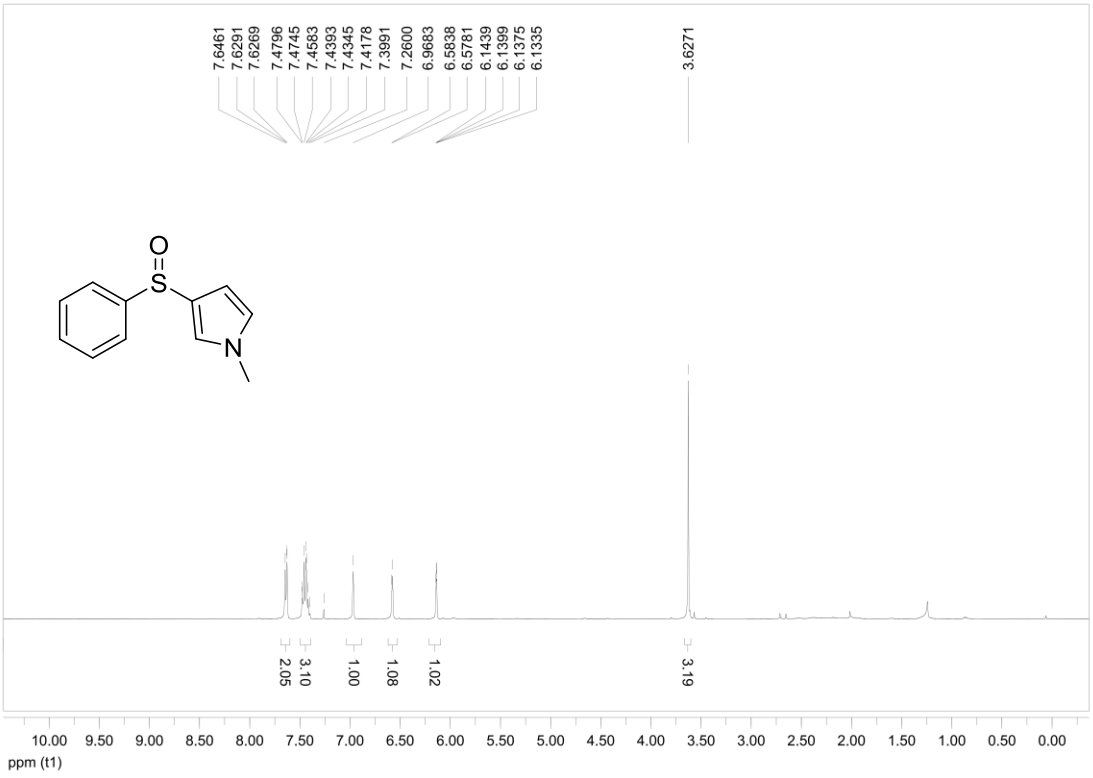


^{13}C NMR (100 MHz, $CDCl_3$)

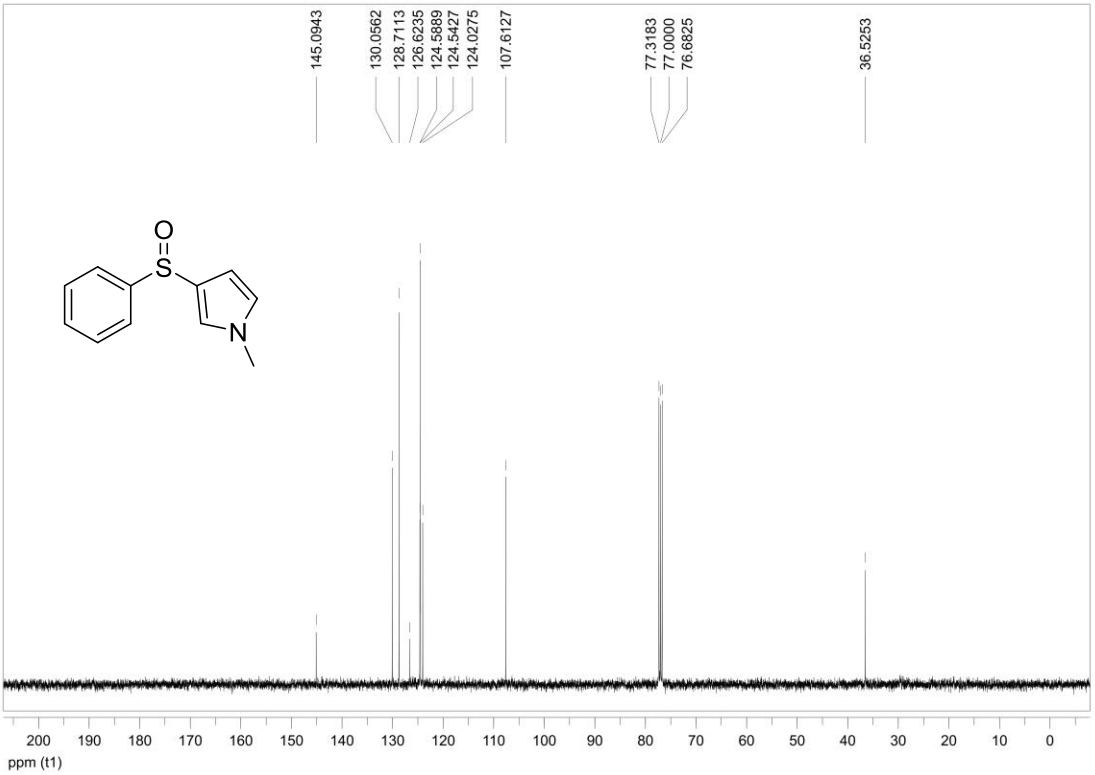


Sulfoxide **8b**

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

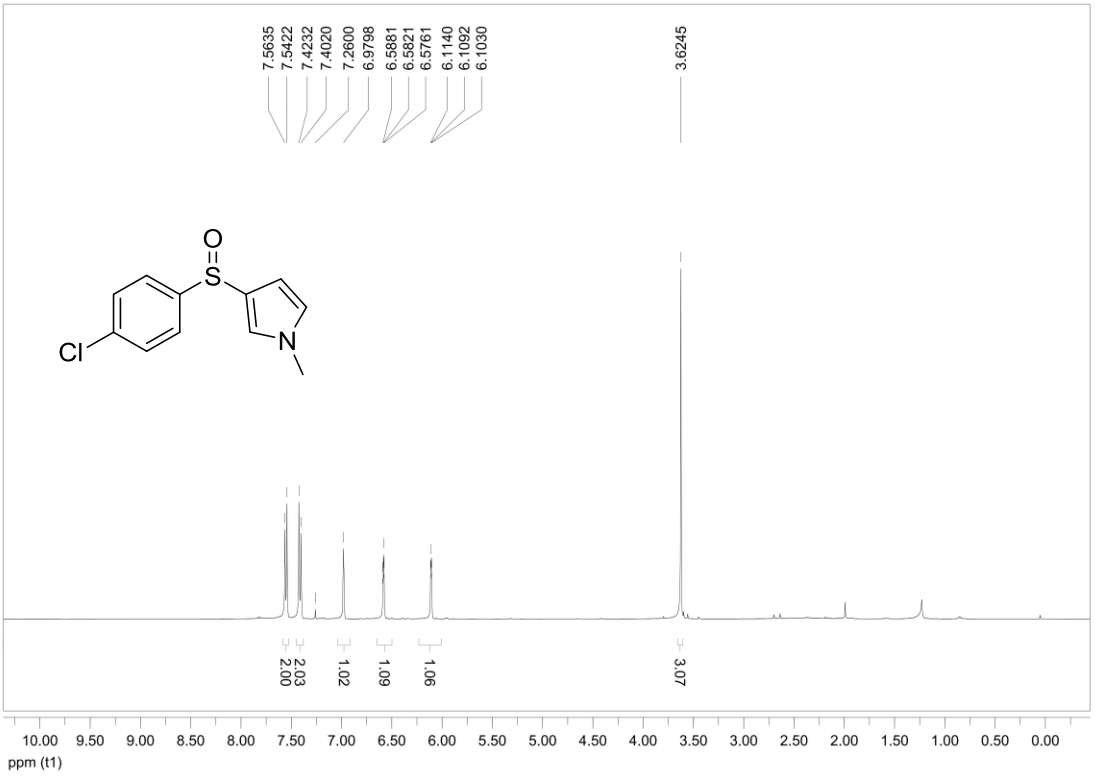


^{13}C NMR (100 MHz, $CDCl_3$)

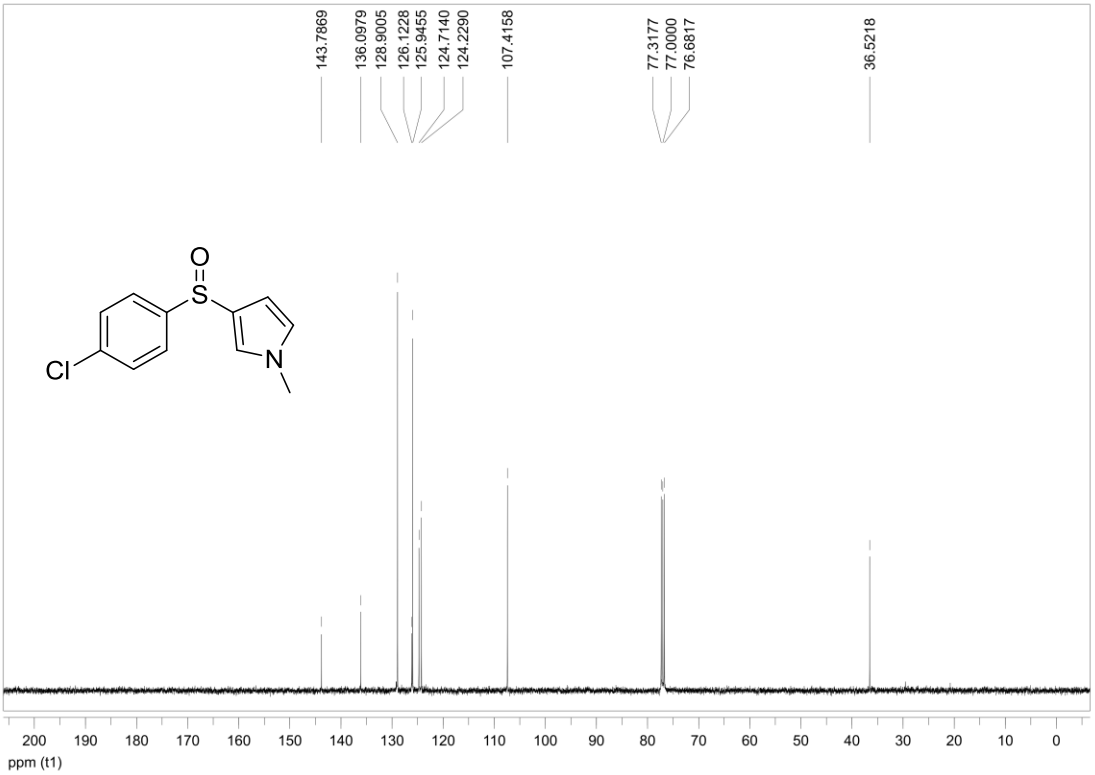


Sulfoxide **8c**

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

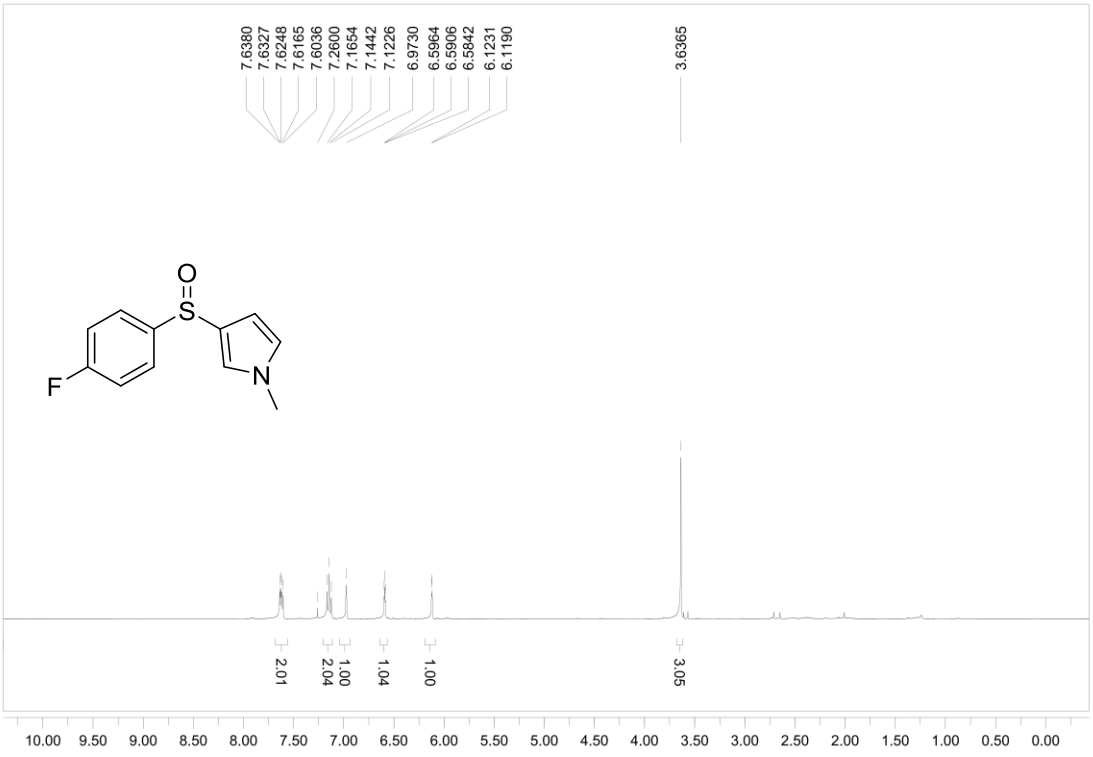


^{13}C NMR (100 MHz, $CDCl_3$)

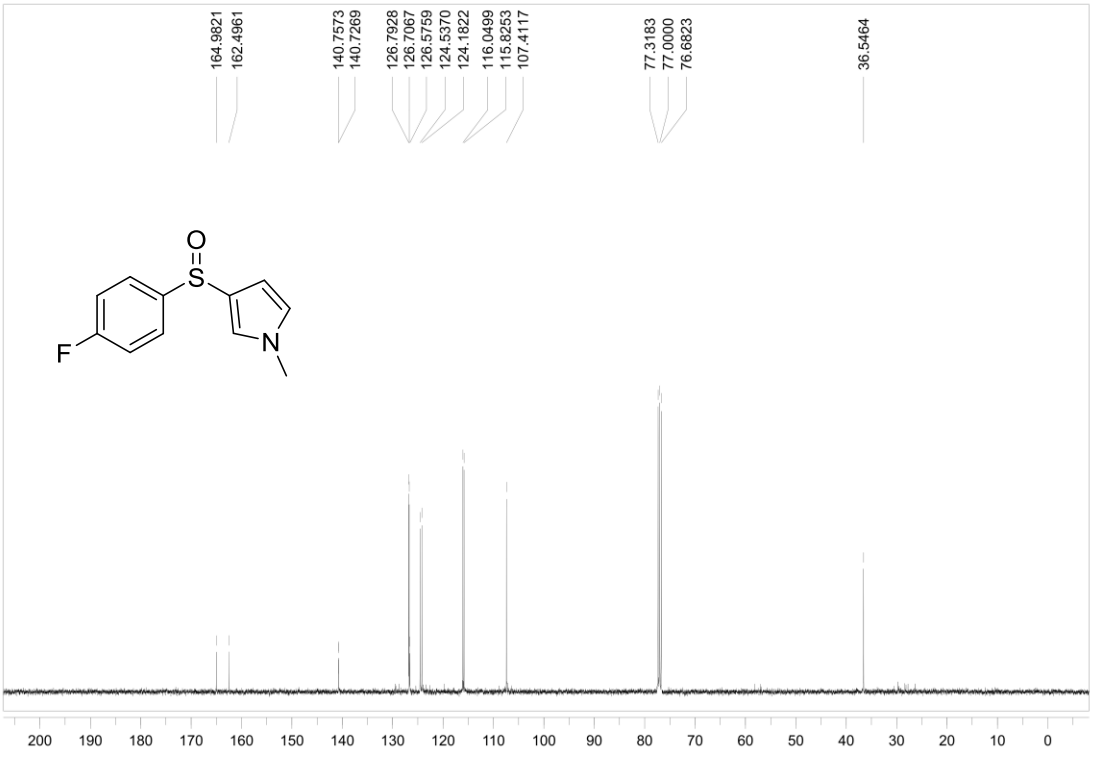


Sulfoxide **8d**

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

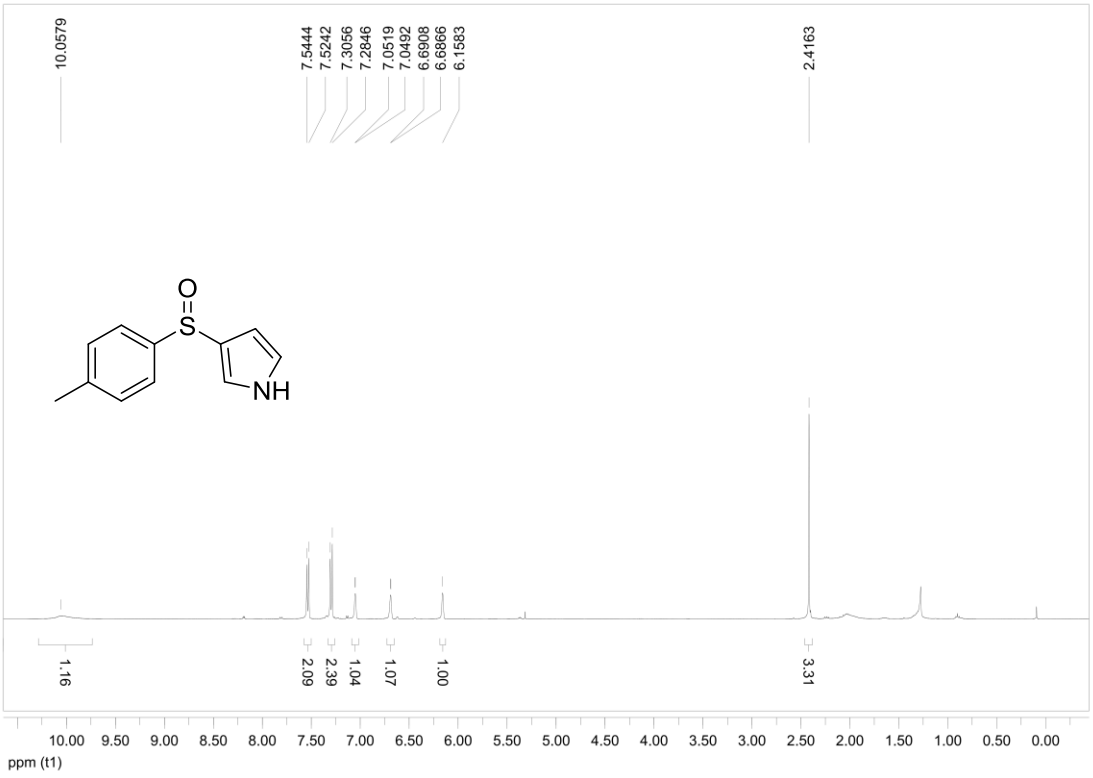


^{13}C NMR (100 MHz, $CDCl_3$)

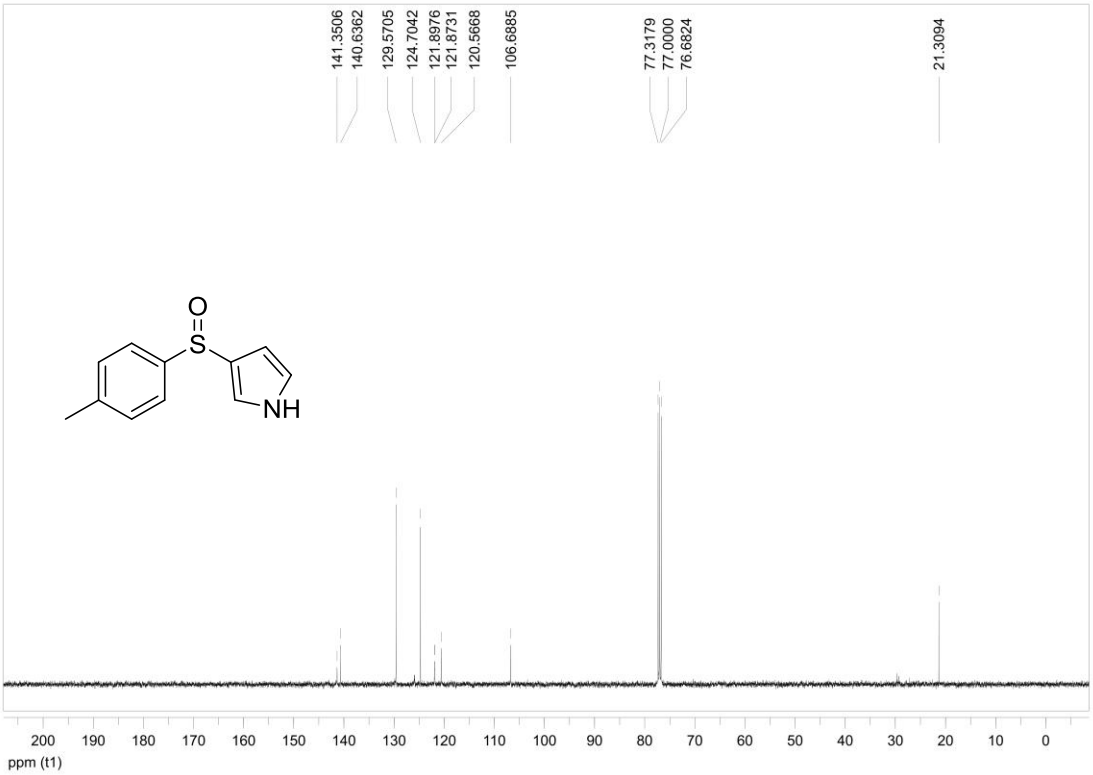


Sulfoxide **8e**

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

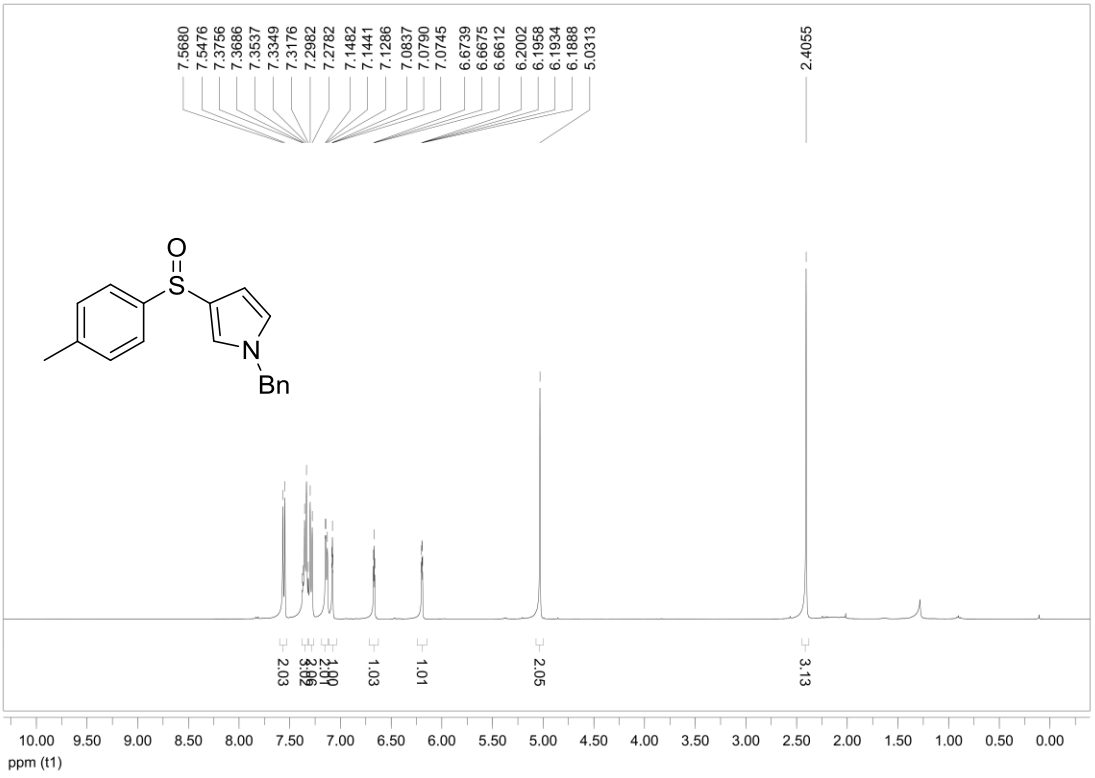


^{13}C NMR (100 MHz, $CDCl_3$)

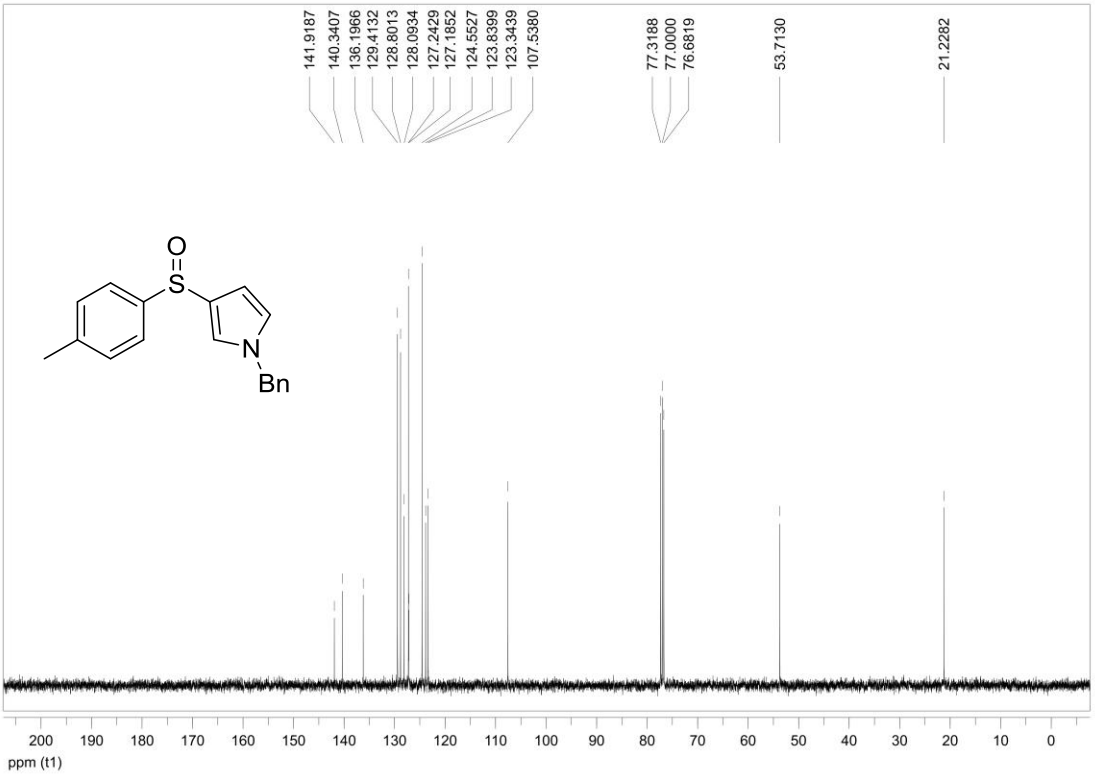


Sulfoxide **8f**

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

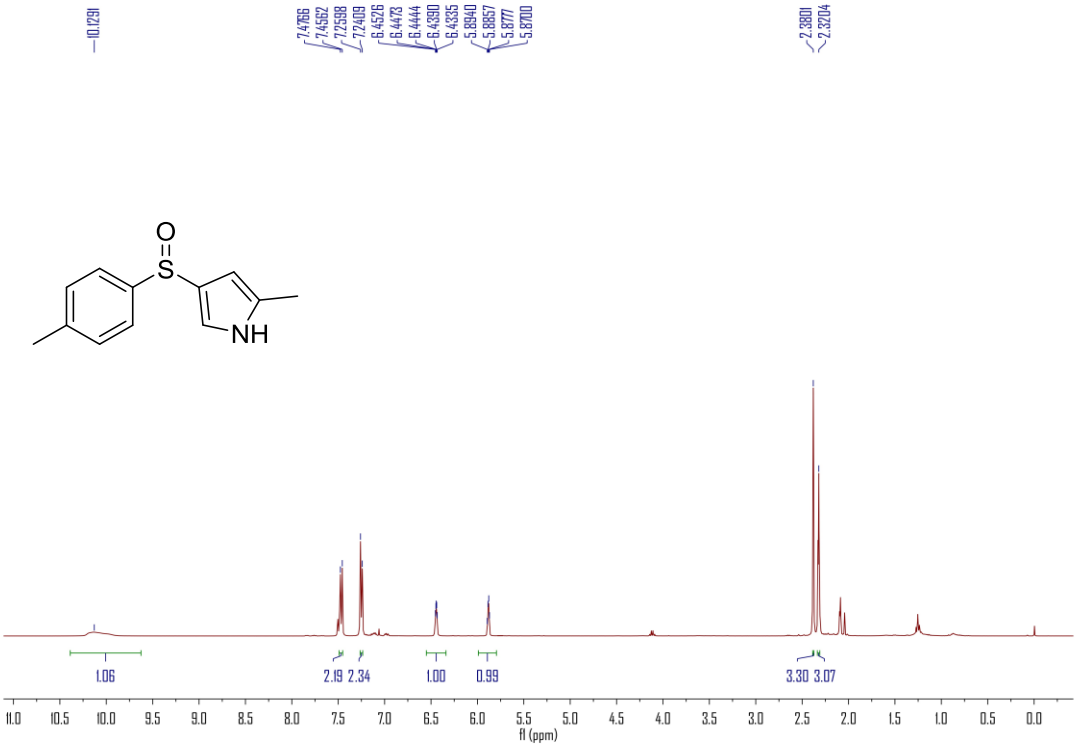


^{13}C NMR (100 MHz, $CDCl_3$)

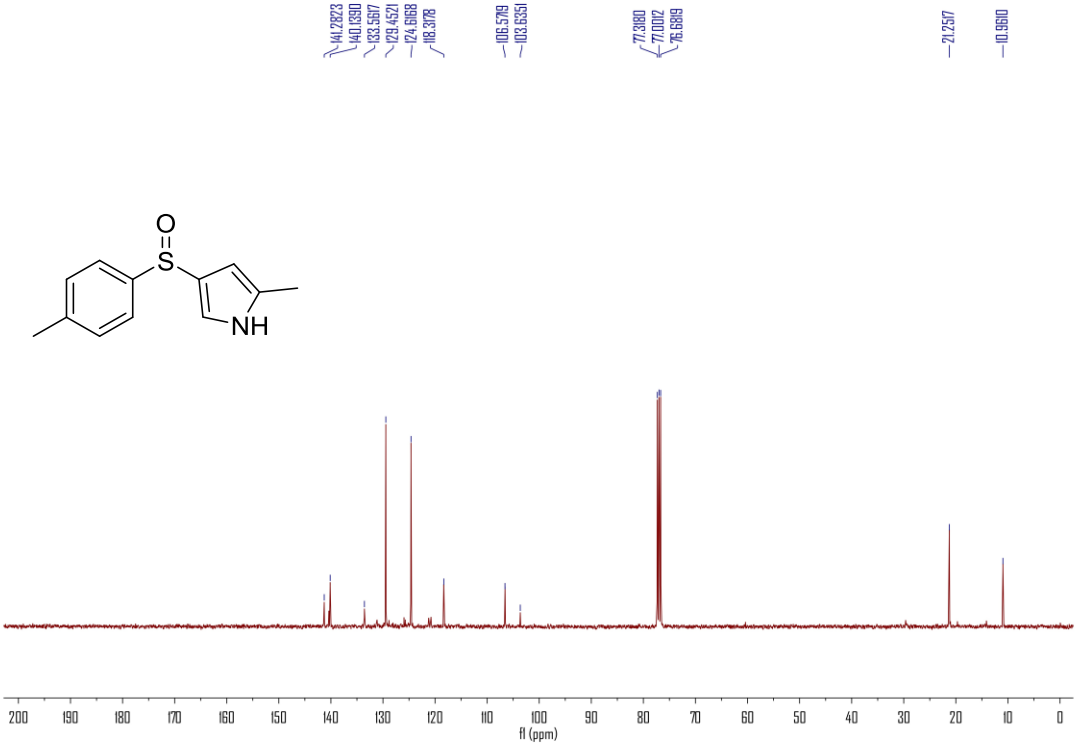


Sulfoxide **8g**

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



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



6. References

1 A. U. Meyer, A. Wimmer and B. König, *Angew. Chem., Int. Ed.* 2017, **56**, 409.

2 M. Harmata, P. Zheng, C. Huang, M. G. Gomes, W. Ying, K. O. Ranyznil, G. Balan and N. L. Calkins, *J. Org. Chem.* 2007, **72**, 683.

3 P. M. Matos, W. Lewis, J. C. Moore, R. A. Stockman, *Org. Lett.* 2018, **20**, 3674.