

Supporting Information
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Supporting Information

TMSOTf-Promoted Sulfinylation of Electron-Rich Aromatics with Sodium Arylsulfonates

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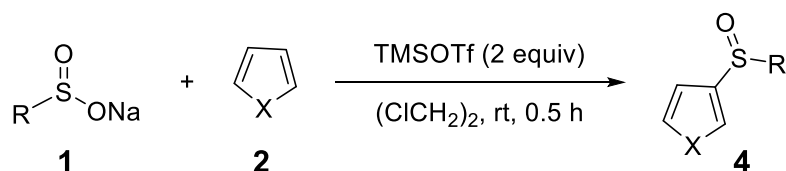
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2. General Information

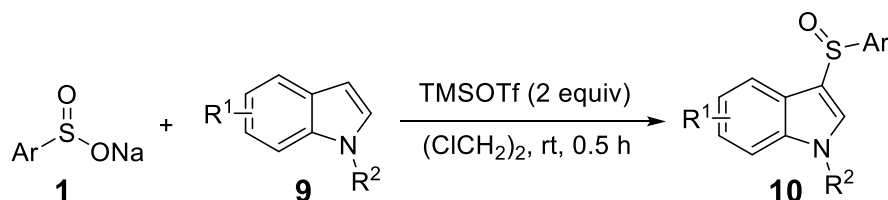
Unless otherwise noted, all reactants or reagents including solvents were obtained from commercial suppliers and used without further purification. TLC plates were visualized by exposure to ultra violet light (UV). High-resolution mass spectra (HRMS) were recorded by using an Electrothermal LTQ-Orbitrap mass spectrometer. Melting points were measured by using a Gongyi X-5 microscopy digital melting point apparatus and are uncorrected. ^1H NMR and ^{13}C NMR spectra were obtained by using a Bruker Avance III 400 MHz NMR 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, d_6 -DMSO: 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, d_6 -DMSO: 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 Sulfoxides

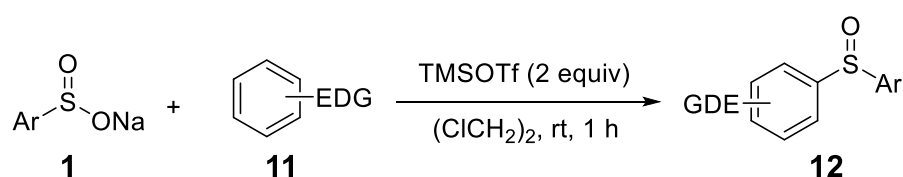
General procedure for the preparation of sulfoxides 4. The mixture of a sodium arylsulfinate (0.2 mmol, 1.0 equiv), a pyrrole/thiophene (0.3 mmol, 1.5 equiv) and TMSOTf (0.4 mmol, 2.0 equiv) in (CICH₂)₂ (1.0 mL) was stirred at 25 °C for 0.5 h, then water (5 mL) and dichloromethane (10 mL) were added. 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 Na₂SO₄, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (ethyl acetate : petroleum ether = 1:1) to afford the desired sulfoxides **4**.



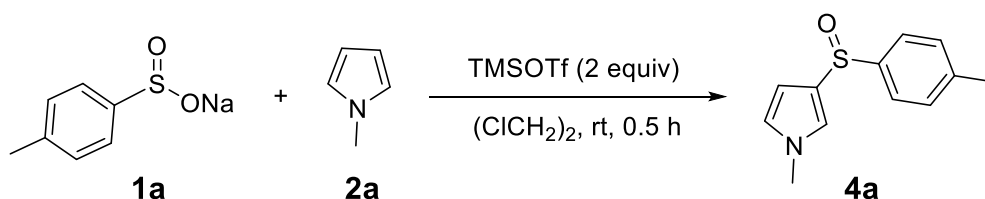
General procedure for the preparation of sulfoxides 10. The mixture of a sodium arylsulfinate (0.2 mmol, 1.0 equiv), an indole (0.4 mmol, 2.0 equiv) and TMSOTf (0.4 mmol, 2.0 equiv) in (CICH₂)₂ (1.0 mL) was stirred at 25 °C for 0.5 h, then water (5 mL) and dichloromethane (10 mL) were added. The two 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 Na₂SO₄, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (ethyl acetate : petroleum ether = 1:1) to afford the desired sulfoxides **10**.



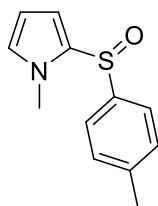
General procedure for the preparation of sulfoxides 12. The mixture of a sodium arylsulfinate (0.2 mmol, 1.0 equiv), an arene (0.4 mmol, 2.0 equiv) and TMSOTf (0.4 mmol, 2.0 equiv) in (CICH₂)₂ (1.0 mL) was stirred at 25 °C for 1 h, then water (5 mL) and dichloromethane (10 mL) were added. The two layers were separated, and the aqueous phase was extracted with dichloromethane (3 × 10 mL). The combined organic extracts were washed by brine, dried over anhydrous Na₂SO₄, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (ethyl acetate : petroleum ether = 1:1) to afford the desired sulfoxides **12**.



Gram-scale experimental procedure for sulfoxide 4a. To a stirred solution of a sodium 4-methylbenzenesulfinate (**1a**, 5.34 g, 30.0 mmol, 1.0 equiv), a *N*-Me-pyrrole (**2a**, 4.0 mL, 45.0 mmol, 1.5 equiv) in (CICH₂)₂ (60.0 mL) was slowly added TMSOTf (10.9 mL, 60.0 mmol, 2.0 equiv) at 0 °C, the reaction was allowed to warm to room temperature and stirred for 0.5 h, then water (100 mL) and dichloromethane (100 mL) were added. The two layers were separated, and the aqueous phase was extracted with dichloromethane (3 × 100 mL). The combined organic extracts were washed by brine, dried over anhydrous Na₂SO₄, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (ethyl acetate : petroleum ether = 1:1) to afford the desired sulfoxide **4a** (yield 81%, 5.32 g).

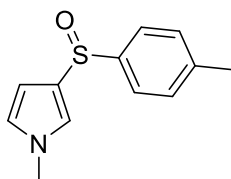


1-Methyl-2-(*p*-tolylsulfinyl)-1*H*-pyrrole (3a)



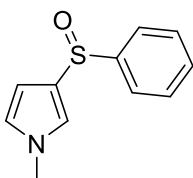
White solid, m.p. = 47–49 °C; ^1H NMR (400 MHz, CDCl_3) δ : 7.43 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 7.9 Hz, 2H), 6.74 (s, 1H), 6.52 (d, J = 1.9 Hz, 1H), 6.12 (s, 1H), 3.56 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 140.5, 139.7, 129.8, 129.7, 128.9, 124.9, 117.2, 108.0, 34.7, 21.2. Data are in accordance to that previously reported.¹

1-Methyl-3-(*p*-tolylsulfinyl)-1*H*-pyrrole (4a)



White solid, m.p. = 84–86 °C; 36.3 mg, 83% yield; ^1H NMR (400 MHz, CDCl_3) δ : 7.53 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 6.95 (t, J = 2.0 Hz, 1H), 6.58 (t, J = 2.5 Hz, 1H), 6.16 (dd, J = 3.0, 1.7 Hz, 1H), 3.64 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 141.9, 140.3, 129.3, 126.8, 124.5, 124.3, 123.9, 107.4, 36.4, 21.2. Data are in accordance to that previously reported.¹

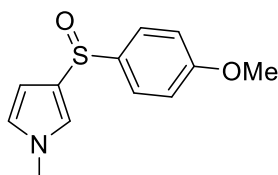
1-Methyl-3-(phenylsulfinyl)-1*H*-pyrrole (4b)



White solid, m.p. = 82–84 °C; 24.2 mg, 59% yield; ^1H NMR (400 MHz, CDCl_3) δ : 7.64 (d, J = 6.8 Hz, 2H), 7.48–7.40 (m, 3H), 6.97 (t, J = 2.0 Hz, 1H), 6.58 (t, J = 2.6 Hz, 1H), 6.14 (dd, J = 3.0, 1.7 Hz, 1H), 3.63 (s, 3H); ^{13}C NMR (100 MHz,

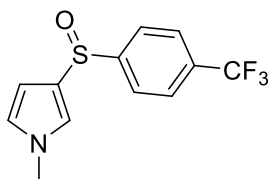
CDCl₃) δ : 145.1, 130.1, 128.7, 126.6, 124.6, 124.5, 124.0, 107.6, 36.5. Data are in accordance to that previously reported.¹

3-((4-Methoxyphenyl)sulfinyl)-1-methyl-1H-pyrrole (4c)



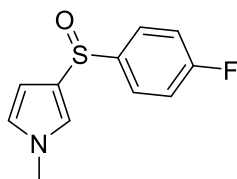
Pale yellow oil, 32.0 mg, 68% yield; ¹H NMR (400 MHz, CDCl₃) δ : 7.59–7.55 (m, 2H), 6.99–6.95 (m, 2H), 6.92 (t, J = 2.0 Hz, 1H), 6.58 (t, J = 2.6 Hz, 1H), 6.14 (dd, J = 2.9, 1.8 Hz, 1H), 3.83 (s, 3H), 3.63 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 161.1, 136.2, 127.0, 126.2, 124.0, 123.9, 114.1, 107.2, 55.3, 36.4; HRMS (ESI) m/z : Calcd for C₁₂H₁₃NaNO₂S [M+Na]⁺: 258.0559. Found: 258.0562.

1-Methyl-3-((4-(trifluoromethyl)phenyl)sulfinyl)-1H-pyrrole (4d)



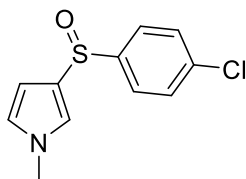
Pale yellow oil, 37.7 mg, 69% yield; ¹H NMR (400 MHz, CDCl₃) δ : 7.74 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.5 Hz, 2H), 7.03 (t, J = 2.0 Hz, 1H), 6.60 (t, J = 2.5 Hz, 1H), 6.10 (dd, J = 3.0, 1.8 Hz, 1H), 3.64 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 149.8, 131.9 (q, J_{C-F} = 32.7 Hz), 125.7, 125.6 (q, J_{C-F} = 3.5 Hz), 125.0, 124.9, 124.4, 123.6 (q, J_{C-F} = 271.3 Hz), 107.5, 36.5; HRMS (ESI) m/z : Calcd for C₁₂H₁₀F₃NaNOS [M+Na]⁺: 296.0327. Found: 296.0334.

3-((4-Fluorophenyl)sulfinyl)-1-methyl-1H-pyrrole (4e)



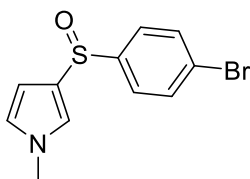
Pale yellow oil, 14.3 mg, 32% yield; ^1H NMR (400 MHz, CDCl_3) δ : 7.65–7.61 (m, 2H), 7.18–7.13 (m, 2H), 6.98 (t, $J = 2.0$ Hz, 1H), 6.60 (t, $J = 2.6$ Hz, 1H), 6.13 (dd, $J = 2.9, 1.7$ Hz, 1H), 3.65 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 163.8 (d, $J_{\text{C-F}} = 250.1$ Hz), 140.9 (d, $J_{\text{C-F}} = 3.0$ Hz), 126.8 (d, $J_{\text{C-F}} = 8.7$ Hz), 124.5, 124.2, 116.0 (d, $J_{\text{C-F}} = 22.4$ Hz), 107.5, 36.6. Data are in accordance to that previously reported.¹

3-((4-Chlorophenyl)sulfinyl)-1-methyl-1H-pyrrole (4f)



Yellow solid, m.p. = 64–66 °C; 39.2 mg, 82% yield; ^1H NMR (400 MHz, CDCl_3) δ : 7.55 (d, $J = 8.5$ Hz, 2H), 7.41 (d, $J = 8.5$ Hz, 2H), 6.98 (t, $J = 2.0$ Hz, 1H), 6.58 (t, $J = 2.4$ Hz, 1H), 6.11 (dd, $J = 2.9, 1.8$ Hz, 1H), 3.62 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 143.8, 136.1, 128.9, 126.1, 125.9, 124.7, 124.2, 107.4, 36.5. Data are in accordance to that previously reported.¹

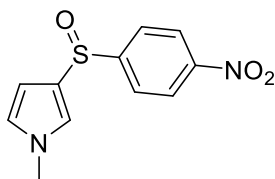
3-((4-Bromophenyl)sulfinyl)-1-methyl-1H-pyrrole (4g)



Colorless oil, 36.8 mg, 65% yield; ^1H NMR (400 MHz, CDCl_3) δ : 7.55 (d, $J = 8.6$ Hz, 2H), 7.47 (d, $J = 8.5$ Hz, 2H), 6.97 (t, $J = 2.0$ Hz, 1H), 6.57–6.56 (m, 1H),

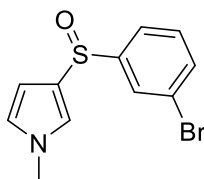
6.09 (dd, $J = 3.0, 1.7$ Hz, 1H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 144.4, 131.7, 126.1, 126.0, 124.7, 124.2, 124.2, 107.3, 36.5; HRMS (ESI) m/z : Calcd for $\text{C}_{11}\text{H}_{10}\text{NaBrNOS}$ $[\text{M}+\text{Na}]^+$: 305.9559. Found: 305.9564.

1-Methyl-3-((4-nitrophenyl)sulfinyl)-1H-pyrrole (4h)



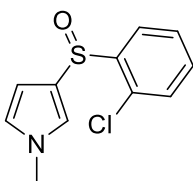
Pale yellow oil, 17.5 mg, 35% yield; ^1H NMR (400 MHz, CDCl_3) δ : 8.30 (d, $J = 8.8$ Hz, 2H), 7.80 (d, $J = 8.8$ Hz, 2H), 7.08 (t, $J = 2.0$ Hz, 1H), 6.62 (t, $J = 2.6$ Hz, 1H), 6.10 (dd, $J = 3.0, 1.7$ Hz, 1H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 153.1, 148.8, 125.6, 125.3, 125.2, 124.7, 123.8, 107.5, 36.7; HRMS (ESI) m/z : Calcd for $\text{C}_{11}\text{H}_{10}\text{NaN}_2\text{O}_3\text{S}$ $[\text{M}+\text{Na}]^+$: 273.0304. Found: 273.0308.

3-((3-Bromophenyl)sulfinyl)-1-methyl-1H-pyrrole (4i)



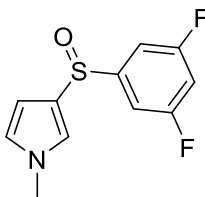
Colorless oil, 36.8 mg, 65% yield; ^1H NMR (400 MHz, CDCl_3) δ : 7.78 (t, $J = 1.8$ Hz, 1H), 7.55–7.52 (m, 2H), 7.32 (t, $J = 7.8$ Hz, 1H), 7.01 (t, $J = 2.0$ Hz, 1H), 6.61 (dd, $J = 2.9, 2.2$ Hz, 1H), 6.15 (dd, $J = 2.9, 1.8$ Hz, 1H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 147.6, 132.9, 130.1, 127.2, 125.8, 124.8, 124.2, 123.0, 122.8, 107.3, 36.5; HRMS (ESI) m/z : Calcd for $\text{C}_{11}\text{H}_{10}\text{NaBrNOS}$ $[\text{M}+\text{Na}]^+$: 305.9559. Found: 305.9565.

3-((2-Chlorophenyl)sulfinyl)-1-methyl-1H-pyrrole (4j)



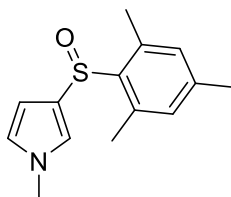
Pale yellow oil, 37.2 mg, 78% yield; ^1H NMR (400 MHz, CDCl_3) δ : 8.13 (dd, J = 7.8, 1.7 Hz, 1H), 7.50 (td, J = 7.5, 1.3 Hz, 1H), 7.37 (td, J = 7.6, 1.7 Hz, 1H), 7.29 (dd, J = 8.0, 1.3 Hz, 1H), 6.94 (t, J = 2.0 Hz, 1H), 6.54 (t, J = 2.6 Hz, 1H), 6.12 (dd, J = 2.9, 1.8 Hz, 1H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 143.0, 131.3, 130.6, 129.7, 127.4, 125.5, 124.8, 124.5, 123.6, 107.6, 36.6; HRMS (ESI) m/z : Calcd for $\text{C}_{11}\text{H}_{10}\text{NaClNOS}$ [$\text{M}+\text{Na}$] $^+$: 262.0064. Found: 262.0069.

3-((3,5-Difluorophenyl)sulfinyl)-1-methyl-1H-pyrrole (4k)



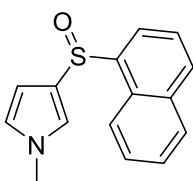
Colorless oil, 14.9 mg, 31% yield; ^1H NMR (400 MHz, CDCl_3) δ : 7.20–7.14 (m, 2H), 7.05 (t, J = 2.0 Hz, 1H), 6.84 (tt, J = 8.5, 2.3 Hz, 1H), 6.62 (d, J = 2.6 Hz, 1H), 6.15 (dd, J = 3.0, 1.8 Hz, 1H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 162.9 (dd, $J_{\text{C-F}}$ = 253.8, 11.4 Hz), 150.1 (t, $J_{\text{C-F}}$ = 7.0 Hz), 125.5, 125.0, 124.5, 107.8 (dd, $J_{\text{C-F}}$ = 19.8, 7.7 Hz), 107.4, 105.4 (t, $J_{\text{C-F}}$ = 25.5 Hz), 36.6; HRMS (ESI) m/z : Calcd for $\text{C}_{11}\text{H}_9\text{NaF}_2\text{NOS}$ [$\text{M}+\text{Na}$] $^+$: 264.0265. Found: 264.0268.

3-(Mesitylsulfinyl)-1-methyl-1H-pyrrole (4l)



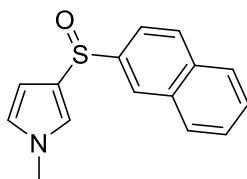
Colorless oil, 41.5 mg, 84% yield; ^1H NMR (400 MHz, CDCl_3) δ : 6.85 (s, 2H), 6.68 (t, $J = 2.1$ Hz, 1H), 6.58 (t, $J = 2.6$ Hz, 1H), 6.06 (dd, $J = 2.9, 1.7$ Hz, 1H), 3.61 (s, 3H), 2.48 (s, 6H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 140.7, 138.6, 136.1, 130.5, 124.9, 123.4, 122.2, 107.6, 36.5, 21.0, 19.3; HRMS (ESI) m/z : Calcd for $\text{C}_{14}\text{H}_{17}\text{NaNOS}$ $[\text{M}+\text{Na}]^+$: 270.0923. Found: 270.0928.

1-Methyl-3-(naphthalen-1-ylsulfinyl)-1H-pyrrole (4m)



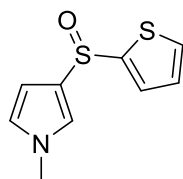
Pale yellow oil, 39.2 mg, 77% yield; ^1H NMR (400 MHz, CDCl_3) δ : 8.36 (dd, $J = 7.2, 1.3$ Hz, 1H), 7.94–7.86 (m, 3H), 7.66 (t, $J = 7.7$ Hz, 1H), 7.48–7.40 (m, 2H), 6.86 (t, $J = 2.0$ Hz, 1H), 6.46–6.45 (m, 1H), 6.12 (dd, $J = 2.9, 1.5$ Hz, 1H), 3.49 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 139.9, 133.3, 130.6, 128.6, 128.5, 126.6, 126.2, 125.8, 125.2, 124.0, 123.5, 122.7, 122.5, 107.9, 36.4; HRMS (ESI) m/z : Calcd for $\text{C}_{15}\text{H}_{13}\text{NaNOS}$ $[\text{M}+\text{Na}]^+$: 278.0610. Found: 278.0616.

1-Methyl-3-(naphthalen-2-ylsulfinyl)-1H-pyrrole (4n)



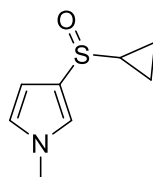
Pale yellow oil, 33.6 mg, 66% yield; ^1H NMR (400 MHz, CDCl_3) δ : 8.35 (s, 1H), 7.96–7.92 (m, 1H), 7.86–7.83 (m, 2H), 7.56–7.52 (m, 2H), 7.44 (dd, $J = 8.6, 1.8$ Hz, 1H), 6.99 (d, $J = 2.1$ Hz, 1H), 6.56 (q, $J = 2.5, 2.1$ Hz, 1H), 6.15 (dd, $J = 3.0, 1.6$ Hz, 1H), 3.59 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 142.2, 133.8, 132.7, 128.6, 128.4, 127.8, 127.2, 126.9, 126.3, 124.7, 124.3, 124.0, 121.2, 107.7, 36.4; HRMS (ESI) m/z : Calcd for $\text{C}_{15}\text{H}_{13}\text{NaNOS}$ $[\text{M}+\text{Na}]^+$: 278.0610. Found: 278.0619.

1-Methyl-3-(thiophen-2-ylsulfinyl)-1H-pyrrole (4o)



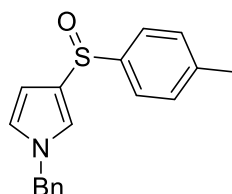
Pale yellow oil, 19.0 mg, 45% yield; ^1H NMR (400 MHz, CDCl_3) δ : 7.54 (dd, J = 5.0, 1.3 Hz, 1H), 7.42 (dd, J = 3.7, 1.3 Hz, 1H), 7.07–7.04 (m, 2H), 6.65 (t, J = 2.6 Hz, 1H), 6.36 (dd, J = 3.0, 1.8 Hz, 1H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 148.4, 130.4, 129.2, 127.2, 126.5, 124.1, 123.7, 107.1, 36.6; HRMS (ESI) m/z : Calcd for $\text{C}_9\text{H}_9\text{NaNOS}_2$ [$\text{M}+\text{Na}$] $^+$: 234.0018. Found: 234.0022.

3-(Cyclopropylsulfinyl)-1-methyl-1H-pyrrole (4p)



Colorless oil, 16.9 mg, 50% yield; ^1H NMR (400 MHz, CDCl_3) δ : 7.01 (d, J = 2.5 Hz, 1H), 6.65 (t, J = 2.7 Hz, 1H), 6.47–6.45 (m, 1H), 3.66 (s, 3H), 2.38–2.31 (m, 1H), 1.31–1.24 (m, 1H), 1.02–0.94 (m, 1H), 0.92–0.78 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 125.5, 123.7, 122.9, 106.3, 36.5, 31.6, 2.61, 2.59; HRMS (ESI) m/z : Calcd for $\text{C}_8\text{H}_{11}\text{NaNOS}$ [$\text{M}+\text{Na}$] $^+$: 192.0454. Found: 192.0459.

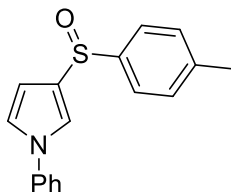
1-Benzyl-3-(*p*-tolylsulfinyl)-1H-pyrrole (4q)



White solid, m.p. = 103–105 °C; 53.1 mg, 90% yield; ^1H NMR (400 MHz, CDCl_3) δ : 7.56 (d, J = 8.1 Hz, 2H), 7.38–7.27 (m, 5H), 7.15–7.07 (m, 3H), 6.67 (t, J = 2.6 Hz, 1H), 6.19 (dd, J = 3.0, 1.8 Hz, 1H), 5.03 (s, 2H), 2.41 (s, 3H); ^{13}C NMR

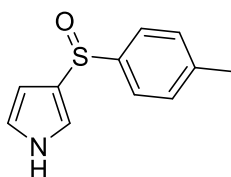
(100 MHz, CDCl₃) δ : 141.9, 140.3, 136.2, 129.4, 128.8, 128.1, 127.2, 127.1, 124.6, 123.8, 123.3, 107.5, 53.7, 21.2. Data are in accordance to that previously reported.¹

1-Phenyl-3-(*p*-tolylsulfinyl)-1*H*-pyrrole (4r)



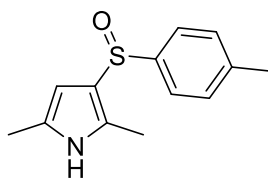
Yellow solid, m.p. = 84–86 °C; 50.0 mg, 89% yield; ¹H NMR (400 MHz, CDCl₃) δ : 7.59 (d, *J* = 8.1 Hz, 2H), 7.44–7.39 (m, 3H), 7.34–7.27 (m, 5H), 7.03 (t, *J* = 2.7 Hz, 1H), 6.33 (dd, *J* = 3.1, 1.7 Hz, 1H), 2.38 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 141.6, 140.6, 139.4, 129.6, 129.5, 129.2, 126.9, 124.6, 121.9, 121.7, 120.9, 108.7, 21.2; HRMS (ESI) *m/z*: Calcd for C₁₇H₁₅NaNOS [M+Na]⁺: 304.0767. Found: 304.0771.

3-(*p*-Tolylsulfinyl)-1*H*-pyrrole (4t)



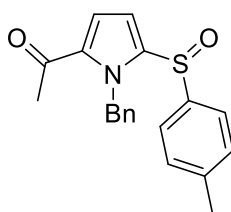
White solid, m.p. = 150–152 °C; 16.4 mg, 41% yield; ¹H NMR (400 MHz, CDCl₃) δ : 10.03 (s, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.03–7.02 (m, 1H), 6.67–6.66 (m, 1H), 6.13 (dd, *J* = 2.8, 1.3 Hz, 1H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ : 141.4, 140.6, 129.6, 124.7, 121.9, 121.9, 120.6, 106.7, 21.3. Data are in accordance to that previously reported.¹

2,5-Dimethyl-3-(*p*-tolylsulfinyl)-1*H*-pyrrole (4u)



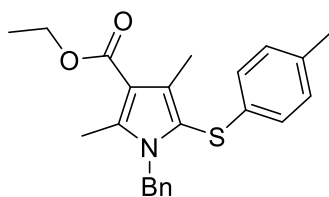
Pale yellow oil, 16.7 mg, 36% yield; ^1H NMR (400 MHz, CDCl_3) δ : 9.74 (br, 1H), 7.50 (d, $J = 8.0$ Hz, 2H), 7.28 (d, $J = 7.8$ Hz, 2H), 5.58 (s, 1H), 2.40 (s, 3H), 2.34 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 141.5, 139.9, 132.5, 129.3, 128.6, 124.5, 120.5, 103.3, 21.2, 12.5, 10.8; HRMS (ESI) m/z : Calcd for $\text{C}_{13}\text{H}_{15}\text{NaNOS}$ $[\text{M}+\text{Na}]^+$: 256.0767. Found: 256.0773.

1-(1-Benzyl-5-(*p*-tolylsulfinyl)-1*H*-pyrrol-2-yl)ethan-1-one (3w)



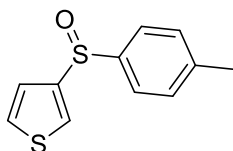
Pale yellow oil, 8.8 mg, 13% yield; ^1H NMR (400 MHz, CDCl_3) δ : 7.54 (d, $J = 8.2$ Hz, 2H), 7.32–7.26 (m, 5H), 7.15 (d, $J = 1.8$ Hz, 1H), 7.12–7.09 (m, 1H), 6.98 (d, $J = 1.8$ Hz, 1H), 5.54 (d, $J = 15.0$ Hz, 1H), 5.50 (d, $J = 15.0$ Hz, 1H), 2.41 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 188.6, 141.3, 141.2, 136.4, 131.7, 130.2, 129.8, 128.7, 127.9, 127.4, 127.4, 124.5, 117.5, 53.2, 27.4, 21.3; HRMS (ESI) m/z : Calcd for $\text{C}_{20}\text{H}_{19}\text{NaNO}_2\text{S}$ $[\text{M}+\text{Na}]^+$: 360.1029. Found: 360.1035.

Ethyl 1-benzyl-2,4-dimethyl-5-(*p*-tolylthio)-1*H*-pyrrole-3-carboxylate (5x)



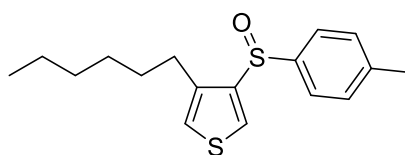
Yellow oil, 35.6 mg, 47% yield; ^1H NMR (400 MHz, CDCl_3) δ : 7.25–7.17 (m, 3H), 6.99 (d, J = 7.9 Hz, 2H), 6.88–6.83 (m, 4H), 6.98 (d, J = 1.8 Hz, 1H), 5.20 (s, 2H), 4.32 (q, J = 6.8 Hz, 2H), 2.47 (s, 3H), 2.44 (s, 3H), 2.27 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 165.7, 139.4, 137.1, 135.1, 134.3, 130.4, 129.6, 128.5, 127.1, 125.9, 125.7, 116.7, 112.3, 59.3, 47.5, 20.8, 14.4, 12.9, 12.5; HRMS (ESI) m/z : Calcd for $\text{C}_{23}\text{H}_{25}\text{NaNO}_2\text{S}$ $[\text{M}+\text{Na}]^+$: 402.1498. Found: 402.1502.

3-(*p*-Tolylsulfinyl)thiophene (4y)



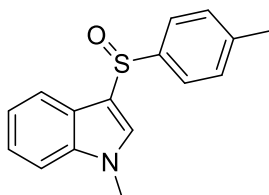
Dark brown oil, 10.2 mg, 23% yield; ^1H NMR (400 MHz, CDCl_3) δ : 7.59–7.53 (m, 4H), 7.30 (d, J = 7.7 Hz, 2H), 7.06–7.03 (m, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 148.2, 141.8, 141.7, 132.0, 131.0, 129.8, 127.1, 124.3, 21.3; HRMS (ESI) m/z : Calcd for $\text{C}_{11}\text{H}_{10}\text{NaOS}_2$ $[\text{M}+\text{Na}]^+$: 245.0065. Found: 245.0072.

3-Hexyl-4-(*p*-tolylsulfinyl)thiophene (4z)



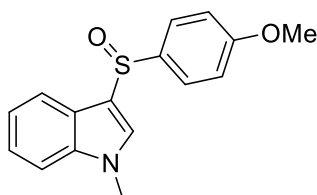
Yellow oil, 38.6 mg, 63% yield; ^1H NMR (400 MHz, CDCl_3) δ : 7.56 (d, J = 8.2 Hz, 2H), 7.45 (d, J = 5.1 Hz, 1H), 7.29 (d, J = 8.0 Hz, 1H), 6.89 (d, J = 5.1 Hz, 1H), 2.89 (t, J = 7.8 Hz, 2H), 2.40 (s, 3H), 1.71–1.57 (m, 2H), 1.38–1.24 (m, 6H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 148.4, 141.7, 141.7, 141.3, 131.2, 129.7, 128.9, 124.5, 31.4, 30.8, 28.9, 28.7, 22.4, 21.3, 13.9; HRMS (ESI) m/z : Calcd for $\text{C}_{17}\text{H}_{22}\text{NaOS}_2$ $[\text{M}+\text{Na}]^+$: 329.1004. Found: 329.1008.

1-Methyl-3-(*p*-tolylsulfinyl)-1*H*-indole (10a)



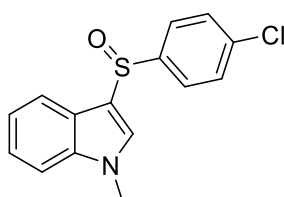
White solid, m.p. = 138–139 °C; 42.0 mg, 78% yield; ¹H NMR (400 MHz, CDCl₃) δ: 7.62 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.34–7.24 (m, 4H), 7.12–7.08 (m, 1H), 3.79 (s, 3H), 2.40 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 140.9, 140.3, 137.6, 132.5, 129.5, 124.8, 124.3, 123.2, 121.3, 119.8, 116.5, 110.0, 33.2, 21.2. Data are in accordance to that previously reported.¹

3-((4-Methoxyphenyl)sulfinyl)-1-methyl-1*H*-indole (10b)



White solid, m.p. = 146–148 °C; 35.3 mg, 62% yield; ¹H NMR (400 MHz, CDCl₃) δ: 7.66 (d, *J* = 7.5 Hz, 2H), 7.49 (s, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.35–7.25 (m, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 2H), 3.84 (s, 3H), 3.81 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 161.2, 137.7, 135.4, 132.2, 126.6, 124.3, 123.2, 121.2, 119.8, 116.9, 114.3, 110.0, 55.3, 33.3. Data are in accordance to that previously reported.²

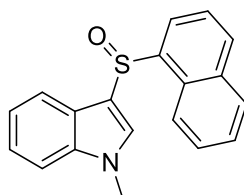
3-((4-Chlorophenyl)sulfinyl)-1-methyl-1*H*-indole (10c)



White solid, m.p. = 144–146 °C; 31.2 mg, 54% yield; ¹H NMR (400 MHz, CDCl₃)

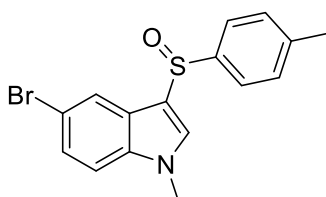
δ : 7.64 (d, J = 8.4 Hz, 2H), 7.54 (s, 1H), 7.45–7.40 (m, 3H), 7.34 (d, J = 8.2 Hz, 1H), 7.27 (t, J = 7.6 Hz, 1H), 7.10 (t, J = 7.5 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 142.9, 137.7, 136.1, 132.9, 129.0, 126.2, 124.0, 123.4, 121.5, 119.7, 115.8, 110.2, 33.3. Data are in accordance to that previously reported.¹

1-Methyl-3-(naphthalen-1-ylsulfinyl)-1H-indole (10d)



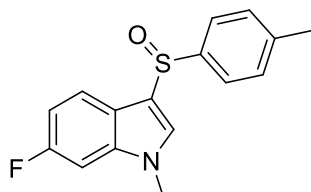
White solid, m.p. = 134–136 °C; 44.5 mg, 73% yield; ^1H NMR (400 MHz, CDCl_3) δ : 8.57 (d, J = 7.2 Hz, 1H), 8.01 (d, J = 8.2 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.79–7.75 (m, 2H), 7.48 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.28–7.23 (m, 3H), 7.20–7.15 (m, 1H), 3.68 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 138.8, 137.3, 133.5, 131.8, 131.0, 128.9, 128.6, 126.7, 126.3, 125.3, 125.2, 123.7, 123.1, 122.5, 121.4, 119.3, 116.3, 110.0, 33.2. Data are in accordance to that previously reported.²

5-Bromo-1-methyl-3-(*p*-tolylsulfinyl)-1H-indole (10e)



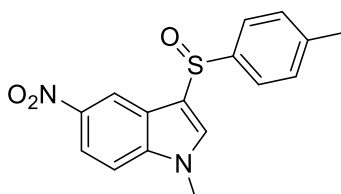
White solid, m.p. = 142–144 °C; 54.1 mg, 78% yield; ^1H NMR (400 MHz, CDCl_3) δ : 7.63 (d, J = 1.5 Hz, 1H), 7.58 (d, J = 8.1 Hz, 2H), 7.43 (s, 1H), 7.32–7.28 (m, 3H), 7.16 (d, J = 8.7 Hz, 1H), 3.75 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 140.6, 140.5, 136.3, 133.1, 129.6, 126.2, 125.8, 124.6, 122.2, 116.4, 114.7, 111.5, 33.4, 21.2. Data are in accordance to that previously reported.¹

6-Fluoro-1-methyl-3-(*p*-tolylsulfinyl)-1*H*-indole (10f)



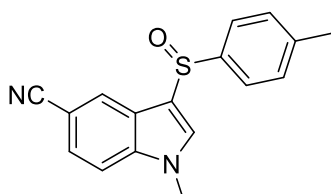
White solid, m.p. = 143–145 °C; 45.3 mg, 79% yield; ¹H NMR (400 MHz, CDCl₃) δ: 7.57 (d, *J* = 8.1 Hz, 2H), 7.48 (s, 1H), 7.35 (dd, *J* = 8.8, 5.2 Hz, 1H), 7.27 (d, *J* = 8.9 Hz, 2H), 6.99 (dd, *J* = 9.2, 1.4 Hz, 1H), 6.83 (dt, *J* = 9.1, 2.0 Hz, 1H), 3.76 (s, 3H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 160.3 (d, *J*_{C-F} = 241.0 Hz), 140.8, 140.5, 138.0 (d, *J*_{C-F} = 11.9 Hz), 132.9, 129.6, 124.8, 121.0 (d, *J*_{C-F} = 10.1 Hz), 120.6, 117.1 (d, *J*_{C-F} = 3.0 Hz), 110.1 (d, *J*_{C-F} = 24.7 Hz), 96.7 (d, *J*_{C-F} = 26.5 Hz), 33.4, 21.2. Data are in accordance to that previously reported.¹

1-Methyl-5-nitro-3-(*p*-tolylsulfinyl)-1*H*-indole (10g)



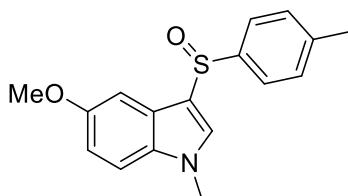
Yellow oil, 40.2 mg, 64% yield; ¹H NMR (400 MHz, CDCl₃) δ: 8.37 (d, *J* = 2.1 Hz, 1H), 8.11 (dd, *J* = 9.1, 2.2 Hz, 1H), 7.62 (s, 1H), 7.61 (d, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 9.1 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 3.87 (s, 3H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 142.6, 141.3, 140.3, 140.2, 134.8, 129.9, 124.7, 123.6, 120.2, 118.7, 116.8, 110.3, 33.8, 21.3. HRMS (ESI) *m/z*: Calcd for C₁₆H₁₄N₂NaO₃S [M+Na]⁺: 337.0617. Found: 337.0623.

1-Methyl-3-(*p*-tolylsulfinyl)-1*H*-indole-5-carbonitrile (10h)



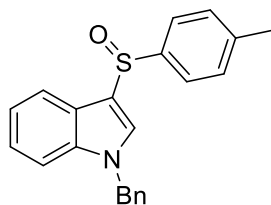
Cyan oil, 38.8 mg, 66% yield; ^1H NMR (400 MHz, CDCl_3) δ : 7.78 (s, 1H), 7.61 (s, 1H), 7.55 (d, $J = 8.1$ Hz, 2H), 7.44 (d, $J = 8.6$ Hz, 1H), 7.37 (d, $J = 8.6$ Hz, 1H), 7.29 (d, $J = 8.0$ Hz, 2H), 3.84 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 141.1, 140.2, 139.2, 134.2, 129.8, 126.1, 125.2, 124.6, 123.9, 119.6, 118.3, 111.1, 104.6, 33.6, 21.2. HRMS (ESI) m/z : Calcd for $\text{C}_{17}\text{H}_{14}\text{N}_2\text{NaOS}$ $[\text{M}+\text{Na}]^+$: 317.0719. Found: 317.0727.

5-Methoxy-1-methyl-3-(*p*-tolylsulfinyl)-1*H*-indole (10i)



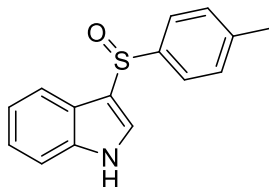
White solid, m.p. = 147–149 °C; 32.3 mg, 54% yield; ^1H NMR (400 MHz, CDCl_3) δ : 7.62 (d, $J = 8.1$ Hz, 2H), 7.42 (s, 1H), 7.29 (d, $J = 8.0$ Hz, 2H), 7.20 (d, $J = 8.9$ Hz, 1H), 6.89 (dd, $J = 8.9, 2.4$ Hz, 1H), 6.84 (d, $J = 2.3$ Hz, 1H), 3.76 (s, 3H), 3.67 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, 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. Data are in accordance to that previously reported.¹

1-Benzyl-3-(*p*-tolylsulfinyl)-1*H*-indole (10k)



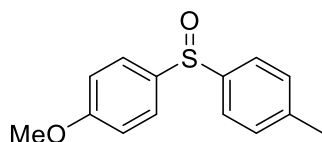
White solid, m.p. = 140–142 °C; 53.6 mg, 78% yield; ^1H NMR (400 MHz, CDCl_3) δ : 7.64 (d, $J = 7.9$ Hz, 2H), 7.59 (s, 1H), 7.49 (d, $J = 8.0$ Hz, 1H), 7.35–7.29 (m, 6H), 7.21 (t, $J = 7.7$ Hz, 1H), 7.17 (d, $J = 7.2$ Hz, 1H), 7.09 (t, $J = 7.5$ Hz, 1H), 5.31 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, 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. Data are in accordance to that previously reported.¹

3-(*p*-Tolylsulfinyl)-1*H*-indole (10l)



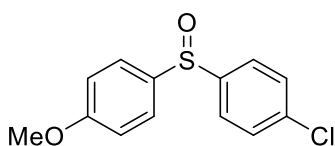
White solid, m.p. = 120–122 °C; 7.7 mg, 15% yield; ¹H NMR (400 MHz, CDCl₃) δ: 10.48 (br, 1H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 1H), 7.16 (d, *J* = 2.3 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 2.38 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) 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. Data are in accordance to that previously reported.¹

1-Methoxy-4-(*p*-tolylsulfinyl)benzene (12a)



Colorless oil, 27.0 mg, 55% yield; ¹H NMR (400 MHz, CDCl₃) δ: 7.55 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 7.3 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 2.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 161.8, 142.5, 141.2, 136.9, 129.8, 127.0, 124.7, 114.7, 55.4, 21.3. Data are in accordance to that previously reported.³

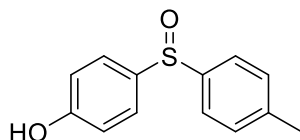
1-Chloro-4-((4-methoxyphenyl)sulfinyl)benzene (12b)



Yellow oil, 25.6 mg, 48% yield; ¹H NMR (400 MHz, CDCl₃) δ: 7.69–7.48 (m, 4H), 7.42 (d, *J* = 8.6 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H); ¹³C NMR (100

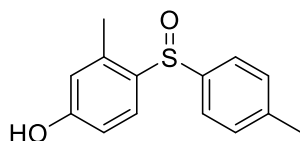
MHz, CDCl₃) δ : 162.2, 144.3, 136.9, 136.2, 129.4, 127.2, 125.9, 114.9, 55.5.
Data are in accordance to that previously reported.⁴

4-(*p*-Tolylsulfinyl)phenol (12c)



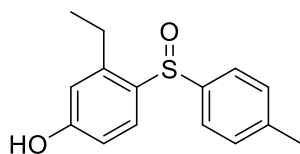
Yellow solid, m.p. = 135–137 °C; 24.1 mg, 52% yield; ¹H NMR (400 MHz, *d*₆-DMSO) δ : 10.14 (s, 1H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 2.32 (s, 3H); ¹³C NMR (100 MHz, *d*₆-DMSO) δ : 160.0, 143.2, 140.5, 135.1, 129.7, 126.6, 123.9, 116.0, 20.7; HRMS (ESI) *m/z*: Calcd for C₁₃H₁₂NaO₂S [M+Na]⁺: 255.0450. Found: 255.0457.

3-Methyl-4-(*p*-tolylsulfinyl)phenol (12d)



Yellow oil, 27.0 mg, 55% yield; ¹H NMR (400 MHz, *d*₆-DMSO) δ : 10.04 (br, 1H), 7.52 (dd, *J* = 8.6, 1.2 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 7.6 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 1H), 6.64 (s, 1H), 2.32 (s, 3H), 2.25 (s, 3H); ¹³C NMR (100 MHz, *d*₆-DMSO) δ : 159.8, 142.2, 140.6, 137.6, 132.7, 129.7, 126.8, 124.9, 117.4, 113.9, 20.7, 18.0; HRMS (ESI) *m/z*: Calcd for C₁₄H₁₄NaO₂S [M+Na]⁺: 269.0607. Found: 269.0615.

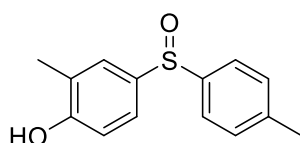
3-Ethyl-4-(*p*-tolylsulfinyl)phenol (12e)



White solid, m.p. = 161–163 °C; 20.2 mg, 39% yield; ¹H NMR (400 MHz, CDCl₃) δ : 8.86 (br, 1H), 7.46 (d, *J* = 8.6 Hz, 1H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* =

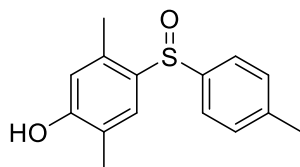
8.1 Hz, 2H), 6.74 (dd, $J = 8.6, 2.4$ Hz, 1H), 6.68 (d, $J = 2.2$ Hz, 1H), 2.79–2.61 (m, 2H), 2.36 (s, 3H), 1.10 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 160.3, 145.2, 141.4, 140.7, 131.0, 129.9, 128.0, 125.6, 116.1, 114.9, 25.0, 21.3, 15.1; HRMS (ESI) m/z : Calcd for $\text{C}_{15}\text{H}_{16}\text{NaO}_2\text{S}$ $[\text{M}+\text{Na}]^+$: 283.0763. Found: 283.0768.

2-Methyl-4-(*p*-tolylsulfinyl)phenol (12f)



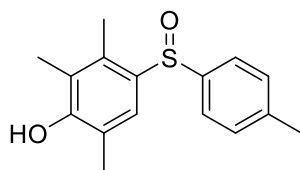
Yellow oil, 27.0 mg, 55% yield; ^1H NMR (400 MHz, CDCl_3) δ : 8.74 (br, 1H), 7.48 (d, $J = 8.0$ Hz, 2H), 7.30–7.24 (m, 4H), 6.85 (d, $J = 8.4$ Hz, 1H), 2.38 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 158.5, 141.3, 141.0, 133.4, 129.8, 128.4, 126.4, 125.3, 124.8, 115.7, 21.3, 16.0; HRMS (ESI) m/z : Calcd for $\text{C}_{14}\text{H}_{14}\text{NaO}_2\text{S}$ $[\text{M}+\text{Na}]^+$: 269.0607. Found: 269.0612.

2,5-Dimethyl-4-(*p*-tolylsulfinyl)phenol (12g)



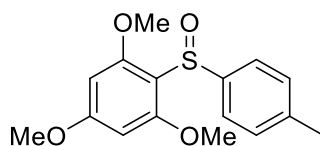
White solid, m.p. = 157–159 °C; 49.4 mg, 95% yield; ^1H NMR (400 MHz, d_6 -DMSO) δ : 9.95 (s, 1H), 7.43 (d, $J = 8.1$ Hz, 2H), 7.39 (s, 2H), 7.30 (d, $J = 8.0$ Hz, 2H), 6.64 (s, 1H), 2.31 (s, 3H), 2.22 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, d_6 -DMSO) δ : 157.9, 142.5, 140.5, 134.6, 132.1, 129.7, 127.0, 124.8, 122.9, 116.6, 20.7, 17.6, 15.5; HRMS (ESI) m/z : Calcd for $\text{C}_{15}\text{H}_{16}\text{NaO}_2\text{S}$ $[\text{M}+\text{Na}]^+$: 283.0763. Found: 283.0767.

2,3,6-Trimethyl-4-(*p*-tolylsulfinyl)phenol (12h)



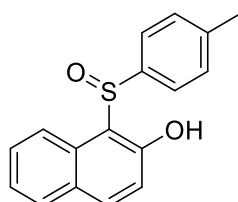
White solid, m.p. = 152–154 °C; 43.8 mg, 80% yield; ^1H NMR (400 MHz, d_6 -DMSO) δ : 8.79 (br, 1H), 7.42 (d, J = 7.9 Hz, 2H), 7.34 (s, 1H), 7.27 (d, J = 7.9 Hz, 2H), 2.29 (s, 3H), 2.20 (s, 6H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, d_6 -DMSO) δ : 155.3, 142.9, 140.4, 133.1, 132.8, 129.7, 124.8, 124.2, 123.7, 123.0, 20.7, 16.7, 14.9, 12.0; HRMS (ESI) m/z : Calcd for $\text{C}_{16}\text{H}_{18}\text{NaO}_2\text{S}$ [$\text{M}+\text{Na}$] $^+$: 297.0920. Found: 297.0925.

1,3,5-Trimethoxy-2-(*p*-tolylsulfinyl)benzene (12i)



Pale yellow oil, 42.8 mg, 70% yield; ^1H NMR (400 MHz, CDCl_3) δ : 7.40 (d, J = 7.8 Hz, 2H), 7.14 (d, J = 7.8 Hz, 2H), 6.00 (s, 2H), 3.75 (s, 3H), 3.65 (s, 6H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 164.7, 161.1, 141.7, 138.7, 128.6, 123.9, 112.6, 91.0, 55.7, 55.2, 21.0. Data are in accordance to that previously reported.³

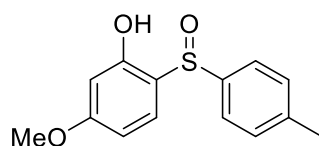
1-(*p*-Tolylsulfinyl)naphthalen-2-ol (12j)



Pale yellow oil, 28.2 mg, 50% yield; ^1H NMR (400 MHz, CDCl_3) δ : 11.72 (s, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 9.0 Hz, 1H), 7.76 (d, J = 8.1 Hz, 1H), 7.64

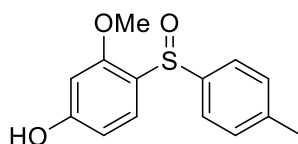
(d, $J = 8.2$ Hz, 2H), 7.50 (t, $J = 7.7$ Hz, 1H), 7.36 (t, $J = 7.5$ Hz, 1H), 7.23 (d, $J = 8.0$ Hz, 2H), 7.09 (d, $J = 9.0$ Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 160.2, 142.3, 140.0, 133.7, 130.6, 130.2, 128.8, 128.0, 127.8, 125.5, 123.9, 121.2, 120.4, 112.8, 21.3; HRMS (ESI) m/z : Calcd for $\text{C}_{17}\text{H}_{14}\text{NaO}_2\text{S}$ $[\text{M}+\text{Na}]^+$: 305.0607. Found: 305.0614.

5-Methoxy-2-(*p*-tolylsulfinyl)phenol (12ka)



Pale yellow oil, 23.1 mg, 44% yield; ^1H NMR (400 MHz, CDCl_3) δ : 10.27 (br, 1H), 7.53 (d, $J = 8.2$ Hz, 2H), 7.27 (d, $J = 7.9$ Hz, 2H), 7.11 (d, $J = 8.6$ Hz, 1H), 6.45 (dd, $J = 8.6, 2.4$ Hz, 1H), 6.39 (d, $J = 2.4$ Hz, 1H), 3.75 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 163.6, 161.0, 141.8, 140.9, 130.0, 127.2, 124.7, 114.8, 107.0, 103.8, 55.3, 21.3; HRMS (ESI) m/z : Calcd for $\text{C}_{14}\text{H}_{14}\text{NaO}_3\text{S}$ $[\text{M}+\text{Na}]^+$: 285.0556. Found: 285.0561.

3-Methoxy-4-(*p*-tolylsulfinyl)phenol (12kb)

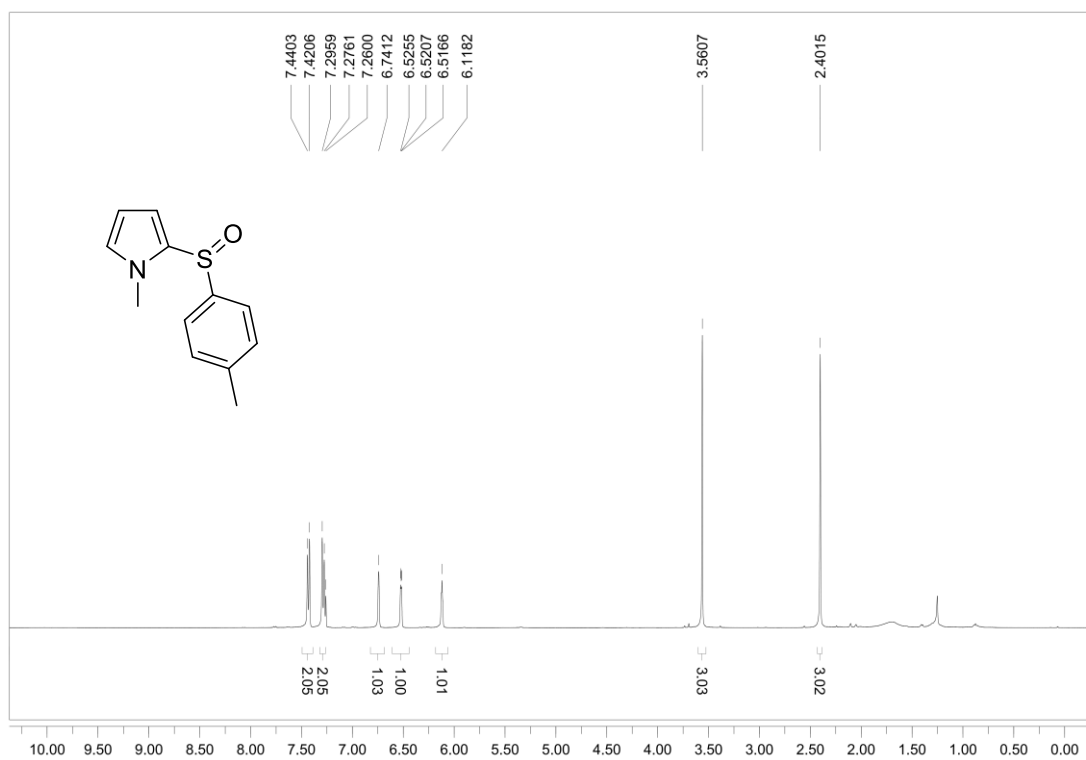


Pale yellow oil, 16.7 mg, 32% yield; ^1H NMR (400 MHz, CDCl_3) δ : 9.37 (br, 1H), 7.49 (d, $J = 8.2$ Hz, 2H), 7.43 (d, $J = 8.6$ Hz, 1H), 7.21 (d, $J = 8.1$ Hz, 2H), 6.55 (dd, $J = 8.6, 2.1$ Hz, 1H), 6.38 (d, $J = 2.0$ Hz, 1H), 3.61 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 162.1, 157.9, 141.3, 140.6, 129.7, 127.1, 125.3, 120.7, 108.8, 99.6, 55.5, 21.3; HRMS (ESI) m/z : Calcd for $\text{C}_{14}\text{H}_{14}\text{NaO}_3\text{S}$ $[\text{M}+\text{Na}]^+$: 285.0556. Found: 285.0564.

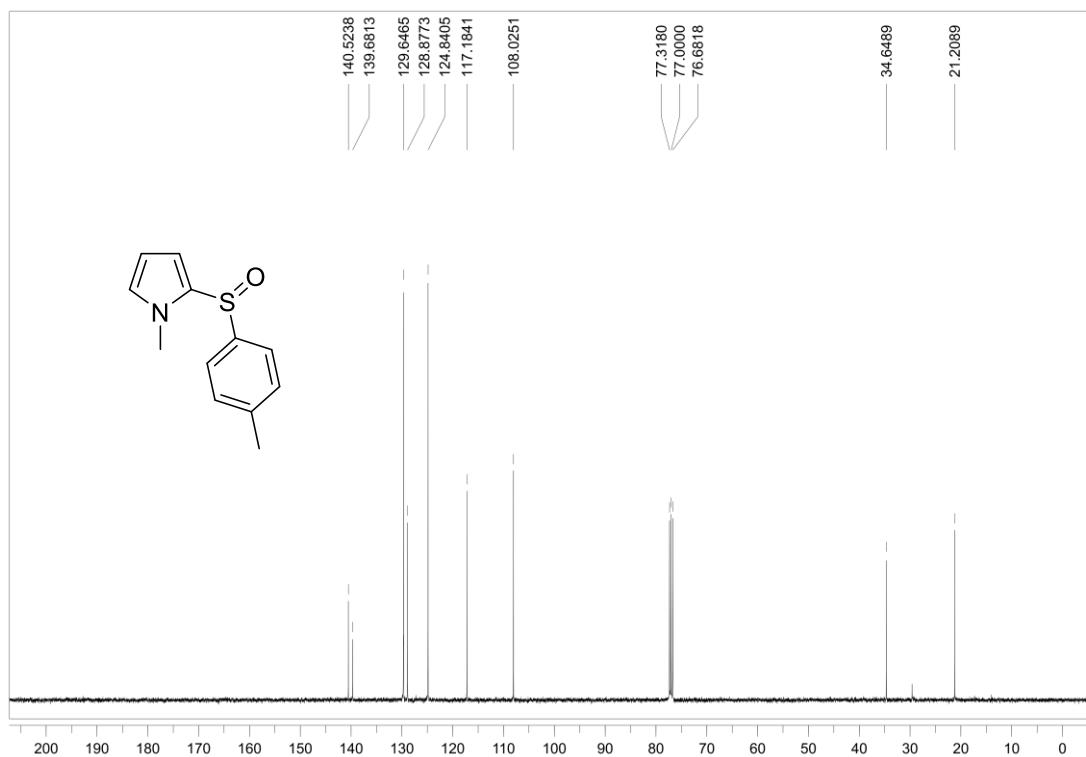
4. NMR Spectra

Sulfoxide **3a**

^1H NMR (400 MHz, CDCl_3)

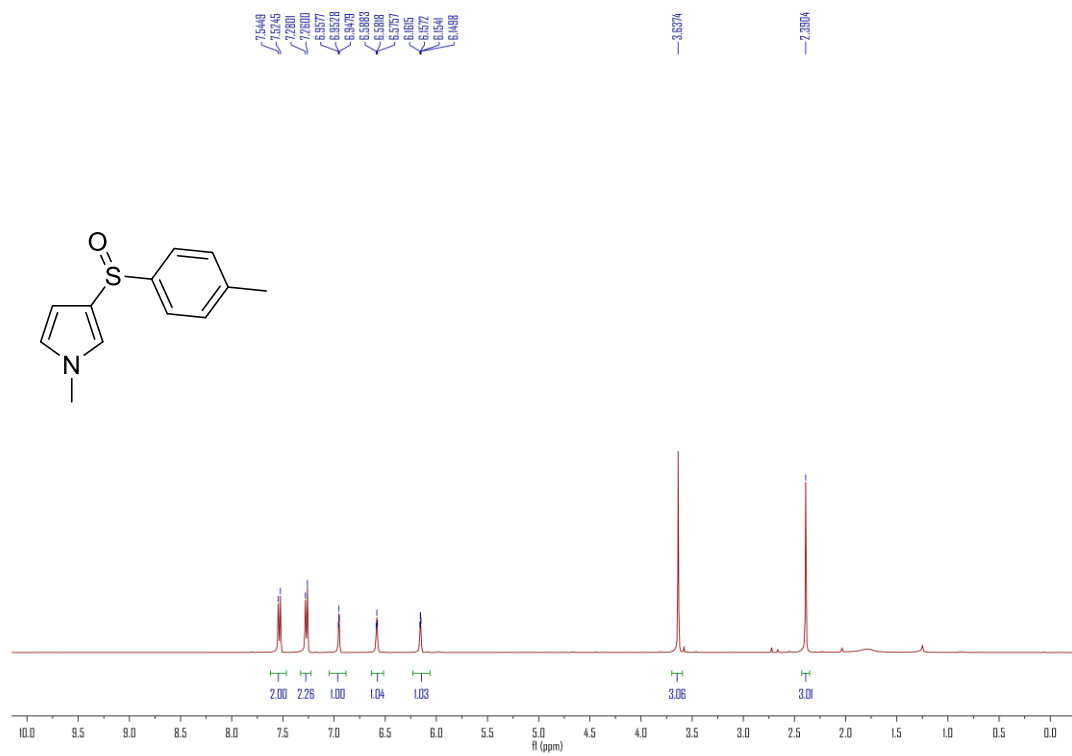


^{13}C NMR (100 MHz, CDCl_3)

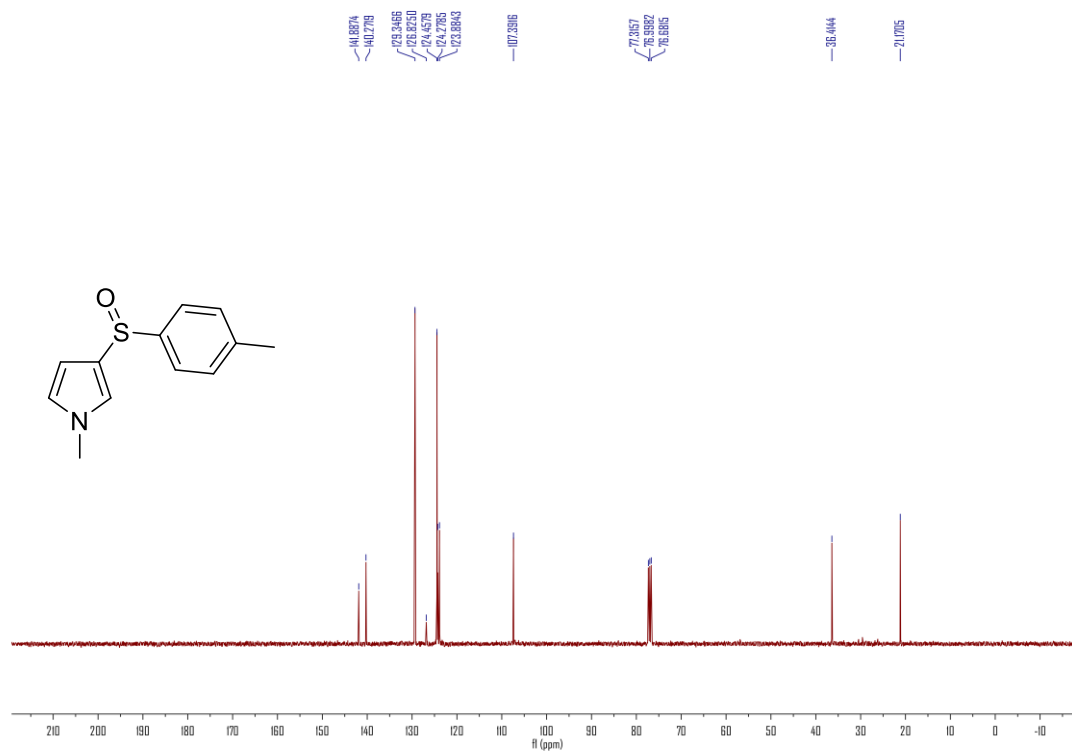


Sulfoxide 4a

^1H NMR (400 MHz, CDCl_3)

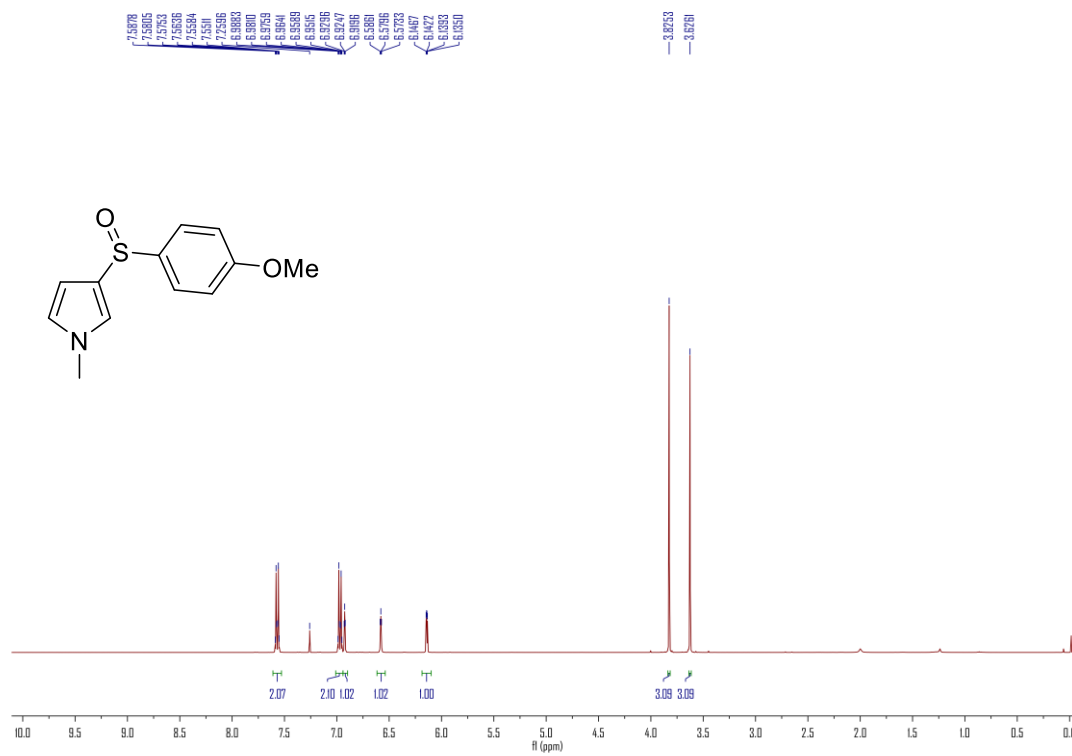


^{13}C NMR (100 MHz, CDCl_3)

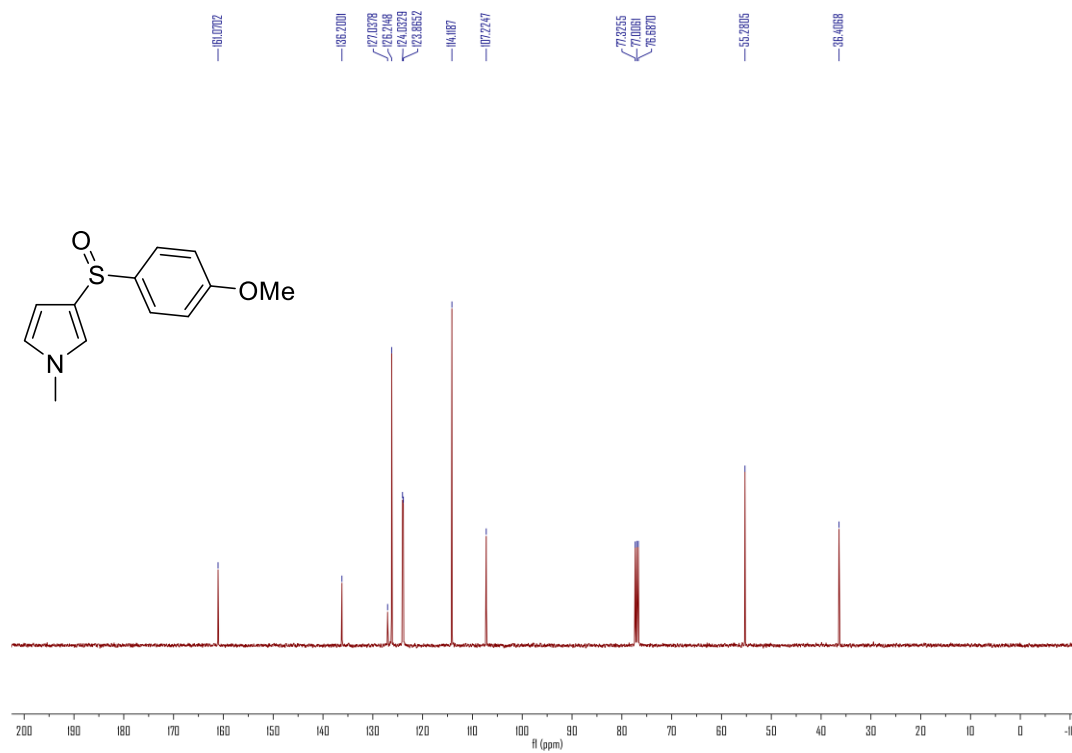


Sulfoxide **4c**

^1H NMR (400 MHz, CDCl_3)

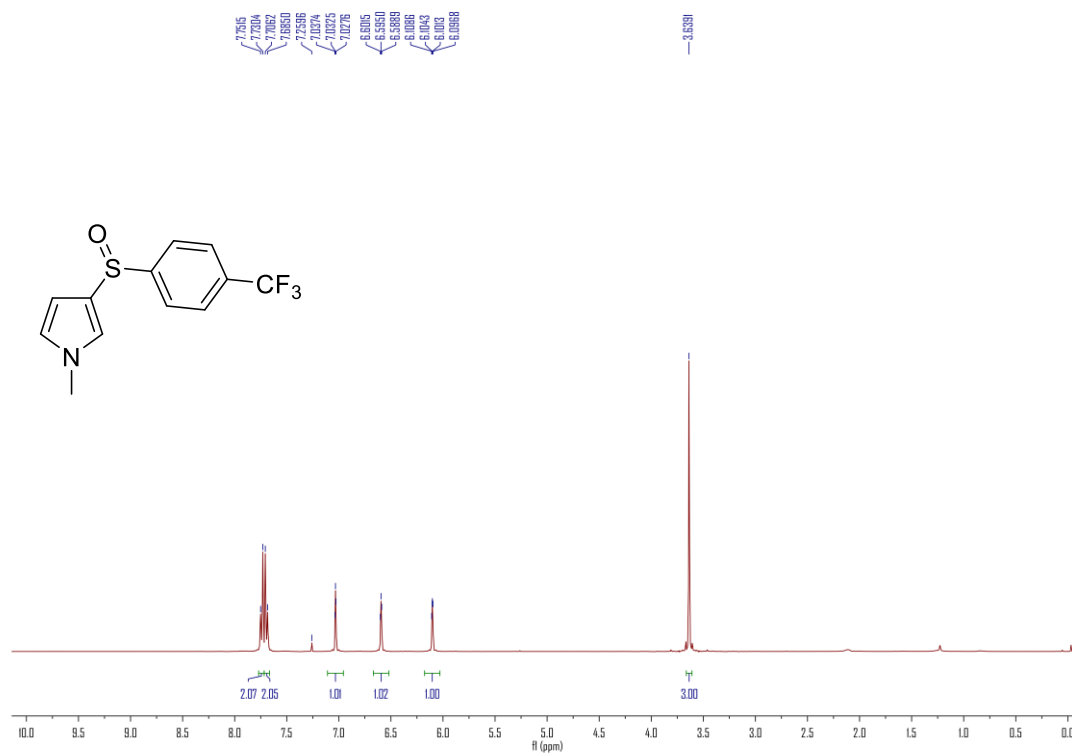


^{13}C NMR (100 MHz, CDCl_3)

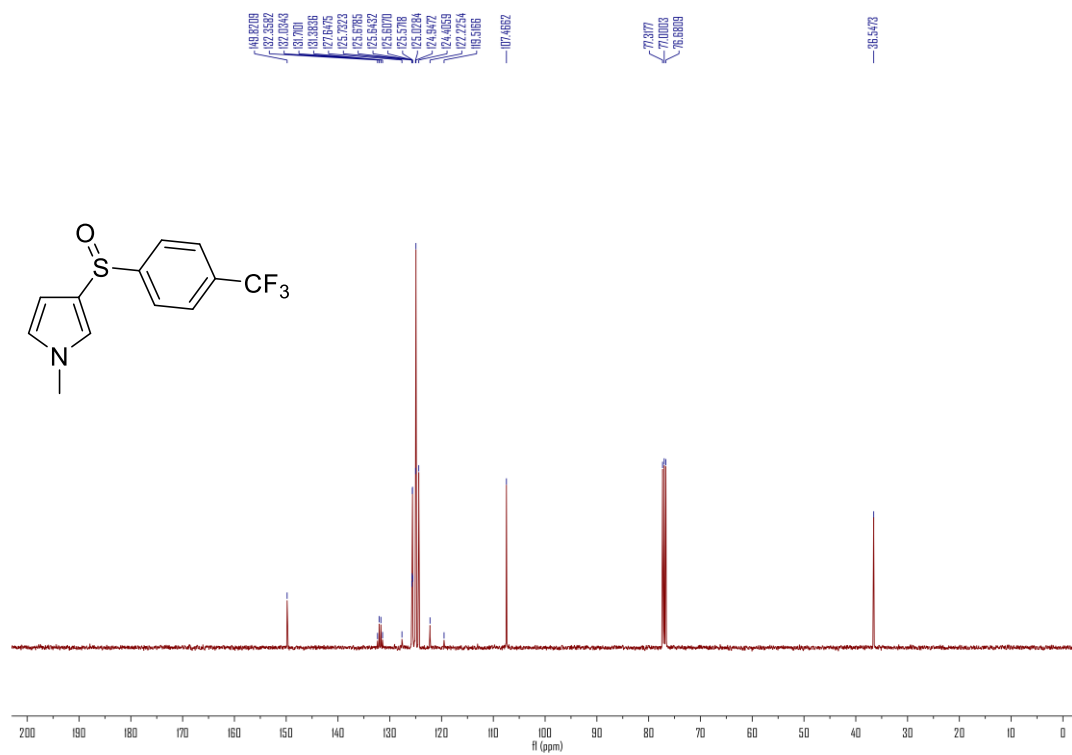


Sulfoxide **4d**

^1H NMR (400 MHz, CDCl_3)

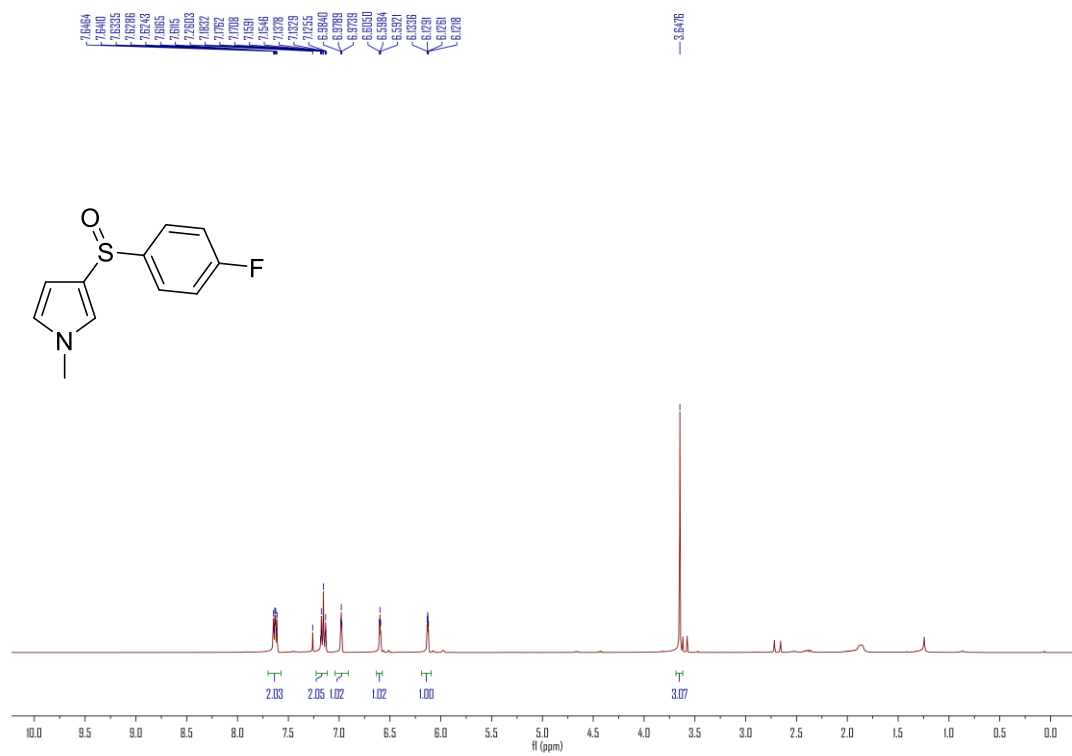


^{13}C NMR (100 MHz, CDCl_3)

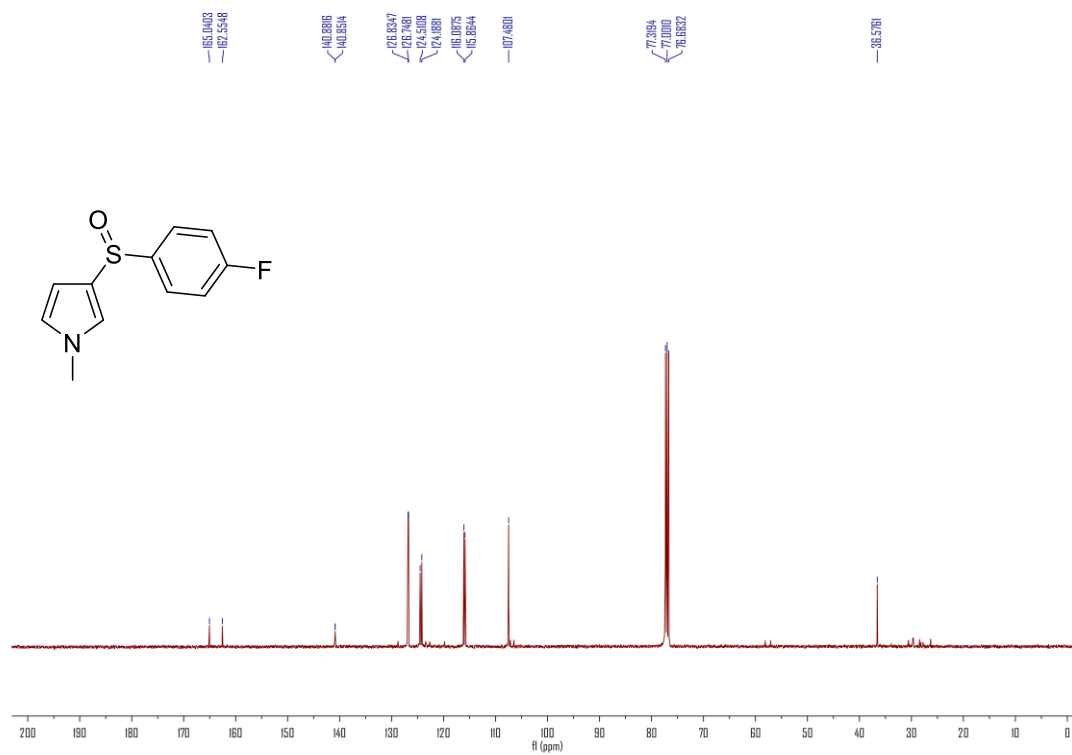


Sulfoxide **4e**

^1H NMR (400 MHz, CDCl_3)

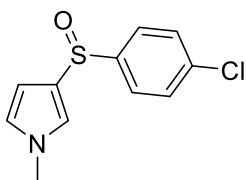
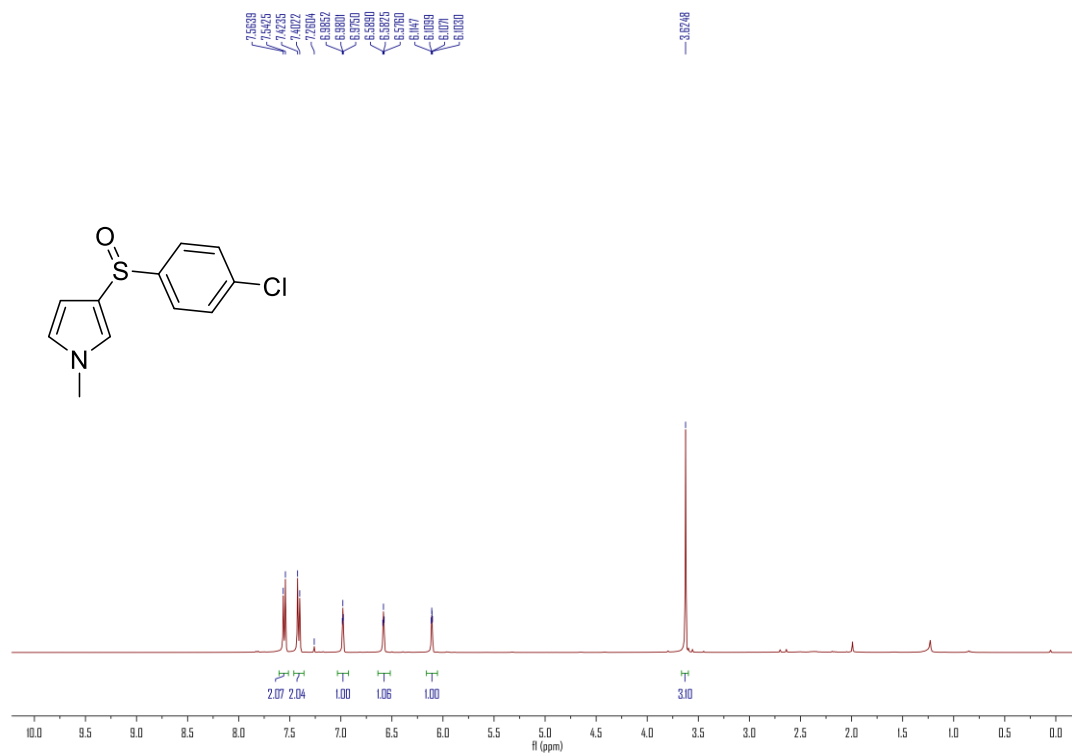


^{13}C NMR (100 MHz, CDCl_3)

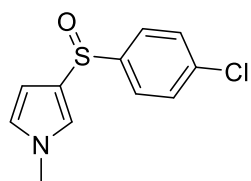
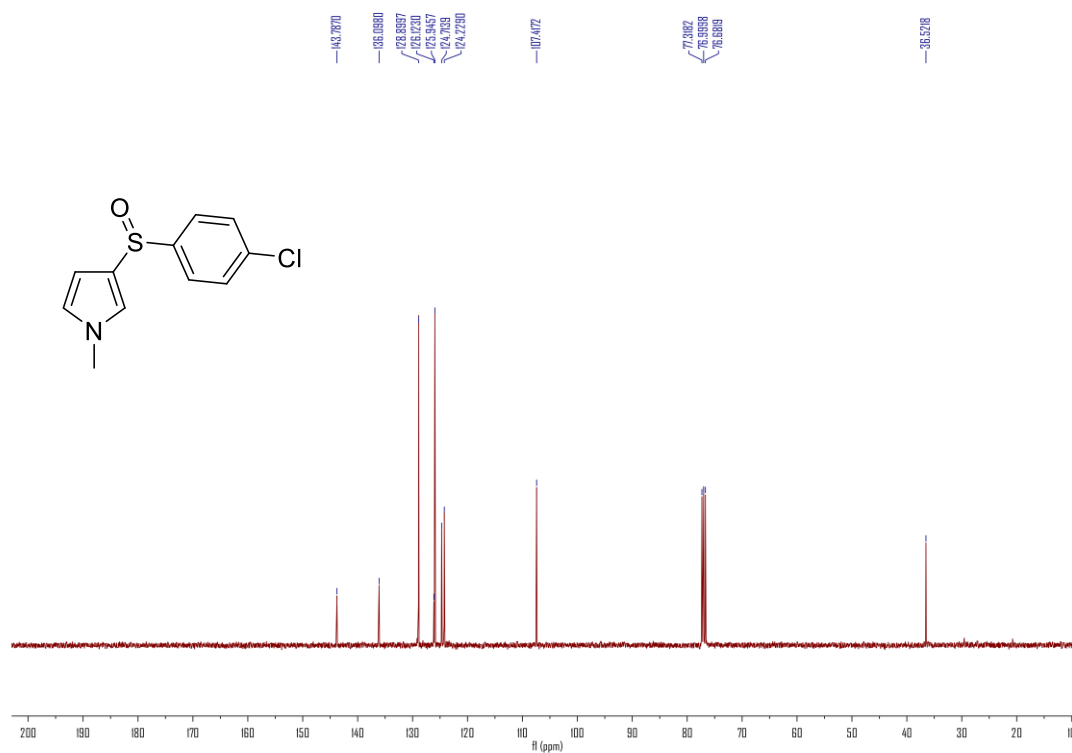


Sulfoxide **4f**

^1H NMR (400 MHz, CDCl_3)

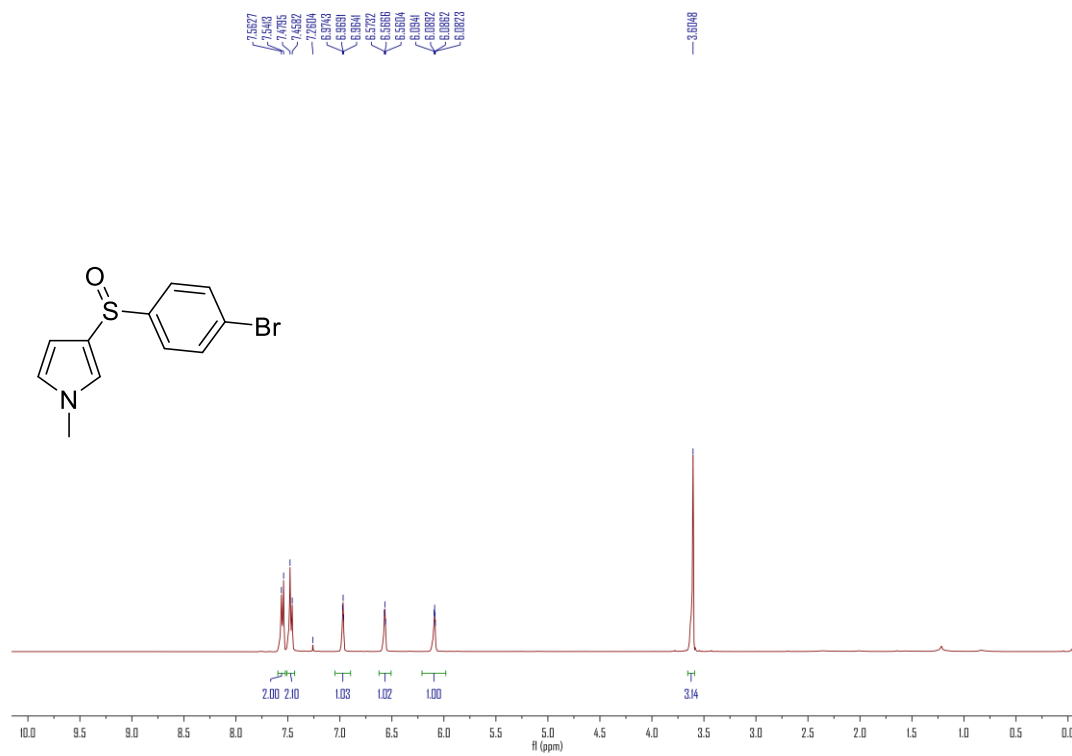


^{13}C NMR (100 MHz, CDCl_3)

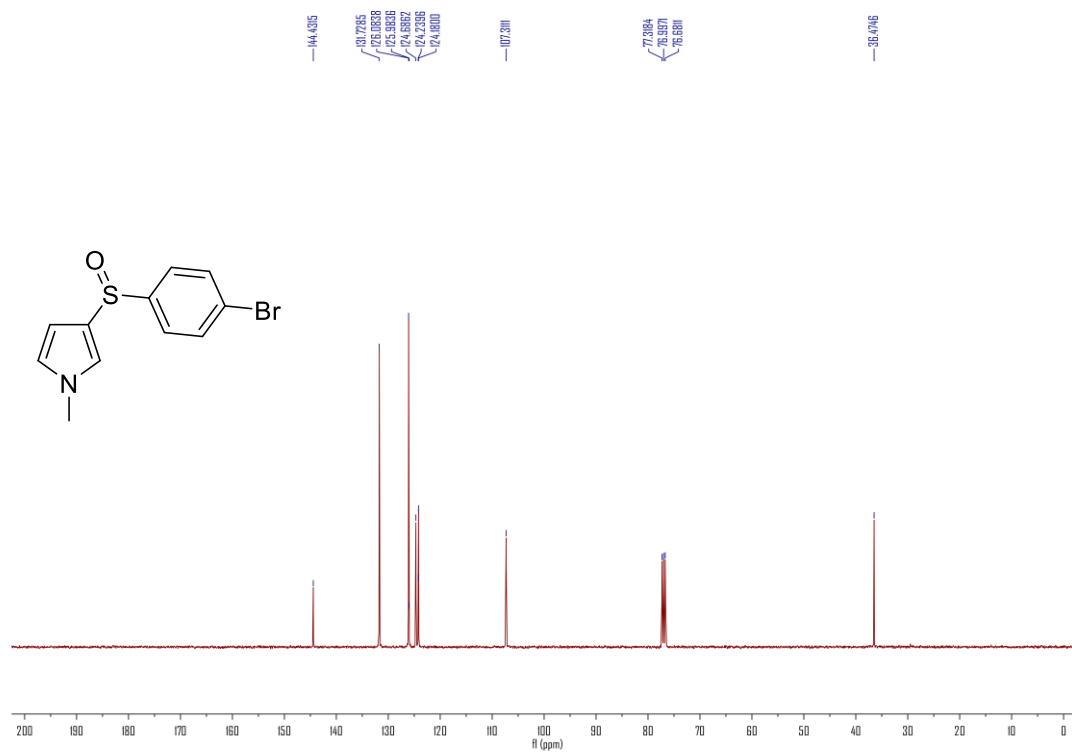


Sulfoxide **4g**

^1H NMR (400 MHz, CDCl_3)

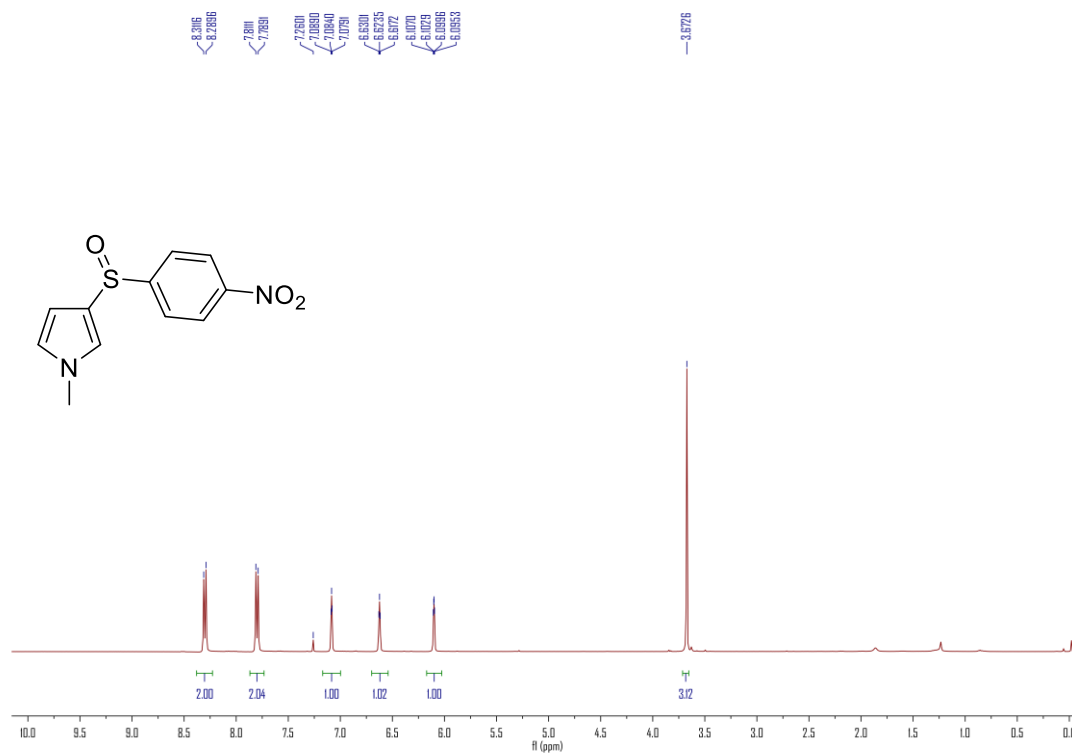


^{13}C NMR (100 MHz, CDCl_3)

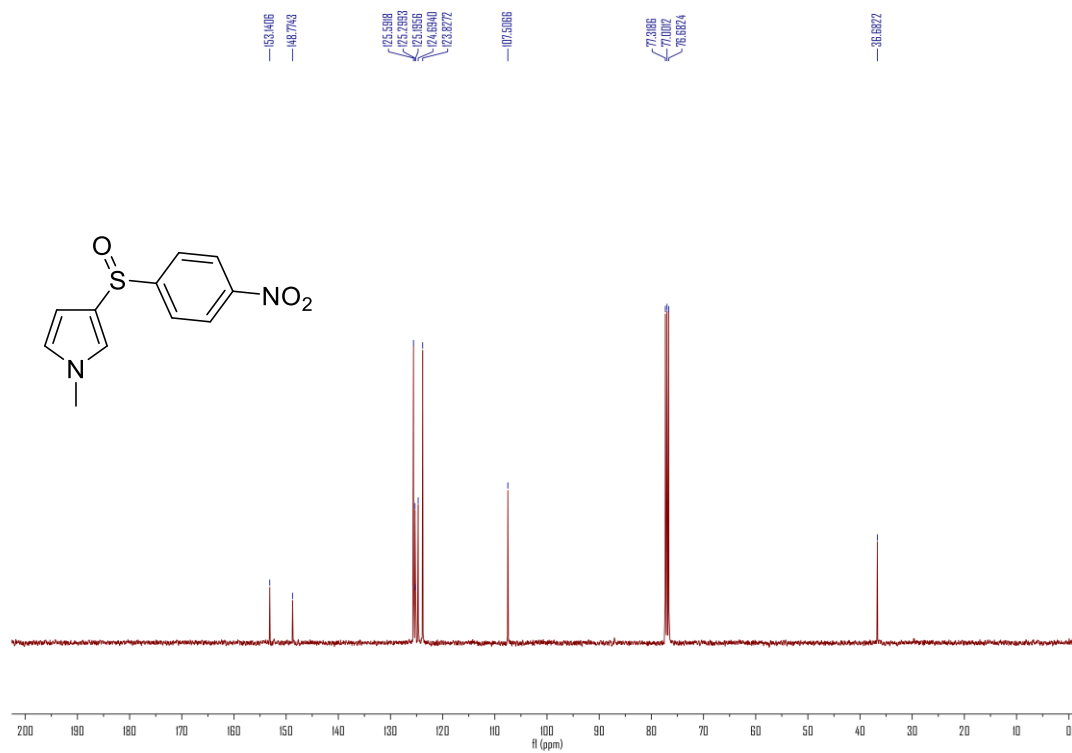


Sulfoxide 4h

^1H NMR (400 MHz, CDCl_3)

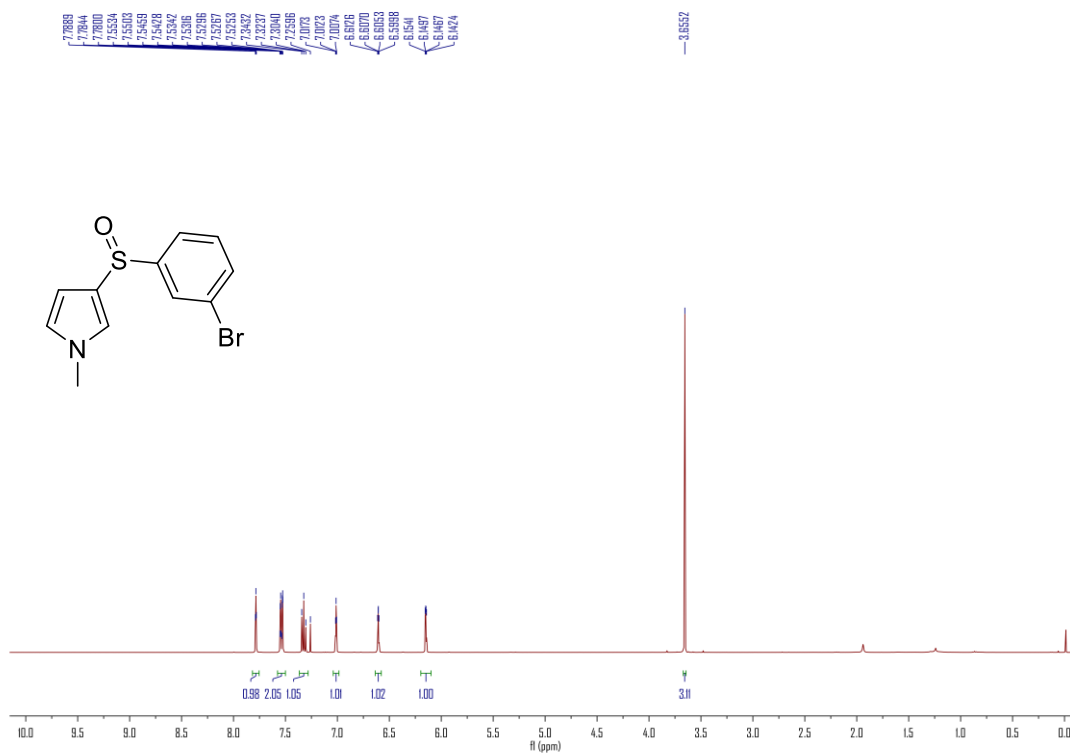


^{13}C NMR (100 MHz, CDCl_3)

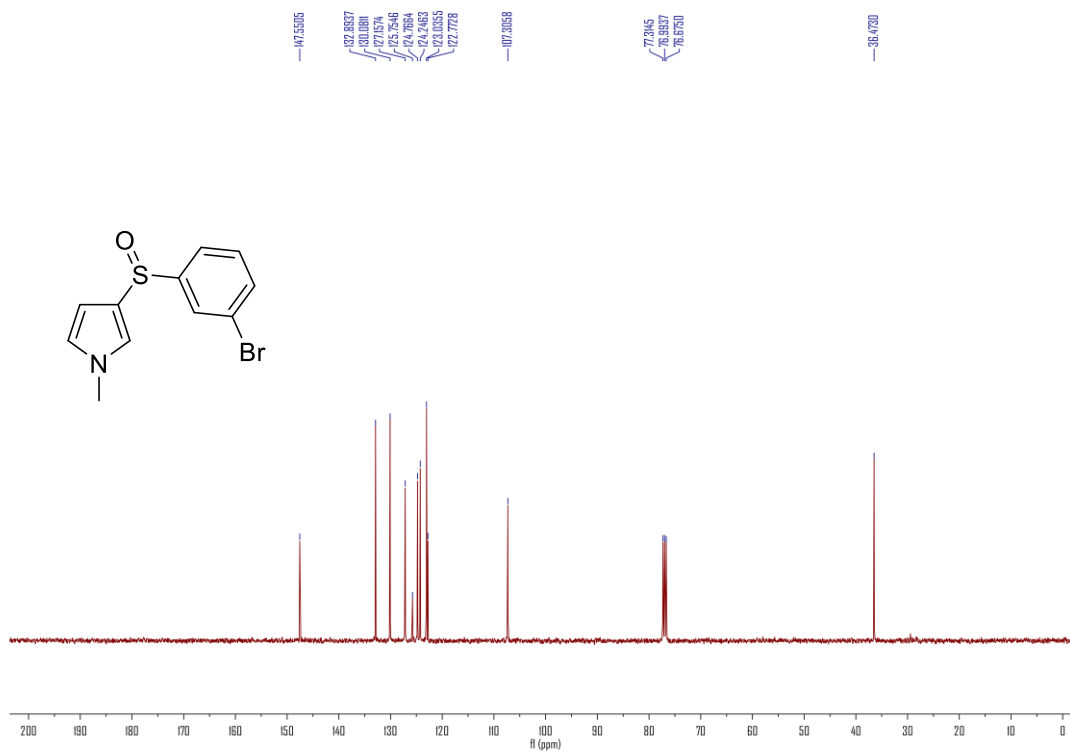


Sulfoxide 4i

^1H NMR (400 MHz, CDCl_3)

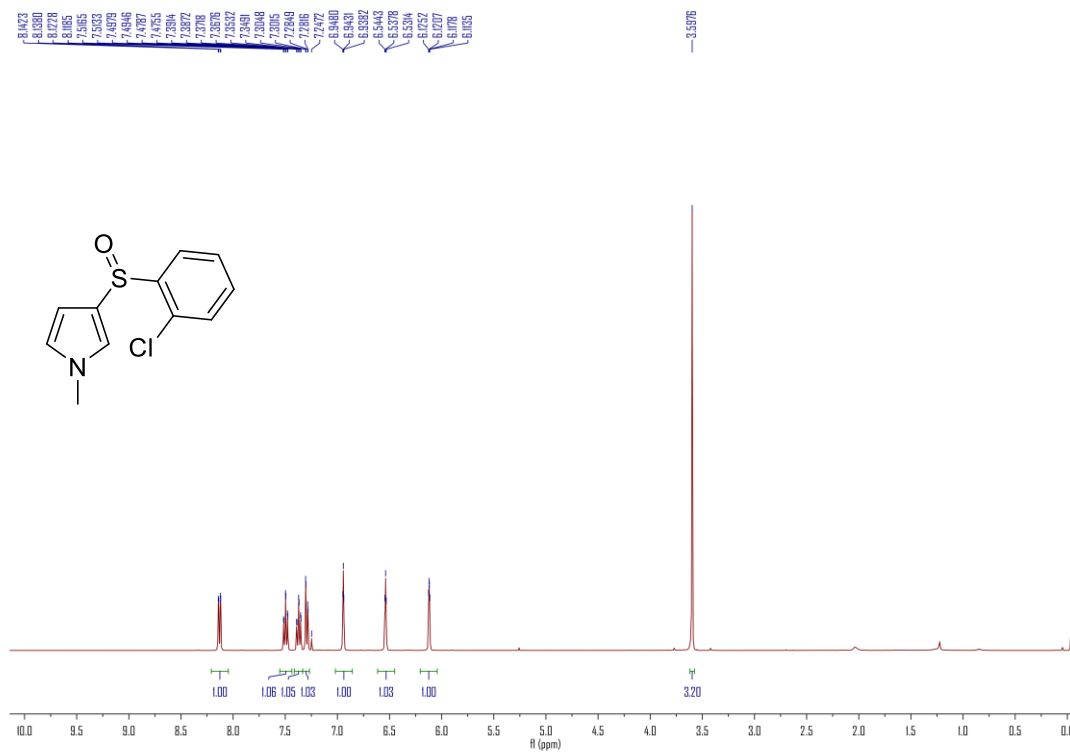


^{13}C NMR (100 MHz, CDCl_3)

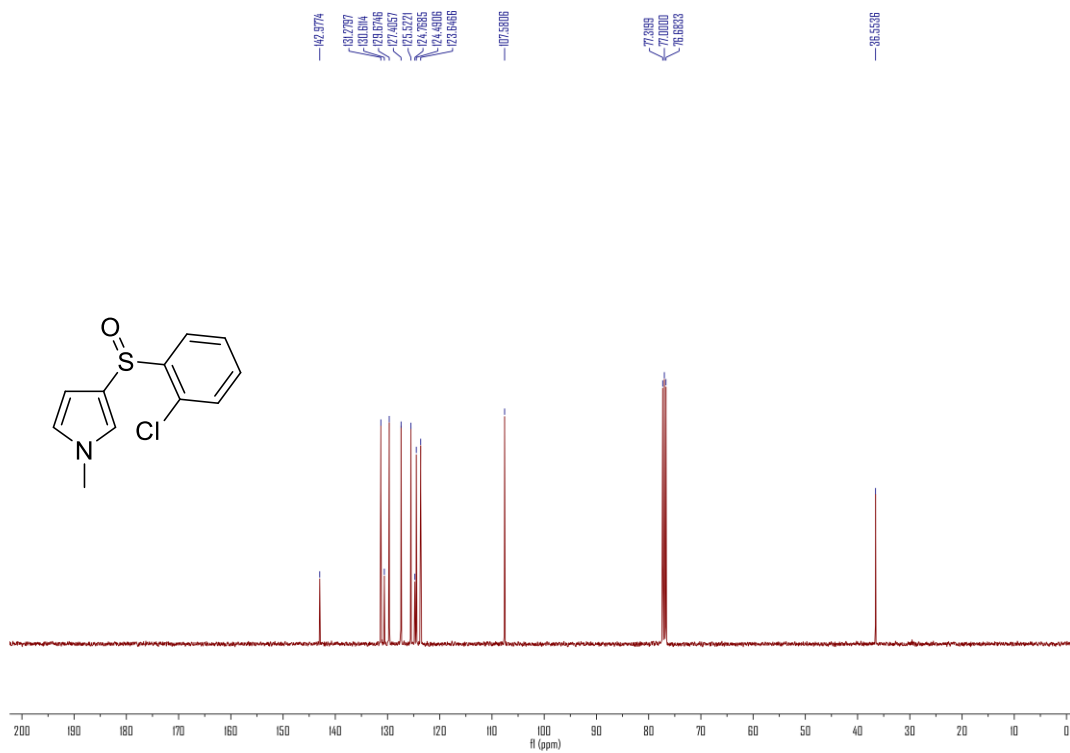


Sulfoxide 4j

¹H NMR (400 MHz, CDCl₃)

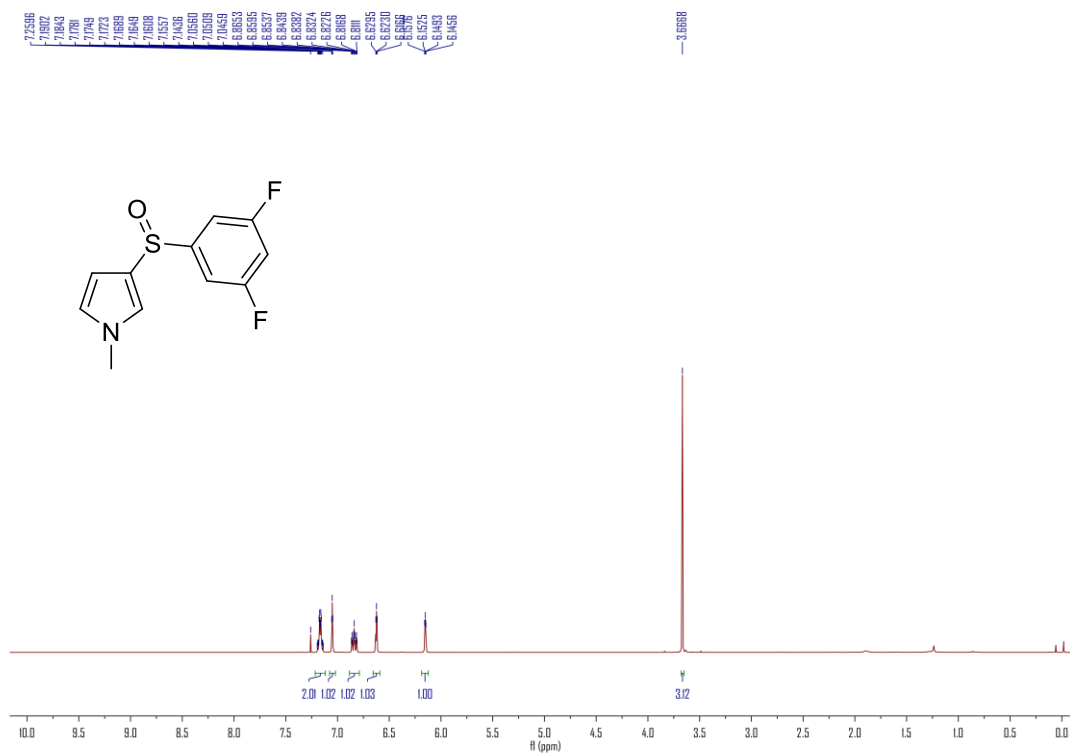


¹³C NMR (100 MHz, CDCl₃)

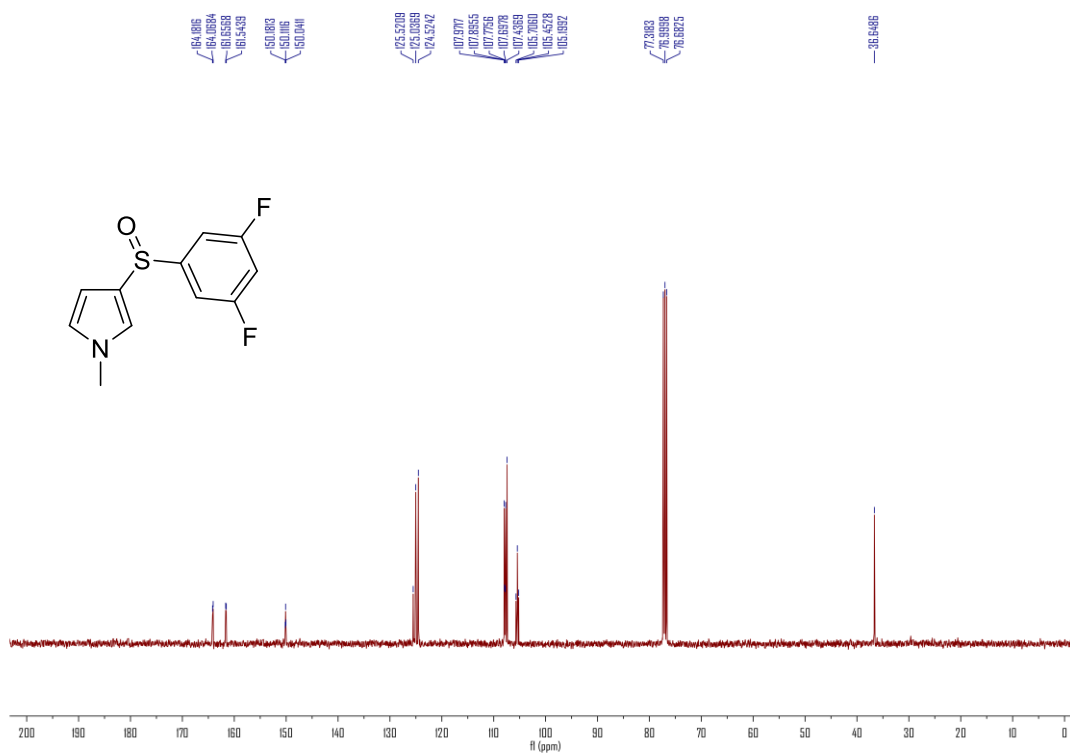


Sulfoxide 4k

^1H NMR (400 MHz, CDCl_3)

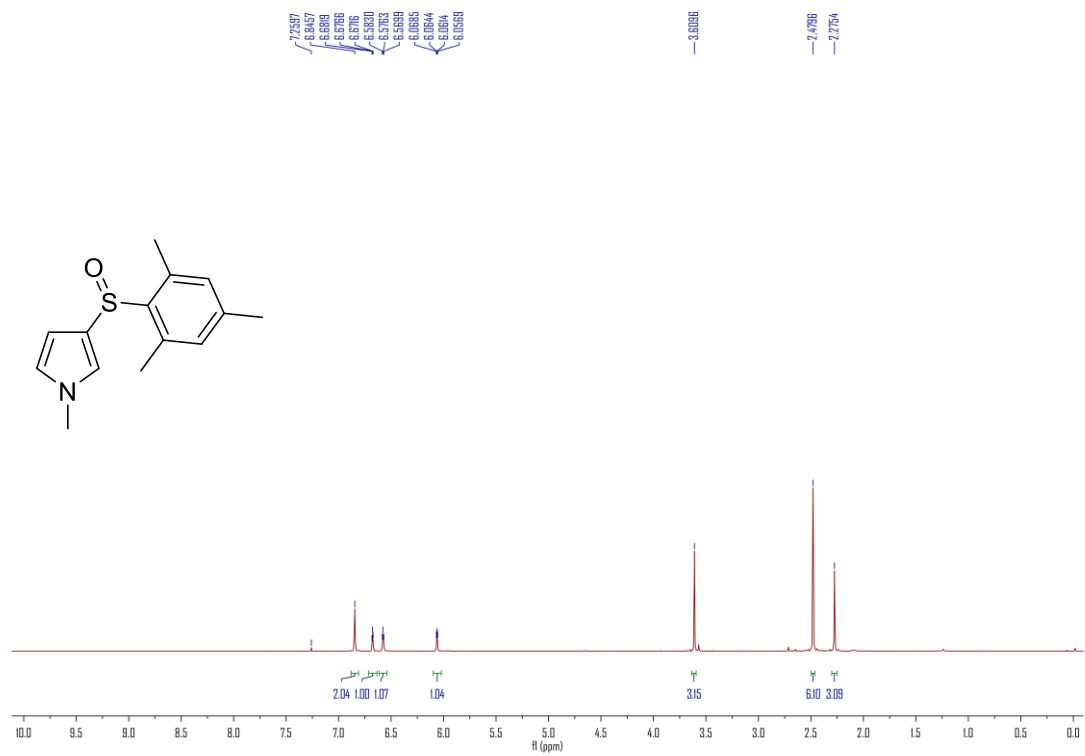


^{13}C NMR (100 MHz, CDCl_3)

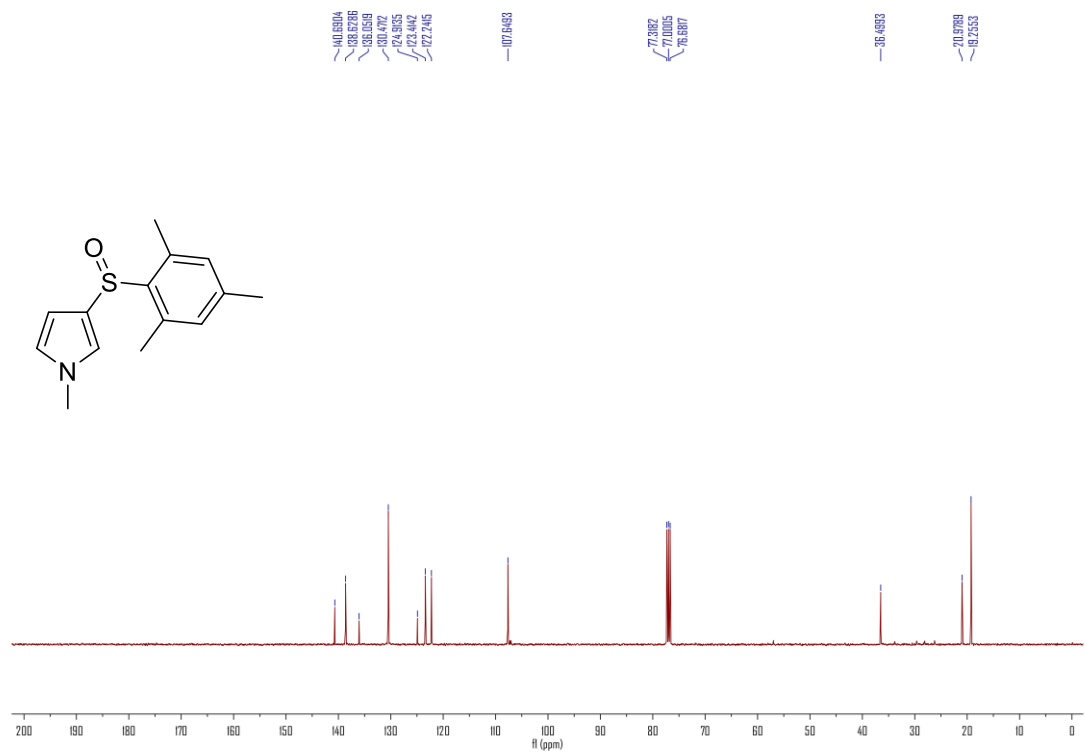


Sulfoxide **4l**

^1H NMR (400 MHz, CDCl_3)

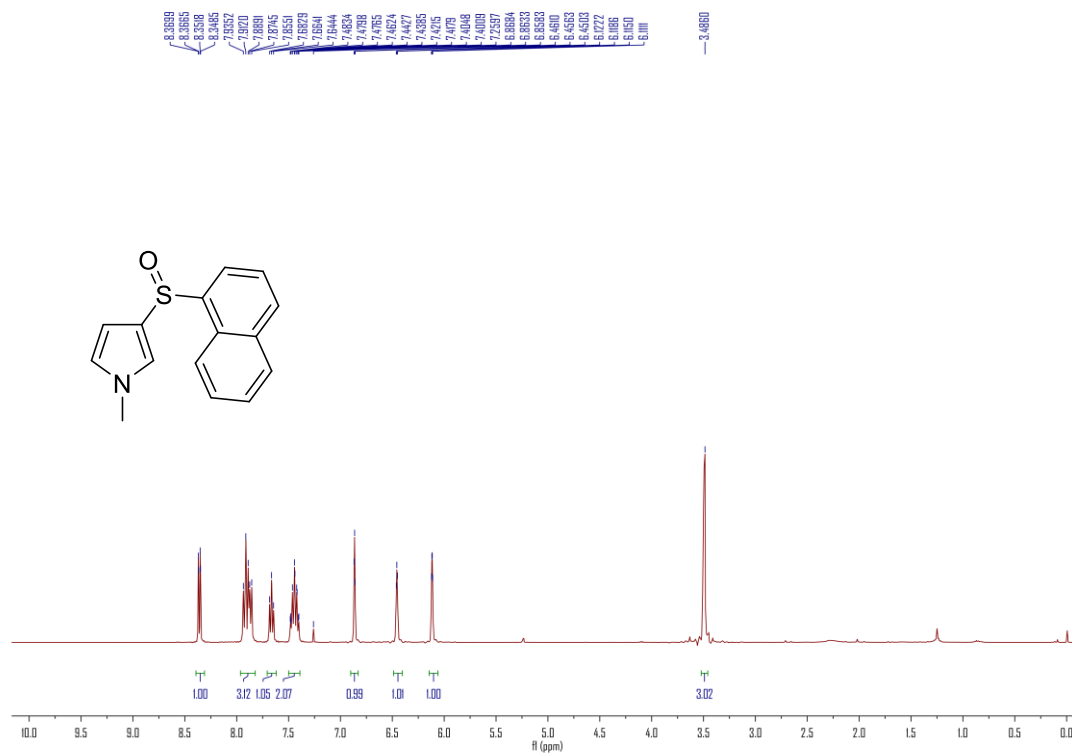


^{13}C NMR (100 MHz, CDCl_3)

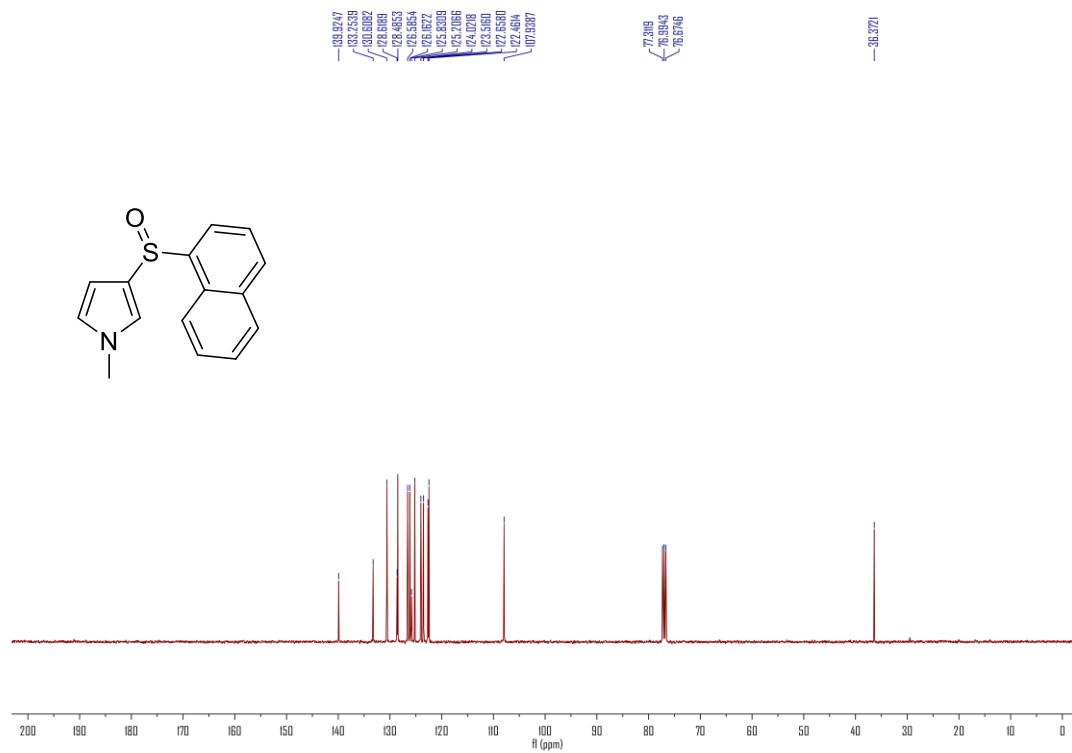


Sulfoxide 4m

¹H NMR (400 MHz, CDCl₃)

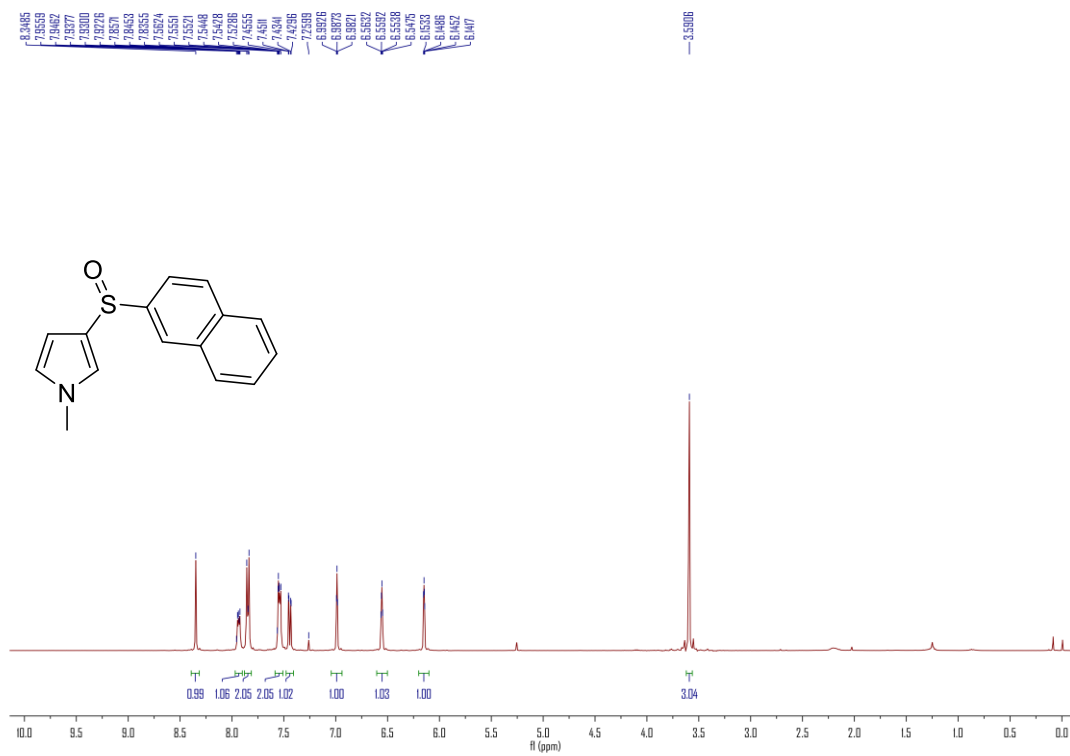


¹³C NMR (100 MHz, CDCl₃)

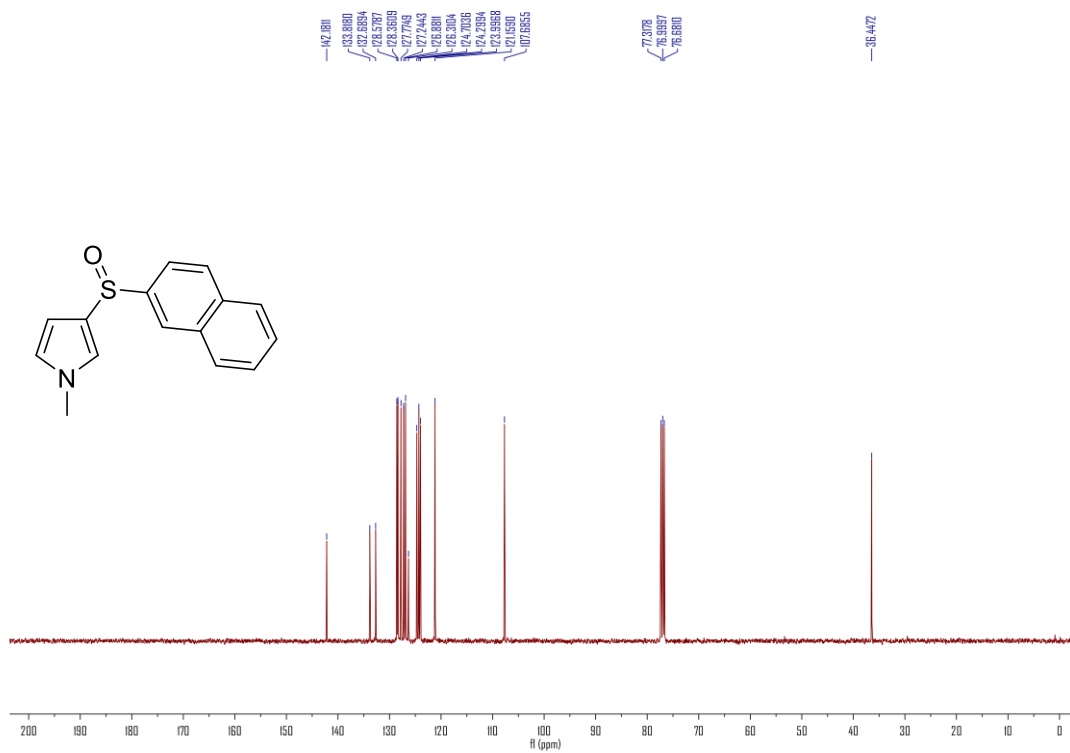


Sulfoxide 4n

¹H NMR (400 MHz, CDCl₃)

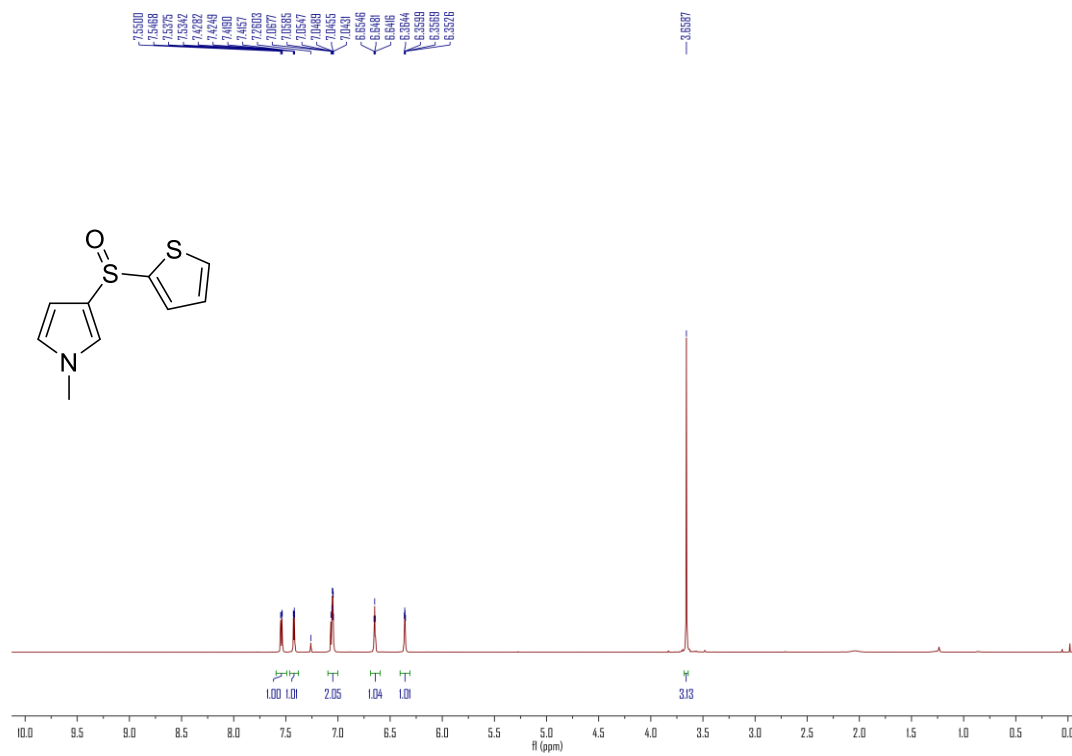


¹³C NMR (100 MHz, CDCl₃)



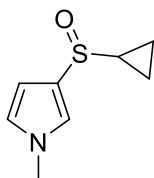
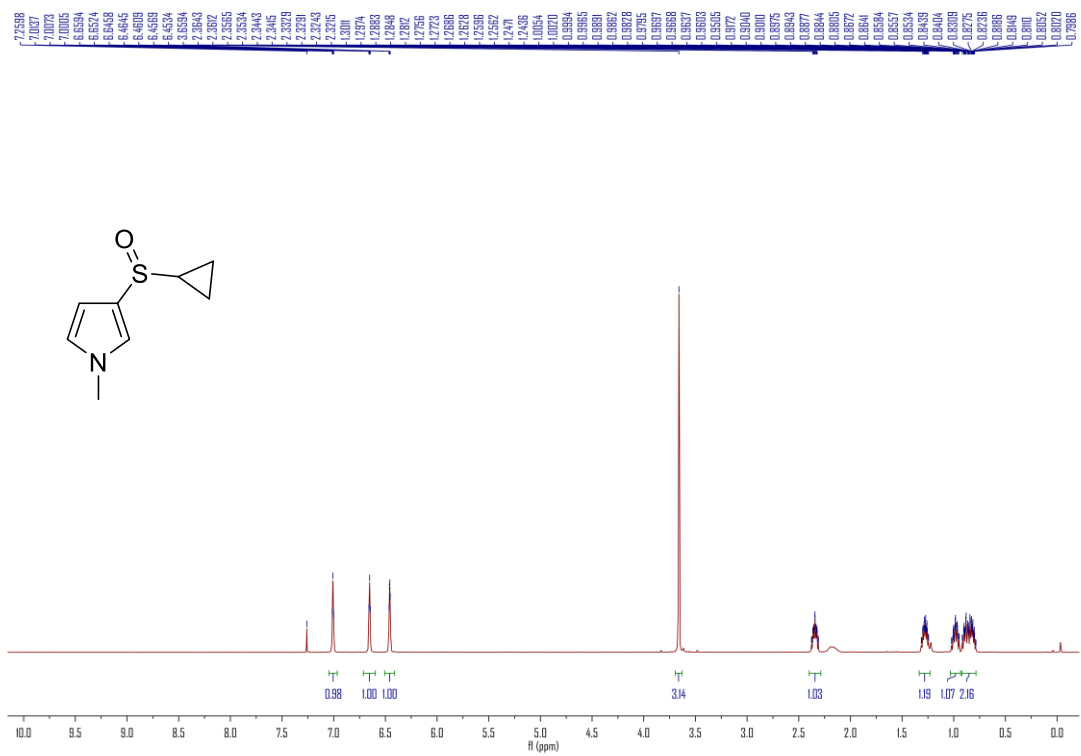
Sulfoxide 4o

^1H NMR (400 MHz, CDCl_3)

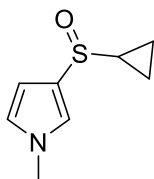
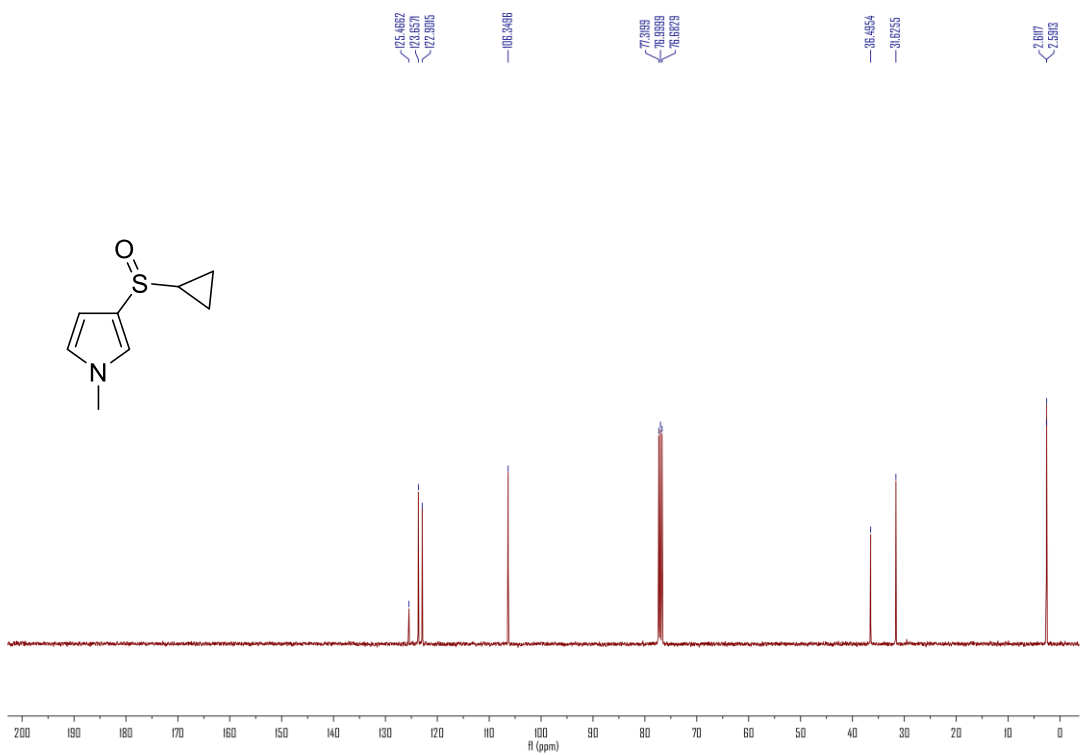


Sulfoxide 4p

¹H NMR (400 MHz, CDCl₃)

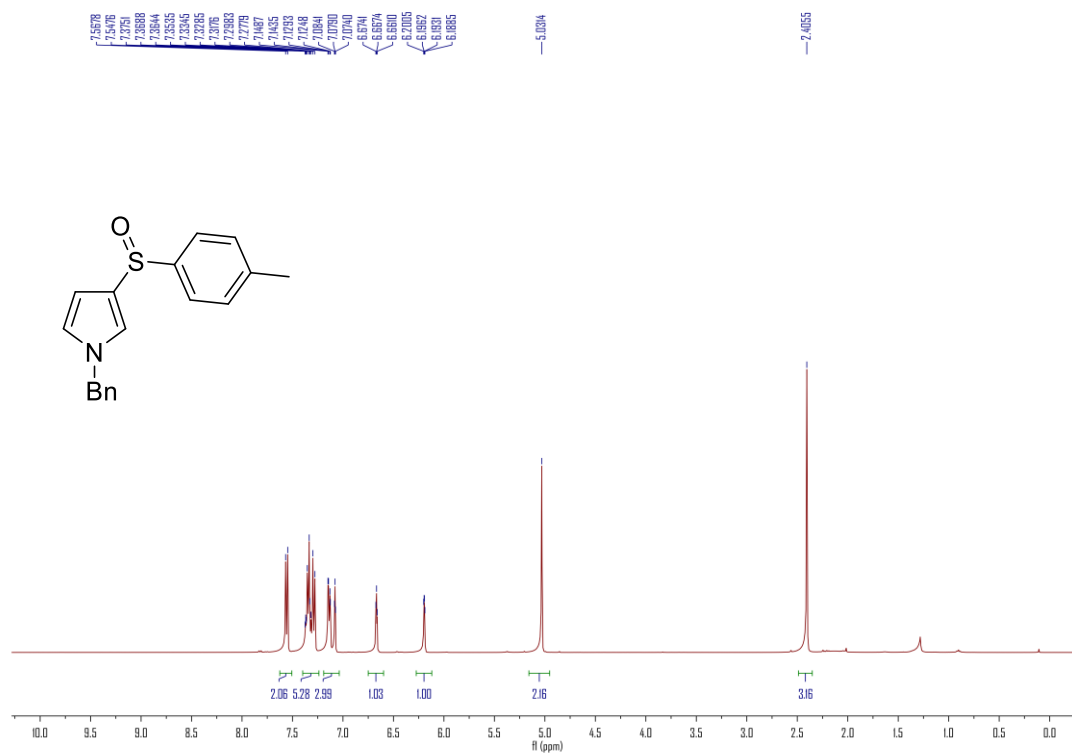


¹³C NMR (100 MHz, CDCl₃)

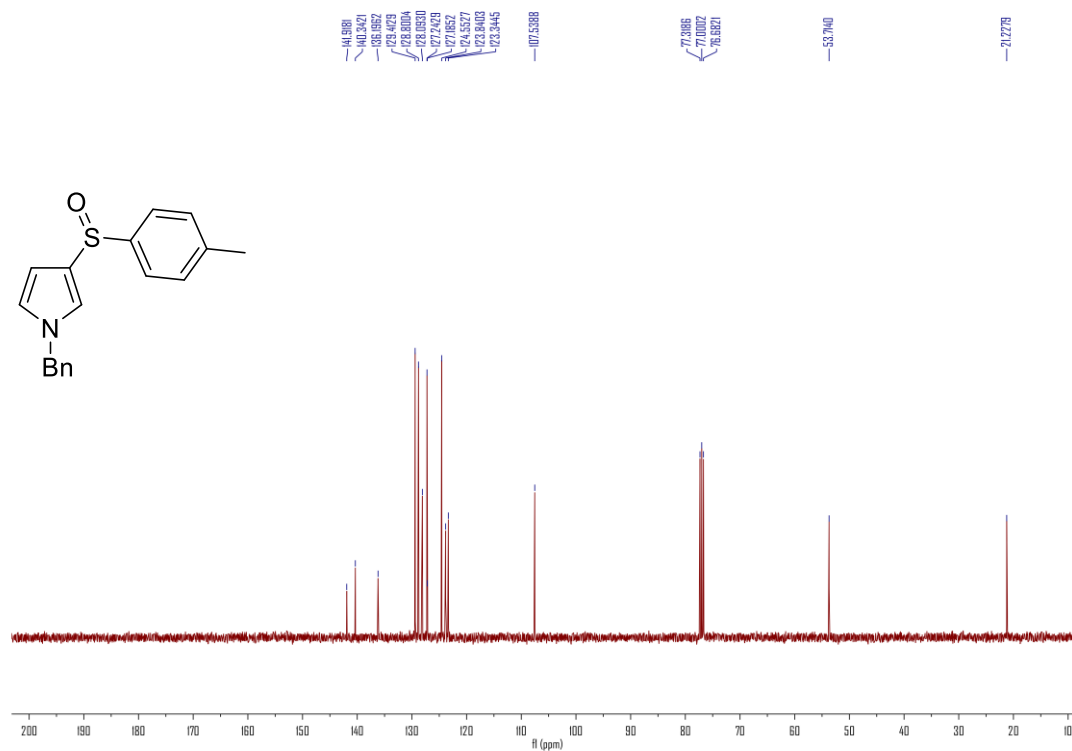


Sulfoxide **4q**

^1H NMR (400 MHz, CDCl_3)

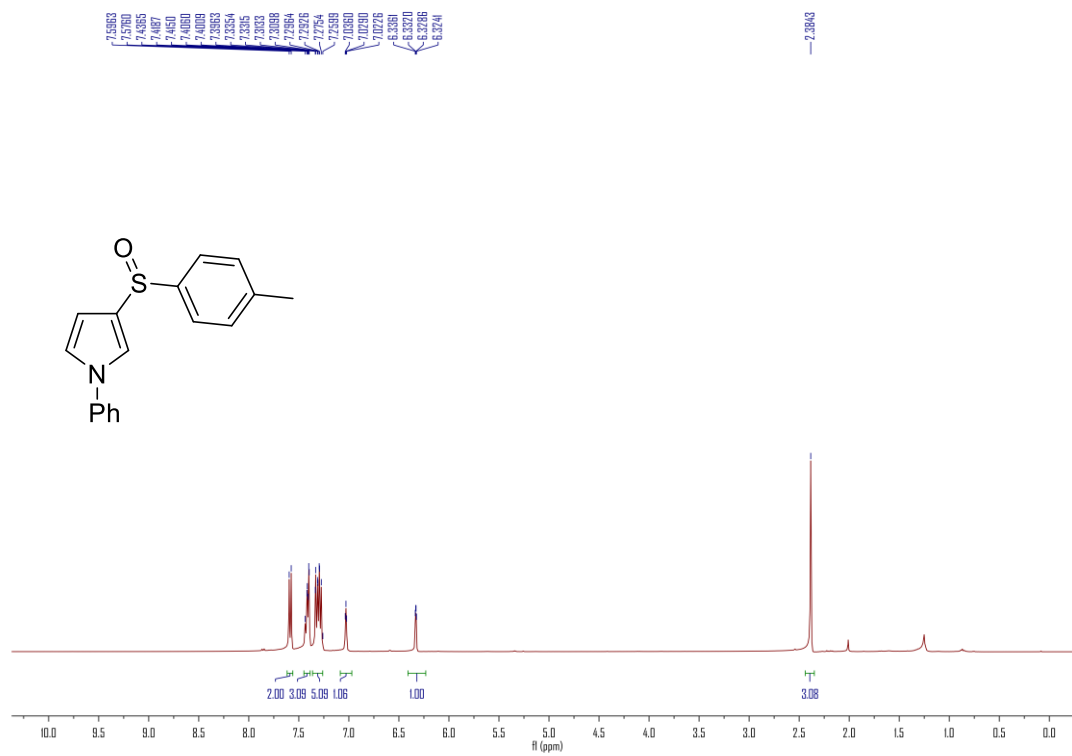


^{13}C NMR (100 MHz, CDCl_3)

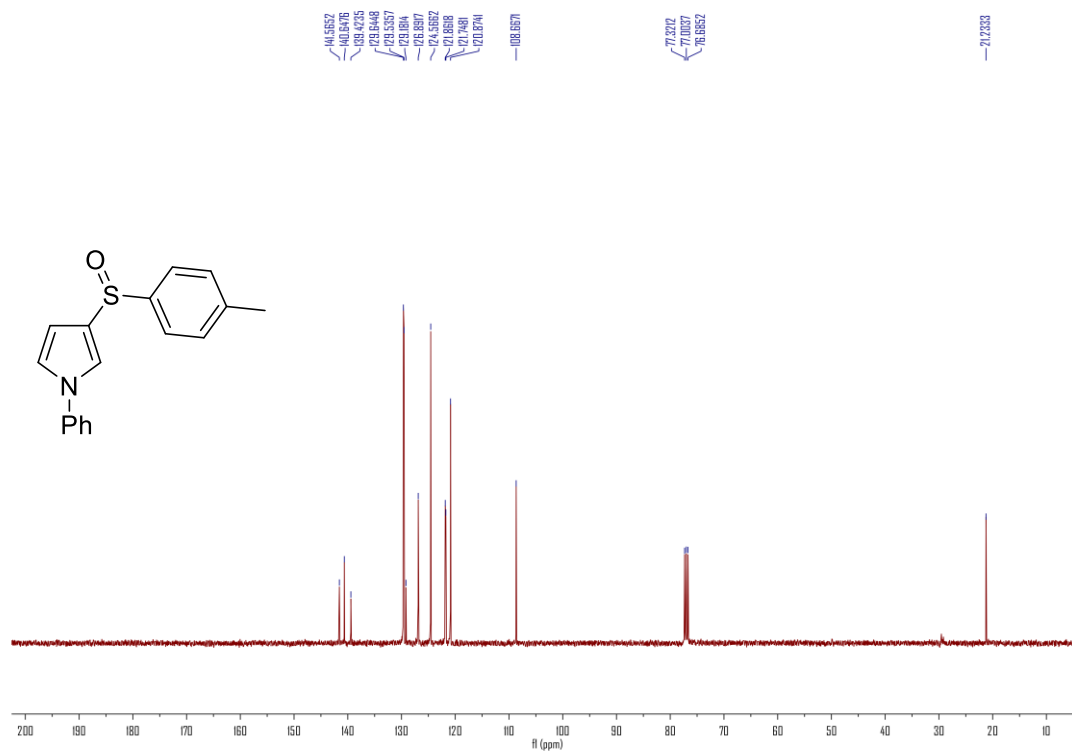


Sulfoxide 4r

^1H NMR (400 MHz, CDCl_3)

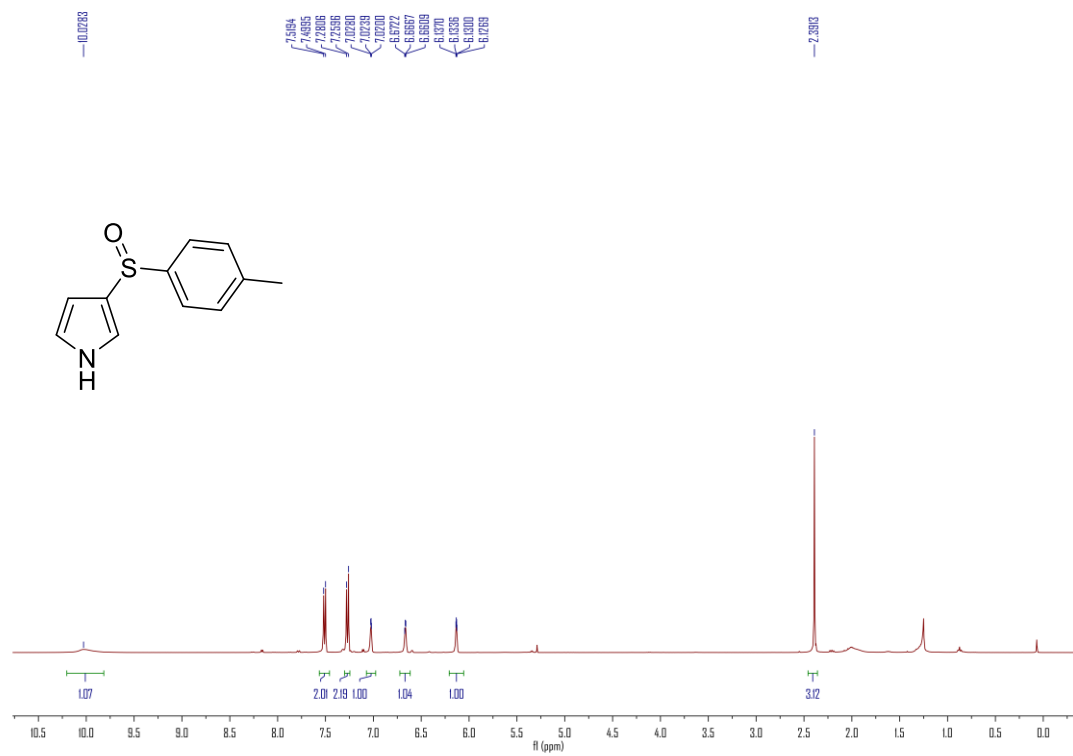


^{13}C NMR (100 MHz, CDCl_3)

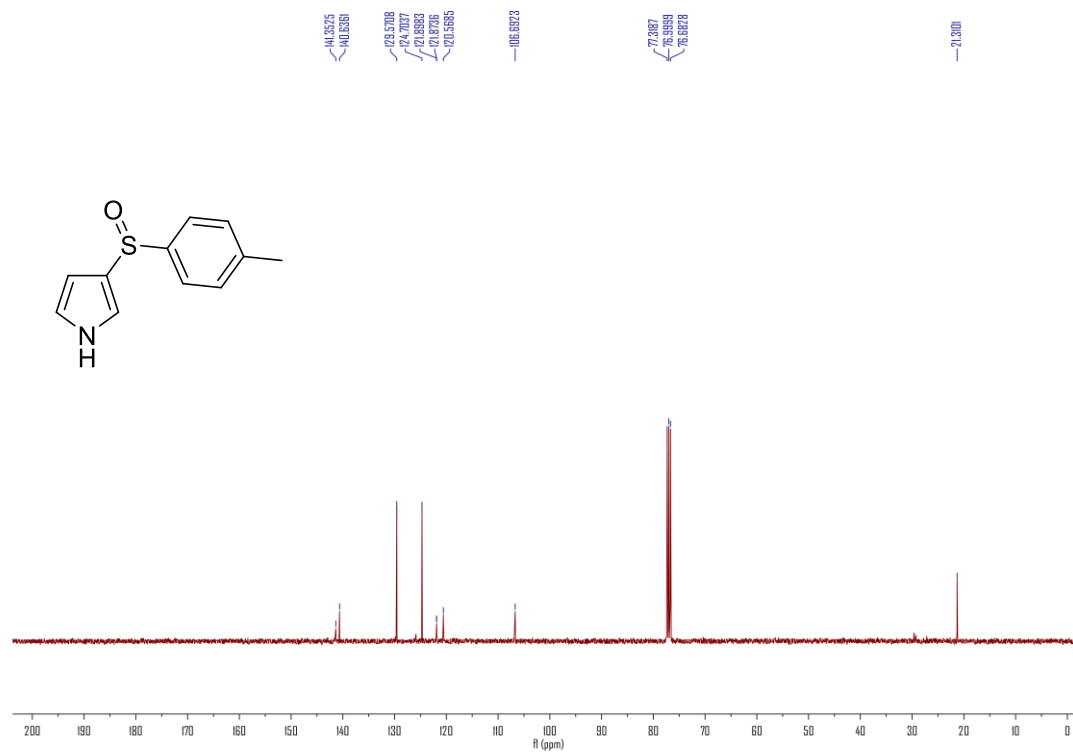


Sulfoxide 4t

^1H NMR (400 MHz, CDCl_3)

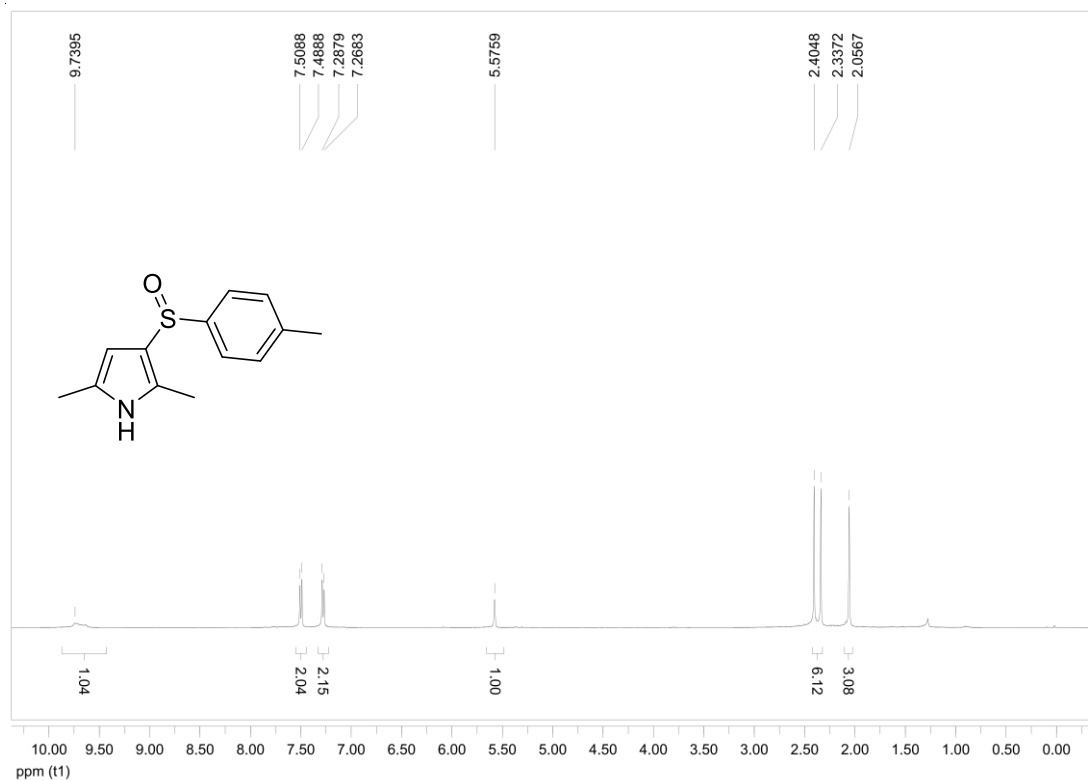


^{13}C NMR (100 MHz, CDCl_3)

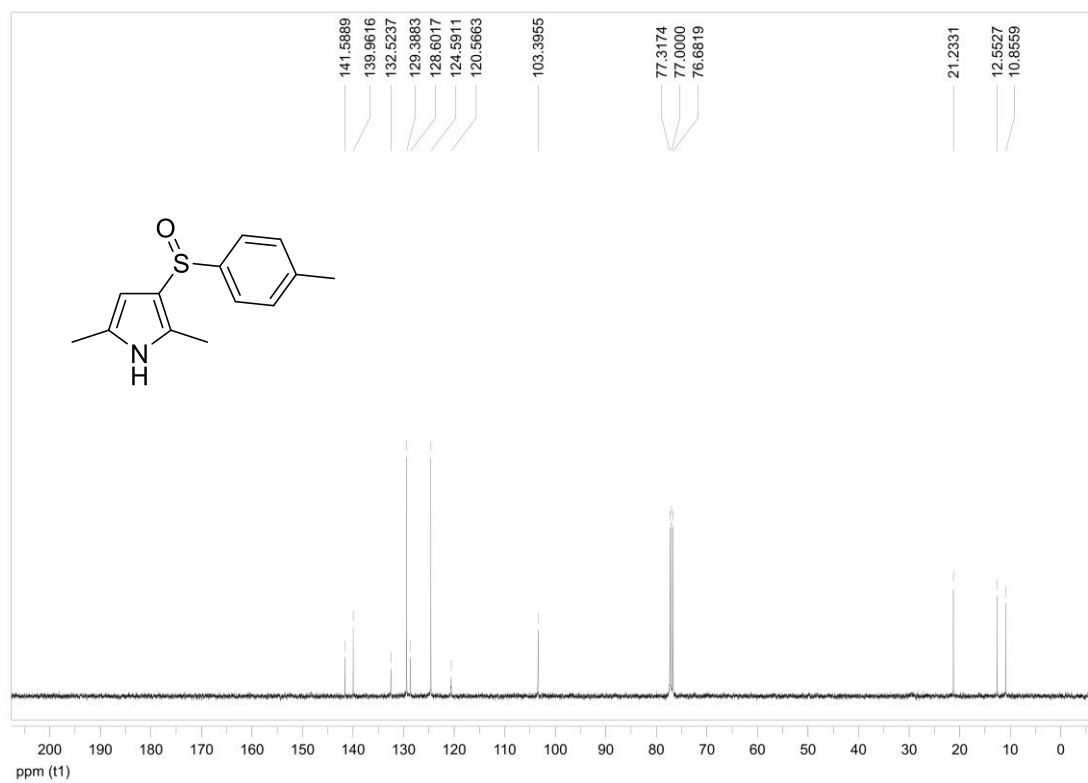


Sulfoxide **4u**

^1H NMR (400 MHz, CDCl_3)

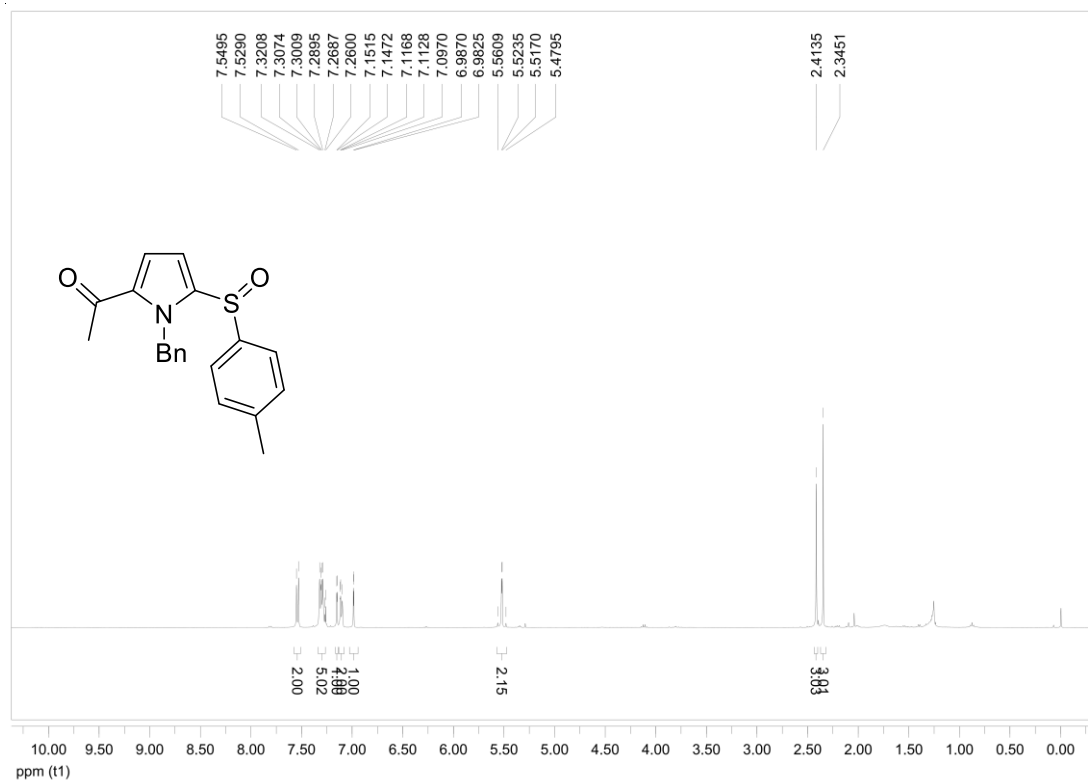


^{13}C NMR (100 MHz, CDCl_3)

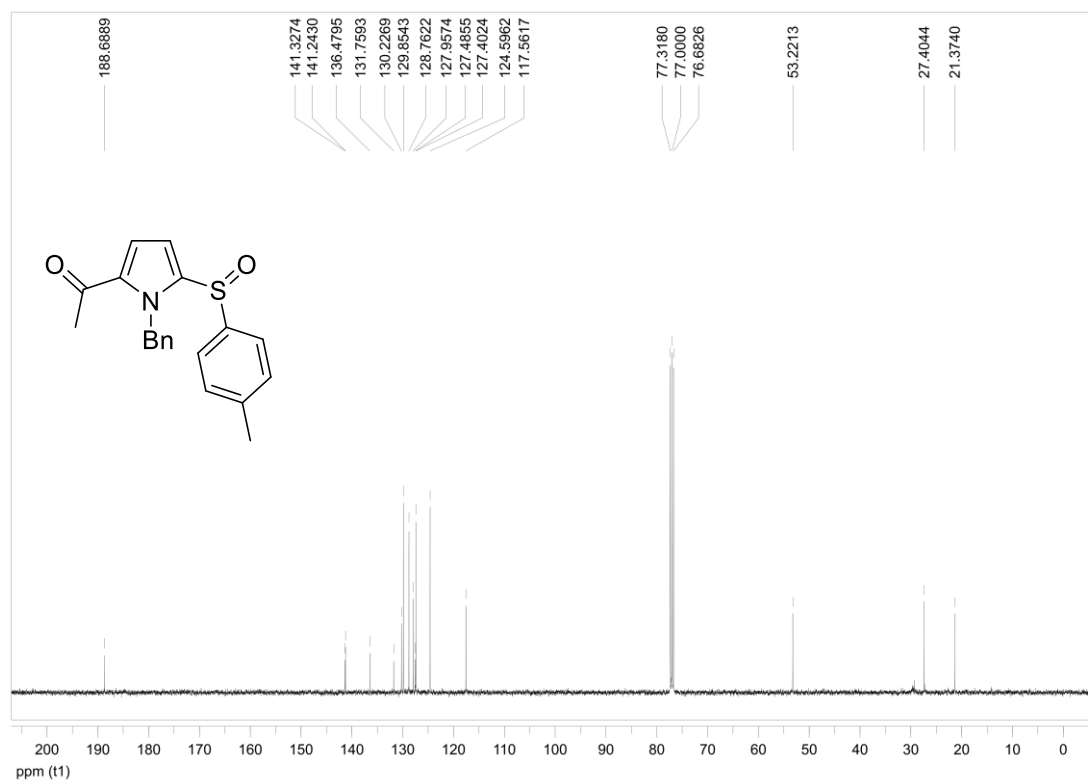


Sulfoxide **3w**

^1H NMR (400 MHz, CDCl_3)

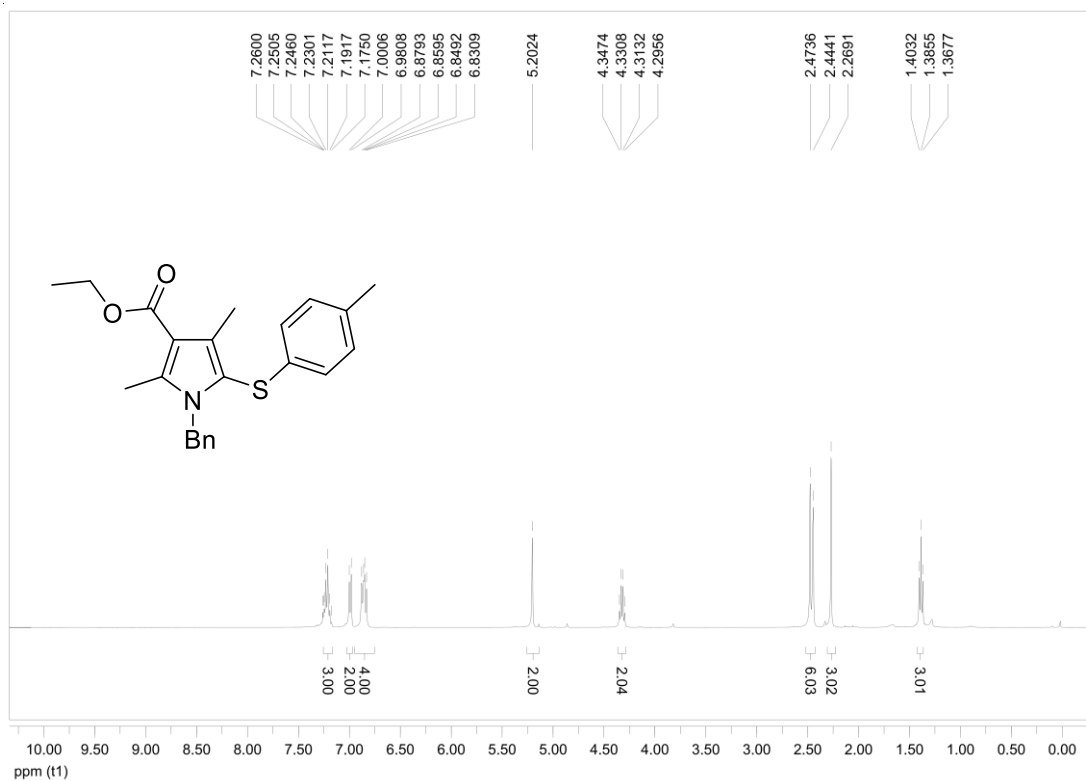


^{13}C NMR (100 MHz, CDCl_3)

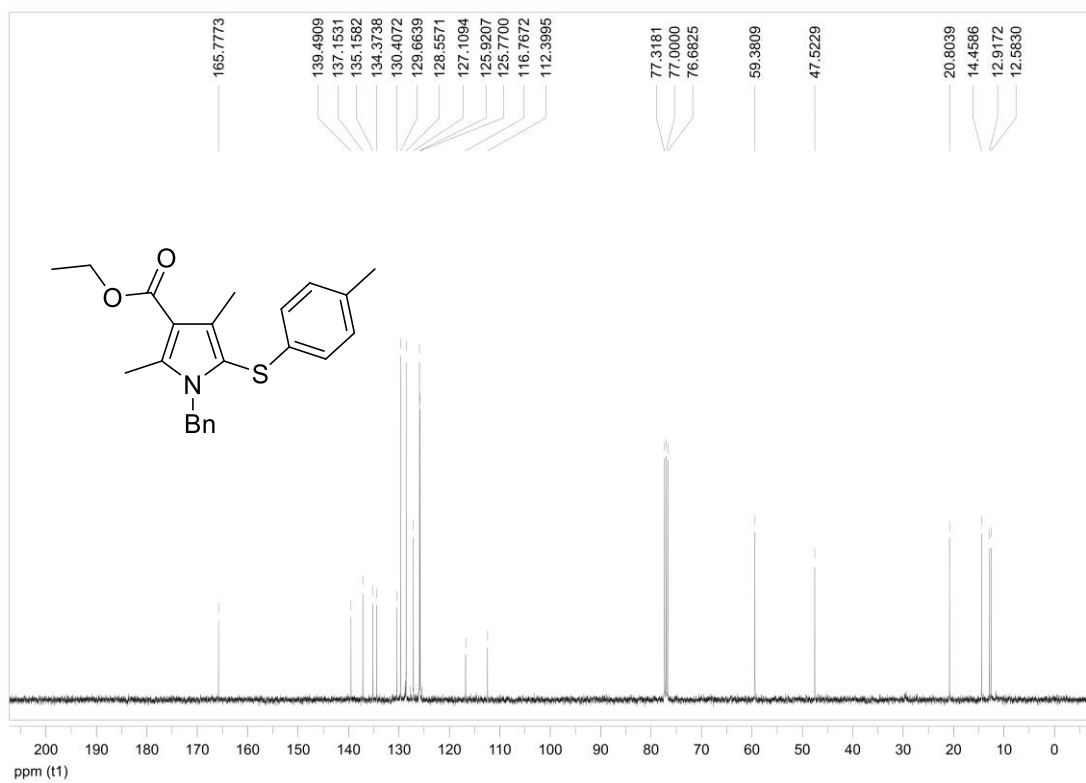


Thioether **5x**

^1H NMR (400 MHz, CDCl_3)

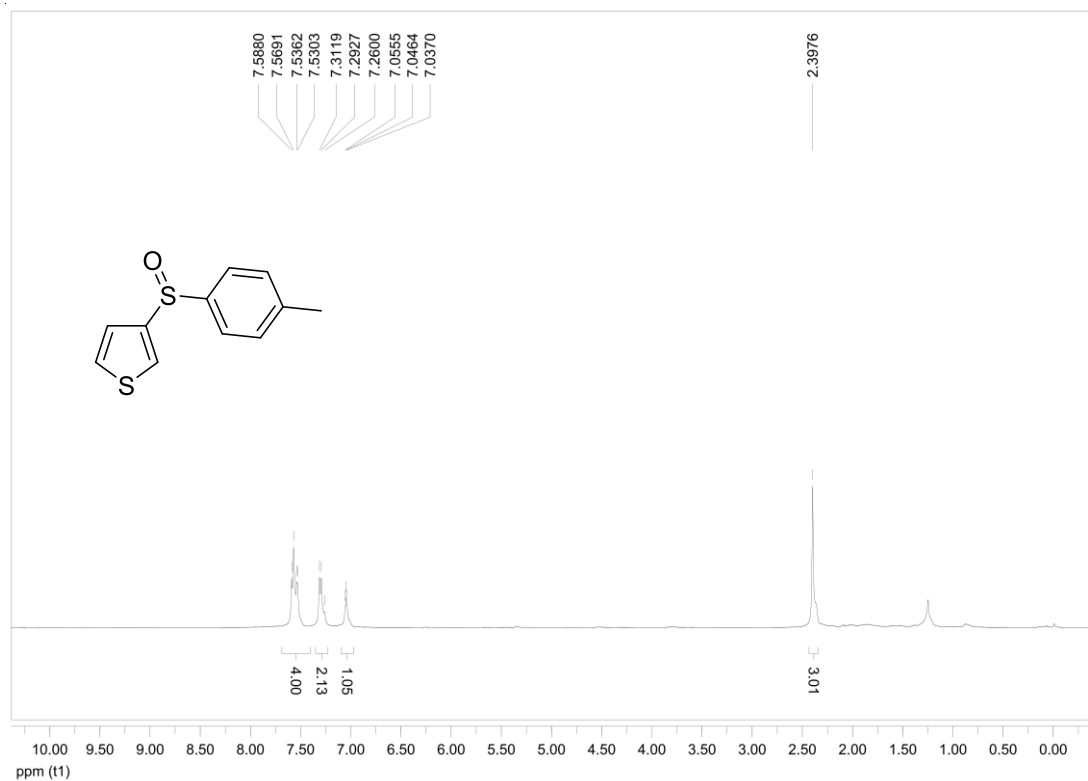


^{13}C NMR (100 MHz, CDCl_3)

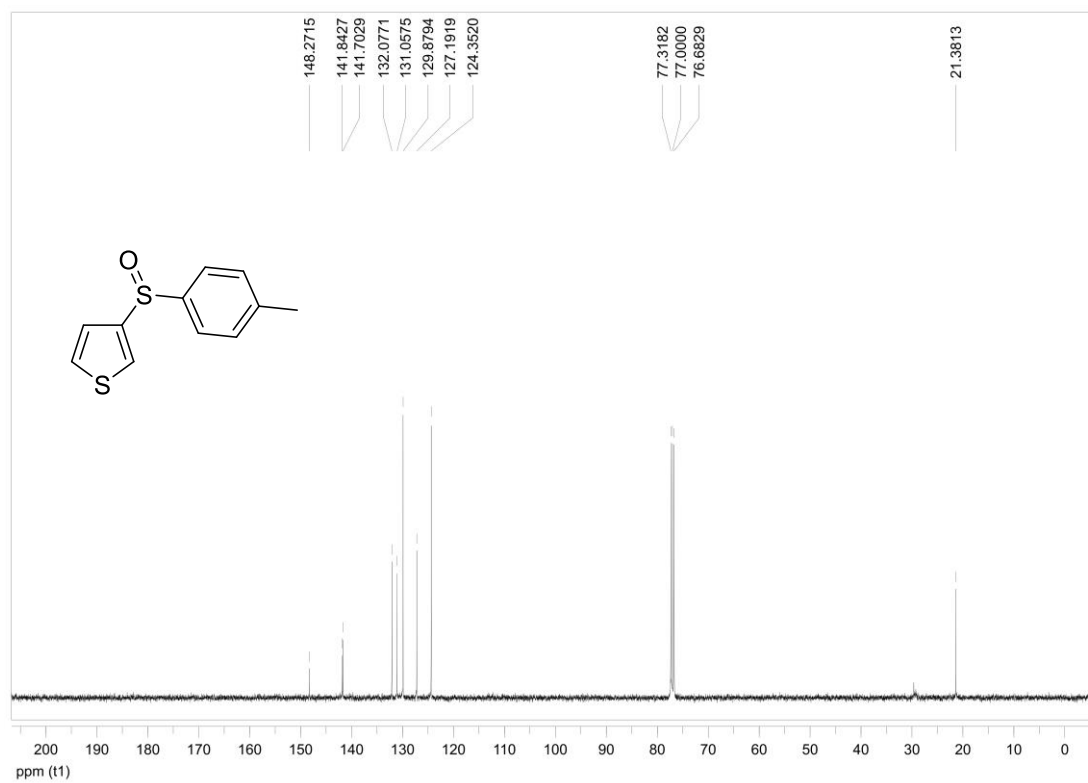


Sulfoxide **4y**

^1H NMR (400 MHz, CDCl_3)

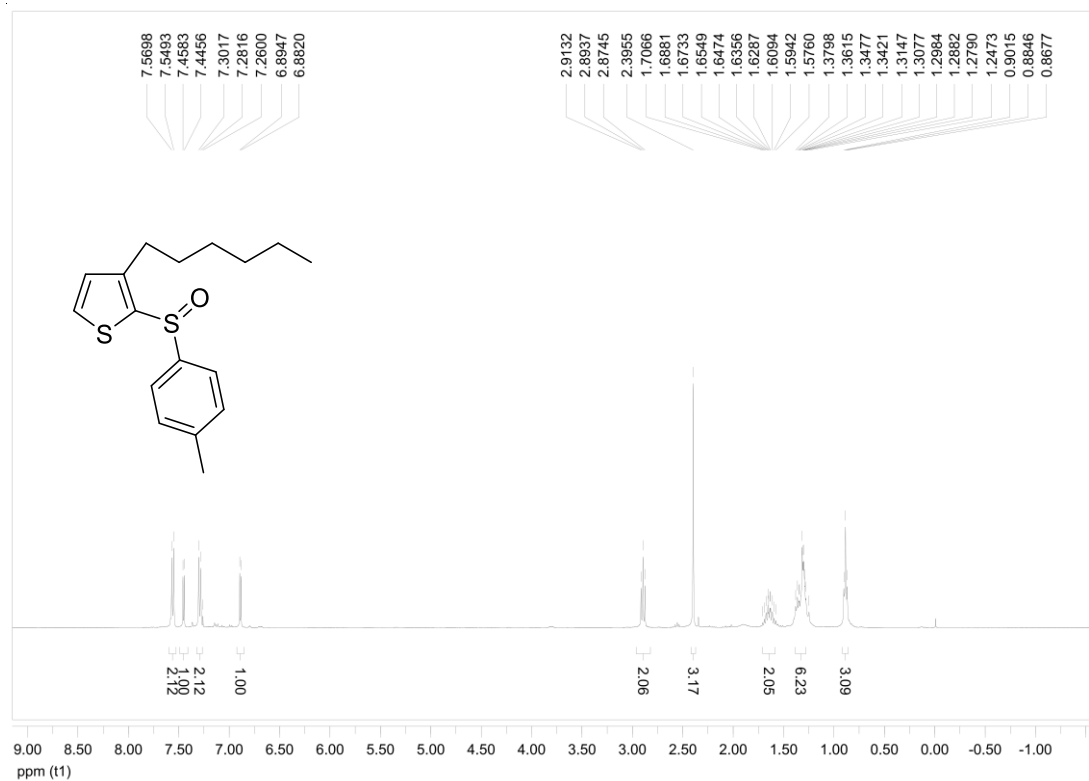


^{13}C NMR (100 MHz, CDCl_3)

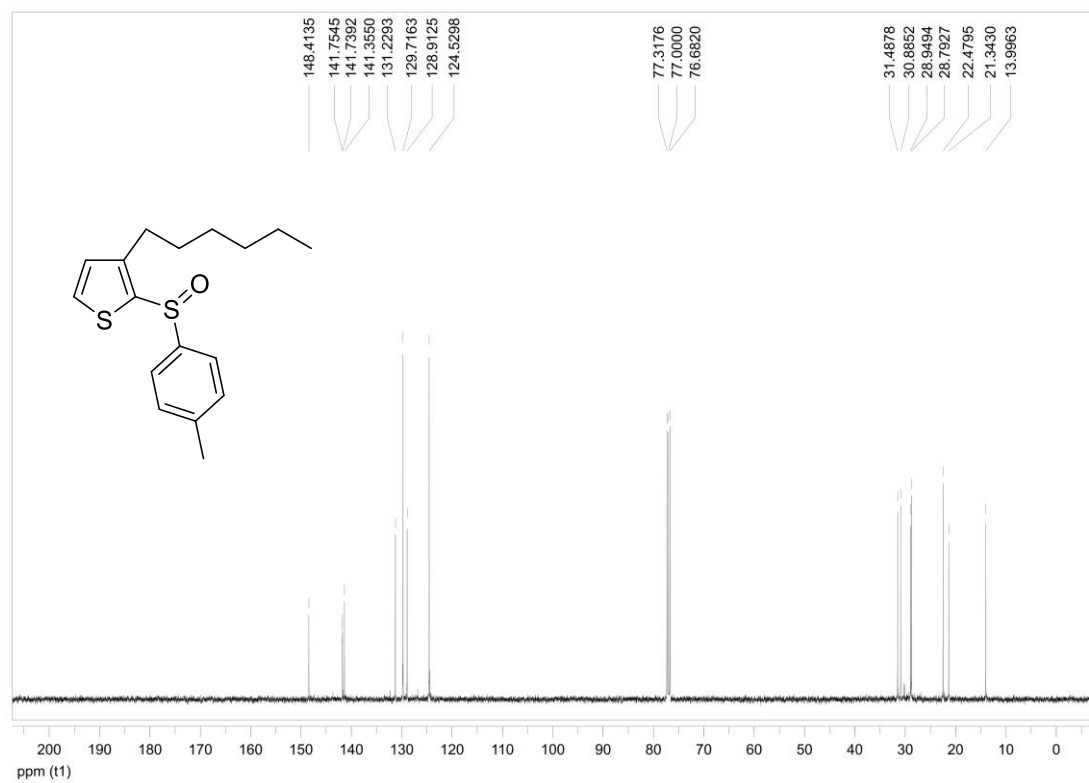


Sulfoxide **4z**

^1H NMR (400 MHz, CDCl_3)

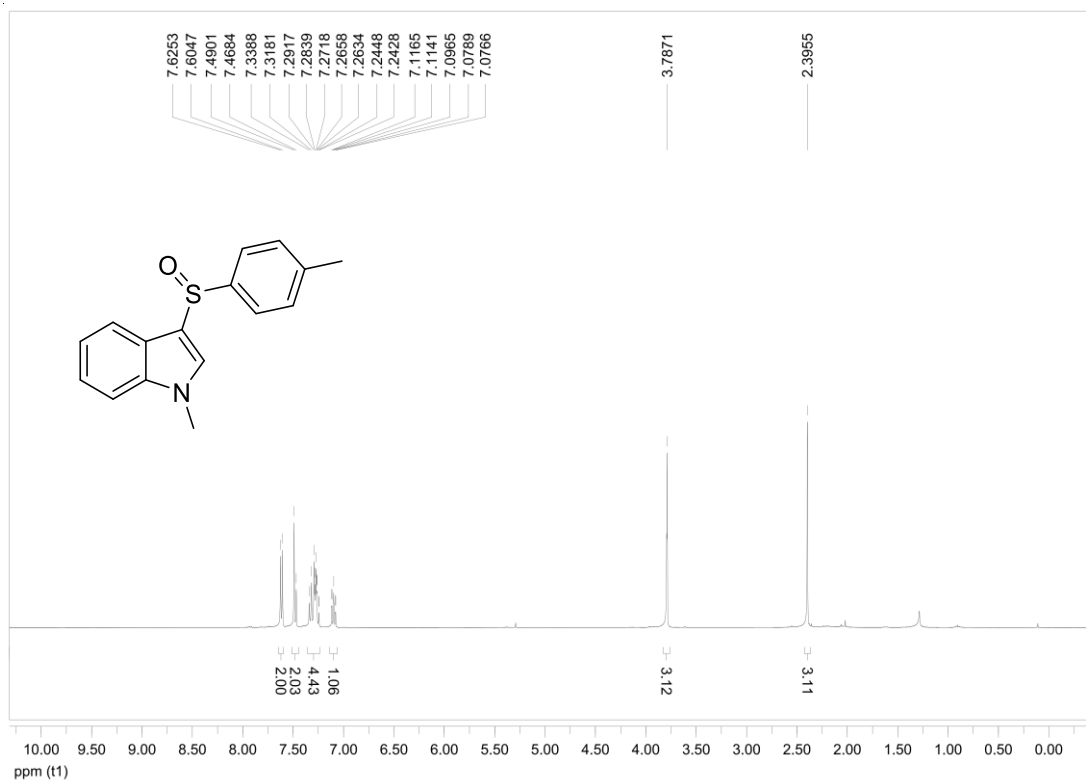


^{13}C NMR (100 MHz, CDCl_3)

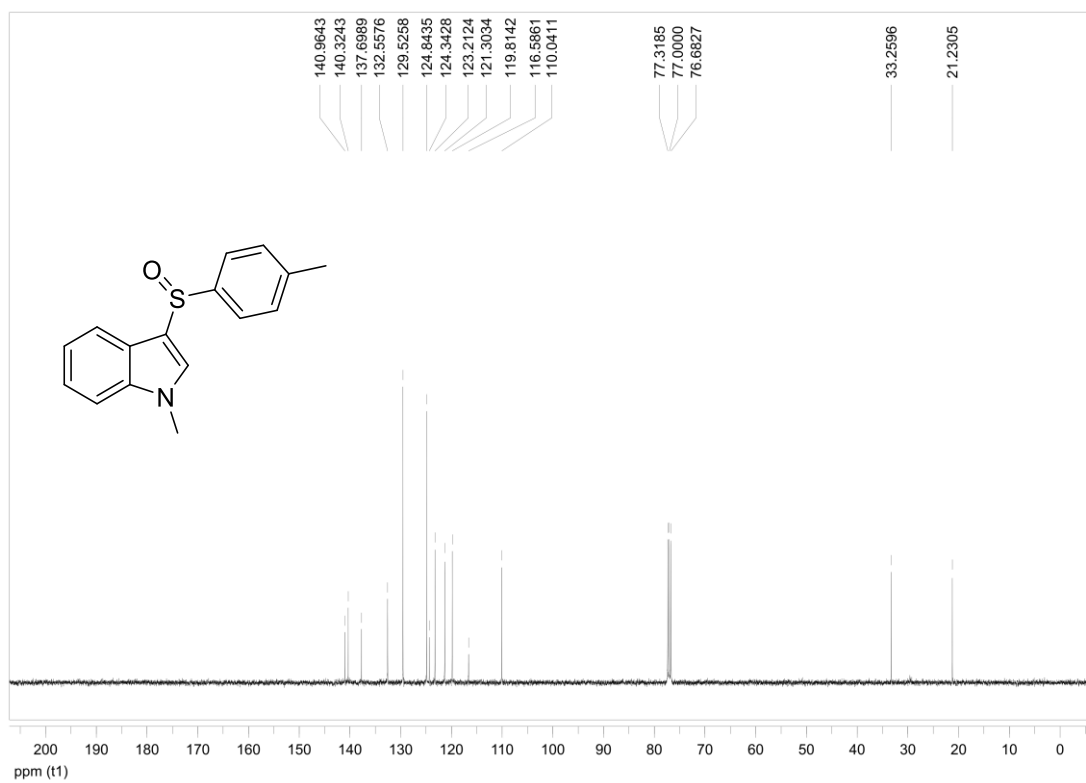


Sulfoxide 10a

^1H NMR (400 MHz, CDCl_3)

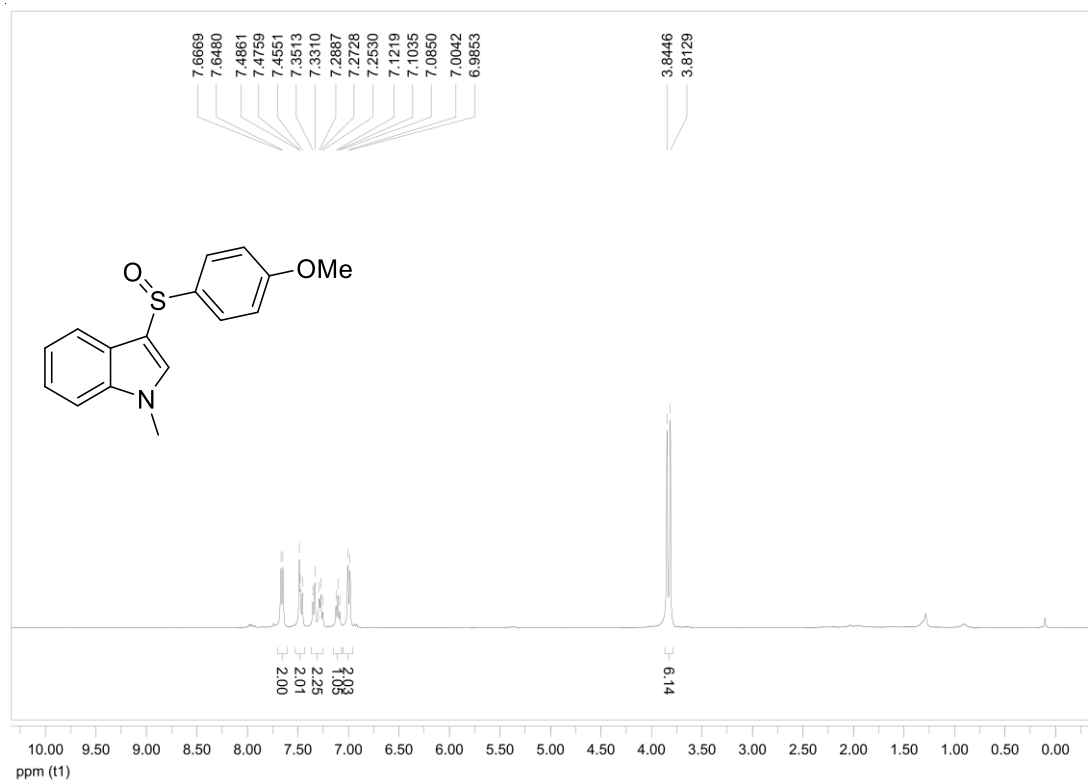


^{13}C NMR (100 MHz, CDCl_3)

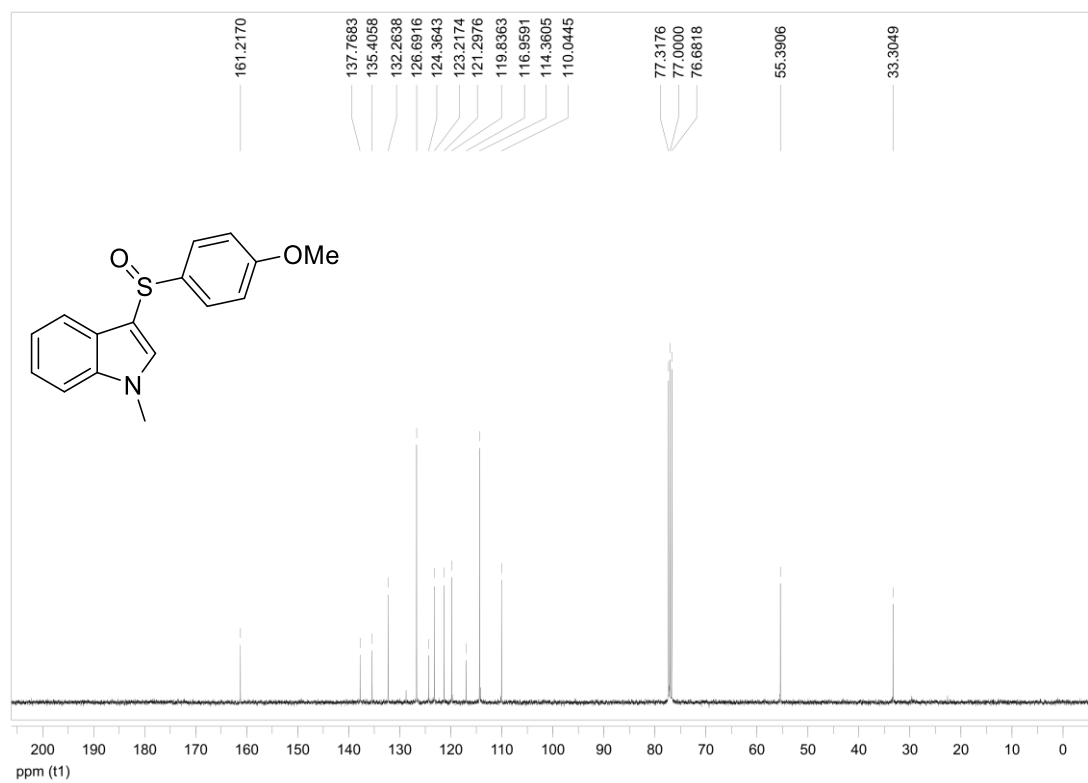


Sulfoxide **10b**

^1H NMR (400 MHz, CDCl_3)

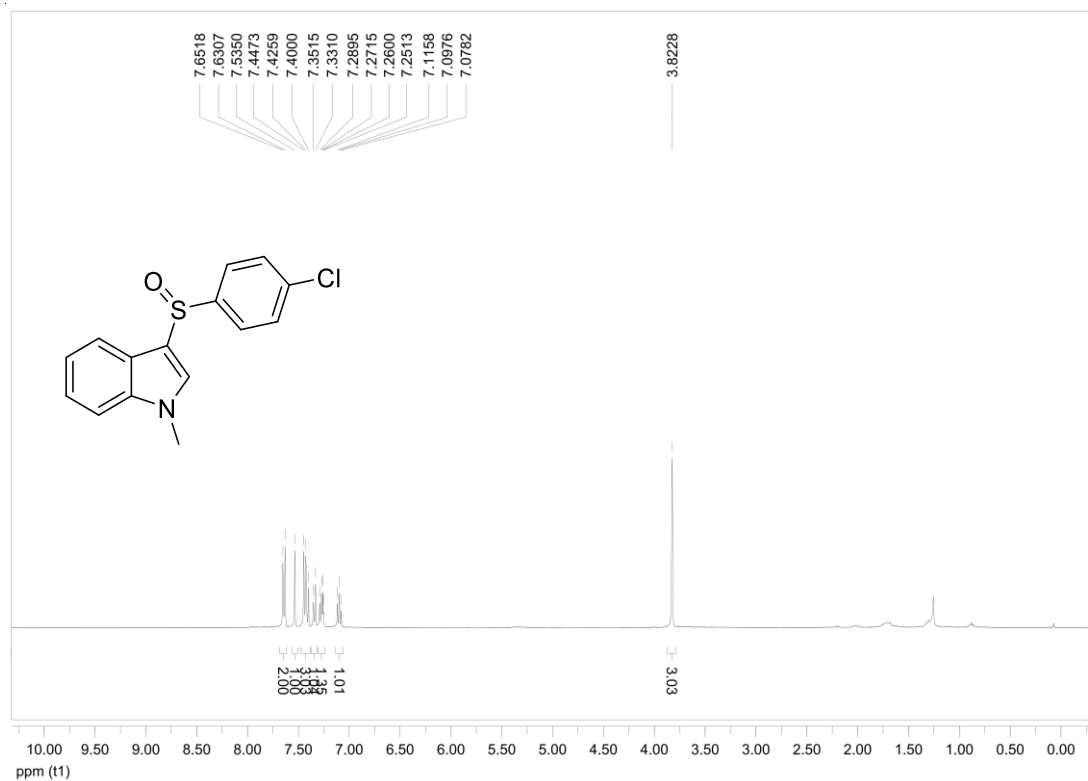


^{13}C NMR (100 MHz, CDCl_3)

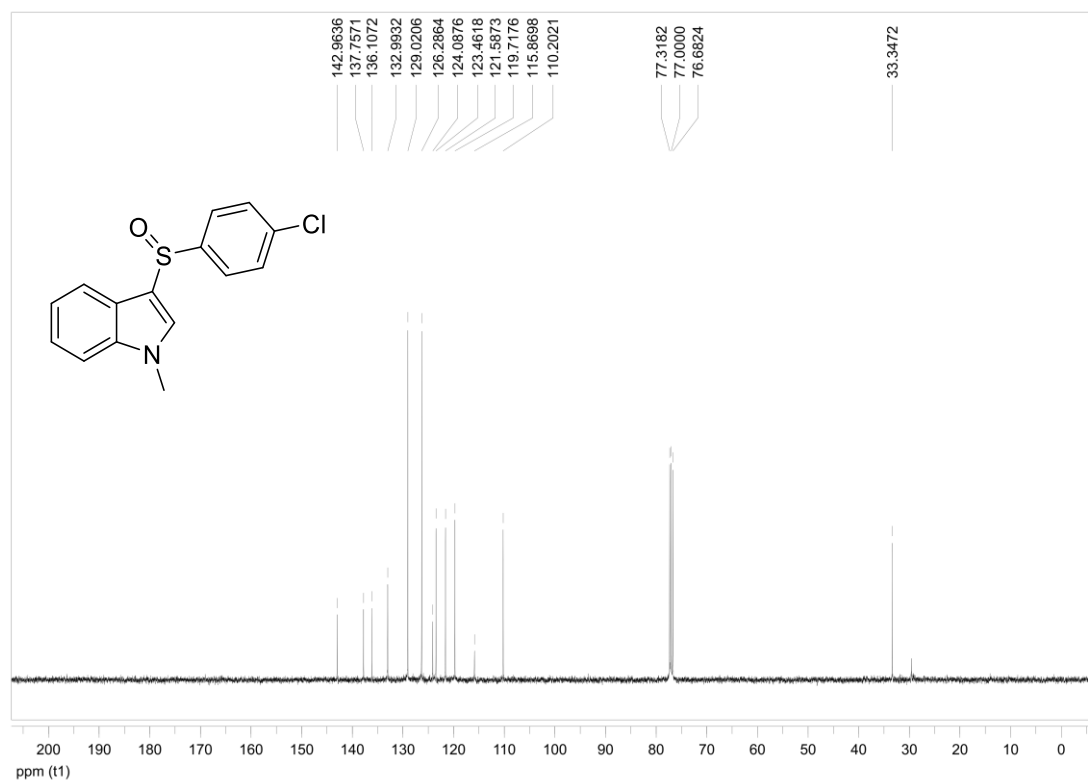


Sulfoxide **10c**

^1H NMR (400 MHz, CDCl_3)

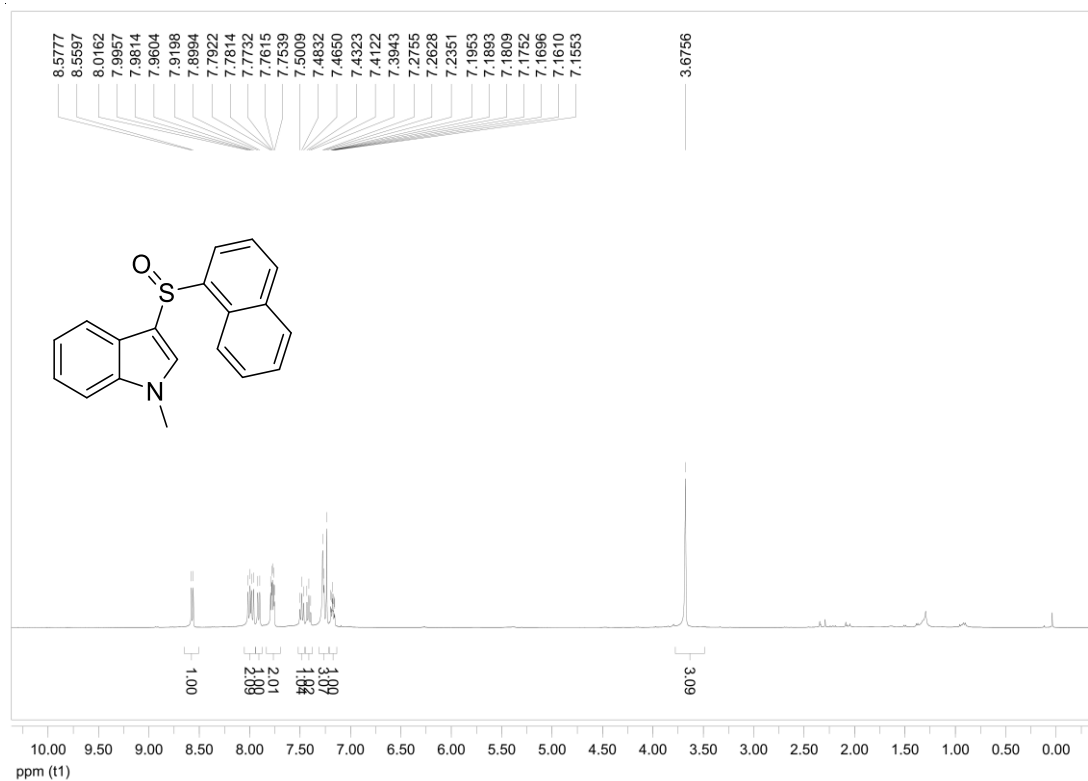


^{13}C NMR (100 MHz, CDCl_3)

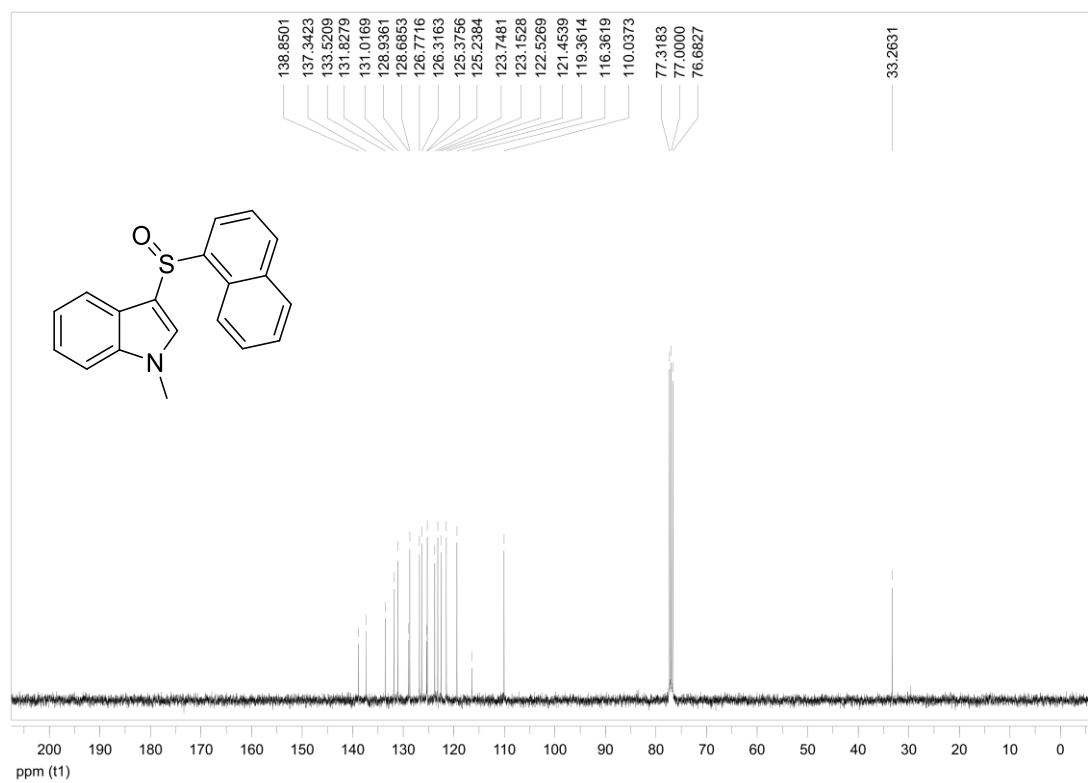


Sulfoxide **10d**

^1H NMR (400 MHz, CDCl_3)

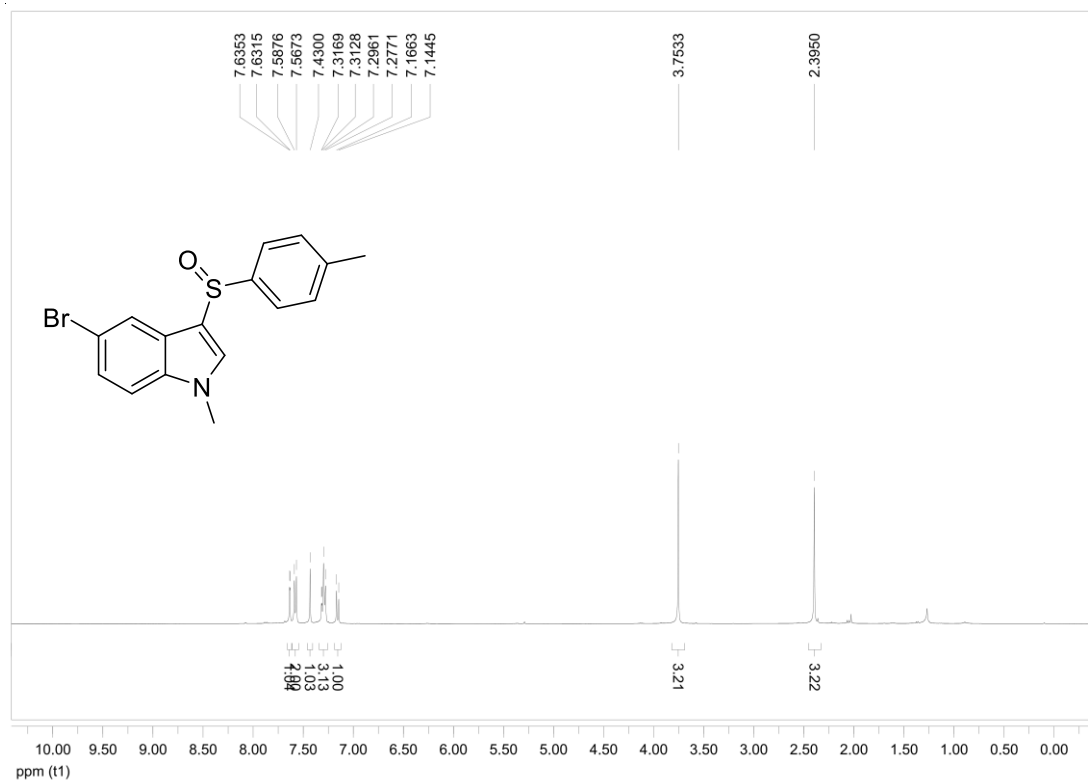


^{13}C NMR (100 MHz, CDCl_3)

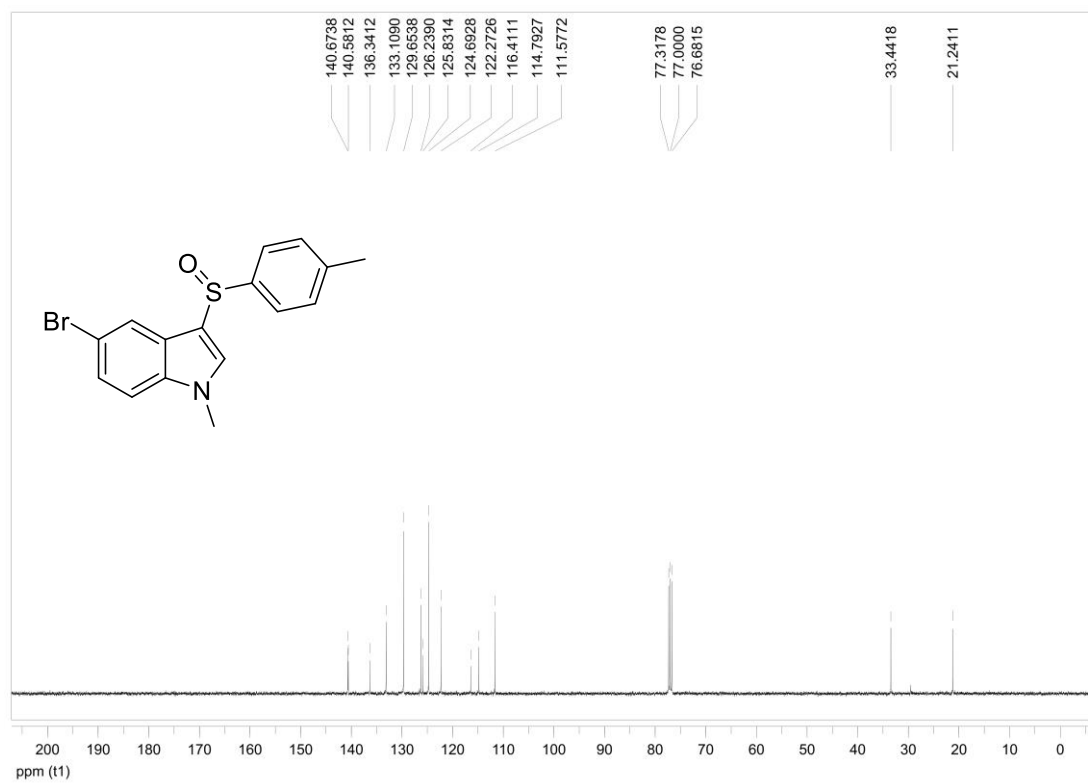


Sulfoxide 10e

^1H NMR (400 MHz, CDCl_3)

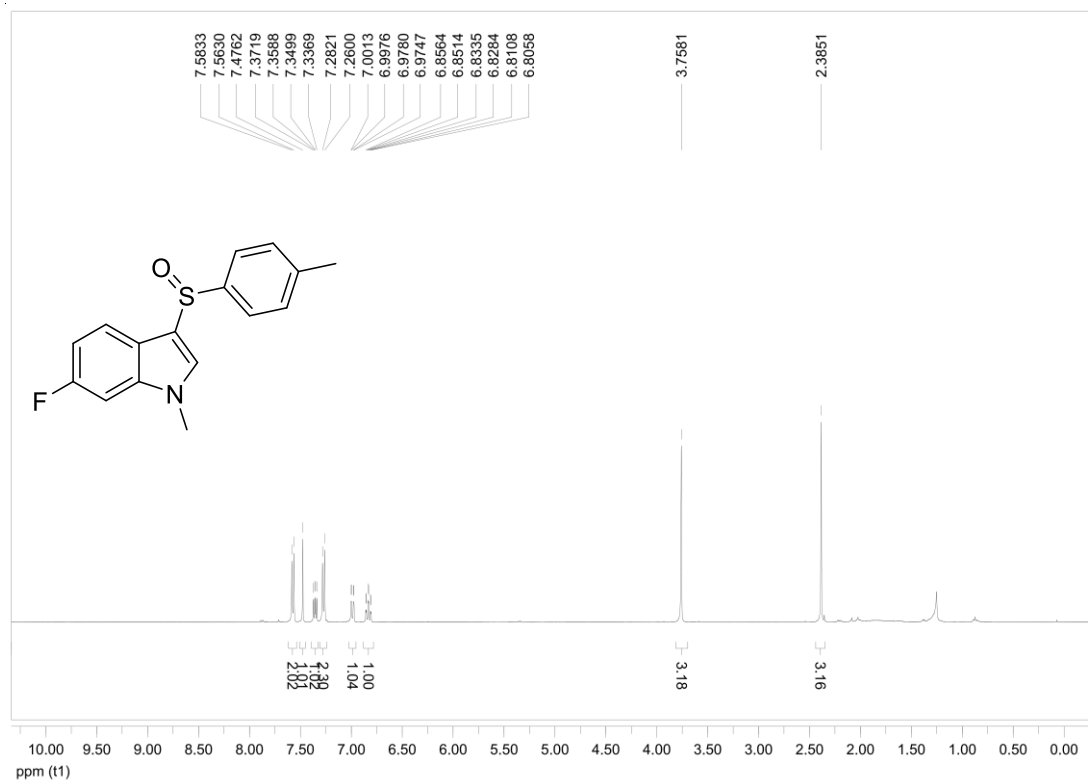


^{13}C NMR (100 MHz, CDCl_3)

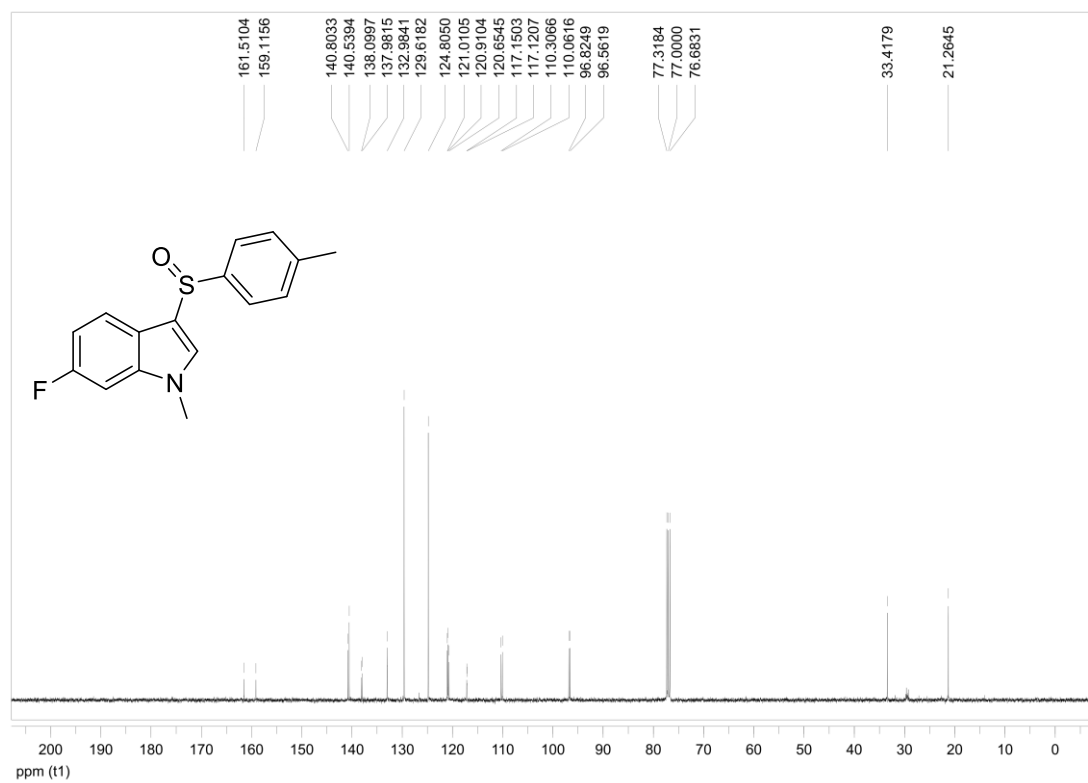


Sulfoxide **10f**

^1H NMR (400 MHz, CDCl_3)

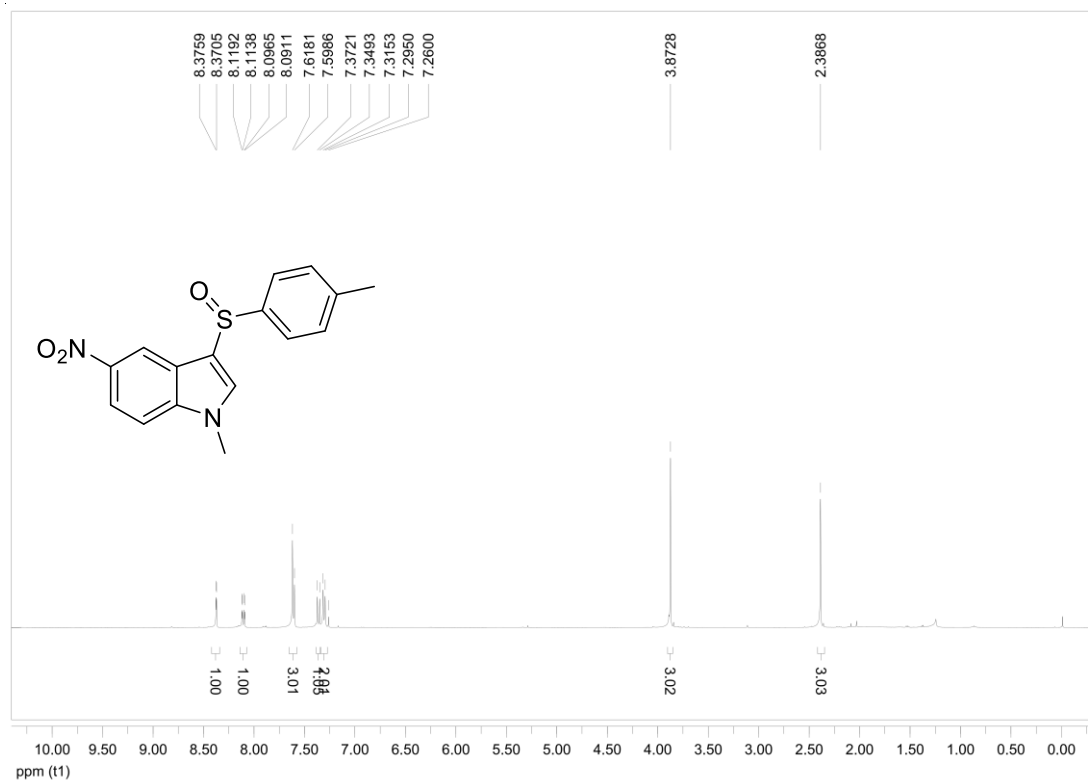


^{13}C NMR (100 MHz, CDCl_3)

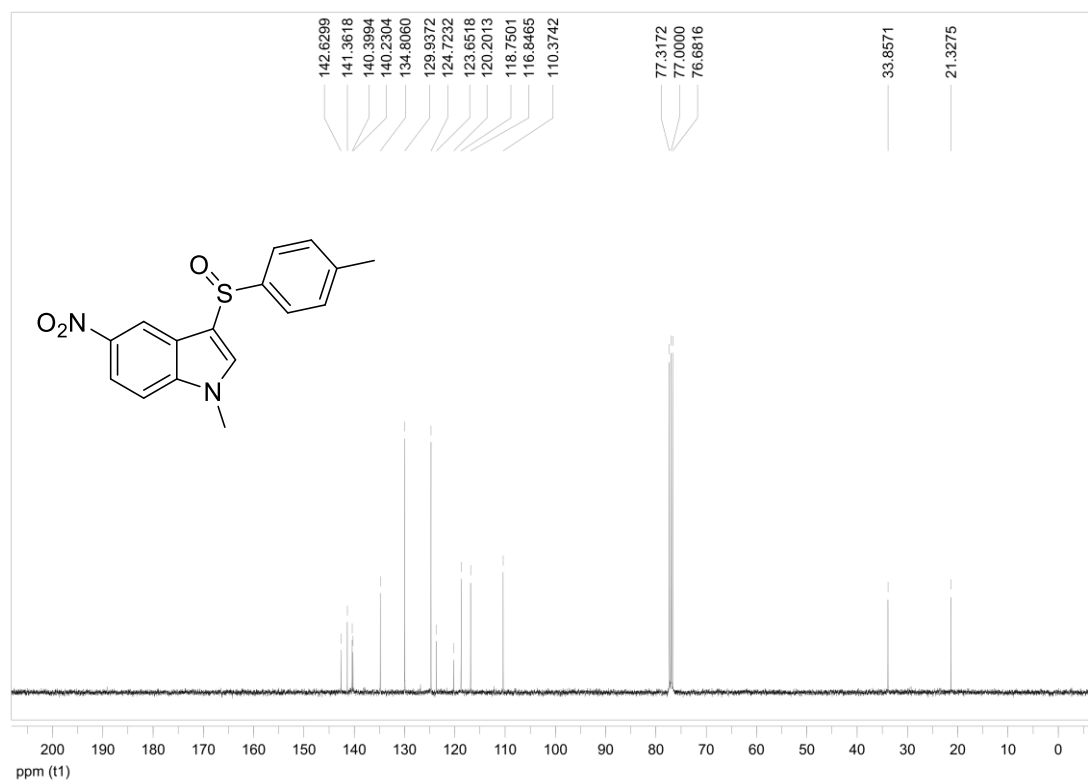


Sulfoxide **10g**

^1H NMR (400 MHz, CDCl_3)

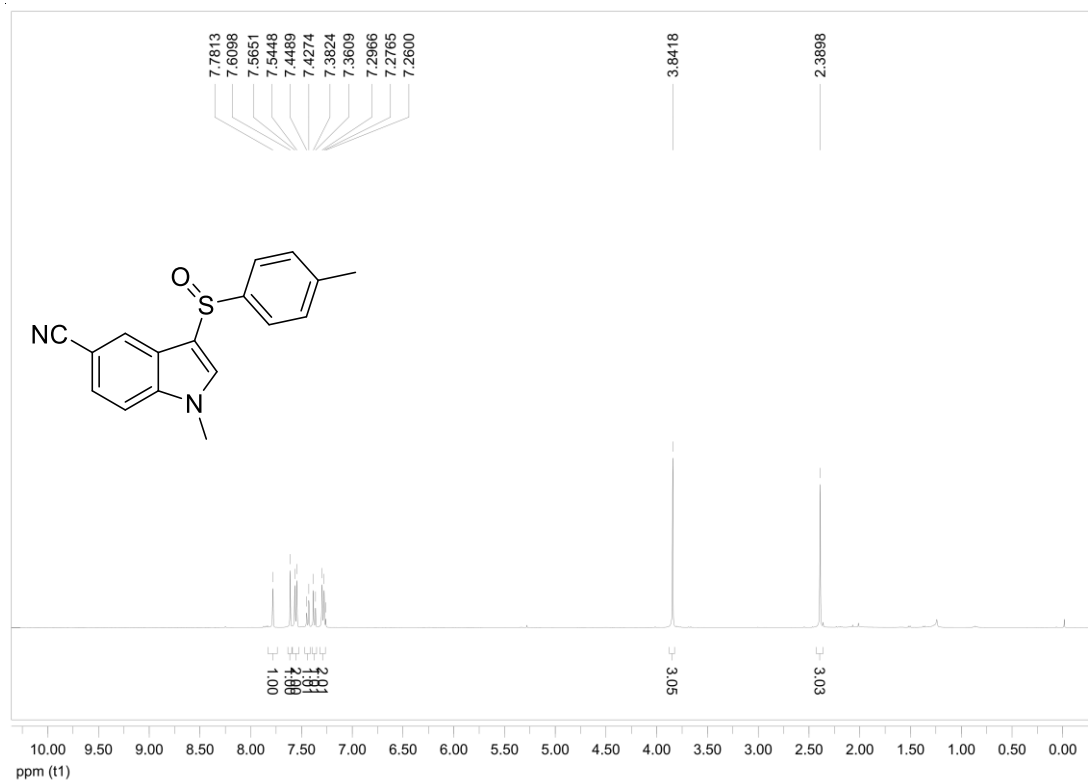


^{13}C NMR (100 MHz, CDCl_3)

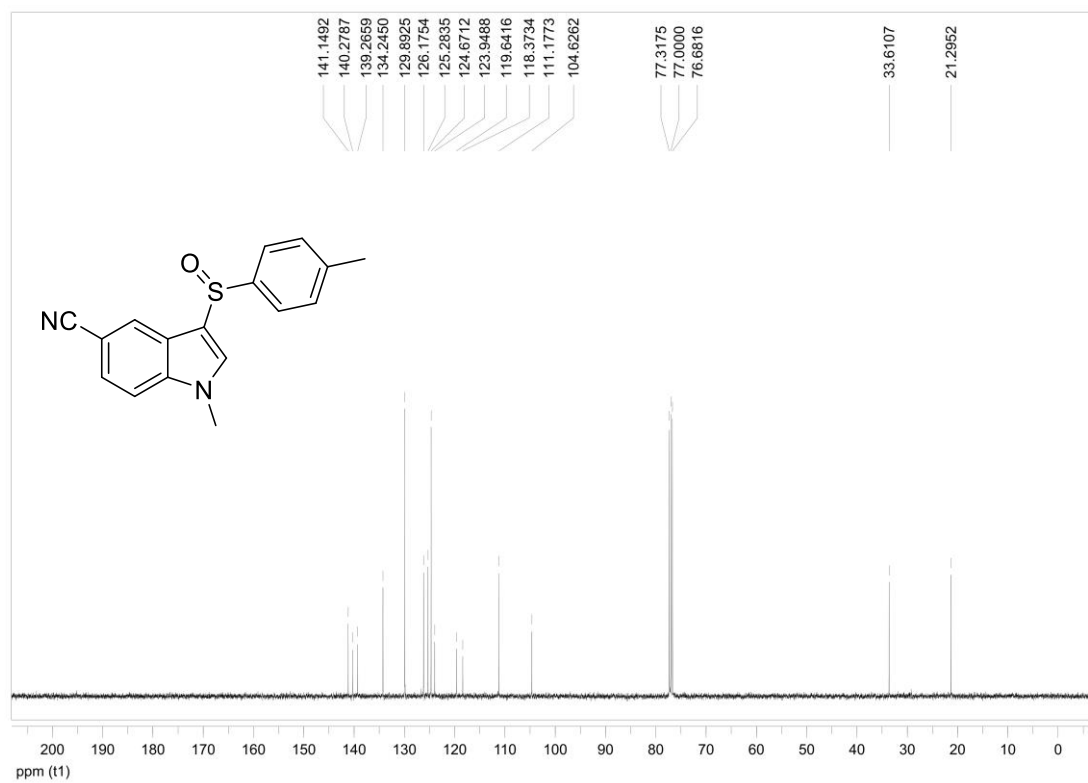


Sulfoxide 10h

^1H NMR (400 MHz, CDCl_3)

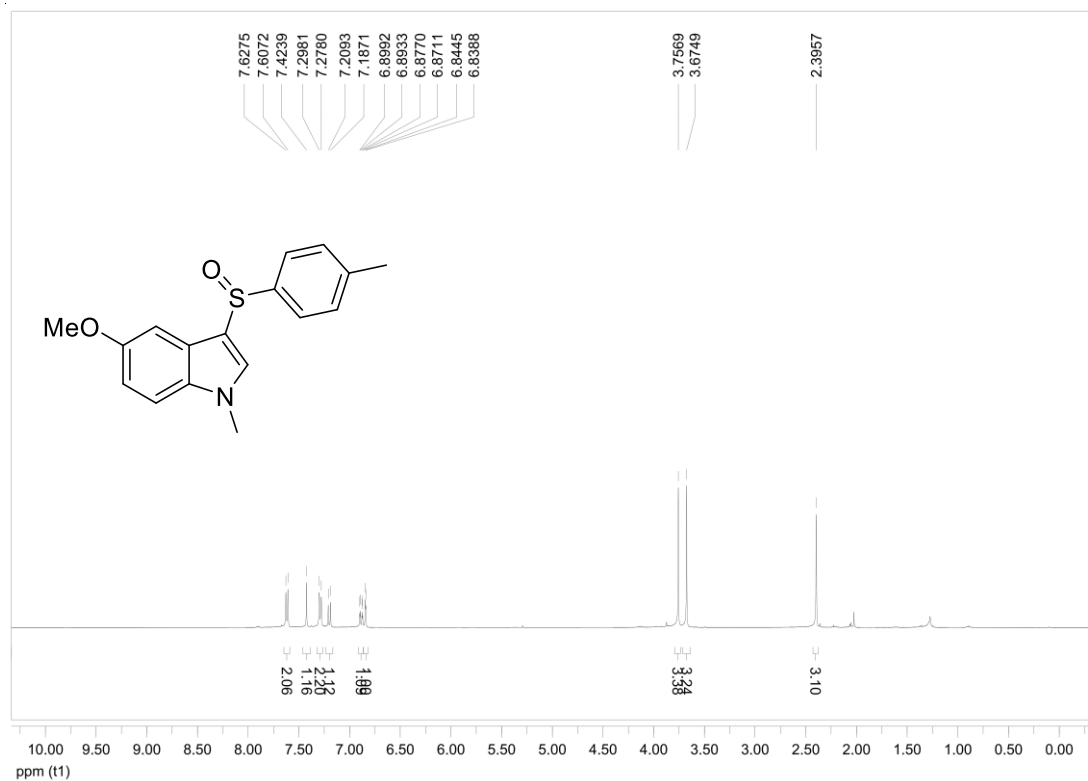


^{13}C NMR (100 MHz, CDCl_3)

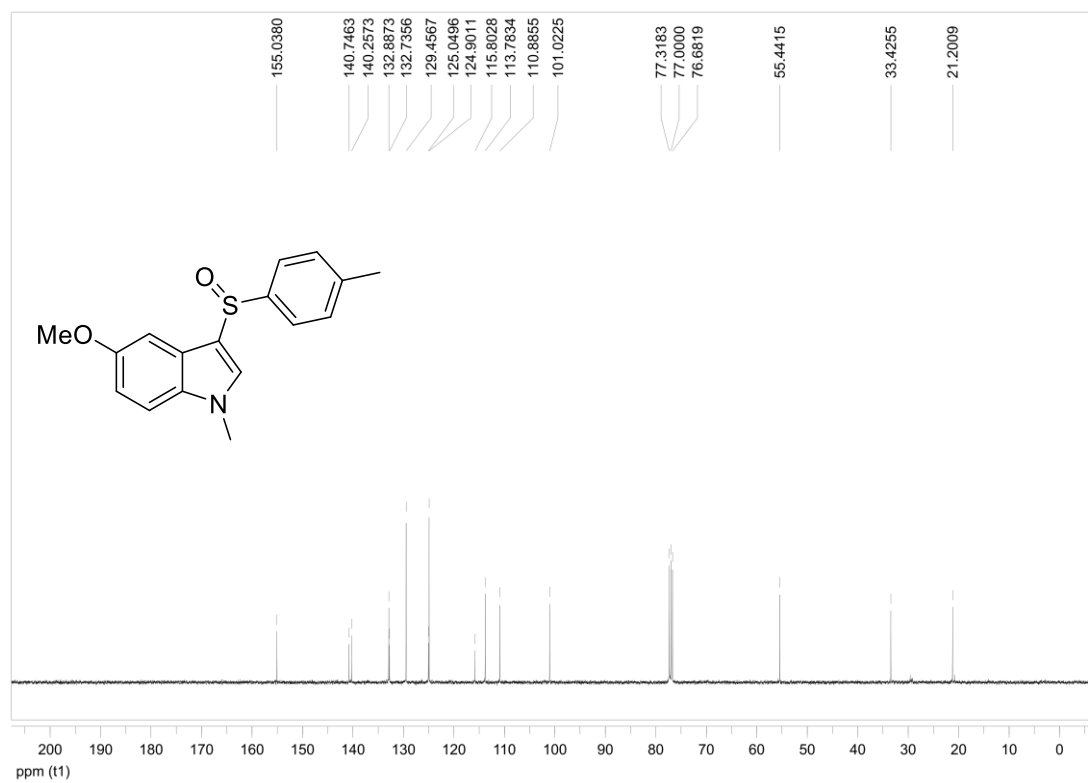


Sulfoxide **10i**

^1H NMR (400 MHz, CDCl_3)

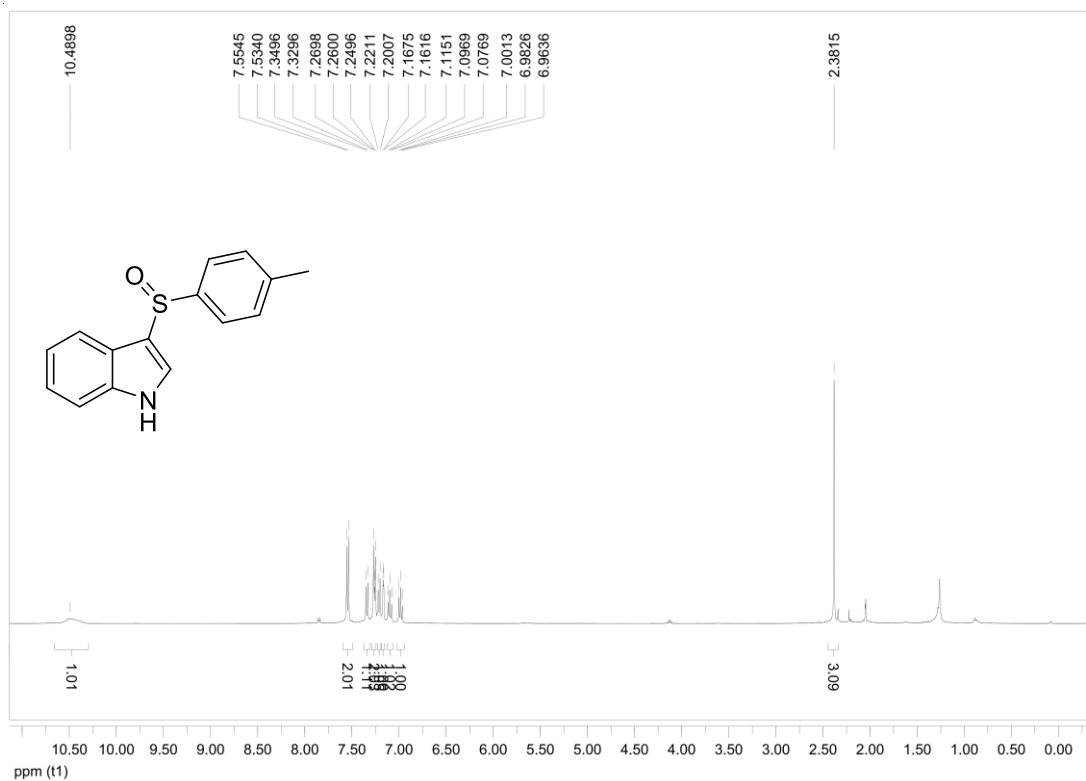


^{13}C NMR (100 MHz, CDCl_3)

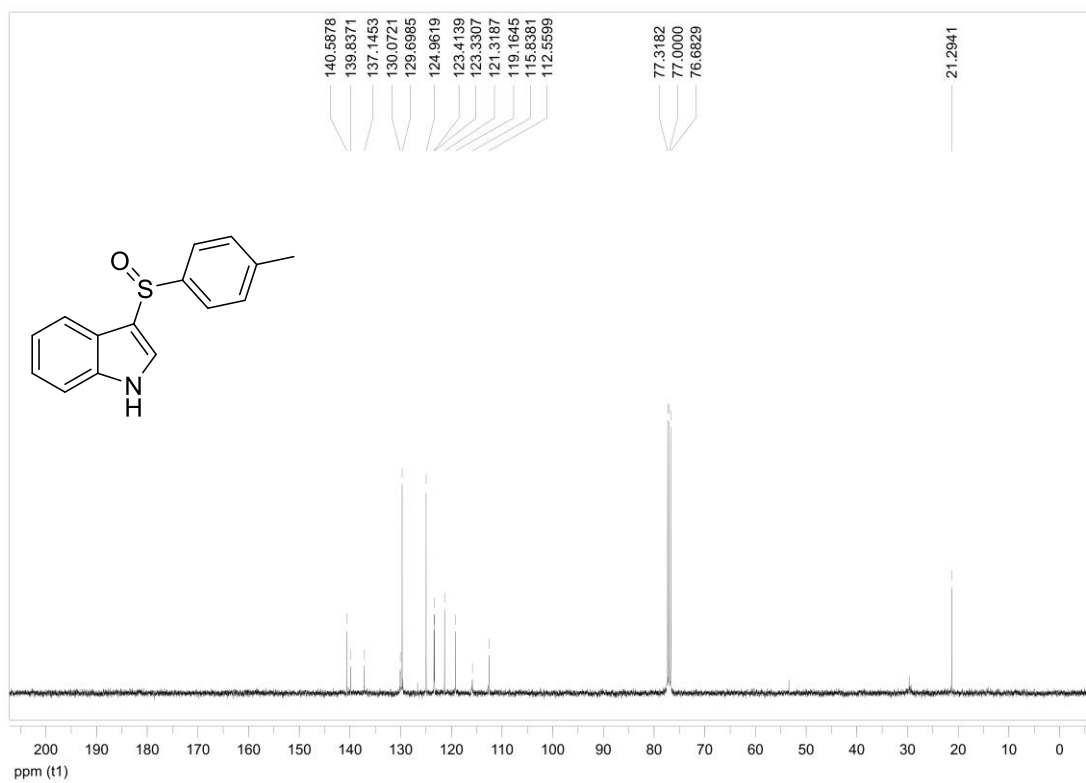


Sulfoxide **101**

^1H NMR (400 MHz, CDCl_3)

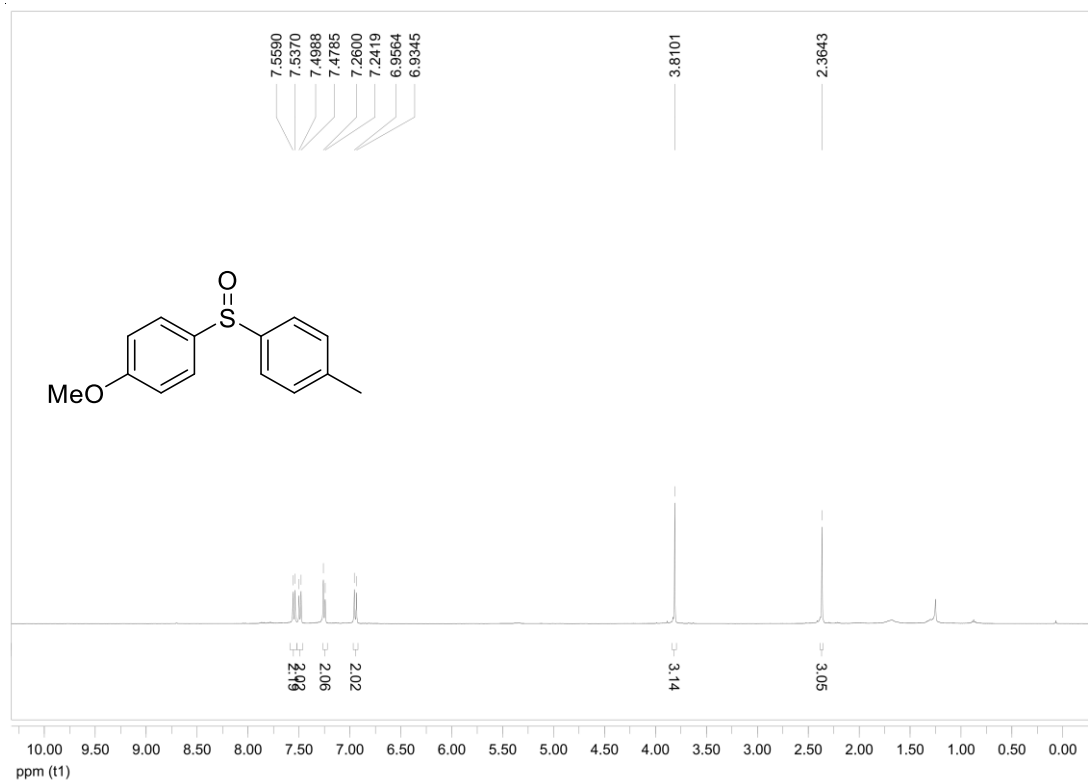


^{13}C NMR (100 MHz, CDCl_3)

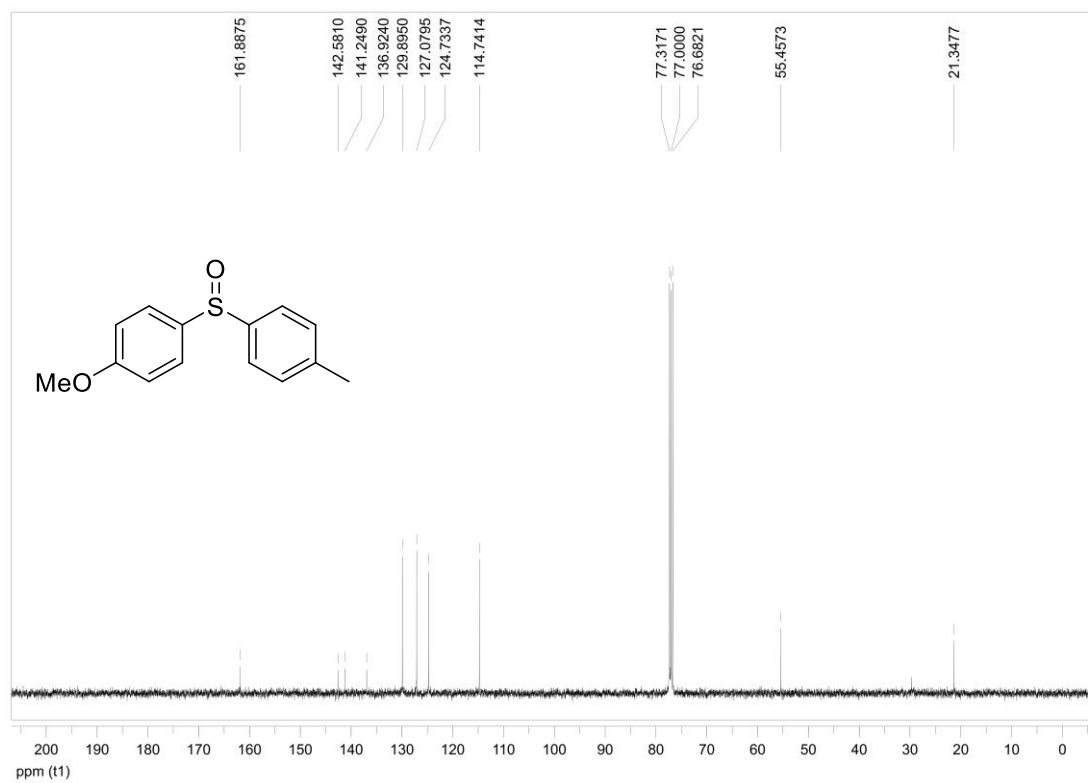


Sulfoxide **12a**

^1H NMR (400 MHz, CDCl_3)

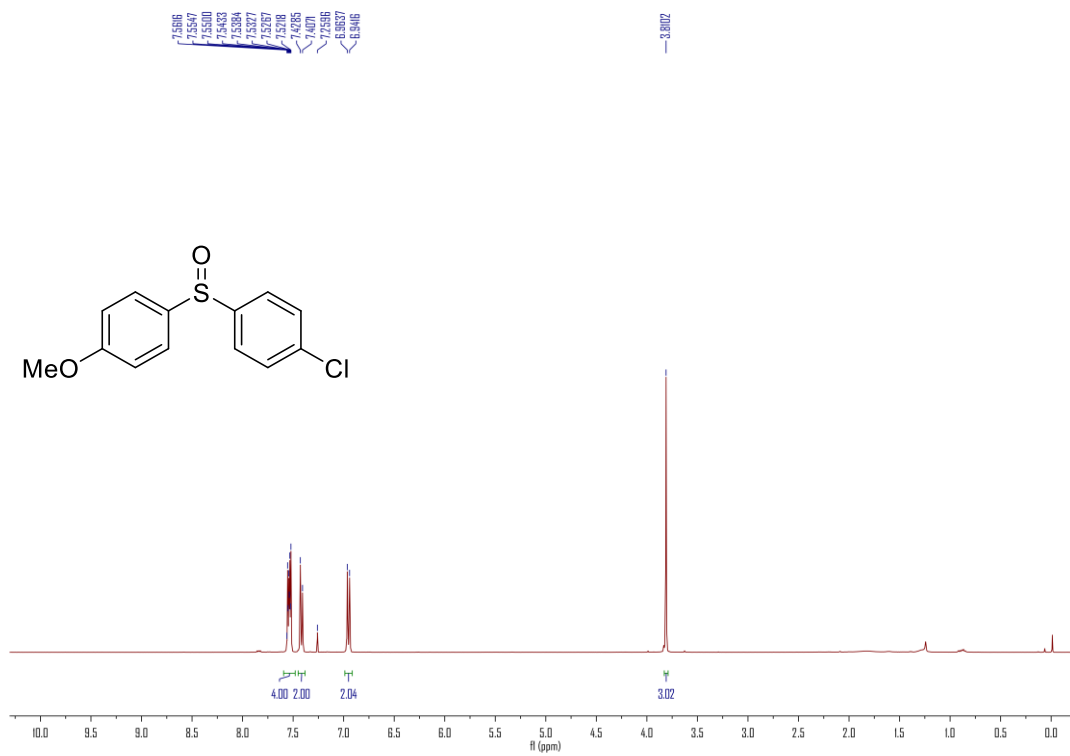


^{13}C NMR (100 MHz, CDCl_3)

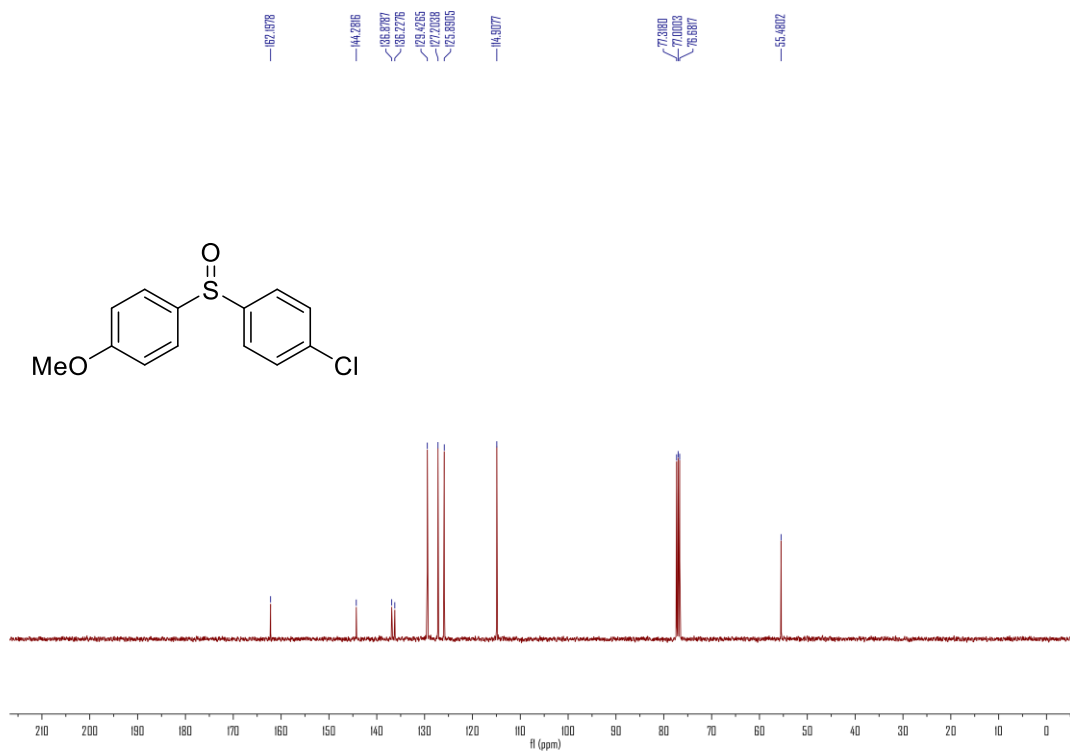


Sulfoxide **12b**

^1H NMR (400 MHz, CDCl_3)

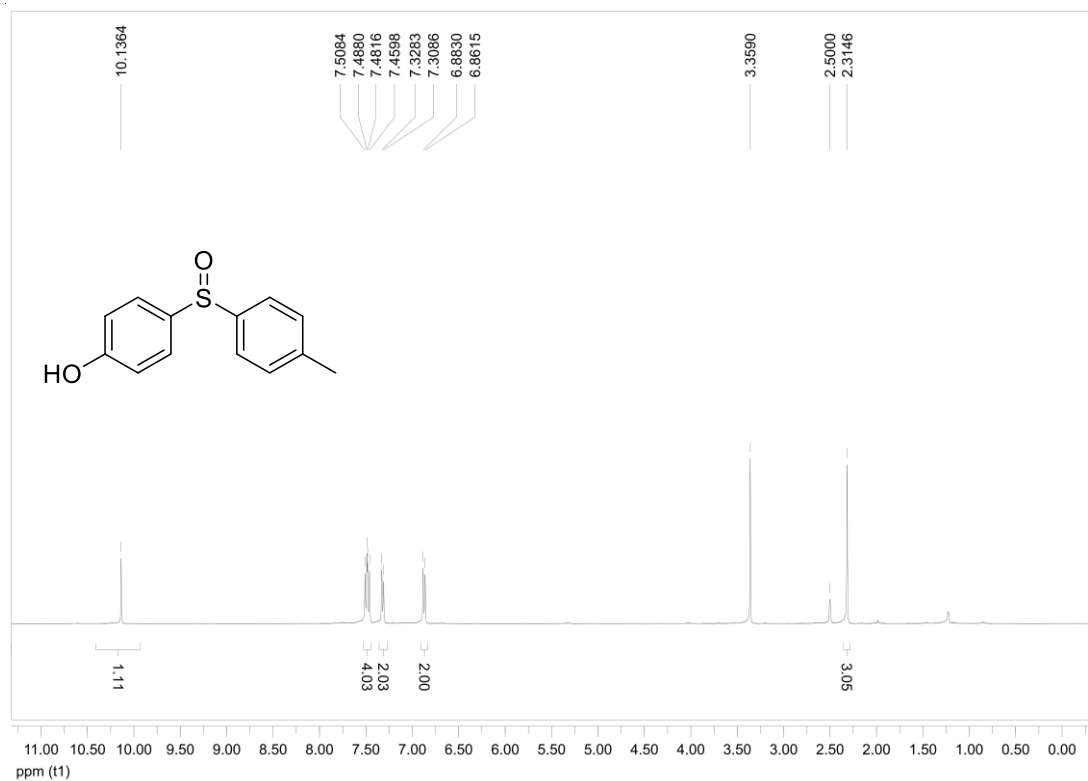


^{13}C NMR (100 MHz, CDCl_3)

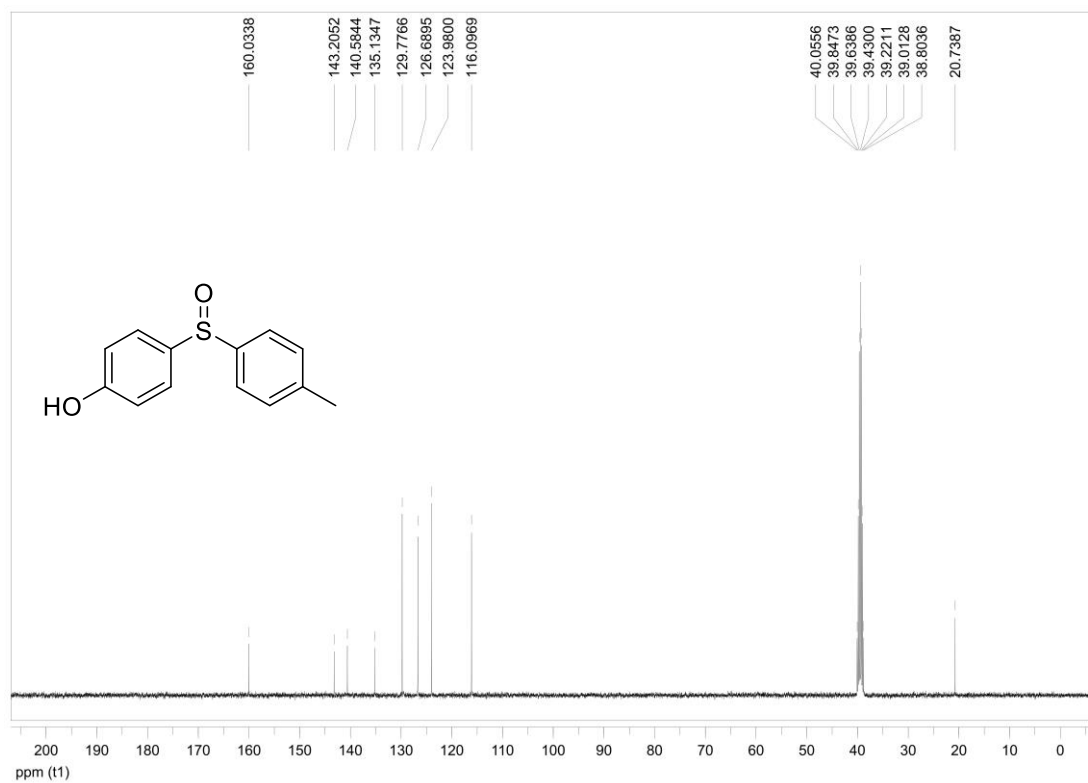


Sulfoxide **12c**

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

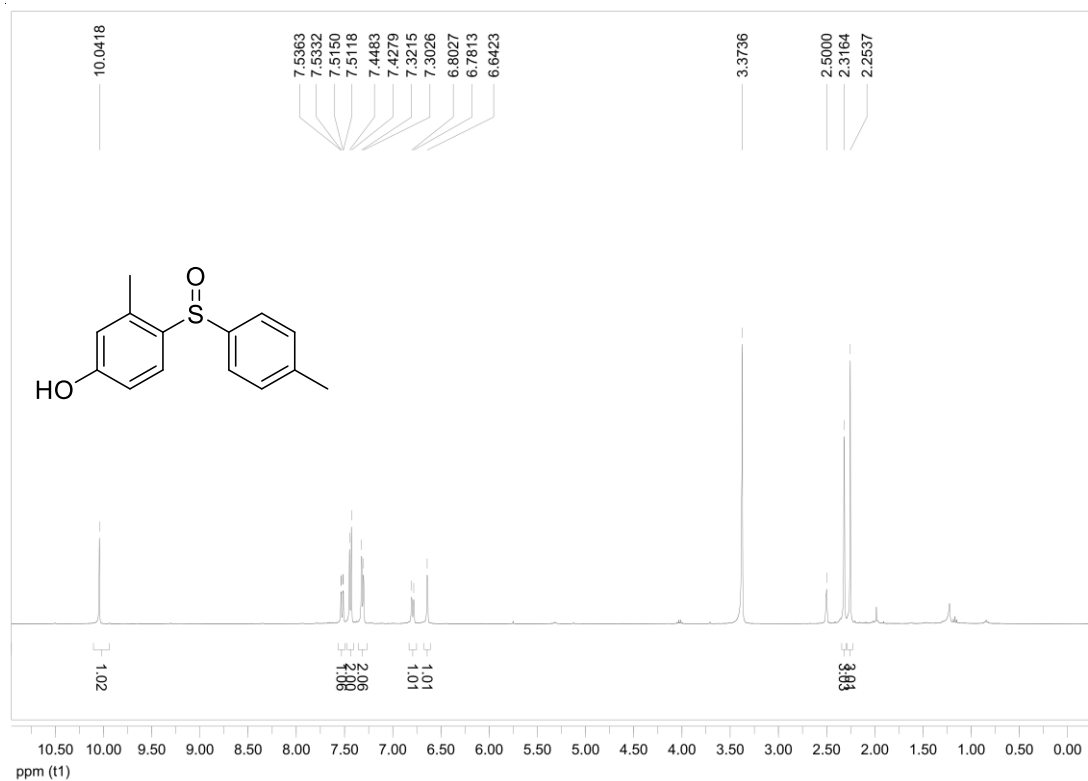


^{13}C NMR (100 MHz, d_6 -DMSO)

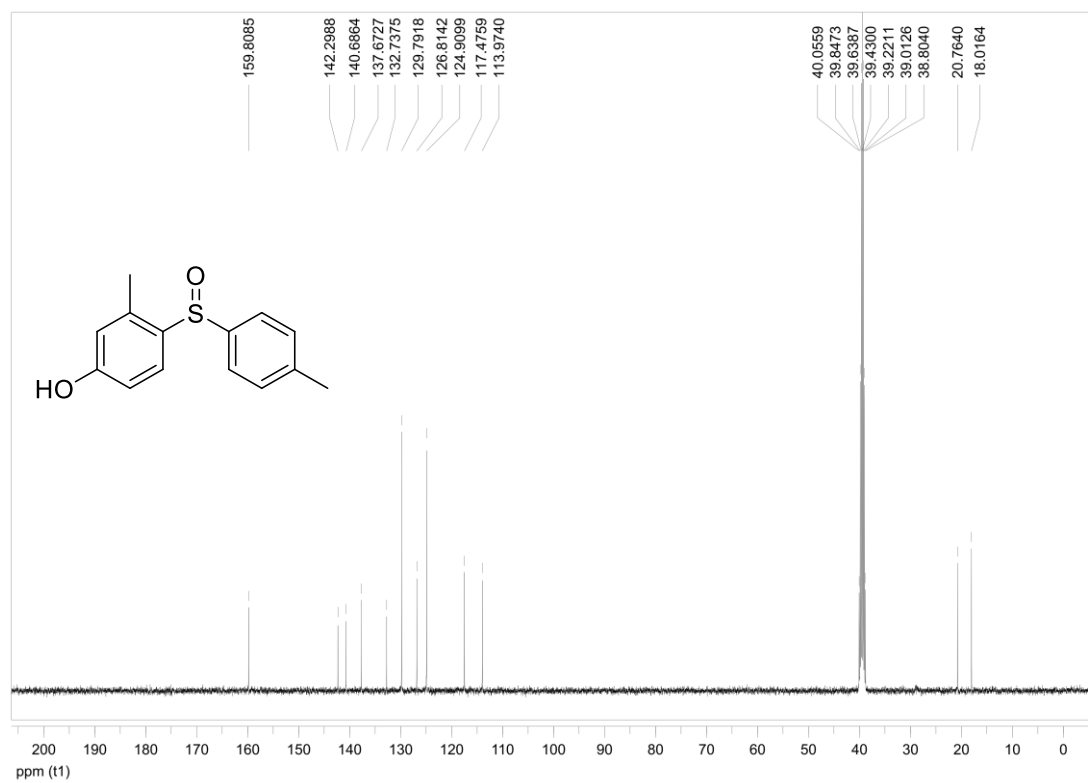


Sulfoxide **12d**

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

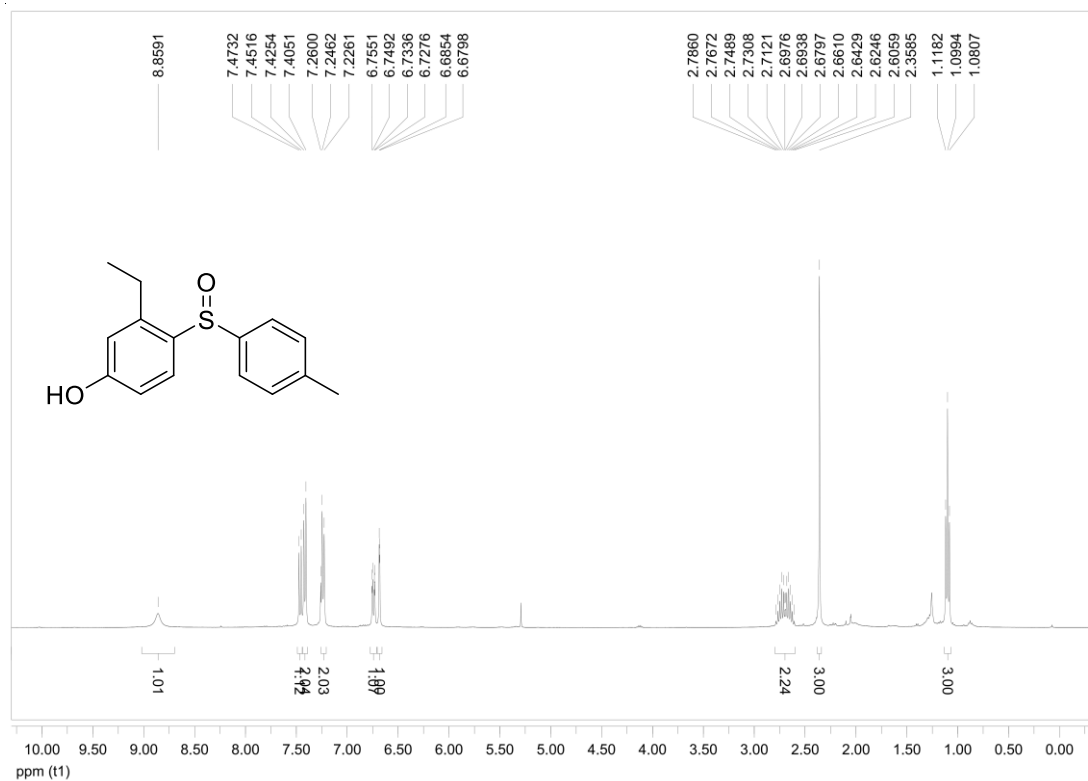


^{13}C NMR (100 MHz, d_6 -DMSO)

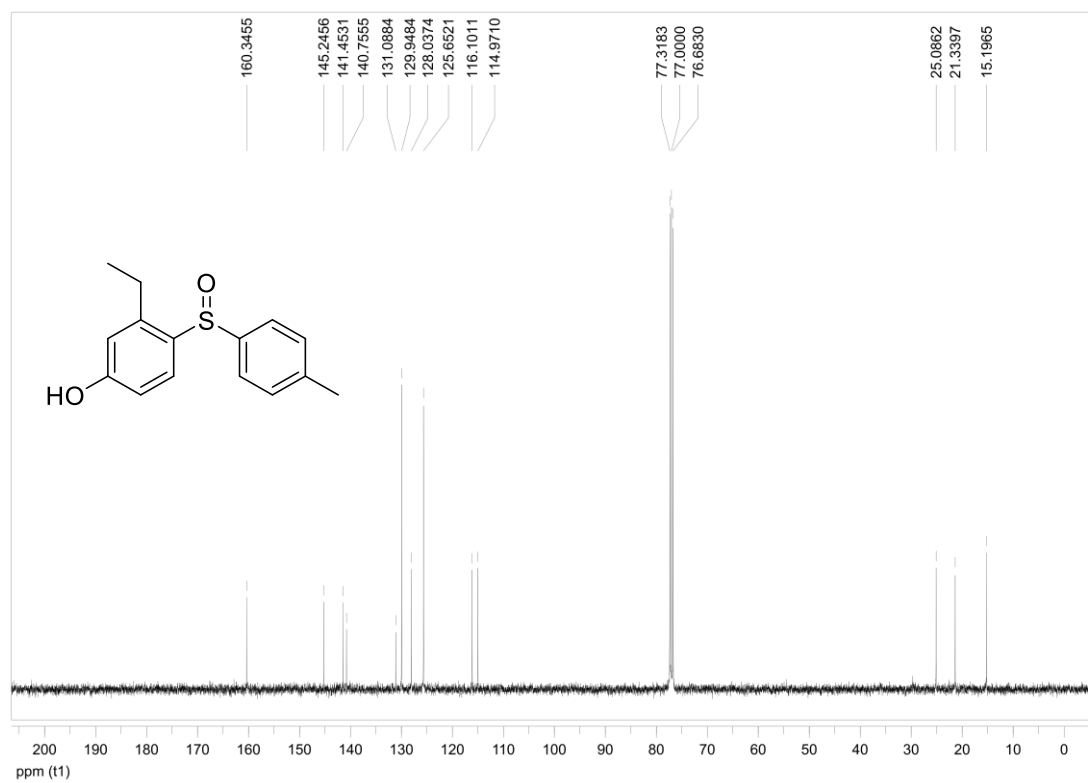


Sulfoxide **12e**

^1H NMR (400 MHz, CDCl_3)

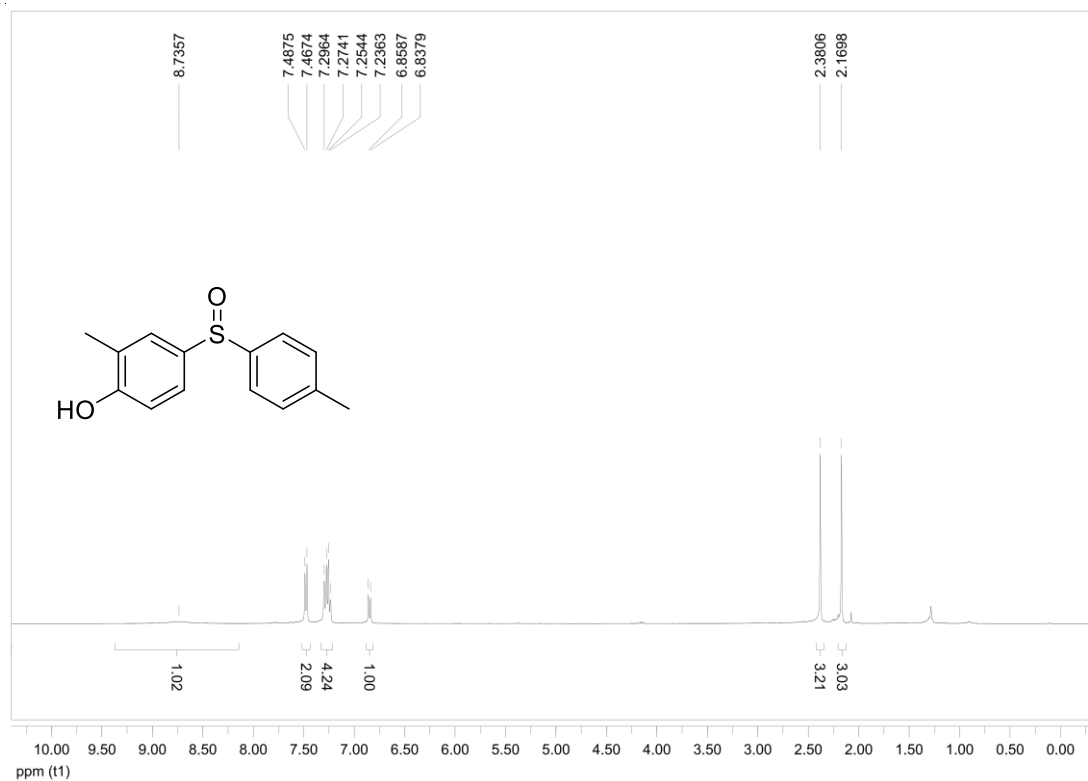


^{13}C NMR (100 MHz, CDCl_3)

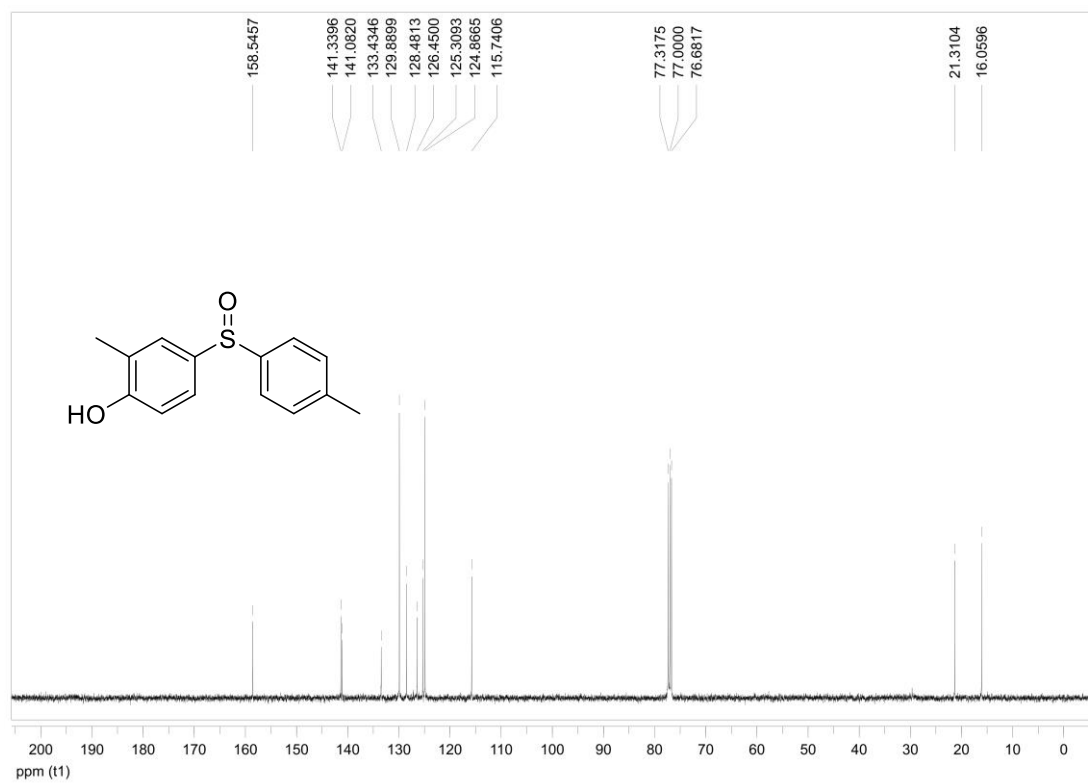


Sulfoxide **12f**

^1H NMR (400 MHz, CDCl_3)

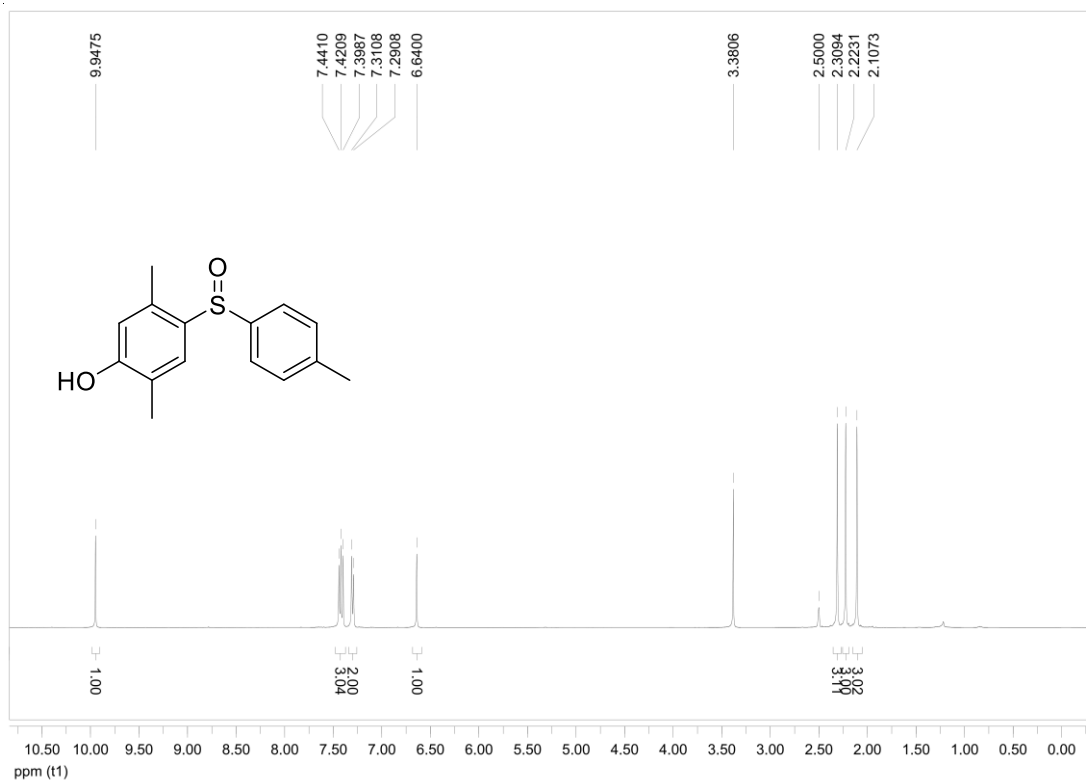


^{13}C NMR (100 MHz, CDCl_3)

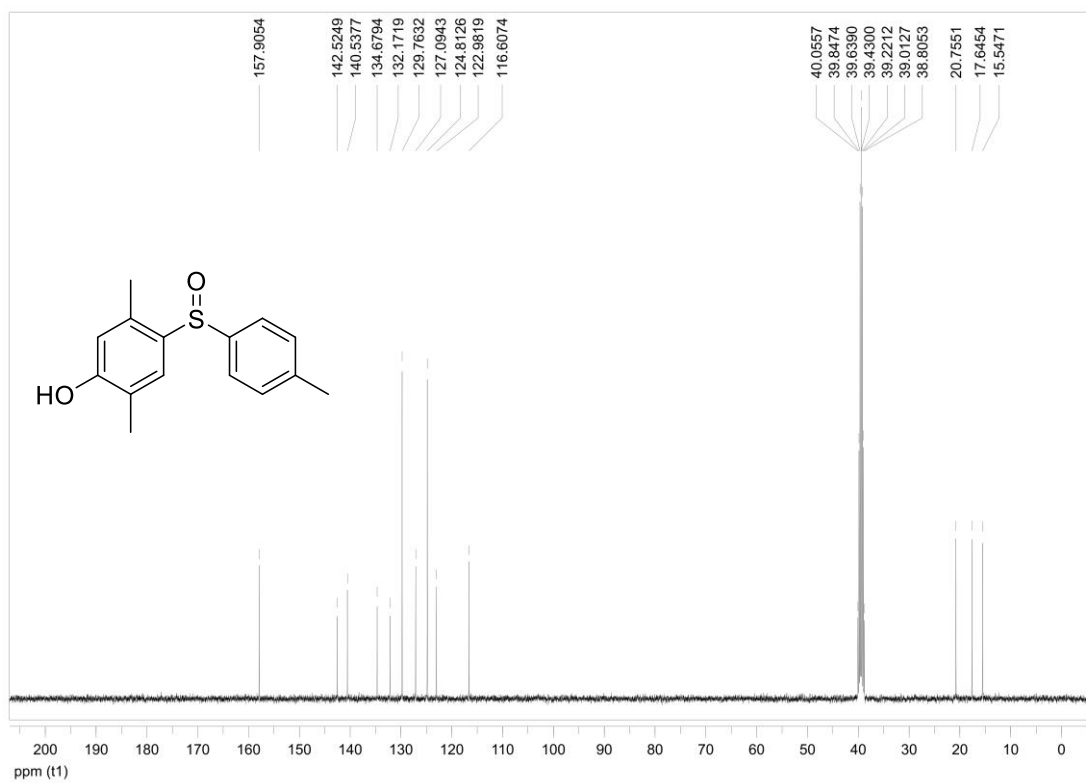


Sulfoxide 12g

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

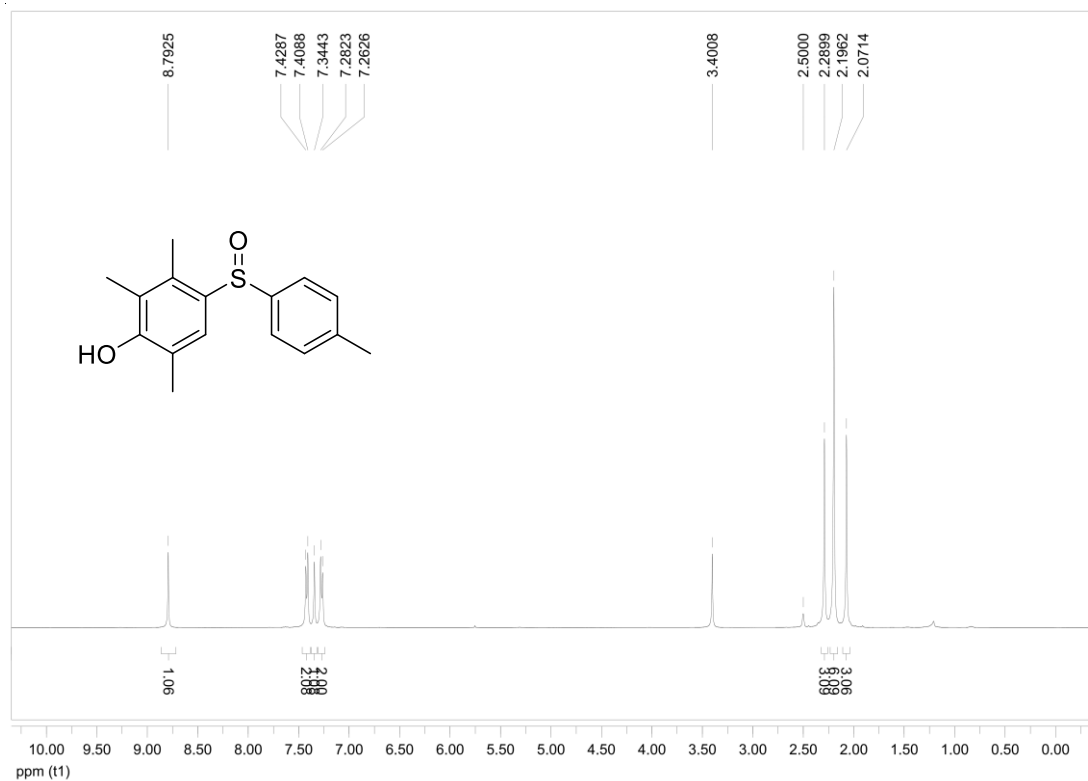


^{13}C NMR (100 MHz, d_6 -DMSO)

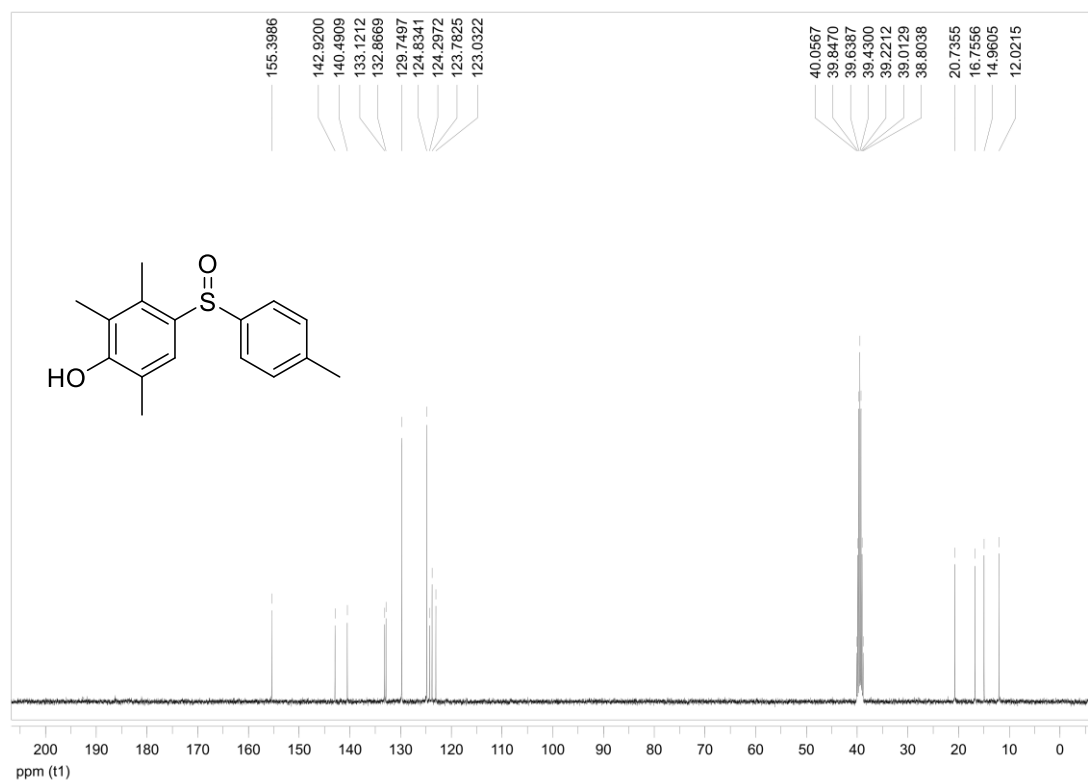


Sulfoxide **12h**

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

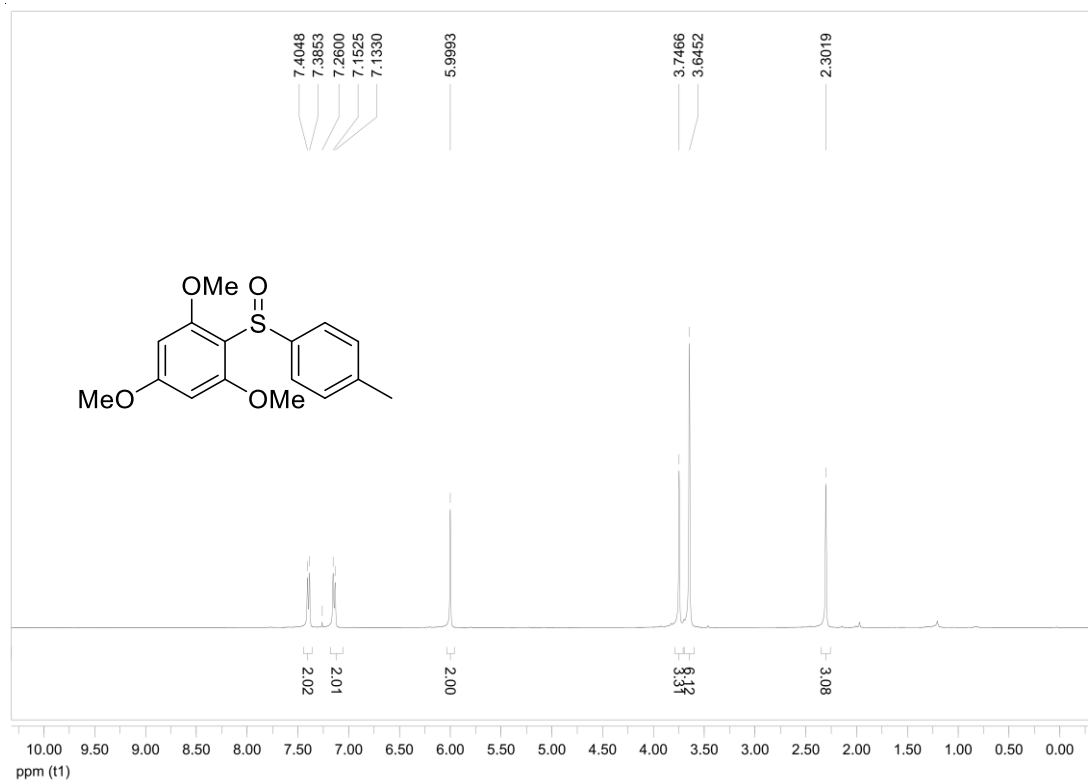


^{13}C NMR (100 MHz, d_6 -DMSO)

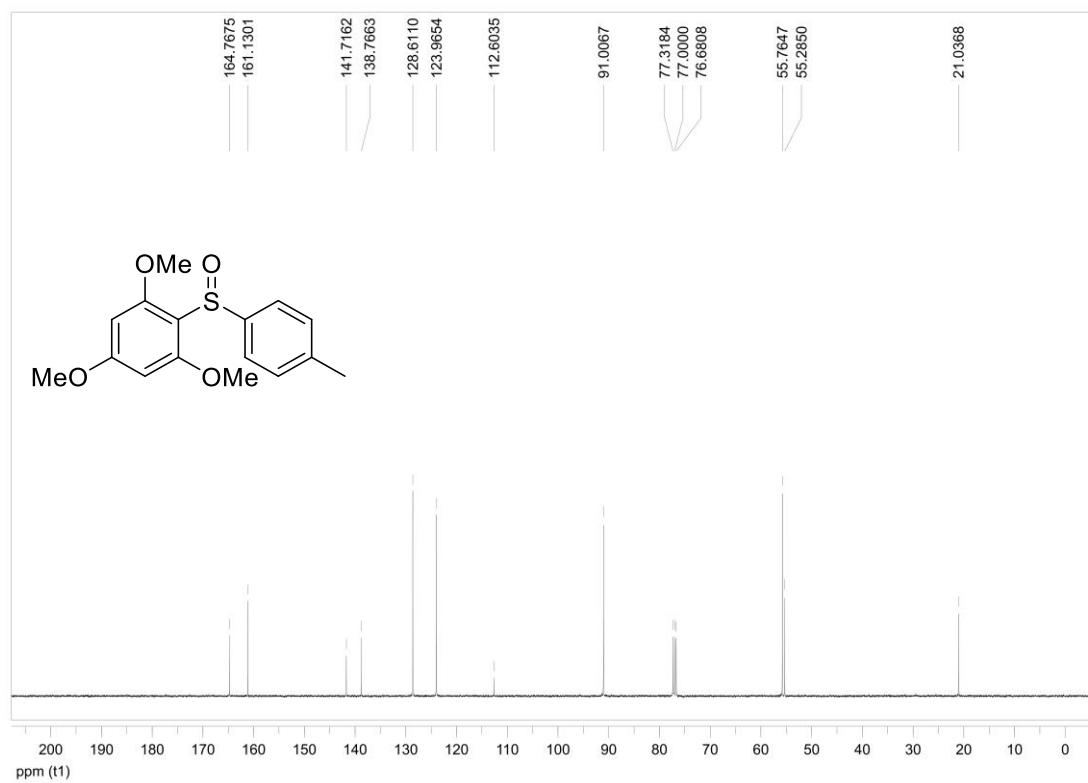


Sulfoxide **12i**

^1H NMR (400 MHz, CDCl_3)

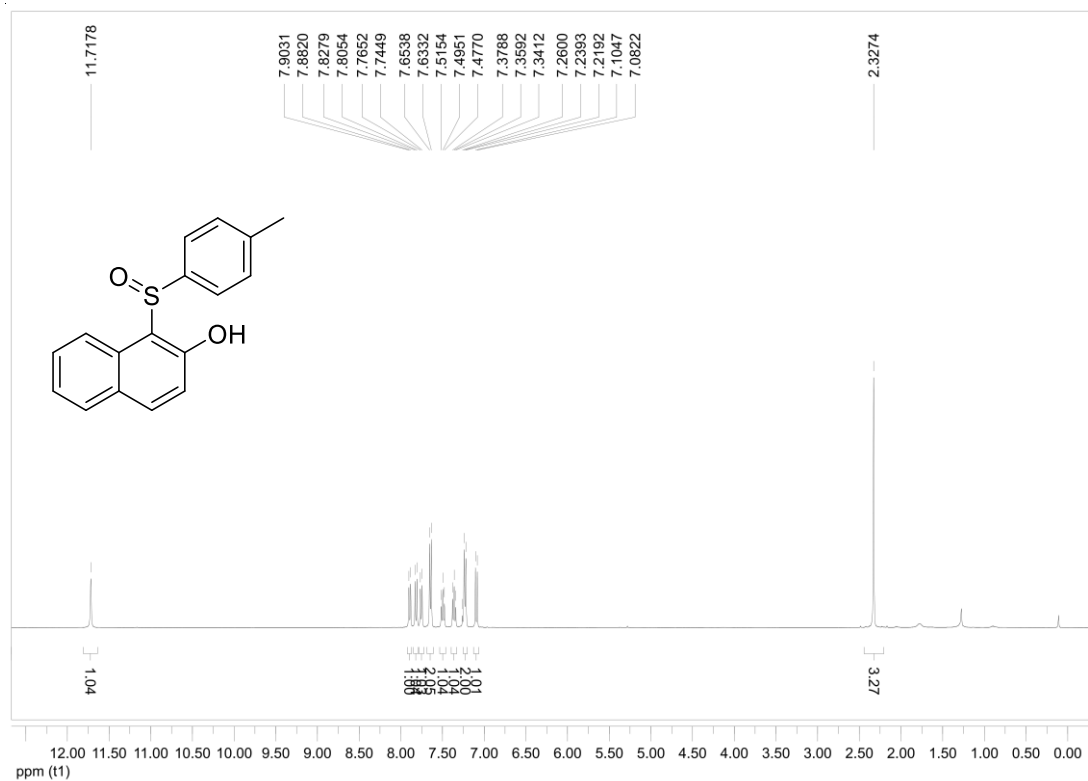


^{13}C NMR (100 MHz, CDCl_3)

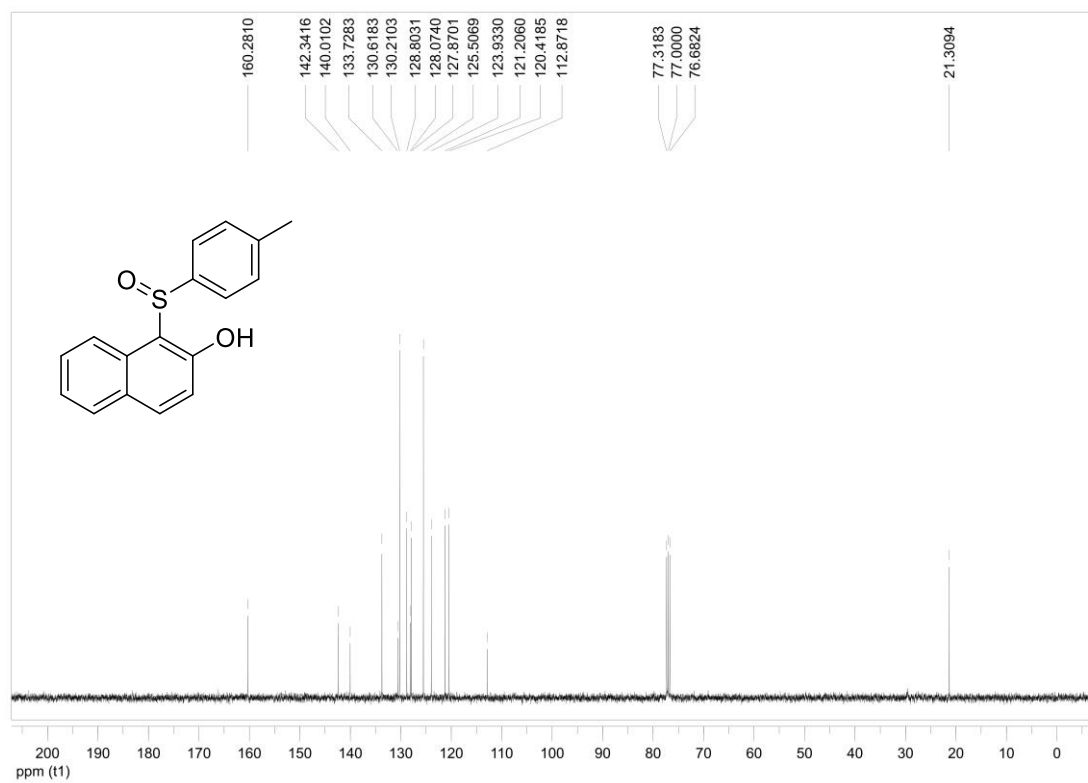


Sulfoxide **12j**

^1H NMR (400 MHz, CDCl_3)

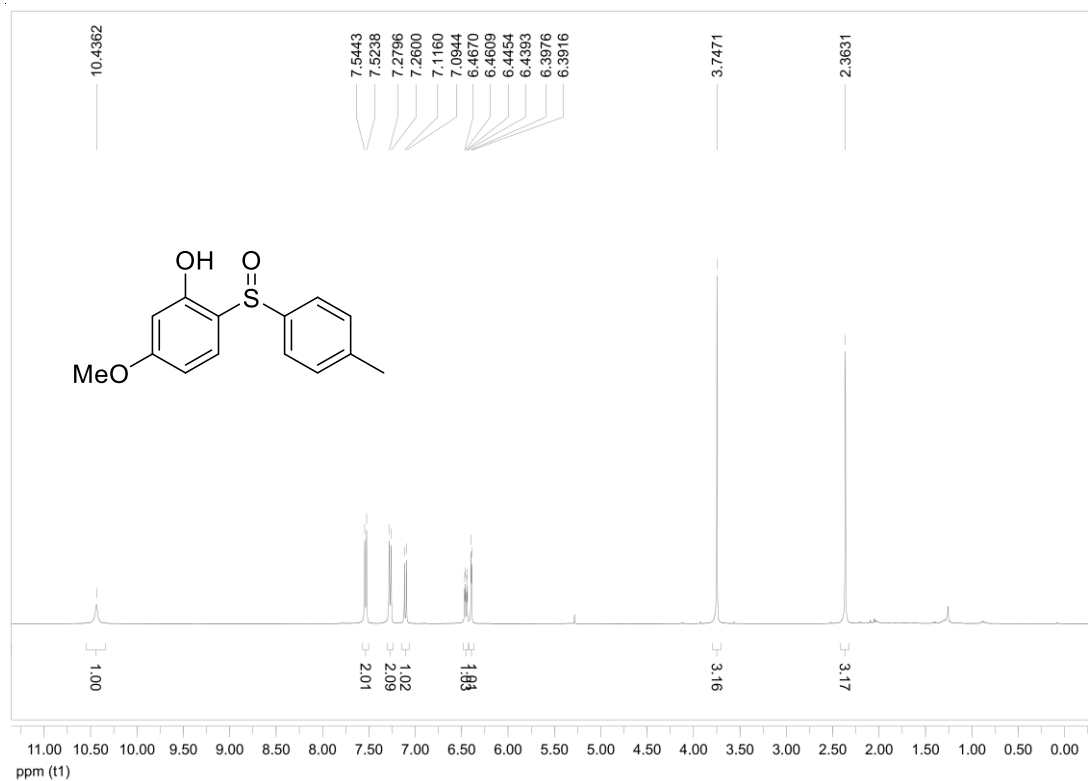


^{13}C NMR (100 MHz, CDCl_3)

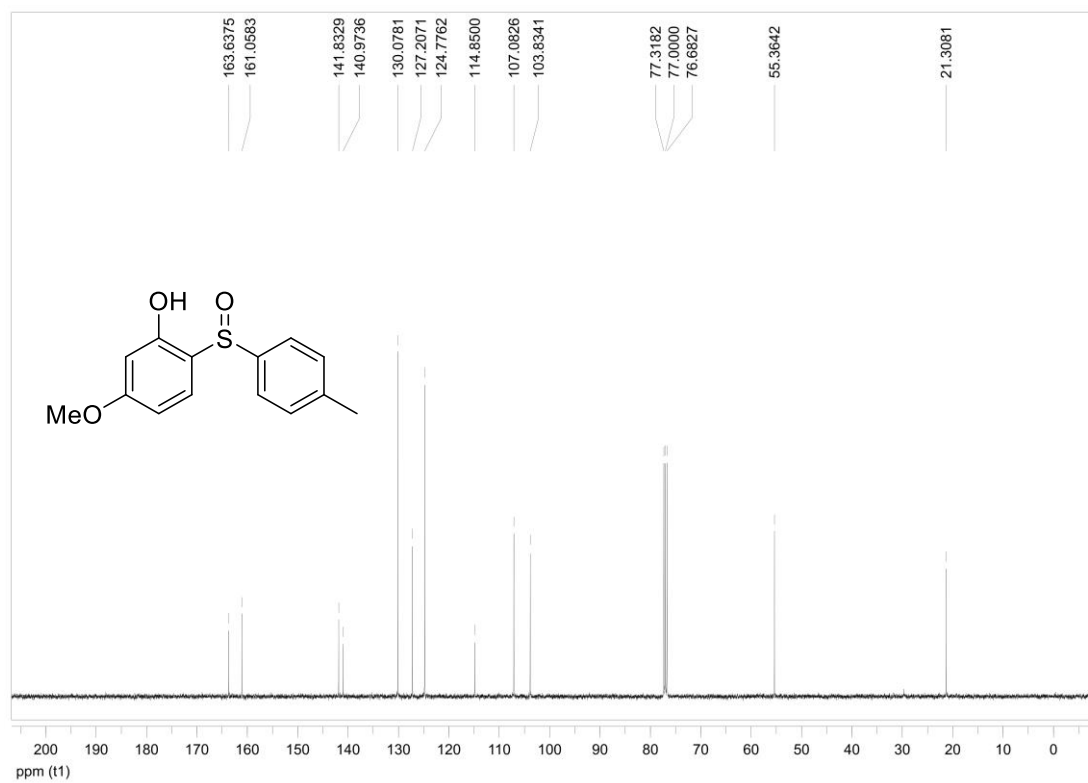


Sulfoxide **12ka**

^1H NMR (400 MHz, CDCl_3)

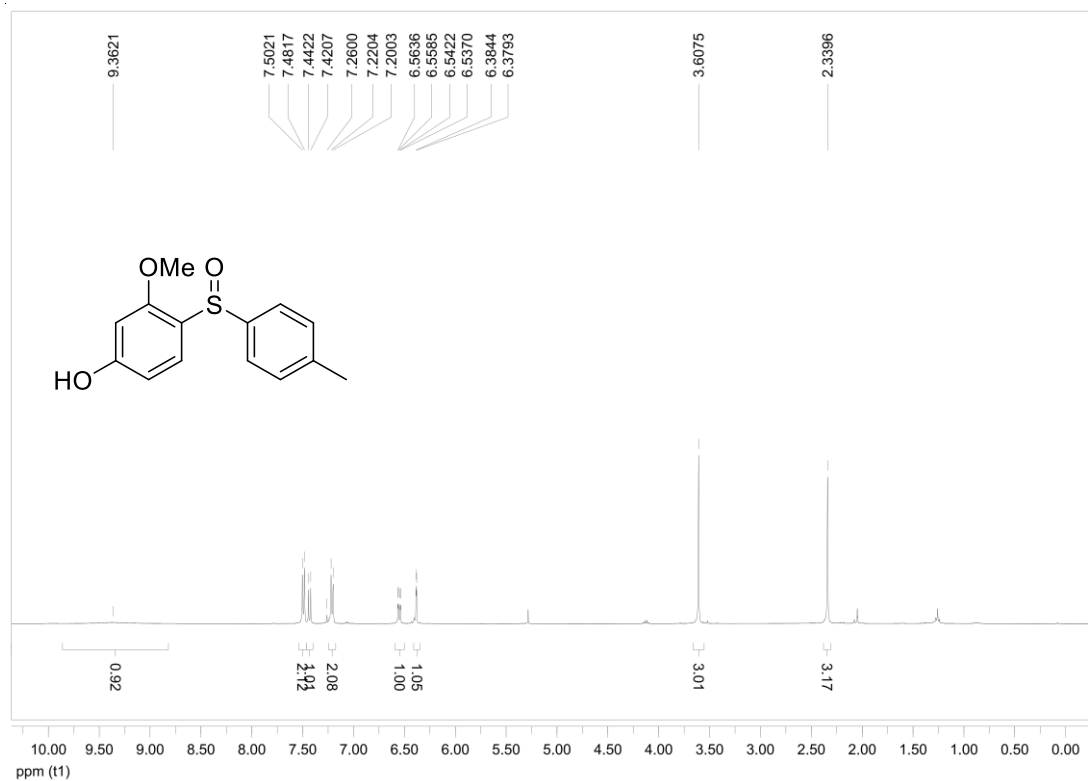


^{13}C NMR (100 MHz, CDCl_3)

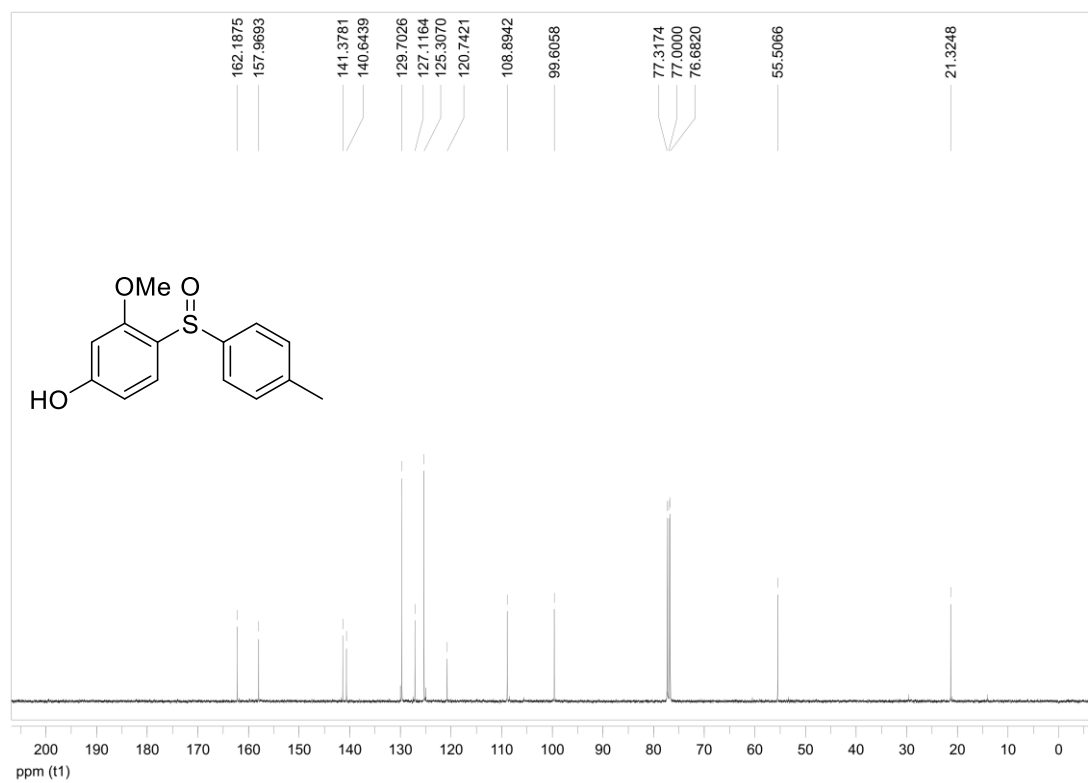


Sulfoxide **12kb**

^1H NMR (400 MHz, CDCl_3)



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



5. References

- 1 Ji, Y. Z.; Zhang, J. Y.; Li, H. J.; Han, C.; Yang, Y. K.; Wu, Y. C. *Org. Biomol. Chem.* **2019**, *17*, 4789.
- 2 Miao, T.; Li, P.; Zhang, Y.; Wang, L. *Org. Lett.* **2015**, *17*, 832.
- 3 Shi, W.; Miao, T.; Li, Y.; Li, P.; Wang, L. *Org. Lett.* **2018**, *20*, 4416.
- 4 Kim, D. H.; Lee, J.; Lee, A. *Org. Lett.* **2018**, *20*, 764.