Supporting Information

TMSOTf-Promoted Sulfenylation of Electron-Rich Aromatics with Sodium Arylsulfinates

Yuan-Zhao Ji,[a] Hui-Jing Li,*[a,b] Hao-Ran Yang,[a] Zheng-Yan Zhang,[a] Li-Jun Xie,[a] and Yan-Chao Wu*[a,b]

[a] School of Marine Science and Technology, Harbin Institute of Technology, Weihai 264209, P. R. China
[b] Weihai Institute of Marine Biomedical Industrial Technology Wendeng District, Weihai 264400, P. R. China

E-mails: lihuijing@iccas.ac.cn, ycwu@iccas.ac.cn
1. Table of Contents

1. Table of Contents S2
2. General Information S3
3. General Procedures for the Preparation of Sulfoxides S4
4. NMR Spectra S25
5. References S73
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. $^1$H 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 ($\delta$ scale) and are referenced to residual protium in the NMR solvents [CDCl$_3$: $\delta$ 7.26, $d_6$-DMSO: $\delta$ 2.50]. Chemical shifts for carbon resonances are reported in parts per million ($\delta$ scale) and are referenced to the carbon resonances of the solvent (CDCl$_3$: $\delta$ 77.0, $d_6$-DMSO: $\delta$ 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 (ClCH$_2$)$_2$ (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 x 10 mL). The combined organic extracts were washed by brine, dried over anhydrous Na$_2$SO$_4$, 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 (ClCH$_2$)$_2$ (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 x 10 mL). The combined organic extracts were washed by brine, dried over anhydrous Na$_2$SO$_4$, 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 (ClCH₂)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 (ClCH₂)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)-1H-pyrrole (3a)**

![Image of 1-Methyl-2-(p-tolylsulfinyl)-1H-pyrrole (3a)]

White solid, m.p. = 47–49 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 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$_3$) $\delta$: 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)-1H-pyrrole (4a)**

![Image of 1-Methyl-3-(p-tolylsulfinyl)-1H-pyrrole (4a)]

White solid, m.p. = 84–86 °C; 36.3 mg, 83% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 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$_3$) $\delta$: 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)-1H-pyrrole (4b)**

![Image of 1-Methyl-3-(phenylsulfinyl)-1H-pyrrole (4b)]

White solid, m.p. = 82–84 °C; 24.2 mg, 59% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 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 C₁₂H₁₃NO₂S [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; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 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$_3$) $\delta$: 163.8 (d, $J_{C-F} = 250.1$ Hz), 140.9 (d, $J_{C-F} = 3.0$ Hz), 126.8 (d, $J_{C-F} = 8.7$ Hz), 124.5, 124.2, 116.0 (d, $J_{C-F} = 22.4$ 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; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 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$_3$) $\delta$: 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; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 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$_3$) $\delta$: 144.4, 131.7, 126.1, 126.0, 124.7, 124.2, 124.2, 107.3, 36.5; HRMS (ESI) m/z: Calcd for C$_{11}$H$_{10}$NaBrNOS [M+Na]$^+$: 305.9559. Found: 305.9564.

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

Pale yellow oil, 17.5 mg, 35% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 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$_3$) $\delta$: 153.1, 148.8, 125.6, 125.3, 125.2, 124.7, 123.8, 107.5, 36.7; HRMS (ESI) m/z: Calcd for C$_{11}$H$_{10}$NaN$_2$O$_3$S [M+Na]$^+$: 273.0304. Found: 273.0308.

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

Colorless oil, 36.8 mg, 65% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 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$_3$) $\delta$: 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 C$_{11}$H$_{10}$NaBrNOS [M+Na]$^+$: 305.9559. Found: 305.9565.
3-((2-Chlorophenyl)sulfinyl)-1-methyl-1H-pyrrole (4j)

Pale yellow oil, 37.2 mg, 78% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 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$_3$) $\delta$: 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 C$_{11}$H$_{10}$NaClNOS [M+Na]$^+$: 262.0064. Found: 262.0069.

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

Colorless oil, 14.9 mg, 31% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 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$_3$) $\delta$: 162.9 (dd, $J_{C-F} = 253.8$, 11.4 Hz), 150.1 (t, $J_{C-F} = 7.0$ Hz), 125.5, 125.0, 124.5, 107.8 (dd, $J_{C-F} = 19.8$, 7.7 Hz), 107.4, 105.4(t, $J_{C-F} = 25.5$ Hz), 36.6; HRMS (ESI) m/z: Calcd for C$_{11}$H$_9$NaF$_2$NOS [M+Na]$^+$: 264.0265. Found: 264.0268.

3-(Mesitylsulfinyl)-1-methyl-1H-pyrrole (4l)
Colorless oil, 41.5 mg, 84% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 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$_3$) $\delta$: 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 C$_{14}$H$_{17}$NaNOS [M+Na]$^+$: 270.0923. Found: 270.0928.

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

Pale yellow oil, 39.2 mg, 77% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 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$_3$) $\delta$: 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 C$_{15}$H$_{13}$NaNOS [M+Na]$^+$: 278.0610. Found: 278.0616.

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

Pale yellow oil, 33.6 mg, 66% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 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$_3$) $\delta$: 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 C$_{15}$H$_{13}$NaNOS [M+Na]$^+$: 278.0610. Found: 278.0619.
1-Methyl-3-(thiophen-2-ylsulfinyl)-1H-pyrrole (4o)

Pale yellow oil, 19.0 mg, 45% yield; \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.54 (dd, \(J = 5.0, 1.3 \text{ Hz}, 1H\)), 7.42 (dd, \(J = 3.7, 1.3 \text{ Hz}, 1H\)), 7.07–7.04 (m, 2H), 6.65 (t, \(J = 2.6 \text{ Hz}, 1H\)), 6.36 (dd, \(J = 3.0, 1.8 \text{ Hz}, 1H\)), 3.66 (s, 3H); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\): 148.4, 130.4, 129.2, 127.2, 126.5, 124.1, 123.7, 107.1, 36.6; HRMS (ESI) m/z: Calcd for C\(_9\)H\(_9\)NaNOS\(_2\) [M+Na]\(^+\): 234.0018. Found: 234.0022.

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

Colorless oil, 16.9 mg, 50% yield; \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.01 (d, \(J = 2.5 \text{ Hz}, 1H\)), 6.65 (t, \(J = 2.7 \text{ Hz}, 1H\)), 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\(_3\)) \(\delta\): 125.5, 123.7, 122.9, 106.3, 36.5, 31.6, 2.61, 2.59; HRMS (ESI) m/z: Calcd for C\(_8\)H\(_{11}\)NaNOS [M+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; \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.56 (d, \(J = 8.1 \text{ Hz}, 2H\)), 7.38–7.27 (m, 5H), 7.15–7.07 (m, 3H), 6.67 (t, \(J = 2.6 \text{ Hz}, 1H\)), 6.19 (dd, \(J = 3.0, 1.8 \text{ Hz}, 1H\)), 5.03 (s, 2H), 2.41 (s, 3H); \(^{13}C\) NMR
13C 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)-1H-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)-1H-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)-1H-pyrrole (4u)**

![Structure Image]

Pale yellow oil, 16.7 mg, 36% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 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$_3$) $\delta$: 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 C$_{13}$H$_{15}$NaNO$_2$S [M+Na]$^+$: 256.0767. Found: 256.0773.

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

![Structure Image]

Pale yellow oil, 8.8 mg, 13% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 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$_3$) $\delta$: 188.6, 141.3, 141.2, 136.4, 131.7, 130.2, 129.8, 128.7, 127.9, 127.4, 124.5, 117.5, 53.2, 27.4, 21.3; HRMS (ESI) m/z: Calcd for C$_{20}$H$_{19}$NaNO$_2$S [M+Na]$^+$: 360.1029. Found: 360.1035.

**Ethyl 1-benzy1-2,4-dimethyl-5-(p-tolylthio)-1H-pyrrole-3-carboxylate (5x)**

![Structure Image]
Yellow oil, 35.6 mg, 47% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 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$_3$) $\delta$: 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 C$_{22}$H$_{25}$NaNO$_2$S [M+Na]$^+$: 402.1498. Found: 402.1502.

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

![Chemical structure of 3-(p-Tolylsulfinyl)thiophene](image)

Dark brown oil, 10.2 mg, 23% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.59–7.53 (m, 4H), 7.30 (d, $J = 7.7$ Hz, 2H), 7.06–7.03 (m, 1H), 7.00 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 148.2, 141.8, 141.7, 132.0, 131.0, 129.8, 127.1, 124.3, 21.3; HRMS (ESI) m/z: Calcd for C$_{11}$H$_{10}$NaOS$_2$ [M+Na]$^+$: 245.0065. Found: 245.0072.

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

Yellow oil, 38.6 mg, 63% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 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$_3$) $\delta$: 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 C$_{17}$H$_{22}$NaOS$_2$ [M+Na]$^+$: 329.1004. Found: 329.1008.
1-Methyl-3-(\(\rho\)-tolylsulfinyl)-1\(H\)-indole (10a)

White solid, m.p. = 138–139 °C; 42.0 mg, 78% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 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\(_3\)) \(\delta\): 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; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 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); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 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; \(^1\)H NMR (400 MHz, CDCl\(_3\))
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); 13C 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; $^1$H 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); 13C 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; $^1$H 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); 13C 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)-1H-indole (10f)

White solid, m.p. = 143–145 °C; 45.3 mg, 79% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 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); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 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)-1H-indole (10g)

Yellow oil, 40.2 mg, 64% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 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); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 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 C\(_{18}\)H\(_{14}\)N\(_2\)NaO\(_3\)S [M+Na]\(^+\): 337.0617. Found: 337.0623.

1-Methyl-3-(p-tolylsulfinyl)-1H-indole-5-carbonitrile (10h)
Cyan oil, 38.8 mg, 66% yield; \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \): 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\(_3\)) \( \delta \): 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 C\(_{17}\)H\(_{14}\)N\(_2\)NaOS [M+Na\(^+\)]: 317.0719. Found: 317.0727.

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

![5-Methoxy-1-methyl-3-(p-tolylsulfinyl)-1H-indole (10i)](image)

White solid, m.p. = 147–149 °C; 32.3 mg, 54% yield; \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \): 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\(_3\)) \( \delta \): 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)**

![1-Benzyl-3-(p-tolylsulfinyl)-1H-indole (10k)](image)

White solid, m.p. = 140–142 °C; 53.6 mg, 78% yield; \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \): 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\(_3\)) \( \delta \): 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)-1H-indole (10l)

White solid, m.p. = 120–122 °C; 7.7 mg, 15% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 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); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 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; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 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); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 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; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 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); \(^{13}\)C 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.¹

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

Yellow solid, m.p. = 135–137 °C; 24.1 mg, 52% yield; ¹H NMR (400 MHz, d₆-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, d₆-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, d₆-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, d₆-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 C$_{15}$H$_{16}$NaO$_2$S [M+Na]$^+$: 283.0763. Found: 283.0768.

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

Yellow oil, 27.0 mg, 55% yield; $^1$H 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 C$_{14}$H$_{14}$NaO$_2$S [M+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; $^1$H 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 C$_{15}$H$_{16}$NaO$_2$S [M+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; $^1$H NMR (400 MHz, $d_6$-DMSO) $\delta$: 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) $\delta$: 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 C$_{16}$H$_{18}$NaO$_2$S [M+Na]$^+$: 297.0920. Found: 297.0925.

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

Pale yellow oil, 42.8 mg, 70% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 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$_3$) $\delta$: 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; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 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$_3$
$\delta$: 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 C$_{17}$H$_{14}$NaO$_2$S [M+Na]$^+$: 305.0607. Found: 305.0614.

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

Pale yellow oil, 23.1 mg, 44% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 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$_3$) $\delta$: 163.6, 161.0, 141.8, 140.9, 130.0, 127.2,

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

Pale yellow oil, 16.7 mg, 32% yield; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 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$_3$) $\delta$: 162.1, 157.9, 141.3, 140.6, 129.7, 127.1,
4. NMR Spectra

Sulfoxide 3a

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide 4a

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide 4b

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide 4c

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide 4d

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide 4e

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide 4f

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide 4g

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide 4h

$^{1}$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide 4i

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide 4j

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide 4k

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide 4I

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide 4m

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide 4n

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide 4o

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide 4p

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide 4q

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide 4r

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide 4t

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide $4u$

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)

S45
Sulfoxide 3w

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Thioether 5x

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide 4y

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide 4z

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide 10a

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide 10b

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide 10c

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide 10d

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)

S53
Sulfoxide 10e

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)

S54
Sulfoxide 10f

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide 10g

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide 10h

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide 10i

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
**Sulfoxide 10k**

$^1$H NMR (400 MHz, CDCl₃)

\[ \text{\includegraphics[width=\textwidth]{hnmr_image}} \]

$^{13}$C NMR (100 MHz, CDCl₃)

\[ \text{\includegraphics[width=\textwidth]{cnmr_image}} \]
Sulfoxide 10l

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide 12a

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide 12b

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
**Sulfoxide 12c**

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

$^{13}$C NMR (100 MHz, $d_6$-DMSO)
Sulfoxide 12d

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

$^{13}$C NMR (100 MHz, $d_6$-DMSO)
Sulfoxide 12e

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
**Sulfoxide 12f**

**$^1$H NMR (400 MHz, CDCl$_3$)**

![$^1$H NMR spectrum](image)

**$^{13}$C NMR (100 MHz, CDCl$_3$)**

![$^{13}$C NMR spectrum](image)
Sulfoxide 12g

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

$^{13}$C NMR (100 MHz, $d_6$-DMSO)
Sulfoxide 12h

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

$^{13}$C NMR (100 MHz, $d_6$-DMSO)
Sulfoxide 12i

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide 12j

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide 12ka

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Sulfoxide 12kb

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
5. References


