# **Supporting Information**

# Exogenous-oxidant-free electrochemical oxidative C-H sulfonylation of arenes/heteroarenes with hydrogen evolution

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## **General information**

Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (boiling point is between 60-90 °C). Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum to the indicated solvent, and they are listed as volume/volume ratios. NMR spectra were recorded on a Bruker spectrometer at 400 MHz (<sup>1</sup>H NMR), 100 MHz (<sup>13</sup>C NMR). Tetramethylsilane was used as an internal standard. All <sup>1</sup>H and <sup>13</sup>C NMR data spectra were reported in delta ( $\delta$ ) units, parts per million (ppm) downfield from the internal standard. Coupling constants are reported in Hertz (Hz). High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument, accurate masses are reported for the molecularion ([M+Na]<sup>+</sup>). Selective ratios were recorded with a Varian GC 2000 gas chromatography instrument with a FID detector. GC-Ms spectra were recorded on a Varian GC-Ms 3900-2100T.

#### **Experimental procedure**

General procedure for the preparation of 3-aryl-benzofurans.<sup>1</sup>



In a nitrogen-filled Schlenk tube,  $Pd(OAc)_2$  (0.6 mg, 0.0025 mmol), <sup>*i*</sup>Bu<sub>3</sub>P•HBF<sub>4</sub> (0.9 mg, 0.003 mmol), phenylboronic acid (73 mg, 0.60 mmol) and 3-bromobenzofuran (99 mg, 0.50 mmol) and 2.80 mL of *n*-butanol. The mixture was pre-stirred at RT for 15 min, and then a solution of NaOH (34 mg, 0.85 mmol) in 0.68 mL of degassed H<sub>2</sub>O was added to initiate the Suzuki reaction. The reaction mixture was stirred vigorously at RT until the 3-bromobenzofuran was fully consumed. At the end of the reaction, the organic phase was separated and the aqueous phase was further extracted with Et<sub>2</sub>O (3 mL x 3). The combined organic extracts were concentrated on a rotary evaporator. The resulting residue was purified by silica gel flash chromatography to obtain the desired coupling product. The title compound was isolated as colorless oil (95 mg, 98% yield) after flash chromatography using hexanes as eluent.

#### General procedure for the preparation of 3-phenyl-5-substituted benzofurans.<sup>2</sup>



**Step 1.** Potassium carbonate (0.05 mol) and potassium iodide (0.005 mol) were added to a mixture of 2-bromo-1-phenylethan-1-one (0.05 mol), phenol (0.05 mol), and dry acetone (60 mL). The reaction mixture was covered with black cloth and was stirred at room temperature for 16 h under nitrogen atmosphere, and then was diluted with 120 mL of  $CH_2Cl_2$ . The solid salts were filtered off and the organic phase was washed with water, dried over  $Na_2SO_4$ . Evaporation gave crude compounds which were directly used for the next reactions without further purification.

**Step 2.** A mixture of 2-phenoxy-1-phenylethan-1-one (10 mmol), polyphosphoric acid (20 g), and toluene (60 mL) was refluxed for 5–6 h. The reaction mixture was cooled to room temperature, poured into water, and extracted with diethyl ether. The organic extracts were dried over  $Na_2SO_4$ , evaporation gave crude compounds. The crude product was purified by silica gel column

chromatography using hexanes as eluent to afford the desired product.

General procedure for the preparation of 2-phenylbenzofuran.<sup>3</sup>



A round bottom flask was charged with bromobenzene (2 mmol), benzofuran-2-ylbor-onic acid (1.1–1.5 equiv.), Pd(PPh<sub>3</sub>)<sub>4</sub> (5–10 mol%), and Cs<sub>2</sub>CO<sub>3</sub> (1.1–1.4 equiv.), into which toluene (16 mL) and MeOH (4 mL) were subsquently added. Then, the reaction mixture was heated in an oil bath at 100–110  $\,^{\circ}$ C until a TLC analysis of an aliquot indicated a complete conversion of the starting materials (12 h). The reaction mixture was then cooled to 23  $\,^{\circ}$ C and quenched with saturated NH<sub>4</sub>Cl solution. Aqueous phase was extracted with ethyl acetate (10 mL x 3), and the combined organic phases were washed with brine (10 mL), dried over MgSO<sub>4</sub>, filtrated and concentrated under reduced pressure to afford the crude furan or benzofuran derivatives. Concentration in vacuum followed by silica gel column purification with petroleum ether/ethyl acetate eluent gave the desired product.

## General procedure for the preparation of sulfonyl hydrazides.<sup>4</sup>

Sulfonyl hydrazides were prepared according to a literature procedure. The hydrazine monohydrate (30 mmol) was added dropwise into the solution of sulfonyl chloride (10 mmol) in THF (50 mL) under nitrogen at 0 °C. Subsequently, the mixture was further stirred at 0 °C for 30 minutes. After the completion of the reaction, the solvent was removed by evaporation, and the residue was extracted with dichloromethane (3 x 20 mL), and the combined organic layer was washed with water, and brine, and dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration in vacuum followed by silica gel column purification with petroleum ether/ethyl acetate eluent gave the desired product in yields range from 70-95%.

#### General procedure for electrochemical oxidative C-H sulfonylation of arenes/heteroarenes:

In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, sulfonyl hydrazides (0.375 mmol),  $K_2CO_3$  (0.375 mmol),  $^nBu_4NBF_4$  (0.1 mmol) were combined and added. The bottle was equipped with graphite rod ( $\phi$  6 mm, about 18 mm immersion depth in solution) as the anode and nickel plate (15 mm × 15 mm × 1 mm) as the cathode and was then charged with nitrogen. Under the protection of N<sub>2</sub>, arenes/heteroarenes (0.25 mmol), purified water (0.5 mL) and CH<sub>3</sub>CN (9.5 mL) were injected respectively into the tubes via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 12 mA at room temperature for 3 h. When the reaction was finished, the pure product was obtained by flash column chromatography on silica gel.





Figure S1. The experimental setup for electrolysis.

**Procedure for cyclic voltammetry (CV):** Cyclic voltammetry was performed in a three-electrode cell connected to a schlenk line under nitrogen at room temperature. The working electrode was a steady glassy carbon disk electrode, the counter electrode a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. 9.5 mL of acetonitrile and 0.5 mL of water containing 0.2 M  $^{n}$ Bu<sub>4</sub>NBF<sub>4</sub> were poured into the electrochemical cell in all experiments. The scan rate is 0.1 V/s, ranging from 0 V to 3.0 V.



Figure S2. Cyclic voltammogram: 1a, 0.1 mmol, 2a, 0.1 mmol, K<sub>2</sub>CO<sub>3</sub>, 0.1 mmol.

#### **Detail descriptions for products**



**2-((4-Chlorophenyl)sulfonyl)-3-phenylbenzofuran (3aa).** The desired pure product was obtained in 87% yield as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.80 (d, *J* = 8.7 Hz, 2H), 7.59 – 7.45 (m, 8H), 7.41 (d, *J* = 8.7 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  154.48, 145.35, 140.50, 138.64, 130.07, 129.43, 129.31, 129.02, 128.51, 128.50, 128.29, 128.14, 127.68, 124.29, 122.29, 112.25. HRMS (ESI) calculated for C<sub>20</sub>H<sub>13</sub>ClNaO<sub>3</sub>S [M+Na]<sup>+</sup>: 391.0166; found: 391.0156.



**2-((2-Chlorophenyl)sulfonyl)-3-phenylbenzofuran (3ab).** The desired pure product was obtained in 75% yield as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.82 (s, 1H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.56-7.47 (m, 8H), 7.39 (t, *J* = 7.9 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  154.56, 145.15, 141.85, 135.28, 133.89, 130.43, 130.06, 129.13, 128.60, 128.54, 128.45, 128.34, 127.91, 127.70, 125.94, 124.35, 122.35, 112.34. HRMS (ESI) calculated for C<sub>20</sub>H<sub>13</sub>CINaO<sub>3</sub>S [M+Na]<sup>+</sup>: 391.0166; found: 391.0170.



**2-((4-Fluorophenyl)sulfonyl)-3-phenylbenzofuran (3ac).** The desired pure product was obtained in 54% yield as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.92 – 7.83 (m, 2H), 7.59 – 7.46 (m, 8H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 8.6 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  165.78 (d, *J* = 256.8 Hz), 154.45, 145.62, 136.24, 130.81 (d, *J* = 9.8 Hz), 130.10, 129.01, 128.59, 128.43, 128.30, 127.86, 127.73, 124.27, 122.29, 116.46 (d, *J* = 22.8 Hz), 112.27. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -102.86. HRMS (ESI) calculated for C<sub>20</sub>H<sub>13</sub>FNaO<sub>3</sub>S [M+Na]<sup>+</sup>: 375.0462; found: 375.0470.



**2-((4-Bromophenyl)sulfonyl)-3-phenylbenzofuran (3ad).** The desired pure product was obtained in 80% yield as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.71 (d, J = 8.6 Hz, 2H), 7.57 (d, J = 8.6 Hz, 2H), 7.55 – 7.43 (m, 8H), 7.29 (t, J = 7.5 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  154.53, 145.33, 139.21, 132.45, 130.11, 129.38, 129.19, 129.06, 128.54, 128.32, 128.23, 127.72, 124.32, 122.33, 112.30. HRMS (ESI) calculated for C<sub>20</sub>H<sub>13</sub>BrNaO<sub>3</sub>S [M+Na]<sup>+</sup>: 434.9661; found: 434.9669.



**3-Phenyl-2-((4-(trifluoromethyl)phenyl)sulfonyl)benzofuran (3ae).** The desired pure product was obtained in 91% yield as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.99 (d, *J* = 8.3 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.56 – 7.47 (m, 7H), 7.32 (t, *J* = 7.5 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  154.71, 144.82, 143.70, 135.30 (q, *J* = 33.1Hz) 130.13, 129.22, 129.02, 128.79, 128.47, 128.40, 127.68, 126.31 (q, *J* = 3.7 Hz) 124.46, 124.37, 123.01 (q, *J* = 271.6 Hz) 122.46, 112.38. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -63.24. HRMS (ESI) calculated for C<sub>21</sub>H<sub>13</sub>F<sub>3</sub>NaO<sub>3</sub>S [M+Na]<sup>+</sup>: 425.0430; found: 425.0436.



**3-Phenyl-2-tosylbenzofuran (3af).** The desired pure product was obtained in 80% yield as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.76 (d, J = 8.3 Hz, 2H), 7.59 – 7.41 (m, 8H), 7.28 (d, J = 7.3 Hz, 1H), 7.24 (d, J = 7.9 Hz, 2H), 2.36 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  154.38, 146.13, 144.90, 137.27, 130.11, 129.75, 128.83, 128.80, 128.20, 128.16, 127.90, 127.82, 127.34, 124.10, 122.18, 112.21, 21.54. HRMS (ESI) calculated for C<sub>21</sub>H<sub>16</sub>NaO<sub>3</sub>S [M+Na]<sup>+</sup>: 371.0712; found: 371.0715.



**3-Phenyl-2-(o-tolylsulfonyl)benzofuran (3ag).** The desired pure product was obtained in 86% yield as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.96 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.36 (m, 9H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 2.40 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  154.22, 145.93, 138.56, 137.83, 133.81, 132.40, 130.12, 129.89, 128.79, 128.55, 128.19, 128.14, 127.61, 127.53, 126.18, 124.19, 122.14, 112.24, 19.78. HRMS (ESI) calculated for C<sub>21</sub>H<sub>16</sub>NaO<sub>3</sub>S [M+Na]<sup>+</sup>: 371.0712; found: 371.0718.



**2-((4-Methoxyphenyl)sulfonyl)-3-phenylbenzofuran (3ah).** The desired pure product was obtained in 54% yield as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.81 (d, *J* = 8.9 Hz, 2H), 7.60 – 7.41 (m, 8H), 7.30 – 7.24 (m, 1H), 6.91 (d, *J* = 8.9 Hz, 2H), 3.81 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  163.85, 154.31, 146.51, 131.66, 130.21, 130.14, 128.89, 128.81, 128.21, 128.07, 127.89, 126.85, 124.09, 122.16, 114.35, 112.21, 55.64. HRMS (ESI) calculated for C<sub>21</sub>H<sub>16</sub>NaO<sub>4</sub>S [M+Na]<sup>+</sup>: 387.0662; found: 387.0667.



**3-Phenyl-2-(phenylsulfonyl)benzofuran (3ai).** The desired pure product was obtained in 81% yield as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.88 (d, *J* = 7.3 Hz, 2H), 7.59 – 7.42 (m, 11H), 7.28 (t, *J* = 7.2 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  154.41, 145.69, 140.10, 133.79, 130.08, 129.11, 128.90, 128.64, 128.30, 128.23, 127.80, 127.73, 124.17, 122.23, 112.24. HRMS (ESI) calculated for C<sub>20</sub>H<sub>14</sub>NaO<sub>3</sub>S [M+Na]<sup>+</sup>: 357.0556; found: 357.0559.



**2-((3,4-Dimethoxyphenyl)sulfonyl)-3-phenylbenzofuran (3aj).** The desired pure product was obtained in 46% yield as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.60 – 7.42 (m, 9H), 7.28 (t,

 $J = 7.8 \text{ Hz}, 1\text{H}, 7.21 \text{ (s, 1H)}, 6.88 \text{ (d, J} = 8.4 \text{ Hz}, 1\text{H}, 3.88 \text{ (s, 3H)}, 3.77 \text{ (s, 3H)}. {}^{13}\text{C NMR} (100 \text{ MHz}, \text{CDCl}_3) \delta 154.21, 153.51, 148.99, 146.58, 131.75, 130.14, 128.96, 128.79, 128.19, 128.08, 127.90, 126.80, 124.09, 122.18, 122.08, 112.18, 110.63, 109.85, 56.09, 55.95. HRMS (ESI) calculated for C<sub>22</sub>H<sub>18</sub>NaO<sub>5</sub>S [M+Na]<sup>+</sup>: 417.0767; found: 417.0774.$ 



**2-(Naphthalen-1-ylsulfonyl)-3-phenylbenzofuran (3ak).** The desired pure product was obtained in 41% yield as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.45 (s, 1H), 7.91 – 7.82 (m, 3H), 7.81 – 7.76 (m, 1H), 7.65 – 7.48 (m, 9H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.30 – 7.23 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 154.49, 145.99, 137.01, 135.25, 132.01, 130.22, 129.83, 129.46, 129.44, 129.34, 128.97, 128.80, 128.31, 128.27, 127.88, 127.84, 127.55, 124.19, 122.47, 122.24, 112.30. HRMS (ESI) calculated for C<sub>24</sub>H<sub>16</sub>NaO<sub>3</sub>S [M+Na]<sup>+</sup>: 407.0712; found: 407.0719.



**3-Phenyl-2-(thiophen-2-ylsulfonyl)benzofuran (3al).** The desired pure product was obtained in 38% yield as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.67 (d, *J* = 3.8 Hz, 1H), 7.62 (d, *J* = 4.9 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 3H), 7.53 – 7.42 (m, 5H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.03 (t, *J* = 4.3 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 154.36, 145.77, 141.16, 134.77, 134.36, 130.06, 128.91, 128.66, 128.40, 128.24, 127.85, 127.77, 127.43, 124.23, 122.27, 112.23. HRMS (ESI) calculated for C<sub>18</sub>H<sub>12</sub>NaO<sub>3</sub>S<sub>2</sub> [M+Na]<sup>+</sup>: 363.0120; found: 363.0119.



**2-((4-Chlorophenyl)sulfonyl)-3-(p-tolyl)benzofuran (3ba).** The desired pure product was obtained in 80% yield as a white solid. <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.81 (d, J = 8.6 Hz, 2H), 7.54 (dd, J = 11.5, 8.2 Hz, 2H), 7.49 (d, J = 8.2 Hz, 1H), 7.47 – 7.41 (m, 4H), 7.33 (d, J = 8.1 Hz,

2H), 7.29 (d, J = 7.4 Hz, 1H), 2.46 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  154.52, 145.05, 140.47, 139.05, 138.68, 129.98, 129.45, 129.32, 129.05, 128.46, 128.34, 127.75, 125.45, 124.22, 122.38, 112.26, 21.42. HRMS (ESI) calculated for C<sub>21</sub>H<sub>15</sub>ClNaO<sub>3</sub>S [M+Na]<sup>+</sup>: 405.0323; found: 405.0331.



**3-(4-(Tert-butyl)phenyl)-2-((4-chlorophenyl)sulfonyl)benzofuran (3ca).** The desired pure product was obtained in 95% yield as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.70 (d, *J* = 8.7 Hz, 2H), 7.49 – 7.35 (m, 7H), 7.30 (d, *J* = 8.6 Hz, 2H), 7.20 (t, *J* = 7.8 Hz, 1H), 1.31 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  154.53, 152.10, 145.21, 140.44, 138.71, 129.82, 129.38, 129.36, 128.41, 128.19, 127.81, 125.47, 125.26, 124.18, 122.51, 112.24, 34.75, 31.28. HRMS (ESI) calculated for C<sub>24</sub>H<sub>21</sub>CINaO<sub>3</sub>S [M+Na]<sup>+</sup>: 447.0792; found: 447.0804.



**3-(4-Chlorophenyl)-2-((4-chlorophenyl)sulfonyl)benzofuran (3da).** The desired pure product was obtained in 39% yield as a white solid. <sup>1</sup>H NMR (400 MHz,CDCl<sub>3</sub>)  $\delta$  7.82 (d, *J* = 8.7 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 1H), 7.53 – 7.43 (m, 8H), 7.33 (t, *J* = 7.5 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  154.57, 145.58, 140.78, 138.48, 135.29, 131.49, 129.61, 129.37, 128.72, 128.68, 127.42, 127.04, 126.96, 124.52, 122.07, 112.42. HRMS (ESI) calculated for C<sub>20</sub>H<sub>12</sub>Cl<sub>2</sub>NaO<sub>3</sub>S [M+Na]<sup>+</sup>: 424.9776; found: 424.9787.



**3-(3-Chlorophenyl)-2-((4-chlorophenyl)sulfonyl)benzofuran (3ea).** The desired pure product was obtained in 77% yield as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.84 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.9 Hz, 1H), 7.53 – 7.43 (m, 8H), 7.32 (t, *J* = 7.5 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  154.50, 145.79, 140.79, 138.39, 134.19, 130.38, 129.90, 129.65, 129.59, 129.41, 129.17, 128.72, 128.47, 127.28, 126.51, 124.55, 122.03, 112.37. HRMS (ESI) calculated for C<sub>20</sub>H<sub>12</sub>Cl<sub>2</sub>NaO<sub>3</sub>S [M+Na]<sup>+</sup>: 424.9776; found: 424.9778.



**2-((4-Chlorophenyl)sulfonyl)-3-(4-(trifluoromethyl)phenyl)benzofuran (3fa).** The desired pure product was obtained in 52% yield as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.82 (dd, J = 15.4, 8.4 Hz, 4H), 7.69 (d, J = 8.1 Hz, 2H), 7.59 (d, J = 8.4 Hz, 1H), 7.56 – 7.43 (m, 4H), 7.34 (t, J = 7.5 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  154.62, 145.95, 140.93, 138.29, 132.51, 131.06 (q, J = 32.5 Hz), 130.61, 129.67, 129.43, 128.85, 127.25, 126.58, 125.32 (q, J = 3.7 Hz), 124.69, 123.94 (q, J = 270 Hz), 121.96, 112.47. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -62.63. HRMS (ESI) calculated for C<sub>21</sub>H<sub>12</sub>ClCF<sub>3</sub>NaO<sub>3</sub>S [M+Na]<sup>+</sup>: 459.0040; found: 459.0043.



**2-((4-Chlorophenyl)sulfonyl)-3-(4-methoxyphenyl)benzofuran (3ga).** The desired pure product was obtained in 50% yield as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.80 (d, *J* = 8.6 Hz, 2H), 7.59 – 7.45 (m, 5H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 8.7 Hz, 2H), 3.90 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  160.24, 154.57, 145.05, 140.48, 138.87, 131.49, 129.45, 129.30, 128.45, 128.12, 127.89, 124.22, 122.39, 120.59, 113.86, 112.30, 55.34. HRMS (ESI) calculated for C<sub>21</sub>H<sub>15</sub>ClNaO<sub>4</sub>S [M+Na]<sup>+</sup>: 421.0272; found: 421.0279.



**2-((4-Chlorophenyl)sulfonyl)-3-(naphthalen-1-yl)benzofuran (3ha).** The desired pure product was obtained in 42% yield as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.90 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.59 – 7.36 (m, 7H), 7.22 – 7.03 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  154.39, 147.06, 140.48, 138.06, 133.37, 131.57, 129.53, 129.44, 129.16, 129.02, 128.57, 128.52, 128.46, 126.35, 126.12, 126.03, 125.20, 125.15, 124.34, 122.58, 112.40. HRMS (ESI) calculated for C<sub>24</sub>H<sub>15</sub>ClNaO<sub>3</sub>S [M+Na]<sup>+</sup>: 441.0323; found: 441.0333.



**2-((4-Chlorophenyl)sulfonyl)-3-(naphthalen-2-yl)benzofuran (3ia).** The desired pure product was obtained in 34% yield as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.03 (s, 1H), 7.99 (d, J = 8.5 Hz, 1H), 7.99 – 7.90 (m, 2H), 7.80 (d, J = 8.6 Hz, 2H), 7.67 – 7.48 (m, 6H), 7.40 (d, J = 8.7 Hz, 2H), 7.33 (t, J = 7.5 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  154.59, 145.56, 140.59, 138.63, 133.28, 132.85, 129.71, 129.48, 129.37, 128.60, 128.26, 128.22, 127.98, 127.88, 127.82, 127.50, 126.92, 126.60, 126.00, 124.41, 122.40, 112.38. HRMS (ESI) calculated for C<sub>24</sub>H<sub>15</sub>ClNaO<sub>3</sub>S [M+Na]<sup>+</sup>: 441.0323; found: 441.0329.



**2-((4-Chlorophenyl)sulfonyl)-3-methylbenzofuran (3ja)**. The desired pure product was obtained in 60% yield as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.00 (d, J = 8.6 Hz, 2H), 7.61 (d, J = 7.9 Hz, 1H), 7.51 (d, J = 8.6 Hz, 2H), 7.50 – 7.40 (m, 2H), 7.36 – 7.27 (m, 1H), 2.64 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  154.70, 144.99, 140.49, 138.96, 129.62, 129.16, 128.35, 128.08, 124.39, 123.75, 121.38, 112.20, 8.60. HRMS (ESI) calculated for C<sub>15</sub>H<sub>11</sub>ClNaO<sub>3</sub>S [M+Na]<sup>+</sup>:



**2-((4-Chlorophenyl)sulfonyl)benzofuran (3ka).**<sup>5</sup> The desired pure product was obtained in 24% yield as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.02 (d, J = 8.7 Hz, 2H), 7.68 (d, J = 7.9 Hz, 1H), 7.58 (s, 1H), 7.52 (d, J = 8.6 Hz, 2H), 7.49 (s, 1H), 7.45 (t, J = 7.8 Hz, 1H), 7.32 (t, J = 8.0 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  156.41, 151.04, 140.86, 137.74, 129.71, 129.67, 128.21, 125.79, 124.39, 123.17, 113.59, 112.39.



**2-((4-Chlorophenyl)sulfonyl)-5-methyl-3-phenylbenzofuran (3la).** The desired pure product was obtained in 60% yield as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.78 (d, *J* = 8.5 Hz, 2H), 7.55 – 7.47 (m, 5H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 9.3 Hz, 2H), 2.37 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  153.04, 145.38, 140.39, 138.80, 134.11, 130.06, 130.01, 129.38, 129.25, 128.92, 128.73, 128.25, 127.94, 127.76, 121.64, 111.77, 21.21. HRMS (ESI) calculated for C<sub>21</sub>H<sub>15</sub>ClNaO<sub>3</sub>S [M+Na]<sup>+</sup>: 405.0323; found: 405.0335.



**2-((4-Chlorophenyl)sulfonyl)-5-methoxy-3-phenylbenzofuran (3ma).** The desired pure product was obtained in 95% yield as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.77 (d, *J* = 8.6 Hz, 2H), 7.55 – 7.47 (m, 5H), 7.44 (d, *J* = 9.1 Hz, 1H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.08 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.85 (d, *J* = 2.5 Hz, 1H), 3.74 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  157.00, 149.57, 145.95, 140.42, 138.74, 129.98, 129.40, 129.25, 128.96, 128.72, 128.34, 128.22, 128.11, 118.58, 112.98, 102.89, 55.81. HRMS (ESI) calculated for C<sub>21</sub>H<sub>15</sub>ClNaO<sub>4</sub>S [M+Na]<sup>+</sup>: 421.0272; found: 421.0286.



**3-((4-Chlorophenyl)sulfonyl)-2-phenylbenzofuran (3na).** The desired pure product was obtained in 42% yield as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.15 (dd, *J* = 6.0, 3.2 Hz, 1H), 7.89 (d, *J* = 6.6 Hz, 2H), 7.68 (d, *J* = 8.7 Hz, 2H), 7.56 – 7.46 (m, 4H), 7.43 – 7.36 (m, 2H), 7.30 (d, *J* = 8.6 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.20, 153.17, 140.71, 139.70, 131.03, 130.06, 129.17, 128.20, 128.05, 127.88, 126.09, 125.21, 124.71, 121.45, 118.13, 111.49. HRMS (ESI) calculated for C<sub>20</sub>H<sub>13</sub>ClNaO<sub>3</sub>S [M+Na]<sup>+</sup>: 391.0166; found: 391.0169.



**2-((4-Chlorophenyl)sulfonyl)-1-phenylnaphtho[2,1-b]furan (30a).** The desired pure product was obtained in 39% yield as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.87 (dd, J = 8.1, 3.9 Hz, 2H), 7.77 – 7.69 (m, 2H), 7.66 (d, J = 9.1 Hz, 1H), 7.56 (d, J = 6.8 Hz, 3H), 7.47 – 7.35 (m, 6H), 7.28 (t, J = 7.7 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  152.97, 145.38, 140.29, 139.00, 130.89, 130.32, 129.72, 129.49, 129.34, 129.19, 129.09, 129.01, 128.53, 128.30, 127.15, 125.36, 122.68, 121.38, 112.25. HRMS (ESI) calculated for C<sub>24</sub>H<sub>15</sub>ClNaO<sub>3</sub>S [M+Na]<sup>+</sup>: 441.0323; found: 441.0329.



**2-((4-Chlorophenyl)sulfonyl)-3-phenylbenzo[b]thiophene (5a)**. The desired pure product was obtained in 54% yield as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.90 (d, J = 8.2 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.46 – 7.39 (m, 3H), 7.39 – 7.30 (m, 3H), 7.27 – 7.15 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  142.32, 140.10, 140.04, 139.84, 139.36, 138.81, 131.64, 130.35, 129.17, 128.85, 128.83, 128.11, 127.72, 125.38, 125.28, 122.38. HRMS (ESI) calculated for C<sub>20</sub>H<sub>13</sub>ClNaO<sub>2</sub>S<sub>2</sub> [M+Na]<sup>+</sup>: 406.9938; found: 406.9942.



**5**-((**4**-Chlorophenyl)sulfonyl)-2,3-dihydrothieno[3,4-b][1,4]dioxine (5b). The desired pure product was obtained in 58% yield as a white solid. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.93 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 8.6 Hz, 2H), 7.21 (s, 1H), 4.38 – 4.33 (m, 2H), 4.25 – 4.19 (m, 2H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  144.16, 141.48, 140.45, 138.61, 129.73, 128.52, 113.36, 108.90, 65.42, 63.79. HRMS (ESI) calculated for C<sub>12</sub>H<sub>9</sub>ClNaO<sub>4</sub>S<sub>2</sub> [M+Na]<sup>+</sup>: 338.9523; found: 338.9527.



**2-((4-Chlorophenyl)sulfonyl)-1-phenyl-1H-pyrrole (5c)**. The desired pure product was obtained in 36% yield as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.48 – 7.37 (m, 1H), 7.38 – 7.27 (m, 4H), 7.27 – 7.20 (m, 3H), 7.13 – 7.05 (m, 2H), 6.92 – 6.85 (m, 1H), 6.34 (dd, *J* = 3.9, 2.7 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  139.95, 139.12, 137.70, 130.20, 129.82, 128.94, 128.84, 128.76, 128.49, 127.80, 119.43, 108.89. HRMS (ESI) calculated for C<sub>16</sub>H<sub>12</sub>ClNNaO<sub>2</sub>S [M+Na]<sup>+</sup>: 340.0169; found: 340.0173.



**2-(4-Chlorophenyl)-3-((4-chlorophenyl)sulfonyl)imidazo[1,2-a]pyridine (5d)**. The desired pure product was obtained in 62% yield as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.09 (d, *J* = 7.1 Hz, 1H), 7.75 – 7.69 (m, 3H), 7.55 (d, *J* = 8.7 Hz, 2H), 7.52 – 7.48 (m, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.7 Hz, 2H), 7.10 (t, *J* = 7.0 Hz, 1H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ 151.92, 146.77, 140.16, 140.09, 135.76, 131.85, 130.79, 129.42, 128.97, 128.10, 127.58, 126.61, 118.07,

117.06, 114.99. HRMS (ESI) calculated for  $C_{19}H_{12}Cl_2N_2NaO_2S$  [M+Na]<sup>+</sup>: 424.9889; found: 424.9898.



**2-((4-Chlorophenyl)sulfonyl)-1,3,5-trimethoxybenzene (5e)**. The desired pure product was obtained in 51% yield as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.88 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 6.06 (s, 2H), 3.82 (s, 3H), 3.78 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  165.31, 160.86, 143.23, 138.32, 128.52, 128.36, 109.90, 91.42, 56.30, 55.48. HRMS (ESI) calculated for C<sub>15</sub>H<sub>15</sub>ClNaO<sub>5</sub>S [M+Na]<sup>+</sup>: 365.0221; found: 365.0223.



2-((4-Chlorophenyl)sulfonyl)-1,3-dimethoxy-5-methylbenzene (5f). The desired pure product was obtained in 56% yield as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.82 (d, *J* = 8.7 Hz, 2H), 7.42 (d, *J* = 8.7 Hz, 2H), 6.39 (s, 1H), 6.24 (s, 1H), 3.81 (s, 3H), 3.61 (s, 3H), 2.80 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  163.84, 159.82, 142.99, 142.80, 138.49, 128.61, 128.41, 119.63, 109.91, 97.31, 55.87, 55.45, 22.81. HRMS (ESI) calculated for C<sub>15</sub>H<sub>15</sub>ClNaO<sub>4</sub>S [M+Na]<sup>+</sup>: 349.0272; found: 349.0277.



1-((4-Chlorophenyl)sulfonyl)-2,3,4,5,6-pentamethylbenzene (5g). The desired pure product was obtained in 40% yield as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.70 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 2.48 (s, 6H), 2.29 (s, 3H), 2.22 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ 

143.26, 141.05, 138.53, 135.45, 135.15, 134.94, 129.14, 127.18, 18.93, 17.86, 16.84. HRMS (ESI) calculated for  $C_{17}H_{19}CINaO_2S$  [M+Na]<sup>+</sup>: 345.0686; found: 345.0694.



**2-((4-Chlorophenyl)sulfonyl)naphthalene (5h**).<sup>6</sup> The desired pure product was obtained in 39% yield as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.60 (d, *J* = 8.6 Hz, 1H), 8.50 (d, *J* = 7.4 Hz, 1H), 8.07 (d, *J* = 8.2 Hz, 1H), 7.87 (t, *J* = 7.4 Hz, 3H), 7.63 – 7.47 (m, 3H), 7.38 (d, *J* = 8.5 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 140.21, 139.49, 135.35, 135.22, 134.10, 129.99, 129.30, 129.06, 128.70, 128.42, 128.20, 126.89, 124.31, 123.95.



**1-((4-Chlorophenyl)sulfonyl)-2,7-dimethoxynaphthalene (5i)**. The desired pure product was obtained in 59% yield as a white solid. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  8.71 (s, 1H), 8.13 (d, *J* = 9.1 Hz, 1H), 7.84 (dd, *J* = 8.6, 6.4 Hz, 3H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 9.1 Hz, 1H), 7.12 (dd, *J* = 9.0, 2.3 Hz, 1H), 3.85 (s, 3H), 3.66 (s, 3H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  159.61, 158.49, 142.68, 137.65, 137.19, 132.19, 130.81, 128.86, 128.65, 124.20, 118.44, 116.31, 111.32, 102.33, 56.57, 55.17. HRMS (ESI) calculated for C<sub>18</sub>H<sub>15</sub>ClNaO<sub>4</sub>S [M+Na]<sup>+</sup>: 385.0272; found: 385.0276.

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# **Copies of product NMR Spectra**



<sup>1</sup>H NMR of compound **3aa** 

<sup>13</sup>C NMR of compound **3aa** 





<sup>13</sup>C NMR of compound **3ab** 





<sup>13</sup>C NMR of compound **3ac** 



<sup>19</sup>F NMR of compound **3ac** 





<sup>13</sup>C NMR of compound **3ad** 





<sup>13</sup>C NMR of compound **3ae** 



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<sup>13</sup>C NMR of compound **3af** 





<sup>13</sup>C NMR of compound **3ag** 





<sup>13</sup>C NMR of compound **3ah** 





<sup>13</sup>C NMR of compound **3ai** 





<sup>13</sup>C NMR of compound **3aj** 





<sup>13</sup>C NMR of compound **3ak** 





<sup>13</sup>C NMR of compound **3al** 





<sup>13</sup>C NMR of compound **3ba** 





<sup>13</sup>C NMR of compound **3ca** 





<sup>13</sup>C NMR of compound **3da** 





<sup>13</sup>C NMR of compound **3ea** 





<sup>13</sup>C NMR of compound **3fa** 







<sup>13</sup>C NMR of compound **3ga** 





<sup>13</sup>C NMR of compound **3ha** 





<sup>13</sup>C NMR of compound **3ia** 





<sup>13</sup>C NMR of compound **3ja** 





<sup>13</sup>C NMR of compound **3ka** 





<sup>13</sup>C NMR of compound **3la** 





<sup>13</sup>C NMR of compound **3ma** 





<sup>13</sup>C NMR of compound **3na** 



<sup>1</sup>H NMR of compound **3na** 



<sup>13</sup>C NMR of compound **30a** 





<sup>13</sup>C NMR of compound **5a** 





90 f1 (ppm) 80 . 170 . 160 . 150 . 140 . 130 120 . 110 100 80 . 70 60 . 50 40 . 30 20 . 10

1



<sup>13</sup>C NMR of compound **5**c





<sup>13</sup>C NMR of compound **5d** 









<sup>13</sup>C NMR of compound **5**g





<sup>13</sup>C NMR of compound **5h** 





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