

## *Supporting information*

# **Photoinduced Photocatalyst-Free Cascade Cyclization of Alkynes with Sodium Sulfinates for the Synthesis of Benzothiophenes and Thioflavones**

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## *Table of Contents for Supporting Information*

1. General considerations.....	2
2. Preparation of the starting materials.....	2
3. General procedure for the synthesis of <b>3a</b> .....	2
4. Characterization data of products.....	3
5. <sup>1</sup> H NMR, <sup>13</sup> C NMR and <sup>19</sup> F NMR spectra of the products.....	27

## 1. General considerations

All reactions were carried out under nitrogen atmosphere.  $^1\text{H}$  NMR  $^{13}\text{C}$  NMR and  $^{19}\text{F}$  NMR spectra were measured on a Bruker Avance NMR spectrometer (600 MHz/151 MHz/565 NMR) in  $\text{CDCl}_3$  as solvent and recorded in ppm relative to internal tetramethylsilane standard.  $^1\text{H}$  NMR data are reported as follows:  $\delta$ , chemical shift; coupling constants ( $J$  are given in Hertz, Hz) and integration. Abbreviations to denote the multiplicity of a particular signal were s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets) and m (multiplet).

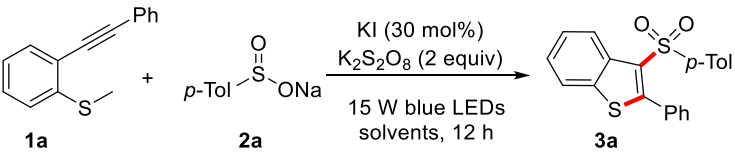
## 2. Preparation of the starting materials

2-alkynylthioanisoles (**1a**) derivatives were prepared according to reported method [5]. The chemicals and solvents were purchased from commercial supplier either Aldrich (USA), Energy Chemical (Shanghai) or Shanghai Chemical Company (P. R. China). All solvents were dried and freshly distilled in  $\text{N}_2$  prior to use. Products were purified by flash chromatography on 200-300 mesh silica gel.

### 3.1 General procedure for the synthesis of **3a** and optimization of solvents.

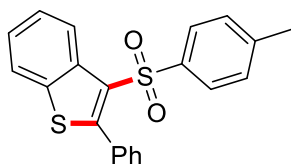
**General procedure 1 (GP 1):** A dry 15 mL tube was charged with 2-alkynylthioanisole (**1a**, 0.20 mmol), sodium sulfinates (**2a**, 0.40 mmol), CH<sub>3</sub>CN:H<sub>2</sub>O (3:1, 2 mL), KI (30 mol%), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (2 equiv) and a magnetic stir bar. Then let the mixture react under 15W blue led light at room temperature and nitrogen atmosphere for 12 hours. After the reaction, the mixture was concentrated to obtain the crude product, and the crude product was further purified by rapid chromatography (silica gel, petroleum ether / ethyl acetate = 30/1 - 15/1) to obtain the required product **3a**.

### 3.2 Optimization of solvents.

				
Entry	Oxidant	Additive	Solvents	Yield (%) <sup>b</sup>
1	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	KI	DMF	26
2	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	KI	Toluene	38
3	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	KI	1,4-dioxane	30
4	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	KI	THF	21
5	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	KI	MeCN	50
6	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	KI	MeCN:H <sub>2</sub> O (1:1)	58
7	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	KI	MeCN:H <sub>2</sub> O (2:1)	69
8	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	KI	MeCN:H <sub>2</sub> O (5:1)	72

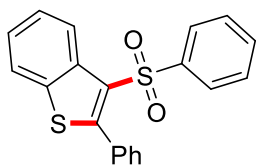
## 4. Characterization Data for Products

### 2-phenyl-3-tosylbenzo[*b*]thiophene (**3a**)<sup>1</sup>



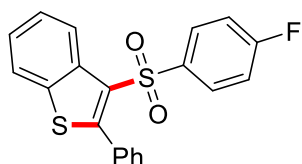
The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 30/1 - 15/1) to afford the **3a** as a white solid (58 mg, 84% yield). **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 8.62 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 8.1 Hz, 1H), 7.53 (d, J = 8.3 Hz, 2H), 7.52 – 7.48 (m, 1H), 7.47 – 7.43 (m, 1H), 7.43 – 7.37 (m, 5H), 7.10 (d, J = 8.1 Hz, 2H), 2.30 (s, 3H). **<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 152.5, 143.9, 139.4, 138.2, 136.1, 131.7, 130.5, 130.3, 129.5, 129.4, 127.6, 127.0, 125.9, 125.6, 124.6, 121.8, 21.5. The characterization data matched the literature [1].

### 2-phenyl-3-(phenylsulfonyl)benzo[*b*]thiophene (**3b**) [2]



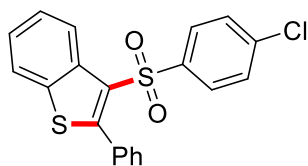
The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 30/1 - 15/1) to afford the **3b** as a white solid (56 mg, 80% yield). **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 8.64 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.64 (dd, J = 8.4, 1.1 Hz, 2H), 7.55 – 7.51 (m, 1H), 7.48 – 7.43 (m, 3H), 7.43 – 7.39 (m, 4H), 7.33 (t, J = 7.9 Hz, 2H). **<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 152.9, 142.3, 138.1, 136.2, 132.9, 131.6, 130.5, 130.0, 129.5, 128.7, 127.7, 126.9, 126.0, 125.6, 124.6, 121.7. The characterization data matched the literature [1].

### 3-((4-fluorophenyl)sulfonyl)-2-phenylbenzo[*b*]thiophene (**3c**) [1]



The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 30/1 - 15/1) to afford the **3c** as a yellow solid (46 mg, 63% yield). **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 8.65 (d, *J* = 8.3 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.64 – 7.59 (m, 2H), 7.56 – 7.51 (m, 1H), 7.49 – 7.43 (m, 2H), 7.42 – 7.38 (m, 4H), 7.01 – 6.94 (m, 2H). **<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 166.0, 164.3, 152.8, 138.3 (d, *J* = 3.1 Hz), 138.1, 136.0, 131.4, 130.5, 130.0, 129.8, 129.7 (d, *J* = 22.7 Hz), 126.9 (d, *J* = 252.1 Hz), 125.7, 124.5, 121.8, 115.9 (d, *J* = 22.8 Hz). The characterization data matched the literature [1].

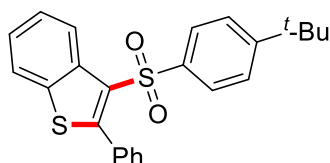
### 3-((4-chlorophenyl)sulfonyl)-2-phenylbenzo[*b*]thiophene (**3d**) [1]



The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 30/1 - 15/1) to afford the **3d** as a yellow solid (57 mg, 75% yield). **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 8.63 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.54 (t, *J* = 8.9 Hz, 3H), 7.50 – 7.44 (m, 2H), 7.43 – 7.38 (m, 4H), 7.28 (d, *J* = 8.6 Hz, 2H). **<sup>13</sup>C NMR (151 MHz,**

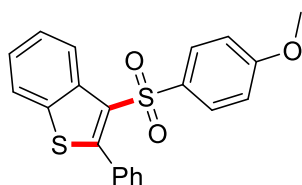
**CDCl<sub>3</sub>**)  $\delta$  153.1, 140.7, 139.5, 138.1, 136.0, 131.4, 130.5, 129.7, 129.6, 129.0, 128.4, 127.7, 126.1, 125.7, 124.5, 121.8. The characterization data matched the literature [3].

**3-((4-(*tert*-butyl)phenyl)sulfonyl)-2-phenylbenzo[*b*]thiophene (3e) [1]**



The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 30/1 - 15/1) to afford the **3e** as a white solid (66 mg, 82% yield). **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**  $\delta$  8.65 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.55 – 7.52 (m, 1H), 7.47 – 7.43 (m, 2H), 7.43 – 7.38 (m, 4H), 7.33 (d, *J* = 8.6 Hz, 2H), 1.26 (s, 9H). **<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)**  $\delta$  156.7, 152.4, 139.2, 138.1, 136.2, 131.7, 130.4, 129.4, 127.6, 126.9, 125.9, 125.7, 125.5, 124.7, 121.7, 35.1, 31.0. The characterization data matched the literature [3].

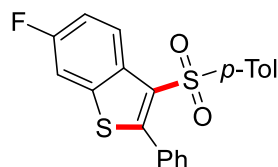
**3-((4-methoxyphenyl)sulfonyl)-2-phenylbenzo[*b*]thiophene (3f) [1]**



The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 15/1 - 7/1) to afford the **3f** as a white solid (58 mg, 77% yield). **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)**  $\delta$  8.56 (d, *J* = 8.4 Hz, 1H),

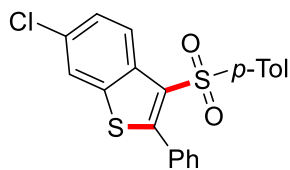
7.73 (d,  $J = 8.1$  Hz, 1H), 7.50 (d,  $J = 9.0$  Hz, 2H), 7.47 – 7.43 (m, 1H), 7.41 – 7.38 (m, 1H), 7.37 – 7.33 (m, 5H), 6.74 – 6.69 (m, 2H), 3.71 (s, 3H).  **$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )**  $\delta$  162.1, 151.0, 137.1, 135.0, 133.0, 130.7, 129.7, 129.4, 128.3, 128.2, 126.6, 124.8, 124.5, 123.6, 120.7, 112.9, 54.5. The characterization data matched the literature [3].

### 6-fluoro-2-phenyl-3-tosylbenzo[*b*]thiophene (**3g**) [1]



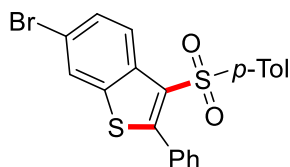
The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 30/1 - 15/1) to afford the **3g** as a brown solid (60 mg, 79% yield).  **$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )**  $\delta$  8.61 (dd,  $J = 9.2, 5.1$  Hz, 1H), 7.50 (d,  $J = 8.3$  Hz, 2H), 7.48 – 7.44 (m, 2H), 7.41 – 7.38 (m, 4H), 7.29 – 7.24 (m, 1H), 7.12 (d,  $J = 8.2$  Hz, 2H), 2.33 (s, 3H).  **$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )**  $\delta$  160.8 (d,  $J = 247.7$  Hz), 152.0 (d,  $J = 3.3$  Hz), 144.0, 139.2 (d,  $J = 4.4$  Hz), 139.1, 132.6, 131.3, 130.5, 130.1, 129.6, 129.4, 127.7, 127.0, 126.1 (d,  $J = 8.9$  Hz), 114.9 (d,  $J = 23.9$  Hz), 107.9 (d,  $J = 25.4$  Hz), 21.5. The characterization data matched the literature [3].

### 6-chloro-2-phenyl-3-tosylbenzo[*b*]thiophene (**3h**) [2]



The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 30/1 - 15/1) to afford the **3h** as a white solid (40 mg, 51% yield). **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 8.57 (d, J = 8.9 Hz, 1H), 7.78 (d, J = 1.9 Hz, 1H), 7.50 – 7.46 (m, 4H), 7.40 (d, J = 4.4 Hz, 4H), 7.12 (d, J = 8.2 Hz, 2H), 2.33 (s, 3H). **<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 152.7, 144.1, 139.1, 139.1, 134.6, 131.9, 131.2, 130.5, 130.3, 129.6, 129.4, 127.7, 127.0, 126.8, 125.6, 121.3, 21.5. The characterization data matched the literature [3].

#### 6-bromo-2-phenyl-3-tosylbenzo[*b*]thiophene (**3i**) [1]

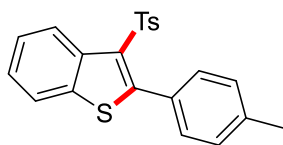


The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 30/1 - 15/1) to afford the **3i** as a yellow solid (60 mg, 68% yield). **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 8.51 (d, J = 8.9 Hz, 1H), 7.94 (d, J = 1.8 Hz, 1H), 7.62 (dd, J = 8.9, 1.8 Hz, 1H), 7.48 (t, J = 7.0 Hz, 3H), 7.40 (d, J = 4.4 Hz, 4H), 7.12 (d, J = 8.2 Hz, 2H), 2.33 (s, 3H). **<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 152.7, 144.1, 139.4, 139.1, 135.0,



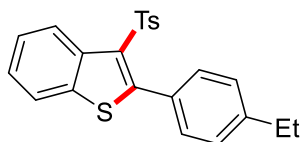
131.1, 130.5, 130.3, 129.7, 129.4, 129.4, 127.7, 127.0, 125.8, 124.2, 119.7, 21.5. The characterization data matched the literature [1].

**2-(*p*-tolyl)-3-tosylbenzo[*b*]thiophene (3j) [1]**



The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 30/1 - 15/1) to afford the **3j** as a white solid (63 mg, 84% yield). **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 8.59 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 8.3 Hz, 2H), 7.51 – 7.47 (m, 1H), 7.42 – 7.37 (m, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 7.9 Hz, 2H), 7.12 (d, J = 8.2 Hz, 2H), 2.43 (s, 3H), 2.31 (s, 3H). **<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 153.0, 143.8, 139.6, 139.5, 138.1, 136.2, 130.4, 129.9, 129.4, 128.7, 128.4, 127.0, 125.8, 125.5, 124.5, 121.7, 21.5, 21.5. The characterization data matched the literature [3].

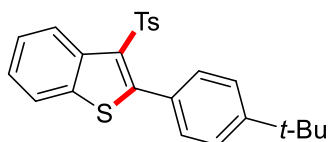
**2-(4-ethylphenyl)-3-tosylbenzo[*b*]thiophene (3k)[3]**



The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 30/1 - 15/1) to afford the **3k** as a white solid (69 mg, 89% yield). **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 8.61 (d, J = 8.4 Hz,

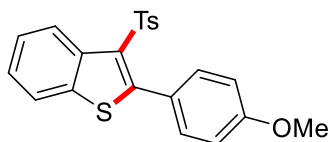
1H), 7.74 (d,  $J = 8.1$  Hz, 1H), 7.54 (d,  $J = 8.3$  Hz, 2H), 7.50 – 7.46 (m, 1H), 7.40 – 7.36 (m, 1H), 7.34 (d,  $J = 8.1$  Hz, 2H), 7.22 (d,  $J = 8.0$  Hz, 2H), 7.09 (d,  $J = 8.2$  Hz, 2H), 2.71 (q,  $J = 7.6$  Hz, 2H), 2.29 (s, 3H), 1.29 (t,  $J = 7.6$  Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  152.9, 145.8, 143.8, 139.5, 138.1, 136.2, 130.5, 130.0, 129.4, 128.9, 127.2, 127.0, 125.8, 125.5, 124.6, 121.7, 28.8, 21.5, 15.4. The characterization data matched the literature. [3]

### 2-(4-(*tert*-butyl)phenyl)-3-tosylbenzo[*b*]thiophene (**3l**) [2]



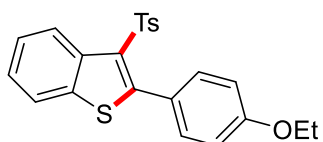
The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 30/1 - 15/1) to afford the **3l** as a white solid (65 mg, 78% yield).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.63 (d,  $J = 8.3$  Hz, 1H), 7.78 (d,  $J = 8.0$  Hz, 1H), 7.52 – 7.48 (m, 3H), 7.43 – 7.37 (m, 3H), 7.36 – 7.32 (m, 2H), 7.08 (d,  $J = 8.1$  Hz, 2H), 2.31 (s, 3H), 1.38 (s, 9H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  152.7, 152.6, 143.6, 139.4, 138.1, 136.3, 130.2, 130.0, 129.2, 128.6, 127.1, 125.8, 125.4, 124.6, 124.6, 121.7, 34.8, 31.3, 21.5. The characterization data matched the literature [1].

### 2-(4-methoxyphenyl)-3-tosylbenzo[*b*]thiophene (**3m**) [1]



The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 15/1 - 7/1) to afford the **3m** as a white solid (59 mg, 76% yield). **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 8.60 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 8.3 Hz, 2H), 7.52 – 7.47 (m, 1H), 7.42 – 7.36 (m, 3H), 7.12 (d, J = 8.2 Hz, 2H), 6.93 (d, J = 8.7 Hz, 2H), 3.88 (s, 3H), 2.32 (s, 3H). **<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 160.6, 152.8, 143.8, 139.5, 138.0, 136.3, 131.9, 129.8, 129.4, 126.9, 125.8, 125.4, 124.5, 123.7, 121.7, 113.1, 55.4, 21.5. The characterization data matched the literature.

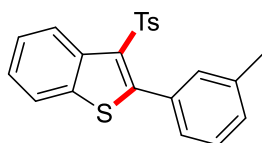
### 2-(4-ethoxyphenyl)-3-tosylbenzo[*b*]thiophene (**3n**)



The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 15/1 - 7/1) to afford the **3n** as a white solid (50 mg, 62% yield). **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 8.61 (d, J = 8.3 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 8.3 Hz, 2H), 7.52 – 7.47 (m, 1H), 7.42 – 7.38 (m, 1H), 7.38 – 7.34 (m, 2H), 7.12 (d, J = 8.1 Hz, 2H), 6.94 – 6.89 (m, 2H), 4.10 (q, J = 7.0 Hz, 2H), 2.32 (s, 3H), 1.46 (t, J = 7.0 Hz, 3H). **<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 160.0, 153.0, 143.7, 139.6, 138.0,

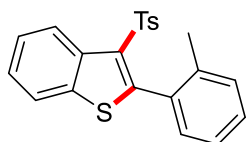
136.3, 131.9, 129.7, 129.3, 126.9, 125.8, 125.4, 124.5, 123.5, 121.6, 113.6, 63.6, 21.5, 14.8. The characterization data matched the literature [2].

**2-(*m*-tolyl)-3-tosylbenzo[*b*]thiophene (**3o**)[3]**



The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 30/1 - 15/1) to afford the **3o** as a white solid (51 mg, 68% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.63 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.55 (d, J = 8.3 Hz, 2H), 7.54 – 7.50 (m, 1H), 7.45 – 7.40 (m, 1H), 7.29 (dd, J = 14.9, 7.5 Hz, 2H), 7.23 (d, J = 7.3 Hz, 1H), 7.17 – 7.11 (m, 3H), 2.38 (s, 3H), 2.34 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 152.7, 143.8, 139.5, 138.1, 137.2, 136.2, 131.5, 131.0, 130.2, 130.1, 129.3, 127.5, 127.1, 125.8, 125.5, 124.6, 121.7, 21.5, 21.3. The characterization data matched the literature [3].

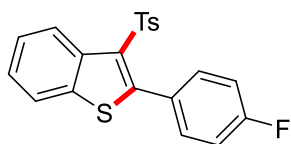
**2-(*o*-tolyl)-3-tosylbenzo[*b*]thiophene (**3p**) [3]**



The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 30/1 - 15/1) to afford the **3p** as a white solid

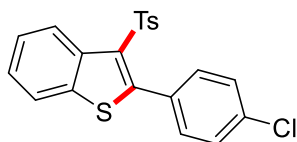
(58 mg, 78% yield). **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 8.66 (d, J = 8.3 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.54 (t, J = 8.4 Hz, 3H), 7.47 – 7.42 (m, 1H), 7.37 (td, J = 7.6, 1.1 Hz, 1H), 7.22 (dd, J = 14.7, 7.2 Hz, 2H), 7.17 – 7.12 (m, 3H), 2.35 (s, 3H), 2.08 (s, 3H). **<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 151.6, 144.0, 139.2, 138.5, 138.1, 135.8, 131.2, 131.0, 130.2, 129.8, 129.6, 129.4, 127.3, 125.8, 125.5, 124.9, 124.5, 121.8, 21.5, 20.2. The characterization data matched the literature.

### 2-(4-fluorophenyl)-3-tosylbenzo[*b*]thiophene (**3q**)[1]



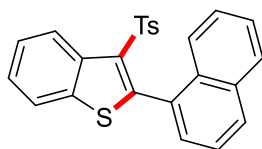
The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 30/1 - 15/1) to afford the **3q** as a yellow solid (54 mg, 71% yield). **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 8.61 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.1 Hz, 1H), 7.53 (t, J = 8.0 Hz, 3H), 7.43 (m, J = 8.6, 6.7, 1.4 Hz, 3H), 7.15 (d, J = 8.2 Hz, 2H), 7.10 (t, J = 8.6 Hz, 2H), 2.34 (s, 3H). **<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 162.7, 151.2, 144.0, 139.3, 138.0, 136.0, 132.4 (d, J = 8.4 Hz), 130.6, 129.4, 127.6, 126.9, 126.0, 125.7, 124.6, 121.7, 114.8 (d, J = 21.9 Hz), 21.5. The characterization data matched the literature.

### 2-(4-chlorophenyl)-3-tosylbenzo[*b*]thiophene (**3r**) [1]



The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 30/1 - 15/1) to afford the **3r** as a yellow solid (55 mg, 70% yield). **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 8.60 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.55 (t, J = 5.8 Hz, 2H), 7.54 – 7.51 (m, 1H), 7.46 – 7.42 (m, 1H), 7.40 – 7.36 (m, 4H), 7.16 (d, J = 8.2 Hz, 2H), 2.35 (s, 3H). **<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 150.8, 144.1, 139.3, 138.1, 136.0, 135.8, 131.8, 130.7, 130.1, 129.5, 127.9, 127.0, 126.0, 125.8, 124.6, 121.7, 21.5. The characterization data matched the literature [3].

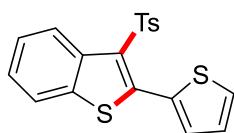
### 2-(naphthalen-1-yl)-3-tosylbenzo[b]thiophene (**3s**)



The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 15/1 - 7/1) to afford the **3s** as a yellow solid (43 mg, 53% yield). **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 8.60 (d, J = 8.4 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 8.3 Hz, 2H), 7.51 – 7.46 (m, 1H), 7.38 (m, J = 8.7, 7.4, 1.6 Hz, 3H), 7.11 (d, J = 8.2 Hz, 2H), 6.94 – 6.90 (m, 2H), 3.86 (s, 3H), 2.30 (s, 3H). **<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 160.6, 152.9, 143.8, 139.6, 138.0, 136.3, 131.9, 131.4, 130.4, 129.8,

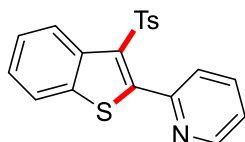
129.4, 126.9, 125.8, 125.4, 124.5, 123.7, 121.7, 113.2, 55.4, 53.5, 31.4, 30.2, 21.5. The characterization data matched the literature.[3]

### 2-(thiophen-2-yl)-3-tosylbenzo[*b*]thiophene (**3t**) [3]



The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 15/1 - 5/1) to afford the **3t** as a yellow solid (56 mg, 77% yield). **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 8.67 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.53 – 7.49 (m, 3H), 7.44 – 7.40 (m, 1H), 7.17 – 7.11 (m, 3H), 2.33 (s, 3H). **<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)** δ 144.6, 143.9, 139.1, 138.2, 136.5, 132.2, 131.0, 130.7, 129.4, 129.3, 127.4, 126.9, 126.0, 125.8, 124.8, 121.5, 21.5. The characterization data matched the literature.

### 2-(3-tosylbenzo[*b*]thiophen-2-yl)pyridine (**3u**)

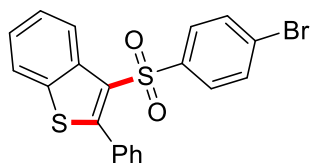


The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 15/1 - 5/1) to afford the **3u** as a white solid (59 mg, 82% yield). **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)** δ 8.71 – 8.68 (m, 1H), 8.45 (d, *J* = 8.3 Hz, 1H), 7.85 – 7.79 (m, 5H), 7.51 – 7.46 (m, 1H), 7.43 –

7.40 (m, 1H), 7.40 – 7.37 (m, 1H), 7.20 (d,  $J = 8.2$  Hz, 2H), 2.32 (s, 3H).

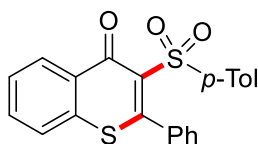
**$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )**  $\delta$  151.1, 150.8, 149.0, 144.0, 138.9, 138.6, 135.8, 135.6, 130.3, 129.6, 127.3, 126.9, 125.9, 125.9, 124.5, 123.9, 122.0, 21.5. The characterization data matched the literature. [2]

### 3-((4-bromophenyl)sulfonyl)-2-phenylbenzo[*b*]thiophene (3v)



The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 15/1 - 5/1) to afford the **3v** as a white solid (65 mg, 76% yield).  **$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )**  $\delta$  8.62 (d,  $J = 6$  Hz, 1H), 7.81 (d,  $J = 6$  Hz, 1H), 7.55 – 7.53 (m, 1H), 7.48 – 7.43 (m, 6H), 7.42 – 7.39 (m, 4H).  **$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )**  $\delta$  153.1, 141.2, 138.1, 136.0, 132.7, 132.0, 131.4, 130.5, 129.7, 128.5, 128.1, 127.7, 126.1, 125.7, 124.5, 121.8.

### 2-phenyl-3-tosyl-4H-thiochromen-4-one (5a)[4]

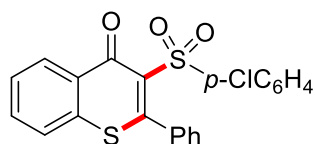


The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 15/1 - 5/1) to afford the **5a** as a white solid (58 mg, 75% yield).  **$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )**  $\delta$  8.20 (d,  $J = 7.9$  Hz, 1H),



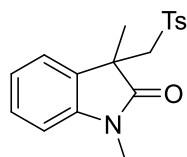
7.84 – 7.73 (m, 2H), 7.61 – 7.54 (m, 1H), 7.52 – 7.34 (m, 7H), 7.19 (d, J = 7.7 Hz, 2H), 2.30 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 175.9, 162.4, 144.0, 138.9, 135.7, 134.9, 132.8, 132.5, 131.6, 130.1, 128.9, 128.7, 128.5, 128.0, 127.9, 125.3, 21.3. The characterization data matched the literature.[4]

### 3-((4-chlorophenyl)sulfonyl)-2-phenyl-4H-thiophene-4-one (5b) [4]



The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 15/1 - 5/1) to afford the **5b** as a yellow solid (66 mg, 80% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.28 (dd, J = 8.1, 1.0 Hz, 1H), 7.91 – 7.86 (m, 2H), 7.58 (td, J = 8.0, 1.4 Hz, 1H), 7.50 – 7.42 (m, 7H), 7.38 – 7.34 (m, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 176.0, 163.2, 140.2, 139.6, 135.7, 134.5, 132.7, 132.6, 131.6, 130.5, 130.3, 129.2, 128.9, 128.7, 128.2, 128.1, 125.3. The characterization data matched the literature.[4]

### 1,3-dimethyl-3-(tosylmethyl)indolin-2-one (6)



The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 15/1 - 5/1) to afford the **6** as a white solid (50 mg, 76% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.38 – 7.37 (m, 2H), 7.30 – 7.27 (m, 1H), 7.16 (d, *J* = 6 Hz, 2H), 7.07 (d, *J* = 6 Hz, 1H), 6.93 – 6.90 (m, 1H), 6.84 (d, *J* = 6 Hz, 1H), 3.85 (d, *J* = 12 Hz, 1H), 3.67 (d, *J* = 18 Hz, 1H), 3.16 (s, 3H), 2.39 (s, 3H), 1.38 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  177.6, 144.3, 143.2, 137.0, 129.6, 129.5, 128.5, 127.8, 124.1, 122.4, 108.3, 61.9, 45.6, 26.5, 25.5, 21.5.

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## 5. $^1\text{H}$ NMR, $^{13}\text{C}$ NMR and $^{19}\text{F}$ NMR spectra of the products

