

Supporting information

A general electron donor-acceptor complex enabled cascade cyclization of alkyne to access sulfur-containing heterocycles

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1. General considerations

All reactions were carried out under nitrogen atmosphere. ^1H NMR ^{13}C NMR and ^{19}F NMR spectra were measured on a Bruker Avance NMR spectrometer (600 MHz/151 MHz/565 NMR) in CDCl_3 as solvent and recorded in ppm relative to internal tetramethylsilane standard. ^1H NMR data are reported as follows: δ , 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

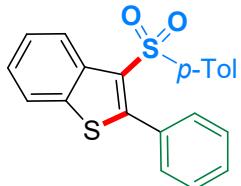
2-alkynylthioanisoles (**1a**) derivatives were prepared according to reported method (W. Liu, Y.-Q. Hu, X.-Y. Hong, G.-X. Li, X.-B. Huang, W.-X. Gao, M.-C. Liu, Y. Xia, Y.-B. Zhou and H.-Y. Wu, *Chem. Commun.*, 2018, **54**, 14148-14151). The chemicals and solvents were purchased from commercial supplier either Aldrich (USA), Energy Chemical (Shanghai) or Shanghai Chemical Company (P. R. China). All solvents were dried and freshly distilled in N_2 prior to use. Products were purified by flash chromatography on 200-300 mesh silica gel.

3. General procedure for the synthesis of **3a**.

A dry 15 mL tube was charged with 2-alkynylthioanisole (**1a**, 0.20 mmol), 4-methylbenzenesulfenic acid (**2a**, 0.40 mmol), CH₃CN:H₂O (1:1, 2 mL), and a magnetic stir bar. Then let the mixture react under 15W blue led light at room temperature and nitrogen atmosphere for 30 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**.

4. Characterization Data for Products

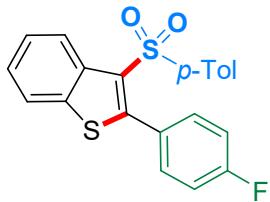
2-phenyl-3-tosylbenzo[*b*]thiophene (**3a**)¹



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 (66.98 mg, 92% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.62 (d, *J* = 8.3 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.52 – 7.48 (m, 1H), 7.47 – 7.37 (m, 6H), 7.10 (d, *J* = 8.1 Hz, 2H), 2.30 (s, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 152.5, 143.9, 139.4, 138.2, 136.1, 131.7, 130.5, 130.3, 129.4, 129.4, 127.6, 127.0, 125.9, 125.6, 124.6, 121.8, 21.5.

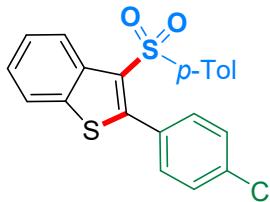
The characterization data matched the literature.¹

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



The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 30/1 - 15/1) to afford the **3b** as a yellow solid (61.88 mg, 81% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.61 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.1 Hz, 1H), 7.53 (d, J = 8.2 Hz, 3H), 7.45 – 7.38 (m, 3H), 7.15 (d, J = 8.2 Hz, 2H), 7.10 (t, J = 8.6 Hz, 2H), 2.34 (s, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 163.5 (d, J = 250.4 Hz), 151.2, 144.0, 139.3, 138.0, 136.0, 132.4 (d, J = 8.4 Hz), 129.4, 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.¹

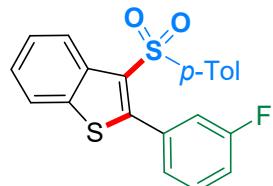
2-(4-chlorophenyl)-3-tosylbenzo[*b*]thiophene (3c**)¹**



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 (66.07 mg, 83% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.60 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.1 Hz, 1H), 7.55 (d, J = 8.3 Hz, 2H), 7.52 (d, J = 7.5 Hz, 1H), 7.44 (t, J = 7.7 Hz, 1H), 7.41 – 7.35 (m, 4H), 7.16 (d, J = 8.2

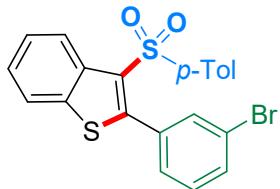
Hz, 2H), 2.35 (s, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 150.8, 144.1, 139.3, 138.1, 136.0, 135.8, 131.8, 130.7, 130.1, 129.5, 127.9, 127.0, 126.0, 125.7, 124.6, 121.7, 21.5. The characterization data matched the literature.¹

2-(3-fluorophenyl)-3-tosylbenzo[b]thiophene (3d)³



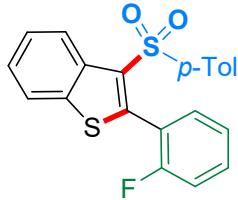
The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 30/1 - 15/1) to afford the **3d** as a yellow solid (60.36 mg, 79% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.62 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 8.3 Hz, 2H), 7.55 – 7.52 (m, 1H), 7.46 – 7.43 (m, 1H), 7.38 (td, J = 8.0, 5.9 Hz, 1H), 7.23 (d, J = 7.7 Hz, 1H), 7.16 (d, J = 8.4 Hz, 3H), 7.11 – 7.07 (m, 1H), 2.35 (s, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 161.7 (d, J = 247.3 Hz), 150.3, 144.1, 139.2, 138.1, 135.9, 133.6 (d, J = 8.1 Hz), 130.9, 129.5, 129.2 (d, J = 8.6 Hz), 127.0, 126.5 (d, J = 3.0 Hz), 126.1, 125.8, 124.7, 121.8, 117.6 (d, J = 22.9 Hz), 116.4 (d, J = 21.1 Hz), 21.5. The characterization data matched the literature.³

2-(3-bromophenyl)-3-tosylbenzo[b]thiophene (3e)³



The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 30/1 - 15/1) to afford the **3e** as a brown solid (72.49 mg, 82% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.65 (d, J = 8.3 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.60 – 7.51 (m, 4H), 7.45 – 7.38 (m, 3H), 7.28 (t, J = 7.8 Hz, 1H), 7.16 (d, J = 8.1 Hz, 2H), 2.35 (s, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 149.9, 144.2, 139.2, 138.1, 135.9, 133.6, 132.9, 132.4, 131.2, 129.5, 129.4, 129.2, 127.1, 126.1, 125.9, 124.7, 121.8, 121.6, 21.6. The characterization data matched the literature.³

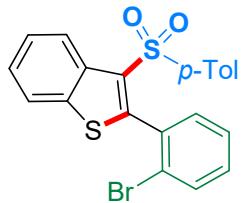
2-(2-fluorophenyl)-3-tosylbenzo[b]thiophene (3f)³



The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 30/1 - 15/1) to afford the **3f** as a yellow solid (59.59 mg, 78% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.47 (d, J = 8.3 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.67 (d, J = 8.3 Hz, 2H), 7.50 – 7.44 (m, 2H), 7.42 – 7.38 (m, 2H), 7.24 – 7.21 (m, 1H), 7.17 (d, J = 8.1 Hz, 2H), 7.15 – 7.11 (m, 1H), 2.32 (s, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 159.8 (d, J = 249.5 Hz), 145.0, 144.1, 138.9 (d, J = 24.5 Hz), 135.5, 132.4,

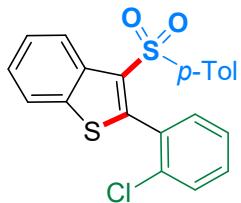
131.8, 131.7 (d, $J = 7.9$ Hz), 129.5, 127.1, 125.9, 125.8, 124.3, 123.5 (d, $J = 3.6$ Hz), 121.9, 119.8, 119.7, 115.5 (d, $J = 21.3$ Hz), 21.5. The characterization data matched the literature.³

2-(2-bromophenyl)-3-tosylbenzo[*b*]thiophene (3g)³



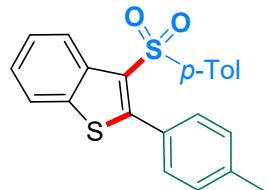
The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 30/1 - 15/1) to afford the **3g** as a brown solid (67.18 mg, 76% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.54 (d, $J = 8.3$ Hz, 1H), 7.80 (d, $J = 8.1$ Hz, 1H), 7.67 (d, $J = 8.3$ Hz, 2H), 7.62 (dd, $J = 8.0, 1.0$ Hz, 1H), 7.53 – 7.49 (m, 1H), 7.45 – 7.38 (m, 3H), 7.32 (td, $J = 7.8, 1.7$ Hz, 1H), 7.17 (d, $J = 8.2$ Hz, 2H), 2.34 (s, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 150.1, 144.2, 138.7, 135.3, 132.9, 132.5, 131.4, 130.9, 129.5, 127.4, 126.6, 125.9, 125.8, 124.5, 124.2, 122.0, 21.6. The characterization data matched the literature.³

2-(2-chlorophenyl)-3-tosylbenzo[*b*]thiophene (3h)³



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 (61.29 mg, 77% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.53 (d, J = 8.3 Hz, 1H), 7.80 (d, J = 8.1 Hz, 1H), 7.66 (d, J = 8.3 Hz, 2H), 7.52 – 7.48 (m, 1H), 7.45 – 7.39 (m, 4H), 7.35 (td, J = 7.3, 1.7 Hz, 1H), 7.17 (d, J = 8.1 Hz, 2H), 2.33 (s, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 148.4, 144.2, 138.8, 138.8, 135.3, 134.2, 132.5, 131.6, 130.9, 130.8, 129.5, 129.4, 127.3, 126.0, 125.9, 125.8, 124.4, 122.0, 21.5. The characterization data matched the literature.³

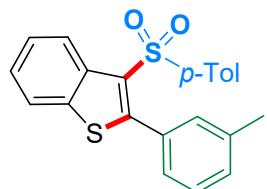
2-(*p*-tolyl)-3-tosylbenzo[*b*]thiophene (**3i**)¹



The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 30/1 - 15/1) to afford the **3i** as a white solid (70.31 mg, 93% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.59 (d, J = 8.3 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 8.3 Hz, 2H), 7.49 (t, J = 7.7 Hz, 1H), 7.39 (t, J = 7.6 Hz, 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), 2.42 (s, 3H), 2.31 (s, 3H). **¹³C NMR (151 MHz, CDCl₃)** 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.

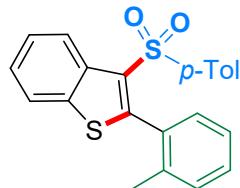
The characterization data matched the literature.¹

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



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 (67.28 mg, 89% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.63 (d, J = 8.3 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.55 (d, J = 8.3 Hz, 2H), 7.53 – 7.50 (m, 1H), 7.44 – 7.41 (m, 1H), 7.29 (dd, J = 14.9, 7.5 Hz, 2H), 7.22 (d, J = 7.3 Hz, 1H), 7.16 – 7.11 (m, 3H), 2.37 (s, 3H), 2.34 (s, 3H). **¹³C NMR (151 MHz, CDCl₃)** 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, 123.3, 121.7, 21.5, 21.3. The characterization data matched the literature.³

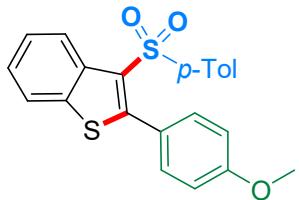
2-(*o*-tolyl)-3-tosylbenzo[*b*]thiophene (3k)³



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 (68.04 mg, 90% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.66 (d, J = 8.3 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.55 (d, J = 8.4 Hz, 3H), 7.46 – 7.42 (m, 1H), 7.29 (dd, J = 14.9, 7.5 Hz, 2H), 7.22 (d, J = 7.3 Hz, 1H), 7.16 – 7.11 (m, 3H), 2.37 (s, 3H), 2.34 (s, 3H).

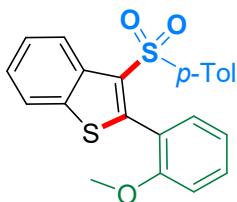
1H), 7.37 (td, $J = 7.6$, 1.0 Hz, 1H), 7.22 (dd, $J = 14.7$, 7.1 Hz, 2H), 7.17 – 7.12 (m, 3H), 2.35 (s, 3H), 2.08 (s, 3H). **^{13}C NMR (151 MHz, CDCl_3)** δ 151.6, 144.0, 139.2, 138.5, 138.1, 135.8, 131.2, 131.0, 130.2, 129.8, 129.6, 129.4, 127.3, 125.8, 125.5, 124.9, 124.5, 121.8, 21.5, 20.2. The characterization data matched the literature.³

2-(4-methoxyphenyl)-3-tosylbenzo[b]thiophene (3l)¹



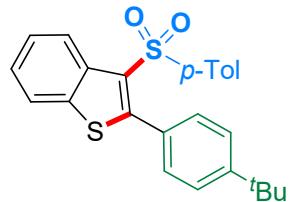
The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 15/1 - 7/1) to afford the **3l** as a white solid (71.71 mg, 91% yield). **^1H NMR (600 MHz, CDCl_3)** δ 8.60 (d, $J = 8.3$ Hz, 1H), 7.77 (d, $J = 8.0$ Hz, 1H), 7.54 (d, $J = 8.3$ Hz, 2H), 7.52 – 7.48 (m, 1H), 7.43 – 7.34 (m, 3H), 7.12 (d, $J = 8.1$ Hz, 2H), 6.93 (d, $J = 8.7$ Hz, 2H), 3.88 (s, 3H), 2.32 (s, 3H). **^{13}C NMR (151 MHz, CDCl_3)** 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.¹

2-(2-methoxyphenyl)-3-tosylbenzo[b]thiophene (3m)



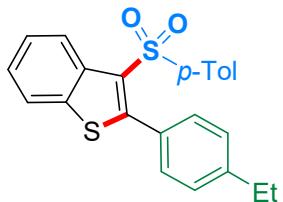
The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 15/1 - 7/1) to afford the **3m** as a white solid (69.34 mg, 88% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.49 (d, J = 8.3 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 8.3 Hz, 2H), 7.47 – 7.44 (m, 1H), 7.44 – 7.40 (m, 1H), 7.39 – 7.36 (m, 1H), 7.30 (dd, J = 7.5, 1.7 Hz, 1H), 7.13 (d, J = 8.1 Hz, 2H), 7.02 (td, J = 7.5, 0.8 Hz, 1H), 6.88 (d, J = 8.3 Hz, 1H), 3.61 (s, 3H), 2.32 (s, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 157.2, 149.0, 143.6, 139.4, 138.8, 135.9, 132.0, 131.2, 130.7, 129.2, 127.1, 125.6, 125.3, 124.3, 121.8, 120.5, 119.8, 110.6, 55.3, 21.5. The characterization data matched the literature.

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



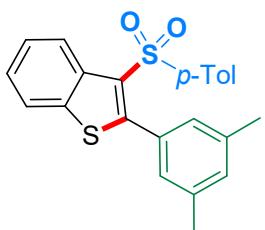
The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 30/1 - 15/1) to afford the **3n** as a yellow solid (77.28 mg, 92% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.63 (d, J = 8.3 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.52 – 7.47 (m, 3H), 7.43 – 7.38 (m, 3H), 7.34 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 8.1 Hz, 2H), 2.31 (s, 3H), 1.38 (s, 9H). **¹³C NMR (151 MHz, CDCl₃)** δ 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.²

2-(4-ethylphenyl)-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 (70.56 mg, 90% yield). **1H NMR (600 MHz, CDCl₃)** δ 8.61 (d, J = 8.3 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 8.3 Hz, 2H), 7.51 – 7.47 (m, 1H), 7.41 – 7.37 (m, 1H), 7.34 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 8.1 Hz, 2H), 2.72 (q, J = 7.6 Hz, 2H), 2.30 (s, 3H), 1.30 (t, J = 7.6 Hz, 3H). **13C NMR (151 MHz, CDCl₃)** δ 152.9, 145.8, 143.8, 139.5, 138.1, 136.2, 130.5, 130.0, 129.3, 128.9, 127.2, 127.0, 125.8, 125.4, 124.6, 121.7, 28.7, 21.5, 15.4. The characterization data matched the literature.³

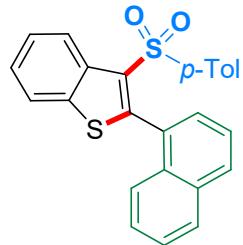
2-(3,5-dimethylphenyl)-3-tosylbenzo[*b*]thiophene (3p**)**



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 (68.21 mg, 87% yield). **1H NMR (600 MHz, CDCl₃)** δ 8.64 (d, J = 8.3

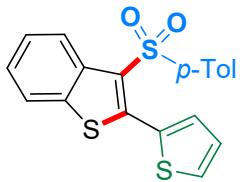
Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.56 (d, J = 8.2 Hz, 2H), 7.51 (t, J = 7.7 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.13 (d, J = 8.1 Hz, 2H), 7.07 (s, 1H), 6.96 (s, 2H), 2.34 (d, J = 5.3 Hz, 9H). **^{13}C NMR (151 MHz, CDCl_3)** δ 152.9, 143.7, 139.6, 138.0, 137.1, 136.2, 131.4, 131.0, 130.1, 129.2, 128.1, 127.1, 125.8, 125.4, 124.6, 121.7, 21.5, 21.2. The characterization data matched the literature.

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



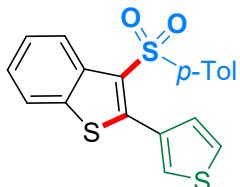
The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 15/1 - 7/1) to afford the **3q** as a yellow solid (70.38 mg, 85% yield). **^1H NMR (600 MHz, CDCl_3)** δ 8.60 (d, J = 8.3 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 8.3 Hz, 2H), 7.51 – 7.45 (m, 1H), 7.41 – 7.35 (m, 3H), 7.11 (d, J = 8.1 Hz, 2H), 6.94 – 6.90 (m, 2H), 3.85 (s, 3H), 2.30 (s, 3H). **^{13}C NMR (151 MHz, CDCl_3)** δ 160.6, 152.9, 143.8, 139.6, 138.0, 136.3, 131.9, 129.8, 129.4, 126.9, 125.8, 125.4, 124.5, 123.7, 121.7, 113.2, 55.4, 21.5. The characterization data matched the literature.

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



The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 15/1 - 7/1) to afford the **3r** as a yellow solid (45.14 mg, 61% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.68 – 8.65 (m, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 8.3 Hz, 2H), 7.53 – 7.48 (m, 3H), 7.44 – 7.40 (m, 1H), 7.15 – 7.11 (m, 3H), 2.33 (s, 3H). **¹³C NMR (151 MHz, CDCl₃)** 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.³

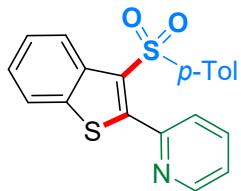
2-(thiophen-3-yl)-3-tosylbenzo[*b*]thiophene (3s**)³**



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 (46.62 mg, 63% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.66 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.54 – 7.48 (m, 4H), 7.43 – 7.38 (m, 1H), 7.34 (dd, J = 5.0, 3.0 Hz, 1H), 7.27 – 7.24 (m, 1H), 7.11 (d, J = 8.1 Hz, 2H), 2.31 (s, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 147.1, 143.9,

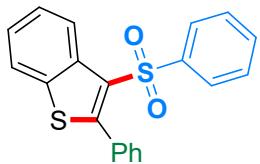
139.3, 137.9, 136.4, 131.1, 130.2, 130.1, 129.4, 127.8, 126.8, 125.9, 125.6, 125.0, 124.6, 121.6, 21.5. The characterization data matched the literature.³

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



The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 15/1 - 5/1) to afford the **3t** as a white solid (43.07 mg, 59% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.69 (dt, J = 4.8, 1.2 Hz, 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), 7.39 – 7.37 (m, 1H), 7.20 (d, J = 8.1 Hz, 2H), 2.32 (s, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 151.2, 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.

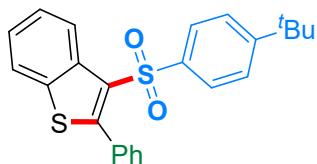
2-phenyl-3-(phenylsulfonyl)benzo[*b*]thiophene (3u)²



The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 30/1 - 15/1) to afford the **3u** as a white solid (63.00 mg, 90% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.64 (d, J = 8.3

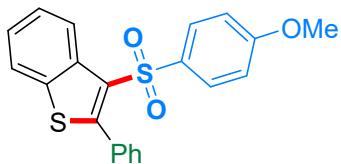
Hz, 1H), 7.80 (d, J = 8.1 Hz, 1H), 7.64 (dd, J = 8.4, 1.1 Hz, 2H), 7.55 – 7.51 (m, 1H), 7.47 – 7.43 (m, 3H), 7.41 (dt, J = 8.3, 3.6 Hz, 4H), 7.33 (dd, J = 8.2, 7.6 Hz, 2H). **^{13}C NMR (151 MHz, CDCl_3)** δ 152.9, 142.3, 138.1, 136.2, 132.9, 131.6, 130.5, 130.0, 129.5, 128.7, 127.7, 126.9, 126.0, 125.6, 124.6, 121.7. The characterization data matched the literature.²

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



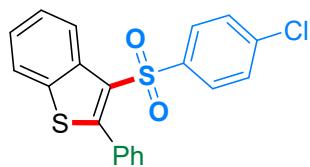
The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 30/1 - 15/1) to afford the **3v** as a white solid (71.46 mg, 88% yield). **^1H NMR (600 MHz, CDCl_3)** δ 8.65 (d, J = 8.3 Hz, 1H), 7.80 (d, J = 8.1 Hz, 1H), 7.58 (d, J = 8.5 Hz, 2H), 7.53 (t, J = 7.7 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.41 (dd, J = 13.7, 7.1 Hz, 4H), 7.33 (d, J = 8.5 Hz, 2H), 1.26 (s, 9H). **^{13}C NMR (151 MHz, CDCl_3)** δ 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.¹

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



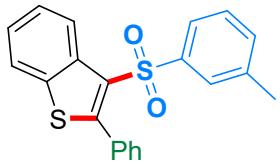
The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 15/1 - 7/1) to afford the **3w** as a white solid (66.12 mg, 87% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.56 (d, J = 8.3 Hz, 1H), 7.72 (d, J = 8.1 Hz, 1H), 7.50 (d, J = 9.0 Hz, 2H), 7.47 – 7.43 (m, 1H), 7.41 – 7.37 (m, 1H), 7.37 – 7.33 (m, 5H), 6.71 (d, J = 9.0 Hz, 2H), 3.71 (s, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 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.¹

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



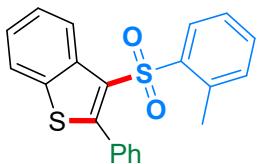
The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 30/1 - 15/1) to afford the **3x** as a yellow solid (64.51 mg, 84% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.63 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.53 (d, J = 8.7 Hz, 3H), 7.48 – 7.44 (m, 2H), 7.43 – 7.39 (m, 4H), 7.28 (d, J = 8.7 Hz, 2H). **¹³C NMR (151 MHz, CDCl₃)** δ 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.¹

2-phenyl-3-(*m*-tolylsulfonyl)benzo[*b*]thiophene (3y**)¹**



The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 30/1 - 15/1) to afford the **3y** as a white solid (66.98 mg, 92% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.67 (d, J = 8.3 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.52 (td, J = 8.3, 7.3, 1.0 Hz, 1H), 7.46 – 7.36 (m, 8H), 7.23 (d, J = 8.2 Hz, 1H), 7.19 (t, J = 7.6 Hz, 1H), 2.24 (s, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 152.6, 142.1, 138.9, 138.1, 136.2, 133.8, 131.6, 130.6, 130.3, 129.5, 128.6, 127.6, 127.4, 126.0, 125.6, 124.7, 124.1, 121.7, 21.2. The characterization data matched the literature.¹

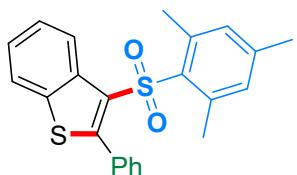
2-phenyl-3-(o-tolylsulfonyl)benzo[b]thiophene (**3z**)³



The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 30/1 - 15/1) to afford the **3z** as a white solid (64.79 mg, 89% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.52 (d, J = 8.3 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.47 (dd, J = 7.9, 0.9 Hz, 1H), 7.42 – 7.38 (m, 1H), 7.35 – 7.32 (m, 1H), 7.25 – 7.21 (m, 1H), 7.20 – 7.12 (m, 5H), 6.95 (d, J = 7.5 Hz, 1H), 6.87 (t, J = 7.7 Hz, 1H), 2.09 (s, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 150.8, 138.9, 136.8, 136.3, 135.7, 131.7,

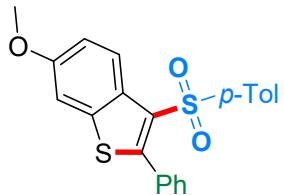
130.9, 130.0, 129.3, 128.6, 128.2, 127.5, 126.6, 124.8, 124.4, 123.8, 120.7, 18.5. The characterization data matched the literature.³

3-(mesitylsulfonyl)-2-phenylbenzo[*b*]thiophene (3aa)



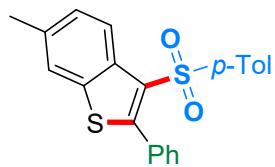
The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 30/1 - 15/1) to afford the **3aa** as a white solid (52.53 mg, 67% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.62 (d, J = 8.3 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.52 – 7.48 (m, 1H), 7.45 – 7.41 (m, 1H), 7.29 – 7.26 (m, 1H), 7.19 – 7.15 (m, 4H), 6.63 (s, 2H), 2.22 (s, 6H), 2.17 (s, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 149.7, 142.5, 139.2, 137.8, 136.7, 136.3, 132.9, 131.5, 131.2, 129.7, 129.0, 127.5, 125.8, 125.3, 124.9, 121.7, 21.9, 20.8. The characterization data matched the literature.

6-methoxy-2-phenyl-3-tosylbenzo[*b*]thiophene (3ab)¹



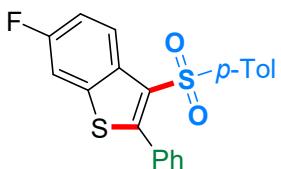
The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 15/1 - 7/1) to afford the **3ab** as a white solid (70.92 mg, 90% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.49 (d, J = 9.1 Hz, 1H), 7.52 (d, J = 8.3 Hz, 2H), 7.46 – 7.43 (m, 1H), 7.42 – 7.38 (m, 4H), 7.23 (d, J = 2.4 Hz, 1H), 7.14 – 7.10 (m, 3H), 3.86 (s, 3H), 2.32 (s, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 158.0, 149.6, 143.8, 139.7, 139.5, 131.8, 130.6, 130.0, 129.9, 129.4, 129.3, 127.6, 126.9, 125.4, 115.8, 104.0, 55.6, 21.5. The characterization data matched the literature.¹

6-methyl-2-phenyl-3-tosylbenzo[b]thiophene (**3ac**)³



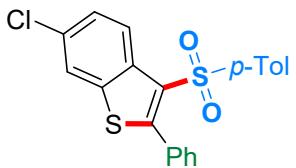
The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 30/1 - 15/1) to afford the **3ac** as a white solid (71.06 mg, 94% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.48 (d, J = 8.5 Hz, 1H), 7.58 (s, 1H), 7.53 (d, J = 8.3 Hz, 2H), 7.47 – 7.44 (m, 1H), 7.43 – 7.38 (m, 4H), 7.33 (dd, J = 8.5, 1.1 Hz, 1H), 7.11 (d, J = 8.2 Hz, 2H), 2.47 (s, 3H), 2.32 (s, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 151.3, 143.7, 139.5, 138.4, 135.8, 133.9, 131.8, 130.5, 130.0, 129.3, 129.3, 127.6, 127.6, 127.0, 124.2, 121.4, 21.5, 21.4. The characterization data matched the literature.³

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



The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 30/1 - 15/1) to afford the **3ad** as a yellow solid (58.83 mg, 77% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.61 (dd, J = 9.2, 5.1 Hz, 1H), 7.50 (d, J = 8.3 Hz, 2H), 7.48 – 7.45 (m, 2H), 7.40 (d, J = 4.1 Hz, 4H), 7.29 – 7.25 (m, 1H), 7.12 (d, J = 8.1 Hz, 2H), 2.33 (s, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 160.8 (d, J = 247.6 Hz), 152.0 (d, J = 3.8 Hz), 144.0, 139.2, 139.1 (d, J = 10.4 Hz), 132.6, 131.3, 130.5, 130.1, 129.6, 129.4, 127.7, 127.0, 126.1 (d, J = 8.8 Hz), 114.9 (d, J = 23.8 Hz), 107.9 (d, J = 25.6 Hz), 21.5. The characterization data matched the literature.¹

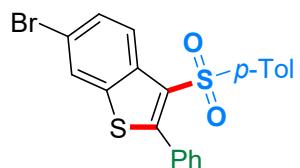
6-chloro-2-phenyl-3-tosylbenzo[*b*]thiophene (3ae**)²**



The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 30/1 - 15/1) to afford the **3ae** as a yellow solid (59.70 mg, 75% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.57 (d, J = 8.9 Hz, 1H), 7.78 (d, J = 1.9 Hz, 1H), 7.51 – 7.46 (m, 4H), 7.40 (d, J = 4.4 Hz,

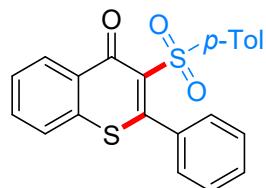
4H), 7.12 (d, J = 8.1 Hz, 2H), 2.33 (s, 3H). **^{13}C NMR (151 MHz, CDCl_3)** δ 152.7, 144.1, 139.1, 139.1, 134.6, 131.9, 131.2, 130.5, 130.3, 129.6, 129.4, 127.7, 127.0, 126.8, 125.6, 121.3, 21.5. The characterization data matched the literature.²

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



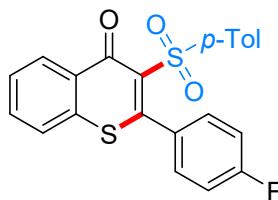
The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 30/1 - 15/1) to afford the **3af** as a yellow solid (63.65 mg, 72% yield). **^1H NMR (600 MHz, CDCl_3)** δ 8.51 (d, J = 8.9 Hz, 1H), 7.94 (d, J = 1.7 Hz, 1H), 7.62 (dd, J = 8.9, 1.8 Hz, 1H), 7.48 (d, J = 8.3 Hz, 3H), 7.40 (d, J = 4.4 Hz, 4H), 7.12 (d, J = 8.1 Hz, 2H), 2.33 (s, 3H). **^{13}C NMR (151 MHz, CDCl_3)** δ 152.7, 144.1, 139.5, 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-phenyl-3-tosyl-4H-thiochromen-4-one (**5a**)⁴



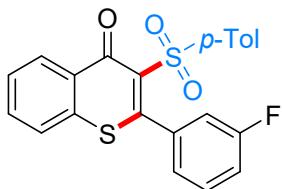
The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 15/1 - 5/1) to afford the **5a** as a white solid (68.21 mg, 87% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.38 – 8.34 (m, 1H), 7.92 (d, J = 8.3 Hz, 2H), 7.63 (td, J = 7.8, 1.4 Hz, 1H), 7.56 – 7.48 (m, 7H), 7.26 (d, J = 8.1 Hz, 2H), 2.38 (s, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 176.1, 162.4, 143.9, 138.9, 135.7, 134.8, 133.1, 132.6, 131.8, 130.3, 129.2, 129.0, 128.8, 128.7, 128.1, 128.1, 125.3, 21.6. The characterization data matched the literature.⁴

2-(4-fluorophenyl)-3-tosyl-4H-thiochromen-4-one (5b)⁴



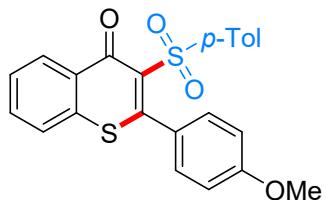
The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 15/1 - 5/1) to afford the **5b** as a yellow solid (46.74 mg, 57% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.37 (dd, J = 8.1, 1.0 Hz, 1H), 7.90 (d, J = 8.3 Hz, 2H), 7.67 – 7.63 (m, 1H), 7.57 – 7.50 (m, 4H), 7.29 – 7.26 (m, 2H), 7.21 (t, J = 8.6 Hz, 2H), 2.40 (s, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 176.1, 163.9 (d, J = 251.0 Hz), 161.1, 144.1, 138.7, 135.5, 133.5, 132.6, 131.8, 130.6, 130.2 (d, J = 8.7 Hz), 129.3, 129.1, 128.8 (d, J = 5.5 Hz), 125.2, 115.5 (d, J = 22.4 Hz), 21.6. The characterization data matched the literature.⁴

2-(3-fluorophenyl)-3-tosyl-4H-thiochromen-4-one (5c)⁴



The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 15/1 - 5/1) to afford the **5c** as a yellow solid (40.18 mg, 49% yield). **$^1\text{H NMR}$ (600 MHz, CDCl_3)** δ 8.39 (dd, $J = 8.2, 1.2$ Hz, 1H), 7.93 (d, $J = 8.3$ Hz, 2H), 7.68 – 7.63 (m, 1H), 7.57 – 7.52 (m, 2H), 7.49 (td, $J = 7.9, 5.7$ Hz, 1H), 7.34 (d, $J = 7.7$ Hz, 1H), 7.29 (d, $J = 8.2$ Hz, 2H), 7.25 – 7.22 (m, 2H), 2.40 (s, 3H). **$^{13}\text{C NMR}$ (151 MHz, CDCl_3)** δ 176.0, 162.0 (d, $J = 248.5$ Hz), 160.4, 144.2, 138.6, 136.5 (d, $J = 8.5$ Hz), 135.4, 133.4, 132.7, 131.7, 129.9 (d, $J = 8.0$ Hz), 129.3, 129.1, 128.9, 125.3, 124.1 (d, $J = 3.0$ Hz), 117.2 (d, $J = 20.9$ Hz), 115.4 (d, $J = 23.4$ Hz), 21.6. The characterization data matched the literature.⁴

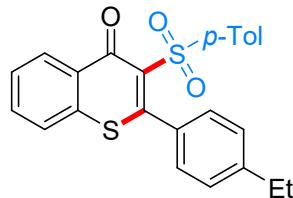
2-(4-methoxyphenyl)-3-tosyl-4H-thiochromen-4-one (5d)⁴



The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 10/1 - 3/1) to afford the **5d** as a white solid (53.17 mg, 63% yield). **$^1\text{H NMR}$ (600 MHz, CDCl_3)** δ 8.33 (dd, $J = 8.5, 1.3$ Hz, 1H), 7.90 (d, $J = 8.3$ Hz, 2H), 7.63 (td, $J = 7.5, 1.4$ Hz, 1H), 7.52

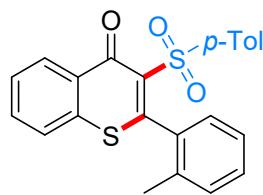
(dd, $J = 8.1, 7.0$ Hz, 4H), 7.27 – 7.24 (m, 2H), 7.02 (d, $J = 8.7$ Hz, 2H), 3.88 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 176.4, 162.3, 161.5, 143.8, 139.1, 135.8, 133.0, 132.4, 131.9, 129.9, 129.2, 129.0, 128.7, 128.5, 126.9, 125.2, 113.7, 55.4, 21.6. The characterization data matched the literature.⁴

2-(4-ethylphenyl)-3-tosyl-4H-thiochromen-4-one (5e)⁴



The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 15/1 - 5/1) to afford the **5e** as a white solid (57.12 mg, 68% yield). ^1H NMR (600 MHz, CDCl_3) δ 8.35 (dd, $J = 8.5, 1.4$ Hz, 1H), 7.91 (d, $J = 8.3$ Hz, 2H), 7.65 – 7.60 (m, 1H), 7.53 – 7.46 (m, 4H), 7.34 (d, $J = 8.1$ Hz, 2H), 7.28 – 7.23 (m, 2H), 2.76 (q, $J = 7.6$ Hz, 2H), 2.39 (s, 3H), 1.31 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 176.2, 162.7, 146.8, 143.8, 139.0, 135.8, 133.0, 132.4, 132.1, 131.8, 129.2, 129.0, 128.7, 128.6, 128.2, 127.6, 125.2, 28.7, 21.6, 15.1. The characterization data matched the literature.⁴

2-(o-tolyl)-3-tosyl-4H-thiochromen-4-one (5f)



The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt : 15/1 - 5/1) to afford the **5f** as a white solid (60.09 mg, 74% yield). **¹H NMR (600 MHz, CDCl₃)** δ 8.42 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 8.3 Hz, 2H), 7.65 – 7.61 (m, 1H), 7.54 – 7.48 (m, 2H), 7.41 (t, J = 7.5 Hz, 1H), 7.33 (t, J = 7.4 Hz, 2H), 7.28 (t, J = 8.2 Hz, 3H), 2.44 (s, 3H), 2.38 (s, 3H). **¹³C NMR (151 MHz, CDCl₃)** δ 175.9, 162.2, 144.0, 138.7, 136.0, 135.9, 134.2, 133.5, 132.5, 131.8, 130.2, 130.0, 129.3, 129.0, 128.9, 128.7, 127.1, 125.4, 125.3, 21.6, 19.9. The characterization data matched the literature.

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5. ¹H NMR, ¹³C NMR and ¹⁹F NMR spectra of the products

