

# Visible-Light-Driven Silver-Catalyzed One-Pot Approach: A Selective Synthesis of Diaryl Sulfoxides and Diaryl Sulfones

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## Supporting Information

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**General Information**

Reactions were performed in a well-dried flask under air atmosphere. Solvents used as reaction media were dried over pre-dried molecular sieves (4 Å) in a microwave oven. Solvents for extraction and chromatography were reagent grade and used as received. Reagents were purified prior to use unless otherwise stated following the guidelines of Perrin and Armarego.<sup>1</sup> Column chromatography was performed with silica gel 60 (70–230 mesh) using a mixture of EtOAc/hexane as eluent. <sup>1</sup>H and <sup>13</sup>C NMR spectra were, respectively, recorded on an Agilent 400 MHz (<sup>1</sup>H NMR), 101 MHz (<sup>13</sup>C NMR) spectrometer in deuterated chloroform (CDCl<sub>3</sub>) with tetramethylsilane (TMS) as an internal reference. Data are reported as (ap = apparent, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad; coupling constant(s) in Hz, integration). Infrared spectra were recorded on a Bruker Tensor 37 FT-IR spectrometer. Mass spectra data were obtained on a Gas Chromatography Mass Spectrometer (Agilent 7890A/5975C GCMS System).

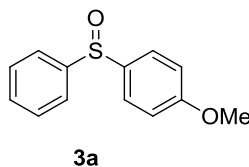
### 1. General procedure for the synthesis of diaryl sulfoxides (A)

Thiol **1** (0.5 mmol, 1.0 equiv), aryl diazonium salt **2** (0.6 mmol, 1.2 equiv), AgNO<sub>3</sub> (0.1 mmol, 0.2 equiv), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (1.5 mmol, 3.0 equiv), and pyridine (1.5 mmol, 3.0 equiv) were dissolved in dry DMSO (0.25 M). The reaction mixture was stirred and irradiated by 4 W green LEDs (530 nm) at room temperature under air atmosphere for 15 h. After the reaction was completed monitored by TLC, water (10 mL) and EtOAc (10 mL) were added, and the mixture was extracted by EtOAc (3 x 10.0 mL). The combined organic layer was dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. Purification by flash chromatography with EtOAc/hexane afforded the corresponding product.

### 2. General procedure for the synthesis of diaryl sulfones (B)

Thiol **1** (0.5 mmol, 1.0 equiv), aryl diazonium salt **2** (0.6 mmol, 1.2 equiv), AgNO<sub>3</sub> (0.1 mmol, 0.2 equiv), and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (1.5 mmol, 3.0 equiv), were dissolved in dry DMF (0.25 M). The reaction mixture was stirred and irradiated by 4 W green LEDs (530 nm) at room temperature under air atmosphere for 15 h. After the reaction was completed monitored by TLC, water (10 mL) and EtOAc (10 mL) were added, and the mixture was extracted by EtOAc (3 x 10.0 mL). The combined organic layer was dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. Purification by flash chromatography with EtOAc/hexane afforded the corresponding product.

### 3. Physical data for the compounds

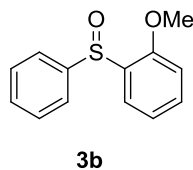


**1-Methoxy-4-(phenylsulfinyl)benzene (3a)**<sup>2</sup>: Prepared according to the general procedure A

using thiophenol and 4-methoxybenzenediazonium tetrafluoroborate. The reaction mixture was purified by flash chromatography using 50% EtOAc/hexane to afford 95 mg (82 % yield) of product as a yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 – 7.59 (m, 2H), 7.58 – 7.55 (m, 2H), 7.46 – 7.38 (m, 3H), 6.96 – 6.92 (m, 2H), 3.77 (s, 3H) ;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.7, 145.5, 136.4, 130.5, 128.9, 126.9, 124.2, 114.5, 55.2; IR 3056, 2939, 2837, 1591, 1493, 1247, 1021, 748, 538  $\text{cm}^{-1}$ ; LRMS (EI); Mass calcd for  $\text{C}_{13}\text{H}_{12}\text{O}_2\text{S}$   $[\text{M}]^+$ : 232.0; found 232.0.

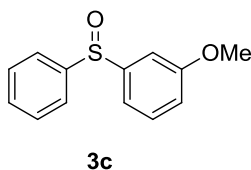
**\*\* 1-Methoxy-4-(phenylsulfinyl)benzene (3a)<sup>2</sup>: 1 mmol reaction scale**

Thiophenol (1.0 mmol, 1.0 equiv), 4-methoxybenzenediazonium tetrafluoroborate (1.2 mmol, 1.2 equiv),  $\text{AgNO}_3$  (0.2 mmol, 0.2 equiv),  $\text{K}_2\text{S}_2\text{O}_8$  (3.0 mmol, 3.0 equiv), and pyridine (3.0 mmol, 3.0 equiv) were dissolved in dry DMSO (0.25 M). The reaction mixture was stirred and irradiated by 4 W green LEDs (530 nm) at room temperature under air atmosphere for 15 h. After the reaction was completed monitored by TLC, water (10 mL) and EtOAc (10 mL) were added, and the mixture was extracted by EtOAc (3 x 10.0 mL). The combined organic layer was dried over anhydrous  $\text{MgSO}_4$ , filtered, and concentrated under reduced pressure. The reaction mixture was purified by flash chromatography using 50% EtOAc/hexane to afford 193 mg (83 % yield) of product as a yellow oil.

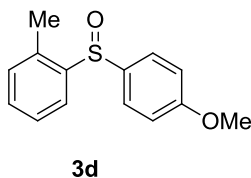


**1-Methoxy-2-(phenylsulfinyl)benzene (3b)<sup>2</sup>:** Prepared according to the general procedure A using thiophenol and 2-methoxybenzenediazonium tetrafluoroborate. The reaction mixture was purified by flash chromatography using 50% EtOAc/hexane to afford 60 mg (52% yield) of product as a pale yellow solid. mp 98–100 °C (lit.<sup>2</sup> 96–98);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92

– 7.90 (m, 1H), 7.72 – 7.69 (m, 2H), 7.43 – 7.37 (m, 4H), 7.16 – 7.12 (m, 1H), 6.85 (d,  $J = 8.3$  Hz, 1H), 3.79 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.6, 145.5, 133.1, 132.1, 130.7, 128.9, 125.2, 124.5, 121.5, 111.0, 55.6; IR 3489, 3060, 2938, 2840, 1584, 1475, 1273, 1036,  $751\text{ cm}^{-1}$ ; LRMS (EI); Mass calcd for  $\text{C}_{13}\text{H}_{12}\text{O}_2\text{S}$   $[\text{M}]^+$ : 232.0; found 232.0.

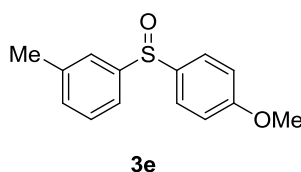


**1-Methoxy-3-(phenylsulfinyl)benzene (3c)**<sup>2</sup>: Prepared according to the general procedure A using thiophenol and 3-methoxybenzenediazonium tetrafluoroborate. The reaction mixture was purified by flash chromatography using 50% EtOAc/hexane to afford 88 mg (76% yield) of product as a yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 – 7.63 (m, 2H), 7.48 – 7.42 (m, 3H), 7.36 – 7.32 (m, 1H), 7.24 – 7.23 (m, 1H), 7.18 – 7.15 (m, 1H), 6.95 (ddd,  $J = 8.2, 2.6, 0.9$  Hz, 1H), 3.81 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.3, 146.8, 145.5, 131.0, 130.2, 129.2, 124.7, 117.3, 116.9, 109.0, 55.5; IR 3469, 3056, 2932, 2836, 1592, 1476, 1237, 1033, 844, 747,  $685, 592, 471\text{ cm}^{-1}$ ; LRMS (EI); Mass calcd for  $\text{C}_{13}\text{H}_{12}\text{O}_2\text{S}$   $[\text{M}]^+$ : 232.0; found 232.0.

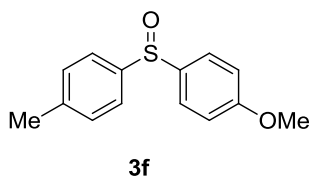


**1-((4-Methoxyphenyl)sulfinyl)-2-methylbenzene (3d)**: Prepared according to the general procedure A using 2-methylbenzenethiol and 4-methoxybenzenediazonium tetrafluoroborate. The reaction mixture was purified by flash chromatography using 50% EtOAc/hexane to afford

79 mg (64% yield) of product as a yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (dd,  $J = 7.8$ , 1.3 Hz, 1H), 7.53 – 7.50 (m, 2H), 7.43 (t,  $J = 7.6$  Hz, 1H), 7.35 (td,  $J = 7.4$ , 1.4 Hz, 1H), 7.14 (d,  $J = 7.5$  Hz, 1H), 6.94 – 6.90 (m, 2H), 3.80 (s, 3H), 2.25 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.9, 142.8, 135.5, 135.2, 130.8, 130.6, 128.3, 126.9, 124.1, 114.7, 55.4, 18.4; IR 3060, 2925, 2842, 1592, 1494, 1254, 1176, 1085, 1030, 830, 758, 533  $\text{cm}^{-1}$ ; HRMS (EI); Mass calcd for  $\text{C}_{14}\text{H}_{14}\text{O}_2\text{S}$   $[\text{M}]^+$ : 246.0715; found 246.0718.

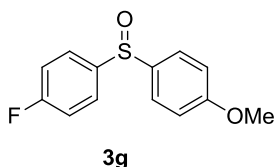


**1-((4-Methoxyphenyl)sulfinyl)-3-methylbenzene (3e):** Prepared according to the general procedure A using 3-methylbenzenethiol and 4-methoxybenzenediazonium tetrafluoroborate. The reaction mixture was purified by flash chromatography using 50% EtOAc/hexane to afford 96 mg (78% yield) of product as a yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 – 7.54 (m, 2H), 7.45 (s, 1H), 7.38 – 7.28 (m, 2H), 7.22 – 7.20 (m, 1H), 6.96 – 6.92 (m, 2H), 3.79 (s, 3H), 2.36 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.9, 145.5, 139.3, 136.7, 131.5, 128.9, 127.1, 124.7, 121.7, 114.7, 55.4, 21.3; IR 3057, 2924, 2838, 1592, 1493, 1248, 1173, 1041, 829, 783, 688, 555, 452  $\text{cm}^{-1}$ ; HRMS (EI); Mass calcd for  $\text{C}_{14}\text{H}_{14}\text{O}_2\text{S}$   $[\text{M}]^+$ : 246.0715; found 246.0714.

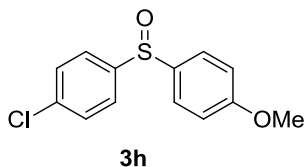


**1-Methoxy-4-(p-tolylsulfinyl)benzene (3f):** Prepared according to the general procedure A using 4-methylbenzenethiol and 4-methoxybenzenediazonium tetrafluoroborate. The reaction

mixture was purified by flash chromatography using 50% EtOAc/hexane to afford 101 mg (82% yield) of product as a yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) 7.55 – 7.52 (m, 2H), 7.49 – 7.47 (m, 2H), 7.23 (d,  $J = 8.1$  Hz, 2H), 6.95 – 6.91 (m, 2H), 3.79 (s, 3H), 2.34 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.8, 142.5, 141.1, 136.9, 129.8, 127.0, 124.6, 114.7, 55.4, 21.3; IR 3049, 2924, 1592, 1493, 1251, 1173, 1042, 810, 619, 537  $\text{cm}^{-1}$ ; LRMS (EI); Mass calcd for  $\text{C}_{14}\text{H}_{14}\text{O}_2\text{S}$   $[\text{M}]^+$ : 246.0; found 246.0.

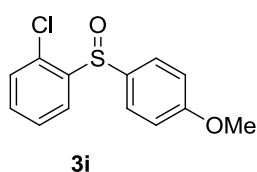


**1-Fluoro-4-((4-methoxyphenyl)sulfinyl)benzene (3g)**<sup>4</sup>: Prepared according to the general procedure A using 4-fluorobenzenethiol and 4-methoxybenzenediazonium tetrafluoroborate. The reaction mixture was purified by flash chromatography using 50% EtOAc/hexane to afford 105 mg (84% yield) of product as a yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 – 7.58 (m, 2H), 7.57 – 7.54 (m, 2H), 7.17 – 7.11 (m, 2H), 6.98 – 6.94 (m, 2H), 3.81 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.9 (d,  $J_{\text{CF}} = 251.2$  Hz), 161.9, 141.3, 136.3 (d,  $J_{\text{CF}} = 0.8$  Hz), 126.8, 126.7 (d,  $J_{\text{CF}} = 8.9$  Hz), 116.3 (d,  $J_{\text{CF}} = 22.5$  Hz), 114.7, 55.3; IR 3063, 2939, 2839, 1589, 1489, 1249, 1024, 825, 534  $\text{cm}^{-1}$ ; LRMS (EI); Mass calcd for  $\text{C}_{13}\text{H}_{11}\text{FO}_2\text{S}$   $[\text{M}]^+$ : 250.0; found 250.0.

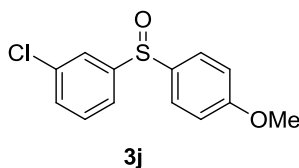


**1-Chloro-4-((4-methoxyphenyl)sulfinyl)benzene (3h)**: Prepared according to the general procedure A using 4-chlorobenzenethiol and 4-methoxybenzenediazonium tetrafluoroborate. The

reaction mixture was purified by flash chromatography using 50% EtOAc/hexane to afford 107 mg (80% yield) of product as a yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 – 7.53 (m, 4H), 7.44 – 7.41 (m, 2H), 6.98 – 6.94 (m, 2H), 3.81 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.1, 144.3, 136.7, 136.2, 129.3, 127.1, 125.8, 114.8, 55.4; IR 3060, 2937, 2838, 1591, 1493, 1249, 1042, 825, 553  $\text{cm}^{-1}$ ; HRMS (EI); Mass calcd for  $\text{C}_{13}\text{H}_{11}\text{ClO}_2\text{S}$   $[\text{M}]^+$ : 266.0168; found 266.0169.



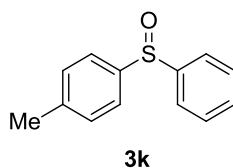
**1-Chloro-2-((4-methoxyphenyl)sulfinyl)benzene (3i):** Prepared according to the general procedure A using 2-chlorobenzenethiol and 4-methoxybenzenediazonium tetrafluoroborate. The reaction mixture was purified by flash chromatography using 10% EtOAc/hexane to afford 81 mg (61% yield) of product as a yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.10 (dd,  $J = 7.8, 1.6$  Hz, 1H), 7.66 – 7.62 (m, 2H), 7.54 – 7.50 (m, 1H), 7.41 – 7.37 (m, 1H), 7.33 – 7.31 (m, 1H), 6.95 – 6.91 (m, 2H), 3.81 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.2, 147.9, 136.0, 135.3, 130.7, 130.3, 127.1, 124.2, 122.5, 114.9, 55.4; IR 3058, 2940, 2838, 1591, 1493, 1408, 1251, 1173, 1044, 829, 680, 560, 454  $\text{cm}^{-1}$ ; HRMS (EI); Mass calcd for  $\text{C}_{13}\text{H}_{11}\text{ClO}_2\text{S}$   $[\text{M}]^+$ : 266.0168; found 266.0166.



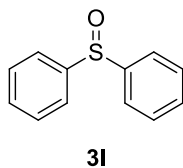
**1-Chloro-3-((4-methoxyphenyl)sulfinyl)benzene (3j):** Prepared according to the general



procedure A using 3-chlorobenzenethiol and 4-methoxybenzenediazonium tetrafluoroborate. The reaction mixture was purified by flash chromatography using 50% EtOAc/hexane to afford 103 mg (77% yield) of product as a yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 – 7.62 (m, 1H), 7.59 – 7.55 (m, 2H), 7.47 – 7.43 (m, 1H), 7.38 – 7.36 (m, 2H), 6.98 – 6.95 (m, 2H), 3.81 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.1, 143.3, 135.3, 131.7, 130.9, 129.9, 128.3, 127.8, 125.5, 114.6, 55.4; IR 3064, 2928, 2840, 1591, 1494, 1252, 1174, 1082, 1026, 830, 759, 545  $\text{cm}^{-1}$ ; HRMS (EI); Mass calcd for  $\text{C}_{13}\text{H}_{11}\text{ClO}_2\text{S}$   $[\text{M}]^+$ : 266.0168; found 266.0170.

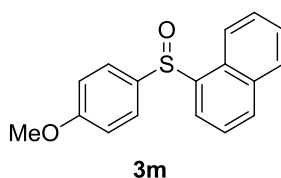


**1-Methyl-4-(phenylsulfinyl)benzene (3k)**<sup>2</sup>: Prepared according to the general procedure A using 4-methylbenzenethiol and benzenediazonium tetrafluoroborate. The reaction mixture was purified by flash chromatography using 30% EtOAc/hexane to afford 87 mg (80% yield) of product as a yellow solid. mp 69–70 °C (lit.<sup>2</sup> 70–71);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 – 7.58 (m, 2H), 7.51 – 7.49 (m, 2H), 7.44 – 7.37 (m, 3H), 7.24 – 7.21 (m, 2H), 2.33 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.7, 142.4, 141.5, 130.8, 129.9, 129.2, 124.9, 124.6, 21.3; IR 3051, 2922, 2857, 1595, 1443, 1042, 810, 748, 689, 620, 533  $\text{cm}^{-1}$ ; LRMS (EI); Mass calcd for  $\text{C}_{13}\text{H}_{12}\text{OS}$   $[\text{M}]^+$ : 216.0; found 216.0.

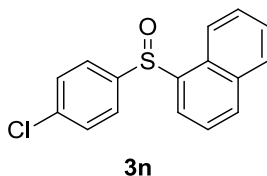


**Sulfinyldibenzene (3l)**<sup>2</sup>: Prepared according to the general procedure A using thiophenol and

benzenediazonium tetrafluoroborate. The reaction mixture was purified by flash chromatography using 30% EtOAc/hexane to afford 82 mg (81% yield) of product as a yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 – 7.63 (m, 4H), 7.48 - 7.41 (m, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.6, 131.0, 129.3, 124.8; IR 3057, 1444, 1091, 1044, 744, 692, 537, 482  $\text{cm}^{-1}$ ; LRMS (EI); Mass calcd for  $\text{C}_{12}\text{H}_{10}\text{OS}$   $[\text{M}]^+$ : 202.0; found 202.0.

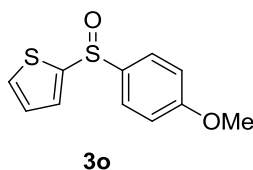


**1-((4-Methoxyphenyl)sulfinyl)naphthalene (3m):** Prepared according to the general procedure A using 4-methoxybenzenethiol and 1-naphthalenediazonium tetrafluoroborate. The reaction mixture was purified by flash chromatography using 50% EtOAc/hexane to afford 107 mg (76% yield) of product as a yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.28 – 8.26 (dd,  $J$  = 7.3, 1.2 Hz, 1H), 8.08 – 8.05 (m, 1H), 7.95 (d,  $J$  = 8.2 Hz, 1H), 7.89 – 7.87 (m, 1H), 7.66 (dd,  $J$  = 8.1, 7.3 Hz, 1H), 7.61 - 7.58 (m, 2H), 7.51 – 7.46 (m, 2H), 6.89 – 6.85 (m, 2H), 3.74 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.8, 140.3, 136.0, 133.6, 131.4, 129.0, 128.8, 127.8, 127.1, 126.5, 125.4, 123.4, 122.3, 114.7, 55.3; IR 3056, 2934, 1591, 1494, 1253, 1044, 770, 529, 436  $\text{cm}^{-1}$ ; HRMS (EI); Mass calcd for  $\text{C}_{17}\text{H}_{14}\text{O}_2\text{S}$   $[\text{M}]^+$ : 282.0715; found 282.0716.

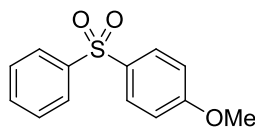


**1-((4-Chlorophenyl)sulfinyl)naphthalene (3n):** Prepared according to the general procedure A

using 4-Chlorobenzenethiol and 1-naphthalenediazonium tetrafluoroborate. The reaction mixture was purified by flash chromatography using 30% EtOAc/hexane to afford 106 mg (74% yield) of product as a white solid. mp 105–107 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.20 – 8.17 (m, 2H), 7.96 (d,  $J$  = 8.2 Hz, 1H), 7.90 – 7.87 (m, 1H), 7.64 – 7.58 (m, 3H), 7.55 – 7.50 (m, 2H), 7.35 – 7.32 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  143.6, 140.0, 137.1, 133.7, 132.0, 129.5, 129.1, 129.0, 127.5, 126.8, 126.6, 125.5, 124.1, 122.3; IR 3056, 1474, 1389, 1049, 769, 565, 498, 429  $\text{cm}^{-1}$ ; HRMS (EI); Mass calcd for  $\text{C}_{16}\text{H}_{11}\text{ClO S}$   $[\text{M}]^+$ : 286.0219; found 286.0217.



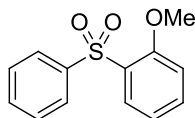
**2-((4-methoxyphenyl)sulfinyl)thiophene (3o):** Prepared according to the general procedure A using thiophene-2-thiol and 4-methoxybenzenediazonium tetrafluoroborate. The reaction mixture was purified by flash chromatography using 10% EtOAc/hexane to afford 85 mg (71% yield) of product as a yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 – 7.61 (m, 2H), 7.56 (dd,  $J$  = 5.0, 1.1 Hz, 1H), 7.50 (dd,  $J$  = 3.7, 1.1 Hz, 1H), 7.05 (dd,  $J$  = 5.0, 3.7 Hz, 1H), 7.02 – 6.98 (m, 2H), 3.84 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.0, 148.6, 136.1, 131.8, 130.7, 127.2, 126.3, 114.7, 55.5; IR 3056, 1589, 1496, 1260, 1039, 729, 532  $\text{cm}^{-1}$ ; HRMS (EI); Mass calcd for  $\text{C}_{11}\text{H}_{10}\text{O}_2\text{S}_2$   $[\text{M}]^+$ : 238.0122; found 238.0120.

**4a**

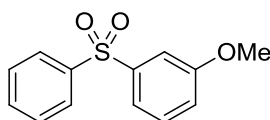
**1-Methoxy-4-(phenylsulfonyl)benzene (4a)**<sup>5</sup>: Prepared according to the general procedure B using thiophenol and 4-methoxybenzenediazonium tetrafluoroborate. The reaction mixture was purified by flash chromatography using 50% EtOAc/hexane to afford 97 mg (78% yield) of product as a yellow solid. mp 90–91 °C (lit.<sup>5</sup> 90–92 °C); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93 – 7.90 (m, 2H), 7.90 – 7.86 (m, 2H), 7.56 – 7.46 (m, 3H), 6.98 – 6.94 (m, 2H), 3.83 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.3, 142.3, 135.6, 133.0, 132.8, 129.8, 129.1, 128.8, 127.2, 114.4, 55.6; IR 3064, 2925, 2845, 1666, 1592, 1496, 1444, 1259, 1147, 1105, 1023, 834, 728, 556 cm<sup>-1</sup>; LRMS (EI); Mass calcd for C<sub>13</sub>H<sub>12</sub>O<sub>3</sub>S [M]<sup>+</sup>: 248.0; found 248.0.

**\*\* 1-Methoxy-4-(phenylsulfonyl)benzene (4a)**<sup>5</sup>: 1 mmol reaction scale

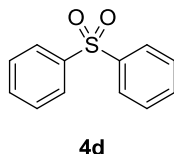
Thiophenol (1.0 mmol, 1.0 equiv), 4-methoxybenzenediazonium tetrafluoroborate (1.2 mmol, 1.2 equiv), AgNO<sub>3</sub> (0.2 mmol, 0.2 equiv), and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (3.0 mmol, 3.0 equiv), were dissolved in dry DMF (0.25 M). The reaction mixture was stirred and irradiated by 4 W green LEDs (530 nm) at room temperature under air atmosphere for 15 h. After the reaction was completed monitored by TLC, water (10 mL) and EtOAc (10 mL) were added, and the mixture was extracted by EtOAc (3 x 10.0 mL). The combined organic layer was dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. The reaction mixture was purified by flash chromatography using 50% EtOAc/hexane to afford 194 mg (78% yield) of product as a yellow solid.

**4b**

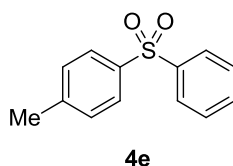
**1-Methoxy-2-(phenylsulfonyl)benzene (4b)**<sup>5</sup>: Prepared according to the general procedure B using thiophenol and 2-methoxybenzenediazonium tetrafluoroborate. The reaction mixture was purified by flash chromatography using 50% EtOAc/hexane to afford 76 mg (61% yield) of product as a white solid. mp 143–145 °C (lit.<sup>5</sup> 142–145 °C); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.16 (d, *J* = 7.9 Hz, 1H), 7.98 – 7.96 (m, 2H), 7.58 – 7.46 (m, 4H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 3.75 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 157.0, 141.5, 135.5, 132.8, 129.8, 128.9, 128.4, 128.3, 120.5, 112.4, 55.8; IR 2944, 2843, 1589, 1479, 1285, 1150, 1094, 1016, 736, 588 cm<sup>-1</sup>; LRMS (EI); Mass calcd for C<sub>13</sub>H<sub>12</sub>O<sub>3</sub>S [M]<sup>+</sup>: 248.0; found 248.0.

**4c**

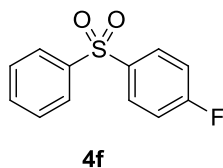
**1-Methoxy-3-(phenylsulfonyl)benzene (4c)**<sup>5</sup>: Prepared according to the general procedure B using thiophenol and 3-methoxybenzenediazonium tetrafluoroborate. The reaction mixture was purified by flash chromatography using 30% EtOAc/hexane to afford 93 mg (75% yield) of product as a yellow solid. mp 89–90 °C (lit.<sup>5</sup> 89–91 °C); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.96 – 7.93 (m, 2H), 7.58 – 7.45 (m, 5H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.08 – 7.06 (m, 1H), 3.82 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.9, 142.6, 141.4, 133.1, 130.3, 129.1, 127.5, 119.7, 119.3, 112.2, 55.5; IR 3065, 1595, 1478, 1307, 1244, 1150, 1101, 1038, 855, 726, 580, 529 cm<sup>-1</sup>; LRMS (EI); Mass calcd for C<sub>13</sub>H<sub>12</sub>O<sub>3</sub>S [M]<sup>+</sup>: 248.0; found 248.0.



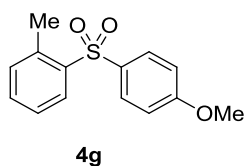
**Sulfonyldibenzene (4d)**<sup>5</sup>: Prepared according to the general procedure B using thiophenol and benzenediazonium tetrafluoroborate. The reaction mixture was purified by flash chromatography using 10% EtOAc/hexane to afford 87 mg (80% yield) of product as a yellow solid. mp 123–124 °C (lit.<sup>5</sup> 123–125 °C);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 – 7.94 (m, 4H), 7.59 – 7.55 (m, 2H), 7.53 – 7.48 (m, 4H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.6, 133.2, 129.3, 127.6; IR 3066, 2925, 1685, 1581, 1445, 1312, 1152, 1103, 997, 758, 685, 561  $\text{cm}^{-1}$ ; LRMS (EI); Mass calcd for  $\text{C}_{12}\text{H}_{10}\text{O}_2\text{S}$   $[\text{M}]^+$ : 218.0; found 218.0.



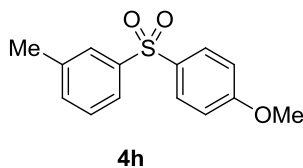
**1-Methyl-4-(phenylsulfonyl)benzene (4e)**<sup>6</sup>: Prepared according to the general procedure B using 4-methylbenzenethiol and benzenediazonium tetrafluoroborate. The reaction mixture was purified by flash chromatography using 30% EtOAc/hexane to afford 89 mg (77% yield) of product as a yellow solid. mp 125–126 °C (lit.<sup>6</sup> 126–127 °C);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 – 7.91 (m, 2H), 7.82 (d,  $J$  = 8.3 Hz, 2H), 7.55 – 7.45 (m, 3H), 7.28 (d,  $J$  = 8.3 Hz, 2H), 2.37 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.1, 141.9, 138.5, 132.9, 129.8, 129.1, 127.6, 127.4, 21.4; IR 3064, 2925, 1594, 1446, 1308, 1153, 815, 743, 712, 651, 549  $\text{cm}^{-1}$ ; LRMS (EI); Mass calcd for  $\text{C}_{13}\text{H}_{12}\text{O}_2\text{S}$   $[\text{M}]^+$ : 232.0; found 232.0.



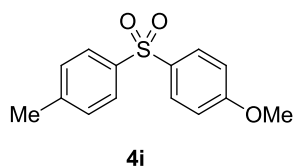
**1-Fluoro-4-(phenylsulfonyl)benzene (4f)**<sup>6</sup>: Prepared according to the general procedure B using thiophenol and 4-fluorobenzenediazonium tetrafluoroborate. The reaction mixture was purified by flash chromatography using 30% EtOAc/hexane to afford 100 mg (85% yield) of product as yellow solid. mp 108–110 °C (lit.<sup>6</sup> 105–107 °C); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.99 – 7.92 (m, 4H), 7.60 – 7.56 (m, 1H), 7.54 – 7.49 (m, 2H), 7.21 – 7.15 (m, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.4 (d,  $J_{CF}$  = 256.0 Hz), 141.5, 137.7, 133.3, 130.5 (d,  $J_{CF}$  = 9.6 Hz), 129.4, 127.6, 116.6 (d,  $J_{CF}$  = 0.8 Hz); IR 3073, 2925, 1588, 1493, 1325, 1154, 844, 730, 712, 685, 549 cm<sup>-1</sup>; LRMS (EI); Mass calcd for C<sub>12</sub>H<sub>9</sub>FO<sub>2</sub>S [M]<sup>+</sup>: 236.0; found 236.0.



**1-((4-Methoxyphenyl)sulfonyl)-2-methylbenzene (4g)**<sup>7</sup>: Prepared according to the general procedure B using 2-methylbenzenethiol and 4-methoxybenzenediazonium tetrafluoroborate. The reaction mixture was purified by flash chromatography using 50% EtOAc/hexane to afford 81 mg (62% yield) of product as a yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.15 (dd,  $J$  = 7.9, 1.3 Hz, 1H), 7.81 – 7.77 (m, 2H), 7.48 – 7.42 (m, 1H), 7.36 (dd,  $J$  = 11.3, 3.9 Hz, 1H), 7.21 (d,  $J$  = 7.5 Hz, 1H), 6.97 – 6.93 (m, 2H), 3.83 (s, 3H), 2.45 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.1, 142.9, 139.4, 137.6, 137.0, 133.2, 132.5, 130.0, 129.8, 129.0, 126.3, 114.2, 55.6, 20.1; IR 2934, 2842, 1665, 1593, 1496, 1325, 1261, 1149, 1023, 805, 759, 712, 583 cm<sup>-1</sup>; LRMS (EI); Mass calcd for C<sub>14</sub>H<sub>14</sub>O<sub>3</sub>S [M]<sup>+</sup>: 262.0; found 262.0.

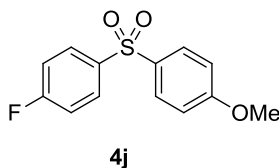


**1-((4-Methoxyphenyl)sulfonyl)-3-methylbenzene (4h)**<sup>8</sup>: Prepared according to the general procedure B using 3-methylbenzenethiol and 4-methoxybenzenediazonium tetrafluoroborate. The reaction mixture was purified by flash chromatography using 20% EtOAc/hexane to afford 84 mg (64% yield) of product as a white solid. mp 80–81 °C (lit.<sup>8</sup> 82–83 °C); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.81 – 7.78 (m, 2H), 7.64 – 7.62 (m, 2H), 7.31 – 7.24 (m, 2H), 6.90 – 6.87 (m, 2H), 3.76 (s, 3H), 2.31 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.3, 142.1, 139.4, 133.6, 133.2, 129.8, 129.0, 127.5, 124.4, 114.4, 55.6, 21.3; IR 2926, 2842, 1594, 1496, 1310, 1261, 1145, 1023, 834, 700, 579, 506 cm<sup>-1</sup>; LRMS (EI); Mass calcd for C<sub>14</sub>H<sub>14</sub>O<sub>3</sub>S [M]<sup>+</sup>: 262.0; found 262.0.

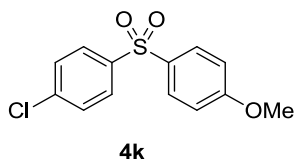


**1-Methoxy-4-tosylbenzene (4i)**<sup>6</sup>: Prepared according to the general procedure B using 4-methylbenzenethiol and 4-methoxybenzenediazonium tetrafluoroborate. The reaction mixture was purified by flash chromatography using 50% EtOAc/hexane to afford 105 mg (80% yield) of product as a yellow solid. mp 99–101 °C (lit.<sup>6</sup> 100–102 °C); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.87 – 7.84 (m, 2H), 7.80 – 7.78 (m, 2H), 7.28 – 7.26 (m, 2H), 6.96 – 6.93 (m, 2H), 3.82 (s, 3H), 2.37 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.2, 143.6, 139.4, 133.5, 129.7, 129.6, 127.3, 114.4, 55.5, 21.4; IR 2925, 2842, 1593, 1494, 1315, 1258, 1149, 1104, 1021, 803, 678, 553 cm<sup>-1</sup>; LRMS (EI); Mass calcd for C<sub>14</sub>H<sub>14</sub>O<sub>3</sub>S [M]<sup>+</sup>: 262.0; found 262.0.

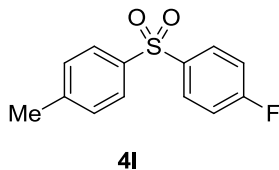




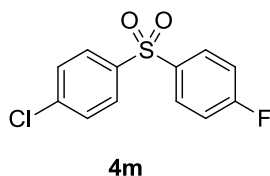
**1-Fluoro-4-((4-methoxyphenyl)sulfonyl)benzene (4j)**<sup>9</sup>: Prepared according to the general procedure B using 4-fluorobenzenethiol and 4-methoxybenzenediazonium tetrafluoroborate. The reaction mixture was purified by flash chromatography using 50% EtOAc/hexane to afford 88 mg (66% yield) of product as a yellow solid. mp 103–105 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95 – 7.90 (m, 2H), 7.88 – 7.84 (m, 2H), 7.19 – 7.13 (m, 2H), 6.99 – 6.95 (m, 2H), 3.85 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.2 (d,  $J_{CF}$  = 255.3 Hz), 163.4, 138.5 (d,  $J_{CF}$  = 3.2 Hz), 132.9, 130.1 (d,  $J_{CF}$  = 9.5 Hz), 129.8, 116.4 (d,  $J_{CF}$  = 22.6 Hz), 114.6, 55.6; IR 3103, 2926, 1592, 1494, 1310, 1259, 1151, 1125, 1024, 834, 681, 553 cm<sup>-1</sup>; LRMS (EI); Mass calcd for C<sub>13</sub>H<sub>11</sub>FO<sub>3</sub>S [M]<sup>+</sup>: 266.0; found 266.0.



**1-Chloro-4-((4-methoxyphenyl)sulfonyl)benzene (4k)**<sup>10</sup>: Prepared according to the general procedure B using 4-chlorobenzenethiol and 4-methoxybenzenediazonium tetrafluoroborate. The reaction mixture was purified by flash chromatography using 50% EtOAc/hexane to afford 99 mg (70% yield) of product as a yellow solid. mp 96–98 °C (lit.<sup>10</sup> 99–100 °C); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.87 – 7.83 (m, 4H), 7.46 – 7.43 (m, 2H), 6.99 – 6.95 (m, 2H), 3.84 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.5, 140.9, 139.4, 132.6, 129.8, 129.4, 128.7, 114.6, 55.6; IR 2929, 2841, 1591, 1496, 1397, 1319, 1258, 1149, 1087, 1012, 847, 802, 754, 665, 600, 553, 472 cm<sup>-1</sup>; LRMS (EI); Mass calcd for C<sub>13</sub>H<sub>11</sub>ClO<sub>3</sub>S [M]<sup>+</sup>: 282.0; found 282.0.

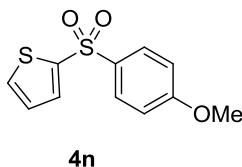


**1-Fluoro-4-tosylbenzene (4l)**<sup>6</sup>: Prepared according to the general procedure B using 4-methylbenzenethiol and 4-fluorobenzenediazonium tetrafluoroborate. The reaction mixture was purified by flash chromatography using 20% EtOAc/hexane to afford 88 mg (70% yield) of product as a yellow solid. mp 87–90 °C (lit.<sup>6</sup> 83–85 °C); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.97 – 7.92 (m, 2H), 7.83 – 7.80 (m, 2H), 7.32 – 7.29 (m, 2H), 7.19 – 7.13 (m, 2H), 2.40 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.3 (d,  $J_{CF}$  = 255.5 Hz), 144.3, 138.3 (d,  $J_{CF}$  = 41.6 Hz), 130.3 (d,  $J_{CF}$  = 9.5 Hz), 130.0, 127.6, 116.5 (d,  $J_{CF}$  = 22.7 Hz), 21.6; IR 2925, 1590, 1492, 1405, 1291, 1236, 1154, 1110, 813, 679, 550 cm<sup>-1</sup>; LRMS (EI); Mass calcd for C<sub>13</sub>H<sub>11</sub>FO<sub>2</sub>S [M]<sup>+</sup>: 250.0; found 250.0.

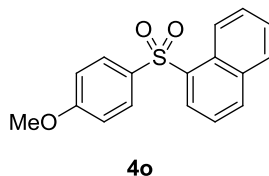


**1-Chloro-4-((4-fluorophenyl)sulfonyl)benzene (4m)**<sup>10</sup>: Prepared according to the general procedure B using 4-chlorobenzenethiol and 4-fluorobenzenediazonium tetrafluoroborate. The reaction mixture was purified by flash chromatography using 10% EtOAc/hexane to afford 104 mg (77% yield) of product as a yellow solid. mp 113–114 °C (lit.<sup>10</sup> 113 °C); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.97 – 7.92 (m, 2H), 7.88 – 7.84 (m, 2H), 7.50 – 7.46 (m, 2H), 7.22 – 7.16 (m, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.5 (d,  $J_{CF}$  = 256.7 Hz), 140.0 (d,  $J_{CF}$  = 8.9 Hz), 137.3, 130.5 (d,  $J_{CF}$  = 9.7 Hz), 129.7, 129.0, 116.7 (d,  $J_{CF}$  = 22.8 Hz); IR 3100, 2926, 1589, 1493, 1395,

1331, 1238, 1154, 1091, 1012, 839, 757, 664, 599, 548  $\text{cm}^{-1}$ ; LRMS (EI); Mass calcd for  $\text{C}_{12}\text{H}_8\text{ClFO}_2\text{S}$   $[\text{M}]^+$ : 270.0; found 270.0.

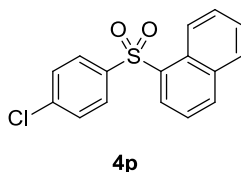


**2-((4-Methoxyphenyl)sulfonyl)thiophene (4n):** Prepared according to the general procedure B using thiophene-2-thiol and 4-methoxybenzenediazonium tetrafluoroborate. The reaction mixture was purified by flash chromatography using 30% EtOAc/hexane to afford 92 mg (72% yield) of product as a yellow solid. mp 114–115  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 – 7.89 (m, 2H), 7.64 (dd,  $J$  = 3.8, 1.3 Hz, 1H), 7.59 (dd,  $J$  = 5.0, 1.3 Hz, 1H), 7.05 (dd,  $J$  = 5.0, 3.8 Hz, 1H), 6.99 – 6.95 (m, 2H), 3.84 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.4, 143.9, 133.5, 133.2, 132.6, 129.5, 127.7, 114.5, 55.6; IR 3099, 2943, 1594, 1497, 1340, 1260, 1147, 1016, 834, 684, 579  $\text{cm}^{-1}$ ; HRMS (EI); Mass calcd for  $\text{C}_{11}\text{H}_{10}\text{O}_3\text{S}_2$   $[\text{M}]^+$ : 254.0071; found 254.0074.



**1-((4-Methoxyphenyl)sulfonyl)naphthalene (4o):** Prepared according to the general procedure B using 4-methoxybenzenethiol and 1-naphthalenediazonium tetrafluoroborate. The reaction mixture was purified by flash chromatography using 30% EtOAc/hexane to afford 109 mg (73% yield) of product as a yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.67 (dd,  $J$  = 8.6, 0.8 Hz, 1H), 8.46 (dd,  $J$  = 7.4, 1.3 Hz, 1H), 8.05 (d,  $J$  = 8.2 Hz, 1H), 7.92 – 7.86 (m, 3H), 7.60 – 7.50 (m, 3H), 6.93 – 6.89 (m, 2H), 3.77 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.1, 136.5, 134.8, 134.1, 133.2, 129.6, 129.4, 128.9, 128.2, 128.1, 126.7, 124.3, 114.3, 55.5; IR 3063, 2943, 2841, 1593,

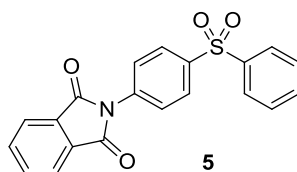
1497, 1320, 1260, 1135, 805, 770, 688, 581  $\text{cm}^{-1}$ ; HRMS (EI); Mass calcd for  $\text{C}_{17}\text{H}_{14}\text{O}_3\text{S}$   $[\text{M}]^+$ : 298.0664; found 298.0666.



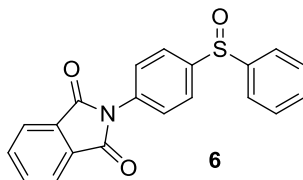
**1-((4-chlorophenyl)sulfonyl)naphthalene (4p):** Prepared according to the general procedure B using 4-chlorobenzenethiol and 1-naphthalenediazonium tetrafluoroborate. The reaction mixture was purified by flash chromatography using 30% EtOAc/hexane to afford 115 mg (76% yield) of product as a yellow solid. mp 102–103 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.61 – 8.58 (m, 1H), 8.51 (dd,  $J$  = 7.4, 1.3 Hz, 1H), 8.10 (d,  $J$  = 8.2 Hz, 1H), 7.91 – 7.88 (m, 3H), 7.64 – 7.52 (m, 3H), 7.43 – 7.40 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.2, 139.6, 135.4, 135.2, 134.2, 130.1, 129.4, 129.1, 128.8, 128.5, 128.3, 126.9, 124.4, 124.0; IR 3087, 2925, 1578, 1475, 1314, 1157, 769, 572, 470  $\text{cm}^{-1}$ ; HRMS (EI); Mass calcd for  $\text{C}_{16}\text{H}_{11}\text{ClO}_2\text{S}$   $[\text{M}]^+$ : 302.0168; found 302.0170.

#### 4. Synthesis of Bioactive compounds

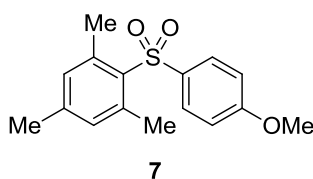
2-(4-mercaptophenyl)isoindoline-1,3-dione and benzenediazonium tetrafluoroborate were reacted in DMF to give sulfone **5**, which shows antibacterial and antifungal activities.<sup>11</sup> Furthermore, when DMSO was used as a solvent, sulfoxide **6**, a potential bioactive compound, was synthesized selectively. Sulfone **7**, which shows EPAC2 antagonist activity,<sup>12</sup> was also synthesized successfully under the optimized reaction conditions. See below for detailed experimental procedures for the synthesis of compound **5**, **6** and **7**.



**2-(4-(phenylsulfonyl)phenyl)isoindoline-1,3-dione (**5**)**<sup>11</sup>: Prepared according to the general procedure B using 2-(4-mercaptophenyl)isoindoline-1,3-dione and benzenediazonium tetrafluoroborate. The reaction mixture was purified by flash chromatography using 50% EtOAc/hexane to afford 162 mg (89% yield) of product as a white solid. mp 224–226 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.97 – 7.95 (m, 2H), 7.82 – 7.77 (m, 4H), 7.71 – 7.68 (m, 2H), 7.62 – 7.60 (m, 2H), 7.55 – 7.47 (m, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.8, 145.1, 144.9, 134.7, 136.1, 134.7, 134.5, 134.1, 131.5, 131.3, 129.5, 126.9, 126.5, 126.0, 125.4, 124.9, 123.9; IR 3057, 1709, 1496, 1367, 1220, 1079, 828, 720, 539 cm<sup>-1</sup>; HRMS (EI); Mass calcd for C<sub>20</sub>H<sub>13</sub>NO<sub>4</sub>S [M]<sup>+</sup>: 363.0565; found 363.0568.



**2-(4-(phenylsulfinyl)phenyl)isoindoline-1,3-dione (6):** Prepared according to the general procedure A using 2-(4-mercaptophenyl)isoindoline-1,3-dione and benzenediazonium tetrafluoroborate. The reaction mixture was purified by flash chromatography using 50% EtOAc/hexane to afford 149 mg (86% yield) of product as a white solid. mp 106–108 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 – 7.94 (m, 2H), 7.80 – 7.78 (m, 2H), 7.46 – 7.43 (m, 2H), 7.42 – 7.31 (m, 7H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.1, 136.8, 134.5, 134.4, 132.2, 131.7, 130.4, 130.1, 129.4, 127.7, 127.0, 123.8; IR 3056, 1714, 1496, 1374, 1262, 1079, 885, 731, 533  $\text{cm}^{-1}$ ; HRMS (EI); Mass calcd for  $\text{C}_{20}\text{H}_{13}\text{NO}_3\text{S}$   $[\text{M}]^+$ : 347.0616; found 347.0620.



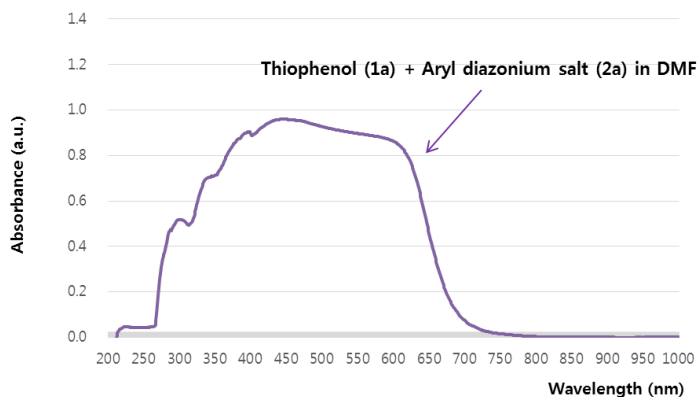
**2-((4-methoxyphenyl)sulfonyl)-1,3,5-trimethylbenzene (7)<sup>12</sup>:**

2,4,6-trimethylbenzenethiol (0.5 mmol, 1.0 equiv), 4-methoxybenzenediazonium tetrafluoroborate (0.75 mmol, 1.5 equiv),  $\text{AgNO}_3$  (0.1 mmol, 0.2 equiv), and  $\text{K}_2\text{S}_2\text{O}_8$  (1.5 mmol, 3.0 equiv), were dissolved in dry DMF (0.25 M). The reaction mixture was stirred and irradiated by 4 W green LEDs (530 nm) at room temperature under air atmosphere for 15 h. After the reaction was completed monitored by TLC, water (10 mL) and EtOAc (10 mL) were added, and the mixture was extracted by EtOAc (3 x 10 mL). The combined organic layer was dried over anhydrous  $\text{MgSO}_4$ , filtered, and concentrated under reduced pressure. The reaction mixture was purified by flash chromatography using 40% EtOAc/hexane to afford 94 mg (65% yield) of product as a yellow solid. mp 133–134 °C (lit.<sup>12</sup> 132–133 °C);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$

7.73 (d,  $J = 8.4$  Hz, 2H), 6.94 – 6.91 (m, 4H), 3.83 (s, 3H), 2.59 (s, 6H), 2.28 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.7, 143.0, 139.7, 135.2, 134.5, 132.1, 129.0, 128.4, 114.0, 55.6, 22.8, 21.0; IR 2933, 2570, 1592, 1493, 1255, 1146, 831, 673, 569  $\text{cm}^{-1}$ ; LRMS (EI); Mass calcd for  $\text{C}_{16}\text{H}_{18}\text{O}_3\text{S}$   $[\text{M}]^+$ : 290.1; found 290.1.

## UV/Vis Spectroscopy

The UV/Vis spectroscopy experiment was carried out to check the absorbance property of the reaction. A noticeable absorbance was observed in the range of green light emission (520-540 nm) when we added thiophenol (**1a**, 0.2 mmol) and 4-methoxybenzenediazonium tetrafluoroborate (**2a**, 0.24 mmol) in DMF (0.25 M). This result indicates that the starting compounds would replace the photocatalyst for the generation of singlet oxygen during the reaction.



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## NMR Spectra

