Supporting Information

Visible-Light-Driven Electron Donor–Acceptor Complex

Induced Sulfonylation of Diazonium Salts with Sulfinates

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1. General Information

Chemicals and anhydrous solvents were purchased from commercial suppliers and used as received. ¹H NMR, ¹³C NMR, and ¹⁹F NMR spectras were recorded by Bruker AV 400 or Bruker AV 500 spectrometers. Chemical shifts (δ) were given in parts per million (ppm) and were measured downfield from internal tetramethylsilane. All High-Resolution Mass Spectra (HRMS) were obtained from AB SCIEX Triple TOF 5600⁺ spectrometer. UV-Vis absorption spectra were recorded by using Shimadzu UV-1800 UV/Vis spectrometer. Flash column chromatography was performed over silica gel (200-300 mesh). The light source was used 18 W LEDs (manufacturer: Xuzhou Facai Lighting Co. Ltd. of China, wavelength: 400 nm purple LEDs, 460 nm blue LEDs, 510 nm green LEDs and white LEDs), less than 1 cm from the light source to the irradiation vessel.

2. Synthesis of Diazonium Salts



General procedure: The diazonium salts were synthesized according to a published procedure.¹ A pre-cooling sodium nitrite (20 mmol) in 15 mL water was added to a mixture solution of HBF₄ (50 wt% in water, 6 mL) and aniline (20 mmol) in water (6 mL) in an ice-water bath. After 1 h of vigorous stirring, the precipitate was collected by filtration, followed by washing with little ice-cold water. The white crystalline was obtained by re-dissolved in acetone and then precipitated with the addition of diethyl ether, then drying to give diazonium salt.

3. Synthesis of Sodium Sulfinates



General procedure: The sodium sulfinates were synthesized according to a published procedure.² Sulfonic acid chloride (10 mmol) was added to a mixture of Na₂SO₃ (20 mmol) and NaHCO₃ (20 mmol) in water (10 mL) and the result mixture was stirred at 80 °C for 10 h. After cooling down to room temperature, the water was removed in vacuum and the residue was extracted in ethanol. Recrystallization from ethanol furnished sodium sulfinate as a white or light yellow solid.

4. Optimization Experiments

Table S1. Optimization of reaction conditions.^a

	N	$J_2^{\oplus} BF_4^{\Theta}$ $NaHCO_3, CH_3CN$	
H ₃ C		+ ONA H ₃ C 400 nm purple LEDs Ar, rt, 12 h	H ₃ CO
	1a	2a	3a
	entry	variations from standard conditions	$\mathbf{3a}^{b}$ (%)
	1	none	88
	2	Na ₂ CO ₃ , instead of NaHCO ₃	84
	3	Cs ₂ CO ₃ , instead of NaHCO ₃	74
	4	K ₃ PO ₄ , instead of NaHCO ₃	78
	5	DCM, instead of CH ₃ CN	40
	6	DMA, instead of CH ₃ CN	32
	7	DMSO, instead of CH ₃ CN	30
	8	1.0 equiv of NaHCO ₃	88
	9	without NaHCO ₃	76
	10	1.0 equiv of 1a	75
	11	white LEDs	13
	12	460 nm blue LEDs	10
	13	510 nm green LEDs	0

14	in the dark	trace			
15	air atmosphere	38			
16	O ₂ atmosphere	trace			
^a Reaction conditions: 1a (0.3 mmol, 1.5 equiv), 2a (0.2 mmol),					
NaHCO ₃ (0.04 mmol, 0.2 equiv), CH ₃ CN [0.2 M], room					
temperature, argon atmosphere, 400 nm purple LEDs, 12 h.					
^b Isolated yield based on 2a .					
	-				

5. General Protocol for the Synthesis of Sulfonylation Products

To a solution of 1 (0.3 mmol, 1.5 equiv) in MeCN (1.0 mL, 0.2 M) was added 2 (0.2 mmol) and NaHCO₃ (3.4 mg, 0.04 mmol) in an oven-dried 8 mL reaction vial. The mixture was bubbled with Ar for 2 min, and the reaction was executed under argon atmosphere. The reaction was then stirred and photolyzed with 15 W 400 nm purple LEDs at distances to the vial of approximately 1 cm for 12 h. Afterwards, the mixture was purified by flash chromatography on silica gel to afford **3** or **4** as solids or liquid.

6. Gram-scale Experiments



A gram-scale experiment for synthesis of **3s** was carried out. To a solution of **1s** (2.00 g, 10.2 mmol) in MeCN (34.0 mL, 0.2 M) was added **2a** (1.21 g, 6.8 mmol) and NaHCO₃ (114 mg, 1.4 mmol) in an oven-dried 50 mL round bottom flask. The mixture was bubbled with Ar for 2 min, and the reaction was executed under argon atmosphere. The reaction was then stirred and photolyzed with 15 W 400 nm purple LEDs at distances to the round bottom flask of approximately 1 cm for 24 h. Afterwards, the mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 3:1) to afford **3s** as dark yellow solid, 1.43 g, 89% yield.

7. Characterization of the Target Products



1-Methoxy-4-tosylbenzene (3a). Purification by chromatography (petroleum

ether/EtOAc = 4:1) afforded **3a** as yellow solid, m.p. 157-159 °C, 36 mg, 88% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, J = 8.3 Hz, 2H), 7.82 (d, J = 9.1 Hz, 2H), 7.40 – 7.34 (m, 2H), 6.95 (d, J = 9.2 Hz, 2H), 3.88 (s, 3H), 2.46 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 165.49, 145.74, 143.49, 130.84, 130.27, 129.92, 127.43, 114.80, 56.00, 21.92. HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₄H₁₅O₃S 263.0736, found 263.0734.



1-Ethoxy-4-tosylbenzene **(3b).** Purification by chromatography (petroleum ether/EtOAc = 4:1) afforded **3b** as yellow oil, 24 mg, 43% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.81 (d, *J* = 9.0 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 9.1 Hz, 2H), 4.11 (q, *J* = 7.0 Hz, 2H), 2.46 (s, 3H), 1.44 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 165.00, 145.69, 143.36, 130.94, 130.28, 129.92, 127.49, 115.20, 64.43, 21.91, 14.70. HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₅H₁₇O₃S 277.0893, found 277.0894.



4,4'-Sulfonylbis(methylbenzene) (3c). Purification by chromatography (petroleum ether/EtOAc = 6:1) afforded 3c as yellow solid, m.p. 158-159 °C, 35 mg, 71% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 2.46 (s, 3H), 2.41 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 147.39, 146.57, 145.96, 130.41, 130.36, 130.27, 129.96, 124.77, 21.96, 21.90. HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₄H₁₅O₂S 247.0787, found 247.0791.



1-(*tert*-Butyl)-4-tosylbenzene **(3d).** Purification by chromatography (petroleum ether/EtOAc = 4:1) afforded **3d** as light yellow solid, m.p. 70-72 °C, 47 mg, 81% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, J = 8.3 Hz, 2H), 7.76 (d, J = 8.7 Hz, 2H), 7.50 (d, J = 8.7 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 2.46 (s, 3H), 1.32 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 159.40, 147.16, 145.93, 130.35, 130.32, 129.94, 126.56, 124.55, 35.51, 31.08, 21.87. HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₇H₂₁O₂S 289.1257, found 289.1249.



1-Fluoro-4-tosylbenzene (3e). Purification by chromatography (petroleum ether/EtOAc = 4:1) afforded **2** as dark yellow solid, m.p. 112-114 °C, 43 mg, 86% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.86 (m, 4H) 7.39 (d, *J* = 7.9 Hz, 2H), 7.22 – 7.06 (m, 2H), 2.47 (s, 3H). ¹³C NMR (125 MHz, DMSO-*d*₆) δ 166.23 (d, *J* = 256.3 Hz), 146.54, 145.26 (d, *J* = 2.6 Hz), 130.40, 130.05, 129.08, 127.26 (d, *J* = 10.3 Hz), 117.48 (d, *J* = 23.6 Hz), 21.30. ¹⁹F NMR (471 MHz, DMSO-*d*₆) δ -101.85. HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₃H₁₂FO₂S 251.0537, found 251.0535.



1-Chloro-4-tosylbenzene **(3f).** Purification by chromatography (petroleum ether/EtOAc = 4:1) afforded **3f** as yellow solid, m.p. 126-128 °C, 36 mg, 67% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 2.48 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 147.59, 146.31, 141.39, 130.53, 130.08, 130.01, 129.88, 125.86, 21.96. HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₃H₁₂ClO₂S 267.0241, found 267.0239.



1-Bromo-4-tosylbenzene **(3g).** Purification by chromatography (petroleum ether/EtOAc = 4:1) afforded **3g** as yellow solid, m.p. 133-135 °C, 50 mg, 80% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.9 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 2.48 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 147.95, 146.34, 133.03, 130.53, 130.15, 130.09, 129.83, 125.91, 21.95. HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₃H₁₂BrO₂S 310.9736, found 310.9726.



4-Tosylbenzonitrile (3h). Purification by chromatography (petroleum ether/EtOAc = 4:1) afforded 3h as light yellow solid, m.p. 136-137 °C, 37 mg, 72% yield. ¹H NMR

(400 MHz, CDCl₃) δ 7.90 (d, J = 8.6 Hz, 2H), 7.86 (d, J = 8.4 Hz, 2H), 7.80 (d, J = 8.6 Hz, 2H), 7.42 (d, J = 8.1 Hz, 2H), 2.49 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 150.98, 146.79, 133.60, 130.67, 130.22, 129.13, 124.82, 117.60, 117.59, 21.99. HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₄H₁₂NO₂S 258.0583, found 258.0586.



1-methyl-4-((4-nitrophenyl)sulfonyl)benzene (**3i**). Purification by chromatography (petroleum ether/EtOAc = 4:1) afforded **3i** as yellow solid, m.p. 165-167 °C, 33 mg, 60% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.35 (d, *J* = 8.9 Hz, 2H), 7.96 (d, *J* = 9.0 Hz, 2H), 7.86 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 2.49 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 152.18, 150.87, 146.90, 130.75, 130.29, 129.11, 125.19, 125.07, 22.01. HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₃H₁₂NO₄S 278.0482, found 278.0472.



1-Ethynyl-4-tosylbenzene **(3j).** Purification by chromatography (petroleum ether/EtOAc = 4:1) afforded **3j** as red oil, 10 mg, 20% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, J = 8.2 Hz, 2H), 7.78 (d, J = 8.6 Hz, 2H), 7.59 (d, J = 8.6 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 3.32 (s, 1H), 2.48 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 148.69, 146.32, 133.34, 130.57, 130.09, 129.87, 128.86, 124.55, 82.57, 81.98, 21.96. HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₅H₁₃O₂S 257.0631, found 257.0631.



1-Chloro-2-tosylbenzene (**3k**). Purification by chromatography (petroleum ether/EtOAc = 4:1) afforded **3k** as yellow oil, 42 mg, 79% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.53 – 7.48 (m, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.32 (ddd, *J* = 8.4, 5.6, 3.1 Hz, 1H), 2.47 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 146.27, 145.32, 138.25, 135.59, 131.42, 130.90, 129.92, 129.34, 127.64, 118.07, 21.96. HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₃H₁₂ClO₂S 267.0241, found 267.0234.



1-chloro-3-tosylbenzene (31). Purification by chromatography (petroleum ether/EtOAc = 4:1) afforded 31 as yellow oil, 47 mg, 88% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.71 (t, *J* = 2.0 Hz, 1H), 7.68 (ddd, *J* = 7.9, 1.9, 1.1 Hz, 1H), 7.51 (ddd, *J* = 8.0, 2.1, 1.1 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 7.6 Hz, 2H), 2.45 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 149.77, 146.43, 135.59, 134.40, 130.65, 130.42, 130.05, 129.42, 123.51, 123.40, 21.83. HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₃H₁₂ClO₂S 267.0241, found 267.0245.



2-Tosylbenzonitrile **(3m).** Purification by chromatography (petroleum ether/EtOAc = 4:1) afforded **3m** as light yellow solid, m.p. 105-107 °C, 33 mg, 64% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.84 – 7.78 (m, 4H), 7.75 – 7.68 (m, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 2.47 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 149.34, 146.90, 134.70, 134.19, 133.76, 130.97, 130.15, 128.11, 117.35, 115.64, 114.88, 21.94. HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₄H₁₂NO₂S 258.0583, found 258.0579.



Methyl(2-tosylphenyl)sulfane **(3n).** Purification by chromatography (petroleum ether/EtOAc = 4:1) afforded **3n** as red oil, 38 mg, 68% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 8.1 Hz, 2H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 1H), 7.14 (t, *J* = 7.7 Hz, 1H), 2.47 (s, 3H), 2.37 (s, 3H). ¹³C NMR (125 MHz, DMSO-*d*₆) δ 146.26, 144.36, 144.22, 136.02, 130.26, 130.08, 127.83, 125.86, 125.01, 119.57, 21.27, 13.93. HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₄H₁₅O₂S₂ 279.0508, found 279.0508.



2-chloro-1-methyl-4-tosylbenzene (30). Purification by chromatography (petroleum ether/EtOAc = 4:1) afforded 30 as red oil, 48 mg, 86% yield. ¹H NMR (400 MHz,

CDCl₃) δ 7.85 (d, J = 8.2 Hz, 2H), 7.79 (d, J = 2.0 Hz, 1H), 7.65 (dd, J = 8.1, 2.0 Hz, 1H), 7.39 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.1 Hz, 1H), 2.48 (s, 3H), 2.44 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 148.12, 146.27, 143.91, 135.73, 131.77, 130.49, 130.06, 129.89, 124.53, 123.34, 21.94, 20.69. HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₄H₁₄ClO₂S 281.0398, found 281.0396.



4-Bromo-2-tosylbenzonitrile (**3p**). Purification by chromatography (petroleum ether/EtOAc = 4:1) afforded **3p** as light yellow solid, m.p. 129-130 °C, 22 mg, 33% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.95 (d, *J* = 1.9 Hz, 1H), 7.85 – 7.79 (m, 3H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.42 (d, *J* = 8.1 Hz, 2H), 2.48 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 149.76, 147.17, 137.40, 134.93, 131.02, 130.25, 128.80, 127.83, 120.78, 114.29, 114.26, 21.99. HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₄H₁₁BrNO₂S 335.9688, found 335.9685.



3-Tosyl-1,1'-biphenyl **(3q).** Purification by chromatography (petroleum ether/EtOAc = 12:1) afforded **3q** as yellow solid, m.p. 197-199 °C, 33 mg, 54% yield. ¹H NMR (500 MHz, CDCl₃) δ 8.03 (t, *J* = 1.9 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.80 (dddd, *J* = 8.9, 8.1, 2.0, 1.1 Hz, 2H), 7.60 – 7.54 (m, 3H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.42 – 7.37 (m, 3H), 2.48 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 149.73, 146.20, 142.90, 139.27, 133.38, 130.51, 130.06, 130.03, 130.00, 129.11, 128.31, 127.19, 123.25, 123.13, 21.92. HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₉H₁₇O₂S 309.0944, found 309.0941.



1-Methyl-4-((4-phenoxyphenyl)sulfonyl)benzene (3r). Purification by chromatography (petroleum ether/EtOAc = 4:1) afforded 3r as yellow oil, 47 mg, 72% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 9.0 Hz, 2H), 7.41 (dd, *J* = 8.6, 7.5 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.07 (dd, *J* = 8.7, 1.1 Hz, 2H), 7.00 (d, *J* = 9.2 Hz, 2H), 2.46 (s, 3H). ¹³C NMR (125 MHz,

CDCl₃) δ 164.00, 154.90, 145.91, 144.44, 130.60, 130.35, 130.33, 129.97, 127.22, 125.37, 120.61, 117.84, 21.91. HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₉H₁₇O₃S 325.0893, found 325.0895.



1-Methyl-3-tosyl-1*H*-pyrazole **(3s).** Purification by chromatography (petroleum ether/EtOAc = 2:1) afforded **3s** as dark yellow solid, m.p. 64-65 °C, 43 mg, 90% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 2.6 Hz, 1H), 7.36 (d, *J* = 7.9 Hz, 2H), 6.65 (d, *J* = 2.6 Hz, 1H), 3.98 (s, 3H), 2.44 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 159.82, 146.09, 132.99, 130.62, 130.05, 129.58, 98.31, 40.32, 21.91. HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₁H₁₃N₂O₂S 237.0692, found 237.0690.



5-Tosylbenzo[d]thiazole (**3t**). Purification by chromatography (petroleum ether/EtOAc = 3:1) afforded **3t** as dark brown oil, 26 mg, 45% yield. ¹H NMR (500 MHz, CDCl₃) δ 9.06 (s, 1H), 8.46 (d, *J* = 1.8 Hz, 1H), 7.96 (d, *J* = 8.7 Hz, 1H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.81 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.36 (d, *J* = 7.7 Hz, 2H), 2.42 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 156.68, 153.59, 147.67, 146.19, 140.34, 130.32, 129.95, 129.75, 122.73, 118.38, 21.78. HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₄H₁₂NO₂S₂ 290.0304, found 290.0302.



4-Methyl-7-tosyl-2H-chromen-2-one **(3u).** Purification by chromatography (petroleum ether/EtOAc = 2:1) afforded **3u** as yellow solid, m.p. 134-136 °C, 46 mg, 73% yield. ¹H NMR (500 MHz, CD₂Cl₂) δ 7.84 (d, *J* = 6.7 Hz, 2H), 7.78 – 7.72 (m, 2H), 7.69 (s, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 6.39 (s, 1H), 2.49 (s, 3H), 2.45 (s, 3H). ¹³C NMR (125 MHz, CD₂Cl₂) δ 159.84, 154.20, 151.82, 150.70, 147.15, 130.80, 130.42, 129.62, 126.37, 125.15, 119.45, 118.02, 113.30, 21.97, 18.91. HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₇H₁₅O₄S 315.0686, found 315.0680.



3,4,6-trimethyl-7-tosyl-2H-chromen-2-one **(3v).** Purification by chromatography (petroleum ether/EtOAc = 4:1) afforded **3v** as yellow solid, m.p. 140-142 °C, 32 mg, 47% yield. ¹H NMR (500 MHz, CD₂Cl₂) δ 7.92 (s, 1H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.19 (s, 1H), 2.48 (s, 3H), 2.38 (s, 3H), 2.29 (s, 3H), 2.17 (s, 3H). ¹³C NMR (125 MHz, CD₂Cl₂) δ 161.01, 156.51, 146.71, 146.22, 145.07, 143.40, 130.84, 130.21, 130.02, 123.41, 119.82, 119.37, 112.72, 21.93, 17.26, 15.38, 13.65. HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₉H₁₉O₄S 343.0999, found 343.0987.



1-bromo-4-(phenylsulfonyl)benzene (4a). Purification by chromatography (petroleum ether/EtOAc = 12:1) afforded 4a as yellow solid, m.p. 106-108 °C, 35 mg, 59% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.97 (dd, J = 8.4, 1.4 Hz, 2H), 7.73 (t, J = 7.5 Hz, 1H), 7.70 – 7.57 (m, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 147.87, 134.98, 133.06, 130.50, 130.33, 129.37, 125.94. HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₂H₁₀BrO₂S 296.9579, found 296.9580.



1-Bromo-4-((4-fluorophenyl)sulfonyl)benzene (4b). Purification by chromatography (petroleum ether/EtOAc = 15:1) afforded 4b as yellow oil, 28 mg, 45% yield. ¹H NMR (500 MHz, DMSO-*d*₆) δ 8.05 (dd, *J* = 5.5, 3.6 Hz, 2H), 7.83 (d, *J* = 7.3 Hz, 2H), 7.74 (d, *J* = 6.8 Hz, 2H), 7.58 (t, *J* = 8.6 Hz, 2H). ¹³C NMR (125 MHz, DMSO-*d*₆) δ 166.23 (d, *J* = 255.4 Hz), 147.22, 133.59 (d, *J* = 10.3 Hz), 133.38, 130.02, 128.03, 126.05, 117.34 (d, *J* = 23.2 Hz). ¹⁹F NMR (471 MHz, DMSO-*d*₆) δ -101.50. HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₂H₉BrFO₂S 314.9485, found 314.9440.



1-bromo-4-((4-chlorophenyl)sulfonyl)benzene (4c). Purification by chromatography

(petroleum ether/EtOAc = 15:1) afforded **4c** as yellow oil, 31 mg, 47% yield. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.97 (d, *J* = 8.7 Hz, 2H), 7.86 – 7.79 (m, 4H), 7.75 (d, *J* = 8.8 Hz, 2H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 147.22, 140.90, 133.38, 132.05, 130.66, 130.10, 130.07, 126.07. HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₂H₉BrClO₂S 330.9190, found 330.9184.



1-bromo-4-((4-methoxyphenyl)sulfonyl)benzene (4d). Purification by chromatography (petroleum ether/EtOAc = 4:1) afforded 4d as yellow oil, 23 mg, 35% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, J = 9.0 Hz, 2H), 7.65 (d, J = 8.9 Hz, 2H), 7.60 (d, J = 8.8 Hz, 2H), 7.03 (d, J = 9.0 Hz, 2H), 3.87 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 164.89, 147.81, 132.92, 132.67, 129.91, 125.77, 123.61, 114.72, 55.87. HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₃H₁₂BrO₃S 326.9685, found 326.9674.



4,4'-Sulfonylbis(methoxybenzene) (4e). Purification by chromatography (petroleum ether/EtOAc = 4:1) afforded 4e as yellow solid, m.p. 129-130 °C, 42 mg, 75% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, *J* = 8.9 Hz, 2H), 7.82 (d, *J* = 9.0 Hz, 2H), 7.04 (d, *J* = 9.0 Hz, 2H), 6.95 (d, *J* = 9.1 Hz, 2H), 3.89 (d, *J* = 3.5 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 165.39, 164.58, 143.41, 132.45, 127.32, 124.87, 114.78, 114.57, 55.97, 55.84. HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₄H₁₅O₄S 279.0686, found 279.0676.



N-(4-((4-Methoxyphenyl)sulfonyl)phenyl)acetamide (4f). Purification by chromatography (petroleum ether/EtOAc = 1:1) afforded 4f as yellow oil, 43 mg, 70% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.42 (s, 1H), 7.84 (d, *J* = 8.8 Hz, 2H), 7.80 – 7.74 (m, 4H), 6.93 (d, *J* = 9.1 Hz, 2H), 3.87 (s, 3H), 2.21 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 169.50, 165.75, 144.17, 143.35, 131.52, 127.50, 119.41, 114.94, 56.03, 24.84. HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₅H₁₆NO₄S 306.0795, found 306.0786.



4-((4-Bromophenyl)sulfonyl)-1,1'-biphenyl (4g). Purification by chromatography (petroleum ether/EtOAc = 12:1) afforded 4g as yellow oil, 34 mg, 46% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 8.5 Hz, 2H), 7.81 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 8.8 Hz, 2H), 7.67 – 7.61 (m, 4H), 7.54 – 7.41 (m, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 147.92, 138.99, 133.08, 131.37, 131.05, 130.33, 129.30, 129.08, 127.97, 127.57, 125.99. HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₈H₁₄BrO₂S 372.9892, found 372.9896.



2-((4-bromophenyl)sulfonyl)naphthalene (4h). Purification by chromatography (petroleum ether/EtOAc = 12:1) afforded 4h as yellow solid, m.p. 115-116 °C, 30 mg, 43% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.60 (s, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.89 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.71 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1H), 7.68 – 7.64 (m, 3H), 7.64 – 7.59 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 147.90, 135.95, 133.03, 132.96, 132.20, 130.30, 130.04, 129.93, 129.70, 129.48, 128.17, 127.97, 125.93, 124.40. HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₆H₁₂BrO₂S 346.9736, found 346.9732.



1-Bromo-4-(methylsulfonyl)benzene (4i). Purification by chromatography (petroleum ether/EtOAc = 8:1) afforded 4i as yellow solid, m.p. 125-126 °C, 22 mg, 47% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 8.8 Hz, 2H), 7.73 (d, *J* = 8.7 Hz, 2H), 3.22 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 147.80, 133.30, 130.76, 125.97, 34.99. HRMS (ESI) m/z: [M + H]⁺ calcd for C₇H₈BrO₂S 234.9423, found 234.9431.



1-Bromo-4-(ethylsulfonyl)benzene (4j). Purification by chromatography (petroleum ether/EtOAc = 6:1) afforded 4j as dark yellow oil, 35 mg, 70% yield. ¹H NMR (500

MHz, CDCl₃) δ 7.81 (d, J = 8.8 Hz, 2H), 7.72 (d, J = 8.8 Hz, 2H), 3.47 (q, J = 7.5 Hz, 2H), 1.49 (t, J = 7.5 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 148.08, 133.25, 130.64, 125.84, 43.04, 7.57. HRMS (ESI) m/z: [M + H]⁺ calcd for C₈H₁₀BrO₂S 248.9579, found 248.9576.



1-Bromo-4-(isopropylsulfonyl)benzene (4k). Purification by chromatography (petroleum ether/EtOAc = 15:1) afforded 4k as yellow oil, 22 mg, 42% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.82 (d, J = 8.8 Hz, 2H), 7.72 (d, J = 8.7 Hz, 2H), 3.82 (p, J = 6.9 Hz, 1H), 1.54 (s, 3H), 1.52 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 148.40, 133.24, 130.57, 125.80, 50.95, 16.12. HRMS (ESI) m/z: [M + H]⁺ calcd for C₉H₁₂BrO₂S 262.9736, found 262.9728.



1-Bromo-4-(butylsulfonyl)benzene (41). Purification by chromatography (petroleum ether/EtOAc = 12:1) afforded 41 as light yellow oil, 23 mg, 41% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 8.7 Hz, 2H), 7.72 (d, *J* = 8.7 Hz, 2H), 3.50 – 3.37 (m, 2H), 1.90 (tt, *J* = 7.9, 6.5 Hz, 2H), 1.52 (h, *J* = 7.4 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 148.05, 133.25, 130.60, 125.86, 47.94, 24.67, 21.90, 13.60. HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₀H₁₄BrO₂S 276.9892, found 276.9880.



1-(Cyclopropylsulfonyl)-4-methoxybenzene (4m). Purification by chromatography (petroleum ether/EtOAc = 4:1) afforded 4m as yellow oil, 16 mg, 38% yield. ¹H NMR (500 MHz, DMSO-*D*₆) δ 7.97 (d, *J* = 9.1 Hz, 2H), 7.22 (d, *J* = 9.0 Hz, 2H), 3.93 (s, 3H), 2.99 (tt, *J* = 7.9, 4.8 Hz, 1H), 1.35 – 1.18 (m, 2H), 1.21 – 1.12 (m, 2H). ¹³C NMR (125 MHz, DMSO-*d*₆) δ 165.47, 142.96, 126.97, 115.47, 56.17, 25.30, 5.32. HRMS (ESI) m/z: [M + H]⁺ calcd for C₁₀H₁₃O₃S 213.0580, found 213.0576.

8. Mechanistic Studies

8.1 TEMPO radical trapping experiments



To a solution of 1a (0.3 mmol, 1.5 equiv) in CH₃CN (1 mL, 0.2 M) was added sodium *p*-toluenesulfinate 2a (0.2 mmol, 1 equiv), NaHCO₃ (0.04 mmol) and TEMPO (0.8 mmol, 4 equiv) in an oven-dried 8 mL reaction vial. The mixture was bubbled with Ar for 2 min, and the reaction executed under argon atmosphere. The reaction was then stirred and photolyzed with 18 W 400 nm purple LEDs at distances to the vial of approximately 1 cm for 12 h. The reaction mixture was then analyzed by HRMS.

The HRMS spectrum showed evidence for the formation of **5** (an adduct of TEMPO and aryl radical) and **6** (an adduct of TEMPO and sulfonyl radical).



Spectrum from 46.wiff (sample 1) - Sample046, Experiment 1, +TOF MS (50 - 800) from 0.068 to 0.077 min



8.2 UV/vis absorption spectrometry between 1a and 2a.



UV/vis absorption spectra between 1a (0.02 M) and 2a (0.02 M) in 1 mL CH₃CN were recorded in 1 cm path quartz cuvettes using a Shimadzu UV-1800 UV/Vis spectrometer.





The stoichiometry of the EDA complexes 1a+2a was calculated using the Job's plot method. The Job's plot of the EDA complex between 1a and 2a was calculated

measuring the absorption of Acetonitrile solutions at 390 nm with different donor/acceptor ratios with constant concentration (0.02 M) of the two components. The absorbance values were plotted against the molar fraction (%) of **1a**. The Job's plot analysis of the EDA complex between **1a** and **2a** showed a maximal absorbance at 50% molar fraction of **1a** indicated the 1:1 stoichiometry of the EDA complex in solution.

8.4 Substrate replaced reaction



To a solution of 1g (0.3 mmol, 1.5 equiv) in CH₃CN (1 mL, 0.2 M) was added *p*-toluenesulfinic acid 7 (0.2 mmol, 1 equiv) in an oven-dried 8 mL reaction vial. The NaHCO₃ was add in 0-2 equivalent. The mixture was bubbled with Ar for 2 min, and the reaction executed under argon atmosphere. The reaction was then stirred and photolyzed with 18 W 400 nm purple LEDs at distances to the vial of approximately 1 cm for 12 h. Afterwards, the mixture was purified by flash chromatography on silica gel to afford **3g** as yellow solid.

9. ¹H NMR and ¹³C NMR Spectra



¹H NMR (400 MHz, CDCl₃)







¹H NMR (400 MHz, CDCl₃)

7.8637 7.8429 7.8173 7.7947 7.3768 7.3768 7.3768 5.9192 6.9192	4.1353 4.1178 4.1002 4.0828	2.4560	1.4535 1.4360 1.4187
2222200	4444	-2	4















¹³C NMR (125 MHz, DMSO-*d*₆)



¹⁹F NMR (471 MHz, DMSO-*d*₆)





¹H NMR (400 MHz, CDCl₃)





S25







¹H NMR (400 MHz, CDCl₃)







¹H NMR (400 MHz, CDCl₃)























¹H NMR (400 MHz, CDCl₃)







S33



















¹H NMR (500 MHz, CDCl₃)











¹H NMR (500 MHz, CD₂Cl₂)



¹³C NMR (125 MHz, CD₂Cl₂)





¹H NMR (500 MHz, CD₂Cl₂)



¹³C NMR (125 MHz, CD₂Cl₂)





220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 fl (ppm)



¹H NMR (500 MHz, DMSO-*d*₆)



¹³C NMR (125 MHz, DMSO-*d*₆)







¹H NMR (400 MHz, DMSO-*d*₆)



¹³C NMR (100 MHz, DMSO-*d*₆)





S45







¹H NMR (400 MHz, CDCl₃)

















¹H NMR (500 MHz, CDCl₃)













10. References

- 1. N. Zhang, Z.-J. Quan, Z. Zhang, Y.-X. Da and X.-C. Wang, *Chem. Commun.*, 2016, **52**, 14234-14237.
- (a) L. K. Liu, Y. Chi and K.-Y. Jen, J. Org. Chem., 1980, 45, 406-410; (b) X. Zhou, J. Luo, J. Liu, S. Peng and G.-J. Deng, Org. Lett., 2011, 13, 1432-1435.