

**An unexpected reaction of aryldiazonium tetrafluoroborates,
sodium metabisulfite, and thiourea under photoinduced
conditions**

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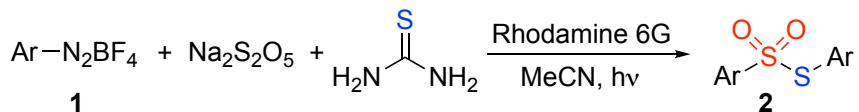
Supporting Information

1. General experimental methods (S2).
2. General experimental procedure and characterization data (S2-S7).
3. ^1H and ^{13}C NMR spectra of compounds **2**, **3** and **4** (S8-S42).

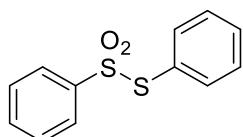
General experimental methods:

Unless otherwise stated, all commercial reagents were used as received. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63 μ m, standard grade). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at \sim 20 Torr at 25–35°C. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 on a Bruker DRX-400 spectrometer operating at 400 MHz and 100 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. High resolution mass spectrometry (HRMS) spectra were obtained on a micrOTOF II Instrument.

General experimental procedure for the photoredox-catalyzed reaction of aryldiazonium tetrafluoroborate **1**, sodium metabisulfite, and thiourea.

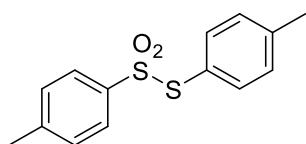


Aryldiazonium tetrafluoroborate **1** (0.4 mmol), sodium metabisulfite (0.4 mmol) and thiourea (0.3 mmol) were combined with Rhodamine 6G (2 mol %) in a tube. The tube was evacuated and backfilled with N₂ three times before the addition of MeCN (2.0 mL). The mixture was then placed around a white CFL (35 W) with a distance of 6 centimeters, and was stirred under light irradiation for 12 hours at room temperature. After completion of reaction as indicated by TLC, the mixture was purified directly by flash column chromatography (EtOAc/n-hexane, 1:16) to provide the desired product **2**.



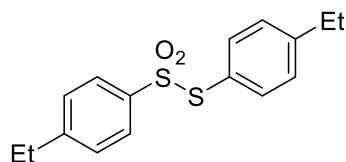
S-phenyl benzenesulfonothioate (2a**)**

White solid. ^1H NMR (400 MHz, CDCl_3): δ 7.56 (d, $J = 8.0$ Hz, 2H), 7.47 – 7.40 (m, 4H), 7.35 – 7.32 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3): δ 143.0, 136.5, 133.6, 131.4, 129.4, 128.8, 127.8, 127.5. HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{11}\text{O}_2\text{S}_2^+$: 251.0195 ($\text{M}+\text{H}^+$), found: 251.0188.



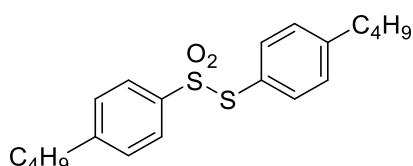
S-(*p*-tolyl) 4-methylbenzenesulfonothioate (2b**)**

White solid. ^1H NMR (400 MHz, CDCl_3): δ 7.46 (d, $J = 7.7$ Hz, 2H), 7.26–7.20 (m, 4H), 7.14 (d, $J = 7.6$ Hz, 2H), 2.42 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 144.5, 142.0, 140.5, 136.4, 130.2, 129.3, 127.6, 124.6, 21.6, 21.4. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{15}\text{O}_2\text{S}_2^+$: 279.0508 ($\text{M}+\text{H}^+$), found: 279.0508.



S-(4-ethylphenyl) 4-ethylbenzenesulfonothioate (2c**)**

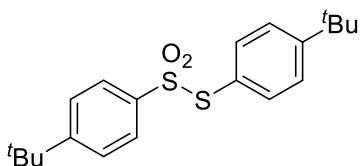
White solid. ^1H NMR (400 MHz, CDCl_3): δ 7.48 (d, $J = 8.3$ Hz, 2H), 7.29 – 7.21 (m, 4H), 7.16 (d, $J = 8.1$ Hz, 2H), 2.74 – 2.64 (m, 4H), 1.24 (q, $J = 7.5$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ 150.7, 148.2, 140.5, 136.6, 129.0, 128.1, 127.7, 124.7, 28.9, 28.7, 15.2, 15.1. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{18}\text{O}_2\text{S}_2\text{Na}^+$: 329.0640 ($\text{M}+\text{Na}^+$), found: 329.0630.



S-(4-butylphenyl) 4-butylbenzenesulfonothioate (2d**)**

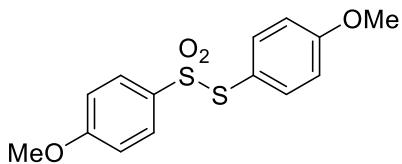
Pale yellow solid. ^1H NMR (400 MHz, CDCl_3): δ 7.45 (d, $J = 8.3$ Hz, 2H), 7.24 (d, $J = 8.1$ Hz, 2H), 7.19 (d, $J = 8.3$ Hz, 2H), 7.12 (d, $J = 8.1$ Hz, 2H), 2.74 – 2.56 (m, 4H), 1.66 –

1.52 (m, 4H), 1.36 – 1.31 (m, 4H), 0.96 – 0.91 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ 149.4, 146.9, 140.3, 136.5, 129.5, 128.6, 127.6, 124.7, 35.5, 35.4, 33.2, 33.1, 22.2, 22.1, 13.9, 13.8. HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{26}\text{O}_2\text{S}_2\text{Na}^+$: 385.1266 ($\text{M}+\text{Na}^+$), found: 385.1261.



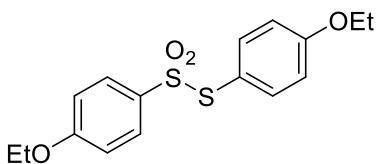
S-(4-(*tert*-butyl)phenyl) 4-(*tert*-butyl)benzenesulfonothioate (2e**)**

White solid. ^1H NMR (400 MHz, CDCl_3): δ 7.49 (d, $J = 8.3$ Hz, 2H), 7.40 (d, $J = 8.0$ Hz, 2H), 7.33 (d, $J = 8.2$ Hz, 2H), 7.29 – 7.26 (m, 2H), 1.33 (s, 9H), 1.31 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3): δ 157.5, 155.0, 140.2, 136.3, 127.4, 126.4, 125.6, 124.6, 35.2, 34.9, 31.1, 31.0. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{27}\text{O}_4\text{S}_2^+$: 363.1447 ($\text{M}+\text{H}^+$), found: 363.1458.



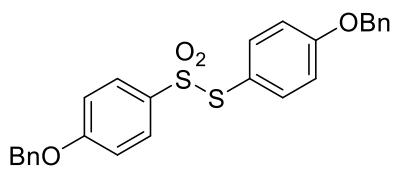
S-(4-methoxyphenyl) 4-methoxybenzenesulfonothioate (2f**)**

White solid. ^1H NMR (400 MHz, CDCl_3): δ 7.50 (d, $J = 8.2$ Hz, 2H), 7.27 (d, $J = 7.5$ Hz, 2H), 6.88 – 6.84 (m, 4H), 3.87 (s, 3H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 163.5, 162.2, 138.3, 134.9, 129.9, 118.9, 114.9, 113.8, 55.7, 55.4. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{15}\text{O}_4\text{S}_2^+$: 311.0406 ($\text{M}+\text{H}^+$), found: 311.0410.



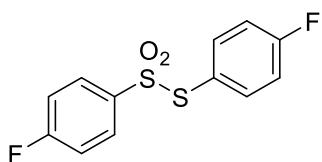
S-(4-ethoxyphenyl) 4-ethoxybenzenesulfonothioate (2g**)**

White solid. ^1H NMR (400 MHz, CDCl_3): δ 7.48 (d, $J = 8.1$ Hz, 2H), 7.24 (d, $J = 7.9$ Hz, 2H), 6.86 – 6.81 (m, 4H), 4.09 – 4.03 (m, 4H), 1.43 (d, $J = 6.1$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ 163.0, 161.6, 138.4, 134.6, 130.4, 129.9, 128.0, 118.7, 115.4, 114.7, 114.2, 64.1, 63.8, 14.7, 14.6. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{18}\text{O}_4\text{S}_2\text{Na}^+$: 361.0539 ($\text{M}+\text{Na}^+$), found: 361.0525.



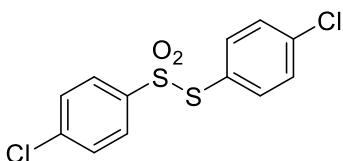
S-(4-(benzyloxy)phenyl) 4-(benzyloxy)benzenesulfonothioate (2h**)**

Pale yellow solid. ^1H NMR (400 MHz, CDCl_3): δ 7.40 – 7.28 (m, 10H), 7.25 – 7.10 (m, 5H), 7.06 (d, J = 8.2 Hz, 1H), 6.99 – 6.87 (m, 2H), 4.92 (s, 4H). ^{13}C NMR (101 MHz, CDCl_3): δ 228.5, 159.0, 158.6, 143.8, 143.4, 136.1, 135.7, 130.2, 129.8, 129.1, 128.7, 128.7, 128.4, 128.2, 127.6, 127.6, 121.8, 121.3, 120.1, 118.9, 112.7, 70.4, 70.2. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{22}\text{O}_4\text{S}_2\text{Na}^+$: 485.0852 ($\text{M}+\text{Na}^+$), found: 485.0841.



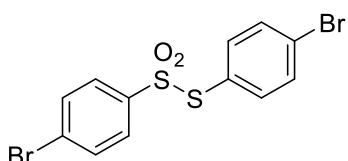
S-(4-fluorophenyl) 4-fluorobenzenesulfonothioate (2i**)**

White solid. ^1H NMR (400 MHz, CDCl_3) δ 7.56 – 7.45 (m, 2H), 7.32 – 7.25 (m, 2H), 7.07 – 7.03 (m, 2H), 7.01 – 6.96 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.9, 166.1, 164.3, 163.6, 138.8 (d, J = 9.1 Hz), 130.4 (d, J = 9.7 Hz), 116.9 (d, J = 22.3 Hz), 116.2 (d, J = 22.8 Hz). HRMS (ESI) calcd for $\text{C}_{12}\text{H}_9\text{O}_2\text{S}_2^+$: 287.0007 ($\text{M}+\text{H}^+$), found: 287.0011.



S-(4-chlorophenyl) 4-chlorobenzenesulfonothioate (2j**)**

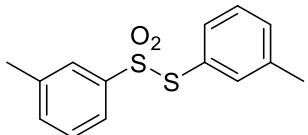
White solid. ^1H NMR (400 MHz, CDCl_3): δ 7.52 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.37 – 7.30 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3): δ 141.3, 140.6, 138.6, 137.7, 129.9, 129.3, 128.9, 126.0. HRMS (ESI) calcd for $\text{C}_{12}\text{H}_9\text{Cl}_2\text{O}_2\text{S}_2^+$: 318.9416 ($\text{M}+\text{H}^+$), found: 318.9426.



S-(4-bromophenyl) 4-bromobenzenesulfonothioate (2k**)**

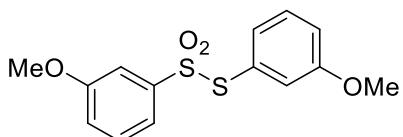
White solid. ^1H NMR (400 MHz, CDCl_3): δ 7.60 (d, J = 8.3 Hz, 2H), 7.52 (d, J = 8.0 Hz,

2H), 7.44 (d, J = 8.1 Hz, 2H), 7.24 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ 141.9, 137.8, 132.9, 132.2, 129.1, 128.9, 127.0. HRMS (ESI) calcd for $\text{C}_{12}\text{H}_9\text{Br}_2\text{O}_2\text{S}_2^+$: 408.8384 ($\text{M}+\text{H}^+$), found: 408.8396.



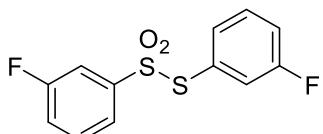
S-(*m*-tolyl) 3-methylbenzenesulfonothioate (**2l**)

Pale yellow solid. ^1H NMR (400 MHz, CDCl_3): δ 7.40 – 7.26 (m, 5H), 7.24 – 7.20 (m, 1H), 7.14 (d, J = 6.8 Hz, 2H), 2.34 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 142.8, 139.4, 139.0, 137.1, 134.3, 133.6, 132.1, 129.1, 128.5, 128.0, 127.6, 124.7, 21.1. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{15}\text{O}_2\text{S}_2^+$: 279.0508 ($\text{M}+\text{H}^+$), found: 279.0504.



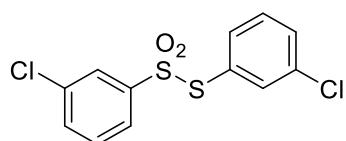
S-(3-methoxyphenyl) 3-methoxybenzenesulfonothioate (**2m**)

White solid. ^1H NMR (400 MHz, CDCl_3): δ 7.36 – 7.32 (m, 1H), 7.27 – 7.19 (m, 1H), 7.23 – 7.16 (m, 1H), 7.12 – 7.10 (m, 1H), 7.02 (m, 2H), 6.96 (d, J = 7.6 Hz, 1H), 6.90 (d, J = 1.8 Hz, 1H), 3.73 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ 159.8, 159.5, 143.9, 130.1, 129.8, 128.8, 128.7, 120.8, 120.7, 119.8, 118.1, 111.6, 55.6, 55.4. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{15}\text{O}_4\text{S}_2^+$: 311.0406 ($\text{M}+\text{H}^+$), found: 311.0401.



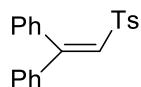
S-(3-fluorophenyl) 3-fluorobenzenesulfonothioate (**2n**)

White solid. ^1H NMR (400 MHz, CDCl_3): δ 7.45 (m, 1H), 7.40 – 7.29 (m, 4H), 7.25 – 7.17 (m, 2H), 7.15 – 7.12 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3): δ 163.4 (d, J = 28.9 Hz), 160.9 (d, J = 30.4 Hz), 144.4, 132.2, 130.7 (dd, J = 14.3, 7.9 Hz), 129.0, 123.3, 123.3, 123.0, 121.1 (d, J = 21.2 Hz), 118.9 (d, J = 21.0 Hz), 114.8 (d, J = 24.7 Hz). HRMS (ESI) calcd for $\text{C}_{12}\text{H}_9\text{F}_2\text{O}_2\text{S}_2^+$: 287.0007 ($\text{M}+\text{H}^+$), found: 287.0014.



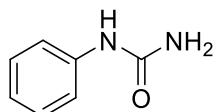
S-(3-chlorophenyl) 3-chlorobenzenesulfonothioate (2o**)**

White solid. ^1H NMR (400 MHz, CDCl_3): δ 7.61 – 7.57 (m, 1H), 7.55 (m, 1H), 7.52 – 7.45 (m, 2H), 7.41 (m, 1H), 7.36 – 7.29 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 136.1, 134.6, 134.0, 131.9, 130.5, 130.1, 127.6, 125.5. HRMS (ESI) calcd for $\text{C}_{12}\text{H}_9\text{Cl}_2\text{O}_2\text{S}_2^+$: 318.9416 ($\text{M}+\text{H}^+$), found: 318.9415.



(2-Tosylethene-1,1-diy) dibenzene (3**)**

Pale yellow solid. ^1H NMR (400 MHz, CDCl_3) δ 7.47 (d, $J = 8.3$ Hz, 2H), 7.38 – 7.34 (m, 2H), 7.32 – 7.28 (m, 4H), 7.24 – 7.18 (m, 2H), 7.15 (d, $J = 8.1$ Hz, 2H), 7.12 – 7.08 (m, 2H), 6.99 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 154.6, 143.6, 139.1, 138.5, 135.5, 130.1, 129.7, 129.2, 128.8, 128.7, 128.5, 128.1, 127.7, 127.6.



1-Phenylurea (4**)**

White solid. ^1H NMR (400 MHz, DMSO) δ 8.50 (d, $J = 4.9$ Hz, 1H), 7.56 – 7.33 (m, 2H), 7.23 – 7.19 (m, 2H), 6.90 – 6.87 (m, 1H), 5.84 (d, $J = 7.2$ Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 156.4, 140.8, 128.9, 121.4, 118.1.

