Supporting Information

A Visible-Light Photocatalytic Thiolation of Aryl, Heteroaryl and Vinyl Iodides

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Experimental Procedures

General Information

Unless otherwise stated, reagents and solvents were purchased from commercial sources and used without further purification. 4-Iodobenzyloxybenzene,\(^1\) tert-butyl 5-ido-1H-indole-1-carboxylate\(^2\) and 2-iodo-1-benzofuran\(^3\) were synthesized according to literature procedures. Vinyl iodides were synthesized according to a literature procedure for the synthesis of \(E\)-iodostyrene\(^4\) or [(1\(E\))-2-iodo-1-methyl-vinyl]-benzene.\(^5\)

\(^1\)H NMR and \(^13\)C NMR spectra were recorded on Bruker 400 Ultrashield (400 MHz), Ascend 400 (400 MHz) or Varian MR-400 spectrometers. Chemical shifts are expressed in parts per million (PPM) and are referenced to the internal solvent peaks.

Mass spectrometric analyses were performed on a Thermo Scientific Q Exactive mass spectrometer fitted with an ASAP ion source. Positive ions were recorded in an appropriate mass range at 140,000 mass resolution. The APCI probe was used without flow of solvent. The nitrogen nebulizing/desolvation gas used for vaporization was heated to 350 °C in these experiments. The sheath gas flow rate was set to 25, the auxiliary gas flow rate to 5 and the sweep gas flow rate to 2 (all arbitrary units). The discharge current was 4 mA and the capillary temperature was 320 °C.

Steady-state luminescent spectra were recorded using a Perkin Elmer LS50 fluorimeter. Samples were excited at 400 nm, slit widths were 2.7 nm and the area under the spectra were used for determining the Stern-Volmer quenching values.

Time-resolved photoluminescence was measured using an Edinburgh Instruments FLSP920 time-correlated single-photon counting spectrometer comprising a pulsed diode laser excitation source operated at 378 nm. Steady-state emission spectra were collected concurrently on this instrument.
Absorption spectra were measured using a Perkin Elmer Lambda 1050 spectrometer. Transient absorption spectra were recorded using an Edinburgh Instruments LP900 spectrometer coupled with a nanosecond pulsed Nd$^{3+}$-YAG laser (Quantel, Brio), operating at 355 nm and 10 Hz repetition rate as the excitation source.

Analytical Thin Layer Chromatography (TLC) was carried out using aluminium-backed Merck Kieselgel KG60 F254 silica plates. The plates were visualised by irradiation with short-wave ultraviolet light. Flash chromatography was performed on Grace Davidson Davisil LC60A 40-63 micron silica gel.

All photoredox reactions were performed using a custom built blue LED photoreactor (Figure S1). The custom reactor was comprised of a square metal frame (100 mm × 110 mm) with 14 blue LEDs (2 × SP-02-V4 LED assembly, each consisting of 7 LXML-PR02-A900 Royal-Blue LUXEON Rebel ES LEDs; [www.luxeonstar.com](http://www.luxeonstar.com)). The photoreactor was fitted with PC cooling fans and heat sinks for temperature control (internal temperature of the reactor typically reaches 27 ± 5 °C overnight). The power of the light source can be varied using an intensity control. The emission output of the light source used was measured using a Princeton Instruments PIXIS 1024BR CCD Detector. The measurement was conducted by shining the LED light indirectly into the aperture of the detector.

**Figure S1.** Custom-built LED photoreactor; a) blue LED assembly; b) PC cooling fans; c) heat sinks; d) intensity control; e) 12 V power supply.
Photoredox cross-coupling reactions

General Procedure A

(Hetero)aryl iodide (0.3 mmol, 1.0 equiv.), dimethyl disulfide (1.2 mmol, 4.0 equiv.), 1,4-diazabicyclo[2.2.2]octane (1.2 mmol, 4.0 equiv.), Ir(ppy)$_3$ (6 μmol, 2 mol%) and DMSO (50.5 μL, 2.0 equiv.) were placed in a 4 mL scintillation vial and taken up in MeCN (3 mL). The vial was sealed with a plastic screw cap and stirred for 24 h at room temperature whilst being irradiated with 10 W blue LED light. The reaction mixture was concentrated under reduced pressure and the residue was purified by flash chromatography on silica to afford the final product.

Product Characterisation Data

![Methyl 4-(methylthio)benzoate (7)](image)

Methyl 4-(methylthio)benzoate (7): prepared according to general procedure A with methyl-4-iodobenzoate (79 mg, 0.3 mmol); purified by flash chromatography, eluting with 10% Et$_2$O/n-pentane, to afford the title product as a white solid (50 mg, 91%).

$^1$H NMR (500 MHz, CDCl$_3$): δ = 7.94 (d, $J = 8.5$ Hz, 2H), 7.24 (d, $J = 8.2$ Hz, 2H), 3.90 (s, 3H), 2.52 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$): δ = 166.8, 145.4, 129.8, 126.2, 124.9, 51.9, 14.8.

Data matched that reported in the literature.$^6$
4-(Methylthio)acetophenone (11): prepared according to general procedure A with 4-iodoacetophenone (74 mg, 0.3 mmol); purified by flash chromatography, eluting with 20% Et₂O/n-pentane, to afford the title compound as a white solid (38 mg, 76%).

¹H NMR (400 MHz, CDCl₃): δ = 7.84 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 2.54 (s, 3H, H), 2.49 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ = 197.3, 146.0, 133.6, 128.9, 125.1, 26.6, 14.9.

Data matched that reported in the literature.⁶

4-(Methylthio)benzonitrile (12): prepared according to general procedure A with 4-iodobenzonitrile (69 mg, 0.3 mmol); purified by flash chromatography eluting with n-pentane, to afford the title compound as a colourless oil (28 mg, 62%).

¹H NMR (400 MHz, CDCl₃): δ = 7.50 (d, J = 8.8 Hz, 2H), 7.23 (d, J = 8.8 Hz, 2H), 2.47 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ = 146.23, 132.27, 125.6, 119.10, 107.76, 14.81.

Data matched that reported in the literature.⁶
1-Methylthio-4-phenylmethoxy benzene (13): prepared according to general procedure A with 4-iodobenzylmethoxybenzene (93 mg, 0.3 mmol); purified flash chromatography eluting with 1% Et₂O/n-pentane, to afford the title compound as a white solid (41 mg, 60%).

\(^1\)H NMR (400 MHz, CDCl₃): \(\delta = 7.43 – 7.32 (m, 5H), 7.25 (d, J = 9.0 \text{ Hz}, 2H), 6.92 (d, J = 9.0 \text{ Hz}, 2H), 5.05 (s, 2H), 2.44 (s, 3H)\)

\(^1^3\)C NMR (100 MHz, CDCl₃): \(\delta = 157.3, 136.9, 130.0, 129.1, 128.6, 127.4, 115.6, 70.1, 18.0\).

Data matched that reported in the literature.⁷

(4-Methoxyphenyl)(methyl)sulfane (14): prepared according to general procedure A with 4-iodoanisole (70 mg, 0.3 mmol); purified by flash chromatography, eluting with 1% Et₂O/n-pentane to afford the title compound as a white solid (25 mg, 55%).

\(^1\)H NMR (400 MHz, CDCl₃): \(\delta = 7.27 (d, J = 9.0 \text{ Hz}, 2H), 6.85 (d, J = 9.0 \text{ Hz}, 2H), 3.79 (s, 3H), 2.44 (s, 3H)\).

\(^1^3\)C NMR (100 MHz, CDCl₃): \(\delta = 158.3, 130.3, 128.9, 114.7, 55.5, 18.2\).

Data matched that reported in the literature.⁸
**2-Methoxythioanisole (15):** prepared according to general procedure A with 2-iodoanisole (70 mg, 0.3 mmol); purified flash chromatography eluting with 1% Et₂O/n-pentane to afford the title compound as a white solid (40 mg, 86%).

^1H NMR (400 MHz, CDCl₃): δ = 7.18 – 7.13 (m, 2H), 6.96 (t, 1H, J = 7.6 Hz), 6.84 (d, J = 8.0 Hz, 1H), 3.90 (s, 3H), 2.44 (s, 3H).

^13C NMR (100 MHz, CDCl₃): δ = 156.3, 128.8, 126.2, 125.9, 121.2, 110.1, 55.8, 14.8.

Data matched that reported in the literature.⁹

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**4-(Methylthio)acetanilide (16):** prepared according to general procedure A with 4-iodoacetanilide (78 mg, 0.3 mmol); purified by flash chromatography, eluting with 1% CH₃OH/CH₂Cl₂ to afford the title compound as an orange solid (27 mg, 50%).

^1H NMR (400 MHz, CDCl₃): δ = 7.43 (d, J = 8.5 Hz, 2H), 7.24 (d, J = 8.5 Hz, 2H), 2.46 (s, 3H), 2.17 (s, 3H).

^13C NMR (100 MHz, CDCl₃): δ = 168.3, 135.6, 133.7, 128.1, 120.6, 24.8, 16.8.

Data matched that reported in the literature.⁶
1-Chloro-4-methylthio benzene (17): prepared according to general procedure A with 4-chloro-iodobenzene (72 mg, 0.3 mmol); purified by flash chromatography, eluting with n-pentane to afford the title compound as a yellow oil (28 mg, 58%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.25$ (d, $J = 9.0$ Hz), 7.17 (d, $J = 9.0$ Hz, 1H), 2.46 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 137.1, 131.0, 129.0, 128.0, 16.2$.

HRMS (ESI) m/z calc. C$_7$H$_8$SCl [M+ H]$^+$ 159.0035, found 159.0031.

Data matched that reported in the literature.$^8$

3-Chlorothioanisole (18): prepared according to general procedure A with 3-chloro-iodobenzene (72 mg, 0.3 mmol); purified by flash chromatography, eluting with n-pentane to afford the title compound as a colorless oil (36 mg, 75%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.20$ (t, $J = 1.6$ Hz), 7.18 (d, $J = 7.6$ Hz, 1H), 7.13 - 7.09 (m, 2H), 2.47 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 140.8, 134.9, 129.9, 126.0, 125.2, 124.6, 15.7$.

Data matched that reported in the literature.$^{10}$
3,5-Diifluorothioanisole (19): prepared according to general procedure A with 1,3-difluoro-
5-iodobenzene (72 mg, 0.3 mmol); purified flash chromatography, eluting with 1% Et₂O/n-
pentane to afford the title compound as a colorless liquid (26 mg, 54%).

^1H NMR (400 MHz, CDCl₃): δ = 6.71 (dd, 2H, J = 8.4 Hz, J = 2.0 Hz), 6.54 (tt, 1H, J = 8.8
Hz, J = 2.0 Hz), 2.45 (s, 3H).

^13C NMR (100 MHz, CDCl₃): δ = 163.3 (dd, J = 249.7 Hz, J = 14.2 Hz), 142.9 (t, J = 9.6
Hz), 108.7 (dd, J = 18.8 Hz, J = 7.8 Hz), 100.4 (t, J = 25.7 Hz), 15.3.

HRMS (ESI) m/z calc. for C₇H₇F₂S [M+H]^+ 161.0237, found 161.0231.

2-(Trifluoromethyl)thioanisole (20): prepared according to general procedure A with 1-
iodo-2-(trifloromethyl)benzene (82 mg, 0.3 mmol); purified by flash chromatography, eluting
with 1% Et₂O/n-pentane to afford the title compound as a colorless liquid (46 mg, 80%).

^1H NMR (400 MHz, CDCl₃): δ = 7.62 (d, 1H, J = 8.0 Hz), 7.48 (t, 1H, J = 7.2 Hz), 7.37 (t, J =
8.0 Hz, 1H), 7.23 (t, J = 7.6Hz, 1H), 2.52 (s, 3H).

^13C NMR (100 MHz, CDCl₃): δ = 137.3, 131.0, 127.0 (q, J = 30.6 Hz), 126.4, 125.7 (q, J =
5.6 Hz), 122.9 (q, J = 272.1 Hz), 123.7, 15.4.

Data matched that reported in the literature.
**2-Bromothioanisole (21):** prepared according to general procedure A with 1-bromo-2-iodobenzene (85 mg, 0.3 mmol); purified by flash chromatography, eluting with n-pentane, to afford the title compound as a colourless liquid (52 mg, 86%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.52$ (d, $J = 6.4$, 1.5 Hz), 7.30 (t, $J = 6$ Hz, 1H), 7.13 (d, $J = 6.4$ Hz), 7.00 (t, $J = 7.2$ 1H), 2.48 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 139.6$, 132.6, 127.8, 125.7, 125.4, 121.7, 15.7.

Data matched that reported in the literature.$^8$

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**2-Methylthio-1,3,5-trimethylbenzene (22):** prepared according to general procedure A with 2-iodo-1,3,5-trimethylbenzene (74 mg, 0.3 mmol); purified by flash chromatography, eluting with n-pentane to afford the title compound as a colorless liquid (24 mg, 48%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 6.93$ (s, 2H), 2.52 (s, 6H), 2.26 (s, 3H), 2.20 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 142.8$, 138.23, 132.0, 129.2, 21.9, 21.2, 18.7.

Data matched that reported in the literature.$^{11}$
9-Phenanthrylmethylsulfide (23): prepared according to general procedure A with 9-iodophenanthrene (91 mg, 0.3 mmol); purified by flash chromatography, eluting with 1% Et<sub>2</sub>O/n-pentane to afford the title compound as a yellow solid (49 mg, 73%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.72 (d, J = 1.6 Hz, 1H), 8.63 (d, J = 8.0 Hz, 1H), 8.36 (dd, J = 8.0, 1.6 Hz, 1H), 7.83 - 7.80 (m, 1H), 7.71 - 7.64 (m, 2H), 7.62 - 7.56 (m, 3H),

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 134.5, 132.0, 130.6, 130.4, 129.0, 127.7, 127.1, 127.0, 126.9, 126.1, 124.9, 123.4, 123.15, 122.7, 16.0.

HRMS (ESI) m/z calc. for C<sub>15</sub>H<sub>13</sub>S [M+H]<sup>+</sup> 225.0732, found 225.0732.

1-Methylthionaphalene (24): prepared according to general procedure A with 1-iodonapthalene (76 mg, 0.3 mmol); purified by flash chromatography, eluting with 1% Et<sub>2</sub>O/n-pentane to afford the title compound as a white solid (48 mg, 92%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.31 (d, J = 8.0 Hz, 1H), 7.86 (dd, J = 8.0, 2.4 1H), 7.69 (d, J = 7.6 Hz, 1H), 7.58-7.50 (m, 2H), 7.46-7.39(m, 2H), 2.59 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 135.98, 133.78, 131.81, 128.69, 126.39, 126.30, 125.99, 125.84, 124.44, 123.77, 16.38.

Data matched that reported in the literature. 8
Methylthiopyrazine (25): prepared according to general procedure A with iodopyrazine (62 mg, 0.3 mmol); purified by flash chromatography, eluting with 20% Et₂O/n-pentane to afford the title compound (32 mg, 85%).

$^1$H NMR (400 MHz, CDCl₃): δ = 8.46 (d, $J = 1.5$ Hz, 1H), 8.36 (dd, $J = 2.5$, 1.5 Hz, 1H), 8.19 (d, $J = 2.5$ Hz, 1H), 2.57 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl₃): δ = 156.0, 145.1, 122.6, 122.1, 18.1.

Data matched that reported in the literature.$^{13}$

2-Methylthiobenzofuran (26): prepared according to general procedure A with 2-iodobenzofuran (73 mg, 0.3 mmol); purified by flash chromatography, eluting with n-pentane to afford the title compound (33 mg, 66%).

$^1$H NMR (400 MHz, CDCl₃): δ = 7.49 – 7.47 (m, 1H), 7.43 (d, $J = 7.2$ Hz), 7.27 – 7.18 (m, 2H), 6.69 (s, 1H), 2.55 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl₃): δ = 156.2, 152.6, 128.9, 124.1, 123.0, 120.2, 110.9, 108.0, 17.2.

Data matched that reported in the literature.$^{14}$
**N-Boc-5-methylthioindole (27):** prepared according to general procedure A with *tert*-butyl 5-iodo-1-H-indole-1-carboxylate (103 mg, 0.3 mmol); purified by flash chromatography, eluting 1% Et<sub>2</sub>O/n-pentane to afford the title compound (51 mg, 64%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.05 (d, J = 8.3 Hz), 7.58 (d, J = 3.4 Hz, 1H), 7.49 (d, J = 1.7 Hz, 1H), 7.29 (dd, J = 8.3, 1.7 Hz), 6.50 (d, J = 3.4 Hz, 1H), 2.52 (s, 3H), 1.67 (s, 9H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 131.5, 126.4, 124.5, 119.9, 115.3, 106.6, 83.6, 28.0, 17.4.

Data matched that reported in the literature.<sup>15</sup>

**2-(Methylthio)pyridine (28):** prepared according to general procedure A with 2-iodopyridine (62 mg, 0.3 mmol); purified by flash chromatography, eluting with 10% Et<sub>2</sub>O/n-pentane, to afford the title compound as a white solid (19 mg, 50%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.44 (dd, J = 5.0, 2.0 Hz, 1H), 7.48 (ddd, J = 8.0, 7.5, 1.9 Hz, 1H), 7.18 (dd, J = 8.0, 1.0 Hz, 1H), 6.97 (ddd, J = 7.5, 5.0, 1.0 Hz, 1H), 2.56 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 160.0, 149.4, 135.7, 121.4, 119.0, 13.2.GW-B1-P2

Data matched that reported in the literature.<sup>16</sup>
2-Methylthiothiophene (29): prepared according to general procedure A with 2-iodothiophene (63 mg, 0.3 mmol); purified by flash chromatography, eluting with n-pentane to afford the title compound as a colourless oil (32 mg, 82%).

\[ \text{H NMR (400 MHz, CDCl}_3\text{): } \delta = 7.28 (dd, J = 4.4, 1.2 \text{ Hz, 1H}), 7.06 (dd, J = 2.4, 1.2 \text{ Hz, 1H}), 6.94 (td, J = 5.2, 3.6 \text{ Hz}), 2.47 (s, 3H). \]

\[ \text{C NMR (100 MHz, CDCl}_3\text{): } \delta = 137.3, 131.2, 128.0, 127.6, 22.4. \]

Data matched that reported in the literature.\(^{17}\)

1-Methylthioisoquinoline (30): prepared according to general procedure A with 1-iodoisooquinoline (77 mg, 0.3 mmol); purified by flash chromatography, eluting with 20% Et\(_2\)O/n-pentane, to afford the title compound as a yellow oil (48 mg, 91%).

\[ \text{H NMR (400 MHz, CDCl}_3\text{): } \delta = 8.32 (d, J = 5.5 \text{ Hz, 1H}), 8.20 (d, J = 8.5 \text{ Hz, 1H}), 7.75 (d, J = 8.0 \text{ Hz, 1H}), 7.66 (dd, J = 8.0, 7.0 \text{ Hz, 1H}), 7.56 (dd, J = 8.5, 7.0 \text{ Hz, 1H}), 7.33 (d, J = 5.5 \text{ Hz, 1H}), 2.70 (3H). \]

\[ \text{C NMR (100 MHz, CDCl}_3\text{): } \delta = 160.1, 141.9, 135.2, 130.2, 127.0, 124.5, 117.0, 12.9. \]

Data matched that reported in the literature.\(^{13}\)
General Procedure B

Vinyl iodide (0.3 mmol, 1.0 equiv.), dimethyl disulfide (1.2 mmol, 4.0 equiv.), 1,4-diazabicyclo[2.2.2]octane (1.2 mmol, 4.0 equiv.) and Ir(ppy)$_3$ (6 µmol, 2 mol %) were placed in a pressure-relief reaction vial and taken up in MeCN (3 mL). The vial was placed in a beaker containing ethylene glycol and heated at 60 °C for 24 h, whilst being irradiated with 10 W blue LEDs. The reaction mixture was concentrated under reduced pressure and the residue was purified by flash chromatography on silica to afford the final product.

Product Characterisation Data

Methyl(styryl)sulfane (31): prepared according to general procedure B with E-1-(2-iodovinyl)benzene (69 mg, 0.3 mmol); purified by flash chromatography, eluting with n-pentane to afford title compound as a colourless oil (20 mg, 45%, Z/E = 1.3:1).

$^1$H NMR (400 MHz, CDCl$_3$): for Z isomer δ = 7.48 (d, $J = 4.0$ Hz, 3H), 7.31 – 7.38 (m, 3H), 6.46 (d, $J = 10.8$ Hz, 1H), 6.23 (d, $J = 10.8$ Hz, 1H), 2.43 (s, 3H); for E isomer δ = 7.20 – 7.26 7.14 (m, 5H), 6.82 (d, $J = 15.2$ Hz, 1H), 6.31 (d, $J = 15.2$ Hz, 1H), 2.41 (s, 3H).

$^{13}$C NMR (400 MHz, CDCl$_3$): δ = 137.2, 137.0, 129.1, 128.8, 128.7, 128.3, 126.8, 125.9, 125.5, 125.4, 124.8, 19.0, 14.9.

HRMS (ESI) m/z calc. for C$_9$H$_{11}$S [M+H]$^+$ 151.0581, found 151.0576.
(4-(tert-Butyl)styryl)(methyl)sulfane (33): prepared according to general procedure B with 1-(tert-butyl)-4-(2-iodovinyl)benzene (86 mg, 0.3 mmol); purified by flash chromatography, eluting with n-pentane to give the title compound as a colourless oil (35 mg, 57%, $Z/E = 1.4:1$).

$^1$H NMR (400 MHz, CDCl$_3$): for $E$ isomer $\delta = 7.33 – 7.31$ (m, 2H), 7.25 – 7.22 (m, 2H), 6.74 (d, $J = 15.4$ Hz, 1H), 6.31 (d, $J = 15.4$ Hz, 1H), 2.38 (s, 3H), 1.31 (s, 9H); for $Z$ isomer $\delta = 7.43 – 7.37$ (m, 4H), 6.43 (d, $J = 10.7$ Hz, 1H), 6.16 (d, $J = 10.7$ Hz, 1H), 2.40 (s, 3H), 1.32 (s, 9H);

$^{13}$C NMR (100 MHz, CDCl$_3$): for both $E$ and $Z$ isomer $\delta = 149.8$, 149.7, 134.4, 134.1, 128.4, 128.0, 125.6, 125.22, 125.17, 125.1, 124.8, 34.6, 34.5, 31.3, 18.9, 14.9.

HRMS (ESI) $m/z$ calc. for C$_{13}$H$_{18}$S $[M]^+$ 206.1129, found 206.1129.

(4-(Methoxystyryl)(methyl)sulfane (34): prepared according to general procedure B with 1-(2-iodovinyl)-4-methoxybenzene (78 mg, 0.3 mmol); purified by flash chromatography, eluting with 5% Et$_2$O/n-pentane to give the title compound as a colourless oil (35 mg, 66%, $Z/E = 0.3:1$).

$^1$H NMR (400 MHz, CDCl$_3$): for $E$ isomer $\delta = 7.25 – 7.21$ (m, 2H), 6.86 – 6.82 (m, 2H), 6.62 (d, $J = 15.4$ Hz, 1H), 6.30 (d, $J = 15.4$ Hz, 1H), 3.80 (s, 3H), 2.37 (s, 3H); for $Z$ isomer $\delta =
7.43 – 7.41 (m, 2H), 6.91 – 6.89 (m, 2H), 6.39 (d, \(J = 10.6\) Hz, 1H), 6.08 (d, \(J = 10.6\) Hz, 1H), 3.82 (s, 3H), 2.40 (s, 3H);

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): for \(E\) isomer \(\delta = 158.7, 126.7, 124.9, 123.3, 114.2, 113.8, 55.4, 15.2\); for \(Z\) isomer \(\delta = 158.4, 130.2, 130.1, 129.9, 126.6, 125.1, 55.4, 18.9\).

HRMS (ESI) \(m/z\) calc. for C\(_{10}\)H\(_{13}\)OS [M+H\(^+\)] = 180.0687, found 180.0681.

![Image 35](image35.png)

**(4-(Bromostyryl)(methyl)sulfane (35):** prepared according to general procedure B with 1-(2-iodovinyl)-4-bromobenzene (93 mg, 0.3 mmol); purified by flash chromatography, eluting with \(n\)-pentane to give the title compound as a colourless oil (21 mg, 31\%, \(Z/E = 1.2:1\)).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): for \(E\) isomer \(\delta = 7.42 – 7.39\) (m, 2H), 7.16 – 7.14 (m, 2H), 6.80 (d, \(J = 15.2\) Hz, 1H), 6.23 (d, \(J = 15.2\) Hz, 1H), 2.38 (s, 3H); for \(Z\) isomer \(\delta = 7.48 – 7.46\) (m, 2H), 7.35 – 7.33 (m, 2H), 6.36 (d, \(J = 10.9\) Hz, 1H), 6.26 (d, \(J = 10.9\) Hz, 1H), 2.42 (s, 3H);

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): for \(E\) isomer \(\delta = 136.2, 135.9, 130.2, 127.0, 120.5, 120.3, 14.9\); for \(Z\) isomer \(\delta = 131.9, 131.5, 120.2, 126.9, 124.2, 123.4, 19.0\).

HRMS (ESI) \(m/z\) calc. for C\(_9\)H\(_{10}\)BrS [M+H\(^+\)] = 228.9687, found 228.9681.

![Image 36](image36.png)

**Methyl(2-phenylprop-1-en-1-yl)sulfane (36):** prepared according to general procedure B with \((E)-(1-iodoprop-1-en-2-yl)benzene (73 mg, 0.3 mmol); purified by flash
chromatography, eluting with \( n \)-pentane to give the title compound as a colourless oil (42 mg, 84%, \( Z/E = 1:2.8 \)).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): for \( E \) isomer \( \delta = 7.40 - 7.34 \) (m, 5H), 5.99 (q, \( J = 1.4 \) Hz, 1H), 2.27 (s, 3H), 2.17 (d, \( J = 1.4 \) Hz, 3 H); for \( Z \) isomer \( \delta = 7.32 - 7.20 \) (m, 5H), 6.29 (q, \( J = 0.9 \) Hz, 1H), 2.40 (s, 3H), 1.38 (d, \( J = 0.9 \) Hz, 1 H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): for \( E \) isomer \( \delta = 128.4, 128.1, 127.6, 127.1, 125.1, 123.9, 24.8, 18.2 \); for \( Z \) isomer \( \delta = 141.9, 140.6, 133.8, 133.0, 126.7, 125.3, 17.6, 17.4 \).

HRMS (ESI) \( m/z \) calc. for C\(_{10}\)H\(_{12}\)S [M]\(^+\) 164.0654, found 164.0654.

![37]

3-(1-(Methylthio)prop-1-en-2-yl)thiophene (37): prepared according to general procedure B with (\( E \))-3-(1-iodoprop-1-en-2-yl)thiophene (75 mg, 0.3 mmol); Purified by flash chromatography, eluting with \( n \)-pentane to give the title compound as a colourless oil (28 mg, 55%, \( Z/E = 1:1.3 \)).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): for \( E \) isomer \( \delta = 7.40 \) (dd, \( J = 2.9, 1.4 \) Hz, 1H), 7.39 (dd, \( J = 5.1, 1.4 \) Hz, 1H), 7.31 (dd, \( J = 5.1, 2.9 \) Hz, 1H), 5.94 (q, \( J = 1.3 \) Hz, 1H), 2.35 (s, 3H), 2.17 (d, \( J = 1.3 \) Hz, 3 H); for \( Z \) isomer \( \delta = 7.26 \) (dd, \( J = 5.1, 2.9 \) Hz, 1H), 7.20 (dd, \( J = 5.1, 1.4 \) Hz, 1H), 7.07 (dd, \( J = 2.9, 1.4 \) Hz, 1H), 6.34 (q, \( J = 1.0 \) Hz, 1H), 2.38 (s, 3H), 2.10 (d, \( J = 1.0 \) Hz, 3 H);

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): for \( E \) and \( Z \) isomers \( \delta = 143.3, 140.9, 128.7, 127.3, 125.7, 124.8, 124.7, 124.5, 123.9, 122.8, 118.5, 24.8, 18.6, 17.5 \).

HRMS (ESI) \( m/z \) calc. for C\(_9\)H\(_{10}\)S\(_2\) [M]+ 171.0302, found 171.0297.
Methyl-(2-(p-tolyl)prop-1-en-1-yl)sulfane (38): prepared according to general procedure B with (E)-1-(1-iodoprop-1-en-2-yl)-4-methylbenzene (77 mg, 0.3 mmol); purified by flash chromatography, eluting with n-pentane to afford the title compound as a colourless oil (46 mg, 91%, Z/E-Ratio: 1:2.6).

$^1$H NMR (400 MHz, CDCl$_3$): for E isomer $\delta = 7.29 – 7.27$ (m, 2H), 7.19 – 7.17 (m, 2H), 5.94 (q, $J = 1.3$ Hz, 1H), 2.35 (s, 3H), 2.25 (s, 3H), 2.14 (d, $J = 1.3$ Hz, 3 H); for Z isomer $\delta = 7.26 – 7.24$ (m, 2H), 7.13 – 7.11 (m, 2H), 6.23 (q, $J = 0.9$ Hz, 1H), 2.38 (s, 3H), 2.34 (s, 3H), 2.11 (d, $J = 0.9$ Hz, 1 H)

$^{13}$C NMR (100 MHz, CDCl$_3$): for E isomer $\delta = 129.11, 128.9, 127.5, 125.1, 124.4, 123.4, 24.9, 21.3, 18.3$; for Z isomer $\delta = 139.2, 137.7, 136.9, 136.4, 133.9, 133.1, 21.1, 17.7, 17.4$. HRMS (ESI) $m/z$ calc. for C$_{10}$H$_{11}$FS [M]$^+$ 178.0816, found 178.0809.

(2-(4-Fluorophenyl)prop-1-en-1-yl)(methyl)sulfane (39): prepared according to general procedure B with (E)-1-fluoro-4-(1-iodoprop-1-en-2-yl)benzene (79 mg, 0.3 mmol); purified by flash chromatography, eluting with n-pentane to afford the title compound as a colourless oil (53 mg, 84%, Z/E-Ratio: 1:2.9).
\( ^1 \text{H} \text{NMR (400 MHz, CDCl}_3 \): for E isomer } \delta = 7.37 – 7.33 \text{ (m, 2H), 7.07 – 7.02 (m, 2H), 5.97 (q, } J = 1.3 \text{ Hz, 1H), 2.26 (s, 3H), 2.13 (d, } J = 1.3 \text{ Hz, 3H); for Z isomer } \delta = 7.32 – 7.28 \text{ (m, 2H), 7.02 – 6.97 (m, 2H), 6.21 (q, } J = 0.4 \text{ Hz, 1H), 2.39 (s, 3H), 2.10 (d, } J = 0.4 \text{ Hz, 3H) } \\

\( ^{13} \text{C} \text{NMR (100 MHz, CDCl}_3 \): for E isomer } \delta = 161.8 \text{ (d, } J = 247 \text{ Hz), 136.6 (d, } J = 3.2 \text{ Hz), 132.8, 129.4 \text{ (d, } J = 7.9 \text{ Hz), 124.2 (d, } J = 1.2 \text{ Hz), 115.1 (d, } J = 21 \text{ Hz), 25.0, 18.2; for Z isomer } \delta = 161.9 \text{ (d, } J = 247 \text{ Hz), 138.2 (d, } J = 3.2 \text{ Hz), 132.2, 126.7 (d, } J = 7.9 \text{ Hz), 125.3 (d, } J = 1.2 \text{ Hz), 115.2 (d, } J = 21 \text{ Hz), 17.8, 17.4.} \\

\text{HRMS (ESI) } m/z \text{ calc. for } C_{10}H_{11}FS [M]^+ 182.0565, \text{ found 182.0560.} \\

\text{General Procedure C} \\
\begin{align*}
\text{MeO}_2\text{C} & \quad + \quad \text{R-S-S-R} \\
\text{fac-Ir(ppy)}_3 & \quad \text{DABCO, DMSO,} \\
\text{MeCN} & \quad 10 \text{ W blue LEDs} \\
\text{24 h} & \quad \text{MeO}_2\text{C} \\
\end{align*}

\text{Methyl 4-iodobenzoate 5 (0.3 mmol, 1.0 equiv.), dialkyl disulfide (1.2 mmol, 4.0 equiv.), 1,4-diazabicyclo[2.2.2]octane (1.2 mmol, 4.0 equiv.), Ir(ppy)}_3 \text{ (6 } \mu \text{mol, 2 mol%) and DMSO (50.5 } \mu \text{L, 2.0 equiv.) were placed in a 4 mL scintillation vial and taken up in MeCN (3 mL). The vial was sealed with a plastic screw cap and stirred for 24 h at room temperature whilst being irradiated with 10 W blue LEDs. The reaction mixture was concentrated under reduced pressure and the residue was purified by flash chromatography on silica to afford the final product.}
Product Characterisation Data

Methyl 4-(ethylthio)benzoate (40): prepared according to general procedure C with diethyl disulfide; purified by flash chromatography, eluting with 10% Et₂O/n-pentane to afford the title compound as a white solid (36 mg, 61%).

\[ ^1H \text{ NMR (400 MHz, CDCl}_3 \] \( \delta = 7.93 \text{ (d, } J = 8.5 \text{ Hz, 2H}), 7.28 \text{ (d, } J = 8.5 \text{ Hz, 2H}), 3.90 \text{ (s, 3H)}, 3.02 \text{ (q, } J = 7.5 \text{ Hz, 2H}), 1.37 \text{ (t, } J = 7.5 \text{ Hz, 3H}). \]

\[ ^13C \text{ NMR (100 MHz, CDCl}_3 \] \( \delta = 167.0, 144.2, 130.0, 126.4, 52.2, 26.3, 14.1. \)

HRMS (ESI) \( m/z \) calc. for C₁₄H₂₀OS \([M]^+\) 196.0612, found 196.0611.

Methyl 4-(butylthio)benzoate (41): prepared according to general procedure C with dibutyl disulfide; purified by flash chromatography, eluting with 10% Et₂OAc/n-pentane to afford the title compound (33 mg, 49%).

\[ ^1H \text{ NMR (400 MHz, CDCl}_3 \] \( \delta = 7.89 \text{ (d, } J = 8.0 \text{ Hz, 1H}), 7.25 \text{ (d, } J = 8.4 \text{ Hz, 2H}), 3.87 \text{ (s, 3H)}, 2.96 \text{ (t, } J = 7.2 \text{ Hz, 2H}), 1.62-1.70 \text{ (m, 2H), 1.41-1.50 (m, 2H), 0.92 (t, } J = 7.2 \text{ Hz 3H}). \]

\[ ^13C \text{ NMR (100 MHz, CDCl}_3 \] \( \delta = 166.9, 144.6, 130.0, 126.7, 126.4, 52.2, 30.9, 22.1, 13.8. \)

Data matched that reported in the literature.\(^{18}\)
Methyl 4-(hexylthio)benzoate (42): prepared according to general procedure C with dihexyl disulfide; purified by flash chromatography, eluting with 10% Et₂OAc/n-pentane to afford the title compound (32 mg, 42%).

\[ \delta = 7.91 \ (d, J = 8.8 \text{ Hz}, 1H), \ 7.28 \ (d, J = 8.0 \text{ Hz}, 2H), \ 3.89 \ (s, 3H), \ 2.98 \ (t, J = 7.2 \text{ Hz}, 2H), \ 1.65-1.73 \ (m, 2H), \ 1.43-1.48 \ (m, 2H), \ 1.25-1.32 \ (m, 4H), \ 0.89 \ (t, 7.2 \text{ Hz}, 3H). \]

\[ \delta = 166.99, 144.6, 130.0, 126.6, 126.4, 52.2, 32.2, 31.5, 29.86, 28.7, 22.7, 14.2. \]

HRMS (ESI) m/z calc. for C\textsubscript{14}H\textsubscript{20}OS [M]+ 252.1221, found 252.1220.

Methyl 4-((2-methoxy-2-oxoethyl)thio)benzoate (43): prepared according to general procedure C with dimethyl 2,2'-disulfanediyldiacetate; purified by flash chromatography, eluting with 5% Et₂OAc/n-pentane to afford the title compound (22 mg, 31%).

\[ \delta = 7.50 \ (d, J = 8.6 \text{ Hz}, 1H), \ 7.58 \ (d, J = 8.4 \text{ Hz}, 2H), \ 3.91 \ (s, 3H), \ 3.58 \ (s, 3H), \ 3.51 \ (s, 2H). \]

\[ \delta = 169.0, 166.5, 142.4, 130.2, 128.6, 126.3, 52.4, 52.1, 40.5, 30.3, 29.6. \]

HRMS (ESI) m/z calc. for C\textsubscript{11}H\textsubscript{12}O\textsubscript{4}S [M]+ 140.9998, found 140.9996.
Methyl 4-((2-((tert-butoxycarbonyl)amino)ethyl)thio)benzoate (44); prepared according to general procedure C with Boc-protected 2,2'-dithio-bis(ethylamine); purified by flash chromatography, eluting with 2% Et₂OAc/n-pentane to afford the title compound (44 mg, 47%).

^1^H NMR (400 MHz, CDCl₃): δ = 7.92 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 8.4 Hz, 2H), 4.9 (s, 1H), 3.80 (s, 3H), 3.36 (q, J = 6.4 Hz, 2H), 3.10 (t, J = 6.4 Hz, 2H), 1.42 (s, 3H).

^1^C NMR (400 MHz, CDCl₃): δ = 166.8, 155.8, 142.8, 130.2, 127.0, 79.7, 52.2, 39.7, 32.7, 32.5, 29.8, 28.5.

HRMS (ESI) m/z calc. for C₁₅H₂₁O₄NS [M]^+ 311.1186, found 311.1186.

Synthesis of semiochemicals

Compound 48 was synthesised according to the general procedure A. 2-Iodophenol (52) (66 mg, 0.3 mmol), dimethyl disulfide (0.108 mL, 1.2 mmol), 1,4-diazabicyclo[2.2.2]octane (135 mg, 1.2 mmol), Ir(ppy)₃ (4 mg, 6 µmol) and DMSO (50.5 µL, 0.6 mmol) were placed in a 4 mL scintillation vial and taken up in MeCN (3 mL). The vial was sealed with a plastic screw cap and stirred for 24 h at room temperature whilst being irradiated with 10 W blue LEDs. The solvent was removed under reduced pressure and the residue was purified by flash
chromatography on silica, eluting with 5 % Et$_2$O/n-pentane to afford 2-(methylthio)phenol 48 as a yellowish oil (39 mg, 93% yield).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.48$ (dd, $J = 6.0$ & 1.6 Hz, 1H), 7.25 (td, $J = 6.0$ & 2.0 Hz, 1H), 6.92 (d, $J = 6.8$ Hz, 1H), 6.82 (td, $J = 6.4$ & 1.6 Hz, 1H), 6.40 (s, 1H). 2.33 (s, 3H).

$^{13}$C NMR (400 MHz, CDCl$_3$): $\delta = 156.2, 134.8, 130.7, 120.9, 114.8, 19.8$.

Data matched that reported in the literature.$^{19}$

Compound 54 was synthesised according to the general procedure A. 2-1odo-1,4-dimethoxybenene (53) (79 mg, 0.3 mmol), dimethyl disulfide (0.108 mL, 1.2 mmol), 1,4-diazabicyclo[2.2.2]octane (135 mg, 1.2 mmol), Ir(ppy)$_3$ (4 mg, 6 $\mu$mol) and DMSO (50.5 $\mu$L, 0.6 mmol) were placed in a 4 mL scintillation vial and taken up in MeCN (3 mL). The vial was sealed with a plastic screw cap and stirred for 24 h at room temperature whilst being irradiated with 10 W blue LEDs. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica, eluting with 2 % Et$_2$O/n-pentane to afford 2-(methylthio)-1,4-dimethoxybenzene as a yellowish oil (40 mg, 72% yield).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 6.77$ (d, $J = 8.2$ Hz, 1H), 6.74 (d, $J = 3.2$ Hz, 1H), 6.62 (dd, $J = 6.8$ Hz, $J = 3.2$ Hz, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 2.43 (s, 3H).

$^{13}$C NMR (400 MHz, CDCl$_3$): $\delta = 156.2, 154.2, 134.8, 130.7, 120.9, 114.8, 56.2, 53.2, 19.8$. 

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S24
A solution of BBr$_3$ in CH$_2$Cl$_2$ (1 M, 2.1 mL, 2.1 mmol) was added dropwise, at -78 °C, to a solution of 4-methoxy-3-(methylthio)benzaldehyde (54) (40 mg, 0.21 mmol) in CH$_2$Cl$_2$ (1 mL). The reaction mixture was stirred at room temperature for 5 h. It was quenched with water and extracted with CH$_2$Cl$_2$ (3 × 10 mL). The combined organic extracts were washed with brine (3 × 30 mL) and dried (MgSO$_4$). The solvent was removed under reduced pressure and the residue purified by flash chromatography on silica, eluting with 10% EtOAc/n-pentane, to give 1,4-dihydroxy-2-(methylthio)benzene (49) as a oil (29 mg, 85% yield).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 6.95 (d, $J$ = 2.8 Hz, 1H), 6.88 (d, $J$ = 8.4 Hz, 1H), 6.77 (d, $J$ = 4.0 Hz, 1H), 6.74-6.75 (m, 2H), 6.16 (s, 1H). 2.38 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 149.1, 141.1, 118.1, 112.5, 111.8, 108.6, 19.9.

Data matched that reported in the literature.$^{19}$

Compound 56 was synthesised according to the general procedure A. 3-Iodo-4-methoxybenzaldehyde (55) (79 mg, 0.3 mmol), dimethyl disulfide (0.108 mL, 1.2 mmol), 1,4-diazabicyclo[2.2.2]octane (135 mg, 1.2 mmol), Ir(ppy)$_3$ (4 mg, 6 $\mu$mol) and DMSO (50.5 $\mu$L, 0.6 mmol) were placed in a 4 mL scintillation vial and taken up in MeCN (3 mL). The vial was sealed with a plastic screw cap and stirred for 24 h at room temperature whilst being irradiated with 10 W blue LEDs. The solvent was removed under reduced pressure and the
residue was purified by flash chromatography on silica, eluting with 10% Et₂O/n-pentane to afford 4-methoxy-3-(methylthio)benzaldehyde (56) as a colourless oil (45 mg, 83% yield).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 9.87\) (s, 1H), 7.67-7.63 (m, 2H), 6.94 (d, \(J = 8.2\) Hz, 1H), 3.98 (s, 3H), 2.49 (s, 3H).

\(^{13}\)C NMR (400 MHz, CDCl\(_3\)): \(\delta = 190.8, 160.8, 130.5, 130.0, 129.6, 125.2, 109.5, 56.4, 14.4\).

Data matched that reported in the literature.\(^{19}\)

A solution of BBr\(_3\) in CH\(_2\)Cl\(_2\) (1 M, 2.7 mL, 2.7 mmol) was added dropwise, at -78 °C, to a solution of 4-methoxy-3-(methylthio)benzaldehyde (56) (50 mg, 0.27 mmol) in CH\(_2\)Cl\(_2\) (1 mL). The reaction mixture was stirred at room temperature for 3 h. It was quenched with water and extracted with CH\(_2\)Cl\(_2\) (3 × 10 mL). The combined organic extracts were washed with brine (3 × 30 mL) and dried (MgSO\(_4\)). The solvent was removed under reduced pressure and the residue purified by flash chromatography on silica, eluting with 20% EtOAc/n-pentane, to give 4-hydroxy-3-(methylthio)benzaldehyde (50) as a white solid (34 mg, 75% yield).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 9.84\) (s, 1H), 8.02 (d, \(J = 2.1\) Hz, 1H), 7.77 (dd, \(J = 8.4, 2.1\) Hz, 1H), 7.35 (br s, 1H), 7.09 (d, \(J = 8.4\) Hz, 1H), 2.38 (s, 3H).

\(^{13}\)C NMR (400 MHz, CDCl\(_3\)): \(\delta = 190.4, 161.4, 136.3, 132.7, 130.4, 123.0, 115.5, 19.5\).

HRMS (ESI) \(m/z\) calc. for C\(_8\)H\(_9\)O\(_2\)S [M+H]\(^+\) 169.0323, found 169.0318.
Sodium borohydride (8 mg, 0.21 mmol) was added in small portions to a solution of 4-hydroxy-3-(methylthio)benzaldehyde (50) (30 mg, 0.18 mmol) in MeOH (1 mL) and the reaction mixture was stirred at room temperature for 14 h. It was quenched with AcOH and concentrated under reduced pressure. The residue was dissolved in CH₂Cl₂ (10 mL), washed with brine (3 × 10 mL), and dried (MgSO₄). The solvent was removed under reduced pressure and the residue purified by flash chromatography by on silica, eluting with 30% EtOAc/n-pentane, to give 4-(hydroxymethyl)-2-(methylthio)phenol (51) as a yellowish solid (27 mg, 90% yield).

¹H NMR (400 MHz, CDCl₃): δ = 7.50 (d, J = 2.1 Hz, 1H), 7.24 (dd, J = 8.3, 2.1 Hz, 1H), 6.96 (d, J = 8.3 Hz, 1H), 6.63 (br s, 1H), 4.60 (s, 2H), 2.34 (s, 3H).

¹³C NMR (400 MHz, CDCl₃): δ = 155.8, 133.6, 133.5, 129.8, 121.1, 114.9, 64.8, 19.8.

HRMS (ESI) m/z calc. for C₉H₁₁O₂S [M+H]⁺ 171.0480, found 171.0474.
Mechanistic Studies

Control experiments

Table S1. The effect of DABCO concentration, light and photocatalyst

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</table>

[a] General conditions: 5 (0.3 mmol), fac-Ir(ppy)_3 (2 mol%), solvent (0.1 M in substrate), 24 h, 10 W blue LEDs; b Yields determined by ¹H NMR spectroscopic analysis using 2,5-dimethylfuran as an internal standard;

Phosphorescence quenching measurements

Samples for steady-state and time-resolved photoluminescence were prepared in the following manner. Dimethyl disulfide was added to an acetonitrile solution of Ir(ppy)_3 (0.01 mM) and made to a given concentration in a volumetric flask. The solution was then transferred to a septum-capped quartz cuvette and deoxygenated immediately prior to measurement by sparging with argon for approximately 10 min. A pre-weighed amount of DABCO or methyl 4-iodobenzoate was dissolved in an acetonitrile solution of Ir(ppy)_3 (0.01 mM) and made to a given concentration in a volumetric flask. The solution was then
transferred to a septum-capped quartz cuvette and deoxygenated immediately prior to measurement by sparging with argon for approximately 10 min.

**Figure S2.** Stern-Volmer plot of Ir(ppy)$_3$ phosphorescence intensity in the presence of methyl 4-iodobenzoate (■), DABCO (▲), dimethyl disulfide (●).

**Transient absorption spectroscopy (TAS) measurements**

Dimethyl disulfide was added to an acetonitrile solution of Ir(ppy)$_3$ (0.1 mM) and made to a given concentration in a volumetric flask. Pre-weighed amounts of either DABCO or methyl 4-iodobenzoate were dissolved in an acetonitrile solution of Ir(ppy)$_3$ (0.1 mM) and made to a given concentration in a volumetric flask. Solutions were deoxygenated immediately prior to measurement by sparging with argon for approximately 6 min.
**Figure S3.** Transient absorption difference spectra of Ir(ppy)$_3$ (0.1 mM) with addition of DABCO (20 mM) recorded at various delay times after excitation. Solutions were prepared in acetonitrile and sparged with argon (6 min) before measurement; $\lambda_{ex} = 355$ nm.

**Figure S4.** Transient absorption difference spectra of Ir(ppy)$_3$ (0.1 mM) with addition of dimethyl disulfide (20 mM) recorded at various delay times after excitation. Solutions were prepared in acetonitrile and sparged with argon (6 min) before measurement; $\lambda_{ex} = 355$ nm.
Disulfide exchange experiments

**Figure S5.** Absorbance spectra of 10 mM dimethyl, diethyl and diphenyl disulfides in acetonitrile, overlaid with the spectral output for the blue LED lamp (see Figure S1). Only absorbance spectrum of diphenyl disulfide (blue trace) overlaps with the emission spectrum of the blue LED lamp (grey area).
$^1$H NMR and $^{13}$C NMR Spectra

CDCl$_3$, 400 MHz

CDCl$_3$, 100 MHz
12

CDCl₃, 400 MHz

12

CDCl₃, 100 MHz
CDCl₃, 400 MHz

CDCl₃, 100 MHz
CDCl₃, 400 MHz

CDCl₃, 100 MHz
CDCl$_3$, 400 MHz

CDCl$_3$, 100 MHz
CDCl$_3$, 400 MHz

CDCl$_3$, 100 MHz
$^{31}$ \text{CDCl}_3, 400 MHz

$^{31}$ \text{CDCl}_3, 100 MHz
CDCl₃, 400 MHz

CDCl₃, 100 MHz
CDCl₃, 400 MHz

CDCl₃, 100 MHz
CDCl₃, 400 MHz

CDCl₃, 100 MHz
CDCl₃, 400 MHz

CDCl₃, 100 MHz
CDCl₃, 400 MHz

CDCl₃, 100 MHz
References