Electronic Supplementary Material (ESI) for *Green Chemistry*
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Supplementary Information for

Eosin Y catalyzed difunctionalization of styrenes using O_2 and CS_2: a direct access to 1,3-oxathiolane-2-thiones

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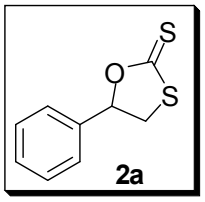
I. General Information: All commercially available reagents were used without further purification unless otherwise specified by a reference. Solvents were purified by the usual methods and stored over molecular sieves. All reactions were performed using oven-dried glassware. Organic solutions were concentrated using a Buchi rotary evaporator. Column chromatography was carried out over silica gel (Merck 100–200 mesh) and TLC was performed using silica gel GF254 (Merck) plates. IR spectra in KBr/neat were recorded on a Perkin-Elmer 993 IR spectrophotometer and ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra were recorded on a Bruker AVII spectrometer in $CDCl_3$ using TMS as internal reference. All chemical shifts are reported in δ/ppm and coupling constants (*J*) in Hertz (Hz). MS (EI) spectra were recorded on double focusing mass spectrometer. Green LEDs (2.50 W, λ = 535 nm) Rebel LED, mounted on a 25 mm cool base was purchased from commercial supplier Luxeon Star LEDs Quadica Developments Inc. 47 6th Concession Rd. Brantford, Ontario N 32 5L7 Canada.

II. General procedure for the synthesis of 1,3-oxathiolane-2-thiones (cyclic dithiocarbonates) 2 (Table 3): CS_2 (1.0 mmol), Cs_2CO_3 (1.0 equiv.) and MeOH (3 mL) were taken in a closed flask and stirred at room temperature for 3 h, to complete the formation of cesium methyl xanthate ($MeO{-}\overset{\overset{S}{\|}}{C}{-}S^{-}Cs^{+}$). Then, styrene **1** (1.0 mmol) and eosin Y (2 mol%) were added to the open flask and the reaction mixture was irradiated with green LEDs [2.50 W, λ = 535 nm] for 8-10 h in open air under stirring at room temperature. After

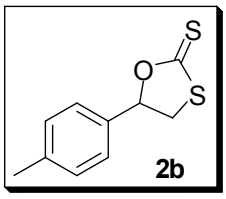
the completion of reaction (as indicated by TLC), it was quenched with water (5 mL) and extracted with ethyl acetate (3 × 5 mL). The organic phase was dried over anhydrous magnesium sulfate and concentrated under reduced pressure to yield the crude product, which was purified by silica gel column chromatography using a mixture of EtOAc-Hexane to give the pure product **2** in high yields (Table 3).

The structure of the products was confirmed by IR, ^{1}H NMR, ^{13}C NMR and MS spectral data.

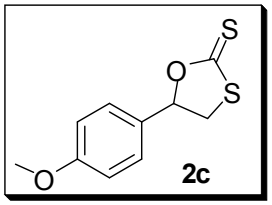
III. Characterization data of compounds **2** are summarized below:



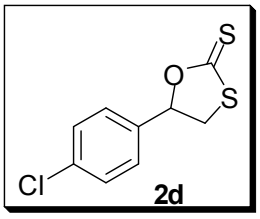
Compound 2a:[1] IR (neat): 1753, 1612, 1585, 1490, 1405, 1184, 723 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.50-7.43 (m, 2H), 7.40-7.32 (m, 3H), 5.31 (dd, 1H $|^{3}J_{HH}|$ 9 Hz, $|^{3}J_{HH}|$ 6 Hz), 3.85 (dd, 1H $|^{2}J_{HH}|$ 11 Hz, $|^{3}J_{HH}|$ 6 Hz), 3.78 (dd, 1H $|^{2}J_{HH}|$ 11 Hz, $|^{3}J_{HH}|$ 9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 211.7, 134.9, 133.0, 130.2, 129.0, 87.4, 46.3. HRMS (EI) calcd. for $C_9H_8OS_2$: 196.0017, found 196.0015.



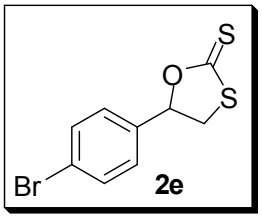
Compound 2b: IR (neat): 2922, 2856, 1714, 1687, 1637, 1570, 1456, 1387, 1123, 857, 672 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.49 (d, 2H $|^{3}J_{HH}|$ 9 Hz), 7.02 (d, 2H $|^{3}J_{HH}|$ 9 Hz), 5.33 (dd, 1H $|^{3}J_{HH}|$ 9 Hz, $|^{3}J_{HH}|$ 6 Hz), 3.84 (dd, 1H $|^{2}J_{HH}|$ 11 Hz, $|^{3}J_{HH}|$ 6 Hz), 3.77 (dd, 1H $|^{2}J_{HH}|$ 11 Hz, $|^{3}J_{HH}|$ 9 Hz), 2.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 213.5, 134.6, 132.0, 130.1, 129.3, 86.9, 47.1, 21.1. HRMS (EI): calcd. for $C_{10}H_{10}OS_2$: 210.0173, found 210.0170.



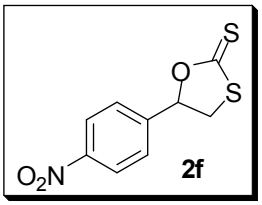
Compound 2c: IR (KBr): 2920, 2839, 1747, 1683, 1630, 1509, 1463, 1259, 1173, 1025, 830 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.32 (d, 2H $|^3J_{HH}|$ 9 Hz), 6.90 (d, 2H $|^3J_{HH}|$ 9 Hz), 5.33 (dd, 1H $|^3J_{HH}|$ 9 Hz, $|^3J_{HH}|$ 6 Hz), 3.78 (s, 3H), 3.63 (dd, 1H $|^2J_{HH}|$ 11 Hz, $|^3J_{HH}|$ 6 Hz), 3.49 (dd, 1H $|^2J_{HH}|$ 11 Hz, $|^3J_{HH}|$ 9 Hz); ^{13}C NMR spectra. ($CDCl_3$, 100 MHz): δ = 214.7, 158.5, 132.7, 127.4, 114.7, 87.2, 55.3, 46.8. HRMS (EI) calcd. for $C_{10}H_{10}O_2S_2$: 226.0122, found 226.0123.



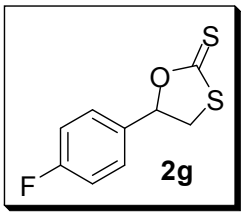
Compound 2d: IR (KBr): 1720, 1630, 1429, 1138, 1057, 834, 729 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.45 (d, 2H $|^3J_{HH}|$ 9 Hz), 7.31 (d, 2H $|^3J_{HH}|$ 9 Hz), 5.37 (dd, 1H $|^3J_{HH}|$ 9 Hz, $|^3J_{HH}|$ 6 Hz), 3.62 (dd, 1H $|^2J_{HH}|$ 11 Hz, $|^3J_{HH}|$ 6 Hz), 3.43 (dd, 1H $|^2J_{HH}|$ 11Hz, $|^3J_{HH}|$ 9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 210.7, 138.3, 133.4, 128.4, 126.7, 87.5, 46.5. HRMS (EI) calcd. for $C_9H_7ClOS_2$: 229.9627, found 229.9624.



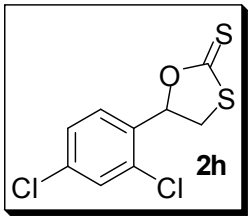
Compound 2e: IR (KBr): 1722, 1637, 1449, 1257, 1196, 1040, 831, 673 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.43 (d, 2H, $|^3J_{HH}|$ 9 Hz), 7.30 (d, 2H $|^3J_{HH}|$ 9 Hz), 5.34 (dd, 1H $|^3J_{HH}|$ 9 Hz, $|^3J_{HH}|$ 6 Hz), 3.60 (dd, 1H $|^2J_{HH}|$ 11 Hz, $|^3J_{HH}|$ 6 Hz), 3.42 (dd, 1H $|^2J_{HH}|$ 11 Hz, $|^3J_{HH}|$ 9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 212.9, 138.5, 131.7, 127.8, 115.2, 87.0, 47.0. HRMS (EI): calcd. for $C_9H_7BrOS_2$ 273.9122, found 273.9124.



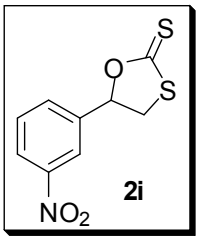
Compound 2f: IR (KBr): 1706, 1662, 1595, 1541, 1445, 1407, 1337, 1147, 1081, 781 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.15 (d, 2H $|^3J_{HH}|$ 9 Hz), 7.58 (d, 2H $|^3J_{HH}|$ 9 Hz), 5.47 (dd, 1H $|^3J_{HH}|$ 9 Hz, $|^3J_{HH}|$ 6 Hz), 3.68 (dd, 1H $|^2J_{HH}|$ 11 Hz, $|^3J_{HH}|$ 6 Hz), 3.47 (dd, 1H $|^2J_{HH}|$ 11 Hz, $|^3J_{HH}|$ 9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 209.3, 147.1, 145.4, 128.8, 124.3, 87.4, 48.2. HRMS (EI): calcd. for $C_9H_7NO_3S_2$: 240.9867, found 240.9866.



Compound 2g: IR (KBr): 1732, 1412, 1137, 1057, 921, 850 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.53-7.46 (m, 2H), 7.29-7.23 (m, 2H), 5.42 (dd, 1H $|^3J_{HH}|$ 9 Hz, $|^3J_{HH}|$ 6 Hz), 3.65 (dd, 1H $|^2J_{HH}|$ 11 Hz, $|^3J_{HH}|$ 6 Hz), 3.47 (dd, 1H $|^2J_{HH}|$ 11 Hz, $|^3J_{HH}|$ 9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 211.6, 160.3, 135.9, 126.4, 115.0, 85.2, 47.5. HRMS (EI) calcd. for $C_9H_7FOS_2$: 213.9922, found 213.9920.

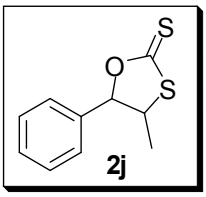


Compound 2h: IR (KBr): 1726, 1563, 1425, 1405, 1123, 1032, 837, 674 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.65 (s, 1H), 7.36 (d, 1H $|^3J_{HH}|$ 8 Hz), 7.24 (d, 1H, $|^3J_{HH}|$ 8 Hz), 5.45 (dd, 1H $|^3J_{HH}|$ 9 Hz, $|^3J_{HH}|$ 6 Hz), 3.68 (dd, 1H $|^2J_{HH}|$ 11 Hz, $|^3J_{HH}|$ 6 Hz), 3.42 (dd, 1H $|^2J_{HH}|$ 11 Hz, $|^3J_{HH}|$ 9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 208.9, 136.0, 134.2, 133.0, 130.8, 128.7, 127.6, 82.9, 47.8. HRMS (EI) calcd. for $C_9H_6Cl_2OS_2$: 263.9237, found 263.9235.



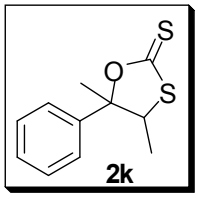
2i

Compound 2i: IR (KBr): 1715, 1639, 1526, 1434, 1417, 1142, 1087, 787 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.24 (s, 1H), 8.22 (dd, 1H $|^3J_{HH}|$ 8 Hz, $|^4J_{HH}|$ 2 Hz), 7.76 (m, 1H), 7.61 (t, 1H $|^3J_{HH}|$ 8 Hz), 5.48 (dd, 1H, $|^3J_{HH}|$ 9 Hz, $|^3J_{HH}|$ 6 Hz), 3.51 (dd, 1H $|^2J_{HH}|$ 11 Hz, $|^3J_{HH}|$ 6 Hz), 3.46 (dd, 1H $|^2J_{HH}|$ 11 Hz, $|^3J_{HH}|$ 9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 210.4, 149.2, 139.7, 132.5, 131.3, 123.7, 121.4, 82.7, 46.9. HRMS (EI): calcd. for $C_9H_7NO_3S_2$: 240.9867, found 240.9865.



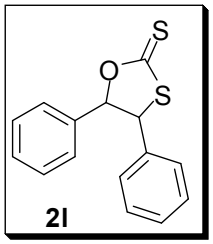
2j

Compound 2j: IR (neat): 2954, 2867, 1709, 1646, 1416, 1394, 1123, 1059, 852, 775 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.34-7.21 (m, 2H), 7.04-6.89 (m, 3H), 5.37 (d, 1H, $|^3J_{HH}|$ 6 Hz), 3.14 (m, 1H), 1.36 (d, 3H, $|^3J_{HH}|$ 6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 212.1, 137.3, 128.6, 127.9, 126.0, 90.7, 49.8, 13.6. HRMS (EI) calcd. for $C_{10}H_{10}OS_2$: 210.0173, found 210.0172.

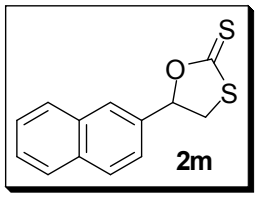


2k

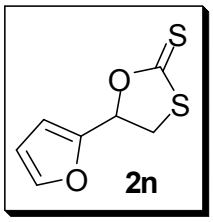
Compound 2k: IR (neat): 2952, 2849, 1716, 1630, 1431, 1351, 1117, 1053, 819, 710 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.42-6.98 (m, 5H), 3.08 (m, 1H), 1.33 (s, 3H), 1.26 (d, 3H, $|^3J_{HH}|$ 6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 211.1, 139.3, 128.9, 128.2, 126.0, 93.1, 57.2, 21.6, 12.9. HRMS (EI) calcd. for $C_{11}H_{12}OS_2$: 224.0330, found 224.0329.



Compound 2l:[1] IR (KBr): 1709, 1481, 1437, 1354, 1140, 1059, 853, 776 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.38-7.29 (m, 7H), 7.26-6.97 (m, 3H), 5.53 (d, 1H $|^{3}J_{HH}|$ 6 Hz), 4.34 (d, 1H $|^{3}J_{HH}|$ 6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 213.1, 139.8, 138.9, 129.6, 129.4, 128.3, 128.0, 127.6, 127.4, 91.2, 58.7. HRMS (EI) calcd. for $C_{15}H_{12}OS_2$: 272.0330, found 272.0330.

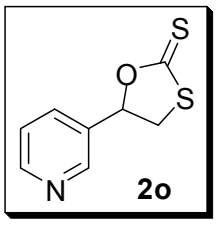


Compound 2m: IR (KBr): 1714, 1445, 1423, 1117, 1043, 910, 772 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.98-7.83 (m, 3H), 7.56 (s, 1H), 7.32-6.96 (m, 3H), 5.46 (dd, 1H $|^{3}J_{HH}|$ 9 Hz, $|^{3}J_{HH}|$ 6 Hz), 3.49 (dd, 1H $|^{2}J_{HH}|$ 11 Hz, $|^{3}J_{HH}|$ 6 Hz), 3.46 (dd, 1H $|^{2}J_{HH}|$ 11 Hz, $|^{3}J_{HH}|$ 9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 213.6, 134.0, 133.7, 128.0, 128.3, 127.6, 127.2, 126.7, 126.3, 125.5, 123.6, 89.4, 49.1. HRMS (EI) calcd. for $C_{13}H_{10}OS_2$: 246.0173, found 246.0172.



Compound 2n: IR (KBr): 1702, 1427, 1407, 1123, 1053, 828, 728, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.59 (s, 1H), 7.63-7.41 (m, 2H), 5.34 (dd, 1H $|^{3}J_{HH}|$ 9 Hz, $|^{3}J_{HH}|$ 6 Hz), 3.48 (dd, 1H $|^{2}J_{HH}|$ 11 Hz, $|^{3}J_{HH}|$ 6 Hz), 3.42 (dd, 1H $|^{2}J_{HH}|$ 11 Hz, $|^{3}J_{HH}|$ 9 Hz); ^{13}C

NMR ($CDCl_3$, 100 MHz): δ = 214.0, 152.3, 140.7, 109.7, 109.2, 87.9, 45.7. HRMS (EI) calcd. for $C_7H_6O_2S_2$: 185.9809, found 185.9806.



Compound 2o: IR (KBr): 3203, 3040, 1724, 1640, 1481, 1413, 1117, 1053, 828, 721, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.43 (s, 1H), 7.76-7.59 (m, 3H), 5.36 (dd, 1H $|^3J_{HH}|$ 9 Hz, $|^3J_{HH}|$ 6 Hz), 3.49 (dd, 1H $|^2J_{HH}|$ 11 Hz, $|^3J_{HH}|$ 6 Hz), 3.42 (dd, 1H $|^2J_{HH}|$ 11 Hz, $|^3J_{HH}|$ 9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 207.8, 147.2, 145.7, 138.8, 132.5, 123.6, 87.5, 47.6. HRMS (EI) calcd. for $C_8H_7NOS_2$: 196.9969, found 196.9967.

References: 1. (*a*) I. Yavari, M. G. Darjani, Z. Hossaini, M. Sabbaghan and N. Hosseini, *Synlett*, 2008, 889; (*b*) N. Kihara, Y. Nakawaki and T. Endo, *J. Org. Chem*., 1995, **60**, 473.