

Supporting Information

Metal-free oxysulfenylation of alkenes with **1-(arylton)pyrrolidine-2,5-diones and alcohols**

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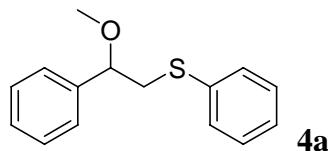
General experimental procedures

All reactions were carried out under nitrogen atmosphere. Proton and carbon magnetic resonance spectra (¹H NMR and ¹³C NMR) were recorded using tetramethylsilane (TMS) in the solvent of CDCl₃ as the internal standard (¹H NMR: TMS at 0.00 ppm, CDCl₃ at 7.26 ppm; ¹³C NMR: CDCl₃ at 77.26 ppm).

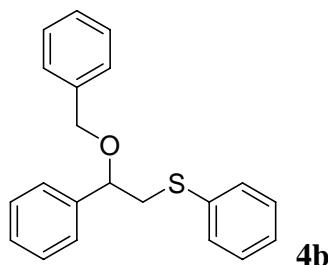
General procedure for synthesis of compounds 4a-ai

A 25 mL Schlenk tube was charged with a magnetic stirrer, alkene (**1**) (0.2 mmol), 1-(arylthio)pyrrolidine-2,5-dione (**2**) (0.3 mmol for entries 1-13, 18-26 and 28-31; 0.5 mmol for entries 14-17; 0.6 mmol for entry 27 in Table 2 of Text), alcohol (**3**) (4.0 mmol for entry 27; 2.0 mmol for the others in Table 2 of Text) and CHCl₃ (1.0 mL) were added to the tube. The tube was sealed, and the mixture was stirred at 80-140 °C till the reaction completed (TLC determination). The resulting mixture was cooled to room temperature, the solvent was removed by a rotary evaporator, and the residue was purified by column chromatography on silica gel using petroleum ether/ ethyl acetate as eluent to give the desired target product (**4**).

Characterization data of compounds 4a-ai

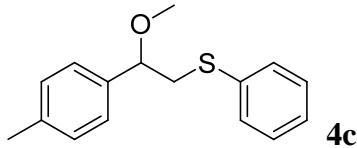


(2-Methoxy-2-phenylethyl)(phenyl)sulfane (4a). Eluent: petroleum ether/ethyl acetate (25:1). Yield 43 mg (88%). Colorless film. ¹H NMR (400 MHz, CDCl₃) δ 7.38-7.32 (m, 6H), 7.30-7.27 (m, 2H), 7.20-7.17 (m, 1H), 4.33-4.30 (m, 1H), 3.33 (dd, *J* = 13.2 Hz, *J* = 8.2 Hz, 1H), 3.27 (s, 3H), 3.14 (dd, *J* = 13.3 Hz, *J* = 4.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 140.6, 136.8, 129.5, 129.0, 128.7, 128.3, 126.9, 126.1, 82.6, 57.2, 41.7. EI-MS: [M]⁺ m/z 244.3.

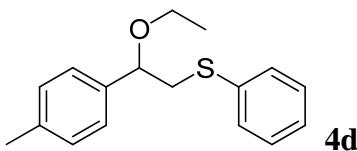


(2-(Benzylxy)-2-phenylethyl)(phenyl)sulfane (4b). Eluent: petroleum ether/ethyl acetate (25:1). Yield 45 mg (70%). Colorless film. ¹H NMR (400 MHz, CDCl₃) δ

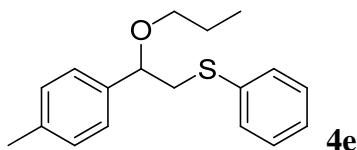
7.44-7.43 (m, 5H), 7.38-7.36 (m, 7H), 7.32-7.19 (m, 3H), 4.63-4.55 (m, 2H), 4.37 (d, J = 11.8 Hz, 1H), 3.48 (dd, J = 13.3 Hz, J = 8.0 Hz, 1H), 3.12 (dd, J = 13.3 Hz, J = 5.1 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 140.8, 138.2, 136.9, 129.4, 129.0, 128.8, 128.5, 128.4, 128.0, 127.8, 127.1, 126.1, 80.2, 71.0, 41.8. EI-MS: $[\text{M}]^+$ m/z 320.1.



(2-Methoxy-2-(*p*-tolyl)ethyl)(phenyl)sulfane (4c). Eluent: petroleum ether/ethyl acetate (25:1). Yield 48 mg (93%). Colorless film. ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.17 (m, 9H), 4.28 (dd, J = 8.0 Hz, J = 5.1 Hz, 1H), 3.34 (dd, J = 13.2 Hz, J = 8.0 Hz, 1H), 3.25 (s, 3H), 3.34 (dd, J = 13.2 Hz, J = 5.1 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 138.0, 137.6, 136.8, 129.4, 128.9, 126.8, 126.1, 82.4, 57.0, 41.6, 21.3. EI-MS: $[\text{M}]^+$ m/z 258.3.

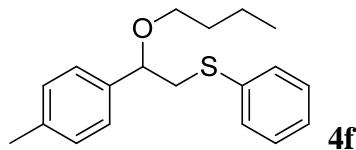


(2-Ethoxy-2-(*p*-tolyl)ethyl)(phenyl)sulfane (4d). Eluent: petroleum ether/ethyl acetate (25:1). Yield 46 mg (86%). Colorless film. ^1H NMR (400 MHz, CDCl_3) δ 7.37-7.33 (m, 2H), 7.29-7.24 (m, 3H), 7.22-7.15 (m, 4H), 4.38 (dd, J = 8.0 Hz, J = 5.3 Hz, 1H), 3.44-3.30 (m, 3H), 3.11 (dd, J = 13.2 Hz, J = 5.3 Hz, 1H), 2.36 (s, 3H), 1.18 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 138.3, 137.8, 136.9, 129.3, 128.9, 126.7, 125.9, 80.6, 64.6, 41.7, 21.3, 15.3. EI-MS: $[\text{M}]^+$ m/z 272.2.

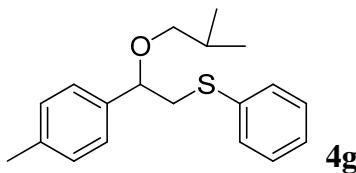


Phenyl(2-propoxy-2-(*p*-tolyl)ethyl)sulfane (4e). Eluent: petroleum ether/ethyl acetate (25:1). Yield 56 mg (99%). Colorless film. ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.35 (m, 2H), 7.30-7.27 (m, 1H), 7.25-7.23 (m, 3H), 7.19-7.17 (m, 3H), 4.39 (dd, J = 8.1 Hz, J = 5.2 Hz, 1H), 3.40-3.22 (m, 3H), 3.12 (dd, J = 13.1 Hz, J = 5.1 Hz, 1H), 2.37 (s, 3H), 1.65-1.53 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 138.4, 137.8, 137.1, 129.3, 129.2, 128.9, 126.7, 125.9, 80.8, 71.0, 41.8, 23.1, 21.3,

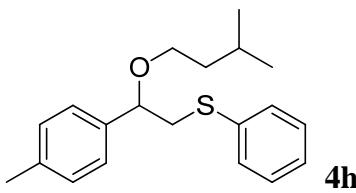
10.8. EI-MS: $[M]^+$ m/z 286.1.



(2-Butoxy-2-(*p*-tolyl)ethyl)(phenyl)sulfane (4f). Eluent: petroleum ether/ethyl acetate (25:1). Yield 55 mg (91%). Colorless film. ^1H NMR (400 MHz, CDCl_3) δ 7.35 (d, $J = 8.2$ Hz, 2H), 7.28-7.24 (m, 7H), 4.37 (dd, $J = 7.9$ Hz, $J = 5.2$ Hz, 1H), 3.38-3.25 (m, 3H), 3.11 (dd, $J = 12.8$ Hz, $J = 5.0$ Hz, 1H), 2.35 (s, 3H), 1.57-1.50 (m, 2H), 1.41-1.33 (m, 2H), 0.88 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 138.4, 137.8, 137.1, 129.3, 129.2, 128.9, 126.7, 125.9, 80.8, 69.1, 41.8, 31.9, 21.3, 19.4, 14.0. EI-MS: $[M]^+$ m/z 300.3.

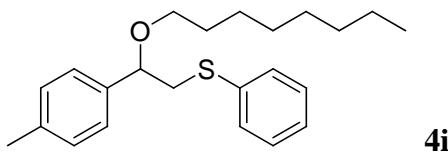


(2-Isobutoxy-2-(*p*-tolyl)ethyl)(phenyl)sulfane (4g). Eluent: petroleum ether/ethyl acetate (25:1). Yield 73 mg (99%). Colorless film. ^1H NMR (400 MHz, CDCl_3) δ 7.37-7.35 (d, $J = 7.1$ Hz, 2H), 7.29-7.17 (m, 7H), 4.37 (dd, $J = 8.2$ Hz, $J = 5.1$ Hz, 1H), 3.36 (dd, $J = 13.2$ Hz, $J = 8.2$ Hz, 1H), 3.14-3.04 (m, 3H), 2.37 (s, 3H), 1.90-1.83 (m, 1H), 0.91-0.89 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 138.4, 137.8, 137.3, 129.3, 129.2, 128.9, 126.8, 125.8, 81.1, 76.2, 41.9, 28.7, 21.3, 19.6, 19.5. EI-MS: $[M]^+$ m/z 300.1.

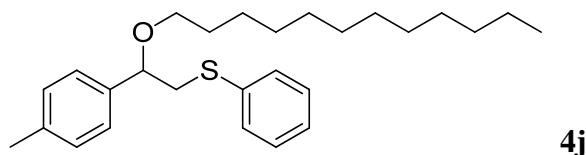


(2-(Isopentyloxy)-2-(*p*-tolyl)ethyl)(phenyl)sulfane (4h). Eluent: petroleum ether/ethyl acetate (25:1). Yield 61 mg (98%). Colorless film. ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.35 (m, 2H), 7.29-7.25 (m, 2H), 7.22-7.16 (m, 5H), 4.38 (dd, $J = 8.1$ Hz, $J = 5.2$ Hz, 1H), 3.40-3.29 (m, 3H), 3.11 (dd, $J = 13.1$ Hz, $J = 5.1$ Hz, 1H), 2.37 (s, 3H), 1.77-1.69 (m, 1H), 1.49-1.42 (m, 2H), 0.89 (d, $J = 6.6$ Hz, 3H), 0.85 (d, $J = 6.6$

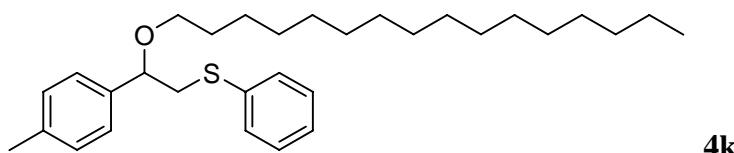
Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 138.4, 137.8, 137.1, 129.3, 129.2, 128.9, 126.7, 125.9, 80.9, 67.7, 41.8, 38.7, 25.0, 22.8, 22.6, 21.3. EI-MS: $[\text{M}]^+$ m/z 314.3.



(2-(Octyloxy)-2-(*p*-tolyl)ethyl)(phenyl)sulfane (4i). Eluent: petroleum ether/ethyl acetate (25:1). Yield 67 mg (95%). Colorless film. ^1H NMR (400 MHz, CDCl_3) δ 7.36-7.34 (m, 2H), 7.28-7.21 (m, 4H), 7.18-7.15 (m, 3H), 4.37 (dd, $J = 8.0$ Hz, $J = 5.3$ Hz, 1H), 3.37-3.24 (m, 3H), 3.11 (dd, $J = 13.1$ Hz, $J = 5.1$ Hz, 1H), 2.36 (s, 3H), 1.57-1.51 (m, 2H), 1.30-1.26 (m, 10H), 0.89 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 138.4, 137.8, 137.1, 129.3, 129.2, 128.9, 126.7, 125.9, 80.8, 69.4, 41.7, 32.0, 29.9, 29.5, 29.4, 26.2, 22.8, 21.3, 14.2. EI-MS: $[\text{M}]^+$ m/z 356.2.

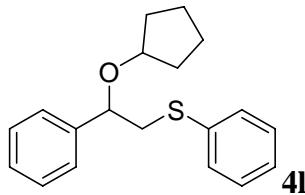


(2-(Dodecyloxy)-2-(*p*-tolyl)ethyl)(phenyl)sulfane (4j). Eluent: petroleum ether/ethyl acetate (25:1). Yield 65 mg (79%). Colorless film. ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.35 (m, 2H), 7.30-7.16 (m, 7H), 4.58 (dd, $J = 8.3$ Hz, $J = 4.9$ Hz, 1H), 3.35-3.18 (m, 2H), 3.11 (dd, $J = 13.1$ Hz, $J = 4.8$ Hz, 1H), 2.37 (s, 3H), 1.92-1.88 (m, 1H), 1.73-1.63 (m, 3H), 1.50-1.29 (m, 3H), 1.25-1.23 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 138.4, 137.8, 137.1, 129.3, 129.2, 128.9, 126.7, 125.9, 80.8, 69.4, 41.7, 32.0, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 26.2, 22.8, 21.3, 14.2. EI-MS: $[\text{M}]^+$ m/z 412.2.

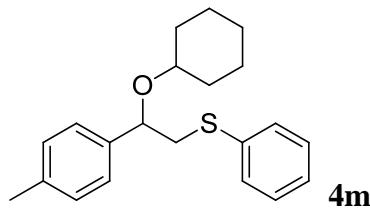


(2-(Hexadecyloxy)-2-*p*-tolylethyl)(phenyl)sulfane (4k). Eluent: petroleum ether/ethyl acetate (25:1). Yield 69 mg (85%). Colorless film. ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.35 (m, 2H), 7.30-7.15 (m, 7H), 4.38 (dd, $J = 8.0$ Hz, $J = 5.3$ Hz, 1H), 3.39-3.25 (m, 3H), 3.12 (dd, $J = 13.1$ Hz, $J = 5.1$ Hz, 1H), 2.37 (s, 3H), 1.59-1.54 (m, 2H), 1.34-1.24 (m, 26H), 0.91 (t, $J = 6.5$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 138.4, 137.8, 137.2, 129.3, 129.2, 128.9, 126.7, 125.9, 80.8, 69.4, 41.7, 32.1, 29.8,

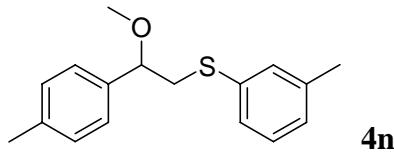
29.7, 29.6, 29.5, 26.3, 22.8, 21.3, 14.3. EI-MS: [M]⁺ m/z 468.3.



(2-(Cyclopentyloxy)-2-p-tolylethyl)(phenyl)sulfane (4l). Eluent: petroleum ether/ethyl acetate (25:1). Yield 46 mg (73%). Colorless film. ¹H NMR (400 MHz, CDCl₃) δ 7.36-7.34 (m, 2H), 7.28-7.23 (m, 4H), 7.18-7.16 (m, 3H), 4.44 (dd, *J* = 8.0 Hz, *J* = 4.7 Hz, 1H), 3.83-3.81 (m, 1H), 3.27 (dd, *J* = 13.2 Hz, *J* = 8.6 Hz, 1H), 3.18 (dd, *J* = 13.0 Hz, *J* = 4.7 Hz, 1H), 2.36 (s, 3H), 1.63-1.59 (m, 2H), 1.57-1.45 (m, 2H), 1.44-1.39 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 138.9, 137.6, 137.3, 129.2, 129.0, 128.9, 126.8, 125.8, 79.4, 76.8, 42.0, 33.2, 31.7, 23.6, 23.5, 21.3. EI-MS: [M]⁺ m/z 298.1.



(2-(Cyclohexyloxy)-2-(p-tolyl)ethyl)(phenyl)sulfane (4m). Eluent: petroleum ether/ethyl acetate (25:1). Yield 41 mg (64%). Colorless film. ¹H NMR (400 MHz, CDCl₃) δ 7.35 (d, *J* = 7.5 Hz, 2H), 7.28-7.14 (m, 7H), 4.37 (dd, *J* = 8.0 Hz, *J* = 5.3 Hz, 1H), 3.37-3.25 (m, 3H), 3.11 (dd, *J* = 13.1 Hz, *J* = 5.2 Hz, 1H), 2.36 (s, 3H), 1.59-1.52 (m, 2H), 1.32-1.26 (m, 18H), 0.90 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 139.3, 137.6, 137.4, 129.2, 128.9, 128.8, 126.7, 125.8, 77.6, 75.6, 42.2, 33.6, 31.4, 25.9, 24.2, 24.0, 21.3. EI-MS: [M]⁺ m/z 326.4.

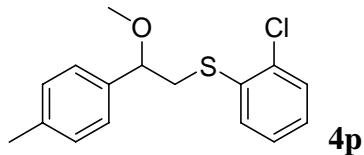


(2-Methoxy-2-p-tolylethyl)(m-tolyl)sulfane (4n). Eluent: petroleum ether/ethyl acetate (25:1). Yield 36 mg (67%). Colorless film. ¹H NMR (400 MHz, CDCl₃) δ 7.29-7.17 (m, 7H), 7.04-6.99 (m, 1H), 4.30 (dd, *J* = 8.0 Hz, *J* = 5.1 Hz, 1H), 3.39-3.30 (m, 1H), 3.28-3.22 (m, 3H), 3.15 (dd, *J* = 13.1 Hz, *J* = 5.2 Hz, 1H), 2.39 (s, 3H), 2.34

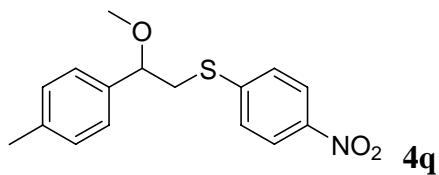
(s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 138.7, 138.0, 137.7, 136.5, 130.0, 129.4, 128.8, 126.9, 126.8, 126.4, 82.5, 57.2, 41.6, 21.5, 21.3. EI-MS: $[\text{M}]^+$ m/z 272.3.



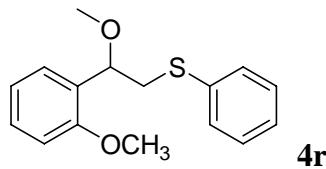
(4-Chlorophenyl)(2-methoxy-2-p-tolylethyl)sulfane (4o). Eluent: petroleum ether/ethyl acetate (25:1). Yield 39 mg (66%). Colorless film. ^1H NMR (400 MHz, CDCl_3) δ 7.26-7.20 (m, 4H), 7.19-7.15 (m, 4H), 4.24 (dd, $J = 8.0$ Hz, $J = 5.0$ Hz, 1H), 3.28 (dd, $J = 13.3$ Hz, $J = 8.1$ Hz, 1H), 3.22 (s, 3H), 3.08 (dd, $J = 13.3$ Hz, $J = 5.1$ Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 138.1, 137.3, 135.3, 132.0, 130.7, 129.4, 129.1, 126.8, 82.3, 57.0, 41.9, 21.3. EI-MS: $[\text{M}]^+$ m/z 292.3, 294.3.



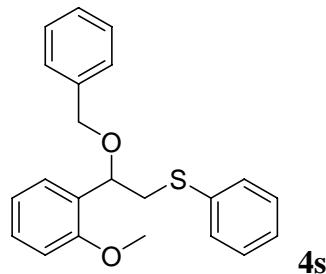
(2-Chlorophenyl)(2-methoxy-2-p-tolylethyl)sulfane (4p). Eluent: petroleum ether/ethyl acetate (25:1). Yield 43 mg (73%). Colorless film. ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.29 (m, 2H), 7.25-7.17 (m, 5H), 7.13-7.08 (m, 1H), 4.33 (dd, $J = 8.3$ Hz, $J = 4.7$ Hz, 1H), 3.33 (dd, $J = 13.0$ Hz, $J = 8.4$ Hz, 1H), 3.26 (s, 3H), 3.12 (dd, $J = 12.9$ Hz, $J = 4.7$ Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 138.1, 137.4, 136.2, 133.9, 129.8, 129.4, 129.1, 127.1, 126.8, 126.7, 82.3, 57.1, 40.6, 21.3. EI-MS: $[\text{M}]^+$ m/z 292.1, 294.1.



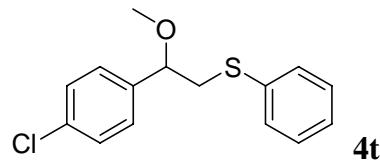
(2-Methoxy-2-p-tolylethyl)(4-nitrophenyl)sulfane (4q). Eluent: petroleum ether/ethyl acetate (25:1). Yield 40 mg (65%). Colorless film. ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, $J = 8.7$ Hz, 2H), 7.31 (d, $J = 8.9$ Hz, 2H), 7.24-7.17 (m, 4H), 4.35 (dd, $J = 8.1$ Hz, $J = 4.8$ Hz, 1H), 3.38 (dd, $J = 13.1$ Hz, $J = 8.1$ Hz, 1H), 3.24-3.19 (m, 4H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.8, 145.1, 138.5, 136.8, 129.6, 126.7, 126.5, 123.9, 82.1, 57.1, 40.0, 21.3. EI-MS: $[\text{M}]^+$ m/z 303.1.



(2-Methoxy-2-(2-methoxyphenyl)ethyl)(phenyl)sulfane (4r). Eluent: petroleum ether/ethyl acetate (25:1). Yield 43 mg (79%). Colorless film. ^1H NMR (400 MHz, CDCl_3) δ 7.44-7.40 (m, 3H), 7.27 (t, J = 7.6 Hz, 3H), 7.16 (t, J = 7.4 Hz, 1H), 7.00 (t, J = 7.4 Hz, 1H), 6.87 (d, J = 8.2 Hz, 1H), 4.80 (dd, J = 9.0 Hz, J = 3.3 Hz, 1H), 3.81 (s, 3H), 3.32 (s, 3H), 3.29-3.28 (m, 1H), 3.11 (dd, J = 13.4 Hz, J = 9.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 137.3, 129.0, 128.9, 128.8, 128.7, 126.5, 125.7, 120.9, 110.4, 76.7, 57.6, 55.3, 40.4. EI-MS: $[\text{M}]^+$ m/z 274.1.

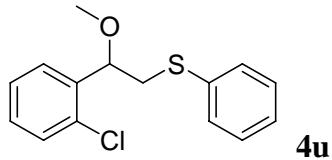


(2-(Benzyl oxy)-2-(2-methoxyphenyl)ethyl)(phenyl)sulfane (4s). Eluent: petroleum ether/ethyl acetate (25:1). Yield 46 mg (66%). Colorless film. ^1H NMR (400 MHz, CDCl_3) δ 7.56 (dd, J = 17.6 Hz, J = 1.6 Hz, 1H), 7.45-7.26 (m, 10H), 7.20-7.15 (m, 1H), 7.05 (t, J = 7.4 Hz, 1H), 6.91 (d, J = 8.2 Hz, 1H), 5.08 (dd, J = 8.7 Hz, J = 3.5 Hz, 1H), 4.57 (d, J = 11.6 Hz, 1H), 4.42 (d, J = 11.6 Hz, 1H), 3.82 (s, 3H), 3.35 (dd, J = 13.6 Hz, J = 3.6 Hz, 1H), 3.23 (dd, J = 13.7 Hz, J = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 157.0, 138.5, 137.5, 129.1, 129.0, 128.9, 128.8, 128.4, 127.9, 127.6, 126.8, 125.7, 121.0, 74.8, 71.6, 40.4. EI-MS: $[\text{M}]^+$ m/z 350.2.

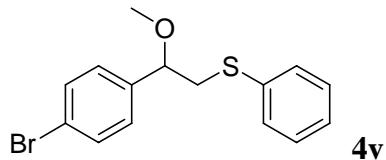


(2-(4-Chlorophenyl)-2-methoxyethyl)(phenyl)sulfane (4t). Eluent: petroleum ether/ethyl acetate (25:1). Yield 44 mg (80%). Colorless film. ^1H NMR (400 MHz, CDCl_3) δ 7.34-7.31 (m, 4H), 7.28-7.23 (m, 4H), 7.20-7.16 (m, 1H), 4.26 (dd, J = 7.6 Hz, J = 5.5 Hz, 1H), 3.30 (dd, J = 13.3 Hz, J = 7.5 Hz, 1H), 3.23 (s, 3H), 3.08 (dd, J =

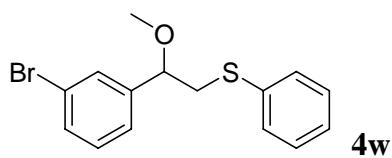
13.3 Hz, $J = 5.4$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 139.1, 136.3, 134.0, 129.6, 129.0, 128.8, 128.3, 126.3, 82.0, 57.2, 41.5. EI-MS: $[\text{M}]^+$ m/z 278.3, 280.1.



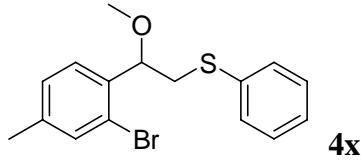
(2-(2-Chlorophenyl)-2-methoxyethyl)(phenyl)sulfane (4u). Eluent: petroleum ether/ethyl acetate (25:1). Yield 30 mg (55%). Colorless film. ^1H NMR (400 MHz, CDCl_3) δ 7.52-7.51 (m, 1H), 7.42-7.40 (m, 2H), 7.34-7.16 (m, 6H), 4.82 (dd, $J = 8.6$ Hz, $J = 3.5$ Hz, 1H), 3.29 (s, 3H), 3.26-3.25 (m, 1H), 3.14 (dd, $J = 13.5$ Hz, $J = 8.6$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 138.1, 136.4, 133.2, 130.0, 129.7, 129.2, 128.9, 127.6, 127.4, 126.3, 78.7, 57.6, 40.5. EI-MS: $[\text{M}]^+$ m/z 278.3.



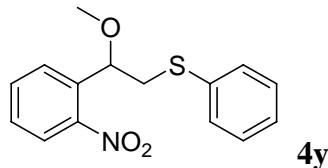
(2-(4-Bromophenyl)-2-methoxyethyl)(phenyl)sulfane (4v). Eluent: petroleum ether/ethyl acetate (25:1). Yield 41 mg (64%). Colorless film. ^1H NMR (400 MHz, CDCl_3) δ 7.47 (d, $J = 7.8$ Hz, 2H), 7.32 (d, $J = 8.1$ Hz, 2H), 7.28-7.25 (m, 2H), 7.19-7.17 (m, 3H), 4.26-4.22 (m, 1H), 3.29 (dd, $J = 13.3$ Hz, $J = 7.5$ Hz, 1H), 3.23 (s, 3H), 3.08 (dd, $J = 13.5$ Hz, $J = 5.3$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 139.6, 136.3, 131.8, 129.6, 129.0, 128.6, 126.3, 122.1, 82.0, 57.2, 41.4. EI-MS: $[\text{M}]^+$ m/z 322.3, 324.3.



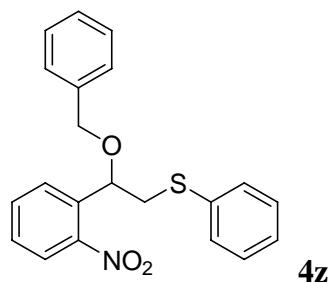
(2-(3-Bromophenyl)-2-methoxyethyl)(phenyl)sulfane (4w). Eluent: petroleum ether/ethyl acetate (25:1). Yield 40 mg (60%). Colorless film. ^1H NMR (400 MHz, CDCl_3) δ 7.45-7.41 (m, 2H), 7.34-7.33 (m, 2H), 7.29-7.25 (m, 2H), 7.22-7.18 (m, 3H), 4.25-4.22 (d, $J = 7.8$ Hz, $J = 5.3$ Hz, 1H), 3.28 (dd, $J = 13.4$ Hz, $J = 7.8$ Hz, 1H), 3.25 (s, 3H), 3.18 (dd, $J = 13.4$ Hz, $J = 5.2$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.1, 136.2, 131.3, 130.3, 129.9, 129.7, 129.1, 126.4, 125.5, 122.9, 82.0, 57.4, 41.5. EI-MS: $[\text{M}]^+$ m/z 322.0, 324.0.



(2-(3-Bromophenyl)-2-methoxyethyl)(phenyl)sulfane (4x). Eluent: petroleum ether/ethyl acetate (25:1). Yield 39 mg (59%). Colorless film. ^1H NMR (400 MHz, CDCl_3) δ 7.43-7.36 (m, 4H), 7.30-7.25 (m, 2H), 7.21-7.14 (m, 2H), 4.73 (dd, $J = 8.6$ Hz, $J = 5.8$ Hz, 1H), 3.28 (s, 3H), 3.26-3.22 (m, 1H), 3.11 (dd, $J = 13.5$ Hz, $J = 8.8$ Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 139.7, 136.5, 136.4, 133.3, 130.1, 128.9, 128.8, 127.5, 126.3, 123.1, 80.8, 57.4, 40.7, 20.9. EI-MS: $[\text{M}]^+$ m/z 336.2, 338.2.

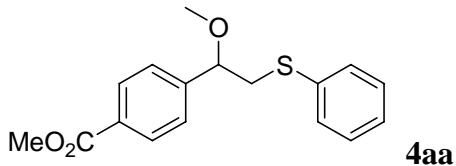


(2-Methoxy-2-(2-nitrophenyl)ethyl)(phenyl)sulfane (4y). Eluent: petroleum ether/ethyl acetate (25:1). Yield 23 mg (40%). Colorless film. ^1H NMR (400 MHz, CDCl_3) δ 7.93 (dd, $J = 8.2$ Hz, $J = 1.1$ Hz, 1H), 7.79 (dd, $J = 7.8$ Hz, $J = 1.3$ Hz, 1H), 7.65(dt, $J = 7.6$ Hz, $J = 1.1$ Hz, 1H), 7.46-7.38 (m, 3H), 7.29-7.24 (m, 2H), 7.20-7.15 (m, 1H), 4.98 (dd, $J = 8.0$ Hz, $J = 3.9$ Hz, 1H), 3.40 (dd, $J = 13.5$ Hz, $J = 3.8$ Hz, 1H), 3.28-3.21 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 148.9, 136.5, 136.0, 133.7, 130.2, 129.0, 128.8, 128.5, 126.5, 124.6, 78.0, 57.8, 41.5. EI-MS: $[\text{M}]^+$ m/z 289.3.

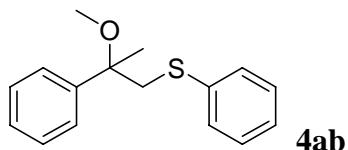


(2-(Benzylxy)-2-(2-nitrophenyl)ethyl)(phenyl)sulfane (4z). Eluent: petroleum ether/ethyl acetate (25:1). Yield 27 mg (37%). Colorless film. ^1H NMR (400 MHz, CDCl_3) δ 7.93 (dd, $J = 8.2$ Hz, $J = 1.2$ Hz, 1H), 7.87 (dd, $J = 7.8$ Hz, $J = 1.0$ Hz, 1H), 7.65 (t, $J = 7.6$ Hz, 1H), 7.47-7.42 (m, 1H), 7.39-7.35 (m, 2H), 6.22 (dd, $J = 7.7$ Hz, $J = 4.1$ Hz, 1H), 6.41 (dd, $J = 21.4$ Hz, $J = 11.5$ Hz, 1H), 3.42 (dd, $J = 13.7$ Hz, $J = 4.2$

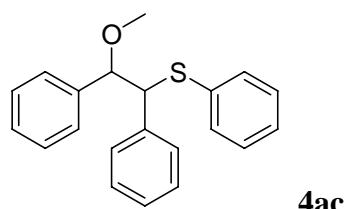
Hz, 1H), 3.33 (dd, J = 13.6 Hz, J = 7.7 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 148.9, 137.4, 136.7, 136.2, 133.7, 130.1, 128.9, 128.8, 128.5, 127.9, 126.4, 124.6, 75.8, 72.0, 41.6. EI-MS: $[\text{M}]^+$ m/z 365.2.



Methyl 4-(1-methoxy-2-(phenylthio)ethyl)benzoate (4aa). Eluent: petroleum ether/ethyl acetate (5:1). Yield 32 mg (53%). Colorless film. ^1H NMR (300 MHz, CDCl_3) δ 8.03 (d, J = 8.3 Hz, 2H), 7.39-7.33 (m, 4H), 7.29-7.24 (m, 2H), 7.21-7.17 (m, 1H), 4.33 (dd, J = 7.7 Hz, J = 5.3 Hz, 1H), 3.92 (s, 3H), 3.31 (dd, J = 13.3 Hz, J = 7.7 Hz, 1H), 3.25 (s, 3H), 3.11 (dd, J = 13.3 Hz, J = 5.3 Hz, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 166.9, 145.8, 136.2, 130.1, 129.9, 129.7, 129.1, 126.9, 126.4, 82.2, 57.4, 52.2, 41.4. EI-MS: $[\text{M}]^+$ m/z 302.2.

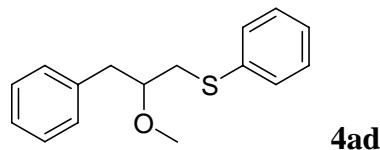


(2-Methoxy-2-phenylpropyl)(phenyl)sulfane (4ab). Eluent: petroleum ether/ethyl acetate (25:1). Yield 35 mg (70%). Colorless film. ^1H NMR (400 MHz, CDCl_3) δ 7.42 (d, J = 7.5 Hz, 2H), 7.37-7.33 (m, 2H), 7.28-7.27 (m, 3H), 7.23-7.19 (m, 2H), 7.12 (d, J = 7.2 Hz, 1H), 3.40 (d, J = 12.5 Hz, 1H), 3.28 (d, J = 12.5 Hz, 1H), 1.71 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.6, 137.6, 129.4, 128.8, 128.4, 127.6, 126.4, 125.9, 79.1, 76.8, 51.0, 47.6, 22.5. EI-MS: $[\text{M}]^+$ m/z 258.3.

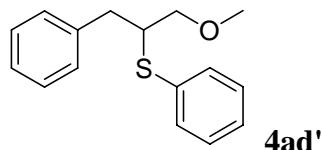


(2-Methoxy-1,2-diphenylethyl)(phenyl)sulfane (4ac). Eluent: petroleum ether/ethyl acetate (25:1). Yield 28 mg (44%). Colorless film. ^1H NMR (400 MHz, CDCl_3) δ 7.25-7.23 (m, 3H), 7.20-7.19 (m, 7H), 7.14-7.12 (m, 3H), 7.10-7.09 (m, 2H), 4.62 (d, J = 5.7 Hz, 1H), 4.37 (d, J = 5.9 Hz, 1H), 3.23 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ

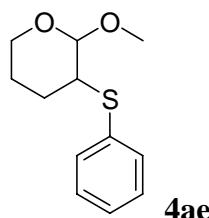
139.0, 138.8, 131.9, 129.4, 128.7, 128.1, 128.0, 127.8, 127.6, 127.2, 126.9, 86.2, 60.3, 57.5. EI-MS: [M]⁺ m/z 320.4.



(2-Methoxy-3-phenylpropyl)(phenyl)sulfane (4ad). Eluenrt: petroleum ether/ethyl acetate (25:1). Yield 20 mg (40%). Colorless film. ¹H NMR (400 MHz, CDCl₃) δ 7.32-7.17 (m, 10H), 3.61-3.54 (m, 1H), 3.25 (s, 3H), 3.02 (dd, *J* = 5.6 Hz, *J* = 4.0 Hz, 2H), 2.94 (d, *J* = 6.2 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 138.2, 136.7, 129.6, 129.3, 129.0, 128.5, 126.5, 126.1, 81.3, 57.6, 39.6, 37.2. EI-MS: [M]⁺ m/z 258.1.

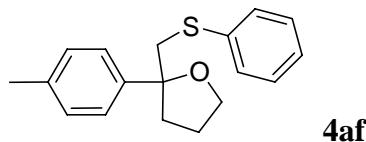


(3-Methoxy-1-phenylpropan-2-yl)(phenyl)sulfane (4ad'). Eluenrt: petroleum ether/ethyl acetate (25:1). Yield 13 mg (25%). Colorless film. ¹H NMR (400 MHz, CDCl₃) δ 7.39-7.37 (m, 2H), 7.31-7.20 (m, 8H), 3.48-3.40 (m, 3H), 3.34 (s, 3H), 3.07 (dd, *J* = 13.8 Hz, *J* = 6.7 Hz, 1H), 2.87 (dd, *J* = 13.9 Hz, *J* = 6.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 138.9, 134.9, 132.1, 129.5, 129.0, 128.4, 127.1, 126.5, 73.5, 59.0, 49.9, 37.9. EI-MS: [M]⁺ m/z 258.3.

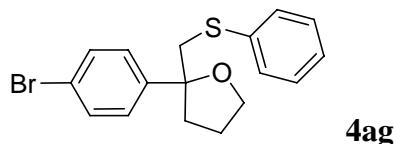


Tetrahydro-2-methoxy-3-(phenylthio)-2H-pyran (4ae). Eluent: petroleum ether/ethyl acetate (25:1). Yield 18 mg (41%). Colorless film. ¹H NMR (300 MHz, CDCl₃) δ 7.47-7.41 (m, 3.2H) (a pair of diastereoisomers was observed, ratio = 1.7: 1), 7.30-7.28 (m, 2H), 7.24-7.20 (m, 2.8H), 4.70 (d, *J* = 3.1 Hz, 0.6H), 4.43 (d, *J* = 4.4 Hz, 1H), 3.92-3.84 (m, 1H), 3.81-3.73 (m, 0.7H), 3.58-3.51 (m, 1.7H), 3.42 (s, 1.8H), 3.41 (s, 3H), 3.31-3.25 (m, 0.6H), 3.23-3.18 (m, 1H), 2.23-2.13 (m, 1H), 1.99-1.83 (m, 2.3H), 1.73-1.64 (m, 2.3H), 1.54-1.49 (m, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 134.9,

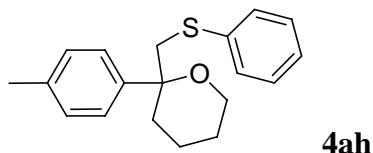
134.8, 131.9, 131.8, 129.0, 128.9, 127.0, 102.3, 99.2, 62.4, 59.1, 55.6, 55.3, 48.9, 47.7, 26.4, 26.1, 25.9, 23.1. EI-MS: $[M]^+$ m/z 224.3.



Tetrahydro-2-((phenylthio)methyl)-2-p-tolylfuran (4af). Eluenrt: petroleum ether/ethyl acetate (25:1). Yield 43 mg (80%). Colorless film. ^1H NMR (600 MHz, CDCl_3) δ 7.32 (d, $J = 8.1$ Hz, 2H), 7.28 (dd, $J = 8.3$ Hz, $J = 0.9$ Hz, 2H), 7.20 (t, $J = 7.8$ Hz, 2H), 7.14-7.10 (m, 3H), 4.04-4.01 (m, 1H), 3.92-3.88 (m, 1H), 3.43 (d, $J = 12.8$ Hz, 1H), 3.32 (d, $J = 12.8$ Hz, 1H), 2.39-2.34 (m, 1H), 2.33 (s, 3H), 2.24-2.20 (m, 1H), 2.04-1.98 (m, 1H), 1.85-1.78 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 142.7, 137.8, 136.7, 129.1, 129.0, 128.8, 125.7, 125.4, 86.1, 68.3, 46.7, 37.0, 26.0, 12.1. EI-MS: $[M]^+$ m/z 284.3.

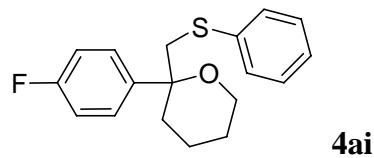


2-(4-Bromophenyl)-tetrahydro-2-((phenylthio)methyl)furan (4ag). Eluenrt: petroleum ether/ethyl acetate (25:1). Yield 51 mg (74%). Colorless film. ^1H NMR (300 MHz, CDCl_3) δ 7.42 (d, $J = 8.5$ Hz, 2H), 7.31-7.11 (m, 7H), 4.07-4.00 (m, 1H), 3.93-3.86 (m, 1H), 3.39 (d, $J = 12.9$ Hz, 1H), 3.30 (d, $J = 12.9$ Hz, 1H), 2.41-2.34 (m, 1H), 2.23-2.14 (m, 1H), 2.10-1.98 (m, 1H), 1.88-1.76 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 144.7, 137.4, 131.3, 129.5, 128.8, 127.4, 125.9, 121.1, 86.0, 68.4, 46.6, 37.2, 26.0. EI-MS: $[M]^+$ m/z 348.3.



Tetrahydro-2-((phenylthio)methyl)-2-p-tolyl-2H-pyran (4ah). Eluenrt: petroleum ether/ethyl acetate (25:1). Yield 49 mg (83%). Colorless film. ^1H NMR (300 MHz, CDCl_3) δ 7.34 (d, $J = 8.2$ Hz, 2H), 7.23-7.06 (m, 7H), 3.79-3.74 (m, 1H), 3.52 (dt, $J = 11.3$ Hz, $J = 2.6$ Hz, 1H), 3.25 (d, $J = 12.5$ Hz, 1H), 3.17 (d, $J = 12.5$ Hz, 1H), 2.35 (s, 3H), 2.00 (dt, $J = 12.4$ Hz, $J = 2.7$ Hz, 1H), 1.73-1.37 (m, 5H). ^{13}C NMR (75 MHz,

CDCl_3) δ 138.9, 137.8, 136.9, 129.3, 129.1, 128.7, 126.9, 125.6, 78.2, 63.0, 49.1, 31.7, 25.9, 21.1, 19.9. EI-MS: $[\text{M}]^+$ m/z 298.2.



2-(4-Fluorophenyl)-tetrahydro-2-((phenylthio)methyl)-2H-pyran (4ai). Eluenrt: petroleum ether/ethyl acetate (25:1). Yield 40 mg (66%). Colorless film. ^1H NMR (300 MHz, CDCl_3) δ 7.43-7.38 (m, 2H), 7.19-6.99 (m, 7H), 3.79-3.74 (m, 1H), 3.48 (dt, $J = 11.4$ Hz, $J = 2.7$ Hz, 1H), 3.24 (d, $J = 12.7$ Hz, 1H), 3.19 (d, $J = 12.7$ Hz, 1H), 2.36 (dt, $J = 13.8$ Hz, $J = 3.2$ Hz, 1H), 1.97 (dt, $J = 12.9$ Hz, $J = 3.7$ Hz, 1H), 1.74-1.59 (m, 2H), 1.53-1.40 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 162.1 (d, $J = 245.7$ Hz), 137.5 (d, $J = 3.1$ Hz), 137.4, 129.3, 128.8 (d, $J = 8.0$ Hz), 128.7, 125.8, 115.3 (d, $J = 21.1$ Hz), 77.9, 63.0, 48.9, 32.0, 25.8, 19.8. EI-MS: $[\text{M}]^+$ m/z 302.2.

¹H and ¹³C NMR spectra of compounds **4a-4ai**

