Highly atom-economic, catalyst- and solvent-free oxidation of sulfides into sulfones using 30% aqueous H_2O_2

Marjan Jereb*

Faculty of Chemistry and Chemical Technology, Aškerčeva 5, 1000 Ljubljana, Slovenia.
E-mail: marjan.jereb@fkkt.uni-lj.si; Fax: ++386-1-241-9220; Tel: ++386-1-241-9248

General information

All transformations were carried under an air atmosphere with stirring at 75 °C. Heterogeneous reaction mixtures were obtained (organic and aqueous phase of H_2O_2 in the case of liquid sulfides) and (solid sulfide and aqueous phase of H_2O_2); no difficulties in this regard were noted. Reactions of the liquid sulfides were carried out in tightly closed conical reactors, while reactions of the solid sulfides were performed in ordinary round flasks equipped with a reflux condenser. Thioanisole, 4-nitrothioanisole, thioxanthone, thiochroman-4-one, 1,3-dithiane, dibenzothiophene, benzo[*b*]thiophene, dimethyl sulfide, phenyl vinyl sulfide and 30% aqueous solution of hydrogen peroxide were obtained from commercial sources and used as received. Most of the other starting sulfides were prepared from the corresponding thiol and haloalkane or benzyl chloride using the literature procedure.[1] 4-Acetylthioanisole, 4-methyl-4'-thiomethylbenzophenone and 4-thiomethylbenzophenone were prepared by Friedel-Crafts reaction using thioanisole and the corresponding acid chloride in dichloromethane in the presence of $AlCl_3$. All crude sulfides were purified by distillation or crystallization. 2-Thiomethylpyridine and 1-methyl-2-thiomethylimidazole were prepared according to the known procedure.[2] In most of the cases, the ^{1}H NMR spectra of the crude reaction mixtures showed signals of the products only, and no visible signals of the impurities.
Crude products were purified by column chromatography (small scale) or crystallization (scale-up). Column chromatography was performed on silica gel (63–200 μm, 70–230 mesh ASTM; Fluka. TLC was performed on Merck-60-F_{254} plates using mixtures of hexane and diethyl ether. The melting points were determined in open-capillaries on Büchi 535 apparatus and on a Leica Galen III Microscope and are uncorrected. Known products were characterized by their ^{1}H NMR and ^{13}C NMR spectra, and also with the melting points when solid. New products were characterized with ^{1}H and ^{13}C NMR spectra, IR, HRMS and/or elemental analysis. The ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance III 500 instrument. Chemical shifts are reported in δ (ppm) values relative to the TMS (δ = 0.00 ppm) and DMSO-d_6 (δ = 2.50 ppm) for ^{1}H NMR, and to the central line of $CDCl_3$ (δ = 77.0 ppm) and to the central line of DMSO-d_6 (39.43 ppm) for ^{13}C NMR. ^{19}F NMR spectra are referred to $CFCl_3$ (δ = 0.00 ppm).

Representative procedure of the non-catalyzed oxidation of the highly volatile sulfide into sulfone using 30% aqueous solution of H_2O_2 under SFRC (scale-up)
The reaction was performed in an Ace pressure tube (15 mL). To a 30% aqueous solution of H_2O_2 (66 mmol, 7.48 g), dimethyl sulfide **1gg** (30 mmol, 1.86 g) was added. Two separated phases turned into one phase after 30 minutes of heating. The tightly closed tube was stirred for 33 h at 75°C. The tube was cooled and H_2O_2 (3 mmol, 0.34 g) was added, and the mixture was stirred for additional 25 h at 75°C (full conversion in 58 h). The reaction mixture was cooled and pure dimethyl sulfone **2gg** (1.63 g) was filtered off. The mother liquor was concentrated in the air furnishing additional 0.84 g, in total (88%) of dimethyl sulfone **2gg**. The product could be used without further purification. The yield is considerably higher in comparison with 1 mmol scale (79%).

Representative procedure of the non-catalyzed oxidation of solid sulfide into sulfone using 30% aqueous solution of H_2O_2 under SFRC (scale-up)

To benzyl phenyl sulfide **1ll** (2 mmol, 0.40 g) a 30% aqueous solution of H_2O_2 was added (4.4 mmol, 0.50 g), and the mixture was heated at 75 °C with stirring for 3 h in a round-bottom flask equipped with a reflux condenser. The mixture was cooled and 2 mmol (0.23 g) of 30% aqueous solution of H_2O_2 were added. **1ll** melted soon after the beginning of heating, and two phases were present for approx. 2 h, and then a white solid crystallized. The heterogeneous reaction mixture was further heated and stirred, and additional H_2O_2 was added (2 mmol, 0.23 g after 8 h and 2 mmol, 0.23 g after 18 h). Full conversion was reached in 27 h. The mixture was cooled, washed with water and product **2ll** filtered off. Crystallization of the crude product from methanol gave **2ll** (0.37 g, 80%) as white solid.

Analogously, 4-methxoxybenzyl 4-methylphenyl sulfide **1nn** was oxidized into its sulfone **2nn**. Sulfide **1nn** (2 mmol, 0.488 g) 30% aqueous solution of H_2O_2 was added (4.4 mmol, 0.50 g), and the mixture was heated at 75°C with stirring for 4 h in a round-bottom flask equipped with a reflux condenser. **1nn** melted soon after beginning of heating, and two phases were present for approx. 1 h, and then a white solid crystallized. The heterogeneous reaction mixture was further heated and stirred, and additional H_2O_2 was added (2 mmol, 0.23 g after 9.5 h and 2 mmol, 0.23 g after 19 h). Full conversion was reached in 27 h. The mixture was cooled, washed with water and product **2nn** was filtered off. Crystallization of the crude product from methanol gave **2nn** (0.43 g, 78%) as white solid.

Phenyl methyl sulfone[3] (**2a**). White crystals, yield 68%, (0.3 mmol of **1a**, 0.66 mmol of H_2O_2), r.t. = 2 h, mp 84–86 °C, lit. 85–87 °C. ^{1}H NMR: δ 3.07 (s, 3H), 7.56–7.61 (m, 2H), 7.65–7.69 (m, 1H), 7.93–7.97 (m, 2H); ^{13}C NMR: δ 44.4, 127.2, 129.3, 133.6, 140.4.

Phenyl ethyl sulfone[3] (**2b**). Colorless oil, yield 65%, (0.3 mmol of **1b**, 0.66 mmol of H_2O_2), r.t. = 3.2 h. ^{1}H NMR: δ 1.28 (t, *J* = 7.5 Hz, 3H), 3.13 (q, *J* = 7.5 Hz, 2H), 7.56–7.60 (m, 2H), 7.65–7.69 (m, 1H), 7.90–7.94 (m, 2H); ^{13}C NMR: δ 7.4, 50.6, 128.2, 129.2, 133.6, 138.4.

Phenyl butyl sulfone[4] (**2c**). Colorless oil, yield 64%, (0.3 mmol of **1c**, 0.66 mmol of H_2O_2), r.t. = 5.75 h, ^{1}H NMR: δ 0.89 (t, *J* = 7.4 Hz, 3H), 1.39 (sext, *J* = 7.4 Hz, 2H), 1.65–1.73 (m, 2H), 3.06–3.11 (m, 2H), 7.55–7.60 (m, 2H), 7.64–7.68 (m, 1H), 7.90–7.93 (m, 2H); ^{13}C NMR: δ 13.5, 21.5, 24.6, 56.0, 128.0, 129.2, 133.6, 139.2.

Phenyl hexyl sulfone[5] (**2d**). Colorless oil, yield 69%, (0.3 mmol of **1d**, 0.66 mmol of H_2O_2), r.t. = 8.25 h. ^{1}H NMR: δ 0.85 (t, *J* = 7.0 Hz, 3H), 1.20–1.30 (m, 4H), 1.31–1.40 (m, 2H), 1.67–1.74 (m, 2H), 3.06–3.11 (m, 2H), 7.55–7.60 (m, 2H), 7.64–7.68 (m, 1H), 7.89–7.93 (m, 2H); ^{13}C NMR: δ 13.9, 22.3, 22.6, 27.9, 31.1, 56.3, 128.0, 129.2, 133.6, 139.2.

Phenyl dodecyl sulfone[6] (**2e**). White crystals, yield 79%, (0.2 mmol of **1e**, 0.22 mmol of H_2O_2 after 0, 3, 4.5 and 9 h), r.t. = 11 h, mp 31–33 °C, lit. 62 °C. ^{1}H NMR: δ 0.88 (t, *J* = 7.1 Hz, 3H), 1.20–1.38 (m, 18H), 1.67–1.74 (m, 2H), 3.05–3.10 (m, 2H), 7.55–7.60 (m, 2H), 7.64–7.68 (m, 1H), 7.89–7.93 (m, 2H); ^{13}C NMR: δ 14.1, 22.6, 22.7, 28.2, 29.0, 29.2, 29.3, 29.4, 29.5, 29.6, 31.9, 56.3, 128.0, 129.2, 133.6, 139.2.

4-Methoxyphenyl methyl sulfone[3] (**2f**). White crystals, yield 95%, (0.3 mmol of **1f**, 0.66 mmol of H_2O_2), 1.5 h, mp 118.1–119.2 °C, lit. 118–120 °C. ^{1}H NMR: δ 3.04 (s, 3H), 3.89 (s,

3H), 7.03 (d, *J* = 8.9 Hz, 2H), 7.87 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR: δ 44.8, 55.7, 114.4, 129.5, 132.2, 163.6.

3-Methoxyphenyl methyl sulfone[7] (**2g**). Colorless oil, yield 87%, (0.3 mmol of **1g**, 0.66 mmol of H_2O_2 after 0 h and 0.33 mmol after 2 h), r.t. = 2.5 h. ^{1}H NMR: δ 3.06 (s, 3H), 3.88 (s, 3H), 7.16–7.20 (m, 1H), 7.43–7.45 (m, 1H), 7.48 (dd, *J* = 8.0, 7.8 Hz, 1H), 7.51–7.54 (m, 1H); ^{13}C NMR: δ 44.4, 55.7, 111.7, 119.4, 120.1, 130.4, 141.6, 160.0.

2-Methoxyphenyl methyl sulfone[8] (**2h**). White crystals, yield 80%, (0.3 mmol of **1h**, 0.66 mmol of H_2O_2 after 0 h and 0.33 mmol after 2 h), r.t. = 3.75 h, mp 88.0–90.0 °C, lit. 88–90 °C. ^{1}H NMR: δ 3.22 (s, 3H), 4.00 (s, 3H), 7.05–7.08 (m, 1H), 7.09–7.13 (m, 1H), 7.57–7.63 (m, 1H), 7.98 (dd, *J* = 7.8, 1.7 Hz, 1H); ^{13}C NMR: δ 42.9, 56.2, 112.2, 120.6, 128.2, 129.6, 135.5, 157.1.

4-Methylphenyl ethyl sulfone[9] (**2i**). White crystals, yield 65%, (0.3 mmol of **1i**, 0.66 mmol of H_2O_2), r.t. = 3 h, mp 48.2–49.5 °C, lit. 50–51 °C. ^{1}H NMR: δ 1.27 (t, *J* = 7.4 Hz, 3H), 2.46 (s, 3H), 3.10 (q, *J* = 7.4 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR: δ 7.5, 21.6, 50.6, 128.2, 129.8, 135.5, 144.6.

4-Fluorophenyl ethyl sulfone[10] (**2j**). Colorless oil, yield 80%, (0.3 mmol of **1j**, 0.66 mmol of H_2O_2), r.t. = 3 h, ^{1}H NMR: δ 1.28 (t, *J* = 7.4, 3H), 3.12 (q, *J* = 7.4, 2H), 7.23–7.28 (m, 2H), 7.91–7.95 (m, 2H); ^{19}F NMR: δ -104.1 (tt, *J* = 8.2, 5.0 Hz, 1F); ^{13}C NMR: δ 7.5, 50.7, 116.6 (d, *J* = 22.6 Hz), 131.1 (d, *J* = 9.6 Hz), 134.5 (d, *J* = 3.1 Hz), 165.8 (d, *J* = 256.3 Hz).

2,4-Difluorophenyl methyl sulfone[11] (**2l**). White crystals, yield 80%, (0.3 mmol of **1l**, 0.66 mmol of H_2O_2), r.t. = 8 h, mp 56.7–59.2 °C. ^{1}H NMR: δ 3.22 (s, 3H), 6.99–7.04 (m, 1H), 7.04-7.10 (m, 1H), 7.97–8.03 (m, 1H); ^{19}F NMR: δ -99.1 (m, 1F), -105.1 (m, 1F); ^{13}C NMR: δ 43.9 (d, *J* = 2.6 Hz), 105.8 (dd, *J* = 25.6, 25.5 Hz), 112.3 (dd, *J* = 22.0, 3.7 Hz), 124.8 (dd, *J* = 15.2, 3.8 Hz), 131.7 (dd, *J* = 10.7, 1.4 Hz), 160.3 (dd, *J* = 257.9, 13.0 Hz), 166.5 (dd, *J* = 259.1, 11.5 Hz).

4-Chlorophenyl methyl sulfone[3] (**2m**). White crystals, yield 79%, (0.2 mmol of **1m**, 0.60 mmol of H_2O_2), 1.5 h, mp 94.1–95.1 °C, lit. 96–98 °C. ^{1}H NMR: δ 3.06 (s, 3H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.90 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR: δ 44.6, 128.9, 129.7, 139.0, 140.5.

3,4-Dichlorophenyl methyl sulfone[12] (**2n**). White crystals, yield 93%, (0.3 mmol of **1n**, 0.90 mmol of H_2O_2), r.t. = 1.75 h, mp 112.1–113.2 °C, lit 112.0 °C. ^{1}H NMR: δ 3.08 (s, 3H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.78 (dd, *J* = 8.4, 2.1 Hz, 1H), 8.05 (d, *J* = 2.1 Hz, 1H); ^{13}C NMR: δ 44.5, 126.5, 129.5, 131.5, 134.2, 138.9, 140.2.

2,5-Dichlorophenyl methyl sulfone[13] (**2o**). White crystals, yield 50%, (0.2 mmol of **1o**, 0.44 mmol of H_2O_2 after 0, 5, 8, and 11 h), r.t. = 12.5 h, mp 85.1–85.9 °C, lit 86–87 °C. ^{1}H NMR: δ 3.28 (s, 3H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.56 (dd, *J* = 8.5, 2.5 Hz, 1H), 8.15 (d, *J* = 2.5 Hz, 1H); ^{13}C NMR: δ 42.6, 130.7, 133.0, 133.8, 134.7, 139.2.

4-Acetylphenyl methyl sulfone[14] (**2p**). White crystals, yield 82%, (0.2 mmol of **1p**, 0.50 mmol of H_2O_2), r.t. = 2 h, mp 128.0.1–129.0 °C, lit. 128.9–129.3 °C. ^{1}H NMR: δ 2.68 (s, 3H), 3.09 (s, 3H), 8.06 (d, *J* = 8.5 Hz, 2H), 8.14 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR: δ 26.9, 44.3, 127.8, 129.1, 140.9, 144.1, 196.6.

4-Nitrophenyl methyl sulfone[3] (**2q**). Pale yellow crystals, yield 85%, (0.3 mmol of **1q**, 0.75 mmol of H_2O_2 after 0 h and after 0.5 h), r.t. = 8 h, mp 138.4–140.1 °C, lit. 139–141 °C. ^{1}H NMR: δ 3.13 (s, 3H), 8.17 (d, *J* = 8.8 Hz, 2H), 8.44 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR: δ 44.3, 124.6, 129.0, 145.9, 150.8.

Cyclopropylmethyl phenyl sulfone[15] (**2s**). Colorless oil, yield 85%, (0.3 mmol of **1s**, 0.66 mmol of H_2O_2), r.t. = 3.5 h. ^{1}H NMR: δ 0.07–0.17 (m, 2H), 0.50–0.61 (m, 2H), 0.96–1.05 (m, 1H), 3.03 (d, *J* = 7.2 Hz, 2H), 7.54–7.60 (m, 2H), 7.64–7.69 (m, 1H), 7.92–7.97 (m, 2H); ^{13}C NMR: δ 4.3, 4.8, 61.3, 128.4, 129.1, 133.6, 139.2.

Phenyl *i*-propyl sulfone[16] (**2t**). Colorless oil, yield 78%, (0.3 mmol of **1t**, 0.66 mmol of H_2O_2), r.t. = 2.5 h. ^{1}H NMR: δ 1.30 (d, *J* = 6.9 Hz, 6H), 3.20 (sept, *J* = 6.9 Hz, 1H), 7.55–7.60 (m, 2H), 7.64–7.69 (m, 1H), 7.87–7.91 (m, 2H); ^{13}C NMR: δ 15.7, 55.5, 129.0, 133.6, 136.9.

Phenyl *s*-butyl sulfone[17] (**2u**). Colorless oil, yield 84%, (0.3 mmol of **1u**, 0.66 mmol of H_2O_2), r.t. = 2.5 h. ^{1}H NMR: δ 0.98 (t, *J* = 7.5 Hz, 3H), 1.27 (d, *J* = 6.9 Hz, 3H), 1.38–1.49 (m, 1H), 1.97–2.07 (m, 1H), 2.92–3.00 (m, 1H), 7.54–7.60 (m, 2H), 7.63–7.68 (m, 1H), 7.86–7.91 (m, 2H); ^{13}C NMR: δ 11.1, 12.5, 22.4, 61.5, 128.9, 129.0, 133.5, 137.3.

Phenyl 2-bromoethyl sulfone[18] (**2v**). White crystals, yield 72%, (0.2 mmol of **1v**, 0.33 mmol of H_2O_2 after 0 h and 0.22 mmol after 1 h), r.t. = 3 h, mp 78–79 °C, lit. 79–80 °C. ^{1}H NMR: δ 3.50–3.63 (m, 4H), 7.59–7.64 (m, 2H), 7.69–7.74 (m, 1H), 7.91–7.95 (m, 2H); ^{13}C NMR: δ 20.8, 58.3, 128.2, 129.6, 134.3, 138.3.

2-Benzenesulfonylacetate[19] (**2w**). Yellow oil, yield 41%, (0.2 mmol of **1w**, 0.33 mmol of H_2O_2 at 0 h and 0.22 mmol after 2.5 h), r.t = 12 h. ^{1}H NMR: δ 1.19 (t, *J* = 7.2 Hz, 3H), 4.12 (s, 2H), 4.15 (q, *J* = 7.2 Hz, 2H), 7.57–7.62 (m, 2H), 7.68–7.72 (m, 1H), 7.94–7.98 (m, 2H); ^{13}C NMR: δ 13.8, 61.0, 62.4, 128.5, 129.2, 134.2, 138.6, 162.3.

(Phenylsulfonyl)acetonitrile[20] (**2x**). White crystals, yield 68%, (0.3 mmol of **1x**, 0.66 mmol of H_2O_2), r.t = 2.25 h, mp 107–109 °C, lit. 110–112 °C. ^{1}H NMR: δ 4.07 (s, 2H), 7.65–7.70 (m, 2H), 7.77–7.82 (m, 1H), 8.03–8.07 (m, 2H); ^{13}C NMR: δ 45.8, 110.3, 128.9, 129.8, 135.4, 136.6.

Phenyl allyl sulfone[21] (**2y**). Colorless oil, yield 80%, (0.3 mmol of **1y**, 0.66 mmol of H_2O_2), r.t. = 4.5 h. ^{1}H NMR: δ 3.80–3.84 (m, 2H), 5.12–5.18 (m, 1H), 5.32–5.36 (m, 1H), 5.75–5.85 (m, 1H), 7.54–7.59 (m, 2H), 7.64–7.68 (m, 1H), 7.86–7.90 (m, 2H); ^{13}C NMR: δ 60.9, 124.6, 124.7, 128.5, 129.0, 133.7, 138.2.

Phenyl vinyl sulfone[22] (**2z**). White crystals, yield 65%, (0.3 mmol of **1z**, 0.66 mmol of H_2O_2), r.t. = 0.85 h, mp 64.5–66.0 °C, lit. 67–68 °C. ^{1}H NMR: δ 6.04 (d, *J* = 9.8 Hz, 1H), 6.45 (d, *J* = 16.5 Hz, 1H), 6.66 (dd, *J* = 16.5, 9.8 Hz, 1H), 7.52–7.57 (m, 2H), 7.61–7.66 (m, 1H), 7.87–7.92 (m, 2H); ^{13}C NMR: δ 127.8, 127.8, 129.3, 133.6, 138.4, 139.5.

Benzyl propargyl sulfone[23] (**2bb**). White crystals, yield 77%, (0.3 mmol of **1bb**, 0.50 mmol of H_2O_2 after 0 h and 0.25 mmol after 0.75 h), r.t. = 1.75 h, mp 108.5–109.6 °C, lit. 108–109 °C. ^{1}H NMR: δ 2.61 (t, *J* = 2.7 Hz, 1H), 3.65 (d, *J* = 2.7 Hz, 2H), 4.44 (s, 2H), 7.39–7.45 (m, 3H), 7.45–7.50 (m, 2H); ^{13}C NMR: δ 42.7, 57.2, 71.8, 76.7, 127.4, 129.2, 129.3, 130.7.

Benzyl ethyl sulfone[24] (**2cc**). White crystals, yield 80%, (0.3 mmol of **1cc**, 0.66 mmol of H_2O_2), r.t. = 3 h, mp 77.5–78.5 °C, lit. 83–84 °C. ^{1}H NMR: δ 1.36 (d, *J* = 7.5 Hz, 3H), 2.86 (q, *J* = 7.5 Hz, 2H), 4.23 (s, 2H), 7.38–7.44 (m, 5H); ^{13}C NMR: δ 6.4, 45.3, 58.7, 128.1, 129.0, 129.1, 130.5.

Benzyl butyl sulfone[25] (**2dd**). White crystals, yield 74%, (0.3 mmol of **1dd**, 0.66 mmol of H_2O_2), r.t. = 4 h, mp 92.4–93.7 °C, lit. 92–95 °C. ^{1}H NMR: δ 0.92 (t, *J* = 7.4 Hz, 3H), 1.41 (sext, *J* = 7.4 Hz, 2H), 1.75–1.83 (m, 2H), 2.79–2.84 (m, 2H), 4.22 (s, 2H), 7.37–7.43 (m, 5H); ^{13}C NMR: δ 13.5, 21.7, 23.7, 50.7, 59.4, 128.1, 129.0, 129.1, 130.5.

2-Pyridyl methyl sulfone[10] (**2ee**). Colorless oil, yield 77%, (0.3 mmol of **1ee**, 0.75 mmol of H_2O_2), r.t. = 11 h. ^{1}H NMR: δ 3.25 (s, 3H), 7.58 (ddd, *J* = 7.6, 4.7, 0.9 Hz, 1H), 7.99 (dt, *J* = 7.8, 1.6 Hz, 1H), 8.11 (m, 1H), 8.75 (m, 1H); ^{13}C NMR: δ 40.0, 121.1, 127.4, 138.2, 150.0, 158.0.

1-Methyl-2-methylsulfonylimidazole[26] (**2ff**). White crystals, yield 50%, (0.3 mmol of **1ff**, 0.99 mmol of H_2O_2), r.t. = 8 h, mp 111.1–112.8 °C, lit. 116–117 °C. ^{1}H NMR: δ 3.37 (s, 3H), 4.00 (s, 3H), 7.01 (br s, 1H), 7.11 (br s, 1H); ^{13}C NMR: δ 34.9, 42.8, 125.3, 128.6, 142.9.

Dimethyl sulfone[27] (**2gg**). White crystals, yield 79%, (1 mmol of **1gg**, 2.2 mmol of H_2O_2), r.t. = 16h, mp 107.0–107.8 °C, lit. 107–108 °C. ^{1}H NMR: δ 2.98 (s, 3H); ^{13}C NMR: δ 42.6.

Ethyl hexyl sulfone[5] (**2hh**). White crystals, yield 90%, (0.3 mmol of **1hh**, 0.66 mmol of H_2O_2), r.t. = 0.85 h, mp 59.1–59.9 °C, lit. 64.5–65.5 °C. ^{1}H NMR: δ 0.90 (t, *J* = 6.9 Hz, 3H), 1.29–1.36 (m, 4H), 1.38–1.49 (m, 5H), 1.79–1.87 (m, 2H), 1.92–3.02 (m, 4H); ^{13}C NMR: δ 6.6, 13.9, 21.9, 22.3, 28.2, 31.2, 46.9, 51.9.

Cyclohexyl ethyl sulfone[28] (**2ii**). White crystals, yield 83%, (0.3 mmol of **1ii**, 0.66 mmol of H_2O_2), r.t. = 3 h, mp 30.3–31.5 °C, lit. 32–34 °C. ^{1}H NMR: δ 1.18–1.36 (m, 3H), 1.39 (t, *J* = 7.5 Hz, 3H), 1.56–1.61 (m, 2H), 1.71–1.77 (m, 1H), 1.91–1.98 (m, 2H), 2.12–2.19 (m, 2H), 2.86 (tt, *J* = 12.2, 3.5 Hz, 1H), 2.95 (q, *J* = 7.5 Hz, 2H); ^{13}C NMR: δ 6.0, 25.0, 25.0, 25.1, 43.6, 60.1.

2-Hydroxyethyl butyl sulfone[1] (**2kk**). Colorless oil, yield 79%, (0.3 mmol of **1kk**, 0.66 mmol of H_2O_2), r.t = 0.75 h, mp 38.6–40.2 °C, lit. 42–43 °C. ^{1}H NMR: δ 0.97 (t, *J* = 7.4 Hz, 3H), 1.49 (sext, *J* = 7.4 Hz, 2H), 1.80–1.87 (m, 2H), 2.55 (br s, 1H), 3.06–3.12 (m, 2H), 3.19–3.23 (m, 2H) 4.10–4.15 (m, 2H); ^{13}C NMR: δ 13.5, 21.7, 23.7, 54.3, 54.7, 56.3.

Benzyl phenyl sulfone[29] (**2ll**). White crystals, yield 81%, (0.3 mmol of **1ll**, 0.66 mmol of H_2O_2 after 0, 1, 1.5 and 2.5 h), r.t. = 4 h, mp 146.2–147.4 °C, lit. 148–150 °C. ^{1}H NMR: δ 4.31 (s, 2H), 7.06–7.10 (m, 2H), 7.24–7.28 (m, 2H), 7.29–7.34 (m, 1H), 7.43–7.48 (m, 2H), 7.58–7.65 (m, 3H); ^{13}C NMR: δ 62.9, 128.1, 128.6, 128.6, 128.7, 128.9, 130.8, 133.7, 137.8.

4-Methoxybenzyl phenyl sulfone[30] (**2mm**). White crystals, yield 81%, (0.3 mmol of **1mm**, 0.66 mmol of H_2O_2 after 0, 1, 1.5 and 2.5 h), r.t. = 5 h, mp 137.0–138.8 °C, lit. 139–140 °C. ^{1}H NMR: δ 3.79 (s, 3H), 4.25 (s, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 7.00 (d, *J* = 8.6 Hz, 2H), 7.43–7.49 (m, 2H), 7.58–7.67 (m, 3H); ^{13}C NMR: δ 55.2, 66.2, 114.0, 119.9, 128.6, 128.9, 132.0, 133.6, 137.9, 160.0.

4-Methoxybenzyl-(4-methylphenyl) sulfone[31] (**2nn**). White crystals, yield 82%, (0.3 mmol of **1nn**, 0.66 mmol of H_2O_2 after 0, 1, 1.5 and 2.5 h), r.t. = 5 h, mp 118.0–119.4 °C, lit. 119–121 °C. ^{1}H NMR: δ 2.42 (s, 3H), 3.79 (s, 3H), 4.23 (s, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 7.00 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR: δ 21.6, 55.2, 62.2, 114.0, 120.1, 128.6, 129.5, 132.0, 135.0, 144.5, 159.9.

4-(Methylsulfonylbenzophenone)[32] (**2oo**). White crystals, yield 87%, (0.3 mmol of **1oo**, 0.75 mmol of H_2O_2 after 0, 1, 3 and 5.5 h), r.t = 8 h, mp 139.0–141.0 °C, lit. 140–141 °C. ^{1}H NMR: δ 3.12 (s, 3H), 7.50–7.55 (m,, 2H), 7.63–7.68 (m, 1H), 7.79–7.83 (m, 2H), 7.96 (d, *J* = 8.4 Hz, 2H), 8.08 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR: δ 44.4, 127.4, 128.6, 130.1, 130.5, 133.4, 136.3, 142.3, 143.4, 195.1.

4-Methyl-4'-(methylsulfonylbenzophenone)[33] (**2pp**). White crystals, yield 87%, (0.3 mmol of **1pp**, 0.75 mmol of H_2O_2 after 0, 1, 3 and 5 h), r.t. = 9 h, mp 190.0–192.0 °C, lit. 192–194 °C. ^{1}H NMR: δ 2.46 (s, 3H), 3.12 (s, 3H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.93 (d, *J* = 8.4 Hz, 2H), 8.07 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR: δ 21.7, 44.4, 127.4, 129.3, 130.3, 130.4, 133.7, 142.8, 143.2, 144.5, 194.8.

Benzo[*b*]thiophene 1,1-dioxide[34] (**2qq**). White crystals, yield 46%, (0.3 mmol of **1qq**, 0.50 mmol of H_2O_2 after 0 h and 0.25 mmol after 1 h), r.t. = 3 h, mp 137.0–139.0 °C, lit. 141–143 °C. ^{1}H NMR: δ 6.72 (d, *J* = 6.9 Hz, 1H), 7.23 (dd, *J* = 6.9, 0.5 Hz, 1H), 7.35–7.39 (m, 1H), 7.51–7.59 (m, 2H), 7.70–7.74 (m, 1H); ^{13}C NMR: δ 121.4, 125.3, 130.6, 130.8, 131.1, 132.3, 133.6, 136.7.

2,3-Dihydro-4(*H*)-1-benzothiopyran-4-one 1,1-dioxide[35] (**2rr**). White crystals, yield 75%, (0.3 mmol of **1rr**, 0.75 mmol of H_2O_2 after 0 h and 0.38 mmol after 1 h), r.t. = 1.5 h, mp 128.8–130.3 °C, lit. 130–130.5 °C. ^{1}H NMR: δ 3.43 (t, *J* = 6.4 Hz, 2H), 3.71 (t, *J* = 6.4 Hz, 2H), 7.73–7.78 (m, 1H), 7.81–7.86 (m, 1H), 8.00–8.05 (m, 1H), 8.11–8.16 (m, 1H); ^{13}C NMR: δ 36.7, 49.2, 123.6, 128.8, 130.2, 133.4, 134.9, 141.3, 190.1.

Dibenzothiophene 5,5-dioxide[36] (**2ss**). White crystals, yield 81%, (0.3 mmol of **1ss**, 0.75 mmol of H_2O_2 after 0, 0.5, 3, 6, 9 and 15 h), r.t = 17.5 h, mp 234–236 °C, lit. 237 °C. ^{1}H NMR: δ 7.51–7.56 (m, 2H), 7.62–7.67 (m, 2H), 7.78–7.82 (m, 2H), 7.82–7.85 (m, 2H); ^{13}C NMR: δ 121.6, 122.2, 130.4, 131.6, 133.9, 137.7.

Thioxanthen-9-one-*S*,*S*-dioxide[37] (**2tt**). Yellow crystals, yield 79%, (0.3 mmol of **1tt**, 0.75 mmol of H_2O_2 after 0, 0.5, 3, 6, 9 and 15 h), r.t = 17.5 h, mp 185.1–186.8 °C, lit. 186–188 °C. ^{1}H NMR: δ 7.77–7.84 (m, 2H), 7.85–7.93 (m, 2H), 8.16–8.23 (m, 2H), 8.32–8.39 (m, 2H); ^{13}C NMR: δ 123.5, 129.2, 130.6, 133.2, 134.6, 140.9, 178.3.

1,3-Dithiane 1,1,3,3-tetraoxide[38] (**2uu**). White crystals, yield 59%, (0.3 mmol of **1uu**, 1.50 mmol of H_2O_2), r.t. = 3 h, mp 309–312 °C. ^{1}H NMR: δ 2.23–2.30 (m, 2H), 3.35–3.40 (m, 4H), 5.25 (s, 2H); ^{13}C NMR: δ 17.4, 49.9, 70.0.

1 J. Morales-Sanfrutos, A. Megia-Fernandez, F. Hernandez-Mateo, M. D. Giron-Gonzalez, R. Salto-Gonzalez and F. Santoyo-Gonzalez, *Org. Biomol. Chem.* 2011, **9**, 851–864.
2 Z. Časar, D. Lorcy, I. Leban and A. Majcen-Le Maréchal, *Acta Chim. Slov*. 2002, **49**, 871–883.
3 C. Yang, Q. Jin, H. Zhang, J. Liao, J. Zhu, B. Yu and J. Deng, *Green. Chem.* 2009, **11**, 1401–1405.

4 A. C. Bonaparte, M. P. Betush, B. M. Panseri, D. J. Mastarone, R. K. Murphy and S. S. Murphree, *Org. Lett.* 2011, **13**, 1447–1449.
5 M. M. Zhao, C. Qu and J. E. Lynch, *J. Org. Chem.* 2005, **70**, 6944–6947.
6 S. R. V. Kandula and P. Kumar, *Tetrahedron* 2006, **62**, 9942-9948.
7 H. Yang, Y. Li, M. Jiang, J. Wang and H. Fu, *Eur. J. Chem*. 2011, **17**, 5562–5660.
8 R. F. Collins and M. Davis, *J. Chem. Soc. (C)*, 1966, 2196–2201.
9 J. K. Crandall and C. Pradat, *J. Org. Chem*. 1985, **50**, 1327–1329.
10 C. Martin, F. Sandrinelli, C. Perrio, S. Perrio and M.-C. Lasne, *J. Org. Chem*. 2006, **71**, 210–214.
11 M. Peyronneau, M.-T. Boisdon, N. Roques, S. Mazières and C. Le Roux, *E. J. Org. Chem*. 2004, 4636–4640.
12 Y. Kato and R. Kimura, *Toxicol. Appl. Pharmacol.* 1997, **145**, 277–284.
13 R. D. Mortimer and W. H. Newsome, *Chemosphere* 1996, **32**, 935–946.
14 P. Hanson, R. A. A. J. Hendrickx and J. R. L. Smith, *Org. Biomol. Chem*. 2008, **6**, 745–761.
15 J.-M. Mattalia, M. Chanon and C. J. M. Stirling, *J. Org. Chem*. 1996, **61**, 1153–1154.
16 F. Schoenebeck, J. A. Murphy, S.-z. Zhou, Y. Uenoyama, Y. Miclo and T. Tuttle, *J. Am. Chem. Soc.* 2007, **129**, 13368–13369.
17 J. T. Mattiza, V. J. Meyer and H. Duddeck, *Magn. Reson. Chem.* 2010, **48**, 192–197.
18 V. N. Matvienko, I. F. Perepichka, A. F. Popov and Z. P. Piskunova, *J. Phys. Org. Chem*. 1994, **7**, 525–533.
19 C. M. Rodríguez, J. M. Ode, J. M. Palazón and V. S. Martín, *Tetrahedron* 1992, **48**, 3571–3576.
20 D. Villemin and A. B. Alloum, *Synth. Commun*. 1990, **20**, 925–932.
21 N. Fukuda and T. Ikemoto, *J. Org. Chem*. 2006, **75**, 4629–4631.
22 G. A. Russell, P. Ngoviwatchai, H. Tashtoush and J. Hershberger, *Organometallics* 1987, **6**, 1414–1419.
23 R. C. Pink, R. Spratt and C. J. M. Stirling, *J. Chem. Soc.* 1965, 5714–5718.
24 I. B. Douglass and B. S. Farah, *J. Org. Chem.* 1959, **24**, 973–975.
25 C. Caupène, C. Martin, M. Lemarié, S. Perrio and P. Metzner, *J. Sulf. Chem.* 2009, **30**, 338–345.
26 G. Vampa, S. Benvenuti, F. Severi, L. Malmusi and L. Antolini, *J. Heterocyclic Chem.* 1995, **32**, 227–234.
27 T. Bruun and N. A. Sorensen, *Acta Chem. Scand.* 1954, **8**, 703–703.
28 M. W. Cronyn and E. Zavarin, *J. Org. Chem*. 1954, **19**, 139–154.
29 A. R. Katritzky, R. Akue-Gedu and A. V. Vakulenko, *Arkivoc* 2007, **(iii)**, 5–12.
30 G. A. Russell and J. M. Pecoraro, *J. Org. Chem.* 1979, **44**, 3990–3991.
31 M. A. Reddy, P. S. Reddy and B. Sreedhar, *Adv. Synth. Catal*. 2010, **352**, 1861–1869.
32 A. Moreau, P. N. P. Rao and E. E. Knaus, *Bioorg. Med. Chem.* 2006, **14**, 5340–5350.
33 M. C. Wilkinson, *Org. Lett.* 2011, **13**, 2232–2235.
34 D. Madec, F. Mingoia, C. Macovei, G. Maitro, G. Giambastiani and G. Poli, *Eur. J. Chem.* 2005, 552–557.
35 M. H. Holshouser, L. J. Loeffler and I. H. Hall, *J. Med. Chem.* 1981, **24**, 853–858.
36 M. Kirihara, J. Yamamoto, T. Noguchi, A. Itou, S. Naito and Y. Hirai, *Tetrahedron* 2009, **65**, 10477–10484.
37 K. Bahrami, M. M. Khodaei, and S. Sohrabnezhad, *Tetrahedron Lett.* 2011, **52**, 6420–6423.
38 A. H. Fawcett, K. J. Ivin and C. D. Stewart, *Org. Magn. Reson.* 1978, **11**, 360–369.