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Green Organocatalytic Oxidation of Sulfides to Sulfoxides and Sulfones

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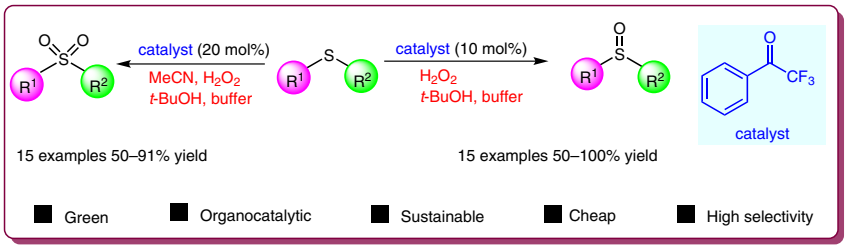


Received: 29.06.2016
Accepted after revision: 26.08.2016
Published online: 21.09.2016
DOI: 10.1055/s-0036-1588315; Art ID: ss-2016-z0467-op

Abstract A highly efficient synthetic methodology towards the selective synthesis of sulfoxides and sulfones is reported using a cheap and green organocatalytic method. Starting from sulfides and using 2,2,2-trifluoroacetophenone as the organocatalyst and H_2O_2 as the oxidant, the high-yielding preparation of sulfoxides or sulfones is described, being dependent on the reaction conditions.

Key words organocatalytic oxidation, sulfoxides, sulfones, hydrogen peroxide, green chemistry

Sulfoxides and sulfones are very important moieties used in medicinal chemistry and especially in the backbone of marketed therapeutics[1] such as Nexium,[2a] Provigil,[2b] the antibacterial Dapsone,[3] Laropiprant[4] and the COX-2 inhibitor Vioxx (Figure 1).[5] They constitute a common motif in agrochemicals[6] and ligands for transition-metal asymmetric catalysis.[7] Also, they are commonly occurring in natural products with active biological character.[8] Moreover, sulfide oxidation is the basis for the catalytic oxidative desulfurization of crude oil, in which sulfur compounds are removed.[9] For all these reasons, selective oxidation of sulfides to either sulfoxides or sulfones is one of the most common challenges in sulfur chemistry.

As a result, numerous strategies for the selective oxidation of sulfides have been reported. The most traditional method involves oxidants such as nitric acid, *m*-chloroperbenzoic acid,[10] UHP,[11] NaClO,[12] $NaIO_4$,[13] Oxone[14] or dimethyldioxirane (Scheme 1, path a).[15] These methods utilize expensive reagents in stoichiometric amounts and require long reaction times. Recently, hydrogen peroxide has been widely employed as the oxidant and a variety of catalysts have been developed. Transition-metal catalysts have been

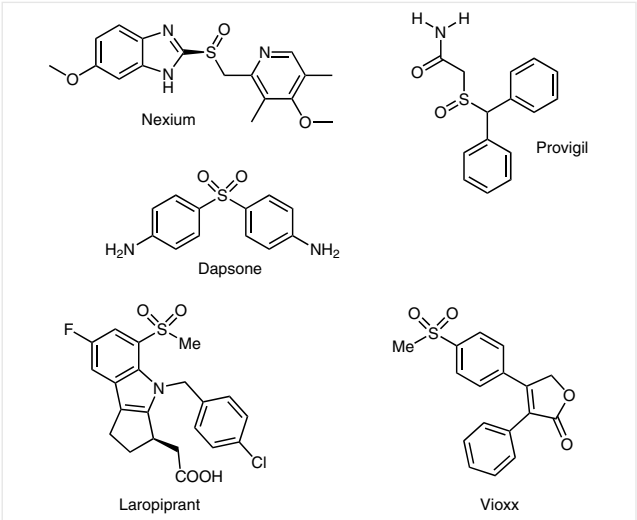
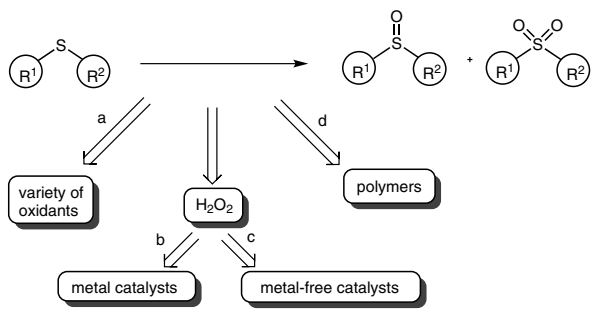


Figure 1 Marketed drugs containing a sulfoxide or a sulfone

reported based on iron,[16] manganese,[17] zinc[18] and a variety of other metals for the activation of hydrogen peroxide (Scheme 1, path b). Unfortunately, drawbacks of metal catalysts, such as toxicity and high levels of inorganic waste, make this method harmful for the environment. Therefore, metal-free catalysts have been developed with examples including enzymes[19] or flavin-based catalysts (Scheme 1, path c).[20] Furthermore, catalyst-free protocols have been devised, but only for sulfone synthesis.[21] Although, polymers[22] have been used to improve the selective oxidation of sulfides, leading to the desired products in good yields, unfortunately, harsh reaction conditions and long reaction times have to be employed (Scheme 1, path d).

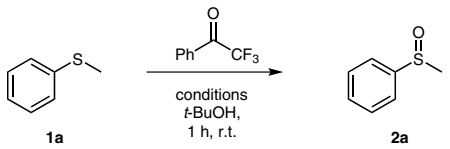
In this work, we employed the green organocatalytic oxidative protocol that was developed in our laboratory,[23] using hydrogen peroxide as the oxidant and 2,2,2-trifluoroac-



Scheme 1 Synthetic pathways for the selective synthesis of sulfoxides and sulfones

etophenone as the catalyst. Herein, we have introduced a cheap, green and environmentally friendly protocol, which achieves the selective oxidation of sulfides to sulfoxides or sulfones, being dependent on the reaction conditions. The advantages of this protocol, such as commercial availability, low-priced reagents, short reaction time and mild reaction conditions, serve to make it one of the most easy and user-friendly oxidation methods (Scheme 1, bottom).

Table 1 Optimization of the Reaction Conditions for the Organocatalytic Synthesis of Sulfoxides



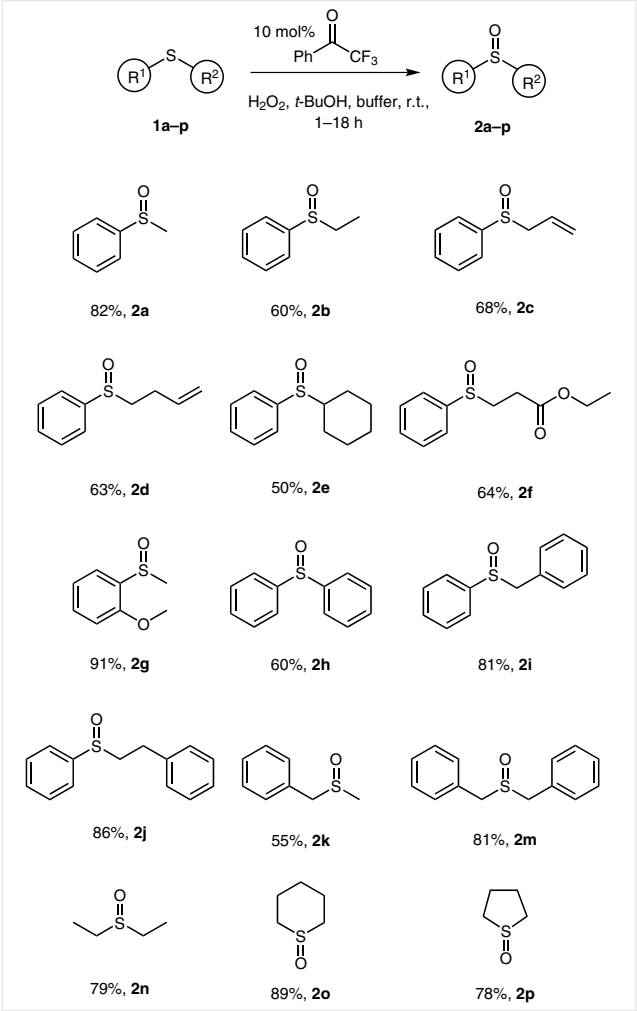
1a **2a**

Entry	Cat. (mol%)[a]	MeCN (equiv)	H_2O_2 (equiv)	Buffer[b]	Yield (%)[c]
1	10	–	1.1	yes	59
2	10	–	3	yes	83
3	0	3	3	no	38
4	0	–	1.5	yes	0
5	10	–	1.5	no	90
6	**10**	**–**	**1.5**	**yes**	**96**

[a] 2,2,2-Trifluoroacetophenone was used as the catalyst.
[b] Aqueous buffer (pH 11) was used.
[c] Yield determined from the crude ^{1}H NMR spectrum.

Initially, we optimized the reaction conditions for the synthesis of sulfoxides (Table 1). Employing 10 mol% of the catalyst, optimization of the amount of hydrogen peroxide in order to improve the yield of the desired sulfoxide was performed (Table 1, entries 1–6). The presence of the catalyst and the aqueous buffer were found to be indispensable for obtaining high yields of the sulfoxide.

Having optimized the reaction conditions, we turned our focus on studying the application of this method with a variety of substrates (Scheme 2). A series of sulfides was tested affording the desired products in excellent yields. Specifically, phenyl sulfides bearing an aliphatic moiety afforded the desired sulfoxides in high to quantitative yields (Scheme 2, products **2a–f**). Furthermore, *ortho*-substituted phenyl sulfide **1g** gave sulfoxide **2g** in excellent yield. When the phenyl sulfide had another substituent containing an aromatic group, the reaction required more time to reach completion affording the desired products in very good

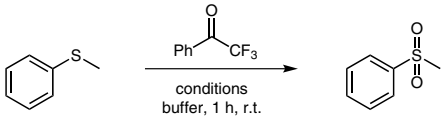


Scheme 2 Substrate scope for the selective organocatalytic oxidation of sulfides to sulfoxides

yields (Scheme 2, products **2h–j**). Moreover, benzyl sulfides were tested and resulted in the isolation of the corresponding products in satisfactory yields (Scheme 2, products **2k** and **2m**). Finally, a range of aliphatic sulfides was oxidized in excellent yields (Scheme 2, products **2n–p**).

In the next step, we studied the synthesis of sulfones (Table 2). Once the amount of the oxidant had been optimized (Table 2, entries 1–4), different polar and non-polar solvents were tested (Table 2, entries 5–12), in order to find the most suitable conditions. Column chromatography proved to be unnecessary in order to isolate the desired sulfone, since the product could be isolated in pure form after the oxidation via simple extractions.

Table 2 Optimization of the Reaction Conditions for the Organocatalytic Synthesis of Sulfones

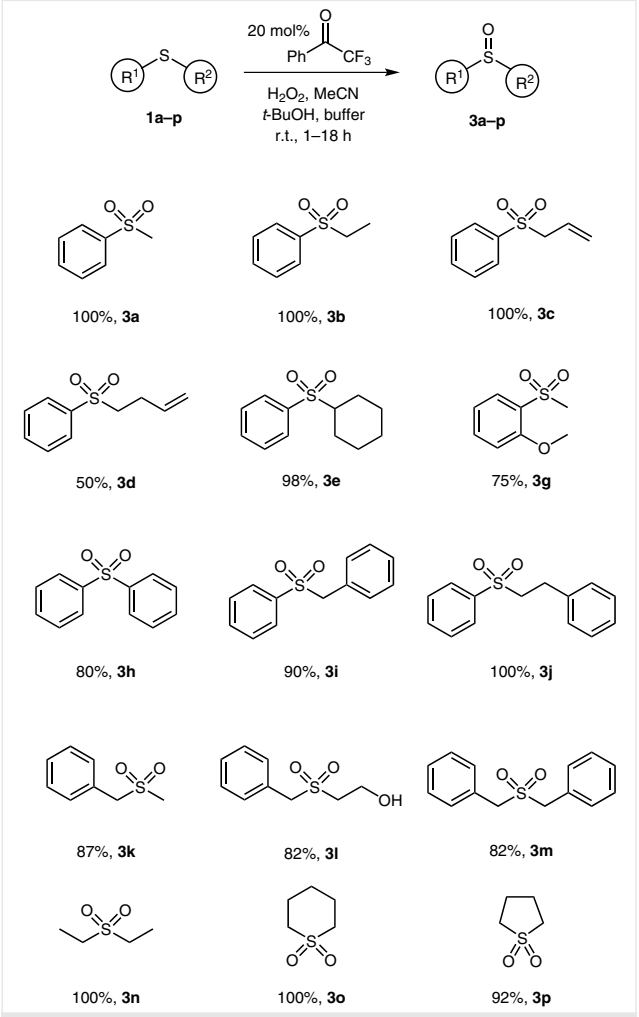


1a **3a**

Entry	Cat. (mol%)[a]	MeCN (equiv)	H_2O_2 (equiv)	Solvent	Yield (%)[b]
1	10	2	2	*t*-BuOH	49
2	10	3	3	*t*-BuOH	88
3	5	3	3	*t*-BuOH	54
4	**20**	**3**	**3**	***t*-BuOH**	**100**
5	20	3	3	EtOAc	80
6	20	3	3	MeOH	85
7	20	3	3	MeCN	64
8	20	3	3	THF	76
9	20	3	3	$CHCl_3$	45
10	20	3	3	toluene	40
11	20	3	3	benzene	39
12	20	3	3	DMSO	5

[a] 2,2,2-Trifluoroacetophenone was used as the catalyst.
[b] Yield determined from the crude ^{1}H NMR spectrum.

Among the substrates that were tested, phenyl sulfides containing an aliphatic moiety afforded the desired sulfones in high yields (Scheme 3, products **3a–e**). An *ortho*-substituted sulfide also underwent the oxidation to give the corresponding phenyl sulfone in very good yield (Scheme 3, product **3g**). Other substituted sulfides bearing an aromatic group were employed successfully, affording the desired products in very good yields (Scheme 3, products **3h–j**). Moreover, benzyl sulfides were transformed into the corresponding sulfones in high yields (Scheme 3, products **3k–m**) via this method. Finally, a range of aliphatic sulfides was successfully oxidized to the corresponding sulfones in excellent yields (Scheme 3, products **3n–p**).



Scheme 3 Substrate scope for the selective organocatalytic oxidation of sulfides to sulfones

Overall, the organocatalytic oxidation of sulfides to sulfoxides requires the presence of a catalyst, aqueous buffer and H_2O_2. The aqueous environment shifts the equilibrium of the ketone–diol of the activated carbonyl group of the catalyst toward the diol, which is oxidized by H_2O_2 to the corresponding perhydrate.[23] We believe that this perhydrate is the active oxidant for the oxidation to the sulfoxide. On the other hand, once MeCN is added to the reaction mixture, Payne's intermediate, which is formed under the basic conditions of the reaction mixture, as well as our previously described organocatalytic system,[23] are in place and shift the oxidation toward sulfone formation.

In conclusion, the selective organocatalytic oxidation of sulfides to sulfoxides or sulfones is described. Utilizing different organocatalytic conditions, the desired products were obtained by employing a cheap and environmentally

friendly organic molecule as the catalyst. This protocol was applied on a variety of aromatic and aliphatic sulfides affording sulfoxides and sulfones in high yields.

Chromatographic purification of the products was accomplished using forced-flow chromatography on Merck® Kieselgel 60 F_{254} (230–400 mesh). Thin-layer chromatography (TLC) was performed on Merck aluminum-backed silica plates (0.2 mm, 60 F_{254}). Visualization of the developed chromatogram was performed by fluorescence quenching using phosphomolybdic acid, anisaldehyde or potassium permanganate stains. Melting points were determined on a Buchi® 530 hot stage apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra (200 MHz and 50 MHz, respectively) were recorded on a Varian® Mercury spectrometer, and are internally referenced to residual solvent signals. Data for ^{1}H NMR are reported as follows: chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s = broad singlet), coupling constant, integration and assignment. Data for ^{13}C NMR are reported in terms of chemical shift (δ). Mass spectra (ESI) were recorded on a Finnigan® Surveyor MSQ LC–MS spectrometer. HRMS spectra were recorded on a Bruker QTOF Maxis Impact spectrometer. Mass spectra and the conversions of the reactions were recorded on a Shimadzu® GCMS-QP2010 Plus gas chromatograph–mass spectrometer utilizing a MEGA® column (MEGA-5, F.T.: 0.25 µm, I.D.: 0.25 mm, length: 30 m, T_{max}: 350 °C, Column ID# 11475).

Organocatalytic Oxidation of Sulfides to Sulfoxides; General Procedure

Sulfide (1.00 mmol) was placed in a round-bottom flask, followed by *t*-BuOH (0.5 mL), 2,2,2-trifluoroacetophenone (17.4 mg, 0.10 mmol), aq buffer solution (0.5 mL, 0.6 M K_2CO_3/4 × 10^{-4} M EDTA disodium salt) and 30% aq H_2O_2 (0.18 mL, 1.50 mmol). The reaction mixture was stirred for 1–18 h. The crude residue was purified using flash column chromatography (40–60% EtOAc in PE) to afford the desired product.

(Methylsulfinyl)benzene (2a)[24]

The reaction mixture was stirred for 1 h.

Colorless oil; yield: 115 mg (82%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.61–7.51 (m, 2 H, ArH), 7.45–7.35 (m, 3 H, ArH), 2.63 (s, 3 H, CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 145.1, 130.8, 129.1, 123.2, 43.5.

MS (ESI): *m*/*z* (%) = 141 (100) $[M + H]^+$.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for C_7H_9OS: 141.0369; found: 141.0374.

(Ethylsulfinyl)benzene (2b)[25]

The reaction mixture was stirred for 3 h.

Colorless oil; yield: 92 mg (60%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.61–7.23 (m, 5 H, ArH), 2.95–2.60 (m, 2 H, CH_2), 1.13 (t, *J* = 7.4 Hz, 3 H, CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 142.9, 130.9, 129.1, 124.1, 50.1, 5.9.

MS (ESI): *m*/*z* (%) = 155 (100) $[M + H]^+$.

(Allylsulfinyl)benzene (2c)[26]

The reaction mixture was stirred for 5 h.

Colorless oil; yield: 113 mg (68%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.58–7.50 (m, 2 H, ArH), 7.47–7.37 (m, 3 H, ArH), 5.70–5.44 (m, 1 H, =CH), 5.26 (d, *J* = 9.3 Hz, 1 H, =C*H*H), 5.12 (d, *J* = 17.4 Hz, 1 H, =CH*H*), 3.52 (dd, *J* = 12.5, 6.1 Hz, 1 H, C*H*H), 3.43 (dd, *J* = 12.5, 7.1 Hz, 1 H, C*H*H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 142.5, 130.9, 128.8, 125.0, 124.1, 123.8, 60.5.

MS (ESI): *m*/*z* (%) = 167 (100) $[M + H]^+$.

(But-3-en-1-ylsulfinyl)benzene (2d)[22]

The reaction mixture was stirred for 1 h.

Colorless oil; yield: 113 mg (63%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.71–7.56 (m, 2 H, ArH), 7.54–7.43 (m, 3 H, ArH), 5.91–5.65 (m, 1 H, =CH), 5.13–5.03 (m, 2 H, $=CH_2$), 2.87 (t, *J* = 7.7 Hz, 2 H, CH_2), 2.62–2.42 (m, 1 H, C*H*H), 2.40–2.23 (m, 1 H, C*H*H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 143.2, 134.8, 131.1, 129.2, 124.0, 117.1, 56.0, 26.2.

MS (ESI): *m*/*z* (%) = 181 (100) $[M + H]^+$.

(Cyclohexylsulfinyl)benzene (2e)[27]

The reaction mixture was stirred for 1 h.

Pale yellow solid; yield: 104 mg (50%); mp 64–65 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.64–7.40 (m, 5 H, ArH), 2.66–2.45 (m, 1 H, CH), 1.94–1.70 (m, 4 H, 4 × CH*H*), 1.66–1.56 (m, 1 H, C*H*H), 1.51–1.08 (m, 5 H, 5 × C*H*H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 141.8, 130.9, 128.9, 125.0, 63.1, 26.2, 25.6, 25.4, 25.3, 24.0.

MS (ESI): *m*/*z* (%) = 209 (100) $[M + H]^+$.

Ethyl 3-(Phenylsulfinyl)propanoate (2f)[28]

The reaction mixture was stirred for 5 h.

Colorless oil; yield: 145 mg (64%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.64–7.47 (m, 2 H, ArH), 7.47–7.34 (m, 3 H, ArH), 4.02 (q, *J* = 7.1 Hz, 2 H, OCH_2), 3.24–3.02 (m, 1 H, C*H*H), 3.01–2.58 (m, 2 H, 2 × C*H*H), 2.56–2.34 (m, 1 H, C*H*H), 1.14 (t, *J* = 7.1 Hz, 3 H, CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.0, 142.2, 131.0, 129.1, 123.8, 60.9, 50.8, 25.9, 13.9.

MS (ESI): *m*/*z* (%) = 227 (100) $[M + H]^+$.

1-Methoxy-2-(methylsulfinyl)benzene (2g)[29]

The reaction mixture was stirred for 18 h.

Pale yellow solid; yield: 155 mg (91%); mp 75–79 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.69 (dd, *J* = 7.5, 1.7 Hz, 1 H, ArH), 7.37–7.25 (m, 1 H, ArH), 7.05 (t, *J* = 7.5 Hz, 1 H, ArH), 6.81 (d, *J* = 8.2 Hz, 1 H, ArH), 3.76 (s, 3 H, OCH_3), 2.65 (s, 3 H, SCH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 154.4, 132.5, 131.7, 124.1, 121.2, 110.3, 55.4, 40.8.

MS (ESI): *m*/*z* (%) = 171 (100) $[M + H]^+$.

Sulfinyldibenzene (2h)[26]

The reaction mixture was stirred for 18 h.

White solid; yield: 121 mg (60%); mp 70–72 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.46–7.09 (m, 10 H, ArH).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 144.9, 131.1, 129.3, 124.7.

MS (ESI): *m*/*z* (%) = 203 (100) $[M + H]^+$.

(Benzylsulfinyl)benzene (2i)[26]

The reaction mixture was stirred for 18 h.

White solid; yield: 175 mg (81%); mp 124–126 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.43–7.24 (m, 5 H, ArH), 7.23–7.05 (m, 3 H, ArH), 6.98–6.81 (m, 2 H, ArH), 4.02 (d, *J* = 12.5 Hz, 1 H, C*H*H), 3.93 (d, *J* = 12.5 Hz, 1 H, C*H*H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 142.4, 130.9, 130.1, 128.8, 128.6, 128.1, 127.9, 124.1, 63.1.

MS (ESI): *m*/*z* (%) = 217 (100) $[M + H]^+$.

(Phenethylsulfinyl)benzene (2j)[30]

The reaction mixture was stirred for 2 h.

Colorless oil; yield: 198 mg (86%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.65–7.51 (m, 2 H, ArH), 7.49–7.31 (m, 3 H, ArH), 7.27–6.98 (m, 5 H, ArH), 3.15–2.73 (m, 4 H, 2 × CH_2).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 143.1, 138.3, 130.6, 128.8, 128.3, 128.1, 126.3, 123.5, 57.7, 27.7.

MS (ESI): *m*/*z* (%) = 231 (100) $[M + H]^+$.

[(Methylsulfinyl)methyl]benzene (2k)[25]

The reaction mixture was stirred for 18 h.

White solid; yield: 85 mg (55%); mp 55–57 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.42–7.36 (m, 5 H, ArH), 4.23 (s, 2 H, CH_2), 2.73 (s, 3 H, CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 133.4, 130.4, 129.0, 128.1, 61.0, 38.9.

MS (ESI): *m*/*z* (%) = 155 (100) $[M + H]^+$.

[Sulfinylbis(methylene)]dibenzene (2m)[26]

The reaction mixture was stirred for 18 h.

White solid; yield: 186 mg (81%); mp 133–135 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.42–7.12 (m, 10 H, ArH), 3.89 (d, *J* = 13.0 Hz, 2 H, 2 × C*H*H), 3.79 (d, *J* = 13.0 Hz, 2 H, 2 × CH*H*).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 129.9, 128.5, 127.9, 56.8.

MS (ESI): *m*/*z* (%) = 231 (100) $[M + H]^+$.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{14}H_{15}OS$: 231.0838; found: 231.0846.

(Ethylsulfinyl)ethane (2n)[31]

The reaction mixture was stirred for 8 h.

Colorless oil; yield: 84 mg (79%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.60 (q, *J* = 7.4 Hz, 4 H, 2 × CH_2), 1.87 (t, *J* = 7.4 Hz, 6 H, 2 × CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 44.5, 6.6.

MS (ESI): *m*/*z* (%) = 107 (100) $[M + H]^+$.

Tetrahydro-2*H*-thiopyran 1-Oxide (2o)[32]

The reaction mixture was stirred for 1 h.

White solid; yield: 105 mg (89%); mp 60–62 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.84–2.43 (m, 4 H, 2 × CH_2), 2.20–1.87 (m, 2 H, CH_2), 1.62–1.22 (m, 4 H, 2 × CH_2).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 48.3, 24.1, 18.6.

MS (ESI): *m*/*z* (%) = 119 (100) $[M + H]^+$.

Tetrahydrothiophene 1-Oxide (2p)[25]

The reaction mixture was stirred for 18 h.

Colorless oil; yield: 81 mg (78%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.96 (t, *J* = 7.5 Hz, 4 H, 2 × CH*H*), 2.19–2.11 (m, 4 H, 4 × C*H*H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 51.0, 22.6.

MS (ESI): *m*/*z* (%) = 105 (100) $[M + H]^+$.

Organocatalytic Oxidation of Sulfides to Sulfones; General Procedure

Sulfide (1.00 mmol) was placed in a round-bottom flask, followed by *t*-BuOH (0.5 mL), 2,2,2-trifluoroacetophenone (34.8 mg, 0.20 mmol), aq buffer solution (0.5 mL, 0.6 M K_2CO_3/4 × 10^{-4} M EDTA disodium salt), MeCN (0.15 mL, 3.00 mmol) and 30% aq H_2O_2 (0.36 mL, 3.00 mmol). The reaction mixture was stirred for 1–5 h. The reaction was quenched with 1 M HCl (5 mL) and extracted with $CHCl_3$ (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo to afford the desired product.

(Methylsulfonyl)benzene (3a)[33]

The reaction mixture was stirred for 1 h.

White solid; yield: 156 mg (100%); mp 88–90 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.02–7.76 (m, 2 H, ArH), 7.71–7.44 (m, 3 H, ArH), 3.02 (s, 3 H, CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 140.3, 133.6, 129.3, 127.2, 44.3.

MS (ESI): *m*/*z* (%) = 157 (100) $[M + H]^+$.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_7H_9O_2S$: 157.0318; found: 157.0321.

(Ethylsulfonyl)benzene (3b)[25]

The reaction mixture was stirred for 1 h.

Colorless oil; yield: 170 mg (100%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.91–7.77 (m, 2 H, ArH), 7.68–7.44 (m, 3 H, ArH), 3.08 (q, *J* = 7.4 Hz, 2 H, CH_2), 1.22 (t, *J* = 7.4 Hz, 3 H, CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 138.1, 133.6, 129.1, 128.0, 50.4, 7.3.

MS (ESI): *m*/*z* (%) = 171 (100) $[M + H]^+$.

(Allylsulfonyl)benzene (3c)[26]

The reaction mixture was stirred for 1 h.

Colorless oil; yield: 182 mg (100%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.86–7.71 (m, 2 H, ArH), 7.64–7.37 (m, 3 H, ArH), 5.86–5.50 (m, 1 H, =CH), 5.23 (d, *J* = 10.1 Hz, 1 H, =C*H*H), 5.06 (d, *J* = 18.3 Hz, 1 H, =C*H*H), 3.76–3.70 (m, 2 H, CH_2).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 137.9, 133.6, 128.8, 128.1, 124.5, 124.3, 60.5.

MS (ESI): *m*/*z* (%) = 183 (100) $[M + H]^+$.

(But-3-en-1-ylsulfonyl)benzene (3d)[22]

The reaction mixture was stirred for 1 h.

Colorless oil; yield: 98 mg (50%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.97–7.76 (m, 2 H, ArH), 7.70–7.40 (m, 3 H, ArH), 5.79–5.53 (m, 1 H, =CH), 5.12–4.81 (m, 2 H, $=CH_2$), 3.30–2.99 (m, 2 H, CH_2), 2.50–2.24 (m, 2 H, CH_2).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 138.8, 133.8, 133.7, 129.3, 128.1, 117.1, 55.3, 26.8.

MS (ESI): *m*/*z* (%) = 197 (100) $[M + H]^+$.

(Cyclohexylsulfonyl)benzene (3e)[34]

The reaction mixture was stirred for 1.5 h.

Yellow solid; yield: 220 mg (98%); mp 71–73 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.95–7.74 (m, 2 H, ArH), 7.71–7.39 (m, 3 H, ArH), 2.99–2.76 (m, 1 H, CH), 2.11–1.95 (m, 2 H, 2 × CH*H*), 2.93–1.73 (m, 2 H, 2 × C*H*H), 1.71–1.54 (m, 1 H, C*H*H), 1.51–0.99 (m, 5 H, 5 × C*H*H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 137.0, 133.5, 128.92, 128.88, 63.3, 25.4, 25.0, 24.9.

MS (ESI): *m*/*z* (%) = 225 (100) $[M + H]^+$.

1-Methoxy-2-(methylsulfonyl)benzene (3g)[21]

The reaction mixture was stirred for 3 h.

White solid; yield: 140 mg (75%); mp 88–90 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.85 (dd, *J* = 8.0, 1.5 Hz, 1 H, ArH), 7.77 (dd, *J* = 8.0, 1.7 Hz, 1 H, ArH), 7.56 (m, 1 H, ArH), 7.36 (td, *J* = 7.8, 1.7 Hz, 1 H, ArH), 3.90 (s, 3 H, OCH_3), 3.11 (s, 3 H, SCH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 157.0, 135.5, 129.4, 128.0, 120.5, 112.5, 56.1, 42.7.

MS (ESI): *m*/*z* (%) = 187 (100) $[M + H]^+$.

Sulfonyldibenzene (3h)[35]

The reaction mixture was stirred for 5 h.

White solid; yield: 174 mg (80%); mp 121–123 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.01–7.85 (m, 4 H, ArH), 7.64–7.32 (m, 6 H, ArH).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 141.3, 133.1, 130.8, 129.1, 129.0, 127.4, 126.9, 124.6.

MS (ESI): *m*/*z* (%) = 219 (100) $[M + H]^+$.

(Benzylsulfonyl)benzene (3i)[26]

The reaction mixture was stirred for 1 h.

White solid; yield: 209 mg (90%); mp 146–148 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.65–7.44 (m, 3 H, ArH), 7.41–7.33 (m, 2 H, ArH), 7.26–7.10 (m, 3 H, ArH), 7.09–6.98 (m, 2 H, ArH), 4.27 (s, 2 H, CH_2).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 137.5, 133.6, 130.6, 130.1, 128.6, 128.3, 124.1, 62.5.

MS (ESI): *m*/*z* (%) = 233 (100) $[M + H]^+$.

(Phenethylsulfonyl)benzene (3j)[36]

The reaction mixture was stirred for 1.5 h.

Colorless oil; yield: 246 mg (100%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.02–7.81 (m, 2 H, ArH), 7.73–7.38 (m, 3 H, ArH), 7.32–6.99 (m, 5 H, ArH), 3.42–3.32 (m, 2 H, CH_2), 3.12–2.90 (m, 2 H, CH_2).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 138.6, 137.1, 133.6, 129.1, 128.5, 128.0, 127.7, 126.6, 57.1, 28.4.

MS (ESI): *m*/*z* (%) = 247 (100) $[M + H]^+$.

[(Methylsulfonyl)methyl]benzene (3k)[25]

The reaction mixture was stirred for 1 h.

White solid; yield: 148 mg (87%); mp 124–126 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.40–7.35 (m, 5 H, ArH), 4.22 (s, 2 H, CH_2), 2.72 (s, 3 H, CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 130.4, 128.9, 128.8, 128.1, 60.9, 38.8.

MS (ESI): *m*/*z* (%) = 171 (100) $[M + H]^+$.

2-(Benzylsulfonyl)ethan-1-ol (3l)[37]

The reaction mixture was stirred for 1 h.

Colorless oil; yield: 164 mg (82%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.51–7.32 (m, 5 H, ArH), 5.56 (br s, 1 H, OH), 4.33 (s, 2 H, CH_2), 4.00 (t, *J* = 6.2 Hz, 2 H, CH_2), 3.07 (t, *J* = 6.2 Hz, 2 H, CH_2).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 130.9, 128.9, 128.8, 127.5, 60.8, 55.9, 53.1.

MS (ESI): *m*/*z* (%) = 201 (100) $[M + H]^+$.

[Sulfonylbis(methylene)]dibenzene (3m)[26]

The reaction mixture was stirred for 1 h.

White solid; yield: 202 mg (82%); mp 151–153 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.46–7.03 (m, 10 H, ArH), 4.13 (s, 4 H, 2 × CH_2).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 130.7, 129.9, 128.7, 127.3, 57.7.

MS (ESI): *m*/*z* (%) = 247 (100) $[M + H]^+$.

(Ethylsulfonyl)ethane (3n)[38]

The reaction mixture was stirred for 1 h.

White solid; yield: 122 mg (100%); mp 73–75 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.87 (q, *J* = 7.5 Hz, 4 H, 2 × CH_2), 1.25 (t, *J* = 7.5 Hz, 6 H, 2 × CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 45.6, 6.1.

MS (ESI): *m*/*z* (%) = 123 (100) $[M + H]^+$.

Tetrahydro-2*H*-thiopyran 1,1-Dioxide (3o)[32]

The reaction mixture was stirred for 1 h.

White solid; yield: 134 mg (100%); mp 101–103 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.99–2.77 (m, 4 H, 2 × CH_2), 2.06–1.85 (m, 4 H, 2 × CH_2), 1.63–1.42 (m, 2 H, CH_2).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 51.8, 24.0, 23.4.

MS (ESI): *m*/*z* (%) = 135 (100) $[M + H]^+$.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_5H_{11}O_2S$: 135.0474; found: 135.0476.

Tetrahydrothiophene 1,1-Dioxide (3p)[25]

The reaction mixture was stirred for 3 h.

Colorless oil; yield: 110 mg (92%).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.93 (t, *J* = 7.5 Hz, 4 H, 4 × C*H*H), 2.16–2.09 (m, 4 H, 4 × CH*H*).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 50.9, 22.5.

MS (ESI): *m*/*z* (%) = 121 (100) $[M + H]^+$.

Acknowledgment

The authors gratefully acknowledge the Operational Program 'Education and Lifelong Learning' for financial support through the NSRF program 'ΕΝΙΣΧΥΣΗ ΜΕΤΑΔΙΣΑΚΤΟΡΩΝ ΕΡΕΥΝΗΤΩΝ (PE 2431)' co-financed by the ESF and the Greek State.

Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0036-1588315.

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