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PAPER

Catalyst-free approach for solvent-dependent selective oxidation of organic sulfides with oxone†

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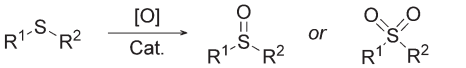
Selective oxidation of sulfides was successfully performed by employing oxone ($2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$) as oxidant without utilization of any catalyst/additive under mild reaction conditions. Notably, the reaction can be controlled by the chosen solvent. When ethanol was used as the solvent, sulfoxides were obtained in excellent yield; the reaction almost exclusively gave the sulfone in water. Furthermore, this protocol worked well for various sulfides to the corresponding sulfoxides in ethanol or sulfones in water.

Introduction

As part of "green" concept,[1] toxic organic solvents are expected to be replaced by alternative non-toxic media and catalyst-free processes could be appealing. Sulfoxides and sulfones, as important synthetic reagents, have been widely used in the preparation of biologically and pharmaceutically significant compounds.[2] Sulfoxides have also emerged as oxotransfer reagents in oxidation processes[3] and as ligands in asymmetric catalysis.[2b] In particular, chiral sulfoxides have been extensively applied in asymmetric synthesis.[4] In this context, much effort has been directed toward the preparation of sulfoxides and sulfones. One of the most favored and straightforward synthetic methods could be selective oxidation of sulfides to sulfoxides or sulfones,[5] respectively, as shown in Scheme 1. Numerous types of oxidants such as molecular oxygen,[6] hydrogen peroxide,[7] organic hydroperoxide,[8] hypervalent iodine[9] and other halogen derivatives[10] have been used for the oxidation of sulfides to date. However, there are some drawbacks in terms of safety, toxicity and abolishment of heavy metals. It is also worth mentioning that a transition metal catalyst, such as Mn,[11] Os,[12] Sc,[13] Ti,[14] V,[15] Re,[16] Ru,[17] Cr,[18] W,[19] Cu,[20] Fe,[21] is required to perform the reaction smoothly in the most cases.

Nevertheless, only a few procedures are suitable for switchable synthesis of sulfoxide or sulfone *via* the oxidation reaction of sulfides with the same oxidant by adjusting a reaction parameter. Hussain *et al.* reported the selective oxidation of sulfides to sulfoxides and sulfones with a borax–H_2O_2 system by varying the pH value of the reaction mixture.[22] Fukuda and co-workers converted various sulfides to the corresponding sulfoxides and sulfones using aqueous NaOCl in the presence of 10 mol% of cyanuric acid under biphasic conditions.[23] 1,3,5-Triazo-2,4,6-triphosphorine-2,2,4,4,6,6-hexachloride could be also successfully utilized as a promoter for oxidation of sulfides with H_2O_2 as oxidant.[24] Very recently, Shi and Wei's group[25] immobilized peroxotungstates onto silica modified with multilayer ionic liquid brushes to promote the oxidation reaction with H_2O_2 as oxidant, affording sulfoxides and sulfones. However, a catalyst or promoter was still required in those processes. Therefore, simple, convenient and environmentally benign methods for switchable oxidation of sulfides to sulfoxides or to sulfones are still highly desired.

Oxone ($2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$), a commercially available salt from Caro's acid (H_2SO_5), is a white, granular, free-flowing solid peroxygen that provides powerful non-chlorine oxidation in a stable, easy-to-handle manner. Furthermore, the byproducts associated with oxone are generally recognized as safe. Currently, oxone has found many applications[26] in oxidation of amines,[27] alcohols,[28] aldehydes[29] and ketones,[30] epoxidation reactions of the alkenes,[31] Baeyer–Villiger reaction[32] and C–H bond oxidation processes[33] due to good stability and high efficiency. In particular, oxone can also be applied to sulfoxidation reactions to form the sulfoxide as major product in aqueous acetone or methanol.[34] Moreover, Kropp *et al.*[35] reported a sulfoxidation method by employing inorganic-supported oxone such as silica gel, alumina. Recently, modified oxone, *e.g.* benzyltriphenylphosphonium peroxymonosulfate, was successfully developed for selective oxidation of aromatic and aliphatic sulfides under nonaqueous and aprotic conditions, which was reported by Hajipour and co-workers.[36]



[O] = halogen, peracids, dioxiranes, hypervalent iodine, alkyl hydroperoxides, hypochlorites, H_2O_2, O_2, etc.
Cat. = Os, Sc, Mo, Ti, V, Re, Ru, Cr, W, Cu, Fe catalyst

Scheme 1 Catalytic oxidation of sulfides.

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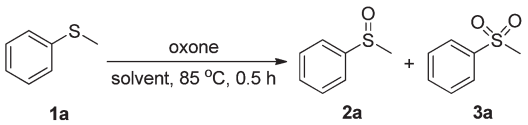
†Electronic supplementary information (ESI) available: Characterization data and copies of the NMR spectra. See DOI: 10.1039/c2gc00027j

Table 1 Solvent effect on oxidation of sulfides with oxone[a]



Entry	Solvent	Conv.[b] (%)	Yield[b] (%) Sulfoxide (**2a**)	Sulfone (**3a**)
1	Toluene	3	<1	<1
2	1,4-Dioxane	32	24	<1
3	Ethyl acetate	12	3	<1
4	Acetone	8	5	<1
5	PC	40	36	2
6	EC	10	7	<1
7	DME	27	23	2
8	DCE	13	9	<1
9	CH_3COOH	>99	59	40
10	DMF	92	60	28
11	CH_3OH	>99	82	15
12	CH_3CN	73	65	4
13	C_2H_5OH	94	86	6
14	H_2O	65	4	57
15[c]	C_2H_5OH	82	76	4
16[c,d]	C_2H_5OH	57	44	1
17[c,e]	C_2H_5OH	36	29	1

[a] Reaction conditions: To a glass tube equipped with a magnetic stir bar, thioanisole (24.8 mg, 0.2 mmol), oxone (92.2 mg, 0.15 mmol), solvent (1 mL) were added, and the mixture was stirred for 0.5 h at 85 °C. PC = propylene carbonate, EC = ethylene carbonate, DME = dimethoxyethane, DCE = 1,2-dichloroethane. [b] Determined by GC with area normalization. [c] Oxone (67.6 mg, 0.11 mmol). [d] Solvent (0.5 mL). [e] Solvent (1.5 mL).

As a part of our continuous interest on selective oxidation reactions,[37] we herein would like to report the selective oxidation of sulfides using ethanol or water as a solvent to afford the corresponding sulfoxides or sulfones, respectively, with good yields. This procedure needs no additional catalysts and the reaction proceeds highly selectively in most cases.

Results and discussion

Influence of different solvents

The exploratory experiments started using thioanisole **1a** as the model substrate. Thus, we have studied the solvent effect, and the results are shown in Table 1. After much experimentation on optimizing solvent, it was found that the use of a less-polar solvent like toluene and 1,4-dioxane afforded phenyl methyl sulfoxide **2a** in low yields (Table 1, entries 1 and 2). Other aprotic solvents such as ethyl acetate, acetone, propylene carbonate, ethylene carbonate, dimethoxyethane, and 1,2-dichloroethane were demonstrated to be inefficient (entries 3–8). High polar DMF and protic solvents like methanol and acetic acid gave good conversions but low selectivity (entries 9–11). Interestingly, the reaction in acetonitrile showed a good reactivity with excellent selectivity toward sulfoxide **2a** (entry 12), similar to Hajipour *et al.*'s report.[36] Excellent conversion and selectivity were achieved in ethanol (entry 13). Surprisingly, strong proton donating solvent, *e.g.* water, worked well but afforded the sulfone compound, *i.e.* phenylmethyl sulfone **3a**, rather than sulfoxide **2a** as major product under the identical reaction conditions (entry 14). In other words, solvent could have a remarkable influence on the reaction outcome, particularly on the selectivity toward sulfoxide **2a** or sulfone **3a**. Further investigation reveals the amount of ethanol could also affect the oxidation result (entries 15–17), presumably being ascribed to variation of oxone dissolution and the concentration of the reactant and reagent originating from changing solvent amount. As a consequence, ethanol and water were employed for further investigation to highly selective formation of the sulfoxides or the sulfone by just switching the solvent.

Table 2 Optimization of the reaction conditions in ethanol[a]

Entry	**1a** : oxone[b]	*T* (°C)	Time (h)	Conv.[c] (%)	Yield[c] (%) **2a**	**3a**
1	1 : 0.55	25	0.5	9	5	0
2	1 : 0.55	60	0.5	51	44	<1
3	1 : 0.55	100	0.5	55	48	4
4	1 : 0.55	60	12	90	85	2
5	1 : 0.60	60	12	>99	89	9
6	1 : 1	60	2	94	90	2
7[d]	1 : 1	60	2	98	7	89
8[d]	1 : 1.5	60	12	>99	0	>99

[a] Reaction conditions: to a glass tube equipped with a magnetic stir bar, thioanisole (24.8 mg, 0.2 mmol), indicated amount of oxone, ethanol (1 mL) as solvent were added, and the mixture was stirred for desired time at reaction temperature. [b] Molar ratio. [c] Determined by GC with area normalization. [d] Water (1 mL) as solvent.

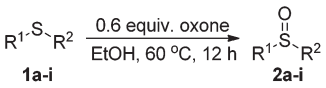
Influence of oxidant amounts and temperature

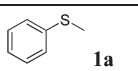
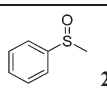
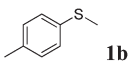
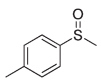
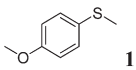
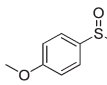
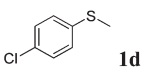
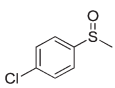
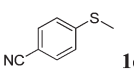
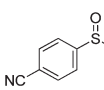
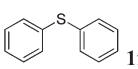
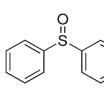
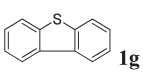
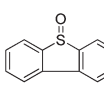
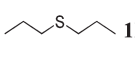
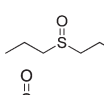
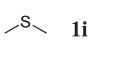
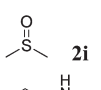
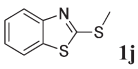
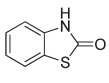
The effect of the reaction parameters was examined by performing the reaction in ethanol, as listed in Table 2. The reaction almost did not occur at 25 °C, while the selectivity would become poor as further rising the temperature to 100 °C (entries 1 and 3). Therefore, the optimized temperature was proved to be 60 °C, at which moderate conversion and excellent selectivity were achieved (entry 2). On the other hand, the conversion could reach 90% by prolonging the reaction time to 12 h and could further attain >99% with near 90% yield of the sulfoxide **2a** by increasing the amount of oxidant (entries 4 and 5). Very interestingly, the sulfone **3a** was obtained in high yield in the presence of 1 equivalent of oxone when water was employed as solvent (entry 7). Finally, the reaction exclusively gave the sulfone **3a** with quantitative yield by prolonging reaction time and increasing the oxone amount (entry 8 *vs.* 7).

Substrate scope

With these results at hand, we next examined how to control this reaction to selectively form different products. The reaction was performed with various sulfides **1a–i** to explore the generality of the sulfoxide formation through ethanol-controlled oxidation of the sulfide. As listed in Table 3, typical sulfides, such as thioanisole **1a** and *p*-tolylmethyl sulfide **1b** gave the corresponding

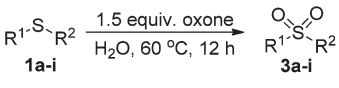
Table 3 Ethanol controlled oxidation of sulfides to sulfoxides[a]

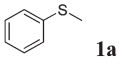
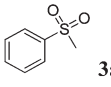
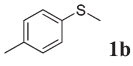
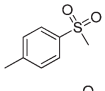
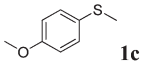
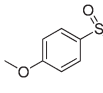
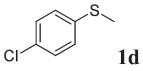
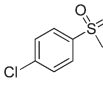
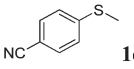
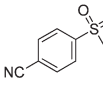
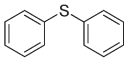
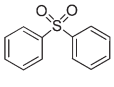
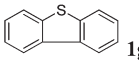
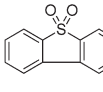
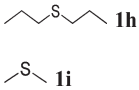
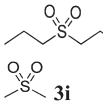
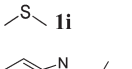
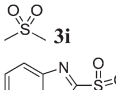


Entry	Substrate	Sulfoxides	Conv.[b] (%)	Yield[c] (%)
1	 **1a**	 **2a**	96	88
2	 **1b**	 **2b**	96	86
3	 **1c**	 **2c**	98	90
4	 **1d**	 **2d**	95	82
5	 **1e**	 **2e**	95	85
6	 **1f**	 **2f**	98	84
7[d]	 **1g**	 **2g**	48	30
8	 **1h**	 **2h**	97	85
9	 **1i**	 **2i**	—[e]	80
10	 **1j**	 **2j**	—[e]	83

[a] Reaction conditions: sulfide (1 mmol), oxone (0.3689 g, 0.6 mmol), ethanol (5 mL) as solvent at 60 °C for 12 h. [b] Determined by GC with area normalization. [c] Isolated yield. [d] 40 h. [e] GC is not suitable for analyzing the compounds with too high or too low boiling point.

Table 4 Water-switchable oxidation of sulfides to sulfones[a]



Entry	Substrate	Sulfone	Conv.[b] (%)	Yield[c] (%)
1	 **1a**	 **3a**	>99	97
2	 **1b**	 **3b**	>99	95
3	 **1c**	 **3c**	>99	94
4	 **1d**	 **3d**	>99	95
5	 **1e**	 **3e**	>99	97
6[d]	 **1f**	 **3f**	>99	94
7[d]	 **1g**	 **3g**	97	95
8	 **1h**	 **3h**	99	94
9	 **1i**	 **3i**	—[e]	93
10	**1j**	**3j**	—[e]	88

[a] Reaction conditions: sulfide (1 mmol), oxone (0.9221 g, 1.5 mmol), water (5 mL) as solvent at 60 °C for 12 h. [b] Determined by GC with area normalization. [c] Isolated yield. [d] SDS (27.2 mg, 10 mol%) was added. [e] GC is not suitable for analyzing the compounds with too high or too low boiling point.

sulfoxides in good yields (entries 1 and 2). Various substituents including –OCH_3, –Cl and –CN could be tolerated and the sulfoxides were obtained in almost excellent yields (entries 3–5). With diphenyl sulfide **1f**, which is generally hard to oxidize,[23] the isolated yield of **2f** reached 84% (entry 6). However, just a low yield (30%) can be obtained with dibenzothiophene sulfoxide **1g** even the reaction time was prolonged to 40 h (entry 7).

Furthermore, the present protocol could be also applicable to the dialkyl sulfides (entries 8 and 9). In the case of methylsulfanyl benzothiazole **1j**, sulfoxidation did not proceed on the 2-position sulfur atom, while the oxidative cleavage of C–S bond took place to afford 2-hydroxybenzothiazole **2j** (entry 10).

On the other hand, we further examined the utility of preparation of the sulfone *via* water-switched oxidation of the sulfide with oxone as an oxidant. As shown in Table 4 substrates **1a–e** were oxidized to afford the corresponding sulfones **3a–e** in almost quantitative yields (entries 1–5). Namely, this protocol can also tolerate several functional groups such as methoxy, chloro, CN. In the case of **1f** and **1g**, sodium dodecyl sulfate (SDS, 10 mol%) as a surfactant is needed to perform the reaction smoothly (entries 6 and 7), probably due to the poor solubility of **1f** and **1g** in H_2O. Moreover, the dialkyl sulfides **1h** and **1i** worked perfect giving the sulfone **3h** and **3i** in 94% and 93% yield, respectively (entries 8 and 9). Methylsulfanyl benzothiazole **1j** also showed good activity to furnish the sulfone product, *i.e.* 2-methanesulfonylbenzothiazole **3j**, in good yield (entry 10). In addition, the sulfone product could be easily separated from the reaction mixture. It is also worth mentioning that the sulfoxide **2a** can further be oxidized with 1 equivalent of oxone to the sulfone **3a** in 99% yield using water as a solvent for a shorter time (2 h).

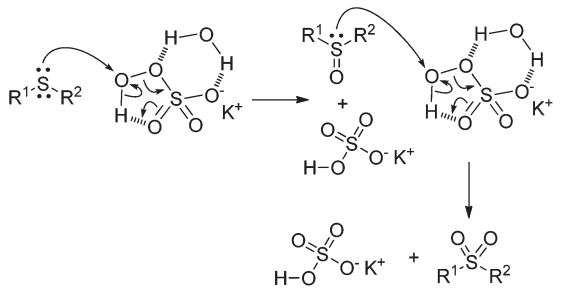
Proposed mechanism

Although the exact reason for the solvent effect is not known, it can be assumed that solubility of oxone and hydrogen bonding formation between oxone and the solvent would be two important factors to control this kind oxone oxidation reaction. To gain

Table 5 Oxidation of sulfide conducted by $K_2S_2O_8$[a]

Entry	Solvent	Conv.[b] (%)	Yield[b] (%) 2a	3a
1	EtOH	7	6	<1
2	H_2O	82	76	5

[a] Reaction conditions: to a glass tube equipped with a magnetic stir bar, thioanisole (49.6 mg, 0.4 mmol), $K_2S_2O_8$ (0.2163 g, 0.8 mmol), $KHSO_4$ (54.5 mg, 0.4 mmol), K_2SO_4 (69.7 mg, 0.4 mmol), solvent (2 mL) were added, and the mixture was stirred for 12 h at 60 °C. [b] Determined by GC with area normalization.



Scheme 2 Proposed reaction pathway for the water-promoted oxidation of sulfide.

a deeper insight into the solvent effect, the **1a** oxidation with potassium persulfate ($K_2S_2O_8$) was carried out in a protic solvent such as ethanol, water under the same reaction conditions as the oxidation with oxone (Table 5).

Ethanol was found to be inactive, possible due to the solubility problem of $K_2S_2O_8$, whereas water gave good yield of the sulfoxide.

The water effect could be attributed not only to the improved solubility but also to possible generation of both an intramolecular hydrogen bond within the oxone molecule[38] and an intermolecular hydrogen bond between H_2O and oxone,[39] leading to formation of the 5-membered ring fused with 6-membered ring as shown in Scheme 2. Therefore, the presence of such hydrogen bonds could allow facile oxygen transfer from the peroxy oxygen of oxone to the sulfide and subsequent to sulfoxide, thus resulting in promotion of the oxidation to formation of the sulfone as the main product (Tables 1 and 4). On the other hand, in the case of ethanol as solvent, ready formation of intramolecular hydrogen bond with the oxone molecule rather than typical intermolecular H-bonding in such a fashion as depicted in Scheme 2, could account for the preferred production of the sulfoxide. When a mixture of ethanol and water was used as a solvent under standard conditions, the product distribution comprising the sulfoxide and the sulfone was dependent on the volume ratio of EtOH/H_2O.[40] All the experiments in this study could support such hypothesis about dependence of the product distribution on hydrogen bond formation.

Conclusions

In conclusion, a protocol for the solvent-controlled oxidative sulfoxidation has been developed with high conversion as well as tunable chemo-selectivity. The noteworthy feature could be that the selective oxidation to the sulfoxide or sulfone can be achieved by changing the solvent and using an inexpensive reagent under safe and mild conditions without any additional reagent. Additionally, the sulfone product could be easily separated from the reaction mixture.

Experimental section

General information

The starting materials were commercially available and were used without further purification except solvents. The products were isolated by column chromatography on silica gel (200–300 mesh) using petroleum ether (60–90 °C) and ethyl acetate. NMR spectra were determined on Bruker 400 in $CDCl_3$. ^1H NMR chemical shifts were referenced to residual solvent as determined relative to $CDCl_3$ (7.26 ppm). The ^{13}C NMR chemical shifts were reported in ppm relative to the carbon resonance of $CDCl_3$ (central peak is 77.0 ppm). ^1H NMR peaks are labelled as singlet (s), doublet (d), triplet (t), and multiplet (m). The coupling constants, *J*, are reported in hertz (Hz). GC-MS data were performed on Finnigan HP G1800 A. GC analyses were performed on a Shimadzu GC-2014 equipped with a capillary column (RTX-wax 30 m × 0.25 μm and RTX-17 30 m × 0.25 μm) using a flame ionization detector. 2-(Methylthio)benzothiazole **1j** was prepared according to previous literature report.[41]

General procedure for the selective oxidation of sulfides to sulfoxides

To a 25 mL glass tube, sulfide (1.0 mmol), oxone (0.3689 g, 0.6 mmol), ethanol (5.0 mL) were added and the mixture was stirred at 60 °C for 12 h. The mixture was cooled to room temperature and added with water (10 mL), then extracted by ethyl acetate (25 mL × 4). After drying with anhydrous Na_2SO_4, the organic residue was analyzed by GC and then purified by column chromatography on silica gel (200–300 mesh) with ethyl acetate/petroleum ether to afford the desired product.

General procedure for the oxidation of sulfides to sulfones

To a 25 mL glass tube, sulfide (1.0 mmol), oxone (0.9221 g, 1.5 mmol), water (5.0 mL) were added and the mixture was stirred at 60 °C for 12 h. The mixture was then cooled to room temperature and extracted by ethyl acetate (25 mL × 4). After drying with anhydrous Na_2SO_4 overnight, the liquid was analyzed by GC. The residue was concentrated under reduced pressure to afford the desired product without further purification except **3j**. All compounds were characterized by ^1H NMR, ^{13}C NMR and mass spectroscopy, which are consistent with those reported in the literature.[7,43,44]

Characterization data for substrate 1j, the oxidation products 2a–j and 3a–j

2-(Methylthio)benzothiazole (1j).[42] The product was obtained as a white solid (3.553 g, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.87 (d, J = 8.1 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.29 (t, J = 7.5 Hz, 1H), 2.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.1, 153.3, 135.1, 126.0, 124.1, 121.3, 120.9, 15.9. EI-MS, m/z (%): 182.08 (100) [M^+].

Phenylmethyl sulfoxide (2a).[9a] The product was obtained as a colorless liquid (0.123 g, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.62–7.60 (m, 2H), 7.51–7.44 (m, 3H), 2.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 145.6, 130.9, 129.2, 123.4, 43.8. EI-MS, m/z (%): 140.00 (79) [M^+].

***p*-Tolylmethyl sulfoxide (2b).**[7c] The product was obtained as a pale yellow liquid (0.133 g, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.50 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 2.66 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 142.3, 141.4, 129.9, 123.4, 43.8, 21.2. EI-MS, m/z (%): 153.99 (30) [M^+].

4-Methoxyphenylmethyl sulfoxide (2c).[7c] The product was obtained as a pale yellow solid (0.153 g, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.70–7.52 (m, 2H), 7.03–7.01 (m, 2H), 3.84 (s, 3H), 2.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 161.9, 136.4, 125.4, 114.8, 55.5, 43.9. EI-MS, m/z (%): 170.00 (19) [M^+].

***p*-Chlorophenylmethyl sulfoxide (2d).**[7c] The product was obtained as a pale yellow solid (0.143 g, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.58 (d, J = 8.5 Hz, 2H), 7.49 (d, J = 8.5 Hz, 2H), 2.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 144.1, 137.2, 129.6, 124.9, 44.0. EI-MS, m/z (%): 175.95 (25) [M^+], 174.03 (61) [M^+].

4-Cyanophenylmethyl sulfoxide (2e).[43] The product was obtained as a white solid (0.140 g, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.83 (d, J = 8.2 Hz, 2H), 7.77 (d, J = 8.1 Hz, 2H), 2.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.4, 133.0, 124.3, 117.7, 114.8, 43.8. EI-MS, m/z (%): 165.00 (88) [M^+].

Diphenyl sulfoxide (2f).[23] The product was obtained as a white solid (0.170 g, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.66–7.64 (m, 4H), 7.49–7.42 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 145.6, 131.0, 129.3, 124.8. EI-MS, m/z (%): 202.01 (100) [M^+].

Dibenzothiophene sulfoxide (2g).[44] The product was obtained as a white solid (0.060 g, 30% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.99 (d, J = 7.6 Hz, 2H), 7.82 (d, J = 7.7 Hz, 2H), 7.61 (t, J = 7.5 Hz, 3H), 7.51 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 145.2, 137.1, 132.5, 129.5, 127.5, 121.9. EI-MS, m/z (%): 200.05 (100) [M^+].

Di(*n*-propyl) sulfoxide (2h).[45] The product was obtained as a colorless liquid (0.114 g, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.72–2.53 (m, 4H), 1.83–1.73 (m, 4H), 1.05 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 54.1, 16.2, 13.3. EI-MS, m/z (%): 135.06 (20) [M^+].

Dimethyl sulfoxide (2i).[46] The product was obtained as a colorless liquid (0.063 g, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.50 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 40.8. EI-MS, m/z (%): 78.00 (50) [M^+].

2-Benzothiazolone (2j).[47] The product was obtained as a white solid (0.125 g, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 10.60 (s, 1H), 7.39 (d, J = 7.8 Hz, 1H), 7.29–7.25 (m, 1H), 7.20–7.12 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 173.6, 135.5, 126.5, 123.8, 123.2, 122.4, 111.9. EI-MS, m/z (%): 151.06 (100) [M^+].

Phenylmethyl sulfone (3a).[23] The product was obtained as a white solid (0.152 g, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.92 (d, J = 7.5 Hz, 2H), 7.66–7.54 (m, 3H), 3.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 140.4, 133.6, 129.3, 127.2, 44.4. EI-MS, m/z (%): 156.01 (25) [M^+].

***p*-Tolylmethyl sulfone (3b).**[7c] The product was obtained as a white solid (0.162 g, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.82 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 7.9 Hz, 2H), 3.03 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 144.7, 137.7, 129.9, 127.4, 44.6, 21.6. EI-MS, m/z (%): 170.03 (51) [M^+].

4-Methoxyphenylmethyl sulfone (3c).[7c] The product was obtained as a white solid (0.175 g, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.87 (d, J = 8.7 Hz, 2H), 7.02 (d, J = 8.7 Hz, 2H), 3.88 (s, 3H), 3.03 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 163.6, 132.2, 129.5, 114.4, 55.7, 44.8. EI-MS, m/z (%): 186.08 (91) [M^+].

***p*-Chlorophenylmethyl sulfone (3d).** The product was obtained as a white solid (0.181 g, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.91–7.88 (m, 2H), 7.58–7.54 (m, 2H), 3.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 140.4, 139.0, 129.7, 128.9, 44.5. EI-MS, m/z (%): 191.98 (24) [M^+], 190.01 (62) [M^+].

4-Cyanophenylmethyl sulfone (3e).[48] The product was obtained as a white solid (0.176 g, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.08 (d, J = 8.3 Hz, 2H), 7.89 (d, J = 8.0 Hz, 2H), 3.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 144.4, 133.2, 128.2, 117.6, 117.0, 44.2. EI-MS, m/z (%): 180.83 (9) [M^+].

Diphenyl sulfone (3f).[23] The product was obtained as a white solid (0.205 g, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.96–7.94 (m, 4H), 7.59–7.49 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 141.6, 133.2, 129.3, 127.7. EI-MS, m/z (%): 217.93 (20) [M^+].

Dibenzothiophene sulfone (3g).[44] The product was obtained as a white solid (0.205 g, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.83–7.78 (m, 4H), 7.66–7.62 (m, 2H), 7.55–7.51 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 137.7, 133.9, 131.6, 130.4, 122.2, 121.6. EI-MS, m/z (%): 216.00 (100) [M^+].

Di(*n*-propyl) sulfone (3h).[45] The product was obtained as a white solid (0.141 g, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.90–2.86 (m, 4H), 1.86–1.76 (m, 4H), 1.02 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 54.2, 15.6, 13.0. EI-MS, m/z (%): 151.05 (22) [M^+].

Dimethyl sulfone (3i).[49] The product was obtained as a white solid (0.088 g, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.97 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 42.6. EI-MS, m/z (%): 94.00 (34) [M^+].

2-Methanesulfonylbenzothiazole (3j).[42] The product was obtained as a white solid (0.188 g, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.20 (d, J = 8.3 Hz, 1H), 8.01 (d, J = 7.8 Hz, 1H), 7.66–7.57 (m, 2H), 3.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.3, 152.4, 136.5, 128.1, 127.7, 125.3, 122.3, 42.4. EI-MS, m/z (%): 212.98 (72) [M^+].

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Notes and references

1 (*a*) C.-J. Li and B. M. Trost, *Proc. Natl. Acad. Sci. U. S. A.*, 2008, **105**, 13197–13202; (*b*) P. Anastas and N. Eghbali, *Chem. Soc. Rev.*, 2010, **39**, 301–312.
2 (*a*) M. C. Carreno, *Chem. Rev.*, 1995, **95**, 1717–1760; (*b*) I. Fernandez and N. Khiar, *Chem. Rev.*, 2003, **103**, 3651–3706; (*c*) E. Wojaczynska and J. Wojaczynski, *Chem. Rev.*, 2010, **110**, 4303–4356; (*d*) K. A. Stingl and S. B. Tsogoeva, *Tetrahedron: Asymmetry*, 2010, **21**, 1055–1074.
3 A. M. Khenkin and R. Neumann, *J. Am. Chem. Soc.*, 2002, **124**, 4198–4199.
4 H. Pellissier, *Tetrahedron*, 2006, **62**, 5559–5601.
5 (*a*) J. Legros, J. R. Dehli and C. Bolm, *Adv. Synth. Catal.*, 2005, **347**, 19–31; (*b*) J. E. Backvall, *Modern oxidation methods*, Wiley-VCH, Weinheim, Germany, 2010.
6 T. Chinnusamy and O. Reiser, *ChemSusChem*, 2010, **3**, 1040–1042.
7 (*a*) F. Shi, M. K. Tse, H. M. Kaiser and M. Beller, *Adv. Synth. Catal.*, 2007, **349**, 2425–2430; (*b*) R. Ricoux, M. Allard, R. Dubuc, C. Dupont, J. D. Marechal and J. P. Mahy, *Org. Biomol. Chem.*, 2009, **7**, 3208–3211; (*c*) C. B. Yang, H. Zhang, J. Liao, J. Zhu, J. G. Deng, Q. P. Jin and B. Yu, *Green Chem.*, 2009, **11**, 1401–1405.
8 For a recent review, see: S. Kumar, S. Verma, S. L. Jain and B. Sain, *Tetrahedron Lett.*, 2011, **52**, 3393–3396.
9 (*a*) J. N. Moorthy, K. Senapati and K. N. Parida, *J. Org. Chem.*, 2010, **75**, 8416–8421; (*b*) J. N. Moorthy, K. Senapati, K. N. Parida, S. Jhulki, K. Sooraj and N. N. Nair, *J. Org. Chem.*, 2011, **76**, 9593–9601.
10 P. Kowalski, K. Mitka, K. Ossowska and Z. Kolarska, *Tetrahedron*, 2005, **61**, 1933–1953.
11 (*a*) M. Hirano, S. Yakabe, J. H. Clark, H. Kudo and T. Morimoto, *Synth. Commun.*, 1996, **26**, 1875–1886; (*b*) F. Voss, E. Herdtweck and T. Bach, *Chem. Commun.*, 2011, **47**, 2137–2139.
12 B. M. Choudary, C. R. V. Reddy, B. V. Prakash, M. L. Kantam and B. Sreedhar, *Chem. Commun.*, 2003, 754–755.
13 M. Matteucci, G. Bhalay and M. Bradley, *Org. Lett.*, 2003, **5**, 235–238.
14 M. A. M. Capozzi, C. Centrone, G. Fracchiolla, F. Naso and C. Cardellicchio, *Eur. J. Org. Chem.*, 2011, 4327–4334.
15 S. L. Jain, B. S. Rana, B. Singh, A. K. Sinha, A. Bhaumik, M. Nandi and B. Sain, *Green Chem.*, 2010, **12**, 374–377.
16 J. B. Arterburn and S. L. Nelson, *J. Org. Chem.*, 1996, **61**, 2260–2261.
17 X. T. Zhou, H. B. Ji, Z. Cheng, J. C. Xu, L. X. Pei and L. F. Wang, *Bioorg. Med. Chem. Lett.*, 2007, **17**, 4650–4653.
18 L. Xu, J. Cheng and M. L. Trudell, *J. Org. Chem.*, 2003, **68**, 5388–5391.
19 A. Bordoloi, A. Vinu and S. B. Halligudi, *Chem. Commun.*, 2007, 4806–4808.
20 I. Gamba, S. Palavicini, E. Monzani and L. Casella, *Chem.–Eur. J.*, 2009, **15**, 12932–12936.
21 J. Legros and C. Bolm, *Angew. Chem., Int. Ed.*, 2003, **42**, 5487–5489.
22 S. Hussain, S. K. Bharadwaj, R. Pandey and M. K. Chaudhuri, *Eur. J. Org. Chem.*, 2009, 3319–3322.
23 N. Fukuda and T. Ikemoto, *J. Org. Chem.*, 2010, **75**, 4629–4631.
24 K. Bahrami, M. M. Khodaei and M. S. Arabi, *J. Org. Chem.*, 2010, **75**, 6208–6213.
25 X. Y. Shi, X. Y. Han, W. J. Ma, J. F. Wei, J. Li, Q. Zhang and Z. G. Chen, *J. Mol. Catal. A: Chem.*, 2011, **341**, 57–62.
26 M. Eissen, M. Strudthoff, S. Backhaus, C. Eismann, G. Oetken, S. Kaling and D. Lenoir, *J. Chem. Educ.*, 2011, **88**, 284–291.
27 (*a*) J. D. Fields and P. J. Kropp, *J. Org. Chem.*, 2000, **65**, 5937–5941; (*b*) K. S. Webb and V. Seneviratne, *Tetrahedron Lett.*, 1995, **36**, 2377–2378.
28 (*a*) C. Bolm, A. S. Magnus and J. P. Hildebrand, *Org. Lett.*, 2000, **2**, 1173–1175; (*b*) M. Hirano, M. Oose and T. Morimoto, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 1046–1047.
29 B. R. Travis, M. Sivakumar, G. O. Hollist and B. Borhan, *Org. Lett.*, 2003, **5**, 1031–1034.
30 M. Uyanik, M. Akakura and K. Ishihara, *J. Am. Chem. Soc.*, 2009, **131**, 251–262.
31 (*a*) Z.-X. Wang, Y. Tu, M. Frohn, J.-R. Zhang and Y. Shi, *J. Am. Chem. Soc.*, 1997, **119**, 11224–11235; (*b*) D. Yang, *Acc. Chem. Res.*, 2004, **37**, 497–505; (*c*) S. E. Denmark, D. C. Forbes, D. S. Hays, J. S. DePue and R. G. Wilde, *J. Org. Chem.*, 1995, **60**, 1391–1407; (*d*) M. Frohn, Z.-X. Wang and Y. Shi, *J. Org. Chem.*, 1998, **63**, 6425–6426; (*e*) N. Hashimoto and A. Kanda, *Org. Process Res. Dev.*, 2002, **6**, 405–406.
32 (*a*) A. Chrobok, *Tetrahedron*, 2010, **66**, 6212–6216; (*b*) M. E. Gonzalez-Nunez, R. Mello, A. Olmos and G. Asensio, *J. Org. Chem.*, 2005, **70**, 10879–10882; (*c*) M. Renz and B. Meunier, *Eur. J. Org. Chem.*, 1999, **1999**, 737–750.
33 P. Liu, Y. G. Liu, E. L. M. Wong, S. Xiang and C. M. Che, *Chem. Sci.*, 2011, **2**, 2187–2195.
34 (*a*) B. M. Trost and D. P. Curran, *Tetrahedron Lett.*, 1981, **22**, 1287–1290; (*b*) K. S. Webb, *Tetrahedron Lett.*, 1994, **35**, 3457–3460; (*c*) F. A. Davis, S. G. Lal and H. D. Durst, *J. Org. Chem.*, 1988, **53**, 5004–5007.
35 P. J. Kropp, G. W. Breton, J. D. Fields, J. C. Tung and B. R. Loomis, *J. Am. Chem. Soc.*, 2000, **122**, 4280–4285.
36 A. R. Hajipour, S. E. Mallakpour and H. Adibi, *J. Org. Chem.*, 2002, **67**, 8666–8668.
37 (*a*) C.-X. Miao, L.-N. He, J.-Q. Wang and J.-L. Wang, *Adv. Synth. Catal.*, 2009, **351**, 2209–2216; (*b*) C.-X. Miao, J.-Q. Wang, B. Yu, W.-G. Cheng, J. Sun, S. Chanfreau, L.-N. He and S.-J. Zhang, *Chem. Commun.*, 2011, **47**, 2697–2699; (*c*) J.-Q. Wang, L.-N. He and C.-X. Miao, *Green Chem.*, 2009, **11**, 1013–1017; (*d*) B. Li, A.-H. Liu, L.-N. He, Z.-Z. Yang, J. Gao and K.-H. Chen, *Green Chem.*, 2012, **14**, 130.
38 O. Ermer and C. Röbke, *Helv. Chim. Acta*, 2003, **86**, 2908–2913.
39 (*a*) V. K. Aggarwal, C. Lopin and F. Sandrinelli, *J. Am. Chem. Soc.*, 2003, **125**, 7596–7601; (*b*) V. K. Aggarwal and G. Y. Fang, *Chem. Commun.*, 2005, 3448–3450.
40 To a glass tube equipped with a magnetic stir bar, thioanisole (24.8 mg, 0.2 mmol), oxone (92.2 mg, 0.15 mmol), and solvent mixture (1 mL) were added, and the mixture was stirred for 0.5 h at 85 °C; V(EtOH) : V(H_2O) = 0.40 : 0.60 mL, conversion: 66%, yield: **2a** (10%), **3a** (56%); V(EtOH) : V(H_2O) = 0.20 : 0.80 mL, conversion: 86%, yield: **2a** (10%), **3a** (76%).
41 R. V. Kumar, K. V. S. R. S. Kumar and K. R. Gopal, *J. Heterocycl. Chem.*, 2005, **42**, 153–156.
42 J. Pospisil and H. Sato, *J. Org. Chem.*, 2011, **76**, 2269–2272.
43 P. Hanson, R. A. A. J. Hendrickx and J. R. L. Smith, *Org. Biomol. Chem.*, 2008, **6**, 745–761.
44 M. Kirihara, J. Yamamoto, T. Noguchi, A. Itou, S. Naito and Y. Hirai, *Tetrahedron*, 2009, **65**, 10477–10484.
45 P. Hanson, R. A. A. J. Hendrickxz and J. R. L. Smith, *New J. Chem.*, 2010, **34**, 65–84.
46 H. E. Gottlieb, V. Kotlyar and A. Nudelman, *J. Org. Chem.*, 1997, **62**, 7512–7515.
47 T. Itoh and T. Mase, *Org. Lett.*, 2007, **9**, 3687–3689.
48 W. Zhu and D. Ma, *J. Org. Chem.*, 2005, **70**, 2696–2700.
49 R. G. Chapman and J. C. Sherman, *J. Org. Chem.*, 2000, **65**, 513–516.

