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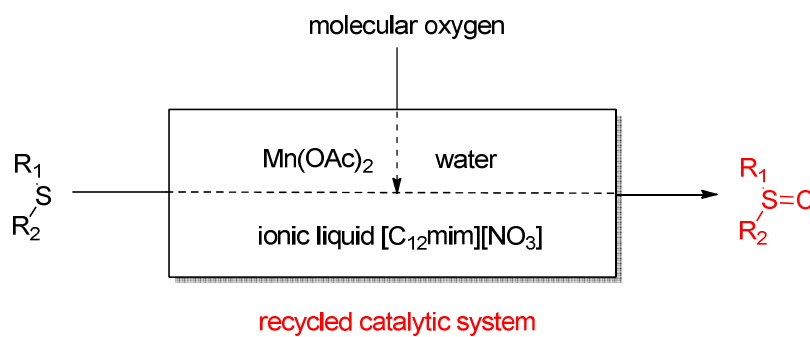
Graphical Abstract

Efficient and convenient oxidation of sulfides to sulfoxides with molecular oxygen catalyzed by $\text{Mn}(\text{OAc})_2$ in ionic liquid $[\text{C}_{12}\text{mim}][\text{NO}_3]$

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Abstract

A simple, efficient, and eco-friendly procedure for aerobic oxidation of sulfides catalyzed by $\text{Mn}(\text{OAc})_2/[\text{C}_{12}\text{mim}][\text{NO}_3]$ has been developed. The reactions afford the target products in good to high yields and no over-oxidation was observed. The products can be easily separated, and the catalytic system can be recycled without loss of catalytic activity.

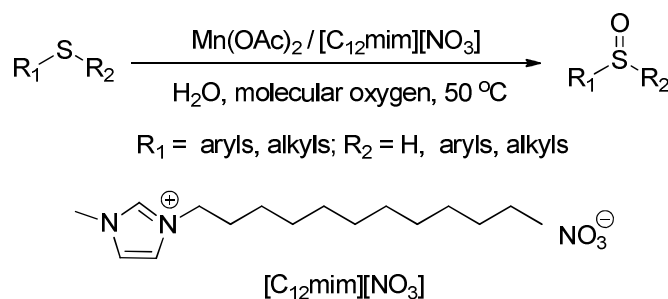
Keywords: oxidation, sulfide, molecular oxygen, manganese acetate, ionic liquid

Sulfoxides are important classes of chemicals commonly used as synthetic intermediates for the construction of various chemically and biologically significant molecules, as well as for the preparation of natural products and drugs.¹ Therefore, there has been tremendous interest in developing efficient methods for the synthesis of these molecules, and a well known method constitutes the oxidation of sulfides. Traditional methods for performing such a transformation generally involve the use of stoichiometric amount of the strongest oxidizing reagents (i.e., peracids, $\text{MeNO}_2/\text{HNO}_3/\text{H}_2\text{SO}_4$, HIO_3 , periodates, etc.).² However, these protocols are generally associated with one or more disadvantages, such as environmental hazards, low yield, harsh or delicate reaction conditions, and a large amount of waste byproducts. Oxidation with ceric ammonium nitrate/ NaBrO_3 ,³ H_5IO_6 / FeCl_3 ,⁴ $\text{AgNO}_3/t\text{-BuOOH}$,⁵ trichloroisocyanuric acid,⁶ H_2O_2 ,⁷ 2-iodoxybenzoic acid,⁸ and other reagents⁹ have also been developed for this conversion. However, some of the procedures are invariably associated with one or more disadvantages such as long reaction times, high temperatures, difficulties in work up, the use of expensive, toxic and moisture sensitive reagents, and difficulties in recycling of the catalyst.

Molecular oxygen is a safe, economical and environmentally-benign reagent, molecular oxygen has recently been utilized as an attractive oxidant for the oxidation of sulfides for the production of these compounds due to cheap price and environmental friendly nature. Therefore, molecular oxygen-based protocols are powerful methods for oxidation of sulfides and attract a great attention, which make the reactions of choice in large and industrial scale applications. A variety of catalytic systems, such as ruthenium,¹⁰ palladium,¹¹ iron,¹² osmate,¹³ gold,¹⁴ and other systems,¹⁵ have been developed for this conversion. However, most of the procedures still suffered from the use of expensive reagents, difficulties in work up, long reaction times, environmental hazards, waste control, etc. Consequently, search for new and environmentally benign synthetic methodologies for oxidation of sulfides that address these drawbacks remains to be of value and interest.

Ionic liquids (ILs) have attracted considerable attention during the past few years due, in some cases, to their favourable properties such as very low vapor pressure, wide liquid temperature range, good ionic conductivity, excellent electrochemical properties, and strong ability to dissolve many chemicals.^{16,17} Therefore, ILs have recently gained recognition of scholars from various fields such as analytical and separation science,¹⁸ chemical synthesis,¹⁹ biocatalytic transformations,²⁰ electrochemistry,²¹ and catalysis.²² In continuation of our interest in exploring green oxidation reactions in ionic liquids, we report

herein a new, efficient and environmentally friendly protocol for the selective aerobic oxidation of sulfides to sulfoxides catalyzed by manganese acetate ($\text{Mn}(\text{OAc})_2$) in ionic liquid 1-dodecyl-3-methylimidazolium nitrate ($[\text{C}_{12}\text{mim}][\text{NO}_3]$) under mild conditions (Scheme 1). Furthermore, we demonstrate that the catalytic system can be recycled and reused without any significant loss of catalytic activity.



Scheme 1 Aerobic oxidation of sulfides to sulfoxides.

To optimize the reaction conditions, methyl(phenyl)sulfane was firstly chosen as the model substrate (Table 1). Eight type of ionic liquids, $[\text{C}_8\text{mim}][\text{NO}_3]$, $[\text{C}_{10}\text{mim}][\text{NO}_3]$, $[\text{C}_{12}\text{mim}][\text{NO}_3]$, $[\text{C}_{12}\text{mim}][\text{NO}_2]$, $[\text{C}_{12}\text{mim}][\text{HSO}_4]$, $[\text{C}_{12}\text{mim}][\text{PF}_6]$, $[\text{C}_{12}\text{mim}][\text{BF}_4]$, and $[\text{C}_{12}\text{mim}]\text{Br}$, were tested with $\text{Mn}(\text{OAc})_2$ as catalyst in the reaction (Table 1, entries 2-9), it was observed that $[\text{C}_{12}\text{mim}][\text{NO}_3]$ demonstrated the best performance (Table 1, entry 4). The different catalytic effects of ILs may be attributed to their different abilities of stabilizing and dissolving O_2 , the catalyst and the substrate. Under reaction conditions, O_2 may be more soluble in $[\text{C}_{12}\text{mim}][\text{NO}_3]$, leading to higher effective concentration of the oxidant, which increases the encounter probabilities between the substrate and reactive species, and so the higher rate and yield of the reaction is observed. As expected, no product was detected in the absence of ionic liquid and catalyst (Table 1, entry 1). Furthermore, the catalyst $\text{Mn}(\text{OAc})_2$, the ionic liquid $[\text{C}_{12}\text{mim}][\text{NO}_3]$ and molecular oxygen are crucial for the oxidation, and the lack of any component can lead to a much lower yield (Table 1, entries 10-12). Besides $\text{Mn}(\text{OAc})_2$, other type of catalysts were also tested in this model reaction (Table 1, entries 13-20), and the results showed that $\text{Mn}(\text{OAc})_2$ demonstrated the best performance. In addition, no over-oxidized product ((methylsulfonyl)benzene) was detected by ^1H NMR analysis of the crude reaction mixtures in all the cases. Therefore, the combination of $[\text{C}_{12}\text{mim}][\text{NO}_3]$ and $\text{Mn}(\text{OAc})_2$ was chosen as the optimal conditions for further exploration.

Table 1 Optimization of the conditions for oxidation of methyl(phenyl)sulfane with molecular oxygen^a

Entry	Ionic liquid	Catalyst	Time / h	Yield / (%) ^b
1	—	—	12	0
2	[C ₈ mim][NO ₃]	Mn(OAc) ₂	2	86
3	[C ₁₀ mim][NO ₃]	Mn(OAc) ₂	2	95
4	[C ₁₂ mim][NO ₃]	Mn(OAc) ₂	2	97
5	[C ₁₂ mim][NO ₂]	Mn(OAc) ₂	2	91
6	[C ₁₂ mim][HSO ₄]	Mn(OAc) ₂	2	58
7	[C ₁₂ mim][PF ₆]	Mn(OAc) ₂	2	69
8	[C ₁₂ mim][BF ₄]	Mn(OAc) ₂	6	37
9	[C ₁₂ mim]Br	Mn(OAc) ₂	2	82
10	—	Mn(OAc) ₂	8	46
11	[C ₁₂ mim][NO ₃]	—	8	52
12	[C ₁₂ mim][NO ₃]	Mn(OAc) ₂	12	76 ^c
13	[C ₁₂ mim][NO ₃]	Cu(OAc) ₂	2	67
14	[C ₁₂ mim][NO ₃]	Co(OAc) ₂	2	74
15	[C ₁₂ mim][NO ₃]	Fe(OAc) ₂	4	58
16	[C ₁₂ mim][NO ₃]	Fe(OAc) ₃	2	77
17	[C ₁₂ mim][NO ₃]	FeSO ₄	2	43
18	[C ₁₂ mim][NO ₃]	FeCl ₃	4	76
19	[C ₁₂ mim][NO ₃]	MnSO ₄	2	61
20	[C ₁₂ mim][NO ₃]	Pd(OAc) ₂	5	78

^a The reactions were carried out with methyl(phenyl)sulfane (0.1 mol), catalyst (0.2 mol), IL (20 mL), and H₂O (10 mL) in the presence of O₂ gas (50 mL min⁻¹) at 50 °C. ^b Isolated yield. ^c The reaction was carried out in the absence of O₂ gas.

In addition, the catalytic system could be typically recovered and reused for subsequent reactions with no appreciable decrease in yields and reaction rates (Figure 1). The recycling process involved the removal of the product from the catalytic system, by a simple extraction with organic solvent. Fresh substrates were then recharged to the aqueous layer of catalytic system and the mixture was heated to react once again.

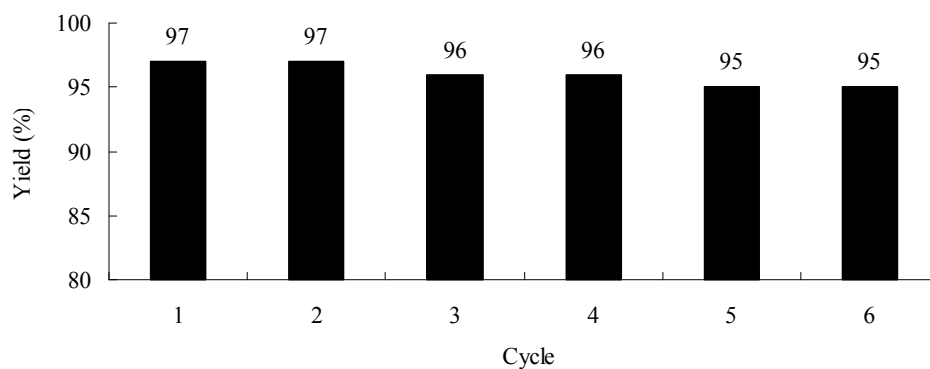
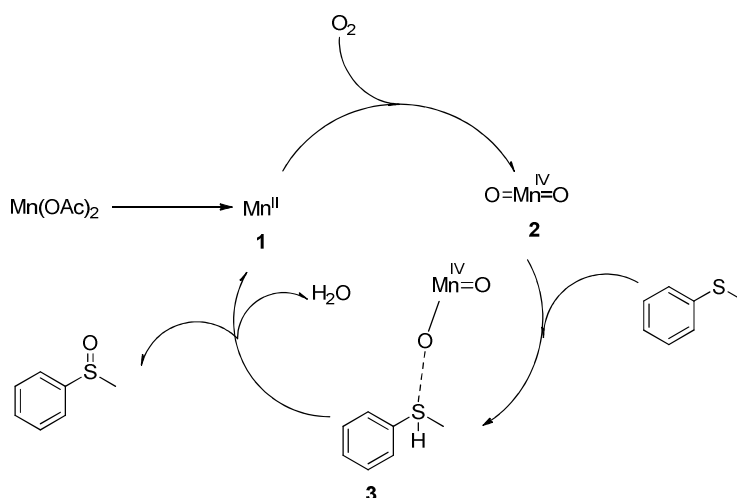


Figure 1 Repeating reactions using recovered catalytic system. The reactions were carried out with methyl(phenyl)sulfane (0.1 mol), recovered catalytic system ($[\text{C}_{12}\text{mim}][\text{NO}_3]$, $\text{Mn}(\text{OAc})_2$ and H_2O), in the presence of O_2 gas (50 mL min^{-1}) at $50 \text{ }^\circ\text{C}$ for 2 h.

According to the literature²³ and the observations in our reactions, taking the oxidation of methyl(phenyl)sulfane with O_2 as an example, a possible mechanism is proposed (Scheme 2). In the reaction, the catalyst $\text{Mn}(\text{OAc})_2$ provides a source of $\text{Mn}(\text{II})$, which reacts with the oxidant O_2 in the ionic liquid $[\text{C}_{12}\text{mim}][\text{NO}_3]$ to form $\text{O}=\text{Mn}(\text{IV})=\text{O}$ (**2**). Then, **2** reacts with the substrate to form transition state **3**. **3** then very rapidly affords $\text{Mn}(\text{II})$ to yield the desired product. The two divalent manganese ions are then re-oxidized to $\text{O}=\text{Mn}(\text{IV})=\text{O}$ by O_2 in $[\text{C}_{12}\text{mim}][\text{NO}_3]$ to complete the catalytic cycle. It looks like that the formation of **3** from **2** and the substrate is the rate-determining step.

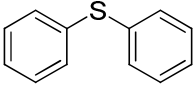
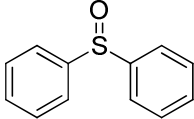
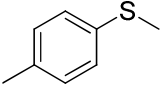
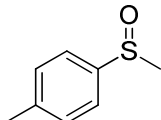
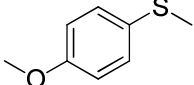
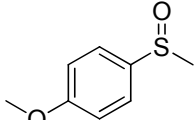
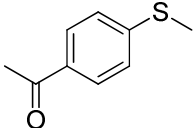
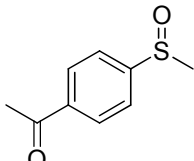
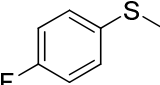
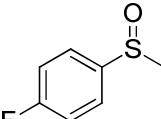
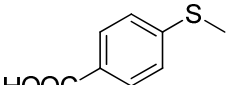
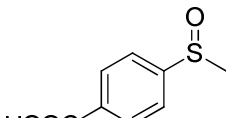
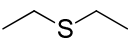
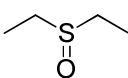
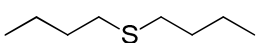
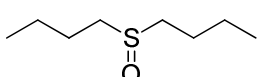


Scheme 2 Possible mechanism for the oxidation of methyl(phenyl)sulfane.

With these results in hand, we subjected other sulfides to the oxidation reactions, and the results are listed in Table 2. It is clear that various types of aryl and alkyl sulfides, can be successfully oxidized to the corresponding sulfoxides in good to high yields (Table 2). Various types of alkyl sulfides can be successfully oxidized to the corresponding sulfoxides (Table 2, entries 9 and 10), whereas the aryl sulfides were less reactive, longer reaction time were needed to reach good yields (Table 2, entries 1-8). It was also observed that the electronic nature of the substituents on the aromatic ring have some impact on the reaction rate. Aryl sulfides, especially those with electron-donating substituents (Table 2, entries 4 and 5), were more reactive than those with or without electron-withdrawing substituents (Table 2, entries 1 and 6-8), excellent yields of the expected sulfoxides were obtained.

Table 2 Catalytic oxidation of sulfides to sulfoxides^a

Entry	Substrate	Product	Time / h	Yield / (%) ^b
1			2	97
2			2	98

3			2	94
4			1.5	97
5			1.5	99
6			4	89
7			4	85
8			4	86
9			1	97
10			1	98

^a Unless otherwise noted, the reactions were carried out with sulfide (0.1 mol), Mn(OAc)₂ (0.2 mol), [C₁₂mim][NO₃] (20 mL), and H₂O (10 mL) in the presence of O₂ gas (50 mL min⁻¹) at 50 °C. ^b Isolated yield.

In conclusion, a new and highly efficient oxidation reaction system using [C₁₂mim][NO₃] in combination with Mn(OAc)₂ has been developed, which is capable of converting sulfides into the corresponding sulfoxides in good to excellent isolated yield. Mild reaction conditions, simplicity of operation, high yields, stability, easy isolation of products, and excellent recyclability of the catalytic system are the attractive features of this methodology. The scope, definition of the mechanism and

synthetic application of this reaction are currently under study in our laboratory.

Experimental

All the chemicals were from commercial sources without any pretreatment. All reagents were of analytical grade. The ionic liquids were synthesized according to the literature procedure.¹⁷ ¹H NMR spectra were recorded on a Bruker 500-MHz spectrometer using CDCl₃ as the solvent with tetramethylsilane (TMS) as an internal standard. High performance liquid chromatography (HPLC) experiments were performed on a liquid chromatograph (Dionex Softron GmbH, America), consisting of a pump (P680) and ultraviolet-visible light detector (UVD) system (170U). The experiments were performed on Diacore C18 column, \varnothing 4.6×250 mm. Elemental analysis were performed on a Vario EL III instrument (Elementar Analysensysteme GmbH, Germany).

General procedure for oxidation reactions

All the three-necked flasks were loaded with sulfide (0.1 mol), Mn(OAc)₂ (0.2 mol), [C₁₂mim][NO₃] (20 mL), and H₂O (10 mL). O₂ gas was bubbled into the flask at the flow rate of 50 mL min⁻¹. The reaction mixture was stirred at 50 °C for an appropriate time (Table 2), the reaction progress was monitored by HPLC. The mixture was then cooled to room temperature and the organic phase was extracted with dichloromethane (3×20 mL). The dichloromethane solution was washed with 5% NaHCO₃ (2×20 mL) and water (3×20 mL), and then dried over anhydrous Na₂SO₄. The solvent was removed and the residue was distilled under vacuum to give the desired pure product. The rest of the ionic liquid and the catalyst were recovered. Fresh substrates were then recharged to the recovered catalytic system and then recycled under identical reaction conditions. The target substrates were characterized by Elemental analysis, ¹H NMR or compared with their authentic samples. Spectroscopic data for selected products is as follows.

(Methylsulfinyl)benzene (Table 2, entry 1)

¹H NMR (500MHz, CDCl₃): δ = 2.71 (s, 3H, CH₃), 7.53-7.57 (m, 4H, Ar-H), 7.73 (m, 1H, Ar-H); Anal. Calcd for C₇H₈OS: C, 59.95; H, 5.73; O, 11.42; S, 22.84. Found: C, 59.97; H, 5.75; O, 11.41; S, 22.87.

(Butylsulfinyl)benzene (Table 2, entry 2)

¹H NMR (500MHz, CDCl₃): δ = 1.07 (t, 3H, CH₃), 1.47-1.58 (m, 4H, CH₂CH₂), 2.91 (m, 2H, CH₂), 7.54-7.79 (m, 5H, Ar-H); Anal. Calcd for C₁₀H₁₄OS: C, 65.84; H, 7.71; O, 8.76; S, 17.55. Found: C, 65.89;

H, 7.74; O, 8.78; S, 17.59.

Sulfinyldibenzene (Table 2, entry 3)

^1H NMR (500MHz, CDCl_3): $\delta = 7.54\text{-}7.59$ (m, 8H, Ar-H), 7.72 (m, 2H, Ar-H); Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{OS}$: C, 71.23; H, 4.96; O, 7.89; S, 15.83. Found: C, 71.25; H, 4.98; O, 7.91; S, 15.85.

1-Methyl-4-(methylsulfinyl)benzene (Table 2, entry 4)

^1H NMR (500MHz, CDCl_3): $\delta = 2.39$ (s, 3H, CH_3), 2.73 (s, 3H, CH_3), 7.42 (m, 2H, Ar-H), 7.59 (m, 2H, Ar-H); Anal. Calcd for $\text{C}_8\text{H}_{10}\text{OS}$: C, 62.27; H, 6.51; O, 10.34; S, 20.75. Found: C, 62.30; H, 6.54; O, 10.37; S, 20.79.

1-Methoxy-4-(methylsulfinyl)benzene (Table 2, entry 5)

^1H NMR (500MHz, CDCl_3): $\delta = 2.71$ (s, 3H, CH_3), 3.87 (s, 3H, OCH_3), 7.21 (m, 2H, Ar-H), 7.59 (m, 2H, Ar-H); Anal. Calcd for $\text{C}_8\text{H}_{10}\text{O}_2\text{S}$: C, 56.39; H, 5.87; O, 18.78; S, 18.83. Found: C, 56.44; H, 5.92; O, 18.80; S, 18.84.

1-(4-(Methylsulfinyl)phenyl)ethanone (Table 2, entry 6)

^1H NMR (500MHz, CDCl_3): $\delta = 2.57$ (s, 3H, CH_3), 2.73 (s, 3H, CH_3), 7.76 (m, 2H, Ar-H), 8.05 (m, 2H, Ar-H); Anal. Calcd for $\text{C}_9\text{H}_{10}\text{O}_2\text{S}$: C, 59.28; H, 5.51; O, 17.55; S, 17.56. Found: C, 59.32; H, 5.53; O, 17.56; S, 17.59.

1-Fluoro-4-(methylsulfinyl)benzene (Table 2, entry 7)

^1H NMR (500MHz, CDCl_3): $\delta = 2.71$ (s, 3H, CH_3), 7.42 (m, 2H, Ar-H), 7.71 (m, 2H, Ar-H); Anal. Calcd for $\text{C}_7\text{H}_7\text{FOS}$: C, 53.13; H, 4.45; F, 12.03; O, 10.09; S, 20.26. Found: C, 53.15; H, 4.46; F, 12.01; O, 10.11; S, 20.27.

4-(Methylsulfinyl)benzoic acid (Table 2, entry 8)

^1H NMR (500MHz, CDCl_3): $\delta = 2.75$ (s, 3H, CH_3), 7.85 (m, 2H, Ar-H), 8.16 (m, 2H, Ar-H), 12.97 (br, 1H, COOH); Anal. Calcd for $\text{C}_8\text{H}_8\text{O}_3\text{S}$: C, 52.11; H, 4.35; O, 26.03; S, 17.38. Found: C, 52.16; H, 4.38; O, 26.06; S, 17.41.

(Ethylsulfinyl)ethane (Table 2, entry 9)

^1H NMR (500MHz, CDCl_3): $\delta = 1.13$ (t, 3H, CH_3), 2.62 (dd, 2H, CH_2); Anal. Calcd for $\text{C}_4\text{H}_{10}\text{OS}$: C, 45.21; H, 9.47; O, 15.03; S, 30.18. Found: C, 45.24; H, 9.49; O, 15.07; S, 30.20.

1-(Butylsulfinyl)butane (Table 2, entry 10)

^1H NMR (500MHz, CDCl_3): $\delta = 0.93$ (t, 3H, CH_3), 1.35-1.42 (m, 4H, CH_2CH_2), 2.55-2.63 (m, 2H, CH_2),

2.67-2.72 (m, 2H, CH₂); Anal. Calcd for C₈H₁₈OS: C, 59.19; H, 11.19; O, 9.83; S, 19.74. Found: C, 59.21; H, 11.18; O, 9.86; S, 19.76.

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References

- 1 G. Solladie, *Heteroatom Chem.*, 2002, **13**, 443; I. Fernández and N. Khiar, *Chem. Rev.*, 2003, **103**, 3651; I. Forristal, *J. Sulfur. Chem.*, 2005, **26**, 163; R. Bentley, *Chem. Soc. Rev.*, 2005, **34**, 609; X. C. Zhao, Q. Zhang, C. Chen, B. S. Zhang, S. Reiche, A. Wang, T. Zhang, R. Schlögl and D. S. Su, *Nano Energy*, 2012, **1**, 624.
- 2 G. Pattenden and L. Roberts, *Tetrahedron Lett.*, 1996, **37**, 4191; R. Mello, A. Olmos, A. Alcalde-Aragonés, A. Díaz-Rodríguez, M. E. G. Núñez and G. Asensio, *Eur. J. Org. Chem.*, 2010, 6200; F. Gasparri, M. Giovannoli, L. Maresca, G. Natile and G. Palmieri, *Synth. Commun.*, 1984, **14**, 1111; M. M. Lakouraj, M. Tajbakhsh, F. Shirini and M. V. A. Tamami, *Synth. Commun.*, 2005, **35**, 775; H. Tohma, S. Takizawa, H. Watanabe, Y. Fukuoka, T. Maegawa and Y. Kita, *J. Org. Chem.*, 1999, **64**, 3519; H. Tohma, T. Maegawa and Y. Kita, *Arkivoc*, 2003, **vi**, 62; F. Ruff, A. Fábrián, Ö. Farkas and Á. Kucsman, *Eur. J. Org. Chem.*, 2009, 2102; V. G. Shukla, P. D. Salgaonkar and K. G. Akamanchi, *J. Org. Chem.*, 2003, **68**, 5422.
- 3 M. H. Ali, D. Kriedelbaugh and T. Wencewicz, *Synthesis*, 2007, 3507.
- 4 S. S. Kim, K. Nehru, S. S. Kim, D. W. Kim and H. C. Jung, *Synthesis*, 2002, 2484.
- 5 R. Das and D. Chakraborty, *Synthesis*, 2011, 277.
- 6 Z. X. Xiong, N. P. Huang and P. Zhong, *Synth. Commun.*, 2001, **31**, 245.
- 7 K. Bahrami, M. M. Khodaei and M. S. Arabi, *J. Org. Chem.*, 2010, **75**, 6208; X. F. Wu, *Tetrahedron Lett.*, 2012, **53**, 4328; M. Kirihara, A. Itou, T. Noguchi and J. Yamamoto, *Synlett*, 2010, 1557; M. M. Khodaei, K. Bahrami and A. Karimi, *Synthesis*, 2008, 1682; S. Hussain, D. Talukdar, S. K. Bharadwaj and M. K. Chaudhuri, *Tetrahedron Lett.*, 2012, **53**, 6512; M. Mba, L. J. Prins and G. Licini, *Org. Lett.*, 2007, **9**, 21; S. Liao, I. Čorić, Q. Wang and B. List, *J. Am. Chem. Soc.*, 2012, **134**, 10765; M. Rahimizadeh, G.

- Rajabzadeh, S. M. Khatami, H. Eshghi and A. Shiri, *J. Mol. Catal. A: Chem.*, 2010, **323**, 59; R. Maggi, S. Chitsaz, S. Loebbecke, C. G. Piscopo, G. Sartori and M. Schwarzer, *Green Chem.*, 2011, **13**, 1121; C. Drago, L. Caggiano and R. F. W. Jackson, *Angew. Chem. Int. Ed.*, 2005, **44**, 7221; A. Rostami, F. Hassanian, A. Ghorbani-Choghamarani and S. Saadati, *Phosphorus Sulfur*, 2013, **188**, 833; H. Egami and T. Katsuki, *J. Am. Chem. Soc.*, 2007, **129**, 8940; T. Yamaura, K. Kamata, K. Yamaguchi and N. Mizuno, *Catal. Today*, 2013, **203**, 76.
- 8 J. N. Moorthy, N. Singhal and K. Senapati, *Tetrahedron Lett.*, 2008, **49**, 80; A. Y. Kuposov and V. V. Zhdankin, *Synthesis*, 2005, 22; V. Satam, A. Harad, R. Rajule and H. Pati, *Tetrahedron*, 2010, **66**, 7659.
- 9 A. Bottoni, M. Calvaresi, A. Ciogli, B. Cosimelli, G. Mazzeo, L. Pisani, E. Severi, D. Spinelli and S. Superchid, *Adv. Synth. Catal.*, 2013, **355**, 191; W. Qian and L. Pei, *Synlett*, 2006, 709; R. S. Varma and K. P. Naicker, *Org. Lett.*, 1999, **1**, 189; A. Ghorbani-Choghamarani and S. Rezaei, *J. Chin. Chem. Soc.*, 2009, **56**, 251; A. Ghorbani-Choghamarani and S. Sardari, *Chin. J. Catal.*, 2010, **31**, 1347; C. V. Reddy and J. G. Verkade, *J. Mol. Catal. A: Chem.*, 2007, **272**, 233; F. Bigi, H. Q. N. Gunaratne, C. Quarantelli and K. R. Seddon, *Comp. Rend. Chim.*, 2011, **14**, 685; P. Zhao, M. Zhang, Y. Wu and J. Wang, *Ind. Eng. Chem. Res.*, 2012, **51**, 6641.
- 10 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; H. B. Ji, T. T. Wang, L. F. Wang and Y. X. Fang, *React. Kinet. Catal. Lett.*, 2007, **90**, 259; H. Tanaka, H. Nishikawa, T. Uchida and T. Katsuki, *J. Am. Chem. Soc.*, 2010, **132**, 12034.
- 11 R. Aldea and H. Alper, *J. Org. Chem.*, 1995, **60**, 8365; W. P. To, Y. Liu, T. C. Lau and C. M. Che, *Chem. Eur. J.*, 2013, **19**, 5654.
- 12 S. E. Martin and L. I. Rossi, *Tetrahedron Lett.*, 2001, **42**, 7147; N. M. Okun, J. C. Tarr, D. A. Hilleshiem, L. Zhang, K. I. Hardcastle and C. L. Hill, *J. Mol. Catal. A Chem.*, 2006, **246**, 11; B. Li, A. H. Liu, L. N. He, Z. Z. Yang, J. Gao and K. H. Chen, *Green Chem.*, 2012, **14**, 130.
- 13 B. M. Choudary, C. R. V. Reddy, B. V. Prakash, M. L. Kantam and B. Sreedhar, *Chem. Commun.*, 2003, 754.
- 14 E. Boring, Y. V. Geletii and C. L. Hill, *J. Am. Chem. Soc.*, 2001, **123**, 1625.
- 15 S. Colonna, N. Gaggero, F. Montanari, G. Pozzi and S. Quici, *Eur. J. Org. Chem.*, 2001, 181; Y. Imada, H. Iida, S. Ono, Y. Masui and S. I. Murahash, *Chem. Asian J.*, 2006, **1**, 136; Y. Ishii, S. Sakaguchi and T. Iwahama, *Adv. Synth. Catal.*, 2001, **343**, 393; A. H. Sun, Z. G. Xiong and Y. M. Xu, *J.*

- Mol. Catal. A: Chem.*, 2006, **259**, 1; Y. Imada, H. Iida, S. Ono and S. I. Murahashi, *J. Am. Chem. Soc.*, 2003, **125**, 2868; H. Claudia, T. Marion and J. Manuela, *Chem. Geol.*, 2013, **342**, 29.
- 16 F. Dommert, K. Wendler, R. Berger, L. D. Site and C. Holm, *ChemPhysChem*, 2012, **13**, 1625; O. Andreussi and N. Marzari, *J. Chem. Phys.*, 2012, **137**, 044508; M. Petkovic, K. R. Seddon, L. P. N. Rebelo and C. S. Pereira, *Chem. Soc. Rev.*, 2011, **40**, 1383.
- 17 S. J. Zhang and X. M. Lu, *Ionic liquids: from fundamental research to industrial applications*, Science Press, Beijing, 2006.
- 18 M. D. Joshi and J. L. Anderson, *RSC Adv.*, 2012, **2**, 5470; P. Sun and D. W. Armstrong, *Anal. Chim. Acta.*, 2010, **661**, 1; S. Stefan and S. Piotr, *Curr. Org. Chem.*, 2011, **15**, 1871.
- 19 N. V. Plechkova and K. R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123; P. Wasserschein and T. Welton, *Ionic liquids in synthesis*, Wiley-VCH, Weinheim, 2008; J. M. Andanson, S. Marx and A. Baiker, *Catal. Sci. Technol.*, 2012, **2**, 1403; A. Rouch, T. Castellan, I. Fabing, N. Saffon, J. Rodriguez, T. Constantieux, J. C. Plaquevent and Y. Génisson, *RSC Adv.*, 2013, **3**, 413.
- 20 F. van Rantwijk, R. M. Lau and R. A. Sheldon, *Trends Biotechnol.*, 2003, **21**, 131; N. Wood, J. L. Ferguson, H. Q. N. Gunaratne, K. R. Seddon, R. Goodacre and G. M. Stephens, *Green Chem.*, 2011, **13**, 1843.
- 21 A. Balducci, W. A. Henderson, M. Mastragostino, S. Passerini, P. Simon and F. Soavi, *Electrochim. Acta*, 2005, **50**, 2233; P. Hapiot and C. Lagrost, *Chem. Rev.*, 2008, **108**, 2238.
- 22 S. Saravanamurugan and A. Riisager, *Catal. Today*, 2013, **200**, 94; V. I. Parvulescu and C. Hardacre, *Chem. Rev.*, 2007, **107**, 2615; H. Olivier-Bourbigou, L. Magna and D. Morvan, *Appl. Catal. A Gen.*, 2010, **373**, 1; Q. Zhang, S. Zhang and Y. Deng, *Green Chem.*, 2011, **13**, 2619; M. Bagherzadeh and S. Ghazali-Esfahani, *Tetrahedron Lett.*, 2013, **54**, 3765.
- 23 C. C. Cosner, P. J. Cabrera, K. M. Byrd, A. M. Thomas and P. Helquist, *Org. Lett.*, 2011, **13**, 2071; J. A. Gonçalves and E. V. Gusevskaya, *Appl. Catal. A: Gen.*, 2004, **258**, 93; M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork and A. A. Abbasi-Larki, *Appl. Catal. A: Gen.*, 2008, **349**, 177; A. M. Kirillov and G. B. Shul'pin, *Coord. Chem. Rev.*, 2013, **257**, 732; S. Lentini, P. Galloni, I. Garcia-Bosch, M. Costas and V. Conte, *Inorg. Chim. Acta*, 2014, **410**, 60; M. Mondal and U. Bora, *RSC Adv.*, 2013, **3**, 18716; M. M. Najafpour, B. Pashaei and S. Nayeri, *Dalton Trans.*, 2012, **41**, 4799.

Graphical Abstract

Efficient and convenient oxidation of sulfides to sulfoxides with molecular oxygen catalyzed by $\text{Mn}(\text{OAc})_2$ in ionic liquid $[\text{C}_{12}\text{mim}][\text{NO}_3]$

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