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Selective and mild oxidation of sulfides to sulfoxides or sulfones using H_2O_2 and Cp′Mo(CO)$_3$Cl as catalysts

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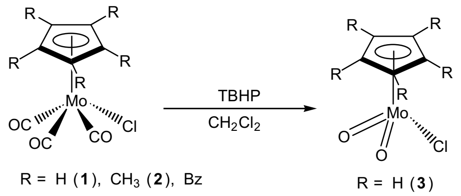
ABSTRACT

Dialkyl, aryl–alkyl, benzylic, and benzothiophenic sulfides are selectively oxidized to sulfoxides or sulfones, with stoichiometric amounts of H_2O_2 (aq) or TBHP, in the presence of complexes Cp′Mo(CO)$_3$Cl, CpMoO$_2$Cl and the mesoporous material MCM-41-2 as catalysts. The use of the thianthrene 5-oxide (SSO) probe shows that CpMo(CO)$_3$Cl/H_2O_2 or TBHP are electrophilic oxidants (Xso $\leqslant$ 15). The same conclusion is drawn from competition experiments with a mixture of p-ClC$_6$H$_4$SCH$_3$ and C$_6$H$_5$SOCH$_3$.

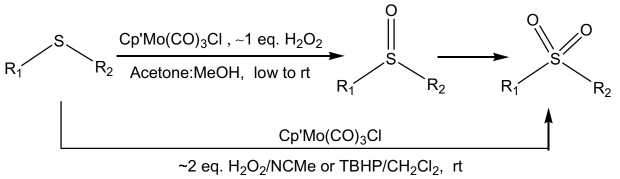
Sulfoxides and sulfones play important roles in synthetic organic chemistry and are important bioactive compounds.[1] Furthermore, sulfoxidation catalysis has assumed special relevance in the deep desulfurization of fuels, due to environmental constraints.[2]

Although there are many reported methods for the oxidation of sulfides to sulfoxides,[3,4] metal-mediated oxidizing systems for the preparation of sulfones are unusual in literature.[5] Only a few reports are available for the selective synthesis of sulfoxides and sulfones with the same reagent system, under adjusted reaction conditions.[6]

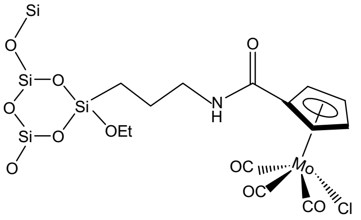
Although complexes MoO$_2$X$_2$L$_2$ are important catalysts for oxygen atom transfer reactions,[7] organometallic oxo complexes have not been so extensively used. Nevertheless, several Cp′MoO$_2$X (X = halide, alkyl) species or more practically their Cp′Mo(CO)$_3$X precursors (Scheme 1) were found to efficiently catalyze olefin epoxidation, with *tert*-butyl hydroperoxide (TBHP), but not with H_2O_2.[8]



Scheme 1.



Scheme 2.



MCM-41-2 (**4**)

These results prompted us to verify the possibility of achievement of a new procedure for the oxidation of sulfides. Herein, we describe the use of complexes [(η^5-C$_5$R$_5$)Mo(CO)$_3$Cl] (R = H (**1**), CH$_3$ (**2**))[8b,9a] and [(η^5-C$_5$H$_5$)MoO$_2$Cl] (**3**)[8b,9b] and the mesoporous

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material MCM-41-2 (**4**)[10] as catalysts for the efficient and selective oxidation of sulfides either to sulfoxides or sulfones (Scheme 2).

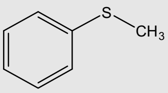
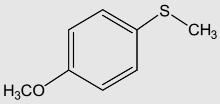
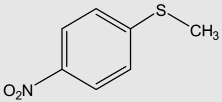
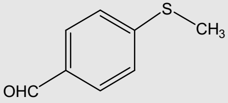
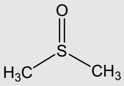
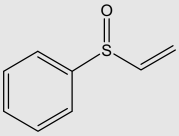
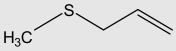
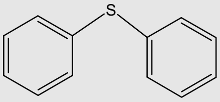
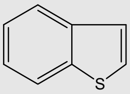
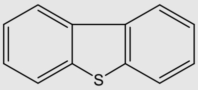
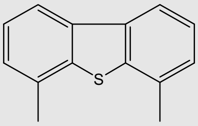
Recently, Poli has revealed the remarkable stability of Cp′Mo(VI) oxo species in aqueous media (through analytical investigations).[11] To the best of our knowledge, our study represents the first example wherein Cp′MoO_2Cl is found to be catalytically efficient with H_2O_2 (aq) as oxidant.

Aryl–alkyl (namely with the electron-withdrawing nitro group), diaryl, and benzothiophenic sulfides were easily oxidized to the corresponding sulfones (Table 1), near to room temperature, using ~2 equiv of H_2O_2 aq (in NCMe) or TBHP. This is a clean, straightforward synthetic method, in which sulfones are readily precipitated as the pure product, in high yields.[12]

The oxidation of BTP is remarkably fast when TBHP is used as oxidant with CH_2Cl_2 as solvent (entries 12 and 15). The time needed for completion of these reactions catalyzed by complexes **1** and **3** is comparable (15 min, at 35 °C). This suggests that the in situ oxidative decarbonylation of complex **1** by TBHP (see

Table 1

Selective oxidation of various functionalized substrates to sulfones using H_2O_2 or TBHP and complexes **1–4**[a]

Entry	Substrate	Catalyst complex	Oxidant	Time (h)	Yield[b] (%) (Conv. %)	Temperature (°C)
1		1	TBHP	15 min 1	(96)[c] (100)	rt
2		1 and 2	H_2O_2	0.5	99 (100)	rt
3		3	H_2O_2	2	(100)	rt
4		1	TBHP	1	85 (100)	rt
5		1	TBHP	6	87	rt
6		1	TBHP	4	76	35
7		2	H_2O_2	2	99	35
8		1	TBHP	1	92 (100)	35
9		2	H_2O_2	4	98	−20 °C to rt
10		1	H_2O_2	3	98	−20 °C to rt
11		2	H_2O_2	5	100	35
12		1 and 2	TBHP	15 min	85 (100)	35
13		1	TBHP; solv.: MeOH	3 8	(28) 78	35
14		2	H_2O_2	5	70	35
15		3	TBHP	15 min	97 (100)	35
16		4	TBHP	4	71	55
17		1 and 2	TBHP	1.5	80	55
18		1	H_2O_2	7	69	35
19		1	TBHP	5	100	rt
20		1	H_2O_2; solv: MeOH/CH_2Cl_2 (4:1)	12	90	35

[a] Reaction conditions: 3.5 mmol of sulfide; 2.0–2.5 equiv of oxidant; 2 mol % of catalyst; 8 ml of solvent: CH_2Cl_2 for TBHP, NCMe for H_2O_2.

[b] Isolated yield. Spectra were compared with literature.[6a,13] Conversion (in brackets) was determined by GC on the reaction mixture (toluene as internal standard). Only sulfone is formed.

[c] Formation of sulfoxide and sulfone.

Scheme 1) is fast and probably gives rise to the same active metal species as complex **3**.[8b] The use of MeOH produces a dramatic slowing effect on the reaction (entry 13), perhaps due to the coordination of this solvent to the Mo(VI) center.[14]

The benzothiophenic compounds DBTP and 4,6-DMDBTP (entries 17–20) could be oxidized in good yields, under very mild conditions. In literature, the oxidation of thiophene derivatives to their sulfones is known to take place over a limited range of metal catalysts and large excess of H_2O_2 and higher reaction temperatures are typically used.[2,15] The oxidation of DBTP at 55 °C, after 1.5 h, in the presence of TBHP/complex **1** (entry 17) is remarkably efficient.

Substrates containing sensitive functional groups such as aldehyde and alkene (entries 6, 7, 9, 10) were selectively oxidized at the sulfur atom, without affecting the C–C double bond. It is important to notice that Cp′Mo(CO)$_3$Cl has been used as an efficient olefin epoxidation catalyst.[8]

The above-mentioned catalytic systems are all homogeneous in nature. At the exploratory level, we have tested the heterogeneous MCM-41-2 (**4**) in the oxidation of BTP by TBHP (entry 16). Compared to the non-supported catalyst (entry 12), longer reaction times at higher temperature were necessary for obtaining comparable isolated yields, in line with previous findings in epoxidation catalysis.[10]

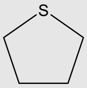
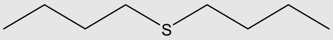
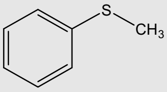
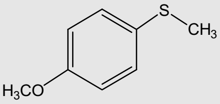
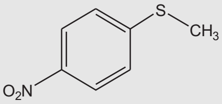
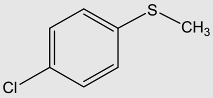
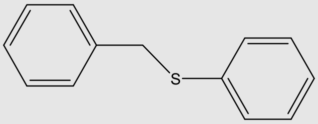
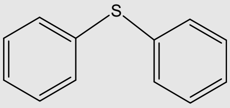
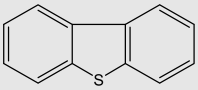
The chemoselective oxidation of sulfides to sulfoxides was also investigated (Scheme 2) and the sulfoxides in Table 2 were isolated using ~1 equiv of oxidant in the appropriate solvent (acetone/MeOH 1:1 for H_2O_2; CH_2Cl_2 for TBHP), from low to rt.[16] In the case of DBTP (entry 9) sulfone formation could not be avoided. There are few reports on the oxidation of DBTP to its sulfoxide,[6c] as the corresponding sulfone is generally obtained.[2,6a,c]

To gain some mechanistic insight on the sulfoxidation reactions, kinetic experiments were performed where *p*-$ClC_6H_4SCH_3$ and $C_6H_5SOCH_3$ (1:1) were in competition for the oxidant (Table 3).[17,18] A much higher oxidative reactivity of *p*-$ClC_6H_4SCH_3$ was observed, as expected.[19,20] When H_2O_2 is used as oxidant, the protic solvent MeOH favors the chemoselective formation of sulfoxide (entries 1 and 2), as in other catalytic systems[18,21a] and this has certainly permitted the straightforward synthesis of sulfoxides in Table 2.

We have also used the thianthrene 5-oxide (SSO) oxidation as a mechanistic probe.[21,22] The results in Table 4 show that SSO was predominantly oxidized at the sulfide and the X_{SO} values unequivocally indicate an electrophilic character for complex **1**/H_2O_2 or

Table 2

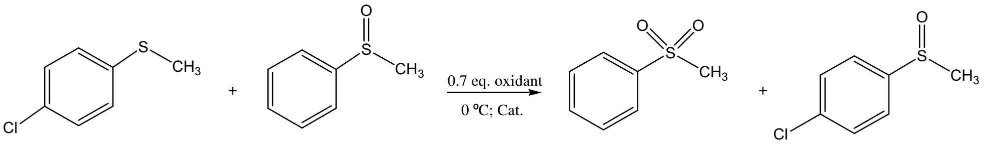
Selective oxidation of sulfides to sulfoxides using H_2O_2 or TBHP and complexes **1** and **2**[a]

Entry	Substrate	Catalyst complex	Oxidant	Time (h)	Yield[b] (%) (Conv. %)
1		1	H_2O_2	2.5	92
2		2	H_2O_2	2	86
3		1	TBHP	15 min, at −20 °C 2.5	(37) 89 (96)
4		1	H_2O_2	2	98
5		2	H_2O_2	3.5	75
6		1	H_2O_2	5	96
7		1	H_2O_2	5.5	92
8		1	H_2O_2	7	95
9		1	H_2O_2	6	60

[a] Reaction conditions: 3.5 mmol of sulfide; 1.1 equiv of oxidant; 2 mol % of catalyst; solv.: CH_2Cl_2 for TBHP, acetone/MeOH (1:1) for H_2O_2; −20 °C to rt.

[b] Isolated yield. Spectra were compared with literature.[4c,6a,13] Conversion (in brackets) was determined by GC. Only sulfoxide is formed.

Table 3
Competitive oxidation of p-$ClC_6H_4SCH_3$ and $C_6H_5SOCH_3$ using H_2O_2 or TBHP and complex **1**[a]

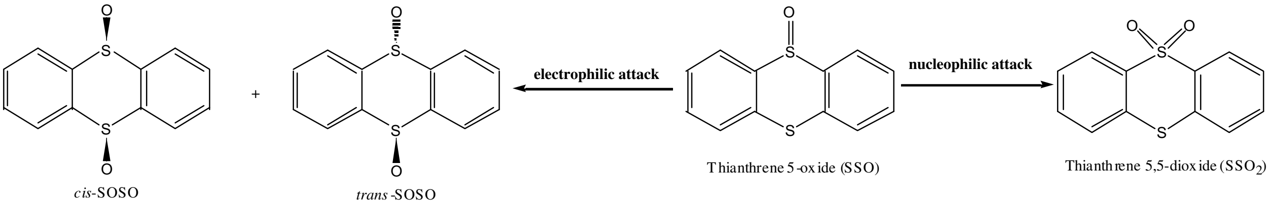


Entry	Oxidant	Solvent	Time (h)	Conv. of p-$ClC_6H_4SCH_3$[b] (%)	Conv. of $C_6H_5SOCH_3$[b] (%)
1	H_2O_2	NCMe	0.5	30	9
2	H_2O_2	Acetone/MeOH (1:1)	3 h	33	–
			5 h 30	66	–
3	TBHP	CH_2Cl_2	2 h	69	–

[a] Reaction conditions: 3.5 mmol of 4-ClTIOAN and 3.5 mmol of TIOANSO; 0.7 equiv of oxidant; 2 mol % of catalyst; at 0 °C.

[b] Conversion determined by GC analysis on the crude reaction mixture (with mesitylene as internal standard).

Table 4
Oxidation of thianthrene 5-oxide (SSO) by H_2O_2 or TBHP catalyzed by complex **1**[a]



Entry	Oxidant (equiv)	Solvent	Time (h)	Conv.[b] (%)	Mass balance[b] (%)	Product distribution[b] (%) SSO_2/*trans*-SOSO/*cis*-SOSO	X_{SO}[c]
1	H_2O_2 (2.0)	CH_2Cl_2/NCMe (2:9)	4	22	97	12/64/24	0.12
2	H_2O_2 (2.0)	CH_2Cl_2/MeOH (1:4)	4	11	71	8/84/8	0.08
3	TBHP (1.0)	CH_2Cl_2	1	86	100	15/78/7	0.15

[a] Reaction conditions: 0.05 mmol of SSO; 1.0–2.0 equiv of oxidant; 2 mol % of catalyst; at rt.

[b] Determined by HPLC analysis of the crude reaction mixture. No over-oxidation product $SOSO_2$ was detected.

[c] XSO = sulfoxide oxidation/total oxidation; calculated according to Ref. 21.

TBHP,[21] in accordance with the competition experiments with $ClC_6H_4SCH_3$ and $C_6H_5SOCH_3$.

The active species in this system is still unknown; a species containing η^2-coordinated peroxide[23], η^1-*tert*-butylperoxo ligand,[7b,14] or a non-cyclopentadienyl containing catalyst[8f] can be suggested on the basis of previous findings.

Regardless of the nature of the intermediate, nucleophilic attack of sulfur then occurs on the electrophilic oxygen atom activated by the Mo(VI) center.

In conclusion, the Cp′Mo(CO)$_3$Cl complexes promote the chemoselective and efficient oxidation of sulfides either to sulfoxides or sulfones, with stoichiometric amounts of TBHP or the 'environmentally friendly' H_2O_2 (aq), under mild reaction conditions. This is the first time Cp′MoO$_2$Cl is found to be catalytically efficient in oxidations with H_2O_2 (aq) and further studies with this system are being developed in our group.

References and notes

1. (a) Kaczorowska, K.; Kolarska, Z.; Mitka, K.; Kowalski, P. *Tetrahedron* **2005**, *61*, 8315–8327 and references cited therein; (b) Simpkins, N. S. Sulfones in Organic Synthesis. In Baldwin, J. E., Magnus, P. D., Eds.; Oxford: Pergamon, 1993.
2. (a) Te, M.; Fairbridge, C.; Ring, Z. *Appl. Catal. A* **2001**, *219*, 267–280; (b) Li, C.; Jiang, Z.; Gao, J.; Yang, Y.; Wang, S.; Tian, F.; Sun, F.; Sun, X.; Ying, P.; Han, C. *Chem. Eur. J.* **2004**, *10*, 2277–2280; (c) Campos-Martin, J.; Capel-Sanchez, M.; Fierro, J. *Green Chem.* **2004**, *6*, 557–569.
3. (a) Yuan, Y.; Bian, Y. *Tetrahedron Lett.* **2007**, *48*, 8518–8520; (b) De Rosa, M.; Lamberti, M.; Pellechia, C.; Scettri, A.; Villano, R.; Soriente, A. *Tetrahedron Lett.* **2006**, *47*, 7233–7235; (c) Massa, A.; De Lorenzo, E. M.; Scettri, A. *J. Mol. Catal. A* **2006**, *250*, 27–29; (d) Hosseinpoor, F.; Golchoubian, H. *Tetrahedron Lett.* **2006**, *47*, 5195–5197; (e) Velusamy, S.; Kumar, A. V.; Saini, R.; Punniyamurthy, T. *Tetrahedron Lett.* **2005**, *46*, 3819–3822; (f) Mekmouche, Y.; Hummel, H.; Ho, R. Y. N.; Que, L., Jr.; Schünemann, V.; Thomas, F.; Trautwein, A. X.; Lebrun, C.; Gorgy, K.; Lepêtre, J.-C.; Collomb, M.-N.; Deronzier, A.; Fontecave, M.; Ménage, S. *Chem. Eur. J.* **2002**, *8*, 1196–1204; (g) Du, G. D.; Espenson, J. H. *Inorg. Chem.* **2005**, *44*, 2465–2471.
4. (a) Bortolini, O.; Di Furia, F.; Modena, G.; Seraglia, R. *J. Org. Chem.* **1985**, *50*, 2688–2690; (b) Bonchio, M.; Carofiglio, T.; Di Furia, F.; Fornasier, R. *J. Org. Chem.* **1995**, *60*, 5986–5988; (c) Batigalhia, F.; Zaldini-Hernandes, M.; Ferreira, A. G.; Malvestiti, I.; Cass, Q. B. *Tetrahedron* **2001**, *57*, 9669–9676.
5. (a) Xu, L.; Cheng, J.; Trudell, M. L. *J. Org. Chem.* **2003**, *68*, 5388–5391; (b) Barker, E.; Ren, T. *Tetrahedron Lett.* **2004**, *45*, 4681–4683.
6. (a) Sato, K.; Hyodo, M.; Aoki, M.; Zheng, X. Q.; Noyori, R. *Tetrahedron* **2001**, *57*, 2469–2476; (b) Sasaki, V.; Ushimaru, K.; Iteya, K.; Nakayama, H.; Yamaguchi, S.; Ichihara, J. *Tetrahedron Lett.* **2004**, *45*, 9513–9515; (c) Bahrami, K. *Tetrahedron Lett.* **2006**, *47*, 2009–2012; (d) Jeyakumar, K.; Chand, D. K. *Tetrahedron Lett.* **2006**, *47*, 4573–4576; (e) Shaabani, A.; Rezayan, A. H. *Catal. Commun.* **2007**, *8*, 1112–1116.
7. (a) Kühn, F. E.; Santos, A. M.; Lopes, A. D.; Gonçalves, I. S.; Herdtweck, E.; Romão, C. C. *J. Mol. Catal. A: Chem.* **2000**, *164*, 25–38; (b) Kühn, F. E.; Groarke, M.; Bencze, É.; Herdtweck, E.; Prazeres, A.; Santos, A. M.; Calhorda, M. J.; Romão, C. C.; Gonçalves, I. S.; Lopes, A. D.; Pillinger, M. *Chem. Eur. J.* **2002**, *8*, 2370–2383; (c) Kühn, F. E.; Santos, A. M.; Abrantes, M. *Chem. Rev.* **2006**, *106*, 2455–2475.
8. (a) Trost, M. K.; Bergman, R. G. *Organometallics* **1991**, *10*, 1172–1178; (b) Abrantes, M.; Santos, A. M.; Mink, J.; Kühn, F. E.; Romão, C. C. *Organometallics* **2003**, *22*, 2112–2118; (c) Freund, C.; Abrantes, M.; Kühn, F. E. *J. Organomet. Chem.* **2006**, *691*, 3718–3729; (d) Martins, A. M.; Romão, C. C.; Abrantes, M.; Azevedo, M. C.; Cui, J.; Dias, A. R.; Duarte, M. T.; Lemos, M. A.; Lourenço, T.; Poli, R. *Organometallics* **2005**, *24*, 2582–2589; (e) Zhao, J.; Santos, A. M.; Herdtweck, E.; Kühn, F. E. *J. Mol. Catal. A: Chem.* **2004**, *222*, 265–271; (f) Pratt, M.; Harper, J. B.; Colbran, S. B. *Dalton Trans.* **2007**, 2746–2748.
9. (a) Kubas, G. J.; Kiss, G.; Hoff, C. D. *Organometallics* **1991**, *10*, 2870–2876; (b) Cousins, M.; Green, M. L. H. *J. Chem. Soc.* **1964**, 1567.
10. Abrantes, M.; Gago, S.; Valente, A. A.; Pillinger, M.; Gonçalves, I. S.; Santos, T. M.; Rocha, J.; Romão, C. C. *Eur. J. Inorg. Chem.* **2004**, 4914–4920.
11. Poli, R. *Chem. Eur. J.* **2004**, *10*, 332–341.
12. *General procedure for preparation of sulfones*: 2.0–2.5 equiv of H_2O_2 (30% aq) or anhydrous TBHP (5–6 M in decane) was added to a solution of the catalyst

(2 mol %) and sulfide (3.5 mmol), in 8 ml of the appropriate solvent (NCMe for H_2O_2; CH_2Cl_2 for TBHP), at rt (or 35 °C). The reaction was monitored by TLC (and GC). After completion, the product precipitated by adding Et_2O/hexane. Pure sulfones were obtained upon recrystallization from CH_2Cl_2/hexane. The purity was ascertained by ^1H NMR, MS and EA. *Vinyl phenyl sulfone* (*entry 9*, Table 1): white solid. IR (ν_{max}, KBr, cm^{-1}): 3108, 3046, 1607, 1583, 1447, 1385, 1306, 1250, 1152. ^1H NMR (300 MHz; $CDCl_3$, δ): 5.97 (d, *J* = 12.0, 1H), 6.39 (d, *J* = 18.0, 1H), 6.64–6.55 (m, 1H), 7.59–7.46 (m, 3H, Ph), 7.83 (d, 2H, Ph). Anal. Calcd $C_8H_8O_2S$: C, 57.14; H, 4.76; S, 19.07. Found: C, 56.95; H, 4.92; S, 19.32. *Allyl methyl sulfone* (*entry 10*): orange oil. IR (ν_{max}, KBr, cm^{-1}): 3093, 2296, 2258, 2055, 1967, 1416, 1302, 1138. ^1H NMR (300 MHz; $CDCl_3$, δ): 1.92 (s, 3H); 3.66 (d, 2H, *J* = 7.2 Hz); 5.43–5.36 (m, 2H); 5.82–5.91 (m, 1H). ESI-MS *m*/*z* Calcd $C_4H_8NaO_2S$ ($[M+Na]^+$): 143.07. Found: 143.1.

13. (a) *The Sadtler Standard Spectra, NMR*; Sadtler Research Laboratories, 12327M, 1972.; (b) Ali, M. H.; Stevens, W. C. *Synthesis* **1997**, 764–768.
14. Veiros, L. F.; Prazeres, A.; Costa, P. J.; Romão, C. C.; Kühn, F. E.; Calhorda, M. J. *Dalton Trans.* **2006**, 1383–1389.
15. (a) Hulea, V.; Fajula, F.; Bousquet, J. *J. Catal.* **2001**, *198*, 179–186; (b) Abrantes, M.; Valente, A. A.; Pillinger, M.; Gonçalves, I. S.; Rocha, J.; Romão, C. C. *Chem. Eur. J.* **2003**, *9*, 2685–2695; (c) Chica, A.; Gatti, G.; Moden, B.; Marchese, L.; Iglesia, E. *Chem. Eur. J.* **2006**, *12*, 1960–1967.
16. *General procedure for preparation of sulfoxides*: 1.1 equiv of H_2O_2 (aq) or TBHP was added to a solution of the catalyst (2 mol %) and sulfide (3.5 mmol), in 8 ml of the appropriate solvent (acetone/MeOH 1:1 for H_2O_2; CH_2Cl_2 for TBHP), at −20 °C. The mixture gradually came to rt. The reaction was monitored by TLC (and GC). After completion, a saturated solution of $NaHCO_3$ (or $Na_2S_2O_5$, 10 ml) was added and it was extracted with CH_2Cl_2 or AcOEt. The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated in vacuum. Pure sulfoxides were isolated upon flash chromatography on silica gel (AcOEt/hexane). The purity was ascertained by ^1H NMR, MS and EA.
17. *Competitive oxidation of p-$ClC_6H_4SCH_3$ and $C_6H_5SOCH_3$*: 0.7 equiv of H_2O_2 (aq) or TBHP was added to a solution containing equal amounts (3.5 mmol) of *p*-$ClC_6H_4SCH_3$ and $C_6H_5SOCH_3$, $CpMo(CO)_3Cl$ (2 mol %) and mesitylene (internal standard), in the selected solvent (5 ml), at 0 °C. The conversion of the substrates was determined by GC analysis.
18. Patonay, T.; Adam, W.; Lévai, A.; Kövér, P.; Németh, M.; Peters, E.-M.; Peters, K. *J. Org. Chem.* **2001**, *66*, 2275–2280.
19. Ballistreri, F. P.; Tomaselli, G. A.; Toscano, R. M.; Conte, V.; Di Furia, F. *J. Am. Chem. Soc.* **1991**, *113*, 6209–6212.
20. Ballistreri, F. P.; Tomaselli, G. A.; Toscano, R. M.; Bonchio, M.; Conte, V.; Di Furia, F. *Tetrahedron Lett.* **1994**, *35*, 8041–8044.
21. (a) Adam, W.; Golsch, D.; Görth, F. C. *Chem. Eur. J.* **1996**, *2*, 255–258; (b) Adam, W.; Golsch, D. *Chem. Ber.* **1994**, *127*, 1111–1113; (c) Bonchio, M.; Conte, V.; De Concilis, M. A.; Di Furia, F.; Ballistreri, F. P.; Tomaselli, G. A.; Toscano, R. M. *J. Org. Chem.* **1995**, *60*, 4475–4480; (d) Adam, W.; Golsch, D. *J. Org. Chem.* **1997**, *62*, 115–119; (e) Adam, W.; Mitchell, C. M.; Saha-Möller, C. R. *J. Mol. Catal. A* **2000**, *154*, 251–255; (f) Adam, W.; Corma, A.; García, H.; Weichold, O. *J. Catal.* **2000**, *196*, 339–344.
22. *General procedure for the oxidation of SSO*: 1.0–2.0 equiv of H_2O_2 (aq) or TBHP was added to a solution containing SSO (0.05 mmol) and $CpMo(CO)_3Cl$ (2 mol %) in the selected solvent (7 ml), at rt. Aliquots were withdrawn, diluted in CH_2Cl_2/EtOH (1:1) and analyzed by quantitative HPLC.
23. (a) Mimoun, H. *J. Am. Chem. Soc.* **1986**, *108*, 3711–3718; (b) Chong, A.; Sharpless, K. B. *J. Org. Chem.* **1977**, *42*, 1587–1590.