Pergamon

Tetrahedron 57 (2001) 9669–9676

TETRAHEDRON

Selective and mild oxidation of sulfides to sulfoxides by oxodiperoxo molybdenum complexes adsorbed onto silica gel

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Received 25 June 2001; accepted 3 October 2001

Abstract—Aliphatic and aromatic sulfides, ketosulfides, sulfinyl acids and esters, and olefinic sulfides were oxidized to sulfoxides using oxodiperoxo complexes of molybdenum coated on silica gel (150 Å pore size) in very high yields. Complete chemoselectivity was observed for the oxidation of all functional sulfides. Sulfones were, however, the main products of the reaction when the complexes were not coated on silica gel. The influence of silica gel as the support of these reactions was also investigated and it was demonstrated that it alters the reactivity of the complex but it is not responsible for the excellent chemoselectivity of the complexes. The complex [$MoO(O_2)_2$(pyrazole) (H_2O)] proved to be more reactive than [$MoO(O_2)_2$(Opyr) (H_2O)]. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

The use of diperoxo complexes of molybdenum for olefin epoxidation is well established[1–3] and since sulfide oxidation can be achieved with reagents used for olefin epoxidation, the use of these complexes for these purpose was examined.

Shurig mentions the use of molybdenum (VI) oxodiperoxo complexes for oxidation of sulfides,[2,3] but to our knowledge there is only a single reported study of the use of these complexes for the preparation of sulfoxides, the paper of the Carofiglio group[4] on the oxidation of thioanisole by hydrogen peroxide catalyzed by Mo(VI) in presence of β-cyclodextrin-based ligands.

Although there are a large number of procedures for oxidation of sulfides to sulfoxides, few of them are highly chemoselective and able to stop at the sulfoxide level.[5]

In this paper we report an efficient oxidation using molybdenum (VI) oxodiperoxo complexes coated on silica gel for conversion of sulfides to sulfoxides. Complete chemoselectivity was observed in the reactions of the oxodiperoxo molybdenum complexes used for all functional sulfides investigated, including alkenes.

2. Results and discussion

Molybdenum (VI) oxodiperoxo complexes such as shown in Fig. 1 [$MoO(O_2)_2$(Opyr) (H_2O)] and [$MoO(O_2)_2$(Pyrazole) (H_2O)], complexes (I) and (II), respectively, are stoichiometric reagents. They were prepared by stoichiometric reaction of the ligands with molybdic acid and hydrogen peroxide by the procedure described by Mimoun et al.[1]

Both complexes were obtained as yellow powder after concentration of the reaction mixture and according to the Mimoun[1] procedure these complexes were dried in the presence of phosphorus pentoxide. Infrared and ultraviolet spectra and microanalysis were used to characterize them (see Section 4).

The series of sulfides selected for these studies is shown in Fig. 2. The series includes aliphatic and aromatic sulfides (1–3), ketosufides (4–12), sulfinyl acids and esters (13–18), and olefinic sulfides (19–27).[6–11]

The oxidation reaction was preliminarily investigated for the sulfides (1)–(3) using the complex (I). The reactions

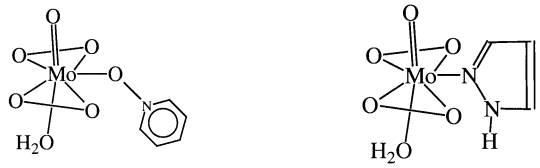

Figure 1. Structures of the aquo (*N*-oxo of pyridine) and of aquo (pyrazol) molybdenum (VI) oxodiperoxo complexes.

Keywords: mild oxidation; oxodiperoxo molybdenum complexes; silica gel; sulfide.

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PII: S0040-4020(01)00969-3

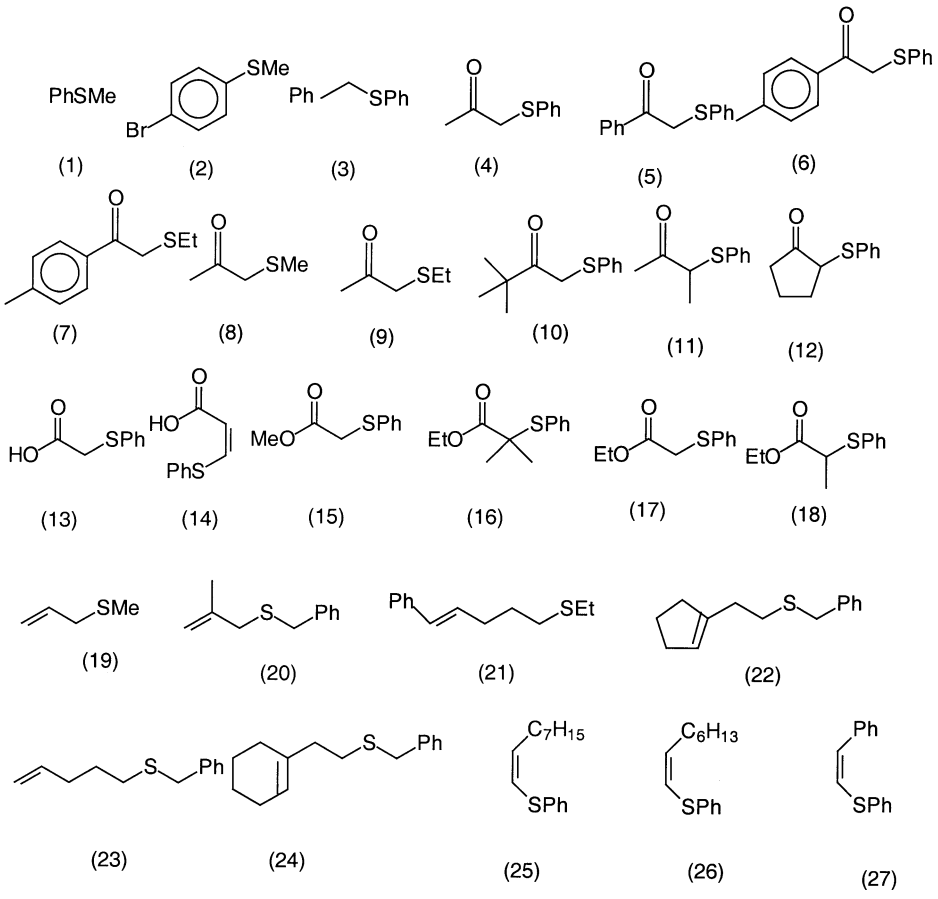

Figure 2. The structures of the used sulfides.

were carried out using methanol:acetonitrile (1:1 v/v) as solvent, however, under these reaction conditions the main products were the corresponding sulfones.

The use of heterogeneous organic reactions by immobilizing the reagent on porous solids has been proved successful.[12–16] The effect of silica gel as support for these reaction was thus investigated by coating complex (I) to silica gel (Davisil, 150 Å pore size) in a weight ratio of 40% of complex to silica.

The adsorbed complex (I) was then used to react with the sulfides (1) to (3), using methanol:acetonitrile (1:5 v/v) as the reaction solvent. The complex was added using a solid addition flask and it was done in portions over a 20 min period. The reactions were followed by thin layer and/or gas chromatography. The main products, this time, were the sulfoxides.

Based on these preliminary results the reactivity of both complexes was investigated. Table 1 shows the results of the oxidation reactions under optimized conditions for the sulfides series (1) to (27), using both molybdenum (VI) oxodiperoxo complexes coated on silica Davisil in a nominal weight ratio of 40%. The reaction conditions were optimized for each sulfide with respect to temperature and reaction time.

The reactions were carried out based on a 1:1 molar ratio of the complexes to the sulfides. Even when a 2:1 molar ratio of the complexes to the sulfide was used the reactions stopped at the sulfoxide stage. Leaving the reactions for a further period of time made little change to the products formed.

The results obtained show that complex (II) reacts about twice as fast as the reactions involving complex (I). Fig. 3 shows the profile of the oxidation reaction of benzyl phenyl sulfide with both complexes exemplifying the greater reactivity of complex (II). In one case, with sulfide 2, oxidation at the stated condition of the reaction with complex (II) gave unwanted sulfone as a major product. However, conducting the reaction at lower temperature (−20 °C) this oxidation was controlled and sulfoxide function was again obtained selectively (see Table 1 entry 2). Traces of sulfones were observed for the reaction of complex (II) with all others sulfides when the reactions were carried out at 0 °C.

The geometrical and electronic structures of these complexes were theoretically investigated at the ab initio level.[16] Good correlation was found between experimental and the calculated geometrical parameters. The relationship between the reactivity of these complexes and their coordination number was also established.

The electronic properties of these complexes were also studied.[17,18] The electronic affinity values computed for complex (I) was 2.24 eV while for complex (II) it was

Table 1. Results of the oxidations of sulfides (1)–(27) with supported complexes (I) and (II)

	Complex (I)[a]		Complex (II)[a]	
Sulfide	Sulfoxide (%)	Time (h)	Sulfoxide (%)	Time (h)
1	97	23	92	12
2[b]	96	11	95	7
3	97	13	97	6
4	88	7	74	5
5	91	10	87	8
6	93	8	92	6
7	97	6	87	4
8	92	9	86	6
9	91	7	84	5
10	97	6	96	3
11	95	10	97	8
12	91	15	90	11
13	92	7	85	3
14	86	14	80	9
15	96	6	92	5
16	97	12	95	6
17	98	8	96	6
18	96	11	94	8
19	83	3	85	1
20	95	15	93	8
21	94	9	91	5
22	98	15	98	7
23	92	16	89	10
24	93	15	90	8
25	97	12	95	9
26	94	12	93	7
27	96	9	94	5

[a] Supported form of the complexes (I) and (II).
[b] Complexes added at −20 °C.

2.93 eV. The comparison of the electronic affinity of both complexes would suggest that complex (II) should be more reactive towards nucleophiles than the complex (I). This predictive behavior was confirmed by the experimental results shown on Table 1.

The sulfides 11, 12 and 18 formed the corresponding sulfoxides, as expected, as a diastereomeric mixture. The yields given in Table 1 for these sulfoxides are for the diastereomeric mixtures.

The results presented in Table 1 show also that the oxidation of sulfides to the corresponding sulfoxides has been achieved with complete chemoselectivity in the presence of a variety of functional groups. It is important to notice that molybdenum (VI) oxodiperoxo complexes have been used, in solution, efficiently as stoichiometric reagents for the oxidation of various organic substrates such as ketones, aliphatic amines and olefins.[1–3]

Trying to establish if the silica was working as a slow-releasing agent and if it was also responsible for the observed chemoselectivity, the reactions of complex (II) with the sulfides 2, 4, 13, 19 and 25 were examined. Complex (II) was selected since it was more reactive than complex (I) and the selected sulfides are representatives of the classes of sulfides investigated.

A comparison was made of the standard reaction conditions with the one using the complex (II) coated to silica added all at once at the beginning of the reaction and by the use of the non-coated complex added as in the standard reaction protocol.

The graphics at Fig. 4 shows the profiles of the oxidations of sulfide 4 at the three examined conditions and illustrates the results found for the other four sulfides also investigated.

When the reactions were carried out as the standard reaction protocol only the corresponding sulfoxides were formed (Fig. 4(a)), however, just by altering the addition condition of the complex, sulfones were also formed (Fig. 4(b)). The use of complex (II) not coated to silica gel and added into portions at 20 min period as in the standard reaction protocol, showed that the use of the silica is important in the reactivity of the complex but not in the chemoselectivity of the reactions. The results for the non-supported reagent (Fig. 4(c)), show that sulfones were formed almost as the sole products of the reactions. However, no epoxidation or Bayer–Villeger products, were obtained at this reaction conditions for any of the functional sulfides.

To demonstrate the utility of the procedure described here, a

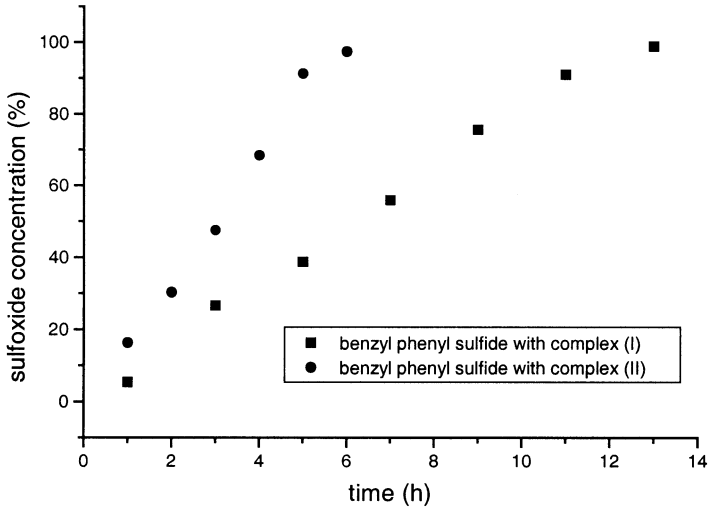

Figure 3. The profile of the oxidation of benzyl phenyl sulfide.

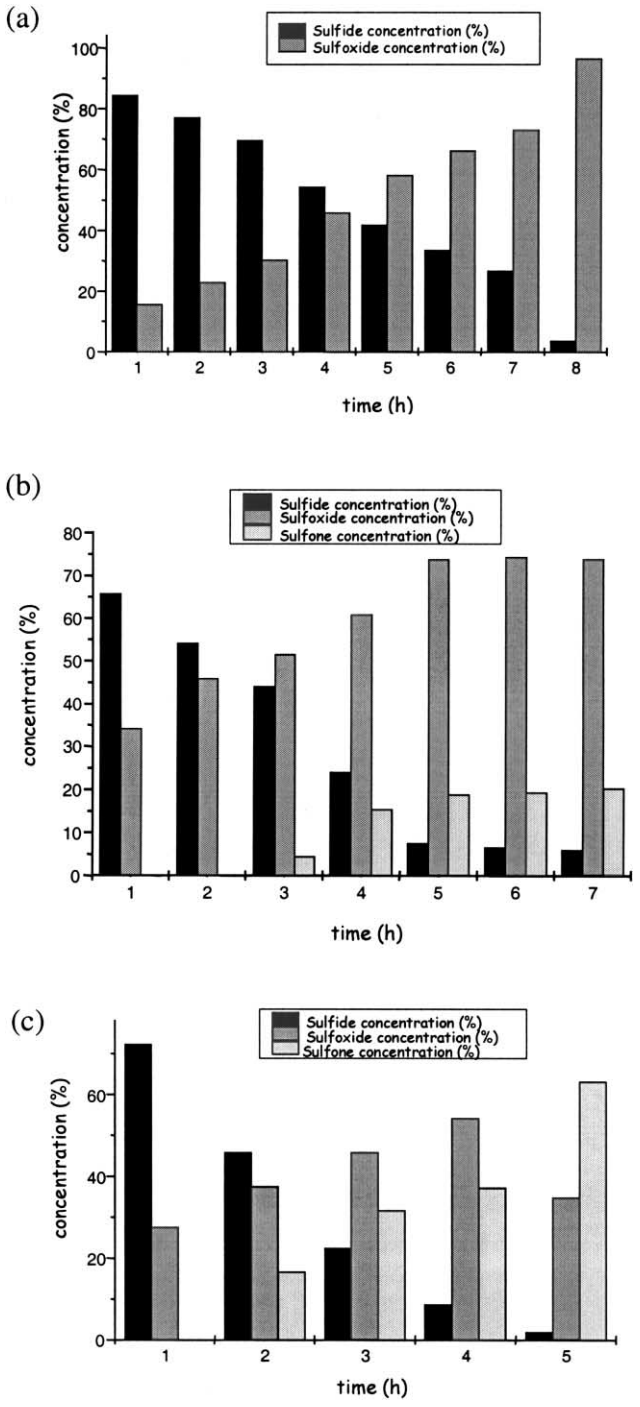

Figure 4. Graphics showing oxidation profiles of the ketosulfide (4) with complex (II) (1:1 molar ratio): (a) Standard oxidation protocol, (b) complex (II) added all at once at the beginning of the reaction and (c) non-coated complex added under the conditions of the standard reaction protocol. No sulfone was formed at condition (a).

hundred fold scale reactions were carried out at the standard reaction conditions for the oxidations of 4-(bromophenyl) methyl sulfide, benzyl phenyl sulfide and allyl methyl sulfide. The sulfoxides were isolated in 90, 91 and 75% yields, respectively. The oxidation reaction of 4-(bromophenyl) methyl sulfide was carried out at $-20\,^{\circ}C$ while for the other two sulfides at $-10\,^{\circ}C$.

The used complex can be reconstituted on the silica by the addition of hydrogen peroxide and then the ligand to the isolated and dried residues of a previous reaction; followed by the addition of a 3 M aqueous solution of sulfuric acid as in the protocol for preparing the complexes. The reconstituted reagents is then dried in presence of phosphorus pentoxide before use. The reconstituted complex (I) was used with success for the oxidation of benzyl phenyl sulfide affording the sulfoxide in 95% isolated yield.

3. Conclusions

The results presented on this paper demonstrated that molybdenum (VI) oxodiperoxo complexes such as shown in Fig. 1 when coated to silica gel can be used for the efficient selective preparation of sulfoxides. Sulfones can be prepared using the complexes uncoated to silica gel. The excellent chemoselectivity of these complexes towards the sulfur group, the high yields obtained and the wide application associated with the easy manipulation makes them a good choice for the use in the oxidation of functional sulfides.

4. Experimental

4.1. General

IR spectra were recorded on a BOMEM MB-Series spectrometer and are reported in wavenumbers (cm^{-1}).

UV–Vis spectra were obtained on a Hitachi instrument in a silica cuvette. Samples for UV–Vis were dissolved in distilled water.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 9.4 and 4.7 T DRX-400 MHz and ARX 200 MHz spectrometer, respectively, in a 5 mm probe at 303 K. Samples were dissolved in $CDCl_3$ and TMS was used as an internal standard. All hydrogen spectra were obtained with spectral width 8117 Hz, pulse width 10.5 μs, acquisition time 4.0 s, relaxation delay 1.0 s and the number of scan adjusted to have a good signal to noise ratio (8–32 scans). The spectra were processed using zero filling and Gaussian window function (LB=−2 and GB=2) when necessary. All ^{13}C NMR spectra were recorded using PENDANT pulse sequence with 1.2 s acquisition time, pulse width 10.0 μs, sweep width 13513 Hz and relaxation delay 1.5 s. The spectra were processed using exponential multiplications with LB=1.0 Hz.

All signals were expressed as ppm downfield from tetramethylsilane used as an internal standard (δ value). Splitting patterns are designated as s (singlet), d (doublet), t (triplet), dt (double triplet), q (quartet), dq (double quartet), m (multiplet).

Microanalysis were recorded on a Fisons Instruments, model EA 1108—CHNS–O.

Melting points were measured using a Microquímica apparatus model MQAPF-301 and are uncorrected.

The reactions were monitored by thin layer chromatography (TLC) using precoated silica gel Merck Kiesegel $60F_{254}$ (10–40 μ) plates and developed in the indicated solvent systems.

The silica gel used in the oxidation reactions as solid support for the complexes was Davisil (200–425 mesh particle size and 150 Å pore size).

The sulfides (1)–(3), (13) and (19) were purchased from Aldrich (Milwaukee, USA). Sulfides (4)–(9) were donated by the group of Dr Liliana Marzorati while sulfides (20)–(24) by the group of Prof Hans Viertler (Instituto de Química, Universidade de S. Paulo, São Paulo, SP, Brazil). The sulfides (25)–(27) were donated to us by the group of Dr Miguel J. Dabdoub Paz (Departamento de Química, Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, Universidade de São Paulo, Ribeirão Preto, SP). All the above cited sulfides were prepared in accordance with the literature work.[6–9] The sulfide (15) was prepared by the reaction of sulfide (13) with diazomethane while sulfides (16) and (18) were prepared in accordance with the works of Burgess and Henderson.[10,11]

Methanol and acetonitrile (HPLC grade, Mallinckrodt Baker, St. Louis, Missouri, USA) were used as received. THF was refluxed with copper (I) chloride, dried and distilled under KOH and stored over sodium metal.

Sulfides and sulfoxides were purified by column chromatography on Silica Gel 60 (70–230 Mesh—ASTM), available from Merck (Darmstadt, Germany).

Organic solutions were concentrated under vacuum on Buchi and Fisaton, evaporator at 20–40 mmHg.

GC analysis was carried out using a GC—17 instrument with a capillary column DB-5 and hydrogen as a carrying gas. Samples for GC were dissolved in ethyl acetate.

4.2. General procedure for the preparation of molybdenum (VI) oxodiperoxo complexes

Molybdenum (VI) oxide was added in portions to an aqueous hydroperoxide solution (30% v/v), at 0°C, under constant stirring. After most of the molybdenum oxide had dissolved, the yellow solution was treated with 1 equiv. of the ligand.

The mixture was stirred for 1 h at room temperature, and then, a 3 M aqueous solution of sulfuric acid was added. A yellow precipitate formed and then filtered through a sintered glass funnel; the solid residue was washed with a solution 1:1 v/v of petroleum ether/2-propanol and concentrated in vacuum. The complexes were recrystallized in 2-propanol at 70°C and dried in a vacuum oven at 60°C in presence of phosphorus pentoxide for 2 days.

4.2.1. Molybdenum (VI) (oxo diperoxo)-pyridine-*N*-oxide (I). Molybdenum (VI) oxide (2.06 g; 19 mmol); 30% v/v aqueous solution hydroperoxide (18 mL), pyridine *N*-oxide (2.03 g; 19 mmol), 3 M aqueous solution of sulfuric acid (5 mL). Yield: 3.21 g (87.2%). Yellow powder; UV (λ_{max}, nm): 210, 256; IR (ν_{max}, KBr, cm^{-1}): 3346, 3118, 1472, 1203, 967, 837, 583, 535. Calcd for [MoO_5(OPy)(H_2O)]: %C, 20.76; %H, 2.42; %N, 4.84. Found: %C, 20.81; %H, 2.30; %N, 4.92.

4.2.2. Molybdenum (VI) (oxo diperoxo)-pyrazole (II). Molybdenum (VI) oxide; (1.48 g; 13 mmol); 30% v/v aqueous solution hydroperoxide (12 mL); pyrazole (1.46 g; 13 mmol); 3 M aqueous solution of sulfuric acid H_2SO_4 (5 mL). Yield: 1.65 g (73%); Yellow powder; UV (λ_{max}, nm): 235, 252; IR (ν_{max}, KBr, cm^{-1}): 3318, 955, 871, 610, 518. Calcd for [MoO_5(Pyrazole) (H_2O)]: %C, 13.74; %H, 2.29; %N, 10.69. Found: %C, 13.85; %H, 2.33; %N, 10.57.

4.2.3. General procedure for coating the molybdenum complexes on silica gel on a 40% ratio. Silica gel (1.15 g) was refluxed in anhydrous THF (10 mL) for 1 h at 85°C. Then the solubilized complex (0.80 g) in hot methanol (30 mL) was slowly added to the silica under reflux. The reaction mixture was kept under reflux for a further 3 h. After cooling, it was concentrated in vacuum and dried in a vacuo oven at 60°C for one day. Coated Complex (I): IR (ν_{max}, KBr, cm^{-1}): 3447, 3118, 1474, 1212, 833. Coated complex (II): IR (ν_{max}, KBr, cm^{-1}): 3423, 1619, 1464, 1208, 960, 850, 529.

4.2.4. Methyl phenyl sulfoxide: a typical protocol. To a stirred solution at −10°C of methyl phenyl sulfide (1) (50 mg; 0.402 mmol) in methanol/acetonitrile (1:5 v/v) (2.5 mL), the coated complex (I) (290 mg; 0.402 mmol), was added in portions using a solid addition flask over a 20 min period. After addition, the reaction was warmed to room temperature and stirred for 23 h The reaction was followed by TLC and GC. Then, the solids were removed using a sintered glass funnel. A saturated solution of sodium hydrogen carbonate (10 mL) was added to the filtrate and then it was extracted with dichlorometane (3×10 mL). The organic phase was separated, dried over anhydrous sodium sulfate and concentrated in vacuum. The sulfoxide was isolated as a colorless oil in 97% yield after purifying by column chromatography using hexane/ethyl acetate (1:1 v/v) as solvent. IR (ν_{max}, KBr, cm^{-1}): 3004, 2922, 1647, 1431, 1037, 957, 751, 690, 530. ^{1}H NMR (400 MHz; $CDCl_3$, δ): 2.73 (s, 3H); 7.49–7.57 (m, 3H); 7.61–7.68 (m, 2H). ^{13}C NMR (50 MHz; $CDCl_3$, δ): 43.35; 122.90; 128.78; 130.45; 145.13. Calcd for C_7H_8OS: %C, 59.91; %H, 5.70; %S, 22.82. Found: %C, 59.98; %H, 5.88; %S, 22.73.

4.2.5. 4-(Bromophenyl) methyl sulfoxide. Isolated as a colorless solid: mp 74–76°C; IR (ν_{max}, KBr, cm^{-1}): 2993, 2906, 1649, 1557, 1039, 942, 811, 680, 505. ^{1}H NMR (400 MHz; $CDCl_3$, δ): 2.72 (s,3H); 7.51 (d, 1H, J=8.7 Hz); 7.68 (d, 1H, J=8.7 Hz). ^{13}C NMR (50 MHz; $CDCl_3$, δ): 43.74; 124.37; 124.60; 149.37; 153.16. Calcd for C_7H_7BrOS: %C, 38.33; %H, 3.19; %S, 14.60. Found: %C, 38.54; %H, 3.08; %S, 14.41.

4.2.6. Benzyl phenyl sulfoxide. Isolated as a white solid: mp 121–122°C; IR (ν_{max}, KBr, cm^{-1}): 2990, 1443, 1030, 743, 684, 480. ^{1}H NMR (400 MHz; $CDCl_3$, δ): 3.98 (d, 1H, J=12.6 Hz); 4.08 (d, 1H, J=12.6 Hz); 6.95–7.00 (m, 2H);

7.20–7.31 (m, 3H); 7.35–7.50 (m, 5H). ^{13}C NMR (50 MHz; $CDCl_3$, δ): 63.39; 124.26; 128.09; 128.29; 128.68; 128.99; 130.20; 130.99; 142.63. Calcd for $C_{13}H_{12}OS$: %C, 72.12; %H, 5.54; %S, 14.79.Found: %C, 72.32; %H, 5.57; %S, 14.93.

4.2.7. 1-Phenylsulfinyl-2-propanone. Isolated as a white solid: mp 74–76°C; IR (ν_{max}, KBr, cm^{-1}): 3056, 2907, 1711, 1352, 1034, 739. ^{1}H NMR (400 MHz; $CDCl_3$, δ): 2.24 (s, 3H); 3.79 (d, 1H, J=13.7 Hz); 3.86 (d, 1H, J=13.7 Hz); 7.52–7.58 (m, 3H); 7.64–7.68 (m, 2H). Calcd for $C_9H_{10}O_2S$: %C, 59.34; %H, 5.49; %S, 17.58. Found: %C, 59.54; %H, 5.41; %S, 17.30.

4.2.8. 1-(Phenylsulfinyl)acetophenone. Isolated as a yellow solid: mp 78–80°C; IR (ν_{max}, KBr, cm^{-1}): 3059, 2912, 1675, 1081, 1045, 749. ^{1}H NMR (400 MHz; $CDCl_3$, δ): 4.29 (d, 1H, J=14.2 Hz); 4.56 (d, 1H, J=14.2 Hz); 7.42–7.53 (m, 5H); 7.56–7.62 (m, 1H); 7.67–7.72 (m, 2H); 7.85–7.90 (m, 2H). ^{13}C NMR (50 MHz; $CDCl_3$, δ): 65.72; 124.03; 128.56; 129.13; 131.33; 133.91; 135.70; 143.02; 191.20. Calcd for $C_{14}H_{12}O_2S$: %C, 68.85; %H, 4.92; %S, 13.11. Found: %C, 68.94; %H, 4.86; %S, 13.03.

4.2.9. 1-Phenylsulfinyl-4-methyl acetophenone. Isolated as a white solid: mp 62–64°C; IR (ν_{max}, KBr, cm^{-1}): 2947, 2835, 1657, 1025, 733. ^{1}H NMR (400 MHz; $CDCl_3$, δ): 2.41 (s, 3H); 4.26 (d, 1H, J=14.1 Hz); 4.55 (d, 1H, J=14.1 Hz); 7.22–7.27 (m, 2H); 7.47–7.52 (m, 3H); 7.67–7.71 (m, 2H); 7.75–7.80 (m, 2H). ^{13}C NMR (50 MHz; $CDCl_3$, δ): 21.65; 41.14; 126.98; 128.80; 129.01; 129.36; 130.42; 132.95; 134.98; 144.37; 193.71. Calcd for $C_{15}H_{14}O_2S$: %C, 69.76; %H, 5.42; %S, 12.40. Found: %C, 69.86; %H, 5.57; %S, 12.50.

4.2.10. 1-Ethylsulfinyl-4-methyl acetophenone. Isolated as a yellow solid: mp 54–55°C; IR (ν_{max}, KBr, cm^{-1}): 2928, 1954, 1670, 1605, 1410, 1014, 812, 447. ^{1}H NMR (400 MHz; $CDCl_3$, δ): 1.40 (t, 3H, J=7.5 Hz); 2.43 (s, 3H); 2.83 (dq, 1H, J=7.5, 13.3 Hz); 2.99 (dq, 1H, J=7.5, 13.3 Hz); 4.25 (d, 1H, J=14.2 Hz); 4.42 (d, 1H, J=14.2 Hz); 7.25–7.33 (m, 2H); 7.84–7.90 (m, 2H). ^{13}C NMR (50 MHz; $CDCl_3$, δ): 14.11; 21.55; 26.21; 36.66; 128.85; 129.18; 129.26; 132.78; 143.94; 194.12. Calcd for $C_{11}H_{14}O_2S$: %C, 62.86; %H, 6.67; %S, 15.23. Found: %C, 62.94; %H, 6.57; %S, 15.26.

4.2.11. 1-Methylsulfinyl-2-propanone. Isolated as a yellow solid: mp 59–60°C; IR (ν_{max}, KBr, cm^{-1}): 2974, 2922, 1725, 1093, 1032, 511. ^{1}H NMR (400 MHz; $CDCl_3$, δ): 2.27 (s, 3H); 3.83 (d, 1H, J=13.7 Hz); 3.92 (d, 1H, J=13.7 Hz); 6.21 (s, 3H). Calcd for $C_4H_8O_2S$: %C, 40.00; %H, 6.67; %S, 26.67. Found: %C, 40.10; %H, 6.70; %S, 26.50.

4.2.12. 1-Ethylsulfinyl-2-propanone. Isolated as a white solid: mp 44–46°C; IR (ν_{max}, KBr, cm^{-1}): 2930, 1713, 1451, 1177, 1022, 754, 610. ^{1}H NMR (400 MHz; $CDCl_3$, δ): 1.33 (t, 3H); 2.75 (m, 2H); 2.29 (s, 3H); 3.61 (d, 1H, J=13.6 Hz); 3.73 (d, 1H, J=13.6 Hz). ^{13}C NMR (50 MHz; $CDCl_3$, δ): 14.20; 26.09; 27.62; 41.63; 203.87. Calcd for $C_5H_{10}O_2S$: %C, 44.77; %H, 7.46; %S, 23.88. Found: %C, 44.86; %H, 7.57; %S, 23.93.

4.2.13. 1-Phenylsulfinyl-3,3-dimethyl-2-butanone. Isolated as a yellow oil. IR (ν_{max}, KBr, cm^{-1}): 2965, 1705, 1580, 1470, 1060, 741, 690, 481. ^{1}H NMR (400 MHz; $CDCl_3$, δ): 1.05 (s, 9H); 3.85 (d, 1H, J=15.3 Hz); 4.21 (d, 1H, J=15.3 Hz); 7.20 (m, 5H). ^{13}C NMR (50 MHz; $CDCl_3$, δ): 26.60; 42.34; 65.28; 127.55; 129.05; 130.22; 135.54; 209.28. Calcd for $C_{12}H_{16}O_2S$: %C, 64.28; %H, 7.14; %S, 14.28. Found: %C, 64.32; %H, 7.16; %S, 14.26.

4.2.14. 3-Phenylsulfinyl-2-butanone. Isolated as a yellow oil. IR (ν_{max}, KBr, cm^{-1}): 3063, 2928, 1709, 1580, 1443, 1157, 1060, 746, 488. ^{1}H NMR (400 MHz; $CDCl_3$, δ): diastereoisomer A: 1.36 (d, 3H, J=7.1 Hz); 2.19 (s, 3H); 3.71 (q, 1H, J=7.1 Hz); 7.49–7.56 (m, 5H); diastereoisomer B: 1.31 (d, 3H, J=7.1 Hz); 2.24 (s, 3H); 3.80 (q, 1H, J=7.1 Hz); 7.56–7.73 (m, 5H). ^{13}C NMR (50 MHz; $CDCl_3$, δ): 14.14; 26.34; 51.80; 127.92; 129.00; 132.58; 132.71; 205.18. Calcd for $C_{10}H_{12}O_2S$: %C, 61.22; %H, 6.12; %S, 16.32. Found: %C, 61.30; %H, 6.08; %S, 16.30.

4.2.15. 2-(Phenylsulfinyl)cyclopentanone. Isolated as a brown oil. IR (ν_{max}, KBr, cm^{-1}): 3059, 2963, 2897, 1738, 1443, 1083, 1043, 825, 750, 694. ^{1}H NMR (400 MHz; $CDCl_3$, δ): diastereoisomer A: 1.86–1.98 (m, 4H); 2.26–2.44 (m, 2H); 3.58 (t, 1H, J=3.8 Hz); 7.25–7.33 (m, 3H); 7.45–7.48 (m, 2H); diastereoisomer B: 1.99–2.20 (m, 4H); 2.69–2.98 (m, 2H); 3.67 (t, 1H, J=3.8 Hz); 7.25–7.33 (m, 3H); 7.45–7.48 (m, 2H). ^{13}C NMR (50 MHz; $CDCl_3$, δ): 22.14; 31.88; 50.13; 58.40; 128.56; 129.01; 130.01; 131.55; 137.31; 217.80. Calcd for $C_{11}H_{12}O_2S$: %C, 63.46; %H, 5.76; %S, 15.38. Found: %C, 63.45; %H, 5.70; %S, 15.41.

4.2.16. Phenylsulfinyl acetic acid. Isolated as a white solid: mp 63–65°C; IR (ν_{max}, KBr, cm^{-1}): 3279, 2965, 2889, 1723, 1421, 1076, 1040, 825, 750, 694. ^{1}H NMR (400 MHz; $CDCl_3$, δ): 3.78 (d,1H, J=13.6 Hz); 3.90 (d, 1H, J=13.6 Hz); 7.52–7.58 (m, 3H); 7.66–7.72 (m, 2H). ^{13}C NMR (50 MHz; $CDCl_3$, δ): 36.65; 127.29; 129.20; 130.14; 134.52; 175.91. Calcd for $C_8H_8O_3S$: %C, 52.11; %H, 4.34; %S, 17.37. Found: %C, 52.20; %H, 4.30; %S, 17.41.

4.2.17. Phenylsulfinyl acrylic acid. Isolated as a white solid: mp 102–104°C; IR (ν_{max}, KBr, cm^{-1}): 3458, 2972, 2891, 1725, 1612, 1423, 1060, 1013, 825, 750, 694. ^{1}H NMR (400 MHz; $CDCl_3$, δ): 5.62 (d, 1H, J=15.0 Hz); 7.90 (d, 1H, J=15.0 Hz); 7.20–7.25 (m, 1H); 7.35–7.44 (m, 2H); 7.47–7.52 (m, 2H). ^{13}C NMR (50 MHz; $CDCl_3$, δ): 112.44; 128.49; 129.48; 131.23; 135.93; 152.98; 170.83. Calcd for $C_9H_8O_3S$: %C, 55.10; %H, 4.08; %S, 16.32. Found: %C, 55.00; %H, 4.18; %S, 16.41.

4.2.18. Methyl 2-(phenylsulfinyl)acetate. Isolated as a yellow oil. IR (ν_{max}, KBr, cm^{-1}): 2927, 1736, 1444, 1045, 749, 691, 487. ^{1}H NMR (400 MHz; $CDCl_3$, δ): 3.72 (s, 3H); 3.68 (d, 1H, J=13.6 Hz); 3.86 (d, 1H, J=13.6 Hz); 7.52–7.59 (m, 3H); 7.66–7.73 (m, 2H). Calcd for $C_9H_{10}O_3S$: %C, 54.54; %H, 5.05; %S, 16.16. Found: %C, 54.45; %H, 5.16; %S, 16.26.

4.2.19. Ethyl 2-(phenylsulfinyl)butanoate. Isolated as a yellow oil. IR (ν_{max}, KBr, cm^{-1}): 2984, 1734, 1454, 1160, 1079, 1048, 854, 755. ^{1}H NMR (400 MHz; $CDCl_3$, δ): 1.21

(t, 3H, J=7.1 Hz); 1.49 (s, 6H); 4.11 (q, 2H, J=7.12 Hz); 7.28–7.40 (m, 3H); 7.45–7.50 (m, 2H). ^{13}C NMR (50 MHz; $CDCl_3$, δ): 13.99; 25.84; 50.84; 61.00; 128.56; 129.25; 131.52; 136.72; 173.76. Calcd for $C_{12}H_{16}O_3S$: %C, 60.00; %H, 6.67; %S, 13.33. Found: %C, 60.10; %H, 6.57; %S, 13.26.

4.2.20. Ethyl (phenylsulfinyl)ethanoate. Isolated as a yellow oil. IR (ν_{max}, KBr, cm^{-1}): 2982, 1734, 1582, 1476, 1028, 743, 479. ^{1}H NMR (400 MHz; $CDCl_3$, δ): 1.21 (t, 3H, J=7.2 Hz); 3.68 (d, 1H, J=13.6 Hz); 3.85 (d, 1H, J=13.6 Hz); 4.15 (q, 2H, J=7.2 Hz); 7.52–7.57 (m, 3H); 7.66–7.73 (m, 2H). ^{13}C NMR (50 MHz; $CDCl_3$, δ): 13.99; 36.65; 61.42; 126.87; 128.93; 129.94; 134.96; 169.56. Calcd for $C_{10}H_{12}O_3S$: %C, 56.60; %H, 5.66; %S, 15.09. Found: %C, 56.54; %H, 5.59; %S, 15.00.

4.2.21. Ethyl 2-(phenylsulfinyl)propanoate. Isolated as a yellow oil. IR (ν_{max}, KBr, cm^{-1}): 1982, 1730, 1455, 1161, 1053, 754, 695. ^{1}H NMR (400 MHz; $CDCl_3$, δ): diastereoisomer A: 1.20 (t, 3H, J=7.1 Hz); 1.48 (d, 3H, J=7.2 Hz); 3.81 (q, 2H, J=7.1 Hz); 4.13 (d, 1H, J=7.2 Hz); 7.50–7.55 (m, 3H); 7.58–7.60 (m, 2H); diastereoisomer B: 1.20 (t, 3H, J=7.1 Hz); 1.48 (d, 3H, J=7.2 Hz); 3.81 (q, 2H, J=7.1 Hz); 4.11 (d, 1H, J=7.2 Hz); 7.50–7.55 (m, 3H); 7.58–7.60 (m, 2H). ^{13}C NMR (50 MHz; $CDCl_3$, δ): 14.00; 17.32; 45.15; 61.00; 127.88; 128.83; 129.05; 132.98; 172.43. Calcd for $C_{11}H_{14}O_3S$: %C, 58.40; %H, 6.19; %S, 14.16. Found: %C, 58.45; %H, 6.16; %S, 14.26.

4.2.22. Allyl methyl sulfoxide. Isolated as a brown oil. IR (ν_{max}, KBr, cm^{-1}): 3088, 3001, 2925, 1649, 1431, 1049, 951, 743. ^{1}H NMR (400 MHz; $CDCl_3$, δ): 2.01 (s, 3H); 3.09 (dt, 2H, J=7.1, 1.1 Hz); 5.08 (dq, 1H, J=1.4, 17.1 Hz); 5.09 (dq, 1H, J=1.1, 10.2 Hz); 5.76 (ddt, 1H, J=7.1, 10.2, 17.1 Hz). ^{13}C NMR (50 MHz; $CDCl_3$, δ): 14.28; 36.86; 116.88; 134.08. Calcd for C_4H_8OS: %C, 46.08; %H, 7.68; %S, 30.72. Found: %C, 46.10; %H, 7.66; %S, 30.76.

4.2.23. 3-Methyl-3-butenyl benzyl sulfoxide. Isolated as a white solid: mp 48–50°C; IR (ν_{max}, KBr, cm^{-1}): 3077, 2919, 1648, 1445, 1036, 894, 758, 703, 470. ^{1}H NMR (400 MHz; $CDCl_3$, δ): 1.72–1.73 (m, 3H); 2.41–2.48 (m, 2H); 2.66–2.74 (m, 2H); 3.96 (d, 1H, J=12.9 Hz); 4.06 (d, 1H, J=12.9 Hz); 4.72–4.73 (m, 1H); 4.80–4.82 (m, 1H); 7.25–7.39 (m, 5H). ^{13}C NMR (50 MHz; $CDCl_3$, δ): 22.40; 30.16; 49.04; 58.40; 112.00; 128.40; 129.02; 129.98; 130.00; 142.46. Calcd for $C_{12}H_{16}OS$: %C, 69.23; %H, 7.69; %S, 15.38. Found: %C, 69.20; %H, 7.65; %S, 15.41.

4.2.24. 5-Phenyl-4-pentenyl benzyl sulfoxide. Isolated as a yellow solid: mp 49–51°C; IR (ν_{max}, KBr, cm^{-1}): 3029, 2927, 1603, 1490, 1123, 1037, 975, 752, 701, 490. ^{1}H NMR (400 MHz; $CDCl_3$, δ): 1.56–1.70 (m, 2H); 1.90–2.10 (m, 2H); 2.22–2.40 (m, 2H); 3.94 (d, 1H, J=12.9 Hz); 4.04 (d, 1H, J=12.9 Hz); 6.12 (dt, 1H, J=7.0, 15.8 Hz); 6.40 (dt, 1H, J=1.4, 15.8 Hz); 7.22–7.40 (m, 10H). ^{13}C NMR (50 MHz; $CDCl_3$, δ): 20.32; 30.65; 36.57; 52.37; 124.08; 127.19; 127.60; 127.75; 128.99; 129.08; 129.16; 129.29; 132.57; 137.09. Calcd for $C_{18}H_{20}OS$: %C, 76.05; %H, 7.04; %S, 11.27. Found: %C, 76.00; %H, 7.08; %S, 11.30.

4.2.25. 2-Cyclopentenyl benzyl sulfoxide. Isolated as a white solid: mp 58–60°C; IR (ν_{max}, KBr, cm^{-1}): 2928, 2840, 1650, 1449, 1027, 971, 767, 695, 479. ^{1}H NMR (400 MHz; $CDCl_3$, δ): 1.80–1.89 (m, 2H); 2.16–2.21 (m, 2H); 2.21–2.30 (m, 2H); 2.50–2.53 (m, 2H); 2.65–2.78 (m, 2H); 3.95 (d, 1H, J=12.8 Hz); 4.05 (d, 1H, J=12.8 Hz); 5.36–5.38 (m, 1H); 7.26–7.41 (m, 5H). ^{13}C NMR (50 MHz; $CDCl_3$, δ): 23.34; 23.96; 32.46; 35.04; 49.25; 58.37; 125.72; 128.39; 129.01; 129.80; 130.02; 141.06. Calcd for $C_{14}H_{18}OS$: %C, 71.79; %H, 7.69; %S, 13.67. Found: %C, 71.86; %H, 7.66; %S, 13.50.

4.2.26. 4-Pentenyl benzyl sulfoxide. Isolated as a yellow solid: mp 46–48°C; IR (ν_{max}, KBr, cm^{-1}): 3076, 2920, 2850, 1633, 1493, 1450, 1024, 913, 768, 699, 483, 388. ^{1}H NMR (400 MHz; $CDCl_3$, δ): 1.80–1.92 (m, 2H); 2.10–2.25 (m, 2H); 2.54–2.61 (m, 2H); 3.94 (d, 1H, J=12.9 Hz); 4.03 (d, 1H, J=12.9 Hz); 4.99 (dq, 1H, J=1.2, 10.3 Hz); 5.01 (dq, 1H, J=1.6, 17.0 Hz); 5.73 (ddt, 1H, J=6.7, 10.3, 17.0 Hz); 7.26–7.31 (m, 2H); 7.33–7.41 (m, 3H). ^{13}C NMR (50 MHz; $CDCl_3$, δ): 21.67; 32.62; 50.22; 58.45; 116.10; 119.09; 128.39; 129.01; 130.01; 130.55; 136.82. Calcd for $C_{12}H_{16}OS$: %C, 69.23; %H, 7.69; %S, 15.38. Found: %C, 69.20; %H, 7.65; %S, 15.41.

4.2.27. 2-Cyclohexenyl benzyl sulfoxide. Isolated as a white solid: mp 66–68°C; IR (ν_{max}, KBr, cm^{-1}): 3064, 2931, 2858, 1637, 1490, 1452, 1033, 912, 768, 699, 483, 388. ^{1}H NMR (400 MHz; $CDCl_3$, δ): 1.48–1.63 (m, 4H); 1.85–1.89 (m, 2H); 1.95–1.99 (m, 2H); 2.15–2.19 (m, 1H); 2.47–2.51 (m, 1H); 2.63–2.70 (m, 2H); 3.95 (d, 1H, J=12.8 Hz); 4.03 (d, 1H, J=12.8 Hz); 5.40–5.42 (m, 1H); 7.25–7.38 (m, 5H). ^{13}C NMR (50 MHz; $CDCl_3$, δ): 22.25; 22.80; 25.21; 28.29; 30.45; 49.38; 58.30; 123.41; 128.36; 128.99; 129.70; 130.03; 134.53. Calcd for $C_{15}H_{20}OS$: %C, 72.58; %H, 8.06; %S, 12.90. Found: %C, 72.59; %H, 8.08; %S, 12.98.

4.2.28. (*Z*)-1-Phenylsulfinyl-2-hepthylethene. Isolated as a yellow oil. IR (ν_{max}, KBr, cm^{-1}): 2927, 2860, 1453, 1038, 738. ^{1}H NMR (400 MHz; $CDCl_3$, δ): 0.86–0.91 (m, 3H); 1.23–1.36 (m, 10H); 2.52–2.66 (m, 2H); 6.18–6.24 (m, 1H); 6.62 (dt, 1H, J=6.8, 15.5 Hz); 7.45–7.52 (m, 5H). ^{13}C NMR (50 MHz; $CDCl_3$, δ): 14.11; 22.66; 29.06; 29.14; 29.21; 31.86; 122.57; 128.76; 128.95; 129.95; 133.78; 136.62. Calcd for $C_{15}H_{22}OS$: %C, 72.00; %H, 8.80; %S, 12.80. Found: %C, 72.10; %H, 8.85; %S, 12.78.

4.2.29. (*Z*)-1-Phenylsulfinyl-2-hexylethene. Isolated as a white oil. IR (ν_{max}, KBr, cm^{-1}): 2928, 2862, 1455, 1040, 741. ^{1}H NMR (400 MHz; $CDCl_3$, δ): 0.89 (t, 3H, J=7.0 Hz); 1.25–1.36 (m, 8H); 2.25 (dq, 2H, J=1.4, 7.3 Hz); 5.82 (dt, 1H, J=7.3, 9.2 Hz); 6.18 (dt, 1H, J=1.4, 9.2 Hz); 7.25–7.35 (m, 5H). ^{13}C NMR (50 MHz; $CDCl_3$, δ): 14.11; 22.63; 28.78; 28.95; 29.13; 33.09; 122.48; 128.65; 128.90; 129.03; 133.72; 136.55. Calcd for $C_{14}H_{20}OS$: %C, 71.18; %H, 8.47; %S, 13.56. Found: %C, 71.10; %H, 8.57; %S, 13.50.

4.2.30. (*Z*)-1-Phenylsulfinyl-2-phenylethene. Isolated as a yellow oil. IR (ν_{max}, KBr, cm^{-1}): 3050, 2888, 1483, 1033, 747. ^{1}H NMR (400 MHz; $CDCl_3$, δ): 6.49 (d, 1H, J=10.7 Hz); 6.59 (d, 1H, J=10.7 Hz); 7.13–7.52 (m, 10H).

Calcd for $C_{14}H_{12}OS$: %C, 73.68; %H, 5.26; %S, 14.03. Found: %C, 73.65; %H, 5.30; %S, 14.13.

4.3. Macroscale oxidation: a typical protocol

4.3.1. 4-(Bromophenyl) methyl sulfoxide. To a stirred solution at −20°C of 4-(bromophenyl) methyl sulfide (2) (8.13 g; 40 mmol) in methanol/acetonitrile (1:5 v/v) (650 mL), the coated complex (I) (28.78 g; 40 mmol), was added in portions using a solid addition flask over a 20 min period. After addition, the reaction was warmed to room temperature and stirred for 13 h. The reaction was followed by TLC and GC. Then, the solids were removed using a sintered glass funnel. A saturated solution of sodium hydrogen carbonate (500 mL) was added to the filtrate and then it was extracted with dichlorometane (3×500 mL). The organic phase was separated, dried over anhydrous sodium sulfate and concentrated in vacuum. The sulfoxide was isolated as a colorless solid in 90% yield.

Acknowledgements

We thank CNPq, CAPES and Fapesp for financial support and for grants.

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