



Development of catalytic sulfoxidation reactions for obtaining sulfonyl- and sulfinyl-based pincer type ligands

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Introduction

Sulfinyl and sulfonyl groups can be found in many different compounds, for example in biologically relevant derivatives, fine chemicals, pharmaceuticals, ligands in catalyst structures, material chemistry, etc.[1] The design and characterization of new compounds containing sulfoxide and/or sulfone moieties, in particular their use in pincer type ligands, represents a topic of importance in our research group as well.[2,3] In the last few years, pincer type ligands that contained such moieties were designed, synthesized then used to obtain *p* block element containing derivatives.[2] The scientific progress to the design and synthesis of such derivatives made us work on finding a process for the synthesis of sulfoxides and sulfones that is easy, cheap and more sustainable. Furthermore, it is of interest to find a system that can selectively lead to either the sulfoxide or the sulfone.

The oxidation of sulfides is a widely employed synthetic route to access sulfoxides and sulfones, utilizing various oxidizing agents such as *meta*-chloro-*perbenzoic* acid (*m*CPBA), HIO₄, oxone, H₂O₂ as oxidizing agents.

In the present work three previously described compounds, decavanadate-based materials were used as catalysts to test their activity in sulfide oxidation reactions: diethylenediammonium decavanadatetratehydrate (NH₄)₂(H₂en)₂[V₁₀O₂₈]·4H₂O (Cat.1), triethylenediammonium decavanadate hexahydrated (H₂en)₃[V₁₀O₂₈]·6H₂O (Cat.2) and tetraammonium decaaqualithium decavanadate [Li₂(H₂O)10](V₁₀O₂₈)(NH₄)₄ (Cat.3). [4]

Table 1. Experimental details, conversion and selectivity data for the oxidation reactions of compound 1

Catalyst	Solvent	Conversion* (%)	Selectivity*(%)	
			2	3
none ^a	MeOH	13	100	0
Cat.1 ^b	MeOH	0	0	0
Cat.1	MeOH	100	64	36
	EG	100	27	73
	H ₂ O	52	68	32
	EtOH	100	16	84
	<i>i</i> -PrOH	100	42	58
Cat.2	MeOH	100	22	78
	EG	81	28	72
	H ₂ O	100	11	89
	EtOH	100	24	76
	<i>i</i> -PrOH	100	32	68
Cat.3	MeOH	100	13	84
	EG	52	53	47
	H ₂ O	100	34	66
	EtOH	100	10	90
	<i>i</i> -PrOH	100	40	60

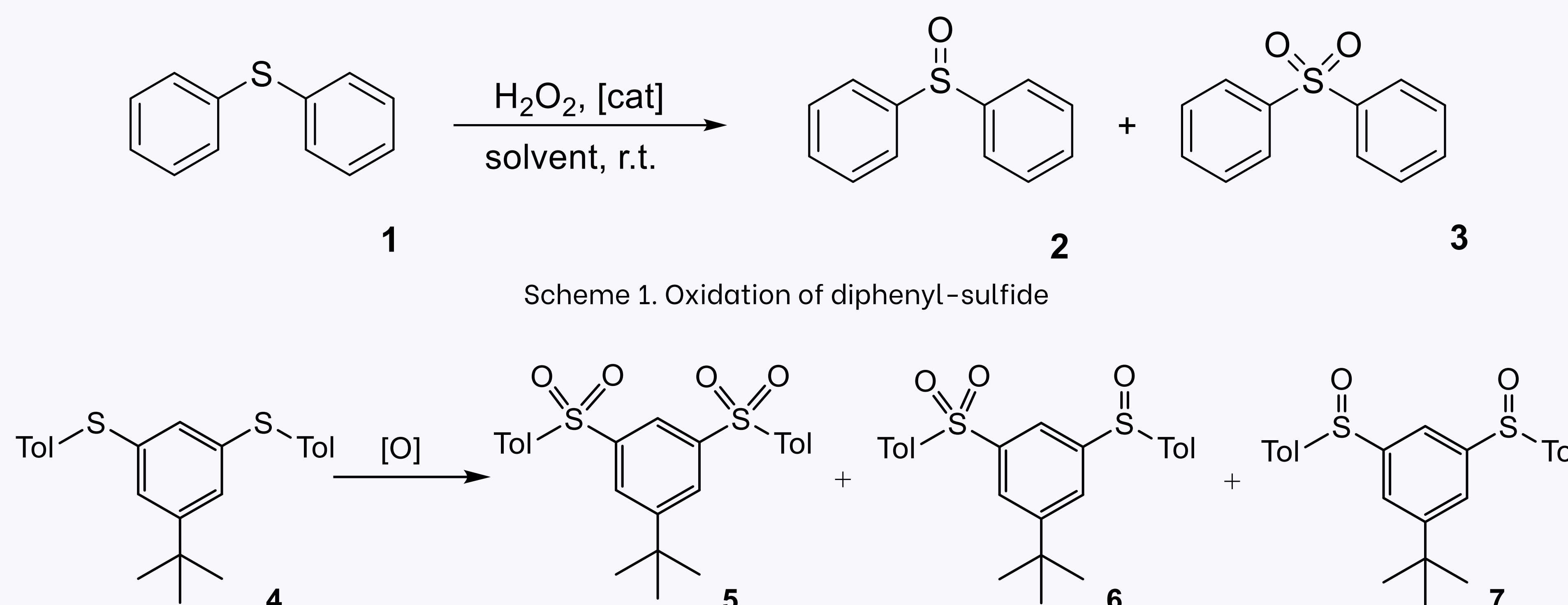
Reaction conditions: diphenyl-sulfide (0.27 mmol), solvent (3 mL), H₂O₂, catalyst (1.5 mol%), room temperature, 2h. ^ano catalyst was used. ^bno H₂O₂ was used. *without separation from reaction mixture, according to ¹H NMR measurements. Methanol (MeOH), ethylene-glycol (EG), water (H₂O), ethanol (EtOH), 2-propanol (*i*-PrOH).

References

- [1] I. Fernández, N. Khair, *Chem. Rev.* 103, 3651. (2003). [2] N. Deak, D. Madec, G. Nemes, *Eur. J. Inorg. Chem.*, 2769. (2020). [3] N. Deak, O. Thillaye du Boullay, S. Mallet-Ladeira, I.T. Moraru, D. Madec, G. Nemes, *Eur. J. Inorg. Chem.*, 3729. (2020). [4] N. Deak, M. Idboumlik, A. Soran, M. Lachkar, B. El Bali, G.Nemes, *Studia UBB Chemia*, LXIX, 3, 7. (2024).

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Scheme 2. Oxidation of 1,3-(para-tolyl sulfide)-5-tertbutyl-benzene

Results and discussions

For the catalytic tests, several criteria were established: reactions were conducted at r.t. (22±2°C), aiming for the shortest possible reaction times. We also prioritized the use of an easily handled oxidant and accessible, low-toxicity solvents. The selection of solvents was initially guided by the principles of green and sustainable chemistry, emphasizing safety, health, and environmental considerations. The catalytic performance of Cat.1-3 under the selected conditions was largely comparable. (Table 1)

In the second part of our study the aim was to investigate and compare various methods for the oxidation of bis-thioether **4**, where we observed that the catalytic oxidation efficiency of Cat.1-3 was highly dependent on the reaction solvent. No substrate conversion was detected in either MeOH or EG with any of the catalysts. However, complete conversion was achieved in H₂O and *i*-PrOH using catalysts Cat.1 and Cat.3 (Table 2).

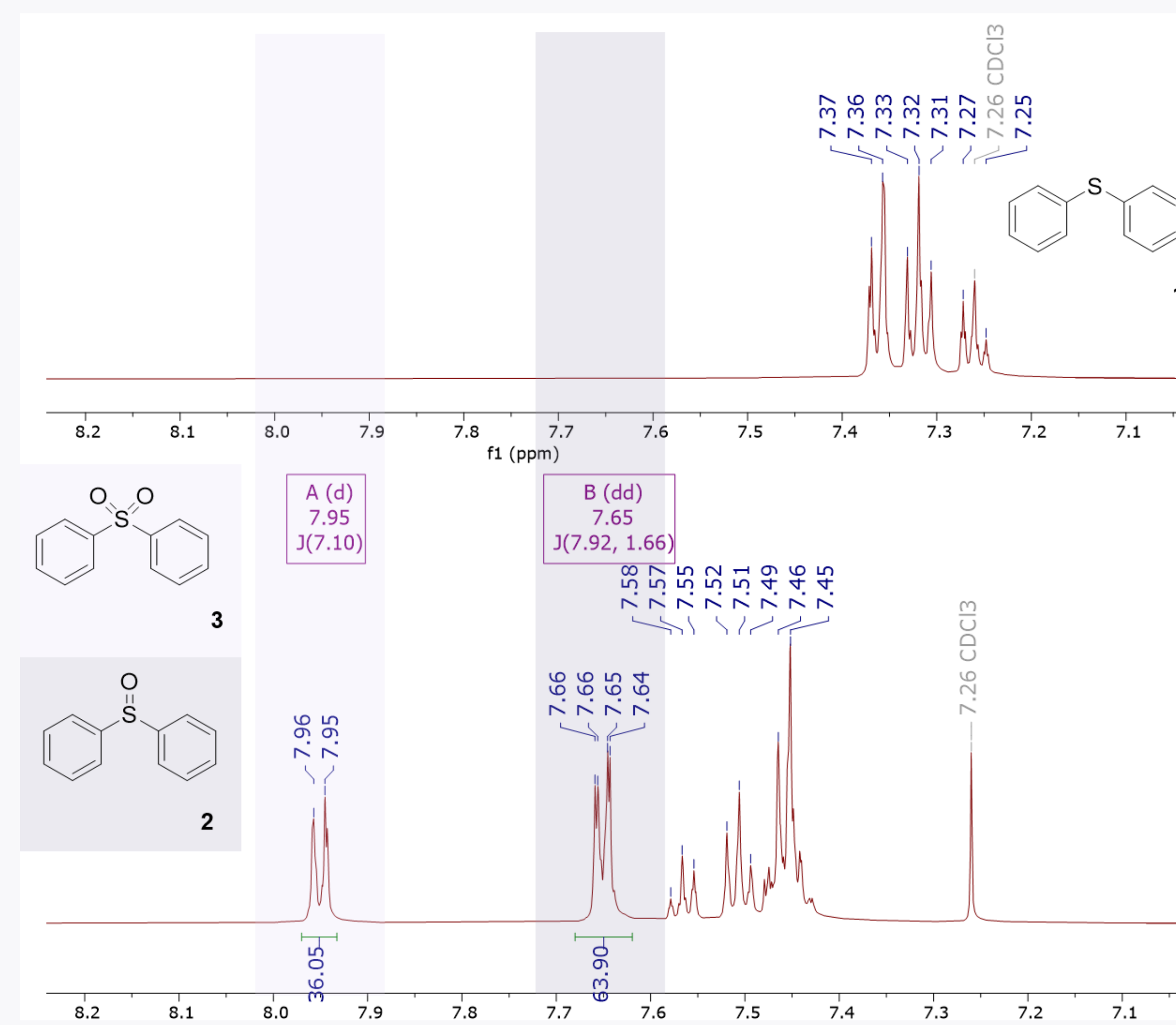


Figure 1. Example for the use of ¹H NMR spectroscopy for calculating the conversion and selectivity of the oxidation reactions.

Table 2. Experimental details, conversion and selectivity data for the oxidation reactions of compound 4

Catalyst	Solvent	Conversion* (%)	Selectivity (%)		
			5	6	7
Cat. 1	MeOH	0	0	0	0
	EG	0	0	0	0
	H ₂ O	100	74.65	25.35	0
	EtOH	0	0	0	0
	<i>i</i> -PrOH	100	36.31	49.32	14.3
Cat. 2	MeOH	0	0	0	0
	EG	0	0	0	0
	H ₂ O	100	29.97	58.39	11.82
	EtOH	71.83	16.54	30.87	21.73
	<i>i</i> -PrOH	40.68	32.34	40.07	25.59
Cat. 3	MeOH	0	0	0	0
	EG	0	0	0	0
	H ₂ O	100	21.04	51.25	27.72
	EtOH	97.5	30.65	29.71	39.64
	<i>i</i> -PrOH	100	19.70	38.11	42.28
none ^a	CH ₂ Cl ₂	100	0	0	100
none ^b	AcOH	100	4.44	36.36	59.2

Reaction condition: 50 mg (0.27 mmol) bis-thioether, 3 mL solvent, 1 mL H₂O₂ 35% solution, 5 mg catalyst (1.5 mol%) were added in a round bottom flask and stirred at room temperature for 48 hour. Water and ethyl-acetate were added, the phases separated, the organic phase washed with ethyl-acetate, then dried under vacuum and analysed by ¹H NMR spectroscopy. ^a *m*CPBA was used as oxidant, reaction at 0 °C, 2h; ^b H₂O₂ was used as oxidant, reaction at room temperature, 48h *without separation from reaction mixture, according to ¹H NMR measurements. Methanol (MeOH), ethylene-glycol (EG), water (H₂O), ethanol (EtOH), 2-propanol (*i*-PrOH).

Conclusion

In this work we investigated the catalytic activity of three decavanadate species in sulfoxidation reactions. Full conversion of the diphenyl-sulfide substrate was observed in a short reaction time (2h), in most solvents (MeOH, EtOH, *i*-PrOH), with low catalyst loading (1.5 mol%). Moreover, Cat.3 showed good results in the recyclability test, giving full conversion of the substrate even after three runs.