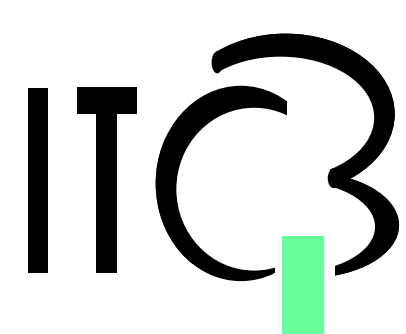


Synthesis, Characterization and Catalytic application of Water Stable η^3 -Allyl Dicarbonyl Complexes of Molybdenum(II)

Carla A. Gamelas,¹ Ana C. Gomes,² Sofia M. Bruno,² Anabela A. Valente,² Martyn Pillinger,² Carlos C. Romão,³ Isabel S. Gonçalves²



¹Escola Superior de Tecnologia de Setúbal, Instituto Politécnico de Setúbal, 2910-761 Setúbal, Portugal;

²Department of Chemistry, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal

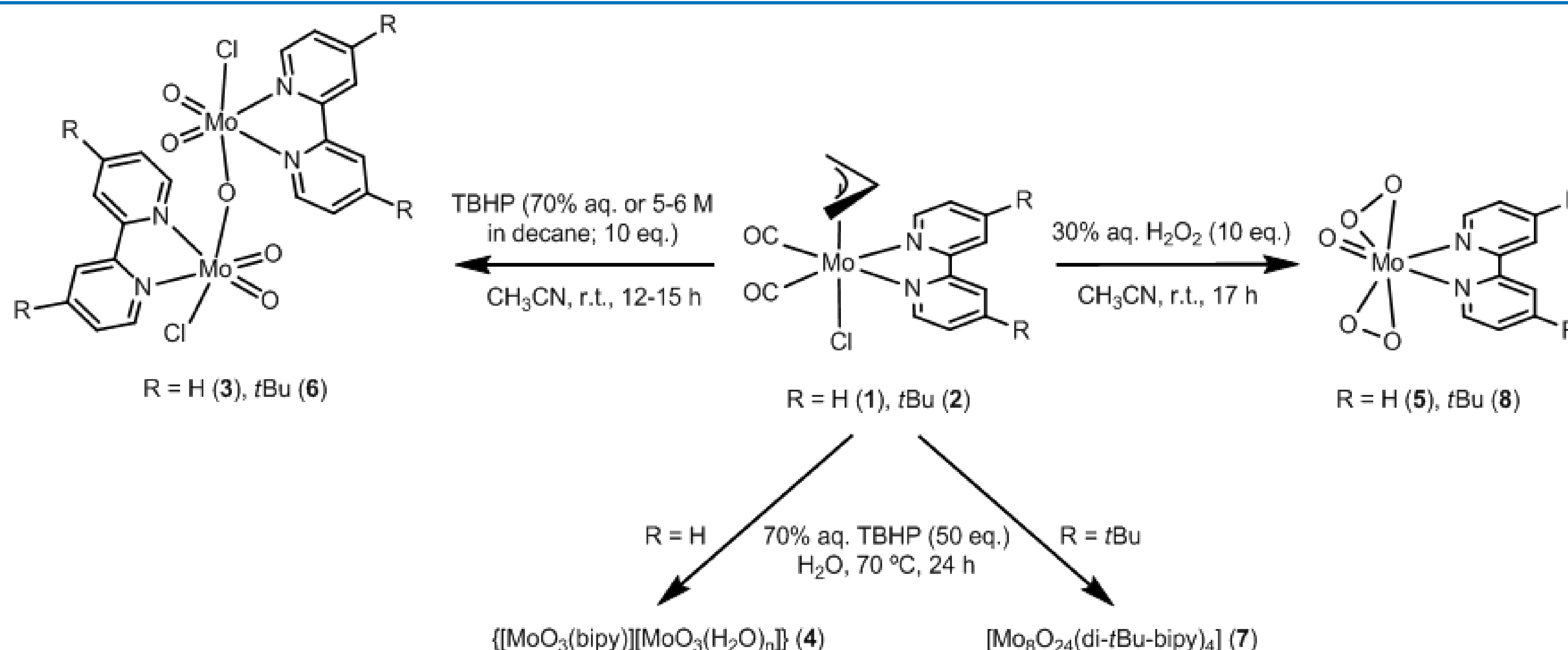
³Instituto de Tecnologia Química e Biológica, UNL, 2781-901 Oeiras, Portugal;



Introduction

Allyl dicarbonyl complexes $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\text{X}(\text{CO})_2(\text{L})_n]$ ($\text{X} = \text{halide}$) have been found to act as catalyst precursors for several reactions, namely the polymerization of dienes and the epoxidation of olefins.¹ In our recent investigations of complexes $\text{cis-}[\text{Mo}(\text{CO})_4(\text{L})]$, we found that the nature of the bidentate ligand L influences the species formed by oxidative decarbonylation and their catalytic performance in olefin epoxidation: with $\text{L} = \text{bipy}$, the organic-inorganic hybrid $[\text{MoO}_3(\text{bipy})]$ is obtained; with $\text{L} = \text{di-}t\text{Bu-bipy}$, the polynuclear complex $[\text{Mo}_8\text{O}_{24}(\text{di-}t\text{Bu-bipy})_4]$ is obtained instead.² Here we report on the use of the complexes $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}(\text{CO})_2(\text{L})]$ ($\text{L} = \text{bipy}$ (**1**), $\text{di-}t\text{Bu-bipy}$ (**2**)) as catalyst precursors in the epoxidation of cyclooctene (Cy) using aqueous TBHP or H_2O_2 as oxidant. Additionally, oxidative decarbonylation was performed for both catalysts, in aqueous media, and the obtained products were characterized and also used as catalysts.

Synthesis



Characterization

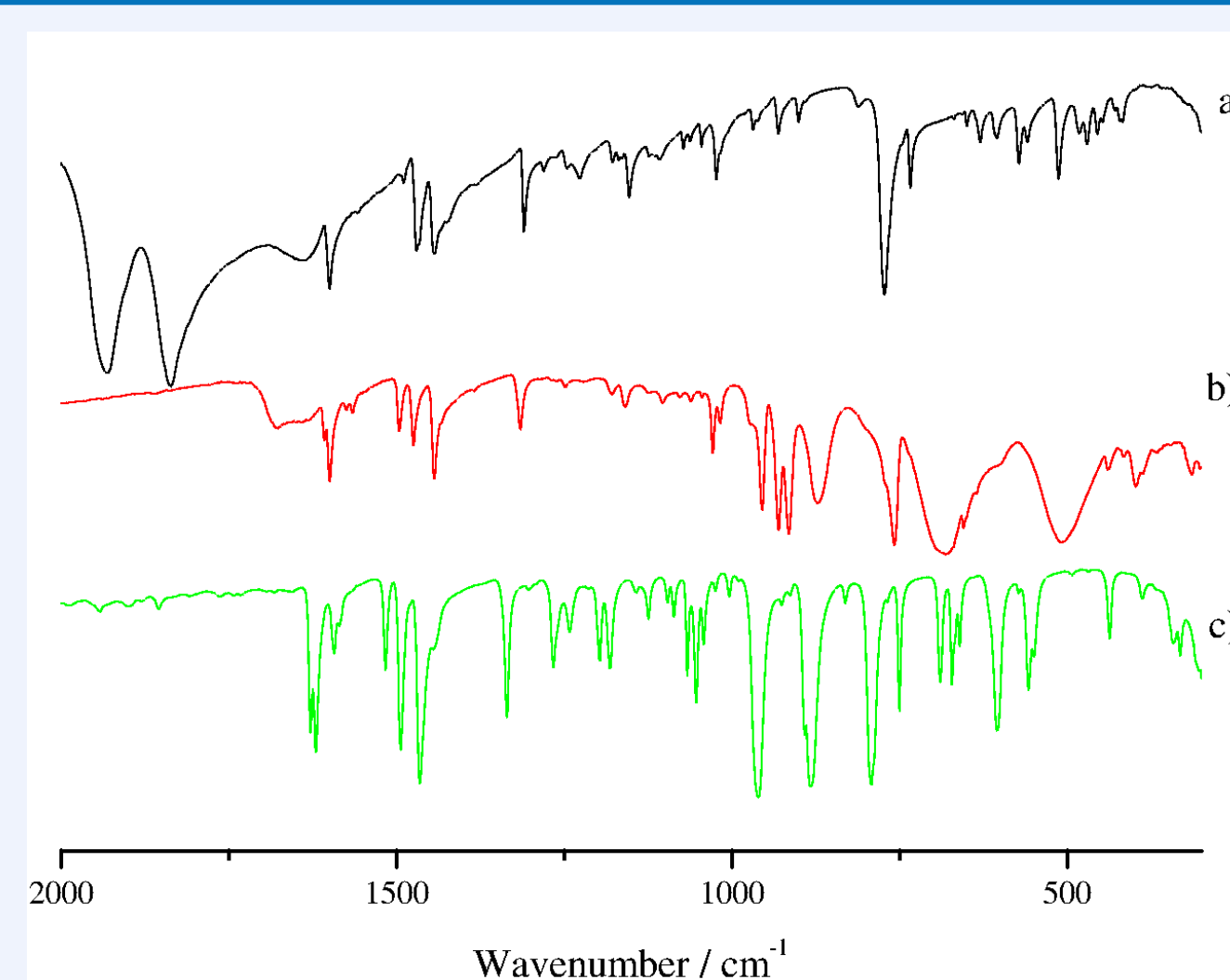
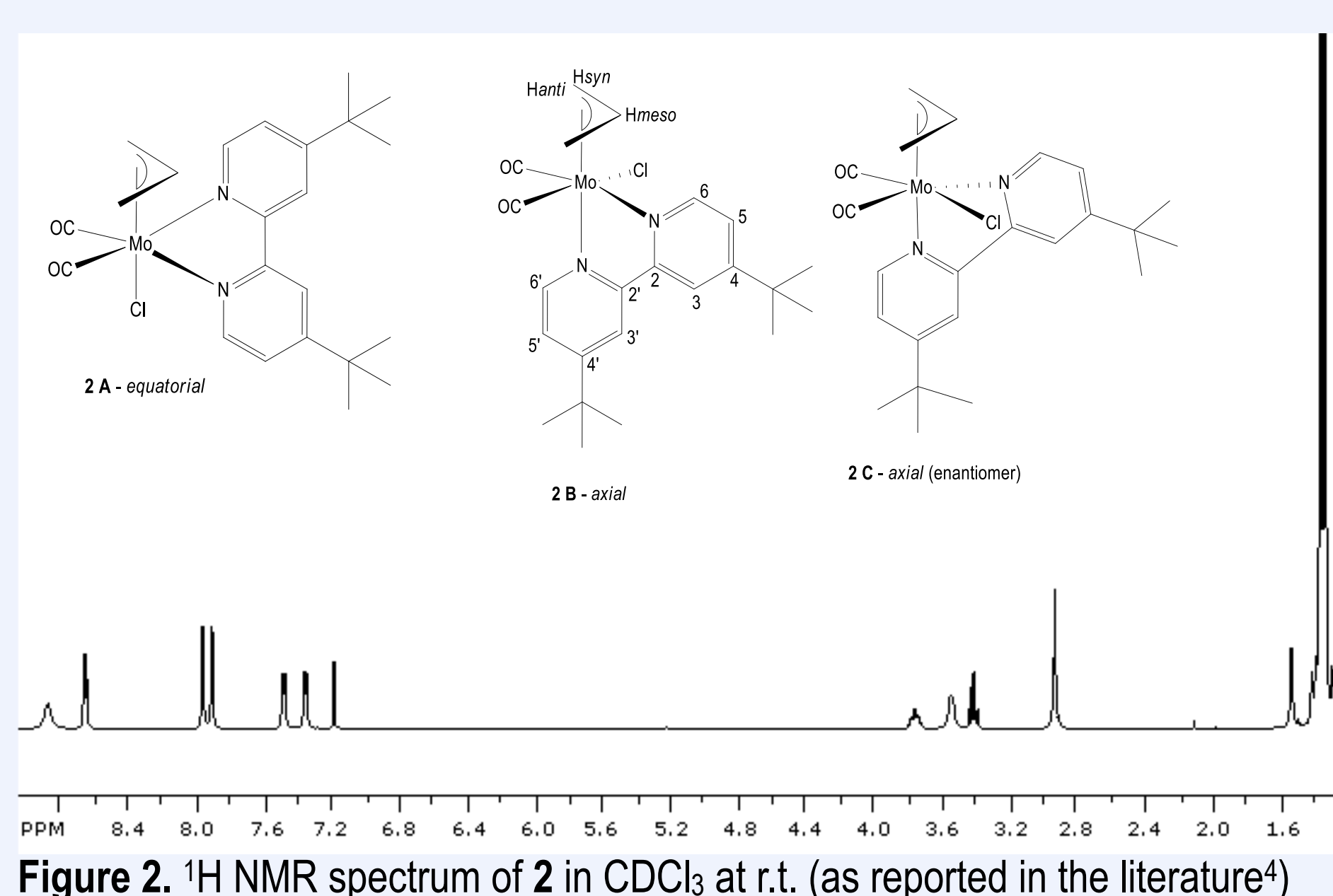
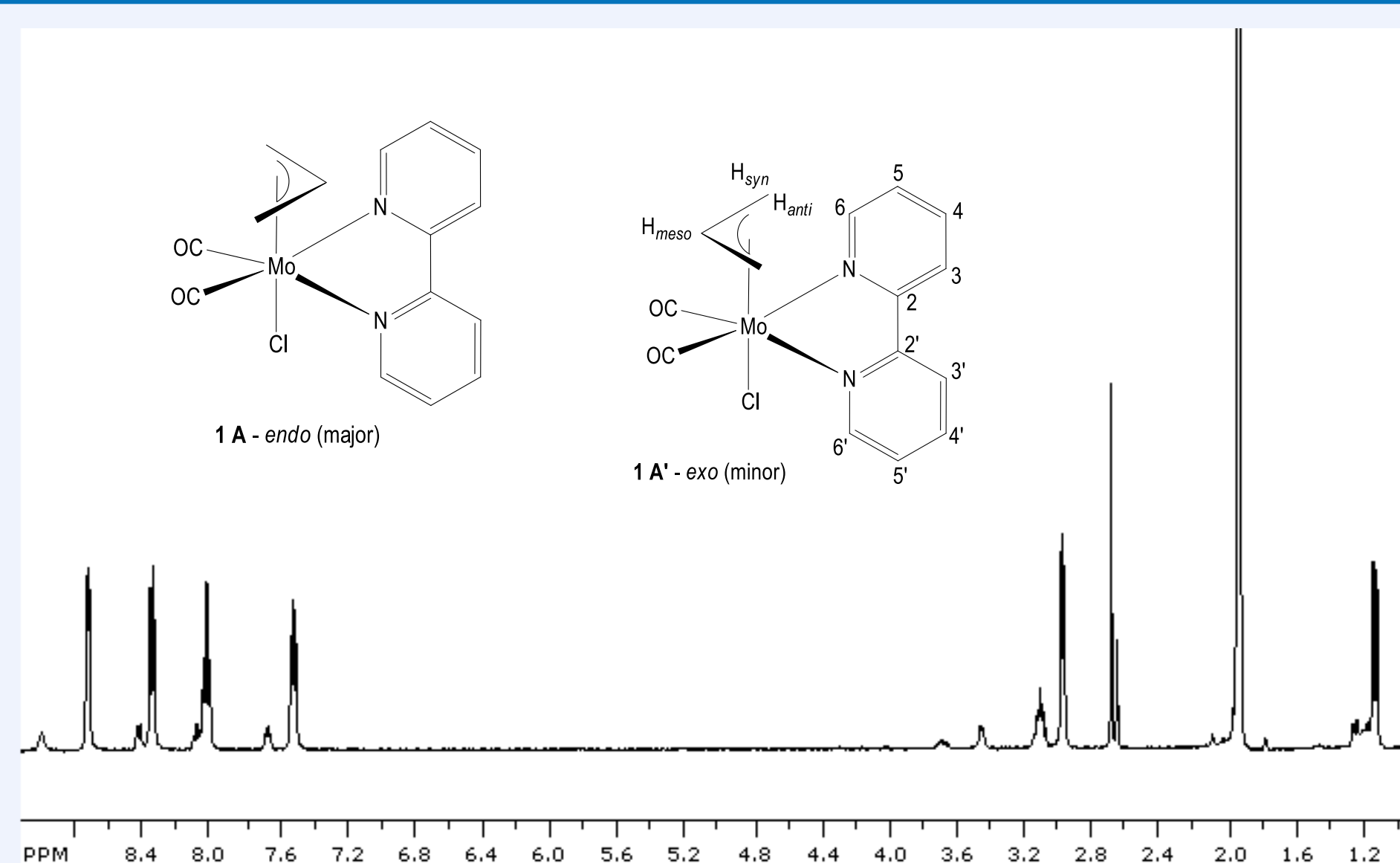


Figure 3. FT-IR spectra of compounds **1** (a), **4** (b), **5** (c)

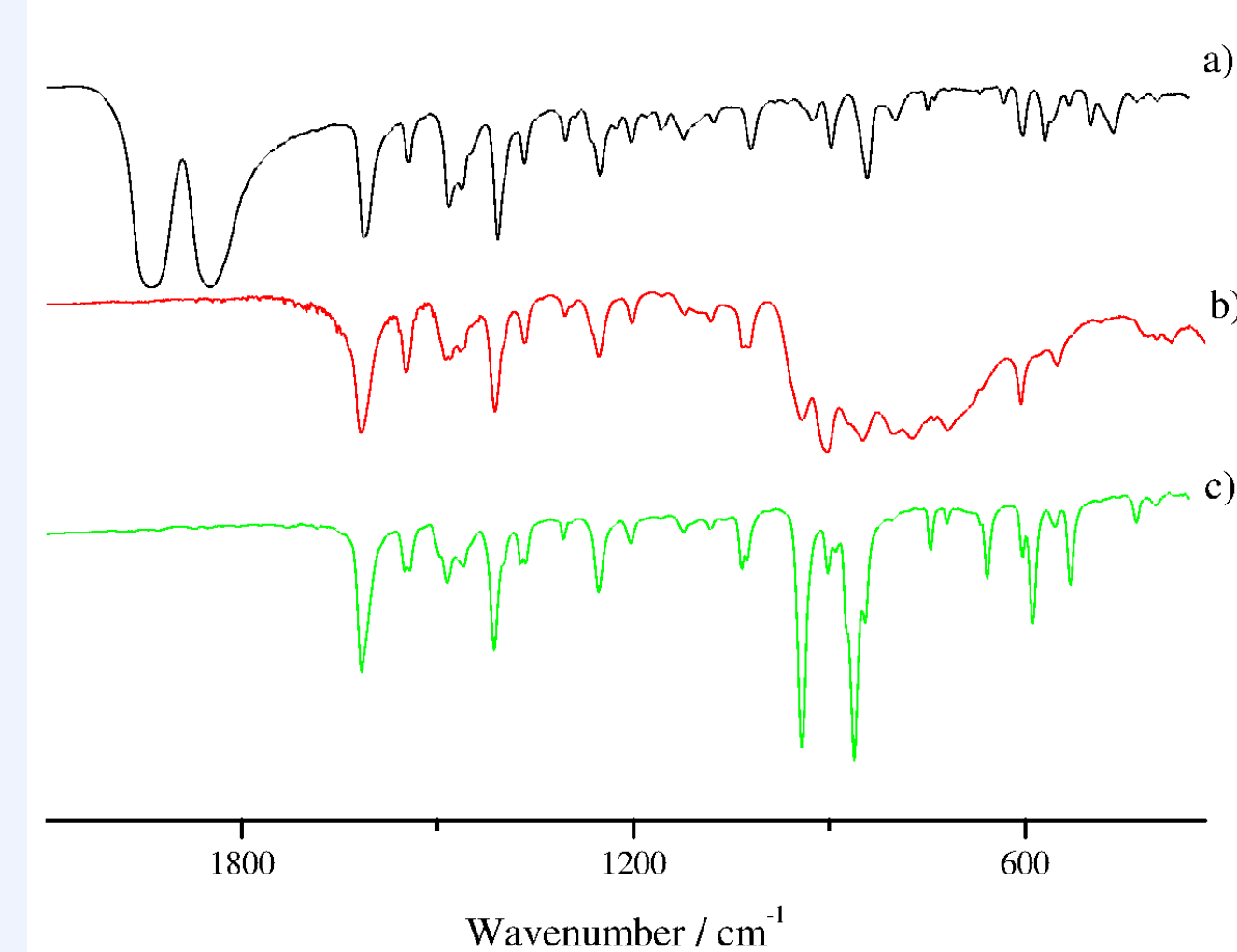


Figure 4. FT-IR spectra of compounds **2** (a), **7** (b), **8** (c)

Compound	Selected FT-IR (cm^{-1})
1	1932vs, 1837vs (CO), 1600m (C=N bipy)
3	1600s (C=N bipy), 931vs, 903vs (Mo=O), 789vs (Mo-O-Mo)
4	955s, 930s, 915s, 868s (Mo=O), 682s (Mo-O-Mo), 514s (OMo ₃)
5	939vs (Mo=O), 861s (O-O), 651m, 583m, 536m (Mo(O ₂) ₂)
7	942 vs, 903vs (Mo=O), 849s, 773s, 719s (Mo-O-Mo)

With the exception of **3**, the oxo Mo(VI) compounds have been previously prepared by different routes: **4**,^{3a} **5**,^{3b} **6**,^{3c} **7**,² and **8**.^{3d}

Catalysis

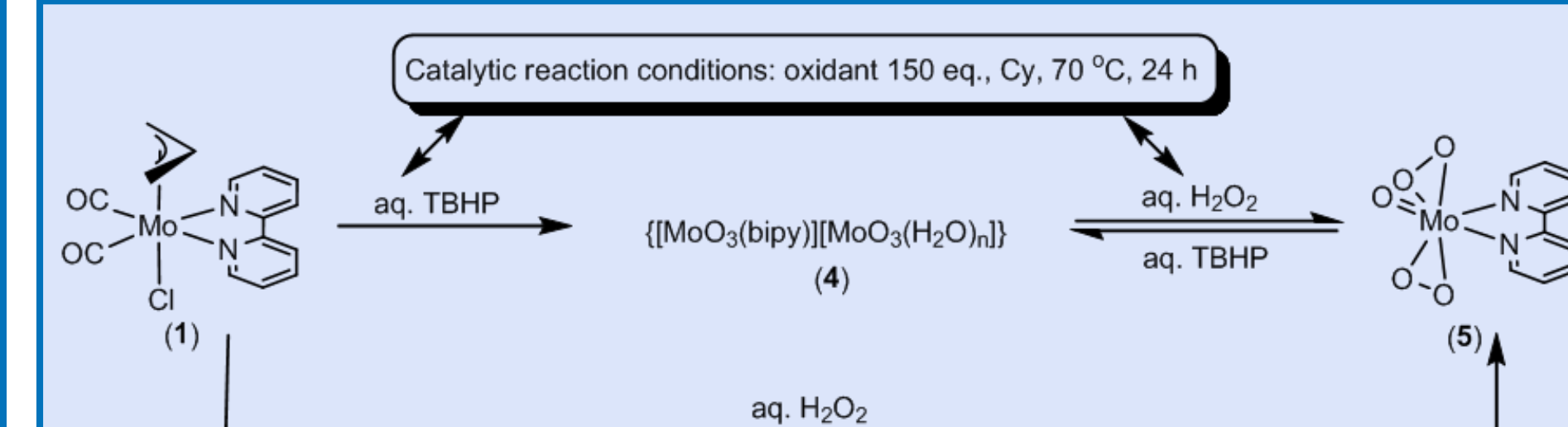


Table 1. Catalytic epoxidation of Cy with TBHP^a

Compound	Solvent	Yield (%) ^b	Identified solid after 24h ^c
1	H_2O	37	4 (TY \approx 60%)
1	CH_3CN	19	4
3	H_2O	32	4
4	H_2O	38	4
5	H_2O	28	4
2	H_2O	87	—
2	CH_3CN	59	—
6	H_2O	96	—
7	H_2O	90	—
8	H_2O	98	—

Table 2. Catalytic epoxidation of Cy with H_2O_2 ^a

Compound	Solvent	Yield (%) ^b	Identified solid after 24h ^c
1	CH_3CN	66	5
3	CH_3CN	71	5
4	CH_3CN	79	5
5	CH_3CN	54	5
2	CH_3CN	26	8
6	CH_3CN	54	8
7	CH_3CN	75	8
8	CH_3CN	81	8

^a mmol of Mo: Cy: oxidant = 0.018:1.8:2.75, 24 h reaction, 70 °C, 800 rpm, total volume \approx 1.25 mL; ^b CyO yield (100% selectivity); ^c solid formed identified by FT-IR spectroscopy; TY = theoretical wt.% yield of product formed.

Conclusions

The η^3 -allyl dicarbonyl complexes $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}(\text{CO})_2(\text{L})]$ ($\text{L} = \text{bipy}$, **1**; $\text{di-}t\text{Bu-bipy}$, **2**) are convenient precursors to oxo Mo(VI) compounds that selectively catalyze the epoxidation of Cy in aqueous media. Reaction of **1** or **2** with the oxidant results in oxidative decarbonylation. When the oxidant is H_2O_2 aq., the oxodiperoxo complexes $\text{MoO}(\text{O}_2)_2(\text{L})$ (**5**, **8**) are formed. By contrast, when the oxidant is TBHP aq., different oxo Mo(VI) compounds are formed, depending on the ligand L and the reaction conditions: oxo-bridged dimers $[\text{MoO}_2\text{Cl}(\text{L})_2]$ (**3**, **6**), the hybrid $[\text{MoO}_3(\text{bipy})][\text{MoO}_3(\text{H}_2\text{O})_n]$ (**4**), the octanuclear complex $[\text{Mo}_8\text{O}_{24}(\text{di-}t\text{Bu-bipy})_4]$ (**7**).

We anticipate that the extension of these studies to other η^3 -allyl dicarbonyl complexes, including chiral derivatives, will provide novel oxo Mo(VI) compounds, possibly active in aqueous catalysis.

References

- [1] Alonso, J. C.; Neves, P.; da Silva, M. J. P.; Quintal, S.; Vaz, P. D.; Silva, C.; Valente, A. A.; Ferreira, P.; Calhorda, M. J.; Felix, V.; Drew, M. G. B. *Organometallics* **2007**, *26*, 5548.
- [2] Amarante, T. R.; Neves, P.; Coelho, A. C.; Gago, S.; Valente, A. A.; Paz, F. A. A.; Pillinger, M.; Gonçalves, I. S. *Organometallics* **2010**, *29*, 883.
- [3] (a) Abrantes, M.; Amarante, T. R.; Antunes, M. M.; Gago, S.; Paz, F. A. A.; Margiolaki, I.; Rodrigues, A. E.; Pillinger, M.; Valente, A. A.; Gonçalves, I. S. *Inorg. Chem.* **2010**, *49*, 6865. (b) Schlemper, E. O.; Schrauzer, G. N.; Hughes, L. A. *Polyhedron* **1984**, *3*, 377. (c) Arzoumanian H.; Bakhtchadjian R. *Trans. Met. Chem.* **2006**, *31*, 681. (d) Amarante, T. R.; Paz, F. A. A.; Gago, S.; Gonçalves, I. S.; Pillinger, M.; Rodrigues, A. E.; Abrantes, M. *Molecules* **2009**, *14*, 3610.
- [4] Rodrigues, C. W.; Limberg, C.; Pritzkow, H. *Chem. Commun.* **2004**, 2734.

Acknowledgments

We are grateful to FCT, POCI 2010, OE and FEDER for general funding, REDE/1517/RMN/2005 and REDE/1504/REM/2005. EST-IPS is acknowledged for a short duration grant to C.A.G. The FCT is acknowledged for a post-doctoral grant to S.M.B. CICECO is acknowledged for financial support (including a post-doctoral grant to A.C.G.).