

Electronic Supporting Information

Molybdenum(VI) Catalysts Obtained from η^3 -Allyl Dicarboxyl Precursors: Synthesis, Characterization and Catalytic Performance in Cyclooctene Epoxidation†

**Carla A. Gamelas,^{a,b} Ana C. Gomes,^c Sofia M. Bruno,^c Filipe A. Almeida Paz,^c
Anabela A. Valente,^c Martyn Pillinger,^c Carlos C. Romão^a and Isabel S.
Gonçalves^{c,*}**

^a*Instituto de Tecnologia Química e Biológica da Universidade Nova de Lisboa, Av. da
República, Estação Agronómica Nacional, 2780-157 Oeiras, Portugal*

^b*Escola Superior de Tecnologia, Instituto Politécnico de Setúbal, 2910-761 Setúbal, Portugal*

^c*Department of Chemistry, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal*

E-mail: igoncalves@ua.pt; Fax: +351 234 370084

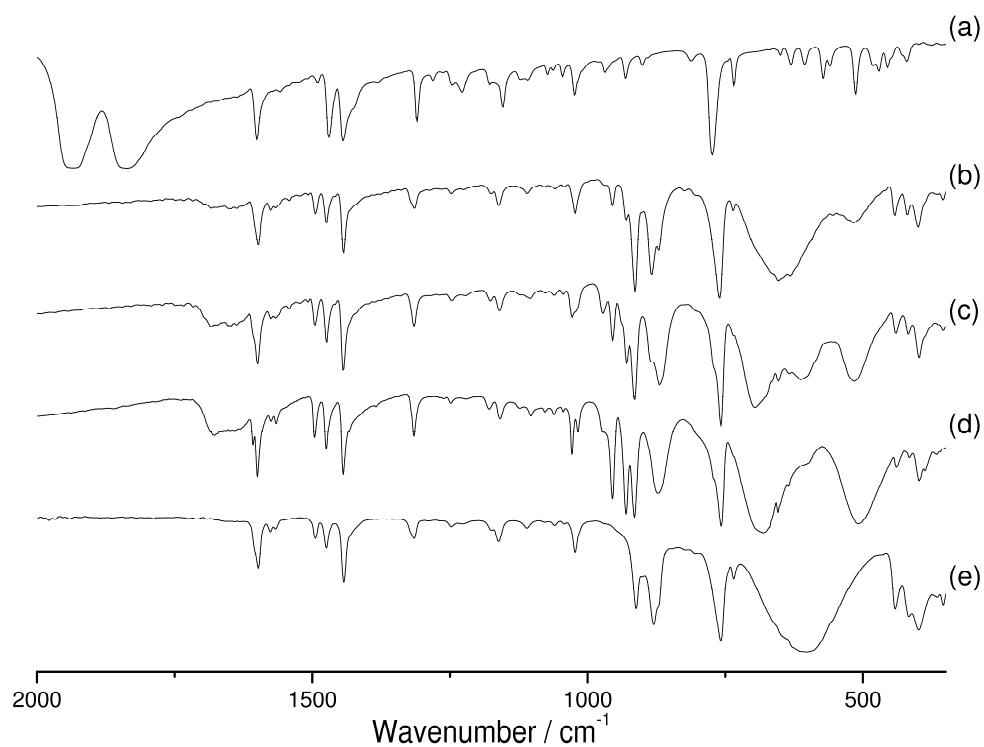


Fig. S1 FT-IR spectra of $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}(\text{CO})_2(\text{bipy})]$ (**1**) (a), **1*** (b), **1-H₂O₂TBHP55** (c), $\{[\text{MoO}_3(\text{bipy})][\text{MoO}_3(\text{H}_2\text{O})]\}_n$ (**4**) (d) and $[\text{MoO}_3(\text{bipy})]$ (e).

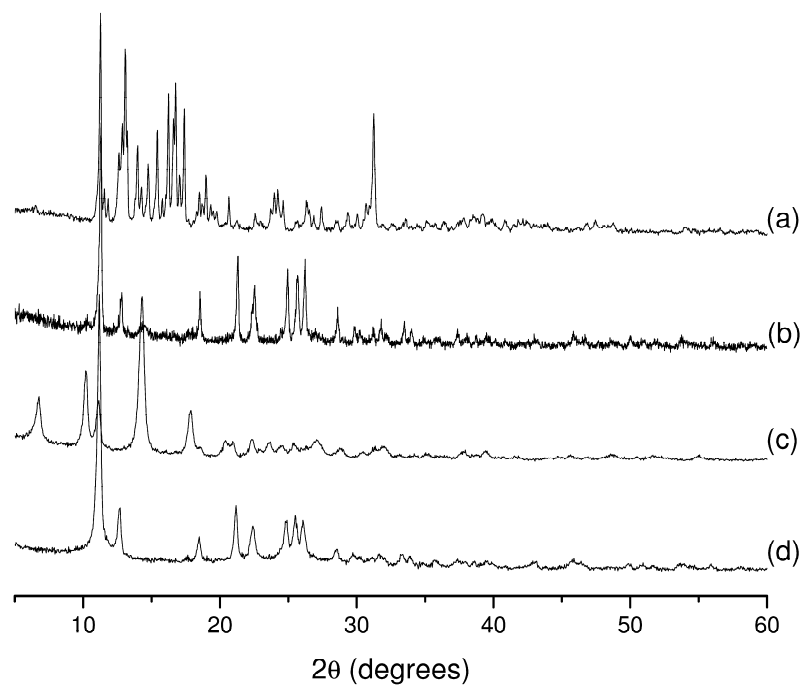


Fig. S2 Power XRD patterns of $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}(\text{CO})_2(\text{bipy})]$ (**1**) (a), **1*** (b), $\{[\text{MoO}_3(\text{bipy})][\text{MoO}_3(\text{H}_2\text{O})]\}_n$ (**4**) (c) and $[\text{MoO}_3(\text{bipy})]$ (d).

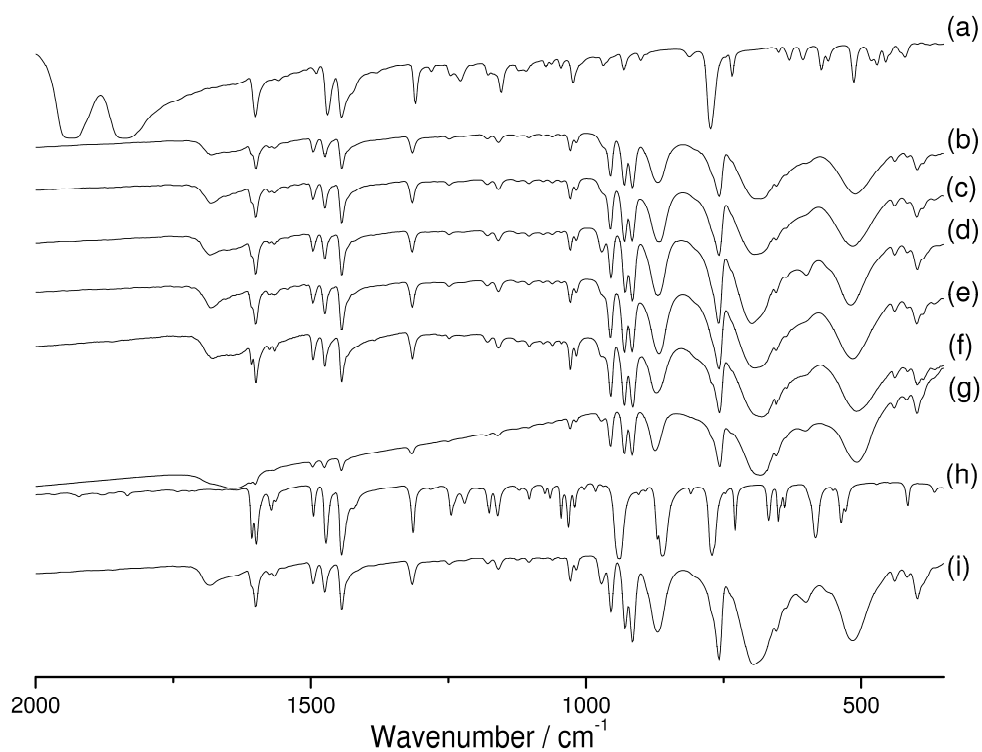


Fig. S3 FT-IR spectra of: $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}(\text{CO})_2(\text{bipy})]$ (**1**) (a); the solids recovered from the reaction of Cy with TBHP in the presence of **1**, at 70 °C, without adding a solvent (b) or using as solvent H₂O (c), ethanol (d) or acetonitrile (e); $\{[\text{MoO}_3(\text{bipy})][\text{MoO}_3(\text{H}_2\text{O})]\}_n$ (**4**) before (f) and after (g) the catalytic reaction using TBHP/H₂O; $\text{MoO}(\text{O}_2)_2(\text{bipy})$ (**5**) before (h) and after (i) the catalytic reaction using TBHP/H₂O.

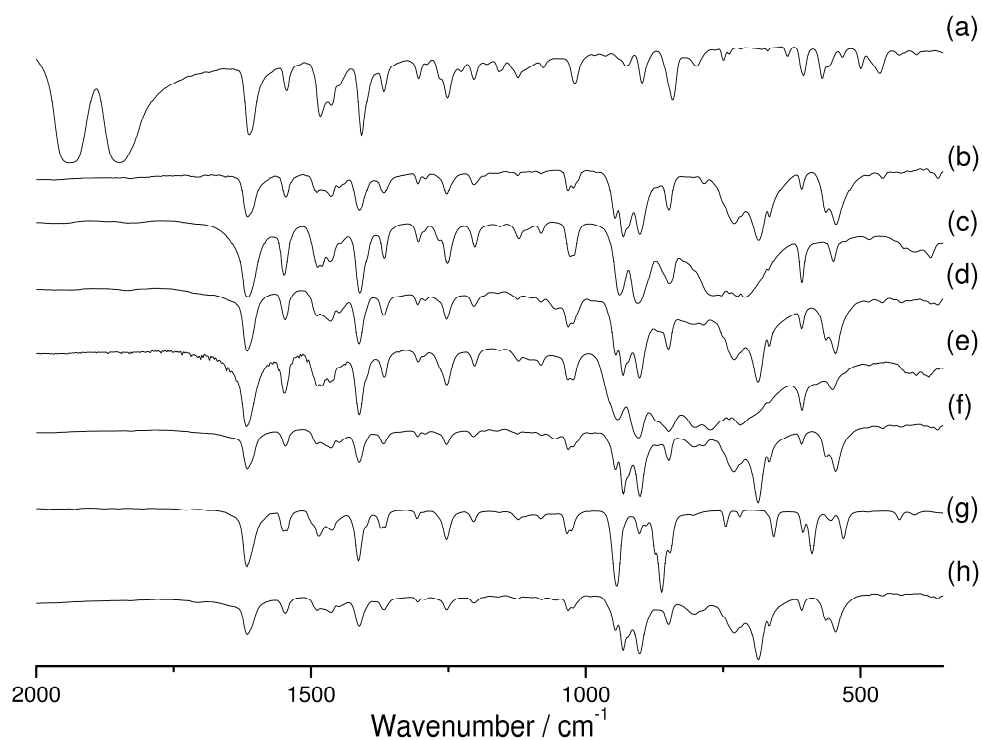


Fig. S4 FT-IR spectra of: $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}(\text{CO})_2(\text{di-}t\text{Bu-bipy})]$ (**2**) (a); the solid (**2***) precipitated from the organic phase of the reaction of Cy with TBHP in the presence of **2**, at 24 h/70 °C, using H_2O as solvent (b); $[\text{MoO}_2\text{Cl}(\text{di-}t\text{Bu-bipy})]_2\text{O}$ (**6**) before (c) and after (d) the catalytic reaction using TBHP/ H_2O ; $[\text{Mo}_8\text{O}_{24}(\text{di-}t\text{Bu-bipy})_4]$ (**7**) before (e) and after (f) the catalytic reaction using TBHP/ H_2O ; $\text{MoO}(\text{O}_2)_2(\text{di-}t\text{Bu-bipy})$ (**8**) before (g) and after (h) the catalytic reaction using TBHP/ H_2O .

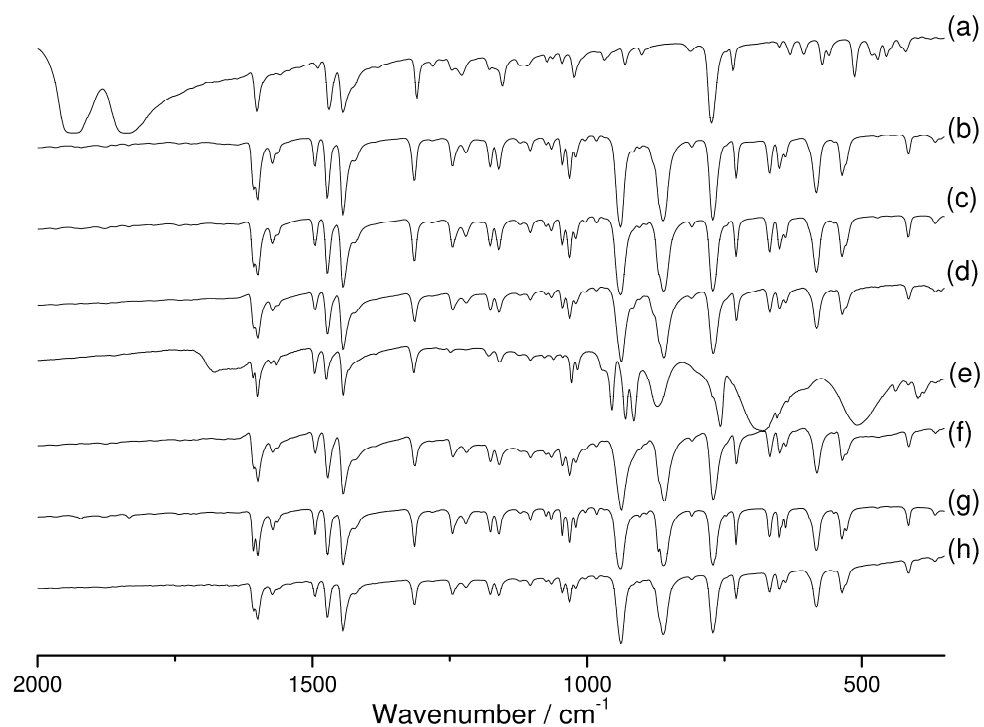


Fig. S5 FT-IR spectra of: [Mo(η^3 -C₃H₅)Cl(CO)₂(bipy)] (**1**) (a); the solids recovered from the reaction of Cy with H₂O₂ in the presence of **1**, at 24 h/70 °C, using as solvent H₂O (b), ethanol (c) or acetonitrile (d); {[MoO₃(bipy)][MoO₃(H₂O)]}_n (**4**) before (e) and after (f) the catalytic reaction using H₂O₂/H₂O; MoO(O₂)₂(bipy) (**5**) before (g) and after (h) the catalytic reaction using H₂O₂/H₂O.

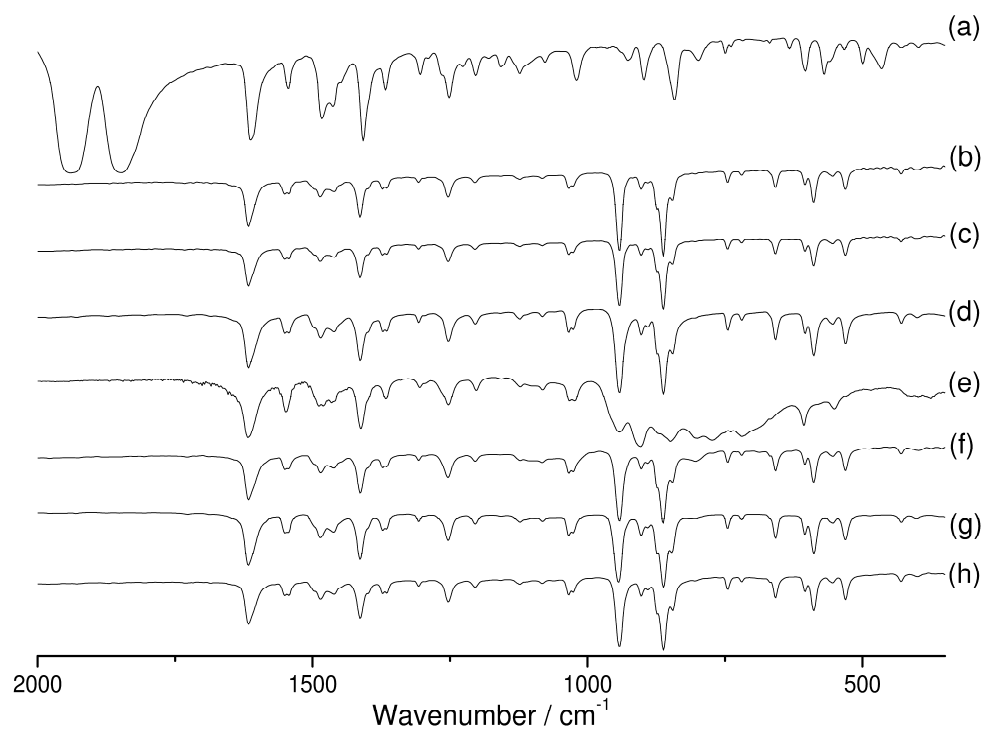


Fig. S6 FT-IR spectra of: [Mo(η^3 -C₃H₅)Cl(CO)₂(di-*t*Bu-bipy)] (**2**) (a); the solids recovered from the reaction of Cy with H₂O₂ in the presence of **2**, at 24 h/70 °C, using as solvent H₂O (b), ethanol (c) or acetonitrile (d); [Mo₈O₂₄(di-*t*Bu-bipy)₄] (**7**) before (e) and after (f) the catalytic reaction using H₂O₂/H₂O; MoO(O₂)₂(di-*t*Bu-bipy) (**8**) before (g) and after (h) the catalytic reaction using H₂O₂/H₂O.

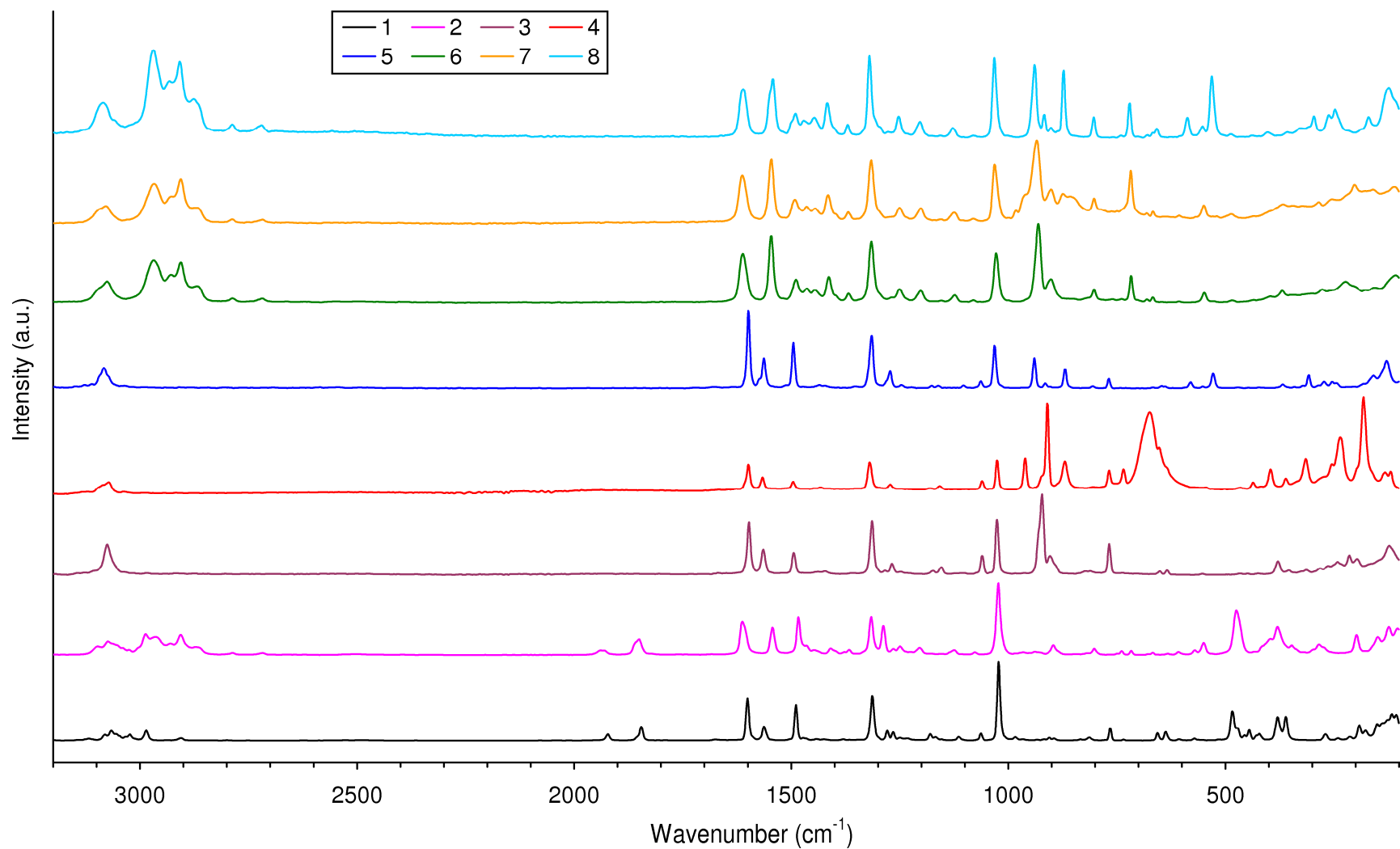


Fig. S7 FT-Raman spectra of $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}(\text{CO})_2(\text{bipy})]$ (**1**), $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}(\text{CO})_2(\text{di-}t\text{Bu-bipy})]$ (**2**), $[\text{MoO}_2\text{Cl}(\text{bipy})]_2\text{O}$ (**3**), $\{[\text{MoO}_3(\text{bipy})][\text{MoO}_3(\text{H}_2\text{O})]\}_n$ (**4**), $\text{MoO}(\text{O}_2)_2(\text{bipy})$ (**5**), $[\text{MoO}_2\text{Cl}(\text{di-}t\text{Bu-bipy})]_2\text{O}$ (**6**), $[\text{Mo}_8\text{O}_{24}(\text{di-}t\text{Bu-bipy})_4]$ (**7**), $\text{MoO}(\text{O}_2)_2(\text{di-}t\text{Bu-bipy})$ (**8**).