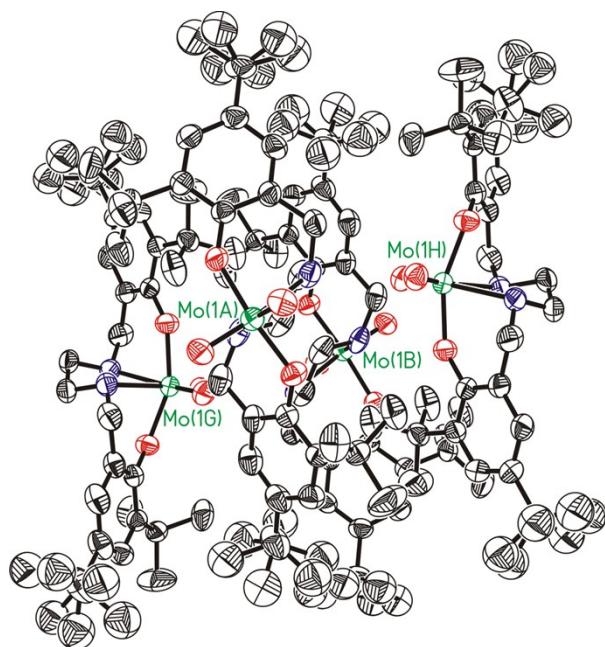


## Supporting Information

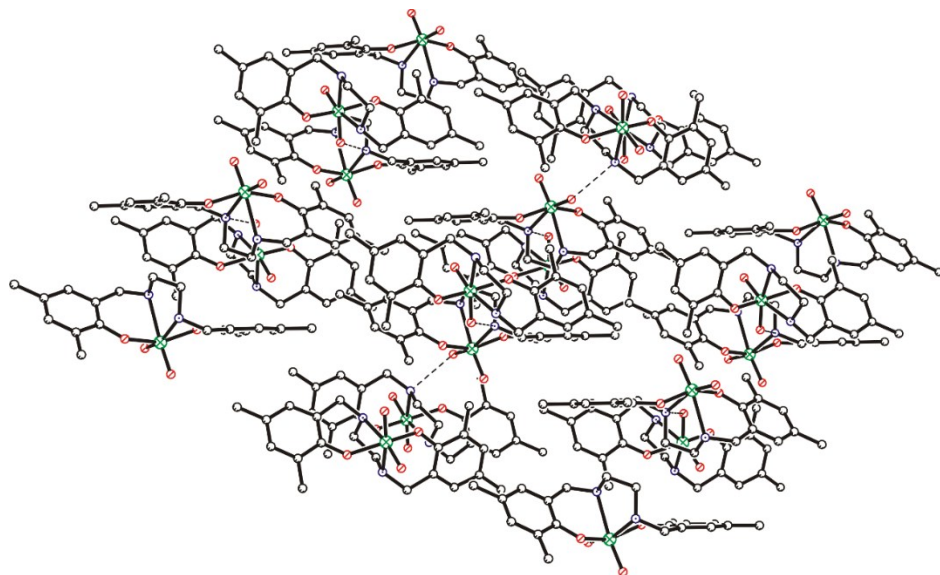
Manuscript ID NJ-ART-09-2017-003551

### Oxygen atom transfer between DMSO and benzoin catalyzed by *cis*-dioxidomolybdenum(VI) complexes of tetradentate Mannich Bases

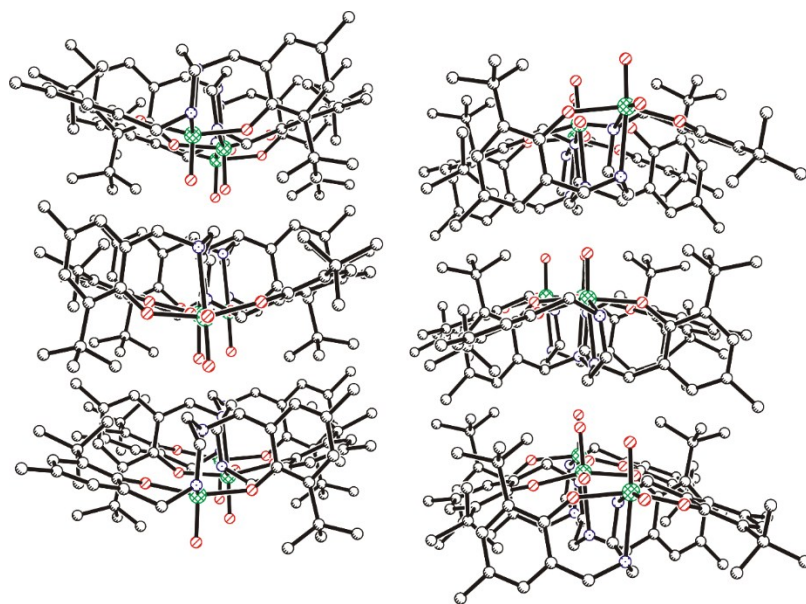
Mannar R. Maurya, Bekele Mengesha, Bhawna Uprety, Nancy Jangra, Reshu Tomar and Fernando Avecilla



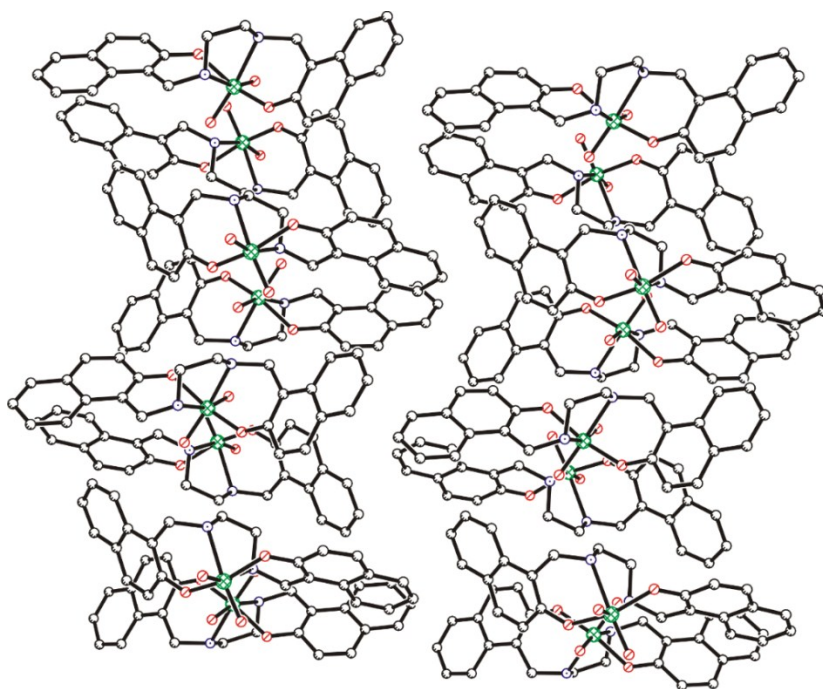
**Fig. S1** View along b axis of the crystal packing of  $[\text{MoO}_2(\text{L}^1)]$  (**1**). All the non-hydrogen atoms are presented by balls and sticks. Hydrogen atoms are omitted for clarity.



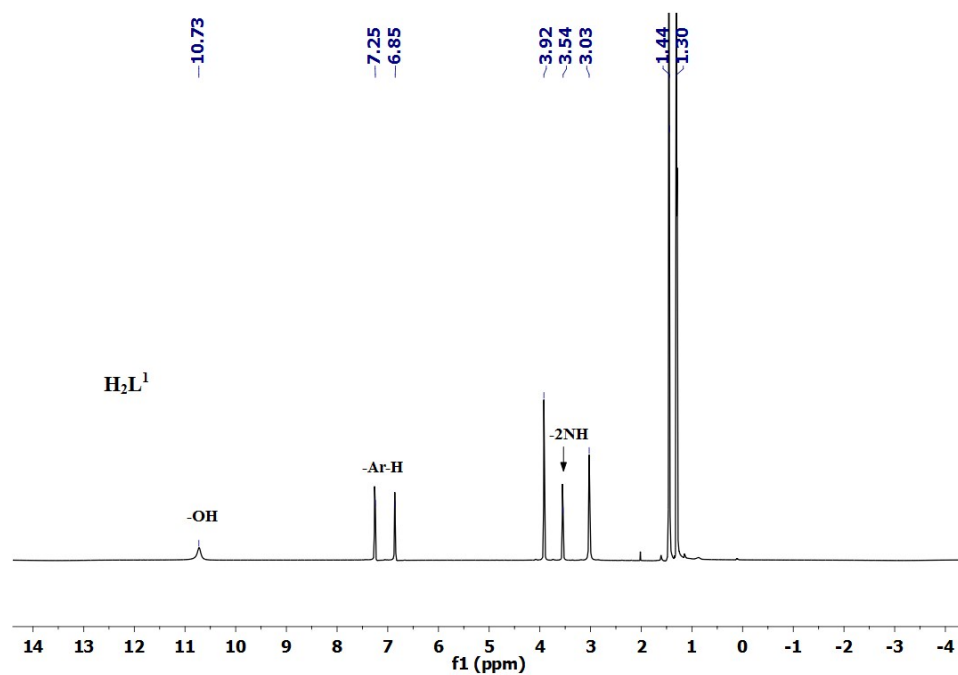
**Fig. S2** Crystal packing of  $[\text{MoO}_2\text{L}^2]$  **2**. All the non-hydrogen atoms are presented by balls and sticks. Hydrogen atoms are omitted for clarity.



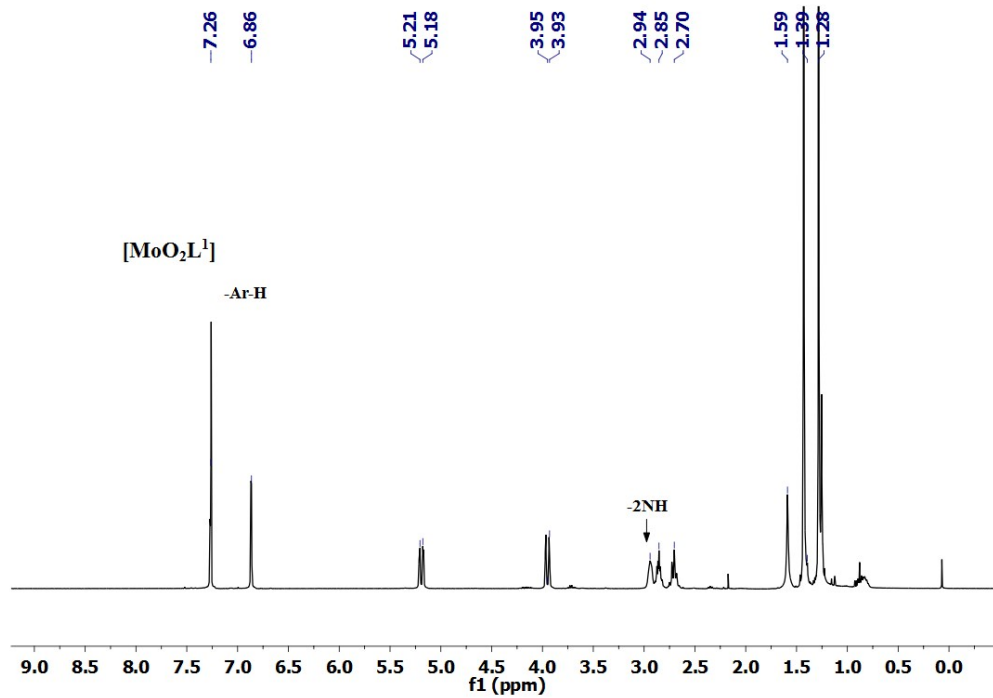
**Fig. S3** Crystal packing of  $[\text{MoO}_2(\text{L}^3)]$  **3**. All the non-hydrogen atoms are presented by balls and sticks. Hydrogen atoms are omitted for clarity.



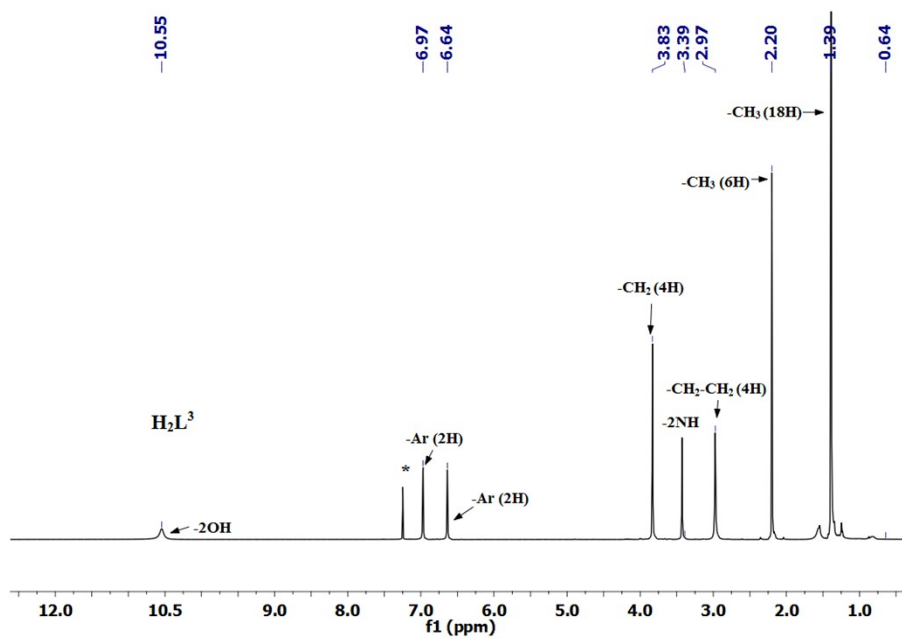
**Fig. S4** Crystal packing of  $[\text{MoO}_2(\text{L}^5)]$  **5**. All the non-hydrogen atoms are presented by balls and sticks. Hydrogen atoms are omitted for clarity.



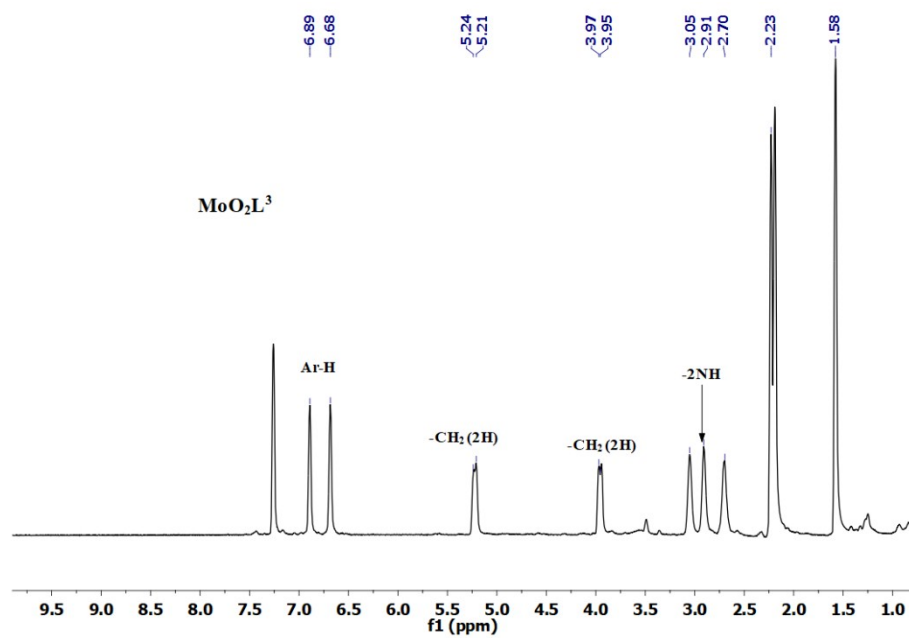
**Fig. S5**  $^1\text{H}$  NMR spectrum of  $\text{H}_2\text{L}^1$  in  $\text{CDCl}_3$



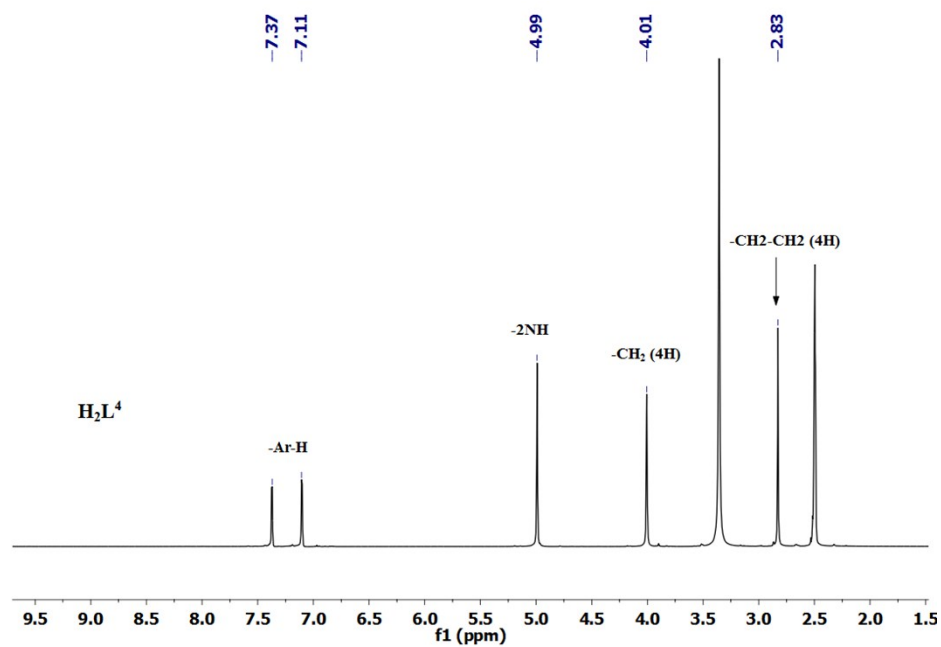
**Fig. S6**  $^1\text{H}$  NMR spectrum of  $[\text{MoO}_2\text{L}^1]$  in  $\text{CDCl}_3$



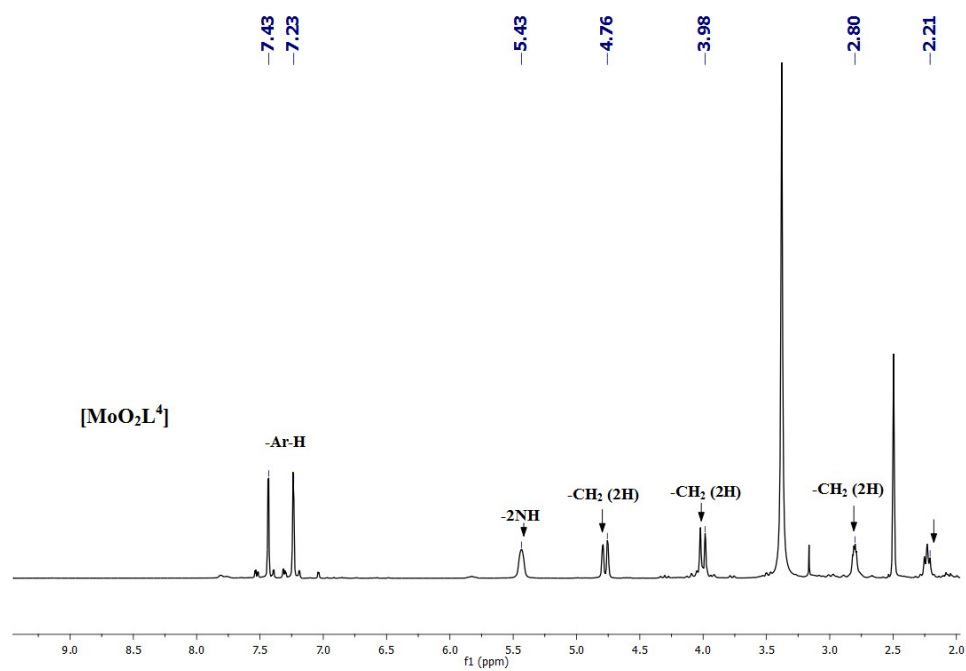
**Fig. S7**  $^1\text{H}$  NMR spectrum of  $\text{H}_2\text{L}^3$  in  $\text{CDCl}_3$ .



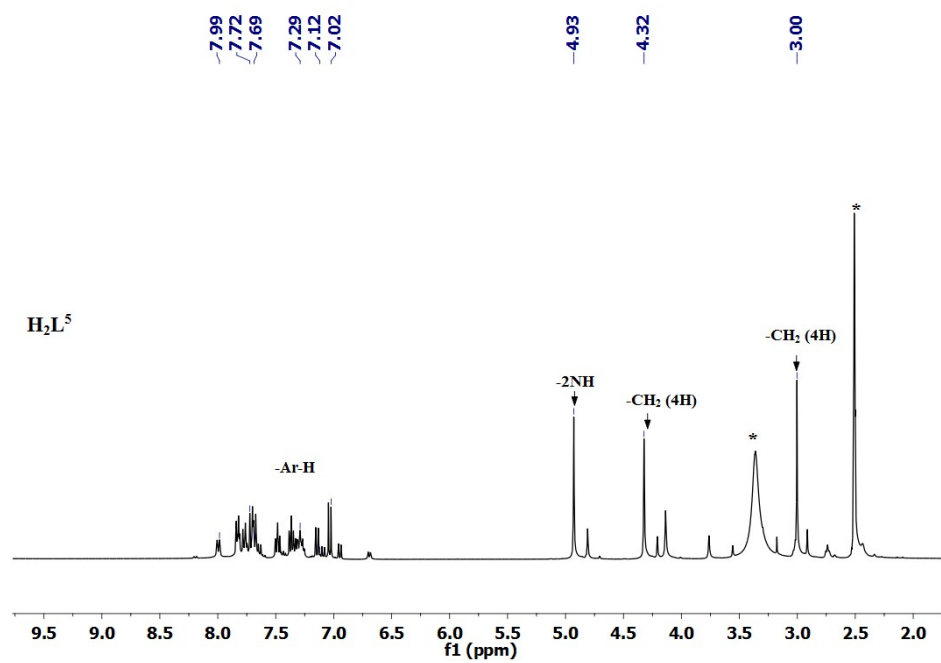
**Fig. S8**  $^1\text{H}$  NMR spectrum of  $[\text{Mo}^{\text{VI}}\text{O}_2\text{L}^3]$  in  $\text{CDCl}_3$ .



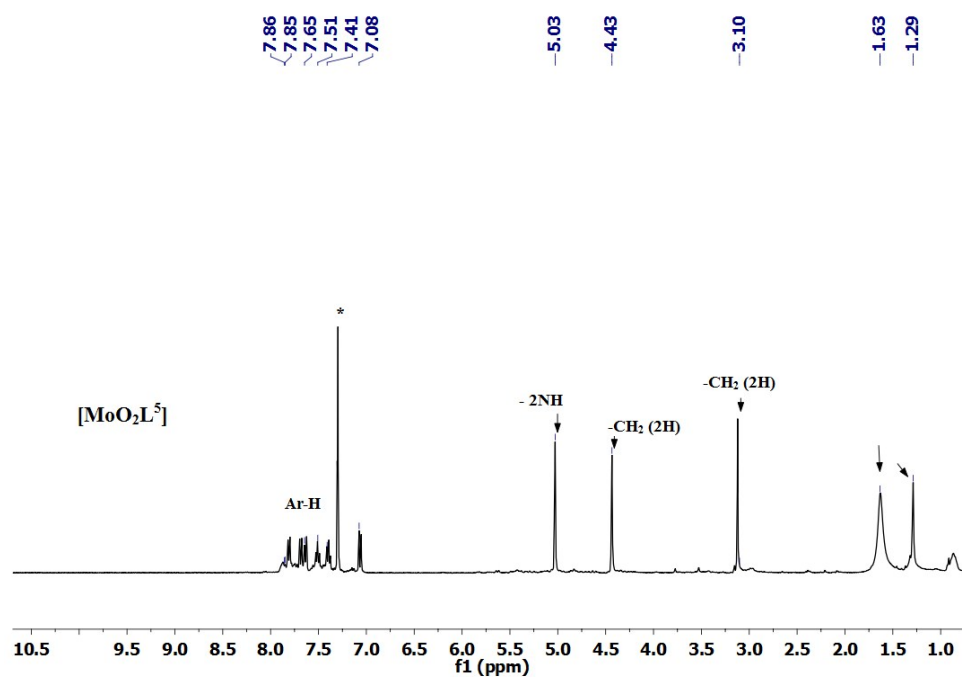
**Fig. S9**  $^1\text{H}$  NMR spectrum of  $\text{H}_2\text{L}^4$  in  $\text{DMSO}-d_6$ .



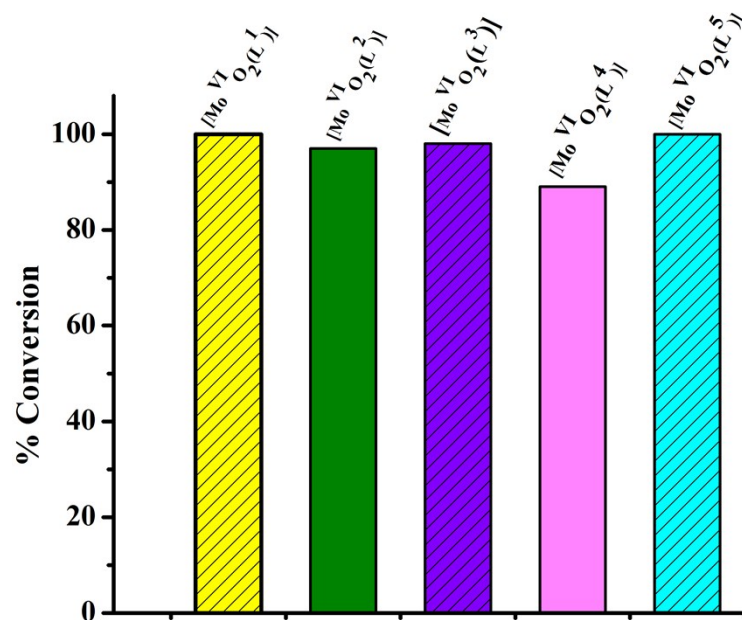
**Fig. S10**  $^1\text{H}$  NMR spectrum of  $[\text{Mo}^{\text{VI}}\text{O}_2\text{L}^4]$  in  $\text{DMSO-d}_6$ .



**Fig. S11**  $^1\text{H}$  NMR spectrum of  $\text{H}_2\text{L}^5$  in  $\text{DMSO-d}_6$ .



**Fig. S12**  $^1\text{H}$  NMR spectrum of  $[\text{Mo}^{\text{VI}}\text{O}_2\text{L}^5]$  in  $\text{CDCl}_3$ .



**Fig. S13** Results for oxygen atom transfer reaction between DMSO and 4-chlorobenzoin catalyzed by *cis*- $[\text{MoO}_2]^{2+}$  complexes (for details, see text).

**Table S1** Dioxidomolybdenum(VI) complexes catalyzed oxygen atom transfer between 4-chlorobenzoin and DMSO in acetonitrile at 80 °C in 18 h of reaction time; conversion, TOF and selectivity data.

Entry	Catalyst	Catalyst [mg, $\mu\text{mol}$ ]	Conv.[%]	Selectivity [%]	TOF [ $\text{h}^{-1}$ ]
1	$[\text{Mo}^{\text{VI}}\text{O}_2(\text{L}^1)]$ <b>1</b>	3.76, 6.02	99	100	46
2	$[\text{Mo}^{\text{VI}}\text{O}_2(\text{L}^2)]$ <b>2</b>	2.73, 6.02	97	100	45
3	$[\text{Mo}^{\text{VI}}\text{O}_2(\text{L}^3)]$ <b>3</b>	3.24, 6.02	98	100	45
4	$[\text{Mo}^{\text{VI}}\text{O}_2(\text{L}^4)]$ <b>4</b>	3.22, 6.02	89	100	41
5	$[\text{Mo}^{\text{VI}}\text{O}_2(\text{L}^5)]$ <b>5</b>	3.00, 6.02	100	100	46

The results of the catalytic OAT reaction between DMSO and 4-chlorobenzoin using different catalysts, show a stark variation while changing the substituent on the phenol rings. Therefore, the complex with naphthyl rings, i.e.  $[\text{MoO}_2(\text{L}^5)]$ (**5**) renders an excellent conversion of 100 %. This conversion drops to 95 – 100 % with alkyl substitution while the chloro substitution further slows down the reaction, and the overall conversion drops to 89 % in 18 h of reaction time for  $[\text{Mo}^{\text{VI}}\text{O}_2(\text{L}^4)]$  (**4**). These results again can directly be correlated with the electronic environment of the *cis*- $[\text{MoO}_2]^{2+}$  core of the catalyst during the catalytic process and its consequences on the reaction mechanism.

The electron withdrawing chloro group exerts an –I effect, destabilizing the reaction intermediate and consequently complex **4** gives the lowest conversion of 89 %. The naphthyl ring reduces the steric hindrance at the *ortho* position, stabilizing the reaction intermediate due to enhanced conjugation and consequently complex **5** gives highest conversion of 100 %. Other substituents have intermediate effect. In 4-chlorobenzoin the reaction intermediate is more stable due to presence of –chloro group at para position which enhance the electron donation through conjugation. Because of that we get the excellent conversion which supports the mechanism.