

## Electronic Supplementary Information (ESI)

### Solventless, Selective and Catalytic Oxidation of Primary, Secondary and Benzylic Alcohols by Merrifield Resin Supported Molybdenum(VI) Complex with H<sub>2</sub>O<sub>2</sub> as an Oxidant

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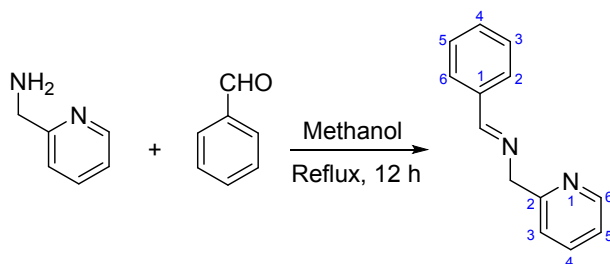
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## Synthesis of homogeneous dioxomolybdenum(VI) Schiff base complex (SB-Mo):

In order to compare the reactivity of the heterogeneous **MR-SB-Mo** with a homogeneous catalyst, a neat dioxomolybdenum(VI) Schiff base complex was synthesized. The ligand for the neat complex was designed in such a way that it provides almost identical coordination environment present in **MR-SB-Mo**.

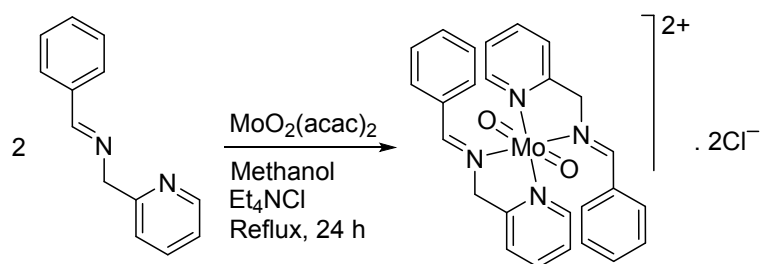
The homogeneous neat complex was synthesized in two steps as follows.

### (a) Synthesis of the ligand



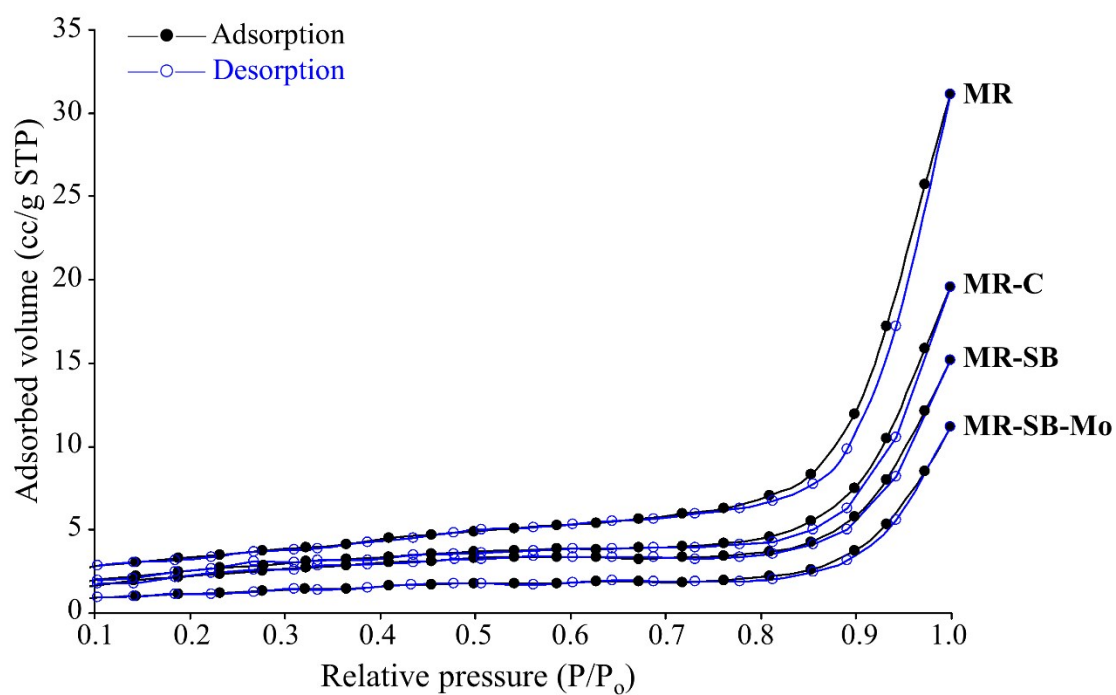
In the typical procedure, the Schiff base ligand was synthesized by refluxing 2.00 g, 18.5 mmol of 2-(aminomethyl)pyridine and 1.96 g, 18.5 mmol of benzaldehyde in 20 mL methanol for 12 h. 1-2 drops of glacial acetic acid was added as catalyst. After completion of the reaction, methanol was removed under reduced pressure and the solid obtained as such was washed thrice with hexane. Finally, the product was dried *in vacuo* (3.58 g, 18.2 mmol, 98.4%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 5.05 (s, 1 H, -CH<sub>2</sub>-), 7.10-7.21 (m, 2 H, Py-H<sub>3,5</sub>), 7.52-7.61 (m, 3 H, Ph-H<sub>3,4,5</sub>), 7.61-7.75 (m, 3 H, Py-H<sub>4</sub> and Ph-H<sub>2,6</sub>), 8.61 (m, 1 H, Py-H<sub>6</sub>), 8.76 (s, 1 H, -CH=N-) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>): 65.9, 121.1, 121.9, 128.6, 129.7, 131.3, 135.8, 136.8, 148.7, 160.3, 162.4 ppm. Elemental analyses for C<sub>13</sub>H<sub>12</sub>N<sub>2</sub> calculated: C, 79.56; H, 6.16; N, 14.27%; found: C, 79.42; H, 6.28; N, 14.05%.

### (b) Synthesis of the neat complex, SB-Mo



1.00 g, 5.1 mmol of the Schiff base ligand and 0.85 g, 2.6 mmol of MoO<sub>2</sub>(acac)<sub>2</sub> were dissolved in 20 mL methanol. To this, 1.69 g, 10.2 mmol of Et<sub>4</sub>NCl (2 equiv. of Schiff base) dissolved in 5 mL of methanol was added. The resulting solution was refluxed for 24 h. After completion of the reaction, the methanol was removed under reduced pressure and the solids were washed thrice with cold dichloromethane:acetonitrile (2:1). Finally, the product was washed thrice with hexane and dried *in vacuo* (1.12 g, 1.9 mmol, 73.1%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 5.08 (s, 2 H, -CH<sub>2</sub>-), 7.18-7.31 (m, 4 H, Py-H<sub>3,5</sub>), 7.51-7.63 (m, 6 H, Ph-H<sub>3,4,5</sub>), 7.63-7.76 (m, 6 H, Py-H<sub>4</sub> and Ph-H<sub>2,6</sub>), 8.74 (m, 2 H, Py-H<sub>6</sub>), 8.98 (s, 2 H, -CH=N-) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>): 66.2, 122.3, 123.1, 128.8, 129.9, 131.1, 136.5, 137.2, 150.3, 161.8,

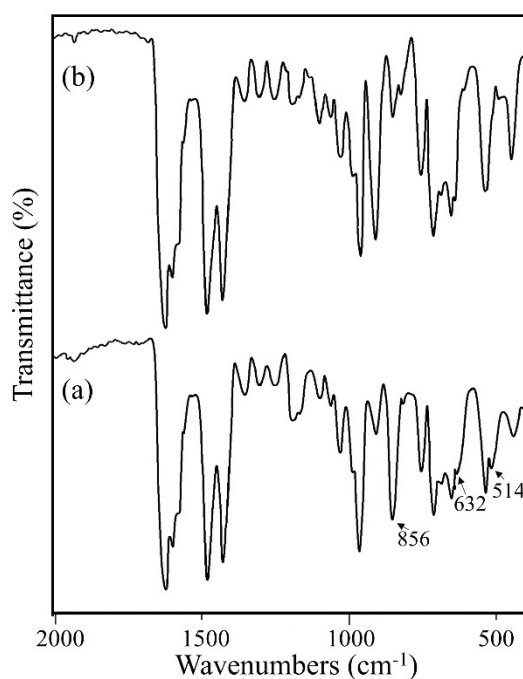
165.7 ppm. MS (ESI+,  $m/z$ ) calculated for  $C_{26}H_{23}MoN_4O_2$   $[M - H]^+$   $m/z = 521.1$ , found 521.1. Elemental analyses for  $C_{26}H_{24}Cl_2MoN_4O_2$  calculated: C, 52.81; H, 4.09; N, 9.47; Mo, 16.23%; found: C, 52.58; H, 3.89; N, 9.34; Mo, 16.08%.



**Fig. S1** The  $N_2$  adsorption–desorption isotherms of MR, MR-C, MR-SB and MR-SB-Mo.

### Isolation of peroxomolybdenum(VI) complex from MR-SB-Mo:

The peroxomolybdenum(VI) complex was formed by treating the **MR-SB-Mo** with excess 30% H<sub>2</sub>O<sub>2</sub>. In the typical procedure, 0.20 g of solid **MR-SB-Mo** was kept in an ice-bath at temperature below 4 °C. Subsequently, 0.50 ml of 30% H<sub>2</sub>O<sub>2</sub> was added to it and allowed the reaction mixture to stand for 4 h (below 4 °C) with occasional stirring. During this time, the polymeric beads became reddish in color. The solid compound was separated by filtration, washed repeatedly with acetonitrile (3 × 3 ml), dried in *vacuo* for 8 h and stored in cool and dry place. The IR spectra shown below were recorded after drying (a) and two days later (b).



**Fig. S2** FT-IR spectra of isolated peroxomolybdenum(VI) complex after (a) drying and (b) two days.

**Table S1** Comparison of catalytic activity for the reported molybdenum-based catalysts towards oxidation of benzyl alcohol.

Sl. No.	Catalyst	Oxidant	TON	TOF (h <sup>-1</sup> )	Ref.
1	CpMo(CO) <sub>3</sub> (C≡CPh)	H <sub>2</sub> O <sub>2</sub>	396	49.5	[1]
2	H <sub>5</sub> PV <sub>2</sub> Mo <sub>10</sub> O <sub>40</sub>	O <sub>2</sub>	405	25.3	[2]
3	PMo <sub>11</sub> / Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O <sub>2</sub>	1125	47	[3]
4	PMA/VAMO	H <sub>2</sub> O <sub>2</sub>	24		[4]
5	PyC <sub>4</sub>	H <sub>2</sub> O <sub>2</sub>	323	190	[5]
6	Polyaniline-MoO <sub>2</sub> (acac) <sub>2</sub>	O <sub>2</sub>	29	2.4	[6]
7	PPh <sub>4</sub> [MoO(O <sub>2</sub> ) <sub>2</sub> (HPEOH)]	H <sub>2</sub> O <sub>2</sub>	630	26.25	[7]
8	[MoO(O <sub>2</sub> ) <sub>2</sub> QO][PPh <sub>4</sub> ]	H <sub>2</sub> O <sub>2</sub>	840	56	[8]
9	[(MoO <sub>2</sub> ) <sub>2</sub> (slsch)(H <sub>2</sub> O) <sub>2</sub> ]	H <sub>2</sub> O <sub>2</sub>	431	144	[9]
10	MoO <sub>2</sub> (acac) <sub>n</sub> -NAP-MgO	O <sub>2</sub>	16.2	1.35	[10]
11	[MoO(O <sub>2</sub> ) <sub>2</sub> (TEDA) <sub>2</sub> ]	H <sub>2</sub> O <sub>2</sub>	96	16	[11]
12	CPS-[MoO <sub>2</sub> (ALGL) <sub>2</sub> ]	O <sub>2</sub>	100		[12]
13	Ph <sub>3</sub> P(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>3</sub> [MoO(O <sub>2</sub> ) <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> )]·2H <sub>2</sub> O	H <sub>2</sub> O <sub>2</sub>	49	8	[13]
<b>14</b>	<b>MR-SB-Mo</b>	<b>H<sub>2</sub>O<sub>2</sub></b>	<b>990</b>	<b>660</b>	<b>This work</b>
<b>15</b>	<b>SB-Mo</b>	<b>H<sub>2</sub>O<sub>2</sub></b>	<b>530</b>	<b>353</b>	<b>This work</b>

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