

## Supporting Information

### Selective aerobic benzylic C-H oxidation co-catalyzed by N-hydroxyphthalimide and Keplerate $\{\text{Mo}_{72}\text{V}_{30}\}$ nanocluster

Abdolreza Rezaeifard,\* Ashkan Khoshyan, Maasoumeh Jafarpour,\* and Mehrdad Pourtahmasb

Catalysis Research Laboratory, Department of Chemistry, Faculty of Science, University of Birjand, Birjand, 97179-414 Iran.

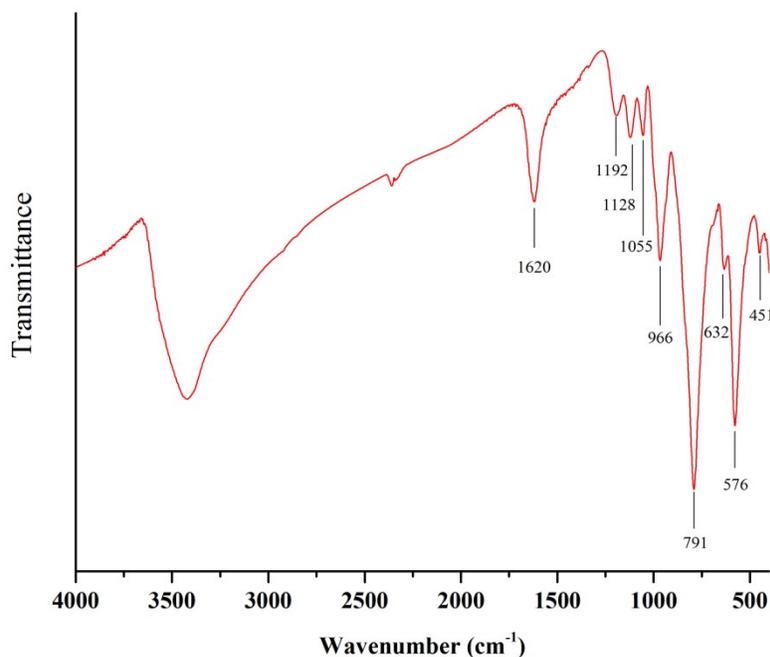


Fig. S1. FT-IR spectra of  $\{\text{Mo}_{72}\text{V}_{30}\}$

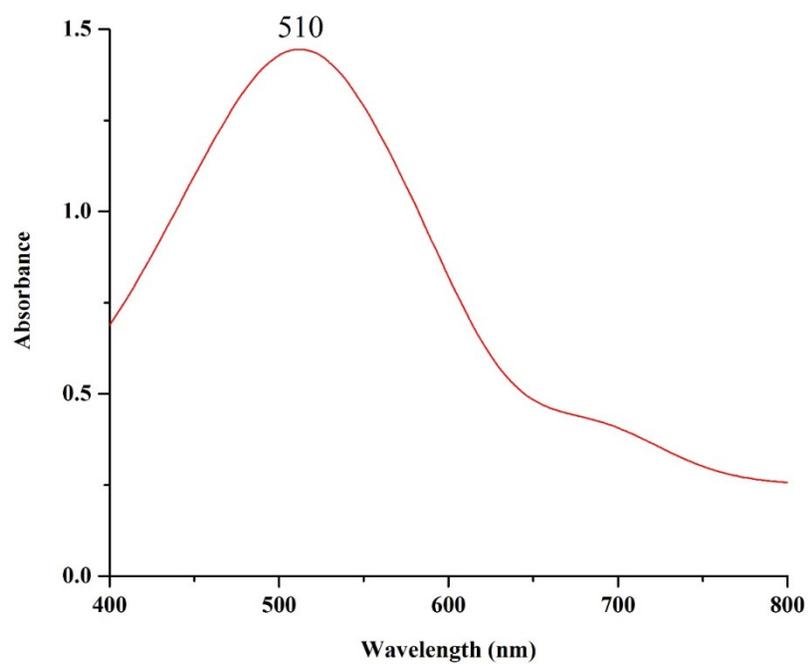


Fig. S2. UV-Vis spectra of {Mo<sub>72</sub>V<sub>30</sub>}

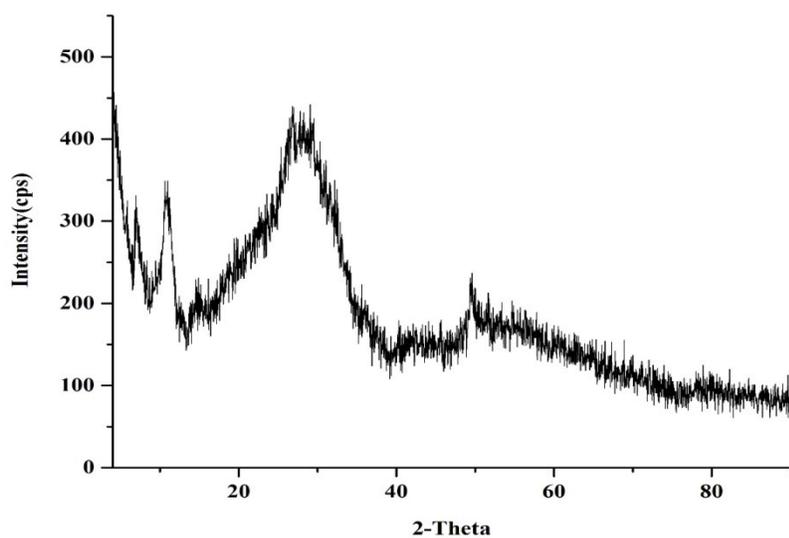


Fig. S3. XRD pattern of {Mo<sub>72</sub>V<sub>30</sub>}

### **-Synthesis of 1-Methyl-3-octadecaneimidazolium bromide ([C<sub>18</sub>mim]Br)**

1-Methyl-3-octadecaneimidazolium bromide ([C<sub>18</sub>mim]Br) was prepared according to literature.<sup>1</sup> 0.79 mL (10 mmol) 1-methyl imidazole and 4 g (12 mmol) of C<sub>18</sub>H<sub>37</sub>Br was dissolved in 15 mL acetonitrile. The resulting solution was refluxed for 24 h. After, cooling in an ice bath; a precipitate appeared. The latter was isolated by filtration and washed with diethyl ether.

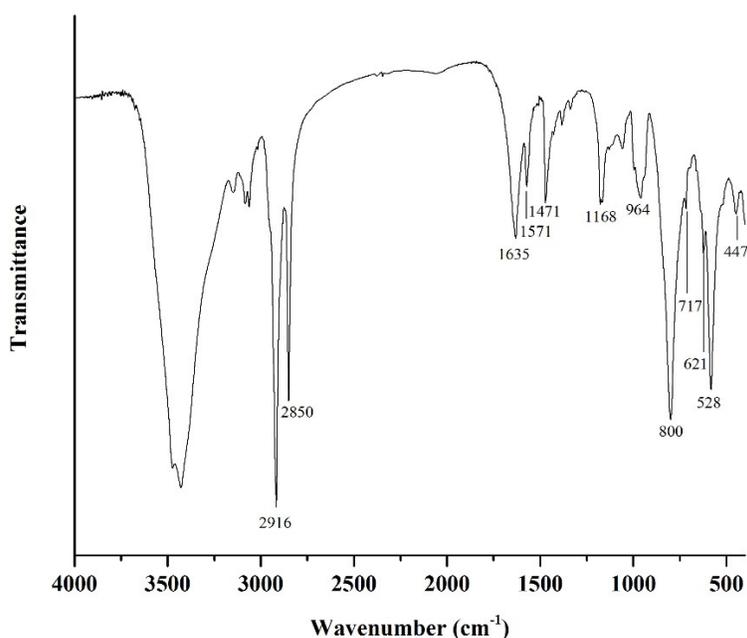
### **-Synthesis of {C<sub>18</sub>mim-Mo<sub>72</sub>V<sub>30</sub>} (C<sub>18</sub>mim: 1-Methyl-3-octadecaneimidazolium)**

{C<sub>18</sub>mim-Mo<sub>72</sub>V<sub>30</sub>} was prepared for the first time according to procedure reported for the synthesis of {C<sub>18</sub>mim-Mo<sub>132</sub>}.<sup>2</sup> The Keplerate-based material was prepared as follows: 0.105g (5.25×10<sup>-3</sup> mmol) {Mo<sub>72</sub>V<sub>30</sub>} was dissolved in 30 mL bidistilled water and then a chloroform (70 mL) solution containing 0.25g (0.6 mmol) [C<sub>18</sub>mim]Br was added. The mixture was stirred for 1 h, where the Keplerate was totally transferred into the organic phase as indicated by the colorless aqueous phase. The organic phase was then separated and the target material was precipitated from the organic phase by addition of an excess of ethanol, isolated by filtration, washed with ethanol and dried in air. Anal. Calcd (%): (mimC<sub>18</sub>H<sub>37</sub>)<sub>22</sub>Na<sub>2</sub>K<sub>10</sub>(VO)[Mo<sub>72</sub>V<sub>30</sub>O<sub>282</sub>(SO<sub>4</sub>)<sub>12</sub>(H<sub>2</sub>O)<sub>m</sub>]<sub>n</sub>H<sub>2</sub>O, n+m=26 (M=22455.7gmol<sup>-1</sup>): C, 25.86, N, 2.74, H, 4.44, S, 1.71. Found: C, 25.90, N, 2.97, H, 4.41, S, 1.47. IR/cm<sup>-1</sup>: 2916 (s), 2850 (s), 1635 (w), 1571 (w), 1471 (m), 1168 (m), 964 (m), 800 (s), 717 (w), 621 (w), 528 (s), 447 (w). The FT-IR, UV-Vis spectra, XRD and TGA of as-prepared {C<sub>18</sub>mim -Mo<sub>72</sub>V<sub>30</sub>} are given as Fig. S4-S7 in supporting information.

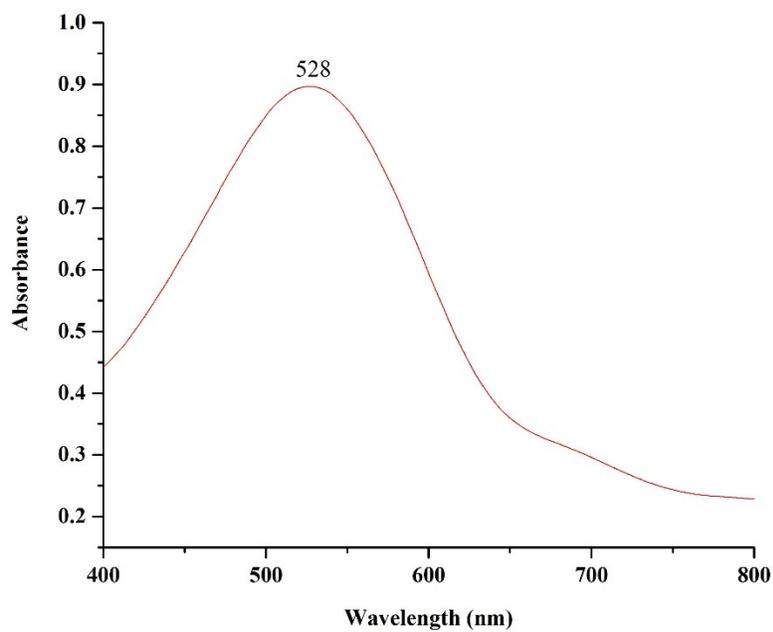
### **-Synthesis of {DODA-Mo<sub>72</sub>V<sub>30</sub>} (DODA: Dioctadecyldimethylammonium)**

{DODA-Mo<sub>72</sub>V<sub>30</sub>} was prepared for the first time according to procedure of {DODA-Mo<sub>132</sub>}.<sup>3</sup> 0.14g (7.3×10<sup>-3</sup> mmol) {Mo<sub>72</sub>V<sub>30</sub>} of the precursor was solubilized in bidistilled water (30 mL) to give a dark purple solution. To this solution was added a large excess of dioctadecyldimethylammonium chloride (DODACl, 0.52 g, 0.89 mmol) solubilized in chloroform (70 mL) under vigorous stirring during 3 hours at room temperature. After almost complete extraction of Keplerate into the organic phase, the latter is separated by decantation and absolute ethanol (about 200 mL) is added, provoking the precipitation of the target compound as a dark purple powder which was isolated by filtration, washed with ethanol and dried in air.

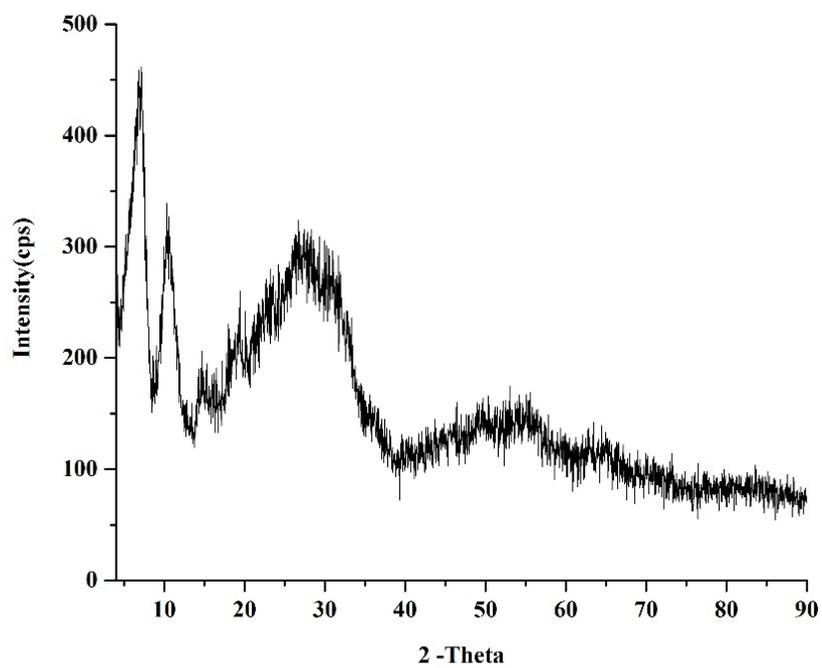
Anal. Calcd. (%):  $(\text{DODA})_{23}\text{Na}_2\text{K}_9(\text{VO})[\text{Mo}_{72}\text{V}_{30}\text{O}_{282}(\text{SO}_4)_{12}(\text{H}_2\text{O})_m].n\text{H}_2\text{O}$ ,  $m+n=15$  ( $M=27510\text{g mol}^{-1}$ ): C, 38.12, N, 1.17, H, 6.79, S, 1.39. Found: C, 38.19, N, 1.72, H, 6.46, S, 1.41. IR/ $\text{cm}^{-1}$ : 2922 (s), 2850 (s), 1637 (w), 1465 (m), 1141 (w), 1058 (w), 968 (m), 800 (s), 638 (w), 584 (s), 447 (w). The FT-IR, UV-Vis spectra, XRD and TGA of as-prepared  $\{\text{DODA-Mo}_{72}\text{V}_{30}\}$  are given as Fig. S8-S11 in supporting information.



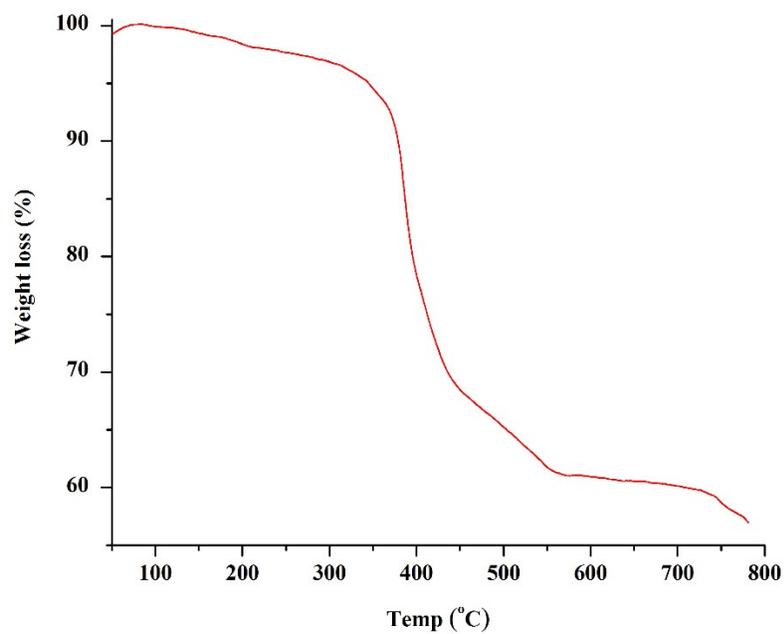
**Fig. S4.** FT-IR spectra of  $\{\text{C}_{18}\text{mim-Mo}_{72}\text{V}_{30}\}$



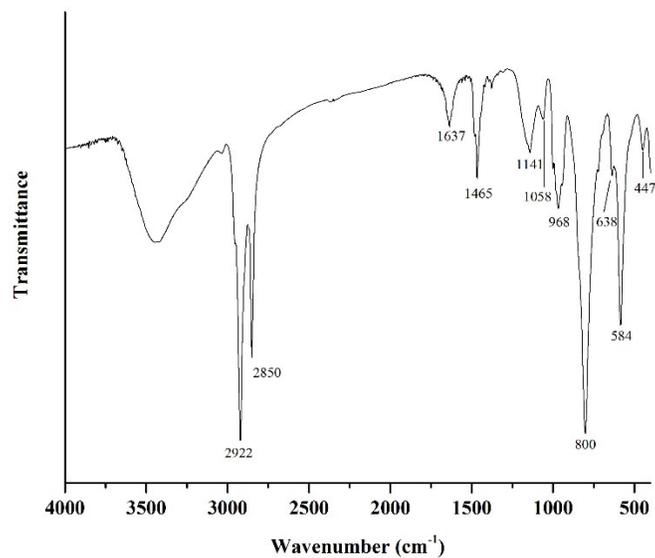
**Fig. S5.** UV-Vis spectra of {C<sub>18</sub>mim-Mo<sub>72</sub>V<sub>30</sub>}



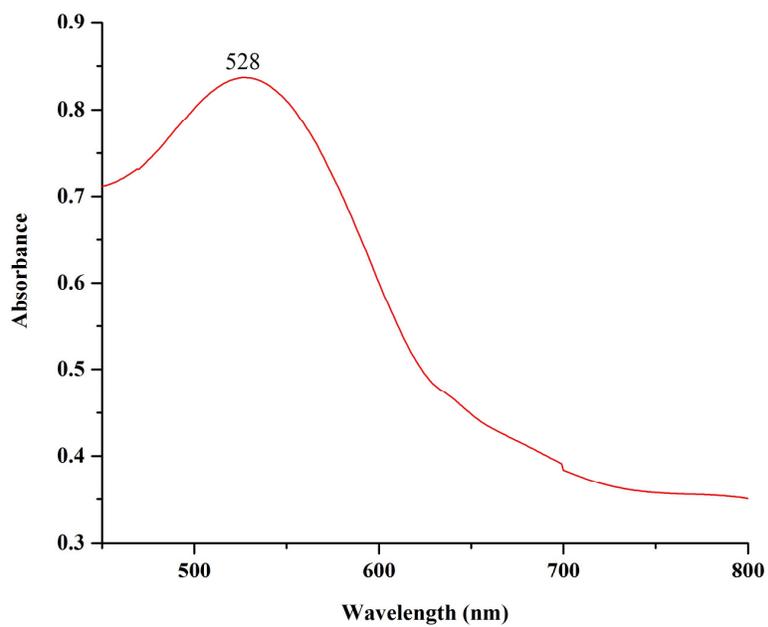
**Fig. S6.** XRD pattern of {C<sub>18</sub>mim-Mo<sub>72</sub>V<sub>30</sub>}



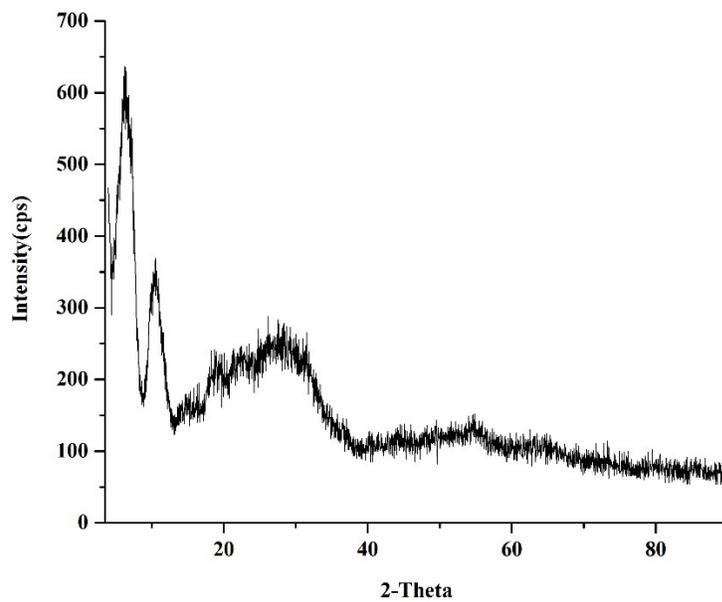
**Fig. S7.** TGA analysis of {C<sub>18</sub>mim-Mo<sub>72</sub>V<sub>30</sub>}



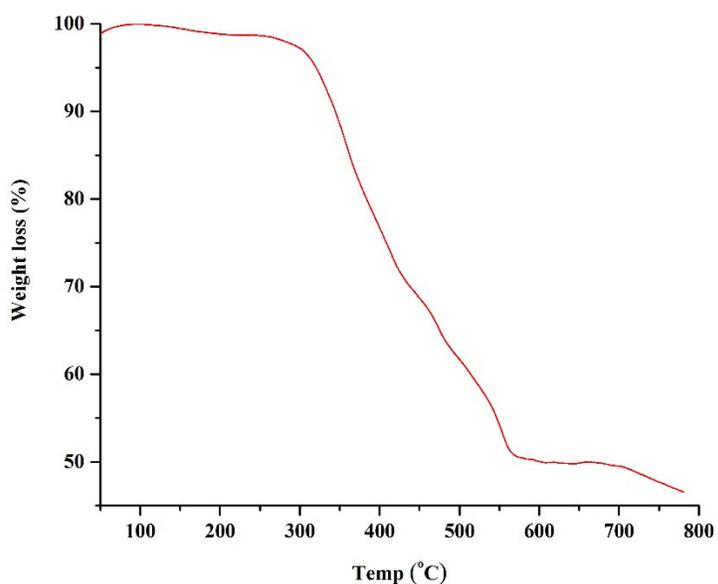
**Fig. S8.** FT-IR spectra of {DODA-Mo<sub>72</sub>V<sub>30</sub>}



**Fig. S9.** UV-Vis spectra of {DODA-Mo<sub>72</sub>V<sub>30</sub>}



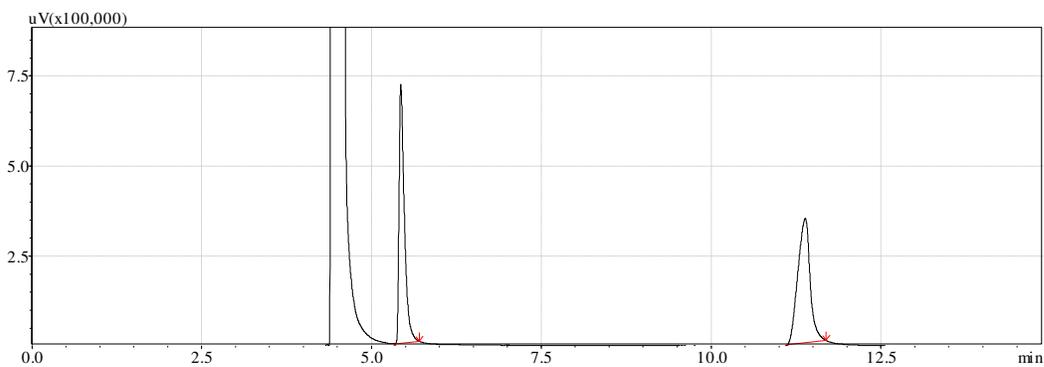
**Fig. S10.** XRD pattern of {DODA-Mo<sub>72</sub>V<sub>30</sub>}



**Fig. S11.** TGA analysis of {DODA-Mo<sub>72</sub>V<sub>30</sub>}

**Fig. S12.** GC traces of standard samples to draw the calibration plot for acetophenone analysis (Table 4, entry 10) using an internal standard method

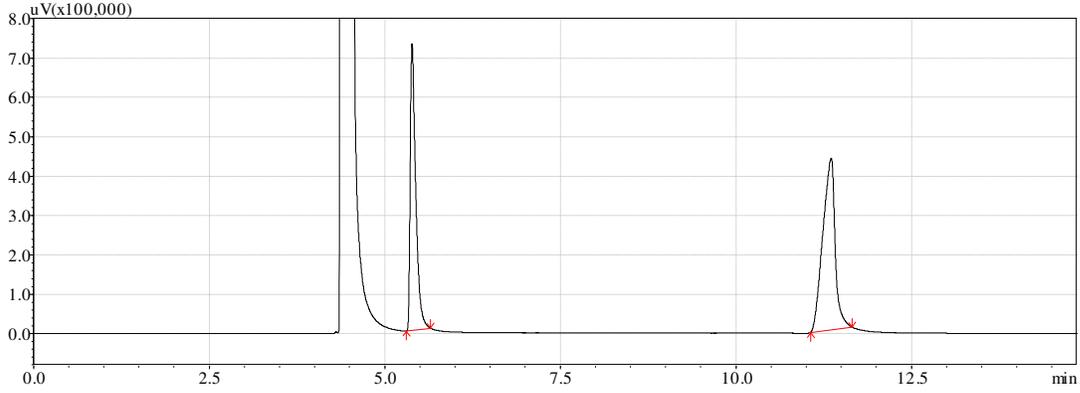
**Standard A) 45 mg of Acetophenone + 55 mg Chlorobenzene (internal standard) in 1 ml EtOAc**



Peak#	Ret.Time	Area	Compound Name
1	5.433	3884221.8	Chlorobenzene
2	11.386	4323755.9	Acetophenone

Concentration of Acetophenone/ Concentration of Chlorobenzene = 1.11

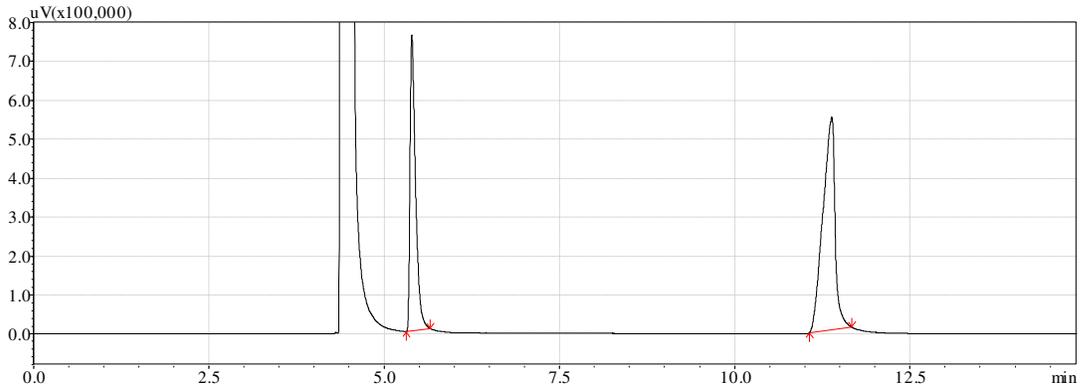
**Standard B) 55 mg of Acetophenone + 55 mg Chlorobenzene (internal standard) in 1 ml EtOAc**



Peak#	Ret.Time	Area	Compound Name
1	5.389	3943072.7	Chlorobenzene
2	11.358	5329802.5	Acetophenone

Concentration of Acetophenone/ Concentration of Chlorobenzene = 1.35

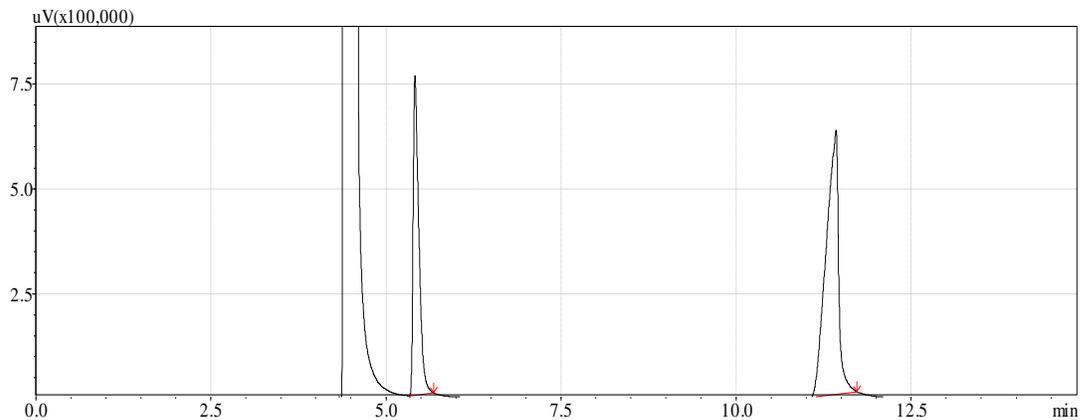
**Standard C) 65 mg of Acetophenone + 55 mg Chlorobenzene (internal standard) in 1 ml EtOAc**



Peak#	Ret.Time	Area	Compound Name
1	5.396	4144634.5	Chlorobenzene
2	11.384	6632839.8	Acetophenone

Concentration of Acetophenone/ Concentration of Chlorobenzene = 1.60

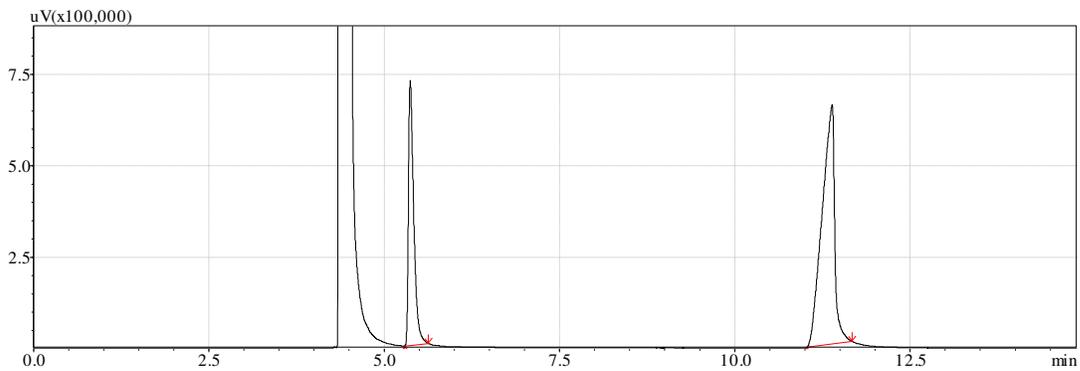
**Standard D) 75 mg of Acetophenone + 55 mg Chlorobenzene (internal standard) in 1 ml EtOAc**



Peak#	Ret.Time	Area	Compound Name
1	5.415	4325191.9	Chlorobenzene
2	11.428	7831586.6	Acetophenone

Concentration of Acetophenone/ Concentration of Chlorobenzene = 1.81

**Standard E) 85 mg of Acetophenone + 55 mg Chlorobenzene (internal standard) in 1 ml EtOAc**

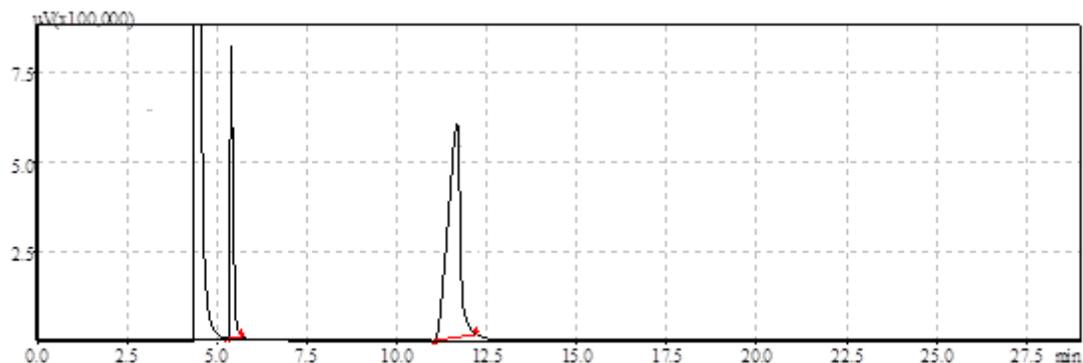


Peak#	Ret.Time	Area	Compound Name
1	5.372	3758925.8	Chlorobenzene
2	11.386	8181693.1	Acetophenone

Concentration of Acetophenone/ Concentration of Chlorobenzene = 2.17

## GC trace of oxidation product

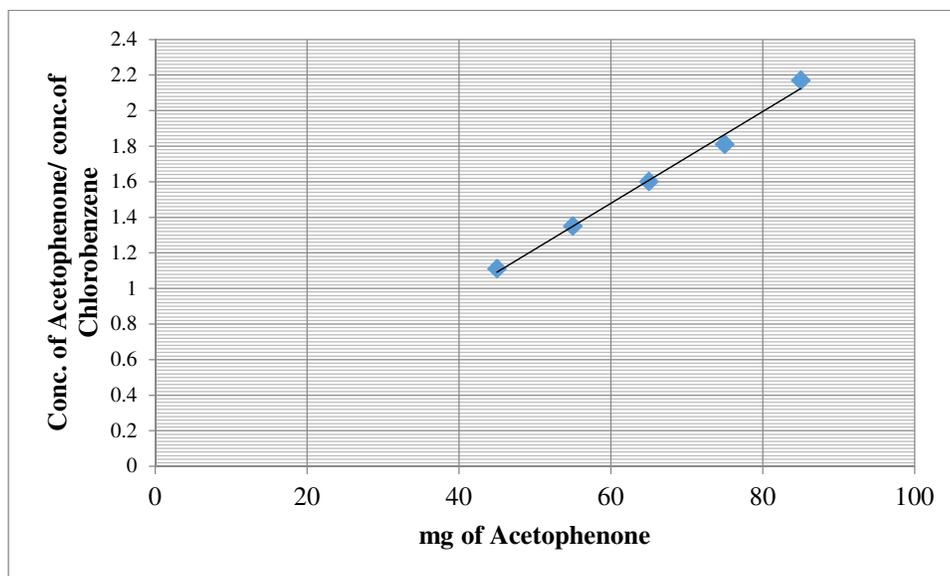
Reaction product (unknown concentration of Acetophenone resulting from 1-phenyl ethanol oxidation, Table 4, entry 10) + 55 mg Chlorobenzene (internal standard) in 1 ml EtOAc



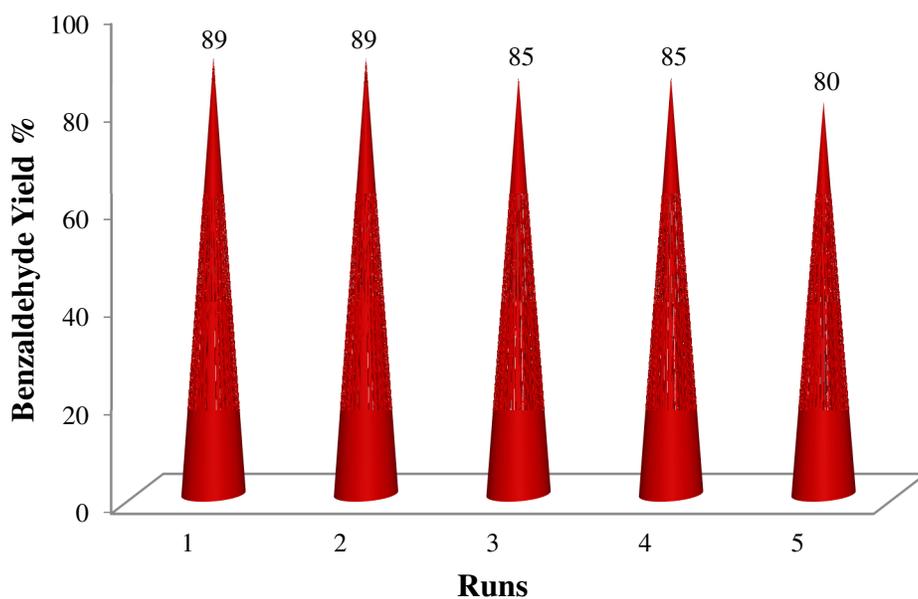
Peak#	Ret.Time	Area	Compound Name
1	5.398	4833867.9	Chlorobenzene
2	11.341	6332366.9	Acetophenone

Concentration of Acetophenone/ Concentration of Chlorobenzene = 1.31

Linear fit of standard data to find out unknown concentration of acetophenone (calibration plot)



From the calibration plot, the concentration of acetophenone in the oxidation of 1-phenyl ethanol (0.5 mmol) with O<sub>2</sub>, co-catalyzed by {Mo<sub>72</sub>V<sub>30</sub>} (5 mg) and NHPI (7.5 mg) in 1 ml EtOAc was found to be 53 mg after 2.5 h which displays 88% yield (100% conversion was observed at this time according to GC trace).



**Fig. S13.** Catalyst recycling in the aerobic oxidation of benzyl alcohol

**References:**

- 1 N. Watfa, S. Floquet, E. Terazzi, M. Haouas, W. Salomon, V. S. Korenev, F. Taulelle, L. Guénée, A. Hijazi, D. Naoufal, C. Piguet and E. Cadot *Soft Matter*, 2015, **11**, 1087–1099.
- 2 N. Watfa, S. Floquet, E. Terazzi, W. Salomon, L. Guénée, K. Buchwalder, A. Hijazi, D. Naoufal, C. Piguet and E. Cadot, *Inorganics*, 2015, **3**, 246–266.
- 3 S. Floquet, E. Terazzi, A. Hijazi, L. Gueneee, C. Piguet and E. Cadot, *New J. Chem.*, 2012, **36**, 865–868.