

Effect of N-based additive on the optimization of liquid phase oxidation of bicyclic, cyclic and aromatic alcohols catalyzed by dioxidomolybdenum(VI) and oxidoperoxidomolybdenum(VI) complexes

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Table S1 Detail of thermogravimetric analysis of complexes

Compounds	Decomp. Temp.	% MeOH		Decomp. Temp.	% MoO ₃	
	[MeOH/ °C]	Calc.	Obs.	[MoO ₃ / °C]	Calc.	Obs.
[Mo ^{VI} O ₂ (L ¹)(MeOH)] 1	159-230	6.00	5.94	553	27.01	26.98
[Mo ^{VI} O ₂ (L ²)(MeOH)] 2	135-200	6.54	6.15	540	29.47	29.00
[Mo ^{IV} O(O ₂)(L ¹)(MeOH)] 3	155-217	5.85	6.13	544	26.32	25.74
[Mo ^{IV} O(O ₂)(L ²)(MeOH)] 4	150-190	6.36	6.47	532	28.63	28.11

Table S2 Conversion of fenchyl alcohol (1.54 g, 0.010 mol) using [Mo^{VI}O₂(L¹)(MeOH)] **1** as catalyst precursor in presence of NEt₃ (0.05 g, 0.0005 mol) in 6 h of reaction time under different reaction conditions

Entry No.	Catalyst [g (mmol)]	H ₂ O ₂ [g (mol)]	CH ₃ CN [mL]	Temp. [°C]	Conv. [%]
1	0.001 (1.8×10 ⁻³)	3.39 (0.030)	5	80	62
2	0.002 (3.8×10 ⁻³)	3.39 (0.030)	5	80	71
3	0.003 (5.6×10⁻³)	3.39 (0.030)	5	80	74
4	0.003 (5.6×10 ⁻³)	2.26 (0.020)	5	80	69
5	0.003 (5.6×10 ⁻³)	4.52 (0.040)	5	80	80
6	0.003 (5.6×10 ⁻³)	3.39 (0.030)	7	80	70
7	0.003 (5.6×10 ⁻³)	3.39 (0.030)	9	80	66
8	0.003 (5.6×10 ⁻³)	3.39 (0.030)	5	70	72
9	0.003 (5.6×10 ⁻³)	3.39 (0.030)	5	60	63

Table S3 Conversion of benzyl alcohol (0.54 g, 0.005 mol) using [Mo^{VI}O₂(L¹)(MeOH)] (**1**) as catalyst precursor and in presence of NEt₃ (0.05 g, 0.0005 mol) in 5 h of reaction time under different reaction conditions.

Entry No.	Catalyst [g (mmol)]	H ₂ O ₂ [g (mmol)]	CH ₃ CN [mL]	Temp. [°C]	Conv. [%]
1	0.001 (1.8×10 ⁻³)	1.13 (10)	5	80	49
2	0.002 (3.8×10⁻³)	1.13 (10)	5	80	66
3	0.003 (5.6×10 ⁻³)	1.13 (10)	5	80	56
4	0.002 (3.8×10 ⁻³)	0.57 (5)	5	80	52
5	0.002 (3.8×10 ⁻³)	1.69 (15)	5	80	45
6	0.002 (3.8×10 ⁻³)	1.13 (10)	7	80	53
7	0.002 (3.8×10 ⁻³)	1.13 (10)	9	80	48
8	0.002 (3.8×10 ⁻³)	1.13 (10)	5	70	56
9	0.002 (3.8×10 ⁻³)	1.13 (10)	5	60	43

Table S4 Conversion of cumic alcohol (0.75 g, 0.005 mol) using [Mo^{VI}O₂(L¹)(MeOH)] (**1**) as catalyst precursor and in presence of NEt₃ (0.05 g, 0.0005 mol) in 8 h of reaction time under different reaction conditions.

Entry No.	Catalyst [g (mmol)]	H ₂ O ₂ [g (mol)]	CH ₃ CN [mL]	Temp. [°C]	Conv. [%]
1	0.001 (1.8×10 ⁻³)	1.69 (0.015)	5	80	37
2	0.002 (3.8×10 ⁻³)	1.69 (0.015)	5	80	45
3	0.003 (5.6×10 ⁻³)	1.69 (0.015)	5	80	43
4	0.002 (3.8×10⁻³)	1.13 (0.010)	5	80	59
5	0.002 (3.8×10 ⁻³)	2.26 (0.020)	5	80	40
6	0.002 (3.8×10 ⁻³)	1.13 (0.010)	3	80	42
7	0.002 (3.8×10 ⁻³)	1.13 (0.010)	7	80	53
8	0.002 (3.8×10 ⁻³)	1.13 (0.010)	5	70	49
9	0.002 (3.8×10 ⁻³)	1.13 (0.010)	5	60	38

Table S5 Conversion of benzyl alcohol ^a and the selectivity of different products.

Catalysts	With additive				Without additive			
	Conv. [%]	a	b	c	Conv. [%]	a	b	c
[Mo ^{VI} O ₂ (L ¹)(MeOH)] 1	66	23	64	13	59	18	67	11
[Mo ^{VI} O ₂ (L ²)(MeOH)] 2	61	21	60	19	54	15	69	16
[Mo ^{VI} O(O ₂)(L ¹)(MeOH)] 3	74	33	52	15	68	31	55	14
[Mo ^{VI} O(O ₂)(L ²)(MeOH)] 4	69	26	49	23	63	17	62	21

^a a: benzaldehyde, b: benzoic acid and c: benzylbenzoate.

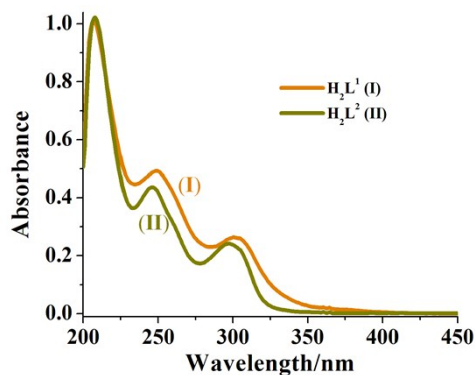


Fig. S1 Electronic spectra (200 to 450 nm range) of two ligands, H₂L¹ **I** and H₂L² **II** recorded in methanol solution. Solution concentration of ligands: H₂L¹: 3.6×10⁻⁴ M and H₂L²: 4.3×10⁻⁴ M.

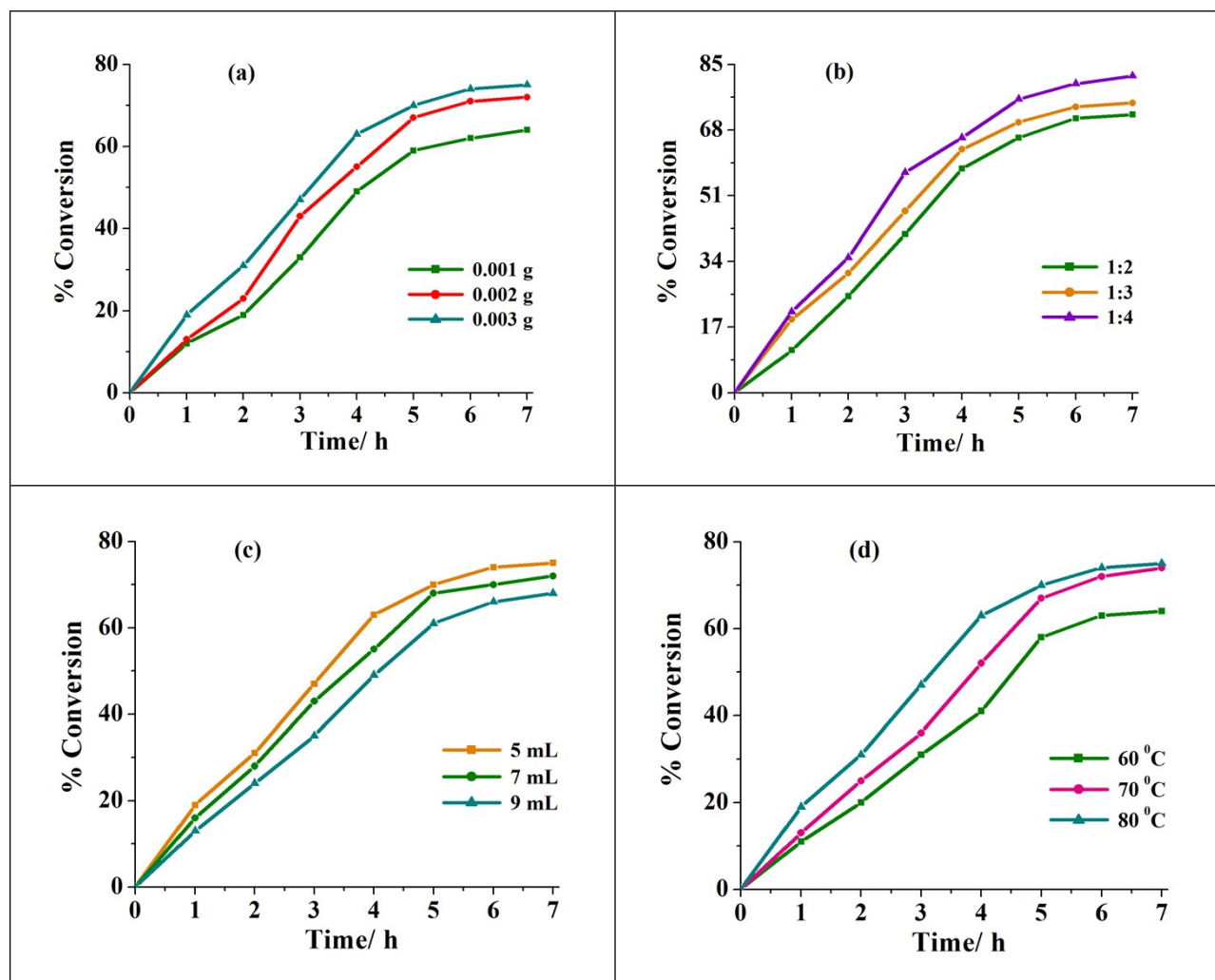


Fig. S2 (a) Effect of variation of amounts of catalyst $[\text{Mo}^{\text{VI}}\text{O}_2(\text{L}^1)(\text{MeOH})]$ (**1**) (0.001, 0.002 and 0.003 g) on the oxidation of fenchyl alcohol. Reaction conditions: fenchyl alcohol (1.54 g, 0.010 mol), 30% H_2O_2 (3.39 g, 0.030 mol), MeCN (5 mL), NEt_3 (0.05 g, 0.0005 mol) at 80 °C for 6 h. (b) Effect of amounts of oxidant i.e. H_2O_2 (0.020, 0.030 and 0.040 mol) on the oxidation of fenchyl alcohol. Reaction conditions: fenchyl alcohol (1.54 g, 0.010 mol), MeCN (5 mL), **1** (0.003 g), NEt_3 (0.05 g, 0.0005 mol) at 80 °C for 6 h. (c) Effect of variation of amount of solvent (5, 7 and 9 mL) on the rate of the oxidation of fenchyl alcohol. Reaction conditions: fenchyl alcohol (1.54 g, 0.010 mol), 30% H_2O_2 (3.39 g, 0.030 mol), **1** (0.003 g), NEt_3 (0.05 g, 0.0005 mol) at 80 °C for 6 h. (d) Effect of different temperatures (60, 70 and 80 °C) on the oxidation of fenchyl alcohol. Reaction conditions: fenchyl alcohol (1.54 g, 0.010 mol), 30% H_2O_2 (3.39 g, 0.030 mol), MeCN (5 mL), **1** (0.003 g) and NEt_3 (0.05 g, 0.0005 mol).

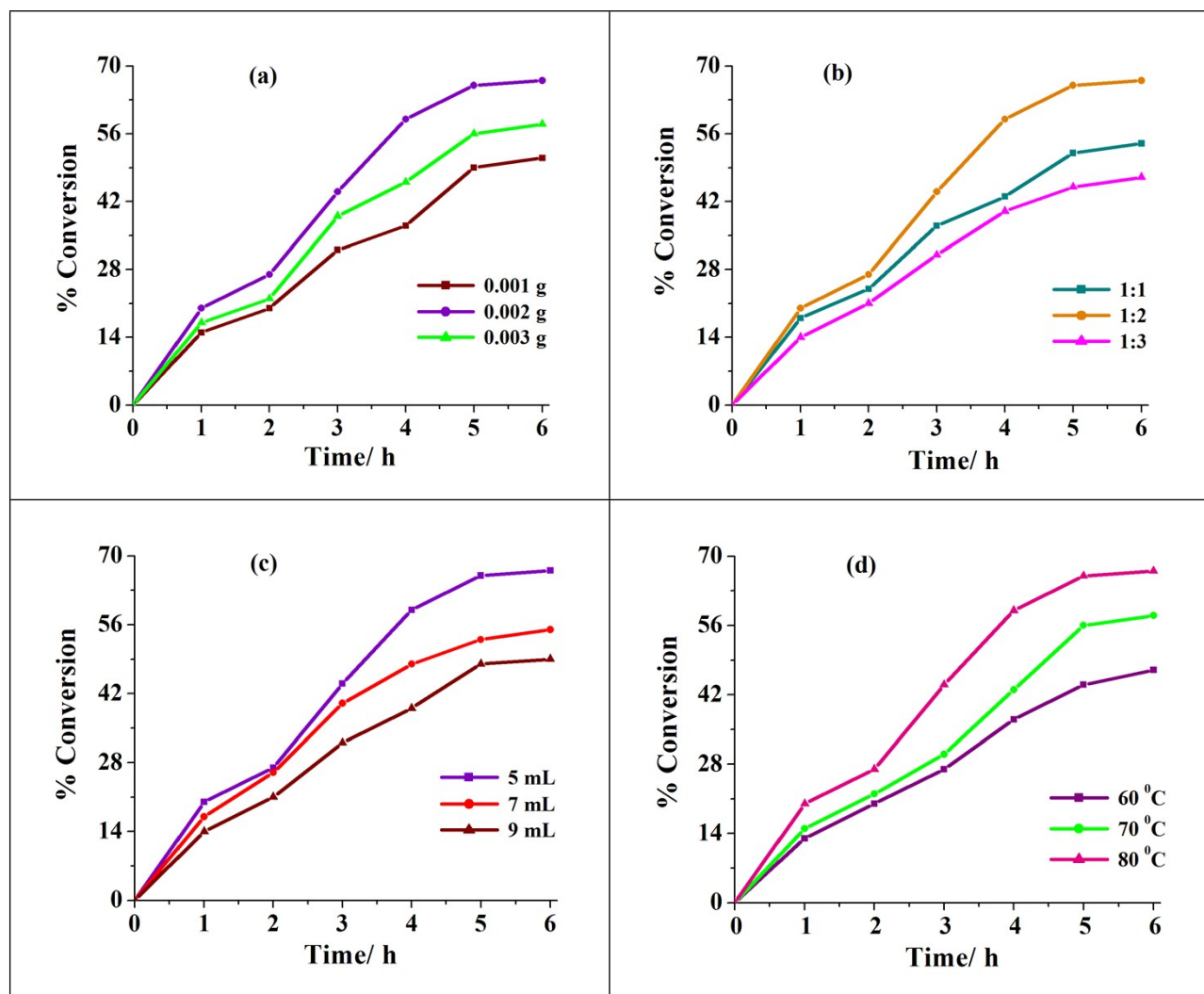


Fig. S3 (a) Effect of variation of amount of catalyst $[\text{Mo}^{\text{VI}}\text{O}_2(\text{L}^1)(\text{MeOH})]$ (**1**) on the oxidation of benzyl alcohol. Reaction conditions: benzyl alcohol (0.54 g, 0.005 mol), 30% H_2O_2 (1.13 g, 0.010 mol), MeCN (5 mL) in presence of NEt_3 (0.05 g, 0.0005 mol) at 80 °C for 5 h. (b) Effect of amount of oxidant i.e. H_2O_2 on the oxidation of benzyl alcohol. Reaction conditions: benzyl alcohol (0.54 g, 0.005 mol), MeCN (5 mL), catalyst (0.002 g) in presence of NEt_3 (0.05 g, 0.0005 mol) at 80 °C for 5 h. (c) Effect of variation of amount of solvent on the rate of the oxidation of benzyl alcohol. Reaction conditions: benzyl alcohol (0.54 g, 0.005 mol), 30% H_2O_2 (1.13 g, 0.010 mol), catalyst (0.002 g) in presence of NEt_3 (0.05 g, 0.0005 mol) at 80 °C for 5 h. (d) Effect of different temperature on the oxidation of benzyl alcohol. Reaction conditions: benzyl alcohol (0.54 g, 0.005 mol), 30% H_2O_2 (1.13 g, 0.010 mol), MeCN (5 mL) and catalysts (0.002 g) in presence of NEt_3 (0.05 g, 0.0005 mol) for 5 h.

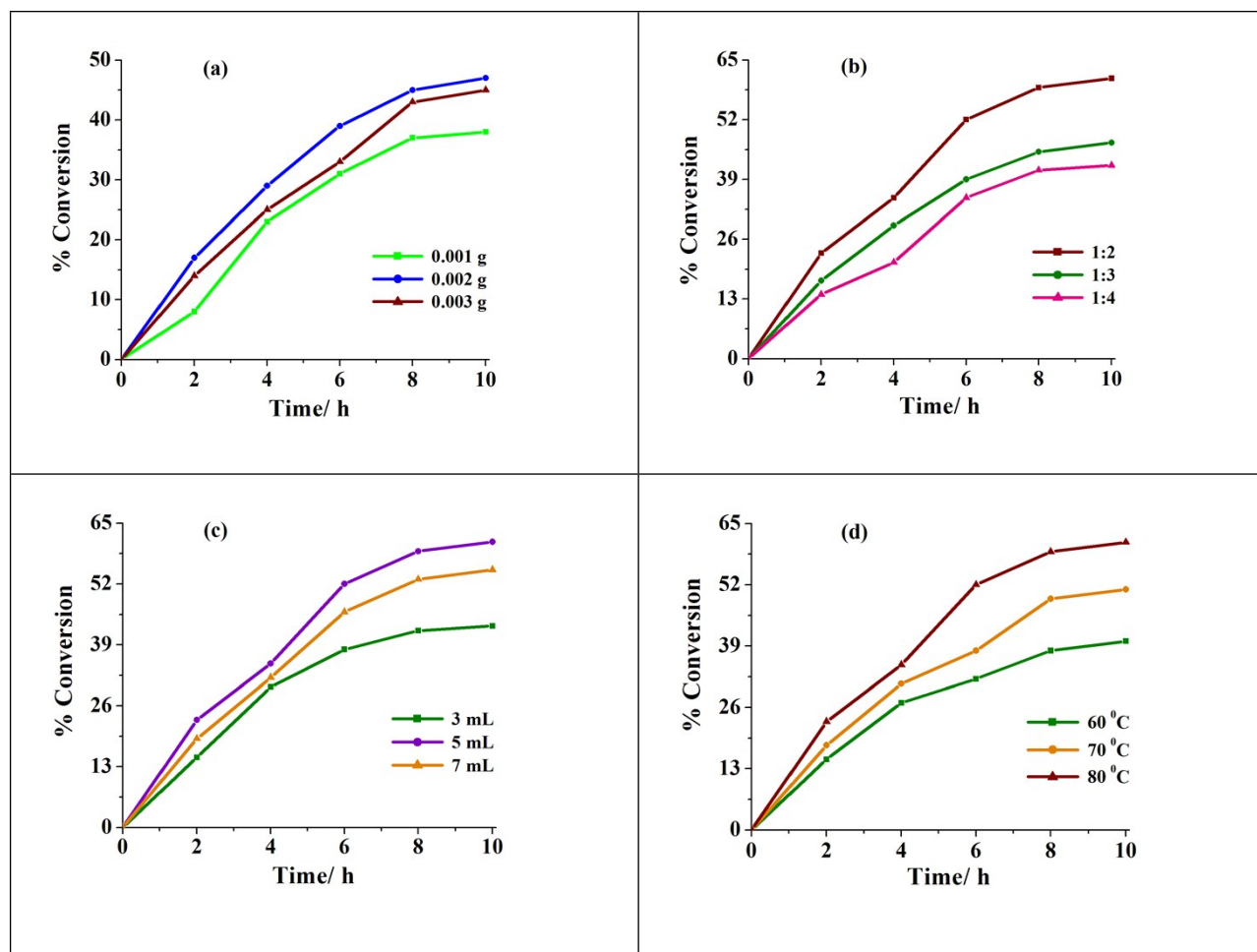


Fig. S4 (a) Effect of variation of amount of catalyst $[\text{Mo}^{\text{VI}}\text{O}_2(\text{L}^1)(\text{MeOH})]$ (**1**) on the oxidation of cumic alcohol. Reaction conditions: cumic alcohol (0.75 g, 0.005 mol), 30% H_2O_2 (1.69 g, 0.015 mol), MeCN (5 mL) in presence of NEt_3 (0.05 g, 0.0005 mol) at 80 °C for 8 h. (b) Effect of amount of oxidant i.e. H_2O_2 on the oxidation of cumic alcohol. Reaction conditions: cumic alcohol (0.75 g, 0.005 mol), MeCN (5 mL), catalyst (0.002 g) in presence of NEt_3 (0.05 g, 0.0005 mol) at 80 °C for 8 h. (c) Effect of variation of amount of solvent on the rate of the oxidation of cumic alcohol. Reaction conditions: cumic alcohol (0.75 g, 0.005 mol), 30% H_2O_2 (1.13 g, 0.010 mol), catalyst (0.002 g) in presence of NEt_3 (0.05 g, 0.0005 mol) at 80 °C for 8 h. (d) Effect of different temperature on the oxidation of cumic alcohol. Reaction conditions: cumic alcohol (0.75 g, 0.005 mol), 30% H_2O_2 (1.13 g, 0.010 mol), MeCN (5 mL) catalysts (0.002 g) in presence of NEt_3 (0.05 g, 0.0005 mol) for 8 h.

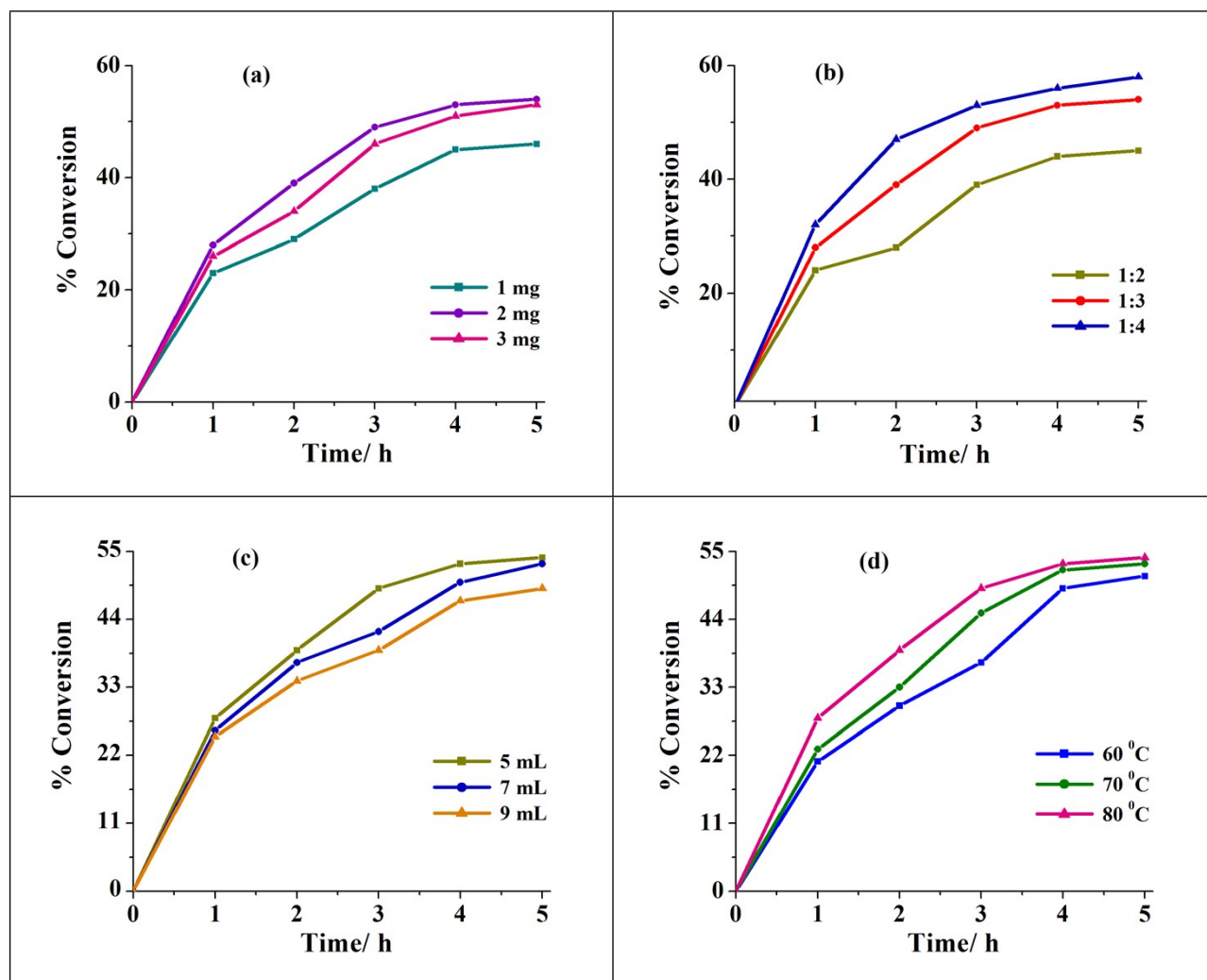


Fig. S5 (a) Effect of variation of amount of catalyst $[\text{Mo}^{\text{VI}}\text{O}_2(\text{L}^1)(\text{MeOH})]$ (**1**) on the oxidation of cyclohexanol. Reaction conditions: cyclohexanol (0.5 g, 0.005 mol), 30% H_2O_2 (1.69 g, 0.015 mol), MeCN (5 mL), NEt_3 (0.05 g, 0.0005 mol) at 80 °C for 4 h. (b) Effect of amount of oxidant i.e. H_2O_2 on the oxidation of cyclohexanol. Reaction conditions: cyclohexanol (0.5 g, 0.005 mol), MeCN (5 mL), catalyst (0.003 g), NEt_3 (0.05 g, 0.0005 mol) at 80 °C for 4 h. (c) Effect of variation of amount of solvent on the rate of the oxidation of cyclohexanol. Reaction conditions: cyclohexanol (0.5 g, 0.005 mol), 30% H_2O_2 (1.69 g, 0.015 mol), catalyst (0.003 g) in presence of NEt_3 (0.05 g, 0.0005 mol) at 80 °C for 4 h. (d) Effect of different temperature on the oxidation of cyclohexanol. Reaction conditions: cyclohexanol (0.5 g, 0.005 mol), 30% H_2O_2 (1.69 g, 0.015 mol), MeCN (7 mL), catalysts (0.003 g) in presence of NEt_3 (0.05 g, 0.0005 mol) for 4 h.