



**CATALYTIC ACTIVITY OF  $(\text{NH}_4)_{42}[\text{Mo}^{\text{VI}}_{72}\text{Mo}^{\text{V}}_{60}\text{O}_{372}(\text{CH}_3\text{COO})_{30}(\text{H}_2\text{O})_{72}]$  AS  
HIGHLY EFFICIENT RECYCLABLE CATALYST FOR THE SYNTHESIS OF  
TETRAHYDROBENZO[*B*]PYRANS IN WATER**

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**Abstract**

Application of  $(\text{NH}_4)_{42}[\text{Mo}^{\text{VI}}_{72}\text{Mo}^{\text{V}}_{60}\text{O}_{372}(\text{CH}_3\text{COO})_{30}(\text{H}_2\text{O})_{72}]$ , a Keplerate-type giant-ball nanoporous isopolyoxomolybdate, as a catalyst for the synthesis of tetrahydrobenzo[*b*]pyran prepared by the reaction of dimedone, malononitrile and aromatic or aliphatic aldehydes in refluxing water. The catalyst was prepared according to a previously published literature procedure using inexpensive and readily available starting materials. Furthermore, the catalyst could be recovered conveniently and reused efficiently such that a considerable catalytic activity still could be achieved after fifth run. Other beneficial features of this new synthetic approach include short reaction time, high yields, clean reaction profiles, and a simple work-up procedure.

**Key words:** Giant-ball nanoporous isopolyoxomolybdate, Keplerate,  $\{\text{Mo}_{132}\}$ , Tetrahydrobenzo[*b*]pyran.

**Introduction**

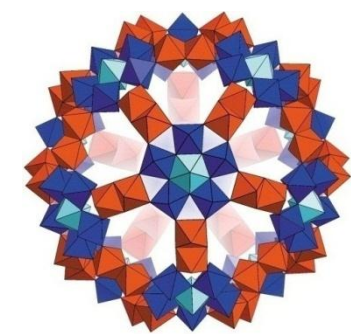
Polyoxometalates (POMs) are polyatomic ions, usually an anion, that consists of three or more transition metal oxyanions linked together by shared oxygen atoms to form a large, closed 3-dimensional framework. The metal atoms are usually group 5 or group 6 transition metals in their high oxidation states. In this state, their electron configuration is  $d^0$  or  $d^1$ . For example, niobium(V), vanadium(V), tantalum(V), molybdenum(VI), and tungsten(VI) are most important transition metals in these structures<sup>i,ii</sup>. These compounds have stimulated many current research activities in a broad range of fields such as catalysis, magnetism, materials science and biomedicine<sup>iii</sup>. Such a stimulation is because of diverse and highly modifiable sizes, shapes, charge densities, acidities and reversible redox potentials of POMs<sup>iv,v</sup>. In recent years, the synthesis of nanotubular materials consisting of POMs such as POMs-including titaniananotubes<sup>vi</sup> and POMs-organic hybrid nanotubes<sup>vii</sup> have been a subject of increasing interest. These new types of nanotubes show the functional properties of POMs

but also the advantages of tubular systems in the application, for example, of catalytic and photochemical properties<sup>vi-ix</sup>.

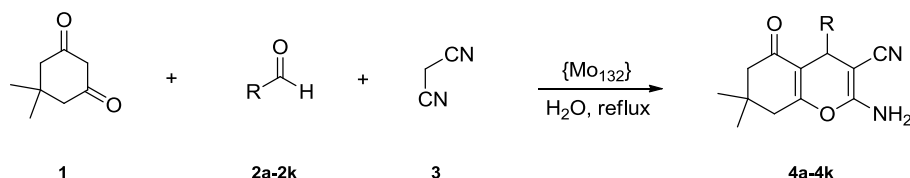
Giant nanosized porous Keplerate-type POMs, reported for the first time by Müller and co-workers<sup>x</sup>, show a large variety of applications in fundamental and applied science, such as in modeling passive cation transport through membranes, encapsulation, nanoseparation chemistry, and magnetic and optics properties<sup>xi,xii</sup>. In spite of these valuable properties, to the authors' knowledge, there are some references in the literature on the use of giant nanosized porous POMs as a catalyst in organic transformations<sup>xiii,xlv,xlvi</sup>.

Tetrahydrobenzo[*b*]pyrans are an important class of oxygen-containing heterocycles with diverse and interesting biological and pharmacological activities such as anti-coagulant, spasmolytic, diuretic, anti-cancer, and anti-anaphylactin characteristics<sup>xiv-xx</sup>. They are also used for the treatment neurodegenerative disease, AIDS associated dementia and down's syndrome as well as for the treatment of schizophrenia and myoclonuse<sup>xxi</sup>. Some 2-amino-4H-pyrans can be useful as photoactive materials<sup>xxii</sup>. Whereas polysubstituted 4H-pyran constitutes a structural unit of a series of natural products<sup>xxiii,xxiv</sup>. According to these excellent properties of the 4H-pyrans, several methods have been reported for the synthesis of these compounds via three components one-pot reactions<sup>xxv-xxxv</sup>. However, many of these methods were associated with use of hazardous organic solvents which is significantly harmful to environment, long duration of reaction, low yield of products, effluent pollution, hard to separate the catalyst and lack of general applicability. Therefore, the development of a new greener and more convenient method using a new catalyst with high catalytic activity for the synthesis of 4H-benzo[*b*]pyrans is highly desirable.

During the course of our recent studies directed towards the development of practical and environmentally friendly procedures for the synthesis of organic compounds using reusable catalysts<sup>xxxvi-xliv</sup>, we investigated the application of the  $(\text{NH}_4)_{42}[\text{Mo}^{\text{VI}}_{72}\text{Mo}^{\text{V}}_{60}\text{O}_{372}(\text{CH}_3\text{COO})_{30}(\text{H}_2\text{O})_{72}]$ , a Keplerate-type giant ball nanoporous isopolyoxomolybdate denoted as  $\{\text{Mo}_{132}\}$  (Fig. 1), as a catalyst for a series of organic transformations. This new reusable catalyst performed well and showed a high level of catalytic activity in the synthesis of 1,2,4,5-tetrasubstituted imidazoles, 1,8-dioxooctahydroxanthenes and 1,8-dioxodecahydroacridines<sup>xlv,xlvi</sup>. This fact prompted us to investigate the catalytic activity of this material in the synthesis of tetrahydrobenzo[*b*]pyrans in water as green solvent (Scheme 1). For the first time, this ball-shaped POM has been characterized using the TEM image by Polarzetal<sup>xlvi</sup>. The TEM picture clearly shows a periodic structure with an average size of approximately 3 nm in diameter. This experimentally obtained diameter fits nicely with the theoretical value for the inner diameter of this ball-shaped POM that calculated to be 2.9 nm<sup>xlviii</sup>.



← 2.9 nm →  
**Fig. 1.** Structure of  $\{\text{Mo}_{132}\}$



**Scheme 1.** {Mo<sub>132</sub>} catalyzed synthesis of tetrahydrobenzo[*b*]pyrans

### Experimental

All chemicals were available commercially and used without additional purification. The catalyst was synthesized according to the literature. Melting points were recorded using a Stuart SMP3 melting point apparatus. The FT-IR spectra of the products were obtained with KBr disks, using a Tensor 27 Bruker spectrophotometer. The <sup>1</sup>H NMR (400 and 500 MHz) spectra were recorded using Bruker 400 and 500 spectrometers.

#### General experimental procedure

A mixture of dimedone **1** (1 mmol), aromatic or aliphatic aldehyde **2a-2q** (1 mmol), malononitrile **3** (1 mmol) and {Mo<sub>132</sub>} (0.08 g) as catalyst in H<sub>2</sub>O (5 ml) was heated under reflux for the appropriate time. The reaction was monitored by TLC. Since the catalyst solubility is very high in cold water, after completion of the transformation, the reaction mixture was allowed to cool down into room temperature. The crude product was collected by filtration, washed with H<sub>2</sub>O and recrystallized from ethanol to give compounds **4a-4k**. The catalyst could be readily recovered from the combined filtrate after evaporation to dryness under reduced pressure and washing with hot ethanol.

#### <sup>1</sup>H NMR and FT-IR data:

**2-amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-benzopyran-3-carbonitrile (4a)** <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 0.97 (s, 3H, CH<sub>3</sub>), 1.05 (s, 3H, CH<sub>3</sub>), 2.10 (d, 1H, *J* = 16.0 Hz, CH<sub>2</sub>, diastereotopic proton), 2.27 (d, 1H, *J* = 16.0 Hz, CH<sub>2</sub>, diastereotopic proton), 2.45–2.55 (m, 2H, CH<sub>2</sub>, diastereotopic protons overlapped with solvent), 4.18 (s, 1H, CH), 7.03 (s br., 2H, NH<sub>2</sub>), 7.10–7.24 (m, 3H, arom-H), 8.16 (t, 2H, *J* = 7.2 Hz, arom-H); FT-IR (KBr disc): ν 3342, 3061, 2982, 1688, 1651, 1489, 1372, 1211, 1167, 828.

**2-amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-benzopyran-3-carbonitrile (4b)** <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 0.95 (s, 3H, CH<sub>3</sub>), 1.03 (s, 3H, CH<sub>3</sub>), 2.10 (d, 1H, *J* = 16.0 Hz, CH<sub>2</sub>, diastereotopic proton), 2.24 (d, 1H, *J* = 16.0 Hz, CH<sub>2</sub>, diastereotopic proton), 2.45–2.55 (m, 2H, CH<sub>2</sub>, diastereotopic protons overlapped with solvent), 4.19 (s, 1H, CH), 7.05 (s br., 2H, NH<sub>2</sub>), 7.17 (d, 2H, *J* = 8.4 Hz, arom-H), 7.34 (d, 2H, *J* = 8.4 Hz, arom-H); FT-IR (KBr disc): ν 3342, 3061, 2982, 1688, 1651, 1489, 1372, 1211, 1167, 828.

**2-amino-4-(4-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-benzopyran-3-carbonitrile (4c)** <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 0.94 (s, 3H, CH<sub>3</sub>), 1.04 (s, 3H, CH<sub>3</sub>), 2.08 (d, 1H, *J* = 16.0 Hz, CH<sub>2</sub>, diastereotopic proton), 2.24 (d, 1H, *J* = 16.0 Hz, CH<sub>2</sub>, diastereotopic proton), 2.42–2.56 (m, 2H, CH<sub>2</sub>, diastereotopic protons overlapped with solvent), 3.71 (s, 3H, OCH<sub>3</sub>), 4.12 (s, 1H, CH), 6.83 (d, 2H, *J* = 8.7 Hz, arom-H), 6.93 (s br., 2H, NH<sub>2</sub>), 7.04 (d, 2H, *J* = 8.7 Hz, arom-H); FT-IR (KBr disc): ν 3342, 3061, 2982, 1688, 1651, 1489, 1372, 1211, 1167, 828.

**2-amino-7,7-dimethyl-4-(3-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-benzopyran-3-carbonitrile (4d)** <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 0.96 (s, 3H, CH<sub>3</sub>), 1.04 (s, 3H, CH<sub>3</sub>), 2.11 (d, 1H, *J* = 16.1 Hz, CH<sub>2</sub>, diastereotopic proton), 2.27 (d, 1H, *J* = 16.1 Hz, CH<sub>2</sub>, diastereotopic proton), 2.55 (s, 2H, diastereotopic proton), 4.42 (s, 1H, CH), 7.17 (s br., 2H, NH<sub>2</sub>), 7.55–7.50 (m, 2H, arom-H), 7.97 (t, 1H, *J* = 1.7 Hz, arom-H), 8.05–8.10 (m, 1H, arom-H); FT-IR (KBr disc): ν 3342, 3061, 2982, 1688, 1651, 1489, 1372, 1211, 1167, 828.

**2-amino-4-(4-fluorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-benzopyran-3-carbonitrile(4e)** <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ0.96 (s, 3H, CH<sub>3</sub>), 1.04 (s, 3H, CH<sub>3</sub>), 2.11 (d, 1H, *J* = 16.2 Hz, CH<sub>2</sub>, diastereotopic proton), 2.26 (d, 1H, *J* = 16.2 Hz, CH<sub>2</sub>, diastereotopic proton), 2.41–2.55 (m, 2H, CH<sub>2</sub>, diastereotopic protons overlapped with solvent), 4.21 (s, 1H, CH), 7.07 (s br., 2H, NH<sub>2</sub>), 7.08–7.23 (m, 4H, arom-H); FT-IR (KBr disc):ν 3342, 3061, 2982, 1688, 1651, 1489, 1372, 1211, 1167, 828.

**2-amino-4-(4-bromophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-benzopyran-3-carbonitrile (4f)** <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ0.96 (s, 3H, CH<sub>3</sub>), 1.05 (s, 3H, CH<sub>3</sub>), 2.11 (d, 1H, *J* = 16.0 Hz, CH<sub>2</sub>, diastereotopic proton), 2.26 (d, 1H, *J* = 16.0 Hz, CH<sub>2</sub>, diastereotopic proton), 2.45–2.55 (m, 2H, CH<sub>2</sub>, diastereotopic protons overlapped with solvent), 4.19 (s, 1H, CH), 7.10 (s br., 2H, NH<sub>2</sub>), 7.12 (d, 2H, *J* = 8.4 Hz, arom-H), 7.50 (d, 2H, *J* = 8.4 Hz, arom-H); FT-IR (KBr disc):ν 3342, 3061, 2982, 1688, 1651, 1489, 1372, 1211, 1167, 828.

**2-amino-4-(3-bromophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-benzopyran-3-carbonitrile (4g)** <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ0.97 (s, 3H, CH<sub>3</sub>), 1.05 (s, 3H, CH<sub>3</sub>), 2.14 (d, 1H, *J* = 16.0 Hz, CH<sub>2</sub>, diastereotopic proton), 2.27 (d, 1H, *J* = 16.0 Hz, CH<sub>2</sub>, diastereotopic proton), 2.45–2.55 (m, 2H, CH<sub>2</sub>, diastereotopic protons overlapped with solvent), 4.22 (s, 1H, CH), 7.13 (s br., 2H, NH<sub>2</sub>), 7.15–7.20 (m, 1H, arom-H), 7.20–7.35 (m, 2H, arom-H), 7.37–7.45 (m, 1H, arom-H); FT-IR (KBr disc):ν 3342, 3061, 2982, 1688, 1651, 1489, 1372, 1211, 1167, 828.

**2-amino-7,7-dimethyl-5-oxo-4-(thiophen-2-yl)-5,6,7,8-tetrahydro-4H-benzopyran-3-carbonitrile (4h)** <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ0.99 (s, 3H, CH<sub>3</sub>), 1.05 (s, 3H, CH<sub>3</sub>), 2.15 (d, 1H, *J* = 16.2 Hz, CH<sub>2</sub>, diastereotopic proton), 2.31 (d, 1H, *J* = 16.2 Hz, CH<sub>2</sub>, diastereotopic proton), 2.44 (d, 1H, *J* = 17.4 Hz, CH<sub>2</sub>, diastereotopic proton), 2.56 (d, 1H, *J* = 17.4 Hz, CH<sub>2</sub>, diastereotopic proton), 4.55 (s, 1H, CH), 6.87 (d, 1H, *J* = 2.8 Hz, arom-H), 6.92 (dd, 1H, *J* = 5.0, 3.4 arom-H), 7.15 (s br., 2H, NH<sub>2</sub>), 7.40 (dd, 1H, *J* = 4.8, 0.8 Hz, arom-H); FT-IR (KBr disc):ν 3342, 3061, 2982, 1688, 1651, 1489, 1372, 1211, 1167, 828.

**2-amino-7,7-dimethyl-4-(4-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-benzopyran-3-carbonitrile (4i)** <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ0.97 (s, 3H, CH<sub>3</sub>), 1.06 (s, 3H, CH<sub>3</sub>), 2.12 (d, 1H, *J* = 16.0 Hz, CH<sub>2</sub>, diastereotopic proton), 2.28 (d, 1H, *J* = 16.0 Hz, CH<sub>2</sub>, diastereotopic proton), 2.45–2.60 (m, 2H, CH<sub>2</sub>, diastereotopic protons overlapped with solvent), 4.38 (s, 1H, CH), 7.22 (s br., 2H, NH<sub>2</sub>), 7.47 (d, 2H, *J* = 8.4 Hz, arom-H), 8.19 (d, 2H, *J* = 8.4 Hz, arom-H); FT-IR (KBr disc):ν 3342, 3061, 2982, 1688, 1651, 1489, 1372, 1211, 1167, 828.

**2-amino-7,7-dimethyl-5-oxo-4-(4-methylphenyl)-5,6,7,8-tetrahydro-4H-benzopyran-3-carbonitrile (4j)** <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ0.95 (s, 3H, CH<sub>3</sub>), 1.05 (s, 3H, CH<sub>3</sub>), 2.09 (d, 1H, *J* = 16.0 Hz, CH<sub>2</sub>, diastereotopic proton), 2.24 (d, 1H, *J* = 16.0 Hz, CH<sub>2</sub>, diastereotopic proton), 2.25 (s, 3H, CH<sub>3</sub>), 2.43–2.57 (m, 2H, CH<sub>2</sub>, diastereotopic protons overlapped with solvent), 4.13 (s, 1H, CH), 6.95 (s br., 2H, NH<sub>2</sub>), 7.02 (d, 2H, *J* = 8.0 Hz, arom-H), 7.08 (d, 2H, *J* = 8.0 Hz, arom-H); FT-IR (KBr disc):ν 3342, 3061, 2982, 1688, 1651, 1489, 1372, 1211, 1167, 828.

**2-amino-4-ethyl-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-benzopyran-3-carbonitrile (4k)** <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ0.70 (t, 3H, *J* = 7.2, CH<sub>3</sub>), 1.03 (s, 3H, CH<sub>3</sub>), 1.05 (s, 3H, CH<sub>3</sub>), 1.30–1.65 (m, 2H, CH<sub>2</sub>, diastereotopic proton), 2.20 (d, 1H, *J* = 16.0 Hz, CH<sub>2</sub>, diastereotopic proton), 2.30 (d, 1H, *J* = 16.0 Hz, CH<sub>2</sub>, diastereotopic proton), 2.37 (d, 1H, *J* = 17.8 Hz, CH<sub>2</sub>, diastereotopic proton), 2.46 (d, 1H, *J* = 17.8 Hz, CH<sub>2</sub>, diastereotopic proton), 3.19 (t, 1H, *J* = 3.6 Hz, CH), 6.93 (s br., 2H, NH<sub>2</sub>); FT-IR (KBr disc):ν 3342, 3061, 2982, 1688, 1651, 1489, 1372, 1211, 1167, 828.

## Results and discussion

The {Mo<sub>132</sub>} catalyst was characterized by FT-IR and UV-Vis spectroscopy as reported in our previous work<sup>xlvi</sup>. For the beginning of this study, 4-chlorobenzaldehyde **2b** was employed as the model aldehyde reacted with dimedone **1** and malononitrile **3**. In order to get the effective reaction conditions, the reaction was optimized in terms of various parameters like catalyst amount, effect of solvent, and influence of temperature (Table 1). Low yields of the product **4b** were obtained in the absence of the catalyst at room temperature or refluxing EtOH or H<sub>2</sub>O (entries 1 and 2) or in the presence of the catalyst under solvent-free conditions at high temperatures (entries 3 and 4) indicating that the catalyst and solvent are necessary for the reaction. As can be seen from Table 1, among the tested solvents such as H<sub>2</sub>O, EtOH, MeOH, CHCl<sub>3</sub>, CH<sub>3</sub>CN, and also solvent-free conditions and various amounts of the catalyst, the reaction was more facile and proceeded to give the highest yield, using 0.08 g of {Mo<sub>132</sub>} in H<sub>2</sub>O at reflux temperature (entry 12). All subsequent reactions were carried out in these optimized conditions.

Encouraged by the remarkable results obtained with the above reaction conditions, and in order to show the generality and scope of this new protocol, we extended the reaction of dimedone **1**, malononitrile **3** with a range of other aromatic or aliphatic aldehydes **2a-2k** under the optimized reaction conditions and the results are summarized in Table 2. As shown, all reactions proceed very clean to give the corresponding tetrahydrobenzo[*b*]pyrans **4a-4k** in high yields over short reaction times. Purity checks with melting points, TLC and the <sup>1</sup>H NMR spectroscopic data reveal that only one product is formed in all cases and no undesirable side-products are observed. The structures of all known products **4a-4k** were deduced from their <sup>1</sup>H NMR and FT-IR spectral data and a comparison of their melting points with those of authentic samples. For example, as shown in Fig. 2, the <sup>1</sup>H NMR spectrum of **4h** in DMSO-d<sub>6</sub> showed two sharp singlet peaks at δ 0.99 ppm and δ 1.06 ppm for two methyl group, multiplet absorption at δ 2.10–2.60 ppm for two methylene groups and a singlet signal at δ 4.55 ppm for amine group as well as the signals in the aromatic region due to 3 aromatic protons in thienyl moiety, indicating the formation of the compound **4h**.


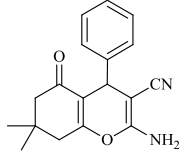
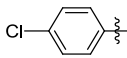
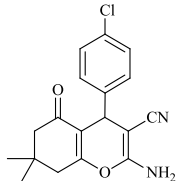
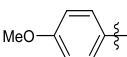
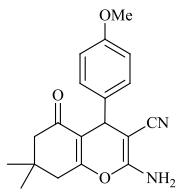
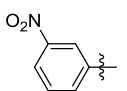
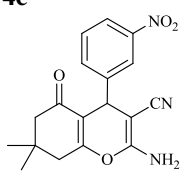
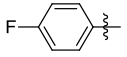
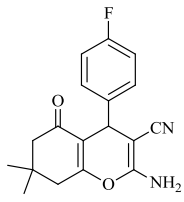
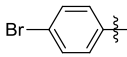
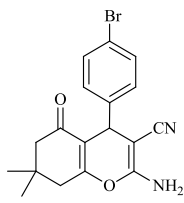
**Table 1.** Optimization of reaction conditions for the synthesis of compound **4b** catalyzed by {Mo<sub>132</sub>}<sup>\*</sup>.

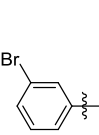
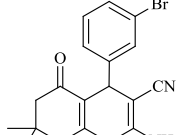

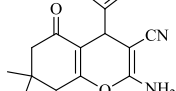
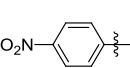
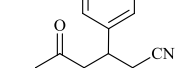
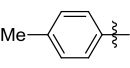
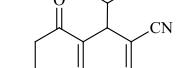

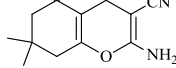
Entry	Catalyst (g)	Solvent	T/°C	Time/min	Isolated Yield/%
1	None	H <sub>2</sub> O	Reflux	90	16
2	None	EtOH	Reflux	90	11
3	0.08	Solvent-free	100	36	27
4	0.08	Solvent-free	120	37	29
5	0.02	EtOH	Reflux	60	17
6	0.04	EtOH	Reflux	47	34
7	0.06	EtOH	Reflux	35	71
8	0.08	EtOH	Reflux	30	84
9	0.02	H <sub>2</sub> O	Reflux	40	26
10	0.04	H <sub>2</sub> O	Reflux	22	57
11	0.06	H <sub>2</sub> O	Reflux	15	89
12	0.08	H <sub>2</sub> O	Reflux	10	96
13	0.08	H <sub>2</sub> O	80	20	88
14	0.08	H <sub>2</sub> O	r.t.	30	82
15	0.1	H <sub>2</sub> O	Reflux	20	95
16	0.02	MeOH	Reflux	50	18
17	0.04	MeOH	Reflux	45	32
18	0.06	MeOH	Reflux	35	82
19	0.08	MeOH	Reflux	25	85
20	0.02	CHCl <sub>3</sub>	Reflux	40	20
21	0.04	CHCl <sub>3</sub>	Reflux	35	41

22	0.06	CHCl <sub>3</sub>	Reflux	30	77
23	0.08	CHCl <sub>3</sub>	Reflux	25	89
24	0.02	CH <sub>3</sub> CN	Reflux	65	13
25	0.04	CH <sub>3</sub> CN	Reflux	55	31
26	0.06	CH <sub>3</sub> CN	Reflux	45	62
27	0.08	CH <sub>3</sub> CN	Reflux	35	80

\* Reaction conditions: dimedone (1 mmol), 4-chlorobenzaldehydes (1 mmol), and malononitrile (1 mmol).

**Table 2.** {Mo<sub>132</sub>} catalyzed synthesis of tetrahydrobenzo[*b*]pyrans <sup>a</sup>

Entry	R	Products <sup>b</sup>	Time/min	Isolated Yield/%	m.p. (°C)	
					Found	Reported
1		 <b>4a</b>	13	92	229-231	228-230 <sup>xxv</sup>
2		 <b>4b</b>	10	96	210-212	211-212 <sup>xxv</sup>
3		 <b>4c</b>	12	88	198-200	200-201 <sup>xxvi</sup>
4		 <b>4d</b>	12	89	212-214	213-214 <sup>xxvi</sup>
5		 <b>4e</b>	10	93	212-214	210-212 <sup>1</sup>
6		 <b>4f</b>	8	92	206-208	207-208 <sup>xxvi</sup>

7			13	95	229-231	228-230 <sup>xlix</sup>
		<b>4g</b>				
8			9	89	212-213	210-212 <sup>xxv</sup>
		<b>4h</b>				
9			11	10	177-179	176-178 <sup>xlix</sup>
		<b>4i</b>				
10			11	85	215-217	215-216 <sup>xxvi</sup>
		<b>4j</b>				
11			15	87	180-182	178-180 <sup>xlix</sup>
		<b>4k</b>				

<sup>a</sup>Reaction conditions: dimedone**1** (1 mmol), aldehyde **2a-2k** (1 mmol), malononitrile**3** (1 mmol), {Mo<sub>132</sub>} (0.08 g), H<sub>2</sub>O (5 ml), reflux.

<sup>b</sup>All the products were characterized according to their FT-IR and <sup>1</sup>H NMR spectral data and comparison of their melting points with those of authentic samples.

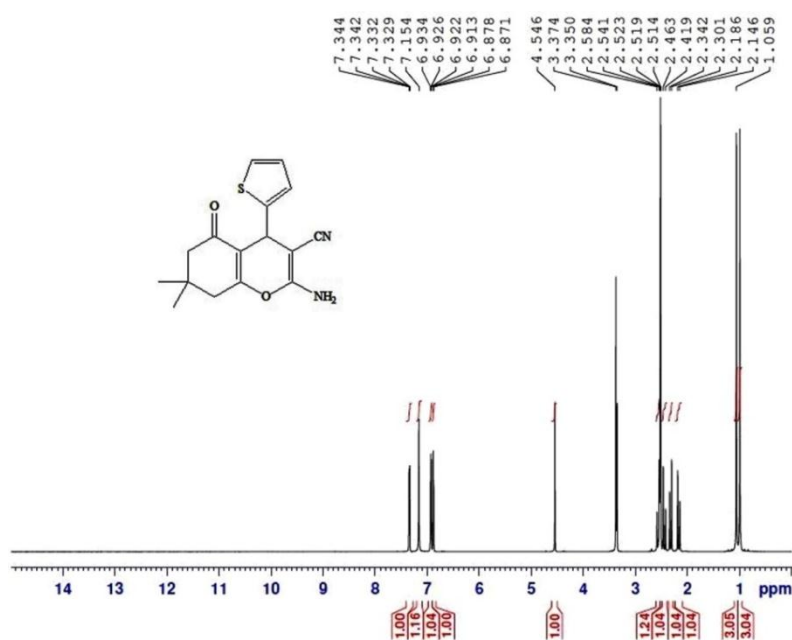
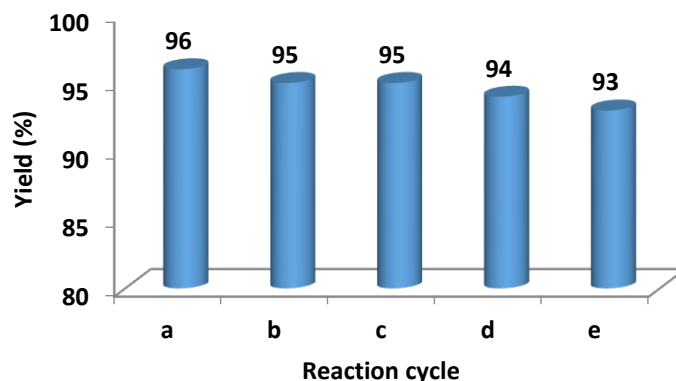


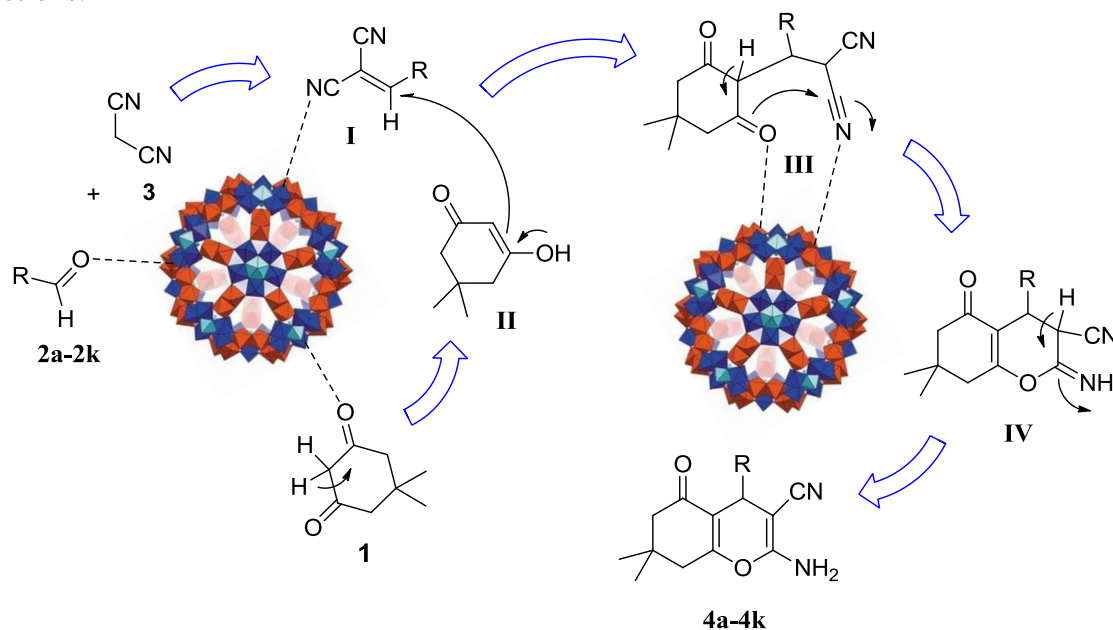
Fig. 2. The <sup>1</sup>H NMR spectrum of compound **4h** in DMSO-d<sub>6</sub> solvent

To test the recyclability of  $\{Mo_{132}\}$ , after completion of the model reaction, the catalyst was recovered according to the procedure described in the experimental section. The separated catalyst was dried at 60 °C under vacuum for 1 h before being reused in a similar reaction. The catalyst could be used at least five times without significant reduction in its activity (96, 95, 95, 94, 93% yields in first to fifth use, respectively) which clearly demonstrates the practical reusability of this catalyst. (Fig. 3a-e).



**Fig. 3.** Effect of recycling on catalytic performance of  $\{Mo_{132}\}$  in the synthesis of **4b** in model reaction.

Although we did not investigate the reaction mechanism, a plausible mechanism for this reaction may proceed as depicted in Scheme 2. On the basis of our previous reports<sup>xlv,xlvi</sup>, it is reasonable to assume that several accessible Mo sites and  $NH_4$  groups in  $\{Mo_{132}\}$  could act as Lewis acid and Brønsted acid centers, respectively, and therefore promote the necessary reactions. The catalyst would play a significant role in increasing the electrophilic character of the electrophiles in the reaction. According to this mechanism, the  $\{Mo_{132}\}$  catalyst would facilitate the formation of intermediates **I**, **II**, **III** and **IV**. Under these conditions, however, attempts to isolate the proposed intermediates failed even after careful monitoring of the reactions.



**Scheme 2.** Plausible mechanism for the  $\{Mo_{132}\}$ -catalyzed formation of tetrahydrobenzo[*b*]pyrans.



## Conclusion

In conclusion, in this paper we showed that  $\{Mo_{132}\}$ , a Keplerate-type giant-ball nanoporous isopolyoxomolybdate, as a highly effective heterogeneous catalyst effectively catalyzes the reaction of dimedone, malononitrile with a range of aromatic or aliphatic aldehydes in refluxing water. This method provided the tetrahydrobenzo[*b*]pyran products in high yields over short reaction time, following a facile work-up process. The catalyst is inexpensive and easily obtained, stable and storable, easily recycled and reused for several cycles with consistent activity.

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