



Original Research article

Successful Application of a Keplerate-type, Giant-ball Nanoporous Isopolyoxomolybdate as a Reusable Green Catalyst for Atom-economy Synthesis of Tetrahydrobenzo[*a*]xanthene-11-ones



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KEYWORDS

Giant-ball nanoporous isopolyoxomolybdate

Keplerate

{Mo₁₃₂}Tetrahydrobenzo[*a*]xanthene-11-ones

ABSTRACT

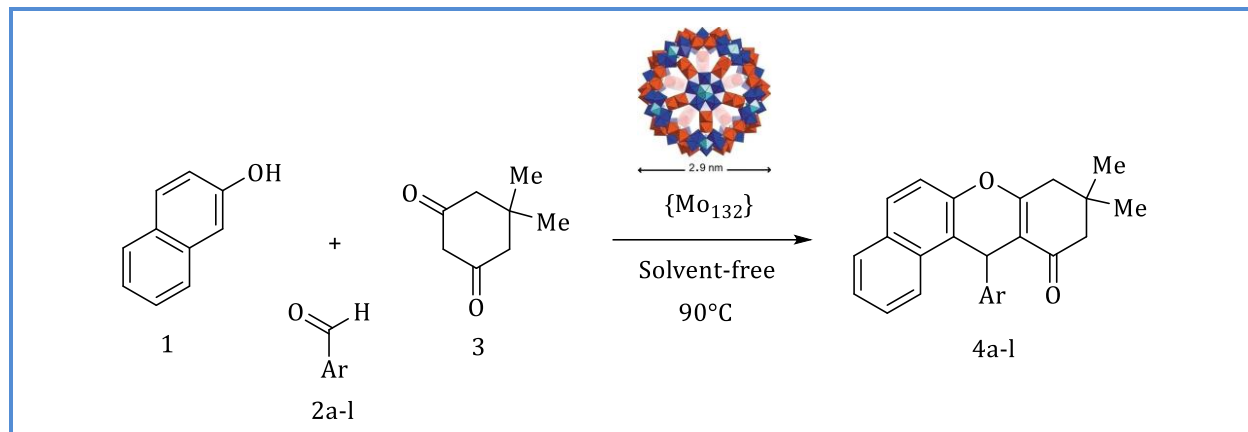
In this study, a new application of a keplerate-type giant-ball nanoporous isopolyoxomolybdate, (NH₄)₄₂[Mo^{VI}₇₂Mo^V₆₀O₃₇₂(CH₃COO)₃₀(H₂O)₇₂], denoted as {Mo₁₃₂}, in the synthesis of tetrahydrobenzo[*a*]xanthene-11-ones *via* a one-pot, three-component reaction of β -naphthol, aryl aldehydes, and dimedone is reported. The reactions were performed under the solvent-free conditions, providing the corresponding products with high atom economy ranging from 90.77% to 92.32%. The catalyst was prepared using inexpensive and readily available materials and could be easily recovered from the reaction mixture by a simple filtration and reused many times with no significant loss of its catalytic activity. High activity of the catalyst, excellent yields, short reaction time, simple procedure with an easy work-up, and the absence of any volatile and hazardous organic solvents are other advantages of the present methodology.

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Graphical Abstract



Introduction

Over the recent decade, several disadvantages of conventional homogeneous acidic catalysts such as H₂SO₄, HCl, HF, H₃PO₄ and FeCl₃ including corrosion, volatility, toxicity, difficulties in separation, recovery, and environmental hazard has attracted much attention to replace them with greener catalysts. In this context, solid acidic catalysts have been widely used in organic transformations [1-5]. These catalysts have many advantages over liquid acid catalysts. They have the advantages of simple separation from liquid reaction media, reusability, and easy handling, and are not corrosive but environmentally benign, presenting fewer disposal problems. Thus the development and use of solid green catalysts are very important in organic syntheses [6-9]. Polyoxometalates (POMs) are a subset of metal oxide cluster compounds consisting of early transition metal atoms in their high oxidation state bridged by oxygen atoms. They are known to have a variety of highly modifiable sizes, shapes, charge densities, acidities, polarities, solubilities and wide-ranging redox potentials, and therefore have been extensively studied in a broad range of fields such as catalysis, magnetism, materials science and biomedicine [10-13]. A number of very large POM anions with a variety of applications in fundamental and applied science have been synthesized and structurally characterized [14-16]. Müller and co-workers [17], for the first time, reported the famous remarkable giant-ball nanosized porous keplerate-type POM, which was formulated as (NH₄)₄₂[Mo^{VI}₇₂Mo^V₆₀O₃₇₂(CH₃COO)₃₀(H₂O)₇₂] and denoted as {Mo₁₃₂} (Figure 1). Polarz *et al.* [18] were the first group to report the characterization of this ball-shaped POM using the transmission electron microscopy (TEM) image. The TEM micrographs clearly showed a periodic structure with an average size of approximately 3 nm in diameter. This experimentally determined that diameter

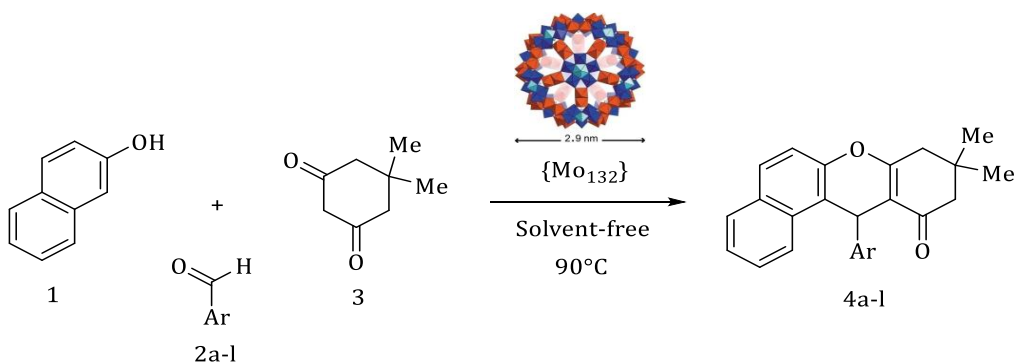
was in good agreement with the theoretical value for the inner diameter of this ball-shaped POM that was calculated to be 2.9 nm [17-19].



Figure 1. Structure of $\{Mo_{132}\}$

Xanthene and benzoxanthene derivatives such as tetrahydrobenzo[*a*]xanthene-11-ones are one of the most privileged classes of heterocyclic compounds that are widely used as anticancer [20], phototoxic [21], anti-inflammatory [22], analgesic [22], antioxidant [23], antimicrobial [24, 25] agents. They have been applied in various industries as dyes in laser technology [26] and also as aurora kinase inhibitor [27]. Due to these useful applications and valuable properties, xanthene derivatives synthesis is very significant. One commonly used method reported for synthesis of tetrahydrobenzo[*a*]xanthene-11-ones involves the one-pot, three-component reaction of β -naphthol, aldehydes, and dimedone initiated by various catalysts such as HBF_4/SiO_2 [28], *N,N'*-dibromo-*N,N'*-1,2-ethanediyl bis(*p*-toluenesulfonamide) [29], SO_3H -functionalized ionic liquids [30], trichloroisocyanuric acid [31], ceric ammonium nitrate [32], *p*-dodecylbenzenesulfonic acid [33], Zr-MCM-41 [34], $Ce(SO_4)_2 \cdot 4H_2O$ [35], metal oxide nanoparticles [36], poly(*N,N'*-dibromo-*N*-ethylnaphtyl-2,7-sulfonamide) [37], and sulfonation of carbonized xylan-type hemicellulose [38]. Although each of these individual methods has its own merits, many suffer from limitations such as the use of halogenated solvents, unsatisfactory yields, prolonged reaction times, expensive catalysts, and tedious isolation procedures. These limitations make further improvements for the synthesis of these compounds.

As part of our research on the development of environmentally friendly methods for synthesis of organic compounds using reusable catalysts [39-46], we previously investigated the application of $\{Mo_{132}\}$ as a catalyst for a series of organic transformations [47-52]. The results revealed that, this new reusable catalyst performed well with a high level of catalytic activity. These facts prompted us to investigate another application of this nanomaterial as catalyst in the synthesis of tetrahydrobenzo[*a*]xanthene-11-ones **4a-l** by one-pot, three-component reaction of β -naphthol **1**, aryl aldehydes **2a-l**, and dimedone **3** (Scheme 1).



Scheme 1. {Mo₁₃₂} catalyzed synthesis of tetrahydrobenzo[*a*]xanthene-11-ones

Experimental

All chemicals were purchased from Merck and Aldrich and used without further purification. Melting points were recorded with a stuart SMP3 melting point apparatus. Fourier transform infrared (FT-IR) spectra were obtained using a tensor 27 Bruker spectrophotometer as KBr disks. The ¹H NMR (300 MHz) spectra were recorded on a Bruker 300 FT spectrometer, in DMSO-*d*₆ as the solvent using tetramethyl silane (TMS) as internal standard.

Synthesis of the keplerate {Mo₁₃₂}

To a solution of (NH₄)₆Mo₇O₂₄·4H₂O (5.6 g, 4.5 mmol) and CH₃COONH₄ (12.5 g, 162.2 mmol) in H₂O (250 mL), N₂H₄·H₂SO₄ (0.8 g, 6.1 mmol) was added, and the resulting solution was stirred for 10 min, during which time it became blue-green in color. The mixture was then treated with 50% CH₃COOH (83 mL) to give a green solution, which was stored in an open 500 mL erlenmeyer flask at 20 °C without stirring. It is noteworthy that the solution became dark brown in color on standing. After 4 days the precipitated red-brown crystals were filtered off, washed with absolute ethanol and diethyl ether, respectively, and finally dried in air [17].

General procedure for the synthesis of tetrahydrobenzo[*a*]xanthene-11-ones 4a-l catalyzed by {Mo₁₃₂}

A mixture of β -naphthol **1** (1 mmol), an aryl aldehyde **2a-l** (1 mmol), dimedone **3** (1 mmol), and {Mo₁₃₂} (0.06 g) was heated in an oil bath at 90 °C for 2-12 min. Upon completion of the transformation, as determined by thin-layer chromatography (TLC), the reaction mixture was cooled to room temperature and diluted with hot ethanol. The catalyst was collected by filtration and washed with a small portion of hot ethanol. The combined filtrates were then concentrated in volume (by half) and allowed to stand at

room temperature until precipitation occurred. The resulting precipitate was collected by filtration, and recrystallized from ethanol to give compounds **4a-l** in excellent yields.

Selected FT-IR and ¹H NMR data

12-(4-chlorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one (**4e**)

FT-IR ($\nu_{\max}/\text{cm}^{-1}$): 3072, 2950, 2871, 1648, 1481, 1370, 1227, 1089, 1018, 816, 749, 658, and 530. ¹H NMR (ppm): δ 0.90 (3H, s), 1.08 (3H, s), 2.15 (1H, d, $J = 16.5$ Hz), 2.36 (1H, d, $J = 16.5$ Hz), 2.60 (1H, d, $J = 17.6$ Hz), 2.72 (1H, d, $J = 17.6$ Hz), 5.60 (1H, s), 7.26 (2H, d, $J = 8.6$ Hz), 7.33 (2H, d, $J = 8.6$ Hz), 7.42-7.47 (1H, m), 7.47-7.50 (1H, m), 7.51-7.55 (1H, m), 7.92-7.98 (2H, m), 8.02 (1H, d, $J = 8.2$ Hz).

9,9-dimethyl-12-(3-nitrophenyl)-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one (**4g**)

FT-IR ($\nu_{\max}/\text{cm}^{-1}$): 3069, 2954, 1648, 1528, 1466, 1353, 1224, 1085, 1026, 811, 752, 678, and 515. ¹H NMR (ppm): δ 0.88 (3H, s), 1.09 (3H, s), 2.17 (1H, d, $J = 16.1$ Hz), 2.39 (1H, d, $J = 16.1$ Hz), 2.65 (1H, d, $J = 17.5$ Hz), 2.75 (1H, d, $J = 17.5$ Hz), 5.81 (1H, s), 7.43-7.55 (4H, m), 7.75-7.80 (1H, m), 7.93-8.02 (3H, m), 8.07 (1H, d, $J = 8.2$ Hz), 8.18 (1H, t, $J = 1.9$ Hz).

12-(4-methoxyphenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one (**4i**)

FT-IR ($\nu_{\max}/\text{cm}^{-1}$): 2951, 1647, 1511, 1460, 1378, 1229, 1173, 1027, 831, 749, and 578. ¹H NMR (ppm): δ 0.91 (3H, s), 1.08 (3H, s), 2.14 (1H, d, $J = 16.5$ Hz), 2.35 (1H, d, $J = 16.5$ Hz), 2.59 (1H, d, $J = 17.6$ Hz), 2.71 (1H, d, $J = 17.6$ Hz), 3.64 (3H, s), 5.53 (1H, s), 6.76 (2H, d, $J = 8.7$ Hz), 7.21 (2H, d, $J = 8.7$ Hz), 7.41-7.46 (1H, m), 7.46-7.50 (1H, m), 7.50-7.55 (1H, m), 7.90-7.95 (2H, m), 8.05 (1H, d, $J = 8.3$ Hz).

12-(4-hydroxyphenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one (**4j**)

FT-IR ($\nu_{\max}/\text{cm}^{-1}$): 3223, 3075, 2952, 1648, 1600, 1511, 1462, 1375, 1230, 1023, 822, 751, 665, and 537. ¹H NMR (ppm): δ 0.91 (3H, s), 1.07 (3H, s), 2.14 (1H, d, $J = 16.1$ Hz), 2.34 (1H, d, $J = 16.1$ Hz), 2.57 (1H, d, $J = 17.5$ Hz), 2.69 (1H, d, $J = 17.5$ Hz), 5.48 (1H, s), 6.58 (2H, d, $J = 8.5$ Hz), 7.09 (2H, d, $J = 8.5$ Hz), 7.41-7.45 (1H, m), 7.45-7.50 (1H, m), 7.50-7.55 (1H, m), 7.88-7.95 (2H, m), 8.05 (1H, d, $J = 8.3$ Hz), 9.20 (1H, s).

Results and discussion

To evaluate the performance of {Mo₁₃₂} as catalyst in the synthesis of tetrahydrobenzo[*a*]xanthene-11-ones, at first, the chosen model reaction between β -naphthol **1** (1 mmol), 4-chlorobenzaldehyde **2e** (1 mmol), and dimedone **3** (1 mmol) was tested in different sets of reaction conditions. A summary of the

optimization experiments is provided in Table 1. Trace amounts of the product 12-(4-chlorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one **4e** were formed at the absence of the catalyst in refluxing H₂O or EtOH and also under solvent-free conditions at high temperature (Entries 1-3), indicating that the catalyst is necessary for the reaction. Due to the advantages of solvent-free conditions in chemical reactions, our investigations on the efficiency of {Mo₁₃₂} in the model reaction were started under solvent-free conditions in different catalyst amounts and temperatures. For finding the best catalyst amount and temperature, an experiment using 0.04 g of the catalyst at 70 °C was tested first. Moderate yield of the product was obtained in this condition (Entry 4). Increasing the amount of the catalyst and temperature increased the yield of the product **4e**. The best result was conducted at the presence of 0.06 g of {Mo₁₃₂} at 90 °C (Entry 12). Higher amount of the catalyst and temperature had no significant effect on the yields and reaction times. Subsequently, our investigation demonstrated that the compound **4e** can be obtained in low to good yields in different solvents including, H₂O, MeOH, EtOH, THF, MeCN, and CHCl₃. However, the reaction time was shorter and yields were higher under the solvent-free conditions. Therefore, solvent-free conditions using 0.06 g of the catalyst at 90 °C was selected in all the subsequent reactions.

Table 1. Optimization of reaction parameters for synthesis of compound **4e** catalyzed by {Mo₁₃₂}^a

Entry	Catalyst (g)	Solvent	T (°C)	Time (min)	Isolated yield (%)
1	-----	H ₂ O	Reflux	90	Trace
2	-----	EtOH	Reflux	90	Trace
3	-----	-----	100	90	Trace
4	0.04	-----	70	20	47
5	0.04	-----	80	20	53
6	0.04	-----	90	15	64
7	0.05	-----	70	15	55
8	0.05	-----	80	12	67
9	0.05	-----	90	10	80
10	0.06	-----	70	12	69
11	0.06	-----	80	10	81
12	0.06	-----	90	7	94
13	0.07	-----	90	7	93
14	0.06	-----	100	7	94
15	0.06	H ₂ O	Reflux	120	27
16	0.06	MeOH	Reflux	90	53
17	0.06	EtOH	Reflux	60	71
18	0.06	THF	Reflux	60	40
19	0.06	MeCN	Reflux	70	52
20	0.06	CHCl ₃	Reflux	80	55

^a Reaction conditions: β -naphthol **1** (1 mmol), 4-chlorobenzaldehyde **2e** (1 mmol), and dimedone **3** (1 mmol)

Having optimized the experimental conditions, we next explored the scope and generality of reaction. Thus, a series of tetrahydrobenzo[*a*]xanthen-11-ones were synthesized using the reaction of β -

naphthol and dimedone with a range of *ortho*-, *meta*- and *para*-substituted aryl aldehydes in the presence of {Mo₁₃₂} under the optimized reaction conditions. As illustrated in Table 2, all aryl aldehydes having substituted electron-donating or electron-withdrawing groups and or none reacted successfully and gave the expected products **4a-l** in excellent yields and short reaction times. However, it was found that the electron-poor aryl aldehydes reacted faster than those electron-rich ones as would be expected. Furthermore, as seen in Figure 2, these reactions have high atom economy ranging from 90.77% to 92.32%, clearly indicated that the {Mo₁₃₂} acts as highly active catalyst in this methodology.

Scheme 1. The condensation of 2-naphthol with 3-nitrobenzaldehyde and thioacetamide

Entry	Ar	Product	Time (min)	Isolated yields (%)	m.p. (°C)	
					Found	Reported
1	C ₆ H ₅	4a	8	90	152-154	150-151 ^[28]
2	3-BrC ₆ H ₄	4b	7	92	169-171	170-171 ^[35]
3	2-ClC ₆ H ₄	4c	10	91	174-176	175-176 ^[35]
4	3-ClC ₆ H ₄	4d	10	93	176-177	173-175 ^[37]
5	4-ClC ₆ H ₄	4e	7	94	190-193	191-193 ^[35]
6	2-O ₂ NC ₆ H ₄	4f	7	90	218-220	220-222 ^[31]
7	3-O ₂ NC ₆ H ₄	4g	3	96	169-171	167-168 ^[31]
8	4-O ₂ NC ₆ H ₄	4h	2	97	176-178	175-177 ^[31]
9	4-MeOC ₆ H ₄	4i	10	89	202-205	201-203 ^[35]
10	4-HOC ₆ H ₄	4j	12	88	222-224	223-226 ^[30]
11	4-MeC ₆ H ₄	4k	12	90	177-178	175-177 ^[35]
12	2-Pyridyl	4l	5	91	195-197	196-198 ^[35]

^a Reaction conditions: β-naphthol **1** (1 mmol), an aryl aldehyde **2a-l** (1 mmol), dimedone **3** (1 mmol), {Mo₁₃₂} (0.06 g), 90 °C, solvent-free

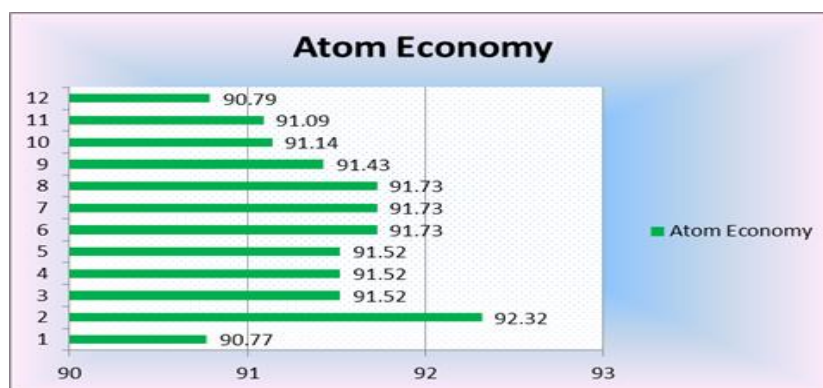


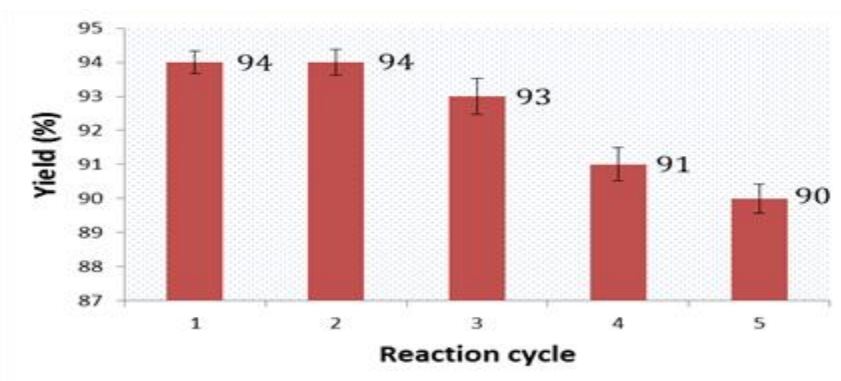
Figure 2. Atom economy for the synthesis of compounds **4a-l** (Entries 1-12 in Table 2)

To show the merit of this method, the efficiency of the catalyst {Mo₁₃₂} was compared with some of those reported for the synthesis of tetrahydrobenzo[*a*]xanthene-11-ones, with respect to the reaction times and temperatures, kind of solvent, and yields of the products (Table 3). According to the obtained results, the current procedure gave high yields of the products in shorter reaction times than the other methods [28-38].

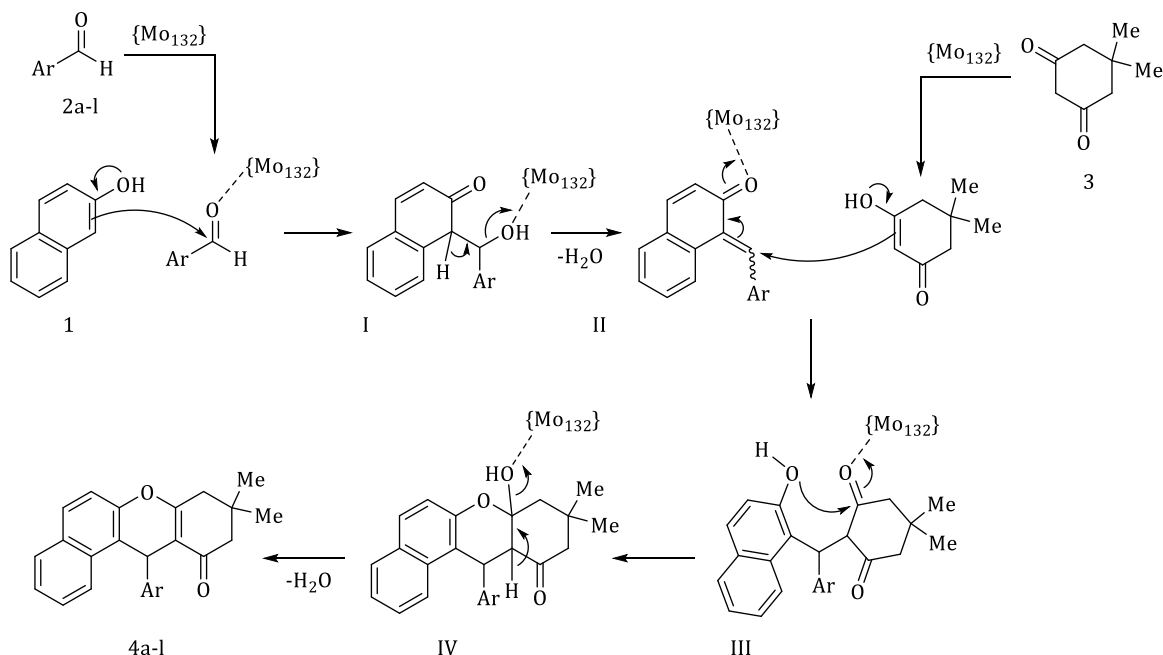
Table 3. Comparison of the catalyst effect in the synthesis of tetrahydrobenzo[*a*]xanthene-11-ones

Catalyst	Conditions			Time (min)	Yield (%)	Ref.
	Solvent	T (°C)	Other			
HF ₄ /SiO ₂	-----	80	-----	55-90	83-95	[28]
<i>N,N'</i> -dibromo- <i>N,N'</i> -1,2-ethanediyl bis(<i>p</i> -toluenesulfonamide)	-----	90	-----	20-95	87-97	[29]
SO ₃ H-functionalized ionic liquids	-----	120	-----	55-95	75-95	[30]
Trichloroisocyanuric acid	-----	110	-----	25-40	74-90	[31]
Ceric ammonium nitrate	CH ₂ Cl ₂ /EtOH	26	Ultrasound	120-144	82-87	[32]
<i>p</i> -dodecylbenzenesulfonic acid	H ₂ O	40-42	Ultrasound	60-240	63-93	[33]
Zr-MCM-41	-----	80	-----	10-20	87-92	[34]
Ce(SO ₄) ₂ ·4H ₂ O	-----	120	-----	8-30	85-97	[35]
Metal oxide nanoparticles	-----	110	-----	8-30	80-97	[36]
Poly(<i>N,N'</i> -dibromo- <i>N</i> -ethyl-naphthyl-2,7-sulfonamide)	-----	110	-----	30-120	70-96	[37]
Sulfonation of carbonized xylan-type hemicellulose	-----	90	-----	120	80-96	[38]
{M ₀₁₃₂ }	-----	90	-----	2-12	88-97	This work

The possibility of recycling and reusing of the {M₀₁₃₂} was examined using the same model reaction under the aforementioned optimized reaction conditions. Upon completion of the first run, hot ethanol was added and the catalyst was collected using a simple filtration. The recycled catalyst was washed with a small portion of hot ethanol, dried under vacuum at 60 °C for 1 h, and then reused in the next run. The catalyst could be used at least five times with a slight reduction in activity (Figure 3) which clearly demonstrated the practical reusability of this catalyst.

**Figure 3.** Reusability of {M₀₁₃₂} for the synthesis of compound **4e**

At the end, a mechanistic rationalization for this reaction was provided (Scheme 2). The $\{Mo_{132}\}$ catalyst has several accessible Mo sites and NH_4 groups, acting 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 the intermediates **I**, **II**, **III** and **IV**.



Scheme 2. Plausible mechanism for the formation of tetrahydrobenzo[*a*]xanthene-11-ones **4a-l** in the presence of $\{Mo_{132}\}$ as catalyst

Conclusions

In this research study, one-pot, three-component reaction of β-naphthol, aryl aldehydes, and dimedone were effectively catalyzed by $\{Mo_{132}\}$, a keplerate-type giant-ball nanoporous isopolyoxomolybdate, under solvent-free conditions, providing the tetrahydrobenzo[*a*]xanthene-11-ones products in excellent yields over short reaction times. The reactions have high atom economy ranging from 90.77 to 92.32%. The catalyst could be readily recycled, and used at least five times without any discernible reduction in its catalytic activity. These features combined with low cost of the catalyst, easy work-up, and the absence of any volatile and hazardous organic solvents makes this method an economical, environmentally benign, and waste-free chemical

process for synthesis of the desired products. A plausible pathway for the formation of the products was also proposed.

Acknowledgements

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Conflict of Interest

We have no conflicts of interest to disclose.

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