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ANOTHER APPLICATION OF A KEPLERATE TYPE GIANT NANOPOROUS ISOPOLYOXOMOLYBDATE AS HIGHLY EFFICIENT REUSABLE CATALYST FOR THE ONE-POT SYNTHESIS OF POLYFUNCTIONALIZED 4*H*-CHROMENES

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Abstract: In this paper, a new application of a Keplerate-typegiant-ball nanoporous isopolyoxomolybdate formulated as $(NH_4)_{42}[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]$ and denoted as ($\{Mo_{132}\}$), was discovered in the one-pot synthesis of several 2-amino-4-aryl-7-hydroxy-4*H*-chromenes by cyclocondensation of resorcinol, aromatic aldehydes, and ethyl cyanoacetate or malononitrile.The reactions were done under solvent-free condition giving the corresponding products in high yields within short reaction times. Other beneficial features of this protocol include ecofriendly catalyst, simple purification procedure, and the recyclability and reusability of the catalyst for up to four consecutive runs.

Keywords: Giant-ball nanoporous isopolyoxomolybdate, Keplerate,$\{Mo_{132}\}$, Polyfunctionalized 4*H*-chromenes, Solvent-free condition

Introduction

Six membered oxygen-containing heterocycles are of great interest because of diverse biological activities[i]. Among them, chromene derivatives have received considerable attention over the past years due to their wide range of various pharmacological properties such as antitumor[ii,iii], antiviral[iv], antifungal[v], anti-inflammatory[vi], antimalarial[vii],antibacterial[viii], anticonvulsant[ix],analgesic[x],and antiproliferative[xi].A number of compounds with chromene moiety are known as potential inhibitors of TNF-α[xii],tumour maker AKR1B10[xiii], NF-κB[xiv], human rhinovirus capsid-binding[xv], hMAO[xvi], AChE[xvii], and aldose reductase[xviii].Furthermore, some drugs containing the chromene motif also found in pigments, cosmetics,and agrochemicals[xix]. Certain derivatives of 4*H*-chromenewas able to induce apoptosis in several cancer cell lines[xx,xxi].

- Because of important properties of chromenes, much attention has been focused on the development of environmentally friendly methodologies for the synthesis of chromene scaffold. Several procedures have been reported for the synthesis of 2-

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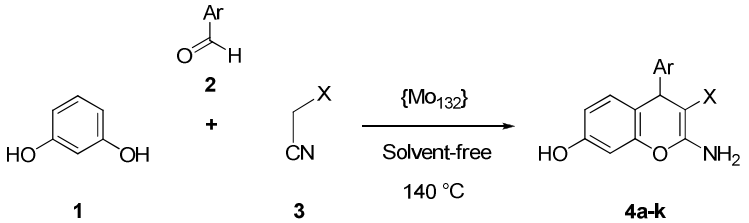
amino-4*H*-chromene including stepwise condensation of salicylaldehydes with 3 equiv of malononitrile[xxii], reaction of malononitrile with in situ generated *ortho*-quinonemethides from 2-(arylsulfonyl)alkyl phenols[xxiii], reaction of resorcinols with benzylidenemalononitriles in the presence of a base as catalyst[xxiv,xxv], or by stepwise reaction of an aromatic aldehyde and ethyl cyanoacetate followed by cyclization with activated phenols or resorcinol in the presence of piperidine as catalyst after refluxing for several hours in ethanol[xxvi,xxvii].Synthesis of these compounds by one-pot reaction of salicylaldehyde, malononitrile, and nitroalkanes catalyzed by DBU has been also reported[xxviii].A perusal of literature reveals that there is an improved method for the synthesis of 2-amino-4-aryl-4*H*-chromenes *via* a one-pot three-component reaction of resorcinol, an aromatic aldehyde, and malononitrile or ethyl cyanoacetate in the presence of a few catalysts including, potassium phthalimide-N-oxyl[xxix],Fe_3O_4nanoparticles[xxx], CuO-CeO_2nanocomposite[xxxi],glucose[xxxii],potassium phthalimide[xxxiii], tungstic acid functionalized mesoporous SBA-15[xxxiv],2,2,2-trifluoroethanol[xxxv],amino-appended *β*-cyclodextrins[xxxvi], and Na_2CO_3[viii].In addition, they can be accessed using ultrasound irradiation in the presence of Fe_3O_4-chitosan nanoparticles[xxxvii],or by electrolysis in the presence of NaBr as an electrolyte[xxxviii].Though each of these methods has its own advantage and provide an improvement in the synthesis of the above mentioned compounds, many suffer disadvantages such as lengthy reaction times, unsatisfactory yields, the use of relatively expensive catalysts, use of organic solvents, and required special conditions using ultrasound irradiation or electrolysis for accelerated synthesis. Hence, there is still a demand for the discovery of new methodologies using new efficient reusable catalysts to overcome these problems.

Recently, $(NH_4)_{42}[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]$, a Keplerate-typegiant-ball nanoporous isopolyoxomolybdate, which is denoted as $\{Mo_{132}\}$,was used in our group as a catalyst for a series of organic transformations[xxxix-xliv]. This nanoporous compound was firstly synthesized and characterized by Müller and co-workers[xlv].The theoretically calculated diameter of this giant-ball nanoporous is 2.9 nm[xlv,xlvi], which is in accord with those experimentally obtained using TEM image byPolarz et al.[xlvii].

Inspired by these facts and also in extension of our previous works on the development of new methodologies in the synthesis of organic compounds using reusable catalysts[xlviii-xlxiii], we report here another application of $\{Mo_{132}\}$ as catalyst in the synthesis of2-amino-4-aryl-7-hydroxy-4*H*-chromenes **4a-k**by one-pot three-component cyclocondensation of resorcinol**1**, aromatic aldehydes**2**, and ethyl cyanoacetateor malononitrile**3** (Scheme 1).



Scheme 1.Synthesis of 2-amino-4-aryl-7-hydroxy-4*H*-chromenes catalyzed by $\{Mo_{132}\}$

Experimental

All chemicals were purchased from Merck and Aldrich and used without purification. Melting points were measured on a Stuart SMP3 melting point apparatus. The ^{1}H spectra were measured in DMSO-$d_6$on a Bruker 300 FT spectrometer using TMS as the internal standard.

Synthesis of the Keplerate {Mo_{132}}. To a solution of $(NH_4)_6Mo_7O_{24}.4H_2O$ (5.6 g, 4.5 mmol) and CH_3COONH_4 (12.5 g, 162.2 mmol) in H_2O (250 ml), $N_2H_4.H_2SO_4$ (0.8 g, 6.1 mmol) was added. The mixture was stirred for 10 min (color change to blue-green) and 50% CH_3COOH (83 ml) subsequently added. The reaction solution, now green, was stored in an open 500-mL Erlenmeyer flask at 20 °C without further stirring (color change to dark-brown). After 4 days the precipitated red-brown crystals were filtered off, washed with absolute ethanol and diethyl ether, respectively, and finally dried in air[xlv].

General procedure for the synthesis of 2-amino-4-aryl-7-hydroxy-4*H*-chromenes 4a-k catalyzed by {Mo_{132}}. A mixture of resorcinol**1** (1 mmol), an aromatic aldehyde **2** (1 mmol), ethyl cyanoacetate or malononitrile**3**(1 mmol) and {Mo_{132}} (0.11 g) was heated in an oil bath at 140 °C for 7-15 min. The reaction was monitored by TLC. Upon completion of the transformation, the reaction mixture was cooled to room temperature and hot ethanol was added. The catalyst was collected by filtration and then washed with a small portion of hot ethanol. The combined filtrates were concentrated and allowed to stand at room temperature until precipitation occurred. The precipitate was recrystallized from ethanol to give compounds **4a-k** in high yields. All the products were known and characterized by IR and ^{1}H NMR (for some cases) spectra and comparison of their melting points with those of authentic samples.

Ethyl 2-amino-7-hydroxy-4-phenyl-4*H*-chromene-3-carboxylate (**4a**):1.05 (t,3H, *J* = 6.9 Hz, CH_3), 3.95 (q,2H, *J* = 6.9 Hz, OCH_2), 4.80 (s,1H, CH), 6.43-6.52 (m,2H, arom-H), 6.98 (d,1H, *J* = 8.4 Hz, arom-H), 7.06-7.26 (m,5H,arom-H), 7.61 (br. s,2H, NH_2), 9.70 (br. s,1H, OH).

2-Amino-7-hydroxy-4-phenyl-4*H*-chromene-3-carbonitrile (**4e**). 4.63 (s,1H, CH), 6.43 (d,1H, *J* = 2.4 Hz, arom-H), 6.50 (dd,1H, J_1= 8.4, J_2 = 2.1 Hz, arom-H), 6.82 (d,1H, *J* = 8.4, arom-H), 6.89 (br. s,2H, NH_2), 7.16-7.35 (m,5H,arom-H), 9.74 (br. s,1H, OH).

2-Amino-7-hydroxy-4-(3-nitrophenyl)-4*H*-chromene-3-carbonitrile (**4h**). 4.92 (s,1H, CH), 6.46 (d,1H, *J* = 2.4 Hz, arom-H), 6.52 (dd,1H, J_1= 8.4, J_2 = 2.4 Hz, arom-H), 6.85 (d,1H, *J* = 8.4, arom-H), 7.06 (br. s,2H, NH_2), 7.60-7.70 (m,2H,arom-H), 8.04 (t,1H, *J* = 2.1 Hz, arom-H), 8.10 (dt,1H, J_1= 7.8, J_2 = 2.1 Hz, arom-H), 9.84 (br,1H, OH).

2-Amino-7-hydroxy-4-(4-methoxyphenyl)-4*H*-chromene-3-carbonitrile (**4i**). 3.72 (s, 3H, OCH_3), 4.57 (s,1H, CH), 6.41 (d,1H, *J* = 2.4 Hz, arom-H), 6.49 (dd,1H, J_1= 8.3, J_2 = 2.4 Hz, arom-H), 6.79 (d,1H, *J* = 8.4, arom-H), 6.84 (br. s,2H, NH_2), 6.87 (d,2H, *J* = 8.7 Hz, arom-H), 7.09 (d,2H, *J* = 8.7 Hz, arom-H), 9.73 (br,1H, OH).

2-Amino-7-hydroxy-4-(4-methylphenyl)-4*H*-chromene-3-carbonitrile (**4j**). 2.26 (s,3H, CH_3), 4.57 (s,1H, CH), 6.40 (d,1H, *J* = 2.4 Hz, arom-H), 6.47 (dd,1H, J_1= 8.4, J_2 = 2.4 Hz, arom-H), 6.77 (d,1H, *J* = 8.4, arom-H), 6.84 (br. s,2H, NH_2), 7.05 (d,2H, *J* = 8.1 Hz, arom-H), 7.11 (d,2H, *J* = 8.1 Hz, arom-H), 9.65 (br,1H, OH).

Results and discussion

In our initial study on the applicability of the {Mo_{132}} in the synthesis of 2-amino-4-aryl-7-hydroxy-4*H*-chromenes, the reaction between resorcinol, 4-chlorobenzaldehyde, and ethyl cyanoacetate for the synthesis of compound **4b** was selected as the test reaction, to optimize the reaction conditions. Because of several advantages of solvent-free conditions such as simpler work-ups, being environmentally friendly, higher yields,reduction of by-products, and faster reactions, we tested the model reaction under solvent-free conditions.The results are summarized in Table 1. A blank reaction without catalyst gave only low yield of the product (entry 1).We were pleased to see that the reaction was efficiently catalyzed by {Mo_{132}}under solvent-free conditions. Among different temperatures and using different

amounts of the catalyst, the reaction was performed well at 140°C in the presence of 0.11 g of the catalyst giving high yield of the product **4b** over short reaction time (entry 10). No significant improvement in the time of the reaction and yield was observed using higher amount of the catalyst and temperature.

Table 1
Optimization of reaction conditions for synthesis of compound**4b**catalyzed by $\{Mo_{132}\}$[a]

Entry	Catalyst (g)	Solvent	T (°C)	Time (min)	Isolated Yield (%)
1	-----	-----	110	120	30
2	0.05	-----	80	75	34
3	0.05	-----	110	35	67
4	0.05	-----	140	30	82
5	0.08	-----	80	30	65
6	0.08	-----	110	30	73
7	0.08	-----	140	25	89
8	0.11	-----	80	25	73
9	0.11	-----	110	25	75
10	0.11	-----	140	15	92
11	0.15	-----	140	20	92
12	0.11	-----	150	20	91
13	0.11	EtOH	Reflux	105	66
14	0.11	MeOH	Reflux	105	50
15	0.11	H_2O	Reflux	120	43
16	0.11	CH_3CN	Reflux	180	40

[a]Reaction conditions: resorcinol(1mmol), 4-chlorobenzaldehyde(1 mmol), and ethyl cyanoacetate(1 mmol). [b]Isolated yields.

In order to establish the generality and effectiveness of the method, a range of 2-amino-4-aryl-7-hydroxy-4*H*-chromenes were prepared by reaction of resorcinol with aromatic aldehydes, and ethyl cyanoacetate or malononitrile under the optimized reaction conditions, and the results are summarizedin Table 2. As shown,all the products were isolated in high yields within short reaction time.This method is effective with a variety of aromatic aldehydes with electron-donating or withdrawing substituents. Under the same conditions, however, the reaction did not proceed when aliphatic aldehydes such as propionaldehyde or isobutyraldehyde were used. All the products were characterized by comparison of their melting points with those of authentic samples and for some cases using ^{1}H NMR spectral data. For example, the ^{1}H NMR spectrum of compound **4a** in DMSO-$d_6$showed atriplet at δ = 1.05 ppm (J = 6.9 Hz) for methyl group, a quartet at δ = 3.95 ppm (J = 6.9 Hz) for methylene group, a singlet at δ = 4.80 ppm for methine group, the characteristic signals at δ = 6.40-7.30 ppm for aromatic protons as well as two single broad bands at δ = 7.61 ppm and δ = 9.70 ppm for the NH_2 and OH groups, respectively.

The reusability of the catalyst was also checked in the model reaction. For this purpose, after completion of the reaction, the catalyst was recovered according to the procedure outlined 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 four times without any significant loss of its activity (92, 91, 91, 89 % yields in first to fourth use, respectively).

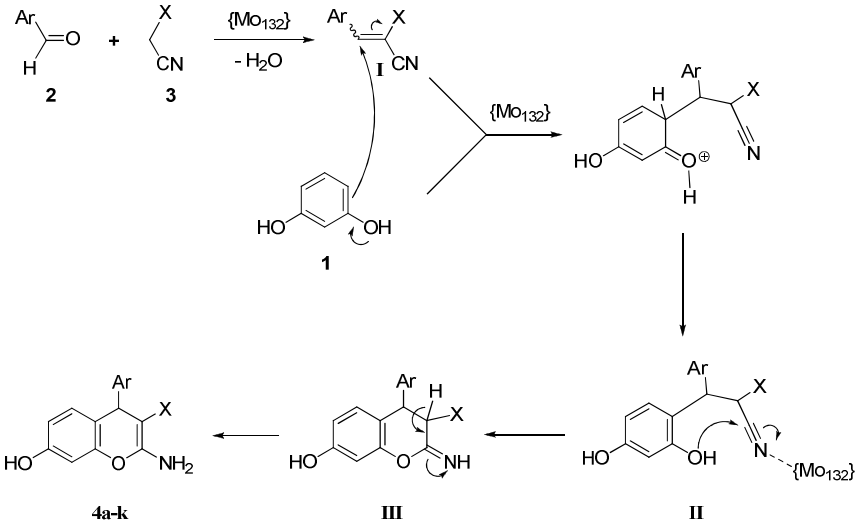
Though, we did not investigate details of the reaction mechanism, the formation of compounds **4a-k** can be explained by the plausible mechanism presented in Scheme 2. On the basis of our previous reports[xxxix,xlii,xliii], we believe that several accessible Mo sites and NH_4 groups in $\{Mo_{132}\}$ can act as Lewis acid and Brönsted acid centers, respectively, and

therefore promote the necessary reactions. The reaction occurs *via* an initial formation of the olefins **I** from the condensation of aryl aldehydes **2** and ethyl cyanoacetateor malononitrile**3**, which suffers nucleophilic attack by resorcinol **1** to give the intermediate **II**. Cyclization of this intermediate followed by tautomerization gave the finalproducts **4a-k***via* the intermediate **III**.

Table 2
Synthesis of 2-amino-4-aryl-7-hydroxy-4*H*-chromenes**4a-k** using $\{Mo_{132}\}$ascatalyst[a]

Entry	Ar	X	Product	Time (min)	Isolated Yield (%)
1	C_6H_5	CO_2Et	**4a**	14	85
2	4-ClC_6H_4	CO_2Et	**4b**	15	92
3	4-FC_6H_4	CO_2Et	**4c**	13	87
4	4-$MeOC_6H_4$	CO_2Et	**4d**	15	80
5	C_6H_5	CN	**4e**	10	82
6	2-ClC_6H_4	CN	**4f**	8	91
7	4-ClC_6H_4	CN	**4g**	7	97
8	3-$O_2NC_6H_4$	CN	**4h**	7	94
9	4-$MeOC_6H_4$	CN	**4i**	8	91
10	4-MeC_6H_4	CN	**4j**	9	90
11	4-HOC_6H_4	CN	**4k**	8	96

[a]Reaction conditions: resorcinol **1** (1 mmol), aromatic aldehydes **2** (1 mmol), and ethyl cyanoacetateor malononitrile**3**(1 mmol), $\{Mo_{132}\}$(0.11 g), 140 ºC, solvent-free.



Scheme 2. Plausible mechanism for the synthesis of 2-amino-4-aryl-7-hydroxy-4*H*-chromenes**4a-k**in the presence of $\{Mo_{132}\}$ as catalyst

Conclusion

In summary, we have reported another application of $\{Mo_{132}\}$, a Keplerate-type giant nanoporousIsopolyoxomolybdate, as catalyst in the synthesis of 2-amino-4-aryl-7-hydroxy-4*H*-chromenes by cyclocondensation of resorcinol, aromatic aldehydes, and ethyl cyanoacetateor malononitrile.Our method has severaladvantages including high yields, short reaction times, inexpensive catalyst, and simple work-up. In addition, thereaction was environmentally friendly because it was solvent-free and the catalyst was recyclable and reusablefor severalcycles with consistent activity.

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