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Fast and Solvent-Free Synthesis of Polyhydroquinolines Catalyzed by a Keplerate Type Giant Nanoporous Isopolyoxomolybdate as a Reusable Catalyst

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A novel application of $(NH_4)_{42}[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]$ catalyst, a Keplerate type giant nanoporous isopolyoxomolybdate, denoted as ($\{Mo_{132}\}$), in the synthesis of polyhydroquinolines is reported. The catalyst was prepared using inexpensive and readily available materials and characterized using FT-IR, and UV spectra. The results showed that this catalyst has high catalytic activity and the desired products were obtained within a few seconds or minutes (for some cases) in high yields under solvent-free conditions at 120 ºC. Furthermore, the catalyst could be recycled after a simple work-up, and reused at least four times without significant reduction in its catalytic activity.

Keywords

Giant nanoporous isopolyoxomolybdate, Keplerate, $\{Mo_{132}\}$, Polyhydroquinolines.

INTRODUCTION

Organic syntheses involving greener process and under solvent-free conditions have been investigated worldwide due to stringent environment and economic regulations.[1-3] In addition, maximizing synthetic efficiency by designing a complexity generating diversity-oriented synthesis is gaining more and more importance in organic synthesis and drug discovery. For this purpose, development and utilization of multicomponent reactions (MCRs) are of prime importance.[4-6] Generally, a product in a MCR is assembled according to a cascade of elementary chemical reactions. Thus, there is a network of reaction equilibria, in which all the starting materials finally flow into an irreversible step yielding the product. The challenge is thus to conduct a MCR in such a way that the network of preequilibrated reactions channels into the main product and does not yield side products.[7] Thus, the developing of new MCRs and improving known MCRs are popular areas of research in current organic chemistry.

The principles of green chemistry have been introduced to eliminate or at least to reduce the use of hazardous materials, such as H_2SO_4 or H_3PO_4 in chemical processes. Cleaner technologies could become possible by making use of the environmental friendly materials, such as the use of solid acids. These catalysts have many advantages over liquid acid catalysts.[8] They 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.

Polyoxometalates (POMs), constituting a large class of metal oxide molecules, are known to have a variety of sizes, structures, electrochemical properties, and chemical reactivities.[9] POMs has been extensively studied because they have many practical applications in

catalysis,[10,11] molecular materials,[12] and corrosion inhibition.[13] In recent decades, uses of some POMs as catalysts for fine organic synthetic processes have been developed and are important for industries related with fine chemicals,[14] including flavors, pharmaceuticals and food industries.[15] In recent years, the synthesis of nanotubular materials consisting of POMs such as POMs-including titania nanotubes[16] and POMs-organic hybrid nanotubes[17] have been a subject of increasing interest. These new types of nanotubes show both the functional properties of POMs but also the advantages of tubular systems in the application, for example, of catalytic and photochemical properties. [16-18] Müller and co-workers, for the first time, reported the famous remarkable giant nanosized porous Keplerate type POM.[19] The Keplerate and giant nanosized porous polyoxometalates show unique features which can be considered as the basis of a new type of nanochemistry and nanomaterials science.[20,21] They find a large variety of applications in fundamental and applied science, such as in modelling passive cation transport through membranes, encapsulation, nanoseparation chemistry, magnetic and optics properties.[22,23] In spite of these valuable properties, to the best of our knowledge, there is only one reference in the literature on the use of giant nanosized porous polyoxometalates as catalyst in epoxidation of olefins[24] and there is no report on the use of them as catalyst in MCRs.

The 1,4-dihydropyridine (1,4-DHP) core is found in a range of compounds exhibiting a broad spectrum of biological activities.[25,26] Some of the representative compounds of this class possess antimicrobial,[27] antitubercular,[28] insecticidal,[29] and neuroprotectant[30] activities. Particularly, 4-aryl-1,4-DHPs are well known as calcium channel blockers and have emerged as one of the most important class of drugs for the treatment of cardiovascular diseases.[31,32] Polyhydroquinolines are a class of fused 1,4-DHPs which have received less attention than other

fused 1,4-DHPs and comparatively very few methods for their preparation have been reported. Polyhydroquinolines are generally synthesized by unsymmetrical Hantzsch reaction which involves the one-pot four-component condensation of dimedone, aldehydes, ammonium acetate, and ethyl acetoacetate using a catalyst such as montmorillonite K-10,[33] Nafion-H,[34] L-proline,[35] vanadium dodecylamino phosphate,[36] trifluoroethanol,[37] FeF_3,[38] $Yb(OTf)_3$,[39] $K_7[PW_{11}CoO_{40}]$,[40] TiO_2 nanoparticles,[41] and $[TBA]_2[W_6O_{19}]$.[42] Synthesis of these compounds using microwave irradiation,[43,44] solar thermal energy,[45] and grinding[46] have also been reported. Nevertheless, in most of these methodologies, the reaction times are long. Also, unsatisfactory yields and tedious isolation procedures are some disadvantages in some of them. These finding make further improvements for the synthesis of these compounds essential.

Due to our interest in the synthesis of heterocyclic compounds,[47-50] and as part of our research on the development of environmentally friendly methods for the synthesis of organic compounds using reusable catalysts,[51-54] we report here the application of a Keplerate type giant nanoporous isopolyoxomolybdate, $(NH_4)_{42}[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]$, denoted as ($\{Mo_{132}\}$) (Figure 1), as highly efficient and reusable novel catalyst to promote the synthesis of polyhydroquinoline derivatives by a one-pot, four-component Hantszch condensation of dimedone, an aldehyde, ammonium acetate, and ethyl acetoacetate under solvent-free conditions (Scheme 1). The diameter of this ball-shaped POM which calculated theoretically is 2.9 nm.[19,20] For the first time this molybdenum cluster has been characterized by the TEM image by Polarz et.al.[21] The TEM picture clearly shows a periodic structure with an average size approximately 3 nm diameter. This experimentally obtained diameter fits nicely with the theoretical value for the inner diameter of the ball-shaped POM. [19,20]

EXPERIMENTAL

Chemicals and Apparatus

All chemicals were available commercially and used without additional purification. The catalyst was synthesized according to the literature. Melting points were recorded on a Stuart SMP3 melting point apparatus. The IR spectra were obtained using a Tensor 27 Bruker spectrophotometer as KBr disks. The ^{1}H NMR (400 and 500 MHz) spectra were recorded with Bruker 400 and 500 spectrometers.

Synthesis of the Keplerate {Mo_{132}}

$N_2H_4.H_2SO_4$ (0.8 g, 6.1 mmol) was added 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). The solution was then stirred for 10 min (color change to bluegreen) and 50% CH_3COOH (83 ml) was subsequently added. The reaction solution, now green, was stored in an open 500-ml Erlenmeyer flask at 20°C without further stirring (slow color change to dark brown). After 4 d the precipitated red-brown crystals were filtered off, washed with absolute ethanol and diethyl ether, respectively, and finally dried in air.[19]

General Procedure for the Synthesis of Polyhydroquinolines 5a-k catalyzed by {Mo_{132}}

A mixture of dimedone **1** (1 mmol), an aldehyde **2a-k** (1 mmol), ammonium acetate **3** (1 mmol), ethyl acetoacetate **4** (1 mmol) and {Mo_{132}} (0.08 g) was heated in an oil bath at 120°C for a few seconds or (for some cases) minutes. The reaction was monitored by TLC. Upon

completion of the transformation, the reaction mixture was cooled to room temperature and hot ethanol was added. This resulted in the precipitation of the catalyst, which was collected by filtration. The catalyst was washed with a small portion of hot ethanol (5 ml). The combined filtrate was concentrated by half and allowed to stand at r.t.. The precipitated solid was collected by filtration, and recrystallized from ethanol to give compounds **5a-k** in high yields.

^{1}H NMR & FT-IR data:

Ethyl 2,7,7-trimethyl-5-oxo-4-phenyl-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (5a)

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.96 (s, 3H, CH_3), 1.10 (s, 3H, CH_3), 1.22 (t, 3H, *J* = 7.1 Hz, CH_3), 2.16-2.39 (m, 4H, $2CH_2$), 2.41 (s, 3H, CH_3), 4.08 (q, 2H, *J* = 7.1 Hz, OCH_2), 5.09 (s, 1H, CH), 6.18 (s br., 1H, NH), 7.13 (t, 1H, *J* = 7.3 Hz, arom-H), 7.22 (t, 2H, *J* = 7.5 Hz, arom-H), 7.33 (d, 2H, *J* = 7.7 Hz, arom-H); IR (KBr, cm^{-1}): υ 3290, 3082, 2957, 1699, 1641, 1611, 1485, 1382, 1215, 1072, 699.

Ethyl 4-(4-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (5b)

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (s, 3H, CH_3), 1.09 (s, 3H, CH_3), 1.21 (t, 3H, *J* = 7.2 Hz, CH_3), 2.13-2.38 (m, 4H, $2CH_2$), 2.40 (s, 3H, CH_3), 4.07 (q, 2H, *J* = 7.2 Hz, OCH_2), 5.03 (s, 1H, CH), 5.95 (s br., 1H, NH), 7.20 (d, *J* = 8.4 Hz, 2H, arom-H), 7.33 (d, *J* = 8.4 Hz, 2H, arom-H); IR (KBr, cm^{-1}): υ 3276, 3206, 3075, 2925, 1703, 1648, 1604, 1491, 1381, 1280, 1215, 1072.

Ethyl 4-(2-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-

carboxylate (5c)

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (s, 3H, CH_3), 1.08 (s, 3H, CH_3), 1.19 (t, 3H, J = 6.8 Hz, CH_3), 2.10-2.35 (m, 4H, $2CH_2$), 2.32 (s, 3H, CH_3), 4.05 (q, 2H, J = 6.8 Hz, OCH_2), 5.40 (s, 1H, CH), 6.14 (s br., 1H, NH), 7.04 (t, J = 7.2 Hz, 1H, arom-H), 7.13 (t, J = 7.2 Hz, 1H, arom-H), 7.25 (d, J = 8.0 Hz, 1H, arom-H), 7.40 (d, J = 7.2 Hz, 1H, arom-H); IR (KBr, cm^{-1}): υ 3290, 3209, 3080, 2959, 1699, 1610, 1493, 1380, 1281, 1217, 1074, 755.

Ethyl 4-(4-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (5d)

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95 (s, 3H, CH_3), 1.10 (s, 3H, CH_3), 1.21 (t, 3H, J = 7.2 Hz, CH_3), 2.15-2.38 (m, 4H, $2CH_2$), 2.40 (s, 3H, CH_3), 4.07 (q, 2H, J = 7.2 Hz, OCH_2), 5.04 (s, 1H, CH), 6.08 (s br., 1H, NH), 7.18 (d, J = 8.4 Hz, 2H, arom-H), 7.26 (d, J = 8.4 Hz, 2H, arom-H); IR (KBr, cm^{-1}): υ 3275, 3192, 3076, 2959, 1706, 1649, 1604, 1489, 1382, 1280, 1214, 1071.

Ethyl 4-(3-hydroxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (5e)

^{1}H NMR (400 MHz, DMSO-d_6): δ 0.87 (s, 3H, CH_3), 1.01 (s, 3H, CH_3), 1.15 (t, 3H, J = 6.8 Hz, CH_3), 1.98 (d, J = 16.4 Hz, 1H, one proton of diastereotopic protons in CH_2), 2.16 (d, J = 16.4 Hz, 1H, one proton of diastereotopic protons in CH_2), 2.28 (d, J = 16.8 Hz, 1H, one proton of diastereotopic protons in CH_2), 2.27 (s, 3H, CH_3), 2.40 (d, J = 16.8 Hz, 1H, one proton of diastereotopic protons in CH_2), 3.98 (q, 2H, J = 6.8 Hz, OCH_2), 4.78 (s, 1H, CH), 6.43-6.61 (m, 3H, arom-H), 6.95 (t, J = 8.0 Hz, 1H, arom-H), 9.03 (s br., 1H, NH or OH), 9.10 (s br., 1H, NH

or OH),; IR (KBr, cm^{-1}): υ 3291, 3079, 2959, 1677, 1609, 1485, 1380, 1278, 1217, 1074.

Ethyl 4-(4-hydroxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (5f): ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.85 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 1.13 (t, 3H, J = 7.2 Hz, CH_3), 1.96 (d, J = 16.8 Hz, 1H, one proton of diastereotopic protons in CH_2), 2.15 (d, J = 16.8 Hz, 1H, one proton of diastereotopic protons in CH_2), 2.25 (s, 3H, CH_3), 2.27 (d, J = 17.2 Hz, 1H, one proton of diastereotopic protons in CH_2), 2.40 (d, J = 17.2 Hz, 1H, one proton of diastereotopic protons in CH_2), 3.96 (q, 2H, J = 7.2 Hz, OCH_2), 4.73 (s, 1H, CH), 6.55 (d, J = 8.4 Hz, 2H, arom-H), 6.92 (d, J = 8.4 Hz, 2H, arom-H), 8.98 (s br., 1H, NH or OH), 9.06 (s br., 1H, NH or OH); IR (KBr, cm^{-1}): υ 3416, 3280, 3207, 3076, 2959, 1687, 1612, 1486, 1380, 1271, 1220.

Ethyl 4-(3-nitrophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (5g)

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95 (s, 3H, CH_3), 1.11 (s, 3H, CH_3), 1.21 (t, 3H, J = 7.2 Hz, CH_3), 2.13-2.39 (m, 4H, $2CH_2$), 2.41 (s, 3H, CH_3), 4.07 (q, 2H, J = 7.2 Hz, OCH_2), 5.17 (s, 1H, CH), 6.23 (s br., 1H, NH), 7.39 (t, J = 8.0 Hz, 1H, arom-H), 7.74 (d, J = 7.6 Hz, 1H, arom-H), 7.97-8.02 (m, 1H, arom-H), 8.13 (t, J = 2.0 Hz, 1H, arom-H); IR (KBr, cm^{-1}): υ 3283, 3211, 3076, 2958, 1704, 1606, 1534, 1487, 1380, 1352, 1280, 1211, 1071.

Ethyl 4-(4-nitrophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (5h)

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (s, 3H, CH_3), 1.12 (s, 3H, CH_3), 1.20 (t, 3H, J = 7.1 Hz,

CH_3), 2.15-2.43 (m, 4H, $2CH_2$), 2.45 (s, 3H, CH_3), 4.08 (q, 2H, J = 7.1 Hz, OCH_2), 5.19 (s, 1H, CH), 6.00 (s br., 1H, NH), 7.51 (d, J = 8.5 Hz, 2H, arom-H), 8.11 (d, J = 8.5 Hz, 2H, arom-H); IR (KBr, cm^{-1}): υ 3275, 3189, 3074, 2966, 1703, 1649, 1607, 1518, 1493, 1378, 1344, 1280, 1215, 1072.

Ethyl 4-(4-methylphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (5i)

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (s, 3H, CH_3), 1.09 (s, 3H, CH_3), 1.24 (t, 3H, J = 7.2 Hz, CH_3), 2.14-2.35 (m, 4H, $2CH_2$), 2.28 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 4.09 (q, 2H, J = 7.2 Hz, OCH_2), 5.03 (s, 1H, CH), 6.41 (s br., 1H, NH), 7.02 (d, J = 7.6 Hz, 2H, arom-H), 7.21 (d, J = 7.6 Hz, 2H, arom-H); IR (KBr, cm^{-1}): υ 3276, 3207, 3077, 2959, 1702, 1605, 1494, 1380, 1281, 1216, 1072.

Ethyl 4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (5j)

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (s, 3H, CH_3), 1.09 (s, 3H, CH_3), 1.23 (t, 3H, J = 7.2 Hz, CH_3), 2.15-2.36 (m, 4H, $2CH_2$), 2.38 (s, 3H, CH_3), 3.75 (s, 3H, OCH_3), 4.09 (q, 2H, J = 7.2 Hz, OCH_2), 5.02 (s, 1H, CH), 6.27 (s br., 1H, NH), 6.75 (d, J = 8.8 Hz, 2H, arom-H), 7.23 (d, J = 8.8 Hz, 2H, arom-H); IR (KBr, cm^{-1}): υ 3276, 3206, 3077, 2957, 1702, 1649, 1605, 1496, 1380, 1280, 1215, 1072.

Ethyl 2,7,7-trimethyl-5-oxo-4-propyl-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (5k)

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.84 (t, 3H, J = 7.2 Hz, CH_3), 1.10 (s, 6H, $2CH_3$), 1.15-1.27 (m, 2H, CH_2), 1.30 (t, 3H, J = 7.2 Hz, CH_3), 1.30-1.43 (m, 2H, CH_2), 2.17-2.37 (m, 4H, $2CH_2$), 2.32 (s, 3H, CH_3), 4.03 (t, 1H, J = 5.2 Hz, CH), 4.10-4.25 (m, 2H, OCH_2), 6.09 (s br., 1H, NH); IR (KBr, cm^{-1}): υ 3277, 3210, 2958, 1699, 1639, 1601, 1489, 1393, 1279, 1216, 1066.

RESULTS AND DISCUSSION

Characterization of the Catalyst

The $\{Mo_{132}\}$ catalyst was characterized by FT-IR and UV/Vis spectroscopy. The FT-IR spectrum of the catalyst shown in Figure 3a exhibits the characteristic vibrational bonds of Mo = O at 969 and 936, the COO and NH_4^+ at 1544 & 1407 as well as H_2O at 2500-3600 & 1618. The locations of these featured peaks for the prepared catalyst as well as other bonds at 855, 792, 725, 628, 568, 514 and 467 were in well agreement with those reported by Müller[19] and Zhou.[20] The UV/Vis spectrum also confirms the structure of the prepared catalyst indicating the characteristic absorption bonds at 213, 232, 265, and 447 nm which are in agreement with literature.[19]

Catalytic Performance of $\{Mo_{132}\}$ in the Synthesis of Polyhydroquinolines

In order to evaluate the catalytic efficiency of $\{Mo_{132}\}$ in the synthesis of polyhydroquinolines and to determine the most appropriate reaction conditions; initially a model study was carried out on the synthesis of compound **5d** by reaction of dimedone **1** (1 mmol), 4-chlorobenzaldehyde **2d** (1 mmol), ammonium acetate **3** (1 mmol), and ethyl acetoacetate **4** (1 mmol) in different sets of reaction conditions (Table 1). As can be seen from Table 1, among the

tested solvents such as EtOH, MeOH, H_2O, CH_2Cl_2, CH_3CN, and also solvent-free conditions and various amounts of the catalyst, the shortest time and best yield was achieved in solvent-free conditions. It was also found that the yield of compound **5d** was strongly affected by the catalyst amount and reaction temperature in solvent-free conditions. No product was obtained in the absence of the catalyst at 120°C following a 60 min reaction time (entry 1) indicating that the catalyst is necessary for the reaction. Increasing the amount of the catalyst and reaction temperature up to 0.08 g and 120°C, respectively, increased the yield of the product **5d**, whereas further increase in both catalyst amount and temperature did not improve the product yield and reaction time.

With optimized conditions in hand, and in order to evaluate the scope of this catalytic transformation, a range of polyhydroquinolines were prepared by the reaction of dimedone, various aldehydes, ammonium acetate, and ethyl acetoacetate. The results are summarized in Table 2. In most cases, the reactions are terminated after a few seconds and for some cases in a few minutes, giving the products **5a-k** in high yields. On the other hand, easy separation of obtained products from the catalyst makes this method useful for the synthesis of polyhydroquinolines.

To further evaluate the overall utility of the current methodology, we compared our results with those of the other methods reported for the synthesis of polyhydroquinolines (Table 3). Our reaction conditions showed a shorter reaction time than all the other conditions and gave high yields of the desired products.

The reusability of $\{Mo_{132}\}$ was also investigated. For this purpose, the synthesis of compound **5d** was again studied under optimized conditions. The $\{Mo_{132}\}$ catalyst was readily recovered from the reaction mixture using the procedure outlined in the experimental section. The separated catalyst was washed with hot ethanol and then dried at 60°C under vacuum for 1 h before being reused in a similar reaction. We found that the catalyst could be reused at least four times with only a slight reduction in activity (Figure 2). Furthermore, the FT-IR spectra of the recovered catalysts were almost identical to the spectrum of the fresh catalyst, indicating that the structure of the catalyst was unchanged by the reaction (Figure 3).

At the end, since the $\{Mo_{132}\}$ catalyst has several accessible Mo sites which can act as Lewis acid centers, we therefore believe that it promotes these reactions by increasing the electrophilic character of the carbonyl groups in the reactions.

CONCLUSION

In conclusion, we showed that $\{Mo_{132}\}$, a Keplerate type giant nanoporous isopolyoxomolybdate, efficiently catalyzes the synthesis of polyhydroquinolines *via* one-pot four-component unsymmetrical Hantzsch condensation of dimedone, aromatic or aliphatic aldehydes, ammonium acetate, and ethyl acetoacetate. The method was very fast and the desired products were obtained within a few seconds or minutes (for some cases) in high yields under solvent-free conditions at 120 ºC. The catalyst can be recycled after a simple work-up, and reused at least four times without substantial reduction in its catalytic activity. The procedure is also advantageous in the sense that it is a solvent-free reaction and therefore operates under environmentally friendly conditions.

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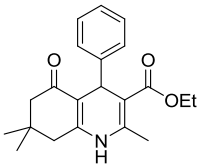
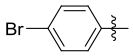
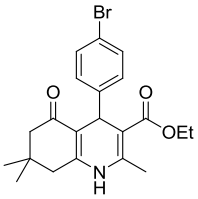
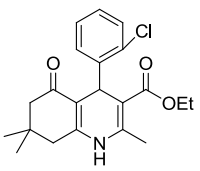
TABLE 1 Optimization of reaction conditions for synthesis of compound **5d** catalyzed by $\{Mo_{132}\}$

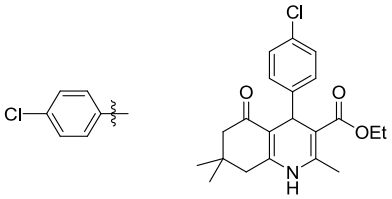
Entry	Catalyst (g)	Solvent	T (°C)	Time (min)	Isolated Yield (%)
1	-----	-----	120	60	-----
2	0.02	-----	100	10	73
3	0.02	-----	120	7	78
4	0.04	-----	100	8	77
5	0.04	-----	120	5	83
6	0.06	-----	100	5	80
7	0.06	-----	120	2	89
8	0.08	-----	100	2	86
9	0.08	-----	120	<1	97
10	0.10	-----	100	2	92
11	0.10	-----	120	<1	96
12	0.08	EtOH	Reflux	60	25
13	0.08	MeOH	Reflux	60	19
14	0.08	H_2O	Reflux	60	32
15	0.08	CH_2Cl_2	Reflux	70	trace
16	0.08	CH_3CN	Reflux	70	trace

Reaction conditions: dimedone **1** (1 mmol), 4-chlorobenzaldehyde **2d** (1 mmol), ammonium acetate **3** (1 mmol), and ethyl acetoacetate **4** (1 mmol)

TABLE 2 {Mo_{132}} catalyzed synthesis of polyhydroquinolines **5a-k**

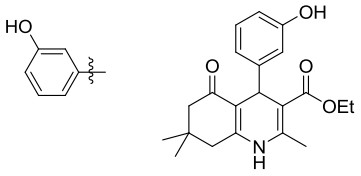
Entry	R	Products	Time (min)	Isolated Yields (%)	m.p. (°C)	
					Found	Reported
1		 **5a**	<1	95	210-212	202-205 [35]
2		 **5b**	<1	94	250-253	251-253 [35]
3			<1	92	205-207	206-208 [42]

5c



4	<1	97	245-247	246-248 [42]

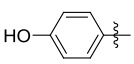
5d

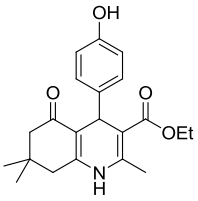


5	2	90	220-223	225-227 [42]

5e

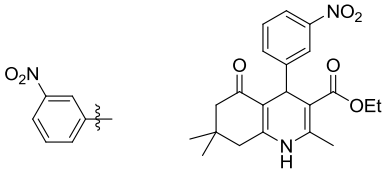
6	1	91	237-240	234-237





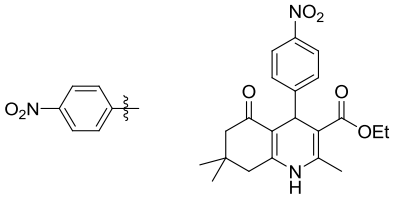
[35]

5f



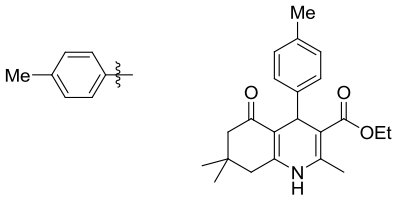
7	<1	95	179-181	176-179 [35]

5g

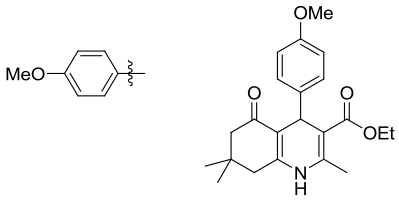


8	<1	91	243-245	241-243 [35]

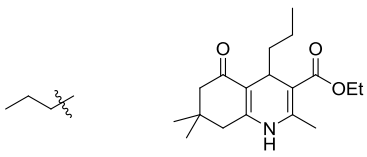
5h

9		<1	92	258-260	260-261 [39]

5i

10		<1	90	256-259	252-254 [35]

5j

11		3	90	148-150	147-148 [39]

5k

Reaction conditions: dimedone **1** (1 mmol), an aldehyde **2a-k** (1 mmol), ammonium acetate **3** (1 mmol), ethyl acetoacetate **4** (1 mmol), $\{Mo_{132}\}$ (0.08 g), 120 ºC, solvent-free.

TABLE 3 Comparison of the efficiencies of different catalysts for the synthesis of polyhydroquinolines

Catalyst	Conditions		Time (min)	Isolated Yield (%)	Ref.
	Solvent	T (°C)			
montmorillonite K-10	EtOH	reflux	20-100	34-95	[33]
Nafion-H	PEG 400/H_2O	50	90-100	88-96	[34]
L-Proline	EtOH	reflux	360-420	81-92	[35]
Vanadium dodecylamino phosphate	MeOH/H_2O	r.t.	90-160	68-83	[36]
trifluoroethanol	trifluoroethanol	70	180	75-98	[37]
FeF_3	EtOH	reflux	60-90	85-95	[38]
$Yb(OTf)_3$	EtOH	reflux	120-480	85-95	[39]
$K_7[PW_{11}CoO_{40}]$	CH_3CN	reflux	25-35	80-90	[40]
TiO_2 nanoparticles	EtOH	reflux	25-45	80-96	[41]
$[TBA]_2[W_6O_{19}]$	----	110	20-40	67-95	[42]
$\{Mo_{132}\}$	----	120	<1-3	90-97	This work

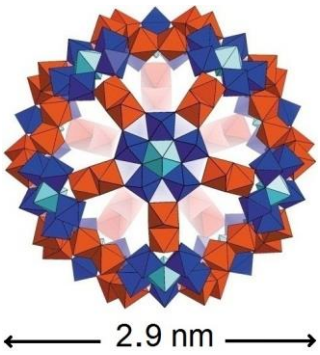


Figure 1. Structure of $\{Mo_{132}\}$

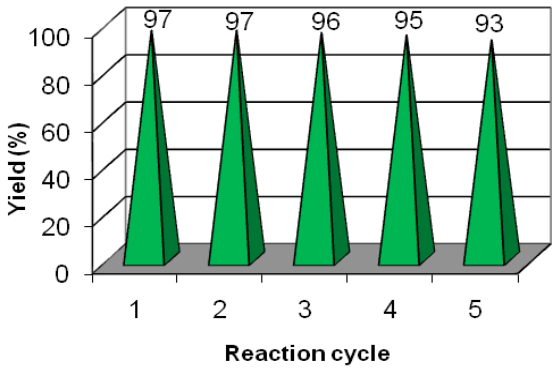


Figure 2. Reusability of {Mo_{132}} for the synthesis of compound **5d**.

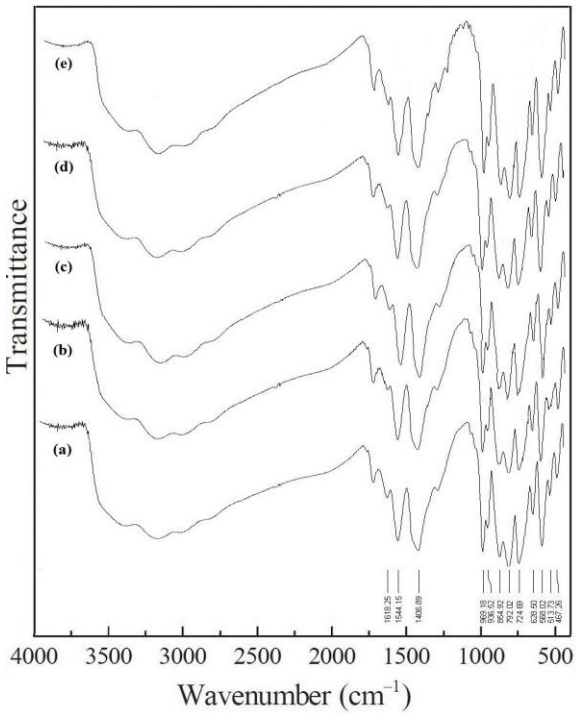
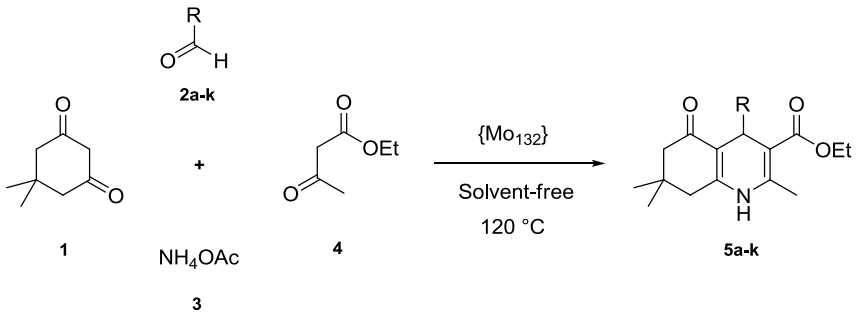


Figure 3. FT-IR spectra of fresh catalyst {Mo_{132}} (a, first run), and recovered catalysts (b-e, second to fifth run, respectively) for synthesis of compound **5d** in model reaction.



Scheme 1. Synthesis of polyhydroquinolines catalyzed by {Mo_{132}}