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Article

Tetrabutylammonium hexatungstate $[TBA]_2[W_6O_{19}]$: Novel and reusable heterogeneous catalyst for rapid solvent-free synthesis of polyhydroquinolines via unsymmetrical Hantzsch reaction

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ABSTRACT

A novel, efficient, and environmentally friendly method for the synthesis of polyhydroquinoline derivatives by a one-pot, four-component unsymmetrical Hantzsch condensation of dimedone, aldehydes, ethyl acetoacetate, and ammonium acetate in the presence of a catalytic amount of tetrabutylammonium hexatungstate $[TBA]_2[W_6O_{19}]$ under solvent-free conditions has been developed. The results showed that this heterogeneous catalyst has high catalytic activity and the desired products were obtained in good to high yields. Moreover, the catalyst was found to be reusable and considerable catalytic activity was still achieved after the fifth run.

1. Introduction

Multicomponent reactions (MCRs) have attracted much interest and are highly regarded in modern organic synthesis and medicinal chemistry because they are one-pot processes that bring together three or more components and show high atom economy and high selectivity [1–4]. MCRs have been widely used in the convergent synthesis of complex and important organic molecules from simple and readily available starting materials, and have emerged as powerful tools for drug discovery [5,6]. The development of new MCRs and improvement of known MCRs are therefore areas of considerable current interest. One such reaction is the synthesis of polyhydroquinolines via the unsymmetrical Hantzsch reaction.

The 1,4-dihydropyridine (1,4-DHP) core is found in a range of compounds exhibiting a broad spectrum of biological activities [7–9]. Some of the representative compounds of this class possess antimicrobial [10], antitubercular [11], insecticidal [12], and neuroprotectant [13] activities. In particular, 4-aryl-1,4-DHPs are well known as calcium-channel blockers and have emerged as one of the most important classes of drugs for the treatment of cardiovascular diseases [14,15]. Recently, 1,4-DHPs have been used as organocatalysts for asymmetric reactions such as hydrogenation of quinolines in the synthesis of alkaloids [16], asymmetric reductive amination of aldehydes [17], and hydrogenation of α,β-unsaturated aldehydes and ketones [18,19].

Polyhydroquinolines are a class of fused 1,4-DHPs that have received less attention than other fused 1,4-DHPs, and comparatively few methods for their preparation have been reported. Polyhydroquinolines are generally synthesized by an unsymmetrical Hantzsch reaction, which involves the one-pot, four-component condensation of dimedone, aldehydes, ethyl acetoacetate, and ammonium acetate, using various promoting agents such as montmorillonite K-10 [20], ionic liquids [21], I_2 [22], FeF_3 [23], $Sc(OTf)_3$ (OTf = trifluoromethanesulfonate) [24], $Yb(OTf)_3$ [25], cerium(IV) ammonium nitrate [26], and trifluoroethanol [27]. Syntheses of these compounds using mi-

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crowave irradiation [28,29], solar thermal energy [30], and grinding [31] have also been reported.

However, most of these methodologies suffer from disadvantages such as unsatisfactory yields, toxic organic solvents, harsh reaction conditions, long reaction times, and the use of relatively expensive reagents. These findings prompted us to perform investigations to find new catalysts that will enable the synthesis of polyhydroquinoline derivatives using simple experimental set-ups and eco-friendly conditions.

The development of environmentally benign, efficient, and economical methods for the synthesis of biologically interesting compounds [32–35] remains a significant challenge in synthetic chemistry. Green chemistry emphasizes the need for environmentally clean synthesis, which involves improvements in selectivity, elimination of hazardous solvents, and easy work-up, using reusable catalysts. As a result, attempts to replace homogeneous catalysts by non-toxic, non-corrosive, easy to handle, and environmentally friendly heterogeneous catalysts have increased rapidly in recent years [36–39]. Reactions under solvent-free conditions have also continued to attract the attention of researchers both from academia and industry [40,41]. This is because solvent-free reactions usually need shorter reaction times and have simpler work-up procedures.

As a result of our interest in the synthesis of heterocyclic compounds [42–45], and as part of our research on the development of environmentally friendly methods for the synthesis of organic compounds using reusable catalysts [46–50], we recently investigated the use of tetrabutylammonium hexatungstate, $[TBA]_2[W_6O_{19}]$, as a catalyst in the Knoevenagel condensation [51], the Biginelli reaction [52], and in the syntheses of biscoumarins [53] and 1,8-dioxodecahydroacridines [54]. This new reusable heterogeneous catalyst performed well and showed high catalytic activity in these transformations. These facts encouraged us to explore the use of this catalyst in the synthesis of polyhydroquinoline derivatives under solvent-free conditions.

2. Experimental

2.1. Synthesis of $[TBA]_2[W_6O_{19}]$

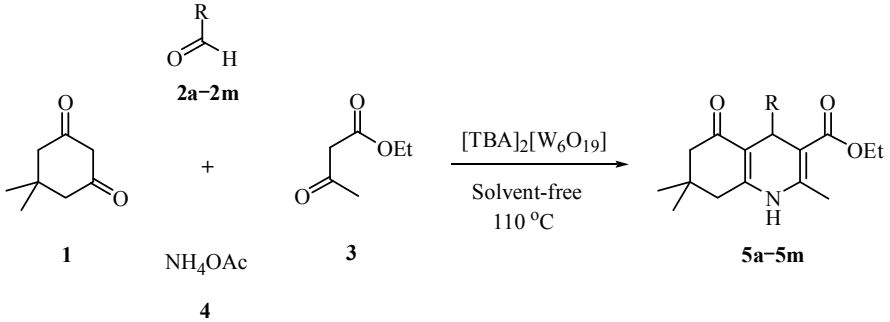
A mixture of sodium tungstate dihydrate ($Na_2WO_4{\cdot}2H_2O$, 99%, 33 g, 0.1 mol), acetic anhydride (40 ml), and *N*,*N*-dimethylformamide (DMF, 30 ml) was heated at 100 °C for 3 h to obtain a white cream. A solution of acetic anhydride (20 ml) and 12 mol/L HCl (18 ml) in DMF (50 ml) was then added drop-wise over a period of time with stirring, and the resulting mixture was filtered to remove the undissolved white solids. A solution of tetrabutylammonium bromide (15.1 g, 0.047 mol) in methanol (50 ml) was then added to the filtrate with rapid stirring to give a white precipitate. The resulting suspension was stirred for 5 min and the product was then collected by filtration. Recrystallization from a minimum amount of hot dimethyl sulfoxide gave the product as colorless diamond-shaped crystals [55].

2.2. General procedure for synthesis of polyhydroquinolines *5a–5m*

A mixture of dimedone **1** (1 mmol), an aldehyde **2a–2m** (1 mmol), ethyl acetoacetate **3** (1 mmol), ammonium acetate **4** (1 mmol), and $[TBA]_2[W_6O_{19}]$ (0.07 mmol, 7 mol%) was heated in an oil bath at 110 °C for 20–30 min. The reaction was monitored using thin-layer chromatography. On completion of the transformation, the reaction mixture was cooled to room temperature and hot ethanol was added. This resulted in precipitation of the catalyst, which was collected by filtration. The product was collected from the filtrate after cooling to room temperature and recrystallized from ethanol to give compounds **5a–5m** in high yields (Scheme 1). The melting points were recorded using a Stuart SMP3 melting-point apparatus. The IR spectra of the products were obtained with KBr disks, using a Tensor 27 Bruker spectrophotometer. The ^1H NMR (400 and 500 MHz) spectra were recorded using Bruker 400 and 500 spectrometers.

Ethyl 2,7,7-trimethyl-5-oxo-4-phenyl-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (**5a**). ^1H NMR (500 MHz, $CDCl_3$): δ 0.97 (s, 3H, CH_3), 1.11 (s, 3H, CH_3), 1.23 (t, 3H, J = 7.1 Hz, CH_3), 2.15–2.39 (m, 4H, $2CH_2$), 2.41 (s, 3H, CH_3), 4.09 (q, 2H, J = 7.1 Hz, OCH_2), 5.01 (s, 1H, CH), 6.18 (s br., 1H, NH), 7.12 (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}): ν 3289, 3219, 3082, 2963, 1699, 1644, 1611, 1485, 1381, 1213, 1072, 761, 698, 530.

Ethyl 4-(4-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (**5b**). ^1H NMR (400 MHz, $CDCl_3$): δ 0.95 (s, 3H, CH_3), 1.09 (s, 3H, CH_3), 1.22 (t, 3H, J = 7.2 Hz, CH_3), 2.14–2.37 (m, 4H, $2CH_2$), 2.39 (s, 3H, CH_3), 4.08 (q, 2H, J = 7.2 Hz, OCH_2), 5.04 (s, 1H, CH), 6.21 (s br., 1H, NH), 7.21 (d, J = 8.4 Hz, 2H, arom-H), 7.34 (d, J = 8.4 Hz, 2H, arom-H); IR (KBr, cm^{-1}): ν 3275, 3206, 3076, 2958, 1703, 1649, 1604, 1487, 1381,



Scheme 1. $[TBA]_2[W_6O_{19}]$-catalyzed synthesis of polyhydroquinoline derivatives.

1280, 1215, 1073, 843, 534.

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), 1.22 (t, 3H, J = 7.2 Hz, CH_3), 2.14–2.39 (m, 4H, $2CH_2$), 2.40 (s, 3H, CH_3), 4.08 (q, 2H, J = 7.2 Hz, OCH_2), 5.05 (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}): ν 3275, 3207, 3077, 2959, 1706, 1649, 1605, 1489, 1382, 1280, 1214, 1071, 844, 535.

Ethyl 4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (**5g**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (s, 3H, CH_3), 1.09 (s, 3H, CH_3), 1.23 (t, 3H, J = 7.2 Hz, CH_3), 2.14–2.36 (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), 6.76 (d, J = 8.8 Hz, 2H, arom-H), 7.24 (d, J = 8.8 Hz, 2H, arom-H); IR (KBr, cm^{-1}): ν 3277, 3207, 3078, 2958, 1701, 1648, 1606, 1495, 1380, 1281, 1216, 850, 537.

Ethyl 4-(4-methylphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (**5h**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.97 (s, 3H, CH_3), 1.09 (s, 3H, CH_3), 1.24 (t, 3H, J = 7.2 Hz, CH_3), 2.13–2.34 (m, 4H, $2CH_2$), 2.27 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 4.09 (q, 2H, J = 7.2 Hz, OCH_2), 5.04 (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}): ν 3276, 3207, 3077, 2959, 1702, 1648, 1605, 1493, 1380, 1282, 1216, 1072, 849, 531.

Ethyl 2,7,7-trimethyl-4-(4-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (**5j**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.94 (s, 3H, CH_3), 1.12 (s, 3H, CH_3), 1.21 (t, 3H, J = 7.1 Hz, CH_3), 2.16–2.44 (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}): ν 3276, 3189, 3075, 2966, 1703, 1649, 1607, 1519, 1493, 1378, 1345, 1280, 1216, 1072, 867, 831, 533.

Ethyl 2,7,7-trimethyl-5-oxo-4-propyl-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (**5m**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.85 (t, 3H, J = 7.2 Hz, CH_3), 1.11 (s, 6H, $2CH_3$), 1.16–1.28 (m, 2H, CH_2), 1.31 (t, 3H, J = 7.2 Hz, CH_3), 1.34–1.47 (m, 2H, CH_2), 2.17-2.38 (m, 4H, $2CH_2$), 2.33 (s, 3H, CH_3), 4.04 (t, 1H, J = 5.6 Hz, CH), 4.11–4.27 (m, 2H, OCH_2), 5.91 (s br., 1H, NH); IR (KBr, cm^{-1}): ν 3278, 3209, 2957, 1699, 1640, 1602, 1489, 1393, 1279, 1216, 1066, 740.

3. Results and discussion

To optimize the reaction conditions, a selected model reaction was carried out with dimedone **1** (1 mmol), 4-chlorobenzaldehyde **2d** (1 mmol), ethyl acetoacetate **3** (1 mmol), and ammonium acetate **4** (1 mmol) under different sets of reaction conditions. The results are summarized in Table 1. The results clearly show that the catalyst is essential, and that the catalytic activity of $[TBA]_2[W_6O_{19}]$ is high, giving **5d** in high yield in a short reaction time. Using $[TBA]_2[W_6O_{19}]$ as the catalyst, we evaluated the reaction in various solvents and under solvent-free conditions. The product yield in refluxing H_2O was low, even after reaction for 240 min (Table 1, entry 15), whereas relatively good yields were obtained in refluxing CH_2Cl_2, CH_3CN, or EtOH (Table 1, entries 16–18). However, the best results in terms of yield, as well as reaction time, were obtained under solvent-free conditions (Table 1, entry 12). It was also found that the yield of compound **5d** was strongly affected by the catalyst amount and reaction temperature under solvent-free conditions. No product was observed when the reaction was carried out under solvent-free conditions without any catalyst, even after a long reaction time (entry 1). The best result was obtained when the reaction was conducted at 110 °C in the presence of 7 mol% of the $[TBA]_2[W_6O_{19}]$ catalyst (Table 1, entry 12).

To determine the generality of this method, the scope of the

Table 1
Effect of $[TBA]_2[W_6O_{19}]$ catalyst amount, solvent, and temperature on model reaction.

Entry	Catalyst (mol%)	Solvent	Temperature (°C)	Time (min)	Yield* (%)
1	—	—	120	120	—
2	3	—	60	40	54
3	3	—	90	40	66
4	3	—	110	20	70
5	3	—	130	20	71
6	5	—	60	40	55
7	5	—	90	20	72
8	5	—	110	20	77
9	5	—	130	20	76
10	7	—	60	40	60
11	7	—	90	20	81
12	7	—	110	20	95
13	7	—	130	20	94
14	8	—	110	20	85
15	7	H_2O	reflux	240	40
16	7	CH_2Cl_2	reflux	240	63
17	7	CH_3CN	reflux	240	65
18	7	EtOH	reflux	240	75

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

Table 2
$[TBA]_2[W_6O_{19}]$-catalyzed synthesis of polyhydroquinoline derivatives **5a**–**5m**.

R	Product[a]	Time (min)	Yield[b] (%)	Melting point (°C)	
				Found	Reported
C_6H_5	**5a**	20	93	214–216	209–210 [22]
4-BrC_6H_4	**5b**	20	90	259–260	254–255 [24]
2-ClC_6H_4	**5c**	30	85	206–208	206–208 [28]
4-ClC_6H_4	**5d**	20	95	246–248	244–246 [26]
3-HOC_6H_4	**5e**	20	86	225–227	218–220 [28]
4-HOC_6H_4	**5f**	20	91	239–241	237–238 [22]
4-$MeOC_6H_4$	**5g**	20	82	257–259	258–259 [24]
4-MeC_6H_4	**5h**	20	88	257–260	260–261 [25]
3-$O_2NC_6H_4$	**5i**	30	83	181–183	178–180 [26]
4-$O_2NC_6H_4$	**5j**	20	83	245–247	244–246 [28]
2-Furyl	**5k**	20	88	240–243	245–247 [26]
Et	**5l**	40	69	163–165	145–146 [25]
n-Pr	**5m**	40	67	165–167	147–148 [25]

Reaction conditions: dimedone **1** (1 mmol), an aldehyde **2a**–**2m** (1 mmol), ethyl acetoacetate **3** (1 mmol), ammonium acetate **4** (1 mmol), $[TBA]_2[W_6O_{19}]$ (0.07 mmol, 7 mol%), 110 °C, solvent-free.
[a] All the products were characterized by their IR spectral data and a comparison of their melting points with those of authentic samples. The structures of some products were also confirmed by ^1H NMR analysis.
[b] Isolated yields.

reaction was investigated using a number of aromatic and aliphatic aldehydes under the optimized reaction conditions; the results are presented in Table 2. The results show that the protocol is useful for different aromatic aldehydes bearing electron-withdrawing and electron-donating substituents in the aromatic rings, giving high yields of the products. Aliphatic aldehydes, however, afforded the corresponding polyhydroquinolines in moderate yields.

The principle advantage of the use of heterogeneous solid catalysts in organic transformations is their reusability. The catalyst was readily recovered from the reaction mixture using the procedure outlined in the experimental section. The separated catalyst was washed with cold 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 used at least five times with only a slight reduction in activity (Fig. 1). Furthermore, retention of the structure of the catalyst was confirmed by comparing the FT-IR spectra of the recovered catalysts (Fig. 2(2)–(5)) with that of the fresh catalyst (Fig. 2(1)) for the model reaction. As shown, these spectra are almost identical.

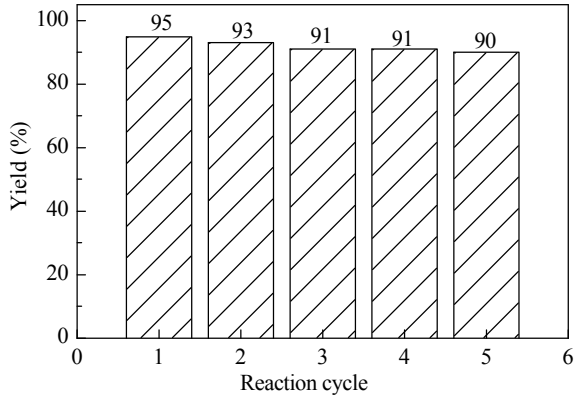


Fig. 1. Reusability of $[TBA]_2[W_6O_{19}]$ for synthesis of compound **5d**.

A mechanistic rationalization for this reaction is provided in Scheme 2. On the basis of our previous reports [51–54], it is reasonable to assume that $[TBA]_2[W_6O_{19}]$ can play a dual role. We therefore propose that the tetrabutylammonium ion $[(n\text{-}Bu)_4N^+]$ induces polarization of the carbonyl groups, whereas the terminal oxygen atoms or the bridging oxygen atom in the polyoxometalate anion, $W_6O_{19}^{2-}$, are slightly basic and can promote the necessary reactions. $[TBA]_2[W_6O_{19}]$ can therefore activate the reactants and also the intermediates in this reaction. As shown in Scheme 2, polyhydroquinolines can be formed either through path **A** or through path **B**. It is proposed that intermediate **I**, in path **A**, is obtained from the reaction of dimedone with an aldehyde, whereas in path **B** the intermediate is formed from the reaction of ethyl acetoacetate with an aldehyde. Intermediate **II** in paths **A** and **B** is obtained from the reaction of ammonium acetate with ethyl acetoacetate

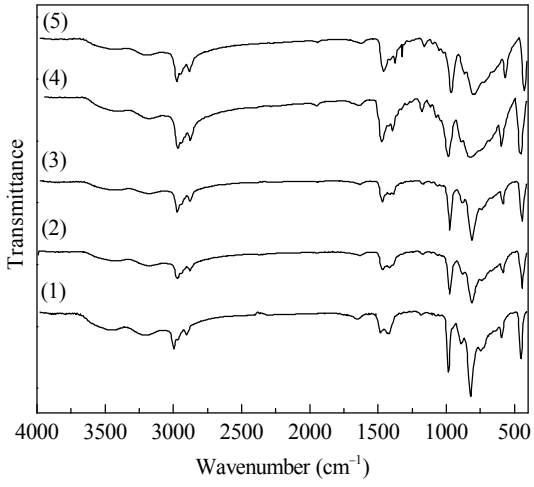
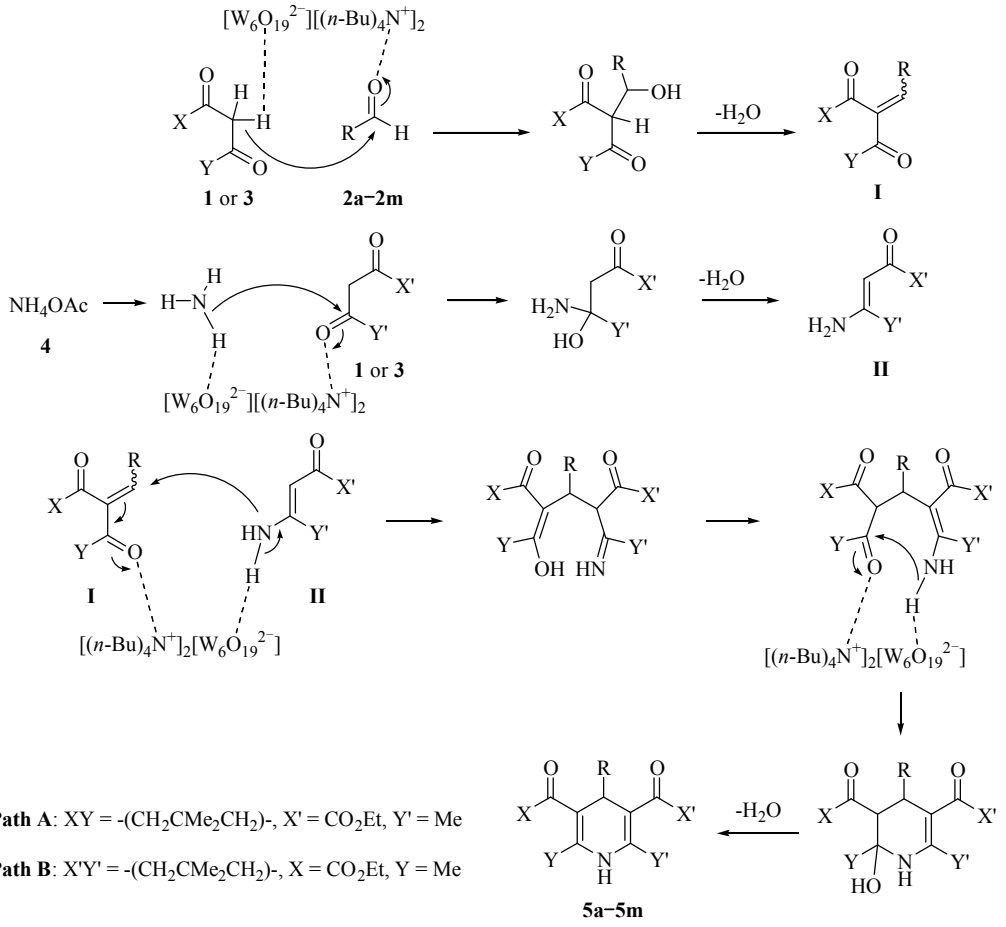


Fig. 2. FT-IR spectra of fresh catalyst ((1), first run), and recovered catalysts ((2–5), second to fifth run, respectively) for synthesis of compound **5d**.



Scheme 2. Plausible mechanism for formation of polyhydroquinolines in the presence of $[TBA]_2[W_6O_{19}]$ as catalyst.

and dimedone, respectively. We propose that $[TBA]_2[W_6O_{19}]$ facilitates the formation of intermediates **I** and **II**, and these intermediates subsequently react together to give the final products **5a–5m**. Under the conditions used, attempts to isolate intermediates **I** and **II** failed, even after careful monitoring of the reactions.

4. Conclusions

A simple, convenient, and practical method was reported for the synthesis of polyhydroquinolines through a one-pot, four-component, unsymmetrical Hantzsch condensation of dimedone, aldehydes, ethyl acetoacetate, and ammonium acetate using $[TBA]_2[W_6O_{19}]$ as a catalyst under solvent-free conditions. The method offers several significant advantages, including short reaction times, high yields of products, easy work-up, and the absence of any hazardous organic solvents. The simplicity of the procedure, combined with the ease of recovery, reusability, and stability of the catalyst, makes this method an economical, environmentally benign, and waste-free chemical process for the synthesis of polyhydroquinolines.

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Graphical Abstract

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Tetrabutylammonium hexatungstate $[TBA]_2[W_6O_{19}]$: Novel and reusable heterogeneous catalyst for rapid solvent-free synthesis of polyhydroquinolines via unsymmetrical Hantzsch reaction

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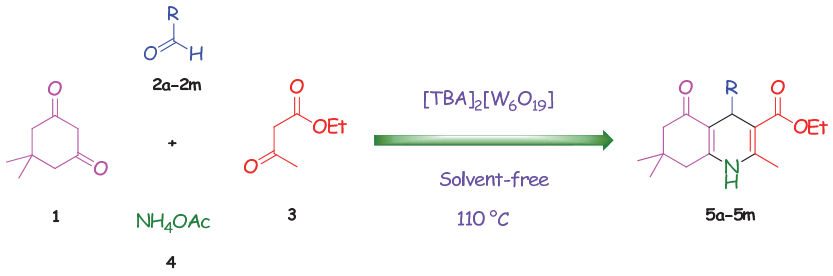

A simple and efficient method for the synthesis of polyhydroquinolines by a one-pot, four-component reaction of dimedone, aldehydes, ethyl acetoacetate, and ammonium acetate, using tetrabutylammonium hexatungstate, $[TBA]_2[W_6O_{19}]$, as a recyclable catalyst under solvent-free conditions is described. The catalyst has high activity and the desired products were obtained in good to high yields.

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