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FULL PAPER

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Synthesis, characterization and application of nano-$CoAl_2O_4$ as an efficient catalyst in the preparation of hexahydroquinolines

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In this work, nano-$CoAl_2O_4$ was prepared and characterized by FT-IR, energy dispersive X-ray analysis (EDX), X-ray diffraction patterns (XRD), scanning electron microscopy (SEM), vibrating sample magnetometer (VSM) and transmission electron microscopy (TEM). Nano-$CoAl_2O_4$ was applied for the synthesis of hexahydroquinoline derivatives by the condensation reaction between ethyl acetoacetate, dimedone and various aldehydes. These reactions were carried out at 80 °C under solvent-free conditions.

KEYWORDS
hantzsch synthesis, hexahydroquinoline, multi-component reaction, nano-$CoAl_2O_4$, solvent-free

1 | INTRODUCTION

Multi-component reactions have an important role in combinatorial chemistry because of the ability to give desired products with high efficiency and atomic economy by the reaction of three or more compounds together in a one step. Additionally, MCRs improve simplicity and synthetic efficiency on the conventional organic synthesis.[1]

Nano Cobalt aluminate (nano-$CoAl_2O_4$) is introduced as a catalyst, pigment layer on luminescent materials and color filter for automotive lamps.[2] Coloration of plastics, fibers, rubber, glass, ceramic bodies, paint and porcelain are other uses of this material because this nano-catalyst is a thermally and chemically stable pigment.[3] For the synthesis of cobalt aluminate oxide several techniques such as sol–gel,[4] EDTA chelating precursor,[5] polymer aerosol pyrolysis,[6] reverse micelle processes,[7,8] oil-in-water,[9] molten salt,[10] hydrothermal,[11] combustion,[12] and Pechini[13] are reported. Heterogeneous catalyst (nano-$CoAl_2O_4$) has many advantages including good selectivity with high stability, reusability and simple recyclability.[14] Some methods for the preparation of polyhydroquinolines have been reported. The three-component condensation reaction of aldehyde with ethyl acetoacetate and ammonia in acetic acid or alcohol are classical method for the synthesis of these compounds.[15–17] Lower yields of the products, usage of an excess of organic solvent and long reaction times are disadvantages of this method. Recently, some investigations have been introduced in order to improve the efficiency of Hantzsch DHPs synthesis, such as [pyridine-SO_3H]Cl,[18] threo-(1S,2S)-2-amino-1-(4′-nitrophenyl)-1,3-propanediol,[19] iron (III) trifluoroacetate,[20] ionic liquid,[21] cerium(IV) ammonium nitrate[22] and $Sc(OTf)_3$.[23] But, some drawbacks still present, for example longer reaction time, non-recyclable catalysts and tedious work-up procedures, low yield that limit the use of these methods.[24] Solvent-free method is an efficient technique for various organic transformations instead of using harmful organic solvents.[25–27] In this work, we have reported a green solvent-free procedure for the synthesis of

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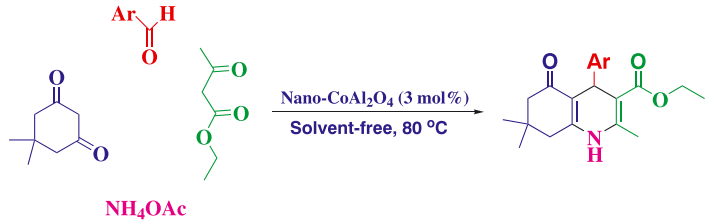


SCHEME 1 The preparation of hexahydroquinolines catalyzed by Nano-$CoAl_2O_4$

polyhydroquinolines using nano-$CoAl_2O_4$ with some advantages including short reaction times, high yields, simplicity of workup and reusability of the catalyst (Scheme 1).

2 | EXPERIMENTAL

2.1 | General

All materials were purchased from Merck and Fluka Chemical Companies. The known products were identified by comparison of their melting points and spectral data with those reported in the literature. The chemical reactions were monitored by TLC using silica gel SIL G/UV 254 plates. The ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were run on Bruker Avance DPX FTNMR spectrometers. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes.

2.2 | Procedure for the preparation of nano-$CoAl_2O_4$

A solution of metal sulfates was prepared by dissolving $CoSO_4.7H_2O$ (3.5 gr, 0.012 mol) and $Al_2(SO_4)_3.18H_2O$ (16.5 g, 0.0495 mol) in 100 ml water with the molar ratio of Co^{+2}/Al^{+3} 1:2 at 50°C. Poly ethylene glycol 4000 (2.5 g) was added to reaction mixture and cooled in ice bath to 5°C. When the solution was stirred, aqueous sodium hydroxide (12 g, 0.3 mol) was added to the obtained mixture. Purple precipitate was formed immediately. The precipitate compound (Nano-$CoAl_2O_4$) was collected by centrifuge and was washed with cold water. Nano $CoAl_2O_4$ was calcinated when it was put in the furnace (800°C) for 6 hours (Figure 1).

2.3 | General procedure for the synthesis of hexahydroquinolines under solvent-free conditions

The mixture of the dimedone (1 mmol), ammonium acetate (1.2 mmol), aldehydes (1 mmol), ethyl acetoacetate (1 mmol) and nano-$CoAl_2O_4$ (0.005 g) as catalyst was stirred at 80 °C for specific time in a 25 ml round-bottomed flask connected to a reflux condenser. Completion of the reaction was identified by TLC (n-hexane/ethyl acetate: 7/3). Ethanol (20 ml) was added to the reaction mixture and heated to dissolve the crude product and starting materials. Then, the nano-$CoAl_2O_4$ catalyst was partly recovered by centrifuge, and the product was purified by the recrystallization in ethanol. The recovered catalyst was reused for four times without reducing the efficiency of the catalyst in the yield of products and reaction times. The spectral data of compounds have been reported in supporting information.

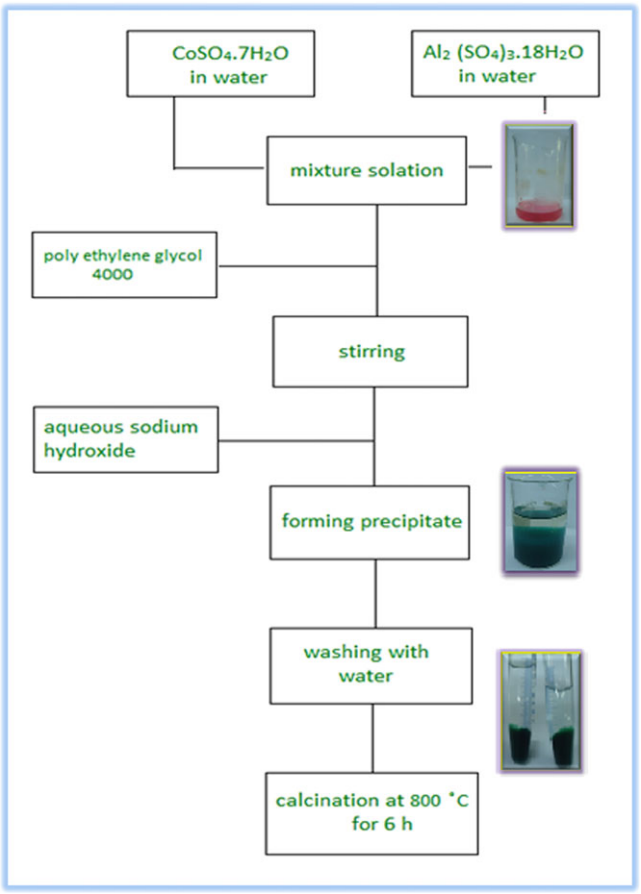


FIGURE 1 The synthesis of nano-$CoAl_2O_4$ powder

3 | RESULTS AND DISCUSSION

Nano-$CoAl_2O_4$ was synthesized and characterized by FT-IR, EDX, XRD, SEM, UV–Vis, VSM and TEM analysis.

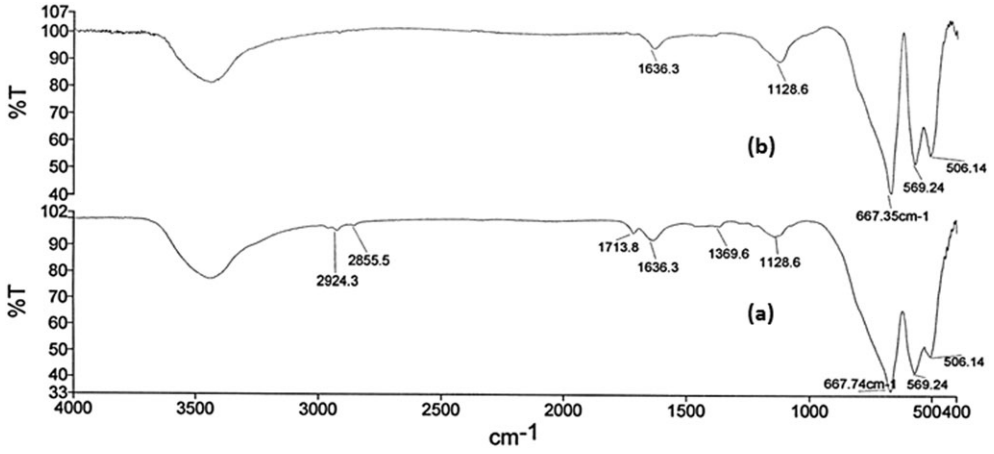


FIGURE 2 FT-IR spectra of the synthesized nano-$CoAl_2O_4$ after calcinations at 600 °C (a) and 800 °C (b) for 6 h

In the IR spectrum of the new catalyst, the stretching vibration of the hydrogen-bonded OH groups was appeared at 3470 cm^{-1}. C–H stretching vibration of absorption band appeared at 2960 cm^{-1} (organic compounds).[28] All of the peaks related to the organic species disappear while the temperature is increased and the rest of absorption peaks related to metal oxygen vibrations become much sharper.[29] The bands at 667.24, 569.24 and 506.14 cm^{-1} of the calcined powders indicate the formation of metal oxide (Co–O and Al–O stretching vibrations).[28] The bending vibration of water molecules appeared at 1654 (Figure 2).[28]

SEM and TEM analysis of the catalyst are given in figures 3 and 4. As SEM images, indicates that the size of the particles is less than 50 nm. Also, the transmission electron microscopy (TEM) analysis approves the same result which was obtained for SEM. So these observations confirm the morphology of the nano catalyst.

XRD pattern of cobalt aluminate was also investigated (Figure 5). Diffraction peaks at various 2θ values including 18.5°, 30.8°, 36.4°, 43.8°, 44.3°, 51.1°, 55.2°, 58.6°, 58.9° and 64.8° are shown in Figure 5. Also, the XRD data, including 2θ, peak width, size of particles and inter planar distance are extracted and shown in Table 1. As shown in Table 1, the

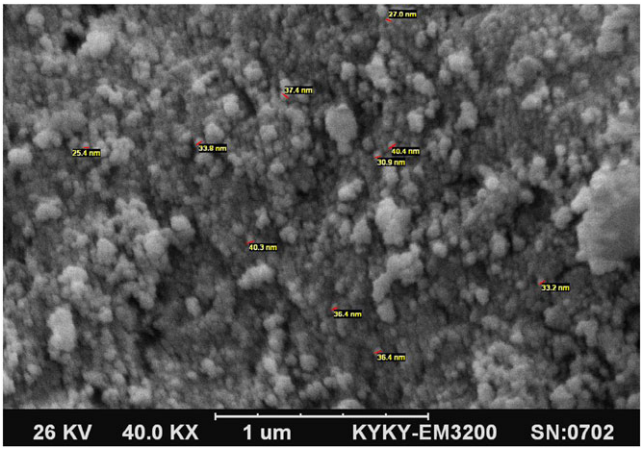


FIGURE 3 The scanning electron microscopy (SEM) of the nano-$CoAl_2O_4$

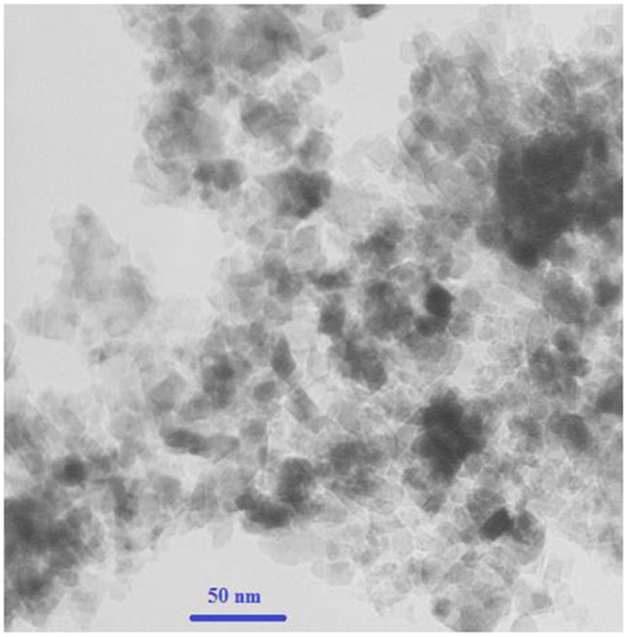


FIGURE 4 The transmission electron microscopy images of the catalyst

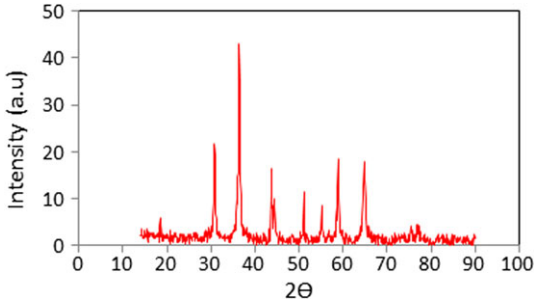


FIGURE 5 The X-ray diffraction (XRD) pattern of nano-$CoAl_2O_4$

TABLE 1 XRD data for the nano-$CoAl_2O_4$

Entry	2Θ	Peak width [FWHM] (degree)	Crystal size (Debye–Scherrer-nm)	Inter planer distance (nm)
1	18.5	0.2	40.25	0.479034
2	30.8	0.33	24.97	0.30131
3	36.4	0.3	27.87	0.246534
4	43.8	0.2	39.18	0.206441
5	44.3	0.3	28.59	0.204226
6	51.1	0.1	88	0.178532
7	55.5	0.2	44	0.289898
8	58.6	0.9	10.12	0.157341
9	58.9	0.4	22.81	0.156612
10	64.8	0.6	15.68	0.143703

size of the size of the crystals is calculated from 10 to 88 nm according to Debye–Scherrer equation.

Energy dispersive spectroscopy (EDS) spectrum of nano-$CoAl_2O_4$ was shown in Figure 6. As it is shown in Figure 6, indicates that the existence of cobalt, aluminium and oxygen in the nano-$CoAl_2O_4$.

The magnetization curve that is shown in Figure 7 determined the values of magnetic moment of nano-$CoAl_2O_4$. The saturation magnetization of nano-$CoAl_2O_4$ was 11 emu/g.

The catalytic activity of nano-$CoAl_2O_4$ was tested for the synthesis of hexahydroquinolines. The multi-component reaction of ethyl acetoacetate (1 mmol), dimedone (0.14 g, 1 mmol), benzaldehyde (1 mmol) and ammonium acetate (0.0925 g, 1.2 mmol) was selected as a model reaction. The model reaction was tested in the presence of different amounts of nano-$CoAl_2O_4$, and in the range of 25 to

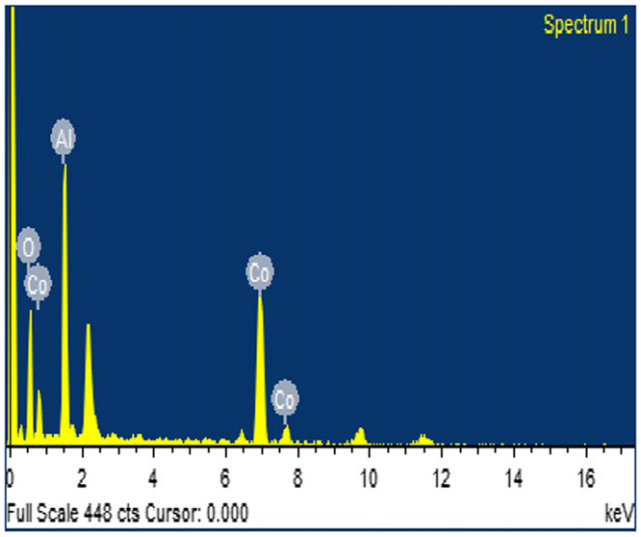


FIGURE 6 The energy-dispersive X-ray spectroscopy (EDX) of the nano-$CoAl_2O_4$

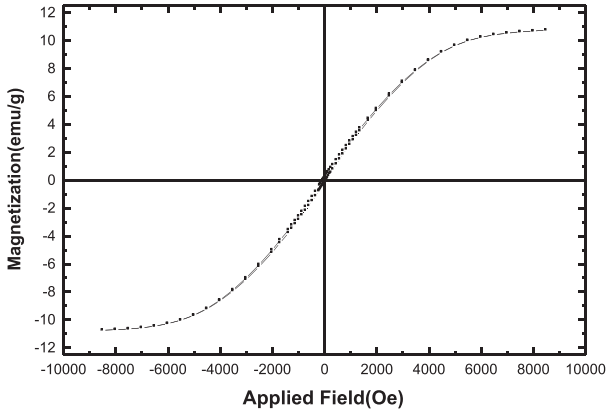


FIGURE 7 Magnetization curve of the prepared catalyst

120 °C under solvent-free conditions. Table 2 shows the results of these optimization experiments. As the results of these reactions, indicates that a catalyst loading of 0.005

TABLE 2 Effect of the catalyst amount and temperature on the reaction between dimedone, ethyl acetoacetate, benzaldehyde, and ammonium acetate

Entry	Catalyst amount (g)	Temp. (°C)	Time (min)	Yield[a] (%)
1	0.001	80	5	71
2	**0.005**	**80**	**3**	**91**
3	0.008	80	4	90
4	0.012	80	4	90
5	0.017	80	3	91
6	0.001	25	25	45
7	0.001	60	9	79
8	0.001	100	4	90
9	0.001	120	4	90

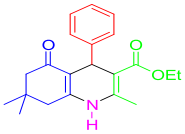
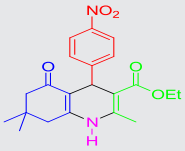
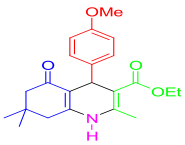
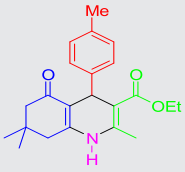
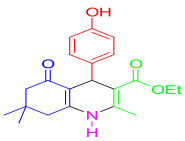
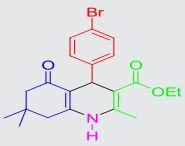
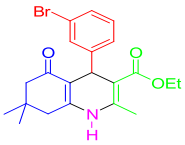
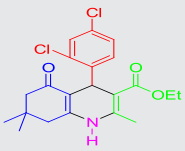
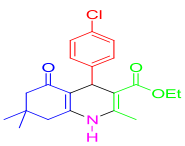
[a]Isolated yield.

TABLE 3 Effect of different solvents on the reaction of dimedone, benzaldehyde and ammonium acetate in the presence of *nano*-$CoAl_2O_4$ (3 mol%)

Entry	Solvent	Yield[a] (%)	Time (min)	Temp. (°C)
1	H_2O	70	60	80
2	CH_2Cl_2	50	60	reflux
3	$CHCl_3$	55	60	reflux
4	n-Hexan	43	60	reflux
5	EtOH	63	60	reflux
6	EtOAC	61	60	reflux
7	CH_3CN	43	60	reflux
8	**-**	**91**	**3**	**80**

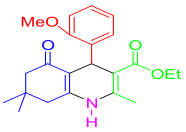
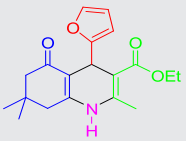
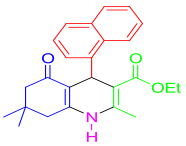
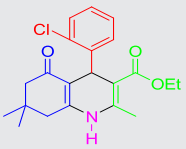
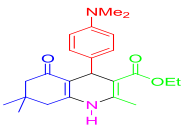
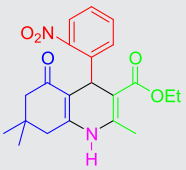
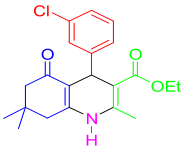
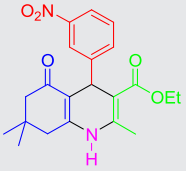
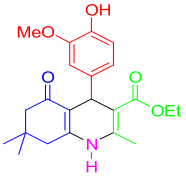
[a]Isolated yield.

TABLE 4 Synthesis of hexahydroquinoline derivatives catalyzed by nano-$CoAl_2O_4$ under solvent-free conditions

Entry	Product	Time (min)	Yield (%)	M.p.°C (lit.)
1		3	91	229–231 (203–205) [30]
2		4	81	244–245 (242–244) [31]
3		4	90	263–265 (257–259) [32]
4		8	90	266–268 (260–261) [32]
5		4	75	234–236 (232–234) [32]
6		8	90	256–258 (255–257) [30]
7		5	85	230–231 (235–237) [30]
8		2	87	243–245 (243–245) [18]
9		8	86	246–248 (245–246) [33]

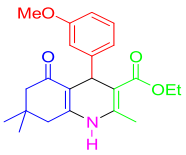
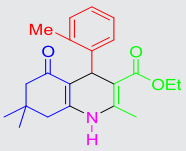
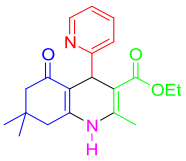
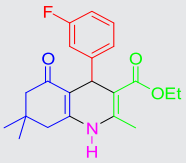
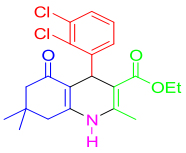
(*Continues*)

TABLE 4 (Continued)

Entry	Product	Time (min)	Yield (%)	M.p.°C (lit.)
10		5	92	249–251 (256–257) [34]
11		11	90	242–245 (245) [35]
12		8	85	235–238 (232–233) [36]
13		7	86	202–205 (207) [35]
14		3	82	235–237 (238–240) [35]
15		3	81	214–217 (205–207) [37]
16		7	85	260–261 (266–268) [36]
17		2	84	186–189 (179–181) [18]
18		6	86	201–202 (200–202) [38]

(*Continues*)

TABLE 4 (Continued)

Entry	Product	Time (min)	Yield (%)	M.p.°C (lit.)
19		7	89	206–208 (202–204) [24]
20		7	85	214–215
21		4	79	157–160
22		3	83	242–245
23		2	89	233–235

gram of catalyst at 80 °C was the best reaction conditions (Table 2, entry 2).

Table 3 shows the comparison of the efficiency of the solution versus solvent-free conditions using a variety of different solvents at 80 °C. Low yields of the products were shown in all of the solvent condition.

Dimedone was reacted with a series of different aryl aldehydes (possessing halogens, electron-donating groups and electron- withdrawing groups), ammonium acetate and ethyl acetoacetate under the optimized reaction conditions. Table 4 shows the results of these reactions. High yields over short reaction times are the main advantages of this method. As we have already tested the recyclability of the nano-$CoAl_2O_4$ in terms of its advantage as a catalyst (0.005 g) to the multi-component reaction of ethyl acetoacetate (1 mmol), ammonium acetate (1.2 mmol), dimedone (1 mmol), and benzaldehyde (1 mmol) at 80 °C. when the reaction was finished, ethanol was added and heated to dissolve the crude product and starting materials. Then the nano-$CoAl_2O_4$ catalyst was partly recovered by centrifuge. The collected catalyst was washed with ethanol, dried and used again in the next reaction. The catalyst was successfully reused for four times (Table 5).

TABLE 5 The reusability of the catalyst

Run	Time (min)	Yield[a] (%)
1	3	91
2	3	89
3	2	91
4	3	90

[a]Isolated yield.

4 | CONCLUSION

In this work, nano-$CoAl_2O_4$ as a recoverable heterogeneous catalyst was prepared and characterized by FT-IR, energy-dispersive x-ray spectroscopy (EDX), X-ray diffraction patterns (XRD), scanning electron microscopy (SEM), vibrating sample magnetometer (VSM) and transmission electron

microscopy (TEM) and used for the one-pot multi-component reaction between aryl aldehydes, ammonium acetate, ethyl acetoacetate and dimedone at 80°C under solvent-free conditions leading to hexahydroquinolines. The advantages of the presented method are high yield, short reaction time, generality, cleaner reaction profile, efficiency, simplicity and reusability of the catalyst.

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