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FULL PAPER

$CoFe_2O_4@SiO_2-NH_2-Co^{II}$ NPs catalyzed Hantzsch reaction as an efficient, reusable catalyst for the facile, green, one-pot synthesis of novel functionalized 1,4-dihydropyridine derivatives

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A magnetically heterogeneous $CoFe_2O_4@SiO_2-NH_2-Co^{II}$ nanoparticle was synthesized by the immobilization of Co (II) complex onto $CoFe_2O_4@SiO_2$ nanoparticles, and the heterogeneous magnetic nanocatalyst was characterized by XRD, TEM, TGA, EDX, and FT-IR techniques. Then, the green and reusable method was introduced for a multicomponent synthesis of 1,4-dihydropyridine derivatives via Hantszch reaction. The synthesis of 1,4-dihydropyridine derivatives was proceeded by the reaction of aldehyde, ethyl acetoacetate, and ammonium acetate in the presence of this magnetic nanocatalyst in EtOH/Water (1:1). Simple work-up, short reaction times, excellent yields (60–96%) as well as green solvent are some advantages of this novel approach, and the corresponding products were purified with no need for chromatographic separation.

KEYWORDS

$CoFe_2O_4@SiO_2-NH_2-Co^{II}$, green synthesis, heterogeneous catalysis, one-pot multicomponent reactions

1 | INTRODUCTION

Recently, bimetallic and mixed metal oxides compounds were most extensively investigated as either heterogeneous catalysts or solid supports.[1,2] In this solid supports, the design of morphologies and properties of the materials is controlled by the presence of two or more metal cations.[3,4] $CoFe_2O_4$, as solid magnetic support, received considerable attention due to its unique thermal stability, magnetic properties, and facile synthesis.[5] Also, active metal center, cost-effectiveness, better flexibility, and high specific surface area make it an appropriate candidate over numerous solid supports.[6] The literature review showed that $CoFe_2O_4$ used as a solid supports in many organic transformations such as epoxidation,[7] isomerization,[8] alkylation,[9] C-C bond formation.[10]

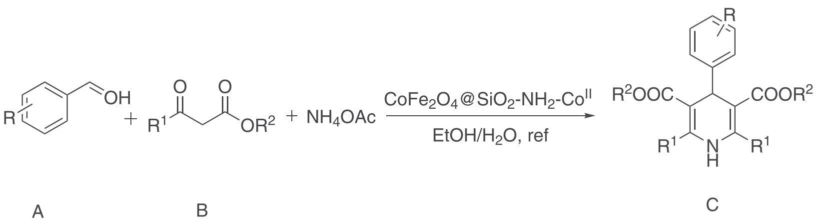
Heterocyclic compounds are also valuable building blocks for the synthesis of bioactive compounds such as medicinal and pharmaceutical products. The 1,4-dihydropyridine compounds as an attractive class of heterocyclic compounds received great attention due to the special properties ranging from anti-microbial,[11] anti-coagulant,[12] anti-oxidant,[13] anti-cancer,[14] anti-tubercular agents,[15] cardiovascular disease,[16] anti-leishmanial and anti-trypanosomal,[17] HIV-1 protease inhibitors[18] to antioxidant activities.[19] Many synthetic protocols which are catalyzed by Et_3N,[20] I_2,[21] polyethylene glycol (PEG-600),[22] $[PVPH]ClO_4$,[23] TMSI,[24] L-proline,[25] nano-γ-Fe_2O_3-SO_3H[26] and NaOH[27] are described for synthesis of different 1,4-dihydropyridine. The drawbacks such as harsh reaction conditions, low yields, expensive and toxic material, and long reaction times or give low yields are still challenges in the synthesis of these heterocyclic compounds. In continuation of developing new synthetic procedure for varied heterocyclic molecules,[28–31] herein, we reported a green and benign method for the synthesis of 1,4-dihydropyridine derivatives *via* multicomponent reaction of aldehyde, ethyl acetoacetate, and ammonium acetate derivatives in the presence of $CoFe_2O_4@SiO_2\text{-}NH_2\text{-}Co^{II}$ nanoparticle in green media (EtOH/water, 1:1) (Scheme 1).

2 | EXPERIMENTAL

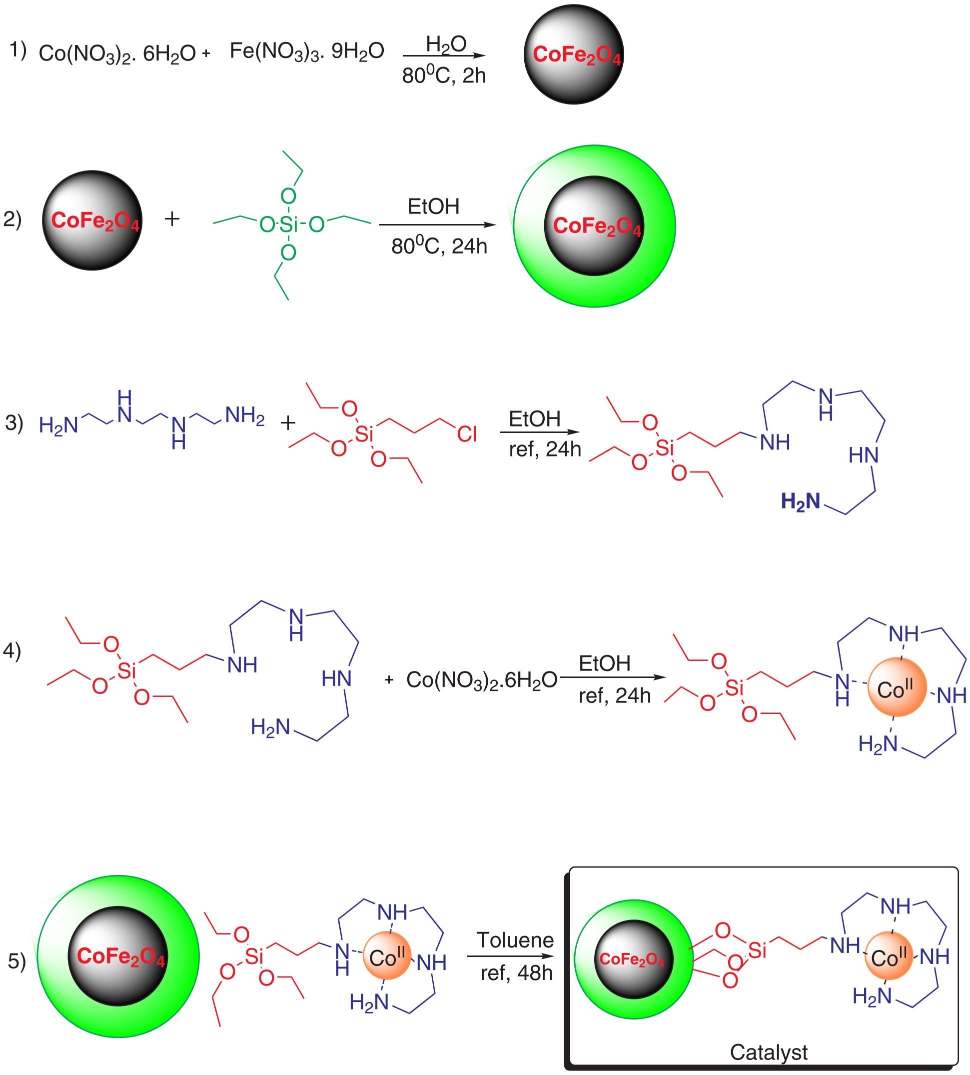
2.1 | Catalyst preparation

2.1.1 | Synthesis of $CoFe_2O_4$ nanoparticles

0.002 mol (0.808 g) of Fe $(NO_3)_3.9H_2O$ and 0.001 mol (0.291 g) Co $(NO_3)_2.6H_2O$ in a molar ratio of 2:1 were dissolved and ultrasonicated for 30 min in water (100 ml). 1 M NaOH solution (20 ml) was added drop by drop to the previous solution and sonicated (30 min). The mixture was then heated for 2 hr at 80 °C. The corresponding



SCHEME 1 The synthesis of 1,4-dihydropyridine derivatives in the presence $CoFe_2O_4@SiO_2\text{-}NH_2\text{-}Co^{II}$ of heterogeneous magnetic nanocatalyst



SCHEME 2 Synthesis of $CoFe_2O_4@SiO_2\text{-}NH_2\text{-}Co^{II}$

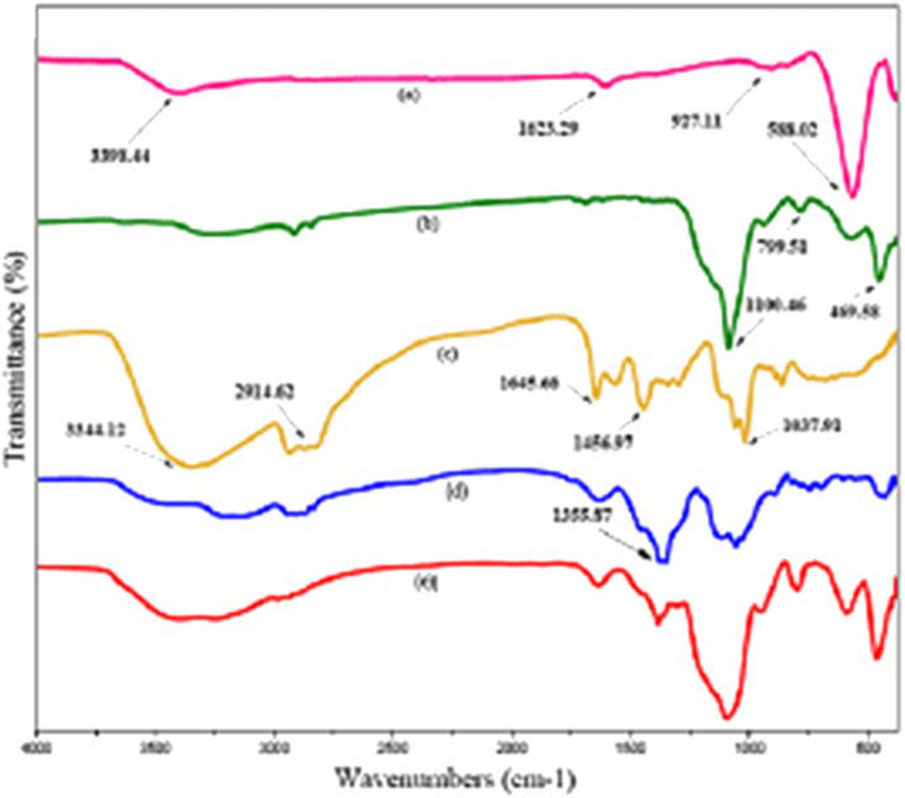


FIGURE 1 FT-IR spectra of Cofe$_2$O$_4$ NPs (a), CoFe$_2$O$_4$@SiO$_2$ NPs (b) PrNH$_2$(c) PrNH$_2$-Co^{II} (d) CoFe$_2$O$_4$@SiO$_2$-NH$_2$-Co ^{II} NPs

black precipitate powder was separated by an external magnet and washed with deionized water until the EtOH- ion free and dried in a vacuum Oven at 80 °C for 10 hr.[32]

2.1.2 | Synthesis of CoFe$_2$O$_4$@SiO$_2$

0.15 gr (0.64 mmol) of CoFe$_2$O$_4$ were mixed in 50 ml EtOH (80%) and dispersed for 30 min. Then, the pH value of the mixture was adjusted to 11–12 by the addition of NH$_3$.H$_2$O, and the mixture was added to the solution. Tetraethylorthosilicate (2 ml) was dropwise added to the mixture, and the mixture was stirred for 20 hr at room temperature. Finally, the resulting powder was separated by an external magnet, washed with deionized water (until neutral), and dried in a vacuum oven at 80 °C for 10 hr.[32]

2.1.3 | Synthesis of NH$_2$-Pr

Triethanolamine (2 mmol) and triethylenetetramine (1 mmol) were dissolved in EtOH (30 mL, Solution 1) and 3-chloropropyltriethoxysilane were dissolved in 20 ml EtOH (Solution 2). Then, the second solution was dropwise added to solution 1 and refluxed for 24 hr at 80 °C. Finally, the solvent was evaporated by a rotary evaporator, and the yellow product was obtained.

2.1.4 | Synthesis of NH2-Pr-CoII

Dissolve 1 mmol of Pr-NH$_2$ in 30 ml of ethanol then dissolve 10 mmol of Co (NO$_3$)$_2$.6H$_2$O in 20 ml of

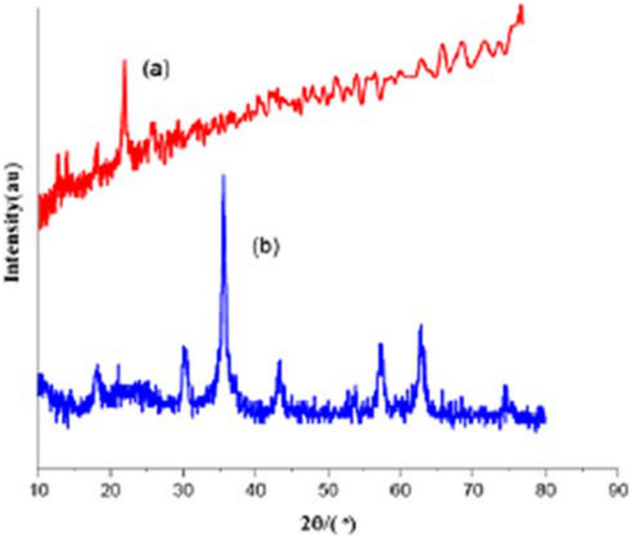


FIGURE 2 XRD patterns of Cofe$_2$O$_4$ NPs (a) and CoFe$_2$O$_4$@SiO$_2$-NH$_2$-Co ^{II} NPs (b)

ethanol and dropwise add to the previous solution. It was refluxed at 80 °C for 24 hr. The obtained precipitate was washed with ethanol and placed at a vacuum oven at 80 °C.

2.1.5 | Synthesis of $CoFe_2O_4@SiO_2$-NH_2-Co^{II}

Apply 0.5 g of Pr-NH_2-Co^{II} precipitate in 30 ml of dry toluene, then add 1 gr of $CoFe_2O_4/SiO_2$ in 70 ml of dry toluene and add the first solution dropwise to the latter for 48 hr at 105 °C reflux. The precipitate was washed with toluene and dried in a vacuum oven at 105 °C for 12 hr. (Scheme 2).

2.2 | Catalyst activity

2.2.1 | General procedure for the Hantzsch reaction

A mixture of aldehyde (1 mmol), ethyl acetoacetate (3 mmol), and ammonium acetate (1 mmol) was added

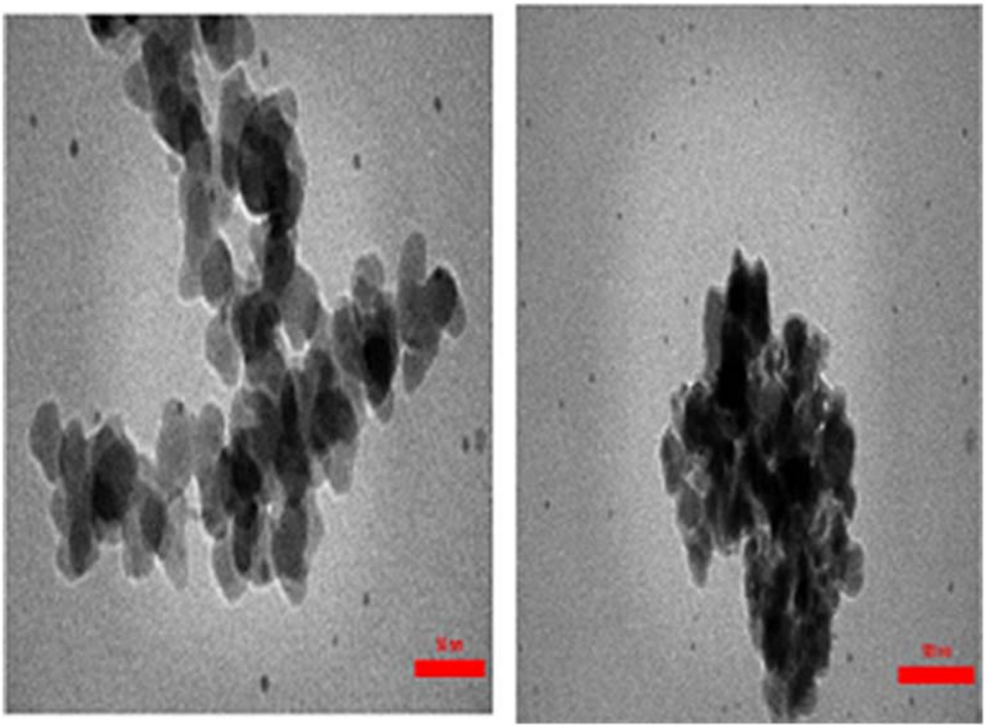
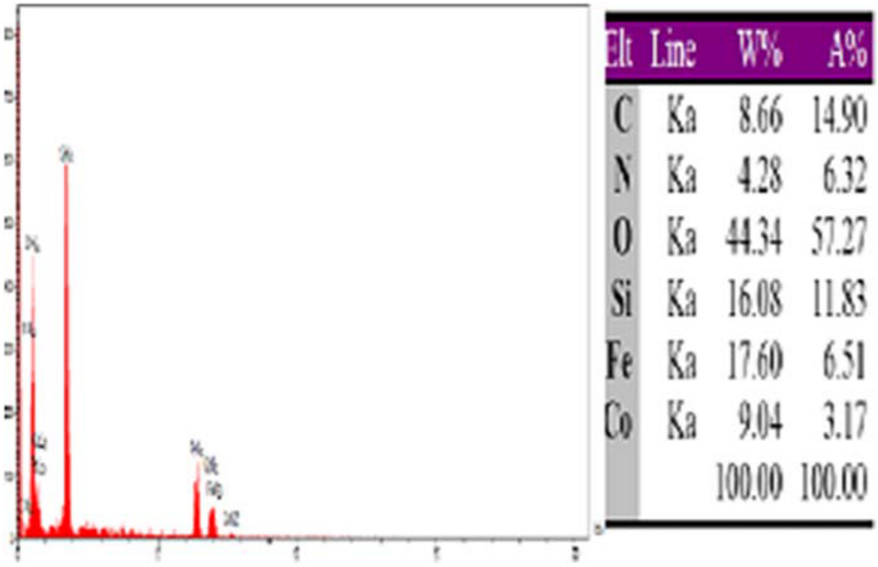


FIGURE 3 TEM image of $CoFe_2O_4@SiO_2$-NH_2-Co ^{II} NPs



Elt	Line	W%	A%
C	Ka	8.66	14.90
N	Ka	4.28	6.32
O	Ka	44.34	57.27
Si	Ka	16.08	11.83
Fe	Ka	17.60	6.51
Co	Ka	9.04	3.17
		100.00	100.00

FIGURE 4 EDAX spectrum of $CoFe_2O_4@SiO_2$-NH_2-Co ^{II} NPs

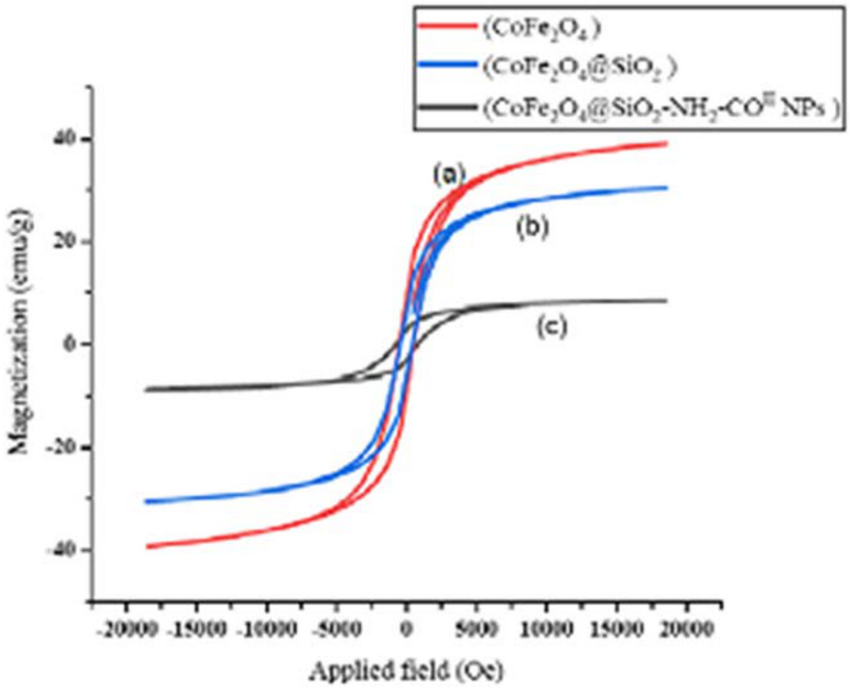
to the EtOH/Water (1:1) containing 0.15 gr $CoFe_2O_4@SiO_2$-NH_2-Co^{II} heterogeneous catalyst. The mixture was heated to reflux for 2 hr, and TLC monitored the reaction. After completion of the reaction, the mixture was cooled down to room temperature and $CoFe_2O_4@SiO_2$-NH_2-Co^{II} separated by an external magnet. Then, the solvent was evaporated by rotary evaporator, and the crude product purified by flash column chromatography (eluent: petroleum ether/ethyl acetate).[33]

3 | RESULTS AND DISCUSSION

3.1 | FT-IR study

IR spectra demonstrated the successful preparation of magnetic $CoFe_2O_4/SiO_2@Pr$-NH_2-Co^{II} magnetic nanoparticles. The peaks are shown at 927 cm^{-1} and 588 cm^{-1} belong to the -OH and Fe-O groups for $CoFe_2O_4$ nanoparticles (Figure 1a). The peak 1100 cm^{-1} is related to the Si-O-Si group attached to the magnetic

FIGURE 5 VSM spectra of $Cofe_2O_4$ NPs (a), $CoFe_2O_4@SiO_2$ NPs (b) $CoFe_2O_4@SiO_2$-NH_2-Co ^{II} NPs (c)



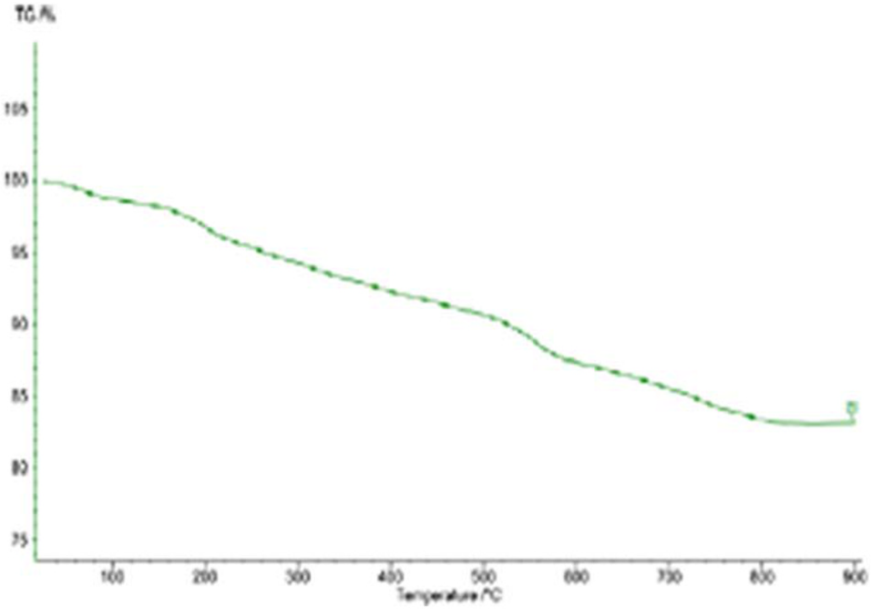


FIGURE 6 TGA thermogram of $CoFe_2O_4@SiO_2$-NH_2-Co ^{II} NPs

core, which demonstrates the fixation of SiO_2 on $CoFe_2O_4$ (Figure 1b). The peak corresponds to 3344 cm^{-1} OH and 2914 cm^{-1} to aliphatic CH and 1645 cm^{-1} to N-H (type I and II amines) (Figure 1c). After Co^{II} stabilization, the OH band of the adsorption band decreased sharply, indicating that the cobalt complex was well stabilized (Figure 1d).

3.2 | X-ray diffraction study

X-ray diffraction is used to study the structure of crystalline materials. The X-ray region of the electromagnetic spectrum lies between the gamma-ray and the UV. Using this spectral region, one can obtain information about the structure, the material of the material, and the quantification of the elements. The XRD spectra of the magnetic nanoparticles are shown in Figure 2. Several strong peaks are seen in area $2\theta = 20–70°$. According to Figure 2a cubic spinel phase corresponds to $CoFe_2O_4$ (JCPDS 22–1086). It has been reported that the concentration of SiO_2 affects the composite structure and decreases the peak. Different X-ray diffraction patterns at $2\theta = 18.1$ °, 20.9 °, 30.2 °, 35.5 °, 43.3 °, 57.2 °, 62.8 °, 74.6 ° from $CoFe_2O_4/SiO_2$@Pr-NH_2-Co^{II} NPs confirm that the particles have polycrystalline structure. The peak in the 18.1 ° region of amorphous SiO_2 indicates that it is well stabilized on $CoFe_2O_4$.

3.3 | TEM study

According to the TEM image, the average size of $CoFe_2O_4/SiO_2$@Pr-NH_2-Co^{II} magnetic nanoparticles is about 20–90 nm (Figure 3). While the size of $CoFe_2O_4$ nanoparticles is about 2–6 nm. The TEM image demonstrates the successful coating of the silica layer around the magnetic core.

3.4 | EDX study

The EDX spectrum shown in Figure 4 shows the percentage of elements, with the presence of all expected major elements (Fe, Co, Si, N, C) present.

3.5 | Vibrating sample magnetometer (VSM) study

Figure 5 shows the VSM pattern of $CoFe_2O_4/SiO_2$@Pr-NH_2-Co^{II} magnetic nanoparticles and shows the magnetic properties of the particle. The nanoparticles exhibit free magnetic behavior. The VSM pattern shows that surface modification by dispersing agents changes the magnetic properties of the nanocomposites, as can be seen in Figure 5. Figure 5a is for $CoFe_2O_4$, and Figure 5b is for $CoFe_2O_4/SiO_2$, and Figure 5c is for $CoFe_2O_4/SiO_2$@Pr-NH_2-Co^{II}. As can be seen, the magnetic properties of the nanoparticles have decreased, but this decrease is not relatively high; the catalyst is easily recoverable by a simple external magnetic field.

3.6 | Thermal gravimetric analysis (TGA)

Figure 6 shows the thermal behavior of magnetic $CoFe_2O_4/SiO_2$@Pr-NH_2-Co^{II} nanoparticles. The $CoFe_2O_4$/

TABLE 1 Optimization of various catalyst for the model reaction

Entry	Catalyst (mg)	Temperature (°C)	Time (hr)	Yield (%)
1	50	Reflux	4.5	65
2	80	Reflux	4	65
3	100	Reflux	3.5	70
4	120	Reflux	2.5	87
5	150	Reflux	2	95
6	180	Reflux	2	96
7	0	Reflux	5	Trace
8	$CoFe_2O_4$	Reflux	2	22
9	$CoFe_2O_4$@SiO_2	Reflux	2	26
10	$CoFe_2O_4$@SiO_2 _NH_2	Reflux	2	28

Reaction conditions: Benzaldehyde (1 mmol), ethyl acetoacetate (1 mmol) and ammonium acetate 1 mmol) in ehanol/water at reflux conditions.

TABLE 2 Optimization of various solvent condition for the model reaction

Entry	Solvent	Temperature (°C)	Time (hr)	Yield* (%)
1	Solvent-free	110	2.5	80
2	*n*-Hexane	Reflux	4.5	30
3	CH_3CN	Reflux	3	77
4	H_2O	Reflux	4	50
6	EtOH	Reflux	2.5	95
7	DCM	Reflux	4.5	42
8	EtOH/H_2O	Reflux	2	95

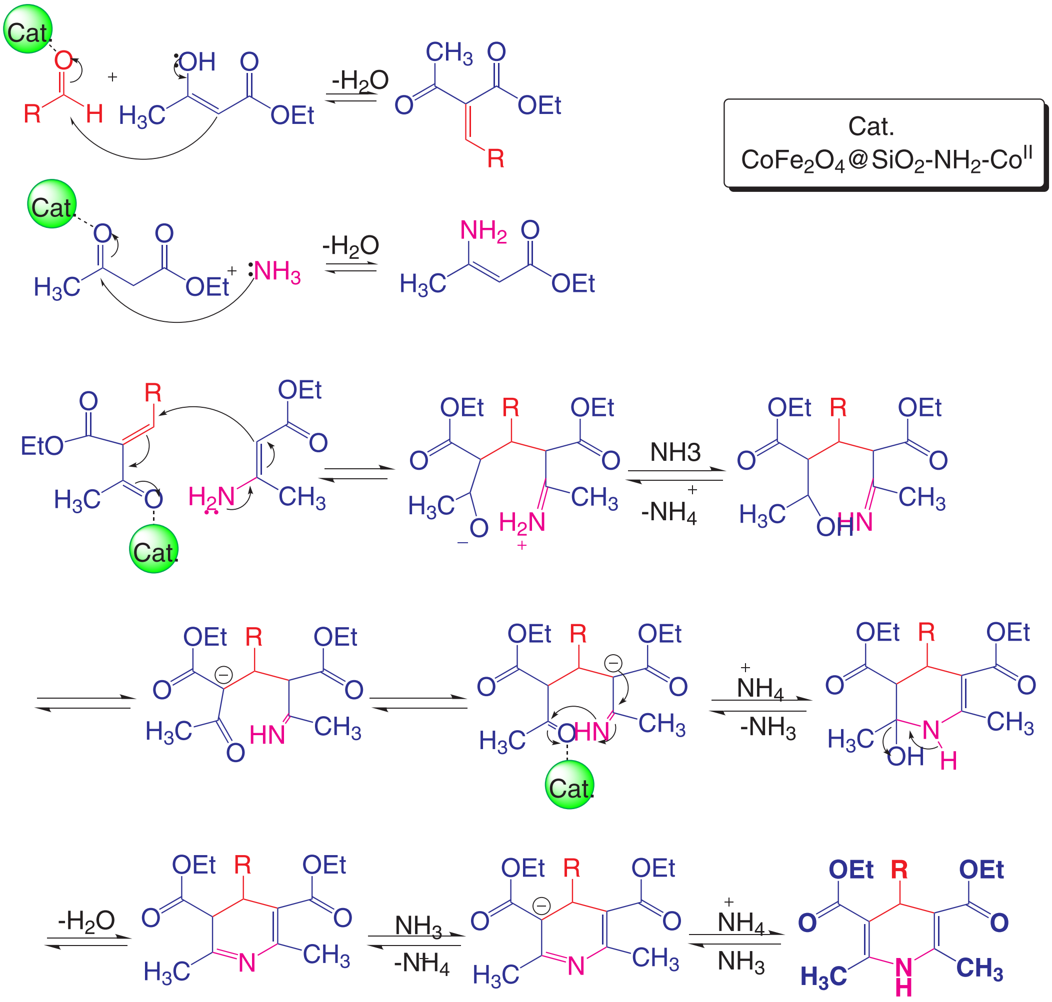
Reaction conditions: Benzaldehyde (1 mmol), ethyl acetoacetate (1 mmol) and ammonium acetate 1 mmol) in the presence of $CoFe_2O_4$@SiO_2-NH_2-Co^{II} (150 mg) in different solvent at reflux conditions.

SiO_2 curve shows weight loss in the range of 90 °C. This weight loss can be attributed to the loss of adsorbed water on the surface as well as the trapped water in the structure of the lattice in the internal OH groups. The second stage is weight loss in the 200 °C region, which can be attributed to the removal of free oxygen. As shown in Figure 6, the water content decreased after incorporation of the Co (II) complex onto $CoFe_2O_4/SiO_2$, indicating that the Co (II) complex was successfully stabilized on the target ligand. Is. The third stage is the weight loss in the 580 °C area that involves the removal of organic compounds.

3.7 | Reaction optimization

In a preliminary attempt for the synthesis of 1,4-dihydropyridine, the reaction of benzaldehyde (1 mmol), ethyl acetoacetate (3 mmol) and ammonium acetate (1 mmol) was performed as a model reaction in the presence of $CoFe_2O_4@SiO_2$ -NH_2-Co^{II} NPs in EtOH/Water (1:1) media and the effect of parameters such as the amount of catalyst, solvent, and temperature were studied on the model reaction. At first, the model reaction was carried out in the absence of the catalyst, and no significant product was obtained (Table 1, entry 7). The model reaction was studied in the presence of the different amounts of catalyst (50–180 mg). When the amount of catalyst was increased from 50 mg to 180 mg, the yield of the reaction was increased to 96% (Table 1, entries 6). Further increase in the amount of catalyst did not increase the yield of the products significantly (Table 1, entries 1–6).

To investigate the effect of the solvent, the model reaction was carried out in different solvents (H_2O, CH_3CN, *n*-Hexane, EtOH, DCM, EtOH/H_2O, solvent-free). Also, the model reaction was carried out in solvent-free conditions, and moderate yield was obtained (Table 2, entry 1). As can be seen in Table 2, the solvent has a significant effect on the yield of the model reaction,



SCHEME 3 The proposed mechanism for the synthesis of 1, 4-dihydropyridine in the presence of $CoFe_2O_4@SiO_2$-NH_2-Co^{II} catalyst

TABLE 3 Synthesis of novel functionalized 1,4-dihydropyridine derivatives by $CoFe_2O_4@SiO_2$-NH_2-Co^{II} catalyst[a]

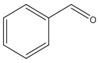
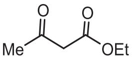
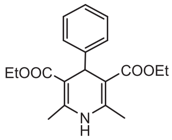
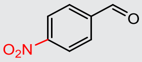
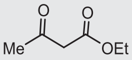
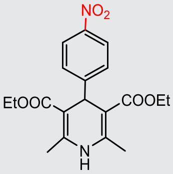
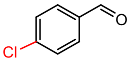
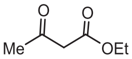
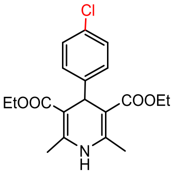
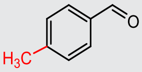
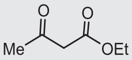
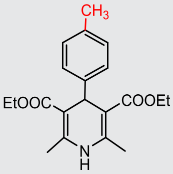
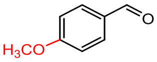
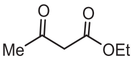
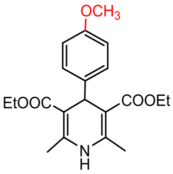
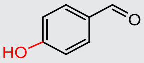
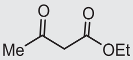
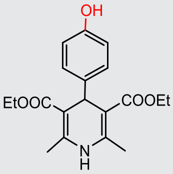
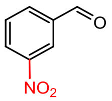
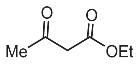
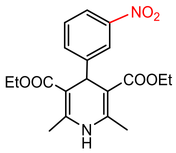
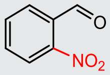
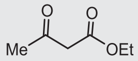
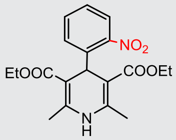
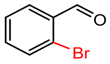
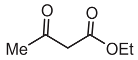
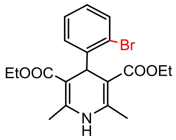
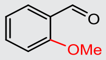
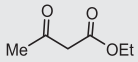
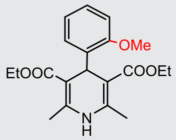
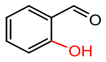
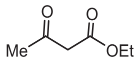
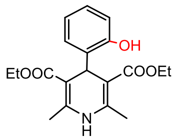
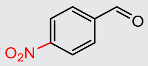
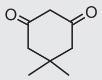
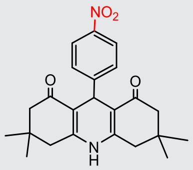
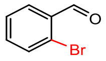
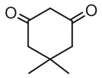
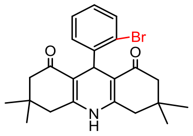
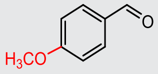
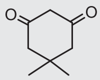
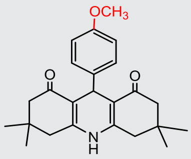
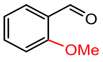
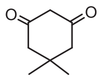
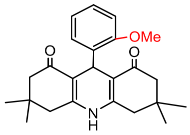
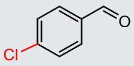
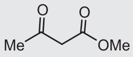
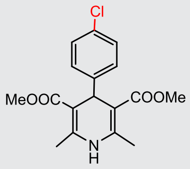
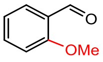
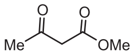
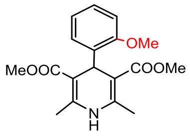
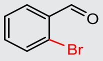
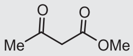
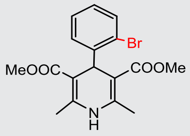
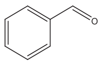
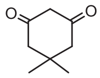
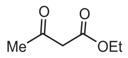
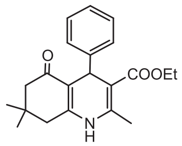
Entry	A	B	Product (C)	Time (h)	Yield *(%)
1				2.5	85
2				2	96
3				2	90
4				3	88
5				3.5	85
6				4	65

TABLE 3 (Continued)

Entry	A	B	Product (C)	Time (h)	Yield *(%)
7				2	93
8				2	90
9				2	89
10				3	83
11				4	60
12				1.5	86
13				1.5	95

(Continues)

TABLE 3 (Continued)

Entry	A	B	Product (C)	Time (h)	Yield *(%)
14				2	96
15				2	85
16				2.5	90
17				3	78
18				2.5	85
19		 And 		0.17	95

Reaction conditions: Benzaldehyde derivatives (1 mmol), diketone or ketoester (1 mmol) and ammonium acetate (1 mmol) in the presence of $CoFe_2O_4@SiO_2\text{-}NH_2\text{-}Co^{II}$ (150 mg) in ethanol at reflux conditions.

TABLE 4 The comparison of $CoFe_2O_4@SiO_2\text{-}NH_2\text{-}Co^{II}$ catalyst with other catalysts

Entry	Catalyst	Solvent	T	Time (hr)	Yield (%)^b	ref
1	$FeWO_4$	DMF	80	4	55	[33]
2	Chitosan NPs	CCl_4	RT	4	55	[35]
3	La_2O_3	Water	RT	3	79	[36]
4	Piperidine	EtOH	RT	72	88	[37]
5	Yb $(PFO)_3$	EtOH	RT	72	87	[38]
6	$CoFe_2O_4@SiO_2\text{-}NH_2\text{-}Co^{II}$	$EtOH/H_2O$	Reflux	2	95	This work

and the best results were obtained in EtOH/Water (1:1) (Table 2, entry 8).

The model reaction was carried out at different temperatures and 80 °C was the optimum temperature.

A probable mechanism for the creation of the target molecule is illustrated in Scheme 3. The Knoevenagel reaction follows through a preliminary generation of benzylidene or imine intermediate, (3), from the condensation of and acetoacetanilide, (1) and aromatic aldehydes, (2). Further, the imine, (3) and 5,5-Dimethyl-1,3-cyclohexanedione, (4) lead to intermolecular Michael addition of carbonyl compounds facilitated by the catalyst to produce another intermediate, (5). Then, the protonated carbonyl is attacked by the amine from ammonium acetate to form the enamine, (6). Intermediate, (6) further undergoes intramolecular cyclization to finally afford functionalized 1,4- dihydropyridine derivative, (7).

Furthermore, the generality of the reaction was investigated for the synthesis of 1,4- dihydropyridine derivatives under optimized conditions (Table 3) and as can be seen, most of the reactants have moderate yields and just ortho and para-hydroxy benzaldehydes have lower yields (Table 3, entries 6 and 11). Also, the efficiency of the was investigated with some reported catalysts[34–38] and as can be seen in Table 4, the present study exhibits advantageous over the other reports including facile preparation of the catalyst, short time of the reaction, and easy separation of the products.

In addition, the reusability of the catalyst was also investigated in the model reaction. Therefore, after the completion of each run, the catalyst was detached from

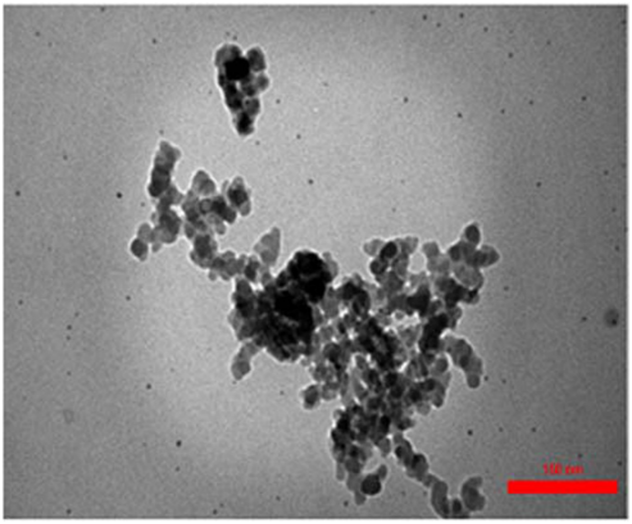


FIGURE 8 TEM image of the reuesd catalyst

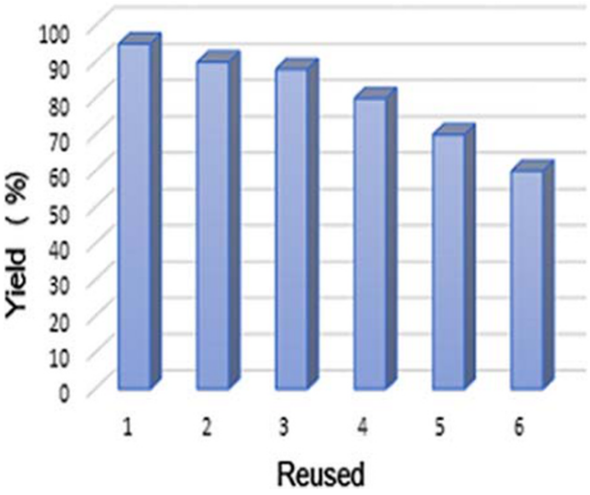


FIGURE 7 The reusibility of the catalyst

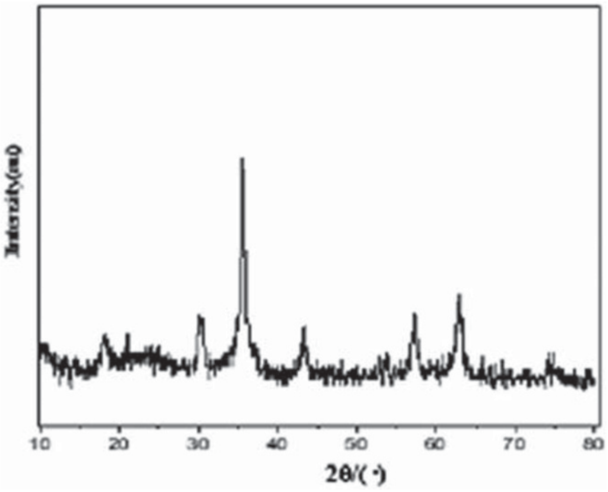


FIGURE 9 XRD pattern of the reuesd catalyst

the reaction mixture and washed with ethanol and dried in an oven at 80 °C for 8 hr. The recycled catalyst applied for the next run and exhibited a little loss of catalytic activity (Figure 7), which is confirmed the use of catalyst.

Co wasn't detected in the reaction solutions based on ICP-AES evaluation via the hot filtration approach. After the solid-free filtrates were subsequently stirred continuously under optimized reaction conditions for its substrates as mentioned above, the results of 1,4-dihydropyridine were significantly less than 5 percent after 12 hr.

For additional investigation, the characterization of this recycled catalyst after two runs (TEM picture (Figure 8), and the XRD spectrum (Figure 9) was accessed along with also the results revealed that the recovered catalyst didn't reveal substantial differences from the arrangement.

4 | CONCLUSIONS

In summary, we developed a robust and efficient recyclable catalyst, $CoFe_2O_4@SiO_2\text{-}NH_2\text{-}Co^{II}$ to use in a four-component one-pot procedure for syntheses of ten novels functionalized pyridine derivatives under green solvent conditions at reflux in good to excellent yields (60–96%). The described protocol has various advantages, including simple work-up, short reaction times, green solvent, impressive yields, easy purification, atom efficiency, makings the procedure attractive. We believe this method will open broader catalytic applications in the fields of organic synthesis and drug discovery.

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CONFLICT OF INTEREST

There are no conflicts to declare.

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