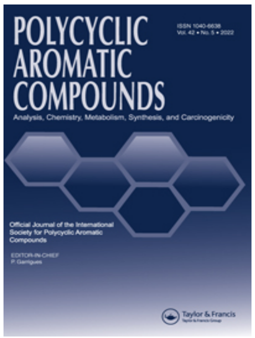

Polycyclic Aromatic Compounds

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/gpol20

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To cite this article: Indah Raya, Mahmoud Kandeel, Forat H. Alsultany, Usama S. Altimari & Surendar Aravindhan (2022): Fabrication and Characterization of a Novel and Efficient Zinc Nanomagnetic Catalyst for Multicomponent Synthesis of Heterocycles, Polycyclic Aromatic Compounds, DOI: 10.1080/10406638.2022.2105908

To link to this article: https://doi.org/10.1080/10406638.2022.2105908

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Fabrication and Characterization of a Novel and Efficient Zinc Nanomagnetic Catalyst for Multicomponent Synthesis of Heterocycles

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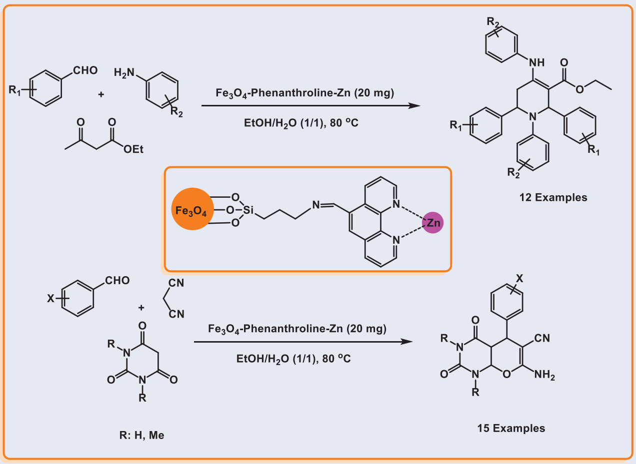
ABSTRACT

The zinc (II) complex supported on magnetic nanoparticles Fe_3O_4 as a novel and efficient magnetically recoverable catalyst (Fe_3O_4-Phenanthroline-Zn) was designed and characterized using the most common spectroscopic techniques including FT-IR spectroscopy, SEM, TEM, EDX, XRD, VSM, and ICP-OES. The Fe_3O_4-Phenantroline-Zn catalyst is shown to be efficient for the multicomponent synthesis of heterocycles including highly substituted piperidines and pyrano[2,3-d]pyrimidines. This system has many advantages, such as excellent level of reusability of magnetic catalysts, high yields, simplicity of separation of catalysts using an external magnet, environmental benignity and ease of handling. To the best of our knowledge, it is the first report on the utilization of zinc nanomagnetic catalyst for the multicomponent synthesis of highly substituted piperidines.



ARTICLE HISTORY
Received 19 May 2022
Accepted 18 July 2022

KEYWORDS
Zinc nanomagnetic catalyst; Fe_3O_4-Phenanthroline-Zn; Highly substituted piperidines; Pyrano[2,3-d]pyrimidines; Magnetic separation

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Supplemental data for this article can be accessed online at http://dx.doi.org/10.1080/10406638.2022.2105908.

Introduction

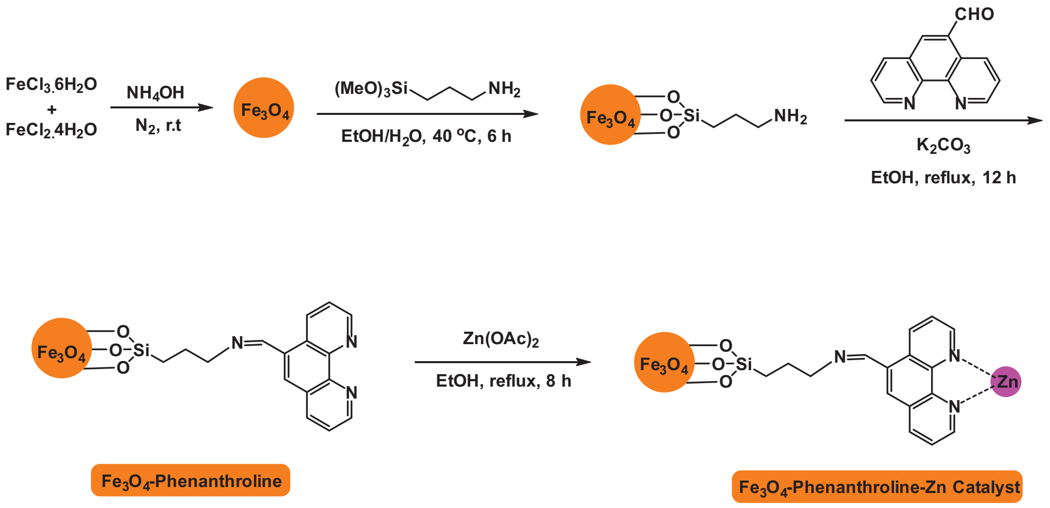
One of the most important goals of chemists is to produce catalysts with high activity and efficiency, complete selectivity, the ability to separate and recover from the reaction mixture, low energy consumption and long life.[1,2] Catalyst performance can be determined by controlling variables such as size, structure, spatial and electron distribution, surface composition, thermal and chemical stability.[3] With the introduction of nanotechnology into the catalyst industry, nanocatalysts have become more prominent. In most cases, these catalysts have shown remarkable properties and have found their way into industrial processes.[4,5] Research in the field of nanocatalysts has always been one of the most interesting topics in Nanochemistry and Green Chemistry.[4,6] Green Chemistry deals with healthy chemical reactions with safe products with maximum efficiency, and minimum consumption of matter and energy.[7–9] Nanocatalysts can lead us to this ideal. Today, magnetic nanoparticles have found a variety of applications due to properties such as large specific surface area and simple separation with an external magnetic field.[10,11] The paramagnetic nature and insolubility of magnetic nanoparticles facilitate the separation of this catalyst from the reaction mixture by an external magnet.[12,13] The physical and chemical properties of magnetic nanoparticles largely depend on the method of synthesis and chemical structure.[14] In most cases, the particle size varies from 1 to 100 nanometers. In recent times, the utilization of magnetic nanoparticles in particular Fe_3O_4 nanoparticles as support for catalysis have received profound attention in organic synthesis.[15–18] A salient feature of magnetic nanoparticle-stabilized catalysts is that they are easily separated from the reaction medium using an external magnetic field, have high catalytic activity and exhibit a high degree of chemical stability.[17,19–21]

Multi-component reactions (MCRs) are one of the most important methods in organic synthesis and medicinal chemistry because of their wide range of applications and significant advantages over conventional linear type syntheses.[22–25] Compared with conventional methods of organic synthesis, MCRs have the advantages such as high-selectivity, higher yield and diversity by varying reaction substrates and simple work-up procedures.[26–29]

Research on heterocyclic chemistry is one of the most important challenges in chemistry science in particular in organic synthesis.[30–32] Synthesis of heterocyclic compounds has attracted great interest due to their wide applicability in life and nature.[33,34] Highly substituted piperidines and pyrano[2,3-d]pyrimidines are very important heterocyclic motifs in the realm of natural and synthetic organic chemistry due to their interesting biological and pharmacological activities such as antitumour, antibacterial, antiviral and anti-inflammatory activities.[35–38] In this paper, we describe the fabrication and characterization of Fe_3O_4-Phenanthroline-Zn nanomaterial and evaluate its catalytic activity for the multicomponent synthesis of highly substituted piperidines and pyrano[2,3-d]pyrimidines. In this method, the zinc complex immobilized on magnetic Fe_3O_4 nanoparticles as catalyst suggested a series of advantages such as magnetic separation, high stability and excellent catalytic-activity. To the best of our knowledge, it is the first report on the utilization of zinc nanomagnetic catalyst for the multicomponent synthesis of highly substituted piperidines.

Result and discussion

The novel zinc (II) complex immobilized on the surface of magnetic nanoparticles modified with phenanthroline (Fe_3O_4-Phenanthroline-Zn) was easily prepared from commercially available and inexpensive reagents according to the procedure summarized in Scheme 1. As illustrated in Scheme 1, the synthesis of a new heterogeneous nanocatalyst was described by functionalization of Fe_3O_4 by AMPTS linker and attachment of phenanthroline to the obtained nano-substrate. Ultimately, Fe_3O_4-Phenanthroline-Zn nanocatalyst was prepared by using a stable interaction between the zinc (II) acetate (that is a sift metal because of its stable electron configuration. The



Scheme 1. Details of fabrication of Fe_3O_4-Phenanthroline-Zn nanomaterial.

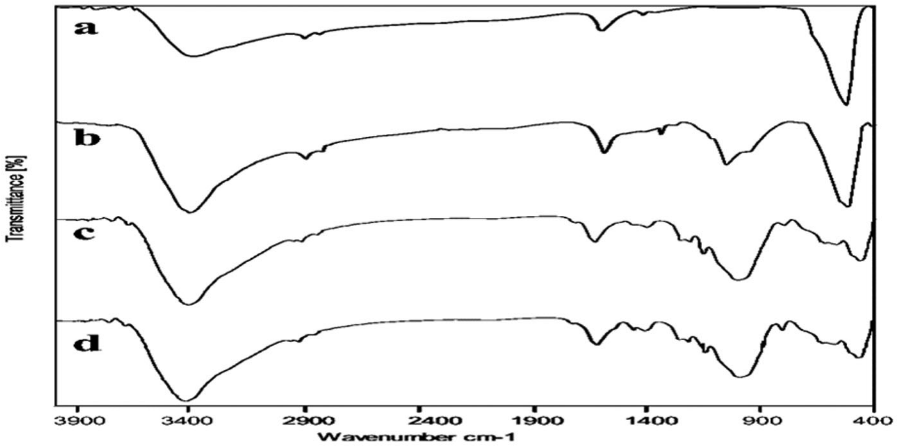


Figure 1. FT-IR spectroscopy of (a) Fe_3O_4, (b) Fe_3O_4@AMPTS, (c) Fe_3O_4-Phenanthroline and (d) Fe_3O_4-Phenanthroline-Zn nanomaterial.

d orbitals of zinc are completely filled and they cannot form metallic bonds. This is the reason why zinc is a soft metal with nitrogenes in pyridine rings (that are borderline due to increased polarizability imparted by the aromatic ring) in the heterogenized ligand (Scheme 1). The structure of Fe_3O_4-Phenanthroline-Zn nanomaterial was characterized by a series of spectroscopic techniques including FT-IR spectroscopy, SEM, TEM, EDX, XRD, VSM, TGA and ICP-OES.

Characterization of catalyst

FT-IR Spectroscopy of Fe_3O_4, Fe_3O_4@AMPTS, Fe_3O_4-Phenanthroline and Fe_3O_4-Phenanthroline-Zn nanomaterial is shown in Figure 1. As shown in Figure 1, a broad peak around 580 cm^{-1} is related to the stretching of Fe–O bond.[39] The existence of Zn in the structure of the catalyst was approved through stretching vibration of C=N bands that appeared at 1629 cm^{-1}, as this band

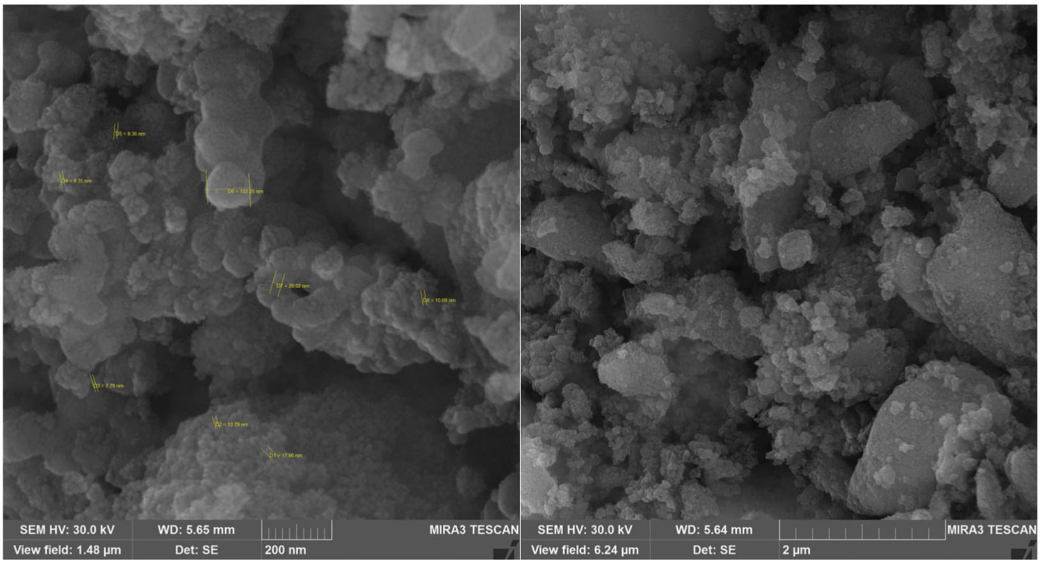
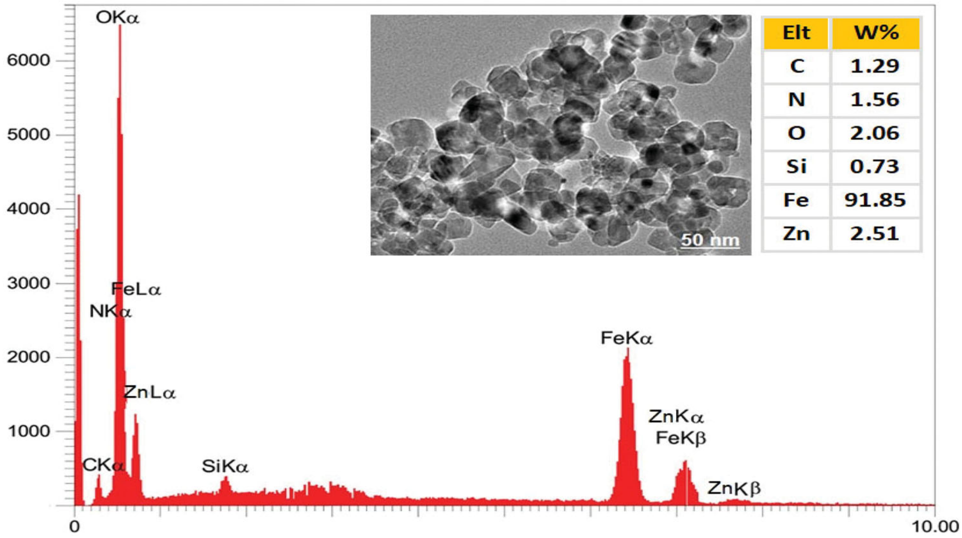


Figure 2. SEM images of Fe_3O_4-Phenanthroline-Zn catalyst at different magnification.



Elt	W%
C	1.29
N	1.56
O	2.06
Si	0.73
Fe	91.85
Zn	2.51

Figure 3. EDX and SEM analysis of Fe_3O_4-Phenanthroline-Zn catalyst.

shifts to lower frequency (1613 cm^{-1}) due to the grafting of Zn (II) complex on the surface of Fe_3O_4-Phenanthroline.[40]

The morphology and size of Fe_3O_4-Phenanthroline-Zn catalyst were determined by SEM and TEM analysis, as shown in Figures 2 and 3. Both the SEM and TEM images demonstrate that the prepared magnetic nanoparticles are spherical, narrowly distributed and well dispersed with average size of less than 15 nm in diameter.

The elemental analysis of Fe_3O_4-Phenanthroline-Zn catalyst was studied by Energy-Dispersive X-ray spectroscopy (EDX). As shown in Figure 2, EDX spectrum of Fe_3O_4-Phenanthroline-Zn catalyst confirmed the presence of Fe, O, N, C, Si and Zn elements in the structure of the catalyst and proved that the magnetic nanoparticle has been successfully synthesized.

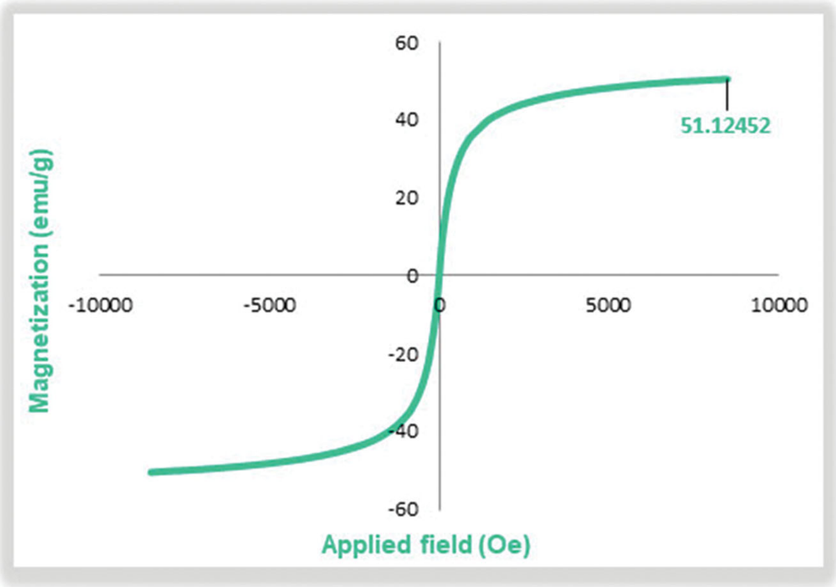


Figure 4. VSM analysis of the Fe_3O_4-Phenanthroline-Zn nanocatalyst.

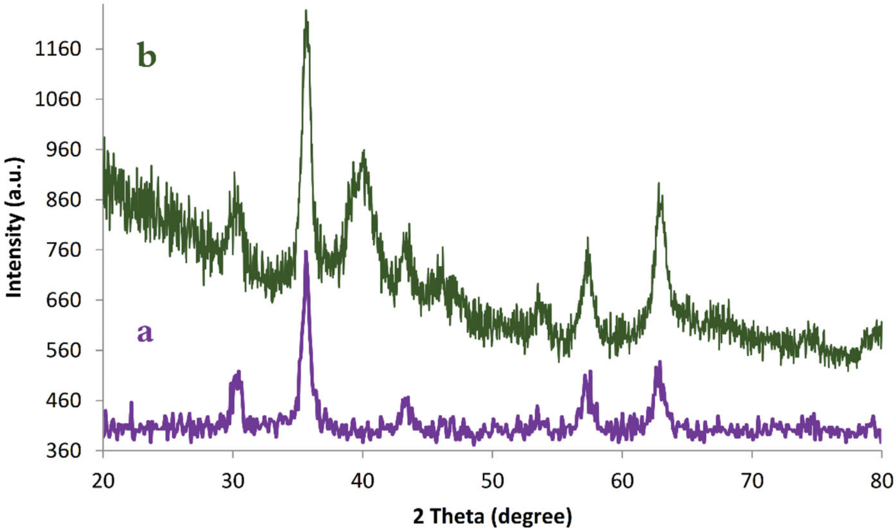


Figure 5. XRD analysis of (a) Fe_3O_4 and (b) Fe_3O_4-Phenanthroline-Zn nanocatalyst.

The magnetic property of Fe_3O_4-Phenanthroline-Zn was checked using Vibrating Sample Magnetometer (VSM) technique at room temperature. Magnetization curve of Fe_3O_4-Phenanthroline-Zn is illustrated in Figure 4. According to the magnetization curves, the saturation of the Fe_3O_4-Phenanthroline-Zn catalyst was about 51.12 emu/g. With superparamagnetic property, the catalyst can be easily recovered by applying an external magnetic field.

The structure of Fe_3O_4-Phenanthroline-Zn nanocatalyst was investigated by X-Ray Difraction (XRD). The XRD pattern of Fe_3O_4-Phenanthroline-Zn nanocatalyst is presented in Figure 5. This analysis affirmed that the surface-modification and conjugation of the Fe_3O_4 nanoparticles did not lead to phase change. Several characteristic peaks at $2\theta = 35.1°$, 41.2°, 50.6°, 63.2°, 67.3° and 74.6° were observed, which are assigned to the (220), (311), (400), (422), (511) and (440) crystallographic faces of magnetite (in good agreement with the standard Fe_3O_4 MNPs XRD spectrum reported in literature). Also, the crystal size was calculated according to Debye–Scherrer formula and the mean crystal size of Fe3O4 NPs and Fe_3O_4-Phenanthroline-Zn was obtained 18.34 nm and 12.27 nm respectively.

In order to determine the amount of Zn on the surface of the catalyst, the ICP-OES (Inductively coupled plasma-optical emission spectrometry) analysis was used which indicated that the exact the amount of Zn, stabilized on surface of Fe_3O_4-Phenanthroline-Zn, is found to be 21.18×10^{-5} mol/g.

After the characterization of Fe_3O_4-Phenanthroline-Zn nanomaterial, its catalytic activity was evaluated in the multicomponent synthesis of highly substituted piperidines. The model reaction of benzaldehyde (2 mmol), ethyl acetoacetate (1 mmol), and aniline (2 mmol) was performed in ethanol under reflux conditions. To establish the reaction conditions, the effects of the catalyst loading, solvent and temperature on the rate and yield of this model reaction were investigated. To illustrate the importance of the nanocatalyst in the reaction, the model reaction was carried out in the absence of zinc nanomagnetic catalyst. As shown in Table 1, only a trace amount of the model product was seen in the absence of catalyst after 120 min (Table 1, Entry 1). As seen in Table 1 (Entries 2–6), when the amount of catalyst increased, the reaction efficiency also increased. But catalytic amount above 20 mg of Fe_3O_4-Phenanthroline-Zn did not significantly affect the reaction progress (Table 1, Entry 7). Next, the influence of solvent and temperature on the model reaction was evaluated; as shown in Table 1, the best results were seen in polar solvents. After comprehensive experiments, 20 mg of Fe_3O_4-Phenanthroline-Zn nanocatalyst in EtOH/H_2O (1/1) (80 °C) was considered as the standardized conditions for the multicomponent synthesis of highly substituted piperidines (Table 1, Entry 13).

After optimization of the reaction conditions, the scope and generality of the multicomponent synthesis of highly substituted piperidines were illustrated with respect to various aromatic aldehydes, ethyl acetoacetate and aniline derivatives. The results of these experiments are listed in Table 2. As shown in Table 2, a library of aromatic aldehydes and amines bearing electron-rich and electron-poor groups at either *ortho-*, *meta-* or *para*-positions of the aromatic ring smoothly participated in these reactions, and the desired products were prepared in good to excellent yields.

A sequential mechanistic pathway attributing to the formation of highly substituted piperidines is outlined in Scheme 2.

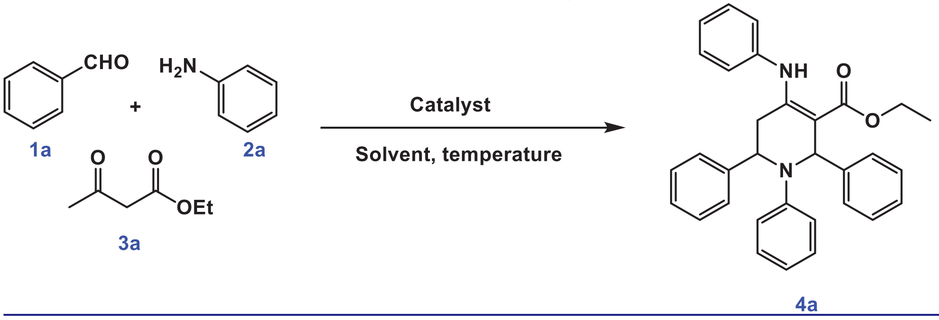
Encouraged by these results, we decided to investigate the activity of this catalytic system in the synthesis of pyrano[2,3-d]pyrimidines. The results of these experiments are listed in Table 3. Under this catalytic system, it could be seen that the reactions proceeded successfully and gave the expected products in high to excellent yields in short reaction times.

A sequential mechanistic pathway attributing to the formation of pyrano[2,3-d]pyrimidines is outlined in Scheme 3.

The reusability of the catalyst is one of the most important advantages and makes it beneficial for commercial applications. Recycling and reusability of the Fe_3O_4-Phenanthroline-Zn catalyst was also examined upon the synthesis of the model products **4a** and **7a** under the standardized conditions. After completion of the reaction, the catalyst was separated easily and rapidly from the product by exposure to an external magnet, and the reaction solution was decanted, magnetically. The remaining nanomagnetic catalyst was washed several times with ethyl acetate and dried to remove residual product, and subjected to the next run. The convenient separation using this strategy minimizes the loss of catalyst during separation. The recovered catalyst could be reused for seven successive times without any significant loss in catalytic efficiency (Figure 6).

Magnetization curve of reused Fe_3O_4-Phenanthroline-Zn after 7 runs is illustrated in Figure 7. According to the magnetization curves, the saturation of the Fe_3O_4-Phenanthroline-Zn catalyst was about 45.82 emu/g. Scanning Electron Microscope (SEM) of Fe_3O_4-Phenanthroline-Zn nanocatalyst catalyst after 7 runs is shown in Figure 7. The SEM image illustrate that these particles are of nearly spherical morphology with a mean diameter of about 10–20 nm. ICP-OES was employed to

Table 1. Optimization of reaction conditions for synthesis of highly substituted piperidines.[a]



Entry	Catalyst	Catalyst (mg)	Solvent (temperature)	Time (min)	Yield%[b]
1		–	EtOH (reflux)	120	Trace
2	Fe_3O_4	20	EtOH (reflux)	120	Trace
3	Fe_3O_4-Phenanthroline	20	EtOH (reflux)	120	Trace
4	Fe_3O_4-Phenanthroline-Zn	5	EtOH (reflux)	60	73
5	Fe_3O_4-Phenanthroline-Zn	10	EtOH (reflux)	50	82
6	Fe_3O_4-Phenanthroline-Zn	15	EtOH (reflux)	40	89
7	Fe_3O_4-Phenanthroline-Zn	20	EtOH (reflux)	30	95
8	Fe_3O_4-Phenanthroline-Zn	25	EtOH (Reflux)	30	95
9	Fe_3O_4-Phenanthroline-Zn	20	H_2O (reflux)	30	94
10	Fe_3O_4-Phenanthroline-Zn	20	CH_3CN (reflux)	30	83
11	Fe_3O_4-Phenanthroline-Zn	20	THF (reflux)	30	49
12	Fe_3O_4-Phenanthroline-Zn	20	Toluene (reflux)	30	56
13	Fe_3O_4-Phenanthroline-Zn	20	PEG (100 °C)	30	81
14	Fe_3O_4-Phenanthroline-Zn	20	Solvent-free (80 °C)	30	87
15	Fe_3O_4-Phenanthroline-Zn	**20**	**EtOH/H_2O (1/1) (80 °C)**	**30**	**98**
14	Fe_3O_4-Phenanthroline-Zn	20	DMF (Reflux)	30	85
15	Fe_3O_4-Phenanthroline-Zn	20	EtOH/H_2O (1/1) (90 °C)	30	98
16	Fe_3O_4-Phenanthroline-Zn	20	EtOH/H_2O (1/1) (70 °C)	30	95
17	Fe_3O_4-Phenanthroline-Zn	20	EtOH/H_2O (2/1) (80 °C)	30	94
18	Fe_3O_4-Phenanthroline-Zn	20	EtOH/H_2O (1/2) (80 °C)	30	92
19	Fe_3O_4-Phenanthroline-Zn	–	– (100 °C)	30	–

[a] Reaction conditions: benzaldehyde (2 mmol), ethyl acetoacetate (1 mmol) and aniline (2 mmol), catalyst, Solvent (3 ml).
[b] Isolated yield.
Bold values signifies the optimized conditions.

determine the exact Zn content of nanomaterial (after 8 times), which was found to be 21.11×10^{-5} mol/g.

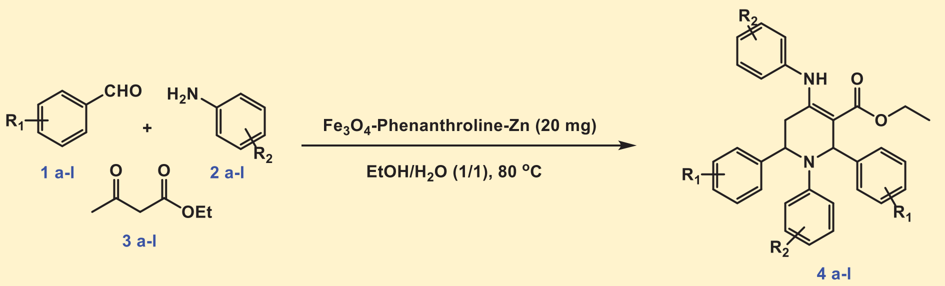
Hot-filtration test

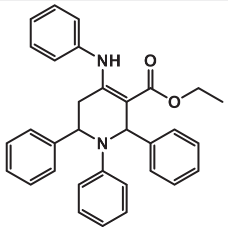
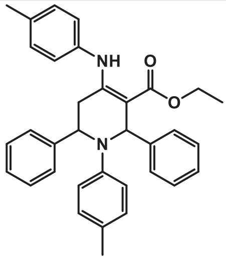
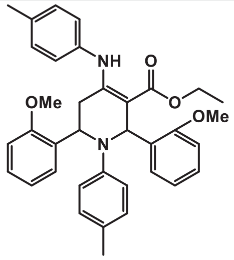
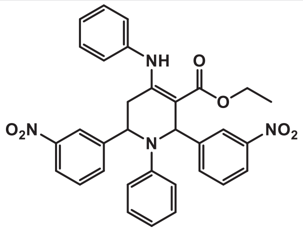
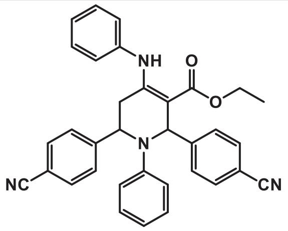
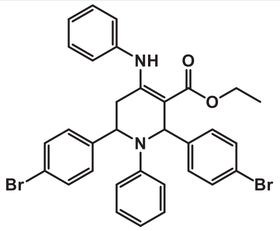
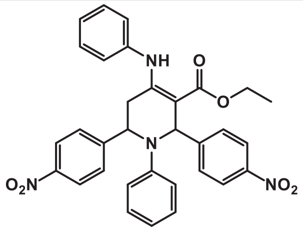
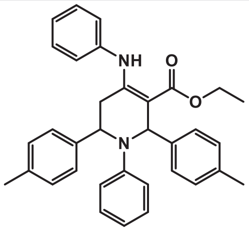
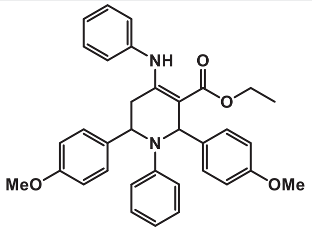
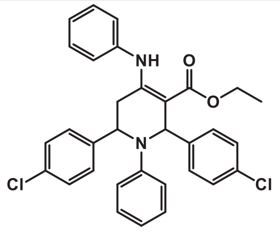
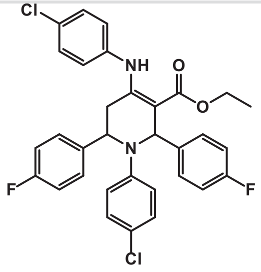
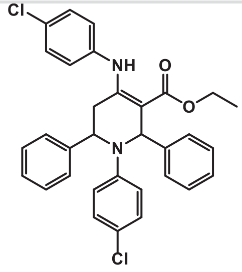
A leaching experiment was conducted to determine the stability of the synthesized magnetic Fe_3O_4-Phenanthroline-Zn catalyst. Keeping the reaction parameters same, a model reaction was catalyzed by Fe_3O_4-Phenanthroline-Zn, After 15 min of the reaction, the catalyst was removed from the reaction mixture via an external magnet and the yield of the product was found to be 71%. Thereafter, the reaction was continued for additional 15 min and the results revealed no significant increment in yield, thus justifying that leaching of active metallic species has been debarred during the course of the reaction.

Competitive study

As presented in Table 4, A comparative study of Fe_3O_4-Phenanthroline-Zn activity with the literature reports shows that the present study shows remarkable advantages over previously published reports. High product yield, short reaction time, magnetic separability and recyclability up

Table 2. Scope of the synthesis of highly substituted piperidines catalyzed by Fe_3O_4-Phenanthroline-Zn nanomaterial.[a]



 4a (30 min, 98%)	 4b (45min, 95%)	 4c (60 min, 91%)
 4d (65min, 92%)	 4e (35 min, 98%)	 4f (25 min, 99%)
 4g (35 min, 96%)	 4h (50 min, 93%)	 4i (75 min, 94%)
 4j (25 min, 98%)	 4k (20 min, 95%)	 4l (30 min, 98%)

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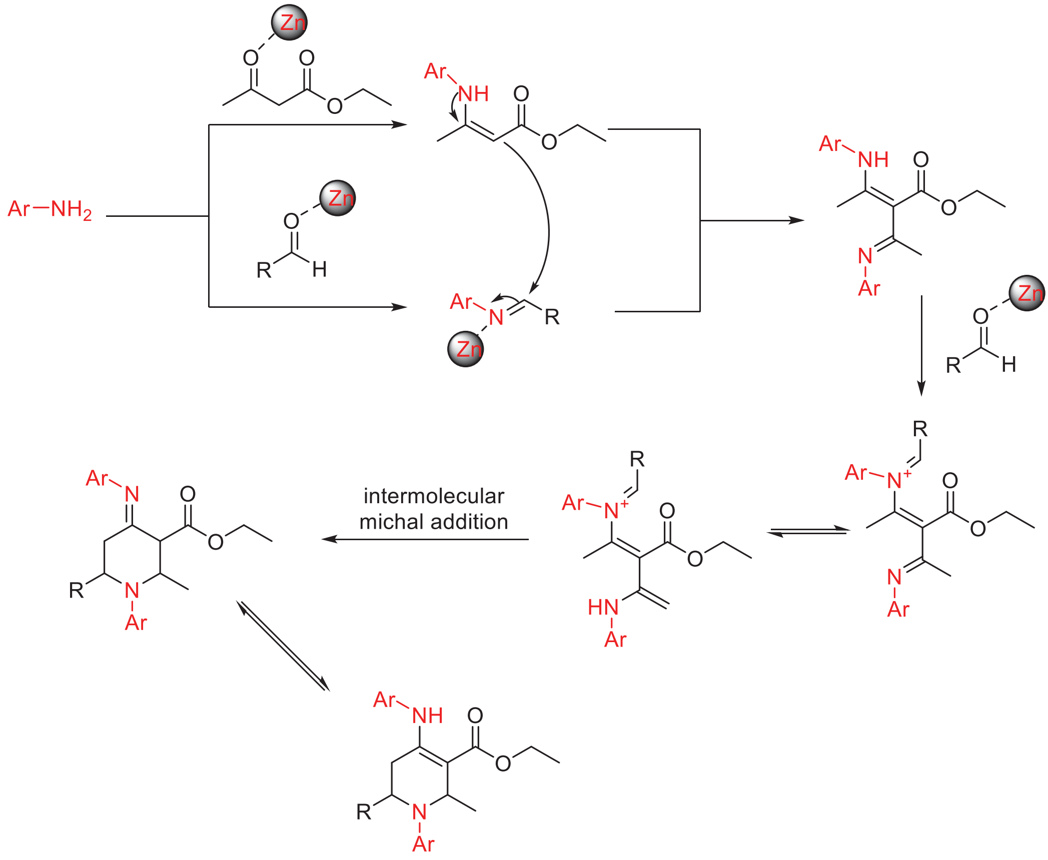
[a] Isolated Yields.



Scheme 2. The plausible mechanistic pathway of the formation of highly substituted piperidines.

to seven consecutive runs are the fascinating attributes of this strategy that makes the protocol economically viable and operationally facile.

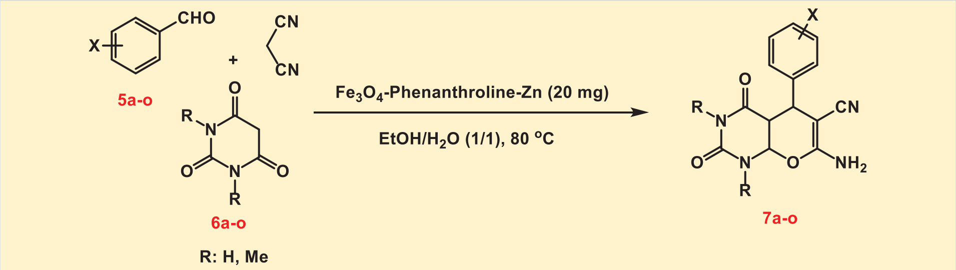
Conclusion

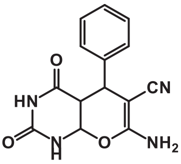
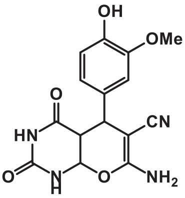
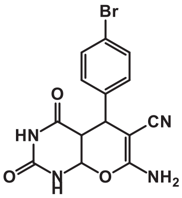
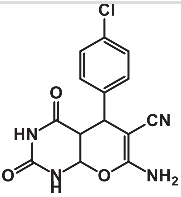
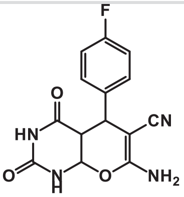
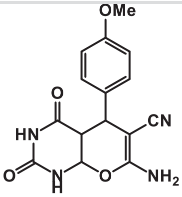
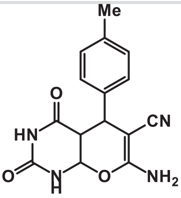
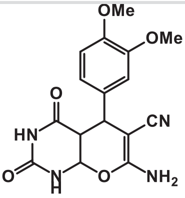
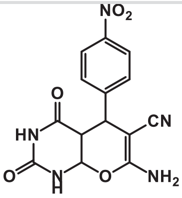
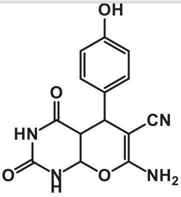
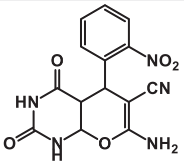
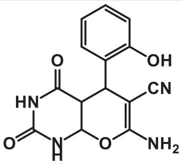
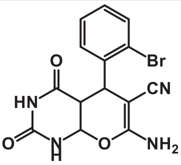
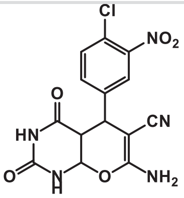
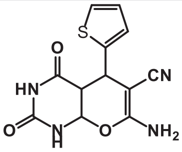
In this paper, we showed that zinc (II) complex supported on magnetic nanoparticles Fe_3O_4 modified with phenanthroline [Fe_3O_4-Phenanthroline-Zn] is an efficient nanomagnetic catalyst for the multicomponent synthesis of highly substituted piperidines and pyrano[2,3-d]pyrimidines. FT-IR spectroscopy, SEM, TEM, EDX, XRD, VSM, and ICP-OES spectroscopic techniques were used to characterize the structure of Fe_3O_4-Phenanthroline-Zn nanomaterial. Catalysis research under green solvents makes also this synthetic protocol ideal and fascinating from the environmental point of view. Interestingly, product separation was readily performed using an external magnet, and the recovered catalyst was reused 7 runs without any notable loss in catalytic activity. To the best of our knowledge, it is the first report on the utilization of zinc nanomagnetic catalyst for the multicomponent synthesis of highly substituted piperidines.

Experimental

Chemicals were purchased from Fisher and Merck. The reagents and solvents used in this work were obtained from Sigma-Aldrich, Fluka or Merck and used without further purification. The infrared spectra (IR) of samples were recorded in KBr disks using a NICOLET impact 410

Table 3. Scope of the synthesis of pyrano[2,3-d]pyrimidines catalyzed by Fe_3O_4-Phenanthroline-Zn nanomaterial.[a]



 7a (25 min, 98%)	 7b (35min, 96%)	 7c (20 min, 99%)
 7d (20 min, 99%)	 7e (20 min, 97%)	 7f (30 min, 97%)
 7g (35 min, 93%)	 7h (30 min, 92%)	 7i (35 min, 97%)
 7j (25 min, 91%)	 7k (20 min, 96%)	 7l (40 min, 92%)
 7m (25 min, 98%)	 7n (25 min, 98%)	 7o (35 min, 98%)

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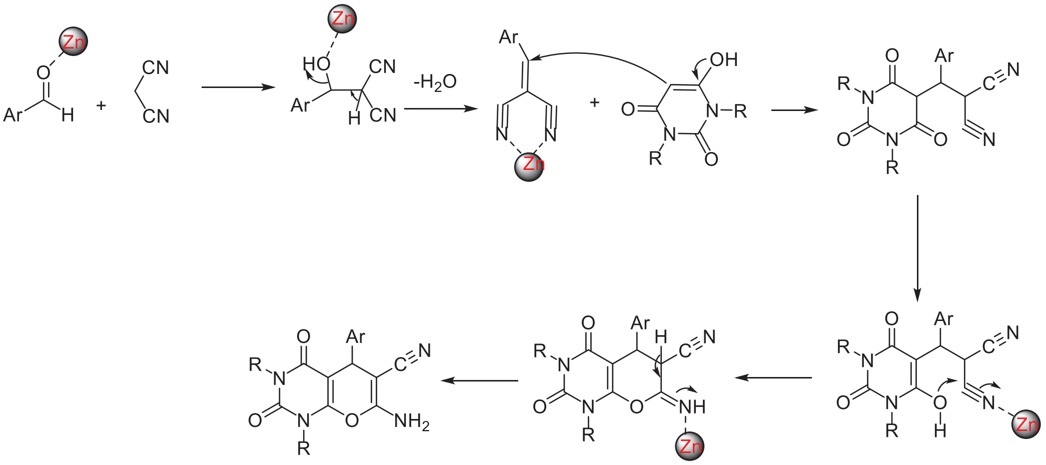
[a] Isolated Yields.



Scheme 3. The plausible mechanistic pathway of the formation of pyrano[2,3-d]pyrimidines.

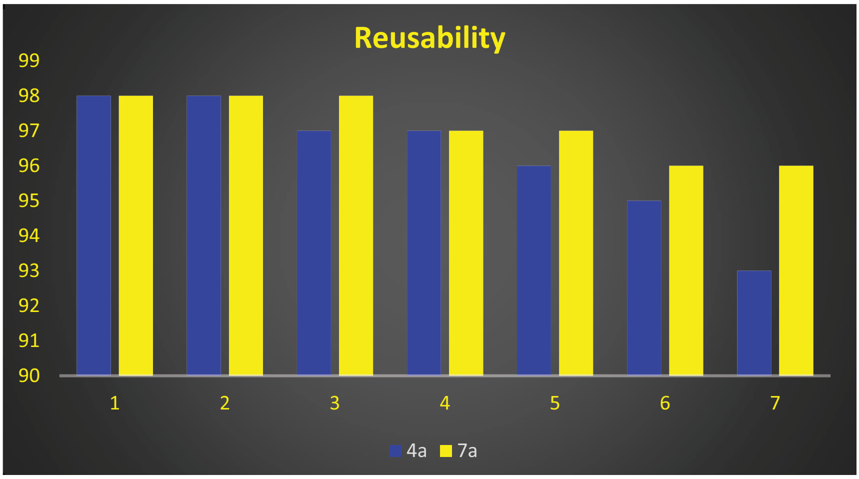


Figure 6. Reusability of Fe_3O_4-Phenanthroline-Zn nanomaterial in the synthesis of model products **4a** and **7a**.

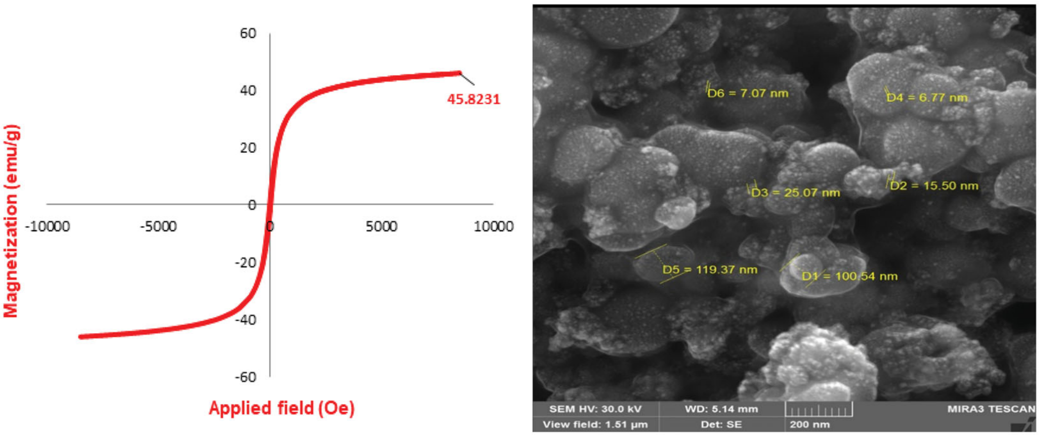


Figure 7. VSM and SEM analysis of Fe_3O_4-Phenanthroline-Zn after 7 runs.

Table 4. Comparison of Fe3O4-Phenanthroline-Zn catalyst with other catalysts in the synthesis of highly substituted piperidines and pyrano[2,3-d]pyrimidines.

Entry		Catalyst	Time	Yield	Ref.
1	Highly substituted piperidines	SBA-15/E-SMTU-Cu^{II}	20	98	[41]
2	Highly substituted piperidines	Fe@SiGu-Prs	20	96	[42]
3	Highly substituted piperidines	Acetic acid	27	90	[43]
4	Highly substituted piperidines	$PbCr_xFe_{12-x}O_{19}$	5	94	[44]
5	Highly substituted piperidines	Fe_3O_4-Phenanthroline-Zn	30	98	This work
6	Pyrano[2,3-d]pyrimidines	Nano-sawdust-OSO_3H	15	94	[45]
7	Pyrano[2,3-d]pyrimidines	MGO-D-NH-$(CH_2)_4$-SO_3H	15	95	[46]
8	Pyrano[2,3-d]pyrimidines	SnO_2/SiO_2	60	94	[47]
9	Pyrano[2,3-d]pyrimidines	$[C_4\ (MIm)_2]\cdot 2HSO_4$	15	88	[48]
10	Pyrano[2,3-d]pyrimidines	Fe_3O_4-Phenanthroline-Zn	25	98	This work

spectrometer. ^{1}HNMR and ^{13}CNMR spectra were recorded with a Bruker DRX-400 spectrometer at 400 and 100 MHz respectively. Nanostructures were characterized using a Holland Philips X, pert X-ray powder diffraction (XRD) diffractometer (Co Kα, radiation= 0.154056 nm), at a scanning speed of 2° min^{-1} from 10° to 80°. Scanning electron microscope (SEM) was performed on an FEI Quanta 200 SEM operated at a 20 kV accelerating voltage. The thermogravimetric analysis (TGA) curves are recorded using a PL-STA 1500 device manufactured by Thermal Sciences. The magnetic measurements were carried out in a vibrating sample magnetometer (VSM, BHV-55, Riken, Japan) at room temperature.

Preparation of the magnetic Fe_3O_4-nanoparticles

The mixture of $FeCl_3.6H_2O$ (5.838 g, 0.0216 mol) and $FeCl_2.4H_2O$ (2.147 g, 0.0108 mol) were dissolved in 100 mL of deionized water in a three-necked bottom (250 mL) under N_2 atmosphere. After that, under rapid mechanical stirring, 10 mL of NH_3 was added to the solution within 30 min with vigorous mechanical stirring. After being rapidly stirred for 30 min, the resultant black dispersion was heated to 80 °C for 30 min. The obtained black precipitate was isolated by magnetic decantation, washed with double-distilled water until neutrality, and further washed twice with ethanol and dried at room temperature.

Preparation of the $Fe_3O_4@SiO_2$

Then the obtained Fe_3O_4 MNPs (2 g) were dispersed in 20 mL of water by sonication for 30 min, and then 2-propanol (200 mL) was added to the reaction mixture. The reaction mixture was stirred using a magnetic stirrer at room temperature. Under continuous stirring, PEG (5.36 g), water (20 mL), ammonia solution (10 mL, 28 wt.%) and 2 mL of tetraethyl orthosilicate (TEOS) were respectively added into the suspension and continuously reacted for 30 h under stirring at room temperature. Then the product ($Fe_3O_4@SiO_2$) was isolated with an external magnet and washed two times with ethanol and distilled water.

Preparation of Fe_3O_4-APTMS

The obtained $Fe_3O_4@SiO_2$ nanoparticles (1.5 g) were dispersed in 250 mL ethanol/water (volume ratio, 1:1) by sonication for 30 min, and then APTMS (2.5 mL) was added to the mixture reaction. The reaction mixture was stirred using mechanical stirring under N_2 atmosphere at 40 °C for 6 h. then, the nanoparticles were re-dispersed in ethanol by sonication for 5 times and separated through magnetic decantation. The nanoparticles product ($Fe_3O_4@SiO_2$-APTMS) was dried at room temperature.

Preparation of Fe_3O_4-Phenanthroline

The MNPs-amine (2.2 g) was dispersed in EtOH (50 mL) by ultrasonic bath for 10 min. Potassium carbonate (1 mmol) and Phenanthroline (10 mmol, 1.8 g) were added and stirred at reflux temperature for 18 h under N_2 atmosphere. Then, the prepared Fe_3O_4-Phenanthroline nanocomposite was separated by magnetic decantation and washed three times with ethanol to remove the unattached substrates. The resulting product was dried at room temperature.

Preparation of the Fe_3O_4-Phenanthroline-Zn catalyst

In the last step, $Zn(OAc)_2$ (6 mmol) was added to Fe_3O_4-Phenanthroline (2.5 g) in absolute ethanol (50 mL) and the resultant mixture was stirred under reflux for 8 h. Finally, the synthesized nanosolid (**Fe_3O_4-Phenanthroline-Zn**) was separated by magnetic decantation. The nanomagnetic catalyst washed several times with absolute ethanol, and dried under vacuum at room temperature.

General procedure for the synthesis of highly functionalized piperidines

A mixture of aldehyde (2 mmol), ethyl acetoacetate (1 mmol), aniline (2 mmol) and Fe_3O_4-Phenanthroline-Zn (20 mg) in ethanol/water (1/1) (3 mL) was stirred at 80 °C. Reaction progress was monitored by TLC (acetone: n-hexane, 2:8). After completion of the reaction, catalyst was separated by external magnet and washed with ethyl acetate, and next, the product was extracted with ethyl acetate (5 mL × 4). The organic layer was dried over anhydrous Na_2SO_4 (1.5 g). Finally, the organic solvents were evaporated, and the corresponding sulfoxides were washed with ethanol and obtained in high to excellent yields.

General procedure for the synthesis of pyrano[2,3-d]pyrimidines

A mixture of aromatic aldehyde (1 mmol), malononitrile (1 mmol), barbituric acid (1 mmol) and Fe_3O_4-Phenanthroline-Zn (20 mg) in ethanol/water (1/1) (3 mL) was stirred at 80 °C. Reaction progress was monitored by TLC (acetone: n-hexane, 2:8). After the completion of the reaction, the catalyst was separated using an external magnet and washed with ethyl acetate. Then, the solvent was evaporated and all products were recrystallized from ethanol. The pure pyrano[2,3-d]pyrimidines derivatives were obtained in excellent yields.

Spectroscopic data

All the products reported here are known compounds and the spectroscopic data was matched literature values. Data for the some of the compounds are given below.[49–53]

Acknowledgement

This work was supported by the Deanship of Scientific Research, Vice Presidency for Graduate Studies and Scientific Research, King Faisal University, Saudi Arabia [Project No. GRANT721].

Disclosure statement

No potential conflict of interest was reported by the author(s).

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