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# ZnCl<sub>2</sub> supported on Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> core–shell nanocatalyst for the synthesis of quinolines *via* Friedländer synthesis under solvent-free condition

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Ebrahim Soleimani, Department of Chemistry, Razi University, Kermanshah 67149-67346, Iran. E-mail: e\_soleimanirazi@yahoo.com A magnetic nanocatalyst of  $Fe_3O_4@SiO_2/ZnCl_2$  was prepared by supporting  $ZnCl_2$ on silica-coated magnetic nanoparticles of  $Fe_3O_4$ . This recoverable catalyst was used for the synthesis of quinolines via Friedländer synthesis from 2-aminoaryl ketones and  $\alpha$ -methylene ketones under solvent-free condition. The prepared catalyst was characterized by FT-IR, TEM, SEM, XRD, EDX, ICP-OES, VSM and BET. It was found that  $Fe_3O_4@SiO_2/ZnCl_2$  showed higher catalytic activity than homogenous  $ZnCl_2$ , and could be reused several times without significant loss of activity.

#### KEYWORDS

magnetite nanocatalyst, ZnCl<sub>2</sub>, quinolines, Friedländer

#### **1 | INTRODUCTION**

In recent years, much attention has been focused on heterogeneous catalysts due to their potential applications for replacing homogenous catalysts in organic chemistry and industry; they exhibit advantages of easy separation of the catalyst from the reaction medium, minimal corrosion, simplify recovery, reusability, green chemical processes, and enhanced product selectivity.<sup>[1]</sup> Among heterogeneous catalysts, supported catalysts on a solid support has attracted significant attention due to a number of advantages as their available active sites, stability, and product separation and their recovery, which are all important factors in organic chemistry and industry.<sup>[2]</sup> Although supported catalysts are available on different supports such as charcoal, alumina, silica and polymers, since silica displays many advantages properties such as excellent stability (chemical as well as thermal), no swelling, high surface area, good accessibility and in addition organic groups can be robustly anchored to the surface to provide catalytic center.<sup>[3]</sup>

Magnetic silica nanoparticles have recently received significant attention due to their chemical inertness, magnetic properties, no toxicity, and excellent thermal stability.<sup>[4]</sup> These favorable properties allow nanoparticles (NPs) to be widely used as a catalyst or supported catalyst for organic syntheses.<sup>[5]</sup> It has been reported that the heterogeneous catalysts supported on MNPs reveal excellent performance in many reactions e.g., hydrolysis, hydrogenation, oxidation, carbon–carbon coupling and reduction.<sup>[6]</sup>

The use of ZnCl<sub>2</sub> has received considerable attention as an inexpensive, nontoxic, commercially available catalyst for various organic transformations. Due to the numerous advantages associated with this eco-friendly compound, ZnCl<sub>2</sub> has been explored as a powerful Lewis acid catalyst for different reactions.<sup>[7]</sup> However, in spite of their potential utility, this homogeneous catalyst present limitations due to the use of toxic and corrosive reagents and the tedious work-up procedure that thus making the process economically and environmentally undesirable. Therefore, in this research, ZnCl<sub>2</sub> was immobilized on the surface of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> core-shell nanoparticles, and then used a magnetic heterogeneous nanocatalyst for the synthesis of quinolines via Friedlander annulation reaction under solvent-free conditions. Advantages and novelty of this new catalyst is easy separation of from reaction medium by applying external magnetic field and reused several times.

It is well known that quinolines exhibit a wide range of biological activities,<sup>[8–10]</sup> and are valuable reagents for the synthesis of nano- and mesostructures with enhanced electronic and photonic properties.<sup>[11]</sup> The classic version of the

Friedländer quinoline synthesis, which combines a 2aminoaryl ketone and a carbonyl compound containing an activated  $\alpha$ -CH acid under acidic or basic conditions by refluxing in an aqueous or alcoholic solution to give quinoline, has been extensively explored.<sup>[12]</sup> In a typical procedure, the catalyst is varied from strong protic inorganic liquid acids,<sup>[13]</sup> such as HCl,  $H_2SO_4$ , and polyphosphoric acid, to Lewis acids,<sup>[14]</sup> such as NaAuCl<sub>6</sub>, and AuCl<sub>3</sub>.3H<sub>2</sub>O, and transition-metals,<sup>[15]</sup> such as ruthenium and palladium. Moreover, the synthesis of these heterocycles has been usually carried out in a polar solvent such as THF, DMF, or DMSO leading to complex isolation and recovery procedures. Therefore, the discovery of a novel and inexpensive catalyst, which can be easily separated and reused, without undesirable contamination, is of prime importance. Therefore, we have prepared a magnetic heterogeneous catalyst of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>/ ZnCl<sub>2</sub>by supporting ZnCl<sub>2</sub> on silica-coated magnetic nanoparticles of Fe<sub>3</sub>O<sub>4</sub>.

In continuation of our efforts to develop new methods in the synthesis of quinolines,<sup>[16]</sup> and magnetic nanocatalysts,<sup>[17]</sup> herein, we wish to report a mild and efficient approach for the synthesis of polysubstituted quinolines via Friedländer annulation using a catalytic amount of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>/ZnCl<sub>2</sub> under solvent-free conditions at 60°C. Accordingly, treatment of 5-chloro-2-aminobenzophenone **1** with  $\alpha$ -methylene ketones **2** in the presence of 20 mol% of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>/ZnCl<sub>2</sub> resulted in the formation of quinolines **3** in high yields (Scheme 1).

#### 2 | RESULTS AND DISCUSSION

#### 2.1 | Preparation and characterization of the catalyst

The Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>/ZnCl<sub>2</sub> nanocatalyst was prepared in three steps; preparation of colloidal iron oxide magnetic nanoparticles (Fe<sub>3</sub>O<sub>4</sub> MNPs) as a magnetic core, coating of silica on Fe<sub>3</sub>O<sub>4</sub> MNPs (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>) as a shell through sol–gel process and incorporation of ZnCl<sub>2</sub> on the surface by an electron interaction between Zn<sup>2+</sup> and surface oxide species<sup>[18]</sup> (for details see Experimental section). The catalyst preparation steps is illustrated in Scheme 2. To prove this claim, each step of the catalyst preparation procedure was investigated by FT-IR to ensure the presence of new

functional groups. Eventually, the nanocatalysts were characterized by different techniques such as XRD, TEM, SEM, EDX, VSM, BET and ICP-OES.

The crystalline structure of magnetite nanoparticles was identified with XRD technique. Figure 1 shows the XRD patterns for Fe<sub>3</sub>O<sub>4</sub> MNPs, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> MNPs and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>/ZnCl<sub>2</sub> MNPs. The XRD pattern of Fe<sub>3</sub>O<sub>4</sub> (Figure 1a) clearly showed six reflection peaks (2 $\theta$ ) at 30°, 35.5°, 43°, 53.8°, 56.9° and 62.5° refer to (220), (311), (400), (422), (511) and (440), confirmed the formation of a cubic spinel ferrite structure, and the crystallite size was calculated from the Scherrer's formula, found to be an average diameter of about 20 nm (Figure 1a). Furthermore, no change observed in the crystalline structure of the  $Fe_3O_4$  core upon coating and immobilization of the magnetite surface by TEOS (Figure 1b) and ZnCl<sub>2</sub> (Figure 1c). After immobilization of ZnCl<sub>2</sub> onto the surface of magnetic nanoparticles, new diffraction peaks were appeared at 21.1 °, 27.4 °, 46.0 ° and 53.5 ° attributed to the ZnCl<sub>2</sub>.<sup>[19]</sup> Furthermore, no change observed in the crystalline structure of the ZnCl<sub>2</sub> after immobilization on surface of Silica. Therefore, there is a possible electronic interaction between Zn<sup>2+</sup> and hydroxyl or surface oxide species on surface in which O atom donates electron to  $Zn^{2+}$ .<sup>[18,19]</sup>

Figure 2 shows the FT-IR spectra of Fe $_3O_4$  MNPs, Fe $_3O_4@SiO_2$  core-shell MNPs and Fe $_3O_4@SiO_2/ZnCl_2$  MNPs.

In Figure 2a (FT-IR of Fe<sub>3</sub>O<sub>4</sub>), the band at 565 cm<sup>-1</sup> is attributed to the vibration of Fe-O bond, while band at 3420 cm<sup>-1</sup> is assigned to the symmetrical stretching vibration of hydroxyl groups (-OHs), indicating the presence of some amount of ferric hydroxide in Fe<sub>3</sub>O<sub>4</sub>. The band at 1620 cm<sup>-</sup> <sup>1</sup> is attributed to the bending vibration of adsorbed water. Figure 2b shows the IR spectrum of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> core-shell MNPs. In comparing Figure 2b with Figure 2a, we have found some new absorption peaks in Figure 2b. The bands at 1088 cm<sup>-1</sup> are related to the asymmetric stretching vibration and the symmetric stretching vibration of Si-O-Si and the band at 960 cm<sup>-1</sup> is assigned to the symmetric stretching vibration of Si-OH. Figure 2c shows the IR spectrum of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>/ZnCl<sub>2</sub> MNPs. In Figure 2c, in addition to bands around 565 cm<sup>-1</sup> (for the stretching vibration of Fe–O bond), around 960 cm<sup>-1</sup> (for the stretching vibration of Si-OH), around 1088 cm<sup>-1</sup> (for the stretching vibration of Si–O–Si),







**FIGURE 1** XRD patterns of (a)  $Fe_3O_4$  MNPs; (b)  $Fe_3O_4$  @SiO<sub>2</sub> MNPs; (c)  $Fe_3O_4$  @SiO<sub>2</sub>/ZnCl<sub>2</sub> MNPs. The arrow mark indicates the (110) diffraction peak of ZnCl<sub>2</sub>



FIGURE 2 FT-IR spectra of (a)  $Fe_3O_4MNPs$ ; (b)  $Fe_3O_4@SiO_2MNPs$ ; (c)  $Fe_3O_4@SiO_2/ZnCl_2MNPs$ 

newer bands at 611 cm<sup>-1</sup>, 735 cm<sup>-1</sup> and 968 cm<sup>-1</sup> are assigned to the stretching vibration of Zn–O band. It reveals that zinc chloride has been successfully grafted onto the surface of  $Fe_3O_4@SiO_2$  core-shell MNPs.

TEM was used to observe the morphology of  $Fe_3O_4@SiO_2/ZnCl_2$ catalyst. Figure 3a shows that the NPs have a core-shell structure with a distinct contrast between silica shells and  $Fe_3O_4$  cores, implying that silica shells ( $Fe_3O_4@SiO_2$ ) successfully coated the hydrophilic  $Fe_3O_4$  NPs. The average size of the cores was found to be ~25–30 nm – a result consistent with the crystallite size of ~20 nm for  $Fe_3O_4$  NPs obtained from XRD. The average size of magnetite-silica core-shell nanoparticles was determined

to be around ~100 nm. The SEM images (Figure 3b–d) shows that, the as-prepared  $Fe_3O_4@SiO_2$  MNPs have a spheroidal morphology and the  $Fe_3O_4@SiO_2/ZnCl_2$  MNPs appear more aggregated and less defined, but they still have a spheroidal shape, with an average size of 90 ± 15 nm.

Furthermore, the Energy dispersive X-ray spectroscopy (EDX) in Figure 4 and Table 1 confirmed the presence of  $ZnCl_2$  on the surface of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>.

The magnetization hysteresis for  $Fe_3O_4@SiO_2/ZnCl_2$ nanoparticle at room temperature is shown in Figure 5. The low  $M_s$  value of  $Fe_3O_4@SiO_2/ZnCl_2$  nanoparticles (38 emu/g) compared to that of magnetite nanoparticles (79.26 emu/g) can be explained by the presence of a thick diamagnetic silica layer surrounding the magnetic core. It is worth mentioning that the  $M_s$  value of the present prepared nanoparticles is much larger than previously published reports.<sup>[20]</sup>

The specific surface area of the samples was measured using a BET method with N<sub>2</sub> adsorption–desorption at  $-196^{\circ}$ C, and the typical results were shown in Figure 6. The BET surface area of Fe<sub>3</sub>O<sub>4</sub> was 38 m<sup>2</sup> g<sup>-1</sup>. After SiO<sub>2</sub> coating, the BET surface area of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> was dramatically increased to  $272m^2$  g<sup>-1</sup>. The BET surface area of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>/ZnCl<sub>2</sub> was decreased to  $224m^2$  g<sup>-1</sup> due to the presence of ZnCl<sub>2</sub>. Although there is still much debating on whether the activity of a catalyst can be directly related to the catalyst surface area, it was generally believed that the adsorption on the catalyst surface would at least help to concentrate the reactant molecules for the reactions.

## 2.2 | Catalytic activity of $Fe_3O_4@SiO_2/ZnCl_2$ in the synthesis of quinolines

We chose the reaction of 2-aminobenzophenone and acetylaceton under solvent-free condition as a model reaction for the optimization study. First, different amounts of the catalyst (entries 1-4) were used for a fixed reaction time of two hours at 60°C. The experimental results showed that the best yield was obtained when 0.07 g of catalyst was used (entry 3). Next, we studied the model reaction at different

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FIGURE 3 (a) TEM image of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>/ZnCl<sub>2</sub> MNPs, SEM images of (b) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> MNPs and (c, d) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>/ZnCl<sub>2</sub> MNPs

temperatures (Table 2, entries 5–7 and 3). The reaction rate increased as the temperature was raised. At 60°C, the good yield of 95% was obtained in a reaction time of 2 h (Table 2, entry 3). Further work indicated that the best results were obtained when the reaction was carried out at 60°C, for 2 h under solvent-free condition using 0.07 g of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>/ZnCl<sub>2</sub> catalyst (Table 2, entry 3). It was also found that this heterogeneous catalyst, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>/ZnCl<sub>2</sub> showed higher catalytic activity than the corresponding homogenous ZnCl<sub>2</sub>.

With the optimized condition established above, we then extended our attempt using various types of acyclic  $\alpha$ -methylene ketones. The results have been summarized in Table 3. In all cases, excellent yields were obtained. This confirms the reliability of the synthetic method.

Finally, for further exploration of the scope and limitation of the method we investigated the reaction of three different cyclic $\alpha$ -methylene ketones with 5-chloro-2aminobenzophenone. Gratifyingly the reaction led to the formation of the corresponding quinolines 3 h–j in high isolated yields (Table 4).

The catalyst was successfully recycled and reused 5 times with 20% loss of its activity, as demonstrated in Figure 7.

#### 2.3 | Proposed mechanism

Possible mechanism for the synthesis quinolines by Lewis acid catalysts has been proposed previously.<sup>[12]</sup> Scheme 3 shows a possible mechanism for this synthesis in the presence of Lewis acid nano paramagnetic  $Fe_3O_4@SiO_2/ZnCl_2$ .

#### **3** | EXPERIMENTAL

#### 3.1 | Materials and techniques

Melting points were taken on an Electrothermal 9100 apparatus and left uncorrected. IR spectra were obtained on a Ray Leigh Wqf-510 Fourier Transform Infrared (FT-IR) spectrophotometer. TEM was performed on a Philips CM10 operated at an 80 kV electron beam accelerating voltage. SEM and EDX were performed on a Philips XL-300 instrument. The sample was sputtered by gold to avoid undesirable electron charging. X-ray diffraction was conducted using a Philips X'pert Pro (PW 3040) X-ray diffractometer with monochromatic Cu-K $\alpha$  radiation (k = 1.54056 Å, 40 kV, 30 mA). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker DRX-250 Avance spectrometer at 250, 400 and 62, 100 MHz. NMR spectra were obtained on solutions in CDCl<sub>3</sub> using tetramethylsilane as an internal standard. The textural structures were measured by N<sub>2</sub>adsorption at - 196°C in a Micromeritics TriStar ASAP 3000 system, and specific surface areas of the as-prepared samples were measured using Brunauer-Emmett-Teller (BET) method. The concentration of copper was estimated using Shimadzu AA-680 flame atomic absorption spectrophotometer and inductively



FIGURE 4 EDX spectrum of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>/ZnCl<sub>2</sub> MNPs

TABLE 1	EDX data (	of Fe <sub>3</sub> O <sub>4</sub>	@SiO <sub>2</sub> /ZnCl <sub>2</sub>	MNPs	(Wt %)
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Sample	C (%)	O (%)	Si (%)	Cl (%)	Fe (%)	Zn (%)	Total (%)
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> /ZnCl <sub>2</sub>	18.44	23.75	16.06	0.19	38.73	2.82	100.00



FIGURE 5 Magnetization loop of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>/ZnCl<sub>2</sub> nanoparticle



FIGURE 6 Nitrogen adsorption/desorption isotherms of Fe<sub>3</sub>O<sub>4</sub> MNPs, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> MNPs and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>/ZnCl<sub>2</sub> MNPs

coupled plasma optical emission spectrometer (ICP-OES) Varian Vista PRO Radial. The magnetic properties of particles were analyzed using Vibrating Sample Magnetometer (VSM, Meghnatis Daghigh Kavir Co., Iran) equipment  $(I_{max} = 150 \text{ A}, P \le 9 \text{ kW})$  at room temperature. All of the chemicals were purchased from Fluka, Merck and Aldrich, and used without further purification.

#### 3.2 | Preparation of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>/ZnCl<sub>2</sub>

Magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles (NPs) were prepared according to the reported method (co-precipitation)<sup>[21]</sup> and coated with silica in the presence of 2-propanol (sol-gel method).<sup>[22]</sup> In brief, 3.0 g of FeCl<sub>3</sub>.6H<sub>2</sub>O and 1.0 g of FeCl<sub>2</sub>.4H<sub>2</sub>O were dissolved in 120 mL deionized water under nitrogen gas with vigorous stirring. Then, NH<sub>3</sub> (28%) was added dropwise into the solution until the pH of the solution reached 11. Stirring was continued for 1 h at 60°C. The color of the bulk solution turned from orange to black immediately. The magnetite precipitate was separated from the solution using a magnet, washed several times with deionized water and ethanol, and left to dry in air. Then, 1.0 g as-synthesized Fe<sub>3</sub>O<sub>4</sub> NPs were mixed with 120 mL isopropyl alcohol in a sealed three-neck flask by ultrasonic treatment for 30 min. 30 mL deionized water, 1.0 mL TEOS (silica precursor), and 4.80 mL ammonia (28 wt%) were added into the mixture of Fe<sub>3</sub>O<sub>4</sub> and isopropyl alcohol at room temperature under mechanical agitation. After 12 h, the final product  $(Fe_3O_4@SiO_2)$  was collected, washed with ethanol and deionized water and dried at 50°C. Then 1.5 g as-synthesized Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> NPs was mixed with 150 mL toluene in a sealed three-neck flask by ultrasonic treatment for 30 min. Then 0.1 g ZnCl<sub>2</sub> were added and the mixed solution was stirred at room temperature for 24 h. The resultant magnetite nanoparticles were collected by an external magnetic field and washed several times with ethanol and deionized water, respectively. Then, the product was dried and activated in a vacuum oven at 60°C for 8 h. The loading of zinc was obtained 6.58 mmol  $g^{-1}$  by inductively coupled plasmaoptical emission spectrometry (ICP-OES).

#### 3.3 | General procedure for the synthesis of quinolines

A mixture of 1.0 mmol 2-aminoaryl ketone, 1.2 mmol  $\alpha$ -CH acid, and 0.07 g catalyst was heated under solvent-free



$\begin{array}{c} CI \\ H_{3}C \\ NH_{2} \end{array} + \begin{array}{c} H_{3}C \\ H_{3}C \\ H_{3}C \end{array} + \begin{array}{c} Ph \\ O $							
Entry	Gram of catalyst (mmol %)	Temperature (°C)	Time (h)	Yield (%) <sup>b</sup>			
1	0.02 (0.13)	60	2	46			
2	0.05 (0.33)	60	2	69			
3	0.07 (0.46)	60	2	95			
4	0.10 (0.66)	60	2	95			
5	0.07 (0.46)	25	12	60			
6	0.07 (0.46)	80	2	96			
7	0.07 (0.46)	100	2	96			

<sup>a</sup>Reaction condition: 2-aminoaryl ketone (1 mmol), acetylaceton (1.2 mmol) and the catalyst under solvent free condition. <sup>b</sup>Isolated yields.



SCHEME 3 Synthesis of 1-(2-Methyl-4-phenyl-quinolin-3-yl)-ethanone

TABLE 3 Synthesis of quinoline derivatives through Friedländer synthesis by catalyst Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>/ZnCl<sub>2</sub>

$\begin{array}{c} Cl \\ H \\ NH_{2} \end{array} \begin{array}{c} Ph \\ NH_{2} \end{array} \begin{array}{c} O \\ R^{2} \end{array} \begin{array}{c} O \\ Fe_{3}O_{4}@SiO_{2}/ZnCl_{2} \\ Solvent-free, 60 \ ^{\circ}C \end{array} \begin{array}{c} Ph \\ NH_{2} \end{array} \begin{array}{c} O \\ R^{2} \end{array} \begin{array}{c} Ph \\ R^{2} \end{array}$							
Entry	R <sup>1</sup>	$\mathbb{R}^2$	Product	Yield % <sup>a</sup> (time, h)	Mp, °C (found)		
1	Me	Me	3a	95 (2)	148		
2	Me	OEt	3b	94 (2)	98		
3	Et	OMe	3c	92 (2)	83		
4	Pr	OMe	3d	93 (3)	82		
5	iPr	OMe	3e	95 (4)	98		
6	CH <sub>2</sub> Cl	OMe	3f	92 (2)	123		
7	CH <sub>2</sub> CO <sub>2</sub> Me	CH <sub>2</sub> CO <sub>2</sub> Me	3 g	90 (2)	124		

<sup>a</sup>Isolated yields.

conditions with stirring at 60°C. After completion of the reaction as indicated by TLC, the catalyst was separated with a magnet from the reaction mixture and washed with hot

ethanol (2–10 mL). Then, the filtrate was concentrated, and the solid product was recrystallized from ethanol. All products are known compounds, which were characterized TABLE 4 Reaction of different cyclic  $\alpha$ -methylene ketones with 5-chloro-2-aminobenzophenone by catalyst Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>/ZnCl<sub>2</sub>

	CI $Ph$ $Ph$ $Ph$ $Ph$ $Ph$ $Ph$ $Ph$ $Ph$	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> /ZnCl <sub>2</sub> Solvent-free, 60 °C	Ph N 3	
Entry	cyclic α-methylene ketones	Product	Yield % <sup>a</sup> (time, h)	Mp, °C (found)
1	cyclohexanone	3 h	94 (2)	157
2	Dimedone	3i	97 (2)	203
3	Tetronic acid	3ј	87 (3)	130

<sup>a</sup>Isolated yields.



**FIGURE 7** Reusability of the catalyst for the synthesis of synthesis of quinolines (model reaction: entry 1, Table 3)

by FT-IR and spectral data and their mp values were compared with literature reports.

#### 4 | CONCLUSION

This work reported on the preparation of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>/ZnCl<sub>2</sub> via functionalization of silica-coated magnetic nanoparticles with ZnCl<sub>2</sub> by one-pot synthesis containing continuously three-step reaction. The core-shell nanoparticles were stable and reusable, non-toxic and inexpensive heterogeneous nanocatalyst with great potential applications in organic syntheses. The Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>/ZnCl<sub>2</sub> MNPs were used as an acid catalyst for the synthesis of different quinolines with 2-aminoaryl ketone and various cyclic or acyclic  $\beta$ -dicarbonyl under solvent-free condition with excellent yields and short time. The major advantage of this catalyst was its ease of the recovery, allowing it to be reused with slightly change in its catalytic activity.

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