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## Sulfamic acid supported on Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> superpara magnetic nanoparticles as a recyclable heterogeneous catalyst for the synthesis of quinolines

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In the present study, for the first time the synthesis of sulfamic acid supported on  $Fe_3O_4@SiO_2$  superpara magnetic nanoparticles as a solid acid catalyst with large density of sulfamic acid groups was suggested. The structural and magnetic properties of functionalized  $Fe_3O_4@SiO_2$  nanoparticles are identified by TEM, IR, VSM, XRD, TGA and elemental analysis. Then, the applicability of the synthesized nanoparticles was tested as a recyclable acidic catalyst for the synthesis of quinoline derivatives, an important class of potentially bioactive compounds. The products are obtained in good to high yields (72–98%) from onepot reaction procedure involving carbonyl compounds and 2-amino benzophenone under solvent-free conditions.

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### 1. Introduction

In recent years, there has been a rapid growth in the development of novel supported compounds such as supported catalysts, reagents and scavengers. Preparing heterogeneous catalysts by immobilizing the homogenous precursors on a solid support is one of the important routes for developing novel heterogeneous catalysts. In most of these cases, the immobilized catalysts so prepared could provide advantages over their unsupported counterparts in terms of easy separation, low toxicity, moisture resistance, air tolerance, easy handling, reusability.<sup>1-3</sup> On a different note, magnetic nanoparticles (MNPs) have gained an increasing interest because of their potential applications such as their uses for cell separation,<sup>4</sup> magnetic resonance imaging,<sup>5</sup> drug delivery systems,<sup>6</sup> protein separation<sup>7</sup> and cancer treatments through hyperthermia.8 Also, magnetic nanoparticles (MNP) can be a good candidate as a support material for heterogeneous catalysts, because of easy synthesis, high surface area, facile separation by magnetic forces, low toxicity and cost.9 According to these attractive properties, many MNP supported catalysts have been designed and widely applied as novel magnetically separated catalysts in traditional metal catalysis,10,11 organocatalysis,12 and even enzyme catalysis.13

The synthesis of quinolines has been of considerable interest to chemists because their oxygen heterocycles may contribute to potential antimalarial, antibacterial, antiasthmatic, antihypertensive, antiinflammatory, antiplatelet and tyro kinase PDGF- RTK inhibiting properties.<sup>14-20</sup> For the synthesis of quinolines, various methods have been reported including the Skraup,<sup>21</sup> Conrad-Limpach-Knorr,22,23 Pfitzinger,24,25 Friedländer26,27 and Combes.28,29 However, the Friedlander condensation is still considered as a popular method for the synthesis of quinoline derivatives.<sup>30-34</sup> In this method, 2-amino benzophenone condenses with ketones or  $\beta$ -diketones to yield quinolines. Nevertheless the development of new synthetic methods for the efficient preparation of heterocycles containing quinoline fragment is therefore an interesting challenge. In this work, for combining the benefits of sulfamic acid and heterogeneous magnetic catalysts, we reveal a new nanometer scale, magnetic, supported, acidic catalyst which can be used for different organic functional group transformations as a catalyst in green processes. Then, we studied its catalytic activity in the synthesis of quinoline derivatives by treatment of 2-amino benzophenone with various carbonyl compounds. Quinoline derivatives were produced with good to high yields (72-98%) under solvent-free conditions.

### 2. Results and discussion

#### 2.1 Catalyst characterization

Due to the reasonable needs to clean and green recovery of the heterogenous catalyst, we synthesized  $Fe_3O_4(@SiO_2 bonded N$ -propyl diethylene tetrasulfamic acid ( $Fe_3O_4(@SiO_2(@PDETSA))$  as a new nanomagnetic heterogeneous systems. Firstly,  $Fe_3O_4$  MNPs were prepared by the reaction of  $FeCl_2 \cdot 4H_2O$ ,  $FeCl_3 \cdot 6H_2O$  with sodium hydroxide in deionized water. For coat silica on  $Fe_3O_4$  MNPs, to mixture  $Fe_3O_4$  and tetraethoxysilane (TEOS) was added NH<sub>3</sub> and was stirred mechanically for 6 h at room

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temperature to produce  $Fe_3O_4@SiO_2$  MNPs. Then,  $Fe_3O_4@SiO_2$ propyl chloride was prepared by the reaction of  $Fe_3O_4@SiO_2$ with (3-chloropropyl) trimethoxy silane in dry toluene for 48 h. Then resulting compound was treated with diethylene triamine in dry toluene for 24 h to give  $Fe_3O_4@SiO_2$  bonded *N*-propyl diethylene triamine ( $Fe_3O_4@SiO_2@PDETA$ ). Finally, the reaction of  $Fe_3O_4@SiO_2@PDETA$  with chlorosulfonic acid at 0 °C gave  $Fe_3O_4@SiO_2$ -bonded *N*-propyl diethylene tetrasulfamic acid ( $Fe_3O_4@SiO_2@PDETSA$ ) (Scheme 1).

The synthesized catalyst was characterized by different methods such as TEM, IR, VSM, XRD, TGA and elemental analysis.

**2.1.1 Transmission electron microscopy (TEM).** The morphology and sizes of (a)  $Fe_3O_4$  and (b)  $Fe_3O_4$ @SiO<sub>2</sub> and (c)

Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PDETSA nanoparticles were observed by transmission electron microscopy (TEM) as shown in Fig. 1.

From TEM images (Fig. 1a), it can be seen that  $Fe_3O_4$  MNPs are uniformly and the average size of  $Fe_3O_4$  MNPs is about 5-8 nm. After being coated with a SiO<sub>2</sub>, the typical core-shell structure of the  $Fe_3O_4$ @SiO<sub>2</sub> can be observed and the average size increases to about 8-10 nm (Fig. 1b). Fig. 1c was showed TEM of  $Fe_3O_4$ @SiO<sub>2</sub>@PDETSA and the average size of MNPs is about 10-12 nm.

**2.1.2 X-ray diffraction (XRD) analysis.** The structural properties of synthesized  $Fe_3O_4$ ,  $Fe_3O_4$ @SiO<sub>2</sub> and  $Fe_3O_4$ @SiO<sub>2</sub>@PDETSA MNPs were analyzed by XRD. As shown in Fig. 2, XRD patterns of the synthesized  $Fe_3O_4$  nanoparticle display several relatively strong reflection peaks in the 2 h region of 20–



X= SO<sub>3</sub>H, H

Scheme 1 Preparation of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> bonded *N*-propyl diethylene tetrasulfamic acid MNPs [Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PDETSA].



Fig. 1 TEM pattern of (a) Fe<sub>3</sub>O<sub>4</sub> MNPs (b) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> MNPs (c) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PDETSA (d) after the five cycles



Fig. 2 XRD pattern of (A) Fe $_3O_4$  MNPs (B) Fe $_3O_4@SiO_2$  MNPs (C) Fe $_3O_4@SiO_2@PDETSA.$ 

80 °C, which is quite similar to those of Fe<sub>3</sub>O<sub>4</sub> nanoparticles reported by other group. The patterns indicate a crystallized structure at  $2\theta$ : 30.2, 35.3, 43.2, 53.5, 57 and 62.5, which are assigned to the (220), (311), (400), (422), (511) and (440) crystallographic faces of magnetite (reference JCPDS card no. 19-629). It can be seen that the Fe<sub>3</sub>O<sub>4</sub> obtained has highly crystalline cubic spinel structure which agrees with the standard Fe<sub>3</sub>O<sub>4</sub> (cubic phase) XRD spectrum (PDF#88-0866). The XRD pattern of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> prepared by the Stöber process, shows an obvious diffusion peak at 13–28 that appeared because of the existence of amorphous silica. For Fe<sub>3</sub>O<sub>4</sub>@ SiO<sub>2</sub>@PDETSA nanoparticles, the broad peak was transferred to lower angles due to the synergetic effect of amorphous silica and DETSA. According to the result calculated by Scherrer equation, it was found that the diameter of  $Fe_3O_4$  nanoparticles obtained was about 8 nm and  $Fe_3O_4$ @SiO<sub>2</sub> microspheres were obtained with a diameter of about 10 nm due to the agglomeration of  $Fe_3O_4$  inside nanospheres and surface growth of silica on the shell. The average sizes of  $Fe_3O_4$ @SiO<sub>2</sub>@PDETSA nanoparticles are calculated to be 12 nm using the Scherrer equation, which are in good accordance with TEM results.

2.1.3 Thermal gravimetric analysis (TGA). The thermal behavior of  $Fe_3O_4$ @SiO\_2@PDETSA MNPs are shown in Fig. 3. A significant decrease in the weight percentage of the  $Fe_3O_4$ @SiO\_2@PDETSA MNPs at about 185 °C that this was evaluated to be ~1.5% according to the TGA analysis. In addition, the analysis showed other decreasing peak appeared at temperature around 650 °C due to the decomposition of the organic spacer



Fig. 3 TGA pattern of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PDETSA MNPs.

group (decomposition of the catalyst). Therefore, the covalent bonds in the catalyst endow it with high thermal stability.

**2.1.4 IR spectra.** The successful conjugation of sulfamic acid onto the surface of the  $Fe_3O_4@SiO_2$  nanoparticles was confirmed by the IR spectra (Fig. 4). The peaks at 3415 and 1010 cm<sup>-1</sup> appear in IR spectra of compound 4A, which are assigned to the -OH and Si-O group, respectively (Fig. 4A). In IR spectra of the  $Fe_3O_4@SiO_2@PDETSA$  MNPs, CH<sub>2</sub> bending at 1480 cm<sup>-1</sup> and Si-C stretching at 1210 cm<sup>-1</sup>are observed as a broad band (Fig. 4B and C). broad band at 3150–3500 cm<sup>-1</sup>, attributed to hydroxyl group of sulfonic acid group (Fig. 4C). The absence of this band in the spectrum of 4B indicates the loss of hydroxyl group of  $Fe_3O_4@SiO_2$ .

**2.1.5 Vibrating sample magnetometer (VSM).** The magnetic properties of the sample containing a magnetite component were studied by a vibrating sample magnetometer (VSM) at 300 K (Fig. 5). Fig. 5 shows the absence of hysteresis phenomenon and indicates that product has superparamagnetism at room temperature. The saturation magnetization values for (A) Fe<sub>3</sub>O<sub>4</sub>, (B)Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> and (C) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PDETSA were 68.4, 43.2 and 36.8 emu g<sup>-1</sup>, respectively. These results indicated that the magnetization of Fe<sub>3</sub>O<sub>4</sub> decreased considerably with the increase of SiO<sub>2</sub> and propyl diethylene tetrasulfamic acid.

**2.1.6 Elemental analysis.** Elemental analysis of Fe<sub>3</sub>O<sub>4</sub>(a) SiO<sub>2</sub>(a)PDETSA gave the following results: N and S 1.54 and 4.69%, respectively. Ratio N:S determined from elemental analysis 3:4 was obtained (Fe<sub>3</sub>O<sub>4</sub>(a)SiO<sub>2</sub>(a)C<sub>7</sub>H<sub>18</sub>N<sub>3</sub>S<sub>4</sub>O<sub>12</sub>). The content of S obtained from elemental analysis showed that typically a loading of 1.4 mmol g<sup>-1</sup> H<sup>+</sup> was obtained.

# 2.2 Catalytic activity of $Fe_3O_4$ (a)SiO<sub>2</sub> (a)PDETSA for the synthesis of quinolines

In order to show the merit of synthesized heterogeneous catalyst in organic reactions,  $Fe_3O_4(@SiO_2 bonded N$ -propyl diethylene tetrasulfamic acid  $[Fe_3O_4(@SiO_2(@PDETSA)]]$  was used, for the synthesis of quinolines by treatment of 2-aminobenzophenone and carbonyl compounds. In order to evaluate



Fig. 4 IR spectra of (A) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> MNPs (B) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PDETA (C) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PDETSA.



Fig. 5 VSM pattern of (A) Fe $_3O_4$  MNPs (B) Fe $_3O_4$ @SiO $_2$  MNPs (C) Fe $_3O_4$ @SiO $_2$ @PDETSA.

the catalytic efficiency of  $Fe_3O_4(@SiO_2(@PDETSA MNPs and to determine the most appropriate reaction conditions; initially a model study was carried out on the synthesis of quinoline 3 (Scheme 2) by the condensation of 2-aminobenzophenone$ **1**and**1**,3-cyclohexadione**2**in different sets of reaction conditions.

In preliminary experiment, this reaction was carried out in various solvents, with  $Fe_3O_4$ @SiO\_2@PDETSA MNPs (0.02 g) as a catalyst. The reaction could be carried out in various solvent and gave product in low yield (Table 1, entries 1–9). It was very surprising that the reaction proceeded in excellent yields (78%) under solvent-free condition (Table 1, entry 10). The reaction proceeded perfectly in high temperature, but the yields decreased when the reaction was carried out in low temperature.

To obtain the optimized reaction conditions, we also changed temperature and the amount of catalyst. The results are summarized in Fig. 6.

Consequently, among the tested temperature and the amount of catalyst, the condensation of 2-aminobenzophenone and 1,3-cyclohexadione was best catalyzed by 0.02 g Fe<sub>3</sub>O<sub>4</sub>OSiO<sub>2</sub>OPDETSA MNPs at 110 °C.

To evaluate catalytic activity of  $Fe_3O_4$ @SiO<sub>2</sub>@PDETSA MNPs, the model reaction was carried out at 110 °C for 45 min under solvent-free condition in the presence of different catalytic systems (0.02 g), separately. The results are shown in Table 2. As it is evident from the results,  $Fe_3O_4$ @SiO<sub>2</sub>@PDETSA MNP was the most effective catalyst in terms of yield of the quinolines (98%) while other catalysts formed the product with the yields of 22–48% (Table 2, entries 1–9). Control experiments indicate that in the absence of the catalyst, the reaction at the same condition gives quinoline in a rather low yield of 20% (Table 2, entry 10).



Scheme 2

Table 1 The effect of various solvent on the synthesis of quinoline 3

Entry	Solvent	Yield <sup>a</sup> %	Yield <sup>b</sup> %
1	H <sub>2</sub> O	5	35
2	MeOH	10	58
3	EtOH	10	58
4	CH <sub>3</sub> CN	5	15
5	THF	_	20
6	CHCl <sub>3</sub>	_	45
7	$CH_2Cl_2$	_	45
8	Dioxane	5	60
9	Ethylene glycol	20	76
10	Solvent-free	25	78

<sup>*a*</sup> Reaction condition: 2-amino-benzophenone (1 mmol), 1,3cyclohexadione (1 mmol), catalyst (0.02 g), solvent (2 mL) at r.t. <sup>*b*</sup> Reaction condition: 2-amino-benzophenone (1 mmol), 1,3cyclohexadione (1 mmol), catalyst (0.02 g), solvent (2 mL) at 80 °C.



Fig. 6 The effect temperature and the amount of catalyst for the synthesis of quinoline 3.

Table 2 One-pot synthesis of quinoline 3 in the presence of various catalytic systems  $a^{a}$ 

$\mathbf{d}^{b}(\%)$

 $^a$  Reaction conditions: 2-aminobenzophenone (1 mmol), 1,3-cyclohexadione (1 mmol), catalyst (0.02 g) at 110  $^\circ\rm C$  under solvent-free condition.  $^b$  The yield refers to pure isolated product.

To establish the generality and applicability of this method, 2-amino-5-chlorobenzophenone/2-aminobenzophenone and carbonyl compounds were subjected to the same reaction condition to furnish the corresponding quinolines (Table 3).

Not only diketones (Table 3, entries 1–12) but also ketones (Table 3, entries 13–17) afforded the desired products in good to excellent yields (72–98%) in short reaction time (45–160 min). It is delighted that the reaction time of 1,3-diphenyl propane-1,3-dione was longer than those of acetylacetone, which is probably due to low reactivity of carbonyl groups. Also, the reaction time of 2-amino-5-chlorobenzophenone and dicarbonyl compounds

was longer than those of 2-aminobenzophenone. The reaction of cyclic diketones took place faster than open chain analogues. These reactions also proceeded with ketone derivatives (Table 3, entries 13–17). In these cases the reaction times are longer. It may be due to the less activity of ketone derivatives than dicarbonyl compounds.

At the end of the reaction, the catalyst could be recovered by an external magnet. The recycled catalyst was washed with dichloromethane and subjected to a second reaction process. The results show that the yield of product after seven runs was only slightly reduced (Fig. 7).

In Table 4, the efficiency of our method for the synthesis of quinolines is compared with some other published works in literature. Each of these methods have their own advantages, but they often suffer from some troubles including the use of organic solvent, necessity of temperature control (entry 2), long reaction time (entries 3–9) and employ of non-recyclable catalyst (entries 6, 7, 10 and 11).

### 3. Experimental

#### 3.1 Chemicals

Reagents and solvents were purchased from Merck or Fluka chemical companies. Purity determinations of the products were accomplished by TLC on silica-gel polygram SILG/UV 254 plates. Melting points were measured on an Electro thermal 9100 apparatus. IR spectra were taken on a Perkin Elmer 781 spectrometer in KBr pellets and reported in cm<sup>-1</sup>.<sup>1</sup> H NMR and <sup>13</sup>C NMR spectra were measured on a Bruker DPX-250 Avance instrument at 250 MHz and 62.9 MHz in CDCl<sub>3</sub> or DMSO-d<sub>6</sub> with chemical shift given in ppm relative to TMS as internal standard. The morphology of the products were determined by using CMPhilips10 model Transmission Electron Microscopy (TEM) at accelerating voltage of 100 kV. Power X-ray diffraction (XRD) was performed on a Bruker D<sub>8</sub>-advance X-ray diffractometer with Cu K $\alpha$  ( $\lambda = 0.154$  nm) radiation. The thermogravimetric analysis (TGA) curves were recorded under air atmosphere using TGA/DTA Shimadzu-50 with platinum pan. The samples were heated in air from 25 to 800 °C with a heating rate of 10 °C min<sup>-1</sup>. The weight losses as a function of temperature were recorded. The magnetic properties were determined by using vibrating sample magnetometer (VSM) leak shore 7200 at 300 K Vsm leak shore.

#### 3.2 Catalyst preparation

**3.2.1 Preparation of Fe\_3O\_4 nanoparticles.** Firstly, 15 g sodium hydroxide (NaOH) was dissolved into 25 mL deionized water. Then, the mixture of 2 g  $FeCl_2 \cdot 4H_2O$ , 5.2 g  $FeCl_3 \cdot 6H_2O$ , 25 mL deionized water and 0.85 mL HCl was added drop by drop with vigorous stirring to make a black solid product. The resultant mixture was heated on water bath for 4 h at 80 °C. The black magnetite solid MNPs were isolated by an external magnet and washed with deionized water and ethanol three times and was then dried at 80 °C for 10 h.

**3.2.2** Preparation of  $Fe_3O_4$  (0.50 g, 2.1 mmol) was dispersed in the mixture of ethanol (100 mL) and

Entry	Substrate 1	Substrate 2	Quinoline 3	Time (min)	$\operatorname{Yield}^{b}(\%)$
1	Ph NH <sub>2</sub>	ů,		45	98
2	CI Ph NH2	ů.		45	95
3	Ph NH <sub>2</sub>	Me Me	O N Me	120	89
4	CI Ph	Me		120	83
5	Ph NH <sub>2</sub>	Me Me		120	90
6	CI Ph	Me Me		120	87
7	Ph NH <sub>2</sub>	Mc O Me		120	98
8	CI Ph NH2			120	92
9	Ph NH <sub>2</sub>	Ph Ph	CI N Ph	160	89
10	CI Ph NH2	o o Ph Ph		120	82
11	Ph NH <sub>2</sub>	Me Me	O N CH <sub>3</sub>	90	95

Entry	Substrate 1	Substrate 2	Quinoline 3	Time (min)	Yield <sup>b</sup> (%)
12		Me Me	CI CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub>	160	88
13	Ph NH <sub>2</sub>			120	83
14	Ph NH <sub>2</sub>			120	93
15	Cl Ph NH <sub>2</sub>			120	75
16				120	89
17	CI NH2			160	77

<sup>*a*</sup> Reaction conditions: 2-amino-5-chlorobenzophenone or 2-amino benzophenone (1 mmol), carbonyl compounds (1 mmol) in the presence of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PDETSA MNPs (0.02 g) at 110 °C under solvent-free condition. <sup>*b*</sup> The yield refers to pure isolated product.



Fig. 7 Recycle of catalyst for the synthesis of quinoline 3.

deionized water (20 mL) for 10 min, Then 2.5 mL of  $NH_3$  was added followed by the addition of tetraethoxysilane (TEOS) (1.5 mL) drop by drop. This solution was stirred mechanically for 6 h at room temperature. Then the product  $Fe_3O_4$ @SiO<sub>2</sub> was separated by an external magnet and was washed with deionized water and ethanol three times and dried at 80  $^\circ C$  for 10 h.

**3.2.3 Preparation of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> bonded propyl chloride** (**Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PC**). Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> (1.0 g) was suspended in dry toluene (30 mL) and then 3-chloropropyl trimethoxy silane (15.0 mL) was added followed by triethyl amine (1 mL) as a catalyst. The suspension was mechanically stirred as it was heated under reflux for 48 h. Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> bonded propyl chloride MNPs were isolated by an external magnet. The collected powder was washed using toluene and ethanol and were dried under vacuum at 80 °C for 4 h to give Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> bonded *N*-propyl chloride (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PC).

3.2.4 Preparation of  $Fe_3O_4$  (20) SiO<sub>2</sub> bonded *N*-propyldiethylenetriamine ( $Fe_3O_4$  (20) SiO<sub>2</sub> (20) Fe<sub>3</sub>O<sub>4</sub> (20) Fe<sub>3</sub>O<sub>4</sub> (20) SiO<sub>2</sub> bonded *N*-propylchloride (1 g) in dry toluene (30 mL),



Table 4 Comparison of results using Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PDETSA MNPs with results obtained by other works for the synthesis of quinolines

Entry	Catalyst	Condition	Yield (%) <sup>a</sup>	Ref.
1	Current	Solvent-free, 110 °C, 45 min	98	_
2	HClO <sub>4</sub> -SiO <sub>2</sub>	$CH_2CN$ , 60 °C, 3 h	92	35
3	PMA-SiO <sub>2</sub>	EtOH, reflux, 8 h	88	36
4	$Zr(DS)_4$	$H_2O$ , reflux, 6 h	90	37
5	$Zr(HSO_4)_4$	$H_2O$ , reflux, 13 h	87	38
6	$CH_3COOH$ (1 eq.)	H <sub>2</sub> O, 60 °C, 6 h	60	39
7	<i>p</i> -TsOH (1 eq.)	H <sub>2</sub> O, 60 °C, 6 h	62	39
8	bmimCl-ZnCl <sub>2</sub>	Ionic liquid, r.t., 24 h	80	40
9	$H_{3}PO_{4}$ (1 eq.)	H <sub>2</sub> O, 60 °C, 12 h	90	39
10	HCl	H <sub>2</sub> O, 100–200 °C, 1 h	68	41

diethylene triamine (15 mL) was added and the mixture was heated under reflux with stirring for 24 h. The reaction was cooled to room temperature and the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> bonded *N*-propyl diethylene triamine MNPs were isolated by an external magnet. The collected compound was washed using toluene and methanol and was dried for 6 h at 80 °C to give Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@PDETA.

3.2.5 Preparation of  $Fe_3O_4@SiO_2$  bonded *N*-propyl diethylene tetrasulfamic acid [ $Fe_3O_4@SiO_2@PDETSA$ ]. To a magnetically stirred mixture of  $Fe_3O_4@SiO_2@PDETA$  (0.5 g) in  $CH_2Cl_2$  (10 mL) at 0 °C, chlorosulfonic acid (1.80 g) was added dropwise over 1 h. After the addition was complete, the mixture was stirred for 12 h until all HCl was removed from the reaction vessel.  $Fe_3O_4@SiO_2$  bonded *N*-propyl diethylene tetrasulfamic acid MNPs were isolated by an external magnet and were washed with methanol and diethyl ether (30 mL) and then dried at room temperature to give  $Fe_3O_4@SiO_2@PDETSA$ .

#### 3.3 Catalytic activity

**3.3.1 General procedure for the preparation of quinoline derivatives.** To a mixture of carbonyl compounds (1.0 mmol) and 2-amino-5-chlorobenzophenone or 2-aminobenzophenone (1.0 mmol) was added  $Fe_3O_4$ @SiO\_2@PDETSA (0.025 g). The mixture was stirred at 110 °C for appropriated reaction time (Table 3). The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was dissolved in acetone and  $Fe_3O_4$ @SiO\_2@PDETSA MNPs were separated by external magnet. Then the solvent was removed from solution under reduced pressure and the resulting product was purified

by recrystallization using ethanol to afford the pure quinoline product in excellent purity and yield. Structural assignments of the products are based on their <sup>1</sup>H NMR, <sup>13</sup>C NMR, MS and IR spectra.

#### 3.4 Selected data

**3.4.1 Compound (entry 2).** 7-Chloro-9-phenyl-3,4-dihydro-1-2*H*-acridinone: yellow solid, m.p. 184–186 °C (lit. [40] 185 °C), IR (KBr, cm<sup>-1</sup>) 3025, 2978, 2874, 1695, 1548, 1475, 1385, 1212, 1078, 1009, 970, 838, 697. <sup>1</sup>HNMR (250 MHz, CDCl<sub>3</sub>)  $\delta$  2.26 (q, 2H, *J* = 6.4 Hz), 2.72 (t, 2H, *J* = 6.4 Hz), 3.37 (t, 2H, *J* = 6.4 Hz), 7.17 (t, 2H), 7.42 (s, 1H), 7.53 (m, 3H), 7.69 (d, 1H, *J* = 8.8 Hz), 8.01 (d, 1H, *J* = 8.8 Hz), MS (*m*/*z*, %): 308((M + 2) – 1, 34), 306 (M – 1, 100), 281(5), 280(29), 278(15), 253(4), 244(10), 215(27), 188(12), 153(17), 120(20), 107(15).

**3.4.2 Compound (entry 6).** Methyl-6-chloro-2-methyl-4phenyl-3-quinolinecarbaoxyl: yellow solid, m.p. 135 °C, (lit. [40] 135 °C), IR (KBr, cm<sup>-1</sup>):  $\nu$ : 3038, 2958, 2900, 1747, 1560, 1458, 1405, 1298, 1237, 1185, 1075, 872, 767. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$  2.74 (s, 3H), 3.56 (s, 3H), 7.25–8.01 (c, 8H). <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>)  $\delta$  23.7, 52.2, 125.2, 125.8, 128.0, 128.5, 128.8, 129.1, 130.5, 131.2, 132.4, 134.9, 145.5, 146.1, 145.9, 154.9, 168.6. MS (m/z, %): 313(M + 2, 31), 311(M+, 100), 296(6), 281(50), 279(97), 254(14), 251(16), 236(4), 211(10), 189(34), 175(52), 108(37), 94(33), 74(17).

**3.4.3 Compound (entry 17).** 2-Chloro-11-phenyl-7,8,9,10tetrahydro-6*H*-cyclohepta[*b*]quinoline: yellow solid, m.p. 196– 198 °C, (lit. [41] 195 °C), IR (KBr, cm<sup>-1</sup>): *v*: 3085, 3052, 2934, 2855, 1618, 1600, 1510, 1465, 1364, 1185, 990, 870, 825, 685, <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta$ : 1.60 (s, 2H), 1.84 (s, 4H), 2.68 (c, 2H) 3.26 (c, 2H), 7.22–7.96 (c, 8H). <sup>13</sup>C NMR (62.9 MHz, CASDEADCl<sub>3</sub>)  $\delta$  26.9, 28.4, 30.7, 31.8, 40.1, 125.1, 127.7, 127.9, 128.6, 129.0, 129.3, 130.3, 131.3, 134.8, 136.9, 144.2, 144.7, 165.1, MS (*m*/*z*, %): 308((M + 2), 33), 306(M - 1, 100), 292(9), 280(15), 277(12), 252(13), 242(17), 228(18), 215(18), 201(10), 188(10), 127(23), 120(25), 107(15).

### Conclusion

In conclusion, the present work provided a new type of heterogeneous for potential synthetic application. Fe<sub>3</sub>O<sub>4</sub>@-SiO<sub>2</sub>@PDETSA MNPs are an efficient and reusable catalyst for the synthesis of quinoline derivatives and is comparable with some other applied catalysts. Products have been achieved by a one-pot coupling reaction of carbonyl compounds and *o*-aminobenzophenone at 110 °C in a short period of time under solvent-free condition. In addition, it is easy to separate and recover the catalyst for another catalytic recycling.

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