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ARTICLE

Synthesis, characterization, and application of Fe_3O_4-SA-PPCA as a novel nanomagnetic reusable catalyst for the efficient synthesis of 2,3-dihydroquinazolin-4(1H)-ones and polyhydroquinolines

Cite this: DOI: 10.1039/xoxxoooooox

Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/xoxxoooooox

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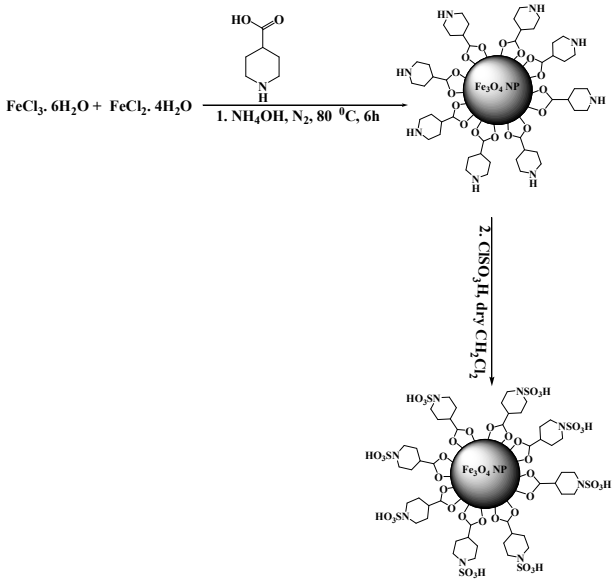
Piperidine-4-carboxylic acid (PPCA) functionalized Fe_3O_4 nanoparticles (Fe_3O_4-PPCA) prepared by the one pot co-precipitation of iron oxide in the presence of PPCA. Grafting of chlorosulfonic acid on the synthesized Fe_3O_4-PPCA nanoparticles afforded sulfamic acid-functionalized magnetic nanoparticles (Fe_3O_4-SA-PPCA). The catalytic activity of Fe_3O_4–SA-PPCA as a novel catalyst was probed through one-pot synthesis of 2,3-dihydroquinazolin-4(1H)-ones and polyhydroquinolines derivatives. The heterogeneous catalyst could be recovered easily and reused many times without significant loss of its catalytic activity.

1 Introduction

Nanoscale materials have been a subject of particular interest due to properties, which differ from their bulk counterparts [1]. They have been used extensively in chemistry [2], physics [3], biology [4] and catalysis [5]. Magnetic nanoparticles have attracted great interest because of their multifunctional physical and chemical properties. Magnetic NPs have many unique magnetic properties such as superparamagnetic, high coercivity, low Curie temperature, high magnetic susceptibility, etc. Among the nanoparticulate transition-metal oxides, magnetite is a common magnetic iron oxide that has a cubic inverse spinel structure with fcc close packed oxygen anions and Fe cations occupying interstitial tetrahedral and octahedral sites [6]. Superparamagnetic magnetite (Fe_3O_4) NP's are getting great interest due to their unique chemical and physical properties. Moreover, the naked iron oxide NPs have high chemical activity, and are easily oxidized in air (especially), generally resulting in loss of magnetism and magnetite dispersibility. Therefore, providing proper surface coating and developing some effective protection strategies (to form core/shell structured materials) to keep the stability of magnetic iron oxide NPs is very important [7]. Practically, it is worthy that in many cases the protecting shells not only stabilize the magnetic iron oxide NPs, but can also be used for further functionalization [8-11]. Heterogeneous catalysts with a matrix structure generally as the magnetically recyclable catalysts (MRCs) are developed in recent years and can be very useful to assist an effective separation and recovery in a liquid-phase reaction by a magnet, especially when the catalysts are in the nanometer-sized range. Therefore, the development of the facile and rapid methods for the preparation of efficient MRCs is still a challenge [12]. In particular, various magnetic nanoparticle-catalysts have been widely employed for promoting different organic reactions [13-15].

2 Results and discussion

In continuation of our recent success in the introduction of new catalysts [16-20], in the present article we describe the preparation of sulfamic acid-functionalized Fe_3O_4 (Fe_3O_4–SA-PPCA) with high magnetic sensitivity and application in Multicomponent reactions.



Scheme 1. Synthesis of Fe_3O_4-SA-PPCA nanoparticles.

2.1 Catalyst characterization

The magnetic nano catalyst, Fe_3O_4-SA-PPCA, is fully characterized by FT-IR, TGA, XRD, SEM, TEM and Vibrating Sample Magnetometer (VSM) analyses. The prepared Fe_3O_4-SA-PPCA NPs catalyst is placed in an aqueous NaCl solution (1 M, 25 mL), where the pH drops instantaneously to ≈ 2.95, indicating ion exchanges between -SO_3H protons and sodium ions.

The thermo gravimetric analysis curves of the piperidine-4-carboxylic acid coated iron oxide and sulfamic acid-functionalized Fe_3O_4 show the mass loss of the organic materials as they decompose upon heating (Fig. 1). Organic groups have been reported to desorb at temperatures above 260 °C. piperidine-4-carboxylic acid coated iron oxide shows three-step weight loss behavior. The initial weight loss up to 100 °C is due to residual water; the weight loss of PPCA modified magnetite NPs appears about 4.5% at 270–450 ◦C which is contributed to the thermal decomposition of the Piperidine-4-carboxylic acid groups. For Fe_3O_4-SA-PPCA MNPs, there is a well-defined mass weight loss of 7.2% between 250 and 465 ◦C related to the breakdown of the PPCA-SA moieties. On the basis of these results, the well grafting of PPCA and SA groups on the MNPs is verified.

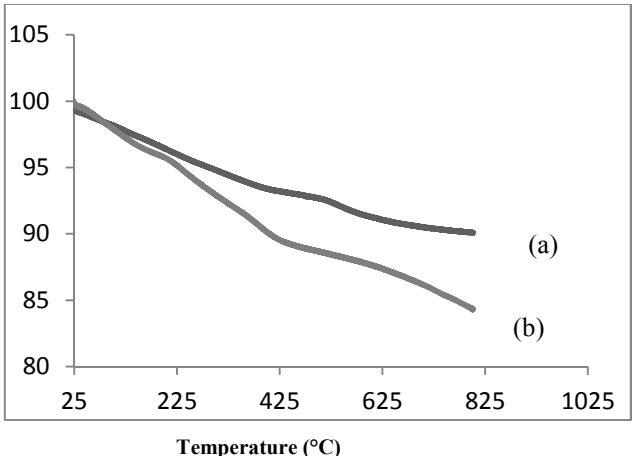


Figure 1. TGA thermograms of (a) Fe_3O_4-PPCA and (b) Fe_3O_4-SA-PPCA.

Fig. 2 shows the FT-IR spectra of both Fe_3O_4-PPCA and Fe_3O_4-SA-PPCA. The Fe–O stretching vibration near 575 cm^{-1} was observed and O-H stretching vibration near 3500 cm^{-1}. In the spectrum of Fe_3O_4–PPCA the peak at 3423 cm^{-1} was probably attributed to the NH groups, which is overlapped by the O–H stretching vibration. The presence of the anchored PPCA group is confirmed by C–H stretching vibrations that appear at 2918 and 2846 cm^{-1} in Fe_3O_4–PPCA spectra. These results provided the evidences that the Piperidine-4-carboxylic acid groups were successfully attached to the surface of Fe_3O_4 nanoparticles as a carboxylate [21]. Reaction of PPCA-Fe_3O_4 with chlorosulfonic acid produces SA-PPCA-MNPs in which the presence of sulfonylmoiety is asserted with 1228 and 1132 cm^{-1} bands in FT-IR spectra. These results were in agreement with the chemical component of the materials prepared.

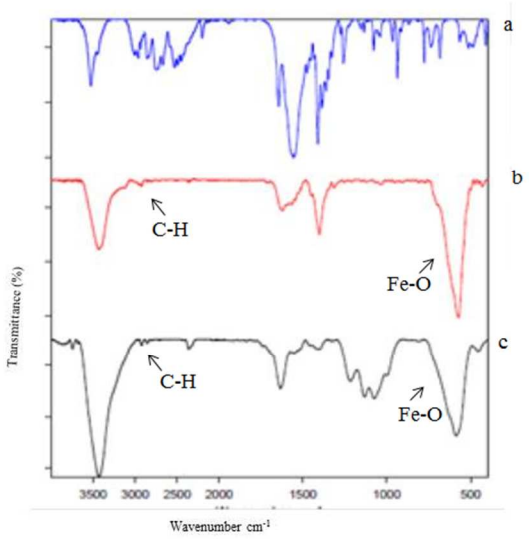


Figure 2. The comparative FT-IR spectra for (a) Pure PPCA (b) Fe_3O_4-PPCA and (c) Fe_3O_4-SA-PPCA.

In order to investigate the crystal structure of the obtained nanoparticles (Fe_3O_4-SA-PPCA) XRD analysis was performed and the resultant pattern of the as-prepared sample is presented in Fig. 3. The XRD pattern indicates that the product consists of magnetite, Fe_3O_4, and the line profile was fitted for observed 7 peaks: (111), (220), (311), (400), (422), (511) and (440).

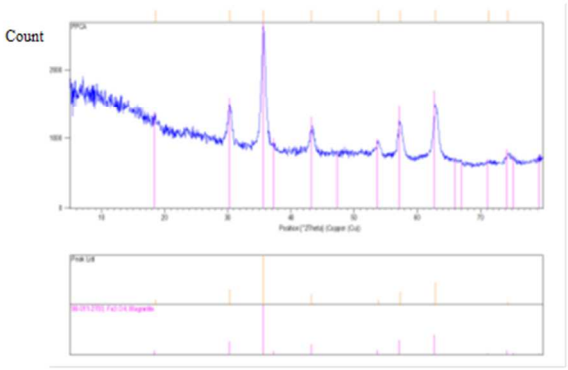


Fig 3. XRD pattern of Fe_3O_4-SA-PPCA nanoparticle.

Magnetic properties of the Fe_3O_4-PPCA-SA were evaluated by vibrating sample magnetometer at room temperature. VSM

measurements showed that the saturation magnetization (Ms) of the catalyst is 48 emu/g.

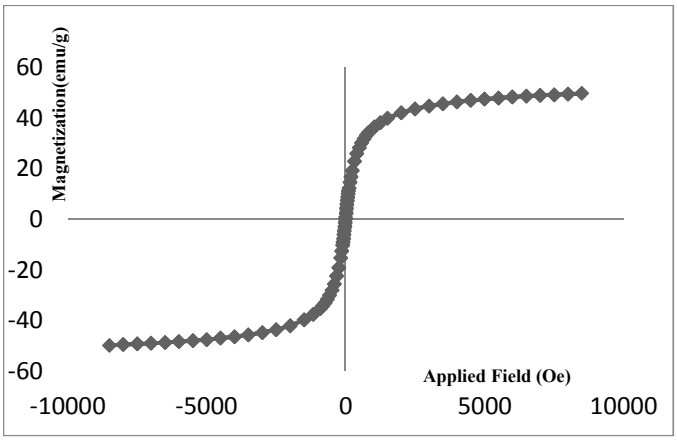


Fig 4. Magnetization curve of Fe_3O_4-SA-PPCA.

The SEM images of Fe_3O_4-PPCA (a) and Fe_3O_4-SA-PPCA (b) was confirmed that the catalyst was made up of uniform nanometer sized particles.

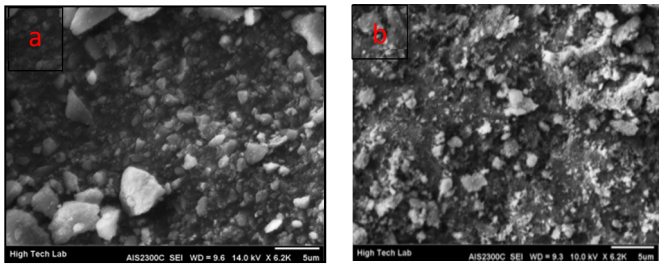


Fig 5. SEM images of Fe_3O_4-PPCA (a) and Fe_3O_4-SA-PPCA (b).

TEM micrographs of described catalyst (Fe_3O_4-PPCA-SA) are given in Fig. 6. Generally, the particles have spherical morphology and their sizes are varying in the range 8–18 nm.

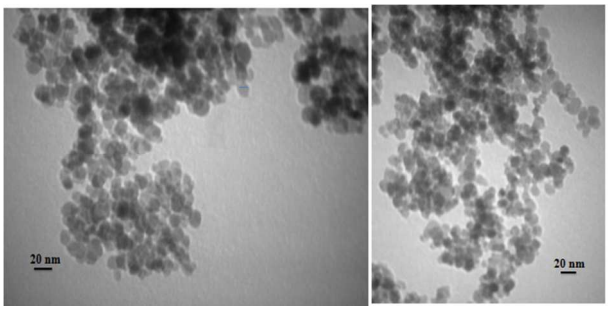


Fig 6. TEM micrographs of Fe_3O_4-PPCA-SA.

2.2 Evaluation of the catalytic activity of Fe_3O_4-SA-PPCA through the synthesis of 2,3-dihydroquinazolin-4(1H)-ones and polyhydroquinolines

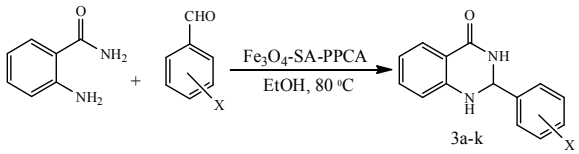
2,3-dihydroquinazolin-4(1H)-ones are an important class of heterocycles with wide range of biological activities including antibacterial, antifungal, anticancer and anticonvulsant activities [22]. Therefore, we investigated catalytic activity of Fe_3O_4-SA-PPCA as a new heterogeneous catalyst in the one-pot synthesis of 2,3-dihydroquinazolin-4(1H)-ones through the reaction of anthranilamide, and aromatic aldehydes. For this purpose, the reaction of p-Clbenzaldehyde and anthranilamide as a simple model reaction was probed to establish the feasibility of the strategy and optimize the reaction conditions.
To investigate the effect of the catalyst, systematic studies are carried out in the presence of different amounts of the catalyst (5, 8, 11, 15 mgr) in ethanol, affording 2,3-dihydroquinazolin-4(1H)-ones with 62%, 63%, 70% and 95% isolated yields, respectively (Table 1, entry 2-5). Thus, the best yield is found in the presence of just 15mg (6.7×10^{-3} mmol) Fe_3O_4-SA-PPCA, and the use of higher amounts of catalyst (18 mg, 7.7×10^{-3} mmol) does not improve the result to an appreciable extent (Table 1, entry 6).

Table 1. Optimization of the catalyst for the synthesis of 2,3-dihydroquinazolin-4(1H)-ones in the presence of different catalytic amount of Fe_3O_4-SA-PPC[a].

Entry	Catalyst (mg)	Time (min)	Yield (%)
1	None	30	0
2	5 (2.1×10^{-3} mmol)	30	62
3	8 (3.4×10^{-3} mmol)	30	63
4	11 (4.7×10^{-3} mmol)	30	70
5	15 (6.7×10^{-3} mmol)	30	95
6	18 (7.7×10^{-3} mmol)	30	96

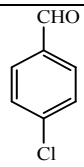
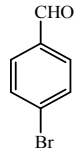
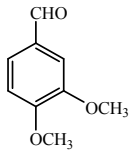
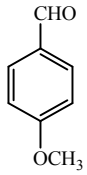
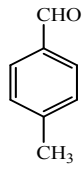
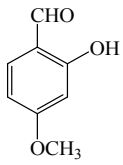
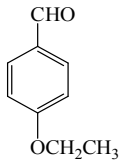
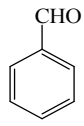
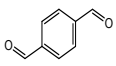
[a] Reaction conditions: anthranilamide (1 mmol), p-Clbenzaldehyde (1 mmol) in EtOH under reflux condition.

Also, this reaction was checked under different temperatures including 25, 40, 60, and 80 °C. The greatest yield in the shortest reaction time was obtained at 80 °C in the presence of 15 mg (6.7×10^{-3} mmol) of catalyst. Using the optimized reaction conditions, this process was demonstrated by the wide range of substituted divers aldehydes to synthesize the corresponding products in excellent yields (Scheme 2, Table 2).



Scheme 2. synthesis of 2,3-dihydroquinazolin-4(1H)-ones.

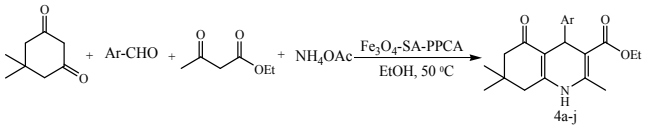
Table 2. Fe_3O_4-SA-PPCA catalyzed the one-pot synthesis of 2,3-dihydroquinazolin-4(1H)-ones in EtOH at 80 °C

Entry	Aldehyde	Product	Time (min)	Yield [a] (%)	M. p. (°C)
1		3a	30	95	201-203 [22]
2		3b	50	95	196-199 [22]
3		3c	30	94	212-214 [22]
4		3d	35	95	191-192 [22]
5		3e	30	95	229-232 [22]
6		3f	80	95	195-198 [23]
7		3g	70	93	171-173 [23]
8		3h	30	91	226-228 [22]
9		3i	75	92 [b]	245-248 [24]

[a] Isolated yield.

[b] Reaction conditions: anthranilamide (2 mmol), terephthalaldehyde (1 mmol) and Fe_3O_4-SA-PPCA (30 mg, 13.4×10^{-3} mmol).

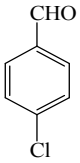
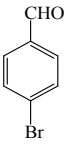
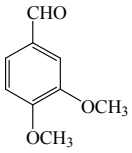
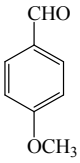
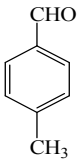
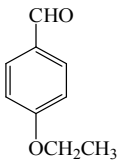
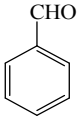
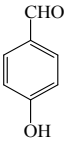
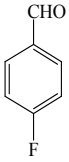
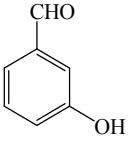
After successfully synthesizing a series of affording 2,3-dihydroquinazolin-4(1H)-ones in excellent yields, we turned our attention towards the synthesis of polyhydroquinolines derivatives. In view of the biological as well as medicinal applications of polyhydroquinoline derivatives, development of efficient and economic method of synthesizing these compounds is a continuous challenge to the chemists. For these reasons, we applied Fe_3O_4-SA-PPCA for the one-pot synthesis of polyhydroquinoline derivatives from four components coupling of aromatic aldehydes, ethyl acetoacetate, dimedone and ammonium acetate [Scheme 3].



Scheme 3. synthesis of polyhydroquinolines.

To obtain the optimal reaction conditions, we evaluated the influence of temperature and different amounts of catalyst on the time and product yield in the reaction of 3,4-dimetoxybenzaldehyde (1 mmol), dimedone (1 mmol), ethyl acetoacetate (1 mmol), and NH_4OAc (1.2 mmol) which was used as a model. 10 mg (4.3×10^{-3} mmol) of Fe_3O_4-SA-PPCA in ethanol at 50 °C was optimal for the desired reaction. Subsequently, a series of differently polyhydroquinoline derivatives were prepared successfully under optimal conditions. The results obtained in the current method are illustrated in Table 3.

Table 3. synthesis of PHQ from dimedone, arylaldehydes, ethyl acetoacetate and ammonium acetate catalyzed by Fe_3O_4-SA-PPCA at 50 °C.[a]

Entry	Aldehyde	Product	Time (min)	Yield[b] (%)	M. p. (°C)
1		4a	120	95	237-238 [25]
2		4b	90	97	248-250 [26]
3		4c	90	93	204-206 [25]
4		4d	120	93	247-248 [27]
5		4e	110	91	252-254 [26]
6		4f	90	97	179-181
7		4g	120	97	216-218 [26]
8		4h	120	97	232-234 [25]
9		4i	90	85	184-186 [25]
10		4j	100	92	221-223 [26]

[a] Reaction conditions: arylaldehyde (1mmol), dimedone (1 mmol),ethyl acetoacetate (1 mmol), NH_4OAc (1.2 mmol) and Fe_3O_4-SA-PPCA (10 mg, 4.3×10^{-3} mmol).
[b] Isolated yield.

The reusability of the catalysts is an important advantage and makes them useful for commercial applications. Thus the recovery and reusability of Fe_3O_4-SA-PPCA were investigated in the synthesis of 2,3-dihydroquinazolin-4(1H)-ones. In these experiments, the reaction mixture was dilute with ethanol and the catalyst was easily and rapidly separated from the product by exposure to an external magnet and decantation of the reaction solution. The remaining magnetic nanocatalyst was further washed with ethanol to remove residual product. Then, the reaction vessel was charged with fresh substrate and subjected to the next. As shown in Fig. 7, the catalyst can be recycled up to 5 runs without any significant loss of its catalytic activity. In addition, one of the attractive features of this novel catalyst system is the rapid and efficient separation of the catalyst by using an appropriate external magnet, which minimizes the loss of catalyst during separation.

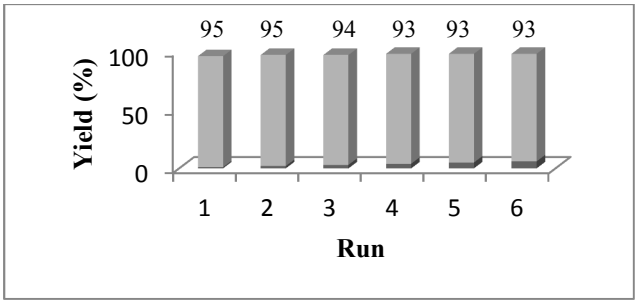


Fig 7. Recyclability of Fe_3O_4-SA-PPCA in the reaction of anthranilamide (1 mmol) and 3,4-dimethoxy benzaldehyde (1 mmol) at reflux condition in EtOH.

In order to investigate the efficiency of this new procedure in comparison with known reported procedures in the literature, the results for the synthesis of 2,3-dihydroquinazolin-4(1H)-one and PHQ derivatives, compared with the best of the well-known data from the literature as outlined in the Table 4. As shown in Table 4, the previously reported procedures suffer from one or more disadvantages such as longer reaction time, using a transition metal catalysts and low yields of products.

Table 4. Comparison of catalytic activity of Fe_3O_4-SA-PPCA with several known catalysts in the synthesis of 2,3-dihydroquinazolin-4(1H)-ones[a] [Entry 1-6] and PHQ[b] [Entry 7-11].

Entry	Catalyst	Condition	Time (min)	Yield (%)	Ref.
1	Beta-cyclodextrin	H_2O, reflux	150	91	[28]
2	$SO4^{2-}/ZrO_2$	EtOH, reflux	7	87	[22]

3	Succinimide-N-sulfonic acid	H_2O, 70° C	60	87	[29]
4	$CuCl_2/Fe_3O_4$-TEDETA	EtOH, reflux	60	95	[23]
5	NH_2SO_3H	H_2O, 70° C	30	86	[30]
6	Fe_3O_4-SA-PPCA	EtOH, reflux	30	95	This work
7	$Yb(OTf)_3$	EtOH, r.t	120	94	[31]
8	MCM-41	90° C, Solvent free	20	87	[27]
9	$PdCl_2$	THF, reflux	270	86	[32]
10	*L*-Proline	H_2O, r.t.	210	72	[33]
11	Fe_3O_4-SA-PPCA	EtOH, 50° C	110	91	This work

[a] Reaction condition: 4-methylbenzaldehyde (1mmol) and anthranilamide (1mmol).
[b] Reaction condition: 4-methylbenzaldehyde, dimedone, ethyl acetoacetate and NH_4OAc.

3 Conclusions

In this study Fe_3O_4-SA-PPCA nanocomposite was synthesized for the first time on a novel one-pot reflux route as a new heterogeneous catalyst. The catalytic activity of Fe_3O_4-SA–PPCA was probed through one-pot synthesis of 2,3-dihydroquinazolin-4(1H)-ones and polyhydroquinoline compounds. The heterogeneous catalyst showed very high conversion rates and could be recovered easily and reused many times without significant loss of its catalytic activity, which makes it useful and attractive for synthesis of these classes of compounds for economic availability and greater selectivity.

4 Experimental

4.1. Materials and instruments

The reagents and solvents used in this work were all purchased from Aldrich and Merck and used without further purification. FT-IR measurements were performed using KBr disc using a NICOLET impact 410 spectrometer. The known products were characterized by comparison of their spectral (^{1}H-NMR, and ^{13}C-NMR, Bruker NMR-Spectrometer FX 400Q) and physical data with those of authentic samples. Powder XRD was collected with a Rigaku-Dmax 2500 diffractometer with nickel filtered Cu Ka radiation (λ = 1.5418 A˚, 40 kV). TEM of the NPs were recorded using a Zeiss-EM10C TEM. Supermagnetic properties of catalyst was measured on Vibrating Sample Magnetometer (VSM) MDKFD.

4.1 General procedure for preparation of 2,3-dihydroquinazolin-4(1H)-ones

The Fe_3O_4-SA-PPCA (15 mg, 6.7×10^{-3} mmol) was added to a mixture of anthranilamide (1 mmol, 0.136 gr) and aldehyde (1 mmol) in ethanol as solvent. Then the mixture was stirred for the appropriate time under reflux condition. The progress was monitored by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature and the catalyst was separated by an external magnet. The products were extracted with ethanol, then EtOH was evaporated under reduced pressure to afford the essentially pure products. In some cases, the product was recrystalized from ethanol for further purification.

4.2 General procedure for the synthesis of polyhydroquinolines

A mixture of dimedone (1 mmol), aldehyde (1mmol), ethyl acetoacetate (1 mmol), ammonium acetate (1.2 mmol) and Fe_3O_4-SA-PPCA as catalyst (10 mg, 4.3×10^{-3} mmol) in ethanol were stirred at 50 °C for an appropriate time. The progress of reaction was monitored by TLC. After completion of the reaction, the catalyst was separated by an external magnet and solvent was evaporated. The residue was extracted by ethyl acetate (3×10 mL) and the combined organic extract was washed with water (3×10 mL), organic layer was dried over anhydrous sodium sulfate and evaporated to dryness. A crude solid was obtained. The pure product was obtained through crystallization from ethanol.

4.3 Representative NMR Data

^{1}H NMR of 2-(2-hydroxy-4-methoxyphenyl)-2,3-dihydroquinazolin-4(1H)-one **3f**: Mp: 195-198; ^{1}H NMR (400 MHz, DMSO): δ = 3.65 (s, 3H), 5.96 (s,1H), 6.27-6.29 (m,1H), 6.38 (s,1H), 6.66-6.68 (m, 2H), 6.98 (s,1H), 7.13-7.15 (m, 1H), 7.21-7.23 (m, 1H), 7.57 (s, 1H), 7.68-7.69 (d, 1H), 9.35 (s, 1H) ppm.
^{1}H and ^{13}C NMR of 2-(4-ethoxyphenyl)-2,3-dihydroquinazolin-4(1H)-one **3g**: Mp: 171-173; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.45 (t, 3H), 4.06 (q, 2H), 5.75 (s, 1H), 5.80-5.85 (m, 1H), 6.66-6.68 (m, 1H), 6.90-6.95 (m, 3H), 7.26 (s,1H), 7.27-7.34 (m, 1H), 7.50-7.51 (m, 2H), 7.95 (s,1H); 13C NMR (100 MHz, $CDCl_3$): δ = 15.9, 64.7, 69.8, 115.6, 116, 116.7, 120.7, 129.7, 129.8, 131.5, 135, 135.1, 148.6, 166.9 ppm.
^{1}H and ^{13}C NMR of Ethyl 4-(4-ethoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate **4f**: Mp: 179-181; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (s, 3H), 1.07 (s, 3H), 1.20-1.21 (m, 3H), 1.37-1.38 (m, 3H), 2.15-2.38 (m, 7H), 3.96 (t, 2H), 4.06 (t, 2H), 4.99 (s, 1H), 5.80 (s, 1H), 6.73 (d, J = 6.4 Hz, 2H), 7.19 (d, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.4, 16.05, 20.3, 28.2, 30.6, 33,7, 36.8, 41,8, 51.9, 60.9, 64.3, 107.3, 113.1, 114.9, 130.1, 140.7, 144.7, 150.2, 158.3, 169, 198 ppm. Anal. Calcd. for $C_{23}H_{29}NO_4$:C, 72.04; H, 7.62; N, 3.65; Found: C, 72.13; H, 6.31; N, 3.74.

Acknowledgements

This work was supported by the research facilities of Ilam University, Ilam, Iran.

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Graphical Abstract

Synthesis, characterization, and application of Fe_3O_4-SA-PPCA as a novel nanomagnetic reusable catalyst for the efficient synthesis of 2,3-dihydroquinazolin-4(1H)-ones and polyhydroquinolines

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Nano magnetic Fe_3O_4-PPCA prepared by one pot co-precipitation of iron oxide with PPCA and used as catalyst for the preparation of DHQs and PHQs.