Received: 10 May 2017 | Revised: 27 June 2017 | Accepted: 29 June 2017

DOI: 10.1002/aoc.3999

FULL PAPER

WILEY Applied Organometallic Chemistry

Sulfamic acid immobilized on amino-functionalized magnetic nanoparticles: A new and active magnetically recoverable catalyst for the synthesis of N-heterocyclic compounds

Lotfi Shiri | Hojatollah Narimani | Mosstafa Kazemi

Department of Chemistry, Faculty of Basic Sciences, Ilam University, PO Box 69315-516, Ilam, Iran

Correspondence
Lotfi Shiri, Department of Chemistry, Faculty of Basic Sciences, Ilam University, PO Box 69315-516, Ilam, Iran.
Email: lshiri47@gmail.com

Sulfamic acid immobilized on amino-functionalized magnetic nanoparticles (MNPs/DETA-SA) was successfully fabricated and characterized using various techniques. Diameters of approximately 15 nm for the MNPs/DETA-SA were observed from scanning electron microscopy images. The as-fabricated nanocomposite was applied as an efficient and magnetically reusable catalyst for the synthesis of 2,3-dihydroquinazoline-4(1*H*)-one and polyhydroquinoline derivatives. All products were obtained in good to excellent yields. Recovery tests confirm that the catalyst can be readily recovered using an external magnet and reused many times without significant loss of its catalytic activity.

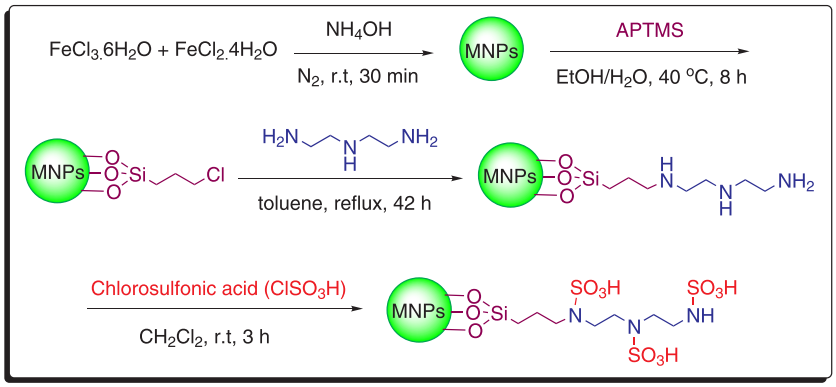
KEYWORDS
2,3-dihydroquinazoline-4(1*H*)-one, magnetically reusable catalyst, MNPs/DETA-SA, polyhydroquinolines

The development of new and efficient nanomaterials as catalyst supports is a real challenge in modern research in catalysis. The immobilization of homogeneous catalysts on supporting materials (such as inorganic silica, organic polymers and other metalliferous oxides) for incorporating the advantages of both heterogeneous and homogeneous catalysis has received much attention as an efficient strategy in catalysis research.[1] In recent times, much regard has been paid to the fabrication and use of magnetic nanoparticles (MNPs) because of a broad range of possible applications.[2] In fact, magnetically separable catalysts are a well-favoured and fascinating strategy for bridging the divide between heterogeneous and homogenous catalysis.[3] The marked advantages of MNPs are easy preparation, large readily available surface area, low toxicity, low cost and operational simplicity.[4] The simple separation of MNP-supported catalysts from products or reaction mixture using an external magnet is the most notable advantage of MNPs.[5] According to these advantages, MNPs can be considered as a promising alternative to other catalyst supports (such as porous/mesoporous catalyst supports).[6]

Catalysis in aqueous media or under solvent-free conditions has recently received special attention in both academic and industrial research.[7]

2,3-Dihydroquinazolin-4(1*H*)-one-based compounds continue to attract significant attention in biosynthesis because of their valuable pharmacological and biological activities.[8,9] They have a vast range of pharmacological and biological activities, such as antitumour, anticancer, analgesic, diuretic and herbicidal activities.[10–12] The general method applicable for the preparation of 2,3-dihydroquinazolin-4(1*H*)-ones is the condensation reaction of 2-aminobenzamide with aldehydes or ketones in the presence of acidic catalysts.[13] In recent times, a range of catalysts for the synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones have been reported in the literature.[14–16]

Catalysis of synthetic reactions by acids is always a fascinating research target in organic synthesis. Since



SCHEME 1 General route for the synthesis of MNPs/DETA-SA

the acids used are often liquid and expensive, their separation from reaction media is the most important concern of organic chemists.[17] Therefore, the design and fabrication of strong solid acids and their application as catalyst in organic reactions is of interest for future organic synthesis, in particular from the green synthetic chemistry point of view.[18,19] The immobilization of acidic functional groups on MNPs can be considered as an ideal and fascinating solution to overcome this drawback, because the catalyst can be readily separated from reaction media using an external magnet. In this paper, we report sulfamic acid immobilized on amino-functionalized magnetic nanoparticles (MNPs/DETA-SA) as a new, efficient and recyclable catalyst for the synthesis of 2,3-dihydroquinazolin-4(1*H*)-one derivatives.

1 | RESULTS AND DISCUSSION

1.1 | Catalyst preparation

The details of the strategy applied for the preparation of sulfamic acid loaded on amino-functionalized MNPs are presented in Scheme 1. The MNPs were prepared by a chemical co-precipitation procedure[5] and covered with 3-chloropropyltrimethoxysilane (CPTMS) by covalent bonds.[1] The reaction of the supported CPTMS with diethylenetriamine (DETA) in toluene under reflux conditions for 42 h produced DETA-functionalized MNPs (MNPs/DETA).[5] Ultimately, the reaction of MNPs/DETA with chlorosulfonic acid in CH_2Cl_2 at room temperature led to MNPs/DETA-SA.

1.2 | Catalyst characterization

The prepared nanosolid catalyst was characterized using Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), vibrating sample magnetometry (VSM), X-ray diffraction (XRD) and thermogravimetric analysis (TGA).

The FT-IR spectra of MNPs, MNPs/CPTMS, MNPs/DETA and MNPs/DETA-SA are displayed in Figure 1. The FT-IR spectrum of MNPs exhibits a stretching vibration at 3401 cm^{-1} which incorporates the contributions from both symmetric and asymmetric modes of the O—H bonds which are attached to the surface of iron atoms (Figure 1a). The presence of MNPs is shown by a strong absorption band at around 570 cm^{-1}, which is attributed to the Fe—O bond of MNPs. The anchoring of CPTMS on MNPs is confirmed by C—H stretching vibrations that appear at 2854 –2922 cm^{-1} (Figure 1b). Also the absorption band at around at 996 cm^{-1} is attributed to Si—O stretching vibration. As shown in Figure 1(c), the functionalization with DETA replacing Cl is confirmed by N—H stretching vibrations that appear at

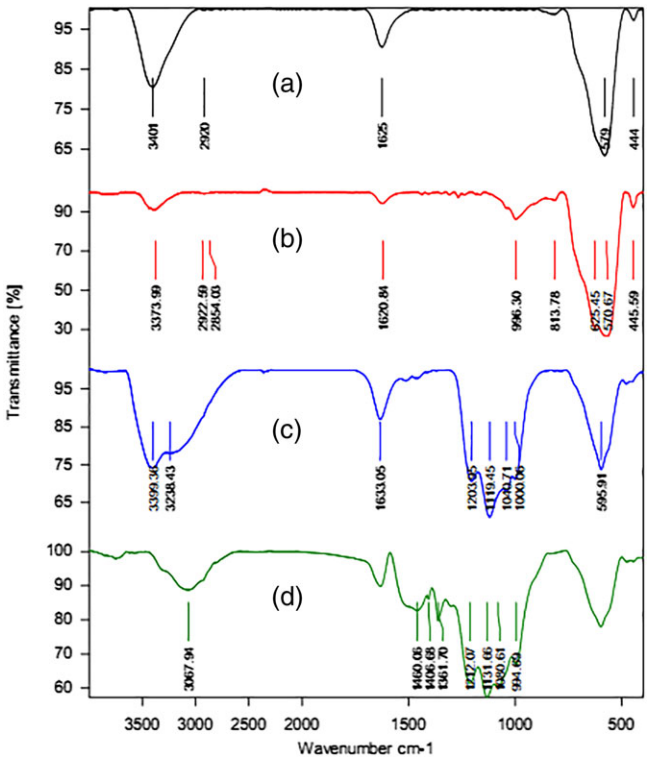


FIGURE 1 FT-IR spectra of MNPs (a), MNPs/CPTMS (b). MNPs/DETA (c) and MNPs/DETA-SA (d)

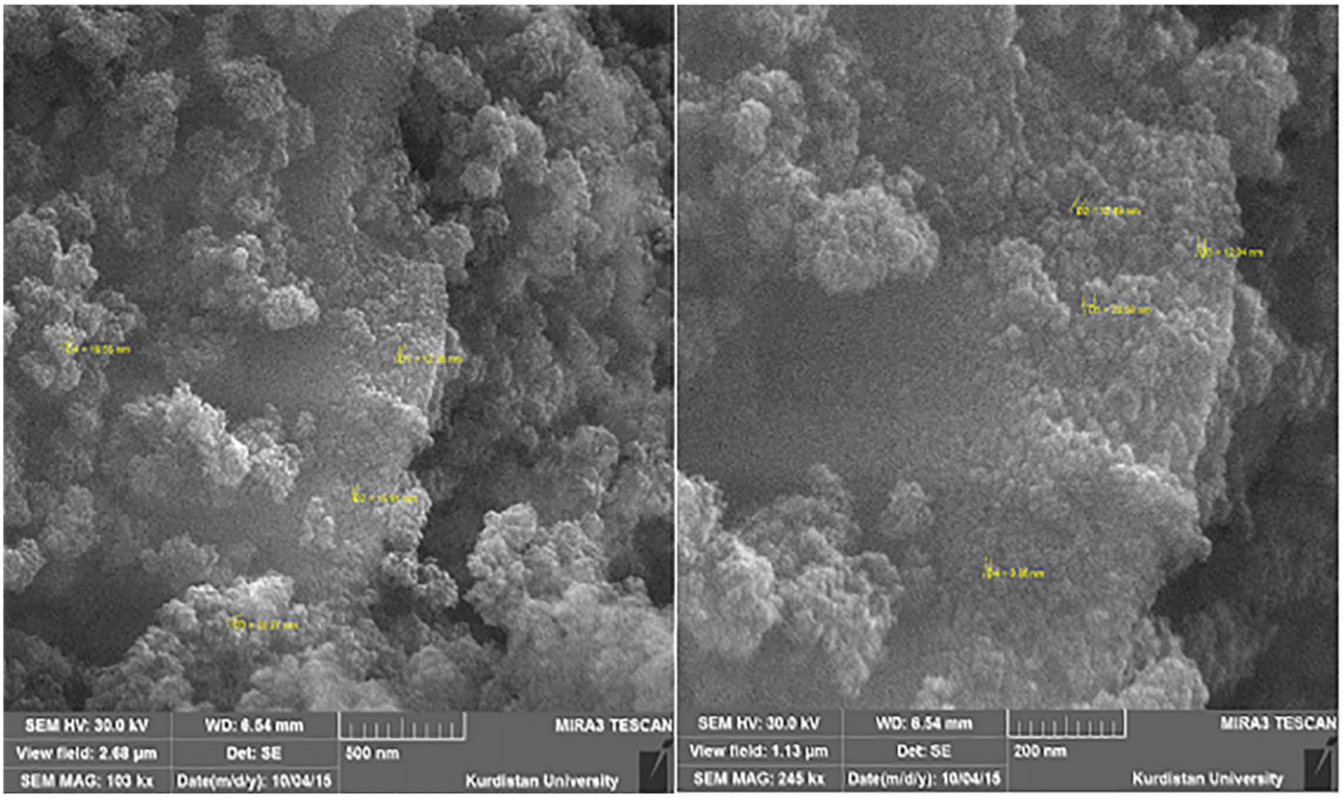


FIGURE 2 SEM images of MNPs/DETA-SA

3399 cm^{-1}. Reaction of MNPs/DETA with chlorosufonic acid produces MNPs/DETA-SA (Figure 1d), in which the presence of SO_3H moiety is evidenced with bands at 1080, 1131 and 1212 cm^{-1}. All of those bands reveal that the surface of MNPs is successfully modified with sulfamic acid.

The morphology and size of the nanocatalyst were evaluated using SEM (Figure 2). The SEM images show that the MNPs/DETA-SA nanoparticles are approximately spherical in shape and tend to agglomerate into larger aggregates. According to Figure 2, the average diameter of the MNPs/DETA-SA nanoparticles is about 15 nm.

The magnetic properties of MNPs and MNPs/DETA-SA were characterized using VSM at ambient temperature. The room temperature magnetization curves of MNPs and MNPs/DETA-SA are shown in Figure 3. The magnetic measurement shows that the MNPs and MNPs/DETA-SA have saturated

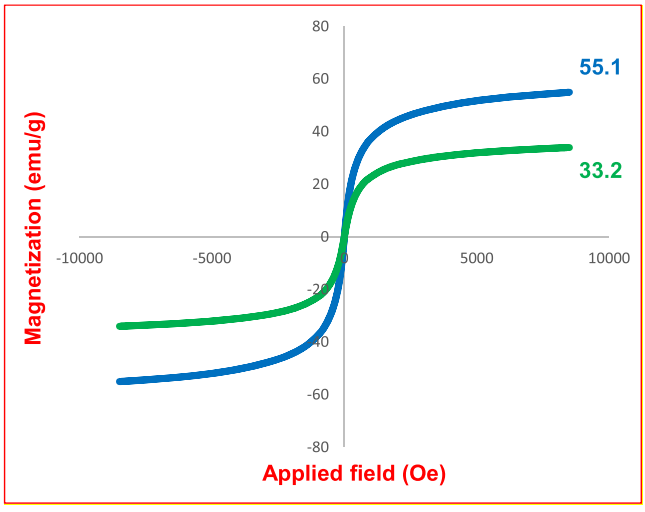


FIGURE 3 Magnetization curves for MNPs (blue) and MNPs/DETA-SA (green) at room temperature

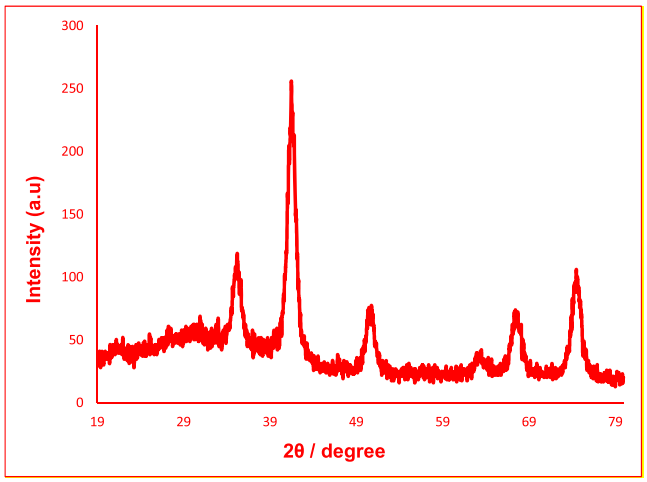


FIGURE 4 XRD pattern of MNPs/DETA-SA

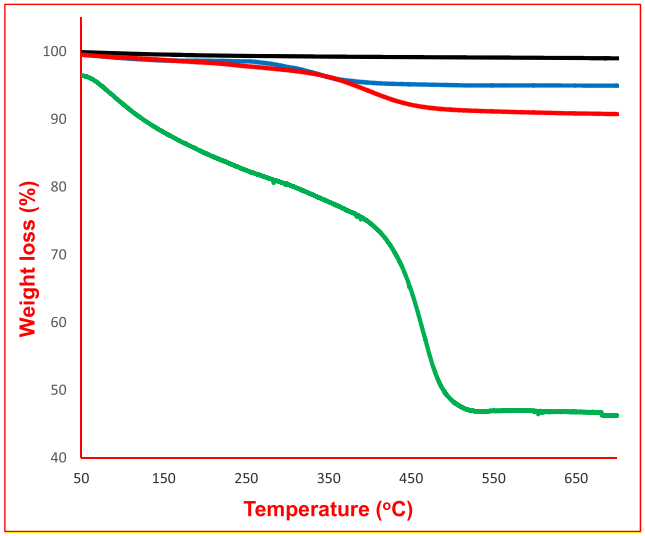
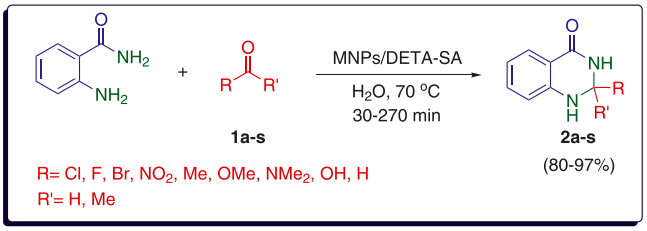


FIGURE 5 TGA curves of bare MNPs (black), MNPs/CPTMS (blue), MNPs/DETA (red) and MNPs/DETA-SA (green)

magnetization values of 55.1 and 33.2 emu g^{-1}, respectively. The decrease of the saturation magnetization can be related to the presence of sulfamic acid groups on the surface of the MNP supports.

In order to investigate the crystal structure of the obtained nanocatalyst (MNPs/DETA-SA), XRD analysis was performed, and the resultant pattern of the as-prepared sample is shown in Figure 4. As can be seen,

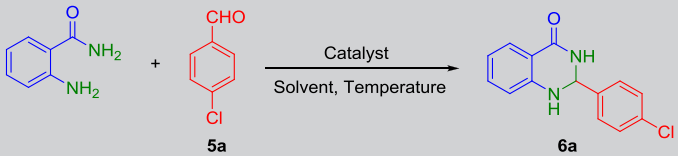


SCHEME 2 MNPs/DETA-SA-catalysed cyclocondensation of anthranilamide with aldehydes/ketones

MNPs/DETA-SA shows several characteristic peaks at 2θ values of 35.2°, 41.3°, 50.5°, 63.2°, 67.4° and 74.5°, in good agreement with the standard XRD pattern of MNPs reported in the literature.[11]

One indication of bond formation between the MNPs and the catalyst can be inferred from TGA. Figure 5 shows the TGA curves for bare MNPs, MNPs/CPTMS, MNPs/DETA and MNPs/DETA-SA. The TGA curves of all samples show a small amount of weight loss below 200 °C, due to desorption of physically adsorbed solvents and surface hydroxyl groups. Organic groups have been reported to desorb at temperatures above 260 °C. The TGA curves of MNPS/CPTMS and MNPS/DETA show mass losses of 5 and 9%, respectively. For MNPs/DETA-SA, there is a well-defined mass loss of 27% between 370 and 520 °C which is related to the breakdown of the DETA-SA moieties. As a result of this

TABLE 1 Optimization of reaction conditions[a]



Entry	Amount of catalyst (mg)	Solvent (temp., °C)	Time (min)	Yield (%)[b]
1	3	H_2O (70)	200	85
2	5	H_2O (70)	105	88
3	10	H_2O (70)	85	93
4	15	H_2O (70)	65	**97**
5	20	H_2O (70)	65	96
6	15	CH_3CN (reflux)	100	91
7	15	EtOH (reflux)	160	89
8	15	THF (reflux)	230	87
9	15	PhMe (reflux)	150	94
10	15	H_2O (60)	90	89
11	15	H_2O (80)	65	95
12	—	H_2O (70)	120	Trace

[a]Reaction conditions: anthranilamide (1.05 mmol) and 4-chlorobenzaldehyde (1 mmol) in the presence of catalyst and solvent (2 ml).

[b]Isolated yield.

TABLE 2 MNPs/DETA-SA-catalysed synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones at 90 °C under solvent-free conditions

Entry	R	R′	Product	Time (min)	Yield(%)[a]	M.p. (°C)
1	4-ClC_6H_5	H	**2a**	65	97	199–201[20]
2	4-$OMeC_6H_5$	H	**2b**	60	95	184–185[20]
3	4-MeC_6H_5	H	**2c**	50	93	223–224[20]
4	4-FC_6H_5	H	**2d**	30	92	197–199[20]
5	4-$NO_2C_6H_5$	H	**2e**	110	88	200–202[20]
6	4-BrC_6H_5	H	**2f**	55	97	201–203[20]
7	4-OHC_6H_5	H	**2 g**	70	91	265–267[13]
8	4-$(Me_2)NC_6H_5$	H	**2 h**	70	96	208–209[20]
9	C_6H_5	H	**2i**	40	94	218–220[20]
10	3-OHC_6H_5	H	**2j**	90	87	230–232[21]
11	3-$NO_2C_6H_5$	H	**2 k**	135	92	193–194[20]
12	3-BrC_6H_5	H	**2 l**	80	86	185–187[20]
13	3-ClC_6H_5	H	**2 m**	90	94	190–192[20]
14	2-$NO_2C_6H_5$	H	**2n**	160	84	190–191[20]
15	2-BrC_6H_5	H	**2o**	115	85	173–174[20]
16	2-$OMeC_6H_5$	H	**2p**	80	91	175–176[20]
17	3,4-$(OMe)_2C_6H_5CHO$	H	**2q**	55	90	209–212[20]
18	Cyclohexanone	—	**2r**	185	83	218–222[20]
19	Ph	Me	**2 s**	270	80	222–224[20]

[a]Isolated yield.

TABLE 3 Optimization of reaction conditions[a]

Entry	Catalyst (mg)	Solvent	Temperature (°C)	Time (min)	Yield (%)[b]
1	5	Solvent-free	90	85	86
2	10	Solvent-free	90	60	89
3	15	Solvent-free	90	35	93
4	20	Solvent-free	90	20	**97**
5	25	Solvent-free	90	20	97
6	30	Solvent-free	90	20	96
7	20	CH_3CN	Reflux	155	79
8	20	THF	Reflux	180	87
9	20	Acetone	Reflux	230	50
10	20	H_2O	Reflux	200	84
11	20	EtOH	Reflux	145	91
12	20	H_2O–EtOH (1:1)	80	160	83
13	20	Solvent-free	70	45	91
14	20	Solvent-free	80	30	94
15	20	Solvent-free	100	20	96
15	—	Solvent-free	90	120	Trace

[a]Reaction conditions: aldehyde (1 mmol), dimedone (1 mmol), ethyl acetoacetate (1 mmol) and ammonium acetate (1.2 mmol).

[b]Isolated yield.

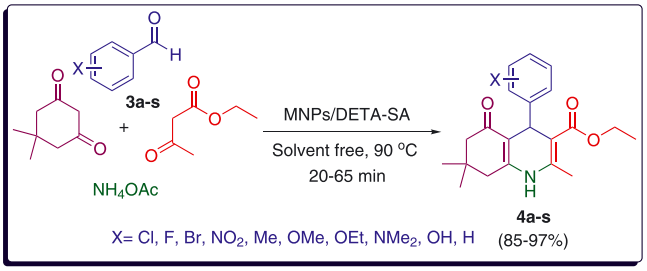
analysis, the grafting of DETA and SA groups on the MNPs is verified.

The loading of sulfamic acid on the surface of the nanocomposite was determined by back titration analysis. The data obtained by back titration show that the amount of sulfamic acid loaded is 1.1 mmol g^{-1}.

1.3 | Catalytic studies

1.3.1 | 2,3-Dihydroquinazolin-4(1*H*)-ones

After characterization of the catalyst, the activity of MNPs/DETA-SA in the one-pot synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones was studied. For this purpose, the reaction of 4-chlorobenzaldehyde and anthranilamide was chosen as a simple model reaction to investigate the possibility of the strategy and optimize the reaction conditions. To evaluate the effect of catalyst loading, systematic studies were carried out in the presence of different amounts of the catalyst (3, 5, 10, 15, 20 mg) in water, affording 2,3-dihydroquinazolin-4(1*H*)-ones in 85, 88, 93, 97 and 97% isolated yields, respectively (Table 1, entries 1–5). As evident from Table 1, the best yield is found in the presence of just 15 mg of MNPs/DETA-SA, and the use of higher amounts of catalyst (20 mg) does not improve the result to an appreciable extent (Table 1, entry 5). Next, under the optimal catalyst amount, the effect of several solvents (such as CH_3CN, EtOH, tetrahydrofuran (THF) and toluene) at reflux temperature was studied (Table 1, entries 4 and 6–9). The best results were obtained in water as solvent. Then, the effect of temperature (60 and 80 °C), under the optimal reaction conditions, on the model reaction was studied, but the obtained results were not satisfactory (Table 1, entries 10 and 11). Finally, the model reaction was conducted in the absence of the catalyst, but only a trace amount of product was observed on TLC plate after 120 min (Table 1, entry 12). Therefore, 15 mg of MNPs/DETA-



SCHEME 3 MNPs/DETA-SA-catalysed synthesis of polyhydroquinolines

TABLE 4 MNPs/DETA-SA-catalysed synthesis of polyhydroquinolines at 90 °C under solvent-free conditions

Entry	Aldehyde	Product	Time (min)	Yield (%)[a]	M.p. (°C)
1	4-ClC_6H_5CHO	**4a**	20	97	236–238[28]
2	4-$OMeC_6H_5CHO$	**4b**	30	93	248–250[28]
3	4-MeC_6H_5CHO	**4c**	25	95	251–253[28]
4	4-FC_6H_5CHO	**4d**	20	94	180–182[28]
5	4-$NO_2C_6H_5CHO$	**4e**	35	90	239–241[29]
6	4-BrC_6H_5CHO	**4f**	40	95	247–251[28]
7	4-OHC_6H_5CHO	**4 g**	35	90	230–233[28]
8	4-$(me)_2NC_6H_5CHO$	**4 h**	25	97	232–234[29]
9	4-$OEtC_6H_5CHO$	**4i**	35	95	178–180[28]
10	C_6H_5CHO	**4j**	50	96	216–218[28]
11	3-ClC_6H_5CHO	**4 k**	30	94	232–234[30]
12	3-$NO_2C_6H_5CHO$	**4 l**	40	90	175–177[29]
13	3-BrC_6H_5CHO	**4 m**	35	91	233–235[29]
14	3-OHC_6H_5CHO	**4n**	65	85	217–219[29]
15	2-$NO_2C_6H_5CHO$	**4o**	55	87	209–211[29]
16	2-ClC_6H_5CHO	**4p**	35	92	207–209[29]
17	2-$OMeC_6H_5CHO$	**4q**	30	93	255–257[31]
18	3,4-$(OMe)_2C_6H_5CHO$	**4r**	25	94	203–205[28]
19	2,4-$(cl)_2C_6H_5CHO$	**4 s**	45	89	240–243[32]

[a]Isolated yield.

TABLE 5 Comparison of activity of various catalysts in the synthesis of products **2a** (entries 1–5) and **4a** (entries 6–10)

Entry	Catalyst	Condition	Time (min)	Yield (%)	Ref.
1	$KAl(SO_4)_2.E_{12}H_2O$	EtOH, reflux	300	80	[33]
2	Glycerosulfonic acid	Glycerol, 80 °C	360	97	[34]
3	Silica sulfuric acid	H_2O,80 °C	180	81	[35]
4	SBNPSA	EtOH, reflux	150	87	[36]
5	MNPs/DETA-SA	H_2O, 70 °C	65	97	This work
6	$PdCl_2$	THF, reflux	240	87	[24]
7	$K_7[PW_{11}CoO_{40}]$	CH_3CN, reflux	30	80	[37]
8	Cu-SPATB/Fe_3O_4	Peg-400, 80 °C	65	98	[28]
9	$[TBA]_2[W_6O_{19}]$	Solvent-free, 110 °C	20	95	[38]
10	MNPs/DETA-SA	Solvent-free, 90 °C	20	97	This work

SA in water at 70 °C were selected as the optimal reaction conditions (Table 1, entry 4).

After the optimization of the reaction conditions, various aldehydes were reacted under the optimum conditions and the corresponding 2,3-dihydroquinazolin-4(1*H*)-one compounds were obtained in good to excellent yields (Scheme 2). The results of these studies are summarized in Table 2. A variety of benzaldehydes bearing electron-donating and electron-withdrawing substituents were successfully employed to prepare the corresponding 2,3-dihydroquinazolin-4(1*H*)-one derivatives in excellent yields. The experimental procedure is very simple and convenient, and has the ability to tolerate a variety of other functional groups (such as hydroxyl, halide, nitro, alkyl and alkoxyl) under the reaction conditions.

1.3.2 | Polyhydroquinolines

Polyhydroquinoline scaffolds are key structural motifs in a diverse range of natural products and pharmaceutically active molecules.[22] Polyhydroquinoline and related derivatives have received great attention in recent times due to their diverse biological activities such as bronchodilator vasodilator, antitumour, anti-atherosclerotic, antidiabetic and geroprotective activities.[23–26] Furthermore, polyhydroquinolines can act as reducing agents for the straight reductive amination of aldehydes and ketones.[27] Considering these valuable applications, we decided to study the catalytic activity of MNPs/DETA-SA in the synthesis of polyhydroquinolines. In this respect, the reaction of 4-chlorobenzaldehyde with dimedone, ammonium acetate and ethylacetoacetate was chosen as a simple model reaction to investigate the possibility of the strategy and optimize the reaction conditions (Table 3). In the synthesis of product **4a**, the best results were obtained when 20 mg of MNPs/DETA-SA was used at 90 °C under solvent-free conditions (Table 3, entry 4).

Based on the observations discussed above, we conducted the same reactions using dimedone, ethylacetoacatate, ammonium acetate and variety of substituted aldehydes under the optimized conditions (Scheme 3). As expected, satisfactory results were obtained, and the results are summarized in Table 4. A wide range of aldehydes was successfully reacted with dimedone, ethylacetoacatate and ammonium acetate to give the polyhydroquinoline derivatives. It is noteworthy that the products were obtained in high yields.

To show the superiority of the present strategy in comparison with other reported procedures, we summarize results for the synthesis of products **2a** and **4a** in Table 5. It is clear that reaction time and product yield are better than those for other protocols reported in the literature. Also the new catalyst is comparable in terms of price, stability, non-toxicity and ease of separation.

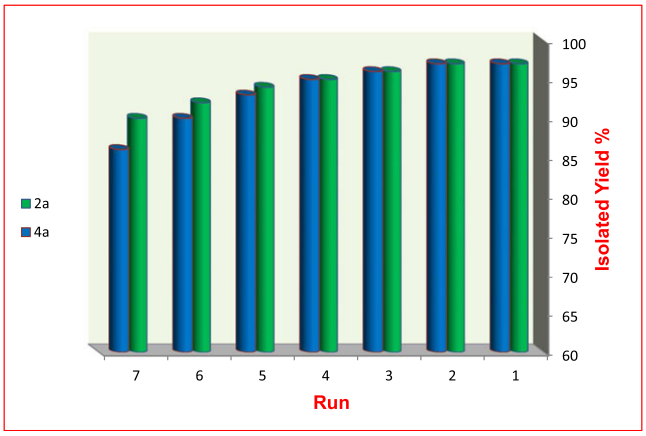


FIGURE 6 Reusability of MNPs/DETA-SA in the synthesis of products **2a** and **4a**

1.4 | Reusability of MNPs/DETA-SA

The recovery and reusability of catalysts is an important aspect in catalytic processes. In this respect, the reusability of MNPs/DETA-SA was investigated in the synthesis of products **2a** and **4a**. In these experiments, after completion of the reaction, the catalyst was easily and rapidly separated from the product using an external magnet. The separated 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 reaction run. As shown in Figure 6, the catalyst can be recycled for up to seven 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 using an appropriate external magnet, which minimizes the loss of catalyst during separation.

2 | CONCLUSIONS

In summary, the preparation of sulfamic acid supported on functionalized MNPs as a versatile and active magnetically recoverable catalyst was described. The prepared acidic nanocatalyst was characterized using FT-IR spectroscopy, TGA, XRD, SEM and VSM. As-fabricated nanosolid showed high catalytic activity in the synthesis of 2,3-dihydroquinazoline-4(1*H*)-one and polyhydroquinoline derivatives. All products were obtained in good to excellent yields. From the environmental point of view, the performance of reactions in water and under solvent-free conditions is a fascinating aspect of this protocol. Reusability studies revealed that the acidic catalyst can be reused many times without significant loss in catalytic efficiency.

3 | EXPERIMENTAL

3.1 | Materials

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. FT-IR spectra of samples were recorded in KBr discs using a Nicolet Impact 410 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker DRX-400 spectrometer at 400 and 100 MHz, respectively. Nanostructures were characterized using a Philips X'pert powder X-ray diffractometer (Co Kα radiation = 0.154056 nm), at a scanning speed of 2° min^{-1} from 10° to 80°. SEM was performed with an FEI Quanta 200 SEM operated at a 20 kV accelerating voltage. TGA curves were recorded using a PL-STA 1500 device manufactured by Thermal Sciences. The magnetic measurements were carried out using VSM (BHV-55, Riken, Japan) at room temperature.

3.2 | Preparation of Fe_3O_4 MNPs

A mixture of $FeCl_3{\cdot}6H_2O$ (5.838 g, 0.0216 mol) and $FeCl_2{\cdot}4H_2O$ (2.147 g, 0.0108 mol) was dissolved in 100 ml of deionized water in a three-necked flask (250 ml) under nitrogen atmosphere. After that, 10 ml of NH_3 was added into 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 black precipitate formed was isolated by magnetic decantation, washed with double-distilled water until neutrality, and further washed twice with ethanol and dried at room temperature.[5]

3.3 | Preparation of MNPs/CPTMS

The obtained MNPs (1.5 g) were dispersed in 250 ml of ethanol–water (1:1 *v*/v) by sonication for 30 min, and then CPTMS (2.5 ml) was added to the reaction mixture. The reaction mixture was stirred using mechanical stirring under nitrogen atmosphere at 40 °C for 8 h. The nanoparticles were then redispersed in ethanol by sonication five times and separated through magnetic decantation. The nanoparticle product (MNPs/CPTMS) was dried at room temperature.[1]

3.4 | Preparation of MNPs/DETA

MNPs/CPTMS (1.5 g) was dispersed in toluene (50 ml) using an ultrasonic bath for 10 min. DETA (2 ml) was added and stirred at 100 °C for 30 h under nitrogen atmosphere. Then, the prepared functionalized MNPs were separated by magnetic decantation and washed three times with ethanol to remove the unattached substrates. The resulting product was dried at room temperature.[5]

3.5 | Preparation of MNPs/DETA-SA

MNPs/DETA (0.5 g) was dispersed in CH_2Cl_2 (10 ml) using an ultrasonic bath for 20 min. Then, chlorosulfonic acid (1.5 ml) was added dropwise over a period of 20 min, and the mixture was stirred for 3 h at room temperature. Functionalized MNPs (MNPs/DETA-SA) were separated by

magnetic decantation, washed four times with dry CH_2Cl_2 and two times with EtOH, and dried at room temperature.

3.6 | General procedure for synthesis of 2,3-Dihydroquinazolin-4(1*H*)-ones

A mixture of anthranilamide (1.05 mmol, 142 mg), aldehyde or ketone and MNPs/DETA-SA (15 mg) in water (2 ml) was stirred at 70 °C. Reaction progress was monitored by TLC (acetone–*n*-hexane, 2:8). After the time specified in Table 2, reaction mass was allowed to cool to room temperature. CH_2Cl_2 (3 × 5 ml) was added to the reaction mixture and the catalyst was separated using an external magnet. CH_2Cl_2 was evaporated under reduced pressure to afford the crude products. The obtained crude products were further recrystallized from ethanol to afford the pure 2,3-dihydroquinazolin-4(1*H*)-ones (80–97%).

3.7 | General procedure for synthesis of Polyhydroquinolines

A mixture of aldehyde (1 mmol), dimedon (1 mmol), ethylacetoacetate (1 mmol), ammonium acetate (1.2 mmol) and MNPs/DETA-SA (20 mg) was stirred at 90 °C under solvent-free conditions. Reaction progress was monitored by TLC (acetone–*n*-hexane, 3:7). After 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 polyhydroquinoline derivatives were obtained in excellent yields (85–97%).

All the products reported here are known compounds and the spectroscopic data matched literature values.

ACKNOWLEDGEMENT

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

ORCID

Mosstafa Kazemi http://orcid.org/0000-0003-4676-720X

REFERENCES

[1] A. Rostami, Y. Navasi, D. Moradi, A. Ghorbani-Choghamarani, *Catal. Commun.* **2014**, *43*, 16.

[2] L. Shiri, A. Ghorbani-Choghamarani, M. Kazemi, *Aust. J. Chem.* **2016**, *69*, 585.

[3] M. Sheykhan, L. Mamani, A. Ebrahimi, A. Heydari, *J. Mol. Catal. A* **2011**, *335*, 253.

[4] A. Ghorbani-Choghamarani, M. Norouzi, *J. Mol. Catal. A* **2014**, *395*, 172.

[5] L. Shiri, A. Ghorbani-Choghamarani, M. Kazemi, *Monatsh. Chem.* **2017**, *148*, 1131.

[6] A. Ying, L. Wang, F. Qiu, H. Hu, J. Yang, *C. R. Chim.* **2015**, *18*, 223.

[7] S. Bonollo, D. Lanari, L. Vaccaro, *Eur. J. Org. Chem.* **2011**, *14*, 2587.

[8] A. Davoodnia, S. Allameh, A. R. Fakhari, *Chin. Chem. Lett.* **2010**, *21*, 550.

[9] A. Ghorbani-Choghamarani, G. Azadi, *RSC Adv.* **2015**, *5*, 9752.

[10] A. Ghorbani-Choghamarani, P. Zamani, *J. Iran. Chem. Soc.* **2012**, *9*, 607.

[11] L. Shiri, M. Kazemi, *Res. Chem. Intermed.* **2017**, *43*, 4813.

[12] J. Safari, S. Gandomi-Ravandi, *C. R. Chim.* **2013**, *16*, 1158.

[13] A. Rostami, A. Tavakoli, *Chin. Chem. Lett.* **2011**, *22*, 1317.

[14] B.-H. Chen, J.-T. Li, G.-F. Chen, *Ultrason. Sonochem.* **2015**, *23*, 59.

[15] M. Abdollahi, A. E. Shabani, *J. Iran. Chem. Soc.* **2014**, *11*, 351.

[16] M. Ghashang, S. S. Mansoor, K. Aswin, *Res. Chem. Intermed.* **2013**, *6168*, 695.

[17] N. Koukabi, E. Kolvari, M. A. Zolfigol, A. Khazaei, B. S. Shaghasemi, B. Fasahatib, *Adv. Synth. Catal.* **2012**, *354*, 2001.

[18] S. Rostamnia, A. Nuri, H. Xin, A. Pourjavadi, S. H. Hosseini, *Tetrahedron Lett.* **2013**, *54*, 3344.

[19] J. Safari, Z. Zarnega, *J. Mol. Catal. A* **2013**, *379*, 269.

[20] L. Shiri, A. Ghorbani-Choghamarani, M. Kazemi, *Appl. Organomet. Chem.* **2017**, *31*, e3596.

[21] A. Ghorbani-Choghamarani, H. Goudarziafshar, P. Zamani, *Chin. Chem. Lett.* **2011**, *22*, 1207.

[22] J. L. Donelson, R. A. Gibbs, S. K. De, *J. Mol. Catal. A* **2006**, *256*, 309.

[23] A. Heydari, S. Khaksar, M. Tajbakhsh, H. R. Bijanzadeh, J. Fluorine, *Chem* **2009**, *130*, 609.

[24] M. Saha, A. K. Pal, *Tetrahedron Lett.* **2011**, *52*, 4872.

[25] K. A. Undale, T. S. Shaikh, D. S. Gaikwad, D. M. Pore, *C. R. Chim.* **2011**, *14*, 511.

[26] K. Sirisha, G. Achaiah, V. M. Reddy, *Arch. Pharm.* **2010**, *343*, 342.

[27] M. A. Zolfigol, M. Safaiee, *Synlett* **2004**, 827.

[28] A. Ghorbani-Choghamarani, B. Tahmasbi, P. Moradi, N. Havasi, *Appl. Organomet. Chem.* **2016**, *30*, 619.

[29] M. Tajbakhsh, H. Alinezhad, M. Norouzi, S. Baghery, M. Akbari, *J. Mol. Liq.* **2013**, *177*, 44.

[30] M. Nasr-Esfahani, J. Hoseini, M. Montazerozohori, R. Mehrabi, H. Nasrabadi, *J. Mol. Catal. A Chem.* **2014**, *382*, 99.

[31] M. Abedini, F. Shirini, M. Mousapour, *Res. Chem. Intermed.* **2016**, *42*, 2303.

[32] M. Mosaddegh, A. Hassankhani, *Arab. J. Chem.* **2012**, *5*, 315.

[33] M. Dabiri, P. Salehi, S. Otokesh, M. Baghbanzadeh, G. Kozehgary, A. A. Mohammadi, *Tetrahedron Lett.* **2005**, *46*, 6123.

[34] M. Hajjami, F. Bakhti, E. Ghiasbeygi, *Croat. Chem. Acta* **2015**, *88*, 197.

[35] S. Bonollo, D. Lanari, L. Vaccaro, *Eur. J. Org. Chem.* **2011**, *14*, 2587.

[36] K. Niknam, N. Jafarpour, E. Niknam, *Chin. Chem. Lett.* **2011**, *22*, 69.

[37] M. M. Heravi, K. Bakhtiari, N. M. Javadi, F. F. Bamoharram, M. Saeedi, *J. Mol. Catal. A Chem.* **2007**, *264*, 50.

[38] A. Davoodnia, M. Khashi, N. Tavakoli-Hoseini, *Chin. J. Catal.* **2013**, *34*, 1173.

How to cite this article: Shiri L, Narimani H, Kazemi M. Sulfamic acid immobilized on amino-functionalized magnetic nanoparticles: A new and active magnetically recoverable catalyst for the synthesis of N-heterocyclic compounds. *Appl Organometal Chem*. 2017;e3999. https://doi.org/10.1002/aoc.3999