

An efficient and one-pot green synthesis of 2-arylsubstituted benzimidazoles catalyzed by nano-Fe₃O₄@silica sulfuric acid as a recyclable nanomagnetic solid acid catalyst

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Abstract

An efficient and green protocol for the synthesis of 2-arylsubstituted benzimidazoles via a condensation reaction of aromatic aldehydes and 1,2-phenylenediamine using nano-Fe₃O₄@SiO₂-SO₃H as a solid acid catalyst in ethanol under reflux conditions has been described. The reactions are completed in short times, and the corresponding benzimidazoles are produced with high yields. The present procedure has several advantages, including short reaction times, high yields of products, facile experiment, simple work-up, eco-friendly reaction conditions, and reusability of the catalyst. The catalyst could simply be separated and recovered by an external magnet and reused several times without appreciable loss of catalytic activity.

Keywords: Fe₃O₄@SiO₂-SO₃H; benzimidazoles; 1,2-phenylenediamine; aromatic aldehydes; green synthesis.

Introduction

Benzimidazoles are an important class of nitrogen-containing heterocyclic compounds that have been reported to possess a wide range of biological and pharmaceutical activities such as antibacterial, anticancers, antifungals, and antivirals [1-3]. Benzimidazole derivatives exhibit significant activity against several viruses such as antimicrobial agents [4], potential antitumor agents [5], influenza [6], herpes (HSV-1) [7] and HIV [8,9]. They also act as topoisomerase inhibitors [10], smooth muscle cell proliferation inhibitors [11], angiotensin II inhibitors [12], and selective neuropeptide YY1

receptor antagonists [13] and have much more importance in organic synthesis [14].

While many strategies are available for the benzimidazoles synthesis, most of these procedures involve the condensation of 1,2-phenylenediamines with carboxylic acids or their derivatives and carbonyl compounds, specially aldehydes [15]. Due to the availability of a wide variety of aldehydes, the condensation of 1,2-phenylenediamine or its derivatives and aldehydes has been extensively used for the synthesis of 2-arylsubstituted benzimidazoles. Various oxidative and catalytic reagents such as FeCl₃.6H₂O

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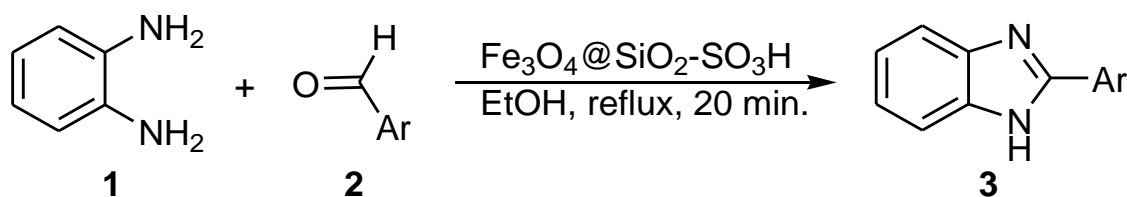
[16], Oxone [17], ionic liquids [18], Yb(OTf)₃ [19], Sc(OTf)₃ [20], In(OTf)₃ [21], I₂/KI/K₂CO₃ [22], KHSO₄ [23], sulfamic acid [24], *p*-TsOH [25], CAN [26], PEG [27], DMP [28], NH₄VO₃ [29], TBAF [30], Co(OH)₂ and CoO [31], SBSA [32], SSA [33], CuO-NP/SiO₂ [34], nano-solid acids [35], TiCl₃OTf [36], VOSO₄ [37], Fe₃O₄@SiO₂/collagen [38], NiEuFe₂O₄ [39] and Fe₃O₄ MNPs [40] have been used in this synthesis. These catalysts are useful to facilitate the synthesis of the desired products, however, most of reported procedures suffer from one or more limitations such as low product yields, prolonged reaction times, tedious work-up procedures, drastic reaction conditions, the use of expensive reagents and toxic solvents, and lack of reusability of the catalyst. Thus, effective, simple and mild methods for the synthesis of 2-arylsubstituted benzimidazoles are still needed.

In recent decades, interest in nanoscale materials for various applications has considerably increased. Nanoparticles have an exceptionally large surface area to volume ratio which is responsible for their widespread advantageous use in catalysis [41]. Acid functionalized heterogeneous nanomaterials have emerged as one of the most useful heterogeneous catalysts due to their numerous applications in organic synthesis [42-50].

Recently, magnetic nanoparticles (MNPs) have been extensively employed for the preparation of heterogeneous catalysts. Because of their paramagnetic properties, the

catalysts can be easily separated by magnetic decantation and reused in many cases without any loss in their activity and selectivity [51-54]. The sulfuric acid functionalized silica-coated magnetite nanoparticles, Fe₃O₄@SiO₂-SO₃H, as a recyclable powerful solid acid catalyst was used in a wide range of organic reactions such as Knoevenagel condensation [55], synthesis of 1,8-dioxooctahydroxanthenes [56], synthesis of indazolo[2,1-*b*]phthalazine-trione and pyrazolo[1,2-*b*]phthalazine-dione derivatives [57], synthesis of amidoalkyl naphthols [58], synthesis of 3,4-dihydropyrimidin-ones/thiones [59], synthesis of indole derivatives [60], synthesis of fused pyrimidines [61], synthesis of spiro [chromeno[2,3-*c*]pyrazole-4,3'-indoline]-diones [62], oxidation of sulfides into sulfoxides [63], protection and deprotection of hydroxyl groups [63], synthesis of substituted quinolines [64], synthesis of pyrazolopyridines [65], and synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones [66,67].

Because of the importance of benzimidazoles as above-mentioned [1-14] and the catalytic strength of Fe₃O₄@SiO₂-SO₃H in chemical transformations [56-68], we now wish describe a new procedure for the synthesis of 2-arylsubstituted benzimidazoles through the condensation of aryl aldehydes with 1,2-phenylenediamine in the presence of catalytic amounts of Fe₃O₄@silica sulfuric acid in EtOH under reflux conditions (Scheme 1).



Scheme 1. Synthesis of 2-arylsubstituted benzimidazoles catalyzed by Fe₃O₄@SiO₂-SO₃H

Experimental

General

All of the commercially available chemicals were purchased from Merck, Fluka and Aldrich and used with no further purification. Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$ were prepared pursuant to the reported procedure [57]. Products were characterized by comparing their physical data, FT-IR, ^1H - and ^{13}C -NMR with authentic samples. Melting points were obtained in open capillary tubes and measured with an electrothermal 9200 apparatus. FT-IR spectra were recorded on KBr Pellets on a Shimadzu IRPresting-21 spectrophotometer in the range of 4000–400 cm^{-1} . NMR spectra were recorded in CDCl_3 on a Bruker Advanced DPX 400 MHz spectrometer using TMS as an internal reference. The reactions were monitored by TLC on silica gel polygram SILG/UV 254 plates. X-ray diffraction (XRD) pattern of catalyst was taken on a Philips X-ray diffractometer Model PW 1840. Scanning electron microscopy (SEM) and energy dispersive X-ray (EDAX) analyses were carried out using a Philips XL30 instrument.

Preparation of magnetic Fe_3O_4 nanoparticles

Superparamagnetic nanoparticles (MNPs) were prepared *via* improved chemical co-precipitation method [57]. According to this method, $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ (6.37 g, 32 mmol) and $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ (15.15 g, 56 mmol) were dissolved in 640 mL deionized water under nitrogen at 80 °C for 1 h, and added to an ammonium hydroxide 25% solution (80 mL) with vigorous mechanical stirring. After the color of bulk solution turned to black, the reaction was carried out for 1 h in N_2 atmosphere. The precipitated particles were washed five times with hot water and separated by magnetic

decantation. Finally, magnetic NPs were dried under vacuum at 70 °C.

Preparation of silica-coated magnetite nanoparticles, $\text{Fe}_3\text{O}_4@\text{SiO}_2$

The synthesized Fe_3O_4 nanoparticles (2 g) were diluted by 450 mL ethanol and 120 mL water. The suspension was dispersed under ultrasonic irradiation for 25 min. Then, 10 mL ammonium hydroxide 25% was added to the suspension under a constant nitrogen flow at room temperature. Next, 2 mL tetraethyl orthosilicate (TEOS) was slowly added to this dispersion under continuous mechanical stirring, and after stirring for 12 h, silica was formed on the surface of magnetite nanoparticles through hydrolysis and condensation of TEOS. The coated nanoparticles were finally separated from the liquid by a magnetic decantation and washed several times with deionized water. Then dried under vacuum at 60 °C overnight [57].

Preparation of silica sulfuric acid-coated magnetite nanoparticles, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$

At first, $\text{Fe}_3\text{O}_4@\text{silica}$ (2.5 g) was poured in a flask containing 75 mL CH_2Cl_2 and dispersed by ultrasonic irradiation for 10 min. Then, chlorosulfonic acid (1.75 g, ca. 1 mL, 15 mmol) diluted in 20 mL CH_2Cl_2 was added drop-wise for a period of 30 min at room temperature. The produced HCl was evolved immediately from the reaction mixture by an inert gas such as nitrogen. After completion of the addition of chlorosulfonic acid, the mixture was shaken for 90 min, while the residual HCl was eliminated. Finally, the resulted $\text{Fe}_3\text{O}_4@\text{silica}$ sulfuric acid was separated from the reaction mixture by an external magnet, washed several times with dried CH_2Cl_2 and dried under vacuum at 60 °C [57].

pH-analysis of the catalyst

To determine pH of the catalyst, Fe₃O₄@SiO₂-SO₃H (0.1 g) was added to a 25 mL of NaCl aqueous solution (1 M, pH = 5.9), and was stirred for 24 h. The pH of the solution was decreased to 2.10, which is equal to a loading of 1.98 mmol SO₃H/g of acidic catalyst.

Typical procedure for the synthesis of 2-arylsubstituted benzimidazoles

To a solution of 1,2-phenylenediamine (1 mmol) and aromatic aldehydes (1 mmol) in EtOH (5 mL), Fe₃O₄@SSA (0.04 g) was added and the mixture was stirred under reflux conditions for 20 minutes (Table 2). Upon the completion of the reaction, as indicated by TLC (EtOAc:*n*-hexane 7:3), the nanocatalyst was removed in the presence of an external magnet. Then, the resulting mixture was cooled down on ice, filtered off and recrystallized from the ethanol to afford the corresponding products in high yields. All of the obtained benzimidazoles are known and identified by comparing their physical and spectroscopic data (IR, NMR) with those of authentic samples [16-40].

Selected Characterization data

2-Phenyl-1H-benzimidazole (3a).

M.p. = 290-291 °C; IR (KBr): $\bar{\nu}$ (cm⁻¹) 3047, 2962, 1462, 1408, 1276, 968, 740, 702; ¹HNMR (CDCl₃, 400 MHz): δ (ppm) 6.73-6.84 (m, 2H), 6.89-7.01 (m, 3H), 7.42-7.53 (m, 2H), 7.87-7.98 (m, 2H), 12.81 (br s, 1H); ¹³CNMR (CDCl₃,

100 MHz): δ (ppm) 110.6, 119.9, 122.7, 123.1, 125.9, 126.6, 127.8, 128.8, 129.0, 129.2, 130.0, 130.1, 151.6.

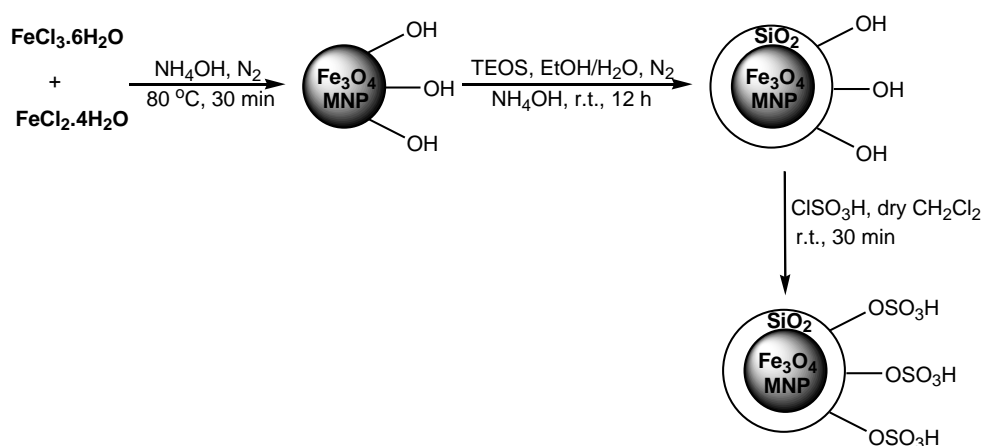
2-(4-Methylphenyl)-1H-benzimidazole (3i).

M.p. = 259-261 °C; IR (KBr): $\bar{\nu}$ (cm⁻¹) 3051, 2958, 1446, 1400, 1273, 964, 752; ¹HNMR (CDCl₃, 400 MHz): δ (ppm) 2.28 (s, 3H), 7.18-7.26 (m, 2H), 7.33-7.41 (m, 2H), 7.49-7.52 (m, 2H), 7.83-7.91 (m, 2H), 12.68 (br s, 1H); ¹³CNMR (CDCl₃, 100 MHz): δ (ppm) 23.5, 110.1, 118.9, 123.0, 123.4, 128.2, 128.9, 130.1, 142.1, 143.5, 151.8.

Results and discussion

In continuation of our studies on magnetic nanocatalysts [69-71], specially nano-Fe₃O₄ encapsulated silica sulfuric acid (Fe₃O₄@SiO₂-SO₃H, Fe₃O₄@SSA) [64-66], herein, we report an efficient and green procedure for the application of Fe₃O₄@SSA as a magnetically recoverable nanocatalyst in the condensation of aryl aldehydes with 1,2-phenylenediamine to produce the desired 2-arylsubstituted benzimidazoles.

In the first step, magnetic nano-Fe₃O₄ was synthesized by coprecipitation from ferrous and ferric ion solutions in basic media. After that, to improve the chemical stability, surface modification was performed by depositing silica on its surface, which was then served as support for SO₃H group as shown in Scheme 2.



Scheme 2. Preparation of Fe₃O₄@SiO₂-SO₃H

The catalyst has been characterized by various techniques, including FT-IR, SEM, EDAX and XRD. The FT-IR spectrum of Fe₃O₄@SiO₂-SO₃H is clearly different from those of Fe₃O₄ and Fe₃O₄@SiO₂ (Fig. 1). The FT-IR analysis of the Fe₃O₄@silica sulfuric acid exhibits a basic characteristic peak at approximately 582 cm⁻¹, which was attributed to the stretching vibrations of the (Fe–O) bond and the bands at 1068, 823 and 439 cm⁻¹ belong to (Si–O)

asymmetric stretching, symmetric stretching and bending vibrations, respectively. The presence of sulfonic acid functional group was confirmed by 1222 and 1141 cm⁻¹ bands that were covered by a stronger absorption of Si–O bond at 1068 cm⁻¹. In addition, the Si–OH group peak at 995 cm⁻¹ was disappeared for Fe₃O₄@silica sulfuric acid. The spectrum also shows a broad OH stretching absorption around 3100–3700 cm⁻¹.

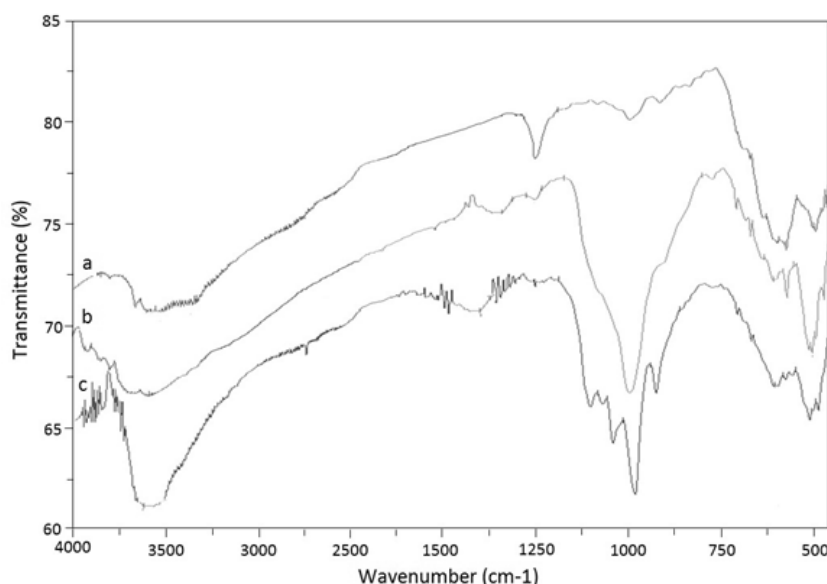


Figure 1. FT-IR spectra of the Fe₃O₄ (a), Fe₃O₄@SiO₂ (b) and Fe₃O₄@SiO₂-SO₃H nanoparticles

The SEM image of Fe₃O₄@SiO₂-SO₃H shows that MNPs have a spherical morphology with nanometer

sized particles less than 50 nm (Figure 2).

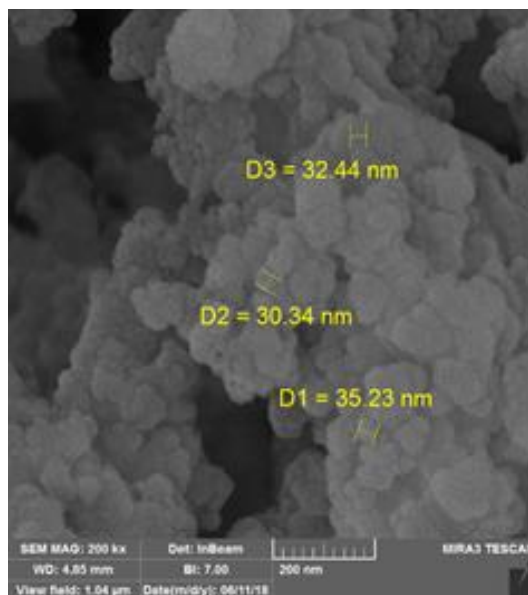


Figure 2. SEM image of Fe₃O₄@SiO₂-SO₃H nanoparticles

The data from EDAX analysis are consistent with our expectations and confirm the presence of iron, oxygen,

silicon and sulfur elements in Fe₃O₄@SiO₂-SO₃H (Figure 3).

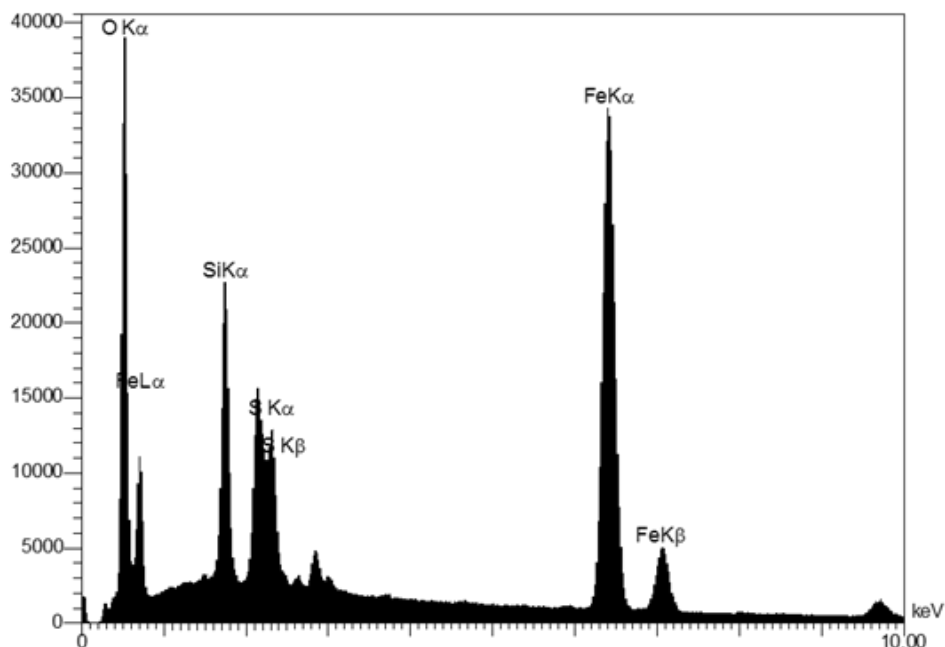


Figure 3. EDAX spectra of Fe₃O₄@SiO₂-SO₃H nanoparticles

The XRD spectrum of Fe₃O₄@SSA is shown in Figure 4. As seen in Figure 4, MNPs display six characteristic peaks at the 2θ values of 30.24, 35.62, 43.26,

53.56, 57.26 and 62.90 [63]. The position and relative intensities of all peaks suitably agree.

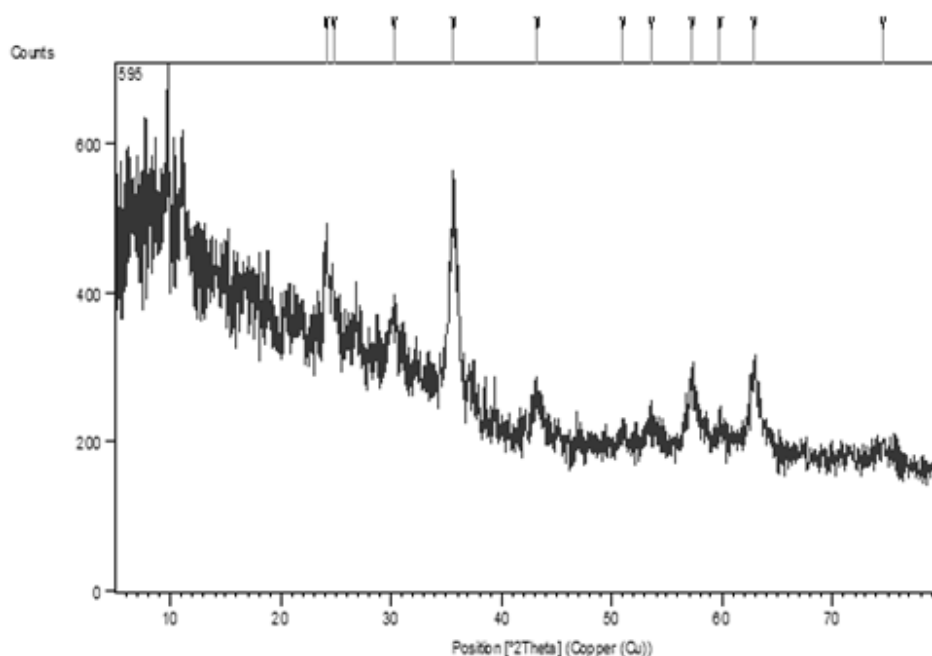


Figure 4. XRD pattern of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$ nanoparticles

After synthesis and characterization of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$, its role as a catalyst was evaluated for the synthesis of 2-arylsubstituted benzimidazoles. We initially investigated a model reaction between 1,2-phenylenediamine and

benzaldehyde in several solvents. From the results provided in Table 1, it was clear that $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$ performed well to give the desired product in EtOH under reflux conditions within 20 min in 91% yield (Table 1, Entry 9).

Table 1. Influence of solvent and $\text{Fe}_3\text{O}_4@\text{SSA}$ loading on the synthesis of **3a**

Entry	Amount of catalyst (g)	Solvent	Condition	Time (min)	Yield (%)
1	0	EtOH	reflux	90	trace
2	0.05	MeCN	reflux	90	75
3	0.05	CH_2Cl_2	reflux	90	trace
4	0.05	CHCl_3	reflux	90	50
5	0.05	EtOAc	reflux	90	trace
6	0.05	H_2O	reflux	90	trace
7	0.05	EtOH	reflux	20	90
8	0.05	EtOH	r.t.	90	67
9	0.04	EtOH	reflux	20	91
10	0.03	EtOH	reflux	20	81

To explore the generality of this procedure, the reaction of 1,2-phenylenediamine with various aldehydes was examined (Table 2). Aldehydes with both electron-donating

and electron-withdrawing groups were reacted with 1,2-phenylenediamine at the optimized reaction conditions and the corresponding products in good to excellent yields were obtained.

Table 2. Synthesis of 2-arylsubstituted benzimidazoles using Fe₃O₄@SSA in EtOH

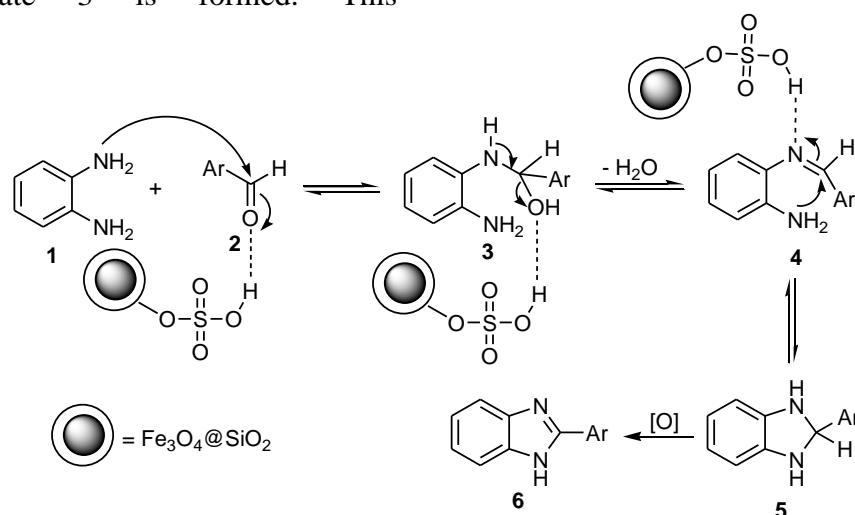
Entry	Ar	Product ^a	Yield (%) ^b	m.p. (°C)	
				Found	Reported
1	C ₆ H ₅	3a	91	290-291	292-294 [35]
2	2-ClC ₆ H ₄	3b	85	230-232	230-232 [36]
3	3-ClC ₆ H ₄	3c	90	194-196	-
4	4-ClC ₆ H ₄	3d	84	279-280	281-282 [38]
5	4-BrC ₆ H ₄	3e	91	279-281	268-270 [35]
6	2-O ₂ NC ₆ H ₄	3f	85	263-265	260 [38]
7	3-O ₂ NC ₆ H ₄	3g	87	185-187	186-188 [38]
8	4-O ₂ NC ₆ H ₄	3h	85	307-309	315-317 [38]
9	4-MeC ₆ H ₄	3i	92	259-261	260-262 [35]
10	4-OMeC ₆ H ₄	3j	90	222-224	222-224 [36]
11	4-Me ₂ NC ₆ H ₄	3k	83	275-277	276-278 [37]
12	2,5-OMeC ₆ H ₃	3l	80	212-214	-

a) All of the products were characterized by IR, ¹H and ¹³C NMR, and their spectra were compared with those of the authentic samples.

b) Isolated yields

Although the detailed mechanism of the reaction is not clear, a plausible rationalization may be advanced to explain the product formation (Scheme 3). Presumably, the aryl aldehyde (2) is first activated by $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$, then 1,2-phenylenediamine (1) attack to the activated carbonyl group, and the intermediate 3 is formed. This

intermediate loses water in an elimination reaction in the presence of catalyst to imine 4. Intramolecular nucleophilic attack and then proton transfer cause ring closure and give compound 5. Finally, aromatization of intermediate 5 under air produces the corresponding 2-aryl benzimidazole (6).



Scheme 3. The proposed mechanism for the synthesis of benzimidazole derivatives

The possibility of recycling the catalyst was tested in the condensation of benzaldehyde with 1,2-phenylenediamine using $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-SO}_3\text{H}$ in ethanol under reflux conditions. Upon completion, the reaction mixture was filtered and the

catalyst was separated by an external magnet and was washed with warm EtOH. The recovered catalyst could be reused at least 4 times without any considerable loss in its catalytic activity (Figure 5).

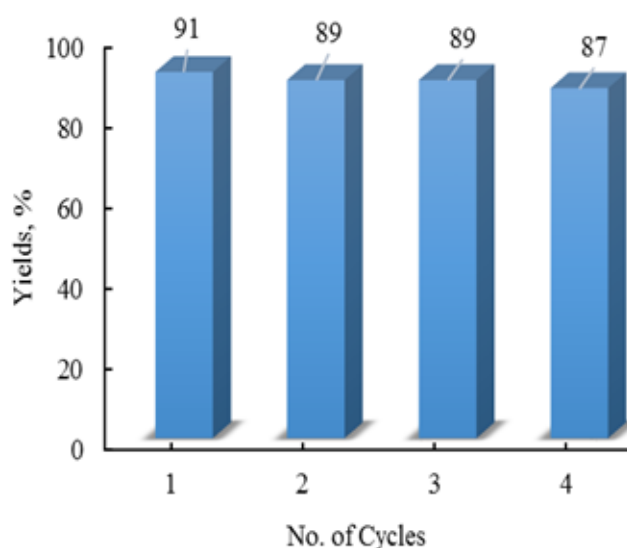


Figure 5. The reusability of catalyst

Table 3 compares the catalytic efficiencies of Fe₃O₄@SiO₂-SO₃H and some of the reported catalysts in the condensation of 1,2-phenylenediamine with benzaldehyde to produce 2-phenyl-

1H-benzoimidazole (**3a**). These data indicated that our procedure is advantageous due to high yield, short reaction time and mild conditions.

Table 3. Efficiency comparison of various catalysts in the synthesis of **3a**

Entry	Catalyst (amount)	Solvent/condition	Time (min)	Yield (%)	Ref.
1	<i>p</i> -TsOH (20 mol%)	DMF/80 °C	10	85	[25]
2	CoO (10 mol%)	EtOH/reflux	300	93	[31]
3	Co(OH) ₂ (10 mol%)	EtOH/reflux	240	96	[31]
4	SSA (0.1 g)	EtOH/reflux	20	91	[33]
5	CuO-NP/SiO ₂ (10 mol%)	MeOH/r.t.	240	93	[34]
6	Nano-ZnO (10 mol%)	EtOH/reflux	100	88	[35]
7	Nano-γ-alumina (10 mol%)	EtOH/reflux	90	88	[35]
8	Nano-ZMS-5 (10 mol%)	EtOH/reflux	85	90	[35]
9	Nano-crystalline SZ (10 mol%)	EtOH/reflux	45	92	[35]
10	TiCl ₃ OTf (10 mol%)	EtOH/r.t.	70	84	[36]
11	VOSO ₄ (3 mol%)	EtOH/r.t.	60	92	[37]
12	Fe ₃ O ₄ @SiO ₂ -SO ₃ H (0.04 g)	EtOH, reflux	20	91	This work

Conclusion

In conclusion, the present study described the synthesis of 2-arylsubstituted benzimidazoles using an efficient nanomagnetic catalyst, Fe₃O₄@SiO₂-SO₃H. This catalytic procedure offers several advantages, such as simple work-up, gentle reaction conditions, use of commercially available and inexpensive starting materials, recyclability and reusability of the catalyst, short time of reactions and high yield of products. Thus, we think that this procedure could be considered as a new and suitable addition to the existent methodologies in this area.

Acknowledgments

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