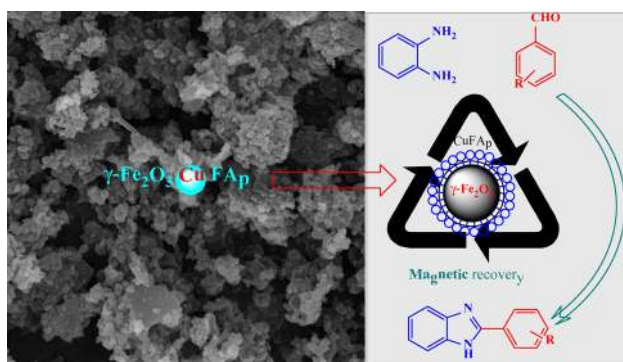CrossMark

ORIGINAL RESEARCH

Copper-incorporated fluorapatite encapsulated iron oxide nanocatalyst for synthesis of benzimidazoles

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Abstract γ-Fe$_2$O$_3$@CuFAp nanocatalyst was synthesized and characterized by several methods including XRD, SEM, TEM, ICP, and FT-IR analyses. The γ-Fe$_2$O$_3$@CuFAp has been used as an efficient recyclable magnetic catalyst for synthesis of benzimidazoles. The γ-Fe$_2$O$_3$@CuFAp was conveniently separated from the reaction mixture by an external magnet, and could be reused at least 12 times without any considerable change in catalytic activity.

Graphical abstract

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Introduction

Benzimidazole is an important structural moiety which is present in many natural and synthetic compounds with a variety of interesting biological activities [1], such as anticancer [2], antiarrhythmic [3], antihistaminic [4], antiulcerative [5], antihypertensives, antiviral, antitumor [1], antibacterial, antifungals [6], anti-inflammatory [7], anticonvulsant, antidiabetic properties [8], and antidepressant [9]. The first benzimidazole was described by Hobrecker in 1872, who obtained 2,5 (or 2,6)-dimethyl-benzimidazole by the reduction of 2-nitro-4-methylacetanilide [10]. Three years later, Ladenburg procured the identical compound by refluxing 3,4-diaminotoluene with acetic acid [11]. Various methodologies have been used for the synthesis of benzimidazole derivatives, which include conversion of esters using an aluminum reagent [12], the oxidative cyclodehydrogenation of Schiff bases, which is generated from *o*-phenylenediamine and aldehydes in the presence of several catalysts [13], such as cabalt(II) chloride hexahydrate [14], iodine [15], cetylpyridinium bromide [16], the condensation of *o*-aryldiamines and aldehyde in refluxing nitrobenzene [17], direct condensation of *o*-aryldiamines and carboxylic acids [18, 19] or their derivatives [20] in the presence of catalysts, such as polyphosphoric acid [21], ionic liquids [22], *p*-TsOH [23], SiO$_2$ as solid support [24], microwave irradiation using polyphosphoric acid [25], and intramolecular *N*-arylations of amidines mediated by potassium hydroxide [26]. Although these reported approaches are significant, but some of them have drawbacks like strict reaction conditions, prolonged reaction period, low yield, expensive catalysts, non-recoverability of the catalysts, use of toxic solvents, and co-occurrence of several side reactions. In this report, we have synthesized a magnetic copper-

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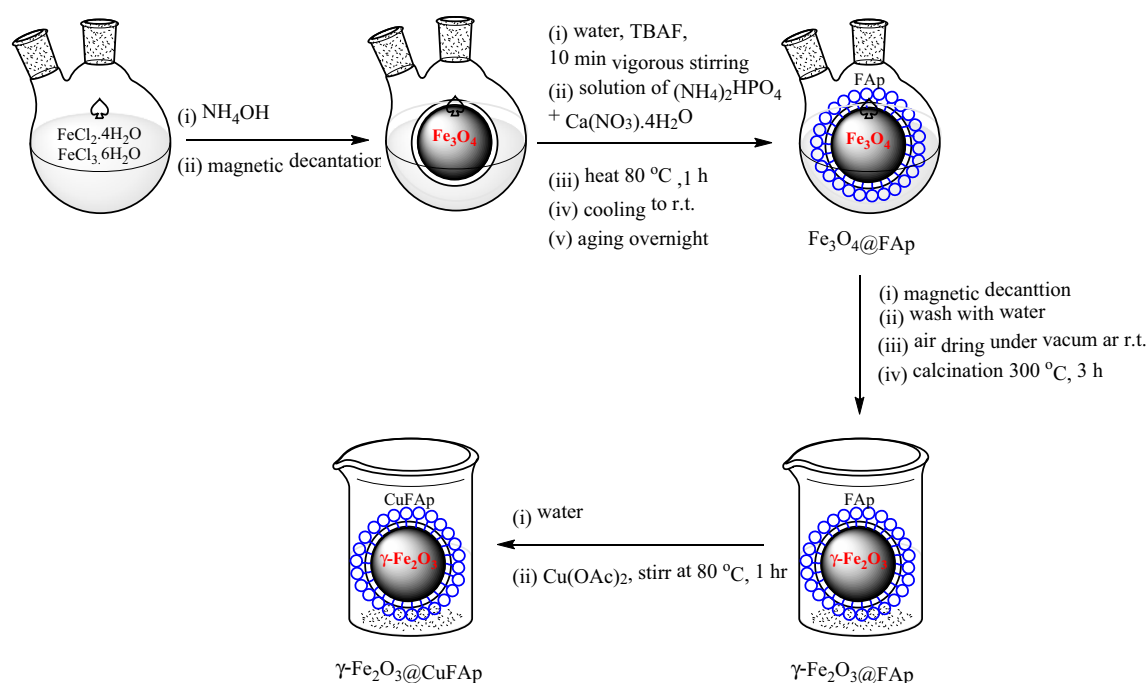
Scheme 1 Synthesis of γ-Fe$_2$O$_3$@CuFAp MNPs

incorporated fluorapatite (γ-Fe$_2$O$_3$@CuFAp) as higly efficient and green catalyst for the preparation of benzimidazoles derivatives.

Experimental part

Materials and reagents

FeCl$_2$·4H$_2$O, FeCl$_3$·6H$_2$O, ammonia solution (25%), Ca(NO$_3$)$_2$·4H$_2$O, (NH$_4$)$_2$HPO$_4$, *o*-phenyl diamine, Cu(OAc)$_2$, TBAF, benzaldehydes, and other organic compounds were purchased from commercial sources.

Physical measurements

Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes. ^{1}H NMR spectra were recorded on a 400 MHz Bruker DRX-400, DMSO-d_6 as solvent, and TMS as an internal standard. FT-IR spectra were determined on an α-Bruker spectrometer. XRD was carried out on a Philips Analytical PC-APD. The Cu contents of samples were determined by ICP-OES on a Varian 730-ES instrument.

Synthesis of nano-Fe$_3$O$_4$ MNPs

Fe$_3$O$_4$ nanoparticles were synthesized by reported chemical co-precipitation technique of ferric and ferrous ions in alkali solution [27–29]. FeCl$_2$·4H$_2$O (0.368 g) and FeCl$_3$·6H$_2$O (1.0 g) were dissolved in deionized water (30 mL) under Ar atmosphere at room temperature. A magnetic stirring bar was added to the flask, and then, an ammonia solution (25%, 10 mL) was added into the mixed Fe(III)/Fe(II) solution with constant stirring at room temperature to increase pH until 11. After 1 h stirring, the black precipitate of Fe$_3$O$_4$ was collected by external magnet and washed with hot water three times.

Synthesis of γ-Fe$_2$O$_3$@FAp MNPs

γ-Fe$_2$O$_3$@FAp nanoparticles were synthesized using reported procedure with minor modifications [17]. The prepared Fe$_3$O$_4$ nanoparticles (0.429 g, 1.85 mmol) were dissolved in 15 mL deionized water and *tetra*-butyl ammonium fluoride (TBAF) (0.78 g, 3 mmol) was added. The solution was stirred vigorously for 10 min at room temperature. A solution of (NH$_4$)$_2$HPO$_4$ (1.19 g, 9 mmol) and Ca(NO$_3$)$_2$·4H$_2$O (3.54 g, 15 mmol) in 30 mL deionized water was added dropwise over 30 min to the mixture
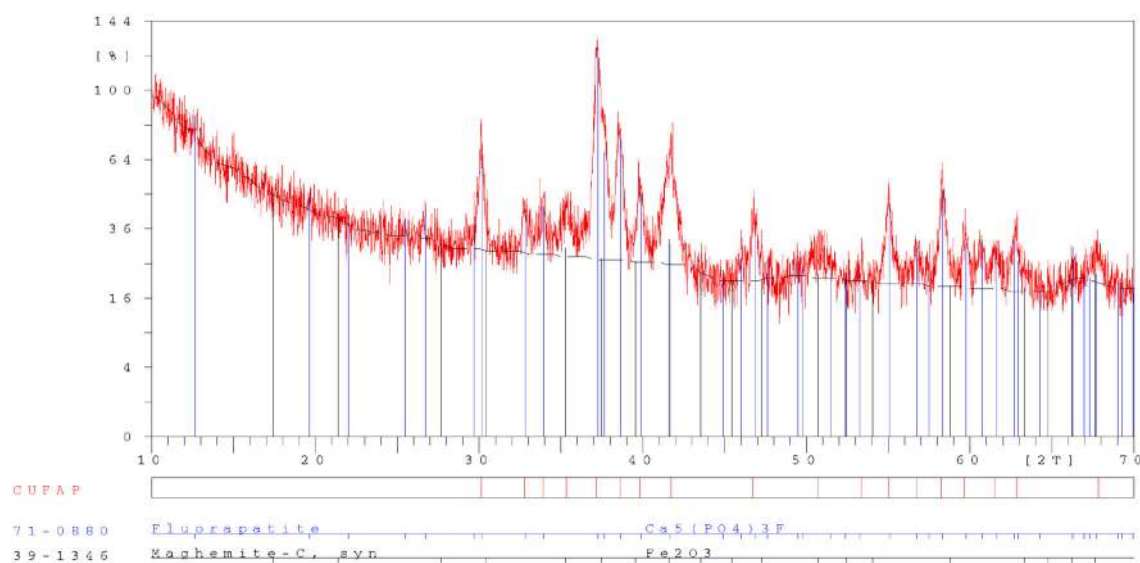
Fig. 1 XRD pattern of γ-Fe$_2$O$_3$@CuFAp NPs

Fig. 2 SEM image of γ-Fe$_2$O$_3$@CuFAp

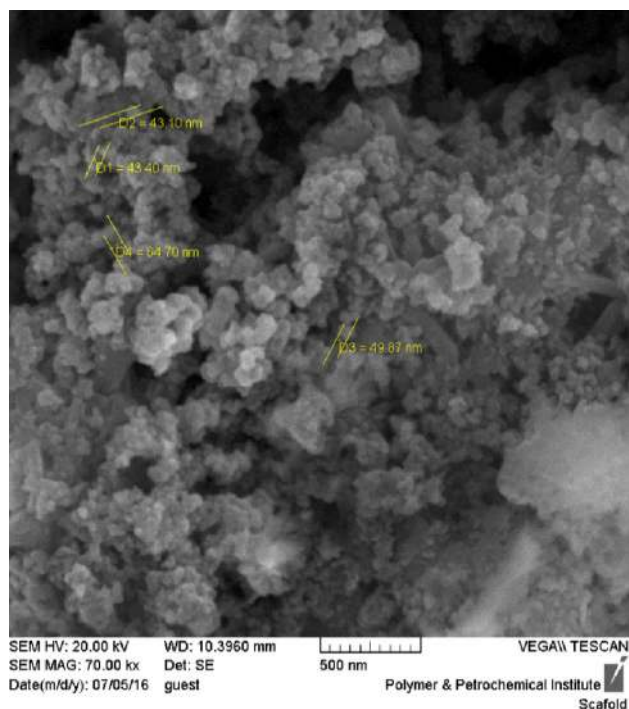**Fig. 3** TEM image of γ-Fe$_2$O$_3$@CuFAp

Fig. 4 FT-IR spectra of γ-Fe$_2$O$_3$@CuFAp

and heated at 80°C for 1 h. Subsequently, it cooled to room temperature and aged overnight. The solution was magnetic decanted and washed with hot deionized water (DW), three times. The product was air-dried and then kept in a furnace at 300°C for 3 h to give a dark-brown powder.
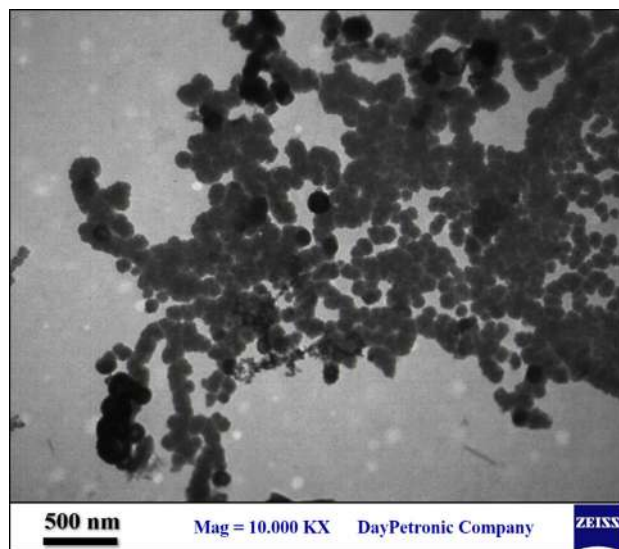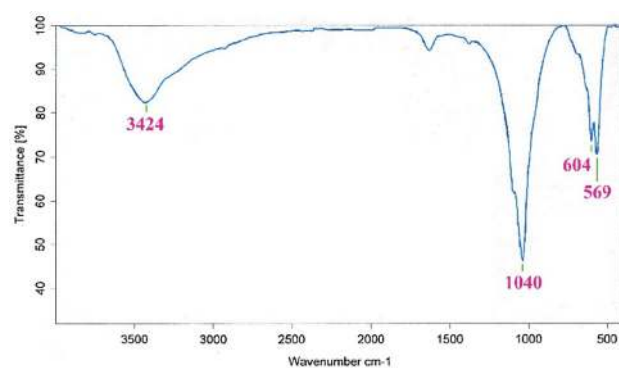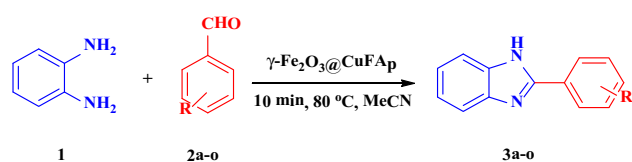
Scheme 2 Synthesis of benzimidazoles

Synthesis of γ-Fe₂O₃@CuFAp MNPs

As shown in Scheme 1, 500 mg γ-Fe₂O₃@FAp was stirred with 8 mmol Cu(NO₃)₂·4H₂O in 100 mL water at room temperature for a period of 2 h. The obtained slurry was magnetic decanted, washed with DW repeatedly, and dried at 100°C yielding γ-Fe₂O₃@CuFAp nanoparticles [30].

General procedure for the synthesis of benzimidazoles

To a mixture of an aldehyde (1 mmol) and 1,2-phenylenediamine (1.2 mmol) in acetonitrile (5 mL), γ-Fe₂O₃@CuFAp (0.04 g) was added. The mixture was stirred at 80°C, and the progress of reaction was monitored by TLC. After completion of the reaction, the catalyst was separated by an external magnet, washed with CH_2Cl_2, dried, and reused for a consecutive run under the same reaction conditions. To obtain the desired product, the

solvent was evaporated and the mixture was extracted with EtOAc (3 × 10 mL). The extract was concentrated, and the crude product was purified by column chromatography using ethyl acetate-*n*-hexane (2:8) as eluent to afford the desired product **3**.

2-Phenyl-1H-benzo[d]imidazole (Table 2, Entry 1)

m.p. 291–293 °C (lit.28, m.p. 292 °C); FT-IR (KBr): $\bar{v}$; 3408, 3043, 1611, 1590, 1465, 755, 706 cm^{-1}, ^{1}H NMR (DMSO-d₆, 400 MHz): δ 12.92 (s, 1H, NH), 8.55 (t, $J = 7.2$ Hz, 1H), 8.19 (d, $J = 8.0$ Hz, 2H), 7.68 (t, $J = 7.2$ Hz, 1H), 7.57–7.50 (m, 3H), 7.26–7.24 (m, 2H).

Results and discussion

Preparation and characterization of the catalyst

As described in the experimental section, Fe₃O₄ NPs were synthesized by a chemical co-precipitation technique of ferric and ferrous ions in alkali solution. Then, Fe₃O₄ NPs were coated with fluorapatite and was heated in the air at 100°C and then kept in the 300°C furnace for 3 h to give a reddish-brown powder γ-Fe₂O₃@FAp NPs. Structure of the catalyst was established by XRD, SEM, TEM, ICP, and FT-IR analyses.

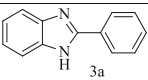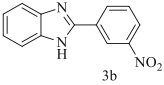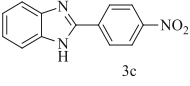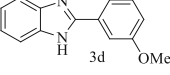**Table 1** Optimization of the synthesis of benzimidazole[a]
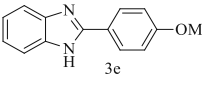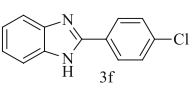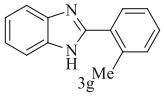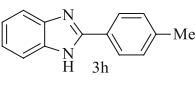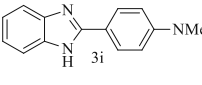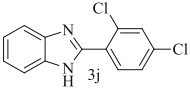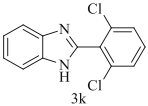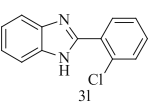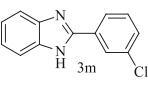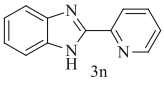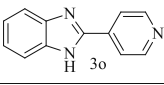
Entry	Catalyst (mg)	T (°C)	Solvent	Additive	Time	Yield[a] (%)
1	γ-Fe₂O₃@CuFAp (50)	80	Acetonitrile	–	8 min	92
2	γ-Fe₂O₃@CuFAp (40)	80	Acetonitrile	–	8 min	94
3	γ-Fe₂O₃@CuFAp (30)	80	Acetonitrile	–	15 min	85
4	γ-Fe₂O₃@CuFAp (20)	80	Acetonitrile	–	1 h	70
5	–	80	Acetonitrile	–	5 h	trace
6	γ-Fe₂O₃@CuFAp (40)	90	Acetonitrile	–	8 min	88
7	γ-Fe₂O₃@CuFAp (40)	70	Acetonitrile	–	8 min	80
8	γ-Fe₂O₃@CuFAp (40)	60	Acetonitrile	–	1 h	55
9	γ-Fe₂O₃@CuFAp (40)	80	H₂O	–	30 min	60
10	γ-Fe₂O₃@CuFAp (40)	80	Toluene	–	8 min	75
11	γ-Fe₂O₃@CuFAp (40)	80	DMF	–	8 min	80
12	γ-Fe₂O₃@CuFAp (40)	80	1,4-Dioxane	–	8 min	70
13	γ-Fe₂O₃@CuFAp (40)	80	AcOH	–	8 min	85
14	γ-Fe₂O₃@CuFAp (40)	80	Acetonitrile	AcOH (0.1 mL)	8 min	89
15	γ-Fe₂O₃@CuFAp (40)	80	Acetonitrile	NaOH (0.1 mL)	8 min	76
16	γ-Fe₂O₃@CuFAp (40)	80	Acetonitrile	NaCl	8 min	88
17	γ-Fe₂O₃@CuFAp (40)	80	Acetonitrile	TBAF	8 min	89
18	γ-Fe₂O₃@FAp (40)	80	Acetonitrile	–	5 h	40

[a] Reaction conditions: *o*-phenylenediamine (1.2 mmol), benzaldehyde (1.0 mmol)

[b] Yield of isolated product

Table 2 γ-Fe$_2$O$_3$@CuFAp catalyzed synthesis of benzimidazoles

Entry	Product	Time (min)	Yield %[a]	M.P (°C) Found	M.P (°C) Reported
1	3a	8	94	291- 293	292 [31]
2	3b	5	92	208- 210	205-206 [31]
3	3c	5	96	> 300	> 300 [31]
4	3d	10	90	212- 214	211-213 [32]
5	3e	10	92	226- 227	226-228 [32]
6	3f	7	95	298- 300	300-302 [31]
7	3g	10	88	210- 212	213-214 [33]
8	3h	10	92	261- 263	269 [31]
9	3i	10	89	228-230	229-230 [31]
10	3j	8	89	219- 221	217-219 [34]
11	3k	9	85	276- 277	275-276 [33]
12	3l	10	89	234- 235	233-234 [34]
13	3m	9	92	229- 231	232-233 [33]
14	3n	10	86	220- 222	220-223 [31]
15	3o	10	89	215- 216	217-218 [35]

Reaction condition: *o*-phenylenediamine (1.2 mmol) to arylaldehyde (1.0 mmol) and γ-Fe$_2$O$_3$@-CuFAp (0.04 g) in 5 ml acetonitrile stirred in 80°C

[a]Isolated products

Characterization of catalyst

XRD analysis

Figure 1 shows the XRD pattern of γ-Fe$_2$O$_3$@CuFAp NPs. The standard XRD data for γ-Fe$_2$O$_3$ and FAp are also depicted in the figure for comparison. Diffraction peaks at around $2\theta = 17.4°, 21.4°, 27.7°, 30.4°, 35.3°, 37.5°, 39.6°, 41.6°$, and 50.7 are readily distinguished from the XRD pattern. They agree with the cubic structure of maghemite (JCPDS file no. 39-1346).

Diffraction peaks at around $2\theta = 12.7°, 19.6°, 25.5°, 26.7°, 29.7°, 30.2°, 32.8°, 33.9, 37.3°, 37.7°, 38.7°, 39.9°, 41.7°, 46.0°, 46.9°, 47.6°, 49.5°, 55.1°, 56.7°, 58.3°, 59.8°, 60.7°, 61.6°, 62.7°, 62.9°$, and $66.3°$ are related to the FAp (JCPDS file no. 71-0880). The average crystallite size was calculated to be 12 nm for γ-Fe$_2$O$_3$ and 25 nm for FAp using the Scherrer equation.

Scanning electron microscopy (SEM)

The synthesized γ-Fe$_2$O$_3$@CuFAp nanoparticles were characterized by SEM (Fig. 2). The SEM image of the catalyst proved its spherical morphology. The average size of synthesized nanoparticles is about 50 nm according to the measurement software.

Transmission electron microscopy (TEM)

TEM image of γ-Fe$_2$O$_3$@CuFAp is presented in Fig. 3. The average size of the nanoparticle was calculated to be 66 nm.

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES)

The ICP-AES was used to exact determination of the copper content of the material synthesized. Analysis confirmed 0.28 mmol Cu per gram of the γ-Fe$_2$O$_3$@CuFAp.

FT-IR

In the FT-IR spectrum of γ-Fe$_2$O$_3$@CuFAp, the bending mode of O–P–O which are overlapping with the stretching vibration of Fe–O appeared at 569 and 604 cm^{-1}. The stretching vibrations of P–O bonds appeared at 1040 cm^{-1}. The strong and broad band at 3024 cm^{-1} corresponds to the O–H groups and adsorbed water. The absence of a medium band at 632 cm^{-1} (relating to the stretching mode of OH in hydroxyapatite) refuses the presence of hydroxyapatite in the structure (Fig. 4).

Catalytic activity of nano γ-Fe$_2$O$_3$@CuFAp for the synthesis of benzimidazoles

We have examined catalytic activity of nano-γ-Fe$_2$O$_3$@CuFAp for the synthesis of benzimidazoles (Scheme 2). At first, the reaction of *o*-phenylenediamine with benzaldehyde was chosen as a model reaction to optimize the reaction conditions (Table 1).

We found that in the presence of 0.04 g of nano γ-Fe$_2$O$_3$@CuFAp, the best yield of the product was obtained at 80°C in acetonitrile (Table 1, Entry 2). To show the role of the catalyst, similar reaction in the absence of the catalyst and in the presence of lower amount of nanomagnetic γ-Fe$_2$O$_3$@CuFAp was also examined. Under these conditions, the reactions led to the formation of the desired product in low yields and long reaction time (Entries 4 and 5).

To establish the generality of this method, the synthesis of various benzimidazoles was studied using different benzaldehydes under optimized reaction conditions (Table 2).

The reaction with aliphatic aldehydes such as acetaldehyde and phenylacetaldehyde resulted in a complex mixture due to aldol condensation.

A plausible mechanism for the formation of benzimidazoles catalyzed by γ-Fe$_2$O$_3$@CuFAp is shown in Scheme 3. The Lewis acid properties of γ-Fe$_2$O$_3$@CuFAp by coordination with the carbonyl group of aldehyde facilitate nucleophilic addition of 1,2-phenylenediamine to the activated aldehyde I to afford intermediate II. In the next step, the catalyst activates intermediate II followed by
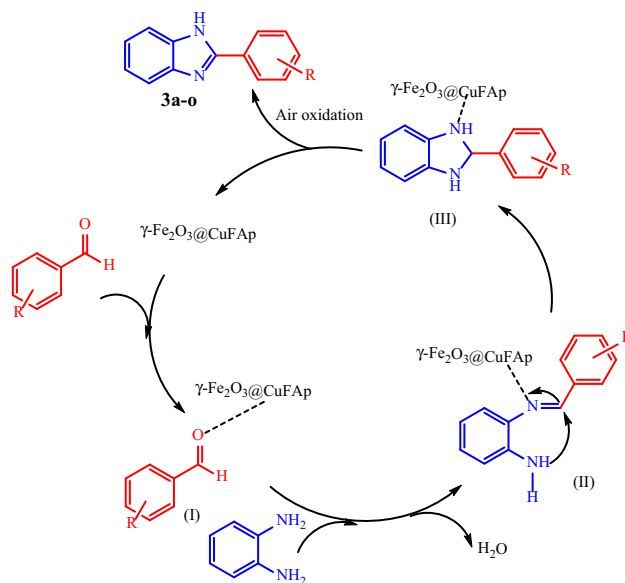
Scheme 3 Plausible mechanism for one-pot synthesis of benzimidazoles catalyzed by γ-Fe$_2$O$_3$@CuFAp

Table 3 Comparison of our results with previously reported data for the synthesis of **3a**

Entry	Catalyst	Solvent	Temperature (°C)	Time	Yield (%)	References
1	Ag_2CO_3/Celite	EtOH	70	3 h	95	[31]
2	DBH	–	50	45 min	95	[32]
3	$Yb(OPf)_3$	Toluene/perfluorodecalin	90	6 h	98	[36]
4	MSI_3PW	$BMI.NTf_2$	40	10 h	99	[37]
5	$T(o\text{-}Cl)PPFe^{III}Cl$	EtOH	r.t	30 min	97	[38]
6	$Co/Ce\text{-}ZrO_2$	–	r.t	10 min	98	[39]
7	Magnetic-CuFAp	CH_3CN	80	8 min	94	This work

intramolecular Michael-type addition to afford the intermediate III. Finally, air oxidation of the intermediate III furnishes the desired products (**3a–o**).

The reusability of a catalyst determines its lifetime. In this regard, the recyclability of $\gamma\text{-}Fe_2O_3$@CuFAp was investigated in a model reaction of *o*-phenylenediamine and benzaldehyde under optimized reaction conditions. The recovered catalyst washed with CH_2Cl_2, dried at room temperature, and reused for a similar reaction. The result showed that after 12 successive runs, catalytic activity of the catalyst was retained without any loss of activity (led to 83% average yield).

To examine the efficiency of the present method for the synthesis of benzimidazoles, preparation of compound **3a** was compared with some of those reported in the literature (Table 3). It is evident from the results that the present protocol shows a very good comparability with previously reported data in terms of reaction times, yield, and reusability of the catalyst.

Conclusions

We have introduced the utilization of $\gamma\text{-}Fe_2O_3$@CuFAp, as a recyclable nanomagnetic catalyst, for green and efficient synthesis of aryl-substituted benzimidazoles through the condensation of 1,2-phenylenediamines with various aryl aldehydes. This method offers some advantages in terms of simplicity of performance, short reaction times, excellent yields, and mild condition. The current protocol could serve as a valuable alternative to known synthetic methods of benzimidazoles and is amenable for iterative combinatorial library generation.

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