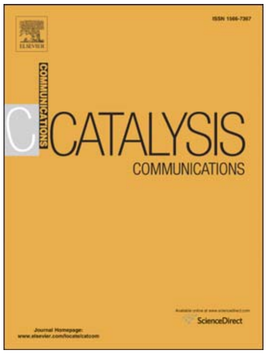

Magnetic carbon nanotube supported Cu ($CoFe_2O_4$/CNT-Cu) catalyst: A sustainable catalyst for the synthesis of 3-nitro-2-arylimidazo[1,2-*a*]pyridines

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Magnetic carbon nanotube supported Cu ($CoFe_2O_4$/CNT-Cu) catalyst: A sustainable catalyst for the synthesis of 3-nitro-2-arylimidazo[1,2-*a*]pyridines

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ABSTRACT

A magnetic carbon nanotube supported Cu catalyst ($CoFe_2O_4$/CNT-Cu) was prepared, characterized and evaluated as a recoverable catalyst for synthesis of 3-nitro-2-arylimidazo[1,2-*a*]pyridines via one-pot three-component reactions of 2-aminopyridines, aldehydes and nitromethane. The reactions proceeded in PEG 400 under aerobic conditions and the products were obtained in good to excellent yields. The catalyst can be successfully recycled for eight runs without appreciable loss of its activity.

Keywords:

Magnetic nanoparticles; Carbon nanotubes; Heterogeneous catalyst; Multi-component reaction; 3-Nitro-2-arylimidazo[1,2-*a*]pyridines

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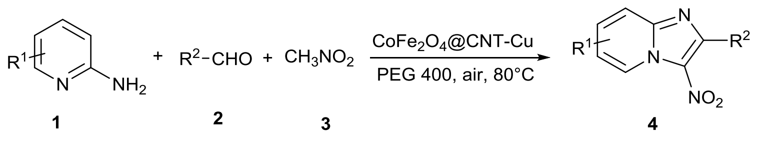
1. Introduction

In view of the principles of green chemistry, the designing of new, efficient reaction protocols, media and catalysts is still important topics of research in organic synthesis. An efficient and recoverable heterogeneous catalyst system constitutes an important aspect of green organic synthesis. In this context, carbon catalysts have been paid much attention as they are cheap and easily obtained. Carbon materials such as activated carbon [1], graphene oxide [2-3], carbon nanofibers [4-5] and carbon nanotubes (CNTs) have been widely used as heterogeneous catalysts. Particularly, CNTs have become one of the most commonly used catalyst supports due to their excellent chemical, thermal, and mechanical stability, inertness, high surface area, and chemically tunable topography. Most importantly, CNTs have rich surface functional groups (mainly hydroxyl and carboxyl), which made CNTs as a suitable support material for metal and metal oxide nanoparticles [6-7]. These catalysts showed high catalytic activity and may be reused for several cycles, but they were difficult to separate from the reaction mixtures, and filtration or high speed centrifugation was usually required. Accordingly, magnetic nanoparticles (NPs) have been emerged as easily reusable catalysts in organic reactions owing to their unique properties such as the remarkable catalytic activity, easy preparation, noncorrosive and nonhazardous nature, eco-friendliness, low cost, as well as facile separation by magnetic force. Magnetic separation is an intriguing alternative to filtration or centrifugation because it reduces loss of catalyst and makes the recovery and reusability of catalyst easier after completion of the reaction [8-10]. Furthermore, replacement of conventional hazardous organic solvents by safe and environmentally benign media is also of key relevance, since organic solvents account for more than 80% of the waste production of a process [11]. Besides, multicomponent reactions (MCRs) are attractive synthetic strategy for the rapid and efficient construction of structurally diverse heterocyclic compounds in a safe, step-economy, convergence, and energy-efficient manner [12-18]. With these aspects of green synthesis in mind, developing new strategies combining magnetic nanocatalysts with carbon nanotubes, environmentally benign media and multicomponent reactions might be one exciting and desirable direction.

Imidazo[1,2-*a*]pyridines represent an important class of *N*-heterocycles and have attactive significant attention due to their various biological and pharmacological activities. Substituted imidazo[1,2-a]pyridines are a characteristic strucral unit present in some naturally occurring products and pharmacologically important molecules. In addition, they have been utilized as dyes [19], electroluminescent [20], and intermediates in chemical synthesis [21]. The wide demand for substituted imidazo[1,2-*a*]pyridines has spurred a vigorous research for the development of new synthetic methods [22-25]. Particularly, 3-nitroimidazo[1,2-a]pyridine can be readily converted to various imidazopyridine derivatives [26]. From a synthetic point of view, methods for obtained 3-nitro-2-arylimidazo[1,2-*a*]pyridines are still limited. In 2012, Yan and co-workers proposed Cu(I)-catalyzed synthesis of 3-nitroimidazo[1,2-a]pyridines by mild oxidative double C–N coupling of nitroolefins with aminopyridines using air as oxidative agent [27]. The group of Jagadhane reported the use of sodium dichloriodide for the efficient synthesis of 3-nitroimidazo[1,2-a]pyridines by the reaction of 2-aminopyridines and nitrostyrenes [28]. More recently, an alternative method to the above coupling reactions has been reported by the group of Itoh employing an iodine source combined with hydrogen peroxide [29]. Despite their effectiveness, some of these methods encounter limitations, such as the use of harmful organic solvents, unsatisfactory yields, long reaction times, narrow substrate scope, or the requirement for advance preparation of nitrostyrenes. Thus, the development of a more efficient catalytic system for accessing these heterocuyclic compounds under environmentally benign conditions is still highly desirable.

Considering the above reports and as a continuation of our research towards the design of magnetic nanocatalysts [30-33] and development of environmentally benign methods for the construction of heterocyclic compounds [34], herein, we describe synthesis and characterization of magnetic recyclable CoFe$_2$O$_4$/CNT-Cu NPs and their application as efficient catalysts for one-pot synthesis of 3-nitro-2-arylimidazo[1,2-a]pyridines by three-component reaction of 2-aminopyridines, aldehydes, and nitromethane in PEG 400 under aerobic conditions (Scheme 1).



Scheme 1. Synthesis of 3-nitro-2-arylimidazo[1,2-*a*]pyridines catalyzed by CoFe$_2$O$_4$/CNT-Cu in PEG 400.

2. Experimental

2.1. General

See in supporting information.

2.2 Preparation of magnetic carbon nanotube supported Cu catalyst ($CoFe_2O_4$/CNT-Cu)

The purchased MWCNTs were dispersed in nitric acid solution (40%) and then placed in an ultrasonic bath for treatment at 80 ^oC for 2 h. The obtained acid-treated MWCNTs were separated by centrifuge, washed with water and ethanol until the pH reached 7.0, and dried under vacuum at 60 ^oC for 8 h.

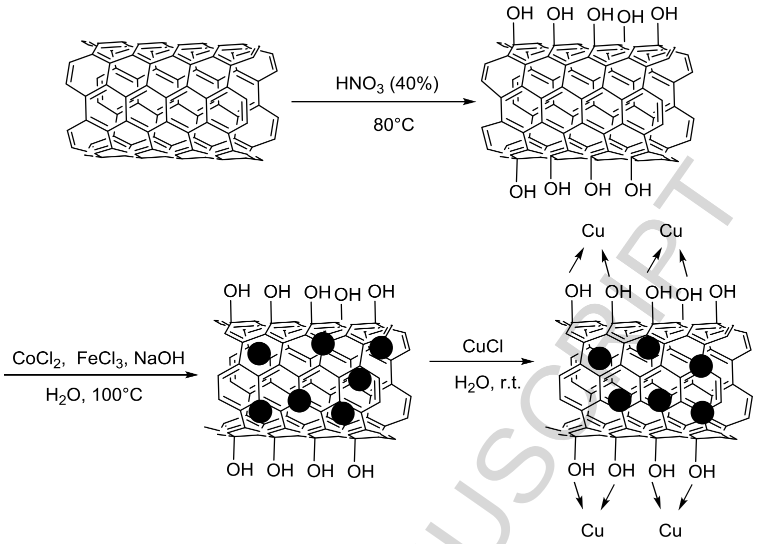
$CoFe_2O_4$-CNT NPs were prepared by a chemical co-precipitation technique using $FeCl_3 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$ and acid-treated carbon nanotubes as precursors. The obtained acid-treated MWCNTs (0.16 g) was dispersed in distilled water (40 ml), and sonicated for 30 min at room temperature. The mixture of $FeCl_3 \cdot 6H_2O$ (2.70 g), $CoCl_2 \cdot 6H_2O$ (1.19 g) and 10 ml distilled water was added to the MWCNTs solution. Then, 25 ml of 3 mol/L NaOH solution and oleic were added slowly into the above solution under vigorous stirring. The mixture was stirred for 1 h at 100 ^oC. The obtained $CoFe_2O_4$-CNT NPs were separated magnetically, washed with water and ethanol until the pH reached 7.0, and dried under vacuum at 60 °C for 24 h.

In order to prepare the supported Cu catalyst, $CoFe_2O_4$/CNT NPs (0.5 g) was dispersed in water (5 ml) by sonication. CuCl (0.2 g) dissolved in water (5 ml) was added to the above solution. After stirring overnight at ambient temperature, the solid was collected using a permanent magnet, followed by washing three times with H_2O. Finally, the obtained $CoFe_2O_4$/CNT-Cu was dried under vacuum at 60 °C for 24 h.

2.3. General procedure for synthesis of imidazo[1,2-a]pyridines in PEG 400

A mixture of 2-aminopyridine (1.0 mmol), benzaldehyde (1.0 mmol), nitromethane (1.1 mmol), and $CoFe_2O_4$/CNT-Cu (0.05 mmol) in PEG 400 (5 ml) was stirred at 80 °C with a reflux condenser under an open atmosphere. After completion of the reaction as monitored by TLC, the reaction mixture was brought to room temperature and diluted with EtOAc (2 ml). The catalyst was separated by a magnetic bar. The organic layer was washed with water and dried with anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was purified through a silica gel column chromatography eluting with an ethyl acetate and petroleum ether mixture to afford the pure product.

3. Results and discussion



Scheme 2. Synthesis of $CoFe_2O_4$/CNT–Cu.

As shown in scheme 2, the catalyst was prepared in a three-step process. At first, raw CNTs were purified and oxidized by nitric acid in an ultrasonic bath at 80 ^oC for 2 h to increase the concentration of oxygen-containing functional groups, finally filtered, thoroughly washed and dried for further use. It has been confirmed that acid treatment could improve the purity of raw CNTs, and introduce hydrophilic groups (such as COOH and OH) to the CNT surface to help adsorb the active metals. Magnetic carbon nanotubes ($CoFe_2O_4$/CNT) were achieved by a chemical co-precipitation technique using $FeCl_3$, $CoCl_2$ and acid-treated carbon nanotube as precursors. CuCl was added to a suspension of $CoFe_2O_4$/CNT in H_2O, while being dispersed by stirring. The magnetic carbon nanotube supported Cu ($CoFe_2O_4$/CNT-Cu) nanoparticles were isolated by magnetic decantation and washed with H_2O and dried. The copper metal amount of the immobilized catalyst was found to be 51.7 % based on inductively coupled plasma mass spectrometry (ICP-MS) analysis.

As shown in Fig. 1 (A), the energy dispersive spectrum (EDS) indicated the presence of Fe, Co, O, C, Cl and Cu in the nanocatalyst. Fig. 1 (B) shows the XRD patterns of the prepared $CoFe_2O_4$/CNT-Cu nanoparticles. The position and relative intensities of observed diffraction peaks appearting at 2θ = 36.5^o, 42.3^o, 50.3^o, 53.8^o and 61.4^o corresponding to the diffractions of (1 2 1), (0 1 4), (4 0 1), (0 1 5) and (3 3 1), well mathed with literature data (JCPDS 22-1066), indicating retention of the crystalline cubic spinel structure during functionalization of $CoFe_2O_4$. The XRD data (JCPDS 001-0793) clearly demonstrates the presence of copper with the characteristic (1 1 1) and (2 2 0) Bragg's peaks located at 2θ = 32.4^o and 47.9^o.

Diffraction peaks at around 39.8° and 73.5° corresponding to the diffractions of (2 0 5) and (3 3 6) are readily recognized from the XRD pattern, The observed diffraction peaks agree well with that of carbon nanotubes (JCPDS 01-0258).

The magnetic properties of the samples $CoFe_2O_4$-CNT-Cu were measured by a vibrating sample magnetometery (VSM) at room temperature. The prepared $CoFe_2O_4$/CNT-Cu is superparamagnetic and the saturation magnetization value is 21.8 emug^{-1} (Fig. 1C). The magnetic behavior of the synthesized nano catalyst is critical for their application, which prevents aggregation and enables them to redisperse rapidly when the magnetic field is removed.

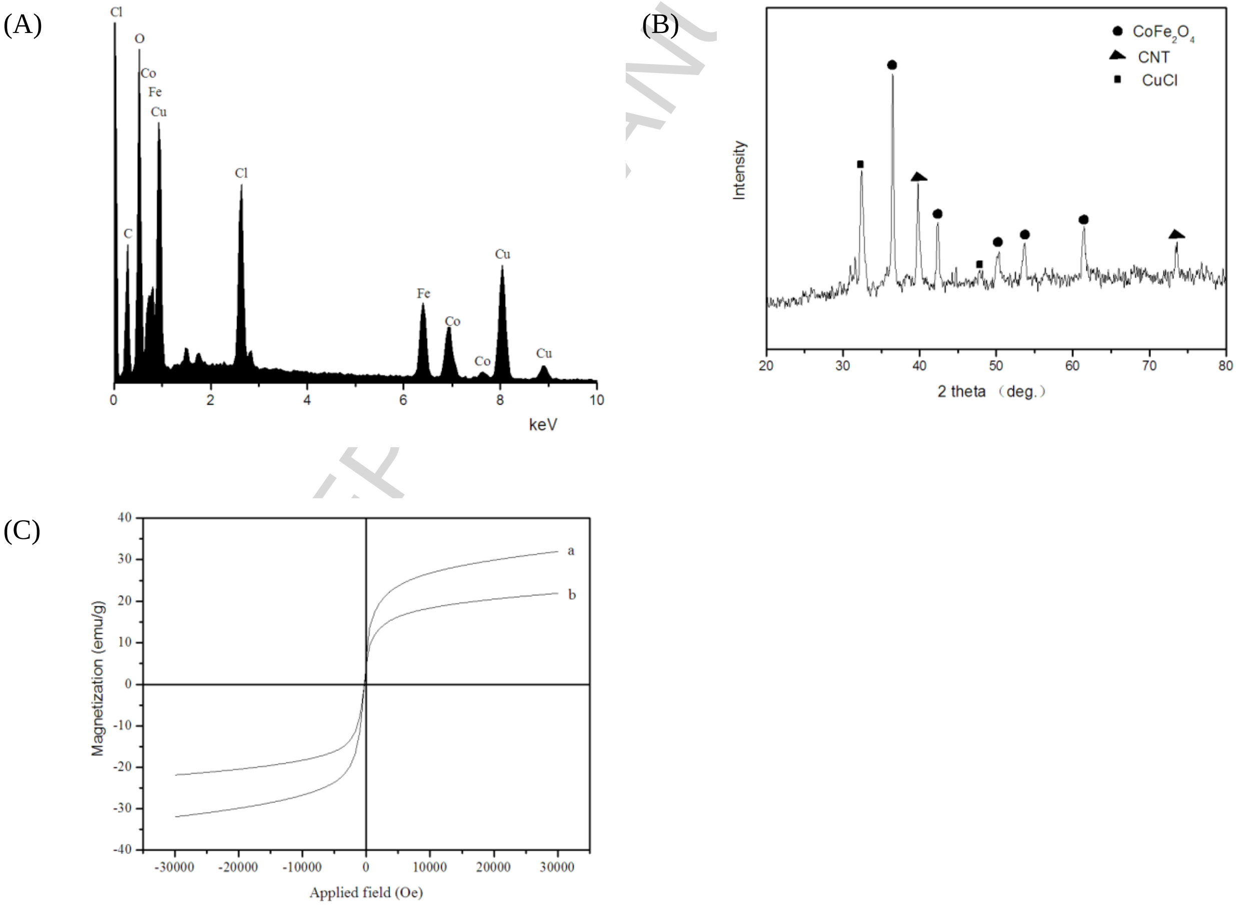


Fig. 1. (A) EDS spectrum of $CoFe_2O_4$/CNT–Cu, (B) XRD pattern of $CoFe_2O_4$/CNT–Cu and (C) magnetization curve of (a) $CoFe_2O_4$/CNT and (b) $CoFe_2O_4$/CNT–Cu.

Fig. 2 shows fourier transform infrared (FT-IR) spectra of carbon nanotubes, acid-treated carbon nanotubes, magnetic $CoFe_2O_4$/CNT nanoparticles and $CoFe_2O_4$/CNT-Cu. The presence of OH and C=O bonds in the acid-treated carbon nano tubes is confirmed by the characteristic peaks appeared at 3457 and

1758 cm^{-1}. The presence of Co-O and Fe-O bonds in the magnetic particles is confirmed by the characteristic peak appeared at 600 cm^{-1}. The absorption at 472 cm^{-1} is assigned to the Cu-O bridge.

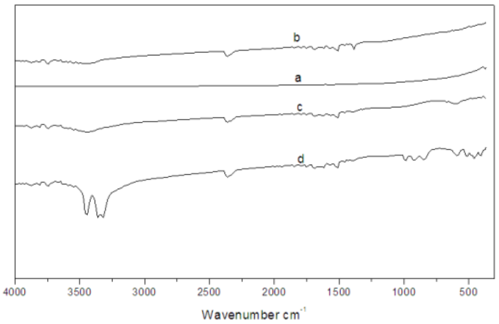


Fig. 2. IR spectra of carbon nanotubes (a), acid-treated carbon nanotubes (b), $CoFe_2O_4$/CNT (c) and $CoFe_2O_4$/CNT–Cu (d).

The shape, size and morphology of the synthesized $CoFe_2O_4$/CNT-Cu NPs were analyzed by using TEM (Fig. 3**)** and SEM (Fig. 4**)**. The average nanopartical diameter of $CoFe_2O_4$/CNT-Cu was estimated to be 50-52 nm based on the TEM image, which is also in accordance with the result calculated by the Debye–Scherrer's equation. The specific surface area of $CoFe_2O_4$/CNT-Cu obtained by the N_2 adsorption isotherms was 26.7 m^{2}g^{-1}.

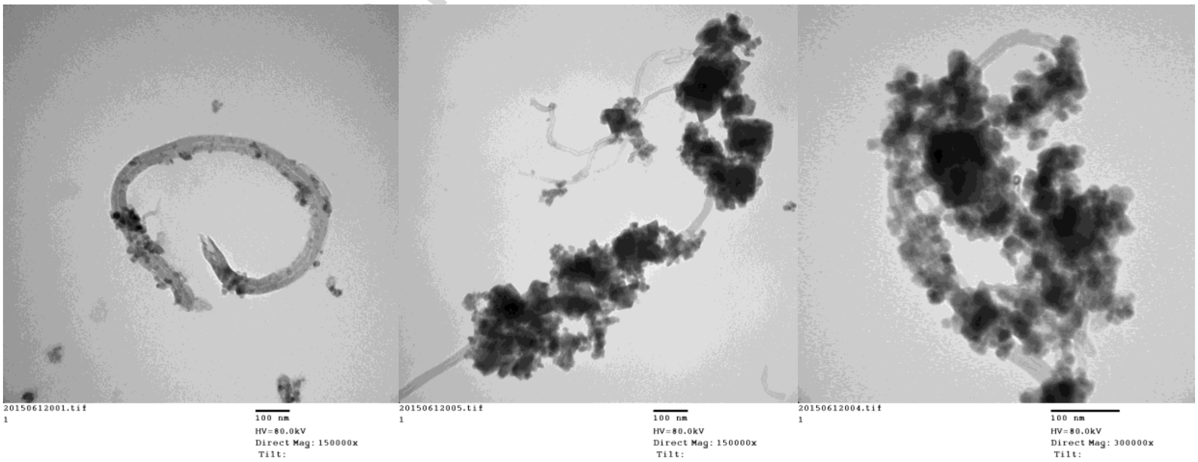


Fig. 3. TEM images of CNT (left), $CoFe_2O_4$/CNT (middle) and $CoFe_2O_4$/CNT–Cu (right).

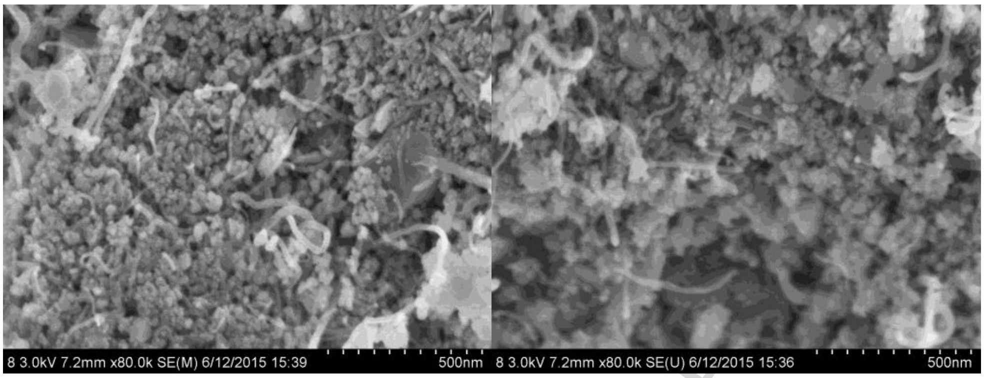


Fig. 4. SEM image of $CoFe_2O_4$/CNT–Cu: fresh (left), after eight reaction cycles (right).

The activity of the prepared catalyst was tested for one-pot reaction of 2-aminopyridine, benzaldehyde and nitromethane under an air atmosphere and the key results are summarized in Table 1. The absence of catalyst failed to give desired product ever after heating the reaction mixture for 6 h in PEG 400 (Table 1, entry 1). Further investigation showed that the reaction occurred smoothly in the presence of $CoFe_2O_4$/CNT-Cu, affording 3-nitro-2-phenylimidazo[1,2-*a*]pyridine (**4a**) in 95% yield (entry 9). The use of $CuCl_2$ as a homogeneous catalyst, showed a drop in reaction rate and gave 65% yield in 6 h (entry 6). In contrast, magnetic nano-Fe_3O_4, γ-Fe_2O_3, $CoFe_2O_4$ and $NiFe_2O_4$ were ineffective for the formation of the expected product. The observed results inferred that copper plays a main catalytic role. We also performed the model reaction in the presence of nano $CuFe_2O_4$, the desired product was obtained in 50% yield. We recently reported that nano $CuFeO_2$ could be used as an efficient catalyst for promoting three-component reaction of 2-aminopyridines, aldehydes and alkynes to give imidazo[1,2-a]pyridines in high yield [34], 81% yield of product was obtained for above model reaction (entry 8).

Next, we screened the effect of the solvent, catalyst loading and temperature. Among the different solvents screened, PEG 400 was found to be the best solvent of choice and afforded the product in high yield. The formatting product **4a** was not observed when the mixture of 2-aminopyridine, benzaldehyde and nitromethane was stirred under reflux temperature or 80 °C in CH_2Cl_2, MeOH, and EtOH in the presence of 5 mol% of $CoFe_2O_4$-CNT-Cu (entries 10-12). When the reaction was conducted in H_2O, EtOH/H_2O (1:1), CH_3CN, DMF and toluene the desired product was obtained in 20%-65% yield (entries 13-17). Based on the fact that PEG plays the role of a ligand in Cu-mediated reaction [35], PEG appeared to play the pivotal role as a solvent and also as a ligand in the present reaction. Furthermore, the relation between the yields of the model reaction and catalyst loading was also studied. The result showed that 5 mol % of catalyst was sufficient to complete the reaction, and further increasing the amount of catalyst to more than 5 mol% showed no significant beneficial effect on the reaction. However, reducing the amount of catalyst led to the declined yield of product (entry 21). Accordingly, the effect of the reaction temperature was investigated. It was found that heating at 80 ^oC gave the best yield while the reaction did not occur at room temperature. Taken together, the optimal reaction conditions included using 5 mol% of $CoFe_2O_4$-CNT-Cu in PEG 400 at 80 ^oC.

Table 1

Optimization of the reaction conditions for the synthesis of 3-nitro-2-phenylimidazo[1,2-*a*]pyridine (**4a**).[a]

Entry	Catalyst	Solvent	Time (h)	Yield (%)
1	no	PEG 400	6	NR
2	nano Fe_3O_4	PEG 400	6	NR
3	nano γ-Fe_2O_3	PEG 400	6	NR
4	nano $CoFe_2O_4$	PEG 400	6	NR
5	nano $NiFe_2O_4$	PEG 400	6	NR
6	$CuCl_2$	PEG 400	6	65
7	nano $CuFe_2O_4$	PEG 400	6	50
8	nano $CuFeO_2$	PEG 400	6	81
9	$CoFe_2O_4$/CNT-Cu	PEG 400	3	95
10	$CoFe_2O_4$/CNT-Cu	CH_2Cl_2	46	NR
11	$CoFe_2O_4$/CNT-Cu	MeOH	6	NR
12	$CoFe_2O_4$/CNT-Cu	EtOH	6	NR
13	$CoFe_2O_4$/CNT-Cu	DMF	6	20
14	$CoFe_2O_4$/CNT-Cu	CH_3CN	6	60
15	$CoFe_2O_4$/CNT-Cu	H_2O	6	50
16	$CoFe_2O_4$/CNT-Cu	EtOH/H_2O (1:1)	6	65
17	$CoFe_2O_4$/CNT-Cu	Toluene	6	40
18[b]	$CoFe_2O_4$/CNT-Cu	PEG 400	6	NR
19[c]	$CoFe_2O_4$/CNT-Cu	PEG 400	3	86
20[d]	$CoFe_2O_4$/CNT-Cu	PEG 400	3	94
21[e]	$CoFe_2O_4$/CNT-Cu	PEG 400	3	82
22[f]	$CoFe_2O_4$/CNT-Cu	PEG 400	3	95

[a] Experimental conditions: 2-aminopyridine (1.0 mmol), benzaldehyde (1.0 mmol), nitromethane (1.1 mmol), catalyst (0.05 mmol) unless otherwise specified in the table, solvent (2 ml), 80 °C, open flask to air.
[b] room temperature.
[c] 60 °C.
[d] 90 °C.
[e] Catalyst (0.02 mmol).
[f] Catalyst (0.10 mmol).

To examine the substrate scope and functional group tolerance of this three-component coupling reaction, we first investigated structurally diverse aldehydes under the optimal conditions. As evidenced in Table 2, various aromatic aldehydes, regardless of the presence of electron-donating or electron-withdrawing functional groups attached to benzene rings could react with 2-aminopyridine and nitromethane smoothly to provide the desired products in high to excellent yields. However, compared to 3- and 4-positions, the substituents at 2-position have slight impact on the result, which might be due to steric hindrance. For example, 2-chlorobenzaldehyde required prolonged reaction time and afforded the desired product **4l** in a relatively lower yield (entry12). Strikingly, this procedure could tolerate a wide range of synthetically useful functional groups such as thioether, C-F bond, C-Cl bond and C-Br bond, which could be used for further transformation at the substituted positions. Also, the present catalytic system showed excellent promise for the transformation of aromatic heterocyclic aldehydes such as thiophene-2-carbaldehyde (entry 17). When the aromatic ring was replaced by a hindered naphthyl group, the desired product **4r** was obtained in 80% yield (entry 18). Subsequently, pyridin-2-amines bearing different functional groups were evaluated. Satisfactorily, 2-aminopyridine having either electron-donating or electron-withdrawing group worked well and delivered the expected products in high to excellent yields.

Table 2.
Scope of reaction of 2-aminopyridines with aldehydes and nitromethane in $CoFe_2O_4$-CNT-Cu/PEG 400 catalytic system.

Entry	R^1	R^2	Product	Time (h)	Yield (%)[a]	mp (°C)	
						Found	Reported
1	H	Ph	**4a**	3	95	176-177	172-174 [27]
2	H	3-$MeOC_6H_4$	**4b**	4	90	146-147	146-148 [36]
3	H	4-$MeOC_6H_4$	**4c**	4	88	171-172	168-170 [27]
4	H	3-$PhOC_6H_4$	**4d**	6	85	146-147	
5	H	4-$CH_3(CH_2)_2OC_6H_4$	**4e**	6	85	135-136	

6	H	4-$CH_3(CH_2)_4OC_6H_4$	**4f**	4	86	96-97	
7	H	4-MeC_6H_4	**4g**	4	92	201-202	204-206 [27]
8	H	4-$CMe_3C_6H_4$	**4h**	4	84	oil	
9	H	4-$MeSC_6H_4$	**4i**	4	90	125-126	
10	H	3-FC_6H_4	**4j**	3	90	213-214	
11	H	4-FC_6H_4	**4k**	3	95	222-223	224-226 [28]
12	H	2-ClC_6H_4	**4l**	6	83	oil	oil [27]
13	H	3-ClC_6H_4	**4m**	4	90	181-182	180-182 [27]
14	H	4-ClC_6H_4	**4n**	3	96	185-186	184-186 [27]
15	H	4-BrC_6H_4	**4o**	3	95	188-190	186-188 [27]
16	H	3-$CF_3C_6H_4$	**4p**	4	90	108-110	
17	H	Thienyl	**4q**	5	86	186-187	188-190 [37]
18	H	1-Naphthyl	**4r**	6	80	116-118	118-120 [27]
19	4-Me	Ph	**4s**	4	91	163-164	156-159 [37]
20	5-F	Ph	**4t**	3	94	156-157	

[a] Isolated yield.

The structures of the prepared products were identified by their IR, ^{1}H NMR, ^{13}C NMR spectra and Mass spectra. The structure of a representative compound **4t** (CCDC 1029046) was also explicitly established by the single-crystal X-ray crystallographic analysis (Fig. S1 in supporting information).

The recyclability is of great importance for applying a catalytic system in industrial processes. The recyclability of the catalyst and PEG 400 was investigated in a model reaction. After completion of the reaction, the reaction mixture was cooled to room temperature, and the product was extracted with ethyl acetate. The catalyst was separated by a magnetic bar. The recovered catalyst was reused in the model reaction to the next round. The efficiency and stability of the catalytic system were found to be very good, even after eight cycles (Fig. 5). SEM images of fresh and recovered catalysts indicated that little morphological changes occurred (Fig. 4). The amount of Cu leaching was also determined by inductively coupled plasma techniques and found that the Cu content after eighth cycle was 0.60 ppm in ethyl acetate. In order to test the recyclability of the used PEG, the PEG was collected after usual workup and dried at 50 ^{o}C under vacuum. The recovered PEG was reused in the next run for the model reaction. The results show that **4a** can be obtained in 85% yield when PEG was reused in the fifth runs.

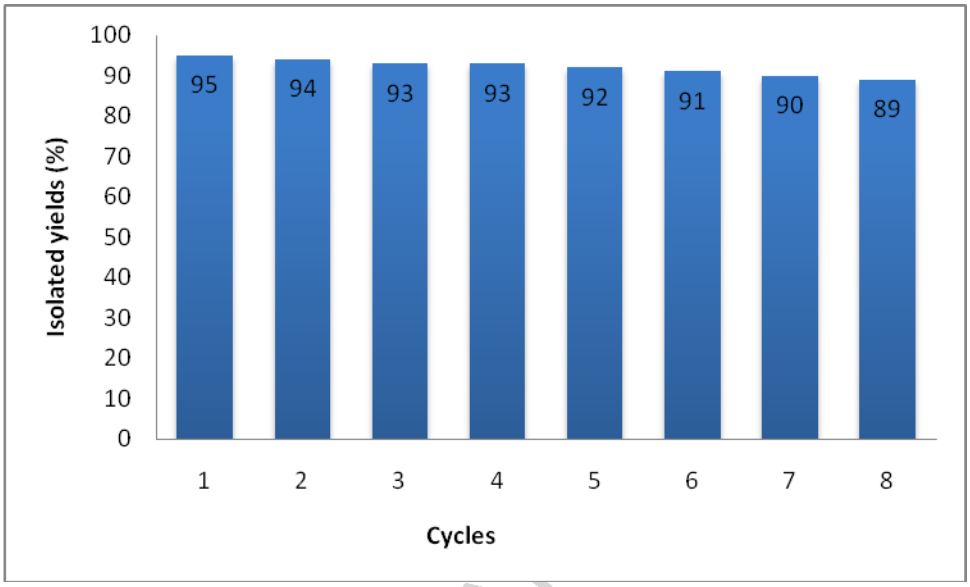
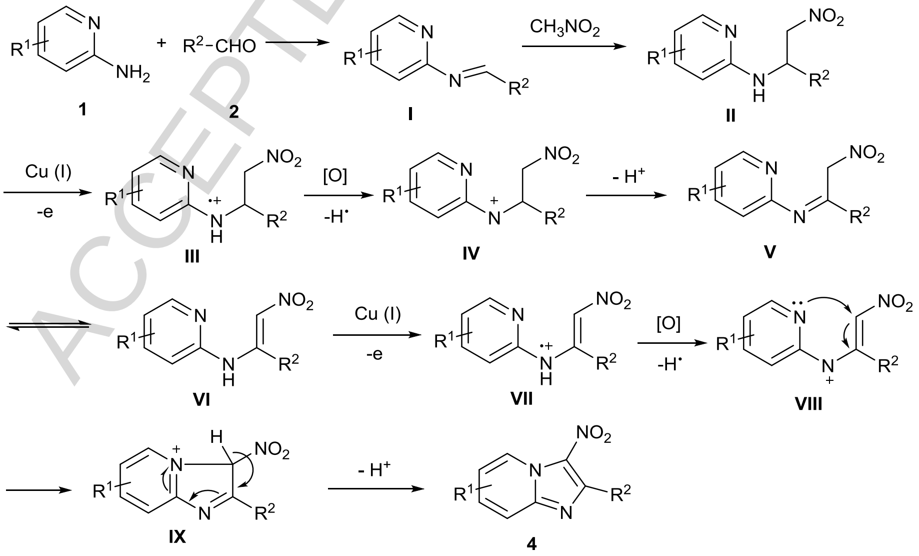


Fig. 5. Reusability of the $CoFe_2O_4$/CNT-Cu.

Finally, based on the observations and previous literature report [36], a probable mechanism for one-pot three-component reactions of 2-aminopyridines, aldehydes and nitromethane has been postulated in Scheme 3.



Scheme 3. Plausible reaction mechanism.

4. Conclusion

In summary, a new kind of $CoFe_2O_4$/CNT-supported Cu catalyst has been firstly prepared by a relatively simple route. It has been demonstrated to be an efficient catalyst for one-pot synthesis of a wide variety of 3-nitro-2-arylimidazo[1,2-*a*]pyridines via one-pot three-component reactions of

2-aminopyridines, aldehydes and nitromethane in PEG 400 under aerobic conditions. More importantly, the magnetic $CoFe_2O_4$/CNT-Cu catalyst can be quickly and completely recovered by simply applying an external magnet and the efficiency remains unaltered even after eight recycles. The experimental simplicity, easily available and economical starting materials, convenient one-pot operation, high yields, wide substrate scope, benign solvent, ecologically clean procedure, efficient recycling reaction system make this methodology a very efficient and green process for the synthesis of biologically important 3-nitro-2-arylimidazo[1,2-*a*]pyridines.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.XXXX

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Graphical Abstract:

Magnetic carbon nanotube supported Cu ($CoFe_2O_4$/CNT-Cu) catalyst: A sustainable catalyst for the synthesis of 3-nitro-2-arylimidazo[1,2-a]pyridines

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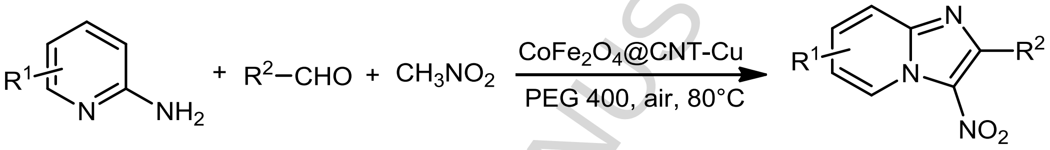

Highlights

- A novel magnetic carbon nanotube supported Cu catalyst was prepared.
- It showed high catalytic activity for the synthesis of 3-nitro-2-arylimidazo[1,2-a]pyridines.
- The catalyst could be easily isolated by magnetic decantation.
- The catalyst was reused several times without significant loss in catalytic activity.