

## Nano-Fe<sub>3</sub>O<sub>4</sub> as a heterogeneous recyclable magnetically separable catalyst for synthesis of nitrogen fused imidazoheterocycles via double C-N bond formation

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### ABSTRACT

An efficient and convenient approach towards the synthesis of nitrogen fused imidazoheterocycles through double C-N bond formation in a single step has been achieved with a good range of substituted phenacyl bromides in the presence of magnetically recoverable Fe<sub>3</sub>O<sub>4</sub> as a green heterogeneous nanocatalyst. The present approach was found to be environmentally benign and economically feasible in view of its ease of application, low cost and easy separation. Developed methodology has several advantages such as wide scope of substrates, easily available catalyst, operationally simple and high yield. Moreover, the magnetically separable catalyst was easily separated from the reaction mixture using an external magnet and recycled up to four times without much lost in its catalytic activity.

**Keywords:** *Magnetically separable nanocatalyst, Imidazoheterocycles, Heterogeneous catalyst, C-N bond formation, Cyclocondensation, Azaheterocycles, Ferrite.*

### 1. Introduction

Fused bicyclic heterocycles containing more than one nitrogen are important structural motifs found in numerous natural products and bioactive molecules [1-3]. Amongst these bicyclic nitrogen fused heterocycles, imidazoheterocycles are privileged scaffolds with wide range of biological activities, especially as antiulcer [4], anticancer [5], anti-inflammatory [6], antiviral [7], immunomodulatory [8], immunosuppressive [9] agents and in the treatment of cystic fibrosis [10].

Several commercially nitrogen fused imidazole drugs, such as imidazopyridine core containing alpidem [11], zolimidine [12], zolpidem [13], necopidem [14], saripidem [14], olprinone [15], imidazo[2,1-b]thiazole core containing levamisole [16] and benzo[d]imidazo[2,1-b]thiazole derivatives (YM-201627 [17]) as well as <sup>11</sup>C-labelled imidazo[2,1-b]benzothiazole [18] have been developed by the modification of imidazole fused

with either pyridine, thiazole or benzothiazole heterocyclic nuclei (Fig. 1). Due to an interesting biological importance displayed on a broad range of therapeutic classes, in the recent years the synthesis of nitrogen bridge bicyclic imidazo[2,1-b] pyridine/thiazole or benzothiazole derivatives have received significant attention from the pharmaceutical industries [19,20].

In the past, few synthetic strategies had been developed for the preparation of imidazoheterocycles, which can be achieved by the condensation reaction of 2-aminopyridine or 2-aminothiazole with two carbon synthones such as phenacyl halide [21-29], diazo aryl ketone [30] or  $\alpha$ -tosyl ketones [31,32] derivatives in presence of the basic or neutral conditions [19,20]. Also, copper catalysed one pot three-component coupling of 2-aminopyridine with aldehyde and acetylene has been reported [33]. Condensation of the bromocarbonyl compound [21-29] with 2-amino pyridine/thiazole compounds in refluxing acetone or ethanol or using different catalysts and reaction conditions requires a long reaction time [19,20]. The proposed reaction process involves the crucial steps for the formation of two C-N bonds, the first step is nucleophilic substitution

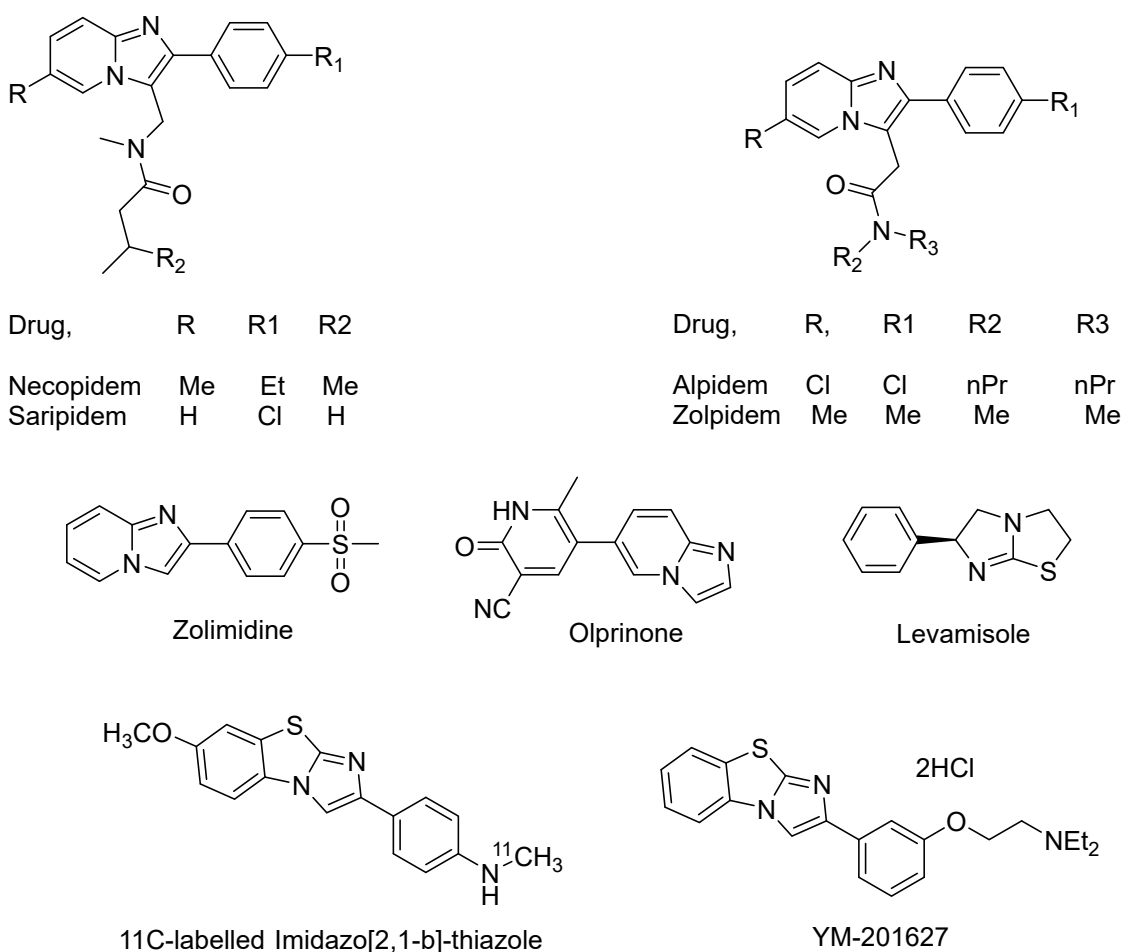
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**Fig. 1.** Fused Imidazoheterocycles based drugs.

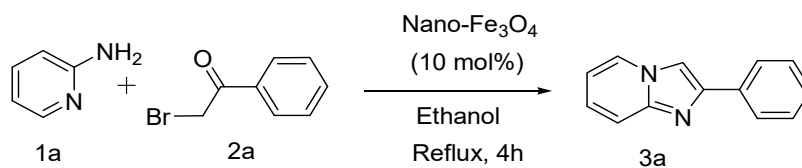
of bromide by nitrogen of 2-aminoheterocycle and the second is dehydrative condensation and preparing the N-fused heterocyclic scaffold.

In recent years, several methods and developments have been reported for the synthesis of imidazo [1,2-*a*]pyridine, imidazo[1,2-*a*]thiazole and imidazo [1,2-*a*]benzothiazole derivatives. In spite of that, these methods have their own merits and drawbacks of green chemistry [21-29]. Many of the developed procedures require harsh reaction conditions, expensive and toxic reagents, tedious work-up, prolonged reaction time, low yields and use of the non-recyclable catalysts; there is no any efficient greener approach. The recovery and reusability of the catalysts are also a major problem. Therefore, the demand for green and eco-friendly procedures using recycled catalysts necessitated developing an alternative method for the synthesis of imidazoheterocycles.

Magnetically separable nano-ferrite ( $\text{Fe}_3\text{O}_4$ ) has attracted much attention in the previous decade, owing to its unique features, low preparation cost, high thermal stability [34-36]. In addition, magnetic

nanoparticles ( $\text{Fe}_3\text{O}_4$ ) show their paramagnetic nature; due to this property, nano- $\text{Fe}_3\text{O}_4$  is very popular as a heterogeneous catalyst and it can be easily separated from the reaction mixture using an external magnet. Magnetic nano- $\text{Fe}_3\text{O}_4$  particles have developed as viable alternatives to conventional materials, because of robust, thermally stable, readily available and high catalytic activities in various organic transformations. The nano-sized particles enhance the exposed surface area of the active component of the catalyst which increases the interaction between reactants and catalysts dramatically [37,38]. The nano-sized catalysts bridge the gap between heterogeneous and homogeneous catalysts and these results in conserving the required characteristics of both systems [36].

Herein, we describe a mild and efficient approach to the synthesis of imidazoheterocycle derivatives through double C-N bond formation using nano- $\text{Fe}_3\text{O}_4$  as catalyst (Scheme 1). To the best of our knowledge, there has been no report on nano-ferrite catalysed synthesis of fused azaheterocycles.



**Scheme 1.** Nano-Fe<sub>3</sub>O<sub>4</sub> catalysed imidazopyridine synthesis reaction.

## 2. Experimental

### 2.1. Chemicals and Instruments

All chemicals were purchased from Sigma-Aldrich and S.D. Finechem companies and used without further purification. Reactions have been monitored by Thin Layer Chromatography on 0.2 mm pre-coated plates of silica gel G60 F254 (Merck). Visualisation was made with UV light or with an iodine vapour. Melting point ranges were determined in open capillaries and are uncorrected. All yields were referred to isolated products after purification. <sup>1</sup>HNMR spectra were recorded on BRUKER AVANCE II 400MHz and <sup>13</sup>CNMR spectra were recorded on BRUKER AVANCE II 100MHz Spectrophotometer in DMSO-d<sub>6</sub> using TMS as the internal standard. The chemical shift values are recorded on δ-scale and the coupling constants (*J*) are in hertz. The X-ray diffraction (XRD) patterns were recorded on Bruker AXS D8 Advance X-ray diffractometer using monochromatic Cu-Kα radiation having wavelength λ = 1.5406 Å. Scanning Electron Microscope (SEM) images were obtained on S-4800 Type-II, HITACHI Japan.

### 2.2. Preparation of Fe<sub>3</sub>O<sub>4</sub> nanoparticles

Fe<sub>3</sub>O<sub>4</sub> nanoparticles were prepared by the quantitative modification of the reported process [39]. FeSO<sub>4</sub>·7H<sub>2</sub>O (6.95 g) and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (10g) were dissolved in 300 mL water in a 500 mL beaker. NH<sub>4</sub>OH (25%) was added slowly to adjust the pH of the solution to 10. Then, the reaction mixture was continuously stirred for 1 h at

60 °C. The precipitated brown coloured nanoparticles were separated by external magnet, washed with water until the pH reached up to 7, then dried at 120 °C for 1 h. Ferrite was characterised by FTIR, XRD and SEM.

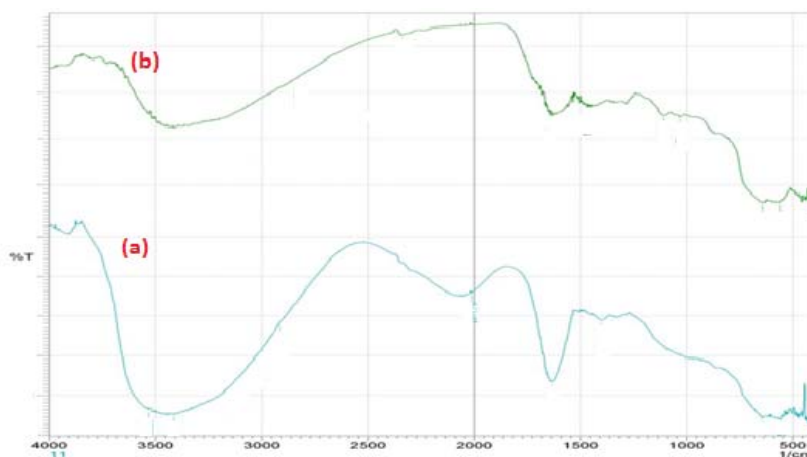
### 2.3. General procedure for the synthesis of imidazoheterocycles:

2-Aminoazaheterocycle (1 mmol), substituted phenacyl bromide (1 mmol) and nano-Fe<sub>3</sub>O<sub>4</sub> (10 mol%) were added into ethanol (5 mL) in a round bottom flask and stirred at refluxed temperature. The progress of the reaction was monitored on TLC (Toluene: Methanol 9:1 v/v). After completion of the reaction, the reaction mixture was diluted with ethyl acetate (10 mL) and the nano catalyst was separated by the external magnet. After separation of catalyst the product was extracted using water, the organic solvent is evaporated and the obtained product was recrystallized with aqueous ethanol.

## 3. Results and Discussion

### 3.1. Catalyst characterization

The FT-IR spectrum analysis suggests two ranges of the absorption bands (Fig. 2). In the range of 400–1000 cm<sup>-1</sup>, two characteristic absorption bands of Fe-O bond were observed at  $\bar{\nu}$  = 570 and 630 cm<sup>-1</sup> for the Fe<sub>3</sub>O<sub>4</sub> MNPs. The second broad absorption band at about 3410 cm<sup>-1</sup> represents a stretching mode of H<sub>2</sub>O molecules and indicates that a large number of OH groups are presented on the surface of the MNPs.



**Fig. 2.** FT-IR spectra of catalyst a) Fresh, b) after 3<sup>rd</sup> run.

The XRD pattern of the Fe<sub>3</sub>O<sub>4</sub> MNPs (Fig. 3) showed a series of diffraction peaks at 2θ° of 30.29°, 35.66°, 43.32°, 53.66°, 57.36°, 63.01° and 74.49° which can be assigned to (220), (311), (400), (422), (511), (440) and (620) planes respectively. The diffraction patterns are well matched with the literature [39] and no diffraction peaks of other impurities was observed.

The SEM analysis suggests that the Fe<sub>3</sub>O<sub>4</sub> MNPs are nanocrystalline morphology of the catalyst (Fig. 4). The image of Fe<sub>3</sub>O<sub>4</sub> MNPs clearly indicates that NPs are uniform in the average particle size range of 60±15 nm. These results are in good harmony with the XRD analysis.

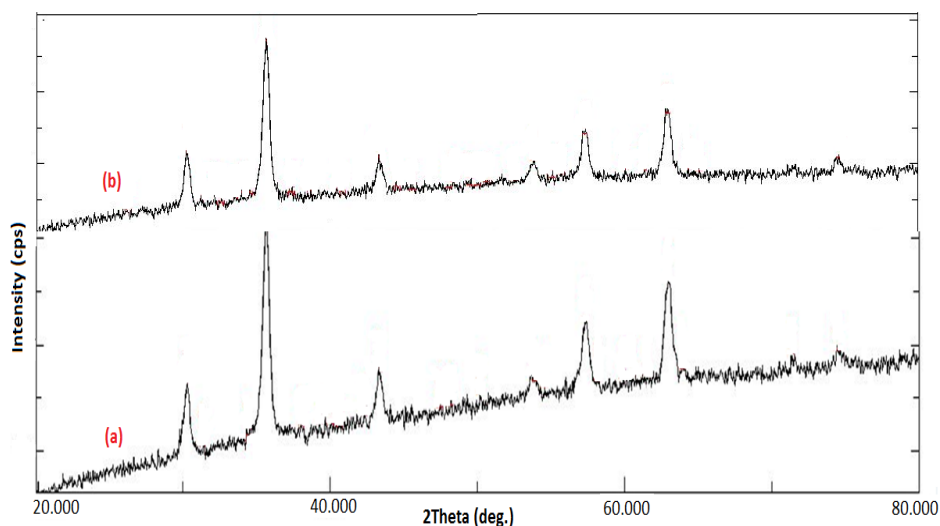


Fig. 3. XRD spectra of catalyst a) Fresh, b) after 3<sup>rd</sup> run.

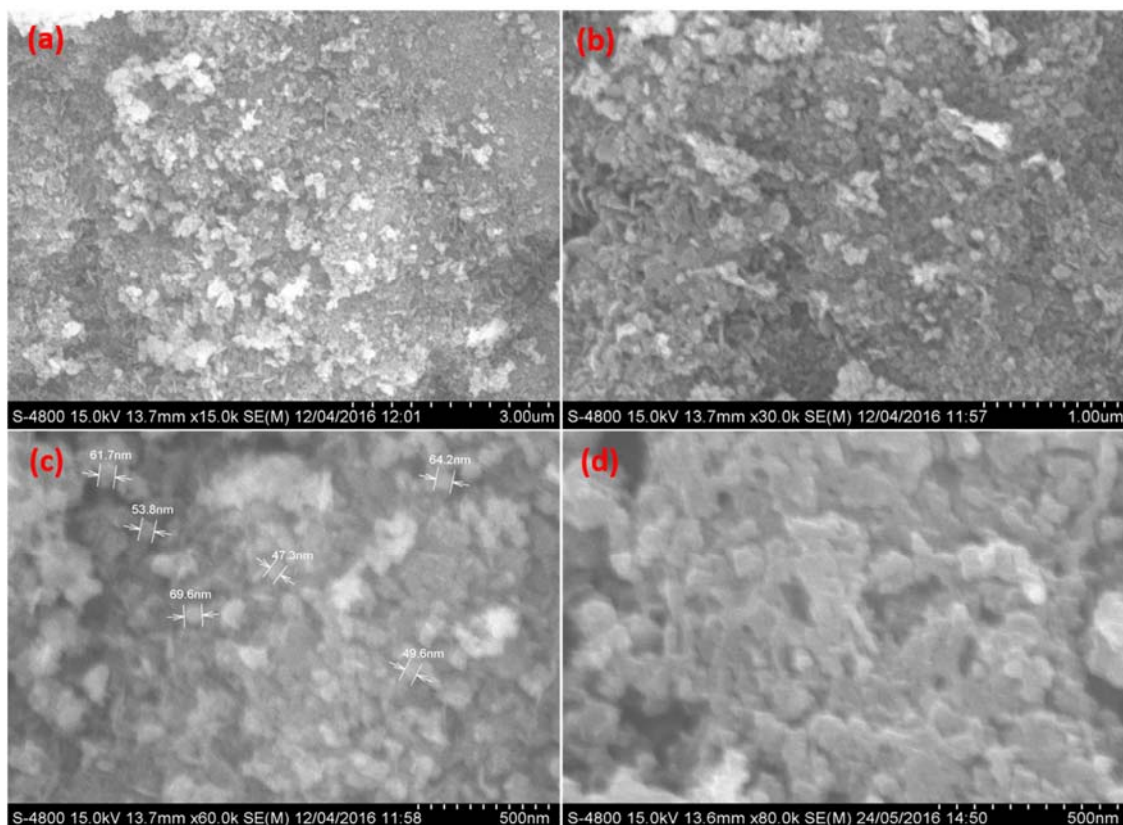
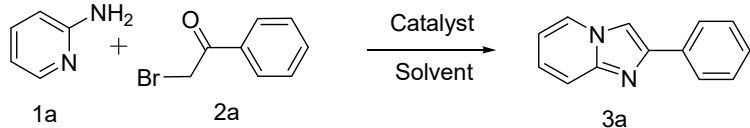


Fig. 4. FEG SEM images of catalyst a-c) Fresh, d) after 3<sup>rd</sup> run.

At the onset of the research, we made a conscious effort to develop a catalytic system that would address the limitations of the previously reported reactions. During the preliminary studies, 2-amino pyridine and phenacyl bromide were used as a model system. A series of experiments were performed to optimize various reaction parameters, such as the catalyst, catalyst loading, solvent, temperature and time (Table 1). Initially we develop the best magnetically separable catalysts; Fe<sub>3</sub>O<sub>4</sub> and MFe<sub>2</sub>O<sub>4</sub> (M= Cu<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup> and Ni<sup>2+</sup>), have been synthesised by thermal decomposition and were subsequently screened for the model system of reaction. Among the catalysts examined, nano-Fe<sub>3</sub>O<sub>4</sub> was found to be the best, providing excellent yields of the desired product 3a (Table 1, entries 1-8). We further

studied catalysts concentration ranging from 5 to 12 mol%; increasing the catalyst loadings from 5 to 10 mol% raises the yield of product 3a up to 91%, Further increase of catalyst concentration to 12 mol% did not improve the yield of 3a (Table 1 entries 8-10). As the solvent has an impact on the overall process, the effect of various solvents (Table 2, entries 1-6) were examined; the best results was obtained with ethanol which afforded 3a in 91% yield (Table 2 entry 1). We also studied the effect of the temperature and the study showed that the yield 3a increases with increasing reaction temperature from 60°C to reflux (Table 2 entry 1, 8). The reaction time was optimized at four hours, a further increase of time to 5 hours did not increases the yield of 3a (Table 1 entry 8, 10).

**Table 1.** Effect of reaction parameters on the imidazopyridine synthesis reaction.<sup>a</sup>



Entry	Catalyst	Catalyst loading (mol %)	Time (h)	Yield (%) <sup>b</sup>
1	None	--	5	43
2	Bulk Fe <sub>3</sub> O <sub>4</sub>	10	5	76
3	Bulk MnFe <sub>2</sub> O <sub>4</sub>	10	5	67
4	Bulk NiFe <sub>2</sub> O <sub>4</sub>	10	5	72
5	Bulk CuFe <sub>2</sub> O <sub>4</sub>	10	5	61
6	Bulk ZnFe <sub>2</sub> O <sub>4</sub>	10	5	68
7	Nano Fe <sub>3</sub> O <sub>4</sub>	10	5	91
<b>8</b>	<b>Nano Fe<sub>3</sub>O<sub>4</sub></b>	<b>10</b>	<b>4</b>	<b>91</b>
9	Nano Fe <sub>3</sub> O <sub>4</sub>	5	5	82
10	Nano Fe <sub>3</sub> O <sub>4</sub>	12	5	91

<sup>a</sup>Reaction conditions: 2-Aminopyridine (1mmol), Phenacyl bromide (1mmol), ethanol (5mL) at reflux temperature.

<sup>b</sup>Isolated yields.

**Table 2.** Effect of solvent, temperature and time on model reaction.<sup>a</sup>

Entry	Solvent	Temp (°C)	Time (h)	Yield (%) <sup>b</sup>
<b>1</b>	<b>Ethanol</b>	<b>reflux</b>	<b>4</b>	<b>91</b>
2	Acetonitrile	reflux	4	81
3	Methanol	reflux	4	54
4	Chloroform	reflux	4	48
5	Water	reflux	4	42
6	DMF	100	4	54
7	Ethanol	reflux	3	82
8	Ethanol	60	4	68

<sup>a</sup>Reaction conditions: 2-Aminopyridine (1mmol), Phenacyl bromide (1mmol), nano-Fe<sub>3</sub>O<sub>4</sub> (10 mol %), solvent (5mL).

<sup>b</sup>Isolated yields.

Having optimized reaction conditions in hand, we explore the substrate scope of the ferrite catalysed *N*-fused heterocycles synthesis by using 2-aminopyridine, 2-aminothiazole or 2-aminobenzothiazole with various substituted phenacyl bromides containing different functional groups. We observed that electron donating and also electron withdrawing substituents provide remarkable yield of products. Gratifyingly this protocol tolerated a variety of common functional groups such as alkyl, ether, halogen and nitro groups regardless of the positions. The results of these reactions are summarized in Table 3.

In order to make our catalytic system more economical, we focused on the reusability of the nano-Fe<sub>3</sub>O<sub>4</sub> catalysts in this cyclisation reaction. The catalysts exhibited remarkable activity observed in all four recycles. After completion of the reaction according to TLC, the reaction mixture was diluted with ethyl acetate. The external magnet was touched to wall of the sealed tube and the reaction mixture was decanted into the small beaker. The catalyst was washed with ethanol (3×5 ml) and dried for 1 h at 120 °C in an oven. Then the catalyst was used directly in the reusability studies. The catalyst was recycled four times (The yields were 91, 86, 81 and 73 %, respectively) and gave constant yields. The third run of recycling catalyst (before fourth run), we have analysed the catalyst by FTIR, XRD and FESEM analysis. All of these analyses clearly match with fresh catalyst.

To determine the ability of nano-Fe<sub>3</sub>O<sub>4</sub> in preparation of imidazopyridine, the efficiency of nano-Fe<sub>3</sub>O<sub>4</sub> for the reaction of 2-Aminopyridine with Phenacyl bromide was compared with previously reported catalysts in the literature, and results are presented in Table 4. Thus, this procedure with nano-Fe<sub>3</sub>O<sub>4</sub> as the catalyst seems superior to other recently reported synthetic methods.

#### 4. Conclusions

We have reported the synthesis of N-bridge fused heterocyclic compounds. In this method, ferrite catalysed two C-N bond formations are the crucial steps for heterocyclisation to deliver the N-fused heterocyclic scaffold. Notably, the current process provides a simple, efficient, environmentally benign and practical route for facial access to valuable azaheterocycles in good yields.

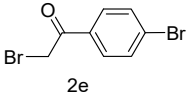
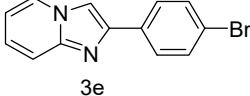
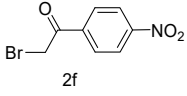
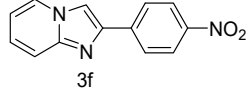
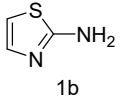
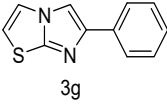
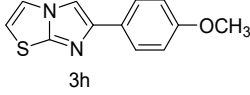
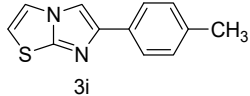
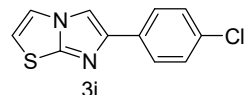
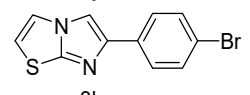
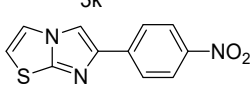
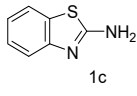
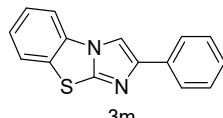
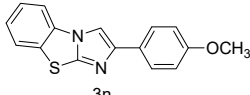
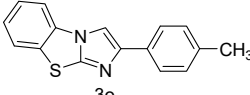
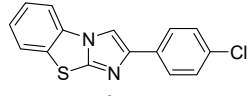
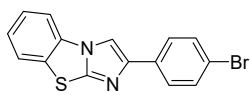
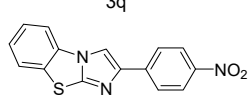
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**Table 3.** Nano-Ferrite catalyzed synthesis of **3a-r**.<sup>a</sup>

Entry	Azole (1)	Phenacyl Bromide (2)	Product (3)	Yield <sup>b</sup> (%)	m.p. (°C)		Ref.
					Found	Reported	
1				91	128-130	129-131	[22]
2	1a			86	132-134	132-134	[22]
3	1a			89	134-136	135-136	[22]
4	1a			90	204-206	206-208	[21]

Table 3. (Continued).

5	1a			84	212-214	214-216	[21]
6	1a			87	204-206	203-207	[21]
7		2a		84	148-150	148-150	[40]
8	1b	2b		82	156-158	154-156	[40]
9	1b	2c		86	142-144	147-149	[40]
10	1b	2d		88	162-164	163-165	[40]
11	1b	2e		84	178-180	181-183	[40]
12	1b	2f		88	234-236	280	[41]
13		2a		74	104-106	106	[17]
14	1c	2b		76	180-182	181	[17]
15	1c	2c		70	120-122	124	[17]
16	1c	2d		80	158-160	160	[17]
17	1c	2e		76	166-168	164	[17]
18	1c	2f		76	286-288	284	[17]

<sup>a</sup>Reaction conditions: 2-Aminoazaheterocycle (1 mmol), substituted phenacyl bromide (1 mmol), nano-Fe<sub>3</sub>O<sub>4</sub> (10 mol %), ethanol (5mL) reflux, time 4h.

<sup>b</sup>Isolated yields.

**Table 4.** Comparison of catalytic activity of Nano Fe<sub>3</sub>O<sub>4</sub> with other reported catalysts used for preparation of imidazopyridine.

Entry	Catalyst (Conc.) <sup>a</sup>	Solvent	Temp. (°C)	Time (h)	Yield (%) <sup>b</sup>	Ref.
1	Catalyst free	Ethanol	50	48	71-80	[23]
2	K <sub>2</sub> CO <sub>3</sub> (1equiv.)	Water	RT	4.3	56	[21]
3	Triethyl amine (1 equiv.)	Water	RT	5.1	55	[21]
4	MgO (1equiv.)	Water	RT	2.1	92	[21]
5	Na <sub>2</sub> CO <sub>3</sub> (1.5 equiv.)	1,4-Dioxane-Water (2:1)	Refluxed	22	94	[27]
6	Neutral Al <sub>2</sub> O <sub>3</sub> (10 equiv.)	Solvent free	RT	3	85	[25]
7	<b>Nano Fe<sub>3</sub>O<sub>4</sub> (10 mol%)</b>	<b>Ethanol</b>	<b>Refluxed</b>	<b>4</b>	<b>91</b>	<b>This work</b>

<sup>a</sup>Compare with 1 equivalent 2-Aminopyridine.<sup>b</sup>Isolated yields.

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