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ORIGINAL PAPER

Using magnetic nanoparticles Fe_3O_4 as a reusable catalyst for the synthesis of pyran and pyridine derivatives via one-pot multicomponent reaction

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Abstract An atom-economical, efficient and mild protocol is described for the synthesis of 2-amino-3-cyanopyridine and 2-amino-3-cyano-4*H*-pyran derivatives in the presence of high surface area Fe_3O_4 as a highly effective heterogeneous catalyst via one-pot multicomponent cyclocondensation reaction.

Keywords Pyran · Pyridine · Magnetic nanoparticles Fe_3O_4 · Multicomponent reaction · Recyclable catalyst · Green chemistry

Introduction

The development of efficient methods for the construction of poly-functionalized heterocyclic compounds has allocated a broad area of organic and medicinal chemistry [1]. Among heterocyclic compounds, 2-amino-3-cyano derivatives have recently received considerable attention due to their potential biological and pharmaceutical activities [2, 3]. 2-amino-3-cyanopyridine and 2-amino-3-cyano-pyran derivatives are one of the most prevalent heterocyclic molecular frame works found in natural products, pharmaceuticals, vitamins, and functional materials [4–7].

Besides, they are useful intermediates [8, 9] and exhibit significant activity as potential antitumor agents, smooth muscle cell proliferation inhibitors, and useful for treatment for intestinal cystitis [10–12].

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In recent years, several methods and developments have been reported for the synthesis of pyran and pyridine [13–17] derivatives; each has its own merits and drawbacks. Many of the standard procedures require long reaction times, harsh reaction conditions, expensive and toxic reagents, solvents, and tedious work-up procedures. Moreover in some cases, a mixture of products is obtained, needing cost-effective column chromatography, naturally resulting in low yields. Heterogeneous catalysis is of supreme importance in many areas of the chemical and energy consuming industries [18, 19].

Conducting the reactions, using heterogenous catalysts should compensate some of drawbacks observed in previously reported reactions. In this kind of reaction, the catalyst can be separated by filtration. However, it is worthy to mention in spite of several advantages, experienced, practically in using of heterogenous catalysts, due to the nano-sized particles used, few limitations to the sustainability are observed [20].

To get around these problems, the use of a heterogeneous catalyst which can be separated practically other than filtration is desirable. Magnetite nanoparticles (Fe_3O_4) have attracted much attention in the past decade, due to their unique features, including, low preparation cost, high thermal and mechanical stability, and adaptability for large-scale production. In addition, their paramagnetic nature allows their facile and effective separation from the reaction mixture, without using standard filtration, required in separation of heterogeneous catalysts. Magnetite nanoparticles (Fe_3O_4) can be easily separated from reaction mixture by using just an external magnet [21].

Thus, in recent years, nano-Fe_3O_4 [22] has attracted a great attention as heterogeneous catalyst [23] due to its simple handling, easy of recovery with an external magnetic field [24, 25]. Magnetic nanoparticles (MNPs) have

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emerged as viable alternatives to conventional materials, as robust, readily available, oxidative stability, biological compatibility, and high catalytic activities in various organic transformations [26–31].

The nano-sized particles increase the exposed surface area of the active component of the catalyst [32, 33], thereby enhancing the contact between reactants and catalyst dramatically [34–38]. These nano-catalyst bridge the gap between homogeneous and heterogeneous catalysis [39], thus preserving the desirable attributes of both systems [40, 41].

Multicomponent reactions (MCRs) [42, 43] have received substantial consideration from the organic community for their innumerable advantages over conventional multistep synthesis [44, 45]. The formation of C–N [46] and C–O [47] bonds by MCRs, which are becoming powerful tools in the modern synthetic chemistry due to their efficiency, atom economy, and convenience in one-pot processes [48].

Recently, we have used nano-Fe_3O_4 as an efficient and easily separable catalyst in different organic reactions [49–51].

In this paper, we wish to report a convenient, green, practical and efficient approach for the synthesis of 2-amino-3-cyanopyridine and 2-amino-3-cyano-4*H*-pyran derivatives via one-pot MCRs using nano-sized magnetic Fe_3O_4 as heterogeneous catalyst.

Experimental

General

Chemicals and solvents were purchased from Merck–Aldrich and used directly with high-grade quality, without any purification. TLC analyses were done using precoated TLC silica gel 60 F_{254} (Merck) plates. Melting points were measured using a capillary tube method with a Barnstead Electrothermal 9200 apparatus. FT-IR spectra were recorded using KBr disks on FT-IR Bruker Tensor 27 instrument in the 500–4000 cm^{-1} region. The vibrational transition frequencies are reported in wave numbers (cm^{-1}). Band intensities are assigned as weak (w), medium (m), and strong (s). All yields refer to isolated products.

Synthesis of catalyst

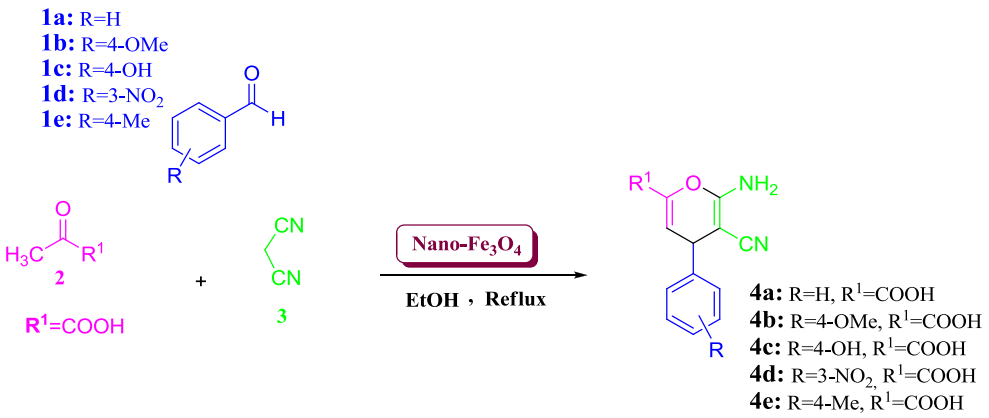
Magnetic nanoparticles Fe_3O_4 were synthesized via a co-precipitation method as described previously [52–55] and applied to the following MCRs as a catalyst.

Synthesis of 2-amino-3-cyano-4*H*-pyran derivatives (4a–4e): general procedure

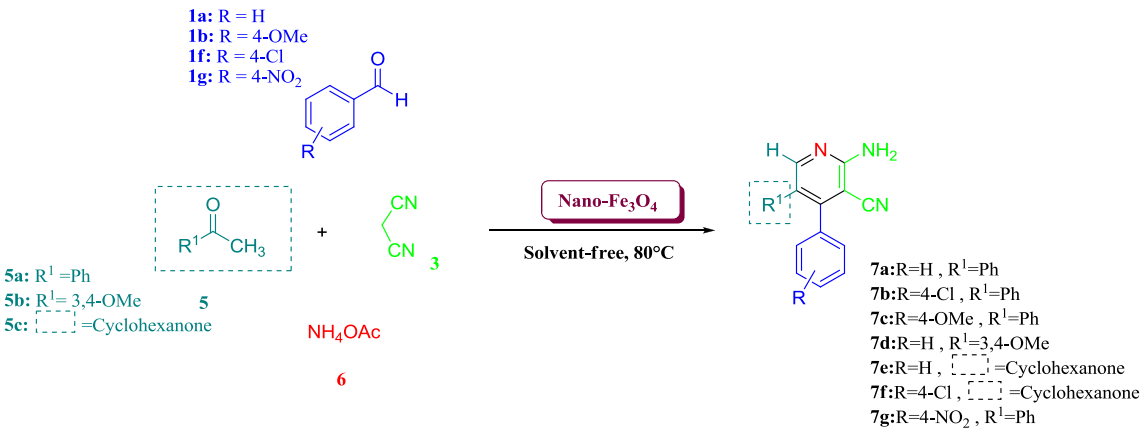
A mixture of an appropriate aromatic aldehyde (1.0 mmol), pyruvic acid (1.0 mmol), and malononitrile (1.2 mmol) was dissolved in ethanol (15 ml). Fe_3O_4 nano-catalyst (0.03 g) was then added to this mixture. This mixture was stirred under reflux. The progress of reaction was monitored by TLC (7:3, n-hexane/ethyl acetate). Upon completion of the reaction, the mixture was cooled to room temperature. Then the catalyst was separated from this mixture by an external magnet and washed with hot acetic acid (5 ml) and ethanol (5 ml), dried in oven, and stored for use in subsequent run under the same conditions. The remaining solution is concentrated to give of 2-amino-3-cyano-4*H*-pyrans as a crude. This crude was crystallized from acetic acid to obtain the pure products. (**4b–e**) (Table 4) (Scheme 1).

Synthesis of 2-amino-3-cyanopyridine derivatives (7a–7g): general procedure

A mixture of an appropriate aromatic aldehyde (1.0 mmol), acetophenone (1.0 mmol), malononitrile (1.0 mmol), ammonium acetate (1.5 mmol), and Fe_3O_4 (0.04 g) was



Scheme 1 Synthesis of 2-amino-3-cyano-4*H*-pyran derivatives (**4a–e**)



Scheme 2 Synthesis of 2-amino-3-cyanopyridine derivatives (**7a–g**)

heated under stirring at 80 °C in an oil bath in solvent-free conditions. The progress of the reaction was monitored by TLC (7:3, n-hexane/ethyl acetate). After completion of the reaction (as indicated in Table 7), the mixture was cooled to room temperature. Then the catalyst was separated from this mixture by an external magnet and washed with hot acetic acid (5 ml) and ethanol (5 ml), dried in oven, and stored for use in subsequent run under the same conditions. The remaining solution is concentrated under reduced pressure to give of 2-amino-3-cyanopyridine as a crude. This crude was crystallized from ethanol to afford the pure products. (**7b–g**) (Table 7) (Scheme 2).

Results and discussion

Initially, for the optimization of the reaction conditions, the reaction of benzaldehyde (**1a**), pyruvic acid (**2**), and malononitrile (**3**) was chosen as a model and was examined under a variety of conditions. Firstly, we used diverse catalysts such as SMI-SO_3H, sulfamic acid, $H_6P_2Mo_{18}O_{62}$, and nano-Fe_3O_4 and also tested the un-catalyzed reaction. The un-catalyzed reaction proceeded sluggishly, monitored the reaction by TLC analysis, and after long reaction time gave **4a** in low yield. Among the catalysts tested, nano-Fe_3O_4 gave the highest yield of **4a** (Table 1, entries 3). The other catalysts examined such as sulfamic acid and $H_6P_2Mo_{18}O_{62}$ were also effective (Table 1, entries 1 and 2). As a result, Fe_3O_4 nano-catalyst was considered as a catalyst of choice to synthesize different derivatives in order to establish the generality of the method. It shows a higher reactivity, and requiring short reaction time. We next investigated the effect of solvents, such as H_2O, CH_3CN, EtOH, and also solvent-free condition for the synthesis of **4a** (Table 2). As it can be seen in Table 2, ethanol was the best solvent regarding the reaction yield (Table 2, entry 2). Additionally, the influence of amount of catalyst and temperature on the progress of model reaction was investigated (Table 3). Consequently, as it can be seen in Table 3, the best result was obtained when 0.03 g of catalyst was used (Table 3, entry 2). Under the optimized reaction conditions concluded, various substituted benzaldehydes were reacted with pyruvic acid and malononitrile in the presence of nano-Fe_3O_4 in refluxing ethanol. All reactions proceeded to completion within 1–1.5 h, and 4*H*-pyrans were isolated in excellent yields. The selected 2-amino-3-cyano-4*H*-pyran derivatives

Table 1 Synthesis of **4a** in the presence of different catalysts in reflux condition

Entry	Catalyst (0.05 g)	Time (min)	Yield (%)[a]
1	Sulfamic acid	180	81
2	$H_6P_2Mo_{18}O_{62}$	60	85
3	Fe_3O_4 NPS	60	91
4	Fe_3O_4 bulk	80	60
5	SMI-SO_3H	180	59
6	–	240	Trace

1.0 mmol (**1a**), 1.0 mmol (**2**), and 1.2 mmol (**3**) in the presence of 0.05 g of catalyst and 4 ml of EtOH

[a] Refers to the isolated yield

Table 2 Synthesis of **4a** in the presence of different solvents

Entry	Solvent	Time (min)	Temperature (°C)	Yield (%)[a]
1	H_2O	180	Reflux	80
2	CH_3CH_2OH	60	Reflux	91
3	CH_3CN	360	Reflux	Trace
4	–	180	100	69

1.0 mmol (**1a**), 1.0 mmol (**2**), and 1.2 mmol (**3**) in the presence of 0.05 g of catalyst and 4 ml of solvent

[a] Refers to the isolated yield

Table 3 Synthesis of **4a** in the presence of different amounts of catalyst and temperatures

Entry	Catalyst (g)	Temperature (°C)	Yield (%)[a]
1	0.02	Reflux	79
2	0.03	Reflux	91
3	0.04	Reflux	91
4	0.05	Reflux	91
5	0.03	70–80	70
6	0.03	90–100	78
7	0.03	110–120	81

1.0 mmol (**1a**), 1.0 mmol (**2**) and 1.2 mmol (**3**)

[a] Refers to the isolated yield

Table 4 Synthesis of 2-amino-3-cyano-4*H*-pyran derivatives (**4a–e**) under optimized conditions

Entry	Product	Time (min)	Yield (%)[a]	Mp (°C)/Lit. Mp [ref]
1	**4a**	60	91	210–214/216–218 [26]
2	**4b**	55	79	274–276/279 [26]
3	**4c**	80	80	256–259/260–262 [26]
4	**4d**	50	68	236–238/240–241 [27]
5	**4e**	65	70	215–217/218–220 [26]

1.0 mmol (**1a**), 1.0 mmol (**2**), and 1.2 mmol (**3**) in the presence of 0.03 g of catalyst and 4 ml EtOH at reflux condition

[a] Refers to the isolated yield

(**4a–e**) were fully characterized, and their physical data were compared with those of authentic compounds and found to be identical (Table 4) [56, 57].

Encouraged by these results, we also examined the catalytic activity of nano-Fe_3O_4 in the synthesis of 2-amino-3-cyanopyridine derivatives **7a**. We performed a one-pot four component reaction of benzaldehyde, **1a**, acetophenone **5**, malononitrile **6**, ammonium acetate **7** as a model reaction under optimal conditions, concluded from nano-Fe_3O_4 catalyzed synthesis of pyran derivatives. Delightfully, the model reaction in optimal conditions gave 90 % yield for the corresponding pyridine derivative, **7a** (Table 5, entry 3). It is significant to note that when the amount of catalyst was decreased from 0.04 to 0.02 g, an appreciable decrease in the yield was observed (Table 6, entries 4–6). Interestingly, the increment in the amount of catalyst did not show any significant effect on the product yield and reaction time. The analysis of the obtained results indicated that the best condition was achieved by carrying out the reaction in the presence of 0.04 g catalyst in solventless conditions (Table 6, entry 4). To study the influence of temperature, the model reaction was carried out at different temperatures (Table 6). The best yield was observed when the reaction was heated at 80 °C in solvent-free conditions (Table 6, entry 4). To establish, the generality of this methodology, we used various substituted benzaldehydes to obtain (**7a–g**). All compounds were known and their structures were confirmed by comparison of physical and spectral data with those of already reported (Table 7) [58–60].

Table 5 Synthesis of **7a** in the presence of different catalysts at 80 °C

Entry	Catalyst (0.05 g)	Time (h)	Yield (%)[a]
1	Sulfamic acid	4	79
2	$H_6P_2Mo_{18}O_{62}$	1	83
3	Fe_3O_4 NPS	0.5	90
4	Fe_3O_4 bulk	3	60
5	SMI-SO_3H	3	56
6	–	6	Trace

1.0 mmol (**1a**), 1.0 mmol (**5a**), 1.0 mmol (**3**), and 1.5 mmol (**6**) in the presence of 0.05 g catalyst

[a] Refers to the isolated yield

Table 6 Optimization conditions for the synthesis of **7a** in the presence of Fe_3O_4 catalyst

Entry	Product	Solvent	Catalyst (g)	Temperature (°C)	Time (h)	Yield (%)[a]
1	**7a**	H_2O	0.04	Reflux	2.15	80
2	**7a**	CH_3CH_2OH	0.04	Reflux	2	75
3	**7a**	CH_3CN	0.04	Reflux	2.5	80
4	**7a**	–	0.04	80	0.5	90
5	**7a**	–	0.02	80	1.45	83
6	**7a**	–	0.03	80	1.30	85
7	**7a**	–	0.05	80	0.5	90
8	**7a**	–	0.04	60	3	86
9	**7a**	–	0.04	70	0.5	87
10	**7a**	–	0.04	100	0.5	90
11	**7a**	–	0.04	120	0.5	90

1.0 mmol (**1a**), 1.0 mmol (**5a**), 1.0 mmol (**3**), and 1.5 mmol (**6**)

[a] Refers to the isolated yield

Table 7 Synthesis of 2-amino-3-cyanopyridine derivatives (**7a–g**) under optimized conditions

Entry	Product	Time (h)	Yield (%)[a]	Mp (°C)/Lit. Mp [ref]
1	**7a**	2	90	186–187/187–189 [28]
2	**7b**	2.15	83	233–235/234–235 [28]
3	**7c**	2.5	83	181–182/179–181 [29]
4	**7d**	2.5	87	207/209–210 [29]
5	**7e**	2.15	86	230–233/230–232 [30]
6	**7f**	2	83	223–225/224–226 [30]
7	**7 g**	3	82	212–213/210–212 [28]

1.0 mmol (**1a**), 1.0 mmol (**5a**), 1.0 mmol (**3**), and 1.5 mmol (**6**) in the presence of 0.04 g catalyst at 80 °C

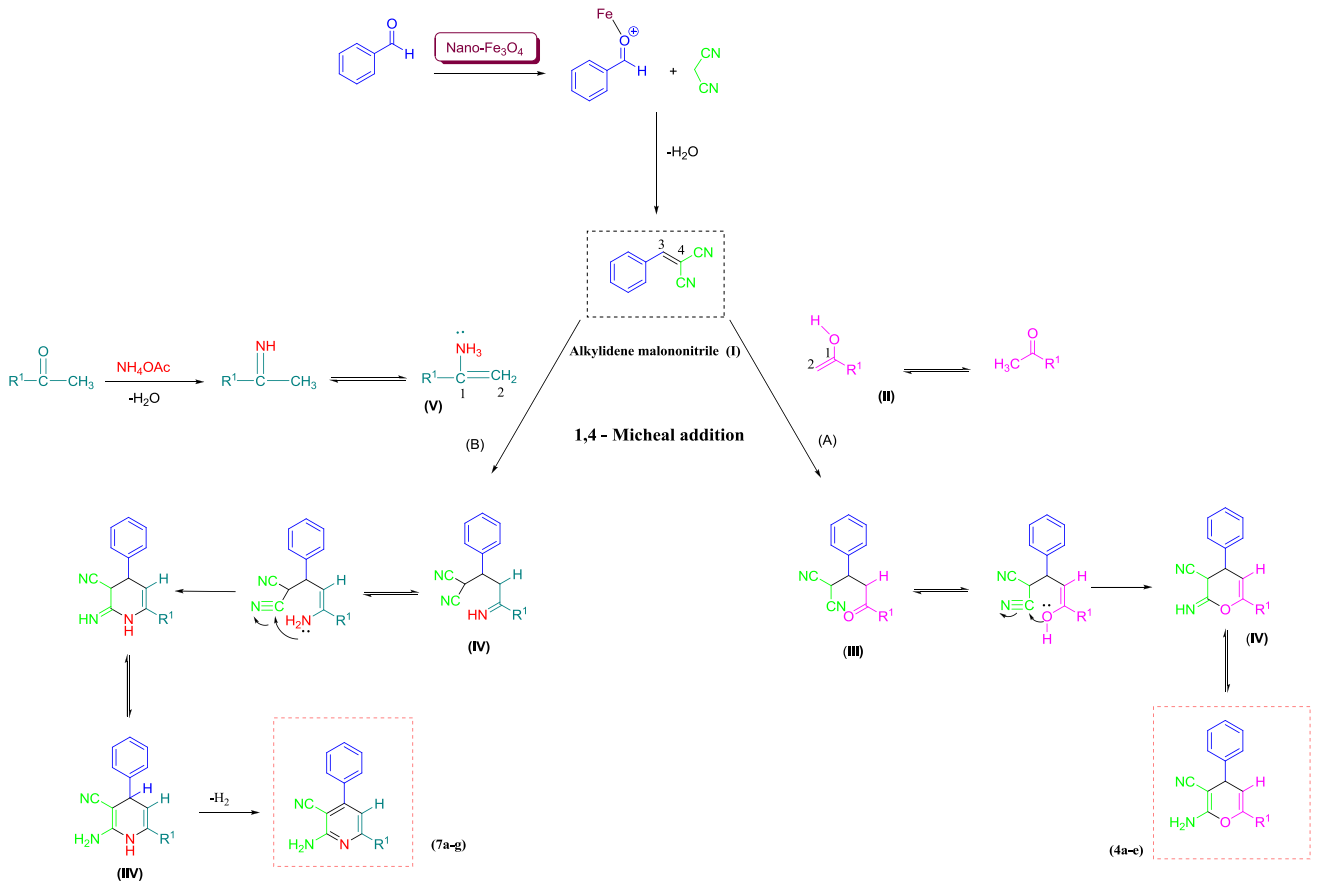
[a] Refers to the isolated yield

A proposed mechanism for the nano-Fe_3O_4-catalyzed formation of 2-amino-3-cyano derivatives is shown in Scheme 3. According to this suggested mechanism, nano-Fe_3O_4 acts as a Lewis acid, playing a significant role in increasing the electrophilic character of the electrophiles. The reaction may proceed via alkylidene malononitrile **I** (generated from condensation of aldehyde with malononitrile). Next via route **A**, the intermediate **III**, formed by the 1,4-Michael addition of tautomerized acetophenone **II** to alkylidene malononitrile **I**. Intermolecular cyclization of this created intermediate **III** affords the desired pyrans (**4a–e**) (Scheme 3) [61].

In similar way, via route **B**, imine **V** (formed from the reaction of an appropriate ketone and ammonium acetate) is added to alkylidene malononitrile **I** via 1,4-Michael addition to give intermediate **VI**, followed by tautomerization and intramolecular cyclization, to afford the intermediate VII which is subjected to oxidative the aromatization of to give the corresponding pyridines (**7a–g**) (Scheme 3) [58].

In practical applications of heterogeneous catalysis, the reusability of the catalyst is important. In this work, we examined the possible recovery and reusability of nano-Fe_3O_4 in the aforementioned reactions.

After completion of the model reactions, the catalyst was recovered from the reaction mixture simply by using an external magnet. The recovered catalyst was suspended in (5 ml) hot acetic acid. This suspension was filtered and washed with diethyl ether and dried. This recovered catalyst was used in both aforementioned reactions. As shown in Fig. 1, the recovered catalyst could be re-used at least 4



Scheme 3 Proposed mechanism of the synthesis of (**4a–e**), (**7a–g**)

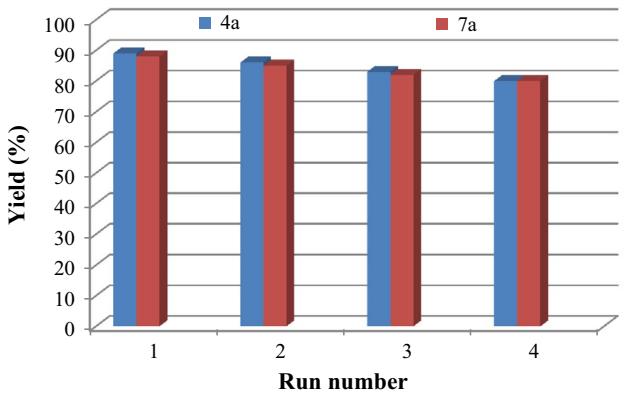


Fig. 1 The recyclability of the Fe_3O_4 in the preparation of **4a** and **7a**

times without a noticeable drop in the product yield and its catalytic activity in the synthesis of **4a** and **7a**. The slight decrease of catalytic activity could be due to the normal loss of the catalyst during the work-up stage (Fig. 1).

Conclusions

In summary, an extremely efficient, mild, facile and economical method for the preparation of poly-functionalized pyridine and pyran derivatives has been developed, via a one-pot MCR, in the presence of high surface area Fe_3O_4 (MNPs) as a highly effective heterogeneous catalyst. The catalysts show environmental friendly character and recyclability, being re-used at least in four consecutive runs without significant loss of catalytic activity. This development in the synthesis of two important heterocyclic systems, in comparison with previously reported methods, not only affords the desired products in excellent yields but also required shorter reaction times. The most important advantage of our protocol is the convenient separation of the commercially purchasable or readily available nano-Fe_3O_4 catalyst from reaction mixture and reusing it in several runs, without appreciable loss of activity.

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