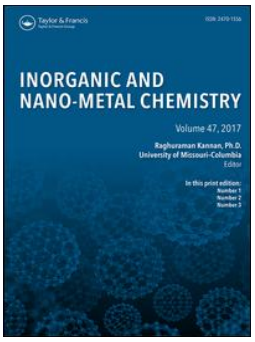

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An expedient and eco-friendly approach for multicomponent synthesis of dihydropyrano[2,3-*c*]pyrazoles using nano-$Al_2O_3/BF_3/Fe_3O_4$ as reusable catalyst

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ABSTRACT

The pyranopyrazole derivatives have many biological activities. They were synthesized *via* a four-component coupling of aromatic aldehyde, malononitrile, ethyl acetoacetate and hydrazine hydrate. In this study, dihydropyrano[2,3-*c*]pyrazoles have been synthesized in the presence of nano-$Al_2O_3/BF_3/Fe_3O_4$ as catalyst in water/ethanol under reflux conditions. The catalyst was removed from the mixture of reaction by an external magnet and was reusable for several times without any loss of its activity. The obtained pyranopyrazoles were characterized by various methods such as FT-IR, ^{1}HNMR and melting point. Easy purification, clean and convenient procedure are some advantages of this method.

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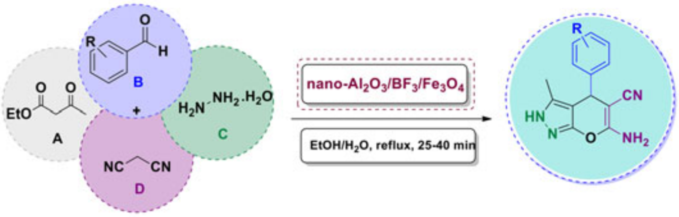
Nano-$Al_2O_3/BF_3/Fe_3O_4$; pyranopyrazole; magnetic catalyst; Lewis acid; multicomponent reaction

GRAPHICAL ABSTRACT



Introduction

The distinctive aspect of multi-component reactions (MCRs) is that the products contain all parts of substrates and creating almost no by-products. Thus, MCRs are an ideal and eco-friendly reaction module by reducing production of waste and energy consumption.[1–3] Final compounds can be obtained with fewer steps, rapidly and in one pot. Therefore, MCRs have been paid attention in modern organic chemistry, such as combinatorial chemistry or medicinal chemistry. So, applications of MCRs are very popular with only a minimum of endeavor and offer a wealth of products.[4,5]

Pyranopyrazole derivatives is getting enormous attention among chemists due to widespread synthetic utilities and potential biological activity[6] such as anticancer,[7] antibacterial,[8] vasodilatory,[9] analgestic properties and Chk1 kinase[10] inhibitory activity and also have acted as insecticidal.[11] Significant attention has been focused on the improvement of new methods for the synthesis of these fused heterocyclic compounds. Most of reported synthetic methods to synthesize pyranopyrazoles implicate the MCR of aldehyde, ethyl acetoacetate, malononitrile and hydrazine hydrate.[6]

Recently, pyranopyrazole synthesis have been promoted by disulfonic acid imidazolium chloroaluminate {[Dsim]$AlCl_4$},[12] γ-alumina,[13] hexadecyltrimethyl ammonium bromide (HTMAB),[14] isonicotinic acid,[15] cinchona alkaloid derivatives,[16] per-6-amino-β-cyclodextrin[17] and silicotungsticacid.[18] Some of these protocols have disadvantages, such as long reaction time, expense and use of toxic organic solvent. Therefore, an important target is the development of effectual, simple and eco-friendly catalysts for the synthesis of pyranopyrazoles.[19–21] Previously, nano-$Al_2O_3/BF_3/Fe_3O_4$ has been synthesized and characterized as a new reusable catalyst.[22] In this study, we wish to report effective and eco-friendly procedure for the synthesis of dihydropyrano[2,3-*c*]pyrazoles in the presence of nano-$Al_2O_3/BF_3/Fe_3O_4$.

Experimental

General

The chemicals were used without any additional purification. The products were characterized by FT-IR, ^{1}H NMR and a comparison of their physical properties with those

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reported in the literature. FT-IR spectra were run on a Bruker, Equinox 55 spectrometer. A Bruker (DRX-400 Avance) NMR was used to record the ^{1}H NMR spectra. Melting points were determined by a Buchi melting point B-540 B.V.CHI apparatus.

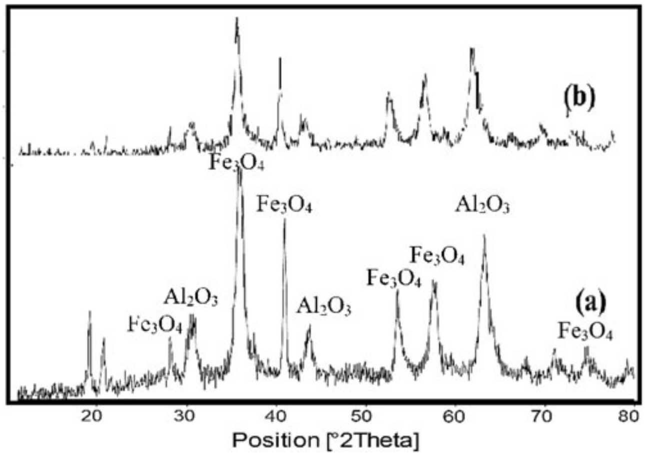


Figure 1. X-ray diffraction (XRD) pattern of (a) fresh and (b) recovered nano-$Al_2O_3/BF_3/Fe_3O_4$.

General procedure for synthesis of dihydropyrano[2,3-c]pyrazoles

A mixture of aromatic aldehyde (1 mmol), malononitrile (0.07 g, 1 mmol), ethyl acetoacetate (0.13 g, 1 mmol), hydrazine hydrate (1.25 mmol) and nano-$Al_2O_3/BF_3/Fe_3O_4$ (0.03 g) has been refluxed in 3 mL water/ethanol (1:2). After completion of the reaction that has been monitored by TLC, the reaction mixture was cooled to room temperature and dissolved in hot ethanol. The catalyst was separated by an external magnet. By adding water to residue, the product was appeared as a pure solid in high yields.

Hot filtration test

A hot filtration test was done to confirm that the nano-catalyst was recoverable heterogeneous one. In this test, a mixture of hydrazine hydrate (1.25 mmol), benzaldehyde (1 mmol), ethyl acetoacetate (1 mmol), malononitrile (1 mmol) and water/ethanol (1:2) (3 mL) was refluxed in the presence of nano-$Al_2O_3/BF_3/Fe_3O_4$ (0.03 g) for 25 min. The catalyst was filtered off from the hot reaction mixture, and the reaction in the filtrate was still monitored. No increase in conversion was observed in the filtrate.

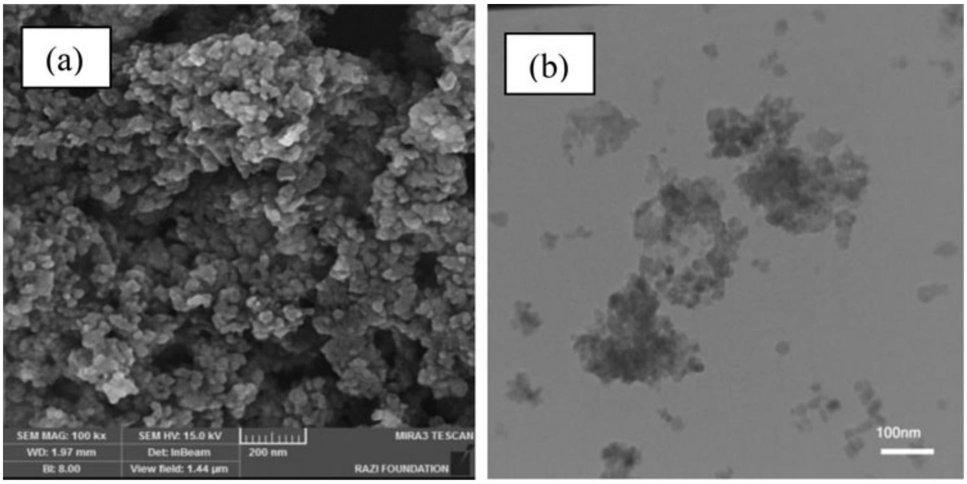
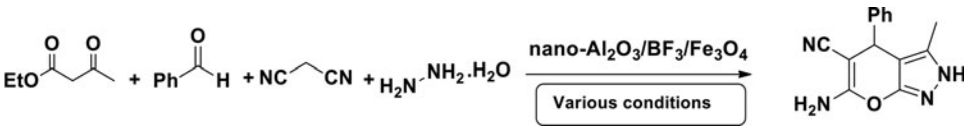


Figure 2. (a) FESEM and (b) TEM image of nano-$Al_2O_3/BF_3/Fe_3O_4$.

Table 1. The condensation reaction of hydrazine hydrate (1.25 mmol), ethyl acetoacetate (1 mmol), malononitrile (1 mmol) and benzaldehyde (1 mmol) in the presence of nano-$Al_2O_3/BF_3/Fe_3O_4$ (0.03 g, 7.3 mol%) under various conditions.



Entry	Solvent	Conditions	Time (min)	Yield[a] (%)
1	solvent-free	R.T.	120	0
2	solvent-free	60 °C	70	40
3	EtOH/H_2O	Reflux	25	90
4	CH_2Cl_2	Reflux	60	15
5	solvent-free	Mixer Mill	15	0
6	EtOH/H_2O	Microwave	5	25
7	EtOH	Ultrasonic	60	35

[a] Isolated yield.

Results and discussion

The XRD pattern of nano-Al_2O_3/BF_3/Fe_3O_4 before and after recycling is shown in Figure 1. The signals at 2θ equal to 37, 45 and 67 are shown nano-γ-Al_2O_3 structure and the values of 2θ equal to 30.27, 35.64, 57.31 and 62.88 with FWHM equal to 0.5510, 0.3936, 0.62298 and 0.6298, respectively, show the existence of Fe_3O_4. Other signal in 2θ equal to 15.73 proves the bonding of flourine to the catalyst backbone. The comparison between XRD pattern of fresh and recovered catalyst shows the high stability of catalyst under reaction conditions.

Table 2. The condensation reaction of hydrazine hydrate (1.25 mmol), ethyl acetoacetate (1 mmol), malononitrile (1 mmol) and benzaldehyde (1 mmol) in the presence of various amounts of nano-Al_2O_3/BF_3/Fe_3O_4.[a]

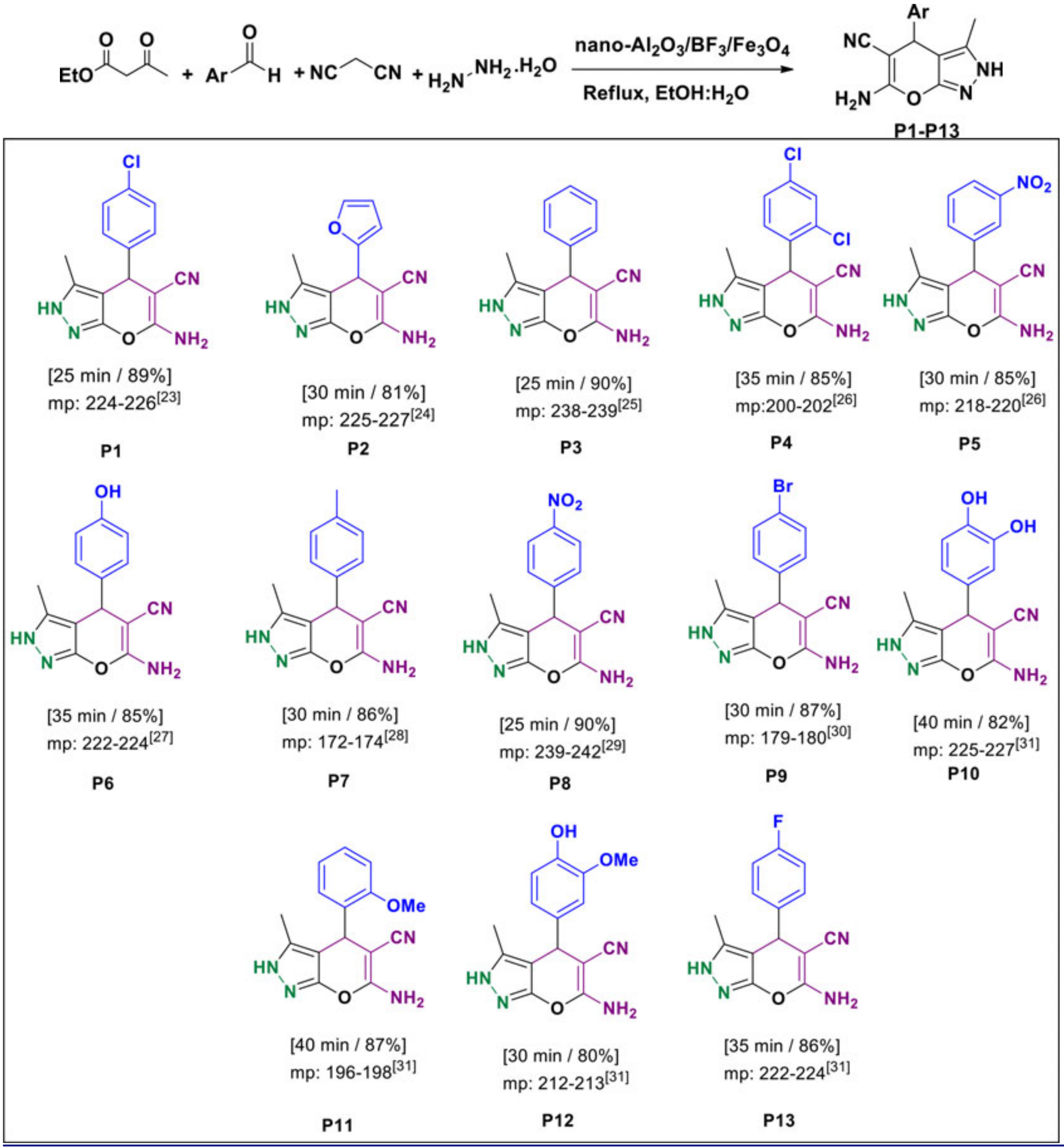
Entry	nano-Al_2O_3/BF_3/Fe_3O_4 (g)	Time (min)	Yield[b] (%)
1	0.007	40	37
2	0.015	30	55
3	0.030	25	90
4	0.040	25	90
5	0.050	25	90
6	0.100	25	88
7	0.150	25	85
8	None	180	None

[a] Condition: reflux in ethanol:H_2O (2:1).
[b] Isolated yield.

In order to investigate the particle size of nano-Al_2O_3/BF_3/Fe_3O_4, FESEM and TEM were measured and presented in Figure 2. In these results, the dimensions of catalyst particles were achieved below 20 nm.

Initially, in order to investigate the activity of nano-Al_2O_3/BF_3/Fe_3O_4 catalyst, in preparation of 6-amino-3-methyl-4-phenyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile, the condensation of benzaldehyde, malononitrile, ethyl acetoacetate and hydrazine hydrate as a model reaction was carried out in the presence of it under various conditions and the results are summarized in Table 1. Among the different conditions screened, ethanol/water gave the product in good yield under reflux condition (Table 1, entry 3).

Table 3. Synthesis of dihydropyrano[2,3-c]pyrazoles derivatives using nano-Al_2O_3/BF_3/Fe_3O_4 in ethanol/water under reflux conditions.[a,b]



[25 min / 89%]
mp: 224-226[23]
P1

[30 min / 81%]
mp: 225-227[24]
P2

[25 min / 90%]
mp: 238-239[25]
P3

[35 min / 85%]
mp:200-202[26]
P4

[30 min / 85%]
mp: 218-220[26]
P5

[35 min / 85%]
mp: 222-224[27]
P6

[30 min / 86%]
mp: 172-174[28]
P7

[25 min / 90%]
mp: 239-242[29]
P8

[30 min / 87%]
mp: 179-180[30]
P9

[40 min / 82%]
mp: 225-227[31]
P10

[40 min / 87%]
mp: 196-198[31]
P11

[30 min / 80%]
mp: 212-213[31]
P12

[35 min / 86%]
mp: 222-224[31]
P13

[a] Isolated yield.
[b] Aldehyde (1 mmol), ethyl acetoacetate (1 mmol), malononitrile (1 mmol), hydrazine hydrate (1.25 mmol) and nano-Al_2O_3/BF_3/Fe_3O_4 (0.03 g).

Other solvent such as CH_2Cl_2 gave the desired products in low yields even after elongated reaction times and also increasing the temperature (Table 1, entry 4). But then, when the reaction was performed under solvent-free conditions in 60 °C, the product was formed in 40% (Table 1, entry 2). Moreover, we have tried to carry out the model reaction using mixer mill, ultrasonic and microwave, but these conditions did not give the product in good yield (Table 1, entries 5–8). To optimize the amount of catalyst and time of reaction, the model reaction was carried out using different amount of catalyst (Table 2).

In the absence of the catalyst, no product was obtained (Table 2, entry 8). On the other hand, by increasing the amount of catalyst the yields of products improved (Table 2, entries 3–7). The highest yield was obtained in 25 min with the use of 0.03–0.05 g of catalyst (Table 2, entries 3–5). Increasing the amount of catalyst up to 0.05 g did not affect observably on the yields of products (Table 2, entries 6, 7). Using nano-Fe_3O_4 as catalyst for promotion of model reaction has produced only 40% yield.

According to the optimized reaction conditions, a variety of aldehydes (containing electron-releasing group or with electron-withdrawing group) have been chosen for synthesis of dihydropyrano[2,3-*c*]pyrazoles in the presence of nano-$Al_2O_3/BF_3/Fe_3O_4$ and the results are presented in Table 3.

A proposed mechanism for preparation of dihydropyrano[2,3-*c*]pyrazoles in the presence of nano-$Al_2O_3/BF_3/Fe_3O_4$ was shown in Scheme 1. BF_3 in nano-$Al_2O_3/BF_3/Fe_3O_4$ as a Lewis acid activates the C=O group in *β*-ketoester and then the pyrazolone formed from the reaction of ethyl acetoacetate and hydrazine hydrate as an intermediate (**5**). In the next step, between aromatic aldehyde and malononitrile, in the presence of catalyst produced compound **6** by Knoevenagel condensation. Ultimately, Michael addition reaction between **5** and **6**, intramolecular cyclization, and aromatization, the desired pyranopyrazole was prepared.

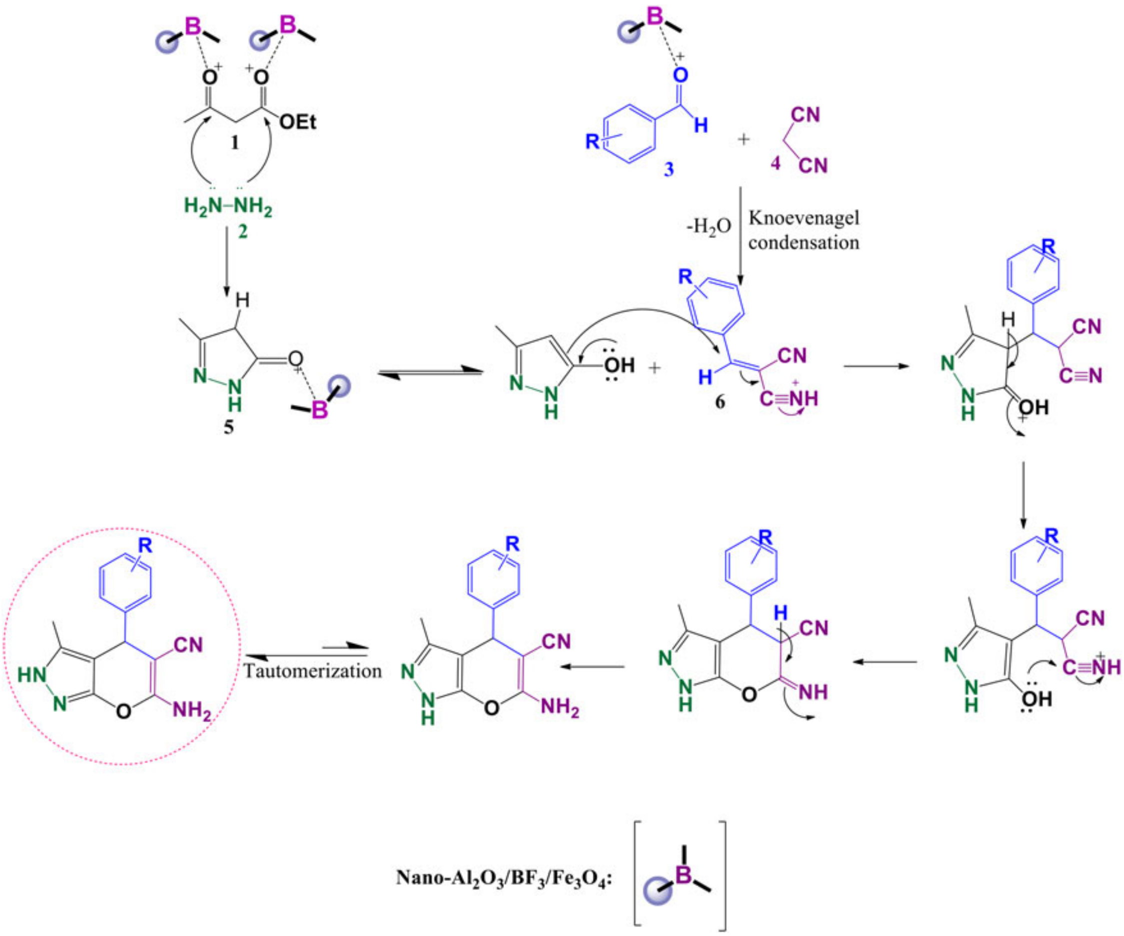
The separated nano-catalyst was reused in the mentioned reaction five times with only a slight decrease in its catalytic activity (Figure 3). Partial loss of activity may be due to blockage of active sites of the catalyst.

As presented in Table 4, the use of nano-$Al_2O_3/BF_3/Fe_3O_4$ resulted in an improved method in terms of reaction time, compatibility with environment, and yield when compared with other reported catalysts. Our reported catalyst has TOF equal to 27.4 h^{-1} and is better than many others.

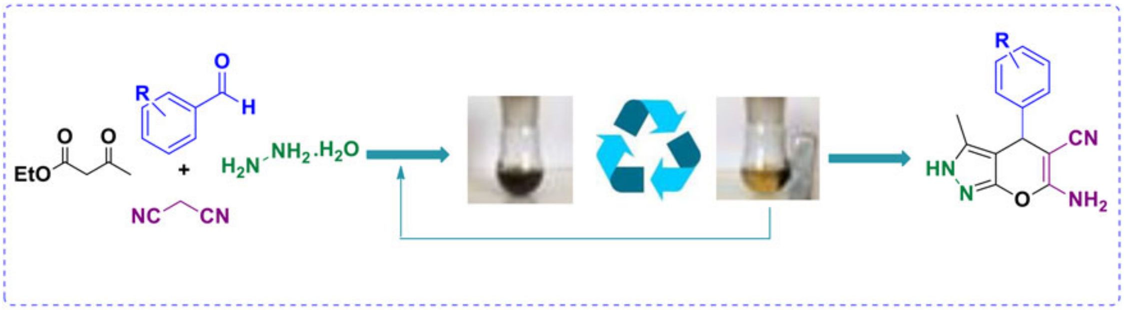
Spectral data for selected compounds

6-Amino-4-(2,4-dichlorophenyl)-3-methyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (Table 3, P4):

Pale yellow solid. M.p. 200–202 °C. FT-IR (ATR)/ῡ(cm^{-1}): 3482, 3243, 3115, 2186, 1638, 1587, 1491, 1408, 1100, 1052, 866, 741.; ^{1}H-NMR (400 MHz, DMSO-d_6)/*δ*



Scheme 1. Proposed mechanism for preparation of dihydropyrano[2,3-c]pyrazoles in the presence of nano-$Al_2O_3/BF_3/Fe_3O_4$.



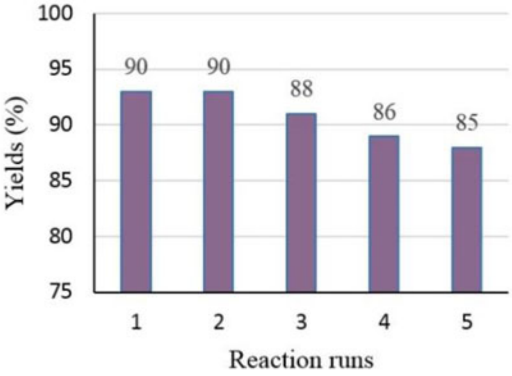


Figure 3. Catalyst recycling experiment.

Table 4. Synthesis of dihydropyrano[2,3-c]pyrazoles in the presence of previously reported catalysts.[a]

Entry	Catalyst (mol%)	Solvent	Conditions	Time (h)	Yield[b] (%)[Ref.]	TOF (h^{-1})
1	CTACl (20)*	H_2O	90 °C	4	88[30]	1.1
2	Isonicotinic acid (10)*	–	85 °C	0.16	90[15]	56.2
3	MorT (10)*	EtOH/H_2O	Reflux	9	92[31]	1.02
4	γ-Alumina (30)**	H_2O	Reflux	0.51	90[13]	5.9
5	$Ba(OH)_2$ (10)***	H_2O	Reflux	1.5	93[32]	6.2
6	Nano-$Al_2O_3/BF_3/Fe_3O_4$ (7.3)	EtOH/H_2O	Reflux	0.45	90[this work]	**27.4**

[a]The used aldehyde: *benzaldehyde, **4-chlorobenzaldehyde, ***3,4,5-trimethoxy benzaldehyde.

ppm: 1.85 (s, 3 H), 5.13 (s, 1 H), 7.07 (s, 2 H), 7.29 (d, $J=8$ Hz, 1 H), 7.47 (dd, $J=8.4$ Hz, $J=2$ Hz, 1 H), 7.65 (d, $J=2.4$ Hz, 1 H), 12.23 (s, 1 H).; 13C NMR (100 MHz, DMSO-d_6)/δ ppm: 161.30, 154.88, 140.07, 135.44, 132.81, 132.10, 128.83, 128.02, 120.25, 96.32, 55.21, 33.07, 9.53.

6-Amino-3-methyl-4-(3-nitrophenyl)-1,4-dihydropyrano [2,3-c]pyrazole-5-carbonitrile (Table 3, P5):

White solid. M.p. 218–220 °C. FT-IR (ATR)/ῡ(cm^{-1}): 3484, 3231, 3120, 2190, 1645, 1597, 1519, 1491, 1410, 1351, 733. ^{1}HNMR (400 MHz, DMSO-d_6)/δ (ppm): 1.82 (s, 3 H), 4.89 (s, 1 H), 7.08 (s, 2 H), 7.64–7.70 (m, 2 H), 8.04 (s, 1 H), 8.13-8.15 (d, $J=8$ Hz, 1 H), 12.23 (s, 1 H).; 13C NMR (100 MHz, DMSO-d_6)/δ ppm: 161.63, 155.17, 148.36, 147.32, 136.38, 134.88, 130.47, 122.33, 121.01, 97.15, 56.59, 36.11, 10.25.

6-Amino-3-methyl-4-(4-nitrophenyl)-1,4-dihydropyrano [2,3-c]pyrazole-5-carbonitrile (Table 3, P8):

White solid. M.p. 239–242 °C. FT-IR (ATR)/ῡ(cm^{-1}): 3475, 3227, 3106, 2195, 1646, 1592, 1513, 1399, 1348, 1163, 1109, 810, 744.; ^{1}H-NMR (400 MHz, Acetone-d_6)/δ ppm: 2 (s, 3 H), 4.88 (s, 1 H), 6.30 (br s, 2 H), 7.55 (d, $J=8$ Hz, 2 H), 8.23 (d, $J=8$ Hz, 2 H), 11.43 (s, 1 H). 13CNMR (100 MHz, DMSO-d_6)/δ ppm: 161.62, 155.15, 152.59, 146.85, 136.36, 132.19, 129.32, 124.38, 120.98, 97.04, 56.37, 36.36, 10.22.

Conclusion

In summary, we have reported an expedient protocol for the preparation of pyranopyrazole derivatives catalyzed by nano-$Al_2O_3/BF_3/Fe_3O_4$ as reusable catalyst under reflux condition in ethanol/water. Meanwhile, some advantage of the presented methodology are low cost, easy work up, simplicity of operation, efficiency, high yields, environmentally benign conditions and short reaction time.

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