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FULL PAPER

Synthesis of pyrano[2,3-*c*]pyrazole derivatives using Fe_3O_4@SiO_2@piperidinium benzene-1,3-disulfonate (Fe_3O_4@SiO_2 nanoparticle-supported IL) as a novel, green and heterogeneous catalyst

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A simple, green and efficient protocol for the one-pot four-component synthesis of pyrano[2,3-*c*]pyrazole derivatives produced from reaction between aryl aldehydes, ethyl acetoacetate, malononitrile and hydrazine hydrate in the presence of nano magnetic piperidinium benzene-1,3-disulfonate was synthesized in water at 60 °C. The Fe_3O_4@SiO_2 nanoparticle-supported IL was designed and synthesized. The present process offers advantages such as clean reaction, short reaction time, good to excellent yield, easy purification and easy recoverable catalyst.

KEYWORDS
Fe_3O_4@SiO_2@piperidinium benzene-1,3-disulfonate, pyrano[2,3-*c*]pyrazole, water solvent

1 | INTRODUCTION

Green chemistry methods continue to progress in important and alternative procedures which aim to conserve resources and reduce costs.[1–3] The focus on green chemistry using environmentally benign mixtures and conditions is one of the most appealing developments in the synthesis of generally used organic compounds.[4] Catalysts supported on magnetic nanoparticles (MNPs), usually iron oxides, can be quickly and easily recovered by external magnetic fields for recycling.[5] The method of magnetic separation, taking advantage of magnetic nano particles, is generally more efficient than filtration or centrifugation as it inhibits loss of the catalyst. The magnetic separation of MNPs is cost-effective and favourable for industrial applications.[6] Presently, abundant investigation is focused on the synthesis of magnetic core-shell structures using coating a SiO_2 shell around preformed NPs.[7] Moreover, the rational design and combination of ionic liquids and magnetic nano particles affords new ionic liquid stabilized on magnetic nano particles (MNPs@ILs) with desirable properties. Therefore, knowledge-based and multifunctional systems can be prepared in good accordance with green chemistry disciplines.[8]

Multi-component reactions (MCRs) play an important part in combinatorial chemistry because of the ability to synthesize compounds purposefully with higher productivity and atom economy by generating structural complexity in a single step from four reactants.[9–11] In addition, MCRs offer the advantage of simplicity and synthetic efficacy over typical chemical reactions. Moreover, the magnetic properties completely recover catalysts by means of an external magnetic field. These advantages become greater if such reactions can be conducted in aqueous media.[12] Pyrano[2,3-*c*]pyrazoles are joined to heterocyclic compounds that possess many biological properties such as fungicidal,[13] bactericidal,[14] vasodilator activities[15] and act as anticancer agents.[16] They also find application as pharmaceutical ingredients and biodegradable agrochemicals.[17,18] Pyrano[2,3-*c*]pyrazoles were first synthesized by a reaction between 3-methyl-5-pyrazolone with tetracyanoethylene.[19]

Herein, we have designed, synthesized and characterized a green Fe_3O_4@SiO_2@piperidinium benzene-1,3-disulfonate and we used it for the synthesis of 6-amino-4-(4-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazoles *via* the one-pot four

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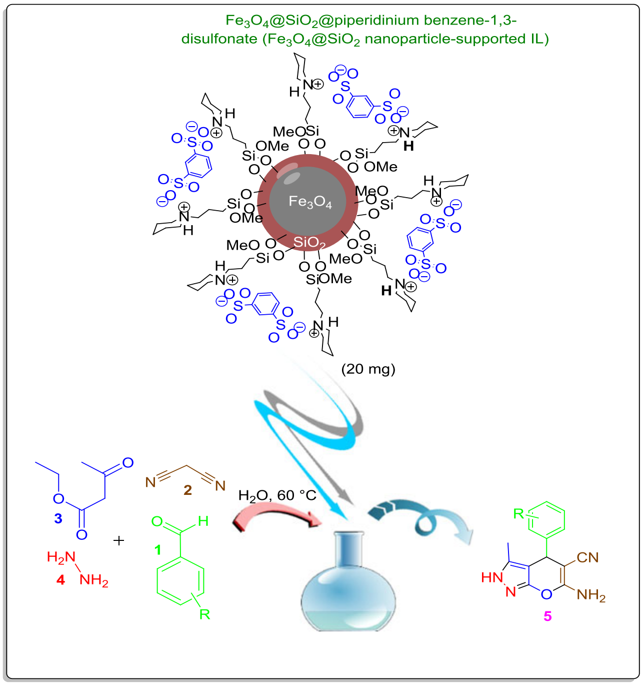
component condensation reaction between aryl aldehydes, ethyl acetoacetate, malononitrile and hydrazine hydrate in water solvent at 60 °C and employed it for the synthesis of pyrano[2,3-*c*]pyrazole derivatives in water solvent at 60 °C (Scheme 1).



SCHEME 1 Synthesis of 6-amino-4-(4-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazoles using Fe_3O_4@SiO_2@piperidinium benzene-1,3-disulfonate as a catalyst

2 | RESULTS AND DISCUSSION

2.1 | Application of Fe_3O_4@SiO_2@piperidinium benzene-1,3-disulfonate

The Fe_3O_4@SiO_2@piperidinium benzene-1,3-disulfonate was produced as reported in our previous research.[20] To optimize the reaction conditions, the condensation reaction of 4-chlorobenzaldehyde with ethyl acetoacetate, malononitrile and hydrazine hydrate was selected as a typical and different amount of Fe_3O_4@SiO_2 nanoparticle-supported IL in a range of 25–90 °C and the optimization was confirmed in water solvent (Table 1). As exposed in Table 1, the best results were obtained when the reaction was achieved using 20 mg of nano magnetic catalyst at 60 °C (Table 1, entry 9). No improvement was detected in the yield of reaction *via* increasing the amount of the catalyst and temperature (Table 1, entries 10–12). Table 1 obviously shows that in the absence of Fe_3O_4@SiO_2 nanoparticle-supported IL, the product was made in low efficiency (Table 1, entries 1 and 2).

To compare the result of the solution with that of water solvent, a mixture of 4-chlorobenzaldehyde with ethyl acetoacetate, hydrazine hydrate and malononitrile as a model using 20 mg of Fe_3O_4@SiO_2 nanoparticle-supported IL in numerous solvents such as H_2O, C_2H_5OH, CH_3CN, CH_3CO_2Et, CH_2Cl_2 and toluene was studied at 60 °C. The results are presented in Table 3. As it can be seen in Table 2, water is clearly the best selection for this reaction. Another purpose for choosing water as a solvent for this

TABLE 1 The effect of quantity of the catalyst and temperature on the synthesis of 6-amino-4-(4-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazoles in water solvent[a]

Entry	Catalyst loading (mg)	Reaction temperature (°C)	Reaction time (min)	Yield[b] (%)
1	—	r.t.	60	10
2	—	90	60	15
3	5	r.t.	10	60
4	5	90	10	65
5	10	r.t.	10	65
6	10	60	8	70
7	10	90	8	75
8	20	r.t.	8	82
9	20	60	8	98
10	20	90	8	98
11	30	r.t.	8	85
12	30	60	8	98

Reaction conditions:

[a] 4-Chlorobenzaldehyde (1 mmol), ethyl acetoacetate (1 mmol), hydrazine hydrate (1 mmol), malononitrile (1 mmol);

[b] Isolated yield.

TABLE 2 The effect of numerous solvents on the synthesis of 6-amino-4-(4-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazoles at 60°C[a]

Entry	Solvent	Reaction time (min)	Yield[b] (%)
1	H_2O	8	98
2	Solvent-free	10	94
3	C_2H_5OH	10	92
4	CH_3CN	15	70
5	CH_3CO_2Et	15	70
6	CH_2Cl_2	45	25
7	Toluene	60	10

Reaction conditions:

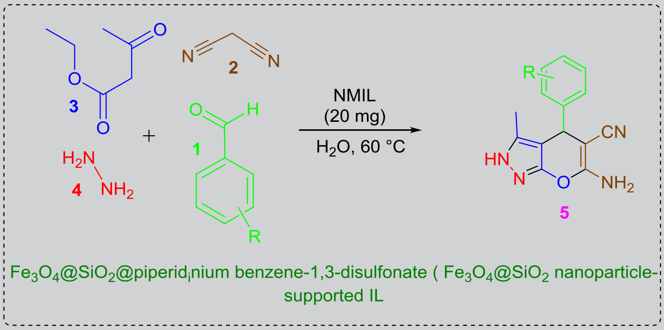
[a] 4-Chlorobenzaldehyde (1 mmol), ethylacetoacetate (1 mmol), hydrazine hydrate (1 mmol), malononitrile (1 mmol);

[b] Isolated yield.

reaction is that water is a safe, cheap, benign and green solvent in comparison with organic solvents. In addition, a mixture of piperidine and benzene-1,3-disulfonic acid was prepared to obtain a free catalyst of piperidinium benzene-1,3-disulfonate. Then, it was used in the model reaction and 15 mol% of this catalyst gave the best results which obtained by the nanocatalyst. Due to the high amount requirement of free catalyst in addition to this fact that it is a homogeneous and non-recyclable catalyst, it is better to use the heterogeneous nanocatalyst.

Stimulated by the significant results, and with the intention of displaying the overview and scope of this new approach, a range of 6-amino-4-(4-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazoles derivatives were produced from the one-pot four-component reaction of ethyl acetoacetate, hydrazine hydrate, various aldehydes and malononitrile using a catalytic amount

TABLE 3 The synthesis of 6-amino-4-(4-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazoles derivatives using 20 mg of Fe_3O_4@SiO_2@piperidinium benzene-1,3-disulfonate[a]



Entry	Aldehyde	R	Reaction time (min)	Yield[b] (%)	M.p (°C)[Ref.]
1	2-Hydroxy-3-methoxybenzaldehyde	H	14	90	240–242
2	Naphtalene-2-carbaldehyde	H	10	92	226–228[21]
3	Biphenyl-4-carbaldehyde	H	12	92	252–254
4	Benzaldehyde	H	11	92	232–234[22]
5	2-Hydroxybenzaldehyde	H	14	90	247–249[23]
6	4-Methoxybenzaldehyde	H	14	91	262–264[22]
7	3-Chlorobenzaldehyde	H	10	96	243–245[23]
8	4-Chlorobenzaldehyde	H	8	98	243–245[23]
9	Furfural	H	10	93	240–242[24]
10	3-Hydroxybenzaldehyde	H	12	92	247–249[23]
11	2-Methoxybenzaldehyde	H	15	90	262–264[22]
12	4-Hydroxybenzaldehyde	H	15	91	247–249[23]
13	3-Bromobenzaldehyde	H	10	97	258–260[24]
14	3-Nitrobenzaldehyde	H	8	96	244–246[23]
15	2-Chlorobenzaldehyde	H	10	94	243–245[23]
16	4-Nitrobenzaldehyde	H	8	98	244–246[23]

Reaction conditions:

[a] Aldehyde (1 mmol), malonitrile (1 mmol), ethylacetoacetate (1 mmol), hydrazine hydrate (1 mmol); water solvent, 60 °C;

[b] Isolated yield

of Fe_3O_4@SiO_2@piperidinium benzene-1,3-disulfonate (20 mg) in water solvent at 60 °C. The results are briefly shown in Table 3. The reaction time of aromatic aldehydes having electron withdrawing groups was rather faster than that of electron donating groups. However meta- and para-substituted aromatic aldehydes produced excellent results, but ortho-substituted aromatic aldehydes produced rather lower yields due to the steric effects.

In another study, recyclability and reusability of the Fe_3O_4@SiO_2 nanoparticle-supported IL was confirmed on the condensation of between 4-chlorobenzaldehyde with malonitrile, ethyl acetoacetate and hydrazine hydrate. At the end of the reaction, Fe_3O_4@SiO_2 nanoparticle-supported IL was separated by magnets then the reaction mixture was decanted and washed with water. The nano magnetic ionic liquid was used without further cleansing after Isolation. Afterwards the recycled catalyst was applied for alternative reaction. Dynamic light scattering (DLS) was applied for definition of particle size in colloidal solution. According to Figure 1, the DLS analysis performed on the freshly prepared catalyst revealed that the average size of the Fe_3O_4@SiO_2@piperidinium benzene-1,3-disulfonate (Fe_3O_4@SiO_2 nanoparticle-supported IL) is 86 nm. The distribution of nanoparticles is about 60 to 100 nm which indicates modest distribution of the nanoparticles. We detected that the catalytic activity of the catalyst was maintained within the limits of the experimental errors for seven continuous runs (Figure 2). Also, comparison of TGA analysis of Fe_3O_4@SiO_2 nanoparticle-supported IL before and after recycling showed the thermal stability of catalyst. Furthermore, FT-IR spectrum of the recycled catalyst (Figure 3) shows the main absorbance bands as mentioned before (for the initial catalyst) in Figure 4e. This confirms that the organic functional groups on the surface of the catalyst were not leached to the reaction solution and grafting process was well done during preparation of the catalyst.

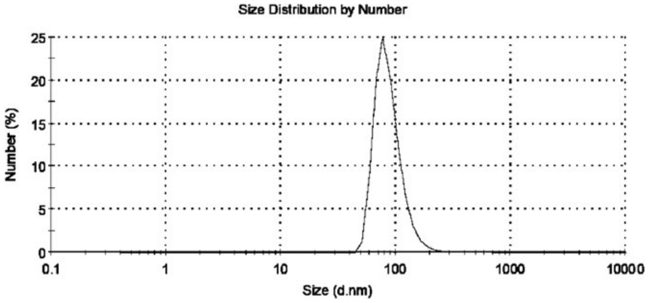


FIGURE 1 Dynamic light scattering size distribution graph of the Fe_3O_4@SiO_2@piperidinium benzene-1,3-disulfonate

A probable mechanism for the synthesis of the 6-amino-4-(4-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazoles (5) is presented in Scheme 3.[22] Firstly, Fe_3O_4@SiO_2@piperidinium benzene-1,3-disulfonate activates the carbonyl group of the ethyl acetoacetate (1) and hydrazine attacks the carbonyl group of the activated ethyl acetoacetate. Then it loses one molecule H_2O, and intramolecular nucleophilic attacks by another NH_2 group of hydrazine to the following carbonyl group of ethyl acetoacetate affords 5-methyl-2,4-dihydro-pyrazol-3-one (6) and removes ethanol. In the next step, the aromatic aldehyde which is activated by nano magnetic catalyst and 5-methyl-2,4-dihydro-pyrazol-3-one (6), attacks to the carbonyl group of the activated aldehyde and removes H_2O, gives 4-benzylidene-5-methyl-2,4-dihydro-3*H*-pyrazol-3-one (7). Then, malononitrile after rearrangement in (8) form, attacks to the double bond in the

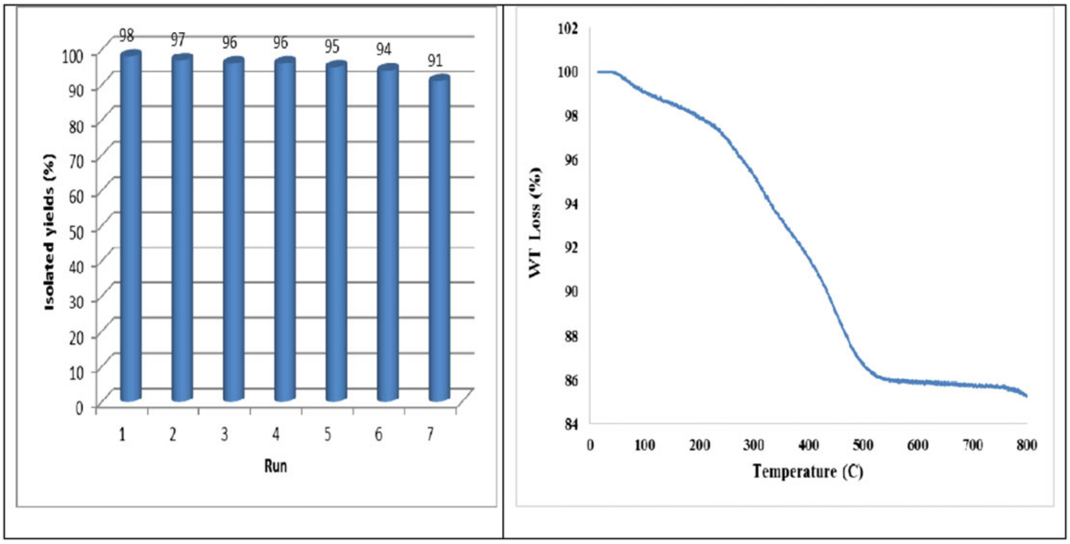


FIGURE 2 Study of the reusability of Fe_3O_4@SiO_2@piperidinium benzene-1,3-disulfonate in 8 minutes (a) and TGA of Fe3O4@SiO2@piperidinium benzene-1,3-disulfonate after recycling (b)

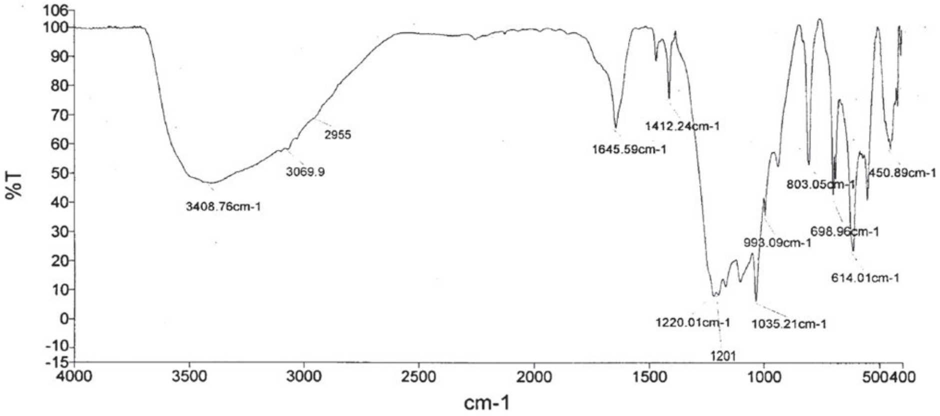


FIGURE 3 FT-IR spectrum of the recycled Fe_3O_4@SiO_2@piperidinium benzene-1,3-disulfonate

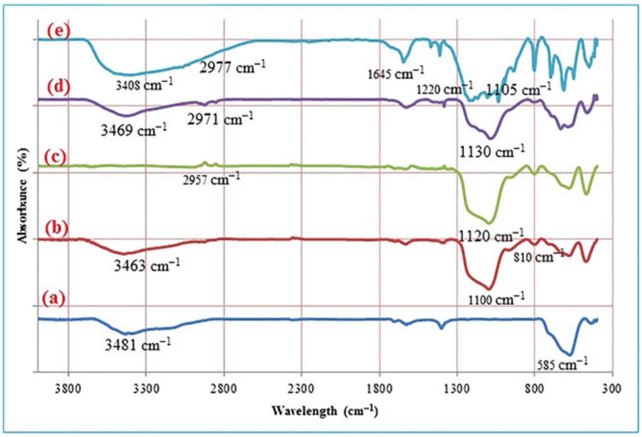
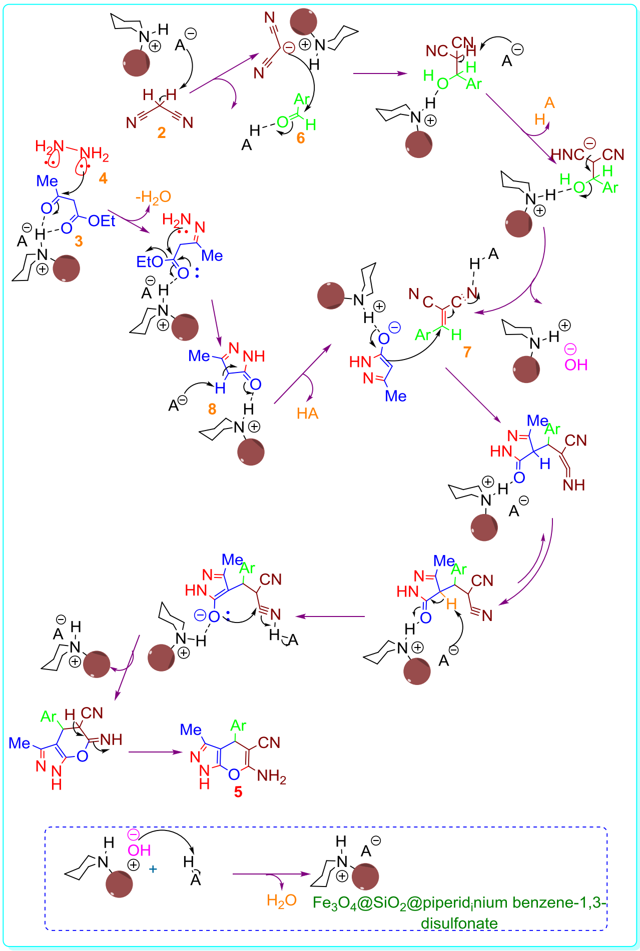


FIGURE 4 The IR spectrum of Fe_3O_4 (a); Fe_3O_4@SiO_2 (b); Fe_3O_4@SiO_2@$(CH_2)_3Cl$ (c); Fe_3O_4@SiO_2@$(CH_2)_3$-piperidine (d); {Fe_3O_4@SiO_2@$(CH_2)_3$-piperidinium}$_2$Benzene-1,3-disulfonate (e)



SCHEME 2 The proposed mechanism for the synthesis of 6-amino-4-(4-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazoles using Fe_3O_4@SiO_2@piperidinium benzene-1,3-disulfonate

4-benzylidene-5-methyl-2,4-dihydro-3*H*-pyrazol-3-one (7), and provides 6-imino-3-methyl-4-phenyl-2,4,5,6-tetrahydropyrano[2,3-*c*]pyrazole-5-carbonitrile (9). Finally, 6-imino-3-methyl-4-phenyl-2,4,5,6-tetrahydropyrano[2,3-*c*] pyrazole-5-carbonitrile (9) after rearrangement, can afford the expected pyrano[2,3-*c*]pyrazole (5) as shown in Scheme 2.

The reaction occurs by primary formation of arylidene malononitrile (**7**) in quantitative yield *via* the Knoevenagel addition of activated malononitrile (**2**) to the activated aromatic aldehyde (**6**) and followed by loss of magnetite nanoparticles tag: piperidinium hydroxide ionic liquid. The creation of the 1,4-dihydropyrano-[2,3-*c*]-pyrazole (**5**) is suggested to include the following tandem reactions: pyrazolone (**8**) formation using reaction between activated ethyl acetoacetate (**3**) and hydrazine Hydrate **4**), Michael addition of pyrazolone (**8**) to arylidene malononitrile (**7**), followed by cyclization and tautomerization (Scheme 2).[31]

To compare the efficiency of {Fe_3O_4@SiO_2@$(CH_2)_3$-piperidinium}$_2$Benzene-1,3-disulfonate catalyst with Fe_3O_4, Fe_3O_4@SiO_2, Fe_3O_4@SiO_2@$(CH_2)_3Cl$ and Fe_3O_4@SiO_2@$(CH_2)_3$-piperidine for the synthesis of 6-amino-4-(4-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazoles, we have tabulated the results of these catalysts to achieve the condensation of 4-chlorobenzaldehyde, ethyl acetoacetate, malononitrile and hydrazine hydrate, in Table 4. As Table 4 displays, magnetic

TABLE 4 Compare the efficiency of MNPs catalyst with other catalysts in the reaction between 4-chlorobenzaldehyde, ethyl acetoacetate, malononitrile and hydrazine hydrate[a]

Entry	Catalyst	Catalyst loading	Time (min)	Yield (%)[b]
1	MNPs catalyst	20 mg	8	98
2	Fe_3O_4	20 mg	60	45
3	$Fe_3O_4@SiO_2$	20 mg	60	35
4	$Fe_3O_4@SiO_2@(CH_2)_3Cl$	20 mg	60	5
5	$Fe_3O_4@SiO_2@(CH_2)_3$-piperidine	20 mg	60	5

Reaction conditions:

[a] 4-Chlorobenzaldehyde (1 mmol), ethylacetoacetate (1 mmol), hydrazine hydrate (1 mmol), malononitrile (1 mmol), H_2O solvent, 60 °C;

[b] Isolated yield.

nanoparticles tag: piperidinium benzene-1,3-disulfonate ionic liquid catalyst has strangely improved the synthesis of dihydropyrano[2,3-*c*]pyrazoles in different terms (reaction time and yield). The reaction time were shorter and the yields were higher when MNPs catalyst was used.

3 | CONCLUSION

In summary, we have developed an efficient, green and environmental friendly process for the synthesis of pyrano[2,3-*c*] pyrazole derivatives by four component cyclocondensation reaction in the presence of $Fe_3O_4@SiO_2$@piperidinium benzene-1,3-disulfonate as a novel and powerful catalyst in water solvent at 60 °C with good to excellent yields. We suggest that the method has also various advantages such as low loading of catalyst, clean reaction, mild reaction conditions, short reaction time, ease of workup, high yields and general applicability for the synthesis of pyrano[2,3-*c*]pyrazole.

3.1 | Experimental

3.1.1 | Preparation of $Fe_3O_4@SiO_2$@piperidinium benzene-1,3-disulfonate

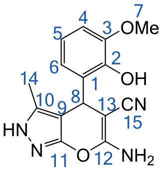
In the beginning, magnetite phase Fe_3O_4 was synthesized *via* adding 3 ml $FeCl_3$ (2 M dissolved in 2 M HCl) to 10.33 mL double distilled water followed using drop wise addition of 2 ml Na_2SO_3 (1 M) for 3 min under magnetic stirring. In the solution color changed from red to light yellow, 80 ml of an $NH_3{\cdot}H_2O$ solution (0.85 M) were added under severe stirring. After 30 min, the magnetite precipitate Fe_3O_4 was washed to pH < 7.5 by distilled water and separated with amagnet. To a mixture containing 1 g of Fe_3O_4, 20 ml water, 80 ml ethanol, 3 ml ammonia and 3 ml tetraethylorthosilicate were added under reflux to attain $Fe_3O_4@SiO_2$.[25–32] Consequently, 3 g of $Fe_3O_4@SiO_2$ and (3-chloropropyl) triethoxysilane (10 mmol) in 80 ml of dry toluene were refluxed under nitrogen for 12 h. The treated $Fe_3O_4@SiO_2@(CH_2)_3$ was filtered, washed twice with dry toluene and anhydrous diethyl ether, and dried at 80 °C for 6 h in vacuum. To prepare piperidine modified magnetic nanoparticles (pi-SCMNPs), 1.0 g silica coated magnetic nanoparticles was added to 50 ml of dry toluene and 3 ml piperidine. The reaction mixture was dispersed for 30 min, and then refluxed with stirring for 72 h. The solid phase was filtered, washed with toluene and ethanol, and dried at 60 °C in vacuum. 1.0 g of pi-SCMNPs was suspended in 50 ml of acetonitrile and 3 ml of benzene-1,3-disulfonic acid was added to this suspension. The mixture was stirred at room temperature for 24 h, then filtered and washed twice with acetonitrile and further washed with deionized water and dried at 60 °C in vacuum.

3.1.2 | General procedure for the preparation of 6-amino-3-methyl-4-phenyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile derivatives

To a mixture of aldehydes (1 mmol), malononitrile (1 mmol), ethyl acetoacetate (1 mmol) and hydrazine hydrate (1 mmol) in a round bottom flask, 20 mg of $Fe_3O_4@SiO_2$@piperidinium benzene-1,3-disulfonate was added as a $Fe_3O_4@SiO_2$ nanoparticle-supported IL and the resulting mixture was vigorously stirred long enough in water solvent at 60 °C (Table 3). After completion of the reaction as observed by TLC (n-hexane/ethyl acetate: 7/3), the catalyst was separated magnetically. The magnetic Fe_3O_4 nanoparticles were washed three to four times with ethanol and then dried at 50 °C for 3 h in order to preserve catalyst and it was used for alternative reaction. The product obtained was pure by TLC and NMR spectroscopy. Subsequently, the products in the aqueous layer was filtered, separated and then the crude product was purified by washing with acetone. In this study, nano magnetic ionic liquid as a catalyst was recycled and reused for seven times without any loss of catalytic activity.

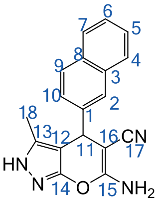
3.2 | Spectral data analysis for compounds

3.2.1 | 6-Amino-4-(2-hydroxy-3-methoxyphenyl)-3-methyl-2,4-dihydropyrano [2,3-c]pyrazole-5-carbonitrile (table 4, entry 1):



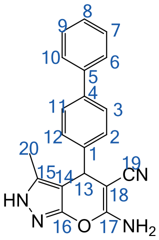
White solid; M.p: 240–242 °C; Yield; 88%; IR (KBr): υ 3468, 3382, 2975, 2845, 2185, 1651, 1617 cm^{-1}, ^{1}H NMR (400 MHz, DMSO-d_6): δ_{ppm} 1.96 (s, 3H, H—C14), 3.79 (s, 3H, H—C7 aliphatic), 4.60 (s, 1H, H—C8), 6.50 (d, 1H, $J = 8$ Hz, H—C4), 6.68 (s, 2H, —NH_2), 6.86 (d, 1H, $J = 8$ Hz, H—C6), 6.95 (dd, 1H, $J = 8$ Hz and $J = 8.0$ Hz, H—C5), 10.39 (s, 2H, —NH, OH); ^{13}C NMR (100 MHz, DMSO-d_6): δ_{ppm} 10.3 (C14), 29.2 (C8), 56 (C7), 55 (C13), 105.4 (C4), 110.5 (C9), 120.5 (C1), 121.3 (C15), 124.3 (C5), 124.7 (C6), 136.9 (C10), 138.3 (C2), 147.1 (C3), 159.5 (C1), 160.5 (C12); Anal. Calc.: C: 60.22, H: 4.97, N: 18.99.

3.2.2 | 6-Amino-3-methyl-4-(naphthalen-2-yl)-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (table 4, entry 2):



White solid; M.p: 226–228 °C; Yield; 90%; IR (KBr): υ 3373, 3311, 3022, 2877, 2192, 1649, 1611 cm^{-1}, ^{1}H NMR (400 MHz, DMSO-d_6): δ_{ppm} 1.76 (s, 3H, H—C18), 4.78 (s, 1H, H—C11), 6.9 (s, 2H, —NH_2), 7.2 (d, 1H, $J = 8$ Hz, H—C4), 7.4 (d, 1H, $J = 8$ Hz, H—C7), 7.7 (dd, 2H, $J = 8$ Hz and $J = 8$ Hz, H—C5,6), 7.8 (m, 3H, $J = 12$ Hz, H—C2,9,10), 12.1 (s, 1H, —NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ_{ppm} 10.1 (C18), 36.9 (C11), 57.5 (C16), 97.8 (C12), 121.2 (C17), 126.1 (C6), 126.21 (C5), 126.29 (C2), 126.7 (C9), 128 (C4), 128.1 (C7), 128.8(C10), 132.5 (C8), 133.2 (C3), 136.2 (C1), 142.1 (C13), 155.2 (C14), 161.3 (C15).

3.2.3 | 4-([1,1′-Biphenyl]-4-yl)-6-amino-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (table 4, entry 3):



White solid; M.p: 252–254 °C; Yield; 90%; IR (KBr): υ 3342, 3376, 3160, 2935, 2837, 2194, 1656, 1612 cm^{-1}, ^{1}H NMR (400 MHz, DMSO-d_6): δ_{ppm} 1.84 (s, 3H, H—C20), 4.66 (s, 1H, H—C13), 6.91 (s, 2H—NH_2), 7.25 (dd, 2H, $J = 8$ Hz and $J = 8$ Hz, H—C7,9), 7.35 (t, 1H, $J = 8$ Hz, H—C8), 7.45 (d, 2H, $J = 8$ Hz, H—C6,10), 7.64 (m, 4H, $J = 10$ Hz, H—C2,3,12,11), 12.13 (s, 1H, —NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ_{ppm} 10.2 (C20), 36.3 (C13), 57.5 (C18), 98 (C14), 121.3 (C19), 127 (C8), 127.2 (C3,11), 127.8 (C6,10), 128.5 (C7,9), 129.3 (C2,12), 136.1 (C1), 139.0 (C4), 140.2 (C15), 144.2 (C5), 155.2 (C16), 161.4 (C17); Anal. Calc.: C: 73.42, H: 5.18, N: 17.32.

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