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Synthesis of pyrano[2,3-*c*]pyrazoles by ionic liquids under green and eco-safe conditions

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Abstract Optimization of a green approach to the synthesis of pyrano[2,3-*c*]pyrazoles based on the one-pot, four-component condensation via a domino Knoevenagel/Michael/cyclization sequence was investigated. This method involved the evaluation of the activity of several ionic liquids (ILs) in various solvents. This one-pot, four-component reaction revealed simplicity, higher yield and lower toxicity advantages over a corresponding three-component method. The effect of reaction parameters including the type and amount of catalyst, type of solvent, reaction temperature and time were studied with respect to yield of pyrano[2,3-*c*]pyrazoles. Catalyst recyclability and time-saving aspects of the reaction suggest that this method presents real alternatives over conventional reaction protocols.

Keywords Green chemistry · Ionic liquids · Pyrano[2,3-*c*]pyrazoles · 1-Phenyl-3-methyl pyrazolone

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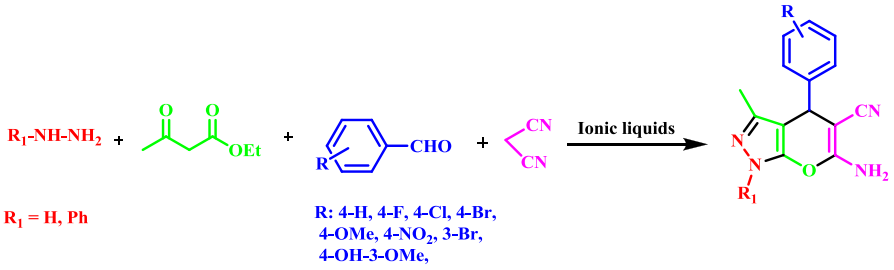
Introduction

Green chemistry is an increasingly important aspect of chemical research devoted to minimizing the use and generation of hazardous substances, organic solvents, and toxic catalysts on the environment [1]. In this context, it is highly desirable to develop environmentally benign processes that can be conducted in an aqueous media due to the low-cost, simple operation and high efficiency in many organic reactions [2]. However, using water is limited by the low solubility of organic compounds. One of the most important strategies to overcome this problem is the use of phase transfer catalysts such as ionic liquids (ILs). Increasing interest in ILs is related to their possible usage as environmentally friendly catalysts and solvents due to their negligible vapor pressure, thermal and chemical stability, solvating ability and easy recyclability [3, 4]. Diverse liquid salts have been produced by the combination of ammonium, pyridinium, or imidazolium cations with various inorganic or organic anions that led to numerous possible applications in the field of heterocyclic compounds synthesis, catalysis, biocatalysis, chemical engineering and electrochemistry [5–7].

Pyrano[2,3-*c*]pyrazoles are an important class of heterocyclic compounds that play an essential role as biologically active compounds and represent an interesting template in medicinal chemistry. Many of these compounds are known for their antimicrobial [8], insecticidal [9] and anti-inflammatory activities [10]. In recent years, several methods for the synthesis of pyrano[2,3-*c*]pyrazoles via multicomponent reactions have been reported. Synthesis of pyrano[2,3-*c*]pyrazole derivatives have been catalyzed by per-6-amino-β-cyclodextrin [11], magnesium oxide [12], piperidine [13], silica-supported tetramethylguanidine (SiO_2TMG) [14], meglumine [15], isonicotinic acid [16], L-proline in ionic liquid media [17], D,L-proline [18] magnetic Fe_3O_4 nanoparticles [19] and catalyst-free [20, 21]. However, there is a scope for further work towards the development of an inexpensive, cleaner and eco-friendly procedure that has a short reaction time.

Biological activity of pyrano[2,3-*c*]pyrazoles and our experience in using ILs as catalysts in the synthesis of heterocyclic compounds [22–24] encouraged us to establish an efficient synthesis route for pyrano[2,3-*c*]pyrazoles via the four-component reaction of hydrazine hydride (or phenyl hydrazine), ethyl acetoacetate, aromatic aldehydes and malononitrile using specific ILs as catalysts (as shown in Scheme 1). This one-pot, four-component reaction showed advantages over a one-



Scheme 1 The preparation of pyranopyrazoles using ILs as catalyst

pot, three-component method of 1-phenyl-3-methyl pyrazolone, aromatic aldehydes and malononitrile in its simple procedure, high yield and low toxicity.

Experimental

Materials and methods

All common reagents and solvents were used as obtained from commercial suppliers without further purifications. Three Brønsted acidic ILs (cat. 1), (cat. 2) and (cat. 3) were prepared according to the procedure reported in the literature [25, 26]. The rest of the ILs (>95 %) were obtained from Shanghai Cheng Jie Chemical, China. Melting points were measured using the capillary tube method with an electrothermal 9200 apparatus. IR spectra were recorded on a JASCO-FT-IR model 5300 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AQS AVANCE-300 spectrometer using TMS as an internal standard. Elemental analysis performed by a Perkin Elmer 2004 (II) CHN analyzer.

Typical procedure for the four-component synthesis of multi-substituted pyranopyrazole derivatives

A mixture of hydrazine hydrate 80 % or phenyl hydrazine (1.2 mmol), ethyl acetoacetate (1 mmol), aromatic aldehydes (1 mmol), malononitrile (1.2 mmol) and 1,3-dimethyl-2-oxo-1,3-bis(4-sulfobutyl) imidazolidine-1,3-diium hydrogen sulfate [DMDBSI]·2HSO$_4$ (10 mol%) in 10 mL of H_2O was stirred at 60 °C for an appropriate period of time. After completion as monitored by TLC (*n*-hexane/ethyl acetate: 7/3), the reaction mixture was cooled to room temperature and the resulting solid was collected by filtration, washed with water (3 × 10 mL) and then dried under vacuum at 80 °C overnight.

Typical procedure for the three-component synthesis of multi-substituted pyranopyrazole derivatives

[DMDBSI]·2HSO$_4$ (10 mol%) was added to a mixture of 1-phenyl-3-methyl pyrazolone (1 mmol), aromatic aldehyde (1 mmol) and malononitrile (1.2 mmol) in 10 mL of EtOH/H_2O (2/1). The reaction mixture was heated at 60 °C for an appropriate period of time. After the reaction was completed, the mixture was cooled to room temperature and the resulting solid was collected by filtration, washed with water (3 × 10 mL) and then dried under vacuum at 80 °C overnight.

Typical procedure for the synthesis of the multi-substituted bispyranopyrazole derivatives

A mixture of hydrazine hydrate or phenyl hydrazine (2.5 mmol), ethyl acetoacetate (2 mmol), terephthalaldehyde (1 mmol), malononitrile (2.5 mmol) and [DMDBSI]·2HSO$_4$ (10 mol%) in 10 mL of H_2O was stirred at 60 °C for an

appropriate period of time. After completion of the reaction, the mixture was cooled to room temperature and the resulting solid was collected by filtration, washed with water (3 × 10 mL) and then dried under vacuum at 80 °C overnight.

Results and discussion

Recently, we observed that the use of $[BSO_3HPy]HSO_4$ as a catalyst resulted in a significant rate acceleration with a high yield in the synthesis of tetraquinazoline-2-amine [27]. Bearing this in mind, we evaluated the catalyst activity of $[BSO_3HPy]HSO_4$ in the four-component reaction between a mixture of phenylhydrazine, ethyl acetoacetate, benzaldehyde and malononitrile to prepare pyrano[2,3-*c*]pyrazole (Scheme 1). The reaction occurred to offer the desired products in medium yields of 60 and 48 % in water and ethanol media, respectively (Table 1, entries 1 and 2). In order to find an effective catalyst and optimize the reaction, a series of ILs with respect to both cation and anion counterparts were screened (Fig. 1).

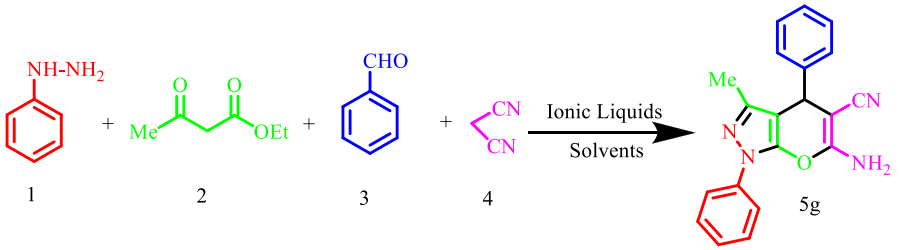
It was observed that almost all of the investigated ILs were capable of catalyzing the desired products, but the model reaction proceeded faster and gave the product in higher yield with $[DMDBSI]\cdot 2HSO_4$ (Table 1, entry 6). It can also be observed that the sulfonic acid ILs effectively catalyze the synthesis of pyrano[2,3-*c*]pyrazole **5g** as indicated from the superior results obtained. [BzMIM]Cl and [AMIM]Br did not significantly increase the yield of the desired product (Table 1, entries 18 and 21).

To adjust the amount of $[DMDBSI]\cdot 2HSO_4$, different experiments were carried out, and it was found that, by increasing the amount of catalyst for the **5g** from 3 to 5, 7 and 10 mol%, the yields increased from 70 to 75, 82 and 85 %, respectively (Table 1, entries 3–6). The use of 10 mol % IL was found to be sufficient to push this reaction forward and a higher catalyst amount (12 and 15 mol%) did not improve the yields of the reaction (Table 1, entries 7 and 8).

Choosing an appropriate solvent has crucial importance for the successful synthesis. To search for the optimal solvent, the model reaction was investigated in the presence of 10 mol% of $[DMDBSI]\cdot 2HSO_4$ using various solvents including ethanol, water, acetonitrile and toluene at 60 °C and also at 120 °C under solvent-free conditions to determine which gave the best results. The results of these comparative experiments are summarized in Table 1. Polar protic solvents such as water and ethanol enhance the rate of reaction (Table 1, entries 6 and 9) while, in the case of non-polar solvent such as toluene, the rate of reaction decreased (Table 1, entry 12). In comparison with organic solvents, water was found to give the best result. This solvent can have substantial effects in realizing the goals of green chemistry.

To optimize the reaction temperature, the reaction was carried out at different temperatures ranging from room temperature to reflux condition in water (30–100 °C). Consequently, 60 °C was found to be the most suitable reaction temperature (Table 2).

Table 1 Effect of different catalysts and solvents on synthesis of compound **5g**



Entry	Reaction conditions	Time (min)	Yield[a] (%)
1	$[BSO_3HPy]HSO_4$ (3 mol%), water	20	60
2	$[BSO_3HPy]HSO_4$ (3 mol%), ethanol	20	48
3	$[DMDBSI]{\cdot}2HSO_4$ (3 mol%),water	15	70
4	$[DMDBSI]{\cdot}2HSO_4$ (5 mol%), water	15	75
5	$[DMDBSI]{\cdot}2HSO_4$ (7 mol%), water	15	82
6	$[DMDBSI]{\cdot}2HSO_4$ (10 mol%), water	15	85
7	$[DMDBSI]{\cdot}2HSO_4$ (12 mol%), water	15	85
8	$[DMDBSI]{\cdot}2HSO_4$ (15 mol%), water	15	85
9	$[DMDBSI]{\cdot}2HSO_4$ (10 mol%), ethanol	15	72
10	$[DMDBSI]{\cdot}2HSO_4$ (10 mol%), acetonitrile	15	55
11	$[DMDBSI]{\cdot}2HSO_4$ (10 mol%), solvent-free, 120 °C	30	70
12	$[DMDBSI]{\cdot}2HSO_4$ (10 mol%), toluene	30	35
13	$[BSO_3HMIM]HSO_4$ (10 mol%), water	15	72
14	$[BSO_3HPy]HSO_4$ (10 mol%), water	15	77
15	$[BSO_3HMIM]CF_3SO_3$ (10 mol%), water	15	80
16	$[BSO_3HPy]CF_3SO_3$ (10 mol%), water	15	78
17	[BMIM]Cl (10 mol%), water	15	71
18	[BzMIM]Cl (10 mol%), water	40	34
19	[BMIM]Br (10 mol%), water	15	53
20	$[BMIM]BF_4$ (10 mol%), water	25	54
21	[AMIM]Br (10 mol%), water	40	25

[a] Isolated yields

These findings confirm the establishment of an efficient and optimized green approach for preparation of pyrano[2,3-*c*]pyrazole in 85 % isolated yield through a one-pot reaction involving a mixture of phenyl hydrazine, ethyl acetoacetate, malononitrile with benzaldehyde in the presence of 10 mol% $[DMDBSI]{\cdot}2HSO_4$ at 60 °C for 15 min.

In comparison to the four-component and one-pot reaction, the three-component reaction including 1-phenyl-3-methyl pyrazolone, aromatic aldehydes and malononitrile underwent the same conditions to yield the target compound (Scheme 2). Similar to the above optimization, different solvents and temperatures in the presence of 10 mol% $[DMDBSI]{\cdot}2HSO_4$ were used for the three-component

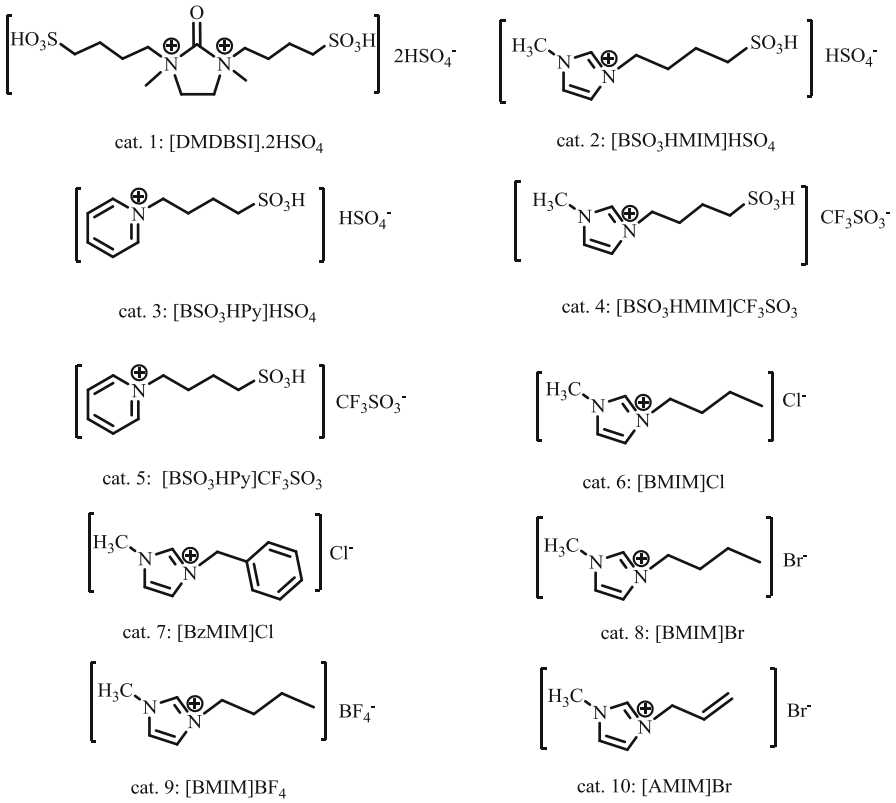


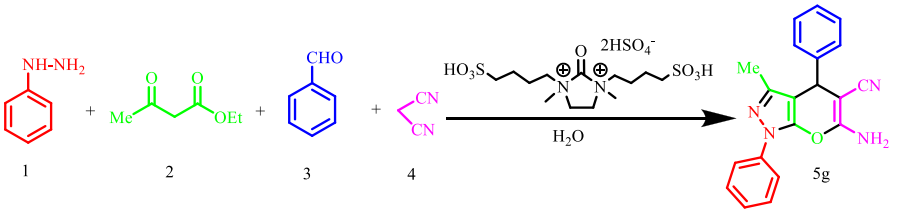
Fig. 1 ILs tested in this study

reaction for the synthesis of compound **5g** (Table 2). It is important to note tha,t when the reaction was carried out in H_2O using [DMDBSI]·$2HSO_4$ as the catalyst, the yield of product **5g** in the four-component reaction reached 85 %. However, the yield of compound **5g** in the three-component reaction decreased when the reaction was attempted in water using the same catalyst. All of the compounds prepared via the four-component one-pot reaction demonstrated the higher yields, simple procedure and atom efficiency for this method compared with three-component reaction.

This optimized protocol was then extended to a variety of hydrazines, and different aldehydes including either electron-withdrawing or electron-donating groups via the four-component reaction. It was found that all these aromatic aldehyde derivatives are suitable for this reaction, giving the desired products in the range of good to excellent yields under water media conditions (Table 3).

In addition, the optimized reaction conditions were tested for the synthesis of multi-substituted bispyrano[2,3-*c*]pyrazole derivatives via the four-component, one-pot synthesis route using methyl acetoacetate, hydrazine (or phenylhydrazine), terephthalaldehyde, and malononitrile at [DMDBSI]·$2HSO_4$ in H_2O at 60 °C that

Table 2 Optimization of reaction time and temperature in presence of 10 mol% [DMDBSI]·2HSO$_4$

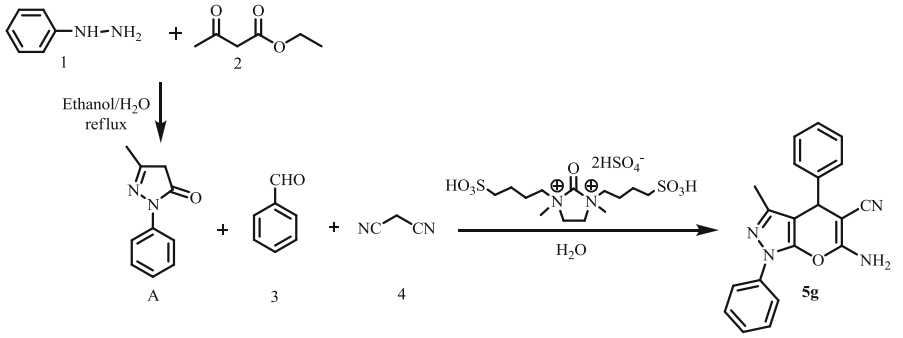


Entry	Temperature (°C)	Time (min)	Yield[c] (%)	
			A[a]	B[b]
1	30	10	40	35
2	40	10	54	50
3	50	10	68	61
4	60	10	80	75
5	70	10	80	75
6	100	10	80	77
7	60	12	82	78
8	60	15	85	80
9	60	18	85	80
10	60	20	85	80

[a] Yields for the four-component one-pot reaction

[b] Yields for the three-component one-pot reaction

[c] Isolated yields

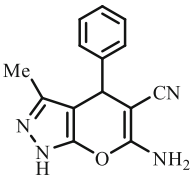
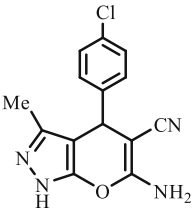
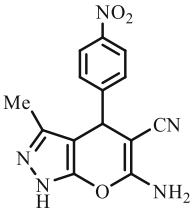
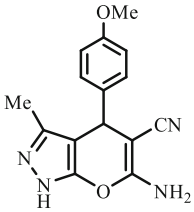
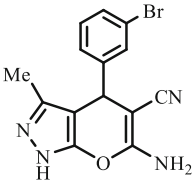
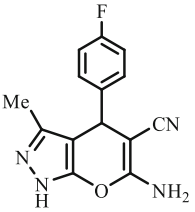
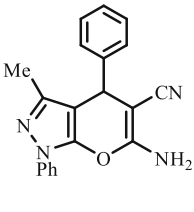
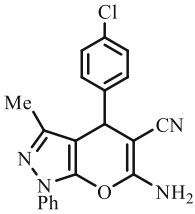
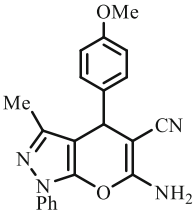
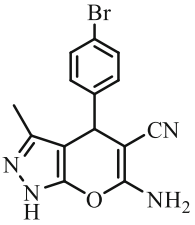
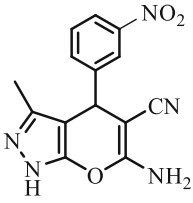
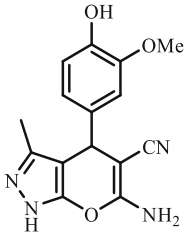
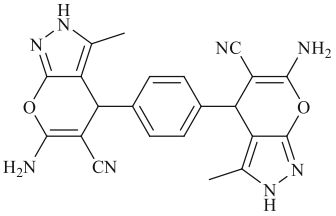
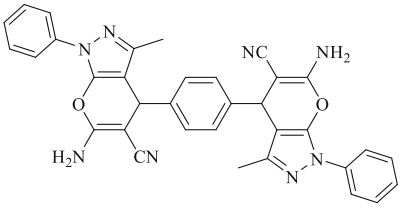


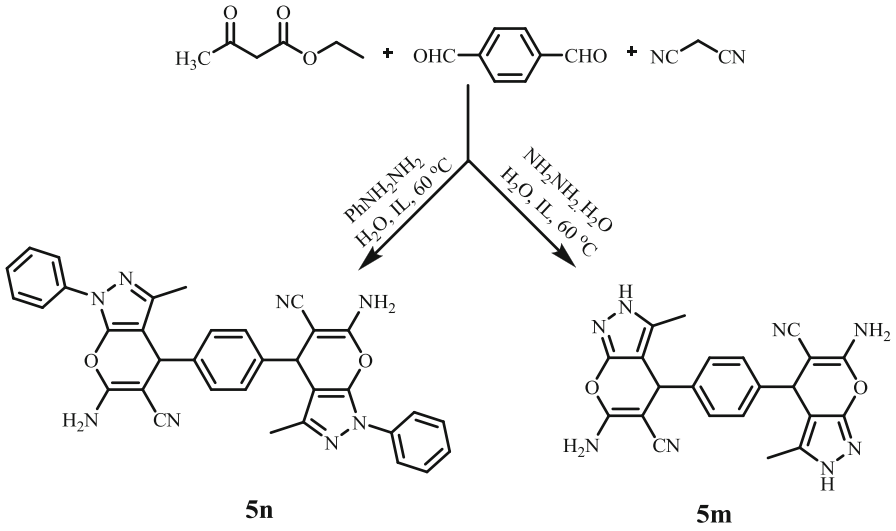
Scheme 2 Three-component reaction for the synthesis of pyranopyrazoles

products **5m** and **5n** were obtained in good yields (Scheme 3). In this study, the obtained products were characterized using melting point, IR, ^{1}H NMR, ^{13}C NMR and CHN (supporting information).

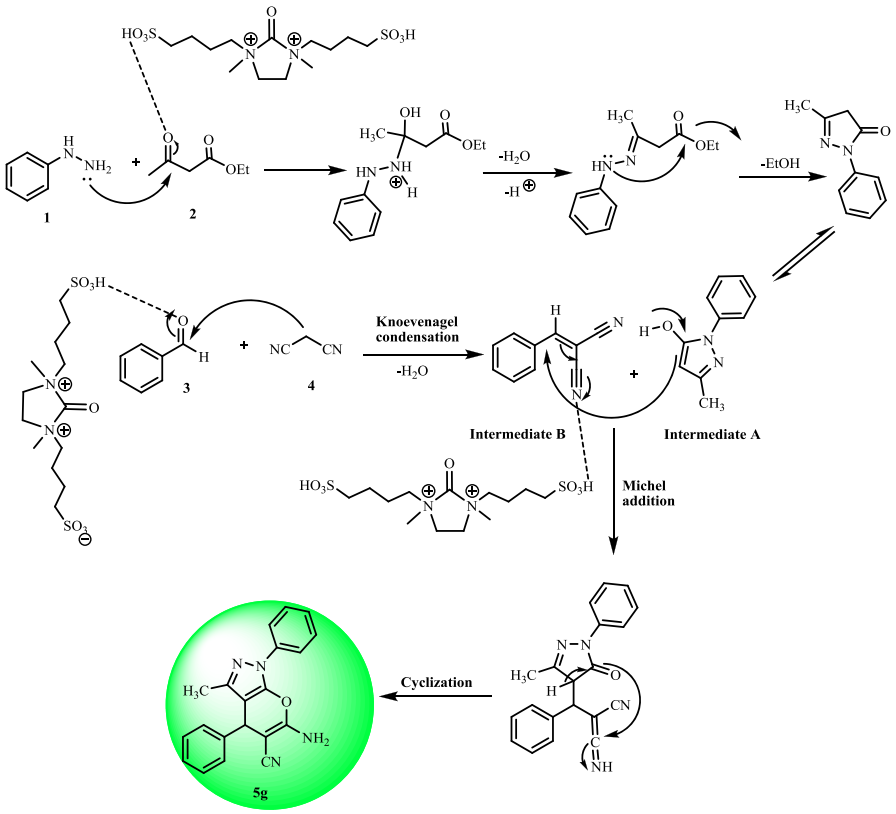
The formation of the desired product **5g** can be explained by the sequence of Knoevenagel condensation and Michael addition followed by cyclization, as shown in Scheme 4. Initially, ethyl acetoacetate is activated by [DMDBSI]·2HSO$_4$. A

Table 3 Synthesis of pyrano[2,3-*c*]pyrazole derivatives in presence of 10 mol% [DMDBSI]·2HSO$_4$ in water media at 60 °C

			
5a, 90 %, 10 min	**5b**, 90 %, 12 min	**5c**, 82 %, 15 min	**5d**, 85 %, 10 min
m.p.: 241–243	m.p.: 234–236	m.p.: 248–250	m.p.: 212
Lit.: [243–244] [15]	Lit.: [234–235] [15]	Lit.: [248–249] [15]	Lit.: [210–212] [15]
			
5e, 80 %, 15 min	**5f**, 78 %, 15 min	**5g**, 85 %, 15 min	**5h**, 88 %, 15 min
m.p.: 219–222	m.p.: 244–246	m.p.: 168–69	m.p.: 173–175
Lit.: [223–224] [17]	Lit.: [244–245] [15]	Lit.: [168–170] [26]	Lit.: [177–178] [25]
			
5i, 85 %, 15 min	**5j**, 86 %, 12 min	**5k**, 80 %, 15 min	**5l**, 76 %, 15 min
m.p.: 170–172	m.p.:178–180	m.p.:196–199	m.p.: 240
Lit.: [173] [28]	Lit.: [178–180] [29]	Lit.: [193–195] [29]	Lit.: [235–237] [29]
			
5m, 78 %, 15 min		**5n**, 74 %, 15 min	
m.p.: 238		m.p.: >300	
Lit.:[238–240] [30]		Lit.: >[300] [30]	



Scheme 3 Synthesis of multi-substituted bispyrano[2,3-*c*]pyrazole derivatives



Scheme 4 Investigation of a possible reaction mechanism for **5g**

Table 4 Comparison of different conditions for the synthesis of **5a**

Catalyst	Reaction condition	Time (min)	Yield (%)	References
L-Proline (10 mol%)	[Bmim]BF_4, 50 °C	10	90	[17]
γ-Alumina (30 mol%)	Solvent-free	35	90	[29]
SiO_2TMG (10 mol%)	Solvent-free, 100 °C	30	96	[14]
Pipiridine (5 mol%)	H_2O, room temperature (r.t.)	10	83	[13]
Et_3N (20 mol%)	EtOH, reflux	15	65	[31]
Catalyst-free	H_2O, 90 °C	240	79	[20]
[Bmim]OH (20 mol%)	50–60 °C	10	88	[32]
Isonicotinic acid (10 mol%)	Solvent-free, 85 °C	10	90	[16]
Meglumine (10 mol%)	EtOH/H_2O (9:1), r.t.	15	95	[15]
[DMDBSI]·$2HSO_4$ (10 mol%)	H_2O, 60 °C	10	90	This work

Table 5 Reusability of catalyst in synthesis of **5g**

Entry	Cycle	Time (min)	Yield (%)
1	1st run	15	85
2	2st run	18	82
3	3st run	20	78
4	4st run	25	71

hydrogen bond between the hydrogen atom of [DMDBSI]·$2HSO_4$ and the carbonyl group of ethyl acetate can expedite the pyrazolone synthesis (intermediate A). In the next step, formation of the arylidene malononitrile (intermediate B) occurs via Knoevenagel condensation between malononitrile and benzaldehyde, followed by loss of water molecules. The next step involves the formation of **5g** via Michael addition of pyrazolone (intermediate A) to arylidene malononitrile (intermediate B), followed by cyclization to give the pyrano[2,3-*c*]pyrazole.

Finally, in order to show the efficiency of the proposed method, [DMDBSI]·$2HSO_4$ catalyst was compared with other catalysts reported earlier for the synthesis of **5a**. As shown in Table 4, the use of [DMDBSI]·$2HSO_4$ leads to a comparable protocol in terms of compatibility with environment, reaction time and yield.

In another study, recyclability of the catalyst was examined upon the condensation of phenyl hydrazine, ethyl acetoacetate, malononitrile and benzaldehyde. After completion of the reaction, the catalyst was extracted by water and separated from the reaction mixture. Subsequently, the water was evaporated and the catalyst was dried in a vacuum at 70 °C overnight. The results showed that the IL could be used at least 4 times without any significant loss in the yield of the reaction (Table 5).

Conclusions

A simple, expeditious, and green method has been established and optimized for the generation of pyrano[2,3-*c*]pyrazoles via four-component reactions in the presence of ILs in water media. The optimized results demonstrated that the yields of 74–90 % could be expected with a reaction time of 10–15 min, and a catalyst amount of 10 mol% using water media in a temperature of 60 °C. Based on such optimized conditions, diverse derivatives were obtained in high yields with a very simple purification procedure avoiding the use of usual column chromatography. The avoidance of using organic solvents and using reusable catalysts together with the facile and fast features of this method provide an alternative route to conventional reaction protocols.

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