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Copper(II) ionic liquid catalyzed cyclization–aromatization of hydrazones with dimethyl acetylenedicarboxylate: a green synthesis of fully substituted pyrazoles†

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The Lewis acid room temperature ionic liquid, [*n*-Bu_4P][$CuBr_3$], was found to be an efficient and reusable catalyst for three component synthesis of fully substituted pyrazoles from the reaction of aldehydes, arylhydrazines and dimethyl acetylenedicarboxylate (DMAD). This catalytic system is simple and chemoselective with high yields.

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Recently, multi-component reactions (MCRs) have been reported to be efficient, fast and environmentally benign processes compared to the complicated stepwise methods.[1] In fact, the importance of MCRs is due to their wide range of applications in pharmaceutical chemistry for the production of diversified structural scaffolds and combinatorial libraries for drug discovery.[2]

Pyrazole derivatives have been extensively used in the core structure of biologically active compounds. For example substituted pyrazoles are used as anti-inflammatory,[3] anti-cancer,[4] anti-angiogenic,[5] monoamine oxidase inhibitor[6] and nitric oxide carrier[7] agents. Due to the importance of these heterocycles, significant efforts have been devoted to find new synthetic methods for preparation of pyrazole derivatives. Some of these known methods are 1,3-dipolar cycloaddition of hydrazones with acetylenic compounds,[8] condensation of 1,3-diketones[9] or chalcones[10] with hydrazines, reaction of arylhydrazines with 3-butynol[11] and condensation of hydrazonoyl chlorides with acetylenic compounds.[12] Pyrazoles and pyrazolines are also prepared by 1,3-dipolar cycloaddition of nitrile imines with acetylenic compounds[13] or cyclic α,β-unsaturated ketones,[14] [3+2] dipolar cycloaddition of 4-halosydnones with 1-haloalkynes,[15] 1,3-dipolar cycloaddition of nitrile imines to benzyne,[16] iodocyclization of acetylenic hydrazides,[17] and cyclization of hydrazone dianions with diethyl oxalate.[18] 1,3-Dipolar cycloaddition of hydrazones with α-oxo-ketenes has been reported for the three-component stereoselective synthesis of pyrazolidinones.[19] Recently, Huang and co-workers reported copper(I)-catalyzed synthesis of pyrazoles in the presence of sodium acetate.[20] However, such reagents were found to be inefficient for the conversion of hydrazones bearing aliphatic and strongly electron donating groups. Also, a stoichiometric amount of base is required for this reaction. Therefore, introduction of new and efficient methods for the synthesis of pyrazole derivatives, which proceed under mild and environmentally benign conditions, is still in demand.

Room temperature ionic liquids as green media or catalysts for environmentally friendly and economically attractive processes have found many applications in organic synthesis,[21] materials science,[22] electrochemistry[23] and separation technology.[24] Due to the wide range of applications of ionic liquids in academic and industrial fields, great development in the structure and property of ionic liquids has been made over the last two decades. In this scope, Sun *et al* developed aerobic oxidation of phenol[25] and 2,3,6-triethylphenol[26] to their corresponding quinones in the presence of [bmim][$CuCl_3$]. Comparison of the results obtained using this catalytic system with some of those reported in the literature using different oxidizing agents or copper(II) salts shows that the reaction is more selective and environmentally friendly using [bmim][$CuCl_3$]. Also the reaction in the presence of catalytic amount of this ionic liquid leads to higher yields and shorter reaction times. In continuation of our interest towards the development of environmentally-friendly methods for heterocyclic synthesis,[27] herein, we report a novel and efficient procedure for the synthesis of pyrazoles by simple cyclization–oxidation of hydrazones with dimethyl acetylenedicarboxylate (DMAD) in the presence of copper(II) ionic liquid, [*n*-Bu_4P][$CuBr_3$], as a reusable catalyst (Scheme 1).

The experimental procedure for these reactions is generally simple and clean, no toxic organic solvent or corrosive substance

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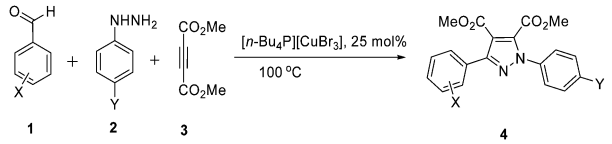
† Electronic supplementary information (ESI) available: Full characterization data for compounds and crystallographic data for compound **4h**. CCDC 867509. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3nj40756j



Scheme 1 Synthesis of pyrazoles *via* cyclization–aromatization of hydrazones with DMAD in the presence of [*n*-Bu_4P][$CuBr_3$].

is used and the corresponding products are obtained in high yields.

In order to achieve the optimized reaction conditions, the reaction of benzaldehyde, phenylhydrazine and DMAD was chosen as a model (Table 1). Initially, the model reaction was carried out in the absence of the catalyst. As shown in Table 1, the reaction was not successful even after prolonged reaction times. Then, the reaction was carried out in the presence of 25 mol% $CuBr_2$ and the corresponding product was obtained in 35% yield after 1 h (Table 1, entry 2). In order to liquefy the reaction mixture for well stirring, we used [*n*-Bu_4P][$CuBr_3$] IL as a catalyst. The results showed that the reaction was carried out efficiently and the desired product was obtained in 87% yield (Table 1, entry 3). Several other Lewis acid ionic liquids such as [bmim][$CuCl_3$], [bmim][$CuBr_3$], [bmim][$FeCl_4$], [bmim][$InCl_4$] and [bmim][$ZnCl_3$] were also tested for this reaction (Table 1, entries 4–8), showing lower yields of the product. It should be mentioned that in the presence of [bmim][$ZnCl_3$], the corresponding pyrazoline was produced as the major product. Next, the effects of temperature and different amounts of catalyst were examined. Lower yields were obtained by decreasing the temperature and the amount of the catalyst, whereas no significant improvement was observed when these parameters were increased (Table 1, entries 9 and 12). Finally, the reaction of benzaldehyde (1 mmol), phenylhydrazine (1 mmol) and DMAD (1.2 mmol) in the presence of [*n*-Bu_4P][$CuBr_3$] (0.25 mmol) at 100 °C was chosen as the optimized reaction conditions.

To survey the scope and generality of this method, a wide range of aldehydes and arylhydrazines were used under the optimized reaction conditions (Table 2). The aldehydes bearing electron-withdrawing or halogen groups in the aromatic ring reacted smoothly with arylhydrazines (phenylhydrazine, *p*-chloro and *p*-tolylhydrazines) and DMAD in the presence of 25 mol% [*n*-Bu_4P][$CuBr_3$] to afford the corresponding fully substituted pyrazoles in good to high yields (Table 2, entries 1–10). The aliphatic aldehydes such as heptanal and butanal (Table 2, entries 11 and 12) also reacted efficiently to give the desired products in good yields. To the best of our knowledge this is the first report using copper based ionic liquids in the synthesis of heterocyclic compounds.

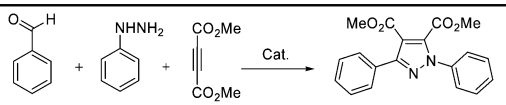
Under the same conditions, the reaction of aldehyde or arylhydrazine bearing strongly electron-donating substituents like 4-methoxybenzaldehyde or 4-methoxyphenylhydrazine produced the corresponding pyrazoline and aromatization didn't occur even after longer reaction times (Scheme 2). But the compounds **5m** and **5n** were oxidized to their corresponding pyrazoles using a stronger oxidant such as H_2O_2 (Scheme 3).

The results indicate that the present protocol is potentially applicable for the chemoselective conversion of aromatic aldehydes bearing electron-withdrawing or halogen groups (chloro, bromo, nitro and cyano) and arylhydrazines (phenylhydrazine, *p*-chloro and *p*-tolylhydrazines) to their corresponding pyrazoles in the presence of aromatic aldehyde or aryl hydrazine containing strongly electron-donating substituents (Scheme 4).

The structure of the products was identified by their IR, mass, ^{1}H and ^{13}C NMR spectra and elemental analysis. Furthermore, the structure of **4h** was confirmed by X-ray crystallographic analysis (CCDC 867509, Fig. 1). The *N*-bound six-membered phenyl ring shows positional disorder between the hydrogen and chlorine atoms at the *para*-position with a refined site occupancy ratio of 0.648(8)/0.352(8). For the crystal data and structure refinement of compound **4h** see ESI.†

A plausible mechanism for this multi-component reaction is illustrated in Scheme 5. At first the intermediate hydrazone **A** is formed by the condensation of aldehyde **1** with hydrazine **2** (it seems that electron-withdrawing groups on the aromatic ring of aldehydes increase the electrophilicity of the carbonyl group towards nucleophilic attack by aryl hydrazine). Then, complexation of Cu(II) with the triple bond of DMAD **3** and subsequent transfer of an electron from DMAD to Cu(II) results in a radical cation intermediate **B** and Cu(I) species.[28] Nucleophilic attack of hydrazone **A** on radical cation **B** provides **C**. One-electron transfer from Cu(I) to **C** gives **D** which upon prototropic shift from nitrogen to carbon gives **E** which in turn converts to **F** by intramolecular nucleophilic attack. The intermediate **F** is transformed to pyrazoline **5** *via* a prototropic shift (in this case, the acidity of hydrogen attached to the carbon of hydrazone is increased due to the presence of electron-withdrawing substituents on the R group and consequently, the conversion of **E** to **F** and finally to **5** is facilitated). Finally, aromatization of **5** under an ambient atmosphere in the presence of Cu(II) catalyst affords the

Table 1 Optimization of the reaction conditions for synthesis of pyrazole **4a**[a]



1 2 3 4

Entry	Catalyst	Time (h)	Yield[b] (%)
1	No catalyst	10	—
2	$CuBr_2$	1	35
3	[*n*-Bu_4P][$CuBr_3$]	1	87
4	[bmim][$CuCl_3$]	1	65
5	[bmim][$CuBr_3$]	1	60
6	[bmim][$FeCl_4$]	1	52
7[c]	[bmim][$InCl_4$]	1	40
8[c]	[bmim][$ZnCl_3$]	1	31
9[d]	[*n*-Bu_4P][$CuBr_3$]	1	79
10[e]	[*n*-Bu_4P][$CuBr_3$]	1	87
11[f]	[*n*-Bu_4P][$CuBr_3$]	1	80
12[g]	[Bu_4P][$CuBr_3$]	1	87

[a] Benzaldehyde (1 mmol), phenylhydrazine (1 mmol) and DMAD (1.2 mmol), catalyst (25 mol%), at 100 °C. [b] Isolated yield. [c] The corresponding pyrazoline was the major product. [d] 20 mol% of catalyst was used. [e] 30 mol% of catalyst was used. [f] Reaction was performed at 90 °C. [g] Reaction was performed at 110 °C.

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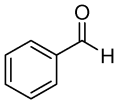
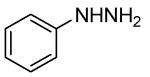
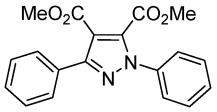
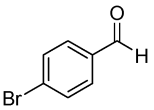
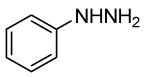
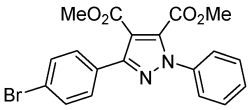
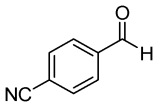
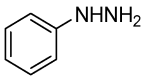
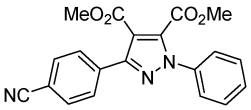
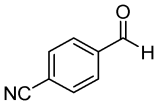
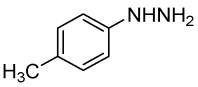
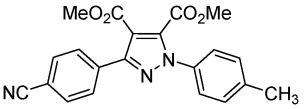
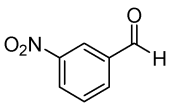
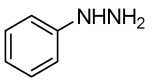
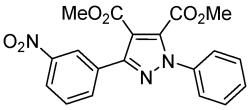
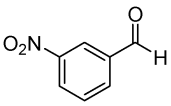
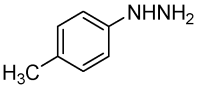
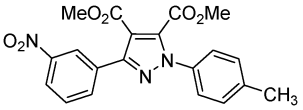
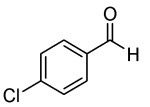
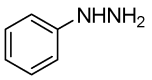
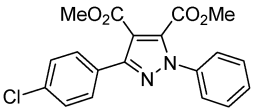
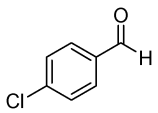
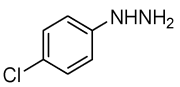
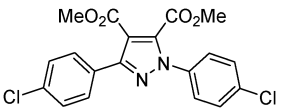
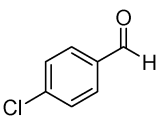
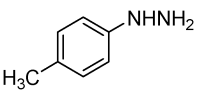
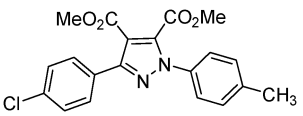
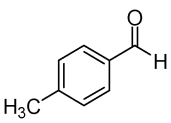
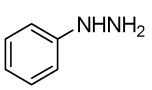
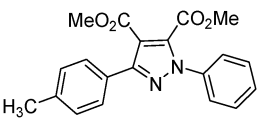
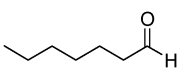
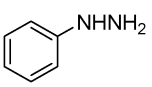
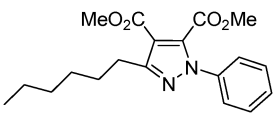
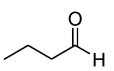
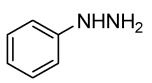
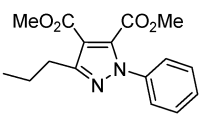
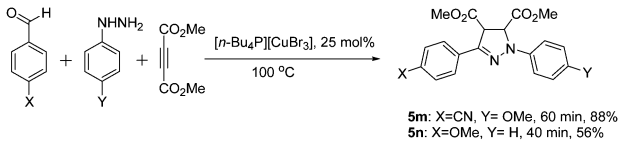
Table 2 Synthesis of pyrazoles *via* cyclization–aromatization of hydrazones with DMAD in the presence of $[n\text{-Bu}_4\text{P}][\text{CuBr}_3]$[a]

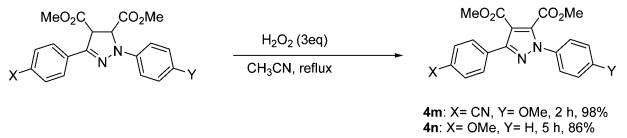
Entry	Aldehyde (**1**)	Hydrazine (**2**)	Product (**4**)		Time (min)	Yield[b] (%)
1				**4a**	60	87
2				**4b**	60	66
3				**4c**	90	91
4				**4d**	90	86
5				**4e**	90	92
6				**4f**	90	85
7				**4g**	60	79
8				**4h**	60	86
9				**4i**	60	75
10				**4j**	60	76
11				**4k**	60	67
12				**4l**	60	72

[a] Aldehyde (1 mmol), phenylhydrazine (1 mmol) and DMAD (1.2 mmol), $[n\text{-Bu}_4\text{P}][\text{CuBr}_3]$ (25 mol%) under solvent-free conditions at 100 °C. [b] Isolated yield.

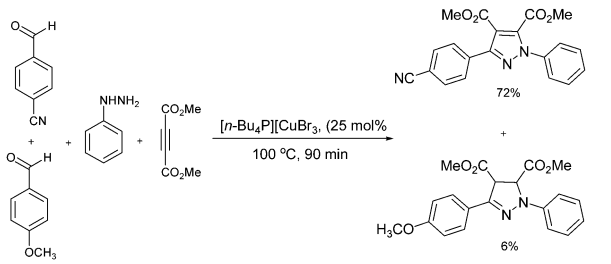
corresponding pyrazole **4** and releases the Cu(II) species for the next catalytic cycle (Scheme 5). To confirm the suggested mechanism, a radical scavenger such as 1,1-diphenylethylene or 2,6-di-*tert*-butylphenol was added to the reaction mixture. Under these conditions, the related hydrazone was observed in the reaction mixture and no further conversion to its corresponding pyrazole occurred. This observation proved the presence of radical species in the reaction. The model reaction was also performed under an argon atmosphere; the product yield was reduced considerably. It is also noteworthy that bubbling oxygen into the reaction mixture accelerated the reaction. These results show that the presence of oxygen is essential. According to the previous works,[25,26] the copper(II) ionic liquid in the presence of oxygen can oxidize the pyrazoline derivatives to pyrazoles.



Scheme 2 Chemoselective synthesis of pyrazoline.



Scheme 3 Oxidation of pyrazolines **5m** and **5n** to their corresponding pyrazoles **4m** and **4n** in the presence of H_2O_2.



Scheme 4 Chemoselective reaction of 4-cyanobenzaldehyde and 4-methoxybenzaldehyde with phenylhydrazine catalyzed by $[n\text{-Bu}_4P][CuBr_3]$.

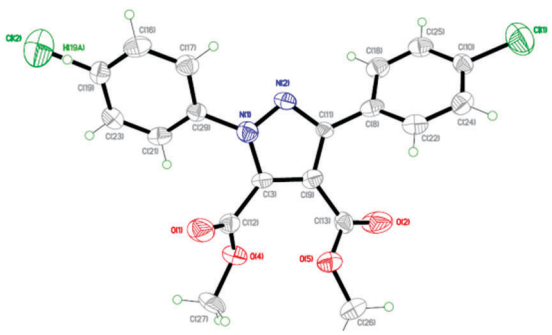
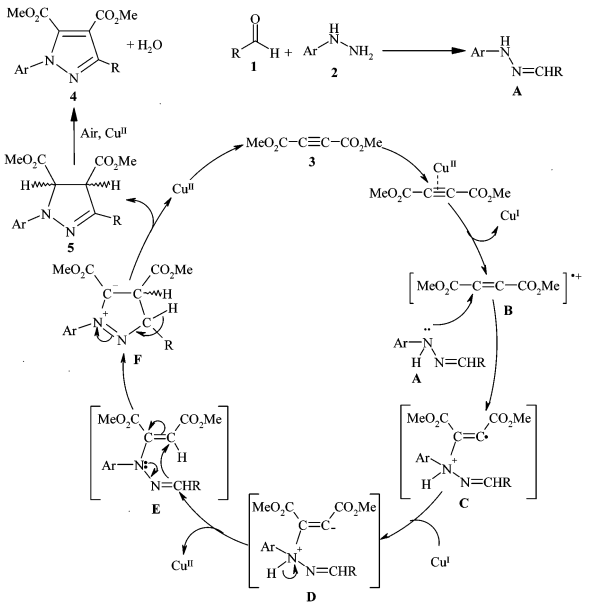


Fig. 1 The crystal structure of compound **4h**.

To check the role of Cu(II) in the oxidation process, the oxidation of dimethyl 1,3-diphenyl-4,5-dihydro-1*H*-pyrazole-4,5-dicarboxylate (the corresponding pyrazoline of **4a**) was investigated in the absence of catalyst; no desired pyrazole was obtained under these conditions. This shows that Cu(II) plays a crucial role in the oxidation step, in addition to activation of DMAD.

It is noteworthy that in comparison with the previous work on the synthesis of pyrazoles using Cu(I) as the catalyst and sodium acetate as the base,[20] in the presence of $[n\text{-Bu}_4P][CuBr_3]$ without any base, the reaction times are shorter (1–1.5 h compared to 10 h) and the yields are higher (66–92% compared to 52–88%). It seems that these two synthetic methods proceed *via* two different pathways.



Scheme 5 Proposed mechanism for the cyclization–aromatization reaction of hydrazone with DMAD.

Reusability and recyclability of a catalyst is of practical importance in minimizing the amount of waste. In this context, we investigated the reusability of this ionic liquid in the model reaction. After completion of the reaction, water (30 ml) was added and the organic materials were filtered. Then, the water was evaporated, the catalyst was dried at 80 °C under reduced pressure for 2 h and reused. The catalyst could be recycled four times with slight loss of its activity (Fig. 2).

In conclusion, we have demonstrated an efficient, novel, eco-friendly and chemoselective method for the synthesis of fully substituted pyrazoles, using Lewis acidic ionic liquid $[n\text{-Bu}_4P][CuBr_3]$ as a reusable catalyst. Short reaction times, simple operation, high yields of products, a green procedure and avoiding toxic organic solvents and reagents are noteworthy advantages of the current method.

Experimental

General information

Melting points were determined using a Stuart Scientific SMP2 apparatus and are uncorrected. FT-IR spectra were obtained as

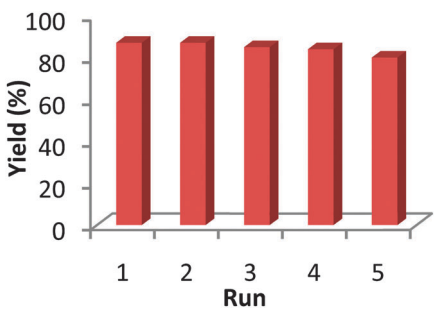


Fig. 2 Reusability of the catalyst for synthesis of **4a**.

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KBr pellets using a Nicolet-Impact 400D instrument in the range of 400–4000 cm^{-1}. ^1H NMR (400 and 500 MHz) and ^{13}C NMR (100 and 125 MHz) spectra were recorded on Bruker-Avance 400 and 500 spectrometers, respectively. All mass spectra were recorded on a Micromass Platform II spectrometer; EI mode at 70 eV. Elemental analysis was carried out using a LECO, CHNS-932 instrument.

General procedure for synthesis of pyrazoles *via* cyclization–aromatization of hydrazones with dimethyl acetylenedicarboxylate. A mixture of aldehyde (1 mmol) and arylhydrazine (1 mmol) was stirred for 20 min. Then, DMAD (1.2 mmol) and [*n*-Bu_4P][$CuBr_3$] (0.25 mmol) were added and the mixture was heated at 100 °C under solvent-free conditions for the appropriate time (Table 2). The progress of the reaction was monitored by TLC (eluent: *n*-hexane–ethyl acetate, 9 : 1). After completion of the reaction, the mixture was cooled to room temperature and water was added (30 ml). The mixture was filtered and the crude product was purified by recrystallization from EtOH to afford the pure product. If necessary, the product was purified by silica gel column chromatography (eluent: *n*-hexane–ethyl acetate: 12/1).

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