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# Morpholinium glycolate as an efficient and reusable catalyst for the synthesis of bis(pyrazol-5-ol) derivatives under solvent-free conditions

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ABSTRACT

In this paper, an environmentally benign access to synthesize Bis(pyrazol-5-ol) derivatives was developed through the one pot pseudo five component condensation reaction of phenyl hydrazine with ethyl acetoacetate, and different aryl/heteroaryl aldehydes using morpholinium glycolate as the homogeneous reusable catalyst under solvent-free conditions at 80 °C. Further, the ionic liquid was prepared and characterized by FT-IR, $^{1}$HNMR, $^{13}$CNMR and TG-DTG techniques. The present synthetic protocol offers excellent yields of the products, short reaction times, clean and simple work up, reusability of catalyst up to five runs, a significant reduction in cost, and eco-efficient alternative to the existing methods.

***Keywords**: Bis(pyrazol-5-ol)s, Morpholinium glycolate, Ionic liquids, Homogeneous catalyst.*

## 1. Introduction

Recently, greener synthetic tools such as multicomponent reactions, ionic liquids (ILs), and solventless reaction conditions have received an enormous attention because of environmental protection laws and global warming effects [1]. Multicomponent reactions (MCRs) have emerged as an essential tool for generating the libraries of drug-like compounds in an eco-friendly manner, and have a distinct edges in comparison to the multi-step reactions [2-4]. On the other hand, fused salts which remain in liquid form at room temperature or below 100 °C were termed as ionic liquids(ILs) [5]. The chemistry of ionic liquids is not new, in fact, in 1914 the first synthesized ionic liquid [$EtNH_3$][$NO_3$] was reported [6]. Since, due to their notable physical and chemical properties, they have found application in different areas such as catalysis [7-12], nanotechnology [13,14], electrochemistry [15], biotechnology [16], engineering processes [17], separations [18] and extractions [19,20]. However, the cost and to some extent the toxicity of few ILs are significant concerns, which can be overcome by the careful selection of anions/cations during the preparations of ionic liquids. Thus, the designing of non-toxic and low-cost ionic liquids is the prime challenge for the chemists. Our literature search at this stage revealed that the morpholinium based ILs exhibits less toxicity, compared to the commonly used tetraalkylammonium, imidazolium, pyridinium based ILs [21].

Pyrazoles are the core structural fragment of many pharmacologically active compounds [22,23]; in fact, in the treatment of Parkinson and Alzheimer diseases, they show inhibitory action against monoamine oxidase [24-26]. Pyrazoles, including 4,4′-(arylmethylene)-bis(3-methyl-1-phenyl-1H- pyrazol-5-ols) have been used as antidepressants [27], anti-inflammatories [28], antipyretics [29], inhibitors of Mycobacterium tuberculosis [30] pesticides [31], fungicides [32], and dyestuffs [33].

Because of these significances, various synthetic protocols have been reported for the synthesis of 4,4'-(arylmethylene) bis (3- methyl-1- phenyl- 1H- pyrazol-5-ol) derivatives [34-37]. These protocols include the use of different catalysts such as Silica-bonded

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N-propylpiperazine sulfamic acid (SBPPSA) [38], Na+-MMT-[pmim]$HSO_4$ [39], Perlite sulfonic acid [40], [$Et_3NH$][$HSO_4$] [41], [cmpy]Cl [42], N-Methylimidazolium perchlorate [43], (DCDBTSD) [44], 2-hydroxy ethyl ammonium propionate [45], and others [46-49]. These protocols are quite satisfactory in many instances, but most of them suffer from certain disadvantages such as the use of an expensive and excess amount of catalyst, lack of reusability of catalyst, prolonged reaction time, moderate yields, harsh reaction conditions, and tedious workup procedures. Thus, the introduction of eco-efficient methods that overcome the mentioned problems is still in demand.

To our continued interest in green synthesis, herein we wish to report the preparation and characterization of morpholinium glycolate (Scheme 1), and its promoting role in the synthesis of Bis(pyrazol-5-ol) derivatives under solvent-free conditions (Scheme 2).

## 2. Experimental

All the chemicals were used from the supplier, except pyrazole-4-carbaldehyde (**3k**) which was prepared according to the reported method [50]. Melting points were measured in an open capillary tube and are uncorrected. All reactions monitoring and purity of the synthesized compounds were performed by TLC on silica-gel 60 F254 aluminium plates. IR spectrum of the compounds was recorded on Thermo Nicolet Avatar 370 FT-IR spectrometer. $^1$HNMR (400 MHz) and $^{13}$CNMR (100 MHz) were carried out on Bruker Advance II 400 spectrometer using DMSO-$d_6$/chloroform-$d$ as solvents. The thermal behavior of the catalyst was studied on Perkin Elmer STA 6000.

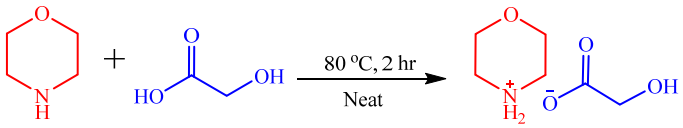
### *2.1. Preparation of Morpholinium glycolate*

To the morpholine (10 mmol) in a 50 mL round bottom flask, glycolic acid (65%, 10 mmol) was added dropwise at room temperature. After addition, the reaction mixture was vigorously stirred at 80 °C for two hours. Finally, the reaction content was cooled, washed with (2 X 15 mL) cyclohexane and dried under reduced pressure to afford a clear brownish liquid (88% yield).

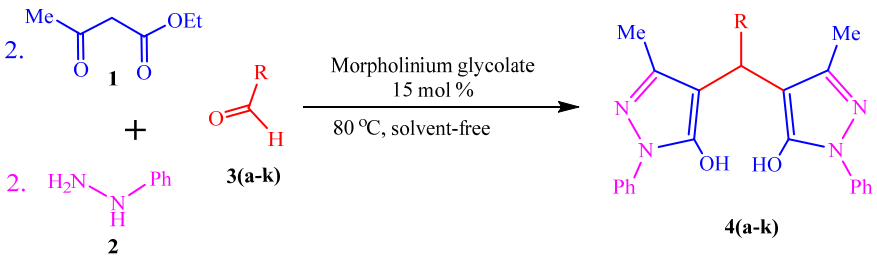
TG-DTG analysis (40 to 730 °C): decomposition point above 206 °C. FT-IR: $\bar{\nu}$= 3600-2640, 1591, 1452, 1405, 1239, 1103 cm$^{-1}$. $^1$HNMR (400 MHz, DMSO-$d_6$): δ= 3.03 (t, $J$ = 4.9 Hz, 4H), 3.67 (s, 2H), 3.75 (t, $J$ = 4.8 Hz, 4H), 4.09 (s, 1H), 6.57 (s, 2H) ppm. $^{13}$CNMR (100 MHz, DMSO-$d_6$): δ= 42.89, 61.54, 63.86, 177.35 ppm.

### *2.2. Synthesis of Bis(pyrazol-5-ol) derivatives(**4a-k**)*

In a 25 mL round bottom flask, a mixture of ethyl acetoacetate (**1**) (2 mmol), phenyl hydrazine (**2**) (2 mmol), aromatic aldehydes (**3a-k**) (1 mmol), and morpholinium glycolate (15 mol %) was heated up to 80 °C with proper stirring for the appropriate time as mentioned in Table **2**. After completion of the reaction (monitored by TLC ethyl acetate: methanol: n-hexane 1:1:8), water (5 mL) was added, and stirring was continued for a few minutes before the reaction was set to cool. The precipitated products were collected by simple filtration and recrystallized from aqueous ethanol (85%) to afford the pure products (**4a-k**) up to 96% yields. The catalyst was recovered from the filtrate under reduced pressure and reused in subsequent cycles. All the products are known except (**4k**) and their physical and spectral data are in agreement with those reported in the literature.




**Scheme 1.** Preparation of morpholinium glycolate.




**Scheme 2.** Synthesis of bis(pyrazol-5-ol) derivatives (4a-k) in the presence of morpholinium glycolate.

*Selected spectral data*

*4,4'-((3-(4-methoxyphenyl)-1-phenyl-1H-pyrazol-4-yl) methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (**4k**):*

Orange solid. m.p.= 198-200 °C. FT-IR (KBr): $\bar{\nu}$= 3133 (OH stretching), 2994 (CH atom), 2835 (CH aliphatic), 1672, 1604, 1502, 1451, 1366, 1323, 1294, 1248, 1179 $cm^{-1}$. $^1$HNMR (400 MHz, $CDCl_3$): δ= 2.25 (s, 6H, $2CH_3$), 3.89 (s, 3H, $OCH_3$), 4.12 (s, 1H, –CH), 7.06 (d, 2H, Ar–H), 7.17-7.25 (m, 3H, Ar–H), 7.34-7.52 (m, 6H, Ar–H), 7.61 (d, 2H, Ar–H), 7.87-7.96 (m, 7H, Ar–H), 10.22 (s, 2H, OH) ppm. $^{13}$CNMR (100 MHz, $CDCl_3$): δ= 13.04, 38.07, 55.44, 110.45, 115.97, 119.32, 123.50, 124.87, 127.74, 128.86, 129.54, 130.69, 134.07, 138.52, 139.42, 160.56 ppm.

## 3. Results and Discussion

In this work, morpholinium glycolate was prepared according to our previously reported method [51], and characterized by FT-IR, $^1$HNMR, $^{13}$CNMR and TG-TDA techniques. After that, its catalytic activity was investigated in the synthesis of bis(pyrazol-5-ol) derivatives.

### *3.1. Catalyst characterization*

The FT-IR spectrum of ionic liquid (Fig. 1) showed the broad peaks in the region of 3600-2640 $cm^{-1}$ which can be related to the overlapping of O–H and N–H stretching groups. The peaks at 2991, 2870 $cm^{-1}$, and 1452 $cm^{-1}$ were ascribed to C–H stretching and bending vibrations respectively. The sharp peak at 1591 $cm^{-1}$ was detected due to ionic carboxyl vibration. Furthermore, the absorption peaks at 1402 $cm^{-1}$ and 1239 $cm^{-1}$ were related to O–H bending and (C-O-C) stretching respectively. These mentioned peaks clearly confirmed the structure of morpholinium glycolate.

The $^1$H and $^{13}$CNMR spectra of morpholinium glycolate were depicted in (Fig. 2). In $^1$HNMR study of the catalyst, the important signal of (–OH) and ($NH_2^+$) protons were observed at δ = 4.09 and δ = 6.57 ppm respectively whereas the methylene (–$CH_2$–) protons were recorded at δ = 3.03, 3.63 and 3.75 ppm. The $^{13}$CNMR peaks of the ionic liquid were detected at 42.89, 61.54, 63.86, and 177.35 ppm. Thermal gravimetric (TG) analysis and differential thermal gravimetric (DTG) analysis of the catalyst were performed in the range of 40 to 730 °C with increasing the temperature to 20 °C per minute. The decomposition of catalyst took place in more than two steps. The weight loss up to 168 °C resulted from the release of an adsorbed water molecule whereas the significant weight loss after 206 °C is attributed to the molecular decomposition of the catalyst. Therefore, based on the thermal analysis (Fig. 3), it is clear that the morpholinium glycolate is thermally stable up to 206 °C.

### *3.2. Catalyst activity*

The catalytic activity of morpholinium glycolate was investigated in the synthesis of the product (**4a**). For this purpose, phenyl hydrazine, ethyl acetoacetate and benzaldehyde were selected as the model substrates. Initially, 15 mol% of morpholinium glycolate as catalyst was used under solvent-free conditions at different temperatures (Table 1, entries 1-18). At room temperature, there was a trace amount of product formed and, as the temperature increases up to 100 °C, the reaction proceeds with higher yields (Table 1, entries 1-7).

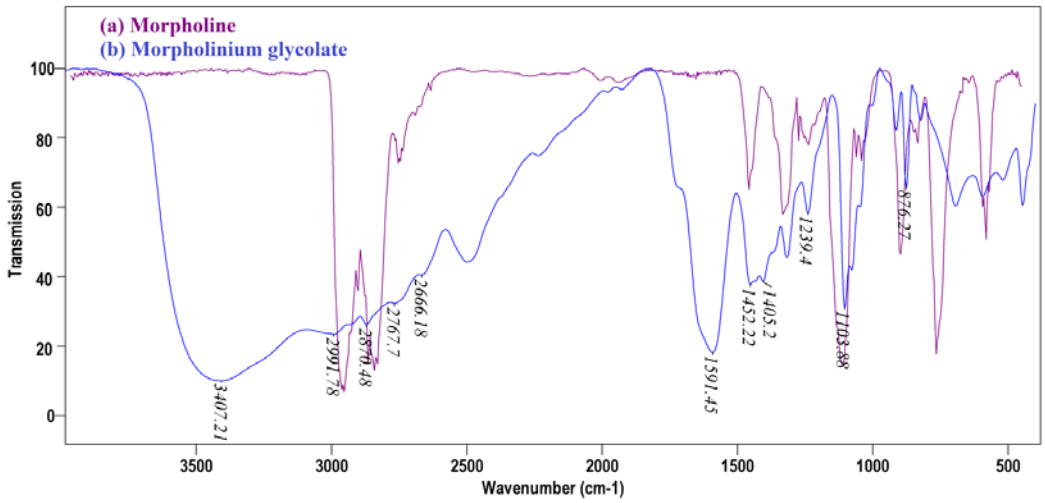



**Fig. 1.** The FT-IR spectrum of (a) morpholine and (b) morpholinium glycolate.

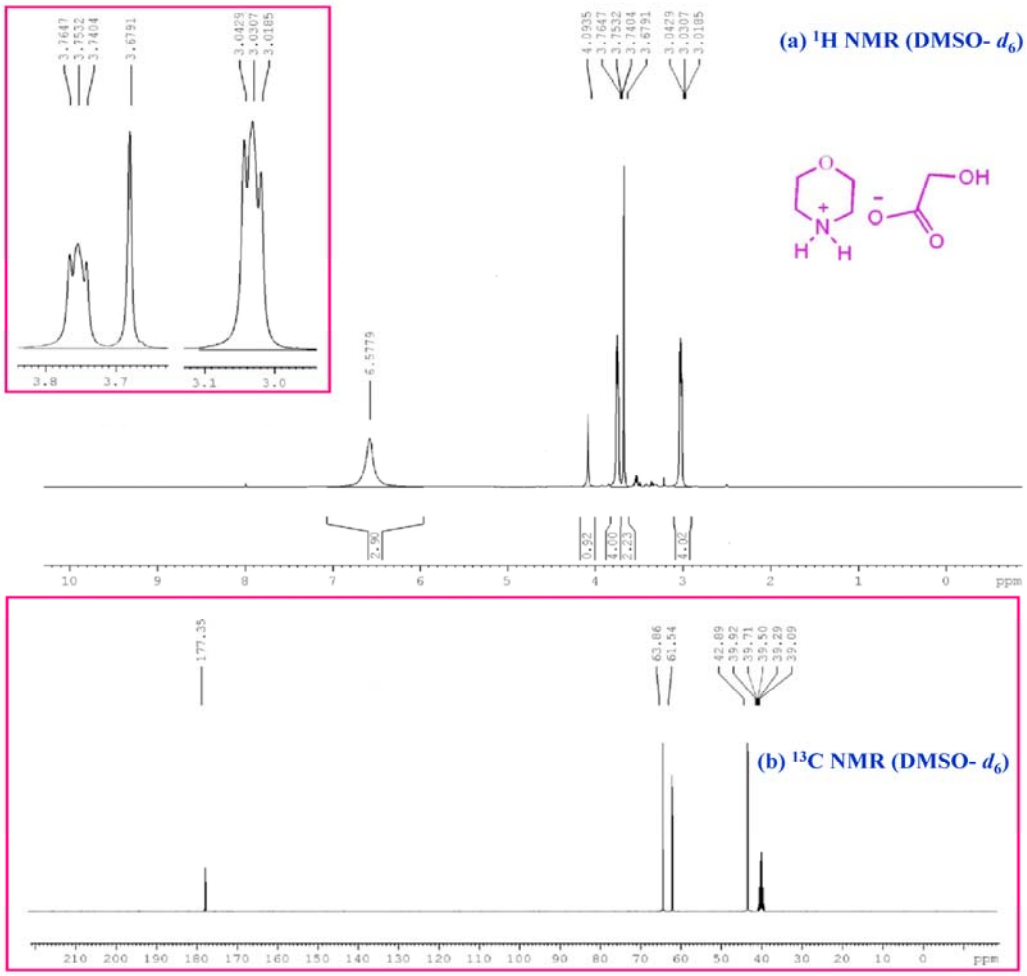



**Fig. 2.** (a) [1]HNMR and (b) [13]CNMR spectra of morpholinium glycolate.

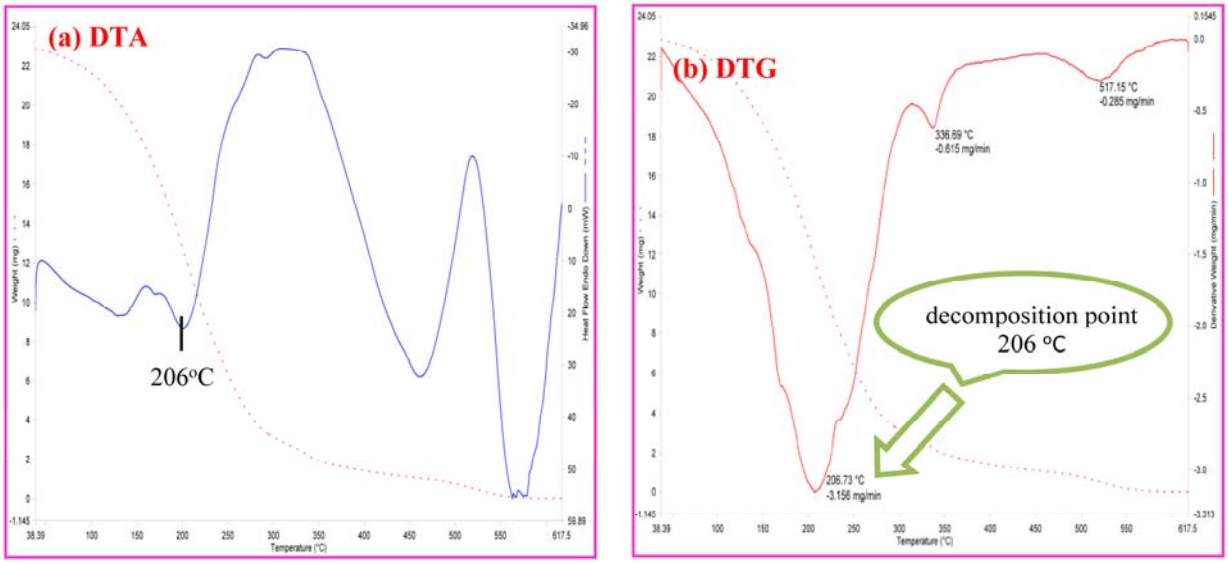



**Fig. 3.** (a) TG, DTA and (b) DTG of morpholinium glycolate.

**Table 1.** Optimization of reaction conditions in the synthesis of (4a)[a] using Morpholinium glycolate as the catalyst.

| Entry | Temp. (°C) | Catalyst (mol%) | Solvent | Time (min)[b] | Yield (%)[c] |
|---|---|---|---|---|---|
| 1 | room temperature | 15 | solvent-free | 150 | 55 |
| 2 | 50 | 15 | solvent-free | 120 | 60 |
| 3 | 60 | 15 | solvent-free | 45 | 68 |
| 4 | 70 | 15 | solvent-free | 30 | 75 |
| **5** | **80** | **15** | **solvent-free** | **10** | **90** |
| 6 | 90 | 15 | solvent-free | 10 | 90 |
| 7 | 100 | 15 | solvent-free | 10 | 90 |
| 8 | 80 | no catalyst | solvent-free | 210 | trace |
| 9 | 80 | 5 | solvent-free | 60 | 30 |
| 10 | 80 | 10 | solvent-free | 35 | 60 |
| 11 | 80 | 20 | solvent-free | 10 | 90 |
| 12 | 80 | 25 | solvent-free | 10 | 90 |
| 13 | reflux | 15 | ethanol | 90 | 70 |
| 14 | reflux | 15 | methanol | 90 | 68 |
| 15 | reflux | 15 | water | 120 | 50 |
| 16 | reflux | 15 | water:ethanol | 90 | 75 |
| 17 | reflux | 15 | acetonitrile | 180 | 45 |
| 18 | reflux | 15 | toluene | 120 | 58 |

[a]Reaction conditions: Ethyl acetoacetate (2 mmol), phenyl hydrazine (2 mmol) and (1 mmol)benzaldehyde.
[b]Reaction progress monitored by TLC.
[c]Isolated yields.

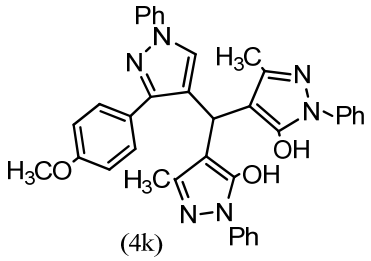
From the obtained result, 80 °C was chosen as the optimum reaction temperature (Table 1, entry 5). Further, the amount of catalyst was evaluated in the model reaction. The result presented in (Table 1, entries 5, 8-12) clearly showed that the best result was obtained for 15 mol% of morpholinium glycolate affording 90% yield (entry 5), and a reaction, without catalyst did not lead to form the product. After that, a variety of solvents such as MeOH, EtOH, $H_2O$, EtOH:$H_2O$, ACN and toluene were screened at reflux temperature in the presence of 15 mol% catalyst (Table 1, entries 13-18). Consequently, the solvent-free condition was found to be better in term of reaction time and product yield.

Encouraged by the significant results, the practicability of this approach was further explored in the synthesis of different bis(pyrazol-5-ol) derivatives (Table 2). Both electron-withdrawing and electron-donating aryl aldehydes were reacted efficiently and furnished the corresponding products in excellent yields (Table 2, entries 1-9). The higher yields and shorter reaction times were observed in the case of aldehydes which have electron-withdrawing groups (Table 2, entries 2-5). Furthermore, Pyrazole-4-carbaldehyde (**3k**) was also reacted smoothly and afforded the product in 92% yield (Table 2, entry 11).

The catalytic activity was also compared with some other reported ILs in the synthesis of compounds (**4a**). The tabulated data (Table 3) clearly indicate that our new catalytic system has the significant edge in terms of reaction time, temperature, yield, simplicity and cost of the procedure.

The probable mechanism for the synthesis of Bis(pyrazol-5-ol) derivatives has been outlined in scheme 3 [43]. At the beginning of reaction, morpholinium glycolate activates the ethyl acetoacetate (**1**), and then phenyl hydrazine (**2**) attacks the carbonyl groups of (**1**) to afford pyrazolone (I), was further rearranged into tautomer (II). In a next step, Knoevenagel type of reaction takes place between activated aldehydes (**3a-k**) and tautomer (II) followed by the liberation of a water molecule to form intermediate (III). Then, Michael addition reaction between intermediate (III) and tautomer (II) is facilitated to form intermediate (IV). Finally, the corresponding products (**4a-k**) are formed by tautomerization and aromatization of intermediate (IV).

**Table 2**. Morpholinium glycolate catalyzed synthesis of bis(pyrazol-5-ol) derivatives (4a-k).[a]

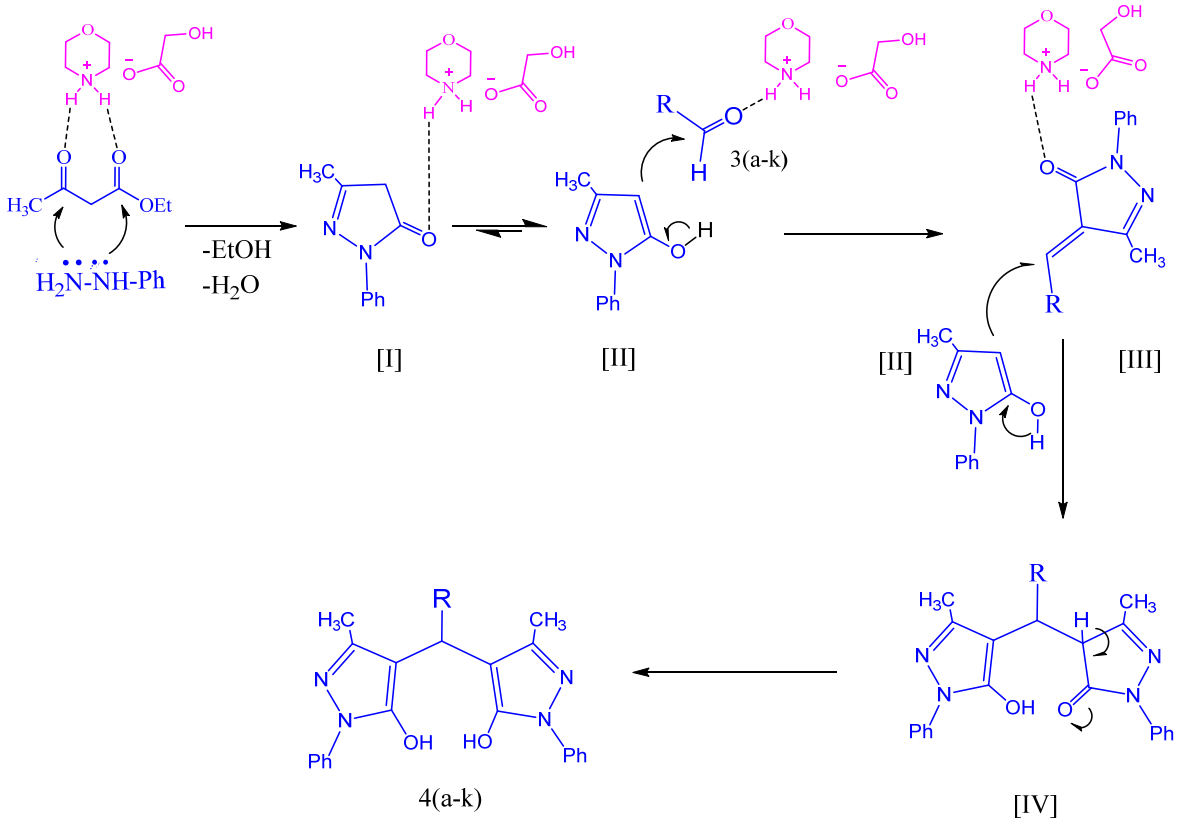
| Entry | R | Product | Time (min)[b] | Yield (%)[c] | m.p. (°C) | | Ref. |
|---|---|---|---|---|---|---|---|
| | | | | | Found | Reported | |
| 1 | $C_6H_5$ | 4a | 10 | 90 | 170-172 | 171-172 | [37] |
| 2 | 4-$ClC_6H_4$ | 4b | 5 | 96 | 208-210 | 207-209 | [37] |
| 3 | 2-$ClC_6H_4$ | 4c | 8 | 91 | 234-236 | 236-237 | [37] |
| 4 | 4-$NO_2C_6H_4$ | 4d | 6 | 96 | 229-231 | 230-232 | [37] |
| 5 | 3- $NO_2C_6H_4$ | 4e | 9 | 92 | 149-150 | 148-150 | [35] |
| 6 | 4-$CH_3C_6H_4$ | 4f | 10 | 90 | 200-202 | 201-202 | [35] |
| 7 | 4-$CH_3OC_6H_4$ | 4g | 12 | 90 | 171-173 | 171-173 | [43] |
| 8 | 4-$HOC_6H_4$ | 4h | 12 | 89 | 154-156 | 155-157 | [38] |
| 9 | 2-$HOC_6H_4$ | 4i | 12 | 85 | 225-227 | 227-229 | [38] |
| 10 | 2-furyl- | 4j | 9 | 86 | 188-190 | 187-189 | [43] |
| 11 | 3k |  (4k) | 10 | 92 | 198-200 | New | This work |

[a]Reaction conditions: Ethyl acetoacetate (2 mmol), phenyl hydrazine (2 mmol) and aldehydes (1mmol) catalyzed by 15 mol% morpholinium glycolate under solvent-free conditions at 80 °C.
[b]Reaction progress monitored by TLC.
[c]Isolated yield.

**Table 3**. Comparison of catalytic activity of Morpholinium glycolate with different ILs in the synthesis of (4a) under solvent-free conditions.

| Entry | Ionic liquids as catalyst | Amount of catalyst (mol%) | Temp. (°C) | Time (min) | Yield (%)[a] | Ref. |
|---|---|---|---|---|---|---|
| 1 | N-Methylimidazolium perchlorate [MIm]$ClO_4$ | 5.4 | 50 | 37 | 90 | [43] |
| 2 | 1-(carboxymethyl)pyridinium chloride [cmpy]Cl | 10 | 110 | 17 | 82 | [42] |
| 3 | 2-Hydroxy ethylammonium propionate (2-HEAP) | 10 | 90 | 30 | 91 | [45] |
| 4 | [$Et_3NH$]$HSO_4$ | 10 | 90 | 45 | 90 | [41] |
| 5 | Na+-MMT-[pmim]$HSO_4$ | 5 | 100 | 14 | 91 | [39] |
| 6 | Morpholinium glycolate | 15 | 80 | 10 | 90 | This work |

[a]Isolated yield.




**Scheme 3.** The proposed mechanism for the synthesis of bis(pyrazol-5-ol) derivatives 4(a-k) using morpholinium glycolate as the catalyst.

### *3.3. Catalyst reusability*

The reusability of morpholinium glycolate in the reaction of ethyl acetoacetate, phenyl hydrazine and benzaldehyde under the optimized reaction conditions was investigated for five runs. After completion of the reaction, 5 mL water was added, and the solid product was separated by simple filtration. The filtrate containing morpholinium glycolate was concentrated under reduced pressure. Then the recovered catalyst was washed with cyclohexane, dried and used directly for subsequent reaction with no considerable drop in its catalytic activity. (The yields for five runs were 91, 91, 90, 88 and 86 %, respectively).

## 4. Conclusions

In outline, the catalyst morpholinium glycolate was fabricated from the commercially available low-cost reagents. Further, their catalytic activity was explored for the synthesis of bis(pyrazol-5-ol) (**4a-k**) derivatives. The solvent-free conditions, utilization of homogeneous reusable catalyst, shorter reaction times, clean and straightforward work up, and excellent yields of the products are the notable features of the current protocol.

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