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# Amberlite-Supported L-Prolinate: A Novel Heterogeneous Organocatalyst for the Three-Component Synthesis of 4*H*-Pyrano[2,3-*c*]pyrazole Derivatives[1]

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**Abstract**—This report describes a new and convenient procedure for heterogenization of L-proline organocatalyst, which is based on non-covalent immobilization of L-proline on the surface of anion-exchange resin amberlite IRA900OH (AmbIRA900OH) as an efficient, cheap, and commercially accessible cationic polymer support. The ion-pair immobilization of L-proline on the surface of amberlite IRA900OH was achieved by treatment of a MeOH/$H_2O$ solution of L-proline with amberlite IRA900OH at 60°C. L-Proline anion was exchanged with hydroxide ion and immobilized via ionic interaction between the carboxylate group of L-prolinate and quaternary ammonium cation of the cationic amberlite support. The prepared heterogeneous organocatalyst was characterized by FTIR, TGA, DTG, XRD, and elemental analysis techniques. The amberlite-supported catalyst was used as an efficient, reusable, and cheap catalyst for the one-pot three-component synthesis of 4*H*-pyrano[2,3-c]pyrazole derivatives in ethanol. The catalyst can be easily recovered and reused by simple filtration for several successive runs with no significant loss of catalytic activity.

**Keywords:** L-proline, anion-exchange resin, organocatalyst, 4*H*-pyrano[2,3-*c*]pyrazole, heterogeneous catalyst

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## INTRODUCTION

Organocatalysis has received great attention during the last years [1]. Organocatalysts have several important advantages, since they are usually robust, inexpensive, readily available, and nontoxic [2]. Organocatalysts are metal-free organic compounds of relatively low molecular weight and simple structure capable of promoting a reaction in substoichiometric amount. At the same time, immobilization and recycling of organocatalysts has experienced a very good growth [3, 4]. Indeed, organocatalysts are usually used in substantial amounts, in some cases up to 30 mol %. This is the main reason for the need of an efficient immobilization and recycling procedure. Moreover, immobilization of an organocatalyst may enhance its activity and stereoselectivity [5].

Immobilization of organocatalyst onto a solid support can be accomplished by either non-covalent linkage such as immobilization via hydrophobic interaction [6, 7], biphasic immobilization [8, 9], and self-supported gel-types and ion-pair immobilization [10, 11] or covalent linkage on supports such as polymers [12, 13], silica [14, 15], magnetite [16], and ionic liquids [17, 18].

One of the most important challenges with catalyst immobilization is to retain the activity and stereoselectivity of the immobilized catalyst. Moreover, another important aspect of immobilized catalysts is separation, which can be achieved by a simple operation such as filtration [19]. Among enantioselective organocatalysts, proline and its derivatives have attracted huge interest and development in the recent years.

The first asymmetric reaction using L-proline was reported in the early 1970s [20]; 30 years later, proline and proline derivatives have been extensively used, especially in asymmetric organocatalyzed aldol-type reactions [21–23]. It should be noted that the immobilization approach requires the use of synthetic derivatives that are more expensive than proline. The latter is commercially available at low cost but is often employed at high catalyst loading. However, attempts

[1] The text was submitted by the authors in English.

to improve or modify its catalytic behavior, taking advantage of specific properties of the support, would justify immobilization in many instances [24].

Pyrans belong to an important class of heterocyclic compounds which exhibit wide range of biological activities [25] and are widely used as cosmetics, pigments, and potentially biodegradable agrochemicals [26]. In view of great importance of pyran derivatives, in recent years efforts have been made to develop new methodologies for the synthesis of these compounds. Most of these methods utilize various catalysts. The most used methods for the synthesis of pyrano[2,3-*c*]-pyrazoles involve three-component cyclocondensation of 3-methyl-1-phenyl-4,5-dihydro-1*H*-pyrazol-5-one with aldehydes and malononitrile. Recently, some new catalysts have been reported for the preparation of this class of compounds [27–32]. Some of these methods suffer from drawbacks such as unsatisfactory yields, extended reaction times, elevated temperatures, tedious work-up, harsh reaction conditions, and the use of expensive reagents. Each method has its own advantages and disadvantages; however, search for a better catalyst for the synthesis of pyrano[2,3-*c*]pyrazoles continues in terms of operational simplicity, reusability, economic viability, and environmental safety.

Due to the current challenges for developing environmentally benign synthetic processes and in continuation of our research on applications of ion-exchange resins for click synthesis of 1,4-disubstituted-1*H*-1,2,3-triazoles [33, 34], we would like to explore the catalytic activity of the ion-exchange resin Amberlite IRA900OH (AmbIRA900OH) as a cationic polymer support for the ion-pair immobilization of L-proline anion via ionic interaction between the carboxylate group of L-prolinate and quaternary ammonium cation of the cationic Amb support. This heterogeneous catalyst was used as an efficient, reusable, cheap, and commercially accessible catalyst for the one-pot three-component synthesis of 4*H*-pyrano[2,3-*c*]pyrazole derivatives in ethanol.

## EXPERIMENTAL

The $^1$H NMR spectra were recorded on a Bruker Avance DPX 400 spectrometer (400 MHz). The X-ray diffraction (XRD) patterns were recorded on a Philips X'PERT-Pro-MPD diffractometer using Cu $K_\alpha$ radiation ($\lambda$ = 1.542 Å); A continuous scan mode was used to collect reflections intensities in the range $5° < 2\theta < 40°$. Fourier transform infrared (FT-IR) spectra (400–4000 cm$^{-1}$) were obtained in KBr using a Thermo Nicolet AVATAR 370 spectrophotometer. The elemental analyses (C, H, and N) were obtained with a Heraeus CHN-O-Rapid analyzer. Thermogravimetric and differential thermogravimetric (TG–DTG) analysis was performed on a Netsch STA449c instrument (sample weight ~10 mg; heating from room temperature to 600°C at a rate of 10 deg/min; alumina sample holders).

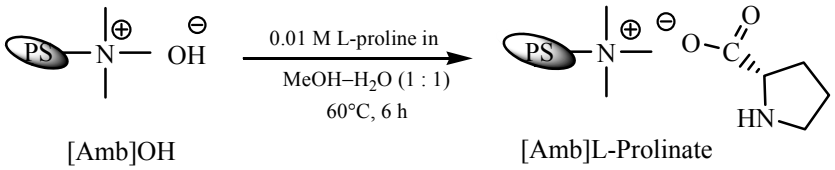
Preparation of the [Amb]-L-prolinate catalyst. Amberlite IRA-900OH (grain size 16–50 mesh, 1 g) was dispersed in 10 mL of a 1 M solution of L-proline in aqueous methanol (1 : 1), and the suspension was heated at 60°C for 6 h. The catalyst was filtered off, washed with aqueous methanol (1 : 1; 2 × 10 mL) and water (2 × 10 mL), and dried under reduced pressure [35–38].

**General procedure for the [Amb]L-prolinate-catalyzed multicomponent synthesis of 4*H*-pyrano[2,3-c]pyrazoles.** A round-bottom flask was charged with 5 mL of ethanol, 1 mmol of 3-methyl-1-phenyl-4,5-dihydro-1*H*-pyrazol-5-one, 1 mmol of the corresponding aldehyde, and 1 mmol of malononitrile, 0.08 g (10 mol %) of [Amb]L-prolinate was added, and the resulting suspension was magnetically stirred on heating under reflux until the reaction was complete (TLC; *n*-hexane–ethyl acetate, 3 : 1). The catalyst was filtered off and washed with hot ethanol (2 × 5 mL). The recovered catalyst was washed with acetone, dried, and stored for further recycling. Crystals of pure 4*H*-pyrano[2,3-*c*]pyrazole derivatives separated from the filtrate. Some products were described previously, and their melting points were compared with the reported values [27–32]. The newly synthesized compounds were characterized by IR and NMR data. Given below are spectral data for some selected 4*H*-pyrano[2,3-*c*]pyrazole derivatives.

**6-Amino-4-(4-methoxyphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (2e).** Yield 0.32 g (89%), pale yellow powder. IR spectrum (KBr), ν, cm$^{-1}$: 3394, 3325, 3059, 2975, 2193, 1661, 1597, 1515, 1397, 1258. $^1$H NMR spectrum, δ, ppm: 1.78 s (3H, $CH_3$), 3.74 s (3H, $OCH_3$), 4.62 s (1H, CH), 6.89 d (2H, CH, $J$ = 8.5 Hz), 7.15 s (2H, CH), 7.17 s (2H, $NH_2$), 7.31 t (1H, CH, $J$ = 7.6 Hz), 7.49 t (2H, CH, $J$ = 7.6 Hz), 7.77 d (2H, CH, $J$ = 8.5 Hz). $^{13}$C NMR spectrum, $\delta_C$, ppm: 12.6, 35.9, 55.1, 58.6, 98.9, 113.8, 119.9, 120.1, 126.2, 128.8, 129.4, 135.6, 137.5, 145.4, 158.2, 159.3.

**6-Amino-3-methyl-4-(3-nitrophenyl)-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (2g).**

**Scheme 1.**




[Amb]OH [Amb]L-Prolinate

Yield 0.33 g (88%), yellow powder. IR spectrum (KBr), ν, $cm^{-1}$: 3436, 3296, 3098, 2190, 1651, 1589, 1517, 1446, 1386, 1349, 1258, 1119. $^1H$ NMR spectrum, δ, ppm: 1.90 s (3H, $CH_3$), 4.81 s (1H, CH), 4.83 s (2H, $NH_2$), 7.36–7.37 m (1H, CH), 7.48–7.51 m (2H, CH), 7.56–7.59 m (1H, CH), 7.66–7.67 m (3H, CH), 8.13 s (1H, CH), 8.19 d (1H, CH, $^3J$ = 7.2 Hz). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 13.0, 36.8, 57.6, 98.0, 120.3, 120.5, 122.7, 126.7, 129.7, 130.7, 135.2, 137.9, 144.5, 145.6, 146.4, 184.4, 160.3.

## RESULTS AND DISCUSSION

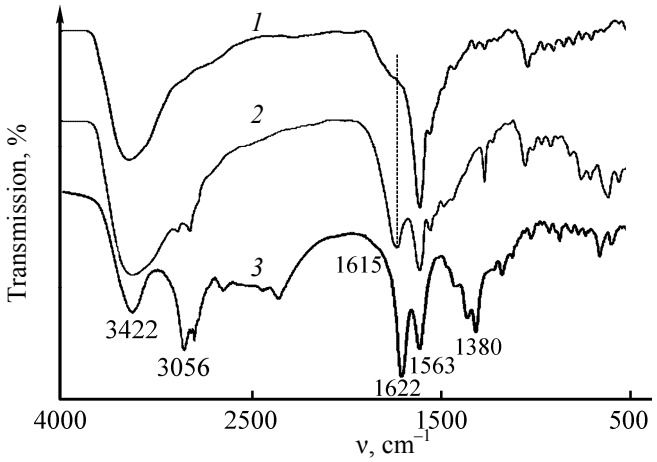
Catalyst preparation. The procedure for ion-pair immobilization of L-prolinate anion on the cationic polymer resin is illustrated by Scheme 1. The strategy consists of building up suitable heterogeneous macroporous polymer-supported L-prolinate catalyst on the surface of commercially available amberlite IRA-900OH (16–50 mesh). Preparation of the heterogeneous polymer-supported L-prolinate catalyst by this procedure is facile and straightforward. Typically, AmbIRA900OH was treated with a 0.01 M solution of L-proline in aqueous methanol at 60°C.

The ion–pair immobilization of L-prolinate anion on the polymer resin was confirmed by comparison of the FT-IR spectra of pure AmbIRA900OH, initial L-proline, and [Amb]L-prolinate hybrid (see figure). Characteristic stretching frequencies of L-proline appeared at 3056 (NH), 1622 ($COO^-$, asym.), and 1380 $cm^{-1}$ ($COO^-$, sym.). These bands are observed as new peaks in the FT-IR spectrum of [Amb]L-prolinate hybrid when compared with the spectrum of pure AmbIRA900OH (Fig. 1). The asymmetric and symmetric $COO^-$ stretching bands of [Amb]L-prolinate were found to shift to lower frequencies, 1615 and 1375 $cm^{-1}$, respectively. The band at 3056 $cm^{-1}$ corresponding to N–H stretching vibrations of L-proline did not change its position in the spectrum of [Amb]L-prolinate. These findings confirmed that L-prolinate anion was successfully loaded onto the polymer surface through ionic interaction (ion-pair binding) between the carboxylate group of L-prolinate and quaternary ammonium cation of the cationic Amb support.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTG) associated with the decomposition profiles of AmbIRA900OH, L-proline, and [Amb]L-prolinate hybrid in a nitrogen atmosphere and the XRD pattern of [Amb]L-prolinate provided further evidences for the immobilization of L-prolinate anion onto the polymer surface (for more information, see [35–38]).

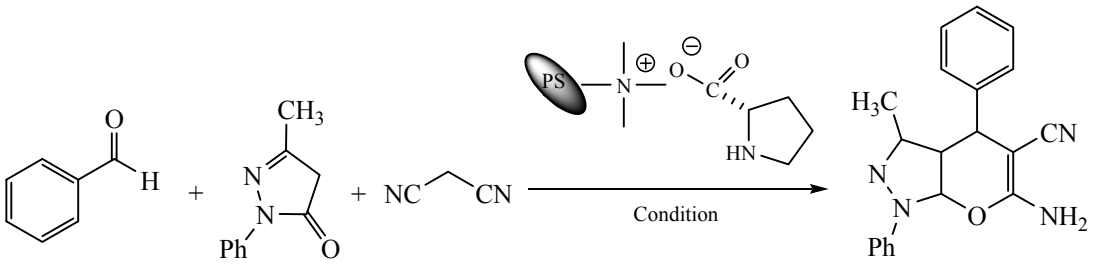
The effect of [Amb]L-prolinate (2–15 mol %) on the model reaction of benzaldehyde with malononitrile and 3-methyl-1-phenyl-4,5-dihydro-1*H*-pyrazol-5-one was studied under different conditions (Table 1). The results clearly indicated that the best yield of 6-amino-3-methyl-1,4-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (**2a**) was achieved by caring out the reaction in the presence of 10 mol % of [Amb]L-prolinate under reflux in ethanol (Table 1, run no. 9). The yield smoothly increased with the catalyst load up to 10 mol %, while the use of larger amounts of the catalyst (15 mol %) did not improve the yield; reduction of he amount of the catalyst led to decreased yield.

In order to explore the scope of this reaction, we conducted the reaction with a series of aromatic aldehydes bearing different substituent groups under the optimal conditions using 10 mol % of [Amb]L-prolinate in ethanol under reflux (Scheme 2, Table 2).




FT-IR spectra of (*1*) [Amb]OH, (*2*) [Amb]L-prolinate, and (*3*) L-proline.

**Table 1.** Reaction of benzaldehyde with malononitrile and 3-methyl-1-phenyl-4,5-dihydro-1*H*-pyrazol-5-one in the presence of [Amb]L-prolinate under different conditions




| Entry | Conditions | Temperature, °C | [Amb]L-prolinate, mol % | Time, min | Yield of **2a**,[a] % |
|---|---|---|---|---|---|
| 1 | No solvent | 100 | 2 | 50 | 50 |
| 2 | $CH_2Cl_2$ | Reflux | 2 | 45 | 60 |
| 3 | $CH_3CN$ | Reflux | 2 | 40 | 65 |
| 4 | THF | 65 | 2 | 45 | 65 |
| 5 | DMF | 100 | 2 | 35 | 68 |
| 6 | $H_2O$/DMF | 100 | 5 | 30 | 70 |
| 7 | $H_2O$ | Reflux | 5 | 35 | 80 |
| 8 | EtOH | Reflux | 5 | 25 | 90 |
| 9 | EtOH | Reflux | 10 | 15 | 98 |
| 10 | EtOH | Reflux | 15 | 15 | 97 |

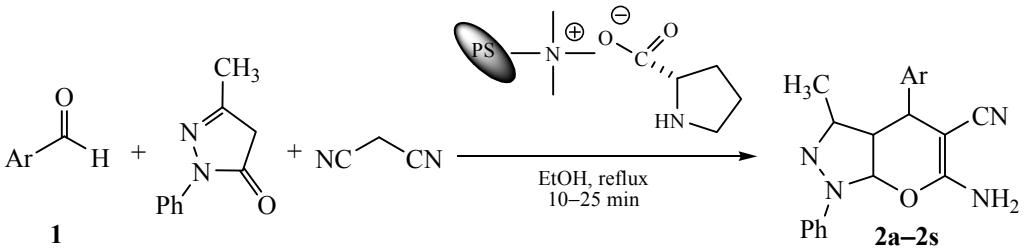
[a] Yield of isolated pure product.

All the products were cleanly isolated by simple filtration and recrystallization from hot ethanol. The data in Table 2 show that aromatic aldehydes with both electron-donating and electron-withdrawing groups smoothly reacted under the given conditions to give target products **2a**–**2s** in good to excellent yields.

Scheme 3 shows a probable reaction mechanism to demonstrate the role of the catalyst. The formation of 4*H*-pyrano[2,3-*c*]pyrazole derivatives involves simultaneously Knoevenagel condensation, Michael addition, and intramolecular cyclization. In the first step, the [Amb]L-prolinate catalyst abstracts a proton from the active methylene group of malononitrile giving rise to carbanion which attacks the carbonyl carbon atom of aromatic aldehyde, and the subsequent loss of water molecule yields α-cyanocinnamonitrile derivative. In the second step, [Amb]L-prolinate catalyst reacts with 3-methyl-1-phenyl-4,5-dihydro-1*H*-pyrazol-5-one to produce enamine intermediate. Michael addition of the latter to the Knoevenagel product, followed by ring closure and deprotonation, yields final 4*H*-pyrano[2,3-*c*]pyrazole.

As a true heterogeneous catalyst, supported catalyst should not leach into the reaction mixture, and the

**Scheme 2.**




**1** **2a–2s**

**Table 2.** Synthesis of 4*H*-pyrano[2,3-*c*]pyrazole derivatives catalyzed by [Amb]L-prolinate

| Entry | Ar | Product no. | Time, min | Yield,[a] % | mp, °C | |
|---|---|---|---|---|---|---|
| | | | | | found | reported |
| 1 | Ph | **2a** | 15 | 98 | 168–170 | 167–171 |
| 2 | 4-Ph$C_6H_4$ | **2b** | 20 | 92 | 190–192 | 190–192 |
| 3 | 4-Me$C_6H_4$ | **2c** | 18 | 94 | 170–171 | 177–179 |
| 4 | 4-CHO$C_6H_4$ | **2d** | 10 | 87 | 235–237 | 234–236 |
| 5 | 4-MeO$C_6H_4$ | **2e** | 25 | 89 | 241–243 | 242–243 |
| 6 | 3,4,5-$(MeO)_3C_6H_2$ | **2f** | 25 | 86 | 194–196 | 194–196 |
| 7 | 3-$O_2NC_6H_4$ | **2g** | 10 | 98 | 190–192 | 189–191 |
| 8 | 4-$O_2NC_6H_4$ | **2h** | 12 | 96 | 196–198 | 197–198 |
| 9 | 2-Cl$C_6H_4$ | **2i** | 18 | 89 | 142–144 | 140–142 |
| 10 | 4-Cl$C_6H_4$ | **2j** | 15 | 87 | 174–176 | 175–178 |
| 11 | 3-Cl$C_6H_4$ | **2k** | 18 | 94 | 159–161 | 158–161 |
| 12 | 2,4-$(Cl)_2C_6H_3$ | **2l** | 15 | 90 | 180–182 | 182–184 |
| 13 | 4-F$C_6H_4$ | **2m** | 12 | 92 | 171–173 | 170–172 |
| 14 | 4-CN$C_6H_4$ | **2n** | 15 | 85 | 215–217 | 217–218 |
| 15 | 4-OH$C_6H_4$ | **2o** | 25 | 89 | 205–207 | 206–207 |
| 16 | 2-OH$C_6H_4$ | **2p** | 20 | 92 | 206–208 | 207–209 |
| 17 | 4-Br$C_6H_4$ | **2q** | 15 | 89 | 184–186 | 184–186 |
| 18 | 4-CN$C_6H_4$ | **2r** | 15 | 90 | 217–220 | 217–219 |
| 19 | Naphthalen-2-yl | **2s** | 18 | 93 | 178–181 | 178–180 |

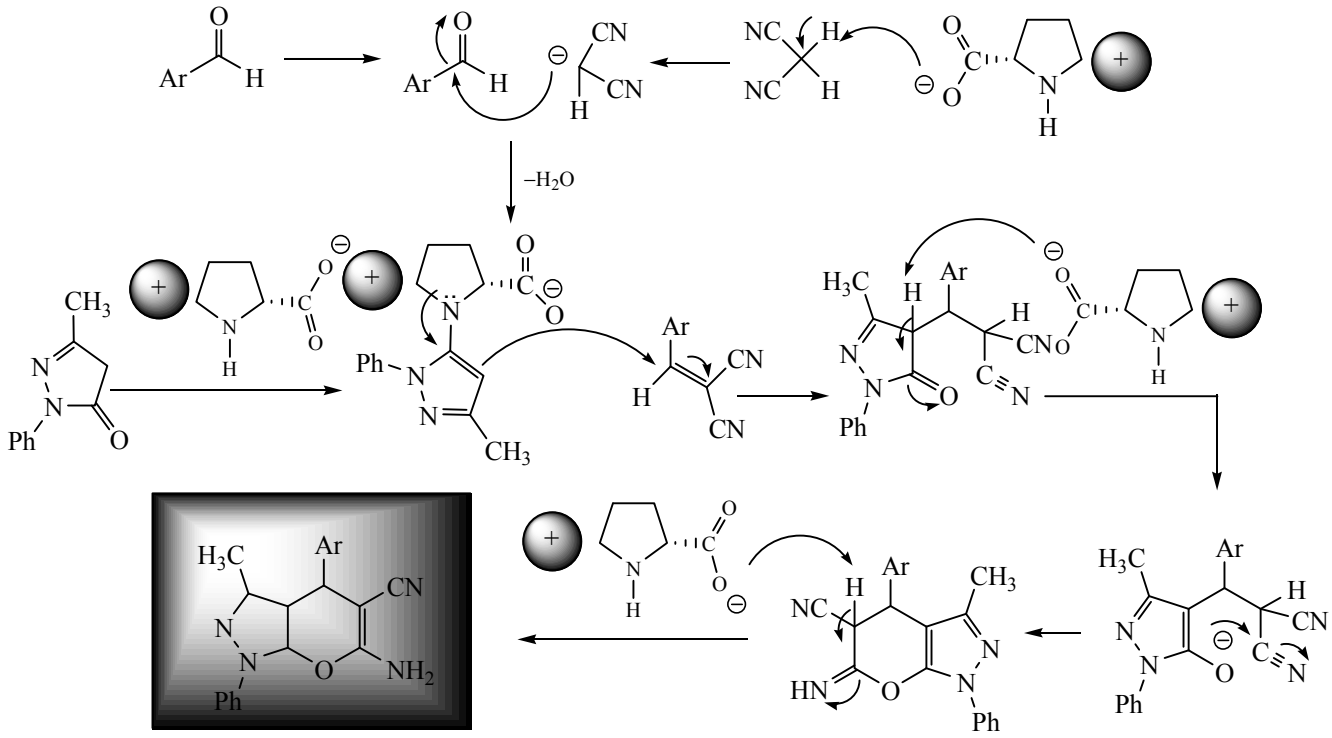
[a] Isolated pure product.

**Table 3.** Comparison of the efficiency of various catalysts and conditions for the reaction of benzaldehyde with malononitrile and 3-methyl-1-phenyl-4,5-dihydro-1*H*-pyrazol-5-one

| Catalysts and reaction conditions | Time, min | Yield, % | Reference |
|---|---|---|---|
| [Amb]L-prolinate (10 mol %), EtOH, reflux | 15 | 98 | This work |
| SBPPSP, EtOH/$H_2O$/100 °C, reflux | 25 | 97 | [27] |
| $H_{14}[NaPW_{12}O_{40}]$, $H_2O$ or EtOH, reflux | 60 | 93 | [28] |
| SB(DBU)Cl, EtOH, rt | 35 | 94 | [29] |
| Nano-$TiO_2$/ $H_{14}[NaP_5W_{30}O_{110}]$, EtOH, ultrasound, 40°C | 15 | 97 | [30] |
| Nano-$La_{0.7}Sr_{0.3}MnO_3$, EtOH, ultrasound, 25°C | 11 | 89 | [31] |
| SnS-NPs@AC, EtOH, reflux | 20 | 91 | [32] |

recyclability of supported catalyst is also important. To estimate recyclability of the proposed catalyst, the reaction of 3-methyl-1-phenyl-4,5-dihydro-1*H*-pyrazol-5-one with benzaldehyde and malononitrile in ethanol was selected again as model. The results are given below.

**Scheme 3.**



| Run no. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| Time(min) | 15 | 15 | 20 | 20 | 20 | 30 | 25 | 25 |
| Isolated yield, % | 98 | 98 | 97 | 97 | 96 | 95 | 94 | 93 |

After completion of the reaction, the mixture was filtered, and the recovered catalyst was washed with acetone and dried before using for next consecutive runs (7 runs). Almost consistent activity was observed over 8 consecutive runs. Thus, [Amb]L-prolinate can be reused up to 8 runs without need to reload, and the difference in the yields between the first and eighth runs is only 5%. The nitrogen content of the fresh and reused catalysts was measured by elemental analysis. It was found that the catalyst lost only 3% of nitrogen after 8 runs. This is a good proof for very low leaching amount of L-proline organocatalyst from [Amb]L-prolinate catalyst into the reaction mixture during 8 runs, indicating that the catalytic ability of [Amb]L-prolinate remained stable after 8 runs in agreement with the recyclability study.

Table 3 compares the efficiency of various catalysts and conditions for the reaction of benzaldehyde, malononitrile, and 3-methyl-1-phenyl-4,5-dihydro-1*H*-pyrazol-5-one. The reaction times for the preparation of 6-amino-3-methyl-1,4-diphenyl-1,4-dihydropyrano-[2,3-*c*]pyrazole-5-carbonitrile by our procedure are shorter than in reported methods. The best yield and short reaction time is attributed to the high efficiency of [Amb]L-prolinate.

## CONCLUSIONS

In conclusion, we have developed a novel and highly efficient protocol for one-pot three component synthesis of 4-*H*-pyrano[2,3-c]pyrazole derivatives in ethanol at 80°C in the presence of amberlite-supported L-prolinate as heterogeneous organocatalyst based on non-covalent ion-pair immobilization of L-proline on the surface of amberlite hydroxide. This methodology made the organocatalyst to be mobile and flexible which not only helped the supported catalyst to be as powerful as its non-supported form, but also made it easily recoverable by simple filtration. The catalyst can be easily recovered and reused for several successive fresh runs with no significant loss of catalytic activity.

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