



Functionalized ionic liquid tagged Cu(II) catalyst: Design, characterization, and application in synthesis of imidazo[1,2-a]pyridine[†]

Sumit Ghosh, Dhiman Kundu, Amrita Dey, Adinath Majee and Alakananda Hajra*

Department of Chemistry, Visva-Bharati (A Central University), Santiniketan-731 235, West Bengal, India

E-mail: alakananda.hajra@visva-bharati.ac.in

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A new ionic liquid tagged Cu(II) catalyst has been prepared by the reaction between imidazolium-based task-specific ionic liquid and CuO. Its catalytic activity has been evaluated in a cascade reaction involving 2-aminopyridine, aldehyde, and terminal alkyne. A bunch of imidazo[1,2-a]pyridines was synthesized efficiently in high yields and the catalyst is easily recyclable without significant loss of catalytic activity. The catalyst structure was established by X-ray crystallography.

Keywords: Ionic liquid tagged Cu(II) catalyst, task-specific ionic liquid, imidazo[1,2-a]pyridine, three-component coupling, re-usability.

1. Introduction

Ionic liquids (ILs), possessing important solvent properties like viscosity and tunable polarity have various applications as efficient alternatives of conventional solvents in electrochemistry, liquid-liquid extractions, catalytic reactions and synthetic chemistry¹. They are known to serve as green solvents by reason of their attractive characteristics like inflammability and low vapor pressure². Ionic liquids, designed to fulfill the targeted job are known as task-specific ionic liquids (TSILs)³. As a consequence, much interest has been paid to design and tuning of imidazolium-based ionic liquids by incorporating the functional group into their side chain⁴. Numerous ionic liquids containing functional groups like amine, amide, ether, alcohol, acid, urea and thiourea into the side chain of imidazolium cation⁵ are already renowned. Several catalytic systems have been developed by adding different metal-catalysts.

However, the TSIL-bonded metal catalyst has been less explored. Metal containing ionic liquids have been realized as catalyst precursors, catalysts, reagents, and potential solvents for several organic conversions and provide eco-friendly protocols^{3,4}. A remarkable catalytic activity of ionic liquid tagged dirhodium(II) carboxylate has been explored in cyclopropanation^{5a}. Literally, ILs got a serious attention as a

reaction medium as well as catalyst after the success of Friedel-Crafts reaction in acidic [EMIM] Cl-AlCl₃ system in 1986^{6a}. Superior catalyst stability relative to common ionic liquids was obtained when PdCl₂ was immobilized in a 2,2'-imidazole-imidazolium ionic liquid which serves as both solvent and ligand^{6b}. Shreeve and co-workers highlighted the palladium species which was an active and highly recyclable catalyst in Heck coupling reaction resulting in very good conversion^{6b}. Significant attempts were also paid to integrate transition metal carbonyl-based organometallic species either with cationic unit or with anionic unit because of their efficient catalytic activity. Welton's group^{6c} reported the preparation of ionic liquid as [BMIM][Co(CO)₄] by the metathesis reaction between [BMIM][Cl] and Na[Co(CO)₄]. Finally, metal-NHC complexes have also incorporated to the IL family by the Waymouth and Hedrick group^{6d}.

Metal complex catalysts with imidazolium tags are generally reused for many times without hampering its efficiency in chemical transformations such as ring-closing olefin metathesis (RCM), hydrogenation, Heck and Suzuki cross-coupling reactions etc. The use of IL supported metal catalysts in synthesis and catalysis is still in its infancy⁷. Moreover, formation of metal chelate complexes involving ionic liquids e.g. the copper(I) complex {[HC(3,5-Me₂pz)₃]-Cu(NCMe)}BF₄

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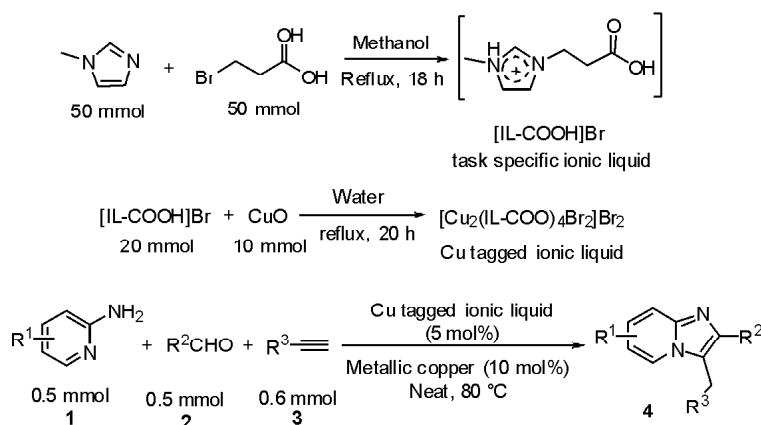
in [bmim]PF₆ and its use as a catalyst to transport -CHCO₂Et units, the dirhodium(II) carboxylate complex containing imidazolium moiety and its use as catalyst in cyclopropanation reactions in ionic liquid have already been reported^{5a,8}. However, none of these reported systems have exhibited X-ray crystal structure.

On the basis of these previous reports and our experiences, it is envisaged that imidazolium based ionic liquids can be used as both ligand and catalyst by incorporating an appropriate coordinating group into their side chain or by including a metal salt with coordinating group of the imidazolium core. Hence, we endeavor to report here in our investigation describing the synthesis, design and X-ray crystal structural analysis of a metal chelate complex prepared from an imidazolium based TSIL that contains carboxylic acid group as a chelating moiety (Scheme 1). These catalysts can be easily recovered and recycled⁹.

The imidazopyridine being a biologically active nitrogen-containing compound, in particular, the imidazo[1,2-*a*]pyridine moiety plays a significant role in the field of biological¹⁰, pharmaceutical resources¹¹ as well as in material science¹². It has great importance for working as antifungal^{13a}, anti-inflammatory^{13b}, antitumor^{13c}, antiviral^{13d}, antibacterial^{13e}, antiprotozoal^{13f}, antipyretic^{13g}, analgesic^{13h}, antiapoptotic¹³ⁱ, hypnoselective, and anxioselective^{13j} substances. Imidazo[1,2-*a*]pyridine is a powerful paradigm in the development

and design of potentially active compounds that are found in some commercially available drugs¹⁴. For example, Zolpidem (I) is utilized for the treatment of insomnia and Alpidem (II) is used as an anxiolytic agent. Olprinone (III) and Zolimidine (IV) are employed for acute heart failure treatment and peptic ulcer treatment respectively. Necopidem (V), and Saripidem (VI) are known to serve as anxiolytic agents (Fig. 1).

Therefore, the synthesis of compounds with imidazo[1,2-*a*]pyridine core attracts considerable attention of organic synthetic chemists because of their remarkable biological activities in medicinal field. Several methods have been also discovered for synthesis of imidazo[1,2-*a*]pyridines, such as by condensation of α -halocarbonyl compounds with 2-aminopyridine^{15a}, one-pot condensations of isonitriles, aldehydes, and 2-aminopyridines^{15b}, Cu-catalyzed three-component reaction of aldehydes, 2-aminopyridines, and alkynes^{15c}, oxidative couplings through C-H activation^{15d}, and very recently, from Morita-Baylis-Hillman acetates of nitroalkenes^{15e}. Our group also developed several efficient synthetic methodologies¹⁶ as well as functionalization methodologies¹⁷ of imidazo[1,2-*a*]pyridines. In continuation of our work to develop newer methodologies for the synthesis of imidazopyridines, as well as on the use of TSIL¹⁸ as a catalyst, herein, we report a new type of ionic liquid tag Cu(II)-catalyst and its uses as a catalyst in the convenient synthesis of imidazo[1,2-*a*]pyridines (Scheme 1).



Scheme 1. Preparation of Cu tagged ionic liquid and synthesis of imidazo[1,2-*a*]pyridines.

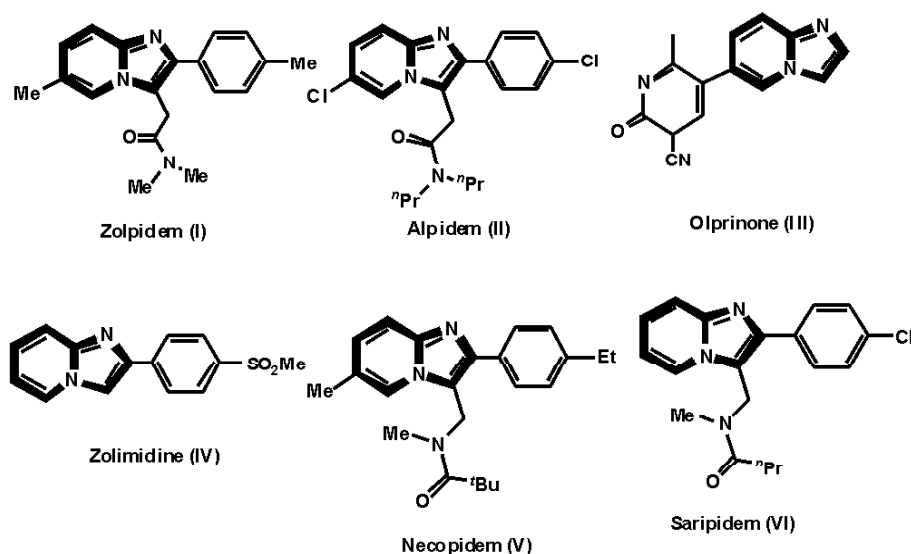


Fig. 1. Imidazo[1,2-a]pyridine containing drugs.

2. Experimental

CuO was initially implemented as metal salt to the TSIL for coordination with the carboxyl group of imidazolium core (cation) to produce Cu-tag ionic liquid. The required 1-methyl-3-(3-ethylcarboxylate)imidazolium bromide was prepared by a single-step reaction of 1-methylimidazole and 3-bromopropionic acid. Carboxyl group, being a bidentate ligand, present in [IL-COOH]Br could perfectly coordinate with Cu(II) ion to facilitate the formation of Cu tagged ionic liquid. A carboxylate complex in water was formed by the reaction of copper(II) oxide with carboxylic acid group of [IL-COOH]Br. The mixture was then filtered to eliminate the excess copper oxide and a green solid was acquired after evaporation of water under reduced pressure. A crystalline solid of Cu tagged ionic liquid was obtained on the slow evaporation of the water from the solution.

Typical experimental procedure for preparation of 1-methyl-3-(3-ethylcarboxylate)imidazoliumbromide:

An equimolar mixture of 1-methylimidazole (50 mmol) and 3-bromopropionic acid (50 mmol) in methanol was refluxed and allowed to react for a period of 18 h. The solution was then cooled to room temperature and the solvent was removed by evaporation under reduced pressure to achieve the crude imidazolium salt. After washing the imidazolium salt with diethyl ether (3×5 ml) the ionic liquid was placed

under vacuum for 5 h.

Typical experimental procedure for synthesis of ionic liquid tagged Cu catalyst:

Copper(II) oxide (10 mmol) was mixed with [IL-COOH]Br (20 mmol) in 10 ml water and the mixture was stirred under reflux for 20 h. The unreacted copper(II) oxide was removed by filtration. Then the water was evaporated under reduced pressure. A green mass was obtained. After recrystallization from water pure crystals were found.

General experimental procedure for preparation of imidazo[1,2-a]pyridines:

A mixture of 2-aminopyridine (0.5 mmol), aldehyde (0.5 mmol), and alkyne (0.6 mmol) was heated at 80°C in neat condition under Ar atmosphere in presence of metallic copper (10 mol%) and ionic liquid tagged Cu catalyst (5 mol%) for the time required to complete the reaction. The reaction mixture was extracted with diethyl ether (3×10 mL). Evaporation of solvent and purification by column chromatography over silica gel provided the corresponding pure imidazo[1,2-a]pyridine derivatives. The ionic liquid tag catalyst left in the reaction vessel was reused for another reaction.

Reusability:

The product was extracted with diethyl ether and the remaining catalyst was reused five times without loss of catalytic activity.

3. Results and discussion

In this, we report the outcome of the reaction between task specific ionic liquids (TSILs) bearing carboxyl group and copper oxide which gave a Cu tagged ionic liquid. The molecular structure of Cu tagged ionic liquid was determined by single crystal X-ray diffraction method (Fig. 2)¹⁹. The two copper(II) ions are located in an octahedral coordination sphere of Cu tagged ionic liquid crystal structure consisting four 1-(2-carboxy-ethyl)-3-methyl-imidazolium cations and four bromide anions (Fig. 2). No water molecule is found to be coordinated here. In this crystal structure, the copper-copper distance is 2.74 Å, which is slightly longer than that of in metallic copper (2.55 Å) and two metal centers are bridged by four 1-(2-carboxy-ethyl)-3-methyl-imidazolium cations i.e. a δ -bond is observed between the two copper(II) ions.

In our initial study, we have chosen 2-aminopyridine (0.5 mmol), benzaldehyde (0.5 mmol) and phenylacetylene (0.6 mmol) as model substrates for three-component coupling reaction to optimize the reaction conditions using different catalytic systems (Table 1). Firstly, the use of 10 mol% metallic copper gave a trace amount of desired product (< 5%) at 80°C temperature after 20 h in neat condition (Table 1, entry 1). However, the use of only 10 mol% CuO furnished the desired products in very low yield (Table 1, entry 2). Notably, the presence of 5 mol% ionic liquid tagged Cu-catalyst improved the yield of the reaction to 75% within 10 h (Table 1, entry 3). Next, we have investigated the role of [IL-COOH]Br in this reaction. No desired product was detected on employing only [IL-COOH]Br (10 mol%) (Table 1, entry 4). But combining the acidic ionic liquid with metallic copper (10 mol%) or CuO (5 mol%) slightly increased the reaction yield

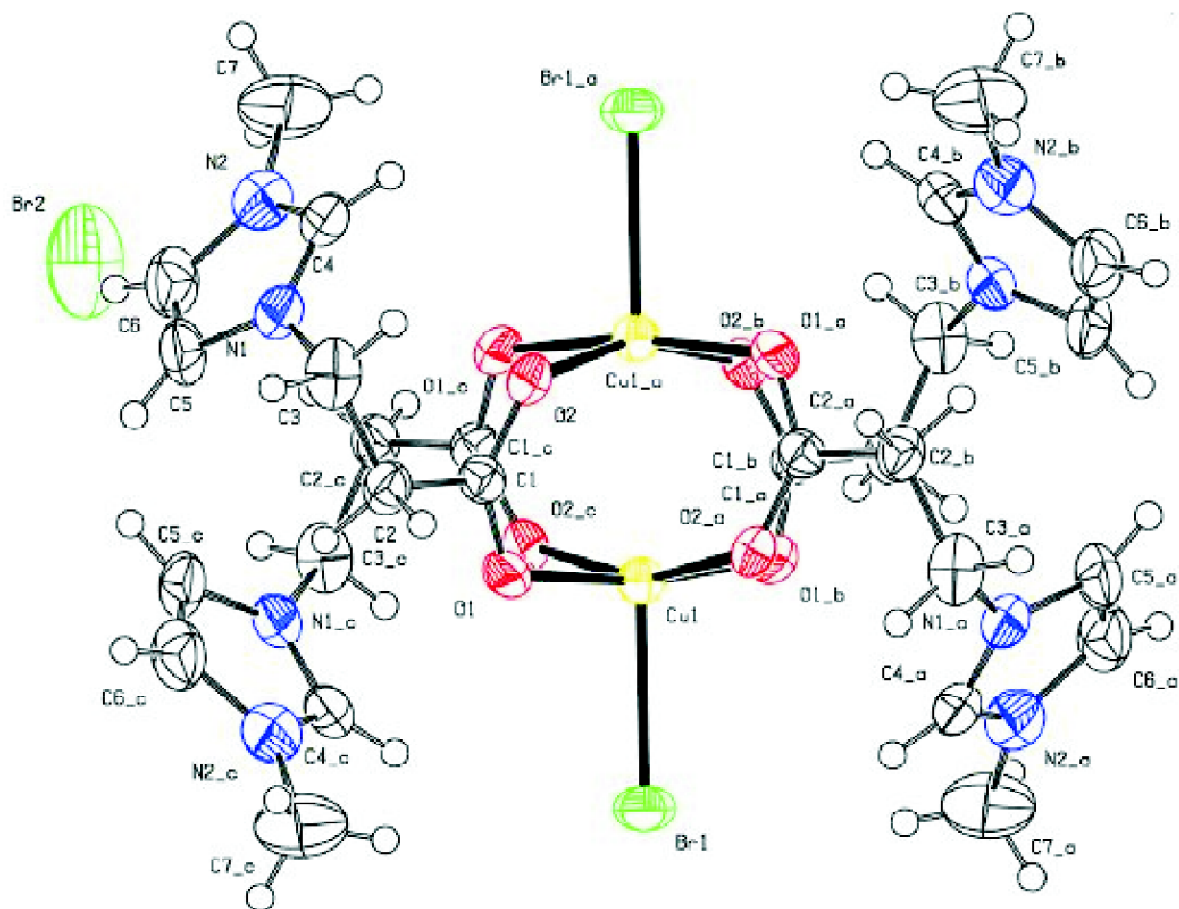
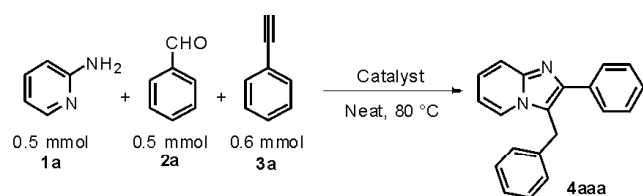


Fig. 2. Crystal structure of ionic liquid tagged Cu(II) catalyst.

to 8% and 35% respectively (Table 1, entries 5 and 6). Delightfully, a significant improvement of the result was observed when the reaction was carried out in presence of binary catalyst such as metallic Cu and ionic liquid tagged Cu-catalyst at the same temperature for 8 h only (Table 1, entry 7). But the combination of metallic Cu (10 mol%) and CuO (5 mol%) as catalyst led to formation of 50% yield of desired product (Table 1, entry 8). So, finally, use of metallic Cu (10 mol%) and ionic liquid tagged Cu-catalyst (5 mol%) as binary catalyst in neat condition under ambient air at 80°C temperature was the optimized reaction condition for this three-component coupling reaction among **1a**, **2a**, and **3a** affording 90% yield of the desired product within 8 h (Table 1, entry 7).

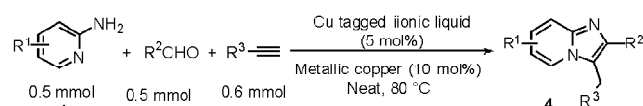
Table 1. Optimization of the reaction conditions^a


| Entry | Catalyst (mol%) | Time (h) | Yield (%) |
|-------|---|----------|-----------|
| 1 | Cu (10) | 20 | < 5 |
| 2 | CuO (10) | 20 | 10 |
| 3 | IL tagged Cu-catalyst (5) | 10 | 75 |
| 4 | [IL-COOH]Br (10) | 20 | 0 |
| 5 | [IL-COOH]Br (10), Cu (10) | 15 | 8 |
| 6 | [IL-COOH]Br (10), CuO (5) | 10 | 35 |
| 7 | Cu (10), IL tagged Cu-catalyst (5) | 8 | 90 |
| 8 | Cu (10), CuO (5) | 8 | 50 |

^aReaction conditions: A mixture of 0.5 mmol of **1a**, 0.5 mmol of **2a** and 0.6 mmol of **3a** in neat condition at reported temperature for mentioned time under open air.

After getting the optimized reaction conditions in hand we began to explore the general applicability of this protocol. Therefore, a variety of electronically divergent aldehydes and alkynes have been tested with 2-aminopyridines under the standard reaction conditions and the results are summarized in Table 2. Benzaldehyde and simple phenylacetylenes were observed to be successfully coupled to 2-aminopyridine followed by cyclization within 9 h to afford the desired product, **4aaa** with excellent yield in presence of the ionic liquid tagged Cu catalyst combining to metallic copper (Table 2, entry 1).

This binary catalyst was all most equally effective for aldehydes and acetylenes containing alkyl or aryl substituents as participants in this cyclization reaction. 4-Ethynyltoluene, *n*-butylacetylene, and *n*-hexylacetylene underwent the cyclization reaction smoothly to produce the desired products (**4aab**, **4aac** and **4aad**) with 86%, 50% and 52% yield respectively (Table 2, entry 2, 3 and 4). The couple of catalyst was also suitable for 4-methyl-2-aminopyridine in this reaction. Aromatic aldehydes bearing different functional groups such as 3-Cl (Table 2, entry 5, **4aba**) and 4-Br (Table 2, entry 6, **4aca**) worked well in this catalytic system providing moderate to excellent yields. The heterocyclic aldehyde such as furan-2-carbaldehyde also performed nicely under this catalytic con-

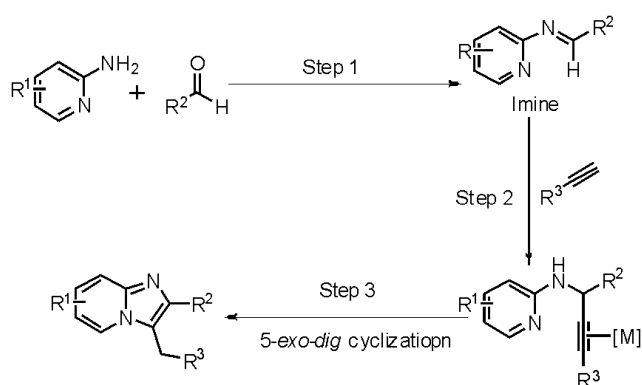
Table 2. Formation of diverse imidazo[1,2-a]pyridines^a


| Entry | R ¹ | R ² | R ³ | Time (h) | Yield (%) | Name |
|-------|----------------|------------------------------------|------------------------------------|----------|-----------|-------------|
| 1 | H | Ph | Ph | 9 | 90 | 4aaa |
| 2 | H | Ph | 4-Me-C ₆ H ₄ | 9 | 86 | 4aab |
| 3 | H | Ph | <i>n</i> Bu | 12 | 50 | 4aac |
| 4 | H | Ph | <i>n</i> Hex | 12 | 52 | 4aad |
| 5 | H | 3-Cl-C ₆ H ₄ | Ph | 9 | 88 | 4aba |
| 6 | H | 4-Br-C ₆ H ₄ | Ph | 9 | 89 | 4aca |
| 7 | H | Furyl | Ph | 10 | 75 | 4ada |
| 8 | 4-Me | Ph | Ph | 10 | 85 | 4baa |
| 9 | 4-Me | 4-CN-C ₆ H ₄ | 4-Me-C ₆ H ₄ | 10 | 82 | 4beb |
| 10 | 4-Me | 4-Me-C ₆ H ₄ | 4-Me-C ₆ H ₄ | 10 | 80 | 4bfb |
| 11 | H | H | Ph | 12 | 50 | 4aga |
| 12 | H | 2-Naphthyl | Ph | 9 | 88 | 4aha |
| 11 | H | H | Ph | 12 | 50 | 4aga |
| 12 | H | 2-Naphthyl | Ph | 9 | 88 | 4aha |
| 13 | H | 1-Naphthyl | Ph | 9 | 80 | 4aia |
| 14 | H | | Ph | 9 | 85 | 4aja |
| 15 | 4-Me | | Ph | 10 | 82 | 4bja |
| 16 | H | <i>i</i> Pr | Ph | 9 | 20 | 4aka |

^aReaction conditions: A mixture of 0.5 mmol of **1**, 0.5 mmol of **2** and 0.6 mmol of **3** with 10 mol% metallic copper catalyst and 5 mol% ionic liquid tagged Cu catalyst in neat condition at reported temperature for mentioned time under open air.

dition to generate the desired product, **4ada** in good yield (Table 2, entry 7). 4-Methylpyridin-2-amine reacted efficiently with benzaldehyde (Table 2, entry 8, **4baa**) and also with 4-CN (Table 2, entry 9, **4beb**) and 4-Me (Table 2, entry 10, **4bfb**) derivatives of benzaldehyde providing excellent yield. Formaldehyde could couple moderately to give 50% yield of the product (Table 2, entry 11, **4aga**). 2-Naphthyl and 1-naphthyl benzaldehyde performed well under the optimized reaction condition affording the desired products in excellent yield (Table 2, entry 12 and 13, **4aha** and **4aia**). The catalytic circumstance was also perfect for the acid sensitive aldehyde such as piperonal which led to an excellent yield of the required coupling product (**4aja** and **4bja**) (Table 2, entries 14 and 15). But aliphatic aldehyde such as *iso*-butylaldehyde afforded low yield of the corresponding product when subjected to the similar reaction condition (Table 2, entry 16, **4aka**).

A plausible reaction mechanism has been outlined in Scheme 2 on the basis of our experiments and literature reports²⁰. This is a three steps reaction in which at first, an imine is formed from aldehyde and 2-aminopyridine. Then, a propargylamine intermediate is produced by the nucleophilic attack of alkyne (activated by Cu-catalyst) to imine. Finally, the desired product, imidazo[1,2-*a*]pyridine is constructed by Cu catalyzed 5-*exo-dig* cyclization of propargylamine²¹.



Scheme 2. The possible reaction pathway.

4. Conclusions

In conclusion, we have successfully designed an ionic liquid tagged Cu catalyst by the reaction between ionic liquid containing carboxyl group and copper oxide. The catalyst structure was characterized by X-ray crystallography. This

newly synthesized ionic liquid tagged copper catalyst has been utilized to develop a facile, general and solvent-free procedure to prepare lot of imidazo[1,2-*a*]pyridine derivatives by three-component coupling reaction of 2-aminopyridines, aldehydes, and terminal alkynes in presence of copper in one pot. We believe our newly developed ionic liquid tag catalyst will open a new door in catalysis.

Acknowledgements

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Supporting Information

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org>

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