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A robust and recyclable ionic liquid-supported copper(II) catalyst for the synthesis of 5-substituted-1*H*-tetrazoles using microwave irradiation

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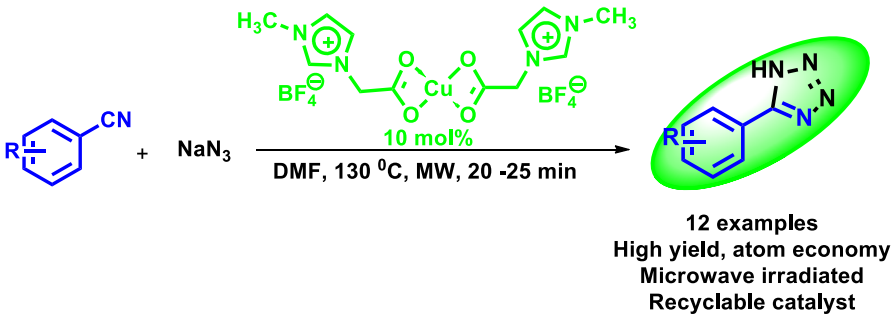
Abstract

A novel and robust ionic liquid-supported copper(II) catalyst has been developed and explored for the efficient synthesis of 5-substituted-1*H*-tetrazoles using microwave irradiation. The ionic liquid-supported catalyst facilitated the efficient isolation of tetrazole products with high purity by simple extraction with organic solvent. Recovered ionic liquid-supported copper(II) catalyst could be recycled for three times for the synthesis of tetrazole products with high purity. This synthetic protocol offers a very clean, convenient, and microwave-assisted environment-friendly method for the efficient synthesis of 5-substituted-1*H*-tetrazoles with high yield.

Graphic abstract



Keywords 1*H*-tetrazoles · (3 + 2) cycloaddition · Microwave irradiation · Ionic liquid

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Introduction

Because of the possession of abundant biological activities such as pharmaceuticals and agrochemicals, nitrogen-containing heterocyclic compounds are getting more and more attention from synthetic chemists [1–3]. Densely substituted tetrazole derivatives are one of the most important classes of compounds widely found in natural products and pharmaceutical molecules owing to their profound bioactivities [4, 5]. Further, this privileged moiety is known as a bioisosteric substituent of carboxylic acid in developing bioactive products as shown in Fig. 1 [6]. Functions of these molecules are commonly found in natural products as well as in many commercial drugs. Hossain et al. [7] isolated and reported the X-ray crystal structure of 6-azidotetrazolo[5,1-a]phthalazine (**A**), a new toxic metabolite of the dinoflagellate Gymnodinium breve. There are tetrazole-containing drug molecules such as losartan (**B**) used for antihypertensive activity, tomelukast (**C**) used for antileukotriene antiasthmatic property, and selective antagonists of NMDA and AMPA receptors (**D**, **E**) used for the treatment of schizophrenia [8, 9].

These nitrogen-containing molecules have noted robustness facilitating their applications in coordination chemistry, in the photographic industry, or as components of special explosives.

In most of the existing studies on 5-substituted-1*H*-tetrazole derivatives, these compounds have been synthesized following (3 + 2) cycloaddition of organic nitriles with sodium azides which was initiated first time by Sharpless and his coworkers in 2001 [10]. Various catalysts utilized for this purpose include both metals and nonmetal catalysts such as Al^{3+} [11], Pd^{0} [12], Zn^{2+} [13], Yb^{3+} [14], Fe^{3+}–Si^{4+} [15], Ag^{+} [16], Ag^{0}NPs [17], Co^{2+} [18], Cu^{2+} [19] Et_3N.HCl [20], I_2 or silica-supported $NaHSO_4$ [21], TBAF [22], chitosan-derived magnetic ionic liquid [23], CAN-HY zeolite [24], activated fuller earth [25], $B(C_6F_5)_3$ [26], 4-(*N*,*N*-dimethylamino)pyridinium acetate [27], Cuttlebone [28], and CAES [29]. Recently, we have demonstrated the synthesis of 5-substituted-1*H*-tetrazole derivatives using both homogeneous Cu(I) catalyst in water and heterogeneous CuO nanoparticles under microwave irradiations [30, 31]. More importantly, most of these methods require the use of hazardous hydrazoic acid and high catalyst loading along with harsh reaction conditions and numerous of them are either not eco-friendly or source of severe environmental pollution. As a result, still there is

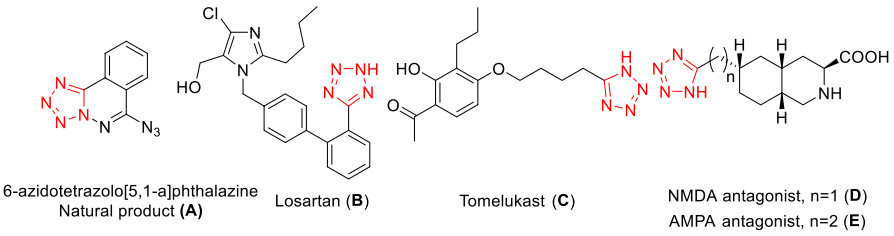


Fig. 1 Examples of bioactive molecules containing the tetrazole core structure

a need to develop a more efficient, simple, milder, and high-yield protocol for the synthesis of 5-substituted-1*H*-tetrazole derivatives.

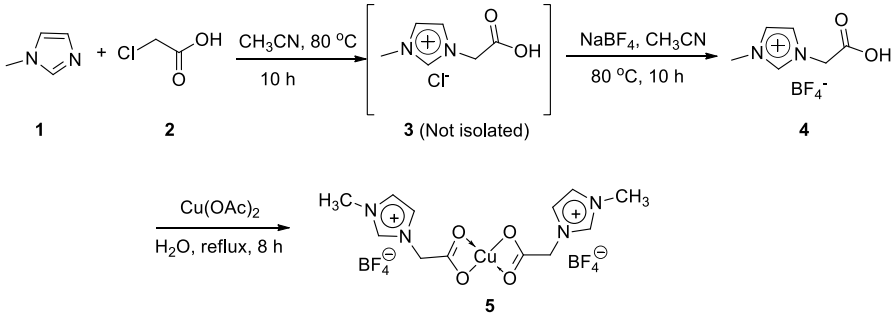
In the last decade, to suite for a particular chemical transformation, task-specific ionic liquids (TSILs) with functional groups tethered covalently to the either cation or anion have been developed [32, 33]. Since then, many low molecular weight TSILs have been used as supported catalysts, reagents, and supported substrates for organic synthesis [34, 35]. By tuning the cation and anion, the entire property of an ionic liquid can be modified which includes thermal stability, vapor pressure, and the solvating ability. Ionic liquid-supported catalysts have the ability to easily separate from the substrate and products after completion of the reaction by adding a less polar organic solvent in which the ionic liquid anchored species is not soluble. At last, the recovered ionic liquid-supported catalyst can be regenerated or reused further to obtain the desired product. Due to these unique characteristics, ionic liquid-supported catalysts are known as excellent heterogeneous catalysts in an effort to stop the environmental degradation and the answer to sustainable development which forms the core of synthetic organic chemistry research. Previously, we have shown the use of task-specific ionic liquids (TSILs) as soluble support for the numerous synthetic transformations to obtain privileged heterocycles under microwave irradiations [35–38]. Moreover, the use of microwave (MW) technology in chemical synthesis is well established. It greatly accelerates the chemical transformation with much higher yields, less waste generation, different reaction selectivities, and mild reaction profile compared to the conventional heating system [39].

As part of our recent report on the diversity-oriented synthesis of bioactive heterocycles [40–44], herein, we wish to report a novel and robust ionic liquid-supported Cu(II)-catalyzed synthesis of 5-substituted 1*H*-tetrazole derivatives under microwave irradiation. The synthetic manipulation involves the recyclable ion-supported Cu(II)-catalyzed microwave-assisted (3 + 2) dipolar cycloaddition of organic nitriles with NaN_3 to obtain the 5-substituted 1*H*-tetrazole derivatives in excellent yields.

Results and discussion

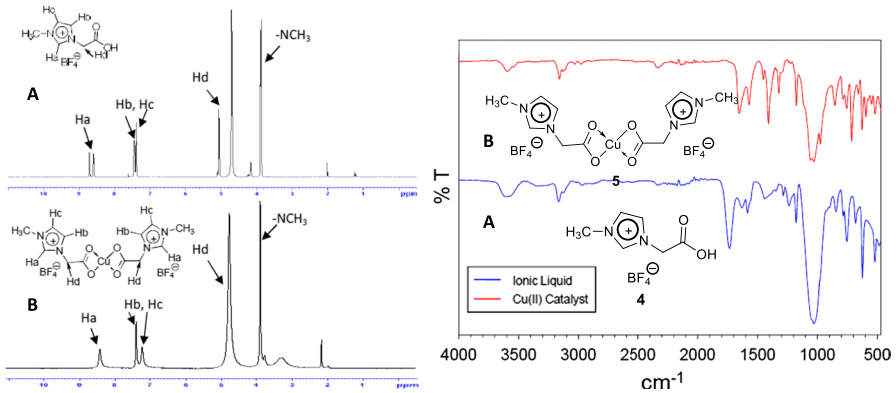
At the onset of our study, the recyclable ionic liquid-supported copper(II) catalyst **5** was synthesized in aqueous solutions in three steps as depicted in Scheme 1. The present strategy toward the synthesis of ionic liquid support **4** equipped with carboxyl group linker, 1-(1-carboxymethyl)-3-methylimidazolium tetrafluoroborate ([carbmmim][BF_4]), was prepared in two steps. The first step involved the reaction of N-methyl imidazole **1** with 2-chloroacetic acid **2** in refluxing CH_3CN solution to obtain the intermediate **3** which underwent anion exchange reaction with $NaBF_4$ to obtain the carboxyl group-functionalized ionic liquid support **4.**

The next step of the catalyst synthesis involved the reaction of carboxyl group-functionalized ionic liquid support **4** with $Cu(OAc)_2$ in refluxing water medium for 8 h to obtain the ionic liquid-supported copper(II) catalyst **5** as pale blue powder with excellent yield. The catalyst was characterized by nuclear magnetic resonance (^1H & ^{13}C NMR), IR, mass spectroscopy, and atomic absorption spectroscopic measurement. Figure 1 demonstrates the quantitative catalyst formation



Scheme 1 Synthesis of ionic liquid-supported Cu(II) catalyst **5** in aqueous medium

by ^{1}H, ^{13}C NMR, IR, and mass spectroscopy in each step with an attached ionic liquid (IL) tag. It has been found that the three protons Ha, Hb, and Hc of free IL-tag appeared at 8.67, 7.41, and 7.40 ppm, respectively, in spectra A, whereas the N-CHd_2 and N-CH_3 protons appeared at 5.03 and 3.68 ppm in Fig. 2. However, the chemical shift of these three protons was shifted to more upfield portion upon reaction with $Cu(OAc)_2$. Similarly, the ^{13}C spectrum of ionic liquid support **4** and catalyst **5** clearly shows all of the carbon present in the structures. Further, Fourier transform infrared spectroscopy (FT-IR) measurements were carried out on ionic liquid support **4** and Cu(II) catalyst **5**. The C=O stretching frequency which is observed at 1745 cm^{-1} in ionic liquid support **4** shifted to 1654 cm^{-1} in ion-bound Cu(II) catalyst **5** due to the electronic reorganization of the double



Entry	Products	Mass	Yields (%)
1	4	$(M\text{-}BF_4)^+$ = 141	95
2	5	$(M\text{-}BF_4)^+$ = 343	92

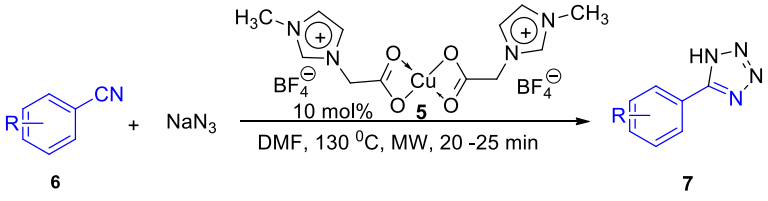
Fig. 2 ^{1}H NMR, IR, and mass spectra of ionic liquid-supported Cu(II) catalyst **5**

bond. The band at around 3600 cm^{-1} is attributed to the –OH stretching vibration, which comes from the surface-adsorbed H_2O. Moreover, the ionic liquid support **4** and Cu(II) catalyst **5** could be confirmed with mass spectra (MS) which are shown in Fig. 2. The copper content of Cu(II) catalyst **5** was found to be 8.5%, on the basis of atomic absorption spectroscopy analysis.

Initially, in order to optimize the reaction condition, we have chosen the reaction of benzonitrile **6a** with NaN_3 as model reaction in Scheme 2. The catalytic activity of ionic liquid-supported Cu(II) catalyst **5** was examined in the reaction between benzonitrile **6a** and NaN_3 under neat condition at 100 °C for 6 h, and the reaction did not yield any 5-phenyl-1*H*-tetrazole **7a** product (Table 1, entry 1). Unfortunately, the reaction did not afford any cyclized product using H_2O-IPA at 100 °C or refluxing THF (Table 1, entries 2, 3), whereas the reaction afforded the cyclized product **7a** in 40% yield in refluxing CH_3CN solution (Table 1, entry 4).

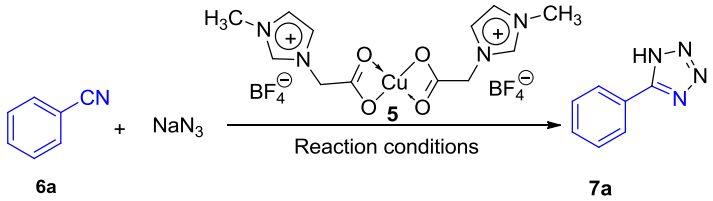
In an effort to increase the yield, the same reaction was repeated in refluxing MeOH solution resulting in the formation of cyclized product **7a** in 60% yield (Table 1, entry 5). However, the yield of the product **7a** did not increase significantly upon prolonging the reaction time to 8 h (Table 1, entry 6). Next we turned our attention for polar aprotic solvents such as DMSO at 130 °C for 6 h, which was proved to be efficient for this reaction with 80% yield of product **7a** (Table 1, entry 7). Apart from DMSO, when the same reaction was carried out in DMF solvent for 6 h at 130 °C, 5-phenyl-1*H*-tetrazole **7a** was formed in 90% yield (Table 1, entry 8). However, to improve the synthetic protocol, the same set of reaction was performed under microwave irradiation for 20 min using DMF as solvent at 130 °C for 320 W to obtain the desired product **7a** in 95% yield (Table 1, entry 9). It is interesting to observe that the yield of the product **7a** did not increase with increasing the catalyst loading up to 15 mol % under microwave irradiation for 20 min (Table 1, entry 10). So the optimum catalyst loading of 10 mol % was sufficient for obtaining the maximum yield of 95% for 5-phenyl-1*H*-tetrazole **7a** derivative.

Table 1 provides the complete optimization study for the (3 + 2) cycloaddition reaction to obtain the 5-phenyl-1*H*-tetrazole **7a**. Subsequently, under metal-free condition the same set of reaction did not yield any cyclized product **7a** (Table 1, entry 11). High-power microwave irradiation allowed us to reduce the reaction time to 20 min compared to several hours under different refluxing conditions. Scheme 1 demonstrates the ionic liquid-supported Cu(II) catalyzed synthesis of



Scheme 2 Ionic liquid-supported Cu(II) catalyzed microwave-assisted synthesis of 5-substituted 1*H*-tetrazoles

Table 1 Optimization of the reaction condition for the synthesis of 5-phenyl-1*H*-tetrazole catalyzed by ionic liquid-supported Cu(II) catalyst



Entry	Cu(II) catalyst	Solvent	Temperature	Time	Yield%[b]
1	10 mol%	No solvent	100 °C	6 h	0
2	10 mol%	H_2O-IPA	100 °C	6 h	0
3	10 mol%	THF	Reflux	6 h	0
4	10 mol%	CH_3CN	Reflux	6 h	40%
5	10 mol%	CH_3OH	Reflux	6 h	60%
6	10 mol%	CH_3OH	Reflux	8 h	60%
7	10 mol%	DMSO	130 °C	6 h	80%
8	10 mol%	DMF	130 °C	6 h	90%
9	10 mol%	DMF	MW[a], 130 °C	20 min	95%
10	15 mol%	DMF	MW[a], 130 °C	20 min	95%
11	No catalyst	DMF	MW[a], 130 °C	20 min	0%

Reaction was performed using **1**a (1 mmol), NaN_3 (1.2 mmol)

[a]Microwave reactions were carried out in microwave model no. CATA R (Catalyst System, Pune) using power 320 W

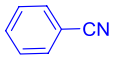
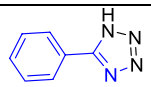
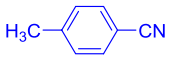
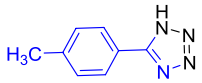
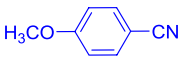
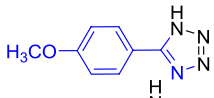
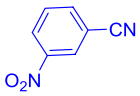
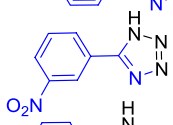
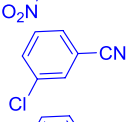
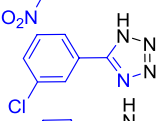
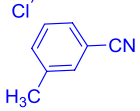
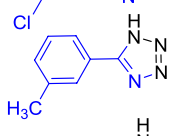
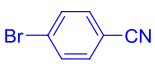
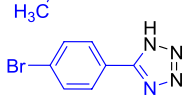
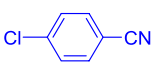
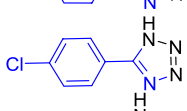
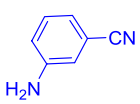
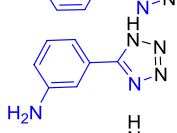
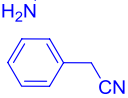
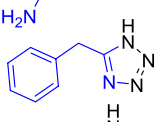
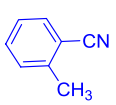
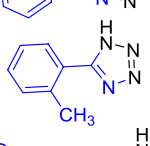
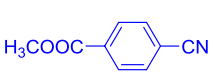
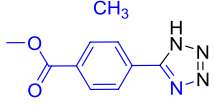
[b]Yield of the isolated product

5-substituted 1*H*-tetrazole derivatives which involves the (3 + 2) cycloaddition reaction under microwave irradiation.

After completion of the reaction, the reaction mixtures were precipitated with cold ether and filtered through fritted funnel to obtain the ionic liquid-supported Cu(II) catalyst. Upon treatment of the supernatant liquid with dil HCl, followed by organic workup, resulted substituted 1*H*-tetrazole derivatives in excellent yields.

Encouraged by the efficient synthetic approach for the desired cycloaddition as described above, we investigated the reaction using a variety of substituted nitriles and NaN_3 as substrates under the same condition. The corresponding 5-substituted-1*H*-tetrazoles **7** were isolated in excellent yields under the present reaction condition as depicted in Table 2.

Table 2 Ionic liquid-supported Cu(II) catalyzed microwave-assisted synthesis of 5-substituted 1*H*-tetrazoles

Entry	R_1—CN	Tetrazole product	Time (min)	Isolated yield[a] (%)
1			20	95
2			25	88
3			25	90
4			20	92
5			22	96
6			25	90
7			22	96
8			20	95
9			25	88
10			25	93
11			25	89
12			22	96

Reaction conditions **6** (1 mmol), NaN_3 (1.5 mmol), ILCu(II) catalyst (10 mol%), DMF (5 mL), 130°C

[a]Yield of the isolated product **7**

The overall reaction time is 20–25 min for the completion of the reaction. The corresponding 5-substituted 1*H*-tetrazole derivatives were obtained with excellent yields after a simple workup involving the precipitation of the reaction mixture with cold ether for the filtration of the catalyst, acidic treatment, and solvent evaporation. Finally, column chromatography purification of crude products

followed by spectroscopic characterization using ^{1}HNMR, ^{13}CNMR, and MS spectroscopy confirmed the formation of desired products. Reaction yields were varied with the substituents present in the aromatic rings. Due to the electrophilic nature of the nitrile moiety attached to the aromatic rings, unsubstituted or electron-withdrawing substituents reacted nicely to obtain the corresponding 1*H*-tetrazole derivatives, whereas electron-donating substituents resulted with lower yields. Unlike aliphatic nitriles where there is no product formation, the benzylic nitrile reacted nicely to obtain the corresponding 1*H*-tetrazole in high yield. However, in an effort to diversify the synthetic methodology, the cycloaddition reaction was performed with 2,6-dimethyl benzonitrile under the same synthetic condition. But the reaction failed to obtain the desired disubstituted tetrazole owing to the steric nature of the substituents present in the benzonitrile. Even the precursor like organic azides failed to produce the desired 1*H*-tetrazole under the optimized reaction condition.

A suggested mechanistic pathway for the (3 + 2) cycloaddition is shown where the ionic liquid-supported Cu(II) catalyst activated the substituted nitriles **6** followed by the addition of NaN_3 resulted the formation of cyclic intermediate. Upon acidic treatment of the cyclic intermediate resulted the generation of 5-substituted-1*H*-tetrazoles **7** in excellent yields. Further, the recyclability of the ionic liquid-supported Cu(II) catalyst **5** was also surveyed and is depicted in Fig. 3.

After a reaction, the reaction mixture was precipitated with cold ether to filter the ionic liquid-supported Cu(II) catalyst through a fritted funnel and was successively washed with cold ether two to three times. After being dried, the catalyst can be reused directly without further purification. The ion-supported Cu(II) catalyst **5** can be recovered, recycled, reused for two consecutive cycles without the loss of catalytic activity.

In summary, ionic liquid-supported Cu(II) catalyst was successfully synthesized and applied as an efficient catalyst in the preparation of library of the 5-substituted-1*H*-tetrazoles in excellent yields under microwave irradiation. The catalyst is thermally stable, green, easy to prepare, and devoid of any drawback associated with homogeneous catalysts. In addition, it can be easily separated from the reaction mixture with cold ether and recovered up to three cycles without the loss of catalytic activity and reaction yield.

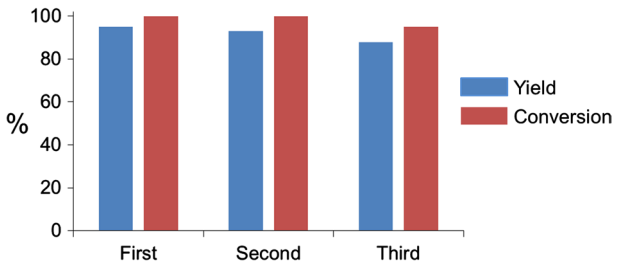


Fig. 3 Ionic liquid-supported Cu(II) catalyzed [3 + 2] cycloaddition reactions of benzonitrile **6a** with sodium azide

Experimental section

General procedure

Unless otherwise indicated, all common reagents and solvents were used as obtained from commercial suppliers without further purification. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded with a Bruker DRX600 spectrometer. Chemical shifts are reported in ppm relative to the internal solvent peak ($\delta = 7.26$ and 77.0 ppm, respectively, for $CDCl_3$). Coupling constants, J, are given in Hz. Multiplicities of peaks are given as: d (doublet), m (multiplet), s (singlet), and t (triplet). GC mass spectra were recorded on a PerkinElmer MS. Microwave-assisted reactions were carried out in a Catalyst Scientific Microwave oven system (model no: CATA R (Catalyst System, Pune) operating at 2450 MHz equipped with glass vial extension by a condenser which was used for performing the reaction. The microwave was equipped with a temperature control system (external probe).

General procedure for the synthesis of ionic liquid support 4

In a round-bottomed flask, a mixture of *N*-methyl imidazole **1** (1.0 equiv) and 2-chloro acetic acid **2** (1.1 equiv) was added to a 5 mL CH_3CN solution and refluxed at 80 °C for 10 h. After completion of the reaction as determined by TLC, to the same reaction mixture was added $NaBF_4$ (1.2 equiv) and continue stirring for at the same temperature for 10 h. After completion, the precipitated NaCl was filtered, and CH_3CN was removed under reduced pressure and washed several times with ether followed by drying to obtain the viscous pale yellow liquid as ionic liquid support **4**.

Ionic liquid-supported Cu(II) catalyst **5**. In a round-bottomed flask, a mixture of carboxyl group-functionalized ionic liquid support **4** (1.0 equiv) and $Cu(OAc)_2$ (0.5 equiv) was added to a 10 mL H_2O solution and refluxed for 8 h. After completion of the reaction, the precipitated blue colored solid was filtered and washed several times with H_2O to obtain the ionic liquid-supported catalyst **5**.

General procedure for the synthesis of 5-substituted-1*H*-tetrazoles (7a) In a round-bottomed flask, a mixture of benzonitrile **6a** (0.052 g, 0.50 mmol, 1.0 equiv) and NaN_3 (0.048 g, 0.75 mmol, 1.5 equiv) was added to a 5 mL DMF containing 10 mol% of ionic liquid-supported Cu(II) catalyst **5**. The reaction mixture was irradiated under microwave heating at 320 W for 20 min at 130 °C. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was precipitated with cold ether and filtered through a fritted funnel to remove the catalyst. The filtrate was acidified with 5 N HCl (10 ml) to neutralize the product and extracted with ether (2×10 ml). The combined organic layer was dried over anhydrous $MgSO_4$. The combined filtrate was subjected to evaporation to obtain the pure compound 5-phenyl-1*H*-tetrazoles **7a** as the product.

1-(1-carboxymethyl)-3-methylimidazolium tetrafluoroborate ([Carbmmim][BF_4]) (4) Pale yellow liquid. ^{1}H NMR (400 MHz, D_2O) δ 8.67 (s, 1H), 7.41(s, 1H), 7.41 (s, 1H), 5.03 (s, 2H), and 3.68 (s, 3H); ^{13}C NMR (100 MHz, D_2O) δ 172.4, 139.8, 125.6, 124.0, 52.2, 38.4; IR (KBr, cm^{-1}): 3574, 3166, 1739, 1579, 1409, 1176 cm^{-1}, MS (FAB) m/z: 141 (M-BF_4^-).

Ionic liquid-supported Cu(II) catalyst (5) Light blue solid. ^{1}H NMR (400 MHz, D_2O) δ 8.44 (s, 1H), 7.40 (s, 1H), 7.23 (s, 1H), and 3.89 (s, 3H); ^{13}C NMR (100 MHz, D_2O) δ 140.4, 126.4, 126.1, 38.4, 32.1; IR (KBr, cm^{-1}): 3519, 3169, 1654, 1570 cm-1, MS (FAB) m/z: 343 (M-BF_4^-).

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