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FULL PAPER

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Supported copper (I) catalyst from fish bone waste: An efficient, green and reusable catalyst for the click reaction toward *N*-substituted 1,2,3-TRIAZOLES

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An eco-efficient, green, and multi-gram procedure is presented for one-pot multi-component synthesis of *N*-substituted 1,2,3-triazoles by using waste fishbone powders supported CuBr (FBPs-CuBr) as catalyst. FBPs-CuBr is found to be an efficient heterogeneous catalyst and a series of 1,2,3-triazoles are obtained in moderate to excellent yields in water under MW irradiation (70–98%). It can be separated conveniently by a simple filtration and reused at least seven consecutive runs with a slight drop in the product yields. Furthermore, the desired product still could be obtained in 80% yield when the scale of the reaction was increased to 40.0 mmol.

KEYWORDS
green synthesis, heterogeneous catalyst, MW irradiation, *N*-substituted 1,2,3-triazoles, waste fishbone powders

1 | INTRODUCTION

As important five-membered nitrogen heterocycles, 1,2,3-triazoles have several biological activities, including antiviral, antifungal, and antitubercular activities.[1–4] Therefore, they represent an important class of biomolecules and have received widespread attention not only from academic research but also from industrial production and application. Recently, it has been reported that *N*-substituted 1,2,3-triazoles have more potential uses than simple 1,2,3-triazole derivatives.[5] However, for the preparation of *N*-substituted 1,2,3-triazoles though copper (I)-catalyzed azide alkyne cycloaddition (CuAAC),[6,7] the starting materials, such as functional alkynes and organic azides were not easily available and expensive. Furthermore, the synthesis of *N*-substituted 1,2,3-triazoles proceed in the presence of copper salts as homogeneous catalyst, which make the separation and recovery of copper catalyst very difficult. In addition, it is probable that the obtained 1,2,3-triazoles can be contaminated by the copper metal in homogeneous catalytic system. So far, many challenges remain and much work still needs to be done. Therefore, an efficient and simple way to synthesize *N*-substituted 1,2,3-triazoles is still necessary.

In order to overcome the above shortcomings, immobilizing the copper salts as heterogeneous catalysts in CuAAC reaction *via* silica,[8–11] magnetic nanoparticles,[12–18] polymers,[19–25] zeolites,[26–29] and charcoal[30,31] have been reported. These heterogeneous catalysts offer several advantages, such as simplification of reaction procedures, easy separation of products, and easy recovery of catalyst. However, a series of laborious, tedious, and time consuming steps are needed during the procedures of catalyst preparation.

In recent years, low-cost and green synthesis of supported catalysts from agricultural wastes and biomass has been found to be of increasing interest. Using agricultural wastes as support materials of catalysts, such as rice husk powders and oyster shell waste,[32–34] not only helps to reuse and recycle waste materials, but also reduces the costs of the supported catalysts. Xiamen is a coastal city of southeast China, and marine fish is one of the most popular seafood in the city. The majority of waste generated by fish processing factory comes from the heads and bones. Although abundant waste fishbones are generated there every day, most of them are abandoned without any pretreatment. Therefore, disposal of fishbone waste in Xiamen is associated with environmental problems. The reasonably utilizing of the surplus waste fishbones has become a new subject of construction of harmonious society at present based on the view of sustainable development. Because fishbone powders contain collagen, noncollagen proteins, carbohydrate, and phosphopeptide, etc., they can be used as an adsorbent for the removal of heavy metal salts from sewage and waste aqueous solution.[35,36] Very recently, Akhlaghinia and co-workers have reported the one-pot synthesis of 1,4-disubstituted 1,2,3-triazoles *via* a three-component reaction between terminal alkynes, organic bromides, and NaN_3 in H_2O by using cuttlebone supported heterogeneous catalyst cuttlebone@$CuCl_2$. The obtained results showed that this protocol was an attractive and environmentally compatible process for the regioselective synthesis of 1,4-disubstituted 1,2,3-triazoles.[37]

In continuation of our efforts to develop green, highly efficient and practical chemical methods as well as our interest on the application of heterogeneous catalysts in organic reactions under MW irradiation,[13,38–41] we report here an environmentally benign and highly efficient one-pot three-component coupling of amines, propargyl bromide and organic azides catalyzed by FBPs-CuBr for the preparation of *N*-substituted 1,2,3-triazoles under MW irradiation in water. To the best of our knowledge, this is the first work that prepares *N*-substituted 1,2,3-triazoles catalyzed by biowaste supported FBPs-CuBr with one-pot three-component and scale-up synthetic strategy. It not only synthesizes *N*-substituted 1, 2, 3-triazoles with low cost, but also reduces the amount of fish bone waste and improves environmental conditions.

2 | RESULTS AND DISCUSSION

2.1 | Preparation and characterization of FBPs-CuBr catalyst

Fleshy and oily materials were removed from raw fish bones with hot deionized water using ultrasonic irradiation until water was clear. The fishbones were put into ethanol to soak and dried. The dried fishbones were roughly crushed using a hammer and then the crushed fish bones were ground into powders with a pestle and mortar, and then screened over 100 mesh sieve (Figure 1b). CuBr was added into FBPs in DMF under the protection of N_2 atmosphere. The obtained mixture was stirred at room temperature. The solid products separated from mother liquor through vacuum filtration and then washed with distilled water to obtain FBPs-CuBr catalyst (Figure 1c).

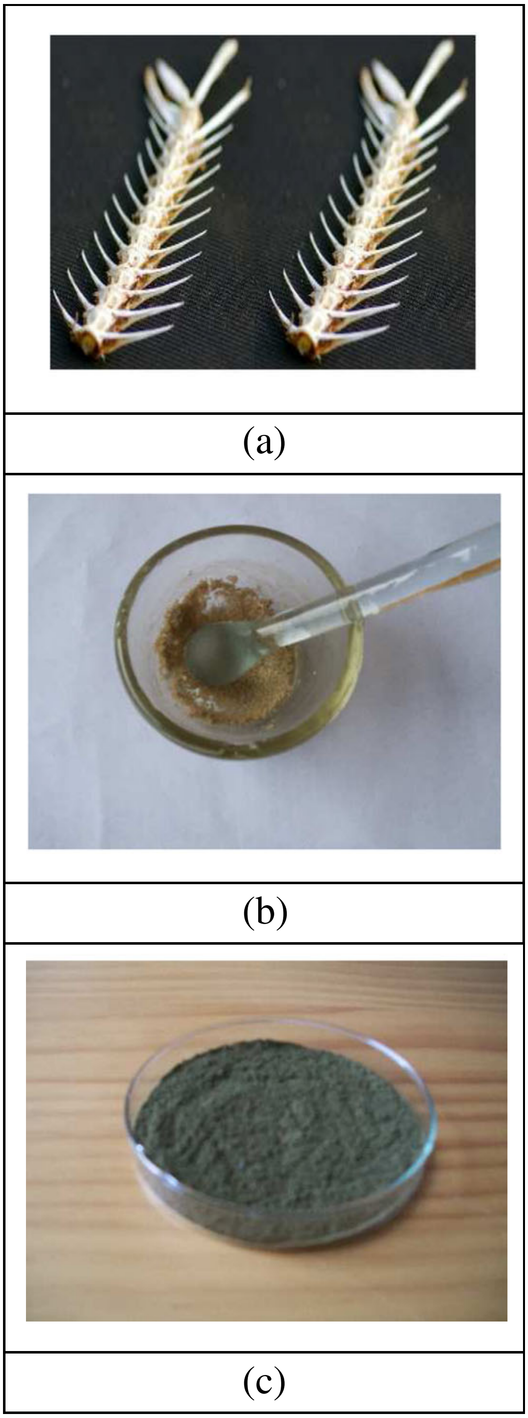


FIGURE 1 (a) fish bone waste; (b) milled FBPs after rinsed thoroughly with hot water; (c) FBPs-CuBr catalyst prepared from fish bone waste

FBPs-CuBr has been characterized using various methods, such as FT-IR, TGA, ICP-AES, XRD and SEM/EDX. At first, FBPs and FBPs-CuBr were characterized using FT-IR spectroscopy (Figure 2). The spectrum of FBPs showed a broad band between 3600 and 3000 cm^{-1} (Figure 2a). It included O–H stretch vibration of HPO_4^{2-}, carbohydrate and adsorbed water. The peaks at near 2925 cm^{-1} and 2852 cm^{-1} were characteristic bands of $–CH_2–$ stretching vibration. The bands 1030 and 750 cm^{-1} characterized the bending vibration of phosphate (O–P). The peaks observed at 1650 and 1535 cm^{-1} were characteristic bands of amide I or amide II bands, respectively. Additionally, the O–P group is also found at 1024 cm^{-1} for FBPs. When FBPs complexed with CuBr, the –C–H stretching peaks of $–CH_2–$ appeared at 2925 and 2852 cm^{-1} were shifted to lower wave numbers 2921 and 2844 cm^{-1}, respectively. The characteristic bands of amide bands appeared at 1650 cm^{-1} was shifted to lower wave number 1647 cm^{-1}. The bending vibration of phosphate (O–P) appeared at 1030 cm^{-1} was shifted to lower wave number 1023 cm^{-1}. Similarly, the $–CO_3^{2-}$ bending vibration absorption peaks at 1428 and 880 cm^{-1} were also shifted to lower wave numbers 1425 and 875 cm^{-1}. The lowering in frequency of the above peaks indicates the formation of the metal–ligand bond. So, it is clear from the above comparison that FBPs-CuBr has been prepared successfully.

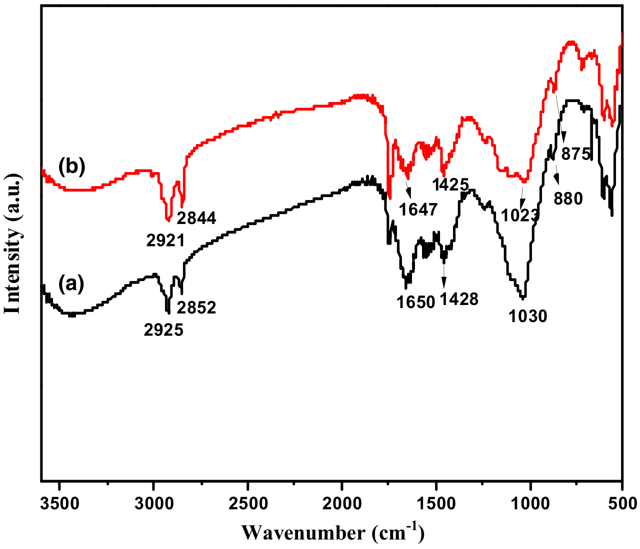


FIGURE 2 FT-IR spectra of FBPs (a) and FBPs-CuBr (b)

The XRD patterns of FBPs and FBPs-CuBr are presented in Figure 3. The obtained XRD patterns of FBPs and FBPs-CuBr displayed the following diffraction peaks (2θ[°]): 25.9, 32.4, 40.1, and 47.1, which can be correlated to the hkl indices (002), (211), (310), and (222), respectively, of hydroxyapatite (JCPDS card number: 09–0432). As shown in Figure 3b, three additional peaks at 2θ = 27.0°, 45.1°, 53.2°, and 72.5° corresponding to the (111), (220), (311) and (331) planes of CuBr were observed in the pattern of the FBPs-CuBr composite, indicating CuBr has been successfully load on the fishbone powders though chemical bonding and physical adsorption.

The thermal behaviors of FBPs and FBPs-CuBr are further investigated by TGA. As shown in Figure 4a and 4b, a slow weight loss occurred over 30–100 °C (about 1.4 wt.%) was observed, which could be assigned to the evaporation of the residual or absorbed water and solvent from the surface of the FBPs and FBPs-CuBr samples. On further heating over a temperature range between 250 °C and 600 °C, it was found that 30% and 43% weight losses occurred for FBPs and FBPs-CuBr samples, respectively. These resulted from the decomposition of protein molecules and other organic substances. It was worth mentioning that FBPs-CuBr possessed good thermal stability (up to 250 °C), which meets the demands for potential applications in catalysis.

Figure 5 showed the EDX mapping images of Cu (red) element, which were from the fresh FBPs-CuBr (a) and the recycled catalyst after 7 consecutive trials (b), respectively. Figure 5a showed the homogeneous distribution of Cu in the fresh FBPs-CuBr catalyst, which meant that CuBr distributed homogeneously in the FBPs instead of forming

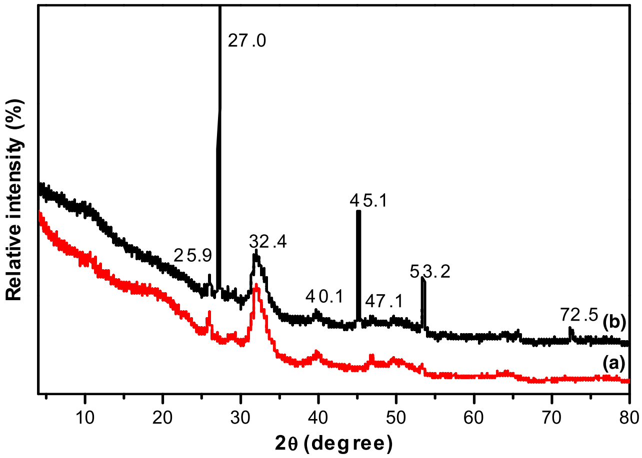


FIGURE 3 XRD patterns of FBPs (a) and FBPs-CuBr (b)

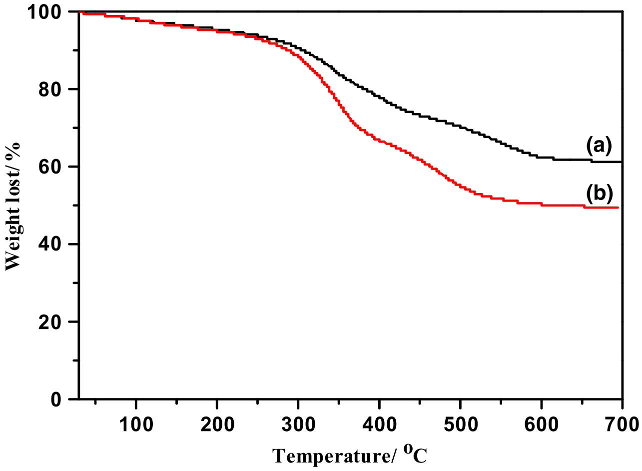


FIGURE 4 TGA curves of FBPs (a) and FBPs-CuBr (b)

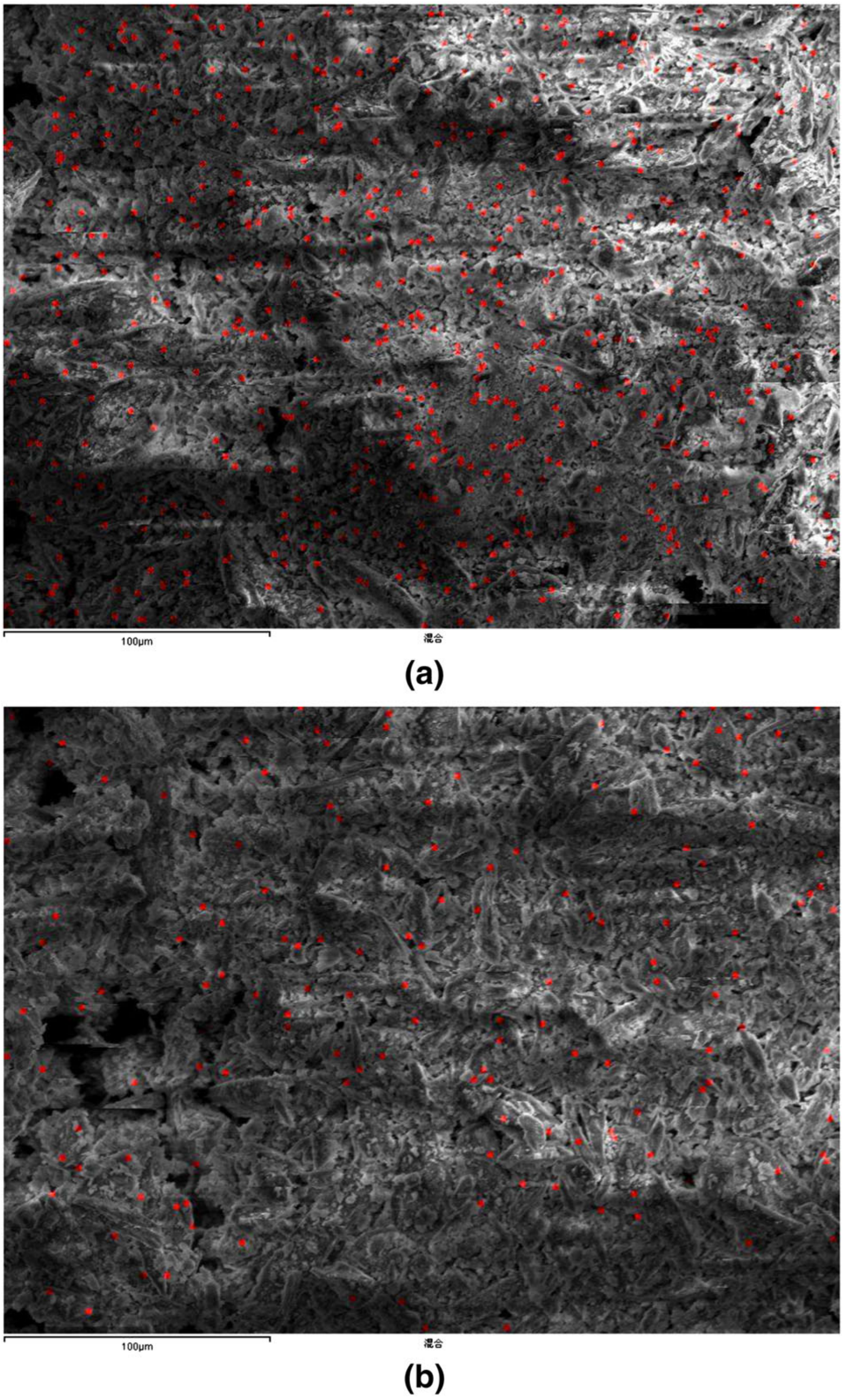


FIGURE 5 EDX elemental mapping images of the surface of FBPs-CuBr (a) and the recycled catalyst after 7 consecutive trials (b)

any fine particles. Obviously, Figure 5b showed the Cu of the recycled catalyst after 7 cycles was lower than the fresh catalyst.

The copper contents of FBPs-CuBr and the reused catalyst after seven recycling were found to be 2.85 wt% and 0.71 wt% by ICP-AES, respectively. It can be further confirmed that the copper contents of catalyst is decreased by the following tests.

XPS analysis is further carried out to determine the composition and the surface electronic state of FBPs-CuBr and FBPs-CuBr after 7 recycling (Figure 6). The XPS spectrum of the Cu2p core level region for the FBPs-CuBr

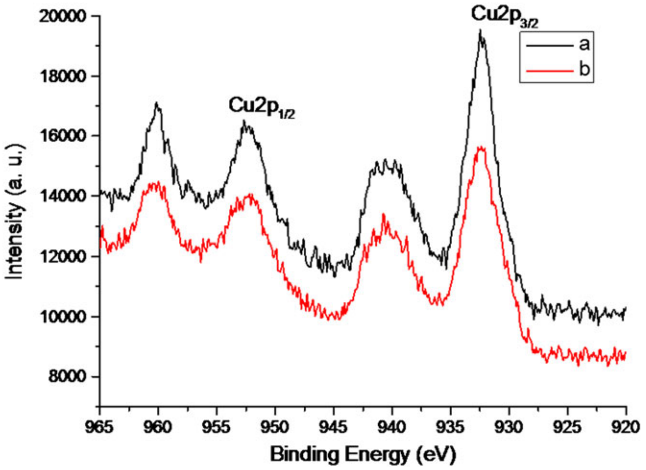
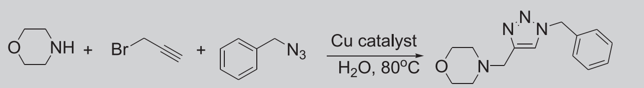


FIGURE 6 XPS Cu2p spectra of FBPs-CuBr (a) and FBPs-CuBr after 7 recycling (b)

TABLE 1 Investigation of various copper salts catalysts in the one-pot synthesis of 4-((1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl)morpholine under MW and conventional heating conditions[a]



Entry	Catalyst	Time[b]/Time[c](min)	Yield[d]/Yield[e] (%)
1	Cu_2O	30/240	36/57
2	CuBr	30/240	54/56
3	$Cu(OAc)_2$	30/240	51/53
4	FBPs-cu$(OAc)_2$	30/240	39/45
5	**FBPs-CuBr**	**30/240/30[c]**	**96/82/31[e]**

[a]0.5 mmol of morpholine, 1.5 mmol of $BrCH_2C\equiv CH$, 1.5 mmol of BnN_3, FBPs-CuBr (5.50 mg, 0.002 mmol Cu), water (5.0 mL), MW, 400 W, 80 °C;

[b,c]Reaction time under MW and conventional heating condition, respectively;

[d,e]Isolated yield of 1, 2, 3-triazole under MW and conventional heating condition, respectively.

catalyst displays main peaks at 932.4 and 952.6 eV, which can be attributed to the binding energy of $Cu2p_{3/2}$ and $Cu2p_{1/2}$, respectively (Figure 6a). These values correspond to the Cu(I) binding energies of CuBr. The binding energies of $Cu2p_{3/2}$ in FBPs-CuBr and the recycled FBPs-CuBr were both found to be around 932.4 eV, suggesting no obvious change in chemical valence of Cu(I) in the supported catalyst after 7 recycling. Especially to deserve to be mentioned, the alkyne-alkyne coupling product was not observed. Herein, the stability of catalyst and the effect of basicity were very vital in the three component reaction. The basicity could drive the rapid formation of propargyl amines and avoid self-coupling product of terminal alkynes. The stability of catalyst could lead to the regioselectivity (1,4-disubstitution) of the three-component CuAAC reaction.

2.2 | Effect of the copper source

In order to determine the optimal catalyst for CuAAC reaction, the catalytic activities of copper salts and supported catalysts were examined in a model reaction using morpholine, propargyl bromide and benzyl azide at 80 °C. The results are summarized in Table 1.

It can be seen that when CuAAC reaction was carried out using homogeneous copper catalysts, such as Cu_2O, CuBr and $Cu(OAc)_2$ for 30 min at 80 °C under MW irradiation, the desired 1,2,3-triazole could be obtained in 36%, 54% and 51% isolated yield, respectively (Table 1, entries 1–3). Unfortunately, these homogeneous copper catalysts cannot be recycled. In order to recycle the copper salts, the supported catalysts, such as FBPs-$Cu(OAc)_2$ and FBPs-CuBr were employed as heterogeneous catalysts. The obtained results showed that when the reaction was carried out using FBPs-$Cu(OAc)_2$ as the catalysts for 30 min at 80 °C under MW irradiation, the desired product could be obtained in low yield of 39% (Table 1, entry 4). To our delight, FBPs-CuBr was found to be the most effective catalyst in terms of isolated yield of the corresponding product (96%, entry 5).

Subsequently, we investigated the activity of the catalysts with respect to time for the formation of the desired 1,2,3-triazole under conventional heating condition. When the supported copper salts, such as FBPs-$Cu(OAc)_2$ and FBPs-CuBr were used as catalysts, the yields were found to be 45% and 82% after 240 min at 80 °C, respectively (Table 1). In addition, when FBPs-CuBr was used as catalyst, the reaction has only a 31% yield after 30 min. Compared with the traditional heating method, the use of MW irradiation could dramatically reduce the reaction time.

In order to further study the regioselectivity (1,4- or 1,5-disubstitution) of the three-component CuAAC reaction, the obtained product has been characterized using NOE technique. In the $^{1}H-{}^{1}H$ NOESY spectrum of the obtained product in $CDCl_3$, the correlation between the triazole proton (Hb) and the adjacent benzyl proton (Hc) was observed (Figure 7). suggesting 4-((1-benzyl-1*H*-1, 2, 3-triazol-4-yl) methyl)morpholine is the only 1,4-disubstitution isomer obtained from the three-component CuAAC reaction by using FBPs-CuBr as catalyst.

2.3 | One-pot synthesis of *N*-substituted 1,2,3-triazoles

Prompted by the aforementioned excellent result of FBPs-CuBr, we further investigate the practicality of the catalyst. Using the optimized reaction condition, the one-pot three-component CuAAC reaction was further expanded to a broader range of various organic amines, propargyl bromide and benzyl azide using FBPs-CuBr as catalyst in order to

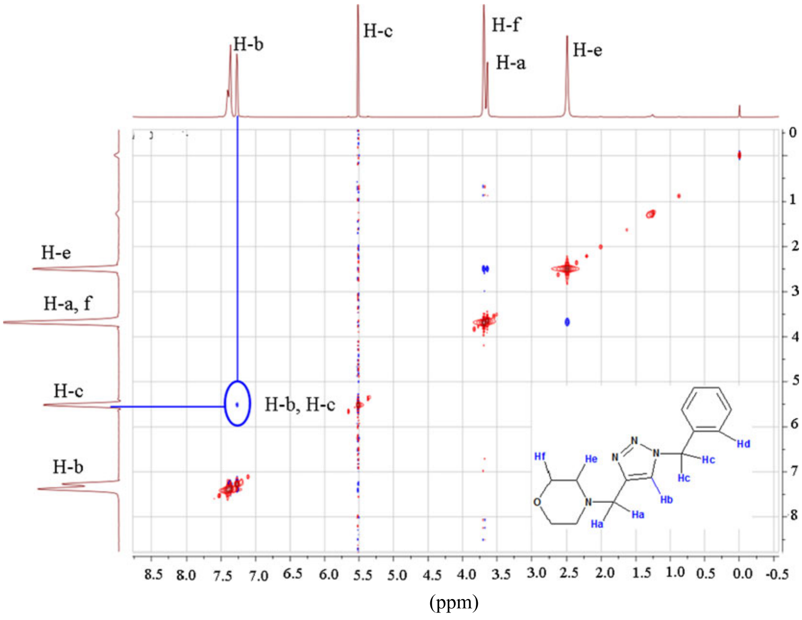
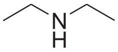
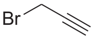
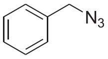
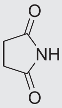
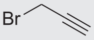
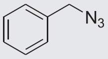
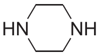
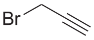
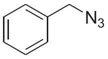
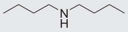
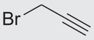
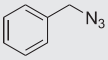
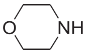
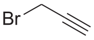
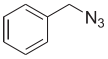
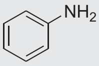
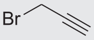
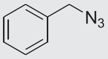
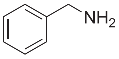
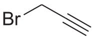
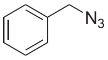
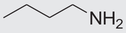
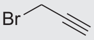
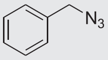
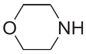
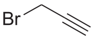
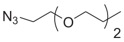


FIGURE 7 2D ^1H – ^1H NOESY spectrum of the prepared 1,2,3-triazole by using FBPs-CuBr catalyst

evaluate the scope and limitations of the method. The obtained results are summarized in Table 2. It was found that most of the reactions proceeded smoothly to give the desired 1,2,3-triazoles in moderate to excellent yields, which obviously indicated the generality and scope of the reaction with respect to various organic amines.

TABLE 2 Synthesis of *N*-substituted 1,2,3-triazoles under the optimized reaction condition[a]

Entry	Amine	Propargyl bromide	Azide	Yield(%)[b]
1				85[8]
2				70[9]
3				85
4				82
5				98
6				93
7				95
8				90
9				84

[a] Reagents and conditions: R^1R^2NH (0.50 mmol), $BrCH_2C \equiv CH$ (0.50 mmol), BnN_3 (0.50 mmol), FBPs-CuBr (5.50 mg, 0.002 mmol Cu), water (5.0 mL), MW, 400 W, 80 °C, 30 min.

[b] Isolated yield.

The yields of the three-component CuAAC reaction of annular secondary amines are higher than open chain secondary amines. Similarly, as for the open chain organic amines, the yield of diethylamine is higher than dibutylamine. However, there are obvious difference in reactivity was observed for the examined reactants with varied electronic properties. For example, the organic amines with electron withdrawing groups (such as succinimide) can react with propargyl bromide/benzyl azide and give moderate yield (Table 2, entry 2, 70%). When using piperazine as starting in the reaction, it is very easy to prepare the corresponding disubstituted bis-1, 2, 3-triazole in 85% yield under the same reaction condition (Table 2, entry 3). Interestingly, this methodology could also be extended to the primary aliphatic and aromatic amines. For example, n-butylamine, phenyl amine, and benzyl amine, the corresponding disubstituted bis-1,2,3-triazoles could also be obtained in excellent yields under the optimized reaction condition (Table 2, entries 6–8).

The copper contents of the obtained 1,2,3-triazoles were detected by atomic absorption spectroscopy (AAS). The exact amount of copper in the isolated final 1,2,3-triazoles (Table 2, entries 1 and 2) were found to be 93 ppm and 147 ppm, respectively. At the same time, the copper contents (Table 2, entries 1 and 2) present in the aqueous phase after extraction with ethyl acetate (10.0 mL × 3) were found to be 850 ppm and 965 ppm, respectively.

2.4 | Recycle use of FBPs-CuBr

For a heterogeneous catalyst, it is very important to investigate its ease of recoverability and reusability. In order to make the FBPs-CuBr catalytic system greener and economical, we focused on recoverability and reusability of FBPs-CuBr on three-component CuAAC reaction of morpholine, propargyl bromide and benzyl azide under the optimized reaction condition. After completion of each run, ethyl acetate was added to dilute the reaction mixture and FBPs-CuBr was recovered from the reaction mixture by a simple filtration. After a simple wash using ethyl acetate and dried, the catalyst was reused directly for the next run under the same condition. The obtained results were shown in Figure 8. The obtained results showed that FBPs-CuBr still kept moderate catalytic activity and the desired product could be obtained in 79% yield after 7 cycles. The result could be explained by the protein, carbohydrate and phosphopeptide molecules on the FBPs surfaces, which play a key role in the chelation of CuBr.

The percentage of copper contents of the fresh and the recycled FBPs-CuBr after seven consecutive trials were determined by ICP-AES analysis. The ICP-AES results showed that the weight percentage of copper content of the recycled FBPs-CuBr after seven cycles was found to be 0.71 wt %, which lower than the fresh catalyst (2.85 wt %). The decrease of yields should be due to the normal loss of the Cu(I) catalyst during the work-up stage.

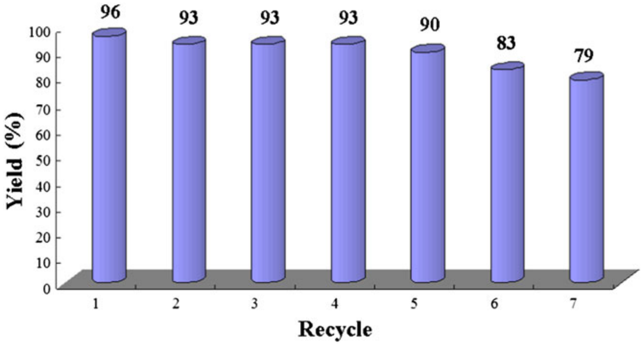


FIGURE 8 Recycling activity of FBPs-CuBr for the synthesis of 1,2,3-triazole by using morpholine, propargyl bromide and benzyl azide as starting materials

TABLE 3 Scale-up synthesis of 4-((1-benzyl-1*H*-1,2,3-triazol-4-yl) methyl) morpholine

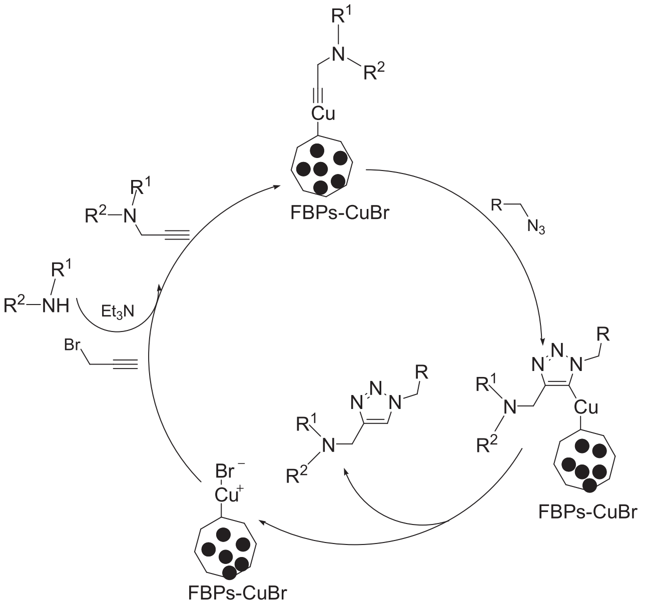
Entry	Scale (mmol)	H_2O (mL)	Isolated yield (%)
1	0.5	5	96
2^{a}	0.5	5	94
3	5	20	94
4^{b}	5	20	90
5	10	40	85
6^{c}	10	40	84
7	20	80	82
8	40	120	80

$^{a\text{–}c}$Catalyst recycled and used for the fifth run.

2.5 | Scale-up synthesis of 4-((1-benzyl-1*H*-1,2,3-triazol-4-yl) methyl) morpholine

Finally, in order to evaluate the feasibility of applying this methodology in a preparative scale, a multi-scale experiment for synthesis of 4-((1-benzyl-1*H*-1,2,3-triazol-4-yl) methyl) morpholine was carried out in the presence of morpholine, propargyl bromide and benzyl azide in water under the optimized reaction condition.

The obtained results were summarized in Table 3. The experimental results showed that the amplification reactions were found to proceed smoothly and the desired product was obtained in good yields (80–96%). When the scales of the reaction were 5 and 10 mmol, the catalyst could be recycled and reused at least 5 times and still maintained good yield (>84%). At last, when the scale of the reaction was 40 mmol, the yield was 80%.



SCHEME 1 A plausible mechanism for the synthesis of *N*-substituted 1,2,3-triazole catalyzed by FBPs-CuBr under MW irradiation

2.6 | Tentative reaction mechanism

A plausible mechanistic pathway for the Cu(I)-catalyzed three-component reaction to form *N*-substituted 1,2,3-triazoles was illustrated in Scheme 1. In the first step, the reaction between a nucleophilic organic amine and propargyl bromide carried out to form propargyl amine by a fast substitution reaction in the presence of Et_3N. Subsequently, the desired copper(I)-acetylide complex was generated by activation of FBPs-CuBr catalyzed C–H bond of terminal alkyne under MW-assisted condition. At last, the copper(I)-acetylide complex was added to organic azide to give the corresponding *N*-substituted 1,2,3-triazoles (Scheme 1).

3 | CONCLUSIONS

In summary, we have successfully developed a new and inexpensive FBPs-CuBr as heterogeneous catalyst from readily available waste FBPs for the first time. FBPs-CuBr showed highly catalytic activity with efficient recycling for the one-pot multicomponent synthesis of *N*-substituted 1,2,3-triazoles from organic amines, propargyl bromide, and benzyl azide under MW irradiation in water. When the scale of the CuAAC reaction was increased to 10.0 mmol, the desired 1,2,3-triazole still could be obtained in 84% yield after 5 recycles. Importantly, when the scale of the reaction was increased to 40.0 mmol, the product still could be obtained in 80% yield. This protocol realizes green, eco-efficient, and multi-gram synthesis of *N*-substituted 1,2,3-triazoles with good yields under mild conditions.

4 | EXPERIMENTAL

4.1 | Materials and instrumentation

All chemicals were purchased from Aladdin Reagent Company (Shanghai, China). The progress of the reaction was monitored by thin layer chromatography using silica gel plates.

The IR spectra were obtained using a FT-IR (4000 ~ 400 cm^{-1}) spectrometer (Nicolet Nexus FT-IR spectrometer, USA) at 4 cm^{-1} resolution and 32 scans. Samples were prepared using the KBr disc method. NMR spectra were acquired in $CDCl_3$ on a Bruker DMX-400 spectrometer at 400 MHz for ^1H NMR, the chemical shifts are given in δ values from TMS as an internal standard. Powder X-ray diffraction (XRD) was used to characterize the crystalline structure of FBPs-CuBr on Bruker D8 Advance (Germany) using Cu Kα radiation. Thermo gravimetric analyzer (TGA) was run on TA instruments TA (USA) DSC2910/SDT2960, samples were heated from 25 to 700 °C at ramp 10 °C/min under N_2. Scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX) was used on the Oxford instruments 7021. The copper contents of *N*-substituted 1,2,3-triazoles prepared by using CuBr and FBPs-CuBr as catalyst were determined by atomic absorption spectrophotometry (AAS) using standard methods with a Varian AA275 atomic absorption spectrophotometer (USA).

4.2 | Preparation of FBPs-CuBr catalyst

Fleshy and oily materials were removed from raw fish bones with hot deionized water using ultrasonic irradiation until water was clear. The fishbones were put into ethanol to soak for 12 h, dried at 80 °C for 12 h. The dried fishbones were roughly crushed using a hammer and then the crushed fish bones were ground into powders with a pestle and mortar, and then screened over 100 mesh sieve (Figure 1 B).

CuBr (0.3 g) was added into FBPs (2.0 g) in DMF (10.0 mL) under the protection of N_2 atmosphere. The obtained mixture was stirred for 24 h at room temperature. The solid products separated from mother liquor through vacuum filtration and then washed with distilled water to obtain FBPs-CuBr catalyst.

4.3 | Synthesis of *N*-substituted 1,2,3-triazoles catalyzed by FBPs-CuBr

N-substituted 1,2,3-triazoles was prepared by one-pot method in two steps: nucleophile substitution reaction between organic amines and propargyl bromide, and the CuAAC reaction between obtained terminal alkynes and benzyl azide.

At first, the nucleophile substitution reaction was carried out as follows: a mixture of water (5.0 ml), Et_3N (1.5 mmol), organic amine (0.5 mmol) and propargyl bromide (0.5 mmol) was stirred vigorously for 10 min at 80 °C under MW irradiation (400 W). Then, benzyl azide (0.5 mmol) and FBPs-CuBr (5.50 mg, 0.002 mmol Cu) were added into the reaction system, the mixture was further heated and stirred under the same conditions until complete consumption of the starting substrates monitored by TLC. Subsequently, the reaction mixture was cooled to room temperature and FBPs-CuBr was isolated by simple filtration, the residual mixture was extracted with ethyl acetate (10.0 mL × 3). The combined organic extracts were washed with saturated brine, and dried (anhydrous $MgSO_4$). After removal of ethyl acetate under reduced pressure, the residue was purified by flash chromatography on silica-gel to give the desired product.

4.4 | Spectroscopic data of the *N*-substituted 1, 2, 3-triazoles

1,4-bis((1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl)piperazine (Table 2, entry 3): FT-IR (KBr disc) cm^{-1}: 3034 (w), 2940 (w), 2874 (m), 2821 (w), 2803 (w), 2785 (w), 2741 (w), 2692(w), 1639 (m), 1550 (m), 1493 (m), 1457 (m), 1373 (m), 1324 (m), 1284 (m), 1208 (m), 1160 (m), 1128 (m), 1048 (m), 1008 (m), 928 (m), 867 (m), 830 (m), 760 (s); ^1H NMR (400 MHz, $CDCl_3$) δ: 7.44–7.37 (m, 12H), 5.52 (s, 4H), 3.70 (s, 4H), 2.59 (s, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.60, 129.13, 128.76, 128.14, 54.16, 53.15, 52.54; MS (ESI): m/z calc. For $C_{24}H_{28}N_8$: 428.24 $[M]^+$, found: 429.52 $[M + H]^+$.

N-((1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl)-*N*-butylbutan-1-amine (Table 2, entry 4): FT-IR (KBr disc) cm^{-1}: 3144 (w), 3080 (w), 3041 (w), 2953 (s), 2874 (m), 2811 (w), 1470 (s), 1382 (m), 1327 (m), 1216 (m), 1057 (m), 724 (s); ^1H NMR (400 MHz, $CDCl_3$) δ: 7.36–7.23 (m, 6H), 5.51 (s, 2H), 3.73 (s, 2H), 2.46–2.33 (m, 4H), 1.42 (dt, J = 15.0, 7.4 Hz, 4H), 1.30–1.20 (m, 4H), 0.85 (t, J = 7.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.26, 134.94, 131.99, 130.86, 130.12, 54.04, 53.54, 49.03, 29.21, 20.57, 13.99; MS (ESI): m/z calc. For $C_{18}H_{28}N_4$: 300.23 $[M]^+$, found: 301.53 $[M + H]^+$.

4-((1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl)morpholine (Table 2, entry 5): FT-IR (KBr disc) cm^{-1}: 3152 (m), 3096 (w), 3033 (w), 2969 (m), 2850 (m), 2811 (m), 1462 (m), 1335 (m), 1279 (m), 1216 (m), 1130 (s), 732 (m); ^1H NMR (400 MHz, $CDCl_3$) δ: 7.41–7.28 (m, 6H), 5.53 (s, 2H), 3.79–3.68 (m, 4H), 3.66 (s, 2H), 2.51 (s, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.63, 129.13, 128.77, 128.11, 122.56, 66.78, 54.16, 53.70, 53.37; MS (ESI): m/z calc. For $C_{14}H_{18}N_4O$: 258.15 $[M]^+$, found: 258.86 $[M]^+$.

N,*N*-bis((1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl) benzenamine (Table 2, entry 6): FTIR (KBr disc) cm^{-1}: 3128 (m), 3073 (m), 3041 (w), 2953 (m), 2938 (m), 2866 (w), 2803 (w) 1462 (m), 1327 (s), 1224 (s), 1128 (s), 732 (s), 708 (w); ^1H NMR (400 MHz, $CDCl_3$) δ: 7.35–7.28 (m, 14H), 6.87–6.86 (m, 2H), 6.77–6.75 (m, 1H), 5.45 (s, 4H), 4.66 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.71, 129.27, 129.08, 128.66, 127.84, 122.00, 54.09, 46.95; MS (ESI): m/z calc. For $C_{25}H_{25}N_7$: 435.22 $[M]^+$, found: 436.14 $[M + H]^+$.

N,*N*-bis((1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl)(phenyl) methanamine (Table 2, entry 7): FTIR (KBr disc) cm^{-1}: 3120 (m), 3065 (m), 3041 (w), 2930 (m), 2834 (m), 1494 (m), 1434 (s), 1382 (s), 1319 (s), 740 (s), 700 (m); ^1H NMR (400 MHz, $CDCl_3$) δ: 7.50–7.28 (m, 17H), 5.52 (s, 4H), 3.74 (s, 4H), 3.65 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.85, 129.08, 129.05, 128.66, 128.28, 127.94, 127.04, 123.10, 57.74, 54.08, 47.58; MS (ESI): m/z calc. For $C_{27}H_{27}N_7$: 449.23 $[M]^+$, found: 450.15$[M + H]^+$.

N,*N*-bis((1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl)butan-1-amine (Table 2, entry 8): FTIR (KBr disc) cm^{-1}: 3136 (s), 3065 (w), 2930 (w), 1597 (s), 1510 (m), 1446 (w), 1367 (m), 1224 (m), 1057 (m), 756 (s), 716 (w); ^1H NMR (400 MHz, $CDCl_3$) δ: 7.52–7.28 (m, 12H), 5.22 (s, 4H), 3.73 (s, 4H), 2.46 (s, 2H), 1.27 (s, 4H), 0.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.85, 129.07, 128.64, 127.95, 122.95, 54.08, 53.34, 47.84, 20.45, 13.95; MS (ESI): m/z calc. For $C_{24}H_{29}N_7$: 415.25 $[M]^+$, found: 416.15 $[M + H]^+$.

4-((1-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-1*H*-1,2,3-triazol-4-yl)methyl)morpholine (Table 2, entry 9): FTIR (KBr disc) cm^{-1}: 3137 (w), 2875 (s), 2817 (s), 1977 (w), 1648 (w), 1551 (s), 1453 (m), 1351 (m), 1328 (m), 1284 (w), 1115 (s), 1049 (m), 1004 (m), 915 (m), 862 (w), 800 (w), 711 (w); ^1H NMR (400 MHz, $CDCl_3$) δ: 7.70 (s, 1H), 4.54 (t, J = 5.1 Hz, 2H), 3.88 (t, J = 5.1 Hz, 2H), 3.73–3.71 (m, 4H), 3.68 (s, 2H), 3.63–3.61 (m, 6H), 3.55 (dd, J = 5.7, 3.2 Hz, 2H), 3.38 (s, 3H), 2.55–2.52 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.67, 123.95, 71.90, 70.51, 69.47, 66.80, 59.02, 53.61, 53.30, 50.19. MS (ESI): m/z calc. For $C_{14}H_{26}N_4O_4$: 314.20 $[M]^+$, found: 315.45 $[M + H]^+$.

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