Cu/SiO$_2$-Pr-NH-Benz as a novel nanocatalyst for the efficient synthesis of 1,4-disubstituted triazoles and propargyl amine derivatives in an aqueous solution

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ABSTRACT

In this work, an innovative nanocatalyst (Cu/SiO$_2$-Pr-NH-Benz) was synthesized and applied to coupling and click reaction in an aqueous solution. This work reports an efficient and straightforward approach for synthesizing diverse propargylamine and 1,2,3-triazole derivatives in excellent yield and short-time reaction. Also, a novel method involving the Cu NPs supported on the SiO$_2$ nanocatalyst as a heterogeneous novel catalyst for the “one-pot” three-component A$^3$-coupling of aldehyde, amine, and alkynes and “one-pot” click reaction between alkyne, benzyl halide, and sodium azide in the water at room temperature was developed. Significant advantageous such as enhanced catalytic activity with efficient recycling for the one-pot synthesis of 1,4-disubstituted triazoles and propargyl amine derivatives and in green condition were observed. Also, after five successive reactions, the catalytic activity of recycled Cu/SiO$_2$-Pr-NH-Benz remained high without significant loss in its intrinsic activity.

1. Introduction

The heterogeneous catalysts have attracted considerable attention because of their wide industrial applications, including cost-effective, acceptable lifetime, fragility, thermal instability, and easy removal compared to homogeneous catalysts [1]. Despite their widespread use, design, and synthesis of heterogeneous catalysts as increasingly selective, efficient, and active, it is still a challenging topic [2]. In recent years, diverse heterogeneous and homogenous catalysts have been applied as catalysts for organic reactions. The heterogeneous catalyst can be used for nanomaterial resulting in a significantly high catalytic activity, a high surface area to volume ratio, excellent selectivity, and exhibit novel characteristics of quantum size effects [3]. The nanomaterial was implemented in the optical, electronic, coating, medical, catalytic, and sensor applications [4, 5] because of their exclusive properties. Although nanomaterials displayed an excellent catalytic activity, they cannot be separated from the reaction conveniently. Therefore, different solid supports have been applied to synthesized heterogeneous catalysts based on nanoparticles such as silica, graphene, zeolites, and carbon nanotubes [4, 5, 6, 7, 8, 9, 10, 11, 12, 13]. Among all, SiO$_2$ is contemplated as one of the most promising support materials owing to diverse morphology, cost-effective, high specific surface area, thermal stability, and conducting properties. Besides, transition metal ions could be anchored or coordinated with a good dispersion on the functioning surface of SiO$_2$ [14]. The highly dispersed copper catalyst has been under intensive study and revealed a promising role in a wide range of catalytic reactions, particularly in complicated reactions such as click and coupling reactions [15].

The azide-alkyne cycloaddition reaction, known as the click reaction, is a promising tool for pharmaceutical and molecular biology applications [16]. The original Huisgen cycloaddition of azide and alkyne could be effectively used for triazole scaffold synthesis but had several demerits, including prolonged reaction time, harsh reaction conditions, and low regioselectivity [17, 18]. The application of Cu(I) catalyst can yield product in high atom economy, exclusive regioselectivity, shortened reaction, broad substrate scope, and under mild reaction conditions. Cu-catalyzed azide-alkyne cycloaddition (Cu-AAC) reaction has been reported for triazole synthesis as an alternative catalyst for click reaction

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Nowadays, incredible efforts have been made to develop catalytic processes to achieve a greener synthesis by reducing chemical waste and the number of synthetic steps and using an eco-friendly solvent to result in target product in good yields and highest rates [22, 23].

Today, the multicomponent and one-pot reaction in which carious starting substrates are amalgamated to provide various scaffolds has been utilized significantly. The multicomponent coupling reaction of amines, aldehydes, and alkynes to synthesize propargylamine as a valuable synthon in preparation of diverse biologically active and natural product compounds has become an exciting challenge in organic synthesis [24]. It was performed in different reaction conditions and solvents such as water, organic media, ionic liquid, or solvent-free conditions to afford various propargylamine. A wide range of different catalysts was utilized in these reactions, including silver, copper, gold, iron, zinc, iridium, and other propargylamine [25, 26, 27].

Copper plays an essential role as a promoter and catalyst in numerous organic reactions such as cycloaddition, coupling, click reactions as well as sigmatropic rearrangements [24, 28, 29]. Copper nanoparticles have been anchored on different silica supports such as MCM and Fumed silica and used for antibacterial and electrochemical applications. However, the potential of these composites in organic catalytic reactions has not been investigated thoroughly. A recent report on copper induction in the
click and A3-coupling reactions prompted us for the present study [30]. This work reports an efficient and straightforward approach for synthesizing diverse propargylamine and 1,2,3-triazole derivatives in eco-friendly condition, excellent yield and short-time reaction. We have designed and developed a method involving the Cu NPs supported on the SiO2 nanocatalyst as a heterogeneous novel catalyst for the “one-pot” three-component A3-coupling of aldehyde, amine, and alkynes and “one-pot” click reaction between alkyne, benzyl halide, and sodium azide in the water at room temperature. These routes’ unique aspects are the enormous scope, high selectivity, cost-effectiveness, and a single-step method that needs nontoxic reagents and environmentally friendly solvents. Therefore, this technique is safe for environs and humans.

Figure 3. FT-IR spectra of (a) SiO2-Pr-Cl, and (b) SiO2-Pr-NH-Benz, and (c) Cu/SiO2-Pr-NH-Benz.

Figure 4. Curves of N2 adsorption-desorption isotherms of (a) SiO2-Pr-NH-Benz, and (b) Cu@SiO2-Pr-NH-Benz.

Table 1. Physical parameters of SiO2-Pr-NH-Benz, and (b) Cu@SiO2-Pr-NH-Benz.

|                  | Surface area (m²/g) | Average Pore diameter (nm) | Pore volume (cm³/g) |
|------------------|---------------------|----------------------------|---------------------|
| SiO2-Pr-NH-Benz  | 159.8               | 30.61                      | 0.316               |
| Cu@SiO2-Pr-NH-Benz | 153.5              | 38.90                      | 0.372               |
2. Experimental

2.1. Synthesis of fumed silica-Pr-Cl nanoparticles

A two-neck round-bottom flask was charged with fumed-silica (2.0 g) and dried out under vacuum at 100°C. Afterward, dry toluene (50 mL) was added at ambient temperature until a diluted mixture was obtained. Then, the mixture was heated under reflux condition for 30 min, followed by a steady addition of (3-chloropropyl) trimethoxysilane (2 mL) to it and refluxed for 72 h. Finally, the fumed silica-Pr-Cl was filtered and washed frequently with EtOH through the Soxhlet apparatus and dried at ambient temperature for 24 h (Figure 1).

2.2. Synthesis of fumed SiO2-Pr-Pyr-Benzimidazole nanoparticles

Fumed SiO2-Pr-Cl (2.0 g) was dried, and then the pertinent 2-amino-Benzimidazole (1.0 g) and toluene (50 mL) were added, and the mixture was heated under reflux for 72 h. Finally, the obtained solid was filtered and washed well with EtOH using Soxhlet apparatus, then dried at room temperature (Figure 2).

2.3. Preparation of Cu@SiO2-Pr-NH-Benzimidazole

The obtained SiO2-Pr-NH-Benz (1 g) were added to a solution of Cu(NO₃)₂ (1 M, 25 mL), ascorbic acid (0.2 g), and the mixture was stirred for 24 h at 50°C. The solid was filtrated, washed four times with doubledistilled water, and dried under vacuum for 10 h to result in Cu@SiO2-Pr-NH-Benz.

2.4. “One-pot” multicomponent A³-coupling reaction by Cu@SiO2-Pr-NH-Benzimidazole nanocatalyst

In a typical procedure, phenylacetylene (1.1 mmol), piperidine (1.1 mmol), aldehyde (1.0 mmol), and Cu@SiO2-Pr-NH-Benz (0.01 g) were added to a 10 mL flask, and 5 mL H₂O was added. The mixture was subjected to ultrasound irradiation for 1 h at room temperature. After the completion of the reaction, the mixture was separated by filtration and

Figure 5. Fe-SEM images of (a) SiO₂-Pr-Cl, (b) Cu@SiO₂-Pr-NH-Benz and (c) TEM image of Cu@SiO₂-Pr-NH-Benz.
washed with H2O and ethanol (310 mL), and filtered. The residue was purified by column chromatography on silica gel using EtOAc/n-hexane as eluent to afford the corresponding pure product (see supporting information; S1–S38).

2.5. “One-pot” multicomponent click reaction by Cu@SiO2-Pr-NH-Benzimidazole nanocatalyst

Phenylacetylene (1 mmol), benzyl bromide derivatives (1 mmol), sodium azide (1 mmol), and Cu@SiO2-Pr-NH-Benz nanocatalyst (0.03 g), and 5 mL H2O were added. The resultant mixture was heated at 70 °C, and TLC monitored the progress of the reaction. Upon completion of the reaction, the mixture cooled to room temperature, and the catalyst was separated by filtration. The solvent was removed in a vacuum to afford the pure product.

3. Result and discussion

3.1. Characterization of Cu@SiO2-Pr-NH-Benz nanocatalyst

The prepared Cu@SiO2-Pr-NH-Benz nanocatalyst was constructed by a three-step procedure to immobilized copper on modified SiO2 for the click and coupling reactions. The prepared supported catalyst Cu/ SiO2-Pr-NH-Benz nanocatalyst was characterized by TGA-DTA, FT-IR, EDX, SEM, and BET analysis. To confirm the preparation of Cu@SiO2-Pr-NH-Benz nanocatalyst, FT-IR spectroscopic study was conducted. The FT-IR spectra of SiO2-Pr-Cl, SiO2-Pr-NH-Benz, and Cu/SiO2-Pr-NH-Benz are shown in Figure 3. The band around 1639 cm⁻¹ and broadband at 3265 cm⁻¹ are attributed to stretching and bending vibrations of the O–H groups. The silica framework (Si–O–Si) resulted in absorption peaks around 821 and 1095 cm⁻¹. The silanol group of silica depicted a band at 917 cm⁻¹, representing the Si–O–C formation, which was formed by the reaction of trimethoxy silyl chloride with the silanol group. However, after the functionalization of fumed-silica with 2-amino benzimidazole, a band is depicted at 3375 and 1649 cm⁻¹, which corresponded to the N–H groups, and the band around 1560 cm⁻¹ is depicted to C=C groups. After immobilization of Cu, these bands' intensity progressively decreased for the sample due to a decrease in the convenience of free silanol groups. The peaks at 3001, 2941, and 1587 cm⁻¹ indicate the distinct attachment.

Also, the N2 adsorption-desorption isotherm was applied to provide insights into pore volume, average pore diameter, specific surface area, and etc (Figure 4). The specific surface area (BET) for SiO2-Pr-NH-Benz and Cu/SiO2-Pr-NH-Benz samples were found to be 159.3 and 153.5 m²g⁻¹, respectively (Figure 4 (a and b)). The BET surface area, pore-volume, and pore size for various samples are represented in Table 1. The nitrogen adsorption/desorption isotherms for SiO2-Pr-NH-Benz and Cu@SiO2-Pr-NH-Benz represent a type IV adsorption isotherm characteristic of a type H1 hysteresis loop with relative pressure ranging from 0.8 to 1.0. These characteristics demonstrate that SiO2 support has a bit mesoporous structure, and still exist after functionalization. The inset figures display the pore size distribution curves for SiO2-Pr-NH-Benz, and Cu@SiO2-Pr-NH-Benz samples, in which the average pore size is about 30 and 39 nm, respectively, which are consistent with the pore size of Brunauer-Emmett-Teller (Figure 4c). The wide particle size distribution is due to the cluster of SiO2 particles, which reduces the support's bulk density, forming large fluffy particles. As presented in Table 1, the catalyst-specific surface area diminished gradually along with the surface's functionalization. As the functionalization enhance, the specific surface area of the catalyst reduced slightly because the functionalization of the
catalyst support surface occupies a certain surface, but it has a specific surface area [31].

The scanning electron microscopy micrograph (SEM) images of functionalized SiO2 and the immobilized copper nanoparticles indicate the changes in the catalyst's morphology after the introduction of the Cu. The nanocatalysts' surface is rough, in accordance with the presence of organic groups on the composite surface (Figure 5 (a,b)). The rough surface increases the catalytic activity of nanocatalysts by enhancing the available catalytic sites. Also, the transmission electron microscopy (TEM) analysis shows that the Cu@SiO2-Pr-NH-Benz did not agglomerate on the surface of SiO2 (Figure 5c). Considering the results of SEM-EDX, attachment of the metal on the surface of the Cu@SiO2-Pr-NH-Benz solid support can be confirmed. The loading metal was found to be 0.0018 mmol/g of the catalyst (0.020 wt%).

Thermogravimetric analysis (TGA) in nitrogen and synthetic air atmosphere was performed from 25 to 970 °C to predict the catalysts' thermal stability. TGA analysis was applied to study the thermal stability of the SiO2-Pr-Cl, SiO2-Pr-NH-Benz, and Cu@SiO2-Pr-NH-Benz nanocatalysts were studied through EDX analysis, which confirmed the presence of Cu in the catalyst along with the other elements, indicating the formation of the desired metal complex. As shown in Figure 6 (a-c), the EDX measurement confirmed that the nanocatalyst contains Si, O, C, Cl, Cu.

Figure 7. TGA-DTA curves of (a) SiO2-Pr-Cl, (b) SiO2-Pr-NH-Benz, and (c) Cu@SiO2-Pr-NH-Benz.

Thermogravimetric analysis (TGA) in nitrogen and synthetic air atmosphere was performed from 25 to 970 °C to predict the catalysts' thermal stability. TGA analysis was applied to study the thermal stability of the SiO2-Pr-Cl, SiO2-Pr-NH-Benz, and Cu@SiO2-Pr-NH-Benz, including the main thermal regions of the polymeric coating decomposition. The TGA results of nanocatalyst demonstrate considerable thermal stability of the catalyst to more than 760 °C, which makes it applicable for implementation in a wide range of reactions with different high temperatures. As shown in Figure 7, the overall weight loss of SiO2-Pr-Cl, SiO2-Pr-NH-Benz, and Cu@SiO2-Pr-NH-Benz was about 13%, 15%, and 19%, which confirmed the functionalization of fumed silica surfaces. The primary decomposition regions determined from TGA-DTA curves exhibited that the organic part's primary decomposition starts from 155 °C, which is higher than that for organic scaffolds. Obtained data are in line with thermal analysis data reported recently.

3.2. The catalytic activity of Cu@SiO2-Pr-NH-Benz for “one-pot” A3 coupling reaction

The catalytic activity of Cu@SiO2-Pr-NH-Benz nanocatalyst was evaluated for the MCR A3 coupling reaction of amine, aldehyde, and alkyne. The model was performed using phenylacetylene, benzaldehyde, and piperidine to optimize various parameters comprising solvent, temperature, time, and catalyst. The results are listed in Table 2.

Herein, we reported a novel Cu-catalyzed one-pot multicomponent coupling reaction. As depicted in Table 2, the investigation was initialized by phenylacetylene, piperidine, and benzaldehyde as model substrates to find the optimal reaction conditions. In order to compare the Cu-catalytic properties, the homocoupling of phenylacetylene has been conducted in H2O. In the absence of a catalyst at 100 °C after 24 h, no product was obtained (Table 2, entry 1). For comparison, Fe3O4@SiO2–NH2–Cu, Cu2O, Fe3O4@CuSiO3, Cu/HM, CuFe2O4, CuSO4/SDS, SiO2-Pr-NH-Benz, and Cu@SiO2-Pr-NH-Benz have been synthesized and examined as a heterogeneous catalyst for the one-pot, three-component A3 coupling reaction to synthesis propargylamine derivatives. When the reaction was repeated in the presence of various catalysts Fe3O4@SiO2–NH2–Cu, Cu2O, Fe3O4@CuSiO3, Cu/HM, CuFe2O4, CuSO4/SDS, and SiO2-Pr-NH-Benz in 5 mL H2O at room temperature for 12 h, the yield of the corresponding product is negligible for the A3 coupling reaction while yielded 30, 55, 65, 73, 0% and 90% of aimed propargylamine with catalysts mentioned above respectively (Table 2, entries 2-6). Among the examined copper-catalysts, the Cu@SiO2-Pr-NH-Benz seemed to be the most active catalyst for the A3 coupling reaction (Table 2, entry 7). In the next step, after optimization of the appropriate catalyst, in order to obtain the best suitable conditions for the synthesis of target propargylamine products, we have optimized the amount of
Table 2. Optimization of A3 coupling reaction conditions.

| Entry | Catalyst (mg) | Solvent | Catalyst (mol%) | Yield, % | Time | Temp  |
|-------|---------------|---------|----------------|---------|------|-------|
| 1     | -             | H2O     | -              | 1       | 2 h  | rt    |
| 2     | Cu2O          | H2O     | 10             | 30      | 12 h | rt    |
| 3     | Fe3O4@CuSiO3  | H2O     | 10             | 55      | 12 h | rt    |
| 4     | Cu/HM, CuFe2O4| H2O     | 10             | 60      | 12 h | rt    |
| 5     | CuSO4/SDS     | H2O     | 10             | 63      | 12 h | rt    |
| 6     | SiO2-Pr-NH-Benz| H2O | 10            | -       | 12 h | rt    |
| 7     | Cu@SiO2-Pr-NH-Benz | H2O  | 10      | 75      | 12 h | rt    |
| 8     | Cu@SiO2-Pr-NH-Benz | H2O  | 5      | 78      | 40 min | rt |
| 9     | Cu@SiO2-Pr-NH-Benz | H2O  | 10      | 82      | 40 min | rt |
| 10    | Cu@SiO2-Pr-NH-Benz | H2O  | 15      | 87      | 40 min | rt |
| 11    | Cu@SiO2-Pr-NH-Benz | H2O  | 20      | 95      | 40 min | rt |
| 12    | Cu@SiO2-Pr-NH-Benz | H2O  | 25      | 95      | 40 min | rt |
| 13    | Cu@SiO2-Pr-NH-Benz | H2O  | 30      | 95      | 40 min | rt |
| 14    | Cu@SiO2-Pr-NH-Benz | H2O  | 20      | Trace   | 100 min | 0 |
| 15    | Cu@SiO2-Pr-NH-Benz | H2O  | 20      | 85      | 35 min | 50 |
| 16    | Cu@SiO2-Pr-NH-Benz | H2O  | 20      | 78      | 40 min | 70 |
| 17    | Cu@SiO2-Pr-NH-Benz | H2O  | 20      | 70      | 50 min | 100 |
| 18    | Cu@SiO2-Pr-NH-Benz | H2O  | 20      | 80      | 150 min | rt |
| 19    | Cu@SiO2-Pr-NH-Benz | H2O  | 20      | 87      | 24 h  | rt    |
| 20    | Cu@SiO2-Pr-NH-Benz | CH3CN | 20      | 56      | 40 min | rt    |
| 21    | Cu@SiO2-Pr-NH-Benz | Solvent-free | 20 | 70      | 40 min | rt    |
| 22    | Cu@SiO2-Pr-NH-Benz | DMF   | 20      | 75      | 40 min | rt    |
| 23    | Cu@SiO2-Pr-NH-Benz | THF   | 20      | 60      | 40 min | rt    |
| 24    | Cu@SiO2-Pr-NH-Benz | CH2Cl2 | 20      | 71      | 40 min | rt    |
| 25    | Cu@SiO2-Pr-NH-Benz | EtOH  | 20      | 82      | 40 min | rt    |

Table 3. Copper-catalyzed one-pot multicomponent A3 coupling reaction.

| Entry | R1      | R2         | R3         | Product | Yield, % | Time (min) |
|-------|---------|------------|------------|---------|----------|------------|
| 1     | Piperidine | -Ph        | Phenyl     | 6a      | 97       | 30         |
| 2     | Piperidine | 3-OH-C6H4  | Phenyl     | 6b      | 80       | 40         |
| 3     | Piperidine | 4-Me-C6H4  | Phenyl     | 6c      | 92       | 35         |
| 4     | Piperidine | 2-OH-C6H4  | Phenyl     | 6d      | 90       | 40         |
| 5     | Piperidine | 2-Me-C6H4  | Phenyl     | 6e      | 81       | 50         |
| 6     | Piperidine | 4-OMe-C6H4 | Phenyl     | 6f      | 93       | 15         |
| 7     | Piperidine | 4-Br-C6H4  | Phenyl     | 6g      | 91       | 8          |
| 8     | Piperidine | 4-Cl-C6H4  | Phenyl     | 6h      | 90       | 34         |
| 9     | Piperidine | 2-naphtaldehyde | Phenyl | 6i      | 93       | 35         |
| 10    | Piperidine | CH3O       | Phenyl     | 6j      | 41       | 80         |
| 11    | Diethylamine | -Ph      | Phenyl     | 6k      | 82       | 50         |
| 12    | Morpholine | -Ph       | Phenyl     | 6l      | 98       | 35         |
| 13    | Piperidine | -Ph       | 2-OMe-C6H4 | 6m      | 88       | 24         |
| 14    | Piperidine | -Ph       | 4-Me-C6H9  | 6n      | 93       | 27         |
| 15    | Piperidine | -Ph       | 4-OMe-C6H4 | 6o      | 91       | 25         |
nanocatalyst. Varying the concentration of Cu@SiO2-Pr-NH-Benz cata-
lyst resulted in yield alteration as expected (Table 2, entry 8–13). We
found that 20 mol% of Cu@SiO2-Pr-NH-Benz nanocatalyst provided a
higher yield than 5 mol%, 10 mol%, 15 mol%. However, increasing the
amount to 25 mol%, and 30 mol% Cu/SiO2-Pr-NH-Benz did not provide a
better yield. The further screening revealed that a lower or higher reac-
tion temperature proved to be not effective without ultrasonic irradiation
(Table 2, entry 14–17). Also, increasing the irradiation time to 150 min
resulted in a yield reduction (Table 2, entry 18). A control experiment
showed that the propargylamine 6a was obtained in 87% yield after an
extended reaction time to 24 h and under ultrasonic irradiation (Table 2,
entry 19). However, it is apparent that the reaction also proceeded in
different solvent-free conditions or with solvents such as DMF, THF, 
CH3CN, CH2Cl2, and EtOH but gave the products in inferior yields
(Table 2, entry 11 and 20–24). Notably, no undesirable byproduct could
be detected under an optimized reaction condition.

Next, we evaluated the substitute effect of amine and aldehyde
(Table 3). In general, good yields were observed with aromatic aldehydes
(Table 3, entry 1–8). However, the aliphatic aldehyde afforded product
6j in only 41% yield (Table 3, entry 10). Reaction with aliphatic amines
diethyleamine seemed to be working quite well (Table 2, entry 11). The
reaction worked efficiently with aliphatic and cyclic amines (Table 3,
entry 12).

### Table 4. Optimization of reaction conditions.

| Entry | Catalyst | Solvent | Catalyst (mol%) | Yield, % | Time | Temp |
|-------|----------|---------|-----------------|---------|------|------|
| 1     | -        | H2O     | -               | -       | 12 h | 55   |
| 2     | CuSO4 (5mol%) | H2O   | 5               | 68      | 5 h  | 55   |
| 3     | MnFe2O4  | H2O     | 5               | 62      | 3.5 h| 55   |
| 4     | SiO2-Pr-SO3H | H2O   | 5               | -       | 5 h  | 55   |
| 5     | Fe2O3@CuSiO3 | H2O   | 5               | 78      | 4 h  | 55   |
| 6     | SiO2-Pr-NH-Benz | H2O   | 5               | -       | 8 h  | 55   |
| 7     | Cu@SiO2-Pr-NH-Benz | H2O   | 5               | 85      | 15 min | 55 |
| 8     | Cu@SiO2-Pr-NH-Benz | H2O   | 10              | 88      | 15 min | 55 |
| 9     | Cu@SiO2-Pr-NH-Benz | H2O   | 15              | 91      | 15 min | 55 |
| 10    | Cu@SiO2-Pr-NH-Benz | H2O   | 20              | 95      | 10 min | 55 |
| 11    | Cu@SiO2-Pr-NH-Benz | H2O   | 25              | 95      | 15 min | 55 |
| 12    | Cu@SiO2-Pr-NH-Benz | H2O   | 30              | 95      | 15 min | 55 |
| 13    | Cu@SiO2-Pr-NH-Benz | EtOH  | 20              | 84      | 20 min | 55 |
| 14    | Cu@SiO2-Pr-NH-Benz | H2O/EtOH | 20         | 89      | 25 min | 55 |
| 15    | Cu@SiO2-Pr-NH-Benz | DMSO  | 20              | 69      | 40 min | 55 |
| 16    | Cu@SiO2-Pr-NH-Benz | THF   | 20              | 49      | 100 min | 55 |
| 17    | Cu@SiO2-Pr-NH-Benz | H2O   | 20              | 61      | 10 min | 0   |
| 18    | Cu@SiO2-Pr-NH-Benz | H2O   | 20              | 73      | 10 min | 25 |
| 19    | Cu@SiO2-Pr-NH-Benz | H2O   | 20              | 95      | 10 min | 75 |
| 20    | Cu@SiO2-Pr-NH-Benz | H2O   | 20              | 95      | 10 min | 100 |

### Table 5. Copper-catalyzed one-pot multicomponent click reaction.

| Entry | R3 | R4 | Product | Yield, % | Time (min) | Temp |
|-------|----|----|---------|----------|------------|------|
| 1     | -Ph | -Ph | 8a      | 98       | 10         | 55   |
| 2     | -Ph | 3,4-Cl-C6H5 | 8b     | 92       | 14         | 55   |
| 3     | -Ph | -CO2Ph | 8c     | 91       | 18         | 55   |
| 4     | -Ph | 3-Me-C6H4 | 8d     | 93       | 13         | 55   |
| 5     | -CH2O-C6H4-NO2 | -CO2Ph | 8e     | 82       | 23         | 55   |
| 6     | Ph  | -CO2Ph | 8f     | 91       | 17         | 55   |
| 7     | Ph  | 4-Br-C6H4 | 8g     | 94       | 13         | 55   |
| 8     | C6H11 | 4-Br-C6H4 | 8h     | 81       | 40         | 55   |
| 9     | Ph  | -Et    | 8i     | 73       | 50         | 55   |
| 10    | Ph  | 2-naphthalene | 8j    | 84       | 18         | 55   |
| 11    | C6H4 | 6-methoxy-naphthalene- | 8k    | 65       | 33         | 55   |
| 12    | -CH2O-C6H4-NO2 | 4-Cl-C6H4 | 8l    | 76       | 26         | 55   |
entry 1–9), affording the desired compound \( \text{6} \) in 80–97% yields. Also, the use of 5-membered ring and 6-membered ring cyclic amine resulted in a good yield of propargylamine \( \text{6} \) (Table 3, entries 1 and 12). Also, alkynes' substituted effect was considered in the reaction with piperidine and benzaldehyde under the optimized condition (Table 3, entries 1 and 13–15). It was exhibited that the different electron-donating groups are bearing -OMe, -Me in the para position, and also -OMe in the ortho position were able to produce the corresponding propargylamine in a good yield and short-reaction time somehow lower than the phenylacetylene group. Incomparable superiorities of our method are quite clear in terms of high yield of synthesized propargylamine, short-reaction time through \( \text{A}\text{3} \) coupling reaction compared with other previously reported catalysts in a one-pot multicomponent manner and under a green condition with maximum efficiency and activity of nanocatalyst.

3.3. The catalytic activity of \( \text{Cu@SiO}_2\text{-Pr-NH-Benz} \) nanocatalyst for “one-pot” click reaction

The catalytic activity of \( \text{Cu@SiO}_2\text{-Pr-NH-Benz} \) nanocatalyst was investigated by choosing the multicomponent reaction between alkyl halides, terminal alkynes, and sodium azide. To find the optimum reaction conditions, a model reaction was chosen, including a mixture of benzyl bromide (1mmol), phenylacetylene (1mmol), and sodium azide (1mmol). The reaction was carried out under different conditions, and the results are presented in Table 4. In the presence of organic ligands, \( \text{Cu@SiO}_2\text{-Pr-NH-Benz} \) was able to improve the productivity of click reaction under mild and green conditions.

To investigate this catalytic system's generality and utility, the catalytic efficiency of \( \text{Cu@SiO}_2\text{-Pr-NH-Benz} \) was examined in click reaction for the “one-pot” synthesis of 1,2,3-triazoles. The best reaction condition was found as 10 mg catalyst in the water and at 55 °C (Table 4). The results demonstrate that in the absence of catalyst, the reaction could not proceed after 12 h in water and at 55 °C (Table 4, Entry 1). However, employing 5 mol% of homogenous copper sulfates catalyst provided

| Entry | Catalyst                          | Conditions         | Time (min) | Yield (%) |
|-------|----------------------------------|--------------------|------------|-----------|
| 1     | Cu/Al                            | Toluene/100 °C     | 22 h       | 94 [25]   |
| 2     | CuNPs@TiO\text{2}                | Solvent free/70 °C | 420        | 90 [32]   |
| 3     | Cu NPs                           | Solvent free/80 °C | 420        | 90 [33]   |
| 4     | Cu/G                             | Toluene/100 °C     | 240        | 95 [34]   |
| 5     | Cu@PMO-1L                        | CH\text{Cl}_2, 70 °C | 24 h       | 96 [35]   |
| 6     | Cu@GNS                           | CH\text{CN}, 83 °C | 300        | 89 [36]   |
| 7     | SiO\text{2}@Cu                   | Toluene, 110 °C    | 300        | 94 [37]   |
| 8     | Cu-MCM-41                        | Solvent free, 110 °C | 150       | 93 [38]   |
| 9     | H-FrO\text{2}@b-Cu@mSiO\text{2}  | Solvent free/110 °C | 15        | 97 [39]   |
| 10    | CS-MCR-Cu@O                      | H\text{2}O/40 °C   | 45         | 95 [30]   |
| 11    | Cu@SiO\text{2}-Pr-NH-Benz        | H\text{2}O/Ultrasound | 30        | 97 [this work] |
Cu@SiO2-Pr-NH-Benz nanocatalyst was deployed to synthesize triazole products in 68% yield (Table 4, Entry 2). As shown in the table, no significant products were observed with SiO2-Pr-SO3H, Fe2O3@Cu-SiO2, and SiO2-Pr-NH-Benz in water after 8 h (Table 4, Entry 4 and 6). It was found that the model reaction in the presence of 5 mol% of Cu@SiO2-Pr-NH-Benz and after 15 min in H2O afforded products in 85% yield and at 55 °C (Table 4, entry 7). Therefore, the excellent yield of 1,4-triazole was observed in the presence of Cu@SiO2-Pr-NH-Benz nanocatalyst and after 15 min.

Increasing the amount of catalyst to 20 mol% improved the yield of model reaction to 95 % in the presence of H2O as short at 55 °C (Table 4, entry 7–12). The solvent effect was also examined by using the various solvents such as DMSO, EtOH, H2O and H2O/EtOH (Table 4, entries 10, 13–16). Table 4, entry 10 depicts that H2O as the solvent results in the shortest reaction time and highest yield, while for other solvents, the yields are lower even for prolonged reactions. Also, the optimal value of temperature was investigated, which demonstrated decreasing the temperature diminish the yield of the reaction, but raising the reaction temperature more than 55 °C does not affect the yield of reaction (Table 4, entries 17–20).

To explore the generality and applicability of the catalyst, and also check the feasibility of CuAAC reaction, terminal alkynes (1 mmol) was reacted with primary halides (1 mmol) and sodium azide (1 mmol) in the presence of Cu@SiO2-Pr-NH-Benz nanocatalyst (20 mol%) at 55 °C in H2O medium under optimal reaction conditions. A series of benzyl bromide phenylacetylene and sodium azide (Table 5). Though, the exceptional yield of 1,4-triazole was observed in the presence of 20 mol% Cu@SiO2-Pr-NH-Benz nanocatalysts after 10 min (Table 4). We have applied the optimal condition to various substrates for the multicomponent one-pot click reaction. To this purpose, various types of substituents for alkynes and alkyl bromides with different electron-withdrawing and electron-donating groups were employed, and the results are shown in Table 5. The results indicate that alkyl halides are bearing various functional groups, including -Br, -Cl, -OH, -Me, and -NO2 were able to produce the corresponding 1,4-disubstituted triazoles (Table 5, Entry 1–8). However, the ethyl halide was less reactive (Table 5, Entry 9). Moreover, it was exhibited that alkyl acetylates had lower yields and resulted in triazole and in longer reaction time (Table 5, Entry 8, and 11). Generally, it has been observed that the aromatic substituted for alkyne and aryl bromide led to high yields for corresponding click reactions.

### 3.4. Revocability and reusability of the catalyst

The reusability and the recyclability of the heterogeneous catalysts are crucial from an economic perspective. The reusing method of the Cu@SiO2-Pr-NH-Benz nanocatalyst was deployed to synthesize triazole scaffolds 8 and propargylamine 6 upon optimized condition. After each cycle’s accomplishment, the solid catalyst was separated from the reaction mixture by filtration, followed by washing several times with ethanol (5 mL) at 50 °C. After drying through vacuum overnight, it was used again in sequential reactions. This investigation exhibited that the catalyst could be recovered and reused at least five times, with only an insignificant loss of its catalytic activity (Figure 8). The results exhibit that the supported catalyst was highly recyclable under the studied reaction conditions, preserving almost unaltered its initial catalytic performance after five times use.

To confirm the stability and reusability of nanocatalyst during the reaction, a comparison between the recovered catalyst and the fresh one was performed applying FT-IR analysis (Figure 9), and no significant changes were observed. The observation confirms that the structure of the recovered catalyst did not change during the reaction.

Further investigation of the heterogeneous character of the Cu@SiO2-Pr-NH-Benz nanocatalyst and the stability was implemented using a hot filtration test. It was examined separating catalysts in half the reaction time; no alter were recognized in the click reaction. The one-pot multi-component reactions do not proceed significantly after the separation of the solid catalyst. In comparison with other reported catalysts for the click reactions, Cu@SiO2-Pr-NH-Benz nanocatalyst represented good catalytic performance in reusability and activity for the A3 coupling reaction (Click reaction (Respectively, Tables 6 and 7).

### 4. Conclusion

In conclusion, a novel SiO2 based nanocatalyst functionalized by benzimidazole scaffolds with immobilized copper nanoparticles as a heterogeneous catalyst was reported. Significant advantages such as enhanced catalytic activity with efficient recycling for the one-pot synthesis of 1,4-disubstituted triazoles and propargyl amine derivatives and in green condition were observed. The unprecedented broad scope of the products of reaction with this novel catalyst was considerable, and facile synthesis of various heterocyclic compounds could be achieved through this procedure. Moreover, this heterogeneous nanocatalyst is stable without copper leaching and aggregation, and also multiple times racemization without loss of catalytic activity makes it eco-friendly. Our investigation to find potential applications in green organic chemistry is ongoing.

### Declarations

**Author contribution statement**

Mahdieh Darroudi, Hossein Rouh: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Mohammad Hasanazadeh: Conceived and designed the experiments.

Nasrin Shadjou: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

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Data will be made available on request.

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The authors declare no conflict of interest.

Additional information

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