

## PAPER

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# Copper-anchored polysulfonamide-modified UiO-66-NH<sub>2</sub>/sodium alginate nanocatalyst for sustainable synthesis of 1,2,3-triazoles†

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An effective nanocomposite comprising a metal–organic framework and porous polysulfonamide–sodium alginate (SA-PS) was developed for phenyl triazole production. The Cu(I) ions were uniformly distributed on the as-prepared UiO-66-NH<sub>2</sub>@SA-PS matrix, coordinated by sulfonamide groups in a bidentate bridging pattern (UiO-66-NH<sub>2</sub>@SA-PS/CuI). The nanocatalyst UiO-66-NH<sub>2</sub>@SA-PS/CuI demonstrated exceptional performance in the synthesis of 1,2,3-triazole derivatives, facilitating high product yields in the reaction of various aryl boronic acids, phenylacetylene, and sodium azide under mild conditions.

## 1. Introduction

The 1,2,3-triazoles are versatile compounds with significant biological and industrial importance. Due to their many potential structural and pharmacological characteristics, they have become a preferred scaffold in medicinal chemistry.<sup>1</sup> Their synthesis, primarily through Huisgen cycloaddition, provides a robust method for accessing a variety of derivatives, thereby supporting extensive research and development in multiple fields of chemistry and medicine.<sup>2</sup> Click chemistry utilizes small fundamental molecular units compiled in combinatorial libraries. These structures rely on selective, straightforward carbon–heteroatom bonds (C–X–C), allowing them to recombine in one-step reactions.<sup>3</sup> This approach aligns with green chemistry principles by enabling the rapid creation of a wide variety of compounds. Click chemistry is currently more prevalent in biological contexts than it is in the chemical phase of drug development, which offers an opportunity to enhance the reactions (Scheme 1).<sup>4</sup> Recent reviews have comprehensively examined the progress of CuAAC reactions, and numerous catalytic copper systems have been reported.<sup>5–8</sup> These systems are categorized into Cu(I) sources, Cu(II) salts or complexes, Cu nanoparticles, Cu MOFs<sup>6</sup> and others. Typical catalysts include Cu(I) sources such as CuI, CuBr, and CuCl.<sup>5–9</sup> Homogeneous Cu(II) salts such as CuSO<sub>4</sub>, CuCl<sub>2</sub> and Cu(OAc)<sub>2</sub>, in combination with sodium ascorbate, have been shown to be effective catalysts for CuAAC reactions.<sup>10</sup> Therefore, a variety of polymer-supported copper catalysts, such

as mPAN-Cu(II),<sup>11</sup> Cu(I)/PVPP-Fe<sub>3</sub>O<sub>4</sub>,<sup>12</sup> Cu@CB-n,<sup>13</sup> Cu(I) NVPMB, <sup>14</sup> PS-PEG-TD2-CuSO<sub>4</sub>,<sup>15</sup> PANFPABuBuX@CuX,<sup>16</sup> and CuX-PBPTP<sup>17</sup> have been successfully employed for this reaction.

The development of biodegradable solid catalysts utilizing renewable biopolymers presents a feasible approach to achieving safer and more sustainable organic synthesis methods, aligning with the principles of green chemistry.<sup>18</sup> In recent decades, heterogeneous catalytic processes have garnered significant interest for their potential to improve the sustainability of chemical reactions.<sup>19,20</sup> By leveraging renewable biopolymers, these catalysts provide an environmentally friendly alternative to conventional systems, enhancing both the safety and efficiency of organic synthesis.<sup>21</sup>

Sodium alginate is a water-soluble biopolymer commonly found in aquatic phytoplankton. This biodegradable polymer consists of chains comprising two monomeric components: 1,4-linked β-D-mannuronic acid and α-L-guluronic acid. Due to the presence of hydroxy (–OH) and carboxylate (–COO<sup>–</sup>) functional groups along its chain, alginate exhibits electrostatic interactions.<sup>22</sup> However, similar to other polymeric gels, pure ionically cross-linked alginate hydrogels possess certain disadvantages, such as structural instability and low mechanical strength, which can limit their practical applications. To improve the physical properties of sodium alginate, graft copolymerization and nanocasting techniques are practical and efficient methods.<sup>23</sup>

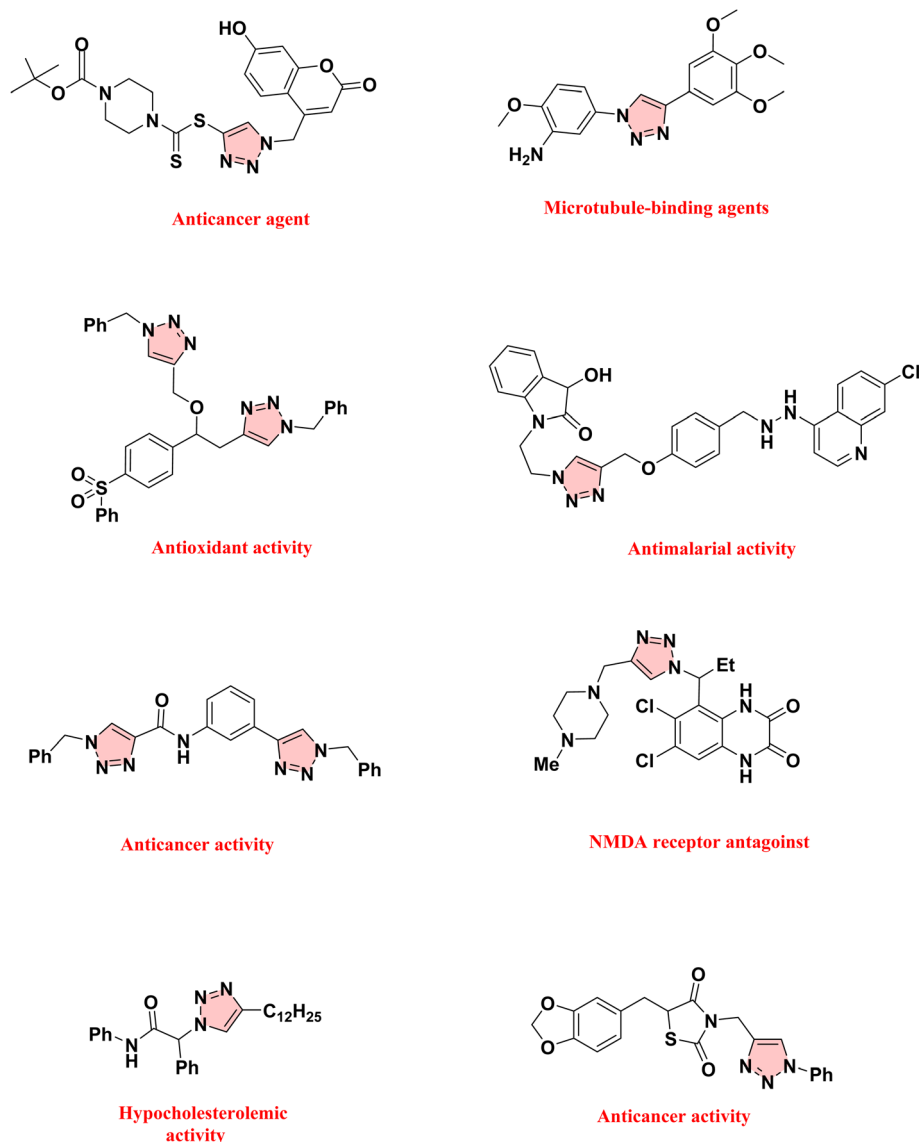
MOFs are highly promising materials due to the versatility and tunability of their orderly crystalline structures.<sup>24,25</sup> Through the integration with carefully engineered polymers to form MOF composites, the shortcomings of pure MOFs can be compensated for, thus achieving synergistic effects for the enhancement and expansion of their performance. MOF/polymer nanocomposites have emerged as promising materials for various applications, including organic reactions.<sup>26–28</sup>

The combination of sodium alginate, polysulfonamide and the metal–organic framework provides an amphiphilic

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Scheme 1 Triazole derivatives with biological activity.

environment for the reaction catalyst. The prepared substrate facilitates effective loading of copper iodide by forming strong bonds with copper iodide nanoparticles. Copper iodide nanoparticles also play a crucial role in improving the reaction conditions as active catalytic species.

In this study, a novel catalyst was designed using the readily accessible UiO-66-NH<sub>2</sub>-functionalized porous sodium alginate-polysulfonamide as a multifunctional heterogeneous support for the immobilization of CuI NPs. The MOF@polymer core-shell catalyst offers a tailored and selective environment for the synthesis of 1,2,3-triazole compounds from the reaction of aryl boronic acids, phenylacetylene, and sodium azide through Huisgen cycloaddition. This study reports the 1,2,3-triazole synthesis, emphasizing the use of a porous sodium alginate-polysulfonamide/copper nanocatalyst supported by a metal-organic framework. This method synthesizes compounds with high efficiency in the presence of an environmentally friendly catalyst (Scheme 1).

## 2. Experimental section

### 2.1 UiO-66-NH<sub>2</sub> synthesis

UiO-66-NH<sub>2</sub> was synthesized using a solvothermal method. Initially, a mixture of 2-aminoterephthalic acid (0.12 g) and zirconium chloride (0.14 g) was dispersed in DMF solvent (50 mL). Subsequently, the solution was transferred to a Teflon-lined autoclave and maintained at 130 °C for 24 h. The sample was immersed in 10 mL of hot EtOH and 10 mL of DMF for 24 h to remove any residual acids trapped inside the pores. Subsequently, it was filtered and dried at 100 °C overnight to obtain the UiO-66-NH<sub>2</sub>.<sup>29,30</sup>

### 2.2 Porous SA-PS synthesis

For polymerization, sodium alginate (0.25 g), *p*-styrene sulfonamide (1.00 g), and SiO<sub>2</sub> nanoparticles (0.05 g) were stirred with a magnet in distilled water (10 mL) at 70 °C. After 10 min, 0.04 g of ammonium persulfate was added to the mixture, and the



reaction mixture was stirred for 2 h with a magnetic stirrer until  $\text{SiO}_2/\text{SA-PS}$  nanoparticles were synthesized and washed with  $\text{H}_2\text{O}$  (5 mL) and  $\text{EtOH}$  (5 mL) to obtain a solid material, which was dried at room temperature under vacuum conditions. Then, the silica in the  $\text{SiO}_2/\text{SA-PS}$  was selectively removed with HF solution. HF solution (10 mL), deionized water (10 mL), and  $\text{SiO}_2/\text{SA-PS}$  nanoparticles (0.5 g) were added in a container. Then, the mixture was stirred at room temperature for 6 h to obtain the prepared porous polymer, washed with  $\text{H}_2\text{O}$  (50 mL) and dried at  $50^\circ\text{C}$ .<sup>31</sup>

### 2.3 Preparation of $\text{UiO-66-NH}_2/\text{SA-PS}$ nanocomposite

The new nanocomposite  $\text{UiO-66-NH}_2/\text{SA-PS}$  was synthesized by the reaction of  $\text{UiO-66-NH}_2$  with porous  $\text{SA-PS}$ .  $\text{UiO-66-NH}_2$  (0.15 g) was dispersed in DMF (5 mL). Then, porous  $\text{SA-PS}$  (0.12 g) in 5 mL DMF was added dropwise to the mixture and stirred for 24 h at  $50^\circ\text{C}$  with a magnetic stirrer. Finally, the sediment obtained was dried in an oven at  $110^\circ\text{C}$  for 24 h to remove the residual solvent to gain  $\text{UiO-66-NH}_2/\text{SA-PS}$ .<sup>31</sup>

### 2.4 Preparation of $\text{UiO-66-NH}_2/\text{SA-PS}/\text{CuI}$ nanocomposite

Subsequently, the resulting  $\text{UiO-66-NH}_2/\text{SA-PS}$  powder (0.1 g) and  $\text{CuI}$  nanoparticles (0.05 g) were added to 20 mL acetonitrile, and the mixture was stirred at  $50^\circ\text{C}$  with a magnetic stir bar for 12 h. The resulting powder was collected by filtration and

washed thoroughly with deionized water (20 mL) and ethanol (20 mL) to remove the unreacted reactant, and then dried (Scheme 2).<sup>31</sup>

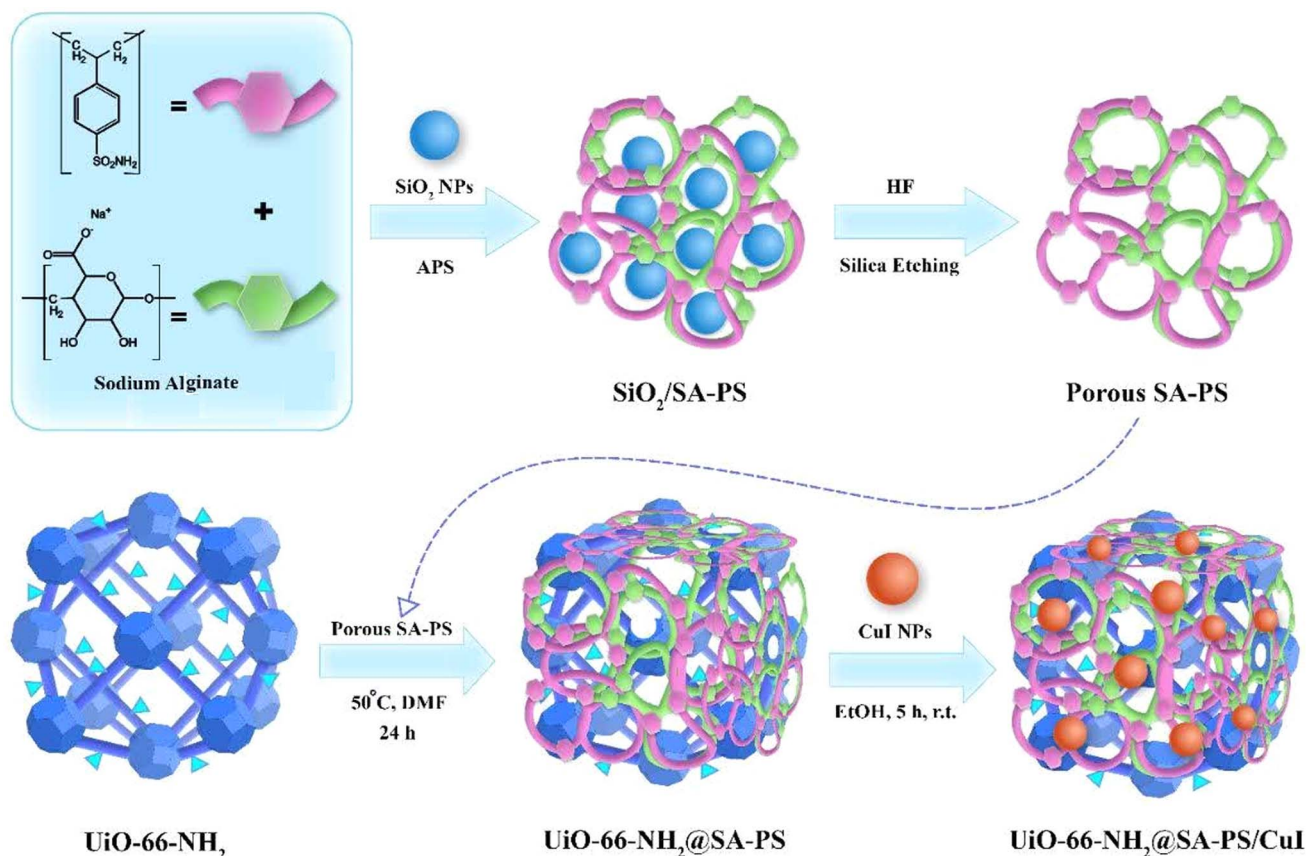
### 2.5 General procedure for 1,2,3-triazole synthesis

A mixture of potassium carbonate (138 mg, 1 mmol), phenylboronic acid (122 mg, 1 mmol), sodium azide (195 mg, 3 mmol) and  $\text{UiO-66@SA/PSA@CuI}$  (10 mg, 0.64 mol%) in  $\text{H}_2\text{O}/\text{EtOH}$  (2 mL) was stirred at  $80^\circ\text{C}$  for 1 h. Then, phenylacetylene (102 mg, 1 mmol) was added to the mixture and stirred for an appropriate time. The progress of reaction was checked using TLC ( $n$ -hexane/ethyl acetate = 10 : 3). After completion of the reaction, the mixture was cooled and then centrifuged to separate the catalyst. After drying, the sediment from the reaction was extracted (ethyl acetate/water = 1 : 2, 30 mL), dried and evaporated, and finally, the crude product was washed with hot  $n$ -hexane (Scheme 3). The amount of copper incorporated in the support was 4.064%, as corroborated using inductively coupled plasma optical emission spectroscopy (ICP-OES).

## 3. Result and discussion

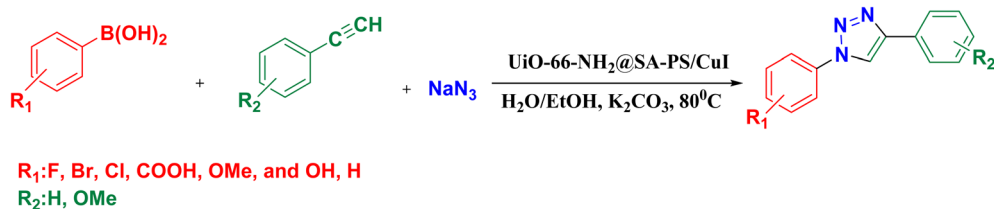
### 3.1 Catalyst activity

Optimization reactions were performed for the reaction of phenylboronic acid **1a**, sodium azide **2a**, and phenylacetylene



Scheme 2 Schematic pathway for the fabrication of  $\text{UiO-66-NH}_2/\text{SA-PS}/\text{CuI}$ .<sup>31</sup>





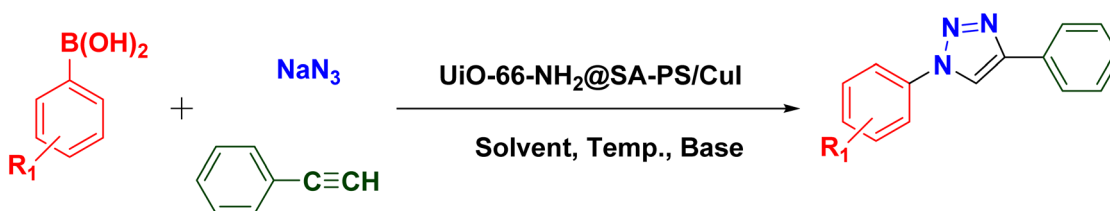
Scheme 3 Schematic pathway for the fabrication of 1,2,3-triazole using UiO-66-NH<sub>2</sub>@SA-PS/CuI nanocomposite.

**3a** to determine the best reaction conditions to yield 1,2,3-triazoles (Table 1) in K<sub>2</sub>CO<sub>3</sub>. UiO-66-NH<sub>2</sub>@SA-PS/CuI is essential for the abovementioned reaction. The best result was achieved when employing 10 mg of UiO-66-NH<sub>2</sub>@SA-PS/CuI catalyst (entry 3), which produced yields of 98%. Further increasing the catalyst dosage beyond 10 mg did not significantly elevate the product yields (entry 4). The reaction did not proceed in the absence of K<sub>2</sub>CO<sub>3</sub> (entry 5). In addition, we performed experiments to investigate different bases for the model reaction. Notably, K<sub>2</sub>CO<sub>3</sub> emerged as the most advantageous base, yielding both the highest output and the shortest reaction time when the model reaction was conducted. This highlights the critical role of base selection in optimizing reaction conditions for the click reaction (entries 6–8).

The choice of solvent significantly influenced the effectiveness of the click reaction, as evidenced by the varying yields

observed across different solvents, which are summarized in Table 1. The catalytic potential in a model reaction was studied using various organic solvents, including PEG, DMF/H<sub>2</sub>O, CH<sub>3</sub>CN/H<sub>2</sub>O, PEG/H<sub>2</sub>O, H<sub>2</sub>O/EtOH, ethanol and water (entries 9–15). When only PEG was employed, its high viscosity resulted in low solubility for the synthesized catalyst, which consequently led to a diminished yield (entry 9). In contrast, using only water allowed phenylboronic acid and the base to dissolve effectively; however, phenylacetylene remained insoluble, resulting in poor yields (entry 10). Conversely, while phenylacetylene dissolved well in ethanol (EtOH), the other components did not, leading to similarly low yields (entry 11). The results presented in Table 1 demonstrate that binary solvent systems are significantly more effective, as they enable the dissolution of all catalytic components (entries 12–14). The EtOH/H<sub>2</sub>O mixture was ultimately selected due to its high

Table 1 Model reaction optimization<sup>a</sup>



| Entry | Cat. (mol%) | Base (mmol)                          | Solvent                             | Yield <sup>b</sup> (%) |
|-------|-------------|--------------------------------------|-------------------------------------|------------------------|
| 1     | —           | K <sub>2</sub> CO <sub>3</sub> (1)   | H <sub>2</sub> O/EtOH               | N.R.                   |
| 2     | 0.32        | K <sub>2</sub> CO <sub>3</sub> (1)   | H <sub>2</sub> O/EtOH               | 85                     |
| 3     | 0.64        | K <sub>2</sub> CO <sub>3</sub> (1)   | H <sub>2</sub> O/EtOH               | 98                     |
| 4     | 0.96        | K <sub>2</sub> CO <sub>3</sub> (1)   | H <sub>2</sub> O/EtOH               | 98                     |
| 5     | 0.64        | —                                    | H <sub>2</sub> O/EtOH               | 55                     |
| 6     | 0.64        | KOH (1)                              | H <sub>2</sub> O/EtOH               | 42                     |
| 7     | 0.64        | Na <sub>2</sub> CO <sub>3</sub> (1)  | H <sub>2</sub> O/EtOH               | 39                     |
| 8     | 0.64        | Cs <sub>2</sub> CO <sub>3</sub> (1)  | H <sub>2</sub> O/EtOH               | 27                     |
| 9     | 0.64        | K <sub>2</sub> CO <sub>3</sub> (1)   | PEG                                 | 30                     |
| 10    | 0.64        | K <sub>2</sub> CO <sub>3</sub> (1)   | H <sub>2</sub> O                    | 10                     |
| 11    | 0.64        | K <sub>2</sub> CO <sub>3</sub> (1)   | EtOH                                | 40                     |
| 12    | 0.64        | K <sub>2</sub> CO <sub>3</sub> (1)   | DMF/H <sub>2</sub> O                | 59                     |
| 13    | 0.64        | K <sub>2</sub> CO <sub>3</sub> (1)   | CH <sub>3</sub> CN/H <sub>2</sub> O | 68                     |
| 14    | (0.64)      | K <sub>2</sub> CO <sub>3</sub> (1)   | PEG/H <sub>2</sub> O                | 72                     |
| 15    | 0.64        | K <sub>2</sub> CO <sub>3</sub> (1)   | H <sub>2</sub> O/EtOH               | 80 <sup>c</sup>        |
| 16    | 0.64        | K <sub>2</sub> CO <sub>3</sub> (2)   | H <sub>2</sub> O/EtOH               | 84                     |
| 17    | 0.64        | K <sub>2</sub> CO <sub>3</sub> (0.5) | H <sub>2</sub> O/EtOH               | 60                     |

<sup>a</sup> Reaction conditions: phenylboronic acid (1 mmol), NaN<sub>3</sub> (3 mmol), phenylacetylene (1 mmol), K<sub>2</sub>CO<sub>3</sub> (1 mmol), and UiO-66-NH<sub>2</sub>@SA-PS/CuI (0.64 mol%) in H<sub>2</sub>O/EtOH (1 : 1, 2 mL) for 90 min. <sup>b</sup> Isolated yield. <sup>c</sup> The reaction was performed at 80 °C.



**Table 2** Comparison efficiency of UiO-66-NH<sub>2</sub>@SA-PS/CuI with different catalysts

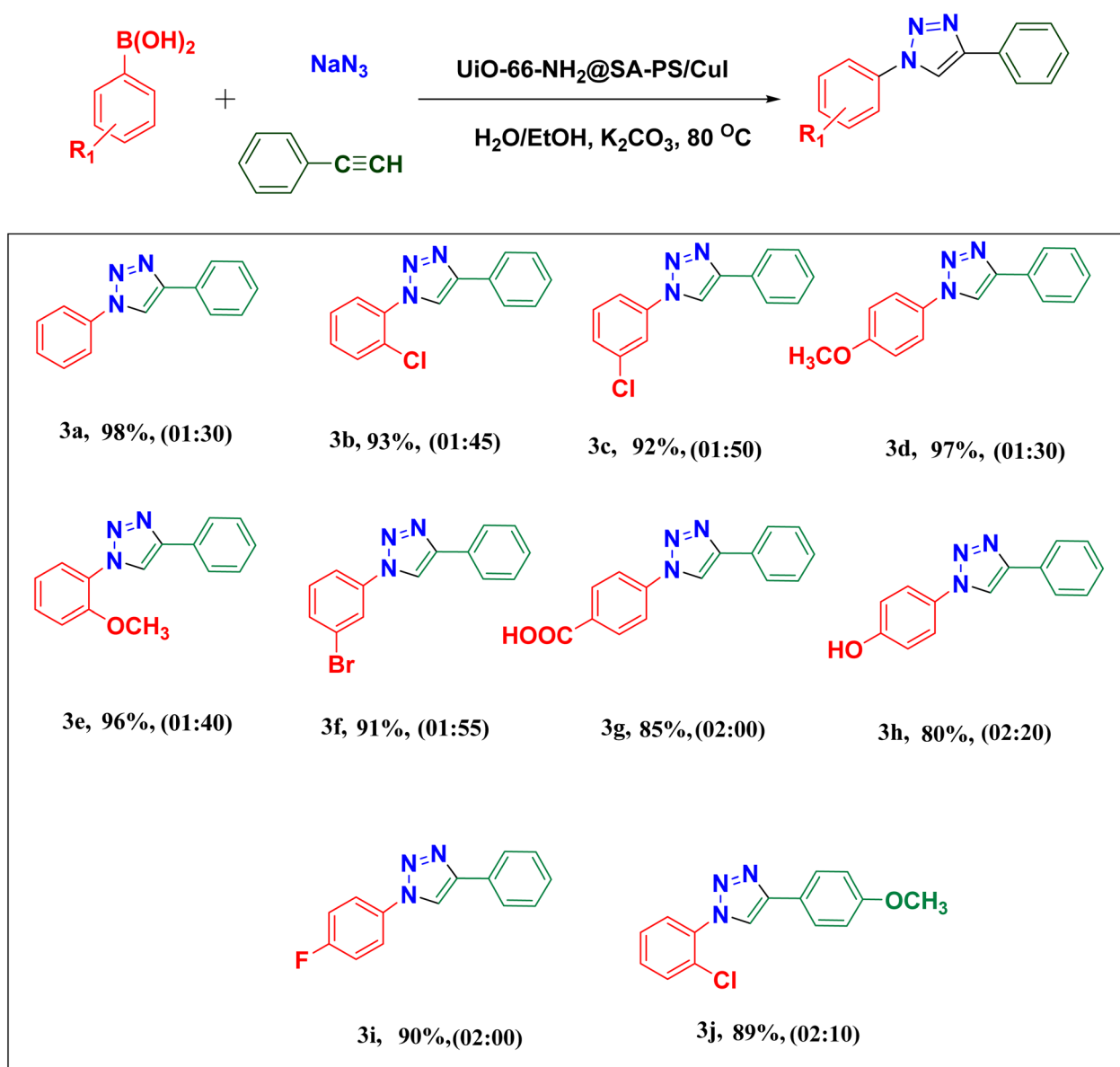
| Entry | Catalyst                                      | Base (mmol)                    | Yield (%) |
|-------|-----------------------------------------------|--------------------------------|-----------|
| 1     | UiO-66-NH <sub>2</sub> (10 mg)                | K <sub>2</sub> CO <sub>3</sub> | 40        |
| 2     | UiO-66-NH <sub>2</sub> @SA (10 mg)            | K <sub>2</sub> CO <sub>3</sub> | 48        |
| 3     | UiO-66-NH <sub>2</sub> @SA-PS (10 mg)         | K <sub>2</sub> CO <sub>3</sub> | 50        |
| 4     | CuI (10 mg)                                   | K <sub>2</sub> CO <sub>3</sub> | 60        |
| 5     | UiO-66-NH <sub>2</sub> @CuI (10 mg)           | K <sub>2</sub> CO <sub>3</sub> | 70        |
| 6     | UiO-66-NH <sub>2</sub> @SA-PS/CuI (0.64 mol%) | K <sub>2</sub> CO <sub>3</sub> | 98        |

catalytic activity and the fact that both solvents are environmentally friendly (entry 2). The evaluation of temperature indicated that 80 °C provides the highest yield (entries 15 vs. 2).

Ultimately, our results revealed that the optimal dosage of K<sub>2</sub>CO<sub>3</sub> catalyst for this reaction was 1 mol (entries 16–17).

Furthermore, the efficiency of the UiO-66-NH<sub>2</sub>@SA-PS/CuI catalyst was compared as shown in Table 2, entries 1–6. The results indicate that the high performance of the synthesized catalyst is related to synergistic effects of UiO-66-NH<sub>2</sub>, porous SA-PS, and CuI NPs (entry 6 vs. 1–5).

To investigate the generality of the copper-catalyzed alkyne-azide cycloaddition reaction, the scope and limitations of this method were investigated using 10 diverse phenylboronic acids. The one-pot reaction of different substituted aryl boronic acids in the presence of H<sub>2</sub>O/EtOH and K<sub>2</sub>CO<sub>3</sub> in MeOH using UiO-66-NH<sub>2</sub>@SA-PS/CuI at 80 °C gave 1,2,3-triazoles. In this catalytic

**Table 3** UiO-66-NH<sub>2</sub>@SA-PS/CuI-catalyzed CuAAC reactions based on the various boronic acids and alkynes<sup>a</sup>

<sup>a</sup> Reaction conditions: phenylboronic acid (1 mmol), NaN<sub>3</sub> (3 mmol), phenylacetylene (1 mmol), K<sub>2</sub>CO<sub>3</sub> (1 mmol) and UiO-66-NH<sub>2</sub>@SA-PS/CuI (0.64 mol%) in H<sub>2</sub>O/EtOH (1 : 1, 2 mL). Isolated yield.



system, the aryl boronic acids bearing either electron-donating or electron-withdrawing groups on the aromatic ring (F, Br, Cl, COOH, OMe, and OH) readily undergo the reaction to afford the corresponding products in good to excellent yields. As shown in Table 3, the presence of an electron-withdrawing substitute in phenylboronic acid extended the reaction time. A simple process to purify the products, without chromatographic purification, was achieved in this study.

Based on literature reports,<sup>32</sup> a plausible mechanism for one-pot CuAAC synthesis has been proposed (Scheme 3), wherein NaN<sub>3</sub> plays the role of azide precursor. Cu(I) species are prone to oxidation to Cu(II) due to their thermodynamic instability.<sup>9</sup> The reaction begins with a boronic acid derivative reacting with sodium azide (NaN<sub>3</sub>) to create an azide group. The UiO-66-NH<sub>2</sub>@SA-PS/CuI catalyst then coordinates with the terminal alkyne, forming a copper-acetylide complex A and releasing a proton (intermediate A). Subsequently, the azide group coordinates with the copper-acetylide complex, leading to a cycloaddition reaction between the azide and the alkyne to produce a triazole ring (intermediates B and C). Thirdly, rearrangement of intermediate C leads to the formation of the copper-metalated triazolide D and releases the catalytic Cu(I) species. Finally, the intermediate C captures a proton to produce the target triazole and regenerate the Cu(I) intermediate. In addition, UiO-66-NH<sub>2</sub>@SA-PS in this catalytic cycle serves as an efficient ligand to tune the activity of Cu(I) species on the catalyst (Scheme 4).<sup>33</sup>

Finally, for practical applications, the recycling of the catalyst was investigated using the model reaction. After completion of the reaction, the catalyst was conveniently and efficiently recovered from the reaction mixture by suction and then subjected to the next run directly without further treatment. As shown in Fig. 1, the catalyst can be reused consecutively at least seven times with comparatively little loss of its catalytic activity. The ICP-AES analysis showed that Cu content in the catalyst

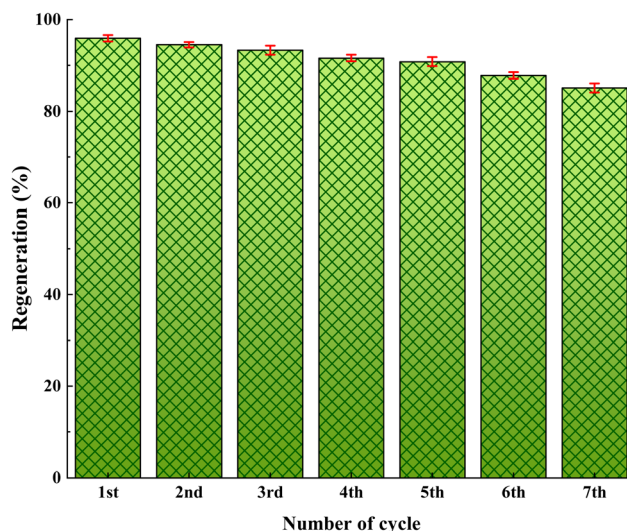
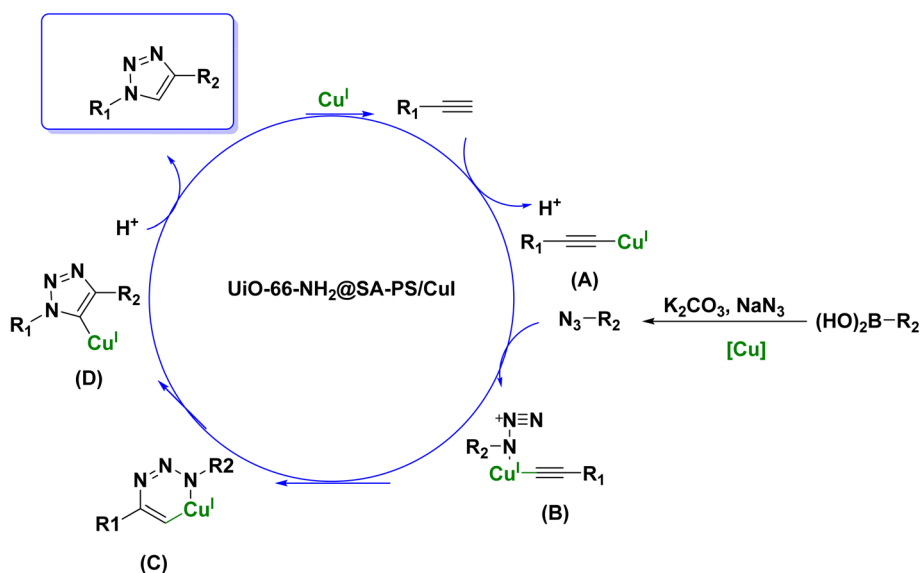


Fig. 1 Recyclability performance of UiO-66-NH<sub>2</sub>@SA-PS/CuI.

after the first run is 3.88%, which is slightly lower than the 4.064% Cu content in fresh catalyst. The slight decrease of the catalytic activity during recycling may be owing to the leaching of copper from the catalyst.

The findings from the click reaction conducted under different conditions are presented in Table 4. This investigation proposes UiO-66-NH<sub>2</sub>@SA-PS/CuI as an environmentally favorable nanocatalyst, leading to improved reaction conditions and enhanced performance (entry 7). The synergy of UiO-66-NH<sub>2</sub>, porous SA-PS and copper iodide nanoparticles shows higher efficiencies and superior catalyst utilization. The UiO-66-NH<sub>2</sub>@SA-PS/CuI catalyst exhibits high yields in short reaction times at mild temperature, with high loading of the catalyst, making performing the reaction effective with only a small amount of the catalyst. Moreover, the UiO-66-NH<sub>2</sub>@SA-PS/CuI



Scheme 4 Proposed mechanism for the UiO-66-NH<sub>2</sub>@SA-PS/CuI-catalyzed CuAAC reaction.



Table 4 Comparison studies

| Entry | Catalyst                                                              | Base                           | Solvent                | T (°C) | Time (h) | Yield (%) | Ref.      |
|-------|-----------------------------------------------------------------------|--------------------------------|------------------------|--------|----------|-----------|-----------|
| 1     | Cu(C <sub>4</sub> H <sub>3</sub> N(CHNCH <sub>3</sub> )) <sub>2</sub> | —                              | EtOH/H <sub>2</sub> O  | 30     | 11.5     | 96        | 34        |
| 2     | Cu-NHC@SiO <sub>2</sub>                                               | Sodium ascorbate               | Ethylene glycol        | 60     | 1        | 96        | 35        |
| 3     | Copper diacetate                                                      | —                              | H <sub>2</sub> O       | 20     | 1        | 94        | 36        |
| 4     | CuO-NiO                                                               | —                              | H <sub>2</sub> O       | 60     | 3        | 85        | 37        |
| 5     | Cu/PANI                                                               | —                              | Ethylene glycol        | 20     | 3        | 75        | 38        |
| 6     | Cu/Al <sub>2</sub> O <sub>3</sub>                                     | K <sub>2</sub> CO <sub>3</sub> | Ball-milling condition | 2      | 2        | 91        | 39        |
| 7     | UiO-66-NH <sub>2</sub> @SA-PS/CuI                                     | K <sub>2</sub> CO <sub>3</sub> | H <sub>2</sub> O/EtOH  | 80     | 0.64     | 98        | This Work |

catalyst is partly formed by sodium alginate and poly-sulfonamide as a non-toxic biopolymer, which makes the catalyst more biodegradable and environmentally friendly. Additionally, the UiO-66-NH<sub>2</sub>@SA-PS/CuI catalyst can be separated from the reaction mixture by centrifugation and easily reused seven times. This suggests that the current method may be a more ideal choice for achieving optimal results in the click reaction.

## 4. Conclusion

An efficient and environmentally friendly method was introduced for 1,4-disubstituted-1,2,3-triazole synthesis using utilizing UiO-66-NH<sub>2</sub>@SA-PS/CuI through click reactions. The easy process avoids the use of hazardous azides, with simple purification. It could be studied for other reactions to be applied for high-yield processes. The excellent activity of the catalyst has been ascribed to the coordination of sulfonamide groups with copper species. Moreover, there is no significant loss of catalytic activity when the catalyst is reused up to seven runs. Therefore, the high catalytic performance, reusability of catalyst, wide substrate scope, short reaction time, and mild conditions are the salient features of this green catalytic process, which make it more competitive for practical applications.

## Data availability

Data is provided within the manuscript or ESI.†

## Conflicts of interest

There are no conflicts to declare.

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