Silica-anchored Cu(I) aminothiophenol complex: An efficient heterogeneous catalyst for synthesis of 1,4-disubstituted 1,2,3-triazoles in water

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ABSTRACT

An efficient method has been developed for synthesis of 1,4-disubstituted 1,2,3-triazoles using the silica-anchored Cu(I) aminothiophenol complex [SiO$_2$-AT-Cu(I)] as a novel heterogeneous catalyst. The prepared catalyst is characterized by the FT-IR spectroscopy, and TGA, SEM, and ICP techniques. Terminal alkynes react with aroyl bromides and sodium azide in the presence of CuI anchored on silica in water at 80°C. The reactions exclusively generate the corresponding regiospecific 1,4-disubstituted 1,2,3-triazoles in good yields. The attractive features of this method are the simple procedure, clean reaction, use of a reusable catalyst, easy workup, and performing a click reaction in water. Moreover, the catalyst can be removed from the reaction mixture by means of simple filtration, and used again for up to five runs without a remarkable loss in its activity.

Keywords: 1,2,3-Triazole, Aroyl bromide, Silica-supported, Click reaction.

1. Introduction

1,2,3-Triazoles have attracted interests over the past few years as their moieties have been widely used in pharmaceuticals, agrochemicals, dyes, photographic materials, and corrosion inhibition. Moreover, 1,2,3-triazoles are important nitrogen heterocycles that display many interesting properties including the anti-bacterial [1], anti-allergic [2-4], anti-HIV [5], GSK-3 inhibiting [6], and anti-neoplastic activities [7].

Copper-catalyzed azide-alkyne cycloaddition (CuAAC), which is also known as the “click reaction”, has become one of the most significant reactions for the preparation of 1,2,3-triazoles [8, 9]. Sharpless et al. used Cu(I) salts to assist the reaction of sodium azide with terminal alkynes to yield 1,4-disubstituted products [10]. Other methods comprise the utilization of Cu(I) stabilizing ligands [11], giving rise to Cu(I) species from Cu nano-size powder [12] and copper nano-clusters [13]. In addition, in the recent years, some methods have been reported for the synthesis of triazoles [14-19]. But some of these methods suffer from long reaction times, expensive reagents, harsh reaction conditions, and use of large quantities of organic solvents, and thus considering the increase of the environmental and economic concerns in the recent years, it is now necessary for chemists to look for environmentally friendly reactions in natural conditions.

Most of the procedures reported for copper-catalyzed azide-alkyne cycloaddition (CuAAC) enjoy simple copper salts such as CuI or Cu(AcO)$_2$ as the catalyst. Although this simple procedure is feasible for many reactions, it has one major drawback, the separation of the catalyst from the reaction mixture is challenging. Thus heterogeneously-catalyzed procedures for this reaction are advantageous. Successful methods include immobilizing or supporting the active homogeneous catalysts on various inorganic supports such as activated carbon [20, 21], zeolites [22] immobilized on surface-modified silica [23], chitosan [24], and copper-supported catalysts on the silica [25-27] that assist in controlling reactivity and selectivity besides the advantage of easy workability.

Among the solvents usually used in organic synthesis, water is quite non-toxic, and the most economical, most abundant, safest, and most environmentally friendly medium. At intervals, water shows a higher reactivity and selectivity compared to the other conventional organic solvents because of its strong hydrogen-bonding potential. These characteristics allow water to act as a
catalyst, a solvent, or a reactant, which is unlike those shown by the conventional organic solvents [28]. In spite of the fact that a large number of CuAAC reactions go on either in organic solvents or in mixtures with water, only a small number of reactions have been reported to occur only in water [29-32]. Thus we investigated a straightforward one-pot synthesis of 1,4-disubstituted 1,2,3-triazoles from aryl bromides, sodium azide, and alkynes catalyzed by the silica-anchored Cu(I) aminothiophenole complex [SiO$_2$-AT-Cu(I)], as an efficient, recyclable, and non-toxic solid catalyst in water (Scheme 1).

2. Experimental

The reagents and solvents used were supplied from Merck, Fluka or Aldrich. Melting points were determined using an electro-thermal C14500 apparatus. The reaction progress and the purity of compounds were monitored using TLC analytical silica gel plates (Merck 60 F254). All the known compounds were identified by comparing their melting points and $^1$H NMR data with those in the authentic samples. The $^1$H NMR (300 MHz) and $^{13}$C NMR (75 MHz) spectroscopies were run on a Bruker Avance DPX-250 FT-NMR spectrometer. The chemical shift values were given as δ values against tetramethylsilane as the internal standard, and the J values were given in Hz. Microanalysis was performed on a Perkin-Elmer 240-B micro-analyzer. Thermo-gravimetric analysis (TGA) curves were recorded using a BAHR STA 503. Scanning electron microscopy (SEM) studies were conducted on a VEGA TESCAN instrument.

2.1. Preparation of new silica-anchored Cu(I) aminothiophenol complex [SiO$_2$-AT-Cu(I)]

2.1.1. Preparation of SiO$_2$-Cl

Silica (1.0 g) was stirred in 100 mL of 1.0 M NaOH at room temperature. Sodium silicate was filtered to remove the undissolved particles. Then 3-(chloropropyl)trimethoxysilane (2.0 mL) was added to the sodium silicate solution. The solution was titrated with nitric acid (3.0 M), and the titration was continued until the pH of the solution reached 3.0. The white gel obtained was separated by centrifugation, washed six times with distilled water and acetone, and dried at room temperature to afford SiO$_2$-Cl as a white powder [33].

2.1.2. Preparation of aminothiophenol functionalized SiO$_2$ (SiO$_2$-AT)

SiO$_2$-Cl (1.00 g) was refluxed with 2-aminothiophenol (4.0 mmol, 0.5 g) in ethanol (20.0 mL) for 24 h in order to replace the terminal chlorine atoms. Then benzaldehyde (4 mmol, 0.4 mL) was added and the mixture was refluxed for 24 h. Finally, SiO$_2$-AT was filtered-off, washed three times with ethanol, and dried at 100 ºC. Elementary analysis showed that the carbon content of SiO$_2$-Cl was 4.2%, which meant that 0.86 mmol/g of pending groups were covalently bonded to the surface of 1.00 g SiO$_2$. Elementary analysis showed that the nitrogen content was 0.32% (0.23 mmol/g), which revealed that the AT loading, around 0.23 mmol/g or near 27% of pending chlorine atom, was changed to AT by this reaction.

2.1.3. Loading with CuI

SiO$_2$-AT (1.00 g) was mixed with CuI (0.07 g, 1.1 mmol) in ethanol (5 mL). The mixture was refluxed for 18 h under an Ar atmosphere. Then it was filtered, and the solid obtained was washed with ethanol and dried at 100 ºC overnight to give SiO$_2$-AT-Cu(I). The copper loading of SiO$_2$-AT-Cu(I) was 0.13% (0.02 mmol g$^{-1}$), determined by the inductively coupled plasma (ICP) technique.

2.2. General procedure for synthesis of 1,4-disubstituted 1,2,3-triazoles (4a-k)

A round-bottom flask was charged with aryl bromide (1.0 mmol), NaN$_3$ (1.2 mmol, 0.08 g), a terminal alkyne (1.0 mmol), SiO$_2$-AT-Cu(I) (0.1 g, 0.002 mmol of Cu), and water (3.0 mL). The mixture was stirred at 80 ºC. Upon completion of the reaction (monitored by TLC), the precipitate formed was washed with warm ethanol (3 × 20 mL) in order to separate the heterogeneous catalyst. The residue was finally purified by crystallization from ethanol to give the desired product (Table 2).

Scheme 1. Synthesis of 1,4-disubstituted 1,2,3-triazoles catalyzed by [SiO$_2$-AT-Cu(I)].
Selected spectral data

1- (4- bromophenyl)-2- (4-phenyl-1H-1,2,3-triazol-1-yl) ethanone (4c):

FT-IR (KBr): $\tilde{\nu} = 3152, 2950, 1700$ (C=O), $1462-1575$ (C=C) cm$^{-1}$. $^1$HNMR (CDCl$_3$, 300 MHz): $\delta = 5.88$ (s, 2H, CH$_2$), 7.37-7.40 (t, 1H, H-Ar), 7.44-7.49 (t, 2H, H-Ar), 7.71-7.74 (d, 2H, H-Ar), 7.87-7.93 (m, 4H, H-Ar), 7.96 (s, 1H, CH of triazole) ppm.

Anal. Calcd. for C$_{16}$H$_{12}$BrN$_3$O: C, 56.16; H, 3.53; N, 12.28; Found: C, 56.34; H, 3.65; N, 12.12.

2- (4- (hydroxymethyl)- 1H- 1,2,3- triazol- 1- yl)- 1- (4-nitrophenyl) ethanone (4e):

FT-IR (KBr): $\tilde{\nu} = 3360$ (OH), 3100, 2910, 1690 (C=O), 1530 (C=C) cm$^{-1}$. $^1$HNMR (CD$_3$COCD$_3$, 300 MHz): $\delta = 4.20$ (s, 1H, OH), 4.59 (s, 2H, CH$_2$), 6.12 (s, 2H, CH$_2$), 7.79 (s, 1H, CH of triazole), 8.2-8.3 (m, 4H, H-Ar) ppm. $^{13}$CNMR (CD$_3$COCD$_3$, 75 MHz): $\delta = 55.9, 67.1, 123.5, 123.9, 129.4, 129.5, 139.1, 148.5, 150.9, 191.0$ ppm; Anal. Calcd. for C$_{11}$H$_{10}$N$_4$O$_4$: C, 50.38; H, 3.84; N, 21.37; Found: C, 50.52; H, 3.65; N, 21.51.

2- (4- (1-hydroxyethyl)- 1H- 1,2,3- triazol- 1- yl)- 1- phenylethanone (4g):

FT-IR (KBr): $\tilde{\nu} = 3200$ (OH), 3110, 2920, 1690 (C=O), 1440-1580 (C=C) cm$^{-1}$. $^1$HNMR (CD$_3$COCD$_3$, 300 MHz): $\delta = 1.53$ (d, 3H, CH$_3$), 4.44 (s, 1H, OH), 5.01-5.07 (q, 1H, CH), 6.13 (s, 2H, CH$_2$), 7.60-7.65 (t, 2H, H-Ar), 7.72-7.77 (t, 1H, H-Ar), 7.86 (s, 1H, CH of triazole), 8.12-8.15 (d, 2H, H-Ar) ppm. $^{13}$CNMR (CD$_3$COCD$_3$, 75 MHz): $\delta = 23.1, 55.5, 62.6, 122.4, 128.1, 128.9, 134, 134.6, 152.9, 191.5$ ppm. Anal. Calcd. for C$_{12}$H$_{13}$N$_3$O$_2$: C, 62.33; H, 5.67; N, 18.17; Found: C, 62.17; H, 5.57; N, 18.34.

2-(4-(2-hydroxypropan-2- yl)- 1H- 1,2,3- triazol-1- yl)-1-phenylethanone (4i):

FT-IR (KBr): $\tilde{\nu} = 3310$ (OH), 3056, 2990, 1690 (C=O), 1450-1540 (C=C) cm$^{-1}$. $^1$HNMR (CDCl$_3$, 300 MHz): $\delta = 1.56$ (s, 6H, CH$_3$), 2.3 (s, 1H, OH), 5.74 (s, 2H, CH$_2$), 7.40-7.45 (t, 2H, H-Ar), 7.54-7.59 (t, 2H, CH-Ar, CH of triazole), 7.86-7.89 (d, 2H, H-Ar) ppm. Anal. Calcd. for C$_{13}$H$_{15}$N$_3$O$_2$: C, 63.66; H, 6.16; N, 17.13; Found: C, 63.48; H, 6.07; N, 17.30.

2- (4- (2- hydroxypropyl)- 1H-1,2,3- triazol-1-yl)- 1-(4-nitrophenyl)ethanone (4j):

FT-IR (KBr): $\tilde{\nu} = 3380$ (OH), 3056, 2995, 1700 (C=O), 1530 (C=C) cm$^{-1}$. $^1$HNMR (CDCl$_3$, 300 MHz): $\delta = 1.71$ (s, 6H, CH$_3$), 2.2 (s, 1H, OH), 5.91 (s, 2H, CH$_2$), 7.66 (s, 1H, CH of triazole), 8.20-8.23 (d, 2H, H-Ar), 8.41-8.44 (d, 2H, H-Ar) ppm. Anal. Calcd. for C$_{13}$H$_{14}$N$_4$O$_4$: C, 53.79; H, 4.86; N, 19.30; Found: C, 53.60; H, 4.77; N, 19.47.

3.3. Catalyst recycling

To recover the catalyst, the separated catalyst was washed twice with warm ethanol (5 mL) and reused after drying.

3. Results and Discussion

3.1. Catalyst preparation

SiO$_2$-AT-Cu(I) was synthesized as shown in Scheme 2, wherein the first step was the synthesis of silica-bonded n-propylchloride according to an earlier report [42]. The second step was the pending chlorine atoms of SiO$_2$-Cl changing to AT by refluxing with 2-AT in ethanol to afford SiO$_2$-AT. Finally, SiO$_2$-AT and CuI were refluxed in ethanol to generate SiO$_2$-AT-Cu(I). The catalyst produced was characterized by FT-IR spectroscopy and the TGA, SEM, and ICP techniques.

3.2. Catalyst characterization

The FT-IR spectra for SiO$_2$ (a), SiO$_2$-Cl (b), and SiO$_2$- AT-Cu(I) (c) are showed in Fig. 1. A broad band was observed in the range of 3400-3300 cm$^{-1}$ in all samples, this band was attributed to the $\tilde{\nu}$ (O-H) stretching of their surface hydroxyl groups. Also the IR spectrum for SiO$_2$ showed major adsorption bands at 1168, 810, and 478 cm$^{-1}$ (Fig. 1a). Moreover, the characteristic band for SiO$_2$ was observed in 1168, it was attributed to the stretching vibrations of its Si-O-Si group. Also low-intensity bands which could be observed at 810 and 478 cm$^{-1}$, were due to the bending vibrations of the Si-O-Si group (Fig. 1a).

The morphology of the SiO$_2$ and SiO$_2$-AT-Cu(I) samples was also investigated by SEM (Fig. 2). It can easily be seen in Fig. 2 that the SiO$_2$ beads have different sizes and roughness. The presence of copper was demonstrated by the change in the particle size and roughness of the surface.

Fig. 3 shows the TG/DTG thermogram for the [SiO$_2$-AT-Cu(I)] catalyst. There is an important weight loss region in the TG curve in the temperature range of 340-400 °C, accompanied by an endothermic peak in the DTG curve, which could be related to the decomposition of the organic residue on the surface of SiO$_2$. 

Scheme 2. Preparation of [SiO₂-AT-Cu(I)].

Fig. 1. FT-IR spectra for SiO₂ (a), SiO₂-Cl (b), and SiO₂-AT-Cu(I) (c).
The last weight loss was observed in the temperature range of 450-500°C, accompanied by another endothermic peak in the DTA curve, which could be related to dehydroxylation of SiO2.

3.3. Catalytic Activity

Preliminary experiments were performed using the reaction of phenacyl bromide with sodium azide and phenylacetylene, as a model reaction, in the presence of SiO2-AT-Cu(I). The reactions were performed using various solvents such as ethanol, methanol, H2O, CH3CN, 1,4-dioxan, THF, DMF, acetone, CH2Cl2, toluene, and CCl4, and in solvent-free conditions. The results obtained are summarized in Table 1. As it can be seen in this table, the highest reaction yield was obtained when H2O was used as the solvent (Table 1, entry 3). To our surprise, the reaction gave lower yields when the reaction was performed under solvent-free conditions (Table 1, entry 12). The conditions with respect to the amount of catalyst were optimized, as shown in Table 1.
Table 1. Optimization of reaction conditions for synthesis of 1-phenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethanone 4a.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Catalyst (mol%)</th>
<th>Temp. (ºC)</th>
<th>Time (h)</th>
<th>Yieldb (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>EtOH</td>
<td>0.2</td>
<td>Reflux</td>
<td>2</td>
<td>83</td>
</tr>
<tr>
<td>2</td>
<td>MeOH</td>
<td>0.2</td>
<td>Reflux</td>
<td>2</td>
<td>81</td>
</tr>
<tr>
<td>3</td>
<td>H2O</td>
<td>0.2</td>
<td>80</td>
<td>2</td>
<td>96</td>
</tr>
<tr>
<td>4</td>
<td>CH3CN</td>
<td>0.2</td>
<td>Reflux</td>
<td>3</td>
<td>66</td>
</tr>
<tr>
<td>5</td>
<td>1,4-dioxan</td>
<td>0.2</td>
<td>Reflux</td>
<td>3</td>
<td>39</td>
</tr>
<tr>
<td>6</td>
<td>THF</td>
<td>0.2</td>
<td>Reflux</td>
<td>4</td>
<td>41</td>
</tr>
<tr>
<td>7</td>
<td>DMF</td>
<td>0.2</td>
<td>80</td>
<td>3</td>
<td>78</td>
</tr>
<tr>
<td>8</td>
<td>Acetone</td>
<td>0.2</td>
<td>Reflux</td>
<td>3</td>
<td>80</td>
</tr>
<tr>
<td>9</td>
<td>CH2Cl2</td>
<td>0.2</td>
<td>Reflux</td>
<td>4</td>
<td>47</td>
</tr>
<tr>
<td>10</td>
<td>Toluene</td>
<td>0.2</td>
<td>80</td>
<td>3</td>
<td>40</td>
</tr>
<tr>
<td>11</td>
<td>CCl4</td>
<td>0.2</td>
<td>Reflux</td>
<td>4</td>
<td>42</td>
</tr>
<tr>
<td>12</td>
<td>Solvent-free</td>
<td>0.2</td>
<td>80</td>
<td>2</td>
<td>25</td>
</tr>
<tr>
<td>13</td>
<td>H2O</td>
<td>0.4</td>
<td>80</td>
<td>2</td>
<td>96</td>
</tr>
<tr>
<td>14</td>
<td>H2O</td>
<td>0.1</td>
<td>80</td>
<td>3</td>
<td>80</td>
</tr>
<tr>
<td>15</td>
<td>H2O</td>
<td>No catalyst</td>
<td>80</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>16</td>
<td>H2O</td>
<td>CuI/SiO2 (0.2)</td>
<td>80</td>
<td>4</td>
<td>77</td>
</tr>
<tr>
<td>17</td>
<td>H2O</td>
<td>0.2</td>
<td>r.t</td>
<td>5</td>
<td>43</td>
</tr>
<tr>
<td>18</td>
<td>H2O</td>
<td>0.2</td>
<td>Reflux</td>
<td>2</td>
<td>95</td>
</tr>
</tbody>
</table>

*aReaction conditions: phenacylbromide (1.0 mmol), phenylacetylene (1.0 mmol), sodium azide (1.2 mmol), catalyst, solvent (3 mL).

*bIsolated yield.

It was found that 0.1 g of [SiO2-AT-Cu(I)] (0.002 mmol CuI) was the optimum condition (Table 1, entry 3). Increasing the amount of catalyst did not increase the yield (Table 1, entry 13). A low concentration of Cu(I) resulted in a decreased yield (Table 1, entry 14). Moreover, when the reaction was carried out in the absence of a catalyst, only a trace amount of the desired product 4a was obtained, even after the reaction time was prolonged to 5 h (Table 1, entry 15), while a moderate yield was observed using CuI with SiO2 (entry 16). Also the effect of temperature on the reaction yield was checked, and the results obtained were tabulated in Table 1. It is obvious that at room temperature, a low yield was obtained (Table 1, entry 17). Increasing the temperature did not improve the reaction yield (Table 1, entry 18).

Under the optimized reaction conditions, the scope of the reaction was explored with various aroyl bromides 1 and alkynes 2. As shown in Table 2, The substituents of the aroyl bromides did not have a clear steric effect on the reaction.

The copper-catalyzed click reaction mechanism comprises the multi-general steps shown in Scheme 3: a) formation of copper(I) acetylide A; b) the first C–N bond formation affords the six-membered ring copper metallacycle B; c) cyclization takes place to yield the copper triazole intermediate C; d) proteolysis of the Cu-C bond gives the triazole product, and regenerates the catalyst.

3.4. Catalyst reusability

The reusability of a catalyst is one of the most significant advantages, and makes it useful for industrial and commercial applications.
Table 2. Synthesis of 1,4-disubstituted 1,2,3-triazoles catalyzed by SiO$_2$-AT-Cu(I)\textsuperscript{a}.

\[
\begin{array}{cccccccc}
\text{Entry} & \text{Aroyl bromide} & \text{Alkyne} & \text{Time (h)} & \text{Product No.} & \text{Product} & \text{Yield}\textsuperscript{b} & \text{m.p. (ºC)} & \text{Ref.} \\
1 & \text{OCH$_3$} & \text{H} & 2 & 4a & \text{OCH$_3$} & \text{96} & 167-169 & 169-171 [34] \\
2 & \text{O$_2$N} & \text{H} & 3 & 4b & \text{O$_2$N} & \text{91} & 183-185 & 184-186 [34] \\
3 & \text{Ph} & \text{H} & 3 & 4c & \text{Ph} & \text{96} & 177-179 & 178-180 [35] \\
4 & \text{Ph} & \text{OH} & 2 & 4d & \text{Ph} & \text{92} & 120-122 & 122-124 [34] \\
5 & \text{O$_2$N} & \text{OH} & 3 & 4e & \text{O$_2$N} & \text{98} & 143-145 & - This work \\
6 & \text{Ph} & \text{OH} & 3 & 4f & \text{Ph} & \text{86} & 157-159 & 159-160 [34] \\
7 & \text{Ph} & \text{OH} & 2 & 4g & \text{Ph} & \text{94} & 127-129 & - This work \\
8 & \text{Ph} & \text{OH} & 3 & 4h & \text{Ph} & \text{83} & 106-108 & 108-110 [36] \\
9 & \text{Ph} & \text{HO} & 2 & 4i & \text{Ph} & \text{90} & 96-98 & - This work \\
10 & \text{O$_2$N} & \text{HO} & 3 & 4j & \text{O$_2$N} & \text{97} & 126-128 & - This work \\
11 & \text{Ph} & \text{HO} & 4 & 4k & \text{Ph} & \text{76} & 167-169 & 168-170 [35] \\
\end{array}
\]

\textsuperscript{a}Reaction conditions: Aroyl bromide (1.0 mmol), alkyne (1.0 mmol), sodium azide (1.2 mmol), catalyst (0.2 mol\%), H$_2$O (3 mL), 80 ºC.

\textsuperscript{b}Isolated yield.
Thus the reusability of the SiO$_2$-AT-Cu(I) catalyst was investigated for the reaction between phenacylbromide, phenylacetylene, sodium azide, and the catalyst in water at 80 °C. The catalyst was recovered by a simple filtration and reused over 5 runs (The yields were 96, 95, 93, 91 and 89 %, respectively) with some decrease in the catalytic activity of the catalyst.

To show the advantages of SiO$_2$-AT-Cu(I) as a heterogeneous catalyst in this reaction, our results and reaction conditions for the synthesis of 1-phenyl-2-(4-phenyl-[1,2,3]triazol-1-yl) ethanone 4a were compared with those of this reaction using the heterogeneous catalysis in previous times (Table 3). The results obtained show that our proposed catalyst is quite comparable with those for the heterogeneous catalyst used regarding the yields.

4. Conclusions

We have demonstrated an environmentally friendly method for the synthesis of 1,4-disubstituted 1,2,3-triazoles using SiO$_2$-AT-Cu(I) as an efficient, new and reusable catalyst. This method offers several advantages such as a shorter reaction time, cleaner reaction, reusability of the catalyst, and high reaction yield. Moreover, this innovative heterogeneous catalyst could be easily separated and reused for at least 5 repeated cycles without a considerable loss in its catalytic activity.

Acknowledgments

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References


Table 3. Synthesis of 1,2,3-triazol 4a using different catalysts and reaction conditions.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>Time (min)</th>
<th>Temp. (°C)</th>
<th>Yield (%)</th>
<th>Ref.</th>
</tr>
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<tr>
<td>1</td>
<td>PEG-400, Cul</td>
<td>water</td>
<td>120</td>
<td>r.t.</td>
<td>74</td>
<td>[37]</td>
</tr>
<tr>
<td>2</td>
<td>P4VPy-Cul</td>
<td>water</td>
<td>25</td>
<td>Reflux</td>
<td>89</td>
<td>[38]</td>
</tr>
<tr>
<td>3</td>
<td>Cul/AK</td>
<td>water</td>
<td>20</td>
<td>Reflux</td>
<td>84</td>
<td>[39]</td>
</tr>
<tr>
<td>4</td>
<td>Amberlyst-supported Cul</td>
<td>CH$_3$CN</td>
<td>60</td>
<td>Reflux</td>
<td>89</td>
<td>[40]</td>
</tr>
<tr>
<td>5</td>
<td>Nano-Fe$_3$O$_4$@TiO$_2$/Cu$_2$O</td>
<td>water</td>
<td>20</td>
<td>Reflux</td>
<td>89</td>
<td>[41]</td>
</tr>
<tr>
<td>6</td>
<td>Cu/Cu(OTF)$_2$</td>
<td>H$_2$O/CH$_3$CN</td>
<td>180</td>
<td>r.t.</td>
<td>91</td>
<td>[35]</td>
</tr>
<tr>
<td>7</td>
<td>SiO$_2$-AT-Cu(I)</td>
<td>Water</td>
<td>120</td>
<td>80</td>
<td>96</td>
<td>This work</td>
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</table>