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# Preparation of $Cu(OAc)_2$/MCM-41 Catalyst and Its Application in the One-Pot Synthesis of 1,2,3-Triazoles in Water

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ABSTRACT: *An efficient one-pot synthesis of 1,2,3-triazoles via the three-component coupling reaction between benzyl or alkyl bromides, terminal alkynes, and sodium azide in the presence of catalytic amounts of $Cu(OAc)_2$/MCM-41 catalyst has been described. This catalyst showed high catalytic activity and 1,4-regioselectivity for the [3 + 2]Huisgen cycloaddition. This method avoids isolation and handling of organic azides, using water as a solvent, and catalyst recycling makes this synthesis a truly green procedure.* © 2012 Wiley Periodicals, Inc. Heteroatom Chem 00:1–7, 2012; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21031

## *INTRODUCTION*

*N*-Heterocyclic compounds such as 1,2,3-triazoles have shown important biological activities, and numerous examples are reported in the literature including anti-HIV activity [1,2], antibacterial activity [3], antiallergic activity [4], and selective $\beta_3$ adrenergic receptor agonism [5]. 1,2,3-Triazoles have also a range of important applications in industries such as dyes, corrosion inhibition, photostabilizers, photographic materials, and agrochemicals [6]. Recently, copper catalysts have been reported for the construction of 1,2,3-triazoles. The "click" chemistry reported by the Sharpless group described that the Cu(I)-catalyzed cycloaddition can be conducted at room temperature and results in 1,4-disubstituted triazoles in high regioselectivity [7]. The required copper(I) catalysts are usually prepared by in situ reduction of copper(II) salts with ascorbate [8], or by comproportionation of copper(0) and copper(II) [9].

The search for alternative cleaner, safer, and environmentally friendly technologies is one of the priorities in chemistry. With this objective, the reduction of wastes, environmentally friendly reagents, and catalysts are important parameters to achieve more sustainable processes [10,11].

Reusable heterogeneous catalysts have attracted a great deal of interest in recent years [12]. Since most of the catalysts are expensive and contaminate the environment, the development of efficient methods for recovery and reuse of the catalysts is a very important aspect in this chemistry. Among various solid supports, silica is usually preferred. With the discovery of the MCM-41-type materials [13], new possibilities for the development of better catalysts supported on siliceous materials have become available [14]. These materials have a high surface area ($\sim 1000\ m^2\ g^{-1}$), a large pore volume, and an ordered hexagonal pore array with pore diameters that can be tuned between 20 and 100 Å.

Here we wish to report an efficient, safe, and green one-pot synthesis of 1,4-disubstituted

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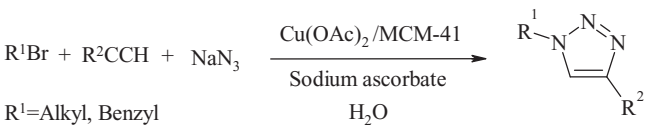



**SCHEME 1**

1,2,3-triazoles from benzyl and alkyl bromides, sodium azide, and alkynes catalyzed by MCM-41-supported copper(II) (Scheme 1). The reactions were carried out in water as a green, nontoxic, and nonflammable solvent, which is recently used as a medium for organic reactions with almost all reaction types explored [15].

## *RESULTS AND DISCUSSION*

The MCM-41-supported copper(II) was readily prepared in two steps. First, MCM-41 was prepared according to our previously published procedure [16]. Then, it was treated with copper(II) acetate in ethanol at 35°C for 8 h to generate the $Cu(OAc)_2$/MCM-41 catalyst.

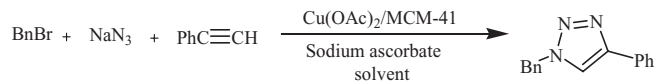
For our initial screening experiments, the 1,3-dipolar cycloaddition reaction between benzyl bromide, sodium azide, and phenylacetylene in a 1:1.1:1 molar ratio was chosen as the model reaction (Table 1).

The reaction was carried out simply by mixing alkyne, benzyl, and alkyl bromides and sodium azide in the presence of a catalytic amount of $Cu(OAc)_2$/MCM-41 (0.04 g). The mixture was catalyzed by the copper(I) catalyst in water, stirring at room temperature and 90°C for 1 h and 15 min, and 1-benzyl-4-phenyl-1*H*-1,2,3-triazole was obtained in 95% and 98% yield, respectively (Table 1, entries 1–2). Further increasing the amount of catalyst did not improve the yield and the reaction time (Table 1, entry 3). The optimum amount of catalyst was 0.04 g as shown in Table 1 (entries 4–5). When benzyl bromide, sodium azide, and phenylacetylene were reacted under similar conditions in the absence of the catalyst, no product was observed after 24 h (Table 1, entry 6). During the course of further optimization of the reaction conditions, various polar and apolar or poorly polar solvents were examined and it was found that the solvent plays a significant role in terms of the reaction rate and isolated yield (Table 1, entries 7–11). As recently reported by other groups [17], apolar solvents did not allow for any transformation (Table 1, entries 10–11). Under the same condition, acetonitrile gave only very low yield of the expected product, whereas the more polar DMF gave the product in moderate yield (Table 1, entries 7–9). Water proved to be the solvent of choice with its fast reaction rate, high yield, cheapness, "green" solvent nature, and environmental acceptability.

To show the generality of this method, we studied the reaction of benzyl and alkyl bromide with a variety of terminal alkynes in the presence of sodium azide under optimum conditions and the results are presented in Table 2.

As can be seen from Table 2, all reactions were highly regioselective toward the 1,4-disubstituted triazoles and afforded the desired products nearly in quantitative yields in most cases. For example,

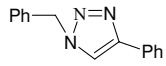
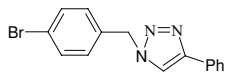
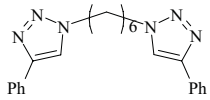
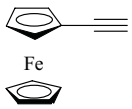
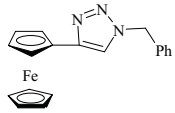
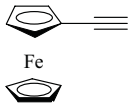
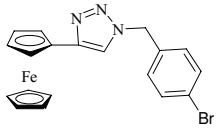
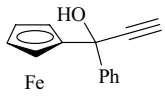
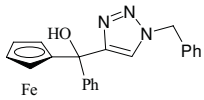
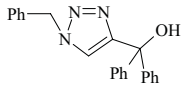
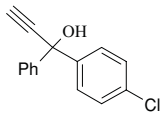
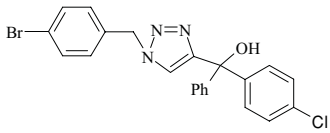
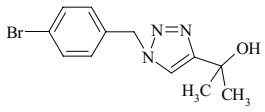
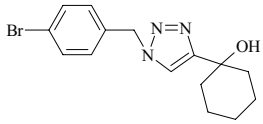
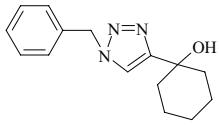
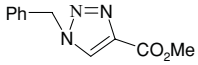
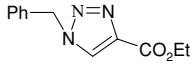
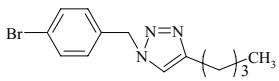
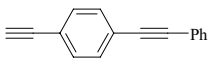
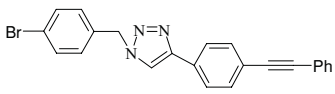
**TABLE 1** Effect of Solvent, Temperature, and Amount of the Catalyst on the One-Pot Synthesis of 1-Benzyl-4-phenyl-1*H*-1,2,3-triazole[a]




| *Entry* | *Catalyst (g)* | *Solvent/Temperature (°C)* | *Time (h)* | *Yield (%)[b]* |
|---|---|---|---|---|
| 1 | $Cu(OAc)_2$/MCM-41 (0.04 g) | $H_2O$/25 | 1 | 95 |
| 2 | $Cu(OAc)_2$/MCM-41 (0.04 g) | $H_2O$/90 | 0.25 | 98 |
| 3 | $Cu(OAc)_2$/MCM-41 (0.05 g) | $H_2O$/90 | 0.25 | 98 |
| 4 | $Cu(OAc)_2$/MCM-41 (0.03 g) | $H_2O$/90 | 0.25 | 75 |
| 5 | $Cu(OAc)_2$/MCM-41 (0.02 g) | $H_2O$/90 | 0.25 | 60 |
| 6 | No catalyst | $H_2O$/90 | 24 | – |
| 7 | $Cu(OAc)_2$/MCM-41 (0.04 g) | DMF/25 | 2 | 25 |
| 8 | $Cu(OAc)_2$/MCM-41 (0.04 g) | DMF/90 | 2 | 40 |
| 9 | $Cu(OAc)_2$/MCM-41 (0.04 g) | $CH_3CN$/25 | 24 | 10 |
| 10 | $Cu(OAc)_2$/MCM-41 (0.04 g) | EtOAc/25 | 24 | – |
| 11 | $Cu(OAc)_2$/MCM-41 (0.04 g) | Toluene/25 | 24 | – |

[a]Reagents and conditions: BnBr (1 mmol), PhC≡CH (1 mmol), $NaN_3$ (1.1 mmol), sodium ascorbate (45 mol%, 0.09 g) and catalyst.
[b]Isolated yield.

**TABLE 2** One-Pot Synthesis of 1,4-Disubstituted 1,2,3-Triazoles from Benzyl or Alkyl Halides, Sodium Azide, and Alkynes[a]

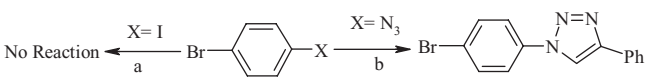
| *Entry* | *Halide* | *Alkyne* | *Product*[b] | *Time (h)* | *Yield (%)*[c] |
|---|---|---|---|---|---|
| 1 | $PhCH_2Br$ | $PhC{\equiv}CH$ |  | 0.25 | 98 |
| 2 | $4\text{-}BrPhCH_2Br$ | $PhC{\equiv}CH$ |  | 0.33 | 98 |
| 3 | $Br(CH_2)_6Br$ | $PhC{\equiv}CH$ |  | 2 | 95 |
| 4 | $PhCH_2Br$ |  |  | 1.25 | 98 |
| 5 | $4\text{-}BrPhCH_2Br$ |  |  | 1.5 | 95 |
| 6 | $PhCH_2Br$ |  |  | 0.5 | 93 |
| 7 | $PhCH_2Br$ |  |  | 0.5 | 98 |
| 8 | $4\text{-}BrPhCH_2Br$ |  |  | 0.75 | 98 |
| 9 | $4\text{-}BrPhCH_2Br$ |  |  | 1.17 | 98 |
| 10 | $4\text{-}BrPhCH_2Br$ |  |  | 0.33 | 95 |
| 11 | $PhCH_2Br$ |  |  | 0.33 | 95 |
| 12 | $PhCH_2Br$ | $MeO_2CC{\equiv}CH$ |  | 0.25 | 83 |
| 13 | $PhCH_2Br$ | $EtO_2CC{\equiv}CH$ |  | 0.33 | 80 |
| 14 | $4\text{-}BrPhCH_2Br$ | $CH_3(CH_2)_3C{\equiv}CH$ |  | 7 | 70 |
| 15 | $4\text{-}BrPhCH_2Br$ |  |  | 12 | 89 |

[a]Reagents and conditions: alkyl or benzyl bromide (1 mmol), terminal alkyne (1 mmol), $NaN_3$ (1.1 mmol), and sodium ascorbate (45 mol%, 0.090 g) catalyzed by $Cu(OAC)_2$/MCM-41 (0.04 g) in water at 90°C.
[b]All products were characterized by spectroscopic data, physical properties, and by comparison with authentic samples.
[c]Yields refer to pure isolated products.

when phenylacetylene reacted with benzyl- and 4-bromobenzyl azides under optimum reaction conditions, the corresponding triazoles were obtained in 98% yields (Table 2, entries 1–2). The reaction of phenylacetylene with dibromohexane gave bistriazole in excellent yield (Table 2, entry 3). We have examined the reaction of terminal acetylene containing a ferrocenyl moiety with benzyl bromides, which also resulted in the corresponding triazoles in very good yields but in longer reaction times (Table 3, entries 4–5). The results presented in Table 2 show that the method can be successfully used for the reaction of benzyl azides and a variety of propargyl alcohols carrying either aryl substituents (entries 6–8) or alkyl substituents (entries 9–11). Notably, methyl and ethyl carboxylate substituted triazoles were also smoothly obtained in good yields (Table 2, entries 12–13). Moreover, alkylacetylene (1-hexyne) gave the corresponding 1,2,3-triazole in moderate yield (Table 2, entry 14). The reaction of 4-bromobenzyl bromide with alkyne containing a terminal and internal acetylene moiety showed that this method is highly selective toward terminal alkyne (Table 2, entry 15).

The reaction of aryl halide (4-bromoiodobenzene) with phenylacetylene was also examined under optimum conditions, but no product was formed. But, when 4-bromophenyl azide reacted with phenylacetylene, the corresponding triazole was formed in good yield after 15 h (Scheme 2). These results suggest that an aryl azide cannot be generated in situ from aryl halide under this condition.

A good feature of this catalyst is that it can be recovered and reused several times without loss of activity. The recyclability of the $Cu(OAc)_2$/MCM-41 catalyst was examined in the reaction of benzyl bromide, phenylacetylene, and sodium azide. The catalyst was recovered by vacuum-filtration onto a sintered-glass funnel, after washing with $CH_2Cl_2$, and drying at 100°C overnight. The resulting catalyst was reused without further purification for the triazole synthesis in a second run of the reaction process with the same substrate. This process repeated for three cycles, and the yield of the triazole did not change significantly.




Condition: (a) PhCCH, $Cu(OAC)_2$MCM-41, $NaN_3$, $H_2O$, sodium ascorbate, 90°C
(b) PhCCH, $Cu(OAC)_2$MCM-41, $H_2O$, sodium ascorbate, 90°C

**SCHEME 2**

## *CONCLUSION*

In conclusion, a safe and efficient three-component reaction for the regioselective generation of 1,4-disubstituted 1,2,3-triazoles in water has been developed. This method avoids isolation and handling of potentially unstable small organic azides and is selective for the preparation of triazole products from terminal (not internal) alkynes and alkyl (not aryl) bromides. Furthermore, $Cu(OAc)_2$/MCM-41 can be recovered and recycled by simple filtration of the reaction solution and reused for four consecutive trials without a decrease in the activity.

## *EXPERIMENTAL*

### *Synthesis and Characterization of $Cu(OAc)_2$/MCM-41 Catalyst*

MCM-41 was prepared according to our previously published paper using sodium silicate as a source of silica and cetyltrimethylammonium bromide as a structure-directing agent [16]. The $Cu(OAc)_2$/MCM-41 catalyst was prepared by adding with stirring the alcoholic solution of copper acetate (200 mg $Cu(OAc)_2$ in 200 mL of ethanol) to 1 g of MCM-41. The preparation was kept in ethyl alcohol for 8 h at 35°C. The material was washed with alcohol and filtered until the filtrate became free from copper ions and further dried at 120°C.

The XRD pattern of $Cu(OAc)_2$/MCM-41 shows three reflections (a very intense peak (100) and two additional high order peaks (110 and 200) with lower intensities). This result is characteristic of a hexagonal pore structure [18]. The nitrogen adsorption–desorption isotherm of the sample was obtained at –196°C, and specific surface area was determined by applying the Brunauer-Emmett-Taylor (BET) equation to the isotherm [19]. The pore size distribution was calculated using the adsorption branch of the isotherm and the Barrett-Joyner-Halenda formula [20]. The nitrogen adsorption–desorption isotherm of $Cu(OAc)_2$/MCM-41 showed irreversible type IV adsorption isotherms as defined by IUPAC for mesoporous materials [18]. The surface area, pore volume, and pore diameter of $Cu(OAc)_2$/MCM-41 were 47.7 $m^2\ g^{-1}$, 0.15 cc $g^{-1}$, and 35.9 Å, respectively.

### *General Procedure for the Preparation of 1,2,3-Triazoles*

To a mixture of alkyl bromide (1 mmol), alkyne (1 mmol), and sodium azide (1.1 mmol) in $H_2O$ (5 mL), the catalyst (0.04 g) and sodium ascorbate (45 mol%, 0.090 g) were added at 90°C. After completion of

the reaction, as monitored by TLC, dichloromethane (15 mL) was added and the reaction mixture was vacuum-filtered through a sintered glass funnel and washed with $CH_2Cl_2$. The combined organic layer was washed with water (30 mL) and saturated NaCl solution (30 mL), dried over anhydrous $Na_2SO_4$, and evaporated in a rotary evaporator. The crude product was purified by crystallization, using a mixture of *n*-hexane and dichloromethane.

*1-Benzyl-4-phenyl-1H-1,2,3-triazole (Entry 1 in Table 2) [17b]*

mp (°C) = 133–134; $^1$H NMR (400 MHz, $CDCl_3$): 5.60 (s, 2H), 7.32–7.44 (m, 8H), 7.70 (s, 1H), 7.83 (d, $J$ = 7.2 Hz, 2H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): 54.25, 119.61, 125.70, 128.07, 128.18, 128.80, 128.82, 129.17, 130.55, 134.68, 148.23 ppm.

*1-(4-Bromobenzyl)-4-phenyl-1H-1,2,3-triazole (Entry 2 in Table 2) [17b]*

mp (°C) = 156–158; $^1$H NMR (400 MHz, $CDCl_3$): 5.54 (s, 2H), 7.20 (d, $J$ = 8.4 Hz, 2H), 7.34 (t, $J$ = 7.4 Hz, 1H), 7.43 (t, $J$ = 7.4 Hz, 2H), 7.53 (d, $J$ = 8.4 Hz, 2H), 7.73 (s, 1H), 7.83 (d, $J$ = 7.2 Hz, 2H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): 53.59, 118.75, 122.97, 125.69, 128.29, 128.86, 129.67, 130.43, 132.34, 133.71, 147.04 ppm.

*4-Phenyl-1-(6-(4-phenyl-1H-1,2,3-triazol-1-yl) hexyl)-1H-1,2,3-triazole (Entry 3 in Table 2)*

mp (°C) = 198–199; $^1$H NMR (400 MHz, $CDCl_3$): 1.41–1.44 (m, 4H), 1.96–1.99 (m, 4H), 4.42 (t, $J$ = 7.0 Hz, 4H), 7.31–7.37 (m, 2H), 7.42–7.46 (m, 4H), 7.77 (s, 2H), 7.84–7.86 (m, 4H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): 25.78, 30.06, 50.09, 119.52, 125.69, 128.17, 128.87, 130.56, 148.23 ppm; Anal. calcd for $C_{22}H_{24}N_6$: C, 70.94; H, 6.49; N, 22.56; found: C, 70.61; H, 6.37; N, 22.85.

*1-Benzyl-4-ferroceneyl-1H-1,2,3-triazole (Entry 4 in Table 2) [21]*

mp (°C) = 158–160; $^1$H NMR (400 MHz, $CDCl_3$): 4.09 (s, 5H), 4.32 (s, 2H), 4.73 (s, 2H), 5.56 (s, 2H), 7.28–7.31 (m, 2H), 7.36 (s, 1H), 7.38–7.41 (m, 3H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): 54.07, 66.73, 68.79, 69.73, 75.66, 118.75, 127.89, 128.69, 129.13, 134.93, 147.28 ppm.

*1-(4-Bromobenzyl)-4-ferroceneyl-1H-1,2, 3-triazole (Entry 5 in Table 2)*

mp (°C) = 174–175; $^1$H NMR (400 MHz, $CDCl_3$): 4.08 (s, 5H), 4.31 (s, 2H), 4.71 (s, 2H), 5.51 (s, 2H), 7.17 (d, $J$ = 7.6 Hz, 2H), 7.37 (s, 1H), 7.53 (d, $J$ = 7.6 Hz, 2H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): 53.42, 66.68, 68.77, 69.63, 75.21, 118.65, 122.86, 129.53, 132.32, 133.91, 147.54 ppm; Anal. calcd for $C_{19}H_{16}FeN_3Br$: C, 54.06; H, 3.82; N, 9.96; found: C, 53.65; H, 3.65; N, 9.92.

*(1-Benzyl)-1H-1,2,3-triazol-4-yl)(phenyl) (ferrocenyl)methanol (Entry 6 in Table 2)*

mp (°C) = 115–116; $^1$H NMR (400 MHz, $CDCl_3$): 3.76 (s, 1H), 4.13–4.25 (m, 9H), 5.50 (d, $J$ = 14.8 Hz, 1H), 5.53 (d, $J$ = 14.8 Hz, 1H), 7.22–7.45 (m, 11H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): 53.43, 66.66, 68.22, 68.28, 68.64, 73.23, 121.15, 126.24, 127.17, 127.77, 127.84, 128.71, 129.13, 134.87, 145.29, 155.06 ppm; Anal. calcd for $C_{26}H_{23}FeN_3O$: C, 69.50; H, 5.16; N, 9.35; Found: C, 69.23; H, 5.01; N, 9.15.

*(1-Benzyl-1H-1,2,3-triazol-4-yl) diphenylmethanol (Entry 7 in Table 2) [22]*

mp (°C) = 135–136; $^1$H NMR (400 MHz, $CDCl_3$): 3.84 (s, 1H), 5.51 (s, 2H), 7.09 (s, 1H), 7.25–7.39 (m, 15 H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): 54.17, 65.33, 122.41, 127.19, 127.53, 127.89, 128.05, 128.75, 129.13, 134.55, 145.63, 158.44 ppm.

*(1-(4-Bromobenzyl)-1H-1,2,3-triazol-4-yl)(4-chlorophenyl)(phenyl)methanol (Entry 8 in Table 2)*

mp (°C) = 124–126; $^1$H NMR (400 MHz, $CDCl_3$): 3.78 (s, 1H), 5.46 (s, 2H), 7.14 (d, $J$ = 8.0 Hz, 2H), 7.28–7.327 (M, 10H), 7.52 (d, $J$ = 8.8 Hz, 2H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): 53.63, 60.33, 76.40, 122.23, 123.04, 127.06, 127.82, 128.22, 128.65, 129.59, 132.37, 133.40, 133.52, 144.10, 145.09, 155.14 ppm; Anal. calcd for $C_{22}H_{17}BrClN_3O$: C, 58.11; H, 3.77; N, 9.24; found: C, 58.28; H, 3.66; N, 9.05.

*2-(1-(4-Bromobenzyl)-1H-1,2,3-triazol-4-yl) propan-2-ol (Entry 9 in Table 2)*

mp (°C) = 116–118; $^1$H NMR (400 MHz, $CDCl_3$): 1.62 (s, 6H), 2.24 (s, 1H), 5.46 (s, 2H), 7.16 (d, $J$ = 8.4 Hz, 2H), 7.37 (s, 1H), 7.52 (d, $J$ = 8.4 Hz, 2H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): 30.43, 53.46, 68.54, 119.01, 122.94, 129.77, 132.31, 133.60, 156.22 ppm; Anal.

calcd for $C_{12}H_{14}BrN_3O$: C, 48.67; H, 4.76; N, 14.19; found:. C, 48.68; H, 4.81; N, 14.18.

### *1-(1-(4-Bromobenzyl)-1H-1,2,3-triazol-4-yl) cyclohexanol (Entry 10 in Table 2)*

mp (°C) = 128–130; $^1$H NMR (400 MHz, $CDCl_3$): 1.53–1.96 (m, 10H), 2.00 (s, 1H), 5.47 (s, 2H), 7.16 (d, $J$= 8.4 Hz, 2H), 7.38 (s, 1H), 7.52 (d, $J$= 8.4 Hz, 2H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): 21.93, 25.32, 38.12, 53.47, 69.58, 119.47, 122.91, 129.73, 132.30, 133.68, 156.42 ppm; Anal. calcd for $C_{15}H_{18}BrN_3O$: C, 53.58; H, 5.40; N, 12.50; found:. C, 53.54; H, 5.49; N, 12.46.

### *1-(1-Benzyl-1H-1,2,3-triazol-4-yl)cyclohexanol (Entry 11 in Table 2)*

mp (°C) = 125–126; $^1$H NMR (400 MHz, $CDCl_3$): 1.31–1.94 (m, 10H), 2.70 (s, 1H), 5.48 (s, 2H), 7.25-7.38 (m, 6H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): 22.35, 38.08, 40.89, 54.13, 69.47, 119.63, 128.10, 128.69, 129.09, 134.68, 156.14 ppm; Anal. calcd for $C_{15}H_{19}N_3O$: C, 70.01; H, 7.44; N, 16.33; found:. C, 69.65; H, 7.62; N, 16.68.

### *Methyl 1-benzyl-1H-1,2,3-triazole-4-carboxylate (Entry 12 in Table 2) [23]*

Mp (°C) = 105–107; $^1$H NMR (400 MHz, $CDCl_3$): 3.94 (s, 3H), 5.59 (s, 2H), 7.29–7.31 (m, 2H), 7.38–7.42 (m, 3H), 7.99 (s, 1H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): 52.22, 54.51, 127.38, 128.31, 129.20, 129.35, 133.64, 140.31, 161.10 ppm.

### *Ethyl 1-benzyl-1H-1,2,3-triazole-4-carboxylate (Entry 13 in Table 2) [24]*

Mp (°C) = 83;$^1$H NMR (400 MHz, $CDCl_3$): 1.39 (t, $J$= 7.2 Hz, 3H), 4.41 (q, $J$= 7.0 Hz, 2H), 5.59 (s, 2H), 7.29–7.31 (m, 2H), 7.38–7.42 (m, 3H), 7.99 (s, 1H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): 14.30, 54.48, 61.33, 127.32, 128.28, 129.16, 129.33, 133.73, 140.67, 160.71 ppm.

### *1-(4-Bromobenzyl)-4-butyl-1H-1,2,3-triazole (Entry 14 in Table 2)*

mp (°C) = 67–68; $^1$H NMR (400 MHz, $CDCl_3$): 0.94 (t, $J$= 7.4 Hz, 3H), 1.33–1.43 (m, 2H), 1.61–1.68 (m, 2H), 2.72 (t, $J$= 7.8 Hz, 2H), 5.47 (s, 2H), 7.14 (d, $J$= 8.8 Hz, 2H), 7.19 (s, 1H), 7.52 (d, $J$= 8.4 Hz, 2H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): 13.82, 22.33, 25.38, 31.48, 53.31, 120.44, 122.77, 129.57, 132.25, 133.98, 148.88 ppm; Anal. calcd for $C_{13}H_{16}BrN_3$: C, 53.07; H, 5.48; N, 14.28; found:. C, 53.23; H, 5.30; N, 14.36.

### *1-(4-Bromobenzyl)-4-(4-(2-phenylethynyl) phenyl)-1H-1,2,3-triazole (Entry 15 in Table 2)*

mp (°C) = 210–210.5; $^1$H NMR (400 MHz, $CDCl_3$): 5.55 (s, 2H), 7.21 (d, $J$= 8.0 Hz, 2H), 7.36–7.37 (m, 3H), 7.53–7.60 (m, 6H), 7.70 (s, 1H), 7.81 (d, $J$= 8.0 Hz, 2H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): 53.60, 89.19, 90.33, 119.76, 123.06, 123.07, 123.13, 125.57, 125.83, 128.39, 129.70, 130.14, 131.62, 132.11, 132.39, 133.56, 147.82 ppm; Anal. calcd for $C_{23}H_{16}BrN_3$: C, 66.68; H, 3.89; N, 10.14; found:. C, 66.15; H, 3.70; N, 10.09.

### *1-(4-Bromophenyl)-4-phenyl-1H-1,2,3-triazole [23]*

mp (°C) = 232–233; $^1$H NMR (400 MHz, $CDCl_3$): 7.39–7.43 (m, 1H), 7.47–7.51 (m, 2H), 7.69–7.74 (m, 4H), 7.92–7.94 (m, 2H), 8.20 (s, 1H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 117.35, 121.90, 122.43, 125.89, 128.62,128.99, 129.94, 132.97, 136.03, 150.64 ppm.

### *Recycling of the Catalyst*

After the reaction had been carried out, the mixture (containing catalyst) was vacuum-filtered onto a sintered-glass funnel and the residue was washed with $CH_2Cl_2$ (10 mL) and dried at 100°C overnight and subjected to a second run of the reaction process with the same substrate.

## *SUPPORTING INFORMATION*

Results of characterization of prepared catalysts using XRD BET methods are available from the corresponding author (r.hosseinzadeh@umz.ac.ir) on request.

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