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Three-Component and Click Strategy for Synthesis of *β*-Hydroxy 1,4-Disubstituted 1,2,3-Triazoles Derivatives Catalyzed by 1,4-Dihydroxyanthraquinone-copper(II) Complex onto Nano $AlPO_4$

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In this work, copper(II) heterogeneous nanocatalyst supported on modified $AlPO_4$ (Cu(II)-DA@Nano $AlPO_4$) was used for the synthesis of some biological active heterocyclic molecules, particularly for the efficient conversion of a wide range of non-activated terminal alkynes to *β*-hydroxy 1,4-disubstituted 1,2,3-triazolethrough a three-component "click" reaction at room temperature in water. The regioselective reactions exclusively gave the corresponding 1,4-disubstituted 1,2,3-triazoles in good to excellent yields. The Cu(II)-nanocatalyst has high catalytic activity, and was recycled ten successive times. This heterogeneous nanocatalyst not only offers substantial improvements in the reaction rates, but also avoids the use of hazardous catalysts, solvents and intermediates. Moreover, the reaction can be performed in large scale.

Keywords: Three component, Triazole, Heterogeneous nanocatalyst, Anthraquinone

INTRODUCTION

Nitrogen containing rings have always been in the center of attention due to their wide range of biological activities. One class of these fascinating compounds is the family of 1,2,3-triazole and its derivatives. These compounds are known for their chemical stability against oxidation, reduction and hydrolysis so that they have large utilities in organic synthesis [1-3] as well as some other applications like drug discovery [4-7], anti-HIV therapy [8,9], fluorescence chemosensors [10], *etc*. [11-17].

Using of 1,2,3-triazoles asheterogeneous catalysts has been tested by incorporating the ring as linker for certain metals and producing metal complexes which are attached to diverse materials [18].

In recent decade, many procedures have been developed to synthesize title compounds. The conventional process which takes advantage of a cycloaddition reaction, necessitates long reaction times and high temperatures, besides it produces a mixture of 1,4- and 1,5-disubstituted triazoles [19-20].

One of the most interesting reactions for synthesizing this class of compounds is the copper(I)-catalyzed reaction [21-44,45] which is reported by Fokin, Sharpless [46,47] and Meldal [48]. By using terminal alkynes this procedure provides exclusively the desired 1,4-disubstitutedtriazoles.

Although copper(I)-catalyzed reaction has many advantages include wide scope of substrates, regiospecifity and high reaction rate, however copper(I) is thermodynamically instable and is prone to oxidation [49-50] and disproportionation [51]. Due to this instability some specific conditions like anhydrous solvents, inert atmosphere and use of ligands to protect the copper nucleus should be present. Generating the copper(I) *in situ* [52-54] is a solution to these drawbacks. This could happen by incorporating copper(II) salts and a reducing agent, normally sodium ascorbate. It is noted that using copper cores with high electron density can accelerate the reaction thus using an electron donating ligand is crucial for performing this reaction well [55].

Because of the reusability and easy production process amino-functionalized nano-materials [56-59,60] have been

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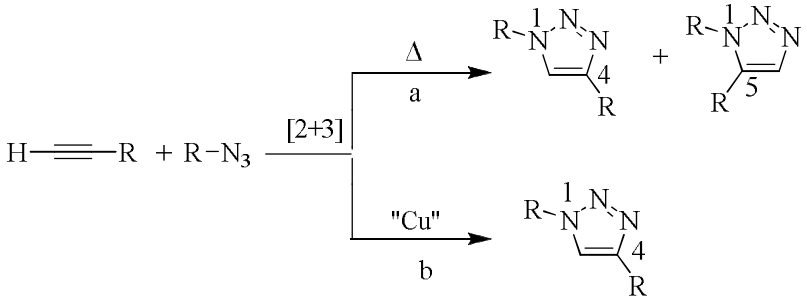


Scheme 1. Conventional procedure for production of the triazole (a) and copper(I)-catalyzed cycloaddition (b)

in great attention in recent decade. In addition, industrial developments need investigating on easy process and inexpensive catalysts. For this purpose, many chemists have taken advantage of amorphous $AlPO_4$ since it has priority over other solids like silica or carbon nanotubes due to particular properties and high value regarding cost. Furthermore, amorphous $AlPO_4$ have been used in covalent immobilization of various class of enzymes and different ligands [56-59].

A reliable and important family of ligands for this reaction is the family of anthracyclines [61]. Anthraquinones specially 1,4-dihydroxyanthraquinone [62] have been proved to have high utility in organic chemistry and produce good metal complexes [62-69].

In continuation of our previous studies [70-72], here in, we provide a one-pot, regioselective, efficient and green procedure to synthesize *β*-hydroxy 1,4-disubstituted 1,2,3-triazoles by using epoxides, terminal alkynes and sodium azide in water under mild conditions in the presence of a Cu(II) heterogeneous nanocatalyst supported on modified $AlPO_4$ as inexpensive, highly stable easily prepared and reusable catalyst. The reactions conducted efficiently to give the 1,4-disubstituted 1,2,3-triazole derivatives in excellent yields.

EXPERIMENTAL

NMR spectra were recorded on a BrukerAvance DPX-250 (^{1}H NMR 250 MHz and ^{13}C NMR 62.9 MHz) spectrometer in pure deuterated solvents with tetramethylsilane as an internal standard. IR spectra were obtained using a Shimadzu FT-IR 8300 spectrophotometer. Mass spectra were determined on a Shimadzu GCMS-QP 1000 EX instruments at 70 or 20 eV. Melting points determined in open capillary tubes in a Büchi-535 circulating oil melting point apparatus. The ICP analysis data were obtained using a Varian Vista-pro analyzer. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica gel PolyGram SILG/UV 254 plates. Column Chromatography was carried out on short columns of silica gel 60 (70-230 mesh) in glass columns (2-3 cm diameter) using 15-30 g of silica gel per one gram crude mixture. Chemical materials were purchased from Fluka, Aldrich and Merck Companies.

General Procedure for the Synthesis of Alkynes Derivatives

A mixture of 2-(prop-2-ynyloxy)-9H-thioxanthen-9-one [73], prop-2-ynyl 3-chlorobenzoate [54], 2-Prop-2-ynyloxy-naphthalene [74], 4-(2-propyn-1-yloxy)benzaldehyde, (5.0 mmol), propargyl bromide (5.5 mmol) and K_2CO_3 (6.0 mmol) in adequate concentration in DMF (50 ml) was stirred out at room temperature for 24 h and poured into ice/water (500 ml). The solution was filtered and the residue was dried. The silica gel column chromatography was used to purify the crude product.

General Procedure for the Synthesis of 1,2,3-Triazole Derivatives in the Presence of a Catalytic Amount of Cu(II)-DA@Nano$AlPO_4$

Epoxide (1.0 mmol), alkyne (1.1 mmol) and sodium azide (1.1 mmol) were mixed and stirred in water (1.0 ml) in the presence of the suitable catalytic amount Cu(II)-DA@Nano $AlPO_4$ (2.0 mol%) at 25 °C. After the completion of the reaction as screened by TLC, the solvent was evaporated and the final product was extracted using

EtOAc (3 × 10 ml), then the combined organic layer was washed out by saturated brine and dried over anhydrous Na_2SO_4. Removal of the solvent to give the crude product, followed by purification on silica gel resulted in the pure β-hydroxy 1,4-disubstituted 1,2,3-triazole derivatives.

Spectral Data for Respective Compounds

2-Phenyl-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)ethanol (3a). Colorless solid; m.p.: 125-127 °C (Lit. [55]:125.5-126.5 °C); IR (KBr): ν = 540 (m), 625 (w), 694 (s), 760 (s), 918 (m), 980 (w), 1072 (s), 1218 (s), 1357 (m), 1458 (s), 1604 (m), 1882 (w), 1952 (w), 2854 (s), 2924 (s), 3078 (m), 3356 (br) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 3.93 (s, 1H), 4.09-4.15 (m, 1H), 4.49-4.59 (m, 1H), 5.60 (dd, 1H, J_1 = 8.2, J_2 = 3.7 Hz), 7.17-7.26 (m, 8H), 7.62-7.69 (m, 3H) ppm. MS: m/z (%) = 267 (M^++2, 0.2), 266 (M^++1, 2.89), 265 (M^+, 6.9), 218 (3.7), 206 (43.1), 178 (9.5), 116 (100.0) base peak, 77 (40).

2-[4-(Hydroxymethyl)-1*H*-1,2,3-triazol-1-yl]-1-phenylethanol (3b). Colourless solid; m.p.: 110-111 °C. (Lit. [55]: 110-111 °C); IR (KBr): ν = 702 (s), 795 (m), 849 (m), 1011 (s), 1084 (s), 1119 (s), 1234 (m), 1454 (s), 2893 (w), 2932 (w), 3167 (s), 3340 (br) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 4.03 (dd, 1H, J_1 = 12.3, J_2 = 3.6 Hz), 4.33-4.46 (m, 3 H), 4.52 (s, 2 H), 5.58 (dd, 1H, J_1 = 8.8, J_2 = 3.8 Hz), 7.13-7.30 (m, 5 H), 7.52 (s, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 53.1, 64.5, 67.1, 122.9, 125.9, 127.1, 128.9, 136.0, 147.3.

1-Phenoxy-3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)propan-2-ol (3c). Colorless solid; m.p.: 124-126 °C (Lit. [55]: 125-126 °C). IR (KBr): ν = 694 (s), 756 (s), 879 (m), 1041 (s), 1080 (s)1118 (s), 1242 (s), 1466 (m), 1497 (m), 1597 (s), 2916 (w), 3086 (w), 3425 (br) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 3.05 (s, 1H), 3.99-4.09 (m, 2H), 4.53-4.61 (m, 2H), 4.71-4.76 (m, 1H), 6.90-7.02 (m, 3H), 7.26-7.43 (m, 5H), 7.74–7.78 (m, 2H), 7.88 (s, 1H). MS: m/z (%) = 297 (M^++2, 1.6), 296 (M^++1, 4.4), 295 (M^+, 7.1), 279 (7.3), 243 (3.7), 222 (5.1), 202 (9.0), 167 (22.1), 149 (62.5), 117 (35.7), 94 (24.2), 77 (51.8), 57 (100.0).

1-(4-Phenyl-1*H*-1,2,3-triazol-1-yl)butan-2-ol (3d). White solid; m.p.: 120-122 °C. IR (KBr): ν = 509 (m), 694 (s), 825 (s), 856 (m), 918 (m), 980 (s), 1080 (s), 1134 (s) 1226 (s) 1427 (m), 1458 (m), 2924 (m), 3140 (w), 3248 (br) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.97 (t, 3H, J = 7.5 Hz), 1.44-1.56 (m, 2H), 3.60 (s, 1H), 3.94-4.04 (m, 1H), 4.08-4.18 (m, 1H), 4.36-4.42 (m, 1H), 7.19-7.30 (m, 3H), 7.57-7.60 (m, 2H), 7.73 (d, 1H, J = 2.5 Hz) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 9.8, 27.4, 59.0, 71.6, 121.2, 125.5, 128.0, 128.6, 130.1, 144.5 ppm.

2-(4-Phenyl-1*H*-1,2,3-triazol-1-yl)cyclohexanol (3e). Colorless solid; m.p.: 178-180 °C. (Lit. [55]: 179-180 °C). IR (KBr): ν = 694 (s), 764 (s), 841 (w), 918 (w), 966 (m), 1049 (s), 1080 (s), 1234 (s), 1358 (w), 1443 (s), 2854 (m), 2932 (s), 3117 (w), 3302 (br). ^1H NMR ($CDCl_3$): δ = 1.40-1.54 (m, 3H); 1.86-2.25 (m, 5H), 3.75 (s, 1H); 4.07-4.16 (m, 2H), 7.28-7.37 (m, 3H); 7.61-7.65 (m, 2 H); 7.72 (s, 1H). MS: m/z (%) = 245 (M^++2, 0.3), 244 (M^++1, 2.6), 243 (M^+, 6.7), 215 (1.5), 203 (2.6), 174 (1.7), 158 (3.7), 117 (100.0) base peak, 81 (55.7), 55 (23.5).

1-(Allyloxy)-3-(4-phenyl-1*H*-1,2,3-triazol-1-yl) propan-2-ol (3f). Colourless solid; m.p.: 70-72 °C. (Lit. [55[: 71.5-72 °C); IR (KBr): ν = 698 (m), 721 (m), 860 (m), 957 (m), 1076 (s), 1165 (s), 1358 (w), 1458 (w), 2970 (m), 3128 (m), 3356 (br) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 3.19 (d, 2H, J = 5.0 Hz), 3.70 (d, 2H, J = 5.4 Hz), 3.96-4.11 (m, 2H), 4.27 (dd, 1H, J_1 = 13.2, J_2 = 2.6 Hz), 4.51 (s, 1H), 4.93 (dd, 1H, J_1 = 17.2, J_2 = 10.3 Hz), 4.99-5.01 (m, 1H), 5.53-5.64 (m, 1H), 6.94-7.06 (m, 3H), 7.36 (dd, 2H, J_1 = 8.2, J_2 = 1.7 Hz), 7.58 (s, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 53.5, 68.9, 71.3, 72.3, 117.4, 121.0, 125.4, 128.0, 128.7, 129.7, 134.2, 147.0. MS: m/z (%) = 260 (M^++1, 5.4), 259 (M^+, 10.5), 230 (4.8), 203 (11.1), 158 (14.9), 132 (16.0), 116 (100.0) base peak, 93 (4.2), 77 (46.2), 57 (37.7).

1-(4-Phenyl-1*H*-1,2,3-triazol-1-yl)propan-2-ol (3g). Light brown solid; m.p.: 114-116 °C. IR (KBr): ν = 509.2 (m), 694 (s), 764 (s), 818 (m), 941 (w), 980 (m), 1080 (s), 1134 (s), 1227 (s), 1373 (m), 1435 (s), 1458 (s), 1612 (w), 2924 (w), 3140 (w), 3210 (br) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.30 (d, 3H, J = 4.5 Hz), 4.17-4.46 (m, 4H), 7.28-7.36 (m, 3H), 7.63 (d, 2H, J = 5), 7.79 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 20.4, 57.4, 66.2, 121.3, 125.4, 128.0, 128.7, 130.1, 147.0 ppm.

1,1,1-Trifluoro-3-(4-phenyl-1*H*-1,2,3-triazol-1-yl) propan-2-ol (3h). Colorless crystal; m.p.: 131-133 °C. IR (KBr): ν = 540 (m), 625 (w), 694 (s), 764 (s), 856 (m), 918 (w), 980 (w), 1072 (s), 1227 (s), 1358 (m), 1805 (w), 1882 (w), 1995 (w), 2878 (w), 2939 (m), 3132 (w), 3325 (br) cm^{-1}. ^1H NMR (DMSO-d_6, 250 MHz): δ = 4.48-4.55 (m,

2H), 4.67-4.75 (m, 1H), 6.90 (d, 1H, *J* = 5 Hz), 7.27-7.35 (m, 1H), 7.39-7.45 (m, 2H), 7.81-7.86 (m, 2H), 8.60 (m, 1H) ppm. ^{13}C NMR (DMSO-d_6, 62.9 MHz): δ = 49.5, 67.1, 67.5, 68.0, 68.5, 79.1, 122.3, 122.5, 125.0, 125.6, 126.8, 127.8, 128.9, 129.3, 130.5, 146.2 ppm.

1-Butoxy-3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)propan-2-ol (3i). Yellow solid; m.p.: 66-68 °C. IR (KBr): ν = 517 (s), 694 (s), 764 (s), 918 (m), 980 (s), 1119 (s), 1219 (s), 1365 (s), 1465 (s), 1581 (w), 1612 (s), 1805 (w), 1882 (m), 1951 (m), 2870 (s), 2955 (s), 3148 (w), 3379 (br) cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.88 (t, 3H, *J* = 7.5 Hz), 1.25-1.40 (m, 2H), 1.47-1.58 (m, 2H), 3.40-3.49 (m, 4H), 4.19-4.38 (m, 3H), 4.54 (dd, 1H, J_1 = 13.5, J_2 = 3.2 Hz), 7.25-7.34 (m, 3H), 7.63-7.67 (m, 2H), 7.83 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 13.9, 19.2, 31.6, 53.5, 69.0, 71.4, 71.8, 121.4, 125.5, 128.0, 128.7, 130.2, 147.2 ppm.

1-Isopropoxy-3-(4-phenyl-1*H*-1,2,3-triazol-1-yl) propan-2-ol (3j). Colorless powder; m.p.: 77-79 °C. IR (KBr): ν = 517 (m), 649 (s), 764 (s), 926 (m), 972 (m), 1080 (s), 1127 (s), 1219 (s), 1335 (w), 1373 (s), 1466 (s), 1612 (m), 1890 (w), 1952 (w), 2862 (w), 2924 (s), 2978 (s), 3356 (br) cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.06 (d, 6H, *J* = 6.0 Hz), 3.33-3.39 (m, 2H), 3.47-3.52 (m, 1H), 3.99 (s, 1H), 4.13 (s, 1H), 4.25-4.33 (m, 1H), 4.44-4.51 (m, 1H), 7.19-7.28 (m, 3H), 7.60-7.63 (m, 2H), 7.78 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 22.0, 53.4, 69.1, 69.2, 72.4, 121.3, 125.5, 128.0, 128.7, 130.3, 147.3 ppm.

2-((1-(2-Hydroxy-3-phenoxypropyl)-1*H*-1,2,3-triazol-4-yl)methoxy)-9H-thioxanthen-9-one (3k). Yellow solid; m.p.: 144-146 °C. IR (KBr): ν = 555 (w), 633 (w), 694 (m), 748 (s), 719 (m), 872 (m), 1041 (s), 1119 (s), 1219 (s), 1296 (m), 1342 (s), 1466 (s), 1597 (s), 1628 (s), 2854 (w), 2924 (s), 3148 (w), 3410 (br) cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 3.37 (s, 1H), 3.96-3.99 (m, 2H), 4.48-4.95 (m, 2H), 4.70-4.75 (m, 1H), 5.26 (s, 2H), 6.84-6.97 (m, 3H), 7.25-7.57 (m, 7H), 7.88 (s, 1H), 8.09 (s, 1H), 8.55 (d, 1H, *J* = 7.5 Hz) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 53.1, 62.0, 68.7, 68.9, 11.8, 114.4, 121.5, 122.9, 126.0, 126.1, 127.4, 128.4, 129.6, 129.7, 129.8, 130.5, 132.1, 133.8, 137.5, 137.7, 156.8, 158.0, 179.6 ppm.

2-((1-(2-Hydroxypropyl)-1*H*-1,2,3-triazol-4-yl) methoxy)-9H-thioxanthen-9-one (3l). Yellow solid; m.p.: 172-174 °C. IR (KBr): ν = 555 (w), 633 (w), 741 (s), 810 (m), 864 (m), 1018 (w), 1057 (m), 1126 (m), 1219 (s), 1288 (m), 1342 (s), 1435 (s), 1589 (s), 1628 (s), 2924 (w), 3155 (w), 3279 (s) cm^{-1}. ^{1}H NMR (DMSO-d_6, 250 MHz): δ = 1.05 (d, 3H, *J* = 5.0 Hz), 3.95-4.02 (m, 1H), 4.18-4.38 (m, 2H), 5.06 (d, 1H, *J* = 5 Hz,), 5.26 (s, 2H), 7.43-7.55 (m, 2H), 7.70-7.73 (m, 3 H), 8.02 (s, 1H), 8.17 (s, 1H), 8.42 (d, 1H, *J* = 10 Hz) ppm. ^{13}C NMR (DMSO-d_6, 62.9 MHz): δ = 20.7, 56.4, 61.4, 65.1, 111.6, 122.6, 125.3, 126.4, 126.4, 126.6, 128.0, 128.4, 129.0, 129.3, 132.6, 136.6, 141.8, 156.8, 178.3 ppm.

2-((1-(3-Butoxy-2-hydroxypropyl)-1*H*-1,2,3-triazol-4-yl)methoxy)-9H-thioxanthen-9-one (3m). Yellow solid; m.p.: 102-104 °C. IR (KBr): ν = 748 (m), 818 (w), 872 (m), 1011 (w), 1119 (s), 1219 (s), 1342 (m), 1435 (w), 1466 (m), 1597 (s), 1628 (s), 2870 (w), 2939 (m), 3155 (w), 3418 (br) cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.89 (t, 3H, *J* = 7.5 Hz), 1.26-1.40 (m, 2H), 1.47-1.58 (m, 2H), 3.03(s, 1H), 3.32-3.50 (m, 4H), 4.16-4.24 (m, 1H), 4.37-4.46 (m, 1H), 4.54-4.61 (m, 1H), 5.30 (s, 2H), 7.25-7.31 (m, 1H), 7.42-7.49 (m, 2H), 7.53-7.62 (m, 2H), 7.85 (s, 1H), 8.13 (d, 1H, *J* = 2.5 Hz), 8.13 (d, 1H, *J* = 7.5 Hz) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 13.8, 19.2, 31.5, 53.0, 62.1, 69.2, 71.5, 11.8, 115.5, 122.9, 126.0, 126.1, 127.4, 128.5, 129.7, 129.8, 130.1, 132.1, 137.4, 142.9, 156.9, 179.5 ppm.

2-((1-(2-Hydroxycyclohexyl)-1*H*-1,2,3-triazol-4-yl) methoxy)-9H-thioxanthen-9-one (3n). Yellow solid; m.p.: 164-166 °C. IR (KBr): ν = 748 (s), 818 (w), 872 (m), 964 (w), 1080 (s), 1126 (m), 1296 (w), 1342 (s), 1466 (s), 1597 (s), 1628 (s), 2862 (w), 2939 (s), 3418 (br) cm^{-1}. ^{1}H NMR (DMSO-d_6, 250 MHz): δ = 1.32 (s, 3H), 1.68-1.95 (m, 5H), 3.74 (s, 1H), 4.16-4.26 (m, 1H), 4.93 (s, 1H), 5.24 (s, 2H), 7.41-7.53 (m, 2H), 7.65-7.69 (m, 3H), 8.02 (s, 1H), 8.21(s, 1H), 8.40 (d, 1H, *J* = 7.5 Hz) ppm. ^{13}C NMR (DMSO-d_6, 62.9 MHz): δ = 23.7, 24.4, 31.9, 34.8, 61.5, 65.8, 71.2, 111.5, 122.6, 123.9, 126.4, 126.5, 127.6, 128.0, 128.4, 129.0, 129.3, 132.6, 136.6, 141.4, 156.9, 178.3 ppm.

2-((1-(2-Hydroxy-3-isopropoxypropyl)-1*H*-1,2,3-triazol-4 yl)methoxy)-9H-thioxanthen-9-one (3o). Yellow solid; m.p.: 127-129 °C. IR (KBr): ν = 486 (s), 555 (s), 633 (s), 663 (s), 748 (s), 818 (s), 872 (s), 938 (w), 1011 (s), 1080 (m), 1126 (s), 1288 (s), 1342 (s), 1404 (m), 1473 (s), 1589 (s), 1635 (s), 2361 (w), 2438 (w), 2870 (w), 2932 (m), 2970 (s), 3063 (w), 3155 (m), 3333 (br) cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.10 (d, 6H, *J* = 7.5 Hz), 3.28-3.33 (m, 2H), 3.44-3.54 (m, 2H), 4.16 (s, 1H), 4.36-4.58 (m, 2H), 5.26 (s,

2H), 7.24-7.52 (m, 5H), 7.84 (s, 1H), 8.09 (s, 1H), 8.55 (d, 1H, *J* = 7.5 Hz) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 21.9, 53.2, 62.0, 68.9, 69.3, 72.4, 111.6, 122.7, 124.7, 125.9, 126.0, 127.3, 127.3, 128.3, 129.5, 129.7, 129.9, 132.0, 133.1, 137.3, 156.8, 179.3 ppm.

2-((1-(3,3,3-Trifluoro-2-hydroxypropyl)-1*H*-1,2,3-triazol-4-yl)methoxy)-9H-thioxanthen-9-one (3p). Yellow solid; m.p.: 120-122 °C. IR (KBr): ν = 555 (w), 741 (s), 810 (m), 864 (m), 1018 (m), 1057 (w), 1142 (s), 1219 (m), 1272 (s), 1342 (s), 1444 (w), 1466 (m), 1589 (s), 1620 (m), 1705 (w), 2762 (w), 2924 (w), 3155 (br) cm^{-1}. ^{1}H NMR (DMSO-d_6, 250 MHz): δ = 4.51-4.58 (m, 2H), 4.65-4.75 (m, 1H), 5.29 (s, 2H), 6.85 (d, 1H, *J* = 5.0 Hz), 7.43-7.57 (m, 2H), 7.60-7.80 (m, 3H), 8.03-8.04 (m, 1H), 8.29 (d, 1H, *J* = 2.5 Hz), 8.43 (d, 1H, *J* = 7.5 Hz) ppm. ^{13}C NMR (DMSO-d_6, 62.9 MHz): δ = 54.5, 66.5, 72.3, 72.7, 73.2, 73.6, 1116.8, 127.9, 131.1, 131.7, 131.7, 132.9, 133.3, 133.8, 134.3, 134.6, 137.9, 141.9, 147.4, 162.0, 183.6 ppm.

2-((1-(2-Hydroxybutyl)-1*H*-1,2,3-triazol-4-yl) methoxy)-9H-thioxanthen-9-one (3q). Yellow solid; m.p.: 150-152 °C. IR (KBr): ν = 748 (s), 719 (m), 864 (m), 1011 (s), 1119 (s), 1219 (s), 1288 (m), 1342 (s), 1412 (m), 1466 (s), 1597 (s), 1628 (s), 2878 (w), 2932 (m), 2932 (m), 3148 (w), 3410 (br) cm^{-1}. ^{1}H NMR (DMSO-d_6, 250 MHz): δ = 0.87 (t, 3H, *J* = 7.5 Hz), 1.19-1.46 (m, 2H), 3.72 (s, 1H), 4.19-4.27 (m, 1H), 4.34-4.41 (m, 1H), 5.03 (d, 1H, *J* = 7.5 Hz), 5.26 (s, 2H), 7.41-7.55 (m, 2H), 7.66-7.76 (m, 3H), 8.01 (d, 1H, *J* = 5.0 Hz), 8.16 (s, 1H), 8.41 (d, 1H, *J* = 7.5 Hz) ppm. ^{13}C NMR (DMSO-d_6, 62.9 MHz): δ = 9.6, 27.9, 55.0, 61.4, 70.2, 111.6, 122.6, 125.4, 126.3, 126.4, 127.6, 127.9, 128.4, 129.0, 129.3, 132.6, 136.6, 141.8, 156.8, 178.2 ppm.

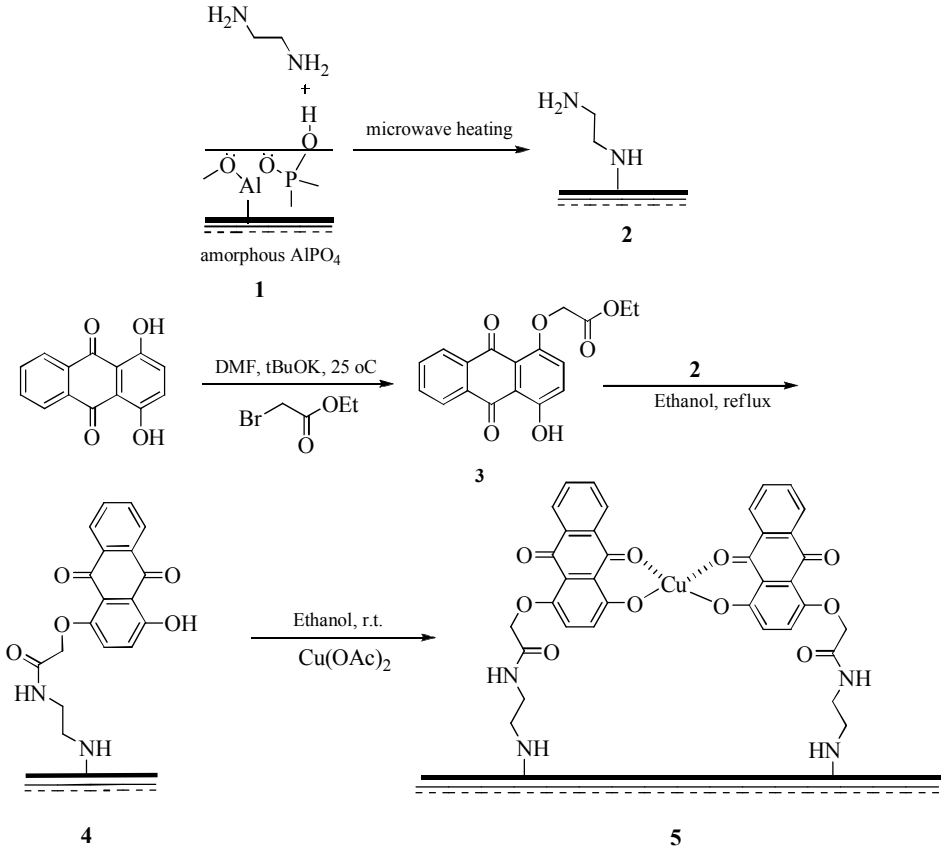
1-(4-((Naphthalen-6-yloxy)methyl)-1*H*-1,2,3-triazol-1-yl)-3-phenoxypropan-2-ol (3r). White crystal; m.p.: 138-140 °C. IR (KBr): ν = 648 (w), 687 (s), 748 (s), 841 (s), 1003 (m), 1041 (m), 1180 (m), 1211 (m), 1365 (w), 1427 (m), 1589 (m), 1628 (w), 1929 (w), 2878 (w), 2924 (w), 3171 (br) cm^{-1}. ^{1}H NMR (DMSO-d_6, 250 MHz): δ = 3.94 (d, 2H, *J* = 5.0 Hz), 4.25 (s, 1H), 4.43-4.52 (m, 1H), 4.59-4.66 (m, 1H), 5.26 (s, 2H), 5.63 (d, 1H, *J* = 5.0 Hz), 6.90-6.95 (m, 3H), 7.17-7.36 (m, 4H), 7.42-7.51 (m, 2H), 7.81 (d, 3H, *J* = 7.5 Hz), 8.26 (s, 1H) ppm. ^{13}C NMR (DMSO-d_6, 62.9 MHz): δ = 52.6, 61.1, 67.8, 69.3, 107.1, 114.4, 118.6, 120.7, 123.6, 125.7, 126.4, 126.7, 127.5, 128.5, 129.3, 129.5, 134.1, 142.2, 155.9, 158.3 ppm.

1-(4-((Naphthalen-6-yloxy)methyl)-1*H*-1,2,3-triazol-1-yl)propan-2-ol (3s). Brown solid; m.p.: 100-102 °C. IR (KBr): ν = 471 (s), 625 (m), 663 (m), 756 (s), 841 (s), 949 (s), 1011 (s), 1057 (m), 1126 (s), 1180 (s), 1219 (s), 1257 (s), 1389 (s), 1466 (s), 1512 (s), 1597 (s), 1628 (s), 1913 (w), 2878 (w), 2939 (w), 2978 (m), 3056 (m)3148 (m), 3371 (br) cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.04 (d, 3H, *J* = 5.0 Hz), 4.05-4.21 (m, 3H), 5.03 (s, 3H), 6.96-7.30 (m, 4H), 7.52-7.60 (m, 4H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 20.5, 57.3, 61.7, 66.4, 107.1, 118.7, 123.9, 124.5, 126.5, 126.9, 127.6, 129.1, 129.6, 134.4, 156.0 ppm.

1-Butoxy-3-(4-((naphthalen-6-yloxy)methyl)-1*H*-1,2,3-triazol-1-yl)propan-2-ol (3t). Brown solid; m.p.: 58-60 °C. IR (KBr): ν = 470 (s), 625 (w), 663 (m), 740 (s), 841 (s), 918 (w), 957 (m), 1011 (s), 1057 (s), 1119 (s), 1180 (s), 1219 (s), 1257 (s), 1389 (s), 1466 (s), 1512 (s), 1570 (s), 1628 (s), 1913 (w), 2870 (s), 2932 (s), 3009 (m), 3055 (w), 3155 (w), 3371 (br) cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.76 (t, 3H, *J* = 7.5 Hz), 1.15-1.23 (m, 2H), 1.35-1.40 (m, 2H), 3.25 (s, 4H), 4.05-4.40 (m, 4H), 5.09 (s, 2H), 7.00-7.31 (m, 4H), 7.58-7.65 (m, 4H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 13.9, 19.2, 31.5, 53.3, 61.8, 69.0, 69.0, 71.4, 71.6, 107.2, 118.7, 123.9, 124.6, 124.7, 126.5, 126.9, 127.6, 129.1, 129.5, 134.4, 156.1 ppm.

1-(3-Chlorophenyl)-2-(1-(2-hydroxy-3-phenoxy-propyl)-1*H*-1,2,3-triazol-4-yl)ethanone (3u). White solid; m.p.: 121-123 °C, IR (KBr): ν = 694.3 (s), 748 (s), 818 (m), 895 (m), 995 (w), 1080 (s), 1126 (s), 1250 (s), 1389 (w), 1427 (w), 1466 (w), 1497 (s), 1597 (s), 1720 (s), 2932 (m), 3070 (w), 3472 (br) cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 3.08 (s, 1H), 4.03-4.37 (m, 5H), 4.53 (s, 2H), 6.90-6.96 (m, 4 H), 7.25-7.35 (m, 3H), 7.50-7.53 (m, 1H), 7.91 (d, 1H, *J* = 7.5 Hz), 8.01 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 61.8, 66.2, 68.5, 68.7, 114.5, 114.7, 121.4, 127.9, 129.6, 129.7, 129.78, 131.4, 133.3, 134.6, 158.3, 165.5, 202.5 ppm.

4-((1-(2-Hydroxy-3-phenoxypropyl)-1*H*-1,2,3-triazol-4-yl)methoxy)benzaldehyde (3v). Light brown; m.p.: 114-116 °C. IR (KBr): ν = 509 (m), 609 (m), 694 (s), 756 (s), 833 (s), 1003 (m), 1049 (s), 1111 (w), 1165 (s), 1250 (s), 1304 (s), 1389 (m), 1427 (m), 1466 (m), 1497 (s), 1597 (s), 1689 (s), 2746 (w), 2878 (w), 2932 (s), 3148 (w), 3364 (br) cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 3.94-4.20 (m, 3H),



Scheme 2. Traditional method for covalent attachment of Cu(II) complex of 1,4-dihydroxyanthraquinone on amino-functionalized amorphous $AlPO_4$

4.46-4.52 (m, 2H), 4.65-4.70 (m, 1H), 5.17 (s, 2H), 6.82-7.02 (m, 5H), 7.20-7.23 (m, 2H), 7.73-7.81 (m, 3H), 9.78 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 53.1, 61.90, 68.7, 68.7, 114.4, 115.0, 121.8, 124.8, 129.6, 130.2, 132.0, 142.9, 158.0, 136.1, 190.9 ppm.

2-(4-Butyl-1*H*-1,2,3-triazol-1-yl)-1-phenylethanol (3w). Oily compound; [54] IR (KBr): ν = 702 (s), 756 (m), 1072 (m), 1229 (m), 1454 (s), 1551 (w), 2932 (m), 3093 (m), 3302 (br) cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.89 (t, 3H, J = 7.3 Hz), 1.24-1.41 (m, 2 H), 1.53-1.65 (m, 2 H), 2.65 (t, 2H, J = 7.5 Hz), 3.73 (s, 1 H), 4.15 (dd, 1H, J_1 = 12.3, J_2 = 3.9 Hz), 4.53 (dd, 1H, J_1 = 12.3, J_2 = 8.4 Hz), 5.60 (dd, 1H, J_1 = 8.2, J_2 = 3.8 Hz), 7.18-7.37 (m, 6H).

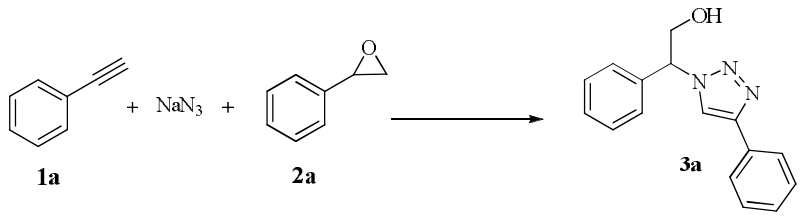
RESULTS AND DISCUSSION

Scheme 2 shows the synthetic procedure of nanocatalyst which consists of five steps [75]. At first, amino-functionalized $AlPO_4$ (2) was synthesized [59] using microwave anchoring of ethylenediamine to the $AlPO_4$ support. Also, using reaction of 1,4-dihydroxy-anthraquinone and ethyl 2-bromoacetate, (4-hydroxy-9,10-dioxo-9,10-dihydro-anthracen-1-yloxy)-acetic acid ethyl ester (3) was synthesized. Then, ligand 3 was attached to $AlPO_4$. Finally, by the reaction of supported ligand 3 and $Cu(OAc)_2$, $AlPO_4$ supported Cu(II) complex of 1,4-dihydroxyanthraquinone was prepared and nanocatalyst was characterized by various characterization techniques [70].

The optimization of Sharpless reaction between 2-phenyl-oxirane, NaN_3, and ethynyl-benzene under different conditions was investigated. According to Table 1, different solvents, temperatures and catalyst loadings were tested.

Initially, the effect of various solvents was checked and it was observed that the reaction had no or less

Table 1. Comparison of Different Solvents for the Synthesis of 3a



Entry	Conditions	Time (h)	Yield (%)[a]
1	Cu(II)-DA@NanoAlPO$_4$ (2 mol%), H_2O, r.t.	3	96
2	Cu(II)-DA@Nano AlPO$_4$ (2 mol%), ethanol, r.t.	4.3	55
3	Cu(II)-DA@Nano AlPO$_4$ (2 mol%), DMSO, r.t.	6	5
4	Cu(II)-DA@Nano AlPO$_4$ (2 mo l%), DMF, r.t.	8	10
5	Cu(II)-DA@Nano AlPO$_4$ (2 mol%), toluene, r.t.	8	3
6	Cu(II)-DA@Nano AlPO$_4$ (2 mol%), 1,4-dioxane, r.t.	8	7
7	Cu(II)-DA@Nano AlPO$_4$ (2 mol%), acetonitrile, r.t.	8	36
8	Cu(II)-DA@Nano AlPO$_4$ (2 mol%), ethanol/water (1:1), r.t.	5	92
9	Cu(II)-DA@Nano AlPO$_4$ (2 mol%), neat, r.t.	8	0
10	Cu(II)-DA@Nano AlPO$_4$ (2 mol%), H_2O, 50 °C	2.3	96
11	Cu(II)-DA@Nano AlPO$_4$ (2 mol%), H_2O, reflux	1.0	96
12	Cu(II)-DA@Nano AlPO$_4$ (5 mol%), H_2O, r.t.	3	97
13	Cu(II)-DA@Nano AlPO$_4$ (1 mol%), H_2O, r.t.	5	78

[a]Isolated yield of product.

improvement in the presence of ethanol, DMSO, toluene, DMF, 1,4-dioxane, acetonitrile, a mixture of ethanol/water (1:1) and even in solvent free conditions. However, the best result obtained in the presence of water (Table 1, entries 1-9)

Second, different catalyst loadings were examined and it was obtained that the optimal amount of Cu(II) catalyst is 2 mol %. By using higher amounts of catalyst no improvements observed and using lower levels of catalyst loading decreased the reaction yield (Table 1, entries 1, 12, and 13).

In the next step, the effect of various temperatures was investigated and according to the obtained data, the best result was in room temperature. Higher temperatures did not have any positive effect on the reaction yield and time (Table 1, entries 10 and 11).

To investigate the scope of reaction, various class of alkynes and epoxides were used in the optimized reaction conditions and their corresponding triazoles were obtained in excellent yields. Both activated and non-activated alkynes carried out the reaction with good to excellent yields.

2-Hydroxy-thioxanthen-9-one was used in this reaction because it shows interesting bio activities and has many

Table 2. The One-pot Three-component Synthesis of 1,4-Disubstituted 1,2,3-Triazoles in the Presence of the Cu(II) Catalyst in Water[a]

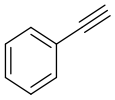
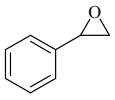
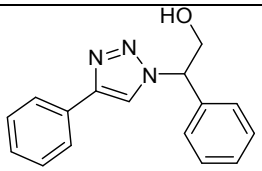
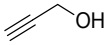
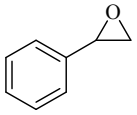
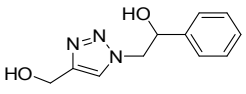
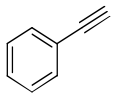
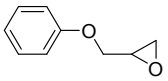
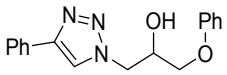
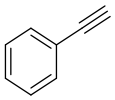
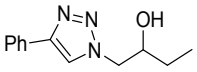
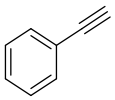
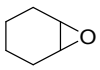
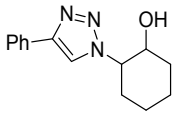
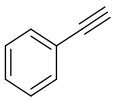
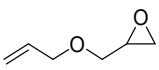
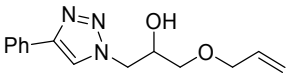
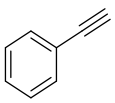
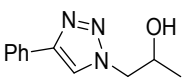
Entry	Alkyne	Epoxide	Product	T (h)	Yield (%)[b]
1	 1a	 2a	 3a	2	96
2	 1b	 2a	 3b	2	91
3	 1a	 2b	 3c	2.5	92
4	 1a	 2c	 3d	2.5	90
5	 1a	 2d	 3e	3	90
6	 1a	 2e	 3f	3	88
7	 1a	 2f	 3g	2.5	91

Table 3. Continued

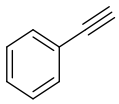
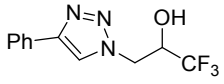
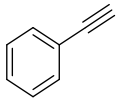
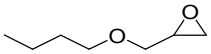
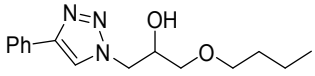
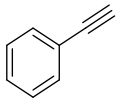
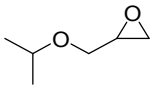
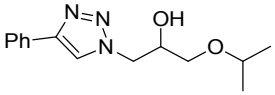
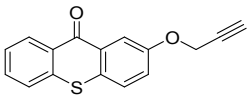
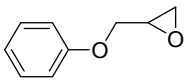
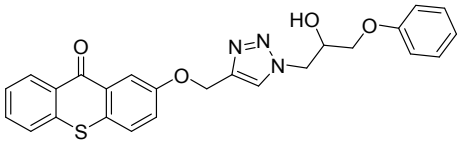
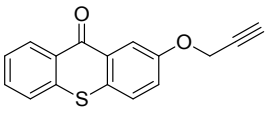
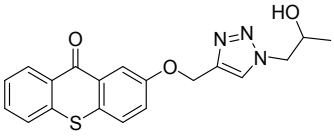
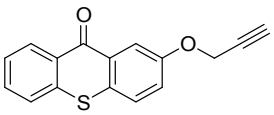
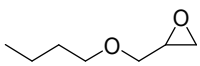
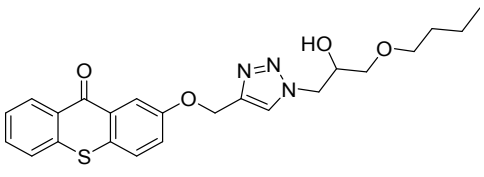
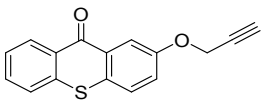
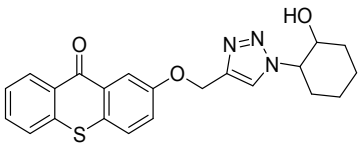
8	 **1a**	 **2g**	 **3h**	1.5	94
9	 **1a**	 **2h**	 **3i**	2	93
10	 **1a**	 **2i**	 **3j**	2	90
11	 **1c**	 **2b**	 **3k**	3	94
12	 **1c**	 **2f**	 **3l**	3	95
13	 **1c**	 **2h**	 **3m**	3	93
14	 **1c**	 **2d**	 **3n**	3	91

Table 4. Continued

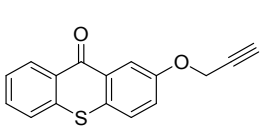
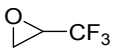
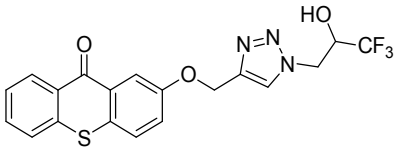
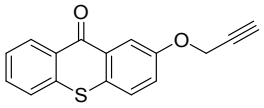
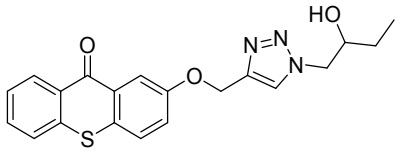
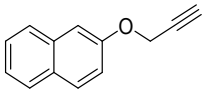
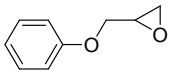
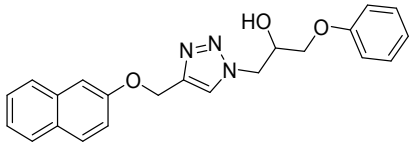
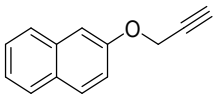
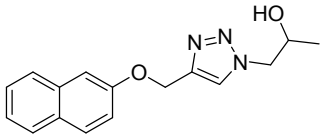
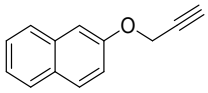
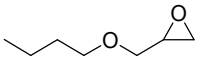
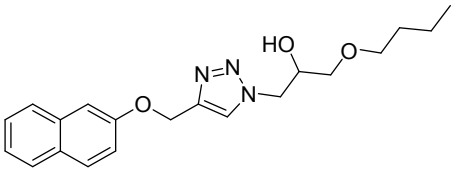
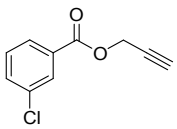
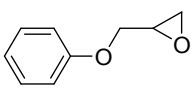
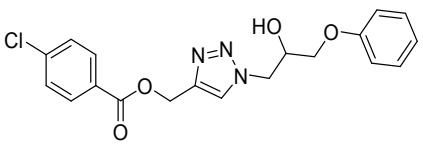
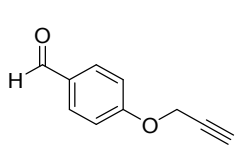
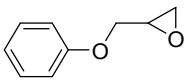
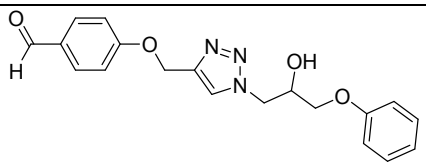
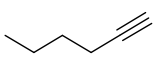
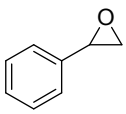
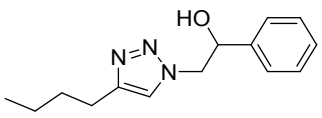
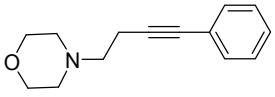
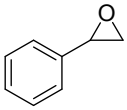
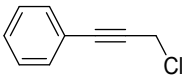
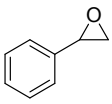
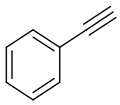
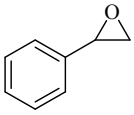
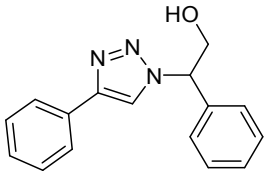
16	 **1c**	 **2g**	 **3p**	2.5	95
17	 **1c**	 **2c**	 **3q**	2.5	93
18	 **1d**	 **2b**	 **3r**	4	84
19	 **1d**	 **2f**	 **3s**	3.5	86
20	 **1d**	 **2h**	 **3t**	4	86
21	 **1e**	 **2b**	 **3u**	3	92

Table 5. Continued

22	 **1f**	 **2b**	 **3v**	3	88
23	 **1g**	 **2a**	 **3w**	1.5	86
24	 **1h**	 **2a**	-		0
25	 **1i**	 **2a**	-		0
26	 **1a**	 **2a**	 **3a**	2	81[c]

[a]Reagents and conditions: organic epoxide (1.0 mmol), alkyne (1.1 mmol), sodium azide (1.1 mmol), Cu(II)-DA@Nano $AlPO_4$ (2 mol%), water (1.0 ml), room temperature. [b]Isolated yield. [c]The reaction was performed on a 10.0 mmol scale.

applications in medicinal chemistry. It was produced according to the literature [76]. Next, it was propargylated and converted to the triazole products. 2-Prop-2-ynyloxy-naphthalene and 3-chloro-benzoic acid ethynyl ester can also carry out the cyclization reaction with azide compounds and provide desired products. Because of diverse utilities of formyl group in organic chemistry we focused to synthesis triazole bearing aldehyde group.

It should be noted that by using internal alkynes no product was observed and the starting materials remained intact.

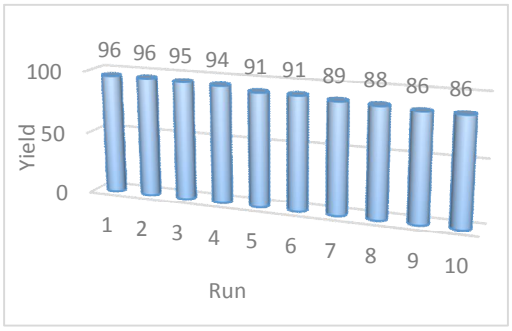


Fig. 1.

As it is shown in Table 2, it was fascinating to see a wide spectrum of epoxides successfully reacted with various alkynes and produce the related triazole in high yields.

Furthermore, we examined the large scale synthesis of 2-phenyl-2-(4-phenyl-[1,2,3]triazol-1-yl)-ethanol (3a) from 2-phenyl-oxirane (10 mmol) and ethynyl-benzene (10 mmol) in the present of 2 mol % catalyst in water at room temperature (Table 2).

Moreover, the reusability of catalyst was examined through the cycloaddition of phenylacetylene, 2-phenyl-oxirane and sodium azide. After the first run the catalyst was recovered by centrifugation and was washed with water and ethyl acetate. Then it was dried under air and reused in a subsequent reaction. As it is depicted in Fig. 1, this heterogeneous catalyst can be easily removed from the reaction mixture and reused several times with minimal decrease in catalytic activity. The activity of Cu(II)-DA@Nano $AlPO_4$ in the synthesis of 1,2,3-triazole derivatives even after 10 runs is still significant.

Next the leaching phenomenon was checked. For this purpose, the catalyst was stirred in H_2O at room temperature for 10 h. Then it was separated from the mixture and the mixture was used in the formation of β-hydroxy 1,4-disubstituted 1,2,3-triazole under the optimized reaction conditions. It was observed that in this situation no product obtained even after 24 h.

All in all, we have provided an efficient and recyclable heterogeneous nano catalyst for the Huisgen 1,3-dipolar cycloaddition reaction and synthesis of various 1,2,3-triazoles. Using a simple filtration, the catalyst can be easily removed from the mixture and reused in 10 subsequent reactions without significant loss of activity. By this reliable process a vast variety of triazoles can be synthesized through the reaction of different epoxides and activated or non-activated alkynes in green conditions. The present reaction provides significant improvement in reaction rate and yield along with avoidance of using any hazardous organic solvents and materials. Furthermore, this procedure can be used for the large scale formation of 1,2,3-triazoles also it has other advantages like easy isolation of products, excellent yields, green process and using a low cost catalyst.

ACKNOWLEDGMENTS

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REFERENCES

[1] B.S. Holla, M. Mahalinga, M.S. Karthikeyan, B. Poojary, P.M. Akberali, N.S. Kumari, Eur. J. Med. Chem. 40 (2005) 1173.

[2] K. Dabak, O. Sezer, A. Akar, O. Anac, Eur. J. Med. Chem. 38 (2003) 215.

[3] W.S. Horne, M.K. Yadav, C.D. Stout, M.R. Ghadiri, J. Am. Chem. Soc. 126 (2004) 15366.

[4] A.D. Moorhouse, A.M. Santos, M. Gunaratnam, M. Moore,S. Neidle, J.E. Moses, J. Am. Chem. Soc. 128 (2006) 15972.

[5] A.D. Moorhouse, J.E. Moses, Chem. Med. Chem. 3 (2008) 715.

[6] C. Mamat, T. Ramenda, F.R. Wuest, Mini-Rev. Org.

Chem. 6 (2009) 21.
[7] M.D. Best, Biochemistry 48 (2009) 6571.
[8] M. Whiting, J.C. Tripp, Y.C. Lin, W. Lindstrom, A.J. Olson, J.H.Elder, K.B. Sharpless, V.V. Fokin, J. Med. Chem. 49 (2006) 7697.
[9] M.J. Giffin, H. Heaslet, A. Brik, Y.-C. Lin, G. Cauvi,C.-H. Wong, D.E. McRee, J.H. Elder, C.D. Stout, B.E. Torbett, J. Med. Chem. 51 (2008) 6263.
[10] S.H. Kim, H.S. Choi, J. Kim, S.J. Lee, D.T. Quang, J.S. Kim,Org. Lett. 12 (2010) 560.
[11] L.-F. Lutz, Angew. Chem. Int. Ed. 46 (2007) 1018.
[12] J. Zhan, D. Tian, H. Li, New J. Chem. 33 (2009) 725.
[13] S.Y. Park, J.H. Yoon, C.S. Hong, R. Souane, J.S. Kim, S.E. Matthews, J. Vicens, J. Org. Chem. 73 (2008) 8212.
[14] K. Chang, L. Su, A. Senthilvelan, W. Chung, Org. Lett. 9 (2007) 3363.
[15] V. Haridas, K. Lal, Y.K. Sharma, S. Upreti, Org. Lett. 10 (2008) 1645.
[16] P. Wu, M. Malkoch, J.N. Hunt, R. Vestberg, E. Kaltgrad,M.G. Finn, V.V. Fokin, K.B. Sharpless, C.J. Hawker, Chem. Commun. 48 (2005) 5775.
[17] G. Franc, A.K. Kakkar, Chem. Eur. J. 15 (2009) 5630.
[18] A.E. Fernandes, A.M. Jonas, O. Riant, Tetrahedron 70 (2014) 1709.
[19] R. Huisgen in 1,3-Dipolar Cycloaddition Chemistry, A. Padwa (Eds.), Wiley, New York, 1984, Chap. 1, pp. 1-176.
[20] C.K. Sha, A.K. Mohanakrishan in Synthetic Applications of 1,3-Dipolar CycloadditionChemistry Toward Heterocycles and Natural Products, A. Padwa, W.H. Pearson (Eds.), Wiley, New York, 2003, pp. 623-680.
[21] M. Liu, O. Reiser, Org. Lett. 13 (2011) 1102.
[22] C. Spiteri, J.E. Moses, Angew. Chem. Int. Ed. 49 (2010) 31.
[23] M. Fuchs, W. Goessler, C. Pilger, C.O. Kappe, Adv. Synth. Catal. 352 (2010) 323.
[24] G.-C. Kuang, H.A. Michaels, J.T. Simmons, R.J. Clark, L. Zhu, J. Org. Chem. 75 (2010) 6540.
[25] A.E. Cohrt, J.F. Jensen, T.E. Nielsen, Org. Lett. 12 (2010) 5414.
[26] J.T. Fletcher, M.E. Keeney, S.E. Walz, Synthesis 19 (2010) 3339.
[27] M. Xu, C. Kuang, Z. Wang, Q. Yang, Y. Jiang. Synthesis 2 (2011) 223.
[28] S. Chandrasekhar, M. Seenaiah, A. Kumar, C.R. Reddy,S.K. Mamidyal, C.G. Kumar, S. Balasubramanian, Tetrahedron Lett. 52 (2011) 806.
[29] K.D. Ha¨nni, D.A. Leigh, Chem. Soc. Rev. 39 (2010) 1240.
[30] J.M. Holub, K. Kirshenbaum, Chem. Soc. Rev. 39 (2010) 1325.
[31] F. Santoyo-Gonzalez, F. Hernandez-Mateo, Chem. Soc. Rev. 38 (2009) 3449.
[32] R.A. Decre'au, J.P. Collman, A. Hosseini, Chem. Soc. Rev. 39 (2010) 1291.
[33] P. Appukkuttan, V.P. Mehtaa, E. Van der Eycken, Chem. Soc. Rev. 39 (2010) 1467.
[34] D. Wang, Na. Li, M. Zhao, W. Shi, C. Ma, B. Chen, Green Chem. 12 (2010) 2120.
[35] C.Le. Droumaguet, C. Wang, Q. Wang, Chem. Soc. Rev. 39 (2010) 1233.
[36] C.O. Kappe, E. Van der Eycken, Chem. Soc. Rev. 39 (2010) 1280.
[37] A.H. El-Sagheer, T. Brown, Chem. Soc. Rev. 39 (2010) 1388.
[38] H.C. Kolb, M.G. Finn, K.B. Sharpless, Angew. Chem. Int. Ed. 40 (2001) 2004.
[39] M.G. Finn, V.V. Fokin, Chem. Soc. Rev. 39 (2010) 1231.
[40] S.K. Mamidyala, M.G. Finn, Chem. Soc. Rev. 39 (2010) 1252.
[41] C.E. Hoyle, A.B. Lowe, C.N. Bowman, Chem. Soc. Rev. 39 (2010) 1355.
[42] D. Urankar, M. Steinbucher, J. Kosjek, J. Kosmrlj, Tetrahedron 66 (2010) 2602.
[43] H. Elamari, F. Meganem, J. Herscovici, C. Girard, Tetrahedron Lett. 52 (2011) 658.
[44] T. Nakamura, T. Terashima, K. Ogata, S.I. Fukuzawa, Org. Lett. 13 (2011) 620.
[45] H. Golchin Hosseini, E. Doustkhah, M.V. Kirillova, S. Rostamnia, G. Mahmoudi, A.M. Kirillov, Applied Catalysis A: General, 2017, doi.org/10.1016/ j.apcata.2017.07.006.
[46] V.V. Rostovtsev, L.G. Green, V.V. Fokin, K.B. Sharpless, Angew. Chem. Int. Ed. 41 (2002) 2596.
[47] K.B. Sharpless, V.V. Fokin, L.G. Green, V.V.

Rostovtsev, Angew. Chem. Int. Ed. 114 (2002) 2708.
[48] C.W. Tornøe, C. Christensen, M. Meldal, J. Org. Chem. 67 (2002) 3057.
[49] M.G. Simmons, C.L. Merril, L.J. Wilson, L.A. Bottomley, K.M. Kadish, J. Chem. Soc. Dalton Trans. (1980) 1827.
[50] C.L. Merrill, L.J. Wilson, T.J. Thamann, T.M. Loehr, N.S. Ferris, W.H. Woodruff, J. Chem. Soc. Dalton Trans. (1984) 2207.
[51] L. Ciavatta, D. Ferri, R. Palombari, J. Inorg. Nucl. Chem. 23 (1983) 1201.
[52] P. Wu, V.V. Fokin, Aldrichimica Acta 40 (2007) 7.
[53] G.C. Tron, T. Pirali, R.A. Billington, P.L. Canonico, G. Sorba, A.A.Genazzanni, Med. Res. Rev. 28 (2008) 278.
[54] P. Appukkuttan, W. Dehaen, V.V. Fokin, E.V.D. Eycken, Org. Lett. 6 (2004) 4223.
[55] H. Sharghi, M. H.Beyzavi, A. Safavi, M.M. Doroodmand, R. Khalifeh, Adv. Synth. Catal. 351 (2009) 2391.
[56] N. Karousis, N. Tagmatarchis, D. Tasis, Chem. Rev., 110 (2010) 5366.
[57] M.W. McKittrick, C.W. Jones, Chem. Mater. 15 (2003) 1132.
[58] J. Zhou, Z. Dong, H. Yang, Z. Shi, X. Zhou, R. Li, Appl. Surf. Sci. 279 (2013) 360.
[59] V. Caballero, F.M. Bautista, J.M. Campelo, D. Luna, R. Luque, J.M. Marinas, A.A. Romero, I. Romero, M. Rodríguez, I. Serrano, J.M. Hidalgo, A. Llobet, J. Mol. Catal. A: Chem. 308 (2009) 41.
[60] S. Rostamnia, N. Nouruzi, H. Xin, R. Luque, Catal. Sci. Technol. 5 (2015) 199.
[61] J.W. Lown, Anthracycline and Anthracenedione-Based Anticanceragents, Chap IV. 1988, pp. 129-161.
[62] L.A. Bigelow, H.H. Reynolds, Org. Synth. 6 (1941) 476.
[63] A. Quach, V. Escax, L. Nicole, P. Goldner, O. Guillot-Noe¨l, P. Aschehoug, P. Hesemann, J. Moreau, D. Gourier, C. Sanchez, J. Mater. Chem. 17 (2007) 2552.
[64] M. Shamsipur, A. Besharati-Seidani, J. Fasihi, H. Sharghi, Talanta. 83 (2010) 674.
[65] M. Barzegar, M.F. Mousavi, H. Khajesharifi, M. Shamsipur, H. Sharghi, IEEE Sens. J. 5 (2005) 392.
[66] A. Rahmani, M.F. Mousavi, S.M. Golabi, M. Shamsipur, H. Sharghi, Chem. Anal. 49 (2004) 359.
[67] S. Riahi, M.F. Mousavi, M. Shamsipour, H. Sharghi, Electroanalysis 15 (2003) 1561.
[68] M. Shamsipur, A. Avanes, M. Javanbakht, M.R. Ganjali, H. Sharghi, Anal. Sci. 18 (2002) 875.
[69] M. Shamsipur, F. Raoufi, H. Sharghi, Talanta 52 (2000) 637.
[70] H. Sharghi, A. Khoshnood, M.M. Doroodmand, R. Khalifeh, J. Iran. Chem. Soc. 9 (2012) 231.
[71] H. Sharghi, P. Shiri, M. Aberi, Mol. Divers. 18 (2014) 559.
[72] H. Sharghi, R. Khalifeh, M.M. Doroodmand, Adv. Synth. Catal. 351 (2009) 207.
[73] H. Sharghi, M. Hosseini-Sarvari, F. Moeini, R. Khalifeh, A.S. Beni, Helvetica Chimica Acta 93 (2010) 435.
[74] H. Sharghi, S. Ebrahimpourmoghaddam, M.M. Doroodmand, A. Purkhosrow, Asian J. Org. Chem. 1 (2012) 377.
[75] H. Sharghi, I. Ghaderi, M.M. Doroodmand, Appl. Organomet. Chem. doi: 10.1002/aoc.3869.
[76] H. Sharghi, A.S. Beni, J. Iran. Chem. Soc. 1 (2005) S33.