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Nanocomposite copper metal as an efficient heterogeneous catalyst in click synthesis of 1,2,3-triazoles in aqueous media

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Abstract: Copper/periodic mesoporous organosilica (Cu/PMO) nanocomposites provided a highly active, reusable, globular, solid-phase catalyst for click chemistry. The reaction proceeds by mixing organohalides, sodium azide, alkyne, and the catalyst in an aqueous medium to afford the desired products. The cost efficiency and recyclability of the catalyst up to six runs without appreciable loss of activity and high yields of products make this procedure greener.

Key words: Mesoporous, organosilica, nanocomposites, click reaction, 1,2,3-triazoles, catalyst

1. Introduction

Click chemistry has become one of the most important concepts in modern chemistry, focusing on efficiently creating molecular diversity from readily available starting materials under simple reaction conditions.[1] Copper (I)-catalyzed organoazide–alkyne cycloaddition (CuAAC)[2] was one of the most credible click-type reactions within the concept of click chemistry.[3–5] This reaction has enabled the practical and efficient preparation of 1,2,3-triazoles from a wide range of substrates with excellent selectivity that cannot be prepared via traditional Huisgen uncatalyzed thermal approaches.[6] Triazoles have attracted considerable interest recently because of their wide usefulness. Among them, 1,2,3-triazoles have received much attention and have been used in variety of synthetic and medicinal chemistry applications such as drug discovery,[7] material science,[8] and bioconjugation.[9] In this regard, heterogeneous catalysis emerges as an important tool and has been frequently used as a green alternative for a broad range of chemical transformations. With the finding that copper metal can be a catalytic species for the synthesis of 1,2,3-triazoles,[10,11] efforts have been devoted to develop new catalytic systems, including heterogeneous catalysis processes, especially copper nanoparticles.[12–17] Additionally, it brings important advantages, such as easy recovery (removal of the catalyst from the reaction media by simple filtration), easy recycling, and enhanced stability of the catalyst, and reactions in water, the solvent used by nature for biological chemistry, which can make synthetic processes cheaper, safer, and greener.[18–20] Regarding our continuous search for reactions catalyzed by mesoporous silica structures as new nanocatalysts, we dedicated our efforts to develop a safe, easy to handle heterogeneous catalyst that could be easily separated from the crude reaction mixture and recycled in a given process.[21,22]

Previous studies showed that Cu/PMO nanocomposite, synthesized by the sol-gel method, was successfully employed to promote three-component β-hydroxy-1,2,3-triazoles synthesis, known as the click reaction, with different methods (Scheme 1).[23–25] We wish to disclose herein our results regarding the performance and

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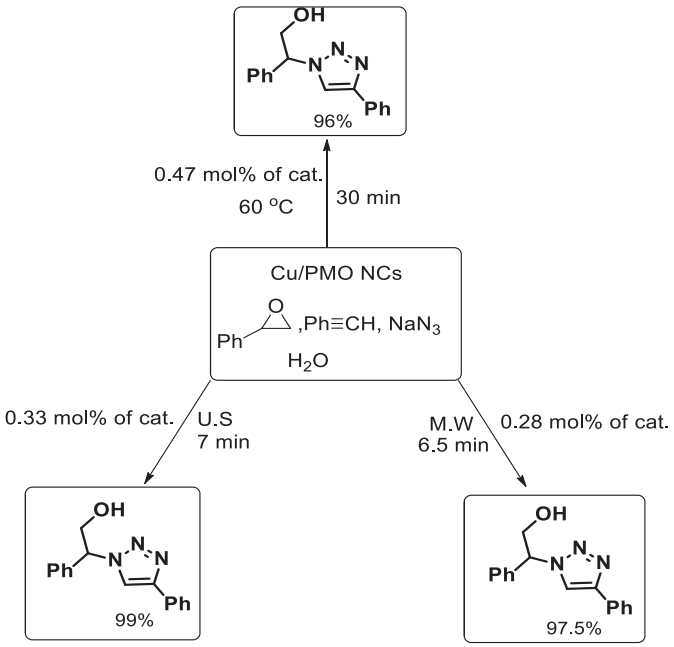
scope of Cu/PMO nanocomposite catalyst in the domino azidolysis of aryl halides and 1,3-dipolar cycloaddition with alkynes, in which 1,2,3-triazoles were synthesized in high yields and short reaction time in aqueous media. A catalyst in amounts of 0.47 mol % promoted the Huisgen 1,3-dipolar cycloaddition of organic azides and terminal alkynes and it was reused without loss of catalytic activity or leaching of copper species.



Scheme 1. Multicomponent synthesis of β-hydroxy-1,2,3-triazoles from styrene oxide, phenylacetylene, sodium azide catalyzed by Cu/PMO NCs in water.

2. Results and discussion

2.1. Preparation of the catalyst

The copper catalyst was readily available by imprinting periodic mesoporous organosilica (PMO) with a recently prepared complex of copper. The latter was obtained by sol-gel process from copper acetate monohydrate, Schiff base, cetyl trimethyl ammonium bromide (CTAB) tetraethylorthosilicate (TEOS), and 3-chloropropyltrimethoxysilane in deionized water under hydrothermal condition (see Supporting Information).

In contrast with most heterogeneous catalysts, our catalyst was ready for use as prepared, after filtration and drying, without any further pretreatment.

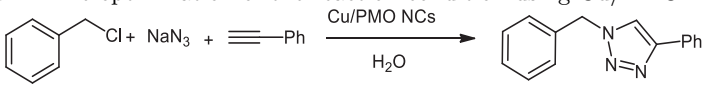
The catalyst was fully characterized by different methods, which revealed the presence of copper imprinted on the PMO (Figures 1-7 of the Supporting Information).

In order to develop an efficient protocol for the Huisgen 1,3-dipolar cycloaddition, a mixture of benzyl chloride, NaN_3, and phenyl acetylene was reacted with different amounts of catalyst, temperatures, and times (Table 1).

As can be seen, the optimized reaction conditions were 0.47 mol % of catalyst and temperature of 60 °C.

After independent optimization of the reaction conditions, different substituted organohalides was efficiently reacted with alkynes under similar conditions to afford the corresponding 1,2,3-triazoles in yields of 82%–96% (Table 2). All the 1,2,3-triazoles were isolated by crystallization. The development of Cu/PMO nanocomposite catalyst with high catalytic efficiency and reusability was our major purpose for this reaction.

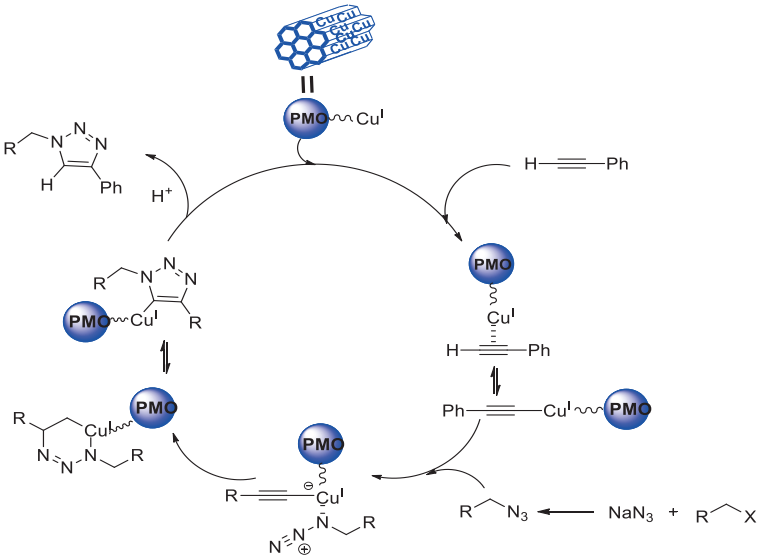
Table 1. The optimization of the reaction condition using Cu/PMO NCs.[a]



Entry	Catalyst (mol %)	Temp. (°C)	T (h)	Yield[b] (%)
1	0.30	60	3	78
2	0.35	60	2	81
3	0.40	60	1.5	84
4	0.47	60	1.5	65
5	0.47	25	1.5	65
6	0.47	90	1.5	94

[a] Reaction conditions: benzyl chloride (1 mmol), phenyl acetylene (1 mmol), NaN_3 (1.1 mmol), H_2O.
[b] Isolated yields.

The reaction mechanism in the alkyne-organoazide cycloaddition catalyzed by Cu/PMO nanocomposite arises from the formation of copper acetylides or copper π-complexes as the real intermediates. On the other hand, the formation of copper (I) triazolide complex as intermediate in the click reaction has been often postulated. Final protonolysis of this type of intermediate would render the triazole product (Scheme 2).

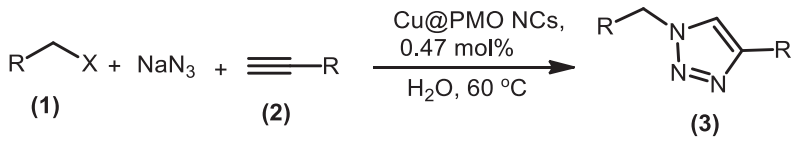


Scheme 2. Mechanistic considerations.

2.2. Compared to some of the catalysts reported

A comparative study on the reactivity of the Cu/PMO nanocomposite with the some reported catalysts of copper to the reaction of benzyl chloride, phenylacetylene, and sodium azide in the optimized condition was carried out, as summarized in Table 3. However, the Cu/PMO nanocomposite was shown to be more active, a low copper loading (0.47 mol %) and mild reaction conditions in comparison with the other catalysts (Table 3, entries 8 vs. 1–7). As can be observed from this table, much higher yields, short reaction times, a low copper loading (0.47 mol %), and mild reaction conditions were obtained for 1,2,3-triazoles with our catalyst in comparison with the other catalysts.

Table 2. Three-component 1,3-dipolar cycloaddition catalyzed by Cu/PMO nanocomposite using organic halides, sodium azide, and alkynes precursors. [a]



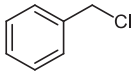
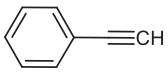
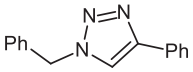
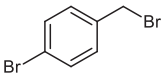
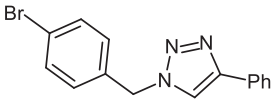
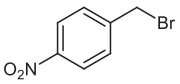
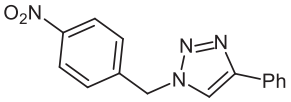
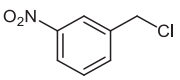
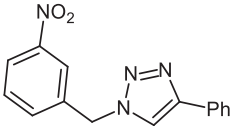
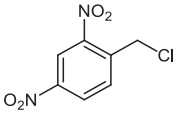
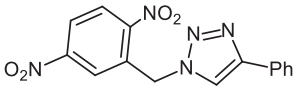
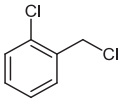
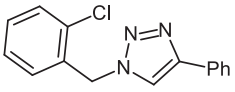
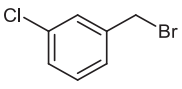
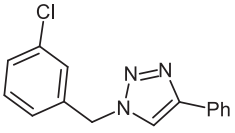
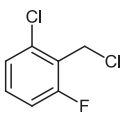
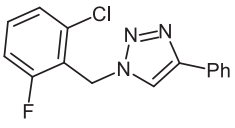
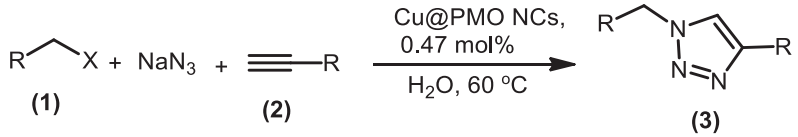
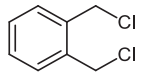
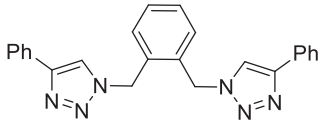
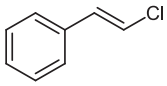
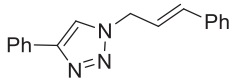
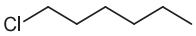
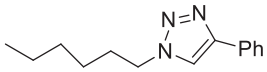
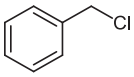
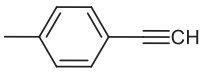
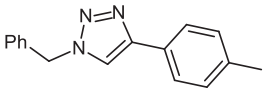
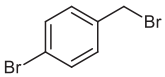
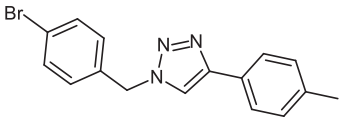
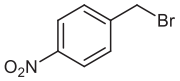
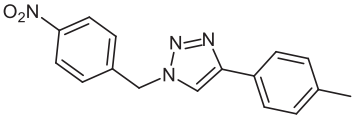
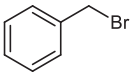
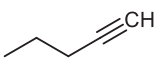
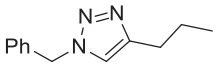
Entry	Organic halide	Alkyne	Triazole	Time (h)	Yield (%)[b]
1	 (1a)	 (2a)	 (3a)	1.5	94
2	 (1b)	(2a)	 (3b)	1.5	92
3	 (1c)	(2a)	 (3c)	1	96
4	 (1d)	(2a)	 (3d)	2	87
5	 (1e)	(2a)	 (3e)	1.5	85
6	 (1f)	(2a)	 (3f)	2	87
7	 (1g)	(2a)	 (3g)	3	84
8	 (1h)	(2a)	 (3h)	3	83

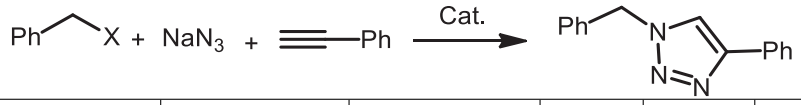
Table 2. Continued.



Entry	Organic halide	Alkyne	Triazole	Time (h)	Yield (%)[b]
9 [c]	 (1i)	(2a)	 (3i)	4	85
10	 (1j)	(2a)	 (3j)	3	89
11	 (1k)	(2a)	 (3k)	4	89
12	 (1l)	 (2b)	 (3l)	1.5	93
13	 (1m)	(2b)	 (3m)	1.5	87
14	 (1n)	(2b)	 (3n)	1.5	95
15	 (1p)	 (2c)	 (3p)	1.5	82

[a] Reaction conditions: 1 (1 mmol), 2 (1 mmol), NaN3 (1.2 mmol), and Cu/PMO nanocomposite (0.47 mol%, 50 mg).
[b] Isolated yield.
[c] 2 mmol of 2a and sodium azide.

Table 3. Synthesis of 1,2,3-triazoles catalyzed by copper on different supports.[a]



Entry	Catalyst	Cat. (mol %)	Solvent	t (°C)	T (h)	Yield (%)	Ref
1	CuNPs/C	0.5	H_2O	70	6	99	[13]
2	Cu ^{II}/HT[c]	10 (mg)	CH_3CN	rt	6	89	[17]
3	CuNPs (Et_3N) [a]	10	THF	65	10 min	98	[15]
4	Cu/Al_2O_3	10	Solvent-free	rt	1	92	[16]
5	Cu nanoclusters	0.1	H_2O/t-BuOH	25	18	99	[26]
6	CuI-USY	10	toluene	rt	15	78	[27]
7	Chitosan Schiff base-copper(I) triflate complexes	10	EtOH/H_2O	25	14	99	[28]
8	Cu@PMO NCs	0.47	H_2O	60	1.5	94	
9	Cu@PMO NCs	0.47	H_2O	rt	8	68	

[a] Reaction condition: organo azide (1 mmol) and phenylacetylene (1 mmol).

2.3. Recyclability of the catalyst

When using a supported catalyst, there is an important problem that the catalyst is readily reusable, which makes its usage an excellent alternative, especially considering environmental and economic aspects. The Cu@PMO NCs catalyst was recovered by the fitted glass filter during filtration, and it was reused in the same reaction under similar conditions without loss of catalytic activity for 6 cycles (Figure).

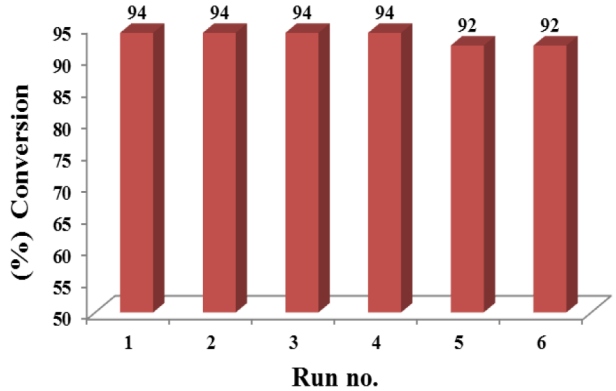


Figure. Recyclability of the Cu@PMO NCs catalytic system.

3. Conclusion

We developed a reusable Cu/PMO NCs catalyst that effectively catalyzed the Huisgen 1,3-dipolar cycloaddition of a variety of alkynes and organic azides, including the three-component cyclization of a variety of alkynes, organic halides, and sodium azide. The products were obtained in good yields with a dramatic reduction in the reaction times and the catalyst was shown to be easily recoverable from the reaction. Moreover, an important feature shown by the catalyst is that it can be reused at least six times without significant loss of activity.

4. Experimental section

All chemicals were purchased from Fluka, Merck, and Aldrich chemical companies. For recorded ^{1}H NMR and ^{13}C NMR spectra we used a Bruker DRX-400 in pure deuterated DMSO-d_6 solvent with tetramethyl silane (TMS) as the internal standard. FT-IR spectra were obtained as KBr pellets on a PerkinElmer 781 spectrophotometer and on an impact 400 Nicolet FT-IR spectrophotometer. TGA was carried out on an STA503 WinTA analyzer from 25 to 900 °C under nitrogen with a heating rate of 10 °C min^{-1}. The XRD patterns were recorded on an X-ray diffractometer (Bruker, D8 ADVANCE, Germany) using Cu-Ka radiation (λ = 0.154056 nm) in the range 2θ = 0.5–5°. The N_2 adsorption/desorption analysis (BET) was performed at –196 °C using an automated gas adsorption analyzer (Tristar 3000, Micromeritics). The scanning electron microscopy (SEM) image was recorded on a JEOL 6400 scanning electron microscope operated at 15 kV.

4.1. General procedure for the synthesis of 1,2,3-triazoles using Cu/PMO NCs

The click reaction of organohalides and alkynes was carried out with treatment of NaN_3 (72 mg, 1.1 mmol), organohalide (1 mmol), alkyne (1 mmol), and Cu/PMO NCs (10 mg, 0.47 mol %) in H_2O (3 mL). The reaction mixture was warmed to 60 °C and monitored by TLC until total conversion of the starting materials. After completion of the reaction, the reaction mixture was filtered off. In order to separate the catalyst from the products, the reaction mixture was dissolved in hot ethanol; subsequently, the whole mixture was directly passed through a sintered glass filter funnel and the excess of solvent was removed under reduced pressure to give the corresponding 1,2,3-triazole compounds (Table 1). Most of the products are known and all of the isolated products gave satisfactory IR and NMR spectra (see Supporting Information).

1-Benzyl-4-phenyl-1H-1,2,3-triazole (3a). Yield: 94%; white solid; mp: 127–129 °C; Lit. [13] (mp: = 128–130 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.82 (s, 2H, CH_2), 7.30 (m, 3H, CH Ar), 7.41 (m, 5H, CH Ar), 7.65 (s, 1H, triazole CH), 7.83 (d, 2H, Ar, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 54.2, 119.6, 125.7, 128.0, 128.2, 128.8, 129.1, 130.6, 134.7, 148.2. IR (KBr): v = 3142, 2921, 1610, 1450, 1358, 1221, 1071, 1043.

1-(4-Bromobenzyl)-4-phenyl-1H-1,2,3-triazole (3b). Yield: 92%; pale yellow solid; mp: 149–152 °C; Lit. [13] (mp: = 150–151 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.63 (s, 2H, CH_2), 7.00–7.42 (m, 5H, CH Ar), 7.56–7.57 (m, 2H, CH Ar), 7.85 (m, 2H, CH Ar), 8.60 (s, 1H, CH triazole): ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 52.8, 121.9, 122.1, 125.6, 128.4, 129.3, 130.6, 131.1, 132.1, 135.8, 147.2; IR (KBr): v = 3080, 2925, 2855, 1593, 1448, 1465, 1353, 1077, 1015, 766, 688.

1-(4-Nitrobenzyl)-4-phenyl-1H-1,2,3-triazole (3c). Yield: 96%; Green solid; mp: 140–143 °C; Lit. [13] (mp: = 140–141 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.70 (s, 2H, CH_2), 7.35–7.46 (m, 5H, CH Ar), 7.74–7.83 (m, 3H, CH Ar), 8.24 (s, 2H, CH Ar & triazole). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 52.1, 119.8, 124.3, 125.7, 128.6, 129.9, 130.1, 141.1, 148.0, 148.6; IR (KBr): v = 3080, 1605, 1520, 1465, 1346, 1219, 1110, 1075, 1046.

1-(3-Nitrobenzyl)-4-phenyl-1H-1,2,3-triazole (3d). Yield: 87%; Green solid; mp: 147–150 °C; Lit. [13] (mp: = 148-151 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.01 (s, 2H, CH_2), 7.18–7.85 (m, 6H, CH Ar), 7.87 (s, 2H, CH Ar), 7.95 (s, 1H, CH Ar), 8.18 (s, 1H, CH triazole).

1-(2,4-Dinitrobenzyl)-4-phenyl-1H-1,2,3-triazole (3e). Yield: 85%; pale yellow solid; mp: 214–218 °C; Lit. [13] (mp: = 215–217 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.17 (s, 2H, CH_2), 7.28–7.36 (m,

2H, CH Ar), 7.43–7.47 (t, 2H, CH Ar), 7.85–7.88 (d, 2H, CH Ar), 8.52–8.56 (d, 1H, CH Ar, J = 8.0 Hz), 8.65 (s, 1H, CH Ar), 8.84 (s, 1H, CH triazole). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 52.1, 119.8, 124.3, 125.7, 128.6, 129.9, 130.1, 141.1, 148.0, 148.6; IR (KBr): v = 3126, 1609, 1536, 1465, 1449, 1400, 1206, 1151, 1074.

1-(2-Chlorobenzyl)-4-phenyl-1H-1,2,3-triazole (3f). Yield: 87%; Green solid; mp: 80–83 °C; Lit. [13] (mp: = 80–83 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.81–5.85 (s, 2H, CH_2), 7.06–7.08 (d, 1H, CH Ar, J = 8.0), 7.22–7.24 (d, 1H, CH Ar, J = 8.0), 7.41–7.50 (m, 6H, CH Ar), 8.22–8.24 (2H, CH Ar & triazole). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 51.7, 121.3, 126.2, 127.4, 128.2, 129.1, 129.7, 130.2, 131.6, 132.6, 132.7, 148.0; IR (KBr): v = 3036, 2924, 1604, 1578, 1478, 1442, 1360, 1319, 1222, 1147, 1101, 1046, 999, 755, 693, 691.

1-(3-Chlorobenzyl)-4-phenyl-1H-1,2,3-triazole (3g). Yield: 84%; Green solid; mp: 90–93 °C; Lit. [13] (mp: = 91–93 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.67 (s, 2H, CH_2), 7.30 (s, 2H, CH Ar), 7.41–7.46 (m, 5H, CH Ar), 7.70–8.00 (s, 2H, CH Ar), 8.64 (s, 1H, CH triazole).

1-(2-Chloro-6-fluorobenzyl)-4-phenyl-1H-1,2,3-triazole (3h). Yield: 83%; Pale green solid; mp: 105–107 °C; Lit. [13] (mp: = 104–107 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.84 (s, 2H, CH_2), 7.35–7.63 (m, 7H, CH Ar), 8.05 (s, 2H, CH Ar). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 53.04, 115.5, 115.7, 118.8, 125.2, 127.1, 128.7, 129.4, 129.6, 129.8, 130.0, 163.38; IR (KBr): v = 3073, 2924, 1740, 1606, 1476, 1455, 1350, 766.

1,3-Bis((4-phenyl-1H-1,2,3-triazol-1-yl)methyl)benzene (3i). Yield: 85%; Green solid; mp: 110–113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.95 (s, 4H, CH_2), 7.30–7.40 (10H, CH Ar), 8.74–7.86 (4H, CH Ar), 8.29 (s, 2H, CH triazole). MS (EI) (70 eV): m/z (%) 392 (9) (M+), 364 (20), 335 (3), 290 (5), 248 (23), 219 (21), 178 (6), 146 (3), 116 (100), 89 (34), 63 (12); IR (KBr): v = 3085, 1608, 1463, 1358, 1221.

1-Cinnamyl-4-phenyl-1H-1,2,3-triazole(3j). Yield: 89%; Pale yellow solid; mp: 131–134 °C; Lit. [13] (mp: = 134 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.25–5.26 (d, 2H, CH_2, J = 4.0 Hz), 6.58–6.61 (m, 1H, CH Ar), 6.76–6.80 (d, 1H, CH Ar, J = 16.0 Hz), 7.30–7.91 (m, 10 H, CH Ar), 8.41 (s, 1H, CH triazole). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 51.4, 121.2, 123.4, 125.1, 127.7, 128.0, 128.7, 130.7, 133.7, 135.7; IR (KBr): v = 3129, 1606, 1461, 1353, 1222.

1-Hexyl (4-phenyl)-1H-1,2,3-triazole) (3k). Yield: 89%; Yellow solid; mp: 75–78 °C; Lit. [13] (mp: = 79–80 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.85 (s, 3H, CH_3), 2.12–2.47 (m, 8H, CH_2), 4.22 (m, 2H, CH_2), 7.12–7.36 (4H, CH Ar), 7.53 (2H, CH Ar & triazole); IR (KBr): v = 2921, 1733, 1458, 1375, 1262, 1081.

1-(Benzyl-4-*p*-tolyl)-1H-1,2,3-triazole) (3l). Yield: 89%; Green solid; mp: 129–130 °C; Lit. [13] (mp: = 130 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.81 (s, 3H, CH_3), 4.13 (s, 2H, CH_2), 7.29–7.40 (3H, CH Ar), 7.86 (2 H, CH Ar), 8.26 (s, 1 H, CH triazole). IR (KBr): v = 2923, 1606, 1495, 1348, 1222, 1004.

1-(4-Bromobenzyl)-4-*p*-tolyl)-1H-1,2,3-triazole) (3m). Yield: 87%; Pale yellow solid; mp: 201–203 °C; Lit. [12] (mp: = 202–204 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.28 (s, 3H, CH_3), 5.00–5.04 (d, 1H, CH_2, J = 15.0 Hz), 5.20–5.24 (d, 1H, CH_2, J = 15.0 Hz), 6.82–6.84 (d, 2 H, CH Ar), 7.00–7.04 (d, 2 H, CH Ar), 7.18–7.24 (m, 5 H, CH Ar & triazole); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 21.4, 52.0, 119.4, 123.0, 125.7, 126.2, 129.6, 129.7, 131.8, 139.2, 140.0, 148.1; IR (KBr): v = 3030, 1625, 1591, 1523, 1485, 1551, 1343, 1226, 1072, 1009, 825, 740.

1-(4-Nitrobenzyl)-4-*p*-tolyl)-1H-1,2,3-triazole) (3n). Yield: 95%; Green solid; mp: 241–243 °C; Lit. [13] (mp: = 243–245 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.25 (s, 3H, CH_3), 4.85 (s, 1H, CH_2),

5.13 (s, 1H, CH_2), 6.97 (d, 4 H, CH Ar), 7.25 (s, 3 H, CH Ar), 7.16–7.24 (s, 2 H, CH Ar & triazole); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 21.4, 52.0, 119.4, 123.0, 125.7, 126.2, 129.6, 129.7, 131.8, 139.2, 140.0, 148.1; IR (KBr): v = 2925, 1608, 1521, 1448, 1343, 1225.

1-(Benzyl-4-ethyl)-1H-1,2,3-triazole) (3p). Yield: 95%; Green solid; mp: 57–58 °C; Lit[13] (mp: = 56–58 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.95 (t, 3H, CH_3), 1.94–2.01 (q, 2H, CH_2), 4.36 (s, 2 H, CH_2), 7.27–7.44 (3 H, CH Ar), 7.75 (s, 1 H, CH triazole), 7.82–7.84 (2 H, CH Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 13.7, 22.0, 27.4, 120.6, 127.8, 128.2, 128.7, 135.0, 150.1; IR (KBr): v = 2924, 1626, 1447, 1238, 1157, 1086.

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