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Synthesis of 1,4-disubstituted 1,2,3-triazoles Catalyzed byEggshell-supported-Cu(I) Metformin Complex as aHeterogeneous Catalyst in Water

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Abstract

An efficient and eco-friendly method has been developed for the synthesis of 1,4-disubstituted 1,2,3-triazoles using the eggshell-supported-Cu(I) metformin complexas a natural and heterogeneous catalyst. The catalyst prepared is characterized by FT-IR spectroscopy, SEM, and ICP techniques. Terminal alkynes were successfully reacted with alkyl chloride and sodium azide in the presence of CuI immobilized on eggshell in water at room temperature. This method offers many advantages such as short reaction times, low cost, use of a reusable catalyst, and simple purification procedures.Moreover, the catalyst could be recovered and recycled four times.

***Keywords*:** 1,2,3-Triazole, Eggshell-supported-Cu(I) metformin, Click reaction.

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Introduction

Today, transition metals have been developed to control the regioselectivity of reactions [1-4].Copper-catalyzed azide-alkyne reactions, used to produce 1,2,3-triazoles, have become the most reported reactions known as click reactions [5-8].Sharpless*et al.* used Cu(I) salts to promote the reaction of azides with terminal alkynes to afford 1,4-disubstituted products [9].Various published procedures for CuAAC reactions favor simple copper salts like CuI, $Cu(AcO)_2$, and $CuSO_4$ as catalysts [10, 12]. Moreover, copper salts as a homogeneous catalyst have many problems such as difficult separation and recycling of the catalyst, cytotoxicity, and environmental pollution. To overcome this problem, designing a heterogeneous catalyst is a useful and applicable method. Heterogeneous catalysis supplies the opportunity for easy separation and recycling of the catalyst, minimization of the metallic waste, easy product purification, and, possibly, continuous or multiple processing of compounds. Several preparations of copper immobilized on supports such as MWCNTs [13], chitosan [14], agarose [15], silica [16], graphene [17] and polymer catalysts [18] have increasingly become more profitable from easy recovery and economical viewpoints. However, most of them suffer from some disadvantages such as low stability, significant leaching after several cycles, and difficult separation. Thus, it is necessary to develop new supports for heterogeneous catalytic systems.

Eggshell waste primarily contains calcium, magnesium carbonate, and protein [19]. In recent years, considerable effort has been made to apply eggshell as value-added products. These major applications include a coating pigment for inkjet printing paper [20],used as an active heterogeneous catalyst for biodiesel synthesis [21] and the starting material for preparing calcium phosphate bio-ceramics [22]. In organic synthesis, numerous different solvents are used. However, water, as a solvent, is rather non-toxic, safe, most eco-friendly, and most economical. At intervals, it has been proved that compared to organic solvents, water have higher reactivity and selectivity owing to the direct result of its significant hydrogen bonding potential. The above-mentioned characteristics are the real reason behind the potential of water causing it to be considered a solvent, a catalyst, and most importantly, a reactant, unlike those seen by the conventional organic solvents [23]. In continuation of our recent success in introducing new catalysts [24-26], we wish to report an efficient, safe, and green one-pot synthesis of 1,4-disubstituted 1,2,3-triazoles from benzyl chloride or alkyl halides, sodium azide, and alkynes catalyzed by eggshell-supported-Cu(I) metforminecomplex in water at 50 ºC.

Experimental

Eggshell powder preparation

Empty chicken eggshells were collected from the household and washed with warm tap water. The adhering membrane was separated manually. Then, the eggshells were washed with distilled water and dried at room temperature [27]. The clean eggshells were dried at room temperature. Then, they were crushed and milled into different particle sizes using a mortar.

Preparation of eggshell-supported Cu(I)-metformin complex

Eggshell powder (1.0 g)was added to a solution of CuI (3.0mmol, 0.60 g) in toluene (5 mL), and the mixture was refluxed for 10 h. Then, metformin (4.0mmol, 0.51 g) was added, and the reaction mixture was refluxed for 12h. The solvent was removed on a rotary evaporator, and the product was dried in an oven at 120 ºC for 10 h. The product formedwas sequentially purified by Soxhlet extraction for 10h with 100 mL of ethanol and acetonitrile to remove the residual reactants or complexes physically adsorbed on the external surface of thematerial. Finally, the solvent was removed on a rotary evaporator, and the product was dried in an oven at 120 ºC for 10 h.Elementary analysis indicated that the nitrogen content was 1.42% (0.2 mmol of metformin/g), and the copper content of eggshell-supported Cu(I)-metformin complex determined by inductively coupled plasma (ICP), was obtained to be 0.95 % (0.15mmol/g).

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

A test tube was charged with an organic halide (1.0 mmol), NaN_3 (1.0 mmol), a terminal alkyne (1.0 mmol), eggshell-supported Cu(I)-metformin complex catalyst (0.28 g, 0.04mmol of Cu), and water (3.0 mL). The mixture was stirred at 50 ºC. Upon completion of the reaction (monitored by TLC), the mixture was extracted using $CHCl_3$ (2×5 mL). The combined organic layers were dried using $MgSO_4$ and evaporated. The residue was finally purified by crystallization from EtOH to give the desired product (Table 2).

(1-(2-chlorobenzyl)-1H-1,2,3-triazol-4-phenyl (4b)

FT-IR (KBr): $\bar{\nu}$ = 3310, 2990, 1580, 1420 cm^{-1}**,** ^{1}HNMR ($CDCl_3$, 300 MHz):δ 5.7 (s, 2H, CH_2), 7.23-7.32 (m, 2H, CH of aromatic), 7.34-7.41 (m, 2H, CH of aromatic), 7.43-7.49 (m, 3H, CH of aromatic), 7.80 (s, 1H, CH of triazol), 7.85 (d, 2H, *J*=5.7 Hz, CH of aromatic).

(1-(2-chlorobenzyl)-1H-1,2,3-triazol-4-yl)methanol (4e)

FT-IR (KBr): $\bar{\nu}$ = 3216, 3104, 2969, 1600, 1472-1586, 678-764 cm^{-1}; ^{1}HNMR ($CDCl_3$, 300 MHz): δ 4.80 (s, 2H, CH_2)**,** 5.68(s, 2H, CH_2), 7.21-7.36 (m, 3H, CH of aromatic),7.44 (d, 1H, *J*=7.8 Hz, CH of aromatic), 7.59 (s, 1H, CH of triazol).

(1-(4-chlorobenzyl)-1H-1,2,3-triazol-4-yl)methanol (4f)

FT-IR (KBr): $\bar{\nu}$ = 3280, 3050, 2983, 1521, 1491, 844, 777 cm^{-1}; ^{1}HNMR ($CDCl_3$, 300 MHz): δ 4.78 (s, 2H, CH_2), 5.50 (s, 2H, CH_2), 7.21 (d, 2H, *J*=8.1 Hz, CH of aromatic), 7.34 (d, 2H, *J*=8.1 Hz, CH of aromatic), 7.49 (s, 1H, CH of triazol); ^{13}C NMR (75 MHz $CDCl_3$): δ 53.4, 56.2, 121.7, 129.3, 129.4, 133.0, 134.8; Anal. Calcd. for $C_{10}H_{10}ClN_3O$: C, 53.70; H, 4.51; N, 18.79. Found: C, 53.88; H, 4.59; N, 18.94.

(1-(4-methylbenzyl)-1H-1,2,3-triazol-4-yl)methanol (4g)

FT-IR (KBr): $\bar{\nu}$ = 3230, 3110, 2990, 1560, 1420 cm^{-1}; ^{1}HNMR ($CDCl_3$, 300 MHz): δ 2.36 (s, 3H, CH_3)**,** 4.77 (s, 2H, CH_2), 5.48 (s, 2H, CH_2), 7.19-7.20 (m, 4H, CH of aromatic), 7.48 (s, 1H, CH of triazol).

2-(1-(2-chlorobenzyl)-1H-1,2,3-triazol-4-yl)propan-2-ol(4k)

FT-IR (KBr): $\bar{\nu}$ = 3290, 3110, 2997, 1580, 1440, 826, 761 cm^{-1}; ^{1}HNMR ($CDCl_3$, 300 MHz): δ 1.64 (s, 6H, $2CH_3$), 2.78 (s, 1H, OH), 5.65 (s, 2H, CH_2), 7.18 (d, 1H, *J*=7.5 Hz, CH of aromatic), 7.25-7.35 (m, 2H, CH of aromatic), 7.43 (d, 1H, *J*=7.8 Hz, CH of aromatic), 7.50 (s, 1H, CH of triazol); ^{13}C NMR (75 MHz $CDCl_3$): δ 30.4, 51.3, 68.5, 119.4, 127.6, 129.9, 130.2, 130.3, 132.5, 133.4, 156.0; Anal. Calcd. for $C_{12}H_{14}ClN_3O$: C, 57.26; H, 5.61; N, 16.69; Found: C, 57.44; H, 5.70; N, 16.85

2-(1-(4-chlorobenzyl)-1H-1,2,3-triazol-4-yl)propan-2-ol (4l)

FT-IR (KBr): $\bar{\nu}$ = 3314, 3100, 2960, 1610, 1480, 826, 761 cm^{-1}; ^{1}HNMR ($CDCl_3$, 300 MHz): δ 1.63 (s, 6H, $2CH_3$), 5.48 (s, 2H, CH_2), 7.21 (d, 2H, *J*=8.4 Hz, CH of aromatic), 7.28 (s, 1H, CH of triazol),7.35 (d, 1H, *J*=8.4 Hz, CH of aromatic); ^{13}C NMR (75 MHz $CDCl_3$): δ 30.4, 53.3, 68.5, 119.1, 129.2, 129.4, 133.1, 134.7, 156.3; Anal. Calcd. for $C_{12}H_{14}ClN_3O$: C, 57.26; H, 5.61; N, 16.69; Found: C, 57.06; H, 5.52; N, 16.84.

2-(1-(4-methylbenzyl)-1H-1,2,3-triazol-4-yl)propan-2-ol (4m)

FT-IR (KBr): $\bar{\nu}$ = 3310, 2970, 1580, 1440, 760, 698 cm^{-1}; ^{1}HNMR ($CDCl_3$, 300 MHz): δ 1.62 (s, 6H, $2CH_3$), 2.37 (s, 3H, CH_3), 2.63 (s, 1H, OH), 5.46 (s, 2H, CH_2), 7.20-7.28 (m, 4H, CH of

aromatic), 7.35 (s, 1H, CH of triazol); ^{13}C NMR (75 MHz $CDCl_3$): δ 21.1, 30.4, 53.9, 68.5, 118.9, 128.2, 129.7, 131.6, 136.6, 156.0; Anal. Calcd. for $C_{13}H_{17}N_3O$: C, 67.51; H, 7.41; N, 18.17; Found: C, 67.69; H, 7.50; N, 18.01.

Results and discussion

A comparison made between the FT-IR spectrum of the eggshell-supported Cu(I)-metformin complex and eggshell demonstrated the presence of the complex inside the eggshell cavities and pores.The IR spectrum for the eggshell showed major adsorption bands at 3431, 2873, 2517, 1421, 875, and 710 cm^{-1}; the characteristic strong phosphate and carbonate bands with absorbed H_2O were observed in the IR spectrum (Figure 1a).

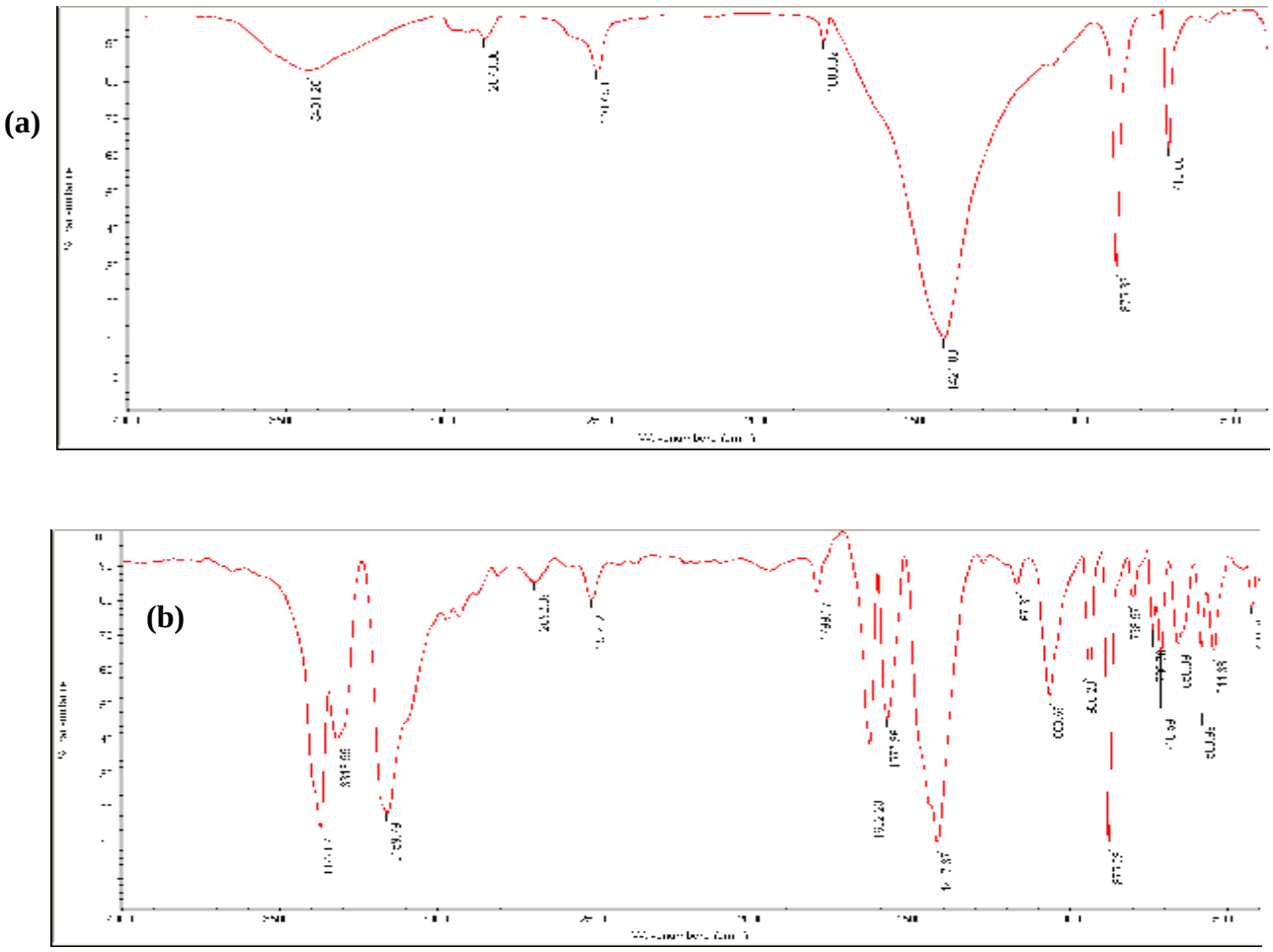


Figure 1. FT-IR spectrum for eggshell.

As expected, the band related to the stretching vibration ν(OH) of uncoordinated H_2O was observed at approximately ~3000 cm^{-1}. A broad band at around 3431 cm^{-1} shows the presence of absorbed

H_2O. The broad band at this region results from overlapping of the hydrogen vibrations in the phosphate group: stretching vibrations of structural–OH and absorbed H_2O. A low intensity band could be observed at 710 cm^{-1}, which was due to the stretching vibration of the P–OH group [28]. In addition, a strong broad band was observed at 1421 cm^{-1}, which was assigned to the stretching vibration of the C–O group. Moreover, an out-of-plane vibration for δ(OCO) was observed at 875 cm^{-1} as a strong band. A medium broad band at 2517 cm^{-1} shows the presence of HCO_3. The data confirm the presence of $CaCO_3$ in the eggshell powder [29]. The IR spectra for the eggshell supported-Cu(I) metformin complex show major bands at 3159 cm^{-1} ν(N-H), 1622 cm^{-1}ν(C=N), and 1577 cm-1 ν(C=C), which are absent in the eggshell IR spectrum (Figure 1b). The scanning electron micrograph (SEM) analysis is another useful tool used to analyze the surface morphology of a catalyst. Figure 2 shows the SEM images of the eggshell catalyst illustrating its porous nature. In general, the high porosity of the microporous eggshell powder provides a large contact area to catalyze the reaction. The presence of Cu(I) metformin complex caused changes demonstrated by the change in the particle size of the eggshell powder and roughness of its surface.

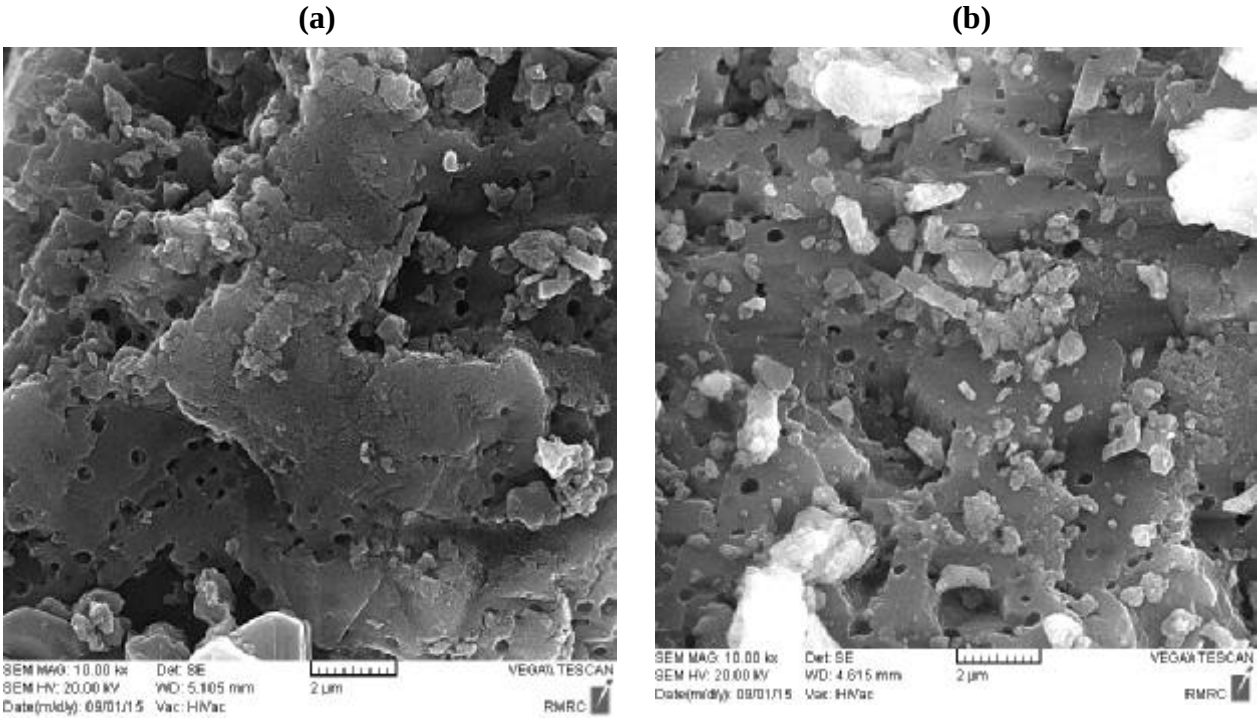
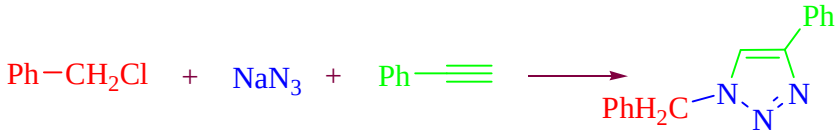


Figure 2. SEMs for eggshell (a) and eggshell-supported-Cu(I)-metformin (b).

To test the catalytic activity of eggshell-supported-Cu(I)-metformin complex in the synthesis of 1,4-disubstituted 1,2,3-triazoles, the reaction between benzyl chloride, sodium azide and phenylacetylene was selected as a model reaction to optimize the reaction conditions, and the results obtained were tabulated in Table 1. The reactions were performed using various solvents,

using H_2O, DMF, CH_3CN, EtOH, THF, toluene, 1,4-dioxane, and in solvent-free conditions at 50 ºC (Table 1). As Table 1 shows, the highest reaction yield was obtained when H_2O was used as the solvent (Table 1, entry 1). To our surprise, the reactions produced lower yields when they were performed under solvent-free conditions (Table 1, entry 8).

Table 1. Optimization of reaction conditions for the synthesis of **4a**[a].



1a **2** **3** **4a**

Entry	Catalyst (g/mol % of Cu)	Solvent	Reaction temp. (°C)	Reaction time (h)	Yield (%)[b]
1	0.27/4	H_2O	50	1	98
2	0.27/4	DMF	50	1	56
3	0.27/4	CH_3CN	50	1	35
4	0.27/4	EtOH	50	1	60
5	0.27/4	THF	50	1	20
6	0.27/4	Toluene	٥٠	1	23
7	0.27/4	1,4-dioxane	50	1	15
8	0.27/4	Solvent-free	50	1	10
9	0.14/2	H_2O	50	5	60
10	0.4/6	H_2O	٥٠	1	98
11	0.27/4	H_2O	RT	10	55
12	0.27/4	H_2O	70	1	97
13	Eggshell (0.27 g)	H_2O	50	24	trace
14	CuI (0.04mmol)	H_2O	50	10	52
15	Eggshell (0.27 g) + CuI (0.04 mmol)	H_2O	50	10	70

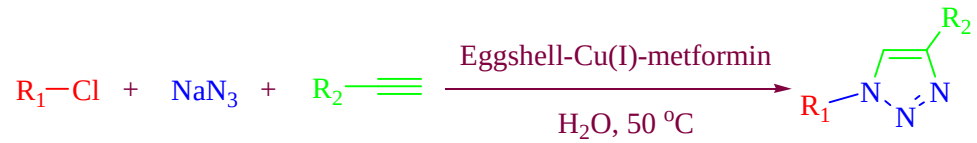
[a]Reaction conditions: benzyl chloride (1.0 mmol), sodium azide (1.0 mmol), phenyl acetylene (1.0 mmol).
[b]Isolated yield.

As Table 1 shows, the concentration of the catalytic copper was optimized. Decrease of the loading of the catalyst to 2 mol% lowered the reaction yield dramatically (Table1, entry 9). However, increase of the amount of catalyst to 6 mol% only shortened the reaction time and did not have any effect on the reaction yield (Table 1, entry 10).Furthermore, the effect of temperature on the conversion was studied. At room temperature and 4 mol% catalyst, the reaction had a low reaction yield (Table 1, entry 11).Increase of the temperature did not improve the reaction yield (Table 1, entry 12). In addition, only a trace amount of the desired product **4a** was obtained when the reaction

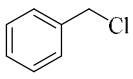
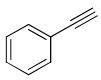
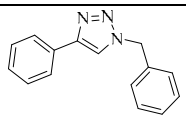
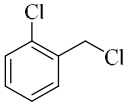
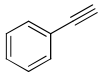
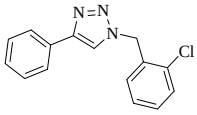
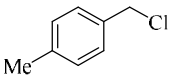
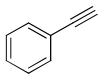
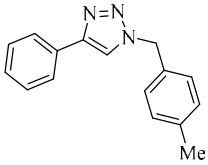
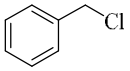
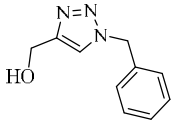
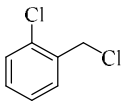
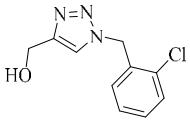
was carried out with eggshell powder (Table 1, entry 13). When the reactions were carried out with CuI alone, leading to poor reaction yields (Table 1, entry 14), while a moderate yield was observed using CuI with eggshell (Table 1, entry 15).

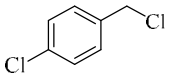
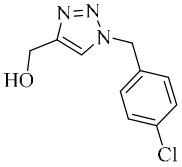
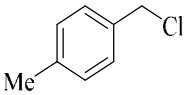
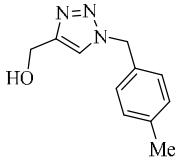
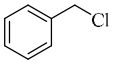
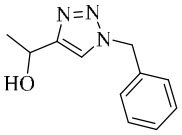
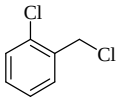
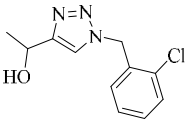
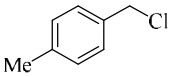
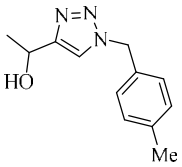
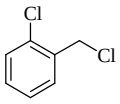
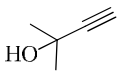
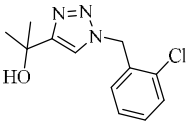
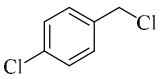
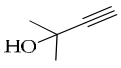
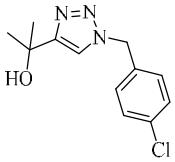
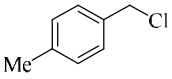
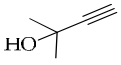
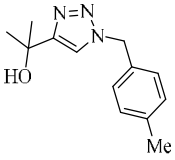
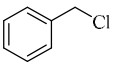
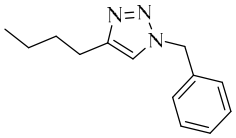
Considering the optimal conditions, the scope of the eggshell-supported Cu(I)-metformin complex catalyzed one-pot CuAAC reactions was investigated for various benzyl chlorides and alkynes. Table 2 presents a summary of the results. The corresponding 1,4-disubstituted 1,2,3-triazoles were isolated as the target products in good yields under reaction conditions from the reaction of benzyl chloride with various terminal alkynes such as phenylacetylene, hexyne, and propargyl alcohols. As Table 2 shows, the steric effects of the substituents at the *ortho*-position of the benzyl chlorides did not have clear effects on the reaction yields.

Table 2. One-pot synthesis of 1,4-disubstituted 1,2,3-triazoles from alkyl cholorides, sodium azide, and alkynes.



1 **2** **3** **4**

Entry	Alkyl choloride	Alkyne	Time (min)	Product	Yield[b] (%)	Mp. (°C)	Lit. [Ref.]
1			۶۰	 **4a**	98	128-130	1127-129 [30]
2			۶۰	 **4b**	87	85-87	88-90 [31]
3			۶۰	 **4c**	۸۸	106-108	106-108 [32]
4			60	 **4d**	91	74-76	78-80 [33]
5			۶۰	 **4e**	78	112-114	110-112 [30]

6			90	 **4f**	91	79-80	This work
7			65	 **4g**	86	83-85	86-88 [34]
8			90	 **4h**	80	78-80	81-83 [35]
9			60	 **4i**	82	58-60	59-61 [30]
10			90	 **4j**	90	47-49	47-49 [36]
11			۹۵	 **4k**	۹۲	100-102	This work
12			60	 **4l**	90	97-99	This work
13			85	 **4m**	93	95-97	This work
14			120	 **4n**	83	61-62	60-62 [37]

[a]Reaction conditions: benzyl chloride derivatives (1.0 mmol), alkyne (1.0 mmol), sodium azide (1.2 mmol), catalyst (0.27g), H_2O (3 mL), 50 °C.[b]Isolated yield.

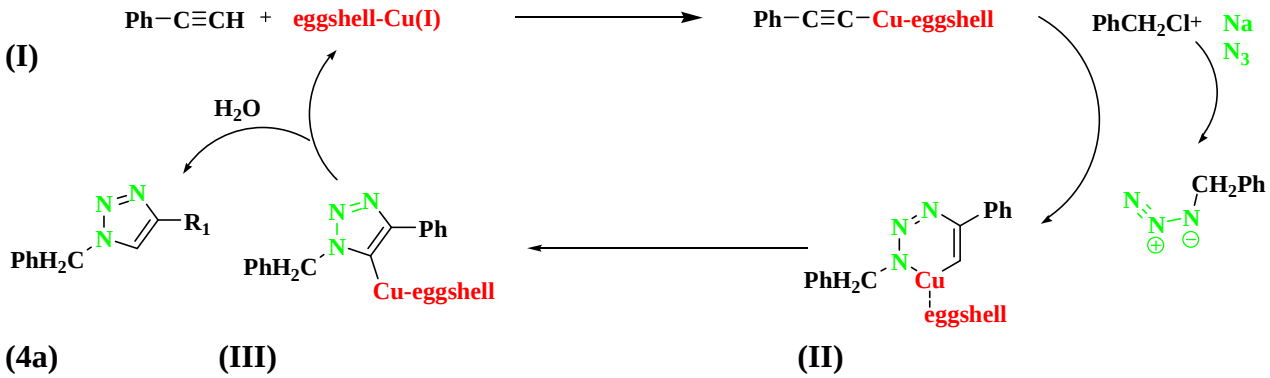
We also investigated the recyclability of eggshell-supported-Cu(I)-metformin complex using the reaction of benzyl chloride, phenylacetylene, and sodium azide, inwater at 50 °C. As Table 3 shows, the catalyst was recovered by a simple filtration and reused over 4 runswith some decrease in the catalytic activity of the catalyst.

Table 3. Synthesis of 1,2,3-triazol **4a** catalyzed by recycled catalyst[a].

Entry	Catalyst	Yield[b]
1	first run	98
2	second run	95
3	third run	91
4	fourth run	88

[a]Reaction conditions: benzyl chloride (1.0 mmol), phenylacetylene(1.0 mmol), sodium azide(1.2 mmol), H_2O(3 mL), 50 °C.
[b]Isolate yield.

A proposed mechanism for the synthesis of 1,2,3-triazole **4a** from benzyl chloride, sodium azide, and phenyl acetylene catalyzed by eggshell-supported-Cu(I)-metformin complex is shown in Scheme 1; a) formation of copper(I) acetylide (I); b) the first C–bond formation affords the six-membered ring copper metallacycle B; c) cyclization takes place to yield the copper triazoleintermediate C; d) proteolysis of the Cu–C bond gives the triazole product, and regenerates the catalyst.



Scheme 1. Proposed mechanism.

A comparative study of the reaction conditions for the synthesis of 1,2,3-triazole **4a** using the methods given in table 4 demonstrates that the proposed protocol is actually better than several other ones. Most of the listed methodologies suffer from some limitations such as long reaction times, harsh reactions, and use of organic solvents.

Table 4. Comparison of the results obtained with previously reported data for the synthesis of **4a**.

Entry	Catalyst (mmol)	Reaction conditions	Reaction time	Yield (%) [ref.]
1	$CuSO_4$ (0.1)	t-BuOH/H_2O, 65 °C	6 h	96 [35]
2	$CuFe_2O_4$ (0.05)	H_2O, 70 °C	3 h	93 [30]
3	Cu-Al_2O_3 (0.06)	H_2O, RT	8 h	92 [38]
4	CuO (0.003)	DMSO, 150 °C	3 h	100 [39]
5	CuNPs (0.1)	THF, 65 °C	10 min	98 [37]
6	SiO_2-CuI (0.5)	EtOH, 78 °C	24 h	91 [40]
7	Eggshell-CuI	H_2O, RT	10 h	85 [This work]

Conclusion

An efficient eggshell-supported-Cu(I)-metformin catalyst was synthesized and applied for clean, and facile synthesis of 1,4-disubstituted 1, 2, 3-triazoles. Cleaner reaction profile, simple, high-to-excellent yields, shorter reaction times, green solvent and easy work-up make this present method an interesting alternative to homogeneous catalysts.

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