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Multicomponent click reaction catalyzed by organic surfactant-free copper sulfide (sf-CuS) nano/micro flowers

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ABSTRACT

The azide-alkyne cycloaddition (Huisgen reaction) is one of the most powerful and widely used copper-mediated reactions. In many such reactions, use of metal or metal oxide nanoparticles as the catalyst is more appealing because of the increased catalytic activity attributed to the large surface to volume ratio. However, the nano/micro particles are synthesized often in the presence of long chain organic molecules as capping or stabilizing agents. These organic molecules cover the active centers and restrict or reduce their catalytic activity. Therefore, we have synthesized the copper sulfide (sf-CuS) nano/micro particles without having organic surfactant molecules as the capping agent. These particles with a flower-like architecture (micro flowers, **mf**) were obtained readily under the supersaturated condition at room temperature. In these particles, the surface was freely available for adsorption and desorption reactions. When utilized as a catalyst in multicomponent cycloaddition reactions, the sf-CuS **mf** exhibited excellent catalytic activity compared with some other nanoparticles with surfactants. This sf-CuS **mf** catalyzed the one-pot synthesis of 1,2,3-triazole and β-hydroxy-1,2,3-triazole effectively from a variety of benzyl bromide derivatives epoxides respectively. Both these reactions proceeded in the presence of azide and phenylacetylene in the water at room temperature. The catalyst was reusable, and there was no catalyst leaching observed during reactions. Synthesis of β-hydroxy triazoles and 1,2,3-triazoles under exceptionally mild conditions with high yields proved the sf-CuS **mf** as the catalyst as a robust and recyclable catalyst.

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1. Introduction

Synthesis of nano/micro particles is fascinating in organic chemistry since they are used as heterogeneous catalysts in organic reactions. The capping agents or surfactants that are used commonly in the synthesis of metal chalcogenides nanoparticles are; amines (hexadecyl amine, alkyl amine), oleic acid, polymers (PVP, PMMA), thiols (do-decane thiol, 1, 6-hexane dithiol) [1–3]. However, the collective properties of nanomaterials are not utilized fully [4–9] because of the presence of organic surfactant molecules around the nano/micro particles that are synthesized *via* conventional chemical synthetic methods. When the metal nano/micro particles are used as a catalyst, the chemical reaction occurs on the surface of the particles. The presence of capping molecules would hide the active centers and restrict or reduce the catalytic activity so that capping agents or surfactant molecules around the particles may contribute negatively to the target applications [10].

In recent years metal is decorated on nanomaterials and these materials are used as heterogeneous catalysts in organic reactions such as heck reaction (Pd/CuO) [11], Suzuki cross-coupling reaction (Pd–CuO@Hol S-1) [12], Sonagashira coupling reaction (Cu/CuO) [13], Heisenberg 1, 3-dipolar reaction (CuNPs/MagSilica) [14], copper(I)-catalyzed synthesis of azoles by Sharpless [15], copper(I)-catalyzed azide-alkyne [3 + 2] cycloaddition by Sharpless and Finn [16] and so on. The substituted triazoles are exciting materials in organic synthesis, coordination chemistry, and N-heterocyclic chemistry [17–21]. Substituted triazoles play an essential role in opening calcium channels in cells, particularly [22] at 1 and 4 positions of triazole. They also show biological activities as anti-cancer, anti-HIV therapy, anti-bacterial [23–27] and anti-allergy molecules [28–30]. Agricultural and industrial applications of such compounds include herbicides, fungicides, agrochemicals [31], optical brighteners [32], fluorescence chemosensory [33] corrosion retarding agents, dyes, and solar cells [34–37]. Further, the heterocyclic compounds that are rich in nitrogen atoms can be

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used as high energy materials [38].

The formation of 1,2,3-triazole derivatives is known to proceed through heisenbug 1,3-dipolar cycloaddition of organic azides and alkynes using CuAAC as a catalyst [38–41]. In recent years, multicomponent click synthesis of 1,2,3-triazoles from both *in-situ* azidolysis of benzyl halide in the presence of alkynes and β-hydroxy-1,2,3-triazoles *via in-situ* azidolysis of epoxides in the presence of alkynes have been developed [42–44]. Some heterogeneous catalysts used in the dipolar cycloaddition are polyurea encapsulated copper(I) chloride [45], CuNP/C [46], $CuFe_2O_4$, [47] Cu/Cu_2O [48], [AQ_2Cu(II)-$APSiO_2$] [49], copper(I)@phosphorated SiO_2 [50] SiO_2–CuI [51], Clay–Cu(II)/$NH_2NH_2 \cdot H_2O$ [52], GO@PTA-Cu [53] and copper(I) in ionic liquids [54]. Albeit several catalytic systems have been used for dipolar cycloaddition, in pursuit of catalyst working under mild condition and developing simple method of production of nano catalyst, we have synthesized surfactant-free copper sulfide (sf-CuS) particles having micro flower (**mf**) like architecture formed by the self-assembly of nanoparticles.

Herein, we report the synthesis of surfactant-free copper sulfide micro flowers (**sf-CuS mf)** in an efficient and straightforward synthetic process, and its practical use in the synthesis of both benzyl halide linked 1,2,3- triazoles and β-hydroxy- 1,2,3-triazoles *via* dipolar cycloaddition of azide and alkyne in the presence of benzyl halide and epoxide. The synthesis described here was performed in water, and so it was safer, greener, and used inexpensive, recyclable surfactant free heterogeneous catalyst. The above synthetic procedure satisfied the most of green chemistry principles such as (a) one-pot multicomponent synthesis (atom economy) (b) reactions in a water medium (green solvent) (c) using of readily separable and recyclable heterogeneous catalyst (d) involving simple workup procedure.

2. Results and discussion

In recent times, the azide-alkyne cycloaddition (Huisgen reaction) has emerged as one of the most powerful and widely utilized copper-mediated reactions. However, many reactions catalyzed by metal or metal oxide nanoparticles are more appealing because of the increased catalytic activity attributed to the large surface to volume ratio. In general, the nano/micro particles used as the catalyst are produced in the presence of long chain organic molecules as capping or stabilizing agents. These capping agents on the nano/micro particles cover the active centers and restrict or reduce their catalytic activity. To outwit this problem, we have developed a method of synthesis of metal chalcogenides without capping agent so that the catalyst surface is freely available for adsorption and desorption reactions [10].

In the present work, we have prepared surfactant-free copper sulfide (**sf-CuS)** under the supersaturated condition in a simple chemical reaction wherein sulphur was dissolved while $LiBH_4$ and $Cu(CH_3COO)_2 \cdot H_2O$ were suspended in dry tetrahydrofuran (THF). The reaction was conducted for 1 h at room temperature and in an inert atmosphere to avoid any oxidation. The partial solubility of the metal source and fast reactivity in the presence of $LiBH_4$ provided a thermodynamically favorable condition [55] which induced the nucleation of particles. Since the reaction was at room temperature, the digestion process was avoided [56–60], which supplemented the formation of black powder of CuS having nano/micro flower like architecture. These micron-sized flower-like particles (**mf**) were formed by the self-assembly of nanoflakes [61]. These metal chalcogenide **mf** were formed under the supersaturated condition, and no surfactant molecules were used during synthesis. The particles were stable, and no agglomeration [10] was observed. The material was characterized by PXRD, SEM, and spectroscopic techniques (Fig. 1) [10]. Since no organic surfactant molecules were surrounding the particles, the catalyst surface was freely available for reactions and that significantly favored high activity in the reactions of click chemistry and epoxy ring opening.

The catalytic activity of sf-CuS **mf** having the unhindered surface in the multicomponent synthesis of 1, 2, 3-triazoles in the dipolar cycloaddition reactions was investigated. The experiments began with optimizing the reaction conditions for the multicomponent synthesis of 1, 2, 3-triazoles from benzyl halide, sodium azide and phenylacetylene (Scheme 1). Later the reaction was extended to the synthesis of β-hydroxy 1, 2, 3-triazoles from epoxy derivatives, sodium azide and phenylacetylene (Scheme 2). This reaction proceeded *via in-situ* ring opening of epoxides followed by the reaction with phenylacetylene. In both reactions, water was used as the solvent at room temperature. The results were very encouraging since the reactions completed in 5–12 h, and yielded of the desired products quantitatively.

In order to optimize the reaction conditions, the reactions were performed by varying the quantity of catalyst and using different solvents. Progress the reaction was monitored by means of TLC. At the end of the reaction, the catalyst was separated by filtration and worked up using ethyl acetate and water. There was no difference in yield and reaction time when catalyst loading was reduced to 15 mg, 10 mg, and 5 mg. However, when 2 mg of the catalyst was used, it required a longer time for the completion of the reaction (above 12 h). Consequently, it was decided to use 5 mg of the catalyst for further studies. Similarly, few more reactions were performed in various solvents to choose the medium of the reaction (Table 1). In DMF 45%, DMSO 20% yield was obtained. Among all solvents tried, water was the best solvent to produce the products in good yields. Other than these solvents no product spot was observed in TLC. Therefore, water was chosen as the reaction

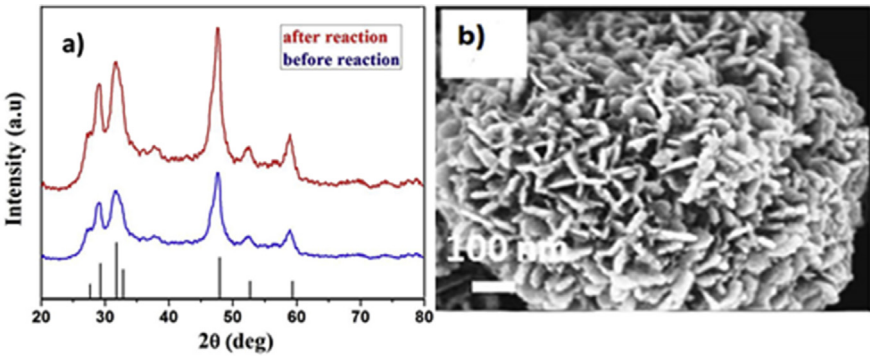
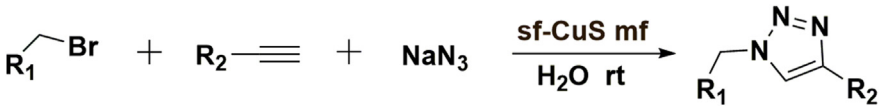
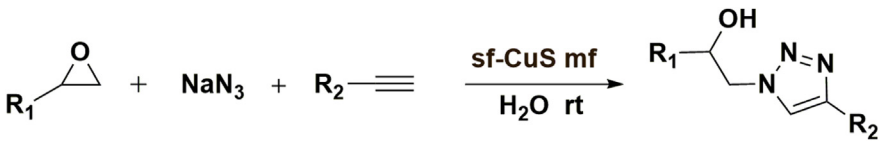


Fig. 1. (a) X-ray diffraction of sf-CuS mf, (b) SEM images of sf-CuS mf.



Scheme 1. Three component syntheis of 1,2,3-triazoles from organic halides catalysed by sf-CuS mf.



Scheme 2. Three component syntheis of β-hydroxy-1,2,3-triazoles from expoxides catalysed by sf-CuS mf in water.

Table 1
Solvent optimization of for the synthesis of Scheme 1 in the model reaction.

Entry	Solvent	time	Yield
1	CH_3OH	24 h	no
2	n-butanol	24 h	no
3	CH_3CN	24 h	no
4	$CHCl_2$	24 h	no
5	$CHCl_3$	24 h	no
6	DMSO	24 h	20%
7	DMF	24 h	45%
8	H_2O	6 h	92%

medium for all reactions.

Different benzyl bromides substituted with halides and methyl were reacted with sodium azide and terminal alkynes to form 1,2,3-triazoles using **sf-CuS mf** as catalyst under optimized condition (Table 2). Similarly, a series of different aryl epoxy, cyclic epoxy and alkyl-substituted epoxy derivatives, sodium azide, and terminal alkynes to form *β*-hydroxy 1,2,3- triazole using **sf-CuS mf** as catalyst and water as solvent at room temperature (Table 3). The crude products from all reactions were purified by column chromatography and then characterized by ^1H and ^{13}C NMR spectral data (Figs. S1–S18). Almost all these reactions (except Table 2, entries 3, 4 and 5) yielded the corresponding product in more 90% yield in water as the solvent.

Though many catalysts are known, the **sf-CuS mf** used here was obtained in a simple reaction condition, and the products were obtained in excellent yield. The performance of the various catalysts in the model reaction (styrene oxide, sodium azide, and phenylacetylene) was compared (Table 4) to understand the effect of **sf-CuS** micro flowers as the catalyst. Most of those catalysts were used at above 60 °C except for Cu/Cu_2O while our CuS was working at the room temperature (This work). Further, most of the literature on Scheme 1 type model reaction was only within benzyl azide and phenylacetylene (two reactants) whereas we are presenting the catalyst which can work in multicomponent reactions.

Leaching study was performed to confirm the heterogeneous catalysis for the reaction shown in Scheme 1. For this purpose, a reaction was stopped after the formation of around 20% product, and the catalyst was separated from the reaction mixture. The reaction was continued without the catalyst for 8 h, but no considerable product formation was observed. This observation explained that the reaction was working under heterogeneous catalysis.

The lifetime of the catalyst and its reusability play an essential role in the practical applications of such heterogeneous systems. In order to take advantage of heterogeneous nature of our catalyst, a set of experiments were performed in which both 1,2,3-triazole from *in-situ* azidolysis of benzyl halide in the presence of alkynes (Scheme 1) and epoxy ring opening followed by cycloaddition of azide (Scheme 2) and phenylacetylene using the recycled **sf-CuS mf**. After the completion of the first reaction, the product was extracted using ethyl acetate, and the catalyst was recovered by simple decantation and dried at 50 °C. A new reaction was performed with new reactants under the same conditions using the recovered **sf-CuS mf**. We have also performed a recycling experiment in Scheme 1 using 5 mmol of reagents. After completion of the reaction, the catalyst was recovered and reused for the next cycle thus confirming that **sf-CuS mf** could be reused for five times with little change in its activity (Fig. 2).

2.1. Experimental procedure

2.1.1. Synthesis of catalyst (sf-CuS)

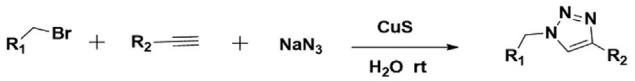
Sulphur (40 mg, 1.3 mmol) was dissolved in 15 mL of dry tetrahydrofuran (THF) in a 50 mL two neck RB flask, to that $LiBH_4$ (59 mg, 2.5 mmol) and $Cu(CH_3COO)_2 \cdot H_2O$ (250 mg, 1.2 mmol) were added. The reaction mixture was stirred at room temperature under nitrogen atmosphere for 1 h. Initially, the color of the solution was dark brown, and after the completion of reaction it turned to dark green along with the evolution of gaseous side product(s). After 1 h, volatile side products and solvent were removed by applying high vacuum. The obtained crude product was washed with methanol (40 mL) followed by THF (40 mL) to remove side products (copper acetate, lithium salt) and unreacted S, and then centrifuged. The residue was dried under vacuum for 6 h to get catalyst as a black powder of **sf-CuS** micro flowers. The catalyst was characterized by PXRD and SEM techniques.

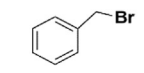
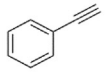
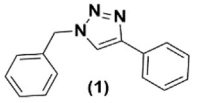
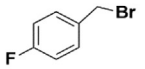
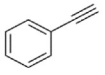
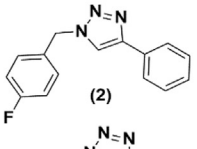
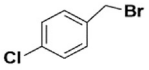
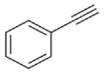
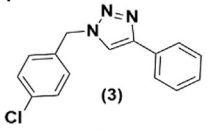
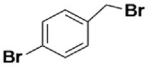
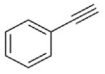
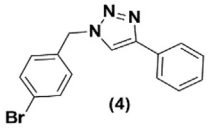
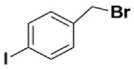
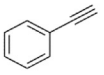
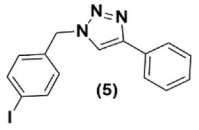
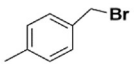
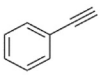
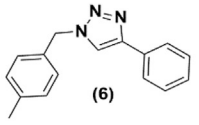
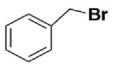
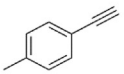
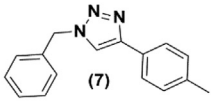
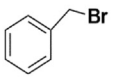
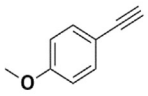
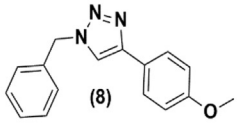
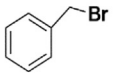
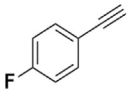
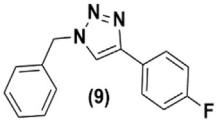
2.1.2. Synthesis of 1, 2, 3-triazole from benzyl bromide derivatives, sodium azide and alkyne

NaN_3 (65 mg, 1.0 mmol), the benzyl bromide (1 mmol), and the alkyne (1 mmol) were added to a suspension of sf-**CuS** (5 mg) in water. The reaction mixture was stirred at room temperature and monitored by TLC until all the starting materials were converted to products. The solid was obtained by filtration and washed by DCM (3 × 10 mL). The ex-traction of aqueous phase with DCM was also performed without loss of product, and collected organic phase were dried with anhydrous Na_2SO_4, and concentrated in vacuum. The product was purified through a silica gel column chromatography as corresponding *β*-hydroxy 1, 2, 3-triazoles. All the products were confirmed by usual spectral methods (^1H NMR, ^{13}C NMR) (*see* Supporting Information S1–S9).

For example: **1-benzyl-4-phenyl-1H-1, 2, 3-triazole:** white solid, mp:128–129 °C; ^1H NMR (500 MHz, $CDCl_3$) $\delta = 7.83–7.81$ (m, 2H), 7.68 (s, 1H), 7.43–7.38 (m, 5H) 7.35–7.32 (m, 3H), 5.59 (s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) $\delta = 148.2, 134.6, 130.5, 129.1, 128.8, 128.1, 128.0, 125.7, 119.4$ and 54.2., HRMS calculated for $C_{15}H_{13}N_3$ $[M+H]^+$: 236.1182, found: 236.1184. (See Supporting Information S1).

Table 2
Synthesis of 1, 2, 3 triazole derivatives by CuS.



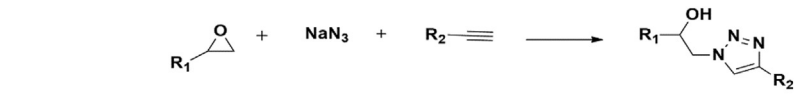
Entry	benzyl bromide (R1)	alkyne (R2)	time	product	yield%
1			6h	 (1)	96%
2			5h	 (2)	95%
3			7h	 (3)	92%
4			9h	 (4)	90%
5			12h	 (5)	87%
6			8h	 (6)	92%
7			6h	 (7)	95%
8			6h	 (8)	96%
9			5h	 (9)	97%

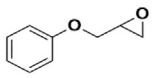
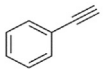
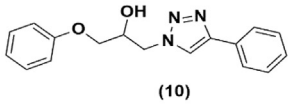
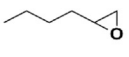
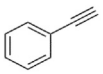
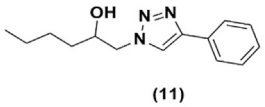
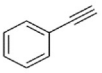
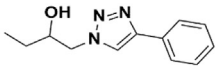
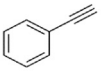
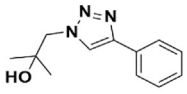
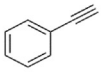
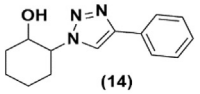
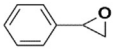
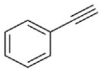
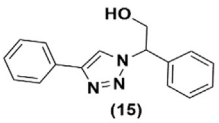
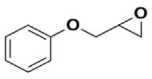
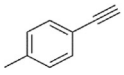
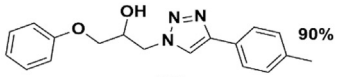
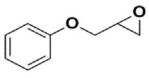
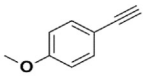
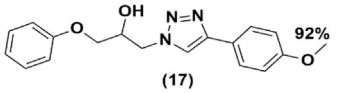
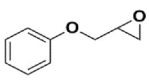
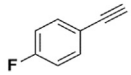
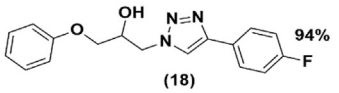
2.1.3. Synthesis of β-hydroxy 1, 2, 3-triazole from benzyl bromide derivatives, sodium azide and alkyne

NaN_3 (65 mg, 1.0 mmol), the epoxide (1 mmol), and the alkyne (1 mmol) were added to a suspension of **sf-CuS** (5 mg). The reaction mixture was stirred at room temperature and monitored by TLC until all the starting materials were converted to products. The solid was obtained by filtration and washed by DCM (3 × 10 mL). The extraction of aqueous phase with DCM was also performed without loss of product, and collected organic phase were dried with anhydrous Na_2SO_4, and concentrated in vacuum. The product was isolated through a silica gel column chromatography as corresponding β-hydroxytriazoles. All the products were confirmed by usual spectral methods (^{1}H NMR, ^{13}C NMR) (See Supporting Information S10–S18).

For example: **3-Phenoxy-2-(4-phenyl-1H-1,2,3- triazol-1-yl) propan-1- ol:** pale yellow solid; mp:126–128 °C; ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 7.89$ (s, 1H), 7.78–7.75 (m, 2H), 7.43–7.39 (m, 2H), 7.34–7.35 (m, 1H), 7.32–7.30 (m, 1H) 7.03–6.99 (m, 1H),

Table 3
Synthesis of β-hydroxy 1, 2, 3-triazole derivatives by CuS.



Entry	epoxide (R1)	alkyne (R2)	time	product	Yield%
1			6h	 (10)	92%
2			8h	 (11)	89%
3			8h	 (12)	86%
4			10h	 (13)	82%
5			12h	 (14)	79%
6			5h	 (15)	91%
7			7h	 (16)	90%
8			7h	 (17)	92%
9			6h	 (18)	94%

6.95–6.92 (m, 2H), 4.75 (dd, $J = 3$ Hz, $J = 11$ Hz, 1H), 4.61–4.54 (m, 2H), 4.09–4.00 (m, 2H), 3.57 (s, 1H). ^{13}C NMR (400 MHz, $CDCl_3$) $\delta = 158.0$, 147.7, 130.2, 129.6, 129.5, 128.8, 128.2, 125.6, 121.6, 121.3, 114.5, 68.9, 68.7 and 53.03 HRMS calculated for $C_{17}H_{17}N_3O_2$ $[M+H]^+$: 296.1398, found: 296.1398. (See Supporting Information S10).

3. Conclusions

Surfactant-free copper sulfide (**sf-CuS)** catalyst has been utilized successfully for one-pot synthesis of triazoles by cycloaddition of both benzyl halide derivatives-alkyne and epoxide derivatives – alkyne in the presence of sodium azide. The desired products were obtained at ambient temperature while the reactions were performed in water. Most of the reactions proceeded faster with the exception of aliphatic epoxide in the case of epoxide derivatives. While in benzyl halide derivatives, less electronegative substituted benzyl halide derivative (Bromo and Iodo) were slower compared with other (flouro and chloro). The catalyst can be recycled and reused for five times without losing its activity.

Table 4
Comparison table of numerous catalysts with various Synthesis of 1, 4-disubstituted β-hydroxy-1, 2, 3-triazoles (for compound 15).

Catalyst	Substrate	Time	Temperature	Yield	Ref.
CPSi	Styrene Oxide	1 h	60 °C	94%	[50]
Cu/Cu_2O	Styrene Oxide	2 h	RT	75%	[48]
$AQ_2Cu(II)$-$APSiO_2$	Styrene Oxide	4 h	60 °C	82%	[49]
$CuFe_2O_4$	Styrene Oxide	6 h	60 °C	87%	[47]
Cu Nano particles	Styrene Oxide	8 h	100 °C	83%	[46]
Cu(I) in Ionic liquids	Styrene Oxide	10 h	80 °C	95%	[54]
Sf-CuS mf	Styrene Oxide	5 h	RT	91%	This work

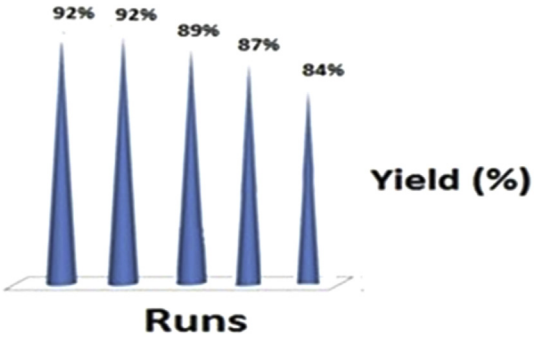


Fig. 2. Recycling results of the sf-CuS mf catalyst in the syntheis of triazoles.

Authors' contributions

Competing interests

No competing interest.

Consent for publication

Not applicable.

Ethics approval and consent to participate

Not applicable.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2019.01.016.

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