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Ultrasound Assisted High-Throughput Synthesis of 1,2,3-Triazoles Libraries: A New Strategy for "Click" Copper-Catalyzed Azide-Alkyne Cycloaddition Using Copper(I/II) as a Catalyst

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Abstract

A series of 1,4-disubstituted 1,2,3-triazoles were prepared by a parallel synthesis protocol utilizing the 3D-supramolecular coordination polymer (SCP) $\{[Cu^{I}(CN)(phen)_2 \cdot Cu^{II}(CN)_2(phen)] \cdot 5H_2O\}$, **1** as a catalyst under ultrasonic irradiations. This work establishes the synergistic action between the mixed valance copper catalyst SCP **1** and ultrasonic irradiation to yield a high-throughput synthesis of 1,4-disubstituted 1,2,3-triazoles libraries. This mixed valance copper(I/II) supramolecular coordination polymer catalyzed azide alkyne cycloaddition reaction protocol allowed a rapid synthesis of the target compounds (10 min) in a parallel fashion with good to excellent yields. Twelve reactions were performed in a single deep well microtiter plate, employing three alkynes and four different azide reagents. From this effort, a total of twelve 1,2,3-triazole were obtained in useful isolated yields. Moreover, unambiguous structural assignment of the obtained regioisomers was determined utilizing Heteronuclear Multiple Bond Correlation (HMBC) 2D NMR techniques as a valuable.

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Extended author information available on the last page of the article

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Graphical Abstract

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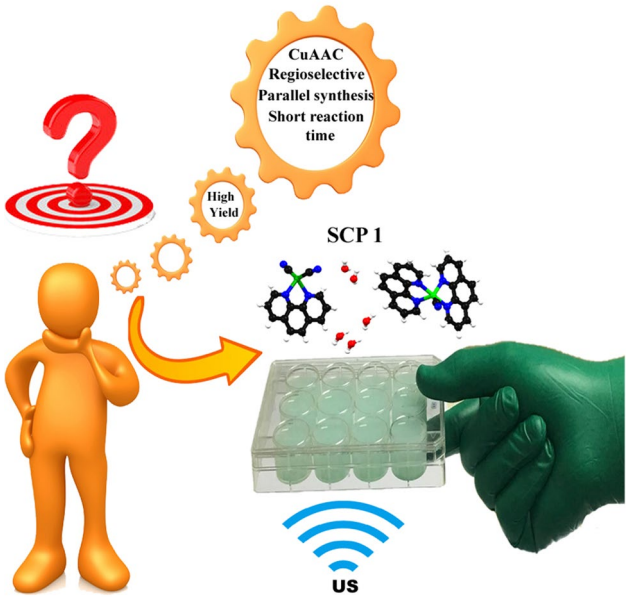


Keywords Supramolecular coordination polymer · Parallel synthesis · CuAAC · Ultrasound · 1,2,3-Triazoles

1 Introduction

1,2,3-Triazoles are an important class of heterocyclic compounds that received significant attention in contemporaneous drug research. It exhibited broad therapeutic applications due to their diverse biological activities [1], such as antimicrobial [2–5], antiviral [6], anti-inflammatory, analgesic [7], anticancer [8–11] and anticonvulsant [12] activities. These privileged scaffolds not only have drawn considerable attention in the field of medicinal chemistry [13] but also, they have prominence in the chemical industry in which these compounds are used as dyes, photostabilizers, and photographic materials [14, 15]. In addition to, 1,2,3-triazole was found to be the most desirable group in the design of functional coatings [16]. Given the above-mentioned paramount importance of these compounds, we found that Dimroth

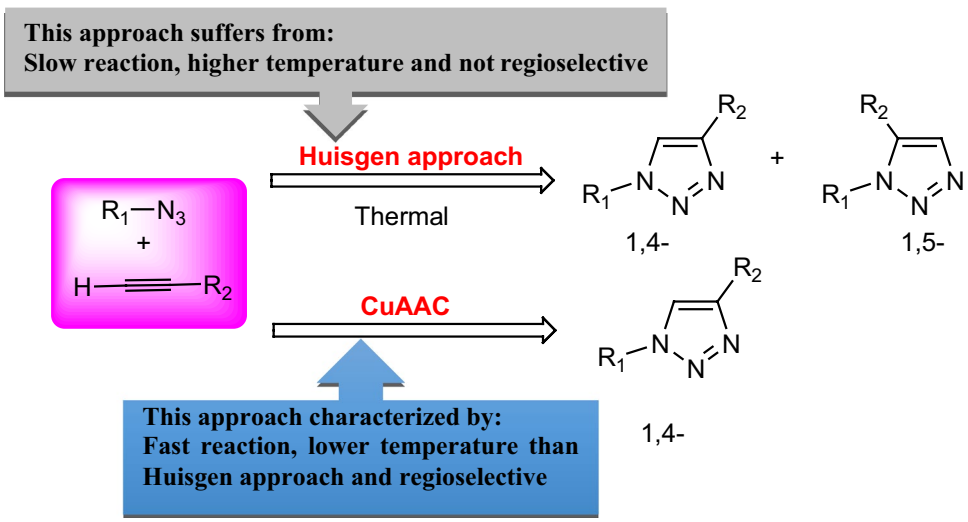


Fig. 1 Huisgen's cycloaddition route to 1,2,3-triazoles and its CuAAC approach

and Fester were first to propose the direct construction of unsubstituted NH-1,2,3-triazole ring by the interaction of hydrogen azide with acetylene [17]. Then in 1963, Huisgen reported the uncatalyzed reaction of 1,3-dipolar cycloaddition of organic azides with alkynes [18] but it was found that the suggested approach of Huisgen, leads to very slow reaction at higher temperature and not regioselective that lead to a mixture of 1,4- and 1,5-regioisomers as represented in Fig. 1. Sharpless et al. developed concept of "click chemistry" that based on the joining of smaller units mimics the approach used by nature to generate substances [19]. Then Huisgen's thermal cycloaddition of azides and alkynes was brought back into focus by Sharpless [20] and Meldal [21] in which they have shown that the copper catalyzed azide alkyne cycloaddition (CuAAC), independently (Fig. 1).

Copper catalyzed azide alkyne cycloaddition reaction is faster, facile and regioselective. Therefore, CuAAC reaction has been gaining huge attention among synthetic chemists [22–27]. Recently, a plethora of publication deals with updated CuAAC reactions and clarified classification for the catalysts used in this reaction. In which the used copper catalysts classified into copper(I) and copper salts or complexes, metallic or nano particle copper and other solid supported copper systems [28]. All these attributes, combined with the potentially favorable physicochemical properties of the resulting triazoles, has propelled the Cu(I)-catalyzed Huisgen cycloaddition to be one of the most popular and efficient reactions within the concept of click chemistry.

In this context, recently Etaiw et al. reported a new effective catalyst based on mixed valence copper(I/II) cyanide supramolecular coordination polymer for dye degradation, antitumor and click reaction [29, 30]. The mixed valence copper cyanide supramolecular coordination polymer is presumed to be in the + 1-oxidation state even though there is evidence that Cu(II) might accelerate the CuAAC reaction [31], possibly by playing a role that complements Cu(I) [32]. The advantages of the mixed valence copper(I, II) catalyst are the ease of prep+/aration and a good catalytic activity. This catalyst was successfully employed for the synthesis of triazoles in excellent yield and short reaction time [30]. Another proof for utilization of mixed valance copper catalyst, very recently released. Ziegler et al. [33] demonstrated an important study show that a dicopper complex with a symmetrically bridging, μ-alkynyl ligand undergoes cycloaddition with an organic azide to yield a symmetrically bridged 1,2,3-triazolide, this reaction embodies a key step that has been postulated in computationally proposed mechanisms of the CuAAC reaction. Moreover, the mixed valance dicopper complex is a competent catalyst for the CuAAC reaction. Finally, suggest that the CuAAC could potentially proceed through mixed-valence dicopper complexes.

Generally, most of employed molecularly defined Cu(I) complexes catalytic system explored for CuAAC reaction needing a few hours to overnight to be completed, but this considered the only disadvantage from our point of view for these catalytic systems. On the other hand, ultrasonic-assisted organic synthesis is a powerful technique that is being used more and more to accelerate organic reaction rate. The notable features of the ultrasound approach are enhanced reaction rates, formation of pure products in high yields, and easier manipulation [34–38]. Moreover, the improvement of synthetic processes by saving energy and time during the preparation of an important products considered the main goal of chemists who believe in chemical sustainability. As the sustainability can be improved by various approaches, some of which are: (i) non-classical energy routes like ultrasound (The use of ultrasound technology appealed to be appropriate, rapid, safe, and sustainable routes) (ii) catalysis, these tools may be helpful in numerous cases. Therefore, herein we report, ultrasound assisted simple, highly efficient, plate-based, parallel synthesis utilizing the successful mixed valence copper(I/II) cyanide supramolecular coordination polymer $\{[Cu^{I}(CN)(phen)_2 \cdot Cu^{II}(CN)_2(phen)] \cdot 5H_2O\}$, **1** as catalyst for copper-catalyzed azide-alkyne cycloaddition to prepare libraries of triazoles. The reaction conducted at room temperature (25 °C) and give good to excellent yields. More importantly, the total time of reaction takes only 10 min for 12 derivatives synthesized parallelly. In this regard, we introduce two important concepts: the first, the concept of 10 min parallel synthesis click reaction and the second, the synergetic action between the mixed valance copper catalyst used and ultrasound, finally we utilized the $^{1}H–^{13}C$ HMBC NMR to unambiguous the structure of the product formed.

2 Results and Discussion

2.1 Characterization of the Catalysts SCP 1, CuCN and $K_3[Cu(CN)_4]$

The room temperature (25 °C) reaction between the aqueous water/ acetonitrile solution of the prepared $K_3[Cu(CN)_4]$ complex and 1,10-phenanthroline (phen) ligand affords the mixed valence Cu(I, II) SCP of the formula $\{[Cu^{I}(CN)(phen)_2 \cdot Cu^{II}(CN)_2(phen)] \cdot 5H_2O\}$, **1**. The chemical composition and the structure of the SCP **1** were affirmed by elemental, spectroscopic analysis and X-ray powder and single crystal diffraction analysis. Comparing the diffractograms of X-ray powder diffraction of the SCP **1** with those of the simulated one, Fig. S1 (see supporting information) indicates that the SCP **1** is identical showing the same 2θ values and the same grid constants. Hence, the bulk material of **1** is iso-structurally identical with their single crystals [29]. The crystal structure of the SCP **1** consists of two molecular structure fragments one of Cu(I) of $[Cu^{I}(CN)(phen)_2]$

and the other fragment contains Cu(II); $[Cu^{II}(CN)_2(phen)]$, Fig. 2. There are five water molecules are connected the two fragments with each other by hydrogen bonds, Fig. 2. The Cu(I) atom in $[Cu^{I}(CN)(phen)_2]$ fragment is coordinated by one terminal cyanide group and two phen ligands forming a distorted trigonal bipyramid geometry, but the Cu(II) in the $[Cu^{II}(CN)_2(phen)]$ fragment is bonded by two cyanide groups and only one phen ligand forming slightly distorted tetrahedral geometry. The oxygen atoms of the water molecules are close packed arranged by short contacts forming an interesting 1D-tape. The water molecules spread between the layers of the $[Cu^{I}(CN)(phen)_2]$ and $[Cu^{II}(CN)_2(phen)]$ fragments forming hydrogen bonds with the terminal cyanide groups and the hydrogen atoms of the phen ligands which expand the structure of the SCP **1** to 3D-framwork, (Fig. S2) (see supporting information). The majority fascinating characteristic in the structure for **1** is its surprising supramolecular interactions, which contain hydrogen bonds of H···N–C type between hydrogen of phen and terminal cyanide groups, π···π stacking interaction between aromatic ligands of phen and C–H···π interactions involving the terminal cyanide and phen ligands, generating an interesting supramolecular building design in the solid state.

By consulting the IR spectra of the SCP **1** and the free ligand (phen), the IR spectrum of the SCP **1** exhibits a strong broad band at 3400 cm^{-1} assigned to the stretching vibrations of the water molecules. Also, the IR spectrum of the SCP **1** shows the bands assigned to the stretching vibrations $\upsilon_{CH(arom)}$ of the phen ligand at 3057, 2930 cm^{-1}. The band at 1615 cm^{-1} corresponds to $\upsilon_{C=N}$ while those at 1588, 1509 and 1460 cm^{-1} are attributed to $\upsilon_{C=C}$ of the phen ligand. The presence of two υ_{CN} IR absorption bands in the IR spectrum of SCP **1** at 2130 and 2088 cm^{-1} supports the presence of two different cyanide groups. It is noteworthy that the $\nu_{C\equiv N}$ bands (2130, 2088 cm^{-1}) of the SCP **1** are different from that of $K_3[Cu(CN)_4]$ (2081 cm^{-1}), which additionally confirms the presence of two different types of cyanide groups. In addition, the ν_{Cu-C} bands at 429 and 435 cm^{-1} confirm the presence of two $(CuCN)_n$ fragments.

2.2 Catalytic Activity Study

Previously, the catalyst SCP **1** described as simple and robust catalyst for azide-alkyne cycloaddition reaction under classical conditions [30]. Here, a new alternative green methodology and cost efficient has been developed for the synthesis of some novel 1,2,3-triazoles by SCP **1** catalyst in a parallel, 12-well plate-based format utilizing ultrasonic irradiation. At the outset, the conditions for the parallel synthesis of 1,2,3-triazoles were optimized by using equimolar mixture of phenyl acetylene (**1a**) as alkyne and 1-(azidomethyl)-4-fluorobenzene (**2a**) as a model reaction on round bottom flask scale (flask mode) utilizing ultrasonic irradiations in presence of SCP **1** copper(I, II) catalyst (Scheme 1).

Noteworthy, three copper catalysts (5 mol%) were scanned for the above model reaction under ultrasonic irradiation. The copper catalysts namely, copper(I)cyanide, potassium tetracyanocuprate complex ($K_3[Cu(CN)_4]$) and mixed valence copper(I, II) SCP **1** were selected. The former three catalysts were chosen which considered the copper precursor of copper cyanide SCP **1** and also, to clarify the advantage of SCP **1** towards the above model reaction (Table 1).

It is clear from results cited in Table 1 that, under ultrasonic irradiations: in absence of catalyst there are no product detected even till 60 min (entry 1), When SCP **1** was used as a copper catalyst, the best yield of the obtained

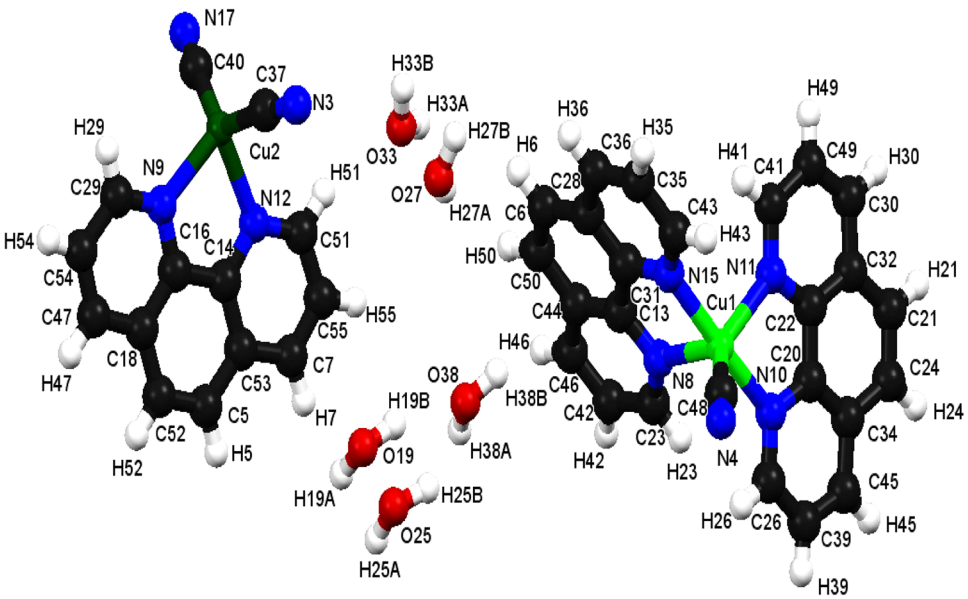


Fig. 2 An ORTEP plot of the asymmetric unit showing the molecular structure of the SCP **1** with the atom labeling scheme

Scheme 1 Optimization of the conditions for CuAAC reaction

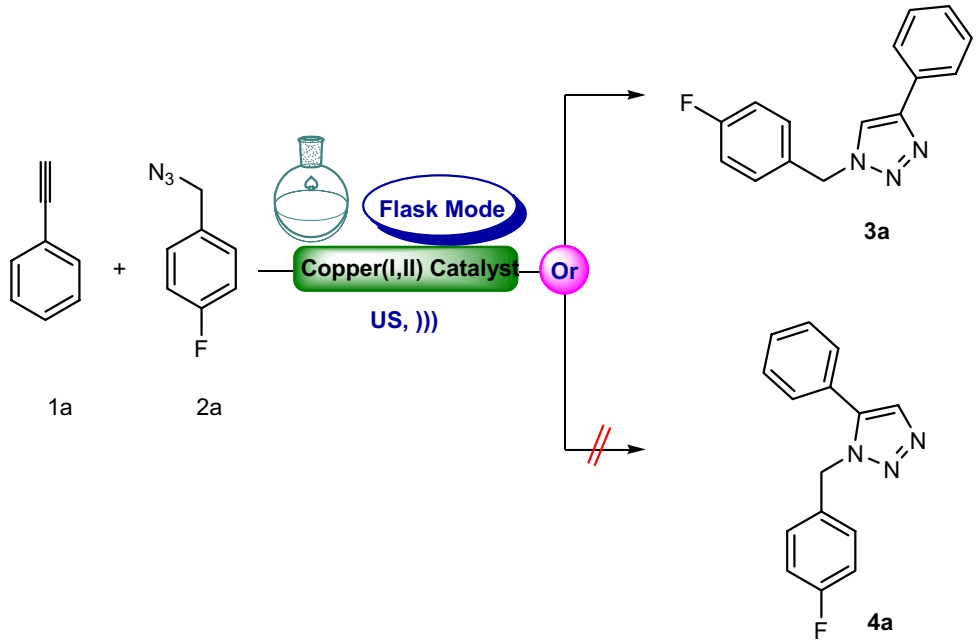


Table 1 Synthesis of compound **3a** using different copper catalysts under ultrasonic irradiation

Entry	Catalyst	Solvent	Temperature (°C)	Time (min)	Yield (%) **3a**
1	Catalyst-free	CH_3CN/H_2O (1:1)	RT (25)	60	ND
2	CuCN	CH_3CN/H_2O (1:1)	RT (25)	30	86
3	$K_3[Cu(CN)_4]$	CH_3CN/H_2O (1:1)	RT (25)	40	75
4	SCP **1**	CH_3CN/H_2O (1:1)	RT (25)	15	99
5	SCP **1**	THF/H_2O (1:1)	RT (25)	15	95
6	SCP **1**	$DMSO/H_2O$ (1:1)	RT (25)	10	95
7	SCP **1**	$Dioxane/H_2O$ (1:1)	RT (25)	10	95
8	**SCP1**	**$Dioxane/H_2O$ (2:1)**	RT (25)	**10**	**99**
9	SCP **1**	Dioxane	RT (25)	30	84
10	SCP **1**	H_2O	RT (25)	60	29
11	SCP **1**	$Dioxane/H_2O$ (2:1)	40	10	99
12	SCP **1**	$Dioxane/H_2O$ (2:1)	60	10	99
13	SCP **1**	$Dioxane/H_2O$ (2:1)	80	10	99

Bold indicates optimum conditions for the reaction

ND not detected

regioisomer was attained (entry 4, 8). When copper(I) cyanide and potassium tetracyanocuprate complex as a source for copper(I) catalysts were used a lower product's yield in longer period was attained (Table 1, entries 2, 3). However, it is noticeable that copper(I) cyanide is more active than tripotassium tetracyanocuprate complex this is may be due to copper(I) cyanide is a coordination polymer. It exists in two polymorphs both of which contain –[Cu–CN]– chains made from linear copper(I) centers linked by cyanide bridges. Copper cyanide with a low-temperature (LT-CuCN) form transforms irreversibly to a second form (high-temperature; HT-CuCN) upon heating above 550 K [39, 40]. In LT-CuCN, the infinite chains are not linear and show a wave-like structure, whereas HT-CuCN is linear and isostructural with AgCN [39, 40]. Copper(I) cyanide is insoluble in water but rapidly dissolves in solutions containing CN^- to form $[Cu(CN)_3]^{2-}$ and $[Cu(CN)_4]^{3-}$, which exhibit trigonal planar and tetrahedral coordination geometry, respectively. These complexes contrast with those of silver and gold cyanides, which form $[M(CN)_2]^-$ ions in solution [41]. Furthermore, raising the reaction temperature to 40, 60, 80 °C, the yield of the obtained target product was remained (99% attained in the same time of the reaction 10 min) (Table 1, entry 11–13). Besides, the solvent played a significant role in

progress of reaction. When dioxane and water were used alone, the yields of desired product were obtained of 84%, 30 min (entry 9) and 29%, 60 min (entry 10) respectively (Table 2, entries 11 and 12). The low yield obtained for the corresponding triazole derivative using pure water as a solvent is attributed to lack of organic material solubility in water. The mixed solvents of CH_3CN/H_2O, THF/H_2O and $DMSO/H_2O$ (1:1, V/V) all afforded excellent yield (Table 2, entries 4–6). As we talk in flask mode, the confirmed optimal synthesis condition should be valid for the plate mode that used for parallel synthesis. Therefore, mixed solvents of THF/H_2O and $DMSO/H_2O$ (1:1, V/V) cannot be used in plate mode (due to solubility issue for material of microplate "polystyrene"). Subsequently, the optimized conditions are using SCP **1** as the catalyst, in presence of solvent dioxane/H_2O mixture (2:1, V/V), under ultrasound-assisted at room temperature. To full optimize the reaction conditions using the best copper catalyst a run of experiments was carried out under changeable catalyst quantities and the reaction progress was monitored by using thin layer chromatography (TLC) for the model reaction (Scheme1) under ultrasonic irradiations. The results obtained from the catalytic test reaction are cited in Table 2.

Initially, for optimization of catalyst's quantity, different mol% of SCP **1** catalyst were tested under the identical reaction situations, where the greatest yield 99% of **3a** was found using 4 mol% of the catalyst and running the process for 10 min (Table 2, entry 4).

The supramolecular catalyst **1** is stable, well-defined non-solvated materials, and soluble in most organic-aqueous solvents, thus making them attractive homogeneous alternatives to copper cyanide and potassium tetra cyanocuprate for potentially promoting the formation of 1,2,3-triazole in high yield in short time. The catalytic activity of the SCP **1** is affected by several factors as the unique three-dimensional open structure through the water molecules which, spread between the layers of the $[Cu^{I}(CN)_2(phen)]$ and $[Cu^{II}(CN)_2(phen)]$ fragments forming H-bonds with the terminal cyanide groups and the hydrogen atoms of the phen ligands (Fig. S2). Alternatively, the 3D-network structure of the SCP **1**, down the projection of the c-axis, consists of fused six-member rings creating box-like structure. Therefore, the superiority of SCP **1** catalyst may be due to that the structure of the SCP **1** contains pores and cavities increases the catalytic activity towards the copper catalyzed azide alkyne cycloaddition reaction forming of 1,2,3-triazole in high yield in short time. As well as, the Cu(I/II) site which forms trigonal bipyramid TBPY-5, (Cu^{I}) and slightly distorted tetrahedral (T-4) (Cu^{II}) geometry play an important role in the formation of 1,2,3-triazole by forming an intermediate octahedral complex. Noteworthy, A mixed-valence Cu(I, II) complex has been hypothesized to be highly efficient in catalysis, since the more Lewis acidic Cu(II) site could enhance activation of the azide substrate [31]. Notably, the above mentioned significant geometric difference between the two copper centers was revealed, with the π-system of the two phen ring ostensibly interacting with the Cu(I) center, while the one phen ring binds more directly to the Cu(II) center, Fig. 2.

Table 2 Optimization of reaction condition for synthesis of **3a** utilizing SCP **1** catalyst

Entry	SCP 1 catalyst (mol%)	Time (min)	Yield (%)
1	1	20	91
2	2	20	93
3	3	10	96
4	**4**	**10**	**99**
5	5	10	99
6	6	10	99

Bold indicates optimum conditions for the reaction

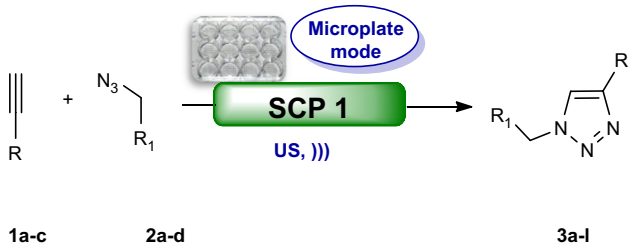
To find the specific effect of ultrasound on these reactions, the previously mentioned reactions were carried out under the optimized conditions in the absence of ultrasound irradiation, it was observed that the reaction time increased considerably, and yield of the products decreased (1 h, 90%). Thus, ultrasound was found to have beneficial effect on the synthesis of 1,2,3-triazole derivative in which decrease time of above reactions from 1 h conventional procedure to 10 min, also, a noticeable improvement in yields of reactions under ultrasonic irradiations. Noteworthy, it is obvious that there is synergistic action between the ultrasonic irradiation in presence of SCP **1** catalyst, in which we examine the effect of ultrasound irradiation technology on the above-mentioned reaction without catalyst (the starting materials were irradiated without catalyst). In addition to, the reaction had been done with SCP **1** catalyst without ultrasound. The effect of ultrasound irradiation can be explained in light of the well-established theory of sonochemistry in which, the passage of a low frequency ultrasonic wave through a liquid generates cavitation bubbles. This phenomenon, known as acoustic cavitation, is the formation, growth, and collapse of highly energetic microbubbles. During the collapse of these microbubbles, extreme conditions of high temperatures and pressures release shockwaves into the reaction medium, generating fragmentation of molecules. The implosion leads to specific effects capable of breaking down chemical bonds [42].

In view of Scheme 1 and contrary to all the research in this regard, in which most of research that deals with CuAAC reaction, write only one regioisomer product like **3a** (1,4-disubstituted-1,2,3-triazole), but we suppose that the above reaction proceeds regioselectively to give also only one product 3**a** or **4a**. Our assumption relies on the product of azide alkyne cycloaddition reaction differed according to

catalyst used (Cu, Ag, Ni or Ru) and alkyne used (terminal or disubstituted) [26, 43–45], and it is frequently difficult to present unequivocal proof of the reaction product structures via ^{1}H NMR. Unfortunately, a plenty of the previously reported results in this regard [46–48] for similar reactions based on one-dimension ^{1}H NMR spectroscopy assume that in the 1,2,3-triazole ring system, N-3 is more electron-rich nitrogen (SP^2 hybridized) than N-1 (SP^3 hybridized); thus, H-4 (present on C-4 that adjacent to N-3) is expected to appear more downfield, typically at a higher chemical shift than H-5 (present on C-5 that adjacent to N-1). We concur with this claim to certain extent, if we have in our hand two ^{1}H NMR spectra for the two regioisomers. In the present case, we have only one ^{1}H NMR spectrum in view of the fact that the reaction proceeded in a regioselective manner. The chemical shift in NMR spectroscopy is considered a tensor not a scalar, so we cannot decide if the obtained chemical shift of the 1,2,3-triazole proton is a lower or higher value. On the other hand, many studies introduce excellent efforts in this situation [49] but given the importance of this reaction in many areas, especially the drug discovery, we still need to clarify a simplified and available method to elucidate the structure of the regioisomer formed. Therefore, it is crucial to rationalize the observed regioselectivity in our reaction. Single crystal X-ray is a useful tool for the unambiguous structure determination of the obtained products, but it is sometimes difficult to access a single crystal of the formed product.

So, we introduce here a simple efficient available tool that enables of structure elucidation for the obtained regioisomer. In which utilization of structure elucidation was conveniently achieved on the basis of the long-range C–H connectivities *via* ^{1}H–^{13}C HMBC, (Fig. 3a) depending on the number correlation between the 1,2,3-triazole proton with its carbons. For example, the number of correlations between the 1,2,3-triazole proton and carbons that are two and three bonds away we can easily determine which isomer formed (Fig. 3a). The presence of three correlations in the ^{1}H–^{13}C HMBC spectrum of the isolated product is conclusive evidence for the proposed structure of **3a** (Fig. 3b). The structure of the product **3a** was confirmed according to elemental analysis and spectral data. IR spectra of the product **3a**.

The above optimized reaction condition for the model reaction (Scheme 1) was chosen to explore the scope and



Scheme 2 Parallel synthesis of twelve 1,2,3-triazole derivatives under ultrasonic irradiation

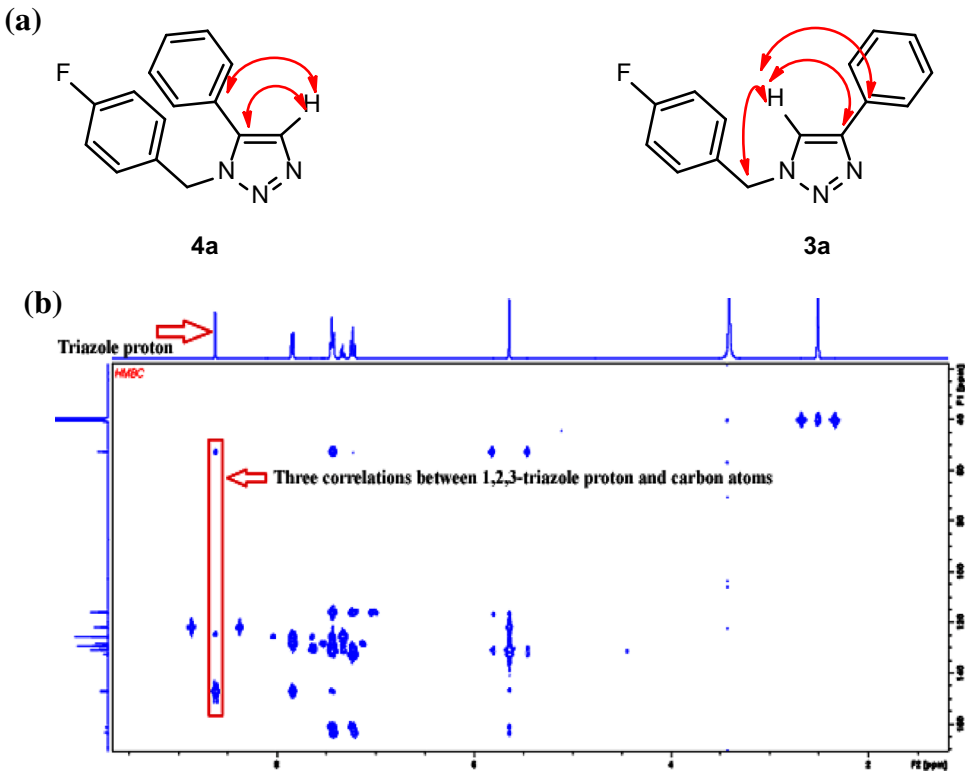


Fig. 3 **a** Number of correlations between the 1,2,3-triazole proton toward carbons in the possible regioselective isomers **3a** and **4a**; **b** number of correlation between the triazole proton and carbon atoms

limitations of this protocol, for small library synthesis of 12 members of 1,2,3-triazole using the azides **2a**–**d** and the alkynes **1a**–**c** in microplate mode (Scheme 2).

We performed twelve reactions in a parallel reaction format (microplate mode). These microplate mode syntheses provided structural diversification of four different azide components that reacted with three alkyne diversity elements (Fig. 4), for the 12 derivatives of 1,4-disubstituted 1,2,3-triazole synthesis.

After charging the 8.7 mL, 12-well polystyrene plate with the appropriate alkynes **1a**–**c** in dioxane/water (2:1), A solution of azide **2a**–**d** in dioxane/water (2:1) was then added to each well followed by a solution of 5 mol% SCP **1** in same solvent. The plate was sealed then vortex mixed for 30 s and allowed sonicated in cleaning bath reactor for 10 min resulting in consumption of the starting material (The progress of reactions was monitored by TLC). Exhilarating, all scanned reactants afforded the corresponding 1,2,3-triazole derivatives under ultrasonic irradiation in 66–99% (Table 3). The easy execution of this parallel reaction format provides rapid access to substituent diversity on the 1,4-disubstiuted 1,2,3-triazoles scaffold by reaction a variety of azides and alkynes in presence of SCP **1** as copper catalyst as shown in Scheme 2.

The mechanism of the CuAAC reaction is very important issue in our case, because we talk about cooperation between two copper centers. Therefore, the proposed mechanism for our reaction depend on the recent study that succeeded in isolation of the dinuclear complexes [50]. It is presumed that, first the alkyne serves as the proton source for the demetallation of the SCP **1**, which regenerates the π,σ-βis(copper) acetylide (intermediate **I**), then on treatment with azide form dimetallated triazole (intermediate **II**) that rapidly forms free triazole **3** as depicted in Scheme 3.

We can summarize our reaction mechanism that proceeds *via* the following steps (i) in situ formation of the σ-bound copper acetylide (Cu^{II}); (ii) Recruitment of a second π-bound copper atom, forming the catalytically active complex (intermediate I); (iii) Reversible coordination of the organic azide to the π-bound copper complex (intermediate II); and (iv) The stepwise annulation events.

Noteworthy, the synergistic action between the ultrasonic irradiation and the SCP **1** catalyst that cause the remarkable improvement in the above-mentioned reactions can be attributed to the well-established theory for the cavitation. The collapse of bubbles caused by cavitation produces intense local heating and high pressures, [51, 52] so reaction time decreases clearly and high % yield obtained. In addition, according to sonochemical reactions classification of Luche [53, 54], the above-mentioned reactions are considered false sonochemistry type in which cavitation effect provides the mechanical energy for all subsequent chemical reactions, including bond scission induced by viscous frictional forces. However, in our opinion the mechanical effect of sonication cannot be the whole reason for the noticeable synergistic effect of ultrasound and the used catalyst on reactivity because there are a variety of homogeneous reactions which are also affected by ultrasonic irradiation. The answer to these questions lies in the actual process of cavitation collapse. The microbubble is not enclosing a vacuum, it contains vapor from the solvent so that, on collapse, these

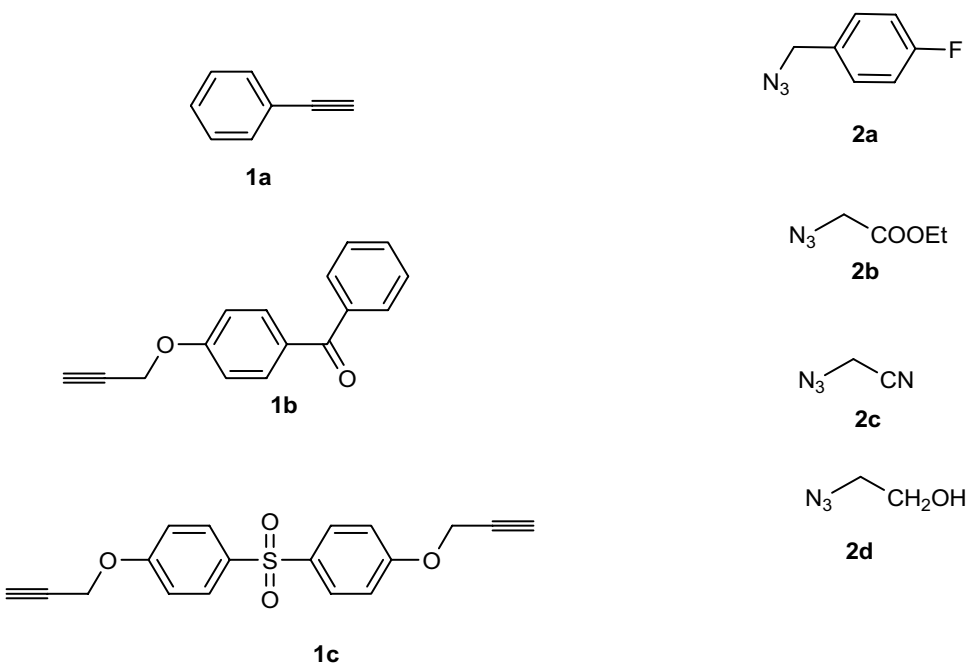
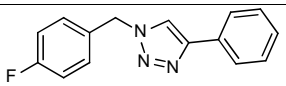
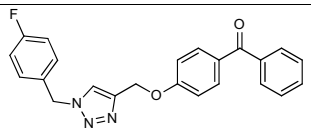
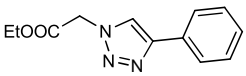
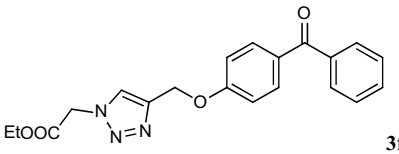
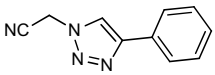
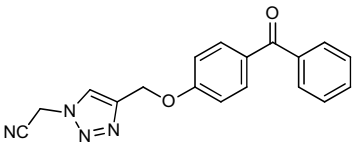
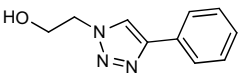
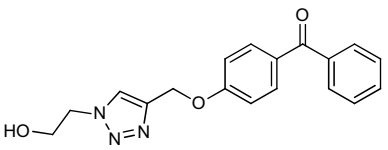
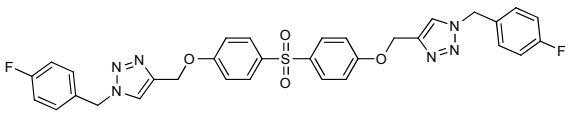
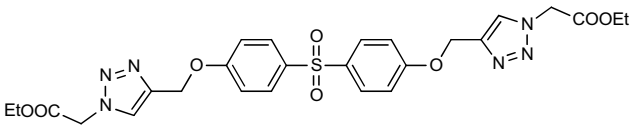
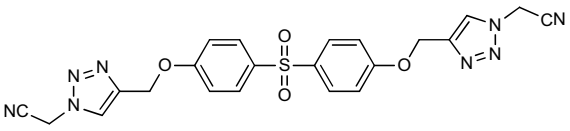
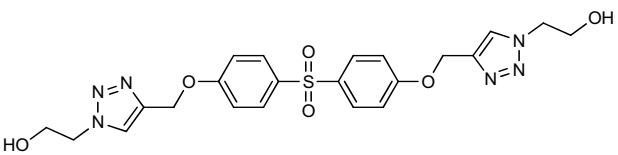
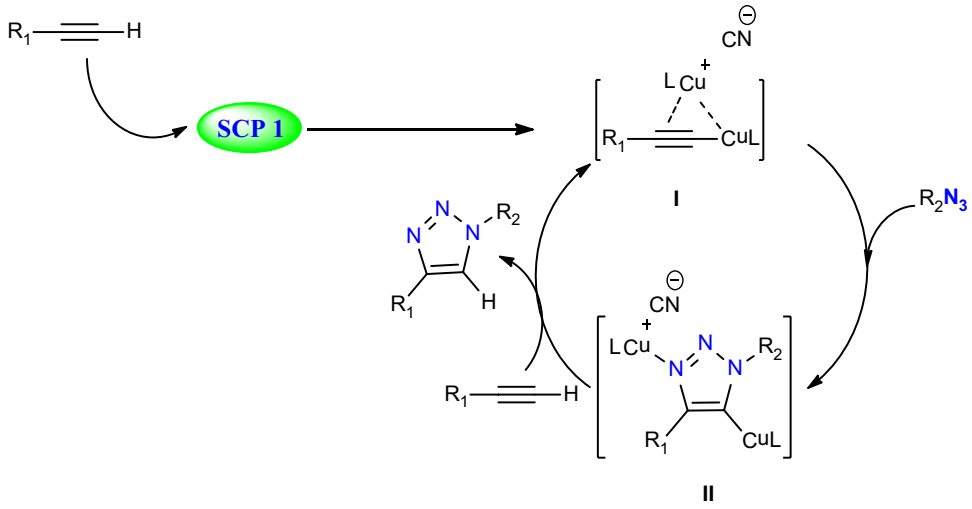


Fig. 4 Azide diversity elements and alkyne diversity elements employed in the library synthesis

Table 3 Library synthesis of 1,4-disubstutied triazole in parallel reaction format under ultrasonic irradiations

Products (Yield %)	
 **3a (99%)**	 **3e (93%)**
 **3b (99%)**	 **3f (95%)**
 **3c (99%)**	 **3g (95%)**
 **3d (96%)**	 **3h (91%)**
 **3i (76%)**	
 **3j (79%)**	
 **3k (79%)**	
 **3l (66%)**	

Scheme 3 Proposed mechanism for mixed valance copper catalyzed the azide alkyne cycloaddition reaction



vapors are subjected to the enormous increases in both temperature and pressure referred to above. Under such extremes the solvent and/or reagent suffers fragmentation to generate reactive species of the radical or carbene type some of which would be high enough in energy to fluoresce. In addition, the shock wave produced by bubble collapse or even by the propagating ultrasonic wave itself could act to disrupt solvent structure which could influence reactivity by altering solvation of the reactive species present [51]. Also, we can interpret the noticeable synergistic action, in light of the supposed mechanism (Scheme 3), in which ultrasound enhancement occur for demetallation step (copper detachment) of SCP **1** to form the intermediate I (slow step) [55].

3 Conclusion

An efficient ultrasound-assisted the parallel synthesis regioselective protocol of 1,4-substituted 1,2,3-triazole libraries catalyzed by the SCP **1** in synthetically useful yields and very short reaction time (10 min) have been developed from a diverse selection of functionalized alkynes and azides. These libraries should prove useful for use in dynamic combinatorial libraries. The remarkable synergistic effect between the ultrasound irradiation and the SCP **1** catalyst on the above-mentioned protocol due to the mechanical effect that produced *via* cavitation and cause the enhancement for the demetallation process of the SCP **1** via alkyne which regenerates the π,σ-bis(copper) acetylide that considered the key species in copper-catalyzed organic reactions. Moreover, 2D (^{1}H–^{13}C) HMBC measurements can be readily utilized for the unambiguous structural characterization of the regioselectivity in the azide, alkyne cycloaddition reactions.

4 Experimental

4.1 Materials and Physical Measurements

All chemicals and solvents used in this study were of analytical grade supplied by Sigma-Aldrich or Merck and used as received. Electronic absorption spectra were recorded on Shimadzu (UV-310l PC) spectrometer. The magnetic susceptibility was determined with Johnson–Matthey susceptometer. Thin-layer chromatography (TLC) was performed on precoated Merck 60 GF254 silica gel plates with a fluorescent indicator, and detection by means of UV light at 254 and 360 nm. The melting points were measured on a Stuart melting point apparatus and are uncorrected. IR spectra were recorded on a Smart iTR, which is an ultra-high-performance, versatile Attenuated Total Reflectance (ATR) sampling accessory on the Nicolet iS10 FT-IR spectrometer. The NMR spectra were recorded on a Bruker Avance III 400 (9.4 T, 400.13 MHz for ^{1}H, 100.62 MHz for ^{13}C and 376.25 MHz for ^{19}F) spectrometer with a 5-mm BBFO probe, at 298 K. Chemical shifts (δ in ppm) are given relative to internal solvent, DMSO-d_6 2.50 for ^{1}H and 39.50 for ^{13}C was used as an external standard. ^{1}H–^{13}C HMBC was acquired and processed using standard Bruker NMR software (Topspin 3.2). Mass spectra were recorded on a Thermo ISQ Single Quadrupole GC–MS. Elemental analyses were carried out on a EuroVector instrument C, H, N, S analyzer EA3000 Series. Sonication was performed by Techno-gaz sonicator (with a frequency of 37 kHz and ultrasonic peak max. 320 W).

The terminal alkynes: 4-(2-propynyloxy)benzophenone (**1b**) [56] and 4,4′-sulfonylbis((prop-2-yn-1-yloxy)benzene) (**1c**) [57] were prepared according to the reported literature. In addition to, the azides: 2-azidoacetonitrile (**2c**)

[58] and 2-azidoethanol (**2d**) [59] were prepared according to the reported literature.

4.2 Catalysts Synthesis

4.2.1 Synthesis of $K_3[Cu(CN)_4]$ Complex

1.790 g (20 mmol) of CuCN was being added, with magnetic stirring, to the solution of 3.906 gm (60 mmol) of KCN in 30 mL of hot H_2O. The solution was filtered off and heated using water bath at 60 °C until the volume of the solution was reduced to its half. Then after, the solvent evaporation was continued in vacuum to dryness. $K_3[Cu(CN)_4]$ was obtained as a solid white product [60, 61], and IR spectrum ($\nu_{Coo} = 2083\ cm^{-1}$ and $\nu_{Cu-C} = 413\ cm^{-1}$).

4.2.2 Synthesis of Mixed Valence Copper SCP $\{[Cu^{I}(CN)(phen)_2 \cdot Cu^{II}(CN)_2(phen)] \cdot 5H_2O\}$ 1

At room temperature, a solution of 99 mg (0.33 mmol) of $K_3[Cu(CN)_4]$ in 30 mL H_2O was added, under gentle stirring to a solution of 60 mg (0.334 mmol) of 1,10-phenanthroline (phen) in 20 mL acetonitrile [29]. During the addition of 1,10-phenanthroline a more intense yellow color solution was formed. The obtained yellow solution was kept under slow evaporation at room temperature (25 °C). The green needle like crystals were resulted from yellow solution after 1 week. The crystals were filtered off after subsequent washing with a mixture of water/acetonitrile and then they were dried in the air overnight, about 70 mg (51% referred to $K_3[Cu(CN)_4]$) of green crystals were obtained. The SCP **1** is light and air stable and insoluble in water, but it is freely soluble in organic solvents. $\mu_{eff.} = 1.95$ BM, Anal. Calc. for **1** ($C_{39}H_{34}N_9O_5Cu_2$): C, 56.0; H, 2.8; N, 15.0%. Found: C, 55.96; H, 2.7; N, 14.9%.

4.3 Typical Procedure for the Catalytic Test Reaction

CAUTION! Organic azides are potentially explosive and should be handle with care. Even if no incident occurred on this scale, the cycloaddition can be highly exothermic and should not be attempted on a larger scale, without being aware of explosion risks.

4.4 Silent Reaction: (Flask Mode)

In 25 mL round bottom flask, loaded with a solution of phenylacetylene (**1a**) (0.105 mmol) in mixture of dioxane/water (2:1, 2 mL). A solution 4-flurobenzylazide (**2a**) (0.1 mmol) in mixture of dioxane/water (2:1, 2 mL) was then added at R.T. (25 °C) the reaction mixture was stirred by magnetic stirrer for 5 min then a solution of SCP **1** (4 mol%) in dioxane/water (2:1, 2 mL) was added to the reaction mixture and stirred at room temperature (25 °C) for 1 h. as examined by TLC. The reaction mixture was filtered and ethyl acetate was added to the filtrate, organic layer was separated and dried over sodium sulfate anhydrous then concentrated in vacuo and the residual solid was taken in ethanol then collected by filtration to give the pure product **3a**.

4.5 Sonicated Reaction: (Flask Mode)

This process was performed on the same scale described above for silent reaction. The reaction was kept at room temperature 25–30 °C which attained by addition or removal of water in ultrasonic bath. The sonochemical reaction was continued for suitable time until the starting materials were no longer detectable by TLC. The products were obtained and purified as described above in silent reaction procedure.

4.6 Sonicated Reaction: (Microplate Mode)

A 8.7 mL, 12-well polystyrene plate was loaded with the appropriate alkynes **1a** (0.105 mmol), **1b** (0.105 mmol) or **1c** (0.0525 mmol) in dioxane/water (2:1, 2 mL). A solution of azide **2a**–**d** (0.1 mmol) in dioxane/water (2:1, 2 mL) was then added to each well followed by a solution of SCP **1** (4 mol%) in dioxane/water (2:1, 2 mL). The plate was sealed with high melt glue gun then sonicated for 10 min at 25 °C resulting in consumption of the starting material (observed by TLC). Noteworthy, a quick temperature rise was observed in most cases after sonication and the triazole crystallized out generally within 5 min (we maintain the temperature in range of 25–30 °C by addition or removal of water in ultrasonic bath). After 10 min, which was selected arbitrarily. Then the content of each well transferred via automatic pipette into 25 mL beaker, and product were obtained and purified as described above in silent reaction procedure.

4.7 Physical and Spectral Data of the Title Compounds 3 Are Listed Below

4.7.1 1-(4-Fluorobenzyl)-4-phenyl-1H-1,2,3-triazole (3a)

mp: 153–155 °C. IR (KBr) (ν_{max}, cm^{-1}): 1499 (N=N), 1452 (C=C). ^{1}HNMR (400 MHz, DMSO): δ_H 5.64 (s, 2H, CH_2), 7.21–7.85 (m, 9H, ArH), 8.63 (s, 1H, triazol H), ^{13}CNMR (100 MHz, DMSO): δ_C 52.69, 115.99, 121.94, 125.62, 128.39, 129.36, 129.55, 130.68, 132.70, 147.15, 163.59, ^{19}F NMR (DMSO): δ_F − 114.00. MS (m/z): 253 (M^+). Anal. Calcd. for $C_{15}H_{12}FN_3$: C, 71.13; H, 4.78; N, 16.59. Found: C, 71.39; H, 4.67; N, 16.44.

4.7.2 Ethyl 2-(4-phenyl-1H-1,2,3-triazol-1-yl)acetate (3b)

mp: 93–95 °C. IR (KBr) (ν_{max}, cm^{-1}): 1736 (C=O ester), 1494 (N=N), 1452 (C=C). ^{1}HNMR (400 MHz, DMSO): δ_H 1.24 (t, 3H, $J=7$ Hz, CH_3), 4.21 (q, 2H, $J=7$ Hz, CH_2) 5.45 (s, 2H, CH_2), 7.35–7.87 (m, 5H, ArH), 8.56 (s, 1H, triazol H), ^{13}CNMR (100 MHz, DMSO): δ_C 14.43, 51.01, 62.06, 123.22, 125.63, 128.46, 129.23, 130.95, 146.86, 167.69. MS (m/z): 231 (M^+). Anal. Calcd. for $C_{12}H_{13}N_3O_2$: C, 62.33; H, 5.67; N, 18.17. Found: C, 62.56; H, 5.60; N, 18.01.

4.7.3 2-(4-Phenyl-1H-1,2,3-triazol-1-yl)acetonitrile (3c)

mp: 70–72 °C. IR (KBr) (ν_{max}, cm^{-1}): 2210 (C≡N), 1495 (N=N), 1450 (C=C). ^{1}HNMR (400 MHz, DMSO): δ_H 5.74 (s, 2H, CH_2), 7.32–7.83 (m, 5H, ArH), 8.51 (s, 1H, triazol H), ^{13}CNMR (100 MHz, DMSO): δ_C 47.22, 114.33, 126.59, 128.01, 129.49, 130.24, 130.47, 149.53. MS (m/z): 184 (M^+). Anal. Calcd. for $C_{10}H_8N_4$: C, 65.21; H, 4.38; N, 30.42. Found: C, 65.34; H, 4.33; N, 30.33.

4.7.4 2-(4-Phenyl-1H-1,2,3-triazol-1-yl)ethanol (3d)

mp: 87–89 °C. IR (KBr) (ν_{max}, cm^{-1}): 3412 (OH), 1495 (N=N), 1448 (C=C). ^{1}HNMR (400 MHz, DMSO): δ_H 3.22 (br s, 1H, OH, D_2O exchangeable), 4.16 (t, 2H, $J=5$ Hz, CH_2), 4.53 (t, 2H, $J=5$ Hz, CH_2), 7.25–7.76 (m, 5H, ArH), 8.66 (s, 1H, triazol H), ^{13}CNMR (100 MHz, DMSO): δ_C 54.63, 60.31, 126.34, 128.43, 129.31, 130.23, 130.64, 148.13. MS (m/z): 189 (M^+). Anal. Calcd. for $C_{10}H_{11}N_3O$: C, 63.48; H, 5.86; N, 22.21. Found: C, 63.67; H, 5.80; N, 22.08.

4.7.5 (4-((1-(4-Fluorobenzyl)-1H-1,2,3-triazol-4-yl) methoxy)phenyl)(phenyl)methanone (3e)

mp: 205–207 °C. IR (KBr) (ν_{max}, cm^{-1}): 1676 (C=O), 1493 (N=N), 1459 (C=C). ^{1}HNMR (400 MHz, DMSO): δ_H 5.23 (s, 2H, CH_2), 5.52 (s, 2H, CH_2), 6.79–7.67 (m, 13H, ArH), 8.35 (s, 1H, triazol H), ^{13}CNMR (100 MHz, DMSO): δ_C 51.75, 61.27, 114.63, 115.73, 115.98, 122.47, 128.87, 129.67, 130.25, 130.47, 130.56, 132.36, 137.98, 144.69, 161.14, 161.43, 194.80, ^{19}FNMR (DMSO): δ_F −112.02. MS (m/z): 387 (M^+). Anal. Calcd. for $C_{23}H_{18}FN_3O_2$: C, 71.31; H, 4.68; N, 10.85. Found: C, 71.47; H, 4.65; N, 10.72.

4.7.6 Ethyl 2-(4-((4-benzoylphenoxy) methyl)-1H-1,2,3-triazol-1-yl)acetate (3f)

mp: 178–180 °C. IR (KBr) (ν_{max}, cm^{-1}): 1721 (C=O ester), 1692 (C=O), 1492 (N=N), 1451 (C=C). ^{1}HNMR (400 MHz, DMSO): δ_H 1.22 (t, 3H, $J=7.08$ Hz, CH_3), 4.19 (q, 2H, $J=7.08$ Hz, CH_2) 5.31 (s, 2H, CH_2), 5.42 (s, 2H, CH_2), 7.22 (d, 2H, $J=8.8$ Hz, ArH), 7.54–7.71 (m, 5H, ArH), 7.76 (d, 2H, $J=8.8$ Hz, ArH), 8.28 (s, 1H, triazol H), ^{13}CNMR (100 MHz, DMSO): δ_C 14.39, 50.86, 61.69, 62.00, 115.09, 126.71, 128.92, 129.70, 130.100, 132.59, 138.13, 142.64, 162.14, 167.64, 182.92, 194.92. MS (m/z): 365 (M^+). Anal. Calcd. for $C_{20}H_{19}N_3O_4$: C, 65.74; H, 5.24; N, 11.50. Found: C, 65.89; H, 5.21; N, 11.38.

4.7.7 2-(4-((4-Benzoylphenoxy) methyl)-1H-1,2,3-triazol-1-yl)acetonitrile (3g)

mp: 162–164 °C. IR (KBr) (ν_{max}, cm^{-1}): 2212 (C≡N), 1679 (C=O), 1493 (N=N), 1442 (C=C). ^{1}HNMR (400 MHz, DMSO): δ_H 5.36 (s, 2H, CH_2), 5.56 (s, 2H, CH_2), 7.13 (d, 2H, $J=8.8$ Hz), 7.39–7.81 (m, 7H, ArH), 8.29 (s, 1H, triazol H), ^{13}CNMR (100 MHz, DMSO): δ_C 45.13, 62.13, 115.43, 117.12, 126.53, 128.69, 129.18, 130.57, 131.15, 132.34, 138.92, 143.15, 162.01, 194.34. MS (m/z): 318 (M^+). Anal. Calcd. for $C_{18}H_{14}N_4O_2$: C, 67.91; H, 4.43; N, 17.60. Found: C, 68.09; H, 4.38; N, 17.47.

4.7.8 (4-((1-(2-Hydroxyethyl)-1H-1,2,3-triazol-4-yl) methoxy)phenyl)(phenyl)methanone (3h)

mp: 213–215 °C. IR (KBr) (ν_{max}, cm^{-1}): 3409 (OH), 1678 (C=O), 1492 (N=N), 1451 (C=C). ^{1}HNMR (400 MHz, DMSO): δ_H 3.31 (br s, 1H, OH, D_2O exchangeable), 4.14 (t, 2H, $J=5.6$ Hz, CH_2), 4.46 (t, 2H, $J=5.6$ Hz, CH_2), 5.59 (s, 2H, CH_2), 7.09 (d, 2H, $J=8.6$ Hz), 7.21–7.86 (m, 7H, ArH), 8.69 (s, 1H, triazol H), ^{13}CNMR (100 MHz, DMSO): δ_C 52.59, 61.39, 62.91, 115.14, 126.07, 128.98, 129.43, 130.02, 130.63, 132.16, 138.74, 142.50, 163.10, 194.06. MS (m/z): 323 (M^+). Anal. Calcd. for $C_{18}H_{17}N_3O_3$: C, 66.86; H, 5.30; N, 13.00. Found: C, 67.02; H, 5.26; N, 12.88.

4.7.9 4,4′-(((Sulfonylbis(4,1-phenylene)) bis(oxy))bis(methylene)) bis(1-(4-fluorobenzyl)-1H-1,2,3-triazole) (3i)

mp: 293–295 °C. IR (KBr) (ν_{max}, cm^{-1}): 1496 (N=N), 1452 (C=C), 1305, 1124 (SO_2). ^{1}HNMR (400 MHz, DMSO): δ_H 5.23 (s, 4H, $2CH_2$), 5.45 (s, 4H, $2CH_2$), 7.21 (d, 4H, $J=8.8$ Hz, ArH), 7.81 (d, 4H, $J=8.8$ Hz, ArH), 8.41 (s, 2H, 2triazol H), ^{13}CNMR (100 MHz, DMSO): δ_C 53.15, 62.13, 115.10, 116.26, 126.24, 129.42, 129.96, 132.17, 133.68, 142.01, 162.38, 166.58. (m/z): 628 (M^+). Anal. Calcd. for $C_{32}H_{26}F_2N_6O_4S$: C, 61.14; H, 4.17; N, 13.37; S, 5.10. Found: C, 61.38; H, 4.13; N, 13.25; S, 5.02.

4.7.10 Diethyl 2,2′-(4,4′-(((sulfonylbis(4,1-phenylene))bis(oxy))bis(methylene)) bis(1H-1,2,3-triazole-4,1-diyl))diacetate (3j)

mp: 257–259 °C. IR (KBr) (ν_{max}, cm^{-1}): 1726 (C=O ester), 1495 (N=N), 1452 (C=C), 1302, 1129 (SO_2). ^{1}HNMR (400 MHz, DMSO): δ_H 1.19 (t, 6H, $J=7.12$ Hz, $2CH_3$), 4.17 (q, 4H, $J=7.12$ Hz, $2CH_2$), 5.27 (s, 4H, $2CH_2$), 5.39 (s, 4H, $2CH_2$), 7.23 (d, 4H, $J=8.88$ Hz, ArH), 7.86 (d, 4H, $J=8.88$ Hz, ArH), 8.24 (s, 2H, 2triazol H), ^{13}CNMR (100 MHz, DMSO): δ_C 14.39, 50.87, 61.85, 62.01, 116.03, 126.75, 129.78, 134.16, 142.23, 162.04, 167.63. (m/z): 584 (M^+). Anal. Calcd. for $C_{26}H_{28}N_6O_8S$: C, 53.42; H, 4.83; N, 14.38; S, 5.48. Found: C, 53.65; H, 4.78; N, 14.23; S, 5.42.

4.7.11 2,2′-(4,4′-(((Sulfonylbis(4,1-phenylene))bis(oxy)) bis(methylene))bis(1H-1,2,3-triazole-4,1-diyl)) diacetonitrile (3k)

mp: 241–243 °C. IR (KBr) (ν_{max}, cm^{-1}): 2210 (C≡N), 1492 (N=N), 1449 (C=C), 1305, 1114 (SO_2). ^{1}HNMR (400 MHz, DMSO): δ_H 5.36 (s, 4H, $2CH_2$), 5.49 (s, 4H, $2CH_2$), 7.17 (d, 4H, $J=8.8$ Hz, ArH), 7.83 (d, 4H, $J=8.8$ Hz, ArH), 8.29 (s, 1H, triazol H), ^{13}CNMR (100 MHz, DMSO): δ_C 48.98, 62.84, 115.61, 117.91, 126.23, 129.17, 133.67, 142.03, 167.19. MS (m/z): 490 (M^+). Anal. Calcd. for $C_{22}H_{18}N_8O_4S$: C, 53.87; H, 3.70; N, 22.85; S, 6.54. Found: C, 54.07; H, 3.67; N, 22.73; S, 6.49.

4.7.12 2,2′-(4,4′-(((Sulfonylbis(4,1-phenylene))bis(oxy)) bis(methylene))bis(1H-1,2,3-triazole-4,1-diyl)) diethanol (3l)

mp: 265–267 °C. IR (KBr) (ν_{max}, cm^{-1}): 3413 (OH), 1495 (N=N), 1455 (C=C), 1313,1107 (SO_2). ^{1}HNMR (400 MHz, DMSO): δ_H 3.31 (br s, 2H, 2 OH, D_2O exchangeable), 4.36 (t, 4H, $J=5.4$ Hz, 2 CH_2), 4.51 (t, 4H, $J=5.4$ Hz, 2 CH_2), 5.51 (s, 2H, CH_2), 7.05 (d, 4H, $J=8.6$ Hz, ArH), 7.81 (d, 4H, $J=8.6$ Hz, ArH), 8.58 (s, 2H, 2 triazol H), ^{13}CNMR (100 MHz, DMSO): δ_C 54.91, 61.23, 63.02, 115.82, 126.45, 128.37, 134.60, 142.18, 167.29. MS (m/z): 500 (M^+). Anal. Calcd. for $C_{22}H_{24}N_6O_6S$: C, 52.79; H, 4.83; N, 16.79; S, 6.41. Found: C, 53.02; H, 4.76; N, 16.68; S, 6.35.

Compliance with Ethical Standards

Conflict of interest The authors declare that they have no conflict of interest.

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