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PAPER

One-pot synthesis of 1,2,3-triazoles from boronic acids in water using Cu(II)–β-cyclodextrin complex as a nanocatalyst†

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We report here the one-pot synthesis of 1,2,3-triazoles of arylboronic acids in water. An efficient method has been developed for the synthesis of 1,2,3-triazoles *via* a one-pot reaction of an arylboronic acid with sodium azide in the presence of Cu_2–β-CD (CD = Cyclodextrin) as a nanocatalyst in water followed by a click cyclization reaction with an alkyne at room temperature in air without any additives. This method is simple, rapid, and high yielding.

Introduction

1,2,3-Triazoles compounds are an important class of organic compounds for both synthetic and medicinal chemistry.[1] 1,2,3-Triazoles are traditionally obtained using the thermal 1,3-dipolar cycloaddition of organic azides with alkynes (Huisgen reaction) that has been known for nearly five decades.[2] In 2002, the groups of Fokin *et al.*[3] and of Medal *et al.*[4] independently reported the Cu(I)-catalyzed azide–alkyne 1,3-dipolar cycloaddition that has attracted a significant attention, due to the formation of 1,4-substituted-1,2,3-triazoles with high regioselectivity and biological properties.[5]

Organic azides are useful intermediates in the synthesis of various heterocyclic compounds specially 1,2,3-triazoles.[6] Although the preparation of alkyl azides is straightforward, methods for the preparation of aryl azides are rather limited. They are prepared from the corresponding amines *via* their diazonium salts,[7] or the reactions of organometallic aryls with *p*-tosyl azide.[8] Recently, copper catalyzed coupling of aryl amines,[9] halides,[10] and boronic acids with an azide sources such as NaN_3, TMSCN and TfN_3 have been reported.[11] Unfortunately, the methods need special ligands or catalysts, organic solvents, specific temperatures, and the limited substrate scope greatly limits the use of these methods. Among the limited methods for the synthesis of arylazides, the coupling of arylboronic acids with sodium azide[11a] has attracted attention due to its compatibility with a variety of functional groups, stability and the lower toxicity of the boronic acids than other organometallic reagents used, and the ease of working up the reaction mixture.

Recently many studies have been reported on the *in situ* generation of required azides in the Cu(I)-catalyzed azide–alkyne 1,3-dipolar cycloaddition reaction.[12]

One-pot synthesis of 1,2,3-triazoles *via* the *in situ* generation of aryl azides in the presence of the alkyne minimizes hazards derived from their isolation and handling. Fokin *et al*. reported the copper catalyzed one-pot synthesis 1,2,3-triazoles from *in situ* generation of azides from aryl halides followed by reaction with an alkyne in the presence of L-proline and sodium ascorbate.[12a] It is worth nothing that due to slow azidonation of aryl halides the above method usually suffers from long reaction times (~overnight) even at elevated temperature. Fokin *et al.* also reported three-component 1,3-dipolar cycloaddition using aliphatic bromides as the azide precursors catalyzed by copper using microwave irradiation.[12b] Moses *et al.* reported an efficient method for the *in situ* generation of aromatic azides from aromatic amines using *tert*-butyl nitrite and azidotrimethylsilane for the synthesis of 1,2,3-triazoles *via* Cu(I)-catalyzed azide–alkyne 1,3-dipolar cycloaddition, but this method suffers from hazards associated with *tert*-butyl nitrile.[12c] In 2010, Alonso *et al.* reported three-component 1,3-dipolar cycloaddition using aliphatic halides as the azide precursors catalyzed by copper nanoparticles on activated carbon.[12d]

With the increasing demand for environmentally friendly methods, organic reactions in aqueous media have attracted much recent attention.[13] Recently we have found that the Cu(II)–β-cyclodextrin complex is an efficient nanocatalyst for the homo- and chemoselective cross-coupling of arylboronic acids under base-free conditions in water.[14] Cu(II)–β-cyclodextrin is a binuclear complex with a good stability constant that can be prepared readily by addition of copper sulfate solution (0.04 M) to a mixture of β-cyclodextrin in sodium hydroxide solution (0.5 M) (Scheme 1).[15]

We have now found that Cu_2–β-CD complex is an effective binuclear macrocyclic nanocatalyst for the one-pot synthesis 1,2,3-triazoles *via* a one-pot reaction of an arylboronic acid with

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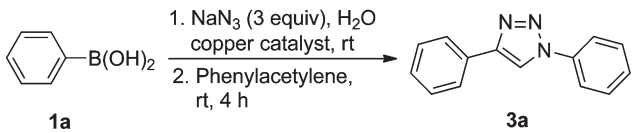
Scheme 1 The suggested formula of Cu(II)–β-CD complex.



Scheme 2 One-pot synthesis **3a** using copper catalysts in water.

Table 1 Copper-catalyzed one-pot synthesis of **3a** from phenylboronic acid (**1a**)

Entry	Catalyst	Mol%	*t* (h)[a]	Yield (%)[b]
1	$Cu(OAc)_2$	10	24	21
2	CuI	10	24	60
3	$CuSO_4$	10	24	28
4	$CuCl_2$	10	24	24
5	$Cu(NO_3)_2$	10	24	58
6	Cu_2–β-CD	5	4	94
7	—	—	24	—
8	β-CD + $CuSO_4$	10	4	<12

[a] Reaction time is the time of formation of phenylazide (first step). [b] Isolated yield of product **3a**.

sodium azide in water followed by a click cyclization reaction with an alkyne at room temperature in air without any additives.

Results and discussion

Initially, treatment of phenylboronic acid **1a** with sodium azide followed by a click cyclization reaction with a phenylacetylene **2a** at room temperature in water was chosen as the model reaction (Scheme 2). When the reaction was carried out using copper(II) acetate ($Cu(OAc)_2$) for 24 h at room temperature, 1,4-diphenyl-1*H*-1,2,3-triazole **3a** was obtained in 21% isolated yield (Table 1). Next, various copper salts were screened in the one-pot synthesis 1,2,3-triazoles of phenylboronic acid **1a** in water (entries 2–5). When the reaction was carried out using copper(I) iodide (CuI) for 24 h at room temperature, triazole **3a** was obtained in 60% yield (entry 2). The reaction yield did not increase when the reaction was carried out using $CuSO_4$, $CuCl_2$ and $Cu(NO_3)_2$ (entries 3–5). Finally, the one-pot reaction of phenylboronic acid (**1a**) with sodium azide in water followed by a click cyclization reaction with an alkyne with 5 mol% of Cu_2–β-CD complex for 4 h at room temperature gave **3a** in 94% isolated yield (entry 6). The blank experiment showed that without Cu_2–β-CD, the reaction could not occur (entry 7). When the reaction was carried out using copper(II) sulfate (0.1 equiv, $CuSO_4$) in the presence of β-CD (0.1 equiv) for 4 h at room temperature, 1,4-diphenyl-1*H*-1,2,3-triazole **3a** was obtained in a very low yield (<12%, entry 8). According to these results, the one-pot reaction of an arylboronic acid with sodium azide in water followed by a click cyclization reaction with an alkyne was examined using Cu_2–β-CD complex at room temperature in air without any additives.

Under the above optimized conditions, arylboronic acids were employed in the coupling reaction with azide in water followed by a click cyclization reaction with an alkyne using Cu_2–β-CD complex at room temperature in air without any additives. The obtained results are summarized in Table 2. The one-pot reaction of different substituted arylboronic acids with sodium azide in water followed by a click cyclization reaction with phenylacetylene using Cu_2–β-CD complex at room temperature in air gave the corresponding 1,2,3-triazoles in excellent yields (entries 2–8).

Arylboronic acid bearing an aldehyde group, in the *para* position gave the corresponding triazole product (entry 8). Arylboronic acid bearing a weakly coordinating group of $-NO_2$ could also be used to obtain the desired product **3c** in 96% yield (entry 3). It is also possible to carry out this reaction for *ortho*-substituted arylboronic acid (entry 2).

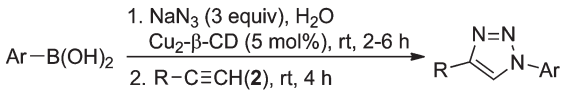
This method was also applied to the one-pot synthesis of the 1,2,3-triazole of 2-naphthylboronic acid. 2-Naphthylboronic acid gave the corresponding triazole **3i** in 94% yield (entry 9).

Treatment of phenylboronic acid with sodium azide in water followed by a click cyclization reaction with different substituted phenyacetylenes using Cu_2–β-CD complex at room temperature in air gave the desired products in excellent yields (entries 10, 11). Finally, the reaction of phenylboronic acid with sodium azide in water in the presence of Cu_2–β-CD followed by a click cyclization reaction with aliphatic alkynes gave the corresponding 1,2,3-triazoles in excellent yields (entries 12–17). Thus, a wide variety of 1,2,3-triazoles were synthesized using the conditions reported herein.

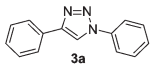
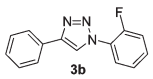
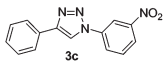
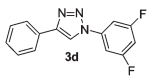
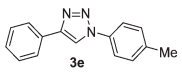
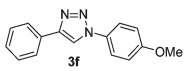
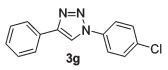
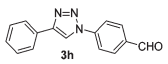
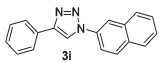
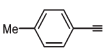
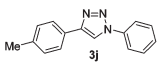
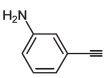
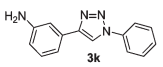
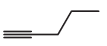
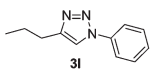
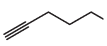
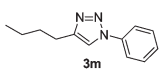
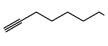
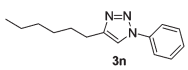
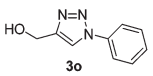
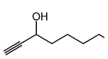
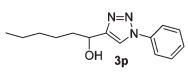
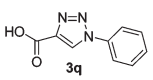
In the previous paper, we presented a proposed mechanism for Cu_2–β-CD catalyzed homocoupling reaction of arylboronic acids.[14] The Cu_2–β-CD played an important role in the formation of a bimetallic aryl copper intermediate, *via* the attack of the hydroxide ligand to the oxophilic boron center, which undergoes subsequent reductive elimination to the symmetrical biaryl compound.[16] In this work, we further investigated the role of the catalyst in the formation of bimetallic aryl copper intermediate.

Transition metal complexes usually have two absorption bands in UV-vis spectroscopy in the visible region leading to their coloration. These bands come from a combination of d–d transfer and charge transfer transition. The charge transfer transition is stronger and out of scale in high concentrations. In the Cu_2–β-CD complex, it is impossible to observe both kinds of absorption due to charge transfer transition between copper and the alkoxide anion. Moreover, sodium azide also has a strong absorption in the UV region that intensifies this phenomenon. The copper sulfate and Cu_2–β-CD show completely different manners in azidation of arylboronic acid that could be observed in their UV-vis spectrum pattern. Fig. 1 shows the UV-vis spectrum of Cu_2–β-CD in aqueous solution (spectrum a). The absorption spectrum of Cu_2–β-CD in aqueous solution containing NaN_3 (spectrum b) becomes similar to that of Cu_2–β-CD in aqueous solution. On the other hand, according to the literature, the reaction of NaN_3 with copper(II) salts gives copper azide.[17] UV-vis spectra of copper(II) sulfate solution and a mixture of copper sulfate with sodium azide show a good interaction of azide with copper(II) (see ESI†). It seems that the hardly soluble copper azide acts a catalyzing reagent in the case of copper sulfate. These results show that there is no interaction between

Table 2 Cu_2–β-CD-catalyzed one-pot reaction of arylboronic acids with sodium azide in water followed by a click cyclization with an alkyne



1 **3**

Entry	Ar (**1**)	Alkyne **2**	Product **3**	*t* (h)	Yield (%)[a]
1	C_6H_5–		 **3a**	4	94
2	*o*-FC_6H_4–		 **3b**	2	94
3	*m*-$NO_2C_6H_4$–		 **3c**	6	95
4	3,5-$F_2C_6H_3$–		 **3d**	2	96
5	*p*-MeC_6H_4–		 **3e**	4	94
6	*p*-$MeOC_6H_4$–		 **3f**	4	97
7	*p*-ClC_6H_4–		 **3g**	4	96
8	*p*-$OHCC_6H_4$–		 **3h**	4	94
9	β-Naphthyl		 **3i**	4	94
10	C_6H_5–		 **3j**	4	95
11	C_6H_5–		 **3k**	4	95
12	C_6H_5–		 **3l**	4	93
13	C_6H_5–		 **3m**	4	89
14	C_6H_5–		 **3n**	4	91
15	C_6H_5–		 **3o**	4	92
16	C_6H_5–		 **3p**	4	90
17	C_6H_5–		 **3q**	4	94

[a] Isolated yields.

Cu_2–β-CD and NaN_3. In contrast to the azide ion, phenylboronic acid interacts very well with the copper ion in Cu_2–β-CD. The addition of phenylboronic acid to an aqueous solution of Cu_2–β-CD changes the absorption spectra (see ESI†). The effect of added phenylboronic acid on the absorption is due to the formation of an intermediate aryl copper complex (see ESI†).[18] The aryl copper intermediate undergoes subsequent reductive azidation to the arylazide compound and the catalyst is regenerated in the solution (spectra c and e). The addition of phenylboronic acid to an aqueous solution of Cu_2–β-CD followed by an addition of NaN_3 also changes the absorption spectra (spectrum e).

We suggest that the Cu_2–β-CD complex is stable in the reaction process and copper ions with cyclodextrin have a synergetic

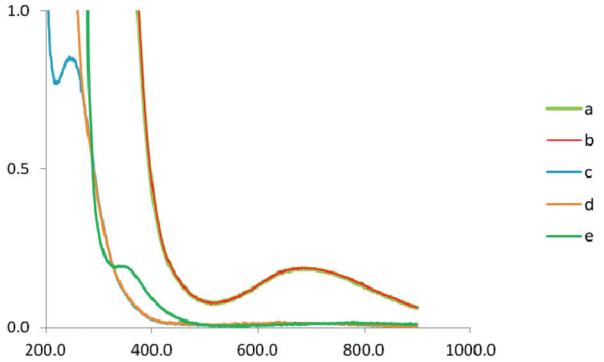
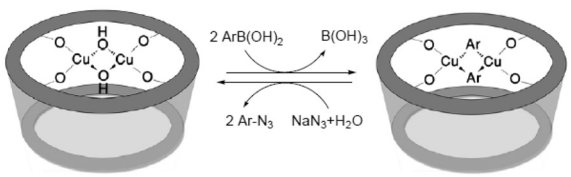


Fig. 1 Spectral properties (UV-vis spectra in cell 0.1 cm) of Cu_2–β-CD in aqueous solution. (a) [Cu_2–β-CD] = 0.06 M in aqueous solution, (b) [Cu_2–β-CD] = 0.06 M in aqueous solution containing 1.8 M of NaN_3. (c) [Cu_2–β-CD] = 0.0006 M in aqueous solution, (d) [Cu_2–β-CD] = 0.0006 M in aqueous solution containing 0.018 M of NaN_3 and (e) [Cu_2–β-CD] = 0.0006 M in aqueous solution containing 0.012 M phenylboronic acid and 0.018 M of NaN_3.

effect to catalyze azidation reaction fast and effectively. Strong evidence to prove this suggestion is the UV-vis spectra of Cu_2–β-CD in the reaction mixture at the end of the typical azidation reaction (see ESI†).

UV-vis spectra of cyclodextrin (CD), 3-nitrophenylazide, and a mixture of CD with 3-nitrophenylazide do not show a good interaction of arylazide with cyclodextrin (see ESI†). However UV-vis of a mixture of Cu_2–β-CD complex with 3-nitrophenylazide shows a good interaction of ayrl azide with the complex.

The data described above lead to the following proposed mechanism for Cu_2–β-CD catalyzed *in situ* azidation of arylboronic acids for the synthesis of 1,2,3-triazoles. The reaction is initiated by transmetallation of the aryl group from B to copper *via* the attack of the hydroxide ligand to the oxophilic boron center. The resulting arylcopper intermediate undergoes subsequent reductive azidation to the arylazide compound (Scheme 3).



Scheme 3 The suggested mechanism of Cu(II)–β-CD catalyzed conversion of aryl boronic acids to aryl azides.

According to literature reports for the Cu-catalyzed azide–alkyne 1,3-dipolar cycloaddition,[5] we believe that the 1,2,3-triazole formation proceeds through attack of the hydroxido ligand of Cu_2–β-CD complex to the terminal hydrogen of acetylene to give copper acetylide. Continuing, coordination of the arylazide to the copper center of the acetylide initiates an azide–alkyne 1,3-dipolar cycloaddition.

Conclusion

We reported here the transition-metal-catalyzed one-pot synthesis of 1,2,3-triazoles *via* a one-pot reaction of an arylboronic acid with sodium azide in water followed by a click cyclization reaction with an alkyne at room temperature in air without any additives. We have developed an efficient Cu catalyzed protocol for the one-pot synthesis of 1,2,3-triazoles of arylboronic acids. Cu_2–β-CD complex was found to be effective catalyst for this transformation, which is readily available and structurally simple as a nanocatalyst.

Experimental

General methods

All melting points were taken on a Yanagimoto and Buchi 510 apparatus and are uncorrected. Mass spectra were recorded on a VG Auto Spec. using electron impact ionization (EI) techniques. NMR spectra were obtained on a Bruker Avance 400 NMR Spectrometer (^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz). UV-vis spectra were obtained on Ultrospec 4000 single beam. Analytical TLC was carried out with plates precoated with silica gel 60 F_{254} (0.25 mm thick). Copper sulfate was recrystallized before use. All solvents were distilled before use.

Preparation of Cu–β-cyclodextrin complex

This complex was prepared by the method described by Matsui *et al.*[15b] In a 250 ml Becker containing 50 ml of 0.5 M NaOH, β-cyclodextrin (1 mmol) was dissolved with stirring. To this clear solution 75 ml of 0.04 M $CuSO_4{\cdot}(H_2O)_5$ (3 mmol) solution was added. A dark blue solution was obtained immediately that was stirred at room temperature. After 6 h, this solution was filtered to remove excess of copper salt which precipitated as a blue solid (copper hydroxide). To this blue solution was added ethanol (about 400 ml) until a light blue suspension was formed, then it was filtrated and wash with ethanol and air-dried at room temperature. This complex was converted to fine powder before use as catalyst.

General procedure for the one-pot synthesis 1,2,3-triazoles of aryl boronic acids

To a mixture of Cu_2CD (0.05 mmol, 65 mg, in this complex the number of water molecule has not been exactly determined so far and so we suppose its molecular weight to be 1300 mg $mmol^{-1}$) in 3 mL distilled water was added arylboronic acid (1 mmol) and sodium azide (3 mmol), and the resulting mixture was stirred at ambient temperature for 4–6 h. The alkyne (1 mmol) was added to the reaction mixture and the mixture was stirred at ambient temperature for 4 h. Water (50 mL) was added to the reaction mixture and extracted with CH_2Cl_2 (2 × 20 ml) and dried over Na_2SO_4. The solvent was removed under reduced pressure to give the crude product. The solid was recrystallized from a solvent mixture CH_2Cl_2–*n*-hexane or CH_2Cl_2–methanol to afford purified 1,2,3-triazoles **3a–q** in 89–97% yields.

1,4-Diphenyl-1*H*-1,2,3-triazole (3a). White solid; mp 170–172 °C (lit.[12a] 165–171 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.27 (s, 1H), 7.95 (d, J = 7.2 Hz, 2H), 7.83 (d, J = 7.6 Hz, 2H), 7.58 (t, J = 8 Hz, 2H), 7.48–7.51 (m, 3H), 7.40 (t, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 132.6, 130.2, 129.8,

128.9, 128.8, 128.4, 128.0, 127.8, 125.8, 120.5; HRMS calcd for $C_{14}H_{12}N_3$ (MH^+): 222.1031 Found: 222.1031.

1-(*o*-Fluorophenyl)-4-phenyl-1,2,3-triazole (3b). White solid; mp 101–102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.37 (s, 1H), 8.04 (t, J = 8 Hz, 1H), 7.95 (d, J = 7.6 Hz, 2H), 7.44–7.51 (m, 3H), 7.34–7.43 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.2 (d, J_{CP} = 249 Hz), 130.1 (d, J_{CP} = 8 Hz), 130.1, 128.9, 128.5, 125.9, 125.3 (d, J_{CP} = 4 Hz), 125.3, 124.8, 117.1, 116.9; HRMS calcd for $C_{14}H_{11}N_3F$(MH^+): 240.937 Found: 240.938.

1-(*m*-Nitrophenyl)-4-pheny-1, 2, 3-triazole (3c). Yellow solid; mp 202–204 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.55 (s, 1H), 8.77 (t, J = 2 Hz, 1H), 8.56 (dd, J = 7.6, 1.2 Hz, 1H), 8.42 (dd, J = 8, 1,6 Hz, 1H), 7.91–7.97 (m, 3H), 7.51 (t, J = 7.6 Hz, 2H), 7.40 (t, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 1149.0, 148.1, 137.6, 132.0, 130.3, 129.5, 128.9, 126.3, 125.8, 123.5, 120.4, 114.9; HRMS calcd for $C_{14}H_{11}N_4O_2$ (MH^+): 267.0882 Found: 267.0877.

1-(3,5-Difluorophenyl)-4-phenyl-1,2,3-triazole (3d). White solid; mp 153–155 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.23 (s, 1H), 7.92 (d, J = 7.6 Hz, 2H), 7.39–7.47 (m, 5H), 6.91–6.96 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.4 (dd, J_{CP} = 250, 14 Hz), 138.6, 129.6, 129.0, 128.8, 125.9, 118.2, 104.0 (t, J_{CP} = 25 Hz), 103.9 (d, J_{CP} = 20 Hz), 103.8; HRMS calcd for $C_{14}H_{10}N_3F_2$ (MH^+): 258.0843 Found: 258.0843.

4-Phenyl-1-*p*-tolyl-1*H*-1, 2, 3-triazole (3e). White solid, mp 159–160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.19 (s, 1H), 9.94 (d, J = 7.2 Hz, 2H), 7.70 (d, J = 7.6 Hz, 2H), 7.49 (t, J = 7.6 Hz, 2H), 7.36–7.41 (m, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:138.9, 134.4, 130.4, 130.3, 128.9, 128.3, 125.8, 120.4, 117.6, 21.1; HRMS calcd for $C_{15}H_{14}N_3$ (MH^+): 236.1188 Found: 236.1198.

1-(*p*-Methoxyphenyl)-4-phenyl-1, 2, 3-triazole (3f). White solid, mp 167–168 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.16 (s, 1H), 7.94 (d, J = 7.6, 2H), 7.72 (d, J = 8.8 Hz, 2H), 7.49 (t, J = 7.2 Hz, 2H), 7.39 (t, J = 7.2 Hz, 1H), 7.07 (d, J = 8.6 Hz, 2H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.8, 130.4, 128.6, 128.3, 125.8, 122.4, 114.8, 55.6; HRMS calcd for $C_{15}H_{14}N_3O$ (MH^+): 252.1137 Found: 252.1143.

1-(*p*-Chlorophenyl)-4-phenyl-1,2,3-triazole (3g). White solid; mp 185–186 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.35 (s, 1H), 8.01 (d, J = 8.8 Hz, 2H), 7.95 (d, J = 7.2 Hz, 2H), 7.73 (d, J = 8.8 Hz, 2H), 7.52 (t, J = 7.6 Hz, 2H), 7.40 (t, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 147.9, 135.9, 133.4, 130.5, 130.4, 129.3, 128.8, 125.8, 122.1, 120.1; HRMS calcd for $C_{14}H_{11}N_3Cl$ (MH^+): 256.0642 Found: 256.0642.

4-(4-Phenyl-1*H*-1,2,3-triazol-1-yl)benzaldehyde (3h). Yellow solid; mp 220–221 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.10 (s, 1H), 9.49 (s, 1H), 8.24 (d, J = 8.8 Hz, 2H), 8.18 (d, J = 8.4 Hz, 2H), 7.97 (d, J = 7.6 Hz, 2H), 7.53 (t, J = 8 Hz, 2H), 7.42 (t, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 192.6, 148.1, 140.9, 136.1, 131.8, 130.4, 129.5, 128.9, 125.8, 120.6, 120.2; HRMS calcd for $C_{15}H_{12}N_3O$ (MH^+): 250.980 Found: 250.980.

1-(β-Naphthyl)-4-phenyl-1,2,3-triazole (3i). White solid; mp 205–207 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.48 (s, 1H), 8.55 (s, 1H), 8.21 (d, J = 8.8 Hz, 2H), 8.05–8.16 (m, 2H), 8.06 (d, J = 7.6 Hz, 2H), 7–61–7.68 (m, 2H), 7.53 (t, J = 7.6 Hz, 2H), 7.41 (t, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 147.9, 134.5, 133.3, 132.8, 130.7, 130.4, 129.5, 128.7, 128.7, 128.4, 128.0, 127.4, 125.8, 120.2, 119.0, 118.0; HRMS calcd for $C_{18}H_{14}N_3$ (MH^+): 272.1188 Found: 272.1183.

1-Phenyl-4-*p*-tolyl-1,2,3-triazole (3j). White solid; mp 171–172 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.19 (s, 1H), 7.83 (m, 4H), 7.57 (t, J = 8 Hz, 2H), 7.48 (t, J = 7.6, 1H), 7.30 (d, J = 9.2 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.3, 129.8, 129.6, 128.7, 127.4, 125.7, 120.5, 117.2, 21.3; HRMS calcd for $C_{15}H_{14}N_3$ (MH^+): 236.1188 Found: 236.1186.

1-Phenyl-4-(*m*-aminophenyl)-1,2,3-triazole (3k). Yellow solid; mp 122–125 °C, ^{1}H NMR (400 MHz, acetone-d_6) δ: 8.86 (s, 1H), 7.98 (d, J = 8 Hz, 2H), 7.64 (t, J = 7.6 Hz, 2H), 7.52 (t, J = 7.6, 1H), 7.38 (d, J = 1.6 Hz, 1H), 7.15–7.22 (m, 2H), 6.71 (dd, J = 7.2, 1.2 Hz, 1H), 4.70–4.90 (br, 2H); ^{13}C NMR (100 MHz, acetone-d_6) δ: 148.9, 148.55, 137.4, 131.4, 129.8, 129.4, 128.4, 120.0, 118.2, 114.2, 114.2, 111.3; HRMS calcd for $C_{14}H_{13}N_4$ (MH^+): 237.1140 Found: 237.1132.

1-Phenyl-4-propyl-1,2,3-triazole (3l). White solid, mp 47–48 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (s, 1H), 7.70 (d, J = 7.6 Hz, 2H), 7.47 (t, J = 7.6 Hz, 2H), 7.37 (t, J = 7.6 Hz, 1H), 2.75 (t, J = 6.8 Hz, 2H), 1.75 (m, 2H), 0.99 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.5, 130.1, 129.2, 128.4, 123.3, 120.9, 27.7, 21.9, 13.8; HRMS calcd for $C_{11}H_{14}N_3$ (MH^+): 188.1188 Found: 188.1184.

1-Phenyl-4-butyl-1,2,3-triazole (3m). White solid; mp 44–46 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (s, 1H), 7.67 (d, J = 8Hz, 2H), 7.43 (t, J = 8 Hz, 2H), 7.33 (t, J = 7.2 Hz, 1H), 2.74 (t, J = 7.2 Hz, 2H), 1.65–1.68 (m, 2H), 1.34–1.37 (m, 2H), 0.90 (t, J = 6.4, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.4, 130.1, 130.0, 129.4, 123.1, 128.8, 30.8, 24.2, 22.2, 13.7; HRMS calcd for $C_{12}H_{16}N_3$ (MH^+): 202.1344 Found: 202.1350.

1-Phenyl-4-hexyl-1,2,3-triazole (3n). White solid; mp 40–42 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (s, 1H), 7.35 (d, J = 7.6 Hz, 2H), 7.50 (t, J = 7.2 Hz, 2H), 7.40 (t, J = 7.2 Hz, 1H), 2.79 (t, J = 7.2 Hz, 2H), 1.70–1.78 (m, 2H), 1.32–1.40 (m, 6H), 0.89 (t, J = 6.8 Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.3, 129.6, 128.3, 120.3, 118.8, 31.6, 29.3, 28.9, 25.6, 22.5, 14.7; HRMS calcd for $C_{14}H_{20}N_3$ (MH^+): 230.1657 Found: 230.1658.

(1-Phenyl-1*H*-1,2,3-triazol-4-yl)methanol (3o). White solid; mp 101–103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.06 (s, 1H), 7.73 (d, J = 7.2 Hz, 2H), 7.53 (t, J = 7.2 Hz, 2H), 7.63 (t, J = 7.6 Hz, 1H), 4.90 (s, 2H), 3.13 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.0, 129.8, 128.8, 120.6, 56.4; HRMS calcd for $C_9H_{10}N_3O$ (MH^+): 176.0824 Found: 176.0817.

1-(1-Phenyl-1,2,3-triazol-4-yl)hexan-1-ol (3p). White solid; mp 75–76 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05 (s, 1H), 7.40 (d, J = 7.6 Hz, 2H), 7.52 (t, J = 7.2 Hz, 2H), 7.44 (t, J = 7.2 Hz, 1H), 5.00–5.08 (br, 1H), 3.18 (br, 1H), 1.93–1.98 (m, 2H), 1.35–1.53 (m, 6H), 0.90 (t, J = 6 Hz, 3H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ: 137.2, 129.7, 129.5, 128.7, 120.5, 115.5, 66.9, 37.4, 31.6, 25.1, 22.6, 14.0; HRMS calcd for $C_{14}H_{20}N_3O$ (MH^+): 246.1606 Found: 246.1606.

1-Phenyl-1, 2, 3-triazole-4-carboxylic acid (3q). White solid; mp 90–92 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ: 9.12 (s, 1H), 8.01 (d, J = 8 Hz, 2H), 7.67 (m, 2H), 7.58 (t, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ: 161.7, 140.8, 136.5, 130.0, 129.4, 126.6, 120.6; HRMS calcd for $C_9H_8N_3O_2$ (MH^+): 190.0617 Found: 190.0615.

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