

Application of magnetic nanoparticle-supported CuBr: a highly efficient and reusable catalyst for the one-pot and scale-up synthesis of 1,2,3-triazoles under microwave-assisted conditions

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An efficient and practical approach was developed to synthesize 1,2,3-triazoles using recyclable Fe₃O₄ magnetic nanoparticle (MNP)-supported copper(i) catalysts *via* a one-pot multi-component copper-catalyzed azide-alkyne cycloaddition (CuAAC) reaction in water. Under microwave irradiation conditions, terminal alkynes reacted quickly with benzyl/alkyl azides, which were generated *in situ* from corresponding primary halides and sodium azide. The 1,2,3-triazoles can be exclusively generated in good to excellent yields and on a multi-gram scale.

Introduction

1,2,3-Triazole derivatives are an important class of organic compounds for medicinal chemistry, which exhibit some biological activity such as antimicrobial activity and anti-HIV activity.^{1–4} Recently, 1,2,3-triazoles were readily prepared from Cu(i)-catalyzed azide-alkyne 1,3-dipolar cycloaddition (CuAAC).^{5,6} The CuAAC click reaction was initially coined by Sharpless and co-workers at the very beginning of the third millennium and has been demonstrated as a powerful tool in numerous scientific fields, due to its superior stereoselectivity, almost quantitative yields, modularity and moderate reaction conditions.^{7–13}

At present, many efforts have been deployed for further developing the CuAAC click reaction to obtain 1,2,3-triazoles, which focused on a one-pot multi-component click reaction.^{14–31} This reaction has drawn great attention because it avoids potential explosion danger in handling small organic azides and minimizes time-consuming workup and purification process.

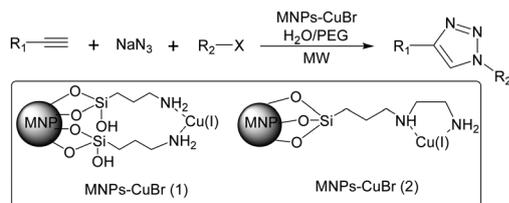
Generally, copper(i) salts and ligands have been used as homogeneous catalyst systems to catalyze one-pot multi-component synthesis of 1,2,3-triazoles from benzyl/alkyl halides, alkynes and sodium azides. However, homogeneous catalysis suffers from many problems such as difficult separation and recycling the expensive catalyst, cytotoxicity and environmental pollution. Alternatively, immobilization of the catalytic system on solid supports can mitigate these problems, as it allows the straightforward removal of the catalyst from the reaction system. In the last few years, numerous methods have been developed to immobilize

copper species on a large variety of solid supports,³² such as charcoal,^{31,33} silica,^{30,34–38} zeolite^{39–42} and polymers.^{43–49} However, the immobilized catalysts are difficult to separate from the solution, only through the use of filter, highspeed centrifugation or precipitation. An ideal solution to this problem is using the magnetic property.

Recently, magnetic nanoparticles (MNPs) have emerged as a smart support for heterogeneous catalysts due to their intrinsic properties such as large surface area, high chemical stability, low toxicity and cost.^{50–52} More importantly, MNPs-supported catalysts can be separated conveniently from the reaction mixtures by an external permanent magnet. Unfortunately, as far as we know, very few MNPs-supported CuAAC catalysts have been developed to generate 1,2,3-triazoles by the CuAAC reaction.^{24,53,54} Furthermore, these methods suffer from some similar drawbacks. For example, R. B. N. Baig *et al.* have recently developed an efficient approach to synthesize 1,2,3-triazoles using magnetically Cu catalyst *via* a one-pot technique in water under microwave irradiation conditions.²⁴ However, the preparation procedure of magnetic Cu catalyst was relatively cumbersome and required expensive reagents, such as reduced glutathione. Furthermore, the catalyst can only be recycled a few times with consistent activity. These approaches may cause environmental or economic concerns when large-scale synthesis is considered. So introduction of low-cost and efficient catalysts which could be used under aqueous conditions to produce the desired 1,2,3-triazoles in a short reaction time at high yield is still in demand.

In order to further improve the practicality and eco-friendliness of the CuAAC reaction, we report here a green, inexpensive and scale-up synthesis of 1,4-disubstituted 1,2,3-triazoles from benzyl/alkyl halides, functional alkynes and sodium azides in water, which

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Scheme 1 MNPs-CuBr catalyzed one-pot synthesis of 1,4-disubstituted 1,2,3-triazoles in water under microwave irradiation conditions.

were catalyzed by heterogeneous, recyclable and commercially available Fe₃O₄-supported Cu(I) catalysts (MNPs-CuBr 1 and 2) *via* a combination of one-pot multi-component CuAAC reaction and microwave irradiation (Scheme 1).

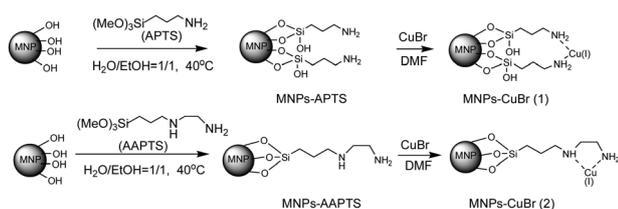
Results and discussion

Preparation and characterization of MNPs-CuBr catalysts 1 and 2

The silanization reaction between the -OH group on the surface Fe₃O₄ MNPs and (MeO)₃Si-groups can easily take place, so 3-aminopropyltrimethoxysilane (APTS) and [3-(2-aminoethylamino)propyl]trimethoxysilane (AAPT) are usually employed to modify the surface of bare MNPs. The bare MNPs were prepared by the conventional coprecipitation method and subsequently reacted with APTS or AAPT to yield amino-modified MNPs. The obtained magnetic materials were then treated with CuBr in *N,N*-dimethylformamide (DMF) at room temperature for 6 h to generate copper(I) catalysts 1 and 2 (Scheme 2).

The copper(I) catalysts 1 and 2 were characterized using various methods. Fig. 1 shows the FT-IR spectra of bare MNPs, APTS-coated MNPs, AAPT-coated MNPs, catalysts 1 and 2. As can be seen from Fig. 1 (lines b and d), the peaks at 3470, 1620 and 585 cm⁻¹ of APTS or AAPT-coated MNPs were characteristic bands of O-H stretching, O-H bending and Fe-O stretching vibrations. The peaks at near 2925 cm⁻¹ and 1050 cm⁻¹ were characteristic bands of -CH₂-stretching vibration and Si-O stretching vibration, indicating that the surface of MNPs was successfully modified with APTS or AAPT. In addition, Fig. 1 (lines b-e) shows the FT-IR spectra of APTS-coated MNPs and AAPT-coated MNPs before and after the complexing reaction with CuBr. The -CH₂- stretching peaks appeared at 2928 and 2927 cm⁻¹ were shifted to 2926 and 2924 cm⁻¹, respectively. This is probably caused by the coordination effect of copper(I) with the monodentate and bidentate ligands APTS and AAPT.

The percentage of nitrogen in the prepared copper(I) catalysts 1 and 2 were found to be 1.055 wt% and 1.554 wt% based on



Scheme 2 Synthetic route of MNPs-CuBr catalysts 1 and 2.

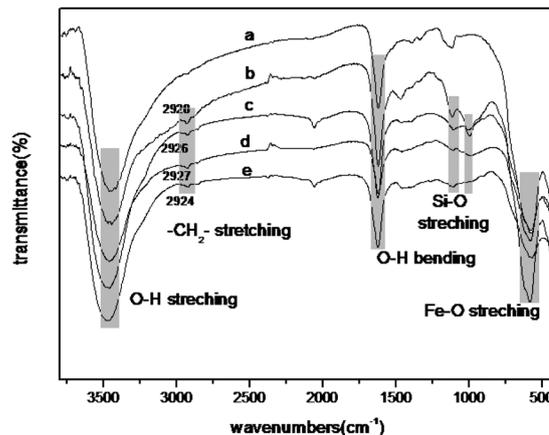


Fig. 1 FT-IR spectra of a: bare MNPs; b: APTS-coated MNPs; c: catalyst 1; d: AAPT-coated MNPs; e: catalyst 2.

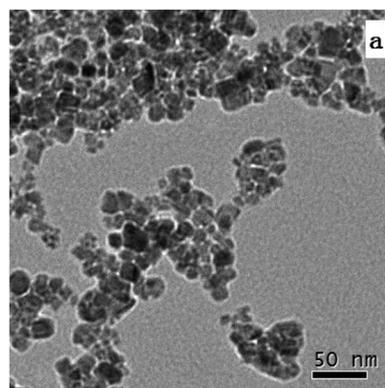


Fig. 2 A TEM image of MNPs-CuBr catalyst 1.

CNS elemental analysis, and the copper(I) contents of them were found to be 2.814 wt% and 4.182 wt% detected by atomic absorption spectroscopy analysis (AAS).

A representative TEM image of the MNPs-CuBr catalyst 1 is shown in Fig. 2, from which it can be seen that most of the particles are quasi-spherical with an average diameter of around 10–20 nm. The obtained results of TEM showed the nano-sized organic-inorganic hybrid materials were obtained.

Fig. 3 shows the X-ray diffraction (XRD) results of the MNPs. The main peaks in XRD at $2\theta = 30.1^\circ, 35.4^\circ, 43.1^\circ, 56.9^\circ$ and 62.5° , corresponded well to the standard magnetite reflections. These main peaks did not change after the attachment of APTS or AAPT even the immobilization of copper(I) species, indicating retention of the crystalline structure during the functionalization process. No copper(I)-related peaks were detected in the XRD pattern of catalyst 1, which was probably caused by copper(I) species dispersed on MNPs in a high level.

The above results suggested strongly that the copper(I) catalysts 1 and 2 were prepared by a simple and practical method.

Effect of catalyst on the one-pot CuAAC reaction in water

The one-pot reaction of benzyl chloride, NaN₃ with phenylacetylene was tested as a model reaction and was explored initially without

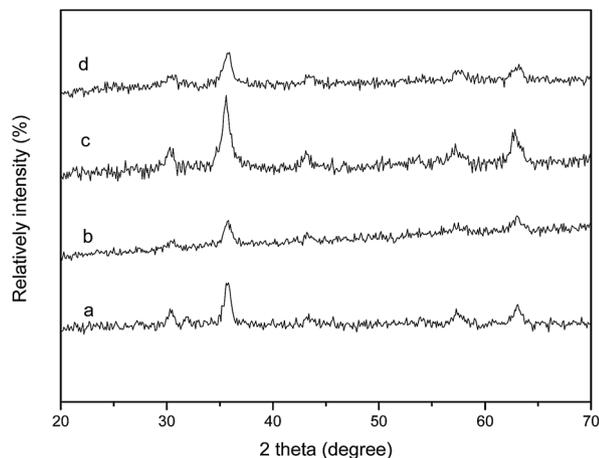


Fig. 3 XRD patterns of a: bare MNPs; b: APTS-coated MNPs; c: catalyst 1; d: catalyst 1 after 7 runs.

any phase transfer catalyst (PTC) using water as a solvent under microwave irradiation for 20 min. Unfortunately, the corresponding 1,2,3-triazole could be obtained in relatively low yield presumably due to the fact that the reactants exist as a non-miscible mixture of oil and water. Therefore, PEG400 as PTC, was applied for this reaction.

The experiment of benzyl chloride (1.5 mmol), NaN_3 (1.5 mmol) and phenylacetylene (1.5 mmol) were carried out by using H_2O (5.0 mL)-PEG400 (1.0 g) as the mixed reaction medium at 80 °C under microwave irradiation. Firstly, when MNP-APTS or MNP-supported $\text{Cu}(\text{II})$ was used as the catalyst, a reaction was still observed, although the yield of the desired product was low (Table 1, entries 1 and 2). Based on these frustrating results, we continued the research to improve the yield of the product by the optimization of the reaction conditions. To our delight, the reaction performed smoothly with the use of **1** and **2** instead of CuBr as the catalyst, and the copper(I) catalyst **1** was more effective than **2** and CuBr salt (Table 1, entries 3–5). As a result, catalyst **1** was used in the subsequent investigations because of its high reactivity, high selectivity and easy separation.

Synthesis of 1,2,3-triazoles catalyzed by copper(I) catalyst **1**

This very promising result encouraged us to extend the reaction to various halides and terminal alkynes so as to demonstrate

Table 1 Effect of the copper source on the one-pot synthesis of 1-benzyl-4-phenyl-1H-1,2,3-triazole^a

Entry	Cu catalyst	Yield ^c (%)
1	MNP-APTS	35
2	MNP-supported $\text{Cu}(\text{II})$ ^b	42
3	CuBr	81
4	Cat. 1	96
5	Cat. 2	90

^a 1.5 mmol of benzyl chloride, 1.5 mmol of NaN_3 , 1.5 mmol of phenylacetylene, 1.46 mol% of catalyst, 20 min. ^b MNP-supported $\text{Cu}(\text{II})$ was prepared from MNP-APTS and $\text{Cu}(\text{OAc})_2$ in DMF. ^c Isolated yield.

the high versatility of our approach. The results are listed in Table 2. As shown in Table 2, the one-pot CuAAC reactions were all smoothly performed in the presence of copper(I) catalyst **1** under microwave irradiation in water, and the 1,4-disubstituted 1,2,3-triazoles were isolated in good to excellent yields, and no formation of the undesired 1,5-isomers.

The reactivity of 4-bromo butane was found to be less reactive than that of benzyl chloride or benzyl bromide (Table 2, entries 1–12). They were more time consuming and lower yielding when 4-bromo butane was treated with the corresponding terminal alkynes. From entries 9 and 10 in Table 2, we reasonably conclude that primary bromides displayed higher activities than their chloride analogues.

Most functional groups such as $-\text{OH}$, $-\text{O}-$, $-\text{COOR}$, $-\text{NR}_1\text{R}_2\text{R}_3$ and $-\text{N}(\text{CO})=$ were highly tolerated (Table 2, entries 1–10), which

Table 2 Copper(I) catalyst **1** used in the one-pot CuAAC reaction for the regioselective formation of 1,4-disubstituted 1,2,3-triazoles under microwave irradiation in water^a

$$\text{R}_1\text{X} + \text{NaN}_3 + \text{R}_2\text{—C}\equiv\text{C—H} \xrightarrow[\text{MW, 80}^\circ\text{C}]{\text{MNP-CuBr (1), H}_2\text{O/PEG}} \text{R}_1\text{—N=N—C(R}_2\text{)=CH—}$$

Entry	Halide	Alkyne	Time ^a (min)	Yield ^b (%)
1			23	92
2			25	90
3			28	90
4			24	91
5			22	93
6			26	89
7			18	93
8			22	91
9			17	92
10			15	92
11			20	94
12			20	96

^a Overall time including heating time and incubating time. ^b Isolated yields.

did not break down under the one-pot CuAAC reaction conditions. However, the yields of 1,2,3-triazoles were significantly affected by the chain length of alkyl halides. When the reaction was carried out using long C-chain alkyl halides ($n \geq 12$) as halide but unfortunately very low conversion was observed on TLC. At the same time, disubstituted alkyl halides, such as 1,6-dibromohexane and 1,10-dibromodecane, were also very difficult to react with phenylacetylene under these optimized reaction conditions and gave complex mixtures. The possible reasons were the low polarity of long chain alkyl halides, its poor microwave absorbing properties, low dielectric constants and the terminal alkynes homocoupling as a side reaction. All products listed in Table 2 have been characterized by FT-IR, ^1H NMR spectroscopy.

Recycling use of catalyst 1

For practical applications of such heterogeneous systems, the reusability is one of the important properties of the catalyst. In this work, we examined the possibility of recovery and reuse of **1** by use of the one-pot CuAAC reaction between phenylacetylene, benzyl chloride and sodium azide. After completion of the model reaction, the catalyst was recovered from the reaction mixture simply by applying an external magnet. Then the recovered catalyst was washed with diethyl ether. After being dried, the catalyst can be reused directly under the same conditions without further purification. As shown in Fig. 4, the catalyst could be recycled and reused at least 7 times without a noticeable drop in the product yield and its catalytic activity. The slight decrease of catalytic activity should be due to the normal loss of the catalyst during the work-up stage.

Furthermore, the TEM images of the used catalyst did not show any significant change in the morphology of catalyst particles and the particle size remained constant at 10–20 nm even after seven reaction cycles, which proved its robustness (Fig. 5b). XRD patterns (Fig. 3d) shows that the crystalline structure of Fe_3O_4 MNP kept the same as well. Moreover, the copper(i) content of the catalyst **1** after seven cycles were found to be 2.582% detected by AAS, which was slightly lower than the catalyst **1** (2.814 wt%). Thus, this makes the process still more cost-effective.

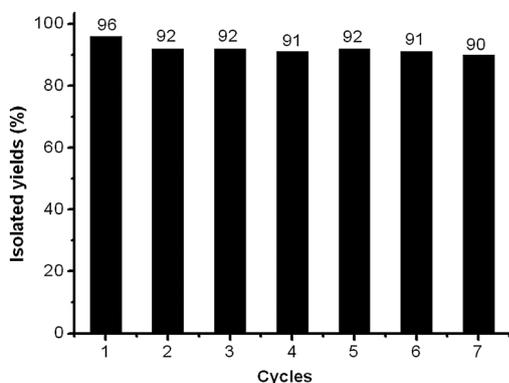


Fig. 4 The recyclability results of copper(i) catalyst **1** for the synthesis of 1,2,3-triazoles.

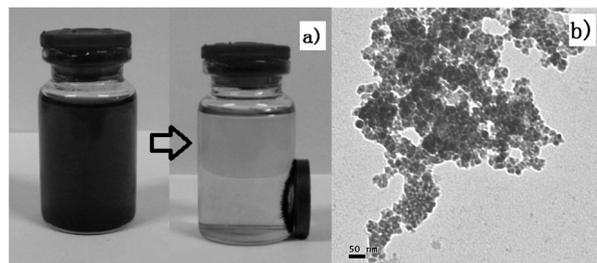


Fig. 5 (a) Photographs showing the magnetic separation of copper(i) catalyst **1**; (b) TEM image of copper(i) catalyst **1** after 7 consecutive trials.

Table 3 Scale-up synthesis of 1-benzyl-4-phenyl-1*H*-1,2,3-triazole

Entry	Scale (mmol)	H ₂ O (mL)	Isolated product (g)	Yield ^a (%)
1	1.5	5	0.34	96
2	30	50	6.42	91
3 ^b	30	50	6.33	90
4 ^c	30	50	6.16	87
5 ^d	30	50	5.64	80
6	60	100	12.13	86

^a Isolated yield. ^b Catalyst recycled from entry 2 and used for 2nd run. ^c 3rd run. ^d 4th run.

Scale-up synthesis of 1-benzyl-4-phenyl-1*H*-1,2,3-triazole

Finally, the scale-up synthesis of the 1,2,3-triazoles was investigated in the case of 1-benzyl-4-phenyl-1*H*-1,2,3-triazole as a model reaction. Encouraged by the above results, we increased the scale of the reaction to 30.0 and 60.0 mmol, keeping the reaction stoichiometry unchanged. The reactions were found to proceed successfully and the corresponding product was obtained in good yield. Importantly, when the scale of the reaction was 30.0 mmol, the catalyst could be recycled and reused at least 4 times. The detailed results were summarized in Table 3.

Conclusion

In summary, we have developed a highly active, easily recoverable and practical heterogeneous catalyst for scale-up synthesis of 1,2,3-triazole derivatives by using a one-pot multi-component CuAAC reaction in water. Microwave irradiation can distinctly shorten the reaction time and simultaneously enhance the yields and purity of 1,2,3-triazoles in comparison with conventional protocols. Furthermore, the performance of catalyst **1** was fully retained after reuse at least 4 times when the scale of the reaction was 30.0 mmol. This contribution can be important for developing a versatile synthetic approach for the scale-up synthesis of 1,2,3-triazole derivatives in a green manner.

Experimental

General

All reagents and solvents were obtained from commercial sources and used without further purification. All the one-pot CuAAC reactions were carried out in a professional microwave reactor equipped with a stirring bar.

The IR spectra were obtained using a Fourier transform infrared (FT-IR) (4000–400 cm^{-1}) spectrometer (Nicolet Nexus FT-IR spectrometer, USA) at 4 cm^{-1} resolution and 32 scans. Samples were prepared using the KBr disc method. The copper(I) contents in the catalysts **1** and **2** were determined by atomic absorption spectrophotometry (AAS) using standard methods with a Varian AA275 atomic absorption spectrophotometer (USA). Size and morphology images of MNPs were obtained by a transmission electron microscope (TEM) (Hitachi H-7650, Japan) operating at 100 kV after a drop of aqueous solution of the nanoparticles was deposited and dried on a copper grid. Powder X-ray diffraction (XRD) was used to characterize the crystalline structure of the nanoparticles on a Bruker D8 Advance (Germany) using Cu K α radiation. NMR spectra were acquired in CDCl_3 or DMSO-d_6 on a Bruker DMX-400 spectrometer at 400 MHz for ^1H NMR, the chemical shifts are given in δ values from TMS as an internal standard.

Preparation of APTS and APTS-coated MNPs

In this study, the APTS and APTS-coated MNPs were produced from bare MNPs using a modified method according to a previously reported procedure (Scheme 2).⁵⁵ Firstly, the naked MNPs were prepared by a chemical coprecipitation method and subsequently were coated with APTS or APTS to prepare amino-functionalized Fe_3O_4 -APTS and Fe_3O_4 -APTS, respectively. In detail, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (5.63 g, 20.8 mmol) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (2.90 g, 10.4 mmol) were dissolved in N_2 purged deionized water (100 mL) under vigorous stirring, the chemical coprecipitation was achieved by adding NaOH aqueous solution (4.5 mol L^{-1}) to adjust the pH value to 10 under vigorous stirring. The solution instantly became black due to the formation of Fe_3O_4 and was then incubated at 60 $^\circ\text{C}$ for 1 h. After that, the synthesized MNPs were washed with hot deionized water and ethanol for three times and then used directly for coating with APTS or APTS. Briefly, the naked MNPs and APTS or APTS with a molar ratio of 2 : 1 were dissolved in 150 mL water/EtOH (V/V = 1/1) solution. The solution was vigorously stirred under N_2 at 40 $^\circ\text{C}$ for 12 h. The synthesized APTS or APTS-coated MNPs were then collected with an external permanent magnet and washed with hot deionized water and ethanol three times and then dried in a vacuum oven at 60 $^\circ\text{C}$.

Preparation of Fe_3O_4 -supported copper(I) catalysts **1** and **2**

In a small Schlenk tube, the Fe_3O_4 -APTS or Fe_3O_4 -APTS (1.00 g) was mixed with CuBr (0.191 g, 1.0 mmol) in DMF (5.0 mL). The mixture was stirred under a N_2 atmosphere at r.t. for 6 h. These inorganic-organic hybrid Fe_3O_4 MNPs-supported copper(I) catalysts were separated by an external permanent magnet, washing with ethanol and ethyl acetate followed by drying under vacuum at 50 $^\circ\text{C}$ overnight for further use.

General procedure for the synthesis of 1,2,3-triazoles catalyzed by copper(I) catalysts **1**

Three substrates primary halides, sodium azide and terminal alkynes in a 1 : 1 : 1 molar ratio followed by adding copper(I) catalyst **1** in a mixture of H_2O (5.0 mL) and PEG400 (1.0 g) in a 10.0 mL round-bottomed flask. The mixture was heated to 80 $^\circ\text{C}$

under microwave irradiation (MW, 480 W) until TLC analysis shows that the reaction is complete. Then the reaction mixture was cooled to room temperature, copper(I) catalyst was isolated by an external permanent magnet, water was removed by rotary evaporation, the crude product was purified by flash chromatography on silica-gel to give the desired 1,2,3-triazoles in 89–96% yields.

1-benzyl-4-(4-hydroxymethyl phenoxy)methyl-1H-1,2,3-triazole (Table 1 entry 1). White solid; FT-IR (KBr disc) cm^{-1} : 3374, 3142, 3066, 3034, 2928, 2872, 1610, 1587, 1510, 1459, 1433, 1386, 1330, 1300, 1238, 1174, 1120, 1010, 860, 825, 746, 719; $^1\text{H-NMR}$ (400 MHz, DMSO-d_6) δ : 8.26 (s, 1H), 7.45–7.28 (m, 5H), 7.23 (d, $J = 8.7$ Hz, 2H), 7.00–6.92 (m, 2H), 5.61 (s, 2H), 5.12 (s, 2H), 5.03 (t, $J = 5.7$ Hz, 1H), 4.42 (d, $J = 5.7$ Hz, 2H).

1-Butyl-4-(4-hydroxymethyl phenoxy)methyl-1H-1,2,3-triazole (Table 2 entry 2). White solid; FT-IR (KBr disc) cm^{-1} : 3372, 3142, 2960, 2933, 2871, 1611, 1586, 1511, 1463, 1383, 1299, 1239, 1175, 1145, 1113, 1010, 860, 828; $^1\text{H NMR}$ (400 MHz, DMSO-d_6) δ : 8.21 (s, 1H), 7.28–7.20 (m, 2H), 7.03–6.95 (m, 2H), 5.12 (s, 2H), 5.05 (dt, $J = 11.4, 5.7$ Hz, 1H), 4.43 (t, $J = 7.0$ Hz, 2H), 4.36 (t, $J = 7.1$ Hz, 2H), 1.86–1.73 (m, 2H), 1.33–1.18 (m, 2H), 0.93–0.84 (m, 3H).

(1-Butyl-1H-1,2,3-triazol-4-yl)methyl benzoate (Table 2 entry 3). White solid; FT-IR (KBr disc) cm^{-1} : 3154, 2956, 2932, 2872, 1720, 1602, 1586, 1471, 1454, 1441, 1383, 1342, 1316, 1272, 1225, 1177, 1147, 1106, 1093, 1069, 1056, 1025, 931, 836, 812, 785, 704; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 8.04 (t, $J = 10.8$ Hz, 2H), 7.69 (s, 1H), 7.58 (dd, $J = 15.2, 8.1$ Hz, 1H), 7.50–7.40 (m, 2H), 5.47 (d, $J = 10.5$ Hz, 2H), 4.37 (t, $J = 7.2$ Hz, 2H), 1.99–1.86 (m, 2H), 1.42–1.29 (m, 2H), 0.95 (dd, $J = 16.8, 9.7$ Hz, 3H).

(1-Benzyl-1H-1,2,3-triazol-4-yl)methyl benzoate (Table 2 entry 4). White solid; FT-IR (KBr disc) cm^{-1} : 3115, 3061, 2966, 2948, 2873, 1714, 1599, 1494, 1450, 1440, 1398, 1314, 1270, 1218, 1119, 1097, 1072, 1051, 1026, 958, 865, 825, 808, 795, 763, 705; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 8.04 (d, $J = 7.6$ Hz, 2H), 7.63 (s, 1H), 7.57 (t, $J = 7.2$ Hz, 1H), 7.42 (dd, $J = 17.6, 9.9$ Hz, 5H), 7.30 (d, $J = 6.2$ Hz, 2H), 5.55 (s, 2H), 5.47 (s, 2H).

1-Benzyl-4-phenoxy)methyl-1H-1,2,3-triazole (Table 2 entry 5). White solid; FT-IR (KBr disc) cm^{-1} : 3136, 2930, 2878, 1595, 1493, 1460, 1430, 1384, 1357, 1335, 1293, 1245, 1221, 1175, 1118, 1079, 1054, 1030, 1006, 985, 891, 858, 819, 755; $^1\text{H-NMR}$ (400 MHz, DMSO-d_6) δ : 8.27 (s, 1H), 7.48–7.19 (m, 7H), 7.15–6.80 (m, 3H), 5.62 (s, 2H), 5.14 (s, 2H).

1-Butyl-4-phenoxy)methyl-1H-1,2,3-triazole (Table 2 entry 6). Pale yellowish oil; FT-IR (KBr disc) cm^{-1} : 3219, 2921, 2852, 1717, 1606, 1590, 1512, 1460, 1374, 1296, 1217, 1175, 1114, 1078, 1028, 970, 929, 826, 751, 694; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 7.58 (s, 1H), 7.24 (t, $J = 7.6$ Hz, 2H), 6.93 (dd, $J = 16.2, 7.9$ Hz, 3H), 5.14 (s, 2H), 4.30 (dt, $J = 14.4, 7.4$ Hz, 2H), 1.89–1.72 (m, 2H), 1.29 (dq, $J = 14.4, 7.1$ Hz, 2H), 0.90 (t, $J = 7.4$ Hz, 3H).

4-[(1-Benzyl-1H-1,2,3-triazol-4-yl)methyl]morpholine (Table 2 entry 7). Pale yellowish solid; FT-IR (KBr disc) cm^{-1} : 3142, 2967, 2853, 2819, 1457, 1329, 1283, 1221, 1114, 1055, 1003, 858, 797, 729; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.40 (dd, $J = 9.0, 3.7$ Hz, 3H), 7.38 (s, $J = 6.2$ Hz, 1H), 7.31–7.26 (m, 2H), 5.53 (s, 2H), 3.79–3.68 (m, 4H), 3.66 (s, 2H), 2.51 (s, 4 H).

1-[(1-Benzyl-1*H*-1,2,3-triazol-4-yl)methyl]pyrrolidine-2,5-dione (Table 2 entry 8). Pale yellowish solid; FT-IR (KBr disc) cm^{-1} : 3142, 3068, 2933, 2859, 1711, 1455, 1430, 1400, 1332, 1175, 1049; ^1H NMR (400 MHz, CDCl_3): δ 7.50 (s, 1H), 7.38 (s, 3H), 7.28 (s, 2H), 5.50 (s, 2H), 4.79 (s, 2H), 2.73 (s, 4H).

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