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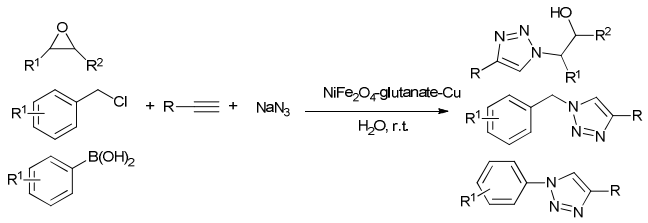
• **Graphical Abstract:**



One-pot three-component synthesis of 1,2,3-triazoles using magnetic $NiFe_2O_4$-glutamate-Cu as an efficient heterogeneous catalyst in water

Jun Lu, Er-Qian Ma, Yu-Heng Liu, Ya-Meng Li, Li-Ping Mo and Zhan-Hui Zhang*

A magnetic $NiFe_2O_4$ supported glutamate-copper catalyst are prepared and applied for the synthesis of a wide variety of 1,2,3-triazoles in water at room temperature.

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One-pot three-component synthesis of 1,2,3-triazoles using magnetic $NiFe_2O_4$-glutamate-Cu as an efficient heterogeneous catalyst in water

Jun Lu[a], Er-Qian Ma[a], Yu-Heng Liu[b], Ya-Meng Li[a], Li-Ping Mo[a] and Zhan-Hui Zhang[a,*]

A novel magnetic $NiFe_2O_4$ supported glutamate-copper catalyst was prepared in a convenient and ecofirendly manner and characterized using FTIR, XRD, EDX, TEM, SEM, XPS and VSM. This magnetic catalyst exhibited excellent catalytic activity for the synthesis of a wide variety of 1,4-disubstituted-1,2,3-triazoles via one-pot three-component click reactions of sodium azide, non-activated terminal alkynes, and different azide precursors such as epoxides, benzyl chloride, and aryl boronic acids at room temperature in water. This procedure has some advantages such as aqueous reaction medium, ambient reaction condition, high yields, wide substrate scope, easy separation of catalyst using an external magnet and efficient recycling.

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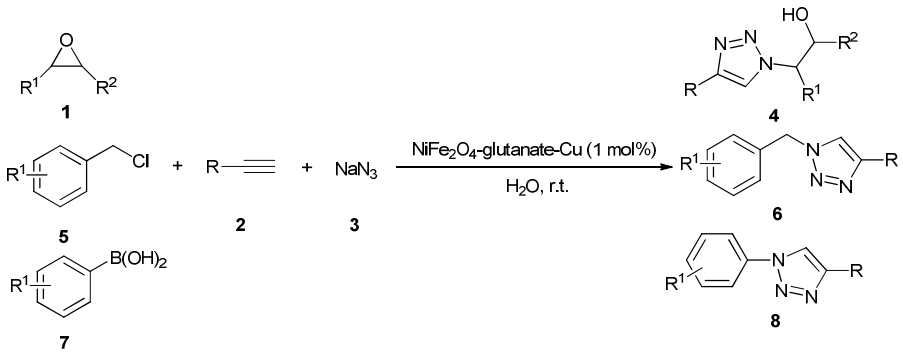
Introduction

Heterocyclic compounds containing nitrogen-atoms occupy an important position in nature product and medical chemistry. 1,2,3-Triazoles are well-known five-membered heterocyclic molecules that have attracted much interest due to their wide range of applications in the fields of pharmaceuticals, agrochemicals, and materials chemistry.[1] The interesting properties of 1,2,3-triazoles encourage the development of convienient and mild methods for their synthesis.[2] The most popular method for the construction of the 1,2,3-triazole framework is Cu(I)-catalyzed 1,3-dipolar Huisgen cycloaddition reaction of azides with alkynes (CuAAC).[3] However, this procedure involves one-pot two component reaction in which azides were prepared prior to the cycloaddition.[4] To overcome this drawback, one-pot three-component methodologies for *in situ* generation of azides have been developed. Various different azide precursors such as epoxides, benzyl halides, and aryl boronic acids have been used in this CuAAC reaction to construct a wide range of 1,4-disubstituted-1,2,3-triazole framework. In general, homogeneous copper (I) catalysts have been used to catalyze these three-component reactions.[5] In order to overcome the difficulty of catalyst separation, some heterogenerous catalytic system have been developed, including Cu(II)-hydrotalcite,[6] Cu(I)-modified zeolite,[7] copper nanoparticles on activated carbon,[8] Cu(I)@phosphorated SiO_2[9] copper supported on the SiO_2 nanoparticle,[10] $CuFe_2O_4$ magnetic nanoparticles[11] for the synthesis of β-hydroxy-1,2,3-triazoles, copper nanoparticles supported on agarose,[12] Cu(I) on waste oyster shell powder,[13] Fe_3O_4 magnetic nanoparticle(MNP)-supported copper(I),[14] Cu(I) on charcoal,[15] copper nanoparticles supported on activated carbon,[16] nano ferrite-glutathione-copper (nano-FGT-Cu),[17] Cu(I) supported on alumina (Cu/Al_2O_3),[18] polymer-supported copper,[19] Cu_2O nanocubes,[20] copper immobilized onto a triazole functionalized magneticnanoparticle,[21] cellulose supported cuprous iodide nanoparticles,[22] supported CuBr on graphene oxide/Fe_3O_4,[23] Cu(II) PBS-bridged PMOs[24] for the synthesis of 1-alkyl-4-aryl-1,2,3-triazoles, and $CuFe_2O_4$ nanoparticles,[25] Fe_3O_4 nanoparticle-supported Cu(II)-β-cyclodextrin complex,[26] clay supported Cu(II)[27] for the synthesis of 1-aryl-1,2,3-triazoles. Despite these achievements, some reported catalytic systems have significant limitations such as the lack of regioselectivity, high temperature, prolonged reaction times and limited substrate scope. Therefore, the further development of simple, efficient, eco-friendly and economically viable processes for the synthesis of 1,2,3-triazoles is still highly desirble.

In view of the principles of green chemistry, the improvement of reaction process, media and catalyst, is still the challenging in the current chemistry. In this regard, multicomponent reactions (MCRs) has been

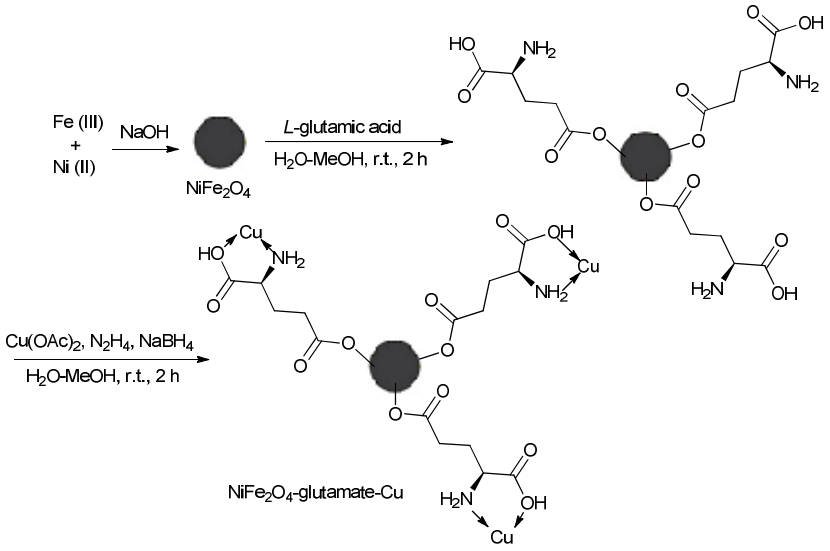
adopted as a practical and extraordinary synthetic tool to create molecular complexity and biologically active heterocyclic compounds in a single reaction vessal ensuring high atom economy, good overall yields and high selectivity, shorter reaction times, operational simplicity, minimizing waster and energy.[28] Furthermore, replacement of conventional hazardous organic solvents by safe and green reaction media has always been a thread in the sustainable chemistry.[29] There is no doubt that, water can be considered as an attractive green solvent, because it is abundant, non-toxic and environmentally benign. Besides, water is also known to enhance the reaction rates and effect the selectivity of a lot of organic transformations owing to its strong hydrogen bonding ability.[30] In addition, for economic and industrial point of view, the development of efficient and recoverable heterogeneous catalyst systems become one of the most important topics of research in organic synthesis. Various materials have been employed as the support to produce heterogeneous catalyst, such as mesoporous silica,[31] activated carbon,[32] polymer,[33] and biomass.[34] Recently, magnetic nanoparticles have emerged as a robust, high-surface-area heterogeneous catalyst support. Magnetic recoverability is an additional attribute of these materials compared to most of the heterogeneous catalyst deployed as it eliminates the necessity of the catalyst filtration or centrifugation after completion of the reaction.[35-37] With these three aspects of green synthesis in mind, the combination of our interest in designing novel magnetic nanocatalysts[38] and the development of environmentally benign syntheic methodologies,[39] herein, we report the preparation, characterization and investigation of catalytic activity of magnetic nano $NiFe_2O_4$-glutamate-Cu for synthesis of a wide variety of 1,4-disubstituted- 1,2,3-triazoles via one-pot three-component click reactions of sodium azide, non-activated terminal alkynes, and different azide precursors such as epoxides, benzyl chloride, and aryl boronic acids in water at room temperature (Scheme 1).



Scheme 1. One-pot synthesis of 1,2,3-triazoles catalyzed by $NiFe_2O_4$-glutamate-Cu in water

Results and discussion

As shown in Scheme 2, the catalyst was prepared in a three-step process. At first, $NiFe_2O_4$ NPs were synthesized by a chemical precipitation technique of $FeCl_3$ and $NiCl_2$ in the basic condition. Then, the anchoring *L*-glutamic acid on the surface of $NiFe_2O_4$ NPs was done in MeOH, followed by the addition of $Cu(OAc)_2$ and $NaBH_4$ at a basic condition, affording the immobilized Cu complex catalyst $NiFe_2O_4$-glutamate-Cu(0). Characterization of the prepared novel magnetic nano catalyst was performed by different physicochemical methods such as X-ray diffracation (XRD), Fourier transform infrared (FT-IR), energy dispersive spectrum (EDS), transmission electron microscopy (TEM), scanning electron microscopy (SEM), vibrating sample magnetometery (VSM), and inductively coupled plasma mass spectrometry (ICP-MS).



Scheme 2 Synthesis of $NiFe_2O_4$-glutamate-Cu

Fig. 1 shows the XRD patterns of the prepared $NiFe_2O_4$-glutamate-Cu(0) nanoparticles. The position and relative intensities of observed diffraction peaks appearting at 2θ = 30.56◦, 36.00◦, 37.2, 57.68◦ and 63.40◦ corresponding to the diffractions of (2 2 0), (3 1 1), (222), (4 2 2) and (4 4 0), well mathed with literature data of $NiFe_2O_4$ (JCPDS 10-0325), indicating retention of the crystalline cubic spinel structure during functionalization of MNPs. The XRD data (JCPDS 01-085-1326) clearly demonstrates the presence of metallic copper with the characteristic (1 1 1) and (2 0 0) Bragg's peaks located at $2\theta = 43.77^{o}$ and $2\theta = 50.81^{o}$

respectively. No impurity peak was observed, indicating that high purity crystalline $NiFe_2O_4$-glutamate-Cu(0) nanoparticles were successfully synthesized.

The FT-IR spectra of $NiFe_2O_4$, $NiFe_2O_4$ anchored with glutamic acid and assembly of magnetic nanoparticles and complex of glutamic acid with Cu ($NiFe_2O_4$-glutamate-Cu) are depicted in Fig. 2. The presence of Fe-O and Ni-O bonds in the magnetic particles is confirmed by the characteristic peaks appeared at 1038 and 411 cm^{-1}, respectively. The absorption at 604 cm^{-1} is assigned to the Cu-O bridge. The bands at 1624, 1482, 1336, 1383,1007, and 946 cm^{-1} are the characteristic absorptions of glutamate, which shows evidence for the formation of a glutamate shell.

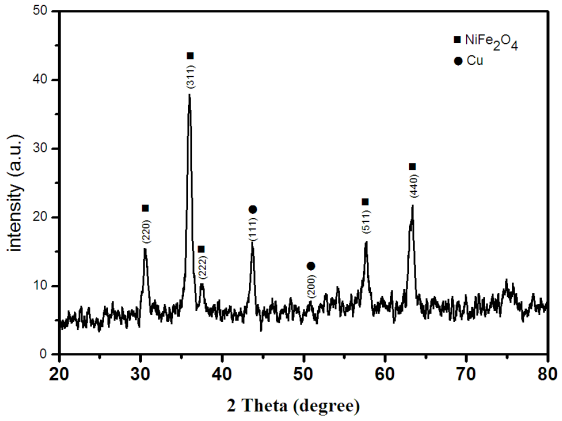


Fig. 1 XRD pattern of $NiFe_2O_4$-glutamate-Cu

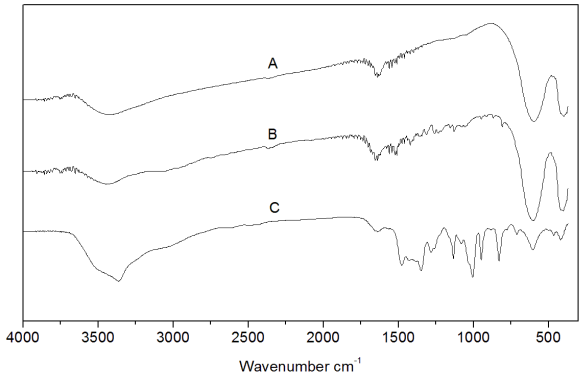


Fig. 2 IR spectra of $NiFe_2O_4$ (A), $NiFe_2O_4$-glutamate (B) and $NiFe_2O_4$-glutamate-Cu (C)

The EDS of $NiFe_2O_4$-glutamate-Cu also shows that the elements, including Fe, Ni, O, C, N and Cu are present in the structure of this material (Fig. 3). Also, to verify the Cu content in the catalyst, it was treated with concentrated HCl and HNO_3 (3/1 ratio of HCl and HNO_3) to

digest the material and then was analyzed by inductively coupled plasma mass spectrometry (ICP-MS) analysis. The Cu content was found to be 10.3%.

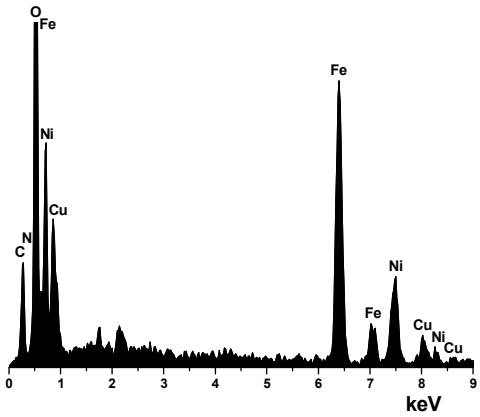


Fig. 3 EDS spectrum of $NiFe_2O_4$-glutamate-Cu

The chemical composition of the $NiFe_2O_4$-glutamate-Cu nanoparticles were also characterized by X-ray photoelectron spectroscopy (XPS) analysis (Fig. 4), which revealed the characteristic peaks for C 1s (283.8 eV), O 1s (530.0 eV), Fe 2p (711.6 eV), Ni 2p (855.7 eV), and Cu 2p (936.7 eV). Furthermore, the high-resolution narrow scan for Cu 2p in $NiFe_2O_4$ displays energy peaks of 2P3/2 and Cu 2P5/2 at 933.2 and 953.3 eV, clearly indicating the formation of the Cu(0) nanoparticles on the $NiFe_2O_4$ nanosheets (Fig. 4b).

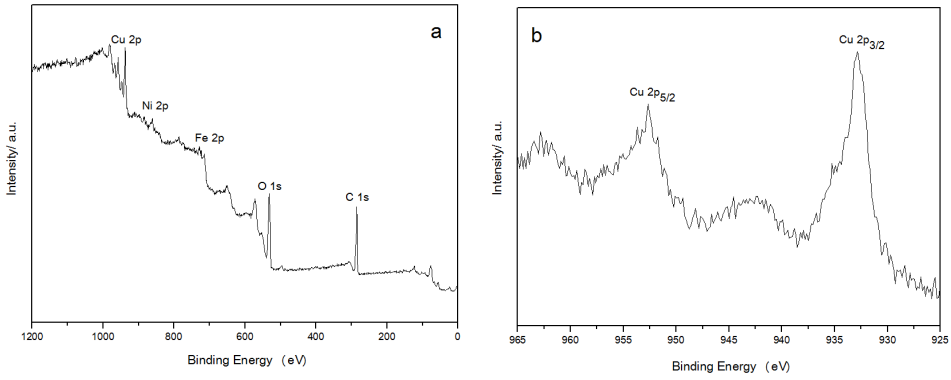


Fig. 4 XPS spectrum of $NiFe_2O_4$-glutamate-Cu: wide scan (a), high-resolution spectrum for the Cu (b).

The shape, size and morphology of the synthesized $NiFe_2O_4$-glutamate-Cu NPs were analyzed by using TEM and SEM. The TEM image shows that $NiFe_2O_4$-glutamate-Cu NPs

have a core-shell structure. Further observation confirmed the formation of a glutamate layer around the $NiFe_2O_4$ nanoparticles (Fig. 5). The SEM image shows that morphology of the particles is spherical or quasi-spherical and the surface configuration of NPs is quite rough with smaller subunits (Fig. 6). The average nanopartical diameter of $NiFe_2O_4$-glutamate-Cu was estimated to be 20-22 nm based on the TEM image, which is also in accordance with the result calculated by the Debye–Scherrer's equation. The specific surface area of $NiFe_2O_4$-glutamate-Cu(0) obtained by the N_2 adsorption isotherms was 37.0 m^2g^{-1}, pore volume was 0.315 $cm^{-3}g^{-1}$ and pore diameter was 11.02 nm.

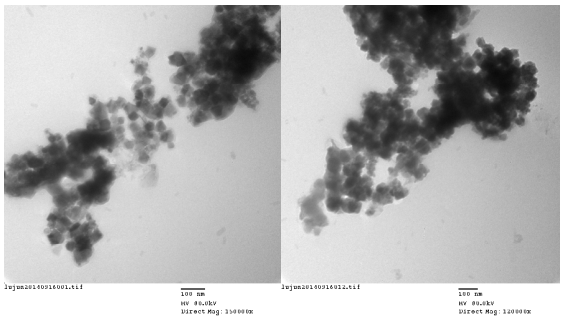


Fig. 5 TEM micrographs of $NiFe_2O_4$-glutamate-Cu: (left) "fresh" catalyst and (right) "recovered" catalyst

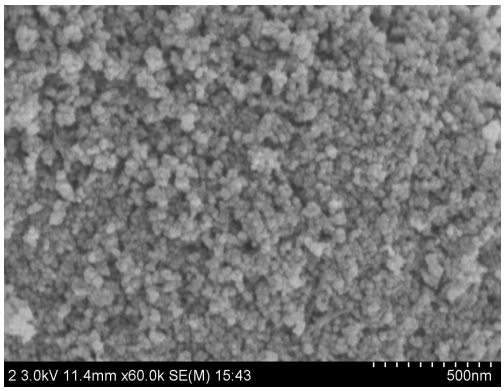


Fig. 6 SEM image of $NiFe_2O_4$-glutamate-Cu

The magnetic properties of the prepared $NiFe_2O_4$-glutamate-Cu(0) were measured by VSM at room temperature with the field sweeping from -30000 to + 30000 Oersted (Fig. 7). The magnetic hysteresis curve of $NiFe_2O_4$-glutamate-Cu(0) revealed that it possessed

superparamagnetic behavior, and its saturation magnetization values was found to be 33.8 $emug^{-1}$, indicating that it could be efficiently separated by an external permanent magnet.

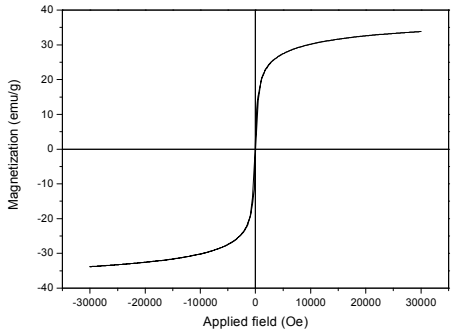
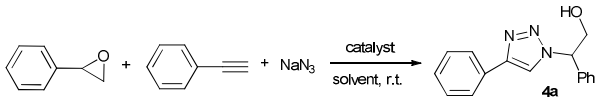


Fig. 7 Magnetization curve of $NiFe_2O_4$-glutamate-Cu

In order to study the efficiency of the prepared $NiFe_2O_4$-glutamate-Cu, the reaction of styrene oxide, sodium azide and ethynylbenzene is adopted as a model reaction. The influence of different parameters such as kinds of catalysts, solvents, catalyst concentration was examined to obtain the best possible combination. When the reaction was attempted without a catalyst in water, that product was not detected even after 6 h (Table 1, entry 1). Some copper salts such as $CuSO_4 \cdot 5H_2O$ and $Cu(OAc)_2 \cdot H_2O$, nano materials such as nano Fe_3O_4, γ-Fe_2O_3, $CoFe_2O_4$, $NiFe_2O_4$, $CuFe_2O_4$ and $CuFeO_2$ were test. However, the reaction efficiency was not imporved. A clear improvement of the yield was observed when CuI, CuCl, $CuFeO_2$ was added, however, the yields are still far from satisfactory. Considering the importance of ligands in the tradional copper-catalyzed reactions, 10-phenantholine (10 mol%) was added to above model reaction in the presence of $CuFeO_2$. It was observed that the yield was significantly improved (entry 12). To our delight, the use of our prepared $NiFe_2O_4$-glutamate-Cu gave **4a** in an excellent yield (entry 13).

Table 1 Screening catalysts for the three-component reaction of styrene oxide, ethynylbenzene and sodium azide[a]



Entry	Catalyst (mol%)	Solvent	Time (h)	Yield (%)
1	no	H_2O	6.0	-
2	$CuSO_4 \cdot 5H_2O$	H_2O	3.0	-
3	$Cu(OAc)_2 \cdot H_2O$	H_2O	3.0	-
4	nano Fe_3O_4	H_2O	3.0	-

5	nano γ-Fe_2O_3	H_2O	3.0	-
6	nano $CoFe_2O_4$	H_2O	3.0	-
7	nano $NiFe_2O_4$	H_2O	3.0	-
8	nano $CuFe_2O_4$	H_2O	3.0	-
9	nano $CuFeO_2$	H_2O	3.0	16
10	CuCl	H_2O	3.0	71
11	CuI	H_2O	3.0	78
12	nano $CuFeO_2$, 10-phenantholine	H_2O	3.0	85
13	$NiFe_2O_4$-glutamate-Cu	H_2O	1.5	95
14	$NiFe_2O_4$-glutamate-Cu	EtOH-H_2O (1:1)	2.0	51
15	$NiFe_2O_4$-glutamate-Cu	EtOH	3.0	-
16	$NiFe_2O_4$-glutamate-Cu	CH_2Cl_2	3.0	-
17	$NiFe_2O_4$-glutamate-Cu	Toluene	3.0	-
18	$NiFe_2O_4$-glutamate-Cu	CH_3CN	3.0	-
19	$NiFe_2O_4$-glutamate-Cu	DMF	3.0	-
20[b]	$NiFe_2O_4$-glutamate-Cu	H_2O	2.0	83
21[c]	$NiFe_2O_4$-glutamate-Cu	H_2O	1.5	85
22[d]	$NiFe_2O_4$-glutamate-Cu	H_2O	1.5	96

[a] Experimental conditions: styrene oxide (1.0 mmol), ethynylbenzene (1.0 mmol), sodium azide (1.1 mmol), catalyst (0.01 mmol), solvent (2 ml), room temperature. [b] catalyst (0.005 mmol). [c] catalyst (0.02 mmol). [d] The reaction was carried out in 50.0 mmmol scale.

Then, the influence of solvents on the reaction was also investigated. Among the different solvents screened, water was found to be the best solvent of choice and afforded the product in high yield. The use of the mixture of ethanol and water afforded the desired product in lower yield. The formatting product **4a** was not observed using ethanol, dichloromethane, toluene, acetonitrile, and *N,N*-dimethylformamide (DMF) as solvents.

The amount of catalyst required for this transformation was investigated. The result showed that 1 mol % of catalyst was sufficient to complete the reaction. The use of excessive catalyst neither increased the yield nor shortened the reaction time, while a decrease in the amount of catalyst decreased the yield. Based on the above results, the optimal conditions were established to be the use of 1 mol% $NiFe_2O_4$-glutamate-Cu as the catalyst in H_2O at room temperature.

Again, in order to demonstrate the practicality of this process, we investigated the scalability of this model reaction on a 50-mmol scale. Indeed, the reaction proceeded similar to the case on a smaller scale and the desired product was obtained in 96% yield in 1.5 h.

(Table 1, entry 22).

For a heterogeneous catalyst, it is important to test the ease of separation, recoverability and reusability in the practical applications. The recyclability of the catalyst was investigated in model reaction. After completion of the reaction, the product was extracted with ethyl acetate. The catalyst was recovered by an external magnet and washed several times with ethyl acetate. Then it was reused in the subsequent run after dying under vacuum at 60 °C. As shown in Fig. 8, the recovered catalyst couble be directly reused in ten successive runs without significant loss of activity. It is clear from the TEM micrograph in Fig. 5 that the catalyst is stable after reaction.

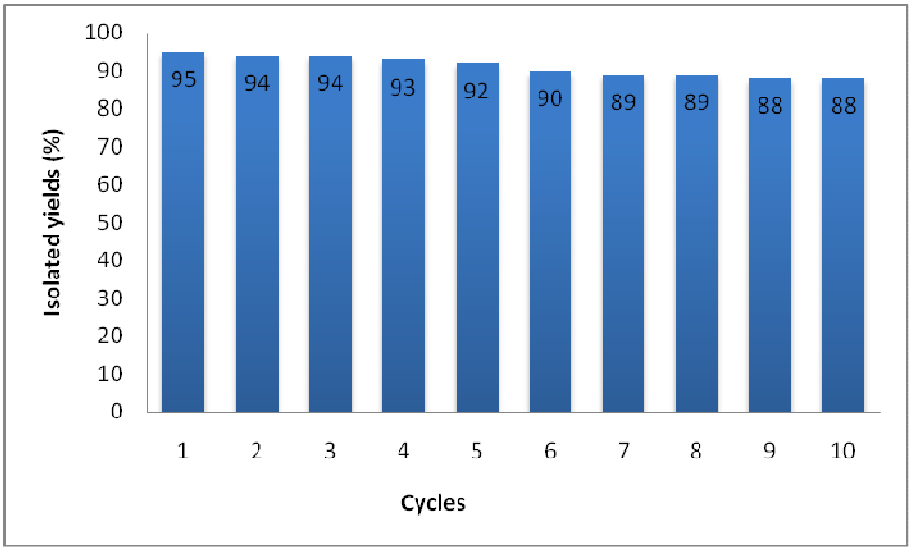


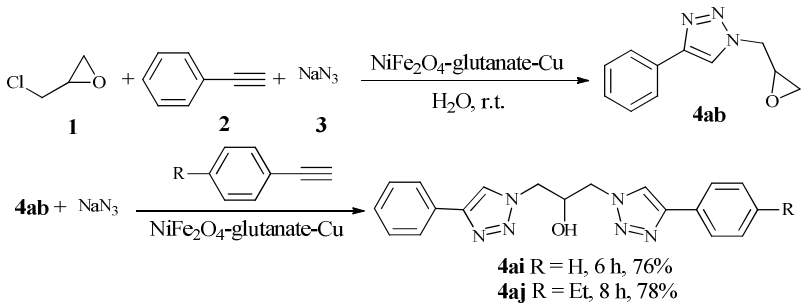
Fig. 8 Reusability of $NiFe_2O_4$-glutamate-Cu in the model reaction

With the optimum reaction conditionds in hand, the scope and generality of this three-component reaction were explored by treating different epoxides, terminal alkynes and sodium azide to generate various hydroxymethylated 1,2,3-triazoles. We first investigated structurally diverse terminal alkynes under the optimal conditions. As shown in Table 2, the reaction is quite general and the corresponding triazoles were obtained in good to excellent yields. Various aryl alkynes, regardless of the presence of electron-donating or electron-withdrawing groups reacted with styrene oxide and sodium azide smoothly to afford the desired products in high to excellent yields with high regioselectivity. Heterocyclic alkyne such as 2-pyridylacetylene worked well and provided the expected in 80% yield (Table 2,

entry 12). Surprisingly, this three-compont reaction also proceeded successfully in the case of aliphatic alkynes although the yields were lower than aryl alkynes (entries 13 and 14).

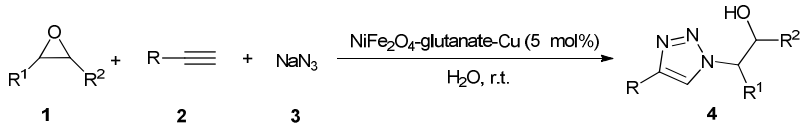
Next, the reactivitities of various epoxides were evaluated. Satisfactorily, styrene oxide having either electron-donating or electron-withdrawing substituents worked well and delivered expected products in high to excellent yields. In the case of 2-monosubstituted aryl epoxides, a major primary alcohol triazole regioisomer was obtained during the reaction, which was consistent with published report.[11] On the other hand, in the case of glycidic ethers, the ring-opening occurred predominantly through an attack by sodium azide at the less substitited carbon atom of the epoxide, followed by cycloaddition with terminal alkynes to afford the major secondary alcohol trizazole regiosiomer, which is agreement with an S_N2 pathway. The probable reason may be that in aryl epoxides the positive charge at benzylic position is stabilized due to conjugation with the phenyl ring, thus leading to the predominant product primary alcohol triazole by nucleopilic attack at the more stable benzylic carbon. Whereas in case of glycidic ethers, steric factor predominates over electronic factors thereby facilitating the attack at the sterically less crowded carbon atom of the epoxide ring. As predicated, some simple aliphatic oxiranes such as 2-(butoxymethyl)oxirane (entry 22), and 2-((allyloxy)methyl)oxirane (entries 24 and 25), secondary alcohol trizazole regiosiomer was obtained as major product corresponding to ring opening at the terminal oxirane carbon, in agreement with an S_N2 pathway. Cyclohexene oxide underwent ring opening exclusively via a *trans*-stereospecific pathway to provide only one *trans* isomer (entries 26-28). Encouraged by these results, the reaction was attempted with an enantiomerically pure chiral epoxide (entry 23). To our satisfaction, the corresponding product (*S*)-**4v** was obtained in high yield with excellent *ee*, indicating no racemization during the reaction.

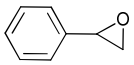
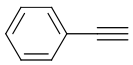
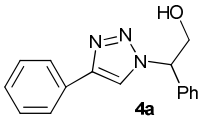
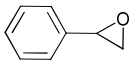
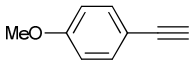
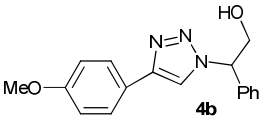
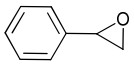
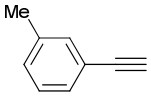
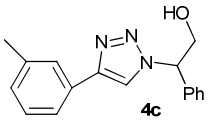
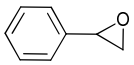
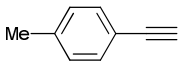
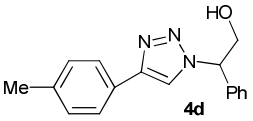
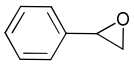
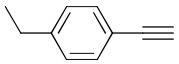
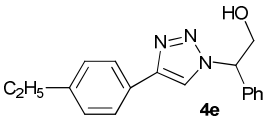
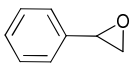
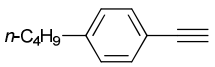
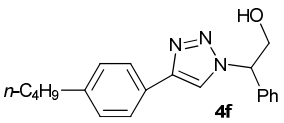
Under the same conditions, epichlorohydrin was also employed in this MCR. It was found that the corresponding epoxytriazoles were obtained in high yields (Table 2, entries 29-35). The resulting product **4ab** can also further react with terminal alkynes and sodium azide to give bis(triazoles) **4ai** and **4aj** (Scheme 3).



Scheme 3. Synthesis of bis(triazoles).

Table 2 Scope of reaction of epoxides with alkynes and sodium azide ctalyzed by magnetic $NiFe_2O_4$-glutamate-Cu



Entry	Epoxide	Alkyne	Product	Time (h)	Yield (%)[a]	m.p. (ºC)
1			 **4a**	1.5	95	126-127 125-127[8]
2			 **4b**	2.5	88	138-139
3			 **4c**	4.0	86	115-116[6]
4			 **4d**	2.0	90	126-127 125-127[9]
5			 **4e**	2.0	93	146-147
6			 **4f**	2.5	92	124-125

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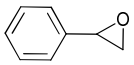
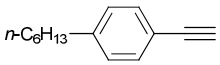
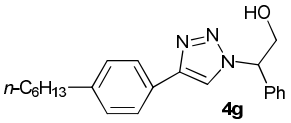
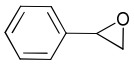
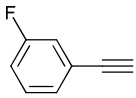
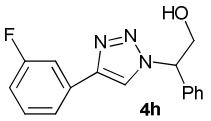
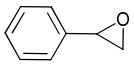
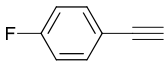
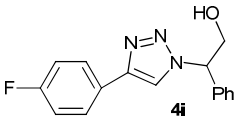
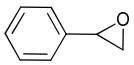
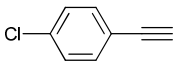
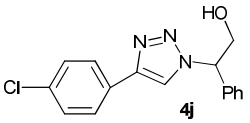
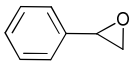
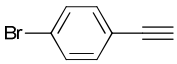
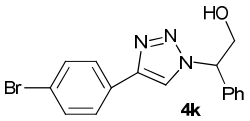
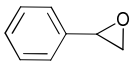
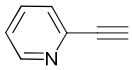
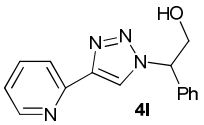
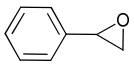
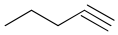
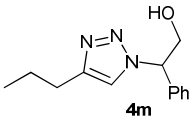
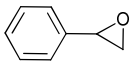
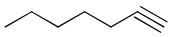
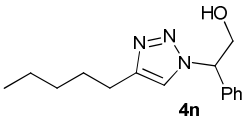
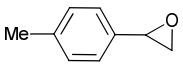
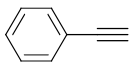
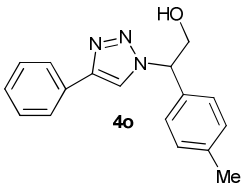
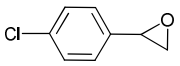
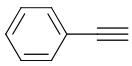
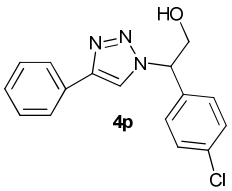
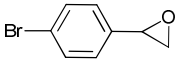
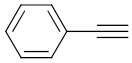
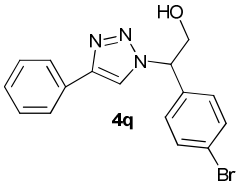
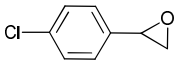
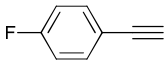
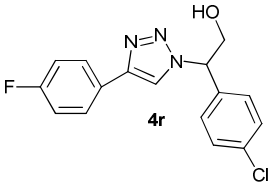
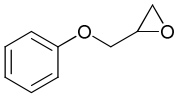
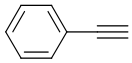
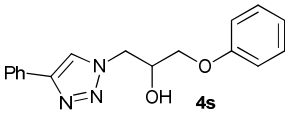
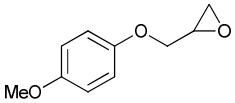
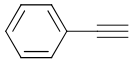
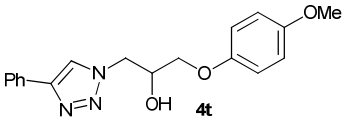
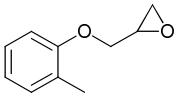
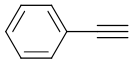
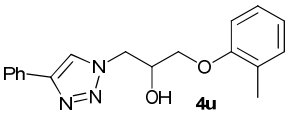
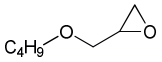
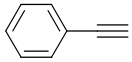
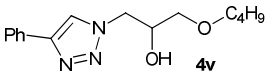
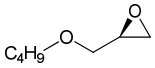
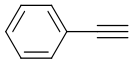
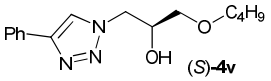
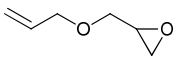
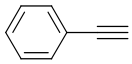
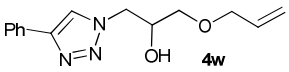
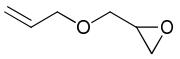
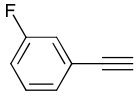
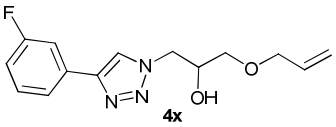
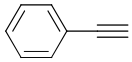
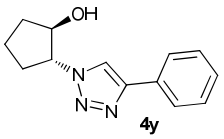
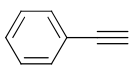
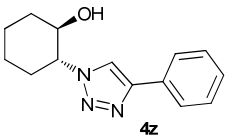
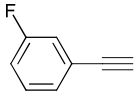
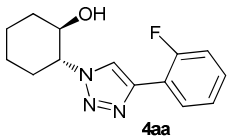
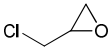
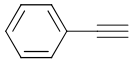
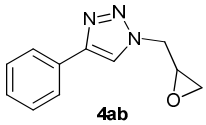
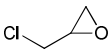
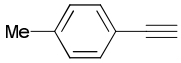
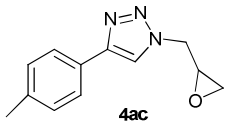
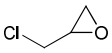
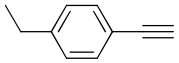
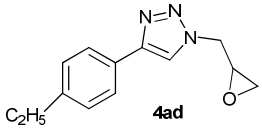
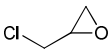
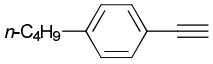
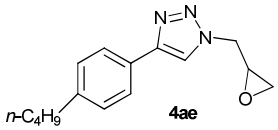
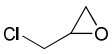
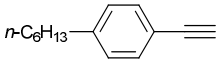
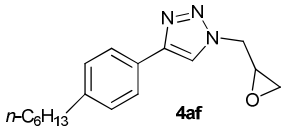
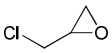
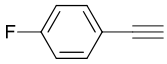
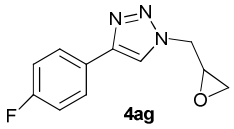
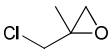
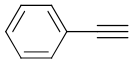
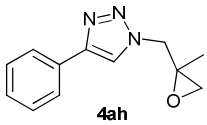
7			 **4g**	2.5	87	105-106
8			 **4h**	2.5	90	114-115[11]
9			 **4i**	2.0	93	99-100
10			 **4j**	2.5	93	128-129
11			 **4k**	3.0	85	149-150
12			 **4l**	4.0	80	130-131 112.7-115.3[8]
13			 **4m**	5.0	71	61-62 62-64[9]
14			 **4n**	6.0	62	oil
15			 **4o**	2.5	90	124-126 125-127[9]
16			 **4p**	5.0	88	140-141 139.6-142.1[8]

17			 **4q**	5.0	85	170-171
18			 **4r**	5.0	80	120-121
19			 **4s**	4.0	86	125-126 125-127[8]
20			 **4t**	2.5	92	110-111[11]
21			 **4u**	2.5	90	oil[11]
22			 **4v**	3.0	90	oil
23[b]			 (*S*)-**4v**	3.0	89	oil
24			 **4w**	2.5	93	71-72 71.5-72[5c]
25			 **4x**	3.0	85	oil
26			 **4y**	2.5	90	oil
27			 **4z**	2.5	89	170-171 168-171[9]

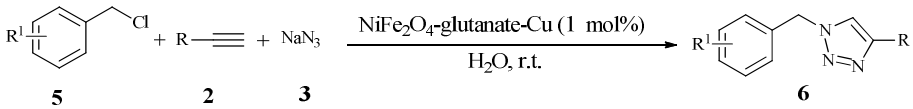
28			 **4aa**	4.0	85	149-150
29			 **4ab**	2.0	95	85-86 82-83[5e]
30			 **4ac**	2.0	90	65-66
31			 **4ad**	2.0	93	146-147
32			 **4ae**	3.0	90	57-58
33			 **4af**	2.5	87	65-66
34			 **4ag**	2.0	93	93-94
35			 **4ah**	3.0	92	oil

[a] Isolated yield. [b] Chiral HPLC conditions: Chiralpak OD-H, hexane/isopropanol = 95:5, flow rate = 1.0 mL/min, wavelength = 245 nm, retention time: 47.3 min (minor), 58.9 nm (major).

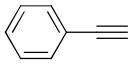
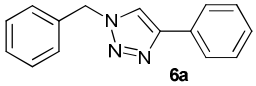
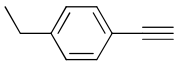
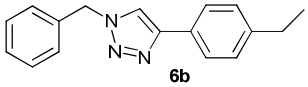
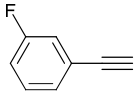
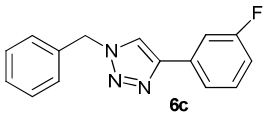
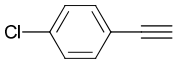
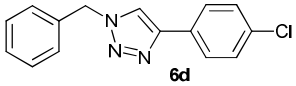
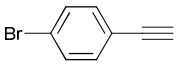
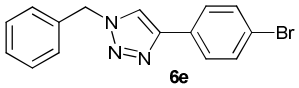
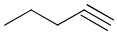
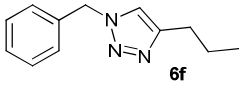
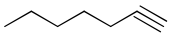
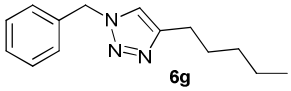
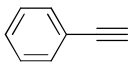
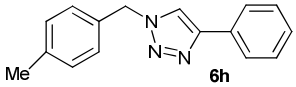
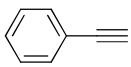
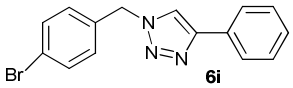
Subsequently, to further demonstrate the applicability of our procedures, we then performed three-component reaction of benzyl chloride, terminal alkynes and sodium azide under above conditions. As shown in Table 3, phenylacetylene derivatives bearing electron-donating or electron-withdrawing substituents on the phenyl group worked well and furnished the corresponding 1-alkyl-4-aryl-1,2,3-triazole derivatives in high yields. While terminal alkyes bearing alkyl groups, as expected, are less reactive in this three-component

reaction, and led to lower yield of products (Table 3, entries 6 and 7). Furthermore, benzyl chloride derivatives bearing an electron-donating or electron-withdrawing group on the phenyl ring underwent the one-pot reaction smoothly and provided the desired product in high yields.

Table 3 Scope of reaction of benzyl chloride with alkynes and sodium azide ctalyzed by magnetic $NiFe_2O_4$-glutamate-Cu



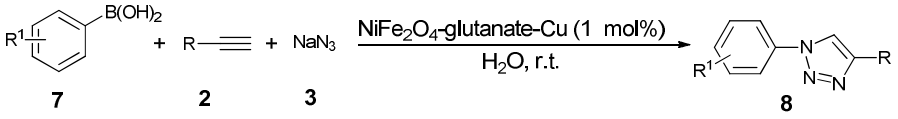
5 **2** **3** **6**

Entry	R^1	Alkyne	Product	Time (h)	Yield (%)	m.p. (ºC)
1	H		 **6a**	4.0	92	130-131 127-130[22]
2	H		 **6b**	6.0	80	oil
3	H		 **6c**	4.5	88	108-109 109-110[5f]
4	H		 **6d**	4.5	85	oil[17]
5	H		 **6e**	5.0	82	151-153 142-144[41]
6	H		 **6f**	7.0	65	oil[13]
7	H		 **6g**	8.5	50	40-41[36e]
8	4-Me		 **6h**	4.5	84	105-106 104-107[22]
9	4-Br		 **6i**	4.0	90	155-156 150-152[5f]

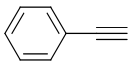
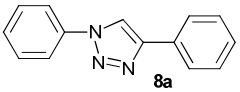
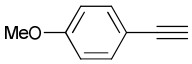
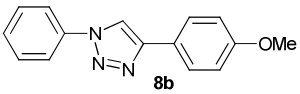
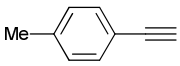
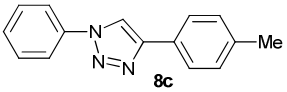
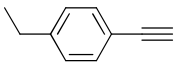
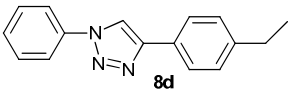
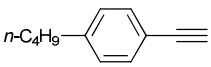
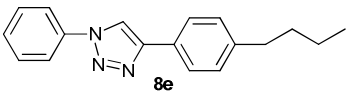
Finally, it was found that this catalytic system can efficiently catalyze one-pot aromatic azidonation of aryl boronic acids followed by regioselective azide-alkyne 1,3-dipolar cyclodaaition reaction to obtain corresponding 1-aryl-1,2,3-triazole derivatives. Various different aromatic and aliphatic alkynes were investivated. As shown in Table 4, the reaction proceeded smoothly with substituted aromatic ethynylbenzenes possessing electronically different substituents and afforded high yields of the desired products (Table 4, entries 1-9). 2-Ethynylthiophene also participated in the reaction and gave 1,4-diary-1,2,3-triazole **8j** in high yield. Under the same reaction conditions, aliphatic alkyne showed less efficiency (Table 4, entry 14). In addition, reaction yields were good for substituted aromatic boronic acids, regardless the electronic nature and substitution pattern on the aryl moiety.

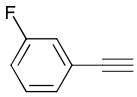
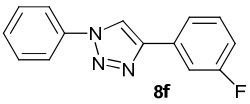
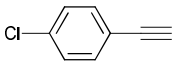
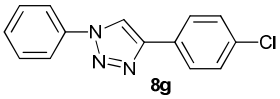
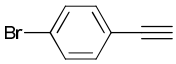
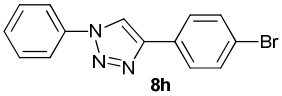
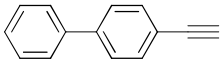
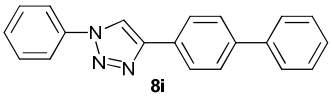
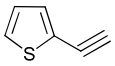
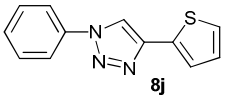
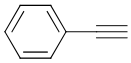
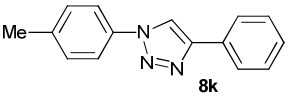
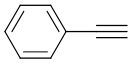
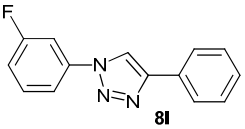
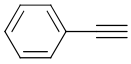
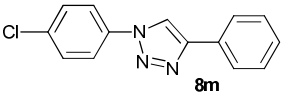
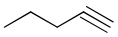
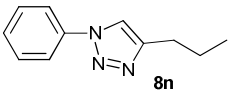
These results successfully demonstrated that this catalytic system can be readily applied to the combinatorial click synthesis of 1,4-disubstitued-1,2,3-triazoles.

Table 4 Scope of reaction of aryl boronic acid with alkynes and sodium azide ctalyzed by magnetic $NiFe_2O_4$-glutamate-Cu



7 **2** **3** **8**

Entry	R^1	Alkyne	Product	Time (h)	Yield (%)	m.p. (ºC)
1	H		 **8a**	3.0	95	176-178 175-177[27]
2	H		 **8b**	5.0	88	157-158 152.5-154.5[42]
3	H		 **8c**	5.0	90	175-176 173-174[5g]
4	H		 **8d**	5.0	89	132-133 128-130[43]
5	H		 **8e**	5.5	86	120-121 118-121[44]

6	H		 **8f**	6.0	85	185-186[45]
7	H		 **8g**	4.0	92	210-211 207-209[43]
8	H		 **8h**	5.5	89	215-216 212-214[43]
9	H		 **8i**	6.0	82	233-234[46]
10	H		 **8j**	4.0	90	132-133 127-129[43]
11	4-Me		 **8k**	4.0	94	168-169 165-167[41]
12	3-F		 **8l**	4.0	94	181-182
13	4-Cl		 **8m**	5.0	92	185-186 224-226[43]
14	H		 **8n**	4.0	65	oil[2d]

Conclusion

In summary, magnetic nano $NiFe_2O_4$ supported glutamate-copper catalyst has been successfully prepared by a relatively simple route. It has been demonstrated to be an efficient catalyst for one-pot synthesis of a wide variety of 1,4-disubstituted-1,2,3-triazoles via three-component click reactions of sodium azide, non-activated terminal alkynes, and different azide precursors such as epoxides, benzyl chloride, and aryl boronic acids in water at room temperature. Aqueous reaction medium, ambient reaction condition, high yields, wide substrate scope, easy separation of catalyst using an external magnet, efficient recycling are outstanding features of this protocol that make it to be an important addition to the existing methods for synthesis of 1,4-disubstituted- 1,2,3-triazoles.

Experimental section

General information

The IR spectra were obtained as KBr pellets or liquid films on KBr pellets with a Bruker-TENSOR 27 spectrometer. XRD measurement was performed on a PANalytical X'Pert Pro X-ray diffractometer using Cu-Kα radiation as the X-ray source in the 2θ range of 20-80^{o}. Transmission electron microscope (TEM) observation was performed by using a Hitachi H-7650 microscope at 80 KV. The morphology of the magnetic nanoparticles was observed by a Hitachi S-4800 SEM instrument. Melting points were determined using an X-4 digital melting point apparatus and are uncorrected. NMR spectra were recorded with a Bruker DRX-500 spectrometer at 500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR using $CDCl_3$ as the solvent and TMS as an internal standard. Mass spectra were performed on a ThermoFinnigan LCQ Advantage instrument with an ESI source (4.5 keV).

Preparation of $NiFe_2O_4$ Magnetic Nanoparticles

To a mixture of $FeCl_3$ (2.7 g) and $NiCl_2$ (1.2 g) in 50 mL water, 25 mL NaOH (1.5 mol/L) and oleic was added slowly. The mixture was stirred for 1h at 80 °C. The obtained precipitated nanoparticles were separated magnetically, washed with water and ethanol until the pH reached 7, and dried under vacuum at 60 °C for 2 h.

Surface Modification of Nano-$NiFe_2O_4$

The obtained nano $NiFe_2O_4$ (0.5 g) was dispersed in a mixture of water and methanol (20 mL, 3:1 volume), and sonicated for 15 min at room temperature. Then, glutamate (0.3 g) dissolved in water (5 mL) was added, and the resulting mixture was stirred for 2 h. The prepared glutamate functionalized magnetic nanoparticles were separated by magnetic decantation, and then washed with water and ethanol, and dried under vacuum at 60 °C for 2 h.

Immobilization of Cu on Magnetic Nanoparticles

Glutamate-functionalized nano-$NiFe_2O_4$ (1 g) was ultrasonically dispersed in a mixture of water and methanol (10 mL, 1:1). $Cu(OAc)_2$ (0.1 g) solution in water (5 ml) was added to the reaction mixture. Hydrazine monohydrate solution in water was added drop wise to adjust the pH of this mixture to 9.0, followed by the addition of 0.1 g of $NaBH_4$. The reaction mixture

was then stirred for 24 h at room temperature. The catalyst was harvested with the aid of a magnet, washed several times with water and ethanol, and dried under vacuum at 60 °C for 2 h.

General procedure for synthesis of 1,2,3-triazoles in water

NaN_3 (1.1mmol), alkyne (1 mmol), epoxide or benzyl chloride, or phenylboronic acid (1 mmol), were added to a suspension of $NiFe_2O_4$-glutamate-Cu (1.0 mol% Cu, 6.3 mg $NiFe_2O_4$-glutamate-Cu) in H_2O (2 mL). The reaction mixture was stirred at room temperature and monitored by TLC. After completion of the reaction, the catalyst was easily removed from reaction mixture using an external magnet. Then, water (30 mL) was added to the resulting mixture, followed by extraction with EtOAc (3×10 mL). The organic layer was dried with $MgSO_4$, concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography eluting with petroleum ether-ethyl acetate to afford the desired products.

Characterization data

2-Phenyl-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)ethanol (4a). White solid; IR (KBr): 3393, 3095, 2928, 1458, 1429, 1223, 1157, 1074, 1051, 1030, 762, 696 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 3.20-3.18 (m, 1H), 4.23 (ddd, *J* = 3.5 Hz, *J* = 9.0 Hz, *J* = 12.5 Hz, 1H), 4.64 (ddd, *J* = 5.0 Hz, *J* = 8.0 Hz, *J* = 12.5 Hz, 1H), 5.67 (dd, *J* = 4.0 Hz, *J* = 8.5 Hz, 1H), 7.27-7.26 (m, 2H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.42-7.38 (m, 5H), 7.69 (s, 1H), 7.70 (d, *J* = 7.0 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 65.1, 67.3, 120.6, 125.7, 127.2, 128.3, 128.8, 129.0, 129.2, 130.2, 136.1, 147.7 ppm. ESI-MS: m/z = 266 $(M+1)^+$.

2-(4-(4-Methoxyphenyl)-1*H*-1,2,3-triazol-1-yl)-2-phenylethanol (4b). White solid; IR (KBr): 3396, 3095, 2929, 1406, 1417, 1255, 1176, 1074, 1051, 1090, 756, 696 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 3.15 (dd, *J* = 5.5 Hz, *J* = 9.5 Hz, 1H), 3.84 (s, 3H), 4.22 (ddd, *J* = 4.0 Hz, *J* = 9.0 Hz, *J* = 13.0 Hz, 1H), 4.63 (ddd, *J* = 5.5 Hz, *J* = 8.5 Hz, *J* = 13.0 Hz, 1H), 5.65 (dd, *J* = 3.5 Hz, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 8.5 Hz, 2H), 7.24-7.26 (m, 2H), 7.42-7.38 (m, 3H), 7.60 (s, 1H)， 7.72 (d, *J* = 8.5 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 55.3, 65.2, 67.3, 114.2, 119.8, 123.0, 127.0, 127.2, 129.0, 129.2, 136.2, 147.6, 159.7 ppm. ESI-MS: m/z = 296 $(M+1)^+$; HRMS calcd. for $C_{17}H_{18}N_3O_2$ $(M+H)^+$: 296.1394; found: 296.1397.

2-Phenyl-2-(4-(*m*-tolyl)-1*H*-1,2,3-triazol-1-yl)ethanol (4c). White solid; IR (KBr): 3419, 3086, 2924, 1491, 1417, 1219, 1136, 1087, 1051, 1028, 775, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 2.38 (s, 3H), 3.15 (dd, *J* = 5.5 Hz, *J* = 9.0 Hz, 1H), 4.22 (ddd, *J* = 4.0 Hz, *J* = 9.0 Hz, *J* = 13.0 Hz, 1H), 4.63 (ddd, *J* = 5.5 Hz, *J* = 8.5 Hz, *J* = 13.0 Hz, 1H), 5.67 (dd, *J* = 4.0 Hz, *J* = 8.5 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 2.0 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.42-7.38 (m, 3H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.64 (s, 1H), 7.68 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 21.4, 65.1, 67.3, 120.5, 122.8, 126.4, 127.2, 128.7, 129.0, 129.1, 129.2, 130.1, 136.1, 138.5, 147.8 ppm. Anal. Calcd for $C_{17}H_{17}N_3O$: C, 73.10; H, 6.13; N, 15.04. Found: C, 73.25; H, 6.27; N, 15.06. ESI-MS: m/z = 280 $(M+1)^+$.

2-Phenyl-2-(4-(*p*-tolyl)-1*H*-1,2,3-triazol-1-yl)ethanol (4d). White solid; IR (KBr): 3385, 3093, 2930, 1456, 1221, 1182, 1074, 1049, 756, 696 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 2.37 (s, 3H), 4.22 (dd, *J* = 3.5 Hz, *J* = 12.5 Hz, 1H), 4.63 (dd, *J* = 8.5 Hz, *J* = 12.5 Hz, 1H), 5.66 (dd, *J* = 3.5 Hz, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.25 (s, 2H), 7.39 (d, *J* = 6.0 Hz, 3H), 7.65 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 21.3, 53.1, 65.3, 67.3, 120.2, 125.6, 127.1, 127.4, 129.0, 129.2, 129.5, 136.1, 138.2, 147.9 ppm. ESI-MS: m/z = 280 $(M+1)^+$.

2-(4-(4-Ethylphenyl)-1*H*-1,2,3-triazol-1-yl)-2-phenylethanol (4e). White solid; IR (KBr): 3392, 3080, 2928, 1489, 1417, 1220, 1116, 1074, 1049, 1030, 754, 696 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.26 (t, *J* = 3.5 Hz, 3H), 2.67 (q, *J* = 7.5 Hz, 2H), 3.17 (dd, *J* = 5.5 Hz, *J* = 9.5 Hz, 1H), 4.22 (ddd, *J* = 4.0 Hz, *J* = 9.0 Hz, *J* = 13.0 Hz, 1H), 4.63 (ddd, *J* = 5.5 Hz, *J* = 8.5 Hz, *J* = 13.0 Hz, 1H), 5.66 (dd, *J* = 4.0 Hz, *J* = 8.5 Hz, 1H), 7.25-7.23 (m, 4H), 7.42-7.38 (m, 3H), 7.65 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 29.7, 32.0, 65.2, 67.3, 120.3, 125.7, 127.2, 128.3, 129.0, 129.1, 130.9, 136.2, 144.5, 147.8 ppm. ESI-MS: m/z = 294 $(M+1)^+$; HRMS calcd. for $C_{18}H_{20}N_3O$ $(M+H)^+$: 294.1601; found: 294.1604.

2-(4-(4-Butylphenyl)-1*H*-1,2,3-triazol-1-yl)-2-phenylethanol (4f). White solid; IR (KBr): 3385, 3080, 2928, 1458, 1437, 1225, 1184, 1076, 1051, 750, 696 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 0.93 (t, *J* = 7.0 Hz, 3H), 1.36 (dd, *J* = 7.0 Hz, *J* = 14.5 Hz, 2H), 1.61 (t, *J* = 7.5 Hz, 2H), 2.62 (t, *J* = 8.0 Hz, 2H), 3.19 (s, 1H), 4.22 (dd, *J* = 3.5 Hz, *J* = 7.0 Hz, 1H), 4.62 (dd, *J* = 11.0 Hz, *J* = 19.5 Hz, 1H), 5.66 (dd, *J* = 3.0 Hz, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 4H), 7.38 (s, 3H), 7.65 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 13.9,

22.3, 33.5, 35.4, 65.3, 67.3, 120.2, 125.6, 127.1, 127.6, 128.9, 129.0, 129.2, 136.1, 143.3, 147.9 ppm. ESI-MS: m/z = 322 $(M+1)^+$; HRMS calcd. for $C_{20}H_{24}N_3O$ $(M+H)^+$: 322.1914; found: 322.1916.

2-(4-(4-Hexylphenyl)-1*H*-1,2,3-triazol-1-yl)-2-phenylethanol (4g). White solid; IR (KBr): 3392, 3080, 2918, 1491, 1411, 1224, 1120, 1074, 1051, 1030, 752, 696 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 0.88 (t, *J* = 6.5 Hz, 3H), 1.30 (s, 5H), 1.60 (dd, *J* = 6.5 Hz, *J* = 14.5 Hz, 3H), 2.62 (t, *J* = 7.5 Hz, 2H), 3.27 (s, 1H), 4.22 (dd, *J* = 12.5 Hz, 1H), 4.63 (dd, *J* = 8.0 Hz, *J* = 12.0 Hz, 1H), 5.66 (dd, *J* = 3.5 Hz, *J* = 8.0 Hz, 1H), 7.25-7.21 (m, 4H), 7.39 (d, *J* = 6.0 Hz, 3H), 7.65 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 14.1, 22.6, 29.0, 31.4, 31.7, 35.8, 65.2, 67.3, 120.3, 125.6, 127.2, 127.6, 128.9, 129.0, 129.1, 136.2, 143.3, 147.8 ppm. ESI-MS: m/z = 350 $(M+1)^+$; HRMS calcd. for $C_{22}H_{28}N_3O$ $(M+H)^+$: 350.2227; found: 350.2232.

2-(4-(3-Fluorophenyl)-1*H*-1,2,3-triazol-1-yl)-2-phenylethanol (4h). White solid; IR (KBr): 3385, 3082, 2924, 1501, 1437, 1226, 1132, 1072, 1051, 779, 675 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 3.12 (s, 1H), 4.23 (d, *J* = 12.0 Hz, 1H), 4.64 (dd, *J* = 8.5 Hz, *J* = 12.0 Hz, 1H), 5.68 (dd, *J* = 3.5 Hz, *J* = 8.0 Hz, 1H), 7.02 (t, *J* = 8.5 Hz, 1H), 7.27 (d, *J* = 2.5 Hz, 2H), 7.43-7.34 (m, 4H), 7.53-7.50 (m, 1H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.71 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 60.2, 62.7, 107.7, 107.9, 110.3 (d, $^2J_{CF}$ = 21.1 Hz), 116.3, 122.5, 124.3, 124.4, 125.7 (d, $^4J_{CF}$ = 8.4 Hz), 127.6 (d, $^3J_{CF}$ = 8.1 Hz), 131.2, 141.8, 158.4 (d, $^1J_{CF}$ = 244.0 Hz) ppm. ESI-MS: m/z = 284 $(M+1)^+$.

2-(4-(4-Fluorophenyl)-1*H*-1,2,3-triazol-1-yl)-2-phenylethanol (4i). White solid; IR (KBr): 3383, 3095, 2932, 1456, 1236, 1180, 1157, 1074, 1053, 1028, 752, 696 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 4.23 (dd, *J* = 3.5 Hz, *J* = 12.5 Hz, 1H), 4.64 (dd, *J* = 8.5 Hz, *J* = 12.5 Hz, 1H), 5.67 (dd, *J* = 3.5 Hz, *J* = 8.0 Hz, 1H), 7.10 (t, *J* = 8.5 Hz, 2H), 7.26 (s, 2H), 7.40 (d, *J* = 6.0 Hz, 3H), 7.66 (s, 1H), 7.76 (dd, *J* = 6.0 Hz, *J* = 8.0 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 65.0, 67.4, 115.8 (d, $^2J_{CF}$ = 21.8 Hz), 120.4, 126.4 (d, $^4J_{CF}$ = 3.3 Hz), 127.2, 127.4(d, $^3J_{CF}$ = 8.0 Hz), 129.0, 129.2, 136.0, 146.7, 162.8 (d, $^1J_{CF}$ = 271.1 Hz) ppm. ESI-MS: m/z = 284 $(M+1)^+$; HRMS calcd. for $C_{16}H_{15}FN_3O$ $(M+H)^+$: 284.1194; found: 284.1195.

2-(4-(4-Chlorophenyl)-1*H*-1,2,3-triazol-1-yl)-2-phenylethanol (4j). White solid; IR (KBr): 3383, 3086, 2929, 1454, 1226, 1186, 1076, 1049, 1028, 756, 715, 696 cm^{-1}; ^1H NMR

($CDCl_3$, 500 MHz) δ 3.15-3.12 (m, 1H), 4.23 (ddd, *J* = 3.0 Hz, *J* = 12.0 Hz, *J* = 21.5 Hz, 1H), 4.64 (ddd, *J* = 6.0 Hz, *J* = 12.5 Hz, *J* = 18.5 Hz, 1H), 5.67 (dd, *J* = 3.5 Hz, *J* = 8.0 Hz, 1H), 7.26 (s, 2H), 7.40-7.37 (m, 5H), 7.69 (s, 1H), 7.72 (d, *J* = 8.5 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 65.1, 67.4, 120.6, 126.9, 127.2, 128.7, 129.0, 129.1, 129.2, 134.1, 135.9, 146.6 ppm. ESI-MS: m/z = 300 $(M+1)^+$; HRMS calcd. for $C_{16}H_{15}ClN_3O$ $(M+H)^+$: 300.0898; found: 300.0894.

2-(4-(4-Bromophenyl)-1*H*-1,2,3-triazol-1-yl)-2-phenylethanol (4k). White solid; IR (KBr): 3383, 3086, 2970, 1470, 1456, 1228, 1072, 1049, 821, 756 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.13 (dd, *J* = 5.5 Hz, *J* = 9.0 Hz, 1H), 4.23 (ddd, *J* = 4.0 Hz, *J* = 9.0 Hz, *J* = 12.5 Hz, 1H), 4.64 (ddd, *J* = 5.5 Hz, *J* = 8.0Hz, *J* = 13.0 Hz, 1H), 5.67 (dd, *J* = 3.5 Hz, *J* = 8.0 Hz, 1H), 7.27 (s, 2H), 7.42-7.37 (m, 3H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.70 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 65.1, 67.4, 120.7, 122.2, 127.2, 128.9, 129.1, 129.2, 130.9, 132.0, 135.9, 146.7 ppm. ESI-MS: m/z = 344 $(M+1)^+$; HRMS calcd. for $C_{16}H_{15}BrN_3O$ $(M+H)^+$: 344.0393; found: 344.0398.

2-Phenyl-2-(4-(pyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)ethanol (4l). White solid; IR (KBr): 3392, 3082, 2953, 1475, 1423, 1234, 1179, 1076, 1058, 1039, 825, 786, 605 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.37 (s, 1H), 4.24 (d, *J* = 11.0 Hz, 1H), 4.63 (t, *J* = 10.5 Hz, 1H), 5.71 (dd, *J* = 3.5 Hz, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 6.5 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 2H), 7.38 (d, *J* = 6.5 Hz, 3H), 7.78 (t, *J* = 8.0 Hz, 1H), 8.11 (s, 1H), 8.17 (d, *J* = 7.5 Hz, 1H), 8.52 (d, *J* = 4.5 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 65.0, 67.4, 120.3, 122.9, 123.0, 127.3, 129.0, 129.1, 135.9, 137.1, 147.9, 149.1, 149.9 ppm. ESI-MS: m/z = 267 $(M+1)^+$.

2-Phenyl-2-(4-propyl-1*H*-1,2,3-triazol-1-yl)ethanol (4m). Oil; IR (KBr): 3414, 2929, 1460, 1419, 1055, 653, 538 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.95 (t, *J* = 7.5 Hz, 3H), 1.77-1.67 (m, 2H), 2.68 (t, *J* = 7.5 Hz, 2H), 2..88-2.86 (m, 1H), 4.18 (ddd, *J* = 4.0 Hz, *J* = 8.5 Hz, *J* = 12.5 Hz, 1H), 4.61 (ddd, *J* = 6.0 Hz, *J* = 8.5 Hz, *J* = 12.5 Hz, 1H), 5.65 (dd, *J* = 4.5 Hz, *J* = 9.0 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.35-7.31 (m, 4H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 13.7, 22.0, 25.4, 27.4, 65.0, 65.8, 120.3, 127.0, 128.4, 128.7, 136.4, 150.1 ppm. ESI-MS: m/z = 232 $(M+1)^+$.

2-(4-Pentyl-1*H*-1,2,3-triazol-1-yl)-2-phenylethanol (4n). Oil; IR (KBr): 3414, 3090, 2930, 1492-, 1435, 1209, 1109, 1068, 752, 600 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.91-0.87

(m, 3H), 1.54-1.48 (m, 2H), 1.74-1.68 (m, 2H), 2.36 (t, *J* = 7.0 Hz, 2H), 2.69 (t, *J* = 7.5 Hz, 2H), 4.19-4.16 (m, 1H), 4.59 (dd, *J* = 8.5 Hz, *J* = 12.0 Hz, 1H), 5.65 (dd, *J* = 4.0 Hz, *J* = 8.5 Hz, 1H), 7.19 (d, *J* = 7.0 Hz, 2H), 7.35-7.27 (m, 4H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 14.0, 22.3, 25.4, 27.8, 30.9, 64.9, 65.8, 120.3, 127.0, 128.5, 128.8, 136.3, 150.3 ppm. ESI-MS: m/z = 260 $(M+1)^+$; HRMS calcd. for $C_{15}H_{21}N_3O$ $(M+H)^+$: 260.1767; found: 260.1763.

2-(4-Phenyl-1*H*-1,2,3-triazol-1-yl)-2-(p-tolyl)ethanol (4o). White solid; IR (KBr): 3385, 3088, 2928, 1511, 1419, 1224, 1155, 1087, 1049, 767, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.36 (s, 3H), 3.13-3.10 (m, 1H), 4.19 (ddd, *J* = 3.5 Hz, *J* = 8.5 Hz, *J* = 12.5 Hz, 1H), 4.62 (ddd, *J* = 4.5 Hz, *J* = 9.0 Hz, *J* = 13.0 Hz, 1H), 5.63 (dd, *J* = 4.0 Hz, *J* = 8.5 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 7.0 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.67 (s, 1H), 7.79 (d, *J* = 7.5 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 16.4, 60.5, 62.4, 115.7, 120.9, 122.4, 123.5, 124.1, 125.1, 125.5, 128.3, 134.3, 142.9 ppm. ESI-MS: m/z = 280 $(M+1)^+$.

2-(4-Chlorophenyl)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)ethanol (4p). White solid; IR (KBr): 3392, 3086, 2935, 1491, 1224, 1157, 1074, 1051, 765, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.14 (s, 1H), 4.24 (d, *J* = 11.5 Hz, 1H), 4.59 (dd, *J* = 8.0 Hz, *J* = 12.0 Hz, 1H), 5.65 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.38-7.32 (m, 3H),7.41 (t, *J* = 7.5 Hz, 2H), 7.70 (s, 1H), 7.79 (d, *J* = 8.0 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 65.0, 66.6, 120.5, 125.7, 128.4, 128.6, 128.9, 129.4, 130.1, 134.6, 135.1, 147.9 ppm. ESI-MS: m/z = 300 $(M+1)^+$.

2-(4-Bromophenyl)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)ethanol (4q). White solid; IR (KBr): 3392, 3082, 2924, 1521, 1419, 1222, 1120, 1074, 1049, 765, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.09 (s, 1H), 4.24 (dd, *J* = 2.5 Hz, *J* = 11.5 Hz, 1H), 4.59 (dd, *J* = 8.0 Hz, *J* = 12.0 Hz, 1H), 5.63 (dd, *J* = 3.5 Hz, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 8.5 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H) 7.70 (s, 1H), 7.79 (d, *J* = 7.5 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 65.0, 66.6, 120.5, 123.2, 125.7, 128.4, 128.9, 130.1, 130.9, 132.4, 135.1, 148.0 ppm. ESI-MS: m/z = 344 $(M+1)^+$; HRMS calcd. for $C_{16}H_{15}BrN_3O$ $(M+H)^+$: 344.0393; found: 344.0399.

2-(4-Chlorophenyl)-2-(4-(4-fluorophenyl)-1*H*-1,2,3-triazol-1-yl)ethanol (4r). White solid; IR (KBr): 3383, 3091, 2928, 1456, 1234, 1157, 1074, 1049, 705cm^{-1}; ^{1}H NMR ($CDCl_3$,

500 MHz) δ 3.11 (s, 1H), 4.23 (dd, *J* = 5.0 Hz, *J* = 11.0 Hz, 1H), 4.59 (t, *J* = 10.0 Hz, 1H), 5.64 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 7.10 (t, *J* = 9.0 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.66 (s, 1H), 7.75 (d, *J* = 5.0 Hz, 1H), 7.77 (d, *J* = 5.5 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 64.9, 66.6, 115.8 (d, $^2J_{CF}$ = 21.8 Hz), 120.3, 126.3 (d, $^4J_{CF}$ = 3.4 Hz), 127.4 (d, $^3J_{CF}$ = 8.0 Hz), 128.6, 129.4, 134.5,135.1, 146.9, 162.8 (d, $^1J_{CF}$ = 246.3 Hz) ppm. ESI-MS: m/z = 318 $(M+1)^+$; HRMS calcd. for $C_{16}H_{14}ClFN_3O$ $(M+H)^+$: 318.0804; found: 318.0808.

1-Phenoxy-3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)propan-2-ol (4s). Oil; IR (KBr): 3086, 2924, 1458, 1236, 1176, 1078, 1043, 763, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.00 (dd, *J* = 6.0 Hz, *J* = 9.5 Hz, 1H), 4.06 (dd, *J* = 5.0 Hz, *J* = 9.5 Hz, 1H), 4.53 (s, 1H), 4.61 (dd, *J* = 7.0 Hz, *J* = 14.0 Hz, 1H), 4.75 (dd, *J* = 3.0 Hz, *J* = 14.0 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 2H), 7.01 (t, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.91 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 29.7, 53.3, 68.9, 114.6, 121.4, 121.6, 125.6, 128.2, 128.8, 129.7, 130.2, 147.5, 158.2 ppm. ESI-MS: m/z = 296 $(M+1)^+$.

1-(4-Methoxyphenoxy)-3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)propan-2-ol (4t). White solid; IR (KBr): 3421, 3086, 2926, 1508, 1458, 1288, 1122, 1076, ,1031, 769, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.19 (d, *J* = 4.5 Hz, 1H), 3.77 (s, 3H), 3.93 (dd, *J* = 6.0 Hz, *J* = 9.5 Hz, 1H), 3.99 (dd, *J* = 5.0 Hz, *J* = 9.5 Hz, 1H), 4.49 (s, 1H),4.58 (dd, *J* = 7.0 Hz, *J* = 14.5 Hz, 1H), 4.72 (dd, *J* = 3.0 Hz, *J* = 14.0 Hz, 1H), 6.84 (t, *J* = 10.5 Hz, 4H), 7.33 (t, *J* = 8.5 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.79 (d, *J* = 7.5 Hz, 2H), 7.89 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 29.7, 55.7, 69.0, 69.7, 114.8, 115.6, 121.3, 125.6, 128.2, 128.8, 130.3, 147.6, 152.3, 154.4 ppm. ESI-MS: m/z = 326 $(M+1)^+$.

1-(4-Phenyl-1*H*-1,2,3-triazol-1-yl)-3-(o-tolyloxy)propan-2-ol (4u). Oil； IR (KBr): 3392, 3120, 2926, 1458, 1244, 1188, 1078, 1028, 750, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.27 (s, 3H), 3.28 (d, *J* = 3.5 Hz, 1H), 4.03 (ddd, *J* = 5.0 Hz, *J* = 9.5 Hz, *J* = 14.5 Hz, 2H), 4.61-4.55 (m, 2H), 4.76 (dd, *J* = 2.0 Hz, *J* = 13.5 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.89 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 29.7, 53.1, 68.9, 69.2, 111.3, 121.2, 121.4, 125.7, 126.6, 127.1, 128.2, 128.9, 130.4, 131.0, 147.8, 156.1 ppm.

ESI-MS: m/z = 310 $(M+1)^+$.

1-Butoxy-3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)propan-2-ol (4v). Oil; IR (KBr): 3419, 3103, 2928, 1458, 1431, 1228, 1130, 1070, 767, 696 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 0.92 (t, *J* = 7.5 Hz, 3H), 1.37 (dd, *J* = 7.5 Hz, *J* = 15.0 Hz, 2H), 1.59-1.54 (m, 2H), 3.40 (dd, *J* = 5.5 Hz, *J* = 9.5 Hz, 1H), 3.49 (ddd, *J* = 4.5 Hz, *J* = 9.5 Hz, *J* = 14.0 Hz, 3H), 4.25 (t, *J* = 10.0 Hz, 1H), 4.43 (dd, *J* = 7.0 Hz, *J* = 14.0 Hz, 1H), 4.59 (dd, *J* = 3.5 Hz, *J* = 14.0 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.88 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 13.9, 19.3, 31.6, 53.2, 69.2, 71.5, 71.6, 121.2, 125.6, 128.1, 128.8, 130.4, 147.5 ppm. ESI-MS: m/z = 276 $(M+1)^+$; HRMS calcd. for $C_{15}H_{22}N_3O_2$ $(M+H)^+$: 276.1707; found: 276.1711.

1-(Allyloxy)-3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)propan-2-ol (4w). White solid; IR (KBr): 3385, 3010, 2930, 1471, 1350, 1136, 1089, 981, 871, 767, 696 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 3.00 (d, *J* = 4.5 Hz, 1H), 3.41 (dd, *J* = 6.0 Hz, *J* = 9.5 Hz, 1H), 3.54 (dd, *J* = 4.5 Hz, *J* = 9.5 Hz, 1H), 4.03 (d, *J* = 5.5 Hz, 2H), 4.27 (d, *J* = 4.0 Hz, 1H), 4.47 (dd, *J* = 7.0 Hz, *J* = 14.0 Hz, 1H), 4.61 (dd, *J* = 3.5 Hz, *J* = 14.0 Hz, 1H), 5.23 (d, *J* = 10.5 Hz, 1H), 5.29 (d, *J* = 17.0 Hz, 1H), 5.90 (ddd, *J* = 5.5 Hz, *J* = 10.5 Hz, *J* = 16.0 Hz, 1H), 7.34 (t, *J* = 7.0 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.91 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 53.2, 69.2, 71.0, 72.5, 117.8, 121.3, 125.6, 128.1, 128.8, 130.4, 134.1, 147.5 ppm. ESI-MS: m/z = 260 $(M+1)^+$.

1-(Allyloxy)-3-(4-(3-fluorophenyl)-1*H*-1,2,3-triazol-1-yl)propan-2-ol (4x). Oil; IR (KBr): 3392, 2924, 1471, 1230, 1118, 1074, 1055, 999, 785, 688 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 3.48-3.45 (m, 1H), 3.55-3.52 (m, 1H), 3.72-3.68 (m, 1H), 4.03 (d, *J* = 5.5 Hz, 2H), 4.29 (s, 1H), 4.41 (ddd, *J* = 2.0 Hz, *J* = 7.5 Hz, *J* = 9.5 Hz, 1H), 4.60 (dd, *J* = 1.5 Hz, *J* = 13.5 Hz, 1H), 5.21 (d, *J* = 10.5 Hz, 1H), 5.28 (d, *J* = 17.0 Hz, 1H), 5.90 (ddd, *J* = 5.5 Hz, *J* = 11.0 Hz, *J* = 16.5 Hz, 1H), 6.99 (t, *J* = 8.0 Hz, 1H), 7.35-7.31 (m, 1H), 7.43 (d, *J* = 10.0 Hz, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.91 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 24.9, 48.7, 53.5, 64.4, 66.4, 67.7, 107.7, 107.9, 110.1 (d, $^2J_{CF}$ = 21.1 Hz), 112.9, 117.1, 125.6 (d, $^4J_{CF}$ = 8.5 Hz), 127.7 (d, $^3J_{CF}$ = 8.6 Hz), 158.3 (d, $^1J_{CF}$ = 244.2 Hz) ppm. ESI-MS: m/z = 278 $(M+1)^+$; HRMS calcd. for $C_{14}H_{17}FN_3O_2$ $(M+H)^+$: 278.1299; found: 278.1303.

2-(4-Phenyl-1*H*-1,2,3-triazol-1-yl)cyclopentanol (4y). Oil; IR (KBr): 3304, 3093, 2928,

1456, 1232, 1074, 1055, 1028, 769, 696 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.81 (ddd, *J* = 8.0 Hz, *J* = 14.0 Hz, *J* = 16.0 Hz, 1H), 1.96-1.90 (m, 2H), 2.21 (ddd, *J* = 6.0 Hz, *J* = 13.0 Hz, *J* = 19.0 Hz, 2H), 2.38 (ddd, *J* = 7.0 Hz, *J* = 14.0 Hz, *J* = 20.5 Hz, 1H), 4.03 (s, 1H), 4.58 (ddd, *J* = 7.0 Hz, *J* = 14.0 Hz, *J* = 22.0 Hz, 2H), 7.31 (t, *J* = 7.0 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 4.5 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 20.2, 29.4, 31.7, 68.1, 77.9, 119.1, 125.7, 128.2, 128.9, 130.5, 147.5 ppm. ESI-MS: m/z = 230 $(M+1)^+$; HRMS calcd. for $C_{13}H_{16}N_3O$ $(M+H)^+$: 230.1288; found: 230.1294.

2-(4-Phenyl-1*H*-1,2,3-triazol-1-yl)cyclohexanol (4z). White solid; IR (KBr): 3306, 3093, 2924, 1456, 1437, 1236, 1165, 1074, 1055, 1028, 767, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.53-1.42 (m, 3H), 2.02-1.88 (m, 3H), 2.24 (d, *J* = 10.0 Hz, 2H), 3.21 (s, 1H), 4.09 (dd, *J* = 5.0 Hz, *J* = 9.5 Hz, 1H), 4.19 (ddd, *J* = 4.5 Hz, *J* = 10.0 Hz, *J* = 13.0 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.75 (d, *J* = 7.5 Hz, 2H), 7.78 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 24.1, 24.8, 31.6, 33.8, 67.2, 72.6, 119.6, 125.5, 128.0, 128.8, 130.4, 146.9 ppm. ESI-MS: m/z = 244 $(M+1)^+$.

2-(4-(3-Fluorophenyl)-1*H*-1,2,3-triazol-1-yl)cyclohexanol (4aa). White solid; IR (KBr): 3317, 3095, 2926, 1458, 1419, 1240, 1199, 1087, 1053, 794, 692 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.53-1.41 (m, 3H), 2.03-1.88 (m, 3H), 2.24 (dd, *J* = 6.0 Hz, *J* = 9.0 Hz, 2H), 2.96 (d, *J* = 3.0 Hz, 1H), 4.07 (ddd, *J* = 5.5 Hz, *J* = 9.5 Hz, *J* = 13.5 Hz, 1H), 4.20 (ddd, *J* = 4.0 Hz, *J* = 9.5 Hz, *J* = 13.5 Hz, 1H), 7.02 (t, *J* = 8.5 Hz, 1H), 7.39-7.34 (m, 1H), 7.48 (d, *J* = 10.0 Hz, 1H) 7.54 (d, *J* = 7.5 Hz, 1H), 7.81 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 19.4, 20.1, 25.0, 26.7, 62.8, 67.8, 107.4, 107.6, 110.0 (d, $^2J_{CF}$ = 20.9 Hz), 115.6, 116.2, 125.5 (d, $^4J_{CF}$ = 8.4 Hz), 127.7 (d, $^3J_{CF}$ = 8.4 Hz), 158.3 (d, $^1J_{CF}$ = 244.1 Hz) ppm. ESI-MS: m/z = 262 $(M+1)^+$; HRMS calcd. for $C_{14}H_{17}FN_3O$ $(M+H)^+$: 262.1350; found: 262.1355.

1-(Oxiran-2-ylmethyl)-4-phenyl-1*H*-1,2,3-triazole (4ab). White solid; IR (KBr): 3392, 3094, 2926, 1458, 1417, 1220, 1176, 1074, 1049, 1026, 761, 696 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 2.56 (t, *J* = 2.0 Hz, 1H), 2.93 (t, *J* = 4.0 Hz, 1H), 3.42-3.40 (m, 1H), 4.37 (dd, *J* = 6.5 Hz, *J* = 15.0 Hz, 1H), 4.87 (d, *J* = 14.5 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.90 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 45.3, 50.1, 51.9, 120.5, 125.8, 128.3, 128.9, 130.4, 148.2 ppm. ESI-MS: m/z = 202 $(M+1)^+$.

1-(Oxiran-2-ylmethyl)-4-(*p*-tolyl)-1*H*-1,2,3-triazole (4ac). White solid; IR (KBr): 3398,

3080, 2922, 1506, 1419, 1220, 1174, 1072, 1047, 746, 663 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 2.38 (s, 3H), 2.58 (dd, *J* = 2.5 Hz, *J* = 4.5 Hz, 1H), 2.93 (t, *J* = 4.5 Hz, 1H), 3.41 (ddd, *J* = 3.0 Hz, *J* = 5.5 Hz, *J* = 9.0 Hz, 1H), 4.36 (dd, *J* = 6.5 Hz, *J* = 15.0 Hz, 1H), 4.86 (dd, *J* = 2.5 Hz, *J* = 14.5 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 2H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.86 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 21.3, 45.3, 50.1, 51.9, 120.2, 125.7, 127.6, 129.6, 138.2, 148.3 ppm. ESI-MS: m/z = 216 $(M+1)^+$; HRMS calcd. for $C_{12}H_{14}N_3O$ $(M+H)^+$: 216.1131; found: 216.1133.

4-(4-Ethylphenyl)-1-(oxiran-2-ylmethyl)-1*H*-1,2,3-triazole (4ad). White solid; IR (KBr): 3400, 3066, 2928, 1521, 1220, 1072, 1047, 761, 677 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.25 (t, *J* = 4.0 Hz, 3H), 2.57 (t, *J* = 2.5 Hz, 1H), 2.68 (q, *J* = 7.5 Hz, *J* = 15.5 Hz, 2H), 2.93 (t, *J* = 4.0 Hz, 1H), 3.42-3.40 (m, 1H), 4.36 (dd, *J* = 6.0 Hz, *J* = 14.5 Hz, 1H), 4.86 (dd, *J* = 2.5 Hz, *J* = 14.5 Hz, 1H), 7.27 (d, *J* = 6.5 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.87 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 28.7, 29.7, 45.3, 50.1, 51.9, 120.2, 125.7, 127.8, 128.4, 144.5, 148.3 ppm. ESI-MS: m/z = 230 $(M+1)^+$; HRMS calcd. for $C_{13}H_{16}N_3O$ $(M+H)^+$: 230.1288; found: 230.1296.

4-(4-Butylphenyl)-1-(oxiran-2-ylmethyl)-1*H*-1,2,3-triazole (4ae). White solid; IR (KBr): 3404, 3064, 2924, 1450, 1419, 1220, 1072, 1049, 746 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 0.94 (t, *J* = 7.5 Hz, 3H), 1.41-1.33 (m, 2H), 1.65-1.59 (m, 2H), 2.57 (dd, *J* = 2.5 Hz, *J* = 4.5 Hz, 1H), 2.64 (t, *J* = 7.5 Hz, 2H), 2.93 (t, *J* = 4.5 Hz, 1H), 3.41 (ddd, *J* = 2.5 Hz, *J* = 4.0 Hz, *J* = 6.5 Hz, 1H), 4.36 (dd, *J* = 6.0 Hz, *J* = 14.5 Hz, 1H), 4.86 (dd, *J* = 2.5 Hz, *J* = 14.5 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.86 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 14.0, 22.3, 33.5, 35.4, 45.3, 50.1, 51.8, 120.2, 125.7, 127.8, 128.9, 143.2, 148.3 ppm. ESI-MS: m/z = 258 $(M+1)^+$; HRMS calcd. for $C_{15}H_{20}N_3O$ $(M+H)^+$: 258.1601; found: 258.1605.

4-(4-Hexylphenyl)-1-(oxiran-2-ylmethyl)-1*H*-1,2,3-triazole (4af). White solid; IR (KBr): 3385, 3101, 2918, 1521, 1419, 1220, 1122, 1072, 1049, 821, 759 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 0.88 (t, *J* = 7.0 Hz, 3H), 1.36-1.29 (m, 6H), 1.63 (t, *J* = 7.0 Hz, 2H), 2.57 (dd, *J* = 2.5 Hz, *J* = 4.5 Hz, 1H), 2.63 (t, *J* = 8.0 Hz, 2H), 2.93 (t, *J* = 4.5 Hz, 1H), 3.41 (ddd, *J* = 2.5 Hz, *J* = 4.0 Hz, *J* = 6.5 Hz, 1H), 4.36 (dd, *J* = 6.5 Hz, *J* = 15.0 Hz, 1H), 4.86 (dd, *J* = 2.5 Hz, *J* = 14.5 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.86 (s, 1H) ppm; ^{13}C NMR

($CDCl_3$, 125MHz) δ 14.1, 22.6, 29.0, 31.4, 31.7, 35.7, 52.9, 63.7, 65.6, 121.2, 125.5, 127.5, 128.9, 143.2, 147.5 ppm. ESI-MS: m/z = 286 $(M+1)^+$; HRMS calcd. for $C_{17}H_{24}N_3O$ $(M+H)^+$: 286.1914; found: 286.1920.

4-(4-Fluorophenyl)-1-(oxiran-2-ylmethyl)-1*H*-1,2,3-triazole (4ag). White solid; IR (KBr): 3392, 3107, 2926, 1498, 1417, 1219, 1159, 1070, 1049, 759, 705 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 2.58 (dd, *J* = 2.5 Hz, *J* = 4.5 Hz, 1H), 2.94 (t, *J* = 4.0 Hz, 1H), 3.41 (ddd, *J* = 3.0 Hz, *J* = 6.5 Hz, *J* = 9.0 Hz, 1H), 4.35 (dd, *J* = 6.5 Hz, *J* = 15.0 Hz, 1H), 4.88 (dd, *J* = 2.5 Hz, *J* = 14.5 Hz, 1H), 7.13 (t, *J* = 8.5 Hz, 2H), 7.80 (d, *J* = 5.5 Hz, 1H), 7.82 (d, *J* = 5.5 Hz, 1H), 7.86 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 45.3, 50.0, 51.9, 115.8 (d, $^2J_{CF}$ = 21.6 Hz), 120.3, 126.7 (d, $^4J_{CF}$ = 3.0 Hz), 127.5 (d, $^3J_{CF}$ = 8.1 Hz), 147.3, 162.7 (d, $^1J_{CF}$ = 270.8 Hz) ppm. ESI-MS: m/z = 220 $(M+1)^+$; HRMS calcd. for $C_{11}H_{11}FN_3O$ $(M+H)^+$: 220.0881; found: 220.0879.

1-((2-Methyloxiran-2-yl)methyl)-4-phenyl-1*H*-1,2,3-triazole (4ah). Oil; IR (KBr): 3392, 3120, 2929, 1460, 1230, 1074, 1045, 1028, 765, 696 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.35 (s, 1H), 2.62 (d, *J* = 4.5 Hz, 1H), 2.74 (d, *J* = 4.5 Hz, 1H), 4.40 (d, *J* = 14.5 Hz, 1H), 4.70 (d, *J* = 15.0 Hz, 1H), 7.34 (t, *J* = 13.0 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.85 (d, *J* = 7.5 Hz, 2H), 7.90 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 18.6, 52.0, 55.1, 55.6, 120.5, 125.7, 128.2, 128.9, 130.5, 148.2 ppm. ESI-MS: m/z = 216 $(M+1)^+$; HRMS calcd. for $C_{12}H_{14}N_3O$ $(M+H)^+$: 216.1131; found: 216.1137.

1,3-Bis(4-phenyl-1*H*-1,2,3-triazol-1-yl)propan-2-ol (4ai).[47] White solid, 252-253 °C; IR (KBr): 3383, 3093, 2924, 1458, 1227, 1159, 1084, 764, 692 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz) δ 4.47-4.39 (m, 3H), 4.64-4.60 (m, 2H), 5.80-5.78 (m, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 4H), 7.85 (d, *J* = 7.0 Hz, 4H), 8.55 (s, 2H) ppm; ^{13}C NMR (DMSO-d_6, 125MHz) δ 53.7, 68.8, 123.0, 125.6, 128.3, 129.4, 131.3, 146.6 ppm. ESI-MS: m/z = 347 $(M+1)^+$;

1-(4-(4-Ethylphenyl)-1*H*-1,2,3-triazol-1-yl)-3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)propan-2-ol (4aj). Yellow solid, 219-220 °C; IR (KBr): 3385, 3088, 2928, 1464, 1226, 1157, 1082, 1028, 762, 691 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz) δ 1.20 (t, *J* = 7.5 Hz, 3H), 2.62 (q, *J* = 7.5 Hz, 2H), 4.42-4.40 (m, 3H), 4.63-4.60 (m, 2H), 5.78 (d, *J* = 4.5 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 7.0 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J*

= 7.5 Hz, 2H), 8.49 (s, 1H), 8.54 (s, 1H) ppm; ^{13}C NMR (DMSO-d_6, 125MHz) δ 16.0, 28.4, 53.67, 53.72, 68.8, 122.6, 123.0, 125.60, 125.63, 128.3, 128.7, 129.4, 131.3, 143.9, 146.60, 146.68 ppm. ESI-MS: m/z = 375 $(M+1)^+$; HRMS calcd. for $C_{21}H_{23}N_6O$ $(M+H)^+$: 375.1928; found: 375.1932.

1-Benzyl-4-phenyl-1*H*-1,2,3-triazole (6a). White solid; IR (KBr): 3198, 3032, 1616, 1508, 669, 489 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.59 (s, 2H), 7.33-7.31 (m, 3H), 7.42-7.37 (m, 5H), 7.66 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 54.2, 119.5 125.7, 128.1, 128.2, 128.8, 129.2, 130.6, 134.7, 148.3 ppm. ESI-MS: m/z = 236 $(M+1)^+$.

1-Benzyl-4-(4-ethylphenyl)-1*H*-1,2,3-triazole (6b). Oil; IR (KBr): 3134, 3032, 1550, 1508, 1159, 781, 669 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.24 (t, *J* = 7.5 Hz, 3H), 2.66 (q, *J* = 7.5 Hz, 2H), 5.58 (s, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.30 (s, 1H), 7.32 (d, *J* = 2.0 Hz, 1H), 7.41-7.37 (m, 3H), 7.62 (s, 1H), 7.23 (d, *J* = 8.0 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 28.5, 29.6, 54.1, 119.0, 125.6, 127.9, 128.1, 128.3, 128.6, 129.0, 130.8, 134.6, 148.2 ppm. ESI-MS: m/z = 264 $(M+1)^+$; HRMS calcd. for $C_{17}H_{18}N_3$ $(M+H)^+$: 264.1495; found: 264.1501.

1-Benzyl-4-(3-fluorophenyl)-1*H*-1,2,3-triazole (6c). Oil; IR (KBr): 3134, 3012, 1558, 1508, 1161, 779, 669 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.59 (s, 2H), 7.41-7.29 (m, 7H), 757-7.51 (m, 2H), 7.66 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 54.2, 119.5 125.7, 128.1, 128.2, 128.8, 129.2, 130.6, 134.7, 148.3 ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 54.3, 112.6 (d, $^2J_{CF}$ = 22.8 Hz), 114.9, 121.3 (d, $^4J_{CF}$ = 2.9 Hz), 127.1, 128.1, 128.90, 128.91, 129.2, 130.4 (d, $^3J_{CF}$ = 8.9 Hz), 134.6, 147.2, 163.9 ppm. ESI-MS: m/z = 254 $(M+1)^+$.

1-Benzyl-4-(4-chlorophenyl)-1*H*-1,2,3-triazole (6d). Oil; IR (KBr): 3246, 3034, 1541, 1496, 1159, 779, 669 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.58 (s, 2H), 7.33-7.31 (m, 2H), 7.40-7.36 (m, 5H), 7.64 (s, 1H), 7.73 (d, *J* = 8.5 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 54.3, 119.5, 127.0, 128.1, 128.9, 129.0, 129.1, 129.2, 133.9, 134.5, 147.2 ppm. ESI-MS: m/z = 270 $(M+1)^+$.

1-Benzyl-4-(4-bromophenyl)-1*H*-1,2,3-triazole (6e). White solid; IR (KBr): 3126, 3012, 1610, 1508, 1168, 1068, 727, 648 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.54 (s, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 7.32-7.29 (m, 2H), 7.54 (t, *J* = 8.5 Hz, 3H), 7.66 (t, *J* = 8.5 Hz, 2H), 7.74 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 52.0, 119.6, 127.1, 127.2, 128.1, 129.0, 129.2, 130.4, 132.0, 132.2, 147.2 ppm. ESI-MS: m/z = 314 $(M+1)^+$.

1-Benzyl-4-propyl-1*H*-1,2,3-triazole (6f). Oil; IR (KBr): 3090, 3034, 1629, 1496, 636, 475 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 0.98 (t, *J* = 7.5 Hz, 3H), 1.80-1.73 (m, 2H), 2.70 (t, *J* = 7.0 Hz, 2H), 5.52 (s, 2H), 7.37-7.30 (m, 6H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 13.8, 22.2, 27.6, 52.5, 103.0, 127.9, 128.2, 128.7, 135.2, 150.2 ppm. ESI-MS: m/z = 202 $(M+1)^+$.

1-Benzyl-4-pentyl-1*H*-1,2,3-triazole (6g). White solid; IR (KBr): 3134, 3034, 1639, 1550, 696, 461 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 0.87 (t, *J* = 7.0 Hz, 3H), 1.33-1.30 (m, 4H), 1.67-1.61 (m, 2H), 2.67 (t, *J* = 7.5 Hz, 2H), 5.47 (s, 2H), 7.21 (s, 1H), 7.24 (d, *J* = 7.5 Hz, 2H), 7.36-7.27 (m, 3H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 14.0, 22.4, 25.7, 29.1, 31.4, 53.9, 120.6, 127.9, 128.5, 129.0, 135.1, 148.9 ppm. ESI-MS: m/z = 230 $(M+1)^+$.

1-(4-Methylbenzyl)-4-phenyl-1*H*-1,2,3-triazole (6h). Oil; IR (KBr): 3158, 3043, 1629, 1545, 678, 480 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 2.35 (s, 3H), 5.52 (s, 2H), 7.22-7.17 (m, 4H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.0 Hz, 2H), 7.61 (s, 1H), 7.78 (d, *J* = 7.5 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 21.2, 54.1, 119.4, 125.7, 128.1, 128.8, 129.5, 129.8, 130.6, 131.7, 138.8, 148.2 ppm. ESI-MS: m/z = 250 $(M+1)^+$.

1-(4-Bromobenzyl)-4-phenyl-1*H*-1,2,3-triazole (6i). White solid; IR (KBr): 3126, 3026, 1654, 1460, 696, 669, 491 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 5.51 (s, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.64 (s, 1H), 7.79 (d, *J* = 8.5 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 53.5, 119.4 123.0, 125.7, 128.3, 128.9, 129.7, 130.4, 132.4, 133.7, 148.4 ppm. ESI-MS: m/z = 314 $(M+1)^+$.

1,4-Diphenyl-1*H*-1,2,3-triazole (8a). White solid; IR (KBr): 3144, 3061, 2364, 1598, 1510, 1456 cm^{-1};^1H NMR ($CDCl_3$, 500 MHz) δ 7.38 (t, *J* = 7.5 Hz 1H), 7.49-7.46 (m, 3H), 7.56 (t, *J* = 7.5 Hz, 2H), 7.80 (d, *J* = 7.5 Hz, 2H), 7.92 (d, *J* = 7.0 Hz, 2H), 8.20 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 117.6, 120.6, 125.9, 128.4, 128.8, 128.9, 129.8, 130.3, 137.1, 148.4 ppm. ESI-MS: m/z = 222 $(M+1)^+$.

4-(4-Methoxyphenyl)-1-phenyl-1*H*-1,2,3-triazole (8b). White solid; IR (KBr): 3107, 3061, 2359, 1599, 1502, 1464, 1067 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 3.87 (s, 3H), 7.00 (d, *J* = 9.0 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.79 (d, *J* = 7.5 Hz, 2H), 7.84 (d, *J* = 8.5 Hz, 2H), 8.11 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 55.4, 114.4, 116.8, 120.5, 123.0, 127.2, 128.7, 129.8, 137.2, 148.3, 159.8 ppm. ESI-MS: m/z = 252 $(M+1)^+$.

1-Phenyl-4-(*p*-tolyl)-1*H*-1,2,3-triazole (8c). White solid; IR (KBr): 3122, 3084, 2359,

1595, 1506, 1489 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 2.40 (s, 3H), 7.27 (d, *J* = 9.5 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.80 (t, *J* = 7.0 Hz, 4H), 8.16 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 21.3, 117.3, 120.5, 125.8, 127.8, 128.7, 129.6, 129.8, 129.8, 134.8, 138.3, 148.5 ppm. ESI-MS: m/z = 236 $(M+1)^+$; HRMS calcd. for $C_{15}H_{14}N_3$ $(M+H)^+$: 236.2912; found: 236.2916.

4-(4-Ethylphenyl)-1-phenyl-1*H*-1,2,3-triazole (8d). White solid; IR (KBr): 2983, 2914, 2359, 1573, 1504, 1454 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.28 (t, *J* = 8.0 Hz, 3H), 2.70 (q, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 2H), 8.16 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 15.5, 28.7, 117.3, 120.5, 125.9, 127.7, 128.4, 128.7, 129.8, 137.1, 144.7, 148.5 ppm. ESI-MS: m/z = 250 $(M+1)^+$.

4-(4-Butylphenyl)-1-phenyl-1*H*-1,2,3-triazole (8e). White solid; IR (KBr): 3113, 2965, 2365, 1568, 1510, 1458 cm^{-1};^1H NMR ($CDCl_3$, 500 MHz) δ 0.95 (t, *J* = 7.0 Hz, 3H), 1.42-1.35 (m, 2H), 1.67-1.61 (m, 2H), 2.66 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.83-7.79 (m, 4H), 8.16 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 14.0, 22.4, 33.6, 35.5, 117.2, 120.5, 125.8, 127.6, 128.7, 129.0, 129.8, 137.2, 143.4, 148.6 ppm. ESI-MS: m/z = 278 $(M+1)^+$.

4-(3-Fluorophenyl)-1-phenyl-1*H*-1,2,3-triazole (8f). White solid; IR (KBr): 3130, 2345, 1610, 1587, 1485, 1066 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.09-7.05 (m, 1H), 7.45-7.41 (m, 1H), 7.48 (t, *J* = 7.0 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 9.5 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7. 80 (d, *J* = 8.0 Hz, 2H), 8.21 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 112.7, 112.9, 115.2 (d, $^2J_{CF}$ = 21.0 Hz), 118.0, 120.6, 121.5 (d, $^4J_{CF}$ = 2.8 Hz), 129.0, 129.9, 130.5 (d, $^3J_{CF}$ = 8.3 Hz), 137.0, 147.4, 163.2 (d, $^1J_{CF}$ = 244.0 Hz) ppm. ESI-MS: m/z = 240 $(M+1)^+$.

4-(4-Chlorophenyl)-1-phenyl-1*H*-1,2,3-triazole (8g). White solid; IR (KBr): 3152, 2346, 1616, 1530, 1500, 796, 542 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.44 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 2H), 8.19 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 117.7, 120.6, 127.1, 128.78, 128.85, 128.94, 129.2, 129.8, 130.9, 147.4 ppm. ESI-MS: m/z = 256 $(M+1)^+$.

4-(4-Bromophenyl)-1-phenyl-1*H*-1,2,3-triazole (8h). White solid; IR (KBr): 3144, 2374, 1616, 1558, 1498, 538 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.48 (t, *J* = 7.0 Hz, 1H), 7.61-7.55

(m, 4H), 7.80-7.78 (m, 4H), 8.20 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 117.7, 120.6, 122.4, 127.4, 128.9, 129.0, 129.9, 130.9, 132.1, 147.4 ppm. ESI-MS: m/z = 300 $(M+1)^+$.

4-([1,1'-Biphenyl]-4-yl)-1-phenyl-1*H*-1,2,3-triazole (8i). White solid; IR (KBr): 3130, 3044, 2382, 1614, 1506, 1467 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.37 (t, *J* = 7.0 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 3H), 7.57 (t, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 7.5 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 8.00 (d, *J* = 8.0 Hz, 2H), 8.24 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 117.6, 120.6, 126.3, 127.5, 127.6, 128.82, 128.86, 129.2, 129.8, 130.9, 137.1, 140.6, 141.2, 148.1 ppm. ESI-MS: m/z = 298 $(M+1)^+$.

1-Phenyl-4-(thiophen-2-yl)-1*H*-1,2,3-triazole (8j). Pale yellow solid; IR (KBr): 3131, 3052, 2346, 1597, 1527, 1481 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.13-7.11 (m, 1H), 7.35 (d, *J* = 4.0 Hz, 1H), 7.49-7.45 (m, 2H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 2H), 8.11 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 117.1, 120.6, 124.6, 125.4, 127.7, 128.9, 129.8, 132.5, 143.5 ppm. ESI-MS: m/z = 228 $(M+1)^+$.

4-Phenyl-1-(p-tolyl)-1*H*-1,2,3-triazole (8k). White solid; IR (KBr): 2916, 2849, 2359, 1558, 1519, 1454 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.44 (s, 3H), 7.38-7.34 (m, 3H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.91 (d, *J* = 7.5 Hz, 2H), 8.15 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 21.1, 117.6, 120.5, 125.9, 128.4, 128.9, 130.3, 130.4, 138.9, 148.3 ppm. ESI-MS: m/z = 236 $(M+1)^+$.

1-(3-Fluorophenyl)-4-phenyl-1*H*-1,2,3-triazole (8l). White solid; IR (KBr): 3128, 3082, 2351, 1608, 1537, 1471, 1065 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.28-7.26 (m, 2H), 7.40 (t, *J* = 7.0 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.54-7.52 (m, 2H), 7.90-7.89 (m, 2H), 8.14 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 105.2, 105.3, 105.37, 105.4, 117.6 (d, $^2J_{CF}$ = 26.6 Hz), 125.9, 128.9 (d, $^3J_{CF}$ = 9.6 Hz), 129.0, 129.6, 130.8, 149.1, 150.1 (d, $^1J_{CF}$ = 246.4 Hz) ppm. ESI-MS: m/z = 240 $(M+1)^+$; HRMS calcd. for $C_{14}H_{11}N_3F$ $(M+H)^+$: 240.0932; found: 240.0934.

1-(4-Chlorophenyl)-4-phenyl-1*H*-1,2,3-triazole (8m). White solid; IR (KBr): 3130, 3097, 2344, 1608, 1558, 1481, 707 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.47 (t, *J* = 7.5 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 3H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 2H), 8.17 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 117.4, 121.7, 125.9, 128.6, 128.8, 129.0, 130.0, 130.9, 132.3, 141.2 ppm. ESI-MS: m/z = 256 $(M+1)^+$.

1-Phenyl-4-propyl-1*H*-1,2,3-triazole (8n). Oil; IR (KBr): 3090, 958, 2343, 1599, 1501, 1465 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 1.02 (t, *J* = 7.5 Hz, 3H), 1.81-1.75 (m, 2H), 2.78 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.69 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125MHz) δ 13.8, 22.7, 27.7, 118.9, 120.4, 128.4, 129.7, 130.9, 149.0 ppm. ESI-MS: m/z = 188 $(M+1)^+$.

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