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Recyclable clay supported Cu (II) catalyzed tandem one-pot synthesis of 1-aryl-1,2,3-triazoles☆

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ABSTRACT

Montmorillonite KSF clay supported CuO nanoparticles efficiently catalyzes one-pot aromatic azidonation of aryl boronic acids followed by regioselective azide–alkyne 1,3-dipolar cycloaddition (CuAAC) reaction producing corresponding 1-aryl-1,2,3-triazole derivatives at room temperature in excellent yields without use of any additives. Investigations on mechanism of CuAAC revealed that sodium azide, which is used as azidonating reagent in one-pot protocol reduces Cu(II) to click-active Cu(I). The catalytic efficiency of another Cu(II) source $CuSO_4$ in combination with NaN_3 for this one-pot CuAAC protocol, further supported our mechanism. This is the first report for use of Cu(II)/NaN_3 catalytic system for CuAAC protocol. The clay–Cu(II) catalyst being ligand-free, leaching-free, easy to synthesize from inexpensive commercially available precursors, recyclable, and environmentally friendly will be highly useful for economical synthesis of 1,4-disubstituted 1,2,3-triazoles.

1. Introduction

In recent years, the Cu(I)-catalyzed azide–alkyne cycloaddition (CuAAC) reaction[1–3] has gained tremendous amount of attention as it finds utility in drug discovery,[4–8] biomolecular ligation,[9] in vivo tagging[10] as well as in polymerization reactions.[11] It is well known that CuAAC reaction occurs only in presence of Cu(I) and does not proceed in presence of Cu(II) or Cu(0); however, Cu (I) salts are prone to redox processes so it is desirable to protect and stabilize the active copper catalysts during CuAAC, which led to discovery of several modified procedures, like using Cu(II)/Cu(0) salts with various additives (e.g., reducing agents)/ligands.[12] The most generalized and widely used version of this reaction involves use of $CuSO_4$/sodium ascorbate catalytic system in aqueous media. As organic azides are explosive in nature, relatively unstable and difficult to isolate, CuAAC strategy involving in situ generation of organic azides from suitable precursors would be highly advantageous and safe. As an efforts toward this aspect, Guo and co-workers[13] developed such protocol using NaN_3/$CuSO_4$/sodium ascorbate catalytic system.

The major limitations of existing CuAAC protocols realized in terms of homogeneous nature of catalysts, thus creating problem during separation of catalyst/product(s) and the requirement of adding reducing agents and stabilizing ligands, which limited their utilization in practical processes. Recent research in this area has concentrated on heterogeneous catalytic systems,[14–17] which have several advantages, such as faster and simpler isolation of the reaction products by filtration, as well as recovery and recycling of the catalyst systems. Cu(I) species immobilized onto various supports, such as silica,[18] zeolites,[19,20] activated charcoal,[21] and amine-functionalized polymers[22] have been reported recently. However, heterogeneous catalysts immobilized with Cu(I) species frequently suffer from the general thermodynamic instability of Cu(I), which results in its easy oxidation to Cu(II) and/or disproportionation to Cu(0) and Cu(II), which limited their utilization in practical processes. Recent studies indicated that immobilized Cu(II) species could be reduced to Cu(I) species by alkyne during homocoupling reaction. However, these protocols require organic solvents to achieve high reactivity, need of inert atmosphere and higher reaction times (48–72 h).[23–26] Xia and co-workers[26] developed ionic liquid based heterogeneous catalysts for efficient synthesis of 1,2,3-triazoles in aqueous medium. In recent studies, hydroxyapatite-supported copper (II) (CuHAP)[27] or Cu(II)–hydrotalcite[28] catalyzed azide–alkyne cycloaddition reaction without use of any base or reducing agents have been reported.

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Herein, we report the use of recyclable heterogeneous clay supported CuO nanoparticles for one-pot synthesis of 1-aryl-1,2,3-triazoles (**1**) from aryl boronic acids (**2**) as depicted in Fig. 1. In the present protocol, sodium azide apart from its role as an azidonation reagent, also acts as a reducing agent producing in situ click-active Cu(I). This one-pot CuAAC protocol also worked well in presence of $CuSO_4/NaN_3$ catalytic system without need of additional reducing agent, which is further support to our finding of sodium azide's role as a reducing agent in CuAAC.

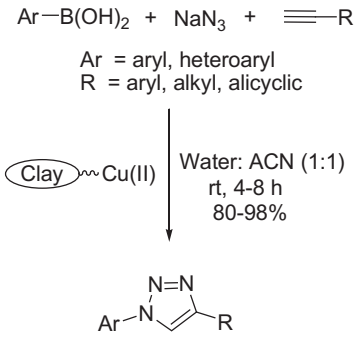


Fig. 1. Clay-supported Cu(II)-catalyzed one-pot synthesis of 1-aryl-1,2,3-trizoles.

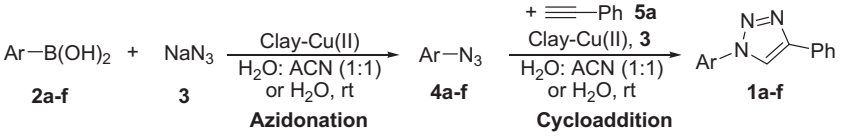
2. Results and discussion

The clay supported Cu(II) catalyst was prepared by treatment of aqueous Cu oligomer with Montmorillonite KSF clay, followed by solvent evaporation, drying in oven and finally calcination at 425 °C for 3 h. Initially, we checked the catalytic performance of clay–Cu(II) catalyst for azide formation from boronic acids in water and ACN: water (1:1) medium at room temperature as depicted in Table 1. Reaction worked in both solvents, however ACN: water (1:1) medium produced higher yields of azides **4a**–**f** with lesser reaction times. 4-Hydroxy phenyl boronic acid required minimal time compared with other aryl boronic acids. Next, we examined the catalytic performance of clay–Cu(II)/NaN_3 catalytic system in click reaction for azides **4a**–**f** with alkyne **5a** (Table 1). The sequence of addition of reactants was found to be very important.[29] A homocoupling of alkyne was observed when all reactants were mixed together at same time.[30] Thus, stirring sodium azide (**3**) and clay–Cu(II) in solvent for 30 min, followed by addition of azide **4a** and alkyne **5a** produced desired triazole **1a**.[31] Similar to azidonation reaction, water: ACN (1:1) solvent was found to be superior to water alone in CuAAC reaction. Phenyl boronic acids, substituted phenyl boronic acids as well as heteroaryl boronic acids participated well in both reactions as depicted in Table 1.

Having successfully developed clay–Cu(II)/NaN_3 catalyzed protocol for aromatic azidonation and CuAAC reaction under identical reaction conditions, it looked obvious to convert these two steps into one-pot protocol for synthesis of 1-aryl-1,2,3-triazoles **1** directly from aryl boronic acids **2**. With known explosive and unstable nature of organic azides and its difficult isolation, this one-pot CuAAC will be highly useful and safe. The model reaction between 4-hydroxy boronic acid **2a**, sodium azide (**3**) and phenyl acetylene (**5a**) was investigated (Table 2). Treatment of **2a** with sodium azide (**3**) in water: ACN (1:1) in presence of clay–Cu(II) catalyst (10 mol %) led to formation of corresponding aryl azide (monitored by TLC). Further on addition of alkyne **5a** produced desired triazole **1a** in 98% yield in total 8 h of reaction time (Table 2, entry 1). Poor yields were obtained in organic solvents viz. *i*-PrOH, THF, MeOH, DMF, DMSO, and acetone (entries 2–7). The ACN: H_2O (1:1) produced corresponding triazole in 98% yield in much lesser time (time, 4 h; entry 8) compared with only water as a solvent (time, 8 h; entry 1). The combination of water: butanol (1:1), however was not able to show improvement over water. Increase in the catalyst loading was able to reduce the reaction time. Loading of 20 mol % catalyst produced desired triazole in 6 h (entry 10). Reduction in catalyst loading, as low as 1 mol % also yielded excellent yield of product **1a** although it required 12 h of reaction time (entry 14). Thus, the 10 mol % of catalyst and water: ACN (1:1) as a reaction medium were found to be optimum by considering reaction time and yield. $CuSO_4$ (10 mol %) also produced excellent yields of **1a** in both water as well as water: ACN (1:1) solvents (entries 15 and 17). Further, the clay–Cu(II) catalyst showed good catalytic efficiency with the recovered catalyst indicating its recyclability over several cycles without significant loss of catalytic activity.[32]

With the optimal conditions in hand, scope of the clay–Cu(II) catalyzed one-pot CuAAC was investigated for variety of boronic acids and alkynes. Various substituted aromatic, and heteroaromatic boronic acids, and different aromatic, alicyclic, and aliphatic alkynes were investigated (Table 3). It was noticed that the triazole products were formed in excellent yields with varying reaction times. The reaction time was dependent on the type of boronic acid but not on the type of alkyne used. 4-Hydroxy phenyl

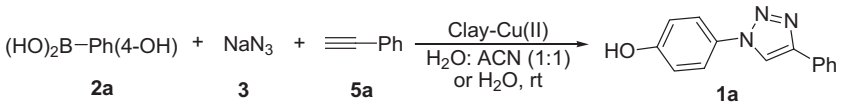
Table 1
Clay–Cu(II)/NaN_3 catalyzed aromatic azidonation[a] and azide–alkyne cycloaddition[b]



		Azidonation			Cycloaddition		
		% Yield[c] (reaction time)[d]			% Yield[c] (reaction time)[d]		
Entry	Ar	Product	Water	ACN:water (1:1)	Product	Water	ACN:water (1:1)
1	–Ph(4-OH)	**4a**	88 (8)	97 (3)	**1a**	94 (1.5)	98 (1)
2	–Ph	**4b**[e]	84 (14)	96 (6)	**1b**[16]	88 (1.5)	97 (1)
3	–Ph(3-CHO)	**4c**	80 (12)	95 (5)	**1c**	90 (2)	97 (1)
4	–Ph(4-OMe)	**4d**	78 (10)	95 (8)	**1d**[16]	90 (1.5)	98 (0.75)
5	-2-OMe pyridin-5-yl	**4e**	82 (8)	98 (3.5)	**1e**	92 (1.5)	98 (0.75)
6	–thiophen-3-yl	**4f**	80 (8)	96 (3.5)	**1f**	92 (1.5)	98 (1)

[a] **2a**–**f** (1 mmol), **3** (2 mmol) and clay–Cu(II) (10 mol %).
[b] **4a**–**f** (1 mmol), **3** (0.6 mmol), **5a** (1.1 mmol) and clay–Cu(II) (10 mol %).
[c] Isolated yields after silica gel column chromatography.
[d] Reaction time in h.
[e] 3 mmol of **3** was used.

Table 2
Catalyst optimization studies for one-pot CuAAC protocol[a]

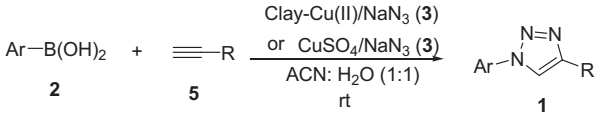


2a 3 5a 1a

Entry	Cu(II) catalyst	Mol % of catalyst	Solvent	Time (h)	Yield[b] (%)
1	Clay–CuO	10	H_2O	8	98
2	Clay–CuO	10	*i*-PrOH	8	40
3	Clay–CuO	10	THF	8	20
4	Clay–CuO	10	MeOH	8	87
5	Clay–CuO	10	DMF	8	65
6	Clay–CuO	10	DMSO	8	62
7	Clay–CuO	10	Acetone	8	30
8	Clay–CuO	10	H_2O/ACN (1:1)	4	98
9	Clay–CuO	10	H_2O/*t*-BuOH (1:1)	8	90
10	Clay–CuO	20	H_2O	6	97
11	Clay–CuO	5	H_2O	8	75
12	Clay–CuO	5	H_2O	12	96
13	Clay–CuO	1	H_2O	5	50
14	Clay–CuO	1	H_2O	12	95
15	$CuSO_4$	10	H_2O	6	97
16	$CuSO_4$	20	H_2O	4	98
17	$CuSO_4$	10	H_2O/ACN (1:1)	4	98

[a] Reagents and reaction conditions: **2a** (1 mmol), **3** (2 mmol), **5a** (1.1 mmol) and Cu(II) catalyst.
[b] Isolated yields after silica gel column chromatography.

Table 3
One-pot synthesis of 1-aryl-1,2,3-triazoles using clay–Cu(II)/NaN_3 or $CuSO_4$/NaN_3-catalyzed CuAAC reaction[a,b]



2 5 1

Entry	Ar	R	Product	Clay–Cu(II)/NaN_3		$CuSO_4$/NaN_3	
				Time (h)	Yield[c] (%)	Time (h)	Yield[c] (%)
1	–Ph(4-OH)	–Ph	**1a**	4	98	2.5	98
2	–Ph	–Ph	**1b**[16]	6	96	3	97
3	–Ph(3-CHO)	–Ph	**1c**	8	85	5	88
4	–Ph(4-OMe)	–Ph	**1d**[16]	6	97	4	98
5	-2-methoxy pyridin-5-yl	–Ph	**1e**	4	96	2.5	97
6	–thiophen-3-yl	–Ph	**1f**	5	95	4	96
7	–Ph(4-OMe)	$-(CH_2)_5CH_3$	**1g**	6	92	3	96
8	–Ph(4-OMe)	$-(CH_2)_7CH_3$	**1h**	6	94	3.5	95
9	–Ph(4-OH)	$-(CH_2)_7CH_3$	**1i**	3	97	2	98
10	–Ph(4-OH)	–cyclohexyl	**1j**	3	98	2	98
11	–Ph	$-CH_2$–NH–Ph(4-F)	**1k**	6	96	3.5	97
12	–naphth-2-yl	–cyclohexyl	**1l**	8	80	5	83
13	–Ph(4-OPh)	–Ph	**1m**	8	80	5.5	85
14	–Ph(4-OMe)	–cyclohexyl	**1n**	6	94	5	96
15	–indol-5-yl	–cyclohexyl	**1o**	8	85	6	90

[a] **2** (1 mmol), **3** (2 mmol), **5** (1.1 mmol) and clay–Cu(II) catalyst (10 mol %) or $CuSO_4$ (10 mol %) in water: ACN (1:1) at room temperature.
[b] The one-pot CuAAC protocol using both catalytic systems also worked in water as reaction medium.
[c] Isolated yields after silica gel column chromatography.

boronic acids gave respective triazoles faster (reaction time, 3–4 h) irrespective of type of alkyne used (entries 1, 9, 10). However, reaction of phenyl boronic acid (non-substituted) required 6 h for completion of the reaction (entries 2 and 11). Reaction of 2-methoxy substituted pyridine-3-yl boronic acid proceeded smoothly and was completed in 4 h (entry 5). Formyl substituted phenyl boronic acid underwent slow reaction and complete conversion was observed in 8 h with 85% isolated yield of desired triazole (entry 3). 4-Methoxyphenyl as well as 4-phenoxyphenyl boronic acids produced corresponding triazoles in 6–8 h (entries 4, 7, 8, 13 and 14). Indol-5-yl boronic acid also participated well in this reaction producing corresponding triazole **1o** in 85% yield (entry 15).

In order to prove the role of sodium azide as reducing agent in CuAAC reaction, a reaction between 4-hydroxy phenyl azide **4a** and phenyl acetylene **5a** was performed using clay–Cu(II) catalyst in the absence of sodium azide. Corresponding triazole was not formed, suggesting that sodium azide plays a crucial role in this CuAAC protocol. Further to generalize our Cu(II)/NaN_3 catalyzed CuAAC protocol, another Cu(II) source viz. $CuSO_4$ was explored. Like, clay–Cu(II) catalyst, $CuSO_4$ also produced excellent yields of triazoles as depicted in Table 3. All synthesized compounds were stable and were fully characterized by NMR, IR, MS and melting point analysis.

The prepared catalyst was characterized for its physical nature. It was found that the prepared clay–Cu(II) catalyst exists in

the form of highly dispersed CuO nanoparticles supported on Montmorillonite KSF (MKSF), as indicated by temperature programmed reduction, X-ray diffraction and scanning electron microscopy (SEM) experiments. The H_2 TPR curve of catalyst showed three reduction peaks, a major peak at 225 °C, small shoulder at 370 °C and a small broad peak at 540 °C. The peak at 225 °C belongs to the reduction of highly dispersed fine CuO particles indicating that these particles are responsible for catalytic activity in CuAAC reaction.[33,34] XRD results were also in agreement with TPR results, suggesting CuO supported on MKSF in the form highly dispersed nanoparticles.[35,36] Further, results of SEM (EDAX) elemental analysis indicated 8.83% Cu content in the prepared catalyst. XRD studies of the used catalyst indicated intercalation of organic species into the clay during organic transformation.[37] Total specific area of Montmorillonite-KSF clay and clay-supported CuO was found to be 37.3514 and 96.4551 m^2/g, respectively.

Fig. 2 shows the high resolution narrow X-ray photoelectron spectra (XPS) for fresh clay supported Cu(II) catalyst, clay–Cu(II) catalyst treated with sodium azide; and $CuSO_4$ treated with NaN_3, recorded to know the oxidation state of Cu after treating with sodium azide. As observed in Fig. 2a, binding energy peaks at 935.6 eV and 955.3 eV can be attributed to 2p3/2 and 2p1/2 spin-orbit split—doublets, respectively, which are characteristic of Cu in+2 oxidation state. On the other hand, when clay–Cu(II) was treated with sodium azide (Fig. 2b) and $CuSO_4$ treated with NaN_3 (Fig. 2c), in addition to the binding energy peaks (935.9 eV, and 955.5 eV in Fig. 2b, and 935.5 eV, and 955.7 eV in Fig. 2c), two additional sets of binding energy peaks at 933.0 eV, and 952.7 eV (Fig. 2b), and 933.1 eV, and 942.2 eV (Fig. 2c) are also observed, which clearly indicates that Cu is present in both +1 and +2 oxidation states.[38,39] These results concluded that Cu(II) gets partially reduced to Cu(I) state after treatment with NaN_3, and thus is present as Cu(II)/Cu(I) mixed valency dinuclear species.

As proved by experimental variation in the CuAAC protocol (CuAAC in presence and in absence of NaN_3) and by XPS analysis, it is evident that sodium azide reduces Cu 2+ to Cu 1+ oxidation state. Thus, the plausible mechanism[40] for one-pot clay–Cu(II)/NaN_3 catalyzed CuAAC reaction is depicted in the Fig. 3.

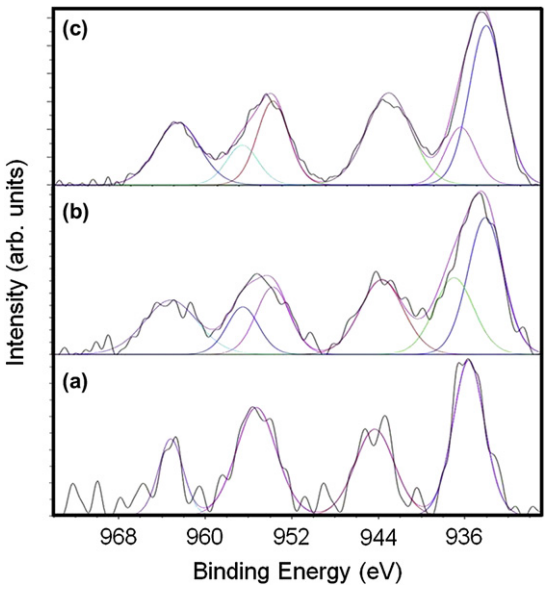


Fig. 2. High resolution narrow X-ray photoelectron spectra (XPS) for (a) fresh clay supported Cu(II) catalyst; (b) clay–Cu(II) catalyst treated with sodium azide; (c) $CuSO_4$ treated with NaN_3.

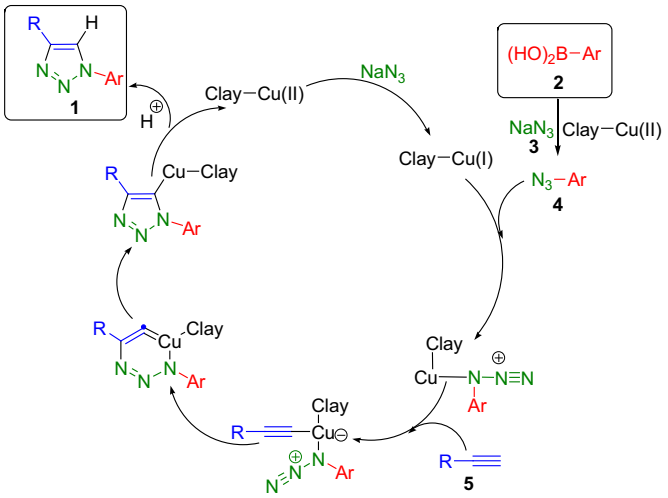


Fig. 3. Plausible mechanism of one-pot CuAAC protocol using clay–Cu(II)/NaN_3 catalyst.

3. Conclusion

In summary, the developed one-pot protocol for synthesis of 1,4-disubstituted 1,2,3-triazoles is highly efficient, economical and safe. The clay–Cu(II) is ligand-free, leaching-free, easy to prepare, easy to handle, environmentally friendly and can be recycled several times without significant loss of catalytic activity; thus it will be highly useful for economical synthesis of 1,4-disubstituted 1,2,3-triazoles. Most importantly the protocol does not require additional reducing agent when NaN_3 is already present in the reaction medium. The use of Cu(II)/NaN_3 catalytic system in CuAAC reaction has been reported for the first time.

4. Experimental section

4.1. General

All chemicals were obtained from Sigma–Aldrich Company and used as received. NMR spectra were recorded on Brucker-Avance DPX FT-NMR 400 MHz instrument. ESI-MS and HRMS spectra were recorded on Agilent 1100 LC and HRMS-6540-UHD machines. Melting points were recorded on digital melting point apparatus. IR spectra were recorded on Perkin–Elmer IR spectrophotometer. Reducible character of the catalyst was determined by Chembet-3000 TPR/TPD/TPO instrument. XRD spectra and Scanning electron micrograph were obtained on XRD Mini-Flex Rigaku Model and Jeol.JEM100C-XII electron microscope, respectively. XPS analysis was performed on a KRATOS-AXIS 165 instrument.

4.2. Preparation and characterization of clay–Cu(II) catalyst

Clay–Cu(II) catalyst was prepared by introducing of calculated amount of aqueous copper oligomer to form a 10% copper deposition on to Montmorillonite KSF and the system was stirred for 15 h followed by filtration and then washed with distilled water several times to remove chlorides. The cake so formed was dried at room temperature, kept overnight in air oven at 110 °C and then powdered and calcined at 425 °C for 3 h. The calcined product is referred to as clay–Cu(II) catalyst and the catalyst so formed was used in the experiments without further activation. Other catalysts with 20 and 5% loading of Cu were also prepared in the same way. Catalyst was characterized using temperature programmed reduction, XRD, and SEM analysis. The reducible character of catalyst

acidity and specific surface area was determined by Chemisorption analyzer, containing a quartz reactor (i.d.=4 mm) and a T.C.D. detector. Prior to TPD studies, samples were pretreated at 250 °C for 2 h in flow of pure nitrogen (99.9%) then cooled to room temperature. After the pre-treatment, samples were saturated with 10% anhydrous ammonia gas until saturated adsorption. The temperature was increased to 80 °C and kept there for 2 h to remove the physisorbed ammonia. Finally the system was heated from 80 to 1200 °C at the rate of 10 °C/min and the desorbed gas was monitored with a T.C.D. detector. All the flow rates were maintained at normal temperature and pressure (NTP). Nitrogen adsorption and desorption was determined at −196 °C by means of an automated adsorption apparatus. X-ray diffractograms were obtained with Cu K-α radiation (1.5418 Å) with scanning rate of 2° per min from 5° to 80°. The X-ray diffraction spectrum (XRD) of the prepared catalyst is shown in Figure S2. To study the morphology, SEM of the sample was carried out using electron microscope with ASID accelerating voltage 15.0 kV. The SEM image of the clay–Cu(II) catalyst is shown in Figure S3.

XPS measurements were obtained on a KRATOS-AXIS 165 instrument equipped with dual aluminum–magnesium anodes using Mg K radiation ($h\nu$=253.6 eV) operated at 5 kV and 15 mA with pass energy 80 eV and an increment of 0.1 eV. Samples were degassed out for several hours in XPS chamber to minimize air contamination to sample surface. To overcome the charging problem, a charge neutralizer of 2 eV was applied and the binding energy of C 1s core level (BE±284.6 eV) of adventitious hydrocarbon was used as a standard. The XPS spectra were fitted using a non-linear square method with the convolution of Lorentzian and Gaussian functions after a polynomial background was subtracted from the raw spectra.

4.3. General procedure for aromatic azidonation

Aryl boronic acids (**2**, 1 mmol) and sodium azide (**3**, 2 mmol) were placed in round bottom flask and subsequently water or water: ACN (1:1) added and stir for 10 min. Then clay–Cu(II) (10 mol %) was added and reaction mixture was stirred vigorously at room temperature for 3–14 h. The completion of reaction was monitored by TLC analysis. After completion of reaction, reaction mixture was extracted with EtOAc (50 mL×3) and dried over anhydrous sodium sulfate. Combined organic layer was concentrated in vacuo and crude reaction mixture was purified by silica gel (#100–200) column chromatography using EtOAc: hexane as eluting solvent to get corresponding aryl azides **4a**–**f** in 80–98% yield. All isolated azides were characterized by comparison of their NMR and MS data with literature values.[13,41–45]

4.4. General procedure for azide–alkyne cycloaddition

Clay supported CuO catalyst (10 mol %) and sodium azide (**3**, 0.6 mmol) were mixed in water or water: ACN (1:1) in round bottom flask and stirred for half an hour. Then organic azides (**4**, 1 mmol) and corresponding alkynes (**5**, 1.1 mmol) were added and reaction mixture was stirred vigorously for specified period of time (10–30 min). Completion of reaction was monitored by TLC. After completion of reaction, reaction mixture was filtered through Whatman® filter paper, residue was washed with EtOAc (50 mL×three times). Organic layer was separated from filtrate and was dried over anhydrous sodium sulfate. Combined organic layer was concentrated in vacuo and crude reaction mixture was purified by silica gel (#100–200) column chromatography using EtOAc: hexane as eluting solvent to get corresponding 1-aryl-1,2,3-triazoles **1a**–**1f** in quantitative yield.

4.5. General procedure for one-pot synthesis of 1,2,3-triazoles (1)

Aryl boronic acid (**2**, 1 mmol) and sodium azide (**3**, 2 mmol) were stirred in water or water: ACN (1:1) for 10 min. Clay supported Cu catalyst (10 mol %) was then added and reaction mixture was stirred for another 30 min. The in situ formation of aryl azide was monitored by TLC. The alkyne (**5**, 1.1 mmol) was added and reaction mixture was stirred at room temperature for specified time duration. The completion of reaction was monitored by TLC. The reaction mixture was filtered through Whatman® filter paper and residue was washed with ethyl acetate. Remaining solid (recovered catalyst) was washed with water, dried (at 100 °C for 3 h) and reused (in case of recyclability experiment). Filtrate was extracted with EtOAc (3×50 mL) and dried over anhydrous sodium sulfate. Combined organic layer was concentrated in vacuo and crude reaction mixture was purified by silica gel (#100–200) column chromatography using EtOAc: hexane as eluting solvent to get corresponding 1-aryl-1,2,3-triazoles **1a**–**1o** in 80–98% yield.

*4.5.1. 1-(4-Hydroxyphenyl)-4-phenyl-1H-1,2,3-triazole (**1a**).* Yield: 98%; white solid; mp 206–208 °C; R_f (40% EtOAc: *n*-hexane) 0.40; ^{1}H NMR (CD_3OD, 400 MHz): δ 8.75 (s, 1H), 7.91 (d, *J*=7.2 Hz, 2H), 7.68 (d, *J*=6.4 Hz, 2H), 7.46 (t, *J*=7.6 Hz, 2H), 7.37 (t, *J*=6.0 Hz, 1H), 6.96 (d, *J*=9.2 Hz, 2H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 157.8, 146.9, 130.4, 128.9, 128.8, 128.1, 125.3, 121.9, 119.5, 116.0; IR (neat): ν_{max} 3139, 1600, 1521, 1231, 1057 cm^{-1}; ESI-MS: *m*/*z* 238 $[M+1]^+$, 260 $[M+Na]^+$; HRMS (ESI+): *m*/*z* 238.0800 calcd for $C_{14}H_{11}N_3O+H^+$ (238.0794).

*4.5.2. 1,4-Diphenyl-1H-1,2,3-triazole (**1b**).*[13] Yield: 96%; white solid; mp 175–177 °C; R_f (30% EtOAc: *n*-hexane) 0.64; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.20 (s, 1H), 7.93 (d, *J*=7.6 Hz, 2H), 7.81 (d, *J*=8.0 Hz, 2H), 7.56 (t, *J*=8.0 Hz, 2H), 7.47 (t, *J*=7.6 Hz, 2H), 7.38 (t, *J*=7.6 Hz, 1H), 7.26 (d, *J*=1.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.5, 137.1, 130.3, 129.8, 128.9, 128.8, 128.4, 125.9, 120.6, 117.6; IR (neat):ν_{max} 3122, 2923, 2360, 1731, 1465, 1239, 1074 cm^{-1}; ESI-MS: *m*/*z* 222 $[M+1]^+$, 244 $[M+Na]^+$.

*4.5.3. 1-(3-Formylphenyl)-4-phenyl-1H-1,2,3-triazole (**1c**).* Yield: 85%; white solid; mp 162–165 °C; R_f (30% EtOAc: *n*-hexane) 0.40; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.13 (s, 1H), 8.30 (d, *J*=7.61 Hz, 2H), 8.19 (d, *J*=7.2 Hz, 1H), 7.99 (d, *J*=7.6 Hz, 1H), 7.94 (d, *J*=7.2 Hz, 2H), 7.77 (t, *J*=8.0 Hz, 1H), 7.50 (t, *J*=5.6 Hz, 2H), 7.41 (t, *J*=4.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 190.8, 148.9, 137.8, 137.7, 130.8, 130.6, 129.9, 129.0, 128.7, 125.9, 125.9, 120.1, 117.4; IR (neat):ν_{max} 3140, 2819, 1700, 1593, 1236, 1015 cm^{-1}; ESI-MS: *m*/*z* 250 $[M+1]^+$, 272 $[M+Na]^+$; HRMS (ESI+): *m*/*z* 250.0986 calcd for $C_{15}H_{11}N_3O+H^+$ (250.0975).

*4.5.4. 1-(4-Methoxyphenyl)-4-phenyl-1H-1,2,3-triazole (**1d**).*[13] Yield: 97%; white solid; mp 155–159 °C; R_f (30% EtOAc: *n*-hexane) 0.53; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.11 9s, 1H), 7.92 (d, *J*=7.2 2H), 7.71 (d, *J*=7.4 Hz, 2H), 7.46 (t, *J*=7.4 Hz, 2H), 7.35 (t, *J*=7.2 Hz, 1H), 7.06 (d, *J*=7.2 Hz, 2H), 3.88 (s, 3H) Hz, 2H, 7.68 (d, *J*=7.6 Hz, 2H), 7.46 (t, *J*=7.4 Hz, 2H), 7.37 (t, *J*=7.2 Hz, 1H), 7.04 (d, *J*=7.2 Hz, 2H), 3.89, (s, 3H); IR (neat):ν_{max} 3130, 2958, 2360, 1726, 1520, 1232, 1044 cm^{-1}; ESI-MS: *m*/*z* 252 $[M+1]^+$.

*4.5.5. 1-(2-Methoxy-pyridin-5-yl)-4-phenyl-1H-1,2,3-triazole (**1e**).* Yield: 96%; light yellow solid; mp 142–144 °C; R_f (40% EtOAc: *n*-hexane) 0.65; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.56 (s, 1H), 8.12 (s, 1H), 8.02 (d, *J*=7.2 Hz, 1H), 7.92 (d, *J*=7.2 Hz, 2H), 7.49 (m, 2H), 7.40 (m, 1H), 6.94 (d, *J*=8.8 Hz, 1H), 4.02 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.1, 148.6, 139.1, 132.0, 130.1, 129.2, 128.5, 128.4, 125.9, 117.9, 111.8, 54.1; IR (neat):ν_{max} 3138, 3045, 1607, 1578, 1229, 1032 cm^{-1}; ESI-MS: *m*/*z* 253

$[M+1]^+$, 275 $[M+Na]^+$; HRMS (ESI+): *m/z* 275.0908 calcd for $C_{14}H_{12}N_4O+Na^+$ (275.0903).

*4.5.6. 1-Thiophen-3-yl-4-phenyl-1H-1,2,3-triazole (**1f**).* Yield: 95%; white solid; mp 164–166 °C; R_f (20% EtOAc: *n*-hexane) 0.43; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.11 (s, 1H), 7.92 (d, *J*=1.6 Hz, 1H), 7.90 (s, 1H), 7.62–7.61 (q, *J*=1.2, 3.2 Hz, 1H), 7.53–7.52 (m, 1H), 7.50–7.48 (m, 1H), 7.68 (m, 1H), 7.44 (m, 1H), 7.38–7.32 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.0, 135.9, 130.2, 128.9, 128.5, 127.3, 125.9, 120.9, 118.0, 114.1; IR (neat):ν_{max} 3103, 1558, 1447, 1231, 1074 cm^{-1}; ESI-MS: *m/z* 228 $[M+1]^+$, 250 $[M+Na]^+$; HRMS (ESI+): *m/z* 250.0415 calcd for $C_{12}H_9N_3S+Na^+$ (250.0409).

*4.5.7. 1-(4-Methoxyphenyl)-4-hexyl-1H-1,2,3-triazole (**1g**).* Yield: 92%; light yellow solid; mp 90–93 °C; R_f (30% EtOAc: *n*-hexane) 0.35; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61 (d, *J*=5.6 Hz, 2H), 7.60 (s, 1H), 6.99 (d, *J*=6.8 Hz, 2H), 3.89 (s, 3H), 2.78 (t, *J*=7.6 Hz, 2H), 1.73 (m, 2H), 1.43–1.30 (m, 6H), 0.91 (t, *J*=6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.6, 149.0, 130.8, 122.1, 119.0, 114.7, 55.6, 31.6, 29.4, 29.0, 25.7, 22.6, 14.1; IR (neat):ν_{max} 3130, 3080, 2926, 2359, 1520, 1254, 1038 cm^{-1}; ESI-MS: *m/z* 260 $[M+1]^+$, 280 $[M+Na]^+$; HRMS (ESI+): *m/z* 260.1738 calcd for $C_{15}H_{21}N_3O+H^+$ (260.1757).

*4.5.8. 1-(4-Methoxyphenyl)-4-octyl-1H-1,2,3-triazole (**1h**).* Yield: 94%; light yellow solid; mp 53–55 °C; R_f (20% EtOAc: *n*-hexane) 0.36; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71–7.61 (m, 3H), 7.03 (d, *J*=6.8 Hz, 2H), 3.89 (s, 3H), 2.82 (t, *J*=7.6 Hz, 2H), 1.72 (m, 2H), 1.43–1.27 (m, 10H), 0.94 (t, *J*=6.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159, 149.0, 132.5, 122.4, 119.0, 114.7, 55.6, 31.9, 30.4, 29.7, 29.5, 29.4, 25.7, 22.7, 14.1; IR (neat):ν_{max} 3125, 2921, 2359, 1727, 1520, 1254, 1046 cm^{-1}; ESI-MS: *m/z* 288 $[M+1]^+$, 310 $[M+Na]^+$; HRMS (ESI+): *m/z* 288.2079 calcd for $C_{17}H_{25}N_3O+H^+$(288.2070).

*4.5.9. 1-(4-Hydroxyphenyl)-4-octyl-1H-1,2,3-triazole (**1i**).* Yield: 97%; light pink solid; mp 98–100 °C; R_f (30% EtOAc: *n*-hexane) 0.29; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64 (s, 1H), 7.58 (d, *J*=6.8 Hz, 2H), 7.06 (d, *J*=7.2 Hz, 2H), 2.79 (t, *J*=7.6 Hz, 2H), 1.76–1.72 (m, 2H), 1.39–1.26 (m, 10H), 0.88 (t, *J*=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.8, 148.8, 129.9, 122.3, 119.5, 116.7, 31.9, 29.4, 29.3, 29.2, 29.2, 25.5, 22.7, 14.1; IR (neat):ν_{max} 3119, 2919, 1599, 1237, 1059 cm^{-1}; ESI-MS: *m/z* 274 $[M+1]^+$, 296 $[M+Na]^+$; HRMS (ESI+): *m/z* 296.1739 calcd for $C_{16}H_{23}N_3O+Na^+$ (296.1733).

*4.5.10. 1-(4-Hydroxyphenyl)-4-cyclohexyl-1H-1,2,3-triazole (**1j**).* Yield: 98%; white solid; mp 167–169 °C; R_f (30% EtOAc: *n*-hexane) 0.31; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60–7.56 (m, 3H), 7.03 (d, *J*=8.8 Hz, 2H), 6.25 (brs, OH), 2.86 (m, 1H), 2.14 (m, 2H), 1.85 (m, 2H), 1.76 (m, 1H), 1.50–1.38 (m, 3H), 1.35–1.23 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.4, 154.0, 130.0, 122.2, 118.1, 116.6, 35.2, 33.0, 26.1, 26.0; IR (neat):ν_{max} 3139, 2926, 2359, 1600, 1519, 1223, 1061 cm^{-1}; ESI-MS: *m/z* 244 $[M+1]^+$, 266 $[M+Na]^+$; HRMS (ESI+): *m/z* 244.1466 calcd for $C_{14}H_{17}N_3O+H^+$ (244.1444).

*4.5.11. 1-Phenyl-4-(4-fluoroanilinomethyl)-1H-1,2,3-triazole (**1k**).* Yield: 96%; white solid; mp 94–96 °C; R_f (60% EtOAc: *n*-hexane) 0.31; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92 (s, 1H), 7.67 (d, *J*=7.2 Hz, 2H), 7.41 (t, *J*=7.6 Hz, 2H), 7.18 (t, *J*=7.6 Hz, 1H), 7.12 (d, *J*=7.6 Hz, 2H), 7.06 (d, *J*=7.6 Hz, 2H), 4.91 (d, *J*=5.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.0, 156.3, 148.3, 132.2, 130.1, 124.2, 122.4, 120.2, 119.8, 119.3, 56.6; IR (neat):ν_{max} 3350, 3120, 2930, 1588, 1513, 1241, 1042 cm^{-1}; ESI-MS: *m/z* 268 $[M]^+$; HRMS (ESI+): *m/z* 268.1175 calcd for $C_{15}H_{13}FN_4+H^+$ (268.1197).

*4.5.12. 1-(Naphth-2-yl)-4-cyclohexyl-1H-1,2,3-triazole (**1l**).* Yield: 80%; white solid; mp 139–141 °C; R_f (20% EtOAc: *n*-hexane) 0.50; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.15 (s, 1H), 8.00 (d, *J*=8.8 Hz, 1H), 7.92–7.87 (m, 3H), 7.81 (s, 1H), 7.58–7.51 (m, 2H), 2.92–2.90 (m, 1H), 2.16 (m, 2H), 1.88 (m, 2H), 1.79 (m, 1H), 1.55–1.39 (m, 4H), 1.36–1.22 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 154.5, 134.8, 133.3, 132.7, 129.9, 128.2, 127.9, 127.3, 126.8, 119.0, 118.1, 117.7, 35.4, 33.0, 29.7, 26.2, 26.1; IR (neat):ν_{max} 3130, 2925, 1569, 1499, 1240, 1040 cm^{-1}; ESI-MS: *m/z* 278 $[M]^+$; HRMS (ESI+): *m/z* 300.1468 calcd for $C_{18}H_{19}N_3+Na^+$ (300.1471).

*4.5.13. 1-(4-Phenoxy-phenyl)-4-phenyl-1H-1,2,3-triazole (**1m**).* Yield: 80%; white solid; mp 171–173 °C; R_f (30% EtOAc: *n*-hexane) 0.73; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.15 (s, 1H), 7.92 (d, *J*=8.3 Hz, 2H), 7.74 (d, *J*=8.9 Hz, 2H), 7.44 (t, *J*=7.7 Hz, 2H), 7.34 (m, 3H), 7.16 (m, 3H), 7.08 (d, *J*=8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.0, 156.4, 148.4, 132.3, 130.0, 128.9, 128.4, 125.9, 124.2, 122.3, 119.5, 119.3, 117.8; IR (neat):ν_{max} 3128, 2921, 2359, 1587, 1514, 1244, 1110 cm^{-1}; ESI-MS: *m/z* 314 $[M+1]^+$; HRMS (ESI+): *m/z* 314.1261 calcd for $C_{20}H_{15}N_3O+H^+$ (314.1288).

*4.5.14. 1-(4-Methoxyphenyl)-4-cyclohexyl-1H-1,2,3-triazole (**1n**).* Yield: 94%; white solid; mp 90–93 °C; R_f (30% EtOAc: *n*-hexane) 0.35; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.62 (m, 3H), 6.98 (d, *J*=6.8 Hz, 2H), 3.82 (s, 3H), 2.82 (m, 1H), 2.18 (m, 2H), 1.90–1.80 (m, 3H), 1.40 (m, 4H), 1.30–1.26 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 159.6, 154.2, 132.5, 121.8, 117.2, 114.7, 50.0, 38.8, 33.1, 29.4, 26.2; IR (neat):ν_{max} 3127, 2926, 2359, 1724, 1518, 1256, 1044 cm^{-1}; ESI-MS: *m/z* 258 $[M+1]^+$; HRMS (ESI+): *m/z* 258.1614 calcd for $C_{15}H_{19}N_3O+H^+$ (258.1601).

*4.5.15. 1-(Indol-5-yl)-4-cyclohexyl-1H-1,2,3-triazole (**1o**).* Yield: 85%; light pink solid; mp 136–139 °C; R_f (30% EtOAc: *n*-hexane) 0.31; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.48 (s, 1H), 7.91 (d, *J*=1.6 Hz, 1H), 7.68 (s, 1H), 7.56–7.47 (m, 2H), 7.33 (t, *J*=2.8 Hz, 1H), 6.63 (t, *J*=2.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 154.0, 135.4, 130.9, 128.0, 126.2, 118.5, 113.2, 111.8, 103.3, 35.4, 33.1, 26.2, 26.1; IR (neat):ν_{max} 3350, 2925, 2359, 1447, 1221, 1044 cm^{-1}; ESI-MS: *m/z* 267 $[M+1]^+$; HRMS (ESI+): *m/z* 267.1632 calcd for $C_{16}H_{18}N_4+H^+$ (267.1604).

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Appendix A. Supplementary data

Spectra of catalyst and all new compounds. Supplementary data associated with this article can be found, in the online version at www.sciencedirect.com. Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/j.tet.2012.07.080.

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29. Mixing together all reactants sodium azide (**3**), organic azide **4a**, alkyne **5a** and clay–Cu(II) catalyst in ACN: H_2O (1:1) at one time and stirring for 1 h led to formation of homo-coupling product of alkyne, however desired triazole **1a** was not formed. The homocoupling product of phenyl acetylene was isolated and characterized using melting point, ^{1}H NMR and MS data. 1,4-diphenylbuta-1,3-diyne: White solid; mp 87–89 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52 (d, J=7. 8 Hz, 4H), 7.40–7.34 (m, 6H); GC–MS: m/z 202 (M^+), 174.2, 150.2, 101.1, 87.9.
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31. Sequence of addition in CuAAC reaction: sodium azide (**3**) and clay–Cu(II) in ACN: water (1:1) were stirred for 30 min. During this period, initial black colored solution turned to grayish yellow. Azide **4a** and alkyne **5a** were then added and reaction mixture was further stirred for another 10–90 min, which led to formation of corresponding triazole product **1a** in excellent yield.
32. Recyclability of the catalyst was checked using model reaction between 4-hydroxy phenyl boronic acid (**2a**), sodium azide (**3**) and phenyl acetylene (**5a**) to prove the heterogeneous nature and its repeated use. The percentage yield of the triazole **1a** was 97, 90, 84, 84 and 86% over five cycles, respectively. The observed decrease in the yield of the reaction could be attributed to the loss of the catalyst during recovery. The % recovery of the catalyst over five cycles was 95, 91, 85, 80 and 78%, respectively. It was noticed that recovery of the catalyst was better when only water was used as reaction medium; however comparatively poor recovery was observed using acetonitrile: water (1:1) as solvent.
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