

Supported NHC-Benzimi@Cu Complex as a Magnetically Separable and Reusable Catalyst for the Multicomponent and Click Synthesis of 1,4-Disubstituted 1,2,3-Triazoles via Huisgen 1,3-Dipolar Cycloaddition

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Abstract

In this paper, we report a novel magnetically separable silica coated copper nano-magnetite NHC-benzimi@Cu complex as heterogeneous catalyst for the multicomponent click reaction via Huisgen 1,3-dipolar cycloaddition reaction of alkyl or aryl halide, sodium azide and terminal alkyne, which affords various1,4-disubstituted 1,2,3-triazoles. The multistep prepared nano catalyst has been characterized by various spectroscopic methods such as FT-IR, TGA, EDX, XRD, TEM and VSM. The heterogeneous nano catalyst structures coated on the copper surface are responsible for the excellent catalyst performances in the reaction. The reusability of the catalyst makes the present protocol more fascinating from an environmental and economic point of view.

Graphic Abstract



Keywords Magnetically retrievable nanocatalyst · Click reaction · Copper iodide · 1,2,3-triazoles · Reusability

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1 Introduction

In recent scenario, the design of a process that minimizes the use, the generation of hazardous substance and reduces environmental impact is a very essential goal in chemistry. The use of benign solvents (e.g. water and ionic liquids) and highly efficient, economic and recoverable catalyst with null toxicity is essential. A significant improvement in catalytic activity can be achieved by synthesizing a nano metal catalyst [1, 2]. In spite of having advantages such as enhanced activity and cost effectiveness, most of the times the separation of nano catalyst becomes valuable due to need of filtration, solvent filtration or centrifugation of the final reaction mixture. In many cases, product and catalyst are insoluble in same solvent, which leads to complexity in work-up. To overcome this problem metal nano particles have been efficiently employed as catalyst in order to recover them by external magnet [3].

Magnetic nano particles usually consist of core shell structure of iron oxide these prevents the aggregation. For this purpose silica is used because of its stability and catalyst functionalized very easily (applied chemistry Nadar ma). From last decade the synthesis of 1,2,3-trizoles has been great interest due to their multifarious applications in pharmaceutical, agrochemicals, corrosion inhibiters etc. [4]. They are found to exhibit wide range of bioactivities such as antiviral [5], anti HIV activity [6], anti-microbial activity [7]. Triazole bridged dendrimers have also been successfully applied as photosensitizer in dye sensitized solar cells (DSSC's) [8] also in various important chemical processes [9]. They have also been evaluated as a novel type of acetyl cholinesterase inhibitors to cure Alzheimer's disease [10], to synthesize potential biological agents [11] as well as to develop anticancer drugs [12].

Herein, we report a simple and efficient synthesis of a nano-ferrite-supported, magnetically recyclable, inexpensive Cu catalyst and its application in Huisgen 1,3-dipolar cycloaddition reaction to synthesize 1,2,3-triazoles via one of the dominant click reaction.

From the last decades, *N*-heterocyclic carbenes (NHCs) have been attracted to researchers as powerful weapon as ligand in organic chemistry and transition metal (TM) catalysis with beyond number of applications in commercially important processes [13–16]. NHCs are easily available, coordinative unsaturation, electron–rich and typical σ –donors, moderate π –acceptors, which sterically requesting structure for complexation with the transition metals. A huge nature of NHC-TM structure is their unremarkable unfaltering quality that is habitually referred to as one of the fundamental advances of these ligands over their phosphine accomplices [17–21]. They are a malleable class of subordinate ligands that have gathered huge consideration for

their capacity to impact different C–C, C–N and C–O bond developments in multicomponent reactions.

In addition they have remarkable properties such as high activity and selectivity with increased stability towards air and moisture, superior catalytic activities, ability to form stable metal complexes, adjustment of electronic and steric parameters, ease of access to their azolium salt precursors and tailor made performance for specific catalytic reactions [22–24]. In spite of these properties NHC-TM complexes have revealed the problem of contamination and recycling of catalyst during organic transformation due to their homogeneous nature [25]. To overcome these problems by replacing homogeneous NHC-complexes with heterogeneous NHCcomplexes with high area support material this gives realm from environmental pollution and economically favorable [26]. Numbers of supporting materials have been reported with NHC-metal complexes for variety of catalytic reaction in the organic synthesis [27-29]. However, despite tremendous advances, there is considerable scope for the further development especially by using magnetic nanoparticles (MNPs) as a support in order to conclude the aim of sustainable and environmentally benign processes.

MNPs have captivated their attention in the field of catalysis due to their technology and chemical application [30, 31]. In recent years, efforts of the scientific community have been directed towards the synthesis of superparamagnetic nanoparticles for the design of magnetically retrievable nanocatalytic systems owing to their exceptional physicochemical properties and rapid response to the applied magnetic field. Amongst, Fe₃O₄ MNPs are robust, inexpensive, easy to prepare, non-toxic, magnetically recoverable and can be reused multiple times for several reaction cycles. Consequently, they have emerged as the viable alternatives to existing solid-supported heterogeneous catalysts [32]. In addition, their high surface region, superparamagnetism, simple surface change by appropriate functionalities and facile retrievability by external magnet has added demanding adaptability for such materials in task explicit catalytic systems [33, 34]. Owing to these properties, they are widely used in synthetic chemistry [35]. Despite remarkable progress, research toward applications of Fe₃O₄ MNPs in the synthesis of magnetically retrievable NHCs is still in its infancy and therefore warrants immediate attention.

Based on aforementioned discussion and in continuation of our studies related to heterogeneous catalysis and multicomponent reaction [36–40], we report herein preparation of magnetic separable nanoparticles decorated N-heterocyclic carbene complex with copper and its application in the synthesis of 1,4-disubstituted 1,2,3-trizoles (Scheme 1).



Scheme 1 Synthesis of 1,4-disubstituted 1,2,3-triazoles by using nano-magnetite NHC-benzimi@Cu (6)

2 Experimental

2.1 General Remarks

All reactions are carried out under air atmosphere in dried glassware conditions. FT-IR data spectra are measured with a Perkin-Elmer one FT-IR spectrophotometer. The samples were examined as KBr discs (~5% w/w). The thermogravimetric analysis (TGA) curves were obtained using instrument SDT Q600 V20.9 Build 20 in the presence of static air at linear heating rate of 10 °C min⁻¹ from 25 to 1000 °C. Elemental analyses were carried out in a Perkin-Elmer 2400, Series II, CHNS/O analyzer and using an energy-dispersive X-ray spectroscopic facility (Hitachi S 4800, Japan). Raman spectroscopy is done by using a Bruker: RFS 27 spectrometer.¹H NMR and ¹³C NMR spectra were recorded with a Bruker Avance (300 MHz for ¹H NMR and 75 MHz for ¹³C NMR) spectrometer using CDCl₃ solvent and tetramethylsilane as an internal standard. The chemical shifts were denoted in parts per million (ppm) and coupling constants are denoted in hertz (Hz). Mass spectra are recorded with a Shimadzu QP2010 gas chromatography-mass spectrometry (GC-MS). X-ray powder diffraction (XRD) was taken by using a Bruker D2 Phaser. Magnetic measurements were performed on Lakeshore magnetometer, USA, Model 7407. The materials are considered by using a PHILIPS CM 200 model with 20-200 kV accelerating voltages. Melting points are determined using MEL-TEMP capillary melting point apparatus and are uncorrected. Fe_3O_4 MNPs (1) [41], silica coated Fe_3O_4 MNPs (2) [42] and all other chemicals were obtained from local suppliers and used without further purification.

2.2 Preparation of 3-Chloropropyl Modified Nano Magnetite (3)

Magneticnano magnetitewere synthesized by co-precipitation method briefly, a mixture of $FeCl_3.6H_2O$ (10 mmol) and $FeCl_2.4H_2O$ (5 mmol) salts were dissolved in 200 mL water An aqueous ammonia solution (28% w/w, 30 mL) was added until the pH = 11. The resulting black dispersion was mixed vigorously for 1 h at room temperature and refluxed for 1 h. The black nano magnetite was separated magnetically from the aqueous solution and were washed with ethanol and dried in an oven at 60 °C. In order to synthesize silica-coated withnano magnetite, nano magnetite (1.0 g) were initially dispersed in 80 mL 4:1 ethanol/water solution and the pH=10 of the solution was adjusted by addition of conc. ammonium hydroxide (12 ml).

Then, 0.5 mL tetraethylorthosilicate (TEOS) was added subsequently. The mixture was stirred vigorously at 40 °C for 12 h. The resultant product was washed three times with ethanol and dried in a vacuum. A mixture of silica coated nano magnetite (**2**) (10 g) and (3-chloropropyl) triethoxysilane (20 mL, 100 mmol) in dry xylene (100 mL) was refluxed in an oil bath. After 24 h, the reaction mixture was cooled, product was isolated by magnetic separation and washed with xylene (4×25 mL), methanol (4×25 mL), deionised water (4×25 mL) and dried under a vacuum at 60 °C and for 12 h to afford 3-chloropropyl modified nano magnetite (3). FTIR (KBr, thin film): v=3408, 2925, 1099, 797, 699, 633, 583 cm⁻¹.

2.3 Preparation of [Nano-Magnetite-Benzimi]Cl (5)

A mixture of **3** (10.0 g) and benzimidazole (**4**) (6 g, 18 mmol) in dimethylformamide (50 mL) was heated at 80 °C in an oil bath. After 72 h, the solid was separated by magnet, washed with MeOH and CH₂Cl₂ and dried under vacuum at 50 °C for 24 h to obtain [Nano magnetite-benzimi]Cl (**5**).IR (KBr, thin film): v = 3428, 2925, 2860, 1654, 1642, 1457, 1387, 1093, 585 cm⁻¹. CHNS elemental analysis observed: %C 13.42, %H 0.36, % N 4.78. Loading of 0.36 mmol functional group per gram of **5** (Scheme 2).

2.4 Preparation of Nano-Magnetite NHC-Benzimi@ Cu (6)

A mixture of **5** (10.0 g), copper iodide (1.9 g, 10 mmol) and NaOtBu (0.096 g, 10 mmol) in THF (50 mL) was heated at 100 °C in an oil bath for 6 h. Afterwards, the mixture was separated by magnet. Washed with the THF and dried under vacuum at 50 °C for 24 h to obtain nano-magnetite NHCbenzimi@Cu (**6**). FT-IR (KBr, thin film): v = 3406, 2893,



Scheme 2 Preparation of nano-magnetite NHC-benzimi@Cu (6)

2828, 1632, 1444, 1320, 1075, 586 cm⁻¹; Elemental analysis observed: %C 13.42, % O 45.51, % Fe 14.30, % Si 19.25, % N 4.78, % Cu 1.41, % I 0.97.

2.5 General Method for Synthesis of 1,4-Disubstituted 1,2,3-Triazoles

In a 50 mL round bottom flask alkyl/aryl halide (1.0 mmol), sodium azide (1.1 mmol), alkyne (1.0 mmol), nano-magnetite NHC-benzimi@Cu (6) (40 mg) was added to above solution and stirred in 5 mL ethanol at 80 °C. The reaction was monitored by thin layer chromatography (TLC) using aluminium backed silica gel 60 (F254) plates. The completion of the reaction, the catalyst was separated magnetically using bar magnet. Finally, the solid obtained was extracted with ethyl acetate and dried over anhydrous Na_2SO_4 the solvent was removed under reduced pressure then the product was purified by silica gel column chromatography.

3 Results and Discussion

The preparation of nano-magnetite complex with copper is outlined in (Scheme 1). Initially, nano magnetite (1) was synthesized by co-precipitations method and coated with silica layer by using TEOS (tetraethyl ortho silicate) afforded silica coated nano magnetite (2) through sol–gel method [41, 42] which on further treatment with (3-chloropropyl)triethoxysilane afforded 3-chloropropyl modified nano magnetite (3). The synthetically fertile chloro group in 3 allowed attachment of ionic liquid like group on the surface of nano magnetite through quaternization with benzimidazole (4) to yield azolium salt precursor acronymed as [nano-magnetitebenzimi] Cl (5). Finally, the complexation of 5 with copper iodide by using NaOtBu as base afforded nano-magnetite NHC-benzimi@Cu (6).

Fourier transform infrared (FT-IR) spectroscopy was employed to monitor reactions involved in the preparation of nano-magnetite NHC-benzimi@Cu (6). The FT-IR spectrum of nano magnetite (1) displayed Fe–O stretching band at 583 cm⁻¹.The formation of silica coated nano magnetite (2) was confirmed by FT-IR peaks at 796, 959 and 1099 cm⁻¹ attributed to Si–O–Si symmetric, Si–O symmetric and Si–O–Si asymmetric stretching modes respectively [43].



Fig. 1 FT-IR spectra of (c) 3-Chloropropyl modified MNPs (3); (d) [Nano-magnetite-benzimi]Cl(5); (e) nano-magnetite NHC-benzimi@Cu(6); (f) Reusednano-magnetite NHC-benzimi@Cu(6)



Fig. 2 TGA curves of bare nano magnetite (1) and nano-magnetite NHC-benzimi@Cu (6)

The FT-IR spectrum of 3-chloropropyl nano magnetite (**3**) displayed characteristic peaks at 3408 cm⁻¹ (O–H stretching), 2925 cm⁻¹ (C–H stretching vibration of propyl group), 1099 cm⁻¹ (Si–O stretching) (Fig. 1c) [44]. The quaternization of **3** with **4** was realized by appearance of three prominent peaks at 1654 cm⁻¹ (C=N stretching vibration), 1642 cm⁻¹(C=C stretching vibration) and 1387 cm⁻¹ (C–N stretching) suggesting the formation of **5** (Fig. 1d) [45].

Finally, the formation of **6** was confirmed by a strong intense band of N–C–N strengthening in the range 1340–1500 cm⁻¹ as a result coordination of NHC carbon ligand with copper metal ion as well as shifting of the characteristic IR absorption peaks to lower frequency values (Fig. 1e) [46, 47].

The thermal stability profiles of bare nano magnetite (1) and nano-magnetite NHC-benzimi@Cu (6) were investigated by TGA analysis over the temperature range of 25-1000 °C at a heating rate of 10 °C min⁻¹. (Fig. 2). In both cases, initial weight loss of 3.68% up to 102 °C and 4.96% up to 111 °C respectively for 1 and 6 is due to evaporation of physically adsorbed water. TGA curve of bare nano magnetite (1) displayed no significant weight loss from 111 to 800 °C which indicates that presence of only iron oxides and no any organic moiety attached on the surface of nano magnetite. In TGA curve of 6, the second weight loss was observed 8.79% in the range of 102–502 °C attributed to loss of surface bound organic scaffolds by thermal decomposition such as (3-chrolopropyl) triethoxy silane and benzimidazole.

The steep weight loss of 15.67% at 700 °C displayed thermal decomposition of copper iodide and major weight loss ascribed to residual silica and metallic oxides which possess high thermal stability.

The presence of copper in its respective energy position suggests the formation of complex **6**. The EDX analysis inform loading of 0.22 mmol of Cu per gram of **6** (Fig. 3). The crystalline material structure and retention of nanomagnetite (**1**) in nano-magnetite NHC-benzimi@Cu (**6**) was investigated by X-ray diffraction (XRD) analysis. The well indexing of all the peaks in a diffractogram to the JCPDS card No. 86–1339 agreed retention of single-phase inverse spinel structure of Fe₃O₄ nano core with high phase purity and crystallinity (Fig. 4).

The characteristic peaks are at 2 θ values of 30.12°, 35.25°, 44.07°, 57.61°, 62.37°, 71.03° and 87.13° are being assigned to the (2 2 0), (3 1 1), (4 0 0), (5 5 1), (4 4 0), (6 2 0) and (6 4 2) crystallographic planes of Fe₃O₄ nano core were observed in the XRD pattern. The most intense peak was observed for (3 1 1) plane are at 2 θ value 35.25°. The broad peaks are at 2 θ from 21° to 32° of the XRD pattern are assigned to the silica phase.

The crystallite size calculated with respect to the most intense peak by using the Scherrer equation was found to







Fig. 4 XRD of nano-magnetite NHC-benzimi@Cu(6) (black); XRD of reused nano-magnetite NHC-benzimi@Cu (6) (blue)

be 51.6 nm. The XRD analysis is revealed preservation of crystallographic structure of nano-magnetite (1) in **6** even after the multi-step functionalization.

The surface morphology of the nano-magnetite NHCbenzimi@Cu (6) was studied by the transmission electron microscopy (TEM). The TEM micrographs show granules with spherical shapes and non-smooth surfaces. Now, TEM images show embedded dark Fe3O4 nano cores surrounded by the grey shell (Fig. 5a, b) [48]. The average nanoparticle size of 6 is found to be 10 nm with a lattice fringe width distance of d(311) = 2.5182 Å, which reveals formation of the perfect crystal structure (Fig. 5c). The selected area of electron diffraction (SAED) patterns are exhibited four strong diffraction rings which were assigned to the (3 1 1), (4 0 0), (3 3 1) and (4 2 2) bright dotted with ring pattern persuade the polycrystalline nature of nano magnetite (1) (Fig. 5d).

The magnetic properties of nano-magnetite (1) and nanomagnetite NHC-benzimi@Cu (6) were evaluated by magnetic hysteresis loops at room temperature using vibrating sample magnetometer (VSM) shown in Fig. 6. The saturation magnetization (Ms) 1 and 6 were found to be 53 emug-1 (Fig. 6a) and 30 emug-1 (Fig. 6b) respectively. The saturation magnetization value of 6 exhibited as comparatively low. This quenching of Ms value is ascribed due to surface functionalization. However, magnetization exhibited by 6 was sufficient to enough for the effective separation by the external magnet.

After this initial success in the synthesis of the designed nano-magnetite NHC-benzimi@Cu (6) catalyst, we focused our attention towards exploring its catalytic activity in the click reaction. Initially a model reaction for Huisgen 1,3-dipolar cycloaddition of benzyl chloride, phenylacetylene and sodium azide. Product was obtained in the extent yield with the 40 mg of catalyst at 80^oC in ethanol (Table 1 entry 7). No significant change in the reaction time and yield of product was observed even though increasing catalytic loading up to 50 mg (in Table 1 entry 6). When catalytic loading was reduced to 20 and 10 mg (Table 2 entry 3–5)



Fig. 5 TEM images of a, b nano-magnetite NHC-benzimi@Cu (6); c nanoparticle shows lattice fringe width; d, e reused nano-magnetite NHC-benzimi@Cu(6); f SAED pattern of nano-magnetite NHC-benzimi@Cu (6)

increases in the time completion for reaction and decreases in the product was observed.

While screening of the catalyst, we investigated the solvent effect according to the green chemistry principle. In water, very poor yield of product was observed and progress of the reaction was observed by (TLC) which did not indicate any appreciable progress in the reaction. After we carried the reaction in the interval of 10 °C temperatures but still there is no progress in the reaction and we got less amount of product. Hence we carried the reaction by changing solvent and temperature. However, the reaction was carried out under reflux condition at 80 °C by using ethanol as a solvent it is noticed that 94% yield of 1,2,3-trizoles was obtained.

Further the screening of solvent was carried out to gives standard reaction condition. It was observed that the very excellent yield of 1,2,3-trizoles was obtained in ethanol up to 94% (Table 2 entry 5) of the yield within a very short time duration.

With the optimuml reaction conditions in hands, the scope and generality of the methodology was evaluated by the reaction using with terminal alkynes and NaN_3 under optimized reaction conditions and observed that all reactions proceeds smoothly furnishing desired product in good yields (Table 3, entries a–j). The results are summarized in Table 3. In all the cases, reactions proceeded smoothly affording to the desired 1, 2, 3-trizoles sin a good to excellent yields.



Fig. 6 a Magnetic curve (VSM) of bare nano-magnetite (1). b Magnetic curve (VSM) of nano-magnetite NHC-benzimi@Cu (6)

(Table 3, entry a, b, c, f) and reactions were clean high yielding without generation of any side product.

The plausible mechanism of the click reaction has been represented in Scheme 3. Initially, the Cu (I) in the catalyst is treated with NaN₃. Nucleophilic attack of benzyl chloride and then the attack of phenyl acetylene provides six membered ring which becomes five membered after the removal of Cu (I). This results in formation of desired product.

To ascertain whether the reactions are truly heterogeneous, leaching studies were performed by analyzing the reaction filtrate after the recovery of nano-magnetite NHCbenzimi@Cu (6) by using the atomic absorption spectroscopy (AAS). Further, the hot filtration test was carried out to confirm the heterogeneous nature of nano-magnetite NHCbenzimi@Cu (6) by using the model reaction. In this test, a mixture of 6 (40 mg), benzyl Chloride (7a; 1.0 mmol), sodium azide (8; 1.1 mmol) phenylacetylene (9a; 1.0 mmol), sodium ascrobate in ethanol (5 mL) was refluxed at 80 °C. The 6 was separated from the hot reaction mixture when 50% conversion was accomplished (GC). The reaction was continued with the filtrate for further 6 h. There was no increase in the yield of the product beyond 50%. In addition, inductively coupled plasma atomic emission spectroscopic (ICP-AES) analysis of filtrate shows absence of copper confirming the heterogeneous nature of 6.

From the green chemistry point of view, recovery and recyclability of the supported catalyst is an unavoidable parameter for industrial and commercial scale that must be tackled for any catalytic process. Thus, the recovery and reusability of nano-magnetite NHC-benzimi@Cu (6) investigated by employing model reaction (Fig. 7).

In brief, after reaction was completed, the 6 was isolated from the reaction mixture by the magnet. The complex 6was washed with a copious amount ethanol to remove the
 Table 1
 Optimization of catalyst loading in synthesis of 1,4-disubstituted 1,2,3-trizoles



Entry	Catalyst	Amount of catalyst (mg)	Time (min)	Yield ^a (%)	TON	$TOF(h^{-1})$
A	Nano-magnetite (1)	200	2880	_	_	_
В	[Nano-magnetite-benzimi]Cl (5)	200	2880	_	-	-
С	Nano-magnetite NHC-benzimi@Cu (6)	10	110	48	21,818	11,990
D	(6)	15	80	50	16,380	11,050
Е	(6)	20	50	60	16,450	10,130
F	(6)	30	30	75	10,330	9570
G	(6)	40 (10 mol%)	20	94	8540	10,200
Н	(6)	50	19	94	4270	5655
Ι	(6)	100	18	95	3450	5560
J	(6)	200	17	95	3430	4590

Present works are highlited in bold

Reaction condition: reaction between benzyl chloride (1 mmol), sodium azide (1.1 mmol), phenyl acetylene (1 mmol) solvent: ethanol, catalyst ^aIsolated yields after column chromatography

 Table 2
 Optimization of solvent in synthesis of 1,4-disbstitued 1,2,3-trizoles



Entry	Solvent	Time (min)	Yield ^a (%)	TON	$TOF(h^{-1})$
1	Dichloromethane	30	35	3181	66
2	DMF	36	80	6454	1490
3	THF	30	60	8545	10,295
4	Water	30	35	3636	993
5	Ethanol	20	94	5000	1250
6	Methanol	30	60	5454	1394
7	Toluene	30	45	4090	846
8	1,4-Dioxane	30	40	3636	389

Present works are highlited in bold

Reaction condition: reaction between benzyl chloride (1 mmol), sodium azide (1.1 mmol), phenyl acetylene (1 mmol) solvent: ethanol, Catalyst, Temp: 80 $^{\circ}$ C

^aIsolated yields after column chromatography

 Table 3
 Nano-magnetite NHC-benzimi@Cu (6) catalyzed synthesis of 1,4-disbstitued 1,2,3-trizoles





Table 3 (continued)



Reaction condition: reaction between benzyl chloride (1 mmol), sodium azide (1.1 mmol), phenyl acetylene (1 mmol) solvent: ethanol, catalyst ^aIsolated yields after column chromatography

organics wedded in the catalyst sites and dried under a vacuum at room temperature. The amounts of necessary reactants were recalculated on the basis of recovered catalyst and recovered catalyst could be reused for 12 times without significant decrease in the yield of the products. Further, the stability of the recycled catalyst was studied by FT-IR spectroscopy, EDX, XRD and TEM analysis of **6**. It is noteworthy to mention that, the FT-IR (Fig. 1f) spectrum of reused **6** still retain the prominent peak patterns of the **6**. The EDX mapping of the **6** after twelve catalytic cycles confirms the integrity of the recycled catalyst. Moreover

TEM analysis of fresh (Fig. 5 a–c) and reused 6 (Fig. 5 d, e) designates that the morphology is preserved even after 12 successive runs.

To demonstrate the importance of nano-magnetite NHCbenzimi@Cu ($\mathbf{6}$) in comparison with other reported methods, we have summarized previous report for synthesis of 1,2,3-trizoles in Table 4. The comparison of the results clearly persuades that the $\mathbf{6}$ is a superior catalyst in terms of the catalyst loading and the reaction time as compared to the reported catalyst. Apart from the listed catalyst in Table no. 4, we found that silica, carbon and magnetic



Scheme 3 Plausible mechanism for the nano-magnetite NHC-benzimi@Cu (6) catalyzed synthesis of 1,4-disubstituted 1,2,3-trizoles



Fig. 7 Reusability of nano-magnetite NHC-benzimi@Cu (6) in the synthesis of 1,4 disubstituted 1,2,3 -triazoles

materials-supported copper species as efficient heterogeneous nanocatalysts in "click" reactions have been also reported with yield 60–98%. However, our catalyst nanomagnetite NHC-benzimi@Cu (6) demonstrate good efficiency compared with other literature survey [49–62].

4 Conclusion

We have refined a highly selective, economical, efficient and ecologically clean procedure for one pot multicomponent synthesis of 1,4-disubstituted 1,2,3-triazoles by click reaction. The reactions were achieved under relatively mild experimental conditions with high yield and easy recovery of catalyst. The reusability without any appreciable loss of activity, ease of work-up short reaction time, magnetically separable and efficient recyclability of the catalyst make it a favorable protocol for the reaction.

Sr. No.	Catalyst	Quantity	Temp (°C)	Solvent	Time (min)	Yield %	Ref.
1	Nano-magnetite NHC-benzimi@Cu	40 mg (10 mol%)	80	Ethanol	20	94	Present work
2	CuNPs/activated carbon	10 mg	70	Water	180	93	49
3	CuFe ₂ O ₄ NPs	10 mol %	RT	Water	60	95	50
4	CuBr on grapheme Oxide/Fe ₃ O ₄ benzyle chloride	5 mol %	80	Water	480	98	51
5	CuFe ₂ O ₄	12 mg	70	Water	240	84	52
6	Fe ₃ O ₄ @ SiO ₂ -caffeine–CuI	25 mg	70	Water	20	94	53
7	Cu	0.5 mol %	80	Water	6 h	96	54
8	[Cu(NHC)]	0.5 mol %	RT	Water	2 h	90	55
9	Cu-ACP-Am-Fe ₃ O ₄ @SiO ₂	40 mg	80	Ethanol	20 min	96	3
10	Cu NPs	40 mg	RT	Methanol	480	75	56
11	GO/Fe ₃ O ₄ -CuBr	5 mol%	80	Water	480	90	57
12	GO/Fe ₃ O ₄ -CuO	10 mg	45	Water	80	97	58
13	SBA-15/Thioamide-Cu(I)	1 mol%	RT	Water	90	95	59
14	Fe3O4@LDH@cysteine-Cu(I)	20 mg	75	Choline azide	25	90	60
15	Cu(II)@Silica	1 mol%	25	water	60	98	61

Table 4 Comparison of different catalyst for synthesis of 10

Present works are highlited in bold

Reaction condition: reaction between benzyl chloride (1 mmol), sodium azide (1.1 mmol), phenyl acetylene (1 mmol) solvent: ethanol, catalyst, temp: 80 °C

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Declarations

Conflict of interest The authors declare no conflict of interest.

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