

FULL PAPER

A sustainable approach for efficient one-pot synthesis of 1-aryl 1,2,3-triazoles using copper iodide supported on 3-thionicotinyl-urea-modified magnetic nanoparticles in DES

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Funding information Tarbiat Modares University An efficient and retrievable copper(I) catalyst was synthesized by immobilizing of copper iodide on 3-thionicotinyl-urea-modified magnetic nanoparticles and characterized using a variety of analysis techniques. The catalytic activity of these nanoparticles was investigated in the one-pot three-component reaction of aryl halides, sodium azide, and terminal alkynes using choline chloride/ PEG deep eutectic mixture as a green and recoverable solvent. The PEGylated deep eutectic solvent (DES), due to its favorable polarity and solubility, can make an effective association of polar and non-polar reactants during the reaction, thereby accelerating the catalysis process. An array of 1-aryl 1,2,3-triazoles were obtained in good to excellent yields. The catalyst system can be readily recovered and reused at least five times with no appreciable loss of its activity.

K E Y W O R D S

1-aryl 1,2,3-triazoles, 3-thionicotinyl-urea-modified magnetic nanoparticles, copper(I) catalyst, deep eutectic solvent

1 | INTRODUCTION

1,2,3-Triazoles, as a significant class of nitrogen heterocyclic compounds, have found widespread applications in chemical, medicinal, pharmaceutical, biological and material sciences.^[1] They exhibit activities such as anticancer,^[2] anti-allergic,^[3] anti-HIV,^[4] anti-bacterial,^[5] and anti-fungal.^[6] Furthermore, they are present in agrochemicals and have also used in the synthesis of dyes, corrosion inhibitors, and photo stabilizers.^[7] The high stability and tolerance of these nitrogen heterocyclic compounds to different conditions and functional groups deserve them to be utilized as ligand for transition metals.^[8] Due to these versatile applications, the

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synthesis of 1,2,3-triazoles has gained prominent attention.^[9] 1,3-Dipolar cycloaddition reaction of azides with alkynes is one of the most approved protocols for the synthesis of triazoles, which was initially put forward by Huisgen et al. They performed this reaction without using any metal catalyst; however, this procedure was associated with high temperature, long reaction times, low product yields, and lack of selectivity.^[10] In later years, Sharpless and Meldal groups independently discovered the improved procedure involving Cu(I)catalyzed azide-alkyne 1,3-dipolar cycloaddition (CuAAC), popularly known as the click reaction, for regioselective synthesis the of 1,4-disubstituted 1,2,3-triazoles.^[11] Since then, the CuAAC reaction has been generally considered as the most attractive protocol for the synthesis of 1,2,3-triazole framework.^[12] A



variety of catalytic systems including Cu(I) salt, Cu(II) salt/reducing agent (sodium ascorbate), and copper(II)/copper(0) comproportionation have been used for click chemistry,^[13] although most of the previous studies on CuAAC reactions are homogeneous and/or involve 1,3-dipolar cycloaddition of pre-isolated organic azides with alkynes, thus subjecting to major limitations such as problematic separation of the catalyst from the reaction medium and/or handling of toxic and potentially explosive organic azides.^[14] In recent years, to avoid the formation of unstable azides, one-pot multicomponent click reactions using in situ generated organic azides from organic halides and NaN₃ have been developed.^[15] The homogeneous catalytic systems have priority in terms of activity and selectivity over heterogeneous catalysts. However, from the standpoint of sustainable chemistry, the use of heterogeneous catalysts is highly desirable because of their recoverability and reusability.^[16] In this regard, a large number of supported copper catalysts have been reported for the synthesis of 1,4-disubstituted 1,2,3-triazoles. They are typically produced by immobilization of copper species on various solid supports such as alumina,^[15] silica,^[17] zeolite,^[18] graphene,^[19] iron oxide,^[20] and polymers.^[21] Among them, magnetic iron oxide nanoparticles have received a remarkable attention for use in catalytic reactions, because of their high catalytic activity and easy separation.^[22] Recently, various heterogeneous copper catalytic systems for the synthesis of 1.4-disubstituted 1.2.3-triazoles from unstable aryl azides and terminal alkynes have been reported,^[19,23] whereas there have been few reports on one-pot multicomponent synthesis of 1,2,3-triazoles from sodium azide, alkynes, and aryl halides as the azide precursors, which most of them have used homogeneous copper catalysts.^[24] Therefore, it might be desirable to develop new methods for the regioselective synthesis of triazoles using effective and recyclable catalytic systems. With this in mind and following our interest in the use of sustainable solvents and catalyst recycling, we decided to study the application of a copper-incorporated magnetic nanocatalyst for the onepot azidation/click reaction of aryl halides in PEGylated DES as a green and sustainable reaction medium. DESs are mixtures formed from Lewis or Brønsted acids and bases, which are able to self-associate via reciprocal hydrogen-bond interactions. Therefore, eutectic mixtures have a melting point lower than those of the individual components.^[25] In recent years, the application of DESs in the field of metal-catalyzed organic considerable attention.^[26] reactions has attracted Choline chloride is a green, inexpensive, and

biodegradable material, which has been known as a salt component in deep eutectic solvents. In continuation of our research on the development of efficient and environmentally benign approach and in the line of our very recent work,^[27] herein, we report the synthesis of silica coated magnetite nanoparticles modified with 1-propyl-3-thionicotinyl-urea as an effective ligand followed by decoration with copper iodide nanoparticles (MNPs@ThNU-CuI). After the characterization of the prepared nanocatalyst, we applied it to efficiently synthesize 1,4-disubstituted 1,2,3-triazoles through the one-pot three-component reaction of terminal alkynes with in situ generated organic azides from aryl iodides and arvl bromides in choline chloride/PEG 200 (1:4) DES.

2 | EXPERIMENTAL SECTION

2.1 | General remarks

All materials were purchased from Merck and Aldrich companies and used without any further purification. The reaction was precisely monitored by thin-layer chromatography (TLC). Preparative TLC was performed on glass plates coated with silica gel 60 F-254 (0.2 mm). Infrared spectra (IR) were recorded using the KBr pellet method on a NICOLET FT-IR 100 spectrometer. The X-ray diffraction (XRD) patterns were obtained at room temperature using a Philips PW1730 diffractometer with Co K α radiation ($\alpha = 1.54056$ Å), 40 kV voltage, 30 mA current, and scanning rate of 0.05°/s over the range of 10-80° for 20. Scanning electron microscopy (SEM) analysis was utilized to study the morphology and size of the catalyst using a TESCAN MIRA III FE-SEM instrument. Energy-dispersive X-ray spectroscopy (EDX) analysis was performed in conjunction with SEM to study the elemental composition of the catalyst. Transmission electron microscopy (TEM) analysis was carried out at 200 kV (Philips model CM300). Thermal gravimetric analysis (TGA) was recorded using a thermal analyzer (SDT Q600) with a heating rate of 20° C min⁻¹ over a temperature range of 25-800°C under flowing argon. Magnetic saturation of the nanoparticles was obtained using a vibrating magnetometer/alternating gradient force magnetometer (VSM/AGFM, MDK Co., Iran). Inductively coupled plasma (ICP) technique was performed using a Varlan Vista-Pro ICP-OE spectrometer. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance (DRX 300 and 500 MHz) in pure deuterated CDCl₃ solvent with tetramethylsilane (TMS) as an internal standard.

2.2 | Preparation of copper iodide immobilized on 3-thionicotinyl-ureamodified magnetic nanoparticles

2.2.1 | Preparation of silica-coated magnetite nanoparticles

Magnetite nanoparticles were prepared by alkaline hydrolysis of iron(II) chloride and iron(III) chloride (molar ratio of 1:2) in an aqueous medium according to the previously reported procedure.^[22a] In order to synthesize silica-coated magnetite nanoparticles, Fe₃O₄ nanoparticles (1.0 g) were dispersed in 80-ml 4:1 ethanol/ water solution, then 1.5 ml of concentrated aqueous ammonia (28 wt%) was added to the suspension until the pH was raised to 10. Subsequently, tetraethyl orthosilicate (TEOS, 1 ml) was added to the reaction vessel, and the mixture was vigorously stirred at 40°C for 18 h. The silica-coated magnetite nanoparticles were collected magnetically and washed several times with water and ethanol before being oven-dried at 60°C for 8 h.

2.2.2 | Synthesis of 3-thionicotinyl-*N*-3-(triethoxysilyl) propyl-urea (1)

A mixture of triethoxy(3-isocyanatopropyl)silane (TESPIC) (5 mmol) and thionicotinamide (5 mmol) was mixed in 40 ml of dry THF and heated at 60° C for 24 h under argon atmosphere. After this period, the solvent was removed using rotatory evaporation. The obtained yellow solid was washed with dry diethyl ether, followed by drying at 40° C under vacuum for 2 h to provide material B.

2.2.3 | Preparation of 1-propyl3-thionicotinyl-urea immobilized on MNPs (MNPs@ThNU) (2) and MNPs@ThNU-CuI (3)

The functionalized magnetic nanoparticles (MNPs@ThNU) were prepared by treating about 1.0 g of Fe_3O_4 @SiO₂ in dry toluene (50 ml) with 3 mmol of precursor 1. The resulting suspension was then refluxed for 36 h under argon atmosphere. The resulting nanoparticles were separated magnetically and washed several times with toluene, ethanol, and diethyl ether, followed by drying at 60°C under vacuum for 8 h to provide MNPs@ThNU. In order to the preparation of MNPs@ThNU-CuI, the resultant nanoparticles (MNPs@ThNU) (1.0 g) and CuI (0.09 g, 0.5 mmol) were suspended in 25 ml of ethanol and refluxed for 6 h under argon atmosphere. The resulting nanoparticles were then

magnetically separated and washed several times with water and ethanol before being dried under vacuum at 60° C for 8 h.

2.3 | Preparation of DESs

DESs were prepared according to the methods reported previously.^[24b,28] In order to synthesize DES, a certain molar ratio (4: 1 or 2: 1) of HBD (PEG 200 or glycerol) and HBA (choline chloride) was mixed and then heated at 80°C under continuous stirring until a homogeneous and transparent liquid was formed. The obtained DESs were used in reactions without any purification.

2.4 | General procedure for the synthesis of 1-aryl 1,2,3-triazoles

A mixture of aryl halides (1.0 mmol), alkynes (1.0 mmol), sodium azide (1.2 mmol), and catalyst (30 mg) was stirred at 90°C in choline chloride/PEG 200 (2 ml, 1:4) for the appropriate time until the reaction was completed as judged by TLC. After completion of the reaction, the reaction medium was diluted by adding hot water (3 ml). The resulting mixture was magnetically decanted, followed by separation of the catalyst. The aqueous phase was extracted with EtOAc (2×15 ml), and then the combined organic phases were concentrated. Finally, the pure products were obtained using chromatography on silica gel. After the catalyst was separated, it was washed with ethanol (3×10 ml) and dried under vacuum for reuse under the same conditions.

3 | RESULTS AND DISCUSSION

3.1 | Catalyst preparation

The process for the synthesis of the MNPs@ThNU-CuI catalyst is schematically depicted in Scheme 1. Silicacoated magnetite nanoparticles (Fe₃O₄@SiO₂) were prepared according to the reported procedures. At first, Fe₃O₄ nanoparticles were prepared by the conventional co-precipitation method. Then, to improve the chemical stability of Fe₃O₄ nanoparticles, the surface of magnetic Fe₃O₄ was modified with a thin layer of silica. On the other hand, the reaction between triethoxy (3-isocyanatopropyl)silane and thionicotinamide resulted in the formation of the material **1**. The final structure of the catalyst (3) was obtained via the reaction of MNPs with material **1** and subsequent treatment with copper iodide.

3.2 | Catalyst characterization

The catalyst was fully characterized using various microscopic and spectroscopic techniques such as FT-IR, XRD, FE-SEM, EDX, TEM, TGA, VSM, and ICP.

FT-IR spectra of triethoxy(3-isocyanatopropyl)silane, material B, Fe₃O₄, Fe₃O₄@SiO₂, MNPs@ThNU, and MNPs@ThNU-CuI are shown in Figure 1a–f. As shown in Figure 1a, the sharp band appearing at 2272 cm⁻¹ is attributed to the NCO group. After the addition of thionicotinamide to isocyanate linker, the isocyanate peak at 2272 cm⁻¹ disappeared, as shown in Figure 1b. Simultaneously, new bands appeared at 1649 cm⁻¹ (C=O stretching vibration), 1579 cm⁻¹ (C=C stretching vibration), 1417 cm⁻¹ (C=C stretching vibration), and 3237 and 3337 cm⁻¹ (stretching vibrations of N–H) in FT-IR spectrum of material B (Figure 1b). Also, the peaks positioned at 2967 and 3042 cm⁻¹ are assigned to C–H stretching vibrations. The characteristic peaks appearing at 590 and 1097 cm⁻¹ are attributed to Fe–O and Si–O stretching vibrations of Fe₃O₄ and SiO₂, respectively (Figure 1d–f). After the immobilization of material B on the surface of the magnetic nanoparticles, the mentioned absorption bands for material B, belonging to C=O and C=C vibrations, were negatively shifted and appeared at 1632 and 1566 cm⁻¹, respectively, in the spectrum of MNPs@ThNU (Figure 1e). These results verify the successful grafting of the organic group on the surface of Fe₃O₄@SiO₂. After supporting of CuI nanoparticles on the surface of the modified magnetic nanoparticles



SCHEME 1 Preparation of MNPs@ThNU-CuI



FIGURE 1 The FT-IR spectra of triethoxy (3-isocyanatopropyl)silane (a), material B (b), Fe_3O_4 (c), Fe_3O_4 @SiO₂ (d), MNPs@ThNU (e), and MNPs@ThNU-CuI (f)

(MNPs@ThNU), it was observed a negative shift in absorption frequency of C=O, and its band was appeared at 1624 cm⁻¹. Further, a slight decrease was observed in the intensity of the absorption peak corresponding to the stretching vibration of C=O bond in the spectrum of MNPs@ThNU-CuI indicating coordination of ligand with copper iodide via C=S and C=O sites (Figure 1f). Although the characteristic weak peak at 670 cm⁻¹ for copper iodide did not appear because of the overlapping of the bands around 600–700 cm⁻¹, the presence of copper iodide in the structure of MNPs@ThNU-CuI can be confirmed by the above-mentioned changes as well as XRD and elemental analyses.^[29]

To determine the crystalline structure of the magnetic nanoparticles, X-ray diffraction (XRD) analysis was performed (Figure 2a-c). As shown in XRD patterns of pure Fe₃O₄ (Figure 2a), Fe₃O₄@SiO₂ (Figure 2b), and MNPs@ThNU-CuI (Figure 2c), characteristic peaks at 20 values of 35.27°, 41.73°, 50.97°, 63.47°, 67.87°, and 74.73° corresponding to diffraction lines (220), (311), (400), (422), (511), and (440), respectively, represent well the crystallinity of the present cubic magnetite in good agreement with the reported values (JCPDS card no. 19-0629). As presented in Figure 2b,c, the broad peaks in the 2θ range from 21° to 30° are assigned to the silica phase, indicating the core-shell structure of the catalyst. In XRD pattern of MNPs@ThNU-CuI, the diffraction peaks located at 20 values of 25.5°, 29.5°, 42.2°, 50.0°, 61.2°, 67.45°, and 77.20° can be ascribed to cubic copper iodide (JCPDS card no. 01-076-0207), which demonstrate the immobilization of copper iodide on MNPs@ThNU (Figure 2c). In addition, the appearance of characteristic peaks of Fe₃O₄@SiO₂ shows that the crystalline structure Applied Organometallic_WILEY⁵ of 14 Chemistry

of magnetic nanoparticles is maintained after each modification.^[30]

The morphological and structural features of the prepared nanoparticles were investigated using the SEM and TEM techniques (Figure 3a,b). The SEM image (Figure 3a) shows that the MNPs@ThNU-CuI catalyst has a nearly spherical morphology with a mean diameter of 43 nm.

Also, as shown in the TEM image of the catalyst, the dark-colored spots can relate to Fe_3O_4 nanoparticles, and the colorless regions can represent the silica shell. The appearance of pale spots in the silica region can indicate the presence of copper iodide nanoparticles on the surface of the functionalized silica-coated magnetite nanoparticles (Figure 3b). SEM and TEM images show that the prepared nanoparticles are uniform in shape and size.

The elemental composition of the obtained nanomaterials was evaluated using EDX analysis. As shown in Figure 3c, EDX pattern obviously approved the presence of the expected elements in the structure of MNPs@ThNU-CuI, namely, carbon, nitrogen, oxygen, silicon, sulfur, iron, copper, and iodine with wt% of 14.46, 7.11, 40.07, 18.44, 0.87, 14.63, 1.78, and 2.64, respectively.

The thermal behaviors of pure Fe_3O_4 nanoparticles and MNPs@ThNU- CuI were characterized by thermogravimetric analysis (Figure 4a,b). TGA curves of both Fe_3O_4 nanoparticles and MNPs@ThNU-CuI show a slight weight loss at temperatures below 150°C, which can be attributed to the physically adsorbed water. The TGA curve of MNPs@ThNU-CuI shows also the other two weight loss steps (Figure 4b). Over the range of 200–800°C, the second and third steps of weight loss



FIGURE 2 The X-ray diffraction patterns of Fe_3O_4 (a), Fe_3O_4 @SiO₂ (b), and MNPs@ThNU-CuI (c)





FIGURE 3 SEM (a), TEM (b), and EDX (c) analysis of the catalyst



FIGURE 4 TGA curves of Fe₃O₄ (a) and MNPs@ThNU-CuI (b)

should correspond to the decomposition of organic moieties (weight loss: 11.78 wt%) and the sublimation of iodine, respectively. These results prove the attachment of 1-propyl-3-thionicotinyl-urea moiety onto the surface of MNPs (0.52 mmol g-1) and also determine the copper content in the catalyst structure (0.3 mmol g⁻¹). Furthermore, the loading amount of copper iodide species was evaluated to be 0.32 mmol g^{-1} using ICP-OES analysis.^[21]

To assess the magnetic behaviors of the pure Fe_3O_4 , Fe_3O_4 @SiO₂, and MNPs@ThNU-CuI, the magnetic hysteresis measurements were carried out in an applied magnetic field sweeping from -10 K to 10 K Oe at room temperature using a vibrating sample magnetometer (Figure 5a,b). The curves showed zero coercivity and zero

FIGURE 5 Magnetization curves of Fe₃O₄ (a) and MNPs@ThNU-CuI (b)



remnants magnetization, indicating the superparamagnetic behavior of the nanoparticles. The saturation magnetization (Ms) values are found to be 26.82 and MNPs@ThNU-CuI, which are much lower than that of pure Fe_3O_4 (Ms value: 63.29 emu g⁻¹). This can be





SCHEME 2 The model reaction between iodobenzene, sodium azide, and phenylacetylene

3.3 | Catalyst activity in the synthesis of 1-aryl 1,2,3-triazoles

The catalytic activity of MNPs@ThNU-CuI was investigated for the synthesis of 1,4-disubstituted-1,2,3-triazoles through the one-pot three-component reactions between aryl halides, sodium azide, and terminal alkynes. For our

 TABLE 1
 Optimization of reaction conditions for one-pot synthesis of 1,4-disubstituted 1,2,3-triazoles^a

Entry	Catalyst (mg)	Cu (mol%)	Solvent	Temp. (°C)	Time (h)	Yield ^b (%)
1	30	0.9	EtOH	Reflux	8	83
2	30	0.9	DMSO	90	8	88
3	30	0.9	DMF	90	8	67
4	30	0.9	Choline azide	90	8	86
5	30	0.9	ChCl/gly (1:2)	90	4	90
6	30	0.9	ChCl/PEG (1:4)	90	4	94
7	30	0.9	ChCl/PEG (1:4)	105	4	92
8	30	0.9	ChCl/PEG (1:4)	75	8	89
9	30	0.9	ChCl/PEG (1:4)	40	14	65
10	20	0.6	ChCl/PEG (1:4)	90	6	86
11	40	1.3	ChCl/PEG (1:4)	90	4	93
12	30 ^c	0.0	ChCl/PEG (1:4)	90	24	N.R
13	0.0	0.0	ChCl/PEG (1:4)	100	24	N.R

^aReaction conditions: phenylacetylene (1.0 mmol), iodobenzene (1.0 mmol), sodium azide (1.2 mmol), and different values of MNPs@ThNU-CuI in solvent (2.0 ml).

^bIsolated yields.

^c30 mg of Fe₃O₄ nanoparticles.

TABLE 2 Multicomponent synthesis of 1,4-disubstituted 1,2,3-triazoles from aryl halides, terminal alkynes, and sodium azide using MNPs@ThNU-Cul^a



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(Continues)



^aReaction conditions: alkyne (1.0 mmol), aryl halide (1.0 mmol), sodium azide (1.2 mmol), and 30 mg of MNPs@ThNU-CuI in choline chloride/PEG (1:4) (2.0 ml). 90°C.

^bIsolated yields.

°The reactions were performed at 95°C.

initial screening experiments, a model reaction between iodobenzene, sodium azide, and phenylacetylene was chosen (Scheme 2).

There has always been a marked dependence of the reaction efficiency on the solvent type, reaction temperature, and amount of catalyst. The results are shown in Table 1. In order to inspect the effect of different solvents, the model reaction was performed in the presence of various solvents, as seen in Table 1, entries 1–6. The results showed that the reactions proceeded in EtOH, DMSO, DMF, choline azide, choline chloride/glycerol (1:2), and choline chloride/PEG 200 with good to excellent yields. Among the examined solvents, choline chloride/PEG 200 (1:4) was found to be the best solvent in terms of time and product yield (Table 1, entry 6). To investigate the effect of temperature on the reaction efficiency, the model reaction was performed at temperatures of 40°, 75°, 90°, and 105°C (Table 1, entries 6–9). The optimum temperature was found to be 90°C. Subsequently, we performed the reaction with different amounts of the catalyst ranging from 20 to 40 mg (0.64 to 1.28 mol% Cu) under ideal conditions (Table 1, entries 6, 10, and 11). When the reaction was performed in the presence of pure Fe₃O₄ in choline chloride/PEG 200 (1:4) at 90°C, we observed no desired product after 24 h (Table 1, entry 12). Also, in the absence of the catalyst, the reaction was not carried out even after a long reaction time (24 h) at high temperature (100°C) (Table 1, entry 13). According to the obtained results, the highest efficiency (yield: 94%) was obtained by carrying out the reaction using 30 mg (0.96 mol%) of MNPs@ThNU-CuI at 90°C in choline chloride/PEG 200 (1:4) (Table 1, entry 6).

To explore the generality of this method, we extended our studies to a variety of aryl halides (aryl iodides and aryl bromides) and alkynes. According to the results shown in Table 2, the reactions of phenylacetylene, 4-methyl phenylacetylene, or 2-pyridylacetylene with sodium azide and aryl iodides bearing electron-rich and electron-deficient groups in a 1:1.2:1 molar ratio were carried out using MNPs@ThNU-CuI (0.96 mol%) at 90-95°C in choline chloride/PEG 200 (1:4), and the corresponding 1,4-disubstituted 1,2,3-triazoles were obtained in good to excellent yields (Table 2, entries 1-10). Not surprisingly, when aryl bromides were used as one of the substrates, a noticeable decrease of the yields was observed (Table 2, entries 11-15). The aliphatic alkyne (propargyl alcohol) as well as aromatic alkynes reacted with iodobenzene and sodium azide by this procedure. However, bromobenzene afforded the same product in a lower yield compared to more reactive aryl iodide (Table 2, entries 10 and 16).

Based on the literature review and our observations, a tentative mechanism for the synthesis of 1,2,3-triazoles has been proposed (Scheme 3). Choline chloride/PEG DES, due to its favorable polarity and solubility, is able to make an effective association of polar and non-polar reactants during the reaction, thus accelerating the catalysis process. First, it is expected that the reaction begins with the coordination of terminal alkyne to MNPs-

supported copper(I) catalyst leading to a π -complex. In the next step, the azide reagent, which has been generated in situ from reaction of sodium azide and the copper catalyst-activated aryl halide assisted by DES, through its lone pair attacks to the central metal of corresponding copper-alkylidine complex resulting in a six-membered metallacycle intermediate. Finally, ring contraction to a copper(I) triazolide complex and subsequent protonolysis affords the desired product as well as regeneration of copper(I) catalyst.

In order to investigate the stability and reusability of the catalyst, the model reaction between iodobenzene, sodium azide, and phenylacetylene was carried out under optimum conditions. In each cycle, after completion of the reaction, the nanocatalyst was easily removed from the reaction mixture using an external magnet, washed with water and ethanol for several times and then dried under vacuum at 70° C to reuse in the next cycle. As shown in Figure 6, MNPs@ThNU-CuI catalyst preserves a reasonable performance in the synthesis of 1,4-disubstituted-1,2,3-triazole after at least five cycles without any appreciable loss of its activity (Figure 6a).

We also measured the amount of leached copper from the heterogeneous metal catalyst during the course of the reaction by ICP-OES analysis. For this purpose, the catalyst was magnetically removed at half of the reaction time, and then the experiment was continued in absence of the catalyst for another 8 h under the same reaction conditions. It was observed no further conversion in residual mixture. The ICP-OES elemental analysis of the filtrate showed the negligible amounts of copper leaching (0.02%) after the first reaction. Moreover, the copper loading amount in the fresh and the recycled catalyst



SCHEME 3 Proposed mechanism for synthesis of 1,4-disubstituted-1,2,3-triazole



FIGURE 6 Recyclability of the nanocatalyst (a) and SEM image of the recovered catalyst (b)

TABLE 3	Comparison of the catalytic efficacy of MNPs@ThNU-CuI with the previously reported catalytic systems for the synthesis of
1,4-diphenyl-	1 <i>H</i> -1,2,3-triazole

Entry	Catalyst (mol% Cu)	Reaction conditions	Time (h)	Temp. (°C)	Yield ^a (%)	Ref.
1	CuI (10)	Iodobenzene, phenylacetylene, NaN ₃ , <i>N</i> , <i>N</i> '-dimethylethylenediamine (20 mol%), sodium ascorbate (10 mol%), ethanol-water (7:3)	15	50	87	Potratz et al. ^[31]
2	CuI (10)	Iodobenzene, phenylacetylene, NaN ₃ , tetrabutylammonium hydroxide/ L-proline, (20 mol%), [BMIM]BF ₄	10	60	88	Yan and Wang ^[24c]
3	Porous Cu(0) (5)	 1-4-Iodoanisole, NaN₃, L-proline (20 mol %), ⁱPr₂NH (20 mol%), DMSO 2-Phenylacetylene 	24/34	80/50	73	Chen et al. ^[32]
4	CuI (20)	 Iodobenzene, NaN₃, DBU (30 mol%), DMSO Phenylacetylene 	2.5/0.5	95/r.t.	93	Jiang et al. ^[24a]
5	CuI (10)	Iodobenzene, phenylacetylene, NaN ₃ , <i>N</i> , <i>N</i> -dimethyl-ethylenediamine (20 mol%), ChCl/glycerol (1:2)	5	75	96	Kafle and Handy ^[24b]
6	CuI@SBA-15/PrEn/ ImPF ₆ (4.1)	 Iodobenzene, NaN₃, L-proline (10 mol %), DMSO/H₂O (2:1) Phenylacetylene 	8/8	r.t./80	93	Hosseini et al. ^[33]
7	CuSO ₄ .5H ₂ O (5)	Iodobenzene, phenylacetylene, NaN ₃ , L-proline (20 mol%), sodium ascorbate (10 mol%), Na ₂ CO ₃ (20 mol%), DMSO/H ₂ O (9:1)	24	65	71	Rizzi et al. ^[34]
8	Fe ₃ O ₄ @SiO ₂ @AMBI/ Cu (20)	Iodobenzene, phenylacetylene, NaN ₃ , sodium ascorbate (30 mol%), DMSO/ H ₂ O	2	100	96	Mehdipour and Khodabakhshi ^[35]
9	MNPs@ThNU-CuI (0.9)	Iodobenzene, phenylacetylene, NaN ₃ , ChCl/PEG (1:4)	4	90	94	_b

^aIsolated yields. ^bThis work. (after five times recycling) was checked by ICP analysis, and it was found that the copper content of the nanocatalyst has not decreased appreciably after the reaction.

FE-SEM analysis was also performed for the recovered MNPs@ThNU-CuI catalyst after five cycles. As can be clearly seen in the SEM image (Figure 6b), the morphology of the catalyst almost has remained constant even after the fifth cycle.

To show the merit of the present approach for the synthesis of 1-aryl 1,2,3-triazoles, the result obtained using MNPs@ThNU-CuI has been compared with some of those reported in the literature. As can be seen in Table 3, the use of MNPs-supported copper(I) catalyst in PEGylated DES as a sustainable and environmentally friendly medium has provided a favorable reaction condition under which the desired product can be obtained in high yield over short reaction time in the presence of a lower catalyst loading. Further, both the catalyst and solvent are able to recover.

4 | CONCLUSIONS

In conclusion, a highly efficient and scalable approach for the one-pot synthesis of 1-aryl 1,2,3-triazoles has been developed using MNPs@ThNU-CuI nanocatalyst through the three-component reaction of terminal alkynes with in situ generated aryl azides from aryl iodides and aryl bromides in sustainable PEGylated DES. The use of magnetic nanocatalyst in DES as an environmentally friendly medium has provided high productivity as well as green and safe conditions. The other key features of the present protocol are as follows: short synthetic route to prepare catalyst, the use of simple and economical reaction conditions, the capability of using a variety of aryl halides and alkynes with moderate to excellent efficiency and the ability to be easily recycled both the magnetic catalyst and solvent.

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AUTHOR CONTRIBUTIONS

sogand mirshafiee: Conceptualization; data curation; formal analysis; funding acquisition; investigation; methodology; project administration; resources. **Arefeh Salamatmanesh:** Conceptualization; data curation; formal analysis; funding acquisition; investigation; methodology; project administration; resources. **Akbar Heydari:** Conceptualization; data curation; formal analysis; funding acquisition; investigation; methodology; project administration; resources; software; supervision; validation; visualization.

CONFLICT OF INTEREST

There are no conflicts of interest to declare.

DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available in the supporting information of this article.

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