

2-(Aminomethyl)benzimidazole/Cu²⁺ immobilized on Fe₃O₄@SiO₂: a convenient magnetic nanocatalyst for click reaction of aryl iodide/benzyl halide, sodium azide and terminal alkyne

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ABSTRACT

In this work, the Fe₃O₄@SiO₂@AMBI/Cu nanocatalyst was synthesized and used as a well-organized magnetic nanocatalyst for the click reaction. This nanocatalyst has effectively catalyzed the cyclization of terminal alkynes and sodium azide with aryl iodide/benzyl halide for the formation of 1,4-disubstituted 1,2,3-triazoles under mild reaction conditions with good to high yields in low reaction time.

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1. Introduction

The term bioorthogonal chemistry was born in 2003 by Bertozzi¹. Bioorthogonal chemistry is about designing reactions that can be achieved in a biological environment and proceeded in living systems. This kind of reactions are posing great biocompatibility and selectivity, also opening new approaches for new innovations in biology by feasible various bond formations in biological systems. From this kind of reactions, click reaction should be mentioned. This reaction was defined in 2001 by Sharpless as an insensitive and easy performing reaction by accessible reagents.²⁻³ In this reaction, triazoles can be synthesized by the reaction of azide and terminal amide and in the presence of Cu as the catalyst. Click chemistry is one of the newest and most operative tools for the synthesis of drug-like heterocyclic compounds with carbon-heteroatom-carbon (C–X–C) bonds that can accelerate the drug discovery improvement and lead to synthesis of biological compounds with anti-HIV, antiviral, antibiotic and antibacterial activities.⁴⁻¹⁰ Until today, many articles have reported click chemistry by various Cu-catalyzed procedures, but due to its importance, it is necessary to develop new methodologies.

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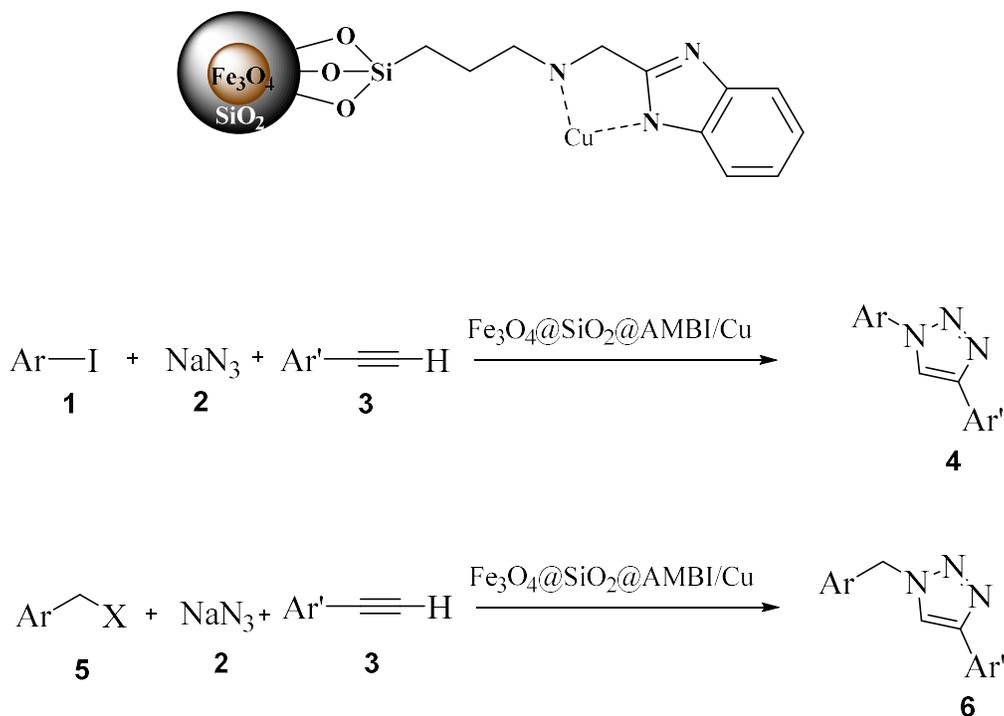
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History of using metal catalysis for heterogeneous catalysis is going back to 60 years ago.¹¹⁻¹³ In heterogeneous catalysis, phase of the catalyst, reactant, and product are different. Thus, the catalyst can be separated from the reaction media more easily compared to homogeneous catalysis. Using transition metals in heterogeneous catalysis, due to their properties, is becoming more and more common during time. Among transition metals, Cu, as an economic and environmentally friendly metal, could be a reliable choice for synthesizing an efficient catalyst. Some of the reported applications of Cu are as followed: selective CO bond cleavage of glycerol¹⁴, reduction of CO₂ electrochemically,¹⁵ catalytic dehydrogenation, catalytic NO reduction¹⁶, and CH activation.¹⁷

In metal catalysis, among various variables that affect the catalytic behavior of the catalyst, the size of the particles, the shape of the particles, the nature of the selected support for immobilizing metal particles on it, and also the nature of other metals present in the structure of the catalyst could be named. According to the influence of the size in the efficiency of the catalyst, synthesizing nanoparticles could be highly beneficial due to their high surface area. As a result, among this explosion of research in the field of nanocatalysis for various reactions such as reduction, oxidation, hydrogenation, electrocatalytic, organic reactions, and photocatalytic reaction, synthesizing metal nanocatalysts with promised properties is even a huge challenge.¹⁸

Herein, to improve previous researches and to prepare effective heterogeneous catalysts to proceed click reaction, the Fe₃O₄@SiO₂@AMBI/Cu nanocatalyst was synthesized using FeCl₃·6H₂O, FeCl₂·4H₂O, NH₄OH, tetraethyl orthosilicate (TEOS), 2-(aminomethyl) benzimidazole dihydrochloride (AMBI), and Cu(OAc)₂, and used as an efficient magnetic nanocatalyst (Scheme 1). This nanocatalyst has effectively catalyzed the synthesis of 1,4-disubstituted-1,2,3-triazoles using terminal aryl alkynes, sodium azide and aryl iodide/benzyl halide with good to high yields in low reaction time (Scheme 1). The most challenging subject of this procedure was the performing of the coupling reaction using Cu-catalyst. This process was carried out successfully in the presence of L-proline with quiet satisfactory results.



Scheme 1. Click reactions using Fe₃O₄@SiO₂@AMBI/Cu nanocatalyst

2. Results and Discussion

FT-IR spectra of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{AMBI}/\text{Cu}$ are illustrated in Figure 1. As illustrated in Figure 1, functional groups of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{AMBI}/\text{Cu}$ can be seen in FT-IR spectra. In the FT-IR spectra of Fe_3O_4 , a broad peak at around $500\text{-}600\text{ cm}^{-1}$ is attributed to the Fe-O group. In $\text{Fe}_3\text{O}_4@\text{SiO}_2$ spectra, in addition to the Fe-O peak, a broad peak at $1050\text{-}1250\text{ cm}^{-1}$ is related to the presence of the Si-O group. Also, in the $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{AMBI}/\text{Cu}$ spectra, in addition to all of the abovementioned peaks, a C=C stretching peak and a characterization peak of N-H are observed at 1649 cm^{-1} and 3400 cm^{-1} , respectively.

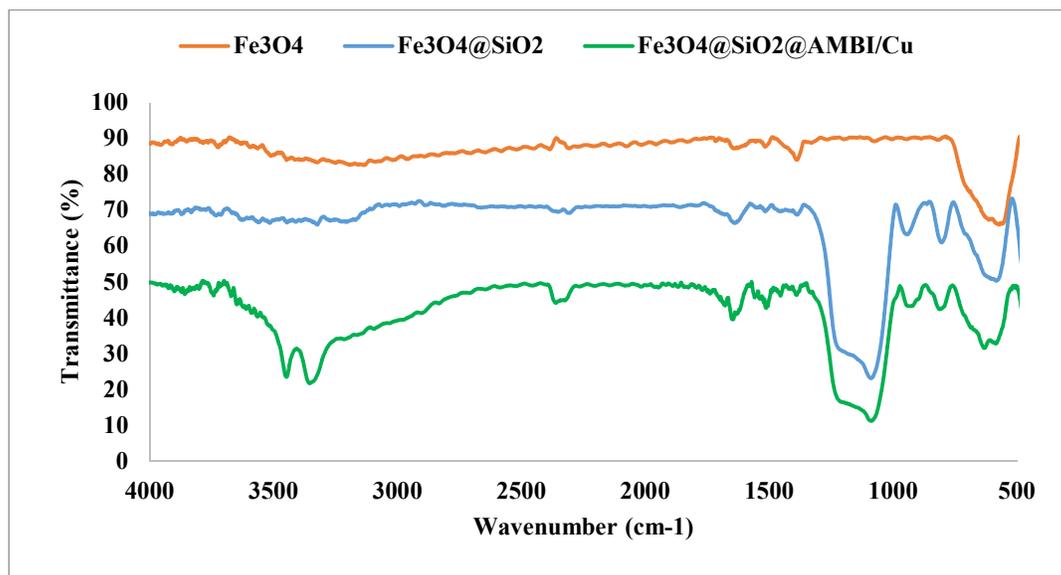


Fig. 1. FT-IR spectra of a) Fe_3O_4 , b) $\text{Fe}_3\text{O}_4@\text{SiO}_2$, and c) $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{AMBI}/\text{Cu}$

The morphology and size of synthesized $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{AMBI}/\text{Cu}$ were studied by SEM and TEM images and they are shown in Figure 2. Consequently, nanoparticles were homogeneously dispersed on Fe_3O_4 as a core with an average diameter of about 20 nm. These analyses revealed that there is no roughness and aggregation present in the surface of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{AMBI}/\text{Cu}$.

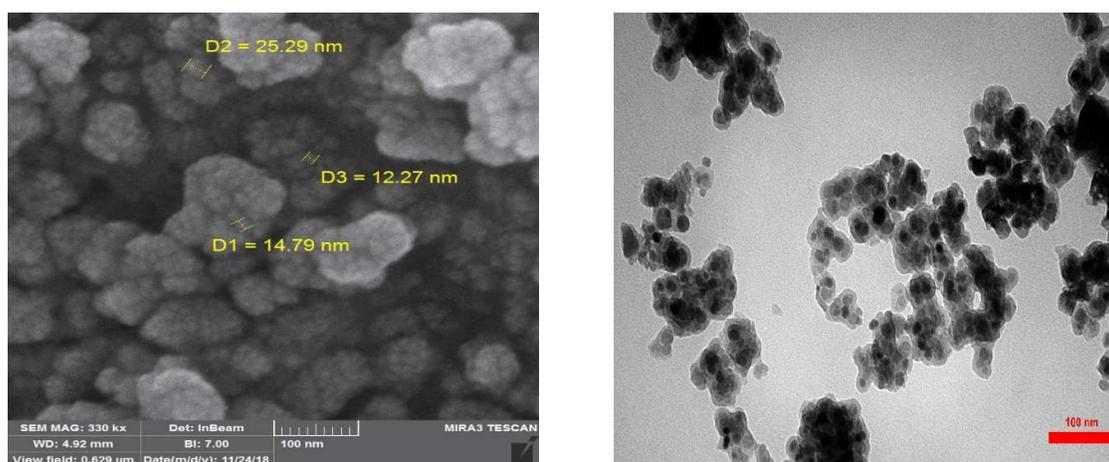


Fig. 2. SEM and TEM spectra of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{AMBI}/\text{Cu}$

The purity and crystalline structure of the synthesized $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{AMBI}/\text{Cu}$ were studied using X-ray diffractions. The XRD pattern of the powders of the final nanocatalyst is indicated in Figure 3. Corresponding peaks of Fe_3O_4 in XRD were observed at $2\theta=30.0, 35.0, 42.0, 52.0, 56.0,$ and $62.0,$ which are similar to the pattern of the reported Fe_3O_4 nanoparticles before.^{19, 30}

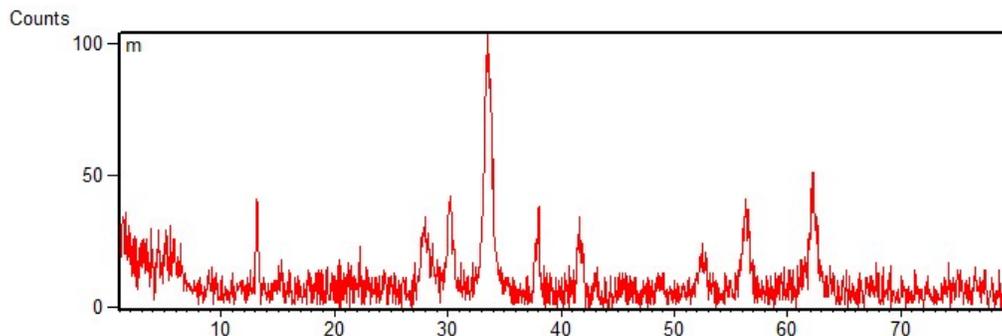


Fig. 3. XRD pattern of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{AMBI}/\text{Cu}$

EDX analysis was performed to study the elemental compositions of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{AMBI}/\text{Cu}$. The EDX spectrum of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{AMBI}/\text{Cu}$ is presented in Figure 4. In this spectrum, the existence of Fe and O has proved the synthesis of Fe_3O_4 . In addition, EDX shows the presence of Cu, N, and Si which proved the successful synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{AMBI}/\text{Cu}$.

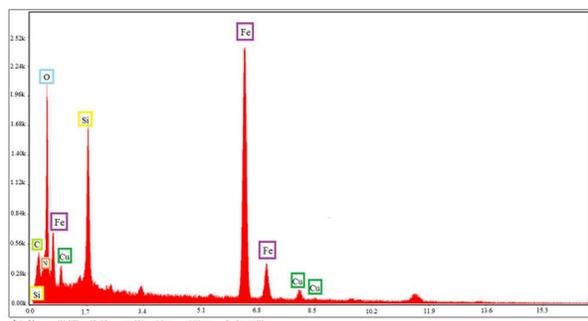


Fig. 4. EDX spectrum of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{AMBI}/\text{Cu}$

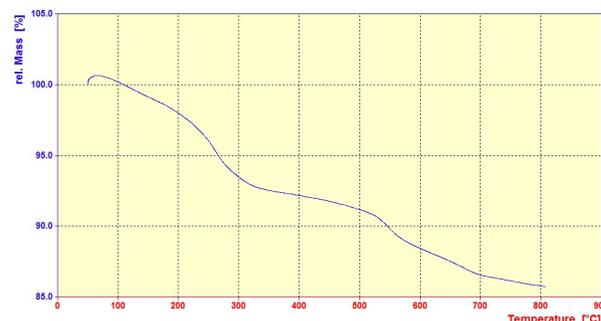


Fig. 5. TGA curve of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{AMBI}/\text{Cu}$

The TGA analysis of the synthesized $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{AMBI}/\text{Cu}$ was taken to understand the stability of it (Figure 5). In TGA, the weight loss under 200°C is related to volatile compounds and the weight loss at about 500°C is related to decomposition of ligand. Furthermore, due to the existence of Cu and Fe_3O_4 , it did not decompose completely at temperatures above 800°C .

2.3 Catalytic activity of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{AMBI}/\text{Cu}$ nanocatalyst

Most of the click reactions which started with aryl iodide need long reaction times and hard conditions. Therefore, we decided to develop this kind of reactions with a new and efficient protocol to proceed this reaction under mild conditions. Initial studies including the optimization of the type of the catalyst, the amount of the catalyst, the reaction time, the reaction temperature, and the type of the base and the solvent were conducted using iodobenzene, phenyl acetylene and sodium azide as the model reaction.

First of all, to understand the best catalyst, various catalysts including CuCl, CuI, Cu_2O , and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{AMBI}/\text{Cu}$ were used. In comparison to other catalytic systems, the best yield was gained using the $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{AMBI}/\text{Cu}$ nanocatalyst. In the next step, in order to optimize the amount of the catalyst, three different amounts of catalysts, including 10, 20, and 30 mg of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{AMBI}/\text{Cu}$ catalyst were used, in which by using 30 mg of catalyst, 96% yield was obtained. For the acquisition of the best temperature of the reaction, after carrying out the reaction in

different temperatures, it was concluded that the optimized temperature is 100°C. Afterwards, different ligands were used (L-proline, picolinic acid, DMEDA, phenantroline, and bipyridine) to carry out coupling reactions of aryl iodide. From the results, it could be concluded that in the presence of L-proline, higher yield of the product was gained. In order to select the best base, NaOH, K₂CO₃, Cs₂CO₃, NaHCO₃, and K₂PO₄ were used and as the result, in the presence of NaOH, the best result was gained. Finally, for the selection of the best solvent, the performance of several solvents was evaluated. In comparison to toluene, dioxane, and EtOH as a solvent, using the combination of H₂O/DMSO yielded to the best results for this reaction (Table 1). By this optimized condition, various derivatives were synthesized (Scheme 2).

Table 1. Optimizing different parameters in the model reaction

Enter	Catalyst	Cat [%]	Ligand	Base	T(°C)	Time(h)	Solvent	Yield[%] ^[a]
1	-	-	L-proline	NaOH	100	12	DMSO/H ₂ O	trace
2	CuCl	20	L-proline	NaOH	100	12	DMSO/H ₂ O	45
3	CuI	20	L-proline	NaOH	100	12	DMSO/H ₂ O	50
4	Cu ₂ O	20	L-proline	NaOH	100	12	DMSO/H ₂ O	40
5	Fe ₃ O ₄ @SiO ₂ @AMBI/Cu	10	L-proline	NaOH	100	2	DMSO/H ₂ O	73
6	Fe ₃ O ₄ @SiO ₂ @AMBI/Cu	20	L-proline	NaOH	100	2	DMSO/H ₂ O	84
7	Fe ₃ O ₄ @SiO ₂ @AMBI/Cu	30	L-proline	NaOH	100	2	DMSO/H ₂ O	96
8	Fe ₃ O ₄ @SiO ₂ @AMBI/Cu	30	picolinic acid	NaOH	100	12	DMSO/H ₂ O	trace
9	Fe ₃ O ₄ @SiO ₂ @AMBI/Cu	30	DMEDA	NaOH	100	12	DMSO/H ₂ O	trace
10	Fe ₃ O ₄ @SiO ₂ @AMBI/Cu	30	2,2'-bipyridine	NaOH	100	12	DMSO/H ₂ O	trace
11	Fe ₃ O ₄ @SiO ₂ @AMBI/Cu	30	1,10-phenanthroline	NaOH	100	12	DMSO/H ₂ O	trace
12	Fe ₃ O ₄ @SiO ₂ @AMBI/Cu	30	L-proline	K ₂ CO ₃	100	8	DMSO/H ₂ O	53
13	Fe ₃ O ₄ @SiO ₂ @AMBI/Cu	30	L-proline	Cs ₂ CO ₃	100	8	DMSO/H ₂ O	63
14	Fe ₃ O ₄ @SiO ₂ @AMBI/Cu	30	L-proline	NaHCO ₃	100	8	DMSO/H ₂ O	54
15	Fe ₃ O ₄ @SiO ₂ @AMBI/Cu	30	L-proline	K ₂ PO ₄	100	8	DMSO/H ₂ O	40
16	Fe ₃ O ₄ @SiO ₂ @AMBI/Cu	30	L-proline	NaOH	100	8	DMSO	71
17	Fe ₃ O ₄ @SiO ₂ @AMBI/Cu	30	L-proline	NaOH	90	8	H ₂ O	77
18	Fe ₃ O ₄ @SiO ₂ @AMBI/Cu	30	L-proline	NaOH	90	8	Toluene	23
19	Fe ₃ O ₄ @SiO ₂ @AMBI/Cu	30	L-proline	NaOH	90	8	Dioxane	32
20	Fe ₃ O ₄ @SiO ₂ @AMBI/Cu	30	L-proline	NaOH	80	8	EtOH	61
21	Fe ₃ O ₄ @SiO ₂ @AMBI/Cu	30	L-proline	NaOH	r.t	4	DMSO/H ₂ O	63

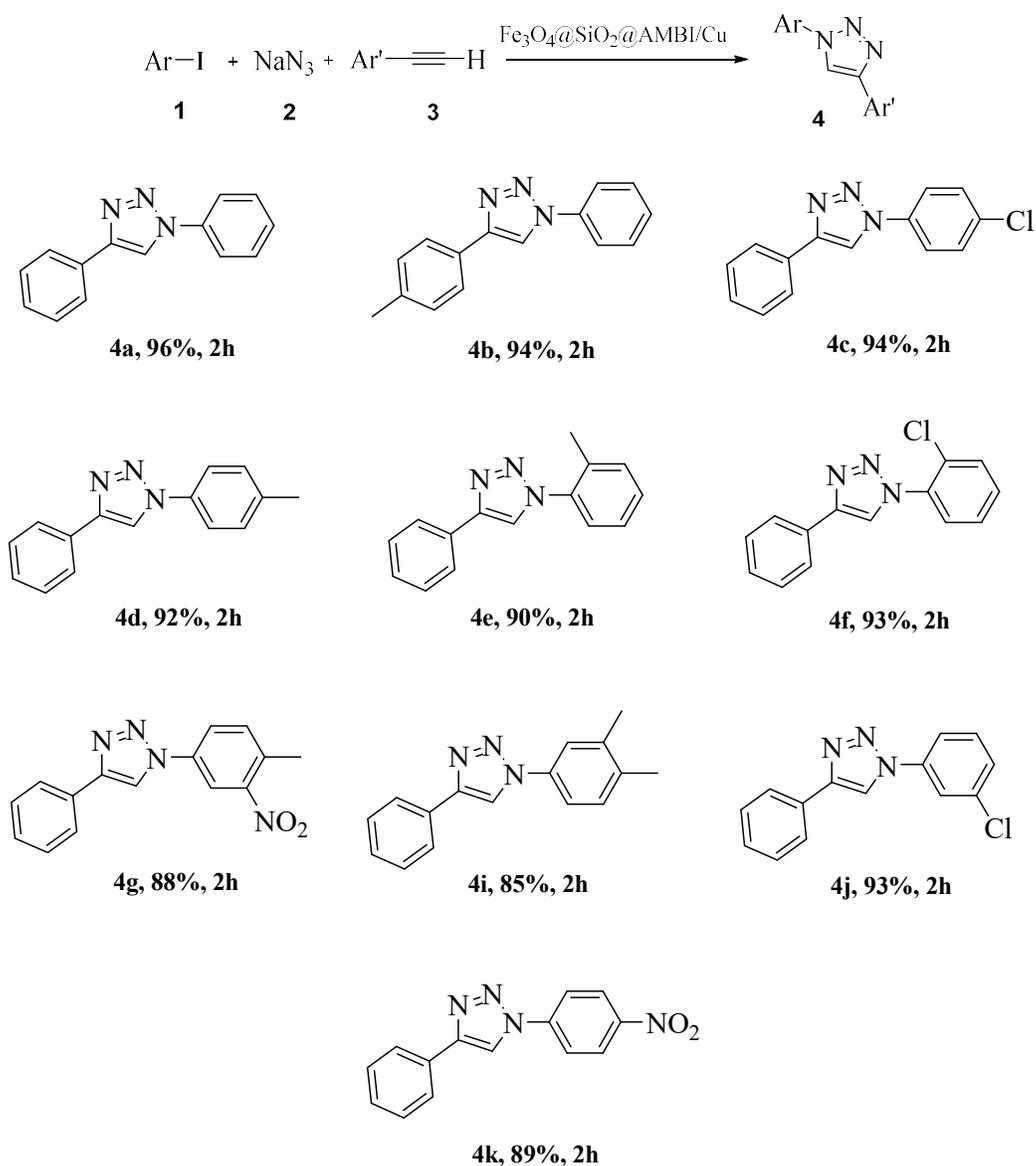
^a Isolated yield

Almost all of the abovementioned optimizing reactions were studied in the reaction of benzyl bromide, phenyl acetylene, and sodium azide as the model reaction.. In this case, the best result was gained using H₂O as the solvent and at 90°C (entry 5, Table 2). Also, different derivatives 1,4-disubstituted 1,2,3-triazoles using benzyl bromide/chloride, aryl alkyne and sodium azide were synthesized by this condition (Scheme 3).

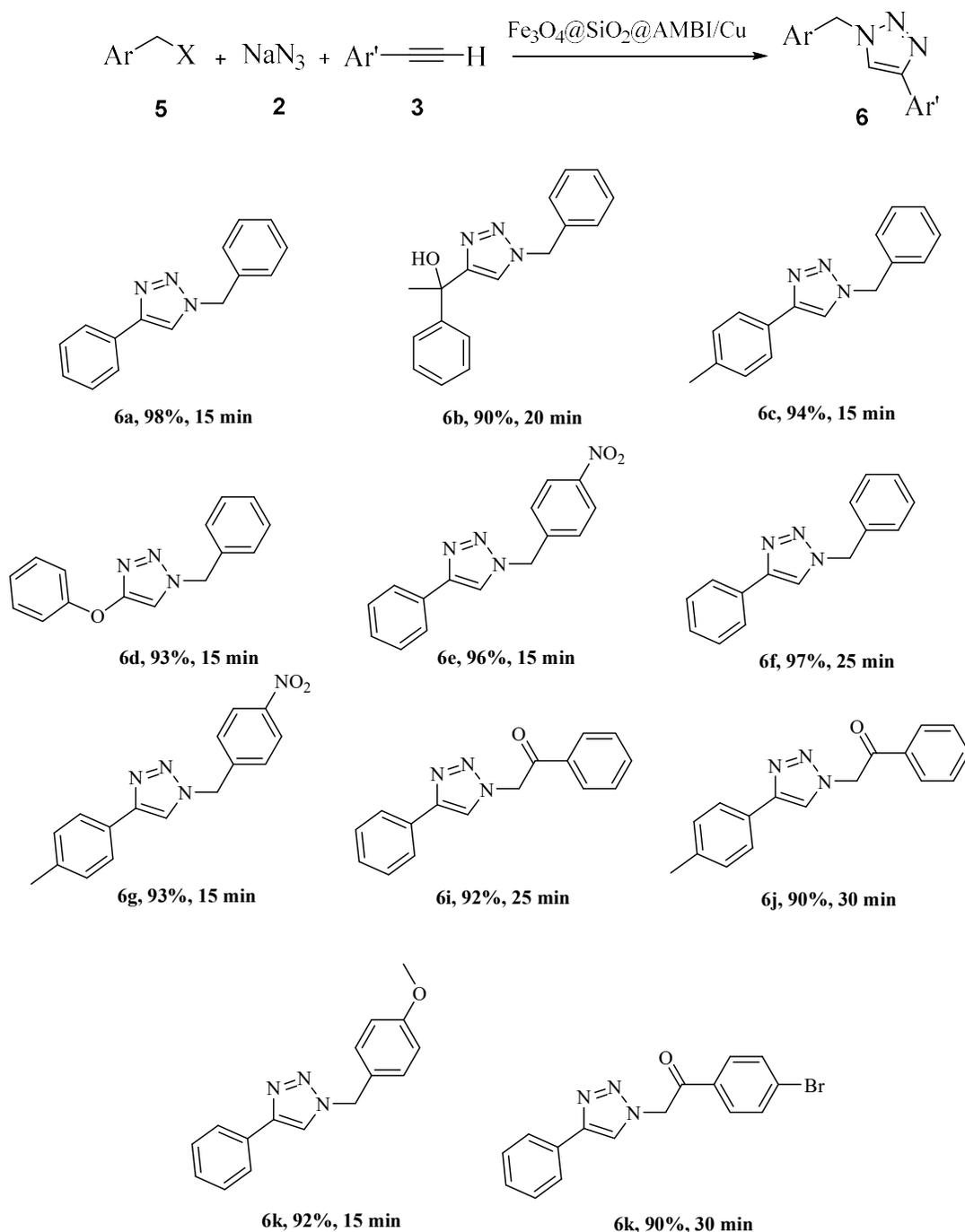
Table 2. Optimizing different parameters in the click reaction of benzyl bromide and phenyl acetylene^a

Enter	Catalyst	Cat [%]	T(°C)	Time(h)	Solvent	Yield[%] ^[a]
1	-	-	50	7	H ₂ O	-
2	-	-	90	8	H ₂ O	21
3	Fe ₃ O ₄ @SiO ₂ @AMBI/Cu	10	90	8	H ₂ O	76
4	Fe ₃ O ₄ @SiO ₂ @AMBI/Cu	20	90	8	H ₂ O	87
5	Fe ₃ O ₄ @SiO ₂ @AMBI/Cu	30	90	0.4	H ₂ O	98
6	Fe ₃ O ₄ @SiO ₂ @AMBI/Cu	40	90	0.4	H ₂ O	98
7	Fe ₃ O ₄ @SiO ₂ @AMBI/Cu	30	r.t	1	H ₂ O	51
8	Fe ₃ O ₄ @SiO ₂ @AMBI/Cu	30	r.t	8	H ₂ O	81
9	Fe ₃ O ₄ @SiO ₂ @AMBI/Cu	30	90	2	Toluene	15
10	Fe ₃ O ₄ @SiO ₂ @AMBI/Cu	30	Reflux	2	CH ₃ OH	65
11	Fe ₃ O ₄ @SiO ₂ @AMBI/Cu	30	Reflux	2	CH ₃ CN	38
12	Fe ₃ O ₄ @SiO ₂ @AMBI/Cu	30	Reflux	1	EtOH/H ₂ O	83
13	Cu/SiO ₂	30	Reflux	12	H ₂ O	95
14	Chitosan-coated Fe ₃ O ₄ /Cu	30	Reflux	12	CH ₂ Cl ₂	94
15	Chitosan/Cu	30	90	4	H ₂ O	98

^a Isolated yield



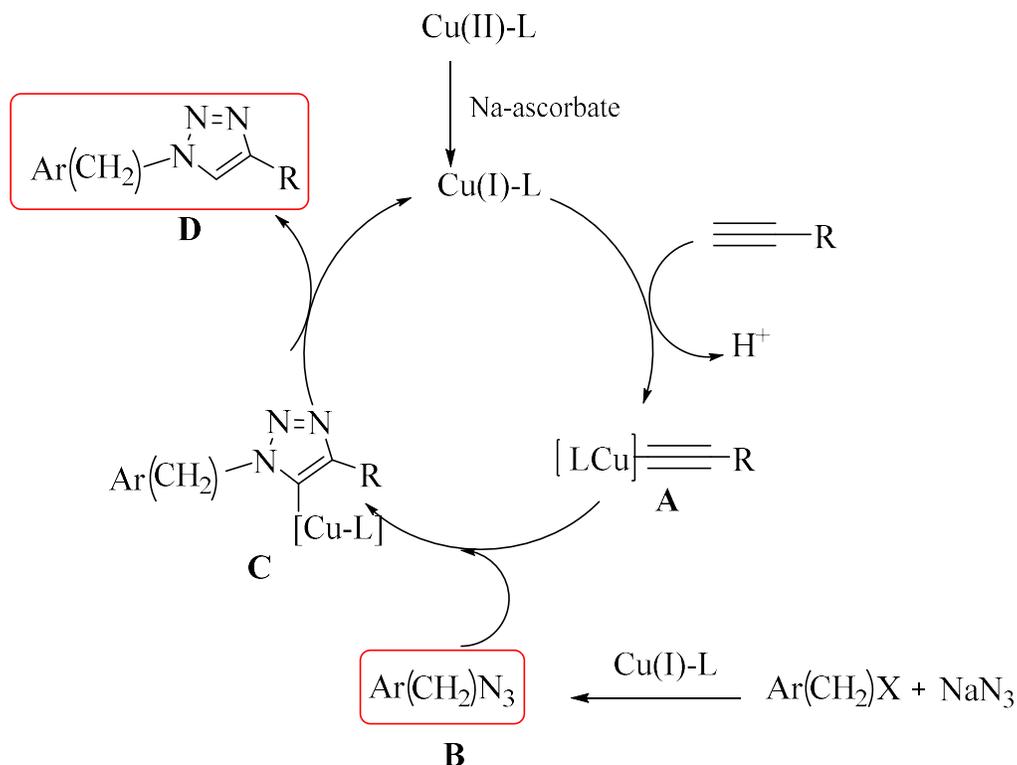
Scheme 2. Substrate scope of 1,4-disubstituted-1,2,3-triazoles using aryl iodide. Optimized reaction conditions: Aryl iodide (1 mmol), aryl alkyne (1 mmol), sodium azide (1.2 mmol), sodium ascorbate (30 mol %), 20 mol % of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{AMBI}/\text{Cu}$, DMSO/ H_2O , 100 °C.



Scheme 3. Substrate scope of 1,4-disubstituted 1,2,3-triazoles using benzyl halide. Optimized reaction conditions: Benzyl bromide (**5a-5e**, **6g-6k**) /benzyl chloride (**5f**) (1 mmol), aryl alkyne (1 mmol), sodium azide (1.2 mmol), sodium ascorbate (30 mol %), 20 mol % of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{AMBI}/\text{Cu}$, H_2O , 80 °C.

2.4 Mechanism

In the suggested mechanism using $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{AMBI}/\text{Cu}$ nanocatalyst in Scheme 4, initially, Cu reacted with sodium azide to form Cu-azide intermediate. Afterwards, by the addition of aryl iodide/benzyl halide, aryl/benzyl azide **B** was obtained. Then, by the activation of alkyne using Cu-catalyst, Cu-alkyne intermediate **A** was formed and by the addition of aryl/benzyl azide, Cu-triazole intermediate **C** was shaped, which led to the final substitution of triazole **D** (Scheme 4).¹⁹



Scheme 4. Proposed mechanism for the synthesis of substituted triazoles

2.5 Reusability of Fe₃O₄@SiO₂@AMBI/Cu nanocatalyst

The stability of Fe₃O₄@SiO₂@AMBI/Cu nanocatalyst was studied by performing 6 different runs under the optimized reaction conditions. The Fe₃O₄@SiO₂@AMBI/Cu nanocatalyst could be easily separated by an external magnet from the reaction media before each upcoming run. The recyclability of the catalyst indicates that the yield of the click reaction using aryl iodide/benzyl halide was decreased slightly from 96% to 89% after 6 runs.

3. Conclusion

To sum up, Fe₃O₄@SiO₂@AMBI/Cu nanocatalyst is successfully synthesized and used in two different click reactions. Following developments of our work could be mentioned here: (1) Synthesis of Fe₃O₄@SiO₂@AMBI/Cu nanocatalyst could be simply achieved in the absence of expensive initial materials. (2) Click reaction using synthesized Fe₃O₄@SiO₂@AMBI/Cu was completed in lower time and milder reaction conditions compared to most of the reported works. (3) The synthesized nanocatalyst could be simply separated, recycled and used after completing the reaction.

Acknowledgement

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4. Experimental

4.1 Materials and Methods

All initial chemicals and materials were purchased from Merck and Aldrich. Also, characterizations were carried out using following instruments: a) FT-IR: Shimadzu FT-IR-8400S spectrophotometer, b) ¹H-NMR: Bruker Avance 500 MHz, c) SEM: KYKY- EM3200 at 26 KV, d) XRD: Jeoljdx-8030, e) TGA: Q50 V6.3 Build 189.

4.2. General procedure

4.2.1 $Fe_3O_4@SiO_2@AMBI/Cu$ nanocatalyst preparation

Fe_3O_4 nanoparticles were synthesized using previous reported literatures. In brief, 5.838g of $FeCl_3 \cdot 6H_2O$ and 2.147 g of $FeCl_2 \cdot 4H_2O$ were added to deionized water under N_2 atmosphere at $85^\circ C$. To this mixture, 10 ml of NH_4OH (25%) was added and stirred for 30min. After the completion of the reaction, produced nanoparticles were separated by an external magnet and dried in a vacuum oven at $60^\circ C$. Next, for the synthesis of $Fe_3O_4@SiO_2$, 0.5mL of tetraethyl orthosilicate (TEOS) was added to the sonicated Fe_3O_4 in 20 mL of deionized water and 70mL of EtOH and was stirred for 8hrs. The resulted compound was separated by an external magnet, washed with water and EtOH, and then dried in a vacuum oven at $60^\circ C$. In the next step, 1g of the synthesized $Fe_3O_4@SiO_2$ was added to Ball-Mill and 0.3g of 2-(aminomethyl)benzimidazole dihydrochloride (98%) (AMBI) plus 0.6g of K_2CO_3 were added. The mixture was milled for 45min at 30Hz. The resulted product was separated by an external magnet and washed 5 times with water and EtOH and then dried in a vacuum oven at $60^\circ C$. This resulted product was dispersed in EtOH. Afterwards, 0.3g of $Cu(OAc)_2$ was added to it and the mixture was refluxed at $80^\circ C$ for 24hrs. Finally, the final product was separated, washed, and dried in an oven.

4.2.2 Click Reaction using aryl iodide

The reaction was carried out using 1mmol of aryl iodide, 1mmol of aryl alkyne, 1.2mmol of sodium azide, 30mol % of sodium ascorbate, and 20 mol % of $Fe_3O_4@SiO_2@AMBI/Cu$ nanocatalyst in DMSO/ H_2O . This combination was stirred for 2 hrs at $100^\circ C$ and the completion of the reaction was followed by thin layer chromatography (TLC). Resulted precipitation was separated and dried in room temperature.

4.2.3 Click reaction using benzyl halide

The reaction was carried out using 1mmol of benzyl bromide/chloride, 1mmol of aryl alkyne, 1.2mmol of sodium azide, 30mol % of sodium ascorbate, and 20mol % of $Fe_3O_4@SiO_2@AMBI/Cu$ nanocatalyst in H_2O . This combination was stirred for 15min h at $80^\circ C$ and the completion of the reaction was followed by thin layer chromatography (TLC). Resulted precipitation was separated and dried in room temperature.

4.3 Physical and Spectral Data

The physical and spectral data of some of the products can be found in the supporting information file.

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