FULL PAPER



Iron oxide modified with pyridyl-triazole ligand for stabilization of gold nanoparticles: An efficient heterogeneous catalyst for A³ coupling reaction in water

Mohammad Gholinejad^{1,2} Hatemeh Zareh¹ | Carmen Najera³

¹ Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), PO Box 45195-1159, Gavazang, Zanjan 45137-66731, Iran
² Research Center for Basic Sciences & Modern Technologies (RBST), Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan 45137-66731, Iran
³ Departamento de Química Orgánica and Centro de Innovación en Química Avanzada (ORFEO-CINQA), Universidad de Alicante, Apdo. 99, E-03080 Alicante, Spain

Correspondence

Mohammad Gholinejad, Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), PO Box 45195-1159, Gavazang, Zanjan 45137-66731, Iran.

Email: gholinejad@iasbs.ac.ir

Carmen Najera, Departamento de Química Orgánica and Centro de Innovación en Química Avanzada (ORFEO-CINQA), Universidad de Alicante, Apdo. 99, E-03080 Alicante, Spain.

Email: cnajera@ua.es

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 Fe_3O_4 nanoparticles were modified with pyridyl-triazole ligand and the new magnetic solid was applied for the stabilization of very small and uniform gold nanoparticles. The resulting magnetic material, Fe_3O_4 @PT@Au, was characterized using various methods. These gold nanoparticles on a magnetic support were applied as an efficient heterogeneous catalyst for the three-component reaction of amines, aldehydes and alkynes (A³ coupling) in neat water with 0.01 mol% Au loading. Using magnetic separation, this catalyst could be recycled for seven consecutive runs with very small decrease in activity. Characterization of the reused catalyst did not show appreciable structural modification.

KEYWORDS

gold nanoparticles, magnetic, propargylamines, pyridyl-triazole, water

1 | INTRODUCTION

Direct C— H bond activation of alkynes is one of the most powerful and reliable methods for converting them to nucleophiles for the construction of carbon–carbon bonds.^[1] Traditional methods for the preparation of alkynylides include the use of stoichiometric amounts of organometallic reagents such as organolithium or

organomagnesium compounds or metal hydrides under strict anhydrous reaction conditions. Another option are metal-catalysed methods for alkyne C- H bond activation.^[2-5] One of the most important applications of the C– H bond activation of terminal alkynes is the preparation of propargylamines by means of a three-component coupling reaction of amines, aldehydes and alkynes (A³ coupling).^[6] Propargylamines are synthetically versatile key molecules in the preparation of many nitrogen-containing biologically active compounds such as β -lactams, oxotremorine analogues, isoquinolines, oxazoles, natural products and agrochemicals.^[7-14]

In addition, propargylamines have applications as therapeutic drug molecules in the treatment of Alzheimer's and Parkinson's diseases.^[15,16] Within the past few years. various transition metals such as copper,^[17–23] silver,^[24,25] iridium.^[26] iron,^[27-29] zinc,^[30] indium^[31] and nickel^[32] have been reported as catalysts for the preparation of propargylamines via A³ coupling reaction under homogeneous or heterogeneous reaction conditions. In recent years, increasing attention has been paid to the catalytic performance of gold, which traditionally was considered as a poor and inactive metal.^[33–35] One of the most important applications of gold as a catalyst was reported by Wei and Li in A³ coupling reaction in which gold activated alkyne C- H bonds.^[36] After reporting this method, some other homogeneous gold catalysts were used for A³ coupling reactions.^[37–51] It should be noted that homogeneous catalysts suffer from the problem of catalyst separation and reuse, and also the problem of product contamination with generally toxic transition metals. Recently, a few heterogeneous and recyclable gold catalysts have been reported for A³ coupling reactions.^[52–69] Along this line, recyclable gold nanoparticles (NPs) of 20 nm in size have been reported for the synthesis of propargylamines in CH₃CN under efficient reaction conditions.^[70]

However, to date limited heterogeneous magnetic catalysts have been reported for A³ coupling reactions.^[71–80] Among the various solids for the preparation of heterogeneous catalysts, magnetic NPs having high surface area and being easy to separate from a reaction mixture are recognized as excellent supports for heterogeneous catalyst design.^[81] In recent years ligands such as phosphoand nitrogen-based ligands were used for rusmodification and stabilization of Fe₃O₄ NPs. Very recently, triazoles have been recognized as excellent ligands for metal catalyst stabilization.^[82-104] These highly stable heterocyclic compounds can be produced by the reaction of terminal alkynes with organic azides catalysed by copper (I) complexes.^[105–107]

In continuation of our interest in heterogeneous catalysis of A³ coupling reactions,^[108,109] we envisaged that the use of new magnetic NPs modified with a pyridyl-triazole ligand could contribute to the stabilization of gold NPs and be applied as an efficient heterogeneous recyclable catalyst for propargylamine preparation via an A³ coupling reaction.

2 **RESULTS AND DISCUSSION**

The ligand, (1-(pyridin-2-ylmethyl)-1*H*-1,2,3-triazol-4-yl) methanol, was prepared by reaction of 2-(bromomethyl)



FIGURE 1 TGA curves of materials 1 and 2



SCHEME 1 Preparation of



FIGURE 2 SEM images of Fe₃O₄@PT@Au (3) at different magnifications



FIGURE 3 EDS mapping images of (a) Au, (b) C, (c) Fe, (d) N, (e) O and (f) Si for **3**

pyridine hydrobromide with NaN₃ and propargylalcohol catalysed by copper (I) iodide. Magnetite NPs were prepared by a co-precipitation method from the reaction of FeCl₃ ·6H₂O and FeCl₂ ·4H₂O salts.^[110] The thus prepared Fe₃O₄ NPs were coated with a thin layer of silica using a sol–gel process to afford core–shell

Fe₃O₄@SiO₂ NPs (Figure S1 in supporting information). Fourier transform infrared spectrum of Fe₃O₄@SiO₂ showed peaks at 1097 and 1627 cm⁻¹ related to Si– O– Fe and bending vibration of water adsorbed on the surface, respectively (Figure S2 in supporting information). Then, chloro group was introduced on



the surface of Fe_3O_4 @SiO₂ NPs by the reaction with 3-chloropropyltrimethoxysilane. The resulting Fe_3O_4 @SiO₂@Cl NPs (1) were allowed to react with the already prepared (1-(pyridin-2-ylmethyl)-1H-1,2,3triazol-4-yl) methanol ligand using sodium hydride as a base. Finally, ligand-modified Fe_3O_4 NPs (2) were treated with NaAuCl₄ ·2H₂O and NaBH₄ to produce the new magnetic supported gold NPs (Fe_3O_4 @PT@Au;



FIGURE 4 EDS spectrum of Fe₃O₄@PT@Au (3)



FIGURE 6 Magnetization curves for Fe_3O_4 , $Fe_3O_4@SiO_2@Cl(1)$, $Fe_3O_4@SiO_2@ligand (2)$ and $Fe_3O_4@PT@Au(3)$



FIGURE 7 XRD pattern of Fe₃O₄@PT@Au (3)



FIGURE 5 TEM images of Fe_3O_4 @PT@Au (3) under different magnifications

3). The preparation is shown in Scheme 1. Based on atomic absorption spectroscopy (AAS) analysis, the amount of Au in Fe₃O₄@PT@Au (3) was found to be 0.01 mmol g^{-1} .

Thermogravimetric analysis (TGA) of **1** showed a twostep weight loss between 25 and 800 °C (Figure 1). The first weight loss was attributed to water and physically adsorbed solvents and the second to the organic residues attached to the surface of the support. The TGA curve of ligand-functionalized solid **2** also showed a two-step weight loss. As shown in Figure 1, with an increase in



FIGURE 8 XPS spectra of Fe_3O_4 @PT@Au (3) in (a) Fe 2p, (b) Au 4f, (c) N 1 s and (d) C 1 s regions

loading of organic compounds, weight losses are observable which confirm the successful addition of the pyridyl-triazole ligand.

Scanning electron microscopy (SEM) images of **3** showed a uniform morphology of these nanoparticles (Figure 2). On the other hand, SEM mapping images confirmed the presence of Au, C, Fe, N, O and Si atoms, which are uniformly located in the structure (Figure 3). In addition, the presence of various elements such as Au, N, Si, Fe and C was confirmed using energy-dispersive X-ray spectroscopy (EDS) (Figure 4).

Furthermore, transmission electron microscopy (TEM) images of **3** at different magnifications showed the presence of highly uniform and mono-dispersed Au NPs supported on the core-shell structure of Fe_3O_4 @PT@Au (Figure 5).

In order to analyse the superparamagnetic properties of the prepared magnetic materials, magnetization curves of Fe₃O₄, **1**, **2** and **3** were studied. Results indicated a significant decrease in magnetization value in Fe₃O₄@SiO₂@Cl compared to Fe₃O₄ confirming the successful attachment of silvl and organic groups (Figure 6). Moreover, after the addition of ligand, a small decrease in magnetization with respect to the previous structure was detected. However, the final Au catalyst, Fe₃O₄@PT@Au, has a magnetization behaviour similar to that Fe₃O₄@SiO₂@ligand NPs. Also, all prepared materials showed zero coercivity and remanence without the presence of hysteresis loops confirming the superparamagnetic nature of the samples.

	Br H +	+ $\overset{H}{\overset{N}}$ + $\overset{Fe_3O_4@PT@Au}{Solvent, T, 1 d}$		
Yield (%) ^b	Temp. (°C)	Solvent	Catalyst (mol%)	Entry
86	50	H ₂ O	0.01	1
100	80	H ₂ O	0.01	2
92	80	H ₂ O	0.007	3
87	80	H ₂ O	0.005	4
30	80	1,4-Dioxane	0.01	5
23	80	DMF	0.01	6
14	80	PhCH ₃	0.01	7
15	80	CH ₃ CN	0.01	8

 TABLE 1
 Optimization of reaction conditions for reaction of 4-bromobenzaldehyde, piperidine and phenylacetylene catalysed by 3^a

^aReaction conditions: 4-bromobenzaldehyde (1 mmol), piperidine (1.5 mmol), phenylacetylene (1.5 mmol) and solvent (2 ml) for 1 d. ^bYields determined by ¹H NMR. 6 of 15 WILEY Organometallic-

TABLE 2 Reactions of aldehydes, amines and alkynes in the presence of Fe₃O₄@PT@Au as catalyst^a

	R ¹ CHO + R ² ₂ NH +	R ³ 3 (0.01 mol%) H ₂ O, 80 °C, 1	$d = R^{1}$	
Entry	R ¹ CHO	R ² ₂ NH	Product	Yield (%) ^b
1	O H	N H		93
2	CI H	N H	Cl N	95
3	CI H	N H		90
4	CI CI	N H		93
5	MeO	N H	OMe N	85
6	O H	N H		90
7	O H	N H		89
8	O H H	N H		86

(Continues)



TABLE 2 (Continued)

	R ¹ CHO + R ² ₂ NH +	R ³ <u>3 (0.01 mol%)</u> H ₂ O, 80 °C, 1	R^1 NR^2_2	
Entry	R ¹ CHO	R ² ₂ NH	Product	Yield (%) ^b
9	O H H	↓ H H		88
10	CHO	N H		76
11	∕∕∕µ ⁰	N H		90
12	о Ч S	N H	S N N	90
13	O H	N H		79
14	O H	N H		87
15	O H	∠N H		93
16	Br H	∠N H	Br N	94

(Continues)

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TABLE 2 (Continued)



^aReaction conditions: aldehyde (1 mmol), amine (1.5 mmol), alkyne (1.5 mmol), H₂O (2 ml), catalyst (10 mg, 0.01 mol%), and during 1 d. ^bIsolated yields after column chromatography.

X-ray diffraction (XRD) analysis of the prepared catalyst showed the presence of Fe₃O₄ NPs by screening Bragg's reflections at $2\theta = 30.18^{\circ}$, 35.5° , 43.4° , 53.5° , 57.2° and 62.8° corresponding to the (210), (311), (400), (422), (511) and (440) planes of Fe₃O₄ NPs, respectively.^[111] Due to low loading weight of Au, peaks relating to metallic gold were weak and appeared at $2\theta = 38^{\circ}$, 44.2° , 65° and 78° (Figure 7).^[112,113]

The X-ray photoelectron spectrum (XPS) of the Fe 2p region shows two main binding energy peaks corresponding to the electronic states of Fe $2p_{3/2}$ and Fe $2p_{1/2}$ which can be deconvoluted into six peaks. Peaks at 710.5 and

723.7 eV are related to Fe (II) and peaks located at 713.1 and 726.1 eV are in good agreement with Fe (III) oxidation state in the Fe₃O₄ phase. The small satellite peaks at 718.2 and 732.7 eV are related to Fe³⁺ in the Fe₂O₃ phase, suggesting that the surface of Fe₃O₄ was partially oxidized to γ -Fe₂O₃ (Figure 8a).^[114–116] In the case of the XPS spectrum for the Au 4f region, a doublet peak at 83.9 and 87.5 eV corresponding to Au(0) was observed, comprising the only Au species in the material (Figure 8b).^[108] Moreover, the N 1 s core-level spectrum confirms the presence of nitrogen by revealing a peak at 399.9 eV (Figure 8c).^[115] The C 1 s XPS spectrum showed

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three peaks centred at 284.6, 286.4 and 288.5 eV, which are related to C– C or C= C, C– N or C– O and C= N forms of carbon, respectively (Figure 8d).^[117–120]

The catalytic activity of 3 was evaluated in the threecomponent coupling reaction of amines, aldehydes and alkynes (A³ coupling). Initial experiments using 4bromobenzaldehyde, piperidine and phenylacetylene were performed to optimize the reaction conditions. Using catalyst 3 (0.01 mol% loading) in water at 50 °C, a yield of 86% for the reaction was obtained (Table 1, entry 1). Moreover, by using 0.01 mol% of catalyst at 80 °C, the reaction took place quantitatively (Table 1, entry 2). By lowering the catalyst amount to 0.007 and 0.005 mol%, lower yields were observed (Table 1, entries 3 and 4). However, using 0.01 mol% of catalyst in other solvents such as 1,4-dioxane, dimethylformamide (DMF), toluene and CH₃CN afforded lower reaction yields (Table 1, entries 5-8). Therefore, we selected water as a green and non-toxic solvent, 0.01 mol% catalyst loading and 80 °C reaction temperature as the most efficient and optimized reaction conditions to study the scope of this A^3 coupling.

The three-component reactions of structurally different aldehydes, amines and alkynes using 0.01 mol% of catalyst 3 were studied. Reactions of aldehydes having electron-withdrawing and electron-donating groups such as - Cl, - Me, - OMe and isopropyl as well as 1-naphthaldehyde with piperidine and phenylacetylene proceeded well and corresponding propargylamines were obtained in high to excellent isolated yields (Table 2, entries 1-10). In the case of the reaction of heptanal as aliphatic aldehyde with piperidine and an phenylacetylene the desired product was obtained in WILEY-Organometallic 9 of 15 Chemistry

90% isolated yield (Table 2, entry 11). Furthermore, of challenging heterocyclic thiophene-3reaction carbaldehyde with piperidine and phenylacetylene proceeded efficiently and the corresponding propargylamine was obtained in 90% yield (Table 2, entry 12). Reaction of 1,1'-biphenyl-4-carbaldehyde with piperidine and phenylacetylene was also studied and results showed the formation of the corresponding product in 79% isolated yield (Table 2, entry 13). It should be noted that in this case the low solubility of aldehydes in water may be responsible for a lower reactivity. Reaction of 1-octyne as aliphatic alkyne with benzaldehyde and piperidine was also studied and the obtained results showed the formation of corresponding product in 87% isolated yield (Table 2, entry 14). In addition, reactions of aldehydes with pyrrolidine or morpholine and phenylacetylene under optimized reaction conditions were investigated. In these cases, A³ coupling reactions proceeded efficiently and afforded the corresponding



FIGURE 9 Recycling of catalyst **3** for the reaction of benzaldehyde, piperidine and phenylacetylene

	Me H + H	Catalyst Solvent, T	Me	
Catalyst	Temp. (°C)	Time (h)	Au (mol%)	Yield (%)
Fe ₃ O ₄ @PT@Au	80	24	0.01	90
Au ₃₈ (SC ₂ H ₄ Ph) ₂₄ ^[48]	80	5	0.01	84
Au NPs ^[61]	75	12	10	83
Au@HS-MCM ^[66]	80	24	2	75
IRMOF-3-LA-Au ^[67]	80	7	1.7	54
NP@Au/NNN-pincer ^[79]	85	8	0.07	83
Fe ₃ O ₄ @Au ^[80]	100	24	10	63
Au@PMO-IL ^[106]	60	24	0.2	88

TABLE 3 Comparison of catalytic activity of Fe_3O_4 @PT@Au with that of other reported Au catalysts in A³ coupling reaction of 4-methylbenzaldehyde, piperidine and phenylacetylene

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propargylamines in high to excellent yields (Table 2, entries 15–22).

The catalytic activity of Fe_3O_4 @PT@Au was compared with that of some previously reported goldcatalysed A^3 coupling reactions (Table 3), showing the efficiency of the present catalyst.

Recycling of heterogeneous noble metal-based catalysts is very important from economic and sustainable chemistry standpoints. Therefore, we studied the recycling of catalyst **3** for the reaction of benzaldehyde, piperidine and phenylacetylene under the optimized reaction conditions. For this purpose, after completion of the reaction, the catalyst was separated using an external magnet and reused in another run of the



FIGURE 10 TEM images of reused catalyst 3 after 10 runs

reaction. Results of this study indicated that on recycling the catalyst for seven consecutive runs a drop in reaction yields of only 6% was observed. However, after the seventh run the yields started to decrease and in the tenth run the product was obtained in a yield of 78% (Figure 9).

TEM images of the reused catalyst after 10 runs showed the preservation of the core-shell structure of the catalyst and the presence of mostly uniform gold NPs and some aggregate species (Figure 10). The TGA curve of reused catalyst after 10 runs had a pattern very similar to that of the fresh catalyst showing that the catalyst structure was stable during the recycling experiments (Figure 11). Comparison of the magnetization curve of reused catalyst after 10 runs with that of fresh catalyst showed very small decrease in the magnetization value and preservation of the superparamagnetic properties suggesting high stability of the catalyst structure during the recycling processes (Figure 12). Finally, XPS analysis of the reused catalyst after 10 runs showed that the Au NPs were in metallic form and Fe, C and N were in forms similar to those of the fresh catalyst (Figure 13).



FIGURE 11 TGA of reused catalyst 3 after 10 runs



FIGURE 12 Magnetization curves of catalyst **3** and of the reused catalyst after 10 runs



FIGURE 13 XPS spectra of reused catalyst **3** after 10 runs in (a) Fe 2p, (b) Au 4f, (c) N 1 s and (d) C 1 s regions

3 | CONCLUSIONS

The synthesized pyridyl-triazole ligand used for modification of Fe_3O_4 NPs was able to stabilize uniform gold NPs. The characterization of these Fe_3O_4 @PT@Au NPs using various methods such as SEM, TEM, AAS, XRD, XPS, TGA, vibrating sample magnetometry and SEM mapping supports the structure of this material. This new magnetic gold composite was applied as a catalyst in A³ coupling reactions. Various aldehydes and amines reacted efficiently with alkynes in water as solvent at 80 °C affording the corresponding propargylamines in high to excellent yields. This catalyst can be easily recovered by simple separation with a magnet and reused for at least seven cycles without appreciate loss of catalytic activity.

4 | EXPERIMENTAL

4.1 | General

All chemicals were purchased from Sigma-Aldrich, Acros and Merck and were used without further purification. All ¹H NMR and ¹³C NMR spectra were recorded with a Bruker spectrometer at 400 MHz and 100 MHz, respectively. Chemical shifts were recorded with reference to tetramethylsilane as the internal standard. TGA was performed at 25–800 °C in an oxygen flow using a NETZSCH STA 409 PC/PG instrument. TEM and SEM images were captured with JEOL JEM-2010 and JEOL JSM 840 instruments, respectively. XPS analyses were performed using a K-Alpha spectrometer. Magnetic measurements were performed using vibrating sample magnetometry (MDK Co., Kashan, Iran). XRD patterns were recorded using a Philips X'Pert Pro instrument. EDS measurements were obtained using a Carl Zeiss Sigma instrument. The content of gold in the catalyst was determined using a Varian AAS instrument.

4.2 | Synthesis of Fe₃O₄ NPs

Magnetic (Fe₃O₄) nanoparticles were prepared using a reported co-precipitation method.^[105] FeCl₃ ·6H₂O (16 mmol, 4.32 g) and FeCl₂ ·4H₂O (8 mmol, 1.59 g) were dissolved in deionized water (250 ml) and stirred for 10 min at room temperature. Then, aqueous ammonia (25%, 13 ml) was added slowly over 20 min and the mixture was stirred at 80 °C for 4 h under argon atmosphere. The black magnetic precipitates were separated using an external magnet and washed with deionized water (3 × 10 ml) and ethanol (3 × 10 ml) and dried in a vacuum oven at 60 °C for 24 h.

4.3 | Synthesis of Fe₃O₄@SiO₂ NPs

The prepared Fe_3O_4 NPs (1 g) were sonicated in ethanol (200 ml) for 30 min. Then, aqueous ammonia (6 ml) and tetraethyl orthosilicate (2 ml) were added and the mixture was stirred for 24 h at room temperature. Then, the reaction mixture was subjected to magnetic separation and the obtained material was washed with deionized water (3 × 10 ml) and ethanol (3 × 10 ml) and dried under vacuum at 60 °C.

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4.4 | Synthesis of Fe_3O_4 $(0.5iO_2)$ $(0.5iO_2)$

Fe₃O₄@SiO₂ NPs (1 g) were sonicated in dried toluene (50 ml) followed by dropwise addition of)3-chloropropyl) trimethoxysilane (1.3 ml). The reaction mixture was refluxed for 24 h under argon atmosphere. Then, the resultant solids were collected using a magnet, washed with ethanol $(3 \times 10 \text{ ml})$, rinsed and dried under vacuum at 60 °C.

4.5 | Synthesis of (1-(Pyridin-2-ylmethyl)-1H-1, 2,3-triazol-4-yl)methanol

2-Bromoethylpyridine hydrobromide (4 mmol, 1 g) and NaN_3 (6 mmol, 0.39 g) were added to stirring solution of acetone (20 ml). In order to dissolve the NaN₃, water (2 ml) was added and the solution was refluxed for 2 h at 60 °C. Then, Et₃N (8 mmol, 1 ml), propargyl alcohol (6 mmol, 0.3 ml) and copper (I) iodide (0.05 mmol, 9.5 mg) were added and the reaction mixture was refluxed for 24 h at 60 °C. The acetone was evaporated and the residue was washed with water and dichloromethane to extract the product to the organic phase. Further purification was achieved using column chromatography with hexane, ethyl acetate and ethanol as eluents. The resulting product was obtained in 84% yield and characterized using ¹H NMR and ¹³C NMR spectroscopies.

4.6 | Synthesis of Ligand-Functionalized Magnetic NPs (2)

Fe₃O₄@SiO₂@Cl (1 g) was sonicated and dispersed in dry 1,4-dioxane (15 ml) for 30 min. In a separate reaction batch, NaH (4 mmol, 0.1 g) was added to (1-(pyridin-2ylmethyl)-1H-1,2,3-triazol-4-yl) methanol (3 mmol, 0.6 g) in dry 1,4-dioxane (15 ml) under argon and the reaction mixture was stirred for 15 min at 25 °C. Then, resulting mixture was added to the flask containing Fe₃O₄@SiO₂@Cl under argon protection and the reaction mixture was stirred at 100 °C for 24 h. The obtained Fe₃O₄@SiO₂@Cl@Ligand (2) was subjected to separation with a magnet and the obtained material was washed with deionized water $(2 \times 10 \text{ ml})$ and ethanol $(2 \times 10 \text{ ml})$ and dried under vacuum at 60 °C.

4.7 | Synthesis of Fe₃O₄@PT@Au Catalyst (3)

Compound 2 (1 g) was sonicated in 12 ml of H_2O- CH₃OH (2:1) for 30 min at room temperature. Then, a solution of NaAuCl₄ ·2H₂O (0.012 mmol, 4.8 mg) was added. Then, an aqueous solution of NaBH₄ (0.3 mmol, 11.3 mg in 1 ml of water) was added slowly and the mixture was stirred for 24 h at room temperature under argon atmosphere. The resulting solid was separated with a magnet, washed with water $(2 \times 10 \text{ ml})$ and ethanol $(2 \times 10 \text{ ml})$ and dried in an oven at 60 °C.

4.8 | General Procedure for Synthesis of **Propargylamines**

The catalyst (10 mg, 0.01 mol%) was added to a mixture of aldehyde (1 mmol), phenylacetylene (1.5 mmol) and amine (1.5 mmol) in water (2 ml) and the mixture was stirred at 80 °C for 24 h under argon atmosphere. After the complication of reaction, the crude products were extracted using ethyl acetate $(4 \times 5 \text{ ml})$. Further purification was performed by column chromatography on silica gel using hexane and ethyl acetate as eluent. All products were known and confirmed using ¹H NMR and ¹³C NMR analyses.

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ORCID

Mohammad Gholinejad D http://orcid.org/0000-0003-0209-4509

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