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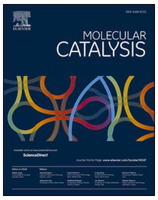

Gold nanoparticle stabilized dithiocarbamate functionalized magnetite carbon as promise clean nanocatalyst for A^3-coupling organic transformation

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A R T I C L E I N F O

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A B S T R A C T

A novel, efficient, and core/shell nanosphere catalyst (Fe_3O_4@C-NHCS-Au^0) was successfully synthesized with a movable magnetite core encapsulated in a carbon shell. It was modified using APTES (3-aminopropyltriethoxysilane) to convert dithiocarbamate (DTC) functional group in the carbon surface though post-modification with CS_2 (carbon disulfide). Au^0-nanoparticles were decorated via DTC binder to improve the catalytic activity. It was applied as a high-efficiency nanocatalyst in promoting three-component A^3 coupling reaction of alkynes, aldehydes, and amines for the synthesis of propargyl amines under the optimized condition.

1. Introduction

Magnetic nanoparticles of magnetite (Fe_3O_4) and its modified core-shell functionalized hybrid materials, are arguably the most extensively studied in chemistry and industry as a green recoverable magnetically catalyst for several organic transformations, e.g. preparation of propargyl amines [1,2]. Functionalized magnetite can be easy the recovery of nanocatalysts effectively from the reaction media by an outer permanent magnetic field [3,4]. Nevertheless, the main limitation of the practical application of Fe_3O_4 is extremely susceptible to oxidative and acidic conditions [5,6]. Maintaining the stability of the magnetite is performed by coating an external protective layer to avoid coagulation mass and corrosion. To achieve this, an effective method is encapsulating Fe_3O_4 nanoparticles by a coating material from organic substance and polymer. Glucose, one of organic coating material can be used as a particle size reduction agent for Fe_3O_4 to manufacture Fe_3O_4@C core-shell nanostructures with a carbon shell and magnetic core [6]. Moreover, in the catalysis of many reactions, core-shell nanocatalysts are very effective [7]. Fe_3O_4@C core-shell nanoparticles have technical applications as a result of useful properties of carbon coating containing naturally porous structure and high stability under extreme conditions. These nanostructures are being utilized in different fields e.g. medicine, catalyst, magnetic resonance imaging (MRI), targeting drug delivery, immunoassay, biology, and separation approaches [8–12]. Common application of Fe_3O_4@C is because of their unique characteristics including great specific surface area, hydrophobic, small size, low toxicity, biocompatibility, chemically inert, great saturation magnetization level, and injectability in industrial uses [13].

The matrices of magnetic nanocomposite as both the support and the nanoparticles stabilizer provide a mechanism for preventing aggregation. Also, magnetic separation instead of centrifugation or filtration decreases wasted catalyst and increases the recoverability [14–16].

In recent years, a large number of multicomponent reactions (MCRs) have been improved as a powerful and efficient tool for assembling complex molecules with significant biologic properties through the several simple and accessible precursors in a one-pot process [17]. Nowadays, the importance and usefulness of MCRs are well-known [18–20]. Among the various MCRs, 3-CR (three-component reaction)

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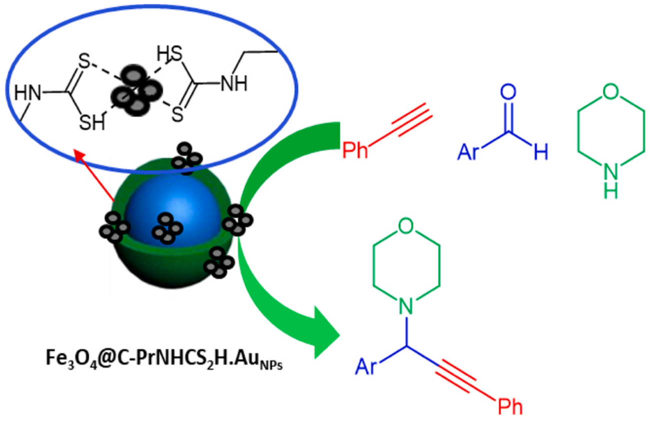


Scheme 1. A^3 coupling reaction over Gold nanoparticle stabilized magnetic carbon.

of amines, aldehydes, and terminal alkynes (the A3 coupling reaction) is a powerful, useful, and selective way for the production of valuable propargylamine compounds [21]. Propargylamines have emerged as synthetically flexible important skeletons and main intermediates for the synthesis of many nitrogenous-including biologic active molecules, e.g. oxotremorine analogs, β-lactams, polyfunctional amino compounds, natural products e.g. fungicides, herbicides, and polymers, agricultural chemicals, pharmaceutical materials as the therapeutic agents of Alzheimer's and Parkinson's disease [21–26].

The traditional procedure for propargylamine production is catalyzed A3-coupling using some transition metal that is performed by nucleophilic addition of Grignard reactants on imines or lithium acetylides [27]. However, reactants in this approach are very sensitive to moisture which requires highly regulated reaction conditions and so the use of the reactants in stoichiometric amounts. In the existence of more active groups of esters, this method is limited [1,28]. A3-coupling, catalytic C–H activation is an alternative eco-friendly and atom-economical process to manufacture of propargyl amines with the theoretical side product only water [29,30].

Recently, direct addition of terminal alkynes on C═N double bonds prepared from either amines and aldehydes or imines in one-pot method via activation of alkynes C—H bond by some noble transition- metal catalysts under both homogeneous by several salts and complexes such as gold,[21,31–33] copper,[21,34,35] silver,[21,33,36,37] zinc,[21,38,39] nickel,[40] iron,[41] mercury,[42] cobalt,[43] iridium,[44] ruthenium,[45] indium,[46] zirconium,[47] rhenium,[48], Polyoxovanadate [49] and so on and heterogeneous [50–58] supported (AgI, AuIII, CuI, etc) and (CuI, AgI, and AuI in ionic liquids) conditions have been successfully utilized to catalyze A3 coupling reaction.

Dithiocarbamates, the soft sulfur donor ligands can be easily stabilized unusually high oxidation states of transition metals. Metal dithiocarbamates have two advantages: (*i*) easy hand working in anhydrous form and chemic stability; (*ii*) good solubility in organic solvents [59–63].

Gold catalysts, especially the catalysts of Au nanoparticles, have attracted much attention, given their comprehensive role as catalysts in the preparation of propargylamine through the activation of C–H (coupling reaction A3) [64–66]. In continuous of our efforts for designing novel nanocomposites and because of high-value of the propargyl amines herein, we reported a magnetic dithiocarbamate-functionalized core/shell nanostructure Fe_3O_4@C, which decorated with the substantial impact of Au0-nanoparticles were utilized as heterogeneous catalysts in the synthesis of propargyl amines under mild reaction conditions with good to excellent yield (Scheme 1).

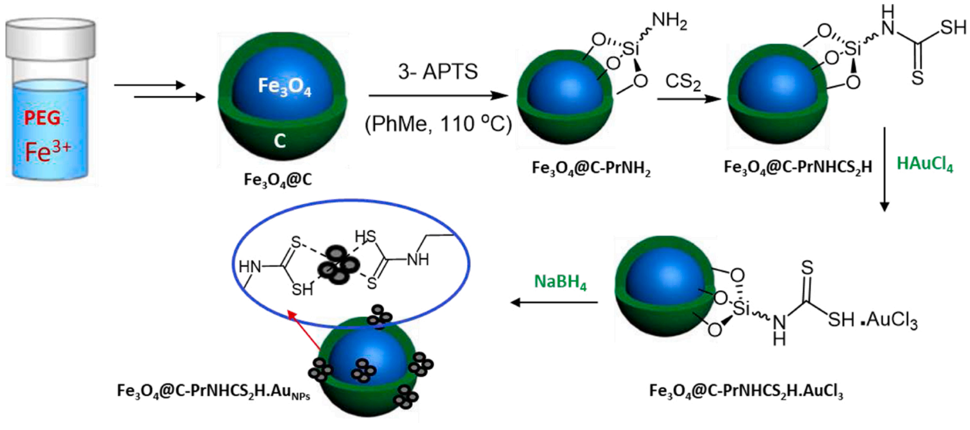
2. Experimental

2.1. Chemicals and apparatus

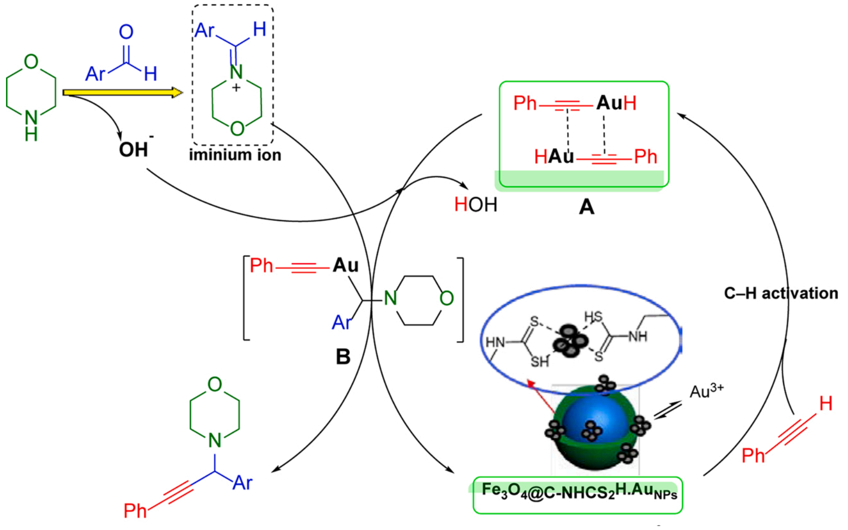
All reagents were obtained commercially from Merck, Sigma, and were used without purification. FT-IR spectra were recorded with a shimadazu IR-640 spectrometer. The crystalline phases of the particles were recognized by Philips-PW1800 diffractometer XRD instrument. The 1H and 13C NMR spectra were recorded on a Bruker Avance 300 spectrometers. Melting points were measured on an Electrothermal 9100 apparatus.

2.2. Synthesis of Fe_3O_4@C-$NHCS_2H$ nanoparticles

Fe_3O_4 nanoparticles were prepared corresponding to the Zhao route [67]. Firstly, $FeCl_3.6H_2O$ (1.5 g, 5.55 mmol) and Polyvinylpyrrolidone (PVP, 1 g), and NaOAc (2 g) were dissolved in EG (ethylene glycol 30 mL) and stirred for 2 h. After transferring the mixture to a Teflon-line autoclave was sealed. After heating it for 10 h at 210 °C, the black sediment was collected by an external magnet after washing with distilled water and ethanol for several times. Encapsulation of prepared Fe_3O_4 nanoparticles with carbon shell was done with an improvement of *literature* [68]. 0.1 g of the synthesized Fe_3O_4 was dispersed under ultrasonication in 30 mL water containing 2.0 g glucose. After transferring the mixture to a Teflon-line autoclave with a 100 mL capacity was heated at for 12.5 h 205 °C. Then, the black solid product was gathered using an external magnet from the mixture and washed for several times with water. Finally, it was dried at 60 °C for 24 h in vacuum. The synthesized Fe_3O_4@C was functionalized corresponding to the *literature* [69]. Fe_3O_4@C (0.1 g) was dispersed with ultrasonication in toluene (10 mL) and after adding 2 mL of APTES to the mixture refluxed



Scheme 2. Schematic way for the immobilization of Au onto the Fe_3O_4@C-$NHCS_2H$.



Scheme 3. A plausible mechanism for the Au-catalyzed A^3-coupling.

for 2 h at 110° C. Finally, the black solid was separated by an external magnet and washed for several times with ethanol. Afterward, it was dispersed in 10 mL methanol and kept it in sonicate condition for 10 min. Finally, 1.1 mL carbon disulfide (CS_2) was added to the reaction mixture and stirred for more than 12 h. The final product Dithiocarbamate functionalized magnetic carbon (Fe_3O_4@C-$NHCS_2H$) was collected using a magnet, washed with ethanol, and dried for 5 h at 60–70 ° C.

2.3. Au $_{NPs}$ immobilization onto the Fe_3O_4@C-$NHCS_2H$

Au nanoparticles on to the dithiocarbamate functionalized magnetic carbon (Fe_3O_4@C-$NHCS_2H$) were immobilized on the support based on *literature* [70]. Typically, 0.3 g of Fe_3O_4@C-$NHCS_2H$ were added to 0.12 M $HAuCl_4$ aqueous solution (10 mL), after 5 min sonication, it was kept for 24 h under stirring. Finally, the black reaction mixture was filtered by an external magnet the obtained solid was washed with ethanol (EtOH) for three times to gain Fe_3O_4@C-$NHCS_2H.AuCl_3$. Then, in a separated vessel, 5 mL of 0.2 mol/L of freshly prepared $NaBH_4$ (in methanol) was prepared and dropwise added to a mixture of prepared Fe_3O_4@C-$NHCS_2H.AuCl_3$ in 50 mL dry methanol during 15 min. After, 30 min, the solid products were collected by an external magnet and washed with methanol, obtaining Fe_3O_4@C-$NHCS_2H.Au_{NPs}$.

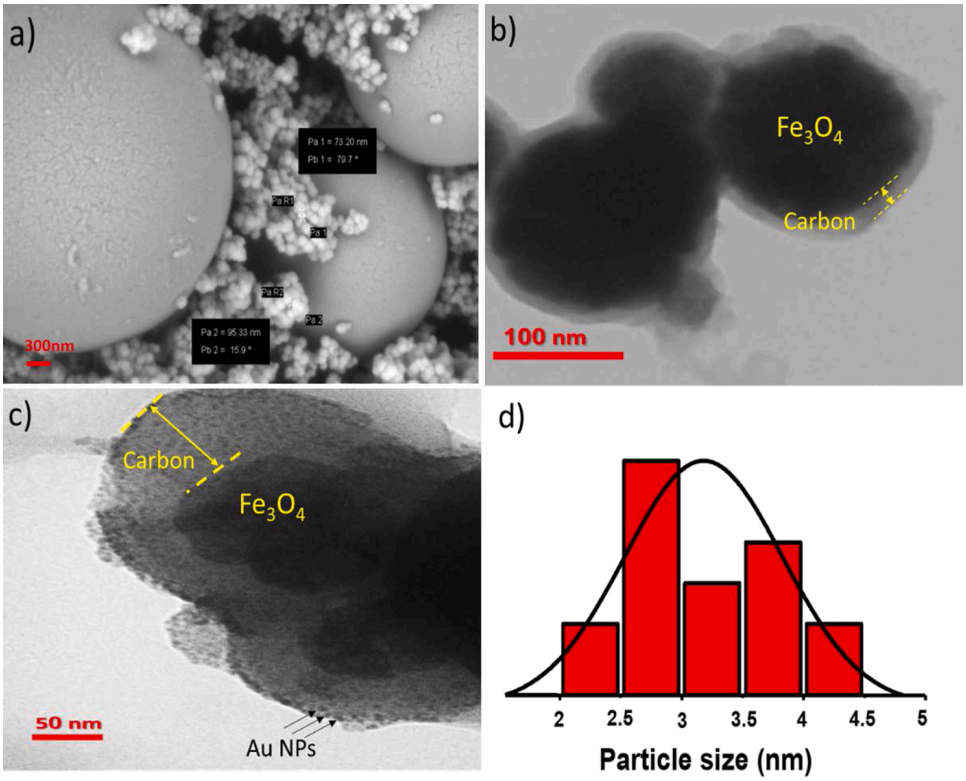


Fig. 1. (a,c) FE-SEM and TEM images of Fe_3O_4@C-$NHCS_2H.Au_{NPs}$ and (b) TEM image of Fe_3O_4@C-$NHCS_2H$, and (d) particle size of Fe_3O_4@C-$NHCS_2H.Au_{NPs}$ microspheres.

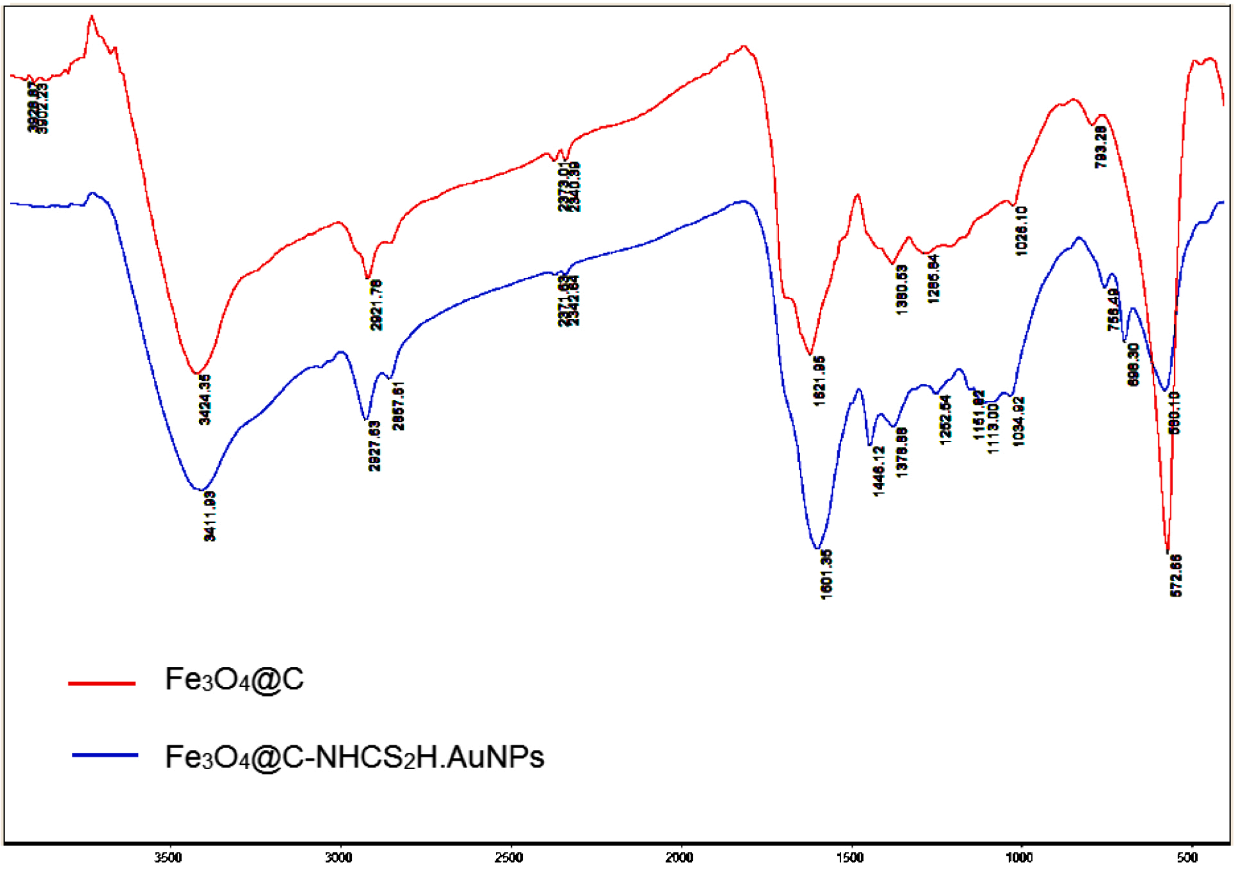


Fig. 2. FTIR spectra of Fe_3O_4@C, and Fe_3O_4@C-$NHCS_2H$.Au_{NPs}.

2.4. General synthesis of propargyl amines

First, 1 mmol of benzaldehyde, 1.2 mmol of morpholine, a 1.3 mmol of phenylacetylene 0.4 g of Fe_3O_4@C-$NHCS_2H$.Au_{NPs}, and 1 mmol of K_2CO_3 were added to 4 mL of $CHCl_3$ and allowed to stirrer at room temperature. The reaction progress was monitored by TLC method. After completion of the reaction, the gold catalyst was removed by an external magnet. The nanocatalyst was then washed with ethyl acetate (3 × 5 mL). The reaction solvent was evaporated to give paste for plate-chromatography. The corresponding propargyl amines were analyzed by physical properties, 1H NMR, and 13C NMR.

1-(1,3-diphenylprop-2-yn-1-yl)piperidine: 1H NMR ($CDCl_3$, 500 MHz): δ_H (ppm) 1.46 (s, 3H, $NCH_2CH_2CH_2$), 1.60–1.66 (m, 6H, $NCH_2CH_2CH_2$), 2.59 (s, 4H, $NCH_2CH_2CH_2$), 4.83 (s, 1H of NCH), 7.32–7.40 (m, *6H of Ar*), 7.53–7.55 (m, *2H of Ar*), 7.65 (d, $3J_{HH}$ =7 Hz, 2 H).

4-(1,3-diphenylprop-2-yn-1-yl)morpholine: 1H NMR ($CDCl_3$, 500 MHz): δ_H (ppm) 2.66 (s, 2H, NCH_2CH_2O), 3.76 (t, $3J_{HH}$ =5.5 Hz, 4H, NCH_2CH_2O), 4.82 (s, 1H of NCH), 7.33–7.41 (m, 6H of Ar), 7.53–7.55 (m, 2H of Ar), 7.64 (d $3J_{HH}$ =7.5 Hz, 2 H). 13C NMR (125 MHz, CDCl3): δ_c (ppm) 62.03 (NCH), 67.17 (NCH_2CH_2O), 85.03 (Ph-C≡C), 88.48 (HCN-C≡C), 122.97, 127.78, 128.23, 128.31, 128.59, 131.81, 137.79.

4-(3-phenyl-1-(p-tolyl)prop-2-yn-1-yl)morpholine: 1H NMR ($CDCl_3$, 500 MHz): δ_H (ppm) 2.66 (s, 3H of Me), 2.71−2.62 (m, 4H, NCH_2CH_2O), 3.80−3.71 (m, 4H, NCH_2CH_2O), 4.87 (s, 1H of NCH), 7.22−7.19 (m, 2H of Ar), 7.36−7.33 (m, 3H of Ar). 13C NMR (125 MHz, CDCl3): δ_c (ppm) 31.7 (CH_3), 50.7 (NCH_2CH_2O), 61.7 (NCH), 67.9 (NCH_2CH_2O), 85.3 (Ph-C≡C), 88.5 (HCN-C≡C), 123.2, 128.3, 128.4, 128.6, 129.1, 131.7, 135.6, 137.6.

1-(1-(2-chlorophenyl)-3-phenylprop-2-yn-1-yl)piperidine: 1H NMR ($CDCl_3$, 500 MHz): δ_H (ppm) 1.44 (t, $3J_{HH}$ =5.5 Hz, 2H, $NCH_2CH_2CH_2$), 1.57–1.61 (m, 4H, $NCH_2CH_2CH_2$), 2.63 (t, $3J_{HH}$ =5.5 Hz, 4H, $NCH_2CH_2CH_2$), 5.12 (s, 1H of NCH), 7.25–7.29 (m, 2H of Ar), 7.34 (t, $3J_{HH}$ =6.5 Hz, 2H of Ar), 7.51–7.53 (m, 1H of Ar), 7.76–7.77 (m, 1H of Ar). 13C NMR (125 MHz, CDCl3): δ_c (ppm) 24.45 ($NCH_2CH_2CH_2$), 26.14 ($NCH_2CH_2CH_2$), 50.70 (NCH), 59.25 ($NCH_2CH_2CH_2$), 85.81 (Ph-C≡C), 87.63 (HCN-C≡C), 123.17, 126.17, 128.13, 128.27, 128.76, 1-(1-(2-chlorophenyl)-3-phenylprop-2-ynyl)morpholine: 1H NMR ($CDCl_3$, 500 MHz): δ_H (ppm) 2.69 (t, $3J_{HH}$ =4.5 Hz, 4H, NCH_2CH_2O), 3.68–3.77 (m, 4H, NCH_2CH_2O), 4.95 (s, 1H of NCH), 7.29–7.36 (m, 5H of Ar), 7.42–7.44 (m, 1H of Ar), 7.51–7.53 (m, 2H of Ar), 7.76 (t, $3J_{HH}$ =2.5 Hz, 1H of Ar).

3. Results and discussion

In the present study, we designed DTC functionalized magnetic core-shell for immobilization ultra-fine Au NPs. In this methodology, the magnetic NPs coated via carbon for functionalized with DTC ligand to be immobilized Au NPs and dispersible in the organic solvent. A schematic illustration of the Fe_3O_4@C-$NHCS_2H$.Au_{NPs} synthesis is shown in Scheme 2.

To verify this speculation, the morphology of the obtained nanosphere has been investigated through FESEM and TEM as shown in (Fig. 1). The FESEM image (Fig. 1a) shown that the of the Fe_3O_4@C-$NHCS_2H$.Au_{NPs} microspheres morphology. The surface of the microsphere with DTC ligand helps for the stabilization of Au NPs and inhibition from agglomeration. From the TEM images can provide more detailed information that enables us to view the spherical Au NPs are well-distributed on the surface of the Fe_3O_4@C-$NHCS_2H$ without significant agglomeration. The size distribution histogram for Au NPs (Fig. 1d) shows a mean diameter of 3.3 ± 0.9 nm, which confirms that Au NPs maintain its high monodispersity profile even after immobilization on the support.

Fig. 2 exhibits the FT-IR spectra of Fe_3O_4@C and the individual Au

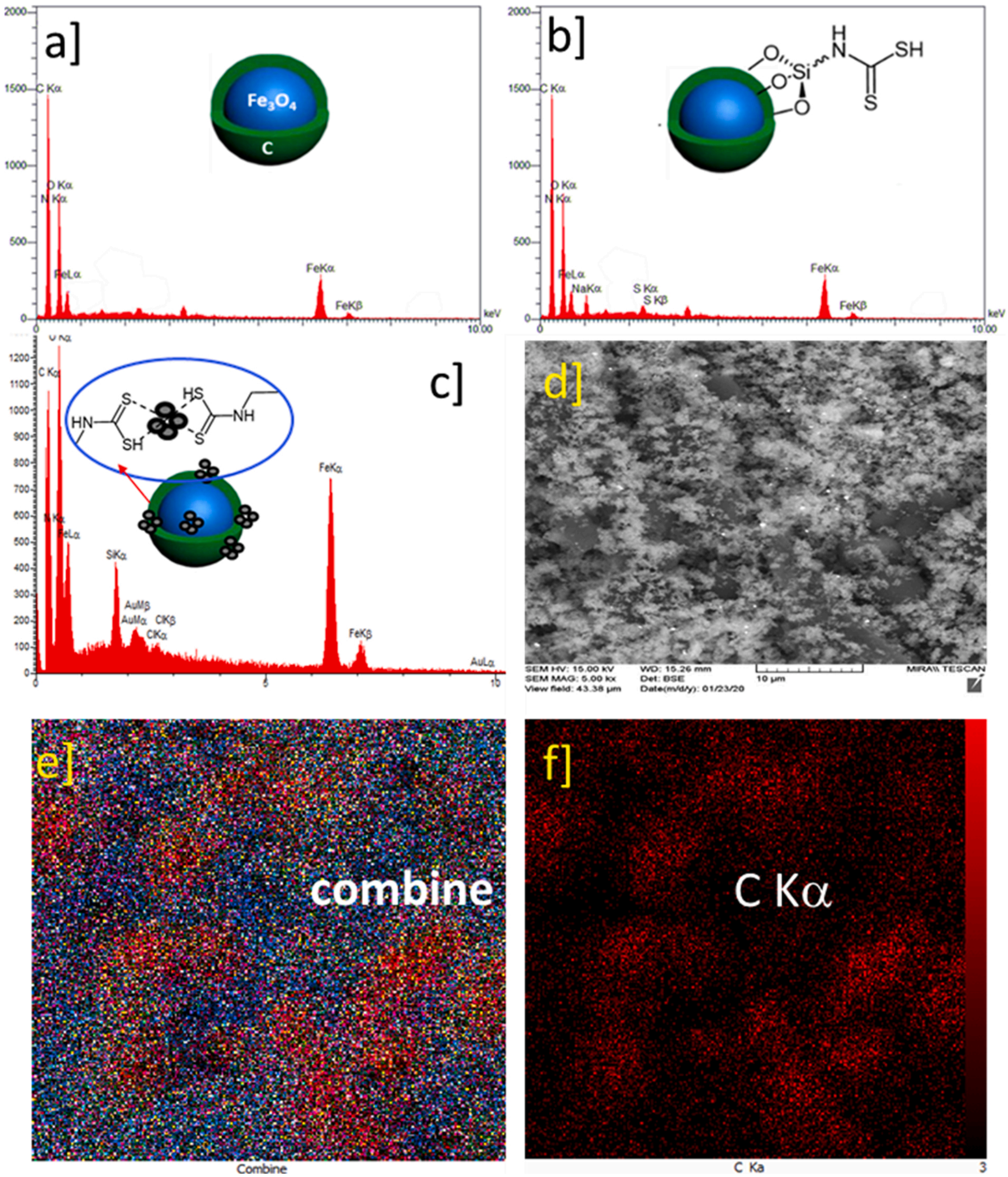


Fig. 3. EDX spectra of Fe_3O_4@C (a), Fe_3O_4@C-$NHCS_2H$ (b), Fe_3O_4@C-$NHCS_2H$.AuNPs microspheres (c). SEM-mapping of Fe3O4@C-NHCS2H.AuNPs (d-f).

nanoparticles synthesized Fe_3O_4@C-$NHCS_2H$.AuNPs in this work. For Fe_3O_4@C, the peaks in the 2900−3000 cm-1 and 3424 cm-1, can be assigned to surface C–H of carbon while O—H functional groups can be attributed to the surface of the carbon. In the spectra of Fe_3O_4@C-$NHCS_2H$.Au nanoparticles, it is worth noting that the peak of Fe_3O_4@C nanoparticles at 1621 cm-1 is red shifted to 1601 cm -1 because of the surface change of bifunctional hybrid nanomaterials. Also, the bands at 1446, 1378, and 1252 cm-1 are assigned to C═S. A characteristic band at 1113 cm-1 can be assigned to the existing CN bonds of DTC. The absorption band at 698 cm−1 referred to the vibration of C–S in the ligand of DTC. These can be proved to the successful synthesis of Fe_3O_4@C-$NHCS_2H$.AuNPs.

To determine the composition of the synthesized metallic Fe_3O_4@C-$NHCS_2H$.AuNPs nanocrystals, EDX spectra and elemental SEM-mapping were recorded, as shown in Fig. 3. The results revealed that the peaks found in the spectrum were derived from C, N, O, S, Au, and Fe atoms, indicating that the purity and successful deposition of Au to Fe_3O_4@C-$NHCS_2H$ microsphere. Wt% of Au in the microsphere was calculated AAS. According to this, the wt% of Au was 1.36 %.

X-ray photoelectron spectra (XPS), one of the most important techniques to determine the oxidation state of surface elements in materials, was used to characterize the Fe_3O_4@C-$NHCS_2H$.AuNPs composites. The XPS spectrum of the gold core levels(4f) shows two intense photo-peaks with maximum BE (binding energy) values of 83.5 and 87.2 eV ascribed

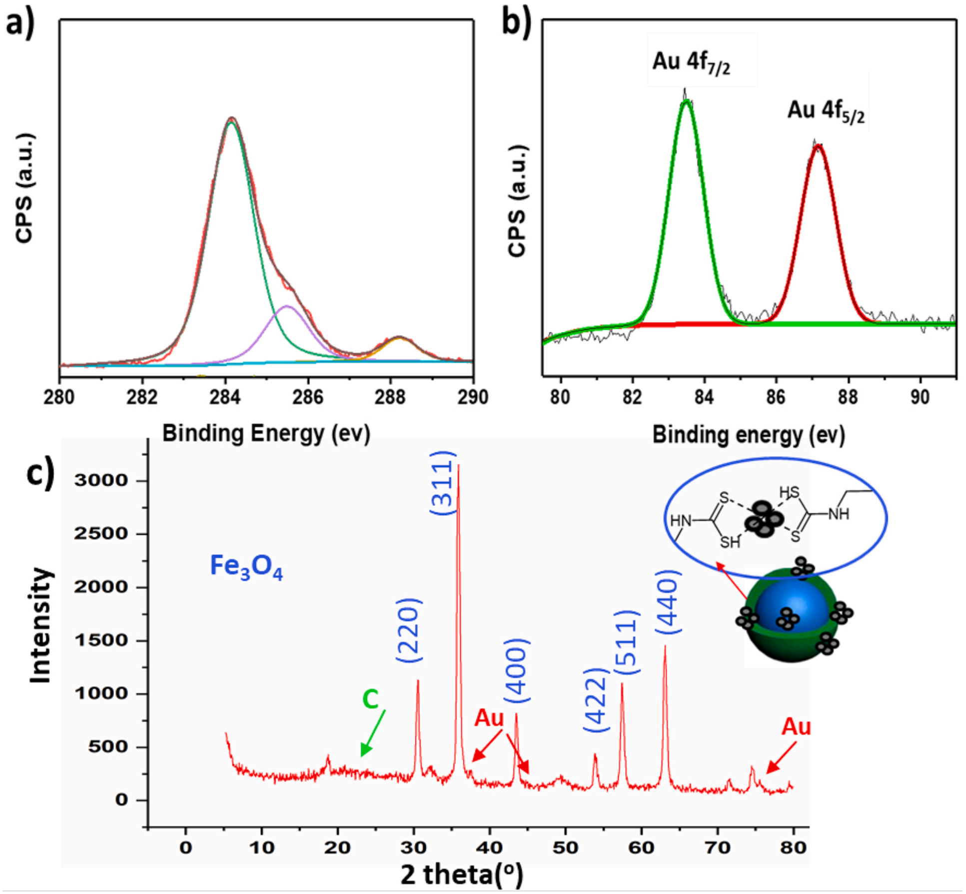
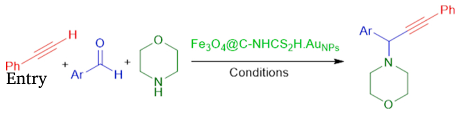


Fig. 4. XPS patterns of Fe_3O_4@C-NHCS$_2$H.Au$_{NPs}$. (a) C1 s; (b) Au 4f. Powder XRD pattern of Fe_3O_4@C-NHCS$_2$H.Au$_{NPs}$ (c).

Table 1
The effect of various solvents [a] on the synthesis of propargylamine.



Entry	Solvent	Base	Temp (°C)	Cat. (mol%)	Time (h)	Yield (%)[b]
1	CH_3CN	KOH	60	0.6	12	68
2	EtOH	KOH	80	0.6	12	35
3	EG	KOH	100	0.6	12	Trace
4	$CHCl_3$	K_2CO_3	60	0.8	12	92

[a] Reaction conditions: morpholine (1.2 mmol), benzaldehyde (1 mmol), and phenylacetylene (1.3 mmol).

[b] Isolated yields.

to the Au 4f7/2 and 4f5/2 doublet, respectively. So, these BE values are consistent with the presence of gold species in the metallic state [71]. The XPS spectrum of the C 1s revealed three peaks located at 284.2, 285.4 and 288.1 eV, which are corresponding to the sp2 bonded carbon in the ligand (C—C), (N—C—C) and (S—C = S) originating from the DTC ligand in structure Fe_3O_4@C, respectively (Fig. 4a, b).

To better understand the crystal structures of as-obtained composite, powder XRD patterns of Fe_3O_4@C-NHCS$_2$H.Au$_{NPs}$ were surveyed (Fig. 4c). The characteristic peaks at $2\theta = 62.6°$, $57.1°$, $53.6°$, $43.2°$, $35.5°$, and $30.2°$ were in good accordance with corresponding Miller index reflection of cubic Fe_3O_4 phase. No obvious peak corresponding to carbon in the XRD pattern demonstrated the amorphous phase of carbon. Also, gold nanoparticles, no remarkable diffraction peaks appeared in the structure of Fe_3O_4@C-NHCS$_2$H.Au$_{NPs}$, which demonstrated that Au NPs were in a low amount.

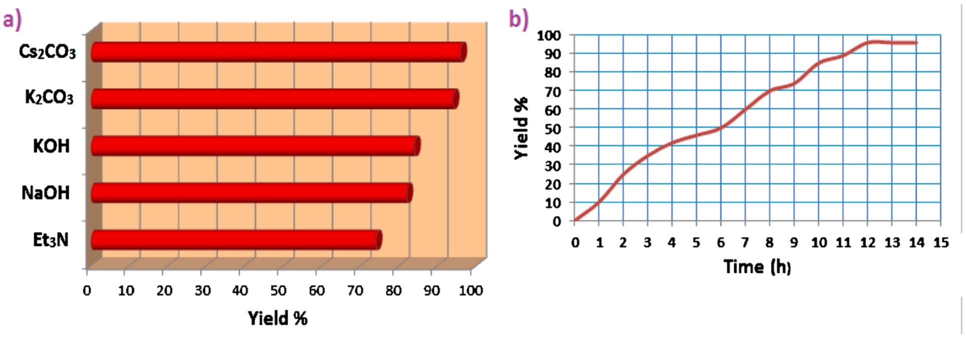


Fig. 5. The base effect (a) and effect of time (b) on the progress of A^3-coupling reaction.

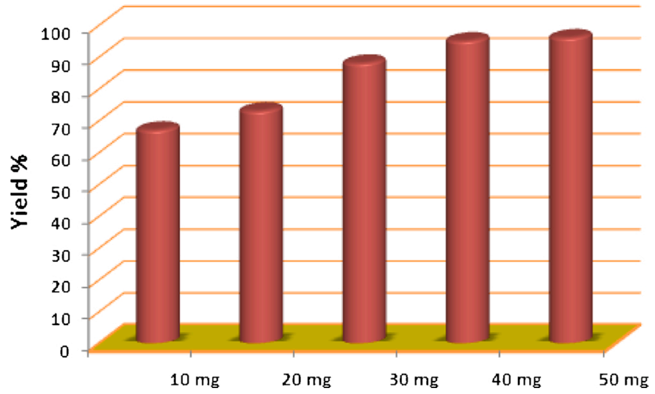


Fig. 6. The effect of mol % of catalysts on A^3-coupling reaction.

3.1. *Catalytic performances*

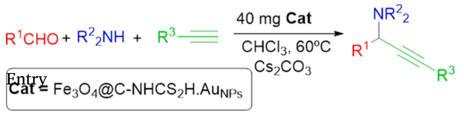
The catalytic activity of the Fe_3O_4@C-$NHCS_2H.Au_{NPs}$ catalyst was examined in the A3-coupling reaction of morpholine, benzaldehyde, and phenylacetylene as the probe reaction. We investigated the effects of temperature, reaction solvents, reaction time, base, and amount of catalyst in A3-coupling. Table 1 summarizes the effects of different solvents and the amount of catalyst. The favorable result was obtained with Fe_3O_4@C-$NHCS_2H.Au_{NPs}$ (40 mg with 0.8 mol% Au NPs) in $CHCl_3$ solvent (Table 1, entry 4).

Different reaction temperatures and base were monitored for observing the activity of Fe_3O_4@C-$NHCS_2H.Au_{NPs}$ in the model reaction. The favorable result was obtained at room temperature and higher than that, no considerable value and change were observed in the reaction yields. For obtaining the best results, Et_3N, NaOH, KOH, K_2CO_3, and Cs_2CO_3 (1 eq) were examined as the base in the model A3-coupling reaction using Fe_3O_4@C-$NHCS_2H.Au_{NPs}$. This test displayed that the best catalytic activity is displayed for Cs_2CO_3 and K_2CO_3 (Fig. 5a). To find an ideal duration for A3 reaction achievement, the reaction progress was screened in each an hour and the reaction kinetics were also shown in Fig. 5b. Start at work, the reaction rate is slow and next, the rate increases along with the reaction progress and finally, the reaction progress (TLC) stops after 12 h. Thus, no considerable change was also observable after 12 h (Fig. 5b).

Several amounts of Fe_3O_4@C-$NHCS_2H.Au_{NPs}$ in terms of Au mol% were tested in the model reaction to obtain an ideal amount of catalyst. Based on this test, the optimal amount of nanocatalyst per each mol of substrate 0.04 g with (0.8 mol% Au NPs) was obtained (Fig. 6).

In command to reach a deeper considerate of whether the proposed catalyst is heterogeneous in nature or not, we performed a series of control experiments such as ICP analysis and HFT (hot filtration test). ICP analysis of A3-coupling reaction indicated that negligible Au leaching occurred. Hot filtration test of the reaction suspension to

Table 2
Synthesis of propargylamine derivatives under the optimized conditions[a].



Entry	R^1	R^2_2NH	R^3	Time (h)	Yield (%) [b]	TON [c]	TOF (h^{-1})[d]	Ref.[e]
1	Ph	Piperidine	Ph	12	**93**	512	43	[72]
2	Ph	Morpholine	Ph	15	**87**	408	27	[73]
3	4-Me-C_6H_4	Piperidine	Ph	18	**83**	–	–	[55]
4	4-Me-C_6H_4	Morpholine	Ph	18	**79**	–	–	[73]
5	2-Cl-C_6H_4	Piperidine	Ph	16	**77**	–	–	[74]
6	2-Cl-C_6H_4	Morpholine	Ph	18	**76**	–	–	[75]
7	4-OMe-C_6H_4	Morpholine	Ph	18	**78**	–	–	[72]
8	2-Me-C_6H_4	Piperidine	Ph	16	**82**	–	–	[74]
9	2-Me-C_6H_4	Morpholine	Ph	18	**78**	–	–	[74]

[a] Reaction conditions: amine (1.2 mmol), aldehyde (1 mmol), and aryl acetylene (1.3 mmol). Yield, TON and TOF calculated based on aldehyde.

[b] Isolated yields.

[c] Turnover number represents the average number of substrate molecules converted into the product per molecule of catalyst.

[d] Turnover number per hour.

[e] Earlier reference of the corresponding product.

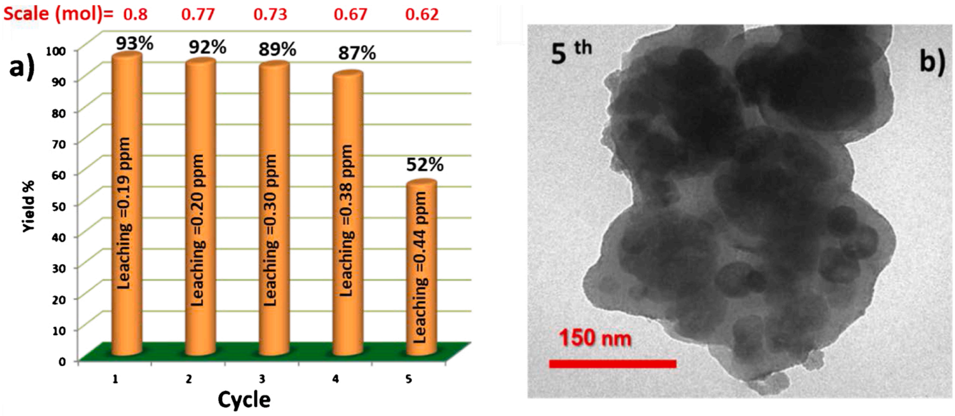


Fig. 7. Recyclability of Fe_3O_4@C-$NHCS_2H.Au_{NPs}$ for the model reaction of A^3-coupling b) TEM image after the 5th recycling of Au-catalyst. Reaction conditions: piperidine (1.2 mmol), benzaldehyde (1 mmol), phenylacetylene (1.3 mmol), K_2CO_3(1 eq), 4 mL $CHCl_3$, 12 h.

Table 3
Comparison of catalytic activity of Fe_3O_4@C-$NHCS_2H$.Au_{NPs} with other catalysts.

Catalyst	Temp (°C)	Time (h)	Solvent	Yield (%)	Ref.
Ag NPs	100	20	PEG	77	[76]
Ag/EOs *orange* NPs	80	8	Toluene	96	[77]
Ag NPs/plant extract	90	18	PEG	83	[78]
Ag_2ONPs(1.8)	100	2	H_2O	92	[79]
Pd NPs@MOF	90	24	Toluene	72	[80]
Fe_3O_4 NPs	80	16	Toluene	75	[81]
MNPs@BiimCu(I)	100	1.5	H_2O	98	[82]
CuNPs	110	6	MeCN	87	[83]
CuNPs@MS	60	20	THF	95	[84]
CuNPs/TiO_2	70	7	–	98	[85]
CuNPs/Magsilica (1.1)	100	1	–	84	[86]
Cu^0-NPs/ montmorillonite	110	3	Toluene	94	[87]
ZnSNPs	reflux	4	MeCN	94	[39]
ZnONPs	90	1.5	–	94	[88]
Cu_2O/ZnONPs	100	1	–	95	[89]
NiONPs	120	22	Toluene	95	[90]
AuNPs	75	5	THF	92	[66]
Au-SH/SO3H(PMO)	70	12	H_2O	98	[91]
Fe_3O_4@PT@Au	80	24	H_2O	90	[92]
Au@SH-CNC	80	24	$CHCl_3$	93	[70]
Au-NCs@Triazine-COP	60	6	$CHCl_3$	87	[74]
Fe_3O_4@C-$NHCS_2H$.Au_{NPs}	60	12	$CHCl_3$	93	This work

remove the insoluble Fe_3O_4@C-$NHCS_2H$.Au_{NPs} which also led to the inhibition of the reaction. ICP analysis and HFT confirmed that the proposed catalyst is truly heterogeneous.

After a successful and careful catalytic study on the A3-coupling of benzaldehyde with morpholine, and phenylacetylene, we found that the reaction can progress with the catalyst. Under the optimized parameters, the reaction was performed in the existence of 40 mg (0.8 mol% Au NPs) of the catalyst at 60 °C and 400 μL $CHCl_3$ as solvent in 12 h under K_2CO_3 base. The reaction of different aldehydes with morpholine and phenylacetylene were performed. Summarized results in Table 2 indicated that in general a wide range of aldehydes could do A3-coupling reaction smoothly and give propargyl amines in high yields and moderate turnover frequency (TOF) numbers and turnover number (TON). It should be noted that the electronic features of the aromatic compounds affect the reaction rate.

For A3-coupling reactions, the Fe_3O_4@C-$NHCS_2H$.Au_{NPs} catalyst was recovered and reused in the same reaction. All the reaction was performed under the optimized factors. At the end of each reaction, the catalyst was rapidly and easily separated from the reaction mixture by a magnet and washed with ethyl acetate several times. Next, the catalyst was dried and reused directly for the next cycle. Therefore, reaction kinetics in each run was similar to the first cycle. After five cycles, a slight decrease in the yields of products observed which is due to a slight waste of catalyst in each recycle (Fig. 7).

According to atomic absorption spectrometry (AAS), negligible Au was detected in the reaction solution until the 5th run, and TEM image revealing the formidable firmness of the nanocatalyst under the examined reaction conditions even after the 5th run Fig. 4b.

Further, the efficiency of Fe_3O_4@C-$NHCS_2H$.Au_{NPs} was compared for the synthesis of the model product with other nanoparticle-based metal catalysts. To have more precise comparison, the reaction condition, time, temperature, solvent, or free-solvent for each protocol were considered, Table 3. As obvious, our procedure is comparable with those of previously reported catalytic systems in terms of yields of the products, temperatures reaction, and time. In addition to this, present nanocatalyst is more effective than the others due to some important benefits such as eco-friendly, stability, recyclability nano-catalyst, etc.

Recently, a possible mechanism for catalyzed A3-coupling proposed by Heaney and co-workers [93]. At first, a dimeric gold (0) acetylide **A** forms via C–H activation of phenylacetylene with Fe_3O_4@C-$NHCS_2H$.Au_{NPs} catalyst. Then, it coordinates with iminium ion to obtain intermediate **B**. Finally, propargylamine yields with the addition of the alkynylide to iminium ion (Scheme 3).

4. Conclusion

In this research, briefly, a novel carbon-based magnetic nanosphere (Fe_3O_4@C-$NHCS_2H$.Au_{NPs}) was synthesized for stabilizing and supporting of gold nanoparticles. It developed as an innovative promise catalyst and effectively green recyclable catalytic system in the synthesis of propargylamine derivatives that were prepared from A3-coupling reaction. Also, this simple procedure presented some significant advantages such as easy handling, the mild conditions of reaction, low toxicity, good to excellent yields of products, and workup and easy separation.

Compliance with ethical standards

The authors declare that they have no conflict of interest.

Author contributions statement

Khadijeh Ojaghi Aghbash: Worked at the Lab and write the manuscript.

Hassan Alamgholiloo: Co-writer and prepared the plots and origin curves.

Nader Noroozi Pesyan: supervisor of the work.

Samad Khaksar: worked the project at Lab.

Sadegh Rostamnia: Managed the work and supervisor of the work.

Declaration of Competing Interest

The authors report no declarations of interest.

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