

Gold Nanoparticles Supported on Polyacrylamide Containing a Phosphorus Ligand as an Efficient Heterogeneous Catalyst for Three-Component Synthesis of Propargylamines in Water

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Abstract Gold nanoparticles supported on a polyacrylamide containing a phosphinite ligand have been synthesized and characterized using different techniques such as TEM, SEM, EDX, XPS and solid UV analyses. The new material was successfully applied as a heterogeneous catalyst for the three component coupling A³ of amines, aldehydes and alkynes to give propargylamines. Reactions are performed in neat water at 80 °C with only 0.05 mol% catalyst loading. The heterogeneous catalyst is recyclable during seven consecutive runs with small decrease in activity.

Key words gold nanoparticles, alkynes, propargylamines, multicomponent reaction, polyacrylamide

Introduction

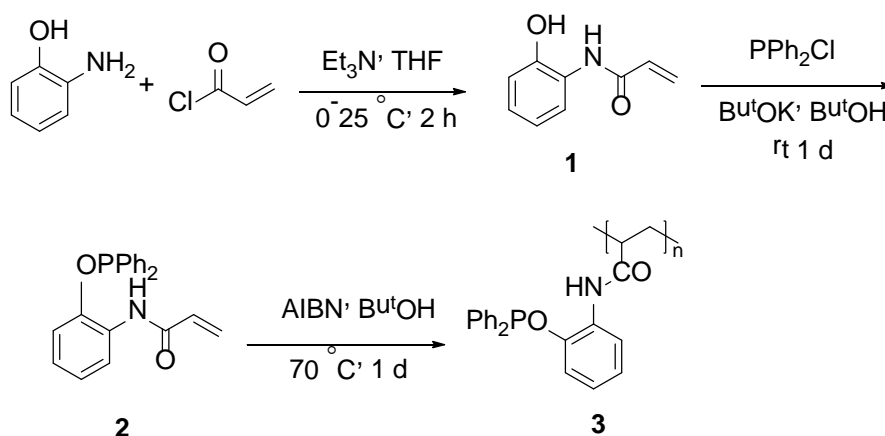
Over the past few decades, transition metals had great impact on developing organic chemistry by introducing of new multifarious catalytic reactions.¹ Gold is one of these transition metals which recently its catalytic properties has been developed as a source of heterogeneous or homogeneous catalysts.² Along this line, oxidation of alcohols³ and carbon monoxide,⁴ hydrogenation of olefins,⁵ cycloaddition reactions,⁶ carbon-heteroatom bond formation,⁷ cyclization of enynes,⁸ deoxygenation of epoxides to alkenes,⁹ and different coupling reactions such as Sonogashira¹⁰ and Suzuki¹¹ reactions are some of the notable applications of gold as a catalyst. Moreover, gold catalysts are well known for their ability to promote activation of C–H bonds for the formation of carbon-carbon or carbon-heteroatom bonds.¹²

Because of extensive pharmaceutical relevance of propargylamines and importance as building blocks in the preparation of nitrogen-containing molecules as well as key intermediates for natural product synthesis, in recent years, great effort has been paid to the synthesis of these compounds. The multicomponent A³ reaction of metal-acetylides with the situ generated imines or iminium ions, from the corresponding primary or secondary amines, is a very useful method for the preparation of propargylamines.¹³ Li and coworkers reported unique property of gold in activation of alkynes in the three component A³ coupling reaction of an aldehyde, an alkyne and an amine for the preparation of propargylamines.¹⁴ After reporting this procedure, different homogenous gold catalysts have been introduced in A³ coupling reactions.¹⁵ However, despite the efficiency of some of these reports, homogenous catalysts suffer from the problem of recovery and catalytic reuse with is economically important for expensive metal catalysts such as gold. Nevertheless, limited heterogeneous gold catalysts have been reported in A³ coupling reactions.¹⁶

Nowadays, polymeric materials have been successfully applied as promising support for the stabilization of metal nanoparticles with a controlled size distribution.¹⁷ Along this line, different polymeric structures have been used for supporting gold nanoparticles.¹⁸ Particularly, phosphorus compounds and therefore polymers containing phosphorus atoms are excellent ligands for stabilization of gold catalysts.¹⁹ Recently, we have reported the synthesis and application of polymer containing phosphorous and nitrogen ligands as a support for stabilization of palladium nanoparticles and its applications in Suzuki-

Miyaura and Sonogashira-Hagihara coupling reactions.²⁰ Also, we have recently reported that gold and copper catalysts supported on periodic mesoporous organosilica with ionic liquid framework (PMO) as an efficient and recyclable catalysts for the three component coupling reaction of aldehydes, alkynes and amines in chloroform.²¹ In continuation with our interest on heterogeneous gold reactions and A³ coupling reaction, herein, we wish to report the synthesis, characterization and application of a polymer containing phosphorous and nitrogen ligands as an excellent support for stabilization of gold nanoparticles and its application as a recyclable catalyst in A³ coupling reactions in neat water.

The polymer containing P,N ligands was synthesized by reaction of 2-aminophenol with acryloyl chloride in the presence of Et₃N in dry THF producing *N*-(2-hydroxyphenyl) acrylamide (**1**). The resulting acrylamide **1** was allowed to react with chlorodiphenylphosphine (PPh₂Cl) using *t*-BuOK as a base in *t*-BuOH as solvent. The obtained phosphinite **2** was subjected to polymerization using 2,2'-azobisisobutyronitrile (AIBN) as initiator in *t*-BuOH for 24 h at 70 °C to afford final polymer containing P,N ligands **3** (Scheme 1).²⁰



Scheme 1 Synthesis of polymer **3**

The final polymer supported gold nanoparticles was easily obtained by treating **3** with NaAuCl₄ salt in aqueous media at room temperature. Thermogravimetric analysis of obtained material showed thermal stability and negligible leaching of organic groups up to 250 °C (Figure 1).

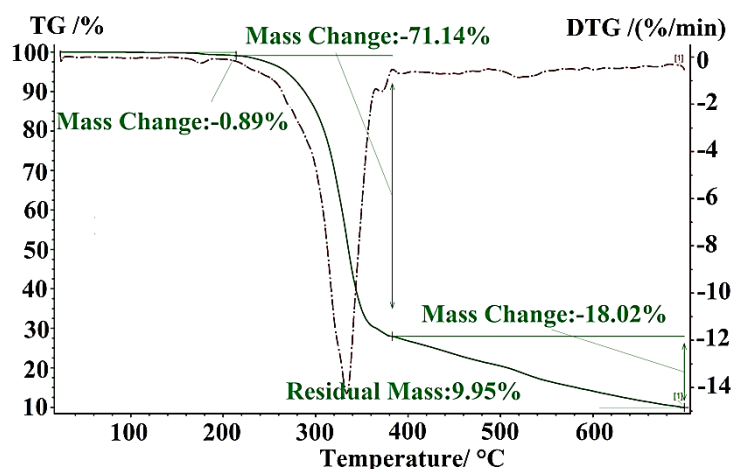


Figure 1 Thermogravimetric diagram of the polymer supported gold nanoparticles

Diffuse reflectance UV visible spectra (DR UV-vis) showed disappearance of related peaks to Au(III) at 230 and 320 nm confirming reduction of Au(III) to Au(0) particles (Figure 2).²²

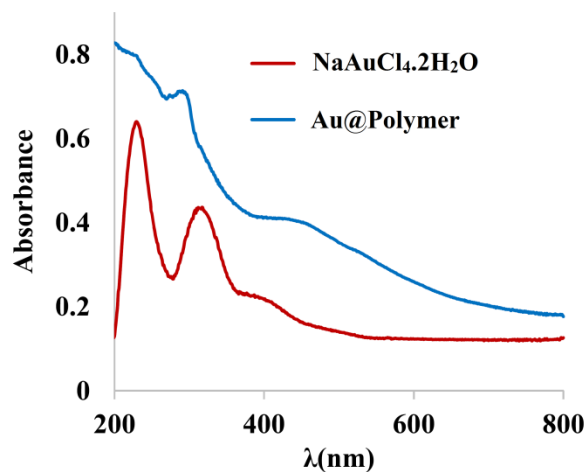


Figure 2 Diffuse reflectance UV visible spectra of the polymer supported gold nanoparticles

SEM image of material showed formation of large sheets in micro scale dimension (Figure 3). Furthermore energy dispersive spectroscopy (EDS) analysis of catalyst obtained from SEM confirmed presence of Au species in the polymer supported Au nanoparticles (Figure 4).

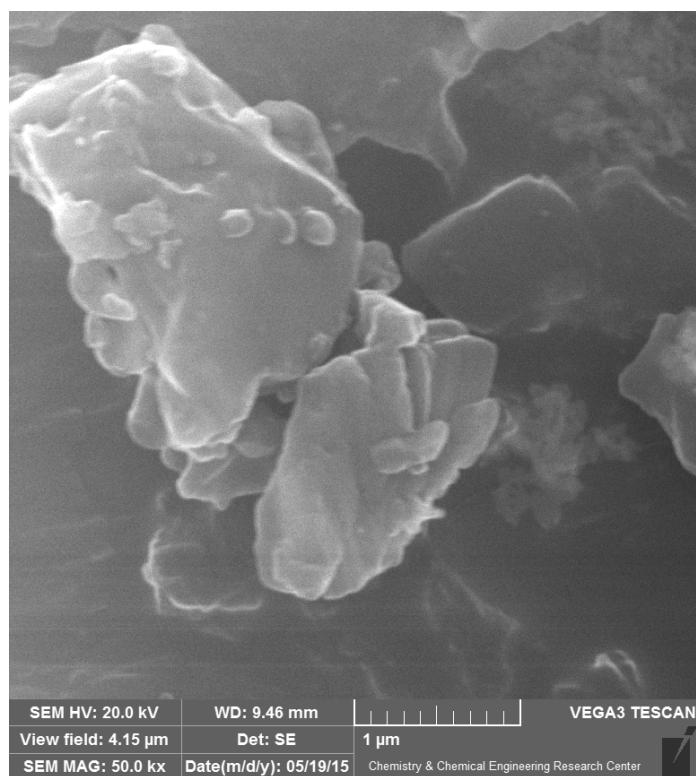


Figure 3 SEM image of the polymer supported gold NPs

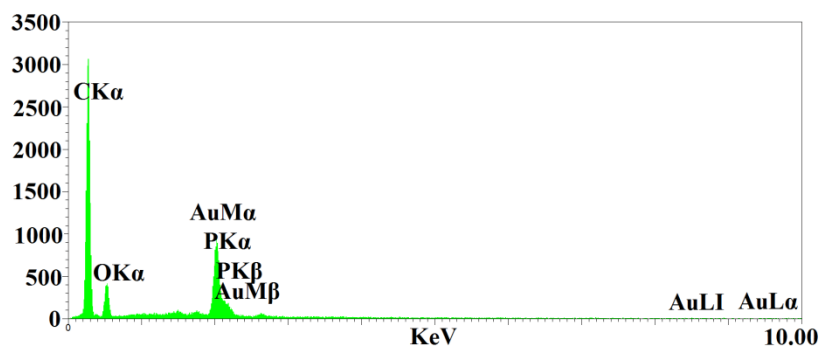


Figure 4 EDS spectrum of the polymer supported gold NPs

TEM images of polymer supported gold NPs showed presence of highly monodispersed nanoparticles in average size of 3-5 nanometers (Figure 5).

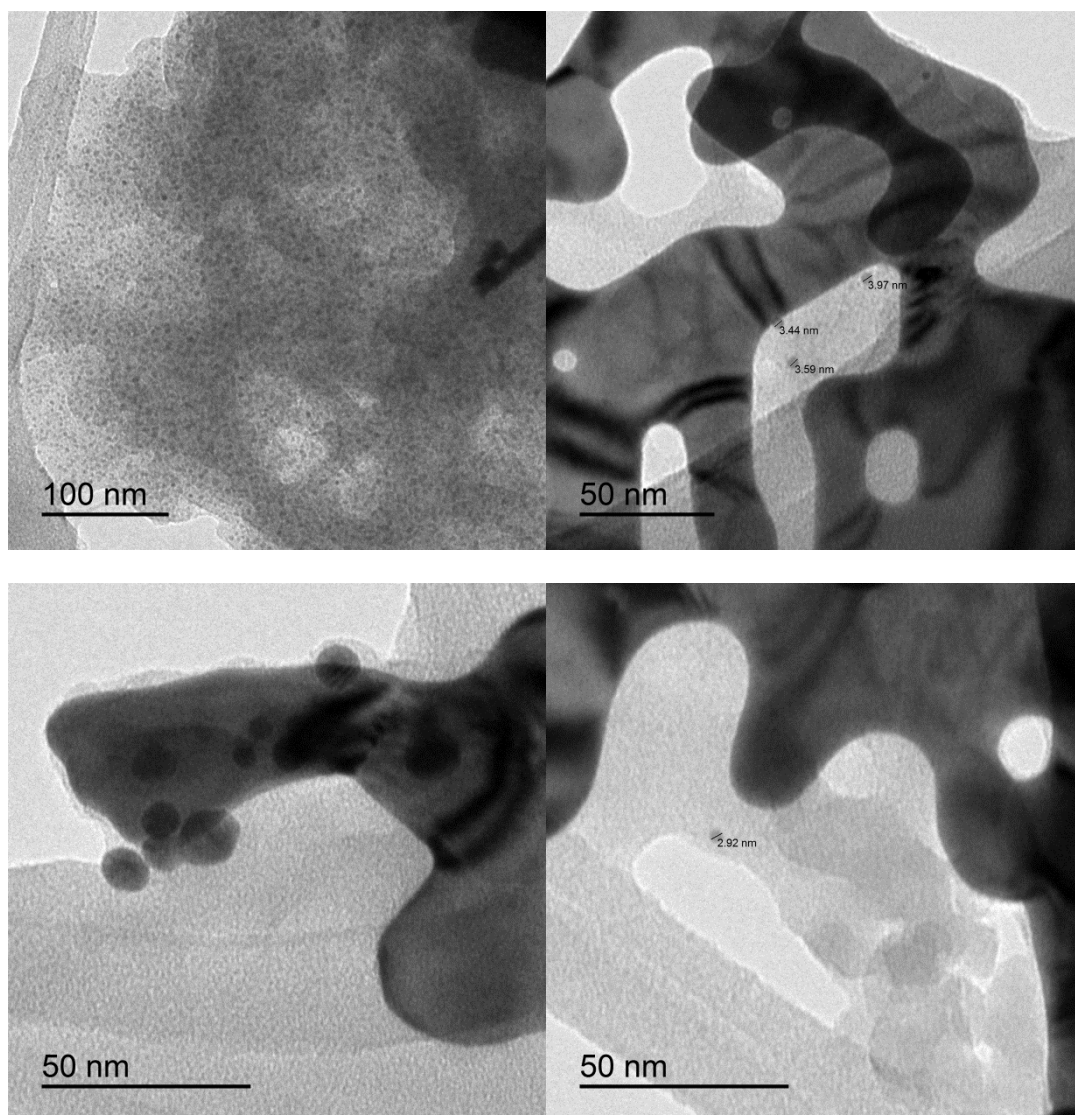


Figure 5 TEM image of polymer supported gold NPs

In the case of the X-ray photoelectron spectrum (XPS) the material showed two doublet peaks for Au 4f_{7/2} and Au 4f_{5/2}. The first doublet with peaks at 84.0 and 87.7 eV is the characteristic peaks for metallic Au and second doublet at/near 85.8 and 89.5 eV) are due to Au³⁺ species.²³ As seen in Figure 6 most of Au is presented in Au(0) state.

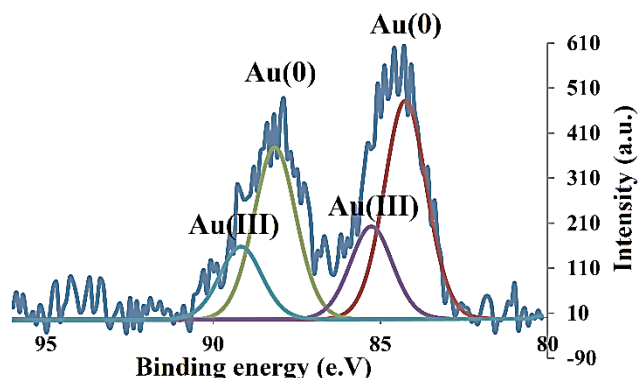
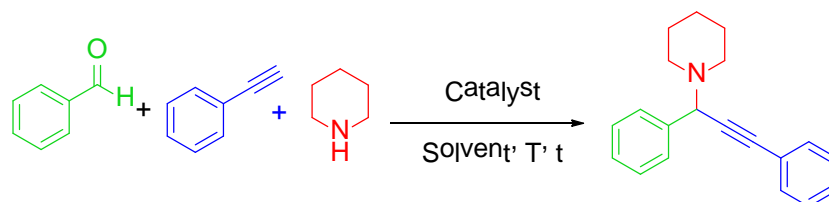


Figure 6 X-ray photoelectron spectroscopy (XPS) of the polymer supported gold NPs

The catalytic activity of polymer supported gold nanoparticles was assessed as a heterogeneous catalyst in the A³ coupling reaction of amine, aldehyde and alkyne. In order to find optimized reaction conditions, the reaction of benzaldehyde, piperidine and phenylacetylene was selected as a model reaction and effect of solvents, catalyst amount and reaction temperature were studied (Table 1). Using 0.5 mol% of catalyst and toluene as a solvent at 100 °C afforded 91% isolated yield and decreasing the reaction temperature to 80 °C gave a lower 40% yield (Table 1, entries 1 and 4). Using other solvents such as DMF, CH₃CN and THF at different temperatures lower yields were obtained (Table 1, entries 2, 3, 5 and 6). However, using CHCl₃ and H₂O the corresponding propargylamine was isolated in 90% and 98% yields at 80 °C and 70 °C, respectively (Table 1, entries 7 and 8). Thus, H₂O was selected as the best solvent and then the effects of catalyst amount and reaction temperature were studied. Decreasing the catalyst loading from 0.5 to 0.05 mol% did not affect reaction yield (Table 1, entries 8-12). However, the use of 0.02 mol% of catalyst cause a decreasing of yield to 80% at 80 °C (Table 1, entry 13). Also, using 0.05 mol% under lower temperatures afford low yield for the reactions (Table 1, entries 14 and 15). As conclusion, we selected H₂O as a solvent, 0.05 mol% catalyst at 80 °C as optimized reaction conditions.

Table 1 Reaction conditions study^a



Entry	Au (mol%)	Solvent	Temp (°C)	Time (h)	Yield ^b (%)
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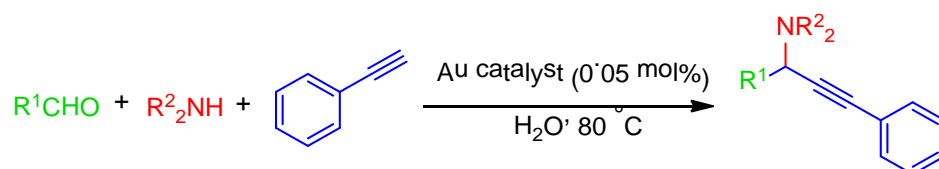
1	0.5	Toluene	100	24	91
2	0.5	DMF	100	24	11
3	0.5	CH ₃ CN	80	24	24
4	0.5	Toluene	80	24	40
5	0.5	DMF	80	24	10
6	0.5	THF	70	24	18
7	0.5	CHCl ₃	70	15	90
8	0.5	H ₂ O	80	24	98
9	0.4	H ₂ O	80	24	99
10	0.2	H ₂ O	80	24	99
11	0.1	H ₂ O	80	24	98
12	0.05	H ₂ O	80	24	97

13	0.025	H ₂ O	80	24	80
14	0.05	H ₂ O	60	24	60
15	0.05	H ₂ O	50	24	18

^a Reaction conditions: benzaldehyde (1 mmol), piperidine (1.5 mmol), phenylacetylene (1.5 mmol), catalyst (see column) and solvent (2 mL). ^b Isolated yield after column chromatography

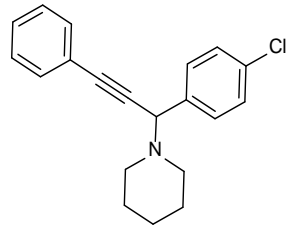
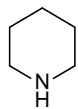
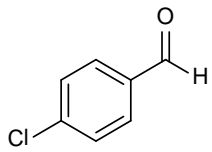
By using the optimized reaction conditions, the synthesis of propargylamines derived from structurally varied aldehydes, secondary amines and phenylacetylene was performed (Table 2). Results on Table 2 indicated that various aromatic aldehydes bearing both electron-withdrawing and electron-donating groups such as 4-Cl, 4-Br, 4-OMe, 4-Prⁱ, 4-Me, 3-Me, and 3,5-Me₂ reacted efficiently with piperidine to afford the corresponding propargylamines in good to excellent yields (Table 2, entries 1-8). Reactions of 2-chlorobenzaldehyde and 2,4-dichlorobenzaldehyde, as relatively sluggish substrates, proceeded well and produced the corresponding propargylamines in high to excellent yields (Table 2, entries 9 and 10). Reaction of 1-naphthalenecarbaldehyde with both piperidine and morpholine took place efficiently giving the corresponding products in high isolated yields (Table 2, entries 11 and 12). In the case of the reaction of furfural as aldehyde with piperidine and morpholine the desired propargylamines were isolated in excellent yields (Table 2, entries 13 and 14). Heptanal as a representative example of aliphatic aldehyde reacted with piperidine and phenylacetylene to afford the desired product in 90% isolated yield (Table 2, entry 15). Also, reaction of benzaldehyde with morpholine and pyrrolidine proceed well and the corresponding propargylamines were obtained in 88% and 98% isolated yield, respectively (Table 2, entries 16 and 17).

Table 2 Reactions of structurally different aldehyde with amines and phenylacetylene^a



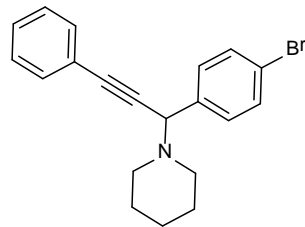
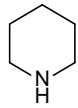
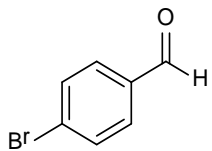
Entry	R ¹ CHO	R ² ₂ NH	Product	Yield ^b (%)
1				98

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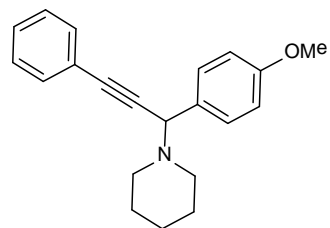
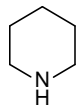
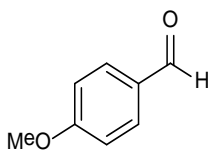
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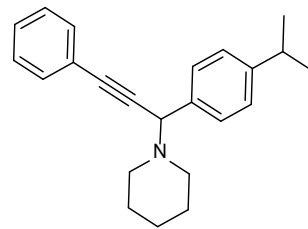
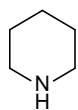
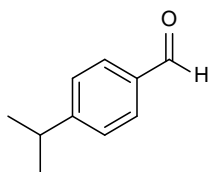
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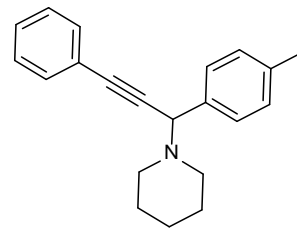
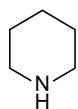
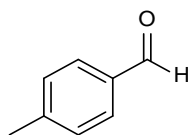
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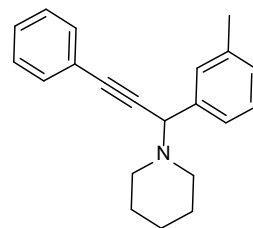
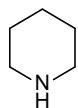
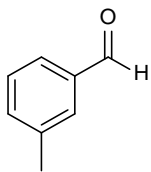
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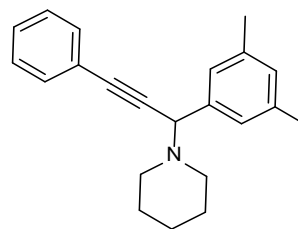
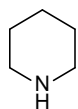
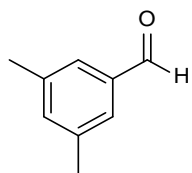
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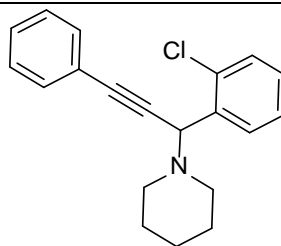
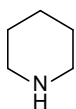
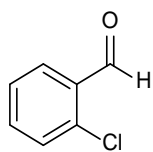
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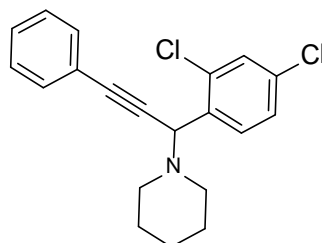
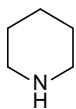
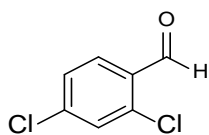
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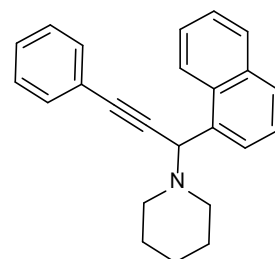
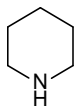
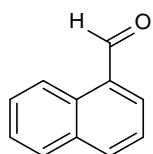
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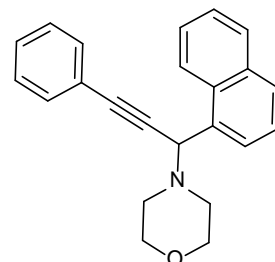
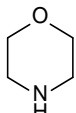
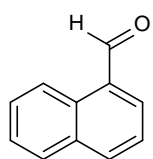
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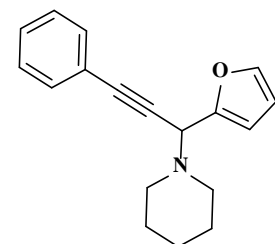
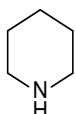
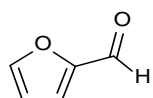
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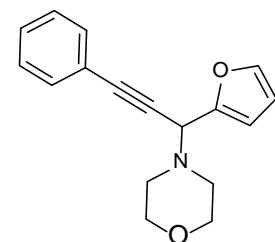
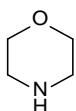
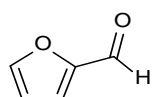
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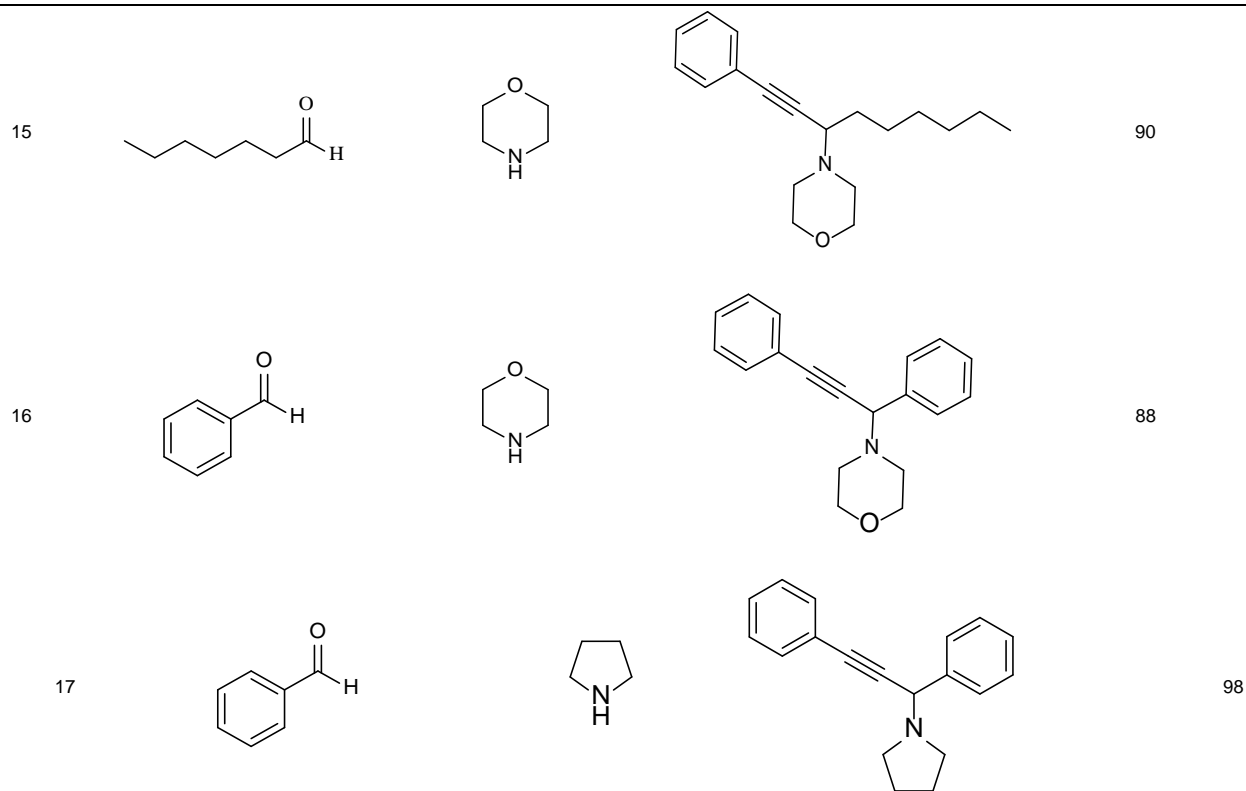


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^a Reaction conditions: aldehyde (1 mmol), amine (1.5 mmol), phenylacetylene (1.5 mmol), catalyst (0.05 mol%) and H₂O (2 mL) were heated at 80 °C during 1 d. ^b Isolated yield after column chromatography.

For the study about the recycling properties of this gold polymer-supported catalyst the standard reaction of benzaldehyde, piperidine and phenylacetylene in H₂O at 80 °C was considered. Results indicated that this catalyst is recyclable during seven consecutive runs of 1 d preserving catalytic activity (Figure 7).

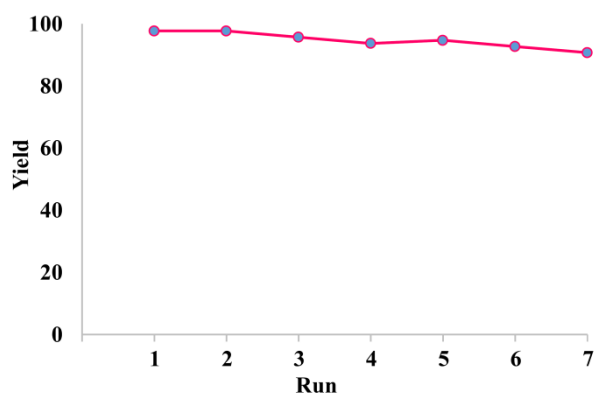


Figure 7 Recycling of the catalyst for the reaction of benzaldehyde, piperidine and phenylacetylene

In order to confirm the heterogeneous nature of the catalyst hot filtration test for the reaction of benzaldehyde, piperidine and phenylacetylene was performed. For this purpose after 5 h reaction, the mixture was filtered off and the obtained aqueous solution was allowed to react for additional 24 h. Results showed that the reaction yield in 5 h (39%) was increased just to 48% after 24 h confirming the heterogeneous character of the catalyst.

In conclusion a new polymer supported gold nanoparticles catalyst has been synthesized, characterized and used as an efficient catalyst for three component coupling reaction of amines, aldehydes and phenylacetylene. Reactions proceed in water as a green solvent and high to excellent yields were obtained. The catalyst was recycle during seven consecutive runs and hot filtration experiments indicated the heterogeneous nature of this polymeric catalyst.

Acknowledgements

The authors are grateful to Institute for Advanced Studies in Basic Sciences (IASBS) Research Council and Iran National Science Foundation (INSF-Grant number of 94010666) for support of this work. C. Nájera is also thankful to The Spanish Ministerio de Economía y Competitividad (MINECO) (projects CTQ2013-43446-P and CTQ2014-51912-REDC), FEDER, the Generalitat Valenciana (PROMETEOII/2014/017) and the University of Alicante for financial support.

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Gold Nanoparticles Supported on Polyacrylamide Containing a Phosphorus Ligand as an Efficient Heterogeneous Catalyst for Three-Component Synthesis of Propargylamines in Water

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