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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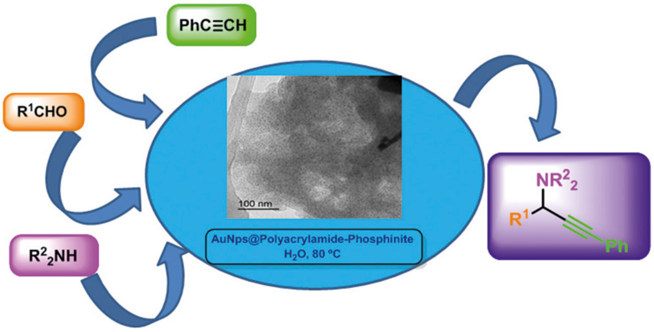

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Abstract Gold nanoparticles supported on a polyacrylamide containing a phosphinite ligand have been synthesized and characterized using different techniques such as TEM, SEM, EDX, XPS, and solid UV analyses. The new material was successfully applied as a heterogeneous catalyst for the three-component A^3 coupling 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.

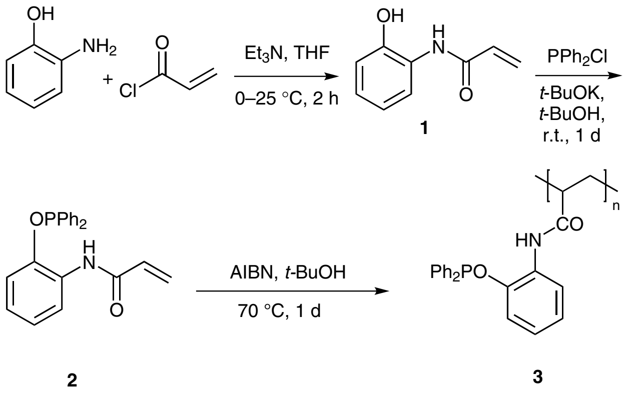
Key words gold nanoparticles, alkynes, propargylamines, multicomponent reaction, polyacrylamide

Over the past few decades, transition metals have had great impact on the development organic chemistry through the introduction of new multifarious catalytic reactions.[1] Gold is one of these transition metals which catalytic properties have been developed recently as a source of heterogeneous or homogeneous catalysts.[2] Along this line, oxidation of alcohols[3] 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 Sonogashira[10] and Suzuki[11] 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 A^3 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 A^3 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 A^3 coupling reactions.[15] However, despite the efficiency of some of these reports, homogenous catalysts suffer from the problem of recovery and catalytic reuse which is economically important for expensive metal catalysts such as gold. Nevertheless, limited heterogeneous gold catalysts have been reported in A^3 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 A^3 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 the stabilization of gold nanoparticles and its application as a recyclable catalyst in A^3 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 Et_3N in dry THF producing *N*-(2-hydroxyphenyl) acrylamide (**1**). The resulting acrylamide **1** was allowed to react with chlorodiphenylphosphine (PPh_2Cl) 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 hours at 70 °C to afford the final polymer containing P,N ligands **3** (Scheme 1).[20]



Scheme 1 Synthesis of polymer **3**

The final polymer-supported gold nanoparticles were easily obtained by treating **3** with $NaAuCl_4{\cdot}2H_2O$ salt in aqueous media at room temperature. Thermogravimetric analysis of the obtained material showed thermal stability and negligible leaching of organic groups up to 250 °C (Figure 1).

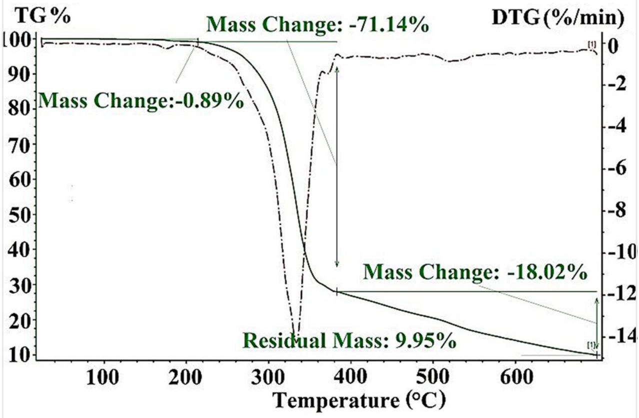


Figure 1 Thermogravimetric diagram of the polymer-supported gold nanoparticles

Diffuse reflectance UV visible spectra (DR UV-Vis) showed disappearance of related peaks to gold(III) at λ = 230 and 320 nm confirming reduction of gold(III) to gold(0) particles (Figure 2).[22]

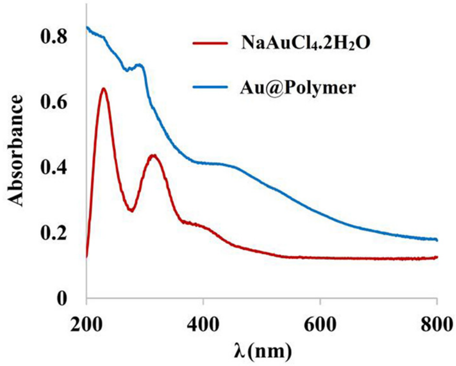


Figure 2 DR UV-vis spectra of the polymer-supported gold nanoparticles

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

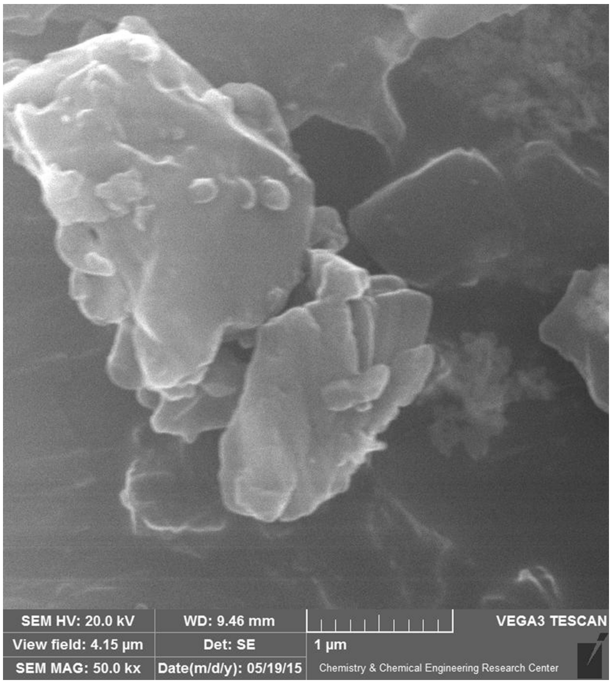


Figure 3 SEM image of the polymer-supported gold nanoparticles

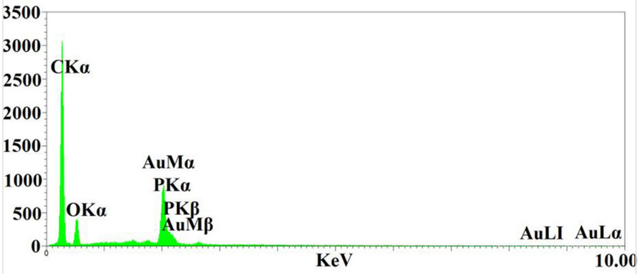


Figure 4 EDS spectrum of the polymer-supported gold nanoparticles

HRTEM images of polymer-supported gold nanoparticles showed the presence of highly monodispersed nanoparticles in an average size of 3–5 nm (Figure 5). It is worth mentioning that formation gold nanoparticles was achieved without using any reducing agents, and the presence of phosphorous atoms in the polymer structure is responsible for reduction and formation of gold nanoparticles.[23]

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 are the characteristic peaks for metallic gold and the second doublet at near 85.8 and 89.5 eV are due to Au^{3+} species.[24] As seen in Figure 6 most of the gold is presented in the gold(0) state.

The catalytic activity of polymer-supported gold nanoparticles was assessed as a heterogeneous catalyst in the A^3 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 effects of solvents, catalyst amount, and reaction temperature were studied (Table 1).

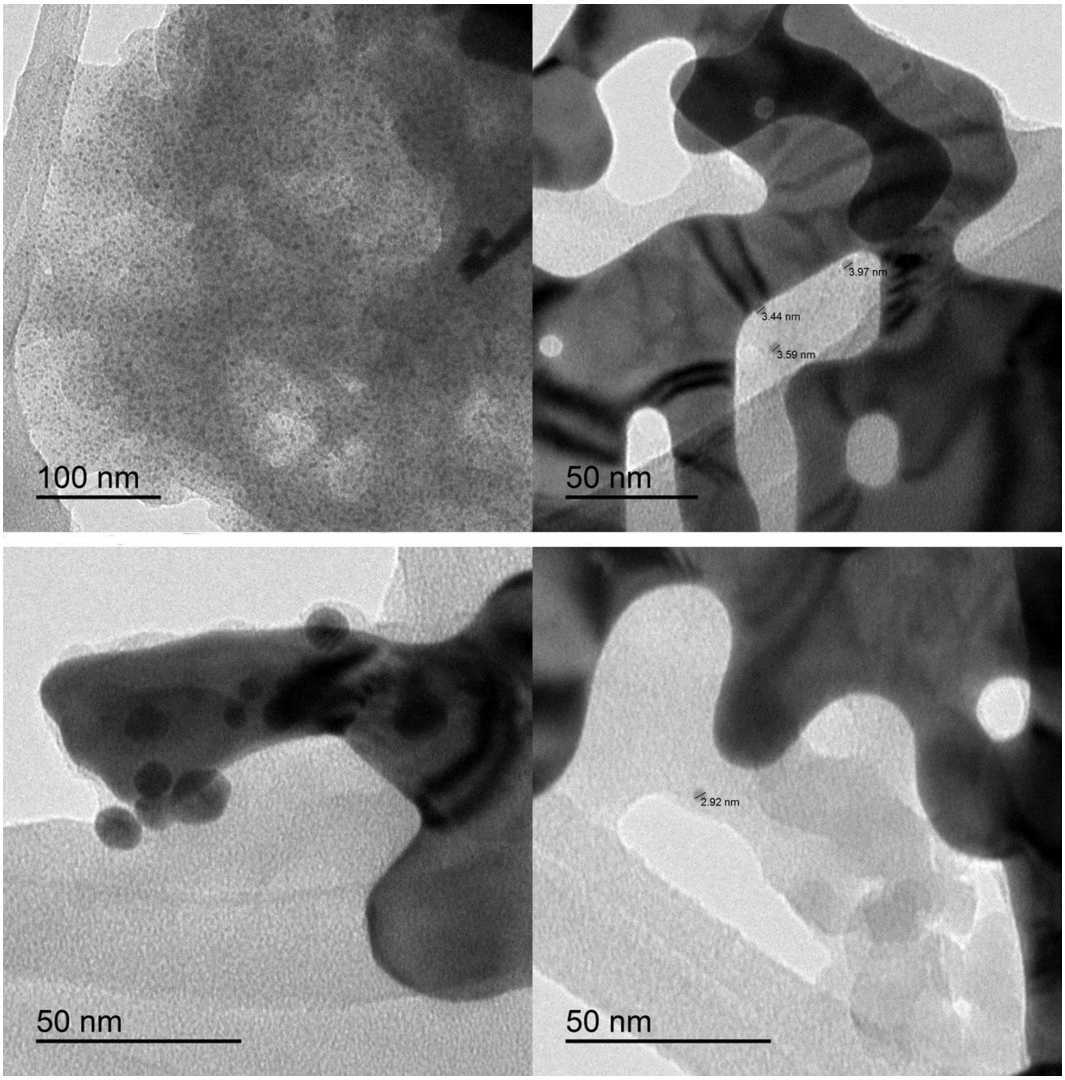


Figure 5 TEM image of polymer-supported gold nanoparticles

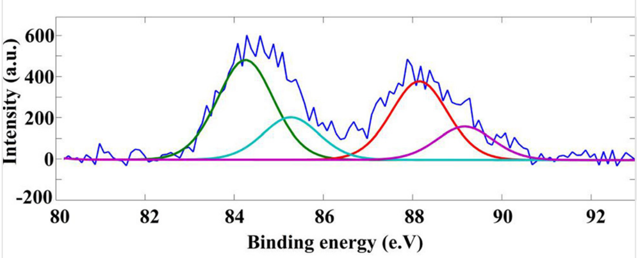
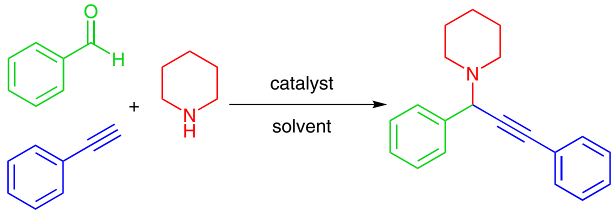


Figure 6 X-ray photoelectron spectroscopy (XPS) of the polymer-supported gold nanoparticles

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, MeCN, and THF at different temperatures lower yields were obtained (Table 1, entries 2, 3, 5 and 6). However, using $CHCl_3$ and H_2O the corresponding propargylamine was isolated in 90% and 98% yields at 70 °C and 80 °C, respectively (Table 1, entries 7 and 8). Thus, H_2O 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 0.025 mol% of catalyst caused 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 H_2O as a solvent and 0.05 mol% catalyst at 80 °C as optimized reaction conditions.

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-*i*-Pr, 4-Me, 3-Me, and 3,5-Me_2 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).[25]

Table 1 Study of Reaction Conditions[a]



Entry	Au (mol%)	Solvent	Temp (°C)	Time (h)	Yield (%)[b]
1	0.5	toluene	100	24	91
2	0.5	DMF	100	24	11
3	0.5	MeCN	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_2O	80	24	98
9	0.4	H_2O	80	24	99
10	0.2	H_2O	80	24	99
11	0.1	H_2O	80	24	98
12	0.05	H_2O	80	24	97
13	0.025	H_2O	80	24	80
14	0.05	H_2O	60	24	60
15	0.05	H_2O	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.

For the study about the recycling properties of this polymer-supported gold catalyst the standard reaction of benzaldehyde, piperidine, and phenylacetylene in H_2O at

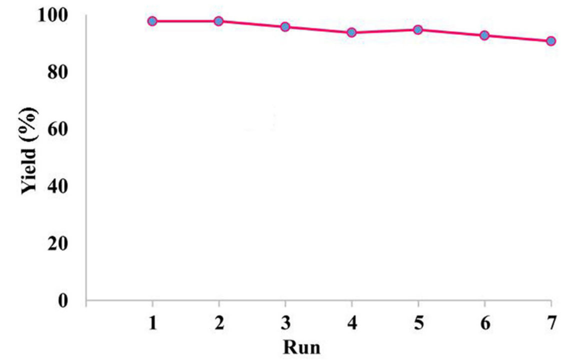
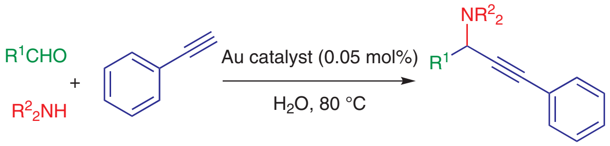


Figure 7 Recycling of the catalyst for the reaction of benzaldehyde, piperidine, and phenylacetylene

80 °C was considered. Results indicated that this catalyst is recyclable during seven consecutive runs of one day preserving catalytic activity (Figure 7).

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 five hours reaction (39% yield), the catalyst was removed from the reaction by filtration and obtained aqueous solution was allowed to react for additional 24 hours. Results showed that the yield of reaction obtained from hot filtration was increased just to 48% after 24 hours. This result confirmed small leaching of catalyst to the solution and heterogeneous character of the catalyst. Furthermore, mercury poisoning for the reaction of benzaldehyde, piperidine, and phenylacetylene was studied. For this purpose after one hour (15%) reaction, mercury(0) (300:1 Hg to Au) was added to the reaction mixture under optimized reaction conditions. Analysis of the reaction after 24 hours showed 29% yield. According the suppression of the reaction, we think again that the reaction may mostly proceed under heterogeneous conditions.[27]

Table 2 Reactions of Structurally Different Aldehydes with Amines and Phenylacetylene[a]



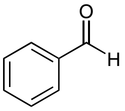
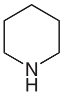
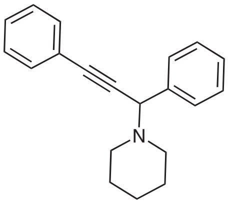
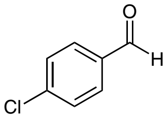
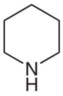
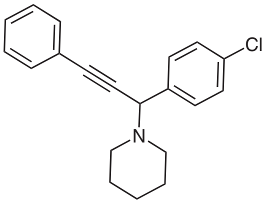
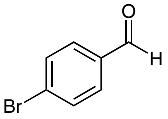
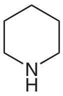
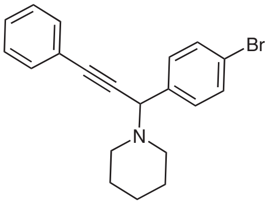
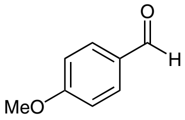
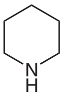
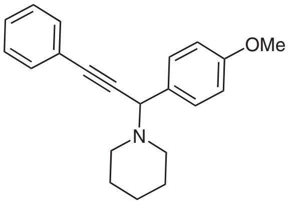
Entry	R^1CHO	$R^2{}_2NH$	Product	Yield (%)[b]
1				98
2				98
3				98
4				97

Table 2 (continued)

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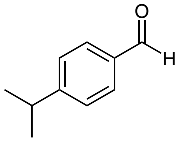
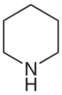
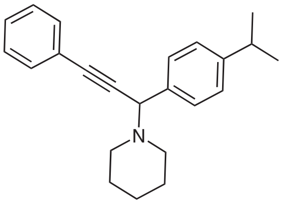
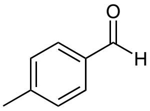
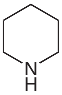
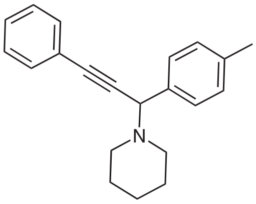
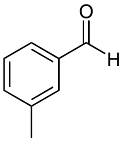
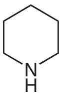
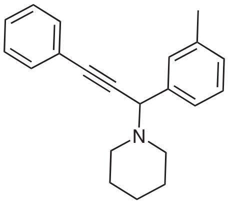
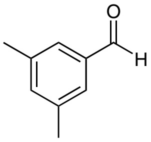
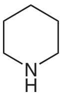
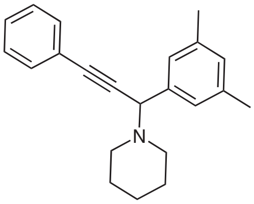
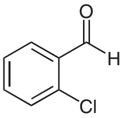
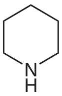
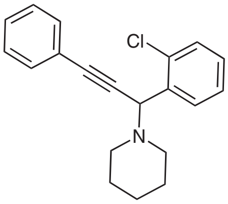
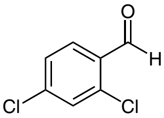
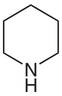
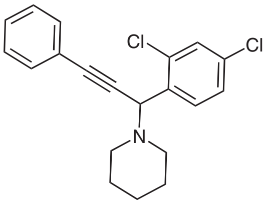
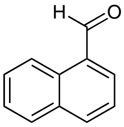
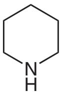
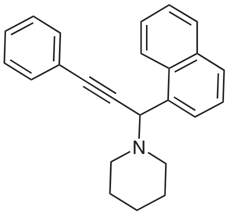
5				76
6				96
7				87
8				74
9				80
10				95
11				73

Table 2 (continued)

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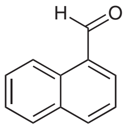
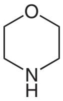
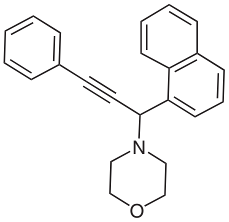
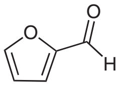
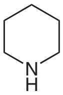
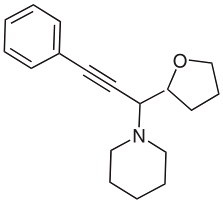
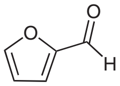
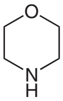
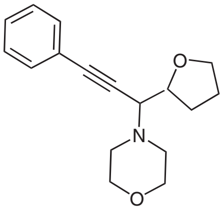
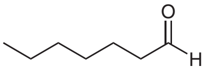
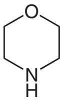
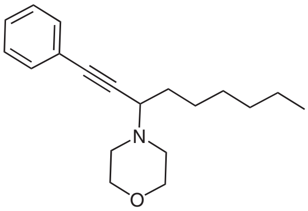
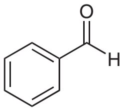
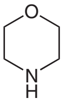
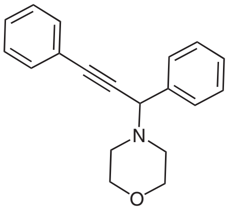
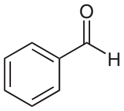
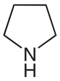
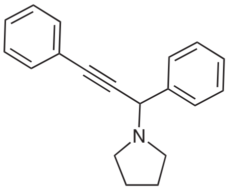
12				89
13				94
14				91
15				90
16				88
17				98

[a] Reaction conditions: aldehyde (1 mmol), amine (1.5 mmol), phenylacetylene (1.5 mmol), catalyst (0.05 mol%), and H_2O (2 mL) were heated at 80 °C during 1 d.

[b] Isolated yield after column chromatography.

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 recycled during seven consecutive runs, and hot filtration experiments indicated the heterogeneous nature of this polymeric catalyst.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1561286.

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(25) A mixture of benzaldehyde (0.100 mL, 1 mmol), piperidine (0.160 mL, 1.5 mmol), phenylacetylene (0.165 mL, 1.5 mmol), catalyst (5 mg containing 0.05 mol% Au), and H_2O (2 mL) was stirred at 80 °C for 1 d. The reaction mixture was cold down to r.t. and then extracted with EtOAc (3 × 10 mL). The organic phase was dried over anhydrous Na_2SO_4 and the solvent evaporated. The resulting propargylamine was purified by column chromatography on silica gel using EtOAc and hexane giving 270 mg (98% yield) of the pure product 1-(1,3-diphenylprop-2-yn-1-yl)piperidine.[26] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57–7.71 (m, 2 H), 7.55–7.56 (m, 2 H), 7.30–7.43 (m, 6 H), 4.90 (s, 1 H), 2.65 (br s, 4 H), 1.64–1.67 (m, 4 H), 1.48–1.51 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.2, 131.8, 128.7, 128.3, 128.2, 128.1, 127.7, 123.2, 88.2, 85.7, 62.4, 50.7, 25.9, 24.3.

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