

Nanoparticles of silver oxide immobilized on different templates: highly efficient catalysts for three-component coupling of aldehyde-amine-alkyne

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Abstract

Silver (I) oxide nanoparticles immobilized on different solid supports were employed in catalyzing an aldehyde-amine-alkyne coupling reaction. It was found that the alumina-supported Ag₂O was the most active catalyst. The scope of the corresponding reaction substrates was extended by virtue of these new catalysts. The feasibility of recycling of the alumina-supported Ag₂O catalyst was also examined.

Keywords: Nanoparticles, templates, three-component coupling

Introduction

Propargylamines are synthetically versatile and key intermediates¹ for preparation of many biologically active nitrogen compounds such as conformationally restricted peptide isosteres, oxotremorine analogues, β -lactams and polyfunctional amino derivatives. A range of efficient and mild metal-catalyzed reactions based upon the nucleophilic addition of in situ generated metal acetylides to imines and enamines have been reported.² Recently, some silver (I) compounds were also used to catalyze A³-coupling (aldehyde-alkyne-amine) reactions to afford propargylamines smoothly.³ On the other hand, the development of nano-metal catalysts⁴ is gaining favor in industry because of their high catalytic activities. Normally, nanoparticles of the catalyst are immobilized on the corresponding templates and therefore they can be separated from the reaction mixture easily, which can allow for the reuse of catalysts and provides for an environmental benign reaction.⁵ Several classes of solids have commonly been used as absorbents in organic chemistry such as alumina, diatomite, silica gels, clays, carbon nanotubes etc.⁶ Furthermore nanoparticles can exhibit special chemical properties.⁷ Methods involving hydroxyapatite-supported copper and layered double hydroxide-supported gold catalyst to construct propargylamine skeleton have been reported respectively.⁸ Herein, we reported that nanoparticles of silver (I) oxide immobilized on different templates catalyze the A³-coupling of

amines, alkynes and aldehydes and give rise to the propargylamines with excellent yields and rapid reaction rates.

Results and Discussion

Initially, we designed and selected a range of templates to support silver oxide. They are silica sphere, diatomite, multi-wall carbon nanotubes (MWCNT) and alumina. In this way, we attempted to obtain different sizes of nanoparticles of silver oxide as potential heterogeneous catalysts. TEM images (Figure 1) show the particle diameters of the silica sphere-, diatomite-, MWCNT- and alumina-supported Ag_2O are mainly in the range of 18-20 nm, 13-16 nm, 10-12 nm and 6-8 nm, respectively. X-ray photoelectron spectroscopy (XPS) analysis indicated that 2.7%, 3.4%, 4.3% and 3.9% of Ag were found in the silica sphere-, diatomite-, MWCNT- and alumina-supported Ag_2O , respectively. X-Ray powder diffraction (XRD) pattern of these catalysts are consistent with their components of these compounds.

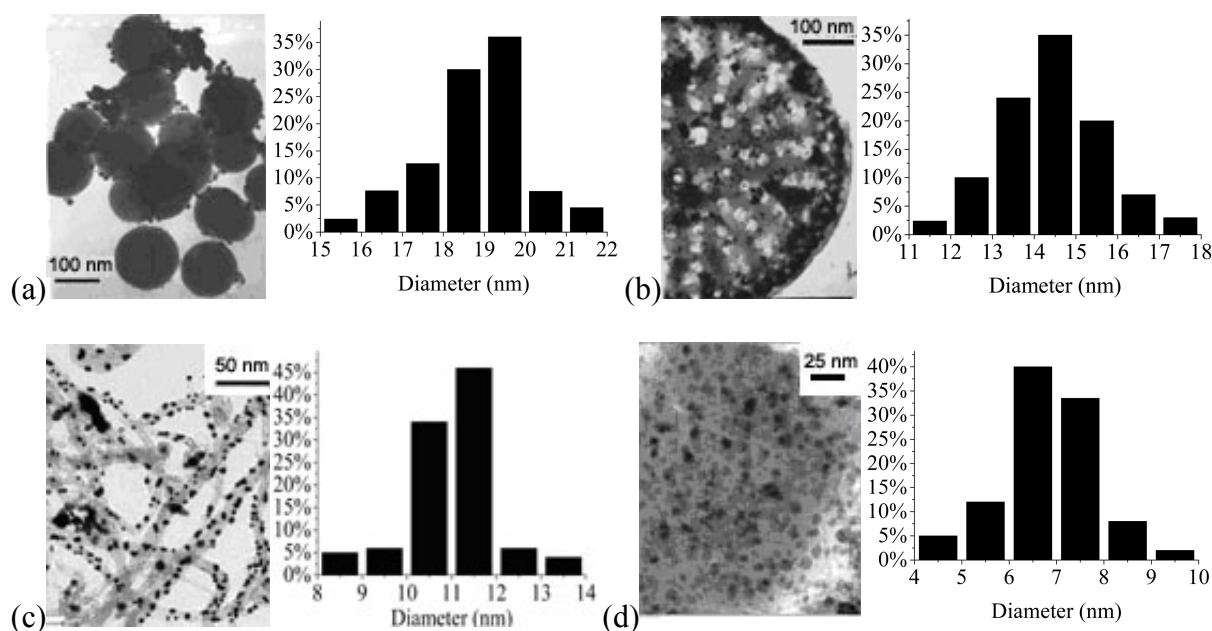


Figure 1. (a) TEM image of Ag_2O /silica-sphere and the particle dispersion. (b) TEM image of Ag_2O /diatomite and the particle dispersion. (c) TEM image of Ag_2O /MWCNT and the particle dispersion. (d) TEM image of Ag_2O /alumina and the particle dispersion.

To examine the catalytic activity of the silver oxide catalysts supported by different templates, benzaldehyde (2 mmol), phenylacetylene (2.4 mmol), diethylamine (3 mmol), water (2 mL), and the corresponding catalyst (50 mg) were mixed in a 10 mL of flask. Then the mixture was stirred and the reaction was carried out at 100 °C. The results are shown in Table 1. It was found that Ag_2O immobilized on the templates (Table 1, entries 1-4) showed much higher catalytic activity

than that without any template (Table 1, entry 5). More importantly, alumina- and MWCNT-supported silver oxide were more efficient, giving 92% and 89% yield in 2 hours (Table 1, entries 3-4) whereas the reactions catalyzed by the silver oxide immobilized on diatomite and silica sphere took a longer time to generate the corresponding products with much lower yields (Table 1, entries 1-2). In the case of alumina-supported Ag_2O , only 1.8% mole of loading catalyst worked well for this coupling reaction. Increasing the catalyst amount did not enhance the yield greatly.

Table 1. A^3 coupling reaction catalyzed by Ag_2O immobilized on different templates

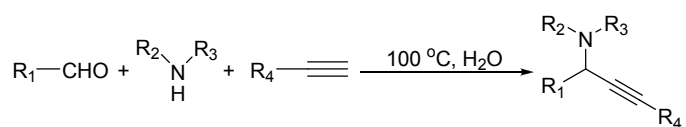
$$\text{PhCHO} + \text{HN} \begin{array}{l} \text{Et} \\ \text{Et} \end{array} + \text{Ph} \text{---} \equiv \xrightarrow{100\text{ }^\circ\text{C}, \text{H}_2\text{O}} \text{Ph} \text{---} \underset{\text{H}}{\text{C}} \text{---} \equiv \text{Ph} \begin{array}{l} \text{Et} \\ \text{N} \text{---} \text{Et} \end{array}$$

entry	catalyst	catalyst amount	isolated yield	reaction time (h)
1	Ag_2O /diatomite	1.5 mol% Ag	52%	4
2	Ag_2O /silica	1.25 mol% Ag	37%	4
3	Ag_2O /MWCNT	2.0 mol% Ag	89%	2
4	Ag_2O /alumina	1.8 mol% Ag	92%	2
5 ^a	Ag_2O (commercial available)	2.1 mol% Ag	29%	12

^aReaction condition: Benzaldehyde (2 mmol), phenylacetylene (2.4 mmol), diethylamines (3 mmol), water (2 mL) and commercial available Ag_2O (5 mg) at 100 °C.

On the basis of the higher catalytic activity, the silver oxide supported by alumina and MWCNT were selected to catalyze the A^3 -coupling reaction. A variety of aldehydes and amines bearing different functional groups were employed as the reaction substrates to explore the scope and generality for the catalyst application. All the results are summarized in Table 2. From Table 2, it was found that various aldehydes such as aromatic, aliphatic and heterocyclic aldehydes could be used as reaction substrates. All of these aldehydes displayed high reactivity under the conditions. Aliphatic aldehydes (Table 2, entries 6-7, 10-15, 17-18) showed a little higher reactivity than aromatic aldehydes (Table 2, entries 1-5, 8-9, 16). As for the aromatic aldehydes, electron-withdrawing groups on the aromatic ring disfavored the reaction (Table 2, entries 2, 8) while electron-donating groups have little influence on the reaction (Table 2, entries 3-5, 16). When dialkylamine, cyclic amine and heterocyclic amine were employed as the reaction substrates, the corresponding reaction also gave the corresponding propargylamines with excellent yields under standard conditions (Table 2, entries 1-18). When a primary amine or an aromatic amine was employed as a substrate, the reaction yield was very low and many side products were observed, perhaps due to the further addition of the generated secondary amine to the aldehyde. As for acetylene substrates, both aromatic alkyne and aliphatic alkyne (Table 2, entries 9-10) displayed high reactivity, giving the corresponding products with excellent yields.

Table 2. A^3 -coupling reaction catalyzed by Ag_2O /alumina and Ag_2O /MWCNT



entry	aldehyde	amine	alkyne	product	yield ^a
1		NH(Et) ₂	Ph-C≡C	1	92% (89%)
2		NH(Et) ₂	Ph-C≡C	2	88% (80%)
3		NH(Et) ₂	Ph-C≡C	3	91% (87%)
4		NH(Et) ₂	Ph-C≡C	4	90% (82%)
5		NH(Et) ₂	Ph-C≡C	5	90% (79%)
6	(CH ₂ O) _n	NH(Et) ₂	Ph-C≡C	6	97% (92%)
7	CH ₃ (CH ₂) ₅ CHO	NH(Et) ₂	Ph-C≡C	7	94% (81%)
8		NH(Et) ₂	Ph-C≡C	8	78% (45%)
9		NH(Et) ₂		9	90% (81%)
10	(CH ₂ O) _n	NH(Et) ₂		10	93% (90%)
11	(CH ₂ O) _n		Ph-C≡C	11	97% (93%)
12			Ph-C≡C	12	95% (81%)
13			Ph-C≡C	13	92% (86%)
14			Ph-C≡C	14	91% (85%)
15	(CH ₂ O) _n		Ph-C≡C	15	98% (89%)
16			Ph-C≡C	16	92% (84%)
17			Ph-C≡C	17	96% (84%)
18	(CH ₂ O) _n		Ph-C≡C	18	92% (86%)

^aIsolated yields catalyzed by Ag₂O/alumina. The data in parentheses were the isolated yields catalyzed by Ag₂O/MWCNT.

Afterwards, we examined the feasibility to use the template-supported Ag₂O in cycle. XPS showed that after the first cycle most of Ag₂O/diatomite and Ag₂O/silica were reduced to Ag (0)

while only a small part of Ag₂O/alumina was reduced. The possible reasons for this low reduction of Ag₂O/alumina are that (1) the faster reaction rate of the A³-coupling catalyzed by Ag₂O/alumina in comparison with that of the reduction of silver (I) and (2) the smaller Ag₂O particles supported by alumina were much more active in catalyzing the reaction due to a good immobilization of silver ion on alumina surface. To test our assumption, benzaldehyde, amine, Ag₂O/alumina and water were stirred at 100 °C. Only after stirring for 10 hours, we observed a completely reduction of silver (I). This indicated that reduction of silver (I) was slower than the A³-coupling reaction. Also, Ag₂O nanoparticles without templates (10-12 nm)⁹ were prepared. When these nanoparticles were used in the coupling reaction, 77% isolated yield was achieved in 4 hours and XRD and XPS showed that most part of the silver (I) was reduced to Ag (0). Ag (0) showed no catalytic activity in this A³-coupling reaction.² All of these experimental results indicated that the generation of Ag (0) resulted in the reduction of the catalytic activity. In Table 3, we presented the results of recycling the alumina-supported Ag₂O in a model reaction of benzaldehyde with phenylacetylene and diethylamine. After each cycle, catalyst was recovered by simple centrifugation and washing by water and ethanol twice, and then was reused for the next cycle. The catalyst exhibited 79%, 50%, 29% yields in the second, third, fourth cycle, respectively (Table 3, entries 3-5).

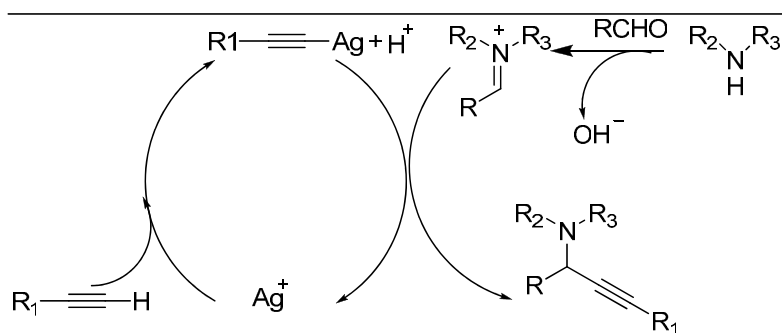
Table 3. Observed XPS binding energy peaks for fresh and recycled Ag₂O/alumina

entry	catalyst (Ag ₂ O)	reaction time (h)	isolated yield	Ag3d _{5/2}	AgM ₄ N ₄₅ N ₄₅	Oxidation State
1	fresh			367.7 eV	357.4	(ϕñ)
2	the 1 st cycle	2	92%	368.1 eV	356.9	(ϕñ)
3	the 2 nd cycle	6	79%	368.0 eV	356.7 358.1	(ϕñ) (0)
4	the 3 rd cycle	8	50%	367.9 eV	356.9 358.2	(ϕñ) (0)
5	the 4 th cycle	14	29%	368.2 eV	—	—

High resolution XPS Ag narrow scan of the fresh alumina-supported silver oxide showed Ag3d_{5/2} at 367.7 eV and AgM₄N₄₅N₄₅ at 357.4 eV, which are attributed to Ag (I) oxidation state. Ag narrow scan in the second (third) cycle showed Ag3d_{5/2} at 368.0 (367.9) eV and AgM₄N₄₅N₄₅ at 358.1 (358.2) eV, which clearly indicated the formation of Ag (0). We deduced that Ag (I) was reduced by the aldehyde in the reaction medium. An ideal template should immobilize Ag (I) tightly so that the reaction can be carried out on the surface of the template. Therefore the key point to keep the catalytic activity in the A³-coupling reaction is to find a proper template to encapsulate nano-Ag₂O tightly and distribute the nanoparticles proportionally.

A succinct mechanism was proposed on the basis of our experimental results together with some literatures.^{2, 3} As shown in Scheme 1, the nucleophilic addition of amine to aldehyde generates iminium, and the reaction of alkyne with Ag (I) gives silver acetylide. The silver

acetylide intermediate then attacks the iminium ion to afford the corresponding propargylamine with the Ag (I) catalyst being released for further reaction.



Scheme 1. Plausible mechanism of the A³-coupling reaction

Conclusions

In conclusion, the nanoparticles of Ag₂O/alumina and Ag₂O/MWCNT were selected as efficient catalysts for the three-component coupling of aldehyde, amine, and alkyne, affording the corresponding propargylamines with high yields and rapid reaction rates. The Ag₂O/alumina can be recycled to some extent. The experimental results indicated that the reduction of Ag (I) is the main reason for the loss of the catalytic activity. This implied that the selection of the template to encapsulate the metal nanoparticles is crucial to keep the catalytic activity, which provides us a clue for exploring the suitable heterogeneous catalyst. Further research is in progress in our laboratory.

Experimental Section

Typical procedure for the preparation of silica sphere-supported Ag₂O nanoparticles

To a flask was added 88 mL of methanol and 12 mL of NH₃·H₂O (25%), then 3.6 mL of Si(OEt)₄ was introduced into the flask, stirring for 30 min. The formed silica sphere was filtered and washed by water and methanol for three times. 50 mL of water and 50 mL of methanol were mixed. To this mixture the obtained silica sphere was introduced and another 2 mmol of AgNO₃ and 15 mmol of CF₃COOH was added, then stirring for 4 hours. The mixture was centrifuged and the residue was transferred into a flask containing 50 mL of solvent (*V*_{water}: *V*_{MeOH} = 1:1). To this flask 15% of n-Bu₄NOH was added dropwise to adjust the pH of the solution up to 10. The silica sphere-supported Ag₂O was obtained by heating the mixture at 80 °C for 1 hour.

Typical procedure for the preparation of diatomite-supported Ag₂O nanoparticles

15 mL of methanol and 15 mL of water were mixed together. To this mixture diatomite (500 mg), AgNO₃ (2 mmol) and 15 mmol of CF₃COOH were added. After the mixture was stirring for 4 hours, the pH of the mixture was adjusted to 10 by adding 0.1 M NaOH dropwise. Then the diatomite-supported Ag₂O was obtained by heating the mixture at 80 °C for 1 hour.

Typical procedure for the preparation of MWCNT-supported Ag₂O nanoparticles

150 mg of MWCNT, 5 mL of 1 M AgNO₃, 185 mL of n-hexane and 1.78 g of bis-(2-ethylhexyl)-sodium sulfosuccinate (AOT) (4 mmol), were added into a 250 mL of flask under vigorous stirring for 6 hours. 15 mL of 1 M NaOH aqueous solution was added dropwise into that solution. After stirring for 5 hours, the reaction mixture was diluted with water and then filtered. The solid was dispersed in water and filtered again, and then the filter cake was washed by water for three times. The solid was then washed by acetone and THF for four times to remove the remainder of water and dried under vacuum for 10 hours at 60 °C, giving the desired MWCNT-supported Ag₂O nanoparticles in good yield.

Typical procedure for A³-coupling reaction

A mixture of benzaldehyde (212 mg, 2 mmol), diethylamine (219 mg, 3 mmol), pehnylacetylene (244 mg, 2.4 mmol) and Ag₂O/alumina catalyst (50 mg) in H₂O (2 mL) was stirred at 100 °C. After completion of the reaction (monitored by TLC), the catalyst was filtered. The product was transferred to the aqueous phase by addition of 10 mL of 2 M HCl and the aqueous phase was washed by EtOAc (3×10 mL). Then the aqueous phase was neutralized and the product was extracted by EtOAc (3×5 mL). Completing evaporation of the organic solvent gave the desired crude product which was purified by column chromatography over silica gel to give high purity product. The filtered catalyst was washed by MeOH (3×5 mL) and dried at 50 °C for 1 hour then was added in the coupling reaction for next cycle.

***N,N*-Diethyl-1,3-diphenylprop-2-yn-1-amine (1).** ¹H NMR (CDCl₃, 300 MHz, ppm): δ = 7.70-7.67 (m, 2 H), 7.51-7.49 (m, 2 H), 7.34-7.30 (m, 6 H), 5.05 (s, 1 H), 2.68-2.52 (m, 4 H), 1.08 (t, J = 7.1 Hz, 6 H). ¹³C NMR (CDCl₃, 75 MHz, ppm): δ = 140.0, 131.9, 128.5, 128.4, 128.2 (two signals overlap), 127.4, 123.6, 87.6, 86.3, 57.2, 44.7, 13.7. IR (Liquid film, cm⁻¹): ν = 3061, 2969, 2932, 2821, 1599, 1490, 1449, 1050, 756, 692. HRMS Calcd. C₁₉H₂₁N (M⁺): 263.1674. Found: 263.1680.

1-(4-Chlorophenyl)-*N,N*-diethyl-3-phenylprop-2-yn-1-amine (2). ¹H NMR (CDCl₃, 300 MHz, ppm): δ = 7.64-7.61 (m, 2 H), 7.51-7.48 (m, 2 H), 7.34-7.30 (m, 5 H), 4.99 (s, 1 H), 2.67-2.47 (m, 4 H), 1.07 (t, J = 4.0 Hz, 6 H). ¹³C NMR (CDCl₃, 75 MHz, ppm): δ = 139.1, 133.4, 132.3, 130.1, 128.8, 128.6 (two signals overlap), 123.6, 88.3, 86.0, 57.0, 45.1, 14.1. IR (Liquid film, cm⁻¹): ν = 3057, 2969, 2932, 2822, 1597, 1488, 1470, 1383, 1287, 1091, 1016, 755, 690. HRMS Calcd. C₁₉H₂₀³⁵ClN (M⁺): 297.1284. Found: 297.1289.

***N,N*-Diethyl-3-phenyl-1-*p*-tolylprop-2-yn-1-amine (3).** ¹H NMR (CDCl₃, 300 MHz, ppm): δ = 7.62-7.52 (m, 4 H), 7.35-7.33 (m, 3 H), 7.20-7.18 (m, 2 H), 5.06 (s, 1 H), 2.75-2.53 (m, 4 H), 2.38 (s, 3 H), 1.12 (t, J = 7.1 Hz, 6 H). ¹³C NMR (CDCl₃, 75 MHz, ppm): δ = 136.9, 136.8,

131.8, 128.8, 128.3 (two signals overlap), 128.0, 123.6, 87.4, 86.5, 56.9, 44.6, 21.1, 13.7. IR (KBr pellet, cm^{-1}): $\nu = 3054, 2969, 2820, 1598, 1509, 1490, 1051, 756, 691$. HRMS Calcd. $\text{C}_{20}\text{H}_{23}\text{N}$ (M^+): 277.1830. Found: 277.1836.

***N,N*-Diethyl-1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-amine (4).** ^1H NMR (CDCl_3 , 300 MHz, ppm): $\delta = 7.60\text{-}7.57$ (m, 2 H), $7.51\text{-}7.48$ (m, 2 H), $7.32\text{-}7.30$ (m, 3 H), $6.90\text{-}6.87$ (m, 2 H), 4.99 (s, 1 H), 3.80 (s, 3 H), $2.67\text{-}2.50$ (m, 4 H), 1.07 (t, $J = 7.1$ Hz, 6 H). ^{13}C NMR (CDCl_3 , 75 MHz, ppm): $\delta = 158.9, 132.0, 131.8, 129.5, 128.3, 128.0, 123.6, 113.5, 87.4, 86.6, 56.6, 55.2, 44.5, 13.7$. IR (KBr pellet, cm^{-1}): $\nu = 2968, 2834, 1610, 1509, 1490, 1464, 1247, 1171, 1038, 833, 756, 691$. HRMS Calcd. $\text{C}_{20}\text{H}_{23}\text{NO}$ (M^+): 293.1780. Found: 293.1786.

1-(Benzo[*d*][1,3]dioxol-6-yl)-*N,N*-diethyl-3-phenylprop-2-yn-1-amine (5). ^1H NMR (CDCl_3 , 300 MHz, ppm): $\delta = 7.50\text{-}7.46$ (m, 2 H), $7.32\text{-}7.30$ (m, 3 H), $7.19\text{-}7.18$ (m, 2 H), 6.78 (d, $J = 8.6$ Hz, 1 H), 5.95 (s, 2 H), 4.94 (s, 1 H), $2.69\text{-}2.47$ (m, 4 H), 1.07 (t, $J = 7.1$ Hz, 6 H). ^{13}C NMR (CDCl_3 , 75 MHz, ppm): $\delta = 147.7, 146.9, 134.1, 131.9, 128.4, 128.2, 123.5, 121.7, 109.0, 107.8, 101.1, 87.6, 86.4, 57.0, 44.6, 13.7$. IR (KBr pellet, cm^{-1}): $\nu = 2969, 2931, 1598, 1503, 1487, 1439, 1234, 1041, 938, 756, 691$. HRMS Calcd. $\text{C}_{20}\text{H}_{21}\text{NO}_2$ (M^+): 307.1572. Found: 307.1580.

***N,N*-Diethyl-3-phenylprop-2-yn-1-amine (6).** ^1H NMR (CDCl_3 , 300 MHz, ppm): $\delta = 7.44\text{-}7.40$ (m, 2 H), $7.30\text{-}7.26$ (m, 3 H), 3.64 (s, 2 H), 2.63 (q, $J = 7.1$ Hz, 4 H), 1.12 (t, $J = 7.1$ Hz, 6 H). ^{13}C NMR (CDCl_3 , 75 MHz, ppm): $\delta = 131.7, 128.2, 127.9, 123.8, 85.0, 84.5, 47.3, 41.5, 12.7$. IR (KBr pellet, cm^{-1}): $\nu = 3058, 2971, 2934, 2819, 2185, 1598, 1489, 1460, 1381, 1321, 1066, 691$. HRMS Calcd. $\text{C}_{13}\text{H}_{17}\text{N}$ (M^+): 187.1361. Found: 187.1366.

***N,N*-Diethyl-1-phenylnon-1-yn-3-amine (7).** ^1H NMR (CDCl_3 , 300 MHz, ppm): $\delta = 7.43\text{-}7.40$ (m, 2 H), $7.30\text{-}7.27$ (m, 3 H), 3.68 (t, $J = 6.8$ Hz, 1 H), $2.76\text{-}2.69$ (m, 2 H), $2.53\text{-}2.46$ (m, 2 H), $1.73\text{-}1.69$ (m, 2 H), 1.69 (br, 2 H), 1.52 (br, 6 H), 1.10 (t, $J = 7.2$ Hz, 6 H), 0.90 (t, $J = 6.5$ Hz, 3 H). ^{13}C NMR (CDCl_3 , 75 MHz, ppm): $\delta = 131.8, 128.3, 127.8, 123.9, 89.3, 84.7, 53.9, 45.0, 34.4, 31.9, 29.2, 26.9, 22.8, 14.2, 13.9$. IR (KBr pellet, cm^{-1}): $\nu = 3057, 2929, 2856, 1598, 1489, 1467, 1380, 1197, 1068, 755, 691$. HRMS Calcd. $\text{C}_{19}\text{H}_{29}\text{N}$ (M^+): 271.2300. Found: 271.2304.

***N,N*-Diethyl-3-phenyl-1-(pyridin-3-yl) prop-2-yn-1-amine (8).** ^1H NMR (CDCl_3 , 300 MHz, ppm): $\delta = 8.92$ (dd, $J = 0.8, 1.4$ Hz, 1 H), 8.53 (dd, $J = 1.2, 4.7$ Hz, 1 H), $8.00\text{-}7.95$ (m, 1 H), $7.52\text{-}7.49$ (m, 2 H), $7.34\text{-}7.32$ (m, 3 H), $7.30\text{-}7.26$ (m, 1 H), 5.06 (s, 1 H), $2.69\text{-}2.52$ (m, 4 H), 1.08 (t, $J = 7.1$ Hz, 6 H). ^{13}C NMR (CDCl_3 , 75 MHz, ppm): $\delta = 150.1, 148.6, 135.8, 135.5, 131.8, 128.3, 128.2, 123.0, 122.90, 88.2, 84.6, 55.1, 44.6, 13.6$. IR (KBr pellet, cm^{-1}): $\nu = 3413, 2970, 2218, 1671, 1576, 1474, 1287, 1054, 756, 692$. HRMS Calcd. $\text{C}_{18}\text{H}_{20}\text{N}_2$ (M^+): 264.1626. Found: 264.1631.

***N,N*-Diethyl-1-phenylhex-2-yn-1-amine (9).** ^1H NMR (CDCl_3 , 300 MHz, ppm): $\delta = 7.63\text{-}7.59$ (m, 2 H), $7.34\text{-}7.32$ (m, 2 H), $7.26\text{-}7.22$ (m, 1 H), 4.80 (s, 1 H), $2.55\text{-}2.40$ (m, 4 H), $2.31\text{-}2.26$ (m, 2 H), $1.63\text{-}1.56$ (m, 2 H), $1.06\text{-}1.00$ (m, 9 H). ^{13}C NMR (CDCl_3 , 75 MHz, ppm): $\delta = 140.7, 128.5, 128.0, 127.1, 87.4, 76.3, 56.7, 44.6, 22.7, 21.0, 13.7$ (two signals overlap). IR (KBr pellet, cm^{-1}): $\nu = 3061, 2966, 2821, 2257, 1601, 1491, 1451, 1381, 1196, 724, 697$. HRMS Calcd. $\text{C}_{16}\text{H}_{23}\text{N}$ (M^+): 229.1830. Found: 229.1822.

***N,N*-Diethylhex-2-yn-1-amine (10).** ^1H NMR (CDCl_3 , 300 MHz, ppm): δ = 3.39-3.38 (m, 2 H), 2.54 (q, J = 7.2 Hz, 4 H), 2.20-2.14 (m, 2 H), 1.56-1.49 (m, 2 H), 1.06 (t, J = 7.2 Hz, 6 H), 0.98 (t, J = 7.3 Hz, 3 H). ^{13}C NMR (CDCl_3 , 75 MHz, ppm): δ = 84.7, 74.4, 47.1, 40.9, 22.4, 20.7, 13.4, 12.5. IR (KBr pellet, cm^{-1}): ν = 2970, 2819, 2260, 1461, 1379, 1322, 1202, 1091, 981, 764. HRMS Calcd. $\text{C}_{10}\text{H}_{19}\text{N}$ (M^+): 153.1517. Found: 153.1509.

1-(3-Phenylprop-2-ynyl)piperidine (11). ^1H NMR (CDCl_3 , 300 MHz, ppm): δ = 7.45-7.41 (m, 2 H), 7.30-7.27 (m, 3 H), 3.47 (s, 2 H), 2.57 (br, 4 H), 1.68-1.61 (m, 4 H), 1.45 (br, 2 H). ^{13}C NMR (CDCl_3 , 75 MHz, ppm): δ = 131.5, 127.9, 127.7, 123.2, 84.9, 84.8, 53.2, 52.8, 48.3, 25.8, 23.8. IR (KBr pellet, cm^{-1}): ν = 3056, 2934, 1876, 1599, 1489, 1442, 1155, 1108, 860, 755, 691. HRMS Calcd. $\text{C}_{14}\text{H}_{17}\text{N}$ (M^+): 199.1361. Found: 199.1352.

1-(4-Methyl-1-phenylpent-1-yn-3-yl)piperidine (12). ^1H NMR (CDCl_3 , 300 MHz, ppm): δ = 7.44-7.41 (m, 2 H), 7.27-7.25 (m, 3 H), 2.98 (d, J = 9.6 Hz, 1 H), 2.65-2.59 (m, 2 H), 2.44-2.37 (m, 2 H), 1.93-1.81 (m, 1 H), 1.61-1.58 (m, 4 H), 1.44-1.41 (m, 2 H), 1.09 (d, J = 6.6 Hz, 3 H), 1.0 (d, J = 6.6 Hz, 3 H). ^{13}C NMR (CDCl_3 , 75 MHz, ppm): δ = 131.8, 128.3, 127.7, 123.9, 87.9, 86.2, 65.8, 50.9, 30.6, 26.4, 24.9, 20.8, 20.0. IR (KBr pellet, cm^{-1}): ν = 2933, 2804, 1598, 1489, 1443, 1323, 1261, 1096, 1005, 755, 690. HRMS Calcd. $\text{C}_{17}\text{H}_{23}\text{N}$ (M^+): 241.183. Found: 241.1822.

1-(5-Methyl-1-phenylhex-1-yn-3-yl)piperidine (13). ^1H NMR (CDCl_3 , 300 MHz, ppm): δ = 7.45-7.41 (m, 2 H), 7.30-7.26 (m, 3 H), 3.61-3.56 (dd, J = 5.8, 9.4 Hz, 1 H), 2.73-2.67 (m, 2 H), 2.52-2.50 (m, 2 H), 1.89-1.87 (m, 1 H), 1.70-1.56 (m, 6 H), 1.49-1.44 (m, 2 H), 0.97 (d, J = 6.9 Hz, 3 H), 0.95 (d, J = 6.8 Hz, 3 H). ^{13}C NMR (CDCl_3 , 75 MHz, ppm): δ = 131.8, 128.3, 127.8, 123.7, 88.2, 85.8, 56.8, 50.7, 42.4, 26.3, 25.5, 24.7, 23.2, 22.2. IR (KBr pellet, cm^{-1}): ν = 3056, 2933, 2804, 2750, 1598, 1573, 1489, 1467, 1158, 1097, 987, 755, 691. HRMS Calcd. $\text{C}_{18}\text{H}_{25}\text{N}$ (M^+): 255.1987. Found: 255.1996.

1-(1-Phenylhex-1-yn-3-yl)piperidine (14). ^1H NMR (CDCl_3 , 300 MHz, ppm): δ = 7.45-7.42 (m, 2 H), 7.30-7.27 (m, 3 H), 3.52-3.47 (dd, J = 5.4, 8.7 Hz, 1 H), 2.72-2.65 (m, 2 H), 2.52-2.47 (m, 2 H), 1.73-1.63 (m, 7 H), 1.49-1.43 (m, 3 H), 0.97 (t, J = 7.5 Hz, 3 H). ^{13}C NMR (CDCl_3 , 75 MHz, ppm): δ = 131.8, 128.3, 127.8, 123.7, 88.3, 85.7, 58.4, 50.7, 35.7, 26.3, 24.7, 20.2, 14.0. IR (KBr pellet, cm^{-1}): ν = 3056, 2931, 2750, 1598, 1489, 1325, 1273, 1158, 1117, 979, 911, 755, 691. HRMS Calcd. $\text{C}_{17}\text{H}_{23}\text{N}$ (M^+): 241.183. Found: 241.1835.

1-(3-Phenylprop-2-ynyl)pyrrolidine (15). ^1H NMR (CDCl_3 , 300 MHz, ppm): δ = 7.42-7.41 (m, 2 H), 7.30-7.26 (m, 3 H), 3.63 (s, 2 H), 2.71-2.70 (m, 4 H), 1.86-1.83 (m, 4 H). ^{13}C NMR (CDCl_3 , 75 MHz, ppm): δ = 131.5, 128.0, 127.7, 123.1, 85.2, 84.2, 52.5, 43.6, 23.6. IR (KBr pellet, cm^{-1}): ν = 2966, 2793, 1649, 1598, 1489, 1322, 1124, 756, 691. HRMS Calcd. $\text{C}_{13}\text{H}_{15}\text{N}$ (M^+): 185.1204. Found: 185.1199.

1-(1-(4-Methoxyphenyl)-3-phenylprop-2-ynyl)pyrrolidine (16). ^1H NMR (CDCl_3 , 300 MHz, ppm): δ = 7.53-7.47 (m, 4 H), 7.32-7.30 (m, 3 H), 6.91-6.88 (m, 2 H), 4.83 (s, 1 H), 3.81 (s, 3 H), 2.68 (br, 4 H), 1.80 (br, 4 H). ^{13}C NMR (CDCl_3 , 75 MHz, ppm): δ = 159.2, 131.9 (two signals overlap), 129.5, 128.3, 128.1, 123.4, 113.7, 87.2, 86.8, 58.6, 55.4, 50.3, 23.6. IR (KBr pellet, cm^{-1}):

¹): $\nu = 2963, 2806, 1609, 1509, 1461, 1248, 1171, 1036, 833, 756, 691$. HRMS Calcd. $C_{20}H_{21}NO$ (M^+): 291.1623. Found: 291.1629.

1-(4-Methyl-1-phenylpent-1-yn-3-yl)pyrrolidine (17). ¹H NMR ($CDCl_3$, 300 MHz, ppm): $\delta = 7.43-7.41$ (m, 2 H), $7.32-7.26$ (m, 3 H), 3.27 (d, $J = 7.8$ Hz, 1 H), $2.76-2.68$ (m, 4 H), $1.95-1.88$ (m, 1 H), 1.80 (br, 4 H), 1.13 (d, $J = 6.6$ Hz, 3 H), 1.06 (d, $J = 6.6$ Hz, 3 H). ¹³C NMR ($CDCl_3$, 75 MHz, ppm): $\delta = 131.8, 128.2, 127.8, 123.7, 87.7, 85.8, 62.6, 50.4, 32.0, 23.6, 20.3, 19.5$. HRMS Calcd. $C_{16}H_{21}N$ (M^+): 227.1674. Found: 227.1669.

4-(3-Phenyl-prop-2-ynyl)morpholine (18). ¹H NMR ($CDCl_3$, 300 MHz, ppm): $\delta = 7.45-7.43$ (m, 2 H), $7.31-7.29$ (m, 3 H), 3.77 (t, $J = 4.5$, 4 H), 3.51 (s, 2 H), 2.64 (t, $J = 4.5$ Hz, 4 H). ¹³C NMR ($CDCl_3$, 75 MHz, ppm): $\delta = 131.6, 128.1, 128.0, 122.9, 85.4, 84.0, 66.7, 52.3, 47.9$. IR (KBr pellet, cm^{-1}): $\nu = 2959, 2854, 2814, 1598, 1489, 1331, 1116, 1006, 862, 757, 692$. HRMS Calcd. $C_{13}H_{15}NO$ (M^+): 201.1154. Found: 201.1159.

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9. Ag₂O nanoparticles were synthesized as follows: 0.01 M NaOH was added to 20 mL of 0.01 M AgNO₃ solution dropwise till the pH up to 10. The mixture was centrifuged and washed by water for several times. Then the silver(I) oxide powder was dried at 100 °C for 4 hours. TEM image showed that the particle size was mainly distributed in the range of 10-12 nm.