



## Highly efficient three-component (aldehyde–alkyne–amine) coupling reactions catalyzed by a reusable PS-supported NHC–Ag(I) under solvent-free reaction conditions

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### ABSTRACT

The development of a highly efficient, polystyrene-supported NHC–Ag(I) catalyst for the three-component coupling reactions of aldehydes, alkynes, and amines ( $A^3$ -coupling) was described. In the presence of PS–NHC–Ag(I) (2 mol %), the  $A^3$ -reactions were carried out at room temperature under solvent-free reaction conditions and the corresponding propargylamines were generated in good to excellent yields. Furthermore, the catalyst could be reused at least 12 times without a significant loss of its catalytic activity.

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The transition-metal catalyzed multi-component reaction is a powerful synthetic tool to access complex structures from simple precursors.<sup>1</sup> In comparison with other transition metals, silver has been virtually untouched as a catalyst for coupling purposes because silver species are commonly considered to have low activity and efficiency, and not to be as good as other late transition metals. But very recently, silver has received more and more attention and is also used as a catalyst or co-catalyst in organic reactions, such as addition,<sup>2</sup> carbon–carbon bond coupling reaction,<sup>3</sup> cyclization,<sup>4</sup> and allylation.<sup>5</sup> In 2003, Li's group developed the first silver-catalyzed three-component coupling of aldehyde, alkyne, and amine ( $A^3$ -coupling),<sup>6</sup> because  $A^3$ -coupling reactions have attracted much attention from organic chemists for the coupling products, propargylamines, which are major skeletons or synthetically versatile building blocks for the preparation of many nitrogen-containing biologically active compounds.<sup>7</sup> There are several transition-metal catalysts, which are able to promote this three-component ( $A^3$ -coupling) reactions. These include Cu(I) salts,<sup>8</sup> Ag(I) salts,<sup>6,9</sup> Au(I)/Au(III) salts,<sup>10</sup> Au(III)–salen complexes,<sup>11</sup> Ir complexes,<sup>12</sup> Hg<sub>2</sub>Cl<sub>2</sub><sup>13</sup> and Cu/Ru bimetallic systems<sup>14</sup> under homogeneous reaction conditions. But all of these catalytic systems suffer from the loss of the precious or hazardous catalysts at the end of the reaction. In order to achieve the recyclability of

the catalysts, Ag(I) and Cu(I) in ionic liquids have been developed by Li et al.<sup>15</sup> and Park et al.,<sup>16</sup> respectively, hydroxyapatite-supported copper (Cu-HAP) and layered double hydroxide supported gold (LDH–AuCl<sub>4</sub>) reported by Likhar et al.<sup>17</sup> heteropolyacid-supported silver (Ag-HPA) observed by Reddy et al.<sup>18</sup> and AgY zeolite prepared by Maggi et al.<sup>19</sup> were successfully used to catalyze  $A^3$ -coupling reactions under heterogeneous reaction conditions with reusability of catalysts. Most recently, Kidwai et al.<sup>20</sup> reported gold- and copper-nanoparticles as reusable catalysts, and Corma et al.<sup>21</sup> developed CeO<sub>2</sub>- and ZrO<sub>2</sub>-stabilized Au(III) as efficient catalysts for the  $A^3$ -coupling reactions. However, almost all of these  $A^3$ -coupling reaction protocols were carried out under heating reaction conditions. It is desirable to develop highly efficient catalysts for  $A^3$ -coupling reactions, which can be carried out at ambient temperature.

In the past decades, *N*-heterocyclic carbenes (NHCs) are widely used as ligands in inorganic and organometallic chemistry since Arduengo and coworkers isolated the first stable *N*-heterocyclic carbenes in 1991.<sup>22</sup> NHCs were first considered as simple phosphine mimics in organometallic chemistry,<sup>23</sup> and increasing experimental data have clearly shown that NHC–metal complexes can surpass their phosphine-based counterparts in both activity and scope. Complexes of *N*-heterocyclic carbenes with virtually every transition metal and many main group elements have been reported.<sup>24</sup> Meanwhile, Nolan's group developed a lot of new NHC–metal complexes, and which were subsequently used to catalyze

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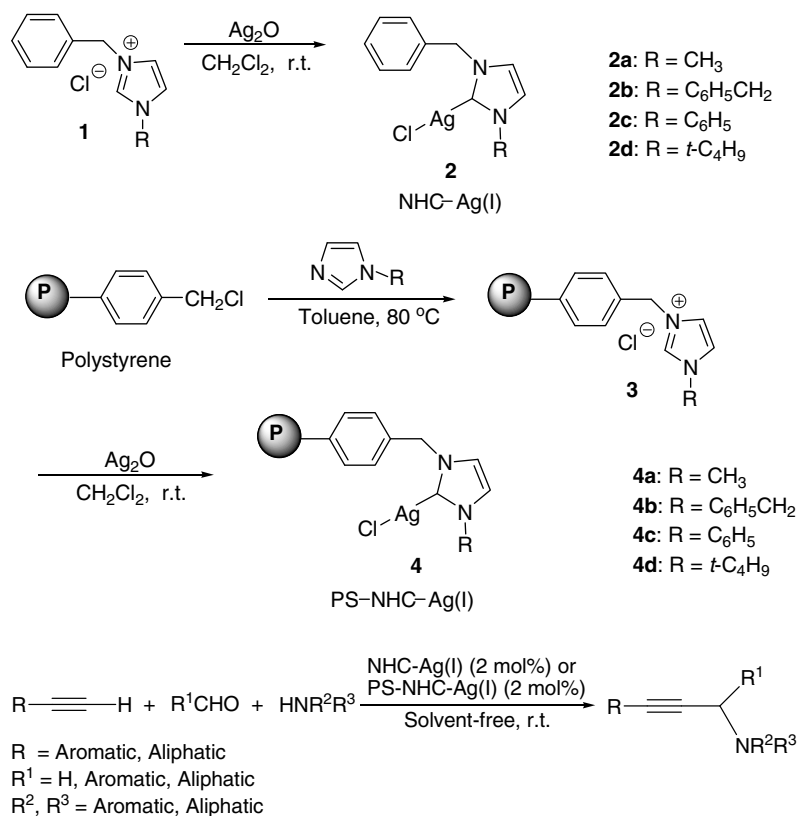
C–C, C–H, C–O, and C–N bond formation reactions efficiently.<sup>25</sup> However, NHC–Ag complexes could be easily synthesized from silver oxide and the corresponding imidazolium salts, while their catalytic activities and applications in organic reactions received little attention.<sup>26</sup>

Environmental concerns associated with chemical processes have encouraged the development of more environmentally friendly methodology for organic reactions. In recent years, immobilizing transition-metal catalysts have received considerable interest. A great deal of efforts have been made for the development of carbon–carbon bond formation reactions catalyzed by supported NHC–metal complexes.<sup>27</sup> As a part of our ongoing interest in the synthesis of propargylamines with A<sup>3</sup>-coupling reactions, we herein report polystyrene-supported NHC–Ag(I) complexes, as well as NHC–Ag(I) complexes, as efficient catalysts for the three-component coupling of aldehydes, alkynes, and amines (A<sup>3</sup>-reactions) under solvent-free conditions at room temperature. The reactions generated the corresponding propargylamines in good to excellent yields. This methodology provided a wide range of substrate applicability and could be applied to aromatic and aliphatic aldehydes, amines, and alkynes. To the best of our knowledge, this is the first example of NHC–Ag(I) or PS–NHC–Ag(I) catalyzed A<sup>3</sup>-coupling reactions (Scheme 1). It is noteworthy that PS–NHC–Ag(I) could be reused at least 12 times without a significant loss of its catalytic activity.

The synthesis of a series of NHC–Ag(I) and PS–NHC–Ag(I) catalysts is illustrated in Scheme 1. They were readily prepared in good yields through a straightforward one- or two-step procedure from commercially available starting materials and reagents.<sup>28</sup> Our initial investigation was focused on the catalytic activity of NHC–Ag(I) and PS–NHC–Ag(I). The above-synthesized catalysts were employed in the A<sup>3</sup>-coupling of *para*-formaldehyde, phenylacetylene, and piperidine (a model reaction) at room temperature in

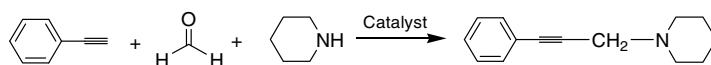
CH<sub>2</sub>Cl<sub>2</sub>. The results are summarized in Table 1. The influence of a substituted group of imidazolium salts in NHC–Ag(I) on their catalytic activity for the A<sup>3</sup>-coupling reaction is C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub> > C<sub>6</sub>H<sub>5</sub> > *t*-C<sub>4</sub>H<sub>9</sub> > CH<sub>3</sub>. It is obvious that the catalytic activity of NHC–Ag(I) decreases for the A<sup>3</sup>-coupling reaction in order: **2b** > **2c** > **2d** > **2a** (Table 1, entries 1–4). This order was also found in the sequence of PS–NHC–Ag(I) catalysts, **4a**–**4d** (Table 1, entries 5–8). The effect of polymer support on the catalytic activity was also investigated, and the results showed that PS–NHC–Ag(I) with polystyrene backbone as support were bestowed with a little higher catalytic activity than their corresponding NHC–Ag(I) analogues (Table 1, **2a** versus **4a**, **2b** versus **4b**, **2c** versus **4c**, and **2d** versus **4d**). As a result, it is evident that **2b** and **4b** are the best catalysts for the A<sup>3</sup>-coupling reaction, and especially, **4b** exhibits the highest catalytic activity. (Table 1, entries 2 and 6). Poor results were observed when Ag<sub>2</sub>O or AgI was used as catalyst (Table 1, entries 9 and 10), and when the reaction was performed in the absence of any silver source, no desired A<sup>3</sup>-coupling product was detected.

The effect of solvent on A<sup>3</sup>-coupling of *para*-formaldehyde, phenylacetylene, and piperidine using **4b** as catalyst was surveyed (Table 2). Among the solvents tested in Table 2, acetone, CH<sub>3</sub>CN, DMSO, and CH<sub>2</sub>Cl<sub>2</sub> were the most suitable reaction media for A<sup>3</sup>-coupling reaction (Table 2, entries 1–4). DMF was inferior and generated the corresponding product in 84% yield (Table 1, entry 5), whereas toluene and THF afforded moderate yields of desired products (Table 1, entries 6 and 7). Poor results were observed when the reactions were carried out in C<sub>2</sub>H<sub>5</sub>OH and H<sub>2</sub>O (Table 1, entries 8 and 9). Surprisingly, 97% yield of the desired product was isolated when the reaction was carried out under neat reaction conditions at room temperature (Table 1, entry 10). To avoid the use of volatile solvents and reduce the environmental pollution, all the three-component coupling reactions were performed under solvent-free reaction conditions. Thus, the optimized reaction



Scheme 1.

**Table 1**  
Effect of silver catalyst on A<sup>3</sup>-coupling reaction<sup>a</sup>

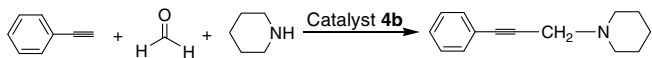


Entry	Catalyst	Solvent	Yield <sup>b</sup> (%)
1	<b>2a</b>	CH <sub>2</sub> Cl <sub>2</sub>	61
2	<b>2b</b>	CH <sub>2</sub> Cl <sub>2</sub>	80
3	<b>2c</b>	CH <sub>2</sub> Cl <sub>2</sub>	74
4	<b>2d</b>	CH <sub>2</sub> Cl <sub>2</sub>	68
5	<b>4a</b>	CH <sub>2</sub> Cl <sub>2</sub>	69
6	<b>4b</b>	CH <sub>2</sub> Cl <sub>2</sub>	90
7	<b>4c</b>	CH <sub>2</sub> Cl <sub>2</sub>	80
8	<b>4d</b>	CH <sub>2</sub> Cl <sub>2</sub>	75
9	Ag <sub>2</sub> O	CH <sub>2</sub> Cl <sub>2</sub>	37
10	AgI	CH <sub>2</sub> Cl <sub>2</sub>	31

<sup>a</sup> Reaction conditions: *para*-formaldehyde (1.0 mmol), piperidine (1.1 mmol), phenylacetylene (1.1 mmol), silver catalyst (2 mol %), CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL), nitrogen atmosphere, at room temperature for 24 h.

<sup>b</sup> Isolated yields.

**Table 2**  
Effect of solvent on A<sup>3</sup>-coupling reaction using **4b** as catalyst<sup>a</sup>



Entry	Catalyst	Solvent	Yield <sup>b</sup> (%)
1	<b>4b</b>	Acetone	95
2	<b>4b</b>	CH <sub>3</sub> CN	91
3	<b>4b</b>	DMSO	90
4	<b>4b</b>	CH <sub>2</sub> Cl <sub>2</sub>	90
5	<b>4b</b>	DMF	84
6	<b>4b</b>	Toluene	69
7	<b>4b</b>	THF	62
8	<b>4b</b>	C <sub>2</sub> H <sub>5</sub> OH	49
9	<b>4b</b>	H <sub>2</sub> O	42
10	<b>4b</b>	Neat	97
11	<b>4b</b>	Neat	71 <sup>c</sup>

<sup>a</sup> Reaction conditions: *para*-formaldehyde (1.0 mmol), piperidine (1.1 mmol), phenylacetylene (1.1 mmol), **4b** (2 mol %), solvent (0.5 mL), nitrogen atmosphere at room temperature for 24 h.

<sup>b</sup> Isolated yields.

<sup>c</sup> PS-NHC-Ag(I) (1 mol %) was used.

conditions for this A<sup>3</sup>-coupling reaction are PS-NHC-Ag(I) catalyst, **4b** (2 mol %) in neat reaction conditions at room temperature for 24 h.

To examine the scope of this three-component coupling reaction, we extended our studies to different combinations of amines, aldehydes, and alkynes. The results are outlined in Table 3. At the beginning of the search for the amine substrate scope, phenylacetylene was used as a model substrate and various amines with different aldehydes were examined (Table 3, entries 1–15). The results indicated that cyclic, heterocyclic, and acyclic secondary aliphatic amines gave excellent yields of the desired products at room temperature with the combination of phenylacetylene-*para*-formaldehyde-amines under standard reaction conditions (Table 3, entries 1–5). Fortunately, secondary aromatic amines also reacted with benzaldehyde and phenylacetylene to give the corresponding products in good yield (Table 3, entry 6).

In order to expand the scope of aldehyde substrates, a combination of phenylacetylene-piperidine-aldehydes was chosen, and various aldehydes were examined. The aliphatic aldehydes, including cyclic and acyclic ones, displayed high reactivity under present reaction conditions (Table 3, entries 7–9). Aromatic aldehydes with both electron-donating and electron-withdrawing functionalities also afforded the corresponding propargylamines in good to excel-

lent yields, and the reaction of aryl aldehydes was also tolerant of *ortho* substitution (Table 3, entries 10–15).

Subsequently, a variety of alkynes were also examined for the A<sup>3</sup>-coupling by using *para*-formaldehyde-*N,N*-dibenzylamine-alkynes manner (Table 3, entries 16–22). As can be seen from the Table 3, the reactivity of both aliphatic and aromatic alkynes was observed, in which aromatic alkynes were often more reactive than aliphatic ones. Aromatic alkynes, including those bearing functional groups, such as methyl, phenyl, chloro, and bromo, were able to undergo three-component-coupling smoothly and generate the corresponding products in excellent yields (Table 3, entries 16–19). The reactions involving terminal aliphatic alkynes also gave both higher conversions and isolated yields under the present reaction conditions (Table 3, entries 20–23). However, no A<sup>3</sup>-reaction product was isolated and starting materials were recovered when ethynyltrimethylsilane was served as terminal alkyne substrate (Table 3, entry 24).




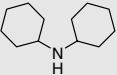

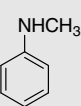


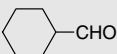















The recyclability of PS-NHC-Ag(I) catalyst **4b** was also investigated. After carrying out the reaction, the catalyst **4b** was separated by simple filtration and washed with acetone (2 mL × 2). After air-dried, it could be reused directly without further purification. The recovered catalyst was used in the next run and almost consistent activity was observed for 12 consecutive cycles (Table 4, entries 1–12). Meanwhile, silver leaching in polystyrene-supported NHC-Ag(I) catalyst **4b** was determined. Inductively coupled plasma (ICP) analysis of the clear filtrates obtained by filtration after the reaction indicated that Ag content is less than 0.1 ppm. However, only trace amount of the desired product was isolated for the model reaction by adding substrates to a filtrate obtained from the filtration of the supported catalyst after the reaction.

**Representative preparation of NHC-Ag(I) catalyst 2b:** In an oven-dried Schlenk flask, 1,3-dibenzylimidazolium chloride **2a** (285 mg, 1.0 mmol) and silver(I) oxide (116 mg, 0.5 mmol) were dissolved/suspended in dichloromethane (10 mL) and stirred at room temperature in the dark for 12 h. The resulting solution was filtered and concentrated, and the silver complex precipitated by addition of excess diethyl ether as a pale crystal, **2b** (243 mg, 62% yield).<sup>28</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.48–7.40 (m, 6H), 7.33–7.26 (m, 4H), 6.98 (s, 2H), 5.34 (s, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 151.1, 135.2, 129.1, 128.9, 127.9, 121.7, 55.8.




**Representative preparation of Merrifield resin supported ionic liquid 3b:** Under nitrogen atmosphere, benzylimidazole (395 mg, 2.5 mmol) and Merrifield resin (2.0 g, loading of benzylchloride, 1.0 mmol g<sup>-1</sup>) were mixed in toluene (15 mL) in a round-bottomed flask. The reaction was carried out at 80 °C for 24 h. Then the solution was filtered and the solid was washed with chloroform (5 mL),

**Table 3**  
A<sup>3</sup>-coupling reaction catalyzed by PS-NHC-Ag(I) catalyst **4b**<sup>a</sup>

$$\text{R}\text{-}\equiv\text{C} + \text{R}^1\text{CHO} + \text{NHR}^2\text{R}^3 \xrightarrow[\text{Solvent-free}]{\text{PS-NHC-Ag(I), } \mathbf{4b}} \text{R}\text{-}\equiv\text{C}\text{-C}(\text{R}^1)\text{-NR}^2\text{R}^3$$

Entry	Alkyne	Aldehyde	Amine	Yield <sup>b</sup> (%)
1	C <sub>6</sub> H <sub>5</sub> C≡CH	CH <sub>2</sub> O		97
2	C <sub>6</sub> H <sub>5</sub> C≡CH	CH <sub>2</sub> O		94
3	C <sub>6</sub> H <sub>5</sub> C≡CH	CH <sub>2</sub> O		95
4	C <sub>6</sub> H <sub>5</sub> C≡CH	CH <sub>2</sub> O		97
5	C <sub>6</sub> H <sub>5</sub> C≡CH	CH <sub>2</sub> O		98
6	C <sub>6</sub> H <sub>5</sub> C≡CH	C <sub>6</sub> H <sub>5</sub> CHO		85 <sup>c</sup>
7	C <sub>6</sub> H <sub>5</sub> C≡CH			94
8	C <sub>6</sub> H <sub>5</sub> C≡CH			91
9	C <sub>6</sub> H <sub>5</sub> C≡CH			90
10	C <sub>6</sub> H <sub>5</sub> C≡CH	C <sub>6</sub> H <sub>5</sub> CHO		92 <sup>c</sup>
11	C <sub>6</sub> H <sub>5</sub> C≡CH	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CHO		95 <sup>c</sup>
12	C <sub>6</sub> H <sub>5</sub> C≡CH	<i>m</i> -ClC <sub>6</sub> H <sub>4</sub> CHO		92 <sup>c</sup>
13	C <sub>6</sub> H <sub>5</sub> C≡CH	<i>o</i> -ClC <sub>6</sub> H <sub>4</sub> CHO		89 <sup>c</sup>
14	C <sub>6</sub> H <sub>5</sub> C≡CH	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CHO		96 <sup>c</sup>
15	C <sub>6</sub> H <sub>5</sub> C≡CH	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CHO		92 <sup>c</sup>
16	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> C≡CH	CH <sub>2</sub> O		96
17	<i>p</i> -C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> C≡CH	CH <sub>2</sub> O		95
18	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> C≡CH	CH <sub>2</sub> O		98
19	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> C≡CH	CH <sub>2</sub> O		96
20	<i>n</i> -C <sub>8</sub> H <sub>17</sub> C≡CH	CH <sub>2</sub> O		90
21	<i>n</i> -C <sub>6</sub> H <sub>13</sub> C≡CH	CH <sub>2</sub> O		89

**Table 3** (continued)

Entry	Alkyne	Aldehyde	Amine	Yield <sup>b</sup> (%)
22	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OCH <sub>2</sub> C≡CH	CH <sub>2</sub> O		85
23	C <sub>2</sub> H <sub>5</sub> O <sub>2</sub> CC≡CH	CH <sub>2</sub> O		87
24	(CH <sub>3</sub> ) <sub>3</sub> SiC≡CH	CH <sub>2</sub> O		0

<sup>a</sup> Reaction conditions: aldehyde (1.0 mmol), amine (1.1 mmol), alkyne (1.1 mmol), PS-NHC-Ag(I), **4b** (2 mol %), nitrogen atmosphere at room temperature for 24 h.

<sup>b</sup> Isolated yields.

<sup>c</sup> At 50 °C for 5 h.

methanol (5 mL), and ethyl acetate (5 mL), respectively, and dried under vacuo at 60 °C. 2.26 g of pale resin was obtained. The loading of the Merrifield resin supported ionic liquid **3b** was quantified via CHN microanalysis and found to be 0.92 mmol g<sup>-1</sup> based on nitrogen percentage. IR (film): 2851, 1353, 1077, 1028 cm<sup>-1</sup>.

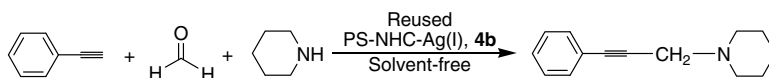
**Representative preparation of PS-NHC-Ag(I) catalyst 4b:** In an oven-dried Schlenk flask, Ag<sub>2</sub>O (116 mg, 0.5 mmol); **3b** (1.1 g), and CH<sub>2</sub>Cl<sub>2</sub> (10 mL) were added. The resulting suspension was stirred at room temperature for 10 h. Then the solution was filtered and the solid was washed with methanol (4 mL) and acetone (4 mL × 2), respectively, and dried under vacuo at 60 °C for 3 h. PS-NHC-Ag(I) catalyst **4b** was obtained as a light gray resin (1.16 g). IR (film): 2907, 1373, 1093, 1020 cm<sup>-1</sup>. The silver amount of the catalyst **4b** was found to be 0.78 mmol g<sup>-1</sup> based on ICP analysis.

**Typical procedure of A<sup>3</sup>-coupling reaction catalyzed by NHC-Ag(I) catalyst 2b:** In an oven-dried Schlenk flask, catalyst **2b** (8 mg, 0.02 mmol), phenylacetylene (110 mg, 1.1 mmol), *para*-formaldehyde (30 mg, 1.0 mmol), piperidine (94 mg, 1.1 mmol), and CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) were added. The mixture was stirred at room temperature for 24 h. After the reaction was completed, ethyl ether (5 mL) was added. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, concentrated, and the residue was purified by flash chromatography on silica gel (eluant:hexane/ethyl acetate = 3:1, V/V) to give the corresponding A<sup>3</sup>-coupling product [1-(3-phenyl-prop-2-yn-1-yl)piperidine] as a colorless oil (160 mg, 80% yield).

**Typical procedure of A<sup>3</sup>-coupling reaction catalyzed by PS-NHC-Ag(I) catalyst 4b:** Under nitrogen atmosphere, PS-NHC-Ag(I) catalyst **4b** (32 mg, contains silver 0.02 mmol), phenylacetylene (110 mg, 1.1 mmol), *para*-formaldehyde (30 mg, 1.0 mmol), and piperidine (94 mg, 1.1 mmol) were added in a 10 mL of Schlenk flask. The mixture was stirred at room temperature for 24 h. After the reaction was completed, ethyl ether (3 mL × 3) was added and the slurry was stirred to ensure removal of the product from the surface of catalyst, then filtered using a sintered glass funnel. The residue was washed with ethyl ether. The combined organics were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, concentrated, and the residue was purified by flash chromatography on silica gel (eluant:hexane/ethyl acetate = 3:1, V/V) to give the corresponding A<sup>3</sup>-coupling product [1-(3-phenyl-prop-2-yn-1-yl)piperidine] as a colorless oil (193 mg, 97% yield).

In summary, we have successfully developed a novel, practical and environmentally friendly method for the syntheses of propargylamines through three-component coupling of aldehydes, amines, and alkynes by using PS-NHC-Ag(I) catalyst **4b** (2 mol %) at room temperature under solvent-free reaction conditions. The reactions generated the corresponding propargylamines in high

**Table 4**  
Successive trials by using reused PS-NHC-Ag(I) catalyst **4b**<sup>a</sup>



Cycle	Yield <sup>b</sup> (%)	Cycle	Yield <sup>b</sup> (%)
1	97	7	93
2	94	8	92
3	96	9	93
4	95	10	92
5	94	11	90
6	94	12	91

<sup>a</sup> Reaction conditions: *para*-formaldehyde (1.0 mmol), phenylacetylene (1.1 mmol), piperidine (1.1 mmol), reused PS-NHC-Ag(I) catalyst **4b** (2 mol %), nitrogen atmosphere at room temperature for 24 h.

<sup>b</sup> Isolated yields.

yields and were applicable to aromatic and aliphatic aldehydes, alkynes, and amines. In addition, this methodology offers a competitive recyclability of the catalyst without a significant loss of its catalytic activity and the catalyst could be readily recovered and reused, thus making this procedure more environmentally acceptable whilst no catalyst leaching was observed. Further investigation on the application of this kind of supported catalysts is still underway in our laboratory.

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