



## Ligand-promoted reaction on silver nanoparticles: phosphine-promoted, silver nanoparticle-catalyzed cyclization of 2-(1-hydroxy-3-arylprop-2-ynyl)phenols

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### ABSTRACT

A highly efficient annulation of 2-(1-hydroxy-3-arylprop-2-ynyl)phenols leading to the key intermediates to synthesize aurones was catalyzed by silver nanoparticles/carbon black-supported silver nanoparticles. In the presence of phosphine ligand, both the catalysts show excellent catalytic activities in the reaction and give the products with good yields as well as excellent regio- and stereo-selectivities in a water-toluene mixed solvent. Furthermore, the catalysts can be recovered and recycled effectively several times.

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In recent years, there has been a great interest in using nanoparticles as catalysts in organic reactions.<sup>1</sup> Because of their easy preparation and being relative stable in air, the nanoparticles of coinage metals such as copper, silver, and gold were widely reported; and there are many excellent examples on their applications as catalysts.<sup>2</sup> In contrast to the many examples of using copper or gold nanoparticles as catalysts for organic reactions, there are only a few reports on using silver nanoparticles (SNPs) as catalysts; and in most of the cases SNPs worked as dehydrogenation catalysts.<sup>3</sup> Herein, we report a novel silver nanoparticle-catalyzed cyclization of 2-(1-hydroxy-3-arylprop-2-ynyl)phenols (**1**) in water, leading to an efficient and expeditious synthesis of aurones (**3**),<sup>4</sup> which have exhibited a wide range of biological activities such as antifungal agents, tyrosinase inhibitors, antioxidant, and others<sup>5</sup> (Scheme 1, route A). With the promotion of a phosphine ligand and water, silver nanoparticles showed extremely high catalytic activities towards the annulation of **1** in good yields as well as excellent regio- and stereoselectivities. To the best of our knowledge, it is also the first example regarding the ligand-promotion observed in silver nanoparticle-catalyzed reactions.<sup>6</sup> Furthermore, the silver nanoparticles could be recovered and reused effectively several times.

Recently, we developed a highly efficient alkynylation-cyclization of terminal alkynes with salicylaldehydes generating substituted 2,3-dihydrobenzofuran-3-ol derivatives (**2**) by using Cy<sub>3</sub>P-silver(I) complex as the catalyst in water (Scheme 1, route

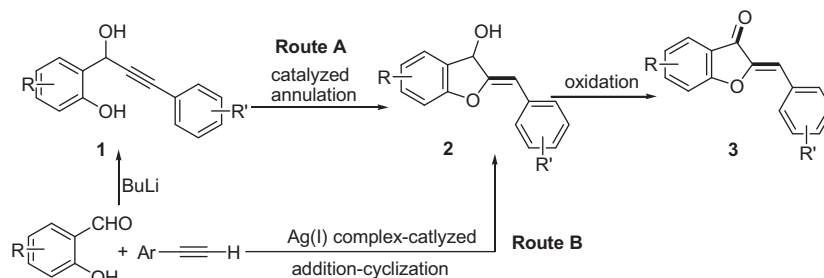
B).<sup>7</sup> During our further studies on the mechanism of the reaction, accidentally, the silver black precipitated on the stir bar, which resulted from the decomposition of Cy<sub>3</sub>P-silver(I) complex, was found to show a certain catalytic activity to the annulation of **1** with the promotion of a phosphine ligand in water.<sup>8</sup> Thus, surfactant-free silver nanoparticle catalysts and carbon black-supported silver nanoparticles (CSNs) catalysts were synthesized and utilized in the cyclization of **1**. The average size of silver nanoparticles is ca. 50 nm based on the TEM image.<sup>9</sup>

The annulation of 2-(1-hydroxy-3-phenylprop-2-ynyl)phenol (**1a**) was selected as the prototype reaction, and some ligands and solvents were examined (Table 1). As demonstrated in Table 1, both SNPs and CSNs showed excellent activities at room temperature to catalyze the cyclization promoted by a phosphine ligand in a water-toluene mixed solvent (entries 1 and 2, Table 1). Although SNPs gave higher activities than CSNs, considering their convenience in handling and storage, the latter were selected for further investigations.<sup>10</sup>

Control experiments in entries 3 and 4 showed that phosphine ligands can promote the cyclization effectively: in the absence of a phosphine ligand, no reaction was observed even at 100 °C, and most starting materials were recovered. A series of phosphine ligands, including both mono- and bidentate ligands, were then screened. Among the monodentate phosphine ligands, Ph<sub>3</sub>P, Cy<sub>3</sub>P, and tri-*o*-tolylphosphine showed good to excellent activities at room temperature, and up to 95% yield of the desired product was obtained with the addition of 10 mol % of *n*-Bu<sub>3</sub>P at 50 °C (entries 2, and 5–7). It is worthy noting that bidentate phosphine ligands such as DPPE and DPPP decreased the catalytic activities

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**Scheme 1.** The synthesis of aurones based on the cyclization of **1**.

(entries 8 and 9). Considering its cost and convenience in handling, we then chose  $\text{PPh}_3$  as the ligand. Even with a lower loading or at low temperature, ca. 90% yields were still achieved with a prolonged reaction time (entries 10–12).

The effect of water in the phosphine-promoted, CSNs/SNPs-catalyzed annulation was also studied. In the absence of water, almost no reaction was observed at room temperature with either SNPs or CSNs as catalysts; whereas much lower yields were observed and a longer reaction time was required even at 100 °C (entries 13–16)

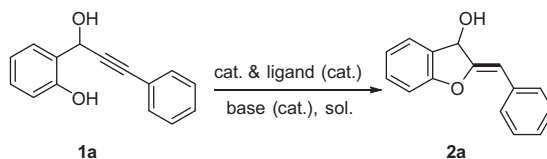
Some N-donor ligands were also evaluated (entries 18–21). Bipyridine exhibited good activity to give the desired product in moderate yields. Noticeably, when *i*-Pr-Pybox was introduced, up to 90% yield of the cyclization product was obtained in 1 h (entry 20).

In order to exclude some other factors probably leading to the same results, several control experiments were also carried out.

Considering phosphine ligands might be easily oxidized under the reaction conditions, triphenylphosphine oxide was utilized alone and together with SNPs, respectively (entries 22 and 23); and no reaction was observed in either case. On the other hand, in order to remove any possible silver ions that remained on the surface, the SNPs catalyst was treated by  $\text{NaBH}_4$  solution before its usage, and no obvious decrease in catalytic activity was observed (entry 24).

Under the optimized reaction conditions (10 mol % of CSNs, 10 mol % of  $\text{PPh}_3$  and 10 mol % of *i*-Pr<sub>2</sub>NEt in water–toluene mixed solvent),<sup>11</sup> the scope of this transformation was examined, and the results are summarized in Table 2. A variety of substituted 2-(1-hydroxy-3-arylprop-2-ynyl)phenols (**2**) with electron donating or electron withdrawing functional groups were compatible under our reaction conditions: all these reactions were completed in 1–3 h, and good to excellent yields were obtained (entries 2–13).

**Table 1**  
Silver nanoparticles-catalyzed cyclization of **1a**<sup>a</sup>



Entry	Catalyst (mol %)	Ligand (mol %)	Base (mol %)	Solvent	Conditions	Result <sup>b</sup>
1	SNPs (10)	$\text{Ph}_3\text{P}$ (10)	<i>i</i> -Pr <sub>2</sub> NEt (10)	Water–toluene	rt, 0.5 h	92%
2	CSNs (10)	$\text{Ph}_3\text{P}$ (10)	<i>i</i> -Pr <sub>2</sub> NEt (10)	Water–toluene	rt, 1 h	92%
3	CSNs (10)	–	<i>i</i> -Pr <sub>2</sub> NEt (20)	Water–toluene	rt, 1 h	ND <sup>c</sup>
4	CSNs (10)	–	<i>i</i> -Pr <sub>2</sub> NEt (20)	Water–toluene	100 °C, 1 h	ND <sup>c</sup>
5	CSNs (10)	$\text{Cy}_3\text{P}$ (10)	<i>i</i> -Pr <sub>2</sub> NEt (10)	Water–toluene	rt, 1.5 h	85%
6	CSNs (10)	<i>n</i> -Bu <sub>3</sub> P (10)	<i>i</i> -Pr <sub>2</sub> NEt (10)	Water–toluene	50 °C, 1 h	95%
7	CSNs (10)	<i>o</i> -Tol <sub>3</sub> P (10)	<i>i</i> -Pr <sub>2</sub> NEt (10)	Water–toluene	rt, 0.5 h	83%
8	CSNs (10)	dppp (10)	<i>i</i> -Pr <sub>2</sub> NEt (10)	Water–toluene	50 °C, 2 h	75%
9	CSNs (10)	dppb (10)	<i>i</i> -Pr <sub>2</sub> NEt (10)	Water–toluene	50 °C, 1 h	85%
10	CSNs (10)	$\text{Ph}_3\text{P}$ (5)	<i>i</i> -Pr <sub>2</sub> NEt (10)	Water–toluene	rt, 3 h	90%
11	CSNs (10)	$\text{Ph}_3\text{P}$ (20)	<i>i</i> -Pr <sub>2</sub> NEt (10)	Water–toluene	rt, 1 h	92%
12	CSNs (10)	$\text{Ph}_3\text{P}$ (10)	<i>i</i> -Pr <sub>2</sub> NEt (10)	Water–toluene	0 °C, 3 h	89%
13	SNPs (10)	$\text{Ph}_3\text{P}$ (10)	<i>i</i> -Pr <sub>2</sub> NEt (10)	Toluene	rt, 1 h	Trace
14	SNPs (10)	$\text{Ph}_3\text{P}$ (10)	<i>i</i> -Pr <sub>2</sub> NEt (10)	Toluene	100 °C, 1 h	82%
15	CSNs (10)	$\text{Ph}_3\text{P}$ (10)	<i>i</i> -Pr <sub>2</sub> NEt (10)	Toluene	rt, overnight	Trace
16	CSNs (10)	$\text{Ph}_3\text{P}$ (10)	<i>i</i> -Pr <sub>2</sub> NEt (10)	Toluene	100 °C, 4 h	63%
17	CSNs (10)	$\text{Ph}_3\text{P}$ (10)	–	Water–toluene	rt, 1 h	7%
18	CSNs (10)	bpy (10)	<i>i</i> -Pr <sub>2</sub> NEt (10)	Water–toluene	rt, 1 h	79%
19	CSNs (10)	Pyridine (10)	<i>i</i> -Pr <sub>2</sub> NEt (10)	Water–toluene	50 °C, 1 h	ND <sup>c</sup>
20	CSNs (10)	<i>i</i> -Pr-Pybox (10)	<i>i</i> -Pr <sub>2</sub> NEt (10)	Water–toluene	rt, 1 h	90%
21	CSNs (10)	<i>i</i> -Pr-Box (10)	<i>i</i> -Pr <sub>2</sub> NEt (10)	Water–toluene	50 °C, 1 h	ND <sup>c</sup>
22	–	$\text{Ph}_3\text{P}=\text{O}$ (10)	<i>i</i> -Pr <sub>2</sub> NEt (10)	Water–toluene	rt, overnight	ND <sup>c</sup>
23	SNPs (10)	$\text{Ph}_3\text{P}=\text{O}$ (10)	<i>i</i> -Pr <sub>2</sub> NEt (10)	Water–toluene	rt to 60 °C, 4 h	Trace
24 <sup>d</sup>	SNPs (10)	$\text{Ph}_3\text{P}$ (10)	<i>i</i> -Pr <sub>2</sub> NEt (10)	Water–toluene	rt, 1 h	86%

<sup>a</sup> Conditions: 2-(1-hydroxy-3-phenylprop-2-ynyl)phenol (0.1 mmol), CSNs (10 mol %, based on silver), SNPs (10 mol %), water (1.5 mL) and toluene (0.5 mL); all reactions were carried out in standard Schlenk system under nitrogen.

<sup>b</sup> Isolated yield.

<sup>c</sup> Not detected.

<sup>d</sup> The SNPs were treated by 0.1 mol/L of  $\text{NaBH}_4$  ethanol solution before their use.

**Table 2**  
Silver nanoparticle-catalyzed cyclization of **1<sup>a</sup>**

Entry	Substrate	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Time (h)	Product	Yield (%) <sup>b</sup>
1	<b>1a</b>	H	H	H	1	<b>2a</b>	92
2	<b>1b</b>	Br	H	H	2	<b>2b</b>	90
3	<b>1c</b>	Cl	H	H	2	<b>2c</b>	88
4	<b>1d</b>	NO <sub>2</sub>	H	H	1.5	<b>2d</b>	90
5	<b>1e</b>	Cl	Cl	H	1.5	<b>2e</b>	83
6	<b>1f</b>	Br	Br	H	1.5	<b>2f</b>	85
7	<b>1g</b>	<i>t</i> -Bu	Br	H	3	<b>2g</b>	93
8	<b>1h</b>	Cl	NO <sub>2</sub>	H	3	<b>2h</b>	88
9	<b>1i</b>	<i>t</i> -Bu	NO <sub>2</sub>	H	2	<b>2i</b>	89
10	<b>1j</b>	H	H	Cl	1	<b>2j</b>	90
11	<b>1k</b>	H	H	OMe	2	<b>2k</b>	91
12	<b>1l</b>	H	H	Me	1.5	<b>2l</b>	90
13	<b>1m</b>	Br	H	Me	1.5	<b>2m</b>	85

<sup>a</sup> Conditions: 2-(1-hydroxy-3-arylprop-2-ynyl)phenols (0.1 mmol), CSNs (10 mol %), PPh<sub>3</sub> (10 mol %), and *i*-Pr<sub>2</sub>NEt (10 mol %) were mixed together and stirred in water (1.5 mL)–toluene (0.5 mL) mixed solvent at room temperature.

<sup>b</sup> Isolated yield.

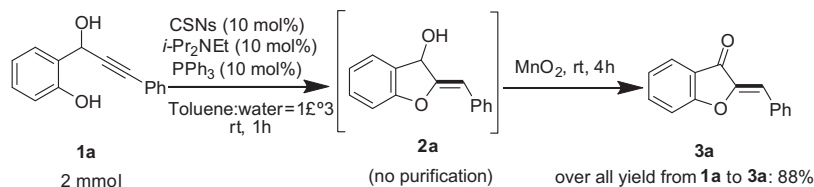
No obvious substituent effect on the rate or yield of the reaction was observed. In all these cases, no other regio- or stereoisomer was observed.

The crude product **2a**, from the cyclization reaction on an enlarged scale following the procedure above, was separated with toluene from water, and was then oxidized by MnO<sub>2</sub> directly without further purification. The final aurone product **3a** was isolated in 88% yield (Scheme 2).

One of the advantages of heterogeneous catalysts is their easy separation from the reaction mixture: they can be recovered and reused readily. We are also interested in recycling the catalysts as well as in the catalytic activity of the annulation. Thus, the solid catalysts were separated and recovered conveniently by centrifugation from the reaction mixture, and then, new solvent, substrate, and fresh phosphine ligand were added. Following this procedure, CSNs, and SNPs were recycled for three times with selected substrates, and the results were listed in Table 3.

With **1a** as the substrate and CSNs as catalyst, an 89% yield was still obtained in the fourth reaction without a distinct decrease compared to the first cycle (entry 1, Table 3). It was noteworthy mentioning here that the reaction time was prolonged in the last three recycles. When **1b** was utilized as a substrate, the same trend was observed (entry 2). On the other hand, with non-supported catalyst (SNPs), the last recycle resulted in a prominent decrease in yield (entry 3).

We suspected that the decreased reaction rate observed in Table 3 might be due to the loss of smaller particles in the process of catalyst recovery<sup>13</sup> and/or the conglomeration of silver nanoparticles.<sup>3a</sup>



**Scheme 2.** Cyclization–oxidation one-pot reaction to aurone **3a**.<sup>12</sup>

**Table 3**  
Application of CSNs and SNPs as a recyclable catalyst in the cyclization of **1a** and **1b<sup>a</sup>**

Entry	Catalyst	Substrate	Yield (%) <sup>b</sup> and reaction time (h)			
			Fresh	Cycle 1	Cycle 2	Cycle 3
1	CSNs	<b>1a</b>	92 (1 h)	90 (8 h)	90 (10 h)	89 (10 h)
2	CSNs	<b>1b</b>	90 (2 h)	85 (8 h)	85 (10 h)	84 (10 h)
3	SNPs	<b>1a</b>	92 (0.5 h)	90 (8 h)	89 (10 h)	75 (10 h)

<sup>a</sup> Conditions: **1a** or **1b** (0.1 mmol), CSNs (10 mol %), PPh<sub>3</sub> (10 mol %), and *i*-Pr<sub>2</sub>NEt (10 mol %) were mixed together and stirred in water (1.5 mL)–toluene (0.5 mL) mixed solvent at room temperature.

<sup>b</sup> Isolated yield.

**Table 4**  
Silver particle-catalyzed cyclization of **1a<sup>a</sup>**

Entry	Conditions	Yield <sup>b</sup>
1	SNPs 10 mol %, Ph <sub>3</sub> P 10 mol %, <i>i</i> -Pr <sub>2</sub> NEt 10 mol %, water–toluene, rt, 0.5 h	92%
2	<b>A</b> 10 mol %, Ph <sub>3</sub> P 10 mol %, <i>i</i> -Pr <sub>2</sub> NEt 10 mol %, water–toluene, rt, 1.5 h	Trace
3	<b>A</b> 10 mol %, Ph <sub>3</sub> P 10 mol %, <i>i</i> -Pr <sub>2</sub> NEt 10 mol %, water–toluene, 60 °C, 1.5 h	85%
4	<b>B</b> 10 mol %, Ph <sub>3</sub> P 10 mol %, <i>i</i> -Pr <sub>2</sub> NEt 10 mol %, water–toluene, rt, 1.5 h	Trace
5	<b>B</b> 10 mol %, Ph <sub>3</sub> P 10 mol %, <i>i</i> -Pr <sub>2</sub> NEt 10 mol %, water–toluene, 60 °C, 1.5 h	87%

<sup>a</sup> Conditions: **1a** (0.1 mmol), catalyst (10 mol %), PPh<sub>3</sub> (10 mol %), *i*-Pr<sub>2</sub>NEt (10 mol %), water (1.5 mL) and toluene (0.5 mL).

<sup>b</sup> Isolated yield.

Thus, in order to further understand the size-effect on the silver-particle catalyst, two kinds of silver catalysts were synthesized without any protective agent by using NaBH<sub>4</sub> (sample **A**) or aqueous hydrazine (sample **B**) as reducing agents, respectively. Their SEM images showed that the average size is around 15 μm.

With the two kinds of silver particles prepared above as catalysts and PPh<sub>3</sub> as the ligand, the cyclization of **1a** was carried out in the water–toluene two-phase system. These larger-sized silver particles showed much lower catalytic activities than the SNPs catalysts (Table 4, entry 1 vs entries 2 and 4). Trace product was observed at room temperature, while ca. 85% yields were obtained at 60 °C with a longer reaction time (entries 3 and 5).

In conclusion, silver nanoparticles and carbon black-supported silver nanoparticles were utilized as highly efficient catalysts for the cyclization of 2-(1-hydroxy-3-arylprop-2-ynyl)phenols with good to excellent yields as well as high regio- and stereo-selectivities. In the reaction, phosphine ligand and water proved to be the key factors that activate the solid catalyst. Furthermore, the nanoparticle catalysts can be recovered and reused at least three times with only decreased reaction rates. The detailed mechanism, the effect of particle size and particle support as well as the scope of the reaction are currently under further investigation.

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### Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.10.065.

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- The dry CSNs catalyst can be stored in air and remains catalytically active for at least one month, while the catalytic activity lasts less than one week for SNPs. The latter can be stored in ethanol for a longer time.
- Typical procedure 1 (entries 1, 2 in Table 1). 2-(1-Hydroxy-3-phenylprop-2-ynyl)phenol (**1a**, 0.1 mmol), SNPs (1.1 mg, 0.01 mmol, 10 mol %) or CSNs (5.1 mg, 0.01 mmol, 10 mol %), 1.7  $\mu$ L of *i*-Pr<sub>2</sub>NEt (0.01 mmol, 10 mol %), and Ph<sub>3</sub>P (2.6 mg, 0.01 mmol, 10 mol %), were added into a 10-mL Schlenk tube<sup>13</sup> with 0.5 mL toluene and 1.5 mL distilled water under nitrogen atmosphere. The mixture was stirred at room temperature for 1 h. The reaction was stopped and extracted with ether (3  $\times$  3 mL). The combined organic phase was dried with Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: 20:1 hexanes/ethyl acetate). Compound **2a** was obtained in 92% yield.
- Typical procedure 2 (Scheme 2). Following the procedure described in typical procedure 1, 2 mmol of 2-(1-hydroxy-3-phenylprop-2-ynyl)phenol (**1a**) was added into a mixed solvent of water (6 mL) and toluene (2 mL), in the presence of CSNs (102 mg, 0.2 mmol, 10 mol %), 34  $\mu$ L *i*-Pr<sub>2</sub>NEt (0.2 mmol, 10 mol %) and Ph<sub>3</sub>P (52.4 mg, 0.2 mmol, 10 mol %). When the reaction was over, the aqueous layer was removed together with the solid catalyst by pipette. The toluene solution was diluted to 5 mL and cooled in an ice bath, and then MnO<sub>2</sub> (6 mmol) was added. The mixture was stirred at room temperature for 4 h, and then, filtered through celite. The solution was concentrated under a reduced pressure, and the residue was purified by flash column chromatography on silica gel (eluent: hexanes/EtOAc 40:1). Compound **3a** was obtained in 88% yield.
- During the catalyst separation by centrifugation, we did notice that some colloidal suspension of SNPs/CSNs was washed away together with the mixed solvent.