

# A Convenient and Efficient Palladium-Catalyzed Carbonylative Sonogashira Transformation with Formic Acid as the CO Source

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**Abstract:** A practical, convenient and efficient palladium-catalyzed carbonylative Sonogashira reaction of aryl iodides has been developed. With formic acid as the CO source and using DCC as the activator, various alkynones were produced in good to excellent yields.

Carbonyl groups are important structural units exist in a large number of organic compounds such as aldehydes, ketones, carboxylic acids and their derivatives, and usually serve as valuable building blocks in the synthesis of natural products, pharmaceuticals, agrochemicals and materials. Among all these carbonyl compounds, alkynones have attracted great attention owing to their multi-functional property and numerous applications in synthetic chemistry.<sup>1</sup> Among them, alkynones represent a powerful platform for the synthesis of numerous heterocyclic compounds,<sup>2</sup> such as pyrroles, pyrazoles, pyrimidines, and quinolones. Traditionally, alkynones were prepared via the cross-coupling reaction of acid chlorides with terminal alkynes<sup>3</sup> (or alkynyl metal<sup>4</sup>). However, despite good reactivity, acid chlorides are not stable and usually need a preparation process which limited the scope of the functional groups tolerance. An alternative approach for the synthesis of alkynones is the transition-metal catalyzed carbonylative Sonogashira coupling reaction,<sup>5</sup> which employs readily accessible aryl halides (or pseudohalides) and terminal alkynes as the starting materials. Since Kobayashi and Tanaka published the first carbonylative Sonogashira reaction in 1981,<sup>5a</sup> a great number of methods have been developed on this subject. However, large percentage of those procedures employs carbon monoxide as the CO source. Although CO gas holds many advantages, its high toxicity and odourless characters hindered the extended applications of those procedures in synthetic chemistry.

Under these backgrounds, several CO surrogates have been developed and applied in carbonylation chemistry during the past decades including metal carbonyls,<sup>6</sup> formamides,<sup>7</sup> aldehyde,<sup>8</sup> formic acid,<sup>9</sup> and oxalyl chloride.<sup>10</sup> However, some drawbacks are still existing, such as stoichiometric metal residuals or acids by-products, special reactors, harsh reaction conditions and so on. The development of general and convenient gaseous CO-free carbonylation methods under mild condition without the influence of accompanied by-product are

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still highly desired. We recently reported the first example on carbonylative Sonogashira coupling with formic acid as the CO source.<sup>9h</sup> With acetic anhydride as the activator, good yields of the desired alkynones can be obtained. However, the prepreparation of acetic formic anhydride and large excess of base to neutralize the in situ formed acetic acid is required. Dicyclohexylcarbodiimide (DCC) has been known as a good dehydration reagent in organic synthesis. We assume that employing DCC as the activator of formic acid, CO can be in-situ generated and DCC will be hydrolyzed to its urea. Due to the poor solubility of urea, it will precipitate out and would not interrupt the following transformation and therefore provide a clean environment for the carbonylative Sonogashira reaction.

With this idea in mind, we present here our newly developed palladium-catalyzed carbonylative Sonogashira method with formic acid as the CO source and dicyclohexylcarbodiimide (DCC) as the activator. The reaction was performed in a one-step one-pot manner; good to excellent yields of the desired alkynones can be prepared under mild conditions with good functional group tolerance.

Table 1 Optimization of the reaction conditions<sup>a</sup>

C) 1a	-l +2	Pd(C Lig Bas HCO DC Solve	OAc) <sub>2</sub> (3 mol%) and (6 mol%) se (2.0 equiv.) OH (2.0 equiv.) C (2.0 equiv.) ent, 30 °C, 20 h	o J 3a	$\mathbf{\tilde{\mathbf{b}}}$
Entry	Ligand	Base	solvent	Temp. (°C)	Yield <sup>b</sup> (%)
1	PPh <sub>3</sub>	Et <sub>3</sub> N	Toluene	30	$79^c$
2	PPh <sub>3</sub>	Et <sub>3</sub> N	Toluene	30	<b>98(97</b> <sup>d</sup> )
3	$PPh_3$	Et <sub>3</sub> N	Toluene	30	38 <sup>e</sup>
4	$PPh_3$	Et <sub>3</sub> N	Toluene	30	75 <sup>f</sup>
5	PPh <sub>3</sub>	Et <sub>3</sub> N	Toluene	60	74
6	$PPh_3$	Et <sub>3</sub> N	Toluene	80	23
7	$PPh_3$	Et <sub>3</sub> N	Toluene	100	8
8	DPPE	Et <sub>3</sub> N	Toluene	30	0
9	DPPF	Et <sub>3</sub> N	Toluene	30	52
10	Xantphos	Et <sub>3</sub> N	Toluene	30	5
11	BINAP	Et <sub>3</sub> N	Toluene	30	3
12	PPh <sub>3</sub>	Et <sub>3</sub> N	THF	30	59
13	$PPh_3$	Et <sub>3</sub> N	DMF	30	42
14	PPh <sub>3</sub>	Et <sub>3</sub> N	CH <sub>3</sub> CN	30	80
15	$PPh_3$	Et <sub>3</sub> N	dioxane	30	84
16	$PPh_3$	DBU	Toluene	30	23
17	$PPh_3$	DIPEA	Toluene	30	13
18	$PPh_3$	$K_2CO_3$	Toluene	30	0
19	PPh <sub>3</sub>	Et <sub>3</sub> N	Toluene	30	93 <sup>g</sup>

<sup>*a*</sup> Reaction conditions: Iodobenzene (1.0 mmol), phenyl acetylene (2.0 mmol), Pd(OAc)<sub>2</sub> (3 mol%), ligand (6 mol %), base (2.0 mmol), HCOOH (2.0 mmol), DCC (2.0 mmol), solvent (4 mL), 30 °C, 24 h. <sup>*b*</sup> GC yield, with dodecane as the internal standard. <sup>*c*</sup> HCOOH (1.5 mmol), DCC (1.5 mmol). <sup>*d*</sup> Isolated yield. <sup>*e*</sup> HCOOH (2.0 mmol), DCC (3.0 mmol). <sup>*f*</sup> Et<sub>3</sub>N (1.0 mmol). <sup>*g*</sup> DIC (2.0 mmol) instead of DCC.

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10.1002/ejoc.201700076

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Initially, iodobenzene 1a and phenyl acetylene 2a were selected as model substrates to this idea. To our delight, using 1.5 equivalent of HCOOH and 1.5 equivalent of DCC as the CO source, the desired product 1,3-diphenylprop-2-yn-1-one 3a was obtained in 79% yield in the presence of 3 mol% Pd(OAc)<sub>2</sub>, 6 mol% PPh<sub>3</sub> and Et<sub>3</sub>N in toluene at 30 °C (Table 1, entry 1). The yield can be further improved to 98% (Table 1, entry 2) when 2 equivalent of CO (2 eq. HCOOH and 2 eq. DCC) was used. The ratio of formic acid and DCC turned out to be crucial for this reaction, excessive DCC decreased the yield dramatically to 38% (Table 1, entry 3). Reducing the amount of base gave a lower yield of 75% (Table 1, entry 4). It should be noted that the reaction temperature also played an important role, when the reaction was performed at higher temperature, the yields of alkynone decreased significantly (Table 1, entries 5-7). This might be resulted from the decomposition of DCC at high temperature. Screening of other phosphine ligands showed that bidentate phosphine ligands are not suitable for this reaction and only a few or trace amount of product was obtained (Table 1. entries 8-11). Further investigations revealed that toluene and Et<sub>3</sub>N are the optimal solvent and base (Table 1, entries 12-18). Additionally, the use of DIC (diisopropylcarbodiimide) instead of DCC as the activator also works well, and the desired product can be obtained in 93% yield (Table 1, entry 19).



**Scheme 1** Substrate scope of the carbonylative Sonogashira reaction<sup>*a*</sup>: variation of aryl iodides. <sup>*a*</sup> Reaction conditions: aryl iodides (1.0 mmol), phenyl acetylene (2.0 mmol), Pd(OAc)<sub>2</sub> (3 mol%), PPh<sub>3</sub> (6 mol %), Et<sub>3</sub>N (2.0 mmol), HCOOH (2.0 mmol), DCC (2.0 mmol), toluene (4 mL), 30 °C, 24 h, isolated yields. <sup>*b*</sup> The reaction was performed at 60 °C.

With the optimized conditions in hand (Table 1 entry 2), we began to investigate the substrates scope of the reaction with various aryl iodides and terminal alkynes. First, as summarized in Scheme 1, a series of aryl iodides was successfully applied to this reaction. Both electron-donating groups and electron-withdrawing groups at the *para* position of the iodobenzenes

were well tolerated and delivered the corresponding alkynones in good to excellent yields (3b-3h). Generally, electron-donating substituents (3b-3e) gave slightly higher yields than electronwithdrawing substituents (3f-3h). Meanwhile, the position of substituents on the iodobenzene influenced the vields significantly due to the steric effect (3i-3k). Parachloroiodobenzene gave a higher yield than metachloroiodobenzene, while ortho-chloroiodobenzene needs to be performed at a higher temperature to give the desired product in moderate yield. Furthermore, 2-naphthyl and heteroaryl iodides were also amenable to the carbonylative coupling reaction, and the corresponding products were conveniently generated in good yields (3I and 3m).



Scheme 2 Substrate scope of the carbonylative Sonogashira reaction <sup>a</sup>: variation of alkynes. <sup>a</sup> Reaction conditions: iodobenzene (1.0 mmol), alkynes (2.0 mmol), Pd(OAC)<sub>2</sub> (3 mol%), PPh<sub>3</sub> (6 mol %), Et<sub>3</sub>N (2.0 mmol), HCOOH (2.0 mmol), DCC (2.0 mmol), toluene (4 mL), 30 °C, 24 h, isolated yields. <sup>b</sup> The reaction was performed at 80 °C.

Then we turned attention to test the generality of the alkyne coupling partner with various substituted alkynes. As demonstrated in Scheme 2, alkyl- and alkoxy-substituted phenyl acetylenes were successfully applied to the carbonylative coupling reaction and gave the corresponding products in good to excellent yields (3n-3r). Interestingly, compared to ortho- and para-substituents, meta-substituted aromatic alkyne gave even higher yields (3n and 3p vs 3o). This might be resulted from the combined effect of steric and conjugate effect. Besides, when halogenated substrates were subjected to this transformation, the coupling reaction proceeded smoothly and delivered the corresponding alkynones. The most electronegative fluoro containing substrate worked better than that of chloro- and bromo-substituents (3s vs 3t and 3u). This can be explained by the stronger electron-withdrawing effect which is benefit for the insertion of alkyne to the acyl palladium intermediate. In addition, 3-thienyl (3v) and alkenyl alkynes (3w) underwent this reaction

at a higher temperature and afforded the desired products in 49% and 85% yields respectively. Moreover, two aliphatic alkynes were successively transformed to their corresponding alkynones in good yields (**3x** and **3y**).

A plausible mechanism was proposed in Scheme 3. Initially, the oxidative addition of the Pd<sup>0</sup> to the aryl iodide 1 give an aryl-palladium complex 4. Then coordination and insertion of 4 with carbon monoxide, which was generated in-situ from formic acid, forms an acyl-palladium intermediate 5. The acylpalladium 5 is then attacked by the terminal alkyne under the assistance of base to generate an alkynyl-palladium complex 6. Finally, reductive elimination produces the final product 3 and meanwhile regenerates Pd<sup>0</sup> for the next catalyst cycle.



Scheme 3 Proposed reaction mechanism.

In conclusion, by employing formic acid as the CO source and DCC as the activator, we have developed a convenient and efficient palladium-catalyzed carbonylative Sonogashira reaction. Under mild conditions, a series of synthetically useful alkynone derivatives were produced in good to excellent yields with good functional group tolerance. No pre-preparation steps and large excess of reagents usage is required here.

## **Experimental Section**

 $Pd(OAc)_2$  (3 mol %),  $PPh_3$  (6 mol %) were transferred into an oven-dried tube which was filled with nitrogen. Toluene (4.0 mL), formic acid (2.0 mmol), alkyne (2.0 mmol) and aryl iodide (1.0 mmol) were added to the reaction tube. After DCC (2.0 mmol) and  $Et_3N$  (2.0 mmol) were added, the tube was sealed and the mixture was stirred at 30 °C for 24 h. After the reaction was completed, the reaction mixture was filtered and concentrated under vacuum. The crude product was purified by column chromatography (EtOAc/hexane = 5/95) on silica gel to afford the alkynone product.

## Acknowledgements

The authors thank the financial supports from NSFC (21472174, 21602201, 21602204) and Zhejiang Natural Science Fund for Distinguished Young Scholars (LR16B020002). X. -F Wu appreciates the general support from Professor Matthias Beller in LIKAT.

**Keywords:** Palladium Catalyst • Carbonylation • Alkynone • Formic acid • CO Surrogate

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See you, CO! A convenient and efficient gaseous CO-free carbonylative Sonogashira reaction has been developed. Employing formic acid as the CO source and DCC as the activator, a series of synthetically useful alkynones were produced in good to excellent yields. Tedious pre-preparation steps and the usage of large excess of reagents can be successfully avoided here. Jin-Bao Peng,\* Fu-Peng Wu, Chong-Liang Li, Xinxin Qi and Xiao-Feng Wu\*

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