# Phosphane-Free Copper-Catalyzed Decarboxylative Coupling of Alkynyl Carboxylic Acids with Aryl Halides under Aerobic Conditions

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A phosphane-free copper-catalyzed decarboxylative crosscoupling reaction of alkynyl carboxylic acids with aryl halides was developed. CuBr (1–5 mol-%) was used as a catalyst in the presence of a  $\beta$ -diketone ligand in air. The reactions of aryl iodides were conducted in the absence of a Pd

## Introduction

Transition-metal-catalyzed cross-coupling reactions can nowadays be considered a cornerstone in organic synthesis.<sup>[1]</sup> Among them, Sonogashira-type reactions.<sup>[2]</sup> which involve the coupling of aryl or alkenyl halides or triflates with terminal alkynes (Scheme 1, type a), have been studied in detail as a powerful tool for preparing acetylene derivatives, which have been used as precursors for natural products, pharmaceuticals, and molecular organic materials.<sup>[3]</sup> Since its introduction in 1975,<sup>[4]</sup> efforts have been made to push the limits of this methodology through the discovery and development of more facile procedures, such as the use of improved metal acetylides as the coupling partners (Scheme 1, type b),<sup>[5,6]</sup> the employment of 2-methyl-3-butyn-2-ol as the acetylene source (Scheme 1, type c),<sup>[7]</sup> as well as the discover of more active catalysts for cross-coupling with unactivated arene chlorides<sup>[8]</sup> or arenes.<sup>[9]</sup> Generally, Sonogashira reactions are performed using a palladium catalyst in the presence or absence of a copper(I) co-catalyst. To satisfy economic concerns, the use of inexpensive metals<sup>[10-12]</sup> as catalysts has been studied. Despite great advances, most methods require the use of oxygen-free reaction conditions to inhibit the Glaser reaction (oxidative homocoupling of terminal alkynes).<sup>[13]</sup> Hence, the development of environmentally benign and efficient methods is still important for continued advancements in this area.

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Scheme 1. Sonogashira-type cross-coupling reactions.

The importance of transition-metal-catalyzed decarboxylative cross-coupling chemistry has grown rapidly in recent years.<sup>[14,15]</sup> Carboxylic acids are among the most common functionalities in organic molecules. They are largely available, stable, and easy to handle and store. Recently, the decarboxylative sp–sp<sup>2</sup> cross-coupling reaction of alkynyl carboxylic acids with aryl halides has been developed.<sup>[16]</sup> All these reactions were performed by using a Pd catalyst in the presence of a phosphane ligand, which is sensitive to air. In addition, the use of an excess amount of tetra-*n*-butylammonium fluoride (TBAF, 2–6 equiv.)<sup>[16f,16h]</sup> or Ag<sub>2</sub>O (1– 2 equiv.)<sup>[16g]</sup> in some cases also limits their application. Herein, we introduce a copper-catalyzed decarboxylative cross-coupling of propiolic acids with aryl halides in air (Scheme 1, type d).

### **Results and Discussion**

Recently, Kolarovič and co-workers reported a CuCl-catalyzed decarboxylation of propiolic acids.<sup>[17]</sup> We have developed a Cu-catalyzed decarboxylative cross-coupling of propiolic acids with amides<sup>[18a]</sup> or terminal alkynes<sup>[18b]</sup> in air. We hypothesized that the decarboxylative cross-coupling of

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# SHORT COMMUNICATION

alkynyl carboxylic acids with aryl halides could be achieved by using a copper catalyst under proper conditions. We initially chose the coupling of 4-nitro-1-iodobenzene (1a) with phenylpropiolic acid (2a) as a model reaction (Table 1). However, no product was observed when the reaction was catalyzed by CuBr (5 mol-%) in DMF at 120 °C (Table 1, Entry 1). Gratifyingly, the expected product, 1-nitro-4-(phenylethynyl)benzene (3a), was obtained in 65% yield when 1,3-diphenylpropane-1,3-dione (L1, 5 mol-%) was added as a ligand in the above catalytic system (Table 1, Entry 2). It is noteworthy that the presence of  $H_2O$ (5 equiv.) led to a dramatic improvement, giving 3a in 95% yield (Table 1, Entry 3). However only a trace amount of 3a was produced when water was used as the solvent (Table 1, Entry 4). It is obvious that the ligand plays a key role in this kind of copper catalysis. Low efficiency was observed when L1 was replaced by  $\beta$ -diketone ligand L2 (Table 1, Entry 5). The reactions did not work when nitrogen-donor ligand L3 or L4 was used (Table 1, Entries 6 & 7). Further investigations indicated that the reaction proceeded smoothly to give an excellent yield even when the loading of CuBr/L1 was reduced to 1 mol-% (Table 1, Entry 8). The use of other catalysts such as  $Cu(OAc)_2$  or  $Cu(acac)_2$  gave a lower yield (Table 1, Entries 9 & 10). Similar high effi-

Table 1. Copper-catalyzed decarboxylative cross-coupling of phenylpropiolic acid (2a) with 4-nitro-1-iodobenzene (1a).<sup>[a]</sup>

O₂N´	+ Ph-==	[C —CO₂H <u>liga</u> solv <b>2a</b> base, 120 °0	u] <del>and</del> Ph— /ent ► Ph— H <sub>2</sub> O C in air	<u></u>	-NO <sub>2</sub>
Ph				Me <sub>2</sub> N NI L4	Me <sub>2</sub>
Entry	[Cu] [mol-%]	Ligand [mol-%]	Base	Solvent	Yield [%] <sup>[b]</sup>
1[c]	CuBr (5)	_	K <sub>2</sub> CO <sub>2</sub>	DMF	NR
2 <sup>[c]</sup>	CuBr(5)	L1 (5)	$K_2CO_3$	DMF	65
3	CuBr (5)	L1 (5)	K <sub>2</sub> CO <sub>3</sub>	DMF	95
4 <sup>[d]</sup>	CuBr (5)	L1 (5)	K <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	trace
5	CuBr (5)	L2 (5)	$K_2CO_3$	DMF	16
6	CuBr (5)	L3 (5)	$K_2CO_3$	DMF	NR
7	CuBr (5)	L4 (5)	$K_2CO_3$	DMF	NR
8	CuBr (5)	L1 (1)	$K_2CO_3$	DMF	96
9	$Cu(OAc)_2(1)$	L1 (1)	$K_2CO_3$	DMF	92
10	$Cu(acac)_2(1)$	L1 (1)	$K_2CO_3$	DMF	84
11 <sup>[e]</sup>	CuBr (1)	L1 (1)	$K_2CO_3$	DCE	NR
12 <sup>[e]</sup>	CuBr (1)	L1 (1)	$K_2CO_3$	CH <sub>3</sub> CN	NR
13	CuBr (1)	L1 (1)	$K_3PO_4$	DMF	93
14	CuBr (1)	L1 (1)	Et <sub>3</sub> N	DMF	NR
15	CuBr(1)	L1 (1)	-	DMF	NR
16 <sup>[f]</sup>	CuBr (1)	L1 (1)	$K_2CO_3$	DMF	<5

[a] Reaction conditions: **1a** (0.5 mmol, 1.0 equiv.), **2a** (0.6 mmol), base (1.0 mmol), H<sub>2</sub>O (5.0 equiv.), copper catalyst, ligand, and solvent (3 mL), 120 °C, 20 h, in air. [b] Isolated yield; NR = no reaction. [c] H<sub>2</sub>O was not added. [d] The reaction was conducted at 100 °C. [e] The reaction was conducted at 80 °C. [f] The reaction was conducted under N<sub>2</sub>.

ciency was obtained by employing  $K_3PO_4$  as the base (Table 1, Entry 13). However, reactions performed in dichloroethane (DCE) or CH<sub>3</sub>CN (Table 1, Entries 11 & 12) in the absence of a base or in the presence of the organic base Et<sub>3</sub>N (Table 1, Entries 14 & 15) did not proceed. Furthermore, a low yield was obtained when the reaction was carried out under an atmosphere of N<sub>2</sub> (Table 1, Entry 16).

To exclude the effect of palladium, the CuBr used in these reactions was analyzed by plasma mass spectrometry (ICP-MS). However, no palladium content was detected in the CuBr catalyst (see the Supporting Information). Furthermore, the reaction of **1a** with **2a** catalyzed by PdCl<sub>2</sub> (0.1 mol-%) instead of CuBr in air only produced **3a** in 60% yield [Equation (1)].



Under the optimized conditions, the scope of this decarboxylative cross-coupling reaction was expanded to a variety of aryl iodides (Table 2). Employing only 1 mol-% of CuBr and L1, iodobenzenes containing a nitro group at the ortho, meta, or para position reacted smoothly with phenylpropiolic acid (2a) to give the corresponding products in good to excellent yields (Table 2, Entries 1-4). However, a low yield was obtained when 4-methoxy-1-iodobenzene (1e) was employed as the substrate under the optimized conditions (Table 2, Entry 5). To improve the efficiency of the reaction with 4-methoxy-1-iodobenzene (1e), screening of different parameters including base, ligand, and catalyst was undertaken (see the Supporting Information). Considering that the iron/copper co-catalytic system<sup>[19]</sup> may affect this transformation, reactions catalyzed by CuBr in the presence of different iron catalysts were investigated (Supporting Information; Table S1, Entries 21–27). However, a low yield was obtained in each case.

On the basis of the above results and the reported efficient decarboxylative cross-coupling reactions with substrates containing a nitro group,<sup>[15,20]</sup> we envisioned that the presence of -NO2 in the catalytic system may improve the decarboxylative transformation. After screening different reaction parameters (see the Supporting Information), we finally found that the expected product 1-methoxy-4-(phenylethynyl)benzene (3e) was formed in the highest yield (63%) when NaNO<sub>2</sub> (1.0 equiv.) was employed with CuBr (5 mol-%) and L1 (Table 2, Entry 6). Moreover, it is surprising that a lower yield was obtained when NaNO<sub>2</sub> was used in the presence of  $H_2O$  (see the Supporting Information). Assisted by NaNO<sub>2</sub>, iodobenzenes bearing electron-withdrawing and electron-donating groups were tolerated in this reaction (Table 2, Entries 6-10). The reaction of 4-bromo-1iodobenzene (1h) with 2b proceeded under these conditions, producing **3h** in 30% yield (Table 2, Entry 11). In addition, the addition of a palladium catalyst did not dramatically improve the yield of this coupling reaction [Table 2, En-



Table 2. The reactions of phenylpropiolic acid (2a) or 4'-methoxy-phenylpropiolic acid (2b) with aryl iodides 1.<sup>[a]</sup>

	$\wedge$		CuBr, L1
R	∰ `` + Ar— <u></u>	-CO <sub>2</sub> I	H <u>additive</u> Ar
		2	DMF, K <sub>2</sub> CO <sub>3</sub> R
	1	2	120 °C in air <b>3</b>
Entry	R (1)	2	Product <sup>[b]</sup>
1	$4-NO_2(1a)$	2a	O₂N──     >─────Ph
	1102(11)		<b>3a</b> (96%)
2	$3 NO_{2} (1h)$	20	< <u> </u>
2	5 1102 (10)	24	<b>3b</b> (98%)
			/ \
3	$2-NO_2(1c)$	2a	$\searrow$
			NO <sub>2</sub> 3c (81%)
			Me
4	4-NO <sub>2</sub> -2-Me (1d)	2a	0₂N—
			- <u> </u>
			<b>3d</b> (96%)
5	4-MeO (1e)	2a	
			<b>3e</b> (20%)
6 <sup>[c]</sup>	4-MeO (1e)	2a	MeO ( Ph
			<b>3e</b> (63%)
			OMe
<b>–</b> [c]	214 0 (16	•	
/101	2-MeO (II)	2a	
			<b>3f</b> (56%)
8 <sup>[c]</sup>	$4-CO_2Me(1g)$	2a	MeO <sub>2</sub> C—〈/ 〉————Ph
	· · · · · · · · · · · · · · · · · · ·		<b>3a</b> (45%)
			Me — Me — Me
9 <sup>[c]</sup>	4-Me (1h)	2b	3b (37%)
			511 (5776)
			Me
· · fal			
$10^{10}$	2-Me (1i)	2b	《 》———— 》——— OMe
			<b>3i</b> (45%)
11 <sup>[c]</sup>	4-Br (1j)	2b	Br
			<b>3</b> j (30%)
1 2 [c,d]	4 Mc (1b)	21	Me————————————————————————————————————
12.11	4-1vie (111)	20	
			<b>3n</b> (19%)

[a] Reaction conditions: 1 (0.5 mmol), 2 (0.6 mmol),  $K_2CO_3$ (1.0 mmol), CuBr (0.005 mmol), L1 (0.005 mmol),  $H_2O$ (2.5 mmol), and DMF (3 mL), 120 °C, 20 h, in air. [b] Isolated yield. [c] 1 (0.25 mmol), 2 (0.3 mmol),  $K_2CO_3$  (0.25 mmol), CuBr (0.0125 mmol), L1 (0.0125 mmol), NaNO<sub>2</sub> (0.25 mmol), and DMF (1.5 mL) were used. [d] PdCl<sub>2</sub> (0.00125 mmol) was added.

try 12; also see Equations (1) and (2) in the Supporting Information].

The reactions of **1a** with variously substituted alkynyl carboxylic acids were then investigated (Table 3). The corresponding diarylacetylenes were produced in good to excellent yields under the optimized conditions (Table 3). Notably, the decarboxylative cross-coupling of heteroarylpro-

piolic acid **2f** proceeded efficiently to give expected product **3m** in 82% yield (Table 3, Entry 5). Moreover, 3-styrylpropiolic acid (**2g**) reacted successfully with **1a** to give the corresponding arylvinylacetylene **3n** in 85% yield (Table 3, Entry 6).

Table 3. The reactions of 4-nitro-1-iodobenzene (1a) with aryl or vinylpropiolic acids  $2.^{\rm [a]}$ 



[a] Reaction conditions: **1a** (0.5 mmol), **2** (0.6 mmol),  $K_2CO_3$  (1.0 mmol), CuBr (0.005 mmol), **L1** (0.005 mmol), H<sub>2</sub>O (2.5 mmol), and DMF (3 mL), 120 °C, 20 h, in air. [b] Isolated yield. [c] **1a** (0.25 mmol), **2** (0.3 mmol),  $K_2CO_3$  (0.5 mmol), CuBr (0.0125 mmol), **L1** (0.0125 mmol), H<sub>2</sub>O (1.25 mmol), and DMF (1.5 mL) was used.

Although, the decarboxylative cross-coupling reactions of phenylpropiolic acid (**2a**) with 4-nitro-1-bromobenzene (**4**) produced expected product **3a** in low yield (Table 4, Entry 1). The reaction in the presence of a trace amount of PdCl<sub>2</sub> (0.5 mol-%) notably increased the yield to 92% (Table 4, Entry 2). Under these conditions, **4** reacted smoothly with propiolic acids containing various aryl or vinyl groups, generating the corresponding products in moderate to good yields (Table 4, Entries 3–7). Notably, 1nitro-4-( $\beta$ -styrylethynyl)benzene (**3p**) was highly stereoselectively generated (*E*/*Z* >99:1; Table 4, Entry 7 vs. Table 3, Entry 6).

### Conclusions

In conclusion, we have developed an efficient copper-catalyzed decarboxylative cross-coupling of aryl halides with alkynyl carboxylic acids. The use of alkynyl carboxylic acid derivatives, which are readily available, easy to store, and simple to handle, as the coupling partner efficiently inhibits Table 4. The reactions of 4-nitro-1-bromobenzene (4) with aryl or vinyl propiolic acids  $2.^{\rm [a]}$ 



[a] Reaction conditions: **4** (0.5 mmol), **2** (0.6 mmol),  $K_2CO_3$  (1.0 mmol), CuBr (0.025 mmol), **L1** (0.025 mmol), PdCl<sub>2</sub> (0.0025 mmol), H<sub>2</sub>O (2.5 mmol), and DMF (3 mL), 120 °C, 20 h, in air. [b] Isolated yield. [c] PdCl<sub>2</sub> was not added.

the formation of dimerization product diynes. All the reactions were conducted in air in the absence of a phosphane ligand. 1,3-Diphenylpropane-1,3-dione as a ligand plays a key role in this kind of copper catalysis. Moreover,  $NaNO_2$ was disclosed to efficiently improve the decarboxylative cross-coupling when a nitro group was not contained in the substrates, although the mechanism is not clear yet. Further studies on the mechanism of the reaction and synthetic applications are ongoing in this laboratory.

### **Experimental Section**

**Typical Procedure:** To a mixture of CuBr (0.005 mmol), 1,3-diphenylpropane-1,3-dione (0.005 mmol), aryl halide (0.5 mmol), alkynyl carboxylic acid (0.6 mmol), and  $K_2CO_3$  (1.0 mmol) was added DMF (3 mL) and the additive(s). The resulting mixture was heated at 120 °C in air for 20 h as monitored by TLC. The reaction mixture was diluted with ethyl acetate (10 mL) and washed with saturated NH<sub>4</sub>Cl (10 mL). The layers were separated, and the aqueous layer was extracted with ethyl acetate (10 mL). The combined organic layers were then concentrated by evaporation, and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the desired product.

**Supporting Information** (see footnote on the first page of this article): Experimental details, characterization data, and <sup>1</sup>H and <sup>13</sup>C NMR spectra for the products included in this paper.

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