



## Nickel-catalyzed oxidative decarboxylative coupling reactions between alkynyl carboxylic acids and arylboronic acids



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### ABSTRACT

Nickel-catalyzed decarboxylative coupling reactions between aryl alkynyl carboxylic acids and arylboronic acids were developed. When aryl alkynyl carboxylic acids were reacted with arylboronic acids in the presence of NiCl<sub>2</sub> (10 mol %), 2,2'-bipyridine (20 mol %), Na<sub>2</sub>CO<sub>3</sub> (1.0 equiv), and Ag<sub>2</sub>CO<sub>3</sub> (1.0 equiv) in DMF at 80 °C for 18 h, the corresponding diaryl alkynes products were formed in moderate to good yields.

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### Introduction

One of the most frequently used methods for the formation of sp<sup>2</sup>–sp carbon–carbon bonds is the Sonogashira reaction, which is a coupling reaction between aryl halides and terminal alkynes in the presence of Pd/Cu catalysts.<sup>1</sup> Since its first report in 1975, this reaction has been modified, improved, and widely employed in organic synthesis, especially in the medicinal and material chemistry fields.<sup>2</sup> Notably, it represents a very useful tool for the synthesis of conjugated polymers bearing an aryl alkyne backbone.<sup>3</sup>

Alkynyl carboxylic acid derivatives such as propiolic acid have received much attention as alkyne sources for the synthesis of aryl alkyne moieties since their decarboxylative coupling reaction was reported in 2008.<sup>4</sup> Alkynyl carboxylic acids offer several advantages. For example, propiolic acid is easier to handle and store as an alkyne source compared to acetylene, and less expensive than other acetylene surrogates such as trimethylsilylacetylene and bis(tributylstannyl)acetylene.<sup>5</sup> In addition, aryl alkynyl carboxylic acid derivatives are easily prepared and no chromatography purification step is required.<sup>6</sup>

In a first Letter, we described the coupling reaction of aryl halides with alkynyl carboxylic acids in the presence of a palladium catalyst. Aryl iodide, bromide, and chloride were successfully used as coupling partners in the decarboxylative coupling reaction

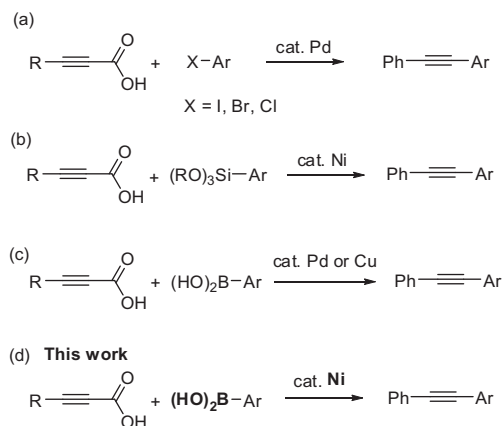
(Scheme 1a).<sup>7</sup> In particular, benzyl bromide and chloride were coupled to give benzyl alkynes in good yields.<sup>8</sup> Recently, the coupling of benzoxazole and indolizine with alkynyl carboxylic acids through decarboxylation was also reported.<sup>9</sup> In addition, the formation of bonds involving heteroatoms such as phosphorus, nitrogen, and sulfur has also been reported using decarboxylative coupling reactions of alkynyl carboxylic acids.<sup>10</sup>

In most cases of decarboxylative coupling reactions, palladium or copper were generally employed as major catalysts, although a few example of nickel catalysts were reported.<sup>11</sup> More recently, we described decarboxylative coupling reactions with organosilanes using a nickel catalyst (Scheme 1b).<sup>12</sup> This success prompted us to develop a nickel-catalyzed decarboxylative coupling using organoboranes. Although the oxidative decarboxylative coupling with aryl boronic acids was reported in the presence of a palladium catalyst or a copper catalyst (Scheme 1c),<sup>13</sup> a nickel-based catalytic system has not been developed so far. Herein, we report a decarboxylative coupling reaction between alkynyl carboxylic acids and organoboranes using a nickel catalyst (Scheme 1d). This method offers several advantages since nickel is abundant and much cheaper than palladium,<sup>14</sup> and a greater variety of organoborane derivatives are commercially available compared to organosilanes.

In order to find the optimal conditions, phenyl propiolic acid (**1a**) and phenylboronic acid (**2a**) were reacted with Na<sub>2</sub>CO<sub>3</sub> and Ag<sub>2</sub>CO<sub>3</sub> under a variety of reaction conditions. First, different nickel sources, ligands, and solvents were tested, and the corresponding results are summarized in Table 1. Reactions conducted in the

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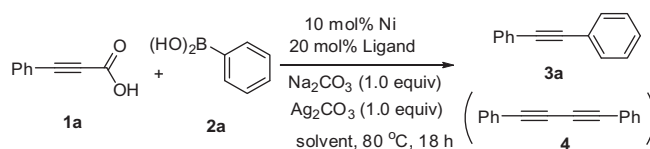
**Scheme 1.** Transition-metal-catalyzed decarboxylative coupling reactions.

presence of Ni(acac)<sub>2</sub>, Ni(OAc)<sub>2</sub>, and Ni(OH)<sub>2</sub> afforded very poor yields of product **3a** (entries 1–3), while Ni(NO<sub>3</sub>)<sub>2</sub> and NiBr<sub>2</sub> provided the desired product in 22% and 28% yields, respectively (entries 4 and 5). The use of NiCl<sub>2</sub> led to an improvement of the product yield to 51% and a decrease of the yield of by-product **4** to 1% (entry 6), whereas NiF<sub>2</sub> gave a very poor yield (entry 7). The replacement of 2,2'-bipyridine (**L1**) with either 4,4'-bis-*tert*-butylbipyridine (**L2**) or 1,10-phenanthroline (**L3**) did not increase the product yield (entries 8 and 9). No product was formed in the reaction with sterically hindered **L4** or *L*-proline (**L5**) (entries 10 and 11). Among the phosphine ligands, only Xantphos (**L9**) provided the desired product in 26% yield (entry 15). With respect to the solvents tested, polar solvents such as DMAc, NMP, and DMSO provided **3a** in 28–45% yields (entries 16–18). However, ethers and aromatic solvents showed no activity (entries 19–22).

Since the decarboxylative coupling reaction between **1a** and **2a** is an oxidative coupling, the oxidant is also an important factor, thus a number of different reagents were tested. As shown in

**Table 1**

Effect of nickel source, ligand, and solvent in the oxidative decarboxylative coupling<sup>a</sup>

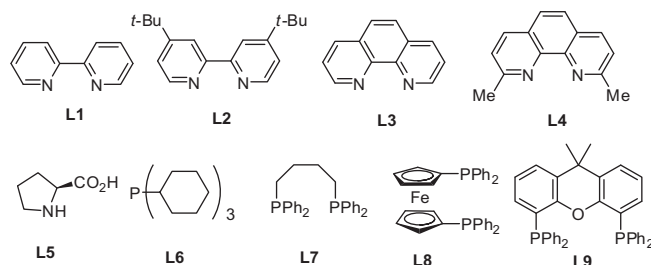


Entry	Ni	Ligand <sup>c</sup>	Solvent	<b>3a</b> yield <sup>b</sup> (%)	<b>4</b> yield <sup>b</sup> (%)
1	Ni(acac) <sub>2</sub>	<b>L1</b>	DMF	9	5
2	Ni(OAc) <sub>2</sub>	<b>L1</b>	DMF	8	4
3	Ni(OH) <sub>2</sub>	<b>L1</b>	DMF	3	2
4	Ni(NO <sub>3</sub> ) <sub>2</sub>	<b>L1</b>	DMF	22	5
5	NiBr <sub>2</sub>	<b>L1</b>	DMF	28	8
6	NiCl <sub>2</sub>	<b>L1</b>	DMF	51	1
7	NiF <sub>2</sub>	<b>L1</b>	DMF	4	2
8	NiCl <sub>2</sub>	<b>L2</b>	DMF	30	19
9	NiCl <sub>2</sub>	<b>L3</b>	DMF	29	2
10	NiCl <sub>2</sub>	<b>L4</b>	DMF	—	1
11	NiCl <sub>2</sub>	<b>L5</b>	DMF	—	4
12	NiCl <sub>2</sub>	<b>L6</b>	DMF	—	6
13	NiCl <sub>2</sub>	<b>L7</b>	DMF	—	12
14	NiCl <sub>2</sub>	<b>L8</b>	DMF	—	22
15	NiCl <sub>2</sub>	<b>L9</b>	DMF	26	5
16	NiCl <sub>2</sub>	<b>L1</b>	DMAc	38	2
17	NiCl <sub>2</sub>	<b>L1</b>	NMP	28	6
18	NiCl <sub>2</sub>	<b>L1</b>	DMSO	45	3
19	NiCl <sub>2</sub>	<b>L1</b>	Diglyme	—	1
20	NiCl <sub>2</sub>	<b>L1</b>	Dioxane	—	5
21	NiCl <sub>2</sub>	<b>L1</b>	Toluene	—	—
22	NiCl <sub>2</sub>	<b>L1</b>	Xylene	—	—

<sup>a</sup> Reaction condition: **1a** (0.3 mmol), **2a** (0.3 mmol), Ni (0.03 mmol), ligand (0.06 mmol), Na<sub>2</sub>CO<sub>3</sub> (0.3 mmol), and Ag<sub>2</sub>CO<sub>3</sub> (0.3 mmol) were reacted at 80 °C for 18 h. The reaction was conducted under air condition.

<sup>b</sup> Determined by gas chromatography with internal standard.

<sup>c</sup> Ligand structure



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