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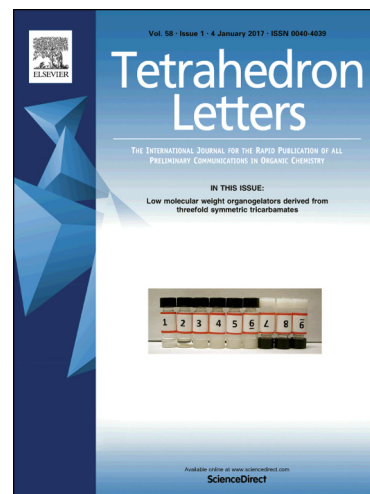
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## Nickel-Catalyzed Decarboxylative Coupling of an Alkynyl Carboxylic Acid with Aryl Iodides

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### ABSTRACT

A decarboxylative coupling reaction with an alkynyl carboxylic acid and aryl iodides in the presence of a nickel catalyst was developed. When the reaction was conducted with NiCl<sub>2</sub> (10 mol%), Xantphos (15 mol%), Mn (1.0 equiv), and Cs<sub>2</sub>CO<sub>3</sub> (1.5 equiv), the desired diaryl alkynes were formed in moderated to good yields. Furthermore, this method does not produce the diyne, which is formed in the homocoupling of alkynyl carboxylic acids.

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### Introduction

Transition metal-catalyzed cross-coupling reactions are among the most important and widely used tools in organic synthesis for the formation of carbon-carbon or carbon-heteroatom bonds.<sup>1</sup> A variety of named reactions, including the Heck,<sup>2</sup> Kumada,<sup>3</sup> Negishi,<sup>4</sup> Stille,<sup>5</sup> Suzuki,<sup>6</sup> Sonogashira,<sup>7</sup> Hiyama,<sup>8</sup> and Buchwald-Hartwig<sup>9</sup> reactions, have been developed and improved over the last four decades. As a coupling substrate, aryl halides are the most commonly employed because they are readily available. Generally, aryl iodides are much more reactive than aryl bromides and chlorides.<sup>10</sup>

Sonogashira first showed that aryl halides are capable of coupling with terminal alkynes in the presence of palladium, copper, and a base to provide aryl alkynes. Since his first report of this reaction in 1979, it has become the most common method for *sp* and *sp*<sup>2</sup> carbon bond formation, and is now known as the Sonogashira reaction.<sup>11</sup> It is very often employed as a useful tool for the synthesis of conjugated polymers in the electroactive material field.<sup>12</sup> Palladium is used as the catalyst for this reaction far more often than other transition metals such as copper and nickel.<sup>13</sup>

As an alternative method, the decarboxylative coupling of alkynyl carboxylic acids has received much attention since we first reported the palladium-catalyzed coupling of alkynyl carboxylic acids and aryl halides in 2008.<sup>14</sup> Alkynyl carboxylic acids such as propiolic acid have been widely employed as

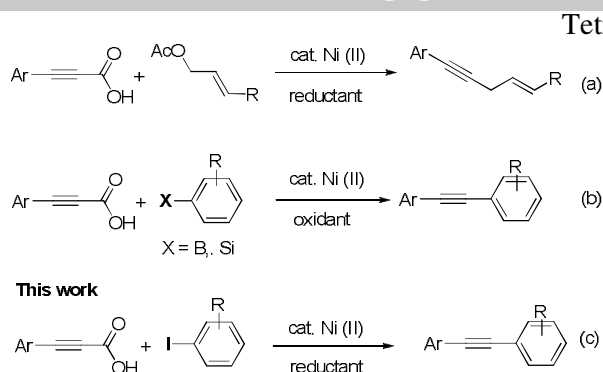
alkyne surrogates, and exhibit good activity in this reaction with a variety of coupling partners.<sup>15</sup> Furthermore, they can be readily prepared in one step without the need for column chromatography for purification.<sup>16</sup>

We have previously reported a number of decarboxylative coupling reactions. For example, synthetic strategies for diaryl alkynes, diynes, diketones, allenes, alkynyl ketones, and alkynyl amides have been developed.<sup>17</sup> In addition, several multicomponent reactions have been developed.<sup>18</sup> These reactions are catalyzed by palladium or copper in most cases, with only a few rare examples of nickel catalysts being reported, even though it is more abundant and less expensive than palladium. The first example of a nickel-catalyzed decarboxylative coupling reaction was that with an allyl acetate, as shown in Figure 1a.<sup>19</sup> Recently, we reported nickel-catalyzed decarboxylative coupling reactions with aryl siloxanes or aryl boronic acids (Figure 1b).<sup>20</sup> These successes prompted us to develop a nickel-catalyzed decarboxylative coupling reaction with aryl halides, which has long been regarded as a challenge.

Herein, we report for the first time the nickel-catalyzed decarboxylative coupling of an alkynyl carboxylic acid and aryl iodides (Figure 1c).

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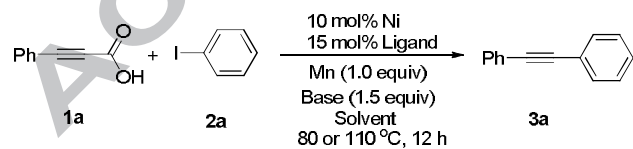
**Figure 1.** Nickel-catalyzed decarboxylative coupling reactions.

To optimize the reaction conditions, phenyl propiolic acid and iodobenzene were chosen as standard substrates. A variety of reaction parameters were investigated, as shown in Table 1. First, we assessed a number of nickel sources. Generally, Ni(COD)<sub>2</sub> is the most frequently employed nickel source in cross-coupling reactions with aryl halides. However, it is very air-sensitive and thus difficult to handle and transport.<sup>21</sup> Therefore, we employed the much more stable nickel(II) as a nickel source in the presence of manganese.<sup>22</sup>

Of the commercially available nickel complexes, only Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O and NiCl<sub>2</sub> provide the coupled product, achieving moderate yields of 44 and 48%, respectively (entries 3 and 4). When Cs<sub>2</sub>CO<sub>3</sub> is employed as a base instead of K<sub>2</sub>CO<sub>3</sub>, the product yield increases to 67% (entry 10); however, other bases such as Na<sub>2</sub>CO<sub>3</sub>, DBU, and DBN result in poor yields (entries 11–13). The reactions with other chelating phosphine ligands such as DPEPhos (**L2**), BINAP (**L3**), and dppf (**L4**) provide only trace amounts of the product (entries 14–16). When the reaction temperature is increased to 110 °C, the desired product is formed in 83% yield (entry 17). When the reaction is run at 110 °C in DMF, toluene, or diglyme, the yields are not satisfactory (entries 18–20).

We also investigated the reaction with different combinations of nickel source and ligand (Figure 2). Three kinds of ligands were tested with Ni(acac)<sub>2</sub> in the presence of Cs<sub>2</sub>CO<sub>3</sub> in DMSO. DPEPhos, BINAP, and dppf afford **3a** in 5, 22, and 64% yields, respectively (entries 21–23). However, the use of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O results in poor yields, irrespective of the phosphine ligand employed (entries 24–26). It is noteworthy that no homocoupled phenyl propiolic acid product, which is 1,4-diphenyl-1,3-butadiyne, is observed in any of the reactions.

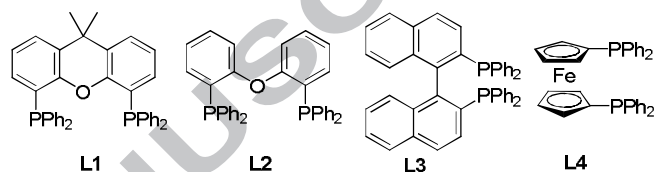
**Table 1.** Screening of Ni source, ligand, base, solvent, and temperature for the decarboxylative coupling reaction.



Entry	Ni	Ligand	Base	Solvent	Temp	Yield (%)
1	Ni(acac) <sub>2</sub>	<b>L1</b>	K <sub>2</sub> CO <sub>3</sub>	DMSO	80	3
2	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	<b>L1</b>	K <sub>2</sub> CO <sub>3</sub>	DMSO	80	1
3	Ni(OAc) <sub>2</sub> ·4H <sub>2</sub> O	<b>L1</b>	K <sub>2</sub> CO <sub>3</sub>	DMSO	80	44
4	NiCl <sub>2</sub>	<b>L1</b>	K <sub>2</sub> CO <sub>3</sub>	DMSO	80	48
5	NiF <sub>2</sub>	<b>L1</b>	K <sub>2</sub> CO <sub>3</sub>	DMSO	80	3
6	Ni(OH) <sub>2</sub>	<b>L1</b>	K <sub>2</sub> CO <sub>3</sub>	DMSO	80	4
7	Ni(Cp) <sub>2</sub>	<b>L1</b>	K <sub>2</sub> CO <sub>3</sub>	DMSO	80	1
8	NiBr <sub>2</sub> ·glyme	<b>L1</b>	K <sub>2</sub> CO <sub>3</sub>	DMSO	80	1

Entry	Ni	Ligand	Base	Solvent	Temp	Yield (%)
9	Ni[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub>	<b>L1</b>	K <sub>2</sub> CO <sub>3</sub>	DMSO	80	1
10	NiCl <sub>2</sub>	<b>L1</b>	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	80	67
11	NiCl <sub>2</sub>	<b>L1</b>	Na <sub>2</sub> CO <sub>3</sub>	DMSO	80	22
12	NiCl <sub>2</sub>	<b>L1</b>	DBU	DMSO	80	17
13	NiCl <sub>2</sub>	<b>L1</b>	DBN	DMSO	80	13
14	NiCl <sub>2</sub>	<b>L2</b>	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	80	5
15	NiCl <sub>2</sub>	<b>L3</b>	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	80	trace
16	NiCl <sub>2</sub>	<b>L4</b>	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	80	trace
17	NiCl <sub>2</sub>	<b>L1</b>	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	110	83
18	NiCl <sub>2</sub>	<b>L1</b>	Cs <sub>2</sub> CO <sub>3</sub>	DMF	110	30
19	NiCl <sub>2</sub>	<b>L1</b>	Cs <sub>2</sub> CO <sub>3</sub>	Toluene	110	20
20	NiCl <sub>2</sub>	<b>L1</b>	Cs <sub>2</sub> CO <sub>3</sub>	Diglyme	110	51
21	Ni(acac) <sub>2</sub>	<b>L2</b>	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	110	5
22	Ni(acac) <sub>2</sub>	<b>L3</b>	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	110	22
23	Ni(acac) <sub>2</sub>	<b>L4</b>	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	110	64
24	Ni(OAc) <sub>2</sub> ·4H <sub>2</sub> O	<b>L2</b>	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	110	13
25	Ni(OAc) <sub>2</sub> ·4H <sub>2</sub> O	<b>L3</b>	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	110	6
26	Ni(OAc) <sub>2</sub> ·4H <sub>2</sub> O	<b>L4</b>	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	110	9

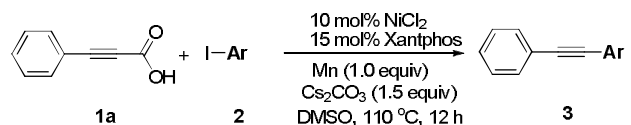
<sup>a</sup>Reaction Conditions: **1a** (0.3 mmol), **2a** (0.6 mmol), Ni (0.03 mmol), ligand (0.045 mmol), Mn (0.3 mmol), and base (0.45 mmol) were reacted in solvent (1.0 mL).



**Figure 2.** Structures of the ligands **L1**–**L4**.

With the optimum conditions established, we investigated the substrate scope of the reaction (Table 2). As expected, phenyl iodide couples with phenyl propiolic acid to give diphenyl acetylene (**3a**) in 88% yield (entry 1). The *ortho*-substituted iodotoluene reacts with low yields in both NiCl<sub>2</sub>/Xantphos and Ni(acac)<sub>2</sub>/dppf (entry 2), while the *meta*- and *para*-substituted iodotoluenes afford the corresponding coupled products in 41 and 79% yields, respectively (entries 3 and 4). Iodoanisoles react at low to moderate yields (entries 5 and 6). 4-Fluoro- and 4-chloroiodobenzene provide the desired products in 42 and 79% yields, respectively (entries 7 and 8). 4-Iodopyridine couples with phenyl propiolic acid to give **3i** in 83% yield (entry 9). Methyl 4-iodobenzoate and 1-iodonaphthalene give the desired products in 47 and 57% yields, respectively (entries 10 and 11). 1-Iodo-4-(trifluoromethyl)benzene afforded **3l** with 82% yield (entry 12). 4-Iodoacetophenone affords the desired product with 16% yield in the presence of NiCl<sub>2</sub>/Xantphos. However, when these reactions are performed with Ni(acac)<sub>2</sub>/dppf, it provide the coupled product **3m** in 39% yield, respectively (entry 13). Aryl iodides bearing cyano or nitro groups do not afford the coupled products under either set of conditions (entries 14 and 15).

**Table 2.** Ni-catalyzed decarboxylative coupling reactions between aryl iodides and phenyl propiolic acid.<sup>a</sup>



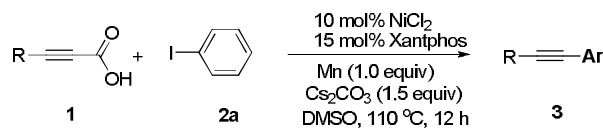
Entry	ArI	Product	Yield <sup>b</sup> (%)
1		<b>3a</b>	88

2		<b>3b</b>	20(27) <sup>c</sup>
3		<b>3c</b>	41
4		<b>3d</b>	79
5		<b>3e</b>	20(66) <sup>c</sup>
6		<b>3f</b>	59
7		<b>3g</b>	42
8		<b>3h</b>	79
9		<b>3i</b>	83
10		<b>3j</b>	47
11		<b>3k</b>	57
12		<b>3l</b>	82(22) <sup>c</sup>
13		<b>3m</b>	16(39) <sup>c</sup>
14		<b>3n</b>	0
15		<b>3o</b>	0

<sup>a</sup>Reaction conditions: **1** (3.0 mmol), **2** (3.0 mmol), NiCl<sub>2</sub> (0.3 mmol), Xantphos (0.45 mmol), Mn (3.0 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (4.5 mmol) were reacted in DMSO at 110 °C, 12 h. <sup>b</sup>Isolated Yield. <sup>c</sup>Ni(acac)<sub>2</sub> (0.3 mmol) and dppe (0.3 mmol) were used instead of NiCl<sub>2</sub>/Xantphos.

To further evaluate this methodology, substituted aryl propiolic acids and alkyl-substituted propiolic acids were employed as coupling partners. The results are summarized in Table 3. Electron donating group substituted-phenyl propiolic acids such as **1b**, **1c** and **1d** afforded the desired product **3p**, **3c** and **3f** with 67%, 77% and 69% yields, respectively (entries 1 – 3). Electron withdrawing group substituted-phenyl propiolic acids also showed good yields (entries 4 and 5). Alkyl-substituted propiolic acids such as hexynoic acid and pentynoic acid gave the desired product **3p** and **3q** with 81% and 85% yields, respectively (entries 6 and 7).

**Table 3.** Ni-catalyzed decarboxylative coupling reactions between aryl or alkyl propiolic acids and phenyl iodide.<sup>a</sup>

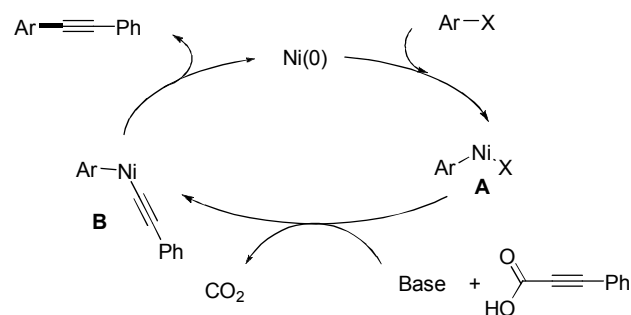


Entry	Propiolic acids	Product	Yield <sup>b</sup> (%)
1		<b>1b</b> <b>3p</b>	67
2		<b>1c</b> <b>3c</b>	77
3		<b>1d</b> <b>3f</b>	69
4		<b>1e</b> <b>3h</b>	77
5		<b>1f</b> <b>3l</b>	82
6		<b>1g</b> <b>3p</b>	81
7		<b>1h</b> <b>3q</b>	85

<sup>a</sup>Reaction conditions: **1** (3.0 mmol), **2a** (3.0 mmol), NiCl<sub>2</sub> (0.3 mmol), Xantphos (0.45 mmol), Mn (3.0 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (4.5 mmol) were reacted in DMSO at 110 °C, 12 h. <sup>b</sup>Isolated Yield.

We attempted to expand this nickel-catalyzed decarboxylative coupling reaction toward aryl bromide and chloride. However, no product was formed.

We have proposed a plausible mechanism for the reaction, as shown in Scheme 1. Ni(II) is reduced to Ni(0) in the presence of manganese.<sup>23</sup> The aryl iodide reacts with Ni(0) to give the oxidative addition complex **A**. The phenyl propiolic acid salt, which is formed by the reaction with Cs<sub>2</sub>CO<sub>3</sub>, reacts with nickel complex **A** to provide the aryl alkynyl nickel complex **B** through a decarboxylative ligand exchange reaction. Finally, reductive elimination affords the desired coupled product and Ni(0).



**Scheme 1.** Proposed mechanism.

In summary, we have developed a synthesis of diaryl alkynes involving the reaction of aryl iodides and phenyl propiolic acid in the presence of a nickel catalyst. To obtain the desired product, NiCl<sub>2</sub> (10 mol%), Xantphos (15 mol%), Cs<sub>2</sub>CO<sub>3</sub> (1.5 equiv), and Mn (1.0 equiv) were employed. This method afforded diaryl alkynes in moderate to good yields. Moreover, this methodology presents several advantages over that used in traditional coupling reactions of this sort: a stable Ni(II) source is employed as the catalyst, and no formation of 1,4-diphenylbutadiene, which is

always produced in palladium- or copper-catalyzed coupling reactions with alkynes, is observed.

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- Theoretically, catalytic amount of manganese can be required to activate the nickel catalyst precursor. However, when 0.5 equivalent of manganese were employed, the yield of product was decreased.

**Highlights**

Decarboxylative coupling reactions with alkynyl  
carboxylic acid and aryl iodides

Nickel-catalyzed decarboxylative coupling

The employment of air stable nickel(II) as a  
catalyst.

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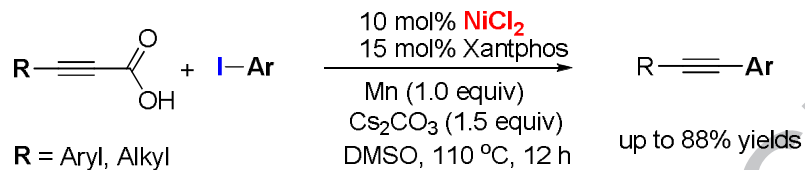
**Graphical Abstract**

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**Nickel-Catalyzed Decarboxylative Coupling of an Alkynyl Carboxylic Acids with Aryl Iodides**

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Yujeong Son, Han-Sung Kim, Ju-Hyeon Lee, Jisun Jang, Chin-Fa Lee\*, Sunwoo Lee\*



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