

# Palladium-Catalyzed Oxidative Carbonylation for the Synthesis of Symmetrical Diaryl Ketones at Atmospheric CO Pressure

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**Abstract:** A mild and efficient synthesis of symmetrical diaryl ketones by palladium-catalyzed oxidative carbonylation of arylboronic acids with carbon monoxide at atmospheric pressure is reported.

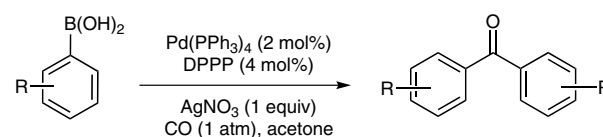
**Key words:** palladium, carbonylation, carbon monoxide, arylboronic acids, diaryl ketone

Palladium-catalyzed carbonylation reactions allow for the straightforward preparation of C–C, C–N, and C–O bonds.<sup>1–3</sup> Among these reactions, palladium-catalyzed carbonylation of aryl halides has been well established over the past decades.<sup>4</sup> The oxidative carbonylation of aryl boronic acids constitute an alternative methodology and has been studied as well.<sup>5</sup> So far, olefins,<sup>6</sup> alkynes,<sup>7</sup> and alcohols<sup>8</sup> have been exploited as nucleophiles.

The synthesis of diaryl ketones have attracted considerable interest, as they are important intermediates<sup>9</sup> in medicinal chemistry<sup>10</sup> and materials sciences.<sup>11,12</sup> A general method for the synthesis of diaryl ketones is intramolecular Friedel–Crafts acylation of aromatics;<sup>13</sup> however, this method requires overstoichiometric amounts of Lewis acid and cannot tolerate many functional groups.

During the past a few decades, transition-metal-catalyzed reactions have provided new approaches to synthesize these compounds.<sup>14</sup> For example, the palladium-catalyzed coupling of arylboronic acids with carboxylic acid derivatives is one of the most efficient ways.<sup>15</sup> Earlier, Suzuki<sup>16</sup> and, more recently, others<sup>17</sup> reported examples of the synthesis of unsymmetrical diaryl ketones via arylboronic acids, carbon monoxide, and aryl iodides in the presence of a palladium catalyst and a suitable base, showing a useful protocol for the synthesis of these compounds. However, most of the papers report products that require two different substrates, such as an aryl halide and a boronic acid. Building upon on our previous work on carbonylation reactions<sup>18</sup> and palladium-catalyzed Heck reaction of aryl boronic acids,<sup>19</sup> we report herein a palladium-catalyzed oxidative carbonylation of aryl boronic acids with carbon monoxide at atmospheric pressure, leading to a

mild and efficient synthesis of symmetrical diaryl ketones (Scheme 1).



**Scheme 1** Palladium-catalyzed oxidative carbonylation for the synthesis of diaryl ketones

Treatment of phenylboronic acid (**1a**) with CO at atmospheric pressure in acetone at 40 °C for 20 hours in the presence of a catalytic amount of Pd(OAc)<sub>2</sub> (1 mol%) and DPPP (2 mol%) gave benzophenone (**2a**) in 31% yield (Table 1, entry 3). Next, we surveyed the blank reaction, which showed that without Pd(OAc)<sub>2</sub> or ligand, no desired product formed (Table 1, entries 1 and 2). When the ligand was switched from DPPP to DavePhos and DPPE, poorer yields were obtained (Table 1, entries 4 and 5). The influence of the palladium source was next examined. It can be seen that Pd(PPh<sub>3</sub>)<sub>4</sub> turned out to be the best precatalyst for the reaction (Table 1, entries 9–14). Oxidants such as BQ (42%), AgOAc (49%), and AgNO<sub>3</sub> (65%) were also screened. It was observed that the reaction gave better results with the use of AgNO<sub>3</sub> as the oxidant (Table 1, entries 12–14). Finally, increasing the amount of Pd(PPh<sub>3</sub>)<sub>4</sub> and DPPP to 2 mol% and 4 mol%, respectively, resulted in benzophenone **2a** being obtained in a yield of 70% (Table 1, entry 13). Based on these conditions, we prolonged the reaction time to 24 hours and, to our delight, we obtained the target product in an excellent yield of 87% (Table 1, entry 14). Hence, the optimized reaction conditions were chosen to be: Pd(PPh<sub>3</sub>)<sub>4</sub> (2 mol%), DPPP (4 mol%), AgNO<sub>3</sub> (1 equiv), acetone as solvent at 40 °C for 24 hours.

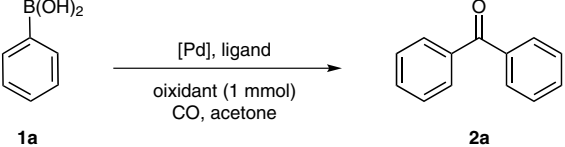
With the optimized reaction conditions in hand,<sup>22</sup> we next examined the scope of arylboronic acids with regard to the formation of benzophenone and derivatives (Table 2). First, 4-substituted boronic acids were explored as substrates. As can be seen, good yields were obtained for substrates bearing either an electron-withdrawing or electron-donating group (**2b–l**, Table 2, entries 2–12). In particular, aryl boronic acids bearing some functional groups, such

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**Table 1** Optimization of Reaction Conditions<sup>a</sup>


Entry	Catalyst	Ligand	Oxidant	Yield (%) <sup>b</sup>
1	–	DPPP	Cu(OAc) <sub>2</sub>	0
2	Pd(OAc) <sub>2</sub>	–	Cu(OAc) <sub>2</sub>	trace
3	Pd(OAc) <sub>2</sub>	DPPP	Cu(OAc) <sub>2</sub>	31
4	Pd(OAc) <sub>2</sub>	DavePhos	Cu(OAc) <sub>2</sub>	18
5	Pd(OAc) <sub>2</sub>	DPPE	Cu(OAc) <sub>2</sub>	11
6	Pd(dba) <sub>2</sub>	DPPP	Cu(OAc) <sub>2</sub>	38
7	Pd(TFA) <sub>2</sub>	DPPP	Cu(OAc) <sub>2</sub>	51
8	PdCl <sub>2</sub>	DPPP	Cu(OAc) <sub>2</sub>	49
9	Pd(PPh <sub>3</sub> ) <sub>4</sub>	DPPP	Cu(OAc) <sub>2</sub>	65
10	Pd(PPh <sub>3</sub> ) <sub>4</sub>	DPPP	BQ	42
11	Pd(PPh <sub>3</sub> ) <sub>4</sub>	DPPP	AgOAc	49
12	Pd(PPh <sub>3</sub> ) <sub>4</sub>	DPPP	AgNO <sub>3</sub>	65
13	Pd(PPh <sub>3</sub> ) <sub>4</sub>	DPPP	AgNO <sub>3</sub>	70 <sup>c</sup>
14	Pd(PPh <sub>3</sub> ) <sub>4</sub>	DPPP	AgNO <sub>3</sub>	87 <sup>d</sup>

<sup>a</sup> Reaction conditions: phenylboronic acid (1 mmol), CO (1 atm), catalyst (1 mol%), oxidant (1 mmol), ligand (2 mol%), solvent (3 mL), 40 °C, 12 h.

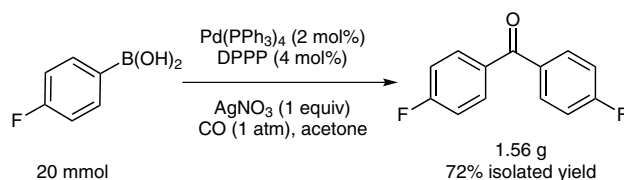
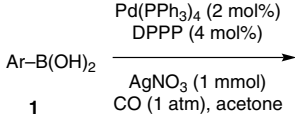
<sup>b</sup> Isolated yield.

<sup>c</sup> Catalyst (2 mol%), ligand (4 mol%), oxidant (1 mmol), solvent (3 mL), 40 °C, 12 h.

<sup>d</sup> The same conditions as in footnote c except for 24 h.

as 4-cyano and 4-trifluoromethoxy, are all viable for the reaction. Next, we surveyed 3- and 2-substituted boronic acids for the reaction. Delightfully, we could obtain benzophenones in good yield (**2l–s**, Table 2, entries 12–19). In particular, the boronic acids with electron-withdrawing substituents gave excellent yields (**2l–v**, Table 2, entries 12–22). Disubstituted boronic acids were also used as substrates; they could be transformed into the target in acceptable yields (**2t–v**, Table 2, entries 20–22). For the sake of generality, we extended the protocol to heteroaryl boronic acids, such as thiophen-3-ylboronic acid. A similar yield of the desired product was obtained with Pd(PPh<sub>3</sub>)<sub>4</sub> as catalyst in 24 hours (**2x**, Table 2, entry 24).

4,4'-Difluorobenzophenone (**2b**)<sup>20</sup> is an important organic compound, which is commonly used as a precursor for polyether ether ketone (PEEK).<sup>21</sup> Usually, it is prepared by the acylation of fluorobenzene with 4-fluorobenzoyl chloride.<sup>20a</sup> By using our method, it can be obtained in a yield of 72% at the gram scale, showing the potential of this protocol in organic synthesis (Scheme 2).

**Scheme 2** Gram-scale synthesis of 4,4'-difluorobenzophenone via carbonylation of (4-fluorophenyl)boronic acid**Table 2** Carbonylation of Aryl Boronic Acids<sup>a</sup>


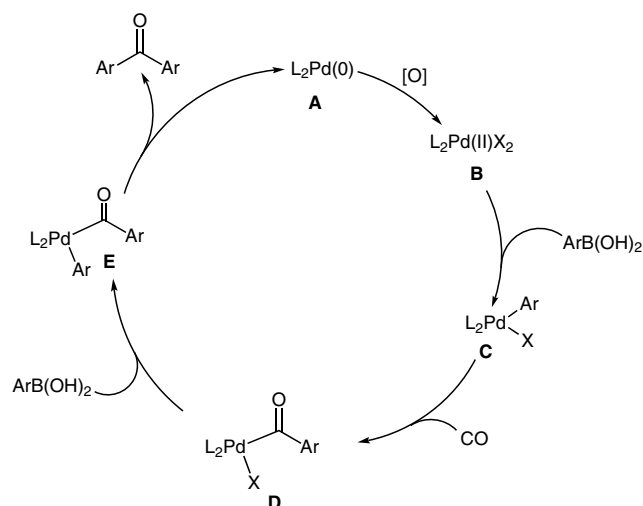
Entry	Ar	Ketone	Yield (%) <sup>b</sup>
1	Ph	<b>2a</b>	74
2	4-FC <sub>6</sub> H <sub>4</sub>	<b>2b</b>	67
3	4-ClC <sub>6</sub> H <sub>4</sub>	<b>2c</b>	62
4	4-NCC <sub>6</sub> H <sub>4</sub>	<b>2d</b>	53
5	4-F <sub>3</sub> CC <sub>6</sub> H <sub>4</sub>	<b>2e</b>	51
6 <sup>c</sup>	4-MeOC <sub>6</sub> H <sub>4</sub>	<b>2f</b>	62
7	4-F <sub>3</sub> COC <sub>6</sub> H <sub>4</sub>	<b>2g</b>	51
8	4-MeC <sub>6</sub> H <sub>4</sub>	<b>2h</b>	74
9	4- <i>t</i> -BuC <sub>6</sub> H <sub>4</sub>	<b>2i</b>	69
10	4-EtC <sub>6</sub> H <sub>4</sub>	<b>2j</b>	43
11 <sup>c</sup>	4-PrC <sub>6</sub> H <sub>4</sub>	<b>2k</b>	41
12	2-FC <sub>6</sub> H <sub>4</sub>	<b>2l</b>	91
13	2-ClC <sub>6</sub> H <sub>4</sub>	<b>2m</b>	75
14	2-MeOC <sub>6</sub> H <sub>4</sub>	<b>2n</b>	63
15	2-MeC <sub>6</sub> H <sub>4</sub>	<b>2o</b>	53
16	3-FC <sub>6</sub> H <sub>4</sub>	<b>2p</b>	82
17	3-ClC <sub>6</sub> H <sub>4</sub>	<b>2q</b>	71
18	3-MeOC <sub>6</sub> H <sub>4</sub>	<b>2r</b>	59
19	3-MeC <sub>6</sub> H <sub>4</sub>	<b>2s</b>	69
20	2,3-(MeO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	<b>2t</b>	63
21	3,5-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	<b>2u</b>	42
22	3,4-F <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	<b>2v</b>	80
23	2-naphthyl	<b>2w</b>	65
24	3-thienyl	<b>2x</b>	71

<sup>a</sup> Reaction conditions: aryl boronic acid (1 mmol), CO (1 atm), Pd(PPh<sub>3</sub>)<sub>4</sub> (2 mol%), ligand (4 mol%), oxidant (1 mmol), solvent (3 mL), 40 °C, 24 h.

<sup>b</sup> Isolated yield.

<sup>c</sup> 36 h.

A possible mechanism for the palladium-catalyzed oxidative carbonylation of arylboronic acids is shown in Scheme 3. Initially, Pd(II) (**B**) is formed by reaction with the oxidant; then transmetalation of the aryl boronic acid with **B** results in the intermediate **C**. After coordination of CO and its subsequent insertion into the Pd–C bond, the palladium acyl intermediate **D** is formed, which can react with another aryl boronic acid to give the ketone product via reductive elimination at the palladium species **E**. Meanwhile, palladium is reduced from Pd(II) to Pd(0) (**A**), the oxidation of which restarts the catalytic cycle.



**Scheme 3** Proposed mechanism for the oxidative carbonylation

In summary, a convenient method for the preparation of symmetric diaryl ketones has been developed. The palladium-catalyzed carbonylation is easy to carry out, allowing for the direct transformation of aryl boronic acids into the corresponding symmetric diaryl ketones under atmospheric CO pressure. The wide scope, mild reaction conditions, and high yields showcase the potential of the method in organic synthesis.

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- (21) Searle, O. B.; Pfeiffer, R. H. *Polym. Eng. Sci.* **1985**, *25*, 474.
- (22) **General Procedure for the Carbonylation of Arylboronic Acids**  
The reaction was carried out in an autoclave containing a 10 mL Teflon reaction tube. Pd(PPh<sub>3</sub>)<sub>4</sub> (0.02 mmol), DPPP (0.04 mmol), and a magnetic stir bar were placed in the tube which was then capped with a stopper and flushed with argon. Then, aryl boronic acid (1 mmol), AgNO<sub>3</sub> (1 mmol), and acetone (3 mL) were added to the tube. The tube was put into the autoclave. Once sealed, the autoclave was purged several times with CO, pressurized to 1 atm at r.t. and then heated in an oil bath at 40 °C for 24 h. The autoclave was then cooled to r.t. and carefully vented to discharge CO in a fume hood. Water (10 mL) was added, and the product was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 15 mL). The organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated. The crude product was purified by column chromatography on silica gel using a mixture of EtOAc and PE as eluent to give the products. The identity and purity of the product was confirmed by <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy and MS or HRMS spectrometry.
- Benzophenone (2a)**  
R<sub>f</sub> = 0.3 (PE–EtOAc, 50:1), yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.83 (d, J = 7.6 Hz, 4 H), 7.62 (t, J = 7.2 Hz, 2 H), 7.51 (t, J = 7.6 Hz, 4 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 196.8, 137.6, 132.4, 130.1, 130.0, 128.3, 128.3 ppm. IR (KBr): 3040, 1658, 1603, 1321, 1274 cm<sup>-1</sup>. ESI-HRMS: m/z calcd for [M + Na<sup>+</sup>]: 205.0621; found: 205.0624.
- Bis(4-fluorophenyl)methanone (2b)**  
R<sub>f</sub> = 0.3 (PE–EtOAc, 50:1), light yellow solid; mp 87–88 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.76–7.72 (m, 4 H), 7.11–7.07 (m, 4 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 193.7, 165.4 (d, J<sub>C-F</sub> = 252.9 Hz), 133.7 (d, J<sub>C-F</sub> = 3 Hz), 132.4 (d, J<sub>C-F</sub> = 9.1 Hz), 115.5 (d, J<sub>C-F</sub> = 21.8 Hz) ppm. IR (KBr): 1647, 1496, 1295, 953, 760 cm<sup>-1</sup>. ESI-HRMS: m/z calcd for [M + Na<sup>+</sup>]: 241.0442; found: 241.0435.
- Bis(4-chlorophenyl)methanone (2c)**  
R<sub>f</sub> = 0.3 (PE–EtOAc, 50:1), solid; mp 127–128 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.72 (d, J = 8.4 Hz, 4 H), 7.46 (d, J = 8.4 Hz, 4 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 193.1, 138.1, 134.5, 130.3, 127.8 ppm. IR (KBr): 2364, 1651, 1585, 1275, 841, 756 cm<sup>-1</sup>. ESI-HRMS: m/z calcd for [M + Na<sup>+</sup>]: 272.9851; found: 272.9844.

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