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## Article

# Carboxylative Suzuki coupling reactions of benzyl chlorides with allyl pinacolborate catalyzed by palladium nanoparticles



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## ABSTRACT

Palladium-catalyzed carboxylative Suzuki coupling reactions of benzyl chlorides with allyl pinacolborate were successfully conducted in the absence of any extra ligand to produce  $\beta,\gamma$ -unsaturated esters in satisfactory to good yields. The carboxylative Suzuki coupling reaction proceeded smoothly under mild conditions in the presence of palladium nanoparticles generated in situ through the formation of a  $\pi$ -benzylpalladium chloride intermediate.

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## 1. Introduction

CO<sub>2</sub> is abundant, inexpensive, nontoxic, and environmentally benign; thus, its chemical fixation and transformation into valuable chemicals that involve new carbon–carbon bond formation has attracted considerable attention [1–6]. In general, strong nucleophilic organometallic reagents (i.e., metal = lithium [7], magnesium [8], aluminum [9,10], or zinc [11–14]) directly undergo a reaction with CO<sub>2</sub> to produce carboxyl-containing organic compounds. However, current methods

for these reactions are limited with respect to functional group tolerance and substrate stability. In contrast to strong nucleophilic organometallic reagents, weak nucleophilic organometallic reagents (i.e., metal = tin [15], silicon [16], or boron [17]) cannot undergo a direct reaction with CO<sub>2</sub> and require the presence of transition-metal catalysts for carboxylation. Among these organometallic reagents, organoboranes are frequently utilized because of their commercial availability, relatively low toxicity, and high tolerance to functional groups. Recently, Hazari et al. [18] reported a type of monodentate carboxylate

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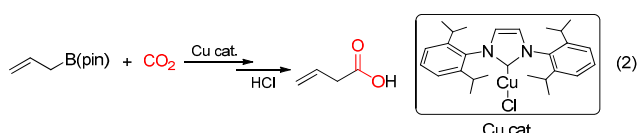
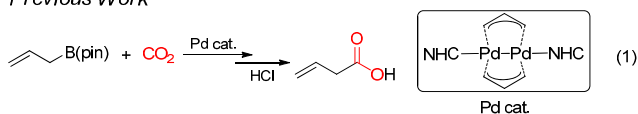
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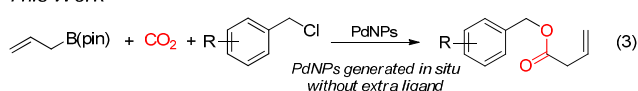
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[[ $\eta^3$ -allyl]Pd(L)(carboxylate) (L = NHC)], which is an efficient catalyst for the carboxylation of allylboranes with CO<sub>2</sub>. Then, they developed an *N*-heterocyclic carbene-supported dimer as an active and stable catalyst for the carboxylation of allylboranes with CO<sub>2</sub> (Eq. (1)) [19]. Duong et al. [20] also studied the carboxylative reaction of allylboronates with CO<sub>2</sub> in the presence of a Cu(I)/NHC catalyst (Eq. (2)). The abovementioned Pd- or Cu-catalyzed carboxylation reactions of allylboranes involved the use of *N*-heterocyclic carbene ligands. The use of carbene ligands is typically disadvantageous because it often leads to air/moisture sensitivity, tedious work-up procedures, and high work-up costs [21–27]. Therefore, the development of a simple and robust catalyst system that allows for the efficient carboxylation of allylboranes with CO<sub>2</sub> without any additional ligands is desirable.

#### Previous Work



#### This Work



Recently, our group reported palladium nanoparticles-catalyzed carbonylative and carboxylative reactions of (chloromethyl)arenes with allyltributylstannane [28–30]. We found that palladium nanoparticles can form in situ, and  $\pi$ -benzyl- $\pi$ -allyl could be used as the carbon-based ligand for palladium nanoparticles [31–33]. Based on our previous study, we hypothesized that the  $\pi$ -allyl involving allylboranes may also be used as a carbon-based ligand for the palladium-catalyzed chemical fixation of CO<sub>2</sub>. As expected, the carboxylative Suzuki coupling reaction of benzyl chlorides with allyl pinacolborate occurred in the presence of palladium nanoparticles (PdNPs) (Eq. (3)). The results are reported in the current work.

## 2. Experimental

All reactions were carried out under a nitrogen atmosphere, unless otherwise noted. The solvents used were purified by standard techniques without special instructions. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on either a Varian Inova-400 spectrometer (400 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C) or a Bruker Avance II-400 spectrometer (400 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C). CDCl<sub>3</sub> and tetramethylsilane were used as a solvent and internal standard, respectively. Infrared spectra were recorded on a NEXUS Fourier transform-infrared spectrometer. High-resolution mass spectra were recorded through gas chromatography-time-of-flight mass spectrometry. All starting materials are commercially available.

## 3. Results and discussion

In the initial study, the reaction of benzyl chloride (**1a**) with allyl pinacolborate in the presence of CO<sub>2</sub> was selected as a model for the optimization of reaction conditions (Table 1). A series of palladium precatalysts, including PdCl<sub>2</sub>, Pd<sub>2</sub>(dba)<sub>3</sub>, Pd(OAc)<sub>2</sub>, and Pd(acac)<sub>2</sub>, were initially tested in tetrahydrofuran (THF) at 50 °C by using TBAB and KF as a stabilizer and an activator, respectively (Table 1 entries 1–4). Among the palladium precatalysts tested, Pd(acac)<sub>2</sub> exhibited the highest catalytic activity, affording the benzyl but-3-enoate (**2a**) in 81% yield (Table 1 entry 4). These results indicated that PdNPs generated in situ from newly formed Pd(0) species possessed higher catalytic activity than those generated from Pd<sub>2</sub>(dba)<sub>3</sub>. No reaction was observed when TBAB was used as a stabilizer in the absence of KF, suggesting that the target reaction was unable to proceed in the absence of an activator (Table 1 entry 5) [34]. Thus, we screened several fluorides (KF, TBAF, and CsF) to determine a suitable activator (Table 1 entries 4, 6, and 7). The mixed products of **2a** and **2a'** were obtained in 53% yield when TBAF was used as the activator for the reaction (Table 1 entry 6), and only a 13% yield of **2a** was obtained when CsF was used as the activator (Table 1 entry 7). These results indicated that KF is the most suitable activator for the carboxylative Suzuki coupling of benzyl chlorides with allyl pinacolborate. Nonpolar (toluene) and polar [THF, dioxane, and *N,N*-dimethyl formamide (DMF)] solvents were then examined (Table 1 entries 4 vs. 8–10). THF was the best solvent. The yield of **2a** decreased to 33% when the reaction was performed for 12 h (Table 1 entry 11). Further studies revealed that no product was generated when the reaction was performed at room temperature (Table 1 entry 12). A similar yield of product **2a**

**Table 1**  
Reaction condition screening <sup>a</sup>.

Entry	Catalyst	Activator	Solvent	Yield <sup>b</sup> (%)
1	PdCl <sub>2</sub>	KF	THF	37
2	Pd <sub>2</sub> (dba) <sub>3</sub>	KF	THF	71
3	Pd(OAc) <sub>2</sub>	KF	THF	50
4	Pd(acac) <sub>2</sub>	KF	THF	81
5	Pd(acac) <sub>2</sub>	None	THF	0
6 <sup>c</sup>	Pd(acac) <sub>2</sub>	TBAF	THF	53
7	Pd(acac) <sub>2</sub>	CsF	THF	13
8	Pd(acac) <sub>2</sub>	KF	Toluene	22
9	Pd(acac) <sub>2</sub>	KF	Dioxane	67
10	Pd(acac) <sub>2</sub>	KF	DMF	29
11 <sup>d</sup>	Pd(acac) <sub>2</sub>	KF	THF	33
12 <sup>e</sup>	Pd(acac) <sub>2</sub>	KF	THF	0
13 <sup>f</sup>	Pd(acac) <sub>2</sub>	KF	THF	80
14 <sup>g</sup>	Pd(acac) <sub>2</sub>	KF	THF	76

<sup>a</sup> Reaction conditions: benzyl chloride (**1a**, 0.5 mmol), allyl pinacolborate (0.6 mmol), CO<sub>2</sub> (2.0 MPa), a Pd catalyst (5 mol%), a stabilizer TBAB (1.4 equiv.), a fluoride activator (2.0 equiv.), and a solvent (5 mL) at 50 °C for 24 h. <sup>b</sup> Isolated yield. <sup>c</sup> A mixture of products **2a** and **2a'** was obtained. <sup>d</sup> The reaction was performed for 12 h. <sup>e</sup> The reaction was performed at room temperature. <sup>f</sup> The reaction was performed at 70 °C. <sup>g</sup> The reaction was performed at 3.0 MPa of CO<sub>2</sub>.

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