

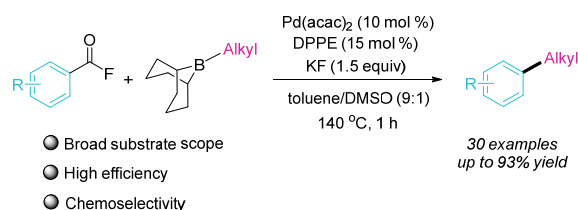
# Palladium-Catalyzed Decarbonylative Alkylation of Acyl Fluorides

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Supporting Information Placeholder



**ABSTRACT:** Palladium-catalyzed decarbonylative alkylation reactions of acyl fluorides have been developed using alkylboranes having  $\beta$ -hydrogens. A wide range of functional groups were well tolerated, even at the high temperature required for decarbonylation. This protocol provides a diverse  $C(sp^2)-C(sp^3)$  bond formation via a highly efficient decarbonylative process. The hemilabile bidentate ligand DPPE plays a crucial role for retardation of the undesired  $\beta$ -hydride elimination.

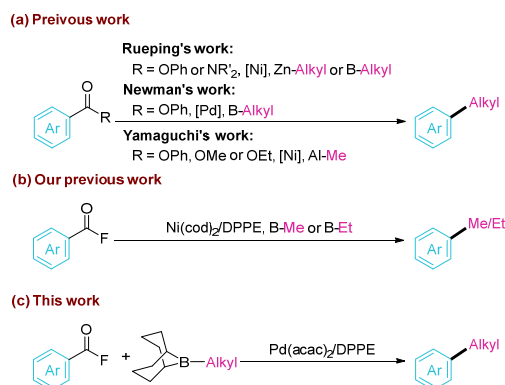
The palladium-catalyzed cross-coupling reactions forming carbon-carbon bonds are important classes in organic chemistry.<sup>1</sup> Particularly, Suzuki–Miyaura cross-coupling reaction has been widely developed and utilized to form diverse C–C bonds.<sup>2</sup> However, when alkylboron reagents are employed as the coupling partners, undesired pathways, especially  $\beta$ -hydride elimination, are unavoidable.<sup>3</sup> As a result, only a few examples have been reported for the construction of  $C(sp^2)-C(sp^3)$  bonds<sup>4,5</sup> compared with its major counterparts,  $C(sp^2)-C(sp^2)$  and  $C(sp^2)-C(sp)$  bonds. Therefore, it is still in a high demand to develop a new synthetic approach to form  $C(sp^2)-C(sp^3)$  bonds.<sup>6</sup>

Over last decades, transformations of carboxylic acids via decarboxylation have attracted much attention in organic synthesis due to their wide abundance, availability and environmentally friendliness.<sup>7</sup> Consequently, carboxylic acid derivatives such as esters and amides have been developed as alternative coupling partners to halogenated electrophiles through decarbonylation.<sup>8</sup> In this context, several research groups have disclosed a series of decarbonylative alkylation reactions of esters<sup>9</sup> and amides<sup>9b</sup> and with alkylboron, -zinc, or -aluminum reagents (Scheme 1a).

On the other hand, acyl fluorides can easily be prepared from the corresponding carboxylic acids<sup>10</sup> and present unique properties under late transition metal catalysis.<sup>11</sup> In some cases, acyl fluorides act as acyl sources in transition-metal-catalyzed reactions to couple with organometallic nucleophiles such as or-

ganozinc, -silicon and -boron reagents to generate various ketones in a retentive manner.<sup>12</sup> While, acyl fluorides have shown powerful faculty as aryl sources for the construction of C–C<sup>13,14,15</sup> and various C–X (X = H,<sup>16</sup> B,<sup>17</sup> Si,<sup>18</sup> and Sn<sup>19</sup>) bonds in a decarbonylative manner. During our continuing studies on the transformation of acyl halides,<sup>20</sup> although we have successfully developed the nickel-catalyzed decarbonylative ethylation (triethylboron) and methylation (methylboroxine) of acyl fluorides, this method could not be applied for other alkylating reagents (Scheme 1b).<sup>21</sup> In order to render our previous work more general, we developed the Pd-catalyzed decarbonylative alkylation of acyl fluorides with a variety of functionalized alkylboranes (Scheme 1c).

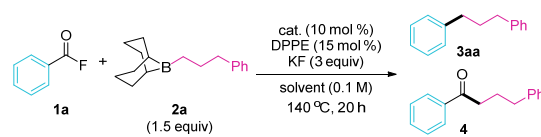
## Scheme 1. Decarbonylative Alkylation of Carboxylic Acid Derivatives



We initially studied the reaction of benzoyl fluoride (**1a**) with *B*-(3-phenylpropyl)-9-borabicyclo[3.3.1]nonane (**2a**), *in-situ* derived from hydroboration of allylbenzene with 9-BBN dimer in toluene (Table S1-6 in the Supporting Information†). Firstly, the Ni(cod)<sub>2</sub>/1,2-bis(diphenylphosphino)ethane (DPPE) catalyst system that showed a superior catalytic activity for ethylation and methylation in our previous work was tested, but only a trace of the products **3aa** and **4** were detected (Table 1, entry 1). In contrast, the combination of Pd(OAc)<sub>2</sub> with DPPE yielded 54% of **3aa** and 8% of **4** (entry 2), indicating that the choice of transition metal catalysts is critical for decarbonylative alkylation. In general,  $\beta$ -hydride elimination of alkylnickel complexes are considered to be more difficult than the alkylpalladium complexes. In some cases, however, nickel complexes are known to cause  $\beta$ -hydride elimination than palladium complexes.<sup>22</sup> When a bulky and electron-rich 1,2-bis(dicyclohexylphosphino)ethane (DCYPE) ligand was employed instead of DPPE, the yield of **3aa** was decreased to 41% (entry 3). To our delight, 71% of **3aa** was obtained with Pd(acac)<sub>2</sub> as the precursor (entry 5), which is comparable to Pd(dba)<sub>2</sub> (entry 4). Further optimizations of the solvents revealed that the toluene/DMSO co-solvent system was efficient, affording **3aa** in 90% yield and ketone **4** was not detected (entry 6).<sup>23</sup> Decreasing of the catalyst loading was found to reduce the yields of the target products (entry 7). It was found that the amount of the base has little effect on the yield (entry 8). Gratifyingly, the reaction could be completed within 1 h, which is highly efficient compared to the previous reports<sup>9</sup> (entry 9). In the control experiments, no desired product was obtained in the absence of the palladium catalyst or the ligand (entries 10 and 11). Given the representative decarbonylative Suzuki-Miyaura coupling<sup>13</sup> and borylation reaction<sup>17b</sup> of acyl fluorides reported by Sanford's group in the absence of the external base under nickel catalysis,<sup>24</sup> only 38% yield of **3aa** was observed without addition of external KF (entry 12). As most importantly, when benzoyl chloride was employed instead of **1a** under the identical reaction conditions, no desired product **3aa** was obtained (entry 13), which revealed that acyl fluorides play a vital role in this transformation.

Encouraged by these results, we examined the scope of acyl fluorides **1** in combination with alkylborane **2a** as the coupling partner under the optimal conditions (Scheme 2). A series of acyl fluorides bearing electron-donating and -withdrawing functional groups could be converted into the corresponding alkylated products **3aa-3na** in moderate to high yields. The use of sterically hindered acyl fluoride **1e** smoothly provided **3ea** in 87% yield. Fluoro (**3ja**), trifluoromethyl (**3ka**, **3la**), cyano (**3ma**) and ketone (**3na**) substituents were well tolerated. Furthermore, not only naphthyl-derived substrates, but heteroaromatic acyl fluorides were also compatible for the present transformation to give **3oa-3ra** in 54-81% yields. However, this transformation could not be applied to cinnamoyl- or 2-(naphthalen-2-yl)acetyl fluorides (See the Supporting Information). Notably, this reaction could afford a large-scale synthesis up to 8.0 mmol with a low dosage of palladium, providing 0.93 g of **3aa** in 59% yield.

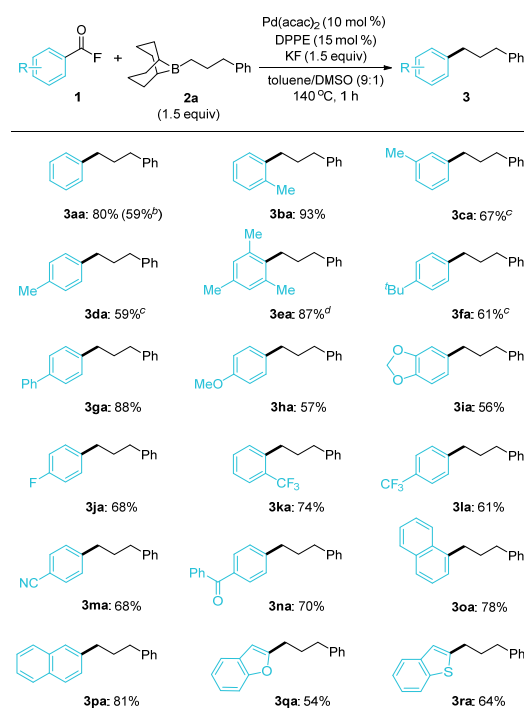
**Table 1. Optimization of the Pd-Catalyzed Decarbonylative Alkylation of Benzoyl Fluoride (**1a**) with Alkylboranes **2a**<sup>a</sup>**



entry	catalyst	solvent <sup>b</sup>	yield (%) <sup>c</sup>	
			<b>3aa</b>	<b>4</b>
1	Ni(cod) <sub>2</sub>	toluene	2	0
2	Pd(OAc) <sub>2</sub>	toluene	54	8
3 <sup>d</sup>	Pd(OAc) <sub>2</sub>	toluene	41	0
4	Pd(dba) <sub>2</sub>	toluene	70	2
5	Pd(acac) <sub>2</sub>	toluene	71	2
6	Pd(acac) <sub>2</sub>	toluene/DMSO	90	0
7 <sup>e</sup>	Pd(acac) <sub>2</sub>	toluene/DMSO	81	0
8 <sup>f</sup>	Pd(acac) <sub>2</sub>	toluene/DMSO	90	0
9 <sup>f,g</sup>	<b>Pd(acac)<sub>2</sub></b>	<b>toluene/DMSO</b>	<b>90 (80)</b>	<b>0</b>
10 <sup>f</sup>	-	toluene/DMSO	0	0
11 <sup>f,h</sup>	Pd(acac) <sub>2</sub>	toluene/DMSO	0	0
12 <sup>f,i</sup>	Pd(acac) <sub>2</sub>	toluene/DMSO	38	0
13 <sup>f,j</sup>	Pd(acac) <sub>2</sub>	toluene/DMSO	0	0

<sup>a</sup>Reaction conditions: **1a** (0.2 mmol), **2a** (1.5 equiv), catalyst (10 mol %), DPPE (15 mol %), KF (3 equiv), toluene (2 mL), 140 °C, 20 h. <sup>b</sup>Toluene (1.8 mL), DMSO (0.2 mL). <sup>c</sup>GC yields, using *n*-dodecane as an internal standard and an isolated yield is shown in parentheses. <sup>d</sup>DCYPE was employed instead of DPPE. <sup>e</sup>Pd(acac)<sub>2</sub> (5 mol %), DPPE (7.5 mol %). <sup>f</sup>KF (1.5 equiv). <sup>g</sup>1 h. <sup>h</sup>Without DPPE. <sup>i</sup>Without KF. <sup>j</sup>Benzoyl chloride was employed instead of **1a**.

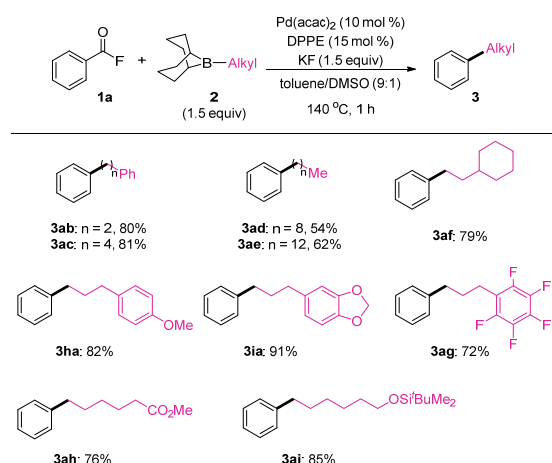
**Scheme 2. Scope of Acyl Fluorides<sup>a</sup>**



<sup>a</sup>Reaction conditions: **1** (0.2 mmol), **2a** (0.3 mmol), Pd(acac)<sub>2</sub> (10 mol %), DPPE (15 mol %), and KF (0.3 mmol), in toluene/DMSO (9:1, 0.1 M) at 140 °C for 1 h under Ar. Isolated yields. <sup>b</sup>Reaction was performed in 8.0 mmol. <sup>c</sup>DCYPE (15 mol %) was used instead of DPPE. <sup>d</sup>20 h.

We subsequently explored the scope of *B*-alkyl-9-BBN reagents **2** using benzoyl fluoride (**1a**) as the electrophile (Scheme 3). Various alkylboranes prepared from hydroboration of the corresponding alkenes were well tolerated to afford decarbonylative products **3ab–3af** under the optimized conditions. The opposite combination of substrates **1** and **2** also afford the same compounds **3ha** and **3ia** in better yields. Relatively, the *B*-alkyl-9-BBN bearing pentafluorophenyl functionality provided the corresponding product **3af** in 79% yield. Moreover, alkylboranes containing ester and silyloxy groups were also suitable for the decarbonylative alkylation and gave the desired products **3ah** and **3ai** in 76% and 85% yields, respectively. Unfortunately, the protocol could not be applied to secondary alkylboron reagents such as 2-methyl-3-phenylpropyl, cyclooctyl derivatives and other alkylboron compounds such as *B*-alkyl(BF<sub>3</sub>K) (see the Supporting Information).

**Scheme 3. Scope of Alkylboranes<sup>a</sup>**

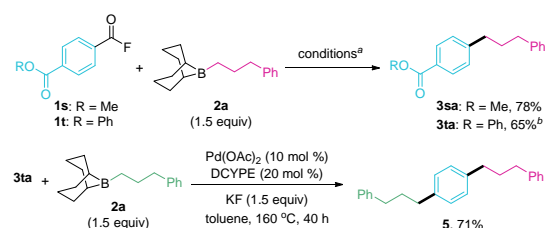


<sup>a</sup>Reaction conditions: **1a** (0.2 mmol), **2** (0.3 mmol), Pd(acac)<sub>2</sub> (10 mol %), DPPE (15 mol %), and KF (0.3 mmol) in toluene/DMSO (9:1, 0.1 M) at 140 °C for 1 h under Ar. Isolated yields.

Next, we explored the chemoselective reactions of the substrates bearing esters and acyl fluoride functionalities (Scheme 4). Under our reaction conditions, the acyl fluoride moieties exclusively reacted with **2a** to deliver the corresponding alkylated products **3sa** and **3ta** in 78% and 65% yields, respectively, remaining ester moieties intact. To demonstrate the utility of this chemoselective alkylation protocol, we used **3ta** as a reactant for the further alkylation under the previously reported reaction condition for esters<sup>9c</sup> and obtained double alkylated product **5** in 71% yield.

According to the related mechanistic studies reported by Schoenebeck<sup>14</sup> and Xie,<sup>25</sup> a plausible reaction mechanism of the present decarbonylative alkylation of acyl fluorides is shown in Scheme 5. Initially, oxidative addition of C(acyl)–F bond to Pd(0) generates acyl(fluoro)palladium(II) complex **A**. Then

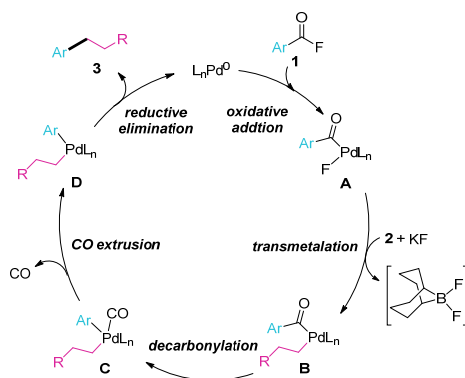
**Scheme 4. Chemoselective and Sequential Alkylation**



<sup>a</sup>Reaction conditions: **1** (0.2 mmol), **2a** (0.3 mmol), Pd(acac)<sub>2</sub> (10 mol %), DPPE (15 mol %), and KF (0.3 mmol) in toluene/DMSO (9:1, 0.1 M) at 140 °C for 1 h under Ar. Isolated yields. <sup>b</sup>130 °C.

transmetalation of **A** with alkylboranes **2** occurs to yield the acyl(alkyl)palladium(II) complex **B** and *B*,*B*-F<sub>2</sub>-9-BBN<sup>26</sup> as the fate of fluorides, supporting that the addition of an external KF is required for the present transformation. Sequentially, the complex **B** undergoes decarbonylation to give complex **C**. Most reported decarbonylation of carboxylic acid derivatives with alkylmetals proceeded with the assistance of the hemilabile bidentate ligands such as DCYPE.<sup>9</sup> Subsequently, aryl(alkyl)palladium(II) complex **D** is formed via CO extrusion from **C**. Finally, reductive elimination affords the alkylated products **3**, regenerating the Pd(0) catalyst. It is noteworthy that even at 140 °C needed for decarbonylation, no  $\beta$ -hydride elimination occurred at all. We carefully monitored the reaction of **1a** with **2h** by the <sup>1</sup>H NMR measurement. Besides the desired coupled products, we observed several unidentified byproducts. However, only a trace of the corresponding alkenes derived from  $\beta$ -hydride elimination of alkylboron reagents was observed. The one of phosphine atoms in the hemilabile bidentate ligand DPPE might open up a coordination site for decarbonylation. While, another possible pathway cannot be ruled out; decarbonylation takes place prior to transmetalation from **A** to aryl(fluoro)palladium(II) complex. Previous DFT calculations of Pd-catalyzed decarbonylative transformations of acyl fluorides indicated that a prior decarbonylation is kinetically unfavorable due to high activation free energy barrier, which suggests that transmetalation might occur prior to decarbonylation.<sup>14,25</sup>

**Scheme 5. Proposed Mechanism**



In summary, we have developed the unprecedented palladium-catalyzed decarbonylative alkylation of acyl fluorides with various alkylboranes. We assume that palladium catalysts are much better than nickel in terms of retarding  $\beta$ -hydride elimination in this work. This method highlights good functional

group tolerance, providing a new approach to the formation of diverse  $C(sp^2)$ – $C(sp^3)$  bonds via decarbonylation. Further applications and studies of detailed mechanistic investigations are currently underway in our laboratory.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures, characterization of new compounds, and spectroscopic data (PDF)

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### Notes

The authors declare no competing financial interests.

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