



Original article

Oxygen-promoted Pd/C-catalyzed Suzuki–Miyaura reaction of potassium aryltrifluoroborates

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ABSTRACT

A simple and highly efficient protocol has been developed for the Pd/C-catalyzed ligand-free Suzuki–Miyaura reaction of potassium aryltrifluoroborates. In this catalytic system, the results demonstrate that oxygen plays a positive role in the cross-coupling reaction. In addition, this catalytic system could be successfully applied to synthesize biaryl compounds containing a carbazole moiety and the catalyst was recycled seven times without significant loss of catalytic activity.

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1. Introduction

In recent years, potassium organotrifluoroborates have been used in the Suzuki–Miyaura reaction, which is one of the most versatile and powerful methods for the carbon–carbon bond formation in the synthesis of biaryl compounds and has been widely developed for its highly efficient and green characteristics [1–4]. Nucleophilic partners of this cross-coupling reaction, the arylboronic acids are not monomeric species, but rather exist as dimeric and cyclic trimeric anhydrides [5]. Moreover, protodeboronation and homocoupling have been prone to competing with the cross-coupling process, particularly for electron-poor arylboronic acids [6,7]. Fortunately, potassium organotrifluoroborate salts offer solutions for these problems. Unlike arylboronic acids, the potassium organotrifluoroborates are monomeric solids, easily prepared from organoboronic acids or esters by the addition of inexpensive potassium hydrogen fluoride (KHF₂) [8]. With very few exceptions, potassium organotrifluoroborates show high stability toward air and water and can be stored indefinitely at room temperature without any precaution [9]. It is an ideal organoboron reagent for organic synthesis.

Significant efforts have been focused on the development of efficient systems for the Suzuki–Miyaura reaction of potassium organotrifluoroborates [10–13], but most of the reported protocols are homogeneous catalytic systems, in which the palladium catalysts are usually not recoverable, and the residual Pd metal in the product could induce serious problems. Therefore, a number of heterogeneous catalysts, which are easily separated and recycled, have come to our attention. Among them, Pd/C is one of the most common heterogeneous catalysts [14,15]. In 2009, LeBlond *et al.* reported the Pd/C-catalyzed cross-coupling of aryl halides with potassium *p*-tolyltrifluoroborate, although longer reaction time and a high loading of catalyst were required [16]. Joucla *et al.* reported a Pd/C-catalyzed approach for the vinylation of aryl halides using potassium vinyltrifluoroborates in *N*-methyl-2-pyrrolidone [17,18].

In the past several years, a series of highly efficient and ligand-free protocols for the Suzuki–Miyaura reaction of aryl boronic acids with aryl halides have been developed by our group [19–22]. In this paper, we describe a simple and efficient approach for the Pd/C-catalyzed ligand-free Suzuki–Miyaura reaction of potassium aryltrifluoroborates with aryl halides in aqueous media. This catalytic system can be successfully applied to synthesize biaryl compounds containing a carbazole moiety, which are important building blocks for the construction of advanced photoelectric materials [23,24]. Importantly, an oxygen-promoting effect was observed in the Pd/C-catalyzed Suzuki–Miyaura reaction of potassium aryltrifluoroborates.

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2. Experimental

2.1. General procedure for the Suzuki–Miyaura reaction of potassium aryltrifluoroborates

A mixture of aryl halide (0.5 mmol), potassium aryltrifluoroborate (0.6 mmol), K_2CO_3 (1.0 mmol), Pd/C (0.5 mol%), ethanol (3 mL), and distilled water (1 mL) was stirred at 80 °C in air for the indicated time. The reaction mixture was added to brine (15 mL) and extracted with ethyl acetate (4×15 mL). The organic solvent was removed under vacuum, and the product was isolated by short-column chromatography.

2.2. Recyclability tests of the Pd/C catalyst

For the first run, a mixture of 4-nitrobromobenzene (0.5 mmol), potassium 9-phenylcarbazolyltrifluoroborate (0.6 mmol), K_2CO_3 (1.0 mmol), Pd/C (1.0 mol%), ethanol (3 mL), and distilled water (1 mL) was stirred at 80 °C in air. The reaction was monitored by TLC. At the end of the reaction, the Pd/C catalyst was recovered by simple filtration, washed with chloroform and water, and dried under vacuum for the next run.

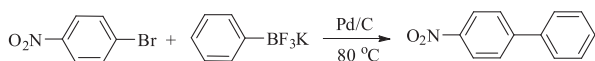
3. Results and discussion

Our group has a long standing interest in the effects of different atmospheres on the Suzuki–Miyaura reaction. Since 2007 we have found that oxygen plays a positive role in the palladium-catalyzed ligand-free Suzuki–Miyaura reaction of aryl boronic acids with aryl halides in different solvents, including polyethylene glycol, organic/water mixed solvents and pure water [4,25,26]. These results inspired us to speculate whether oxygen could also promote the Suzuki–Miyaura reaction of potassium phenyltrifluoroborates with aryl halides. Therefore, the Pd/C-catalyzed Suzuki–Miyaura reaction of 4-nitrobromobenzene with potassium phenyltrifluoroborate was performed in the different atmospheres (Table 1). The cross-coupling gave the product in 51% yield in a nitrogen atmosphere (Table 1, entry 2). However, the cross-coupling performed in air provided a 91% yield within the same reaction time, which is much faster than that in nitrogen (Table 1, entry 1). Excitingly, the same cross-coupling reaction carried out in an oxygen atmosphere was completed in 15 min (Table 1, entry 3). It is clear that oxygen promotes the Pd/C-catalyzed Suzuki–Miyaura reaction of potassium phenyltrifluoroborate under aqueous conditions. Consequently, we carried out all the reactions in air for the study.

After having optimized the reaction conditions such as solvents, bases and catalysts (see Supporting information), we further investigated the scope and limitations of substrates under the conditions of 75% aqueous ethanol as solvent, K_2CO_3 as base, Pd/C

Table 1

The effects of different atmospheres on the Pd/C-catalyzed Suzuki–Miyaura reaction of 4-nitrobromobenzene with potassium aryltrifluoroborate.^a



Entry	Atmosphere	Time (min)	Yield ^b (%)
1	Air	20	91
2	N ₂	20	51 ^c
3	O ₂	15	98

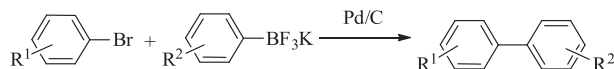
^a Reaction conditions: 4-nitrobromobenzene (0.5 mmol), potassium phenyltrifluoroborate (0.6 mmol), Pd/C (0.5 mol%), K_2CO_3 (1.0 mmol), EtOH/H₂O (3 mL/1 mL).

^b Isolated yield.

^c The EtOH and H₂O were degassed.

Table 2

The Suzuki–Miyaura reaction of aryl halides with potassium aryltrifluoroborates.^a



Entry	R ¹	R ²	Time (min)	Yield (%) ^b
1	4-CN	H	20	91
2	4-NO ₂	H	25	95
3	4-CHO	H	25	93
4	4-COCH ₃	H	30	95
5	4-OCH ₃	H	50	78
6	4-OH	H	30	91
7	4-CF ₃	4-CH ₃	27	95
8	4-CN	4-CH ₃	35	96
9	4-CN	4-OCH ₃	30	90
10	4-OCH ₃	4-OCH ₃	60	70
11	4-NO ₂	4-CH ₃	25	93
12	4-NO ₂	3-CH ₃	120	79
13	4-NO ₂	2-CH ₃	120	46
14	2-CN	H	30	94
15	2-CN	4-CH ₃	25	97

^a Reaction conditions: aryl halide (0.5 mmol), potassium aryltrifluoroborate (0.6 mmol), Pd/C (0.5 mol%), K_2CO_3 (1.0 mmol), EtOH/H₂O (3 mL/1 mL), 80 °C, in air. The reaction was monitored by TLC.

^b Isolated yield.

(0.5 mol %) as catalyst at 80 °C in air. As shown in Table 2, in general, most of the reactions gave biaryl derivatives in high yields. The electronic nature of the substituent has some influence on the reactivity of the cross-coupling reactions. It is clear that 4-substituted aryl bromides containing electron-withdrawing groups showed a slightly higher reactivity than those containing electron-donating groups, due to the effect of these substituents on the reactivity of C–Br bond (Table 2, entries 1–6). Either 4-methyl or 4-methoxy-substituted potassium phenyltrifluoroborates could complete the reactions smoothly (Table 2, entries 7–9). Increasing the steric effect could decrease the reactivity of the substrates (Table 2, entries 12 and 13). Unexpectedly, the *ortho*-substituted substrate, 2-bromobenzonitrile, reacted with potassium phenyltrifluoroborate or potassium *p*-tolyltrifluoroborate, providing the desired products in 94% and 97% yields, respectively (Table 2, entries 14 and 15).

The present protocol was also extended to the synthesis of useful nitrogen-based heterobiaryl compounds. The results are summarized in Table 3. The cross-coupling of 5-bromo-2-methoxypyridine with potassium *p*-tolyltrifluoroborate gave 5-bromo-2-phenylpyridine in a 93% yield (Table 3, entry 2). Using potassium *o*-tolyltrifluoroborate as the nucleophilic partner, the cross-coupling was completed in 120 min, providing an 86% yield (Table 3, entry 3). As for 6-substituted 2-bromopyridines, both 2-bromo-6-methoxypyridine and 2-bromo-6-fluoropyridine provided good to excellent yields of the desired products (Table 3, entries 4–6). Other nitrogen-based heterobiaryls also achieved good results (Table 3, entries 7–10), whereas 2-bromothiophene was less active and generated the product in 44% yield (Table 3, entry 11). In this heterogeneous catalytic system, the reaction between *N*-heteroaryl chloride and potassium phenyltrifluoroborate achieved a moderate yield (Table 3, entry 12).

In recent years, carbazole derivatives have been extensively used as functional building blocks for the synthesis of small molecules, oligomers or polymers, and also as host materials because of their high triplet energy and good hole-transporting ability [27,28]. In this catalytic system, a series of aryl substituted 9-phenylcarbazolyl derivatives have been successfully synthesized via the Pd/C-catalyzed Suzuki–Miyaura reaction of aryl bromides with potassium 9-phenylcarbazolyltrifluoroborate. The results presented in Table 4 show that the aryl bromides bearing

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