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Palladium-Catalyzed Amide Synthesis via Aminocarbonylation of Arylboronic Acids with Nitroarenes

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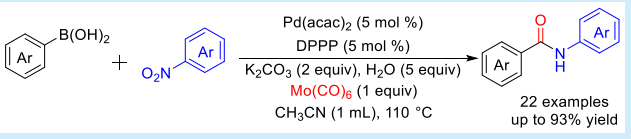
Supporting Information

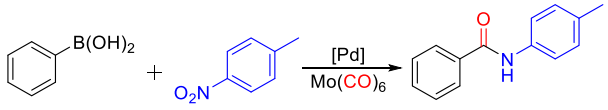
ABSTRACT: A palladium-catalyzed aminocarbonylation of aryl boronic acids with nitroarenes for the synthesis of amides has been developed. A wide range of substrates were well-tolerated and gave the corresponding amides in moderate to good yields. No external oxidant or reductant was needed in this procedure. This procedure provides a redox-economical process for the synthesis of amides.



Amide is one of the most essential structural motifs in life science and also widely exists in natural products and pharmaceutical compounds as well as organic materials.[1,2] Traditionally, amides are synthesized by the reaction between carboxylic acids and amines. Although this reaction is thermodynamically favorable, it suffers from the high activation energy due to the formation of the ammonium salt. Thus the direct amidation of acid with amine usually requires a high reaction temperature. To drive the equilibrium to the right, three strategies were usually used: (1) using an activated carboxylic acid derivative such as acid chloride or anhydride; (2) using an additional reagents such as HATU, HOBt, or PyBOP as the catalyst; and (3) transamidation with the other amides.[3] An alternative strategy for amide synthesis is the transition-metal-catalyzed aminocarbonylation of aryl halides with amines as the nucleophile.[4] Compared with amines, the direct use of nitroarenes as nitrogen sources is more attractive because nitroarenes are generally less expensive than the corresponding anilines. Several research groups, including Beller, Driver, Hu, and us, have demonstrated that nitroarenes could serve as an alternate nitrogen source in aminocarbonylation reactions.[5] For example, Hu and coworkers developed a nickel-catalyzed reductive aminocarbonylation of aryl halides with nitroarenes using $Co_2(CO)_8$ as a CO surrogate.[6] Both aryl iodides and bromides were tolerated, and a broad substrate scope had been achieved. Herein we report a new palladium-catalyzed aminocarbonylation of aryl boronic acids with nitroarenes for the synthesis of amides.[7] No external reductant or oxidant was needed in this procedure.

Initially, phenylboronic acid **1a** and 4-nitrotoluene **2a** were selected as the model substrates for this aminocarbonylation reaction. To our delight, using $Mo(CO)_6$ as a solid CO source and K_2CO_3 as the base, the desired amide **3aa** was successfully obtained in 50% yield using the $Pd(acac)_2$/DPPP catalyst system in 1,4-dioxane (Table 1, entry 1). Subsequently, a series of acidic and basic additives were tested in this reaction, and it was found that K_2CO_3 was optimal. Acidic additive PTS·H_2O resulted in a lower yield of **3aa** (Table 1, entry 2). Only a trace amount of product **3aa** was detected when another base such as Cs_2CO_3, K_3PO_4, or NEt_3 was used (see Table S1). Then, various palladium catalysts were screened for this reaction. Unfortunately, reduced yields were observed with these

Table 1. Optimization of the Reaction Conditions[a]



1a **2a** **3aa**

entry	palladium	ligand	1a/2a	solvent	yield (%)[b]
1	$Pd(acac)_2$	DPPP	1:2	dioxane	50
2[c]	$Pd(acac)_2$	DPPP	1:2	dioxane	17
3	$Pd(TFA)_2$	DPPP	1:2	dioxane	29
4	$PdCl_2$	DPPP	1:2	dioxane	18
5	$Pd(OAc)_2$	DPPP	1:2	dioxane	trace
6	$Pd(acac)_2$	DPPP	1:1.5	dioxane	17
7	$Pd(acac)_2$	DPPP	1:1	dioxane	trace
8	$Pd(acac)_2$	DPPP	1.5:1	dioxane	7
9	$Pd(acac)_2$	DPPP	2:1	dioxane	14
10[d]	$Pd(acac)_2$	DPPP	1:2	dioxane	62
11[d]	$Pd(acac)_2$	DPPP	1:2	DME	54
12[d]	$Pd(acac)_2$	DPPP	1:2	CH_3CN	74(70)[e]
13[d]	$Pd(acac)_2$	DPPF	1:2	CH_3CN	46
14[d]	$Pd(acac)_2$	DPEphos	1:2	CH_3CN	15
15[d]	$Pd(acac)_2$	Xantphos	1:2	CH_3CN	18

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (1 mmol), palladium catalyst (5 mol %), ligand (5 mol %), $Mo(CO)_6$ (1 equiv), K_2CO_3 (2 equiv), solvent (1 mL), 20 h. [b]Yields were determined by GC using dodecane as an internal standard. [c]PTS·H_2O (20 mol %) was used instead of K_2CO_3. [d]H_2O (5 equiv) was added. [e]Isolated yield. DME: dimethoxyethane.

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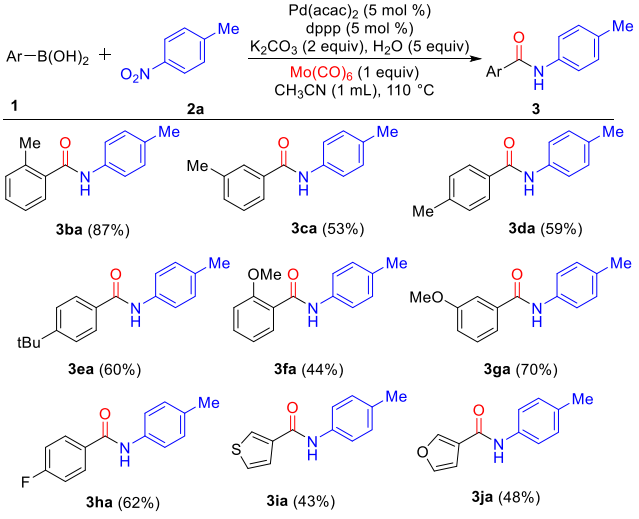
Org. Lett. XXXX, XXX, XXX–XXX

catalysts (see Table S2). When $Pd(TFA)_2$, $PdCl_2$, and $Pd(OAc)_2$ were used as the catalysts, **3aa** was obtained in 29%, 18%, and trace yields, respectively (Table 1, entries 3−5). The ratio of phenylboronic acid and nitroarene played an important role in this reaction. Reducing the amount of nitroarene to 1.5 equiv decreased the yield of **3aa** to 17% (Table 1, entry 6). Only a trace amount of **3aa** was obtained when 1 equiv of nitroarene was used (Table 1, entry 7). When excess phenylboronic acid against nitroarene was used, the amide product **3aa** could also be obtained, albeit in lower yields (Table 1, entries 8 and 9). In our experience, the addition of water usually plays a significant role in the reduction of nitroarenes because it serves as the hydrogen source.[8] Indeed, the yield of **3aa** was improved to 62% when 5 equiv of water was added in the reaction (Table 1, entry 10). Subsequently, various solvents were examined in this reaction. Ether solvent such as dimethoxyethane was effective and provided the product **3aa** in 54% yield (Table 1, entry 11). CH_3CN was found out to be the optimal solvent and produced **3aa** in 74% yield (Table 1, entry 12). Screening of the bidentate phosphine ligands revealed that DPPP was optimal. When DPPF, DPEphos, or Xantphos was used as the ligand, **3aa** was obtained in 46, 15, or 18% yield, respectively (Table 1, entries 13−15). Notably, 55% of the desired amide can still be obtained by decreasing the loading of palladium catalyst to 2 mol %.

With the optimized conditions in hand (Table 1, entry 12), we began to investigate the substrate scope of this transformation with various arylboronic acids and nitroarenes. First, as summarized in Scheme 1, we investigated the substrate

Scheme 1. Substrate Scope of Arylboronic Acids[a]

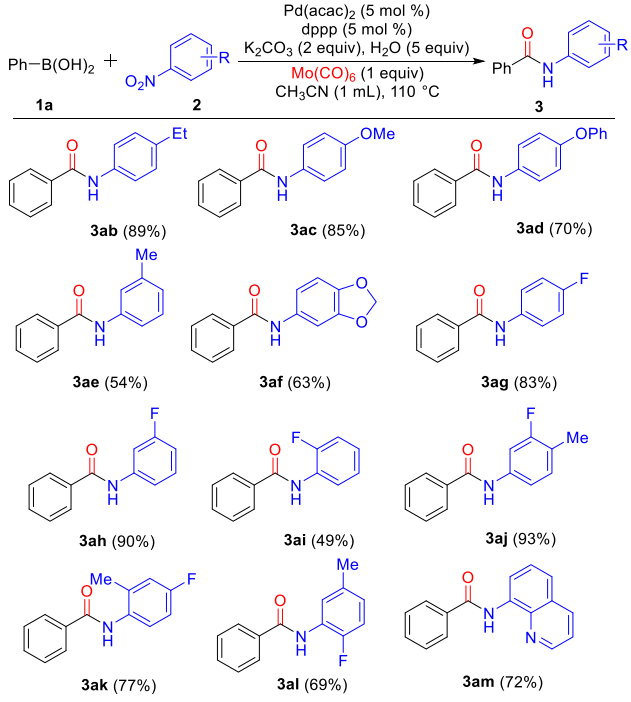


[a]Reaction conditions: arylboronic acid (0.5 mmol), 4-nitrotoluene **2a** (1 mmol), $Pd(acac)_2$ (5 mol %), DPPP (5 mol %), $Mo(CO)_6$ (1 mmol), K_2CO_3 (2 equiv), MeCN (1 mL), 110 °C, 20 h, isolated yields.

scope of the arylboronic acids. A series of different substituted phenylboronic acids were successfully applied under our standard reaction conditions, and the corresponding amides were obtained in moderate to good yield (Scheme 1, **3ba**−**ha**). Both electron-donating-group- and electron-withdrawing-group-substituted phenylboronic acids were well tolerated. Fluoride was compatible in this aminocarbonylation reaction and produced the corresponding product in 62% yield (**3ha**). In addition, heteroaryl boronic acids were also suitable substrates for this transformation. For example, thiophen-3-ylboronic acid **1i** and furan-3-ylboronic acid **1j** reacted successfully with 4-nitrotoluene **2a** and provided the corresponding products **3ia** and **3ja** in 43 and 48% yield, respectively.

Subsequently, we turned our attention to examine the generality of this aminocarbonylation reaction with respect to nitroarenes. As illustrated in Scheme 2, a range of nitro-

Scheme 2. Substrate Scope of Nitroarenes[a]



[a]Reaction conditions: phenylboronic acid **1a** (0.5 mmol), nitroarenes (1 mmol), $Pd(acac)_2$ (5 mol %), DPPP (5 mol %), $Mo(CO)_6$ (1 mmol), K_2CO_3 (2 equiv), MeCN (1 mL), 110 °C, 20 h, isolated yields.

benzenes with various substitutions at different positions of the benzene ring were applied under the optimized conditions (Table 1, entry 12). The corresponding amides were successfully prepared in moderate to good yield (Scheme 2). The electronic properties of the substituents on the benzene ring did not significantly affect the reaction yields. Both electron-donating and electron-withdrawing groups substituted nitrobenzene at the para position were well tolerated and produced the corresponding products in good to excellent yield (Scheme 2, **3ab**, **3ac**, **3ad**, and **3ag**). The steric effect of the substituents dramatically affected the yields (Scheme 2, **3ah** vs **3ai**). Moreover, this aminocarbonylation reaction also works well for nitroheteroarene. For instance, 8-nitroquinoline **2m** smoothly reacted with phenylboronic acid **1a** and produced the corresponding amide **3am** in 72% yield.

On the basis of these results and previous literature, a plausible catalytic cycle for this aminocarbonylation reaction is proposed, as shown in Scheme 3. Initially, the transmetalation of phenylboronic acid with Pd(II) gives a phenyl−palladium complex, which is transformed into an acyl−palladium intermediate after the coordination and insertion of CO

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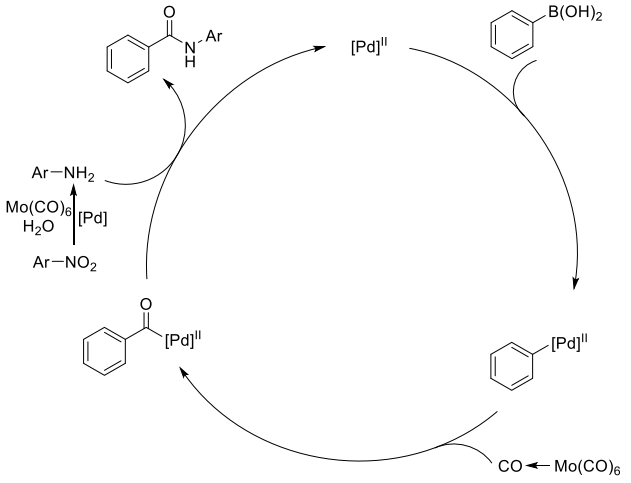
Org. Lett. XXXX, XXX, XXX−XXX

Scheme 3. Plausible Catalytic Cycle



from $Mo(CO)_6$. At the same time, the nitroarene is reduced by $Mo(CO)_6$ in the presence of water to give aromatic amine.[8] The nucleophilic attack of amine on the acyl−palladium intermediate releases the desired product and Pd(II) for the next catalytic cycle.

In summary, we have developed a palladium-catalyzed aminocarbonylation of aryl boronic acids with nitroarenes for the synthesis of amides. A range of substituted amides were prepared in moderate to good yield from easily available aryl boronic acids and nitroarenes. No external reductant or oxidant is needed in this procedure. The reaction proceeded in a CO-gas-free and redox-economic manner, where $Mo(CO)_6$ was used as a solid CO source and nitroarene was used as a cheap and abundant nitrogen source.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b01772.

General comments, general procedure, optimization details, analytic data, and NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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