Organic LETTERS

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Dioxygen-Promoted Pd-Catalyzed Aminocarbonylation of Organoboronic Acids with Amines and CO: A Direct Approach to Tertiary Amides

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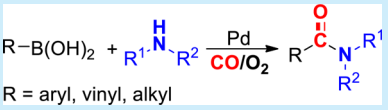
Supporting Information

ABSTRACT: A direct approach from organoboronic acids and amines to tertiary amides via Pd-catalyzed aerobic aminocarbonylation has been developed. The presence of O_2 significantly promotes the efficiency of this transformation. This method uses commercially available organoboronic acids and cheap CO and O_2 (1 atm), which renders amides an easy synthesis with broad substrate scope and high functional group tolerance.

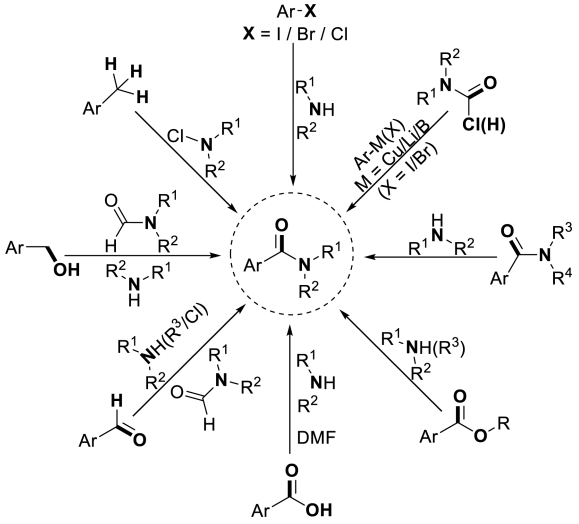


Amide is one of the most important structural motifs found ubiquitously in pharmaceuticals, natural products, insect repellents, polymers, and synthetic intermediates.[1] Traditionally, amide synthesis is the condensation of amines with carboxylic acids or amine acylation with acid derivatives, such as acyl chlorides, anhydrides, or active esters.[2] These methods, however, are limited in their applications by the need for harsh conditions and poor atom-economy. In the last few decades, many attractive approaches for the direct synthesis of tertiary amides have been developed from various starting materials, including methylarenes,[3] alcohols,[4] aldehydes,[5] carboxylic acids,[6] aryl esters,[7] carboxamides,[8] carbamoyl chlorides,[9] and aryl halides,[10] through different mechanistic processes (Scheme 1).[11] In particular, the aminocarbonylation of aryl halides with carbon monoxide (CO) and amines has been widely studied, since the three-component coupling reaction was first reported by Heck in 1974.[12] This strategy has become a powerful tool to synthesize amide, owing to the unique ability of CO serving as an excellent carbonyl group source.[13]

In light of our continuous interest in oxidative carbonylative reactions,[14] we envisioned that the aerobic oxidative aminocarbonylation of organoboronic acids would be of great interest[15] since the nontoxic organoboronic acids are air-/moisture-stable and widely commercially available.[16] Amide synthesis from organoboronates was commonly documented with carbamoyl chlorides (Scheme 2a).[9b,d,17] More recently, the approach with *N*-chloroamines generated in situ with NCS was recently achieved by Wu's group under high CO pressure (Scheme 2b).[18] In contrast, the direct aminocarbonylation of organoboronates with amines has rarely been studied. Herein, we report a simple approach to tertiary amides directly from organoboronic acids and amines with CO and O_2 (balloon) (Scheme 2c).

Initially, the aminocarbonylation of (4-methoxyphenyl) boronic acid (**1a**) with *N*-methyl-1-phenylmethanamine (**2a**) catalyzed by $[Pd(PPh_3)_2Cl_2]$ was investigated under a CO/O_2 mixture. After screening of additives and cocatalysts, the desired product *N*-benzyl-4-methoxy-*N*-methylbenzamide (**3a**) was obtained in 51% when 10 mol % of CuCl was loaded (entry 1, Table 1). We then conducted several control experiments. The reaction did not work in the absence of Pd catalyst (entry 2). CuCl cocatalyst could improve the efficiency of this transformation (cf. entries 1 and 3). As we screened the solvent, the yield increased to 61% when the reaction proceeded in DMSO (entry 4). When the reaction was exposed under pure CO atmosphere without O_2, **3aa** was still obtained in 48% yield

Scheme 1. Reported Syntheses of Tertiary Benzamides



Received: September 27, 2016

DOI: 10.1021/acs.orglett.6b02913
Org. Lett. XXXX, XXX, XXX−XXX

Scheme 2. Amide Syntheses from Organoboronic Reagents

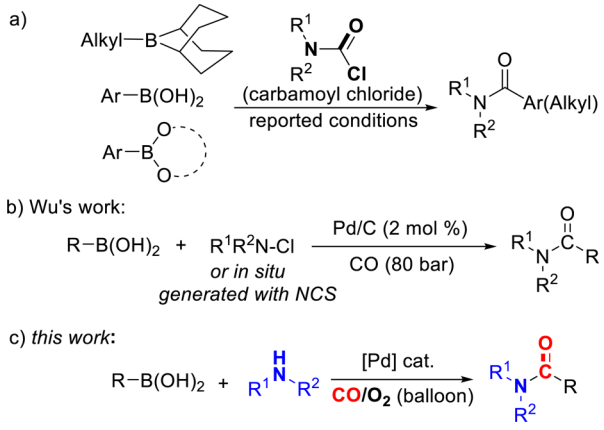
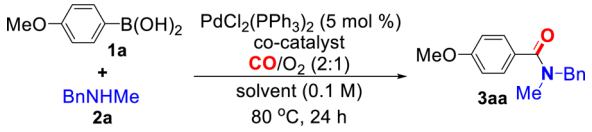


Table 1. Condition Optimization for Aminocarbonylation of Organoboronic Acid 1a[a]



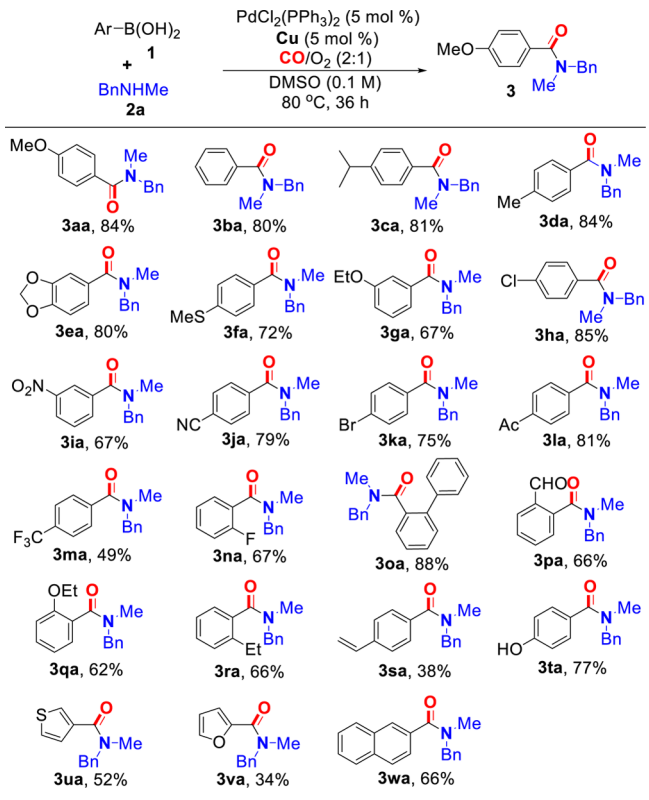
entry	cocatalyst	solvent	yield[b] (%)
1	CuCl (10 mol %)	MeCN	51
2[c]	CuCl (10 mol %)	MeCN	0
3		MeCN	37
4	CuCl (10 mol %)	DMSO	61
5[d]	CuCl (10 mol %)	DMSO	48
6	CuCl (5 mol %)	DMSO	80
7	Cu (5 mol %)	DMSO	79
8[e,f]	**Cu (5 mol %)**	**DMSO**	**84**
9[e−g]	Cu (5 mol %)	DMSO	22
10[e,f,h]	Cu (5 mol %)	DMSO	74
11[e,f]		DMSO	65

[a]Reaction conditions: **1a** (0.4 mmol), **2a** (0.44 mmol), $PdCl_2(PPh_3)_2$ (0.02 mol), CO/O_2 (2:1, balloon), 80 °C, 24 h. [b]Isolated yields. [c]Without $PdCl_2(PPh_3)_2$. [d]Under pure CO without O_2. [e]1.3 equiv of **2a** was employed. [f]Stirred for 36 h. [g]CO/Ar (2:1, balloon) was used instead of CO/O_2 (2:1, balloon). [h]CO/air (2:1, balloon) was used instead of CO/O_2 (2:1, balloon).

(entry 5). It is interesting to note that 80% of **3aa** was produced when the loading of CuCl was decreased to 5 mol % (entry 6). After screening of copper catalysts and other metal cocatalysts, the copper powder showed a similar capacity, providing benzamide **3aa** in 79% yield (entry 7). However, increasing the temperature or the volume ratio of CO/O_2 resulted in decline in yield (see the SI). Using powdered copper as the cocatalyst, 84% yield of **3aa** was obtained by employing 1.3 equiv of **2a** and prolonging the reaction time to 36 h (entry 8). It is noteworthy that the efficiency decreased significantly when the reaction was carried out under CO/Ar (2:1, balloon) instead of CO/O_2 (2:1, balloon) (cf. entries 8−10), which demonstrates that the O_2 functions not only as a gas diluting the CO concentration but also as an oxidant to promote the reaction. Considering the effect of copper powder, we also conducted a reaction in the absence of copper (entry 11), which afforded **3aa** in 65% yield.

In order to test the general applicability of this optimization, the substrate scope of organoboronic acids was investigated (Scheme 3). Phenylboronic acid (**1b**) proceeded well in this

Scheme 3. Pd-Catalyzed Aminocarbonylation of Organoboronic Acids[a]



[a]Standard conditions: **1** (0.4 mmol), **2a** (1.3 equiv), $Pd(PPh_3)Cl_2$ (0.02 mmol), Cu (0.02 mmol), CO/O_2 (2:1, balloon), DMSO (4.0 mL), 80 °C, 36 h. Isolated yields.

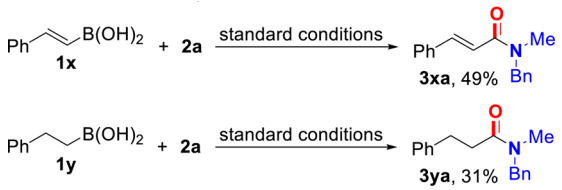
transformation, giving product **3ba** in 80% yield. Both aryl boronic acids containing electron-donating groups and electron-withdrawing groups at the aryl rings produced the desired amides in good yields (**3ca**−**ma**). Generally, the efficiencies of the electron-deficient substrates were slightly lower than those of the electron-rich substrates (**3ia**, **3ma**). The *ortho*-substituted aryl boronic acids also underwent the reaction smoothly (**3na**, **3pa**−**ra**). Additionally, a high yield was obtained when 1,1′-biphenyl-2-ylboronic acid (**1o**) was applied to this system. Some heteroaromatic substrates also performed successfully in this reaction. The yield of product from furan-2-ylboronic acid (**1v**) was found to be lower than that from thiophene-3-ylboronic acid (**1u**). To our delight, substrates with functional groups such as the nitro, cyano, bromo, formyl, vinyl, and exposed hydroxyl group were well tolerated in this protocol (**3ia**−**ka**, **3pa**, **3sa**, **3ta**), affording the corresponding amide products in moderate to high yields.

To further study the scope of this protocol, other organoboronic acids, such as vinylboronic acid and alkylboronic acid, were also investigated. Satisfactorily, the products *α,β*-unsaturated acylamide (**3xa**, Scheme 4) and alkyl acylamide (**3ya**) were also successfully obtained under the standard conditions.

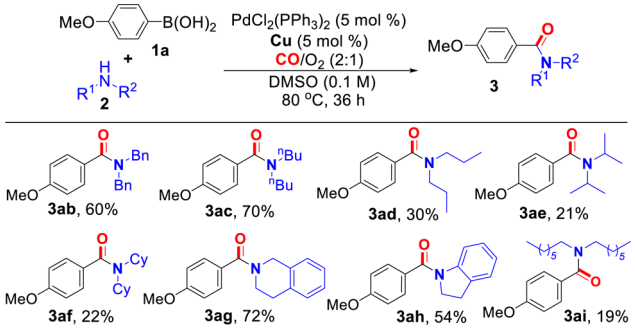
Next, we evaluated the methodology with other secondary amines (Scheme 5). Moderate yields were obtained when dibenzylamine (**2b**), alkyl secondary amine dibutylamine (**2c**), and cyclic secondary amine (**2g**) were employed as the substrates. The reactions of dipropylamine (**2d**), diisopropylamine (**2e**), dicyclohexylamine (**2f**), and even di-*n*-octylamine

DOI: 10.1021/acs.orglett.6b02913
Org. Lett. XXXX, XXX, XXX−XXX

Scheme 4. Pd-Catalyzed Aminocarbonylation of Vinylboronic Acid and Alkylboronic Acid



Scheme 5. Pd-Catalyzed Aminocarbonylation of Organoboronic Acid 1a with Different Amines[a]

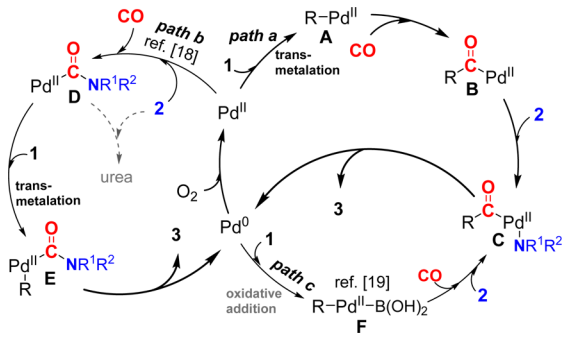


[a]Standard conditions: **1a** (0.4 mmol), **2** (1.3 equiv), $Pd(PPh_3)Cl_2$ (0.02 mmol), Cu (0.02 mmol), CO/O (2:1, balloon), DMSO (4.0 mL), 80 °C, 36 h. Isolated yields.

(**2i**) bearing long-chain alkyl groups also afforded products, respectively, though with an array of lower yields between 19 and 30%. No desired product was detected from the bidentate amine DMEDA (see the SI). Apparently, the strong coordinative amines would retard the reaction. Product was not obtained when a tertiary amine was employed as the N-partner (see the SI). Five-menbered cyclic amine indoline (**2h**) performed well to give the product **3ah** in 54% yield.

According to our previous work[14b] and the above observed results, a comprehensive mechanism is proposed in Scheme 6.

Scheme 6. Proposed Comprehensive Mechanism



Three pathways are possible: (1) Path a begins with the transmetalation of the Pd^{II} catalyst and **1** forming an arylpalladium species **A**, which provides the intermediate **B** by CO insertion. Then, the generated intermediate undergoes reductive elimination to produce the amide product **3**. (2) In some cases, trace amounts of urea products could be detected, which indicates an alternative pathway through the carbamic Pd species (**D**) that is formed by insertion of CO into N–Pd^{II} bond (path b).[19] Then, **E** is generated through transmetalation process of Pd species **D** with **1**. (3) Alternatively, the oxidative addition of arylboronic acids to Pd(0) produces **F**,[20] which subsequently undergoes CO insertion and ligand exchange with amines to form intermediate **C**. Finally, the desired product **3** is produced via the reductive elimination of **C** and **E**. The control experiments demonstrate that the presence of O_2 significantly promotes the efficiency of this transformation (entries 8–10), which suggests an aerobic oxidative process regenerating Pd(II) catalyst by O_2 to complete the catalytic circle. However, although it has been demonstrated by several techniques, such as scanning electron microscopy and X-ray diffraction analysis, that copper powder can be in situ oxidized by O_2 into active species Cu(I),[21] the function of copper in this transformation is still not completely clear.

In summary, we have developed a simple Pd-catalyzed tertiary amide synthesis from readily available organoboronic acids, amines, and CO in the presence of O_2. This method contributes to a direct access to tertiary amides with broad substrate scopes and high functional group tolerance. The use of cheap common metal catalysts under ambient pressure makes this reaction easily operated. An aerobic oxidative process is involved in this transformation. Further studies on the mechanistic details and reactions with other amines are underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02913.

Research details, experimental procedures, full characterization of products, and NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from National Basic Research Program of China (973 Program) (Grant No. 2015CB856600), National Natural Science Foundation of China (Nos. 21325206 and 21632001), the National Young Top-notch Talent Support Program, and the Peking University Health Science Center (BMU20150505) is greatly appreciated. We thank Kai Wu in this group for reproducing the results of **3ba** and **3ah**.

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DOI: 10.1021/acs.orglett.6b02913
Org. Lett. XXXX, XXX, XXX−XXX