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DOI: 10.1039/C6GC03465A

Journal Name

COMMUNICATION

Copper-catalyzed oxidative coupling reaction of arylboronic acids, amines and carbon dioxide using molecular oxygen as the oxidant

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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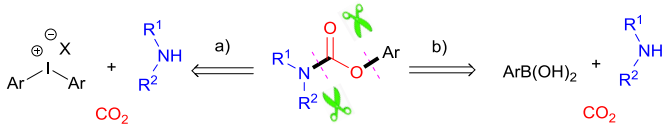
A Cu-catalyzed oxidative coupling reaction of arylboronic acids, amines and carbon dioxide is descried for the first time. The reaction tolerates a wide range of functional groups, providing a convenient protocol for the synthesis of various *O*-aryl carbamates. The successful development of the transformation was enabled by the use of $BF_3{\cdot}OEt_2$ as the promoter and molecular oxygen as the oxidant. Mechanistic studies suggested that Cu^{II} carbamato complex is involved in the catalytic transformation.

The global warming and climate challenge has motivated synthetic chemists to develop new and efficient methodologies for converting carbon dioxide (CO_2) into valuable chemicals, not only because CO_2 is the major anthropogenic greenhouse gas but also because CO_2 is a nontoxic, abundantly available and renewable C1 resource.[1]

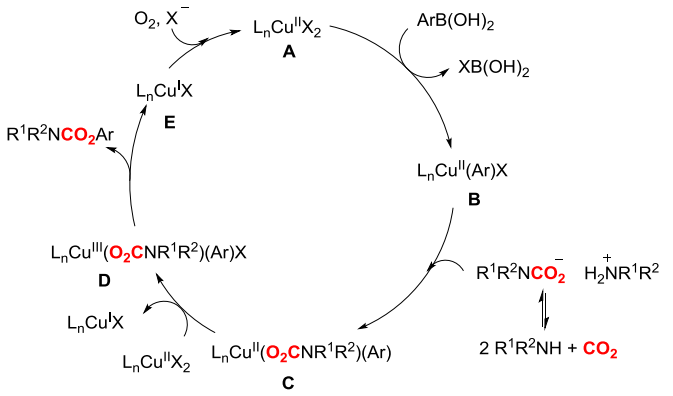
One of the promising examples in this field is the conversion of CO_2 into organic carbamates, which are ubiquitous moieties in a large number of functionalized molecules with many important applications in chemistry related fields. [2-4] While a wide variety of CO_2-based methods has been developed to access different classes of carbamates,[5] the direct synthesis of *O*-aryl carbamates from CO_2 remains outstanding challenges. The highly toxic phosgene ($COCl_2$) and its derivatives are still the basic raw materials for the production of such compounds in both laboratory preparation and industrial applications.[4d-f, 6]



Scheme 1. Strategies for the synthesis of *O*-aryl carbamates.

Only recently, we demonstrated a straightforward access to *O*-aryl carbamates via a base-promoted three-component reaction of CO_2, amines and diaryliodonium salts (Scheme 1, a).[7a] However, this transformation requires the preformation of the diaryliodonium salts and generates a stoichiometric amount of aryl iodides as the byproducts. Our continuous interest in converting CO_2 into organic carbamates[7] urged us to develop a more convenient approach to *O*-aryl carbamates via the use of easily available aryl donors while with minimal waste production.

Arylboronic acids are commercially available, comparatively stable and nontoxic compounds. Over the past decades, they have been widely used as coupling partners for the C-C bond and C-heteroatom bond forming reactions including the Pd-catalyzed Suzuki-Miyaura coupling reaction and the Cu-mediated Chan-Evans-Lam cross-coupling reaction.[8] However, to the best of our knowledge, they have not yet been applied for the assembly of *O*-aryl carbamates to date. We envisioned that a more convenient route to *O*-aryl carbamates might be achieved by a copper-catalyzed oxidative coupling between CO_2, amines and arylboronic acids (Scheme 1, b). The reaction mechanism was hypothesized in Scheme 2: the arylboronic acid initially undergoes transmetalation with complex **A** to



Scheme 2. Hypothetical new pathway for the synthesis of *O*-aryl carbamates

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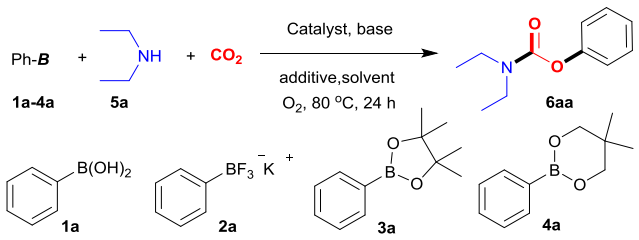
generate intermediate **B**. Then, coordination exchange of **B** with in situ generated carbamate anion gives species **C**, which would be oxidized to Cu^{III} species **D** via disproportionation. Finally, the reductive elimination of **D** affords the desired product.

With the above hypothesis in mind, we set out to examine the reaction of phenylboronic acid (**1a**), diethylamine (**5a**) and CO_2 under various conditions. Initially, the reaction was conducted in the presence of $Cu(OAc)_2$ as the catalyst and pyridine as the base under a molecular oxygen atmosphere, but only trace amount of desired product **6aa** was detected, and the amination prouduct,[8f] *N*,*N*-diethylaniline was formed as the major product (Table 1, entry 1). To our surprise, switching the catalyst to Cu_2O led to formation of **6aa** in 10% yield (entry 2). After a thorough investigation we were pleased to find that, upon addition of 3 equivalents of $BF_3{\cdot}OEt_2$ with respect to **1a**, the reaction became faster and furnished **6aa** in an excellent yield (entry 3). Control experiments showed that, besides $BF_3{\cdot}OEt_2$, Cu_2O, pyridine and molecular oxygen are all essential in affording the product (entries 4-6). Among various copper sources tested, Cu_2O was uniquely efficient in promoting the reaction (entries 3, 4, 7 and 8). In addition, replacement of $BF_3{\cdot}OEt_2$ with HBF_4 or CsF completely suppress the reaction (entries 11 and 12). Replacing pyridine with DBU, TEA or DMAP led to very poor product yields (entries 13-15), presumably because the pyridine serve as both base and ligand in the reaction. Further screenings showed that DCM was the most effective solvent (see Supporting Information, Table S1). The reaction temperature and time were also optimized and it was found that 80 °C and 24 h are optimal for the reaction (see Supporting Information, Table S2 and S3). In parallel to **1a**, other boronic acid derivatives (**2a**, **3a** and **4a**) were proven to be less effective coupling partners (entries 16-18).

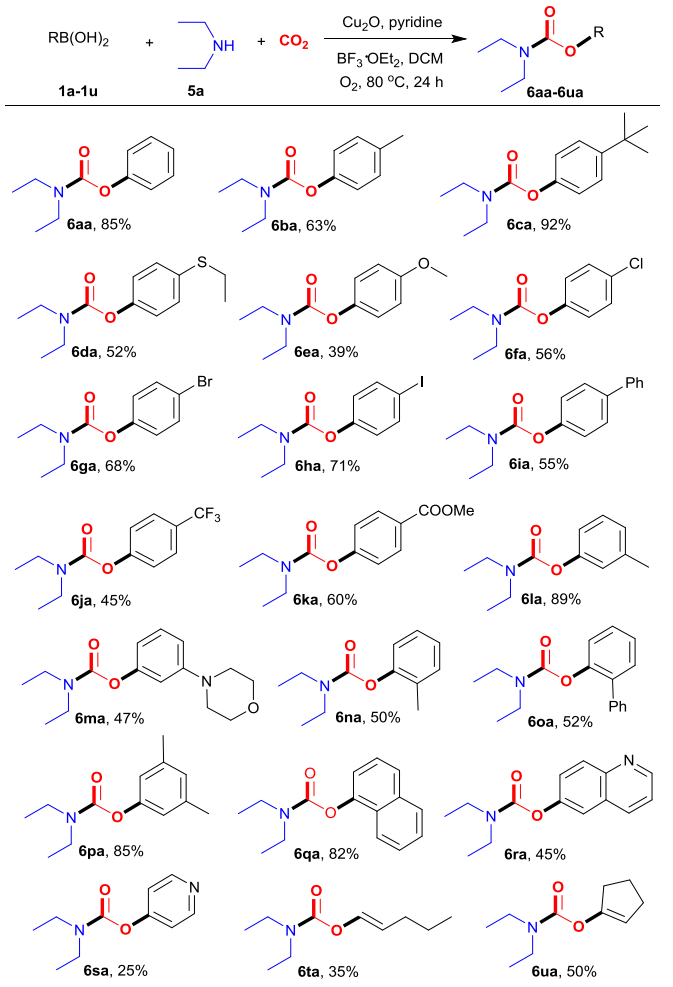
With the optimal reaction conditions in hand, we then tried to explore the generality and limitations of the protocol. First, we focused on the variation of arylboronic acids in combination with diethyl amine and CO_2. As shown in Scheme 3, all the tested arylboronic acids underwent smooth oxidative coupling reactions to furnish the *O*-aryl carbamates in moderate to excellent yields upon isolation. Both electron-donating and electron-withdrawing substituents, such as

Table 1. Optimization of Reaction Conditions.[a]



Entry	Ph-*B*	Catalyst	Base	Additive	Yield [%][b]
1	**1a**	$Cu(OAc)_2$	pyridine	-	trace[c]
2	**1a**	Cu_2O	pyridine	-	10
3	**1a**	Cu_2O	pyridine	$BF_3{\cdot}OEt_2$	91 (85)
4	**1a**	-	pyridine	$BF_3{\cdot}OEt_2$	0
5	**1a**	Cu_2O	-	$BF_3{\cdot}OEt_2$	trace
6[d]	**1a**	Cu_2O	pyridine	$BF_3{\cdot}OEt_2$	trace
7	**1a**	$Cu(OAc)_2$	pyridine	$BF_3{\cdot}OEt_2$	trace
8	**1a**	$CuCl_2$	pyridine	$BF_3{\cdot}OEt_2$	trace
9	**1a**	CuI	pyridine	$BF_3{\cdot}OEt_2$	trace
10	**1a**	CuO	pyridine	$BF_3{\cdot}OEt_2$	trace
11	**1a**	Cu_2O	pyridine	HBF_4	0
12	**1a**	Cu_2O	pyridine	CsF	0
13	**1a**	Cu_2O	DBU	$BF_3{\cdot}OEt_2$	trace
14	**1a**	Cu_2O	TEA	$BF_3{\cdot}OEt_2$	trace
15	**1a**	Cu_2O	DMAP	$BF_3{\cdot}OEt_2$	33
16	**2a**	Cu_2O	pyridine	$BF_3{\cdot}OEt_2$	37
17	**3a**	Cu_2O	pyridine	$BF_3{\cdot}OEt_2$	19
18	**4a**	Cu_2O	pyridine	$BF_3{\cdot}OEt_2$	34

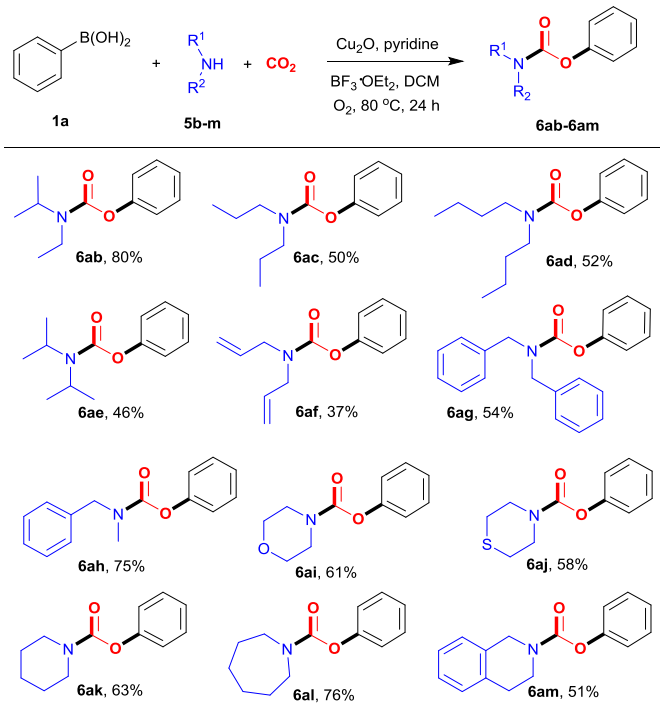
[a] Reaction conditions: organoboron reagent (0.5 mmol), **5a** (2.5 mmol), catalyst (10 mol%), base (3 equiv), additive (3 equiv), CH_2Cl_2 (3 mL), O_2 (0.4 MPa), total pressure (4.0 MPa), 80 °C, 24 h. [b] GC yield with dodecane as internal standard; number in parentheses is the yield of isolated product. [c] *N*,*N*-diethylaniline was isolated in 18% yield as the major product. [d] The reaction was carried out in the absence of molecular oxygen.



Scheme 3. Substrate scope with respect to boronic acids. Reaction conditions: **1** (0.5 mmol), **5a** (2.5 mmol), Cu_2O (10 mol%), pyridine (3 equiv), $BF_3{\cdot}OEt_2$ (3 equiv), DCM (3 mL), O_2 (0.4 MPa), total pressure (4.0 MPa), 80 °C, 24 h. Yields of the isolated products are shown.

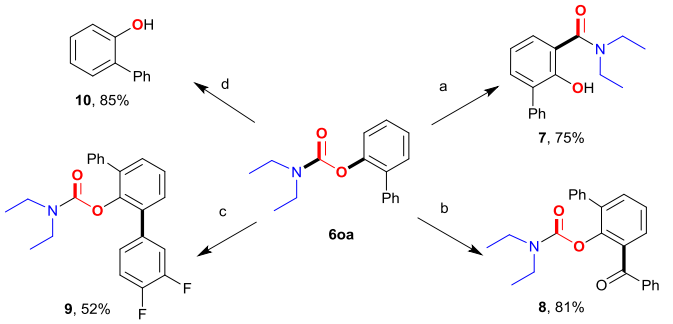
methyl, methoxy, ethylthio, ester, morpholino and trifluoromethyl, are well tolerated. Notably, products, arising from arylboronic acids bearing halogen functionalities (**1f**-**h**), would offer the potentials for elaboration of complex molecules via further transformations. *O*rtho-substituted substrates (**1n** and **1o**) gave the corresponding products (**6na** and **6oa**) in slightly lower yields than their meta- or para-substituted analogues, which are associated with the influence of steric hindrance. In addition to mono-substituted boronic acids, polysubstituted substrate **1p** and fused one **1q** also served as effective coupling partners to yield the desired products (**6pa** and **6qa**) in high yields. Moreover, heteroaryl boronic acids (**1r** and **1s**) were compatible with the transformation, albeit the yields were somewhat low. Gratifyingly, vinylboronic acids (**1t** and **1u**) were able to couple with amine **5a** and CO_2, resulting in vinyl carbamates (**6ta** and **6ua**) with retention of the stereoconfiguration of C=C bond (see **6ta**), and these products are difficult to prepare or inaccessible with the conventional methods.

Subsequently, we turned our attention to examine the amines (Scheme 4). Various acyclic secondary amines were able to give rise to the *O*-aryl carbamates (**6ab**-**6ah**) in moderate to high yields. Both the sterically hindered diisopropylamine and the unsaturated diallylamine could give the desired products (**6ae** and **6af**) albeit in lower yields. Pleasingly, the methodology was found to be suitable for the transformation of different cyclic amines, affording the products in 51-76% yields (**6ai**-**6ao**). However, when primary amine such as *n*-butylamine was employed, only trace of the desired product was detected, and *N*-butylaniline was formed as the major product via the direct amination of **1a**.[8f] Anilines did not participate in the reaction, leading to the recovery of the substrates.



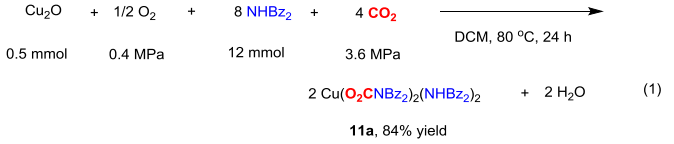
Scheme 4. Substrate scope of amines. Reaction conditions: **1a** (0.5 mmol), **5** (2.5 mmol), Cu_2O (10 mol%), pyridine (3 equiv), $BF_3{\cdot}OEt_2$ (3 equiv), DCM (3 mL), O_2 (0.4 MPa), total pressure (4.0 MPa), 80 °C, 24 h. Yields of the isolated products are shown.

To demonstrate the synthetic utility of the new protocol, product **6oa** were employed for further transformations to prepare a range of functionalized products. As shown in scheme 5, **6oa** could efficiently undergo Fries rearrangement[9] and decarboxylative acylation[10] to afford **7** and **8** in 75% and 81% yields, respectively. The Pd-catalyzed *o*-arylation of **6oa** with *o*-difluorobenzene also gave product **9** in a satisfactory yield.[4d] Moreover, the use of **10** equiv of NaOH in refluxing ethanol led to a phenol derivative upon hydrolysis.[11]

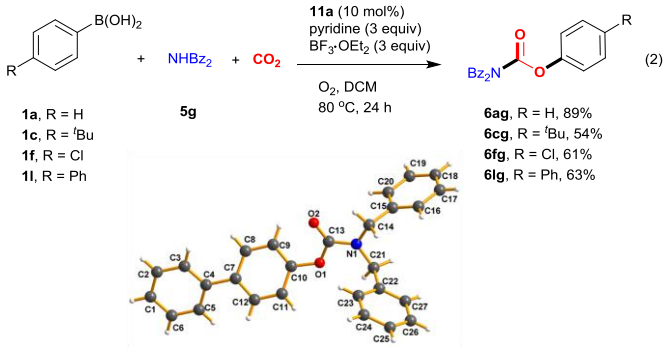


Scheme 5. Versatile transformations of the *O*-aryl Carbamate products. Reaction conditions: (a) **6oa** (0.5 mmol), LDA (1.2 equiv), THF, -78 °C to room temperature, 8 h. (b) **6oa** (0.3 mmol), $PdOAc)_2$ (5 mol%), $(NH_4)_2S_2O_8$ (0.45 mmol), TfOH (20 mol%), DCE (2 mL) in pressure tubes. (c) **6oa** (0.2 mmol), benzene (1 mL), $Pd(OAc)_2$ (10 mol%), $Na_2S_2O_8$ (10 mol %), TFA (5 equiv), 48 h. (d) **6oa** (0.5 mmol), NaOH (10 equiv), EtOH (50 ml), reflux, 8 h.

Preliminary mechanistic studies were also conducted. Initially, we treated Cu_2O with dibenzylamine and CO_2 in the presence of molecular oxygen in CH_2Cl_2 at 80 °C for 24 h. To our delight, a blue-violet Cu^{II} carbamato complex, $Cu(O_2CNBz_2)_2(NHBz_2)_2$ (**11a**), which was previously reported by Dell'Amico and co-workers, [12] was obtained in 84% yield (eq 1).

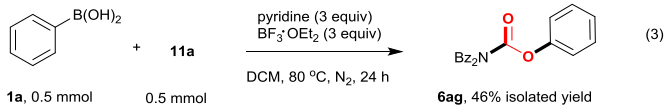


As expected, this complex was able to serve as a catalyst to facilitate the reactions of a variety of aryl boronic acids with dibenzylamine and CO_2 under the standard conditions, affording the corresponding carbamates (**6ag**-**6lg**) in moderate to high yields (eq 2). The structure of the product **6lg** was confirmed unambiguously by X-ray crystallography.[13] These results strongly suggested that carbamato complex of copper(II) of formula $Cu(O_2CNR_2)_2(NHR_2)_2$, might be formed in situ and act as the catalytically active species. It should be pointed out that in these cases, pyridine, $BF_3{\cdot}OEt_2$, and oxygen are all required for the reaction, which is consistent with the results obtained with Cu_2O as catalyst (see Supporting Information, Table S4).

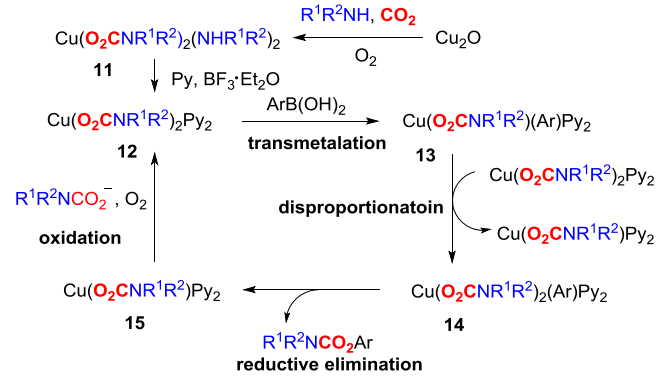


X-ray structure of **6lg**

Furthermore, although it has long been regarded that carbomato metal complexes generally exhibit no reactivity to nucleophiles,[14] we found that the stoichiometric reaction of **11a** with phenylboronic acid (**1a**) in the presence of pyridine and $BF_3{\cdot}OEt_2$ gave the desired product **6ag** in a moderate yield (eq 2), revealing that the *N,N*-dialkylcarbamato group could transfer from their metal complexes to the aryl ring of the boronic acids under our conditions. Note that the unprecedented reaction could proceed under a N_2 atmosphere. Thus, the molecular O_2 is not involved from such a complex to the terminal product.



Based on the above findings and previous reports,[5, 7-8, 15-16] a plausible catalytic cycle of the newly developed three-component reaction is proposed in Scheme 6. Initially, Cu^{II} carbamato complex **11** forms from Cu_2O, amine and CO_2 in the presence of molecular oxygen. With the assistance of $BF_3{\cdot}OEt_2$, **11** would undergo ligand exchange with pyridine to give the active Cu^{II} species **12**. Then, the transmetallation of boronic acid **1** with **12** gives species **13**. Upon a disproportionation-like process with another equivalent of **12**, a higher oxidation state Cu^{III} complex **14** is then generated. Finally, the reductive elimination of **14** would yield the carbamate product along with liberation of Cu^{I} species **15**, which is oxidized by O_2 to regenerate **12**.



Scheme 6. Proposed catalytic cycle for the Cu-catalyzed oxidative coupling of amines, CO_2 and arylboronic acids.

Conclusions

we have developed the first copper-catalyzed oxidative coupling of arylboronic acids, amines and CO_2 by using molecular O_2 as a green oxidant. The reaction provides a practical protocol for the synthesis of a wide range of functionalized *O*-aryl carbamates. The key to the success is the identification of a catalytic system involving the use of cost-effective copper(I) oxide as a pre-catalyst, $BF_3{\cdot}OEt_2$ as the promoter. Mechanistic studies suggests that a Cu^{II} complex $Cu(O_2CNR_2)_2(NHR_2)_2$ acts as the catalytically active species for the transformation. Further work focusing on product forming details and applications of the method in synthetic diversity is currently ongoing in our laboratory.

Acknowledgements

We thank the Ministry of Science and Technology of the People's Republic of China (2016YFA0602900), the National Natural Science Foundation of China (21572071 and 21420102003) and the Fundamental Research Funds for the Central Universities (2015zz038) for financial support.

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13 CCDC 1490993 (**6lg**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_reques/cif.

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View Article Online
DOI: 10.1039/C6GC03465A

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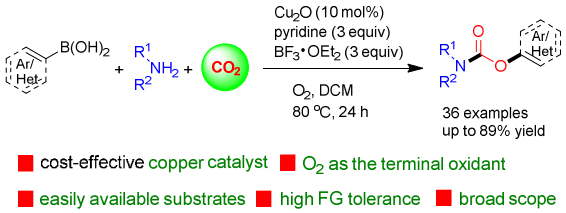

A Cu-catalyzed oxidative coupling of arylboronic acids, amines and carbon dioxide is descried, providing a route to *O*-aryl carbamates.