Cross-Coupling

International Edition: DOI: 10.1002/anie.201500074
German Edition: DOI: 10.1002/ange.201500074

Visible-Light-Mediated Chan–Lam Coupling Reactions of Aryl Boronic Acids and Aniline Derivatives**

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Abstract: *The copper(II)-catalyzed aerobic oxidative coupling reaction between aryl boronic acids and aniline derivatives was found to be improved significantly under visible-light-mediated photoredox catalysis. The substrate scope of this oxidative Chan–Lam reaction was thus expanded to include electron-deficient aryl boronic acids as viable starting materials.*

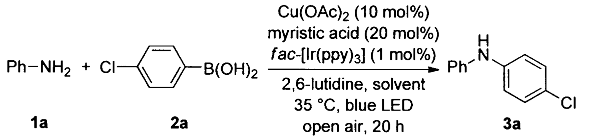
The use of sunlight as a nearly inexhaustible source of clean energy to enable sustainable organic synthesis has gained considerable attention in recent years.[1] This is, in part, due to the recognition of the synthetic potential of photoexcited metal polypyridyl complexes to act as single-electron redox mediators to activate organic substrates by oxidation or reduction and generate reactive open-shell radical intermediates that can undergo additional chemical transformations. Furthermore, the emergence of linking photoredox catalysis with other modes of catalytic activation has expanded the synthetic utility of visible-light photocatalysis, and has led to the discovery of novel reactivities and improved reaction conditions.[2,3]

Owing to their ubiquitous presence in a wide range of molecules that are important in the biological and material sciences, the construction of carbon–nitrogen bonds by transition-metal-catalyzed cross-coupling reactions represents an important area of research.[4] As such, the discovery of a mild copper-promoted cross-coupling reaction between nitrogen nucleophiles and aryl boronic acids by Chan[5] and Lam[6] has led to the rapid development of this transformation and the refinement of the original reports to include other heteroatom nucleophiles with catalytic amounts of copper salts in the presence of various oxidants.[7] Despite these advances, relatively high catalyst loadings and/or a limited substrate scope are characteristics of the Chan–Lam coupling reaction. Although not explicitly stated in the literature, our working hypothesis was that the current limitations associated with the Chan–Lam reaction are related to the difficulty in accessing the key Cu^{III} intermediate. For instance, the Cu^{II}-catalyzed aerobic coupling reaction between aniline derivatives and aryl boronic acids, which was reported by Buchwald co-workers, requires vigorous stirring in an oversized reaction vessel to obtain the *N*,*N*-diaryl amines in satisfactory yields.[8] It was assumed that these conditions facilitated the efficient oxidation of the copper intermediate by improving the oxygen uptake. Furthermore, the Chan–Lam reaction was found to be sensitive to the electronic properties of the aryl boronic acids, and aryl boronic acids bearing electron-withdrawing substituents were found to be poor substrates. This electronic effect could be rationalized by the difficulty associated with the oxidation of Cu^{II} complexes bearing electron-deficient aryl groups. In this context, we hypothesized that the productive combination of copper and photoredox catalysis could solve the problem of accessing the reactive Cu^{III} intermediate.

As part of our ongoing studies exploring the synthetic utility of visible-light photocatalysts,[9] we herein disclose an efficient aerobic coupling reaction between aniline derivatives and aryl boronic acids that is catalyzed by a copper(II) salt and an iridium-based photocatalyst under irradiation with a blue-light-emitting diode (LED).

We began our initial investigations by examining the Cu^{II}-catalyzed aerobic coupling reaction between aniline (**1a**) and 4-chlorophenylboronic acid (**2a**) using *fac*-[Ir(ppy)$_3$] (tris[2-phenylpyridinato-C^2,*N*]iridium) as the visible-light photoredox catalyst (Table 1). Gratifyingly, when the conditions

Table 1: Optimization of the *fac*-[Ir(ppy)$_3$]-assisted Cu^{II}-catalyzed Chan–Lam reaction of aniline (**1a**) and the electron-deficient aryl boronic acid **2a** under blue LED irradiation.[a]



Entry	Solvent	Yield[b] [%]
1	toluene	54
2	MeOH	54
3	DMF	31
4	$MeNO_2$	29
5	MeCN	83
6	PhCN	90
7[c]	toluene/MeCN (1:1)	>95

[a] Reaction conditions: **1a** (0.25 mmol), **2a** (0.38 mmol), $Cu(OAc)_2$ (0.025 mmol, 10 mol%), myristic acid (0.050 mmol, 20 mol%), *fac*-[Ir(ppy)$_3$] (0.0025 mmol, 1 mol%), and 2,6-lutidine (0.25 mmol) in the indicated solvent (0.5 mL) at 35 °C for 20 h in open air under blue LED irradiation. [b] Yield based on **1a** and determined by ^1H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. [c] $c = 0.25$ M.

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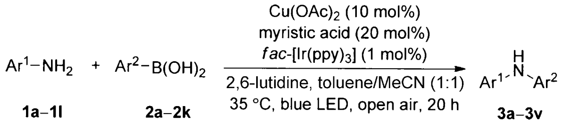
[**] This work was partially supported by a Grant-in-Aid for Science Research from the Japan Society for the Promotion of Science (JSPS), the Global COE Program (Chemistry Innovation through Cooperation of Science and Engineering), the University of Tokyo, the Japan Science and Technology Agency (JST), and the Ministry of Education, Culture, Sports, Science and Technology (MEXT, Japan).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201500074.

originally reported by Buchwald et al. were modified slightly by introducing *fac*-[Ir(ppy)$_3$]as a co-catalyst under blue LED irradiation, the desired *N*,*N*-diaryl amine **3a** was obtained in moderate yield (entry 1). By screening various solvents (entries 2–6), we found that the visible-light-mediated Chan–Lam reaction occurred efficiently in nitrile-based solvents (entries 5–6). Furthermore, because of the difficulties associated with removing benzonitrile, we re-examined the solvents and found that a 1:1 mixture of toluene and acetonitrile provided the desired product **3a** in excellent yield (entry 7). Finally, we performed control experiments and determined that the copper catalyst, the visible-light photoredox catalyst, and blue LED irradiation were all essential components of the aerobic oxidative C–N coupling reaction.[10]

With the optimized conditions in hand, we examined the substrate scope of the Cu^{II}-catalyzed aerobic coupling reaction between primary aryl amines **1a**–**1l** with electron-deficient aryl boronic acids **2a**–**2i** under visible-light-mediated photoredox conditions (Table 2). When aniline derivatives **1a**–**1d**, which bear slightly electron-donating substituents, were subjected to the Chan–Lam reaction with 4-chlorophenylboronic acid (**2a**), the desired *N*,*N*-diaryl amines **3a**–**3d** were obtained in excellent yields (entries 1–4). On the other hand, when *para*-anisidine (**1e**) was utilized as a substrate, the yield was moderate, and there was virtually no difference between the visible-light-mediated conditions and the control reaction (entry 5). Whereas the halogen-substituted aniline derivatives **1f** and **1g** proved to be excellent coupling partners for the aerobic C–N bond-forming reaction (entries 6 and 7), the more electron-deficient anilines **1h**–**1l** provided the desired products in moderate to good yields (entries 8–12). Next, we investigated different electron-deficient aryl boronic acids. We found that aryl boronic acids substituted with halogens (**2b** and **2c**) were viable substrates to furnish the *N*,*N*-diaryl amines **3m** and **3n** in good to excellent yields (entries 13 and 14). In contrast, visible-light-mediated Chan–Lam reactions with the electron-poor aryl boronic acids **2e** and **2g** were only moderately successful in most cases (entries 15–18).[11] We also examined the effect of different chlorine substitution patterns and found that the *meta*-substituted aryl boronic acid **2h** provided the desired product **3s** in modest yield (entry 19), whereas 2-chlorophenylboronic acid (**2i**) showed very poor reactivity (entry 20). Although our studies had thus far focused on Chan–Lam coupling reactions of aniline derivatives **1a**–**1l** with the electron-deficient aryl boronic acids **2a**–**2i**, we also examined the more electron-rich aryl boronic acids **2j** and **2k** and found them to be viable substrates to provide the corresponding *N*,*N*-diaryl amines **3u** and **3v** in good to excellent yields (entries 21 and 22).[12]

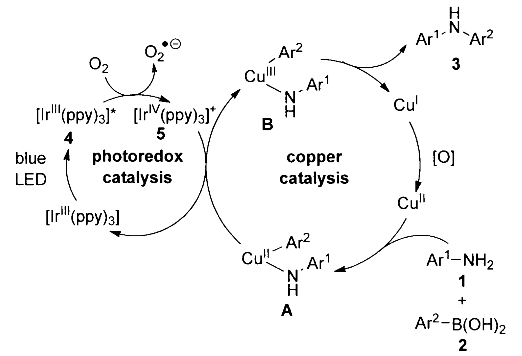
Table 2: Substrate scope for the Cu^{II}-catalyzed Chan–Lam coupling reaction of aniline derivatives **1a**–**1l** and electron-deficient aryl boronic acids **2a**–**2k** under visible-light-mediated photoredox catalysis.[a]



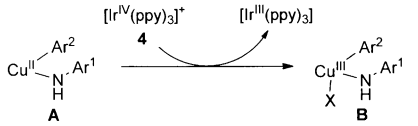
Entry	Ar^1	Ar^2	Product	Yield[b] [%]
1	Ph (**1a**)	4-Cl-C$_6$H$_4$ (**2a**)	**3a**	93 (7)
2	4-Me-C$_6$H$_4$ (**1b**)	4-Cl-C$_6$H$_4$ (**2a**)	**3b**	100 (23)
3	3-Me-C$_6$H$_4$ (**1c**)	4-Cl-C$_6$H$_4$ (**2a**)	**3c**	95 (11)
4	2-Me-C$_6$H$_4$ (**1d**)	4-Cl-C$_6$H$_4$ (**2a**)	**3d**	100 (12)
5	4-MeO-C$_6$H$_4$ (**1e**)	4-Cl-C$_6$H$_4$ (**2a**)	**3e**	43 (37)
6	4-Br-C$_6$H$_4$ (**1f**)	4-Cl-C$_6$H$_4$ (**2a**)	**3f**	91 (7)
7	4-Cl-C$_6$H$_4$ (**1g**)	4-Cl-C$_6$H$_4$ (**2a**)	**3g**	100 (9)
8	4-CN-C$_6$H$_4$ (**1h**)	4-Cl-C$_6$H$_4$ (**2a**)	**3h**	71 (15)
9	4-CO$_2$Et-C$_6$H$_4$ (**1i**)	4-Cl-C$_6$H$_4$ (**2a**)	**3i**	42 (11)
10	4-Ac-C$_6$H$_4$ (**1j**)	4-Cl-C$_6$H$_4$ (**2a**)	**3j**	47 (13)
11	4-CF$_3$-C$_6$H$_4$ (**1k**)	4-Cl-C$_6$H$_4$ (**2a**)	**3k**	72 (15)
12	3,5-Cl$_2$-C$_6$H$_3$ (**1l**)	4-Cl-C$_6$H$_4$ (**2a**)	**3l**	55 (10)
13	Ph (**1a**)	4-F-C$_6$H$_4$ (**2b**)	**3m**	79 (12)
14	Ph (**1a**)	4-Br-C$_6$H$_4$ (**2c**)	**3n**	89 (12)
15	Ph (**1a**)	4-CF$_3$-C$_6$H$_4$ (**2d**)	**3o**	85 (19)
16	Ph (**1a**)	4-CN-C$_6$H$_4$ (**2e**)	**3p**	43 (5)
17	Ph (**1a**)	4-Ac-C$_6$H$_4$ (**2f**)	**3q**	47 (18)
18	Ph (**1a**)	4-CO$_2$Me-C$_6$H$_4$ (**2g**)	**3r**	62 (19)
19	Ph (**1a**)	3-Cl-C$_6$H$_4$ (**2h**)	**3s**	65 (17)
20	Ph (**1a**)	2-Cl-C$_6$H$_4$ (**2i**)	**3t**	<5 (<2)
21[c]	Ph (**1a**)	Ph (**2j**)	**3u**	100[12]
22[c]	Ph (**1a**)	4-MeO-C$_6$H$_4$ (**2k**)	**3v**	76 (70)[8]

[a] Reaction conditions: **1** (0.25 mmol), **2** (0.38 mmol), Cu(OAc)$_2$ (0.025 mmol, 10 mol%), myristic acid (0.050 mmol, 20 mol%), *fac*-[Ir(ppy)$_3$] (0.0025 mmol, 1 mol%), 2,6-lutidine (0.25 mmol), toluene/MeCN (1:1, 1.0 mL), 35 °C, 20 h, open air, blue LED irradiation. [b] Yield of isolated products **3a**–**3v** based on the amounts of **1a**–**1l**. Yields shown in parentheses are of the isolated products **3a**–**3t** for the reactions performed in the absence of *fac*-[Ir(ppy)$_3$] and blue LED irradiation. [c] Using 5 mol% of Cu(OAc)$_2$ and 10 mol% of myristic acid.

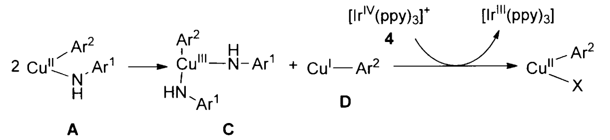
A tentative mechanism for the *fac*-[Ir(ppy)$_3$]-catalyzed Chan–Lam coupling reaction of aromatic amines **1** and aryl boronic acids **2** under blue LED irradiation is shown in Scheme 1.[13] Initially, the Cu catalyst could undergo ligand exchange and transmetalation with aromatic amine **1** and aryl boronic acid **2** to generate Cu amide **A**. Concurrently, a light-induced metal-to-ligand charge transfer of *fac*-[Ir(ppy)$_3$] would result in the formation of photoexcited complex **4** ($E_{1/2}{}^{IV/*III} = -1.73$ V vs. SCE),[1e] which could be oxidatively quenched with O$_2$ ($E_{1/2red} = -0.92$ V vs. SCE)[14] to produce the oxidizing Ir complex **5** and generate superoxide.[15] Based on our working hypothesis, this single-electron oxidant could facilitate the oxidation of Cu amide **A** to the key Cu^{III} intermediate **B**,[16] which regenerates the *fac*-[Ir(ppy)$_3$] to complete the photoredox catalytic cycle. Reductive elimination of **B** would furnish the desired cross-coupling product **3** and a Cu^I salt, which, upon oxidation by air, would regenerate the Cu^{II} catalyst to complete the Cu catalytic cycle. Two potential pathways to access the reactive Cu^{III} intermediate **B** through single-electron oxidation by a photoexcited [Ir(ppy)$_3$] complex can be considered. In the first case, the direct oxidation of Cu^{II} amide **A** by either the photoexcited [Ir(ppy)$_3$]* **4** ($E_{1/2}{}^{*III/II} = 0.31$ V vs. SCE) or the oxidatively quenched [Ir(ppy)$_3$]$^+$ **5** ($E_{1/2}{}^{IV/III} = 0.77$ V vs. SCE)[1e] is possible to generate the key Cu^{III} intermediate **B**. Conversely,



Direct oxidation of Cu^{II} by photoexcited [Ir(ppy)$_3$]



Regeneration of Cu^{II} by photoexcited [Ir(ppy)$_3$]



Scheme 1. Proposed reaction mechanism for the visible-light-mediated Chan–Lam coupling reaction of aniline derivatives **1** with aryl boronic acids **2**.

two equivalents of **A** may undergo a redox disproportionation reaction[15] to generate Cu^{III} amide **C** and aryl Cu^{I} species **D**, which could be re-oxidized to Cu^{II} by the photoexcited [Ir(ppy)$_3$] complex. Although experimental evidence to determine which of these two scenarios is operating has yet to be obtained, the pathway involving re-oxidation of the Cu^{I} species ($E_{1/2}^{II/I} \approx 0.32$ V vs. Fc$^+$/Fc)[17] is more likely as the iridium complexes used in this study are relatively weak single-electron oxidants.

Finally, although our proposed mechanism assumes that an oxidatively quenched photocatalyst is responsible for the key oxidation step, an alternative oxidant could be singlet oxygen ($^1O_2$) produced by photosensitization with the triplet excited state of *fac*-[Ir(ppy)$_3$].[18] However, the introduction of various known chemical traps for $^1O_2$ did not significantly hinder the visible-light-mediated Chan–Lam reaction in most cases.[19]

In conclusion, a modified procedure for the copper-catalyzed Chan–Lam reaction of aniline derivatives and aryl boronic acids was developed. Through the productive merger of copper and photoredox catalysis, the substrate scope of this oxidative coupling reaction was expanded to include electron-deficient aryl boronic acids as viable starting materials. Further studies on the mechanism of this visible-light-mediated process and the utility of photoexcited metal polypyridyl complexes as redox mediators for efficient transition-metal-catalyzed cross-coupling reactions are currently underway.

Experimental Section

Typical procedure for the Cu^{II}-catalyzed aerobic coupling reactions of aniline derivatives **1a**–**1l** with aryl boronic acids **2a**–**2i** under visible-light photoredox catalysis: *fac*-[Ir(ppy)$_3$] (0.0017 g, 0.0026 mmol, 1 mol %), Cu(OAc)$_2$ (0.0048 g, 0.026 mmol, 10 mol %), myristic acid (0.0120 g, 0.053 mmol, 20 mol %), aryl boronic acid **2a** (0.0586 g, 0.375 mmol), aniline derivative **1a** (24 μL, 0.263 mmol), 2,6-lutidine (31 μL, 0.268 mmol), and toluene/MeCN (1:1, 1 mL) were added to a 2 mL screw-cap vial. The vial was closed with a cap with a small puncture, and the reaction mixture was stirred for 20 h under blue LED irradiation (owing to the heat generated by the LED lamp, the ambient temperature became 35 °C). Next, the crude reaction mixture was passed through a plug of silica gel, concentrated under reduced pressure, and the resulting organic residue was purified by preparative thin-layer chromatography (EtOAc/*n*-hexane 1:4) to afford *N*,*N*-diaryl amine **3a** (0.0499 g, 0.245 mmol, 93 %) as a light-brown solid.

Keywords: C–N coupling · copper catalysis · cross-coupling · oxidation · photocatalysis

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[10] For additional data pertaining to the optimization studies and control experiments, see the Supporting Information.

[11] The effectiveness of the visible-light-mediated Chan–Lam reaction does not seem to completely reflect the strength of the electron-withdrawing ability of the substituents on the aryl boronic acids. Other factors, such as functional-group incompatibility, may skew the results to some degree, but do not affect the overall trend.

[12] As the yields obtained for **3u** and **3v** through the visible-light-mediated Chan–Lam reaction are similar to those in the original report by Buchwald and Antilla (Ref. [8]), from a practical point of view, the Buchwald conditions are superior. On the other hand, it was found that the Chan–Lam reaction of aniline (**1a**) and phenyl boronic acid (**2j**) using only 1 mol% of $Cu(OAc)_2$ and 2 mol% of myristic acid provided only trace amounts of **3u**, whereas the addition of 1 mol% of $[Ir(ppy)_3]$ under blue LED irradiation provided **3u** in 59% yield.

[13] Emission quenching experiments were conducted, and it was revealed that a $Cu(OAc)_2$/myristic acid complex, air, and *N,N*-diaryl amine **3a** could act as quenchers of photoexcited $[Ir(ppy)_3]$. This would suggest a more complex catalytic cycle. However, control studies strongly suggest that the quenching of $Cu(OAc)_2$ and **3a** are non-productive processes. For discussions of the control experiments and the Stern–Volmer plots, see the Supporting information.

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[19] At this stage, we cannot rule out the possibility that $^1O_2$ plays a role in the visible-light-mediated Chan–Lam reaction as the yields of *N,N*-diaryl amine **3a** were lower in the presence of organic substrates that are known to react with $^1O_2$. For detailed experimental results, see the Supporting Information.

Received: January 5, 2015

Communications

Cross-Coupling

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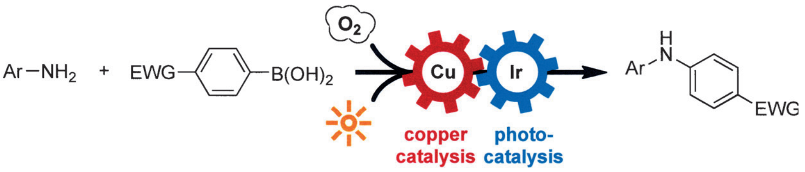
Visible-Light-Mediated Chan–Lam Coupling Reactions of Aryl Boronic Acids and Aniline Derivatives



Two are better than one: The copper(II)-catalyzed aerobic oxidative coupling reaction between aryl boronic acids and anilines is significantly improved by the addition of visible-light-mediated photoredox catalysts. The substrate scope of this Chan–Lam reaction was thus expanded to include electron-deficient aryl boronic acids.