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Visible-Light Photoredox Borylation of Aryl Halides and Subsequent Aerobic Oxidative Hydroxylation

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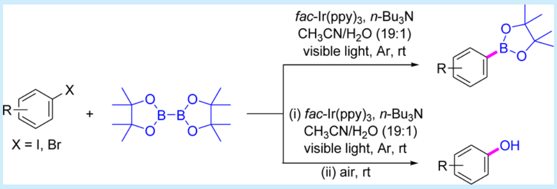
Supporting Information

ABSTRACT: Efficient and practical visible-light photoredox borylation of aryl halides and subsequent aerobic oxidative hydroxylation were developed. The protocols use readily available aryl halides and bis(pinacolato)diboron as the starting materials, *fac*-Ir(ppy)$_3$ as the photocatalyst, and corresponding arylboronic esters and phenols were obtained in good yields. The methods show some advantages including simple equipment, mild conditions, easy operation, and wide substrate scope. Therefore, they should provide a valuable strategy for chemical transformations.



Arylboronic acids and esters are important building blocks for the formation of aryl carbon−carbon or carbon−heteroatom bonds.[1] Traditional synthetic methods use couplings of arylmetallic intermediates with trialkyl borates, followed by transesterification or hydrolysis. Some drawbacks include limited functional group tolerance and anhydrous conditions.[2] Recently, transition-metal-catalyzed borylation of aryl halides was a popular strategy, and some efficient methods were built to convert aryl C−X bonds to C−B bonds.[3] Several transition-metal-free borylations of aryl halides were also established.[4] More interestingly, direct C−H borylation in the presence[5] or absence[6] of transition metals was presented. In addition, aromatic nitrogen-containing compounds such as amines,[7] diazonium salts,[8] and aryl triazenes[9] are also used as starting materials to prepare arylboronic acid derivatives. Although these methods are useful, the limited substrates, harsh conditions, special additives, and/or longer times are usually observed. Recently, photoinduced chemical transformations with UV[10] and visible light[11] have emerged as a powerful activation protocol, and some interesting reactions have been developed via photoinduced aryl carbon−halogen bond dissociation.[12,13] Very recently, several groups reported metal-free UV photoinduced borylation of haloarenes,[14] in which specialized equipment was required. Distinctly, it is more convenient and practical to use domestic light sources and standard laboratory glassware in visible-light photocatalysis, and the electron transfer between the catalysts and substrates upon photoexcitation makes a reaction milder than the analogous energy-transfer characteristics of UV photochemistry.[15] Recently, eosin-Y-catalyzed borylation of aryldiazonium salts under irradiation of visible light was developed.[16] Furthermore, synthesis of phenols from arylboronic acids has been well-developed.[17] Recently, two groups independently described visible-light-induced aerobic oxidative hydroxylation of arylboronic acids under [Ru(bpy)$_3$Cl$_2$]·6H$_2$O[18a] or methylene blue catalysis.[18b] As our continuing study on visible-light photoredox catalysis,[19] we report an efficient and practical visible-light photoredox borylation of aryl halides and subsequent aerobic oxidative hydroxylation.

First, visible-light photoredox borylation of 1-iodo-4-methoxybenzene (**1e**) with 1.5 equiv of bis(pinacolato)diboron (**2**) was selected as the model to optimize conditions including photocatalysts, additives, solvents, time, and amount of reactants. As shown in Table 1, three transition-metal photocatalysts, *fac*-Ir(ppy)$_3$ (**A**), [Ir(ppy)$_2$](dtbbpy)PF$_6$ (**B**), and[Ru(bpy)$_3$]Cl$_2$ (**C**), were screened using 2.0 equiv of ^{n}Bu$_3$N as the additive and MeCN as the solvent under Ar atmosphere and irradiation of visible light with 23 W compact fluorescent light (CFL) for 24 h (entries 1−3), and *fac*-Ir(ppy)$_3$ provided the highest yield (entry 1). No reaction was observed in the absence of ^{n}Bu$_3$N (entry 4). Yields increased when the amount of ^{n}Bu$_3$N was increased (entries 5 and 6). Reaction in a mixed solvent of MeCN and water led to higher yields (entries 7 and 8). When 2.0 equiv of **2** was used, an 89% yield was afforded (entry 9). Methanol was not a suitable solvent (entry 10). Yield decreased when the time was shortened (compare entries 9, 11, and 12). We attempted Et$_3$N and diisopropylethylamine (DIPEA) as additives, and they provided lower yields (entries 13 and 14). No reaction occurred in the absence of light (entry 15).

With optimized visible-light photoredox conditions, the substrate scope for borylation of **1** with **2** was surveyed. As shown in Table 2, aryl iodides displayed reactivity higher than that of aryl bromides. Note that electron effects on the aryl iodides did not show obvious difference in reactivity, but aryl bromides containing electron-withdrawing groups exhibited higher reactivity than those containing electron-donating groups. Halonaphthalenes and 4-halobiphenyl were good substrates (**3q−s**). Reaction of 1,4-dibromobenzene with 4.0 equiv of **2** provided bisborylating product **3t** in 70% yield. The visible-light photoredox borylation displayed tolerance of various functional

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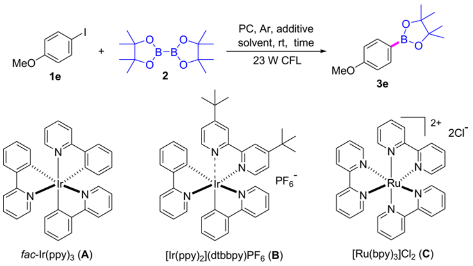
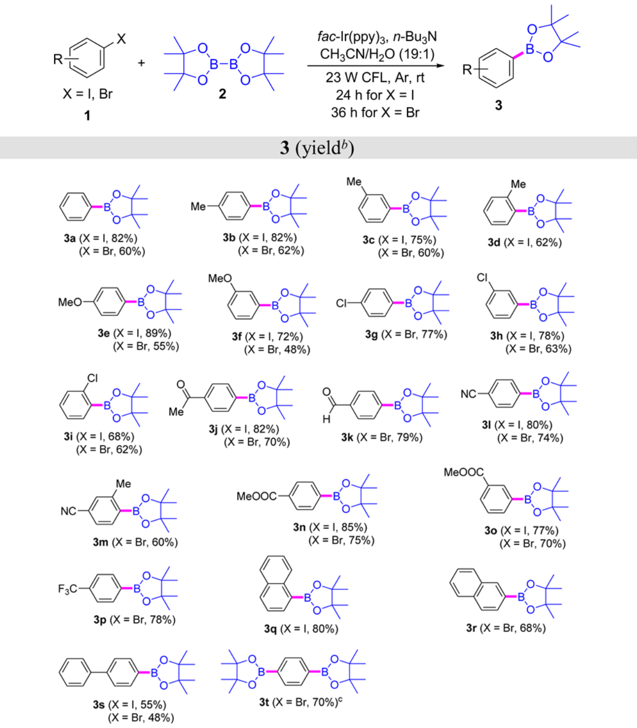
Table 1. Optimization of Conditions for Visible-Light Photoredox Borylation of 1e with 2[a]



entry	PC	additive (equiv)	solvent	time (h)	yield (%)[b]
1[c]	**A**	$^{n}Bu_3N$ (2)	MeCN	24	25
2[c]	**B**	$^{n}Bu_3N$ (2)	MeCN	24	6
3[c]	**C**	$^{n}Bu_3N$ (2)	MeCN	24	trace
4[c]		$^{n}Bu_3N$ (2)	MeCN	24	NR
5[c]	**A**	$^{n}Bu_3N$ (4)	MeCN	24	32
6[c]	**A**	$^{n}Bu_3N$ (5)	MeCN	24	44
7[c]	**A**	$^{n}Bu_3N$ (5)	MeCN/H_2O (9:1)	24	72
8[c]	**A**	$^{n}Bu_3N$ (5)	MeCN/H_2O (19:1)	24	80
9[d]	**A**	$^{n}Bu_3N$ (5)	MeCN/H_2O (19:1)	24	89
10[d]	**A**	$^{n}Bu_3N$ (5)	CH_3OH	24	62
11[d]	**A**	$^{n}Bu_3N$ (5)	MeCN/H_2O (19:1)	12	76
12[d]	**A**	$^{n}Bu_3N$ (5)	MeCN/H_2O (19:1)	36	89
13[d]	**A**	NEt_3 (5)	MeCN/H_2O (19:1)	24	58
14[d]	**A**	DIPEA (5)	MeCN/H_2O (19:1)	24	60
15[d,e]	**A**	$^{n}Bu_3N$ (5)	MeCN/H_2O (19:1)	24	NR

[a] Reaction conditions: Ar atmosphere and visible-light irradiation, **1e** (0.2 mmol), photocatalyst (PC) (2.0 μmol), additive (0.4−1.0 mmol), solvent (2.0 mL), rt (~25 °C), 12−36 h in a sealed Schlenk tube. [b] Isolated yield. [c] 0.3 mmol of **2**. [d] 0.4 mmol of **2**. [e] No light. NR = No reaction.

Table 2. Substrate Scope for Visible-Light Photoredox Borylation of 1 with 2[a]



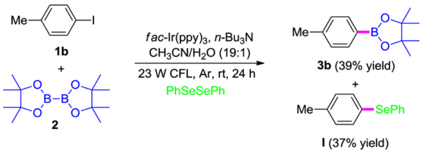
[a] Reaction conditions: Ar atmosphere and visible-light irradiation 23 W CFL, **1** (0.2 mmol), **2** (0.4 mmol), *fac*-Ir(ppy)$_3$ (2.0 μmol), $^{n}Bu_3N$ (1.0 mmol), MeCN (1.9 mL), H_2O (0.1 mL), rt (~25 °C), 24 or 36 h in a sealed Schlenk tube. [b] Isolated yields. [c] 0.8 mmol of **2**.

groups including ethers (**3e,f**), C−Cl bond (**3g−i**), ketone (**3j**), aldehyde (**3k**), nitriles (**3l,m**), esters (**3n,o**), and CF_3 (**3p**).

To disclose the mechanism for the borylation of aryl halides, reaction of **1e** with **2** in the presence of diphenyl diselenide was performed under the standard conditions, and **3b** and **I** were obtained in 39 and 37% yields, respectively (Scheme 1). The experiment showed that the aryl radical was generated during the reaction. Furthermore, electron spin resonance (ESR) spectra of various mixtures were recorded under visible-light irradiation (λ > 420 nm) using 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) as the radical trapping agent (Figure 1). (a) When treatment of iodobenzene (**1a**) (50 mM), *fac*-Ir(ppy)$_3$ (1 mol %), tributylamine (TBA) (50 mM), **2** (50 mM), and DMPO (100 mM) was performed, two groups of radical signals were observed as follows: a sextet peak signal (marking with the stars) with a *g* value of 2.003, AN = 1.46 mT, AH = 2.15 mT corresponding to a carbon-centered radical, and the other quartet peak signal (marked with triangles) with a *g* value of 2.002, AN = 1.35 mT, AH = 1.49 mT corresponding to a nitrogen-centered radical (Figure 1a). (b) Only weak radical signals were observed in the absence of **2** (Figure 1b), which displayed that **2** could promote formation of radicals. (c) No radical signal was observed in the absence of **1a** (Figure 1c), and the experiment showed that aryl halide was an electron acceptor. (d) A result similar to that in Figure 1c was found without addition of TBA (Figure 1d), which indicated that TBA was a radical initiator.

A possible mechanism for the visible-light photoredox borylation of aryl halides is proposed in Scheme 2 according to the results above. Treatment of **2** with water in the presence of TBA (n-Bu_3N) leads to **A** and **B**.[14b] Irradiation of photocatalyst

Scheme 1. Control Experiment in the Presence of PhSeSePh for Mechanism Investigation



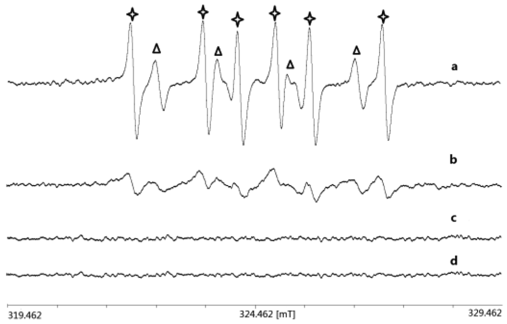


Figure 1. ESR spectra of various mixtures under irradiation of visible light for 6 min: (a) mixture of **1a** (50 mM), *fac*-Ir(ppy)$_3$ (1 mol %), TBA (50 mM), **2** (50 mM), and DMPO (100 mM) in CH_3CN; (b) mixture of **1a** (50 mM), [*fac*-Ir(ppy)$_3$] (1 mol %), TBA (50 mM), and DMPO (100 mM) in CH_3CN; (c) mixture of TBA (50 mM), *fac*-Ir(ppy)$_3$ (1 mol %), **2** (50 mM), and DMPO (100 mM) in CH_3CN; (d) mixture of **1a** (50 mM), *fac*-Ir(ppy)$_3$ (1 mol %), **2** (50 mM), and DMPO (100 mM) in CH_3CN.

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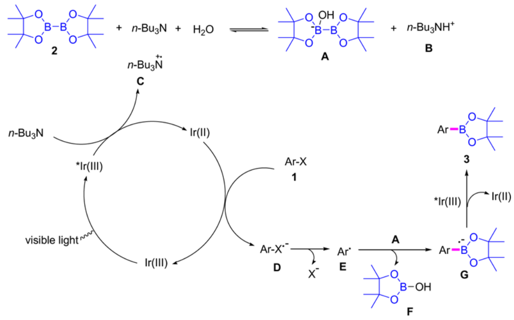
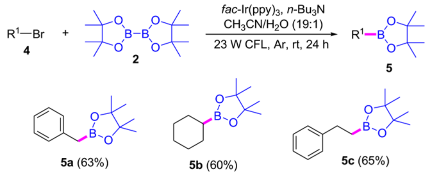
Scheme 2. Proposed Mechanism for Visible-Light Photoredox Borylation of Aryl Halides (4) with 2



Ir(III) with visible light gives the excited-state *Ir(III), and a single-electron transfer of *n*-Bu$_3$N to *Ir(III) provides Ir(II) leaving **C**. Reaction of Ir(II) with aryl halide (**1**) donates radical anion **D**, regenerating photocatalyst Ir(III). Desorption of halogen anion (X$^-$) from **D** gives aryl radical **E**, and treatment of **E** with **A** affords radical anion **G**. Finally, one single-electron transfer of **G** to *Ir(III) provides the target product (**3**) and Ir(II).

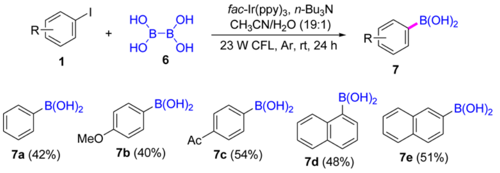
Inspired by the excellent results above, we extended the substrate scope to alkyl bromides. As shown in Scheme 3, reaction of alkyl bromides with **2** under the standard conditions provides alkylboronic esters in moderate yields. We also attempted reaction of aryl iodides with bisboronic acid (**6**), and the corresponding arylboronic acids were obtained (Scheme 4). Unfortunately, the reaction was inferior to the borylation of aryl halides using **2** as the borylating agent.

Scheme 3. Visible-Light Photoredox Borylation of 4 with 2



5a (63%) **5b** (60%) **5c** (65%)

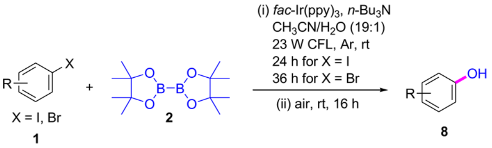
Scheme 4. Visible-Light Photoredox Borylation of 1 with 6



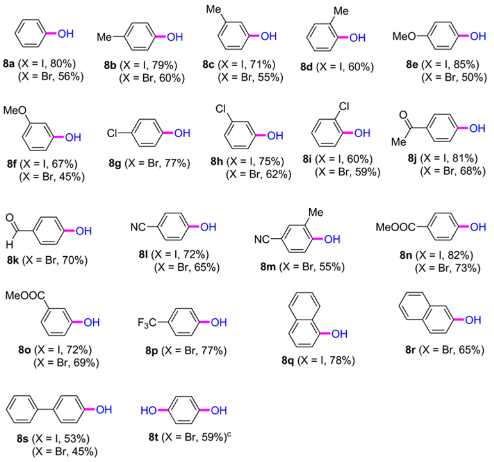
7a (42%) **7b** (40%) **7c** (54%) **7d** (48%) **7e** (51%)

In 2012, photoredox-catalyzed oxidation of boronic acids and esters was described.[18a] As shown in Table 3, we investigated one-pot, two-step, visible-light photoredox synthesis of phenols from **1**, including borylation of aryl halides and hydroxylation of arylboronic esters. For borylation of aryl halides, the visible-light photoredox catalytic conditions were the same as those in Table 2. When the borylation of aryl halides was complete, the sealed Schlenk tube was opened, and the subsequent aerobic oxidative hydroxylation of arylboronic esters for 16 h provided the corresponding phenols with various functional groups. The mechanism is similar to that in previous literature.[18] Therefore, it is easy to make phenols using **1** and **2** as the starting materials.

Table 3. Substrate Scope for One-Pot, Two-Step, Visible-Light Photoredox Synthesis of Phenols from 1[a]



8 (yield[b])



8a (X = I, 80%) (X = Br, 56%)
8b (X = I, 79%) (X = Br, 60%)
8c (X = I, 71%) (X = Br, 55%)
8d (X = I, 60%)
8e (X = I, 85%) (X = Br, 50%)
8f (X = I, 67%) (X = Br, 45%)
8g (X = Br, 77%)
8h (X = I, 75%) (X = Br, 62%)
8i (X = I, 60%) (X = Br, 59%)
8j (X = I, 81%) (X = Br, 68%)
8k (X = Br, 70%)
8l (X = I, 72%) (X = Br, 65%)
8m (X = Br, 55%)
8n (X = I, 82%) (X = Br, 73%)
8o (X = I, 72%) (X = Br, 69%)
8p (X = Br, 77%)
8q (X = I, 78%)
8r (X = Br, 65%)
8s (X = I, 53%) (X = Br, 45%)
8t (X = Br, 59%)[c]

[a] Reaction conditions: Ar atmosphere and visible-light irradiation with 23 W CFL, **1** (0.2 mmol), **2** (0.4 mmol), *fac*-Ir(ppy)$_3$ (2.0 μmol), N^{n}Bu$_3$ (1.0 mmol), MeCN (1.9 mL), H$_2$O (0.1 mL), rt (~25 °C), same borylation time as in Table 2 in a sealed Schlenk tube; 16 h in an opened Schlenk tube. [b] Isolated yields. [c] 0.8 mmol of **2**.

In summary, we have developed an efficient and practical visible-light photoredox borylation of aryl halides with bis(pinacolato)diboron under catalysis of *fac*-Ir(ppy)$_3$, and the subsequent aerobic oxidative hydroxylation of the obtained arylboronic esters in air provided various phenols. Reactions were performed at room temperature and exhibited good functional group tolerance. Therefore, the present methods show some advantages for the synthesis of arylboronic esters and phenols. We believe that the novel discovery will find wide applications in some fields.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02553.

Experimental details and figures (PDF)

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Notes

The authors declare no competing financial interest.

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