Photoinduced Divergent Deaminative Borylation and Hydrodeamination of Primary Aromatic Amines

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Photoinduced Divergent Deaminative Borylation and Hydrodeamination of Primary Aromatic Amines

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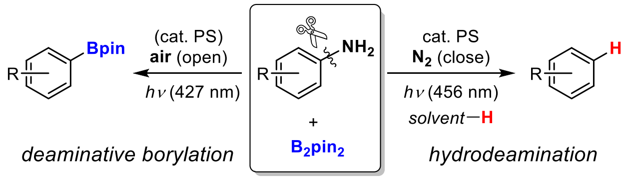


ABSTRACT: We have developed the divergent deaminative borylation and hydrodeamination of primary aromatic amines using bis(pinacolato)diboron. These transformations can be switched by the reaction conditions. Mechanistic and computational studies have suggested that the cleavage of the C–N bond and the formation of C–B bond are unlikely to involve free aryl radical intermediates. However, hydrodeamination is shown to proceed via hydrogen atom transfer between the corresponding aryl radical and an ethereal solvent.

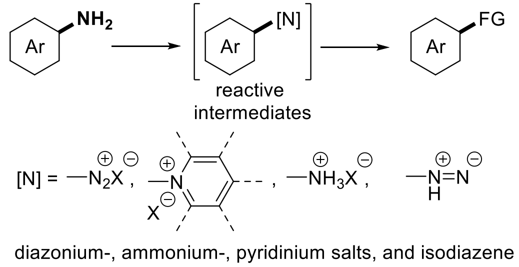
Transformation via aromatic C–N bond cleavage is a promising method for synthetic applications, because arylamine moieties are common among synthetic intermediates, natural products, and pharmaceuticals. In particular, primary aromatic amines (Ar–NH_2) are readily available industrially from the reduction of the corresponding nitroarenes. However, transformations via C–N bond cleavage of Ar–NH_2 remain challenging[1] because of the high dissociation energy of the C–N bond,[2] the poor leaving ability of the NH_2 group, and the reactive N–H bond.[3] Hence, the transformations of Ar–NH_2 that have been developed typically involve intermediates bearing relatively reactive C–N bonds, such as diazonium salts (Ar–N_2X),[4] pyridinium salts,[5] aryl ammonium salts ($ArNH_3X$),[6] and amide[7] derivatives. Levin's group recently achieved the hydrodeamination of primary amines via isodiazene intermediates prepared using an anomeric amido reagent.[8] Overall, direct C–N bond transformations of Ar–NH_2, bypassing intermediates such as Ar–N_2X and Katritzky salts, are still challenging, even though directing-group-assisted ruthenium-catalyzed direct deaminative arylation of Ar–NH_2 was achieved.[9]

Recently, we developed the photoinduced deaminative borylation of unreactive aromatic amines.[10] Zhang and coworkers later reported activation of the unreactive C–N bond of anilines via photoinduced aerobic borylation.[11] However, in these reaction systems, borylation of Ar–NH_2 have not been thoroughly investigated, and hydrodeamination of Ar–NH_2 was not examined. Herein, we report the deaminative borylation and hydrodeamination of Ar–NH_2 upon irradiation with visible light,[12] in which the reactions can be switched by changing the reaction conditions (Scheme 1b). Control experiments and density functional theory (DFT) calculations were also conducted for mechanistic studies.

We first investigated a reaction of 4-biphenylamine (**1a**) based on our previous borylation system:[10] 2.0 equiv of bis(pinacolato)diboron (B_2pin_2), 20 mol% of pyrene, with UV irradiation (365 nm) under N_2 (Table 1, entry 1). The reaction in cyclopentyl methyl ether (CPME) afforded

Scheme 1. Deaminative Transformations of Primary Aromatic Amines

(a) Transformations via reactive intermediates



(b) **This work**: Photoinduced divergent deaminative transformations

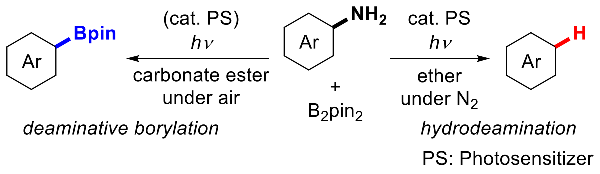
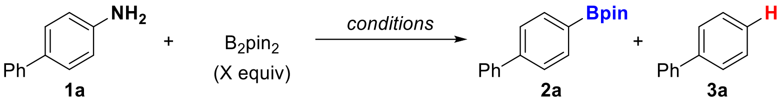


Table 1. Optimization for Deaminative Borylation and Hydrodeamination of 1a



entry	X	PS (mol%)	solvent (M)	atmosphere	light source	time (h)	conv. (%) of **1a**[a]	yield (%)[a]		ratio
								2a	**3a**	**2a**:**3a**
1	2	pyrene (20)	CPME (0.1)	N_2 (close)	A	18	48	10	22	31:69
2	4	pyrene (20)	BTF (0.33)	N_2 (close)	A	18	73	26	8	76:24
3	4	none	BTF (0.33)	N_2 (close)	A	18	74	40	5	89:11
4	4	none	BTF (0.33)	air (open)	A	18	89	55	6	90:10
5	4	none	BTF (0.33)	air (open)	B	18	64	54	1	98: 2
6	4	none	BTF (0.67)	air (open)	B	18	76	67	3	97: 3
7	4	none	DMC (0.67)	air (open)	B	18	91	88 (83)[b]	<1	>98:<2
8	2	pyrene (20)	diglyme (0.1)	N_2 (close)	A	24	62	10	30	25:75
9	2	**PS1** (5)	diglyme (0.1)	N_2 (close)	C	24	88	10	43	19:81
10[c]	2	**PS1** (5)	diglyme (0.1)	N_2 (close)	C	24	93	10	66	13:87
11[c],	2	**PS1** (5)	diglyme (0.05)	N_2 (close)	C	48	96	8	76 (68)[b]	10:90
12[c]	0	**PS1** (5)	diglyme (0.05)	N_2 (close)	C	48	<1	<1	<1	-

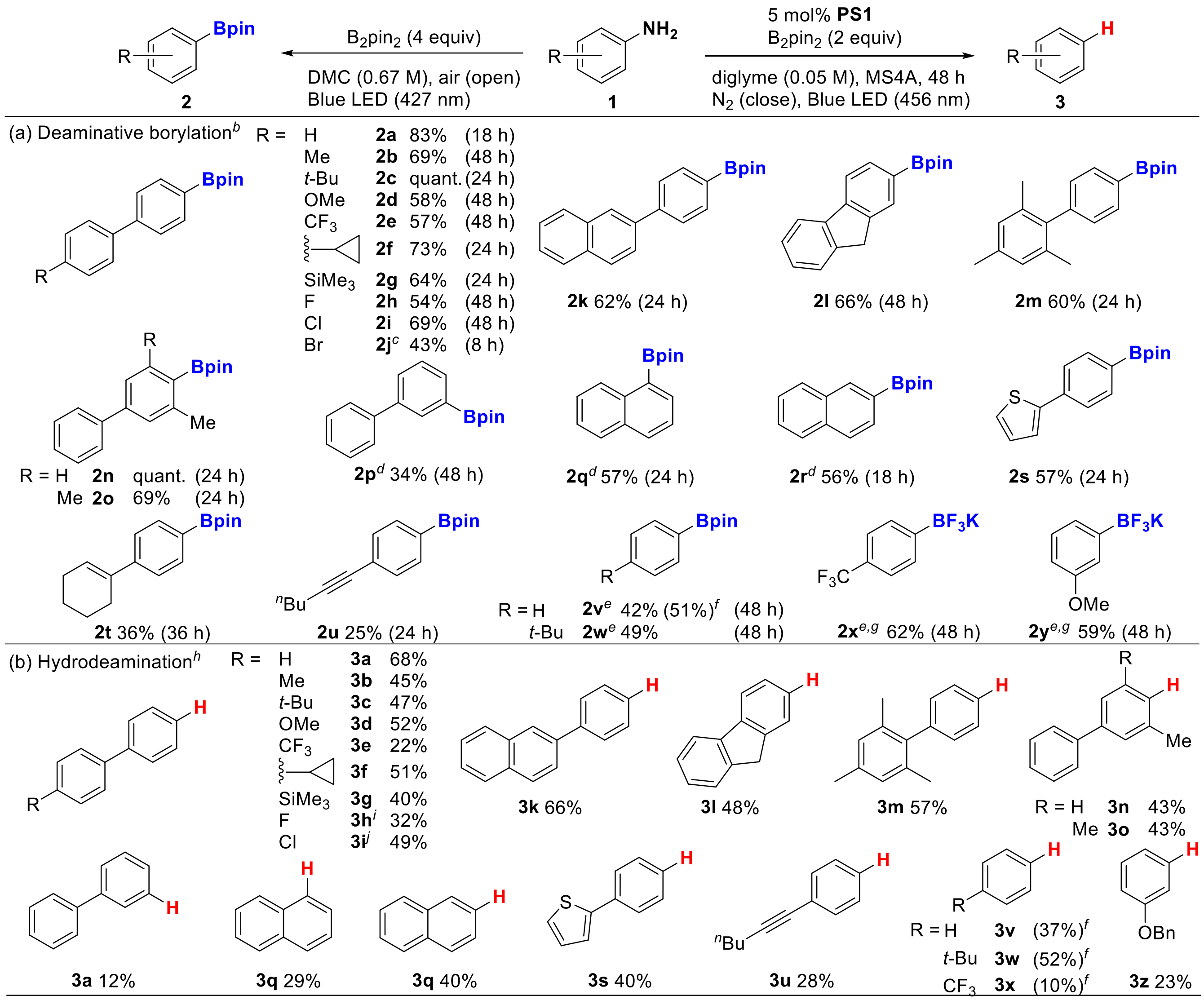
[a]Determined by GC. [b]Isolated yield is reported in parentheses. [c]With molecular sieve 4A. PS: photosensitizer, A: UV (365 nm), B: blue LED (427 nm), C: blue LED (456 nm), CPME: cyclopentyl methyl ether, BTF: benzotrifluoride, **PS1**: [Ir(dF(Me)ppy)$_2$bpy]PF$_6$.

4-biphenylboronic acid pinacol ester (**2a**) in 10% yield, together with biphenyl (**3a**) in 22% yield (**2a**:**3a** = 31:69). This result inspired us to explore reaction conditions with higher yields and selectivities for products **2a** and **3a**. First, the improvement of the yield and selectivity of the deaminative borylated product **2a** was investigated (Table 1, entries 2–7). In benzotrifluoride (BTF, 0.33 M), **2a** was obtained as the major product (**2a**:**3a** = 76:24) (entry 2). Surprisingly, the yield of **2a** and the selectivity for **2a** increased in the absence of pyrene (**2a**:**3a** = 89:11) (entry 3). Changing the atmosphere from N_2 to air[13] was effective, **2a** being obtained in 55% yield (entry 4).[14] The selectivity for **2a** was improved (**2a**:**3a** = 98:2) by changing the light source from UV (365 nm) to a blue LED (427 nm) (entry 5). Moreover, a higher concentration (0.67 M) gave a 67% yield of **2a** (entry 6). Solvent screening revealed that dimethyl carbonate (DMC) gave the best result, affording **2a** in 88% yield and suppressing the formation of **3a** (entry 7 and Table S3). Next, we developed the selective hydrodeamination of **1a** to **3a** (entries 8–12). Investigation of various ethereal solvents under UV irradiation (Table S9) revealed that diglyme was the best solvent, affording **3a** in 30% yield (entry 8). After screening several photosensitizers and light sources (Table S10), the combination of [Ir(dF(Me)ppy)$_2$bpy]PF$_6$ (**PS1**) and irradiation at 456 nm was found to improve the selectivity of **3a** (entry 9). The addition of molecular sieve 4A improved the yield of **3a** (entry 10) and the prolonged reaction time and the lower concentration gave **3a** in 76% yield with high selectivity of **3a** (entry 11).[15] Furthermore, the absence of B$_2$pin$_2$ did not afford **3a** at all, indicating the reaction system required B$_2$pin$_2$ (entry 12).

Next, we investigated the deaminative borylation and hydrodeamination of various primary aromatic amines (Scheme 2). Biphenyl amines **1a**–**1e** containing electron-donating or electron-withdrawing groups were borylated. Cyclopropyl (**1f**) and trimethylsilyl groups (**1g**) were tolerated in this reaction. The borylation of biphenyl amines **1h**–**1j** containing F, Cl, or Br atoms also proceeded without loss of the halogen atoms. 4-(2-Naphthyl)aniline (**1k**) was transformed into **2k** in 62% yield. 2-Amino fluorene (**1l**) and 4-mesityl-aniline (**1m**) were converted into **2l** and **2m** in 66% and 60% yield, respectively. Biphenyl amines with a methyl group (or groups) in the *ortho*-positions, **1n** and **1o**, were also borylated in moderate yields. Notably, the corresponding *N*,*N*-dimethyl amines remained intact under our previously reported conditions.[10] Borylation of aniline **1p** with a phenyl group at the *meta*-position was facilitated by use of a photosensitizer (9-mesityl-10-methylacridinium tetrafluoroborate) to afford **2p** in 34% yield. Moreover, 1-naphthylamine (**1q**) and 2-naphthylamine (**1r**) were transformed into **2q** and **2r** in 57% and 56% yields, respectively. The reaction of 4-(thiophen-2-yl)aniline **1s** afforded **2s** in 57% yield. The borylation of anilines **1t** and **1u** with alkenyl and alkynyl groups at the *para*-position proceeded, giving **2t** and **2u** with the unsaturated bonds retained. The reaction system was also applicable to aniline (**2v**) and anilines with an electron-donating or electron–withdrawing group at the *para*-position, **1w** and **1x**, in diglyme as solvent. The borylation of *m*-anisidine (**1y**) provided **2y** in 59% yield after treatment with KHF$_2$.

The substrate scope of hydrodeamination was investigated. The hydrodeamination of aminobiphenyls **1a**–**1e** containing an electron-donating group gave **3a**–**3e** Aminobiphenyls with cyclopropyl or trimethylsilyl substituents were also good substrates, giving **3f** and **3g** in 51% and 40%

Scheme 2. Substrate Scope of Deaminative Borylation and Hydrodeamination[a]

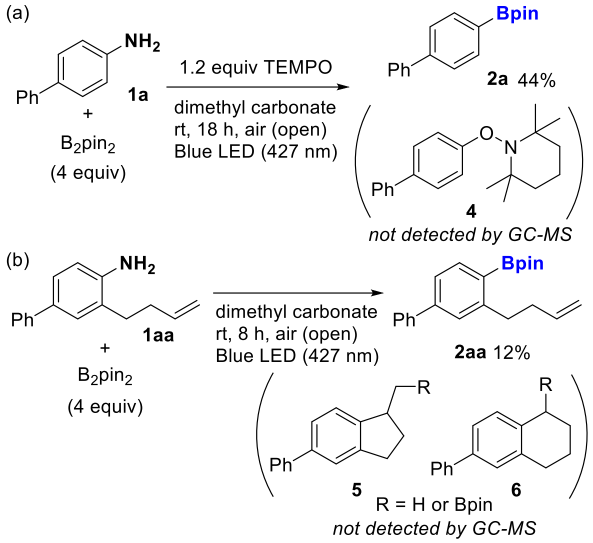


[a]Isolated yield. [b]Conditions: primary aromatic amine (0.200 mmol), B_2pin_2 (0.800 mmol, 4.0 equiv), DMC (0.30 mL, 0.67 M), Blue LED (427 nm), air (open). [c]B_2pin_2 (6.0 equiv), 9-mesityl-10-methylacridinium tetrafluoroborate (0.50 mol%). [d]B_2pin_2 (6.0 equiv), 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mol%). [e]Diglyme (0.20 mL, 1.0 M). [f]GC yield in parentheses. [g]Treatment with KHF_2. [h]Conditions: primary aromatic amine (0.200 mmol), B_2pin_2 (0.400 mmol, 2.0 equiv), diglyme (4.0 mL, 0.050 M), MS4A (40.0 mg), Blue LED (456 nm), N_2 (close). [i]8 h. [j]Mixture with 3% of **3a**. DMC: dimethyl carbonate.

yields, respectively. The reaction of aminobiphenyls **1h** and **1i** containing a halogen atom proceeded. However, in the hydrodeamination of **1i**, the further dechlorination was also detected. 4-(2-Naphthyl)aniline (**1k**), aminofluorene (**1l**), and 4-mesitylaniline (**1m**) were suitable for producing **3k–3m** in moderate yields. Aminobiphenyls bearing methyl group(s), **1n** and **1o,** afforded **3n** and **3o** in 43% and 43% yields, respectively. The reaction of **1p** with B_2pin_2 provided biphenyl **3a,** albeit in low yield. Moreover, the 1- and 2-naphthylamines **1q** and **1r** were converted into naphthalene (**3q**) in 29% and 40% yields, respectively. 2-Phenylthiophene **3s** was obtained in 40% yield from 4-(2-thienyl)aniline (**1s**). Hydrodeamination of anilines with an alkynyl group (**1u**) afforded **3u**. Furthermore, aniline (**1v**) was converted to benzene (**3v**) in 37% yield. In the case of the ^{t}Bu-, CF_3-, and benzyloxy-substituted anilines **1w**, **1x**, and **1z,** borylated products **3w**, **3x** and **3z** were also formed.

A series of experiments was conducted to elucidate the reaction mechanisms of deaminative borylation and hydrodeamination. First, we investigated the relationship between aromatic C–N bond cleavage and C–B bond formation. Borylation in the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as a radical-trapping reagent under an aerobic atmosphere gave **2a** in 44% yield (Scheme 3a), whereas the adduct **4** between TEMPO and the aryl radical corresponding to **1a** was not observed by GC-MS. Moreover, the borylation of biphenyl amine **1aa** bearing an alkene moiety afforded only the borylated product **2aa** without formation of the cyclic products **5** or **6** derived from the corresponding aryl radicals (Scheme 3b). The results suggest that the C–N bond cleavage and C–B bond formation proceed faster than the above radical trapping reactions or are unlikely to involve an aryl radical intermediate.

Scheme 3. Control Experiments for Deaminative Borylation



We conducted ESR spin-trapping and trapping-reagent experiments for reactive oxygen species, namely, the radical anion ($O_2^{\bullet-}$) and singlet oxygen ($^1O_2$).[16] The reaction of the $O_2^{\bullet-}$-trapping reagent 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) with **1a** resulted in observation of a signal indicating a radical species (presumably $O_2^{\bullet-}$) in the ESR spectrum (Scheme S1 and Figure S11). A $^1O_2$ trapping experiment was conducted using benzyl methyl sulfide (Scheme S2 and Figure S13), and produced a 10% yield of the corresponding sulfoxide, evidently formed by the reaction between the sulfide and $^1O_2$.[17] These results suggest that deaminative borylation involves the generation of $O_2^{\bullet-}$ and $^1O_2$.[18]

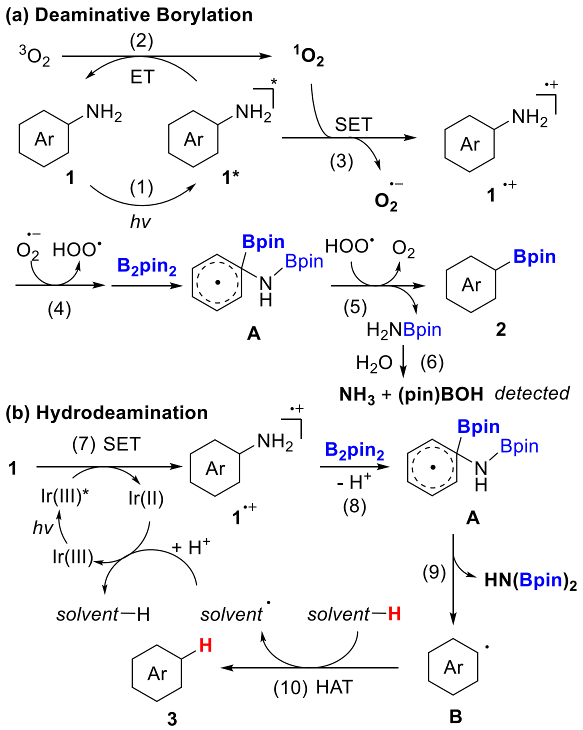
Next, we investigated the reaction mechanism of hydrodeamination by means of deuterium labelling experiments. The hydrodeamination of **1a** in THF-d_8 afforded **3a**-*d* in 38% yield (76%D) (Scheme S5). The result indicates that hydrodeamination involves hydrogen atom transfer (HAT) from an ethereal solvent to an aryl radical. The generation of aryl radicals from **1a** was supported by the hydrodeamination of **1aa** (containing an alkene moiety) which yielded the corresponding 5- and 6-memberd cyclic compounds **7** and **8** (Scheme S6).

Based on the above experiments and on DFT calculations (Figures S29–32), the proposed mechanisms of deaminative borylation and hydrodeamination are shown in Scheme 4. In the deaminative borylation (Scheme 4a and Figures S30–S31), we can consider the following stages: (1) irradiation (427 nm) of the aromatic amine **1** gives the excited state **1***;[19] (2) $^3O_2$ is excited to $^1O_2$ via energy transfer (ET) from **1***; (3) single-electron transfer (SET) from **1*** to $^1O_2$ produces $\mathbf{1}^{\bullet+}$ and $O_2^{\bullet-}$, computational insight suggesting that SET from **1*** to $^1O_2$ is more favorable than SET to $^3O_2$ by 10.3 kcal/mol (Figure S29); (4) deprotonation of $\mathbf{1}^{\bullet+}$ by $O_2^{\bullet-}$ and sequential reaction with B_2pin_2 afford intermediate **A** via the formation of C–B and N–B bonds, with cleavage of the B–B bond; (5) cleavage of the C–N bond proceeds after protonation of **A** by $HOO^\bullet$, generating **2** and amino borane (H_2NBpin); and (6) the hydrolysis of H_2NBpin affords NH_3 and (pin)BOH[20] as byproducts.

In the hydrodeamination (Scheme 4b and Figure S32), the proposed stages are as follows: (7) SET from **1** to Ir(III)* affords $\mathbf{1}^{\bullet+}$;[21] (8) $\mathbf{1}^{\bullet+}$ provides intermediate **A** through the subsequent reaction of $\mathbf{1}^{\bullet+}$ with B_2pin_2, accompanied by deprotonation; (9) **A** then decomposes into aryl radical **B** and $HN(Bpin)_2$ without the protonation of **A**; and (10) hydrogen atom transfer (HAT) between **B** and the ethereal solvent affords **3**.

In summary, we have developed a photoinduced divergent deaminative borylation and hydrodeamination of primary aromatic amines that does not require the use of relatively reactive species such as diazonium salts. These two transformations can afford a variety of organoboron and deaminated aromatic compounds with various functional groups. Mechanistic and computational studies have revealed that cleavage of the C–N bond and the formation of C–B bonds in deaminative borylation are unlikely to involve aryl free-radical intermediates, but that hydrodeamination involves hydrogen atom transfer from an ethereal solvent to an aryl radical, which is generated along with the elimination of aminoborane. We hope that this study presents a new approach to the deaminative transformation of primary aromatic amines.

Scheme 4. Proposed Reaction Mechanisms



ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures, characterization data, ^1H and ^{13}C NMR spectra, and computational details (PDF)

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Notes

The authors declare no competing financial interest.

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(13) Since we finished optimizing the deaminative borylation conditions, the similar aerobic reaction system has been reported by Zhang's group (ref. 11).

(14) Air (close) and oxygen atmosphere systems decreased product's yield (Table S5). The other oxidants did not give better results (Table S6).

(15) More than 2 equiv of B_2pin_2 or higher concentration resulted in more formation of borylation product **2a** (Tables S11 and S12).

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(18) Borylation of corresponding oxidized compounds to **1a**, such as azobenzene did not proceed at all (Scheme S4).

(19) In UV-vis absorption spectrum of **1a** in DMC solution, the absorption band spread up to ca. 500 nm, which suggested that **1a** is possibly excited under irradiation at 427 nm (Figure S18). The mechanism of excitation state related with aniline derivatives is unclear.

(20) Considering the generation of excess (pin)BOH compared to the yield of **2a**, (pin)BOH is likely to produce via the reaction with the singlet oxygen and B_2pin_2 as well as hydrolysis of H_2NBpin. See Scheme S3 for the detail.

(21) Based on redox potentials of Ir(III)* ($E_{\text{red}}^{\text{III*/II}}$= ca. +1.19 V vs. SCE) and **1** (E_{ox} = +0.99 V vs. SCE), the SET process is feasible (Figures S26–28).