Halogen-bonding-promoted Photo-induced C–X Borylation of Aryl Halide using Phenol Derivatives

Kazuki Matsuo, Eiji Yamaguchi*, Akichika Itoh*

Gifu Pharmaceutical University, 1-25-4, Daigaku-Nishi, Gifu, Gifu 501-1196, Japan

keyword

C–X borylation, aryl halides, halogen bonding complex, photo reaction

ABSTRACT

This study investigates the photo-induced C–X borylation reaction of aryl halides by forming a halogen-bonding complex. The method employs 2-naphthol as a halogen-bonding acceptor and proceeds under mild conditions without a photoredox catalyst under 420 nm blue light irradiation. The method is highly chemoselective, broadly functional group tolerant, and provides concise access to corresponding boronate esters. Mechanistic studies reveal that forming the halogen-bonding complex between aryl halide and naphthol acts as an electron donor-acceptor complex to furnish aryl radicals through photo-induced electron transfer.

INTRODUCTION

Visible light-mediated photoexcitation of small molecules has been used for various useful reactions to specific reactivity derived from electrically excited open-shell chemical species.[1] On the contrary, direct photochemical activation of small molecules requires strong energy such as ultraviolet light. Moreover, indirect methods *via* activation of expensive transition metal-based photocatalysts with visible light response are frequently used.[2] Photochemical reactions using electron donor-acceptor (EDA) complexes, a new type of non-covalent bonding proposed by Mulliken, have recently attracted much attention as an alternative methodology to photocatalysis.[3] EDA complexes are formed by the coordination between two molecules, such as electron donors and electron acceptors. In many cases, the energy of this transition is in the visible light region, and one electron is transferred from the electron donor to the electron acceptor, leading to a reactive open-shell intermediate (Figure 1a).[4] Various aggregation modes of EDA complexes are reported, and π-π interactions and hydrogen bonds are frequently used in the organic photochemistry, but recently n-σ interactions such as halogen-bonding interactions have been attracting attention.[5]

Halogen-bonding interactions compared with other intermolecular non-covalent interactions such as hydrogen bonding possess an advantage: the halogen-bond interaction has a greater directionality mainly, due to which, the positive electrostatic potential region, σ-hole, is located at the center of the C-X axis, resulting in a nearly linear structure with an angle of 160° to 180°.[6] Moreover, since the photochemical activation of EDA complex through halogen-bonding interaction is the aggregation between the organic halide and the electron donor, selective activation of the organic halide and generation of radical carbon species only by fragmentation of the anion radical species generated are potentially possible. (Figure 1b).[5]
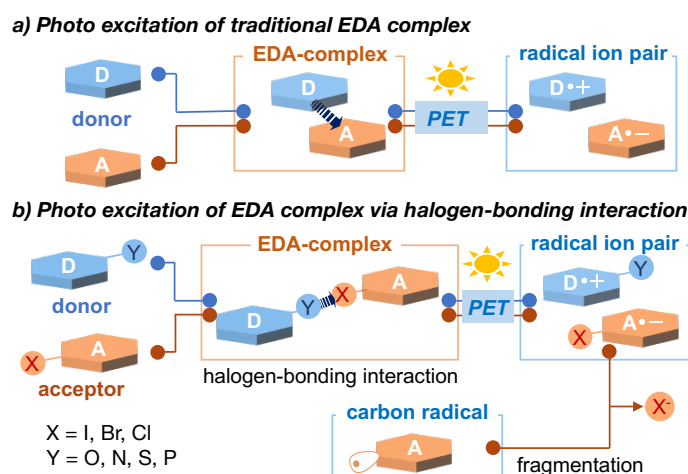

a) Photo excitation of traditional EDA complex

b) Photo excitation of EDA complex via halogen-bonding interaction

X = I, Br, Cl
Y = O, N, S, P

Figure 1. (a) Classical EDA complex theory. (b) A halogen-bonding strategy to produce *C*-centered radical species. PET: photo-induced electron transfer.

Arylboronic esters have been recognized as useful reagents and building blocks in contemporary synthetic organic chemistry due to many catalytic C–C bond formations, such as Suzuki-Miyaura cross-coupling.[7] The classical method for the preparation of aryl boronates is the reaction using pyropholic lithium reagents (RLi) or Grignard reagents (RMgX) with boron-based electrophiles (Scheme 1a).[8] On the contrary, the transition-metal-catalyzed borylation reaction as an alternative approach to constructing C(sp2)–B bond has been developed from haloarenes and aromatic hydrocarbons as the corresponding boronic acids/esters.[9–15] These are robust methodologies to produce organoboron compounds. However, they require expensive transition metal catalysts and high temperatures. Hence, there has been much interest in developing alternative methods using photoreaction in recent years.[16] For example, the "UV light" induced borylation of haloarenes using quaternary aryl ammonium salts under transition metal-free conditions was reported by Li et al.[17] and Larionov et al.[18] Moreover, Jiao and coworkers reported a noble organocatalytic reaction for the borylation of unactivated aryl chlorides by photoactivation of *in situ*-generated SED (single electron donor) complex.[19] The key to this photo-induced borylation is the formation of aryl radicals.

Therefore, we estimated that developing a simple and rapid methodology for generating aryl radicals would lead to novel photo-induced borylation.

We have recently developed the use of an *in situ*-generated halogen-bonding complex to enable the photo-induced transformation of olefins *via* ATRA reactions.[20] Therefore, inspired by the methods, we started to challenge the development of the direct borylation of aryl halides using halogen-bonding interaction (Scheme 1b). Herein, we report a photochemical C–X bond borylation reaction using novel aryl radical generation strategy through the halogen-bonding EDA complex.
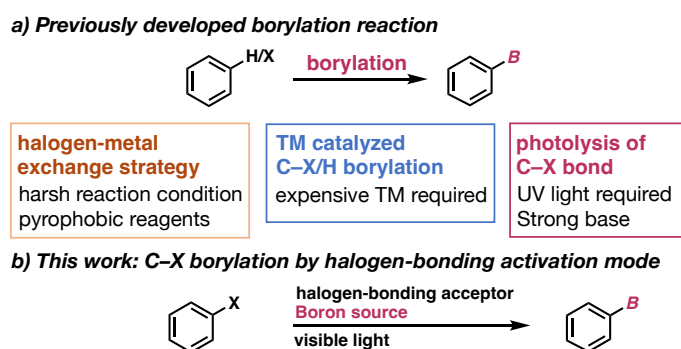
Scheme 1. (a) Traditional borylation tachnology. (b) This work: photo-induced C–X borylation mediated by halogen-bonding complex.

RESULTS AND DISCUSSION

To validate our proposal, we studied the radical borylation reaction of haloarenes **1**. Present experiments were conducted in acetonitrile (MeCN) using commercially available bis (pinacolato) diboron **2a** as a cheap and stable boron source. Our overarching goal was to define a strategy that permits the predictable and mild activation of substrates that would be inert to other practical approaches, including photoredox catalysis. Therefore, 4-iodoanisole **1a**, which is difficult to activate by photocatalysis reductively, was selected as the precursor of aryl radicals.[21] After carefully screening the conditions, it was found that the optimal reaction conditions include the use of a 3 W 420 nm LED as the light source, MeCN as the solvent, and performing the reaction at room temperature under Ar atmosphere to furnish the desired borylation product **4a** in 92% yield (Table 1, entry 1).[22] According to the base screening results, we found that NaOH and KOH were also an efficient base for the photochemical C–I borylation reaction (entry 1 vs. entries 2–5). Other solvents, such as THF, MeOH, and DMF, were proved inferior (entries 6–8). Control experiments revealed the essential role of K_2CO_3, 2-NpOH, and photoirradiation on the observed reactivity (entries 9–11). The desired borylated product 4a was formed when the reaction was under an oxygen atmosphere, albeit in a slightly low yield (entry 12). Finally, when a catalytic amount of 2-NpOH was employed, the borylation reaction proceeded catalytically, albeit the yield of the desired product decreased (entry 13).

Table 1. Optimization study for C–I borylation reaction of **1a**[a].
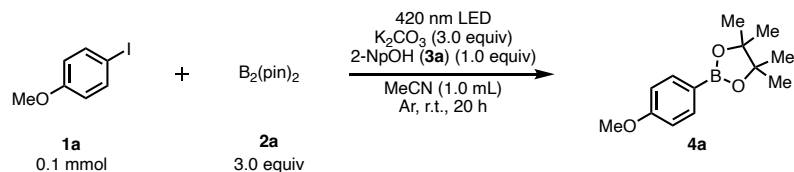
Entry	Changed from standard conditions	Yield (%)
1	-	95(92)
2	Na$_2$CO$_3$ instead of K$_2$CO$_3$	10
3	Cs$_2$CO$_3$ instead of K$_2$CO$_3$	87
4	NaOH instead of K$_2$CO$_3$	94
5	KOH instead of K$_2$CO$_3$	93
6	THF instead of MeCN	10
7	MeOH instead of MeCN	29
8	DMF instead of MeCN	50
9	w/o K$_2$CO$_3$	3
10	w/o 2-NpOH (**3a**)	10
11	dark or dark at 50 ºC	trace
12	under O$_2$	64
13	**3a** (0.1 equiv)	64

[a] Yield was determined by ^{1}H NMR analysis of crude reaction mixture using 1,1,2,2 tetrachloroethane as an internal standard. The number in parenthesis is isolated yield.

  Further, we explored the scope of the photo-induced borylation using optimized reaction conditions (Figure 2). Iodoarenes with electron-donating substituents, regardless of the substitution pattern, were converted to the corresponding arylboronic esters in moderate to excellent yields (**4a-g**). Moreover, a scale-up experiment was also conducted to furnish corresponding boronate (**4a**) ester in 81% yield. The sterically hindered substrates **1h** and **1i** reacted well to give arylboronate **4h** and **4i** in moderate yields. Naturally, the unsubstituted haloarene **1j** reacted sufficiently to obtain the desired product **4j**. Additionally, we have shown that bromoarene **2j** can also be adapted using a strong base, albeit in moderate boronate ester yield (KO^{t}Bu). Borylation of halogenated iodoarenes bearing fluoro (**4k**), chloro (**4l**), bromo (**4m**), and iodo (**4n**) groups was also demonstrated. Fluorine substituents with weak ability as halogen-bonding donors gave the corresponding borylated products in good yields, but for chlorine-, bromine-, and iodine-substituted substrates, undesired diborylation reactions proceeded, and the yields significantly decreased. Unfortunately, although haloarenes with strong electron-deficient substituents, such as CF$_3$ groups (**4u** and **4v**) are known to be good halogen-bonding donors, the borylation reaction did not proceed properly under

optimal reaction conditions. Furthermore, aryl halides with carbonyls (**4q-t**), such as ketones, aldehydes, esters, and cyanides, which are unstable under basic conditions, gave the desired borylated products (**5q-t**) without decomposition in any case under the reaction conditions.[19] It should be noted that the borylation reaction proceeded smoothly even with relatively inert bromoarenes. Interestingly, in the case of 4-halo benzaldehyde (**4s**), the reaction proceeds without adding phenol as a halogen-bonding acceptor, suggesting that the C–X bond's direct hemolysis may proceed a different pathway for this substrate.[23] Substrates with protected or unprotected hydroxyl or amino groups could be converted smoothly to the corresponding borylation products (**4u–4ai**). Although these substrates (**1u–1ai**) may interfere with the halogen-bond formation, they were used in this reaction without yield loss. The fact that unprotected phenols and anilines can be directly converted to boronates suggests that the reaction is highly valuable. Excellent yields were obtained for the biphenyl and naphthyl substrate (**4aj–4al**). The halogen-bonding interaction initiated the borylation reaction of aromatic halide, promoted by phenol **2**, provided a range of borylated heteroarenes in moderate to excellent yield (**4am–4au**). Additionally, the borylated substrate (B(pin); **1av** and B(dan); **1aw**) also applied to the present borylation; the C–I bond was converted to C–B bond in 92% for **4av** and 60% for **4aw**, respectively.

Further experiments demonstrated that this method is compatible with the functionalization of biorelevant compounds. It allowed the late-stage introduction of boronate ester into menthol-derived aryl iodide (**1ax**) and protected glucose-derived aryl iodide (**1ay**) in a single step. Finally, we applied our strategy to perform other boron sources, such as bis (neopentyl glycolato) diboron (**2b**) and bis (hexylene glycolato) diboron (**2c**). This transformation, using other boron sources, afforded the corresponding borylated product (**5a** and **5b**) in excellent yield. However, the use of tetrahydroxydiboron resulted in no reaction, which is suspected to be due to the acid-base reaction between diboron and the base proceeded.
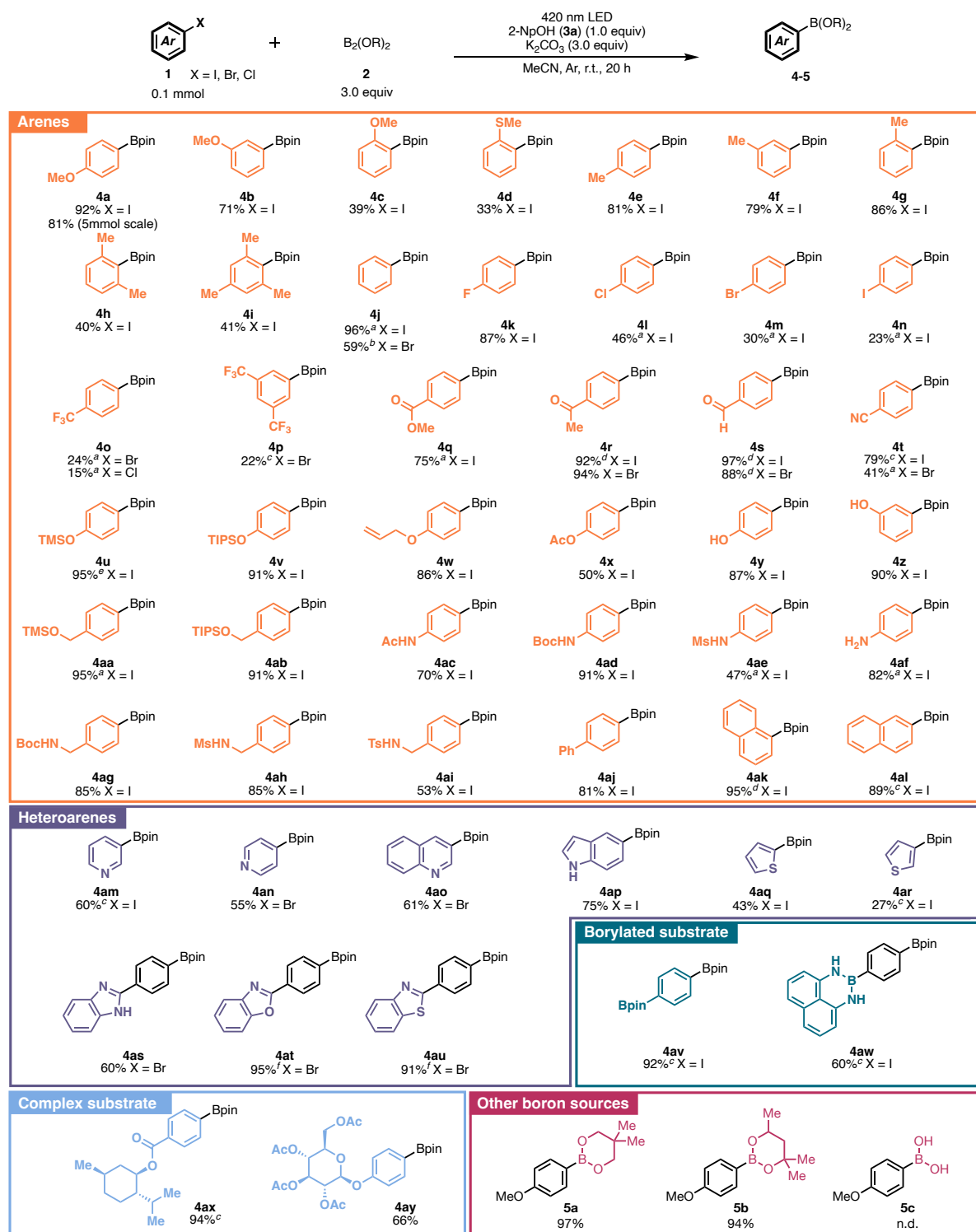
Figure 2. Substrate scope for C–I borylation reaction. Reaction conditions: **1**, **2**, or **3** (0.1 mmol, 1.0 equiv), diboron reagents (3.0 equiv), K_2CO_3 (3.0 equiv), 2-NpOH (1.0 equiv) in 1.0 mL of MeCN, irradiated under 420 nm LED at room temperature for 20 h. Yields of isolated products are reported. [a] 1-NpOH (1.0 equiv) was used instead of 2-NpOH. [b] KO^{t}Bu (1.0 equiv) was used instead of K_2CO_3. [c] 2,6-Cl_2-C_6H_3OH (1.0 equiv) was used instead of 2-

NpOH. [d] Without 2-NpOH. [e] After column chromatography, the deprotected product was isolated.[24f] 4-Ph-C$_6$H$_4$OH (1.0 equiv) was used instead of 2-NpOH.

Several controlled experiments were carried out (Scheme 3). We hypothesize that the aryl radicals are generated by forming EDA complexes and irreversible fragmentation through PET, as shown in Scheme 3a. First, the effect of phenolic hydroxyl groups was investigated (Scheme 3b). The reaction using preformed potassium naphthoxide gave the corresponding boronate (**4a**). In contrast, the reaction did not proceed when corresponding methyl-protected naphthol was used. This is indicated that the phenoxide formed from phenol with base in the reaction mixture may have promoted the reaction. We also discovered that 2-NpOK was used instead of 2-NpOH in MeCN, showing a significant redshift to the visible region when preformed. The shoulder peak was observed at approximately 420–450 nm (Scheme 3b, blue line vs. gray line). The addition of iodobenzene did not affect their UV absorption (Scheme 3b, orange line). Moreover, we observed the formation of a 1:1 complex between 2-naphtoxide and **1a** with a binding constant (Ka) of 0.99 M^{-1} in DMSO-d_6 using a ^{1}H NMR titration method and Job's plot analysis (Scheme 3c, See ESI, Figure S1–4). Since these results are similar to the previous results[5e] and are sufficient to rule out the formation of EDA complexes by π-π* interaction or n-π* interaction, such as the independent reporting by Miyake and Melchior,[25,26] we hypothesize that the formation of EDA complexes by halogen-bonding interactions is the key to initiating the reaction.

We performed several controlled experiments to determine aryl radical generation through PET after forming EDA complexes through halogen-bonding interaction (Scheme 3d). When the reaction using 2-iodo-allylphenol **1az** was used as a substrate, borylation reaction proceeded after radical cyclization reaction to furnish **4az** in 39% yield (Scheme 3d, eq. 1). Moreover, methyl 2-iodobenzoate 1ba to the reaction resulted in no desired product formation and gave the C–C and C–O forming cyclic product **6** in 11% yield (Scheme 3d, eq. 2). This byproduct is thought to be formed by a similar pathway as that using hypervalent iodine compounds by Miyake.[25] Therefore, the aryl radical intermediate formed after PET reacts with the phenoxy radical to form a C–C bond. The byproduct can be obtained by rearrangement and removal of water.[27] When the reaction was subjected to the optimized condition with the addition of radical scavengers, such as TEMPO, the desired product formation was significantly suppressed; instead, the formation of TEMPO adducts of aryl radicals **7a** was obtained (Scheme 3d, eq. 3).[28] At the same time, 7b is formed by the reaction of TEMPO with the acetonitrile radical generated by the hydrogen atom abstraction from acetonitrile by the phenoxy radical generated *in situ*.[29]
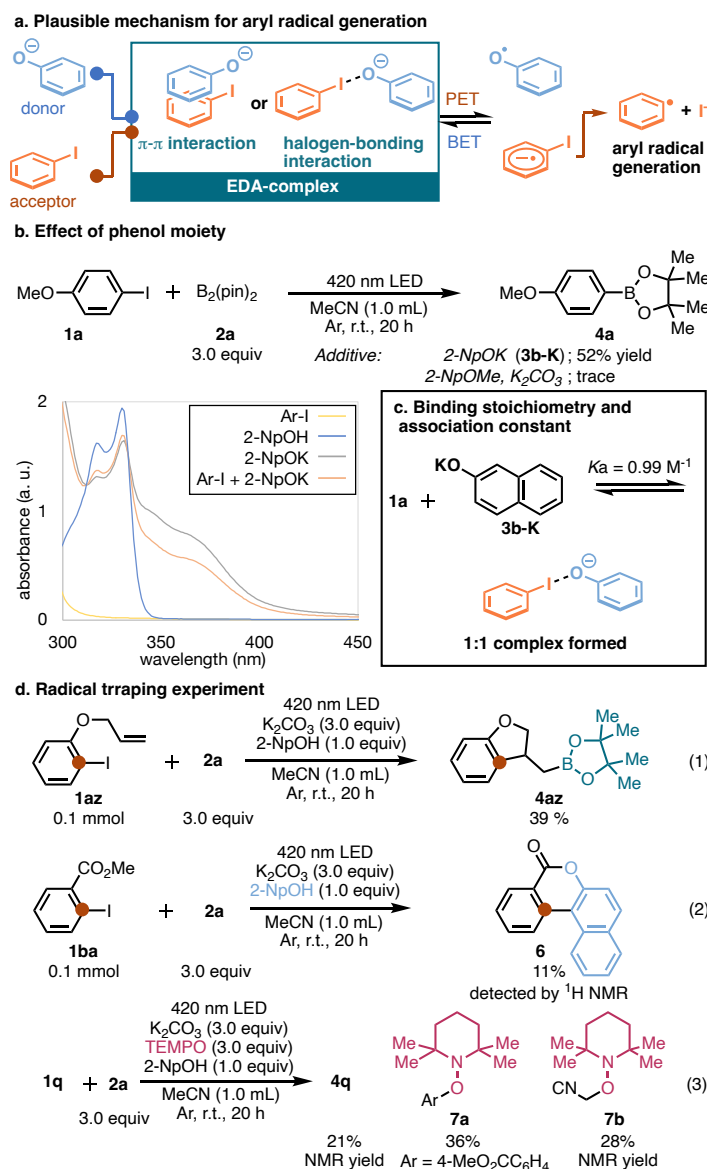
Scheme 3. Controlled experiments. (a) A plausible mechanism for aryl radical generation step. (b) The reaction employs potassium 2-naphtoxide and 2-MeO-Np and UV/Vis spectrum. (c) Investigation of binding stoichiometry and association constant. (d) Intermolecular and intramolecular radical trapping experiments. [a] Isolated yield.

Based on the previously reported results and our experimental evidence, the possible reaction pathway for geeeranting the aryl radical is shown in Scheme 4.[5e,25,30,31.] The reaction was initiated by photoexcitation of the halogen-bonding complex **A** to produce the excited state **B** under irradiation of 420 nm LED. The photoexcitation of B undergoes ET to an aryl halide, producing an aryl radical anion **C** and phenoxy radical. After the fragmentation of **C**, the generated aryl radical **D** reacts with the *in situ* formed borate **E** to produce an arylboronate **4** and boryl radical anion **F**.[31] The radical anion **F** can also be viewed as an anionic based stabilized boryl radical. Finally, **F** is oxidized by the phenoxy radical to form the borate **G**.
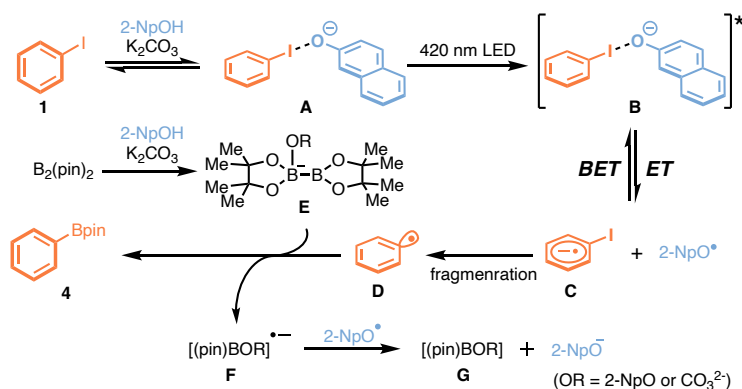
Scheme 4. Plausible reaction mechanism for photo-induced borylation reaction aryl halide.

CONCLUSION

In summary, the photo-induced borylation of aryl halides promoted by phenol derivatives *via* halogen bonding was investigated. The borylation of aryl halides with $B_2(pin)_2$ afforded various products in moderate to good yields when irradiated at 420 nm. The photoactivated borylation from our study revealed that an EDA complex between aryl halides and phenoxides was a crucial intermediate in the subsequent charge separation processes that led to the formation of aryl radical. Furthermore, this is the first reported example of a methodology using phenol as an acceptor for the halogen-bond. Further efforts are focused on extending this new methodology to other classes of compounds for photocatalysis, including inactive aryl halides or alkyl halides.

■ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at @@@@. [1]

H, $^{13}C\{^1H\}$ and ^{19}F NMR spectra, UV/Vis spectra, results of full detailed optimization study experiments, and characterization of all compounds synthesized.

■AUTHOR INFORMATION

Corresponding Author

Correspondence to E.Y. and A.I.

Eiji Yamaguchi (yamaguchi@gifu-pu.ac.jp)

Akichika Itoh (itoha@gifu-pu.ac.jp)

Competing interests

The authors declare no competing interests.

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