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Redox-Neutral Borylation of Aryl Sulfonium Salts via C−S Activation Enabled by Light

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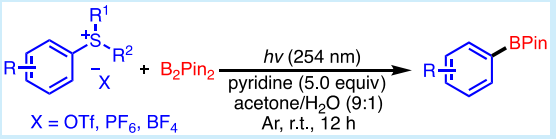
Supporting Information

ABSTRACT: Reported here is a novel photoinduced strategy for the borylation of aryl sulfonium salts using bis(pinacolato)diboron as the boron source. This method exploits redox-neutral aryl sulfoniums to gain access to aryl radicals via C−S bond activation upon photoexcitation under transition-metal-free conditions. Therefore, it grants access to diverse arylboronate esters with good performance from easily available aryl sulfoniums accompanied by mild conditions, operational simplicity, and easy scalability.



Organosulfur compounds have long played a prominent role in organic synthesis and in the construction of novel chemical structures and architectures.[1] Highly selective activation and functionalization of C−S bond can accurately modify extremely useful *S*-containing molecules like natural products, drug molecules, and bioactive intermediates. Although C−S bond has much lower bond dissociation enthalpies (BDE) than those of other C−X bonds (X = H, C, O, N, halo),[2] the activation of C−S bond in sulfides was comparatively scanty due to their bad smell and strong affinity to transition metals than other chemical bonds. To address this dilemma, recently, the readily installed sulfoniums, which are also bench-stable and easy-to-handle, have been used as promising coupling partners or building blocks instead of conventional sulfides for organic synthesis.[1h,3] For one thing, the C−S bond of sulfoniums can be cleaved more easily than those of sulfides thanks to their electron deficiency. For another, neutral sulfur fragments eliminated from sulfoniums would be less poisonous to metallic catalysts than anionic *S*-containing species. In this context, the seminal work of Umemoto on fluoro-alkylation via C−S bond cleavage of fluoroalkylated sulfonium salts paved the road to the application of sulfonium salts in the construction of chemical bonds.[4] Additionally, since the pioneering work of Liebeskind on cross-coupling reactions of aryl sulfoniums with various organometallic reagents,[5] transition-metal catalyzed and metal-free cross-coupling reactions of aryl sulfoniums[1h] such as arylation,[6] alkenylation,[7] alkynylation,[8] borylation,[9] alkoxycarbonylation[10] cyanation,[11] and fluorination[12] have also been well studied.

In recent years, photoredox catalysis has become a powerful synthetic strategy in organic chemistry via activation and functionalization of various chemical bonds.[13] Particularly, this attractive alternative to traditional catalysis relies primarily on the generation of a wide array of active radical intermediates through homolytic cleavage of different chemical bonds enabled by light. In the context of photoinduced C−S bond activation, although a pioneering photolysis of sulfonium bromide through radical pathway was reported early in 1969,[14] only a few examples were involved in practical application for the construction of chemical bonds.[15] Very recently, the Ritter group reported a promising and practical strategy for site-selective and versatile aromatic C−H functionalization through C−S bond cleavage of sulfonium salts under photoredox catalysis.[16] Nevertheless, the development and expansion of more general and efficient strategies for the activation and functionalization of C−S bond through photoredox catalysis would be still highly desirable.

Aromatic boronic acids and arylboronates are widely used in organic synthesis, material science, and drug discovery as key building blocks.[17] Although traditional transition metal catalytic strategies toward borylation were versatile and well-studied,[18,19] very recently, photoredox catalysis has opened up a radical-involving path[20] that can easily gain access to borylation reactions via photoinduced activation of various chemical bonds like the C−halo bond,[21] C−N bond,[22] C−C bond,[23] C−O bond,[24] and even C−H bond.[25] Inspired by these findings, we envisioned that the open-shelled intermediates could also be accessed upon excitation by light through a homolytic cleavage of an activated C−S bond of sulfoniums; thus, a photoinduced borylation via C−S activation could be achieved.[26] Therefore, as part of our efforts to develop photoredox catalytic strategies for the activation and construction of chemical bonds,[27] we herein report a transition-metal-free and redox-neutral borylation of aryl sulfoniums enabled by light. The present protocol is featured with mild conditions, operational simplicity, good functional groups tolerance, and easy scalability. Additionally, a radical pathway was proposed according to our preliminary mechanism study.

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Studies were commenced with the UV−vis adsorption test of a typical aryl sulfonium salt **S1**. Obviously, a UV−vis spectrum showed that sulfonium **S1** exhibited a characteristic absorption band around 233 nm (Figure 1), which indicated

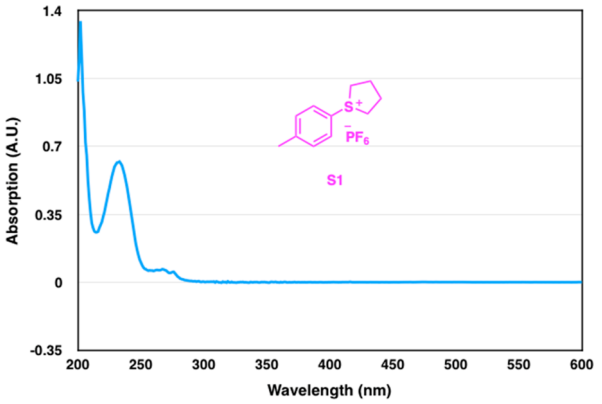
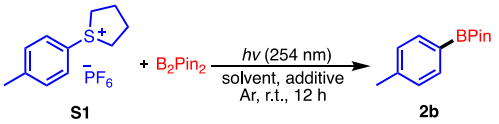


Figure 1. UV−vis absorption spectrum of sulfonium **S1** in acetonitrile.

that UV-irradiation could help to excite aryl sulfoniums. Therefore, the borylation of sulfonium **S1** under UV-irradiation (254 nm) using B_2Pin_2 (bis(pinacolato)diboron) as the borylation reagent was chosen as the model reaction for the optimization of reaction conditions (for details, see Table S1 in Supporting Information). As a result, atetone/H_2O (v/v = 9:1) was found to be the best solvent due to the better solubility of sulfonium salts in the presence of water (Table 1, entry 3). Additionally, 3.5 equiv of B_2Pin_2 were necessary for a satisfactory yield of the desired borylated product (Table 1, entries 3−5). At the same time, pyridine proved to be necessary and also the best additive, which played the role of activating B_2Pin_2.[23b] And an 82% NMR yield for **2b** could be obtained accompanied by an 81% isolated yield in the presence of 5.0 equiv of pyridine (Table1, entries 6−9). Last, it was proven that the borylation of sulfonium could not proceed in dark at all, which could convince the indispensable role of photoirradiation to the sulfonium in the absence of any other catalysts (Table 1, entry 10). Given the ease of the modification for aryl sulfonium salts, several different sulfonium salts were synthesized and their activity toward borylation was also evaluated. To our delight, all the sulfonium salts were compatible with our protocol under the optimal conditions. Notably, the relatively simple sulfonium triflate **1b**, which can be easily synthesized by simple methylation of corresponding methyl aryl sulfide, displayed the same activity just as sulfonium **S1** under the identical reaction conditions. Considering the much easier synthesis of sulfonium triflates, we subsequently evaluated the scope of sulfonium triflates under the optimal reaction conditions.

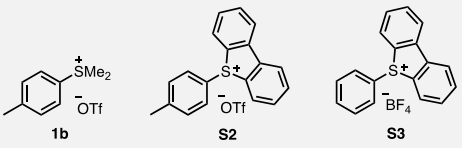
Inspiringly, a wide array of aryl sulfonium triflates were compatible to the present borylation protocol and a variety of functional groups were tolerated (Table 2). Generally, *para*-substituted aryl sulfoniums bearing electron-donating groups, such as methyl, *tert*-butyl, hydroxyl, methoxy, and allyloxy, could deliver the borylation products with good yields, which were better than that of phenyl sulfonium (Table 2, **2a**−**f**). Additionally, sulfoniums with either acetal or ketal at the *para*-position could also be converted to the desired boronate esters with upper-moderate yields (Table 2, **2g** and **2h**). When it comes to the sulfoniums with electron-withdrawing groups at

Table 1. Selected Results for the Optimization of Reaction Conditions[a]



entry	solvent	B_2Pin_2 (equiv)	additive (equiv)	yield[b] (%)
1	CH_3CN	3.5	Py (1.5)	15
2	acetone	3.5	Py (1.5)	46
3	acetone/H_2O (9:1)	3.5	Py (1.5)	69
4	acetone/H_2O (9:1)	2.0	Py (1.5)	52
5	acetone/H_2O (9:1)	4.0	Py (1.5)	68
6	acetone/H_2O (9:1)	3.5	Py (3.0)	71
7	acetone/H_2O (9:1)	3.5	Py (4.0)	77
8	**acetone/H_2O(9:1)**	**3.5**	**Py (5.0)**	**82 (81)**[c]
9	acetone/H_2O (9:1)	3.5	None	43
10[d]	acetone/H_2O (9:1)	3.5	Py (5.0)	ND
11[e]	**acetone/H_2O(9:1)**	**3.5**	**Py (5.0)**	**81**[c]
12[f]	acetone/H_2O (9:1)	3.5	Py (5.0)	69[c]
13[g]	acetone/H_2O (9:1)	3.5	Py (5.0)	65[c]

[a]Reaction conditions: **S1** (0.1 mmol); solvent, 1.0 mL; *hv* (254 nm); Ar; rt; 12 h. [b]NMR yield with mesitylene as internal standard. [c]Isolated yield. [d]The reaction was conducted in dark. [e]**1b** instead of **S1**. [f]**S2** instead of **S1**. [g]**S3** instead of **S1**. Py: pyridine; ND: not detected.



the *para*-position, both fluoro- and chloro-substituted ones showed good activity toward the borylation (Table 2, **2i** and **2j**). However, only moderate yields could be obtained for bromo- and trifluoromethyl substituted sulfoniums (Table 2, **2k** and **2l**), which might be ascribed to the instability of the radical intermediates. Notably, sulfonate derivated sulfonium could also be delivered to the corresponding boronate ester with a satisfactory yield (Table 2, **2m**). Subsequently, *meta*-substituted sulfonium triflates were evaluated. It was found that 3-methyl sulfonium could be converted to 3-methyl boronate ester in high yield (Table 2, **2n**). Besides, interestingly, not only the electron-rich sulfoniums but also the electron-deficient ones could deliver the desired products smoothly with moderate to good yields (Table 2, **2o**−**u**). For *ortho*-substituted sulfonium triflates, it was observed that only 2-methyl and 2-fluoro sulfonium triflates could be converted to their corresponding boronate ester with medium to good yields (Table 2, **2v** and **2y**). However, other sulfonium triflates with substitutes such as methoxy, hydroxyl, and chloro at the *ortho*-position displayed poor reactivity toward this light-enabled borylation (Table 2, **2w**, **2x**, **2z**). With the aim to further explore the synthetic utility of this methodology, a scale-up synthesis of arylboronate ester was then carried out. Delightedly, a 73% isolated yield of 4-Me-phenyl boronate ester **2b** was obtained when 5 mmol of **1b** was treated under the optimal reaction conditions (Table 2, 2b), revealing that our strategy was effective on large scale. Nevertheless, the present borylation protocol was not compatible with both benzyl and alkyl sulfonium salts, and the sulfoniums were

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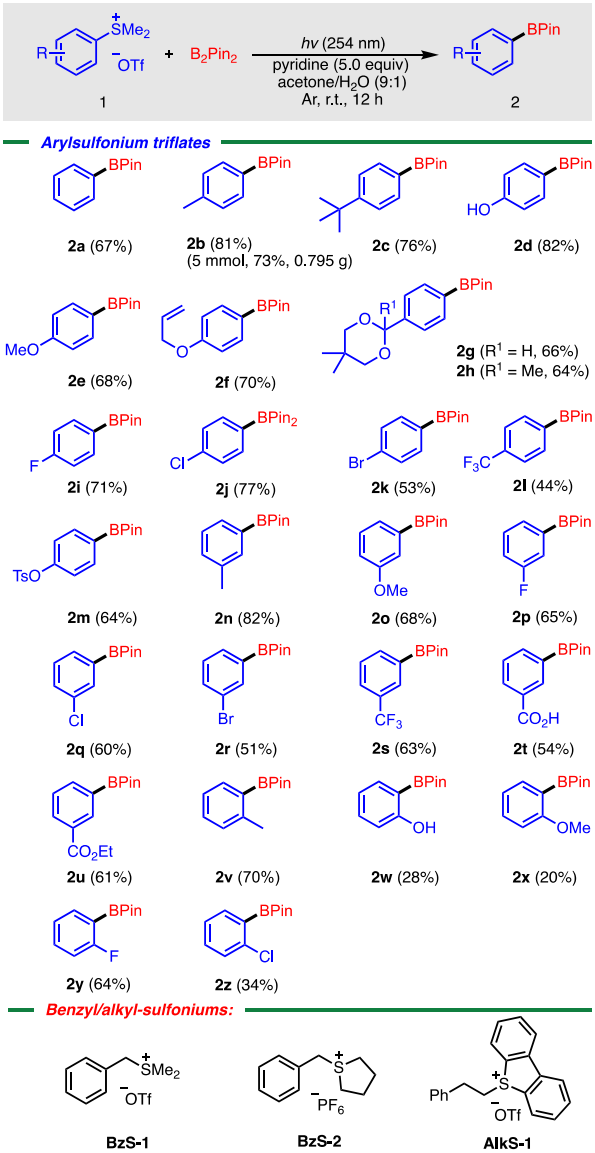
Table 2. Scope of Aryl Sulfonium Triflates[a]



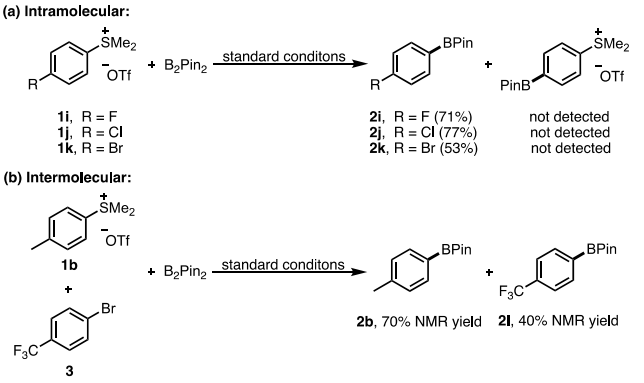
[a]Reaction conditions: sulfonium triflates (0.1 mmol); B_2Pin_2 (3.5 equiv); pyridine (5.0 equiv); acetone/H_2O (9:1), 1.0 mL; *hν* (254 nm); Ar; rt; 12 h.

decomposed via demethylation or ring-opening reaction (Table 2, **BzS-1**, **BzS-2**, **AlkS-1**).

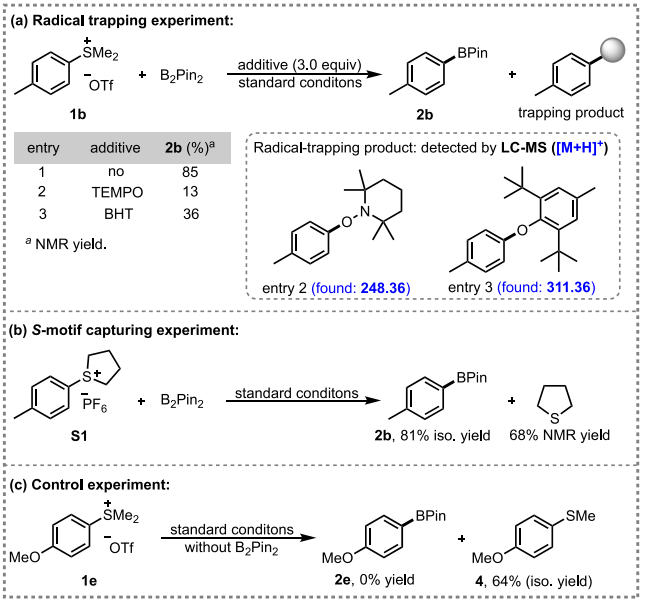
Aryl-halides have been widely used as building blocks in both transition metal catalyzed[9a,18,19] and photoredox catalyzed borylation systems.[16,21] Based on the results of our study, intramolecularly, borylation of 4-halo-aryl sulfoniums **1i**–**k** furnished the corresponding borylation products with the halo-groups nearly untouched (Scheme 1a). Intermolecularly, aryl sulfonium still exhibited better activity toward borylation compared with even extremely activated aryl-halide **3** (Scheme 1b). These results clearly underline the much more competitive activity of the C–S bond in sulfonium compared with that of conventional C–halo bonds[21c] toward identical transformation under the present reaction system.

In order to gain insight into the reaction mechanism, several control experiments were conducted (Scheme 2). First, it was observed that the borylation reaction was significantly suppressed when 3.0 equiv of a radical scavenger, like

Scheme 1. Chemoselective Evaluation



Scheme 2. Mechanism Study



TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) and BHT (2,6-di-*tert*-butyl-4-methylphenol), was added, respectively (Scheme 2a). Additionally, the trapped products by TEMPO and BHT were also detected via LC-MS (Scheme 2a). These results evidenced that an aryl-radical intermediate was formed via the C(sp^2)–S bond cleavage of the aryl sulfonium under UV-irradiation during the reaction. Furthermore, when sulfonium hexafluorophosphate **S1** was treated under the optimal reaction conditions, the corresponding *S*-motif decomposed from **S1**, i.e., tetrahydrothiophene, was detected by NMR in 68% yield (Scheme 2b). This result could also be powerful evidence for the photoinduced cleavage of the C(sp^2)–S bond of sulfonium. Notably, no borylated product was detected when sulfonium triflate **1e** was treated in the absence of B_2Pin_2 (Scheme 2c). Instead, the demethylation product **4** was isolated in 64% yield, which was formed via the cleavage of the C(sp^3)–S bond of sulfonium. Consequently, the cleavage of the C(sp^2)–S bond of sulfonium would be favorable in the presence of B_2Pin_2 under UV-irradiation, which might ascribed to the stability of the subsequently formed radical intermediate.

In view of the experimental results obtained above, we believe that this borylation reaction proceeded through a radical process that was initiated via the photoexcitation of aryl

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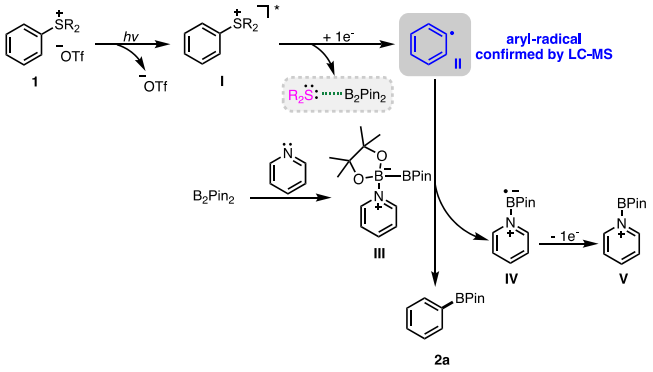
sulfonium **1** with the formation of an excited state **I** (Scheme 3). Consequently, the key aryl-radical **II** would be generated

Scheme 3. Proposed Reaction Mechanism



through the cleavage of the activated C(sp^2)−S bond via a reductive single electron transfer (SET) process in the presence of B_2Pin_2. At the same time, the neutral *S*-motif, namely dialkyl-thioether, was released from intermediate **I** and could be stabilized by binding to B_2Pin_2 by electron donation. On the other hand, pyridine could bind to the boron center of B_2Pin_2 to give a hereroleptic complex **III**, which could be seen as an activated borylation reagent. Thus, borylation of the aryl-radical intermediate by boron transfer from **III** afforded the target borylated product, along with the pyridine-complexed boryl-radical **IV**. The open-shell intermediate **IV** was finally transferred to the corresponding pyridinium **V** through a SET-oxidative process.

In conclusion, a novel and efficacious strategy for the generation of an aryl radical from aryl sulfoniums via C−S bond activation under photoirradiation has been reported, thus enabling the transition-metal-free borylation reaction. A wide range of arylboronates can be easily prepared, representing a practical application of aryl sulfonium salts in photoredox organic synthesis. Furthermore, this methodology will likely also be of great help to the late-stage functionalization of boron-based compounds for the synthesis of much more complex organic molecules.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.9b03850.

General information, experimental procedures, compound characterizations, and NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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