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To be cited as: *Chem. Eur. J.* 10.1002/chem.202004692

Link to VoR: https://doi.org/10.1002/chem.202004692

WILEY-VCH

10.1002/chem.202004692

(*o*-Phenylenediamino)borylstannanes: Efficient Reagents for Borylation of Various Alkyl Radical Precursors

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Dedicated to Professor Ilhyong Ryu on the occasion of his 70th birthday

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Abstract: (*o*-Phenylenediamino)borylstannanes were newly synthesized to achieve radical boryl substitutions of a variety of alkyl radical precursors. Dehalogenative, deaminative, decharcogenative, and decarboxylative borylations proceeded in the presence of a radical initiator to give the corresponding organic boron compounds. Radical clock experiments and computational studies have provided insights into the mechanism of the homolytic substitution (S_H2) of the borylstannanes with alkyl radical intermediates. DFT calculation disclosed that the phenylenediamino structure lowered the LUMO level including the vacant *p*-orbital on the boron atom to enhance the reactivity to alkyl radicals in S_H2. Moreover, C(sp^3)-H borylation of THF was accomplished using the triplet state of xanthone.

Alkyl boronates represent valuable synthetic intermediates that are readily transformed into various functional compounds.[1–6] Therefore, much effort has been spent into the development of efficient synthetic methods. Amazing progress has been made in transition-metal-catalyzed borylations.[7–10] On the other hand, protocols mediated by main-group-element reagents without transition metal catalysts have also been promising. Electrophilic borylation of organometallic compounds[11] and hydroboration of alkenes[12] are recognized as practical methods, but these methods suffer from incompatibility with functional groups and poor regioselectivity, respectively. Several borylating reagents have been used to accomplish boryl substitution reactions leading to alkyl boronates without transition metal catalysts (Figure 1A). Boryllithium has been employed in the borylation of alkyl chlorides,[13] but their high level of reactivity narrows both the substrate scope and the functional group tolerance. Although borylsilanes act as borylating reagents, applicable substrates are limited to primary alkyl bromides and silylation proceeds as an unavoidable side-reaction.[14] Boron dianion cluster ($B_6H_6^{2-}$) reacts with primary and secondary sulfonates as well as primary alkyl bromides and iodides to give alkylboronic esters,[15] but only one boron atom in the cluster is consumed for C-B bond formation and other boron atoms become waste. Recently, trapping alkyl radical intermediates by diboron compounds has opened a new avenue for the access to various aliphatic boronic esters (Figure 1B).[16] To date, various radical precursors including alkyl halides,[17–21] carboxylic acid,[22–26] amine,[27–29] and alcohol derivatives[30–32] have been revealed as applicable substrates for radical borylations. Available substrates are restricted, however, by their own reduction potentials because the generation of alkyl radical intermediates from the substrates relies on single electron transfer (SET) in almost all cases. Therefore, the use of alkyl chlorides as substrates remains challenging due to their lower reduction potentials (Table S1) regardless of the ready availability. Melchiorre has reported the borylation of alkyl chlorides using an organocatalyst (Figure 1C), but the applicable substrates are limited to primary benzylic and allylic chlorides.[19]

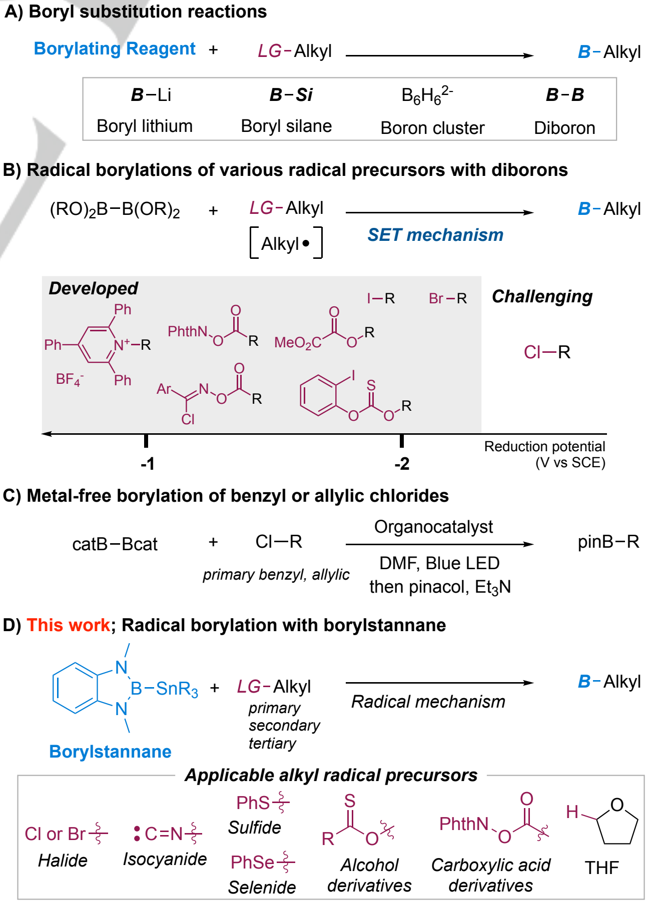

Figure 1. (A) Borylating reagents giving aliphatic boron compounds in boryl substitutions. (B) Radical borylations using diborons and the chart of reduction potentials of each radical precursor. (C) Borylation of alkyl chlorides using a nucleophilic organocatalyst. (D) This work; Radical borylation with borylstannane.

Herein, we report that (*o*-phenylenedamino)borylstannanes were newly synthesized and employed as borylating reagents to access aliphatic boronates from various alkyl chlorides including secondary and tertiary ones (Figure 1D). Borylstannanes were used for radical reactions for the first time. The present method allows the borylation of isocyanides, selenides, sulfides, and alcohol or carboxylic acid derivatives. In particular, this is the first report of radical borylative desulfurization and deselenation. In addition, radical $C(sp^3)$-H borylation of THF was achieved using photoexcited aryl ketone via the process of hydrogen atom transfer (HAT).

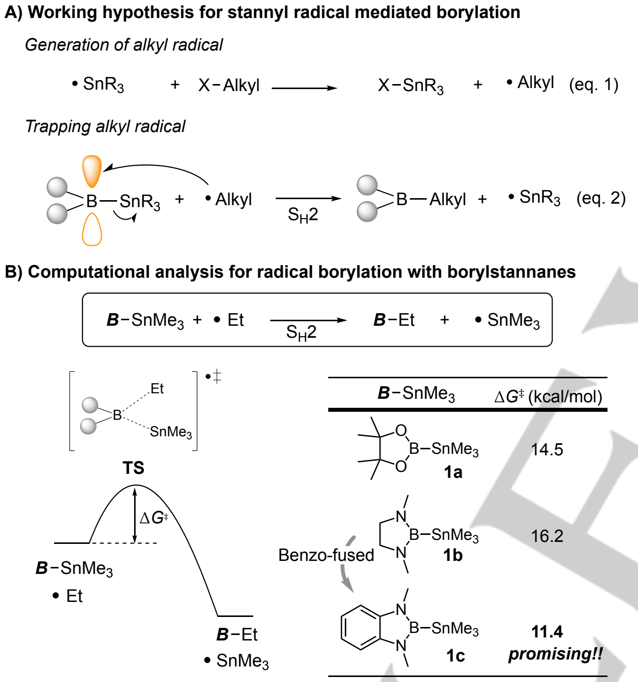

Figure 2. (A) Working hypothesis for borylation using borylstannanes. (B) Computational studies of the radical borylation step using borylstannane **1a**-**1c** ((U)M062X/6-31+G(d,p) for H, B, C, N, O and LANL2DZ for Sn).

A working hypothesis for radical borylation with borylstannanes is depicted in Figure 2A. First, trialkylstannyl radicals react with alkyl radical precursors (X-Alkyl) to afford alkyl radicals (eq. 1).[33,34] Next, the reaction of borylstannanes with the alkyl radicals proceeds via an S_H2 mechanism (eq. 2).[35–37] To examine candidates that could be efficient borylstannanes, we estimated the activation energy of the reaction of alkyl radicals with borylstannanes via DFT calculation (Figure 2B). The reaction of pinacolateborylstannane **1a** with an ethyl radical proceeded via the S_H2 mechanism, and its activation energy is a feasible value. A synthetic method for **1a**, however, has unfortunately not been developed, which likely is because of its unstable nature.[38] A higher activation barrier was estimated for reaction of the known isolable borylstannane **1b**, which possesses an ethylenediamino group.[39,40] The present radical borylation would proceed via the interaction of a vacant *p*-orbital at the boron atom with the SOMO of the alkyl radical (eq. 2). Therefore, we expected phenylenediaminoborylstannane **1c** to improve the efficiency of radical borylation, because the energy level of the LUMO, which includes the vacant *p*-orbital of the boron atom, is lowered by the benzo-fusion on the ethylenediaminoboryl group to allow a more feasible interaction with the SOMO of alkyl radicals. In fact, the activation energy of the borylation using **1c** is lower than that of either **1a** or **1b**.

We started screening borylating reagents in the borylation of alkyl chloride **2a** based on our calculation results (Table 1). The synthesis of borylstannanes **1c-1f** was successfully achieved via electrophilic substitution of (*o*-phenylenediamino)borylbromides with stannyllithium. They were isolated using silica gel column chromatography and kept at room temperature under a nitrogen atmosphere. In particular, borylstannane **1c** was characterized by X-ray crystallographic analysis, which revealed a trigonal planar structure for the boron center and a tetrahedral structure for the tin center. The bond length of B-Sn (2.249(4) Å) is longer than the reported B-Si (2.03 Å) bond of $(pin)B-SiPhMe_2$.[41] By using (phenylenediamino)borylstannane **1c,** the reaction of **2a** in the presence of V-40 as a radical initiator at 100 °C successfully gave the borylated product **A**. Because the formed diamonoboryl product **A** was too air-sensitive for storage, it was treated with pinacol under acidic conditions to quantitatively form the alkylboronate **3a** as an isolable compound. Tributylstannyl-substituted one **1d** proved to be the best borylating reagent. In contrast, the reaction of **1b** resulted in a low yield as expected from the calculated result discussed in Figure 2. Dichloro-substituted borylstannane **1e** gave a lower yield than **1d**. *N*,*N*'-di-isopropyl-substituted borylstannane **1f** afforded a moderate yield probably owing to the steric hindrance. Borylsilanes (**1g** and **1h**) and diboron **1i** both failed in reactions that were either sluggish or non-existent, respectively. These results underscore the advantage of a stannyl radical over either silyl or boryl radicals in terms of the proposed radical chain mechanism (Figure 2A). Our extensive screening of radical initiators, solvents and reaction temperatures is described in the Supporting Information (Tables S2-3).

Table 1. Comparison of Reactivities Between Borylating Reagents in the Reaction of Phenethyl Chloride **2a**.[a]

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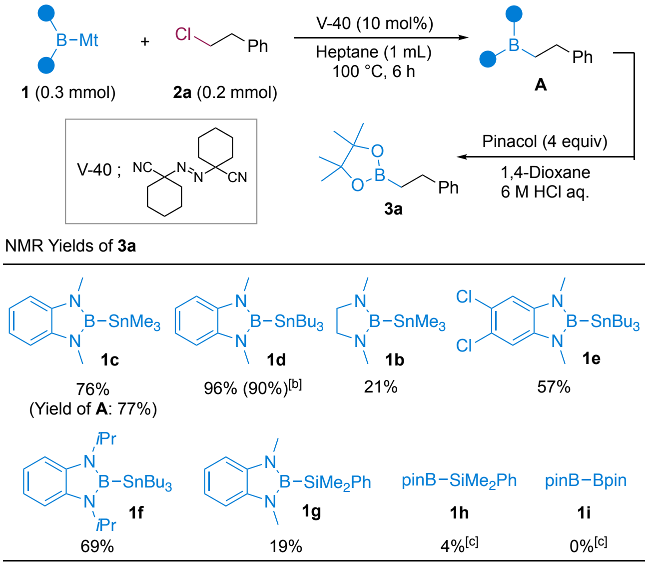
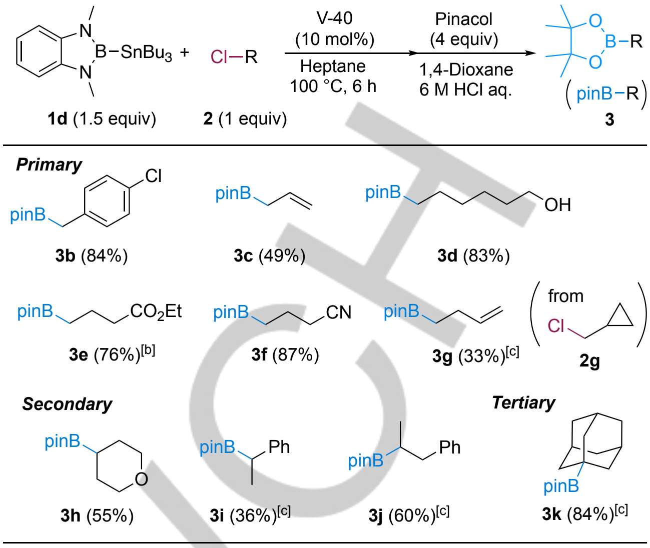


[a] Borylating reagent **1** (0.3 mmol), 2-phenethyl chloride **2a** (0.2 mmol), V-40 (0.02 mmol), and heptane (1 mL) at 100 °C for 6 h; pinacol (0.8 mmol), 1,4-dioxane (1 mL), 6 M HCl aq (1 mL), rt, 2 h. Yields were determined by ^{1}H NMR analysis. [b] The yield of isolated product **3a** is shown. [c] Without pinacol treatment.

With the optimized conditions in hand, the scope of alkyl chlorides was evaluated (Table 2). *p*-Chlorobenzyl chloride successfully underwent borylation to give boronate **3b** with an intact aryl chloride moiety.[42] Allyl chloride also gave the allyl boronate **3c**, which shows the alkene moiety is tolerated, but the yield was moderate because the stability and less reactivity of the allyl radical disturbs the borylation. Primary alkyl chlorides bearing hydroxy, ethoxycarbonyl, and cyano groups were converted into the corresponding boronates (**3d**-**3f**) in high yields. The reaction of cyclopropylmethyl chloride **2g** gave the ring-opening product **3g** exclusively,[43] which supported the radical mechanism. It is noteworthy that secondary and tertiary alkyl chlorides were applicable to the present borylation in contrast to the previous reactions.[19] 4-Chlorotetrahydropyran and 1-phenethyl chloride worked well to afford the target products (**3h** and **3i**). 2-Chloro-1-phenylpropane turned out to be a suitable substrate for this reaction, giving boronate **3j**. 1-Chloroadamane smoothly provided the corresponding boronate **3k**.

Table 2. Substrate Scope of Alkyl Chlorides.[a]



[a] Borylstannane **1d** (0.6 mmol), alkyl chloride **2** (0.4 mmol), V-40 (0.04 mmol), and heptane (2 mL) at 100 °C for 6 h; pinacol (1.6 mmol), 1,4-dioxane (2 mL), 6 M HCl aq (2 mL), rt, 2 h. Yields of isolated products are shown. [b] TsOH•H_2O (4 equiv) was used instead of HCl. [c] Borylstannane **1d** (0.6 mmol), alkyl chloride **2** (0.2 mmol), V-40 (0.1 mmol).

Borylstannane **1d** was applied to the reaction with other alkyl radical sources instead of alkyl chlorides (Table 3). Deaminative borylation of isocyanides, which are readily prepared from amines, was accomplished under the same conditions as the borylation of alkyl chlorides. Benzylic isocyanides (**2l**, **2m**) and cyclohexyl isocyanide **2n** were transformed into the corresponding boronic esters.[44] Deselenative borylation of phenyl selenide **2o** proceeded to give β-oxyboronic esters. *p*-Methylbenzyl phenyl sulfide **2p** was used as a radical precursor and the radical borylative desulfurization proceeded in a good yield.[45] Xanthate **2q** from cholesterol and thionocarbamate **2r** from epiandrosterone reacted with the retention of stereochemistry and good diastereoselectivity. Decarboxylative borylation of phthalimide esters (**2s**, **2t**) from proline and indomethacin successfully afforded the corresponding products.

Table 3. A Series of Radical Boprylations Using Various Radical Sources.[a]

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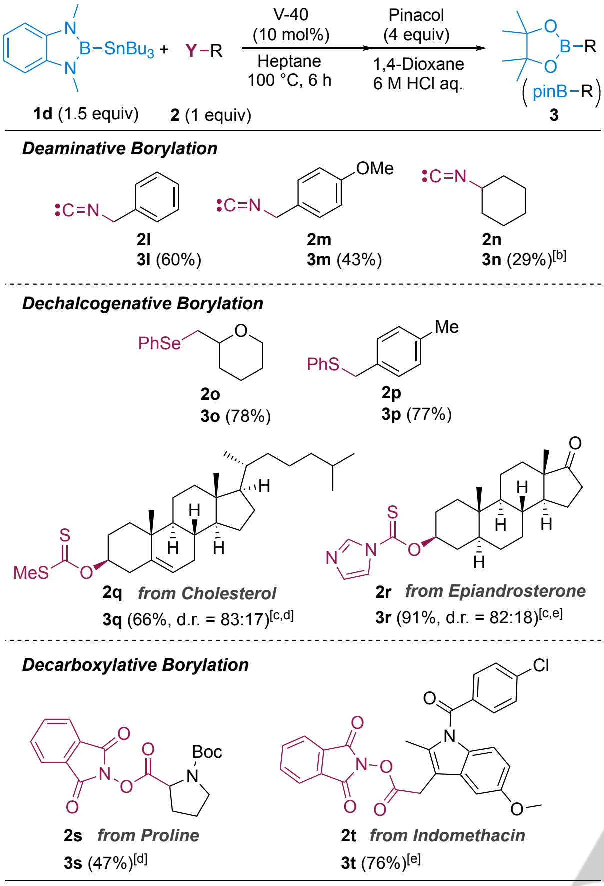


[a] Borylstannane **1d** (0.3 mmol), alkyl radical precursor **2** (0.2 mmol), V-40 (0.02 mmol), and heptane (1 mL) at 100 °C for 6 h; pinacol (0.8 mmol), 1,4-dioxane (1 mL), 6 M HCl aq (1 mL), rt, 2 h. Yields of isolated products are shown. [b] Reaction temperature: 120 °C. [c] Borylstannane **1d** (0.6 mmol), alkyl radical precursor **2** (0.2 mmol), V-40 (0.1 mmol). [d] TsOH·H$_2$O (4 equiv) was used instead of HCl. [e] 1,4-Dioxane was used instead of heptane.

We performed radical clock experiments[46–48] to evaluate the reaction rate for the S$_H$2 step. 6-Bromo-1-hexene **2u** was reacted with an excess amount of borylstannane **1** (Figure 3). The pseudo-first-order rate constant for the homolytic substitution reaction of the borylstannane with 5-hexen-1-yl radical **B** was estimated from the product ratio (***Linear***/***Cyclic***), the concentration of borylstannane, and the known cyclization rate constant (Figure 3A, eq. 3). Then, the rate constants for radical borylations of 5-hexen-1-yl radical **B** using **1c** and **1d** at 80 °C were estimated to be 4.7 x 10^6 /M·s and 2.6 x 10^6 /M·s, respectively (Figure 3B). These rate constants for the borylation of 5-hexen-1-yl radical **B** were found to be slightly larger than that for the reduction with Bu$_3$SnH (1.1 x 10^6 /M·s at 80 °C).[48] In addition, the radical clock experiment was performed at different reaction temperatures and an Eyring plot gave the activation parameters: Δ$H^‡$ (2.68 kcal/mol), Δ$S^‡$ (22.0 cal/mol·K), and the activation energy Δ$G^‡$ (9.23 kcal/mol) (Figure S4). The experimental value of Δ$G^‡$ almost matched the calculations (11.4 kcal/mol in Figure 2B).

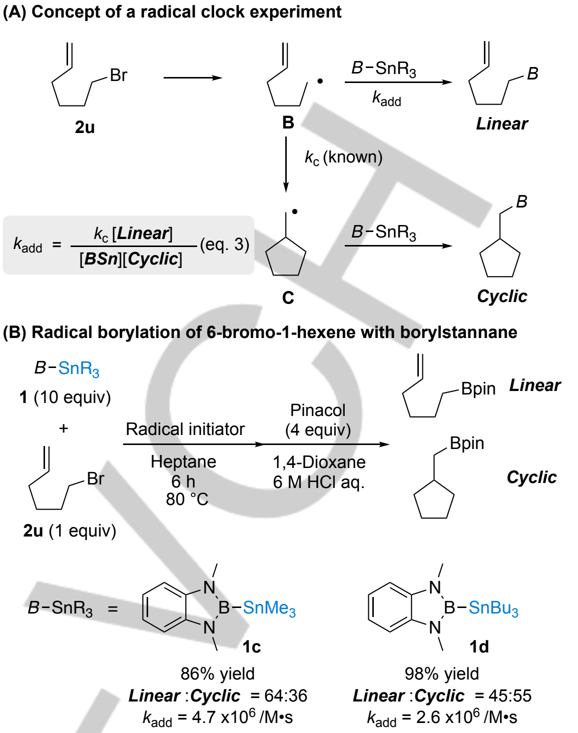


Figure 3. (A) Concept of the radical clock experiment using borylstannane. (B) Radical borylation of 6-bromo-1-hexene with borylstannane **1c** and **1d**.

The reaction mechanism for borylation of alkyl chlorides is presented in Figure 4A. In this reaction, alkyl radical **4** generated from the decomposition of V-40 reacts with borylstannane **1d** to form tributylstannyl radical **5**. The generated stannyl radical **5** reacts with alkyl chloride **2**, which leads to alkyl radical **6** and stannyl chloride **7**. The radical **6** is trapped by borylstannane **1d** to give the corresponding borylated product **8**, and stannyl radical **5** is regenerated. NBO analysis for the transition state of the S$_H$2 reaction between the ethyl radical and borylstannane **1c** revealed a significant interaction between SOMO (ethyl radical) and LP* (boron) (Figure 4B). This interaction is evident in the α spin-set and is estimated to amount to 49.8 kcal/mol. Considering the fact that the vacant *p*-orbital of the boron plays a vital role in the S$_H$2 mechanism, we evaluated the LUMOs of **1b** and **1c** (Figure 4C). In the case of **1c**, the vacant *p*-orbital of the boron effectively conjugates with the orbital on the phenylenediamine structure to delocalize the LUMO. On the other hand, the vacant *p*-orbital of the boron in **1b** is isolated. Therefore, the lower energy level of the LUMO of **1c** allows a larger interaction with the SOMO of the alkyl radical, which enables efficient borylation.

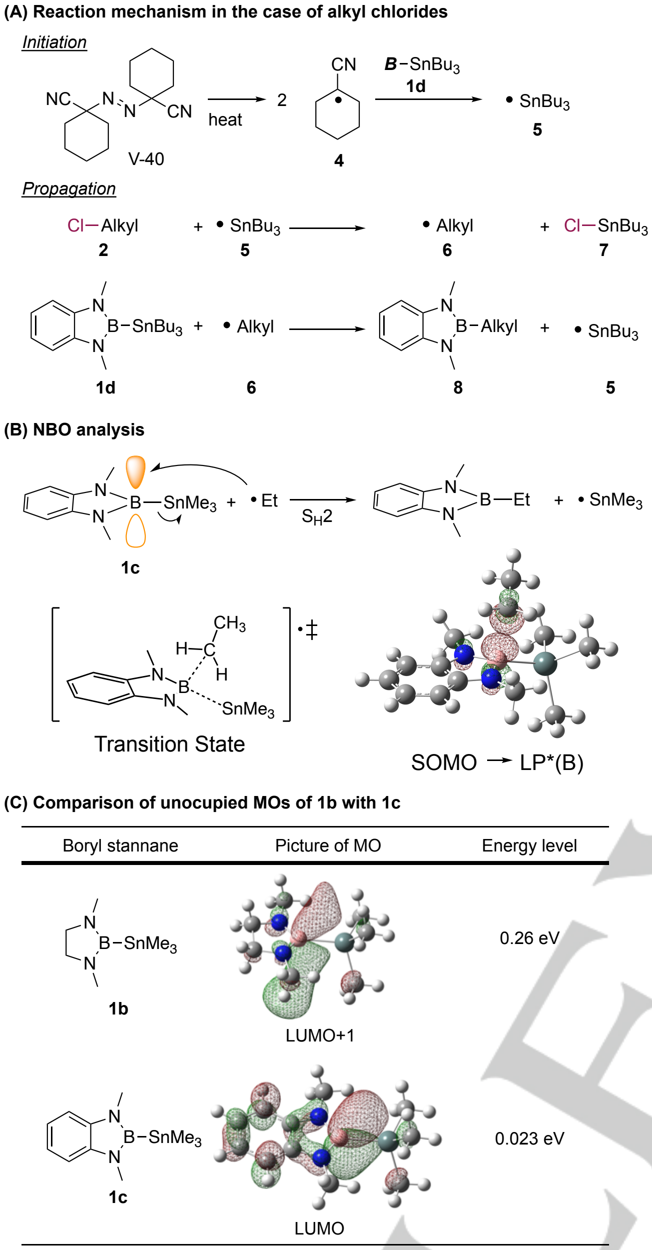
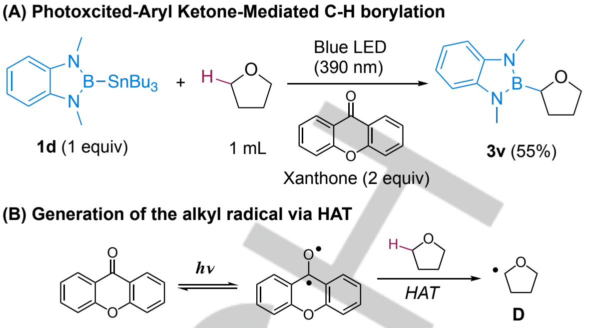


Figure 4. (A) Reaction mechanism when using alkyl chlorides. (B) Gauss View representation of key orbitals for the transition state. (SOMO --> LP*(boron) (49.8 kcal/mol) (UM062X/6-31+G(d,p) for H, B, C, N and LANL2DZ for Sn). (C) Unoccupied molecular orbitals of **1b** and **1c** (M062X/6-31+G(d,p) for H, B, C, N and LANL2DZ for Sn)

Instead of a borylation of the carbon-heteroatom bond using a radical initiator, we tackled C-H borylation with borylstannane via a radical pathway. Aggarwal reported the attractive C(sp^3)-H borylation of alkanes via HAT.[49] In our strategy, the HAT process undergoes by using the triplet state of aryl ketone to access alkyl radicals.[50–52] Therefore, via the use of xanthone under light irradiation, a radical C-H borylation of THF with borylstannane **1d** was carried out. Gratifyingly, the mono-borylated product **3v** was obtained (Scheme 1-A). The key for this reaction was the generation of a nucleophilic radical **D** via the HAT of a photoexcited aryl ketone (Scheme 1-B and Figure S7).



Scheme 1. (A) Radical C-H borylation of THF with borylstannane. Borylstannane **1d** (0.1 mmol), THF (1 mL), and xanthone (0.2 mmol) at room temperature under visible light irradiation for 12 h. An NMR yield of the product **3v** is shown. (B) The key step for generating an alkyl radical.

In conclusion, we have developed novel borylstannanes for borylating reagents. Various types of alkyl radical precursors were successfully applied toward dehalogenative-, deaminative-, dechalgenative-, decarboxylative-, and C(sp^3)-H borylation. The *o*-phenylenediamino structure in borylstannanes enables high efficiency for trapping alkyl radicals via S_H2 reactions. The present method provides a useful approach for syntheses of alkyl boronates, which are widely used in organic synthesis. Further investigations into the utility of borylstannanes in radical reactions are now under way.

Acknowledgements

This work was supported by JSPS KAKENHI grant number JP15H05848 in the Middle Molecular Strategy, and also by grant numbers JP16K05719, JP18K19079, JP18H01977, and JP19K05455. Y. N. acknowledges support from the Mitsui Chemicals Award in Synthetic Organic Chemistry, and from the Shorai Foundation for Science and Technology.

Keywords: boron • borylstannane • main group elements • radical reactions • tin

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[42] When 4-chlorotoluene was used for the present radical borylation, no borylation product was observed and the starting material was recovered.

[43] The yield of **3g** in the crude product determined by ^{1}H NMR was moderate (53%). However, the isolated yield was decreased during the purification by silica gel column chromatography.

[44] The generation of the radical would be very slow and the isocyanide **2n** is decomposed under heating conditions. Thus, the yield of **3n** was low. In fact, isocyanide **2n** was not recovered and the complicated by-products were observed.

[45] When 2-phenylethyl phenyl sulfide was employed as a radical precursor, the yield of the desired product was very low (11% yield). The simple alkyl radicals are hardly generated from alkylsulfides because C-S bonds are stronger than C-Cl bonds. Thus, the generation of the stabilized radical such as benzyl radical is necessary for the desulfurizative borylation.

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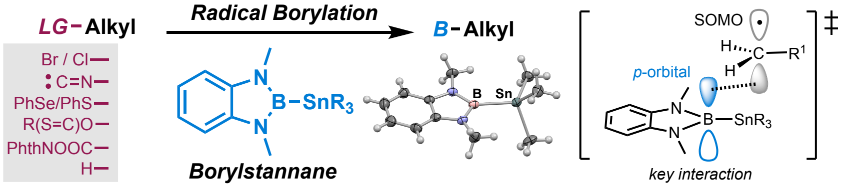

Newly synthesized (*o*-phenylenediamino)borylstannanes were utilized for radical borylations. Various alkyl radical precursors were applicable to dehalogenative-, deaminative-, dechalgenative-, decarboxylative-, and C-H borylation. The interaction of the *p*-orbital on the boron atom with the SOMO of the alkyl radical was a key to this reaction.