PhD. Thesis

Development of Borylation Methods for Allenes and Arynes

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Contents

1. General Introduction

1.1. Organoboron Compounds

Organoboron compounds have been useful synthetic intermediates due to their C–B bonds have been able to be converted into various bonds (C–C, C–O, C–N, C–halogen, C–metal, etc.).[1–10] The Lewis acidity of boron atoms can show the weak polarization in C–B bonds to generate nucleophilic carbon atoms in organoboron chemistry. In 1938, Johnson group reported that electron-rich C–B bonds were oxidized to C–O bonds by peroxides or oxygen (Figure 1B).[11–14] In 1956, Brown group also reported that the oxidation of C-B bonds after hydroboration of alkenes (Figure 1C).[15–17] Recently, C–heteroatom bonds, i.e., C–N and C–halogen bonds, were able to be constructed from C–B bonds (Figure 1D).[9] Another essential role of the organoboron compounds is a carbanion equivalent through transmetallation process with transition metal catalysts (Figure 2).[5] The substituents on the boron atom can be transferred to the palladium or other transition metals *via* activation of the boron center with Lewis bases, which has been commonly used for the generation of the organometallic species.[18–22] Thus, organoboron compounds are nowadays recognized as versatile synthetic intermediates in organic synthesis.

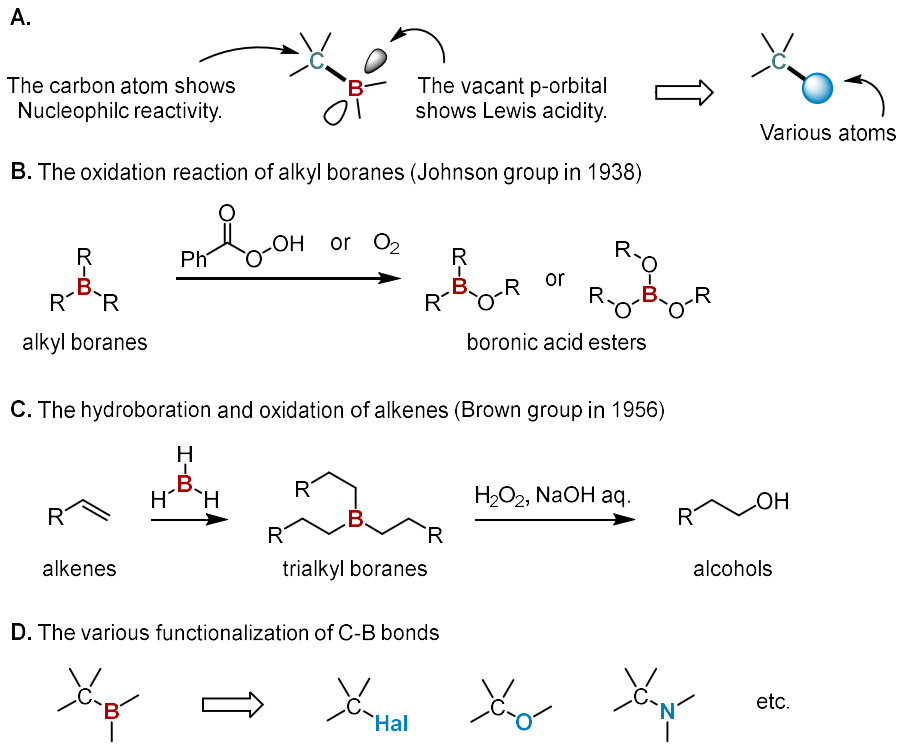


Figure 1. Transformation of C–B bonds to other bonds

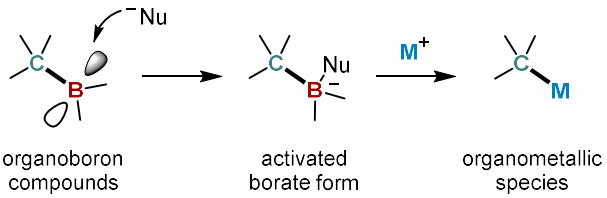


Figure 2. Organoboron compounds as transmetallation reagents. (M = Pd, Ni, Rh, Cu, Fe, etc.)

Boron-containing organic molecules have also been well explored as functional organic materials for optical, electronic, and pharmaceutical applications.[23–29] Triaryl boron moieties are used as electron-acceptor units in optical and electronic materials, i.e., fluorescent materials, electron transport materials (Figure 3).[23–29,30] Moreover, the innovative and practical examples of boron-containing drugs are the bortezomib, an anti-cancer agent that acts as a proteasome inhibitor and tavaborole, an anti-fungal drug (Figure 4).[28,31] The introduction of boron atoms in drug molecules can sometimes have positive effects. Furthermore, many types of boron catalysts have been developed (Figure 5).[29] For example, chiral oxazaborolidines are used as the catalyst for asymmetric hydrogenation of ketones, which is known as Corey-Bakshi-Shibata reduction.[32–36]

Organoboron compounds are important for synthesizing multi-functional organic materials. The development of novel organoboron compounds will contribute to numerous research fields. In this thesis, I focus on the synthesis of stereodifined organoboron compounds functionalized as alkenyl and diaryl borinic acid esters.

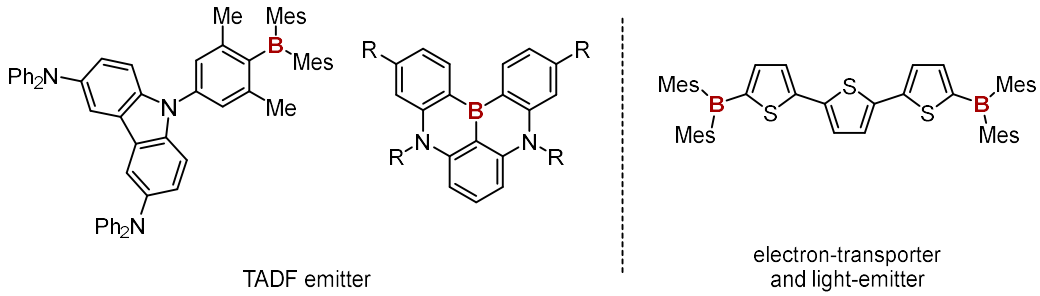


Figure 3. Applications of organoboron compounds in material chemistry

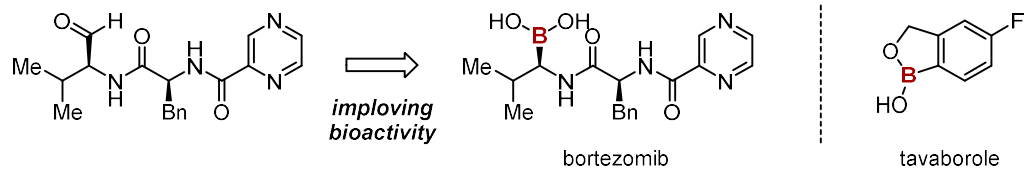


Figure 4. Boron-containing drugs “Bortezomib” and tavaborole in pharmaceuticals

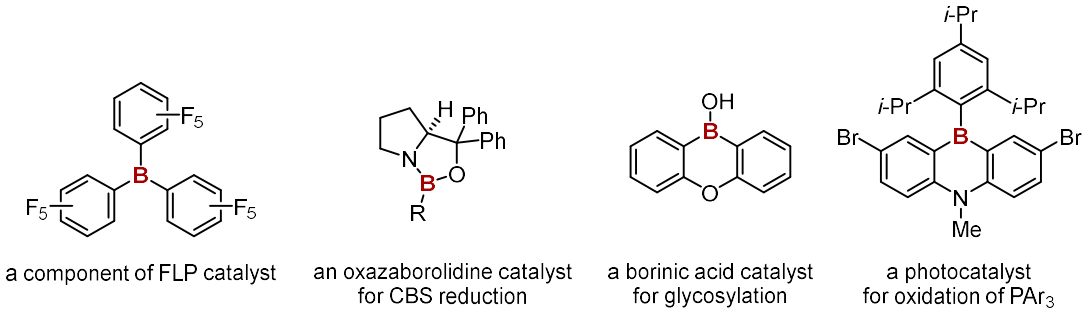


Figure 5. Applications of organoboron compounds in catalysts

1.2. Borylation Reactions of Organic Molecules

Traditionally, stoichiometric reactions of synthesizing organoboron compounds have been developed.[1,2] In 1860, Frankland group first synthesized an organoboron compound via nucleophilic substitution on an electrophilic boronic atom with an organozinc reagent (Figure 6A).[3,4] Such classical procedure, including boronic esters and halo boron compounds as electrophilic boron sources, and organolithium, -magnesium, and -zinc compounds for the nucleophilic organometallic reagents, has still been used for synthesizing the organoboron compound. Brown group developed a practical hydroboration reaction for introducing a boron atom in organic molecules in 1956 (Figure 6B).[15–17] The hydroboration of multiple bonds affords *anti*-Markovnikov-type organoboron compounds, which can be used for the preparation of alcohols via oxidation of the boron atom.

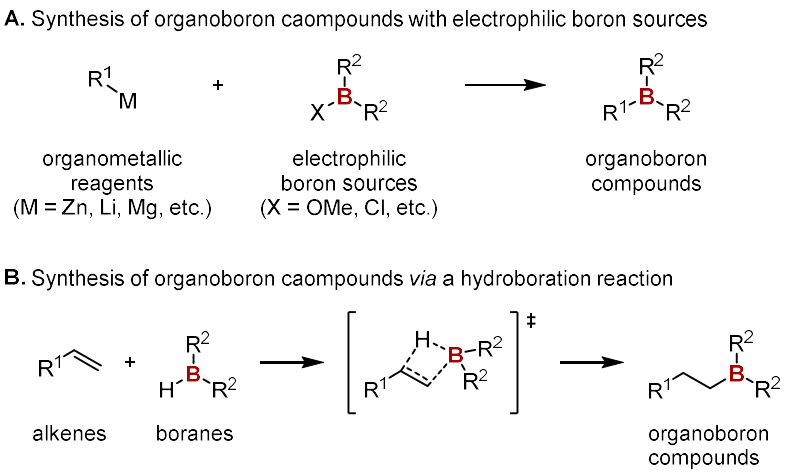


Figure 6. Traditional preparation methods of organoboron compounds

Recently, catalytic borylation methods are also used for preparing the organoboron compounds. In 1985, the first catalytic reaction is a rhodium-catalyzed hydroboration of alkenes using catechol boronate as a boron source by the Nöth group (Figure 7A).[37] This reaction was suitable for terminal alkenes with *anti*-Markovnikov selectivity to give the corresponding terminal alkyl boronates.[38,39] In 1995, Miyaura and Ishiyama developed a palladium-catalyzed borylative substitution of aryl halides with a diboron reagent as the boron source (Figure 7B).[40–43] Moreover, Hartwig group reported the first catalytic borylation of C(sp3)–H bonds with iridium- and rhodium catalyst in 2000 (Figure 7C).[44–46] Furthermore, Ishiyama and Hartwig found an iridium complex can catalyze the C(aryl)–H bond borylation reaction in 2002 (Figure 7D).[47,48] To date, many types of catalytic borylation reactions have been developed after those pioneering works.[49–54]

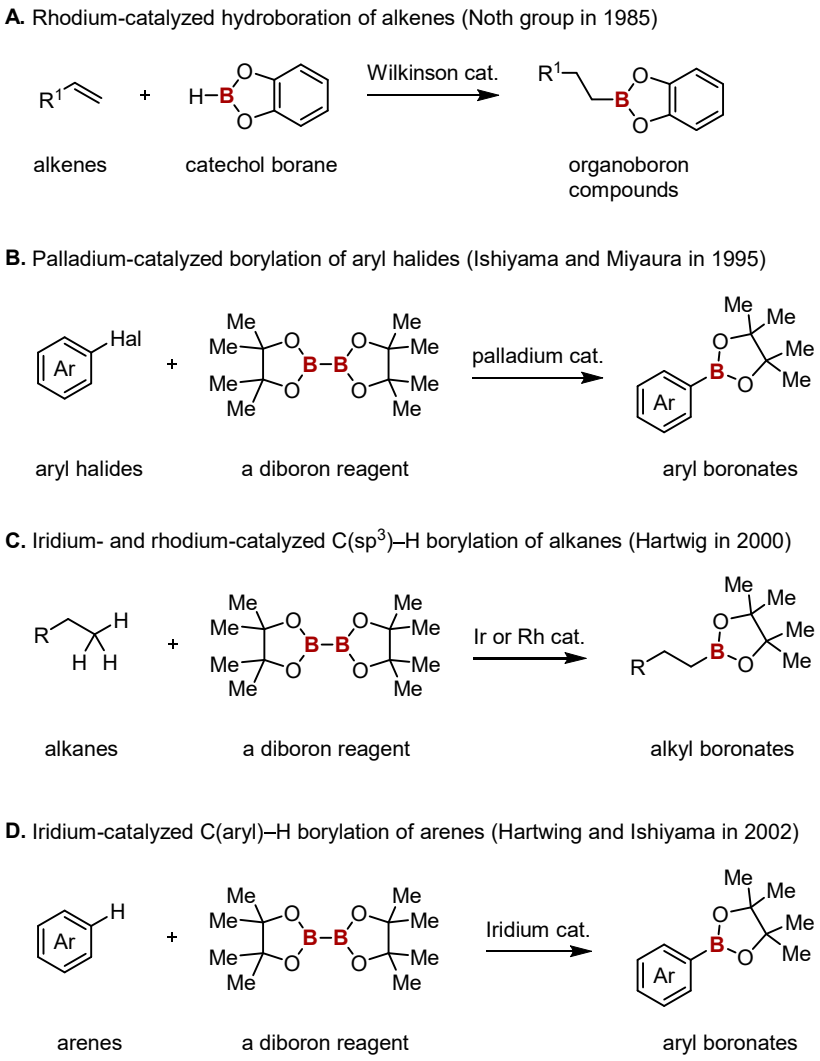


Figure 7. Catalytic preparation methods of organoboron compounds

1.3. Copper(I)-catalyzed Borylation Reactions with Diboron Reagents

In 2000, Hosomi and Ito group and Miyaura and Ishiyama group respectively developed the copper(I)-catalyzed borylation reaction of multiple bonds with a bis(pinacolate) diboron as the boron source (Figure 8A).[55–58] The catalytic amount of active species, boryl copper(I) intermediate, is generated *in situ* via *σ*-bond metathesis between the diboron reagent and a copper(I) alkoxide (Figure 8B).[59–61] The 1,2-addition of the boryl copper(I) species to enone substrates affords the alkyl copper(I) intermediate, and the subsequent protonation gives the corresponding hydroboration product with regeneration of the copper(I) alkoxide. This formal conjugate addition of the pinacolato boron group indicates the nucleophilicity of the boron atom, even though boron atoms have a strong electrophilic nature in general, mainly due to

the vacant π-orbital of the boron atom.[59] To date, a variety of electrophiles has been found to be suitable for the borylation reactions, for example, conjugated esters, allylic electrophile, carbonyl compounds, and imines (Figure 9).[59–61] In 2005 and 2007, Ito and Sawamura group developed the copper(I)-catalyzed enantiospecific and enantioselective *γ*-borylation of allylic electrophiles to furnish allylic boronates (Figure 10).[62,63] Recently, Ito group also reported that electron-deficient aromatic rings allowed to react with the boryl copper(I) species (Figure 11).[64–66]

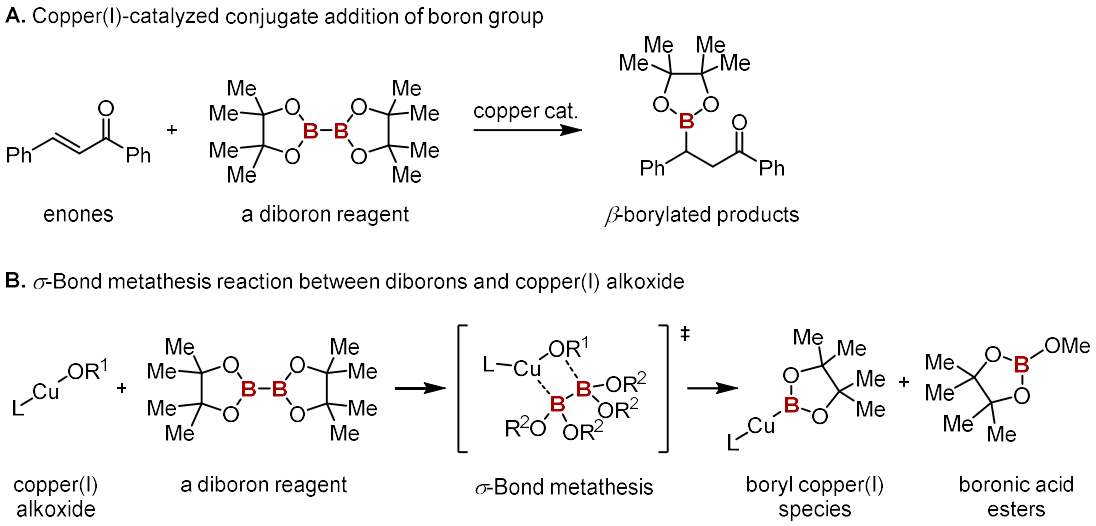


Figure 8. Pioneering works on borylation reactions with copper(I)-boron species

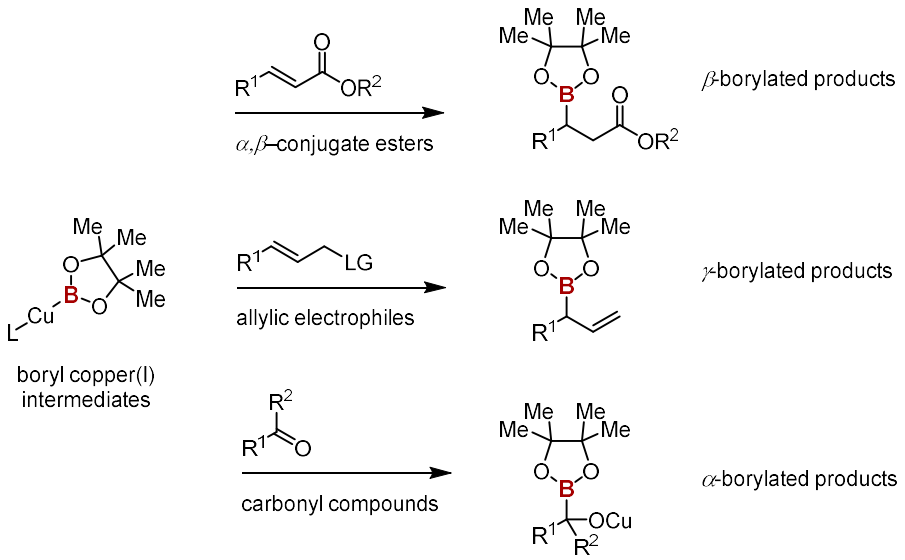


Figure 9. Reactions of various electrophiles with boryl copper(I) species

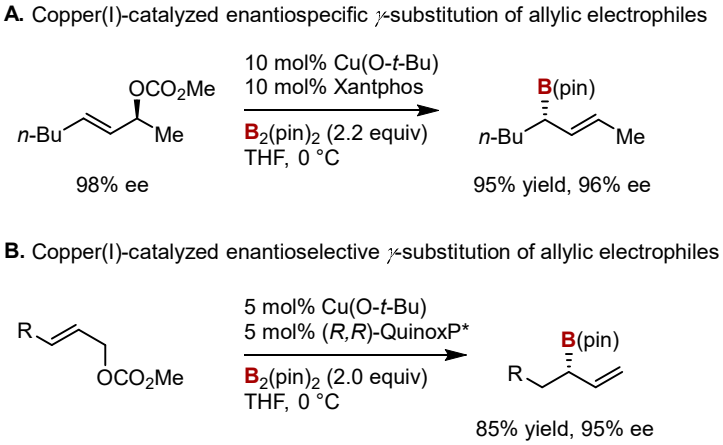


Figure 10. *γ*-Borylation of allylic electrophiles

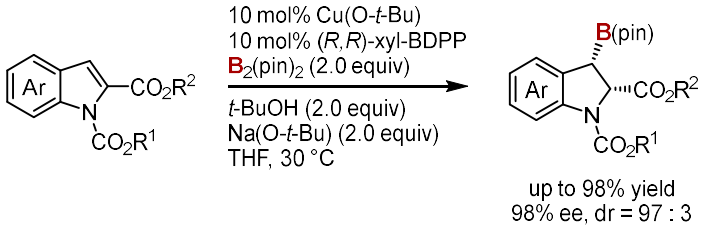


Figure 11. Dearomative asymmetric borylation of indole derivatives

In 2000–2001, Miyaura and Ishiyama reported that terminal alkynes produce alkenyl boronates by boryl copper(I) species (Figure 12).[56,57] This reaction proceeds *via* the boryl cupration (1,2-di-metallation) of the multiple bonds, then the generation of alkenyl copper(I) intermediate, which implies the boryl copper(I) species shows the reductive nature of multiple bonds. After that, many types of borylation reactions of the other multiple bonds have been developed, including alkenes, allenes, dienes, and en-ynes (Figure 13).[59–61] The trapping of the intermediate with several electrophiles allows difunctionalization reaction of multiple bonds.[67,68] Nevertheless, these three-component couplings are challenging due to the chemoselectivity issue, the reactions are useful for the preparation of highly functionalized and organoboron synthetic intermediates.

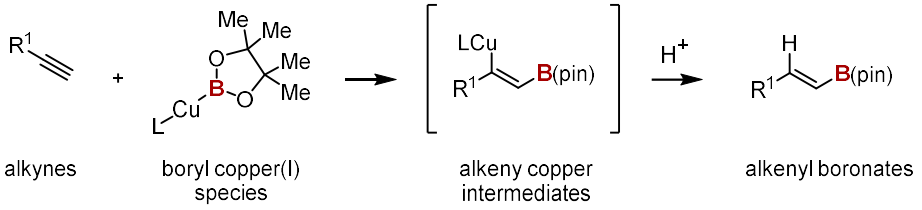


Figure 12. Copper(I)-catalyzed hydroboration of terminal alkynes

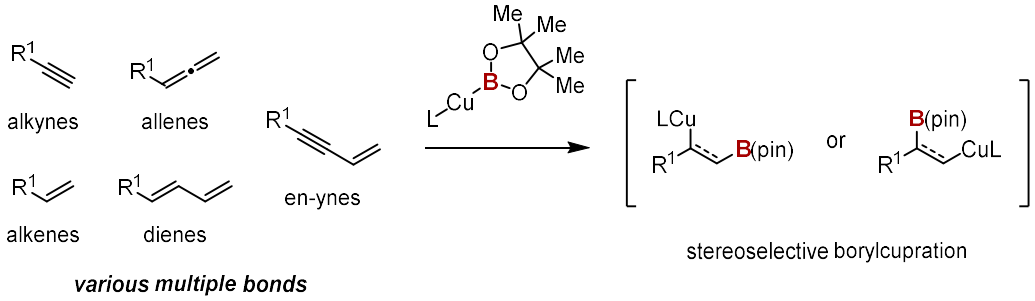
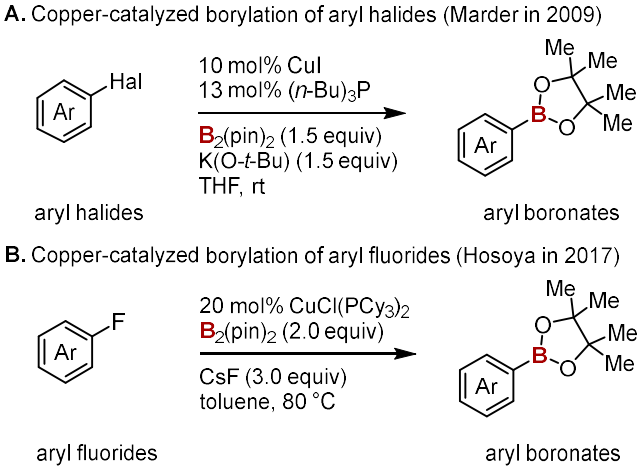


Figure 13. Copper(I)-catalyzed boryl-functionalization reactions of multiple bonds

The copper(I)-boron species are also able to proceed the boryl substitution of aryl and alkyl halides. In 2009, Marder group reported the first Miyaura borylation of aryl halides with copper(I) catalyst and diboron reagent (Figure 14A).[69] In 2017, Hosoya group achieved a copper(I)-catalyzed Miyaura borylation of fluoro arenes, which proceeds *via* a radical process (Figure 14B).[70] Moreover, Steel group, Marder group, Liu group and Ito group respectively reported the boryl substitution reaction of alkyl halides (Figure 14C).[71,72] Based on these pioneering works, the exploration of new borylation reactions of various multiple bonds still has been ongoing.



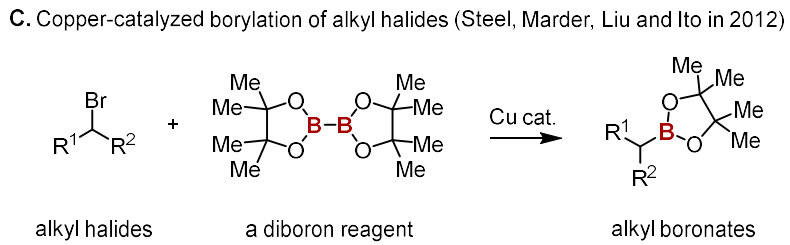


Figure 14. Copper(I)-catalyzed boryl substitution reactions on arenes

1.4. Boryl-Functionalization of Terminal Allenes with Copper(I) Catalyst

Allenes have two consecutive carbon-carbon double bonds. In the allene structure, the terminal carbon has sp^2-hybrid orbital, and the internal carbon has sp-hybrid orbital.[73] *Mono*-, *di*-, *tri*-, *tetra*-substituted allenes have been synthesized and widespread synthetic applications as electrophiles and nucleophiles have been developed.[74] Since the first borylation reaction of *mono*- or *gem*-disubstituted allenes was reported by Ishiyama and Miyaura in 1998, various catalytic- or non-catalytic borylation reactions of allenes have been developed, such as diboration, hydroboration, carboboration, aminoboration and silylboration, to afford alkenyl boronates or allylic boronates (Figure 15, upper side).[74] In the boryl-functionalization reactions of terminal allenes, various copper(I)-catalyzed boryl-functionalization of allenes to afford alkenyl boronates or allylic boronates have been explored (Figure 15, middle side).[75] The borylcupration of terminal allenes normally generates the allylcopper intermediates, which have the equilibrium between the internal alkene and the terminal alkene. Then, several nucleophiles trap those intermediates to afford the linear-type internal alkenes (α-position) and the branch-type terminal alkenes (γ-position). The major selectivity of the alkenyl boronate products is the latter type. As well as the allylboration reaction, the trapping electrophiles with allylcopper intermediate **1** possibly proceeds *via* six-membered-type transition state to afford the branch-type terminal alkenes. On the other hand, the reaction, which affords linear-type internal alkenes, was first achieved by Hoveyda group in 2014 with allylic phosphate electrophiles.[76] In the same year, Tsuji and Fujihara also developed similar reaction conditions.[77] Moreover, Brown group revealed aryl iodides could be used as the electrophiles for the linear-type selectivity.[78] In these reactions, bulky NHC ligands were used to afford the allylcopper intermediate **1**. Then, the oxidative addition of electrophiles was proceeded on the copper atom. After the reductive elimination, the linear-type internal alkenes were furnished. In chapters 2 and 3, the novel copper(I)-catalyzed boryl-functionalization methods for terminal allenes were developed using alkyl halide in chapter 2 or silylboranes in chapter 3.

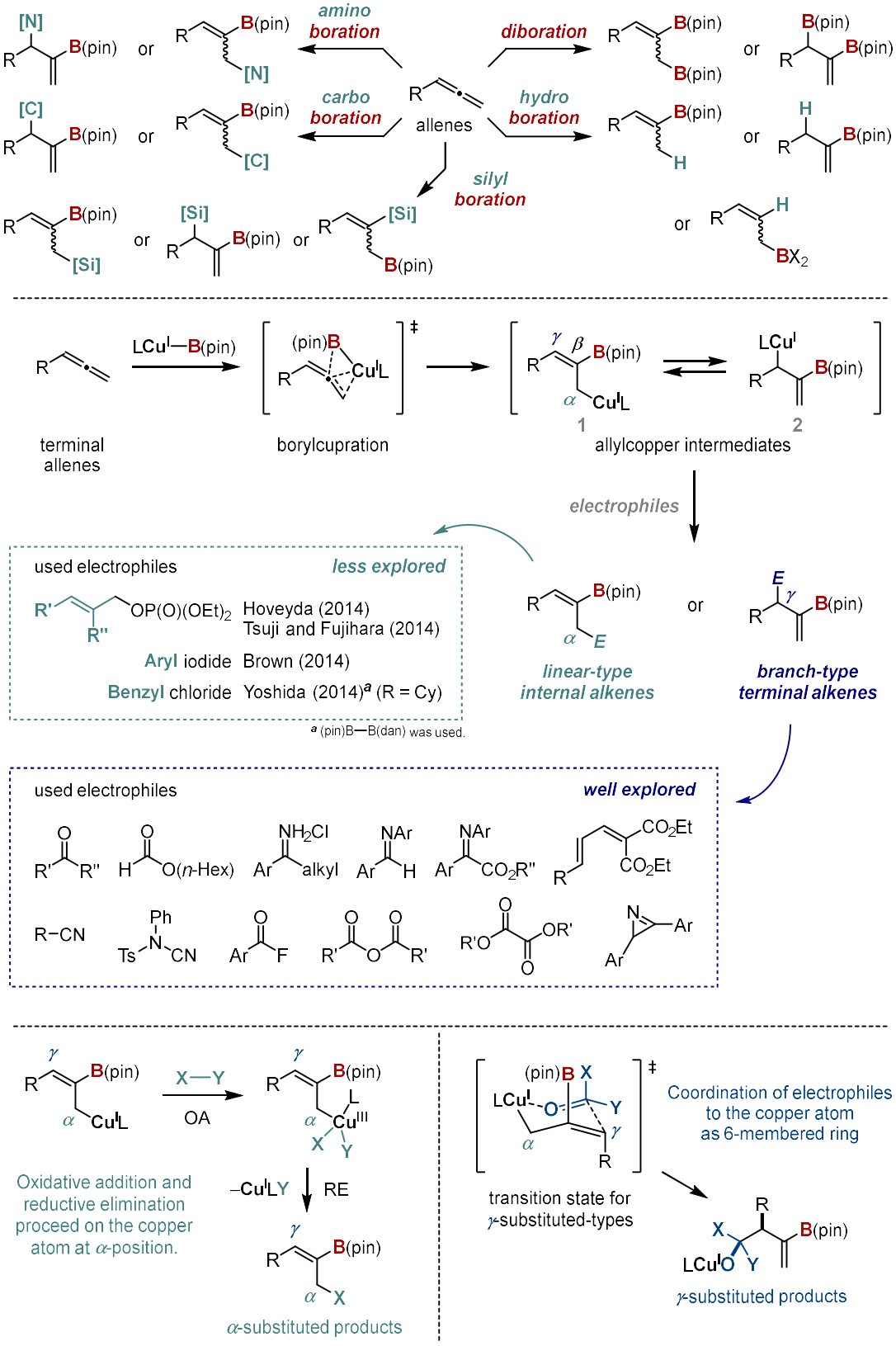


Figure 15. Regioselective boryl-functionalization for *mono*-substituted terminal allenes

For the related alkylboration reaction in chapter 2, in 2018, Ozawa and Ito reported the intramolecular alkylboration of *mono*-substituted terminal allenes using a copper(I)-catalyst to afford alkenyl boronates bearing cyclobutyl moieties (Figure 16, left).[75] Interestingly, intramolecular alkylboration of allenes shows γ-alkylation selectivity due to difference in the kinetic stability of copper(III)-cyclic intermediate before the reductive elimination steps. Moreover, in 2021, Ozawa and Ito reported the intermolecular alkylboration of *gem*-disubstituted terminal allenes with inverse regioselectivity to afford the allylic boronates bearing tetrasubstituted alkenes (Figure 16, right).[75] In this case, the steric repulsion between substituents on allenes and B(pin), and the space, which fits non-substituted side of terminal allenes lead to the inverse selectivity of borylcupration step to afford allylic boronates. In these reactions, structures of substituents on allenes and reaction fields controlled by ligands on the copper center are strongly related to the regioselectivity of the products.The related silylboration reactions are described in the introduction of chapter 3.

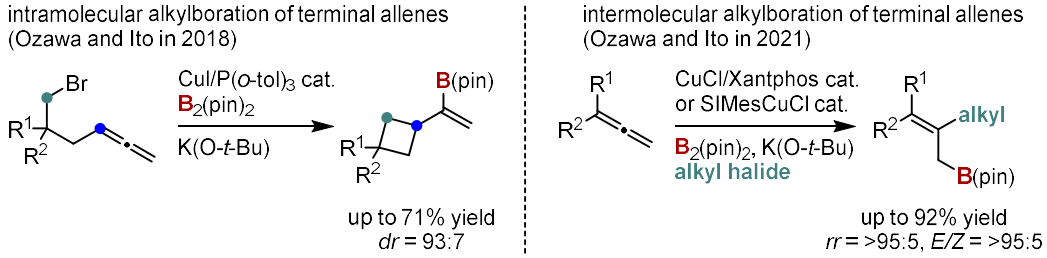


Figure 16. Regioselective boryl-functionalization for *mono*-substituted terminal allenes

1.5. Boryl-Functionalization of Arynes

Arynes are useful electrophilic intermediates, which have highly strained transient triple bonds on aromatic rings, and many methods for their generation and application to synthetic organic chemistry have been investigated.[79,80] To date, various arylation reactions have developed by means of their highly reactive carbon-carbon triple bond. Well-known aryne-generation methods are listed in Figure 17. Traditionally, arynes have been generated by a metalation of *ortho*-dihaloarenes.[81] This aryne intermediate immediately reacts with aryl-metal species under −78 °C *in situ* and it usually afforded diaryl-type products.[82] Since 1960, *ortho*-diazonium benzoate has been used as an aryne precursor.[83] This precursor has potentially explosive under by heat of about room temperature. Thus, it is generated *in situ* and used for reactions in the same flask. In 1983, Kobayashi developed silyl-triflate-type aryne precursor. It is gently activated by weak bases like CsF, KF, TBAF, Cs_2CO_3, K_2CO_3 etc.[79] This Kobayashi precursor has been applied to many aryne-containing reactions and it has been the most famous aryne precursor today.[80] After that, Furukawa and Suzuki respectively developed the aryne precursors, which are activated by organomagnesium

reagents or organolithium reagents.[84] In 2008, Kim group reported palladium-catalyzed generation of arynes *via* oxidative addition of the Ar–Br bond to palladium(0)-catalyst.[85] In 2013, Hosoya group achieved a generation of arynes from precursors using a B(pin) group as an acceptor for bases.[86] The relatively strong Lewis acidity of the boron atom promotes the coordination of butyl lithium reagents to the boron center below 0 °C and arynes gradually generate. Recently, the aryne precursor activated by LiHMDS was reported by Stuart.[87] This is easily prepared and air-stable iodonium salt, whose iodonium group is a leaving group. Furthermore, it has been known that chloranes bromanes, iodanes and oxonium salt have shown the reactivity of aryne precursors mildly activated by carbonate salts or phosphate salts.[88] Moreover, triple bonds on hetero-rings "hetero-arynes" have also been developed and applied to synthetic routes of complicated natural products and bioactive compounds.[89]

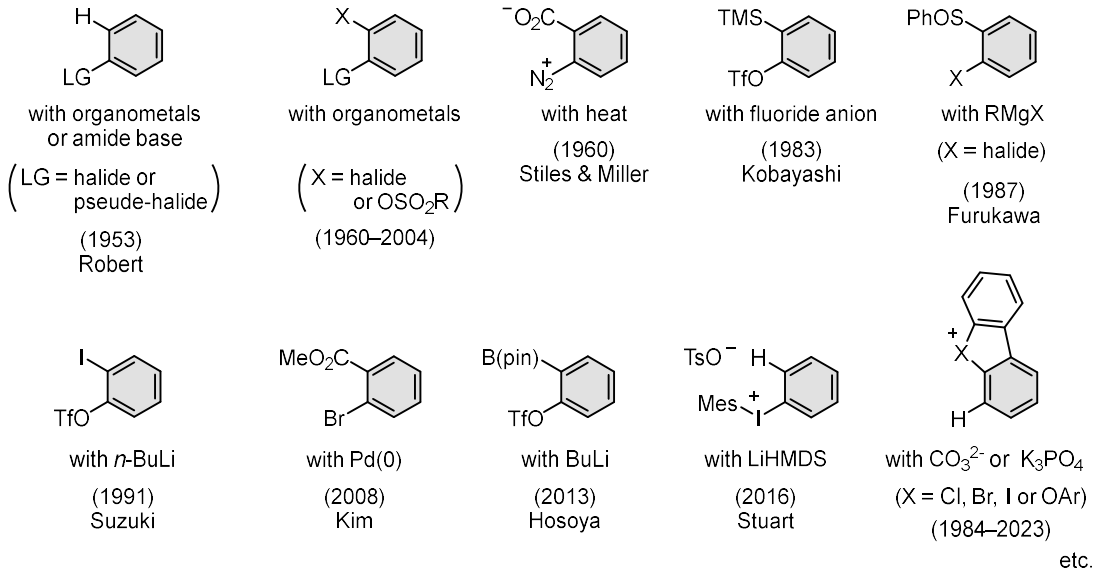


Figure 17. Representative aryne precursors

Arynes have possible four conjugation structures such as alkyne form, cumulene form, zwitterion form and diradical form.[90a] In these structures, most stable form is the alkyne form in terms of experimental and computational analysis (Figure 18a).[90b] In the experimental studies of arynes, several aryne-nickel complexes were isolated at the range from –90 °C to room temperature by NMR and single crystal X-ray analysis from 1985 to 2016 (Figure 18b).[91] In 2002, Wenger isolated the first palladium-aryne complex as a single crystal.[92] The benzyne-metal complexes are reactive as electrophiles and easy to become dimers or oligomers.[91,92] Today, three types of reactivities of arynes have been developed (Figure 18c).[80] One of the reactions is insertion reaction. Insertion reactions into various σ-bonds and π-bonds have been developed such as C–C, C–N, C–P, C–S, C–H, Si–N, Sn–Sn, Si–Si, B–B

etc.[80] Moreover, the reaction of arynes with catalytic, such as Pd, Ni, Pt and Cu catalyst, or stoichiometric organometal species, such as R–BX_2, R–SnX_3, R–MgX, R–ZnX, R–Li, has been reported to generate arylmetal species *in situ*. Also, three-component coupling reactions have been developed.[80] Electrophilic arynes are captured by nucleophiles, followed by the trapping aryl anion by electrophiles to produce the coupling products. The nucleophiles tend to have heteroatoms such as oxygen, nitrogen, sulfur, phosphorus, bromine. Furthermore, various cyclization reactions have been also reported. The reagents for the cyclization include alkenes, 1,3-dienes, azides, 1,3-diple-type reagents etc.[80]

Borylation of arynes has been the attractive method to obtain the 1,2-boryl-functionalized aromatic rings in one step. The pioneering work of this area is shown in Figure 19. In 2010, Yoshida achieved the first diboration of arynes with platinum(0)-catalyst.[93a] In this case, the catalytic amount of platinum(II)-B(pin) species, which was generated after the oxidative addition of $B_2(pin)_2$ to the platinum(0) atom, performed the boryl-metalation of arynes as the active species. After the borylation of the aryl-platinum bonds *via* reductive elimination, the desired 1,2-diboryl arenes were furnished and palatinum(0) species was regenerated. Moreover, the copper(I)-catalyzed diboration of arynes has been reported in 2012.[93b] The copper(I)-complexes, $B_2(pin)_2$ and potassium fluorides generated the borylcopper(I)-active species and it proceeded the borylcupration of arynes. After that, Oestreich applied the platinum(0)-catalyzed diboration conditions to the diboration of indolynes in 2015.[94] Uchiyama focused on the borylzincate nucleophilic species, which was formed by the diboron, dialkylzinc reagents and alkoxide bases.[95] The author used the borylzincate reagents and arynes, which were generated from 1,2-dihaloarenes as electrophiles, to afford the *ortho*-borylated arylzinc species *in situ*. Then, the added electrophiles captured them to produce the final products. Hydroboration of arynes also developed by Taniguchi and Curran. The first example was reported in 2013.[96a] They used the NHC-borane complexes as stable hydride source to obtain the hydroborated arene products in moderate to high yields. Furthermore, the aryne intermediates, which were generated by the intramolecular cyclization of the triyne-type substrates *in situ*, could afford the multifunctionalized borylarenes in one pot operation.[96b] Recently, Mizoguchi and Sasakura achieved the first carboboration of arynes with alkenylboronates activated by alkyllithium reagents in 2022.[97] They used the [B(pin), OTf]-type aryne precursor and sec-butyllithium for generation of arynes under the cold temperature condition. The nucleophilic addition of the activated alkenylborate species to arynes afforded aryl anion intermediates. Following 1,2-metallate rearrangement and the coordination of the aryl anion to the boron atom furnished the boron-containing cyclic intermediate as shown in the last scheme. The isolated products were obtained after oxidation with hydrogen peroxide aqueous solution in

up to 82% yield. According to these previously reported reactions, aryne insertion reactions into boron-metal bonds, boron-hydrogen bonds and boron-carbon bonds have been developed. However, insertion reactions of arynes into boron-oxygen bonds have been unexplored.

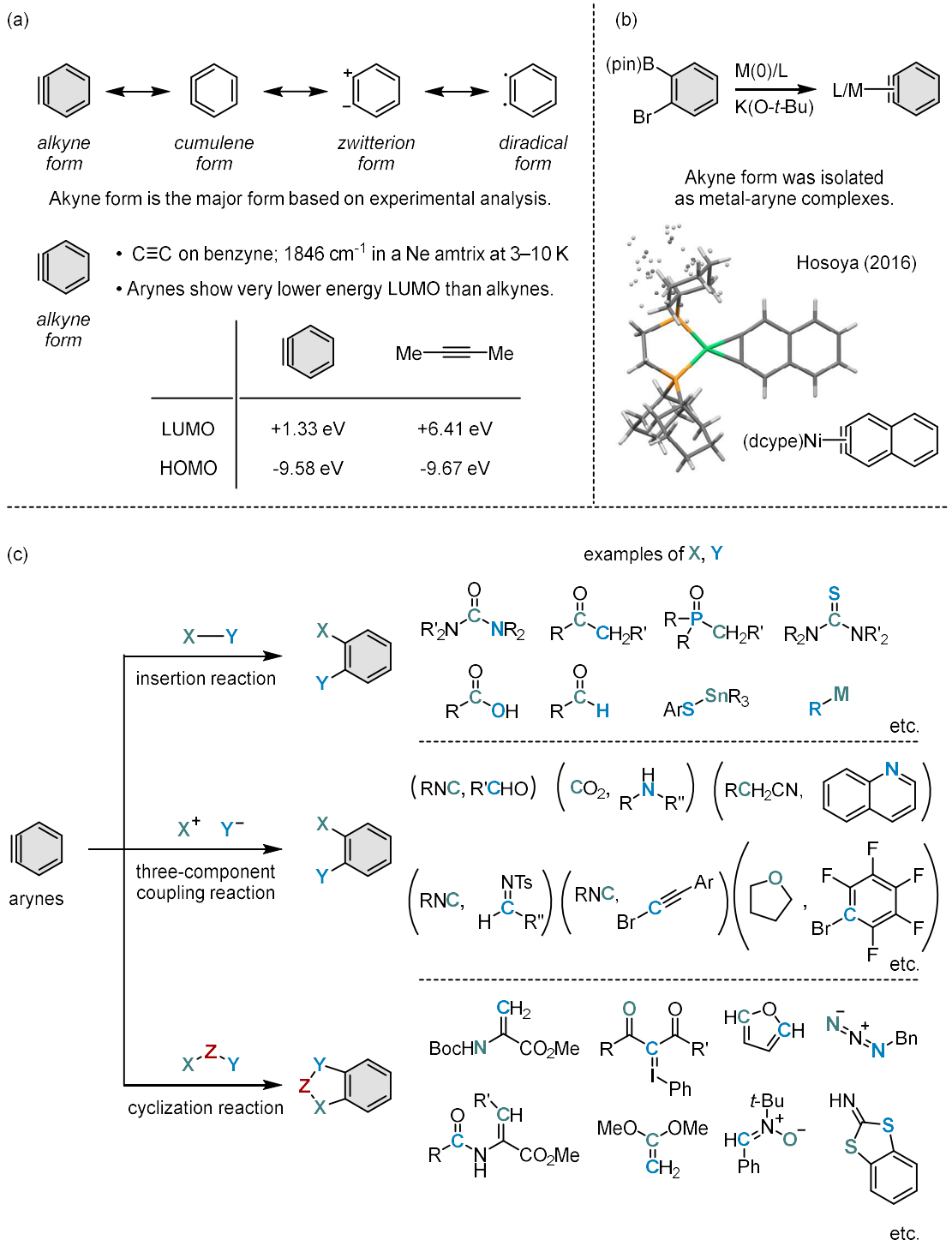


Figure 18. The reactivity of arynes

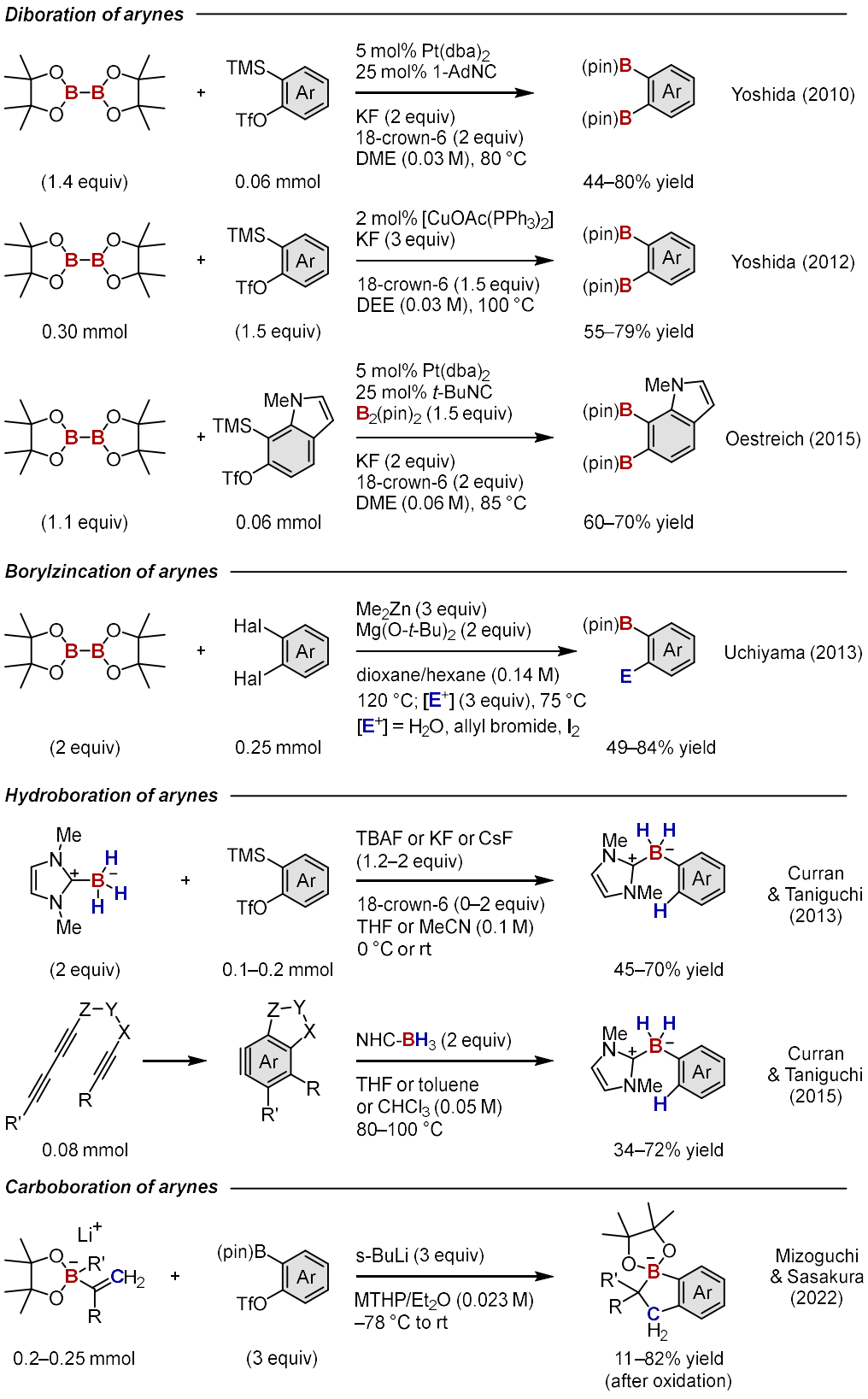


Figure 19. Borylation reactions of aryne intermediates

1.6. Selective Boron–Oxygen Bond Activation of Boronic Acid Derivatives

The B–O bond activation reactions are listed in Figure 20. Traditionally, the activation of B–O bond have been achieved by the protonation of the trialkoxylborate species.[1–5] The protonation and deoxylation from the boron center furnish the corresponding boronates or boronic acids (Figures 20a and 20b). Also, dehydroxylation reactions with dehydrating reagents afford the boroxines or boronic acid esters (Figure 20c and 20d).[1–5] Moreover, for synthesizing more stable boronic acid ester derivatives than boronic acid esters, MIDA borate, B(dan)-type compounds and cyclic triolborates have been developed, which contains dehydroxylation steps.[98] Synthesizing trifluoroborate salts with fluorinating reagents contains the dehydroxylation step (Figure 20e).[21] Additionally, high Lewis acidic boron reagents such as boron trichloride or boron tribromide promote the exchange reaction between a boron–oxygen bond and a boron–halogen bond (Figure 20f).[99] In 2014–2016, Blum developed the ring-closing intramolecular oxyboration of alkynes by alkoxyl catecholboronates and gold(I) catalyst (Figure 20g).[100] In this reaction, CF_3CO_2Na weakly coordinates the boron center to generate the catalytic amount of four-coordinated borate species *in situ*. Then, the nucleophilic addition of the oxygen atom in the borate to the alkyne is activated by gold(I) to generate the borylated benzofuran structure. In 2013 and 2014, Aggarwal reported the diastereo- and enantioselective allylboration reactions using aldehydes or ketones (Figure 20i).[101] In this reaction, trifluoroacetic acid anhydride (TFAA) was used as the activation reagent of borate species in the six-membered-ring-type transition state. In this transition state, TFAA is coordinated by the oxygen atom in the boron-containing five-membered ring moiety. Then, the boron-oxygen bond is cleaved to form the borinic acid ester. Recently, Dong reported the first ox-Matteson reaction in 2022 (Figure 20h).[102] In this reaction, the active species is trialkoxylborates generated by the coordination of the bormomethyllithium reagent. Then, the heating promotes the 1,2-rearrangement of the alkoxide group to afford the carbon-inserted products. The Matteson-type reactions, which affords mixture of *O*-migration products and *C*-migration products, have already been reported by Matteson and Aggarwal respectively.[103] In the carbene chemistry, Kusama reported the [1,2]-boron-Brook rearrangement to afford the one-carbon-inserted boron-containing six-membered rings using the photolysis of acylsilane compounds (Figure 20j).[104] According to these synthetic methods, there are five-types of boron-oxygen bond activation methods, **(i)** protic or Lewis acid promoted deoxygenation of tri- or dialkoxyl borate species, boronic acids such as (a), (b), (e), (f) and (i), **(ii)** oxygen atom exchanging such as (c), (d) and (j), **(iii)** benzofuran synthesis approach as (g), **(iv)** oxa-Matteson approach as (h). In chapter 4, I developed the novel ring-opening boron–oxygen bond cleavage method *via* oxyboration reaction of arynes to afford borinic acid cyclic esters.

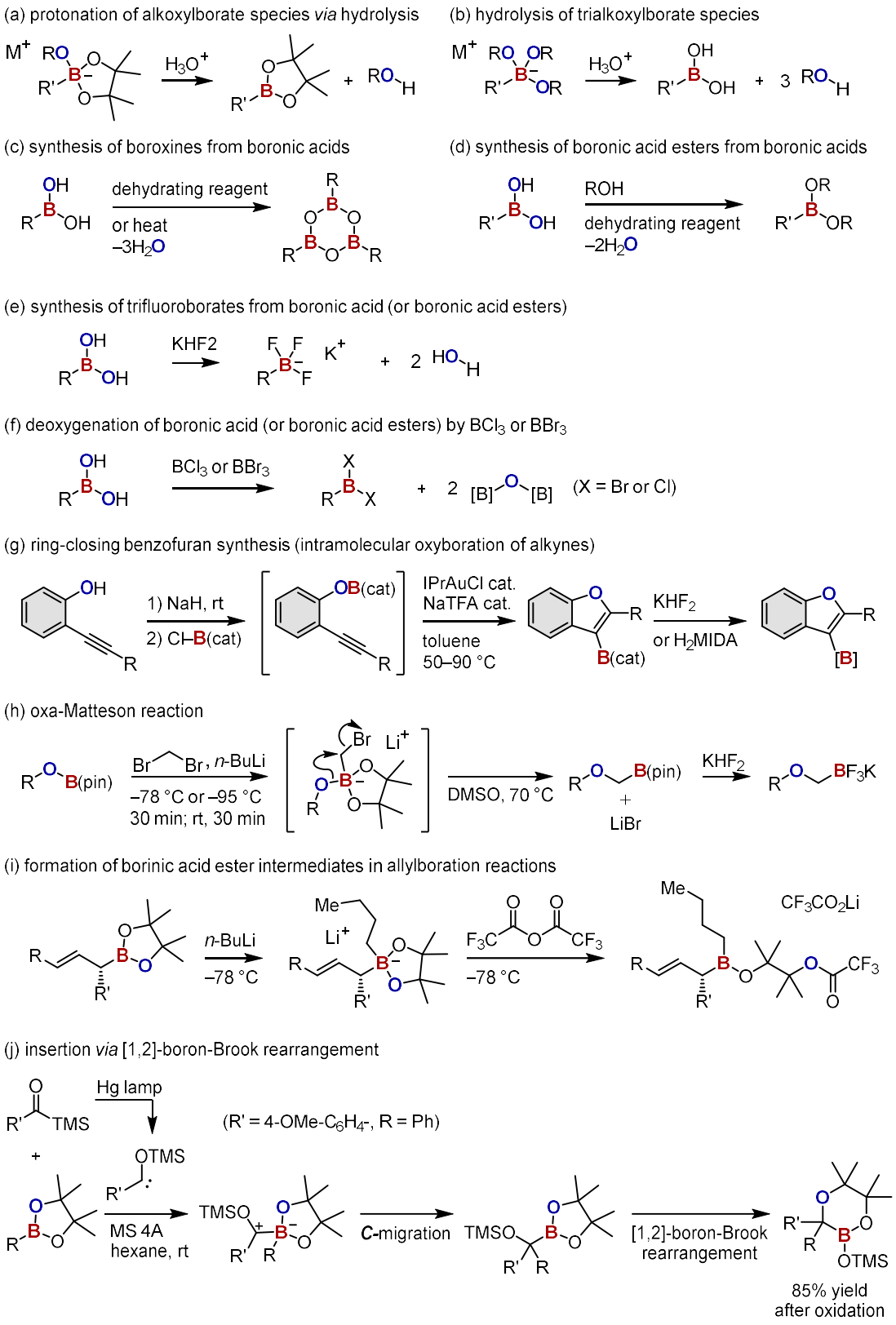


Figure 20. B–O bond activation in boron-containing compounds

1.7. Purpose of This PhD. Thesis

In this thesis, the purpose was to develop novel borylation methods of unique unsaturated carbon–carbon multiple bonds, which are allenes with two consecutive double bonds and arynes with electrophilic triple bonds on arenes.

1.8. References

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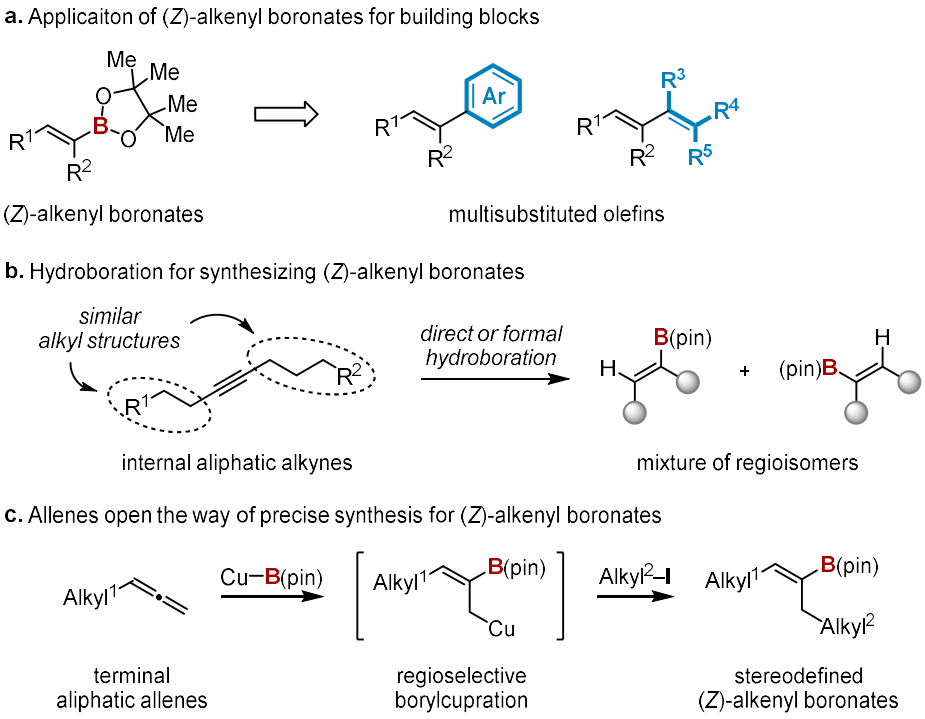
2. Copper(I)-Catalyzed Linear-Selective Alkylboration of Terminal Allenes for Synthesis of (*Z*)-Alkenyl Boronates

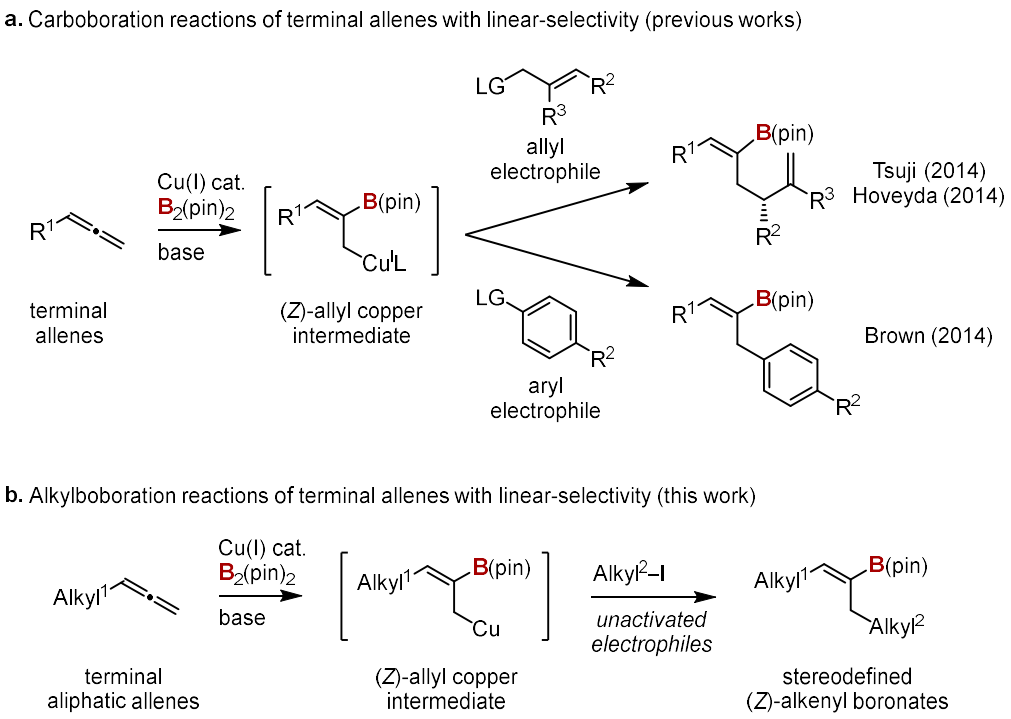
2.1. Introduction

Alkenyl boronates are widely used organometallic reagents due to the high stereospecificity in their applecations,[1–3] for example, Suzuki–Miyaura cross-coupling reaction. For this reason, stereoselective synthesis of alkenyl boronates is an important issue. In the case of synthesizing multi-substituted olefins such as styrene and diene derivatives shown in Scheme 1a, (*Z*)-alkenyl boronates are useful precursors for the sterically congested *cis*-alkene structure.[2,4] However, the synthesis of alkenyl boronates that have similar alkyl substituents ($Alkyl^1$ and $Alkyl^2$) is challenging (Scheme 1b).[2,5] Although catalytic and non-catalytic hydroboration reactions of internal alkynes are developed to access the internal alkenyl boronates,[6] the reactions show low regioselectivity without a directing group such as propargylic heteroatoms.[7,8] Recent significant development of synthetic methods has expanded the variety of alkenyl boronates. However, precise synthesis of aliphatic (*Z*)-alkenyl boronates still has crucial limitations.[9-12] Therefore, I planned to synthesize the alkenyl boronates *via* a copper(I)-catalyzed three-component coupling between *mono*-substituted allenes, alkyl iodides, and $B_2(pin)_2$, which is an intermolecular alkylboration of terminal allenes (Scheme 1c).[13] Perfectly controlling of the regio-, stereo-, and chemoselectivity, nucleophilic borylation of *mono*-substituted allenes and subsequent alkylation were able to furnish the (*Z*)-alkenyl boronates bearing two different alkyl groups. Carboboration of allenes is one of the direct and useful ways to access (*Z*)-alkenyl boronates (Scheme 2).[13] The regio- and stereoselective borylcupration of the terminal double bond of the *mono*-substituted allenes generate (*Z*)-allyl copper(I) intermediates, and the following carbon–carbon bond formation at the *α*-position with carbon electrophiles affords (*Z*)-alkenyl boronates. In 2014, Tsuji,[14a] Hoveyda,[14b] and Brown[14c] respectively reported intermolecular carboboration reactions of terminal allenes, and the corresponding products were obtained with high stereoselectivity (Scheme 2a).[15] However, those reactions have limitations of using allyl and aryl electrophiles, which are stable in basic conditions due to competing elimination of the leaving group with *β*-proton is avoided in such electrophiles. On the other hand, the use of simple alkyl electrophiles for the carboboration reaction is expected to be more challenging due to the side reactions caused by the decomposition of the alkyl electrophiles *via* *β*-elimination to produce alkenes.[8,16] Furthermore, a direct boryl substitution reaction of alkyl electrophiles can also proceed as a major side reaction consuming the boron reagents and the electrophiles.[17] Recently, Ito group developed the first intermolecular alkylboration of *gem*-disubstituted allenes for the synthesis of allylic boronates.[16g] In this reaction, the

corresponding three-component coupling products were obtained in high yield with suppressing direct borylation reactions of alkyl halides. Therefore, I expected a reaction of terminal allenes with alkyl halides, and a diboron reagent were able to produce the (*Z*)-alkenyl boronates if the high controlled regioselectivity of the borylcupration and subsequent alkylation proceeded (Scheme 2b). Based on these synthetic strategies, I developed the intermolecular alkylboration reaction of *mono*-substituted terminal allenes for the synthesis of (*Z*)-alkenyl boronates. Directing groups were not necessary for allene moieties and alkyl halide moieties to proceed the stereoselective construction of sterically congested alkenyl boron structures. Moreover, various R^1 substituents was suitable for this reaction, including *prim*-, *sec*-, and *tert*-alkyl groups and also heteroatom substituents.



Scheme 1. Copper(I)/$B_2(pin)_2$ system-catalyzed synthesis of alkenyl boronates *via* a carboboration reaction of *mono*-substituted terminal allenes.



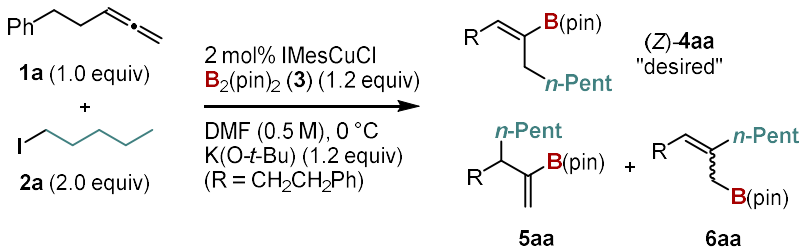
Scheme 2. Copper(I)/$B_2(pin)_2$ system-catalyzed synthesis of alkenyl boronates *via* carboboration reactions of *mono*-substituted terminal allenes.

2.2. Results and Discussions

First, the reaction conditions were investigated using an allene **1a** and an alkyl halide **2a** as standard substrates. The various conditions are shown in Table 1. In this reaction, the desired isomer (**4**), the regioisomer of alkylation (**5**) and that of borylcupration (**6**) were given. However, the regioselectivity of borylcupration [(**4**+**5**)/**6**] was perfectly controlled in most cases. Therefore, the regioselectivity is not described otherwise noted. The reaction under the standard conditions produced the alkenyl boronate (*Z*)-**4aa** in high yield (entry 1: 90%, *E*/*Z* = 1:99, **4**/**5** = >99:1). The selectivity and yield were slightly decreased at the higher temperature 30 °C (entry 2: 88%, *E*/*Z* = 2:98, **4**/**5** = 98:2). SIMes and IPr ligands showed relatively slow reaction rates and selectivity was higher than IMes ligand (entries 3 and 4: 48–78%, *E*/*Z* = 8:92–1:99, **4**/**5** = 97:3–99:1). A monodentate phosphine was also applicable (entry 5: 80%, *E*/*Z* = 1:99, **4**/**5** = 99:1). On the other hands, bidentate phosphine ligand was not suitable to this reaction (entry 6: 19%, *E*/*Z* = 2:98, **4**/**5** = 67:33). A non-polar and aprotic solvent gave the product in low yield (entry 7: 33%, *E*/*Z* = 1:99, **4**/**5** = 98:2). On the contrary, a polar solvent, tetrahydrofuran (THF), afforded the product in high yield (entry 8: 73%, *E*/*Z* = 1:99, **4**/**5** = 99:1). However, the yield was lower than the reaction in dimethylformamide (DMF). The structure of the bases did not largely affect the yield and selectivity (entries 9–

11: 79–89%, *E*/*Z* = 1:99, **4**/**5** = 98:2–99:1). The reaction was successfully proceeded at the lower catalyst loading, 0.5 mol % of copper(I) catalyst (entry 12: 76%, *E*/*Z* = 1:99, **4**/**5** = 99:1). Moreover, the desired product **4** could be obtained in high yield from a combination of 1.0 equivalent of allene **1a**, alkyl halide **2a**, diboron reagent **3**, and base K(O-*t*-Bu) (entry 13: 82%, *E*/*Z* = 1:99, **4**/**5** = 98:2). Based on these experiments, the catalyst system and reaction conditions optimized to achieve high reactivity and chemoselectivity.

Table 1. Reaction optimization



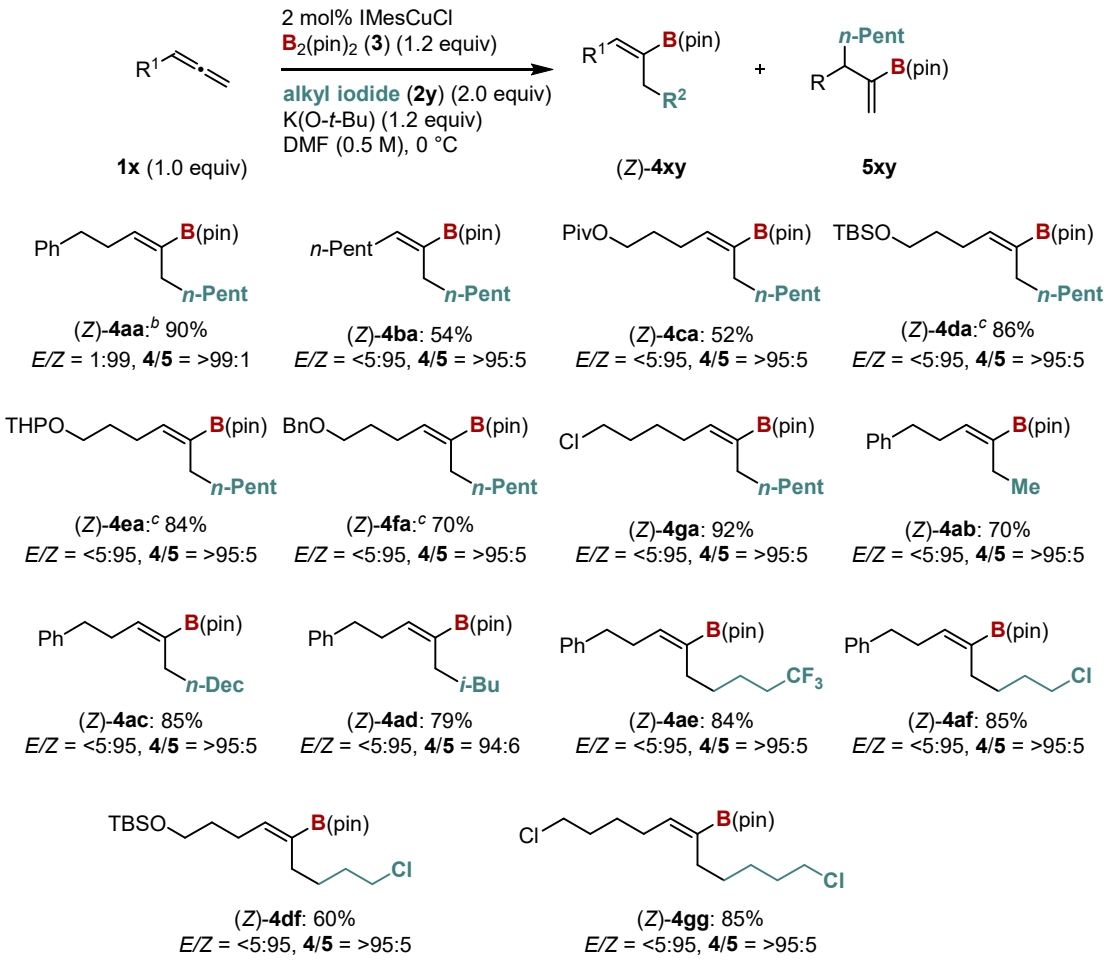
entry	variation from standard conditions	yield of **4** [%][b]	*E*/*Z* of **4** [%][c]	**4**/**5** [%][c]
1	none	90	1:99	>99:1
2	temperature: 30 °C	88	2:98	98:2
3	catalyst: SIMesCuCl	78	1:99	99:1
4	catalyst: IPrCuCl	48	8:92	97:3
5	catalyst: CuCl/PCy_3	80	1:99	99:1
6	catalyst: CuCl/Xantphos	19	2:98	67:33
7	solvent: toluene	33	1:99	98:2
8	solvent: THF	73	1:99	99:1
9	base: Li(O-*t*-Bu)	81	1:99	99:1
10	base: Na(O-*t*-Bu)	89	1:99	99:1
11	base: KOMe	79	1:99	98:2
12	catalyst: 0.5 mol %	76	1:99	99:1
13	w/ 1.0 equiv of reagents[d]	82	1:99	98:2

[a]Standard conditions: IMesCuCl (0.025 mmol), **1a** (0.5 mmol), **2a** (1.0 mmol), **3** (0.6 mmol), and K(O-*t*-Bu) (0.6 mmol) in DMF (1.0 mL). The consumption of the substrate **1a** was confirmed by GC analysis of the reaction mixture. The regioselectivity of borylcupration (**4**+**5**)/**6** was >99:1, which was determined by GC analysis. [b]Isolated yield. [c]Determined by GC analysis of the reaction mixture. [d]IMesCuCl (0.025 mmol), **1a** (0.5 mmol), **2a** (0.5 mmol), **3** (0.5 mmol), and K(O-*t*-Bu) (0.5 mmol) in DMF (1.0 mL).

Then, the substrate scope was investigated using the standard conditions (Table 2). The model substrate and a similar simple *primary*-alkyl-substituted substrate gave the borylated products in high yield with excellent regio- and stereoselectivity [(*Z*)-**4aa**: 90%, *E*/*Z* = <5:95, **4**/**5** = >95:5, (*Z*)-**4ba**: 54%, *E*/*Z* = <5:95, **4**/**5** = >95:5]. Pivaloyl (Piv), silyl (TBS), tetrahydropyranyl (THP), and benzyl (Bn) groups tolerated in this reaction [(*Z*)-**4ca**, (*Z*)-**4da**, (*Z*)-**4ea**, (*Z*)-**4fa**: 52–86%, *E*/*Z* = <5:95, **4**/**5** = >95:5]. A chloride group remained under these conditions [(*Z*)-**4ga**: 92%, *E*/*Z* = <5:95, **4**/**5** = >95:5]. However, phenyl allene produced a stereo-mixture of the product (72%, *E*/*Z* = 45:55), which would be caused by the easy 1,3-allylic isomerization of the allyl copper(I) intermediate. Next, I investigated the scope of alkyl

halides. Short and long alkyl groups were applicable to the R^2 substituent [(*Z*)-**4ab**, (*Z*)-**4ac**: 70–85%, *E*/*Z* = <5:95, **4**/**5** = >95:5]. In the case of *iso*-butyl iodide as the electrophile, the product was obtained in high yield, although the regioselectivity was slightly decreased [(*Z*)-**4ad**: 79%, *E*/*Z* = <5:95, **4**/**5** = 94:6]. A trifluoromethyl and chloro group tolerated under the conditions [(*Z*)-**4ae**, (*Z*)-**4af**, (*Z*)-**4df**, (*Z*)-**4gg**: 60–85%, *E*/*Z* = <5:95, **4**/**5** = >95:5]. Those types of alkenyl boronates are inaccessible *via* other transition-metal-catalyzed hydroboration of alkynes, although multi-step synthesises were reported.[6–12] However, *sec*-alkyl iodide, like iodocyclohexane, was not suitable to this reaction (<5%).[16f]

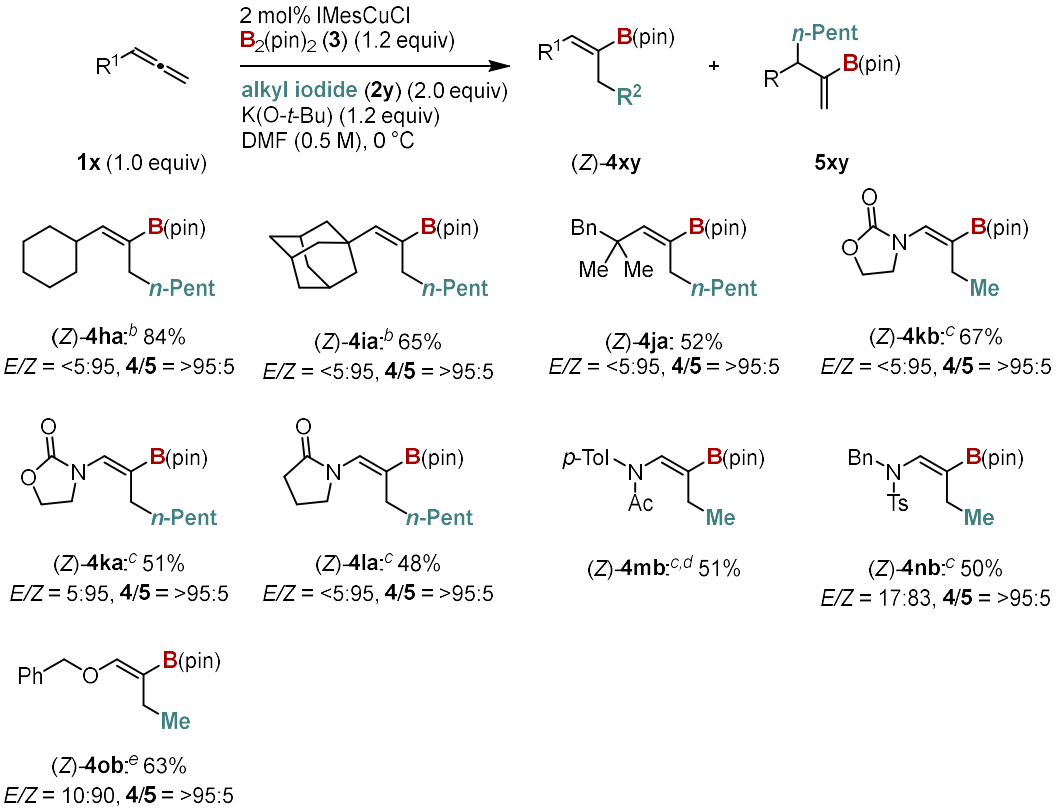
Table 2. Substrate scope[a]



[a]Standard conditions: IMesCuCl (0.025 mmol), **1x** (0.5 mmol), **2y** (1.0 mmol), **3** (0.6 mmol), and K(O-*t*-Bu) (0.6 mmol) in DMF (1.0 mL). Isolated yield. The *E*/*Z* values of **4** and the **4**/**5** selectivity were determined by ^{1}H NMR analysis after silica-gel column chromatography. [b]The *E*/*Z* values of **4** and the **4**/**5** selectivity were determined by GC analysis of the reaction mixture. [c]10 mol % of IMesCuCl was used.

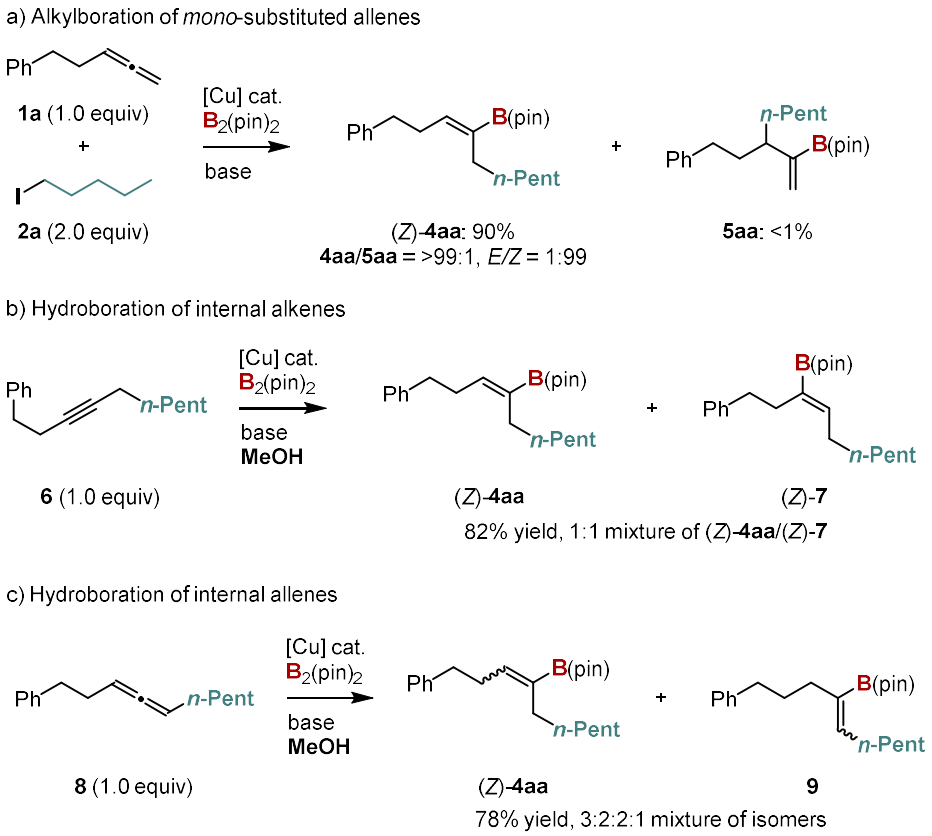
Then, the reaction was applied to other bulky and functionalized substrates (Table 3). *sec*- and *tert*-Alkyl-substituted allenes afforded the corresponding products with good selectivity [(*Z*)-**4ha**, (*Z*)-**4ia**, (*Z*)-**4ja**: 52–84%, *E*/*Z* = <5:95, **4**/**5** = >95:5]. Also, I applied heteroatom-substituted allenes to the substrate of this reaction.[18] After further optimization of the copper(I) catalyst, CuCl/(*o*-tol)$_3$P was found to give the desired carboborated product of allenamides in moderate yields [(*Z*)-**4kb**, (*Z*)-**4ka**, (*Z*)-**4la**, (*Z*)-**4mb**: 48–67%, *E*/*Z* = ≤5:95, **4**/**5** = >95:5]. A methylated product of the tosyl-protected amine substrate was given in moderate yield with slightly decreased stereoselectivity [(*Z*)-**4nb**: 50%, *E*/*Z* = 17:83, **4**/**5** = >95:5]. On the other hand, the addition of other alkyl chains, like a *n*-pentyl group, could not proceed; the elimination of the tosyl group was observed as the major side reaction. Using IPrCuCl catalyst, the borylated product of an allenyl ether was obtained [(*Z*)-**4ob**: 63%, *E*/*Z* = 10:90, **4**/**5** = >95:5].

Table 3. Scope of bulkier allenes and functionalized allenes[a]



[a]Standard conditions: IMesCuCl (0.025 mmol), **1x** (0.5 mmol), **2y** (1.0 mmol), **3** (0.6 mmol), and K(O-*t*-Bu) (0.6 mmol) in DMF (1.0 mL). Isolated yield. The *E*/*Z* values of **4** and the **4**/**5** selectivity were determined by ^{1}H NMR analysis after silica-gel column chromatography. [b]10 mol % of IMesCuCl was used. [c]5 mol % of CuCl and (*o*-tol)$_3$P was used instead of IMesCuCl. The reaction was performed in DMF (0.31 M). [d]The *E*/*Z* values of **4** and the **4**/**5** selectivity could not be determined by GC and NMR analysis. [e]5 mol % of IPrCuCl was used instead of IMesCuCl. The reaction was performed in THF (0.5 M).

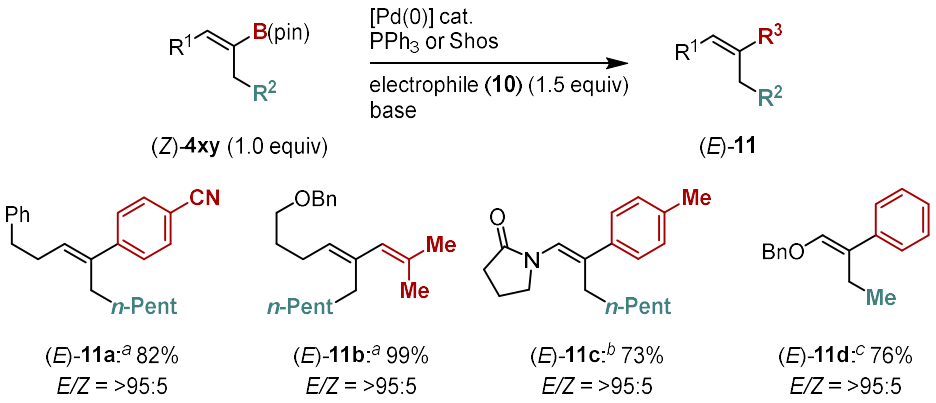
To demonstrate the advantage of this reaction compared to other synthetic methods of (*Z*)-alkenyl boronates, three types of copper(I)-catalyzed borylation reactions were carried out; (a) the alkylboration of terminal allene **1a**, (b) hydroboration reaction of an internal alkyne **6**, and (c) hydroboration reaction of an internal allene **8** (Scheme 3). The three-component coupling reaction between allene **1a**, alkyl halide **2a**, and a diboron reagent **3** selectively gave the corresponding alkenyl boronate (*Z*)-**4aa** in high yield [(*Z*)-**4aa**: 90%, *E*/*Z* = 1:99, **4**/**5** = >99:1; Scheme 2a]. Contrary, the hydroboration of internal alkyne **6** using methanol as the proton source produced the desired product (*Z*)-**4aa** and the regioisomer (*Z*)-**7** with poor regioselectivity [82% in total, 1:1 mixture of (*Z*)-**4**/(*Z*)-**7**; Scheme 2b]. Moreover, the hydroboration of internal allene **8** furnished the regio- and stereoisomers of borylation product [78% in total, 3:2:2:1 mixture of isomers; Scheme 2c]. Although other synthetic approaches, including transition-metal-catalyzed reactions and some multi-step synthesises, are conceivable, I assumed that this reaction developed in this study is one of the most efficient and general approaches for (*Z*)-alkenyl boronates in the absence of directing groups.



Scheme 3. Competition of synthetic approach of (*Z*)-alkenyl boronates.

Then I performed the Suzuki–Miyaura cross-coupling reactions as the derivatization of obtained alkenyl boronates. The coupling with an aryl bromide and an alkenyl bromide afforded the corresponding products, respectively [(*E*)-**11a**, (*E*)-**11b**: 82–99%, *E*/*Z* = >95:5]. The coupling products of an enamide and an alkenyl ether were also obtained in good yield with high stereospecificity [(*E*)-**11c**, (*E*)-**11d**: 73–76%, *E*/*Z* = >95:5].

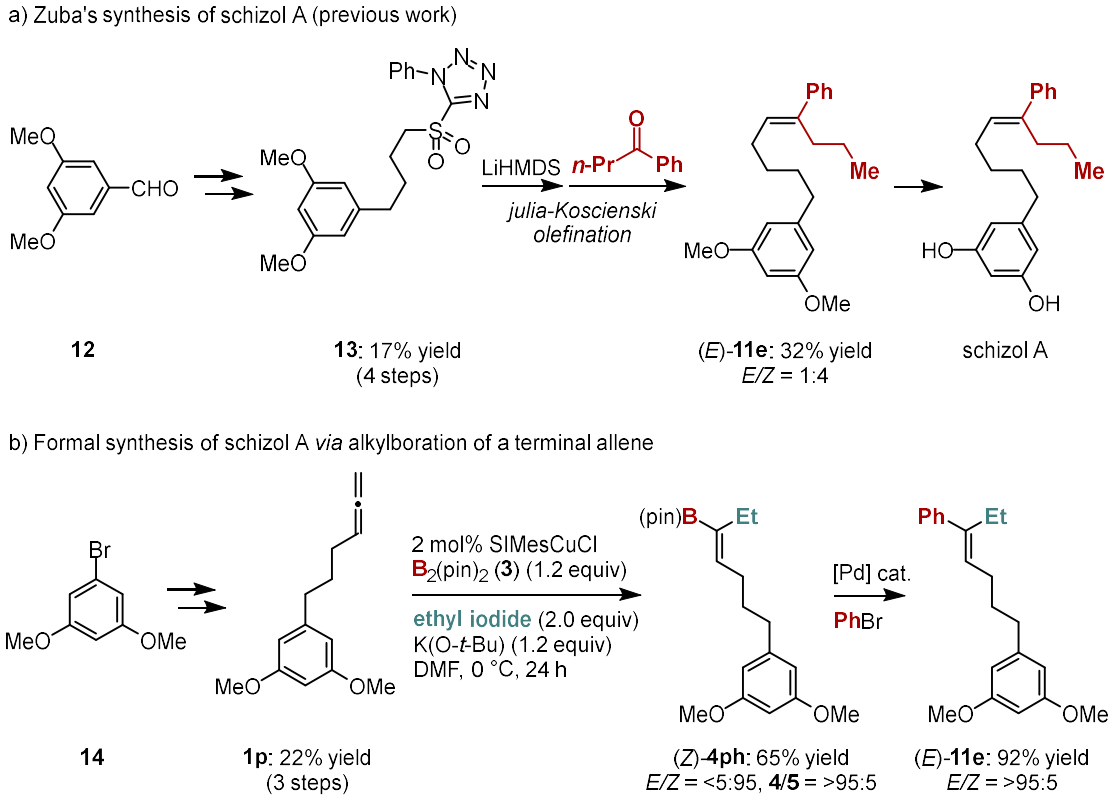
Table 4. Suzuki–Miyaura cross-coupling of (*Z*)-alkenyl boronates[a]



[a]Isolated yield. [b]Conditions: [Pd]/SPhos cat. and NaOH in THF/H_2O. [c]Conditions: [Pd]/PPh_3 cat. and Cs_2CO_3 in THF. [d]Conditions: [Pd]/PPh_3 cat. and KOH in THF/H_2O.

Schizol A is a marine natural product first isolated and characterized in 2017 by the Zubía group (Scheme 4a, right).[19] It has a trisubstituted alkene moiety with two long alkyl groups in *cis* orientation. The Zubía group also attempted to synthesize schizol A from commercially available aldehyde **12** (Scheme 4a). The direct precursor of schizol A, (*E*)-**11e**, was synthesized *via* Julia–Koscienski olefination as the key step for construction of the alkene. However, the poor stereoselectivity was reported for the desired (*E*)-stereoisomer (*E*/*Z* = 1:4).

We decided to apply our selective synthesis of (*Z*)-alkenyl boronates to synthesizing the precursor of schizol A, (*E*)-**11e**, *via* the alkylboration of a terminal allene **1p** (Scheme 4b). First, the terminal allene **1p** was obtained through three-step synthesis from a commercially available aryl bromide **14** in 14% yield. After that, the alkylboration was performed under standard conditions with ethyl iodide. The product (*Z*)-**4ph** was obtained in moderate yield with excellent regio- and stereoselectivity (65% yield, *E*/*Z* = <5:95, **4**/**5** = >95:5). The successive Suzuki–Miyaura cross-coupling reaction afforded (*E*)-**11e** in high yield (92% yield, *E*/*Z* = >95:5). Therefore, I succeeded the stereoselective synthesis of the trisubstituted alkene structure for schizol A.

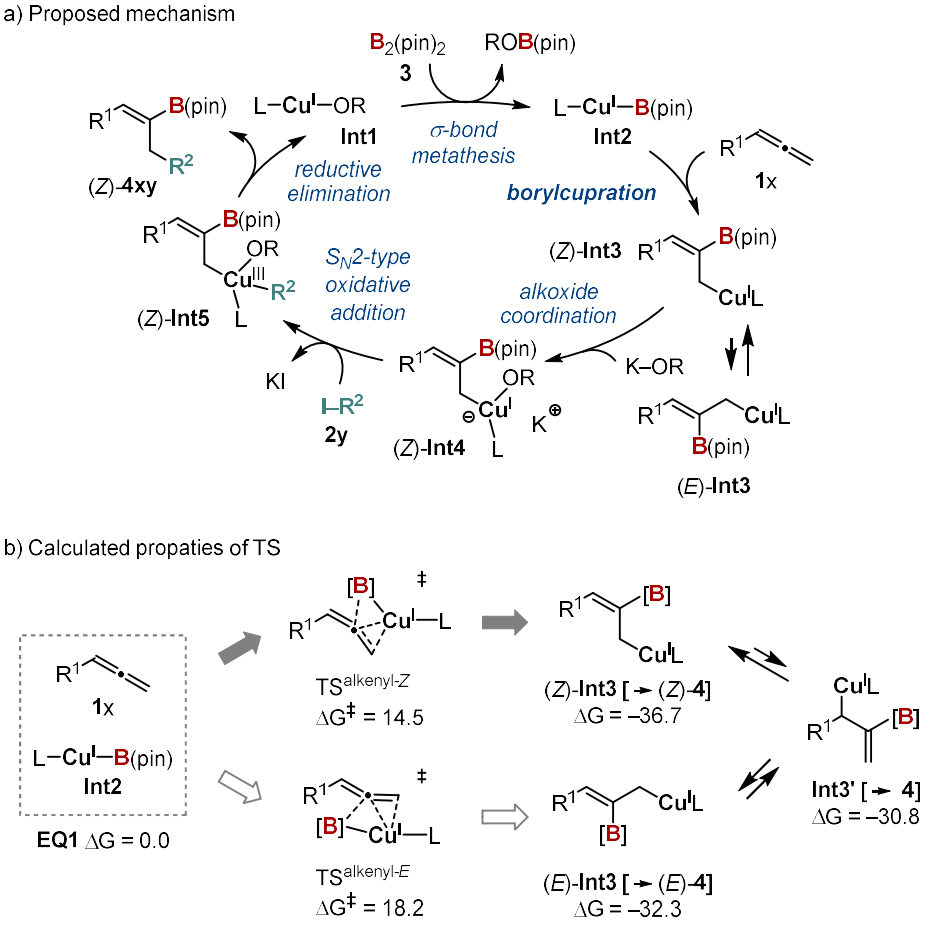


Scheme 4. Competition of synthetic approach of schizol A.

I illustrated the proposed mechanism in Scheme 5a. A *σ*-bond metathesis between a diboron reagent **3** and the copper(I) alkoxide **Int1**, which is generated *in situ* from a copper(I) chloride complex and an alkoxide base, produces the boryl copper(I) species **Int2**. After that, the borylcupration of allenes **1** forms allyl copper(I) intermediate **Int3**. Then, the coordination of alkoxide to the cooper(I) centre to form the cuprate species **Int4**,[20,21] S_N2-type oxidative addition to alkyl halide **2** gives a transient copper(III) intermediate **Int5**, which would be a transition state of the concerted alkylation mechanism. Finally, reductive elimination generates the copper(I) alkoxide catalyst **Int1** and the desired product **4**.

To obtain detailed insight into the regio- and stereoselectivity of borylcupration of terminal allenes in this reaction, the transition state (TS) **TS**^{alkenyl} and the resulting allyl copper(I) intermediate **Int3** were calculated using the density functional theory (DFT) method (Scheme 5b). The calculation was conducted with IMesCuB(pin) as the model catalyst and methyl allene as the model substrate, respectively. The TS connecting to (*Z*)-**Int3** is located 3.7 kcal/mol lower than that connecting to (*E*)-**Int3**. This result indicates that the formation of (*Z*)-**Int3** is more kinetically favored than that of (*E*)-**Int3**. Moreover, (*Z*)-**Int3** is more thermodynamically stable than (*E*)-**Int3** and another allyl copper(I) isomer **Int3'**, which lead

to produce **5**. These intermediates are connected to each other by 1,3-allylic isomerization of allyl copper(I) species. Thus, I assumed that the production of (*Z*)-**Int3** and (*Z*)-**4** is both kinetically and thermodynamically favorable, compared to paths for other isomers.



Scheme 5. Mechanistic study of alkylboration of terminal allenes.

The DFT calculations were performed at ωB97X-D/SDD for Cu and 6-311+G(d,p) for the other atoms/SMD(DMF)//ωB97X-D/SDD for Cu and 6-31G(d) for the other atoms/SMD(DMF) level of theory.

2.3. Conclusions

I have developed the copper(I)-catalyzed intermolecular alkylboration of terminal allenes to furnish the (*Z*)-alkenyl boronates. Various allenes and alkyl halides, including could be used as substrates. This method is able to prepare the (*Z*)-alkenyl boronates that have two similar alkyl groups. They are difficult to synthesize *via* other borylation reactions of multiple bonds such as hydroboration of internal alkynes and allenes.

2.4. Experimental Details

2.4.1. Instruments and Chemicals

Materials were commercially available and purified by standard procedures unless otherwise noted. Solvents were purchased from commercial suppliers, degassed *via* three freeze-pump-thaw cycles, and dried over molecular sieves (MS 4A). NMR spectra were recorded on JEOLJNM-ECX400P,JNM-ECS400 and JNM-ECA600 spectrometers (1H: 400 MHz, 13C: 100 MHz). Tetramethylsilane (1H, δ 0.00) and CDCl3 (13C, δ 77.0) were employed as the external standards, respectively. CuCl (224332-25G, ≥99%) and K(O-t-Bu) (659878-5G, 99.99%) were purchased from Sigma-Aldrich Co. and used without further purification. GLC analyses were conducted with a Shimadzu GC-2014 or GC-2025 equipped with a ULBON HR-1 glass capillary column (Shinwa Chemical Industries) and an FID detector. Recycle preparative gel chromatography (GPC) was performed with JAILC-9101 using CHCl3 as an eluent. High-resolution mass spectra were obtained at the Global Facility Center, Hokkaido University and GC-MS & NMR Lab., Faculty of Agriculture, Hokkaido University.

2.4.2. General Experimental Procedure

IMesCuCl (0.010 mmol), bis(pinacolato)diboron (**3**) (0.60 mmol), and K(O-t-Bu) (0.60 mmol) were placed in an oven-dried reaction vial under argon atmosphere. Then, the vial was sealed with a screw cap containing a Teflon™-coated rubber septum. Dry DMF (1.0 mL) was added in the vial through the rubber septum using a syringe. After stirred for 15 min, the reaction mixture was cooled to 0 ℃ for 10 min, **1x** (0.50 mmol) and **2y** (1.0 mmol) were added to the mixture. After the reaction mixture was stirred at 0 ℃ for 24 h, the reaction mixture was passed through a short silica gel column (Φ: 10 mm, height of the silica-gel column: 90 mm) with Et_2O/hexane (10/90) eluent. The crude material was purified by flash column chromatography (SiO_2, Et_2O/hexane, 0:100–20:80) to give the corresponding alkenyl boronate (*Z*)-**4xy**. After that, the regioselectivity and stereoselectivity were determined by ^1H NMR analysis and ^{13}C NMR analysis.

2.4.3. Substrate Preparation Procedure and Characterization

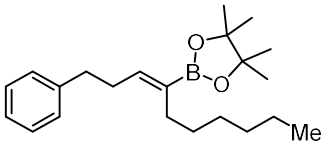
Terminal allenes (**1a**–**1j**,[26] **1k**,[27] **1l**,[28] **1m**,[29] **1n**[30] and **1o**[31]), an internal alkyne (**7**[32]), and an internal allene (**9**[33]) were prepared according to literature procedures. The ^1H and ^{13}C NMR spectra of known compounds were confirmed with literatures (**1a**,[24] **1b**,[35] **1c**,[36] **1d**,[36] **1e**,[37] **1f**, [38] **1g**,[39] **1h**,[24] **1i**,[40] **1j**,[41] **1k**,[27] **1l**,[28] **1m**,[29] **1n**,[30] **1o**,[31] and **7**[32]). All alkyl iodides (**2a**–**2h**) were purchased from commercial suppliers (Tokyo Chemical Industry Co. and Sigma-Aldrich Co.).

The internal allene **9** was synthesized according to literature procedure.[8] It was obtained

in 88% yield (521 mg, 2.43 mmol, colorless oil). ^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.89 (t, *J* = 6.7 Hz, 3H), 1.22–1.42 (m, 6H), 1.88–1.99 (m, 2H), 2.26–2.35 (m, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 5.04–5.16 (m, 2H), 7.14–7.33 (m, 5H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 14.1 (CH_3), 22.5 (CH_2), 28.8 (CH_2), 30.7 (CH_2), 31.3 (CH_2), 35.5 (CH_2), 90.2 (CH), 91.5 (CH), 125.7 (CH), 128.2 (CH), 128.5 (CH), 141.9 (C), 203.9 (C). HRMS-EI (m/z): $[M]^+$ calcd for $C_{16}H_{22}$, 214.1722; found, 214.1720.

2.4.4. Characterization of Products

(*Z*)-4,4,5,5-Tetramethyl-2-(1-phenyldec-3-en-4-yl)-1,3,2-dioxaborolane [(*Z*)-4aa].

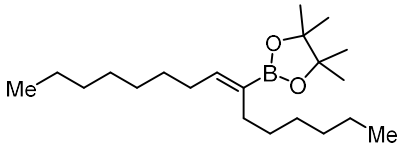


(*Z*)-**4aa**

The borylation reaction was conducted with 72.1 mg (0.500 mmol) of **1a**. The product (*Z*)-**4aa** was obtained in 90% yield with *E*/*Z* = 1:99, **4**:**5** = >99:1 (154.0 mg, 0.450 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.87 (t, *J* = 7.0 Hz, 3H), 1.17–1.34 (m, 8H), 1.26 (s, 12H), 2.06–2.14 (m, 2H), 2.40–2.47 (m, 2H), 2.66–2.73 (m, 2H), 6.35 (t, *J* = 7.0 Hz, 1H), 7.15–7.22 (m, 3H), 7.24–7.32 (m, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 14.1 (*C*H_3), 22.6 (*C*H_2), 24.7 (*C*H_3), 28.5 (*C*H_2), 29.2 (*C*H_2), 30.0 (*C*H_2), 30.7 (*C*H_2), 31.8 (*C*H_2), 35.6 (*C*H_2), 83.0 (*C*), 125.8 (*C*H_2, 128.3 (*C*H), 133.1 (br, B–*C*), 142.2 (*C*), 144.4 (*C*H). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{22}H_{35}O_2{}^{11}B$, 342.2734; found, 342.2726.

(*Z*)-4,4,5,5-Tetramethyl-2-(pentadec-7-en-7-yl)-1,3,2-dioxaborolane [(*Z*)-4ba].

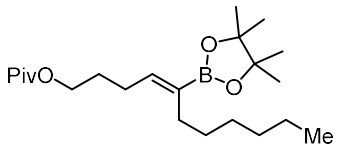


(*Z*)-**4ba**

The borylation reaction was conducted with 68.9 mg (0.498 mmol) of **1b**. The product (*Z*)-**4ba** was obtained in 54% yield with *E*/*Z* = <5:95, **4**:**5** = >95:5 (96.4 mg, 0.269 mmol, colorless oil).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.88 (t, *J* = 6.7 Hz, 6H), 1.21–1.34 (m, 18H), 1.25 (s, 12H), 2.08–2.14 (m, 4H), 6.27 (t, *J* = 6.7 Hz, 1H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 14.1 (*C*H_3), 22.7 (*C*H_2), 24.7 (*C*H_3), 24.8 (*C*H_2), 28.49 (*C*H_2), 28.53 (*C*H_2), 29.2 (*C*H_2), 29.5 (*C*H_2), 30.2 (*C*H_2), 31.8 (*C*H_2), 31.9 (*C*H_2), 82.9 (*C*), 146.0 (*C*H). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{21}H_{41}O_2{}^{11}B$, 336.3203; found, 336.3199.

(*Z*)-5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)undec-4-en-1-yl pivalate [(*Z*)-4ca].

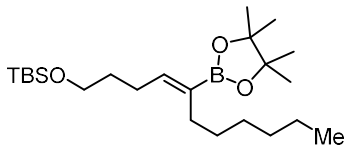


(*Z*)-**4ca**

The borylation reaction was conducted with 91.1 mg (0.500 mmol) of **1c**. The product (*Z*)-**4ca** was obtained in 52% yield with *E*/*Z* = <5:95, **4**:**5** = >95:5 (99.5 mg, 0.260 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.87 (t, *J* = 6.7 Hz, 3H), 1.20 (s, 9H), 1.22–1.33 (m, 8H), 1.25 (s, 12H), 1.73 (quintet, *J* = 7.0 Hz, 2H), 2.11 (t, *J* = 6.8 Hz, 2H), 2.21 (q, *J* = 7.0 Hz, 2H), 4.06 (t, *J* = 6.7 Hz, 2H), 6.25 (t, *J* = 7.0 Hz, 1H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 14.1 (*C*H_3), 22.6 (*C*H_2), 24.7 (*C*H_3), 24.9 (*C*H_2), 27.2 (*C*H_3), 28.2 (*C*H_2), 28.5 (*C*H_2), 29.3 (*C*H_2), 30.1 (*C*H_2), 31.8 (*C*H_2), 38.7 (*C*), 64.0 (*C*H_2), 83.0 (*C*), 144.0 (*C*H), 178.6 (*C*). HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{22}H_{41}O_4{}^{11}BNa$, 403.2994; found, 403.2993.

(*Z*)-*tert*-Butyldimethyl{[5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undec-4-en-1-yl]oxy}silane [(*Z*)-4da].

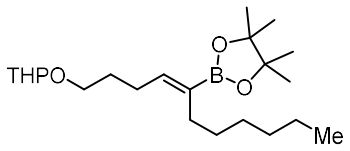


(*Z*)-**4da**

The borylation reaction was conducted with 106.1 mg (0.500 mmol) of **1d**. The product (*Z*)-**4da** was obtained in 86% yield with *E*/*Z* = <5:95, **4**:**5** = >95:5 (177.0 mg, 0.431 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.04 (s, 6H), 0.85–0.91 (m, 3H), 0.89 (s, 9H), 1.21–1.33 (m, 8H), 1.25 (s, 12H), 1.60 (quintet, *J* = 6.7 Hz, 2H), 2.10–2.21 (m, 4H), 3.61 (t, *J* = 6.7 Hz, 2H), 6.28 (t, *J* = 7.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): –5.3 (*C*H_3), 14.1 (*C*H_3), 18.3 (*C*), 22.7 (*C*H_2), 24.7 (*C*H_3), 24.9 (*C*H_2), 25.9 (*C*H_3), 28.4 (*C*H_2), 29.2 (*C*H_2), 30.1 (*C*H_2), 31.9 (*C*H_2), 32.4 (*C*H_2), 62.8 (*C*H_2), 82.9 (*C*), 145.2 (*C*H). HRMS-EI (*m*/*z*): $[M–Me]^+$ calcd for $C_{22}H_{44}O_3Si^{11}B$, 395.3157; found, 395.3153.

(*Z*)-2-[1-(Benzyloxy)undec-4-en-5-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(*Z*)-4ea].

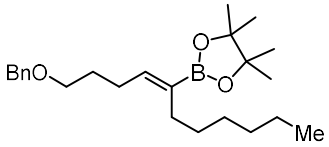


(*Z*)-**4ea**

The borylation reaction was conducted with 91.4 mg (0.501 mmol) of **1e**. The product (*Z*)-**4ea** was obtained in 84% yield with *E*/*Z* = <5:95, **4**:**5** = >95:5 (159.5 mg, 0.421 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.87 (t, *J* = 6.7 Hz, 3H), 1.20–1.34 (m, 8H), 1.25 (s, 12H), 1.47–1.62 (m, 4H), 1.66–1.74 (m, 3H), 1.78–1.88 (m, 1H), 2.12 (t, *J* = 6.7 Hz, 2H), 2.16–2.28 (m, 2H), 3.40 (dt, *J* = 12.9 and 6.7 Hz, 1H), 3.47–3.52 (m, 1H), 3.74 (dt, *J* = 12.9 and 6.7 Hz, 1H), 3.84–3.90 (m, 1H), 4.57–4.59 (m, 1H), 6.28 (t, *J* = 6.7 Hz, 1H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 14.1 (*C*H_3), 19.6 (*C*H_2), 22.7 (*C*H_2), 24.7 (*C*H_3), 25.2 (*C*H_2), 25.5 (*C*H_2), 28.5 (*C*H_2), 29.22 (*C*H_2), 29.25 (*C*H_2), 30.1 (*C*H_2), 30.7 (*C*H_2), 31.9 (*C*H_2), 62.2 (*C*H_2), 67.1 (*C*H_2), 82.9 (*C*), 98.7 (*C*H), 144.9 (*C*H). HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{22}H_{41}O_4{}^{11}BNa$, 403.2994; found, 403.2993.

(*Z*)-2-[1-(Benzyloxy)undec-4-en-5-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(*Z*)-4fa].

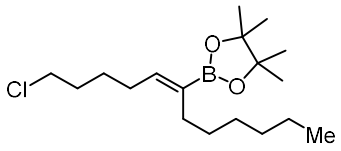


(*Z*)-**4fa**

The borylation reaction was conducted with 94.2 mg (0.500 mmol) of **1f**. The product (*Z*)-**4fa** was obtained in 70% yield with *E*/*Z* = <5:95, **4**:**5** = >95:5 (135.3 mg, 0.350 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.87 (t, *J* = 7.0 Hz, 3H), 1.20–1.34 (m, 8H), 1.25 (s, 12H), 1.72 (quintet, *J* = 7.0 Hz, 2H), 2.12 (t, *J* = 6.8 Hz, 2H), 2.22 (q, *J* = 7.0 Hz, 2H), 3.48 (t, *J* = 6.7 Hz, 2H), 4.50 (s, 2H), 6.26 (t, *J* = 7.0 Hz, 1H), 7.26–7.34 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 14.1 (*C*H_3), 22.6 (*C*H_2), 24.7 (*C*H_3), 25.1 (*C*H_2), 28.5 (*C*H_2), 29.16 (*C*H_2), 29.24 (*C*H_2), 30.1 (*C*H_2), 31.9 (*C*H_2), 70.0 (*C*H_2), 72.8 (*C*H_2), 83.0 (*C*), 127.4 (*C*H), 127.6 (*C*H), 128.3 (*C*H), 138.6 (*C*), 144.8 (*C*H). HRMS-EI (*m*/*z*): $[M–Me]^+$ calcd for $C_{23}H_{36}O_3{}^{11}B$, 371.2762; found, 371.2758.

(*Z*)-2-(1-Chlorododec-5-en-6-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(*Z*)-4ga].

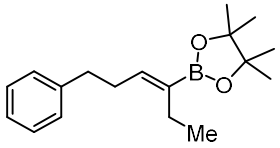


(*Z*)-**4ga**

The borylation reaction was conducted with 65.9 mg (0.504 mmol) of **1g**. The product (*Z*)-**4ga** was obtained in 91% yield with *E*/*Z* = <5:95, **4**:**5** = >95:5 (150.4 mg, 0.458 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.88 (t, *J* = 6.7 Hz, 3H), 1.23–1.33 (m, 8H), 1.25 (s, 12H), 1.50–1.58 (m, 2H), 1.76–1.83 (m, 2H), 2.09–2.19 (m, 4H), 3.53 (t, *J* = 6.7 Hz, 2H), 6.24 (t, *J* = 6.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 14.1 (*C*H_3), 22.6 (*C*H_2), 24.7 (*C*H_3), 26.4 (*C*H_2), 27.6 (*C*H_2), 28.5 (*C*H_2), 29.2 (*C*H_2), 30.1 (*C*H_2), 31.9 (*C*H_2), 32.3 (*C*H_2), 45.0 (*C*H_2), 83.0 (*C*), 144.6 (*C*H). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{18}H_{34}O_2Cl^{11}B$, 328.2344; found, 328.2349.

(*Z*)-4,4,5,5-Tetramethyl-2-(6-phenylhex-3-en-3-yl)-1,3,2-dioxaborolane [(*Z*)-4ab].

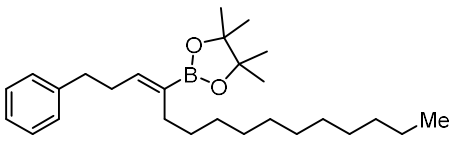


(*Z*)-**4ab**

The borylation reaction was conducted with 71.8 mg (0.498 mmol) of **1a**. The product (*Z*)-**4ab** was obtained in 70% yield with *E*/*Z* = <5:95, **4**:**5** = >95:5 (100.4 mg, 0.349 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.91 (t, *J* = 7.4 Hz, 3H), 1.27 (s, 12H), 2.12 (q, *J* = 7.4 Hz, 2H), 2.42–2.48 (m, 2H), 2.68–2.72 (m, 2H), 6.34 (t, *J* = 7.0 Hz, 1H), 7.16–7.22 (m, 3H), 7.25–7.31 (m, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 14.7 (*C*H_3), 21.8 (*C*H_2), 24.7 (*C*H_3), 30.4 (*C*H_2), 35.6 (*C*H_2), 83.0 (*C*), 125.8 (*C*H), 128.3 (*C*H), 142.1 (*C*), 144.0 (*C*H). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{18}H_{27}O_2{}^{11}B$, 286.2107; found, 286.2102.

(*Z*)-4,4,5,5-Tetramethyl-2-(1-phenylpentadec-3-en-4-yl)-1,3,2-dioxaborolane [(*Z*)-4ac].



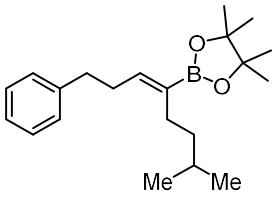
(*Z*)-**4ac**

The borylation reaction was conducted with 72.1 mg (0.500 mmol) of **1a**. The product (*Z*)-**4ac** was obtained in 85% yield with *E*/*Z* = >95:5, **4**:**5** = >95:5 (174.9 mg, 0.424 mmol,

colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.88 (t, *J* = 6.9 Hz, 3H), 1.17–1.35 (m, 18H), 1.26 (s, 12H), 2.06–2.15 (m, 2H), 2.39–2.48 (m, 2H), 2.65–2.73 (m, 2H), 6.35 (t, *J* = 6.9 Hz, 1H), 7.15–7.22 (m, 3H), 7.25–7.32 (m, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 14.1 (*C*H_3), 22.7 (*C*H_2), 24.7 (*C*H_3), 28.5 (*C*H_2), 29.3 (*C*H_2), 29.5 (*C*H_2), 29.6 (*C*H_2), 29.7 (*C*H_2), 30.1 (*C*H_2), 30.7 (*C*H_2), 31.9 (*C*H_2), 35.6 (*C*H_2), 82.9 (*C*), 125.7 (*C*H), 128.3 (*C*H), 133.2 (br, B–*C*), 142.2 (*C*), 144.4 (*C*H). HRMS-EI (*m*/*z*): [M]$^+$ calcd for $C_{27}H_{45}O_2{}^{11}B$, 412.3517; found, 412.3511.

(*Z*)-4,4,5,5-Tetramethyl-2-(7-methyl-1-phenyloct-3-en-4-yl)-1,3,2-dioxaborolane [(*Z*)-4ad].

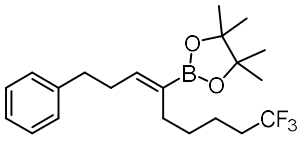


(*Z*)-**4ad**

The borylation reaction was conducted with 72.1 mg (0.500 mmol) of **1a**. The product (*Z*)-**4ad** was obtained in 79% yield with *E*/*Z* = >95:5, **4**:**5** = >95:5 (129.6 mg, 0.395 mmol, colorless oil).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.87 (d, *J* = 6.8 Hz, 6H), 1.12–1.20 (m, 2H), 1.26 (s, 12H), 1.45–1.56 (m, 1H), 2.04–2.17 (m, 2H), 2.38–2.49 (m, 2H), 2.63–2.76 (m, 2H), 6.33 (t, *J* = 7.2 Hz, 1H), 7.12–7.23 (m, 3H), 7.23–7.32 (m, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 22.6 (*C*H_3), 24.7 (*C*H_3), 26.4 (*C*H_2), 27.9 (*C*H), 30.6 (*C*H_2), 35.6 (*C*H_2), 39.3 (*C*H_2), 82.9 (*C*), 125.8 (*C*H), 128.3 (*C*H), 133.2 (br, B–*C*), 142.2 (*C*), 144.1 (*C*H). HRMS-EI (*m*/*z*): [M]$^+$ calcd for $C_{21}H_{33}O_2{}^{11}B$, 328.2577; found, 328.2578.

(*Z*)-4,4,5,5-Tetramethyl-2-(9,9,9-trifluoro-1-phenylnon-3-en-4-yl)-1,3,2-dioxaborolane [(*Z*)-4ae].



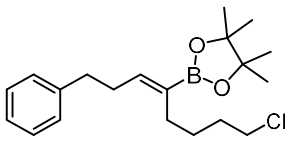
(*Z*)-**4ae**

The borylation reaction was conducted with 72.1 mg (0.500 mmol) of **1a**. The product (*Z*)-**4ae** was obtained in 84% yield with *E*/*Z* = <5:95, **4**:**5** = >95:5 (158.7 mg, 0.415 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.25 (s, 12H), 1.28–1.37 (m, 2H), 1.45–1.53 (m, 2H), 1.96–2.08 (m, 2H), 2.12 (t, *J* = 7.6 Hz, 2H), 2.39–2.47 (m, 2H), 2.67–2.74 (m, 2H), 6.40 (t, *J*

= 7.0 Hz, 1H), 7.16–7.22 (m, 3H), 7.24–7.31 (m, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 21.6 (q, *J* = 3.0 Hz, *C*H_2), 24.7 (*C*H_3), 27.9 (*C*H_2), 29.0 (*C*H_2), 30.8 (*C*H_2), 33.7 (q, *J* = 28.3 Hz, *C*H_2), 35.5 (*C*H_2), 83.1 (*C*), 125.8 (*C*), 127.4 (q, *J* = 294.6 Hz, *C*), 128.3 (*C*), 132.0 (br, B–*C*), 142.0 (*C*), 145.4 (*C*H). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{21}H_{30}F_3O_2{}^{11}B$, 382.2295; found, 382.2288.

(*Z*)-2-(8-Chloro-1-phenyloct-3-en-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(*Z*)-4af].

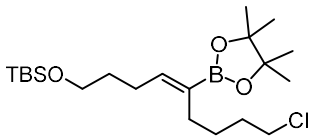


(*Z*)-**4af**

The borylation reaction was conducted with 72.2 mg (0.500 mmol) of **1a**. The product (*Z*)-**4af** was obtained in 85% yield with *E*/*Z* = <5:95, **4**:**5** = >95:5 (148.8 mg, 0.425 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.26 (s, 12H), 1.42 (quintet, *J* = 7.0 Hz, 2H), 1.72 (quintet, *J* = 7.0 Hz, 2H), 2.13 (t, *J* = 7.0 Hz, 2H), 2.41–2.47 (m, 2H), 2.68–2.72 (m, 2H), 3.51 (t, *J* = 7.0 Hz, 1H), 6.39 (t, *J* = 7.0 Hz, 1H), 7.17–7.20 (m, 3H), 7.26–7.30 (m, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 24.7 (*C*H_3), 27.2 (*C*H_2), 27.5 (*C*H_2), 30.8 (*C*H_2), 32.3 (*C*H_2), 35.5 (*C*H_2), 45.1 (*C*H_2), 83.1 (*C*), 125.8 (*C*H), 128.3 (*C*H), 142.0 (*C*), 145.3 (*C*H). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{20}H_{30}O_2Cl{}^{11}B$, 348.2031; found, 348.2025.

(*Z*)-*tert*-Butyl{[9-chloro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)non-4-en-1-yl]oxy}dimethylsilane [(*Z*)-4df].

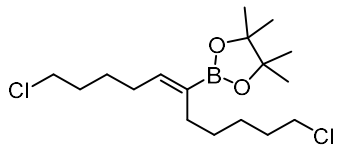


(*Z*)-**4df**

The borylation reaction was conducted with 104.4 mg (0.492 mmol) of **1d**. The product (*Z*)-**4df** was obtained in 60% yield with *E*/*Z* = <5:95, **4**:**5** = >95:5 (125.0 mg, 0.300 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.04 (s, 6H), 0.89 (s, 9H), 1.25 (s, 12H), 1.48 (dt, *J* = 15.3, 7.0 Hz, 2H), 1.57–1.64 (m, 3H), 1.76 (dt, *J* = 15.3, 7.0 Hz, 2H), 2.16 (dt, *J* = 14.1, 7.0 Hz, 4H), 3.54 (t, *J* = 6.7 Hz, 2H), 3.61 (t, *J* = 6.7 Hz, 2H), 6.32 (t, *J* = 7.0 Hz, 1H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): –5.3 (*C*H_3), 18.3 (*C*), 24.7 (*C*H_3), 25.0 (*C*H_2), 25.9 (*C*H_3), 27.3 (*C*H_2), 27.5 (*C*H_2), 32.3 (*C*H_2), 32.4 (*C*H_2), 45.1 (*C*H_2), 62.7 (*C*H_2), 83.0 (*C*), 146.1 (*C*H). HRMS-EI (*m*/*z*): $[M–Me]^+$ calcd for $C_{20}H_{39}O_3SiCl{}^{11}B$, 401.2454; found, 401.2445.

(*Z*)-2-(1,11-Dichloroundec-5-en-6-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(*Z*)-4gg].

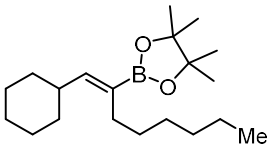


(*Z*)-**4gg**

The borylation reaction was conducted with 65.5 mg (0.501 mmol) of **1g**. The product (*Z*)-**4gg** was obtained in 85% yield with *E*/*Z* = <5:95, **4**:**5** = >95:5 (148.3 mg, 0.426 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.26 (s, 12H), 1.31–1.46 (m, 4H), 1.51–1.58 (m, 2H), 1.74–1.83 (m, 4H), 2.13 (t, *J* = 7.0 Hz, 2H), 2.17 (t, *J* = 7.0 Hz, 2H), 3.53 (t, *J* = 6.8 Hz, 2H), 3.54 (t, *J* = 6.8 Hz, 2H), 6.27 (t, *J* = 7.0 Hz, 1H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 24.7 (*C*H_3), 26.4 (*C*H_2), 26.7 (*C*H_2), 27.6 (*C*H_2), 28.2 (*C*H_2), 29.2 (*C*H_2), 32.3 (*C*H_2), 32.6 (*C*H_2), 44.9 (*C*H_2), 45.1 (*C*H_2), 83.1 (*C*), 145.0 (*C*H). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{17}H_{31}O_2Cl_2{}^{11}B$, 348.1797; found, 348.1796.

(*Z*)-2-(1-Cyclohexyloct-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(*Z*)-4ha].

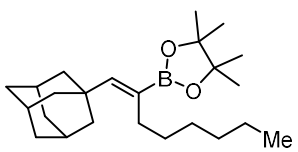


(*Z*)-**4ha**

The borylation reaction was conducted with 62.0 mg (0.507 mmol) of **1h**. The product (*Z*)-**4ha** was obtained in 83% yield with *E*/*Z* = <5:95, **4**:**5** = >95:5 (134.6 mg, 0.420 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.88 (t, *J* = 6.3 Hz, 3H), 1.05–1.34 (m, 13H), 1.25 (s, 12H), 1.53–1.74 (m, 5H), 2.11 (t, *J* = 6.3 Hz, 2H), 2.29–2.40 (m, 1H), 6.06 (d, *J* = 9.4 Hz, 1H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 14.1 (*C*H_3), 22.6 (*C*H_2), 24.7 (*C*H_3), 25.9 (*C*H_2), 26.1 (*C*H_2), 28.7 (*C*H_2), 29.2 (*C*H_2), 30.6 (*C*H_2), 31.8 (*C*H_2), 32.7 (*C*H_2), 37.4 (*C*H), 82.9 (*C*), 151.1 (*C*H). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{20}H_{37}O_2{}^{11}B$, 320.2890; found, 320.2885.

(*Z*)-2-[1-(Adamantan-1-yl)oct-1-en-2-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(*Z*)-4ia].

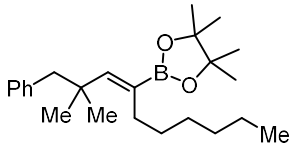


(*Z*)-**4ia**

The borylation reaction was conducted with 87.8 mg (0.504 mmol) of **1i**. The product (*Z*)-**4ia** was obtained in 64% yield with *E*/*Z* = <5:95, **4**:**5** = >95:5 (121.0 mg, 0.325 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.86–0.90 (m, 3H), 1.22–1.35 (m, 8H), 1.24 (s, 12H), 1.65–1.70 (m, 6H), 1.79–1.83 (m, 6H), 1.93–1.97 (m, 3H), 2.24–2.28 (m, 2H), 5.94 (s, 1H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 14.1 (*C*H_3), 22.6 (*C*H_2), 24.7 (*C*H_3), 24.8 (*C*), 28.8 (*C*H), 29.6 (*C*H_2), 29.8 (*C*H_2), 31.1 (*C*H_2), 31.8 (*C*H_2), 36.8 (*C*H_2), 42.6 (*C*H_2), 82.9 (*C*), 153.6 (*C*H). HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{24}H_{41}O_2{}^{11}BNa$, 395.3096; found, 395.3092.

(*Z*)-2-(2,2-Dimethyl-1-phenyldec-3-en-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(*Z*)-4ja].

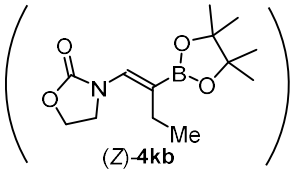


(*Z*)-**4ja**

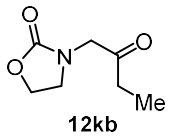
The borylation reaction was conducted with 86.1 mg (0.500 mmol) of **1j**. The product (*Z*)-**4ja** was obtained in 52% yield with *E*/*Z* = <5:95, **4**:**5** = >95:5 (96.4 mg, 0.260 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.87 (t, *J* = 6.8 Hz, 3H), 1.11 (s, 6H), 1.23–1.31 (m, 8H), 1.25 (s, 12H), 2.19–2.24 (m, 2H), 2.72 (s, 2H), 6.18 (s, 1H), 7.12–7.26 (m, 5H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 14.1 (*C*H_3), 22.6 (*C*H_2), 24.7 (*C*H_3), 28.3 (*C*H_3), 29.5 (*C*H_2), 29.7 (*C*H_2), 30.6 (*C*H_2), 31.8 (*C*H_2), 38.7 (*C*), 49.2 (*C*H_2), 83.0 (*C*), 125.8 (*C*H), 127.5 (*C*H), 130.7 (*C*H), 139.1 (*C*), 152.3 (*C*H). HRMS-EI (*m*/*z*): $[M–Me]^+$ calcd for $C_{23}H_{36}O_2{}^{11}B$, 355.2813; found, 355.2809.

3-(2-Oxobutyl)oxazolidin-2-one (12kb)



(*Z*)-**4kb**



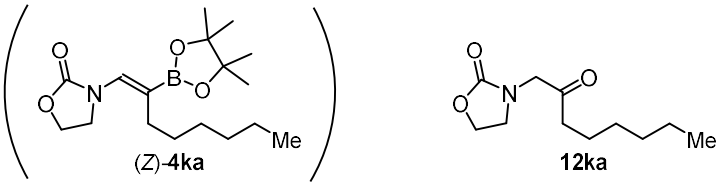
12kb

The borylation reaction was conducted with 62.6 mg (0.500 mmol) of **1k**. To remove an undesired boryl substitution product of the alkyl halide and hydroboration product of the allene for the further purification and the determination of the regioselectivities, the oxidation of the boryl groups was performed. The corresponding ketone product **12kb** was obtained in 51% yield with **4**:**5** = >95:5 (40.4 mg, 0.257 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.12 (t, *J* = 7.3 Hz, 3H), 2.47 (q, *J* = 7.4 Hz, 2H), 3.68 (t, *J* = 8.0 Hz, 2H), 4.10 (s, 2H), 4.41 (t, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 7.4

(CH_3), 33.2 (CH_2), 45.2 (CH_2), 52.6 (CH_2), 62.3 (CH_2), 158.9 (*C*), 205.3 (*C*). HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_7H_{11}O_3NNa$, 180.0631; found, 180.0628.

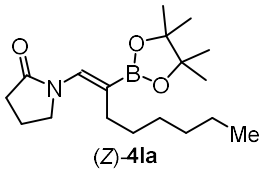
3-(2-Oxooctyl)-1,3-oxazolidin-2-one (12ka)



The borylation reaction was conducted with 62.6 mg (0.500 mmol) of **1k**. To remove an undesired boryl substitution product of the alkyl halide and hydroboration product of the allene for the further purification and the determination of the regioselectivities, the oxidation of the boryl groups was performed. The corresponding ketone product **12ka** was obtained in 51% yield with **4**:**5** = >95:5 (54.8 mg, 0.257 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.88 (t, *J* = 7.0 Hz, 3H), 1.22–1.36 (m, 6H), 1.61 (quintet, *J* = 7.2 Hz, 2H), 2.42 (t, *J* = 7.4 Hz, 2H), 3.67 (t, *J* = 7.8 Hz, 2H), 4.08 (s, 2H), 4.40 (t, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 14.0 (CH_3), 22.4 (CH_2), 23.3 (CH_2), 28.7 (CH_2), 31.4 (CH_2), 39.9 (CH_2), 45.0 (CH_2), 52.7 (CH_2), 62.1 (*C*H), 158.7 (*C*), 204.8 (*C*). HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{11}H_{19}O_3NNa$, 236.1257; found, 236.1260.

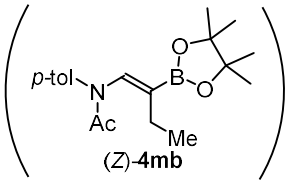
1-[(*Z*)-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oct-1-en-1-yl]pyrrolidin-2-one [(*Z*)-4la]



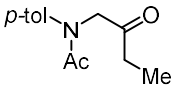
The borylation reaction was conducted with 61.6 mg (0.500 mmol) of **1l**. The product (*Z*)-**4la** was obtained in 48% yield with *E*/*Z* = <5:95, **4**:**5** = >95:5 (76.8 mg, 0.239 mmol, colorless solid).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.88 (t, *J* = 7.0 Hz, 3H), 1.21–1.40 (m, 20H), 2.08 (quintet, *J* = 7.6 Hz, 2H), 2.22 (t, *J* = 7.1 Hz, 2H), 2.42 (t, *J* = 8.2 Hz, 2H), 3.85 (t, *J* = 7.1 Hz, 2H), 7.23 (s, 1H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 13.9 (CH_3), 18.6 (CH_2), 22.4 (CH_2), 24.5 (CH_3), 27.5 (CH_2), 29.1 (CH_2), 30.0 (CH_2), 31.4 (CH_2), 31.6 (CH_2), 48.0 (CH_2), 83.0 (*C*), 113.7 (br, B–*C*), 132.6 (*C*H), 174.9 (*C*). HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{18}H_{32}O_3{}^{11}BNNa$, 344.2371; found, 344.2371.

***N*-(2-Oxobutyl)-*N*-(*p*-tolyl)acetamide (12mb)**



(*Z*)-**4mb**

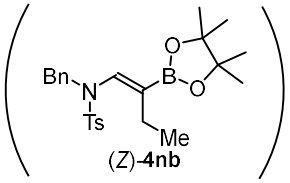


12mb

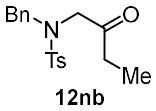
The borylation reaction was conducted with 93.6 mg (0.500 mmol) of **1m**. To remove an undesired boryl substitution product of the alkyl halide and hydroboration product of the allene for the further purification and the determination of the regioselectivities, the oxidation of the boryl groups was performed. The corresponding ketone product **12mb** was obtained in 48% yield with **4**:**5** = >95:5 (55.9 mg, 0.240 mmol, colorless oil).

^{1}H NMR (399 MHz, $CDCl_3$, δ): 0.91 (t, *J* = 7.4 Hz, 3H), 1.63 (sixtet, *J* = 7.3 Hz, 2H), 1.91 (s, 3H), 2.36 (s, 3H), 2.40 (t, *J* = 7.4 Hz, 2H), 4.39 (s, 2H), 7.19 (s, *J* = 8.0 Hz, 4H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 13.6 (*C*H_3), 16.9 (*C*H_2), 21.0 (*C*H_3), 21.9 (*C*H_3), 41.8 (*C*H_2), 58.8 (*C*H_2), 127.6 (*C*H), 130.2 (*C*H), 137.9 (*C*), 141.0 (*C*), 170.8 (*C*), 204.9 (*C*). HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{14}H_{19}O_2NNa$, 256.1308; found, 256.1312.

***N*-Benzyl-*N*-(2-oxobutyl)-4-methylbenzenesulfonamide (12nb)**



(*Z*)-**4nb**

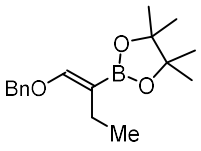


12nb

The borylation reaction was conducted with 149.7 mg (0.500 mmol) of **1n**. To remove an undesired boryl substitution product of the alkyl halide and hydroboration product of the allene for the further purification and the determination of the regioselectivities, the oxidation of the boryl groups was performed. The corresponding ketone product **12nb** was obtained in 60% yield with **4**:**5** = >95:5 (99.6 mg, 0.301 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.90 (t, *J* = 7.2 Hz, 3H), 2.25 (q, *J* = 7.4 Hz, 2H), 2.45 (s, 3H), 3.86 (s, 2H), 4.37 (s, 2H), 7.20–7.38 (m, 7H), 7.75 (d, *J* = 6.7 Hz, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 7.2 (*C*H_3), 21.5 (*C*H_3), 32.5 (*C*H_2), 52.0 (*C*H_2), 54.5 (*C*H_2), 127.4 (*C*H), 128.1 (*C*H), 128.7 (*C*H), 128.8 (*C*H), 129.6 (*C*H), 134.9 (*C*), 136.1 (*C*), 143.6 (*C*), 206.4 (*C*). HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{18}H_{21}O_3NNaS$, 354.1134; found, 354.1137.

(*Z*)-2-(1-(Benzyloxy)prop-1-ene-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [(*Z*)-4ob]

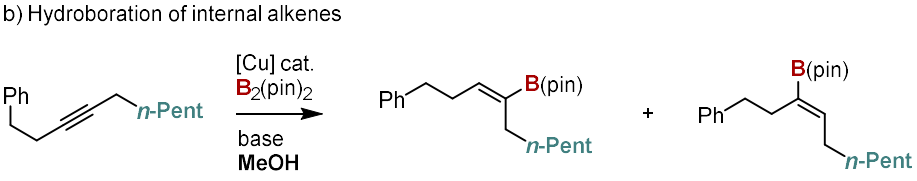


(*Z*)-**4ob**

The borylation reaction was conducted with 74.6 mg (0.500 mmol) of **1o**. The product (*Z*)-**4ob** was obtained in 63% yield with **4**:**5** = >95:5 (91.3 mg, 0.317 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.98 (t, *J* = 7.4 Hz, 3H), 1.24 (s, 12H), 2.16 (q, *J* = 7.4 Hz, 2H), 4.92 (s, 2H), 6.74 (s, 1H), 7.27–7.38 (m, 5H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 14.7 (*C*H_3), 18.4 (*C*H_2), 24.6 (*C*H_3), 74.0 (*C*H_2), 82.5 (*C*), 108.4 (Br, B–*C*), 126.9 (*C*H), 127.7 (*C*H), 128.4 (*C*H), 137.5 (*C*), 156.3 (*C*H). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{17}H_{25}O_3{}^{11}B$, 288.1900; found, 288.1894.

2.4.5. Control Experiments

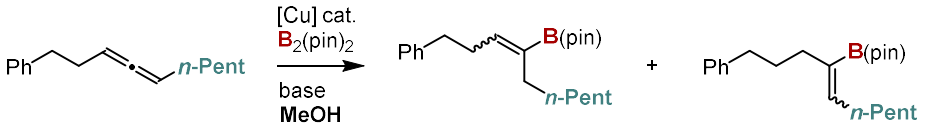


6 (1.0 equiv) (*Z*)-**4aa** (*Z*)-**7**

82% yield, 1:1 mixture of (*Z*)-**4aa**/(*Z*)-**7**

IMesCuCl (0.0050 mmol), bis(pinacolato)diboron (**3**) (0.300 mmol) and K(O-*t*-Bu) (0.300 mmol) were placed in a round-bottomed flask under argon atmosphere. After that, dry DMF (0.5 mL) was added in the flask through the rubber septum using a syringe. After stirring for 30 min at room temperature, **6** (0.252 mmol) and MeOH (0.500 mmol) were added to the mixture. Then, the reaction mixture was cooled to 0 ℃. After the substrate **6** was consumed, the reaction mixture was passed through a short silica gel column (Φ: 10 mm, height of the silica-gel column: 90 mm) with Et_2O/hexane (10/90) eluent. The crude material was purified by flash column chromatography (SiO_2, Et_2O/hexane, 0:100–20:80) to give the corresponding borylated products in 82% NMR yield, 1:1 mixture of (*Z*)-**4aa**/(*Z*)-**7**.

c) Hydroboration of internal allenes

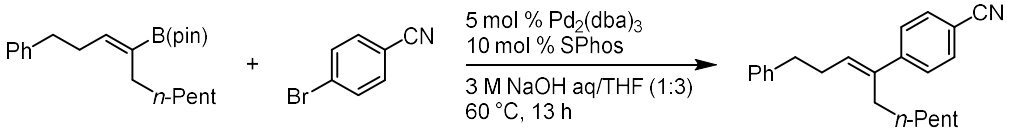


8 (1.0 equiv) (*Z*)-**4aa** **9**

78% yield, 3:2:2:1 mixture of isomers

IMesCuCl (0.0050 mmol), bis(pinacolato)diboron (**3**) (0.300 mmol) and K(O-*t*-Bu) (0.300 mmol) were placed in a round-bottomed flask. After that, dry DMF (0.5 mL) was added in the flask through the rubber septum using a syringe. After stirring for 30 min at room temperature, **8** (0.250 mmol) and MeOH (0.500 mmol) were added to the mixture. Then, the reaction mixture was cooled to 0 ℃. After the substrate was consumed, the reaction mixture was passed through a short silica gel column (Φ: 10 mm, height of the silica-gel column: 90 mm) with Et_2O/hexane (10/90) eluent. The crude material was purified by flash column chromatography (SiO_2, Et_2O/hexane, 0:100–20:80) to give the corresponding borylation products in 78% yield, 3:2:2:1 mixture of isomers.

2.4.6. Suzuki–Miyaura Cross-coupling Reaction of Borylation Products

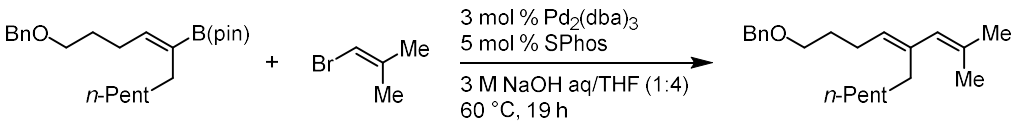


(*Z*)-**4aa** (1.5 equiv) (*E*)-**11a**

The Suzuki–Miyaura cross-coupling reaction of (*Z*)-**4aa** was conducted according to the literature procedure.[43] (*Z*)-**4aa** (0.251 mmol), 4-bromobenzonitrile (0.375 mmol), $Pd_2(dba)_3$ (0.005 mmol) and SPhos (0.01 mmol) were dissolved in THF (2.25 mL) in an oven-dried reaction vial under argon atmosphere. After the addition of 3 M NaOH aqueous solution (0.75 mL), the mixture was stirred at 60 ℃ for 13 h. Then, the mixture was quenched by addition of water (5 mL) and extracted three times with Et_2O (10 mL ×3). The combined organic layer was washed with brine, dried over $MgSO_4$ followed by filtration. After evaporation, the crude material was purified by silica gel chromatography (Et_2O/hexane, 0:100–3:97) to give the product (*E*)-**11a** in 82% yield [the product was obtained as a mixture with 4-bromobenzonitrile, (*E*)-**11a**: 75.5 mg, 0.206 mmol and 4-bromobenzonitrile, 0.055 mmol].

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.85 (t, *J* = 6.9 Hz, 3H), 1.16–1.28 (m, 8H), 2.38–2.46 (m, 2H), 2.53 (q, *J* = 7.6 Hz, 2H), 2.77 (t, *J* = 7.6 Hz, 2H), 5.76 (t, *J* = 7.4 Hz, 1H), 7.18–7.24 (m, 3H), 7.28–7.33 (m, 2H), 7.37–7.40 (m, 2H), 7.56–7.60 (m, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 14.0 (*C*H_3), 22.5 (*C*H_2), 28.4 (*C*H_2), 29.1 (*C*H_2), 29.3 (*C*H_2), 30.6 (*C*H_2), 31.5 (*C*H_2), 35.8 (*C*H_2), 109.9 (*C*), 119.1 (*C*), 126.0 (*C*H), 126.8 (*C*H), 128.35 (*C*H), 128.41 (*C*H), 130.7 (*C*H),

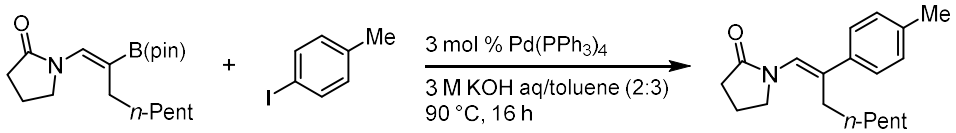
132.0 (*C*H), 139.7 (*C*), 141.5 (*C*), 147.9 (*C*). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{23}H_{27}N$, 317.2144; found, 317.2143.



(*Z*)-**4fa** (1.7 equiv) (*E*)-**11b**

The Suzuki–Miyaura cross-coupling reaction of (*Z*)-**4fa** was conducted according to the literature procedure.[43] In an oven-dried reaction vial, 1-Bromo-2-methylprop-1-ene (0.342 mmol), $Pd_2(dba)_3$ (0.006 mmol), SPhos (0.010 mmol) were placed under argon atmosphere. (*Z*)-**4fa** (0.201 mmol) in dry THF (2.0 mL) was added, followed by addition of 3 M NaOH aq. (0.70 mL). Then, the mixture was warmed to 60 ℃ and stirred for 19 h. After the reaction mixture was cooled to room temperature, it was quenched by H_2O and extracted with Et_2O three times. The combined organic layer was then dried over $MgSO_4$. After filtration, the solvents were removed by evaporation. The crude mixture was purified by flash column chromatography (SiO_2, Et_2O/hexane, 0:100–5:95) to give the coupling product (*E*)-**11b** (64.8 mg, 0.198 mmol, 99%) as colorless oil.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.87 (t, *J* = 6.3 Hz, 3H), 1.22–1.33 (m, 8H), 1.70–1.75 (m, 8H), 2.03 (t, *J* = 7.0 Hz, 2H), 2.18 (q, *J* = 7.0 Hz, 2H), 3.50 (t, *J* = 6.3 Hz, 2H), 4.51 (s, 2H), 5.15 (t, *J* = 7.0 Hz, 1H), 5.55 (s, 1H), 7.26–7.35 (m, 5H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 14.1 (*C*H_3), 19.3 (*C*H_3), 22.6 (*C*H_2), 24.5 (*C*H_2), 26.4 (*C*H_3), 28.6 (*C*H_2), 29.2 (*C*H_2), 30.0 (*C*H_2), 31.0 (*C*H_2), 31.8 (*C*H_2), 69.9 (*C*H_2), 72.9 (*C*H_2), 127.4 (*C*H), 127.6 (*C*H), 127.8 (*C*H), 128.3 (*C*H), 132.7 (*C*), 138.0 (*C*), 138.6 (*C*). HRMS-EI (*m*/*z*): $[M–Me]^+$ calcd for $C_{21}H_{31}O$, 299.2375; found, 299.2376.

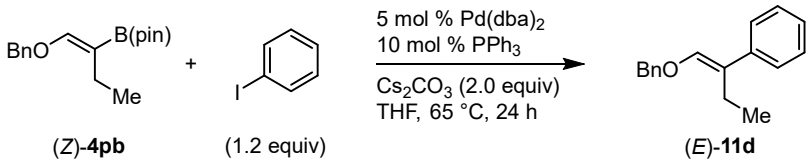


(*Z*)-**4la** (3.0 equiv) (*E*)-**11c**

The Suzuki–Miyaura cross-coupling reaction of (*Z*)-**4la** was conducted according to the literature procedure.[29] (*Z*)-**4la** (0.100 mmol) and $Pd(PPh_3)_4$ (0.0030 mmol) were placed in an oven-dried reaction vial under argon atmosphere. Dry toluene (0.3 mL) was added in the vial through the rubber septum using a syringe. After the addition of 4-tolyl iodide (0.300 mmol) and 3 M KOH aq. (0.2 mL) into the vial, the mixture was stirred at 90 ℃ for 16 h. After celite filtration, the celite washed with DCM and the mixture of the filtrate dried over $MgSO_4$ followed by filtration. After evaporation, the crude material was purified by silica gel chromatography

(EtOAc/hexane, 15:85–25:75) to give the coupling product (*E*)-**11c** in 73% yield (20.9 mg, 0.0732 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.85 (t, *J* = 6.7 Hz, 3H), 1.16–1.47 (m, 8H), 2.14 (quintet, *J* = 7.5 Hz, 2H), 2.34 (s, 3H), 2.40–2.58 (m, 4H), 3.77 (t, *J* = 7.1 Hz, 2H), 6.49 (s, 1H), 7.12 (d, *J* = 8.6 Hz, 3H), 7.24 (m, *J* = 8.2 Hz, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 14.0 (*C*H_3), 19.0 (*C*H_2), 21.1 (*C*H_3), 22.6 (*C*H_2), 28.8 (*C*H_2), 29.5 (*C*H_2), 30.0 (*C*H_2), 30.6 (*C*H_2), 31.6 (*C*H_2), 49.3 (*C*H_2), 121.7 (*C*H), 126.6 (*C*H), 128.9 (*C*H), 132.7 (*C*), 136.7 (*C*), 138.0 (*C*), 175.1 (*C*). HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{19}H_{27}ONNa$, 308.1985; found, 308.1986.

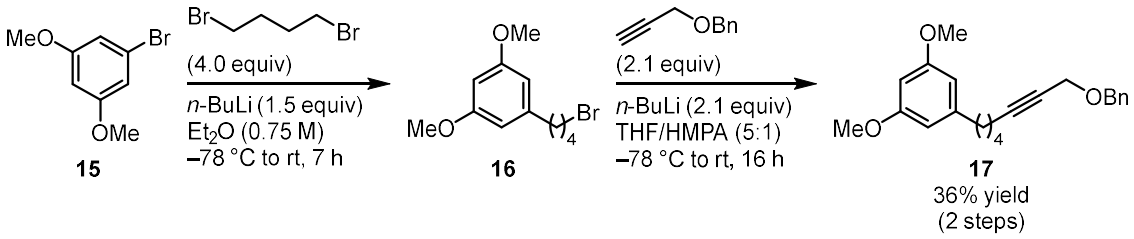


(*Z*)-**4pb** (1.2 equiv) (*E*)-**11d**

The Suzuki–Miyaura cross-coupling reaction of (*Z*)-**4la** was conducted according to the literature procedure.[44] In an oven-dried reaction vial, $Pd_2(dba)_3$ (0.0030 mmol), PPh_3 (0.010 mmol) and Cs_2CO_3 (0.200 mmol) were placed under a nitrogen atmosphere. Dry THF (0.5 mL) was added through the rubber septum using a syringe. After the addition of iodobenzene (0.119 mmol) and (*Z*)-**4pb** (0.100 mmol), the mixture was stirred at 65 ℃ for 24 h. After the substrate was consumed, the reaction mixture was passed through a short silica gel column (*Φ*: 10 mm, height of the silica-gel column: 90 mm) with Et_2O/hexane (10/90) eluent. The crude material was purified by flash column chromatography (SiO_2, Et_2O/hexane, 0:100–2:98) to give the corresponding coupling product (*E*)-**11c** in 76% yield (21.4 mg, 0.0755 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.02 (t, *J* = 7.4 Hz, 3H), 2.58 (q, *J* = 7.6 Hz, 2H), 4.91 (s, 2H), 6.42 (s, 1H), 7.15–7.40 (m, 10H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 13.1 (*C*H_3), 20.4 (*C*H_2), 74.0 (*C*H_2), 112.1 ©, 125.7 (*C*H), 125.9 (*C*H), 127.3 (*C*H), 127.9 (*C*H), 128.3 (*C*H), 128.5 (*C*H), 137.6 (*C*), 139.5 (*C*), 143.1 (*C*H). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{17}H_{18}O$, 238.1358; found, 238.1356.

2.4.7. Formal Total Synthesis of schizol A

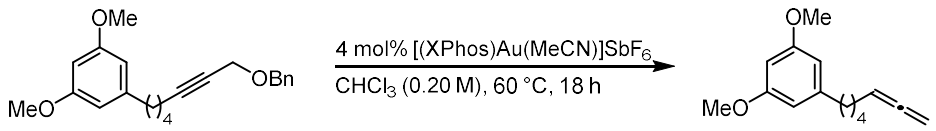


In a vacuum dried 50 mL two-neck round-bottomed flask, aryl bromide **15** was dissolved

in Et_2O (20 mL) under a nitrogen atmosphere. After cooled to −78 °C, to this solution was added *n*-BuLi (22.5 mmol) dropwise and the mixture was warmed up to 0 °C. After stirred for 30 min, the reaction mixture was cooled to −78 °C again. Then, to the reaction mixture was added 1,4-dibromobutane (7.1 ml, 60 mmol) dropwise and the mixture was warmed up to room temperature. After 7 h, the resulting mixture was diluted with water (30 ml) and extracted with Et_2O three times. The combined organic layer was then dried over Mg_2SO_4. After filtration, the solvents were removed by evaporation. The crude product was purified by flash column chromatography to give the mixture of corresponding coupling product **16** and 1,3-dimethoxybenzene (colorless oil).

In a vacuum dried 50 mL two-neck round-bottomed flask, propargyl ether was dissolved in THF (30 mL) under a nitrogen atmosphere. After cooled to −78 °C, to this solution was added *n*-BuLi (16.2 mmol) dropwise and the mixture was warmed up to 0 °C. After stirred for 30 min, to the reaction mixture was added HMPA (7.7 ml) and alkyl bromide **16** solution in THF (10 ml). The reaction mixture was warmed up to room temperature and stirred for 16 h. After the reaction was completed, the reaction mixture was cooled to 0 °C and diluted with water (20 ml). The resulting mixture was extracted with Et_2O three times, and the combined organic layer was then dried over Mg_2SO_4. After filtration, the solvents were removed by evaporation. The crude product was purified by flash column chromatography to give the corresponding inner alkyne **17** in 36% yield (1.84 g, 5.43 mmol, colorless oil) in 2 steps.

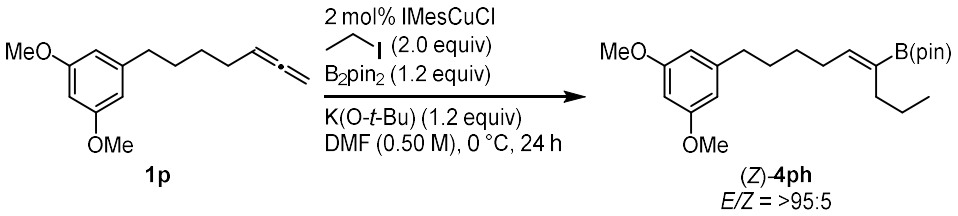
^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.52–1.63 (m, 2H), 1.74 (quintet, *J* = 7.4 Hz, 2H), 2.27 (tt, *J* = 6.6 Hz, 2.2 Hz, 2H), 2.58 (t, *J* = 7.6 Hz, 2H), 3.77 (s, 6H), 4.15 (t, *J* = 2.2 Hz, 2H), 4.58 (s, 2H) , 6.30 (t, *J* = 2.0 Hz, 1H) , 6.35 (d, *J* = 2.0 Hz, 2H), 7.25–7.39 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 18.6 (*C*H_2), 28.0 (*C*H_2), 30.2 (*C*H_2), 35.6 (*C*H_2), 55.1 (*C*H_3), 57.6 (*C*H_2), 71.2 (*C*H_2), 76.0 (*C*), 86.8 (*C*), 97.5 (*C*H), 106.3 (*C*H), 127.6 (*C*H), 128.0 (*C*H), 128.3 (*C*H), 137.5 (*C*), 144.6 (*C*), 160.6 (*C*). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{22}H_{26}O_3$, 338.1882; found, 338.1879.



[(XPhos)Au(MeCN)]SbF_6 (33.8 mg, 0.0356 mmol) were placed in an oven-dried reaction vial. After the vial was sealed with a screw cap containing a Teflon®-coated rubber septum, the vial was connected to a vacuum/nitrogen manifold through a needle. It was evacuated and then backfilled with nitrogen. This cycle was repeated three times. Dry $CHCl_3$ (4.5 mL) and inner alkyne **17** were added to the vial through the rubber septum using a syringe and the reaction mixture was warmed up to 60 °C. After stirring for 24 h, the reaction mixture was

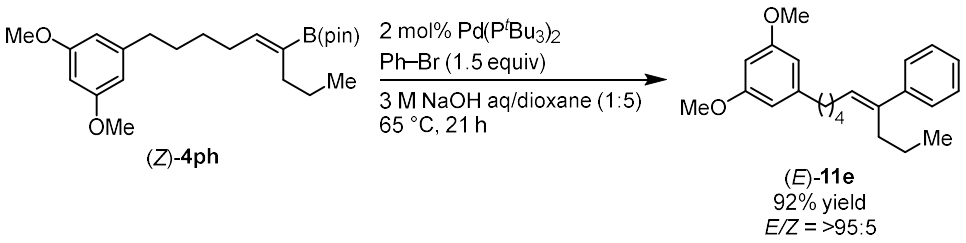
cooled to room temperature and passed through a short silica gel column (Φ: 10 mm, the height of the silica-gel column: ca. 30 mm) eluting with Et_2O/hexane (10/90). The crude material was purified by flash column chromatography to give the corresponding allene product **1p** in 62% yield (129.1 mg, 0.556 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.46 (quintet, *J* = 7.5 Hz, 2H), 1.65 (quintet, *J* = 7.6 Hz, 2H), 1.99–2.08 (m, 2H), 2.56 (t, *J* = 7.6 Hz, 2H), 3.78 (s, 6H), 4.62–4.68 (m, 2H), 5.09 (quintet, *J* = 6.7 Hz, 1H), 6.30 (t, *J* = 2.3 Hz, 1H), 6.34 (d, *J* = 2.3 Hz, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 28.0 (*C*H_2), 28.7 (*C*H_2), 30.6 (*C*H_2), 36.0 (*C*H_2), 55.1 (*C*H_3), 74.6 (*C*H_2), 89.8 (*C*H), 97.5 (*C*H), 106.4 (*C*H), 145.0 (*C*), 160.6 (*C*), 208.4 (*C*). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{15}H_{20}O_2$, 232.1463; found, 232.1459.



IMesCuCl was prepared according to the literature.[42] In an argon-filled grove-box, IMesCuCl (4.5 mg, 0.0111 mmol), bis(pinacolato)diboron (**3**) (169.6 mg, 0.668 mmol), and K(O-*t*-Bu) (75.0 mg, 0.668 mmol) were placed in an oven-dried reaction vial. After the vial was sealed with a screw cap containing a Teflon™-coated rubber septum, dry DMF (1.11 mL) was added in the vial through the rubber septum using a syringe. After stirred for 15 min, the reaction mixture was cooled to 0 ℃. After stirred at 0 ℃ for 10 min, **1p** (129.1 mg, 0.556 mmol) and ethyl iodide (173.1 mg, 1.11 mmol) were added to the mixture. The reaction mixture was stirred at 0 ℃ for 24 h. After the reaction was completed, the reaction mixture was passed through a short silica gel column (*Φ*: 10 mm, height of the silica-gel column: 90 mm) with Et_2O/hexane (10/90) eluent. The crude material was purified by flash column chromatography (SiO_2, Et_2O/hexane, 0:100–20:80) to give the corresponding alkenyl boronate (*Z*)-**4ph** in 65% yield with *E*/*Z* = <5:95, **4**:**5** = >95:5 (141.1 mg, 0.363 mmol, colorless oil).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.88 (t, *J* = 7.0 Hz, 3H), 1.29 (s, 12H), 1.30–1.49 (m, 4H), 1.63 (quintet, *J* = 7.5 Hz, 2H), 2.04–2.20 (m, 4H), 2.55 (t, *J* = 7.6 Hz, 2H), 3.78 (s, 6H), 6.25–6.32 (m, 2H), 6.32–6.37 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 14.0 (*C*H_3), 23.3 (*C*H_2), 24.7 (*C*H_3), 28.3 (*C*H_2), 28.8 (*C*H_2), 30.5 (*C*H_2), 31.0 (*C*H_2), 36.1 (*C*H_2), 55.2 (*C*H_3), 82.9 (*C*), 97.6 (*C*H), 106.4 (*C*H), 132.3 (br, B–*C*), 145.1 (*C*), 145.7 (*C*H), 160.6 (*C*). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{23}H_{37}O_4{}^{11}B$, 388.2789; found, 388.2779.



The Suzuki–Miyaura cross-coupling reaction of (*Z*)-**4ph** was conducted according to the literature procedure.[29] Under argon atmosphere, Pd(P^{t}Bu$_3$)$_4$ (1.0 mg, 0.0020 mmol) were placed in an oven-dried reaction vial. Dry 1,4-dioxane (0.5 mL) was added in the vial through the rubber septum using a syringe. After the addition of (*Z*)-**4ph** (38.8 mg, 0.100 mmol), bromobenzene (18.8 mg, 0.120 mmol) and 3 M NaOH aqueous solution (0.1 mL) into the vial, the mixture was warmed to 65 ℃. After stirred for 21 h, the reaction mixture was cooled to room temperature and passed through a short silica gel column (*Φ*: 10 mm, height of the silica-gel column: 90 mm) with Et_2O/hexane (10/90) eluent. The crude material was purified by flash column chromatography to give the corresponding coupling product **11e** in 92% yield with *E*/*Z* = >95:5 (31.0 mg, 0.0916 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.87 (t, *J* = 7.4 Hz, 3H), 1.35 (sextet, *J* = 3.5 Hz, 2H), 1.49 (quintet, *J* = 7.0 Hz, 2H) ,1.68 (quintet, *J* = 8.2 Hz, 2H), 2.22 (q, *J* = 7.2 Hz, 2H), 2.46 (t, *J* = 7.6 Hz, 2H), 2.58 (t, *J* = 7.6 Hz, 2H), 3.78 (s, 6H) , 5.64 (t, *J* = 7.2 Hz, 1H), 6.30 (t, *J* = 2.5 Hz, 1H), 6.35 (d, *J* = 2.0 Hz, 2H), 7.18–7.24 (m, 1H), 7.26–7.35 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 14.0 (*C*H_3), 21.8 (*C*H_2), 28.4 (*C*H_2), 29.5 (*C*H_2), 30.9 (*C*H_2), 31.7 (*C*H_2), 36.2 (*C*H_2), 55.2 (*C*H_3), 97.6 (*C*H), 106.4 (*C*H), 126.3 (*C*H), 126.4 (*C*H), 128.1 (*C*H), 129.0 (*C*H), 140.0 (*C*), 143.4 (*C*), 145.1 (*C*), 160.7 (*C*). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{23}H_{30}O_2$, 338.2246; found, 338.2244.

2.5. Computational Details

2.5.1. Computational Methods

All geometry optimizations and thermal energy correction calculations (frequency analyses) using density functional theory (DFT) were performed with the Gaussian 16 (revision C.01)[45] suite of programs. The thresholds defined in Gaussian 16 were used. The geometry optimizations were carried out at ωB97X-D[46] level of theory with a mixed basis set [SDD[47] for Cu atom, and 6-31G(d)[48] for the other atoms]. The solvation effect of DMF was included in the calculations using SMD solvation model.[48] Harmonic frequency calculations were conducted at the same level of theory on the optimized geometries to check all the stationary points as either minima or first-order saddle points. Intrinsic reaction coordinate

(IRC)[49] calculations were carried out to confirm the transition states connecting the correct reactants and products on the potential energy surface. Moreover, the self-consistent field (SCF) energies of the optimized molecular systems were corrected at a higher level of theory. For these reasons, I chose ωB97X-D[46] functional with another mixed basis set [SDD[47] for Cu atom, and 6-311+G(d,p)[48] for the other atoms]. The solvation effect of DMF was included in the calculations with SMD solvation model.[48]

2.5.2. Calculated Properties of All Structures

Table S1. Calculated energies and parameters of the optimized structures.

Structure	SCF energy [hartree]	*H* [hartree]	*TS* [hartree]	*G* [hartree]
Substrate **1**	–155.962079	–155.872210	0.032649	–155.904859
Catalyst **Int2**	–155.873154	–1532.181045	0.103293	–1532.284338
TS$^{\text{alkenyl-}Z}$	–1688.762278	–1688.054519	0.111634	–1688.166153
TS$^{\text{alkenyl-}E}$	–1688.757495	–1688.049891	0.110283	–1688.160174
(*Z*)-**Int3**	–1688.846123	–1688.135629	0.112073	–1688.247702
(*E*)-**Int3**	–1688.840612	–1688.129926	0.110694	–1688.240620
Int3'	–1688.838475	–1688.128026	0.110235	–1688.238261

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3. Regio- and Stereoselective Silaboration of Terminal Allenes with Copper(I)-Catalyst

3.1. Introduction

Functionalized organoboron compounds, like alkenyl and allylic boronic acid esters, and organosilicon compounds, like alkenyl and allylic silanes, are recognized as useful building blocks in organic synthesis.[1,2] Therefore, silyl boryl compounds bearing alkenyl and allylic moieties are expected to be more attractive than the simple organoboron and -silicon compounds. Stepwise derivatizations of the borylated and silylated carbons can increasingly construct complex skeletons.

Silaboration of allenes with silylboranes is one practical preparation method of silyl boryl compounds (Figure 21a).[3–5] This method can potentially produce alkenyl and allylic boronates (the upper and lower arrows, respectively). Commonly, the regioselectivity of the reaction affords the alkenyl boron and an allylic silane structure (the upper arrow).[4] For this selectivity, many types of palladium-catalyzed reactions have been developed.[6] On the other hand, the regioselectivity producing the allylic boronate and alkenyl silane structure is very rare (the lower arrow),[5] i.e., only two examples have been reported to our knowledge. One example has been reported by the Cheng group; a combination of palladium catalyst and an alkenyl iodide gave the allylic boronates.[7a] After that, the Stratakis group reported a gold nanoparticle on TiO_2 also catalyzes the same reaction.[7b] However, this rare regioselectivity is limited to those expensive metal-catalyzed reactions.

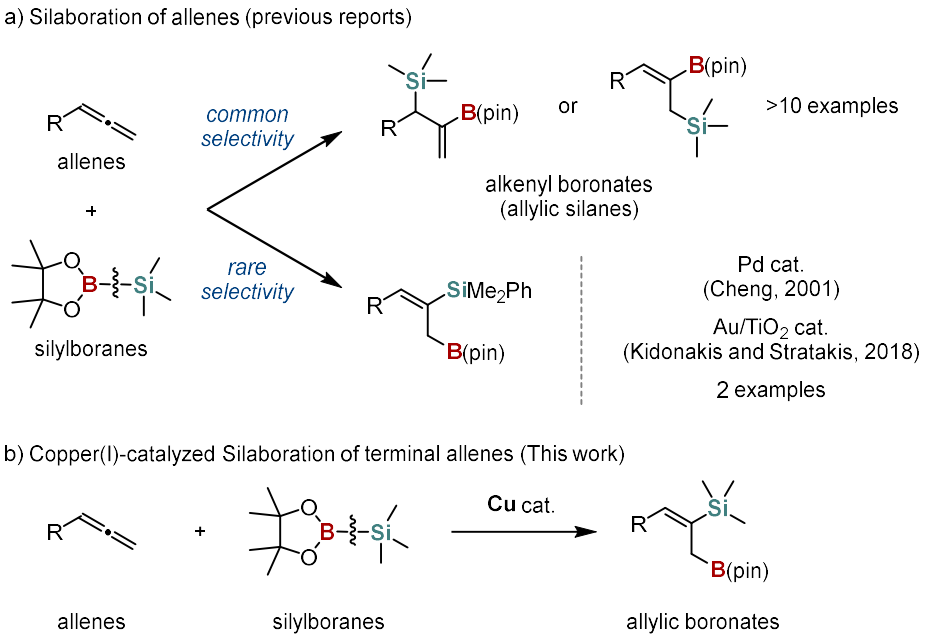


Figure 21. Silyl boryl compounds and methods for their synthesis from allenes.

Recently, I focused on the synthesis of multisubstituted allylic boronates *via* borylation of allenes with a copper(I)/$B_2(pin)_2$ system.[8] Based on the study, I anticipated that silaboration of allenes with a copper(I)/R_3Si–B(pin) system could also furnish the rare-selectivity product with a silyl copper(I) active species.[9,10] As a nucleophilic silyl group on the silyl copper(I) intermediate is introduced at the 2-position of the allenes to produce the alkenyl silane moiety.[11,12]

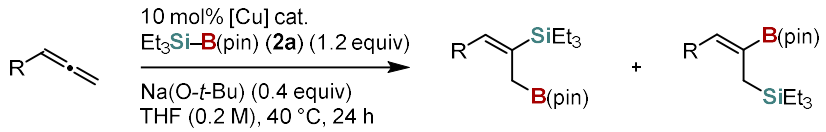
Herein, I developed the first copper(I)-catalyzed silaboration of terminal allenes (Figure 21b). The reaction proceeds with the rare regioselectivity to produce allylic boronic acid esters bearing alkenyl silane moiety under mild reaction conditions (Figure 21b, the lower arrow). The products were obtained in high yield with high regio- and stereoselectivity (up to 93% yield, r.r. = >95:5, *E*/*Z* = >95:5). Moreover, I demonstrated the derivatization of both the C–B bond and C–Si bond for the synthesis of multi-functionalized molecules.

3.2. Results and Discussions

I started the reaction optimization from the conditions for a copper(I)-catalyzed regio- and stereoselective silaboration of alkynes, which was reported by the Shintani group,[10b] I investigated the suitable catalyst with phenethyl allene **1a** as a model substrate (Table 1). The stereoselectivity of allylic boronate **3** was exellent otherwise noted (*E*/*Z* = <5:95). Copper(I) iodide, which is the optimal catalyst precursor for the silaboration of alkynes,[10b] gave the desired product in good yield with high regioselectivity (entry 1: 98%, **3**/**4** = 96:4). However, other copper(I) salts, copper(I) chloride and copper(I) acetate, were not suitable to this reaction, although the regioselectivity was slightly increased (entry 2: 48%, **3**/**4** = >99:1; entry 3: 65%, **3**/**4** = >99:1). A cationic copper(I) salt, $[Cu(MeCN)_4]BF_4$, did not afford the product (entry 4: trace). Also, I found copper(I) 2-thiophenecarboxylate (CuTC)[10a] was effective in this reaction to produce the desired product in high yield with good regioselectivity (entry 5: 94%, **3**/**4** = 97:3). On the other hand, a divalent copper salt was not effective in this reaction (entry 6: 66%, **3**/**4** = >99:1). Next, I tested copper(I) catalysts bearing phosphine ligands and *N*-heterocyclic carbene (NHC) ligands. Unfortunately, the yields were low to moderate (entry 7: 55%, **3**/**4** = >99:1; entry 8: 58%, **3**/**4** = >99:1; entry 9: 38%, **3**/**4** = >99:1). Based on the above results, CuI and CuTC were found to be suitable copper sources to this reaction. For the model substrate **1a**, both CuI and CuTC gave the product almost quantitatively with high regioselectivity, although the selectivity was slightly decreased compared to the small-scale reactions (entry 10: 98%, **3**/**4** = 94:6; entry 11: >99%, **3**/**4** = 92:8). For a substrate with an *n*-octyl group as another *prim*-alkyl group (**1b**), CuTC showed the better results than CuI (entry 12: 77%, **3**/**4** = 87:13; entry 13: 89%, **3**/**4** = 88:12). Also, in the case of cyclohexyl allene **1c**, CuTC was more effective than CuI (entry 14: 61%, **3**/**4** = >99:1;

entry 15: 72%, **3**/**4** = >99:1). Therefore, I selected CuTC as an optimal catalyst precursor for this silaboration reaction of terminal allenes.

Table 5. Optimization of a copper(I) catalyst



1x (*E*)-**3xa** *E*/*Z* = >95:5 (*Z*)-**4xa**

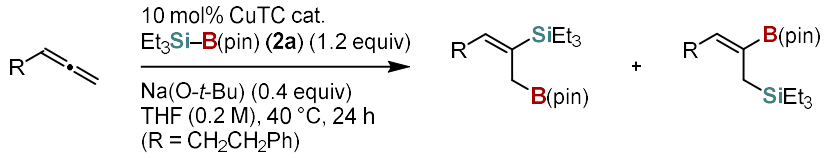
entry	[Cu] cat.	R–	yield [%]	**3**/**4** [%]
1	CuI	$PhCH_2CH_2$–	98	96:4
2	CuCl	$PhCH_2CH_2$–	48	>99:1
3	CuOAc	$PhCH_2CH_2$–	65	>99:1
4	$[Cu(MeCN)_4]BF_4$	$PhCH_2CH_2$–	trace	-
5	CuTC	$PhCH_2CH_2$–	94	97:3
6	$CuCl_2$	$PhCH_2CH_2$–	66	>99:1
7	CuI/Xantphos	$PhCH_2CH_2$–	55	>99:1
8	CuI/PPh_3	$PhCH_2CH_2$–	58	>99:1
9	IMesCuCl	$PhCH_2CH_2$–	38	>99:1
10[b]	CuI	$PhCH_2CH_2$–	98	94:6
11[b]	CuTC	$PhCH_2CH_2$–	>99	92:8
12[b]	CuI	*n*-Octyl–	77	87:13
13[b]	CuTC	*n*-Octyl–	89	88:12
14[b]	CuI	Cy–	61	>95:5
15[b]	CuTC	Cy–	72	>95:5

[a]Standard conditions: [Cu] cat. (0.025 mmol), **1a** (0.25 mmol), **2a** (0.30 mmol), and Na(O-*t*-Bu) (0.10 mmol) in THF (1.25 mL). The yield and regioselectivity (**3**/**4**) were determined by GC analysis of the reaction mixture using an internal standard. [b][Cu] cat. (0.05 mmol), **1a** (0.50 mmol), **2a** (0.60 mmol), and Na(O-*t*-Bu) (0.20 mmol) in THF (2.5 mL). The yield and regioselectivity (**3**/**4**) were determined by ^{1}H NMR analysis of the crude material using an internal standard.

Next, the other reaction conditions were tested in Table 6. Entry 1 is the standard condition to compare it with other conditions. The higher concentration condition gave almost the same results as the standard conditions (entry 2: 93%, **3**/**4** = 95:5). When I used a potassium base as the additive, dropped the yield was shown (entry 3: 79% yield, **3**/**4** = >99:1). Also, a lithium base afforded trace amount of the product. The equivalent of the base was found to be important; both half (0.2 equiv) and double (0.8 equiv) amount of the base resulted in decreasing in the yield (entry 5: 38% yield, **3**/**4** = >99:1, entry 6: 84% yield, **3**/**4** =

92:8). The yield was dramatically dropped at the lower reaction temperature (entry 7: 13% yield, **3**/**4** = >99:1).

Table 6. Optimization of other reaction conditions



1a (*E*)-**3aa** *E*/*Z* = >95:5 (*Z*)-**4xa**

entry	Change from standard conditions	yield [%]	**3**/**4** [%]
1	none	94	97:3
2	base: Na(O-*t*-Bu), 0.5 M	93	95:5
3	base: K(O-*t*-Bu), 0.5 M	79	>99:1
4	base: Li(O-*t*-Bu), 0.5 M	trace	-
5	base: Na(O-*t*-Bu) (0.2 equiv)	38	>99:1
6	base: Na(O-*t*-Bu) (0.8 equiv)	84	92:8
7	temperature: 30 ℃	13	>99:1

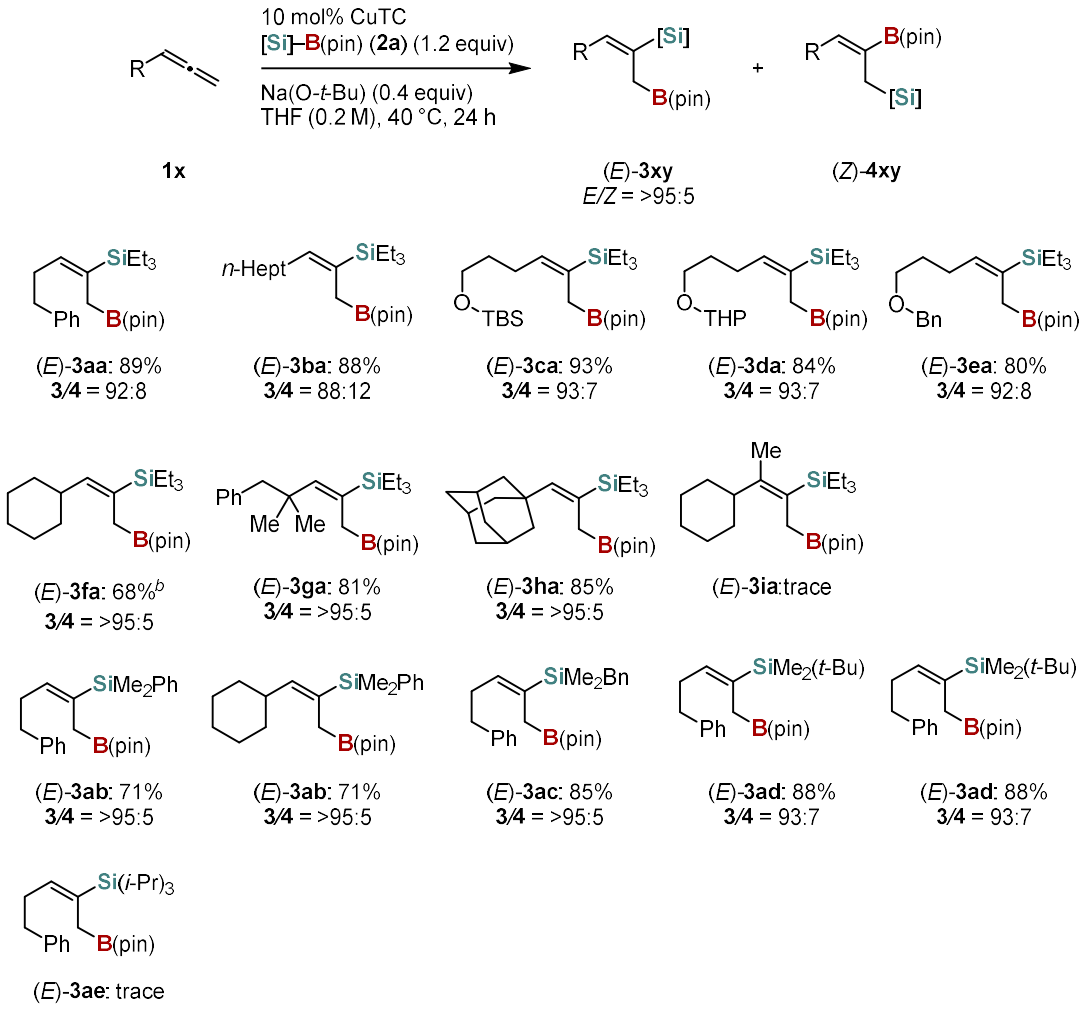
[a]Standard conditions: [Cu] cat. (0.025 mmol), **1a** (0.25 mmol), **2a** (0.30 mmol), and Na(O-*t*-Bu) (0.10 mmol) in THF (1.25 mL). The yield and regioselectivity (**3**/**4**) were determined by GC analysis of the reaction mixture using an internal standard.

Then, the substrate scope of allenes and silylboranes was investigated in Table 7. The stereoselectivity was *E*/*Z* = <5:95 otherwise noted. The silaboration products of the model substrates bearing *prim*-alkyl groups were given in high yield with high regioselectivity [(*E*)-**3aa**: 89%, **3**/**4** = 92:8; (*E*)-**3ba**: 88%, **3**/**4** = 88:12]. The TBS, THP, and Bn groups for protection of a hydroxyl group were tolerated [(*E*)-**3ca**: 93%, **3**/**4** = 93:7; (*E*)-**3da**: 84%, **3**/**4** = 93:7; (*E*)-**3ea**: 80%, **3**/**4** = 92:8]. A cyclohexyl allene also furnished the product in good yield with perfect regio- and stereoselectivity [(*E*)-**3fa**: 68%, **3**/**4** = >95:5]. Also, the bulkier substituents were applicable to this reaction [(*E*)-**3ga**: 93%, **3**/**4** = >95:5; (*E*)-**3da**: 85%, **3**/**4** = >95:5]. Unfortunately, a *gem*-disubstituted allene gave merely trace amounts of the regioselectivity-inverted product, the alkenyl boronate **4** [(*Z*)-**4ia**: trace].

As the next step, the scope of silylboranes was investigated. Me_2PhSi–B(pin) afforded the corresponding products in good yield with perfect regioselectivity [(*E*)-**3ab**: 71%, **3**/**4** = >95:5; (*E*)-**3fb**: 61%, **3**/**4** = >95:5]. After that, silylboranes having trialkyl silyl groups were tested, which were synthesized according to the procedure previously reported.[13] The Bn-group-substituted silylborane afforded the product in good yield [(*E*)-**3ac**: 85%, **3**/**4** = >95:5]. The TBS group could also be added in excellent yield with high regioselectivity [(*E*)-**3ad**: 93%,

3/**4** = 93:7]. Unfortunately, a bulky silyl group was not reactive in this silaboration reaction [(*E*)-**3ae**: trace].

Table 7. Substrate scopes



[a]Standard conditions: [Cu] cat. (0.05 mmol), **1a** (0.50 mmol), **2a** (0.60 mmol), and Na(O-*t*-Bu) (0.20 mmol) in THF (2.5 mL). Isolated yield. The regioselectivity (**3**/**4**) was determined by ^{1}H NMR analysis after silica-gel column chromatography. [b]The product was isolated after oxidation of the boryl group.

For the application of the silyl boryl compounds obtained in this reaction were attempted in Figure 22. The allylboration reaction of benzaldehyde with various allylic boronates (*E*)-**3** afforded the homo-allylic alcohols **6** in high yield with excellent diastereoselectivity without the loss of alkenyl silane moieties (Figure 22a; **6a**: 80%; **6b**: 77%; **6c**: 88%). Moreover, a sequential functionalization of the boryl and silyl groups were performed. The oxidation of the boryl group did not lose the alkenyl silane structure to give the product (*E*)-**8** in high yield

(Figure 22b; 95%). After the protection of the hydroxy group, the silyl group could be converted to the iodine in high yield [(*E*)-**9**, 79%]. The stereochemistry of the alkene structure was not decreased through these stepwise derivatizations (*E*/*Z* = >95:5).

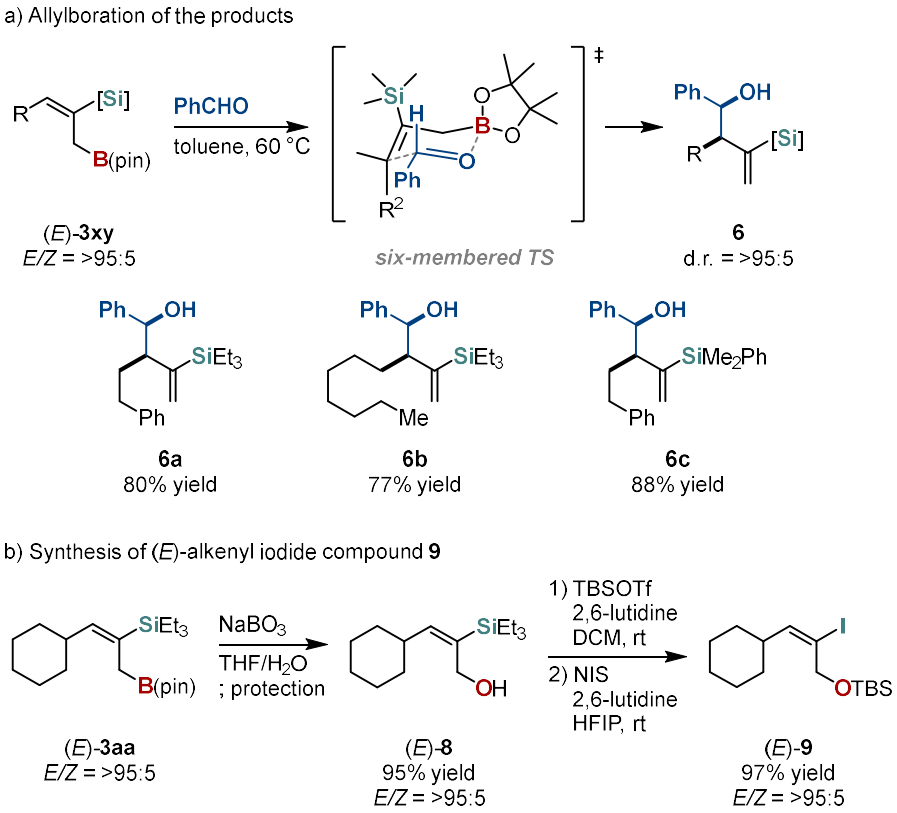


Figure 22. Derivatizations of C–B and C–Si bonds

The proposed mechanism is shown in Figure 23a. The copper(I) alkoxide **Int1** is generated from the copper(I) salt in the presence of an alkoxide base. The σ-bond metathesis between **Int1** and the silylborane **2** generates the silyl copper(I) intermediate **Int2**. After that, the nucleophilic silyl group on the copper(I) in **Int2** is inserted into the electrophilic carbon center in the allene *via* (*E*)-**TS1** to afford the allylic copper(I) intermediate (*E*)-**Int3**. Finally, the σ-bond metathesis between (*E*)-**Int3** and the silylborane **2** *via* (*E*)-**TS2** gave the product (*E*)-**3** and regenerate the silyl copper(I) intermediate **Int2**.

To gain detailed insight into the regio- and stereoselectivity-determining mechanism, the transition state of silylcupration **TS1** was analyzed by means of density functional theory (DFT) calculations. The calculations were conducted at ωB97X-D/Def2-SVP/SMD(THF) level of theory.[14] A TMS group and a methyl allene were used as the calculation models. Also, one molecule of THF was used as the ligand of copper(I) since 2-thiophenecarboxylate in

CuTC is expected to be exchanged with THF molecule in THF solvation. The ligation of THF is stronger than thiophene, which was confirmed by DFT analysis (see Supporting Information). The major product (*E*)-**3** is produced *via* (*E*)-**TS1**. The nucleophilic silyl group on the silyl copper(I) is connected to the electrophilic carbon atom of the allene. This match of electronic effects should promote the major path. For the stereoisomer (*Z*)-**3**, the silyl copper(I) intermediate inserts from the side of the methyl group of the allene substrate. The steric congestion between the silyl group and the methyl group destabilizes the structure, as a result, suppresses this minor path of stereoisomer. For the regioisomer **4**, there are not the interaction of nucleophilic and electrophilic groups in the TS (**TS1'**). Therefore, this electronic disadvantage prevents this minor path of the regioisomer.

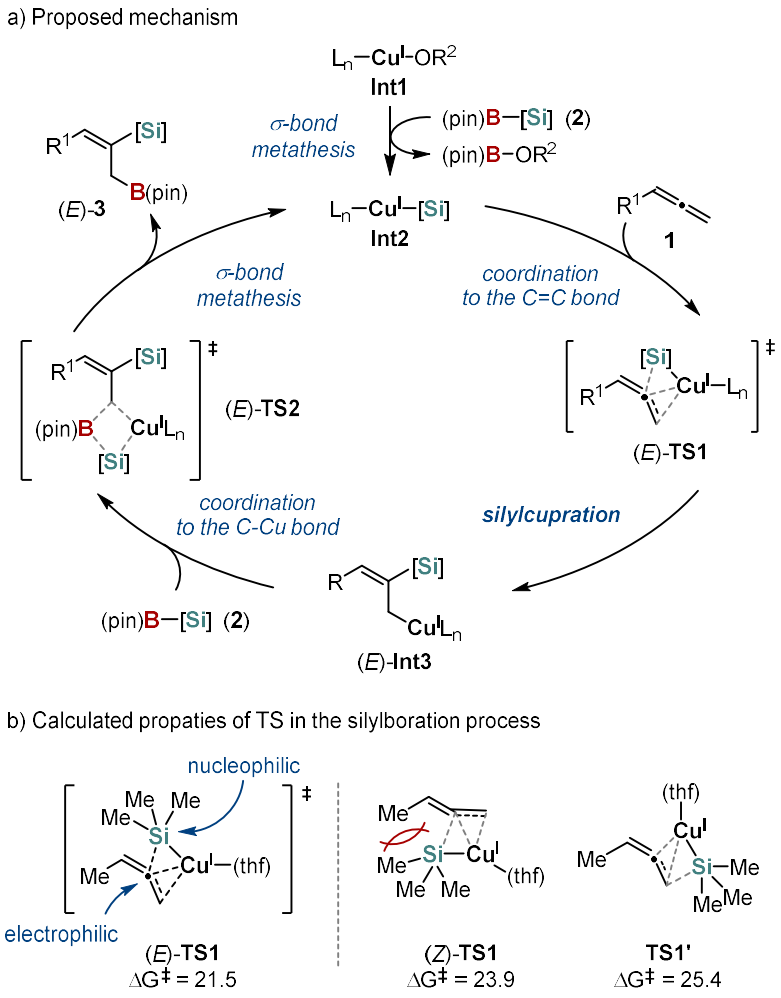


Figure 23. Proposed mechanism and computational study

3.3. Conclusion

In conclusion, I developed the first copper(I)-catalyzed silaboration reaction of terminal allenes. The product has an allylic boronate moiety and an alkenyl silane moiety. This is rare regioselectivity in the silaboration of allenes. The alkene structure was constructed with high stereoselectivity. Allene substrates bearing *prim*-, *sec*- and *tert*-alkyl groups and a variety of silyl groups in the silylboranes were applicable in this reaction. Moreover, the boryl and silyl groups in the products could be transformed into other functional groups with high stereospecificity.

3.4. Experimental Details

3.4.1. Instruments and Chemicals

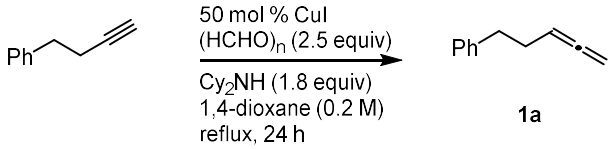
Materials were commercially available and purified by standard procedures unless otherwise noted. Also, solvents were commercially available, degassed *via* three freeze-pump-thaw cycles, and dried over molecular sieves (MS 4A). NMR spectra were recorded on JEOL JNM-ECX400P and JNM-ECS400 spectrometers (^{1}H: 400 MHz, ^{13}C: 100 MHz). Tetramethylsilane (^{1}H, δ 0.00) and $CDCl_3$ (^{13}C, δ 77.0) were employed as the external standards, respectively. Copper(I) 2-thiophenecarboxylate (CuTC) (Tokyo Chemical Industry, C2312) and Na(O-*t*-Bu) (Tokyo Chemical Industry, S0450) were purchased and used as received. GLC analyses were conducted with a Shimadzu GC-2014 or GC-2025 equipped with a ULBON HR-1 glass capillary column (Shinwa Chemical Industries) and an FID detector. High-resolution mass spectra were obtained at the Global Facility Center, Hokkaido University.

3.4.2. General Experimental Procedure

CuTC (0.05 mmol) and Na(O-*t*-Bu) (0.20 mmol) were placed in an oven-dried vial under argon atmosphere. After the vial was sealed with a screw cap containing a Teflon™-coated rubber septum, dry THF (2.5 mL) and **2a** (0.60 mmol) were successively added to the vial through the rubber septum using a syringe. After the mixture was stirred for 15 min, **1a** (0.50 mmol) was added to the mixture. After being stirred for 24 h at 40 ℃, the reaction mixture was passed through a short pad of silica gel (*Φ*: 10 mm, the height of the silica gel: 90 mm), with Et_2O/hexane (10/90) eluent. The crude material was purified by flash column chromatography (silica gel, Et_2O/hexane, 0:100–2:98) to give the corresponding silaboration product (*E*)-**3aa** as a colorless oil. Finally, the regioselectivity and stereoselectivity were determined by ^{1}H NMR analysis.

3.4.3. Substrate Preparation Procedure and Characterization

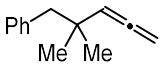
Terminal allenes **1a**–**1h** were prepared according to a general preparation procedure (GPP1) described below. A *gem*-disubstituted allene **1i** was prepared according to the reference.[41] Silylboranes **2a** and **2c**–**2e** were prepared according to a general preparation procedure (GPP2) described below. Silylborane **2b** was purchased from commercial suppliers (Tokyo Chemical Industry Co.). The ^{1}H and ^{13}C NMR spectra of known compounds were confirmed with literatures (**1a**,[42] **1b**,[43] **1c**,[44] **1d**,[45] **1e**,[42] **1f**,[44] **1h**,[46] **2a**,[47] **2b**–**2e**[47]).



1a

The terminal allene **1a** was synthesized according to the literature procedure.[48] In an oven-dried round-bottomed flask, but-3-yn-1-ylbenzene (2.60 g, 20 mmol), CuI (2.00 g, 10 mmol), and paraformaldehyde (50 mmol) were dissolved in dry 1,4-dioxane (100 mL) under a nitrogen atmosphere. After the addition of dicyclohexylamine (6.53 g, 36 mmol) into the flask, the mixture was refluxed overnight. After the mixture was evaporated and filtered through a pad of celite with hexane as eluent. The crude material was then purified by silica gel chromatography (hexane eluent) to give the allene product **1a** as a colorless oil.

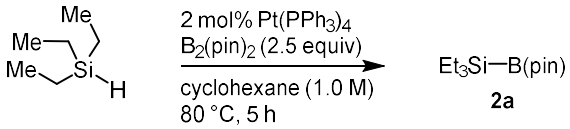
(2,2-Dimethylpenta-3,4-dien-1-yl)benzene. (1g)



1g

1g was prepared according to GPP1. It was obtained in 44% yield (2.37 g, 13.7 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.01 (s, 6H), 2.61 (s, 2H), 4.68 (d, *J* = 6.7 Hz, 2H), 5.10 (t, *J* = 6.7 Hz, 1H), 7.13–7.29 (m, 5H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 27.5 (*C*H_3), 35.2 (*C*), 49.4 (*C*H_2), 76.4 (*C*H_2), 100.4 (*C*H), 125.9 (*C*H), 127.6 (*C*H), 130.6 (*C*H), 138.8 (*C*), 206.4 (*C*). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{13}H_{16}$, 172.1252; found, 172.1246.



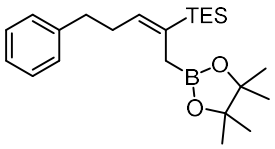
2a

The terminal silylborane **2a** was synthesized according to the literature procedure.[47] In

an oven-dried round-bottomed flask, $Pt(PPh_3)_4$ (0.200 mmol) and bis(pinacolato)diboron (25.0 mmol), and then triethylsilane (10.1 mmol) were dissolved in cyclohexane (10 mL). After being stirred at 80 °C for 5 h, the reaction mixture was passed through a short pad of silica gel (*Φ*: 10 mm, the height of the silica gel: 90 mm) with Et_2O/hexane (10/90) eluent. The crude material was purified by flash column chromatography (silica gel, Et_2O/hexane, 0:100–2:98) to give the silylborane product **2a** as a colorless oil.

3.4.4. Characterization of Products

(*E*)-Triethyl[5-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-en-2-yl]silane. [(*E*)-3aa]

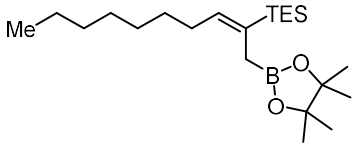


(*E*)-**3aa**

The reaction was conducted with 72.1 mg (0.500 mmol) of **1a**. The product (*E*)-**3aa** was obtained in 89% yield with *E*/*Z* = >99:1, **3**:**4** = 92:8 (172.5 mg, 0.446 mmol, colorless oil). The stereochemistry of the product was confirmed by H-H COSY and HMQC experiments of the product. The stereochemistry of the alkene structure was confirmed by NOESY experiment of the product.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.56 (q, *J* = 7.8 Hz, 6H), 0.90 (t, *J* = 8.0 Hz, 9H), 1.21 (s, 12H), 1.70 (s, 2H), 2.41 (q, *J* = 7.3 Hz, 2H) , 2.71 (t, *J* = 7.6 Hz, 2H) , 5.69 (t, *J* = 6.5 Hz, 1H) , 7.13–7.31 (m, 5H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 2.6 (*C*H_2), 7.4 (*C*H_3), 14.4 (*C*H_2), 24.8 (*C*H_3), 30.8 (*C*H_2), 35.6 (*C*H_2), 82.9 (*C*), 125.5 (*C*H), 128.1 (*C*H), 128.4 (*C*H), 133.8 (*C*), 139.2 (*C*H), 142.6 (*C*). HRMS-EI (*m*/*z*): [M–Me]$^+$ calcd for $C_{22}H_{42}{}^{11}BO_2Si$, 371.2578; found, 371.2579.

(*E*)-Triethyl[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dec-2-en-2-yl]silane. [(*E*)-3ba]



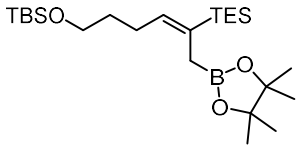
(*E*)-**3ba**

The reaction was conducted with 69.1 mg (0.500 mmol) of **1b**. The product (*E*)-**3ba** was obtained in 88% yield with *E*/*Z* = >95:5, **3**:**4** = 89:11 (168.0 mg, 0.442 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.57 (q, *J* = 7.8 Hz, 6H), 0.91 (t, *J* = 7.8 Hz, 9H), 1.21 (s, 12H), 1.22–1.45 (m, 13H), 1.70 (s, 2H) , 2.07 (q, *J* = 7.0 Hz, 2H) , 5.64 (t, *J* = 6.5 Hz, 1H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 2.7 (*C*H_2), 7.5 (*C*H_3), 14.1 (*C*H_3), 14.3 (*C*H_2), 22.7 (*C*H_2), 24.8

(CH_3), 28.9 (CH_2), 29.3 (CH_2), 29.39 (CH_2) , 29.45 (CH_2), 31.9 (CH_2), 82.9 (*C*), 132.7 (*C*), 140.7 (*C*H). HRMS-EI (*m*/*z*): [M–Me]$^+$ calcd for $C_{21}H_{42}{}^{11}BO_2Si$, 365.3047; found, 365.3044.

(*E*)-*tert*-Butyldimethyl{[5-triethylsilyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-4-en-1-yl]oxy}silane. [(*E*)-3ca]

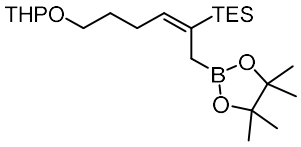


(*E*)-**3ca**

The reaction was conducted with 106.0 mg (0.499 mmol) of **1c**. The product (*E*)-**3ca** was obtained in 93% yield with *E*/*Z* = >95:5, **3**:**4** = 93:7 (172.5 mg, 0.463 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.05 (s, 6H), 0.57 (q, *J* = 7.8 Hz, 6H), 0.85–0.97 (m, 18H), 1.21 (s, 12H), 1.62 (quintet, *J* = 7.2 Hz, 2H), 1.71 (s, 2H), 2.12 (q, *J* = 7.0 Hz, 2H), 3.61 (t, *J* = 6.8 Hz, 2H), 5.64 (t, *J* = 6.3 Hz, 1H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): –5.3 (CH_3), 2.6 (CH_2), 7.5 (CH_3), 14.4 (CH_2), 18.4 (*C*), 24.8 (CH_3), 25.1 (CH_2), 26.0(CH_3), 32.5(CH_2), 63.0 (CH_2), 82.9 (*C*), 133.5 (*C*), 139.7 (*C*H). HRMS-EI (*m*/*z*): [M–Et]$^+$ calcd for $C_{22}H_{46}{}^{11}BO_3Si_2$, 425.3079; found, 425.3072.

(*E*)-Triethyl[6-(tetrahydro-pyran-2-yloxy)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-2-en-2-yl]silane. [(*E*)-3da]

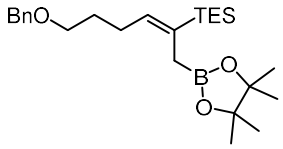


(*E*)-**3da**

The reaction was conducted with 91.1 mg (0.500 mmol) of **1d**. The product (*E*)-**3da** was obtained in 84% yield with *E*/*Z* = >95:5, **3**:**4** = 94:6 (177.3 mg, 0.418 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.57 (q, *J* = 7.8 Hz, 6H), 0.90 (t, *J* = 7.6 Hz, 9H), 1.21 (s, 12H), 1.46–1.91 (m, 10H), 2.16 (quintet, *J* = 6.4 Hz, 2H), 3.39 (q, *J* = 7.4 Hz, 1H), 3.49 (t, *J* = 5.7 Hz, 1H) , 3.75 (q, *J* = 7.5 Hz, 1H), 3.86 (t, *J* = 9.4 Hz, 1H) , 4.59 (t, *J* = 7.0 Hz, 1H) , 5.65 (t, *J* = 6.5 Hz, 1H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 2.6 (CH_2), 7.4 (CH_3), 14.3 (CH_2), 19.5 (CH_2), 24.7 (CH_3), 25.5 (CH_2), 25.5(CH_2), 29.4(CH_2), 30.7 (CH_2) , 62.1(CH_2), 67.2 (CH_2), 82.9 (*C*), 98.7 (*C*H) , 133.6 (*C*), 139.6 (*C*H). HRMS-ESI (*m*/*z*): [M+Na]$^+$ calcd for $C_{23}H_{45}{}^{11}BO_4SiNa$, 447.3073; found, 447.3062.

(*E*)-Triethyl[6-benzyloxy-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-2-en-2-yl]silane. [(*E*)-3ea]

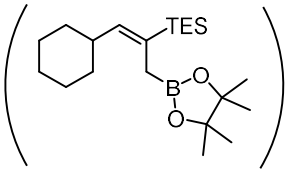


(*E*)-**3ea**

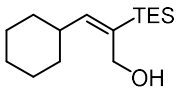
The reaction was conducted with 94.4 mg (0.501 mmol) of **1e**. The product (*E*)-**3ea** was obtained in 80% yield with *E*/*Z* = >95:5, **3**:**4** = 94:6 (173.0 mg, 0.402 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.56 (q, *J* = 7.8 Hz, 6H), 0.90 (t, *J* = 7.8 Hz, 9H), 1.20 (s, 12H), 1.68–1.80 (m, 4H), 2.17 (q, *J* = 7.1 Hz, 2H), 3.48 (t, *J* = 6.8 Hz, 2H), 4.50 (s, 2H), 5.63 (t, *J* = 6.5 Hz, 1H), 7.22–7.37 (m, 5H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 2.6 (*C*H_2), 7.4 (*C*H_3), 14.7 (*C*H_2), 24.7 (*C* H_3), 25.3 (*C*H_2), 29.4 (*C*H_2), 70.1 (*C*H_2), 72.8 (*C*H_2), 82.9 (*C*), 127.4 (*C*H), 127.6 (*C*H), 128.3 (*C*H), 138.7 (*C*), 139.5 (*C*H). HRMS-EI (*m*/*z*): $[M–Et]^+$ calcd for $C_{23}H_{38}{}^{11}BO_3Si$, 401.2684; found, 401.2686.

(*E*)-Triethyl[1-cyclohexyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-2-en-2-yl]silane. [(*E*)-3fa]



(*E*)-**3fa**

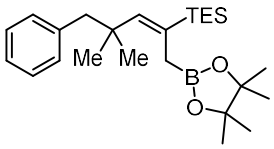


(*E*)-**8**

The reaction was conducted with 61.3 mg (0.502 mmol) of **1f**. The product (*E*)-**3fa** was obtained as a mixture with small amounts of an unidentified impurity. In order to remove the impurity, (*E*)-**3fa** was treated with $NaBO_3$•$4H_2O$ (221.6 mg, 1.44 mmol) as an oxidant for the boron atom in THF/H_2O (2.2 mL/1.4 mL). The mixture was stirred at room temperature overnight. After the reaction was completed, the reaction mixture was extracted with Et_2O, and the extract was dried over $MgSO_4$. After solids were filtered off, the solvents were removed under reduced pressure. The crude material was purified by flash column chromatography (silica gel, EtOAc/hexane, 0:100–6:94) to give the alcohol product (*E*)-**8** in 68% yield (2 steps) with *E*/*Z* = >95:5, **3**:**4** = >95:5 (87.4 mg, 0.343 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.88 (t, *J* = 6.7 Hz, 3H), 1.23–1.33 (m, 8H), 1.25 (s, 12H), 1.50–1.58 (m, 2H), 1.76–1.83 (m, 2H), 2.09–2.19 (m, 4H), 3.53 (t, *J* = 6.7 Hz, 2H), 6.24 (t, *J* = 6.7 Hz, 1H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 14.1 (*C*H_3), 22.6 (*C*H_2), 24.7 (*C*H_3), 26.4 (*C*H_2), 27.6 (*C*H_2), 28.5 (*C*H_2), 29.2 (*C*H_2), 30.1 (*C*H_2), 31.8 (*C*H_2), 32.3 (*C*H_2), 45.0 (*C*H_2), 83.0 (*C*), 144.6 (*C*H). HRMS-EI (*m*/*z*): $[M–Et]^+$ calcd for $C_{13}H_{25}OSi$, 225.1675; found, 225.1680.

(*E*)-Triethyl[4-dimethyl-5-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-en-2-yl]silane. [(*E*)-3aa]

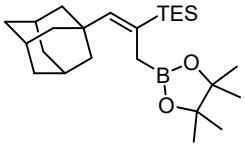


(*E*)-**3ga**

The reaction was conducted with 86.3 mg (0.501 mmol) of **1g**. The product (*E*)-**3ga** was obtained in 81% yield with *E*/*Z* = >95:5, **3**:**4** = >95:5 (168.2 mg, 0.406 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.55 (q, *J* = 7.5 Hz, 6H), 0.91 (t, *J* = 7.6 Hz, 9H), 1.11 (s, 9H), 1.21 (s, 12H), 1.87 (s, 2H), 2.69 (s, 2H), 5.44 (s, 1H), 7.14–7.26 (m, 5H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 2.9 (*C*H_2), 7.5 (*C*H_3), 15.3 (*C*H_2), 24.8 (*C*H_3), 28.7 (*C*H_3), 39.2 (*C*), 49.1 (*C*H_2), 83.0 (*C*), 125.6 (*C*H), 127.4 (*C*H), 130.7 (*C*H), 132.5 (*C*), 139.5 (*C*), 146.7 (*C*H). HRMS-EI (*m*/*z*): $[M–Me]^+$ calcd for $C_{21}H_{41}O_2{}^{11}B$, 399.2891; found, 399.2880.

(*E*)-Triethyl[1-adamanthyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-2-en-2-yl]silane. [(*E*)-3ha]

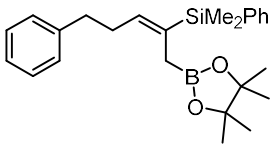


(*E*)-**3ha**

The reaction was conducted with 87.1 mg (0.500 mmol) of **1h**. The product (*E*)-**3ha** was obtained in 85% yield with *E*/*Z* = >95:5, **3**:**4** = >95:5 (176.1 mg, 0.423 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.54 (q, *J* = 7.9 Hz, 6H), 0.91 (t, *J* = 7.8 Hz, 9H), 1.23 (s, 12H), 1.61–1.73 (m, 6H), 1.75–1.85 (m, 6H), 1.87–1.99 (m, 5H), 5.22 (s, 1H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 2.9 (*C*H_2), 7.5 (*C*H_3), 14.9 (*C*H_2), 24.8 (*C*H), 28.8 (*C*H_3), 37.0 (*C*H_2), 37.8 (*C*), 42.7 (*C*H_2), 83.0 (*C*), 130.5 (*C*), 148.6 (*C*H). HRMS-EI (*m*/*z*): $[M–Me]^+$ calcd for $C_{24}H_{42}{}^{11}BO_2Si$, 401.3047; found, 401.3056.

(*E*)-Dimethyl-phenyl[5-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-en-2-yl]silane. [(*E*)-3ab]

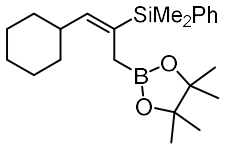


(*E*)-**3ab**

The reaction was conducted with 72.1 mg (0.500 mmol) of **1a**. The product (*E*)-**3ab** was obtained in 71% yield with *E*/*Z* = >95:5, **3**:**4** = >95:5 (144.2 mg, 0.355 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.33 (s, 6H), 1.16 (s, 12H), 1.73 (s, 2H) , 2.41 (q, *J* = 7.4 Hz, 2H) , 7.61 (t, *J* = 7.8 Hz, 2H) , 7.82 (t, *J* = 6.5 Hz, 1H) , 7.14–7.37 (m, 8H) , 7.45–7.55 (m, 2H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): –3.1 (*C*H_3), 14.4 (*C*H_2), 24.7 (*C*H_3), 30.9 (*C*H_2), 35.4 (*C*H_2), 83.0 (*C*), 134.2(*C*H) , 135.3(*C*), 138.8 (*C*), 139.8 (*C*H), 142.4 (*C*), 125.6 (*C*H) , 127.5 (*C*H) , 128.2 (*C*H) , 128.5 (*C*H) , 128.6 (*C*H). HRMS-EI (*m*/*z*): [M–Me]$^+$ calcd for $C_{24}H_{32}{}^{11}BO_2Si$, 391.2265; found, 391.2263.

(*E*)-Dimethylphenyl[1-cyclohexyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-2-en-2-yl]silane. [(*E*)-3fb][9]

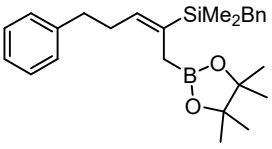


(*E*)-**3fb**

The reaction was conducted with 61.1 mg (0.500 mmol) of **1f**. The product (*E*)-**3fb** was obtained in 61% yield with *E*/*Z* = >95:5, **3**:**4** = >95:5 (117.7 mg, 0.306 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.31 (s, 6H), 0.97–1.35 (m, 6H), 1.16 (s, 12H), 1.59–1.78 (m, 6H) , 2.29 (q, *J* = 10.3 Hz, 1H) , 5.58 (d, *J* = 9.0 Hz, 1H) , 7.28–7.34 (m, 3H) , 7.47–7.56 (m, 2H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): –3.0 (*C*H_3), 14.2 (*C*H_2), 24.7 (*C*H_3), 26.0 (*C*H_2), 26.2 (*C*H_2), 32.5 (*C*H_2), 37.9 (*C*H), 82.9(*C*), 127.4 (*C*H) , 128.5 (*C*H), 131.4 (*C*), 134.2 (*C*H), 139.2 (*C*), 146.8 (*C*H). HRMS-EI (*m*/*z*): [M–Me]$^+$ calcd for $C_{22}H_{34}{}^{11}BO_2Si$, 369.2421; found, 369.2419.

(*E*)-Benzyldimethyl[5-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-en-2-yl]silane. [(*E*)-3ac]

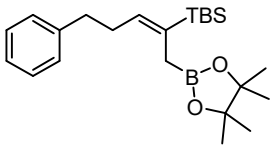


(*E*)-**3ac**

The reaction was conducted with 72.1 mg (0.500 mmol) of **1a**. The product (*E*)-**3ac** was obtained in 85% yield with *E*/*Z* =>95:5, **3**:**4** = >95:5 (179.2 mg, 0.426 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): –0.02 (s, 6H), 1.21 (s, 12H), 1.77 (s, 2H), 2.14 (s, 2H), 2.39 (q, *J* = 7.3 Hz, 2H) , 2.68 (t, *J* = 7.8 Hz, 2H) , 5.71 (t, *J* = 6.6 Hz, 1H) , 6.90–7.08 (m, 3H) , 7.13–7.31 (m, 7H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): –4.0 (*C*H_3), 14.4 (*C*H_2), 24.8 (*C*H_3), 25.2 (*C*H_2), 30.8 (*C*H_2) , 35.4 (*C*H_2), 83.1 (*C*), 123.7(*C*H) , 125.6(*C*H) , 127.9(*C*H) , 128.2(*C*H) , 128.3(*C*H) , 128.4(*C*H) , 135.5(*C*) , 138.9(*C*H), 140.6 (*C*), 142.4 (*C*). HRMS-EI (*m*/*z*): [M–Me]$^+$ calcd for $C_{25}H_{34}{}^{11}BO_2Si$, 405.2421; found, 405.2421.

(*E*)-*tert*-Butyl-dimethyl-[5-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-en-2-yl]silane. [(*E*)-3ab]

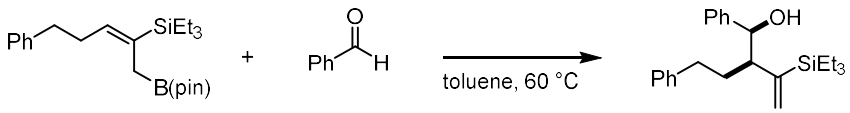


(*E*)-**3ad**

The reaction was conducted with 72.1 mg (0.500 mmol) of **1a**. The product (*E*)-**3aa** was obtained in 88% yield with *E*/*Z* =>95:5, **3**:**4** = 93:7 (170.4 mg, 0.441 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.02 (s, 6H), 0.84 (s, 9H), 1.21 (s, 12H), 1.77 (s, 2H), 2.39 (q, *J* = 7.3 Hz, 2H) , 2.71 (t, *J* = 8.0 Hz, 2H) , 5.72 (t, *J* = 6.5 Hz, 1H) , 7.14–7.31 (m, 5H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): –6.1 (*C*H_3), 15.5 (*C*H_2), 17.3 (*C*), 24.8 (*C*H_3), 27.0 (*C*H_3) , 30.8 (*C*H_2) , 35.5 (*C*H_2), 83.0 (*C*), 125.6(*C*H) , 128.2(*C*H) , 128.4(*C*H), 134.8(*C*), 139.7(*C*H), 142.5(*C*). HRMS-EI (*m*/*z*): [M–Me]$^+$ calcd for $C_{22}H_{36}{}^{11}BO_2Si$, 371.2578; found, 371.2596.

3.4.5. Derivatization of the boryl and silyl groups



(*E*)-**3aa** (2.0 equiv) **6a**

Allylic boronate (*E*)-**3aa** (38.8 mg, 0.100 mmol) and benzaldehyde (20.4 μL, 0.200 mmol) were dissolved in dry toluene (1.0 mL) in a vial. After 24 h stirring at 60 ℃, the reaction mixture was passed through a short pad of silica gel (*Φ*: 10 mm, the height of the silica gel: 90 mm) with Et_2O/hexane (10/90) eluent. The crude product was purified by flash column chromatography (silica gel, Et_2O/hexane, 0:100–94:6) to give homo-allylic alcohol **6a** in 80% yield (29.3 mg, 0.0799 mmol, colorless oil). The diastereoselectivity of the reaction (stereochemistry of the product) is estimated according to a plausible six-membered transition state of the reaction (Figure S1).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.53–0.73 (m, 6H), 0.93 (t, *J* = 7.8 Hz, 9H), 1.65–1.78 (m, 1H), 1.85–1.99 (m, 1H), 2.06 (s, 1H), 2.18–2.29 (m, 1H), 2.51–2.63 (m, 1H), 2.72 (dt, *J* = 10.2, 6.6 Hz, 1H), 4.68 (d, *J* = 2.3 Hz, 1H), 5.73 (d, *J* = 2.0 Hz, 1H), 5.98 (d, *J* = 1.6 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 2H), 7.08–7.38 (m, 8H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 3.0 (*C*H_2), 7.3 (*C*H_3), 27.7 (*C*H_2), 33.7 (*C*H_2), 50.0 (*C*H), 73.9 (*C*H), 125.6 (*C*H), 126.1 (*C*H), 126.9 (*C*H), 127.4 (*C*H_2), 128.1 (*C*H), 128.2 (*C*H), 128.2 (*C*H), 142.6 (*C*), 150.2 (*C*). HRMS-EI (*m*/*z*): [M–Et]$^+$ calcd for $C_{22}H_{29}OSi$, 337.1988; found, 337.1981.

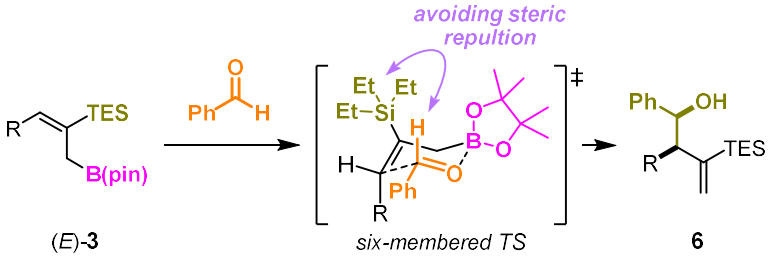
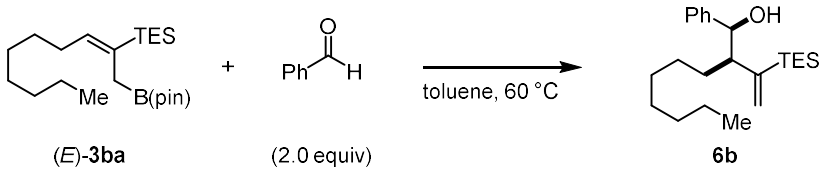
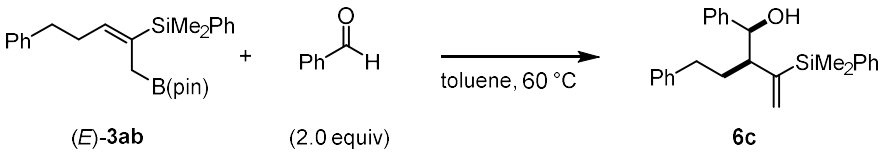


Figure S1. Plausible transition state of allylboration reaction.



This allylboration reaction was conducted with 168.0 mg (0.442 mmol) of (*E*)-**3ba** as above. The product **6b** was obtained in 77% yield (122.6 mg, 0.340 mmol, colorless oil).

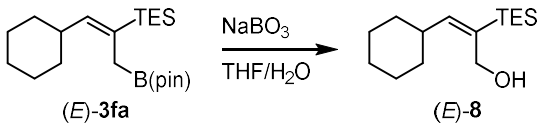
^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.53–0.72 (m, 6H), 0.84 (t, *J* = 7.4 Hz, 3H), 0.93 (t, *J* = 7.8 Hz, 9H), 1.03–1.33 (m, 11H), 1.53–1.67 (m, 1H), 2.06 (d, *J* = 2.0 Hz, 1H), 2.65 (dt, *J* = 11.3, 3.3 Hz, 1H), 4.61–4.67 (m, 1H), 5.66 (d, *J* = 2.3 Hz, 1H), 5.88 (d, *J* = 1.6 Hz, 1H), 7.19–7.39 (m, 5H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 2.9 (*C*H_2), 7.3 (*C*H_3), 14.0 (*C*H_3), 22.6 (*C*H_2), 25.9 (*C*H_2), 27.4 (*C*H_2), 29.1 (*C*H_2), 29.8 (*C*H_2), 31.8 (*C*H_2), 50.3 (*C*H), 74.1 (*C*H), 126.1 (*C*H), 126.7 (*C*H), 127.1 (*C*H_2), 127.9 (*C*H), zz142.9 (*C*), 150.2 (*C*). HRMS-EI (*m*/*z*): [M–Et]$^{+}$ calcd for $C_{21}H_{35}OSi$, 331.2457; found, 331.2470.



The allylboration reaction was conducted with 144.2 mg (0.355 mmol) of (*E*)-**3ab** according to the procedure as above. The product **6c** was obtained in 88% yield (120.5 mg, 0.312 mmol, colorless oil).

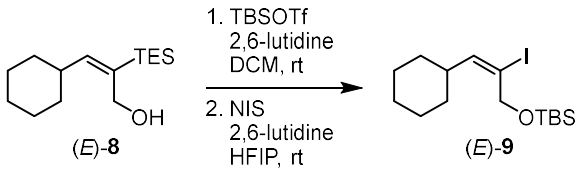
^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.36 (s, 3H), 0.40 (s, 3H), 1.62–1.73 (s, 1H), 1.80–1.94 (m, 2H), 2.06–2.17 (m, 1H), 2.43–2.53 (m, 1H), 2.60–2.67 (m, 1H), 4.44–4.50 (m, 1H), 5.78–5.84 (m, 1H), 5.95–6.01 (m, 1H), 6.94 (d, *J* = 7.0 Hz, 2H), 7.04–7.26 (m, 8H), 7.33–7.43 (m, 3H), 7.47–7.56 (m, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): –2.7 (*C*H_3), –2.6 (*C*H_3), 28.2 (*C*H_2), 33.7 (*C*H_2), 50.4 (*C*H), 74.7 (*C*H), 128.0 (*C*H_2), 128.1 (*C*H), 128.2 (*C*H), 128.3 (*C*H), 128.4 (*C*H), 129.5 (*C*H), 134.3 (*C*H), 137.7 (*C*), 142.7 (*C*), 142.9 (*C*), 151.8 (*C*). HRMS-EI (m/z):

[M+Na]+ calcd for C26H30ONaSi, 409.1958; found, 409.1950.



(*E*)-**3fa** (*E*)-**8**

(*E*)-**3fa** (131.7 mg, 0.361 mmol) was treated with $NaBO_3$•$4H_2O$ (221.6 mg, 1.44 mmol) as an oxidant for the boron atom in THF/H_2O (2.2 mL/1.4 mL). The mixture was stirred at room temperature overnight. After the substrate was consumed, the reaction mixture was extracted with Et_2O and dried over $MgSO_4$. After solids were filtered off, the solvents were removed under reduced pressure. The crude material was purified by flash column chromatography (silica gel, EtOAc/hexane, 0:100–6:94) to give the alcohol product (*E*)-**8** in 95% yield (87.4 mg, 0.343 mmol, colorless oil).



(*E*)-**8** (*E*)-**9**

(*E*)-**8** (25.5 mg, 0.100 mmol) was dissolved in CH_2Cl_2 (850 μL) under a nitrogen atmosphere in a dried vial. To the mixture was successively added 2,6-lutidine (17.4 μL, 0.150 mmol) and TBSOTf (22.6 μL, 0.125 mmol) at 0 ℃. After the reaction mixture was stirred for 2 h, quenched with 1 M HCl aqueous solution (2 mL). The mixture was extracted with CH_2Cl_2 and washed by brine. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane eluent to give TBS-protected product (27.6 mg, 0.0748 mmol, 75%) as a colorless oil.

The TBS-protected product (27.6 mg, 0.0748 mmol) was dissolved in HFIP (300 μL). 2,6-Lutidine (5.6 mg, 0.0524 mmol) was added at 0 ºC under a nitrogen atmosphere. NIS (25.2 mg, 0.112 mmol) was added to the mixture at 0 ºC and stirred for 1 h. After the substrate was consumed, the reaction mixture was quenched with water (3 mL) and extracted with hexane three times (3 mL×3). The combined organic layer was washed by saturated aqueous $Na_2S_2O_3$, saturated aqueous $NaHCO_3$, and water. The combined organic layer was dried over Na_2SO_4. After filtration, the solvents were removed under reduced pressure. The crude material was purified by flash column chromatography (silica gel, ether/hexane, 0:100–2:98) to give the corresponding iodinated product (*E*)-**9** (79%, 22.6 mg, 0.0594 mmol) as a colorless oil.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.12 (s, 6H), 0.93 (m, 9H), 1.00–1.38 (m, 5H), 1.52–1.79

(m, 5H), 2.37 (q, *J* = 10.5 Hz, 1H), 4.24 (s, 2H), 6.14 (d, *J* = 9.8 Hz, 1H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): –5.0 (*C*H_3), 18.4 (*C*), 25.6 (*C*H_2), 25.7 (*C*H_2), 25.9 (*C*H_3), 32.8 (*C*H_2), 40.7 (*C*H), 65.4 (*C*H_2), 101.8 (*C*), 148.2 (*C*H). HRMS-EI (*m*/*z*): $[M–Me]^+$ calcd for $C_{14}H_{26}IOSi$, 365.0798; found, 365.0803.

3.5. Computational Details

3.5.1. Computational Methods

All geometry optimizations and thermal energy correction calculations (frequency analyses) by means of density functional theory (DFT) were performed with the Gaussian 16 (revision C.01) suite of programs.[50] The thresholds defined in Gaussian 16 were used. The geometry optimizations were carried out at ωB97X-D[51] level of theory with Def2-SVP[52,53] as a basis set. The solvation effect of THF was included in the calculations with SMD solvation model.[54] Harmonic frequency calculations were conducted at the same level of theory on the optimized geometries to check all the stationary points as either minima or first-order saddle points. Intrinsic reaction coordinate (IRC)[55] calculations were carried out to confirm the transition states connecting the correct reactants and products on the potential energy surface.

3.5.2. Calculated Properties of All Structures

The ligation energies of thiophene and THF were compared in Figure S2. The ligation energy of THF was found to be larger than that of thiophene by 12.3 kcal/mol. Thus, a 2-thiophenecarboxylate ligand in CuTC is assumed to be exchanged with the THF molecule in THF solvent.

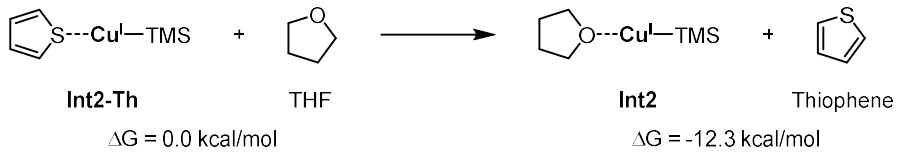


Figure S2. Gibbs free energies of silyl copper(I) species coordinated by thiophene or THF.

Table S2. Calculated properties of the optimized structures.

Structure	SCF energy [hartree]	*H* [hartree]	*TS* [hartree]	*G* [hartree]
Silyl copper **Int2Th**	–2602.114258	–2601.919219	0.061950	–2601.981169

Silyl copper **Int2**	–2281.633908	–2281.387487	0.062003	–2281.449490
THF	–232.216279	–232.093122	0.033731	–232.126853
Thiophene	–552.718215	–552.645913	0.032151	–552.678064
Allene **1**	–155.808704	–155.718632	0.032940	–155.751572
(*E*)-**TS1**	–2437.432162	–2437.095233	0.071502	–2437.166735
(*Z*)-**TS1**	–2437.429865	–2437.093144	0.069805	–2437.162949
TS1'	–2437.427254	–2437.089462	0.071161	–2437.160623

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10. For examples of silaboration reactions with a rare regioselectivity, see refs 16 and 17.

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4. Ring Expansion of Aryl Boronates *via* Oxyboration of Arynes

4.1. Introduction

The Aryne intermediates are important class of tools that enable the 1,2-difunctionalization of aromatic rings.[1,2] Their unique reactivity have found widespread use in the construction of highly functionalized bioactive compounds.[1,2] Recently, the borylative functionalization of arynes has been a especially active research area since this method allows producing highly functionalized arylboron synthetic reagents in organic synthesis (Figure 24a).[3–7] In 2010, Yoshida and coworkers reported the first borylation of arynes.[3a] They found that the borylation of arynes using Cu(I) catalyst/$B_2(pin)_2$ system resulted in the formation of 1,2-diborylated arenes.[3a] Also, Oestreich developed a diboration of indolyne derivatives with a platinum(0) catalyst in 2015.[4] In 2013, Uchiyama reported the borylation zincation system of arynes using dialkylzinc species and $B_2(pin)_2$.[5] Moreover, Curran and Taniguchi later reported the hydroboration of arynes using *N*-heterocyclic carbene (NHC)-borane complexes.[6] In 2022, Mizoguchi and Sakurai reported the carboborylative cyclization of arynes with vinylboronates *via* 1,2-metallate rearrangement.[7] Despite the very significant progress that has been made in aryne borylation chemistry, there are still no reports of aryne insertion into B–O bonds.[1–7] The achievement of such aryne oxyboration transformations is very difficult since it requires the selective activation of B–O bonds. They have a relatively high bond dissociation energy (BDE) of 806 kJ/mol compared to boron-containing chemical bonds, like B–B (297 kJ/mol), B–H (330 kJ/mol), and B–C (448 kJ/mol) bonds.[8] However, overcoming this challenge would open new avenues to functionalized arylboron compounds that are difficult to prepare by other means.

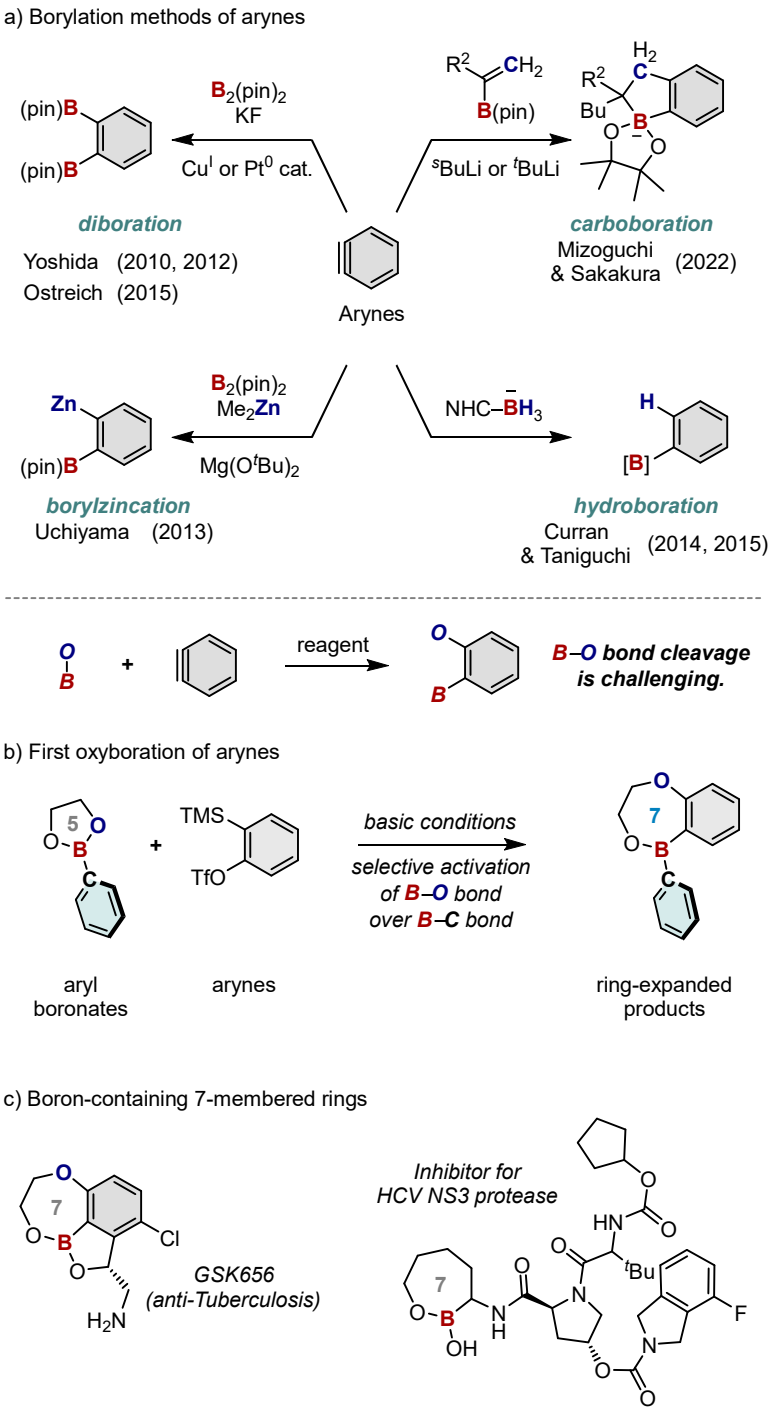


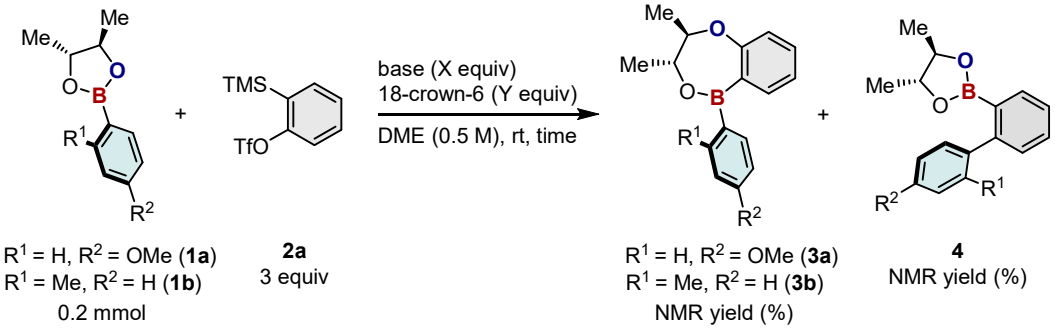
Figure 24. Borylation of arynes

4.2. Results and Discussions

First, to investigate this reaction, I optimized the reaction between 2-(4-methoxyphenyl)-4,5-dimethyl-1,3,2-dioxaborolane (**1a**) and aryne precursor **2a** in the presence of a fluoride base and 18-crown-6 in Table 8. Using CsF as a base furnished the desired oxyboration

product **3a** in moderate yield (entry 1, 41% yield). Notably, the carboboration product **4** was not obtained. No product formation was observed in the reaction with KF as a base (entry 2). The use of RbF as a base also afforded the desired product **3a**, but the yield remained moderate (entries 3 and 4, 43% and 41% yields, respectively). Unfortunately, increasing the amount of CsF and 18-crown-6 (6 equiv) hardly improved (entry 5, 48% yield). I surmised that the low yields might be due to the ring-opening decomposition of the cyclic borinic acid ester product **3a** under the basic reaction conditions. Therefore, I decided to use 4,5-dimethyl-2-(*o*-tolyl)-1,3,2-dioxaborolane (**1b**) as the substrate (entry 6), and the desired ring-expanded product **3b** was obtained in excellent yield (entry 6, 70%). It suggested that steric congestion around the boron center improves the stability of **3** toward undesired decomposition. Finally, I tested the reaction in the absence of 18-crown-6. As a result, it caused significantly decreased the yield of **3b** (entry 7, 29% yield).

Table 8. Optimization of oxyboration reaction



R^1 = H, R^2 = OMe (**1a**)
R^1 = Me, R^2 = H (**1b**)
0.2 mmol

2a
3 equiv

R^1 = H, R^2 = OMe (**3a**)
R^1 = Me, R^2 = H (**3b**)
NMR yield (%)

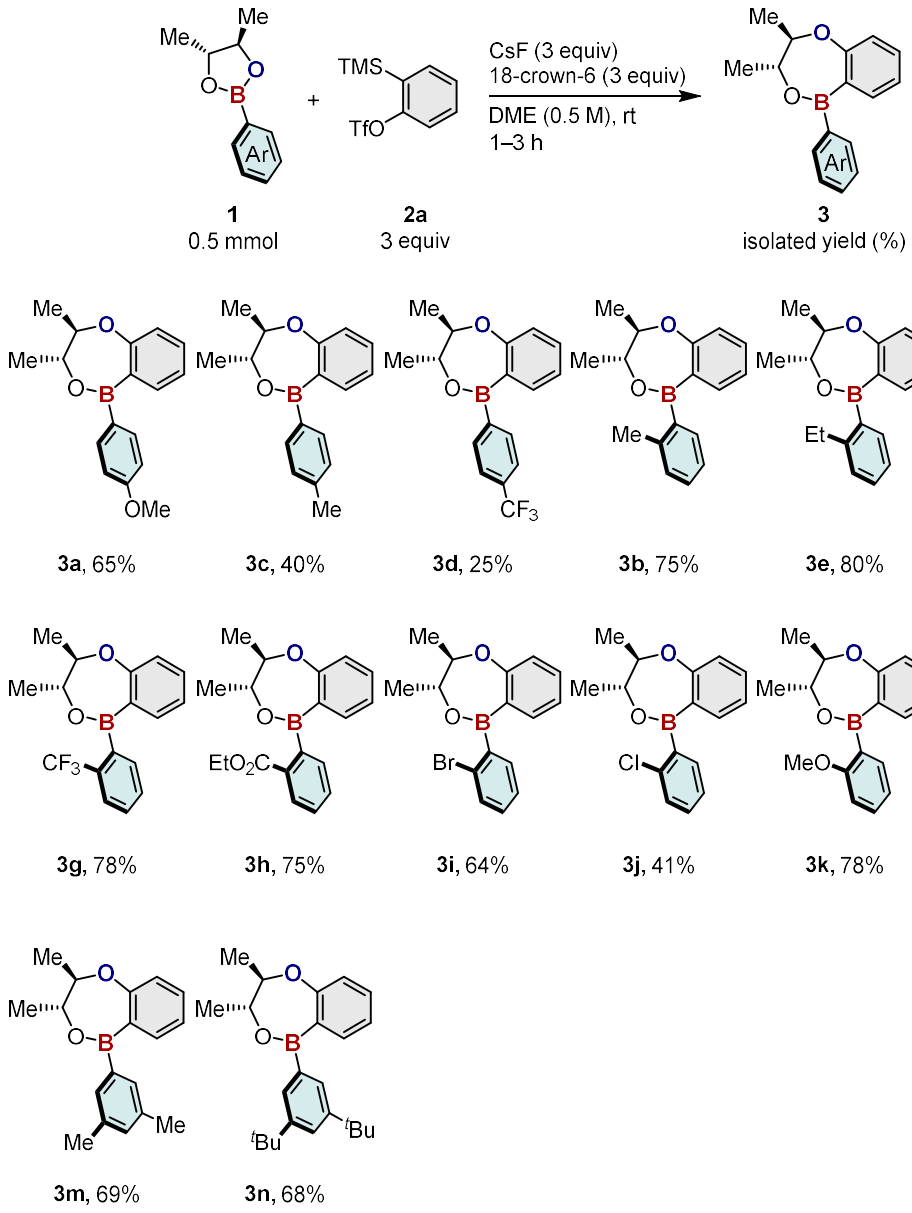
4
NMR yield (%)

entry	R^1	R^2	base	X (equiv)	Y (equiv)	time (h)	yield of **3** (%)[b]	yield of **4** (%)[b]
1	H	OMe	CsF	3	3	1.5	41	<5
2	H	OMe	KF	3	3	3	<5	<5
3	H	OMe	RbF	3	3	3	43	<5
4	H	OMe	RbF	3	3	1	41	<5
5	H	OMe	CsF	6	6	1.5	48	<5
6	Me	H	CsF	3	3	1.5	70	<5
7	Me	H	CsF	3	0	1.5	29	<5

[a]Standard conditions: boronate **1** (0.2 mmol), aryne precursor **2a** (0.6 mmol), base, and 18-crown-6 in 1,2-dimethoxyethane (0.4 mL). [b]The yields of **3** and **4** were determined *via* NMR analysis using 1,2-dibromomethane as an internal standard.

Having determined the optimal conditions, I examined the substrate scope in Table 9. The ring-expanded 7-membered borinic acid esters were able to be isolated after flash silica gel column chromatography without significant decrease in the product yields. The reactions of substrates bearing *para*-substituents on the benzene ring, like methoxy (**1a**), methyl (**1c**), and trifluoromethyl (**1d**) groups afforded the corresponding oxyboration products (**3a**, **3c**, and **3d**) in low-to-moderate yields (65%, 40%, and 25% yield, respectively). The electron-withdrawing trifluoromethyl group of **1d** increased the Lewis acidity of the boron center, resulted in the undesired decomposition of **3d**. Next, I investigated *ortho*-substituted arylboronates (**1b**, **1e**–**1k**). Since the *ortho*-substituents can improve the stability of the products under basic conditions, the desired products (**1b**, **1e**–**1k**) were obtained in good yields (41–80%). Notably, both sterically-hindered- and electron-deficient substrates were well tolerated. Moreover, naphthalene-substituted substrate **1l** also underwent the oxyboration to give the desired product **3l** in good yield (71%). Furthermore, I found that the reactions with *meta*-substituted substrates (**1m** and **1n**) proceeded smoothly to give the ring-expanded products (**3m** and **3n**) in good yields. However, the use of alkenyl- and alkyl boronates resulted in complex mixtures.

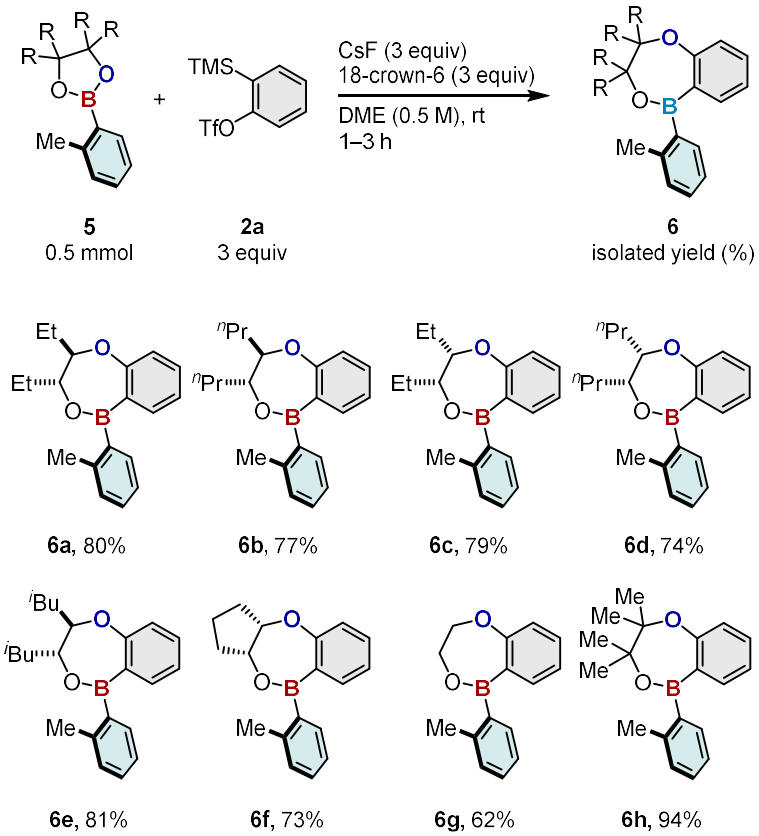
Table 9. Substrate scope of aryl boronic acid esters



Subsequently, I turned our attention to the effect of the dialkoxyl part (Table 10). Various alkyl substituents were tolerated under the present conditions, and the corresponding products (**6a**–**6e**) were obtained in good-to-high yields (74–81%). The trans/cis stereochemistry of the substituents did not affect the reactivity (**6a**, 80% and **6c**, 79%). For the cyclopentyl moiety (**5f**), the oxyboration reaction proceeded to afford the corresponding boron-containing bicyclic compound (**6f**) in 73% yield. Ethylene glycol derivative **5g** also underwent the borylative ring expansion to give the desired product **6g** in good yield (62%).

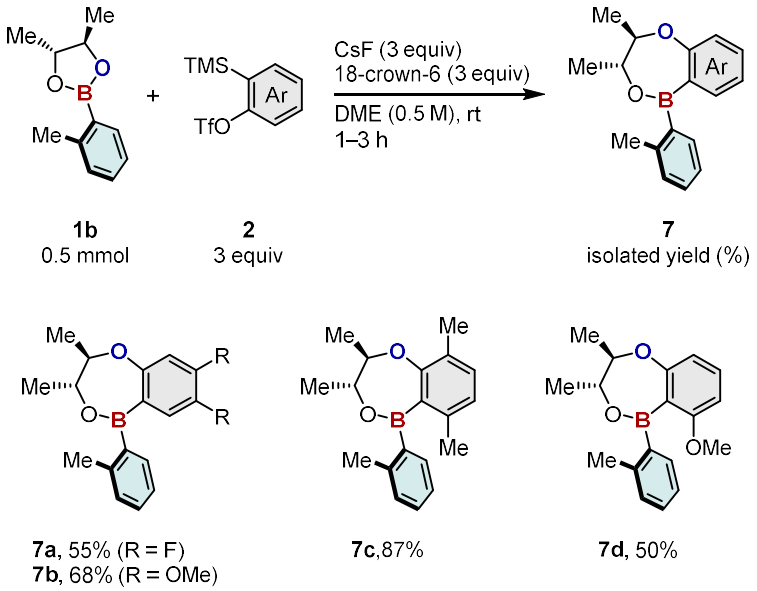
Moreover, the pinacol-containing boronate **5h** afforded the highly stable product **6h** in excellent yield (94%). I also used attempted to use acyclic boronates in the oxyboration reaction; however, they did not afford the desired products (see the Supporting Information for details).

Table 10. Effect of the boron side



After that, other aryne precursors with substitution at the benzene ring were tested in Table 11. An electron-deficient aryne precursor containing fluorine atoms (**2b**) afforded the corresponding oxyboration product **7a** in 55% yield. Also, good yield (68%) was obtained when an electron-rich aryne precursor (**2c**) was employed as the substrate to give the corresponding product **7b**. The reaction of a sterically demanding aryne precursor (**2d**) proceeded smoothly to give the desired product **7c** in excellent yield (87%). I presume that the steric effect of the alkyl substituents on the benzene ring increased the stability of **7c** under the basic reaction conditions, resulting in the good yield.

Table 11. Reactions with various arynes



Furthermore, an unsymmetrical aryne precursor **2e** was used for the oxyboration reaction of the boronate **1b**, and the regioselective oxyboration of **1b** was achieved to afford **7d** in 50% yield. The structure of **7d** was detected *via* single-crystal X-ray diffraction analysis in Figure 25. Interestingly, I realized that the 7-membered ring structure of **7d** was similar to the 7-membered carbocycle in a bioactive compound KGP-156.[11a] Molander suggested that a boron–oxygen single bond can be regarded as isoelectronic to a carbon–carbon double bond.[11b] Considering the structural similarity between **7d** and KGP-156, as well as the prevalence of cycloheptene skeletons in many other bioactive compounds, the products obtained by means of our oxyboration are potentially bioisosteres for drug discovery.[11c-e]

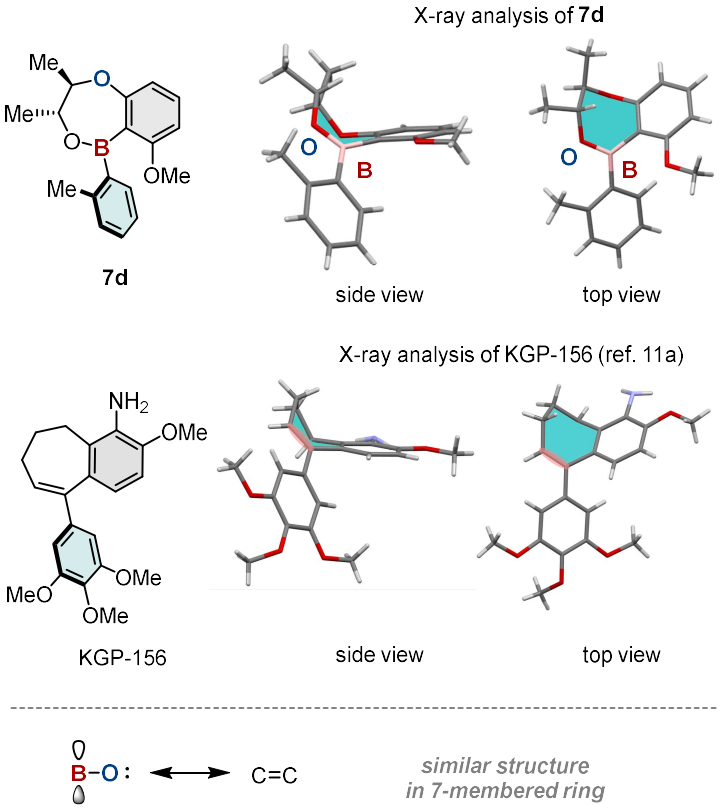
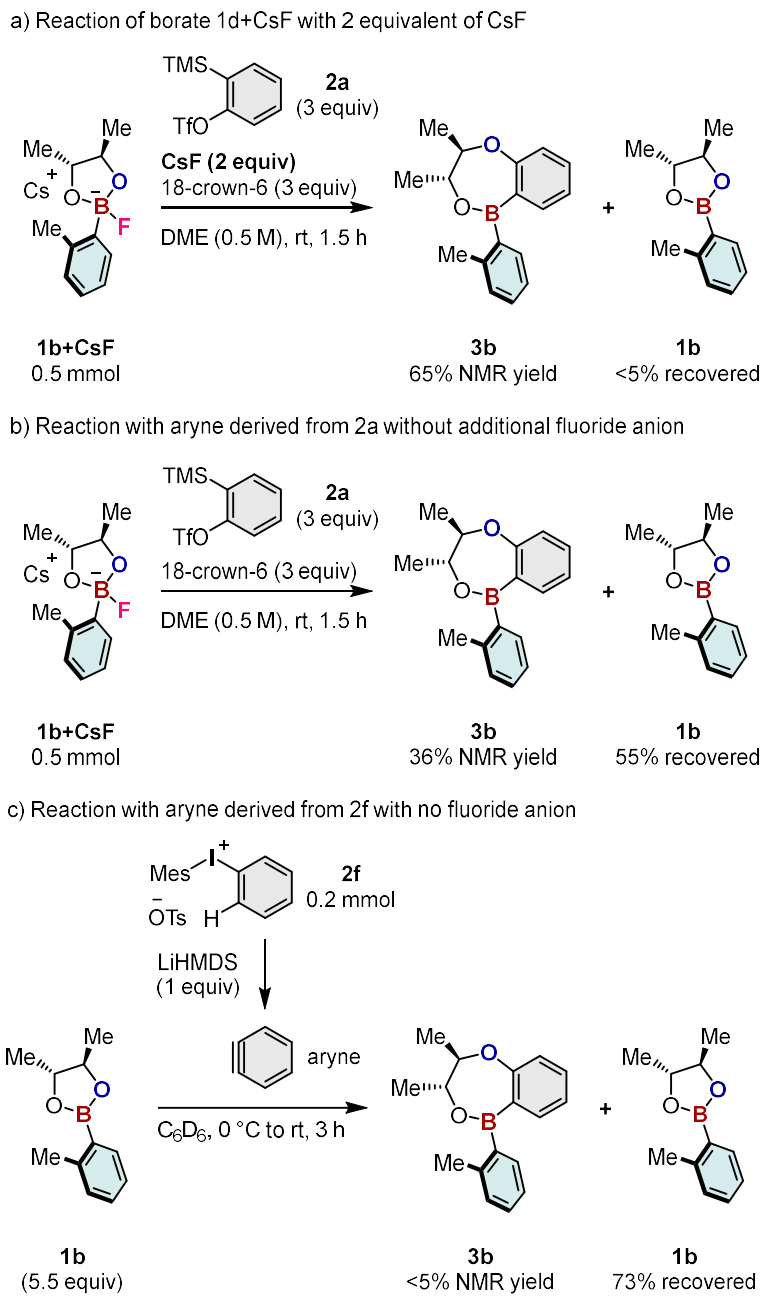


Figure 25. X-ray single-crystal analysis of 7d and KGP-156

To obtain detailed mechanistic insight, I carried out several control experiments (Scheme 6). I prepared the fluorinated borate of **1b** (**1b+CsF**) and applied it to oxyboration with CsF (2 equiv) and aryne precursor **2a** (Scheme 6A).[12] The desired product **3b** was obtained in 65% yield. It was comparable to the yield in the reaction using **1b** (Table 2, 75%). Importantly, even though in the absence of CsF, the reaction of **1b+CsF** afforded **3b**, albeit in lower yield (36% yield) (Scheme 6B). Moreover, I found that **3b** was not obtained and **1b** was recovered (73%) when an aryne intermediate derived from the iodonium salt **2f** and lithium bis(trimethylsilyl)amide (LiHMDS) were used for the oxyboration reaction (Scheme 6C).[13] ^{11}B NMR analysis of the reaction mixture showed that bulky LiHMDS did not coordinate the boron center of the boronate **1b**, and the corresponding boron ate complex did not form in the reaction (See the Supporting Information for details). Based on these results, it suggested that the fluorinated borate was an active species in the aryne oxyboration, and that the borate can also serve as a fluoride anion source for the activation of the aryne precursor **2a**.



Scheme 6. Experimental mechanistic studies

Finally, I conducted density functional theory (DFT) calculations to reveal the mechanistic details of the oxyboration between borate species and arynes. The reaction pathways were systematically explored by means of the artificial force-induced reaction (AFIR) method,[14] which utilizes an artificial force to trigger possible reactions for the generation of a reaction network automatically. The resulting reaction network was analyzed, and all the pathways with accessible barriers were further optimized and summarized (Figure

26). The pathways corresponding to the oxyboration of arynes (i.e., B–O bond cleavage) and the arylboration of arynes (i.e., B–C bond cleavage) are indicated by the colors blue and orange, respectively. In both cases, the first step is the nucleophilic attack of the oxygen atom to the aryne, which immediately generates an oxonium and a carbanion on the aryne intermediates. The formation of the oxonium cation significantly weakens the B–O bond and promotes the nucleophilic attack of the carbanion on the boron atom. As a result, the boron–oxygen bond cleavage pathway (*via* **TS-1B**) has a relatively low free energy barrier of only +19.6 kJ/mol. On the other hand, the boron–carbon bond cleavage pathway (*via* **TS-1A**) has a large barrier of +118.7 kJ/mol. Therefore, my calculations suggest that the oxyboration is greatly preferred over the arylboration, in good agreement with our experimental observations. Notably, further calculations for a non-fluorinated arylboronate highlighted the critical role that fluorine-substitution plays. In the case of the non-fluorinated boron, the binding of the oxygen atom to the benzyne is energetically unfavorable (ΔG = +75.3 kJ/mol). Moreover, the subsequent boron–oxygen bond cleavage was found to have a barrier of +85.9 kJ/mol, which was dramatically higher barrier than that for the fluorinated borate ($\Delta G^{\ddagger}$ = +19.6 kJ/mol), as no oxonium cation was formed and the boron–oxygen bond was not weakened. The reason that oxonium formation does not occur in the case of non-fluorinated arylboronate is probably because the boron is only three-coordinate and remains highly electron-deficient (i.e., having only 6 electrons). Therefore, the formation of oxonium in the vicinity of this highly electron-deficient B atom greatly destabilizes the system. These results strongly suggest the importance of including fluorides in the reaction system. The formation of the borate with CsF would increase the nucleophilicity of the oxygen on the boryl group, promoting the nucleophilic attack of the oxygen on benzyne to form Int-1 (ΔG = –25.0 kJ/mol). Because of the weakened boron–oxygen bond, the subsequent ring expansion *via* boron–oxygen bond cleavage would proceed rapidly to form the 7-membered borinic acid cyclic ester.

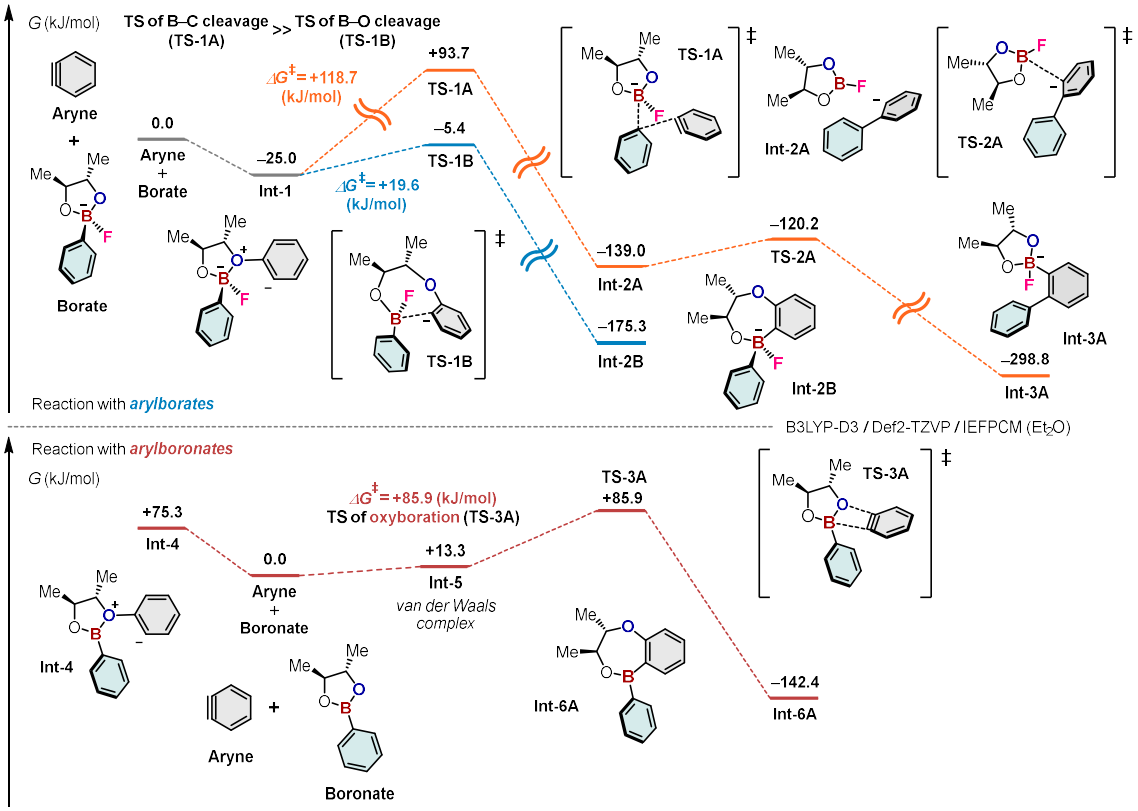


Figure 26. Computational studies on the oxyboration/arylboration processes

B3LYP-D3/Def2-TZVP//B3LYP-D3/Def2-TZVP level of theory using IEF-PCM solvation model (solvent = Et_2O)

4.3. Conclusion

In conclusion, the first example of the oxyboration of arynes to produce ring-expanded cyclic borinic acid esters was achieved. Experimental and computational studies suggested that this unprecedented borylative ring expansion proceeds *via* the bond–oxygen bond activation of the *in situ* formed borate species by arynes.

4.4. Experimental Details

4.4.1. Instruments and Chemicals

Materials were commercially available and purified by standard procedures unless otherwise noted. The solvents were also commercially available and further dried over molecular sieves (MS 4A). NMR spectra were recorded on JEOL JNM-ECX400P, JNM-ECS400, and JNM-ECA600 spectrometers (^{1}H: 400 MHz, ^{13}C: 100 MHz, ^{11}B: 126 MHz). Tetramethylsilane (^{1}H, δ 0.00), $CDCl_3$ (^{13}C, δ 77.00), fluorobenzene (19F, δ –113.60), and $BF_3{\cdot}OEt_2$ (^{11}B, δ 0.00) were employed as the external standards, respectively. GLC analyses

were conducted with a Shimadzu GC-2014 or GC-2025 equipped with a ULBON HR-1 glass capillary column (Shinwa Chemical Industries) and an FID detector. Recycle preparative gel chromatography (GPC) was conducted with LC-5060using $CHCl_3$ as an eluent. High-resolution mass spectra were obtained at the Global Facility Center, Hokkaido University.

4.4.2. General Experimental Procedure

In the case of solid arylboronates

In an oven-dried reaction vial, arylboronates (**1**) (0.50 mmol), CsF (1.5 mmol) and 18-crown-6 (1.5 mmol) were placed under argon atmosphere. After the vial was sealed with a screw cap containing a Teflon™-coated rubber septum, dry DME (1.0 mL) was added to the vial through the rubber septum using a syringe. After that, 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (1.5 mmol) were added to the mixture. The reaction mixture was stirred at ambient temperature until the arylboronates were consumed. After the reaction was completed, the reaction mixture was passed through a short silica-gel column (*Φ*: 15 mm, height of the silica-gel column: 30 mm) with Et_2O eluent. The crude material was purified by flash column chromatography (SiO_2, Et_2O/hexane, 0:100–10:90) to furnish the corresponding diarylborinic acid esters (**3**).

In the case of liquid arylboronates

In an oven-dried reaction vial, CsF (227.8 mg, 1.5 mmol, 3.0 equiv) and 18-crown-6 (396.5 mg, 1.50 mmol, 3.0 equiv) were placed under argon atmosphere. After the vial was sealed with a screw cap containing a Teflon™-coated rubber septum, dry DME (1.0 mL) was added in the vial through the rubber septum using a syringe. After that, arylboronates (**1**) (0.50 mmol, 1.0 equiv) were added to the mixture, followed by 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (447.5 mg, 1.5 mmol, 3 equiv). The reaction mixture was stirred at ambient temperature until the arylboronates were consumed. After the reaction was completed, the reaction mixture was passed through a short silica-gel column (*Φ*: 15 mm, height of the silica-gel column: 30 mm) with Et_2O eluent. The crude material was purified by flash column chromatography (SiO_2, Et_2O/hexane, 0:100–10:90) to give the corresponding diarylborinic acid esters (**3**)

4.4.3. Substrate Preparation Procedure and Characterization

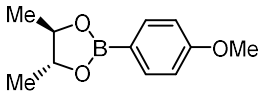
The aryne precursors (**2a**,[15] **2b**,[15] **2c**,[15] **2d**,[16] **2e**,[17] **2f**,[18] **2g,**[19] **2h**[20]), boronic acid esters[21] (**1a**–**1p**) were prepared according to literature procedures. The ^1H and ^{13}C NMR spectra of known compounds were confirmed with reported literatures (**2a**,[15] **2b**,[15] **2c**,[15] **2d**,[16] **2e**,[17] **2f**,[18]

2g,[19] **2h**[20]). Other reagents were commercially available (KANTO KAGAKU Co., Tokyo Chemical Industry Co., and Sigma-Aldrich Co.).

General procedure for synthesizing aryl boronates

An aryl boronic acid (5.0 mmol, 1.0 equiv), $MgSO_4$ (662.0 mg, 5.5 mmol, 1.1 equiv), ether (5.0 mL) and a diol (5.0 mmol, 1.0 equiv) were placed in a test tube under air atmosphere. After stirring at ambient temperature for 4h, the reaction mixture was filtered, and the solvent were evaporated. The crude mixture was purified by silica-gel column chromatography (hexane/Et_2O) to five the corresponding arylboronates (**1**) or (**5**).

(*4R,5R*)-2-(4-Methoxyphenyl)-4,5-dimethyl-1,3,2-dioxaborolane (1a).

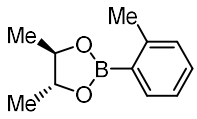


1a

The boronate **1a** was synthesized according to a literature procedure.[21] The corresponding product **1a** was obtained in 93% yield (959.4 mg, 4.66 mmol, white solid).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.38 (d, *J* = 5.8 Hz, 6H), 3.83 (s, 3H), 4.12–4.19 (m, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 20.9 (*C*H_3), 55.0 (*C*H_3), 80.4 (*C*H), 113.4 (*C*H), 136.5 (*C*H), 162.2 (C). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 30.5 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{11}H_{15}{}^{11}BO_3$, 206.1111; found, 206.1110.

(*4R,5R*)-4,5-Dimethyl-2-(*o*-tolyl)-1,3,2-dioxaborolane (1b).

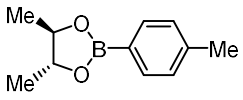


1b

The boronate **1b** was synthesized according to a literature procedure.[21] The corresponding product **1b** was obtained in 85% yield (804.0 mg, 4.23 mmol, white solid).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.39 (d, *J* = 6.4 Hz, 6H), 2.54 (s, 3H), 4.13–4.20 (m, 2H), 7.15–7.18 (m, 2H), 7.33 (dt, *J* = 7.2, 3.6 Hz, 1H), 7.77–7.82 (m, 1H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 21.1 (*C*H_3), 22.2 (*C*H_3), 80.2 (*C*H), 124.7 (*C*H), 129.9 (*C*H), 131.0 (*C*H), 136.1 (*C*H), 145.0 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$, δ): 31.1 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{11}H_{15}{}^{11}BO_2$, 190.1162; found, 190.1159.

(*4R,5R*)-4,5-Dimethyl-2-(*p*-tolyl)-1,3,2-dioxaborolane (1c).

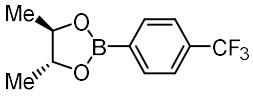


1c

The boronate **1c** was synthesized according to a literature procedure.[21] The corresponding product **1c** was obtained in 77% yield (736.4 mg, 3.87 mmol, white solid).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.39 (d, *J* = 5.9 Hz, 6H), 2.37 (s, 3H), 4.13–4.20 (m, 2H), 7.20 (d, *J* = 7.4 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 20.9 (*C*H_3), 21.7 (*C*H_3), 80.5 (*C*H), 128.6 (*C*H), 134.8 (*C*H), 141.5 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 30.8 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{11}H_{15}{}^{11}BO_2$, 190.1162; found, 190.1165.

(*4R,5R*)-4,5-Dimethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (1d).

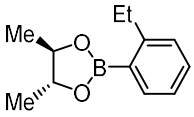


1d

The boronate **1d** was synthesized according to a literature procedure.[21] The corresponding product **1d** was obtained in 85% yield (1034.6 mg, 4.24 mmol, white solid).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.38 (d, *J* = 5.5 Hz, 6H), 4.18–4.25 (m, 2H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.92 (d, *J* = 7.8 Hz, 2H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 20.6 (*C*H_3), 80.9 (*C*H), 124.18 (*C*H), 124.2 (*C*F_3, q, *J* = 272.3 Hz), 124.4 (*C*H), 132.8 (*C*, q, *J* = 32.1 Hz), 135.1 (*C*H). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. 19F NMR (369 MHz, $CDCl_3$, δ): –63.6 (s, 3F). ^{11}B NMR (126 MHz, $CDCl_3$, δ): 30.3 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{11}H_{12}{}^{11}BF_3O_2$, 244.0879; found, 244.0877.

(*4R,5R*)-2-(2-Ethylphenyl)-4,5-dimethyl-1,3,2-dioxaborolane (1e).



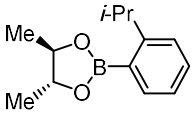
1e

The boronate **1e** was synthesized according to a literature procedure.[21] The corresponding product **1e** was obtained in 87% yield (885.7 mg, 4.34 mmol, colorless oil).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.20 (t, *J* = 7.4 Hz, 3H), 1.39 (d, *J* = 5.6 Hz, 6H), 2.87–2.96 (m, 2H), 4.13–4.20 (m, 2H), 7.16–7.23 (m, 2H), 7.34–7.40 (m, 1H), 7.77–7.82 (m, 1H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 17.0 (*C*H_3), 21.1 (*C*H_3), 28.8 (*C*H_2), 80.2 (*C*H), 124.9 (*C*H), 128.4 (*C*H), 131.1 (*C*H), 136.2 (*C*H), 151.5 (*C*). A carbon directly attached to a boron atom

was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 31.1 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{12}H_{17}{}^{11}BO_2$, 204.1318; found, 204.1319.

(*4R,5R*)-2-(2-Isopropylphenyl)-4,5-dimethyl-1,3,2-dioxaborolane (1f).

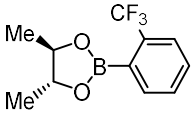


1f

The boronate **1f** was synthesized according to a literature procedure.[21] The corresponding product **1f** was obtained in 87% yield (947.5 mg, 4.34 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.23 (d, *J* = 6.7 Hz, 6H), 1.39 (d, *J* = 5.1 Hz, 6H), 3.67 (sept, *J* = 6.9 Hz, 1H), 4.13–4.20 (m, 2H), 7.17 (t, *J* = 7.0 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 7.0 Hz, 1H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 21.2 (*C*H_3), 24.3 (*C*H_3), 24.5 (*C*H_3), 31.6 (*C*H), 80.2 (*C*H), 124.6 (*C*H), 124.9 (*C*H), 131.1 (*C*H), 135.9 (*C*H), 155.7 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 31.1 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{13}H_{19}{}^{11}BO_2$, 218.1475; found, 218.1476.

(*4R,5R*)-4,5-Dimethyl-2-(2-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (1g).

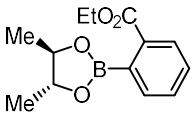


1g

The boronate **1g** was synthesized according to a literature procedure.[21] The corresponding product **1g** was obtained in 61% yield (739.1 mg, 3.03 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.41 (d, *J* = 5.9 Hz, 6H), 4.20–4.27 (m, 2H), 7.49–7.56 (m, 2H), 7.65–7.70 (m, 1H), 7.75–7.80 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 20.3 (*C*H_3), 80.6 (*C*H), 124.4 (*C*F_3, q, *J* = 273.1 Hz), 125.0 (*C*H), 129.9 (*C*H), 130.5 (*C*H), 133.8 (*C*, q, *J* = 31.3 Hz), 134.9 (*C*H). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. 19F NMR (369 MHz, $CDCl_3$, δ): –60.5 (s, 3F). ^{11}B NMR (126 MHz, $CDCl_3$, δ): 30.9 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{11}H_{12}{}^{11}BF_3O_2$, 244.0879; found, 244.0884.

Ethyl 2-((*4R,5R*)-4,5-dimethyl-1,3,2-dioxaborolan-2-yl)benzoate (1h).

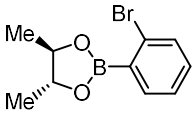


1h

The boronate **1h** was synthesized according to a literature procedure.[21] The corresponding product **1h** was obtained in 91% yield (1124.9 mg, 4.53 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.39 (t, *J* = 7.0 Hz, 3H), 1.44 (d, *J* = 5.9 Hz, 6H), 4.21–4.28 (m, 2H), 4.33–4.45 (m, 2H), 7.39–7.46 (m, 1H), 7.50–7.56 (m, 2H), 7.97 (d, *J* = 7.4 Hz, 1H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 14.3 (*C*H_3), 20.6 (*C*H_3), 61.4 (*C*H_2), 80.7 (*C*H), 128.6 (*C*H), 128.9 (*C*H), 131.87 (*C*H), 131.90 (*C*H), 133.7 (*C*), 168.2 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 31.4 (br, s). HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{13}H_{18}{}^{11}BO_4$, 249.1293; found, 249.1290.

(*4R,5R*)-2-(2-Bromophenyl)-4,5-dimethyl-1,3,2-dioxaborolane (1i).

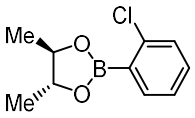


1i

The boronate **1i** was synthesized according to a literature procedure.[21] The corresponding product **1i** was obtained in 81% yield (1037.4 mg, 4.07 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.42 (d, *J* = 5.9 Hz, 6H), 4.20–4.27 (m, 2H), 7.24–7.32 (m, 2H), 7.54–7.59 (m, 1H), 7.68–7.74 (m, 1H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 21.0 (*C*H_3), 80.7 (*C*H), 126.3 (*C*H), 128.3 (*C*), 132.1 (*C*H), 132.9 (*C*H), 137.1 (*C*H). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 30.5 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{10}H_{12}{}^{11}BBrO_2$, 254.0110; found, 254.0113.

(*4R,5R*)-2-(2-Chlorophenyl)-4,5-dimethyl-1,3,2-dioxaborolane (1j).



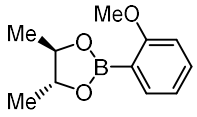
1j

The boronate **1j** was synthesized according to a literature procedure.[21] The corresponding product **1j** was obtained in 84% yield (880.3 mg, 4.18 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.42 (d, *J* = 5.9 Hz, 6H), 4.19–4.26 (m, 2H), 7.21–7.28

(m, 1H), 7.32–7.39 (m, 2H), 7.76 (d, *J* = 6.7 Hz, 1H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 21.0 (*C*H_3), 80.7 (*C*H), 125.9 (*C*H), 129.6 (*C*H), 132.1 (*C*H), 137.0 (*C*H), 139.8 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 30.4 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{10}H_{12}{}^{11}BClO_2$, 210.0615; found, 210.0618.

(*4R,5R*)-2-(2-Methoxyphenyl)-4,5-dimethyl-1,3,2-dioxaborolane (1k).

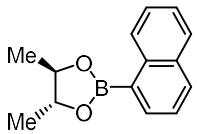


1k

The boronate **1k** was synthesized according to a literature procedure.[21] The corresponding product **1k** was obtained in 25% yield (260.1 mg, 1.26 mmol, white solid) after GPC separation.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.40 (d, *J* = 6.4 Hz, 6H), 3.87 (s, 3H), 4.16–4.22 (m, 2H), 6.87–6.89 (m, 1H), 6.93–6.98 (m, 1H), 7.40–7.46 (m, 1H), 7.75 (dd, *J* = 7.2, 3.6 Hz, 1H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 20.9 (*C*H_3), 55.6 (*C*H_3), 80.2 (*C*H), 110.2 (*C*H), 120.2 (*C*H), 132.8 (*C*H), 137.2 (*C*H), 164.2 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 30.7 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{10}H_{12}{}^{11}BClO_2$, 206.1111; found, 206.1110.

(*4R,5R*)-4,5-Dimethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborolane (1l).

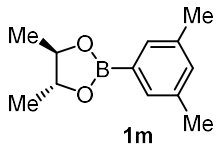


1l

The boronate **1l** was synthesized according to a literature procedure.[21] The corresponding product **1l** was obtained in 91% yield (1033.9 mg, 4.57 mmol, colorless oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.47 (d, *J* = 6.3 Hz, 6H), 4.25–4.32 (m, 2H), 7.46–7.50 (m, 2H), 7.51–7.56 (m, 1H), 7.83–7.86 (m, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 8.08–8.12 (m, 1H), 8.76 (d, *J* = 8.6 Hz, 1H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 21.1 (*C*H_3), 80.4 (*C*H), 125.0 (*C*H), 125.5 (*C*H), 126.4 (*C*H), 128.3 (*C*H), 128.4 (*C*H) 131.8 (*C*H), 133.2 (*C*), 135.9 (*C*H), 136.9 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 31.2 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{14}H_{15}{}^{11}BO_2$, 226.1162; found, 226.1162.

(*4R,5R*)-2-(3,5-Dimethylphenyl)-4,5-dimethyl-1,3,2-dioxaborolane (1m).

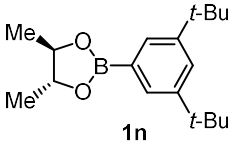


1m

The boronate **1m** was synthesized according to a literature procedure.[21] The corresponding product **1m** was obtained in 67% yield (687.1 mg, 3.37 mmol, white solid).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.39 (d, *J* = 5.5 Hz, 6H), 2.32 (s, 6H), 4.13–4.20 (m, 2H), 7.11 (s, 1H), 7.44 (s, 2H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 20.9 (*C*H_3), 21.2 (*C*H_3), 80.5 (*C*H), 132.4 (*C*H), 133.1 (*C*H), 137.2 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 30.7 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{12}H_{17}{}^{11}BO_2$, 204.1318; found, 204.1318.

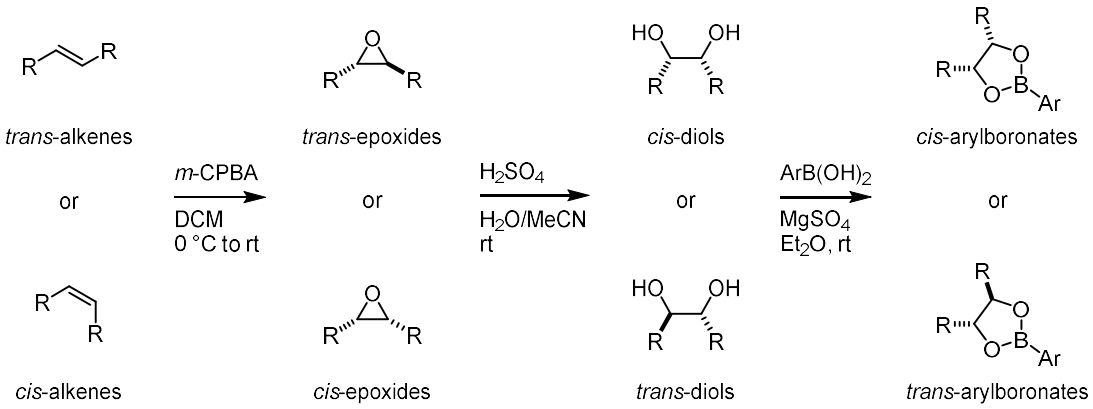
(*4R,5R*)-2-(3,5-Di-*tert*-butylphenyl)-4,5-dimethyl-1,3,2-dioxaborolane (1n).



1n

The boronate **1n** was synthesized according to a literature procedure.[21] The corresponding product **1n** was obtained in 79% yield (1139.9 mg, 3.95 mmol, white solid).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.34 (s, 18H), 1.40 (d, *J* = 6.4 Hz, 6H), 4.14–4.21 (m, 2H), 7.55 (t, *J* = 2.0 Hz, 1H), 7.67 (d, *J* = 1.6 Hz, 2H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 21.1 (*C*H_3), 31.5 (*C*H_3), 34.8 (*C*), 80.5 (*C*H), 125.6 (*C*H), 128.8 (*C*H), 150.0 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 31.1 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{18}H_{29}{}^{11}BO_2$, 288.2258; found, 288.2262.

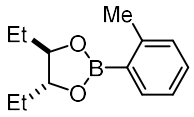


Scheme S1. Synthesis of various diols and corresponding arylboronates

The diols for preparation of corresponding aryl boronate (**5**) were synthesized according to a literature procedure.[22]

Alkene (8-10 mmol) and CH_2Cl_2 (0.5 M) were placed in a round-bottom flask. *m*-CPBA (1.2 equiv) was added to the reaction mixture at 0 °C, and they were stirred at ambient temperature. After the alkene was completely consumed, saturated $Na_2S_2O_3$ aqueous solution was added at 0 °C. The crude mixture was filtered and washed with saturated $NaHCO_3$ aqueous solution for three times. After the washing with brine and it was dried with Na_2SO_4, the organic phase was concentrated under reduced pressure. This crude mixture of epoxide was used for the next hydrolysis reaction without further purification. To the round-bottom flask containing an epoxide, MeCN/H_2O (v/v = 3:1, 0.2 M) was added, followed by conc. H_2SO_4 aqueous solution (3.6 M, 1.0 equiv). After the reaction mixture was stirred at ambient temperature for 30 min, the organic phase was extracted by ether three times. It was washed with brine for three times and dried with Na_2SO_4. The obtained crude diols were used for synthesizing aryl boronate (**5**) without further purification.

***trans*-4,5-Diethyl-2-(*o*-tolyl)-1,3,2-dioxaborolane (5a).**

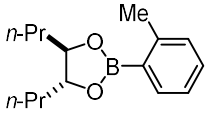


5a

The boronate **5a** was synthesized according to a literature procedure.[21] *cis*-3-Hexene (8.0 mmol) was used for the diol synthesis, and 2-methylphenylboronic acid (679.8 mg, 5.0 mmol) was used for the arylboronates synthesis. The corresponding product **5a** was obtained in 72% yield (791.2 mg, 3.63 mmol, colorless oil) based on the amount of the boronic acid.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.03 (t, *J* = 7.4 Hz, 6H), 1.67 (quint, *J* = 7.4 Hz, 4H), 2.55 (s, 3H), 4.03–4.09 (m, 2H), 7.15–7.19 (m, 2H), 7.31–7.35 (m, 1H), 7.81 (d, *J* = 7.4 Hz, 1H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 9.2 (*C*H_3), 22.2 (*C*H_3), 29.2 (*C*H_2), 83.1 (*C*H), 124.7 (*C*H), 129.9 (*C*H), 130.9 (*C*H), 136.1 (*C*H), 145.0 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 30.8 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{13}H_{19}{}^{11}BO_2$, 218.1475; found, 218.1477.

***trans*-4,5-Dipropyl-2-(*o*-tolyl)-1,3,2-dioxaborolane (5b).**

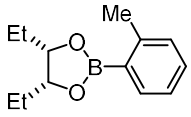


5b

The boronate **5b** was synthesized according to a literature procedure.[21] *cis*-4-Octene (10.0 mmol) was used for the diol synthesis, and 2-methylphenylboronic acid (679.8 mg, 5.0 mmol) was used for the arylboronates synthesis. The corresponding product **5b** was obtained in 79% yield (977.7 mg, 3.97 mmol, colorless oil) based on the amount of the boronic acid.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.98 (t, *J* = 7.4 Hz, 6H), 1.40–1.69 (m, 8H), 2.54 (s, 3H), 4.07–4.12 (m, 2H), 7.14–7.20 (m, 2H), 7.29–7.35 (m, 1H), 7.78–7.82 (m, 1H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 14.0 (*C*H_2), 18.4 (*C*H_2), 22.2 (*C*H_3), 38.4 (*C*H_3), 82.2 (*C*H), 124.7 (*C*H), 129.8 (*C*H), 130.9 (*C*H), 136.1 (*C*H), 145.0 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 30.8 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{15}H_{23}{}^{11}BO_2$, 246.1788; found, 246.1788.

***cis*-4,5-Diethyl-2-(*o*-tolyl)-1,3,2-dioxaborolane (5c).**

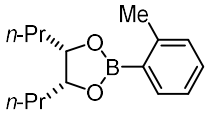


5c

The boronate **5c** was synthesized according to a literature procedure.[21] *trans*-3-Hexene (8.0 mmol) was used for the diol synthesis, and 2-methylphenylboronic acid (679.8 mg, 5.0 mmol) was used for the arylboronates synthesis. The corresponding product **5c** was obtained in 32% yield (353.2 mg, 1.62 mmol, colorless oil) based on the amount of the boronic acid.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.09 (t, *J* = 7.4 Hz, 6H), 1.54–1.65 (m, 4H), 2.56 (s, 3H), 4.37–4.43 (m, 2H), 7.14–7.21 (m, 2H), 7.30–7.36 (m, 1H), 7.79–7.85 (m, 1H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 10.8 (*C*H_2), 22.2 (*C*H_3), 24.0 (*C*H_3), 81.1 (*C*H), 124.7 (*C*H), 129.8 (*C*H), 130.9 (*C*H), 136.2 (*C*H), 145.1 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 31.1 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{13}H_{19}{}^{11}BO_2$, 218.1475; found, 218.1474.

***cis*-4,5-Dipropyl-2-(*o*-tolyl)-1,3,2-dioxaborolane (5d).**

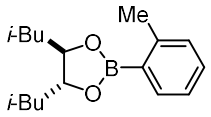


5d

The boronate **5d** was synthesized according to a literature procedure.[21] *trans*-4-Octene (10.0 mmol) was used for the diol synthesis, and 2-methylphenylboronic acid (679.8 mg, 5.0 mmol) was used for the arylboronates synthesis. The corresponding product **5d** was obtained in 70% yield (858.8 mg, 3.49 mmol, colorless oil) based on the amount of the boronic acid.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.99 (t, *J* = 7.2 Hz, 6H), 1.39–1.73 (m, 8H), 2.55 (s, 3H), 4.46–4.51 (m, 2H), 7.14–7.19 (m, 2H), 7.33 (dt, *J* = 7.2, 3.6 Hz, 1H), 7.79–7.83 (m, 1H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 14.1 (*C*H_2), 19.6 (*C*H_2), 22.2 (*C*H_3), 33.0 (*C*H_3), 79.4 (*C*H), 124.7 (*C*H), 129.8 (*C*H), 130.9 (*C*H), 136.2 (*C*H), 145.1 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 31.1 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{15}H_{23}{}^{11}BO_2$, 246.1788; found, 246.1790.

***trans*-4,5-Diisobutyl-2-(*o*-tolyl)-1,3,2-dioxaborolane (5e).**

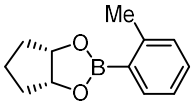


5e

The alkene, (*Z*)-2,7-dimethyloct-4-ene, was synthesized from isobutyraldehyde (1.72 g, 20 mmol) and (2-methylbutyl)triphenylphosphonium bromide (8.27 g, 20 mmol) *via* Wittig reaction according to literature.[23] The boronate **5e** was synthesized from 2-methylphenylboronic acid (5.0 mmol) and the crude mixture of (*Z*)-2,7-dimethyloct-4-ene.[21] The corresponding product **5e** was obtained in 53% yield (726.7 mg, 2.65 mmol, colorless oil) based on the amount of the boronic acid.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.98 (d, *J* = 1.6 Hz, 6H), 1.00 (d, *J* = 2.4 Hz, 6H), 1.36 (dddd, *J* = 21.6, 13.6, 7.8, 3.6 Hz, 2H), 1.59–1.66 (m, 2H), 1.90 (sept, *J* = 6.7 Hz, 2H), 2.54 (s, 3H), 4.08–4.14 (m, 2H), 7.14–7.19 (m, 2H), 7.32 (dt, *J* = 7.6, 2.0 Hz, 1H), 7.80 (dd, *J* = 7.6, 1.2 Hz, 1H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 22.3 (*C*H_3), 23.3 (*C*H_3), 25.0 (*C*H_2), 45.4 (*C*H), 81.4 (*C*H), 124.7 (*C*H), 129.8 (*C*H), 130.9 (*C*H), 136.2 (*C*H), 145.0 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 31.0 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{17}H_{27}{}^{11}BO_2$, 274.2102; found, 274.2106.

***cis*-2-(*o*-Tolyl)tetrahydro-4*H*-cyclopenta[*d*][1,3,2]dioxaborolane (5f).**



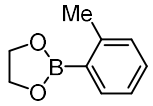
5f

The boronate **5f** was synthesized according to a literature procedure.[21] The corresponding product **5f** was obtained in 90% yield (904.6 mg, 4.48 mmol, colorless oil) based on the amount of the boronic acid.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.57–1.73 (m, 4H), 1.98–2.04 (m, 2H), 2.52 (s, 3H), 4.95–

5.02 (m, 2H), 7.14–7.20 (m, 2H), 7.33 (dt, *J* = 7.6, 3.8 Hz, 1H), 7.73–7.78 (m, 1H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 21.5 (*C*H_2), 22.3 (*C*H_3), 34.8 (*C*H_2), 82.4 (*C*H), 124.8 (*C*H), 129.8 (*C*H), 130.9 (*C*H), 136.1 (*C*H), 144.9 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 30.8 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{12}H_{15}{}^{11}BO_2$, 202.1162; found, 202.1160.

2-(*o*-Tolyl)-1,3,2-dioxaborolane (5g).



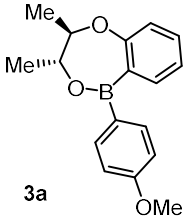
5g

The boronate **5g** was synthesized according to a literature procedure.[21] The corresponding product **5g** was obtained in 90% yield (728.0 mg, 4.49 mmol, colorless oil) based on the amount of the boronic acid.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 2.54 (s, 3H), 4.37 (s, 4H), 7.16–7.21 (m, 2H), 7.34 (dt, *J* = 7.2, 3.6 Hz, 1H), 7.78–7.83 (m, 1H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 22.3 (*C*H_3), 65.8 (*C*H), 124.8 (*C*H), 129.9 (*C*H), 131.1 (*C*H), 136.2 (*C*H), 145.0 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 31.6 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_9H_{11}{}^{11}BO_2$, 162.0848; found, 162.0849.

4.4.4. Characterization of Products

(*3R,4R*)-1-(4-Methoxyphenyl)-3,4-dimethyl-3,4-dihydro-1*H* benzo[*c*][1,5,2]dioxaborepine (3a).



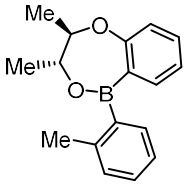
3a

The borylation reaction was conducted with 0.499 mmol of **1a**. The corresponding product **3a** was obtained in 65% yield (91.4 mg, 0.324 mmol, pale yellow solid).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.32 (d, *J* = 6.4 Hz, 3H), 1.40 (d, *J* = 6.4 Hz, 3H), 3.86 (s, 3H), 4.15–4.22 (m, 1H), 4.31–4.38 (m, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.98–7.02 (m, 1H), 7.08–7.13 (m, 1H), 7.39–7.44 (m, 1H), 7.57 (dd, *J* = 7.2, 3.1 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 17.3 (*C*H_3), 19.1 (*C*H_3), 55.1 (*C*H_3), 75.5 (*C*H), 84.1 (*C*H), 113.1 (*C*H), 121.4 (*C*H), 122.2 (*C*H), 132.1 (*C*H), 137.35 (*C*H), 137.39 (*C*H), 160.1 (*C*), 160.9 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar

relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 44.5 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{17}H_{19}{}^{11}BO_3$, 282.1425; found, 282.1424.

(*3R,4R*)-3,4-Dimethyl-1-(*o*-tolyl)-3,4-dihydro-1*H*-benzo[*c*][1,5,2]dioxaborepine (3b).

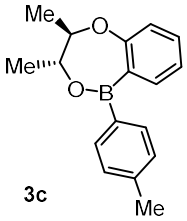


3b

The borylation reaction was conducted with 0.500 mmol of **1b**. The corresponding product **3b** was obtained in 75% yield (100.1 mg, 0.376 mmol, pale yellow oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.41 (d, *J* = 6.4 Hz, 3H), 1.43 (d, *J* = 7.2 Hz, 3H), 2.36 (s, 3H), 4.27–4.34 (m, 1H), 4.40–4.46 (m, 1H), 6.90–6.94 (m, 1H), 6.97–7.00 (m, 1H), 7.17–7.21 (m, 2H), 7.26–7.31 (m, 1H), 7.35–7.43 (m, 3H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 17.3 (*C*H_3), 19.6 (*C*H_3), 22.5 (*C*H_3), 78.2 (*C*H), 82.0 (*C*H), 119.3 (*C*H), 120.9 (*C*H), 124.6 (*C*H), 128.7 (*C*H), 129.4 (*C*H), 132.8 (*C*H), 133.4 (*C*H), 140.6 (*C*H), 140.8 (*C*), 162.7 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 45.3 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{17}H_{19}{}^{11}BO_2$, 266.1476; found, 266.1477.

(*3R,4R*)-3,4-Dimethyl-1-(*p*-tolyl)-3,4-dihydro-1*H*-benzo[*c*][1,5,2]dioxaborepine (3c).

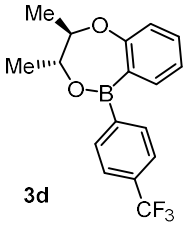


3c

The borylation reaction was conducted with 0.500 mmol of **1c**. The corresponding product **3c** was obtained in 40% yield (53.4 mg, 0.201 mmol, white solid).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.34 (d, *J* = 6.3 Hz, 3H), 1.40 (d, *J* = 6.7 Hz, 3H), 2.40 (s, 3H), 4.23 (quint, *J* = 6.7 Hz, 1H), 4.33 (quint, *J* = 6.7 Hz, 1H), 7.00 (d, *J* = 8.2 Hz, 1H), 7.08 (t, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.39–7.44 (m, 1H), 7.55–7.61 (m, 1H), 7.73 (d, *J* = 7.8 Hz, 2H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 17.3 (*C*H_3), 19.2 (*C*H_3), 21.7 (*C*H_3), 76.0 (*C*H), 83.8 (*C*H), 121.1 (*C*H), 121.9 (*C*H), 128.4 (*C*H), 132.3 (*C*H), 135.4 (*C*H), 138.0 (*C*H), 140.8 (*C*), 160.6 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 44.7 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{17}H_{19}{}^{11}BO_2$, 266.1476; found, 266.1479.

(*3R,4R*)-3,4-Dimethyl-1-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1*H*-benzo[*c*][1,5,2]dioxaborepine (3d).

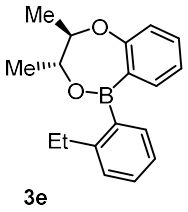


3d

The borylation reaction was conducted with 0.500 mmol of **1d**. The corresponding product **3d** was obtained in 25% yield (40.6 mg, 0.127 mmol, pale yellow oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.38 (d, *J* = 5.9 Hz, 3H), 1.43 (d, *J* = 5.5 Hz, 3H), 4.28–4.37 (m, 2H), 7.00–7.09 (m, 2H), 7.43–7.47 (m, 1H), 7.49–7.52 (m, 1H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.89 (d, *J* = 7.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 17.4 (*C*H_3), 19.2 (*C*H_3), 77.3 (*C*H), 83.4 (*C*H), 120.7 (*C*H), 121.7 (*C*H), 124.0 (*C*H), 124.269 (*C*H), 124.270 (q, *J* = 272.3 Hz, *C*F_3), 131.9 (q, *J* = 32.1 Hz, *C*), 133.1 (*C*H), 135.0 (*C*H), 138.6 (*C*H), 161.7 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 44.1 (br, s). 19F NMR (369 MHz, $CDCl_3$, δ): –63.4 (s, 3F). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{17}H_{16}{}^{11}BF_3O_2$, 320.1193; found, 320.1196.

(*3R,4R*)-1-(2-Ethylphenyl)-3,4-dimethyl-3,4-dihydro-1*H*-benzo[*c*][1,5,2]dioxaborepine (3e).

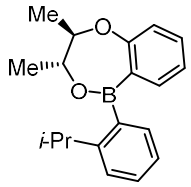


3e

The borylation reaction was conducted with 0.501 mmol of **1e**. The corresponding product **3e** was obtained in 80% yield (112.7 mg, 0.402 mmol, pale yellow solid).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.17 (t, *J* = 7.6 Hz, 3H), 1.41 (d, *J* = 9.6 Hz, 3H), 1.43 (d, *J* = 9.2 Hz, 3H), 2.63–2.78 (m, 2H), 4.31 (quint, *J* = 6.3 Hz, 1H), 4.43 (quint, *J* = 6.4 Hz, 1H), 6.90 (t, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.23–7.26 (m, 1H), 7.30–7.43 (m, 4H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 16.6 (*C*H_2), 17.3 (*C*H_3), 19.7 (*C*H_3), 29.3 (*C*H_3), 78.3 (*C*H), 82.0 (*C*H), 119.2 (*C*H), 120.8 (*C*H), 124.7 (*C*H), 127.9 (*C*H), 128.7 (*C*H), 132.7 (*C*H), 133.4 (*C*H), 140.8 (*C*H), 147.3 (*C*), 162.8 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 45.5 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{18}H_{21}{}^{11}BO_2$, 280.1632; found, 280.1632.

(*3R,4R*)-1-(2-Isopropylphenyl)-3,4-dimethyl-3,4-dihydro-1*H*-benzo[*c*][1,5,2]dioxaborepine (3f).

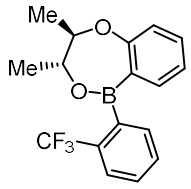


3f

The borylation reaction was conducted with 0.501 mmol of **1e**. The corresponding product **3e** was obtained in 78% yield (114.7 mg, 0.390 mmol, pale yellow solid).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.21 (d, *J* = 7.2 Hz, 3H), 1.22 (d, *J* = 6.8 Hz, 3H), 1.40 (d, *J* = 6.8 Hz, 3H), 1.44 (d, *J* = 6.8 Hz, 3H), 3.03 (sept, *J* = 6.8 Hz, 1H), 4.27–4.33 (m, 1H), 4.42–4.48 (m, 1H), 6.85–6.92 (m, 1H), 6.96–7.00 (m, 1H), 7.16–7.21 (m, 1H), 7.27–7.31 (m, 1H), 7.32–7.41 (m, 4H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 17.3 (*C*H_3), 19.8 (*C*H_3), 24.2 (*C*H_3), 24.5 (*C*H_3), 34.0 (*C*H), 78.6 (*C*H), 81.7 (*C*H), 119.1 (*C*H), 120.7 (*C*H), 124.5 (*C*H), 124.8 (*C*H), 128.6 (*C*H), 131.8 (*C*H), 133.5 (*C*H), 141.1 (*C*H), 151.5 (*C*), 163.0 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 45.3 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{19}H_{23}{}^{11}BO_2$, 294.1789; found, 294.1790.

(*3R,4R*)-3,4-Dimethyl-1-(2-(trifluoromethyl)phenyl)-3,4-dihydro-1*H*-benzo[*c*][1,5,2]dioxaborepine (3g).



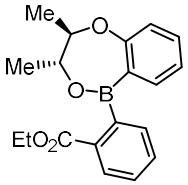
3g

The borylation reaction was conducted with 0.500 mmol of **1g**. The corresponding product **3g** was obtained in 78% yield (125.5 mg, 0.392 mmol, white solid).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.38 (d, *J* = 6.7 Hz, 3H), 1.45 (d, *J* = 6.7 Hz, 3H), 4.28 (quint, *J* = 6.7 Hz, 1H), 4.48 (quint, *J* = 6.5 Hz, 1H), 6.84–6.90 (m, 1H), 6.97–7.00 (m, 1H), 7.14–7.17 (m, 1H), 7.38–7.55 (m, 4H), 7.68 (d, *J* = 7.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 17.4 (*C*H_3), 19.7 (*C*H_3), 79.5 (*C*H), 81.4 (*C*H), 119.0 (*C*H), 120.7 (*C*H), 125.1 (q, *J* = 273.5 Hz, *C*F_3), 125.3–125.5 (m, *C*H), 128.1 (*C*H), 130.4 (*C*H), 131.9 (*C*H), 132.1 (q, *J* = 30.8 Hz, *C*), 133.8 (*C*H), 139.7 (*C*–B), 141.1 (*C*H), 163.9 (*C*). ^{11}B NMR (126 MHz, $CDCl_3$, δ): 43.7 (br, s). 19F NMR (369 MHz, $CDCl_3$, δ): –58.7 (s, 3F). HRMS-EI (*m*/*z*): $[M]^+$ calcd for

$C_{17}H_{16}{}^{11}BF_3O_2$, 320.1193; found, 320.1192.

Ethyl 2-{(*3R,4R*)-3,4-dimethyl-3,4-dihydro-1*H*-benzo[*c*][1,5,2]dioxaborepin-1-yl}benzoate (3h).

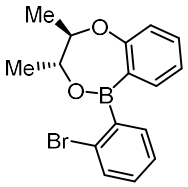


3h

The borylation reaction was conducted with 0.501 mmol of **1h**. The corresponding product **3h** was obtained in 75% yield (121.1 mg, 0.374 mmol, white solid).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.26 (t, *J* = 7.2 Hz, 3H), 1.35 (d, *J* = 6.4 Hz, 3H), 1.46 (d, *J* = 6.4 Hz, 3H), 4.19–4.34 (m, 2H), 4.44–4.56 (m, 2H), 6.75–6.81 (m, 1H), 6.93–7.01 (m, 2H), 7.28–7.32 (m, 1H), 7.40–7.48 (m, 2H), 7.53–7.59 (m, 1H), 8.01 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 14.3 (*C*H_3), 18.2 (*C*H_3), 20.2 (*C*H_3), 61.5 (*C*H_2), 79.1 (*C*H), 81.5 (*C*H), 118.9 (*C*H), 120.8 (*C*H), 127.6 (*C*H), 128.6 (*C*H), 130.7 (*C*H), 132.38 (*C*H), 132.46 (*C*H), 132.8 (*C*H), 139.4 (*C*), 163.3 (*C*), 168.9 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 41.8 (br, s). HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{19}H_{22}{}^{11}BO_4$, 325.1606; found, 325.1603.

(*3R,4R*)-1-(2-Bromophenyl)-3,4-dimethyl-3,4-dihydro-1*H*-benzo[*c*][1,5,2]dioxaborepine (3i).



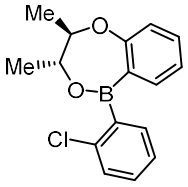
3i

The borylation reaction was conducted with 0.500 mmol of **1i**. The corresponding product **3i** was obtained in 64% yield (105.8 mg, 0.320 mmol, white solid).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.43 (d, *J* = 6.7 Hz, 3H), 1.47 (d, *J* = 7.0 Hz, 3H), 4.27 (quint, *J* = 6.7 Hz, 1H), 4.50 (quint, *J* = 6.7 Hz, 1H), 6.90 (t, *J* = 7.0 Hz, 1H), 6.98 (d, *J* = 8.6 Hz, 1H), 7.20–7.26 (m, 1H), 7.28–7.35 (m, 3H), 7.38–7.44 (m, 1H), 7.54 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 17.3 (*C*H_3), 19.8 (*C*H_3), 79.4 (*C*H), 81.3 (*C*H), 119.0 (*C*H), 120.8 (*C*H), 125.5 (*C*H), 126.3 (*C*H), 129.8 (*C*H), 131.8 (*C*H), 132.9 (*C*H), 133.9 (*C*H), 141.0 (*C*), 163.6 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 43.1 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd

for $C_{16}H_{16}{}^{11}BBrO_2$, 330.0424; found, 330.0424.

(*3R,4R*)-1-(2-Chlorophenyl)-3,4-dimethyl-3,4-dihydro-1*H*-benzo[*c*][1,5,2]dioxaborepine (3j).

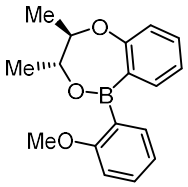


3j

The borylation reaction was conducted with 0.500 mmol of **1j**. The corresponding product **3j** was obtained in 41% yield (58.2 mg, 0.203 mmol, white solid).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.42 (d, *J* = 6.4 Hz, 3H), 1.46 (d, *J* = 6.4 Hz, 3H), 4.30–4.37 (m, 1H), 4.46–4.52 (m, 1H), 6.87–6.93 (m, 1H), 6.96–7.01 (m, 1H), 7.27–7.32 (m, 3H), 7.33–7.38 (m, 2H), 7.39–7.43 (m, 1H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 17.2 (*C*H_3), 19.8 (*C*H_3), 79.3 (*C*H), 81.3 (*C*H), 119.0 (*C*H), 120.7 (*C*H), 125.9 (*C*H), 128.7 (*C*H), 129.7 (*C*H), 132.9 (*C*H), 133.8 (*C*H), 136.5 (*C*H), 140.9 (*C*), 163.4 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 43.4 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{16}H_{16}{}^{11}BClO_2$, 286.0929; found, 286.0930.

(*3R,4R*)-1-(2-Methoxyphenyl)-3,4-dimethyl-3,4-dihydro-1*H*-benzo[*c*][1,5,2]dioxaborepine (3k).

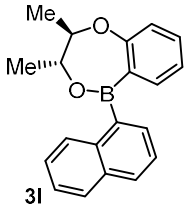


3k

The borylation reaction was conducted with 0.501 mmol of **1k**. The corresponding product **3k** was obtained in 78% yield (110.8 mg, 0.393 mmol, colorless oil).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.41 (d, *J* = 6.8 Hz, 3H), 1.44 (d, *J* = 6.8 Hz, 3H), 3.72 (s, 3H), 4.30–4.36 (m, 1H), 4.41–4.47 (m, 1H), 6.86–6.93 (m, 2H), 6.94–7.01 (m, 2H), 7.32–7.40 (m, 4H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 16.9 (*C*H_3), 19.7 (*C*H_3), 55.4 (*C*H_3), 78.5 (*C*H), 81.4 (*C*H), 110.3 (*C*H), 118.9 (*C*H), 120.4 (*C*H), 120.5 (*C*H), 130.0 (*C*H), 133.2 (*C*H), 140.9 (*C*H), 161.9 (*C*H), 162.4 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 44.8 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{17}H_{19}{}^{11}BO_3$, 282.1425; found, 282.1422.

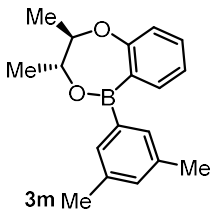
(*3R,4R*)-3,4-Dimethyl-1-(naphthalen-1-yl)-3,4-dihydro-1*H*-benzo[*c*][1,5,2]dioxaborepine (3l).



The borylation reaction was conducted with 0.500 mmol of **1l**. The corresponding product **3l** was obtained in 71% yield (107.7 mg, 0.356 mmol, white solid).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.47 (d, *J* = 2.3 Hz, 3H), 1.49 (d, *J* = 2.7 Hz, 3H), 4.38–4.44 (m, 1H), 4.53 (quint, *J* = 6.6 Hz, 1H), 6.83–6.90 (m, 1H), 7.02–7.05 (m, 1H), 7.33–7.37 (m, 1H), 7.38–7.51 (m, 4H), 7.60–7.64 (m, 1H), 7.88 (t, *J* = 9.0 Hz, 2H), 8.08 (d, *J* = 8.6 Hz, 1H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 17.4 (*C*H_3), 19.7 (*C*H_3), 78.4 (*C*H), 82.3 (*C*H), 119.5 (*C*H), 121.0 (*C*H), 125.0 (*C*H), 125.4 (*C*H), 125.6 (*C*H), 128.5 (*C*H), 128.9 (*C*H), 129.3 (*C*H), 132.4 (*C*H), 133.3 (*C*), 133.5 (*C*H), 135.9 (*C*), 140.7 (*C*H), 162.5 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 45.4 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{20}H_{19}{}^{11}BO_2$, 302.1476; found, 302.1474.

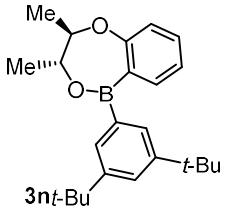
(*3R,4R*)-1-(3,5-Dimethylphenyl)-3,4-dimethyl-3,4-dihydro-1*H*-benzo[*c*][1,5,2]dioxaborepine (3m).



The borylation reaction was conducted with 0.500 mmol of **1m**. The corresponding product **3m** was obtained in 69% yield (97.2 mg, 0.347 mmol, pale yellow oil).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.34 (d, *J* = 6.4 Hz, 3H), 1.42 (d, *J* = 6.4 Hz, 3H), 2.35 (s, 6H), 4.24 (quint, *J* = 6.3 Hz, 1H), 4.33 (quint, *J* = 6.3 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 7.06–7.13 (m, 2H), 7.40–7.45 (m, 3H), 7.56–7.59 (m, 1H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 17.3 (*C*H_3), 19.2 (*C*H_3), 21.3 (*C*H_3), 76.2 (*C*H), 83.6 (*C*H), 120.9 (*C*H), 121.8 (*C*H), 132.3 (*C*H), 132.4 (*C*H), 132.9 (*C*H), 136.9 (*C*), 138.3 (*C*H), 160.8 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 44.6 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{18}H_{21}{}^{11}BO_2$, 280.1632; found, 280.1635.

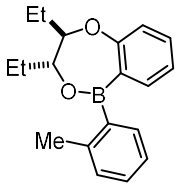
(*3R,4R*)-1-(3,5-Di-*tert*-butylphenyl)-3,4-dimethyl-3,4-dihydro-1*H*-benzo[*c*][1,5,2]dioxaborepine (3n).



The borylation reaction was conducted with 0.500 mmol of **1n**. The corresponding product **3n** was obtained in 68% yield (124.0 mg, 0.340 mmol, pale yellow oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.35 (s, 18H), 1.36 (d, *J* = 8.2 Hz, 3H), 1.42 (d, *J* = 6.3 Hz, 3H), 4.26 (quint, *J* = 6.3 Hz, 1H), 4.34 (quint, *J* = 6.3 Hz, 1H), 6.99–7.03 (m, 1H), 7.04–7.09 (m, 1H), 7.40–7.45 (m, 1H), 7.54–7.56 (m, 1H), 7.59–7.62 (m, 1H), 7.67 (d, *J* = 2.4 Hz, 2H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 17.5 (*C*H_3), 19.3 (*C*H_3), 31.5 (*C*H_3), 34.8 (*C*), 76.3 (*C*H), 83.7 (*C*H), 120.8 (*C*H), 121.7 (*C*H), 124.8 (*C*H), 129.3 (*C*H), 132.3 (*C*H), 138.5 (*C*H), 149.5 (*C*), 161.1 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 46.6 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{24}H_{33}{}^{11}BO_2$, 364.2573; found, 364.2581.

***trans*-3,4-Diethyl-1-(*o*-tolyl)-3,4-dihydro-1*H*-benzo[*c*][1,5,2]dioxaborepine (6a).**

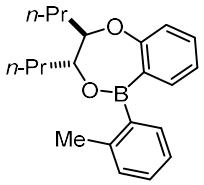


6a

The borylation reaction was conducted with 0.501 mmol of **5a**. The corresponding product **6a** was obtained in 80% yield (117.8 mg, 0.400 mmol, pale yellow oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.07 (t, *J* = 7.4 Hz, 3H), 1.10 (t, *J* = 7.4 Hz, 3H), 1.67–1.93 (m, 4H), 2.36 (s, 3H), 4.18–4.27 (m, 2H), 6.86–6.92 (m, 1H), 6.98–7.02 (m, 1H), 7.15–7.21 (m, 2H), 7.27–7.42 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 10.4 (*C*H_2), 10.5 (*C*H_2), 22.5 (*C*H_3), 22.6 (*C*H_3), 26.6 (*C*H_3), 82.1 (*C*H), 84.2 (*C*H), 119.2 (*C*H), 120.5 (*C*H), 124.6 (*C*H), 128.5 (*C*H), 129.3 (*C*H), 132.4 (*C*H), 133.5 (*C*H), 140.3 (*C*), 140.8 (*C*H), 162.3 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 45.3 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{19}H_{23}{}^{11}BO_2$, 294.1789; found, 294.1793.

***trans*-3,4-Dipropyl-1-(*o*-tolyl)-3,4-dihydro-1*H*-benzo[*c*][1,5,2]dioxaborepine (6b).**

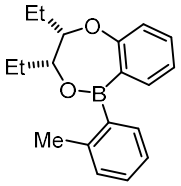


6b

The borylation reaction was conducted with 0.500 mmol of **5b**. The corresponding product **6b** was obtained in 77% yield (124.3 mg, 0.386 mmol, yellow solid).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.92–0.98 (m, 6H), 1.44–1.55 (m, 2H), 1.57–1.77 (m, 5H), 1.80–1.90 (m, 1H), 2.35 (s, 3H), 4.24–4.34 (m, 2H), 6.86–6.91 (m, 1H), 6.96–7.00 (m, 1H), 7.16–7.21 (m, 2H), 7.27–7.30 (m, 1H), 7.30–7.36 (m, 2H), 7.37–7.42 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 13.9 (*C*H_2), 19.03 (*C*H_3), 19.10 (*C*H_3), 22.6 (*C*H_3), 31.4 (*C*H_2), 35.6 (*C*H_2), 80.7 (*C*H), 82.8 (*C*H), 119.2 (*C*H), 120.5 (*C*H), 124.6 (*C*H), 128.5 (*C*H), 129.3 (*C*H), 132.3 (*C*H), 133.5 (*C*H), 140.3 (*C*), 140.8 (*C*H), 162.3 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 45.6 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{21}H_{27}{}^{11}BO_2$, 322.2102; found, 322.2104.

***cis*-3,4-Diethyl-1-(*o*-tolyl)-3,4-dihydro-1*H*-benzo[*c*][1,5,2]dioxaborepine (6c).**

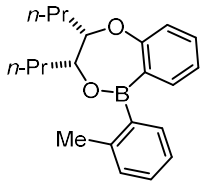


6c

The borylation reaction was conducted with 0.500 mmol of **5c**. The corresponding product **6c** was obtained in 79% yield (115.8 mg, 0.394 mmol, pale yellow oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.11 (t, *J* = 7.4 Hz, 6H), 1.57–1.78 (m, 3H), 1.82–1.94 (m, 1H), 2.35 (s, 3H), 4.09 (q, *J* = 4.7 Hz, 1H), 4.32 (q, *J* = 4.6 Hz, 1H), 6.84–6.90 (m, 1H), 7.02 (d, *J* = 8.6 Hz, 1H), 7.17–7.21 (m, 2H), 7.25–7.30 (m, 1H), 7.33–7.42 (m, 3H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 10.8 (*C*H_3), 11.0 (*C*H_3), 22.6 (*C*H_3), 23.7 (*C*H_2), 25.6 (*C*H_2), 83.6 (*C*H), 86.0 (*C*H), 118.1 (*C*H), 120.4 (*C*H), 124.6 (*C*H), 128.2 (*C*H), 129.3 (*C*H), 131.7 (*C*H), 133.5 (*C*H), 139.9 (*C*), 141.9 (*C*H), 164.2 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 45.0 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{19}H_{23}{}^{11}BO_2$, 294.1789; found, 294.1790.

***cis*-3,4-Dipropyl-1-(*o*-tolyl)-3,4-dihydro-1*H*-benzo[*c*][1,5,2]dioxaborepine (6d).**

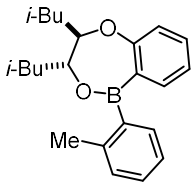


6d

The borylation reaction was conducted with 0.500 mmol of **5d**. The corresponding product **6d** was obtained in 74% yield (118.5 mg, 0.368 mmol, pale yellow oil).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.95 (t, *J* = 7.4 Hz, 3H), 0.98 (t, *J* = 7.0 Hz, 3H), 1.42–1.54 (m, 2H), 1.57–1.74 (m, 5H), 1.81–1.90 (m, 1H), 2.34 (s, 3H), 4.18 (q, *J* = 4.0 Hz, 1H), 4.40 (q, *J* = 4.0 Hz, 1H), 6.85–6.90 (m, 1H), 7.00–7.04 (m, 1H), 7.16–7.22 (m, 2H), 7.26–7.28 (m, 1H), 7.30–7.34 (m, 1H), 7.36–7.42 (m, 2H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 13.9 (*C*H_3), 14.0 (*C*H_3), 19.3 (*C*H_2), 19.6 (*C*H_2), 22.6 (*C*H_3), 32.8 (*C*H_2), 34.5 (*C*H_2), 82.0 (*C*H), 84.3 (*C*H), 118.2 (*C*H), 120.4 (*C*H), 124.6 (*C*H), 128.2 (*C*H), 129.3 (*C*H), 131.7 (*C*H), 133.5 (*C*H), 139.8 (*C*), 141.9 (*C*H), 164.2 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 47.1 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{21}H_{27}{}^{11}BO_2$, 322.2102; found, 322.2104.

***trans*-3,4-Diisobutyl-1-(*o*-tolyl)-3,4-dihydro-1*H*-benzo[*c*][1,5,2]dioxaborepine (6e).**

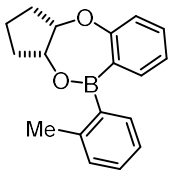


6e

The borylation reaction was conducted with 0.500 mmol of **5e**. The corresponding product **6e** was obtained in 81% yield (142.2 mg, 0.406 mmol, pale yellow oil).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.92–0.98 (m, 12H), 1.35–1.47 (m, 2H), 1.66–1.74 (m, 1H), 1.81–2.06 (m, 3H), 2.34 (s, 3H), 4.29–4.38 (m, 2H), 6.86–6.91 (m, 1H), 6.95–6.99 (m, 1H), 7.16–7.22 (m, 2H), 7.27–7.30 (m, 1H), 7.30–7.36 (m, 2H), 7.37–7.42 (m, 1H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 21.6 (*C*H_2), 21.7 (*C*H_2), 22.6 (*C*H_3), 23.4 (*C*H_3), 23.6 (*C*H_3), 24.4 (*C*H_3), 24.6 (*C*H_3), 37.9 (*C*H), 42.4 (*C*H), 79.4 (*C*H), 81.6 (*C*H), 119.3 (*C*H), 120.5 (*C*H), 124.6 (*C*H), 128.5 (*C*H), 129.4 (*C*H), 132.4 (*C*H), 133.5 (*C*H), 140.4 (*C*), 140.8 (*C*H), 162.1 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 45.4 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{23}H_{31}{}^{11}BO_2$, 350.2416; found, 350.2419.

5-(*o*-Tolyl)-2,3,3a,10a-*cis*-tetrahydro-1*H*,5*H*-benzo[*c*]cyclopenta[*f*][1,5,2]dioxaborepine (6f).

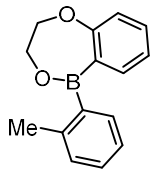


6f

The borylation reaction was conducted with 0.501 mmol of **5f**. The corresponding product **6f** was obtained in 73% yield (102.1 mg, 0.367 mmol, pale yellow solid).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.60–1.71 (m, 1H), 1.89–2.17 (m, 5H), 2.43 (s, 3H), 4.51–4.58 (m, 2H), 7.06–7.20 (m, 4H), 7.29–7.33 (m, 2H), 7.37–7.48 (m, 2H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 19.8 (*C*H_2), 22.7 (*C*H_3), 29.1 (*C*H_2), 30.6 (*C*H_2), 78.0 (*C*H), 88.6 (*C*H), 120.3 (*C*H), 123.8 (*C*H), 124.6 (*C*H), 129.9 (*C*H), 132.2 (*C*H), 135.6 (*C*H), 137.0 (*C*H), 143.1 (*C*), 162.7 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 46.2 (br, s). HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{18}H_{20}{}^{11}BO_2$, 279.1547; found, 279.1551.

1-(*o*-Tolyl)-3,4-dihydro-1*H*-benzo[*c*][1,5,2]dioxaborepine (6g).

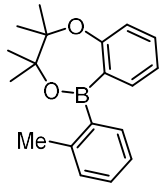


6g

The borylation reaction was conducted with 0.501 mmol of **5g**. The corresponding product **6g** was obtained in 62% yield (73.5 mg, 0.309 mmol, orange oil).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 2.34 (s, 3H), 4.46–4.50 (m, 2H), 4.52–4.57 (m, 2H), 6.90 (t, *J* = 7.2 Hz, 1H), 6.99–7.04 (m, 1H), 7.17–7.22 (m, 2H), 7.27–7.32 (m, 1H), 7.34–7.38 (m, 1H), 7.39–7.45 (m, 2H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 22.5 (*C*H_3), 70.2 (*C*H_2), 72.9 (*C*H_2), 118.5 (*C*H), 120.7 (*C*H), 124.6 (*C*H), 128.5 (*C*H), 129.4 (*C*H), 131.9 (*C*H), 133.7 (*C*H), 140.2 (*C*), 142.0 (*C*H), 164.5 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 46.0 (br, s). HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{15}H_{16}{}^{11}BO_2$, 239.1234; found, 239.1238.

3,3,4,4-Tetramethyl-1-(*o*-tolyl)-3,4-dihydro-1*H*-benzo[*c*][1,5,2]dioxaborepine (6h).



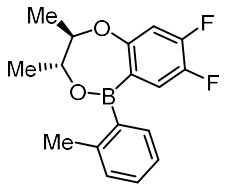
6h

The borylation reaction was conducted with 0.500 mmol of **5h**. After **5h** was consumed, water (0.5 mL) was added, and the reaction mixture was stirred 24 h. After that, the reaction mixture was passed through a short silica gel column (*Φ*: 15 mm, height of the silica-gel column: 30 mm) eluting with Et_2O. The crude material was purified by flash column chromatography (SiO_2, Et_2O/hexane, 0:100–3:97) to give the corresponding diarylborinic acid ester **6h**.

The product **6h** was obtained in 94% yield (138.3 mg, 0.470 mmol, yellow solid).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.41 (s, 6H), 1.45 (s, 6H), 2.36 (s, 3H), 6.80–6.86 (m, 1H), 6.92–6.96 (m, 1H), 7.15–7.22 (m, 2H), 7.26–7.28 (m, 1H), 7.29–7.34 (m, 2H), 7.36–7.41 (m, 1H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 22.5 (*C*H_3), 26.2 (*C*H_3), 83.08 (*C*H_2), 83.11 (*C*H_2), 119.5 (*C*H), 119.8 (*C*H), 124.5 (*C*H), 128.2 (*C*H), 129.3 (*C*H), 132.1 (*C*H), 133.7 (*C*H), 140.2 (*C*), 141.1 (*C*H), 161.9 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 44.3 (br, s). HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{19}H_{23}{}^{11}BO_2$, 294.1789; found, 294.1790.

(*3R,4R*)-7,8-Difluoro-3,4-dimethyl-1-(*o*-tolyl)-3,4-dihydro-1*H*-benzo[*c*][1,5,2]dioxaborepine (7a).



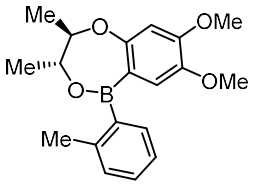
7a

The borylation reaction was conducted with 0.500 mmol of **1b** and 1.501 mmol of 4,5-difluoro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2b**. The corresponding product **7a** was obtained in 55% yield (83.4 mg, 0.276 mmol, brown oil).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.397–1.402 (m, 3H), 1.41–1.42 (m, 3H), 2.35 (s, 3H), 4.28 (quint, *J* = 6.3 Hz, 1H), 4.41 (quint, *J* = 6.3 Hz, 1H), 6.78 (dd, *J* = 12.0, 6.0 Hz, 1H), 7.08–7.13 (m, 1H), 7.17–7.21 (m, 2H), 7.29–7.32 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 17.2 (*C*H_3), 19.6 (*C*H_3), 22.4 (*C*H_3), 78.3 (*C*H), 82.7 (*C*H), 108.3 (d, *J* = 18.2 Hz, *C*), 124.8 (*C*H), 127.0 (q, *J* = 17.3 Hz, *C*), 129.1 (*C*H), 129.6 (*C*H), 132.7 (*C*H), 140.7 (*C*), 145.2 (dd, *J*

= 229.2, 12.5 Hz, *C*H), 153.3 (dd, *J* = 239.9, 14.4 Hz, *C*H), 159.4 (d, *J* = 9.6 Hz, *C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 46.2 (br, s). 19F NMR (369 MHz, $CDCl_3$, δ): –130.7 (s, 1F), –148.2 (s, 1F). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{17}H_{17}{}^{11}BF_2O_2$, 302.1287; found, 302.1287.

(*3R,4R*)-7,8-Dimethoxy-3,4-dimethyl-1-(*o*-tolyl)-3,4-dihydro-1*H*-benzo[*c*][1,5,2]dioxaborepine (7b).

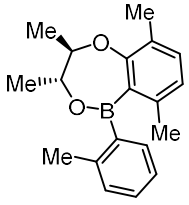


7b

The borylation reaction was conducted with 0.500 mmol of **1b** and 1.498 mmol of 4,5-dimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2c**. The corresponding product **7b** was obtained in 68% yield (111.7 mg, 0.342 mmol, white solid).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.40 (d, *J* = 6.8 Hz, 3H), 1.42 (d, *J* = 6.8 Hz, 3H), 2.37 (s, 3H), 3.61 (s, 3H), 3.89 (s, 3H), 4.22–4.28 (m, 1H), 4.38–4.45 (m, 1H), 6.53 (s, 1H), 6.78 (s, 1H), 7.15–7.21 (m, 2H), 7.25–7.30 (m, 1H), 7.35–7.38 (m, 1H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 17.3 (*C*H_3), 19.7 (*C*H_3), 22.5 (*C*H_3), 55.8 (*C*H_3), 56.2 (*C*H_3), 78.3 (*C*H), 81.9 (*C*H), 102.4 (*C*H), 121.5 (*C*H), 124.6 (*C*H), 128.5 (*C*H), 129.4 (*C*H), 132.5 (*C*H), 140.5 (*C*), 143.2 (*C*), 153.6 (*C*), 158.8 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 44.3 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{19}H_{23}{}^{11}BO_4$, 326.1687; found, 326.1689.

(*3R,4R*)-3,4,6,9-Tetramethyl-1-(*o*-tolyl)-3,4-dihydro-1*H*-benzo[*c*][1,5,2]dioxaborepine (7c).



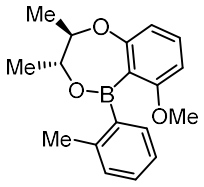
7c

The borylation reaction was conducted with 0.500 mmol of **1b** and 1.498 mmol of 3,6-dimethyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2d**. The corresponding product **7c** was obtained in 87% yield (128.3 mg, 0.436 mmol, white solid).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.24–1.26 (m, 3H), 2.77 (d, *J* = 6.0 Hz, 3H), 1.96 (s, 3H), 2.26 (s, 3H), 2.37 (s, 3H), 4.15–4.24 (m, 1H), 4.30–4.38 (m, 1H), 6.83 (d, *J* = 8.0 Hz, 1H),

7.10–7.18 (m, 3H), 7.24–7.29 (m, 1H), 7.39–7.43 (m, 1H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 16.4 (*C*H_3), 17.1 (*C*H_3), 18.8 (*C*H_3), 21.8 (*C*H_3), 22.2 (*C*H_3), 73.8 (*C*H), 85.6 (*C*H), 125.0 (*C*H), 125.6 (*C*H), 127.8 (*C*), 129.8 (*C*H), 129.9 (*C*H), 132.7 (*C*H), 134.8 (*C*H), 140.6 (*C*), 142.6 (*C*), 155.2 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 47.1 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{19}H_{23}{}^{11}BO_2$, 294.1789; found, 294.1791.

(*3R,4R*)-9-methoxy-3,4-dimethyl-1-(*o*-tolyl)-3,4-dihydro-1*H*-benzo[*c*][1,5,2]dioxaborepine (7d)



7d

The borylation reaction was conducted with 0.500 mmol of **1b** and 1.500 mmol of 2-methoxy-6-(trimethylsilyl)phenyl trifluoromethanesulfonate **2e**. The corresponding product **7d** was obtained in 50% yield (74.6 mg, 0.252 mmol, white solid).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.24 (d, *J* = 6.3 Hz, 3H), 1.38 (d, *J* = 6.3 Hz, 3H), 2.42 (s, 3H), 3.57 (s, 3H), 4.15–4.22 (m, 1H), 4.25–4.32 (m, 1H), 6.65 (dd, *J* = 11.8, 7.8 Hz, 2H), 7.09–7.15 (m, 2H), 7.23–7.28 (m, 1H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 7.4 Hz, 1H). ^{13}C NMR (98 MHz, $CDCl_3$, δ): 16.7 (*C*H_3), 18.7 (*C*H_3), 22.4 (*C*H_3), 55.5 (*C*H_3), 74.3 (*C*H), 84.7 (*C*H), 106.8 (*C*H), 115.8 (*C*H), 124.5 (*C*H), 129.6 (*C*H), 129.7 (*C*H), 132.2 (*C*H), 135.4 (*C*H), 143.0 (*C*), 158.1 (*C*), 163.4 (*C*). A carbon directly attached to a boron atom was not detected, likely due to quadropolar relaxation. ^{11}B NMR (126 MHz, $CDCl_3$, δ): 46.2 (br, s). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{18}H_{21}{}^{11}BO_3$, 296.1582; found, 296.1584.

4.4.5. Optimization of Reaction Conditions

The optimizations of boron sources (Figure S3) and bases (Scheme S2) were performed as general experimental procedure.

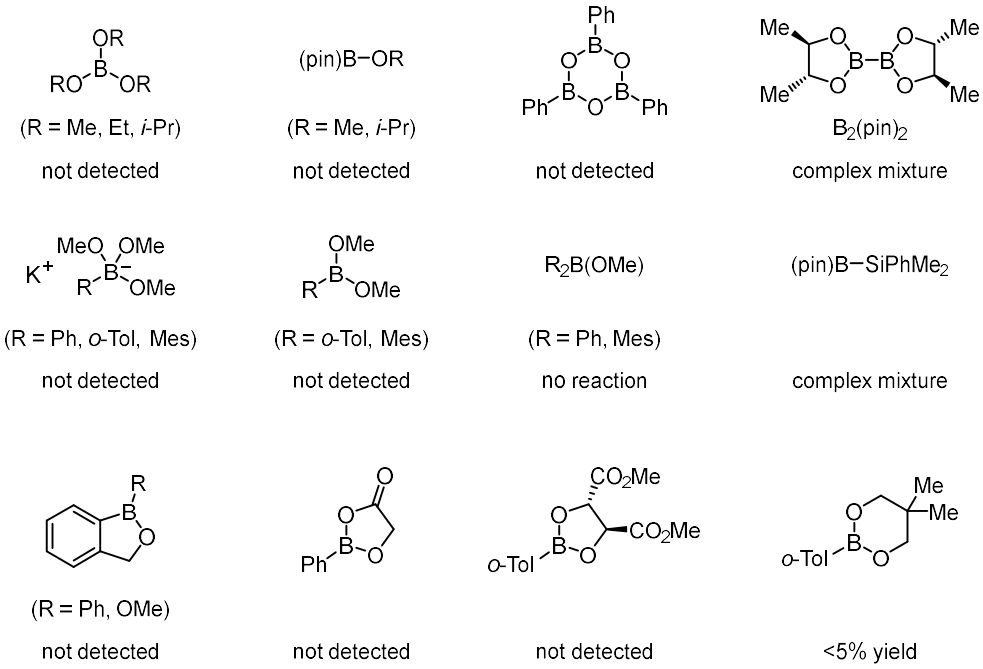
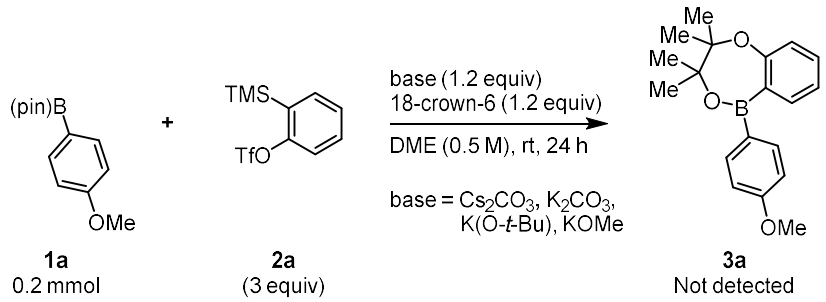
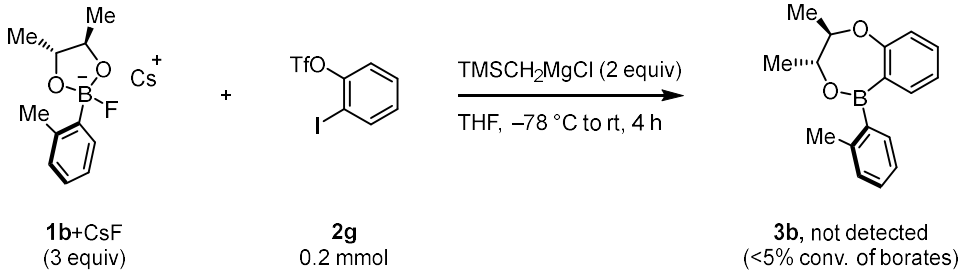


Figure S3. Optimization of boron sources

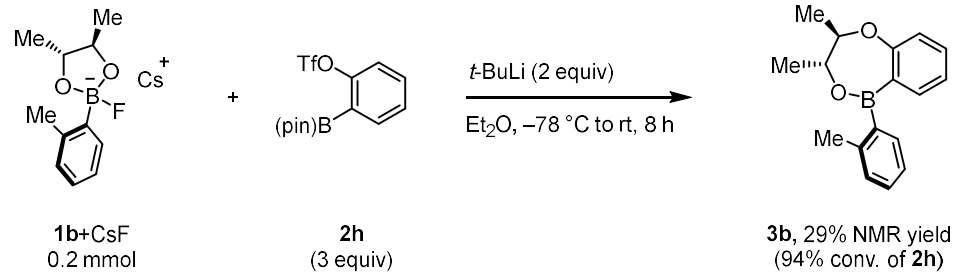


Scheme S2. Optimization of bases



Scheme S3. Oxyboration of aryne precursor **2g**

This reaction was conducted according to the literature procedure.[19] Arylboronate **1b** (114.0 mg, 0.60 mmol, 3.0 equiv) was placed in an oven-dried reaction vial. In an argon-filled grove-box, CsF (91.0 mg, 0.60 mmol, 3.0 equiv) was placed in the same vial. After the vial was sealed with a screw cap containing a Teflon™-coated rubber septum, dry THF (1.2 mL) was added to the vial through the rubber septum using a syringe. After the mixture was stirred at rt for 1 h, the solvent was evaporated under reduced pressure. Then, dry THF (1.0 mL) and 2-iodophenyl trifluoromethanesulfonate **2g** (70.6 mg, 0.20 mmol, 1.0 equiv) were added at -78 °C. After 15 min, $TMSCH_2MgCl$ (1.0 M in THF, 0.4 mmol, 0.4 mL, 2.0 equiv) was added dropwise. The reaction mixture was gradually warmed to rt for 4 h. Then, it was passed through a short silica-gel column (*Φ*: 15 mm, height of the silica-gel column: 30 mm) eluting with Et_2O. The crude mixture was analyzed by GC and ^1H NMR measurements. As a result, the desired product **3b** was not detected.



1b+CsF
0.2 mmol

2h
(3 equiv)

3b, 29% NMR yield
(94% conv. of **2h**)

Scheme S4. Oxyboration of aryne precursor **2h**

This reaction was conducted according to the literature procedure.[20] Arylboronate **1b** (38.1 mg, 0.20 mmol, 1.0 equiv) was placed in an oven-dried reaction vial. In an argon-filled grove-box, CsF (30.4 mg, 0.20 mmol, 1.0 equiv) was placed in the same vial. After the vial was sealed with a screw cap containing a Teflon™-coated rubber septum, dry THF (0.4 mL) was added to the vial through the rubber septum using a syringe. After the mixture was stirred at rt for 1 h, the solvent was evaporated under a reduced pressure. Then, dry Et_2O (2.0 mL) and 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl trifluoromethanesulfonate **2h** (211.5 mg, 0.60 mmol, 3.0 equiv) were added at -78 °C. After 15 min at -78 °C, *t*-BuLi (1.6 M in *n*-pentane, 0.6 mmol, 0.375 mL, 3.0 equiv) was added dropwise. The reaction mixture was gradually warmed to rt for 8 h. Then, it was passed through a short silica-gel column (*Φ*: 15 mm, height of the silica-gel column: 30 mm) eluting with Et_2O. The desired product **3b** was afforded in 29% yield by ^1H NMR analysis.

4.4.6. Unsuccessful Compounds

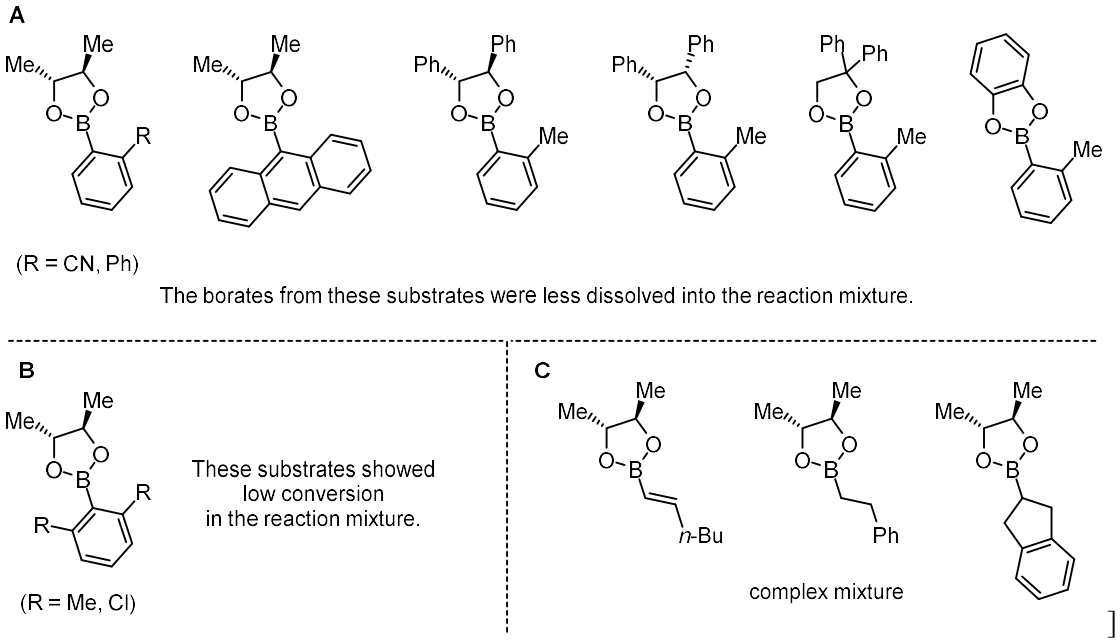


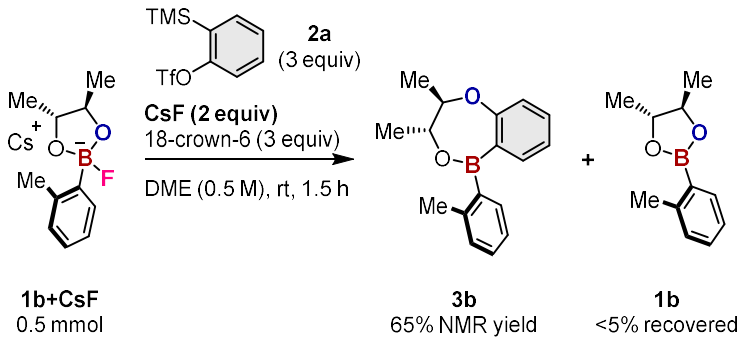
Figure S4. Unsuccessful compounds

A. Fluorinated borate species from these arylboronates were little soluble in the reaction solution. As a results, the desired products were not given.

B. The conversion of these arylboronates were poor due to the hindered boron–oxygen bond.

C. These alkenyl- and alkylboronates afforded a complex mixture. Moreover, the products were decomposed in the way of silica-gel column chromatography.

4.4.7. Control Experiments



Scheme S5. The reaction of arylborate **1b**+CsF with 2 equivalent of CsF

In an oven-dried reaction vial, arylboronate **1b** (0.500 mmol) was placed. Under an argon atmosphere, CsF (0.500 mmol) was placed in the same vial. After the vial was sealed with a screw cap containing a Teflon™-coated rubber septum, dry THF (1.00 mL) was added to the vial through the rubber septum using a syringe. After the mixture was stirred at ambient temperature for 30 min, the solvent was evaporated under reduced pressure. Then, CsF (1.00 mmol) and 18-crown-6 (1.50 mmol) were added in an argon-filled grove-box. After the vial was sealed with a screw cap containing a Teflon™-coated rubber septum, dry 1,2-dimethoxyethane (1.00 mL) was added to the vial through the rubber septum using a syringe. Then, 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (1.50 mmol) were added to the mixture. The reaction mixture was stirred at ambient temperature for 90 min. The reaction mixture was passed through a short silica-gel column (*Φ*: 15 mm, height of the silica-gel column: 30 mm) with Et_2O eluent. The desired product **3b** was afforded in 65% yield by ^1H NMR analysis.

^{11}B NMR of 1b+CsF in THF-d_8 (Figure S5) revealed that CsF smoothly coordinated to arylboronate **1b**. In addition, in the THF solution, arylboronate **1b** (0.5 mmol) proceeded oxyboration reaction with aryne precursor **2a** to afford product **3b** in 80% NMR yield under the optimized conditions.

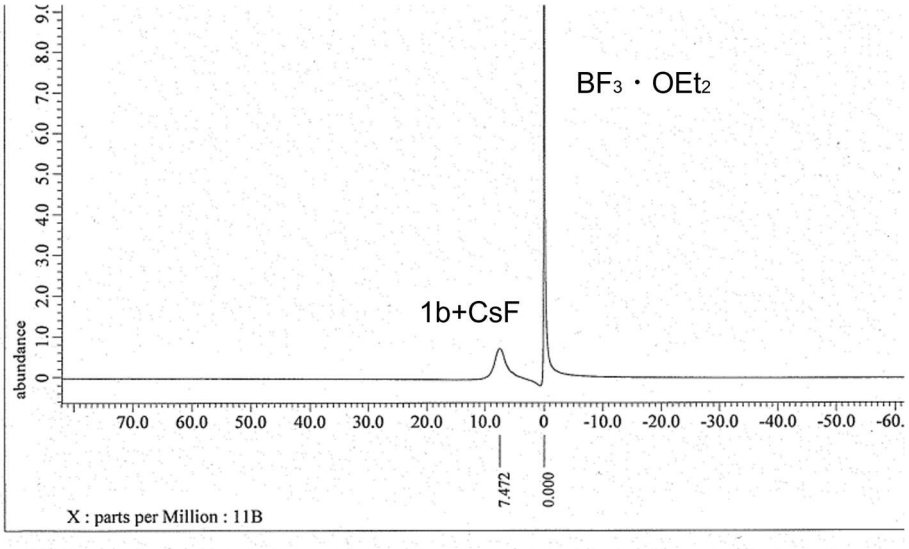


Figure S5. ^{11}B NMR of **1b** (0.5 mmol) in THF-d_8 (1.0 mL) at ambient temperature for 0.5 h

In Figure S6, arylboronates **1b** (0.500 mmol) were placed in an oven-dried reaction vial. Under an argon atmosphere, CsF (1.50 mmol) and 18-crown-6 (1.50 mmol) were placed in the same vial. After the vial was sealed with a screw cap containing a Teflon™-coated rubber septum, THF-d_8 (1.0 mL) was added to the vial through the rubber septum using a syringe.

After 0.5 h, ^{11}B NMR analysis was performed.

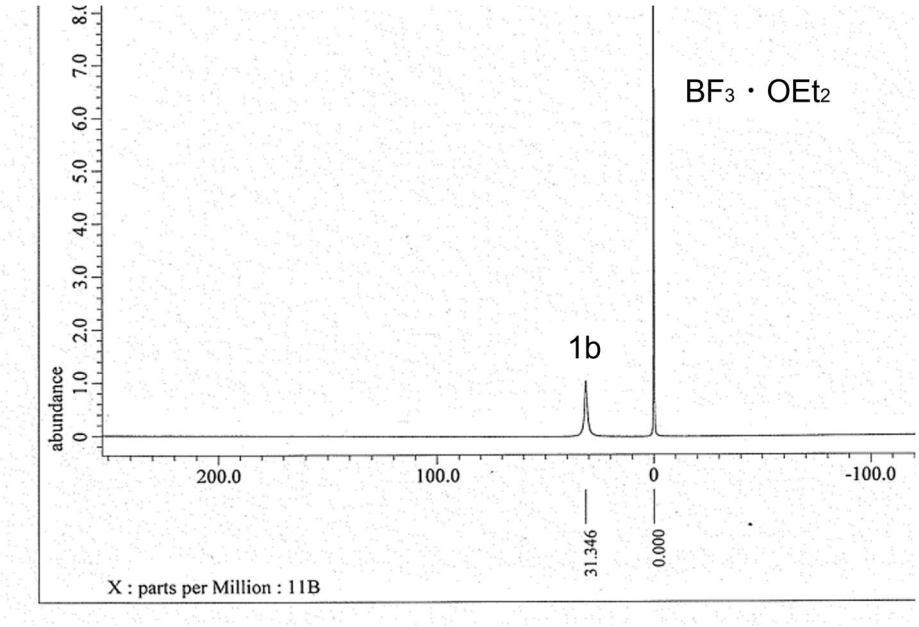
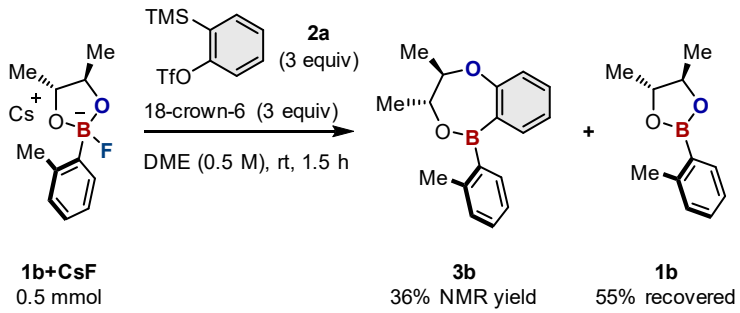


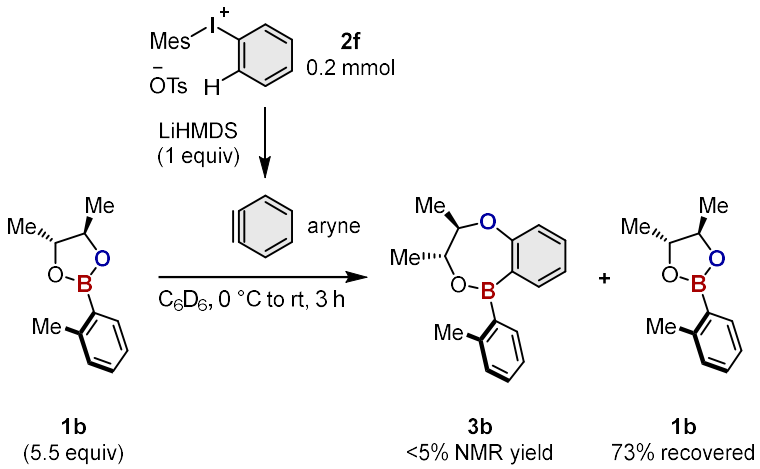
Figure S6. ^{11}B NMR of **1b** in THF-d_8



Scheme S6. Reaction of arylborate **1b**+CsF

In an oven-dried reaction vial, arylboronate **1b** (0.50 mmol) was placed. Under an argon atmosphere, CsF (0.50 mmol) was placed in the same vial. After the vial was sealed with a screw cap containing a Teflon^{TM}-coated rubber septum, dry THF (1.00 mL) was added to the vial through the rubber septum using a syringe. After the mixture was stirred at ambient temperature for 30 min, the solvent was evaporated under reduced pressure. In an argon-filled grove-box, 18-crown-6 (1.50 mmol) were added. After the vial was sealed with a screw cap containing a Teflon^{TM}-coated rubber septum, dry 1,2-dimethoxyethane (1.0 mL) was added to the vial through the rubber septum using a syringe. Finally, 2-(trimethylsilyl)phenyl

trifluoromethanesulfonate **2a** (1.5 mmol) was added to the mixture. The reaction mixture was stirred at ambient temperature for 1.5 h. The reaction mixture was passed through a short silica-gel column (*Φ*: 15 mm, height of the silica-gel column: 30 mm) with Et_2O eluent. The desired product **3b** was afforded in 36% yield by ^1H NMR analysis.



Scheme S7. Reaction of arylboronate **1b** with arynes generated from iodonium salt **2f**

This reaction was conducted according to the literature procedure.[32] In an oven-dried reaction vial, arylboronate **1b** (1.1 mmol) and iodonium salt **2e** (0.20 mmol) were placed. Then, dry benzene-d_6 (2.8 mL) was added to the vial through the rubber septum using a syringe under an argon atmosphere. After the mixture was stirred in an ice bath for 5 min, LiHMDS (0.2 mmol) in benzene-d_6 (0.2 mL) were added to the mixture dropwise. The reaction mixture was gradually warmed to ambient temperature for 3 h. Then, the reaction mixture was passed through a short silica-gel column (*Φ*: 15 mm, height of the silica-gel column: 30 mm) with Et_2O eluent. As a result, the desired product **3b** was not afforded.^{11}B NMR of **1b**+LiHMDS in C_6D_6 (Figure S7) revealed that LiHMDS did not coordinate to arylboronate **1b**.

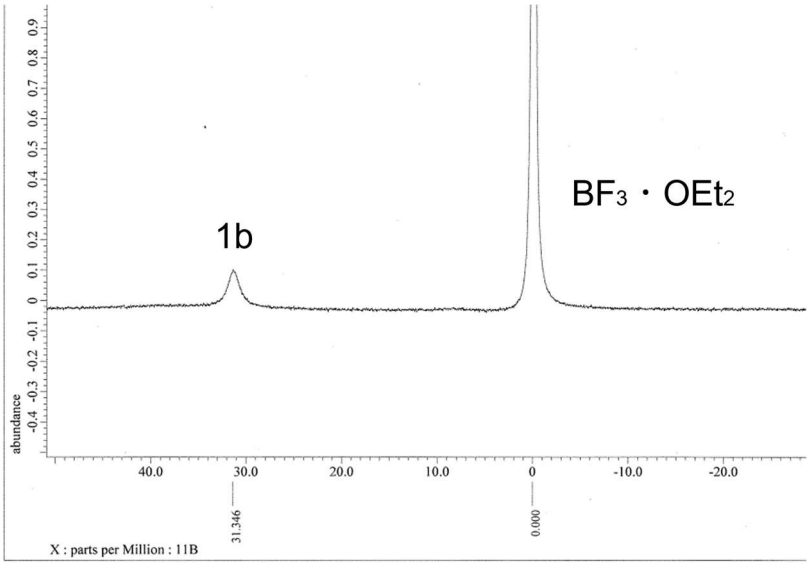


Figure S7. ^{11}B NMR of **1b** (0.2 mmol) + LiHMDS (0.2 mmol) in benzene-d_6 (3.0 mL) at ambient temperature for 2 h

In Figure S8, in an oven-dried reaction vial, arylboronates **1b** (0.20 mmol) were placed. LiHMDS (0.2 mmol) was placed in the same vial under an argon atmosphere. After the vial was sealed with a screw cap containing a Teflon™-coated rubber septum, C_6D_6 (3.0 mL) was added to the vial through the rubber septum using a syringe. After 2 h, ^{11}B NMR analysis was conducted.

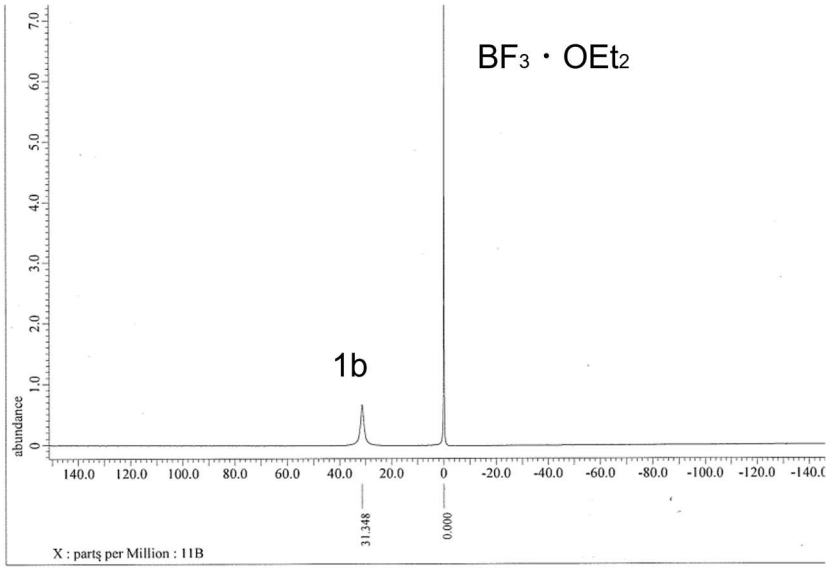
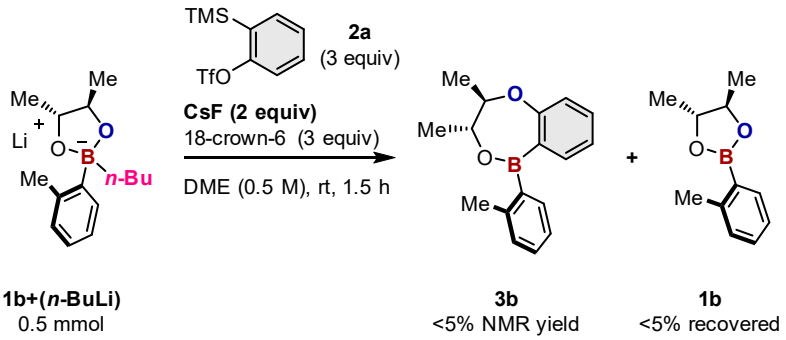


Figure S6. ^{11}B NMR of **1b** in benzene-d_6



Scheme S8. Reaction of arylborate **1b**+(*n*-BuLi) with 2 equiv of CsF

In an oven-dried reaction vial, arylboronate **1b** (0.50 mmol) was placed under argon atmosphere. After the vial was sealed with a screw cap containing a Teflon™-coated rubber septum, THF (1.0 mL) and *n*-BuLi (1.6 M in *n*-hexane, 0.5 mmol) was added at 0 °C through the rubber septum using a syringe. After the mixture was stirred at ambient temperature for 1 h, the solvent was evaporated under reduced pressure. Then, under an argon atmosphere, CsF (1.0 mmol) and 18-crown-6 (1.50 mmol) were added. After the vial was sealed with a screw cap containing a Teflon™-coated rubber septum, dry 1,2-dimethoxyethane (1.0 mL) was added in the vial through the rubber septum using a syringe. Finally, 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (447.6 mg, 1.5 mmol, 3 equiv) was added to the mixture. The reaction mixture was stirred at ambient temperature for 1.5 h. The reaction mixture was passed through a short silica-gel column (*Φ*: 15 mm, height of the silica-gel column: 30 mm) eluting with Et_2O. The desired product **3b** was not detected by ^1H NMR analysis.

4.4.7. Single Crystal X-ray analysis of 7d

The stereochemistry of **7d** was confirmed by X-ray crystallographic analysis. The detailed information was summarized in Figure S9 and Table S3.

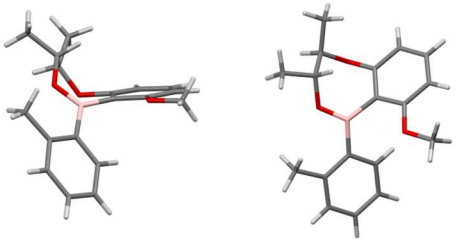


Figure S9. Solid-state structure of **7d**

Table S3. Summary of X-ray crystallographic information of **7d**

CCDC Number	2301195
Empirical Formula	$C_{18}H_{21}BO_3$
Formula Weight	296.16
Crystal System	monoclinic
Crystal Size / mm	0.1×0.1×0.1
a / Å	7.65950(10)
b / Å	11.42840(10)
c / Å	9.9394(2)
α / °	90
β / °	110.729
γ / °	90
V / Å^3	813.73(2)
Space Group	$P2_1$
Z value	2
D_{calc} / g cm^{-3}	1.209
Temperature / K	153
$2\theta_{max}$ / °	152.958
μ / cm^{-1}	0.635
No. of Reflections	Total: 10243
	Unique: 3262
	R_{int} = 0.0372
R_1[a]	0.0341
wR_2[b]	0.0871
GOF[c]	1.090
Max./Mini. peak *I*[d] / Å^3	0.15 e$^-$/−0.15 e$^-$
Flack parameter	0.11(10)

4.5. Computational Details

4.5.1. Computational Methods

All the calculations were performed at the DFT level of theory with the B3LYP hybrid functional[24] in Gaussian 16.[25] Considering the dispersion properly, an explicit dispersion correction term (D3) developed by Grimme and co-workers,[26] was also employed in the DFT calculations. The Def2-TZVP basis set[27] was used for all the atoms involved in this study during both the geometry optimization and the single-point calculation processes.

Considering the solvation environment in which the molecule stays, the implicit solvation model, IEF-PCM,[28] is applied to all the calculations involved in this study with diethyl ether (ε= 4.2400) used as the solvent. The AFIR method[29] was applied to explore all the pathways with accessible barriers. All the minima and transition states were fully optimized without any constraints. Frequency calculations were carried out to characterize all the optimized structures as local minima or transition states. Transition states were identified by having one imaginary frequency. An intrinsic reaction coordinate (IRC) calculation[30] was performed for each transition state to ensure it connected the correct reactants and products. The free energies were computed at 298.15 K and 1 atm.

4.5.1. Calculated Properties of All Structures

(**E**: Electronic Energy; **G**: Gibbs Free Energy at 298.15 Kelvin and under 1 atm)

Aryne

(**E** = -231.00486485 a.u.; **G** = -230.95660150 a.u.)

0 1

C	1.036831254924	0.004303738863	-3.733567676013
C	-0.098070086571	-0.343854713462	-2.976350136397
C	2.086294257870	0.326320265003	-2.896139446711
H	-1.004540102620	-0.622001026571	-3.501274075637
C	-0.098070061292	-0.343854705582	-1.573991117240
C	2.086294111609	0.326320220165	-1.654201894839
H	-1.004540080945	-0.622001019720	-1.049067206222
C	1.036831292511	0.004303750672	-0.816773575898
H	1.037906550748	0.004591155911	0.263760685169
H	1.037906590768	0.004591167721	-4.814101973213

Borate

(**E** = -664.58776554 a.u.; **G** = -664.41157076 a.u.)

-1 1

B	0.239386945041	0.837550345563	-4.504421347903
O	1.612715762807	0.868271321861	-5.054227209512
O	-0.425089926860	2.029649064927	-5.081380816149
C	0.341069985433	2.452504627371	-6.190142240299
H	0.435872243575	4.511790927692	-5.570769680960
C	0.147617088626	3.934576452327	-6.452308622528

H	-0.899164324539	4.150539790906	-6.674755145344
H	0.752691273800	4.265451364711	-7.300901491664
C	1.775295781734	2.043975017992	-5.817801814888
C	2.698458711768	1.811381849041	-7.000750146913
H	3.685346008933	1.492042062186	-6.659657692677
H	2.292090956725	1.031476095280	-7.649053886648
H	2.820819871128	2.726206196220	-7.587344922398
H	2.202689195030	2.843319007163	-5.184264831030
H	0.047788801616	1.886521376953	-7.092878071719
C	0.186084924852	0.874662553472	-2.879325667232
C	-0.959558390620	0.490834138968	-2.170481812608
C	1.265994106769	1.343289975557	-2.122157584207
C	-1.032249078602	0.575240879470	-0.782047427592
C	1.211869935537	1.430619184782	-0.732434563428
C	0.057185300501	1.048470110440	-0.054552670536
H	-1.812590881606	0.111766290533	-2.722741994522
H	2.172506775275	1.636004712526	-2.641447731105
H	-1.936024892054	0.270912465622	-0.264906079629
H	2.068906654098	1.795140453212	-0.175980703893
H	0.007754992974	1.114657314513	1.026303048745
F	-0.422331259944	-0.369127038281	-4.963003068361

TS-1A

(**E** = -895.57697874 a.u.; **G** = -895.33250624 a.u.)

-1 1

C	-1.787896049170	-2.183683867783	0.854051110685
C	-1.945890294082	-3.572963943966	0.863797496967
C	-0.498839919664	-1.755939365280	0.594661915407
H	-2.928746952262	-3.992914393683	1.045694411224
C	-0.854486024761	-4.416107402244	0.640101024429
C	0.550820364260	-2.490300729244	0.396628246653
H	-0.997558083657	-5.492424993189	0.652752836818
C	0.417719513835	-3.880827667307	0.407027565866
H	1.256412810871	-4.554295117954	0.248045596957
H	-2.624816480176	-1.521110163667	1.028915033034
B	-0.280926311655	0.393044797586	-1.129908711397

O	0.925359397453	-0.173218501665	-1.698196546207
O	-0.218496209139	1.840067476708	-1.409030488192
C	0.901587791169	2.088122212278	-2.238089720004
H	1.835521854264	3.473863579381	-0.881014454034
C	1.521905611639	3.437859266596	-1.926692248462
H	0.800767182406	4.239836168763	-2.095735482193
H	2.393241038777	3.622653814348	-2.561020333456
C	1.820801056255	0.884131378419	-1.979077337746
C	2.743184577268	0.521182632906	-3.125927870767
H	3.334144728214	-0.360901318204	-2.874567205361
H	2.159542342567	0.300077585335	-4.022212218240
H	3.429491243131	1.342650728956	-3.347835201818
H	2.428192887568	1.102802810945	-1.083471325711
H	0.594359484946	2.068339876491	-3.298289911514
C	-0.390784817128	0.269616452573	0.584266568210
C	-1.581891237667	0.851134046355	1.090190352887
C	0.768552019892	0.478508728230	1.369200496331
C	-1.613071136130	1.572200221447	2.272997781194
C	0.756908987121	1.211549850558	2.539882072426
C	-0.441923528790	1.759331601765	3.004968750212
H	-2.488859577936	0.752558577240	0.505673745242
H	1.682068280727	-0.006363435923	1.043785825853
H	-2.543558200052	2.004300772418	2.623312215360
H	1.668865591926	1.344054875022	3.110596867243
H	-0.462053277624	2.317859532843	3.933147024651
F	-1.452583677393	-0.189773493054	-1.679643099548

Int-1

(**E** = -895.62581496 a.u.; **G** = -895.37770499 a.u.)

-1 1

C	-0.938324096854	-1.894250233504	-0.387970413913
C	-1.011046158408	-3.111427363412	0.281460351767
C	0.319747984721	-1.329949871302	-0.555625560518
H	-1.971597355007	-3.585024289825	0.446827555254
C	0.167826638038	-3.703499856701	0.731553008611
C	1.536604608356	-1.833524654656	-0.159996598643

H	0.127278286423	-4.654883571040	1.254919232246
C	1.393604669495	-3.071158139961	0.503936136403
H	2.283349375622	-3.580404945288	0.877619468715
H	-1.829011786599	-1.397125754545	-0.753702078623
B	-0.541179648915	1.308162699477	-0.661525712435
O	0.258565913697	-0.031305630915	-1.247523389395
O	0.406179507985	2.307708849005	-1.045392438092
C	1.113679674118	1.901357646133	-2.205017515481
H	2.989986562614	2.692655610222	-1.512634986477
C	2.348308113989	2.760175320586	-2.393118241122
H	2.060440506273	3.802829272717	-2.534049311085
H	2.917488520127	2.439900147980	-3.268244132421
C	1.434120403218	0.421789834708	-1.982245096884
C	1.617551472924	-0.388944129660	-3.244563594236
H	1.832778435773	-1.427242510830	-2.997996913389
H	0.718720386202	-0.345820981662	-3.862520179054
H	2.456354388903	0.010751818743	-3.818673634313
H	2.286323418548	0.300505231364	-1.312285407440
H	0.464231198035	1.993980214074	-3.088571413932
C	-0.809539767215	1.208837217112	0.908022659981
C	-2.104306254587	1.113275955592	1.425515208849
C	0.250688492894	1.233451549389	1.820758180928
C	-2.338124406633	1.047129901020	2.796745544815
C	0.031504880211	1.163542434315	3.191872977877
C	-1.267850993951	1.071125278267	3.685097655838
H	-2.942177903044	1.088877756243	0.738702302116
H	1.265169722514	1.294876794014	1.445936650053
H	-3.352403211621	0.973422271157	3.172274295268
H	0.871259279876	1.175561746944	3.876955310296
H	-1.443189151532	1.014961097091	4.753050943452
F	-1.723346310251	1.313840191045	-1.426325068034

Int-2A

(**E** = -895.66929157 a.u.; **G** = -895.42113547 a.u.)

-1 1

C	-1.174504390742	-2.337155328126	0.824614297616

C	-1.005345359511	-3.623201243246	0.324652711045
C	-0.061174866069	-1.521136247081	1.091961260886
H	-1.866363200736	-4.251403423039	0.124055851737
C	0.286937065219	-4.088456788629	0.094022936012
C	1.277704031677	-1.954932163200	0.898384414463
H	0.438584682789	-5.088188601636	-0.306782580472
C	1.377636961215	-3.265498996175	0.388781949628
H	2.367796444532	-3.686065769481	0.200581156101
H	-2.181913117459	-1.980115452457	1.020977575428
B	-0.933663960750	1.658289867682	-2.024305250163
O	-0.540899803454	0.369119006333	-2.187734489485
O	0.059548635175	2.557432405612	-1.781218360194
C	1.309976549382	1.814787835712	-1.818846022232
H	1.634315747246	1.949902302328	0.300355884178
C	2.166245906364	2.169623250389	-0.625432370120
H	2.432960969158	3.227311628277	-0.644406193979
H	3.083633364414	1.577363856984	-0.637021778896
C	0.880635994806	0.324543142013	-1.869030577313
C	1.621548286607	-0.509717856172	-2.885911864385
H	1.253535524555	-1.535690700176	-2.867646722523
H	1.498088421261	-0.101475895733	-3.891698674441
H	2.685407518659	-0.528264206321	-2.641028957828
H	0.977166463909	-0.132431329245	-0.882888735617
H	1.813632832146	2.095086614358	-2.750079900658
C	-0.307875633911	-0.127814472548	1.557940381266
C	-1.381528340484	0.635795947346	1.076952632685
C	0.559650240357	0.486708650496	2.471811174327
C	-1.576731097444	1.952994740758	1.480626562221
C	0.361349794650	1.797680027759	2.886899831321
C	-0.706260070713	2.543439587529	2.390550114739
H	-2.052935493807	0.201969707355	0.346890333837
H	1.405161324957	-0.086086437590	2.830111336573
H	-2.400343173405	2.522993985898	1.066888152152
H	1.047335680670	2.244772914549	3.597530229219
H	-0.851986570490	3.570499038952	2.702500135296
F	-2.211223633243	2.032446982929	-2.126244487960

TS-2A

(**E** = -895.66266180 a.u.; **G** = -895.41396084 a.u.)

-1 1

C	-1.286837596731	-2.279487090673	1.334872763258
C	-1.045496958544	-3.479847986698	0.676709338564
C	-0.442924136311	-1.171185948902	1.137108825970
H	-1.693573835140	-4.334378082464	0.839349345318
C	0.045576294593	-3.564879229004	-0.185718455403
C	0.687386109991	-1.208717588693	0.278931359649
H	0.247351526123	-4.494296635055	-0.713739108648
C	0.870255507545	-2.451149884952	-0.359285802826
H	1.704474408574	-2.570645966288	-1.056206867121
H	-2.127697377285	-2.219706620476	2.021017268881
B	-0.530475508955	0.721331542040	-1.884287514514
O	0.044061756698	-0.122687455245	-2.790878931935
O	0.227402582546	1.797118860546	-1.524157629094
C	1.515734773377	1.630371487701	-2.161359616450
H	2.456283090155	0.989516942129	-0.370440155727
C	2.621588451317	1.749531628796	-1.136804625583
H	2.621119169138	2.740930785561	-0.680994703969
H	3.592955105206	1.587333041752	-1.612105014201
C	1.443330455496	0.231967699504	-2.836035116546
C	1.950798097820	0.199132712086	-4.260169738809
H	1.849127616800	-0.802261859649	-4.680444701574
H	1.391243892958	0.899331858216	-4.884404740004
H	3.007088541214	0.477148006372	-4.288178763311
H	1.970673465902	-0.494388926364	-2.213567579290
H	1.600282500572	2.412498254728	-2.924394979572
C	-0.764225711844	0.090595066795	1.863506128975
C	-2.082555994967	0.506011593745	2.098088039022
C	0.262477142663	0.919547288034	2.335576638514
C	-2.362747415548	1.689704854973	2.773637833927
C	-0.011175440552	2.098844090968	3.015815091496
C	-1.328343379693	2.493386594503	3.242261842715
H	-2.901870158873	-0.091332796740	1.717612130579

H	1.281641321424	0.617558613699	2.134867913010
H	-3.393469746521	1.990052068688	2.924660012787
H	0.806507007446	2.715388822560	3.372394603749
H	-1.544024045706	3.416027472608	3.767764749544
F	-1.803836027877	0.596437095193	-1.511746438387

Int-3A

(**E** = -895.73371599 a.u.; **G** = -895.48197325 a.u.)

-1 1

C	-0.874221974835	-2.285403178090	1.716112839815
C	-0.516125498849	-3.496115921535	1.139103846513
C	-0.719529752766	-1.069024948861	1.032835833966
H	-0.639857245579	-4.420373191886	1.691567445314
C	0.007230290847	-3.501147283934	-0.148614280009
C	-0.194064902785	-1.056234581764	-0.279822032564
H	0.292467148517	-4.435138373931	-0.620338856959
C	0.156793585369	-2.297320012237	-0.828482589036
H	0.545507796393	-2.306365262729	-1.839995909411
H	-1.264809115258	-2.275825148116	2.727426770444
B	0.029154799248	0.268104403756	-1.223557045173
O	0.171206519831	-0.075390727829	-2.658395489571
O	1.296223316562	0.961408910671	-0.884608272411
C	1.908383099261	1.363406093812	-2.092526890453
H	3.834132183505	0.534719221306	-1.600665197173
C	3.411320708567	1.488353775048	-1.925754032405
H	3.652895332907	2.243611010825	-1.175332935759
H	3.886723770361	1.778924172117	-2.866604931208
C	1.456870469159	0.295359246883	-3.100785802825
C	1.428069500684	0.756281139082	-4.547306769587
H	1.068808772192	-0.044427000835	-5.196755488777
H	0.756411029747	1.610837142730	-4.654873570207
H	2.425794400079	1.048880655731	-4.886154650980
H	2.145122398797	-0.566374444855	-3.014358855887
H	1.499614163242	2.337055376825	-2.416897231135
C	-1.123426371420	0.166067579452	1.760985019283
C	-2.358117689204	0.227776495165	2.417877206747

C	-0.274208219613	1.273450383444	1.855017085495
C	-2.735564977271	1.354232865543	3.140866936403
C	-0.647309095106	2.398122208821	2.580239615480
C	-1.878351717819	2.446031974769	3.228669727187
H	-3.038991241139	-0.611356925982	2.342652644042
H	0.671133768798	1.256106739456	1.331350876383
H	-3.702485052136	1.380582758951	3.629393654182
H	0.027176514310	3.244430699650	2.636543287501
H	-2.168209125858	3.325919347494	3.790239234891
F	-1.099822519355	1.155789659799	-1.093073041705

TS-1B

(**E** = -895.61937384 a.u.; **G** = -895.37023794 a.u.)

-1 1

C	-0.857766850428	-2.611826081439	-1.503492817411
C	-1.211561029013	-3.513539317946	-0.504227873529
C	0.149777806320	-1.675936578166	-1.248973651538
H	-1.995119484250	-4.242414423254	-0.682687618729
C	-0.547629202423	-3.463862572723	0.719562315280
C	0.864176054537	-1.571242823392	-0.058327337583
H	-0.816002149070	-4.155487079954	1.514073532785
C	0.461820970213	-2.511441371491	0.907439275470
H	0.948992568755	-2.505772255346	1.885321213850
H	-1.362868743866	-2.621788157393	-2.465475465132
B	-0.461554118062	1.289408126533	-0.135493847483
O	0.353083949267	-0.800404442947	-2.335372659939
O	0.677868985870	1.693482129264	-0.732226318751
C	0.992535751704	1.510957686058	-2.125138799245
H	2.950371121747	2.404590764332	-1.936049689591
C	2.014146677475	2.582394871951	-2.469512505892
H	1.631576484899	3.559982845696	-2.173305765694
H	2.218934336406	2.603771284498	-3.539565949961
C	1.479934484015	0.071939647739	-2.344530814226
C	2.191577718479	-0.131432582334	-3.676368400679
H	2.423467111612	-1.190558514148	-3.794041435975
H	1.555402075045	0.171866652817	-4.512650593201

H	3.125259299977	0.430407045885	-3.728189317255
H	2.129570141284	-0.192823924204	-1.505094767086
H	0.084442355112	1.653271918951	-2.720351647575
C	-0.614653531054	1.355072881048	1.416653712108
C	-1.853386553206	1.121316024128	2.024544158642
C	0.480397330233	1.642210347788	2.241116820573
C	-1.997747192484	1.170458963487	3.407418108681
C	0.343985140210	1.695143690545	3.622045704975
C	-0.897957744798	1.459158837482	4.208853468558
H	-2.709762794420	0.885600240808	1.404436188674
H	1.448359623064	1.807052436732	1.786068891961
H	-2.963317423742	0.978757369151	3.859924895993
H	1.203812396076	1.911723311148	4.244701957816
H	-1.005011457226	1.494218880600	5.286510899415
F	-1.550116886253	0.978296764092	-0.874867847300

Int-2B

(**E** = -895.68666032 a.u.; **G** = -895.43494045 a.u.)

-1 1

C	0.065279901893	-2.996975197785	-1.582603217621
C	-0.278067121527	-3.826009111733	-0.521092617293
C	0.053595257169	-1.610915980160	-1.424547986938
H	-0.268119800168	-4.902473926858	-0.646794772207
C	-0.622094645340	-3.255210777644	0.698674260481
C	-0.303067831639	-0.993829567181	-0.216272412950
H	-0.889495533890	-3.883403255198	1.540846439992
C	-0.627832416230	-1.867769682370	0.830542514426
H	-0.907051833406	-1.441098355105	1.786882083300
H	0.343311765334	-3.407222822660	-2.546235795994
B	-0.413640263360	0.646508051145	-0.051102366106
O	0.358915821491	-0.889108619466	-2.562459852885
O	0.752467151370	1.362794520237	-0.596199062910
C	0.989761629168	1.410995165856	-1.979297443737
H	2.981370161082	2.242206532213	-1.784314625388
C	2.016141130619	2.515981464978	-2.219355337328
H	1.671792906993	3.426001322615	-1.726931831502

H	2.157471368990	2.729196830485	-3.279690130731
C	1.451890746639	0.048820296046	-2.519886745238
C	1.992883193061	0.089357784162	-3.941222949085
H	2.190708709763	-0.926078303360	-4.286520979468
H	1.261887592096	0.542884538519	-4.614866359627
H	2.918789885349	0.660774171382	-3.998371297132
H	2.216367351942	-0.338727402700	-1.835599197566
H	0.063746981836	1.659390097984	-2.518519884895
C	-0.542065064428	1.078859983845	1.512932882663
C	-1.780426211365	1.340709065001	2.108915878125
C	0.585525839835	1.170360330298	2.338644983061
C	-1.894833865976	1.677630106235	3.457076499903
C	0.489654415175	1.505402279961	3.686279865878
C	-0.757028336233	1.760446979723	4.254305899225
H	-2.674204059767	1.280836150904	1.497598546186
H	1.560830067165	0.976728505052	1.906109294502
H	-2.870938399747	1.876675829493	3.886645705493
H	1.384363777690	1.568445939589	4.296622576985
H	-0.839116265962	2.021770307241	5.303110146039
F	-1.619211295079	1.066393486533	-0.764247932706

Boronate

(**E** = -564.55228079 a.u.; **G** = -564.37462133 a.u.)

0 1

B	0.675293263641	1.802846976201	-4.116638236688
O	1.931132734612	1.888432553682	-4.663724980441
O	-0.318193105097	2.180569727223	-4.985160059216
C	0.287409778554	2.449350051928	-6.270803310258
H	-0.054793563105	4.571641571712	-6.188477558103
C	-0.255808632658	3.733129702208	-6.857769845577
H	-1.332395927402	3.659544501814	-7.013347823690
H	0.217488990609	3.935558884588	-7.821174753751
C	1.808131452771	2.469047227346	-5.982551106049
C	2.645221758564	1.702212189330	-6.982041598534
H	3.699771555401	1.737090031747	-6.707562558960
H	2.327565064762	0.658688169445	-7.022099870558

H	2.534631496430	2.138298897416	-7.977287061749
H	2.161314866280	3.503378484332	-5.913266045300
H	0.042741137152	1.605513477934	-6.924570095843
C	0.406615169753	1.326569791573	-2.664052539997
C	-0.900590892564	1.231248474130	-2.168414848406
C	1.464935998683	0.979927814944	-1.813480259751
C	-1.143995974215	0.805050957655	-0.868203170794
C	1.227301154446	0.552100566104	-0.512735355179
C	-0.078880848287	0.464689358159	-0.038640842697
H	-1.731161828935	1.494703262430	-2.812062908306
H	2.482263548365	1.047692252454	-2.179657802492
H	-2.160257781322	0.737212085895	-0.500054762365
H	2.056254881824	0.287280457409	0.131965393783
H	-0.266299073100	0.131857074090	0.974890776339

Int-4

(**E** = -795.54942243 a.u.; **G** = -795.30253430 a.u.)

0 1

C	-0.193767376991	-2.406830115152	-0.580659601326
C	0.115660178750	-3.645077368517	-0.024375626339
C	0.745981012655	-1.424019042498	-0.342999018007
H	-0.560855322627	-4.480714781117	-0.149877825006
C	1.307665584246	-3.787622583680	0.691369629062
C	1.921615648934	-1.426407198257	0.305792645366
H	1.551638419361	-4.751020895812	1.127087544880
C	2.181619284388	-2.709648920713	0.843838064712
H	3.096668429129	-2.882519646778	1.406811175582
H	-1.103713907037	-2.234586646038	-1.140844326442
B	0.031729688708	1.137601232843	-0.204925850363
O	0.310272690806	-0.033885262018	-0.991232211559
O	0.386614239755	2.236112207277	-0.906816100327
C	0.870647945609	1.887529513164	-2.225417373934
H	2.878803458316	2.553883559345	-1.845403976205
C	2.085240360301	2.715950383515	-2.575748894454
H	1.826753470542	3.774326108678	-2.589812161695
H	2.455157959795	2.439150402190	-3.564595390717

C	1.147503718875	0.382354383107	-2.156829938602
C	0.769777332505	-0.415347966998	-3.375145726897
H	0.968882096207	-1.474623828206	-3.220216544075
H	-0.284293458133	-0.278665249868	-3.619417422849
H	1.371311457071	-0.075519955647	-4.220121174888
H	2.170680153075	0.184558295451	-1.833325522688
H	0.054191668231	2.086861891579	-2.924730536158
C	-0.649582865444	1.190755313462	1.175699385101
C	-0.891881037176	2.463608395800	1.720680501459
C	-1.057699813079	0.068478510445	1.911505087499
C	-1.514738949144	2.610354114956	2.951932685084
C	-1.686433056139	0.214424213406	3.141201665961
C	-1.914628031352	1.483390681414	3.664292685047
H	-0.584515510141	3.343472796697	1.169803049186
H	-0.875344062441	-0.925082222139	1.530186665367
H	-1.688401437576	3.599336575441	3.356743888600
H	-1.992856991647	-0.663600069361	3.695411623337
H	-2.400319229154	1.594078407472	4.625890220677

Int-5

(**E** = -795.56632155 a.u.; **G** = -795.32617562 a.u.)

0 1

C	2.154965285998	1.918030003063	2.935214882313
C	1.824345388432	0.569153415850	2.704448464099
C	2.450095337433	2.548616592247	1.741837332080
H	1.562561157677	-0.051646899143	3.553194283813
C	1.812609949909	0.003649715173	1.421902969606
C	2.437435620395	2.043920550028	0.606988349702
H	1.533521026638	-1.036490023314	1.305526931102
C	2.130513526463	0.741877145606	0.266305656106
H	2.103059773724	0.310935808243	-0.723007749530
H	2.159597356428	2.354799752078	3.923524399188
B	-1.003150254398	-0.222342864028	-0.522689697627
O	-0.709641724550	0.775787930205	-1.416429120286
O	-1.713648750484	0.213870284855	0.564640737120
C	-1.971270161508	1.627740504960	0.400004801436

H	-0.547107345254	2.224111205614	1.895709403223
C	-1.600319312446	2.380164500014	1.659148425240
H	-2.203793354694	2.041303479985	2.501786953185
H	-1.772125472523	3.449966867187	1.520433900449
C	-1.142443048850	2.031727987650	-0.845989400920
C	-1.904724626694	2.845834898680	-1.867620346087
H	-1.272761705995	3.074079517474	-2.726338966542
H	-2.782805660228	2.297326643636	-2.213716694624
H	-2.235421586063	3.787763793155	-1.424478644022
H	-0.240274090733	2.566817718010	-0.534499923452
H	-3.040443755792	1.738609220226	0.193102439884
C	-0.545670942738	-1.693841632395	-0.710162845952
C	-0.869050989339	-2.673828923097	0.237363096307
C	0.235883586743	-2.068265964260	-1.810737128929
C	-0.426542104582	-3.983200288956	0.092584322142
C	0.681318918575	-3.376289382986	-1.961031378111
C	0.350611252765	-4.335533693008	-1.007808488823
H	-1.468485779679	-2.400496134379	1.097308293869
H	0.497968692249	-1.322813351124	-2.551959715130
H	-0.684126899508	-4.728920917198	0.834516122261
H	1.285977486684	-3.649382052408	-2.816994973399
H	0.697927660123	-5.355047657320	-1.121844728507

TS-3A

(**E** = -795.54777064 a.u.; **G** = -795.29849830 a.u.)

0 1

C	0.262951926591	-2.978738996969	1.663344812111
C	-1.020174447402	-3.429587849000	1.979020879327
C	0.506775431435	-1.937013974022	0.738357153268
H	-1.152609706640	-4.236847183320	2.691987082643
C	-2.146760055470	-2.851121035422	1.388307560926
C	-0.658867210626	-1.463879791318	0.241809273805
H	-3.142407122026	-3.196312300975	1.635959805152
C	-1.974628356281	-1.812903506440	0.477066993048
H	-2.811766679908	-1.317016334078	0.002335511237
H	1.100538711481	-3.462729255607	2.161457463184

B	0.503230127675	0.682522292982	-0.410241558151
O	-0.507790008779	-0.297825138143	-0.776264802567
O	1.327365568412	0.890631758016	-1.453195954117
C	1.077636936809	-0.033434103440	-2.538155829621
H	2.319367201642	-1.592490006966	-1.746337444133
C	2.230738353517	-1.005854628648	-2.661635483652
H	3.160330881857	-0.463612026111	-2.833793414286
H	2.060171814674	-1.680065050108	-3.503346970936
C	-0.274106545398	-0.701262654600	-2.198914618197
C	-1.448153876283	-0.242150845498	-3.024178331737
H	-2.372938519926	-0.692735942892	-2.665091496109
H	-1.543258833863	0.844256381055	-2.993940200330
H	-1.295449990839	-0.548253366778	-4.060652247716
H	-0.186035847373	-1.784228555081	-2.173606007151
H	0.974667958281	0.567990931520	-3.442211949846
C	0.469866814376	1.516358493171	0.880982379393
C	1.522902484673	2.406596081477	1.138168074457
C	-0.590425946283	1.455878144500	1.795804090452
C	1.521571904719	3.203302710121	2.275271264645
C	-0.598468796011	2.258100082405	2.928599677963
C	0.459172852453	3.130410834152	3.171652038430
H	2.349361815115	2.467628727452	0.441044034586
H	-1.408979358534	0.768706729023	1.627115783316
H	2.345402779690	3.879981585499	2.464012051612
H	-1.424233792629	2.199703686884	3.626334524653
H	0.456109900270	3.750634979812	4.059390072624

Int-6A

(**E** = -795.63798626 a.u.; **G** = -795.38545887 a.u.)

0 1

C	-0.031157453637	-1.783769243955	1.705414080935
C	-0.608170971453	-3.034598309686	1.898841107808
C	-0.264108255253	-1.044056800361	0.540540540025
H	-0.408167485042	-3.591382708370	2.805387845528
C	-1.451728889181	-3.562662133644	0.926336010066
C	-1.111846206969	-1.606575208175	-0.422519379792

H	-1.912949375177	-4.531275895471	1.073700815657
C	-1.709202862581	-2.846545411734	-0.238612674626
H	-2.371299453336	-3.232687628301	-1.002836700926
H	0.621108211209	-1.375309507659	2.467781009469
B	0.417177339156	0.335170231686	0.237470533689
O	-1.445652669483	-0.874163995622	-1.541096892898
O	0.884628112012	0.622532953951	-1.012257740636
C	0.934773749241	-0.304867166278	-2.105053819632
H	1.466096335256	-2.159946331388	-1.065882863299
C	1.861604867387	-1.483664489621	-1.820245635225
H	2.829552697995	-1.111460769563	-1.481814648622
H	2.016906438445	-2.049973098141	-2.740329493796
C	-0.482519530026	-0.696996539533	-2.594790039938
C	-1.081473028236	0.360226298085	-3.503986045771
H	-2.095984124988	0.081204865148	-3.788440231543
H	-1.114750588080	1.321770972387	-2.989193189447
H	-0.483257301271	0.466184930236	-4.409851576105
H	-0.388314938155	-1.645811361917	-3.137723288466
H	1.384274001776	0.265222163413	-2.920809867892
C	0.619992647830	1.451596676874	1.315807187142
C	1.546518242046	2.485818937230	1.106925104945
C	-0.118775555061	1.472716488280	2.507925580205
C	1.735940429078	3.488319662908	2.048865243630
C	0.057497160670	2.479011046407	3.451422125850
C	0.989275153817	3.486860911217	3.224963604882
H	2.123884980629	2.494941319043	0.190625881201
H	-0.851055557403	0.696979040686	2.694323050295
H	2.461228617220	4.272653235219	1.869564211368
H	-0.529949737846	2.478305260814	4.361374347612
H	1.132369657197	4.269561098544	3.959921780184

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5. Summary

Organoboron compounds have been widely used as versatile synthetic building blocks in organic synthesis. Over the decades, their applications to functional organic materials, such as luminescent materials, organocatalyst and pharmaceuticals, have also attracted the interest of researchers. In Chapter 1, the development of novel functionalized organoboron compounds and their stereoselective synthetic methods with copper(I)/diboron systems were featured.

In Chapter 2, I developed a new methodology for the regioselective alkylboration of terminal allenes. This approach achieved the precise synthesis of (*Z*)-alkenyl boronates whose substituents were very similar to each other. The mild reaction conditions showed the wide functional-group-tolerance, which was enough to achieve formal synthesis of complicated bioactive compound, schizol A, in good yield with excellent regioselectivity for the first time. The reaction mechanism of regio- and stereoselective borylcupration of terminal allenes was revealed using the DFT calculation and (*Z*)-alkenyl boronates were the easiest to be produced in terms of the Gibbs free energies.

In Chapter 3, the copper(I)-catalyzed silaboration was achieved to furnish allylic-boronate-alkenyl-silane products. Silylborane reagents and copper(I) catalyst explored the rare selectivity compared with that of previous silaboration reactions of allenes. The various silylboranes and terminal allenes were able to be applied to this silaboration reaction. Moreover, in terms of the DFT calculations, the regioselective silylcupration was the key step to furnish allylic-boronate-alkenyl-silane products.

In chapter 4, the first ring expansion of aryl boronates through insertion of arynes was developed. This reaction proceeded under mild basic condition at ambient temperature smoothly to afford various ring expanded products “diaryl borinic acid cyclic esters.” From the single crystal X-ray analysis, one of the obtained products showed good similarity between its boron-oxygen bond of the ring structure and carbon-carbon double bond of a cycloheptene ring in KGP-156. The DFT calculations and experimental mechanistic studies revealed that the *mono*-fluorinated borate species efficiently proceed the oxyboration of arynes to furnish the corresponding cyclic borinic acid esters.

Though this thesis, I developed new approaches to introduce the boryl group into allenes and arynes with copper(I) catalysts or without catalysts. The use of unique multiple bonds such as allenes and arynes showed the interesting reactivity and selectivity respectively. Based on these described reaction conditions, substrate scopes and reaction mechanisms in the borylation reaction of allenes and arynes, the unconventional discovery in borylation chemistry and the synthetic application of allenes and arynes would be created in the future.

6. List of publications

Chapter 2 : Copper(I)-Catalyzed Linear-Selective Alkylboration of Terminal Allenes for Synthesis of (*Z*)-Alkenyl Boronates

Ozawa, Y.;† Shiratori, Y.;† Koriyama, H.; Endo, K.; Iwamoto, H.; Ito, H. †*Co-first author.*

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Chapter 3 : Regio- and Stereoselective Silaboration of Terminal Allenes with Copper(I)-Catalyst

Ozawa, Y.; Koriyama, H.; Shiratori, Y.; Ito, H

ACS Org. Inorg. Au **2023**, *3*, 104–108.

Chapter 4 : Ring Expansion of Aryl Boronates *via* Oxyboration of Arynes

Shiratori, Y.; Jiang, J.; Kubota, K.; Maeda, S.; Ito, H.

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