Organocatalytic Diboration and Silaboration Based on Pyridine-Mediated Activation of Boron-Containing σ-Bond

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Contents

General Introduction

Boron, the fifth element which has vacant p-orbital with lower electron negativity than carbon, has gained much attention in organic chemistry to explore characteristic molecular functions in various research fields by incorporating boron in organic molecules. Boron-containing organic compounds have indeed been used as reagents for organic synthesis[1] and as functional molecules such as molecular catalysts,[2] fluorescent materials,[3] and pharmaceuticals (Figure 1).[4] As a variety of new molecular functions are explored and recognized widely, the development of efficient and precise synthetic protocols of boron-containing organic molecules are in high demand.

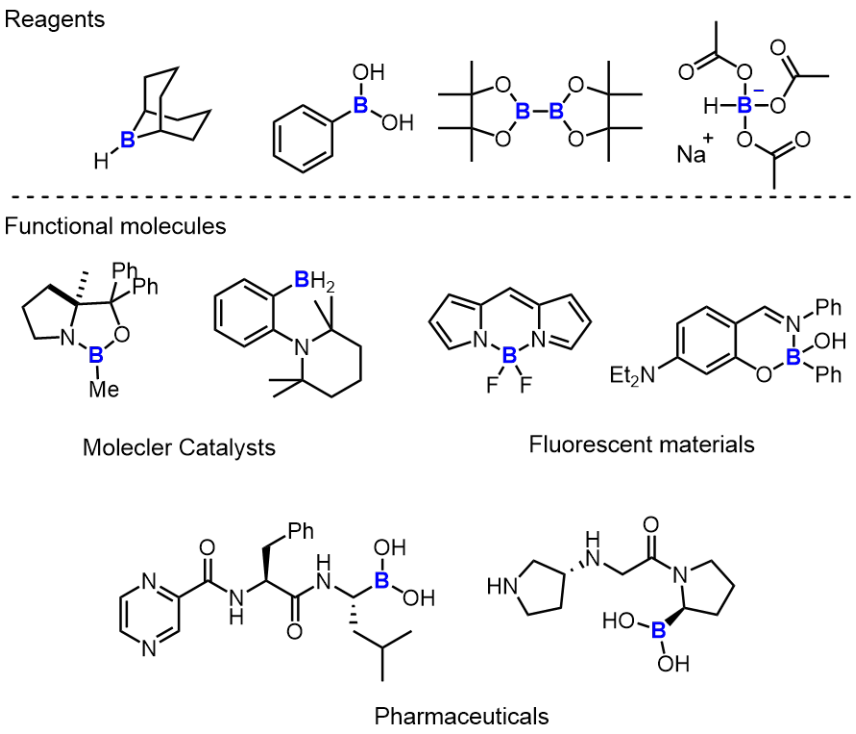
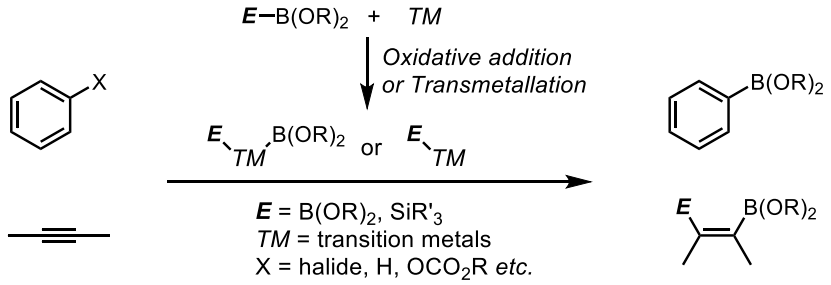


Figure 1. Examples of Boron-Containing Functional Molecules

Organoboron compounds have been synthesized conventionally through reactions of organometallic reagents with boron electrophiles or by thermal hydroboration of unsaturated molecules.[5] In addition to these, various synthetic methods based on transition metal-catalyzed activation of boron-containing σ-bonds have been developed in more recent years (Scheme 1).[6] In particular, transition metal-catalyzed addition of σ-bonds between boron and nonhydrogen element allows characteristic molecular transformations in which simultaneous introduction of boron and the nonhydrogen

element into organic molecules in a single step.[7] The most representative example is shown by the rapid development of a variety of diboration reactions of unsaturated organic molecules using tetraalkoxydiboron reagents. Remarkably, the diboron reagents not only enabled diborations, but also mild generation of reactive borylmetal species, which are of high utility in catalysis, under very mild reaction conditions. Furthermore, the chemistry of the diboron catalysis stimulated the development of further synthetic transformations using reagents containing boron-silicon, boron-tin, boron-halogen, and even boron-carbon bonds. It should be remarked here that establishment of a new mode of the activation of boron-containing σ-bonds have an enormously large impact on the development of new synthetic protocols for the synthesis of boron-containing organic molecules, leading ultimately to the development of new functional molecules.

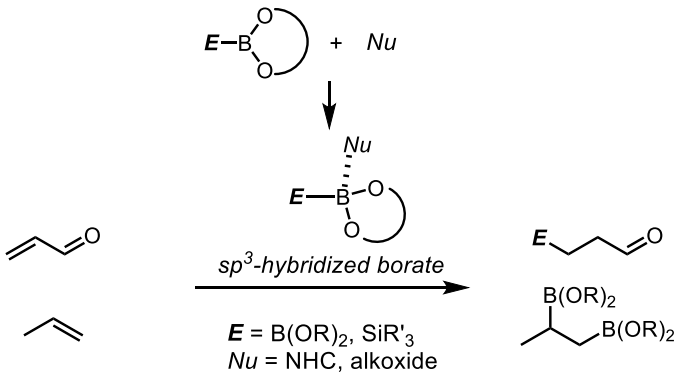


Scheme 1. Transition-metal-catalyzed borylation via boron–element σ-bond activation

Since around 2000, organocatalytic reactions have been revisited, gaining close attention especially in asymmetric organic synthesis to take advantage of using simple, nonmetallic chiral organic compounds as catalysts.[8] In material and drug synthesis, organocatalytic reactions are very attractive from the viewpoint of not only the cost of synthesis, but also the low content of metallic contaminants in the final products. It seems to be interesting to use organic compounds as a catalyst for activation of boron-containing σ-bonds, since new mode of activation may lead to the development of new synthetic protocols of boron-containing organic molecules as seen in the development of transition-metal catalyzed diboration and related borylation reactions. Establishment of novel reactions, which proceed with high chemo-, regio-, and stereo-selectivities, can be expected highly by the organocatalytic borylation reactions.

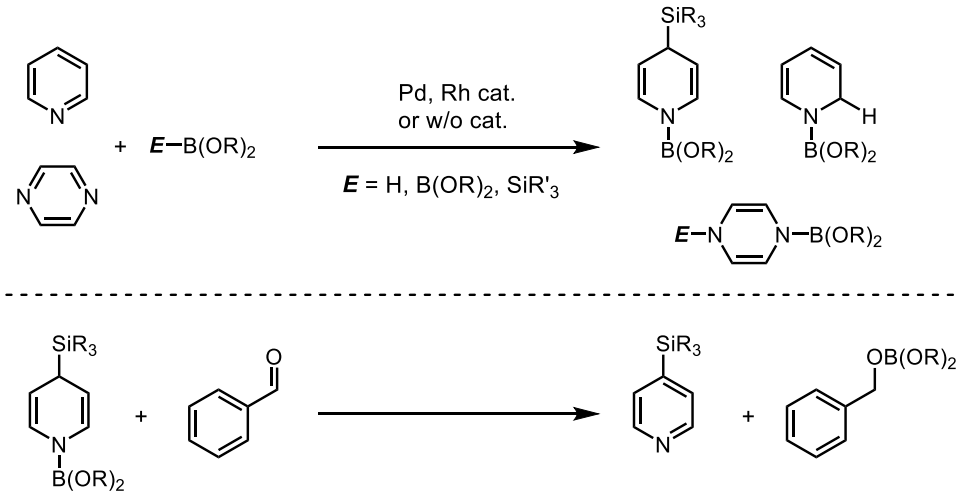
One of the important early findings on the organocatalytic activation of boron-boron and boron–silicon bonds is use of *N*-heterocyclic carbenes (NHCs) and alkaline metal alkoxides (Scheme 2). Hoveyda and coworkers have reported NHC-catalyzed conjugate borylation and silylation of α,β-unsaturated carbonyl compounds.[9] Fernández and coworkers have reported an alkoxide-catalyzed diboration of alkenes.[10] A key

mechanistic feature of these reactions is that NHC and alkoxide attack the boron center of $(RO)_2B–B(OR)_2$ and $R'_3Si–B(OR)_2$ to form tetracoordinated sp^3-hybridized borate intermediates, by which the boron–boron and boron–silicon bonds are polarized, making the remaining boryl and silyl groups more nucleophilic. This mode of activation of boron-boron and boron–silicon bonds has significantly contributed to the rapid progress of the research field of organocatalytic borylation and silylation.[11] As an important variant based on this concept, Sawamura and coworkers reported diboration and silaboration of acetylene carboxylates, where the reactions proceed through alkynyl- or allenyloxyborates generated from the reaction of substrates with organocatalysts.[12, 13]



Scheme 2. Organocatalytic borylation via sp^3-hybridized borate

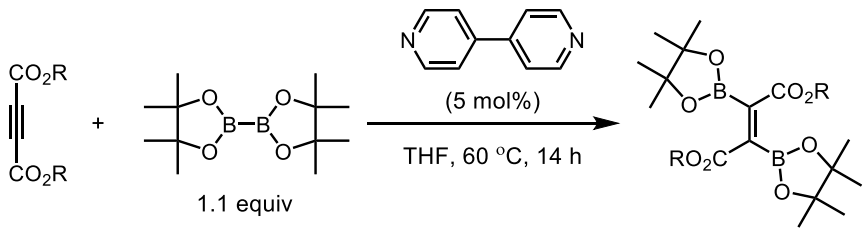
Based on the research background described above, the author focused on the use of nitrogen-containing aromatic compounds as new organocatalysts for effective activation of boron-containing nonpolar σ-bond. This idea stems from two previous findings. Firstly, boron-silicon bond is activated by pyridines and pyrazines in their stoichiometric reaction with silylborane to form N-borylated dihydropyridines[14] and dihydropyrazines (Scheme 3, top).[15] It is assumed that formation of thermodynamically stable boron-nitrogen bond is a driving force of these dearomatizing addition reactions. Secondly, the N-boryldihydropyridine undergoes boryl transfer to aldehydes to form pyridine and alkoxyborane (Scheme 3, bottom).[14a] The thermodynamic driving force of this process is presumed to be formation of aromatic ring along with the formation of the boron oxygen bond. The author envisioned that combining these two elementary processes, which contain dearomatization and rearomatization of nitrogen-containing aromatic ring, in a cascade manner may enable new catalytic processes, in which nitrogen-containing aromatic compounds serves as a catalyst to shuttle the boryl group.



Scheme 3. Previous findings about dearomatizing borylation and aromatizing boryl transfer

In this thesis, the author describes the activation of boron-containing σ-bonds by pyridines and their organocatalytic use in diboration and silylborination of unsaturated molecules. Outline of the thesis is given below.

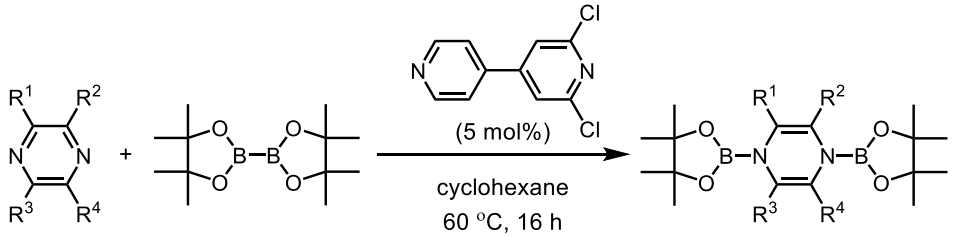
In chapter 1, the author describes an efficient *trans* addition of diborons to acetylenedicarboxylates in the presence of a catalytic amount of 4,4'-bipyridine. This reaction achieves stereoselective synthesis of (*E*)-2,3-diborylfumarates, which have never been obtained by conventional transition-metal-catalyzed reactions that follow selective *cis*-addition. Nonradical mechanism starting from nucleophilic attack of bipyridine to alkyne and following formation of allenyloxyborate is proposed.



Scheme 4. 4,4'-Bipyridine catalyzed diboration of acetylenedicarboxylates

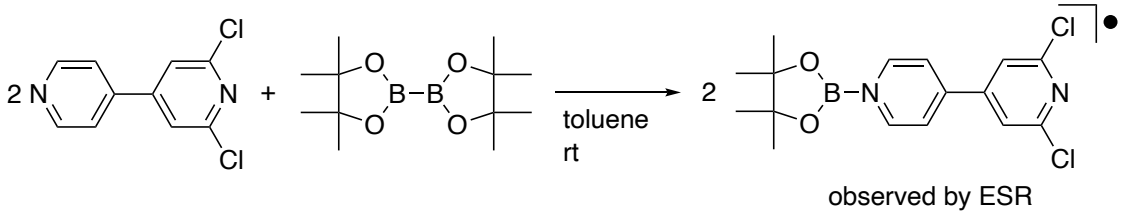
In chapter 2, the author describes diboration of substituted pyrazines which hardly undergoes the diboraion in the absence of a catalyst. Use of a catalytic amount of 2,6-dichloro-4,4'-bipyridine as a catalyst allowed efficient formation of *N*,*N*′-diboryl-1,4-dihydropyrazines. This catalytic reaction consists of two elementary reactions; (1)

transition-metal-free addition of diboron to 4,4'-bipyridine to form diborylbipyridinylidene with dearomatization of the two pyridine rings, and (2) boryl transfer from *N*,*N*′-diborylbipyridinylidene to pyrazine to afford *N*,*N*′-diboryldihydropyrazine with reforming of 4,4'-bipyridine. The two elementary steps can be regarded as "reductive addition" and "oxidative elimination", which are interestingly compared with "oxidative addition" and "reductive elimination" in the typical elementary steps for transition-metal-catalyzed addition reactions.



Scheme 5. 4,4'-Bipyridne catalyzed dearomatizing *N*,*N'*-diboration of pyrazines

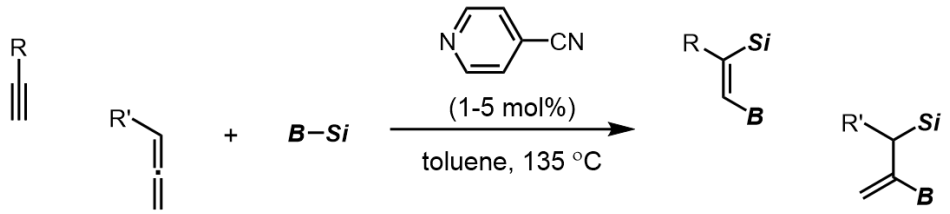
In chapter 3, the author describes a mechanistic study on the 4,4'-bipyridine catalyzed diboration of pyrazines presented in chapter 2. Intermediary radical species was detected by ESR measurement of the reaction of 2,6-dichloro-4,4'-bipyridine and bis(pinacolato)diboron. Based on this observation, radical processes involving 4,4'-bipyridine-stabilized boryl radical were evaluated by DFT calculation. The mechanism of the catalysis was assumed by the calculated activation barriers of the elementary processes and heat of formation of the products in each process. It was indicated that the major path involves the homolytic cleavage of the boron–boron bond, which is facilitated by coordination of 4,4'-bipyridine to boron atom. Thus generated 4,4'-bipyridine-stabilized boryl radicals shuttle boryl radicals to pyrazine to end up with the formation of *N*,*N'*-diboryl-4,4'-bipyridinylidene.



Scheme 6. The key elemental reaction forming 4,4'-bipyridine-stabilized boryl radical

In chapter 4, the author describes an organocatalytic regio- and stereoselective *cis*-addition of silylboronic esters to the carbon–carbon triple bond of propiolic acid esters. This reaction was effectively promoted by a catalytic amount of 4-cyanopyridine to form

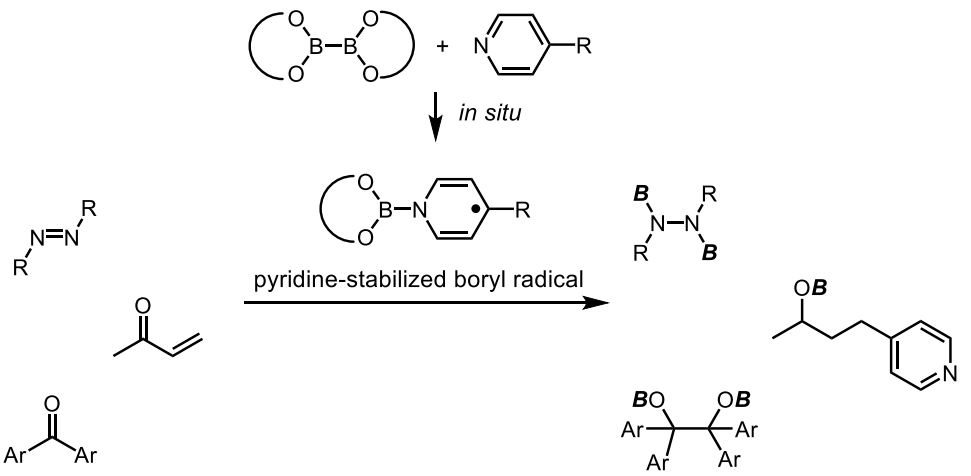
(*Z*)-3-boryl-2-silylacrylates. The same *cis*-1,2-addition fashion was also promoted by other pyridine catalysts such as 2,6-dichloro-4,4'-bipyridine and 4-(3,5-dichlorophenyl)pyridine. In contrast, selective 1,1-silaboration was induced by non-pyridine catalysts such as tertiary phosphines, alkoxides, and *N*-heterocyclic carbenes, indicating that the *cis*-1,2-silaboration is characteristic reaction mode for pyridine catalysts. Ethynylbenzene derivatives and terminal allenes also took part in the 4-cyanopyridine-catalyzed 1,2-silaboration.



Scheme 6. 4-Cyanopyridine catalyzed 1,2-silaboration of alkynes and allenes

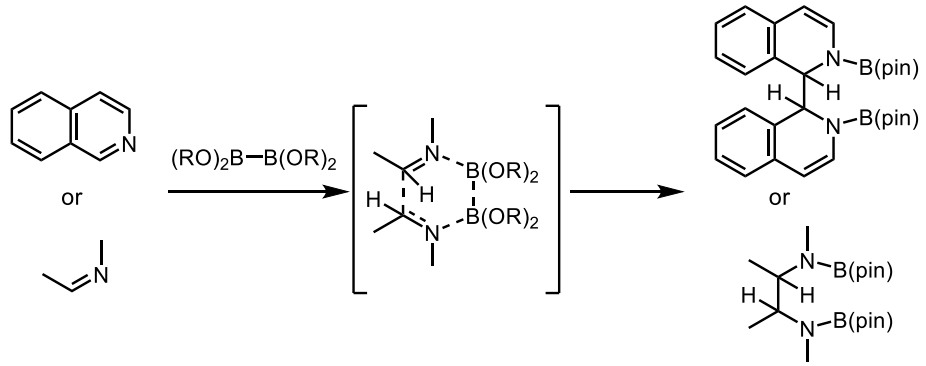
In summary, the author established efficient borylation reactions based on new organocatalytic activation of boron-containing σ-bond using various types of pyridines as catalysts. Thus, established transformations are attractive for cost-effective, metal-free synthesis of boron-containing organic compounds. It should be noted that much progress has been recorded on organocatalytic borylation following the author's study since 2012. Before ending this chapter, the author would like to introduce recent variants associated with boron–boron bond activation using pyridine derivatives as a catalyst or a substrate.

Several variants involving formation of pyridine-stabilized boryl radical through homolytic cleavage of boron–boron bonds have been reported after publication of the author's work presented in chapter 2. Li et. al. reported 4-cyanopyridine-catalyzed *N*,*N*'-diboration of azo compounds,[16] 4-pyridylation of ketones and enones,[17] and C-C bond formation of aldehydes and 1,1-diarylethylene.[18] Jiao et. al. reported 4-phenylpyridine-catalyzed borylation of aryl halide using KOMe as a co-catalyst.[19] Chung et. al reported isonicotinate-catalyzed pinacol coupling of diarylketone.[20] Cai et. al. reported 4-cyanopyridine-catalyzed hydroboration of stylene.[21] Mashima and co-workers reported 4,4'-bipyridine-catalyzed reduction of nitroarenes.[22]



Scheme 7. Pyridine-catalyzed borylation via pyridine-stabilized boryl radical

The other important variant is a [3.3] sigmatropic rearrangement of isoquinolines[23] or imines.[24] In this reaction, both boron–boron bond cleavage and carbon–carbon bond formation are suggested to take place simultaneously without formation of boryl radical species. By using chiral diboron reagent, chiral diamines were synthesized in a highly enantioselective manner.



Scheme 8. Sigmatropic rearrangement via cleavage of boron–boron σ-bond

It should be noted again that establishing new mode of bond activation opens up new possibility for a series of new synthetic transformations. In this thesis, the author demonstrates that pyridine derivatives have high potential to serve as catalysts for activation of boron-containing σ-bonds. The findings have indeed stimulated further development of new synthetic reactions for boron-containing molecules as shown by the recent reports on the new borylation reactions from other groups.

1) Coca, A. *Boron Reagent in Synthesis*; American Chemical Society, **2018**.
2) Corey, E. J.; Bakshi, R. K.; Shibata, S. *J. Am. Chem. Soc.* **1987**, *109*, 5551. For reviews: (a) Deloux, L., Srebnik, M. *Chem. Rev.*, **1993**, *93*, 763. (b) Dimitrijevic, E., Taylor, M. S. *ACS Catal.* **2013**, *3*, 945. (c) Taylor, M. S. *Acc Chem. Res.* **2015**, *48*, 295. (d)Rao, B., Kinjo, R. *Chem.: Asian J.* **2018**, *13*, 1279. (e) Ma, Y., Lou, S.-J., Hou, Z. *Chem. Soc. Rev.*, **2021**, *50*, 1945.
3) For reviews: (a) Loudet, A. Burgess, K. *Chem. Rev.* **2007**, *107*, 4891. (b) Liu, Z., Jiang, Z., Yan, M., Wang, X. *Front. Chem.*, **2019**, *7*, 712. (c) Li, D., Chen, Y., Liu, Z. *Chem. Soc. Rev.*, **2015**, *44*, 8097. (c) Thareja, S., Zhu, M., Ji, X., Wang, B. *Heterocycl. Commun.*, **2017**, *23*, 137.
4) For reviews: (a) Hey-Hawkins, E., Teixidor, C. V. *Boron-Based Compounds: Potential and Emerging Applications in Medicine*; John Wiley & Sons, **2018**. (b) Soriano-Ursúa, M. A., Das, B. C., Trujillo-Ferrara, J. G. *Expert Opin. Ther. Patents*, **2014**, *24*, 485.
5) (a) Brown, H. C., Cole, T. E. *Olganometallics* **1983**, *2*, 1316. (b) Das, K. K., Paul, S., Panda, S. *Org. Biomol. Chem.*, **2020**, *18*, 8939-8974.
6) Hall, D. G. *Boronic Acids: Preparation and Applications in Organic Synthesis, Medicine and Materials 2nd Edition*; Wiley VCH, **2011**.
7) Reviews on transition-metal-catalyzed addition of B–B and Si–Si bonds: (a) Beletskaya, I.; Moberg, C. *Chem. Rev.* **2006**, *106*, 2320. (b) Burks, H. E.; Morken, J. P. *Chem. Commun.* **2007**, 4717. (c) Suginome, M.; Ohmura, T. In *Boronic Acids second edition*, ed. D. Hall, Wiley-VCH, 2011, vol. 1, pp 171. (d) Takaya, J.; Iwasawa, N. *ACS Catal.* **2012**, *2*, 1993. (e) M. B. Ansell, J. Spencer, O. Navarro, *ACS Catal.* **2016**, *6*, 2192. (f) Wang, M., Shi, Z. *Chem. Rev.* **2020**, *120*, 7348.
8) For reviews: (a) List, B. *Chem. Rev.* **2007**, *107*, 5413. (b) Shaikh, I. R. *J. Catalysts* **2014**, 402860. (c) Stephan, D. W., Erker, G. *Angew. Chem. Int. Ed.* **2015**, *54*, 6400.
9) (a) Lee, K.-S., Zhugralin, A. R., Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 7253. (b) Lee, K.-S., Zhugralin, A. R., Hoveyda, A. H. *J. Am. Chem. Soc.* **2010**, *132*, 12766. (c) O'Brien, J. M., Hoveyda, A. H. *J. Am. Chem. Soc.* **2011**, *133*, 7712.
10) Miralles, N., Cid, J., Cuenca, A. B., Carbó, J., Fernández, E. *Chem. Commun.* **2015**, *51*, 1693.
11) For reviews: (a) Dewhurst, R. D., Neeve, E. C., Marder, T. B. *Chem. Commun.* **2015**, *51*, 9594. (b) Cuenca, A. B., Shishido, R., Ito, H., Fernández, E. *Chem. Soc. Rev.* **2017**, *46*, 415. (c) Wen, Y., Deng, C., Xie, J., Kang, X. *Molecules* **2019**, *24*, 101.
12) Nagao, K., Ohmiya, H., Sawamura, M. *Org. Lett.* **2015**, *17*, 1204.
13) Morinaga, A., Nagao, K., Ohmiya, H., Sawamura, M. *Angew. Chem. Int. Ed.* **2015**,

54, 15859.

14) (a) Oshima, K.; Ohmura, T.; Suginome, M. *J. Am. Chem. Soc.* **2011**, *133*, 7324. (b) Oshima, K.; Ohmura, T.; Suginome, M. *J. Am. Chem. Soc.* **2012**, *134*, 3699.
15) Oshima, K., Ohmura, T., Suginome, M. *Chem. Commun.* **2012**, *48*, 8571.
16) Wang, G., Zhang, H., Zhao, J., Li, W., Cao, J., Zhu, C., Li, S. *Angew. Chem. Int. Ed.*, **2016**, *55*, 5985.
17) Wang, G., Cao, J., Gao, L., Chen, W., Huang, W. Cheng, X. Li, S. *J. Am. Chem. Soc.*, **2017**, *139*, 3904.
18) Cao, J., Wang, G., Gao, L., Cheng, X. Li, S. *Chem. Sci.*, **2018**, *9*, 3664.
19) Zhang, L., Jiao, L. *J. Am. Chem. Soc.*, **2017**, *139*, 607.
20) Jo, J., Kim, S., Choi, J.-H., Chung, W. *Chem. Commun.*, **2021**, *57*, 1360-1363.
21) Xu, R., Lu, G., Cai, C. *New J. Chem.*, **2018**, *42*, 16456.
22) (a) Hosoya, H., Castro, L. C. M., Sultan, I., Nakajima, Y., Ohmura, T., Sato, K., Tsurugi, H., Suginome, M., Mashima, K. *Org. Lett.*, **2019**, *21*, 9812. (b) Qi, J.-Q., Jiao, L. *J. Org. Chem.*, **2020**, *85*, 13877.
23) (a) Chen, D., Xu, G., Zhou, Q. Chung, L. W., Tang, W. *J. Am. Chem. Soc.*, **2017**, *139*, 9767-9770. (b) Zhou, Q., Tang, W., Chung, L. W. *J. Organomet. Chem.*, **2018**, *864*, 97.
24) Zhou, M., Li, K., Chen, D., Xu, R., Xu, G., Tang, W. *J. Am. Chem. Soc.*, **2020**, *142*, 10337.

Chapter 1

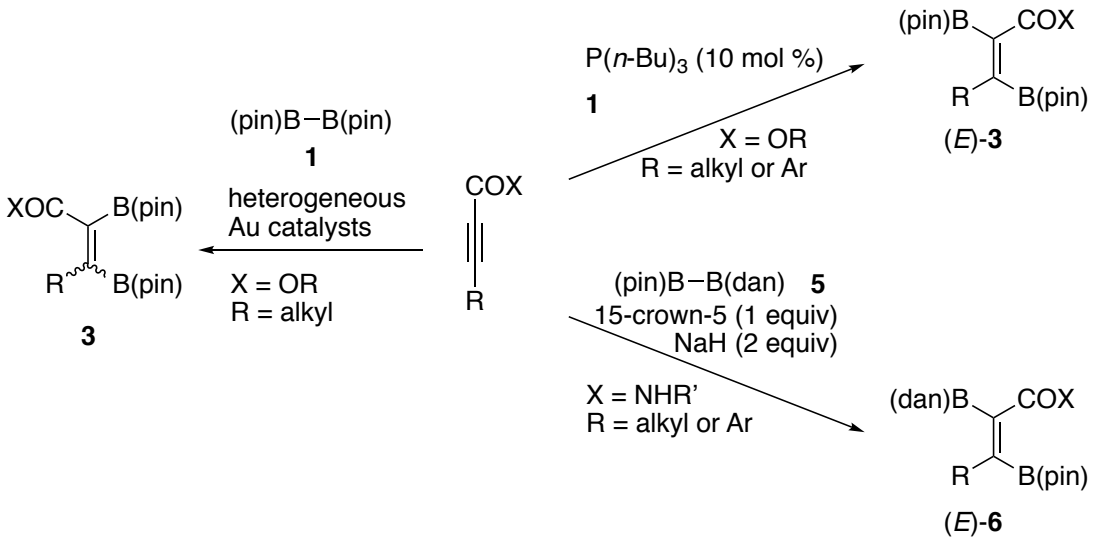
4,4’-Bipyridine-Catalyzed Stereoselective *trans*-Diboration of Acetylenedicarboxylates Giving 2,3-Diborylfumarates

ABSTRACT

Acetylenedicarboxylates undergo *trans*-addition of tetraalkoxydiboron in THF at 60 °C in the presence of 4,4’-bipyridine (5 mol %) as a catalyst to give 2,3-diborylfumarates in good yields with high stereoselectivity.

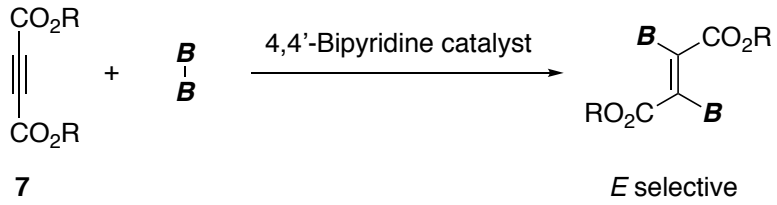
Introduction

Catalytic diboration of alkynes with diboron reagents such as bis(pinacolato)diboron (**1**) provides stereoselective accesses to diborylalkenes.[1] Since the first report by Ishiyama, Miyaura, and coworkers in 1993,[2a] transition metal catalysts have been used for stereoselective *cis*-1,2-diboration of a broad range of terminal and internal alkynes.[2,3] A recent report on cobalt-catalyzed 1,1-diboration makes diboration-based organic transformations more valuable.[4] However, it is interesting to note that the transition-metal-catalyzed diboration has never been applied to alkynes in which the carbon–carbon triple bond is conjugated with carbonyl groups, except for nonstereoselective diboration of alkynoates **2a** and **2b** using heterogeneous gold catalysts (Scheme 1, left).[3a,3b,5] This particular limitation of transition metal catalysts has been overcome by transition-metal-free catalysts.[6,7,8,9] Sawamura and coworkers have reported P(*n*-Bu)$_3$-catalyzed diboration of 3-aryl- and 3-alkylpropiolates **2**, leading to the stereoselective formation of (*E*)-α,β-diborylacrylates (*E*)-**3** through *trans*-1,2-addition to **1** (Scheme 1, top right).[6] Santos and coworkers have also reported *trans*-1,2-diboration of alkynoic amides **4**, which is promoted by NaH/15-crown-5 (Scheme 1, bottom right).[7] 1,1-Diboration of propiolates has also been accomplished using a catalytic amount of *t*-BuOLi.[8] However, even those organocatalytic diborations have been hardly applicable to acetylenedicarboxylates **7**, which have been recognized as reactive substrates in related catalytic element–element additions such as bis-silylation,[10] silastannation,[11] and silaboration.[12]



Scheme 1. 1,2-Diboration of alkynes conjugated with carbonyl groups

Recently, the author reported diboration of substituted pyrazines with **1**, where 4,4'-bipyridines are effective catalysts to activate the boron–boron σ bond of **1**.[13] This study triggered the development of diboron-based borylations by pyridine-based catalysts.[14] Herein, the author describes the first diboration of acetylenedicarboxylates **7** to afford 2,3-diborylfumarates in the presence of 4,4'-bipyridine as an effective catalyst (Scheme 2).



7 *E* selective

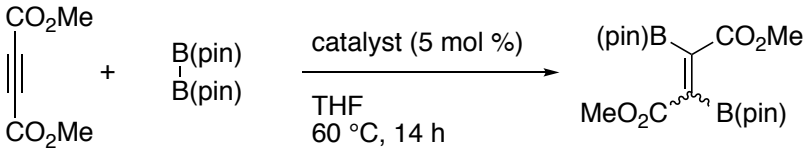
Scheme 2. This work: Stereoselective *trans*-1,2-diboration of acetylenedicarboxylates

Results and Discussions

The reaction of dimethyl acetylenedicarboxylate (**7a**) with **1** was carried out under conditions established for diboration of other alkynes (entries 2-4, Table 1). In the presence of $Pt(PPh_3)_4$ (5 mol %), **7a** underwent addition of **1** in DMF at 110 °C to give **8a** in low yield as a mixture of stereoisomers (38%, *E*:*Z* = 14:86, entry 2). No reaction took place when the reaction was carried out either with P(*n*-Bu)$_3$ (5 mol %) in THF at 80 °C or *t*-BuOLi (5 mol %) in CH_3CN at 60 °C (entries 3 and 4), although these conditions have been effective for diboration of alkynoates [Schemes 1(b) and 1(c)]. ICy, which was used as a catalyst for 1,4-addition of **1** to ethyl crotonate,[15] did not promote the diboration of **7a** (entry 5).

The author then turned his attention to 4,4'-bipyridines **9a**-**e**, some of which have been effective catalysts for the addition of **1** to substituted pyrazines (entries 6-10).[13] In the presence of **9a**-**e** (5 mol %), the addition of **1** to **7a** took place efficiently in THF at 60 °C to give the adduct **8a** in 70–88% yields. The stereochemistry of the product was assigned by X-ray crystallographic analysis (Figure 1), which revealed that the reaction gave the *E*-isomer stereoselectively. The stereoselectivity was affected by the electronic nature of the 4,4'-bipyridines: 4,4'-bipyridines **9a**-**c** bearing electron-withdrawing groups resulted in high stereoselectivity (*E*:*Z* = >99:1, entries 6–8), whereas lower selectivity was observed in the reaction with 4,4'-bipyridine **9d** bearing the electron-donating methyl group (*E*:*Z* = 93:7, entry 9). Unsubstituted 4,4'-bipyridine **9e** showed high catalyst activity and high stereoselectivity for the *E* isomer, giving (*E*)-**8a** in 76% isolated yield after purification by silica gel column chromatography (entry 10).

Table 1. Screening of catalysts[a]



7a **1** (1.1 equiv) **8a**

entry	catalyst	yield (%)[b]	*E*:*Z*[b]
1	none	NR	–
2[c]	$Pt(PPh_3)_4$	38	14:86
3[d]	P(*n*-Bu)$_3$	NR	–
4[e]	*t*-BuOLi	NR	–
5	ICy[f]	NR	–
6	**9a** ($R^1 = R^2 = Cl$)	61	>99:1
7	**9b** ($R^1 = Cl$, $R^2 = H$)	87	>99:1
8	**9c** ($R^1 = CF_3$, $R^2 = H$)	70	>99:1
9	**9d** ($R^1 = Me$, $R^2 = H$)	85	93:7
10	**9e** ($R^1 = R^2 = H$)	88 (76)[g]	98:2
11	**10a** ($R^3 = H$)	83	69:31
12	**10b** ($R^3 = Me$)	77	55:45
13	**10c** ($R^3 = OMe$)	67	59:41
14	**10d** ($R^3 = NMe_2$)	41	56:44
15	**10e** ($R^3 = Ph$)	82	82:18
16	**10f** ($R^3 = CO_2Et$)	74	93:7
17	**10g** ($R^3 = CN$)	13	87:13
18	**10h** ($R^4 = Me$, $R^5 = H$)	40	53:47
19	**10i** ($R^4 = H$, $R^5 = Me$)	76	65:35
20	**10j** ($R^4 = H$, $R^5 = OMe$)	90	80:20
21	**10k** ($R^4 = H$, $R^5 = CO_2Me$)	63	96:4
22	isoquinoline (**10l**)	48	87:13

[a] **7a** (0.20 mmol), **1** (0.22 mmol), and catalyst (0.010 mmol) were stirred in THF (0.2 mL) at 60 °C for 14 h, unless otherwise noticed. [b] Determined by GC. [c] In DMF at 110 °C. [d] At 80 °C. [e] In CH_3CN at 60 °C. [f] Generated in situ from ICy•HCl with *t*-BuONa. [g] Yield of isolated *E*-isomer.

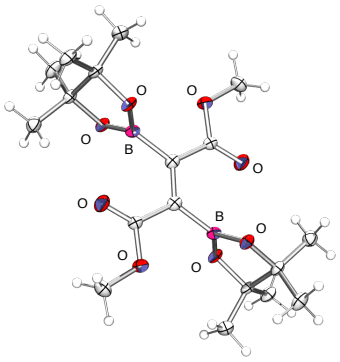
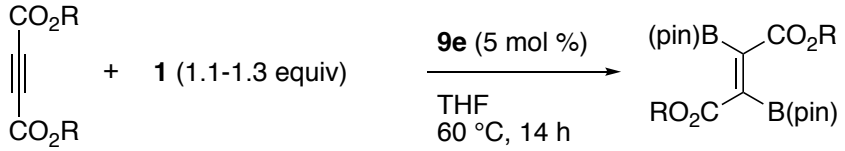


Figure 1. ORTEP drawing of (*E*)-**8a** at the 50% probability level

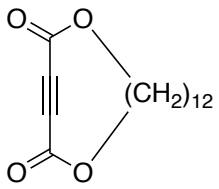
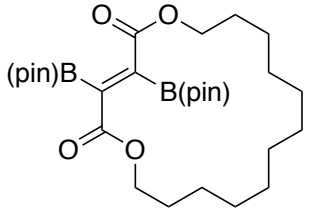
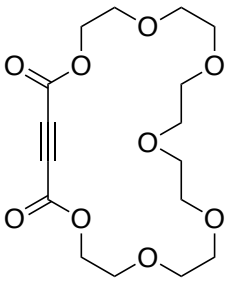
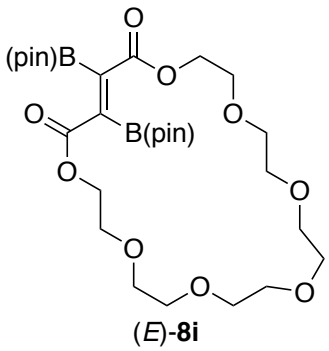
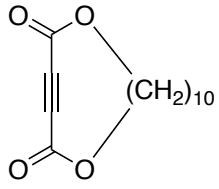
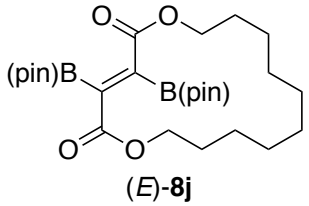
The author also tested pyridines **10a**–**k**, some of which have been reported as efficient catalysts for catalytic borylation reactions using **1** (entries 11–21).[14] Although diboration of **7a** proceeded efficiently in the presence of pyridine (**10a**, 5 mol %), the stereoselectivity was rather low (*E*:*Z* = 69:31, entry 11). The results obtained with 4-substituted pyridines **10b**–**g** are summarized as follows: (1) catalyst efficiency is not higher than the parent **10a**, and (2) pyridines **10b**–**d** bearing electron-donating substituents resulted in low stereoselectivity, whereas better stereoselectivity was observed in the reaction with **10e**–**g** having electron-withdrawing groups. Pyridines **10h**–**k** bearing a substituent at the 2- or 3-positions also served as catalysts with comparable yields and stereoselectivity (entries 18–21). Isoquinoline (**10l**), which could undergo reductive coupling in the reaction with **1**,[14e] also worked as a catalyst for diboration (entry 22).

Various acetylenedicarboxylates **7** were used in the reactions with **1** using **9e** as a catalyst (5 mol %) (Table 2). Diethyl and diisopropyl esters **7b** and **7c** underwent addition of **1** in THF at 60 °C to give the corresponding 2,3-diborylfumarates (*E*)-**8b** and (*E*)-**8c** in 74 and 73% yields, respectively (entries 1 and 2). Alkyl esters **7d** and **7e** bearing Cl and Br on the alkyl chain also gave (*E*)-**8d** and (*E*)-**8e** in 71 and 77% yields, respectively (entries 3 and 4). In the reaction of allyl ester **7f**, **1** added selectively to the carbon–carbon triple bond with the carbon–carbon double bonds remained intact (entry 5). It should be remarked that in the reaction of propargyl ester **7g**, the diboration took place chemoselectively at the internal carbon–carbon triple bond, leaving terminal carbon–carbon triple bonds untouched (entry 6). Eighteen- and twenty three-membered cyclic alkynes **7h** and **7i** also underwent the diboration to give the *E* isomers of **8h** and **8i** preferentially (*E*:*Z* = 73:27–75:25, entries 7 and 8). In contrast, the reaction of a substrate having smaller sixteen-membered alkyne **8j**, afforded the diboration product in moderate yield with low stereoselectivity (entry 9).

Table 2. 4,4'-Bipyridine-catalyzed diboration of **7**[a]

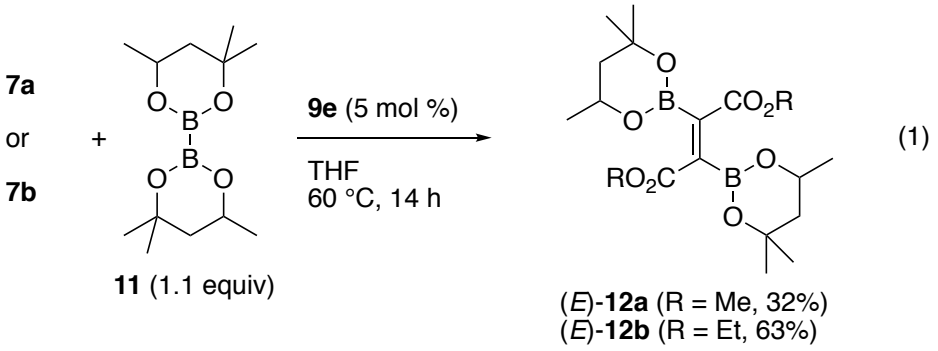


7 (*E*)-**8**

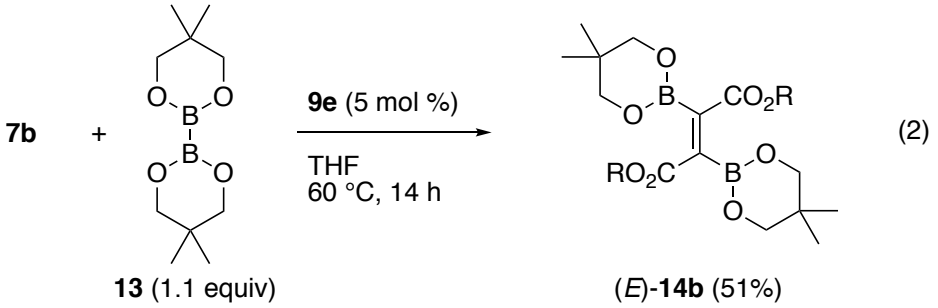
entry	substrate	product	yield (%)[b]
1	**7b** (R = Et)	(*E*)-**8b**	74
2	**7c** (R = *i*-Pr)	(*E*)-**8c**	74
3	**7d** [R = $(CH_2)_3Cl$]	(*E*)-**8d**	71
4	**7e** [R = $(CH_2)_3Br$]	(*E*)-**8e**	77
5	**7f** [R = $CH_2CH{=}CH_2$]	(*E*)-**8f**	74
6	**7g** [R = $CH_2C{\equiv}CH$]	(*E*)-**8g**	50
7	 **7h**	 (*E*)-**8h**	(99)[c], 52
8	 **7i**	 (*E*)-**8i**	(91)[d], 50
9	 **7j**	 (*E*)-**8j**	(58)[e], 27

[a] **7** (0.20 mmol), **1** (0.22-0.26 mmol), and **9e** (0.010 mmol) in THF (0.2 mL) were stirred at 60 °C for 14 h. [b] Isolated yield of *E* isomer. [c] ^{1}H NMR yield (*E*:*Z* = 73:27). [d] ^{1}H NMR yield (*E*:*Z* = 75:25). [e] ^{1}H NMR yield (*E*:*Z* = 66:34).

Hexylene glycol- and neopentyl glycol-derived diborons **11** and **13** showed comparable reactivity with **1** in the 4,4'-bipyridine-catalyzed diboration of **7a** and **7b** (eqs. 1 and 2). Such a broad scope of diboron reagents is in sharp contrast to the P(*n*-Bu)$_3$ catalyst system,[6] in which only **1** served as a diboration reagent.



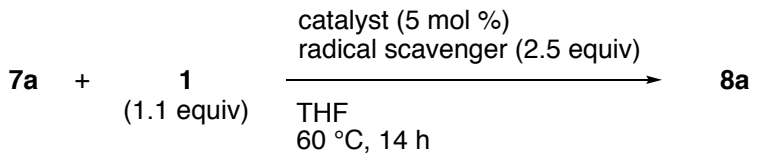
(1)



(2)

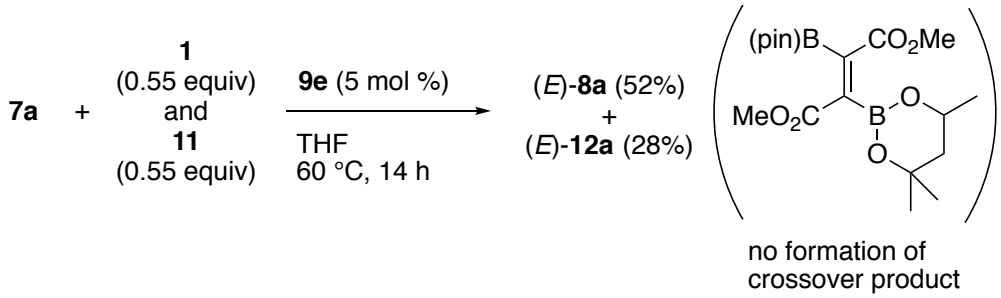
There have been reports on the nucleophilic conjugate addition of **10a** to **7a**.[16] On the other hand, pyridines have also been known as effective catalysts for B–B bond activation of **1** via a radical pathway.[14a-d,14f] In the **9**- or **10**-catalyzed diboration of **7**, the latter reaction pathway is not likely because of the following experimental results: (1) typical radical scavengers (TEMPO and cyclohexa-1,4-diene) did not affect the reaction of **7a** with **1** (Scheme 3a); (2) no crossover product was observed in the reaction of **7a** with **1** (0.55 equiv) and **11** (0.55 equiv) (Scheme 3b). Therefore, the author proposes a mechanism based on the reaction pathway involving the nucleophilic conjugate addition of the pyridine-based catalyst to **7** as an initial step (Scheme 4), which is related to the mechanism proposed for P(*n*-Bu)$_3$-catalyzed diboration of alkynoates (Scheme 1b, top).[6] Nucleophilic attack of **9** or **10** on **7** forms **A**,[16] which reacts with diboron to afford **B**. Transfer of the boryl group gives ylide **C**, which is then converted to cyclic intermediate **D**. Ring-opening takes place with the release of **9** or **10** to afford the product. In the reaction with **9** or electron-deficient **10**, the *E* isomer is formed directly from **D** due to the high elimination abilities of these pyridines. In contrast, stepwise ring-opening and elimination of pyridines via **E** takes place in the reaction of electron-neutral or -rich **10**, resulting in the formation of an *E*/*Z* mixtures.[17]

(a) Reaction in the presence of radical scavengers



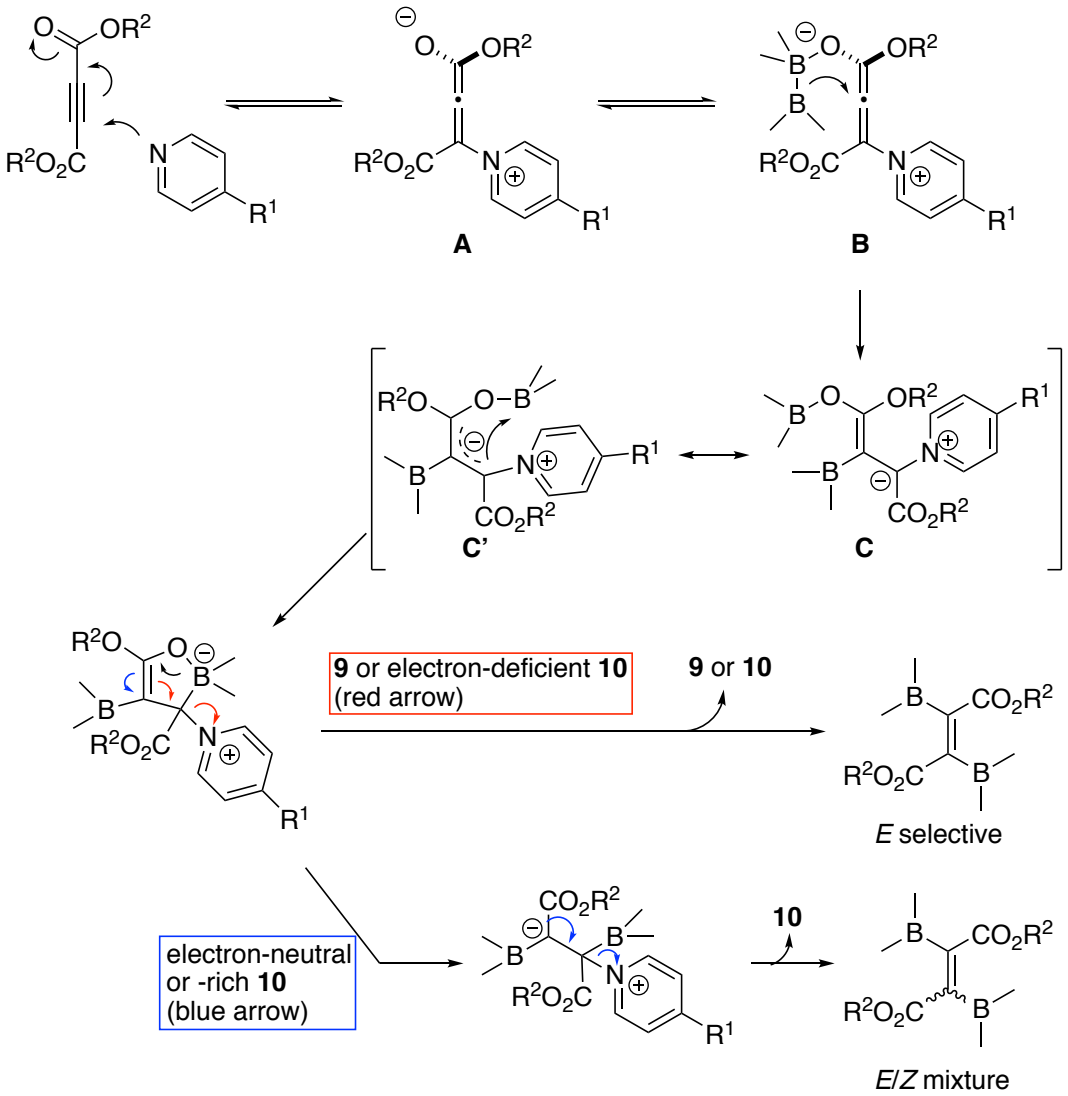
	catalyst: **9e**		catalyst: **10a**	
radical scavenger	GC yield	*E*:*Z*	GC yield	*E*:*Z*
TEMPO	91%	98:2	83%	65:35
cyclohexa-1,4-diene	97%	98:2	83%	69:31

(b) Crossover experiment



Scheme 3. Mechanistic investigation

Attempts on Suzuki-Miyaura coupling of (*E*)-**8b** with aryl halides under the typical coupling conditions were failed due to fast protodeborylation.



Scheme 4. Possible mechanism

Conclusion

In conclusion, the author has established the first diboration of acetylenedicarboxylates using 4,4'-bipyridine as a catalyst, which afforded *trans*-1,2-diboration products in good yields. A mechanism involving the nucleophilic conjugate addition of the pyridine catalyst to the substrates is proposed, that contrasts with the recent reports on the B–B bond activation by pyridine-based catalysts through a radical pathway.

Experimental Section

General

All reactions were performed in glove box or using Schlenk technique under an atmosphere of nitrogen with magnetic stirring. Materials were weighted by an electric balance, Sartorius CPA225D (readability: 0.01 mg). Column chromatography was performed with Ultra Pure Silica Gel (SILICYCLE, pH 7.0, 40-63 μm, 60 Å) or CHROMATOREX DIOL MB100-40/75 (Fuji Silysia Chemical Ltd.). Gas chromatography (GC) was performed by Shimadzu GC-2014 with Agilent J&W GC Column DB-1 (ϕ 0.32 mm x 15 m). Gel Permeation Chromatography (GPC) was performed by Japan Analytical Industry LC-908 with series-connected JAIGEL-1H (ϕ 20 mm x 600 mm) and JAIGEL-2H (ϕ 20 mm x 600 mm). ^{1}H NMR spectra were recorded on a Varian 400-MR (399.89 MHz) spectrometer. ^{13}C NMR spectra were recorded on a Varian 400-MR (100.55 MHz) spectrometer. ^{11}B NMR spectra were recorded on a Varian 400-MR (128.30 MHz) spectrometer. ^{1}H NMR data were reported as follows: chemical shifts in ppm downfield from tetramethylsilane, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant (*J*), and integration. ^{13}C and ^{11}B NMR data were reported in ppm downfield from tetramethylsilane (^{13}C) and BF_3•OEt_2 (^{11}B), respectively. High resolution mass spectra were recorded on a Thermo Scientific Exactive (ESI, APCI, DART) spectrometer. Infrared (IR) spectra were recorded on a Shimadzu FTIR-8400 spectrometer attached MIRacle (ZnSe).

Materials

Tetrahydrofuran (THF, Kanto, dehydrated stabilizer free) was purchased and used without further purification. Bis(pinacolato)diboron (**1**), bis(hexylene glycolato)diboron (**11**), and bis(neopentyl glycolato)diboron (**13**) were purchased from Boron Molecular and purified by recrystallization (pentane) before use. Dimethyl acetylenedicarboxylate (**7a**, TCI) and diethyl acetylenedicarboxylate (**7b**, TCI) were distilled before use. Other acetylenedicarboxylates **7c-g** were synthesized from acetylenedicarboxylic acid (TCI) with the corresponding alcohols. For preparation of **7h**, **7i**, and **S1**, see below. $Pt(PPh_3)_4$ was prepared by the reported method.[18] *t*-BuOLi (Wako), ICy•HCl (TCI), *t*-BuONa (TCI), and 4,4'-bipyridine (**9e**, TCI) was used as received from commercial sources. Substituted 4,4'-bipyridines **9a-d** were prepared by the method reported previously.[19] P(*n*-Bu)$_3$ (TCI), pyridines **10a** (Wako), **10b** (TCI), **10c** (TCI), **10d** (Wako), **10e** (TCI), **10f** (TCI), **10g** (TCI), **10h** (TCI), **10i** (TCI), **10j** (TCI), **10k** (TCI), and isoquinoline (**10l**, TCI) were purchased and distilled before use. 2,2,6,6-Tetramethylpiperidine 1-oxyl (TEMPO, TCI)

and cyclohexa-1,4-diene (TCI) were used as received from commercial source.

*Preparation of 1,6-dioxacyclooctadec-3-yne-2,5-dione (**7h**)*[20]: A 2000 mL two-necked, round-bottomed flask, equipped with a Dimroth condenser and a magnetic stirring bar, was charged with acetylenedicarboxylic acid (345 mg, 3.0 mmol) and 1,12-dodecanediol (618 mg, 3.0 mmol). The flask was evacuated and backfilled with nitrogen. Toluene (dry, 600 mL) and $Hf(OTf)_4$ (232 mg, 0.30 mmol) were added to the flask, and the mixture was reacted at 110 °C with stirring for 24 h. After cooling to room temperature, silica gel (0.7 g) was added to the flask and volatiles were removed by a rotary evaporator. The silica gel was collected and charged with a column. 1,6-Dioxacyclooctadec-3-yne-2,5-dione (**7h**, 431 mg, 51%) was obtained as colorless oil after purification by column chromatography on silica gel (Ultra Pure Silica Gel; eluent: hexane:EtOAc = 19:1). **7h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.29-4.33 (m, 4H), 1.67-1.75 (m, 4H), 1.36-1.51 (m, 8H), 1.25-1.36 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9, 74.9, 67.9, 29.3, 28.8, 28.3, 27.3, 26.4. HRMS (APCI, positive) *m/z* calcd for $C_{16}H_{25}O_4^+$ $[M + H]^+$: 281.1747, found: 281.1742.

*Preparation of 1,4,7,10,13,16,19-heptaoxacyclotricos-21-yne-20,23-dione (**7i**)*: According to the procedure for preparation of **7h**, acetylenedicarboxylic acid (302 mg, 2.6 mmol) was reacted with hexaethylene glycol (760 mg, 2.7 mmol) in toluene (dry, 500 mL) at 110 °C for 19 h in the presence of $Hf(OTf)_4$ (180 mg, 0.23 mmol). **7i** (344 mg, 36%) was obtained as brown oil after purification by column chromatography on silica gel (Ultra Pure Silica Gel; eluent: $CHCl_3$:MeOH = 1:0 to 3:1). **7i**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.37-4.42 (m, 4H), 3.62-3.76 (m, 20H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.8, 74.9, 71.4, 71.3, 71.0, 70.6, 68.4, 66.1. HRMS (APCI, positive) *m/z* calcd for $C_{16}H_{25}O_9^+$ $[M + H]^+$: 361.1493, found: 361.1482.

*Preparation of 1,6-dioxacyclohexadec-3-yne-2,5-dione (**7j**)*: According to the procedure for preparation of **7h**, acetylenedicarboxylic acid (286 mg, 2.5 mmol) was reacted with 1,10-decanediol (446 mg, 2.6 mmol) in toluene (dry, 500 mL) at 110 °C for 58 h in the presence of $Hf(OTf)_4$ (108 mg, 0.14 mmol). **7j** (43 mg, 7%) was obtained as brown oil after purification by column chromatography on silica gel (Ultra Pure Silica Gel; eluent: hexane:Et_2O = 19:1 to 10:1). **7j**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.30-4.36 (m, 4H), 1.70-1.80 (m, 4H), 1.40-1.52 (m, 8H), 1.25-1.37 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.7, 76.2, 69.2, 29.6, 29.2, 28.2, 27.3. HRMS (APCI, positive) *m/z* calcd for $C_{14}H_{21}O_4^+$ $[M + H]^+$: 253.1434, found: 253.1426.

Screening of catalyst (Table 1)

*Reaction of **7a** with **1** under catalyst-free conditions (entry 1)*

In a glove box, a glass tube having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with **1** (56 mg, 0.22 mmol), THF (0.2 mL), and **7a** (28 mg, 0.20 mmol). The tube was sealed by the stopcock and was taken out from the glove box. The mixture was heated at 60 °C with stirring for 14 h. After cooling to room temperature, Bn_2O (40 mg, 0.20 mmol, internal standard) was added, and the resulting mixture was analyzed by GC. No reaction took place.

*Reaction of **7a** with **1** in the presence of $Pt(PPh_3)_4$ (entry 2)*

This reaction was carried out according to the reported procedure.[21] In a glove box, a glass tube having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with $Pt(PPh_3)_4$ (0.010 mmol), **1** (62 mg, 0.24 mmol), DMF (0.8 mL), and **7a** (28 mg, 0.20 mmol). The tube was sealed by the stopcock and was taken out from the glove box. The mixture was heated at 110 °C with stirring for 14 h. After cooling to room temperature, Bn_2O (40 mg, 0.20 mmol, internal standard) was added, and the resulting mixture was analyzed by GC. **8a** was formed in 38% yield (*E*:*Z* = 14:86).

*Reaction of **7a** with **1** in the presence of P(n-Bu)$_3$ (entry 3)*

This reaction was carried out according to the reported procedure.[6] In a glove box, a glass tube having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with **1** (63 mg, 0.25 mmol), THF (0.2 mL), **7a** (29 mg, 0.21 mmol), and P(*n*-Bu)$_3$ (2.1 mg, 0.010 mmol). The tube was sealed by the stopcock and was taken out from the glove box. The mixture was heated at 80 °C with stirring for 14 h. After cooling to room temperature, Bn_2O (39 mg, 0.20 mmol, internal standard) was added, and the resulting mixture was analyzed by GC. No reaction took place.

*Reaction of **7a** with **1** in the presence of t-BuOLi (entry 4)*

This reaction was carried out according to the reported procedure.[8] In a glove box, a glass tube having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with *t*-BuOLi (0.74 mg, 0.0090 mmol), **1** (62 mg, 0.24 mmol), CH_3CN (0.2 mL), and **7a** (28 mg, 0.20 mmol). The tube was sealed by the stopcock and was taken out from the glove box. The mixture was heated at 60 °C with stirring for 14 h. After cooling to room temperature, Bn_2O (38 mg, 0.19 mmol, internal standard) was added, and the resulting mixture was analyzed by GC. No reaction took place.

*Reaction of **7a** with **1** in the presence of ICy (entry 5)*

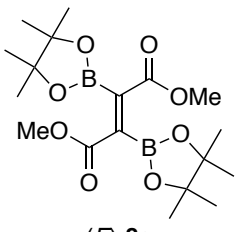
This reaction was carried out according to the reported procedure.[15] In a glove box, a glass tube having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with ICy•HCl (2.5 mg, 0.0090 mmol), *t*-BuONa (0.90 mg, 0.0090 mmol), **1** (65 mg, 0.26 mmol), THF (0.2 mL), and **7a** (28 mg, 0.20 mmol). The tube was sealed by the stopcock and was taken out from the glove box. The mixture was heated at 60 °C with stirring for 14 h. After cooling to room temperature, Bn_2O (40 mg, 0.20 mmol, internal standard) was added, and the resulting mixture was analyzed by GC. No reaction took place.

*Reaction of **7a** with **1** in the presence of **9** or **10** (entries 6–22)*

General Procedure: In a glove box, a glass tube having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with **9** or **10** (0.010 mmol), **1** (56 mg, 0.22 mmol), THF (0.2 mL), and **7a** (28 mg, 0.20 mmol). The tube was sealed by the stopcock and was taken out from the glove box. The mixture was heated at 60 °C with stirring for 14 h. After cooling to room temperature, Bn_2O (40 mg, 0.20 mmol, internal standard) was added, and the resulting mixture was analyzed by GC to determine the yield of **8a** and the ratio of *E*:*Z*.

*4,4'-Bipyridine (**9e**)-catalyzed diboration of **7a** with **1** (entry 10)*

In a glove box, a glass tube having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with **9e** (1.5 mg, 0.010 mmol), **1** (63 mg, 0.25 mmol), THF (0.2 mL), and **7a** (29 mg, 0.21 mmol). The tube was sealed by the stopcock and was taken out from the glove box. The mixture was heated at 60 °C with stirring for 14 h. ^{1}H NMR analysis of the crude mixture indicated that (*E*)-**8a** was formed in 88% yield. The product (*E*)-**8a** (62 mg, 76%) was obtained as a white solid after purification by GPC (eluent: $CHCl_3$).



(*E*)-**8a**

Dimethyl 2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)fumarate [(*E*)-8a]

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 6H), 1.33 (s, 24H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 149.3 (broad, *C*–B), 84.4, 52.6, 24.7. ^{11}B NMR (128 MHz, $CDCl_3$) δ 28.5. HRMS (ESI, positive) *m/z* calcd for $C_{18}H_{31}B_2O_8^+$ $[M + H]^+$: 397.2200, found: 397.2198. Chemical shifts in C_6D_6: ^{1}H NMR (400 MHz, C_6D_6) δ 3.19 (s, 6H), 1.32 (s, 24H). ^{13}C NMR (101 MHz, C_6D_6) δ 168.6, 150.2 (broad, *C*–B), 84.2, 51.9, 25.0. ^{11}B NMR (128 MHz, C_6D_6) δ 30.5.

(*Z*)-**8a** was relatively unstable under air, thus isolation of it by chromatography was failed. The following ^{1}H NMR chemical shifts were collected from spectrum of the crude mixture. (*Z*)-**8a**: ^{1}H NMR (400 MHz, C_6D_6) δ 3.42 (s, 6H), 1.10 (s, 24H).

X-ray crystallographic analysis of (*E*)-8a

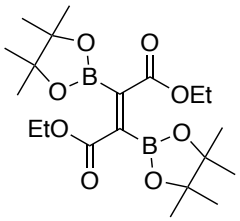
Single crystal of (*E*)-**8a** was obtained from toluene solution and mounted in the loop. The data was collected on a Rigaku R-AXIS imaging plate area detector with graphite-monochromated Mo $K\alpha$ radiation operating at 50 kV and 40 mA at −173 °C. Data was processed with direct methods SHELX-97[22] and SIR97.[23] Empirical absorption correction was applied to the crystal.[24] All non-hydrogenatoms were refined anisotropically.

Table S1. Crystal data and structure refinement for (*E*)-**8a**

Empirical formula	$C_{18}H_{30}B_2O_8$	
Formula weight	396.04	
Temperature	100 K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 9.932(2) Å	α = 90°
	b = 9.9448(19) Å	β = 93.313(4)°
	c = 10.673(2) Å	γ = 90°
Volume	1048.8(4) $Å^3$	
Z	2	
Density (calculated)	1.254 Mg/m^3	
Absorption coefficient	0.095 mm^{-1}	
F(000)	424	
Crystal size	0.600 x 0.600 x 0.600 mm^3	
Theta range for data collection	3.41 to 27.43°	
Index ranges	-12<=h<=12, -11<=k<=12, -13<=l<=13	
Reflections collected	9526	
Independent reflections	2388 [*R*(int) = 0.0233]	
Completeness to theta = 27.43°	99.7%	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2388 / 0 / 132	
Goodness-of-fit on F^2	1.072	
Final *R* indices [I>2sigma(I)]	*R*1 = 0.0418, *wR*2 = 0.1001	
R indices (all data)	*R*1 = 0.0506, *wR*2 = 0.1092	
Largest diff. peak and hole	0.460 and -0268 e.$Å^{-3}$	
weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0456P)^2 + 0.5339P]$ where $P = (F_o^2 + 2F_c^2)/3$	

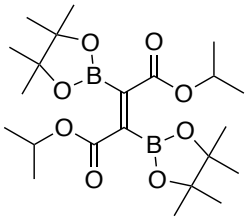
4,4'-Bipyridine-catalyzed diboration of acetylenedicarboxylates 7 with 1 (Table 2)

General Procedure: In a glove box, a glass tube having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with **9e** (1.6 mg, 0.010 mmol), **1** (56 mg, 0.22 mmol), THF (0.2 mL), and **7** (0.20 mmol). The tube was sealed by the stopcock and was taken out from the glove box. The mixture was heated at 60 °C with stirring for 14 h. After cooling to room temperature, the volatiles were removed from the reaction mixture under reduced pressure. The residue was purified by column chromatography on silica gel, GPC, or recrystallization to afford (*E*)-**8**.



(*E*)-**8b**

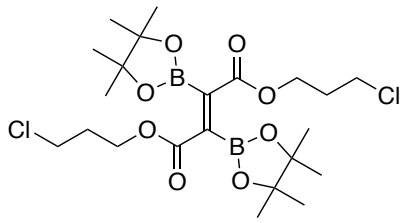
Diethyl 2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)fumarate [(*E*)-8b, entry 1]: According to the general procedure, the reaction was carried out using **9e** (1.6 mg, 0.010 mmol), diethyl acetylenedicarboxylate (**7b**, 34 mg, 0.20 mmol), and **1** (62 mg, 0.24 mmol) in THF (0.2 mL) at 60 °C for 14 h. The product (*E*)-**8b** (63 mg, 74%) was obtained as a white solid after purification by GPC (eluent: $CHCl_3$). Geometry of the carbon–carbon double bond was confirmed as *E* by conversion of the product to (*E*)-**8a** under standard transesterification conditions (see section 6). (*E*)-**8b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.23 (q, J = 7.2 Hz, 4H), 1.33 (s, 24H), 1.29 (t, J = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 149.8 (broad, *C*–B), 84.2, 61.7, 24.8, 14.1. ^{11}B NMR (128 MHz, $CDCl_3$) δ 28.8. HRMS (ESI, positive) *m/z* calcd for $C_{20}H_{35}B_2O_8^+$ $[M + H]^+$: 425.2513, found: 425.2497.



(*E*)-**8c**

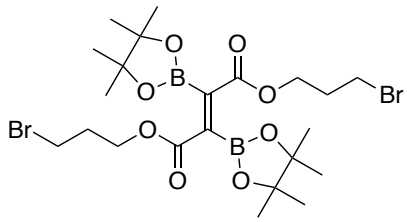
Diisopropyl 2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)fumarate [(*E*)-8c, entry 2]: According to the general procedure, the reaction was carried out using **9e** (1.6 mg, 0.010 mmol), diisopropyl acetylenedicarboxylate (**7c**, 39 mg, 0.20 mmol), and **1** (63 mg, 0.25 mmol) in THF (0.2 mL) at 60 °C for 14 h. The product (*E*)-**8c** (65 mg, 74%)

was obtained as a white solid after purification by GPC (eluent: $CHCl_3$). Geometry of the carbon–carbon double bond was assigned on the analogy of that of (*E*)-**8a**. (*E*)-**8c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.07 (sept, J = 6.0 Hz, 2H), 1.32 (s, 24H), 1.26 (d, J = 6.0 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 84.0, 69.2, 24.8, 21.9. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ 28.7. HRMS (ESI, positive) *m/z* calcd for $C_{22}H_{39}B_2O_8^+$ $[M + H]^+$: 453.2826, found: 453.2822.



(*E*)-**8d**

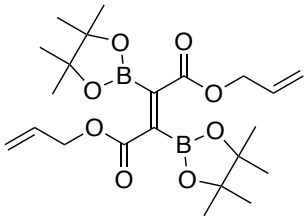
Di(3-chloropropyl) 2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)fumarate [(*E*)-8d, entry 3]: According to the general procedure, the reaction was carried out using **9e** (1.6 mg, 0.010 mmol), di(3-chloropropyl) acetylenedicarboxylate (**7d**, 54 mg, 0.20 mmol), and **1** (56 mg, 0.22 mmol) in THF (0.2 mL) at 60 °C for 14 h. The product (*E*)-**8d** (75 mg, 71%) was obtained as a white solid after purification by column chromatography on silica gel (CHROMATOREX DIOL, eluent: hexane:$CHCl_3$ = 5:1 to 3:1). Geometry of the carbon–carbon double bond was assigned on the analogy of that of (*E*)-**8a**. (*E*)-**8d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.35 (t, J = 6.0 Hz, 4H), 3.61 (t, J = 6.4 Hz, 4H), 2.12 (quint, J = 6.4 Hz, 4H), 1.33 (s, 24H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 150.0 (broad, *C*–B), 84.4, 62.4, 41.0, 31.7, 24.9. ^{11}B NMR (128 MHz, $CDCl_3$) δ 28.1. HRMS (ESI, positive) *m/z* calcd for $C_{22}H_{37}B_2Cl_2O_8^+$ $[M + H]^+$: 521.2046, found: 521.2040.



(*E*)-**8e**

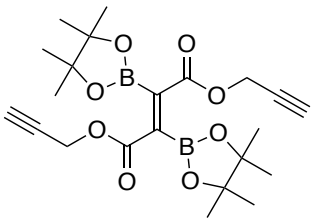
Di(3-bromopropyl) 2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)fumarate [(*E*)-8e, entry 4]: According to the general procedure, the reaction was carried out using **9e** (1.5 mg, 0.010 mmol), di(3-bromopropyl) acetylenedicarboxylate (**7e**, 73 mg, 0.20

mmol), and **1** (57 mg, 0.22 mmol) in THF (0.2 mL) at 60 °C for 14 h. The product (*E*)-**8e** (96 mg, 77%) was obtained as a white solid after purification by GPC (eluent: $CHCl_3$). Geometry of the carbon–carbon double bond was assigned on the analogy of that of (*E*)-**8a**. (*E*)-**8e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.33 (t, J = 6.0 Hz, 4H), 3.45 (t, J = 6.4 Hz, 4H), 2.20 (quint, J = 6.4 Hz, 4H), 1.33 (s, 24H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 149.9 (broad, *C*–B), 84.4, 63.4, 31.8, 29.2, 24.9. ^{11}B NMR (128 MHz, $CDCl_3$) δ 28.9. HRMS (ESI, positive) *m/z* calcd for $C_{22}H_{37}B_2Br_2O_8^+$ $[M + H]^+$: 611.1015, found: 611.1003.



(*E*)-**8f**

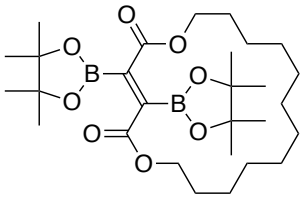
Diallyl 2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)fumarate [(*E*)-8f, entry 5]: According to the general procedure, the reaction was carried out using **9e** (1.6 mg, 0.010 mmol), diallyl acetylenedicarboxylate (**7f**, 40 mg, 0.20 mmol), and **1** (59 mg, 0.23 mmol) in THF (0.2 mL) at 60 °C for 14 h. The product (*E*)-**8f** (68 mg, 74%) was obtained as a white solid after purification by GPC (eluent: $CHCl_3$). Geometry of the carbon–carbon double bond was assigned on the analogy of that of (*E*)-**8a**. (*E*)-**8f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91 (ddt, J = 17.2, 10.0, 6.0 Hz, 2H), 5.35 (d, J = 17.2 Hz, 2H), 5.23 (d, J = 10.0 Hz, 2H), 4.69 (d, J = 6.0 Hz, 4H), 1.32 (s, 24H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 131.7, 118.8, 84.3, 66.3, 24.8. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.2. HRMS (ESI, positive) *m/z* calcd for $C_{22}H_{35}B_2O_8^+$ $[M + H]^+$: 449.2513, found: 449.2504.



(*E*)-**8g**

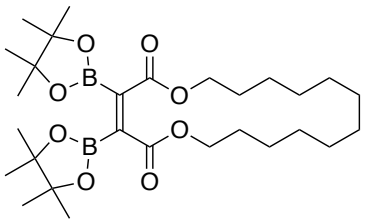
Di(prop-2-yn-1-yl) 2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)fumarate [(*E*)-8g, entry 6]: According to the general procedure, the reaction was carried out using **9e** (1.5 mg, 0.010 mmol), dipropargyl acetylenedicarboxylate (**7g**, 35 mg, 0.18 mmol),

and **1** (54 mg, 0.21 mmol) in THF (0.2 mL) at 60 °C for 14 h. The product (*E*)-**8g** (41 mg, 50%) was obtained as a colorless crystal after recrystallization (THF, 1.5 mL) followed by washing with THF (3 x 0.3 mL). Geometry of the carbon–carbon double bond was assigned on the analogy of that of (*E*)-**8a**. (*E*)-**8g**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.78 (d, J = 2.4 Hz, 4H), 2.46 (t, J = 2.4 Hz, 2H), 1.34 (s, 24H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 149.3 (broad, *C*–B), 84.6, 76.9, 75.7, 53.4, 24.8. ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.3. HRMS (ESI, positive) *m/z* calcd for $C_{22}H_{31}B_2O_8^+$ $[M + H]^+$: 445.2200, found: 445.2190.



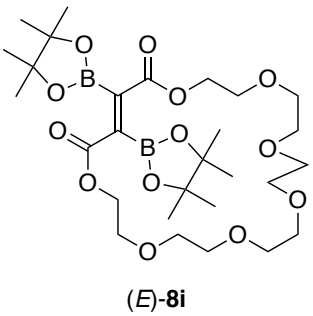
(*E*)-**8h**

(*E*)-3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,6-dioxacyclooctadec-3-ene-2,5-dione [(*E*)-8h, entry 7]: According to the general procedure, the reaction was carried out using **9e** (1.5 mg, 0.010 mmol), 1,6-dioxacyclooctadec-3-yne-2,5-dione (**7h**, 56 mg, 0.20 mmol), and **1** (66 mg, 0.26 mmol) in THF (0.4 mL) at 60 °C for 14 h. ^{1}H NMR analysis of the crude mixture indicated that **8h** was formed in 99% yield (*E*:*Z* = 73:27). The product (*E*)-**8h** (56 mg, 52%) was obtained as a colorless oil after purification by GPC (eluent: $CHCl_3$). Geometry of the carbon–carbon double bond was confirmed as *E* by conversion of the product to (*E*)-**8a** under standard transesterification conditions. (*E*)-**8h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.69 (ddd, J = 10.8 Hz, 8.0 Hz, 3.2 Hz, 2H), 3.90 (ddd, J = 10.8 Hz, 7.2 Hz, 3.2 Hz, 2H), 1.64-1.76 (m, 2H), 1.51-1.64 (m, 4H), 1.41-1.51 (m, 2H), 1.32 (s, 12H), 1.30 (s, 12H), 1.08-1.38 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 84.1, 66.0, 29.5, 28.8, 28.4, 27.7, 26.2, 24.9 (4C of *C*H_3), 24.8 (4C of *C*H_3). The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ 28.3. HRMS (APCI, positive) *m/z* calcd for $C_{28}H_{49}B_2O_8^+$ $[M + H]^+$: 535.3608, found: 535.3601. IR (neat) 1709 ($\nu_{C=O}$) cm^{-1}.



(*Z*)-**8h**

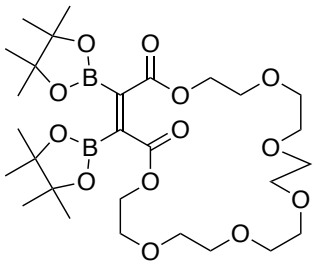
(*Z*)-3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,6-dioxacyclooctadec-3-ene-2,5-dione [(*Z*)-8h]: The titled compound was synthesized by **10a**-catalyzed reaction to obtain spectroscopic data of the *Z* isomer. According to the general procedure, the reaction was carried out using **10a** (1.0 μL, 0.010 mmol), 1,6-dioxacyclooctadec-3-yne-2,5-dione (**7h**, 59 mg, 0.21 mmol), and **1** (61 mg, 0.24 mmol) in THF (0.4 mL) at 60 °C for 14 h. ^{1}H NMR analysis of the crude mixture indicated that **8h** was formed in 99% yield as a mixture of *E* and *Z* isomers (*E*:*Z* = 39:61). (*Z*)-**8h** (42 mg, 38%, yellow oil) was obtained with (*E*)-**8h** (33 mg, 29%, colorless oil) after purification by GPC (eluent: $CHCl_3$). (*Z*)-**8h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.18 (t, *J* = 6.8 Hz, 4H), 1.64 (quint, *J* = 6.8 Hz, 4H), 1.31 (s, 24H), 1.25-1.40 (m, 16H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 84.9, 64,8, 27.8, 27.2, 26.8, 26.7, 24.9, 24.7. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ 27.8. HRMS (APCI, positive) *m/z* calcd for $C_{28}H_{49}B_2O_8^+$ $[M+H]^+$: 535.3608, found: 535.3605. IR (neat) 1724 ($\nu_{C=O}$) cm^{-1}.



(*E*)-**8i**

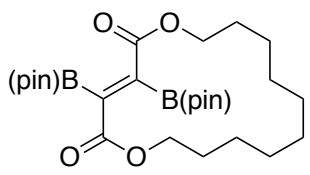
(*E*)-21,22-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4,7,10,13,16,19-heptaoxacyclotricos-21-ene-20,23-dione [(*E*)-8i, entry 8]: According to the general procedure, the reaction was carried out using **9e** (1.7 mg, 0.010 mmol), 1,4,7,10,13,16,19-heptaoxacyclotricos-21-yne- 20,23-dione (**7i**, 73 mg, 0.20 mmol), and **1** (62 mg, 0.24 mmol) in THF (0.2 mL) at 60 °C for 14 h. ^{1}H NMR analysis of the crude mixture indicated that **8i** was formed in 91% yield (*E*:*Z* = 75:25). The product (*E*)-**8i** (62 mg, 50%) was obtained as a white solid after purification by GPC (eluent: $CHCl_3$). Geometry of the carbon–carbon double bond was assigned as *E* on the analogy of that of (*E*)-**8h**. (*E*)-**8i**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.84 (ddd, J = 12.0, 8.4, 2.4 Hz, 2H), 3.94 (ddd, J = 12.0, 4.4, 2.4 Hz, 2H). 3.57-3.76 (m, 20H), 1.33 (s, 12H), 1.32 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 149.6 (broad, C–B), 84.2, 71.8, 70.9, 70.4 (two non-equivalent carbons overlapped), 68.9, 64.6, 24.81 (4C of CH_3), 24.78 (4C of CH_3). ^{11}B NMR (128 MHz, $CDCl_3$) δ 27.9. HRMS (APCI, positive) *m/z* calcd for $C_{28}H_{49}B_2O_{13}^+$ $[M + H]^+$: 615.3354, found: 615.3345. IR (neat) 1707 ($\nu_{C=O}$) cm^{-1}.



(*Z*)-**8i**

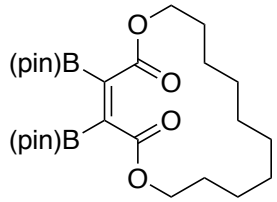
(*Z*)-21,22-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4,7,10,13,16,19-heptaoxacyclotricos-21-ene-20,23-dione [(*Z*)-8i]: The titled compound was synthesized by **10a**-catalyzed reaction to obtain spectroscopic data of the *Z* isomer. According to the general procedure, the reaction was carried out using **10a** (1.3 mg, 0.020 mmol), 1,4,7,10,13,16,19-heptaoxacyclotricos-21-yne-20,23-dione (**7i**, 70 mg, 0.19 mmol), and **1** (62 mg, 0.24 mmol) in THF (0.2 mL) at 60 °C for 14 h. ^{1}H NMR analysis of the crude mixture indicated that **8i** was formed as a mixture of *E* and *Z* isomers. (*Z*)-**8i** (29 mg, 24%, yellow oil) was obtained with (*E*)-**8i** (24 mg, 20%, white solid) after purification by GPC (eluent: $CHCl_3$). (*Z*)-**8i**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.29-4.33 (m, 4H), 3.70-3.74 (m, 4H), 3.59-3.67 (m, 16H), 1.29 (s, 24H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 84.9, 70.9, 70.83, 70.80, 70.7, 69.0, 64.7, 24.8. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ 28.2. HRMS (DART, positive) *m/z* calcd for $C_{28}H_{49}B_2O_{13}^+$ $[M+H]^+$: 615.3354, found: 615.3338. IR (neat) 1726 ($\nu_{C=O}$) cm^{-1}.



(*E*)-**8j**

(*E*)-3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,6-dioxacyclooctadec-3-

ene-2,5-dione [(*E*)-8j, entry 7]: According to the general procedure, the reaction was carried out using **9e** (1.8 mg, 0.010 mmol), 1,6-dioxacyclohexadec-3-yne-2,5-dione (**7j**, 39 mg, 0.15 mmol), and **1** (59 mg, 0.23 mmol) in THF (0.2 mL) at 60 °C for 14 h. ^{1}H NMR analysis of the crude mixture indicated that **8j** was formed in 58% yield (*E*:*Z* = 66:34). The products (*E*)-**8j** (21 mg, 27%, brown oil) and (*Z*)-**8j**(8 mg, 11%, yellow oil) were obtained after purification by GPC (eluent: $CHCl_3$). Geometry of the carbon–carbon double bond was assigned on the analogy of that of (*E*)- and (*Z*)-**8j**. [(*E*)-**8j**]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.69 (ddd, J = 10.8, 7.2, 3.2 Hz, 2H), 3.88 (ddd, J = 10.8, 8.0, 3.2 Hz, 2H), 1.70-1.81 (m, 2H), 1.39-1.60 (m, 6H), 1.30 (s, 12H), 1.28 (s, 12H), 1.20-1.39 (m, 6H), 1.10-1.20 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 84.2, 67.2, 29.60, 29.58, 28.1, 27.5, 24.8, 24.6. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ 28.7. HRMS (APCI, positive) *m/z* calcd for $C_{26}H_{45}B_2O_8^+$ $[M + H]^+$: 507.3295, found: 507.3290. IR (neat) 1713 ($\nu_{C=O}$) cm^{-1}.

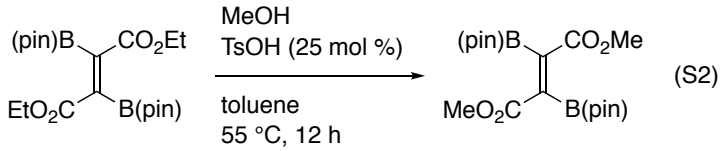


(*Z*)-**8j**

(*Z*)-3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,6-dioxacyclohexadec-3-ene- 2,5-dione [(*Z*)-8j]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.25-4.29 (m, 4H), 1.60-1.69 (m, 4H), 1.31 (s, 24H), 1.26-1.34 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 84.9, 63.5, 28.5, 26.9, 25.6, 24.9, 24.3. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ 28.2. HRMS (APCI, positive) *m/z* calcd for $C_{26}H_{45}B_2O_8^+$ $[M + H]^+$: 507.3295, found: 507.3288. IR (neat) 1724 ($\nu_{C=O}$) cm^{-1}.

Confirmation of the double bond geometry of 8b and 8h

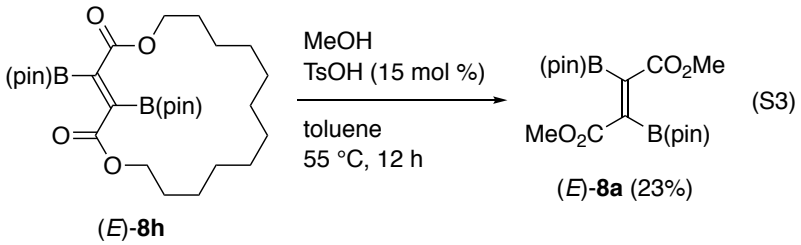
The geometry of the double bond was confirmed by a conversion to stereo-defined (*E*)-**8a** through transesterification.



(*E*)-**8b** (*E*)-**8a** (96%) (S2)

*Transesterification of (E)-**8b** (eq. S2)*: A 10 mL Schlenk flask, equipped with a magnetic stirring bar, was charged with **8b** (43 mg, 0.10 mmol) and *p*-toluenesulfonic

acid monohydrate (4.7 mg, 0.025 mmol). The flask was evacuated and backfilled with nitrogen. Toluene (0.5 mL) and MeOH (2 mL) were added to the flask, and the mixture was heated at 55 °C with stirring for 12 h. After cooling to room temperature, the volatiles were removed from the reaction mixture under reduced pressure. The residue was purified by column chromatography on silica gel (CHROMATOREX DIOL; eluent: hexane:$CHCl_3$ = 3:1) to afford (*E*)-**8a** (39 mg, 96%).



(*E*)-**8h** (*E*)-**8a** (23%)

*Transesterification of (E)-**8h** (eq. S3)*: A 10 mL Schlenk flask, equipped with a magnetic stirring bar, was charged with (*E*)-**8h** (28 mg, 0.053 mmol) and *p*-toluenesulfonic acid monohydrate (1.6 mg, 0.0080 mmol). The flask was evacuated and backfilled with nitrogen. Toluene (0.5 mL) and MeOH (2 mL) were added to the flask, and the mixture was heated at 55 °C with stirring for 12 h. After cooling to room temperature, the volatiles were removed from the reaction mixture under reduced pressure. The residue was purified by column chromatography on silica gel (CHROMATOREX DIOL; eluent: hexane:$CHCl_3$ = 3:1) to afford (*E*)-**8a** (4.8 mg, 23%).

Notes and References

1) For reviews, see: a) Marder, T. B., Norman, N. C., *Top. Catal.* **1998**, *5*, 63. b) Ishiyama, T., Miyaura, N., *J. Organomet. Chem.* **2000**, *611*, 392. c) Dembitsky, V. M., Ali, H. A., Srebnik, M., *Adv. Organomet. Chem.* **2004**, *51*, 193. d) Miyaura, N., *Bull. Chem. Soc. Jpn.* **2008**, *81*, 1535. e) Suginome, M., Ohmura, T., In *Boronic Acids, 2nd Ed.* D. G. Hall Ed. 2011, Wiley-VCH, pp 171. f) Takaya, J., Iwasawa, N., *ACS Catal.* **2012**, *2*, 1993. g) Barbeyron, R., Benedetti, E., Cossy, J., Vasseur, J.-J., Arseniyadis, S., Smietana, M., *Tetrahedron* **2014**, *70*, 8431. h) Neeve, E. C., Geler, S. J., Mkhalid, I. A. I., Westcott, S. A., Marder, T. B., *Chem. Rev.* **2016**, *116*, 9091. i) Cuenca, A. B., Shishido, R., Ito, H., Fernández, E., *Chem. Soc. Rev.* **2017**, *46*, 415.
2) For Pt catalyst, see: a) Ishiyama, T., Matsuda, N., Miyaura, M., Suzuki, A., *J. Am. Chem. Soc.* **1993**, *115*, 11018. b) Ishiyama, T., Matsuda, N., Murata, M., Ozawa, F., Suzuki, A., Miyaura, N., *Organometallics* **1996**, *15*, 713. c) Lesley, G., Nguyen, P., Taylor, N. J., Marder, T. B., Scott, A. J., Clegg, W., Norman, N. C., *Organometallics* **1996**, *15*, 5137. d) Iverson, C. N., Smith, M. R., *Organometallics* **1996**, *15*, 5155. e) Maderna, A., Pritzkow, H., Siebert, W., *Angew. Chem. Int. Ed. Eng.* **1996**, *35*, 1501. f) Anderson, K. M., Lesley, M. J. G., Norman, N. C., Orpen, A. G., Starbuck, J., *New J. Chem.* **1999**, *23*, 1053. g) Mann, G., John, K. D., Baker, R. T., *Org. Lett.* **2000**, *2*, 2105. h) Thomas, R. L., Souza, F. E. S., Marder, T. B., *J. Chem. Soc., Dalton Trans.* **2001**, 1650. i) Ali, H. A., Quntar, A. E. A. A., Goldberg, I., Srebnik, M., *Organometallics* **2002**, *21*, 4533. j) Lillo, V., Mata, J., Ramírez, J., Peris, E., Fernández, E., *Organometallics* **2006**, *25*, 5829. k) Carson, M. W., Giese, M. W., Coghlan, M. J., *Org. Lett.* **2008**, *10*, 2701. l) Prokopcová, H., Ramírez, J., Fernández, E., Kappe, C. O., *Tetrahedron Lett.* **2008**, *49*, 4831. m) Grirrane, A., Corma, A., Garcia, H., *Chem. Eur. J.* **2011**, *17*, 2467. n) Bauer, F., Braunschweig, H., Gruss, K., Kupfer, T., *Organometallics* **2011**, *30*, 2869. o) Jiao, J., Hyodo, K., Hu, H., Nakajima, K., Nishihara, Y., *J. Org. Chem.* **2014**, *79*, 285. p) Hyodo, K., Suetsugu, M., Nishihara, Y., *Org. Lett.* **2014**, *16*, 440. q) Alonso, F., Moglie, Y., Pastor-Pérez, L., Sepúlveda-Escribano, A., *ChemCatChem* **2014**, *6*, 857. r) Khan, A., Asiri, A. M., Kosa, S. A., Garcia, H., Grirrane, A., *J. Catal.* **2015**, *329*, 401. s) Mora-Radó, H., Bialy, L., Czechtizky, W., Méndez, M., Harrity, J. P. A., *Angew. Chem. Int. Ed.* **2016**, *55*, 5834.
3) For Au catalyst, see: a) Chen, Q., Zhao, J., Ishikawa, Y., Asao, N., Yamamoto, Y., Jin, T., *Org. Lett.* **2013**, *15*, 5766. b) Kidonakis, M., Stratakis, M., *Eur. J. Org. Chem.* **2017**, 4265. For Co catalyst, see: c) Adams, C. J., Baber, R. A., Batsanov, A. S., Bramham, G., Charmant, J. P. H., Haddow, M. F., Howard, J. A. K., Lam, W. H., Lin, Z., Marder,

T. B., Norman, N. C., Orpen, A. G., *Dalton Trans.* **2006**, 1370. d) Ferrand, L., Lyu, Y., Rivera-Hernández, A., Fallon, B. J., Amatore, M., Aubert, C., Petit, M., *Synthesis* **2017**, *49*, 3895. For Cu catalyst, see: e) Lillo, V., Fructos, M. R., Ramírez, J., Braga, A. A. C., Maseras, F., Díaz-Requejo, M. M., Pérez, P. J., Fernández, E., *Chem. Eur. J.* **2007**, *13*, 2614. f) Yoshida, H., Kawashima, S., Takemoto, Y., Okada, K., Ohshita, J., Takaki, K., *Angew. Chem. Int. Ed.* **2012**, *51*, 235. For Pd catalyst, see: g) Braunschweig, H., Kupfer, T., Lutz, M., Radacki, K., Seeler, F., Sigritz, R., *Angew. Chem. Int. Ed.* **2006**, *45*, 8048. h) Ansell, M. B., da Silva, V. H. M., Heerdt, G., Braga, A. A. C., Spencer, J., Navarro, O., *Catal. Sci. Technol.* **2016**, *6*, 7461. For Fe catalyst, see: i) Nakagawa, N., Hatakeyama, T., Nakamura, M., *Chem. Eur. J.* **2015**, *21*, 4257. For Ir catalyst, see: j) Iwadate, N., Suginome, M., *J. Am. Chem. Soc.* **2010**, *132*, 2548.

4) Krautwald, S., Bezdek, M. J., Chirik, P. J., *J. Am. Chem. Soc.* **2017**, *139*, 3868.
5) 1-Alkynylphosphonates have been applied to platinum-catalyzed diboration. See ref. 2i.
6) Nagao, K., Ohmiya, H., Sawamura, M., *Org. Lett.* **2015**, *17*, 1304.
7) Verma, A., Snead, R. F., Dai, Y., Slebodnick, C., Yang, Y., Yu, H., Yao, F., Santos, W. L., *Angew. Chem. Int. Ed.* **2017**, *56*, 5111.
8) Morinaga, A., Nagao, K., Ohmiya, H., Sawamura, M., *Angew. Chem. Int. Ed.* **2015**, *54*, 15859.
9) For transition-metal-free diboration of alkynes other than alkynes conjugated with carbonyl groups, see: a) Nagashima, Y., Hirano, K., Takita, R., Uchiyama, M., *J. Am. Chem. Soc.* **2014**, *136*, 8532. b) Yoshimura, A., Takamachi, Y., Han, L.-B., Ogawa, A., *Chem. Eur. J.* **2015**, *21*, 13930. c) Kojima, C., Lee, K.-H., Lin, Z., Yamashita, M., *J. Am. Chem. Soc.* **2016**, *138*, 6662. d) Yoshimura, A., Takamachi, Y., Mihara, K., Saeki, T., Kawaguchi, S., Han, L.-B., Nomoto, A., Ogawa, A., *Tetrahedron* **2016**, *72*, 7832.
10) a) Okinoshima, H., Yamamoto, K., Kumada, M., *J. Organomet. Chem.* **1975**, *86*, C27. b) Sakurai, H., Kamiyama, Y., Nakadaira, Y., *J. Am. Chem. Soc.* **1975**, *97*, 931.
11) a) Mitchell, T. N., Wickenkamp, R., Amamria, A., Dicke, R., Schneider, U., *J. Org. Chem.* **1987**, *52*, 4869. b) Murakami, M., Morita, Y., Ito, Y., *J. Chem. Soc., Chem. Commun.* **1990**, 428.
12) Ansell, M. B., Spencer, J., Navarro, O., *ACS Catal.* **2016**, *6*, 2192.
13) a) Ohmura, T., Morimasa, Y., Suginome, M., *J. Am. Chem. Soc.* **2015**, *137*, 2852. See also: b) Oshima, K., Ohmura, T., Suginome, M., *Chem. Commun.* **2012**, *48*, 8571.
14) a) Wang, G., Zhang, H., Zhao, J., Li, W., Cao, J., Zhu, C., Li, S., *Angew. Chem. Int. Ed.* **2016**, *55*, 5985. b) Zhang, L., Jiao, L., *J. Am. Chem. Soc.* **2017**, *139*, 607. c) Wang,

G., Cao, J., Gao, L., Chen, W., Huang, W., Cheng, X., Li, S., *J. Am. Chem. Soc.* **2017**, *139*, 3904. d) Candish, L., Teders, M., Glorius, F., *J. Am. Chem. Soc.* **2017**, *139*, 7440. e) Chen, D., Xu, G., Zhou, Q., Chung, L. W., Tang, W., *J. Am. Chem. Soc.* **2017**, *139*, 9767. f) Cheng, W.-M., Shang, R., Zhao, B., Xing, W.-L., Fu, Y., *Org. Lett.* **2017**, *19*, 4291.

15) Lee, K., Zhugralin, A. R., Hoveyda, A. H., *J. Am. Chem. Soc.* **2009**, *131*, 7253.
16) a) Diels, O., Alder, K., *Liebigs Ann. Chem.* **1932**, *498*, 16. b) Acheson, R. M., Taylor, G. A., *J. Chem. Soc.* **1960**, 1691. c) Nair, V., Sreekanth, A. R., Abhilash, N., Biju, A. T., Devi, B. R., Menon, R. S., Rath, N. P., Srinivas, R., *Synthesis* **2003**, 1895. For a review, see: d) Nair, V., Deepthi, A., Ashok, D., Raveendran, A. E., Paul, R. R., *Tetrahedron* **2014**, *70*, 3085.
17) Isomerization between *E* and *Z* isomers was not observed under the catalytic conditions.
18) Ugo, R., Cariati, F., La Monica, G., *Inorg. Synth.* **1968**, *11*, 105.
19) Ohmura, T., Morimasa, Y., Suginome, M., *J. Am. Chem. Soc.* **2015**, *137*, 2852.
20) de Léséleuc, M., Collins, S. K., *Chem. Commun.* **2015**, *51*, 10471.
21) Ishiyama, T., Matsuda, N., Miyaura, M., Suzuki, A., *J. Am. Chem. Soc.* **1993**, *115*, 11018.
22) Sheldrick, G. M., SHELX-97. *Programs for Crystal Structure Analysis.*; University of Göttingen: Germany, **1997**.
23) Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G., Spagna, R., *J. Appl. Cryst.* **1999**, *32*, 115.
24) Higashi, T., ABSCOR. *Program for Absorption Correction.*; Rigaku Corporation: Japan, 1995.

Chapter 2

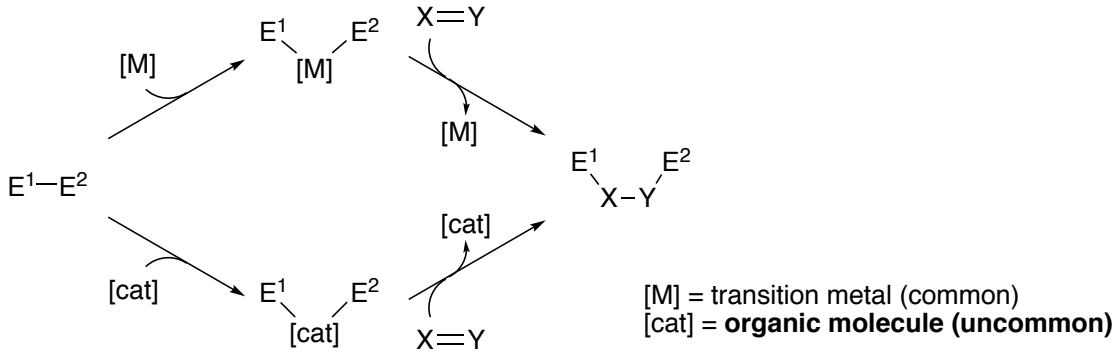
Organocatalytic Diboration Involving "Reductive Addition" of a Boron–Boron σ-Bond to 4,4'-Bipyridine

ABSTRACT

A 4,4'-bipyridine-based catalyst system for diboration of pyrazine derivatives was established. The catalyst cycle consists of the following two steps: (1) reductive addition of the boron–boron bond of bis(pinacolato)diboron to 4,4'-bipyridine to form *N*,*N'*-diboryl-4,4'-bipyridinylidene, and (2) oxidative boryl transfer from the intermediate to pyrazine to give *N*,*N'*-diboryl-1,4-dihydropyrazine with regeneration of 4,4'-bipyridine.

Introduction

Transition metal catalysts have played privileged roles in the development of catalytic additions of nonpolar σ-bonds E^1–E^2 such as H–H, B–B, and Si–Si bonds across carbon–carbon and carbon–heteroatom multiple bonds.[1,2] A key feature of transition metal catalysts is their high ability to activate nonpolar σ-bonds, mainly through oxidative addition to form E^1–[M]–E^2 (Scheme 1, top).[3] This ability has been recently extended to the activation of C–H and C–C bonds, leading to the exciting development of new catalytic transformations.[4]



Scheme 1. Catalytic Addition Reaction of E^1–E^2 to X=Y

On the other hand, rapid progress in organocatalysis has also enabled activation of nonpolar σ-bonds. It has been shown that H–H bond is successfully activated by a frustrated Lewis pair (FLP) catalyst, allowing organocatalytic hydrogenation of carbon–nitrogen and carbon–carbon double bonds.[5,6] Moreover, diboration of alkenes in the presence of a catalytic amount of Lewis bases such as *t*-BuONa or Cs_2CO_3 has been demonstrated.[7,8,9] These new reactions clearly suggest further development of useful transformations through organocatalytic activation of nonpolar σ-bonds.

Is it then possible to generate an intermediate E^1–[cat]–E^2 in organocatalytic addition reactions (Scheme 1, bottom)?[10,11] Because the organocatalyst is formally reduced, the elementary step to form the E^1–[cat]–E^2 species is now regarded as formal "reductive addition." Transfer of E^1 and E^2 from E^1–[cat]–E^2 species to unsaturated organic molecules results in the formation of an addition product. In the current paper, the author discusses the organocatalytic addition proceeding through formation of isolable E^1–[cat]–E^2 intermediates, taking 4,4'-bipyridine-catalyzed diboration of pyrazines as an example.

Suginome group has recently reported that nitrogen-containing aromatic compounds undergo addition of boron reagents to give the dearomatized products.[12,13,14] Silaboration[12a] and hydroboration[12b] of pyridines take place at 50 °C in the presence of palladium and rhodium catalysts. Further, they established an addition of

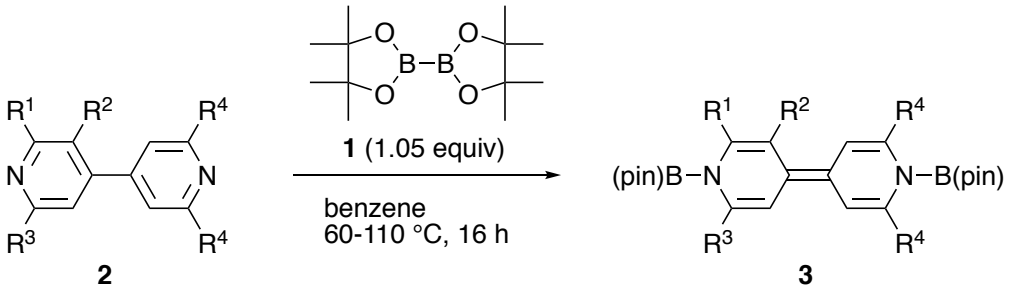
bis(pinacolato)diboron (**1**)[15] to sterically unhindered pyrazines, which proceeds efficiently at room temperature even in the absence of transition metal catalysts.[13] A possible driving force of the reactions is formation of stable boron–nitrogen bonds. The author turned his attention to diboration of bipyridines, in which aromaticity at the two aromatic rings is lost simultaneously.

Results and Discussions

Reaction of 4,4'-bipyridine (**2a**) with **1** (1.05 equiv) was carried out in benzene (entry 1, Table 1). Because two adjacent pyridine rings would lose aromaticity, the addition reaction of **1** into **2a** was expected to be rather unfavorable. However, the author found that the reaction took place efficiently at 110 °C (bath temperature) to give *N*,*N'*-diboryl-4,4'-bipyridinylidene **3a** as a yellow solid in 94% yield after 16 h.[16] Although dearomatized **3a** was air and moisture sensitive both in a solid state and in a solution, it was thermally stable and could be stored under inert atmosphere at room temperature for at least 3 months.

Substituted 4,4'-bipyridines **2b**-**2j** were subjected to reaction with **1** in benzene (entries 2-10, Table 1). 2-Methyl-4,4'-bipyridine (**2b**) underwent addition of **1** at 110 °C to afford **3b** (entry 2). The isolated yield was moderate, because of its relatively high solubility in benzene. 2-Chloro- (**2c**) and 2-fluoro-4,4'-bipyridine (**2d**) were more reactive than **2a** and **2b**: the reaction with **1** proceeded smoothly at 60 °C to give **3c** and **3d** in moderate yields (entries 3 and 4).[17] Addition of **1** to 3-methoxy-, 3-chloro-, and 3-fluoro-4,4'-bipyridines **2e**-**2g** also took place at 60-110 °C to give **3e**-**3g** (entries 5-7). 2,6-Dimethyl-4,4'-bipyridine (**2h**) afforded the corresponding product in moderate yield (entry 8), whereas no reaction took place for 2,2',6,6'-tetramethyl-4,4'-bipyridine (**2j**, entry 10). These results indicate that steric hindrance around both nitrogen atoms retards the reaction, as observed in the reaction of pyrazine.[13] 2,6-Dichloro-4,4'-bipyridine (**2i**) may undergo the addition of **1** at 60 °C, but no desired adduct **3i** was obtained probably because **3i** was unstable under these conditions (entry 9).

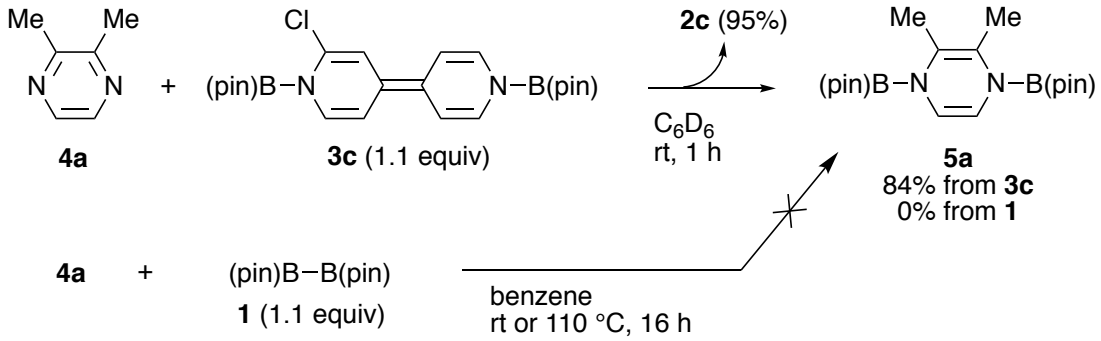
Table 1. Addition of **1** to 4,4'-Bipyridines **2**[a]



entry	R^1	R^2	R^3	R^4		temp (°C)	% yield[b]
1	H	H	H	H	**2a**	110	94 (**3a**)
2	Me	H	H	H	**2b**	110	50 (**3b**)
3	Cl	H	H	H	**2c**	60	65 (**3c**)
4	F	H	H	H	**2d**	60	60 (**3d**)
5	H	OMe	H	H	**2e**	110	62 (**3e**)
6	H	Cl	H	H	**2f**	60	56 (**3f**)
7	H	F	H	H	**2g**	60	93[f] (**3g**)
8	Me	H	Me	H	**2h**	110	61 (**3h**)
9	Cl	H	Cl	H	**2i**	60	0[g] (**3i**)
10	Me	H	Me	Me	**2j**	110	0[h] (**3j**)

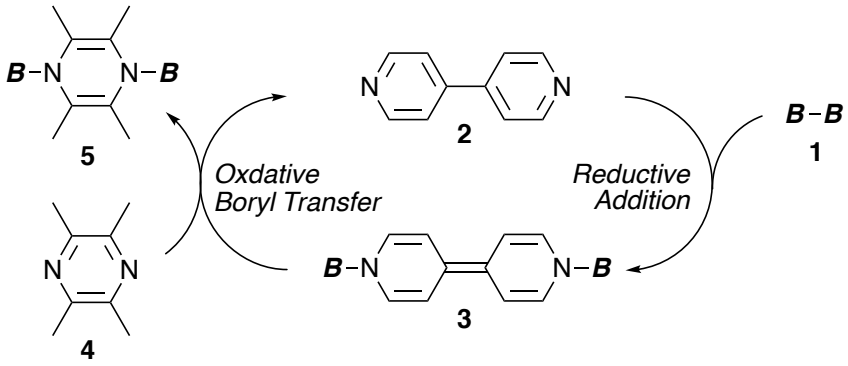
[a] **1** (0.21 mmol) and **2** (0.20 mmol) in benzene (0.4 mL) was stirred at 110 °C for 16 h. [b] Isolated yield based on **2**. [c] For 4 h with **1** (1.5 equiv). [d] For 10 h. [e] For 24 h. [f] Including $O[B(pin)]_2$ (4%) that could not be removed. [g] No desired product was obtained. [h] No reaction took place.

In the course of examination of the synthesis and reactivity of **3**, the author found that boryl groups on **3c** migrated to 2,3-dimethylpyrazine (**4a**) within 1 h even at room temperature, giving *N,N'*-diboryl-1,4-dihydropyrazine **5a** in high yield (Scheme 2, top).[18] It is interesting to note that no borylation of **4a** took place in the attempted direct diboration with diboron **1** at room temperature or even under reflux in benzene (Scheme 2, bottom).[13] The formation of **5a** was accompanied by quantitative formation of bipyridine **2c** (Scheme 2, top). These results suggest that the diboration of sterically demanding pyrazine is enabled by using a diboration product of bipyridine **2** as an intermediate, instead of using diboron **1** directly.

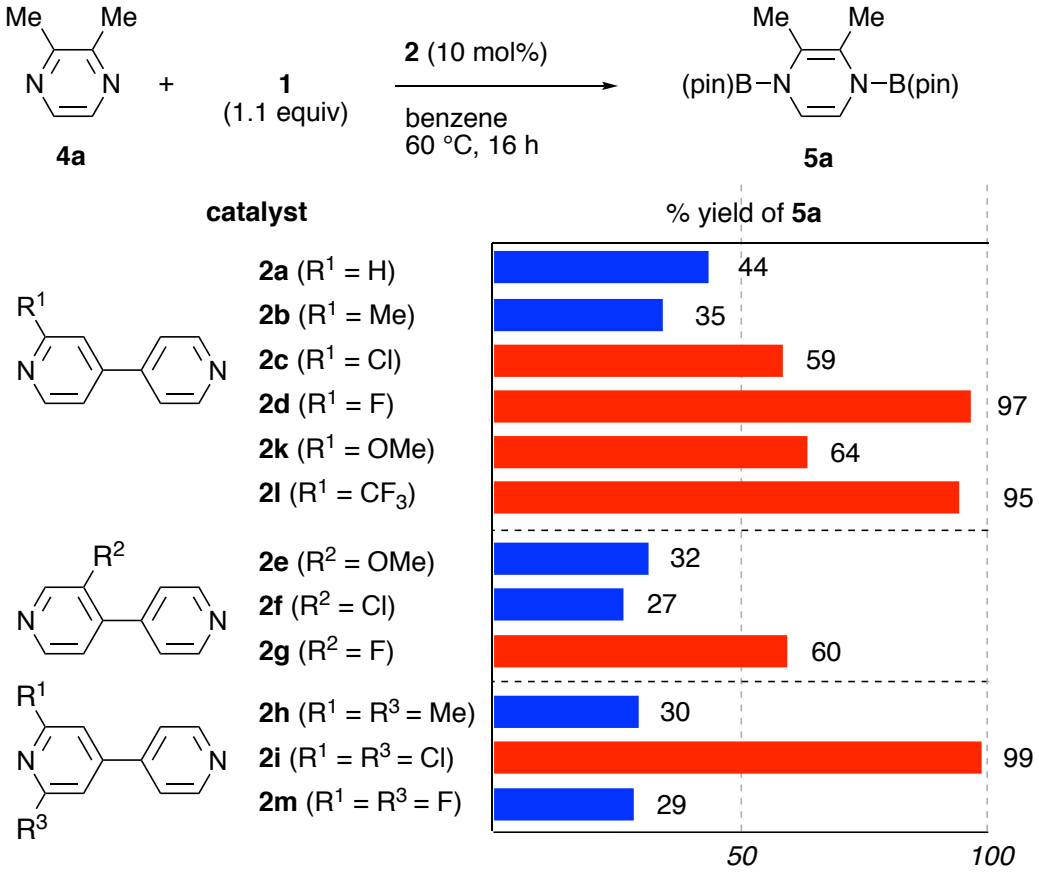


Scheme 2. Boryl Transfer from **3i** to **4a**

A new organocatalytic diboration of sterically hindered **4** was designed as shown in Scheme 3. The catalytic cycle consists of the following two steps: (1) reductive addition of the B–B bond of diboron **1** to bipyridine **2** to form a dearomatized intermediate **3**, and (2) oxidative boryl transfer from **3** to pyrazine **4** to give **5** with regeneration of **2**. This catalytic reaction indeed worked well as expected. A reaction of **4a** with **1** (1.1 equiv) in benzene at 60 °C in the presence of **2a** (R^1 = H, 10 mol %) afforded **5a** in 44% yield (Scheme 4). As mentioned above, no reaction took place in the absence of **2**, even at 110 °C (Scheme 2, bottom), indicating significant rate acceleration was accomplished by the catalytic amount of **2a**.



Scheme 3. Possible Catalytic Cycle



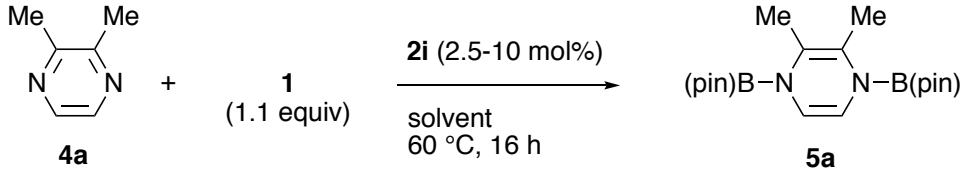
Scheme 4. Screening of Catalysts for Addition of **1** to **4a**[a]

The catalyst efficiency of 4,4'-bipyridines was highly dependent on the substituent at the C2 position (Scheme 4). The yields of **5a** were improved by **2c** (R^1 = Cl), **2d** (R^1 = F), **2k** (R^1 = OMe), and **2l** (R^1 = CF_3), whereas **2b** (R^1 = Me) resulted in lower yields. These results indicate that the catalyst efficiency correlates closely with inductive effect of the substituents, and that the bipyridines bearing stronger electron-withdrawing groups achieve higher catalyst efficiency (**2d**, **2l** > **2c**, **2k** > **2a** > **2b**). The substituents at the C3 positions also affected the catalyst efficiency. The product **5a** was formed in moderate yield with **2g** (R^2 = F), whereas **2e** (R^2 = OMe) and **2f** (R^2 = Cl) gave **5a** in low yields. These results indicate the effect of the dihedral angle made by the two pyridine rings. The author finally found that **2i** (R^1 = R^3 = Cl) showed the highest catalyst efficiency. Unexpectedly low catalyst efficiency of **2m** (R^1 = R^3 = F) could be attributed to excessive electron deficiency on the pyridine ring because of the double substitution of the fluorine atoms.

The catalyst efficiency was improved further by changing the solvent from benzene to THF or cyclohexane (Table 2). The **2i**-catalyzed reaction in cyclohexane resulted in

high yield formation of **5a** with lower catalyst loading (5 mol %, entry 4). Dearomatized **5a** was thermally stable and could be purified by distillation. The catalyst loading could be reduced to 2.5 mol %, although elevated reaction temperature (80 °C) was required (entry 5).

Table 2. Reaction Conditions for **2i**-Catalyzed Addition of **1** to **4a**[a]



4a **5a**

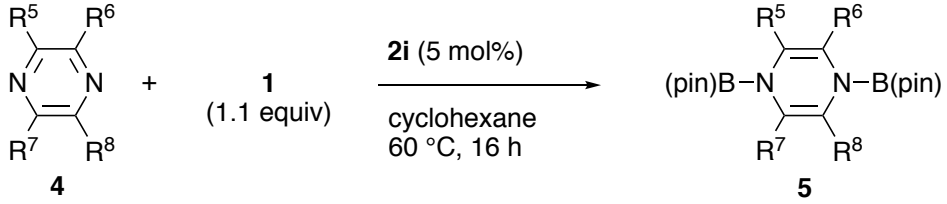
entry	catalyst loading (mol %)	solvent	% yield[b]
1	10	benzene	99
2	5	benzene	66
3	5	THF	91
4	5	cyclohexane	99 (84)[c]
5	2.5	cyclohexane	71

[a] **1** (0.44 mmol), **2i** (0.010-0.040 mmol), and **4a** (0.40 mmol) were stirred in a solvent (0.2 mL) at 60 °C for 16 h unless otherwise noted. [b] ^{1}H NMR yield based on **4a**. [c] Isolated yield based on **4a**. [d] At 80 °C.

To examine the scope of the catalytic B–B bond cleavage by 4,4'-bipyridine, pyrazine derivatives **4b**-**4i** were subjected to diboration with **1** using **2i** as a catalyst (Table 3).[19,20] In the presence of **2i** (5 mol %), 2-ethoxy-3-methylpyrazine (**4b**) underwent addition of **1** in cyclohexane at 60 °C to give **5b** in good yield (entry 1). In diboration of 2,3-dichloropyrazine (**4c**), **2c** gave better catalyst efficiency than **2i** (entry 2). Although 2,5-dimethylpyrazine (**4d**) reacted with **1** slowly in the absence of the catalyst to afford **5d** (23% yield at 110 °C), the reaction was accelerated in the presence of **2i**, resulting in the formation of **5d** in 88% yield at 60 °C (entry 3). Diboration of trisubstituted 2-chloro-3,6-dimethylpyrazine (**4e**) also took place efficiently to give **5e** in high yield (entry 4). 2,3,5,6-Tetramethylpyrazine (**4f**) did not undergo diboration at all under these conditions, probably because of its steric hindrance. However, the author found that **4f** underwent diboration by increasing the catalyst loading (10 mol %) at an elevated reaction temperature (110 °C) (entry 5). Also, diborylated efficiently were sterically demanding 2,3-disubstituted quinoxalines **4g** and **4h** and phenazine (**4i**), in which the loss of aromaticity is reduced because of the polycyclic aromatic structure (entries 6-8).[21] It

should again be noted that, without catalys **2i**, no or only inefficient reactions took place (Table 3, yields in parentheses).

Table 3. Organocatalytic Diboration of Pyrazine Derivatives **4**[a]



entry	R^5	R^6	R^7	R^8		% yield	
1	OEt	Me	H	H	**4b**	78 (0)	**5b**
2	Cl	Cl	H	H	**4c**	57 (0)	**5c**
3	Me	H	H	Me	**4d**	88 (23)	**5d**
4	Me	Cl	H	Me	**4e**	82 (0)	**5e**
5	Me	Me	Me	Me	**4f**	58 (0)	**5f**
6	–CH=CH–CH=CH–		Me	Me	**4g**	83 (<1)	**5g**
7	–CH=CH–CH=CH–		Ph	Ph	**4h**	96 (0)	**5h**
8	–CH=CH–CH=CH–		–CH=CH–CH=CH–		**4i**	99 (0)	**5i**

[a] **1** (0.44 mmol), **2i** (0.020 mmol, 5 mol %), and **4** (0.40 mmol) were stirred in cyclohexane (0.2 mL) at 60 °C for 16 h uless otherwise noted. [b] Isolated yield based on **4**. In parenthesis, ^{1}H NMR yield of the reaction at 110 °C for 16 h in the absence of the bipyridine catalyst. [c] **2c** (9 mol %) was used instead of **2i**. [d] **2i** (10 mol%). [e] At 110 °C. [f] A gram scale reaction of **4g** (3 mmol) in THF using **2i** (8 mol %), giving **5g** (1.0g).

Conclusion

In conclusion, the author has established a conceptually new organocatalytic addition reaction of nonpolar E^1–E^2 bond to unsaturated substrates with formation of E^1–[cat]–E^2 as a key catalyst intermediate via reductive addition of E^1–E^2 bond to 4,4'-bipyridines used as an organocatalyst. Remarkable catalyst efficiency of 4,4'-bipyridines has been demonstrated in diboration of sterically hindered pyrazines. The mechanism involving organocatalytic σ-bond activation would be a new tool for organic transformations as an alternative to transition-metal-catalyzed reactions.

Experimental Section

General

All reactions were performed in glove box or using Schlenk technique under an atmosphere of nitrogen with magnetic stirring. Materials were weighted by an electric balance, Sartorius CPA225D (readability: 0.01 mg). Column chromatography was performed with Ultra Pure Silica Gel (SILICYCLE, pH 7.0, 40-63 μm, 60 Å). ^{1}H NMR spectra were recorded on a Varian 400-MR (399.89 MHz) spectrometer. ^{13}C NMR spectra were recorded on a Varian 400-MR (100.55 MHz) spectrometer. ^{11}B NMR spectra were recorded on a Varian 400-MR (128.30 MHz) spectrometer. ^{1}H NMR data were reported as follows: chemical shifts in ppm downfield from tetramethylsilane, multiplicity (s = singlet, d = doublet, t = triplet, and m = multiplet), coupling constant (*J*), and integration. ^{13}C and ^{11}B NMR data were reported in ppm downfield from tetramethylsilane (^{13}C) and BF_3•OEt_2 (^{11}B), respectively. High resolution mass spectra (HRMS) were recorded on Thermo Scientific Exactive (ESI, DART) and JEOL JMS-MS700 (EI) spectrometers.

Materials

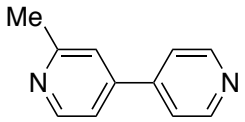
Solvents and reagents: Tetrahydrofuran (THF, Wako) was degassed by purging with argon (15 min + 10 min) and then dried by The Ultimate Solvent System (GlassContour). Benzene (Wako) and cyclohexane (nacalai tesque) were distilled over calcium hydride and degassed prior to use. Bis(pinacolato)diboron (**1**) was purchased from ChemICHIBA or Boron Molecular and was purified by recrystallization from pentane before use. 2,3-Dimethylpyrazine (**4a**, TCI), 2-ethoxy-3-methylpyrazine (**4b**, TCI), 2,3-dichloropyrazine (**4c**, TCI), 2,5-dimethylpyrazine (**4d**, TCI), and 3-chloro-2,5-dimethylpyrazine (**4e**, TCI) were distilled before use. 2,3,5,6-Tetramethylpyrazine (**4f**, TCI), 2,3-dimethylquinoxaline (**4g**, TCI), 2,3-diphenylquinoxaline (**4h**, Wako), and phenazine (**4i**, TCI) ware used as received from commercial sources.

4,4'-Bipyridines: 4,4'-Bipyridine (**2a**, TCI) was used as received from commercial sources. Substituted 4,4'-bipyridines **2b-j** and **2m** were prepared by Suzuki-Miyaura coupling of the corresponding 4-halopyridines with 4-pyridylboron reagents. 2-Methoxybipyridine (**2k**) was prepared by coupling reaction of **2c** with sodium methoxide. 2-Trifluoromethylpyridine (**2l**) was obtained by trifluoromethylation of **2a**.

Preparation of 4-pyridylboronic acid:[22] A mixture of toluene (15 mL), NaOH aq (5N, 15 mL) and H_2O (40 mL) was cooled to 0 ºC. 4-Bromopyridine hydrochloride (9.6 g, 50 mmol, TCI) was added slowly into the mixture with stirring. The resulting mixture was

stirred at 0 °C for 30 min. The organic materials were extracted with toluene (12 mL x 2). After drying over anhydrous sodium sulfate, the toluene solution of 4-bromopyridine was degassed purging with nitrogen. A three-necked round-bottomed flask, equipped with a dropping funnel and a magnetic stirrer bar, was evacuated and backfilled with nitrogen. The toluene solution of 4-bromopyridine, $B(O\textit{i}\text{-}Pr)_3$ (11.6 g, 61 mmol), toluene (40 mL), and THF (20 mL) were added into the flask and the solution was cooled to –78 ºC. *n*-BuLi (1.6 M in hexane, 50 mmol) was added dropwise to the solution via the dropping funnel. After 1 hour stirring, aqueous hydrogen chloride (2 N, 50 mL) was added to the reaction mixture and the resulting mixture was warmed to room temperature. The water layer was collected and neutralized with aqueous sodium hydroxide (5 N). A white precipitate formed was collected and washed with water (20 mL x 2). After dried in vacuo, 4-pyridylboronic acid (4.9 g, 80%) was obtained as a white solid.

General procedure for Suzuki-Miyaura coupling of 4-halopyridines with 4-pyridylboron reagents: A two-necked, round-bottomed flask, equipped with a Dimroth condenser, a rubber septum, and a magnetic stirring bar, was charged with a palladium complex (0.20 mmol), a phosphine ligand (1.0 mmol), a base (30 mmol), a 4-halopyridine (10 mmol), and a 4-pyridylboron reagent (12 mmol). The flask was evacuated and backfilled with nitrogen. 1,4-Dioxane (24 mL) and H_2O (10 mL) were added to the flask. The resulting mixture was reacted at 110 °C using an oil bath with stirring. The reaction was monitored by GC. After cooling to room temperature, the organic materials were extracted with EtOAc, and the extracts were washed with brine. After drying over anhydrous sodium sulfate, the mixture was concentrated. The product **2** was obtained after purification by column chromatography on silica gel.

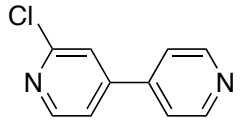


2b

2-Methyl-4,4'-bipyridine (2b)

According to the general procedure, 4-bromo-2-methylpyridine[23] (1.1 g, 6.2 mmol) and 4-pyridylboronic acid (1.0 g, 8.1 mmol) were reacted in 1,4-dioxane/H_2O (16 mL/7 mL) at 110 °C in the presence of $Pd_2(dba)_3$•$CHCl_3$ (52 mg, 0.050 mmol), PCy_3 (34 mg, 0.12 mmol) and K_3PO_4 (2.5 g, 12 mmol). The product **2b** (0.93 g, 91%) was obtained after column chromatography on silica gel (eluent: CH_2Cl_2:MeOH = 19:1). **2b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60-8.74 (m, 2H), 8.62 (d, J = 5.2 Hz, 1H), 7.50-7.53 (m, 2H), 7.39 (s, 1H), 7.33 (d, J = 5.2 Hz, 1H) 2.65 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 150.8,

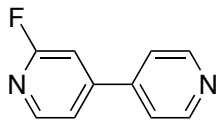
150.1, 146.1, 146.0, 121.6, 121.2, 118.7, 24.7. HRMS (ESI, positive) *m/z* calcd for $C_{11}H_{11}N_2^+$ $[M + H]^+$: 171.0917, found: 171.0913.



2c

2-Chloro-4,4'-bipyridine (2c)

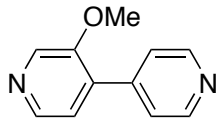
According to the general procedure, 2-chloro-4-iodopyridine (2.4 g, 10 mmol, TCI) and 4-pyridylboronic acid (1.5 g, 12 mmol) were reacted in 1,4-dioxane/H_2O (24 mL/10 mL) at 110 °C in the presence of $Pd(OAc)_2$ (44 mg, 0.20 mmol), PPh_3 (229 mg, 0.87 mmol) and K_2CO_3 (4.1 g, 30 mmol). The product **2c** (1.1 g, 59%) was obtained after column chromatography on silica gel (eluent: CH_2Cl_2:MeOH = 19:1). **2c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, J = 5.2 Hz, 2H), 8.52 (d, J = 5.2 Hz, 1H), 7.58 (s, 1H), 7.50-7.53 (m, 2H), 7.46 (dd, J = 5.2, 1.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.8, 150.9, 150.7, 148.9, 144.5, 122.3, 121.5, 120.4. HRMS (ESI, positive) *m/z* calcd for $C_{10}H_8ClN_2^+$ $[M + H]^+$: 191.0371, found: 191.0366.



2d

2-Fluoro-4,4'-bipyridine (2d)

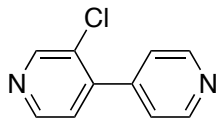
According to the general procedure, 2-fluoro-4-iodopyridine[24] (2.3 g, 10 mmol) and 4-pyridylboronic acid (1.5 g, 12 mmol) were reacted in 1,4-dioxane/H_2O (24 mL/10 mL) at 110 °C in the presence of $Pd_2(dba)_3$•$CHCl_3$ (54 mg, 0.050 mmol), PCy_3 (35 mg, 0.12 mmol) and K_3PO_4 (4.3 g, 20 mmol). The product **2d** (1.3 g, 74%) was obtained after column chromatography on silica gel (eluent: CH_2Cl_2:MeOH = 19:1). **2d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76-8.80 (m, 2H), 8.37 (d, J = 5.2 Hz, 1H), 7.58 (d, J = 5.2 Hz, 2H), 7.44 (ddd, J_{HH} = 5.2, 1.6 Hz, $^3J_{HF}$ = 1.6 Hz, 1H), 7.17-7.19 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7 (d, $^1J_{CF}$ = 238.4 Hz), 151.0 (d, $^3J_{CF}$ = 8.5 Hz), 150.2, 148.9 (d, $^3J_{CF}$ = 15.5 Hz), 145.3, 121.8, 119.5 (d, $^4J_{CF}$ = 3.8 Hz), 107.6 (d, $^2J_{CF}$ = 38.0 Hz). HRMS (ESI, positive) *m/z* calcd for $C_{10}H_8FN_2^+$ $[M + H]^+$: 175.0666, found: 175.0664.



2e

3-Methoxy-4,4'-bipyridine (2e)

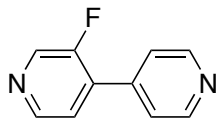
According to the general procedure, 4-bromopyridine hydrochloride (0.98 g, 5.1 mmol) and (3-methoxypyridin-4-yl)boronic acid[25] (1.3 g, 8.3 mmol) were reacted in 1,4-dioxane/H_2O (16 mL/7 mL) at 110 °C in the presence of $Pd_2(dba)_3$•$CHCl_3$ (55 mg, 0.050 mmol), PCy_3 (34 mg, 0.12 mmol) and K_3PO_4 (2.6 g, 12 mmol). The product **2e** (410 mg, 43%) was obtained after column chromatography on silica gel (eluent: CH_2Cl_2:EtOAc:MeOH = 18:6:1). **2e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68-7.71 (m, 2H), 8.43 (s, 1H), 8.38 (d, J = 4.8 Hz, 1H), 7.51-7.53 (m, 2H), 7.28 (d, J = 4.8 Hz, 1H), 3.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5, 149.3, 144.3, 143.1, 134.7, 134.6, 124.1, 124.0, 56.5. HRMS (ESI, positive) *m/z* calcd for $C_{11}H_{11}N_2O^+$ $[M + H]^+$: 187.0866, found: 187.0865.



2f

3-Chloro-4,4'-bipyridine (2f)

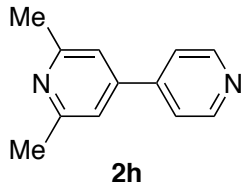
According to the general procedure, 3-chloro-4-iodopyridine[26] (3.3 g, 14 mmol) and 4-pyridylboronic acid (2.1 g, 17 mmol) were reacted in 1,4-dioxane/H_2O (32 mL/8 mL) at 110 °C in the presence of $Pd(OAc)_2$ (53 mg, 0.24 mmol), PPh_3 (216 mg, 0.82 mmol) and K_2CO_3 (6.1 g, 44 mmol). The product **2f** (1.4 g, 53%) was obtained after column chromatography on silica gel (eluent: CH_2Cl_2:MeOH = 19:1). **2f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74-8.76 (m, 2H), 8.72 (d, J = 0.4 Hz, 1H), 8.59 (d, J = 4.8 Hz, 1H), 7.39-7.41 (m, 2H), 7.27 (dd, J = 4.8, 0.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6, 150.2, 148.3, 145.0, 144.4, 129.9, 124.8, 123.6. HRMS (ESI, positive) *m/z* calcd for $C_{10}H_8ClN_2^+$ $[M + H]^+$: 191.0371, found: 191.0365.



2g

3-Fluoro-4,4'-bipyridine (2g)

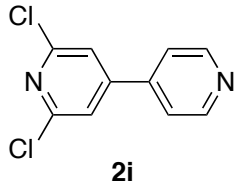
According to the general procedure, 3-fluoro-4-iodopyridine エラー! ブックマークが定義されていません。 (2.2 g, 10 mmol) and 4-pyridylboronic acid (1.5 g, 12 mmol) were reacted in 1,4-dioxane/H_2O (24 mL/10 mL) at 110 °C in the presence of $Pd_2(dba)_3$•$CHCl_3$ (45 mg, 0.040 mmol), PCy_3 (29 mg, 0.10 mmol) and K_3PO_4 (4.3 g, 20 mmol). The product **2g** (1.1 g, 65%) was obtained after column chromatography on silica gel (eluent: CH_2Cl_2:MeOH = 19:1). **2g**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75-8.78 (m, 2H), 8.61 (d, $^3J_{HF}$ = 2.4 Hz, 1H), 8.55 (dd, J = 4.8, 0.8 Hz, 1H), 7.54-7.57 (m, 2H), 7.43 (dd, J_{HH} = 4.8 Hz, $^4J_{HF}$ = 6.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5 (d, $^1J_{CF}$ = 258.6 Hz), 150.3, 146.5 (d, $^3J_{CF}$ = 9.4 Hz), 141.0, 139.6 (d, $^2J_{CF}$ = 24.8 Hz), 133.2 (d, $^3J_{CF}$ = 10.1 Hz), 123.5 (d, $^2J_{CF}$ = 31.7 Hz), 123.3. HRMS (ESI, positive) *m/z* calcd for $C_{10}H_8FN_2^+$ $[M + H]^+$: 175.0666, found: 175.0661.



2h

2,6-Dimethyl-4,4'-bipyridine (2h)

According to the general procedure, 4-bromopyridine hydrochloride (0.20 g, 1.0 mmol, TCI) and 2,6-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine[27] (0.29 g, 1.2 mmol) were reacted in 1,4-dioxane/H_2O (1.5 mL/0.5 mL) at 80 °C in the presence of $Pd(OAc)_2$ (23 mg, 0.10 mmol), PPh_3 (134 mg, 0.51 mmol) and K_2CO_3 (0.43 g, 3.1 mmol). The product **2h** (76 mg, 40%) was obtained after column chromatography on silica gel (eluent: $CHCl_3$:AcOEt = 1:3). **2h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69-8.72 (m, 2H), 7.49-7.51 (m, 2H), 7.19 (s, 2H), 2.61 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 150.7, 146.4, 146.3, 121.6, 118.3, 24.7. HRMS (ESI, positive) *m/z* calcd for $C_{12}H_{13}N_2^+$ $[M + H]^+$: 185.1073, found: 185.1069.

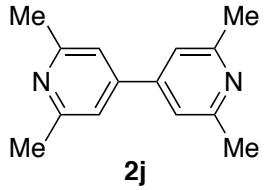


2i

2,6-Dichloro-4,4'-bipyridine (2i)

According to the general procedure, 4-bromopyridine hydrochloride (1.8 g, 9.0 mmol, TCI) and 2,6-dichloro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine[27] (2.7 g,

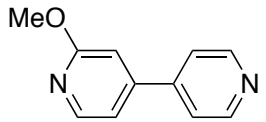
9.7 mmol) were reacted in 1,4-dioxane/H_2O (32 mL/8 mL) at 110 °C in the presence of $Pd(OAc)_2$ (33 mg, 0.15 mmol), PPh_3 (163 mg, 0.73 mmol) and K_2CO_3 (4.3 g, 31 mmol). The product **2i** (0.82 g, 41%) was obtained after column chromatography on silica gel (eluent: CH_2Cl_2:EtOAc:MeOH = 24:8:1). **2i**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, J = 5.2 Hz, 2H), 7.54 (d, J = 5.2 Hz, 2H), 7.51 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9, 150.8, 150.2, 144.3, 121.8, 121.0. HRMS (ESI, positive) *m/z* calcd for $C_{10}H_7Cl_2N_2^+$ [M + H]$^+$: 224.9981, found: 224.9975.



2j

2,2',6,6'-Tetramethyl-4,4'-bipyridine (2j)

According to the general procedure, 2,6-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine[28] (121 mg, 0.52 mmol), and 4-bromo-2,6-dimethylpyridine[29] (90 mg, 0.48 mmol) were reacted in 1,4-dioxane/H_2O (0.8 mL/0.3 mL) at 110 °C in the presence of $Pd(OAc)_2$ (13 mg, 0.06 mmol), PPh_3 (67 mg, 0.25 mmol) and K_2CO_3 (277 mg, 2.0 mmol). The product **2j** (79 mg, 0.37 mmol, 77%) was obtained after column chromatography on silica gel (eluent: CH_2Cl_2:EtOAc = 1:4). **2j**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (s, 4H), 2.60 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 147.0, 118.4, 24.6. HRMS (ESI, positive) *m/z* calcd for $C_{14}H_{17}N_2^+$ [M + H]$^+$: 213.1386, found: 213.1380.

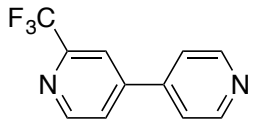


2k

2-Methoxy-4,4'-bipyridine (2k)

2-Chloro-4,4'-bipyridine **2c** (103 mg, 0.54 mmol) and sodium methoxide (47 mg, 0.86 mmol) were reacted in toluene (1.0 mL) at 110 °C in the presence of $Ni(cod)_2$ (21 mg, 0.080 mmol) and dppf (69 mg, 0.13 mmol). After 24 hours, the reaction mixture was cooled at room temperature, then extracted with EtOAc. The organic layer was dried with sodium sulfate. The product **2k** (50 mg, 50%) was obtained after column chromatography on silica gel (eluent: CH_2Cl_2: MeOH = 19:1). **2k**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71-8.73 (m, 2H), 8.28 (d, J = 5.2 Hz, 1H), 7.50-7.53 (m, 2H), 7.11 (dd, J = 5.6, 1.6 Hz, 1H),

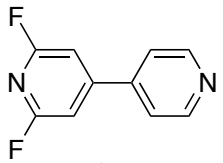
6.97-6.99 (m, 1H), 4.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 150.6, 148.4, 148.0, 146.0, 121.6, 114.9, 108.9, 53.8. HRMS (ESI, positive) *m/z* calcd for $C_{11}H_{11}N_2O^+$ [M + H]$^+$: 187.0866, found: 187.0863.



2l

2-Trifluoromethyl-4,4'-bipyridine (2l)

The titled compound was synthesized trifluoromethylation of **2a** according to the reported method.[30] A Schlenk tube was charged 4,4'-bipyridine (0.19 mg, 1.2 mmol), zinc trifluoromethanesulfinate (0.83 mg, 2.5 mmol, Aldrich) and CH_2Cl_2/H_2O (5 mL/2 mL). The mixture was cooled at 0 ºC, and added *tert*-butyl hydroperoxide (5.5 M in decane, 0.9 mL, Fluka,) dropwise with vigorous stirring. The reaction mixture was warmed to room temperature and stirred for 19h. Then the mixture was added saturated $NaHCO_3$ aq (30 mL) and extracted with CH_2Cl_2 (30 mL x 3). The organic layer was dried with Na_2SO_4. The product **2l** (39 mg, 14%) was obtained after column chromatography on silica gel (eluent: CH_2Cl_2:EtOAc = 1:1). **2l**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, J = 4.8 Hz, 1H), 8.80 (d, J = 4.4 Hz, 2H), 7.92 (s, 1H), 7.74 (d, J = 4.8 Hz, 1H), 7.58 (d, J = 4.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.10, 150.97, 149.6 (q, $^2J_{CF}$ = 34.8 Hz), 147.6, 144.5, 124.2, 121.6, 121.5 (q, $^1J_{CF}$ = 272.5 Hz), 118.5 (q, $^3J_{CF}$ = 2.3 Hz). HRMS (ESI, positive) *m/z* calcd for $C_{11}H_8F_3N_2^+$ [M + H]$^+$: 225.0634, found: 225.0626.



2m

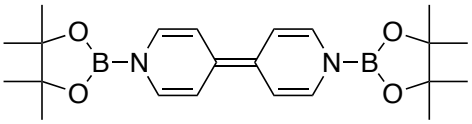
2,6-Difluoro-4,4'-bipyridine (2m)

According to the general procedure, 4-bromopyridine hydrochloride (0.49 g, 2.5 mmol, TCI) and 2,6-difluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine[27] [containing 20% of 2,6-difluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine, 0.56 g, 2.3 mmol] were reacted in THF/H_2O (5 mL/1 mL) at 70 °C in the presence of $Pd(OAc)_2$ (9.3 mg, 0.041 mmol), PPh_3 (57 mg, 0.22 mmol) and K_2CO_3 (0.70 mg, 5.1 mmol). The product **2m** (152 mg, 34%) was obtained after column chromatography on silica gel (eluent: CH_2Cl_2:EtOAc = 4:1). **2m**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78-8.81

(m, 2H), 7.50-7.52 (m, 2H), 7.07 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6 (dd, $^1J_{CF}$ = 246.2 Hz, $^3J_{CF}$ = 15.5 Hz), 155.3, 150.4, 144.3, 121.7, 104.4 (dd, $^2J_{CF}$ = 27.1 Hz, $^4J_{CF}$ = 13.9 Hz). HRMS (ESI, positive) *m/z* calcd for $C_{10}H_7F_2N_2^+$ $[M + H]^+$: 193.0572, found: 193.0567.

Addition of Bis(pinacolato)diboron (1) to 4,4'-Bipyridines 2 (Table 1)

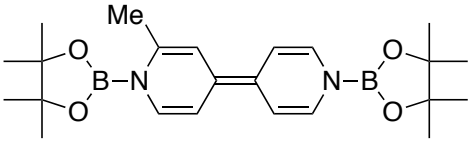
General Procedure: In a glove box, a glass tube (outside diameter: 20 mm) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with **1** (0.21 mmol), **2** (0.20 mmol), and benzene (0.4 mL). Mixing them at room temperature generally resulted in a colored homogeneous solution (dark orange-brown or yellow). The tube was sealed by the stopcock and was taken out from the glove box. The mixture was stirred at 60 or 110 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). A colored precipitate (bright orange or yellow) was formed on the inside wall of the tube. After 16 h, the tube was taken into glove box, and the solution was removed from the tube by decantation. The solid was rinsed with benzene (0.5 mL x 3) and pentane (0.5 mL x 3) then dried in vacuo. The *N*,*N*'-diboryl-4,4'-bipyridinylidene **3** was obtained as a yellow solid with high purity. Although **3a**-**h** were extremely sensitive to air and moisture both in a solid state and in a solution, they were thermally stable and could be stored under inert atmosphere at room temperature for at least 3 months. The NMR measurements were performed using a NMR sample tube having PTFE stopcock (J. Young). The HRMS experiments (EI or DART) were accomplished by minimizing exposure to air.



3a

1,1'-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*,1'*H*-4,4'-bipyridinylidene (3a, entry 1)

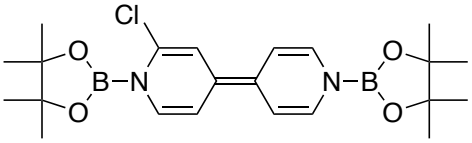
According to the *General Procedure*, 4,4'-bipyridine (**2a**) (32 mg, 0.21 mmol) was reacted with **1** (57 mg, 0.22 mmol) in benzene (0.4 mL) at 110 °C for 16 h. The product **3a** (80 mg, 94%) was obtained as an air sensitive yellow solid. All attempts to purify the compound by distillation were failed. **3a**: ^{1}H NMR (400 MHz, C_6D_6) δ 6.57 (d, J = 8.4 Hz, 4H), 5.74 (d, J = 8.4 Hz, 4H), 0.95 (s, 24H). ^{13}C NMR (101 MHz, C_6D_6) δ 126.1, 112.5, 110.3, 83.9, 24.6. ^{11}B NMR (128 MHz, C_6D_6) δ 23.1 (broad). HRMS (EI, positive) *m/z* calcd for $C_{22}H_{32}B_2N_2O_4^+$ $[M]^+$: 410.2543, found: 410.2552.



3b

2-Methyl-1,1'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*,1'*H*-4,4'-bipyridinylidene (3b, entry 2)

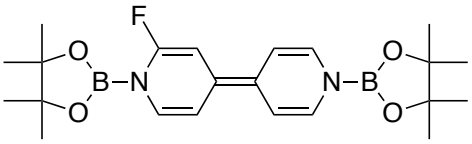
According to the *General Procedure*, 2-methyl-4,4'-bipyridine (**2b**) (57 mg, 0.30 mmol) was reacted with **1** (88 mg, 0.35 mmol) in benzene (0.4 mL) at 110 °C for 16 h. The product **3b** (44 mg, 50%) was obtained as an air sensitive yellow solid. **3b**: ^{1}H NMR (400 MHz, C_6D_6) δ 6.82 (d, J = 8.0 Hz, 1H), 6.62 (dd, J = 8.0, 1.2 Hz, 1H), 6.56 (dd, J = 8.0, 1.2 Hz, 1H), 5.90 (dd, J = 8.4, 2.4 Hz, 1H), 5.84 (dd, J = 8.4, 2.4 Hz, 1H), 5.81 (dd, J = 8.4, 2.4 Hz, 1H), 5.66 (d, J = 0.8 Hz, 1H), 2.09 (d, J = 0.8 Hz, 3H), 0.97 (s, 12H), 0.94 (s, 12H). ^{13}C NMR (101 MHz, C_6D_6) δ 135.0, 126.1, 125.8, 113.7, 110.7, 110.4, 110.3, 109.3, 83.8, 83.1, 24.6, 24.5, 22.6. ^{11}B NMR (128 MHz, C_6D_6) δ 23.1 (broad). HRMS (DART, positive) *m/z* calcd for $C_{23}H_{35}B_2N_2O_4^+$ $[M + H]^+$: 425.2777, found: 425.2770.



3c

2-Chloro-1,1'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*,1'*H*-4,4'-bipyridinylidene (3c, entry 3)

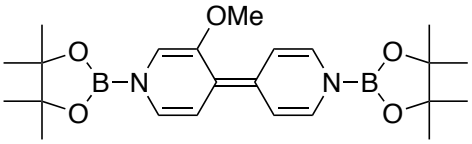
According to the *General Procedure*, 2-chloro-4,4'-bipyridine (**2c**) (38 mg, 0.20 mmol) was reacted with **1** (77 mg, 0.30 mmol) in benzene (0.4 mL) at 60 °C for 4 h. The product **3c** (58 mg, 65%) was obtained as an air sensitive yellow solid. **3c**: ^{1}H NMR (400 MHz, C_6D_6) δ 6.66 (d, J = 8.0 Hz, 1H), 6.56 (dd, J = 8.0, 1.2 Hz, 1H), 6.52 (dd, J = 8.0, 1.2 Hz, 1H), 5.99 (d, J = 2.4 Hz, 1H), 5.67 (dd, J = 8.0, 2.4 Hz, 1H), 5.65 (dd, J = 8.0, 2.4 Hz, 1H), 5.56 (dd, J = 8.0, 2.4 Hz, 1H), 0.98 (s, 12H), 0.94 (s, 12H). ^{13}C NMR (101 MHz, C_6D_6) δ 126.9, 126.8, 114.2, 112.5, 112.0, 110.1, 109,9, 109.6, 84.0, 83.7, 24.54, 24.47 (two peaks may be overlapped with the peaks of C_6D_6). ^{11}B NMR (128 MHz, C_6D_6) δ 23.0 (broad). HRMS (DART, positive) *m/z* calcd for $C_{22}H_{32}B_2ClN_2O_4^+$ $[M + H]^+$: 445.2231, found: 445.2211.



3d

2-Fluoro-1,1'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*,1'*H*-4,4'-bipyridinylidene (**3d, entry 4**)

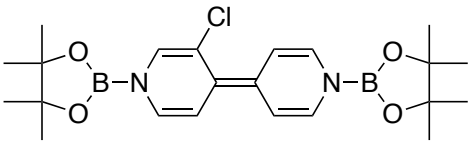
According to the *General Procedure*, 2-fluoro-4,4'-bipyridine (**2d**) (35 mg, 0.20 mmol) was reacted with **1** (55 mg, 0.22 mmol) in benzene (0.4 mL) at 60 °C for 10 h. The product **3d** (51 mg, 60%) was obtained as an air sensitive yellow solid. **3d**: ^{1}H NMR (400 MHz, C_6D_6) δ 6.52-5.56 (m, 3H), 5.65-5.74 (m, 2H), 5.49 (dd, J = 8.8, 2.4 Hz, 1H), 5.39 (dd, J = 2.0 Hz, $^{3}J_{HF}$ = 12.0 Hz, 1H), 0.96 (s, 12H), 0.95 (s, 12H). ^{13}C NMR (101 MHz, C_6D_6) δ 153.3 (d, $^{1}J_{CF}$ = 253.2 Hz), 126.7, 126.0, 125.7, 114.0 (d, $^{3}J_{CF}$ = 7.0 Hz), 111.9 (d, $^{3}J_{CF}$ = 5.4 Hz), 110.4, 110.2, 110.1, 88.3 (d, $^{2}J_{CF}$ = 21.7 Hz), 84.0, 83.8, 24.6, 24.5. ^{11}B NMR (128 MHz, C_6D_6) δ 22.7 (broad). HRMS (DART, positive) *m/z* calcd for $C_{22}H_{32}B_2FN_2O_4^+$ $[M + H]^+$: 429.2527, found: 429.2517.



3e

3-Methoxy-1,1'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*,1'*H*-4,4'-bipyridinylidene (**3e, entry 5**)

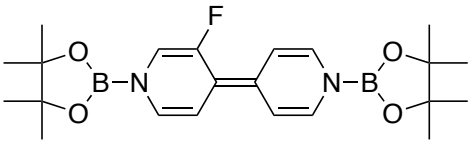
According to the *General Procedure*, 3-methoxy-4,4'-bipyridine (**2e**) (38 mg, 0.20 mmol) was reacted with **1** (61 mg, 0.24 mmol) in benzene (0.4 mL) at 110 °C for 16 h. The product **3e** (55 mg, 62%) was obtained as an air sensitive yellow solid. **3e**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.28 (dd, J = 8.4, 2.4 Hz, 1H), 6.60-6.68 (m, 3H), 6.21 (d, J = 1.2 Hz, 1H), 5.88 (d, J = 8.0 Hz, 1H), 5.87 (dd, J = 8.4, 2.4 Hz, 1H), 3.10 (s, 3H), 1.00 (s, 12H), 0.94 (s, 12H). ^{13}C NMR (101 MHz, C_6D_6) δ 149.2, 127.1, 125.2, 124.1, 114.4, 114.0, 111.0, 110.3, 109.2, 107.0, 83.9 (O*C*Me$_2$, overlapped), 54.8, 24.61, 24.55. ^{11}B NMR (128 MHz, C_6D_6) δ 23.0 (broad). HRMS (DART, positive) *m/z* calcd for $C_{23}H_{35}B_2N_2O_5^+$ $[M + H]^+$: 441.2727, found: 441.2724.



3f

3-Chloro-1,1'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*,1'*H*-4,4'-bipyridinylidene (**3f, entry 7**)

According to the *General Procedure*, 3-chloro-4,4'-bipyridine (**2f**) (39 mg, 0.20 mmol) was reacted with **1** (55 mg, 0.21 mmol) in benzene (0.4 mL) at 60 °C for 24 h. The product **3f** (51 mg, 56%) was obtained as an air sensitive yellow solid. **3f**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.35 (dd, J = 8.4, 2.4 Hz, 1H), 6.77 (d, J = 1.2 Hz, 1H), 6.63 (dd, J = 8.4, 1.2 Hz, 1H), 6.58 (dd, J = 8.4, 1.2 Hz, 1H), 6.37 (dd, J = 8.0, 1.2 Hz, 1H) 5.74 (dd, J = 8.4, 2.4 Hz, 1H), 5.70 (d, J = 8.0 Hz, 1H), 0.93 (s, 12H), 0.91 (s, 12H). ^{13}C NMR (101 MHz, C_6D_6) δ 127.6, 127.2, 126.0, 124.2, 119.6, 116.3, 112.4, 111.4, 110.8, 109.9, 84.2, 84.1, 24.52, 24.47. ^{11}B NMR (128 MHz, C_6D_6) δ 23.0 (broad). HRMS (DART, positive) *m/z* calcd for $C_{22}H_{32}B_2ClN_2O_4^+$ $[M + H]^+$: 445.2231, found: 445.2228.

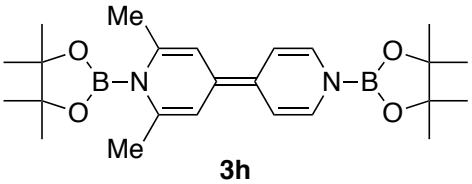


3g

3-Fluoro-1,1'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*,1'*H*-4,4'-bipyridinylidene (**3g, entry 8**)

According to the *General Procedure*, 3-fluoro-4,4'-bipyridine (**2g**) (34 mg, 0.20 mmol) was reacted with **1** (55 mg, 0.21 mmol) in benzene (0.4 mL) at 60 °C for 16 h. The product **3g** was obtained as an air sensitive yellow solid as a mixture of (pin)B–O–B(pin) (**S1**)[31] [80 mg, **3g** (93%) + **S1** (4%), calculated based on ^{1}H NMR analysis in C_6D_6]. Complete removal of **S1** by washing benzene and pentane was failed. **3g**: ^{1}H NMR (400 MHz, C_6D_6) δ 6.75 (dd, J = 8.4, 2.4 Hz, 1H), 6.58-6.65 (m, 2H), 6.56 (d, J = 8.0 Hz, 1H), 6.44 (d, 8.0 Hz, 1H), 5.67-5.73 (m, 2H), 0.93 (s, 12H), 0.92 (s, 12 H). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.32 (dd, J = 8.4, 1.6 Hz, 1H), 6.13-6.23 (m, 4H), 5.66 (dd, J = 8.0 Hz, $^{5}J_{HF}$ = 9.2 Hz, 1H), 5.63 (dd, J = 8.4, 2.0 Hz, 1H), 1.252 (s, 12H), 1.246 (s, 12H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 153.9 (d, $^{1}J_{CF}$ = 240.8 Hz), 127.9, 126.4 (d, $^{4}J_{CF}$ = 3.8 Hz), 125.1, 112.0 (d, $^{3}J_{CF}$ = 6.2 Hz), 111.8 (d, $^{3}J_{CF}$ = 18.5 Hz), 111.4 (d, $^{2}J_{CF}$ = 44.9 Hz), 109.9 (d, $^{4}J_{CF}$ = 10.8 Hz), 109.0, 105.6 (d, $^{2}J_{CF}$ = 15.4 Hz), 84.7, 84.6, 24.8 (CH_3, overlapped). Assignments of $^{2}J_{CF}$, $^{3}J_{CF}$, and $^{4}J_{CF}$ were based on DEPT. ^{13}C NMR data in C_6D_6 is not given because of

low solubility. ^{11}B NMR (128 MHz, C_6D_6) δ 23.0 (broad). HRMS (DART, positive) *m/z* calcd for $C_{22}H_{32}B_2FN_2O_4^+$ $[M + H]^+$: 429.2527, found: 429.2514. **S1**[31]: ^{1}H NMR (400 MHz, C_6D_6) δ 1.01 (s, 24H). ^{13}C NMR (101 MHz, C_6D_6) δ 82.9, 24.6. ^{11}B NMR (128 MHz, C_6D_6) δ 22.6.



3h

2,6-Dimethyl-1,1'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*,1'*H*-4,4'-bipyridinylidene (3h, entry 8)

According to the *General Procedure*, 2,6-dimethyl-4,4'-bipyridine (**2h**) (36 mg, 0.20 mmol) was reacted with **1** (53 mg, 0.21 mmol) in benzene (0.4 mL) at 110 °C for 16 h. The product **3h** (53 mg, 61%) was obtained as an air sensitive yellow solid. **3h**: ^{1}H NMR (400 MHz, C_6D_6) δ 6.62 (d, J = 8.4 Hz, 2H), 5.94 (d, J = 8.4 Hz, 2H), 5.74 (s, 2H), 2.12 (s, 6H), 0.98 (s, 12H), 0.94 (s, 12H). ^{13}C NMR (101 MHz, C_6D_6) δ 136.3, 125.8, 114.6, 111.0, 110.8, 110.4, 83.8, 82.6, 24.6, 24.3, 23.5. ^{11}B NMR (128 MHz, C_6D_6) δ 23.2 (broad). HRMS (DART, positive) *m/z* calcd for $C_{24}H_{37}B_2N_2O_4^+$ $[M + H]^+$: 439.2934, found: 439.2931.

Reaction of 2,6-dichloro-4,4'-bipyridine (2i) with 1 (entry 9)

According to the *General Procedure*, 2,6-dichloro-4,4'-bipyridine (**2i**) (45 mg, 0.20 mmol) was reacted with **1** (114 mg, 0.45 mmol) in benzene (0.4 mL) at 60 °C. Although **2i** was consumed after 16 h, no desired product **3i** was formed, which was confirmed by ^{1}H NMR analysis of the reaction mixture. Similar result was also obtained in the reaction at room temperature.

Reaction of 2,2',6,6'-tetramethyl-4,4'-bipyridine (2j) with 1 (entry 10)

According to the *General Procedure*, 2,2',6,6'-tetramethyl-4,4'-bipyridine (**2j**) (34 mg, 0.16 mmol) was reacted with **1** (45 mg, 0.18 mmol) in benzene (0.4 mL) at 110 °C. However, no reaction took place at all after 16 h, which was confirmed by ^{1}H NMR analysis of the reaction mixture.

Boryl Transfer from 3c to 2,3-Dimethylpyrazine (4a) (Scheme 2, top)

In a glove box, a 4-mL vial, equipped with a magnetic stirring bar, was charged with **3c** (50 mg, 0.11 mmol), 2,3-dimethylpyrazine (**4a**, 11 mg, 0.10 mmol), and C_6D_6 (1.0 mL).

The mixture was reacted at room temperature with magnetic stirring. After 1 h, dibenzyl ether (10 mg, 0.050 mmol, internal standard) was added to the solution. ^{1}H NMR analysis of the resulting mixture indicated formation of *N*,*N'*-diboryl-1,4-dihydropyrazine **5a** (84%) and 2-chloro-4,4'-bipyridine (**2c**, 95%). For characterization data of **5a**, see section 7.

Reaction of 4a with 1 in the Absence of 2 (Scheme 2, bottom)

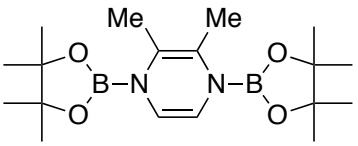
2,3-Dimethylpyrazine (**4a**, 21 mg, 0.20 mmol) was stirred with **1** (56 mg, 0.22 mmol) in benzene (0.2 mL) at room temperature. No reaction took place after 16 h, which was confirmed by ^{1}H NMR analysis of the reaction mixture. The reaction did not proceed at all even at 110 °C (bath temperature) for 16 h.

Screening of Catalyst for Addition of 1 to 4a (Scheme 4)

General Procedure: In a glove box, a glass tube (outside diameter: 20 mm) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with **1** (0.44 mmol), **4a** (0.40 mmol), **2** (0.040 mmol) and benzene (0.2 mL). The tube was sealed by the stopcock and was taken out from the glove box. The mixture was stirred at 60 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). After 16 h, the tube was cooled to room temperature, and dibenzyl ether (40 mg, internal standard) was added to the solution. The resulting mixture was performed to ^{1}H NMR analysis to determine the yield of **5a**. For characterization data of **5a**, see section 7.

Reaction Conditions for 2i-Catalyzed Addition of 1 to 4a (Table 2)

General Procedure: In a glove box, a glass tube (outside diameter: 20 mm) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with **1** (0.44 mmol), **4a** (0.40 mmol), **2i** (0.010-0.040 mmol) and solvent (0.2 mL). The tube was sealed by the stopcock and was taken out from the glove box. The mixture was stirred at 60 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). After 16 h, the tube was cooled to room temperature, and dibenzyl ether (39.6 mg, internal standard) was added to the solution. The resulting mixture was performed to ^{1}H NMR analysis to determine the yield of **5a**.



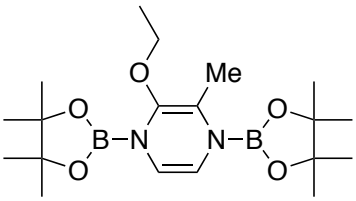
5a

2,3-Dimethyl-1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyrazine (**5a, entry 4**)

In a glove box, a glass tube (outside diameter: 20 mm) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with **1** (116 mg, 0.45 mmol), **4a** (42 mg, 0.39 mmol), **2i** (4.5 mg, 0.020 mmol) and cyclohexane (0.2 mL). The tube was sealed by the stopcock and was taken out from the glove box. The mixture was stirred at 60 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). After 16 h, the tube was cooled to room temperature and the crude mixture was transferred to a flask for Kugelrhor under atmosphere of nitrogen. The product **5a** (120 mg, 84%) was obtained as an air sensitive white solid after distillation (135 °C/0.15 mmHg). **5a**: ^{1}H NMR (400 MHz, C_6D_6) δ 6.15 (s, 2H), 2.02 (s, 6H), 1.01 (s, 24H). ^{13}C NMR (101 MHz, C_6D_6) δ 120.2, 117.3, 82.5, 24.6, 16.7. ^{11}B NMR (128 MHz, C_6D_6) δ 22.7 (broad). HRMS (DART, positive) *m/z* calcd for $C_{18}H_{33}B_2N_2O_4^+$ $[M + H]^+$: 363.2621, found: 363.2610.

Organocatalytic Diboration of Pyrazine Derivatives 4 (Table 3)

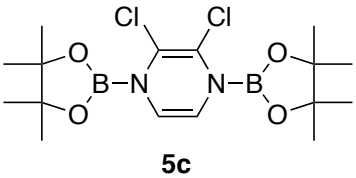
General Procedure: In a glove box, a glass tube (outside diameter: 20 mm) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with **1** (0.44 mmol), **4** (0.40 mmol), **2i** (4.5 mg, 0.020 mmol) and cyclohexane (0.2 mL). The tube was sealed by the stopcock and was taken out from the glove box. The mixture was stirred at 60 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). After 16 h, the tube was cooled to room temperature and the crude mixture was transferred to a flask for Kugelrhor under atmosphere of nitrogen. The product **5** was obtained after distillation under reducing pressure. Although **5a-i** were sensitive to air and moisture, they were more stable than **3a-h**. The relative stability under air was increased in the order of **3a-h** < **5a-f** < **5g-i**. The NMR measurements were performed using a NMR sample tube having PTFE stopcock (J. Young). The HRMS experiments for **5a-f** (DART) were accomplished by minimizing exposure to air.



5b

2-Ethoxy-3-methyl-1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyrazine (**5b, entry 1**)

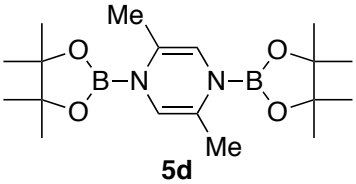
According to the *General Procedure*, 2-ethoxy-3-methylpyrazine (**4b**) (56 mg, 0.41 mmol) was reacted with **1** (113 mg, 0.44 mmol) in cyclohexane (0.2 mL) at 60 °C for 16 h. The product **5b** (125 mg, 78%) was obtained as an air sensitive white solid after distillation by Kugelrhor (125 °C/0.10 mmHg). **5b**: ^{1}H NMR (400 MHz, C_6D_6) δ 6.06 (d, J = 5.4 Hz, AB pattern, 1H), 6.05 (d, J = 5.4 Hz, AB pattern, 1H), 3.78 (q, J = 7.2 Hz, 2H), 2.18 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H), 1.01 (s, 12H), 1.00 (s, 12H). ^{13}C NMR (101 MHz, C_6D_6) δ 138.0, 117.6, 116.1, 109.8, 82.5 (O*C*Me$_2$, overlapped), 66.2, 24.63, 24.59, 15.1, 14.2. ^{11}B NMR (128 MHz, C_6D_6) δ 22.4 (broad). HRMS (DART, positive) *m/z* calcd for $C_{19}H_{35}B_2N_2O_5^+$ $[M + H]^+$: 393.2727, found: 393.2714.



5c

2,3-Dichloro-1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyrazine (**5c, entry 2**)

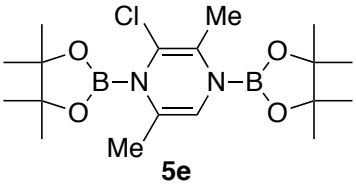
According to the *General Procedure* using **2c** (7.0 mg, 0.037 mmol, 9 mol %) instead of **2i**, 2,3-dichloropyrazine (**4c**) (61 mg, 0.41 mmol) was reacted with **1** (115 mg, 0.45 mmol) in cyclohexane (0.2 mL) at 60 °C for 16 h. The product **5c** (95 mg, 57%) was obtained as an air sensitive white solid after distillation by Kugelrhor (130 °C/0.10 mmHg). **5c**: ^{1}H NMR (400 MHz, C_6D_6) δ 5.92 (s, 2H), 0.96 (s, 24H). ^{13}C NMR (101 MHz, C_6D_6) δ 118.8, 117.7, 83.7, 24.5. ^{11}B NMR (128 MHz, C_6D_6) δ 22.6 (broad). HRMS (DART, positive) *m/z* calcd for $C_{16}H_{27}B_2Cl_2N_2O_4^+$ $[M + H]^+$: 403.1529, found: 403.1518.



5d

2,5-Dimethyl-1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyrazine (5d, entry 3)

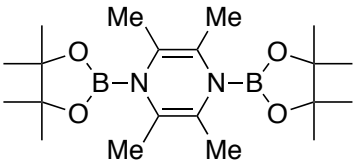
According to the *General Procedure*, 2,5-dimethylpyrazine (**4d**) (43 mg, 0.40 mmol) was reacted with **1** (115 mg, 0.45 mmol) in cyclohexane (0.2 mL) at 60 °C for 16 h. The product **5d** (128 mg, 88%) was obtained as an air sensitive white solid after distillation by Kugelrhor (135 °C/0.15 mmHg). **5d**: ^{1}H NMR (400 MHz, C_6D_6) δ 5.79 (d, J = 1.2 Hz, 2H), 1.90 (d, J = 1.2 Hz, 6H), 1.00 (s, 24H). ^{13}C NMR (101 MHz, C_6D_6) δ 122.8, 113.3, 82.3, 24.6, 18.2. ^{11}B NMR (128 MHz, C_6D_6) δ 22.6 (broad). HRMS (DART, positive) *m/z* calcd for $C_{18}H_{33}B_2N_2O_4^+$ $[M + H]^+$: 363.2621, found: 363.2610.



5e

3-Chloro-2,5-dimethyl-1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyrazine (5e, entry 4)

According to the *General Procedure*, 3-chloro-2,5-dimethylpyrazine (**4e**) (58 mg, 0.40 mmol) was reacted with **1** (116 mg, 0.46 mmol) in cyclohexane (0.2 mL) at 60 °C for 16 h. The product **5e** (133 mg, 82%) was obtained as an air sensitive white solid after distillation by Kugelrhor (115 °C/0.10 mmHg). **5e**: ^{1}H NMR (400 MHz, C_6D_6) δ 6.07 (d, J = 1.2 Hz, 1H), 2.23 (d, J = 1.2 Hz, 3H), 2.04 (s, 3H), 1.01 (s, 12H), 0.95 (s,12H). ^{13}C NMR (101 MHz, C_6D_6) δ 126.7, 126.6, 118.8, 116.4, 82.9, 82.8, 24.64, 24.57, 17.2, 16.8. ^{11}B NMR (128 MHz, C_6D_6) δ 22.8 (broad). HRMS (DART, positive) *m/z* calcd for $C_{18}H_{31}B_2ClN_2O_4^+$ $[M]^+$: 396.2153, found: 396.2139.

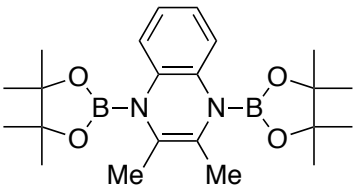


5f

2,3,5,6-Tetramethyl-1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyrazine (5f, entry 5)

According to the *General Procedure* using **2i** (8.9 mg, 0.040 mmol, 10 mol %), 2,3,5,6-tetramethylpyrazine (**4f**) (56 mg, 0.41 mmol) was reacted with **1** (115 mg, 0.45 mmol) in cyclohexane (0.2 mL) at 60 °C for 16 h. The product **5f** (93 mg, 58%) was obtained as an

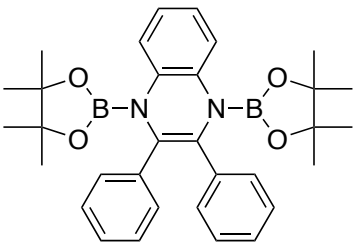
air sensitive white solid after distillation by Kugelrhor (130 °C/0.10 mmHg). **5f**: ^{1}H NMR (400 MHz, C_6D_6) δ 2.13 (s, 12H), 1.04 (s, 24H). ^{13}C NMR (101 MHz, C_6D_6) δ 125.5, 82.0, 24.6, 17.3. ^{11}B NMR (128 MHz, C_6D_6) δ 23.1 (broad). HRMS (DART, positive) *m/z* calcd for $C_{20}H_{37}B_2N_2O_4^+$ $[M + H]^+$: 391.2934, found: 391.2922.



5g

2,3-Dimethyl-1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydroquinoxaline (**5g, entry 6**)

According to the *General Procedure* using **2i** (55 mg, 0.24 mmol, 8 mol %), 2,3-dimethylquinoxaline (**4g**) (0.47 g, 3.0 mmol) was reacted with **1** (0.80 g, 3.1 mmol) in THF (3.0 mL) at 60 °C for 16 h in the presence of **2i** (55 mg, 0.24 mmol). The product **5g** (1.0 g, 83%) was obtained as a relatively air sensitive white solid after distillation by Kugelrhor (140 °C/0.10 mmHg). **5g**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.69-7.72 (m, 2H), 6.98-7.02 (m, 2H), 2.13 (s, 6H) 1.00 (s, 24H). ^{13}C NMR (101 MHz, C_6D_6) δ 139.4, 125.3, 123.4, 121.8, 82.7, 24.6, 17.6. ^{11}B NMR (128 MHz, C_6D_6) δ 23.4 (broad). HRMS (DART, positive) *m/z* calcd for $C_{22}H_{35}B_2N_2O_4^+$ $[M + H]^+$: 413.2777, found: 413.2764.

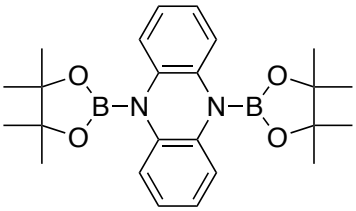


5h

2,3-Diphenyl-1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydroquinoxaline (**5h, entry 7**)

According to the *General Procedure*, 2,3-diphenylquinoxaline (**4h**) (112 mg, 0.40 mmol) was reacted with **1** (115 mg, 0.45 mmol) in cyclohexane (0.2 mL) at 60 °C for 16 h. The product **5h** (206 mg, 96%) was obtained as a relatively air sensitive white solid after distillation by Kugelrhor (185 °C/0.10 mmHg). **5h**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.91-7.96 (m, 2H), 7.56-7.59 (m, 4H), 7.09-7.13 (m, 2H), 6.94-6.99 (m, 4H), 6.87-6.92 (m,

2H), 0.83 (s, 24H). ^{13}C NMR (101 MHz, C_6D_6) δ 140.4, 139.2, 133.4, 131.5, 127.1, 127.0, 123.9, 121.1, 82.7, 24.3. ^{11}B NMR (128 MHz, C_6D_6) δ 23.4 (broad). HRMS (DART, positive) *m/z* calcd for $C_{32}H_{39}B_2N_2O_4^+$ $[M + H]^+$: 537.3090, found: 537.3075.

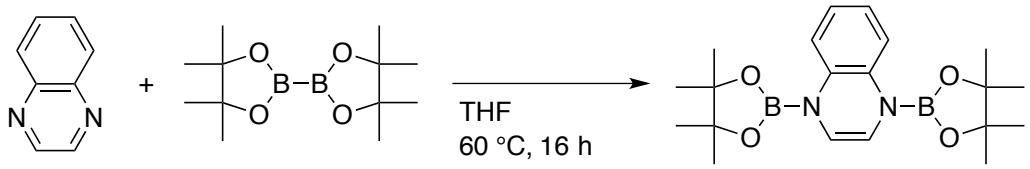


5i

5,10-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5,10-dihydrophenazine (5i, entry 8)

According to the *General Procedure*, phenazine (**4i**) (75 mg, 0.41 mmol) was reacted with **1** (116 mg, 0.45 mmol) in cyclohexane (0.4 mL) at 60 °C for 16 h. The product **5i** (181 mg, 99%) was obtained as a relatively air sensitive white solid after distillation by Kugelrhor (170 °C/0.10 mmHg). **5i**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.72-7.75 (m, 4H), 6.99-7.02 (m, 4H), 0.98 (s, 24H). ^{13}C NMR (101 MHz, C_6D_6) δ 138.6, 123.9, 122.7, 83.2, 24.6. ^{11}B NMR (128 MHz, C_6D_6) δ 23.8 (broad). HRMS (ESI, positive) *m/z* calcd for $C_{24}H_{33}B_2N_2O_4^+$ $[M + H]^+$: 435.2621, found: 435.2613.

Diboration of Quinoxaline (S2)



S2 **1** **S3** (57%)

Quinoxaline (**S2**, TCI, used after recrystallization from petroleum ether) underwent addition of **1** in THF at 60 °C to give **S3** in the absence of 4,4'-bipyridine catalyst. In a glove box, a glass tube (outside diameter: 20 mm) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with **1** (125 mg, 0.49 mmol), **S2** (55 mg, 0.42 mmol) and THF (0.2 mL). The tube was sealed by the stopcock and was taken out from the glove box. The mixture was stirred at 60 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). After 16 h, the tube was cooled to room temperature and the crude mixture was transferred to a flask for Kugelrhor under atmosphere of nitrogen. The product **S3** (92 mg, 57%) was obtained as a relatively air sensitive white solid after distillation by Kugelrhor (150 °C/0.15

mmHg). 1,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydroquinoxaline (**S3**): ^{1}H NMR (400 MHz, C_6D_6) δ 7.76-7.79 (m, 2H), 6.82-6.85 (m, 2H), 6.09 (s, 2H), 0.99 (s, 24H). ^{13}C NMR (101 MHz, C_6D_6) δ 135.2, 124.0, 120.2, 115.7, 83.1, 24.6. ^{11}B NMR (128 MHz, C_6D_6) δ 23.2 (broad). HRMS (ESI, positive) *m/z* calcd for $C_{20}H_{30}B_2N_2O_4^+$ $[M]^+$: 384.2392, found: 384.2372.

Note and References

1) *The Handbook of Homogeneous Hydrogenation*, de Vries, J. G., Elsevier, C. J. eds., Wiley-VCH, 2006.
2) Reviews on transition-metal-catalyzed addition of B–B and Si–Si bonds: (a) Beletskaya, I., Moberg, C. *Chem. Rev.* **2006**, *106*, 2320. (b) Burks, H. E., Morken, J. P. *Chem. Commun.,* **2007**, 4717. (c) Suginome, M., Ohmura, T., In *Boronic Acids second edition*, ed. D. Hall, Wiley-VCH, 2011, vol. 1, pp 171. (d) Takaya, J., Iwasawa, N. *ACS Catal.,* **2012**, *2*, 1993.
3) (a) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 2nd ed., John Wiley and Sons: New York, 1994. (b) Hartwig, J. F. *Organotransition Metal Chemistry*, University Science Books, California, 2010. For oxidative addition of B–B to Rh(I) and Pt(0), see: (c) Ishiyama, T., Matsuda, N., Miyaura, N., Suzuki, A. *J. Am. Chem. Soc.,* **1993**, *115*, 11018. (d) Nguyen, P., Lesley, G., Taylor, N. J., Marder, T. B., Pickett, N. L., Clegg, W., Elsegood, M. R. J., Norman, N. C. *Inorg. Chem.,* **1994**, *33*, 4623. (e) Ishiyama, T., Matsuda, N., Murata, M., Ozawa, F., Suzuki, A., Miyaura, N. *Organometallics,* **1996**, *15*, 713.
4) Selected reviews: (a) Jun, C.-H. *Chem. Soc. Rev.,* **2004**, *33*, 610. (b) Murakami, M., Matsuda, T. *Chem. Commun.,* **2011**, *47*, 1100. (c) Arockiam, P. B., Bruneau, C., Dixneuf, P. H. *Chem. Rev.,* **2012**, *112*, 5879. (d) Yamaguchi, J., Yamaguchi, A. D., Itami, K. *Angew. Chem. Int. Ed.,* **2012**, *51*, 8960. (e) Kuhl, N., Hopkinson, M. N., Wencel-Delord, J., Glorius, F. *Angew. Chem. Int. Ed.,* **2012**, *51*, 10236.
5) (a) Chase, P. A., Welch, G. C., Jurca, T., Stephan, D. W. *Angew. Chem. Int. Ed.,* **2007**, *46*, 8050. (b) Spies, P., Schwendemann, S., Lange, S., Kehr, G., Fröhlich, R., Erker, G. *Angew. Chem. Int. Ed.,* **2008**, *47*, 7543. For recent reviews, see: (c) Stephan, D. W. *Org. Biomol. Chem.,* **2012**, *10*, 5740. (d) Stephan, D. W., Erker, G. *Top. Curr. Chem.,* **2013**, *332*, 85. (e) Hounjet, L. J., Stephan, D. W. *Org. Process Res. Dev.,* **2014**, *18*, 385. (f) Paradies, J. *Angew. Chem. Int. Ed.,* **2014**, *53*, 3552.
6) *t*-BuOK-catalyzed hydrogenation of ketones with H_2 has also been reported. (a)

Walling, C., Bollyky, L. *J. Am. Chem. Soc.,* **1961**, *83*, 2968. (b) Walling, C., Bollyky, L. *J. Am. Chem. Soc.,* **1964**, *86*, 3750. (c) Berkessel, A., Schubert, T. J. S., Müller, T. N. *J. Am. Chem. Soc.,* **2002**, *124*, 8693.

7) (a) Bonet, A., Pubill-Ulldemolins, C., Bo, C., Gulyás, H., Fernández, E. *Angew. Chem. Int. Ed.,* **2011**, *50*, 7158. (b) Bonet, A., Sole, C., Gulyás, H., Fernández, E. *Org. Biomol. Chem.,* **2012**, *10*, 6621. (c) Blaisdell, T. P., Caya, T. C., Zhang, L., Sanz-Marco, A., Morken, J. P. *J. Am. Chem. Soc.,* **2014**, *136*, 9264. (d) Miralles, N., Cid, J., Cuenca, A. B., Carbó, J. J., Fernández, E. *Chem. Commun.,* **2015**, *51*, 1693. For related diboration using stoichiometric amount of an alkoxide, see: (e) Nagashima, Y., Hirano, K., Takita, R., Uchiyama, M. *J. Am. Chem. Soc.,* **2014**, *136*, 8532.

8) α,β-Unsaturated carbonyl compounds and imines also undergo addition of diboron under organocatalytic conditions, giving β-boryl carbonyl compounds and α-boryl alkylamine derivatives, respectively. (a) Lee, K., Zhugralin, A. R., Hoveyda, A. H. *J. Am. Chem. Soc.,* **2009**, *131*, 7253 and *J. Am. Chem. Soc.,* **2010**, *132*, 12766 (additions & corrections); (b) Bonet, A., Gulyás, H., Fernández, E. *Angew. Chem. Int. Ed.,* **2010**, *49*, 5130. (c) Pubill-Ulldemolins, C., Bonet, A., Bo, C., Gulyás, H., Fernández, E. *Chem. Eur. J.,* **2012**, *18*, 1121. (d) Wu, H., Radomkit, S., O'Brien, J. M., Hoveyda, A. H. *J. Am. Chem. Soc.,* **2012**, *134*, 8277. (e) Solé, C., Gulyás, H., Fernández, E. *Chem. Commun.,* **2012**, *48*, 3769. (f) Wen, K., Chen, J., Gao, F., Bhadury, P. S., Fan, E., Sun, Z. *Org. Biomol. Chem.,* **2013**, *11*, 6350.

9) For reviews, see: (a) Cid, J., Gulyás, H., Carbó, J. J., Fernández, E. *Chem. Soc. Rev.,* **2012**, *41*, 3558. (b) Gulyás, H., Bonet, A., Pubill-Ulldemolins, C., Solé, C., Cid, J., Fernández, E. *Pure Appl. Chem.,* **2012**, *84*, 2219.

10) FLP-catalyzed hydrogenation involves formation of a highly polarized $[H–LA]^-[H–LB]^+$ species as a catalyst intermediate via heterolytic cleavage of H–H bond (LA: Lewis acid; LB: Lewis base). See ref. 5. Related organocatalytic activation of H–Si and H–B bonds: (a) Parks, D. J., Piers, W. E. *J. Am. Chem. Soc.,* **1996**, *118*, 9440. (b) Parks, D. J., Blackwell, J. M., Piers, W. E. *J. Org. Chem.,* **2000**, *65*, 3090. (c) Piers, W., Marwitz, A. J. V., Mercier, L. G. *Inorg. Chem.,* **2011**, *50*, 12252. (d) Eisenberger, P., Bailey, A. M., Crudden, C. M. *J. Am. Chem. Soc.,* **2012**, *134*, 17384.

11) Lewis base-catalyzed diboration involves formation of $sp^2–sp^3$ hybridized diboron as a catalyst intermediate via nucleophilic attack of the Lewis base to the boron center. See ref. 7 and 8. See also following references that involve structurally characterized $sp^2–sp^3$ hybridized diboron: (a) Clegg, W., Dai, C., Lawlor, F. J., Marder, T. B., Nguyen, P., Norman, N. C., Pickett, N. L., Power, W. P., Scott, A. J. *J. Chem. Soc. Dalton Trans.,* **1997**, 839. (b) Gao, M., Thorpe, S. B., Kleeberg, C., Slebodnick, C.,

Marder, T. B., Santos, W. L. *J. Org. Chem.,* **2011**, *76*, 3997. (c) Kleeberg, C. K., Crawford, A. G., Batsanov, A., Hodgkinson, P., Apperley, D. C., Cheung, M. S., Lin, Z., Marder, T. B. *J. Org. Chem.,* **2012**, *77*, 785.

12) (a) Oshima, K., Ohmura, T., Suginome, M. *J. Am. Chem. Soc.,* **2011**, *133*, 7324; (b) Oshima, K., Ohmura, T., Suginome, M. *J. Am. Chem. Soc.,* **2012**, *134*, 3699.

13) Oshima, K., Ohmura, T., Suginome, M. *Chem. Commun.,* **2012**, 48, 8571.

14) Catalytic hydroboration of pyridines reported from other groups: (a) Arrowsmith, M., Hill, M. S., Hadlington, T., Kociok-Köhn, G., Weetman, C. *Organometallics,* **2011**, *30*, 5556. (b) Intemann, J., Lutz, M., Harder, S. *Organometallics,* **2014**, *33*, 5722. (c) Dudnik, A. S., Weidner, V. L., Motta, A., Delferro, M., Marks, T. J. *Nat. Chem.,* **2014**, *6*, 1100. Transition-metal-free addition of Ph_2P–B(pin) to pyridine and acridine: (d) Daley, E. N., Vogels, C. M., Geier, S. J., Decken, A., Doherty, S., Westcott, S. A. *Angew. Chem. Int. Ed.,* **2015**, *54*, 2121.

15) (1) (a) Nöth, H. *Z. Naturforsch.,* **1984**, *39b*, 1463. (b) Ishiyama, T., Murata, M., Ahiko, T., Miyaura, N. *Org. Synth.,* **2000**, *77*, 176.

16) A related compound, *N*,*N'*-bis(dimesitylboryl)-4,4'-bipyridinylidene, has been reported. (a) Lichtblau, A., Kaim, W., Schulz, A., Stahl, T. *J. Chem. Soc., Perkin Trans., 2* **1992**, 1497. (b) Lichtblau, A., Hausen, H.-D., Schwarz, W., Kaim, W. *Inorg. Chem.,* **1993**, *32*, 73.

17) The adducts **3c** and **3d** were relatively unstable under the reaction conditions, thus the reaction at 110 °C resulted in significant degrease of the yields because of product decomposition.

18) For precedents of *N*,*N'*-diboryl-1,4-dihydropyrazines, see refs. 13 and 16.

19) (1) Although dearomatized **5** were air and moisture sensitive, they were thermally stable and could be purified by distillation.

20) There has been much interest in the chemistry of 1,4-dihydropyrazines, including their synthetic utilities and structural features as exemplified below. Applications in inorganic synthesis: (a) Saito, T., Nishiyama, H., Tanahashi, H., Kawakita, K., Tsurugi, H., Mashima, K. *J. Am. Chem. Soc.,* **2014**, *136*, 5161. Studies focused on the antiaromatic character arising from their conjugated cyclic 8π-electron structure: (b) Kaim, W. *Angew. Chem. Int. Ed.,* **1981**, *20*, 599. (c) Kaim, W. *J. Am. Chem. Soc.,* **1983**, *105*, 707. (d) Lichtblau, A., Ehlend, A., Hausen, H.-D., Kaim, W. *Chem. Ber.,* **1995**, *128*, 745. See also ref. 16. Studies focused on their electron-rich ring systems: (e) Kaim, W. *Angew. Chem. Int. Ed.,* **1981**, *20*, 600. (f) Brook, D. J. R., Haltiwanger, R. C., Koch, T. H. *J. Am. Chem. Soc.,* **1991**, *113*, 5910. (g) Brook, D. J. R., Haltiwanger, R. C., Koch, T. H. *J. Am. Chem. Soc.,* **1992**, *114*, 6017. Studies on their

key role in the structure of redox-active biological molecules: (h) Goto, T., Kishi, Y. *Angew. Chem. Int. Ed.,* **1968**, *7*, 407. (i) Walsh, C. *Acc. Chem. Res.,* **1980**, *13*, 148.

21) The parent quinoxaline underwent addition of **1** at 60 °C in the absence of the bipyridine catalyst (see Experimental Section).

22) Nishida, M., Torii, A., Yoshida, T. Japan patent JP2006-96714A.

23) Comins, D. L., Mantlo, N. B. *J. Org. Chem*., **1985**, *50*, 4410.

24) Rocca, P., Cochennec, C., Marsais, F., Thomas-dit-Dumont, L., Mallet, M., Godard, A., Quéguiner, G. *J. Org. Chem.,* **1993**, *58*, 7832.

25) This compound was prepared via *ortho*-lithiation of 3-methoxypyridine with lithium isopropylamide followed by treatment with B(O*i*-Pr)$_3$. Bouillon, A., Lancelot, J.-C., Collot, V., Bovy, P. R., Rault, S. *Tetrahedron,* **2002**, *58*, 4369.

26) Rocca, P., Marsais, F., Godard, A., Queguiner, G. *Tetrahedron,* **1993**, *49*, 49.

27) This compound was prepared by iridium-catalyzed C–H borylation of 2,6-dimethylpyridine. Ishiyama, T., Takagi, J., Hartwig, J. F., Miyaura, N. *Angew. Chem. Int. Ed.,* **2002**, *41*, 3056.

28) This compound was prepared by iridium-catalyzed C–H borylation of 2,6-dichloropyridine. See ref. 6.

29) Murphy, J. M., Liao, X., Hartwig, J. F. *J. Am. Chem. Soc.,* **2007**, *129*, 15434.

30) Fujihara, Y., Dixon, J. A., O'Hara, F., Funder, E. D., Dixon, D. D., Rodriguez, R. A., Baxter, R. D., Herlé, B., Sach, N., Collins, M. R., Ishihara, Y., Baran, P. S. *Nature,* **2012**, *492*, 95.

31) Hawkeswood, S., Stephan, D. W. *Dalton Trans.,* **2005**, 2182.

Chapter 3

4,4’-Bipyridine-Catalyzed Diboration of Pyrazines: Modified Reaction Mechanism Involving 4,4’-Bipyridine-Stabilized Boryl Radical

ABSTRACT

The mechanism of 4,4’-bipyridine-catalyzed diboration of pyrazines was studied by experimental observation of the intermediates and by theoretical calculations. Intermediary radical species were detected by ESR measurement of the reactions of 2,6-dichloro-4,4'-bipyridines with bis(pinacolato)diboron and identified by simulation. Based on these observations, radical processes involving 4,4’-bipyridine-stabilized boryl radicals were evaluated by DFT calculations combined with single-component artificial force induced reaction (SC-AFIR). The results of calculations indicate that a radical transfer process from 4,4’-bipyridine-stabilized boryl radical to pyrazine is a major pathway in the catalytic reaction. The origin of the high catalytic efficiency of 2,6-dichloro-4,4'-bipyridine is ascribed to the effect of the chlorine atom on the stability of the corresponding *N*,*N*’-diboryl-4,4’-bipyridinylidene.

Introduction

Transition-metal-free borylations with tetraalkoxydiboron reagents have provided practical and cost-effective methods to prepare boron-containing organic compounds.[1] Recent rapid progress in borylation reactions involving nitrogen-containing aromatic compounds as substrates or catalysts is particularly noteworthy from both synthetic and mechanistic viewpoints.[2]

In 2012, we reported an addition reaction of tetraalkoxydiboron to pyrazines that afforded dearomatized *N*,*N'*-diboryl-1,4-dihydropyrazines (diboration of pyrazines).[3] Although this noncatalytic conversion was applicable only to the parent pyrazine and to monosubstituted pyrazines, diboration of di-, tri-, and tetra-substituted pyrazines was later achieved in 2015 by using 4,4'-bipyridines as catalysts, such as **1a**-**c** (Figure 1A).[4] For example, addition of bis(pinacolato)diboron (**3**) to 2,3-dimethylpyrazine (**2**) proceeded in benzene at 60 °C in the presence of 4,4'-bipyridine (**1a**, 10 mol %) to afford *N*,*N'*-diboryl-2,3-dimethyl-1,4-dihydropyrazine (**4**) in 44% yield (Figure 1B). The catalytic efficiency was improved by using chlorine-substituted 4,4'-bipyridines: 59% yield with 2-chloro-4,4'-bipyridine (**1b**) and 99% yield with 2,6-dichloro-4,4'-bipyridine (**1c**). For this reaction, we proposed a mechanism involving *N*,*N'*-diboryl-4,4'-bipyridinylidene (**5**) as an intermediate (Figure 1C) based on the reaction of **1b** with **3** to afford **5b**, as well as on the efficient boryl transfer from **5b** to **2** to afford **4** and **1b** (Figure 1D).

In 2016, for the reaction of **3** with 4-cyanopyridine, Li and coworkers reported the formation of a 4-cyanopyridine-stabilized boryl radical on the basis of their Electron Spin Resonance (ESR) studies.[5,6] Subsequently, other pyridine-stabilized boryl radicals have been observed by ESR in the reaction of **3** with 4-(4-cyanophenyl)pyridine[7] or **3** with 4-phenylpyridine/MeOK.[8] Most recently, Qi and Jiao reported the results of calculations on the reaction of bis(neopentylglycolato)diboron with **1a**, for which the generation of a 4,4'-bipyridine-stabilized boryl radical was proposed.[9] These studies prompted us to revisit our 4,4'-bipyridine-catalyzed diboration to examine in detail the reaction mechanism by ESR analysis and by conducting the density functional theory (DFT) calculations based on single-component artificial force induced reaction (SC-AFIR).[10] Herein, we propose a mechanism involving radical intermediate **6•** (Figure 1E), the stability of which depends on the substituents, as theoretically determined by DFT computational analysis.

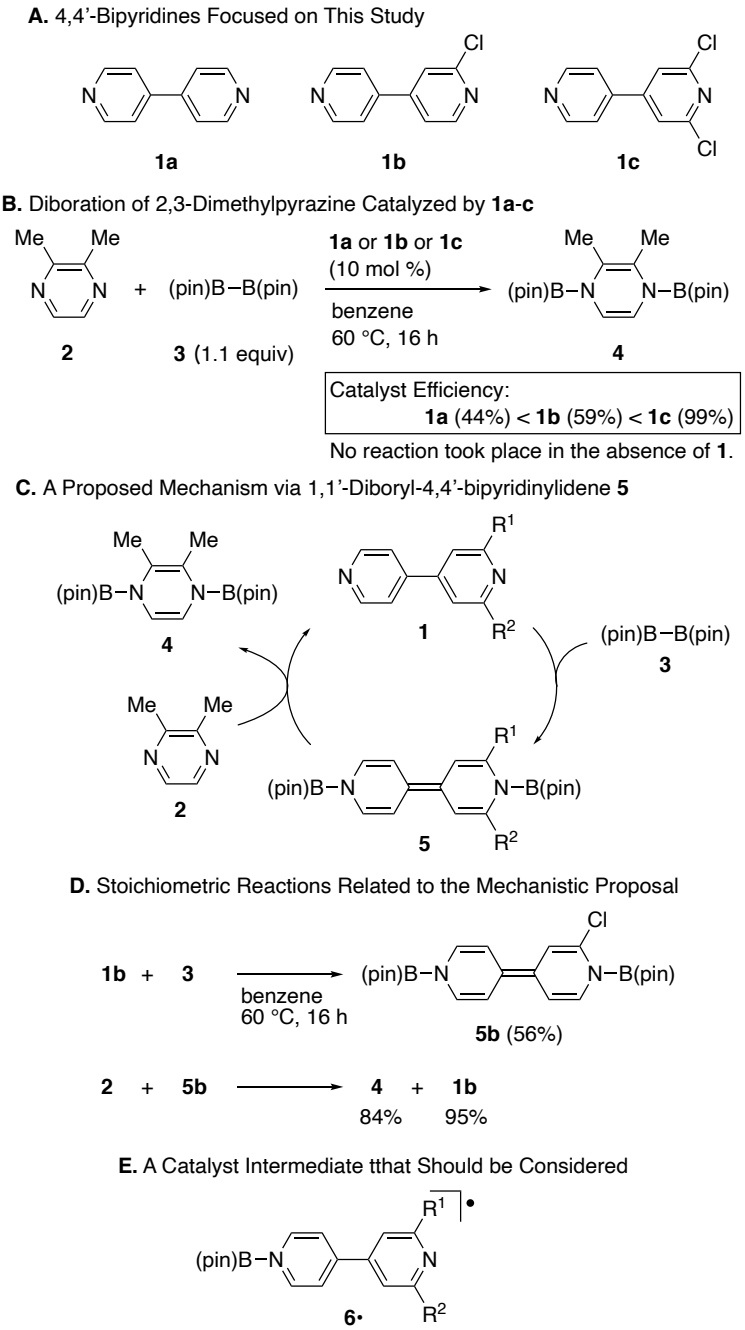


Figure 1. 4,4'-Bipyridine-Catalyzed Diboration of Pyrazines

Experimental

Materials. 2,6-Dichloro-4,4'-bipyridine (**1c**) was prepared by Suzuki-Miyaura coupling of 4-bromopyridine hydrochloride with 2,6-dichloro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (**9**).[4] Bis(pinacolato)diboron (**3**) was purchased from Boron Molecular and purified by recrystallization (pentane) before use.

2,6-Dichloro-4,4'-bipyridine-2',3',5',6'-*d*$_4$ (1c-*d*$_4$). The titled compound was synthesized from 4-aminopyridine (**7**) through three steps (Figure 2). The conversion of **7** to **7-*d*$_4$** was carried out according to the method reported previously.[11] A stainless-steel autoclave, equipped with a glass reaction vessel and a magnetic stirring bar, was charged with 5% Pd/C (65.7 mg), **7** (330 mg, 3.51 mmol), and D_2O (14 mL). The resulting mixture was stirred at 160 °C under H_2 atmosphere for 20 h. After cooling to room temperature, the reaction mixture was diluted with MeOH and filtrated to remove insoluble materials. The filtrate was concentrated to afford 4-aminopyridine-2,3,5,6-*d*$_4$ (**7-*d*$_4$**, 325 mg, 3.31 mmol, 94%, >97% D). This reaction was carried out twice, and combined **7-*d*$_4$** was used for the next conversion. A 50 mL two-neck flask, equipped with a magnetic stirring bar and a rubber septum, was charged with **7-*d*$_4$** (449 mg, 4.58 mmol) and hydrobromic acid (48%, 3 mL). The flask was cooled to 0 °C by an ice/water bath. Bromine (2.34 g, 14.6 mmol) was added dropwise to the flask. The flask was cooled to –10 °C by an ice/water/NaCl bath. An aqueous solution of $NaNO_2$ (886 mg with 1.4 mL of H_2O) was added dropwise to the flask over 30 min. The resulting mixture was stirred for 10 min at –10 °C and then for 30 min at room temperature. To quench the reaction, saturated aqueous Na_2SO_3 solution was added to the flask at 0 °C until the solution became colorless. The solution was made basic by adding aqueous NaOH solution (5 N), and the organic materials were extracted with Et_2O. After drying the organic phase over anhydrous sodium sulfate, the solution was treated with ethereal solution of HCl (1 M, 5.2 mL), and the resulting precipitate was collected by filtration. 4-Bromopyridynium chloride-2,3,5,6-*d*$_4$ (**8-*d*$_4$**, 741 mg, 3.73 mmol, 81%) was obtained after drying in vacuo. A 100 mL two-neck flask, equipped with a magnetic stirring bar, a rubber septum, and a Dimroth condenser with three-way stopcock, was charged with $Pd(OAc)_2$ (11.6 mg, 0.0517 mmol), PPh_3 (53.6 mg, 0.204 mmol), K_2CO_3 (1.01 g, 7.31 mmol), **8-*d*$_4$** (494 mg, 2.49 mmol), and **9**[12] (836 mg, 3.05 mmol). The flask was evacuated and backfilled with nitrogen. 1,4-Dioxane (10 mL) and degassed H_2O (3 mL) were added to the flask, and the resulting mixture was stirred at 100 °C overnight. After cooling to room temperature, the organic materials were extracted with AcOEt, and the extract was washed with brine and dried over anhydrous sodium sulfate. The product **1c-*d*$_4$** (180 mg, 0.79 mmol, 32%) was obtained as a white solid after column chromatography on silica gel (eluent: CH_2Cl_2:EtOAc:MeOH = 24:8:1) and preparative recycle GPC (eluent: $CHCl_3$). **1c-*d*$_4$**: ^{1}H NMR (600 MHz, C_6D_6) δ 6.70 (s). ^{2}H NMR (77 MHz, C_6H_6) δ 8.45 (broad s), 6.34 (broad s). ^{13}C NMR (151 MHz, C_6D_6) δ 151.5, 150.7, 150.6 (t, *J* = 27 Hz, *C*D), 142.1, 120.7, 120.6 (t, *J* = 25 Hz, *C*D). HRMS (EI, positive) *m/z* calcd for $C_{10}H_2D_4N_2Cl_2^+$ $[M]^+$: 228.0154, found: 228.0154.

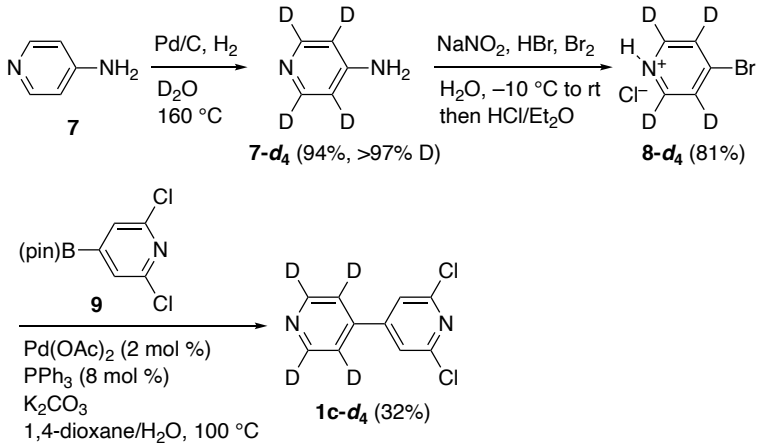


Figure 2. Synthesis of **1c-*d*$_4$**

Measurement of ESR. A glassware with a glass tube having a liquid reservoir attached to the tip of the ESR sample tube (quartz) in a T-shape was used for the experiment (see Supporting Information). The glassware was charged with **1c** (12.0 mg, 0.053 mmol) and **3** (6.7 mg, 0.026 mmol), and toluene (dehydrogenated over CaH_2 and K mirror, degassed by Freeze-Pump-Thaw, 0.2 mL) was transferred to the glassware under vacuum. **1c** and **3** began to dissolve in toluene and the solution began to take on a brown color. The resulting solution was degassed by Freeze-Pump-Thaw, and then the glass tube was burned off under vacuum to seal the glassware. ESR spectra were measured with a Bruker EMX spectrometer.

Simulation of ESR Spectra. Geometry of radical **6c•** was optimized using density functional theory UB3LYP/6-311G+(d,2p) in Gaussian16.[13] The calculated hyperfine coupling constants (HFCCs) were used as starting values for simulation. HFCCs of ^{2}H and lower abundance isotopes such as ^{10}B, ^{37}Cl and ^{13}C were neglected. Simulated spectra fitted to observed spectra were obtained by modifying the calculated HFCCs.

DFT Calculation. The mechanism for diboration of **2** catalyzed by **1a**–**1c** was investigated by DFT method combined with a systematic reaction path search method, single-component artificial force induced reaction (SC-AFIR).[10] The SC-AFIR calculations at the PM6 level[14] were performed specifying atoms in the rings of reactants as target atoms and a model collision energy parameter g = 150 kJ/mol. The obtained AFIR paths were refined by the locally updated plane method[15] to gain approximate

transition state (TS) structures for further TS optimizations. After the TS optimizations, intrinsic reaction coordinate calculations were performed to conform the path connections. Harmonic vibrational frequency calculations were performed to check whether the obtained structures correspond to local minima or saddle points on potential energy surface. The structure optimizations and frequency calculations were performed at the spin-unrestricted M06-L[16]/6-31+G* level. The Gibbs energies under the experimental conditions were estimated using harmonic frequency values. All calculations were carried out using a developer's version of GRRM combined with Gaussian09.[17] In Figures 5–8, $\Delta\Delta G^{\ddagger}$ is Gibbs energy difference between the highest transition state and the initial state. ΔG is Gibbs energy difference between the final state and the initial state. In Figures 5–8, 10, and 11, Gibbs free energy values were evaluated at the experimental temperature (333.15 K).

Results and Discussions

Observation of Radical Species

The previously reported ESR spectra of boryl radicals stabilized by 4-cyanopyridine,[5] 4-(4-cyanophenyl)pyridine,[7] and 4-phenylpyridine[8] are rather complex, and simulated spectra with hyperfine coupling constants (HFCCs) have only been calculated for the 4-phenylpyridine-stabilized boryl radical.[8b] Therefore, we first examined the reaction of a partially deuterated derivative **1c-*d*$_4$**, which was expected to give a simpler ESR spectrum.[18] Compound **1c-*d*$_4$**, which was prepared by Suzuki-Miyaura coupling of 4-bromopyridinium chloride-2,3,5,6-d_4 (**8-*d*$_4$**) with 4-pyridylboronic acid (**9**) (Figure 2), was mixed with **3** in toluene and the resulting brown solution was subjected to ESR measurement. As shown in Figure 3(a-1), generation of a radical species was confirmed. The simulated spectrum shown in Figure 3(a-2), which is based on the HFCC values given in Figure 4, shows good agreement with the observed spectrum. A radical generated from **1c** and **3** was then measured by ESR spectroscopy, and a more complex spectrum was obtained, as shown in Figure 3(b-1). Based on the HFCC values assigned for the **6c-*d*$_4$•**, simulation was carried out to afford HFCC values (Figure 4) that lead the spectrum shown in Figure 3(b-2). These results offer reasonable support for the formation of **6c-*d*$_4$•** and **6c•**.

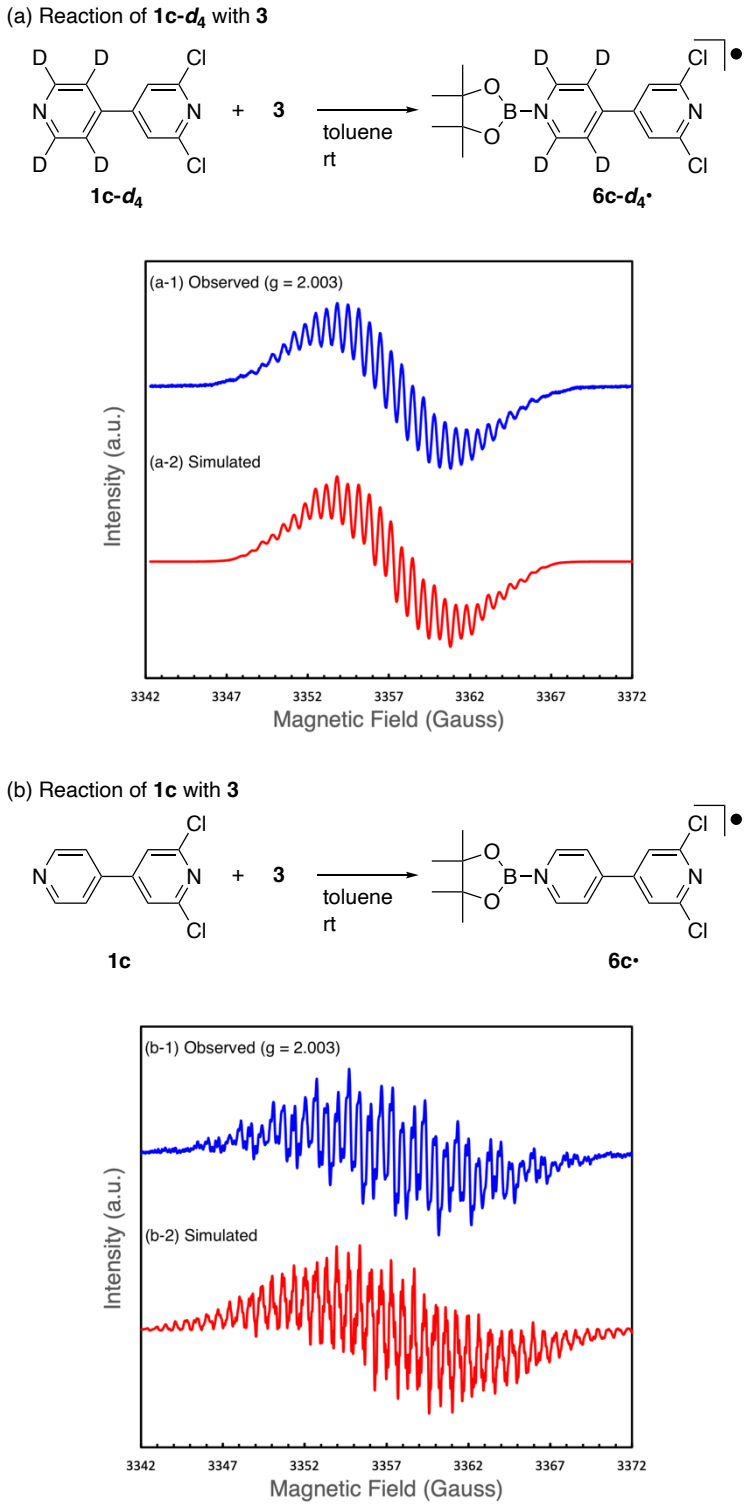
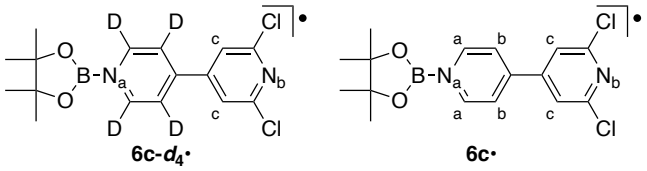


Figure 3. ESR Measurements and Simulations



HFCC / Gauss	*a* (^{11}B)	*a* (^{35}Cl)	*a* ($^{14}N_a$)	*a* ($^{14}N_b$)	*a* ($^{1}H_a$)	*a* ($^{1}H_b$)	*a* ($^{1}H_c$)
Simulated (**6c-*d*$_4$•**)	1.32	0.59	0.73	1.42	0.00	0.00	3.32
Simulated (**6c•**)	1.32	0.59	0.73	1.42	4.75	1.07	3.32
Calculated (**6c•**)	–1.64	–0.27	1.02	1.68	–5.00	0.87	–2.90

Figure 4. Hyperfine Coupling Constants (HFCCs) for **6c-*d*$_4$•** and **6c•**

Theoretical Calculation of Possible Radical Processes

Having confirmed the formation of 4,4'-bipyridine-stabilized boryl radical **6c-*d*$_4$•** and **6c•**, we then performed theoretical calculations on the reaction mechanism of **1a**-catalyzed diboration of **2** with **3** to afford **4** (Figure 1B). The activation free energy ($\Delta\Delta G^{\ddagger}$) of the radical initiation process, i.e., the reaction of **1a** (2 equiv) with **3** to afford two equivalents of 4,4'-bipyridine-stabilized boryl radical **6a•** (Eq. A1, Figure 5), was calculated to be 93.0 kJ/mol.[19] The subsequent radical transfer processes from **6a•** were then evaluated (Eqs. A2–A4, Figure 6). The reasonable activation barrier ($\Delta\Delta G^{\ddagger}$ = 83.8 kJ/mol) of Eq. A2, in which the cleavage of the boron–boron bond of **3** and the formation of the nitrogen–boron bond with **6a•** and **1a** take place to afford **5a** and **6a•**, indicates that Eq. A2 is a possible process to generate **5a**.[19] Eqs. A3 and A4 show the reaction of **6a•** with **2** to afford pyrazine-stabilized radical **10•**. The activation barrier ($\Delta\Delta G^{\ddagger}$ = 82.0 kJ/mol) of Eq. A4, in which diboron **3** is not involved, is kinetically more favorable than Eq. A3. The $\Delta\Delta G^{\ddagger}$ values of Eqs. A1–A4 are values that can be overcome with sufficient frequency at the experimental temperature used (60 °C).

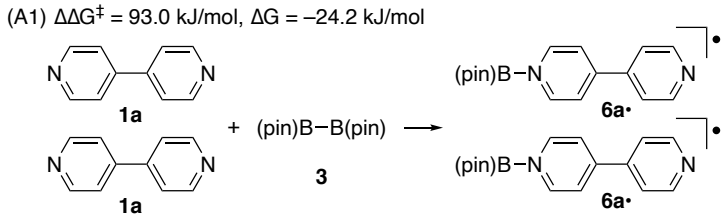


Figure 5. Radical Initiation Process

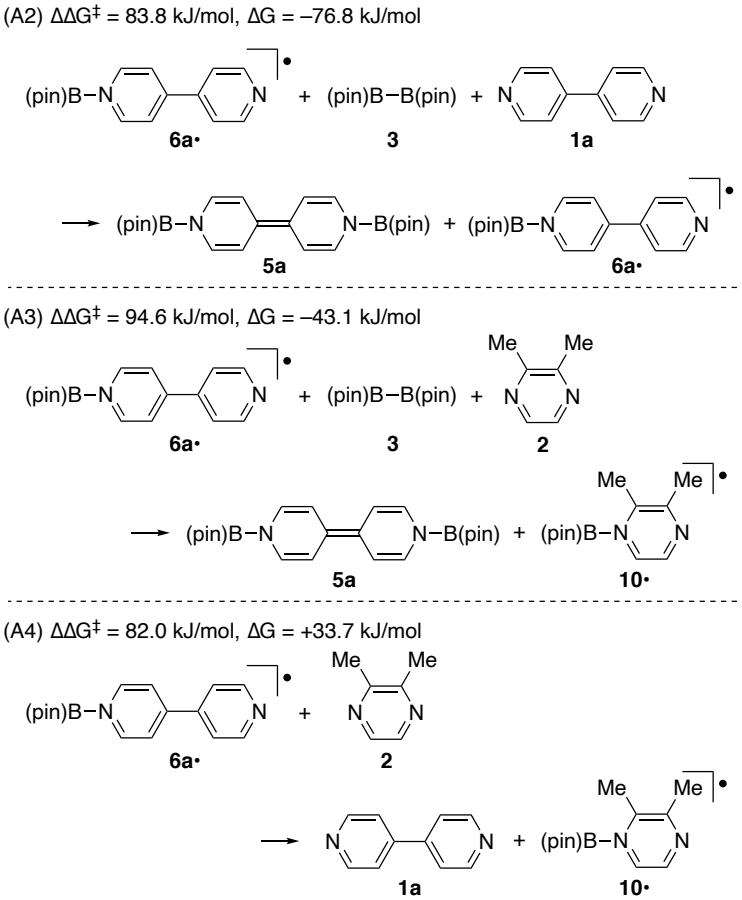


Figure 6. Possible Radical Transfer Processes from **6a•**

The radical transfer processes from pyrazine-stabilized boryl radical **10•**, which afford final product **4**, were then evaluated (Eqs. A5–A7, Figure 7). Among them, the reaction of **10•** with **5a** ($\Delta\Delta G^{\ddagger}$ = 33.9 kJ/mol, Eq. A7) is much more kinetically favorable than the reactions involving **3** and **1a** ($\Delta\Delta G^{\ddagger}$ = 91.9 kJ/mol, Eq. A5) or **3** and **2** ($\Delta\Delta G^{\ddagger}$ = 94.3 kJ/mol, Eq. A6).

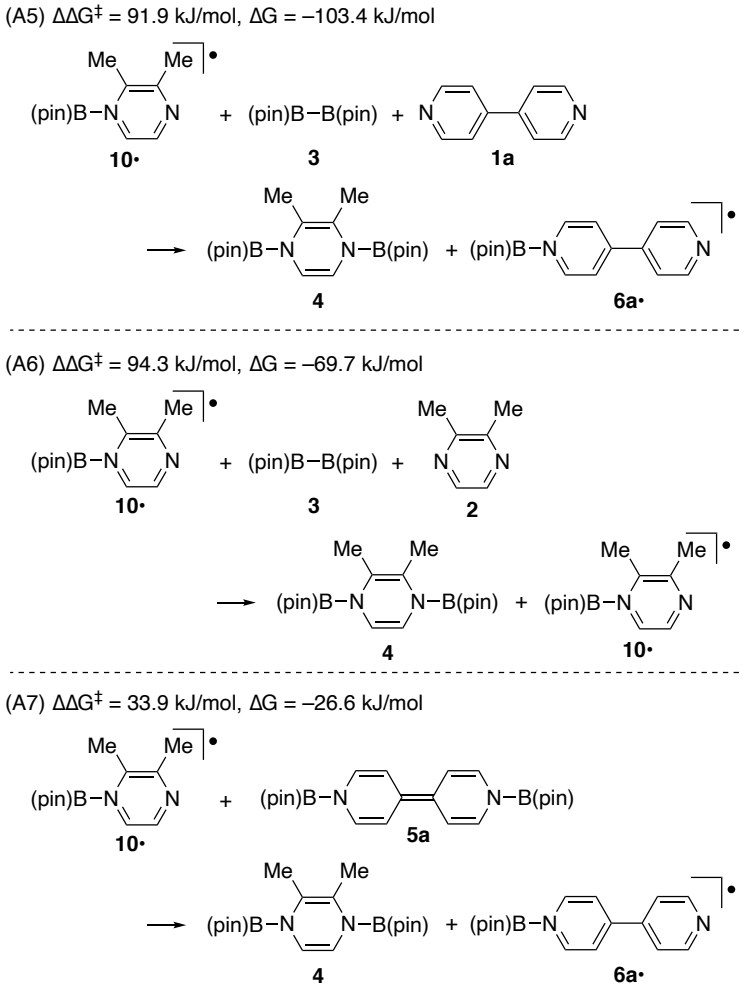


Figure 7. Possible Radical Transfer Processes from **10•**

Finally, the radical termination processes were evaluated (Eqs. A8–A10, Figure 8). In the reaction of **6a•** with **10•**, formation of **1a** and **4** (Eq. A8, $\Delta\Delta G^{\ddagger}$ = 8.9 kJ/mol) is kinetically more favorable than that of **5a** and **2** (Eq. A9, $\Delta\Delta G^{\ddagger}$ = 33.7 kJ/mol). Disproportionation of **6a•** to afford **1a** and **5a** (Eq. A10, $\Delta\Delta G^{\ddagger}$ = 21.5 kJ/mol) is also kinetically favorable, and in addition to Eq. A2 this is a possible process for production of **5a**.[19]

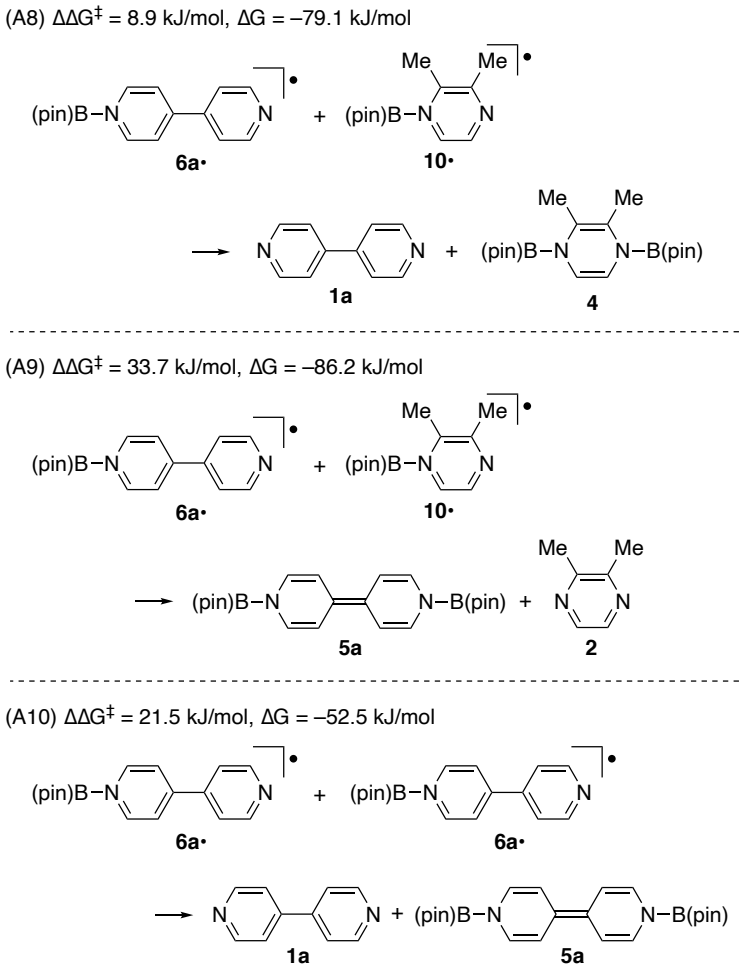


Figure 8. Possible Radical Termination Processes

Based on the results of the calculations, a reasonable reaction mechanism for **1a**-catalyzed diboration of **2** is proposed as shown in Figure 9. The first step is formation of the radical **6a•** by the reaction of **1a** with **3** (Eq. A1). Reaction of **6a•** with **2** is the second step, which affords **10•** and **1a** (Eq. A4, path *a*). Finally, **10•** reacts with **6a•** to give **4** and **1a** (Eq. A8). Disproportionation of **6a•** to form **5a** and **1a** (Eq. A10) is another possible path to produce **4**, which is formed by the reaction of **5a** with **10•** (Eq. A7) (path *b*). Compound **5a** is also formed through the reaction of **6a•**, **3**, and **1a** (Eq. A2).

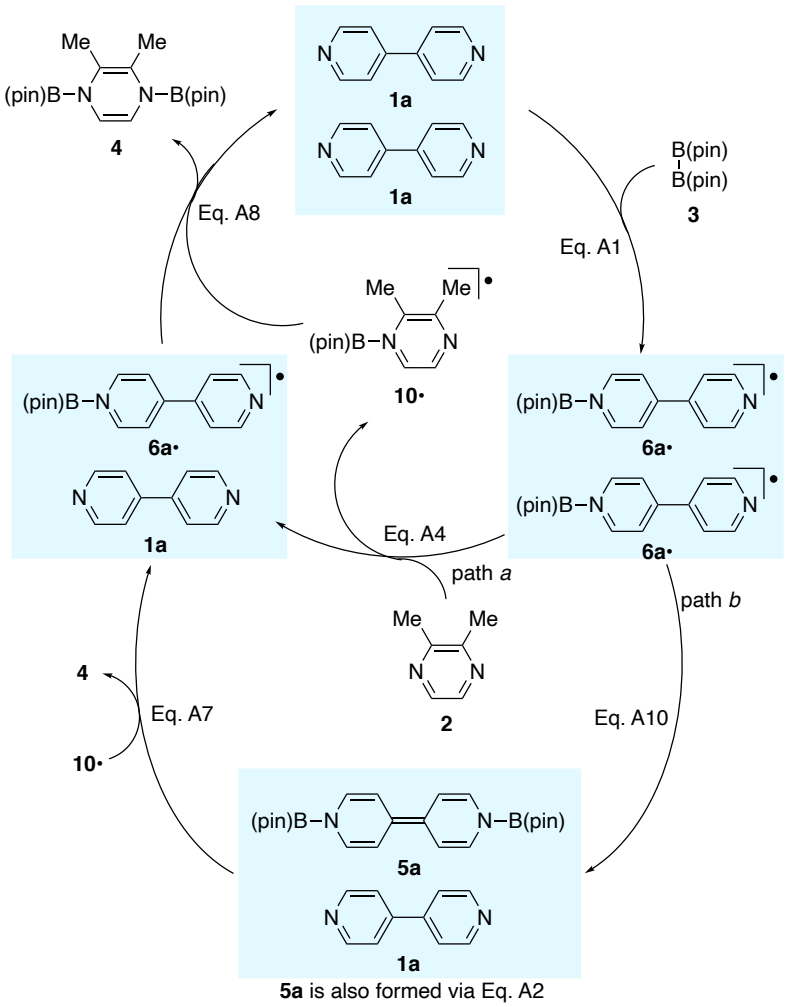


Figure 9. A Possible Reaction Mechanism for **1a**-Catalyzed Diboration of **2**

Effect of Chlorine on Catalyst Efficiency

As described above, the efficiency of **1a**-catalyzed diboration of **2** under the experimental conditions was moderate (44% yield of **4** at 60 °C for 16 h), but the catalyst efficiency was improved by using chlorine-substituted **1b** (59% yield) and **1c** (99% yield). The moderate catalyst efficiency of **1a** can be understood by considering the stability of the intermediate **5a**. The heat of formation of **5a** is ΔG = –76.7 kJ/mol (the sum of free energy change in Eqs. A1 and A10), which is lower and thus thermodynamically more favored than that of **4** (ΔG = –69.7 kJ/mol, i.e., the sum of free energy change in Eqs. A3 and A7). Furthermore, **5a** is readily formed from **6a•** through Eq. A10. Therefore, it is concluded that **5a** is a resting state of the catalytic cycle and that it inhibits the turnover by decreasing the concentration of **6a•**.

For further understanding of the effect of chlorine substituents on the catalyst

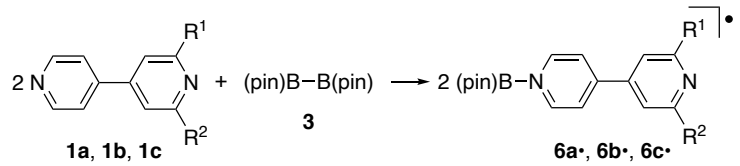
efficiency, we calculated the activation free energy $\Delta\Delta G^{\ddagger}$ and free energy change ΔG for the reactions with chlorine-substituted **1b** and **1c**. The results of the ten elementary processes corresponding to Eqs. A1–A10 for each, i.e., Eqs. B1–B10 and Eqs. C1–C10, are given in the Supporting Information. We first evaluated the effect of chlorine on the radical initiation process [Figure 10(a)],[20] however, no appreciable differences of the $\Delta\Delta G^{\ddagger}$ values between Eqs. A1 (93.0 kJ/mol), B1 (99.0 kJ/mol), and C1 (99.2 kJ/mol) indicate that the chlorine does not affect this stage.

By examining these conditions, we found that chlorine substitution has a remarkable effect on processes A–C10, in which **6a–c•** disproportionate to **1a–c** and **5a–c** [Figure 10(b)]. Although processes A10, B10, and C10 are all reversible, as judged from $\Delta\Delta G^{\ddagger}$ for the forward and backward reactions (14.9–71.1 kJ/mol), the forward reaction C10, in which dichlorine-substituted **6c•** is converted into **1c** and **5c**, is found to be thermodynamically unfavorable, as judged by the large positive ΔG (+23.0 kJ/mol). We evaluated processes A2, B2, and C2, in which **5a–c** are also formed from **6a–c•** [Figure 10(c)], and found that processes B2 and C2, involving mono- and dichlorine substituted catalysts **1b** and **1c**, were unfavorable as judged by the large $\Delta\Delta G^{\ddagger}$ values (117.8 and 156.7 kJ/mol). Therefore, the use of dichlorine-substituted catalyst **1c** is advantageous because it avoids formation of **5c**, which could limit the catalysis turnover.

Free energy changes for processes A–C1 and A–C10 along with the relative free energy of the final products (**4** + **1** + **1**) are shown in Figure 11. From the free energy change in processes A–C1, the radical intermediate **6c•** is calculated to be 9.45 kJ/mol more stable than **6a•**. This indicates that the chlorine on the pyridine ring contributes towards the stabilization of the key radical intermediate in the catalysis. A more significant effect of the chlorine substitution is indicated by the 56.6 kJ/mol destabilization of *N*,*N'*-diboryl-4,4'-bipyridinylidene **5**, which has been assumed to be the turnover-limiting state in the catalysis. Indeed, in the conversion of **6•** into **5** in processes A–C10, although the parent bipyridine system favors production of **5a** thermodynamically, chlorine substitution makes this step highly thermodynamically unfavorable [Figure 10(b)]. The calculated stabilities of **5a**, **5b**, and **5c** are consistent with the experimental results: i.e., whereas **5a** and **5b** are formed in the reaction of **3** with **1a** and **1b**, respectively, no formation of **5c** was observed in the reaction of **3** with **1c**.[4]

Based on the findings discussed above, the effect of chlorine can be summarized as follows: (1) the chlorine substitution makes formation of the key radical species **6•** more favorable and (2) prevents the formation of turnover-limiting **5**. As a result, high concentration of catalytically active **6•** is maintained throughout the reaction, leading to high efficiency of the overall diboration in the reaction catalyzed by **5c**.

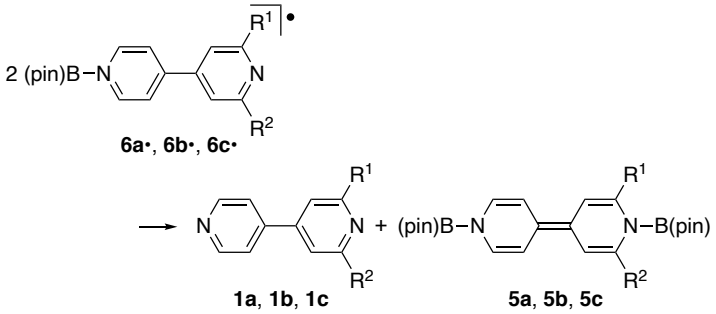
(a) Comparison of Eqs. A1, B1, and C1



1a, **1b**, **1c** **6a•**, **6b•**, **6c•**

			ΔΔG‡ (kJ/mol)		
Eq.	R^1	R^2	forward	backward	ΔG (kJ/mol)
A1	H	H	93.0	117.2	–24.2
B1	Cl	H	99.0	128.7	–24.7
C1	Cl	Cl	99.2	142.3	–43.1

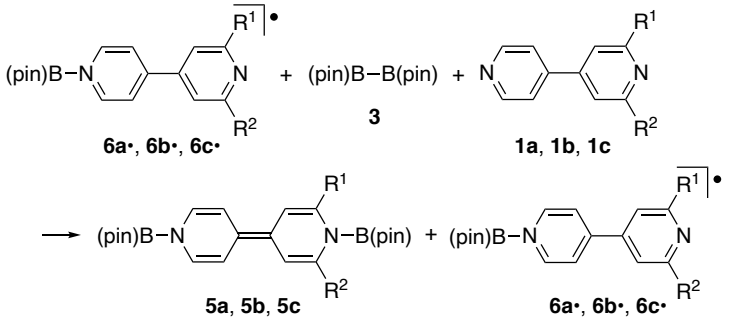
(b) Comparison of Eqs. A10, B10, and C10



6a•, **6b•**, **6c•** **1a**, **1b**, **1c** **5a**, **5b**, **5c**

			ΔΔG‡ (kJ/mol)		
Eq.	R^1	R^2	forward	backward	ΔG (kJ/mol)
A10	H	H	21.5	61.8	–52.5
B10	Cl	H	36.1	25.8	–19.3
C10	Cl	Cl	71.1	14.9	+23.0

(c) Comparison of Eqs. A2, B2, and C2



6a•, **6b•**, **6c•** **1a**, **1b**, **1c** **5a**, **5b**, **5c** **6a•**, **6b•**, **6c•**

			ΔΔG‡ (kJ/mol)		
Eq.	R^1	R^2	forward	backward	ΔG (kJ/mol)
A2	H	H	83.8	160.6	–76.8
B2	Cl	H	117.8	166.7	–48.9
C2	Cl	Cl	156.7	176.8	–20.1

Figure 10. Evaluation of Effect of Chlorine on Activation Barriers. $\Delta\Delta G^{\ddagger}$ is Gibbs energy difference between the highest transition state and the initial state (forward) or the final state (backward). ΔG is Gibbs energy difference between the final state and the initial state of each elementary process. See Supporting Information for full reaction profiles of these elementary processes.

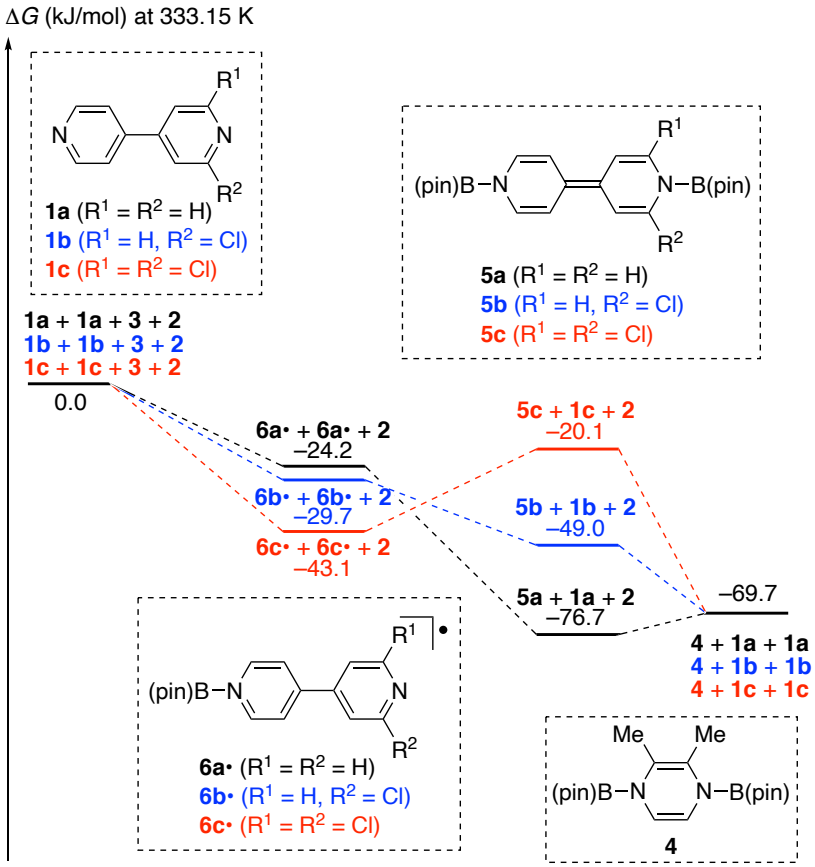


Figure 11. Relative Stabilities of the Possible Reaction Intermediates (**6a•**, **6b•**, **6c•**, **5a**, **5b**, and **5c**) and Product **4**

Conclusion

We observed 4,4'-bipyridine-stabilized boryl radicals by ESR study of the reaction of bis(pinacolato)diboron **3** with 2,6-dichloro-4,4'-bipyridine **1c** and its partially deuterated derivative **1c-*d*$_4$**. Based on these observations, we used a theoretical computational approach to revisit the mechanism of 4,4'-bipyridine-catalyzed diboration of pyrazines. The results revealed that a major path is radical transfer from 4,4'-bipyridine-stabilized boryl radical **6•** to pyrazine **2** to afford pyrazine-stabilized boryl radical **10•**, which reacts with **6•** to afford *N*,*N'*-diboryl-1,4-dihydropyrazine **4**. A path via *N*,*N'*-diboryl-4,4'-bipyridinylidene **5** that was proposed previously is concluded to constitute a minor path in the reaction catalyzed by **1c**. The high catalyst efficiency of 2,6-dichloro-4,4'-bipyridine **1c** arises from destabilization of the corresponding *N*,*N'*-diboryl-4,4'-bipyridinylidene **5c**, thereby maintaining a high concentration of the boryl radical.

References and Notes

1) For a review see: (a) Palau-Lluch, G., Sanz, X., Cascia, E. L., Civit, M. G., Miralles, N., Cuenca, A. B., Fernández, E. *Pure Appl. Chem.* **2015**, *87*, 181. (b) Cuenca, A. B., Shishido, R., Ito, H., Fernández, E. *Chem. Soc. Rev.* **2017**, *46*, 415–430. (c) Hirano, K., Uchiyama, M. *Adv. Synth. Catal.* DOI: 10.1002/adsc.202001610.
2) (a) Farre, A., Soares, K., Briggs, R. A., Balanta, A., Benoit, D. M., Bonet, A. *Chem. Eur. J.*, **2016**, 22, 17552. (b) Ohmura, T., Morimasa, Y., Suginome, M., *Chem. Lett.,* **2017**, *46*, 1793. (c) Wang, G., Cao, J., Gao, L., Chen, W., Huang, W., Cheng, X., Li, S. *J. Am. Chem. Soc.* **2017**, *139*, 3904. (d) Candish, L., Teders, M., Glorius, F. *J. Am. Chem. Soc.,* **2017**, *139*, 7440. (e) Chen, D., Xu, G., Zhou, Q., Chung, L. W., Tang, W., *J. Am. Chem. Soc.,* **2017**, *139*, 9767. (f) Cheng, W.-M., Shang, R., Zhao, B., Xing, W.-L., Fu, Y. *Org. Lett.,* **2017**, *19*, 4291. (g) Pinet, S., Liautard, V., Debiais, M., Pucheault, M. *Synthesis* **2017**, *49*, 4759. (h) Hu, J., Wang, G., Li, S., Shi, Z. *Angew. Chem. Int. Ed.,* **2018**, *57*, 15227. (i) Gao, L., Wang, G., Cao, J., Yuan, D., Xu, C., Guo, X., Li, S. *Chem. Commun.* **2018**, *54*, 11534. (j) Xu, R., Lu, G.-P., Cai, C. *New J. Chem.* **2018**, *42*, 16456. (k) Morimasa, Y., Kabasawa, K., Ohmura, T., Suginome, M., *Asian J. Org. Chem.,* **2019**, *8*, 1092. (l) Cao, J., Wang, G., Gao, L., Chen, H., Liu, X., Cheng, X., Li, S. *Chem. Sci.,* **2019**, *10*, 2767. (m) Maekawa, Y., Ariki, Z. T., Nambo, M., Crudden, C. M. *Org. Biomol. Chem.,* **2019**, *17*, 7300. (n) Zhang, L., Jiao, L. *J. Am. Chem. Soc.,* **2019**, *141*, 9124. (o) Hosoya, H., Castro, L. C. M., Sultan, I., Makajima, Y., Ohmura, T., Sato, K., Tsurugi, H., Suginome, M., Mashima, K. *Org. Lett.,* **2019**, *21*, 9812. (p) Koniarczyk, J. L., Greenwood, J. W., Alegre-Requena, J. V., Paton, R. S., McNally, A. *Angew. Chem. Int. Ed.* **2019**, *58*, 14882. (q) Yang, H., Zhang, L., Zhou, F.-Y., Jiao, L. *Chem. Sci.* **2020**, *11*, 742. (r) Zhang, L., Wu, Z.-Q., Jiao, L. *Angew. Chem. Int. Ed.,* **2020**, *59*, 2095. (s) Ma, Y., Pang, Y., Chabbra, S., Reijerse, E. J., Schnegg, A., Niski, J., Leutzsch, M., Cornella, J. *Chem. Eur. J.* **2020**, *26*, 3738. (t) Li, L., Wu, Z., Zhu, H., Robinson, G. H., Xie, Y., Schaefer, H. F. *J. Am. Chem. Soc.,* **2020**, *142*, 6244. (u) Zhou, M., Li, K., Chen, D., Xu, R., Xu, G., Tang, W. *J. Am. Chem. Soc.,* **2020**, *142*, 10337. (v) Jo, J., Kim, S., Choi, J.-H., Chung, W.-J., *Chem. Commun.* **2021**, *57*, 1360. (w) Castro, L. C. M., Sultan, I., Nishi, K., Tsurugi, H., Mashima, K., *J. Org. Chem.* **2021**, *86*, 3287.
3) Oshima, K., Ohmura, T., Suginome, M., *Chem. Commun.,* **2012**, *48*, 8571.
4) Ohmura, T., Morimasa, Y., Suginome, M. *J. Am. Chem. Soc.,* **2015**, *137*, 2852.
5) Wang, G., Zhang, H., Zhao, J., Li, W., Cao, J., Zhu, C., Li, S. *Angew. Chem. Int. Ed.,* **2016**, *55*, 5985.

6) For pyridine-stabilized diorganoboryl radicals, see (a) Köster, R., Bellut, H., Benedikt, G., Ziegler, E. *Liebigs Ann. Chem.* **1969**, *724*, 34. (b) Schlüter, K., Berndt, A. *Angew. Chem. Int. Ed.* **1980**, *19*, 57.
7) Cao, J., Wang, G., Gao, L., Cheng, X., Li, S., *Chem. Sci.,* **2018**, *9*, 3664.
8) (a) Zhang, L., Jiao, L. *J. Am. Chem. Soc.,* **2017**, *139*, 607. (b) Zhang, L., Jiao, L. *Chem. Sci.,* **2018**, *9*, 2711.
9) Qi, J.-Q., Jiao, L. *J. Org. Chem.,* **2020**, *85*, 13877.
10) Maeda, S., Harabuchi, Y., Takagi, M., Saita, K., Suzuki, K., Ichino, T., Sumiya, Y., Sugiyama, K., Ono, Y. *J. Comput. Chem.,* **2018**, *39*, 233-250.
11) Esaki, H., Ito, N., Sakai, S., Maegawa, T., Monguchi, Y., Sajiki, H. *Tetrahedron,* **2006**, *62*, 10954.
12) This compound was prepared by iridium-catalyzed C–H borylation of 2,6-dichloropyridine. Ishiyama, T., Takagi, J., Hartwig, J. F., Miyaura, N. *Angew. Chem. Int. Ed.,* **2002**, *41*, 3056.
13) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, *Gaussian 16, Revision C.01*; Gaussian, Inc., Wallingford CT, 2016.
14) Stewart, J. J. P. *J. Mol. Model.,* **2007**, *13*, 1173-213.
15) Choi, C., Elber, R., *J. Chem. Phys.,* **1991**, *94*, 751-760.
16) Zhao, Y., Truhlar, D. G *J. Chem. Phys.,* **2006**, *125*, 194101-194118.
17) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R.

Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09, Revision D.01*; Gaussian, Inc., Wallingford CT, 2013.

18) ESR study on a partially deuterated 4-phenylpyridine-stabilized boryl radical has been reported. See ref. 8b.

19) A related calculation study on the reaction of bis(neopentylglycolato)diboron (B_2nep_2) has been reported by Qi and Jiao. See ref. 9.

20) The substituent effect on the reaction of **3** with pyridines to form pyridine-stabilized boryl radicals has been evaluated. See ref. 7.

Chapter 4

Pyridine-Based Catalysts for Organocatalytic Regioselective syn-Silaboration of Terminal Alkynes and Allenes

ABSTRACT

The first transition-metal-free silaboration of terminalalkynes and allenes was established using pyridine-based catalysts. In the presence of 4-cyanopyridine (1–2 mol %), alkyl propiolatesunderwent regio- and stereoselective addition of silylboronic estersin toluene at 135 °C to afford (*Z*)-3-boryl-2-silylacrylates in good yields. 2,6-Dichloro-4,4'-bipyridine and 4-(3,5-dichlorophenyl)pyridine also exhibited high catalyst efficiency for the1,2-silaboration of ethyl propiolate, whereas 1,1-silaboration was induced by P(n-Bu)3, *t*-BuOK, and ICy to afford ethyl 3-boryl-3-silylacrylates as *Z*/*E* mixtures. The silaboration of ethynylbenzenesand terminal allenes was also accelerated by 4-cyanopyridine catalyst to afford (*Z*)-*β*-boryl-*α*-silylstyrenes and *β*-borylallylsilanes in a regioselective manner.

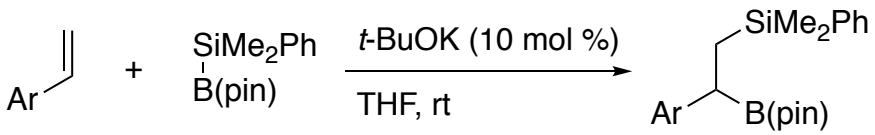
Introduction

Transition-metal-free catalytic reactions involving the activation of B–E bonds (E = B, Si) have received increasing attention as a new tool for the synthesis of organoboron and organosilicon compounds.[1] *N*-Heterocyclic carbens,[2] tertiary phosphines,[3] and organic and inorganic bases (including alkoxide and carbonate salts)[4] have been developed as effective catalysts for the transfer of E into α,β-unsaturated carbonyl compounds and imines through conjugate or direct addition fashions. The bases also catalyze substitution reactions of aryl halides,[5] vinyl epoxides,[6] vinyl aziridines,[6] allylic alcohols,[7] and α-(boryloxy)alkylboronates.[8,9]

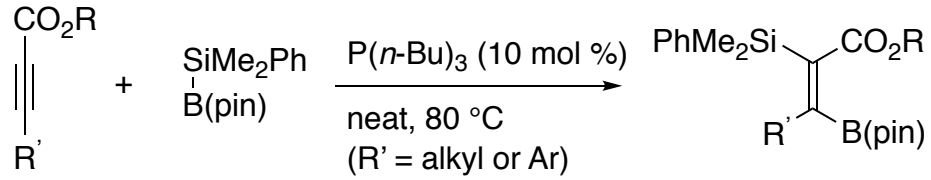
In addition to such borylation and silylation reactions, the diboration and silaboration of carbon–carbon unsaturated compounds, where C–B and C–E bonds are formed simultaneously, have also been studied under transition-metal-free catalytic conditions.[10] Diboration of alkenes, allenes, and alkynes has been carried out using catalysts such as Cs_2CO_3,[11] *t*-BuONa,[11] *t*-BuOLi,[12] P(*n*-Bu)$_3$,[13] $(PhS)_2/h\nu$ [14] and $PPh_3/h\nu$[15] which make diboration cost effective as well as otherwise inaccessible stereoisomers now accessible.[12,13] In contrast to the recent rapid progress made in diboration, transition-metal-free catalytic silaboration is still largely unexplored. Indeed, the preceding examples are limited to the reactions of styrenes with *t*-BuOK catalyst [Scheme 1 (a)] and alkynoates with P(*n*-Bu)$_3$ catalyst [Scheme 1 (b)].[13,16] In effort to make the transition-metal-free catalytic silaboration a more valuable tool in organic synthesis, exploration of new catalysts with a broader substrate scope is highly desirable.

The author has recently reported on transition-metal-free catalytic addition reactions of diboron reagents to substituted pyrazines[17] and acetylenedicarboxylates,[18] where the B–B bond of diboron is activated efficiently by 4,4'-bipyridines used as catalyst. Based on our findings and on the related borylation by pyridine-based catalysts,[19] the auther envisioned that pyridines, including 4,4'-bipyridines, would also be efficient catalysts for activation of the B–Si bond of silylboronic esters. Herein, we describe the first transition-metal-free silaboration of terminal alkynes and allenes using pyridine-based catalysts [Scheme 1 (c)]. The silaboration of terminal alkynes takes place regio- and stereoselectively to afford the corresponding adducts as single isomers.

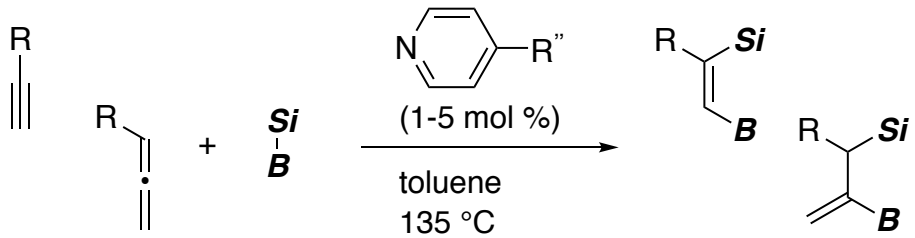
(a) *t*-BuOK Catalyst (ref. 16)



(b) P(*n*-Bu)$_3$ Catalyst (ref. 13)



(c) Pyridine-Based Catalysts (This Work)



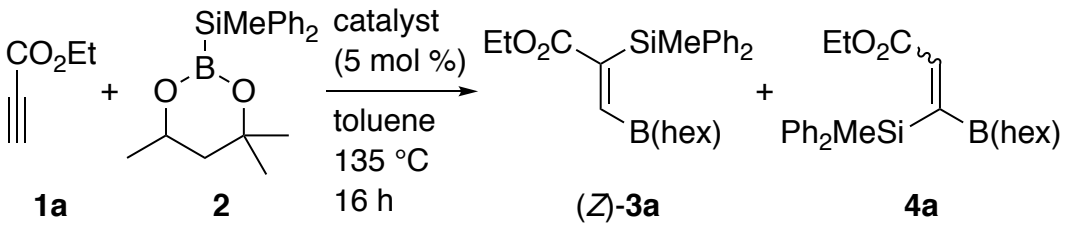
Scheme 1. Transition-Metal-Free Catalytic Silaboration of C–C Unsaturated Bonds

Organocatalytic silaboration of ethyl propiolate (**1a**) was investigated using hexylene glycol-derived silylboronic ester $MePh_2Si$–B(hex) (**2**) (Table 1). Whereas only a trace amount of the adduct was formed in toluene at 135 °C for 16 h in the absence of catalyst (entry 1), **1a** underwent addition of **2** efficiently in the presence of Me- and Cl-substituted 4,4'-bipyridines **5b**-**5e** (5 mol %) (entries 3–6). The reaction afforded (*Z*)-3-boryl-2-silylacrylate **3a** in 51–73% yields through *syn*-1,2- addition with regioselective introduction of the boryl and silyl groups into the terminal and internal carbons of the alkyne moiety, respectively. Cl-substituted 4,4'-bipyridines **5c** and **5e** (entries 4 and 6) showed higher catalyst efficiency than Me-substituted **5b** and **5d** (entries 3 and 5). In sharp contrast, no catalyst activity was observed with unsubstituted 4,4'-bipyridine (**5a**) (entry 2), although it showed high catalyst performance in the diboration of acetylenedicarboxylates.[18] The reaction was also promoted by 4-arylpyridines **6a**–**6c**, where Cl-substituted **6c** showed high catalyst performance (entries 6–8). High catalyst efficiency was also achieved with ethyl isonicotinate (**6g**) and 4-cyanopyridine (**6h**) (entries 13 and 14), whereas parent pyridine (**6d**), 4-picoline (**6e**), and 4-(dimethylamino)pyridine (**6f**) showed low catalyst efficiencies (entries 10–12). These

results indicate that the conjugated functional groups at the C4 position enhance performance of the pyridine catalysts. The **6h**-catalyzed silaboration could be carried out with low catalyst loading (1 mol %); here, **3a** was obtained in 83% isolated yield (entry 15). The cyano group should be on the C4 position; otherwise the yield of **3a** was low (entries 16 and 17). It is noted that P(*n*-Bu)$_3$, *t*-BuOK, and ICy, which have been known to be effective catalysts for Si–B bond activation,[2,13,16a] induced 1,1-silaboration to afford 3-boryl-3-silylacrylate **4a** as a *Z*/*E* mixture (entries 18–20).

Various propiolates were subjected to the organocatalytic silaboration using **6h** (1 mol %) as catalyst (Scheme 2). Methyl, *n*-octyl, and isobutyl propiolates **1b**–**1d** underwent the silaboration with **2** efficiently to afford **3b**–**3d** in 73–77% yields. The reaction of isopropyl propiolate **1e** was slower, and no addition to *t*-butyl propiolate (**1f**) took place, indicating that the reaction is rather sensitive to the steric bulkiness of the alkyl groups. A chloro group on the alkyl substituent was tolerable under the reaction conditions; 3-chloropropyl acrylate **3g** was obtained in 79% yield. The reaction of (2-bromophenyl)methyl propiolate (**1h**) afforded **3h** in moderate yield. In the silaboration of but-1-en-4-yl propiolate (**1i**), **3i** was formed in 69% yield; here, the terminal alkene moiety was left untouched. Cinnamyl propiolate **1j**, which potentially undergoes cleavage of the carbon–oxygen bond in the palladium-catalyzed silaboration, afforded **3j** in 63% yield. The catalyst **6h** also promoted the addition of Me_2PhSi–B(pin) (**7**) and $MePh_2Si$–B(pin) (**9**) to **1a**, although yields of the adducts (*Z*)-**8** and (*Z*)-**10** were moderate. The addition of sterically demanding Ph_3Si–B(pin) (**11**) proceeded at a higher reaction temperature (150 °C) to afford **12**, albeit in low yield.

Table 1. Catalyst Screening[a]



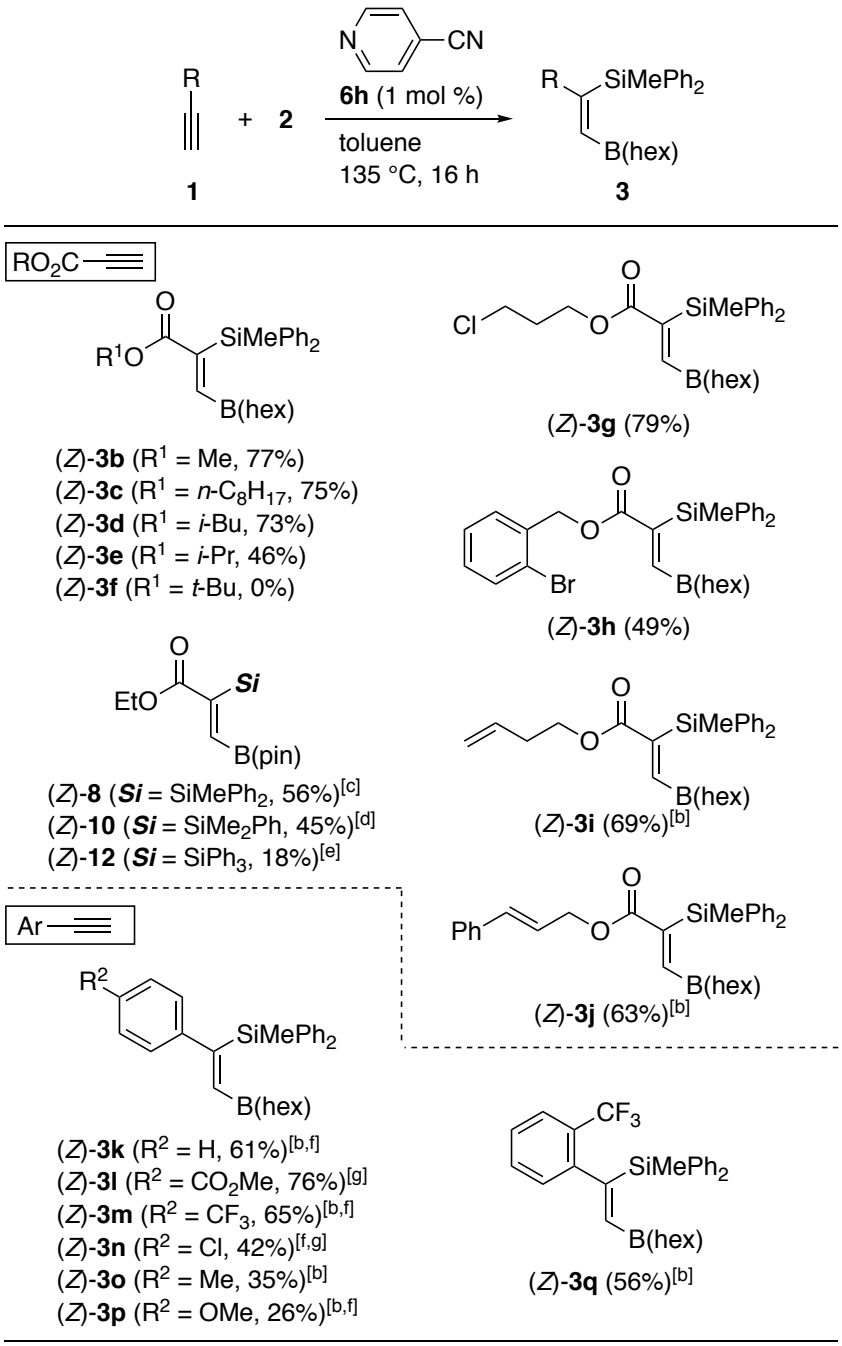
1a **2** (*Z*)-**3a** **4a**

entry	catalyst	% yield[b] (*Z*)-**3a**	% yield[b] **4a**
1	none	trace	0
2	**5a** ($R^1 = R^2 = H$)	trace	0
3	**5b** ($R^1 = H$, $R^2 = Me$)	51	0
4	**5c** ($R^1 = H$, $R^2 = Cl$)	64	0
5	**5d** ($R^1 = R^2 = Me$)	55	0
6	**5e** ($R^1 = R^2 = Cl$)	73	0
7	**6a** ($R^3 = H$)	21	0
8	**6b** ($R^3 = Me$)	59	0
9	**6c** ($R^3 = Cl$)	81	0
10	**6d** ($R^4 = H$)	8	0
11	**6e** ($R^4 = Me$)	12	0
12	**6f** ($R^4 = NMe_2$)	trace	0
13	**6g** ($R^4 = CO_2Et$)	70	0
14	**6h** ($R^4 = CN$)	85	0
15[c]	**6h**	88 (83)[d]	0
16	**6i** ($R^5 = H$, $R^6 = CN$)	9	0
17	**6j** ($R^5 = CN$, $R^6 = H$)	39	0
18	P(*n*-Bu)$_3$	0	63 (*Z*:*E* = 67:33)
19	*t*-BuOK	0	65 (*Z*:*E* = 58:42)
20	ICy[e]	0	92 (*Z*:*E* = 69:31)

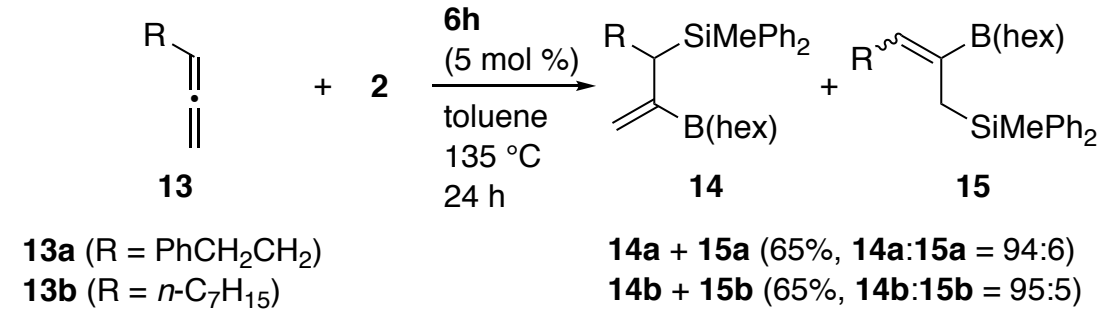
[a] **1a** (0.20 mmol), **2** (0.24 mmol), and a catalyst (0.010 mmol) were reacted in toluene at 135 °C for 16 h. [b] Determined by GC. [c] 1 mol % of **6h** was used. [d] Isolated yield. [e] Generated in situ from ICy•HCl with *t*-BuONa.

Ethynylbenzene (**1k**) also underwent the regioselective *syn*-addition of **2** in the presence of **6h** (2 mol %) to afford (*Z*)-*β*-boryl-*α*-silylstyrene **3k** in 61% yield. Methyl 4-ethynylbenzoate (**1l**) and 1-ethynyl-4-(trifluoromethyl)benzene (**1m**) reacted with **2** efficiently to afford **3l** and **3m** in good yields, whereas the silaboration of 1-ethynyl-4-methylbenzene (**1o**) and 1-ethynyl-4-methoxybenzene (**1p**) were slow, affording the adducts **3o** and **3p** in low yields. Sterically demanding 1-ethynyl-2-trifluoromethylbenzene (**1q**) also underwent addition of **2** to afford **3q** in 56% yield. Diethyl acetylenedicarboxylate (**1r**), methyl 3-phenylpropiolate (**1s**), and 1-phenyl-1-propyne (**1t**) did not afford the corresponding silaboration products in the reaction with **2** in toluene at 135 °C for 24 h when using **6h** (5 mol %). These results indicate that the **6h**-catalyzed silaboration is suitable for conversion of the terminal alkynes conjugated with either a carbonyl group or an electron-deficient aryl group.

Besides alkynes, terminal allenes **13** also underwent **6h**-catalyzed silaboration (Scheme 3).[20] In the presence of **6h** (5 mol %), addition of **2** to 5-phenyl-1,2-pentadiene (**13a**) took place in toluene at 135 °C to afford *β*-borylallylsilane **14a** and a small quantity of isomer **15a** (65%, **14a**:**15a** = 94:6). 1,2-Decadiene (**13b**) also underwent the silaboration selectively at the internal carbon–carbon double bond (65%, **14b**:**15b** = 95:5). It is noteworthy that the regio- and stereoselectivity was found to be identical to that of the palladium-catalyzed silaboration.



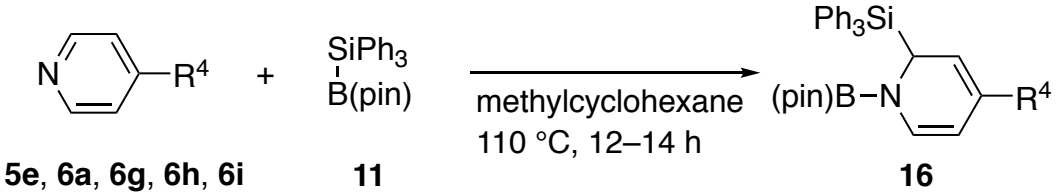
Scheme 2. Silaboration of Alkynes Catalyzed by **6h**. [a] **1** (0.20 mmol), **2** (0.24 mmol), and **6h** (0.0020 mmol) were reacted in toluene at 135 °C for 16 h. Isolated yields of **3** were given. [b] **6h** (2 mol %) was used. [c] $MePh_2Si$–B(pin) (**7**) was used instead of **2**. [d] Me_2PhSi–B(pin) (**9**) was used instead of **2**. [e] Ph_3Si–B(pin) (**11**) was used instead of **2**. The reaction was carried out with **11** (0.30 mmol) at 150 °C for 16 h. The yield was determined by ^1H NMR. [f] Reaction was carried out for 24 h. [g] **6h** (5 mol %) was used.



Scheme 3. Silaboration of Allenes Catalyzed by **6h**

As mentioned, the **6h**-catalyzed silaboration of terminal alkynes and allenes proceeded with the identical regio- and stereoselectivity to that afforded by a palladium catalyst.[21] Considering the possibility that the pyridine compounds used for the silaboration were contaminated with a trace amount of a transition metal, and this contamination was a true catalyst, we carried out ICP-MS analysis of **6h**. Analysis revealed no late transition metals, including palladium (results were as follows: < 0.1 ppm for Co, Ru, Rh, Ir, Pd, Pt, Ag, and Au; < 1 ppm for Fe, Ni, and Cu). We therefore conclude that the additions of **2** to **1** and **13** were accelerated significantly by **6h**.

Table 2. Transition-Metal-Free Silaboration of Pyridines[a]

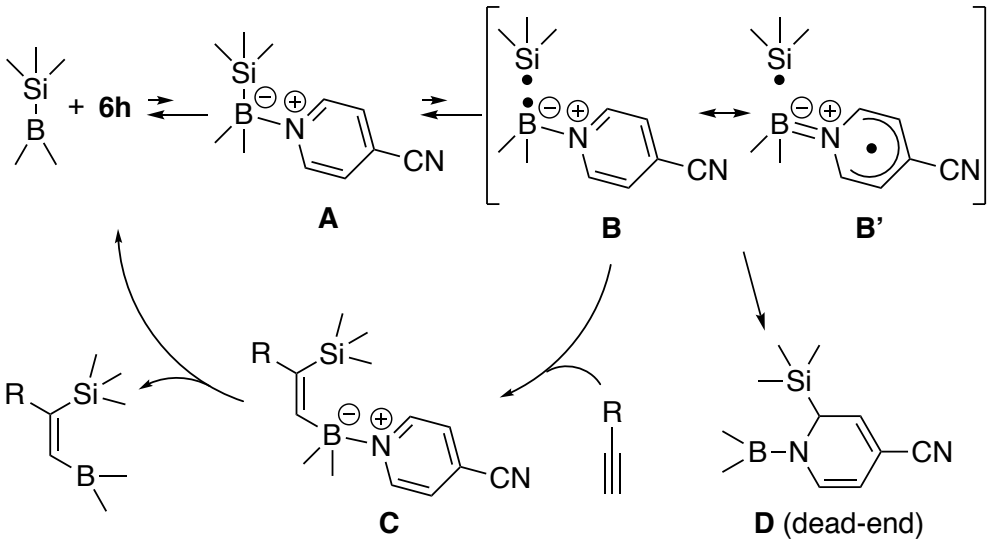


entry	pyridine	yield (%)[b]
1	**5e** (R^4 = 2,6-dichloropyridin-4-yl)	20 (**16a**)
2	**6a** (R^4 = Ph)	no reaction
3	**6g** (R^4 = CO_2Et)	17 (**16b**)
4	**6h** (R^4 = CN)	36 (**16c**)
5[c]	**6h**	(21)[d] (**16c**)
6	**6i** (3-cyanopyridine)	no reaction

[a] **6** (0.10 mmol) and **11** (0.10 mmol) were reacted in methylcyclohexane at 110 °C for 12–14 h. [b] Determined by 1H NMR. [c] **6h** (0.55 mmol) and **11** (0.50 mmol) were reacted in methylcyclohexane at 120 °C for 4 h. [d] Isolated yield.

To understand the mechanism of **6h**-catalyzed silaboration, we first investigated stoichiometric reactions of **6h** with silylboronic esters under transition-metal-free conditions. We found that **6h** underwent 1,2-addition of **11** at 110 °C to afford *N*-boryl-2-silyl-1,2-dihydropyridine **16c**, albeit in low yield (entry 4, Table 2).[22,23] The dearomatized **16c** could be isolated in 21% yield in the reaction under modified conditions (120 °C, 4 h) (entry 5). The dearomatizing addition of **11** to **5e** and **6g** also took place to afford **16a** and **16b**, respectively (entries 1 and 3). On the other hand, **6a** and **6i** did not undergo the addition reaction under the same conditions (entries 2 and 6). These results indicate that cleavage of the Si–B bond of **11** was only achieved with the pyridines that showed high catalyst performance (entries 6, 13, and 14 in Table 1).

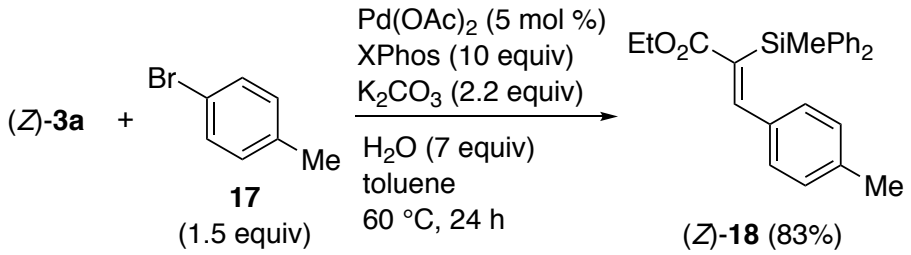
Based on the result shown in Table 2, we assumed the dearomatized *N*-boryl-2-silyl-1,2-dihydropyridine **16** to be an intermediate. However, the reaction of isolated **16c** with **1a** (10 equiv) in toluene at 150 °C did not afford the silaboration product **12** after 16 h, although **16c** decomposed completely at that temperature.[24] This result indicates that *N*-boryl-2-silyl-1,2-dihydropyridine is not involved as an intermediate in the catalytic cycle.



Scheme 4. Possible Mechanism

From these results, we assumed a mechanism in which the Si–B bond is activated by **6h** coordinated onto the boron atom (**A**, Scheme 4). The mechanism involves homolytic cleavage of the Si–B bond, which forms a boryl radical stabilized by **6h**.[25] The generated radical pair **B** rapidly adds to the carbon–carbon triple bond in a *syn* fashion. This addition may take place in an almost concerted manner, as no crossover products were obtained in the reaction of **1a** with **2** (0.57 equiv) and **9** (0.59 equiv) under the same

reaction conditions.[24] The absence of reactive alkyne may result in the formation of **D** as a dead-end product. It is also suggested that the more nucleophilic pyridine-boryl radical preferentially attacks the more electron-deficient alkyne terminus, resulting in the observed regioselectivity.



Scheme 5. Suzuki-Miyaura Coupling of (*Z*)-**3a**

The silaboration products (*Z*)-**3** would be useful synthetic intermediates in the preparation of stereo-defined functionalized organosilicon compounds through conversion of the boryl group. An application in Suzuki-Miyaura coupling is demonstrated as an example (Scheme 5). An ethyl ester (*Z*)-**3a** was reacted with 4-bromotoluene (**17**) in toluene in the presence of a palladium catalyst bearing XPhos as a ligand and K_2CO_3 as a base. The carbon–carbon bond formation took place efficiently at 60 °C with retention of the double bond geometry to afford (*Z*)-3-aryl-2-silylacrylate **18** (83%), which is an isomer that cannot be synthesized by radical or metal-catalyzed hydrosilylation of 3-arylpropiolates.[26]

Conclusion

In conclusion, the auther has established the silaboration of alkyl propiolates, ethynylarenes, and terminal allenes using 4-cyanopyridine as catalyst. The reactions proceed with the identical regio- and stereoselectivity to that afforded by a palladium catalyst. Therefore, this method is a cost-effective alternative to transition-metal-catalyzed silaboration.

Experimental Section

General

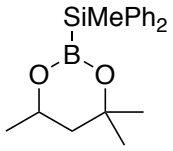
All reactions were performed in glove box or using Schlenk technique under an atmosphere of nitrogen with magnetic stirring. Materials were weighted by electric balances, Sartorius CPA225D or Shimadzu AP225WD (readability: 0.01 mg). Column chromatography was performed with Ultra Pure Silica Gel (SILICYCLE, pH 7.0, 40-63 μm, 60 Å) or CHROMATOREX DIOL MB100-40/75 (Fuji Silysia Chemical Ltd.). Gas chromatography (GC) was performed by Shimadzu GC-2014 with Agilent J&W GC Column DB-1 (ϕ 0.32 mm x 15 m). Gel Permeation Chromatography (GPC) was performed by Japan Analytical Industry LC-908 with series-connected JAIGEL-1H (ϕ 20 mm x 600 mm) and JAIGEL-2H (ϕ 20 mm x 600 mm). ^{1}H NMR spectra were recorded on a Varian 400-MR (399.89 MHz) spectrometer. ^{13}C NMR spectra were recorded on a Varian 400-MR (100.55 MHz) spectrometer. ^{11}B NMR spectra were recorded on a Varian 400-MR (128.30 MHz) spectrometer. ^{1}H NMR data were reported as follows: chemical shifts in ppm downfield from tetramethylsilane, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant (*J*), and integration. ^{13}C and ^{11}B NMR data were reported in ppm downfield from tetramethylsilane (^{13}C) and BF_3•OEt_2 (^{11}B), respectively. High resolution mass spectra were recorded on Thermo Scientific Exactive (ESI, APCI) or JEOL JMS-SX102A (EI) spectrometers.

Materials

Toluene (Kanto, dehydrated, super plus grade) was purchased and used without further purification. Methylcyclohexane was distilled over calcium hydride and degassed. 4,4'-Bipyridine (**5a**, TCI), *t*-BuOK (nacalai), ICy•HCl (TCI), and *t*-BuONa (TCI) were used as received from commercial sources. Substituted 4,4'-bipyridines **5b-e** were prepared by the method reported previously.[17a] P(*n*-Bu)$_3$ (TCI), pyridines **6a** (TCI), **6d** (Wako), **6e** (TCI), **6f** (Wako), **6g** (TCI), **6h** (TCI), **6i** (TCI), and **6j** (TCI) were purchased and distilled before use. Silylboronic esters **2**, **7**, **9**, and **11** were synthesized according to the reported method.[27] Alkynes **1a** (TCI), **1b** (Wako), **1f** (TCI), **1k** (TCI), **1l** (TCI), **1m** (TCI), **1n** (TCI), **1o** (TCI), **1p** (TCI), and **1q** (Sigma-Aldrich) were purchased and distilled before use. Propiolic acid esters **1c**,[28] **1d**, **1e**, **1g**,[29] **1h**, **1i**,[30] and **1j**[31] were synthesized by condensation of propiolic acid (TCI) with the corresponding alcohols under the conditions using *p*-toluenesulfonic acid (for **1c**, **1d**, **1e**, **1g**, **1i**) or *N*,*N'*-dicyclohexylcarbodiimide (DCC) and 4-(*N*,*N*-dimethylamino)pyiridine (DMAP) (for **1h**, **1j**).[28] Allenes **13a** and **13b** were prepared by the reaction of methyl propargyl ether with

the corresponding Grignard reagents in the presence of catalytic amount of CuBr.[32] Followings are new compounds.

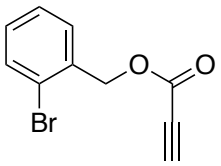
2-(Methyldiphenylsilyl)-4,4,6-trimethyl-1,3,2-dioxaborinane (2)



2

The titled compound was synthesized from methyldiphenylsilyl lithium (30.0 mmol) with 2-isopropoxy-4,4,6-trimethyl-1,3,2-dioxaborinane (65.0 mmol) according to the reported procedure.[27] **2** (7.2 g, 74%) was obtained after Kugelrohr distillation (120 °C/0.2 Torr). **2**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.63 (m, 4H), 7.28-7.33 (m, 6H), 4.21 (dqd, J = 12.0, 6.4, 3.2 Hz, 1H), 1.83 (dd, J = 14.0, 3.2 Hz, 1H), 1.56 (dd, J = 14.0, 12.0 Hz, 1H), 1.32 (s, 3H), 1.29 (s, 3H), 1.26 (d, J = 6.4 Hz, 3H), 0.53 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 135.2, 128.6, 127.7, 71.0, 64.7, 46.6, 31.4, 28.6, 23.3, –4.4. ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.4. HRMS (EI, positive) *m/z* calcd for $C_{19}H_{24}BO_2Si^+$ $[M - H]^+$: 323.1633, found: 323.1634.

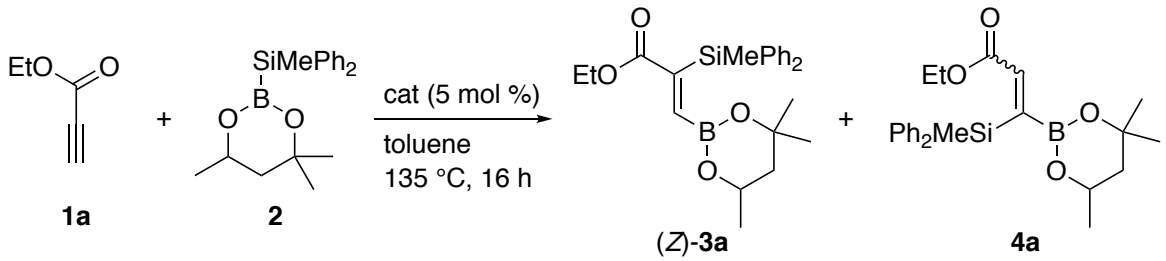
2-Bromobenzyl propiolate (1h)



1h

The titled compound was synthesized from propiolic acid (1.6 g, 22 mmol) with (2-bromophenyl)methanol (3.7 g, 20 mmol) in Et_2O using DCC (4.6 g, 22 mmol) and DMAP (0.25 g, 2.0 mmol).[28] **1h** (2.5 g, 52%) was obtained as a white solid after column chromatography on silica gel [Ultra Pure Silica Gel (SILICYCLE, pH 7.0, 40-63 μm, 60 Å), eluent: hexane:Et_2O = 10:1]. **1h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, J = 7.6, 1.2 Hz, 1H), 7.44 (dd, J = 7.6, 1.2 Hz, 1H), 7.34 (td, J = 7.6, 1.2 Hz, 1H), 7.22 (td, J = 7.6, 1.2 Hz, 1H), 5.32 (s, 2H), 2.93 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4, 134.1, 133.1, 130.3, 127.8, 123.7, 75.5, 74.5, 67.5. HRMS (EI, positive) *m/z* calcd for $C_{10}H_7BrO_2^+$ $[M]^+$: 237.9624, found: 237.9631.

Catalyst Screening (Table 1)

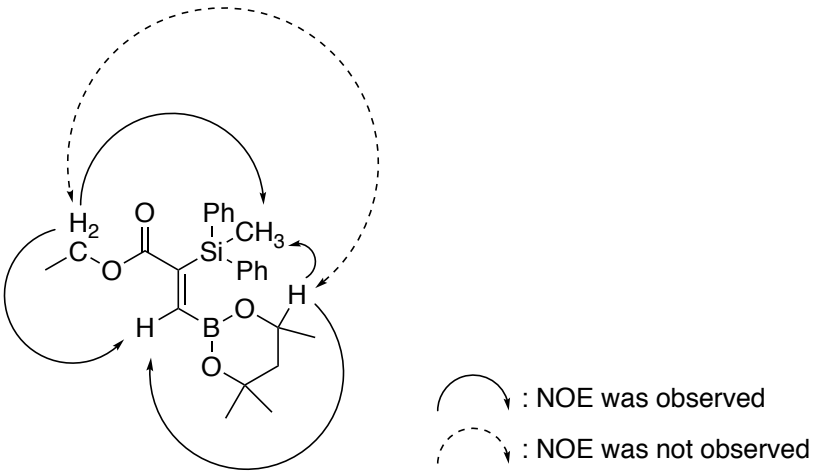


1a **2** (*Z*)-**3a** **4a**

General Procedure: In a glove box, a glass tube (outside diameter: 20 mm) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with a catalyst (0.010 mmol), ethyl propiolate (**1a**, 20 mg, 0.20 mmol), **2** (77 mg, 0.24 mmol), and toluene (0.4 mL). The tube was sealed by the stopcock and was taken out of the glove box. The mixture was stirred at 135 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). After 16 h, the tube was cooled to room temperature, and tetradecane (39 mg, 0.20 mmol, internal standard) was added. The resulting mixture was analyzed by GC to determine the yield of the silaboration products (*Z*)-**3a** and **4a**.

Ethyl (*Z*)-2-(methyldiphenylsilyl)-3-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)acrylate [(*Z*)-3a] (entry 15)

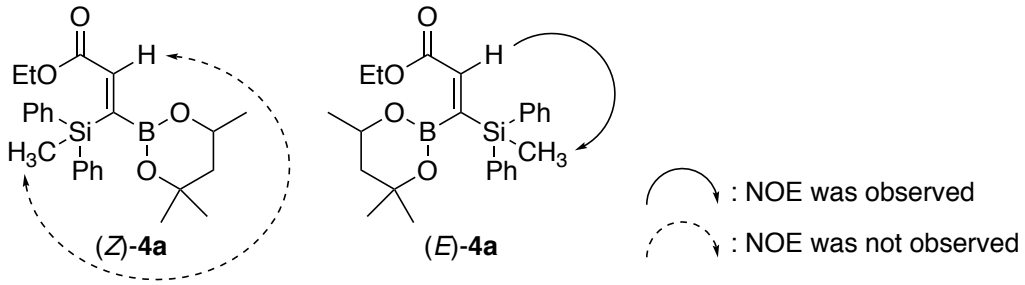
According to the general procedure, the reaction was carried out using **6h** [0.0020 mmol, 20 μL from 0.10 M stock solution, which was prepared using 2 mL volumetric flask with **6h** (20.8 mg, 0.20 mmol) and toluene], **1a** (20 mg, 0.20 mmol), and **2** (78 mg, 0.24 mmol). The product (*Z*)-**3a** (70 mg, 0.17 mmol, 83%) was obtained after purification by column chromatography on silica gel [Ultra Pure Silica Gel (SILICYCLE, pH 7.0, 40-63 μm, 60 Å), eluent: hexane:AcOEt = 19:1 to 9:1; then CHROMATOREX DIOL MB100-40/75 (Fuji Silysia Chemical), eluent: hexane:Et_2O = 9:1]. *Note: The second column chromatography was effective to remove silicon-containing impurities formed from **2**.* (*Z*)-**3a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.62 (m, 4H), 7.30 (s, 1H), 7.26-7.34 (m, 6H), 3.89 (q, J = 7.2 Hz, 2H), 3.70 (dqd, J = 11.6, 6.0, 2.8 Hz, 1H), 1.43 (dd, J = 13.6, 2.8 Hz, 1H), 1.07 (s, 3H), 1.01 (d, J = 6.0 Hz, 3H), 0.97 (t, J = 7.2 Hz, 3H), 0.95 (s, 3H), 0.92 (dd, J = 13.6, 11.6 Hz, 1H), 0.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 152.0 (broad, *C*–B), 148.1, 137.4, 137.1, 135.0, 134.9, 129.03, 128.98, 127.7 (two peaks overlapped), 71.6, 64.8, 60.5, 45.1, 30.8, 28.0, 22.5, 14.0, –2.2. ^{11}B NMR (128 MHz, $CDCl_3$) δ 25.3. HRMS (ESI, positive) *m/z* calcd for $C_{24}H_{31}BO_4SiNa^+$ $[M + Na]^+$: 445.1977, found: 445.1969. The structure of this compound was confirmed by NOE.



Ethyl 3-(methyldiphenylsilyl)-3-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)acrylate (4a) (entry 20)

According to the general procedure, the reaction was carried out using ICy•HCl (2.50 mg, 0.0060 mmol), NaO*t*-Bu (1.03 mg, 0.010 mmol), **1a** (18 mg, 0.18 mmol), and **2** (78 mg, 0.24 mmol). GC analysis of the crude mixture (internal standard: tridecane) indicated no formation of **3a** and formation of **4a** (92%, *Z*:*E* = 69:31). The *Z* and *E* isomers were separable by column chromatography on silica gel [Ultra Pure Silica Gel (SILICYCLE, pH 7.0, 40-63 μm, 60 Å), eluent: hexane:Et_2O = 10:1]. (*Z*)-**4a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.56 (m, 4H), 7.27-7.32 (m, 6H), 6.89 (s, 1H), 3.93 (dqd, *J* = 12.0, 6.0, 2.8 Hz, 1H), 3.22 (q, *J* = 7.2 Hz, 2H), 1.50 (dd, *J* = 14.0, 2.8 Hz, 1H), 1.07 (s, 3H), 1.02 (d, *J* = 6.0 Hz, 3H), 1.02 (t, *J* = 7.2 Hz, 3H), 1.02 (s, 3H), 0.96 (dd, *J* = 14.0, 12.0 Hz, 1H), 0.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 155.3 (*C*–B, not observed by 1D BCM, observed by 2D HMBC), 141.2, 138.5, 138.2, 134.83, 134.81, 128.7 (two peaks overlapped), 127.6 (two peaks overlapped), 71.5, 65.2, 60.3, 45.3, 30.9, 27.8, 22.8, 14.1, –2.9. ^{11}B NMR (128 MHz, $CDCl_3$) δ 26.7. HRMS (ESI, positive) *m/z* calcd for $C_{24}H_{31}BO_4SiNa^+$ $[M + Na]^+$: 445.1977, found: 445.1970. A ^{1}H/^{13}C correlation between H_3C–Si (δ 0.78) and *C*–B (δ 155.3) was observed by 2D HMBC, indicating both the boryl and silyl groups are bound to the identical carbon. The *Z*-geometry of the double bond was determined by NOE. (*E*)-**4a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.60 (m, 4H), 7.28-7.42 (m, 6H), 6.34 (s, 1H), 4.12-4.24 (m, 3H), 1.61 (dd, *J* = 13.6, 3.2 Hz, 1H), 1.27 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.21 (dd, *J* = 13.6, 11.6 Hz, 1H), 1.12 (s, 3H), 1.11 (d, *J* = 6.0 Hz, 3H), 0.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 161.2 (*C*–B, not observed by 1D BCM, observed by 2D HMBC), 138.3, 135.5, 135.4, 129.5, 127.8, 71.3, 65.3, 60.7, 45.8, 31.1, 27.5, 23.0, 14.4, –3.6. ^{11}B NMR (128 MHz, $CDCl_3$) δ 27.4. HRMS (ESI, positive) *m/z* calcd for $C_{24}H_{31}BO_4SiNa^+$ $[M + Na]^+$: 445.1977, found: 445.1970. A ^{1}H/^{13}C

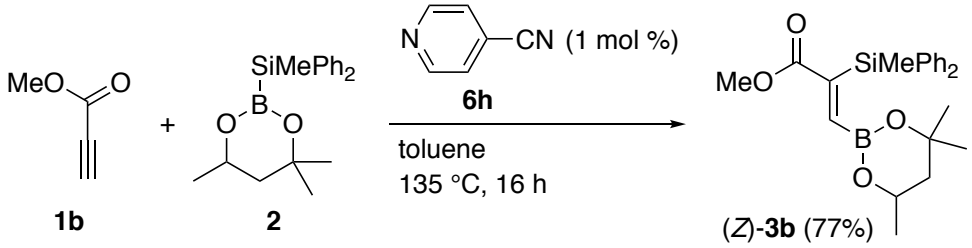
correlation between H_3C–Si (δ 0.72) and *C*–B (δ 161.2) was observed by 2D HMBC, indicating both the boryl and silyl groups are bound to the identical carbon. The *E*-geometry of the double bond was determined by NOE.



Silaboration of Alkynes Catalyzed by 6h (Scheme 2)

General Procedure: In a glove box, a glass tube (outside diameter: 20 mm) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with **6h** [0.0020 mmol, 20 μL from 0.10 M stock solution, which was prepared using 2 mL volumetric flask with **6h** (20.8 mg, 0.20 mmol) and toluene], **1** (0.20 mmol), **2** (0.24 mmol), and toluene (0.4 mL). The tube was sealed by the stopcock and was taken out of the glove box. The mixture was stirred at 135 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). After 16 h, the tube was cooled to room temperature, and the volatiles were removed under reducing pressure. The product (*Z*)-**3** was purified by column chromatography on silica gel or GPC.

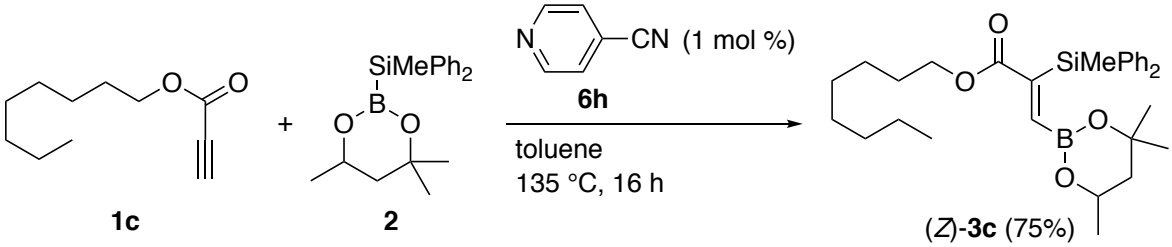
The reaction of 1b with 2 to afford methyl (*Z*)-2-(methyldiphenylsilyl)-3-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)acrylate [(*Z*)-3b]



According to the general procedure, the reaction was carried out using **6h** [0.0020 mmol, 20 μL from 0.10 M stock solution, which was prepared using 2 mL volumetric flask with **6h** (20.8 mg, 0.20 mmol) and toluene], **1b** (16 mg, 0.19 mmol), and **2** (80 mg, 0.25 mmol). The product (*Z*)-**3b** (60 mg, 0.15 mmol, 77%) was obtained after purification by column chromatography on silica gel [Ultra Pure Silica Gel (SILICYCLE, pH 7.0, 40-63 μm, 60

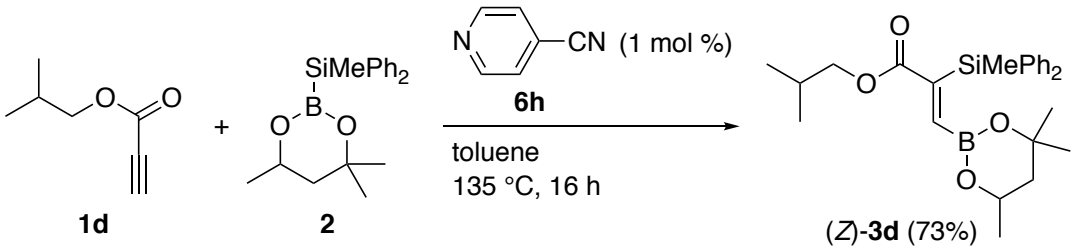
Å), eluent: hexane:AcOEt = 19:1 to 9:1; then CHROMATOREX DIOL MB100-40/75 (Fuji Silysia Chemical), eluent: hexane:Et_2O = 9:1]. (*Z*)-**3b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.62 (m, 4H), 7.28-7.36 (m, 6H), 7.28 (s, 1H), 3.69 (dqd, J = 11.6, 6.0, 2.8 Hz, 1H), 3.43 (s, 3H), 1.43 (dd, J = 13.6, 2.8 Hz, 1H), 1.06 (s, 3H), 0.99 (d, J = 6.0 Hz, 3H), 0.94 (s, 3H), 0.92 (dd, J = 13.6, 11.6 Hz, 1H), 0.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 148.0, 137.2, 136.9, 135.1, 135.0, 129.1, 129.0, 127.8 (two peaks overlapped), 71.6, 64.8, 51.5, 45.1, 30.8, 28.0, 22.5, –2.2. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ 25.3. HRMS (ESI, positive) *m/z* calcd for $C_{23}H_{29}BO_4SiNa^+$ $[M + Na]^+$: 431.1820, found: 431.1813.

The reaction of 1c with 2 to afford *n*-octyl (*Z*)-2-(methyldiphenylsilyl)-3-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)acrylate [(*Z*)-3c]



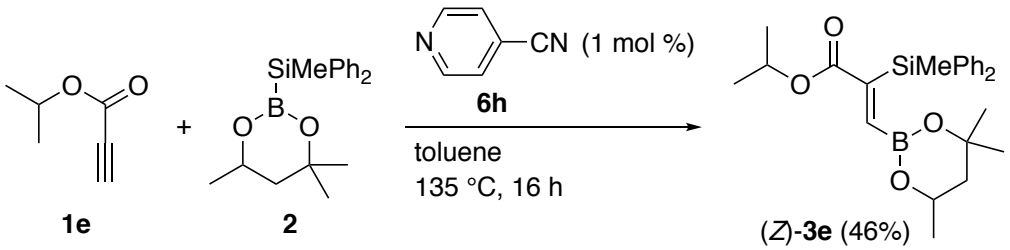
According to the general procedure, the reaction was carried out using **6h** [0.0020 mmol, 20 μL from 0.10 M stock solution, which was prepared using 2 mL volumetric flask with **6h** (20.8 mg, 0.20 mmol) and toluene], **1c** (35 mg, 0.19 mmol), and **2** (78 mg, 0.24 mmol). The product (*Z*)-**3c** (72 mg, 0.14 mmol, 75%) was obtained after purification by column chromatography on silica gel [Ultra Pure Silica Gel (SILICYCLE, pH 7.0, 40-63 μm, 60 Å), eluent: hexane:AcOEt = 19:1 to 9:1, twice]. (*Z*)-**3c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.62 (m, 4H), 7.32 (s, 1H), 7.26-7.36 (m, 6H), 3.78-3.88 (m, 2H), 3.69 (dqd, J = 11.6, 6.4, 2.8 Hz, 1H), 1.43 (dd, J = 14.0, 2.8 Hz, 1H), 1.07 (s, 3H), 1.09-1.37 (m, 12H), 1.00 (d, J = 6.4 Hz, 3H), 0.95 (s, 3H), 0.87-0.95 (m, 1H), 0.88 (t, J = 7.2 Hz, 3H), 0.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.7, 152.0 (broad, *C*–B), 148.0, 137.4, 137.1, 135.0, 134.9, 129.03, 128.99, 127.8 (two peaks overlapped), 71.6, 64.83, 64.78, 45.1, 31.9, 30.8, 29.31, 29.26, 28.5, 28.0, 26.0, 22.8, 22.5, 14.3, –2.1. ^{11}B NMR (128 MHz, $CDCl_3$) δ 25.2. HRMS (ESI, positive) *m/z* calcd for $C_{30}H_{43}BO_4SiNa^+$ $[M + Na]^+$: 529.2916, found: 529.2916.

The reaction of 1d with 2 to afford isobutyl (*Z*)-2-(methyldiphenylsilyl)-3-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)acrylate [(*Z*)-3d]



According to the general procedure, the reaction was carried out using **6h** [0.0020 mmol, 20 μL from 0.10 M stock solution, which was prepared using 2 mL volumetric flask with **6h** (20.8 mg, 0.20 mmol) and toluene], **1d** (24 mg, 0.19 mmol), and **2** (79 mg, 0.24 mmol). The product (*Z*)-**3d** (64 mg, 0.14 mmol, 73%) was obtained after purification by column chromatography on silica gel [Ultra Pure Silica Gel (SILICYCLE, pH 7.0, 40-63 μm, 60 Å), eluent: hexane:AcOEt = 19:1 to 9:1; then CHROMATOREX DIOL MB100-40/75 (Fuji Silysia Chemical), eluent: hexane:Et_2O = 9:1]. (*Z*)-**3d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.62 (m, 4H), 7.32 (s, 1H), 7.27-7.36 (m, 6H), 3.68 (dqd, J = 11.6, 6.4, 2.8 Hz, 1H), 3.66 [dd (AB pattern), J = 10.4, 6.4 Hz, 1H], 3.62 [dd (AB pattern), J = 10.4, 6.4 Hz, 1H], 1.66 (nonet, J = 6.4 Hz, 1H), 1.42 (dd, J = 13.6, 2.8 Hz, 1H), 1.07 (s, 3H), 1.00 (d, J = 6.4 Hz, 3H), 0.95 (s, 3H), 0.90 (dd, J = 13.6, 11.6 Hz, 1H), 0.78 (s, 3H), 0.73 (d, J = 6.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.7, 152.2 (broad, *C*–B), 148.0, 137.4, 137.0, 135.1, 135.0, 129.1, 129.0, 127.8 (two peaks overlapped), 71.6, 70.9, 64.8, 45.1, 30.8, 28.1, 27.7, 24.5, 19.20, 19.19, –2.1. ^{11}B NMR (128 MHz, $CDCl_3$) δ 25.5. HRMS (ESI, positive) *m/z* calcd for $C_{26}H_{35}BO_4SiNa^+$ $[M + Na]^+$: 473.2290, found: 473.2284.

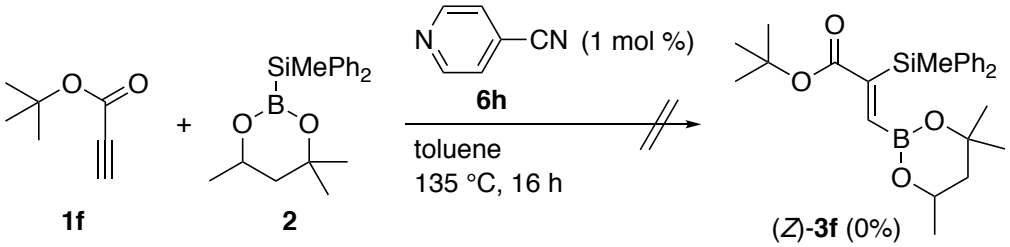
The reaction of 1e with 2 to afford isopropyl (*Z*)-2-(methyldiphenylsilyl)-3-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)acrylate [(*Z*)-3e]



According to the general procedure, the reaction was carried out using **6h** [0.0020 mmol, 20 μL from 0.10 M stock solution, which was prepared using 2 mL volumetric flask with **6h** (20.8 mg, 0.20 mmol) and toluene], **1e** (22 mg, 0.20 mmol), and **2** (79 mg, 0.24 mmol). The product (*Z*)-**3e** (39 mg, 0.090 mmol, 46%) was obtained after purification by column chromatography on silica gel [Ultra Pure Silica Gel (SILICYCLE, pH 7.0, 40-63 μm, 60 Å), eluent: hexane:AcOEt = 19:1 to 9:1; then CHROMATOREX DIOL MB100-40/75

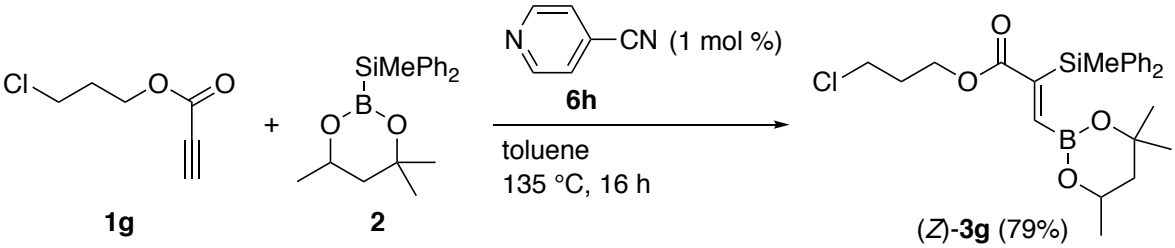
(Fuji Silysia Chemical), eluent: hexane:Et_2O = 9:1]. (*Z*)-**3e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.62 (m, 4H), 7.31 (s, 1H), 7.26-7.35 (m, 6H), 4.79 (sept, J = 6.4 Hz, 1H), 3.70 (dqd, J = 12.0, 6.4, 2.8 Hz, 1H), 1.44 (dd, J = 14.0, 2.8 Hz, 1H), 1.08 (s, 3H), 1.01 (d, J = 6.4 Hz, 3H), 0.96 (s, 3H), 0.95 (d, J = 6.4 Hz, 3H), 0.93 (d, J = 6.4 Hz, 3H), 0.88-0.98 (m, 1H), 0.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 151.6 (broad, *C*–B), 148.3, 137.5, 137.3, 135.0, 134.9, 128.98, 128.96, 127.8 (two peaks overlapped), 71.6, 68.0, 64.8, 45.1, 30.8, 28.1, 22.5, 21.6, 21.5, –2.2. ^{11}B NMR (128 MHz, $CDCl_3$) δ 25.3. HRMS (ESI, positive) *m/z* calcd for $C_{25}H_{33}BO_4SiNa^+$ [M + Na]$^+$: 459.2133, found: 459.2129.

An attempt of the reaction of 1f with 2 to obtain *tert*-butyl (*Z*)-2-(methyldiphenylsilyl)-3-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)acrylate [(*Z*)-3f]



According to the general procedure, the reaction was carried out using **6h** [0.0020 mmol, 20 μL from 0.10 M stock solution, which was prepared using 2 mL volumetric flask with **6h** (20.8 mg, 0.20 mmol) and toluene], **1f** (23 mg, 0.19 mmol), and **2** (79 mg, 0.24 mmol). The desired product (*Z*)-**3f** did not observed by GCMS and ^{1}H NMR analyses after reaction at 135 °C for 16 h.

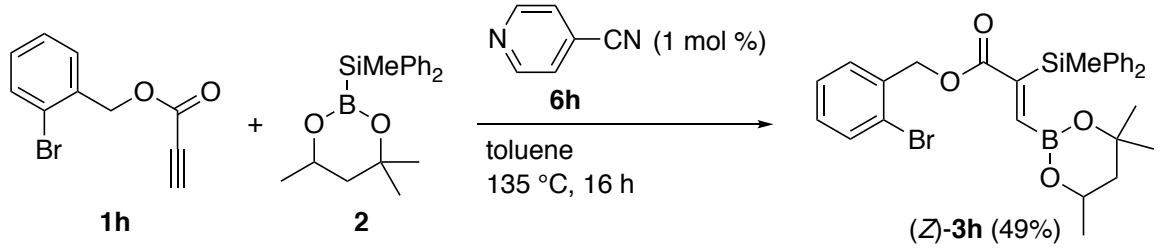
The reaction of 1g with 2 to afford 3-chloroprop-1-yl (*Z*)-2-(methyldiphenylsilyl)-3-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)acrylate [(*Z*)-3g]



According to the general procedure, the reaction was carried out using **6h** [0.0020 mmol, 20 μL from 0.10 M stock solution, which was prepared using 2 mL volumetric flask with **6h** (20.8 mg, 0.20 mmol) and toluene], **1g** (28 mg, 0.20 mmol), and **2** (78 mg, 0.24 mmol). The product (*Z*)-**3g** (72 mg, 0.15 mmol, 79%) was obtained after purification by column

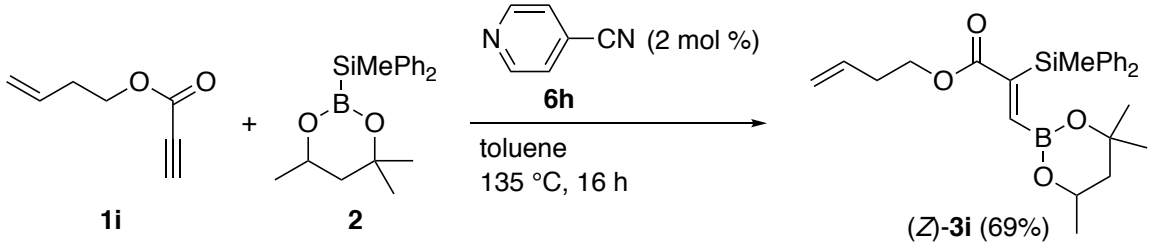
chromatography on silica gel [Ultra Pure Silica Gel (SILICYCLE, pH 7.0, 40-63 μm, 60 Å), eluent: hexane:AcOEt = 19:1 to 9:1; then CHROMATOREX DIOL MB100-40/75 (Fuji Silysia Chemical), eluent: hexane:Et_2O = 9:1]. (*Z*)-**3g**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.61 (m, 4H), 7.34 (s, 1H), 7.28-7.38 (m, 6H), 3.95-4.04 (m, 2H), 3.71 (dqd, J = 11.6, 6.4, 3.2 Hz, 1H), 3.22 (t, J = 6.4 Hz, 2H), 1.72-1.78 (m, 2H), 1.44 (dd, J = 13.6, 3.2 Hz, 1H), 1.08 (s, 3H), 1.02 (d, J = 6.4 Hz, 3H), 0.96 (s, 3H), 0.93 (dd, J = 13.6, 11.6 Hz, 1H), 0.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 147.4, 137.2, 136.9, 134.93, 134.86, 129.19, 129.15, 127.9 (two peaks overlapped), 71.7, 64.9, 61.2, 45.1, 41.3, 31.6, 30.8, 28.1, 22.5, –2.2. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ 25.3. HRMS (ESI, positive) *m/z* calcd for $C_{25}H_{32}BClO_4SiNa^+$ $[M + Na]^+$: 493.1744, found: 493.1739.

The reaction of 1h with 2 to afford 2-bromobenzyl (*Z*)-2-(methyldiphenylsilyl)-3-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)acrylate [(*Z*)-3h]



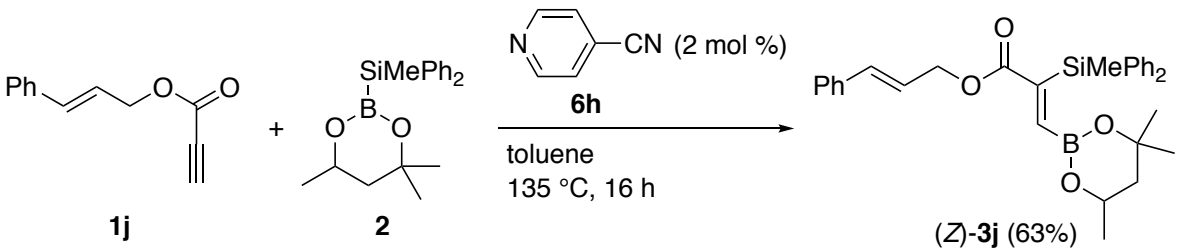
According to the general procedure, the reaction was carried out using **6h** [0.0020 mmol, 20 μL from 0.10 M stock solution, which was prepared using 2 mL volumetric flask with **6h** (20.8 mg, 0.20 mmol) and toluene], **1h** (48 mg, 0.20 mmol), and **2** (81 mg, 0.25 mmol). The product (*Z*)-**3h** (55 mg, 0.10 mmol, 49%) was obtained after purification by Gel Permeation Chromatography (GPC), which was performed by Japan Analytical Industry LC-908 with series-connected JAIGEL-1H (ϕ 20 mm x 600 mm) and JAIGEL-2H (ϕ 20 mm x 600 mm). (*Z*)-**3h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.62 (m, 4H), 7.50 (dd, J = 7.6, 1.6 Hz, 1H), 7.41 (s, 1H), 7.26-7.37 (m, 6H), 7.08-7.17 (m, 2H), 6.99 (dd, J = 7.2, 2.0 Hz, 1H), 5.02 [d (AB pattern), J = 13.6 Hz, 1H], 4.98 [d (AB pattern), J = 13.6 Hz, 1H], 3.70 (dqd, J = 11.6, 6.0, 3.2 Hz, 1H), 1.43 (dd, J = 13.6, 3.2 Hz, 1H), 1.08 (s, 3H), 1.01 (d, J = 6.0 Hz, 3H), 0.96 (s, 3H), 0.92 (dd, J = 13.6, 11.6 Hz, 1H), 0.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 147.2, 137.0, 136.7, 135.5, 135.2, 135.0, 132.6, 129.7, 129.4, 129.2, 129.1, 127.8 (two peaks overlapped), 127.4, 123.2, 71.7, 65.8, 64.9, 45.1, 30.8, 28.1, 22.5, –2.1. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ 25.2. HRMS (ESI, positive) *m/z* calcd for $C_{29}H_{32}BBrO_4SiNa^+$ $[M + Na]^+$: 585.1239, found:585.1233.

The reaction of 1i with 2 to afford 3-buten-1-yl (*Z*)-2-(methyldiphenylsilyl)-3-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)acrylate [(*Z*)-3i]



According to the general procedure, the reaction was carried out using **6h** [0.0040 mmol, 40 μL from 0.10 M stock solution, which was prepared using 2 mL volumetric flask with **6h** (20.8 mg, 0.20 mmol) and toluene], **1i** (26 mg, 0.21 mmol), and **2** (78 mg, 0.24 mmol). The product (*Z*)-**3i** (65 mg, 0.14 mmol, 69%) was obtained after purification by column chromatography on silica gel [Ultra Pure Silica Gel (SILICYCLE, pH 7.0, 40-63 μm, 60 Å), eluent: hexane:AcOEt = 19:1 to 9:1; then CHROMATOREX DIOL MB100-40/75 (Fuji Silysia Chemical), eluent: hexane:Et_2O = 9:1]. (*Z*)-**3i**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.81 (s, 1H), 7.68-7.76 (m, 4H), 7.11-7.21 (m, 6H), 5.37-5.49 (m, 1H), 4.84-4.87 (m, 1H), 4.80-4.84 (m, 1H), 3.80-3.91 (m, 2H), 3.41 (dqd, J = 12.0, 6.0, 2.8 Hz, 1H), 1.89-1.96 (m, 2H), 0.933 (s, 3H), 0.925 (s, 3H), 0.89 (d, J = 2.8 Hz, 1H), 0.83 (d, J = 6.0 Hz, 3H), 0.73 (s, 3H), 0.66 (dd, J = 13.6, 12.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 147.9, 137.4, 137.0, 135.0, 134.9, 134.3, 129.1, 129.0, 127.8 (two peaks overlapped), 117.0, 71.6, 64.8, 63.8, 45.1, 32.9, 30.8, 28.0, 22.5, –2.2. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ 25.3. HRMS (ESI, positive) *m/z* calcd for $C_{26}H_{33}BO_4SiNa^+$ $[M + Na]^+$: 471.2133, found: 471.2127.

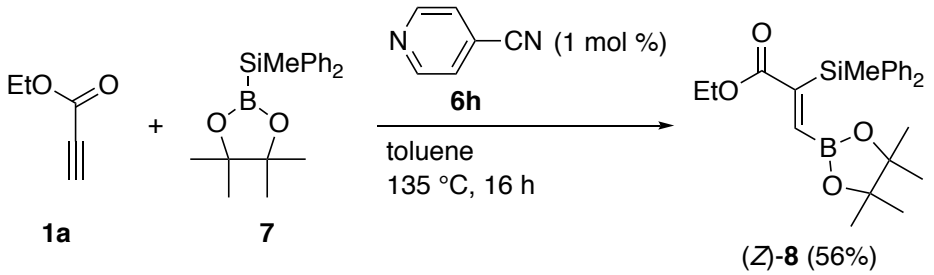
The reaction of 1j with 2 to afford cinnamyl (*Z*)-2-(methyldiphenylsilyl)-3-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)acrylate [(*Z*)-3j]



According to the general procedure, the reaction was carried out using **6h** [0.0040 mmol, 40 μL from 0.10 M stock solution, which was prepared using 2 mL volumetric flask with **6h** (20.8 mg, 0.20 mmol) and toluene], **1j** (37 mg, 0.20 mmol), and **2** (77 mg, 0.24 mmol).

The product (*Z*)-**3j** (63 mg, 0.12 mmol, 63%) was obtained after purification by column chromatography on silica gel [Ultra Pure Silica Gel (SILICYCLE, pH 7.0, 40-63 μm, 60 Å), eluent: hexane:AcOEt = 19:1 to 9:1; then CHROMATOREX DIOL MB100-40/75 (Fuji Silysia Chemical), eluent: hexane:Et_2O = 9:1]. (*Z*)-**3j**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.63 (m, 4H), 7.34 (s, 1H), 7.22-7.35 (m, 11H), 6.42 (d, J = 16.0 Hz, 1H), 5.94 (dt, J = 16.0, 6.0 Hz, 1H), 4.50 (d, J = 6.0 Hz, 2H), 3.70 (dqd, J = 12.0, 6.0, 2.8 Hz, 1H), 1.44 (dd, J = 14.0, 2.8 Hz, 1H), 1.07 (s, 3H), 1.01 (d, J = 6.0 Hz, 3H), 0.95 (s, 3H), 0.93 (dd, J = 14.0, 12.0 Hz, 1H), 0.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 147.9, 137.3, 137.0, 136.6, 135.1, 135.0, 133.6, 129.10, 129.06, 128.6, 128.0, 127.8 (two peaks overlapped), 126.7, 123.5, 71.6, 65.1, 64.9, 45.1, 30.8, 28.0, 22.5, –2.2. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ 25.2. HRMS (ESI, positive) *m/z* calcd for $C_{31}H_{35}BO_4SiNa^+$ $[M + Na]^+$: 533.2290, found: 533.2284.

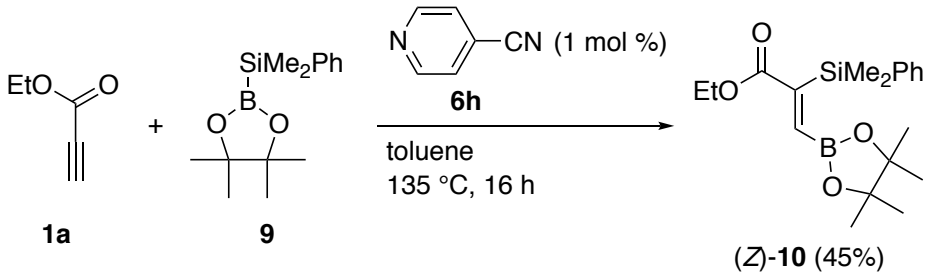
The reaction of 1a with 7 to afford ethyl (*Z*)-2-(methyldiphenylsilyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate [(*Z*)-8]



According to the general procedure, the reaction was carried out using **6h** [0.0020 mmol, 20 μL from 0.10 M stock solution, which was prepared using 2 mL volumetric flask with **6h** (20.8 mg, 0.20 mmol) and toluene], **1a** (18 mg, 0.19 mmol), and **7** (83 mg, 0.26 mmol). The product (*Z*)-**8** (44 mg, 0.10 mmol, 56%) was obtained after purification by column chromatography on silica gel [Ultra Pure Silica Gel (SILICYCLE, pH 7.0, 40-63 μm, 60 Å), eluent: hexane:AcOEt = 19:1 to 9:1; then CHROMATOREX DIOL MB100-40/75 (Fuji Silysia Chemical), eluent: hexane:Et_2O = 9:1]. (*Z*)-**8**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.59 (m, 4H), 7.28-7.36 (m, 6H), 7.08 (s, 1H), 3.84 (q, J = 7.2 Hz, 2H), 0.96 (s, 12H), 0.95 (t, J = 7.2 Hz, 3H), 0.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 154.6, 136.8, 135.0, 129.2, 127.7, 84.0, 60.7, 24.7, 13.9, –2.2. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ 28.6. HRMS (ESI, positive) *m/z* calcd for $C_{24}H_{31}BO_4SiNa^+$ $[M + Na]^+$: 445.1977, found: 445.1973.

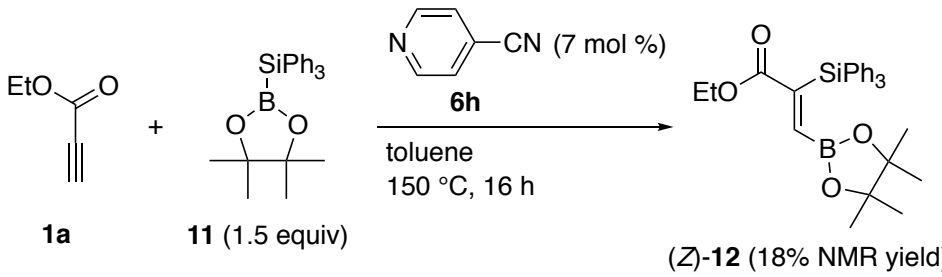
The reaction of 1a with 9 to afford ethyl (*Z*)-2-(dimethylphenylsilyl)-3-(4,4,5,5-

tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate [(*Z*)-10]



According to the general procedure, the reaction was carried out using **6h** [0.0020 mmol, 20 μL from 0.10 M stock solution, which was prepared using 2 mL volumetric flask with **6h** (20.8 mg, 0.20 mmol) and toluene], **1a** (19 mg, 0.19 mmol), and **9** (61 mg, 0.23 mmol). The product (*Z*)-**10** (31 mg, 0.090 mmol, 45%) was obtained after purification by column chromatography on silica gel [Ultra Pure Silica Gel (SILICYCLE, pH 7.0, 40-63 μm, 60 Å), eluent: hexane:AcOEt = 19:1 to 9:1; then CHROMATOREX DIOL MB100-40/75 (Fuji Silysia Chemical), eluent: hexane:Et_2O = 9:1]. (*Z*)-**10**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.58 (m, 2H), 7.28-7.33 (m, 3H), 7.03 (s, 1H), 4.05 (q, J = 7.2 Hz, 2H), 1.16 (t, J = 7.2 Hz, 3H), 1.14 (s, 12H), 0.50 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 154.9, 138.8, 134.1, 128.9, 127.7, 84.1, 60.7, 24.9, 14.2, –1.1. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ 28.9. HRMS (ESI, positive) *m/z* calcd for $C_{19}H_{29}BO_4SiNa^+$ $[M + Na]^+$: 383.1820, found: 383.1818.

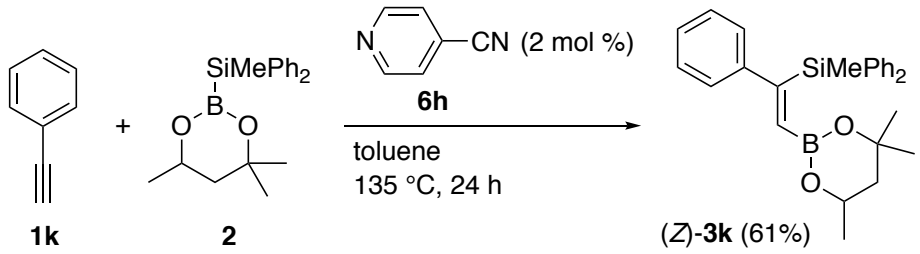
The reaction of 1a with 11 to afford ethyl (*Z*)-2-(triphenylsilyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate [(*Z*)-12]



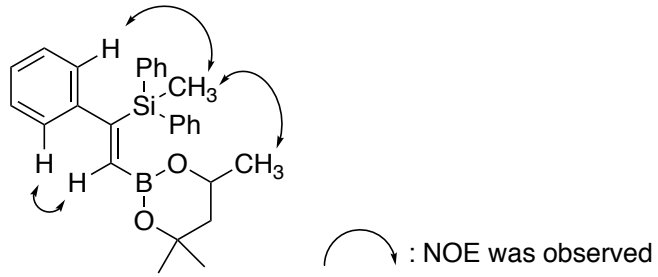
According to the general procedure, the reaction was carried out at 150 °C for 16 h using **6h** (1.4 mg, 0.014 mmol), **1a** (20 mg, 0.20 mmol), **11** (115 mg, 0.30 mmol), and toluene (0.4 mL). ^{1}H NMR analysis of the crude reaction mixture indicated that the product (*Z*)-**12** was formed in 18% yield. Purification of (*Z*)-**12** by Gel Permeation Chromatography (GPC) was attempted, but it did not obtained as a pure form. Therefore, only ^{1}H NMR and HRMS data were collected. (*Z*)-**12**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.68 (m, 6H), 7.29-7.41 (m, 9H), 7.18 (s, 1H), 3.77 (q, J = 7.2 Hz, 2H), 0.87 (t, J = 7.2 Hz, 3H), 0.80 (s,

12H). HRMS (ESI, positive) *m/z* calcd for $C_{29}H_{33}BO_4SiNa^+$ $[M + Na]^+$: 507.2133, found: 507.2135.

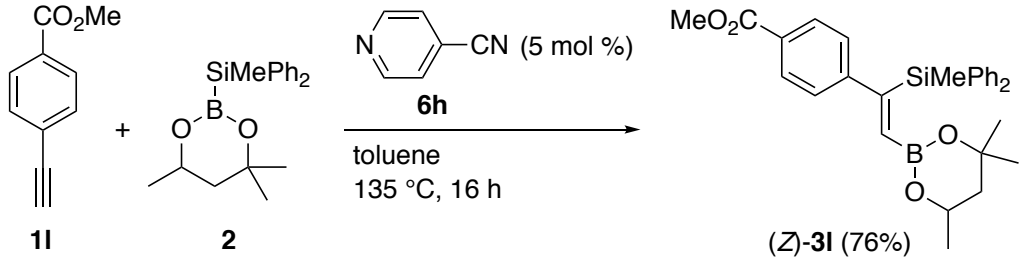
The reaction of 1k with 2 to afford (*Z*)-1-(methyldiphenylsilyl-2-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)-1-phenylethene [(*Z*)-3k]



According to the general procedure, the reaction was carried out using **6h** [0.0040 mmol, 40 μL from 0.10 M stock solution, which was prepared using 2 mL volumetric flask with **6h** (20.8 mg, 0.20 mmol) and toluene], **1k** (21 mg, 0.20 mmol), and **2** (78 mg, 0.24 mmol). The product (*Z*)-**3k** (53 mg, 0.12 mmol, 61%) was obtained after purification by column chromatography on silica gel [Ultra Pure Silica Gel (SILICYCLE, pH 7.0, 40-63 μm, 60 Å), eluent: hexane:Et_2O = 49:1 to 11:1]. (*Z*)-**3k**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.71 (m, 2H), 7.52-7.56 (m, 2H), 7.25-7.39 (m, 6H), 7.04-7.16 (m, 5H), 6.55 (s, 1H), 3.56 (dqd, *J* = 11.6, 6.0, 2.8 Hz, 1H), 1.40 (dd, *J* = 13.6, 2.8 Hz, 1H), 1.06 (s, 3H), 0.94 (d, *J* = 6.0 Hz, 3H), 0.90-0.98 (m, 1H), 0.89 (s, 3H), 0.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 148.6, 144.8 (*C*–B, detected by 2D HMQC), 138.5, 137.5, 135.6, 135.2, 129.0, 128.7, 127.8, 127.7 (two peaks overlapped), 126.9, 125.9, 71.2, 64.4, 45.2, 30.9, 28.0, 22.5, –0.6. ^{11}B NMR (128 MHz, $CDCl_3$) δ 25.2. HRMS (APCI, positive) *m/z* calcd for $C_{27}H_{32}BO_2Si^+$ $[M + H]^+$: 427.2259, found: 427.2254. The structure of this compound was confirmed by NOE.

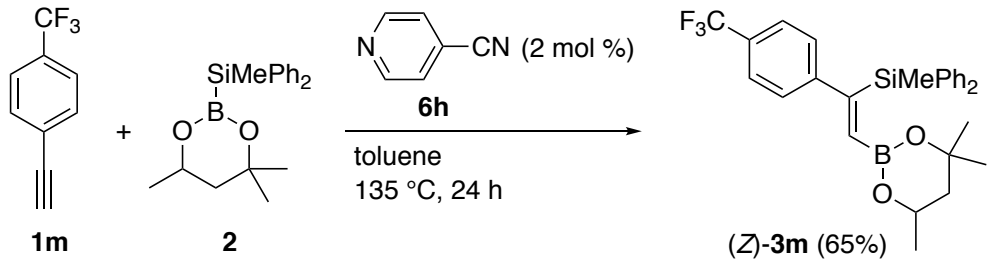


The reaction of 1l with 2 to afford (*Z*)-1-(methyldiphenylsilyl-2-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)-1-(4-methoxycarbonylphenyl)ethene [(*Z*)-3l]



According to the general procedure, the reaction was carried out using **6h** (1.3 mg, 0.010 mmol), **1l** (35 mg, 0.22 mmol), and **2** (78 mg, 0.24 mmol). The product (*Z*)-**3l** (80 mg, 0.16 mmol, 76%) was obtained after purification by column chromatography on silica gel [Ultra Pure Silica Gel (SILICYCLE, pH 7.0, 40-63 μm, 60 Å), eluent: hexane:AcOEt = 19:1 to 9:1; then CHROMATOREX DIOL MB100-40/75 (Fuji Silysia Chemical), eluent: hexane:Et_2O = 9:1]. (*Z*)-**3l**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.82 (m, 2H), 7.63-7.68 (m, 2H), 7.50-7.55 (m, 2H), 7.25-7.39 (m, 6H), 7.08-7.12 (m, 2H), 6.56 (s, 1H), 3.86 (s, 3H), 3.59 (dqd, *J* = 11.6, 6.0, 2.8 Hz, 1H), 1.42 (dd, *J* = 14.0, 2.8 Hz, 1H), 1.06 (s, 3H), 0.96 (d, *J* = 6.0 Hz, 3H), 0.91-0.99 (m, 1H), 0.90 (s, 3H), 0.52 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 157.3, 153.7, 145.8 (*C*–B, detected by 2D HMQC), 137.9, 137.0, 135.5, 135.1, 129.24, 129.16, 128.9, 127.8 (two peaks overlapped), 127.6, 127.0, 71.4, 64.5, 52.0, 45.2, 30.9, 28.0, 22.5, –0.9. ^{11}B NMR (128 MHz, $CDCl_3$) δ 24.9. HRMS (ESI, positive) *m/z* calcd for $C_{29}H_{33}BO_4SiNa^+$ $[M + Na]^+$: 507.2133, found: 507.2132.

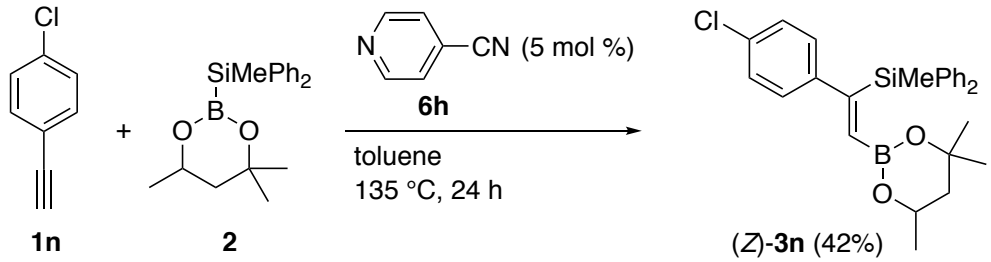
The reaction of 1m with 2 to afford (*Z*)-1-(methyldiphenylsilyl-2-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)-1-(4-trifluoromethylphenyl)ethene [(*Z*)-3m]



According to the general procedure, the reaction was carried out using **6h** [0.0040 mmol, 40 μL from 0.10 M stock solution, which was prepared using 2 mL volumetric flask with **6h** (20.8 mg, 0.20 mmol) and toluene], **1m** (34 mg, 0.20 mmol), and **2** (78 mg, 0.24 mmol). The product (*Z*)-**3m** (34 mg, 0.13 mmol, 65%) was obtained after purification by column chromatography on silica gel [Ultra Pure Silica Gel (SILICYCLE, pH 7.0, 40-63 μm, 60 Å), eluent: hexane:Et_2O = 32:1 to 11:1]. (*Z*)-**3m**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.68 (m, 2H), 7.50-7.54 (m, 2H), 7.26-7.40 (m, 8H), 7.10-7.15 (m, 2H), 6.55 (s, 1H), 3.59 (dqd, *J* = 11.6, 6.0, 2.8 Hz, 1H), 1.42 (dd, *J* = 13.6, 2.8 Hz, 1H), 1.07 (s, 3H), 0.96 (d, *J* =

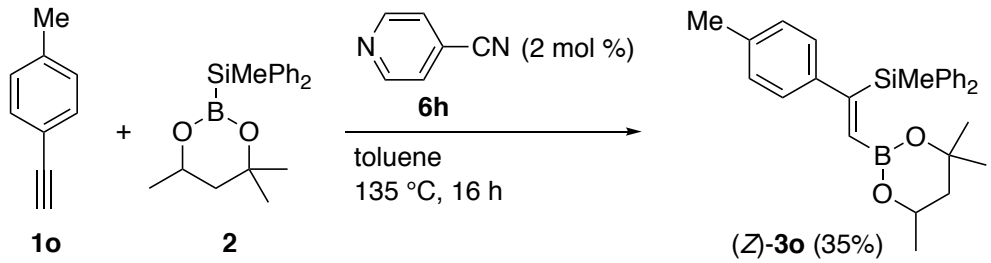
6.0 Hz, 3H), 0.91-0.99 (m, 1H), 0.91 (s, 3H), 0.51 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 152.3, 146.1 (broad, *C*–B), 137.7, 136.8, 135.5, 135.1, 129.2, 129.0, 128.0 (q, $^2J_{CF}$ = 32 Hz), 127.8 (two peaks overlapped), 127.2, 124.8 (q, $^3J_{CF}$ = 3.9 Hz), 124.6 (q, $^1J_{CF}$ = 270 Hz), 71.4, 64.6, 45.2, 30.9, 28.0, 22.5, –0.9. ^{11}B NMR (128 MHz, $CDCl_3$) δ 25.3. HRMS (APCI, positive) *m/z* calcd for $C_{28}H_{31}BF_3O_2Si^+$ $[M + H]^+$: 495.2133, found: 495.2125.

The reaction of 1n with 2 to afford (*Z*)-1-(methyldiphenylsilyl-2-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)-1-(4-chlorophenyl)ethene [(*Z*)-3n]



According to the general procedure, the reaction was carried out using **6h** (1.1 mg, 0.010 mmol), **1n** (27 mg, 0.20 mmol), and **2** (78 mg, 0.24 mmol). The product (*Z*)-**3n** (38 mg, 0.080 mmol, 42%) was obtained after purification by column chromatography on silica gel [Ultra Pure Silica Gel (SILICYCLE, pH 7.0, 40-63 μm, 60 Å), eluent: hexane:Et_2O = 49:1 to 13:1]. (*Z*)-**3n**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.67 (m, 2H), 7.49-7.54 (m, 2H), 7.26-7.38 (m, 6H), 7.07-7.11 (m, 2H), 6.95-7.00 (m, 2H), 6.52 (s, 1H), 3.57 (dqd, *J* = 12.0, 6.0, 2.8 Hz, 1H), 1.41 (dd, *J* = 14.0, 2.8 Hz, 1H), 1.06 (s, 3H), 0.95 (d, *J* = 6.0 Hz, 3H), 0.90-0.98 (m, 1H), 0.89 (s, 3H), 0.51 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6, 147.1, 138.0, 137.1, 135.6, 135.1, 131.7, 129.1, 128.9, 128.3, 127.9, 127.8 (two peaks overlapped), 71.3, 64.5, 45.2, 30.9, 28.0, 22.5, –0.8. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ 24.4. HRMS (APCI, positive) *m/z* calcd for $C_{27}H_{31}BClO_2Si^+$ $[M + H]^+$: 461.1869, found: 461.1865.

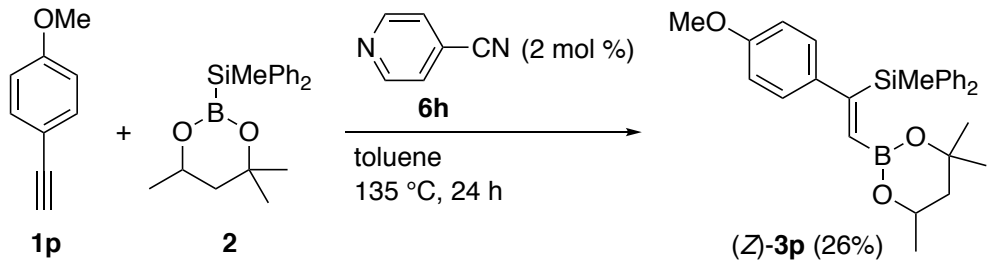
The reaction of 1o with 2 to afford (*Z*)-1-(methyldiphenylsilyl-2-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)-1-(4-methylphenyl)ethene [(*Z*)-3o]



According to the general procedure, the reaction was carried out using **6h** [0.0040 mmol,

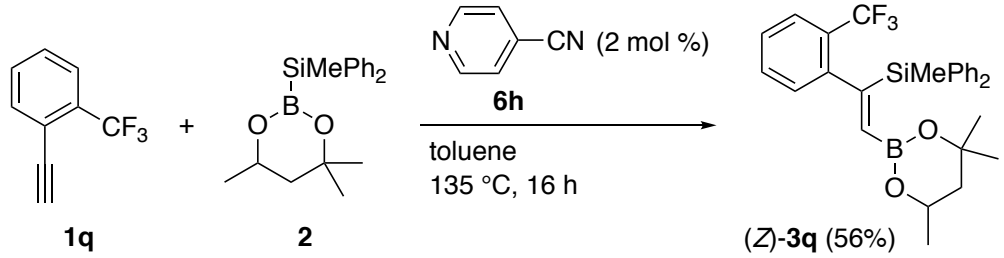
40 μL from 0.10 M stock solution, which was prepared using 2 mL volumetric flask with **6h** (20.8 mg, 0.20 mmol) and toluene], **1o** (22 mg, 0.19 mmol), and **2** (77 mg, 0.24 mmol). The product (*Z*)-**3o** (29 mg, 0.070 mmol, 35%) was obtained after purification by column chromatography on silica gel [Ultra Pure Silica Gel (SILICYCLE, pH 7.0, 40-63 μm, 60 Å), eluent: hexane:Et_2O = 49:1 to 15:1]. (*Z*)-**3o**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.73 (m, 2H), 7.51-7.58 (m, 2H), 7.26-7.40 (m, 6H), 6.92-7.01 (m, 4H), 6.54 (s, 1H), 3.54 (dqd, *J* = 11.6, 6.0, 2.8 Hz, 1H), 2.26 (s, 3H), 1.39 (dd, *J* = 14.0, 2.8 Hz, 1H), 1.06 (s, 3H), 0.93 (d, *J* = 6.0 Hz, 3H), 0.89-0.97 (m, 1H), 0.88 (s, 3H), 0.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 145.6, 143.8 (broad, *C*–B), 138.7, 137.6, 135.7, 135.4, 135.2, 128.9, 128.7, 128.5, 127.6 (two peaks overlapped), 126.9, 71.2, 64.3, 45.2, 30.9, 28.0, 22.5, 21.2, –0.5. ^{11}B NMR (128 MHz, $CDCl_3$) δ 24.7. HRMS (APCI, positive) *m/z* calcd for $C_{28}H_{34}BO_2Si^+$ $[M + H]^+$: 441.2416, found: 441.2408.

The reaction of 1p with 2 to afford (*Z*)-1-(methyldiphenylsilyl-2-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)-1-(4-methoxylphenyl)ethene [(*Z*)-3p]



According to the general procedure, the reaction was carried out using **6h** [0.0040 mmol, 40 μL from 0.10 M stock solution, which was prepared using 2 mL volumetric flask with **6h** (20.8 mg, 0.20 mmol) and toluene], **1p** (23 mg, 0.17 mmol), and **2** (78 mg, 0.24 mmol). The product (*Z*)-**3p** (21 mg, 0.050 mmol, 26%) was obtained after purification by column chromatography on silica gel [Ultra Pure Silica Gel (SILICYCLE, pH 7.0, 40-63 μm, 60 Å), eluent: hexane:Et_2O = 49:1 to 4:1]. (*Z*)-**3p**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.71 (m, 2H), 7.51-7.56 (m, 2H), 7.26-7.39 (m, 6H), 6.98-7.03 (m, 2H), 6.66-6.71 (m, 2H), 6.53 (s, 1H), 3.74 (s, 3H) 3.55 (dqd, *J* = 11.6, 6.0, 2.8 Hz, 1H), 1.39 (dd, *J* = 14.0, 2.8 Hz, 1H), 1.06 (s, 3H), 0.94 (d, *J* = 6.0 Hz, 3H), 0.90-0.97 (m, 1H), 0.89 (s, 3H), 0.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 157.0, 143.8 (broad, *C*–B), 141.1, 138.7, 137.6, 135.6, 135.1, 129.0, 128.7, 128.1, 127.7 (two peaks overlapped), 113.2, 71.2, 64.3, 55.3, 45.2, 30.9, 28.0, 22.5, –0.5. ^{11}B NMR (128 MHz, $CDCl_3$) δ 25.0. HRMS (APCI, positive) *m/z* calcd for $C_{28}H_{34}BO_3Si^+$ $[M + H]^+$: 457.2365, found: 457.2358.

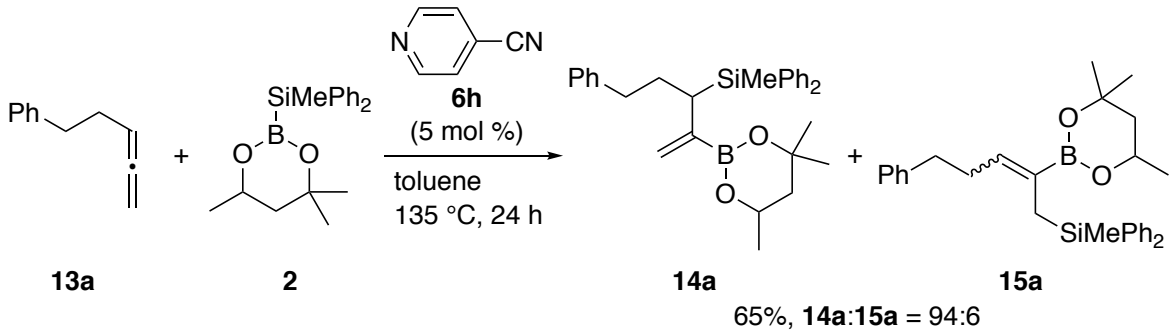
The reaction of 1q with 2 to afford (*Z*)-1-(methyldiphenylsilyl-2-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)-1-(2-trifluoromethylphenyl)ethene [(*Z*)-3q]



According to the general procedure, the reaction was carried out using **6h** [0.0040 mmol, 40 μL from 0.10 M stock solution, which was prepared using 2 mL volumetric flask with **6h** (20.8 mg, 0.20 mmol) and toluene], **1q** (34 mg, 0.20 mmol), and **2** (76 mg, 0.24 mmol). The product (*Z*)-**3q** (55 mg, 0.11 mmol, 56%) was obtained after purification by column chromatography on silica gel [Ultra Pure Silica Gel (SILICYCLE, pH 7.0, 40-63 μm, 60 Å), eluent: hexane:$CHCl_3$:Et_2O = 30:3:1 to 50:5:2]. (*Z*)-**3q**: ^{1}H NMR [400 MHz, $CDCl_3$, Rotamers **A** and **B** (53:47) were observed.] δ 7.56-7.61 (m, **A** 2H and **B** 2H), 7.38-7.54 (m, **A** 3H and **B** 3H), 7.06-7.36 (m, **A** 8H and **B** 8H), 6.80-6.87 (m, **A** 1H and **B** 1H), 6.38 (s, **A** 1H and **B** 1H), 3.63-3.77 (m, **B** 1H), 3.50-3.63(m, **A** 1H), 1.39-1.46 (m, **A** 1H and **B** 1H), 0.88-1.06 (m, **A** 10H and **B** 10H), 0.61 (s, **B** 3H), 0.52 (s, **A** 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 155.7, 147.4, 145.1 (broad, C–B), 138.1, 137.7, 137.4, 136.8, 135.8, 135.5, 135.2, 135.1, 130.6, 130.5, 129.6, 129.2, 128.8, 128.7, 127.6, 127.42, 127.37, 126.2 (q, $^2J_{CF}$ = 27 Hz), 126.0, 125.8, 125.4, 124.7 (q, $^1J_{CF}$ = 273 Hz), 71.2, 64.6, 64.5, 45.4, 30.8, 27.9, 22.6, –1.5. Several peaks overlap the peaks observed between 125 to 131 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ 24.4. HRMS (ESI, positive) *m/z* calcd for $C_{28}H_{30}BF_3O_2SiNa^+$ $[M + Na]^+$: 517.1952, found: 517.1947.

Silaboration of Allenes Catalyzed by 6h (Scheme 3)

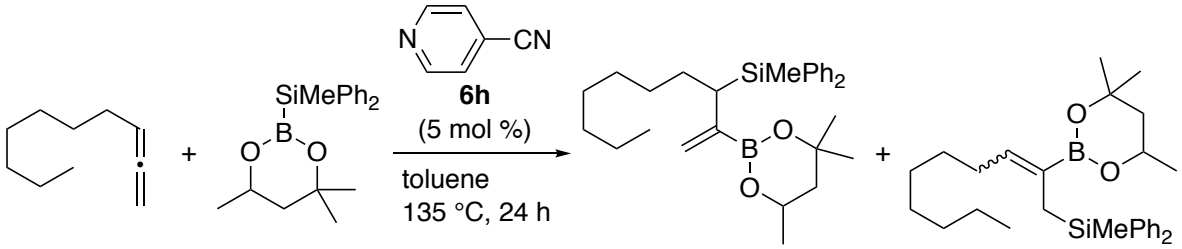
The reaction of 13a with 2 to afford 3-(methyldiphenylsilyl)-2-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)-5-phenylpent-1-ene (14a)



In a glove box, a glass tube (outside diameter: 20 mm) having PTFE stopcock (J. Young),

equipped with a magnetic stirring bar, was charged with **6h** (1.1 mg, 0.010 mmol), **13a** (28 mg, 0.20 mmol), **2** (78 mg, 0.24 mmol), and toluene (0.4 mL). The tube was sealed by the stopcock and was taken out of the glove box. The mixture was stirred at 135 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). After 24 h, the tube was cooled to room temperature, and the volatiles were removed under reducing pressure. The product **14a** (60 mg, 0.13 mmol, 65%) was obtained as a mixture with **15a** (**14a**:**15a** = 96:4) after purification by column chromatography on silica gel [Ultra Pure Silica Gel (SILICYCLE, pH 7.0, 40-63 μm, 60 Å), eluent: hexane:Et_2O = 99:1 to 11:1]. **14a** and **15a** were separable by Gel Permeation Chromatography (GPC), which was performed by Japan Analytical Industry LC-908 with series-connected JAIGEL-1H (ϕ 20 mm x 600 mm) and JAIGEL-2H (ϕ 20 mm x 600 mm). **14a**: ^{1}H NMR [400 MHz, $CDCl_3$, a mixture of diastereomers **A** and **B** (1:1)] δ 7.45-7.52 (m, **A** 2H and **B** 2H), 7.20-7.40 (m, **A** 10H and **B** 10H), 7.12-7.19 (m, **A** 1H and **B** 1H), 7.07-7.11 (m, **A** 2H and **B** 2H), 5.88 (d, J = 2.8 Hz, **A** 1H or **B** 1H), 5.87 (d, J = 2.8 Hz, **A** 1H or **B** 1H), 5.40 (d, J = 2.8 Hz, **A** 1H or **B** 1H), 5.37 (d, J = 2.8 Hz, **A** 1H or **B** 1H), 4.01 (dqd, J = 11.6, 6.0, 2.8 Hz, **A** 1H or **B** 1H), 3.91 (dqd, J = 11.6, 6.0, 2.8 Hz, **A** 1H or **B** 1H), 2.65-2.76 (m, **A** 2H and **B** 2H), 2.35-2.47 (m, **A** 1H and **B** 1H), 1.93-2.06 (m, **A** 2H or **B** 2H), 1.76-1.88 (m, **A** 2H or **B** 2H), 1.58 (dd, J = 13.6, 2.8 Hz, **A** 1H or **B** 1H), 1.56 (dd, J = 13.6, 2.8 Hz, **A** 1H or **B** 1H), 1.19 (s, **A** 3H or **B** 3H), 1.16 (d, J = 6.0 Hz, **A** 3H or **B** 3H), 1.12 (d, J = 6.0 Hz, **A** 3H or **B** 3H), 1.12 (s, **A** 3H or **B** 3H), 1.09 (s, **A** 3H or **B** 3H), 1.08 (s, **A** 3H or **B** 3H), 1.05-1.14 (m, **A** 1H and **B** 1H), 0.46 (s, **A** 3H and **B** 3H). ^{13}C NMR [101 MHz, $CDCl_3$, a mixture of two diastereomers (1:1)] δ 143.3, 143.2, 137.6 (two peaks overlapped), 136.44, 136.37, 135.43, 135.39, 135.3, 135.2, 129.1 (two peaks overlapped), 129.0, 128.9, 128.8, 128.7, 128.2 (two peaks overlapped), 127.7 (two peaks overlapped), 127.54, 127.47, 125.5 (two peaks overlapped), 123.8, 123.5, 70.64, 70.62, 64.6, 64.5, 45.55, 45.51, 35.1, 34.9, 31.35, 31.30, 31.1 (two peaks overlapped), 29.5, 28.9, 28.3, 28.0, 23.2, 23.0, –6.0, –6.5. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ 24.3. HRMS (ESI, positive) *m/z* calcd for $C_{30}H_{37}BO_2SiNa^+$ $[M + Na]^+$: 491.2548, found: 491.2545.

The reaction of 13b with 2 to afford 3-(methyldiphenylsilyl)-2-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)-dec-1-ene (14b)



13b **2** **14b** **15b**

65%, **14b**:**15b** = 95:5

In a glove box, a glass tube (outside diameter: 20 mm) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with **6h** (1.0 mg, 0.010 mmol), **13b** (27 mg, 0.19 mmol), **2** (77 mg, 0.24 mmol), and toluene (0.4 mL). The tube was sealed by the stopcock and was taken out of the glove box. The mixture was stirred at 135 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). After 24 h, the tube was cooled to room temperature, and the volatiles were removed under reducing pressure. The product **14b** (58 mg, 0.13 mmol, 65%) was obtained as a mixture with **15b** (**14b**:**15b** = 95:5) after purification by column chromatography on silica gel [Ultra Pure Silica Gel (SILICYCLE, pH 7.0, 40-63 μm, 60 Å), eluent: hexane:Et_2O = 99:1 to 11:1]. **14b**: ^{1}H NMR [400 MHz, $CDCl_3$, a mixture of diastereomers **A** and **B** (1:1)] δ 7.57-7.64 (m, **A** 2H and **B** 2H), 7.42-7.47 (m, **A** 2H and **B** 2H), 7.22-7.39 (m, **A** 6H and **B** 6H), 5.79 (d, J = 3.2 Hz, **A** 1H or **B** 1H), 5.78 (d, J = 3.2 Hz, **A** 1H or **B** 1H), 5.29 (d, J = 3.2 Hz, **A** 1H or **B** 1H), 5.28 (d, J = 3.2 Hz, **A** 1H or **B** 1H), 3.99 (dqd, J = 12.0, 6.0, 2.8 Hz, **A** 1H or **B** 1H), 3.89 (dqd, J = 12.0, 6.0, 2.8 Hz, **A** 1H or **B** 1H), 2.67 (dd, J = 12.0, 3.6 Hz, **A** 1H or **B** 1H), 2.66 (dd, J = 12.0, 3.6 Hz, **A** 1H or **B** 1H), 1.58-1.72 (m, **A** 1H and **B** 1H), 1.47-1.58 (m, **A** 2H and **B** 2H), 1.17 (s, **A** 3H or **B** 3H), 1.15 (d, J = 6.0 Hz, **A** 3H or **B** 3H), 1.12 (s, **A** 3H or **B** 3H), 1.10 (d, J = 6.0 Hz, **A** 3H or **B** 3H), 1.08 (s, **A** 3H or **B** 3H), 1.07 (s, **A** 3H or **B** 3H), 1.02-1.40 (m, **A** 11H and **B** 11H), 0.85 (t, J = 6.8 Hz, **A** 3H and **B** 3H), 0.479 (s, **A** 3H or **B** 3H), 0.477 (s, **A** 3H or **B** 3H). ^{13}C NMR [101 MHz, $CDCl_3$, a mixture of two diastereomers (1:1)] δ 137.9 (two peaks overlapped), 136.94, 136.85, 135.5, 135.4, 135.31, 135.25, 129.0 (two peaks overlapped), 128.69, 128.66, 127.7 (two peaks overlapped), 127.51, 127.46, 123.5, 123.3, 70.6, 70.5, 64.6, 64.4, 45.54, 45.47, 32.1 (two peaks overlapped), 31.3, 31.1, 30.0, 29.6 (two peaks overlapped), 29.5, 29.3 (two peaks overlapped), 29.1, 28.9 (two peaks overlapped), 28.7, 28.2, 28.0, 23.2, 23.0, 22.8 (two peaks overlapped), 14.3 (two peaks overlapped), –6.0, –6.4. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ 24.2. HRMS (ESI, positive) *m/z* calcd for

$C_{29}H_{43}BO_2SiNa^+$ $[M + Na]^+$: 485.3018, found: 485.3011.

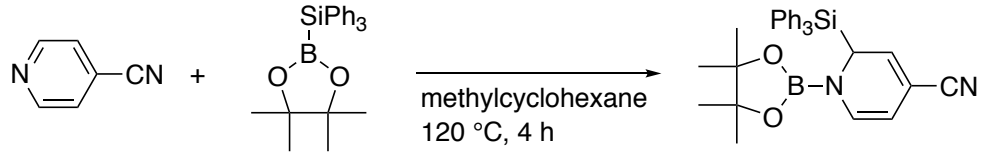
Transition-Metal-Free Silaboration of Pyridines (Table 2)

General Procedure: In a glove box, a glass tube (outside diameter: 20 mm) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with **5** or **6** (0.10 mmol), **11** (0.10 mmol), and methylcyclohexane (0.2 mL). The tube was sealed by the stopcock and was taken out of the glove box. The mixture was stirred at 110 °C by a heating magnetic stirrer with an oil bath. After 12–14 h, the tube was cooled to room temperature, and dibenzyl ether (0.050 mmol, internal standard) was added. The resulting mixture was analyzed by ^{1}H NMR to determine the yield of the silaboration products **16**.

In the reaction of **6h** with **5e** (entry 1), formation of **16a** (20%) was indicated by the following specific peaks: ^{1}H NMR (400 MHz, C_6D_6) δ 6.53 (d, J = 7.2 Hz, 1H), 5.26 (d, J = 7.2 Hz, 1H), 5.19 (d, J = 7.2 Hz, 1H), 4.52 (dd, J = 7.2, 1.6 Hz, 1H).

In the reaction of **6h** with **6g** (entry 3), formation of **16b** (17%) was indicated by the following specific peaks: ^{1}H NMR (400 MHz, C_6D_6) δ 6.71 (d, J = 6.8 Hz, 1H), 6.53 (d, J = 7.6 Hz, 1H), 5.56 (dd, J = 7.6, 1.6 Hz, 1H), 5.31 (d, J = 6.8 Hz, 1H).

The reaction of 6h with 11 to afford 4-Cyano-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(triphenylsilyl)-1,2-dihydropyridine (16c) (entry 5)



6h (1.1 equiv) **11** **16c** (21%)

In a glove box, a glass tube (outside diameter: 20 mm) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with **6h** (57 mg, 0.55 mmol), **11** (193 mg, 0.50 mmol), and methylcyclohexane (0.4 mL). The tube was sealed by the stopcock and was taken out of the glove box. The mixture was stirred at 120 °C using a magnetic stirrer with an oil bath. After 4 h, the solution color was changed to dark brown and a precipitate was formed. (*Note: Extension of reaction time made the reaction messier.*) The tube was cooled to room temperature and was brought in a glove box. The reaction mixture (both liquid and solid) was transferred into 30 mL round bottom flask using THF as a solvent for dissolving the compounds. The volatiles were removed under reducing pressure. The residues were dissolved in cyclohexane (7–8 mL) and pentane (7–8 mL). (*Note: **11** was more soluble than **6h** in cyclohexane, whereas in pentane **11** was less soluble than **6h**. The product **16c** was less soluble than **6h** and **11** in both cyclohexane*

and pentane.) The solvents were evaporated slowly under reducing pressure to precipitate **16c** as a glossy brown solid. (*Note: Fine adjustment of the solvent ratio was important to obtain **16c** with high purity as well as in reasonable yield.*) The solid was collected by suction filtration. Then the solid was placed in a 4 mL vial, and it was washed with pentane containing a small amount of cyclohexane (pentane:cyclohexane = ca. 100:1) by decantation to remove remaining **6h** and **11** (twice). After removing the remaining solvents in vacuo, **16c** (52 mg, 21%) was obtained as a brown solid. **16c**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.61-7.64 (m, 6H), 7.13-7.19 (m, 9H), 6.25 (d, J = 7.6 Hz, 1H), 5.61 (dt, J = 6.8, 1.2 Hz, 1H), 4.99 (d, J = 6.8 Hz, 1H), 4.46 (dd, J = 7.6, 1.2 Hz, 1H), 0.70-1.00 (m, 6H), 0.65-0.90 (m, 3H), 0.50-0.70 (m, 3H). This compound was unstable in $CDCl_3$. ^{13}C NMR (101 MHz, C_6D_6) δ 137.0, 134.8, 132.3, 131.4, 130.2, 128.2, 117.8, 110.4, 103.7, 83.5, 47.4, 24.9. ^{11}B NMR (128 MHz, C_6D_6) δ 22.2. HRMS (ESI, positive) *m/z* calcd for $C_{30}H_{31}BN_2O_2SiNa^+$ $[M + Na]^+$: 513.2140, found: 513.2152.

ICP-MS Analysis of 4-Cyanopyridine (6h)

We ordered ICP-MS analysis of 4-cyanopyridine for SHIMADZU TECHNO-RESEARCH, Inc. A copy of the report is shown on the next page.

Report Number: MKC-06208

TEST REPORT

Date of Issue: 1 June 2017
Order Number: 46102006

To: Kyoto University
Graduate School of Engineering

SHIMADZU TECHNO-RESEARCH, INC.
1, Nishinokyo-Shimoaicho, Nakagyo-ku, Kyoto-City, Kyoto 604-8436, Japan
Phone: +81-75-811-3181 FAX: +81-75-821-7837

The analysis results are reported below.

Title: Measurement of Elemental Impurities

Client : Kyoto University
Graduate School of Engineering
Department of Synthetic Chemistry and Biological Chemistry

Sample : 4-cyanopyridine (1pc)

Date of Reception : 24 April 2017 (Delivered by Client's Courier)

Analysis Method : A sample (0.10 g) was placed in a 100 mL PTFE digestion vessel. Nitric acid (4 mL) and ultrapure water (4 mL) was added to the vessel, and the vessel was attached to a rotor of microwave instrument. The sample was conducted to microwave digestion (maximum temperature 230 °C). After cooling the vessel to room temperature, the resulting solution was transferred to a measuring flask (PP). Ultrapure water was added to the flask to make it 40 mL in total. Dilute hydrochloric acid solution, which was prepared from hydrochloric acid with ultrapure water (1:9, v/v), was added to make it 80 mL in total. The resulting solution was analyzed by an ICP-MS instrument.

Instrument : Inductively coupled plasma mass spectrometer, 7700x (Agilent Technologies, Inc.)
Microwave digestion system, ETHOS-TC (Milestone Srl)

Analysis Result :

Analyte	Unit	Result
Fe	µg/g	<1
Co	µg/g	<0.1
Ni	µg/g	<1
Cu	µg/g	<1
Ru	µg/g	<0.1
Rh	µg/g	<0.1
Pd	µg/g	<0.1
Ag	µg/g	<0.1
Ir	µg/g	<0.1
Pt	µg/g	<0.1
Au	µg/g	<0.1

(1) '<' indicates that each result was less than the quantitative limit.

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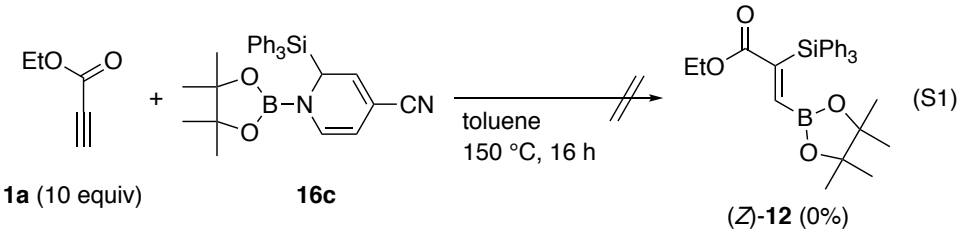
Documented by Teruko TOYODA
Verified by Shinji Shimada
Approved by Atsukiro Hayashi

SHIMADZU TECHNO-RESEARCH, INC.

(1/1)

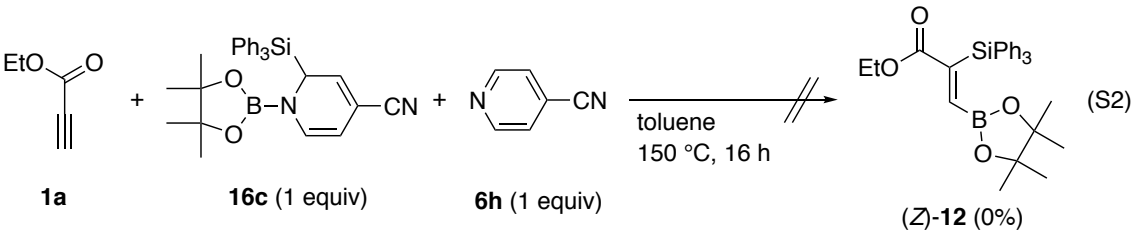
Mechanistic Investigations

Stoichiometric Reaction of 1a with 16c (Eqs. S1, S2, and S3)

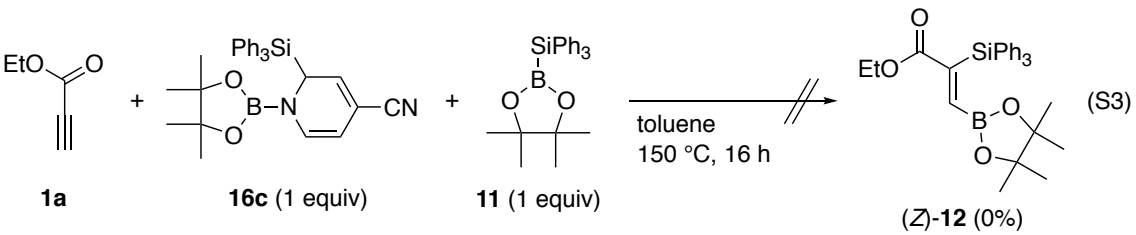


1a (10 equiv) **16c** (*Z*)-**12** (0%)

In a glove box, a glass tube (outside diameter: 20 mm) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with **16c** (40 mg, 0.081 mmol), toluene (0.4 mL), and **1a** (78 mg, 0.80 mmol). The tube was sealed by the stopcock and was taken out of the glove box. The mixture was stirred at 150 °C by a magnetic stirrer with oil bath. No formation of (*Z*)-**12** was observed by GCMS and ^{1}H NMR analyses after 16 h, although **16c** was decomposed completely.



1a **16c** (1 equiv) **6h** (1 equiv) (*Z*)-**12** (0%)

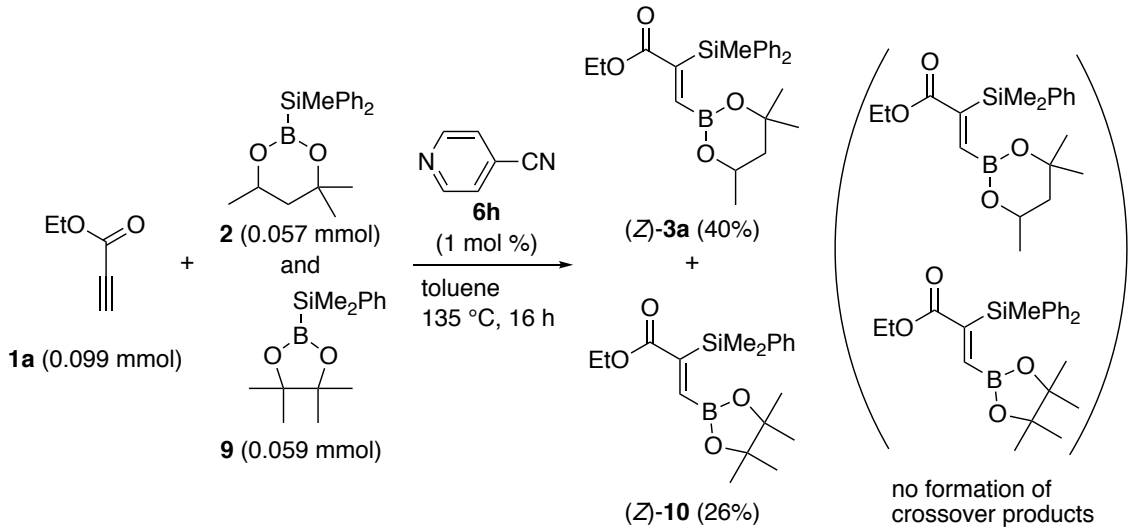


1a **16c** (1 equiv) **11** (1 equiv) (*Z*)-**12** (0%)

We also carried out the reaction of **1a** with **16c** (1 equiv) in the presence of either **6h** (1 equiv) or **11** (1 equiv) to check the following two possibilities: (1) **6h** is required for transfer of the boryl and silyl groups from **16c** to **1a**, and (2) **16c** promotes addition of **11** into **1a** (Eqs. S2 and S3). However, both the reactions did not afford (*Z*)-**12**, therefore we concluded that **16c** is a dead-end of the **6h**-catalyzed silaboration.

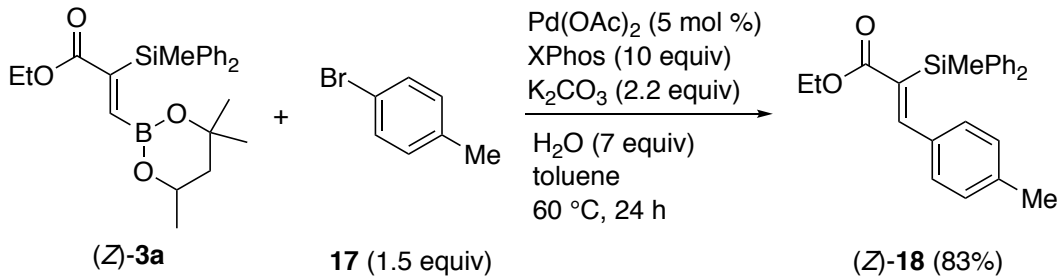
Crossover Experiment (Scheme S1)

Scheme S1. 6h-Catalyzed Reaction of 1a with 2 and 9



In a glove box, a glass tube (outside diameter: 20 mm) having PTFE stopcock (J. Young), equipped with a magnetic stirring bar, was charged with **6h** [0.0010 mmol, 10 μL from 0.10 M stock solution, which was prepared using 2 mL volumetric flask with **6h** (20.8 mg, 0.20 mmol) and toluene], **1** (9.8 mg, 0.099 mmol), **2** (18 mg, 0.057 mmol), **9** (15 mg, 0.59 mmol), and toluene (0.2 mL). The tube was sealed by the stopcock and was taken out of the glove box. The mixture was stirred at 135 °C by a heating magnetic stirrer with an aluminum heating block (hole size: 21 mm diameter x 33 mm depth). After 16 h, the tube was cooled to room temperature, and tetradecane (20 mg, 0.098 mmol, internal standard) was added to the mixture. GC analysis of the mixture indicated that (*Z*)-**3a** and (*Z*)-**10** were formed in 40 and 26% yields, respectively, whereas no cross-over products were formed.

Suzuki-Miyaura Coupling of (Z)-3a (Scheme 5)



In a glove box, a glass tube having PTFE stopcock (J. Young), equipped with magnetic stirring bar, was charged with $Pd(OAc)_2$ (1.12 mg, 0.0050 mmol), XPhos (6.19 mg, 0.012 mmol), K_2CO_3 (39 mg, 0.22 mmol), (*Z*)-**3a** (40 mg, 0.090 mmol), 4-bromotoluene (**17**,

26 mg, 0.15 mmol), and toluene (0.6 mL). The tube was sealed by the stopcock and was taken out of the glove box. The stopcock was removed temporally under argon flow. Degassed water (13 μL) was added to the tube, and the tube was sealed by the stopcock again. The mixture was reacted at 60 °C for 24 h. After cooling to room temperature, water (10 mL) was added to the tube. The organic materials were extracted with Et_2O (20 mL x 3), and the combined organic layer was washed with water (10 mL x 3), brine (10 mL x 1), and dried over anhydrous sodium sulfate. The product (*Z*)-**18** (30 mg, 83%) was obtained after purification by column chromatography on silica gel (eluent: hexane:Et_2O = 9:1). (*Z*)-**18**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.50-7.56 (m, 4H), 7.27-7.37 (m, 6H), 7.07 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 8.0 Hz, 2H), 3.88 (q, J = 7.2 Hz, 2H), 2.26 (s, 3H), 0.92 (t, J = 7.2Hz, 3H), 0.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 155.8, 139.1, 137.0, 134.8, 134.1, 133.5, 129.2 (two peaks overlapped), 128.6, 127.9, 60.8, 21.4, 13.8, –2.0. HRMS (ESI, positive) *m/z* calcd for $C_{25}H_{26}O_2SiNa^+$ $[M + Na]^+$: 409.1594, found: 409.1588.

Notes and References

1) For reviews, see: (a) Cid, J., Gulyás, H., Carbó, J. J., Fernández, E. *Chem. Soc. Rev.,* **2012**, *41*, 3558–3570 (b) Dewhurst, R. D., Neeve, E. C., Braunschweig, H., Marder, T. B. *Chem. Commun.,* **2015**, *51*, 9594–9607 (c) Cuenca, A. B., Shishido, R., Ito, H., Fernández, E. *Chem. Soc. Rev.,* **2017**, *46*, 415–430.
2) (a) Lee, K., Zhugralin, A. R., Hoveyda, A. H. *J. Am. Chem. Soc.,* **2009**, *131*, 7253–7255 (b) O'Brien, J. M., Hoveyda, A. H. *J. Am. Chem. Soc.,* **2011**, *133*, 7712–7715 (c) Wu, H., Radomkit, S., O'Brien, J. M., Hoveyda, A. H. *J. Am. Chem. Soc.,* **2012**, *134*, 8277–8285.
3) (a) Bonet, A., Gulyás, H., Fernández, E. *Angew. Chem. Int. Ed.,* **2010**, *49*, 5130–5134 (b) Pubill-Ulldemolins, C., Bonet, A., Gulyás, H., Bo, C., Fernández, E. *Org. Biomol. Chem.,* **2012**, *10*, 9677–9682.
4) (a) Pubill-Ulldemolins, C., Bonet, A., Bo, C., Gulyás, H., Fernández, E. *Chem. Eur. J.,* **2012**, *18*, 1121–1126 (b) Solé, C., Gulyás, H., Fernández, E. *Chem. Commun.,* **2012**, *48*, 3769–3771 (c) Wen, K., Chen, J., Gao, F., Bhadury, P. S., Fan, E., Sun, Z. *Org. Biomol. Chem.,* **2013**, *11*, 6350–6356.
5) Yamamoto, E., Izumi, K., Horita, Y., Ito, H. *J. Am. Chem. Soc.,* **2012**, *134*, 19997–20000.
6) Sanz, X., M. Lee, G., Pubill-Ulldemolins, C., Bonet, A., Gulyás, H., Westcott, S. A., Bo, C., Fernández, E. *Org. Biomol. Chem.,* **2013**, *11*, 7004–7010.
7) Miralles, N., Alam, R., Szabó, K. J., Fernández, E. *Angew. Chem. Int. Ed.,* **2016**, *55*, 4303–4307.
8) Wang, L., Zhang, T., Sun, W., He, Z., Xia, C., Lan, Y., Liu, C., *J. Am. Chem. Soc.,* **2017**, *139*, 5257–5264.
9) Transition-metal-free photoinduced borylation has also reported. (a) Fawcett, A., Pradeilles, J., Wang, Y., Mutsugam, T., Myers, E. L., Aggarwal, V. K. *Science,* **2017**, *357*, 283–286 (b) Wu, J., He, L., Nobel, A., Aggarwal, V. K. *J. Am. Chem. Soc.,* **2018**, *140*, 10700–10704.
10) For reviews on diboration and silaboration, see: (a) Ohmura, T., Suginome, M., *Bull. Chem. Soc. Jpn.,* **2009**, *82*, 29–49 (b) Suginome, M., Ohmura, T., in *Boronic Acids Second Edition, Vol. 1* (Ed.: D. G. Hall), Wiley-VCH, **2011**, pp. 171–212 (c) Oestreich, M., Hartmann, E., Mewald, M. *Chem. Rev.,* **2013**, *113*, 402–441 (d) Delvos, L. B., Oestreich, M. in *Science of Synthesis Knowledge Updates 2017/1* (Ed: M. Oestreich), Thieme, Stuttgart, **2017**, pp 65-176.
11) (a) Bonet, A., Pubill-Ulldemolins, C., Bo, C., Gulyás, H., Fernández, E. *Angew. Chem.*

Int. Ed., **2011**, *50*, 7158–7161 (b) Bonet, A., Sole, C., Gulyás, H., Fernández, E. *Org. Biomol. Chem.,* **2012**, *10*, 6621–6623 (c) Blaisdell, T. P., Caya, T. C., Zhang, L., Sanz-Marco, A., Morken, J. P. *J. Am. Chem. Soc.,* **2014**, *136*, 9264–9267 (d) Miralles, N., Cid, J., Cuenca, A. B., Carbó, J. J., Fernández, E. *Chem. Commun.,* **2015**, *51*, 1693–1696.

12) Morinaga, A., Nagao, K., Ohmiya, H., Sawamura, M. *Angew. Chem. Int. Ed.,* **2015**, *54*, 15859.

13) Nagao, K., Ohmiya, H., Sawamura, M. *Org. Lett.,* **2015**, *17*, 1304–1307.

14) Yoshimura, A., Takamachi, Y., Han, L.-B., Ogawa, A. *Chem. Eur. J.,* **2015**, *21*, 13930–13933.

15) Yoshimura, A., Takamachi, Y., Mihara, K., Saeki, T., Kawaguchi, S., Han, L.-B., Nomoto, A., Ogawa, A. *Tetrahedron,* **2016**, *72*, 7832–7838.

16) (a) Ito, H., Horita, Y., Yamamoto, E. *Chem. Commun.,* **2012**, *48*, 8006–8008 (b) Yamamoto, E., Shishido, R., Seki, T., Ito, H. *Organometallics,* **2017**, *36*, 3019–3022.

17) (a) Ohmura, T., Morimasa, Y., Suginome, M., *J. Am. Chem. Soc.,* **2015**, *137*, 2852–2855. See also: (b) Oshima, K., Ohmura, T., Suginome, M. *Chem. Commun.,* **2012**, *48*, 8571–8573.

18) Ohmura, T., Morimasa, Y., Suginome, M. *Chem. Lett.,* **2017**, *46*, 1793–1796.

19) (a) Wang, G., Zhang, H., Zhao, J., Li, W., Cao, J., Zhu, C., Li, S. *Angew. Chem. Int. Ed.,* **2016**, *55*, 5985 (b) Zhang, L., Jiao, L., *J. Am. Chem. Soc.,* **2017**, *139*, 607 (c) Wang, G., Cao, J., Gao, L., Chen, W., Huang, W., Cheng, X., Li, S. *J. Am. Chem. Soc.,* **2017**, *139*, 3904 (d) Candish, L., Teders, M., Glorius, F. *J. Am. Chem. Soc.,* **2017**, *139*, 7440 (e) Pinet, S., Liautard, V., Debiais, M., Pucheault, M. *Synthesis,* **2017**, *49*, 4759–4768 (f) Chen, D., Xu, G., Zhou, Q., Chung, L. W., Tang, W. *J. Am. Chem. Soc.,* **2017**, *139*, 9767 (g) Cheng, W.-M., Shang, R., Zhao, B., Xing, W.-L., Fu, Y. *Org. Lett.,* **2017**, *19*, 4291 (h) Hu, J., Wang, G., Li, S., Shi, Z. *Angew. Chem. Int. Ed.,* **2018**, *57*, 15227–15231 (i) Xu, R., Lu, G.-P., Cai, C. *New J. Chem.*, 2018, 42, 16456–15450.

20) For transition-metal-catalyzed silaboration of allenes, see: (a) Onozawa, S., Hatanaka, Y., Tanaka, M. *Chem. Commun.,* **1999**, 1863–1864 (b) Suginome, M., Ohmori, Y., Ito, Y. *Synlett*, **1999**, 1567–1568 (c) Suginome, M., Ohmori, Y., Ito, Y. *J. Organomet. Chem.,* **2000**, *611*, 403–413 (d) Suginome, M., Ohmura, T., Miyake, Y., Mitani, S., Ito, Y., Murakami, M. *J. Am. Chem. Soc.,* **2003**, *125*, 11174–11175 (e) Ohmura, T., Suginome, M. *Org. Lett.,* **2006**, *8*, 2503–2506 (f) Ohmura, T., Taniguchi, H., Suginome, M. *J. Am. Chem. Soc.,* **2006**, *128*, 13682–13683.

21) Suginome, M., Matsuda, T., Nakamura, H., Ito, Y. *Tetrahedron,* **1999**, *55*, 8787–8800.

22) For palladium-catalyzed silaboration of pyridines, see: Ohmura, T., Oshima, K.,

Suginome, M. *J. Am. Chem. Soc.,* **2011**, *133*, 7324–7327.

23) Although the 1,2-silaboration of **6h** was also observed in the reactions with **2** or **9**, yields of the corresponding adducts were lower than that in the reaction with **11**.

24) For details, see Experimental section.

25) For borylation reactions in which involvement of pyridine-boryl radical is proposed, see refs. 19a–e and 19g–i. For other reports related to pyridine-boryl radical, see: (a) Köster, R., Bellut, H., Benedikt, G., Ziegler, E. *Liebigs Ann. Chem.,* **1969**, *724*, 34–55 (b) Schlüter, K., Berndt, A. *Angew. Chem. Int. Ed.,* **1980**, *19*, 57–58 (c) Zhang, L., Jiao, L. *Chem. Sci.,* **2018**, *9*, 2711–2722 (d) Cao, J., Wang, G., Gao, L., Cheng, X., Li, S. *Chem. Sci.,* **2018**, *9*, 3664–3671 (e) Gao, L., Wang, G., Cao, J., Yuan, D., Xu, C., Guo, X., Li, S. *Chem. Commun.,* **2018**, *54*, 11534–11537 (f) Cao, J., Wang, G., Gao, L., Chen, H., Liu, X., Cheng, X., Li, S. *Chem. Sci.,* **2019**, *10*, 2767–2772.

26) Radical hydrosilylation of ethyl 3-phenylpropiolate with $HSi(SiMe_3)_3$ gives (*E*)-3-phenyl-2-silylacrylate via *syn*-hydrosilylation. See: Kopping, B., Chatgilialoglu, C., Zehnder, M., Giese, B. *J. Org. Chem.,* **1992**, *57*, 3994.

27) Suginome, M., Matsuda, T., Ito, Y. *Organometallics,* **2000**, *19*, 4647–4649.

28) Balas, L., Jousseaume, B., Langwost, B. *Tetrahedron Lett.,* **1989**, *30*, 4525–4526.

29) Sato, E., Mawatari, Y., Sadahiro, Y., Yamada, B., Tabata, M., Kashiwaya, Y. *Polymer,* **2008**, *49*, 1620–1628.

30) Kraff, M. E., Romero, R. H., Scott, I. L. *J. Org. Chem.,* **1992**, *57*, 5277–5278.

31) Ma, S., Lu, X. *J. Org. Chem.,* **1993**, *58*, 1245–1250.

32) (a) Brandsma, L. "Synthesis of Acetylenes, Allenes and Cumulenes" Elsevier, 2004 (b) Moreau, J.-L., Gaudemar, M. *J. Organomet. Chem.,* **1976**, *108*, 159.

List of Publications

Chapter 1

4,4'-Bipyridine-catalyzed Stereoselective *trans*-Diboration of Acetylenedicarboxylates to 2,3-Diborylfumarates

Toshimichi Ohmura, Yohei Morimasa, and Michinori Suginome

Chem. Lett., **2017**, *46*, 1793-1796.

Chapter 2

Organocatalytic Diboration Involving "Reductive Addition" of a Boron–Boron σ-Bond to 4,4'-bipyridine

Tochimichi Ohmura, Yohei Morimasa, and Michinori Suginome

J. Am. Chem. Soc., **2015***, 137*, 2852-2855

Chapter 3

Mechanism of 2,6-Dichloro-4,4'-Bipyridine-Catalyzed Diboration of Pyrazines Involving a Bipyridine-Stabilized Boryl Radical

Toshimichi Ohmura, Yohei Morimasa, Tomoya Ichino, Yusuke Miyake, Yasujiro Murata, Michinori Suginome, Kunihiko Tajima, Tetsuya Taketsugu, and Satoshi Maeda

Bull. Chem. Soc. Jpn. Accepted.

Chapter 4

Pyridine-Based Organocatalysts for Regioselective *syn*-1,2-Silaboration of Terminal Alkynes and Allenes

Yohei Morimasa, Kosuke Kabasawa, Toshimichi Ohmura, and Michinori Suginome

Asian J. Org. Chem., **2019**, *8*, 1092-1096.