Ph.D. thesis

Synthesis of Silylborane Compounds and Their Applications

（シリルボラン化合物の合成とその応用）

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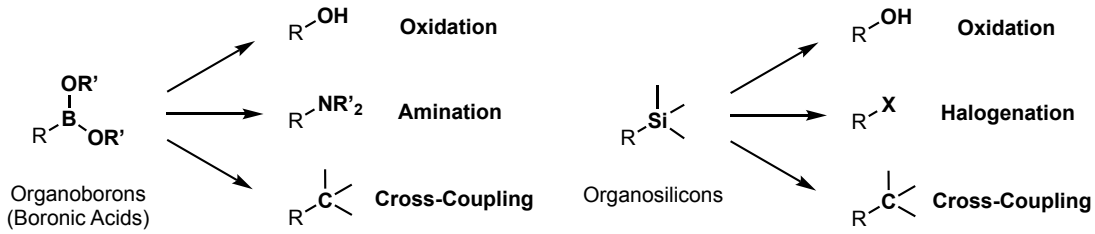
Contents

General Introduction

Organoboron and organosilicon compounds are an important class of organometallic reagents in organic synthesis and have received extensive interests in various research field such as pharmaceuticals, agrochemicals and organic materials.[1, 2] They are generally low toxic, and exhibit air- and moisture-stable compared to other organometallic reagents such as organolithium or Grignard reagents (Scheme 1). On the other hand, organoboron and organosilicon compounds can be easily activated under the appropriate conditions and show sufficient reactivities for the use in organic synthesis. They can be utilized as reagents for various transformation reactions such as oxidation, amination, cross-coupling, and halogenation.

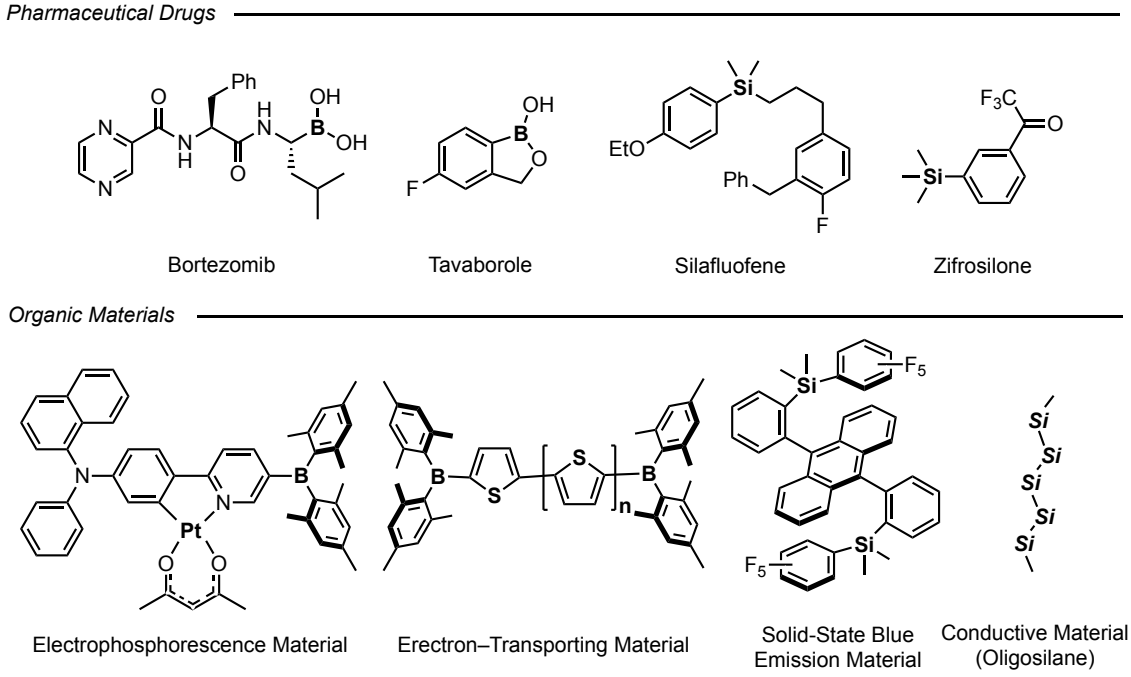
Scheme 1. Synthetic Importance of Organoboron and Organosilicon Compounds in Organic Chemistry.



High Air- and Moisture-Stable, Low Toxic, Sufficient Reactivity, Various Transformation

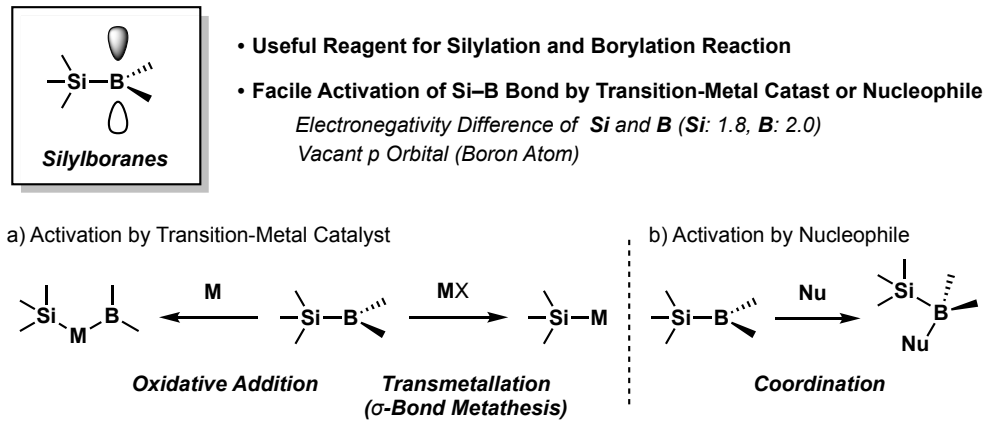
For these reasons, the derivatives of organoboron and organosilicon compounds are used as synthetic intermediates for the synthesis of pharmaceuticals, agrochemicals and organic materials. Furthermore, some organoboron and organosilicon compounds have recently attracted a great deal of attention as important molecules for pharmaceuticals and organic emissive materials because they exhibit bioactivities or unique photophysical properties (Scheme 2).[1,2]

Scheme 2. Applications of Organoboron and Organosilicon Compounds for Pharmaceuticals and Organic Materials.



Silylborane compounds containing silicon–boron bonds have been widely utilized as versatile reagents for preparing organoboron and -silicon compounds in the organic synthesis (Scheme 3).[3] The Si–B interelement bonds in silylborane compounds are generally inert with appropriate substitution at the boron atom, while the difference of electronegativity between boron and silicon enables the facile activation of the Si–B bond by a transition-metal catalyst. The Si–B bonds are generally activated by transition-metal catalyst via two types of activation modes. First, the oxidative addition of Si–B bond to

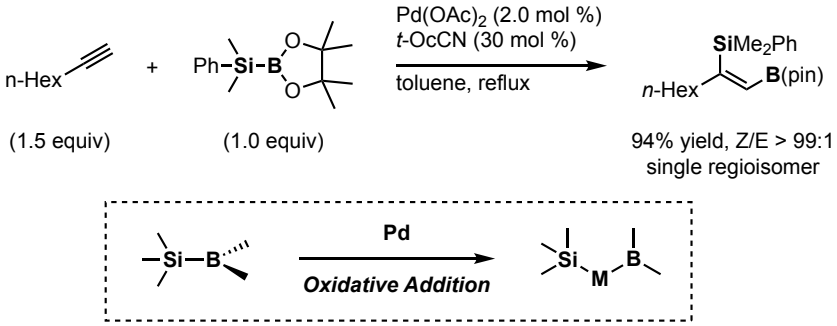
Scheme 3. General Reactivity of Silylborane Compounds.[3]



transition metal catalysts (Ni, Pd, Pt etc.) generate the (boryl)(silyl)metal intermediate (Scheme 3a, left side). This is the most frequently used activation method and has led to considerable progress in the catalytic silaboration of unsaturated C–C bonds. Second, transmetallation between silylborane compounds and transition metal catalysts (Cu, Rh etc.) produces silyl metal intermediates which are silicon nucleophiles (Scheme 3a, right side). The Si–B bonds can be also activated by Lewis bases (Nu) because of the high Lewis acidity of the sp^2-hybridized boron atom derived from the vacant *p*-orbital (Scheme 3b). A variety of Lewis bases can coordinate to the boron center to form the silylborane/Lewis base ate complexes where are also silicon nucleophiles. Therefore, silylborane compounds have recently received considerable attention as silicon pronucleophiles because silylboranes can produce silicon nucleophiles in the presence of the transition-metals or bases under mild conditions.

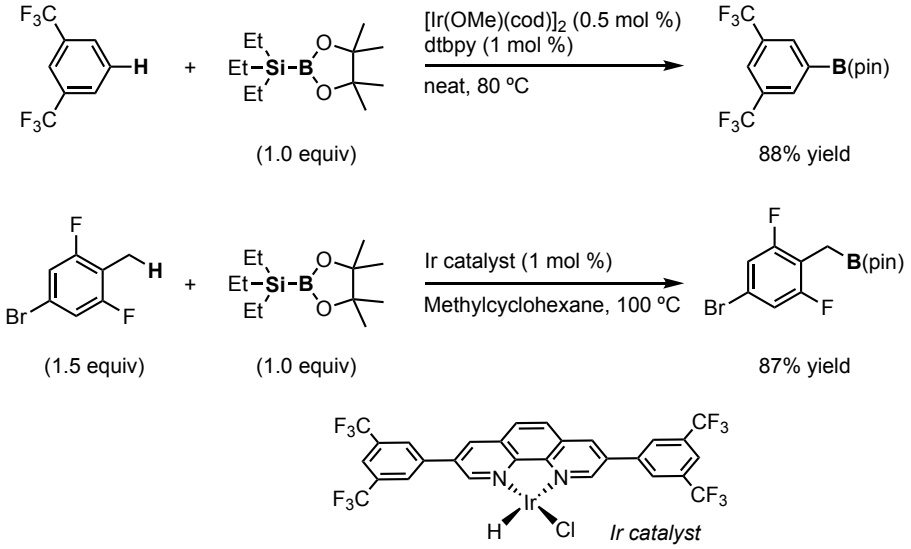
In 1996, Suginome, Ito, and co-workers reported the palladium-catalyzed regioselective silaboration reaction of terminal alkynes via Si–B bond activation by an oxidative addition (Scheme 4)[4]. In this reaction, (boryl)(silyl)Pd(II) species are formed by the oxidative addition of the Si–B bond in silylborane to Pd(0) and acts as the active catalyst species. This reaction is the pioneering work for the applications of silylborane compounds in organic synthesis.

Scheme 4. Palladium-Catalyzed *Z*-Selective Silaboration of Terminal Alkynes.[4]



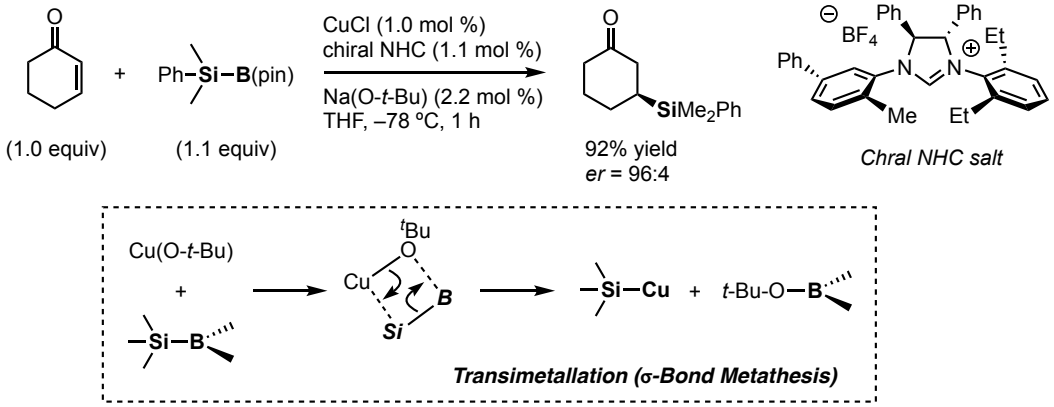
The combination of silylborane compounds and the iridium(I)/dtbpy catalyst also allows for the C–H borylation reaction of aromatic or benzylic C–H bonds (Scheme 5)[5]. Hartwig and co-worker reported that aromatic or benzylic C–H bonds underwent the iridium-catalyzed borylations with triethylsilylborane to produce the corresponding products in high yield.

Scheme 5. Iridium-Catalyzed C–H Borylation with Triethylsilylborane.[5]



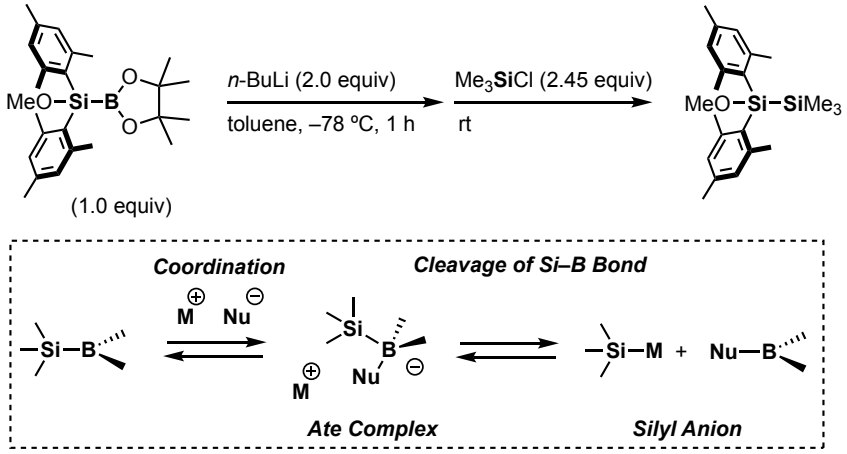
In 2010, the first example of copper(I)-catalyzed silyl conjugate addition to α,β-unsaturated carbonyl compounds using silylboranes was reported by Hoveyda and co-workers (Scheme 6)[6]. Nucleophilic silylcopper(I) species are generated *in situ* as active catalyst species from the reaction of chiral NHC/copper(I) complex with silylborane via σ-bond metathesis. The activation of Si–B bond by transmetallation with copper alkoxide catalysts has been recognized as the most standard technique in organosilicon chemistry. The conjugate silyl addition to 2-cyclohexen-1-one proceeded efficiently to produce the chiral β-silyl ketone in high yield with excellent enantioselectivity.

Scheme 6. Copper(I)-Catalyzed Enantioselective Silyl Conjugate Addition to α,β-Unsaturated Carbonyl Compounds.[6]



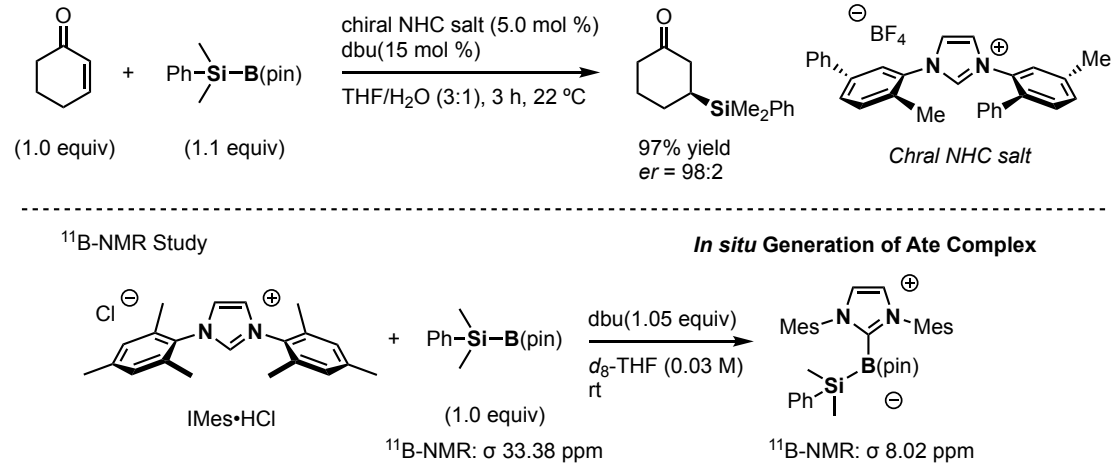
The Si–B bonds in silylborane compounds can be also activated by a variety of Lewis bases because of the high Lewis acidity of the sp^2-hybridized boron atom derived from the vacant *p*-orbital (Scheme 3b). In 2001, Kawachi, Tamao, and co-worker disclosed that the stoichiometric boron-metal exchange reaction in silylborane compounds with organolithium reagents (Scheme 7).[7] In this reaction, the Si–B bonds in silylborane compounds are activated by the coordination of the organolithium reagent, and then the silyl lithium is formed by the cleavage of Si–B bonds. This is the pioneering work for the activation of Si–B bonds by nucleophiles.

Scheme 7. Generation of Silyl Anion Species by the Reaction of Silylboranes with Nucleophiles.[7]



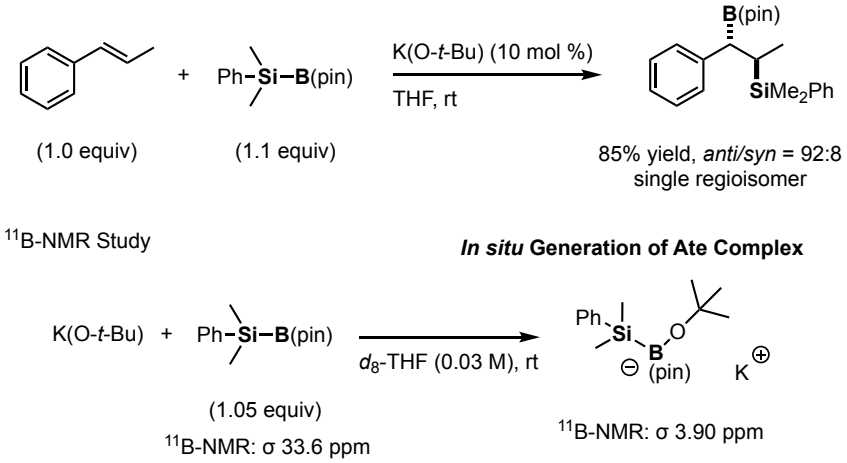
N-Heterocyclic carbenes (NHC) are also used as bases and activate the Si–B bonds in silylborane compounds to generate the silicon nucleophiles. In 2011, Hoveyda and co-workers first reported that NHC-catalyzed silyl conjugate addition to α,β-unsaturated carbonyl compounds (Scheme 8).[8] The reaction of α,β-unsaturated carbonyl compounds with a silylborane compound in the presence of the catalytic amount of a chiral imidazolium salt and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at room temperature produced the conjugate silylation products in high yield with excellent enantioselectivity. The *in situ* ^{11}B-NMR analysis suggested that the silylborane/NHC ate complex are generated in the reaction mixture.

Scheme 8. Chiral NHC-Catalyzed Silyl Conjugate Addition to α,β-Unsaturated Carbonyl Compounds.[8]



Alkoxide bases can also activate the Si–B bonds to form the silicon nucleophiles. In 2012, Ito and co-workers reported the alkoxide base-catalyzed silaboration reaction of aromatic alkene with silylborane compounds as the first examples of transition-metal free, base-mediated silaboration of aromatic alkenes (Scheme 9).[9] Aromatic alkenes underwent the silaboration reaction effectively in the presence of 10 mol % of K(O-*t*-Bu) to afford the silaboration product in high yield with excellent regioselectivity. The *in situ* ^{11}B-NMR analysis suggested that the silylborane/alkoxide base ate complex are formed in the reaction mixture. Later, they also developed the formal nucleophilic boryl substitution of

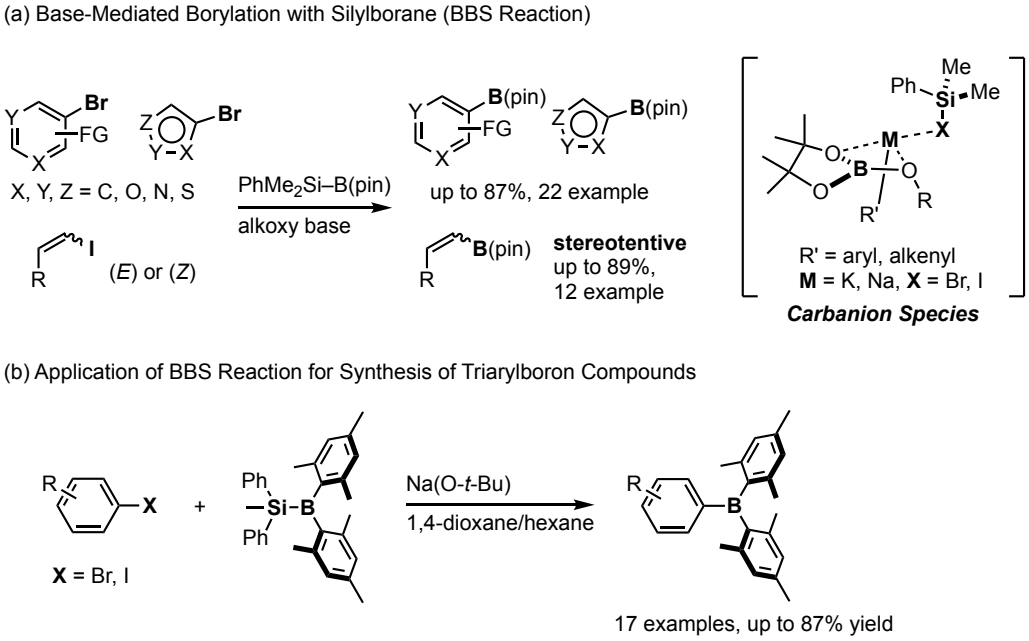
Scheme 9. K(O-*t*-Bu) Catalyzed Silaboration of Aromatic Alkenes.[9]



aryl-, alkenyl- and alkyl halides with a silylborane and an alkoxy base (Scheme 10a)[10]. In this reaction mechanism, the Si–B bonds in the silylborane compound are activated by an

alkoxide base to generate the silylborane/alkoxide base ate complex (**B**ase-Mediated **B**orylation with **S**ilylborane, BBS reaction). Then, this silicon nucleophile reacts with the organohalide to produce the carbanion species as the key intermediate. Furthermore, the BBS Method was applied to the synthesis of triarylborane compounds, which exhibit the unique optical properties (Scheme 10b)[10d].

Scheme 10. Formal Nucleophilic Boryl Substitution of Aryl-, Alkenyl- and Alkyl Halides with a Silylborane and an Alkoxy Base.[10]

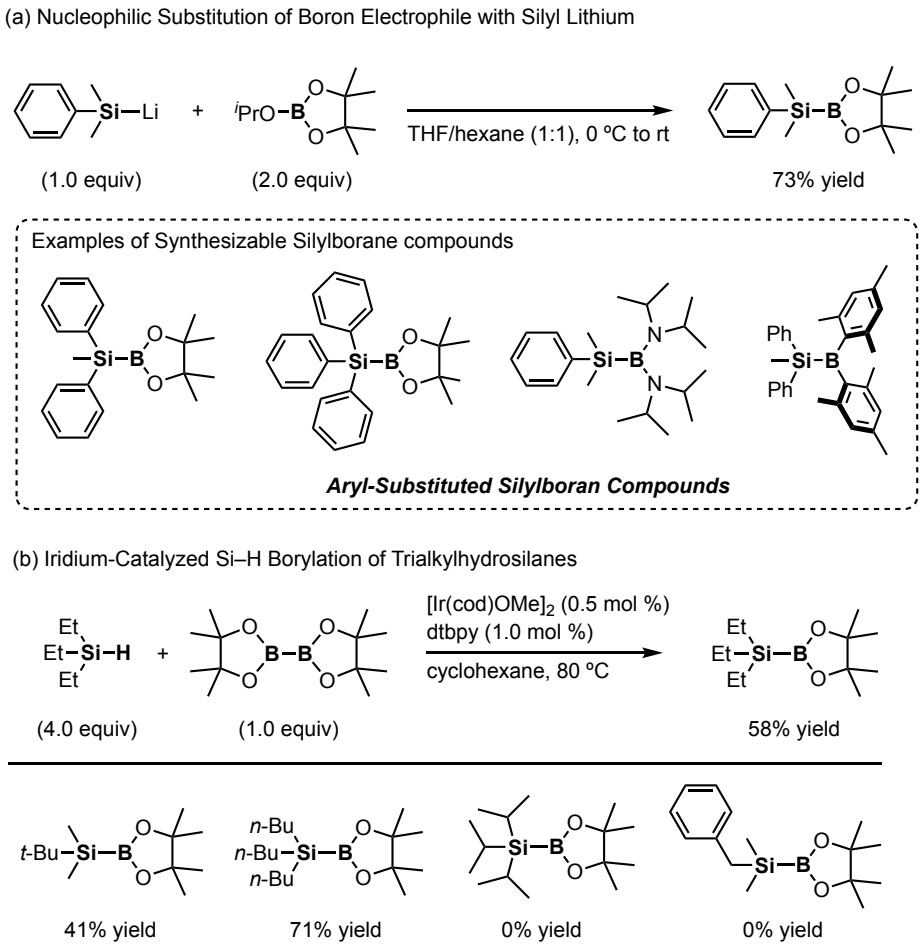


The first preparation of compounds containing a silicon–boron (Si–B) bond was reported by Seyferth and Ryschkewitsch in 1960.[11] Early research interests were mainly focused on exploring their physical properties, but their applications to organic synthesis are more recent. From the pioneering work reported by Suginome, Ito and co-workers in 2000, silylboranes have been widely used as versatile organometallic reagents for introducing a boryl- and a silyl group into organic molecules.[12] Actually, a lot of silaboration and silylation reactions using silylboranes have been developed to expand the scope of organosilicon and organoboron compounds.[3,13,14] However, practically synthesizable silylboranes, especially trialkylsilylboranes are still quite limited. A conventional method for the preparation of silylborane compounds is the stoichiometric reaction of silyl anions and a boron electrophile to form the corresponding aryl-substituted silylboranes such as $PhMe_2Si$–B(pin).[12] However, trialkylsilylboranes cannot be directly synthesized by this approach due to the limitation derived from the generation

of silyl anions. Silyl anions are generally formed by reactions of chlorosilanes with alkali metals (K, Na and Li), while this method are limited to the preparation of aromatic groups-substituted silyl anions $Ar_{3-n}R_nSi–M$ (n = 0–2, M = K, Na or Li) because of the lower reduction of the aryl-substituted chlorosilanes and the disilane intermediates.

Alternatively, trialkylsilylboranes are synthesized by an iridium-catalyzed direct borylation of trialkylhydrosilanes with bis(pinacolato)diboron $B_2(pin)_2$ developed by Hartwig and co-workers.[5a] Although this approach is significantly useful for the simple, small size of trialkylsilylboranes, this method does not enable synthesizing sterically hindered silylboranes such as triisopropylsilyl (TIPS) boronate and also aromatic group-containing silylboranes due to the competition with undesired aromatic C–H borylation reactions.[15]

Scheme 11. Synthetic Methods of Silylborane Compounds.[5a, 12]



$PhMe_2Si–B(pin)$ has been the most frequently utilized in the reactions using silylborane compounds probably due to the good reactivity and relatively simple

preparation. Indeed, most silylation and silaboration reactions using silylborane have been developed by the use of $PhMe_2Si$–B(pin), and only a few examples using Et_3Si–B(pin) were reported recently. Therefore, installable silyl- and boryl-groups into organic compounds using silylboranes are significantly limited. Additionally, $PhMe_2Si$–B(pin) is an air- and moisture-sensitive reagent, which greatly reduces the practical utility in organic synthesis. Thus, the development of new protocols for the synthesis of new types of silylboranes would allow access to a vast range of valuable organosilicon compounds that are inaccessible by previously reported methods. Given these aspects, the author has realized that the development of a general and efficient synthetic method for various classes of silylborane compounds as well as their new transformations should give substantial impact on both silylation and borylation chemistry.

Chapter 1 describes the synthesis of new, bulky tris(trimethylsilyl)silyl boronate esters $(TMS)_3Si$–$B(OR)_2$. Tris(trimethylsilyl)silyl boronate pinacol and hexylene glycol esters [$(TMS)_3Si$–B(pin) and $(TMS)_3Si$–B(hg)] were prepared in 46 and 61% yields, respectively by the reaction of tris(trimethylsilyl)silyl potassium with the corresponding boron electrophiles. Notably, these silyl boronate esters exhibited high stability to air and silica gel, and were applied to the transition-metal-free boryl substitution of aryl halides, providing the desired borylated products in high yields with excellent B/Si ratios (up to 96% yield, B/Si = 99:1). These new silyl boronate esters were also applied to a sequential borylation/cross-coupling process with various aryl halides, as well as the base-mediated silaboration of styrene.

Chapter 2 describes the iridium-catalyzed C–H dimesitylborylation of benzofuran derivatives with a silyldimesitylborane. The direct dimesitylborylation of benzofuran derivatives *via* a C–H activation catalyzed by an iridium(I)/*N*-heterocyclic carbene (NHC) complex in the presence of Ph_2MeSi–$BMes_2$ afforded the corresponding dimesitylborylation products in good to high yield with excellent regioselectivity. This method provides a straightforward route to donor-(π-spacer)-acceptor systems with intriguing solvatochromic luminescence properties.

Chapter 3 describes the development of a new synthetic method for trialkylsilylboranes compounds by a rhodium or platinum catalyzed direct borylation of hydrosilanes with bis(pinacolato)diboron. The developed conditions allow synthesizing new trialkylsilylboranes bearing bulky alkyl groups as well as sensitive functional groups that are inaccessible by previously reported methods. We demonstrate the use of these compounds as silyl anion equivalents in organic transformations and significantly expanded the scope of synthesizable organosilicon compounds.

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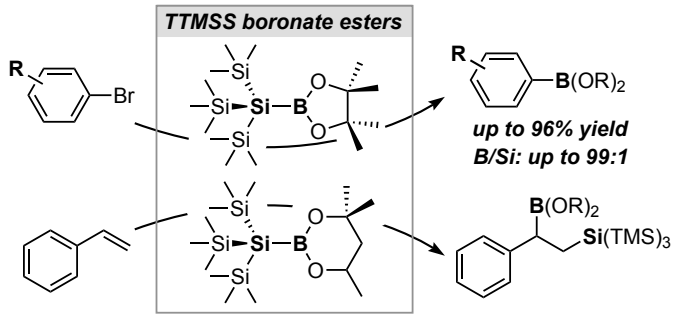
Chapter 1.

Synthesis of Novel Bulky, Air- and Moisture-Stable Tri(trimethylsilyl)silyl Boronate Esters

Abstract

Novel, bulky tris(trimethylsilyl)silyl boronate pinacol and hexylene glycol esters [$(TMS)_3Si$–B(pin) and $(TMS)_3Si$–B(hg)] were synthesized in 46 and 61% yields, respectively by the reaction of tris(trimethylsilyl)silyl potassium with the corresponding boron electrophiles. Notably, these silyl boronate esters showed high stability toward air and silica gel, and could be applied to the transition-metal-free boryl substitution of aryl halides, producing the desired borylated products in high yields with excellent B/Si ratios (up to 96% yield, B/Si = 99:1). These new silyl boronate esters could also be applied to a sequential borylation/cross coupling process with various aryl halides, as well as the base-mediated silaboration of styrene.



Introduction

Silyl boronate esters, represented by $PhMe_2Si$–B(pin) (**1a**) have been widely utilized as useful reagents for preparing organo-boron and -silicon compounds.[1] These organometallic compounds have been used as invaluable building blocks since the compounds have stable C–Si or C–B bonds, which can be transformed to various carbon-carbon or carbon-heteroatom bonds.[2,3] Ito and co-workers have developed the transition-metal-free boryl substitution of aryl halides with silyl boronate ester **1a** and alkoxy base (**B**ase-mediated **B**orylation with **S**ilyl boronate esters, denoted as **BBS,** Figure 1a, b).[4,5] This reaction produces easy access to various aryl-, heteroaryl- and alkenyl boronate esters because it can be operated under mild conditions with high reactivity without a transition-metal catalyst. This BBS strategy can also be applied to directly prepare triarylboranes, which have numerous potential applications in materials science, from various organic halides.[4d] However, there still remains several drawbacks should be improved: the silylation is concomitantly occurred in this BBS method (typical borylation/silylation ratio, 90:10–96:4); the silylborane reagents [typically PhMe2SiB(pin)] are not stable in air and moisture, which lessens the utility of this

reaction. Although there exist several reactions using the silyl boronate ester reagent in the presence of air or water, significant decomposition of silyl boronate esters after storage of the reagents in air is usually observed.[6]

Mechanistic studies have suggested that this reaction proceeds via the halogenophilic attack of a silicon nucleophile on the halogen atom of an aryl halide, generating the corresponding aryl anion intermediate. The subsequent nucleophilic attack of the arylanion determines the borylation/silylation (B/Si) ratio of the products (Figure 1a, path **a** or **b**). Based on this mechanism, the author envisioned that the use of silyl boronate esters bearing a bulky silyl group would improve the B/Si selectivity of the BBS by suppressing the undesired pathway (path **b**). As for the usability issue of silyl boronate ester compound, $PhMe_2Si$–B(pin) (**1a**) is sensitive to air and moisture. Although several analogous silyl boronate esters[1,7,8] have been reported, very little is known about the stability of these compounds. Hartwig and co-workers reported the Ir-catalyzed borylation of hydrosilanes and prepared several trialkyl silyl boronate esters, including Et_3Si–B(pin) (**1b**), which they purified by column chromatography over silica gel.[8] These compounds are fairly stable, but their reactivity in base-mediated reactions was not studied. It is needed to develop a new silyl boronate ester reagent that show good bench stability as well as excellent reactivity and selectivity in the reactions with alkoxy bases. The author envisioned that silyl boronate esters bearing considerable steric bulk would be sufficiently stabilized kinetically to tolerate air and moisture (Figure 1c). With this in mind, we focused on the use of a tris(trimethylsilyl)silyl [$(TMS)_3Si$] group,[9,10] which is comparable in size to a *t*-butyl group.[9b]

Herein, the author reported the first synthesis of silyl boronate esters [$(TMS)_3Si$–$B(OR)_2$] bearing a tris(trimethylsilyl)silyl [$(TMS)_3Si$] group,[9,10] which exibit high selectivity in the BBS and silaboration reactions with excellent air/moisture stability. Notably, these silyl boronates were readily purified by column chromatography over silica gel, highlighting their stability. Additionally, these silyl boronate ester reagents could be applied to transition-metal-free boryl substitution of aryl halides,[4] providing the corresponding aryl boronates in high yields with high B/Si ratios (up to 99/1). The author also conducted the KOMe-mediated silaboration of styrene[11,12] using silyl boronate esters.

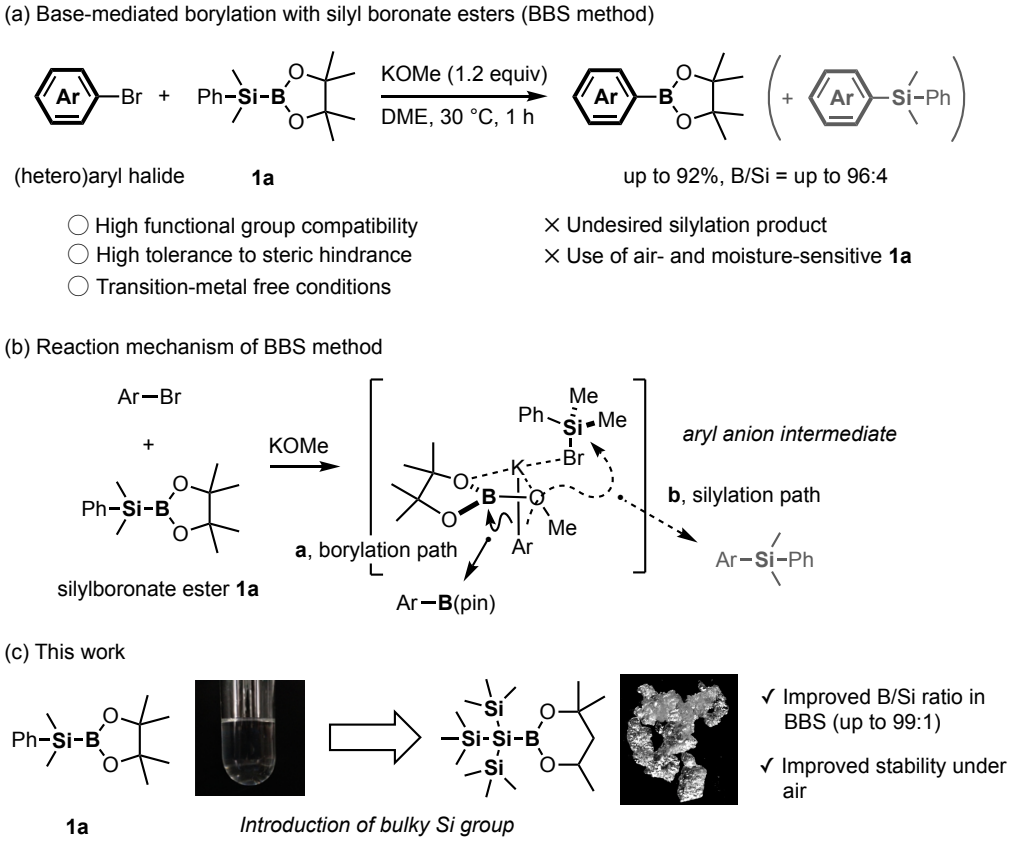
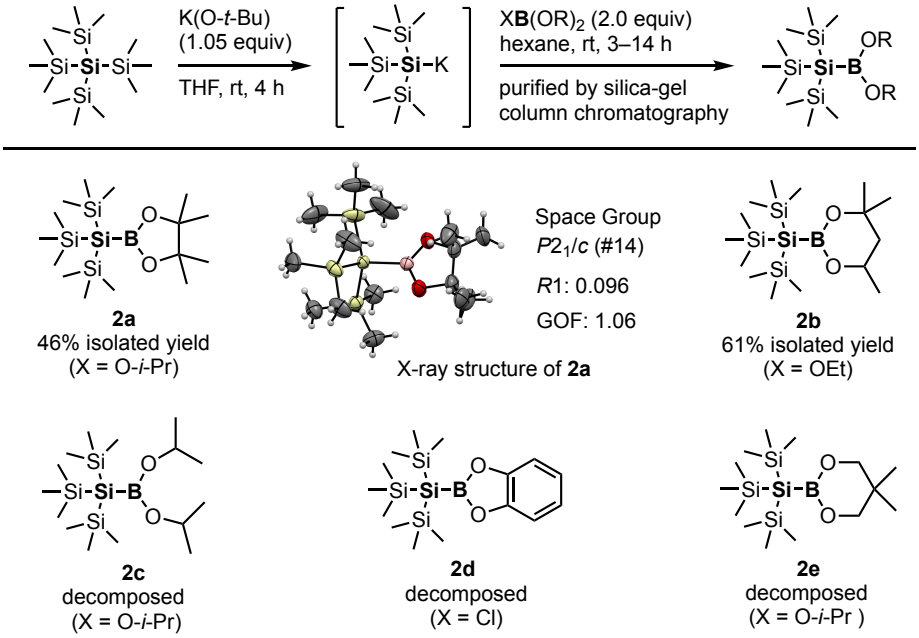


Figure 1. (a) Base-mediated borylation with silyl boronate esters (BBS). (b) Mechanism of BBS method. (c) Concept of this work.

Results and Discussion

The author initially investigated the synthesis of tris(trimethylsilyl)silyl boronate esters, which have different alkoxy substituents on their boron atom (Table 1). Tris(trimethylsilyl)silyl pinacol borane [$(TMS)_3Si$–B(pin) (**2a**)] was obtained in 46% yield as a colorless solid using *in situ*-generated tris(trimethylsilyl)silyl potassium and *i*-PrOB(pin). This compound was successfully purified by column chromatography over silica gel. Tris(trimethylsilyl)silyl boronic acid hexylene glycol ester [$(TMS)_3Si$–B(hg), (**2b**)] was also synthesized in the same manner (**2b**, 61% yield, colorless solid). Unfortunately, however, tris(trimethylsilyl)silyl boronate esters bearing a diisopropoxy (**2c**), catecholato (**2d**) or neopentyl glycolato (**2e**) moiety decomposed during column chromatography over silica gel although the corresponding silylboronate esters seemed formed in the reaction mixtures based on the GC analyses.

Table 1. Synthesis of $(TMS)_3Si$–$B(OR)_2$[a].



[a]Reaction conditions: A mixture of $(TMS)_4Si$ (1.0 equiv) and K(O-*t*-Bu) (1.05 equiv) in THF [0.50 M to $(TMS)_4Si$] was stirred for 4 h at rt. The reaction was concentrated *in vacuo*, diluted with hexane [0.50 M to $(TMS)_4Si$] and treated with X-$B(OR)_2$ (2.0 equiv), before being stirred for 3–14 h. Compounds **2c**–**2e** decomposed during column chromatography over silica gel.

The molecular structure of **2a** was confirmed by single crystal X-ray analysis (Supporting Information). The Si–B bond length of **2a** [2.015(5) Å] was found to be shorter than a *B*–silyl borazine bearing a $(TMS)_3Si$ group [$(TMS)_3Si(Me)_2B_3N_3(Me)$] [B–Si length, 2.097(5) Å],[10a] and even shorter than the sum of the covalent radii of B and Si

(2.05 Å). Although $(TMS)_3Si$ is well-known as a bulky group, these comparisons suggest that steric congestion around the Si–B bond is not considerable because the substituents around B and Si atoms [$(TMS)_3Si$ and pinacol] are far from each other.

Encouraged by the successful preparation of the $(TMS)_3Si$ boronate esters, the author proceeded to evaluate their stability under air (Figure 2). Fortunately, $(TMS)_3Si$–B(pin) (**2a**) remained unchanged after 48 h at room temperature in toluene under air. In contrast, only less than 20% of $PhMe_2Si$–B(pin) (**1a**) was left after 5 h under the same conditions. $(TMS)_3Si$–B(hg) (**2b**) also exhibited greater stability to air than $PhMe_2Si$–B(pin) (**1a**), although the recovery of **2b** was 83% under the same conditions after 48 h. The stability of Et_3Si–B(pin) (**1b**) was similar to that of **2a**. The stability of silyl boronate esters **1a**, **2a** and **2b** to silica gel was also examined based on their recovery from silica gel swelled with hexane at room temperature under air for 1 h. These results revealed that the stabilities were of the order **2a** > **2b** > **1a** (Recovery yields: 95%, 85%, 64%, respectively. For details, see Experimental Section), which was consistent with the stability of these compounds under air.

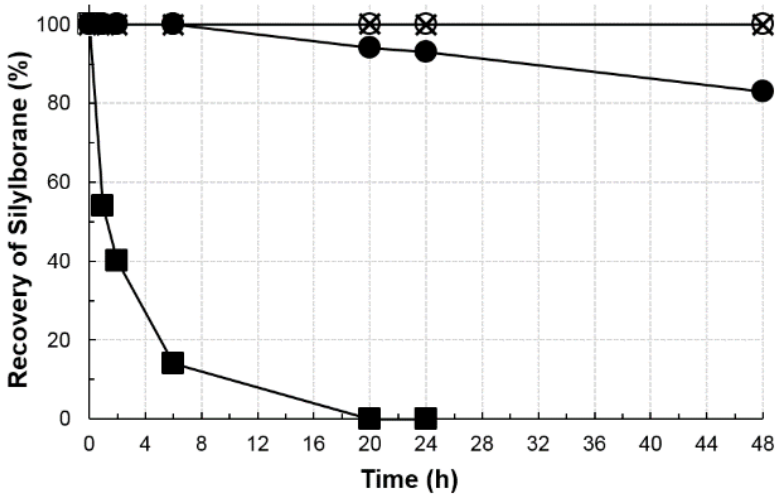
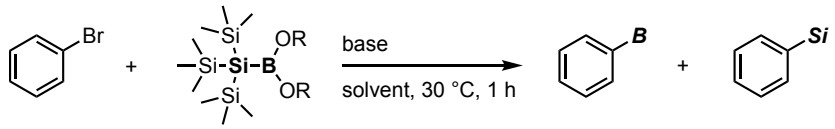


Figure 2. Stability of Silyl Boronate Esters under Air: $PhMe_2Si$–B(pin) **1a** (■), Et_3Si–B(pin) **1b** (×), $(TMS)_3Si$–B(pin) **2a** (○), $(TMS)_3Si$–B(hg) **2b** (●), Conditions: A solution of silyl boronate esters **1a**, **1b, 2a**, or **2b** (0.2 mmol) in toluene (1.0 mL) was stirred at room temperature. After a set time, the recovery of the silyl boronate ester was determined by GC.

To explore the applicability of these silyl boronate ester reagents to organic synthesis, the author explored the boryl substitution of phenyl bromide with $(TMS)_3Si$–B(pin) **2a** and $(TMS)_3Si$–B(hg) **2b** (Table 2).[4] The author initially examined the reaction of **2a** with phenyl bromide **3a** in the presence of KOMe using DME as a solvent, which provided the desired borylated product in 63% yield with a B/Si ratio (**4a**/**5a** + **5b**) of 89:11 (Table 2, entry 1. For details, see Experimental Section). The use of silyl boronate ester **2b** instead of **2a** led to the improvement in the yield and B/Si ratio (80%, B/Si = 93:7, Table 2, entry 2), thus, all of the subsequent optimization reactions were performed using **2b**. The use of NaOMe afforded similar results to those obtained with KOMe, whereas LiOMe failed to afford the desired products (Table 2, entries 3 and 4). The best results were obtained using the bulky base K(O-*t*-Bu) (Table 2, entry 5). Na(O-*t*-Bu) and Li(O-*t*-Bu) also exhibited better yields and B/Si selectivities than their methoxide counterparts (Table 2, entries 6 and 7).

Table 2. Optimization of the Reaction Conditions for the Borylation of **3a** with $(TMS)_3Si$–$B(OR)_2$/Alkoxy Base.[a]



3a (1.0 equiv) | **2a** or **2b** | **4**: **4a**: ***B*** = **B**(pin), **4a'**: ***B*** = **B**(hg) | **5**: **5a**: ***Si*** = TMS, **5b**: ***Si*** = $(TMS)_3Si$

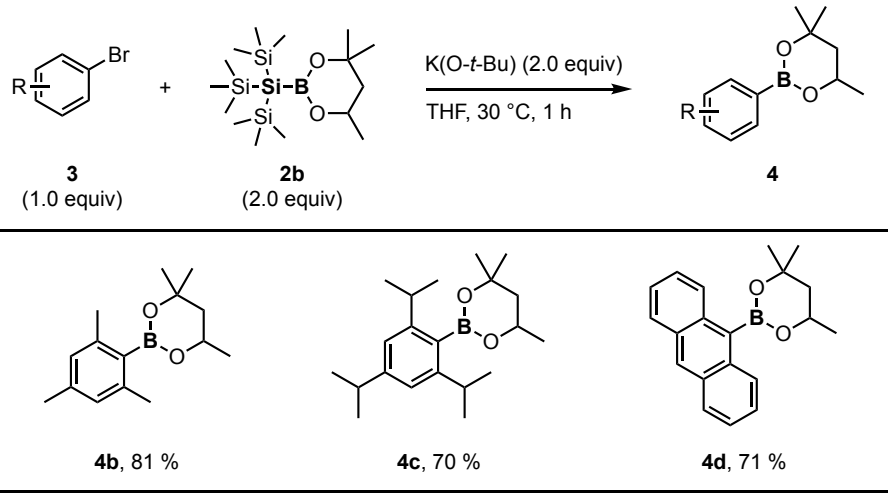
entry	**Si–B**	base (equiv)	solvent	yield(%)[b]	**4**/(**5a** + **5b**)[c]
1[d]	**2a**	KOMe (2.0)	DME	63	89/11
2	**2b**	KOMe (2.0)	DME	80	93/7
3	**2b**	NaOMe (2.0)	DME	80	90/10
4	**2b**	LiOMe (2.0)	DME	0	–
5	**2b**	K(O-*t*-Bu) (2.0)	DME	94	98/2
6	**2b**	Na(O-*t*-Bu) (2.0)	DME	91	96/4
7	**2b**	Li(O-*t*-Bu) (2.0)	DME	75	94/6
8	**2b**	K(O-*t*-Bu) (2.0)	THF	95 (76)[e]	96/4
9[f]	**2b**	K(O-*t*-Bu) (1.2)	DME	64	95/5
10[g]	**2b**	K(O-*t*-Bu) (2.0)	DME	62	97/3
11[h]	**2b**	K(O-*t*-Bu) (2.0)	DME	96	99/1
12	**1b**	K(O-*t*-Bu) (2.0)	THF	0	–

[a]Reaction conditions unless specified otherwise: silylboronate ester (2 equiv) and a base in a solvent was stirred for 10 min at 650 rpm at 30 °C, after which **3a** (0.3 mmol) was added. The resultant mixture was stirred for 1 h at 30 °C. [b]GC yield of **4a** or **4a'**. [c]Ratio of **4a** or **4a'** to **5a** + **5b**. [d]Reaction time: 3 h. [e]Isolated yield after sequantial boryl substitution/Suzuki-Miyaura cross coupling. [f]1.5 equiv of **2b** was used. [g]PhCl was used as a substrate. [h]PhI was used as a substrate.

The use of DME instead of THF had very little impact on the yield or selectivity (Table 2, entry 8). The author also investigated the reaction with 1.5 equiv of **2b**, which resulted in a lower yield (64%, B/Si = 95:5, Table 2, entry 9). The effect of the leaving group of the aryl halide was also examined. Chlorobenzene afforded the corresponding borylated product in good yield and high selectivity (62%, B/Si = 97:3, entry 10), whereas iodobenzene provided an excellent yield and higher selectivity (96%, B/Si = 99:1, entry 11). In contrast, the reaction of bromobenzene with Et_3Si–B(pin) (**1b**), which shows similar stability of **2b**, resulted in no reaction (Table 2, entry 12).

With the optimized reaction conditions in hand, the author examined the borylation of hindered arylbromides with **2b** (Table 3). Pleasingly, sterically hindered aryl bromides **3b–d** also reacted with **2b** to produce the corresponding products in high yields (**4b**: 81%, **4c**: 70%, **4d**: 71%).

Table 3. Substrate Scope for the Boryl Substitution of Aryl Halides using $(TMS)_3Si$–B(hg)/K(O-*t*-Bu).[a]

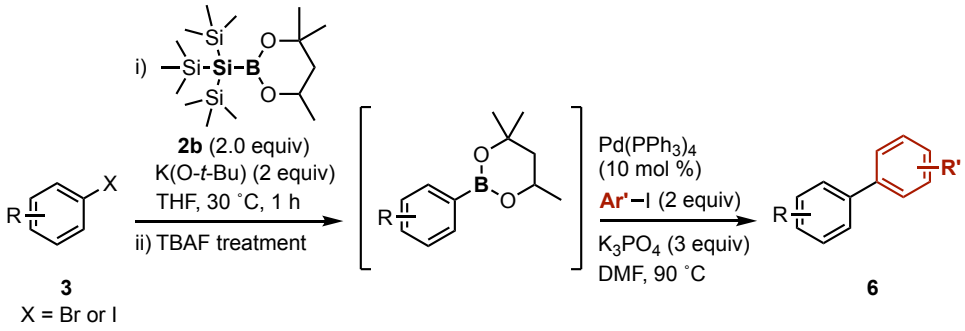


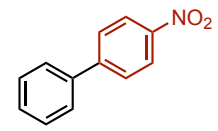
[a]Reaction conditions: a mixture of silylboronate ester **2b** (2.0 equiv) and K(O-*t*-Bu) (2.0 equiv) in THF was stirred for 10 min at 650 rpm and 30 °C. Aryl bromide **3** (0.3 mmol) was added, and the resulting mixture was stirred for 1 h at 30 °C.

The author also investigated the possibility of a one-pot borylation/Suzuki cross coupling sequence to further investigate the functional group compatibility of **2b** and the overall utility of this reaction (Table 4). Electron-neutral and electron-rich aryl bromides readily underwent the borylation, followed by a cross coupling with 4-nitroiodobenzene, to produce the corresponding products in high yield (**6a**: 76%, **6e**: 85%, **6f**: 75%). Reactions with aryl bromides or iodides bearing an electron-withdrawing group (i.e., fluoro, *t*-butyl or ethyl ester, or amide group) also proceeded effectively to give the

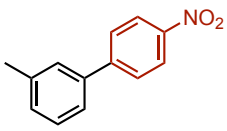
desired products in good yields (**6g**: 74%, **6h**: 57%, **6i**: 62%, **6j**: 61%). Notably, two sulfur-containing aryl bromides also underwent the one-pot borylation/cross coupling to give the desired products in good yields (**6k**: 75%, **6l**: 79%). **2a** and **2b** could also be used as reagents for the base-mediated silaboration of alkenes,[11] which can provide access to synthetically useful 1,2-bismetallated products.

Table 4. Substrate Scope for the Boryl Substitution of Aryl Halides with $(TMS)_3Si$–B(hg)/K(O-*t*-Bu).[a]

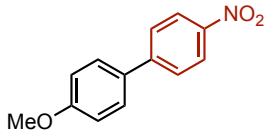




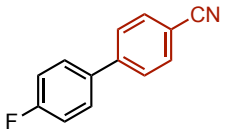
6a, 76% (X = Br)



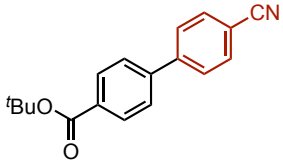
6e, 85% (X = Br)



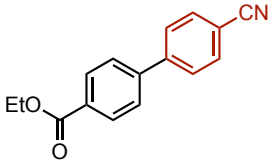
6f, 75% (X = Br)



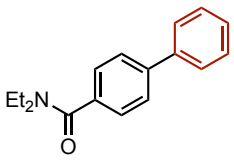
6g, 74% (X = Br)



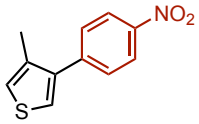
6h, 57% (X = I)



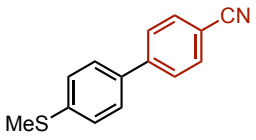
6i, 62% (X = I)



6j, 61% (X = Br)



6k, 75% (X = Br)

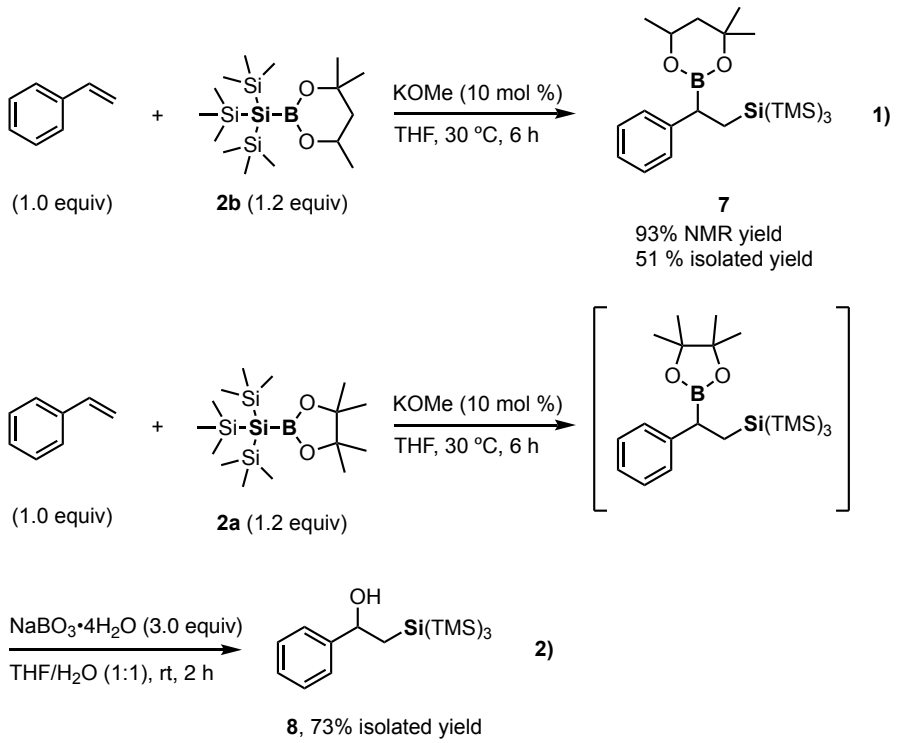


6l, 79% (X = Br)

[a]Isolated yield.

The silaboration of styrene with **2b** in the presence of a catalytic amount of KOMe produced the desired silaborated product **7** in high yield (93% NMR yield). In addition, the one-pot, base-mediated silaboration of styrene with **2a**/$NaBO_3$ oxidation afforded the corresponding alcohol **8** in 73% yield (Scheme 1). Contrary, the reaction of styrene with Et_3Si–B(pin) (**1b**) in the presence a catalytic amount of KOMe showed no reactivity.

Scheme 1. Silaboration of Styrene with Silyl Boronate Ester **2a** or **2b** in the presence of KOMe.



Summary

In summary, the author has developed new air- and moisture stable TTMSS boronate esters. These reagents showed high stability for extended periods at room temperature in solution, and also exhibited good stability to silica gel. Furthermore, these reagents were successfully utilized in the boryl substitution of aryl halides with K(O-*t*-Bu), as well as the silaboration of styrene in the presence of catalytic KOMe.

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Experimental

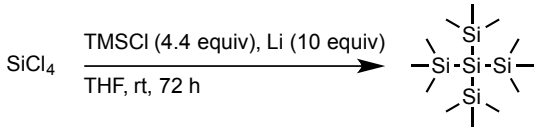
Table of Contents

1. General and Materials.

Materials were obtained from commercial suppliers and purified by standard procedures unless otherwise noted. Dry solvents for the reaction were also purchased from commercial suppliers and used as received unless otherwise noted. DME was distilled from sodium benzophenone ketyl, and further dried over molecular sieves 4A (MS4A) prior to use. THF was degassed via three freeze-pump-thaw cycles, and further dried over MS4A prior to use. K(O-*t*-Bu) (>97.0%) purchased from Tokyo Chemical Industry Co. (TCI) were used as received. Silica Gel 60 N (40–100 μm, spherical, neutral) purchased from Kanto Chemical Co. was used as received. *tert*-Butyl 4-iodobenzoate[1] and *N*, *N*-diethyl-4-iodobenzamide[2] were synthesized according to the literature procedures. NMR spectra were recorded on JEOL JNM-ECX400P and ECS-400 spectrometers (^{1}H: 400 MHz, ^{13}C: 100 MHz, ^{11}B: 127 MHz, and ^{29}Si: 79.5 MHz). Tetramethylsilane (^{1}H and ^{29}Si) and $CDCl_3$ (^{13}C) were employed as internal standards, respectively. $BF_3 \cdot Et_2O$ was used as an external standard for ^{11}B NMR analysis. Multiplicity was reported as follows: s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet. GLC analyses were conducted with a Shimadzu GC-2014 or GC-2025 equipped with ULBON HR-1 glass capillary column (Shinwa Chemical Industries) and a FID detector. 1,4-Diisopropylbenzene was used as the internal standard for determining GC yield. GC yield was determined by GC analysis

of the crude reaction mixture. Mesitylene was used as the internal standard for determining NMR yield. NMR yield was determined by ^{1}H-NMR analysis of the crude reaction mixture. High-resolution mass spectra were recorded at the Global Facility Center for Instrumental Analysis, Hokkaido University.

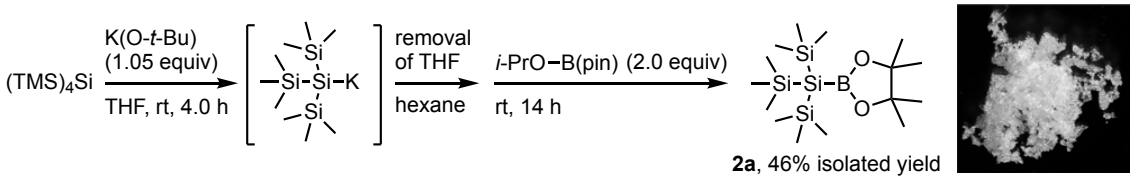
2. Preparation of Tetrakis(trimethylsilyl)silane.



Tetrakis(trimethylsilyl)silane was prepared according to literature procedures.[3] A 500 mL two-necked, round-bottomed flask equipped with an inlet adapter with a 3-way stopcock and a glass magnetic stirrer bar were oven-dried over 20 min. After cooling to rt, lithium (7.0 g, 1.0 mol, 10 equiv) was added to the flask, then evacuated and refilled with nitrogen three times. THF (100 mL) and TMSCl (47.8 g, 440 mmol, 4.4 equiv) was added via a syringe. At the same time, a solution of $SiCl_4$ was prepared by diluting $SiCl_4$ (17.0 g, 100 mmol, 1.0 equiv) in 200 mL of THF. The $SiCl_4$ solution was added dropwise to the mixture of TMSCl and lithium over 1 h at 0 °C. The mixture was vigorously stirred for 3 days at room temperature. After completion of the reaction, the brown mixture was directly filtrated through a short silica-gel column with hexane/Et_2O (80:20) to remove salts and excess lithium. The resulting brown solid was purified by recrystallization from acetone, and then purified by silica-gel chromatography with hexane as the eluent to give tetrakis(trimethylsilyl)silane [13.26 g, 41.3 mmol, 41% isolated yield] as a white solid. ^{1}H and ^{13}C NMR spectra were in agreement with those in the literature.[3]

3. Synthesis of Tris(trimethylsilyl)silyl Boronate Ester 2a and 2b.

3-1. Procedure for Preparation of Tris(trimethylsilyl)silyl Boronate Ester 2a.



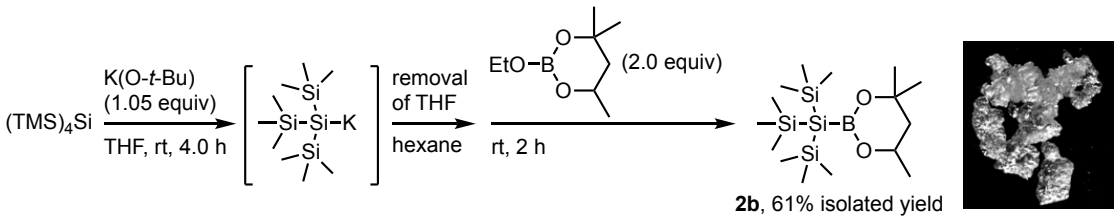
2a, 46% isolated yield

A 300 mL two-necked, round-bottomed flask equipped with an inlet adapter with a three-way stopcock and a glass magnetic stirrer bar were oven-dried over 20 min. After cooling to rt, tetrakis(trimethylsilyl)silane (11.0 g, 33.0 mmol, 1.0 equiv) was added to the flask, then evacuated and refilled with nitrogen three times, and THF (33.0 mL) was

added via a syringe. Then, a THF solution of K(O-*t*-Bu) (1.05 M, 33.0 mL, 34.7 mmol) was added to the flask via a syringe. After the resultant solution was stirred for 4 h at room temperature, the solvent was removed under reduced pressure, and hexane (66.0 mL) was added to the flask. Then, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12.3 g, 66.0 mmol, 2.0 equiv) was added in one portion to the mixture. After the resultant solution was stirred for 14 h at rt, the completeness was checked by GC analysis. Then, the mixture was directly filtered through a short silica-gel column with hexane as the eluent. After removal of the solvents under reduced pressure, the crude product was purified by silica-gel column chromatography with hexane as the eluent to give tris(trimethylsilyl)silyl boronate ester **2a** (5.70 g, 15.2 mmol, 46% isolated yield) as a white solid (m.p. = 94.3 °C).

^{1}H NMR (396 MHz, $CDCl_3$, δ): 0.18 (s, 27H), 1.19 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 2.1 (*C*H_3), 25.0 (*C*H_3), 82.8 (*C*). ^{11}B NMR (127 MHz, $CDCl_3$, δ): 37.3. ^{29}Si NMR (78.7 MHz, $CDCl_3$, δ): –101.2 (*Si*Me_3), –128.0 (*Si*$(SiMe_3)_3$). HRMS-EI (*m*/*z*): $[M-CH_3]^+$ calcd for $C_{14}H_{36}{}^{10}BO_2{}^{28}Si_4$, 358.19217; found, 358.19201.

3-2. Procedure for Preparation of Tris(trimethylsilyl)silyl Boronate Ester 2b.



A 50 mL two-necked, round-bottomed flask equipped with an inlet adapter with a three-way stopcock and a glass magnetic stirrer bar were oven-dried over 20 min. After cooling to rt, tetrakis(trimethylsilyl)silane (3.21 g, 10.0 mmol, 1.0 equiv) was added to the flask, then evacuated and refilled with nitrogen three times, and THF (10.0 mL) was added via a syringe. Then, a THF solution of K(O-*t*-Bu) (1.0 M, 10.5 mL, 10.5 mmol) was added to the flask via a syringe. After the resultant solution was stirred for 4 h at room temperature, the solvent was removed under reduced pressure, and hexane (20.0 mL) was added to the flask. Then, 2-ethoxy-4,4,6-trimethyl-1,3,2-dioxaborinane (3.44 g, 20.0 mmol, 2.0 equiv) was added in one portion to the mixture. After the resultant solution was stirred for 2 h at rt, the completeness of the reaction was checked by GC. Then the mixture was directly filtered through a short silica-gel column with hexane as the eluent. After removal of the solvents under reduced pressure, the crude product was purified by silica-gel column chromatography with hexane as the eluent to give tris(trimethylsilyl)silyl boronate ester **2b** (2.28 g, 6.09 mmol, 61% isolated yield) as a

white solid (m.p. = 30.9 °C).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.16 (s, 27H), 1.20 (d, J = 6.7 Hz, 3H), 1.22 (s, 3H), 1.25 (s, 3H), 1.44 (dd, J = 12.0, 13.5 Hz, 1H), 1.78 (dd, J = 2.9, 13.5 Hz, 1H), 4.13 (ddq, J = 3.1, 6.0, 12.0 Hz, 1H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 2.0 (CH_3), 23.4 (CH_3), 28.4 (CH_3), 31.4 (CH_3), 46.6 (CH_2), 64.4 (CH), 70.6 (C). ^{11}B NMR (127 MHz, $CDCl_3$, δ): 34.4. ^{29}Si NMR (78.7 MHz, $CDCl_3$, δ): –99.6 ($SiMe_3$), –122.7 ($Si(SiMe_3)_3$). HRMS-EI (m/z): $[M]^+$ calcd for $C_{15}H_{39}{}^{11}BO_2{}^{28}Si_4$, 374.21202; found, 374.21137.

4. General Experimental Procedures.

4-1. General Procedure for Boryl Substitution of Aryl Halides with 2b: Procedure A.

Tris(trimethylsilyl)silyl boronate ester **2b** (224.8 mg, 0.60 mmol, 2.0 equiv) was placed in a vial with a screw cap containing a teflon-coated rubber septum under air. Then, the reaction vial was connected to a vacuum-nitrogen manifold through a needle, and it was evacuated and refilled with nitrogen three times. After THF (2.40 mL) was added to the vial, a THF solution of K(O-*t*-Bu) (1.0 M, 0.60 mL, 0.60 mmol, 2.0 equiv) was added to the vial via a syringe. The reaction solution was stirred for 10 min at 30 ºC, then aryl halide (0.30 mmol) was then added dropwise to the vial with a syringe through the rubber septum. After 1 h, the reaction mixture was analyzed by GC to check completeness of the reaction. Then the mixture was directly filtered through a short silica-gel column with hexane/Et_2O (90:10) as an eluent. After removal of the solvents under reduced pressure, the crude product was purified by silica-gel column chromatography with 0−1.4% hexane/Et_2O eluent to give the corresponding borylated product.

4-2. General Procedure for Sequential Boryl Substitution with 2b and Suzuki-Miyaura Coupling: Procedure B.

Tris(trimethylsilyl)silyl boronate ester **2b** (224.8 mg, 0.60 mmol, 2.0 equiv) was placed in a 20 mL-Schenk flask with a magnetic stirrer bar under air. Then, the flask was connected to a vacuum-nitrogen manifold through a needle, and it was evacuated and refilled with nitrogen three times. After THF (2.40 mL) was added to the flask, a THF solution of K(O-*t*-Bu) (1.0 M, 0.60 mL, 0.60 mmol, 2.0 equiv) was added to the flask via a syringe. The reaction solution was stirred for 10 min at 30 ºC, then an aryl halide (0.30 mmol) was added dropwise to the vial with a syringe. After 1 h, the completeness of the reaction was checked by GC. Then, the solution was cooled to −10 ºC followed by the addition of TBAF (0.50 M THF solution, 1.20 mL) to remove a byproduct,

tetrakis(trimethylsilyl)silane. The resultant solution was stirred for 1 h at the same temperature. After that, the solvent was removed under reduced pressure. K_3PO_4 (191.0 mg, 0.90 mmol, 3.0 equiv), 1-iodo-4-nitrobenzene (149.4 mg, 0.60 mmol, 2.0 equiv), $Pd(PPh_3)_4$ (34.7 mg, 0.03 mmol, 10 mol %), and DMF (1.20 mL) were successively added to the flask. The reaction solution was heated to 90 ºC and stirred overnight. After that, the reaction mixture was cooled to room temperature, and H_2O was added to the mixture, and then extracted with hexane/AcOEt (4:1) three times. The combined organic layer was dried over $MgSO_4$ followed by filtration and evaporation. The crude product was purified by silica-gel column chromatography to give the corresponding coupling product.

4-3. General Procedures for the Stability Evaluation of Silylboranes under air (toluene solution, Figure 2).

$PhMe_2Si$–B(pin) **1a**[4], $(TMS)_3Si$–B(pin) **2a**, $(TMS)_3Si$–B(hg) **2b** or Et_3Si–B(pin) **1b**[5] (0.2 mmol) was placed in a vial with a screw cap containing a teflon-coated rubber septum under air. Then, the reaction vial was connected to a balloon filled with air through a needle. After toluene (1.0 mL) was added to the vial, the mixture was stirred for a certain time. After that, the mixture was analyzed by GLC and ^{1}H-NMR analysis. The yield of the recovered silylborane was determined by GC analysis.

4-4. General Procedures for the Stability Evaluation of Silylboranes under air (neat).

$PhMe_2Si$–B(pin) **1a**[4], $(TMS)_3Si$–B(pin) **2a**, or $(TMS)_3Si$–B(hg) **2b** (0.30 mmol) was placed in a vial. Then, the vial was covered with aluminum foil and was left to stand for a certain time under air. After that, the mixture was analyzed by GLC and ^{1}H-NMR analysis. The yield of the recovered silylborane was determined by GC analysis. Results are presented in Figure S1.

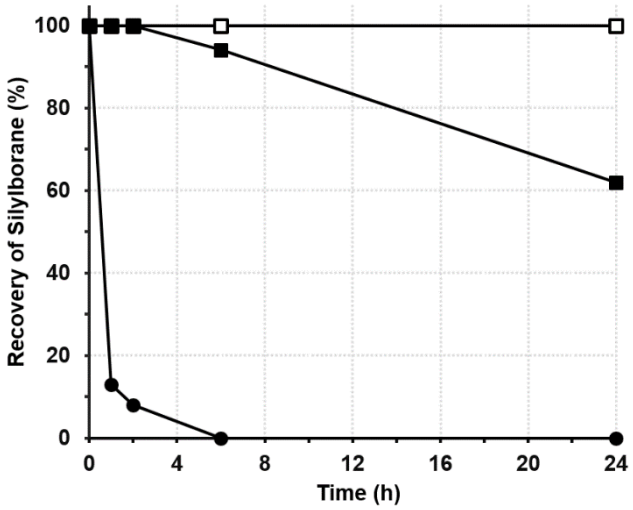


Figure S1. Stability of silylboranes under air (neat): $PhMe_2Si$–B(pin) **1a** (●), $(TMS)_3Si$–B(pin) **2a** (□), $(TMS)_3Si$–B(hg) **2b** (■).

4-5. General Procedures for the Stability Evaluation of Silylboranes on Silica-Gel Column.

$PhMe_2Si$–B(pin) **1a**[4], $(TMS)_3Si$–B(pin) **2a**, or $(TMS)_3Si$–B(hg) **2b** (0.30 mmol) was loaded on a silica gel column (weight 2.5 g, diameter 1.2 cm, length 4.4 cm) swollen with hexane, and held in the column at rt for 1 h. Silylborane in the silica–gel column was eluted by hexane/Et_2O (95:5) as the eluent within 5 min. The yield of the recovered silylborane was determined by GC analysis. Results are presented in Figure S2.

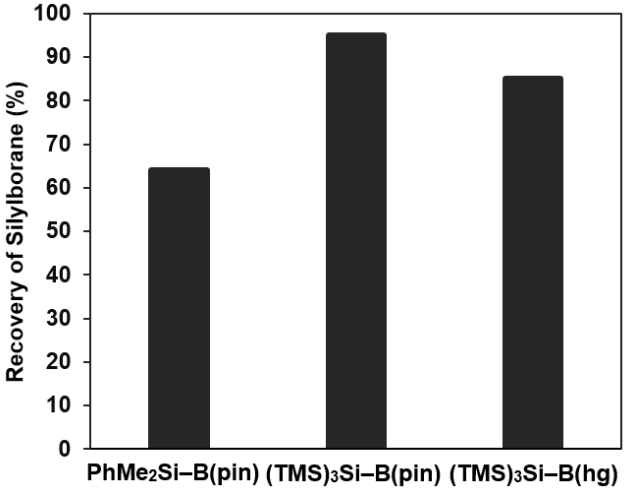
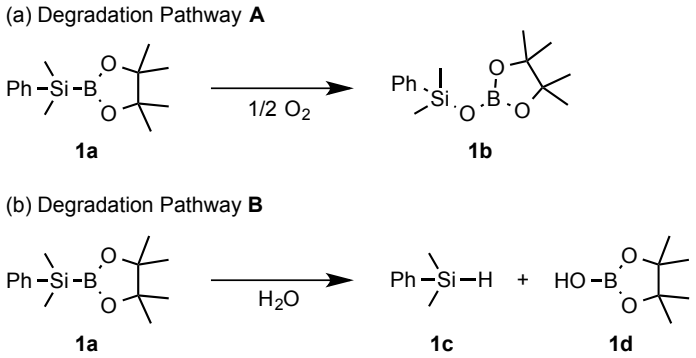


Figure S2. Stability of silylboranes on silica-gel.

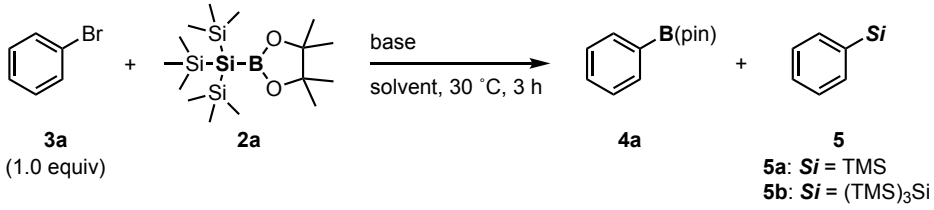
4-6. Consideration of the Analysis of the Chemical Stability of Silylboronate Esters under Air or in Silica-Gel.

In the investigation of air stability of $PhMe_2Si$–B(pin) (**1a**), degradation product only Si-O-B compound **1b** was observed by GC-MS analysis, suggesting that degradation under air proceeded via degradation pathway A (Scheme S1). Meanwhile, $PhMe_2Si$–B(pin) (**1a**) in silica-gel seemed to decompose via degradation pathway A and B since both **1b** and $PhMe_2SiH$ **1c** were observed by GC analyses. $(TMS)_3Si$–O–B(hg) was also observed as the sole degradation product in the investigation of air stability of **2b** based on GC and GC-MS analyses.



Scheme S1. Potential Degradation Pathways of Silylboronate Esters.

5. Optimization of the Reaction Conditions for Borylation of Bromobenzene with Silylborane 2a/Alkoxy Base.[a]

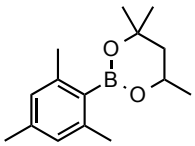


entry	Si–B **2a** (equiv)	base (equiv)	solvent	yield (%)[b]	***B*/*Si*** [c]
1	1.5	KOMe (1.2)	DME	48	90:10
2	1.5	NaOMe (1.2)	DME	32	84:16
3	1.5	K(O-*t*-Bu) (1.2)	DME	21	73:27
4	1.5	Na(O-*t*-Bu) (1.2)	DME	9	65:35
5	2.0	KOMe (2.0)	DME	63	89:11
6	2.0	KOMe (2.0)	THF	38	87:13

[a]Reaction conditions: silylboronate ester **2a** and a base in a solvent was stirred for 10 min at 650 rpm at 30 °C, after which **3a** (0.3 mmol) was added. The resultant mixture was stirred for 1 h at 30 °C. [b]GC yield of **4a** or **4a'**. [c]Ratio of **4a** to **5a** + **5b**.

6. Characterization of Boryl Substitution Products.

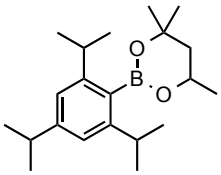
2-Mesityl-4,4,6-trimethyl-1,3,2-dioxaborinane (4b).



The reaction was performed according to the general procedure **A** with **3b** (59.8 mg, 0.30 mmol). After the borylation reaction completed, the reaction mixture was directly filtered through a short silica-gel column with hexane/Et_2O (90:10) as the eluent. After removal of the solvents under reduced pressure, the crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 98.6:1.4) as the eluent to give the corresponding borylated product **4b** (58.6 mg, 0.242 mmol, 81% isolated yield) as a pale yellow liquid.

^1H and ^{13}C NMR spectra were in agreement with the literature.[6] ^1H NMR (401 MHz, $CDCl_3$, δ): 1.32 (d, *J* = 6.7 Hz, 3H), 1.35 (s, 3H), 1.41 (s, 3H), 1.63 (dd, *J* = 11.8, 13.8 Hz, 1H), 1.91 (dd, *J* = 3.0, 13.8 Hz, 1H), 2.22 (s, 3H), 2.31 (s, 6H), 4.38 (ddq, *J* = 2.9, 6.0, 12.0 Hz, 1H), 6.75 (s, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 21.2 (*C*H_3), 21.9 (*C*H_3), 23.2 (*C*H_3), 28.0 (*C*H_3), 31.2 (*C*H_3), 46.3 (*C*H_2), 65.3 (*C*H), 71.4 (*C*), 127.2 (*C*H), 132.0 (brs, *C*–B), 137.8 (*C*), 140.0 (*C*). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{15}H_{23}{}^{10}BO_2$, 245.18274; found, 245.18223.

2-(2,4,6-Triisopropylphenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane (4c).

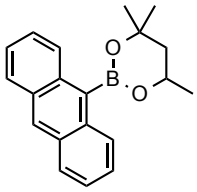


The reaction was performed according to the general procedure **A** with **3c** (85.2 mg, 0.30 mmol). After the borylation reaction completed, the reaction mixture was directly filtered through a short silica-gel column with hexane/Et_2O (85:15) as the eluent. After removal of the solvents under reduced pressure, the crude product was purified by silica-gel column chromatography with hexane/CH_2Cl_2 (100:0 to 75:25) as the eluent, then purified again by silica-gel column chromatography with hexane/Et_2O (100:0 to 99:1) as the eluent to give the corresponding borylated product **4c** (69.5 mg, 0.210 mmol, 70% isolated yield) as a white solid.

^1H NMR (392 MHz, $CDCl_3$, δ): 1.20 (d, *J* = 6.7 Hz, 6H), 1.25 (d, *J* = 6.7 Hz, 6H), 1.27 (d, *J* = 6.7 Hz, 6H), 1.30 (d, *J* = 6.3 Hz, 3H), 1.33 (s, 3H), 1.40 (s, 3H), 1.66 (dd, *J* = 11.8, 13.7 Hz, 1H), 1.90 (dd, *J* = 2.7, 14.1 Hz, 1H), 2.82 (septet, *J* = 6.9 Hz, 1H), 2.91 (septet,

J = 7.0 Hz, 2H), 4.37 (ddq, J = 3.0, 6.0, 12.0 Hz, 1H), 6.91 (s, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 23.2 (*C*H$_3$), 24.1 (*C*H$_3$), 24.2 (*C*H$_3$) 24.5 (*C*H$_3$), 27.8 (*C*H$_3$), 31.3 (*C*H$_3$), 34.3 (*C*H), 34.5 (*C*H), 46.1 (*C*H$_2$), 65.1 (*C*H), 71.3 (*C*), 119.8 (*C*H), 132.2 (brs, *C*–B), 148.8 (*C*), 150.4 (*C*). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{21}H_{35}{}^{10}BO_2$, 329.27664; found, 329.27567.

2-(Anthcen-10-yl)-4,4,6-trimethyl-1,3,2-dioxaborinane (4d).

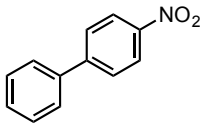


The reaction was performed according to the general procedure **A** with **3d** (77.1 mg, 0.30 mmol). After the borylation reaction completed, the reaction mixture was directly filtered through a short silica-gel column with hexane/Et_2O (90:10) as the eluent. After removal of the solvents under reduced pressure, the crude product was purified by silica-gel column chromatography with hexane/CH_2Cl_2 (100:0 to 75:25) as the eluent, then purified again by silica-gel column chromatography with hexane/Et_2O (99.8:0.2 to 97:3) eluent. Finally, the crude mixture was purified by recrystallization from hexane to give the corresponding borylated product **4d** (64.7 mg, 0.213 mmol, 71% isolated yield) as a white solid.

^{1}H NMR (401 MHz, $CDCl_3$, δ): 1.45 (d, *J* = 6.4 Hz, 3H), 1.49 (s, 3H), 1.63 (s, 3H), 1.95 (dd, *J* = 11.8, 13.8 Hz, 1H), 2.11 (dd, *J* = 2.6, 14.2 Hz, 1H), 4.64 (ddq, *J* = 3.1, 6.1, 12.0 Hz, 1H), 7.38−7.47 (m, 4H), 7.96 (dd, *J* = 2.0, 7.2 Hz, 2H), 8.14 (dd, *J* = 1.6, 4.8 Hz, 2H), 8.40 (s, 1H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 23.2 (*C*H$_3$), 28.3 (*C*H$_3$), 31.2 (*C*H$_3$), 46.4 (*C*H$_2$), 65.9 (*C*H), 72.3 (*C*), 124.7 (*C*H), 125.1 (*C*H), 127.6 (*C*H), 128.4 (*C*H), 128.7 (*C*H), 131.3 (*C*), 134.3 (*C*). The carbon directly attached to the boron atom was not detected, likely due to quadropolar relaxation. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{20}H_{21}O_2{}^{10}B$, 303.16709; found, 303.16739.

7. Characterization of Products from Sequential Procedure of Boryl Substitution and Suzuki-Miyaura Coupling.

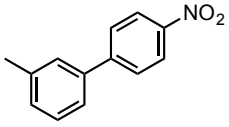
4-Phenylnitrobenzene (6a).



The borylation reaction was performed according to the general procedure **B** with **3a** (47.0 mg, 0.30 mmol). After the borylation reaction completed, the reaction mixture was cooled to −10 ºC followed by the addition of TBAF (0.5 M THF solution, 1.2 mL) to remove a byproduct, tetrakis(trimethylsilyl)silane. The resultant solution was stirred for 1 h at the same temperature. After that, solvent was removed under reduced pressure. K_3PO_4 (191.9 mg, 0.90 mmol, 3.0 equiv), 1-iodo-4-nitrobenzene (149.2 mg, 0.60 mmol, 2.0 equiv), $Pd(PPh_3)_4$ (35.0 mg, 0.03 mmol, 10 mol %), and DMF (1.2 mL) were successively added to the flask. The reaction solution was heated to 100 ºC and stirred overnight. After that, the reaction mixture was cooled to room temperature, and H_2O was added to the mixture, and then extracted with hexane/AcOEt (4:1) three times. The combined organic layer was dried over $MgSO_4$ followed by filtration and evaporation. The crude product was purified by silica-gel column chromatography with hexane/CH_2Cl_2 (100:0 to 75:25) as the eluent to give the corresponding coupling product **6a** (45.6 mg, 0.229 mmol, 76% isolated yield over 2 steps) as a white solid.

^1H and ^{13}C NMR spectra were in agreement with those in the literature.[7] ^1H NMR (392 MHz, $CDCl_3$, δ): 7.42−7.54 (m, 3H), 7.61–7.66 (m, 2H), 7.72–7.78 (m, 2H), 8.28–8.33 (m, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 124.1 (*C*H), 127.3 (*C*H), 127.8 (*C*H), 128.9 (*C*H), 129.1 (*C*H), 138.7 (*C*), 147.0 (*C*), 147.6 (*C*). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{12}H_9{}^{14}N_1O_2$, 199.0633; found, 199.06288.

3-Methyl-4'-nitro-1,1'-biphenyl (6e).

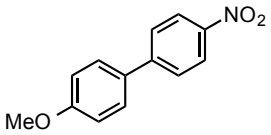


The reaction was performed according to the general procedure **B** with 3-bromotoluene (51.2 mg, 0.30 mmol). After the borylation reaction completed, the reaction mixture was cooled to −10 ºC followed by the addition of TBAF (0.5 M THF solution, 1.2 mL) to remove a byproduct, tetrakis(trimethylsilyl)silane. The resultant solution was stirred for 1 h at the same temperature. After that, solvent was removed under reduced pressure. K_3PO_4 (191.5 mg, 0.90 mmol, 3.0 equiv), 1-iodo-4-nitrobenzene (149.1 mg,

0.60 mmol, 2.0 equiv), $Pd(PPh_3)_4$ (34.8 mg, 0.03 mmol, 10 mol %), and DMF (1.2 mL) were successively added to the flask. The reaction solution was heated to 90 ºC and stirred overnight. After that, the reaction mixture was cooled to room temperature, and H_2O was added to the mixture, and then extracted with hexane/AcOEt (4:1). The combined organic layer was dried over $MgSO_4$ followed by filtration and evaporation. The crude product was purified by silica-gel column chromatography with hexane/CH_2Cl_2 (100:0 to 80:20) as the eluent to give the corresponding coupling product **6e** [54.5 mg, 0.256 mmol, 85% isolated yield over 2 steps] as a white solid.

^1H and ^{13}C NMR spectra were in agreement with the literature.[8] ^1H NMR (392 MHz, $CDCl_3$, δ): 2.45 (s, 3H), 7.27 (d, J = 5.9 Hz, 1H), 7.37−7.44 (m, 3H), 7.71–7.76 (m, 2H), 8.27–8.32 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.5 (*C*H_3), 124.0 (*C*H), 124.5 (*C*H), 127.7 (*C*H), 128.1 (*C*H), 129.0 (*C*H), 129.6 (*C*H), 138.7 (*C*), 138.9 (*C*), 146.9 (*C*), 147.7 (*C*). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{13}H_{11}NO_2$, 213.07898; found, 213.07884.

4-Methoxy-4'-nitro-1,1'-biphenyl (6f).

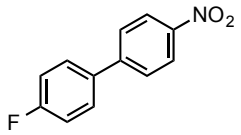


The reaction was performed according to the general procedure **B** with 4-bromoanisole (56.1 mg, 0.30 mmol). After the borylation reaction completed, the reaction mixture was cooled to −10 ºC followed by the addition of TBAF (0.5 M THF solution, 1.2 mL) to remove a byproduct, tetrakis(trimethylsilyl)silane. The resultant solution was stirred for 1 h at the same temperature. After that, solvent was removed under reduced pressure. K_3PO_4 (191.7 mg, 0.90 mmol, 3.0 equiv), 1-iodo-4-nitrobenzene (149.4 mg, 0.60 mmol, 2.0 equiv), $Pd(PPh_3)_4$ (34.7 mg, 0.03 mmol, 10 mol %), and DMF (1.2 mL) were successively added to the flask. The reaction solution was heated to 90 ºC and stirred overnight. After that, the reaction mixture was cooled to room temperature, and H_2O was added to the mixture, and then extracted with hexane/AcOEt (4:1). The combined organic layer was dried over $MgSO_4$ followed by filtration and evaporation. The crude product was purified by silica-gel column chromatography with hexane/CH_2Cl_2 (100:0 to 70:30) as the eluent to give the corresponding coupling product **6f** [51.3 mg, 0.224 mmol, 75% isolated yield over 2 steps] as a yellow solid.

^1H and ^{13}C NMR spectra were in agreement with the literature.[8] ^1H NMR (392 MHz, $CDCl_3$, δ): 3.88 (s, 3H), 7.00–7.05 (m, 2H), 7.56–7.62 (m, 2H), 7.67–7.73 (m, 2H), 8.25–8.30 (m, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 55.4 (*C*H_3), 114.6 (*C*H), 124.1 (*C*H), 127.0 (*C*H), 128.5 (*C*H), 131.0 (*C*), 146.5 (*C*), 147.2 (*C*), 160.4 (*C*). HRMS-EI (*m/z*): $[M]^+$ calcd

for $C_{13}H_{11}NO_3$, 229.07389; found, 229.07349.

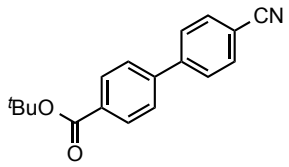
4-Fluoro-4'-nitro-1,1'-biphenyl (6g).



The reaction was performed according to the general procedure **B** with 4-bromofluorobenzene (52.5 mg, 0.30 mmol). After the borylation reaction completed, the reaction mixture was cooled to −10 ºC followed by the addition of TBAF (0.5 M THF solution, 1.2 mL) to remove a byproduct, tetrakis(trimethylsilyl)silane. The resultant solution was stirred for 1 h at the same temperature. After that, solvent was removed under reduced pressure. K_3PO_4 (190.8 mg, 0.90 mmol, 3.0 equiv), 1-iodo-4-nitrobenzene (149.5 mg, 0.60 mmol, 2.0 equiv), $Pd(PPh_3)_4$ (34.6 mg, 0.03 mmol, 10 mol %), and DMF (1.2 mL) were successively added to the flask. The reaction solution was heated to 90 ºC and stirred overnight. After that, the reaction mixture was cooled to room temperature, and H_2O was added to the mixture, and then extracted with hexane/AcOEt (4:1). The combined organic layer was dried over $MgSO_4$ followed by filtration and evaporation. The crude product was purified by silica-gel column chromatography with 0 − 20% hexane/CH_2Cl_2 as the eluent. Then the crude mixture was purified by recrystallization from hexane/CH_2Cl_2 to give the corresponding coupling product **6g** [48.4 mg, 0.223 mmol, 74% isolated yield over 2 steps] as a white solid.

^{1}H and ^{13}C NMR spectra were in agreement with the literature.[8] ^{1}H NMR (401 MHz, $CDCl_3$, δ): 7.16–7.23 (m, 2H), 7.57−7.64 (m, 2H), 7.67–7.73 (m, 2H), 8.28–8.33 (m, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 116.1 (d, *J* = 21.7 Hz, *C*H), 124.1 (*C*H), 127.6 (*C*H), 129.1 (d, *J* = 8.5 Hz, *C*H), 134.8 (d, *J* = 2.8 Hz, *C*), 146.5 (*C*), 147.0 (*C*), 163.3 (d, *J* = 251 Hz, *C*). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{12}H_8{}^{19}FNO_2$, 217.05391; found, 217.05332.

***tert*-Butyl 4-(4-cyanophenyl)benzoate (6h).**

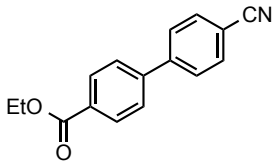


The reaction was performed according to the general procedure **B** with *t*-butyl 4-iodobenzoate (91.3 mg, 0.30 mmol). After the borylation reaction completed, the reaction mixture was cooled to −10 ºC followed by the addition of TBAF (0.5 M THF solution, 1.2 mL) to remove a byproduct, tetrakis(trimethylsilyl)silane. The resultant solution was

stirred for 1 h at the same temperature. After that, solvent was removed under reduced pressure. K_3PO_4 (191.1 mg, 0.90 mmol, 3.0 equiv), 4-iodobenzonitrile (137.4 mg, 0.60 mmol, 2.0 equiv), $Pd(PPh_3)_4$ (34.7 mg, 0.03 mmol, 10 mol %), and DMF (1.2 mL) were successively added to the flask. The reaction solution was heated to 90 ºC and stirred overnight. After that, the reaction mixture was cooled to room temperature, and H_2O was added to the mixture, and then extracted with hexane/AcOEt (4:1). The combined organic layer was dried over $MgSO_4$ followed by filtration and evaporation. The crude product was purified by silica-gel column chromatography with hexane/Et_2O (98:2 to 86:14) as the eluent, then purified again by silica-gel column chromatography with hexane/EtOAc (100:0 to 95:5) as the eluent. Finaly, the crude mixture was purified by recrystallization from hexane/CH_2Cl_2 to give the corresponding coupling product **6h** [47.4 mg, 0.170 mmol, 57% isolated yield over 2 steps] as a white solid.

^1H and ^{13}C NMR spectra were in agreement with the literature.[9] ^1H NMR (392 MHz, $CDCl_3$, δ): 1.62 (s, 9H), 7.61–7.66 (m, 2H), 7.69–7.78 (m, 4H), 8.07–8.12 (m, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 28.1 (*C*H_3), 81.3 (*C*) 111.6 (*C*), 118.7 (*C*), 127.0 (*C*H), 127.8 (*C*H), 130.1 (*C*H), 132.0 (*C*), 132.6 (*C*H), 142.8 (*C*), 144.5 (*C*), 165.2 (*C*). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{18}H_{17}NO_2$, 279.12593; found, 279.12544.

Ethyl 4-(4-cyanophenyl)benzoate (6i).

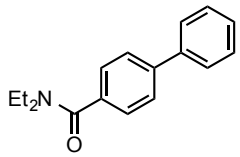


The reaction was performed according to the general procedure **B** with ethyl 4-iodobenzoate (82.4 mg, 0.30 mmol). After the borylation reaction completed, the reaction mixture was cooled to −10 ºC followed by the addition of TBAF (0.5 M THF solution, 1.2 mL) to remove a byproduct, tetrakis(trimethylsilyl)silane. The resultant solution was stirred for 1 h at same temperature. After that, solvent was removed under reduced pressure. K_3PO_4 (190.7 mg, 0.90 mmol, 3.0 equiv), 4-iodobenzonitrile (137.3 mg, 0.60 mmol, 2.0 equiv), $Pd(PPh_3)_4$ (34.8 mg, 0.03 mmol, 10 mol %), and DMF (1.2 mL) were successively added to the flask. The reaction solution was heated to 90 ºC and stirred overnight. After that, the reaction mixture was cooled to room temperature, and H_2O was added to the mixture, and then extracted with hexane/AcOEt (4:1). The combined organic layer was dried over $MgSO_4$ followed by filtration and evaporation. The crude product was purified by silica-gel column chromatography with hexane/Et_2O (97:3 to 85:15) as the eluent to give the corresponding coupling product **6i** [46.9 mg, 0.187 mmol, 62%

isolated yield over 2 steps] as a white solid.

^{1}H and ^{13}C NMR spectra were in agreement with the literature.[10] ^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.43 (t, *J* = 7.1 Hz, 3H), 4.42 (q, *J* = 7.1 Hz, 2H), 7.63–7.68 (m, 2H), 7.70−7.79 (m, 4H), 8.13–8.18 (m, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 14.3 (*C*H_3), 61.2 (*C*H_2) 111.7 (*C*), 118.7 (*C*), 127.1 (*C*H), 127.9 (*C*H), 130.3 (*C*H), 130.5 (*C*), 132.7 (*C*H), 143.3 (*C*), 144.4 (*C*), 166.1 (*C*). HRMS-EI (m/z): $[M]^+$ calcd for $C_{16}H_{13}NO_2$, 251.09463; found, 251.09422.

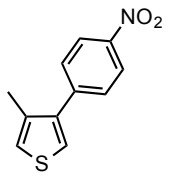
***N,N*-Diethylbiphenyl-4-carboamide (6j).**



The reaction was performed according to the general procedure **B** with 4-bromo-*N,N*-dimethylbenzamide (77.2 mg, 0.30 mmol). After the borylation reaction completed, the reaction mixture was cooled to −10 ºC followed by the addition of TBAF (0.5 M THF solution, 1.2 mL) to remove a byproduct, tetrakis(trimethylsilyl)
silane. The resultant solution was stirred for 1 h at same temperature. After that, solvent was removed under reduced pressure. K_3PO_4 (191.2 mg, 0.90 mmol, 3.0 equiv), iodobenzene (122.9 mg, 0.60 mmol, 2.0 equiv), $Pd(PPh_3)_4$ (34.8 mg, 0.03 mmol, 10 mol %), and DMF (1.2 mL) were successively added to the flask. The reaction solution was heated to 90 ºC and stirred overnight. After that, the reaction mixture was cooled to room temperature, and H_2O was added to the mixture, and then extracted with hexane/AcOEt (4:1). The combined organic layer was dried over $MgSO_4$ followed by filtration and evaporation. The crude product was purified by silica-gel column chromatography with hexane/EtOAc (95:5 to 70:30) as the eluent to give the corresponding coupling product **6j** [46.4 mg, 0.183 mmol, 61% isolated yield over 2 step] as a yellow solid.

^{1}H and ^{13}C NMR spectra were in agreement with the literature.[11] ^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.16 (brs, 3H), 1.26 (brs, 3H), 3.33 (brs, 2H), 3.57 (brs, 2H), 7.35−7.39 (m, 1H), 7.44−7.48 (m, 4H), 7.58−7.63 (m, 4H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 12.9 (*C*H_3), 14.2 (*C*H_3) 39.2 (*C*H_2), 43.2 (*C*H_2), 126.8 (*C*H), 127.0 (*C*H), 127.6 (*C*H), 128.8 (*C*H), 136.0 (*C*), 140.3 (*C*), 141.9 (*C*), 171.0 (*C*). HRMS-EI (*m/z*): $[M+H]^+$ calcd for $C_{17}H_{20}NO$, 254.15394; found, 254.15392.

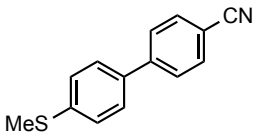
3-Methyl-4-(4-nitrophenyl)thiophene (6k).



The reaction was performed according to the general procedure **B** with 3-bromo-4-methylthiophene (53.4 mg, 0.30 mmol). After the borylation reaction completed, the reaction mixture was cooled to −10 ºC followed by the addition of TBAF (0.5 M THF solution, 1.2 mL) to remove a byproduct, tetrakis(trimethylsilyl)silane. The resultant solution was stirred for 1 h at the same temperature. After that, solvent was removed under reduced pressure. K_3PO_4 (191.6 mg, 0.90 mmol, 3.0 equiv), 1-iodo-4-nitrobenzene (150.0 mg, 0.60 mmol, 2.0 equiv), $Pd(PPh_3)_4$ (34.9 mg, 0.03 mmol, 10 mol %), and DMF (1.2 mL) were successively added to the flask. The reaction solution was heated to 90 ºC and stirred overnight. After that, the reaction mixture was cooled to room temperature, and H_2O was added to the mixture, and then extracted with hexane/AcOEt (4:1). The combined organic layer was dried over $MgSO_4$ followed by filtration and evaporation. The crude product was purified by silica-gel column chromatography with hexane/CH_2Cl_2 (95:5 to 75:25) as the eluent. Then the mixture was purified by recrystallization from CH_2Cl_2/hexane to give the corresponding coupling product **6k** [49.1 mg, 0.224 mmol, 75% isolated yield over 2 steps] as a pale yellow solid.

^{1}H and ^{13}C NMR spectra were in agreement with the literature.[12] ^{1}H NMR (401 MHz, $CDCl_3$, δ): 2.30 (s, 3H), 7.07−7.12 (m, 1H), 7.33 (d, *J* = 3.2 Hz, 1H), 7.54–7.59 (m, 2H), 8.25–8.30 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 15.5 (*C*H$_3$) 123.2 (*C*H), 123.6 (*C*H), 124.8 (*C*H), 129.1 (*C*H), 135.6 (*C*), 140.7 (*C*), 143.6 (*C*), 146.7 (*C*). HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{11}H_{10}NO_2S$, 220.04322; found, 220.04368.

4'-(Methylthio)biphenyl-4-carbonitrile (6l).



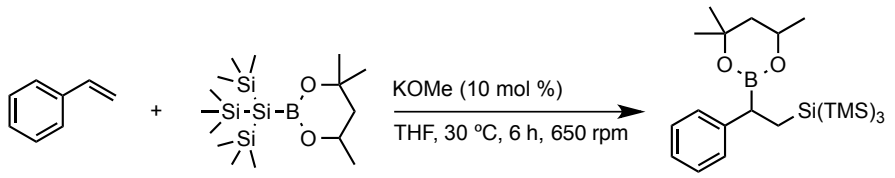
The reaction was performed according to the general procedure **B** with 4-bromothioanisole (61.3 mg, 0.30 mmol). After the borylation reaction completed, the reaction mixture was cooled to −10 ºC followed by the addition of TBAF (0.5 M THF solution, 1.2 mL) to remove a byproduct, tetrakis(trimethylsilyl)silane. The resultant solution was stirred for 1 h at the same temperature. After that, solvent was removed under reduced pressure. K_3PO_4 (191.4 mg, 0.90 mmol, 3.0 equiv), 4-iodobenzonitrile

(137.3 mg, 0.60 mmol, 2.0 equiv), $Pd(PPh_3)_4$ (34.7 mg, 0.03 mmol, 10 mol %), and DMF (1.2 mL) were successively added to the flask. The reaction solution was heated to 90 °C and stirred overnight. After that, the reaction mixture was cooled to room temperature, and H_2O was added to the mixture, and then extracted with hexane/AcOEt (4:1). The combined organic layer was dried over $MgSO_4$ followed by filtration and evaporation. The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 92:8) as the eluent to give the corresponding coupling product **6l** [53.4 mg, 0.237 mmol, 79% isolated yield over 2 steps] as a white solid.

^1H and ^{13}C NMR spectra were in agreement with the literature.[13] ^1H NMR (396 MHz, $CDCl_3$, δ): 2.54 (s, 3H), 7.32–7.37 (m, 2H), 7.50–7.55 (m, 2H), 7.64–7.74 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 15.4 (*C*H_3), 110.6 (*C*), 118.9 (*C*), 126.6 (*C*H), 127.2 (*C*H), 127.4 (*C*H), 132.6 (*C*H), 135.5 (*C*), 139.8 (*C*), 144.8 (*C*). HRMS-EI (*m/z*): $[M]^+$ calcd for $C_{14}H_{11}NS$, 225.06122; found, 225.06121.

8. Silaboration of Styrene with 2a or 2b.

8-1. Procedure for Silaboration of styrene with Siylborane 2b.



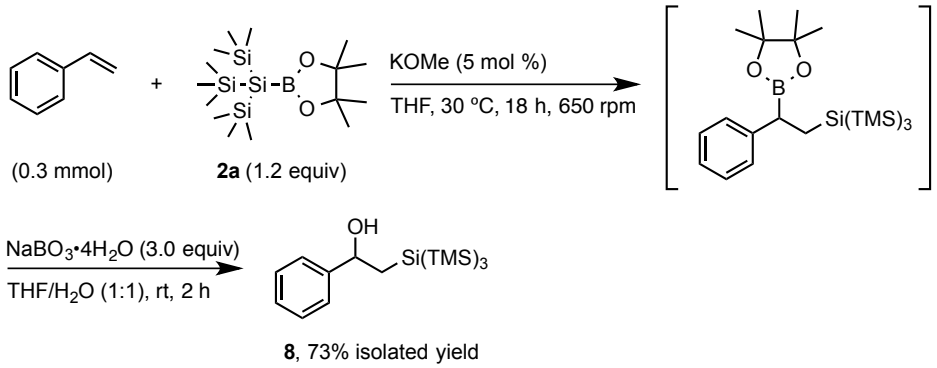
(0.3 mmol) **2b**, (1.2 equiv) **7**, 93% NMR yield (51 % isolated yield)

Tris(trimethylsilyl)silyl boronate ester **2b** (134.5 mg, 0.36 mmol, 1.2 equiv) was placed in a vial with a screw cap containing a teflon-coated rubber septum in the air. After the vial was placed in a glove box, KOMe (2.1 mg, 0.03 mmol, 10 mol %) was placed in the vial and sealed by the screw cap. After the vial was removed from the glove box, connected to the nitrogen/vacuum manifold line, THF (0.6 mL) was added to the vial. The reaction solution was stirred for 10 min at 30 °C, then styrene (31.5 mg, 0.30 mmol) was added dropwise with syringe. After 6 h, the reaction mixture was analyzed by GC to check completeness of the reaction. The reaction mixture was filtrated through filter paper with hexane and concentrated under reduced pressure. The crude product was purified by bulb-to-bulb distillation to give silaborated product **7** (72.8 mg, 0.152 mmol, 51% isolated yield] as a white solid.

^1H NMR (401 MHz, $CDCl_3$, 1:1 diastereomeric mixture, δ): 0.12 (s, 13.5H), 0.14 (s,

13.5H), 0.96 (dd, J = 4.2, 14.2 Hz, 0.5H), 1.02 (dd, J = 5.2, 14.4 Hz, 0.5H), 1.09 (s, 1.5H), 1.15 (s, 1.5H), 1.16 (s, 1.5H), 1.18 (s, 1.5H), 1.19 (s, 1.5H), 1.20 (s, 1.5H), 1.32 (dd, J = 8.0, 11.2 Hz, 0.5H), 1.36 (dd, J = 8.6, 11.8 Hz, 0.5H), 1.55–1.68 (m, 2H), 2.20–2.25 (m, 1H), 4.04 (ddq, J = 3.1, 6.1, 12.0 Hz, 1H), 7.04–7.09 (m, 1H), 7.19–7.21 (m, 1H). ^{13}C NMR (99 MHz, $CDCl_3$, 1:1 diastereomeric mixture, δ): 1.30 (CH_3), 1.32 (CH_3), 9.4 (CH_2), 9.6 (CH_2), 22.9 (CH_3), 23.0 (CH_3), 27.8 (CH_3), 27.9 (CH_3), 31.0 (CH_3), 31.1 (CH_3), 34.7 (brs, *C*–B), 45.6 (CH_2), 45.7 (CH_2), 64.6 (*C*H), 64.7 (*C*H), 70.6 (*C*), 124.4 (*C*H), 124.5 (*C*H), 127.70 (*C*H), 127.77 (*C*H), 127.85 (*C*H), 127.92 (*C*H), 147.9 (*C*), 148.4 (*C*) . HRMS-EI (*m/z*): $[M-CH_3]^+$ calcd for $C_{22}H_{44}{}^{10}BO_2Si_4$, 462.25477; found, 462.25412.

8-2. Procedure for Sequential Silaboration of Styrene with Silylborane 2a and Oxidation of Boryl Group.

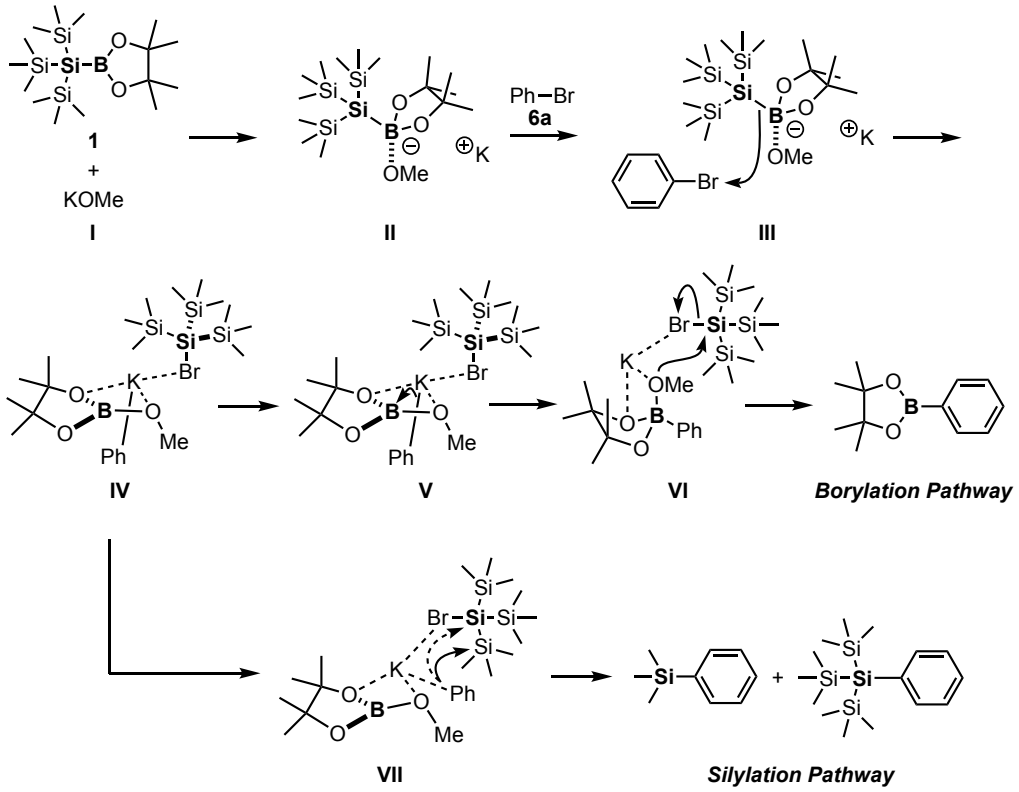


Tris(trimethylsilyl)silyl boronate ester **2a** (134.8 mg, 0.36 mmol, 1.2 equiv) was placed in a vial with a screw cap containing a silicon-coated rubber septum in the air. After the vial was placed in a glove box, KOMe (1.0 mg, 0.015 mmol, 5.0 mol %) was placed in the vial. After the vial was removed from the glove box, THF (0.6 mL) was added to the vial. The reaction solution was stirred for 10 min at 30 °C, then styrene (31.5 mg, 0.30 mmol) was added dropwise with syringe. After 18 h, the reaction mixture was analyzed by GC to check completeness of the reaction. The reaction mixture was filtrated through filter paper with hexane and concentrated under a reduced pressure. The crude mixture was transferred to a 50 mL eggplant flask with a magnetic stirrer bar and the solvent was removed under a reduced pressure. Then, THF (3.0 mL), N_2-bubbled H_2O (3.0 mL), and $NaBO_3{\cdot}4H_2O$ (139.4 mg, 0.90 mmol, 3.0 equiv) were successively added to the flask, and the resultant mixture was stirred for 2 h at room temperature. After that, the reaction mixture was extracted with three times with Et_2O, washed with NaCl saturated aqueous solution, dried over $MgSO_4$, and filtered. The crude mixture was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 98.8:1.2) as the eluent to give the corresponding alcohol **8** (81.0 mg, 0.220 mmol, 73% isolated yield

over 2 steps) as a white solid.

^{1}H NMR (401 MHz, $CDCl_3$, δ): 0.18 (s, 27H), 1.33 (d, J = 4.8 Hz, 1H), 1.34 (d, J = 9.6 Hz, 1H), 1.69 (brs, 1H), 4.74 (dd, J = 5.0, 8.6 Hz, 1H), 7.22−7.28 (m, 1H), 7.33−7.36 (m, 4H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 1.2 (CH_3), 20.3 (CH_2) 74.4 (*C*H), 125.3 (*C*H), 127.4 (*C*H), 128.6 (*C*H), 147.8 (*C*). HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{17}H_{36}ONaSi_4$, 391.17354; found, 391.17361.

9. Hypothetical Reaction Mechanism of Boryl Substitution.



Scheme S2. Proposed Reaction Mechanism for Boryl Substitution of Aryl Halide with Silylborane **2a**.[14]

10. Single Crystal Structure Analysis of 2a.

Single crystal X-ray structural analyses of **2a** were carried out on a Rigaku R-AXIS RAPID diffractometer using graphite monochromated Mo-K□ radiation (Figure S3, Table S1). The structure was solved by direct methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure crystallographic software package except for refinement, which was performed using SHELXL-2014.[15]

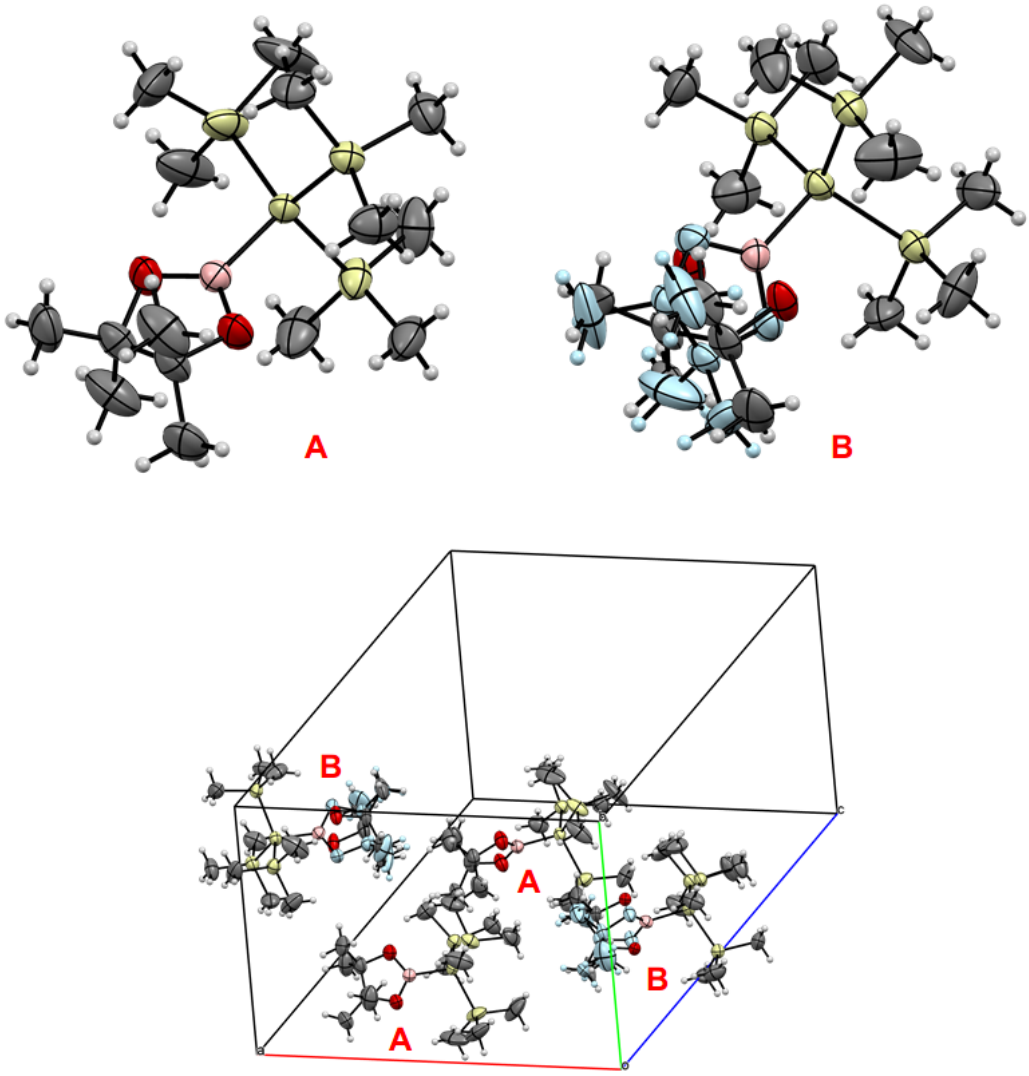


Figure S3. Single-crystal structure of **2a**: The single crystal of **2a** contains two crystallographically independent molecules (**A** and **B**), where **B** molecules exhibit rotational disorder at pinacol borane moiety. One set of a disordered segment is colored with light-blue.

Table S1. Summary of X-ray crystallographic data for **2a**.

Compound	**2a**
CCDC Name	1540097
Empirical Formula	$C_{15}H_{39}BO_2Si_4$
Formula Weight	374.62
Crystal System	monoclinic
Crystal Size / mm	0.550 × 0.491 × 0.304
a / Å	16.806(16)
b / Å	13.2018(13)
c / Å	23.003(2)
α / °	90
β / °	103.707(3)
γ / °	90
V / Å^3	4958.7(8)
Space Group	$P2_1/c$ (#14)
Z value	8
D_{calc} / g·cm^{-3}	1.004
Temperature / K	123
$2\theta_{max}$ / °	50.1
μ (MoK$_\alpha$) / cm^{-1}	2.431
No. of Reflections Measured	Total: 55313 Unique : 8761 (R_{int} = 0.0852)
Residuals: R_1 (I > 2.00σ (I)) / %	8.34
Residuals: wR_2 (All reflections) / %	21.36
Goodness of Fit (GOF)	1.076
Maximum peak in Final Diff. Map / Å^3	0.39 e$^-$
Minimum peak in Final Diff. Map / Å^3	–0.78 e$^-$

10. Reference of Experimental Section

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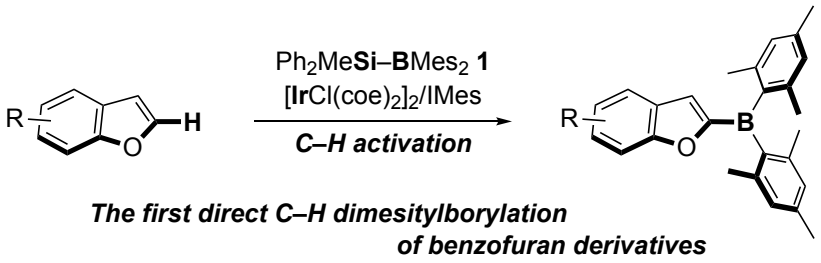
Chapter 2.

Iridium-Catalyzed C–H Dimesitylborylation of Benzofuran Derivatives with Silyldimesitylborane

Abstract

The direct dimesitylborylation of benzofuran derivatives via the iridium-catalyzed C–H activation has been achieved. The C–H dimesitylborylation of benzofuran derivatives in the presence of iridium(I)/*N*-heterocyclic carbene (NHC) complex catalyst and $Ph_2MeSi–BMes_2$ furnished the corresponding dimesitylborylation products in good to high yield with excellent regioselectivity. Our method provides a straightforward route to construct a donor-(π-spacer)-acceptor (D-π-A) system, which often exhibits intriguing solvatochromic luminescence properties.

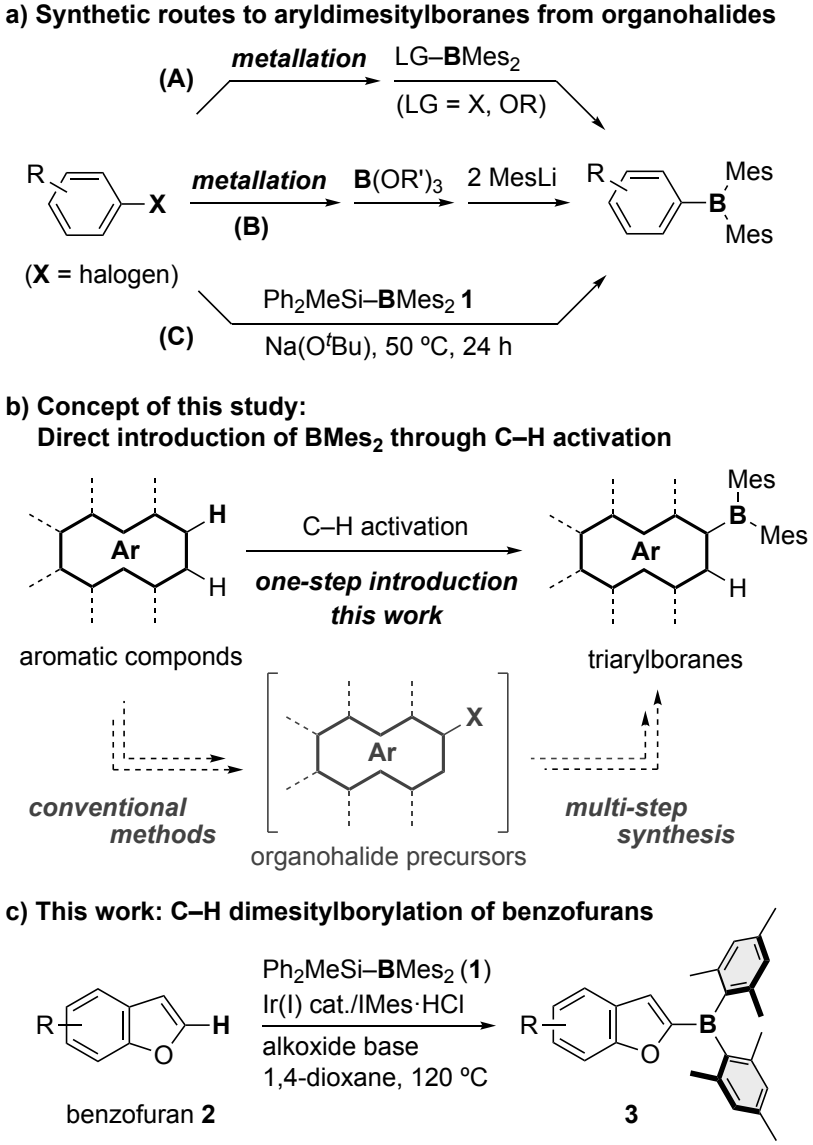


The first direct C–H dimesitylborylation of benzofuran derivatives

Introduction

Boron-containing π-conjugated compounds such as triarylboranes have received a great deal of attention as important materials due to their unique photophysical and electronic properties. These properties arise from the pπ-π* conjugation between the vacant p-orbital of the boron atom and the π*-orbital of the connected carbon-based π-conjugated moieties.[1] A dimesitylboryl ($BMes_2$) group is frequently used in this context because of its high π-electron-accepting abilities and its desirable stability in air. However, methods to introduce $BMes_2$ groups into aromatic compounds are still highly limited. A conventional method for the transfer of $BMes_2$ groups is the nucleophilic substitution of $BMes_2$ electrophiles ($Mes_2B–X$; X = halogen or OR) with organometallic reagents (Ar–M; M = Li, Mg) generated from organic halides via halogen-metal exchange [Scheme 1a, (A)].[2,3] $BMes_2$ groups can also be introduced into aromatic compounds by the reaction of aryl boronic acid esters with MesLi [Scheme 1a, (B)].[2,4] Recently, our group reported the direct dimesitylborylation of aryl halides with silyldimesitylborane $Ph_2MeSi–BMes_2$ and Na(O^{t}Bu), i.e., **B**ase-mediated **B**orylation with **S**ilylborane (BBS reaction) [Scheme 1a, (C)].[5,6] Although the corresponding dimesitylborylation products are obtained in good yield using both methods, a stoichiometric amount of bases or organometallic reagents is needed. Furthermore, in both reactions, the availability of the $BMes_2$ compounds significantly depends on the availability of the preceding organohalide

precursors, which are often difficult to access, especially in case of highly functionalized organic halides. Therefore, more efficient and direct methods are required to improve the availability of triarylborane compounds for the introduction into organic compounds.



Scheme 1. a) Synthetic Routes to Aryldimesitylboranes from Organohalides. b) Schematic Illustration of the Concept of This Study. c) This Work: Direct Dimesitylborylation of Benzofurans via an Iridium-Catalyzed C–H Activation.

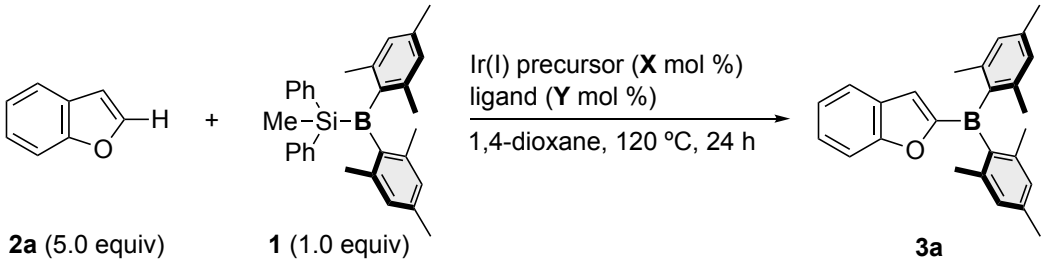
Iridium-catalyzed aromatic C–H borylations[7,8] using diboron or silylborane compounds[9] is a powerful method for the synthesis of arylboron compounds, and have been often used for the synthesis of organic materials,[10] natural products,[11] and fine chemicals.[11] This method allows us the direct borylation of C–H bonds in aromatic

compounds without requiring any halogenated intermediates and providing the corresponding arylboronates in high yield with excellent regioselectivity. Therefore, the direct introduction of $BMes_2$ into aromatic compounds via iridium-catalyzed C–H borylations may potentially provide a novel method for the synthesis of boron-containing organic compounds with a triarylborane structure [Scheme 1b]. This method thus enables a late-stage introduction of the $BMes_2$ group,[12] which would be advantageous especially for the compilation of compound libraries with complicated structures for screening purposes. However, no previous examples of the synthesis of triarylboranes with this strategy have been reported yet. Most examples of C–H borylations introduce boronate groups [$B(OR)_2$] such as B(pin), and only one example for the introduction of $B(9\text{-BBN})_2$ (9-BBN: 9-borabicyclo[3.3.1]nonan) has been reported.[13] Herein, the author disclosed the first example of the direct introduction of $BMes_2$ into benzofuran derivatives (**2**) via an iridium-catalyzed C–H activation using $Ph_2MeSi–BMes_2$ (**1**)[14] as the borylation reagent [Scheme 1c]. The C–H dimesitylborylation proceeds effectively in the presence of $[Ir(Cl)(coe)_2]_2$/IMes (IMes: 1,3-dimesitylimidazol-2-ylidene; coe: cyclooctene) to produce the corresponding dimesitylborylation products in good to high yield with excellent regioselectivity. Some of the dimesitylborylation products obtained showed a pronounced solvatochromic luminescence properties due to their donor-(π-spacer)-acceptor (D-π-A) structure.

Results and Discussion

The author initially investigated the optimum reaction conditions for the iridium-catalyzed C–H dimesitylborylation of benzofuran (**2a**) with **1** (Table 1),[15] beginning by screening a series of different ligands (Table 1; entries 1–6). For that purpose, The reactions of benzofuran **2a** were performed with Ph_2MeSi–$BMes_2$ **1** in the presence of $[Ir(OMe)(cod)]_2$ (2.5 mol %; cod: 1,5-cyclooctadiene) and a series of different ligands in 1,4-dioxane at 120 ºC. The use of IMes·HCl/K(O^{t}Bu) (10 mol %) provided **3a** in 48% yield (Table 1; entry 1). The silylated product was also observed as a side product. The presence of K(O^{t}Bu) was needed to generate the Ir–NHC complex catalyst *in situ*. 4,4-Di-*tert*-butyl-2,2'-bipyridine (dtbpy; 5.0 mol %) and 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4phen; 5.0 mol %), which are effective ligands for typical Ir-catalyzed C–H borylation reactions, did not facilitate the dimesitylborylation of the C–H bonds of **2a** (entries 2 and 3). Using monodentate (10 mol %) or bidentate (5.0 mol %) phosphines such as triphenylphosphine (PPh_3), tri-*tert*-butylphosphine (P^{t}Bu$_3$) and 1,2-bis(dicyclohexylphosphino)ethane (dcpe) did not furnish **3a** efficiently (entries 4–6; 0–13%). These results suggest that the presence of NHC ligands is crucial to promote the dimesitylborylation of **2a** efficiently. Therefore, the author further investigated various Ir(I) precursors and NHC ligands (Table 1; entries 7–15). In the presence of $[Ir(Cl)(coe)_2]_2$ (2.5 mol %) and IMes·HCl/K(O*t*Bu) (10 mol %), **3a** was obtained in 69% yield (entry 7). The use of $[Ir(Cl)(cod)]_2$ (2.5 mol %) resulted in a slightly lower yield of **3a** (58% yield; entry 8). Using Crabtree's catalyst $[Ir(cod)(Py)(PCy_3)][PF_6]$ (5.0 mol %; Py: pyridine) produced **3a** in merely 5% yield (entry 9). The cationic iridium catalyst $[Ir(cod)_2][BAr^F{}_4]$ [5.0 mol %; Ar^F: 3,5-bis(trifluoromethyl)phenyl] exhibited good reactivity (65% yield; entry 10), similar to that of $[Ir(Cl)(coe)_2]_2$. Diminishing the catalyst loading {$[Ir(Cl)(coe)_2]_2$ (2.5 mol %) and IMes·HCl/K(O*t*Bu) (5.0 mol %)} also provided **3a** in high yield (75% ^{1}H NMR yield; 59% isolated yield; entry 11). The use of other NHC ligands such as SIMes, IPr, or ICy decreased the yield of **3a** (SIMes: 64%; IPr: 10%; ICy: 11%; entries 12–14). [(IMes)IrCl(cod)] prepared in advance afforded **3a** in high yield (70% yield; entry 15). **3a** was not obtained in the absence of IMes (entry 16). Moreover, using H–$BMes_2$ instead of Ph_2MeSi–$BMes_2$ did not produce any **3a** (Table S5).[16] Therefore, the optimal conditions to obtain a maximum of **3a** involve $[Ir(Cl)(coe)_2]_2$ (2.5 mol %) and IMes (5.0 mol %).[17] Under these conditions, the silylation side product was formed in 29% yield.

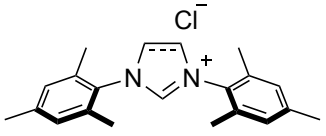
Table 1. Optimization of the Reaction Conditions for the Iridium-Catalyzed C–H Borylation of Benzofuran (**2a**) Using **1**.[a]



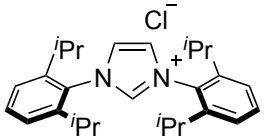
2a (5.0 equiv) **1** (1.0 equiv) **3a**

entry	Ir(I) precursor (mol %)	ligand [Y mol %]	yield (%)[b]
1	$[Ir(OMe)(cod)]_2$ (2.5)	IMes•HCl (10)[c]	48
2	$[Ir(OMe)(cod)]_2$ (2.5)	dtbpy (5.0)	0
3	$[Ir(OMe)(cod)]_2$ (2.5)	Me_4phen (5.0)	0
4	$[Ir(OMe)(cod)]_2$ (2.5)	PPh_3 (10)	0
5	$[Ir(OMe)(cod)]_2$ (2.5)	P^tBu_3 (10)	13
6	$[Ir(OMe)(cod)]_2$ (2.5)	dcpe (5.0)	0
7	$[IrCl(coe)_2]_2$ (2.5)	IMes•HCl (10)[c]	69
8	$[IrCl(cod)]_2$ (2.5)	IMes•HCl (10)[c]	58
9	$[Ir(cod)(Py)PCy_3][PF_6]$ (5.0)	IMes•HCl (10)[c]	5
10	$[Ir(cod)_2][BAr^F{}_4]$ (5.0)	IMes•HCl (10)[c]	65
11	$[IrCl(coe)_2]_2$ (2.5)	IMes•HCl (10)[c]	75 (59)
12	$[IrCl(coe)_2]_2$ (2.5)	SIMes•HCl (10)[c]	64
13	$[IrCl(coe)_2]_2$ (2.5)	IPr•HCl (10)[c]	10
14	$[IrCl(coe)_2]_2$ (2.5)	ICy•HCl (10)[c]	11
15	[(IMes)IrCl(cod)] (5.0)	–	70
16	$[IrCl(coe)_2]_2$ (2.5)	–	0

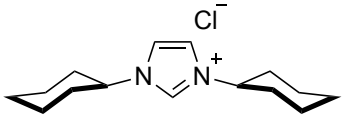
[a] Reaction conditions: **1** (0.10 mmol), **2a** (0.50 mmol), Ir(I) precursor (0.0025 or 0.005 mmol) and ligand (0.005 or 0.01 mmol) in 1,4-dioxane (0.5 mL) at 120 °C for 24 h. [b] ^{1}H-NMR yield of **3a**. 1,1,2,2-tetrachloroethane was used as an internal standard. The isolated yield of **3a** is shown in the parentheses. [c] K(O*t*Bu) (Y mol %) was added to the reaciton mixture.



IMes·HCl, SIMes·HCl



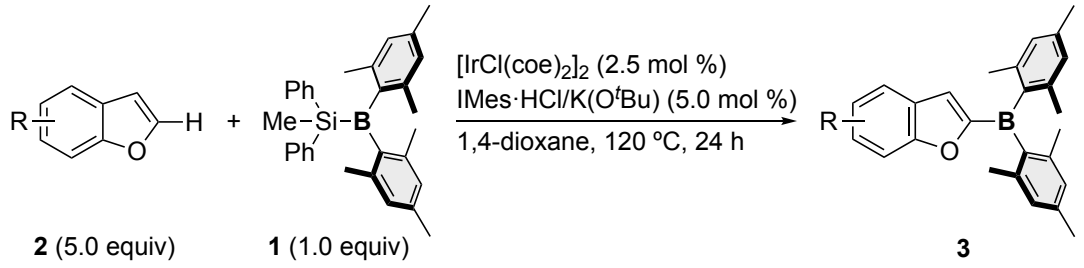
IPr·HCl



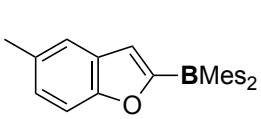
ICy·HCl

With the optimized conditions in hand, the author proceeded to examine the substrate scope for this C–H dimesitylborylation (Table 2).[18] 5-Methylbenzofuran (**2b**) reacted with **1** to produce the corresponding borylation product (**3b**) in high yield (73%). Substrates bearing two methyl groups such as 5,7-dimethyl- (**2c**), 4,6-dimethyl- (**2d**), and 4,7-dimethylbenzofuran (**2e**) afforded **3c**, **3d**, and **3e**, respectively, in good yield (**3c**: 77%; **3d**: 69%; **3e**: 62%). The reaction of 5-chlorobenzofuran (**2f**) proceeded effectively without any side reactions involving the C–Cl bond, even though some transition-metal catalysts exhibit high reactivity for the cleavage of such C–Cl bonds. Unfortunately, furan substrate **2g** did not readily engage in the C–H dimesitylborylation.[19] The optimized catalyst system also worked well for benzofuran derivatives bearing aromatic rings at the 5-position (**2h**–**2k**) to give the corresponding products in good yield (**3h**: 62%; **3i**: 68%; **3j**: 67%; **3k**: 58%). The reaction of 9-carbazolyl-substituted benzofuran **2l** produced **3l** in good yield (66%). The molecular structure of **3l** was confirmed by a single-crystal x-ray diffraction analysis (Figure 1). These results indicate high reactivity of this C–H dimesitylborylation only toward benzofuran derivatives. This unique reactivity allowed the site-selective C–H dimesitylborylation of the benzofuran moiety in **2m**, which bears an additional furan substituent (Scheme 2).

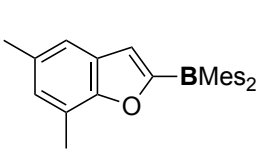
Table 2. Substrate Scope for the Ir-catalyzed C–H Dimesitylborylation of Substituted Benzofuran Derivatives.[a]



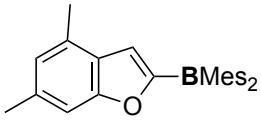
2 (5.0 equiv) **1** (1.0 equiv) **3**



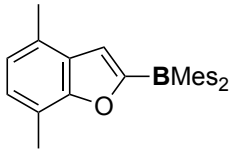
3b, 73 (60)%



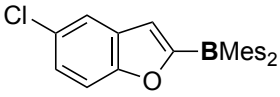
3c, 77 (60)%



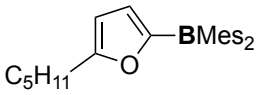
3d, 69 (64)%



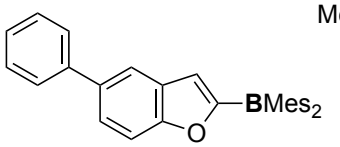
3e, 62 (52)%



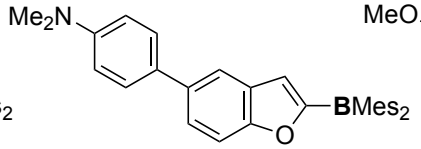
3f, 74 (42)%



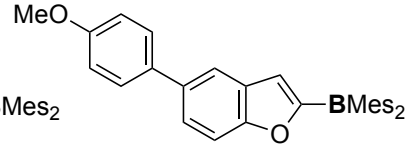
3g, 16%[b]



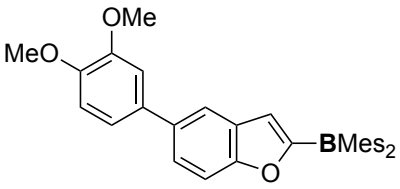
3h, 62 (40)%



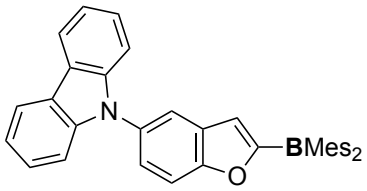
3i, 68 (60)%



3j, 67 (57)%



3k, 58 (53)%



3l, 66 (59)%

[a] Reaction conditions: **1** (0.10 mmol), **2** (0.50 mmol), $[IrCl(coe)_2]_2$ (0.0025 mmol), IMes·HCl/KO*t*Bu (0.01 mmol) in 1,4-dioxane (0.5 mL) at 120 °C. The yield of the products was determined by ^{1}H-NMR analysis using 1,1,2,2-tetrachloroethane as the internal standard. Isolated product yield values are shown in the parentheses. [b] Identified based on ^{1}H-NMR spectroscopy and GC-MS spectrometry.

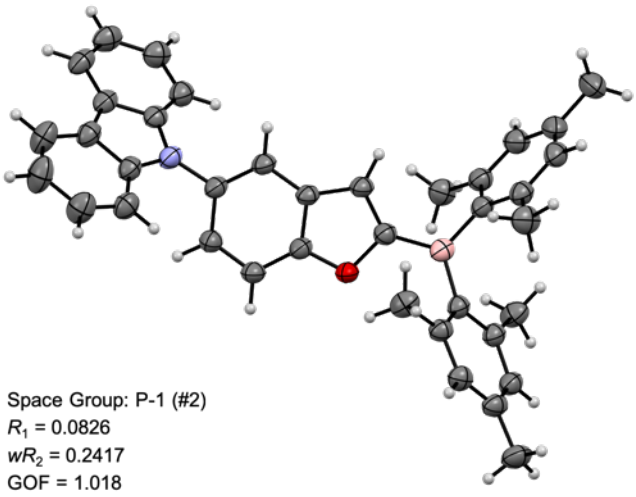
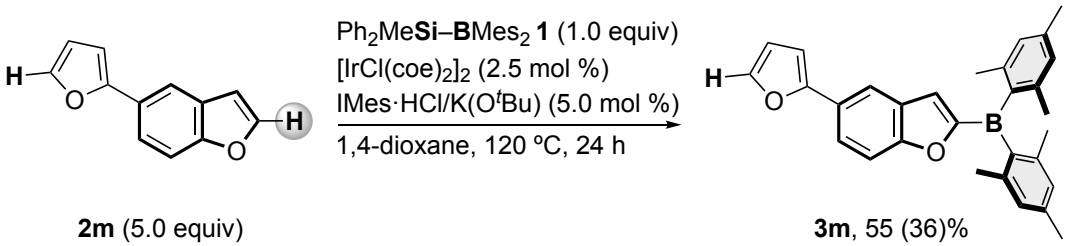


Figure 1. Crystal Structure of **3l** with Thermal Ellipsoids at 50% Probability. Color Code: Grey: Carbon; White: Hydrogen; Pink: Boron; Red: Oxygen; Pale Purple: Nitrogen.



Scheme 2. Site-Selective C–H Dimesitylborylation of Benzofuran **2m**, Which Bears an Additional Furan Substituent.

Dimesitylborylation product **3i** showed pronounced solvatochromic luminescence properties due to the D-π-A structure, which includes the benzofuran moiety and the phenyl spacer (Figure 2). The absorption and emission spectra of **3i** were measured in various solvents. Two absorption maxima (λ_{abs} = 290 and 350 nm) were observed that were relatively unaffected by the solvent polarity (Figure S1). Yet, the author obtained seven different emission spectra for **3i** (λ_{ex} = 365 nm) in seven different solvents (hexane, toluene, Et_2O, CH_2Cl_2, THF, acetone and CH_3CN) (Figure 2). All spectra of **3i** showed a broad band with a distinct emission maximum ($\lambda_{em, max}$) ranging from 455 nm to 722 nm (hexane: $\lambda_{em, max}$ = 455 nm, Φ_{em} = 29.4%; toluene: $\lambda_{em, max}$ = 504 nm, Φ_{em} = 43.5%; Et_2O: $\lambda_{em, max}$ = 536 nm, Φ_{em} = 43.5%; CH_2Cl_2: $\lambda_{em, max}$ = 587 nm, Φ_{em} = 59.4%; THF: $\lambda_{em, max}$ = 602 nm, Φ_{em} = 50.0%; acetone: $\lambda_{em, max}$ = 667 nm, Φ_{em} = 29.4%; CH_3CN: $\lambda_{em, max}$ = 722

nm, Φ_{em} = 43.5%), which demonstrates that $\lambda_{em,\ max}$ changes with the solvent polarity. These results indicate that **3i** shows properties that are characteristic for push-pull solvatoluminescent dyes. Thus, the Ir-catalyzed C–H dimesitylborylation of substituted benzofuran derivatives described in this article enables the rapid construction of the D-π-A systems found in such dyes.

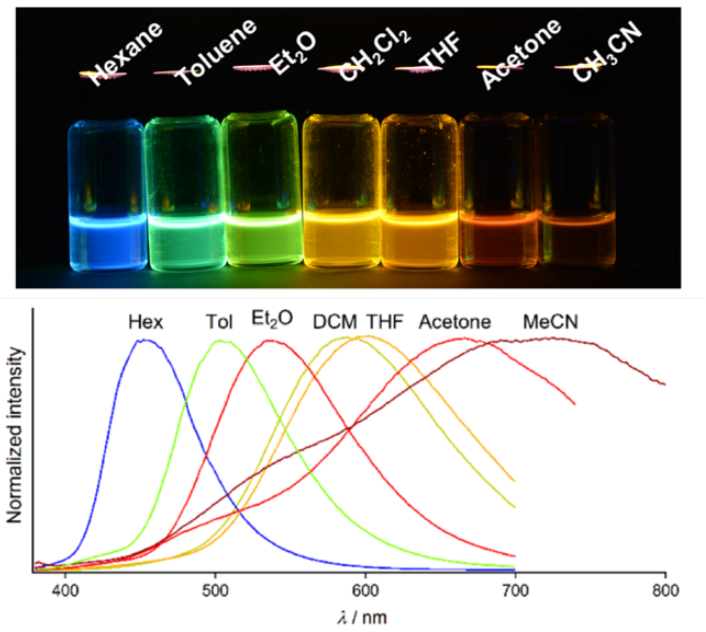
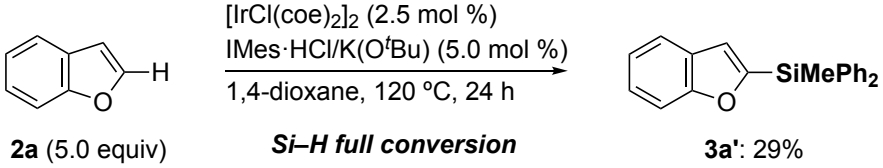


Figure 2. Photograph and Emission Spectra of **3i** in Various Solvents under Irradiation from UV light (λ_{ex} = 365 nm; 10 μM).

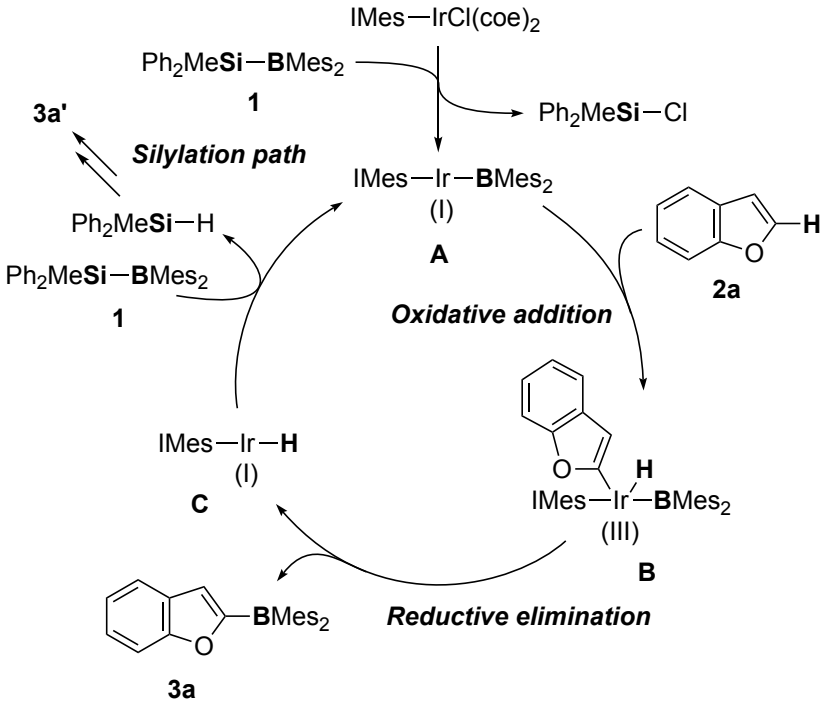
Silylation products were observed as the main side products of this dimesitylborylation reactions. To gain insight into the mechanism of their generation, a control experiment was performed (Scheme 3). The reaction between **2a** and Ph_2MeSi–H instead of Ph_2MeSi–$BMes_2$ led to the formation of the silylation product **3a'** in 29% yield.[20–22] This result suggests that Ph_2MeSi–H, which would be produced as a by-product in the borylation reaction, reacts with **2a** to give the silylation side product.



2a (5.0 equiv) ***Si–H full conversion*** **3a'**: 29%

Scheme 3. Control Experiment Using $PhMe_2Si$–H instead of **1**.

Based on previous mechanistic studies[9, 23] for the Ir-catalyzed C–H borylation of aromatic compounds with bis(pinacolate)diboron and silylborane, and considering the results of my control experiments, the author would like to propose a plausible reaction mechanism for this C–H dimesitylborylation (Scheme 4). The NHC-Ir(I) complex formed *in situ* could initially react with $Ph_2MeSi–BMes_2$ (**1**) to produce monoboryliridium(I) complex **A** as an active catalyst species. The subsequent oxidative addition of a C–H bond at the 2-position in **2a** to complex **A** would produce Ir(III) complex **B**. This regioselectivity could be assigned to the high acidity of the C–H bond in the benzofuran ring.[24] Reductive elimination of the desired dimesitylborylation product (**3a**) would lead to the generation of Ir(I)-hydride complex **C**. Finally, the oxidative addition of **1** to complex **C**, followed by a reductive elimination of $Ph_2MeSi–H$, would regenerate Ir(I) complex **A**. Additionally, $Ph_2MeSi–H$ would rapidly engage in a side reaction of **2a** to provide the silylated benzofuran **3a'** via a C–H activation process. Moreover, it seems feasible to assume that the Ir(III) complexes $[Ir(B)_n(Si)_{3–n}]$ (n = 1 or 2) are formed *in situ* and act as actual active catalytic species.[9, 23] At present, the author speculates that the formation of the monoboryliridium(I) complex **A** would be favored relative to that of $[Ir(B)_n(Si)_{3–n}]$ (n = 1 or 2) due to the presence of bulky boryl and silyl groups.[25]



Scheme 4. Possible Reaction Mechanism for the Ir(I)-Catalyzed C–H Dimesitylborylation of Benzofuran Derivatives.

Summary

In summary, the author has developed a novel method for the C–H dimesitylborylation of benzofuran derivatives, which is the first example of a direct dimesitylborylation of aromatic compounds through C–H activation using a catalyst system based on an Iridium(I)/*N*-heterocyclic carbene complex. These reactions produce the corresponding dimesitylborylation products in good to high yield with excellent regioselectivity. This method thus allows the one-step introduction of luminescent functionality into non-luminescent heteroarenes at a late stage in their synthesis, which should considerably promote the synthesis of novel organic materials. Detailed mechanistic studies and efforts to expand the substrate scope are currently in progress in the author's laboratory.

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15) For further optimizations of the reaction conditions, see the supporting information.
16) Preliminary experiments for the reaction using H–$BMes_2$ instead of Ph_2MeSi–$BMes_2$ were also conducted. For details, see the supporting information (Table S5).
17) For examples of aromatic C–H borylation reactions using Ir/NHC catalyst systems, see: a) G. D. Rey, C. F. Rentzsch, D. V. Preysing, T. Scherg, M. Mühlhofer, E. Herdtweck, W. A. Herrmann, *J. Organomet. Chem.* **2006**, *691*, 5725; b) C. F. Rentzsch, E. Tosh, W. A. Herrmann, F. E. Kühn, *Green Chem.* **2009**, *11*, 1610.
18) Reactions of heteroaromatic substrates other than benzofuran and furan were also investigated. However, these compounds did not effectively engage in this reaction. For details, see the supporting information.
19) The presence of the borylation product in the reaction mixture was ascertained based on a combined GC, GC-MS, and ^{1}H NMR analysis.
20) Other silicon-derived by-products such as Ph_2MeSi–$SiMePh_2$, Ph_2MeSi–O–$SiMePh_2$, and Ph_2MeSi–OH were not observed by GC and GC-MS in the reaction mixture. For details, see the supporting information.
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Experimental

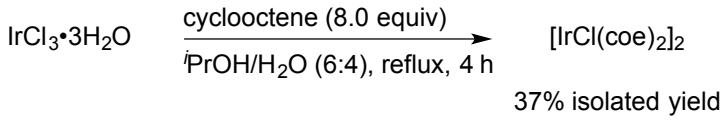
Table of Contents

1. General and Materials.

All reactions were performed in oven-dried glassware using conventional Schlenk techniques under a static pressure of nitrogen or argon. Materials were obtained from commercial suppliers and purified by standard procedures unless otherwise noted. 2,3-Benzofuran (>99.0%) was purchased from Tokyo Chemical Industry Co. (TCI) and distilled under reduced pressure prior to use. Dry solvents for the reaction were also purchased from commercial suppliers, degassed via three freeze-pump-thaw cycles, and further dried over molecular sieves (MS4A) prior to use. K(O-*t*-Bu) (>97.0%) purchased from Tokyo Chemical Industry Co. (TCI) were used as received. Silica Gel 60 N (40–100 μm, spherical, neutral) purchased from Kanto Chemical Co. was used as received. Silyldimesitylborane $Ph_2MeSi–BMes_2$ **1** was synthesized according to the literature procedures[1]. NMR spectra were recorded on JEOL JNM-ECX400P and ECS-400 spectrometers (^{1}H: 400 MHz, ^{13}C: 100 MHz, and ^{11}B: 127 MHz). Tetramethylsilane (δ = 0.00 ppm for ^{1}H-NMR) and $CDCl_3$ (δ = 77.0 ppm for ^{13}C-NMR) were employed as external standards, respectively. $BF_3·Et_2O$ was used as an external standard for ^{11}B NMR analysis. Multiplicity was reported as follows: s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet. 1,1,2,2-Tetrachloroethane was used as an internal standard for determining NMR yield. NMR yield was determined by quantitative ^{1}H-NMR analysis of the crude reaction mixture. GLC analyses were conducted with a Shimadzu GC-2014 or GC-2025 equipped with ULBON HR-1 glass capillary column (Shinwa Chemical Industries) and a FID detector. Recycle preparative gel chromatography (GPC) was conducted with JAILC-9101 using $CHCl_3$ as an eluent.

Emission spectra were recorded on Hitachi F-7000 spectrometer. Emission quantum yields were recorded on a Hamamatsu Quantaurus-QY spectrometer with an integrating sphere. Single crystal X-ray structural analyses were carried out on a Rigaku R-AXIS RAPID diffractometer using graphite monochromated Mo-K_α radiation. The structure was solved by direct methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure crystallographic software package except for refinement, which was performed using SHELXL program. High-resolution mass spectra were recorded at the Global Facility Center for Instrumental Analysis, Hokkaido University.

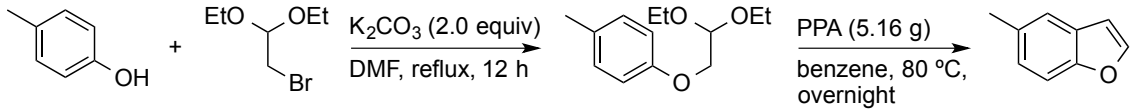
2. Preparation of Iridium (I) Precursor $[IrCl(coe)_2]_2$.[2]



Chlorobis(cyclooctene)iridium (I) dimer was prepared according to literature procedures[2]. A oven-dried, two-necked round-bottomed flask equipped with a condenser, an inlet adapter with a three-way stopcock and a Teflon®-coated magnetic stirrer bar was charged with $IrCl_3$•$3H_2O$ (528 mg, 1.50 mmol), then evacuated and refilled with nitrogen three times. The mixed solvents of ^{i}PrOH (5.7 mL) and water (3.3 mL), which were degassed by N_2 bubbling, were added to the flask via a syringe. Then, cyclooctene (coe) (1.32 g, 1.56 mL, 12.0 mmol, 8.0 equiv) was added to the flask and the resulting mixture was heated to 100 °C (reflux). After the reaction mixture was stirred at 4 h under reflux, the mixture was cooled to room temperature. The reaction mixture was cooled to 0 °C, then the yellow-orange solid was precipitated. The solvents were removed from the flask via a syringe and the precipitate was dried under reduced pressure to afford the desired iridium complex [500 mg, 0.56 mmol, 37% isolated yield] as a yellow-orange solid.

3. Preparation of Starting Materials.

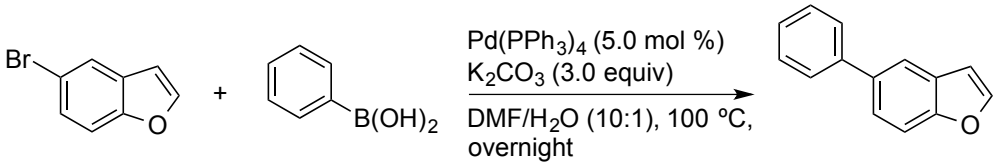
3-1. Preparation of 5-Methylbenzofuran (2b): Representative Procedures for Preparation of 2b–2f, S2; Procedure A[3].



A 100 mL, two-necked round-bottomed flask equipped with a condenser, an inlet adapter with a three-way stopcock and a Teflon®-coated magnetic stirrer bar was charged with 4-methylphenol (1.62 g, 15.0 mmol), bromoacetaldehyde diethyl acetal (3.55 g, 18.0 mmol, 1.2 equiv) and K_2CO_3 (4.15 g, 30.0 mmol, 2.0 equiv). Then, they were dissolved in dimethylformamide (19 mL), and the resulting reaction mixture was stirred at 150 °C (reflux) for 12 h. After cooled to room temperature, the reaction mixture was quenched with water and extracted with hexane/EtOAc (4:1) three times. The combined organic layer was washed with saturated aqueous NaCl and dried over $MgSO_4$, followed by filtration and evaporation. The crude product was purified by silica-gel column chromatography with hexane/EtOAc (100:0 to 90:10) as the eluent to give the **S1** [3.02 g, 13.4 mmol, 90% yield] as a colorless oil. ^{1}H NMR spectrum was in agreement with it in the literature[4].

S1 (3.00 g, 13.4 mmol) and polyphosphoric acid (PPA) (5.16 g) were placed in an oven-dried, 200 mL, two-necked flask equipped with a condenser, an inlet adapter with a Three-way stopcock and a Teflon®-coated magnetic stirrer bar. Benzene (30 mL) was added to the flask via syringe and the resulting mixture was stirred at 80 °C overnight. After cooled to room temperature, the reaction mixture was quenched with water and extracted with Et_2O three times. The combined organic layer was washed with saturated aqueous $NaHCO_3$, saturated aqueous NaCl and dried over $MgSO_4$, followed by filtration and evaporation. The crude product was purified by silica-gel column chromatography with hexane as the eluent to give the **2b** (685 mg, 5.18 mmol, 35% yield) as a colorless oil. ^{1}H and ^{13}C NMR spectra were in agreement with those in the literature[4].

3-2. Preparation of 5-Phenylbenzofuran (2h): Representative Procedures for Preparation of 2h–2k; Procedure B.



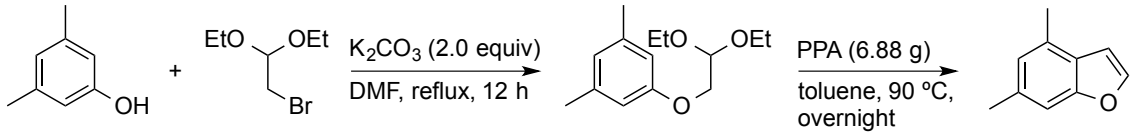
S2 (1.5 equiv) **2h**, 89%

A 100 mL, two-necked round-bottomed flask equipped with a condenser, an inlet adapter with a Three-way stopcock and a Teflon®-coated magnetic stirrer bar was charged with **S2** (391 mg, 2.00 mmol), phenylboronic acid (488 mg, 3.20 mmol, 1.5 equiv), $Pd(PPh_3)_4$ (116 mg, 0.1 mmol, 5.0 mol %) and K_2CO_3 (829 mg, 6.00 mmol, 3.0 equiv). Then, they were dissolved in DMF/H_2O (25 mL/2.5 mL, 10:1) and the resulting reaction mixture was stirred at 100 °C overnight. After cooled to room temperature, the reaction mixture was quenched with water and extracted with hexane/EtOAc (4:1) three times. The combined organic layer was washed with saturated aqueous NaCl and dried over $MgSO_4$, followed by filtration and evaporation. The crude product was purified by silica-gel column chromatography with hexane/CH_2Cl_2 (100:0 to 95:5) as the eluent to give the **2h** [344 mg, 1.77 mmol, 89% yield] as a white solid. ^1H and ^{13}C NMR spectra were in agreement with those in the literatures[5].

3-3. Characterization of Benzofuran Derivatives.

Benzofuran **2a** and 2-pentylfuran **2g** were purchased from Tokyo Chemical Industry Co. (TCI) and distilled under reduced pressure prior to use. Benzofuran derivatives **2b**[4], **2c**[6], **2d**, **2e**[6], **2f**[4] and **S2**[4] were synthesized according to Procedure A. 5-Arylbenzofurans **2h**[5], **2i**[5], **2j**[5], **2k** and **2m**[7] were synthesized according to Procedure B. All spectroscopic data matched those reported[4-7].

4, 6-Dimethylbenzofuran (2d).



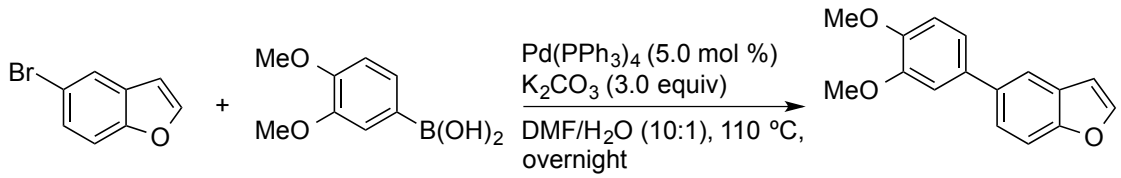
(1.2 equiv) **S3**, quant. **2d**, 40%

2d (1.18 g, 8.07 mmol) was prepared from 4-bromophenol (2.44 g, 20.0 mmol) as a colorless oil according to the procedure **A**.

^1H NMR (392 MHz, $CDCl_3$, δ): 2.42 (s, 3H), 2.47 (s, 3H), 6.71 (dd, J = 1.0, 2.4 Hz, 1H), 6.86 (d, J = 2.4 Hz, 1H), 7.14 (s, 1H), 7.52 (s, 1H). ^{13}C NMR (99 MHz, $CDCl_3$, δ):

18.5 (*C*H$_3$), 21.5 (*C*H$_3$), 105.0 (*C*H), 109.0 (*C*H), 124.5 (*C*H), 124.6 (*C*), 130.4 (*C*), 134.3 (*C*), 143.7 (*C*H), 155.2 (*C*). HRMS-EI (*m*/*z*): [M]$^+$ calcd for $C_{10}H_{10}O$, 146.0732; found, 146.0738.

5-(3', 4'-Dimethoxyphenyl)benzofuran (2k).

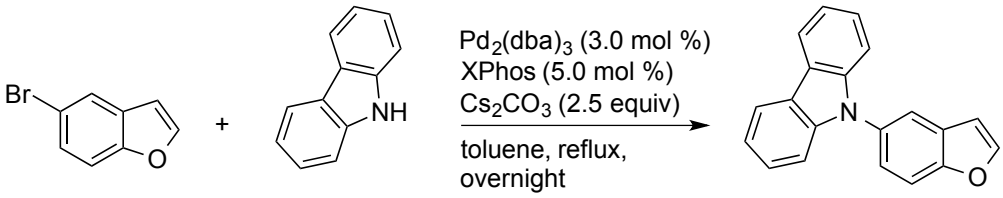


S2 (1.2 equiv) **2k**, 92%

2k (940 mg, 3.70 mmol) was prepared from 4-bromophenol (788 mg, 4.00 mmol) as a white solid (m.p. = 118-121 °C) according to the procedure **B**.

^{1}H NMR (396 MHz, $CDCl_3$, δ): 3.94 (s, 3H), 3.97 (s, 3H), 6.82 (dd, *J* = 1.2, 2.4 Hz, 1H), 6.96 (d, *J* = 8.3 Hz, 1H), 7.13 (d, *J* = 2.4 Hz, 1H), 7.16 (dd, *J* = 2.4, 8.3 Hz, 1H), 7.49 (dd, *J* = 2.0, 8.7 Hz, 1H), 7.55 (d, *J* = 8.7 Hz, 1H), 7.66 (d, *J* = 2.0 Hz, 1H), 7.75 (d, *J* = 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 55.88 (*C*H$_3$), 55.93 (*C*H$_3$), 106.7 (*C*H), 110.7 (*C*H), 111.4 (*C*H), 119.3 (*C*H), 119.5 (*C*H), 123.7 (*C*H), 127.9 (*C*), 134.6 (*C*), 136.3 (*C*), 145.5 (*C*H), 148.2 (*C*), 149.0 (*C*), 154.2 (*C*). HRMS-EI (*m*/*z*): [M]$^+$ calcd for $C_{16}H_{14}O_3$, 254.0943; found, 254.0942.

3-4. Preparation of 9-(Benzofuran-5-yl)-9*H*-carbazole (2l)[8].



S2 (1.2 equiv) **2l**, 65%

A 100 mL, two-necked round-bottomed flask equipped with a condenser, an inlet adapter with a Three-way stopcock and a Teflon®-coated magnetic stirrer bar was charged with carbazole (403 mg, 2.40 mmol, 1.2 equiv), $Pd_2(dba)_3$ (55.0 mg, 0.06 mmol, 3.0 mol %), XPhos (47.5 mg, 0.10 mmol, 5.0 mol %) and Cs_2CO_3 (1.63 g, 5.00 mmol, 2.5 equiv). Then the flask was evacuated and refilled with nitrogen three times. They were dissolved in toluene (20 mL), and **S2** (396 mg, 2.0 mmol) was added to the flask. The resulting mixture was stirred at 112 °C overnight. After cooled to room temperature, the reaction mixture was quenched with water and extracted with Et_2O three times. The combined organic layer was washed with saturated aqueous NaCl and dried over $MgSO_4$,

followed by filtration and evaporation. The crude product was roughly purified by silica-gel column chromatography with hexane/CH_2Cl_2 (100:0 to 92:8) as the eluent, followed by the recrystallization from hexane/CH_2Cl_2 to give the **2l** [370 mg, 1.31 mmol, 65% yield] as a white solid (m.p. = 131-134 °C).

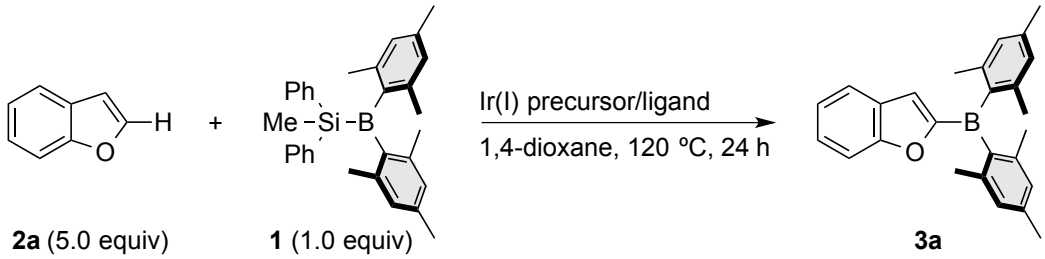
^{1}H NMR (396 MHz, $CDCl_3$, δ): 6.83 (dd, *J* = 1.0, 2.0 Hz, 1H), 7.27 (ddd, *J* = 1.2, 6.7, 7.5 Hz, 2H), 7.31–7.36 (m, 2H), 7.39 (ddd, *J* = 1.2, 7.1, 7.9 Hz, 2H), 7.43 (dd, *J* = 2.4, 8.7 Hz, 1H), 7.68 (d, *J* = 8.7 Hz, 1H), 7.73 (dd, *J* = 2.4, 3.5 Hz, 2H), 8.15 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 106.8 (*C*H), 109.7 (*C*H) 112.6 (*C*H) 119.7 (*C*H), 120.15 (*C*H), 120.25 (*C*H), 123.1 (*C*), 123.8 (*C*H), 125.9 (*C*H), 128.6 (*C*), 132.6 (*C*), 141.5 (*C*), 146.4 (*C*H), 153.9 (*C*). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{20}H_{13}{}^{14}N_1O_1$, 283.0997; found, 283.0993.

4. General Experimental Procedure for Direct Dimesitylborylation of Benzofuran.

$[IrCl(coe)_2]_2$ (2.2 mg, 0.0025 mmol, 2.5 mol %), IMes•HCl (1.8 mg, 0.0050 mmol, 5.0 mol %), KO^{t}Bu (0.6 mg, 0.0050 mmol, 5.0 mol %) and (diphenylmethylsilyl)dimesitylborane **1** (44.7 mg, 0.10 mmol, 1.0 equiv) were placed in a vial with a screw cap containing a Teflon®-coated rubber septum in a glove box under an argon atmosphere. After the reaction vial was removed from the glove box, 1,4-dioxane (0.5 mL) was added to the vial via a syringe. The resulting mixture was stirred for 10 min at rt, and then benzofuran (0.50 mmol, 5.0 equiv) was added dropwise to the vial. After the resulting mixture was stirred at 120 °C for 24 h, the reaction mixture was analyzed by GC to check completeness of the reaction. The mixture was directly filtered through a short silica-gel column with Et_2O as an eluent, then the resultant solution was concentrated under reduced pressure. 1,1,2,2-Tetrachloroethane was added to this mixture as an internal standard, and the NMR yield was determined by quantitative ^{1}H NMR analysis. After that, 1,1,2,2-tetrachloroethane was removed under reduced pressure. The crude product was roughly purified by silica-gel column chromatography with hexane/CH_2Cl_2 eluent (100:0 to 95:5) to give the mixture of a borylated product and a silylated product. And then, this mixture was further purified by recrystallization or GPC to give the desired borylated product.

5. Optimization Studies.

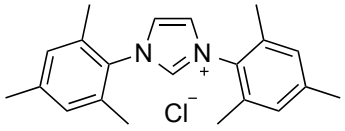
Table S1. Investigation of Various Ligands in C–H Dimesitylborylation of Benzofuran 2a.



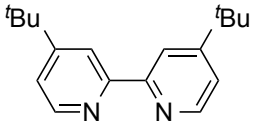
2a (5.0 equiv) **1** (1.0 equiv) **3a**

Entry	Ir(I) precursor (mol %)	ligand (mol %)	yield (%)[a]
1[b]	**[Ir(OMe)(cod)]$_2$ (2.5)**	**IMes·HCl (10)**	**48**
2	[Ir(OMe)(cod)]$_2$ (2.5)	dtbpy (5.0)	0
3	[Ir(OMe)(cod)]$_2$ (2.5)	Me$_4$phen (5.0)	0
4	[Ir(OMe)(cod)]$_2$ (2.5)	PPh$_3$ (10)	0
5	[Ir(OMe)(cod)]$_2$ (2.5)	P^{t}Bu$_3$ (10)	13
6	[Ir(OMe)(cod)]$_2$ (2.5)	dcpe (5.0)	0

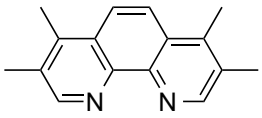
[a] NMR yield. 1,1,2,2-Tetrachloroethane was used as an internal standard.
[b] K(O^{t}Bu) (10 mol %) was added as a base to generate free carbene *in situ*.



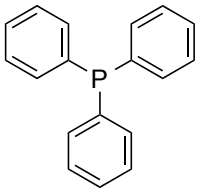
IMes•HCl



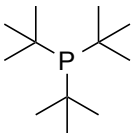
dtbpy



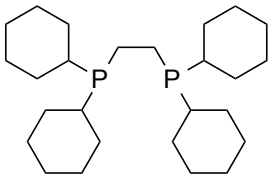
Me$_4$phen



PPh$_3$

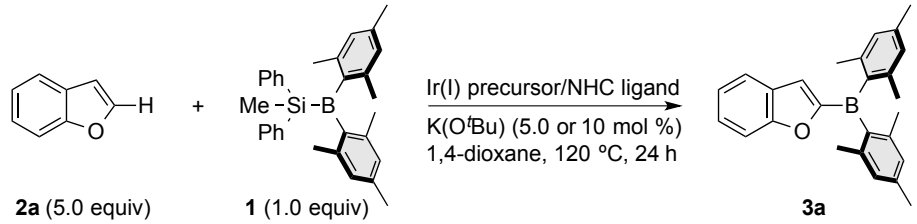


P^{t}Bu$_3$



dcpe

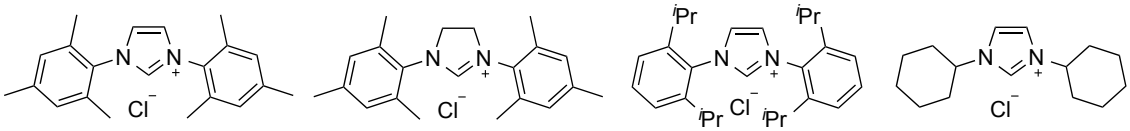
Table S2. Screening of Ir(I) Precursors and NHC ligands.



2a (5.0 equiv) **1** (1.0 equiv) **3a**

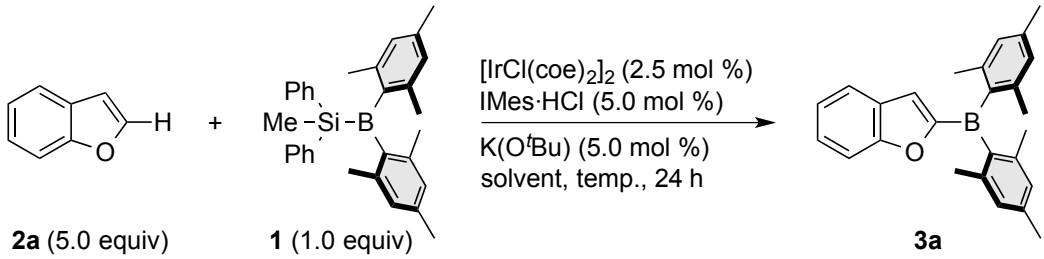
Entry	Ir(I) precursor (mol %)	ligand (mol %)	K(O^{t}Bu) (**X** mol %)	yield (%)[a]
1	$[Ir(OMe)(cod)]_2$ (2.5)	IMes·HCl (10)	10	48
2	**$[IrCl(coe)_2]_2$ (2.5)**	**IMes·HCl (10)**	**10**	**69**
3	$[IrCl(cod)]_2$ (2.5)	IMes·HCl (10)	10	58
4	$[Ir(cod)(Py)(PCy_3)][PF_6]$ (5.0)	IMes·HCl (10)	10	5
5	$[Ir(cod)_2]$BARF (5.0)	IMes·HCl (10)	10	65
6	**$[IrCl(coe)_2]_2$ (2.5)**	**IMes·HCl (5.0)**	**5.0**	**75**
7	$[IrCl(coe)_2]_2$ (2.5)	SIMes·HCl (5.0)	5.0	64
8	$[IrCl(coe)_2]_2$ (2.5)	IPr·HCl (5.0)	5.0	10
9	$[IrCl(coe)_2]_2$ (2.5)	ICy·HCl (5.0)	5.0	11
10	**[Ir(IMes)(cod)Cl] (5.0)**	–	–	**70**
11	$[IrCl(coe)_2]_2$ (2.5)	–	–	0
12	–	IMes·HCl (5.0)	5.0	0
13	–	–	5.0	0

[a] NMR yield. 1,1,2,2-Tetrachloroethane was used as an internal standard.



IMes•HCl SIMes•HCl IPr•HCl ICy•HCl

Table S3. Investigation of Solvents and Reaction Temperature.

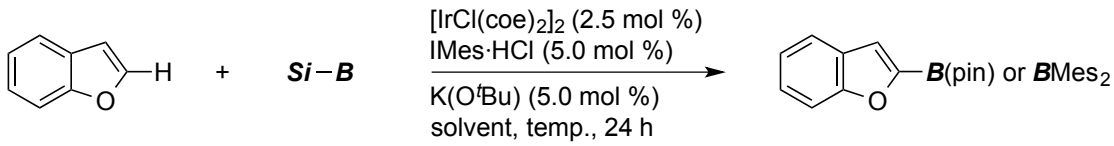


2a (5.0 equiv) **1** (1.0 equiv) **3a**

Entry	solvent	temp (°C)	yield (%)[a]
1	**1,4-dioxane**	**120**	**75 (59)**
2	1,4-dioxane	100	63
3	1,4-dioxane	80	0
4	CPME	120	72
5	$^{n}Bu_2O$	120	74
6	DME	120	70

[a] NMR yield. 1,1,2,2-Tetrachloroethane was used as an internal standard.

Table S4. C–H Dimesitylborylation of Benzofuran Using Various Silylboranes.

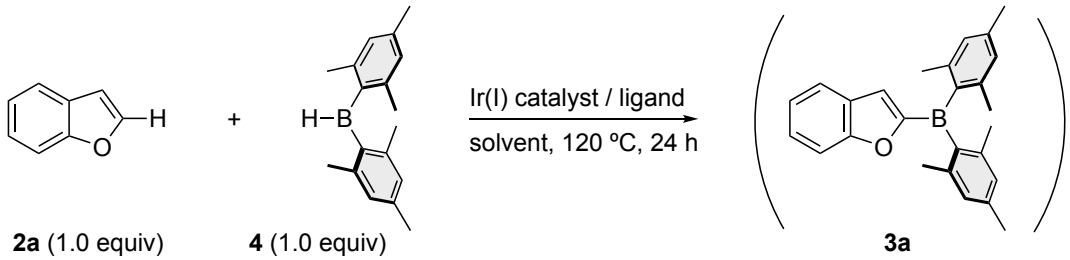


2a (5.0 equiv) **1** (1.0 equiv) NMR yield

Entry	***Si*–*B***	yield (%)[a]
1	Ph_2MeSi–$BMes_2$ **1**	70
2	$PhMe_2Si$–B(pin)	56
3	Et_3Si–B(pin)	0
4	$(TMS)_3Si$–B(pin)	0

[a] NMR yield. 1,1,2,2-Tetrachloroethane was used as an internal standard.

Table S5. Preliminary Experiments for Dimesitylborylation Using Dimesitylborane **4**

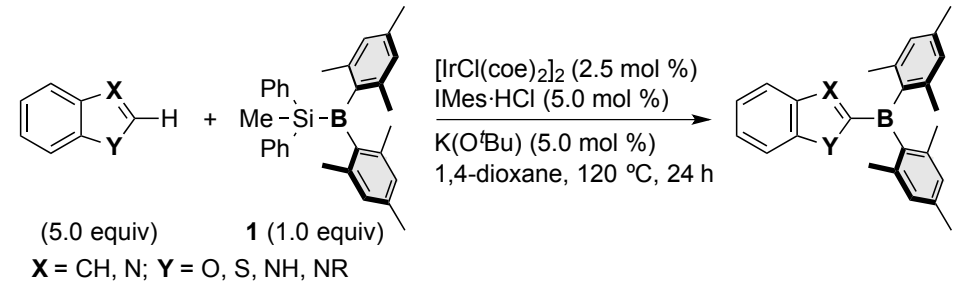


2a (1.0 equiv) **4** (1.0 equiv) **3a**

Entry	Ir(I) precursor (mol %)	ligand (mol %)	solvent	yield (%)[a]
1	[(IMes)IrCl(cod)] (10)	-	1,4-dioxane	N.D.
2	[(IMes)IrCl(cod)] (10)	-	DME	N.D.
3	[(IMes)IrCl(cod)] (10)	-	Mesitylene	N.D.
4	[(SIMes)IrCl(cod)] (10)	-	DME	N.D.
5	[(ICy)IrCl(cod)] (10)	-	DME	N.D.
6	$[Ir(OMe)(cod)]_2$ (5.0)	dtbpy (10)	DME	N.D.
7	$[Ir(OMe)(cod)]_2$ (5.0)	TMPhen (10)	DME	N.D.
8	[(IMes)IrCl(cod)] (10)	IPr•HCl (5.0)	DEE[b]	N.D.

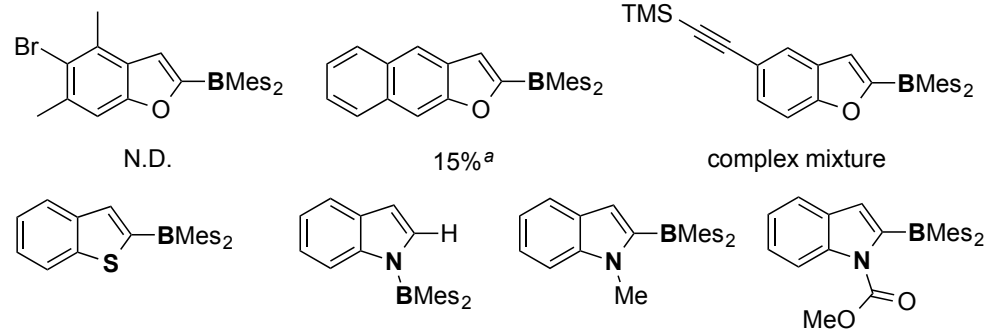
[a] NMR yield. 1,1,2,2-Tetrachloroethane was used as an internal standard. [b] 1,2-Diethoxyethane

Table S6. Unsuccessful Heteroaromatic Substrates in C–H Dimesitylborylation.



(5.0 equiv) **1** (1.0 equiv)

X = CH, N; **Y** = O, S, NH, NR



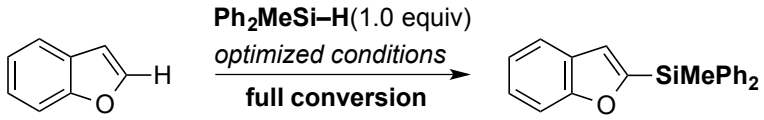
N.D. 15%[a] complex mixture

23%[a] (31%)[b] 67%[c] N.D N.D

N.D N.D.

[a] NMR yield. 1,1,2,2-Tetrachloroethane was used as an internal standard. [b] NMR yield when 5 mol % of $[IrCl(coe)_2]_2$ and 10 mol % ICy·HCl was used. [c] Isolated yield.

6. Control Experiments for Reaction Mechanism of C–H Dimesitylborylation. Reaction using $Ph_2MeSi–H$ instead of 1 under Optimized Condition.

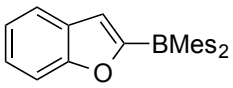


2a (5.0 equiv) **3a'**: 29%

$Ph_2MeSi–H$ was synthesized according to the literature procedure[17]. $[IrCl(coe)_2]_2$ (2.2 mg, 0.0025 mmol, 2.5 mol %), IMes•HCl (1.8 mg, 0.0050 mmol, 5.0 mol %), KO^{t}Bu (0.6 mg, 0.0050 mmol, 5.0 mol %) were placed in a vial with a screw cap containing a Teflon®-coated rubber septum in a glove box under an argon atmosphere. After the reaction vial was removed from the glove box, 1,4-dioxane (0.5 mL) and $Ph_2MeSi–H$ (19.7 mg, 0.10 mmol, 1.0 equiv) were added to the vial via a syringe. The resulting mixture was stirred for 10 min at rt, and then benzofuran (**2a**) (0.50 mmol, 59.2 mg, 5.0 equiv) was added dropwise to the vial. After the resulting mixture was stirred at 120 °C for 24 h, the reaction mixture was analyzed by GC to check completeness of the reaction. The mixture was directly filtered through a short silica-gel column with Et_2O as an eluent, then the resultant solution was concentrated under reduced pressure. 1,1,2,2-Tetrachloroethane was added to this mixture as an internal standard, and the NMR yield was determined by ^1H NMR analysis. $Ph_2MeSi–SiMePh_2$[12], $Ph_2MeSi–OH$[13, 14] and $Ph_2MeSi–O–SiMePh_2$[15, 16] were not detected in the reaction mixture by GC and GC-MS analysis compared to authentic samples ($Ph_2MeSi–D$[10, 11], $Ph_2MeSi–SiMePh_2$[12], $Ph_2MeSi–OH$[13, 14] and $Ph_2MeSi–O–SiMePh_2$[15, 16] were prepared according to literature procedures[10-16].).

7. Characterization of Dimesitylborylated Products.

(Benzo[*b*]furan-2-yl) dimesitylborane (3a).

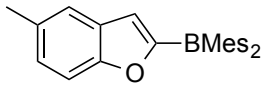


The reaction was performed with $Ph_2MeSi–BMes_2$ **1** (44.7 mg, 0.10 mmol, 1.0 equiv) and **2a** (59.1 mg, 0.50 mmol, 5.0 equiv). The NMR yield of **3a** in crude mixture was 75%. The product **3a** was obtained as a viscous liquid in 59% yield (21.6 mg, 0.0590 mmol) after purification by silica-gel column chromatography (hexane/CH_2Cl_2, 100:0 to 95:5) and GPC.

^1H NMR (396 MHz, $CDCl_3$, δ): 2.12 (s, 12H), 2.32 (s, 6H), 6.86 (s, 4H), 7.21–7.26 (m, 1H), 7.29 (d, J = 1.0 Hz, 1H), 7.39 (ddd, J = 1.6, 7.5, 8.2 Hz, 1H), 7.55 (dd, J = 1.0, 8.5

Hz, 1H), 7.61–7.64 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.3 (*C*H$_3$), 23.0 (*C*H$_3$), 112.5 (*C*H), 122.78 (*C*H), 122.83 (*C*H), 125.5 (*C*H), 127.4 (*C*H), 128.3 (*C*H), 139.1 (*C*), 139.9 (br, B–*C*), 141.3 (*C*), 158.9 (*C*), 167.4 (brs, B–*C*). ^{11}B NMR (127 MHz, $CDCl_3$, δ): 64.1. HRMS-EI (m/z): $[M]^+$ calcd for $C_{26}H_{27}{}^{10}BO$, 365.2191; found, 365.2196.

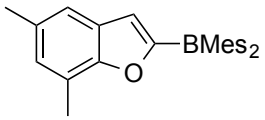
Dimesityl (5-methylbenzo[*b*]furan-2-yl) borane (3b).



The reaction was performed with Ph_2MeSi–$BMes_2$ **1** (45.0 mg, 0.10 mmol, 1.0 equiv) and **2b** (66.0 mg, 0.50 mmol, 5.0 equiv). The NMR yield of **3b** in crude mixture was 73%. The product **3b** was obtained as a white solid (m.p. = 75-80 °C) in 60% yield (22.7 mg, 0.0597 mmol) after purification by silica-gel column chromatography (hexane/CH_2Cl_2, 100:0 to 94:6) and GPC.

^{1}H NMR (396 MHz, $CDCl_3$, δ): 2.12 (s, 12H), 2.32 (s, 6H), 2.44 (s, 3H), 6.85 (s, 4H), 7.21 (dd, *J* = 1.6, 8.3 Hz, 1H), 7.22 (d, *J* = 1.2 Hz, 1H), 7.39 (t, *J* = 1.0 Hz, 1H), 7.44 (d, *J* = 8.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.3 (*C*H$_3$, *C*H$_3$), 23.0 (*C*H$_3$), 112.0 (*C*H), 122.2 (*C*H), 125.3 (*C*H), 128.2 (*C*H), 128.4 (*C*), 129.1 (*C*H), 132.3 (*C*), 139.0 (*C*), 139.9 (br, B–*C*), 141.2 (*C*), 157.4 (*C*), 167.5 (br, B–*C*). ^{11}B NMR (127 MHz, $CDCl_3$, δ): 63.8. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{27}H_{29}{}^{10}BO$, 379.2348; found, 379.2338.

(5,7-Dimethylbenzo[*b*]furan-2-yl) dimesitylborane (3c).

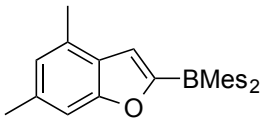


The reaction was performed with Ph_2MeSi–$BMes_2$ **1** (44.6 mg, 0.10 mmol, 1.0 equiv) and **2c** (73.5 mg, 0.50 mmol, 5.0 equiv). The NMR yield of **3c** in crude mixture was 77%. The product **3c** was obtained as a white solid (m.p. = 168-171 °C) in 60% yield (23.6 mg, 0.0598 mmol) after purification by silica-gel column chromatography (hexane/CH_2Cl_2, 100:0 to 96:4) and GPC.

^{1}H NMR (401 MHz, $CDCl_3$, δ): 2.11 (s, 12H), 2.32 (s, 6H), 2.39 (s, 3H), 2.46 (s, 3H), 6.84 (s, 4H), 7.03 (s, 1H), 7.20 (s, 1H), 7.21 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 15.3 (*C*H$_3$), 21.2 (*C*H$_3$), 21.3 (*C*H$_3$), 23.1 (*C*H$_3$), 119.6 (*C*H), 122.2 (*C*), 126.1 (*C*H), 127.8 (*C*), 128.1 (*C*H), 129.8 (*C*H), 132.3 (*C*), 138.8 (*C*), 140.1 (br, B–*C*), 141.3 (*C*), 156.6 (*C*), 167.3 (brs, B–*C*). ^{11}B NMR (127 MHz, $CDCl_3$, δ): 63.3. HRMS-EI (*m*/*z*): $[M]^+$ calcd for

$C_{28}H_{31}{}^{10}BO$, 393.2504; found, 393.2489.

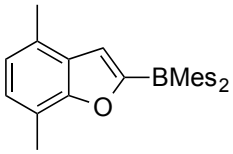
(4,6-Dimethylbenzo[*b*]furan-2-yl) dimesitylborane (3d).



The reaction was performed with $Ph_2MeSi–BMes_2$ **1** (45.2 mg, 0.10 mmol, 1.0 equiv) and **2d** (73.1 mg, 0.50 mmol, 5.0 equiv). The NMR yield of **3d** in crude mixture was 69%. The product **3d** was obtained as a viscous liquid in 64% yield (25.2 mg, 0.0639 mmol) after purification by silica-gel column chromatography (hexane/CH_2Cl_2, 100:0 to 94:6) and GPC.

^{1}H NMR (401 MHz, $CDCl_3$, δ): 2.12 (s, 12H), 2.32 (s, 6H), 2.44 (s, 3H), 2.45 (s, 3H), 6.86 (s, 4H), 6.87 (s, 1H), 7.17 (s, 1H), 7.29 (d, *J* = 1.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 18.7 (*C*H$_3$), 21.3 (*C*H$_3$), 22.0 (*C*H$_3$), 23.1 (*C*H$_3$), 109.8 (*C*H), 124.6 (*C*H), 124.8 (*C*H), 126.1 (*C*), 128.2 (*C*H), 132.6 (*C*), 138.4 (*C*), 138.9 (*C*), 140.0 (br, B–*C*), 141.3 (*C*), 159.4 (*C*), 166.5 (br, B–*C*). ^{11}B NMR (127 MHz, $CDCl_3$, δ): 63.2. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{28}H_{31}{}^{10}BO$, 393.2504; found, 393.2496.

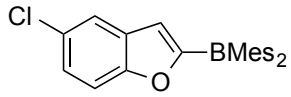
(4,7-Dimethylbenzo[*b*]furan-2-yl) dimesitylborane (3e).



The reaction was performed with $Ph_2MeSi–BMes_2$ **1** (44.8 mg, 0.10 mmol, 1.0 equiv) and **2e** (73.0 mg, 0.50 mmol, 5.0 equiv). The NMR yield of **3e** in crude mixture was 62%. The product **3e** was obtained as a white solid (m.p. = 199-203 °C) in 52% yield (20.4 mg, 0.0517 mmol) after purification by silica-gel column chromatography (hexane/CH_2Cl_2, 100:0 to 94:6) and recrystallization from hexane.

^{1}H NMR (401 MHz, $CDCl_3$, δ): 2.12 (s, 12H), 2.33 (s, 6H), 2.45 (s, 6H), 6.86 (s, 4H), 6.93 (d, *J* = 7.2 Hz, 1H), 7.10 (d, *J* = 7.2 Hz, 1H), 7.31 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 15.1 (*C*H$_3$), 18.5 (*C*H$_3$), 21.3 (*C*H$_3$), 23.1 (*C*H$_3$), 119.9 (*C*), 122.8 (*C*H), 125.1 (*C*H), 127.8 (*C*), 128.1 (*C*H), 128.2 (*C*H), 130.4 (*C*), 138.8 (*C*), 140.2 (br, B–*C*), 141.4 (*C*), 157.9 (*C*), 166.5 (brs, B–*C*). ^{11}B NMR (127 MHz, $CDCl_3$, δ): 63.3. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{28}H_{31}{}^{10}BO$, 393.2504; found, 393.2492.

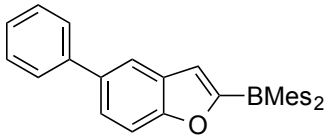
(5-Chlorobenzo[*b*]furan-2-yl) dimesitylborane (3f).



The reaction was performed with $Ph_2MeSi–BMes_2$ **1** (44.7 mg, 0.10 mmol, 1.0 equiv) and **2f** (76.0 mg, 0.50 mmol, 5.0 equiv). The NMR yield of **3f** in crude mixture was 74%. The product **3f** was obtained as a viscous liquid in 42% yield (17.0 mg, 0.0424 mmol) after purification by silica-gel column chromatography (hexane/CH_2Cl_2, 100:0 to 96:4) and GPC.

^{1}H NMR (396 MHz, $CDCl_3$, δ): 2.10 (s, 12H), 2.32 (s, 6H), 6.86 (s, 4H), 7.20 (d, J = 1.0 Hz, 1H), 7.34 (dd, J = 2.2, 8.5 Hz, 1H), 7.47 (d, J = 9.1 Hz, 1H), 7.58 (d, J = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.3 (*C*H$_3$), 23.0 (*C*H$_3$), 113.5 (*C*H), 122.0 (*C*H), 124.2 (*C*H), 127.6 (*C*H), 128.3 (*C*H), 129.4 (*C*), 139.4 (*C*), 141.3 (*C*), 157.1 (*C*); Two signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation. ^{11}B NMR (127 MHz, $CDCl_3$, δ): 64.6. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{26}H_{26}{}^{10}BO^{35}Cl$, 399.1802; found, 399.1798.

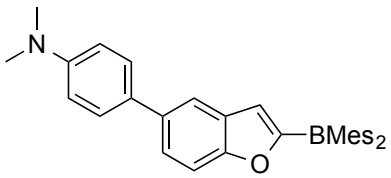
Dimesityl (5-phenylbenzo[*b*]furan-2-yl) borane (3h).



The reaction was performed with $Ph_2MeSi–BMes_2$ **1** (45.0 mg, 0.10 mmol, 1.0 equiv) and **2h** (98.0 mg, 0.50 mmol, 5.0 equiv). The NMR yield of **3h** in crude mixture was 62%. The product **3h** was obtained as a white solid (m.p. = 200-202 °C) in 40% yield (17.8 mg, 0.0402 mmol) after purification by silica-gel column chromatography (hexane/CH_2Cl_2, 100:0 to 88:12), GPC and recrystallization from CH_2Cl_2/Hexane.

^{1}H NMR (401 MHz, $CDCl_3$, δ): 2.14 (s, 12H), 2.33 (s, 6H), 6.87 (s, 4H), 7.31–7.37 (m, 2H), 7.41–7.47 (m, 2H), 7.56–7.65 (m, 4H), 7.79 (t, J = 1.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.3 (*C*H$_3$), 23.1 (*C*H$_3$), 112.6 (*C*H), 121.1 (*C*H), 125.6 (*C*H), 127.0 (*C*H), 127.37 (*C*H), 127.41 (*C*H), 128.3 (*C*H), 128.8 (*C*H), 136.6 (*C*), 139.2 (*C*), 139.9 (brs, B–*C*), 141.3 (*C*), 141.4 (*C*), 158.5 (*C*), 168.1 (brs, B–*C*). ^{11}B NMR (127 MHz, $CDCl_3$, δ): 64.0. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{32}H_{31}{}^{10}BO$, 441.2504; found, 441.2492.

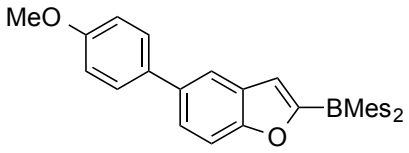
4-[2-(Dimesitylboranyl) benzo[*b*]furan-5-yl]-*N, N*-dimethylaniline (3i).



The reaction was performed with $Ph_2MeSi–BMes_2$ **1** (45.2 mg, 0.10 mmol, 1.0 equiv) and **2i** (118.5 mg, 0.50 mmol, 5.0 equiv). The NMR yield of **3i** in crude mixture was 68%. The product **3i** was obtained as a viscous yellowish green liquid in 60% (29.1 mg, 0.0599 mmol) yield after purification by silica-gel column chromatography (hexane/CH_2Cl_2, 100:0 to 65:35) and GPC.

^{1}H NMR (401 MHz, $CDCl_3$, δ): 2.14 (s, 12H), 2.33 (s, 6H), 2.99 (s, 6H), 6.82 (d, J = 8.4 Hz, 2H), 6.87 (s, 4H), 7.31 (d, J = 1.0 Hz, 1H), 7.49 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.8 Hz, 1H), 7.61 (dd, J = 1.6, 8.8 Hz, 1H), 7.73 (d, J = 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.3 (*C*H$_3$), 23.1 (*C*H$_3$), 40.6 (*C*H$_3$), 112.5 (*C*H), 112.8 (*C*H), 119.9 (*C*H), 125.7 (*C*H), 127.0 (*C*H), 128.0 (*C*H), 128.3 (*C*H), 128.7 (*C*), 129.4 (*C*), 136.7 (*C*), 139.1 (*C*), 139.9 (brs, B–*C*), 141.3 (*C*), 149.7 (*C*), 158.0 (*C*), 167.9 (brs, B–*C*). ^{11}B NMR (127 MHz, $CDCl_3$, δ): 63.6. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{34}H_{36}{}^{10}BO^{14}N$, 484.2926; found, 484.2911.

Dimesityl [5-(4-methoxyphenyl) benzo[*b*]furan-2-yl)] borane (3j).

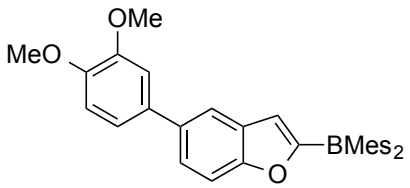


The reaction was performed with $Ph_2MeSi–BMes_2$ **1** (45.1 mg, 0.10 mmol, 1.0 equiv) and **2j** (112.6 mg, 0.50 mmol, 5.0 equiv). The NMR yield of **3j** in crude mixture was 67%. The product **3j** was obtained as a white solid (m.p. = 92-98 °C) in 57% yield (26.9 mg, 0.0569 mmol) after purification by silica-gel column chromatography (hexane/CH_2Cl_2, 100:0 to 70:30) and GPC.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 2.14 (s, 12H), 2.33 (s, 6H), 3.85 (s, 3H), 6.87 (s, 4H), 6.96–7.01 (m, 2H), 7.32 (s, 1H), 7.49–7.54 (m, 2H), 7.59 (d, J = 1.2 Hz, 2H), 7.73 (t, J = 1.4 Hz, 1H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 21.3 (*C*H$_3$), 23.1 (*C*H$_3$), 55.3 (*C*H$_3$), 112.6 (*C*H), 114.2 (*C*H), 120.5 (*C*H), 125.6 (*C*H), 127.2 (*C*H), 128.3 (*C*H), 128.4 (*C*H), 128.8 (*C*), 133.9 (*C*), 136.2 (*C*), 139.1 (*C*), 139.8 (brs, B–*C*), 141.3 (*C*), 158.2 (*C*), 158.9 (*C*),

168.0 (brs, B–*C*). ^{11}B NMR (127 MHz, $CDCl_3$, δ): 64.0. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{33}H_{33}{}^{10}BO_2$, 471.2610; found, 471.2604.

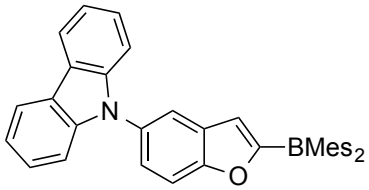
[5-(3,4-Dimethoxyphenyl) benzo[*b*]furan-2-yl] dimesitylborane (3k).



The reaction was performed with Ph_2MeSi–$BMes_2$ **1** (45.1 mg, 0.10 mmol, 1.0 equiv) and **2k** (127.4 mg, 0.50 mmol, 5.0 equiv). The NMR yield of **3k** in crude mixture was 58%. The product **3k** was obtained as a viscous liquid in 53% yield (26.5 mg, 0.0527 mmol) after purification by silica-gel column chromatography (hexane/Et_2O, 100:0 to 80:20) and GPC.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 2.14 (s, 12H), 2.33 (s, 6H), 3.93 (s, 3H), 3.95 (s, 3H), 6.87 (s, 4H), 6.96 (d, *J* = 8.2 Hz, 1H), 7.10 (d, *J* = 1.6 Hz, 1H), 7.14 (dd, *J* = 2.0, 8.2 Hz, 1H), 7.33 (s, 1H), 7.60 (d, *J* = 1.6 Hz, 2H), 7.75 (t, *J* = 1.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.3 (*C*H_3), 23.0 (*C*H_3), 55.9 (*C*H_3), 110.7 (*C*H), 111.4 (*C*H), 112.6 (*C*H), 119.6 (*C*H), 120.6 (*C*H), 125.5 (*C*H), 127.2 (*C*H), 128.3 (*C*H), 128.7 (*C*), 134.4 (*C*), 136.4 (*C*), 139.2 (*C*), 139.8 (brs, B–*C*), 141.2 (*C*), 148.4 (*C*), 149.1 (*C*), 158.2 (*C*), 168.1 (brs, B–*C*). ^{11}B NMR (127 MHz, $CDCl_3$, δ): 64.2. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{34}H_{35}{}^{10}BO_3$, 501.2716; found, 501.2707.

9-[2-(Dimesitylboranyl) benzo[*b*]furan-5-yl)-9*H*-carbazole (3l).

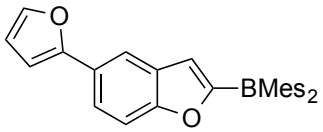


The reaction was performed with Ph_2MeSi–$BMes_2$ **1** (45.1 mg, 0.10 mmol, 1.0 equiv) and **2l** (142.4 mg, 0.50 mmol, 5.0 equiv). The NMR yield of **3l** in crude mixture was 66%. The product **3l** was obtained as a white solid (m.p. = 242-246 °C) in 59% yield (31.5 mg, 0.0593 mmol) after purification by silica-gel column chromatography (hexane/CH_2Cl_2, 100:0 to 80:20) and recrystallization from CH_2Cl_2/hexane.

^{1}H NMR (401 MHz, $CDCl_3$, δ): 2.18 (s, 12H), 2.34 (s, 6H), 6.89 (s, 4H), 7.28 (ddd, *J* = 1.7, 6.4, 8.0 Hz, 2H), 7.33–7.43 (m, 5H), 7.54 (dd, *J* = 1.8, 8.6 Hz, 1H), 7.75 (d, *J* = 8.8

Hz, 1H), 7.78 (d, J = 2.0 Hz, 1H), 8.15 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.3 (*C*H$_3$), 23.1 (*C*H$_3$), 109.7 (*C*H), 113.7 (*C*H), 119.8 (*C*H), 120.3 (*C*H), 121.4 (*C*H), 123.2 (*C*), 125.0 (*C*H), 125.9 (*C*H), 127.0 (*C*H), 128.4 (*C*H), 129.3 (*C*), 132.7 (*C*), 139.4 (*C*), 139.7 (brs, B–*C*), 141.3 (*C*), 141.4 (*C*), 157.7 (*C*), 168.9 (brs, B–*C*). ^{11}B NMR (127 MHz, $CDCl_3$, δ): 65.6. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{38}H_{34}{}^{10}BO^{14}N$, 530.2770; found, 530.2761.

[5-(Furan-2-yl) benzo[*b*]furan-2-yl] dimesitylborane (3m).



The reaction was performed with Ph_2MeSi–$BMes_2$ **1** (44.7 mg, 0.10 mmol, 1.0 equiv) and **2m** (92.1 mg, 0.50 mmol, 5.0 equiv). The NMR yield of **3m** in crude mixture was 55%. The product **3m** was obtained as a viscous liquid in 36% yield (15.7 mg, 0.0363 mmol) after purification by silica-gel column chromatography (hexane/CH_2Cl_2, 100:0 to 95:5) and GPC.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 2.13 (s, 12H), 2.33 (s, 6H), 6.47 (dd, J = 2.0, 3.1 Hz, 1H), 6.61 (d, J = 2.7 Hz, 1H), 6.87 (s, 4H), 7.30 (d, J = 1.2 Hz, 1H), 7.47 (d, J = 1.6 Hz, 1H), 7.55 (d, J = 9.0 Hz, 1H), 7.72 (dd, J = 2.0, 9.0 Hz, 1H), 7.91 (d, J = 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.3 (*C*H$_3$), 23.0 (*C*H$_3$), 104.4 (*C*H), 111.6 (*C*H), 112.7 (*C*H), 117.7 (*C*H), 124.2 (*C*H), 125.5 (*C*H), 126.3 (*C*), 128.3 (*C*H), 128.6 (*C*), 139.2 (*C*), 139.8 (br, B–*C*), 141.3 (*C*), 141.9 (*C*H), 154.0 (*C*), 158.3 (*C*), 168.2 (brs, B–*C*). ^{11}B NMR (127 MHz, $CDCl_3$, δ): 64.0. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{30}H_{29}{}^{10}BO_2$, 431.2297; found, 431.2291.

8. Optical Properties of Product 3i.

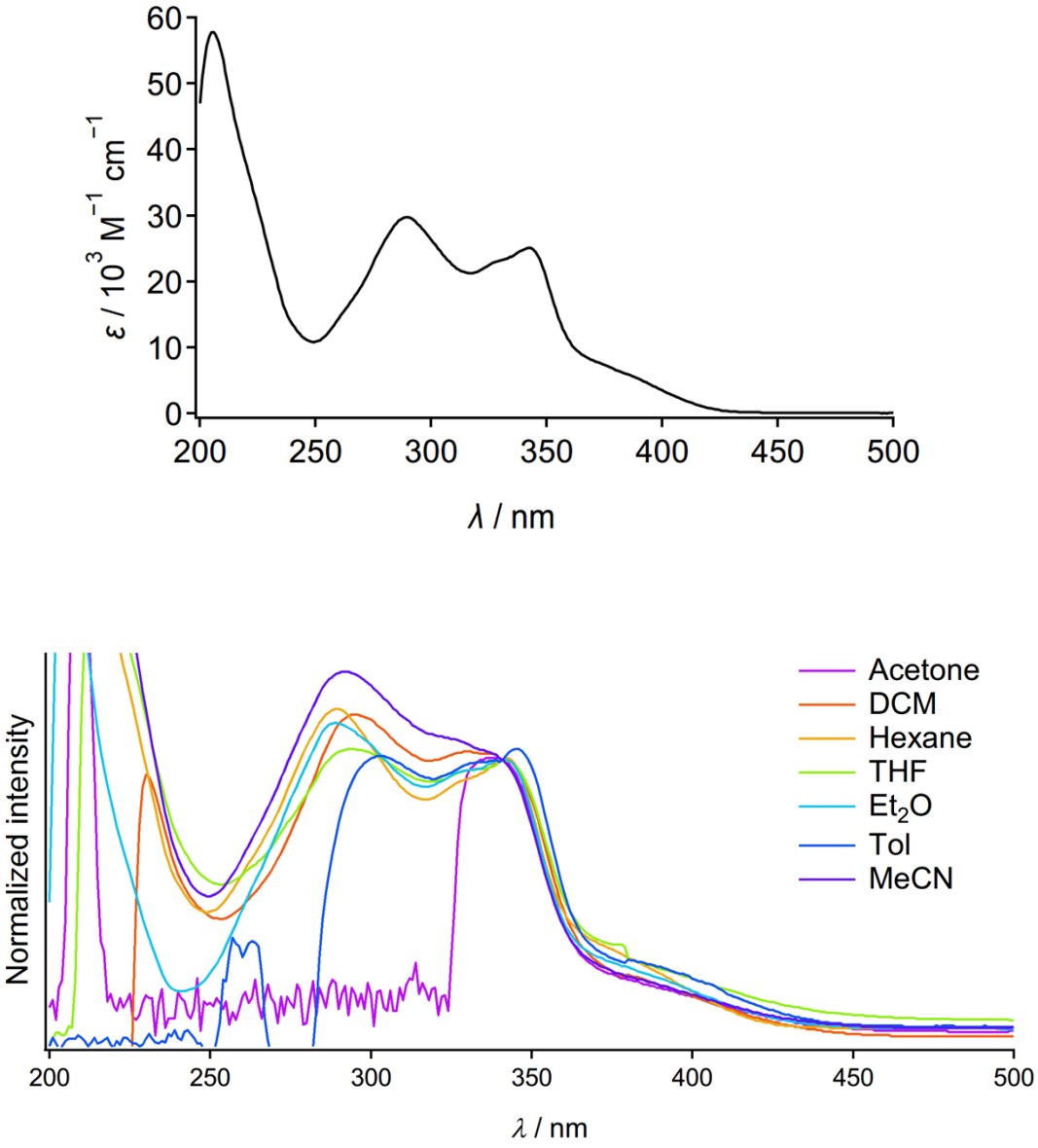


Figure S1. Absorption Spectrum of Solutions of Product **3i** (c = 10 × 10^{-6} M) in hexane (upper) and various solvents (lower).

9. Single Crystal X-Ray Analysis of Product 3l.

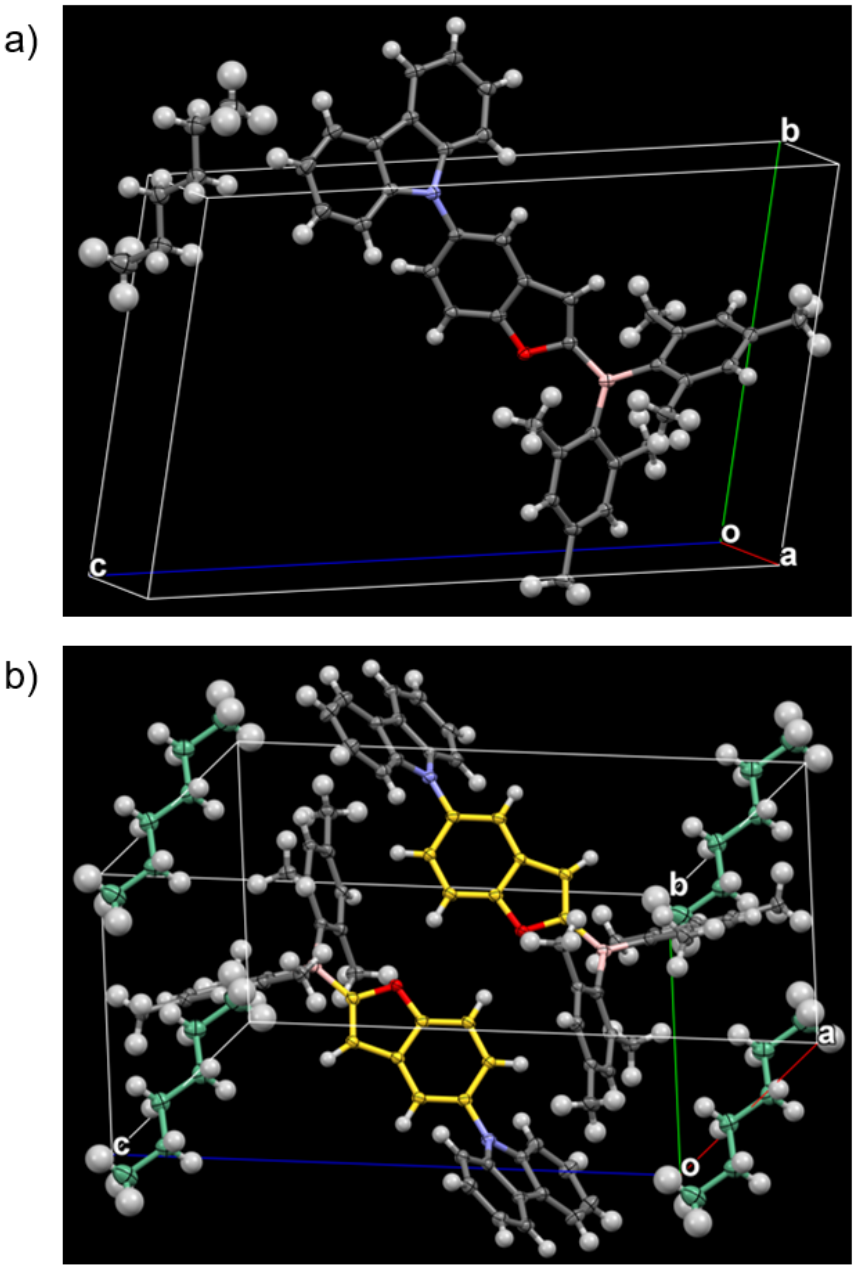


Figure S2. Single crystal structure of **3l** which contains 0.5 equiv of hexane molecule. In b), carbons of benzofuran moiety and hexane are colored in orange and green, respectively.

Crystallographic parameters: *P*-1, triclinic, $C_{41}H_{41}BNO$, M_w = 574.60, a = 8.0210(3) Å, b = 11.8245(4), c = 18.3551(8) Å, α = 101.392(3)°, β = 102.418(4)°, γ = 98.424(3)°, V = 1633.86(12) Å^3,ρ_{calc} = 1.168 cm^{-3}, R_1 = 8.26 %, wR_2 = 24.17 %, GOF = 1.018.

10. Reference of Experimental Section.

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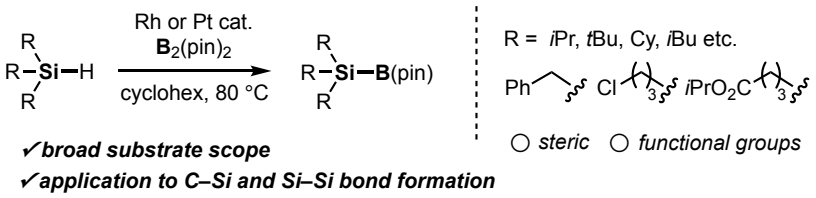
Chapter 3.

Development of Novel Synthetic Method for Trialkylsilylborane Compounds

Abstract

Silylboranes are an important class of organometallic reagents in organic synthesis., serving as silyl anion equivalents in the presence of the transition-metal catalysts or bases. However, synthesizable silylboranes are still quite limited. In particular, the synthesis of trialkylsilylboranes bearing steric hindrance or functional groups has not been reported. Here, the author reported the use of a rhodium or a platinum catalyst for direct borylation of hydrosilanes with bis(pinacolato)diboron. The developed conditions allow synthesizing new trialkylsilylboranes bearing bulky alkyl groups as well as sensitive functional groups that are inaccessible by previously reported methods. The author demonstrated the use of these compounds as silyl anion equivalents in organic transformations and significantly expanded the scope of synthesizable organosilicon compounds.

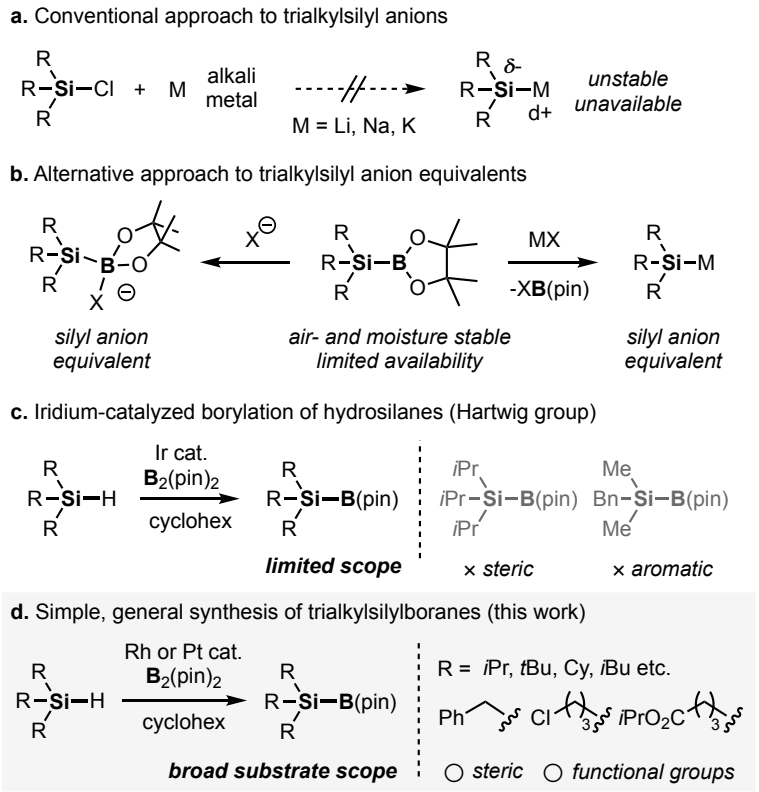


Introduction

Silyl anions represent a class of important organometallic species for silicon–carbon and silicon–silicon bond formation reactions in organic synthesis.[1] Conventionally, the generation of silyl anions is accomplished by reactions of chlorosilanes with alkali metal (K, Na and Li) or reactions of hydrosilanes with alkali metal hydride.[2] However, these methods are limited to the preparation of aromatic groups-substituted silyl anions $Ar_{3-n}R_nSi–M$ (n = 0–2, M = K, Na or Li).[3] Thus, preparation of trialkylsilyl anions has been a longstanding challenge in silicon chemistry (Scheme 1a).

Recent investigations have increasingly focused on exploiting a transmetallation from silylboranes with bases or metal catalysts for the generation of silyl anion equivalents that provides efficient routes to various silicon compounds (Scheme 1b).[4–6] This approach has significantly expanded the scope of synthesizable organosilicon compounds because trialkylsilyl anion equivalents can be prepared. Despite recent significant progress on nucleophilic silylation chemistry with silylboranes, the development of a general synthetic route to trialkylsilylboranes bearing complex structures or functional groups has remained elusive. A conventional method involves stoichiometric reactions between silyl

anions and boron electrophiles to form the corresponding aryl-substituted silylboranes such as $PhMe_2Si–B(pin)$.[7] However, trialkylsilylboranes cannot be synthesized by this approach. To overcome these limitations, transition-metal-catalyzed strategies under mild conditions are desirable. In this context, Hartwig and co-workers have developed an iridium-catalyzed direct borylation of trialkylhydrosilanes with bis(pinacolato)diboron $B_2(pin)_2$ (Scheme 1c).[8] Although this pioneering approach is remarkable, their method does not enable synthesizing sterically hindered silylboranes such as triisopropylsilyl (TIPS) boronate and also aromatic group-containing silylboranes due to the competition with undesired aromatic C–H borylation reactions (Scheme 1c)[9]. Therefore, synthesizable trialkylsilylboranes are highly limited, and $Et_3S–B(pin)$ was utilized as a silicon pronucleophile in most of the silylation reactions with silylboranes.



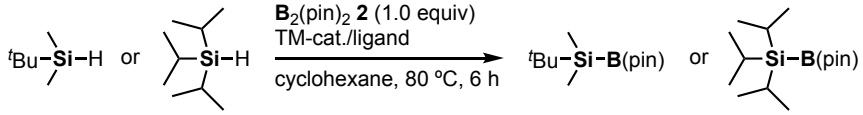
Scheme 1. Synthesis of Trialkylsilyl Anion Equivalents.

In the past decades, transition-metal-catalyzed borylation of C–H bonds has attracted considerable research interest, and various catalytic systems (*e.g.* Ir, Rh, Ru, Ni, Fe, Co, and Pt) have been developed.[10] In contrast, few examples have been reported on the transition-metal-catalyzed borylation of Si–H bonds, which are analogs of C–H bonds. To my knowledge, the iridium-catalyzed borylation of trialkylhydrosilanes with $B_2(pin)_2$ reported by Hartwig group is the only one example.[8] Inspired by these pioneering studies, we envisioned that transition-metal C-H borylation catalysts other than iridium could also be utilized for Si–B bond formation and provide unique reactivity profiles. Here, the author reported the development of general synthetic routes to trialkylsilylboranes via rhodium- or platinum-catalyzed hydrosilane borylation reactions (Scheme 1d). Compared to Hartwig's conditions, the developed systems show a substantially broadened substrate scope. Specifically, the author found that a rhodium catalytic system is particularly effective for the borylation of sterically hindered trialkylsilanes and allows the first synthesis of the TIPS-type silylborane. The author also discovered that a platinum catalyst shows unprecedented high chemoselectivity and allows the first examples of the synthesis of benzyl-group-substituted silylborane and sensitive-functional-group containing trialkylsilylboranes. Furthermore, we investigated their application in organic transformations and demonstrated that these new trialkylsilylboranes can be utilized as silyl anion equivalents, which are difficult to access by previously reported methods. The present study is not a simple extension of the Hartwig's work but represents the development of a new catalytic system for robust Si–H borylation of trialkylhydrosilanes that renders various trialkylsilyl anion equivalents applicable to organic synthesis.

Results and Discussion

The author initially investigated the reactivity of various C–H borylation catalysts in the Si–H borylation of trialkylsilane with $B_2(pin)_2$ (Table 1). As a result of the preliminary investigation using *tert*-butyldimethylsilane (TBS–H) **1a** as the model substrate, the author found that rhodium-, platinum- and nickel-catalytic systems showed higher reactivity than iridium-catalytic system reported by Hartwig group (entries 1–4; For details of the preliminary investigation, see Experimental Section).[8] Also, the reaction of bulky triisopropylsilane (TIPS–H) **1b** with the rhodium catalyst ($[Rh(OMe)(cod)]_2$, ICy·HCl and KO^{t}Bu) produced the corresponding borylated product **3b** in 40% yield, while the reactions with platinum-, nickel- and iridium-catalysts didn't produce **3b** (entry 5–8). Therefore, the author conducted further optimization study for rhodium-catalyzed borylation of hydrosilanes (Table 2; For details of optimization study, see Experimental Section).

Table1. Preliminary Experiments for Transition-Metal Catalyzed Borylation of Trialkylsilanes.[a]



1a **1b** **3a** **3b**

trialkylsilane (4.0 equiv)

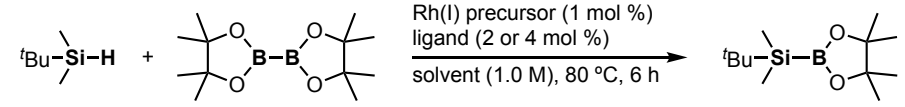
entry	**Si**–H	catalytic system (mol %)	yield [%][b]
1	**1a**	[**Rh**(OMe)(cod)]$_2$ (1.0)/ICy•HCl/K(O^{t}Bu) (4.0)	73
2	**1a**	**Pt**(PPh$_3$)$_4$ (2.0)	86
3[c]	**1a**	**Ni**(cod)$_2$ (2.0)/ICy•HCl / K(O^{t}Bu) (4.0)	77
4	**1a**	[**Ir**(OMe)(cod)]$_2$ (1.0)/dtbpy (2.0)	61
5	**1b**	[**Rh**(OMe)(cod)]$_2$ (1.0)/ICy•HCl/K(O^{t}Bu) (4.0)	40[d]
6	**1b**	**Pt**(PPh$_3$)$_4$ (2.0)	trace[d]
7[c]	**1b**	**Ni**(cod)$_2$ (2.0)/ICy•HCl/K(O^{t}Bu) (4.0)	trace[d]
8	**1b**	[**Ir**(OMe)(cod)]$_2$ (1.0)/dtbpy (2.0)	n.d.[d, e]

[a]Reaction Conditions: trialkylsilane (4.0 equiv), **2** (0.5 mmol), catalyst and ligand in cyclohexane (0.5 mL) at 80 °C for 6 h. [b]GC yield. Tetracosane was used as an internal standard. [c]THF was used as a solvent instead of cyclohexane. [d]GC yield after 24 h. [e]Not detected. Boebel, T. A.; Hartwig, J. F. *Organometallics* **2008**, *27*, 6013.

The author initially screened a series of ligands to identify a more efficient catalytic system (Table 2, entry 1–6). The reaction of **1a** with **2** (1.2 equiv) in the presence of $[Rh(OMe)(cod)]_2$ (1 mol %) and ICy·HCl (4.0 mol %) proceeded smoothly to furnish the corresponding product **3a** in 53% yield (Table 1; entry 1). The presence of KO^{t}Bu was needed to generate the Rh–NHC complex catalyst *in situ*. The use of 4,4-Di-*tert*-butyl-

2,2’-bipyridine (dtbpy; 2.0 mol %) and 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4phen; 2.0 mol %) led to the low yield of **3a** (entries 2 and 3). Using monodentate (4.0 mol %) or bidentate (2.0 mol %) phosphines such as triphenylphosphine (PPh_3), 2-dicyclohexylphosphino-2’,6’-dimethoxybiphenyl (SPhos) and 1,2-bis(diphenylphosphino)ethane (dppe) did not also generate **3a** efficiently (entries 4–6). These results suggest that the presence of NHC ligands is essential to promote the Si–H borylation of **1a** efficiently. Therefore, the author further examined various NHC ligands (Table 2; entries 7–12). The screening of various NHC ligands revealed that ICy·HCl was the best NHC ligand for this Si–H borylation, and **3a** was obtained in 51% yield using ICy·HCl (entry 7). IMe·HCl also showed high reactivity to produce **3a** in 45% yield (entry 8). The use of bulky NHC ligands such as IMes·HCl (entry 9), IPr·HCl (Pr: 2,6-diisopropylphenyl; entry 10), I^{t}Bu·HCl (entry 10) and IAd·HCl (Ad: 1-adamantyl; entry 12) resulted in the low yield of **3a** (entry 9–12). The borylation using $[RhCl(cod)]_2$ exhibited similar reactivity to $[Rh(OMe)(cod)]_2$ (entry 13). The effects of solvents were also examined (entry 14–16), and the use of DMF improved the yield of **3a** (entry 14, 72% yield). Finally, **3a** was obtained in 87% yield (78% isolated yield; entry 17) by increasing the equivalent of $B_2(pin)_2$ (2.5 equiv). These results revealed that the rhodium-catalytic system was effective for the borylation of bulky trialkylsilanes.

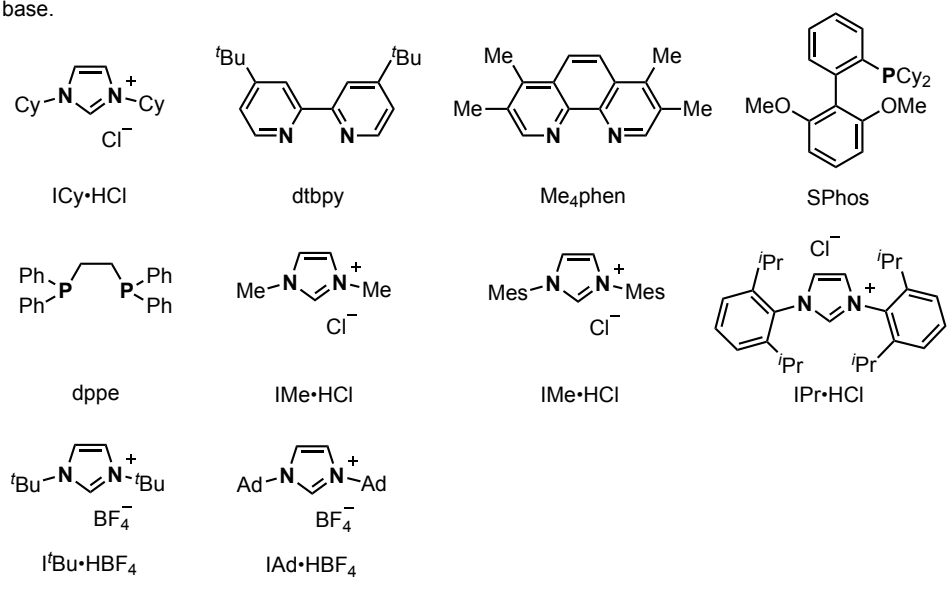
Table 2. Optimization of the Reaction Conditions for the Rhodium-Catalyzed Si–H Borylation of Trialkylsilane (**1a**).[a]



1a (0.5 mmol) **2** (**X** equiv) **3a**

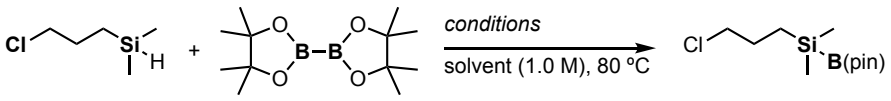
entry	X	Rh(I) precursor	ligand (mol %)	solvent	yield (%)[b]
1	1.2	$[Rh(cod)(OMe)]_2$	ICy•HCl (4.0)[c]	THF	53
2	1.2	$[Rh(cod)(OMe)]_2$	dtbpy (2.0)	THF	4
3	1.2	$[Rh(cod)(OMe)]_2$	Me_4phen (2.0)	THF	7
4	1.2	$[Rh(cod)(OMe)]_2$	PPh_3 (4.0)	THF	11
5	1.2	$[Rh(cod)(OMe)]_2$	SPhos (4.0)	THF	trace
6	1.2	$[Rh(cod)(OMe)]_2$	dppe (2.0)	THF	trace
7	1.2	$[Rh(cod)(OMe)]_2$	ICy•HCl (4.0)[c]	THF	51
8	1.2	$[Rh(cod)(OMe)]_2$	IMe•HCl (4.0)[c]	THF	45
9	1.2	$[Rh(cod)(OMe)]_2$	IMes•HCl (4.0)[c]	THF	8
10	1.2	$[Rh(cod)(OMe)]_2$	IPr•HCl (4.0)[c]	THF	14
11	1.2	$[Rh(cod)(OMe)]_2$	I^{t}Bu•HBF_4 (4.0)[c]	THF	27
12	1.2	$[Rh(cod)(OMe)]_2$	IAd•HBF_4 (4.0)[c]	THF	28
13	1.2	$[Rh(cod)Cl]_2$	ICy•HCl (4.0)[c]	THF	54
14	1.2	$[Rh(cod)(OMe)]_2$	ICy•HCl (4.0)[c]	DMF	72
15	1.2	$[Rh(cod)(OMe)]_2$	ICy•HCl (4.0)[c]	Dioxane	42
16	1.2	$[Rh(cod)(OMe)]_2$	ICy•HCl (4.0)[c]	cyclohexane	53
17	**2.5**	**$[Rh(cod)(OMe)]_2$**	**ICy•HCl (4.0)[c]**	**DMF**	**87 (78)**

[a]Reaction Conditions: TBS–H **1a** (0.5 mmol), **2** (1.2 or 2.5 equiv), Rh(I) precursor (0.005 mmol) and ligand (0.01 or 0.02 mmol) in solvent (0.5 mL) at 80 °C for 6 h. [b]GC yield. Tetracosane was used as an internal standard. Isolated yield is shown in the parentheses. [c]KO^{t}Bu (4 mol %) was added as a base.



Subsequently, the optimized condition for the rhodium catalytic system was applied to the borylation of functional-group containing trialkylsilanes (Table 3). However, trialkylsilane bearing chloro group **1c** didn't undergo the borylation effectively (entry 1). The author also investigated the borylations of **1c** with platinum- and nickel-catalytic system (entry 2, 3). Consequently, the author found that **1c** underwent the platinum-catalyzed borylation to give the corresponding product **3c**, albeit low yield (22% yield, entry 2)[11].

Table 3. Rhodium-, Platinum- and Nickel-Catalyzed Si–H Borylation of Trialkylsilane Containing Chloro Group.[a]



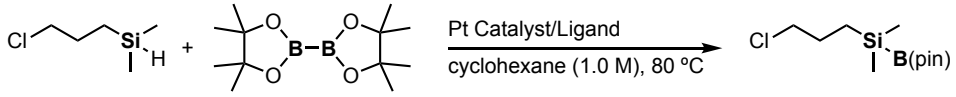
1c **2** (2.5 equiv) **3c**, trace

entry	reaction conditions (mol %)	yield [%][b]
1	[**Rh**(OMe)(cod)]$_2$ (1.0)/ICy•HCl/K(O^{t}Bu) (4.0), DMF	trace
2	**Pt**(PPh$_3$)$_4$ (2.0), cyclohexane	**22**
3	**Ni**(cod)$_2$ (2.0)/ICy•HCl / K(O^{t}Bu) (4.0), cyclohexane	n.d.[c]

[a]Reaction Conditions: trialkylsilane (0.5 mmol), **2** (2.5 equiv), catalyst and ligand in solvent (0.5 mL) at 80 °C. [b]GC yield. Tetracosane was used as an internal standard. [c]Not detected.

Then, further optimization of reaction conditions for the platinum-catalytic system was conducted (Table 4, For details of optimization study, see Experimental Section). The reaction of **1c** with $B_2(pin)_2$ **2** (1.2 equiv) in the presence of $Pt(PPh_3)_4$ produced the corresponding product **3c** in 22% yield (entry 1). Increasing the amount of catalyst loading (2.0 mol %) and **2** (2.5 equiv) drastically improved the yield of **3c** (72%; entry 2). The use of $Pt(dba)_2$ or $Pt(dba)_2$/ ICy·HCl resulted in a moderate yield of **3c** (57% yield, respectively; entry 3,4). Karstedt catalyst showed high reactivity to furnish **3c** in 82% yield (entry 5). The reaction using Pt on Carbon (5 wt% on activated carbon) proceeded smoothly to give **3c** in 85% yield (50% isolated yield; entry 6) as the best result. Pt on Al_2O_3 was also examined and produced **3c** in slightly lower yield (77% yield; entry 7).

Table 4. Optimization of the Reaction Conditions for the Platinum-Catalyzed Si–H Borylation of Trialkylsilane (**1c**).[a]



1c (1.0 equiv) **2** (**X** equiv) **3c**

entry	X	Pt Catalyst (mol %)	ligand (mol %)	time (h)	yield (%)[b]
1	1.2	$Pt(PPh_3)_4$ (1.0)	–	20	22
2	2.5	$Pt(PPh_3)_4$ (2.0)	–	23	72
3	2.5	$Pt(dba)_2$ (2.0)	–	6	57
4	2.5	$Pt(dba)_2$ (2.0)	ICy•HCl (4.0)[c]	6	57
5	2.5	Karstedt catalyst (2.0)	–	6	82
6	**2.5**	**Pt on Carbon (2.0)**	–	**1**	**85 (50)**
7	2.5	Pt on Al_2O_3 (2.0)	–	24	77

[a]Reaction Conditions: trialkylsilane (0.5 mmol), **2** (1.2 or 2.5 equiv), catalyst and ligand in solvent (0.5 mL) at 80 °C. [b]GC yield. Tetracosane was used as an internal standard. Isolated yield is shown in the parentheses. [c]KO^{t}Bu (4 mol %) was added as a base.

To explore the scope of the present rhodium- and platinum-catalyzed Si–H borylations, a variety of trialkylsilanes was tested (Table 5). The iridium-catalyzed borylations were also explored to compare the reactivities of the rhodium, platinum, and iridium catalytic systems. First, the author examined the borylations of sterically hindered trialkylsilanes (Table 5. **3a**–**3j**).

TBS–H **1a** underwent the borylation catalyzed by rhodium and platinum effectively, although iridium catalytic system furnished trace amount of the product. The reaction of TIPS–H **1b** in the presence of $[Rh(OMe)(cod)]_2$/ICy also proceeded smoothly to give the desired silylborane **3a** in good yield (56%). The use of Pt/C resulted in a lower yield of **3a** (20%). $[Ir(OMe)(cod)]_2$/dtbpy exhibited no reactivity to **1b**. A tricyclohexylsilane **1d** also underwent the rhodium-catalyzed borylation, albeit low yield (30%). The molecular structure of **3d** was confirmed by a single-crystal X-ray diffraction analysis (Figure 1). The developed rhodium-catalyzed condition could be applied to trialkylsilanes bearing β-branched alkyl group **1e**–**1h** and methoxy group **1i** (**3e**: 73%; **3f**:75%; **3g**: 20%; **3h**: 52%; **3i**: 50%). The two-fold Si–H borylation of **1j** also provided the corresponding product **3j** in excellent yield (86%). Then, the author investigated functional-group-containing trialkylsilanes (Table 5, **3c**, **3k**, **3l**). Trialkylsilane **1k**, **1k'** containing the benzyl group using Pt/C were efficiently converted into the desired silylborane **3k**, **3k'** without any side reactions (63%, 49%, respectively). The molecular structure of **3k** was determined by a single-crystal X-ray diffraction analysis (Figure 1). In contrast, the iridium catalytic system provided the C–H borylation products in the phenyl group, and the rhodium

catalytic system furnished the mixture of the Si–H and C–H borylation products. The present platinum-catalyzed condition could be applied to trialkylsilanes containing chloro (**1c**, **1c'**), ester group (**1l**) to give the corresponding products in good yield (**3c**: 50%; **3c'**: 50%; **3l**: 42%). The simple, small trialkylsilanes provided the corresponding products in high yields under each condition using iridium, rhodium and platinum catalysts (Table 5, **3m**–**3p**). The liner or cyclic alkyl group substituted hydrosilanes **1m**, **1n**, **1o**, and **1p** underwent the borylations effectively.

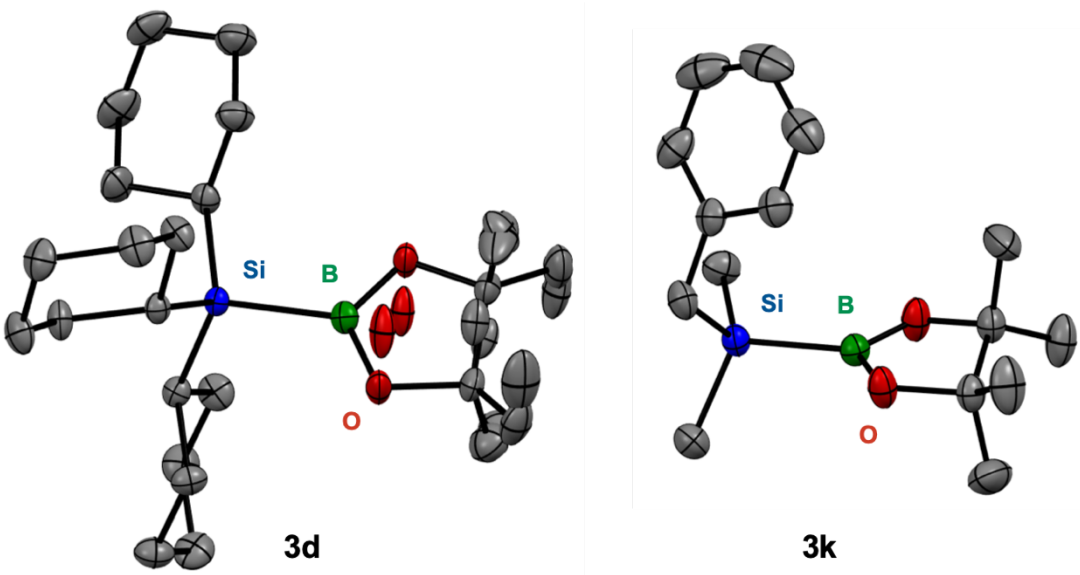
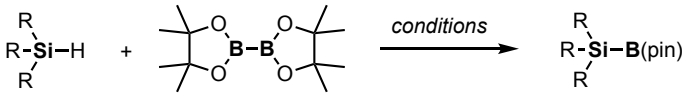


Figure 1. Crystal Structure of **3d** and **3k** with Thermal Ellipsoids at 50% Probability. Hydrogen atoms are omitted for clarity. The B(pin) moiety of **3d** is disordered. Color Code: Grey: Carbon; Green: Boron; Blue: Silicon; Red: Oxygen.

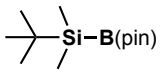
Table 5. Substrate Scope for Si–H Borylation with Rhodium and Platinum Catalysts.[a]



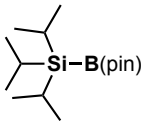
1 **2** (2.5 equiv) **3**

[Rh]: [Rh(OMe)(cod)]$_2$ (1 mol %), ICy·HCl/K(O-*t*-Bu) (4 mol %), DMF, 80 °C
[Pt]: Pt/C (2 mol %), cyclohexane, 80 °C
[Ir]: [Ir(OMe)(cod)]$_2$ (1 mol %), dtbpy (2 mol %), cyclohexane, 80 °C

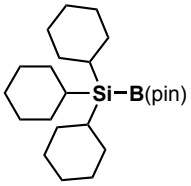
sterically hindered trialkylsilylboranes



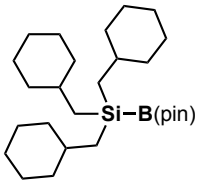
3a
[Rh]: 78 (87)%,
[Pt]: 56 (78)%, [Ir]: (7)%



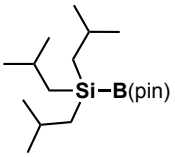
3b
[Rh]: 58%[b], [Pt]: 20%
[Ir]: 0%[c]



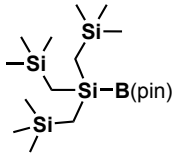
3d
[Rh]: 30%[b]



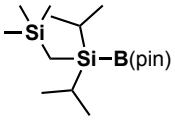
3e
[Rh]: 73%[b], [Ir]: 0%[c]



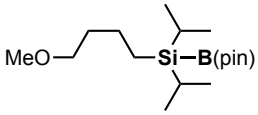
3f
[Rh]: 75%[b], [Ir]: 0%[c]



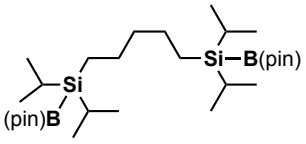
3g
[Rh]: 20%[b]



3h
[Rh]: 52%[b], [Ir]: 0%[c]

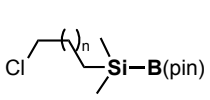


3i
[Rh]: 50%



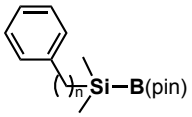
3j
[Rh]: 86%, [Ir]: 0%

phenyl- and functional-groups-containinig trialkylsilylboranes



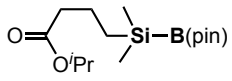
3c (n = 1)
[Pt]: 50 (85)%, [Rh]: (30)%
[Ir]: (37)%

3c' (n = 2)
[Pt]: 50 (70)%, [Ir]: (10)%



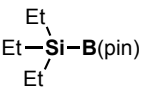
3k (n = 1)
[Pt]: 63%, [Rh]: trace
[Ir]: 0%

3k' (n = 3)
[Pt]: 49 (67)% [Ir]: (24)%

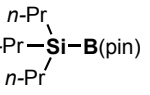


3l
[Pt]: 42 (65)%, [Ir]: 0%

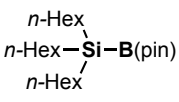
simple trialkylsilylboranes



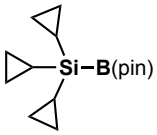
3m
[Rh]: 66%, [Pt]: 62%
[Ir]: 57%



3n
[Rh]: 66%, [Pt]: 52%
[Ir]: 35%



3o
[Rh]: 77%, [Pt]: 63%
[Ir]: 58%

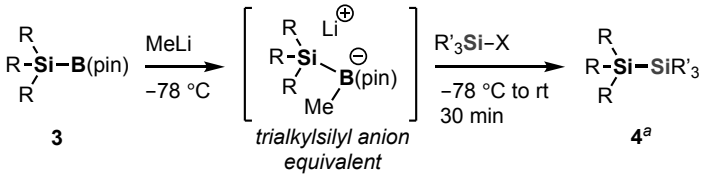


3p
[Rh]: 63%[b], [Pt]: 42%
[Ir]: 55%[c]

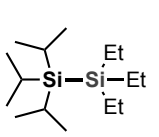
[a]Isolated yields are given. GC yields were shown in the parentheses. Tetracosane was used as an internal standard. [b]The reaction was carried out with [Rh(OMe)(cod)]$_2$ (2.0 mol %) and ICy•HCl/KO^{t}Bu (8.0 mol %). [c]The reaction was carried out with [Ir(OMe)(cod)]$_2$ (2.0 mol %) and dtbpy (4.0 mol %)

Subsequently, the author turned my attention to the application of the obtained trialkylsilylboranes. First, the author focused on the silicon-silicon cross-coupling reactions of silyl electrophiles with trialkylsilylboranes in the presence of nucleophiles (Table 6 and supporting information).[12] A silicon-silicon bond formation is an important step in the synthesis of oligosilanes with unique electronic and optical properties. The reactions of silyl electrophiles with silyl anion equivalents derived from silylboranes and nucleophiles could easily produce the oligosilanes. Therefore, the author envisioned that various oligosilanes, which are difficult to access by precedented methods, could be synthesized using trialkylsilylboranes prepared by the rhodium- or platinum-catalyzed Si–H borylations. Indeed, the reactions of bulky trialkylsilylboranes **3a**–**3d** and **3f** proceeded effectively to afford the corresponding disilanes in high yield, respectively (**4a**: 73%; **4b**:92%; **4c**: 91%; **4d**: 77%). Pleasingly, silylborane **3c** containing chloro group could be applied to the Si–Si coupling reaction with TIPS-OTf (**4e**: 78%). Dichloro-silanes and -disilanes also underwent the reactions to give the tri- or tetrasilanes in good yield. The unsymmetrical trisilane **4f** was obtained using **3a** and **3b**, albeit in low yield (**4f**: 35%). Tricyclohexylsilyl- and triisopropyl-groups could be introduced into dichloro-silane or disilane to give the **4g**, **4h** in moderate yield (**4g**: 55%; **4h**: 61%) if the 2.0 equivalent of **3d** or **3a** were used. The molecular structure of **4g** was confirmed by a single-crystal X-ray diffraction analysis (Figure 2).

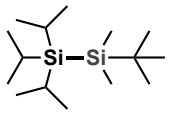
Table 6. Use of Trialkylsilylboranes as Silyl Anion Equivalents in Silicon–Silicon Cross-Coupling Reactions.[12]



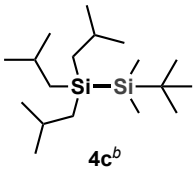
3 | *trialkylsilyl anion equivalent* | **4**[a]



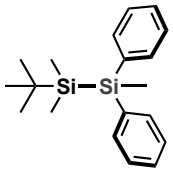
4a[b]
73% yield



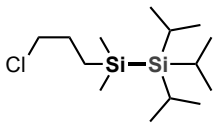
4b[b]
92% yield



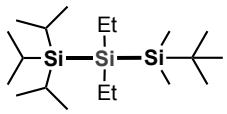
4c[b]
91% yield



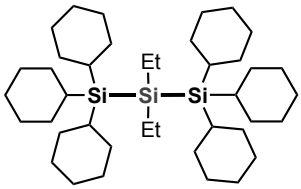
4d[b]
77% yield



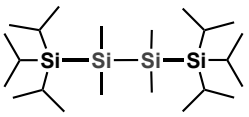
4e[b]
78% yield



4f[c]
35% yield



4g[d]
55% yield



4h[d]
61% yield

[a]Isolated yield are given. [b]Conditions: **3** (0.2 mmol), MeLi (1.1 M in Et_2O, 0.27 mL), silyl electrophile (X = Cl or OTf, 0.4 mmol) in THF (1.0 mL). [c]Conditions: **3a** (0.2 mmol), **3b** (0.2 mmol), MeLi (1.1 M in Et_2O, 0.44 mL), Et_2SiCl_2 (0.2 mmol) in THF (3.0 mL). [d]Conditions: **3** (0.4 mmol), MeLi (1.1 M in Et_2O, 0.41 mL), silyl electrophile (0.2 mmol) in THF (2.0 mL).

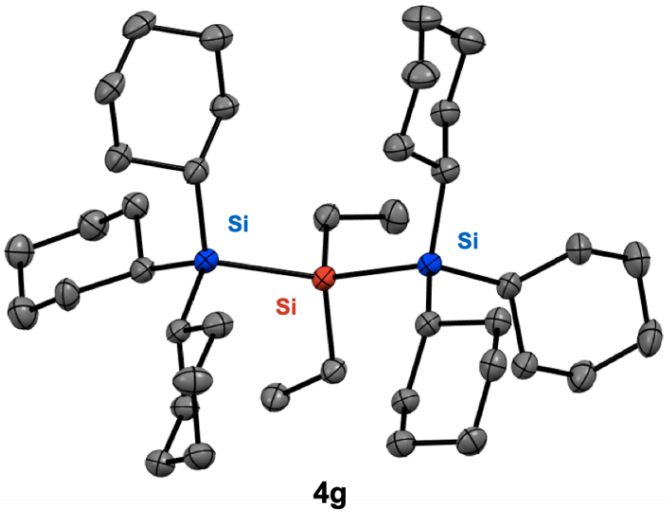
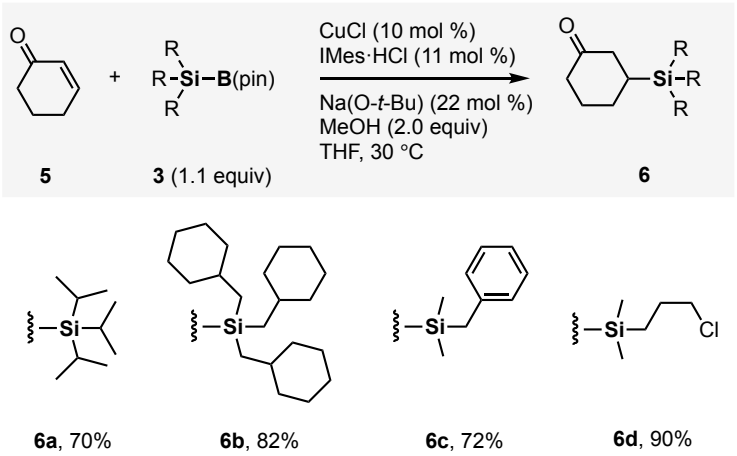


Figure 2. Crystal Structure of **4g** with Thermal Ellipsoids at 50% Probability. Hydrogen atoms are omitted for clarity. Color Code: Grey: Carbon; Blue: Silicon derived from a silylborane; Red: Silicon derived from a silyl electrophile.

Second, the author investigated the reactivities of the obtained trialkylsilylboranes in transition-metal catalyzed reactions. Copper (I)-catalyzed silyl conjugate addition to 2-cyclohexen-1-one with bulky trialkylsilylboranes proceeded effectively to afford the silylation products in high yield, respectively (Table 7, **6a**: 70%; **6b**: 82%).[13] Functional-group-containing trialkylsilylboranes **3c** and **3k** were also used as silylation reagents to produce the corresponding products in high yield, respectively (**6c**: 72%; **6d**: 90%).

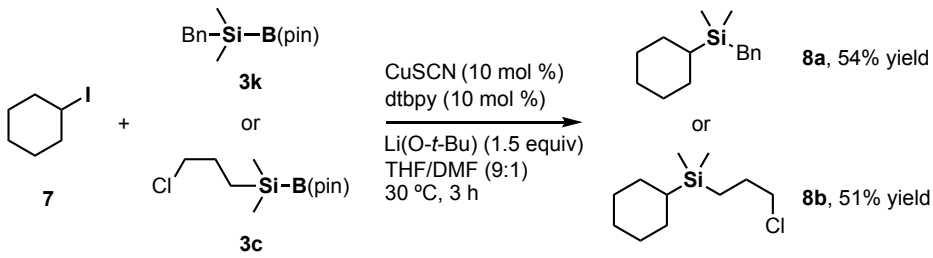
Table 7. Copper (I)-Catalyzed Silyl Conjugate Addition to α,β-Unsaturated Ketone with Various Trialkylsilylboranes.[a]



[a]Conditions: **5** (0.2 mmol), **3** (0.22 mmol), CuCl (0.02 mmol), IMes·HCl (0.022 mmol), Na(O-*t*-Bu) (0.044 mmol) and MeOH (0.4 mmol) in THF (0.6 mL). Isolated yields are given.

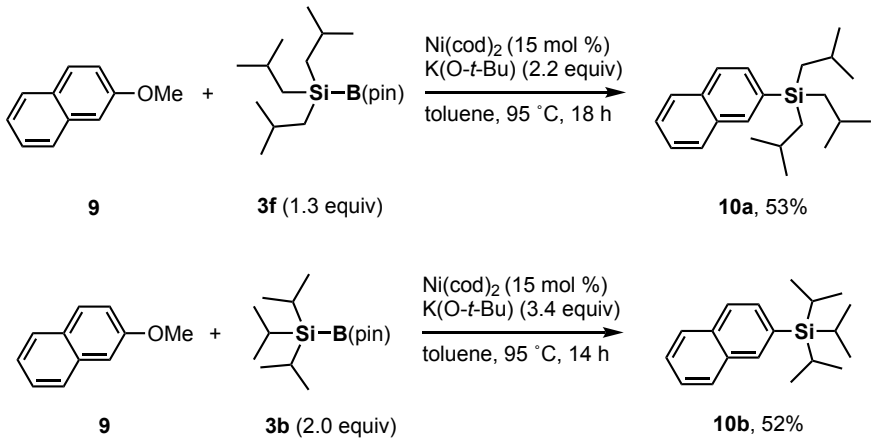
Copper (I)-catalyzed radical silylation of an alkyl iodide with Functional-Group-Containing trialkylsilylboranes was also examined (Scheme 2).[14] Iodocyclohexane underwent the silylations with trialkylsilylboranes **3k** and **3c** to give the corresponding silylation products in moderate yield (**8a**: 54%; **8b**: 51%).

Scheme 2. Copper (I)-Catalyzed Radical Silylation of Alkyl Iodine with Functional-Group-Containing Trialkylsilylboranes.[14]



Sterically hindered trialkylsilylboranes **3f** and **3b** can be applied to the nickel-catalyzed silylation of aryl methyl ethers (Scheme 3).[15] The reactions of 2-methoxynaphthalene with **3f** or **3b** furnished the silylation products in moderate yield, respectively (**10a**: 53%; **10b**: 52%). The results of silicon-silicon cross-coupling reactions and transition-metal catalyzed reactions with various trialkylsilylboranes demonstrates the synthetic utility of this study, and various trialkylsilyl group can be introduced into organic molecules.

Scheme 3. Nickel-catalyzed Silylation of Aryl Methyl Ether with Sterically Hindered Trialkylsilylboranes.[15]



Summary

In conclusion, the author developed the new synthetic method for trialkylsilylborane compounds by the rhodium- or platinum-catalyzed direct borylation of hydrosilanes with bis(pinacolato)diboron. The developed conditions allow the synthesis of new trialkylsilylboranes bearing bulky alkyl groups as well as sensitive functional groups that are inaccessible by previously reported methods. The author demonstrated the use of these trialkylsilylboranes as silyl anion equivalents in organic transformations and significantly expanded the scope of synthesizable organosilicon compounds.

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Experimental

Table of Contents

1. General and Materials.

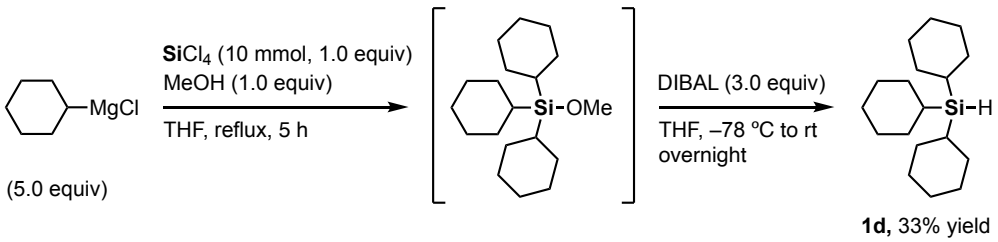
All reactions were performed in oven-dried glassware using conventional Schlenk techniques under a static pressure of nitrogen or argon. Materials were obtained from commercial suppliers and used as received unless otherwise noted. Dry solvents for the reaction were purchased from commercial suppliers, degassed via three freeze-pump-thaw cycles, and further dried over molecular sieves (MS4A) prior to use. Cyclohexane purchased from Tokyo Chemical Industry Co. (TCI) were dried over CaH_2 and distilled prior to use. 1,3-Dicyclohexylimidazolium chloride (ICy·HCl, >98.0%) and K(O-*t*-Bu) (>97.0%) purchased from Tokyo Chemical Industry Co. (TCI) were used as received. $[Rh(OMe)(cod)]_2$ was prepared according to the literature procedures[1]. Pt/C (Platinum on Carbon extent of labeling: 5 wt % loading, matrix activated carbon support) and $[Ir(OMe)(cod)]_2$ purchased from Sigma-Aldrich Co. were used as received. Silica Gel 60 N (40–100 μm, spherical, neutral) purchased from Kanto Chemical Co. was used as received. NMR spectra were recorded on JEOL JNM-ECX400P, ECS-400 and ECZR spectrometers (^{1}H: 400 MHz, ^{13}C: 100 MHz, ^{11}B: 127 MHz, ^{29}Si: 79.5 MHz). Tetramethylsilane (δ = 0.00 ppm for ^{1}H-NMR and ^{29}Si-NMR) and $CDCl_3$ (δ = 77.0 ppm for ^{13}C-NMR) were employed as external standards, respectively. $BF_3·Et_2O$ was used as

an external standard for ^{11}B NMR analysis. Multiplicity was reported as follows: s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, m = multiplet. Mesitylene was used as an internal standard for determining NMR yield. NMR yield was determined by quantitative ^{1}H-NMR analysis of the crude reaction mixture. GLC analyses were conducted with a Shimadzu GC-2014 or GC-2025 equipped with ULBON HR-1 glass capillary column (Shinwa Chemical Industries) and a FID detector. 1,4-Diisopropylbenzene was used as an internal standard for determining GC yield. Recycle preparative gel chromatography (GPC) was conducted with JAILC-9101 using $CHCl_3$ as an eluent. Single crystal X-ray structural analyses were carried out on a Rigaku XtaLAB AFC11 (RCD3) and XtaLAB PRO MM007 diffractometer using graphite monochromated Mo-K_α or Cu- K_α radiation. The structure was solved by direct methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the Olex2 crystallographic software package except for refinement, which was performed using SHELXL-2013. High-resolution mass spectra were recorded at the Global Facility Center for Instrumental Analysis, Hokkaido University.

2. Substrate Synthesis

Trialkylhydrosilanes **1a**, **1b**, **1m**, **1n**, and **1o** were purchased from commercial suppliers (Tokyo Chemical Industry Co. or Sigma-Aldrich Co.) and used as received unless otherwise noted. **1c** was prepared according to the literature procedure.[2] **1k'** was prepared according to the same procedure for **1e** and ^{1}H and ^{13}C NMR spectra of **1k'** were in agreement with those in the literature.[3]

Preparation of Tricyclohexylsilane (1d)



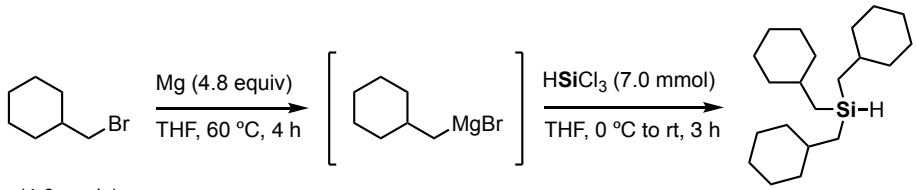
The reaction was performed according to the literature procedure.[4,5] A oven-dried 100 mL, two-necked round-bottomed flask was charged with tetrachlorosilane $SiCl_4$ (1.7 g, 10 mmol) and THF (2.0 mL). MeOH (320.4 mg, 10 mmol, 1.0 equiv) was added dropwise to the vial, and the mixture was stirred for 30 min at room temperature.

Cyclohexylmagnesium chloride (1.0 M in 2-methyltetrahydrofuran, 50 mL, 50 mmol, 5.0 equiv) was added dropwise to the mixture, and then the resulting mixture was stirred at 80 °C (reflux) for 30 h. After cooled to room temperature, the resulting mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O three times. The combined organic layer was washed with saturated aqueous NaCl and dried over Na_2SO_4, followed by filtration and evaporation to give the crude product. The crude product was used in the next step without further purification.

In an oven-dried 100 mL, two-necked round-bottomed flask, the obtained crude material was dissolved in toluene (20 mL) under nitrogen atmosphere. After the mixture was cooled to –78 °C, DIBAL (ca. 1.0 M in toluene, 30 mL, 30 mmol) was added dropwise to the mixture, and the resulting mixture was stirred for 1 h at –78 °C. Then, the reaction mixture was allowed to warm to room temperature and stirred overnight. The resulting suspension was quenched by the addition of 1 M HCl aqueous solution. The mixture was extracted with Et_2O three times, and dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography (SiO_2, hexane) and GPC to afford the corresponding silane **1d** (924.7 mg, 3.32 mmol, 33% yield by 2 steps) as a colorless viscous oil.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.80–0.93 (m, 3H), 1.11–1.32 (m, 15H), 1.71 (d, J = 7.4 Hz, 15H), 3.19 (q, J = 2.2 Hz, 1H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 22.0 (*C*H), 27.0 (*C*H_2), 28.3 (*C*H_2), 29.4 (*C*H_2). HRMS–EI (*m/z*): $[M]^+$ calcd for $C_{18}H_{34}{}^{28}Si$, 278.2430; found, 278.2432.

Preparation of Tri(cyclohexylmethyl)silane (1e)



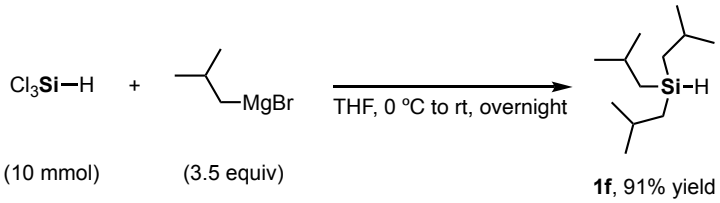
In an oven-dried 50 mL, two-necked round-bottomed flask equipped with a condenser was placed dry magnesium turnings (816.8 mg, 33.6 mmol, 4.8 equiv) under nitrogen atmosphere. After the magnesium was further flame dried under nitrogen atmosphere, a crystal of I_2 and THF (28 mL) were added to the flask. Then, (bromomethyl)cyclohexane (3.87 mL, 28 mmol, 4.0 equiv) was slowly added to the reaction mixture at room temperature. After the mixture was stirred for 4 h at 60 °C, the heating was stopped and the mixture was allowed to cool to room temperature.

(Cyclohexlymethyl)magnesium bromide in THF solution prepared above was

transferred to another oven-dried 100 mL, two-necked round-bottomed flask. Then, trichlorosilane $HSiCl_3$ (708 μL, 7.0 mmol, 1.0 equiv) was added dropwise to the flask at 0 °C, and the resulting mixture was stirred for 3 h at room temperature. The resulting mixture was quenched with 1 M HCl aqueous solution and extracted with Et_2O three times. The combined organic layer was washed with saturated aqueous NaCl and dried over Na_2SO_4, followed by filtration and evaporation. The crude product was purified by flash chromatography (SiO_2, hexane) and GPC to afford the corresponding silane **1e** (1.56 g, 4.88 mmol, 70% yield) as a colorless viscous oil. ^1H and ^{13}C NMR spectra were in agreement with those in the literature.[6]

^1H NMR (392 MHz, $CDCl_3$, δ): 0.54 (dd, J = 3.7, 7.3 Hz, 6H), 0.84–0.99 (m, 6H), 1.05–1.29 (m, 9H), 1.29–1.41 (m, 3H), 1.56–1.77 (m, 15H), 3.86 (sept, J = 3.3 Hz, 1H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 21.5 (CH_2), 26.3 (CH_2), 26.6 (CH_2), 34.8 (CH), 36.6 (CH_2). HRMS–EI (*m/z*): $[M–C_7H_{13}]^+$ calcd for $C_{14}H_{27}{}^{28}Si$, 223.1882; found, 223.1882.

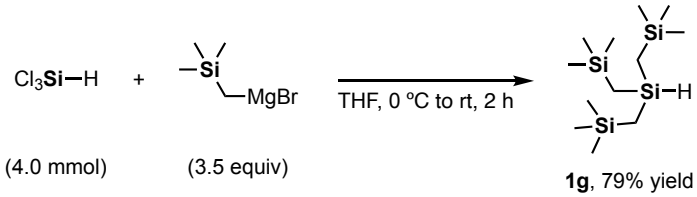
Preparation of Triisobutylsilane (1f)



Isobutylmagnesium chloride (2.0 M in THF, 17.5 mL, 35 mmol, 3.5 equiv) and THF (20 mL) were added to an oven-dried 100 mL, two-necked round-bottomed flask. After the mixture was cooled to 0 °C, trichlorosilane $HSiCl_3$ (1.0 mL, 10 mmol, 1.0 equiv) was added dropwise to the flask at 0 °C, and the resulting mixture was stirred overnight at room temperature. The resulting mixture was quenched with 1 M HCl aqueous solution and extracted with Et_2O three times. The combined organic layer was washed with saturated aqueous NaCl and dried over $MgSO_4$, followed by filtration and evaporation. The crude product was purified by flash chromatography (SiO_2, pentane) to afford the corresponding silane **1f** (1.82 g, 9.1 mmol, 91% yield) as a colorless liquid.

^1H NMR (401 MHz, $CDCl_3$, δ): 0.58 (dd, J = 3.3, 7.0 Hz, 6H), 0.95 (d, J = 6.4 Hz, 18H), 1.76 (nonet, J = 6.7 Hz, 3H), 3.85 (sept, J = 3.4 Hz, 1H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 23.0 (CH_2), 25.4 (CH), 25.9 (CH_3). HRMS–EI (*m/z*): $[M–CH_3]^+$ calcd for $C_{11}H_{25}{}^{28}Si$, 185.1726; found, 185.1729.

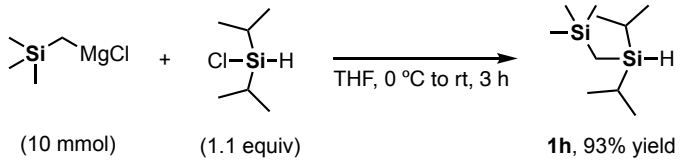
Preparation of Tris[(trimethylsilyl)methyl]silane (1g)



(Trimethylsilyl)methylmagnesium chloride (1.0 M in THF, 14 mL, 14 mmol, 3.5 equiv) was added to an oven-dried 100 mL, two-necked round-bottomed flask. After the mixture was cooled to 0 °C, trichlorosilane $HSiCl_3$ (1.0 mL, 4.0 mmol, 1.0 equiv) was added dropwise to the flask at 0 °C, and the resulting mixture was stirred overnight at room temperature. The resulting mixture was quenched with 1 M HCl aqueous solution and extracted with Et_2O three times. The combined organic layer was washed with saturated aqueous NaCl and dried over Na_2SO_4, followed by filtration and evaporation. The crude product was purified by flash chromatography (SiO_2, hexane) to afford the corresponding silane **1g** (916.6 mg, 3.15 mmol, 79% yield) as a colorless liquid.

^{1}H NMR (396 MHz, $CDCl_3$, δ): –0.22 (d, J = 4.0 Hz, 6H), 0.04 (s, 27H), 4.07 (sept, J = 3.6 Hz, 1H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 0.97 (CH_3), 3.1 (CH_2). HRMS–EI (*m/z*): $[M–CH_3]^+$ calcd for $C_{11}H_{31}{}^{28}Si_4$, 275.1503; found, 275.1497.

Preparation of [(Diisopropylsilyl)methyl]trimethylsilane (1h)

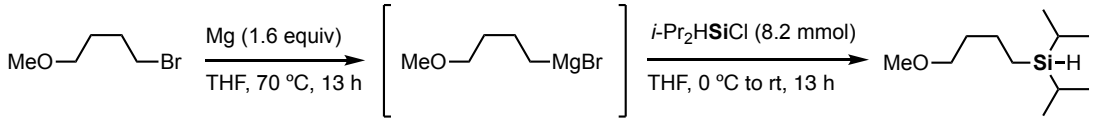


(Trimethylsilyl)methylmagnesium chloride (1.0 M in THF, 10 mL, 10 mmol, 1.0 equiv) was added to an oven-dried 100 mL, two-necked round-bottomed flask. After the mixture was cooled to 0 °C, chlorodiisopropylsilane *i*-Pr_2HSiCl (1.9 mL, 11 mmol, 1.1 equiv) was added dropwise to the flask at 0 °C, and the resulting mixture was stirred overnight at room temperature. The resulting mixture was quenched with 1 M HCl aqueous solution and extracted with Et_2O three times. The combined organic layer was washed with saturated aqueous NaCl and dried over Na_2SO_4, followed by filtration and evaporation. The crude product was purified by flash chromatography (SiO_2, pentane) to afford the corresponding silane **1h** (1.89 g, 9.33 mmol, 93% yield) as a colorless viscous oil.

^{1}H NMR (401 MHz, $CDCl_3$, δ): –0.35 (d, J = 4.0 Hz, 2H), 0.04 (s, 9H), 0.88–0.97 (m, 2H), 1.00 (dd, J = 2.4, 6.4 Hz, 12H), 3.52 (sept, J = 1.9 Hz, 1H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): –6.7 (CH_2), 0.69 (CH_3), 11.6 (CH), 18.6 (CH_3), 18.8 (CH_3). HRMS–EI (*m/z*):

$[M–CH_3]^+$ calcd for $C_9H_{23}{}^{28}Si_2$, 187.1338; found, 187.1339.

Preparation of Diisopropyl(4-methoxybutyl) silane (1i)



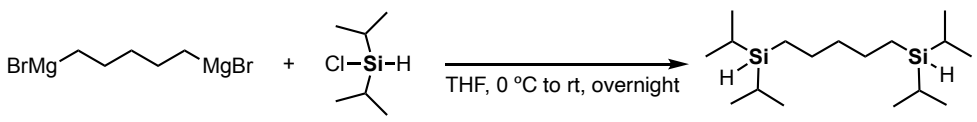
(1.3 equiv) **1i**, 83% yield

In an oven-dried 50 mL, two-necked round-bottomed flask equipped with a condenser was placed dry magnesium turnings (322.1 mg, 13.2 mmol, 1.6 equiv) under nitrogen atmosphere. After the magnesium was further flame dried under nitrogen atmosphere, a crystal of I_2 and THF (11 mL) were added to the flask. Then, 1-Bromo-4-methoxybutane (1.4 mL, 11 mmol, 1.3 equiv) was slowly added to the reaction mixture at room temperature. After the mixture was stirred for 3 h at 70 °C, the heating was stopped and the mixture was allowed to cool to room temperature.

In an oven-dried 100 mL round bottomed flask, chlorodiisopropylsilane (1.4 mL, 8.2 mmol) was dissolved in THF (40 mL) under nitrogen atmosphere. After the reaction mixture was cooled to 0 °C, a THF solution of 4-methoxybutylmagnesium bromide (1.0 M, 11 mL, 11 mmol) was added dropwise to the reaction mixture, and the mixture was warmed to room temperature. After stirred for 13 h, the resulting suspension was quenched by the addition of 1 M HCl aqueous solution. The mixture was extracted with Et_2O three times and dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography with pentane/Et_2O eluent (100:0 to 98:2) to afford the corresponding silane **1i** (1.38 g, 6.8 mmol, 83%) as a colorless oil.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.60–0.65 (m, 2H), 0.94–1.05 (m, 14H), 1.40–1.49 (m, 2H), 1.62 (quint, J = 7.1 Hz, 2H), 3.33 (s, 3H), 3.38 (t, J = 6.5 Hz, 2H), 3.41–3.42 (m, 1H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 8.23 (CH_2), 10.5 (CH), 18.7 (CH_3), 19.0 (CH_3), 21.9 (CH_2), 33.4 (CH_2), 58.5 (CH_3), 72.5 (CH_2). HRMS-EI (m/z): $[M–{}^iPr]^+$ calcd for $C_8H_{19}O^{28}Si$, 159.1205; found, 159.1206.

Preparation of 1,5-Bis(diisopropylsilyl)pentane (1j)



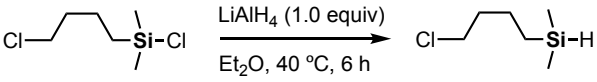
(8.0 mmol) (2.2 equiv) **1j**, 93% yield

Pentamethylenebis(magnesium bromide) (0.5 M in THF, 16 mL, 8.0 mmol, 1.0 equiv)

and THF (16 mL) were added to an oven-dried 100 mL, two-necked round-bottomed flask. After the mixture was cooled to 0 °C, chlorodiisopropylsilane (3.0 mL, 17.6 mmol, 2.2 equiv) was added dropwise to the flask at 0 °C, and the resulting mixture was stirred overnight at room temperature. The resulting mixture was quenched with 1 M HCl aqueous solution and extracted with Et_2O three times. The combined organic layer was washed with saturated aqueous NaCl and dried over $MgSO_4$, followed by filtration and evaporation. The crude product was purified by flash chromatography (SiO_2, hexane) to afford the corresponding silane **1j** (1.89 g, 9.33 mmol, 93% yield) as a colorless viscous oil.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.54–0.64 (m, 4H), 0.92–1.05 (m, 28H), 1.34–1.43 (m, 6H), 3.38–3.43 (m, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 8.3 (*C*H_2), 10.6 (*C*H), 18.8 (*C*H_3), 19.1 (*C*H_3), 24.9 (*C*H_2), 37.6 (*C*H_2). HRMS-EI (*m*/*z*): $[M–^iPr]^+$ calcd for $C_{14}H_{33}{}^{28}Si_2$, 257.2121; found, 257.2120.

Preparation of (4-Chlorobutyl)dimethylsilane (1c')

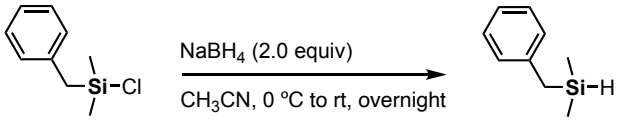


(1.3 equiv) **1c'**, 78% yield

The reaction was performed according to the literature procedure[9]. In an oven-dried 100 mL, two-necked round bottomed flask, $LiAlH_4$ (262.8 mg, 6.9 mmol) was dissolved in EtO_2 (20 mL) under nitrogen atmosphere. Then (4-chlorobuthyl)dimethylchlorosilane (3.6 mL, 20 mmol) was added dropwise to the reaction mixture, and the mixture was warmed to 40 °C. After stirred for 6 h, the resulting suspension was quenched by the addition of H_2O. The mixture was then extracted with Et_2O three times and dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO_2, hexane) to afford the corresponding silane **1c'** (2.35 g, 15.6 mmol, 78% yield) as a colorless oil.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.08 (d, *J* = 3.9 Hz, 6H), 0.60 (td, *J* = 3.1, 8.2 Hz, 2H), 1.50–1.55 (m, 2H), 1.81 (quint, *J* = 7.1 Hz, 2H), 3.55 (t *J* = 6.7 Hz, 2H), 3.83–3.88 (m, 1H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): –4.55 (*C*H_3), 13.3 (*C*H_2), 21.7 (*C*H_2), 35.8 (*C*H_2), 44.7 (*C*H_2). HRMS-EI (*m*/*z*): $[M–CH_3]^+$ calcd for $C_5H_{12}Cl^{28}Si$, 135.0397; found, 135.0392.

Preparation of Benzyldimethylsilane (1k)

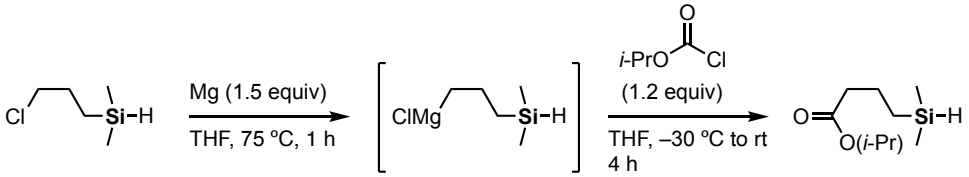


(20 mmol) **1k**, 78% yield

The reaction was performed according to the literature procedure.[4] Benzyldimethylchlorosilane (3.7 mL, 20 mmol, 1.0 equiv) was added dropwise to a suspension of $NaBH_4$ (1.5 g, 40 mmol, 2.0 equiv) in CH_3CN (30 mL) at 0 °C under nitrogen atmosphere. The reaction mixture was allowed to warm to room temperature and stirred overnight. Then, the resulting suspension was quenched by the addition of 1 M HCl aqueous solution. The mixture was extracted with Et_2O three times, and dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography (SiO_2, pentane) to afford the corresponding silane **1k** (2.33 g, 15.5 mmol, 78% yield) as a colorless oil. ^1H and ^{13}C NMR spectra were in agreement with those in the literature.[7]

^1H NMR (401 MHz, $CDCl_3$, δ): 0.06 (d, J = 4.0 Hz, 6H), 2.16 (d, J = 3.2 Hz, 2H), 3.95 (non, J = 3.5 Hz, 1H), 7.04 (d, J = 6.8 Hz, 2H), 7.08 (t, J = 7.6 Hz, 1H), 7.18–7.26 (m, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): –4.7 (*C*H_3), 24.2 (*C*H_2), 124.2 (*C*H), 128.1 (*C*H), 128.3 (*C*H), 140.0 (*C*H). HRMS–EI (*m/z*): $[M]^+$ calcd for $C_9H_{14}{}^{28}Si$, 150.0865; found, 150.0867.

Preparation of Isopropyl 4-(dimethylsilyl)butanoate (1l).



1c (20 mmol) **1l**, 33% yield

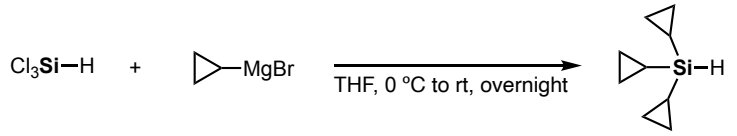
The reduction was performed according to the literature procedure[2]. In an oven-dried 100 mL, two-necked round-bottomed flask equipped with a condenser was placed dry magnesium turnings (739.2 mg, 30.4 mmol, 1.5 equiv) under nitrogen atmosphere. After the magnesium was further flame dried under nitrogen atmosphere, a crystal of I_2 and THF (30 mL) were added to the flask. Then, (3-chloropropyl)dimethylsilane **1c** (3.2mL, 20 mmol) was slowly added to the reaction mixture at room temperature. After the mixture was stirred for 1 h at 75 °C, the heating was stopped and the mixture was allowed to cool to room temperature.

In an oven-dried 100 mL round bottomed flask, isopropyl chloroformate (2.8 mL, 24

mmol, 1.2 equiv) was dissolved in THF (14 mL) under nitrogen atmosphere. After the reaction mixture was cooled to –30 °C, a THF solution of 3-(dimethyldilyl)propylmagnesium chloride (0.67 M, 30 mL, 20 mmol) was added dropwise to the reaction mixture and the mixture was warmed to room temperature. After stirred for 4 h, the resulting suspension was quenched by the addition of 1 M HCl aqueous solution. The mixture was the extracted with Et_2O three times and dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography with pentane/Et_2O eluent (100:0 to 97:3) to afford the corresponding silane **1l** (1.25 g, 6.65 mmol, 33%) as a colorless oil.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.08 (d, J = 4.3 Hz, 6H), 0.59–0.64 (m, 2H), 1.23 (d, J = 6.3 Hz, 6H), 1.63–1.71 (m, 2H), 2.30 (t, J = 7.4 Hz, 2H), 3.85 (sept, J = 3.5 Hz, 1H), 5.01 (sept, J = 6.3 Hz, 1H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): –4.67 (*C*H_3), 13.8 (*C*H_2), 20.1 (*C*H_2), 21.8 (*C*H_3), 37.8 (*C*H_2), 67.2 (*C*H), 173.0 (*C*). HRMS-EI (*m*/*z*): $[M–CH_3]^+$ calcd for $C_8H_{17}O_2{}^{28}Si$, 173.0998; found, 173.0998.

Preparation of Tricyclopropylsilane (1p)



Cyclopropylmagnesium bromide (0.5 M in THF, 40 mL, 20 mmol, 3.3 equiv) was added to an oven-dried 100 mL, two-necked round-bottomed flask. After the mixture was cooled to 0 °C, trichlorosilane $HSiCl_3$ (0.60 mL, 6.0 mmol, 1.0 equiv) was added dropwise to the flask at 0 °C, and the resulting mixture was stirred overnight at room temperature. The resulting mixture was quenched with 1 M HCl aqueous solution and extracted with Et_2O three times. The combined organic layer was washed with saturated aqueous NaCl and dried over Na_2SO_4, followed by filtration and evaporation. The crude product was purified by flash chromatography (SiO_2, pentane) to afford the corresponding silane **1p** (637.5 mg, 4.19 mmol, 70% yield) as a colorless liquid.

^{1}H NMR (396 MHz, $CDCl_3$, δ): –0.96 (dddd, J = 3.0, 6.7, 9.8, 16.5 Hz, 3H), 0.32–0.37 (m, 6H), 0.56–0.62 (m, 6H), 3.25 (q, J = 3.1 Hz, 6H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): –9.4 (*C*H), 1.24 (*C*H_2). HRMS-EI (*m*/*z*): $[M–H]^+$ calcd for $C_9H_{15}{}^{28}Si$, 151.09430; found, 151.09446.

3. General Experimental Procedures for Si–H Borylation of Trialkylsilanes.

3-1. General Procedures for Rhodium-Catalyzed Si-H Borylation: Procedure A.

$[Rh(OMe)(cod)]_2$ (2.4 mg, 0.005 mmol, 1.0 mol %), ICy·HCl (5.4 mg, 0.020 mmol, 4.0 mol %), and bis(pinacolato)diboron (317.4 mg, 1.25 mmol, 2.5 equiv) were placed in a vial with a screw cap containing a Teflon®-coated rubber septum under air. Then, K(O-*t*-Bu) (2.2 mg, 0.020 mmol, 4.0 mol %) was also added to the vial in a glove box under an argon atmosphere. After the reaction vial was removed from the glove box, DMF (0.5 mL) was added to the vial via a syringe. The resulting mixture was stirred for 5 min at rt, then trialkylsilane **1a** (58.1 mg, 0.50 mmol, 1.0 equiv) was added dropwise to the vial. After the resulting mixture was stirred at 80 °C for 6 h, the reaction mixture was analyzed by GC to check the completeness of the reaction. The mixture was directly filtered through a short silica-gel column with Et_2O as an eluent, then the resultant solution was concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography with hexane/EtOAc eluent (100:0 to 95:5) to give the corresponding product **3a** in 78% yield (94.2 mg, 0.39 mmol) as a white solid.

3-2. General Procedure for Platinum-Catalyzed Si-H Borylation: Procedure B.

Platinum on carbon (5 wt % loading, matrix activated carbon support) (1.9 mg, 0.01 mmol, 2.0 mol %) and bis(pinacolato)diboron (316.3 mg, 1.25 mmol, 2.5 equiv) were placed in a vial with a screw cap containing Teflon®-coated rubber septum under air. Then, the reaction vial was connected to a vacuum-nitrogen manifold through a needle, and it was evacuated and refilled with nitrogen three times. Cyclohexane (0.50 mL) was added to the vial via a syringe. Trialkylsilane **1a** (58.1 mg, 0.50 mmol, 1.0 equiv) was added dropwise to the vial. After the resulting mixture was stirred at 80 °C for 1 h, the reaction mixture was analyzed by GC to check the completeness of the reaction and determine GC yield of the product (77% GC yield). The mixture was directly filtered through filter paper with Et_2O as an eluent, then the resultant solution was concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography with hexane/Et_2O eluent (100:0 to 95:5) to give the corresponding product **3c** in 56% yield (68.1 mg, 0.28 mmol) as a white solid.

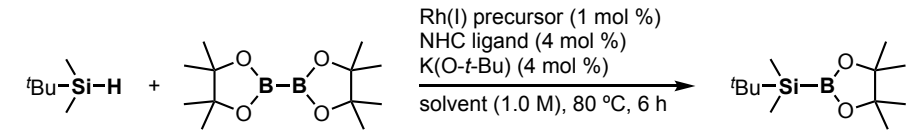
3-3. General Procedure for Iridium-Catalyzed Si-H Borylation: Procedure C.

$[Ir(OMe)(cod)]_2$ (3.3 mg, 0.005 mmol, 1.0 mol %), dtbpy (2.7 mg, 0.010 mmol, 2.0 mol %), and bis(pinacolato)diboron (317.4 mg, 1.25 mmol, 2.5 equiv) were placed in a vial with a screw cap containing a Teflon®-coated rubber septum under air. Then, the

reaction vial was connected to a vacuum-nitrogen manifold through a needle, and it was evacuated and refilled with nitrogen three times. Cyclohexane (0.5 mL) was added to the vial via a syringe. The resulting mixture was stirred for 5 min at rt, then trialkylsilane **1a** (58.1 mg, 0.50 mmol, 1.0 equiv) was added dropwise to the vial. After the resulting mixture was stirred at 80 °C for 6 h, the reaction mixture was analyzed by GC to check the completeness of the reaction and determine GC yield of the product (8% GC yield).

4. Optimization Study for Rh- and Pt-Catalyzed Si–H Borylation.

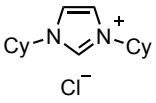
Table S1. NHC Ligand Screening.[a]

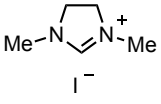


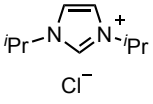
1b (0.5 mmol) **2** (1.2 equiv) **3b**

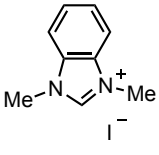
entry	Rh(I) precursor	ligand	solvent	yield (%)[b]
1	$[Rh(cod)(OMe)]_2$	ICy•HCl	THF	53
2	**$[Rh(cod)(OMe)]_2$**	**ICy•HCl**	**DMF**	**72 (62)**
3	$[Rh(cod)(OMe)]_2$	SIMe•HI	DMF	**70**
4	$[Rh(cod)(OMe)]_2$	**L1**	DMF	55
5	$[Rh(cod)(OMe)]_2$	**L2**	DMF	37
6	$[Rh(cod)(OMe)]_2$	**L3**	DMF	33
7	$[Rh(cod)(OMe)]_2$	**L4**	DMF	57
8	$[Rh(cod)(OMe)]_2$	**L5**	DMF	56
9	$[Rh(cod)(OMe)]_2$	**L6**	DMF	62
10	$[Rh(cod)(OMe)]_2$	**L7**	DMF	N.D.
11	[(ICy)RhCl(cod)][c]		DMF	40

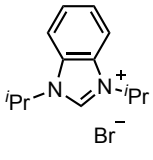
[a]Reaction Conditions: TBS–H **1b** (0.5 mmol), **2** (1.2 equiv), Rh(I) precursor (0.005 mmol) and ligand (0.02 mmol) in solvent (0.5 mL) at 80 °C for 6 h. [b]GC yield. Tetracosane was used as an internal standard. Isolated yield is shown in the parentheses.

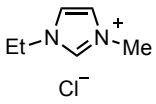

ICy•HCl

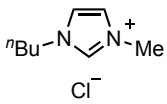

SIMe•HI

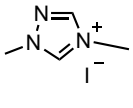

L1


L2


L3


L4


L5


L6

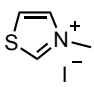
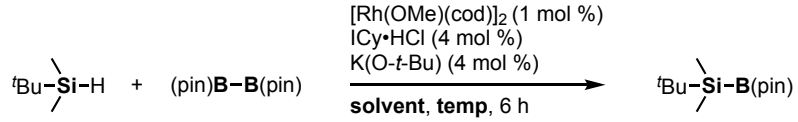

L7

Table S2. Solvent Screening and Investigation of Reaction Temperature.[a]

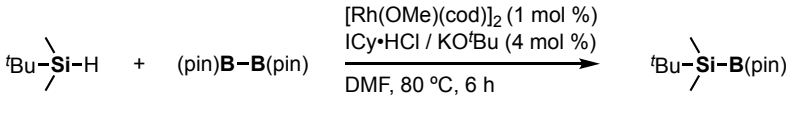


1b (0.5 mmol) **2** (1.2 equiv) **3b**

entry	solvent (1.0 M)	temp (ºC)	yield (%)[b]
1	**DMF**	**80**	**72 (62)**
2	DMA	80	59
3	DMI	80	32
4	NMP	80	14
5	CH_3CN	80	15
6	cyclohexane	80	53
7	toluene	80	48
8	DME	80	49
9	1,4-dioxane	80	41
10	$^nBu_2O$	80	48
11	CPME	80	51
12	DMF	70	47
13	DMF	60	44

[a]Reaction Conditions: TBS–H **1b** (0.5 mmol), **2** (1.2 equiv), Rh(I) precursor (0.005 mmol) and ligand (0.02 mmol) in solvent (0.5 mL) at 80 °C for 6 h. [b]GC yield. Tetracosane was used as an internal standard. Isolated yield is shown in the parentheses.

Table S3. Investigation of Equivalents of Silane and Diboron.[a]

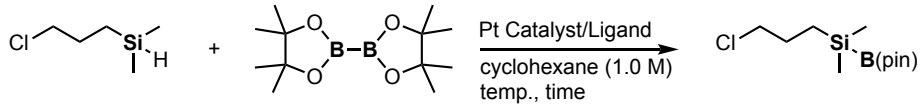


(**X** equiv) (**Y** equiv) GC yield
(1.0 equiv = 0.5 mmol)

entry	***Si***–H (**X** equiv)	$\boldsymbol{B}_2(pin)_2$ (**Y** equiv)	yield (%)[b]
1	1.0 (0.5 mmol)	1.2	72 (62)
2	1.0	1.5	76
3	1.0	2.0	75
4	**1.0**	**2.5**	**87 (78)**
5	1.5	1.0 (0.5 mmol)	65
6	2.0	1.0	62
7	2.5	1.0	60

[a]Reaction Conditions: TBS–H **1b** (**X** mmol), **2** (**Y** equiv), Rh(I) precursor (0.005 mmol) and ligand (0.02 mmol) in solvent (0.5 mL) at 80 °C for 6 h. [b]GC yield. Tetracosane was used as an internal standard. Isolated yield is shown in the parentheses.

Table S4. Optimization of Reaction Conditions for Pt Catalytic System.



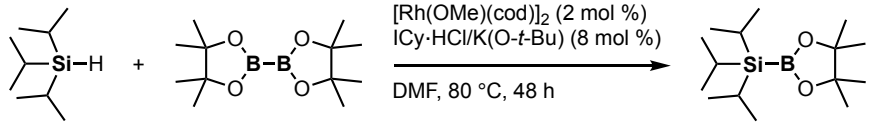
1k (1.0 equiv) **2** (2.5 equiv) **3k**

entry	Pt catalyst (mol %)	ligand	temp. (ºC)	time (h)	yield (%)[b]
1	$Pt(PPh_3)_4$ (2.0)	–	80	23	72
2	$Pt(dba)_2$ (2.0)	–	80	6	57
3	$Pt(dba)_2$ (2.0)	ICy•HCl (4.0)	80	6	57
4	Karstedt catalyst (2.0)	–	80	6	82
5	**Pt on Carbon (2.0)**	–	**80**	**1**	**85 (50)**
6	Pt on Al_2O_3 (2.0)	–	80	24	77
7	Pt on Carbon (2.0)	–	50	6	77
8	Pt on Carbon (2.0)	–	rt	24	73
9[c]	Pt on Carbon (2.0)	–	80	23	70

[a]Reaction Conditions: **1k** (0.5 mmol), **2** (2.5 equiv), Pt catalyst (0.01 mmol) in cyclohexane (0.5 mL). [b]GC yield. Tetracosane was used as an internal standard. Isolated yield is shown in the parentheses. [c]Octane was used an solvent.

5. Large-Scale Synthesis of Trialkylsilylborane.

Large-Scale Synthesis of 3b.

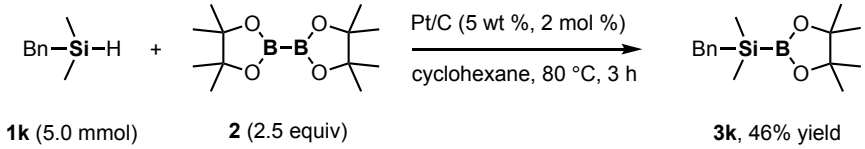


1b (5.0 mmol) **2** (2.5 equiv) **3b,** 61% yield

$[RhCl(cod)]_2$ (49.7 mg, 0.10 mmol, 2.0 mol %), ICy·HCl (107.9 mg, 0.40 mmol, 8.0 mol %), and bis(pinacolato)diboron (3.17 g, 12.5 mmol, 2.5 equiv) were placed in a vial with a screw cap containing a Teflon®-coated rubber septum under air. Then, K(O-*t*-Bu) (44.9 mg, 0.40 mmol, 8.0 mol %) was also added to the vial in a glove box under an argon atmosphere. After the reaction vial was removed from the glove box, DMF (5.0 mL) was added to the vial via a syringe. The resulting mixture was stirred for 5 min at rt, then triisopropylsilane **1b** (789.6 mg, 5.0 mmol, 1.0 equiv) was added dropwise to the vial. After the resulting mixture was stirred at 80 °C for 48 h, the reaction mixture was analyzed by GC to check the completeness of the reaction. The mixture was directly filtered through a short silica-gel column with Et_2O as an eluent, then the resultant solution was concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography with hexane/EtOAc eluent (100:0 to 95:5) to give the corresponding product **3b** in 61% yield (864.5 mg, 3.0 mmol) as a colorless oil. ($[RhCl(cod)]_2$ is the effective precursor for Si–H

borylation as well as $[Rh(OMe)(cod)]_2$. Additionally, $[RhCl(cod)]_2$ is commercially available, and cheaper than $[Rh(OMe)(cod)]_2$.).

Large-Scale Synthesis of 3k.

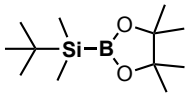


1k (5.0 mmol) **2** (2.5 equiv) **3k**, 46% yield

Platinum on carbon (5 wt % loading, matrix activated carbon support) (19.7 mg, 0.10 mmol, 2.0 mol %) and bis(pinacolato)diboron (3.16 g, 12.5 mmol, 2.5 equiv) were placed in a vial with a screw cap containing Teflon®-coated rubber septum under air. Then, the reaction vial was connected to a vacuum-nitrogen manifold through a needle, and it was evacuated and refilled with nitrogen three times. Cyclohexane (5.0 mL) was added to the vial via a syringe. Benzyldimethlysilane **1k** (750.1 mg, 5.0 mmol, 1.0 equiv) was added dropwise to the vial. After the resulting mixture was stirred at 80 °C for 3 h, the reaction mixture was analyzed by GC to check the completeness of the reaction. The mixture was directly filtered through filter paper with Et_2O as an eluent, then the resultant solution was concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography with hexane/Et_2O eluent (100:0 to 95:5) to give the corresponding product **3k** in 46% yield (637.0 mg, 2.31 mmol) as a white solid.

6. Characterization of Silylborane Products.

***tert*-Butyldimethyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (3a).**

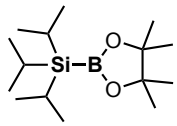


3a

The reaction was performed with **1a** (58.1 mg, 0.50 mmol) according to the procedure **A** and **B**. The product **3a** was obtained as a white solid in 78% yield (94.2 mg, 0.39 mmol, procedure **A**) and 56% yield (68.1 mg, 0.28 mmol, procedure **B**), respectively.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.01 (s, 6H), 0.91 (s, 9H), 1.23 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): –6.5 (*C*H_3), 16.2 (*C*), 25.0 (*C*H_3), 27.0 (*C*H_3), 82.9 (*C*). ^{11}B NMR (127 MHz, $CDCl_3$, δ): 34.4. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{12}H_{27}{}^{10}BO_2{}^{28}Si$, 241.19097; found, 241.19110.

Triisopropyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (3b).

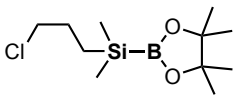


3b

The reaction was performed with **1b** (79.7 mg, 0.50 mmol) according to the procedure **A** and **B**. The product **3b** was obtained as a colorless oil in 58% yield (83.1 mg, 0.29 mmol, procedure **A**) and 20% yield (28.9 mg, 0.10 mmol, procedure **B**), respectively.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.04–1.10 (m, 21H), 1.23 (s, 12H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 11.0 (*C*H), 19.6 (*C*H_3), 25.0 (*C*H_3), 82.7 (*C*). ^{11}B NMR (127 MHz, $CDCl_3$, δ): 34.5. ^{29}Si NMR (79 MHz, $CDCl_3$, δ): –4.5. HRMS-EI (*m*/*z*): $[M–CH_3]^+$ calcd for $C_{14}H_{30}{}^{10}BO_2{}^{28}Si$, 268.21444; found, 268.21463.

(4-Chloropropyl)dimethyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (3c).



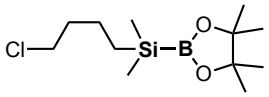
3c

The reaction was performed according to the general procedure **B** with **1c** (68.5 mg, 0.50 mmol). The product **3c** was obtained in 50% yield (65.9 mg, 0.25 mmol) as a colorless oil.

^{1}H NMR (396 MHz, $CDCl_3$, δ): 0.08 (s, 6H), 0.67–0.71 (m, 2H), 1.23 (s, 12H), 1.77–1.84 (m, 2H), 3.51 (t, J = 6.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): –4.15 (*C*H_3), 12.5

(CH_2), 25.0 (CH_3), 28.3 (CH_2), 47.9 (CH_2), 83.2 (C). ^{11}B NMR (127 MHz, $CDCl_3$, δ): 34.2 (s). HRMS–EI (*m/z*): $[M–CH_3]^+$ calcd for $C_{10}H_{21}{}^{10}BClO_2Si$, 246.1129; found, 246.1125.

(4-Chlorobuthyl)dimethyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (3c').

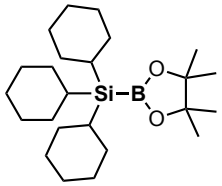


3c'

The reaction was performed according to the general procedure **B** with **1k'** (75.1 mg, 0.50 mmol). The product **3c'** was obtained in 50% yield (68.7 mg, 0.25 mmol) as a colorless oil.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.07 (s, 6H), 0.58–0.63 (m, 2H), 1.24 (s, 12H), 1.44–1.52 (m, 2H), 1.80 (quint, J = 7.1 Hz, 2H), 3.54 (t, J = 6.7 Hz, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): –4.13 (CH_3), 14.0 (CH_2), 21.8 (CH_2), 25.0 (CH_3), 36.0 (CH_2), 44.8 (CH_2), 83.1 (C). ^{11}B NMR (127 MHz, $CDCl_3$, δ): 34.4 (s). HRMS–EI (*m/z*): $[M–CH_3]^+$ calcd for $C_{11}H_{23}{}^{10}BClO_2Si$, 260.1285; found, 260.1285.

Tricyclohexyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (3d).

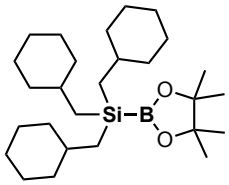


3d

The reaction was performed with **1d** (139.7 mg, 0.50 mmol) according to the procedure **A**. The product **3d** was obtained 30% yield (60.0 mg, 0.15 mmol) as a white solid.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.85–0.96 (m, 3H), 1.12–1.32 (m, 27H), 1.61–1.80 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 22.7 (CH), 25.0 (CH_3), 27.2 (CH_2), 28.6 (CH_2), 29.5 (CH_2), 82.6 (C). ^{11}B NMR (127 MHz, $CDCl_3$, δ): 35.1. HRMS-EI (*m/z*): $[M–CH_3]^+$ calcd for $C_{23}H_{42}{}^{10}BO_2{}^{28}Si$, 388.30834; found, 388.30934.

Tris(cyclohexylmethyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (3e).

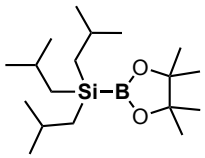


3e

The reaction was performed with **1e** (159.7 mg, 0.50 mmol) according to the procedure **A**. The product **3e** was obtained in 73% yield (164.1 mg, 0.37 mmol) as a white solid.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.59 (d, *J* = 6.7 Hz, 6H), 0.84–0.97 (m, 6H), 1.04–1.28 (m, 9H), 1.22 (s, 12 H), 1.31–1.44 (m, 3H), 1.67–1.72 (m, 15H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 22.2 (*C*H_2), 24.9 (*C*H_3), 26.3 (*C*H_2), 26.7 (*C*H_2), 35.1 (*C*H), 36.9 (*C*H_2), 82.8 (*C*). ^{11}B NMR (126 MHz, $CDCl_3$, δ): 34.8. HRMS-EI (*m*/*z*): $[M–C_7H_{13}]^+$ calcd for $C_{20}H_{38}{}^{10}BO_2{}^{28}Si$, 348.2770; found, 348.27685.

Triisobutyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (3f).

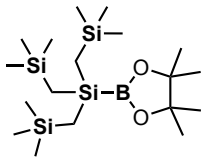


3f

The reaction was performed with **1f** (100.9 mg, 0.50 mmol) according to the procedure **A**. The product **3f** was obtained 75% yield (121.9 mg, 0.37 mmol) as a colorless oil.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.64 (d, *J* = 7.4 Hz, 6H), 0.93 (d, *J* = 6.3 Hz, 18H), 1.22 (s, 12H), 1.78 (sept, *J* = 6.7 Hz, 3H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 23.5 (*C*H_2), 24.9 (*C*H_3), 25.6 (*C*H), 26.4 (*C*H_3), 82.9 (*C*). ^{11}B NMR (127 MHz, $CDCl_3$, δ): 34.8. HRMS-EI (*m*/*z*): $[M–CH_3]^+$ calcd for $C_{17}H_{36}{}^{10}BO_2{}^{28}Si$, 310.26139; found, 310.26076.

[{(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silanetriyl}tris(methylene)]tris (trimethylsilane) (3g).



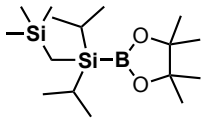
3g

The reaction was performed with **1g** (146.0 mg, 0.50 mmol) according to the procedure **A**. The product **3g** was obtained 20% yield (42.4 mg, 0.10 mmol) as a colorless

oil.

^{1}H NMR (392 MHz, $CDCl_3$, δ): –0.16 (s, 6H), 0.04 (s, 27H), 1.23 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 1.7 (*C*H_3), 3.7 (*C*H_2), 25.3 (*C*H_3), 83.0 (*C*). ^{11}B NMR (127 MHz, $CDCl_3$, δ): 34.0. HRMS-EI (*m*/*z*): $[M–CH_3]^+$ calcd for $C_{17}H_{42}{}^{10}BO_2{}^{28}Si_4$, 400.23912; found, 400.23910.

[{diisopropyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silyl}methyl]trimethyl silane (3h).

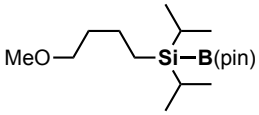


3h

The reaction was performed with **1h** (101.9 mg, 0.50 mmol) according to the procedure **A**. The product **3h** was obtained 52% yield (85.4 mg, 0.26 mmol) as a colorless oil.

^{1}H NMR (396 MHz, $CDCl_3$, δ): –0.29 (s, 2H), 0.05 (s, 9H), 0.90–0.99 (m, 2H), 1.10 (d, *J* = 5.1 Hz, 12H), 1.22 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): –5.4 (*C*H_2), 1.5 (*C*H_3), 12.4 (*C*H), 18.9 (*C*H_3), 19.1 (*C*H_3), 25.1 (*C*H_3), 82.8 (*C*). ^{11}B NMR (127 MHz, $CDCl_3$, δ): 34.4. HRMS-EI (*m*/*z*): $[M–CH_3]^+$ calcd for $C_{15}H_{34}{}^{10}BO_2{}^{28}Si_2$, 312.22267; found, 312.22229.

Diisopropyl(4-methoxybutyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (3i).

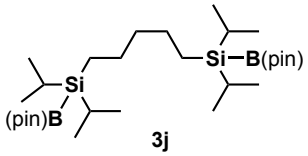


3i

The reaction was performed according to the general procedure A with **1i** (99.6 mg, 0.49 mmol). The product **3i** was obtained in 50% yield (81.5 mg, 0.25 mmol) as a colorless oil.

^{1}H NMR (396 MHz, $CDCl_3$, δ): 0.62–0.66 (m, 2H), 0.99–1.06 (m, 14H), 1.22 (s, 12H), 1.38–1.47 (m, 2H), 1.61 (quint, *J* = 7.0 Hz, 2H), 3.33 (s, 3H), 3.37 (t, *J* = 6.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 8.99 (*C*H_2), 11.0 (*C*H), 18.9 (*C*H_3), 19.2 (*C*H_3), 21.7 (*C*H_2), 25.0 (*C*H_3), 33.7 (*C*H_2), 58.5 (*C*H_3), 72.6 (*C*H_2), 82.8 (*C*). ^{11}B NMR (127 MHz, $CDCl_3$, δ): 34.4 (s). HRMS–EI (*m/z*): $[M–CH_3]^+$ calcd for $C_{16}H_{34}{}^{10}BO_3Si$, 312.2407; found, 312.2406.

1,5-Bis[diisopropyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silyl]pentane (3j).

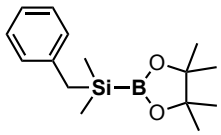


3j

The reaction was performed with **1j** (58.1 mg, 0.50 mmol) according to the procedure **A**. The product **3j** was obtained 86% yield (238.3 mg, 0.43 mmol) as a colorless oil.

^{1}H NMR (396 MHz, $CDCl_3$, δ): 0.56–0.65 (m, 4H), 0.98–1.05 (m, 28H), 1.22 (s, 24H), 1.31–1.42 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 9.0 (*C*H_2), 11.1 (*C*H), 19.0 (*C*H_3), 19.2 (*C*H_3), 24.9 (*C*H_2), 25.0 (*C*H_3), 38.4 (*C*H_2), 82.7 (*C*). ^{11}B NMR (127 MHz, $CDCl_3$, δ): 34.4. HRMS-EI (*m/z*): $[M+Na]^+$ calcd for $C_{29}H_{62}{}^{10}B_2O_4{}^{28}Si_2$, 573.43376; found, 573.43423.

Benzyldimethyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (3k).

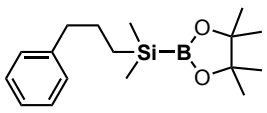


3k

The reaction was performed according to the general procedure **B** with **1k** (74.4 mg, 0.50 mmol). The product **3k** was obtained in 63% yield (85.9 mg, 0.31 mmol) as a white solid.

^{1}H NMR (396 MHz, $CDCl_3$, δ): 0.04 (s, 6H), 1.21 (s, 12H), 2.17 (s, 2H), 7.14–7.18 (m, 3H), 7.02–7.05 (m, 3H), 7.16–7.20 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): –4.21 (*C*H_3), 34.7 (*C*H_2), 25.0 (*C*H_3), 83.2 (*C*), 123.8 (*C*H), 128.0 (*C*H), 128.1 (*C*H), 140.7 (*C*). ^{11}B NMR (127 MHz, $CDCl_3$, δ): 34.2 (s). HRMS–EI (*m/z*): $[M–CH_3]^+$ calcd for $C_{14}H_{22}{}^{10}BO_2Si$, 260.1518; found, 260.1516.

Dimethyl(3-phenylpropyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (3k').



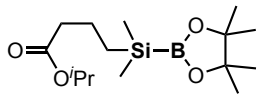
3k'

The reaction was performed according to the general procedure **B** with **1k'** (89.1 mg, 0.50 mmol). The product **3k'** was obtained in 49% yield (74.3 mg, 0.24 mmol) as a colorless oil.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.05 (s, 6H), 0.63–0.67 (m, 2H), 1.22 (s, 12H), 1.60–

1.70 (m, 2H), 2.63 (t, J = 7.6 Hz, 2H), 7.14–7.18 (m, 3H), 7.25–7.29 (m, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): –4.06 (*C*H_3), 14.7 (*C*H_2), 25.0 (*C*H_3), 26.7 (*C*H_2), 39.7 (*C*H_2), 83.0 (*C*), 125.5 (*C*H), 128.1 (*C*H), 128.4 (*C*H), 142.8 (*C*). HRMS–EI (*m/z*): $[M–CH_3]^+$ calcd for $C_{16}H_{26}{}^{10}BO_2Si$, 288.1831; found, 288.1832.

Isopropyl 4-[dimethyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silyl)]butanoate (3l).

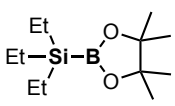


3j

Platinum on carbon (2.1 mg, 0.01 mmol, 2.0 mol %) and bis(pinacolato)diboron (126.5 mg, 0.50 mmol, 1.0 equiv) were placed in a vial with a screw cap containing Teflon-coated rubber septum under air. Then, the reaction vial was connected to a vacuum-nitrogen manifold through a needle, and it was evacuated and refilled with nitrogen three times. Cyclohexane (0.50 mL) was added to the vial via a syringe. **1j** (283.0 mg, 1.50 mmol, 3.0 equiv) was added dropwise to the vial. After the resulting mixture was stirred at 80 °C for 22 h, the reaction mixture was analyzed by GC to check the completeness of the reaction and determine GC yield of the product (65% GC yield). The mixture was directly filtered through filter paper with Et_2O as an eluent, then the resultant solution was concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography with hexane/Et_2O eluent (100:0 to 97:3) to give the corresponding product **1q** in 42% yield (65.3 mg, 0.21 mmol) as a colorless oil.

^{1}H NMR (396 MHz, $CDCl_3$, δ): 0.07 (s, 6H), 0.59–0.64 (m, 2H), 1.22 (s, 3H), 1.23 (s, 14H), 1.62–1.70 (m, 2H), 2.29 (t, J = 7.3 Hz, 2H), 5.00 (quint, J = 6.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): –4.17 (*C*H_3), 14.5 (*C*H_2), 20.4 (*C*H_2), 21.8 (*C*H_3), 24.9 (*C*H_3), 38.2 (*C*H_2), 67.1 (*C*H), 83.0 (*C*), 173.2 (*C*). ^{11}B NMR (127 MHz, $CDCl_3$, δ): 34.3 (s). HRMS–EI (*m/z*): $[M–CH_3]^+$ calcd for $C_{14}H_{28}{}^{10}BO_4Si$, 298.1886; found, 298.1879.

Triethyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (3m).

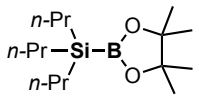


3m

The reaction was performed with **1m** (61.2 mg, 0.53 mmol) according to the general procedure **A**, **B** and **C**. The product **3m** was obtained as a colorless oil in 66% yield (84.7 mg, 0.35 mmol, procedure **A**), 62% yield (76.4 mg, 0.32 mmol, procedure **B**), and 57% yield (70.3 mg, 0.29 mmol, procedure **C**), respectively.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.59 (q, *J* = 7.8 Hz, 6H), 0.97 (t, *J* = 7.8 Hz, 9H), 1.23 (s, 12H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 2.89 (*C*H_2), 8.29 (*C*H_3), 25.0 (*C*H_3), 82.8 (*C*). ^{11}B NMR (127 MHz, $CDCl_3$, δ): 34.5 (s). HRMS–EI (*m/z*): $[M–CH_3]^+$ calcd for $C_{11}H_{24}{}^{10}BO_2Si$, 226.1675; found, 226.1672.

Tripropyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (3n).

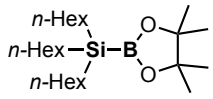


3n

The reaction was performed with **1n** (81.2 mg, 0.51 mmol) according to the general procedure **A**, **B** and **C**. The product **3n** was obtained as a colorless oil in 66% yield (96.3 mg, 0.34 mmol, procedure **A**), 52% yield (74.4 mg, 0.26 mmol, procedure **B**), and 35% yield (48.9 mg, 0.17 mmol, procedure **C**), respectively.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.58–0.62 (m, 6H), 0.97 (t, *J* = 7.3 Hz, 9H), 1.22 (s, 12H), 1.32–1.41 (m, 6H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 14.6 (*C*H_2), 18.3 (*C*H_2), 18.4 (*C*H_3), 25.0 (*C*H_3), 82.8 (*C*). ^{11}B NMR (127 MHz, $CDCl_3$, δ): 35.0 (s). HRMS–EI (*m/z*): $[M–CH_3]^+$ calcd for $C_{14}H_{30}{}^{10}BO_2Si$, 268.2144; found, 268.2143.

Trihexyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (3o).

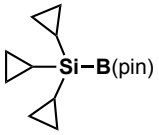


3o

The reaction was performed with **1o** (143.2 mg, 0.50 mmol) according to the general procedure **A**, **B** and **C**. The product **3o** was obtained as a colorless oil in 77% yield (159.2 mg, 0.39 mmol, procedure **A**), 63% yield (129.2 mg, 0.31 mmol, procedure **B**), and 58% yield (118.5 mg, 0.29 mmol, procedure **C**), respectively.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.59 (t, *J* = 7.8 Hz, 6H), 0.86–0.89 (m, 9H), 1.22 (s, 12H), 1.24–1.31 (m, 24H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 11.7 (*C*H_2), 14.1 (*C*H_3), 22.6 (*C*H_2), 24.7 (*C*H_2), 24.9 (*C*H_3), 31.6 (*C*H_2), 33.3 (*C*H_2), 82.8 (*C*). ^{11}B NMR (127 MHz, $CDCl_3$, δ): 35.1 (s). HRMS–EI (*m/z*): $[M–CH_3]^+$ calcd for $C_{23}H_{48}{}^{10}BO_2Si$, 394.3553; found, 394.3556.

Tricyclopropyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (3p).



3p

The reaction was performed with **1p** (76.0 mg, 0.50 mmol) according to the general procedure **A**, **B** and **C**. The product **3p** was obtained as a colorless oil in 63% yield (87.0 mg, 0.31 mmol, procedure **A**), 42% yield (58.7 mg, 0.21 mmol, procedure **B**), and 55% yield (75.9 mg, 0.27 mmol, procedure **C**), respectively.

^{1}H NMR (392 MHz, $CDCl_3$, δ): –0.47 (tt, J = 6.7, 9.8 Hz, 3H), 0.35–0.40 (m, 6H), 0.52–0.58 (m, 6H), 1.19 (s, 12H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): –8.6 (*C*H), 1.1 (*C*H_2), 24.9 (*C*H_3), 82.8 (*C*). ^{11}B NMR (127 MHz, $CDCl_3$, δ): 33.2. HRMS-EI (*m*/*z*): $[M–CH_3]^+$ calcd for $C_{14}H_{24}{}^{10}BO_2{}^{28}Si$, 262.16749; found, 262.16759.

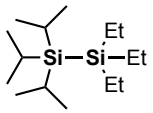
7. General Procedures for Silicon–Silicon Coupling Reaction of Silylboranes with Silyl Electrophiles.

7-1. General Procedures for Si–Si Coupling Reaction: Procedure D.

Trialkylsilylborane **3** (0.2 mmol, 1.0 equiv) was placed in a vial with a screw cap containing a Teflon®-coated rubber septum under nitrogen. It was dissolved in THF (1.0 mL), and the mixture was cooled to –78 °C. Then, MeLi (1.1 M in Et_2O, 0.27 mL, 1.5 equiv) was added to the vial. After the mixture was stirred at –78 °C for 10 min, silyl chloride or triflate was added dropwise to the vial at –78 °C. The mixture was allowed to warm to room temperature and stirred for 30 min. After that, the reaction mixture was analyzed by GC to check the completeness of the reaction. The mixture was quenched by the addition of EtOH and filtered through a short silica-gel column with Et_2O as an eluent, then the resultant solution was concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography with hexane eluent to give the corresponding product **4**. Further purification by GPC was conducted if needed.

7-2. Characterization of Si–Si Coupling Products.

1,1,1-Triethyl-2,2,2-triisopropyldisilane (4a).

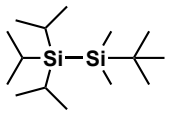


4a

The reaction was performed with **3a** (56.7 mg, 0.20 mmol) and TES–Cl according to the procedure **D**. The product **4a** was obtained in 73% yield (40.0 mg, 0.15 mmol) as a colorless oil after the prification by GPC.

^{1}H NMR (401 MHz, $CDCl_3$, δ): 0.74 (q, J = 7.9 Hz, 6 H), 1.01 (t, J = 7.8 Hz, 9H), 1.09 (d, J = 6.0 Hz, 18H), 1.12–1.22 (m, 3H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 5.3 (CH_2), 8.6 (CH_3), 12.4 (CH), 20.0 (CH_3). ^{29}Si NMR (79 MHz, $CDCl_3$, δ): –9.9, –3.0. HRMS-EI (m/z): $[M]^+$ calcd for $C_{15}H_{36}{}^{28}Si_2$, 272.23555; found, 272.23539.

1-(*tert*-Butyl)-2,2,2-triisopropyl-1,1-dimethyldisilane (4b).



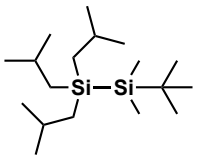
4b

The reaction was performed with **3a** (56.6 mg, 0.20 mmol) and TBS–OTf according

to the procedure **D**. The product **4b** was obtained in 92% yield (50.0 mg, 0.18 mmol) as a colorless oil after the prification by silica-gel column chromatography with hexane eluent.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.13 (s, 6H), 0.96 (s, 9H), 1.12 (d, J = 6.7 Hz, 18H), 1.17–1.29 (m, 3H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): –2.3 (*C*H_3), 12.6 (*C*H), 18.2 (*C*), 20.1 (*C*H_3), 28.3 (*C*H_3). ^{29}Si NMR (79 MHz, $CDCl_3$, δ): –7.8, –3.0. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{15}H_{36}{}^{28}Si_2$, 272.23555; found, 272.23585.

1-(*tert*-Butyl)-2,2,2-triisobutyl-1,1-dimethyldisilane (4c).

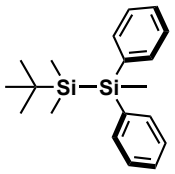


4c

The reaction was performed with **3f** (65.2 mg, 0.20 mmol) and TBS–OTf according to the procedure **D**. The product **4c** was obtained in 91% yield (57.4 mg, 0.18 mmol) as a colorless oil silica-gel column chromatography with hexane eluent.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.04 (s, 6H), 0.72 (d, J = 7.1 Hz, 6H), 0.93 (d, J = 3.5 Hz, 18H), 0.95 (s, 9H), 1.92 (nonet, J = 6.6 Hz, 3H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): –4.3 (*C*H_3), 18.2 (*C*), 25.0 (*C*H_2), 25.7 (*C*H), 26.9 (*C*H_3), 28.2 (*C*H_3). ^{29}Si NMR (79 MHz, $CDCl_3$, δ): –14.8, –8.7. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{18}H_{42}{}^{28}Si_2$, 314.28250; found, 314.28246.

1-(*tert*-Butyl)-1,1,2-trimethyl-2,2-diphenyldisilane (4d).

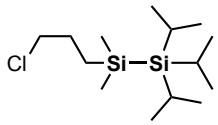


4d

The reaction was performed with **3c** (45.1 mg, 0.19 mmol) and Ph_2MeSi–Cl according to the procedure **D**. The product **4d** was obtained in 79% yield (47.9 mg, 0.15 mmol) as a colorless oil after the prification by GPC.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.12 (s, 6H), 0.68 (s, 3H), 0.82 (s, 9H), 7.30–7.36 (m, 6H), 7.49–7.56 (m, 4H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): –5.2 (*C*H_3), –3.3 (*C*H_3), 18.2 (*C*), 27.7 (*C*H_3), 127.8 (*C*H), 128.6 (*C*H), 134.9 (*C*H), 137.9 (*C*). ^{29}Si NMR (79 MHz, $CDCl_3$, δ): –23.1, –8.4. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{19}H_{28}{}^{28}Si_2$, 312.17295; found, 312.17269.

1-(3-Chloropropyl)-2,2,2-triisopropyl-1,1-dimethyldisilane (4e).

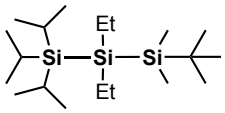


4e

The reaction was performed with **3k** (52.5 mg, 0.20 mmol) and TIPS–Cl according to the procedure **D**. The product **4e** was obtained in 78% yield (45.9 mg, 0.16 mmol) as a colorless oil after the prification by GPC.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.16 (s, 6H), 0.71–0.78 (m, 2H), 1.09 (d, J = 6.3 Hz, 18H), 1.12–1.26 (m, 3H), 1.75–1.85 (m, 2H), 3.51 (t, J = 6.9 Hz, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): –1.4 (*C*H_3), 11.9 (*C*H), 14.3 (*C*H_2), 19.8 (*C*H_3), 27.9 (*C*H_2), 48.0 (*C*H_2). ^{29}Si NMR (79 MHz, $CDCl_3$, δ): –17.2, –3.8. HRMS-EI (*m*/*z*): $[M–iPr]^+$ calcd for $C_{11}H_{26}{}^{35}Cl^{28}Si_2$, 249.12616; found, 249.12604.

1-(*tert*-Butyl)-2,2-diethyl-3,3,3-triisopropyl-1,1-dimethyltrisilane (4f).



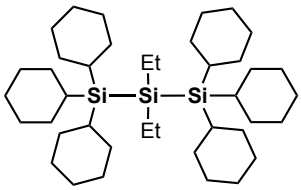
4f

Trialkylsilylborane **3a** (56.8 mg, 0.20 mmol, 1.0 equiv) was placed in a vial with a screw cap containing a Teflon®-coated rubber septum under nitrogen. It was dissolved in THF (0.7 mL), and the mixture was cooled to –78 °C. After MeLi (1.1 M in Et_2O, 0.45 mL, 4.5 equiv) was added dropwise to the mixture, the mixture was stirred at –78 °C for 10 min. Then, the reaction mixture was added dropwise to dichlorodiethylsilane (31.5 mg, 0.20 mmol, 1.0 equiv) in THF solution (0.7 mL) at –78 °C, and the resulting mixture was stirred for 30 min at rt. After the mixture was recooled to –78 °C, TBS–Li in THF solution prepared from **3c** and MeLi at –78 °C for 10 min was added slowly to the mixture. After the resulting mixture was allowed to warm to room temperature and stirred for 1 h, the reaction mixture was analyzed by GC to check the completeness of the reaction. The mixture was quenched by the addition of EtOH and filtered through a short silica-gel column with Et_2O as an eluent, then the resultant solution was concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography with hexane eluent and GPC to give the corresponding product **4f** in 35% yield (24.2 mg, 0.067 mmol) as a colorless oil.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.12 (s, 6H), 0.90–0.99 (m, 13H), 1.04–1.11 (m, 6H), 1.13 (d, J = 7.1 Hz, 18H), 1.19–1.31 (m, 3H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): –2.8 (*C*H_3),

5.1 (*C*H_2), 10.6 (*C*H_3), 13.2 (*C*H), 19.1 (*C*), 20.3 (*C*H_3), 28.1 (*C*H_3). ^{29}Si NMR (79 MHz, $CDCl_3$, δ): –35.1, –5.4, 2.1. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{19}H_{46}{}^{28}Si_3$, 358.2908; found, 358.2904.

1,1,1,3,3,3-Hexacyclohexyl-2,2-diethyltrisilane (4g).

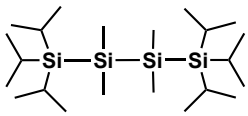


4g

Trialkylsilylborane **3d** (80.9 mg, 0.20 mmol, 2.0 equiv) was placed in a vial with a screw cap containing a Teflon®-coated rubber septum under nitrogen. It was dissolved in THF (0.5 mL), and the mixture was cooled to –78 °C. After MeLi (1.1 M in Et_2O, 0.45 mL, 4.5 equiv) was added dropwise to the mixture, the mixture was stirred at –78 °C for 1 h. Then, the reaction mixture was added dropwise to dichlorodiethylsilane (15.7 mg, 0.10 mmol, 1.0 equiv) in THF solution (0.5 mL) at –78 °C. After the mixture was allowed to warm to room temperature and stirred for 2 h, the reaction mixture was analyzed by GC to check the completeness of the reaction. The mixture was quenched by the addition of EtOH and filtered through a short silica-gel column with Et_2O as an eluent, then the resultant solution was concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography with hexane eluent. Futhermore, the remaining mixture was recrystallized from hexane in the freezer to give the corresponding product **4g** in 55% yield (35.3 mg, 0.055 mmol) as a white solid.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.91–1.01 (m, 4H), 1.01–1.12 (m, 12H), 1.12–1.31 (m, 18H), 1.31–1.43 (m, 12H), 1.66–1.92 (m, 30H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 6.4 (*C*H_2), 10.8 (*C*H_3), 26.2 (*C*H), 27.1 (*C*H_2), 28.9 (*C*H_2), 30.2 (*C*H_2). ^{29}Si NMR (79 MHz, $CDCl_3$, δ): –34.0, –6.2. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{34}H_{65}{}^{28}Si_3$, 430.33026; found, 430.32966.

1,1,1,4,4,4-Hexaisopropyl-2,2,3,3-tetramethyltetrasilane (4h).



4h

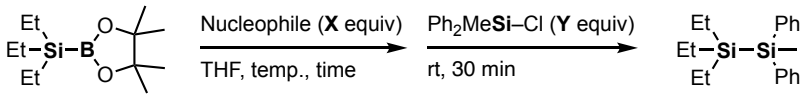
Trialkylsilylborane **3a** (114.4 mg, 0.40 mmol, 2.0 equiv) was placed in a vial with a screw cap containing a Teflon®-coated rubber septum under nitrogen. It was dissolved in

THF (1.0 mL), and the mixture was cooled to –78 °C. After MeLi (1.1 M in Et_2O, 0.41 mL, 2.25 equiv) was added dropwise to the mixture, the mixture was stirred at –78 °C for 30 min. Then, the reaction mixture was added dropwise to 1,2-dichlorotetramethyldisilane (37.7 mg, 0.20 mmol, 1.0 equiv) in THF solution (1.0 mL) at –78 °C. After the mixture was allowed to warm to room temperature and stirred for 1 h, the reaction mixture was analyzed by GC to check the completeness of the reaction. The mixture was quenched by the addition of EtOH and filtered through a short silica-gel column with Et_2O as an eluent, then the resultant solution was concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography with hexane eluent to give the corresponding product **4h** in 61% yield (52.7 mg, 0.12 mmol) as a colorless oil.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.32 (s, 12H), 1.11 (d, J = 6.7 Hz, 36H), 1.18–1.29 (m, 6H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): –1.2 (*C*H_3), 12.8 (*C*H), 20.1 (*C*H_3). ^{29}Si NMR (79 MHz, $CDCl_3$, δ): –44.8, –2.5. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{22}H_{54}{}^{28}Si_4$, 430.33026; found, 430.32966.

7-3. Optimization Study for Si–Si Coupling.

Table S5. Optimization of Reaction Conditions for Si–Si Coupling.[a]



3m (0.2 mmol)

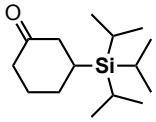
entry	Nucleophile (**X** equiv)	**Y**	**temp.** (ºC)	**time.** (min)	yield (%)[b]
1	MeLi (1.5)	2.0	–78	10	**88**
2	^{n}BuLi (1.5)	2.0	–78	10	84
3	PhLi (1.5)	2.0	–78	10	**88**
4	MeMgBr (1.5)	2.0	–78	10	N.D.
5	MeMgBr (1.5)	2.0	0	10	N.D.
6	PhMgBr (1.5)	2.0	–78	10	N.D.
7	$(TMS)_2NK$ (1.5)	2.0	–78	10	**88**
8	K(O-*t*-Bu) (1.5)	2.0	–78	10	74
9	K(O-*t*-Bu) (1.5)	2.0	rt	10	51
10	MeLi (1.5)	2.0	–78	1	85
11	MeLi (1.5)	2.0	–78	30	86
12	MeLi (1.5)	2.0	0	10	74
13	MeLi (1.0)	1.0	–78	10	76

[a]Reaction Conditions: **3m** (0.5 mmol), Nucleophile (**X** equiv), and Ph_2MeSi–Cl (**Y** equiv) in THF (1 mL). [b]GC yield. 1,4-Diisopropylbenzene was used as an internal standard.

8. General Procedures for Copper (I)-Catalyzed Silyl Conjugate Addition to α,β-Unsaturated Ketone with Various Trialkylsilylboranes.[8]

A vial with a screw cap containing a Teflon®-coated rubber septum was charged with copper chloride (2.0 mg, 0.020 mmol, 10 mol %), IMes·HCl (7.5 mg, 0.022 mmol, 11 mol %), and trialkylsilylborane (0.22 mmol, 1.1 equiv) under air. Then, Na(O-*t*-Bu) (4.2 mg, 0.022 mmol, 22 mol %) was added to the vial in a glove box under an argon atmosphere. After the reaction vial was removed from the glove box, THF (0.6 mL) was added to the vial via a syringe. The resulting mixture was stirred for 10 min at 30 °C, 2-cyclohexen-1-one **5** (0.2 mmol, 1.0 equiv) and MeOH (10 μL, 2.0 equiv) were added dropwise to the vial. After the resulting mixture was stirred at 30 °C for 2 h, the reaction mixture was analyzed by GC to check the completeness of the reaction. The mixture was directly filtered through a short silica-gel column with Et_2O as an eluent, then the resultant solution was concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography to give the corresponding product **6**.

3-(Triisopropylsilyl)cyclohexan-1-one (6a).

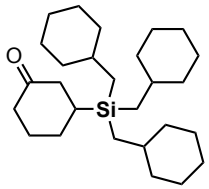


6a

The reaction was performed with **4** (19.2 mg, 0.20 mmol) and **1f** (62.7 mg, 0.22 mmol) for 24 h at 60 °C. The corresponding product **6a** was obtained in 89% yield (45.5 mg, 0.18 mmol) as a white solid after purification by silica-gel column chromatography with hexane/EtOAc eluent (100:0 to 95:5).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.07–1.18 (m, 21H), 1.39–1.47 (m, 1H), 1.62–1.75 (m, 2H), 1.88–1.97 (m, 1H), 2.15–2.23 (m, 1H), 2.29–2.45 (m, 4H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 10.9 (*C*H), 19.1 (*C*H_3), 25.0 (*C*H), 27.6 (*C*H_2), 30.3 (*C*H_2), 42.1 (*C*H_2), 43.9 (*C*H_2), 212.5 (*C*). HRMS–EI (*m/z*): $[M–i\text{-}Pr]^+$ calcd for $C_{12}H_{23}O^{28}Si$, 211.1518; found, 211.1518.

3-[Tris(cyclohexylmethyl)silyl]cyclohexan-1-one (6b).

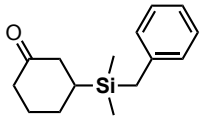


6b

The reaction was performed with **4** (19.1 mg, 0.20 mmol) and **1j** (98.1 mg, 0.22 mmol) for 24 h at 60 °C. The corresponding product **6b** was obtained in 82% yield (68.0 mg, 0.16 mmol) as a viscous liquid after purification by silica-gel column chromatography with hexane/EtOAc eluent (100:0 to 96:4) and GPC.

^{1}H NMR (392 MHz, $CDCl_3$, δ): .0.53 (d, J = 6.7 Hz, 6H), 0.89–0.98 (m, 6H), 1.06–1.27 (m, 10H), 1.32–1.43 (m, 3H), 1.48 (td, J = 3.4, 12.9 Hz, 1H), 1.60–1.76 (m, 16H), 1.83 (d, J = 13.3 Hz, 1H), 2.13–2.20 (m, 2H), 2.27–2.43 (m, 3H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 21.2 (CH$_2$), 26.1 (CH$_2$), 26.6 (CH$_2$), 26.6 (CH$_2$), 27.4 (CH), 30.0 (CH$_2$), 34.2 (CH), 37.2 (CH$_2$), 42.1 (CH$_2$), 43.0 (CH$_2$), 213.1 (C). HRMS–APCI (m/z): $[M+H]^+$ calcd for $C_{27}H_{49}O^{28}Si$, 417.3547; found, 417.3545.

3-(Benzyldimethylsilyl)cyclohexan-1-one (6c).

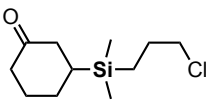


6c

The reaction was performed with **4** (19.8 mg, 0.21 mmol) and **1g** (60.2 mg, 0.22 mmol) for 4 h at 30 °C. The corresponding product **6c** was obtained in 82% yield (41.4 mg, 0.17 mmol) as a viscous liquid after purification by silica-gel column chromatography with hexane/EtOAc eluent (100:0 to 94:6).

^{1}H NMR (392 MHz, $CDCl_3$, δ): –0.03 (d, J = 3.9 Hz, 6H), 1.15 (ddt, J = 3.3, 12.0, 13.1 Hz, 1H), 1.46 (ddd, J = 3.6, 12.8, 25.8 Hz, 1H), 1.65–1.84 (m, 2H), 2.10–2.22 (m, 4H), 2.26–2.42 (m, 3H), 6.99 (d, J = 7.1 Hz, 2H), 7.08 (t, J = 7.3 Hz, 1H), 7.22 (t, J = 7.6 Hz, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): –5.68 (CH$_3$), –5.62 (CH$_3$), 23.3 (CH$_2$), 26.0 (CH$_2$), 26.5 (CH), 29.7 (CH$_2$), 41.9 (CH$_2$), 42.3 (CH$_2$), 124.1 (CH), 128.0 (CH), 128.2 (CH), 139.4 (C), 212.5 (C). HRMS–EI (m/z): $[M]^+$ calcd for $C_{15}H_{22}OSi$, 246.1440; found, 246.1440.

3-[(3-Chloropropyl)dimethylsilyl]cyclohexan-1-one (6d).



6d

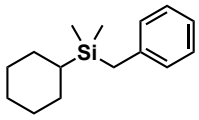
The reaction was performed with **4** (19.2 mg, 0.20 mmol) and **1p** (58.4 mg, 0.22 mmol) for 2 h at 30 °C. The corresponding product **6d** was obtained in 94% yield (44.0

mg, 0.19 mmol) as a viscous liquid after purification by silica-gel column chromatography with hexane/EtOAc eluent (100:0 to 94:6).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.01 (d, *J* = 3.1 Hz, 6H), 0.62–0.67 (m, 2H), 1.14 (ddt, *J* = 3.4, 11.9, 13.1 Hz, 1H), 1.46 (ddd, *J* = 3.4, 12.8, 25.4 Hz, 1H), 1.66–1.85 (m, 4H), 2.10–2.23 (m, 2H), 2.26–2.36 (m, 2H), 2.37–2.44 (m, 1H), 3.51 (t, *J* = 6.7 Hz, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): –5.59 (*C*H_3), 10.9 (*C*H_2), 26.0 (*C*H_2), 26.9 (*C*H), 27.4 (*C*H_2), 29.8 (*C*H_2), 41.9 (*C*H_2), 42.3 (*C*H_2), 47.8 (*C*H_2), 212.5 (*C*). HRMS–APCI (*m/z*): $[M+H]^+$ calcd for $C_{11}H_{22}OCl^{28}Si$, 233.1123; found, 233.1122.

9. General Procedures for Copper (I)-Catalyzed Radical Silylation of Alkyl Iodine with Functional-Group-Containing Trialkylsilylboranes.[9]

Benzyl(cyclohexyl)dimethylsilane (8a).

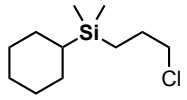


8a

A vial with a screw cap containing a Teflon®-coated rubber septum was charged with copper thiocyanate CuSCN (2.4 mg, 0.020 mmol, 10 mol %), dtbpy (5.4 mg, 0.020 mmol, 10 mol %), and trialkylsilylborane **3k** (82.7 mg, 0.30 mmol, 1.5 equiv) under air. Then, Li(O-*t*-Bu) (23.9 mg, 0.30 mmol, 1.5 equiv) was added to the vial in a glove box under an argon atmosphere. After the reaction vial was removed from the glove box, THF (0.90 mL) and DMF (0.10 mL) were added to the vial via a syringe. The resulting mixture was stirred for 10 min at 0 °C, and then iodocyclohexane **7** (42.2 mg, 0.20 mmol, 1.0 equiv) was added dropwise to the vial at 0 °C. After the resulting mixture was stirred at 30 °C for 3 h, the reaction mixture was analyzed by GC to check the completeness of the reaction. The mixture was directly filtered through a short silica-gel column with Et_2O as an eluent, then the resultant solution was concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography with hexane eluent to give the corresponding product **8a** (24.9 mg, 0.11 mmol, 54%) as a colorless liquid.

^{1}H NMR (392 MHz, $CDCl_3$, δ): –0.11 (s, 6H), 0.62 (tt, *J* = 3.1, 12.5 Hz, 1H), 1.01–1.30 (m, 5H), 1.61–1.79 (m, 5H), 2.06 (s, 2H), 6.96–7.01 (m, 2H), 7.03–7.09 (m, 1H), 7.17–7.23 (m, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): –5.6 (*C*H_3), 23.6 (*C*H_2), 24.8 (*C*H), 26.9 (*C*H_2), 27.4 (*C*H_2), 28.0 (*C*H_2), 123.7 (*C*H), 128.07 (*C*H), 128.13 (*C*H), 140.6 (*C*). HRMS–EI (*m/z*): $[M]^+$ calcd for $C_{15}H_{24}{}^{28}Si$, 232.1647; found, 232.1647.

(3-Chloropropyl)(cyclohexyl)dimethylsilane (8b).



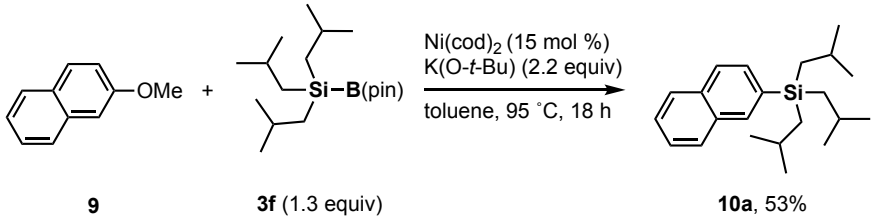
8b

A vial with a screw cap containing a Teflon®-coated rubber septum was charged with copper thiocyanate CuSCN (2.4 mg, 0.020 mmol, 10 mol %), and dtbpy (5.4 mg, 0.020 mmol, 10 mol %), under air. Then, Li(O-*t*-Bu) (23.8 mg, 0.30 mmol, 1.5 equiv) was also added to the vial in a glove box under an argon atmosphere. After the reaction vial was removed from the glove box, THF (0.90 mL) and DMF (0.10 mL) were added to the vial via a syringe. The resulting mixture was stirred for 10 min at 0 °C, and then trialkylsilylborane **1p** (78.7 mg, 0.30 mmol, 1.5 equiv) and iodocyclohexane **7** (42.2 mg, 0.20 mmol, 1.0 equiv) was added dropwise to the vial at 0 °C. After the resulting mixture was stirred at 30 °C for 3 h, the reaction mixture was analyzed by GC to check the completeness of the reaction. The mixture was directly filtered through a short silica-gel column with Et_2O as an eluent, then the resultant solution was concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography with hexane eluent to give the corresponding product **8b** (22.3 mg, 0.10 mmol, 51%) as a colorless liquid.

^{1}H NMR (392 MHz, $CDCl_3$, δ): –0.07 (s, 6H), 0.53–0.65 (m, 3H), 1.00–1.29 (m, 5H), 1.61–1.80 (m, 7H), 3.50 (t, J = 6.9 Hz, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): –5.5 (CH_3), 11.2 (CH_2), 25.1 (CH), 26.9 (CH_2), 27.4 (CH_2), 27.8 (CH_2), 28.0 (CH_2), 48.2(CH_2). HRMS–EI (*m/z*): $[M–C_6H_{11}]^+$ calcd for $C_5H_{12}{}^{35}Cl^{28}Si$, 135.0397; found, 135.0395.

10. General Procedures for Nickel-catalyzed Silylation of Aryl Methyl Ether with Sterically Hindered Trialkylsilylboranes.[10]

Triisobutyl (naphthalen-2-yl)silane (10a).

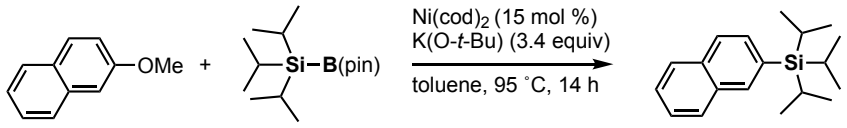


9 **3f** (1.3 equiv) **10a**, 53%

A vial with a screw cap containing a Teflon®-coated rubber septum was charged with 2-methoxynaphthalene **9** (31.9 mg, 0.20 mmol, 1.0 equiv) under air. Then, $Ni(cod)_2$ (8.3 mg, 0.030 mmol, 15 mol %) and K(O-*t*-Bu) (49.6 mg, 0.44 mmol, 2.2 equiv) were also added to the vial in a argon-filled glove box. The reaction vial was removed from the glove box, and toluene (1.0 mL) and trialkylsilylborane **3f** (84.9 mg, 0.26 mmol, 1.3 equiv) were added to the vial via a syringe. After the resulting mixture was stirred 18 h at 95 °C, the reaction mixture was analyzed by GC to check the completeness of the reaction. The mixture was directly filtered through a short silica-gel column with Et_2O as an eluent, then the resultant solution was concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography with hexane eluent and GPC to give the corresponding product **10a** (34.6 mg, 0.11 mmol, 53%) as a white solid.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.89 (d, *J* = 6.7 Hz, 18H), 0.93 (d, *J* = 7.4 Hz, 6H), 1.80 (nonet, *J* = 6.7 Hz, 3H), 7.47–7.50 (m, 2H), 7.60 (dd, *J* = 1.0, 7.8 Hz, 1H), 7.78–7.89 (m, 3H), 7.99 (s, 1H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 24.1 (*C*H_2), 24.9 (*C*H), 26.5 (*C*H_3), 125.6 (*C*H), 126.0 (*C*H), 126.5 (*C*H), 127.6 (*C*H), 128.0 (*C*H), 130.7 (*C*H), 132.9 (*C*), 133.4 (*C*), 134.6 (*C*H), 136.9 (*C*). HRMS–EI (*m/z*): $[M]^+$ calcd for $C_{22}H_{34}{}^{28}Si$, 326.2430; found, 326.2424.

Triisopropyl(naphthalen-2-yl)silane (10b).



9 **3b** (2.0 equiv) **10b**, 52%

A vial with a screw cap containing a Teflon®-coated rubber septum was charged with 2-methoxynaphthalene (31.8 mg, 0.20 mmol, 1.0 equiv) under air. Then, $Ni(cod)_2$ (8.3 mg, 0.030 mmol, 15 mol %) and K(O-*t*-Bu) (76.3 mg, 0.68 mmol, 3.4 equiv) were also

added to the vial in a argon-filled glove box. The reaction vial was removed from the glove box, and toluene (1.0 mL) and trialkylsilylborane **3b** (113.7 mg, 0.40 mmol, 2.0 equiv) were added to the vial via a syringe. After the resulting mixture was stirred 14 h at 95 °C, the reaction mixture was analyzed by GC to check the completeness of the reaction. The mixture was directly filtered through a short silica-gel column with Et_2O as an eluent, then the resultant solution was concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography with hexane eluent and GPC to give the corresponding product **10b** (29.6 mg, 0.10 mmol, 52%) as a white solid.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.11 (d, J = 7.8 Hz, 18H), 1.51 (sept, J = 7.5 Hz, 3H), 7.44–7.51 (m, 2H), 7.57 (dd, J = 1.0, 8.0 Hz, 1H), 7.78–7.88 (m, 3H), 7.99 (s, 1H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 10.9 (*C*H), 18.6 (*C*H_3), 125.6 (*C*H), 126.1 (*C*H), 126.4 (*C*H), 127.6 (*C*H), 128.1 (*C*H), 131.7 (*C*H), 132.5 (*C*), 132.9 (*C*), 133.5 (*C*), 135.9 (*C*H). HRMS–EI (*m/z*): $[M]^+$ calcd for $C_{19}H_{28}O^{28}Si$, 284.19603; found, 284.19554.

11. Single Crystal X-ray Analysis of 3d, 3k, and 4g.

Table S6. Summary of X-ray crystallographic data for 3d, 3k, and 4g.

Compound	**3d**	**3k**	**4g**
CCDC Name	1987433	1987434	1987435
Empirical Formula	$C_{24}H_{45}BO_2Si$	$C_{15}H_{25}BO_2Si$	$C_{40}H_{76}Si_3$
Formula Weight	404.50	276.25	641.27
Crystal System	orthorhombic	orthorhombic	triclinic
Crystal Size / mm^3	0.694 × 0.623 × 0.19	0.7 × 0.7 × 0.6	0.2 × 0.05 × 0.05
a / Å	10.03550(10)	12.8389(6)	14.1385(6)
b / Å	12.25900(10)	15.4902(7)	17.3628(5)
c / Å	19.9447(2)	16.8273(8)	17.4795(4)
α / °	90	90	101.869(2)
β / °	90	90	108.310(3)
γ / °	90	90	97.402(3)
V / $Å^3$	2453.70(4)	3346.6(3)	3899.2(2)
Space Group	$P2_12_12_1$	*Pbca*	*P*-1
Z value	4	8	4
D_{calc} / $g \cdot cm^{-3}$	1.095	1.097	1.092
Temperature / K	293(2)	293(2)	123.0
$2\theta_{max}$ / °	152.876	55.75	153.524
μ / mm^{-1}	0.947 (CuK_α)	0.136 (MoK_α)	1.288 (CuK_α)
No. of Reflections Measured	Total: 9243 Unique : 4560 (R_{int} = 0.0667)	Total: 25488 Unique : 3559 (R_{int} = 0.0269)	Total: 39810 Unique : 15365 (R_{int} = 0.0681)
R_1 (I > 2.00σ (I)) / %	0.0556	0.0376	0.0662
wR_2 (All reflections) / %	0.1414	0.1044	0.1888
Goodness of Fit (GOF)	1.076	1.064	1.071
Maximum peak in Final Diff. Map / $Å^3$	0.36 e^-	0.26 e^-	0.57 e^-
Minimum peak in Final Diff. Map / $Å^3$	–0.76 e^-	–0.23 e^-	–0.59 e^-
Flack parameter	0.032(18)	-	-

12. References of Experimental Section.

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List of Publications

Chapter 1.

Tris(trimethylsilyl)silyl Boronate Esters: Novel Bulky, Air- and Moisture-Stable Silylboronate Ester Reagents for Boryl Substitution and Silaboration Reactions

Yamamoto, E.; Shishido, R.; Seki, T.; Ito, H.
Organometallics **2017**, *36*, 3019–3022.

Chapter 2.

The Direct Dimesitylborylation of Benzofuran Derivatives via Iridium-Catalyzed C–H Activation with Silyldimesitylborane

Shishido, R.; Sasaki, I.; Seki, T.; Ishiyama, T.; Ito, H.
Chem. Eur. J. **2019**, *25*, 12924–12928.

Chapter 3.

A Simple, General Synthesis of Trialkylsilylboranes and Their Use as Silyl Anion Equivalents in Organic Synthesis

Shishido, R.; Uesugi, M.; Kubota, K.; Ito, H.
To be submitted.

Other Publications

1. Direct Introduction of a Dimesitylboryl Group Using Base-Mediated Substitution of Aryl Halides with Silyldimesitylborane

   Yamamoto, E.; Izumi, K.; Shishido, R.; Seki, T.; Tokodai, N.; Ito, H.
   Chem. Eur. J. **2016**, *22*, 17547–17551.

2. Bench-Stable Stock Solutions of Silicon Grignard Reagents: Application to Iron and Cobalt-Catalyzed Radical C(sp^3)–Si Cross-Coupling Reactions

   Xue, W.; Shishido, R.; Oestreich, M.
   Angew. Chem. Int. Ed. **2018**, *57*, 12141–12145. "*Very Important Paper* (VIP)"

3. Transition-metal-free B–B and B–interelement reactions with organic molecules

   Cuenca, A. B.; Shishido, R.; Ito, H.; Fernández, E.
   Chem. Soc. Rev. **2017**, *46*, 415–430.

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