Ph D. Thesis

Development of Efficient Synthesis of Organometallic Compounds Using Functionalized Organoboron Compounds

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Contents

I General Introduction

Organoboron compounds, which have a boryl group on their skeletons, are one of the most attractive synthetic reagents for organic transformations (Figure 1).[1,2] C–B bonds can be transformed into C–heteroatom or C–C bonds under appropriate reaction conditions. In 1938, Johnson reported the oxidation of a C–B bond into C–O–B structure by the treatment with peroxides.[3–6] Additionally, in 1956, Brown reported a hydroboration/oxidation method for the oxidation of double bonds.[7-9] Furthermore, recently, amination and halogenation were also reported.[10] On the other hand, in 1979, Suzuki reported a C–C bond formation reaction catalyzed by a Pd complex, which is well known as Suzuki-Miyaura cross-coupling.[11-16] Therefore, organoboron compounds are regarded as indispensable synthetic reagents.

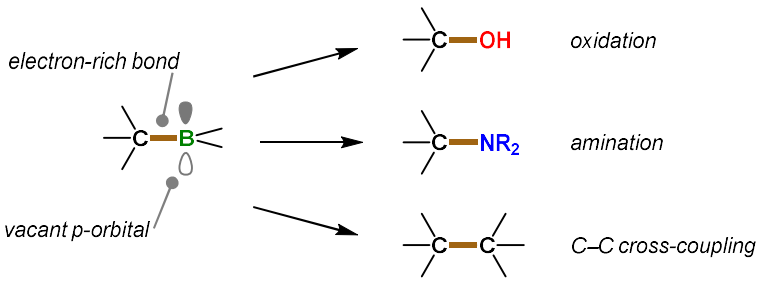


Figure 1. The synthetic utility of organoboron compounds.

Similar to carbon-based organoboron compounds, silylboranes containing a Si-B bond have been studied as easy-to-handle silylation reagents (Figure 2).[17–19] In 1960, Seyferth and Ryschkewitsch reported the synthesis of *B*-silyl borazine as the first silylborane.[20] While the physical property of Si-B bonds was investigated in the early period, their synthetic utility of them has been focused on since the pioneering study by Ito and Suginome in 1996. Ito and Suginome prepared silylboranes via reactions between a silyllithium and boron electrophiles to form Si-B bonds and applied them to a Pd-catalyzed sila-boration reaction of alkynes.[17] As both silicon and boron groups are regarded as useful functional groups that can form various C-heteroatom bonds, such reactivity of silylboranes has attracted great attention and various silylation, borylation, and sila-boration reactions have been developed.[19] These investigations revealed three activation pathways of silylboranes (Figure 2). First is the oxidative addition of a transition-metal into an interelement Si-B bond to afford active silylboryl metal species which can react with unsaturated bonds.[21] Second, the nucleophilic attack of bases to the vacant p orbital of the boron atom produces silylborates, which are regarded as silicon nucleophiles due to their electron-rich feature.[22] These silylborates lead to transmetalation of the silyl group to a metal center in a transition-metal catalytic system or direct nucleophilic silylation to electrophiles. Additionally, an exceptional nucleophilic borylation reaction of organohalides via this activation mode was also reported by Ito.[23] Third, direct lithiation of silylboranes by the treatment with MeLi was

reported by Kawachi and Tamao in 2001.[24] These three activations have in common that they generate nucleophilic silicon species. Due to the electron-positivity of silicon, the generation of nucleophilic silicon species is difficult while electrophilic silicon reagents are widely employed in synthetic chemistry. Therefore, silylboranes are indispensable nucleophilic silicon reagents and have great potential to expand the hitherto silicon chemistry which has been limited by poor accessibility of silicon nucleophiles.

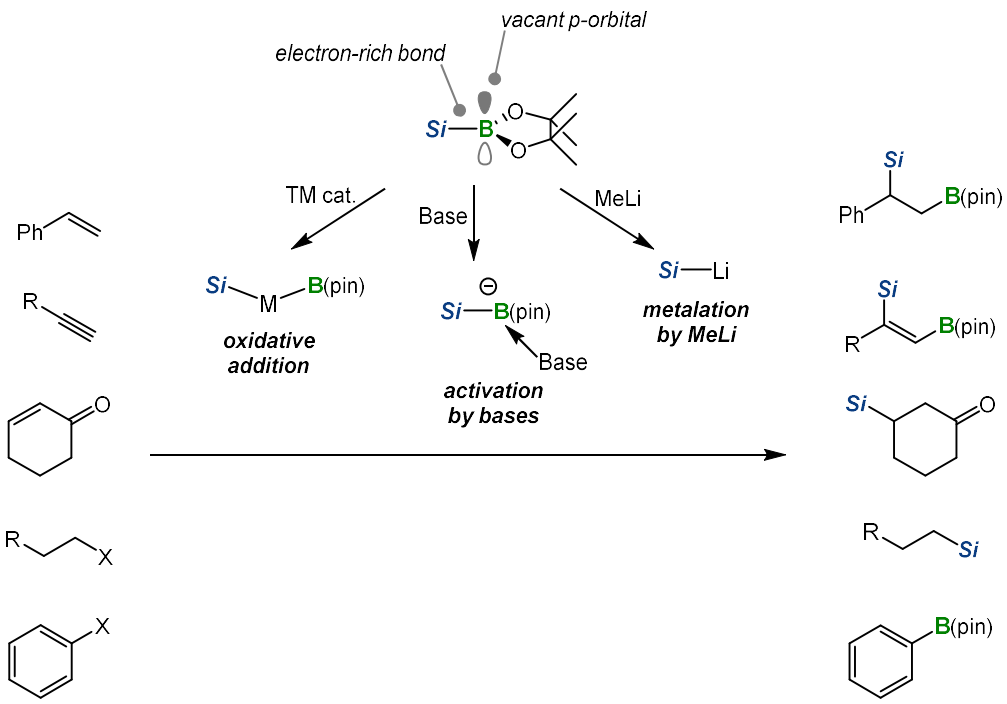


Figure 2. The synthetic utility of silylboranes

Functionalized organoboron compounds bearing a boryl group and another functional group in their skeletons are expected to be more important synthetic reagents because they have two reactivity to form more complicated molecular structures (Figure 3). Also, boron-containing organic molecules often have attractive optical and electronic properties, biological activities, and reactivities (Figure 4).[25-31] Because triarylboron moiety has a high electron capacity, they are used as electron-acceptors in organic materials such as fluorescent, electron-transport, and sensor materials.[25-29,32] In pharmaceutical science, since boronic acids work as bioisosteres of carboxylic acids, α-amino boronic acids are regarded as a mimic of α-amino acids and related peptide drugs such as Bortezomib were developed.[30,33] Borane-based catalysts were also investigated.[31] Tris(pentafluorophenyl)borane is a highly strong Lewis acid and is employed as a Lewis acid catalyst or a part of frustrated Lewis pairs.[34] For these attractive applications of organoboron compounds, functionalized organoboron compounds should be useful as starting materials. Although borylation methods have been well-established, direct

borylation of complex organoboron materials would be failed due to their functional groups. Instead, synthesis from functionalized organoboron compounds through simple transformations could give more complex organoboron compounds. Thus, efficient and facile synthetic methods of functionalized organoboron compounds are required.

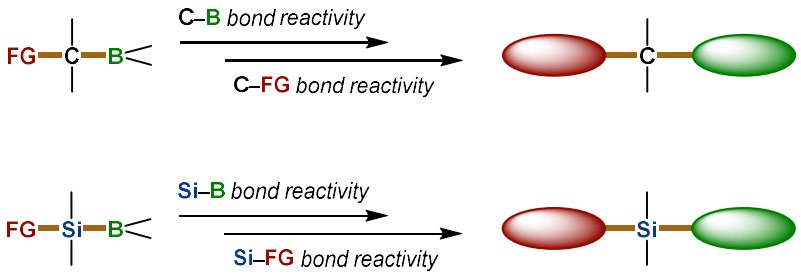


Figure 3. The synthetic potentials of functionalized organoboron compounds.

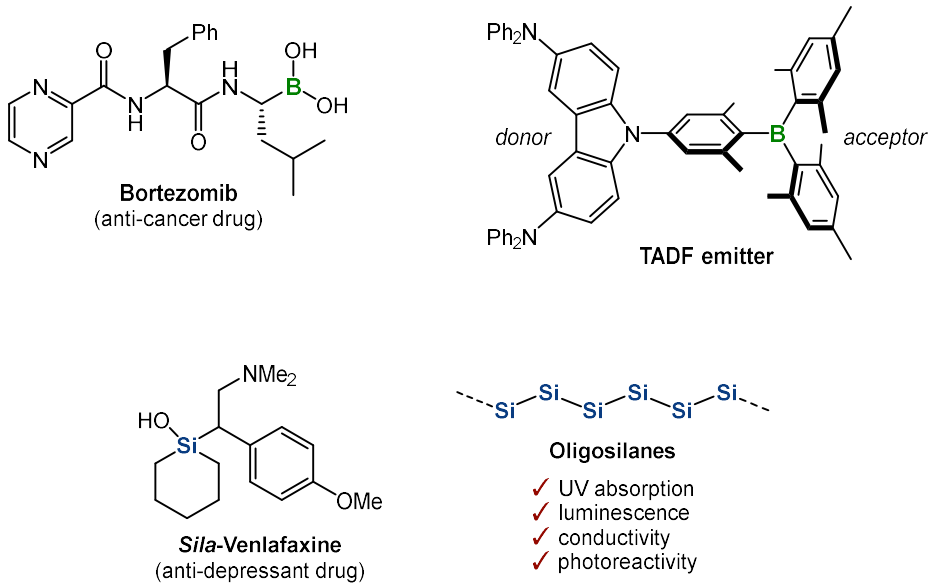
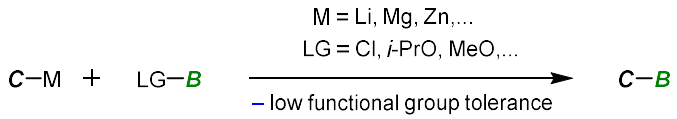


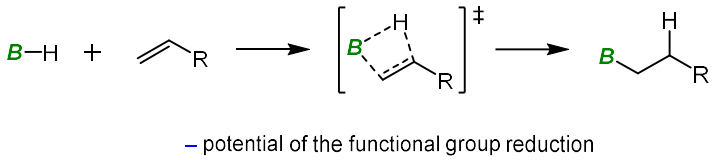
Figure 4. Remarkable organoboron and -silicon compounds.

Among many reported synthetic methods of organoboron compounds, recently developed transition-metal-catalyzed borylation reactions are particularly important for the synthesis of functionalized organoboron compounds because classic stoichiometric borylation reactions involve the reaction using high reactive organometallic species leading to low functional compatibility. In 1860, Frankland reported the first preparation of organoboron compounds using organozinc reagents and boronic esters (Scheme 1).[35,36] Organolithiums and –magnesiums are also employed as nucleophiles. On the other hand, in 1956, Brown reported hydroboration reactions of unsaturated bonds using hydroboranes (Scheme 2).[7-9] However, these methods often cannot be applied to

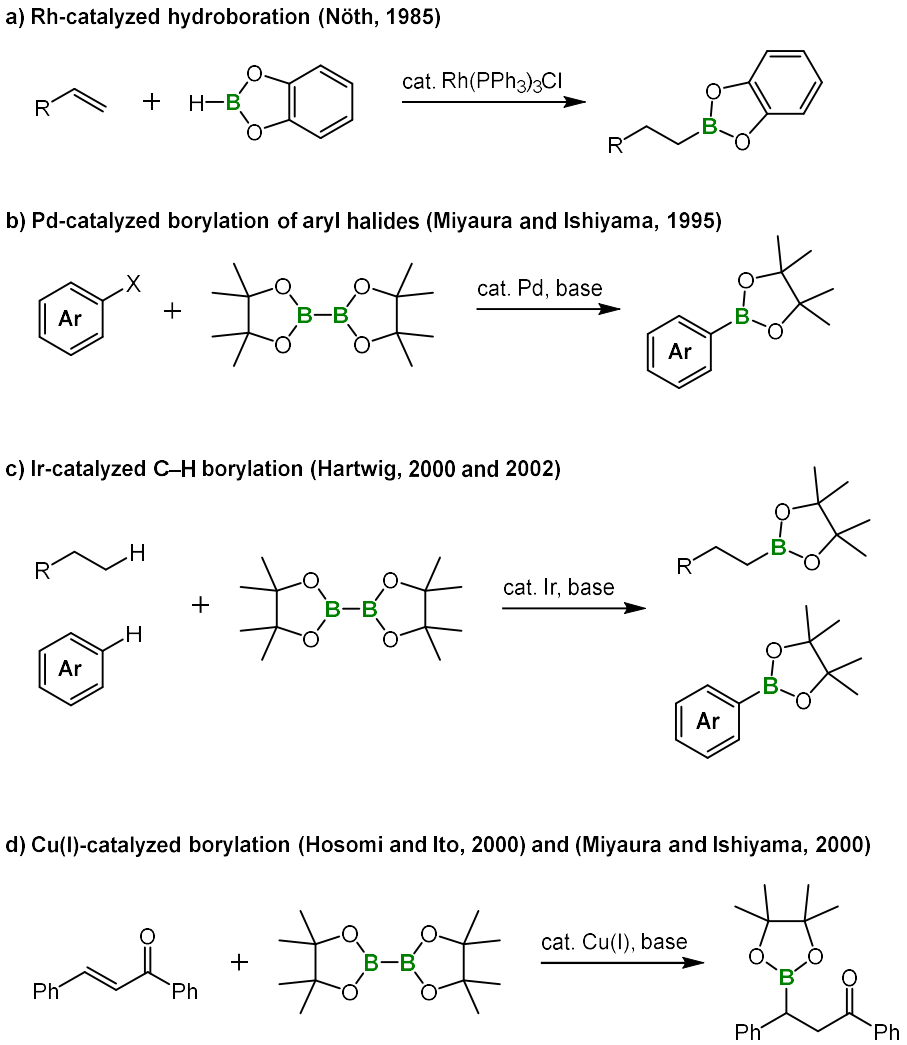
functionalized substrates due to high reactivities of organometals and hydroboranes. Compared to these classic borylation reactions under harsh conditions, transition-metal-catalyzed borylation reactions can produce borylated products under milder conditions (Scheme 3). In 1985, Nöth reported the first catalytic hydroboration of unactivated alkenes using Rh complex as a catalyst (Scheme 3a).[37] Miyaura and Ishiyama also reported Pd-catalyzed borylation of aryl halides(Scheme 3b).[38,39] Furthermore, Hartwig has reported remarkable Ir- and Rh-catalyzed C–H borylation since 2000 (Scheme 3c).[40-43] Compared to expensive Pd, Ir, and Rh catalysts, inexpensive Cu catalysts were reported in 2000 by the Hosomi-Ito group and the Miyaura-Ishiyama group, independently (Scheme 3d).[44-47] Based on these frontrunner borylation reactions, various catalytic borylation reactions have been reported.[48-53] In particular, Cu(I)-catalyzed borylation using bis(pinacolato)diboron is one of the most well-studied methods and various substrates can be transformed into the corresponding organoboron compounds. Thus, C-B bond formation reactions have been drastically built up, leading to the preparation of carbon-based organoboron compounds easily by various synthetic routes.



Scheme 1. Preparation of organoboron compoun ds using organometals and boron electrophiles.



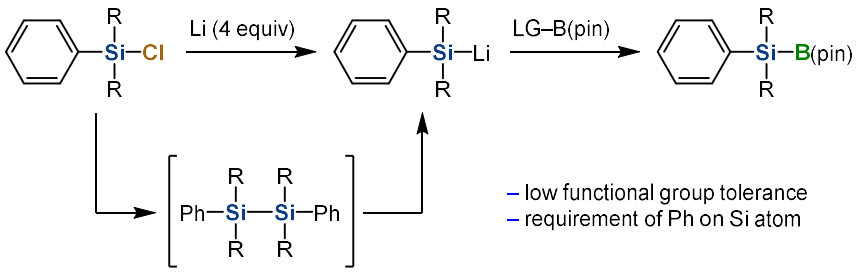
Scheme 2. Hydroboration reaction.



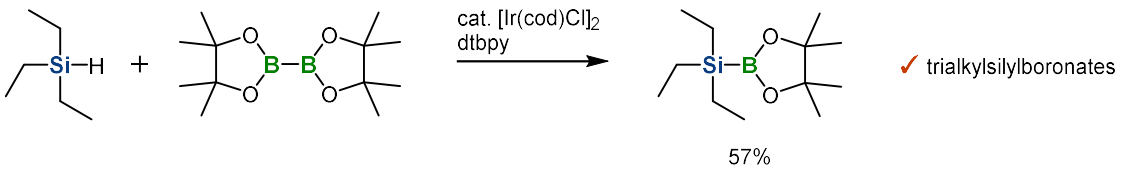
Scheme 3. Catalytic borylation reactions

Synthetic methods of silylboranes have also been developed by many researchers.[17–19] Classically, silylboranes were prepared via the reaction between silyl anions and boron electrophiles (Scheme 4). In 1960, Seyferth and Ryschkewitsch reported the synthesis of a silylated borazine as the first silylboranes (Scheme 4a).[20] Additionally, in 1996, Ito and Suginome reported the first synthesis of silyl(pinacilato)boronate which is commonly employed for organic synthesis today (Scheme 4b).[17] However, the scope of silylboranes is limited due to the limitation of the generation of silyllithiums. Generally, silyllithiums are generated by the reduction of chlorosilanes with alkali metals (Li, Na, and K) and this reduction requires at least one phenyl group on the silicon atom to promote Si–Si cleavage of the disilane intermediate produced by reductive homo-coupling of chlorosilanes.[54,55] The use of highly reactive alkali metals and the requirement of a phenyl group severely limit available silyllithiums. On the other hand, in 2008, Hartwig reported the first catalytic preparation method, the Ir-catalyzed Si–H borylation reaction between hydrosilanes and bis(pinacolato)diboron to form

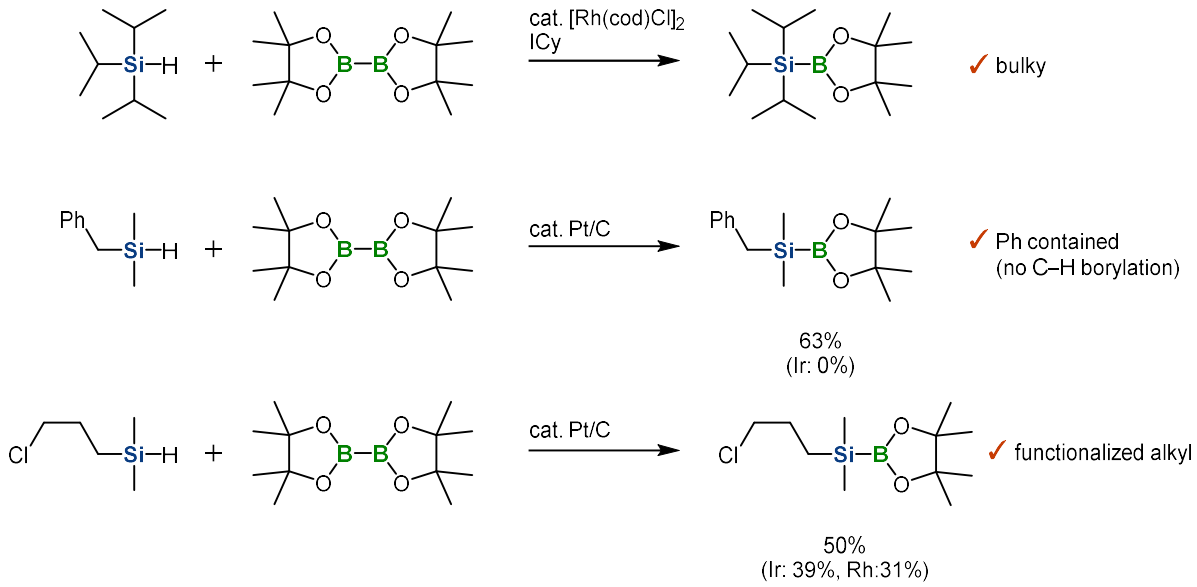
silylboronates (Scheme 5).[56] Noteworthy, this Ir catalytic system can produce trialkylsilylboronates which cannot be prepared by the classic method because of the requirement of a phenyl group on the silicon atom. Furthermore, in 2020, Ito reported Rh and Pt catalytic systems (Scheme 6).[57] Compared to Ir catalysis, Rh catalysis can be applied to bulky silanes such as triisoprorylsilane and Pt catalysis tolerates functional groups. Thus, the chemical space of silylboranes has been dramatically expanded by recently developed transition-metal-catalyzed Si–H borylation reactions.



Scheme 4. The synthesis of silylboranes via the reaction between silyl anions and boron electrophiles



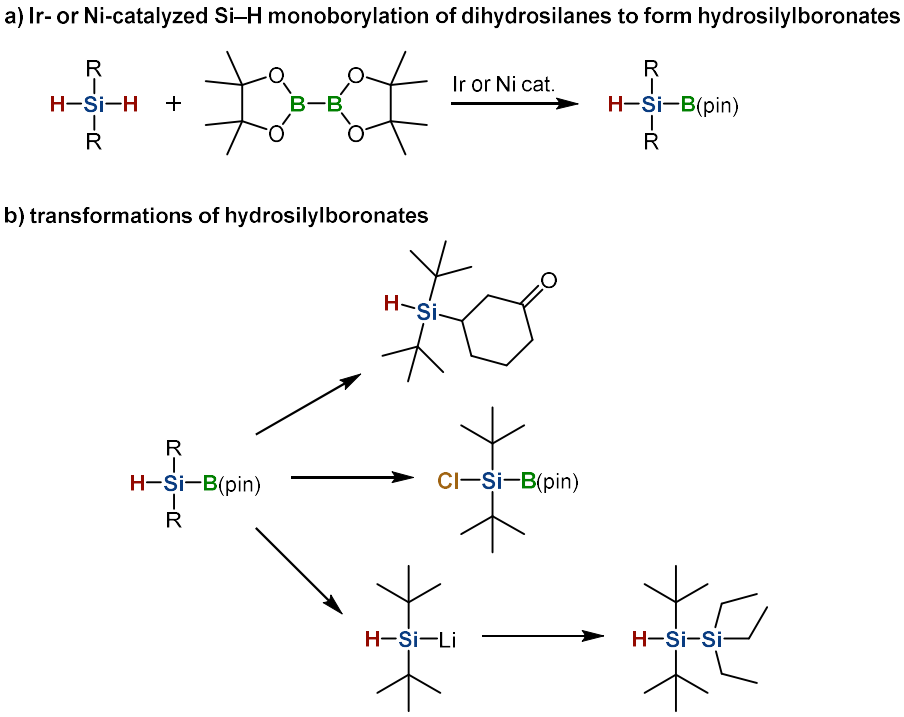
Scheme 5. Ir-catalyzed Si–H borylation of hydrosilanes reported by Hartwig.



Scheme 6. Recently developed Rh and Pt catalytic systems for Si–H borylation.

With this background in the synthesis of organoboron compounds, I have studied the synthesis of functionalized organoboron compounds and their applications. Especially, I focused on the synthesis of functionalized silylboronates because recently developed Si–H borylation opened the way to novel silylboronates. As above mentioned, silylboronates can be used as silicon nucleophiles which are generally difficult to generate. The expanded range of silylboronates promotes synthetic applications of silyl nucleophiles and could enable the creation of novel silicon-based compounds.

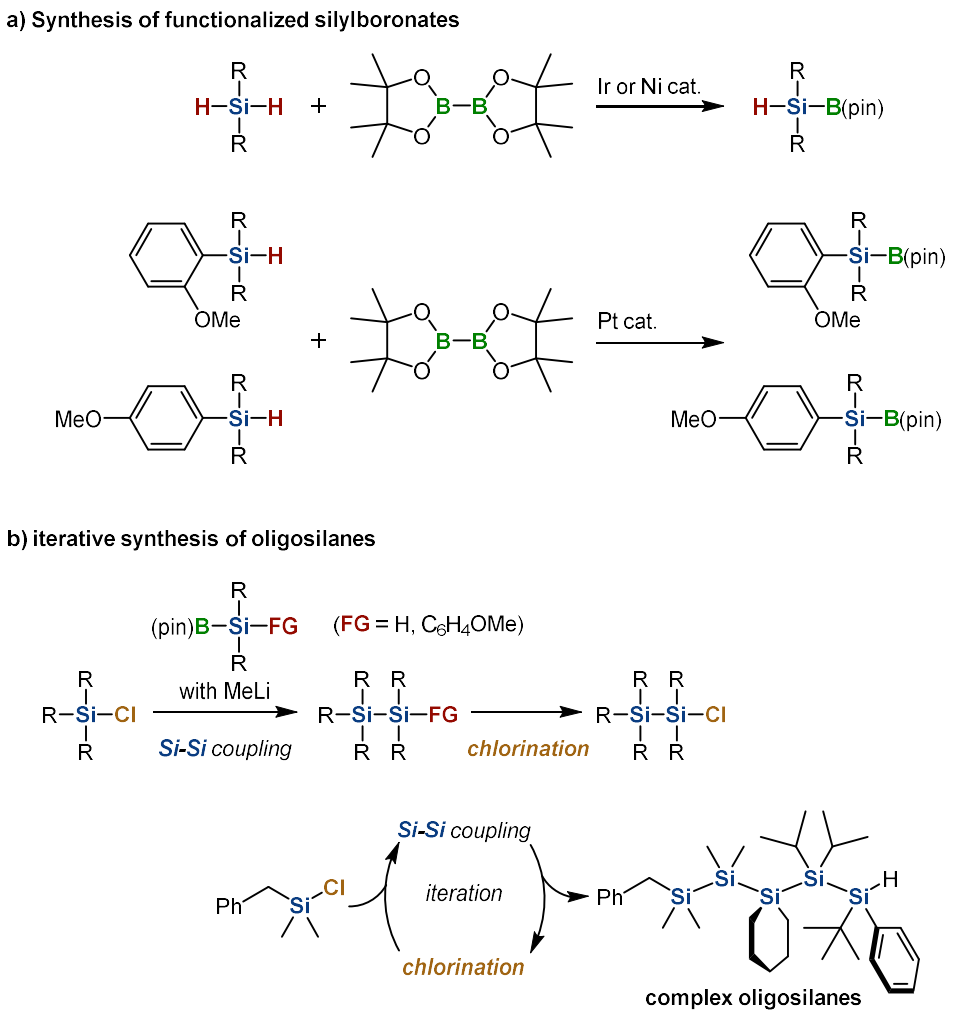
In chapter 2, I report transition-metal-catalyzed monoborylations of dihydrosilanes to form hydrosilylboronates (Scheme 7).[61] Hydrosilylboronates are a class of functionalized silylboronates, which have an active Si–H bond. I found efficient Ir and Ni catalytic systems for the desired Si–H borylation. Obtained hydrosilylboronates applied to the previously reported silylation reactions and produced the corresponding organosilicon compounds. Further, I also report the first spectroscopic evidence of the dialkylhydrosilyl lithium generated by the activation of the hydrosilylboronate with MeLi.



Scheme 7. Overview of chapter 2.

In chapter 3, I describe the iterative synthesis of oligosilanes using functionalized silylboronates produced by transition-metal catalyzed Si–H borylation reactions (Scheme 8).[62] I prepared methoxyphenyl-substituted silylboronates via Pt-catalyzed Si–H borylation and hydrogen-substituted ones via monoborylation of dihydrosilanes described in chapter 2. The present iterative oligosilane synthesis includes two key reactions: Si–Si cross-coupling and chlorination of the oligosilane

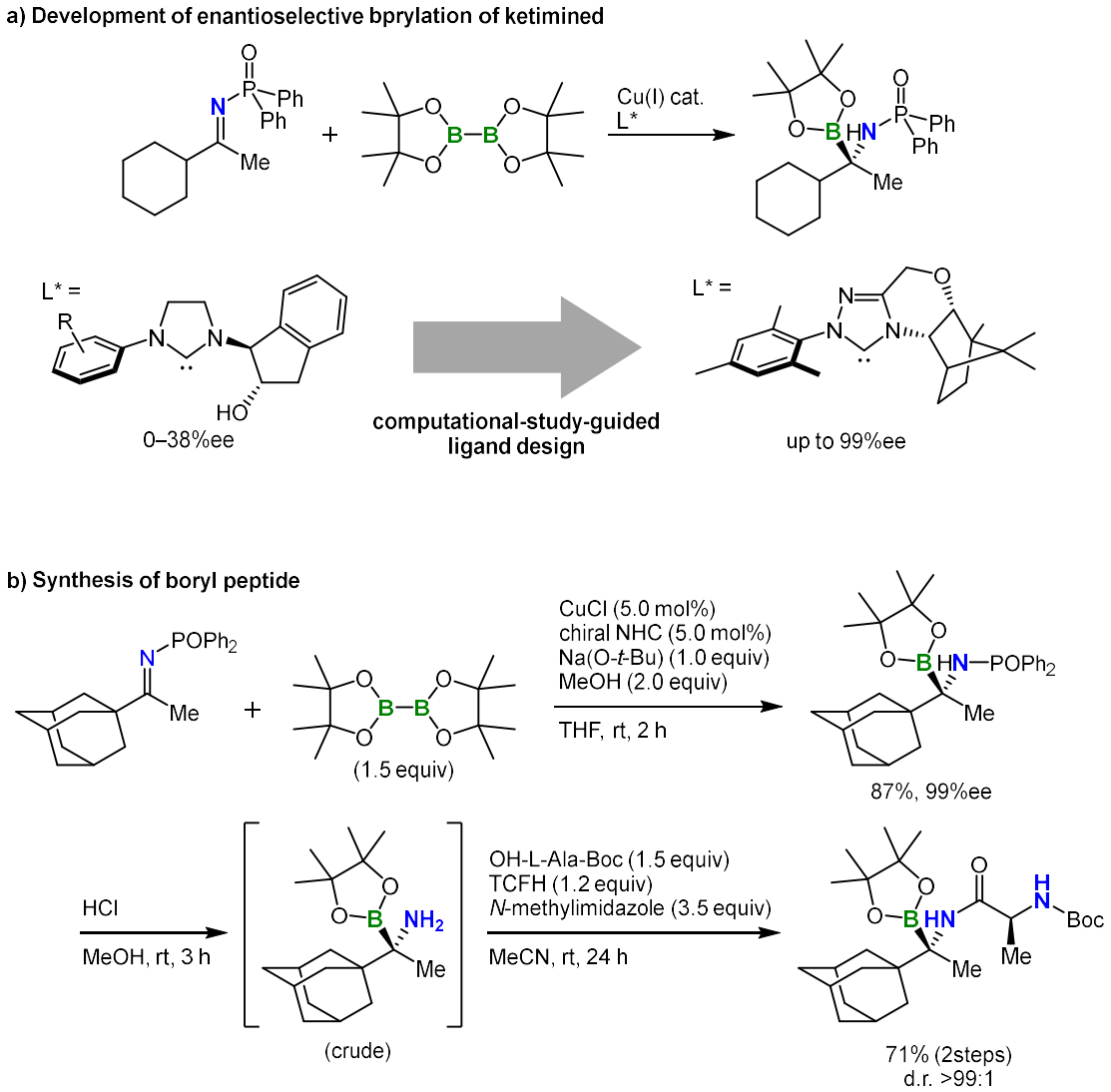
terminals. Si-Si cross-coupling is accomplished by the generation of silyl anions via the activation of silylboronates with MeLi and subsequent reaction with chlorosilanes. The second key step, chlorination, is carried out using another functional group of functionalized silylboronates, methoxyphenyl and hydrogen; these groups on the silicon atom were reported to be readily chlorinated. The advantage of the present iterative synthesis is various oligosilanes can be produced by changing the order of introduced blocks even with limited building blocks. Therefore, the present method allows the synthesis of structurally complicated oligosilanes while classic methods such as the reductive homo-coupling of dichlorosilanes can produce only simple structures.



Scheme 8. Overview of chapter 3.

I also investigated the synthesis of carbon-based functionalized organoboron compounds. In chapter 4, I report the synthesis of chiral α-amino boronates via Cu(I)-catalyzed enantioselective hydroboration of ketimines (Scheme 9).[63] Previously, Ito reported enantioselective hydroborylation of

ketones catalyzed by Cu(I)/chiral NHC complex (Scheme 9a).[64] However, when this catalytic system was applied to ketimines instead of ketones, enantioselectivity was greatly decreased (Scheme 9b). In order to overcome this problem, I tried computational analysis of this reaction with DFT calculation. Based on the structure of transition states, a NHC ligand with a large protruding substituent was expected to enhance enantioselectivity. With this expectation, I tested several NHC candidates and finally found a suitable NHC ligand with a camphor moiety. The obtained α-amino boronates can be converted into peptidyl boronic acids.



Scheme 9. Overview of chapter 4.

References

1) Boronic Acids: Preparation, Applications in Organic Synthesis and Medicine; Hall, D. G., Ed.; Wiley-VCH, Weinheim, 2011; Vols 1–2.
2) Fyfe, J. W. B.; Watson, A. J. B. Recent Developments in Organoboron Chemistry: Old Dogs, New Tricks. *Chem* **2017**, *3*, 31–55.
3) Snyder, H. R.; Kuck, J. A.; Johnson, R. J. Organoboron Compounds, and the Study of Reaction Mechanisms. Primary Aliphatic Boronic Acids. *J. Am. Chem. Soc.* **1938**, *60*, 105–111.
4) Johnson, J. R.; Van Campen, M. G.; Grummitt, O. Organoboron Compounds. II. The Reducing Action of Some Organoboronic Acids. *J. Am. Chem. Soc.* **1938**, *60*, 111–115
5) Johnson, J. R.; Snyder, H. R.; Van Campen, M. G. Organoboron Compounds. III. Reactions of Tri-n-Butylborine. *J. Am. Chem. Soc.* **1938**, *60*, 115–121.
6) Johnson, J. R.; Van Campen, M. G. Organoboron Compounds. IV. Reaction of Tri-nButylborine with Peroxides and with Oxygen. Mechanism of Autoöxidation. *J. Am. Chem. Soc.* **1938**, *60*, 121–124.
7) Brown, H. C.; Subba Rao, B. C. A New Technique for the Conversion of Olefins into Organoboranes and Related Alcohols. *J. Am. Chem. Soc.* **1956**, *78*, 5694–5695.
8) Brown, H. C.; Subba Rao, B. C. Hydroboration of Olefins. A Remarkably Fast RoomTemperature Addition of Diborane to Olefins. *J. Org. Chem.* **1957**, *22*, 1136–1137.
9) Brown, H. C.; Zweifel, G. Hydroboration. IX. The Hydroboration of Cyclic and Bicyclic Olefins-Stereochemistry of the Hydroboration Reaction. *J. Am. Chem. Soc.* **1961**, *83*, 2544– 2551.
10) Sandford, C.; Aggarwal, V. K. Stereospecific Functionalizations and Transformations of Secondary and Tertiary Boronic Esters. *Chem. Commun.* **2017**, *53*, 5481–5494.
11) Miyaura, N.; Suzuki, A. Palladium-Catalyzed Cross-Coupling Reactions of Organoboron Compounds. *Chem. Rev.* **1995**, *95*, 2457–2483.
12) Miyaura, N.; Suzuki, A. Stereoselective Synthesis of Arylated (E)-Alkenes by the Reaction of Alk-1-Enylboranes with Aryl Halides in the Presence of Palladium Catalyst. *J. Chem. Soc. Chem. Commun.* **1979**, 866–867.
13) Miyaura, N.; Yamada, K.; Suzuki, A. A New Stereospecific Cross-Coupling by the PalladiumCatalyzed Reaction of 1-Alkenylboranes with 1-Alkenyl or 1-Alkynyl Halides. *Tetrahedron Lett.* **1979**, *20*, 3437–3440.
14) Miyaura, N. Cross-Coupling Reaction of Organoboron Compounds via Base-Assisted Transmetalation to Palladium(II) Complexes. *J. Organomet. Chem.* **2002**, *653*, 54–57.
15) Lennox, A. J. J.; Lloyd-Jones, G. C. Selection of Boron Reagents for Suzuki-Miyaura Coupling. *Chem. Soc. Rev.* **2014**, *43*, 412–443.
16) Enantioselective, Rhodium-Catalyzed 1,4-Addition of Organoboron Reagents to ElectronDeficient Alkenes. In Organic Reactions; John Wiley & Sons, Inc.: Hoboken, NJ, USA,

2017; Vol. 93, pp 1–686.

17) Cuenca, A. B.; Shishido, R.; Ito, H.; Fernandez, E. Transition-metal-free B–B and B–interelement reactions with organic molecules. *Chem. Soc. Rev.* **2017**, *46*, 415–430.

18) (a) Suginome, M.; Nakamura, H.; Ito, Y. Regio- and Stereo-selective Silaboration of Alkynes catalyzed by Palladium and Platinum Complexes. *Chem. Commun.* **1996**, 2777–2778. (b) Suginome, M.; Matsuda, T.; Ito, Y. Convenient Preparation of Silylboranes. *Organometallics* **2000**, *19*, 4647–4649. (c) Ohmura, T.; Matsuda, K.; Furukawa, H.; Suginome, M. Synthesis of Silylboronic Esters Functionalized on Silicon. *Organometallics* **2007**, *26*, 1291–1294.

19) (a) Oestreich, M.; Hartmann, E.; Mewald, M. Activation of the Si–B Interelement Bond: Mechanism, Catalysis, and Synthesis. *Chem. Rev.* **2013**, *113*, 402–441. (b) Ohmura, T.; Suginome, M. Silylboronates as New Tools in Organic Synthesis. *Bull. Chem. Soc. Jpn.* **2009**, *82*, 29–49. (c) Xue, W.; Oestreich, M. Beyond Carbon: Enantioselective and Enantiospecific Reactions with Catalytically Generated Boryl- and Silylcopper Intermediates. *ACS Cent. Sci.* **2020**, *6*, 1070–1081. (d) Feng, J.-J.; Mao, W.; Zhang, L.; Oestreich, M. Activation of the Si–B Interelement Bond Related to Catalysis. *Chem. Soc. Rev.* **2021**, *50*, 2010–2073.

20) (a) Seyferth, D.; Kögler, H. P. Preparation of organosilicon-substituted borazenes. *J. Inorg. Nucl. Chem.* **1960**, *15*, 99–104. (b) Cowley, A. H.; Sisler, H. H.; Ryschkewitsch, G. E. The chemistry of borazine. III. B–silyl boranzines. *J. Am. Chem. Soc.* **1960**, *82*, 501–502.

21) (a) Cui, B.; Jia, S.; Tokunaga, E.; Shibata, N. Defluorosilylation of fluoroarenes and fluoroalkanes. *Nat. Commun.* **2018**, *9*, 4393–4400. (b) Zarate, C.; Nakajima, M.; Martin, R. A mild and ligand-free Ni-catalyzed silylation via C–OMe cleavage. *J. Am. Chem. Soc.* **2017**, *139*, 1191– 1197. (c) Guo, L.; Chatupheeraphat, A.; Rueping, M. Decarbonylative silylation of esters by combined nickel and copper catalysis for the synthesis of arylsilanes and heteroarylsilanes. *Angew. Chem., Int. Ed.* **2016**, *55*, 11810– 11813. (d) Tani, Y.; Yamaguchi, T.; Fujiwara, T.; Terao, J.; Tsuji, Y. Copper-catalyzed silylative allylation of ketones and aldehydes employing allenes and silylboranes. *Chem. Lett.* **2015**, *44*, 271– 273.

22) (a) Morimasa, Y.; Kabasawa, K.; Ohmura, T.; Suginome, M. Pyridine-based organocatalysts for regioselective syn-1,2-silaboration of terminal alkynes and allenes. *Asian J. Org. Chem.* **2019**, *8*, 1092–1096. (b) Kojima, K.; Nagashima, Y.; Wang, C.; Uchiyama, M. In situ generation of silyl anion species through Si–B bond activation for the concerted nucleophilic aromatic substitution of fluoroarenes. *ChemPlusChem* **2019**, *84*, 277–280. (c) Gu, Y.; Shen, Y.; Zarate, C.; Martin, R. A mild and direct site-selective sp2-C–H silylation of (poly)azines. *J. Am. Chem. Soc.* **2019**, *141*, 127–132. (d) Liu, X.-W.; Zarate, C.; Martin, R. Base-mediated defluorosilylation of C(sp2)–F and C(sp3)–F bonds. *Angew. Chem., Int. Ed.* **2019**, *58*, 2064–2068. (e) Gao, P.; Wang, G.; Xi, L.; Wang, M.; Li, S.; Shi, Z. Transition-metal-free defluorosilylation of fluoroalkenes with silylboronates. *Chin. J. Chem.* **2019**, *37*, 1009–1014.

23) (a) Yamamoto, E.; Izumi, K.; Horita, Y.; Ito, H. Anomalous Reactivity of Silylborane: Transition-Metal-Free Boryl Substitution of Aryl, Alkenyl, and Alkyl Halides with Silylborane/Alkoxy Base Systems. *J. Am. Chem. Soc.* **2012**, *134*, 19997–20000. (b) Yamamoto, E.; Ukigai, S.; Ito, H. Boryl substitution of functionalized aryl-, heteroaryl- and alkenyl halides with silylborane and an alkoxy base: expanded scope and mechanistic studies. *Chem. Sci.* **2015**, *6*, 2943–2951. (c) Uematsu, R.; Yamamoto, E.; Maeda, S.; Ito, H. Taketsugu, T. Reaction Mechanism of the Anomalous Formal Nucleophilic Borylation of Organic Halides with Silylborane: Combined Theoretical and Experimental Studies. *J. Am. Chem. Soc.* **2015**, *137*, 4090–4099. (d) Yamamoto, E.; Izumi, K.; Shishido, R.; Seki, T.; Tokodai, N.; Ito, H. Direct Introduction of a Dimesitylboryl Group Using Base-Mediated Substitution of Aryl Halides with Silyldimesitylborane. *Chem. Eur. J.* **2016**, *22*, 17547-17551. (e) Yamamoto, E.; Maeda, S.; Taketsugu, T.; Ito, H. Transition-Metal-Free Boryl Substitution Using Silylboranes and Alkoxy Bases. *Synlett* **2017**, *28*, 1258-1267. (f) Yamamoto, E.; Shishido, R.; Seki, T.; Ito, H. Tris(trimethylsilyl)silylboronate Esters: Novel Bulky, Air- and Moisture-Stable Silylboronate Ester Reagents for Boryl Substitution and Silaboration Reactions. *Organometallics* **2017**, *36*, 3019-3022.

24) (a) Kawachi, A.; Minamimoto, T.; Tamao, K. Boron–Metal Exchange Reaction of Silylboranes with Organometallic Reagents: A New Route to Arylsilyl Anions. *Chem. Lett.* **2001**, *30*, 1216–1217. (b) Kajiwara, T.; Takeda, N.; Sasamori, T.; Tokitoh N. Synthesis of Alkali Metal Salts of Borylsilyl Anions Utilizing Highly Crowded Silylboranes and Their Properties. *Organometallics* **2008**, *27*, 880–893.

25) *Recent Advances in Boron-Containing Materials*; Aydin, M., Ed.; IntechOpen, 2019.

26) Ren, Y.; Jäkle, F. Merging Thiophene with Boron: New Building Blocks for Conjugated Materials. *Dalton. Trans.* **2016**, *45*, 13996–14007.

27) Haque, A.; Al-balushi, R. A.; Raithby, P. R.; Khan, M. S. Recent Advances in π-Conjugated N^C-Chelate. *Molecules* **2020**, *25*, 2645.

28) Lee, H.; Karthik, D.; Lampande, R.; Ryu, J. H.; Kwon, J. H. Recent Advancement in Boron-Based Efficient and Pure Blue Thermally Activated Delayed Fluorescence Materials for Organic Light-Emitting Diodes. *Front. Chem.* **2020**, *8*, 1–16.

29) Dhiman, A.; Giribabu, L.; Trivedi, R. π-Conjugated Materials Derived From Boron-Chalcogenophene Combination. A Brief Description of Synthetic Routes and Optoelectronic Applications. *Chem. Rec.* **2021**, *21*, 1738–1770.

30) Song, S.; Gao, P.; Sun, L.; Kang, D.; Kongsted, J.; Poongavanam, V.; Zhan, P.; Liu, X. Recent Developments in the Medicinal Chemistry of Single Boron Atom-Containing Compounds. *Acta Pharm. Sin. B* **2021**, *11*, 3035–3059.

31) Pineschi, M. Boron Reagents and Catalysts for the Functionalization of Strained Heterocycles. *Adv. Synth. Catal.* **2021**, 2325–2339.

32) Qi, Y.; Cao, X.; Zou, Y.; Yang, C. Multi-Resonance Organoboron-Based Fluorescent Probe for Ultra-Sensitive, Selective and Reversible Detection of Fluoride Ions. *J. Mater. Chem. C* **2021**, *9*, 1567–1571.

33) Adams, J.; Behnke, M.; Chen, S.; Cruickshank, A. A.; Dick, L. R.; Grenier, L.; Klunder, J. M.; Ma, Y. T.; Plamondon, L.; Stein, R. L. Potent and Selective Inhibitors of the Proteasome: Dipeptidyl Boronic Acids. *Bioorganic Med. Chem. Lett.* **1998**, *8*, 333–338.

34) B(C6F5)3 の触媒と FLP のレビュー探す

35) Frankland, E.; Duppa, B. On Boric Ethide. *Proc. R. Soc. London* **1860**, *10*, 568–570.

36) Frankland, E.; Duppa, B. Vorläufige Notiz Über Boräthyl. *Justus Liebigs Ann. Chem.* **1860**, *115*, 319–322.

37) Männig, D.; Nöth, H. Catalytic Hydroboration with Rhodium Complexes. *Angew. Chem., Int. Ed.* **1985**, *24*, 878–879.

38) Ishiyama, T.; Murata, M.; Miyaura, N. Palladium(0)-Catalyzed Cross-Coupling Reaction of Alkoxydiboron with Haloarenes: A Direct Procedure for Arylboronic Esters. *J. Org. Chem.* **1995**, *60*, 7508–7510.

39) Takagi, J.; Takahashi, K.; Ishiyama, T.; Miyaura, N. Palladium-Catalyzed Cross-Coupling Reaction of Bis(Pinacolato)Diboron with 1-Alkenyl Halides or Triflates: Convenient Synthesis of Unsymmetrical 1,3-Dienes via the Borylation-Coupling Sequence. *J. Am. Chem. Soc.* **2002**, *124*, 8001–8006.

40) Waltz, K. M.; He, X.; Muhoro, C.; Hartwig, J. F. Hydrocarbon Functionalization by Transition Metal Boryls. *J. Am. Chem. Soc.* **1995**, *117*, 11357–11358.

41) Waltz, K. M.; Hartwig, J. F. Functionalization of Alkanes by Isolated Transition Metal Boryl Complexes. *J. Am. Chem. Soc.* **2000**, *122*, 11358–11369.

42) Chen, H.; Schlecht, S.; Semple, T. C.; Hartwig, J. F. Thermal, Catalytic, Regiospecific Functionalization of Alkanes. *Science* **2000**, *287*, 1995–1997.

43) Takagi, J.; Sato, K.; Hartwig, J. F.; Ishiyama, T.; Miyaura, N. Iridium-Catalyzed C–H Coupling Reaction of Heteroaromatic Compounds with Bis(pinacolato)diboron: Regioselective Synthesis of Heteroarylboronates. *Tetrahedron Lett.* **2002**, *43*, 5649–5651.

44) Ito, H.; Yamanaka, H.; Tateiwa, J.; Hosomi, A. Boration of an α,β-Enone Using a Diboron Promoted by a Copper(I)–Phosphine Mixture Catalyst. *Tetrahedron Lett.* **2000**, *41*, 6821–6825.

45) Takahashi, K.; Ishiyama, T.; Miyaura, N. Addition and Coupling Reactions of Bis(pinacolato)diboron Mediated by CuCl in the Presence of Potassium Acetate. *Chem. Lett.* **2000**, *57*, 982–983.

46) Takahashi, K.; Ishiyama, T.; Miyaura, N. A Borylcopper Species Generated from Bis(pinacolato)diboron and Its Additions to α,β-Unsaturated Carbonyl Compounds and Terminal Alkynes. *J. Organomet. Chem.* **2001**, *625*, 47–53.

47) Neeve, E. C.; Geier, S. J.; Mkhalid, I. A. I.; Westcott, S. A.; Marder, T. B. Diboron(4) Compounds: From Structural Curiosity to Synthetic Workhorse. *Chem. Rev.* **2016**, *116*, 9091– 9161.

48) Mkhalid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. C–H Activation for the Construction of C–B Bonds. *Chem. Rev.* **2010**, *110*, 890–931.

49) Hartwig, J. F. Regioselectivity of the Borylation of Alkanes and Arenes. *Chem. Soc. Rev.* **2011**, *40*, 1992–2002.

50) Xu, L.; Wang, G.; Zhang, S.; Wang, H.; Wang, L.; Liu, L.; Jiao, J.; Li, P. Recent Advances in Catalytic C−H Borylation Reactions. *Tetrahedron* **2017**, *73*, 7123–7157.

51) Kuroda, Y.; Nakao, Y. Catalyst-Enabled Site-Selectivity in the Iridium-Catalyzed CH Borylation of Arenes. *Chem. Lett.* **2019**, *48*, 1092–1100.

52) Wang, M.; Shi, Z. Methodologies and Strategies for Selective Borylation of C–Het and C–C Bonds. *Chem. Rev.* **2020**, *120*, 7348–7398.

53) Yadagiri, B.; Daipule, K.; Singh, S. P. Photoinduced Borylation Reactions: An Overview. *Asian J. Org. Chem.* **2021**, *10*, 7–37.

54) (a) Lerner, H.-W. Silicon Derivatives of Group 1, 2, 11, 12 elements. *Coord. Chem. Rev.* **2005**, *249*, 781–798. (b) Sekiguchi, A.; Lee, V. Y.; Nanjo, M. Lithiosilanes and Their Application to the Synthesis of Polysilane Dendrimers. *Coord. Chem. Rev.* **2000**, *210*, 11–45. (c) Kawachi, A.; Tamao, K. Preparation and Reaction of Functionalized Silyllithiums. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 945–955.

55) (a) Rahman, N. A.; Fleming, I; Zwicky, A. B. Failure in Several Attempts to Prepare Arylsilyl-lithium Reagents by the Gilman Cleavage of Disilanes with Lithium. *J. Chem. Res.*, *Miniprint* **1992**, 2401–2409. (b) Lee, T. W. Corey, E. J. (2-Methoxyphenyl)dimethylsilyl Lithium and Cuprate Reagents Offer Unique Advantages in Multistep Synthesis. *Org. Lett.* **2001**, *3*, 3337–3339.

56) Boebel, T. A.; Hartwig, J. F. Iridium-Catalyzed Preparation of Silylboranes by Silane Borylation and Their Use in the Catalytic Borylation of Arenes. *Organometallics* **2008**, *27*, 6013–6019.

57) Shishido, R.; Uesugi, M.; Takahashi, R.; Mita, T.; Ishiyama, T.; Kubota, K.; Ito, H. General Synthesis of Trialkyl- and Dialkylarylsilylboranes: Versatile Silicon Nucleophiles in Organic Synthesis. *J. Am. Chem. Soc.* **2020**, *142*, 14125–14133.

58) Takeuchi, T.; Shishido, R.; Kubota, K.; Ito, H. Synthesis of Hydrosi-lylboronates via the Monoborylation of a Dihydrosilane Si–H Bond and Their Application for the Generation of Dialkylhydrosilyl Anions. *Chem. Sci.* **2021**, *12*, 11799–11804.

59) Takeuchi, T.; Roy, A.; Ito, H. Iterative Synthesis of Oligosilanes Using Methoxyphenyl- and Hydrogen-Substituted Silylboronates as Building Blocks: General Synthetic Method for Complex Oligosilanes. *under revision*.

60) Kubota, K.; Miura, D.; Takeuchi, T.; Osaki, S.; Ito, H. Synthesis of Chiral α-Amino Tertiary Boronates via the Catalytic Enantioselective Nucleophilic Borylation of Dialkyl Ketimines. *ACS*

Catal. **2021**, *11*, 6733–6740.

61) Kubota, K.; Osaki, A.; Jin, M.; Ito, H. Copper(I)-Catalyzed Enantioselective Nucleophilic Borylation of Aliphatic Ketones: Synthesis of Enantioenriched Chiral Tertiary α-Hydroxyboronates. *Angew*. *Chem*., *Int*. *Ed*. **2017**, *56*, 6646– 6650.

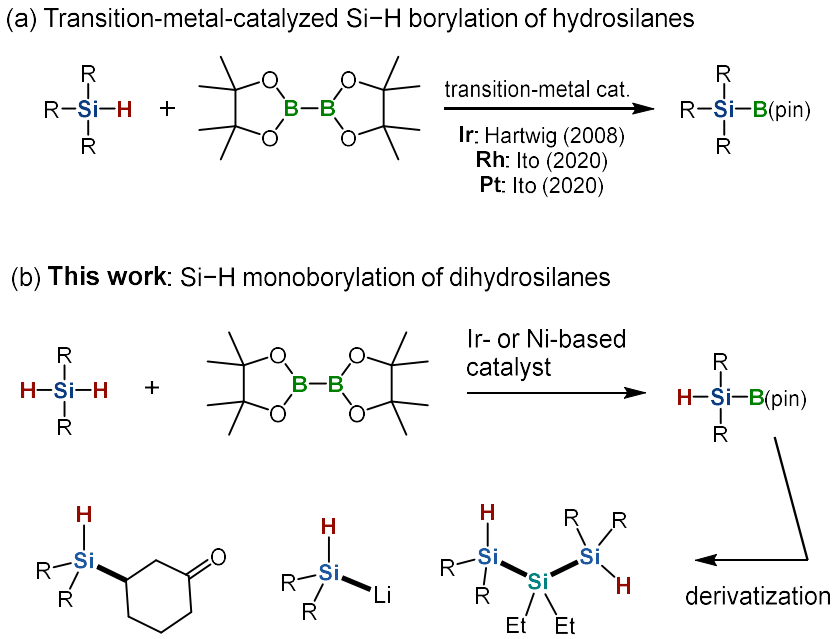
II Synthesis of Hydrosilylboronates via the Transition-Metal-Catalyzed Monoborylation of dihydrosilanes

2.1: Introduction

Silicon-based compounds have many applications in catalyst design, drug discovery, materials science, and polymer chemistry.[1] The development of new reagents for the synthesis of organosilicon compounds is important for a broad range of scientific fields.[1] Since the pioneering study of Suginome and Ito in 1996, silylboronates have become indispensable silylation reagents on account of their reactivity and the ease with which they can be handled.[1–3] In the presence of a transition-metal catalyst or a base, silylboronates can be easily activated and used as silicon nucleophiles for reactions with a electrophiles. [1–3] Given their high synthetic utility, the development of efficient preparation methods of silylboronates would expand the range of silicon-based compounds that are synthetically accessible.

The typical preparation method of silylboronates involves a reaction between a silyl anion and a boron electrophile.[2] As silyl anions are in most cases produced by the reduction of chlorosilanes with alkali metals, the variety of substituents tolerated on the silicon atom is quite limited; moreover, at least one aromatic group is required at the silicon center to promote the reduction of chlorosilanes and disilane intermediates.[4,5] Additionally, due to the harsh reduction conditions, this method suffers from low functional-group compatibility. Therefore, only a limited range of silylboronates can be prepared using this approach.

Instead, the direct Si–H borylation of hydrosilanes is being a valuable complementary method for the synthesis of silylboronates (Scheme 1a).[6,7] In 2008, Hartwig reported a pioneering Si–H borylation of trialkylhydrosilanes with bis(pinacolato)diboron [$B_2(pin)_2$] catalyzed by Ir complex. This reaction forms trialkylsilylboronates, which cannot be synthesized using the conventional reduction based on alkali metals.[6] In 2020, Ito group reported that rhodium- and platinum- Si–H borylation of trialkylhydrosilanes. Ito method can produce bulky and functionalized trialkylsilylboronates that are difficult to access via either the iridium-catalyzed borylation or the conventional reduction method (Scheme 1a).[7]



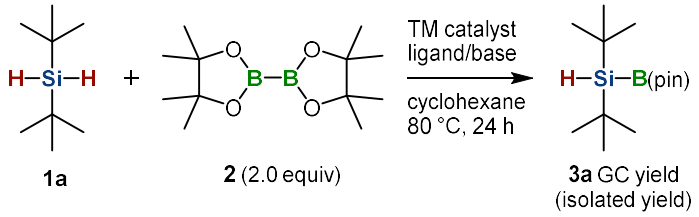
Scheme 1. Transition-metal-catalyzed Si–H borylation of hydrosilanes.

In the present study, we discovered that the monoborylation of a dihydrosilane Si−H bond can be achieved in the presence of iridium- or nickel-based catalysts, yielding hydrosilylboronates that bear a hydrogen atom at the silicon center (Scheme 1b). In 2004, Tokitoh and co-workers reported the first synthesis of diarylhydrosilylboronates via the insertion of a silylene into a H–B bond.[8] Although this pioneering study is remarkable, the substituents on the silicon atom are limited to extremely bulky aryl moieties, such as mesityl and 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl groups, due to the highly reactive silylene species involved in the reaction.[8] The monoborylation approach reported here is applicable to the synthesis of dialkylhydrosilylboronates and alkylarylhydrosilylboronates from easily accessible dihydrosilanes. These hydrosilylboronates are difficult to access by any other means. Furthermore, we demonstrate that these hydrosilylboronates can be used as novel silicon nucleophiles in the presence of a transition-metal catalyst or base. Moreover, we report the first $^{29}Si\{^{1}H\}$ NMR spectroscopic evidence for the formation of (t-Bu_2)HSiLi, generated via the reaction of (t-Bu_2)HSi–B(pin) with MeLi. Although the synthesis of disilylhydrosilyl lithium compounds has already been reported by Iwamoto, Kira and co-workers[5f], this is the first example of the formation of dialkylhydrosily lithium species.

2.2: Results and Discussion

We started optimization of the reaction conditions for the borylation of di-*tert*-butylsilane (**1a**) with $B_2(pin)_2$ (**2**) in the presence of a variety of transition-metal catalysts (Table 1). Initially, I investigated

an iridium-based catalytic system, as originally reported by Hartwig (entry 1).[6] The reaction using $[Ir(cod)Cl]_2$/4,4'-di-*tert*-butyl-2,2'-dipyridyl (dtbpy) (**L1**) as the catalyst in cyclohexane at 80 °C gave the desired product (**3a**) in 68% yield (entry 1). Notably, the di-borylated product was not detected. We also attempted the reaction with Rh and Pt catalysts.[7] Unfortunately, the rhodium catalyst resulted in a complex product mixture (**3a**: <1%; entry 2), and the platinum catalyst produced **3a** in 36% yield (entry 3). To improve the iridium catalytic system, we used NHC ligands instead of dtbpy (**L1**).[7] ICy·HCl (**L2**) resulted in 43% yield of **3a** (entry 4), whereas the use of **L3**, which is an NHC ligand that contains a pyridine moiety, provided a slightly higher yield than dtbpy (**L1**) (73%, entry 5).[9] We found that **3a** could be obtained in 71% yield (entry 6) even at a lower catalyst loading (0.5 mol%). Although there aren't any reports in the literature on the borylation of Si–H bonds using a nickel catalyst,[10] we discovered that nickel-based catalysts are also effective for the monoborylation of **1a**. While the formation of **3a** was not observed when $Ni(cod)_2$/1,3-dimesitylimidazolium chloride (IMes·HCl) (**L4**) was employed (**3a**: <1%; entry 7), the use of **L2** instead of **L4** afforded **3a** in 50% yield (entry 8). However, the reproducibility of the reaction was unsatisfactory under these conditions. After an extensive screening of the reaction conditions, we found that when the reaction was carried out in *n*-octane at 120 °C, **3a** was obtained in 54% yield with excellent reproducibility (entry 9). I also demonstrated that **3a** can be isolated in 63% yield using column chromatography on silica gel (entry 6).



entry	TM catalyst (mol%)	ligand (mol%)	base (mol%)	yield (%)[a]
1	$[Ir(cod)Cl]_2$ (2.5)	**L1** (5)	none	68
2[b]	$[Rh(cod)Cl]_2$ (2.5)	**L2** (10)	K(O-*t*-Bu) (20)	<1
3	Pt/C (5)	none	none	36
4	$[Ir(cod)Cl]_2$ (2.5)	**L2** (10)	K(O-*t*-Bu) (15)	43
5	$[Ir(cod)Cl]_2$ (2.5)	**L3** (5)	K(O-t-Bu) (10)	73
6	**$[Ir(cod)Cl]_2$ (0.5)**	**L3 (5)**	**K(O-t-Bu) (2)**	**71 (63)**
7	$Ni(cod)_2$ (5)	**L4** (10)	K(O-*t*-Bu) (10)	<1
8	$Ni(cod)_2$ (5)	**L2** (10)	K(O-*t*-Bu) (10)	43–55[c]
9[d]	**$Ni(cod)_2$ (5)**	**L2 (10)**	**K(O-*t*-Bu) (10)**	**51–59**[c]

[a]GC yield (isolated yield). [b]DMF instead of cyclohexane. [c]4 runs. [d]*n*-Octane instead of cyclohexane, 120°C.

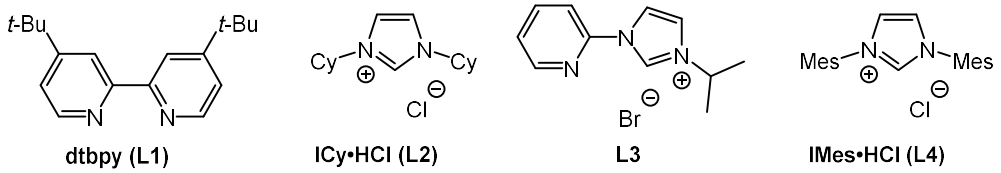
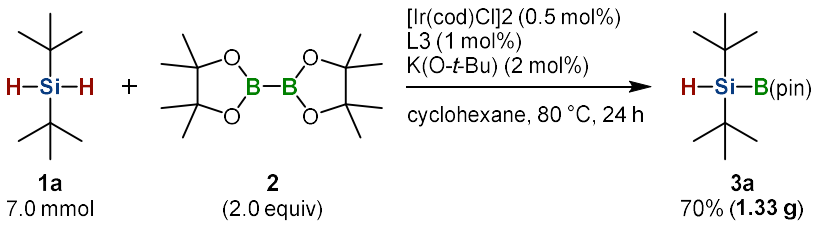


Table 1. Optimization of reaction conditions.

Additionally, a gram-scale synthesis of **3a** successfully gave the desired product even with 0.5 mol% catalyst loading (70%, Scheme 2).



Scheme 2. Gram-scale Synthesis

The molecular structure of **3a** was confirmed by single-crystal X-ray diffraction analysis (Figure 1). Although several conformers of **3a** were observed in the disordered structure, the presence of a silicon-boron bond was confirmed unambiguously.

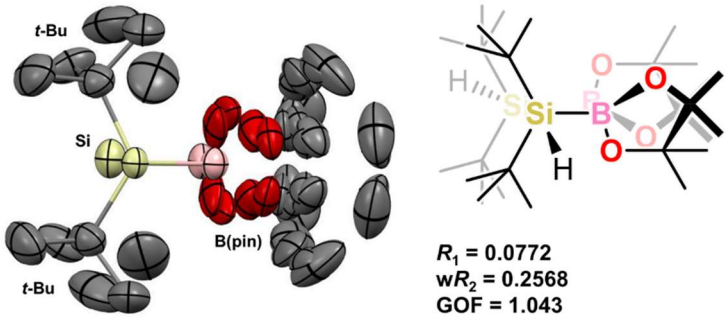


Figure 1. SC-XRD of **3a**.

With the optimized conditions in hand, substrate scope of the present Si–H monoborylation was investigated (Scheme 3). Dicyclohexylsilylboronate (**3b**) was obtained via both of the iridium- and nickel-catalyzed borylation reactions of the corresponding dihydrosilane (**1b**) [24% and 38% GC yield (29% isolated yield), respectively]. Next, the monoborylation of a dihydrosilane bearing a tertiary and a primary alkyl group (**1c**) was investigated. The desired dialkylhydrosilylboronate (**3c**) was obtained in low yield using the iridium catalyst (11% isolated yield). The nickel catalyst was more effective for the borylation of **1c**, generating **3c** in 43% isolated yield. I found that the sterically less hindered dialkyldihydrosilane **1d** did not provide **3d** under either set of conditions (Scheme 3c). speculated that less hindered dihydrosilanes could potentially undergo fast dehydrogenative coupling with another dihydrosilane molecule, facilitated by the metal catalyst, to form silicon-based oligomers,[11] thus impeding the desired borylation reaction.

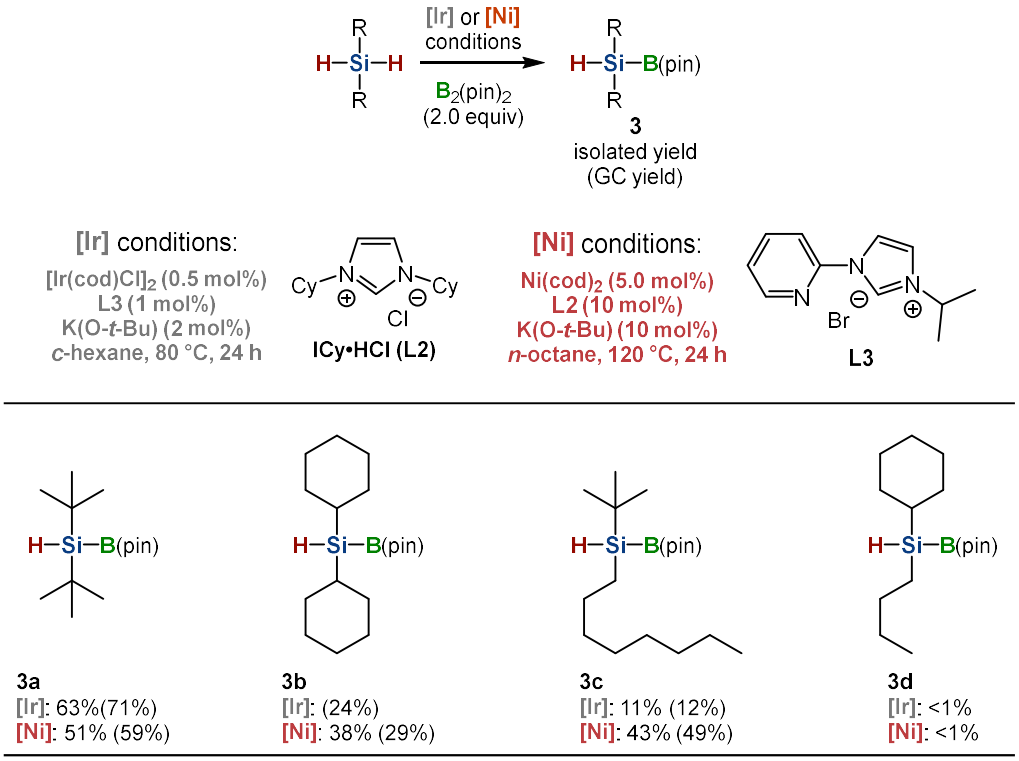


Table 2. Scope of dialkyldihydrosilanes.

Furthermore, aryl-substituted dihydrosilanes were employed for the present monoborylation reaction (Table 3). Pleasingly, *t*-BuPhHSi–B(pin) (**3e**) was obtained from both the iridium- and nickel-based catalytic systems in 57% and 31% yield, respectively. Unfortunately, sterically less hindered $CyPhSiH_2$ (**1f**) and *n*-$BuPhSiH_2$ (**1g**) did not produce the corresponding hydrosilylboronates (**3f** and **3g**). In these cases, the formation of oligosilanes produced by dehydrogenative homo-coupling was observed,[11] suggesting that the presence of a bulky *t*-Bu group on the silicon atom is necessary for efficient Si–H monoborylation. Unfortunately, the borylation of diphenylsilane resulted in complex mixture. Next, the steric effect of the aryl group was investigated. *Para*-tolyl- and *meta*-tolyl-substituted hydrosilylboronates **3h** and **3i** were obtained in yields comparable to that of **3e**. However, *ortho*-tolyl-substituted hydrosilylboronate **3j** was not obtained by the Si–H monoborylation using the iridium-based catalyst; this is probably due to a competing benzylic C–H borylation.[12] In contrast, the nickel-based catalyst afforded **3j** in good yield (59% isolated yield). Hydrosilylboronate **3k**, which bears a 4-$MeOC_6H_4$ group, was also obtained in a yield comparable to that of **3e**. Notably, these hydrosilylboronates (**3e** and **3h**–**3k**) show high stability toward air and moisture and can be isolated by flash column chromatography on silica gel.

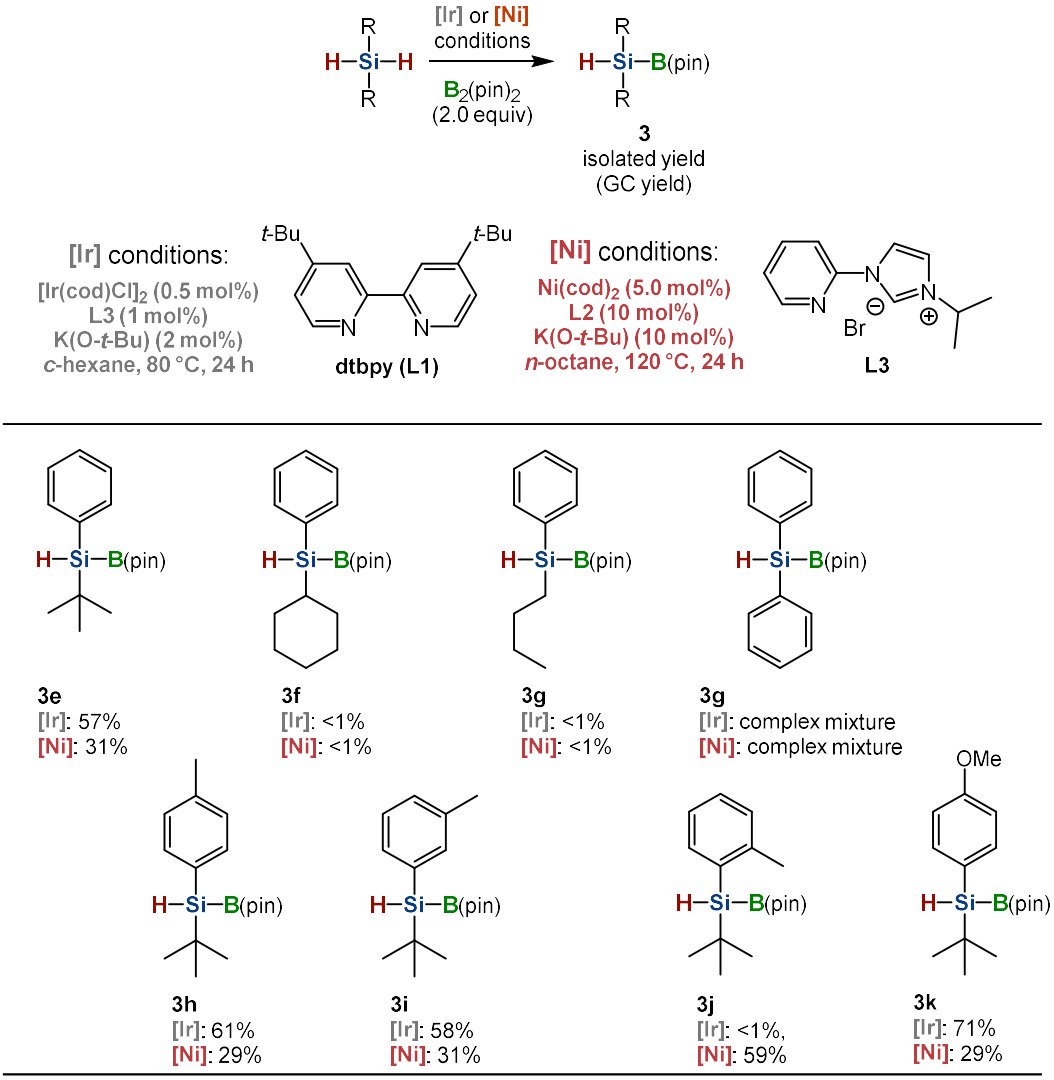
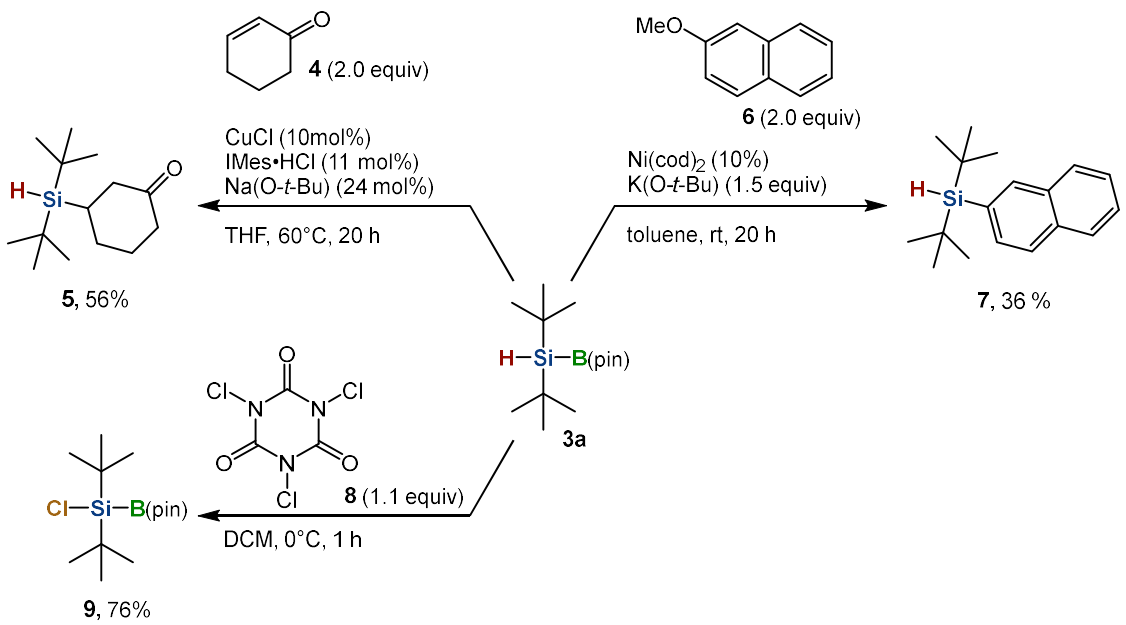


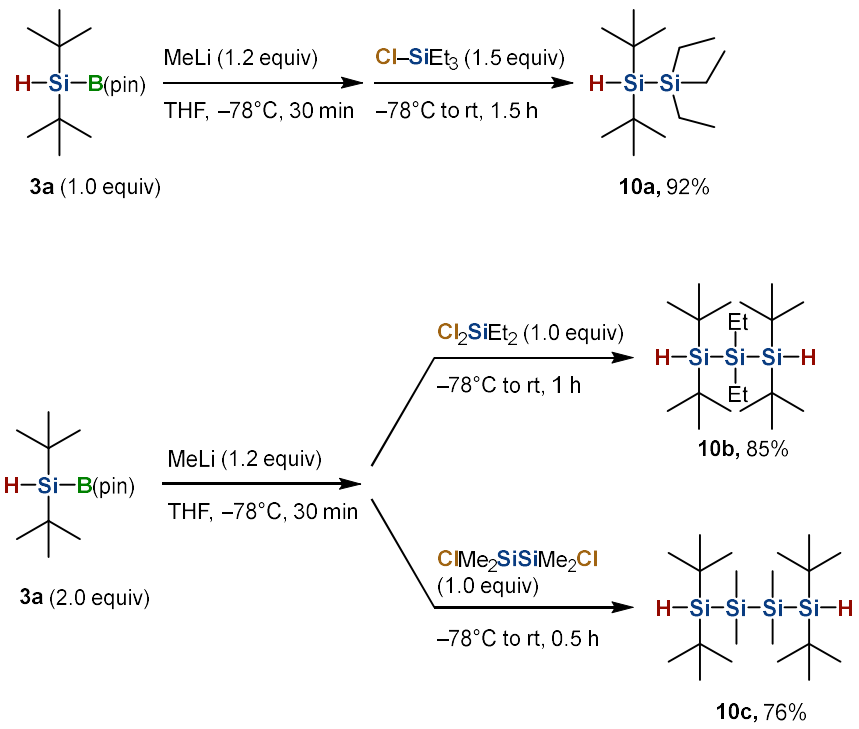
Table 2. Scope of alkylaryldihydrosilanes

To demonstrate the synthetic utility of the newly synthesized hydrosilylboronates, transformations of **3a** was investigated (Scheme 3). A copper(I)-catalyzed conjugated silylation of cyclohexenone (**4**) with **3a** proceeded to form the desired β-silylated ketone (**5**) in 56% yield.[13] Furthermore, a nickel-catalyzed silylation of 2-methoxynaphthalene **6** with **3a** produced the corresponding aryl silane (**7**) in 36% yield.[14] In addition to nucleophilic silylations, **3a** could also be applied to a Si–H bond-functionalization reaction. For example, the chlorination of a Si–H bond in **3a**, when treated with trichloroisocyanuric acid (**8**), furnished chlorosilylborane **9** in 76% yield.[15]



Scheme 3. Transformations of **3a**.

Since oligosilanes are interesting material candidates,[16] I carried out silicon−silicon cross-coupling reactions between newly synthesized silylboronate **3a** and various silyl chlorides after the activation by MeLi (Scheme 4).[7,17] The silicon−silicon coupling between **3a** and triethylsilyl chloride in the presence of methyl lithium (MeLi) afforded the corresponding Si−H bond-bearing disilane (**10a**) in excellent yield (92%). Furthermore, Si–Si coupling with dichlorodiethylsilane and 1,2-dichlorotetramethyldisilane proceeded smoothly to form the desired trisilane (**10b**) and tetrasilane (**10c**) in 85% and 76% yield, respectively. The silicon−silicon coupling products could be transformed using Si–H reactivity to give more complex oligosilanes.



Scheme 4. Si–Si cross-coupling using **3a**.

Finally, I investigated *in situ* $^{29}Si\{^1H\}$ NMR experiments to confirm the formation of a hydrosilyl anion in the reaction of **3a** with MeLi. Kawachi and Tamao have reported the formation of Ph_3SiLi during the reaction of Ph_3Si–B(pin) with MeLi.[17] More recently, Ito reported the formation of *i*-Pr_3SiLi during the reaction of *i*-Pr_3Si–B(pin) with MeLi.[7] Although Iwamoto and Kira reported the generation of disilylhydrosilyllithium in the reaction between disilyldihydrosilanes and bulky strong bases[5f], to the best of our knowledge, the generation of a dialkylhydrosilyllithium species has not been reported so far.[5f] In the present study, I attempted to produce the dialkylhydrosilyl anion of **3a** via treatment with MeLi in THF-d_8 (Figure 2). I observed a new ^{29}Si signal (σ 14.2 ppm), which was attributed to silyllithium **11**, in the $^{29}Si\{^1H\}$ NMR spectrum at room temperature (Figure 2a). Furthermore, the ^{29}Si–^7Li coupling of **11** was observed at –95 °C (σ 11.8 ppm, quartet, J [^{29}Si–^7Li] = 50 Hz) (Figure 2b). These results indicate that (t-Bu)$_2$HSiLi (**11**) is generated *in situ*. This is in agreement with the reports from Kawachi and Ito group on the heterolytic cleavage and the formation of silyl anion species Ph_3SiLi and *i*-Pr_3SiLi.[7,17] To the best of our knowledge, this is the first $^{29}Si\{^1H\}$ NMR spectroscopic evidence for the formation of a dialkylhydrosilyllithium species.

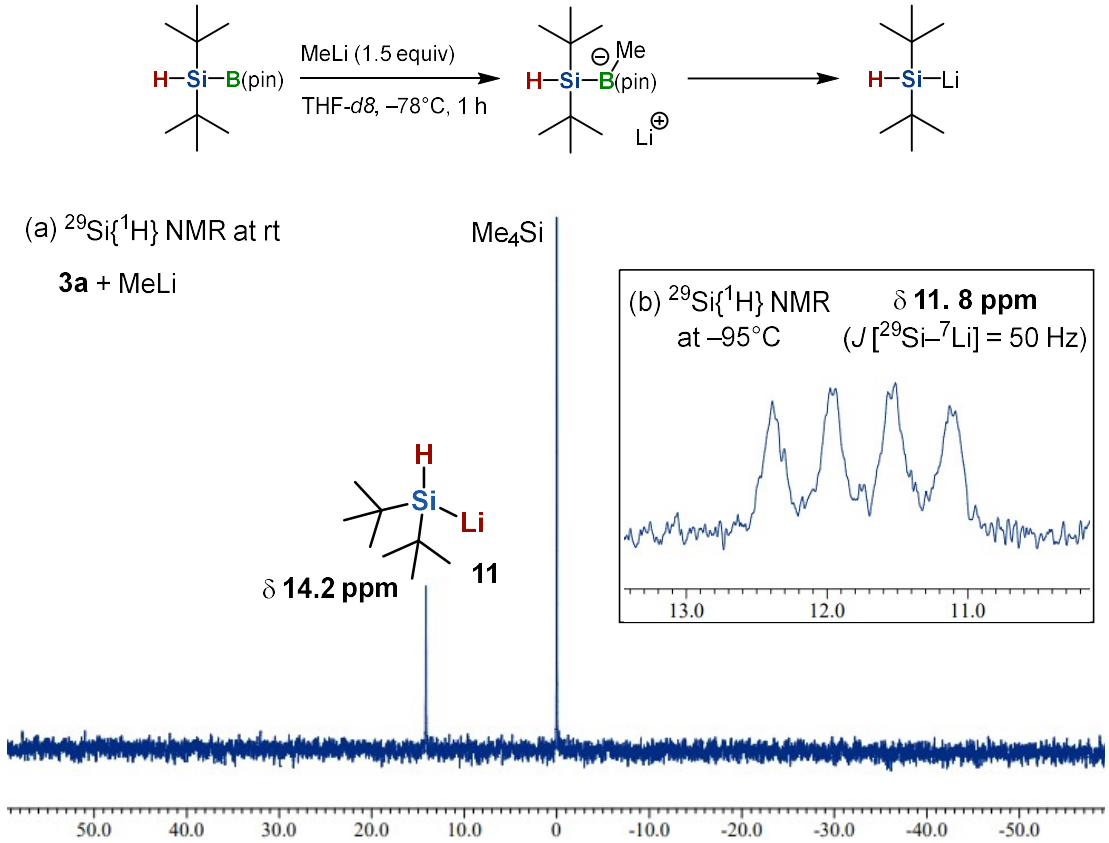


Figure 2. $^{29}Si\{^{1}H\}$ NMR experiments of the activation of 3a with MeLi.

2.3: Conclusion

In conclusion, I developed iridium- and nickel-catalyzed monoborylations of dihydrosilanes to produce hydrosilylboronates. Notably, these silylboronates bear a reactive hydrogen atom at the silicon center. Importantly, these hydrosilylboronates can be used as novel silicon nucleophiles in the presence of activating transition-metal catalysts or bases. Furthermore, the first $^{29}Si\{^{1}H\}$ NMR spectroscopic evidence for the formation of a $(t\text{-Bu})_2HSiLi$ species was reported.

2.4: References

1) (a) *Organosilicon Chemistry: Novel Approaches and Reactions*, eds., T. Hiyama, M. Oestreich, Wiley-VCH, Weinheim, 2020; (b) *Silicon in Organic, Organometallics, and Polymer Chemistry*, Ed., M. A. Brook, Wiley-Interscience Publication, 2000; (c) A. B. Cuenca, R. Shishido, H. Ito, E. Fernandez, *Chem. Soc. Rev.*, **2017**, *46*, 415−430.

2) (a) M. Suginome, H. Nakamura, Y. Ito, *Chem. Commun.* **1996**, 2777−2778; (b) M. Suginome, T. Matsuda, Y. Ito, *Organometallics*, **2000**, *19*, 4647−4649. (c) T. Ohmura, K. Masuda, H. Furukawa, M. Suginome, *Organometallics*, **2007**, *26*, 1291− 1294.

3) (a) M. Oestreich, E. Hartmann, M. Mewald, *Chem. Rev.*, **2013**, *113*, 402−441; (b) T. Ohmura, M. Suginome, *Bull. Chem. Soc. Jpn.*, **2009**, *82*, 29−49; (c) W. Xue, M. Oestreich, *ACS Cent. Sci.*, **2020**, *6*, 1070−1081; (d) J.-J. Feng, W. Mao, L. Zhang, M. Oestreich, *Chem. Soc. Rev.* **2021**, *50*, 2010−2073.

4) For reviews on silyl anions, see: (a) H.-W. Lerner, *Coord. Chem. Rev.*, **2005**, *249*, 781−798; (b) A. Sekiguchi, V. Y. Lee, M. Nanjo, *Coord. Chem. Rev.*, **2000**, *210*, 11−45; (c) A. Kawachi, K. Tamao, *Bull. Chem. Soc. Jpn.*, **1997**, *70*, 945−955.

5) For examples of the generation of functionalized silyl lithium compounds, see: (a) K. Tamao, A. Kawachi, Y. Ito, *J. Am. Chem. Soc.*, **1992**, *114*, 3989−3990; (b) K. Tamao, A. Kawachi, *Organometallics*, **1995**, *14*, 3108−3111; (c) A. Kawachi, K. Tamao, *Organometallics*, **1996**, *15*, 4653−4656; (d) A. Kawachi, K. Tamao, *J. Am. Chem. Soc.*, **2000**, *122*, 1919−1926; (e) A. Kawachi, Y. Oishi, T. Kataoka, K. Tamao, *Organometallics*, **2004**, *23*, 2949−2955; (f) T. Iwamoto, J. Okita, C. Kabuto, M. Kira, *J. Am. Chem. Soc.*, **2002**, *124*, 11604−11605.

6) T. A. Boebel, J. F. Hartwig, *Organometallics*, **2008**, *27*, 6013−6019.

7) R. Shishido, M. Uesugi, R. Takahashi, T. Mita, T. Ishiyama, K. Kubota, H. Ito, *J. Am. Chem. Soc.*, **2020**, *142*, 14125−14133.

8) T. Kajiwara, N. Takeda, T. Sasamori, N. Tokitoh, *Organometallics*, **2004**, *23*, 4723−4734.

9) M. Peter, R. Breinbauer, *Tetrahedron Lett.*, **2010**, *51*, 6622–6625.

10) For examples of nickel-catalyzed C−H bond borylation reactions, see: (a) T. Furukawa, M. Tobisu, N. Chatani, *Chem. Commun.*, **2015**, *51*, 6508−6511; (b) H. Zhang, S. Hagihara, K. Itami, *Chem. Lett.*, **2015**, *44*, 779−781; (c) A. Das, P. K. Hota, S. K. Mandal, *Organometallics*, **2019**, *38*, 3286−3293.

11) For selected examples of the dehydrogenative coupling of silanes mediated by transition-metal catalysts, see: (a) H.-G. Woo, T. D. Tilley, *J. Am. Chem. Soc.*, **1989**, *111*, 8043−8044; (b) L. Rosenberg, C. W. Davis, J. Yao, *J. Am. Chem. Soc.*, **2001**, *123*, 5120−5121; (c) P. Diversi, F. Marchetti, V. Ermini, S. Matteoni, *J. Organomet. Chem.*, **2000**, *593–594*, 154–160; (d) T. Baumgartner, W. Wilk, *Org. Lett.*, **2006**, *8*, 503–506; (e) M, Itazaki, K. Ueda, H. Nakazawa, *Angew. Chem., Int. Ed.*, **2009**, *48*, 3313–3316.

12) S. H. Cho, J. F. Hartwig, J. Am. Chem. Soc. 2013, 135, 8157−8160.

13) K.-S. Lee, A. H. Hoveyda, *J. Am. Chem. Soc.*, **2010**, *132*, 2898−2900.

14) C. Zarate, M. Nakajima, R. Martin, *J. Am. Chem. Soc.*, **2017**, *139*, 1191−1197.

15) S. Varaprath, D. H. Stutts, *J. Organomet. Chem.*, **2007**, *692*, 1892−1897.

16) (a) T. Karatsu, *J. Photochem. Photobiol.*, *C*, **2008**, *9*, 111−137; (b) H. Tsuji, J. Michl, K. Tamao, *J. Organomet. Chem.*, **2003**, *685*, 9−14.

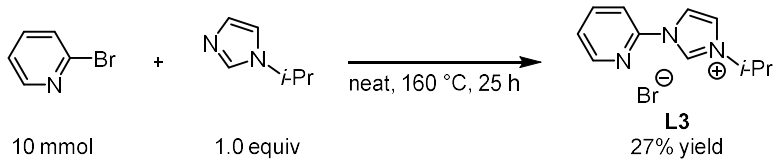
17) A. Kawachi, T. Minamimoto, K. Tamao, *Chem. Lett.*, **2001**, *30*, 1216−1217.

2.5: Experimental Details

Instrumentation and Chemicals

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 reactions were purchased from commercial suppliers, degassed via three freeze-pump-thaw cycles, and further dried over molecular sieves (MS4A) before use. $[Ir(cod)Cl]_2$ (>93%), $Ni(cod)_2$ (>97%), K(O-*t*-Bu) (>97%), ICy·HCl (>98.0%) and di-*tert*-butylsilane (**1a**) were purchased from TCI and used as received. Bis(pinacolato)diboron $[B_2(pin)_2]$ was recrystallized prior to use. Silica Gel 60 N (40–100 μm, spherical, neutral) purchased from Kanto Chemical Co. was used as received. GLC analyses were conducted with a Shimadzu GC-2014 or GC-2025 equipped with ULBON HR-1 glass capillary column (Shinwa Chemical Industries) and an FID detector. n-$C_{13}H_{28}$ 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. NMR spectra were recorded on JEOL JNM-ECX400P, ECS-400 (^{1}H: 400 MHz, ^{13}C: 100 MHz, ^{29}Si: 79.5 MHz), JNM-ECA600, and ECZ600R/S3 (^{29}Si: 120 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. $BF_3 \cdot Et_2O$ 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, sept = septet, m = multiplet. High-resolution mass spectra were recorded at the Global Facility Center for Instrumental Analysis, Hokkaido University. Single crystal X-ray structural analyses were carried out on a Rigaku XtaLAB AFC11 (RCD3) and XtaLAB PRO MM007 diffractometer using graphite monochromated Mo-Kα or Cu- Kα 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.

Preparation of L3

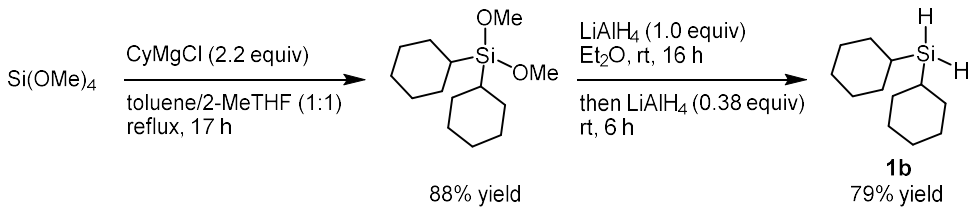


This reaction was performed according to the literature procedure.[1] 2-Bromopyridine (1.00 mL, 10.0 mmol) was added dropwise to 1-isopropylimidazole (1.10 g, 10.0 mmol, 1.00 equiv) under nitrogen atmosphere. The reaction mixture was allowed to warm to 160 °C and stirred for 25 h. After cooling to room temperature, the mixture was washed with hexane. The resulting solid was purified

by recrystallization from $Et_2O/CHCl_3$ to afford the corresponding imidazolium salt **L3** (0.718 g, 2.68 mmol, 27% yield) as a brown needle crystal.

^{1}H NMR (399 MHz, $CDCl_3$, δ): 1.74 (d, J = 6.8 Hz, 6H), 5.25 (sept, J = 6.7 Hz, 1H), 7.39 (q, J = 1.7 Hz, 1H), 7.47 (dd, J = 4.8, 7.6 Hz, 1H), 8.10 (td, J = 1.6, 8.1 Hz, 1H), 8.33 (t, J = 1.8 Hz, 1H), 8.48–8.55 (m, 1H), 8.80 (d, J = 8.0 Hz, 1H), 12.02 (t, J = 1.6 Hz, 1H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 23.2 (CH_3), 54.1 (CH_2), 115.2 (*C*H), 119.0 (*C*H), 120.0 (*C*H), 125.0 (*C*H), 134.6 (*C*H), 140.5 (*C*H), 145.9 (*C*), 148.8 (*C*H). HRMS-ESI (m/z): $[M–Br]^+$ calcd for $C_{11}H_{14}N_3$, 188.1182; found 188.1184.

Preparation of 1b



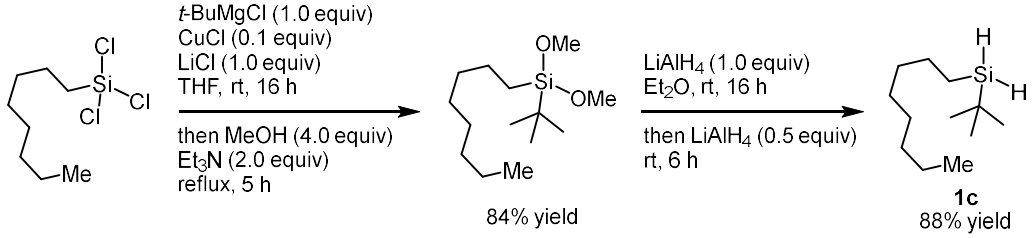
The reactions were performed according to the literature procedure.[2] Cyclohexylmagnesium chloride (1.0 M in 2-MeTHF, 55.0 mL, 55.0 mmol, 2.20 equiv) was added dropwise to tetramethyl orthosilicate (3.83 g, 25.0 mmol) in toluene (55.0 mL) under nitrogen atmosphere. The reaction mixture was stirred for 17 h at 120 °C (reflux). After cooling to room temperature, the reaction was quenched with saturated NH_4Cl aqueous solution and extracted with Et_2O three times. The combined organic layer was dried over $MgSO_4$, followed by filtration and evaporation. The residue was purified by Kugelrohr distillation under reduced pressure (36 Pa, bath temp. 130 °C) to afford dicyclohecyldimethoxysilane (5.68 g, 22.2 mmol, 88% yield) as a colorless oil.

^{1}H NMR (391 MHz, $CDCl_3$, δ): 0.81–0.91 (m, 2H), 1.12–1.35 (m, 10H), 1.62–1.82 (m, 10H), 3.57 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 24.1 (*C*H), 26.9 (CH_2), 27.1 (CH_2), 27.9 (CH_2), 50.7 (CH_3). HRMS-EI (m/z): $[M]^+$ calcd for $C_{14}H_{28}O_3Si$, 256.1859; found 256.1854.

Dicyclohexyldimethoxysilane (5.18 g, 20.0 mmol) was added dropwise to a suspension of $LiAlH_4$ (0.761 g, 20.0 mmol, 1.00 equiv) in Et_2O (20.0 mL) under nitrogen atmosphere. The reaction mixture was stirred for 16 h at room temperature. Then, $LiAlH_4$ (0.286 g, 7.53 mmol, 0.375 equiv) was added to the reaction mixture in one portion. After stirring for 6 h, the reaction was quenched by water. The mixture was filtered through a celite pad. The resulting solution was dried over $MgSO_4$, followed by filtration and evaporation. The residue was purified by Kugelrohr distillation under reduced pressure (50 Pa, bath temp. 110 °C) to afford the corresponding silane **1b** (3.12 g, 15.9 mmol, 79% yield) as a colorless oil.

^{1}H NMR (401 MHz, $CDCl_3$, δ): 0.82–0.98 (m, 2H), 1.13–1.34 (m, 10H), 1.60–1.81 (m, 10H), 3.38 (t, J = 3.0 Hz, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 20.5 (*C*H), 26.7 (CH_2), 27.8 (CH_2), 29.6 (CH_2). HRMS-EI (m/z): $[M]^+$ calcd for $C_{12}H_{24}Si$, 196.1647; found 196.1646.

Preparation of 1c



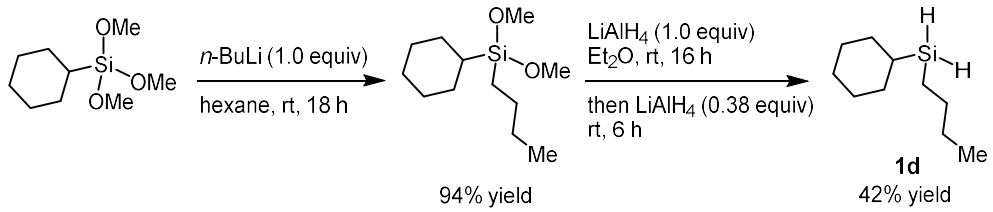
The reactions were performed using a modified literature procedure.[3] *tert*-Butylmagnesium chloride (2.0 M in THF, 15.0 mL, 30.0 mmol, 1.00 equiv) was added dropwise to the mixture of *n*-octyltrichlorosilane (7.27 g, 29.4 mmol), copper(I) chloride (0.302 g, 3.05 mmol, 0.104 equiv), and lithium chloride (1.27 g, 30.0 mmol, 1.02 equiv) in THF (30.0 mL) under nitrogen atmosphere. The reaction was stirred for 16 h at room temperature. Then, MeOH (5.00 mL, 120 mmol, 4.08 equiv) and Et_3N (8.50 mL, 60.0 mmol, 2.04 equiv) were added to the reaction mixture. The resulting mixture was stirred for 5 h at 85 °C (reflux). After cooling to room temperature, the reaction mixture was filtered and extracted with hexane three times. The combined organic layer was dried over $MgSO_4$, followed by filtration and evaporation. The residue was purified by Kugelrohr distillation under reduced pressure (63 Pa, bath temp. 130 °C) to afford *tert*-butyldimethoxy(octyl)silane (6.46 g, 24.8 mmol, 84% yield) as a colorless oil.

^{1}H NMR (401 MHz, $CDCl_3$, δ): 0.63–0.69 (m, 2H), 0.88 (t, J = 6.8 Hz, 3H), 0.94 (s, 9H), 1.22–1.37 (m, 10 H), 1.38–1.48 (m, 2H), 3.58 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 10.1 (CH_2), 14.1 (CH_3), 19.2 (C), 22.7 (CH_2), 23.2 (CH_2), 26.4 (CH_3), 29.2 (CH_2), 29.3 (CH_2), 31.9 (CH_2), 33.8 (CH_2), 51.1 (CH_3). HRMS-EI (m/z): $[M–^tBu]^+$ calcd for $C_{10}H_{23}O_2Si$, 203.1467; found 203.1463.

tert-Butyldimethoxy(octyl)silane (6.24 g, 24.0 mmol) was added dropwise to a suspension of $LiAlH_4$ (0.913 mg, 24.0 mmol, 1.00 equiv) in Et_2O (24.0 mL) under nitrogen atmosphere. The reaction mixture was stirred for 16 h at room temperature. Then, $LiAlH_4$ (0.452 mg, 12.0 mmol, 0.500 equiv) was added to the reaction mixture in one portion. After stirring for 6 h at 30 °C, the reaction was quenched by water. The mixture was filtered through a celite pad. The resulting solution was dried over $MgSO_4$, followed by filtration and evaporation. The residue was passed through silica-gel column chromatography (hexane as eluent). The crude product was purified by Kugelrohr distillation under a reduced pressure further purified by distillation (7.0 hPa, bath temp. 150 °C) to afford the corresponding silane **1c** (4.30 g, 21.2 mmol, 88% yield) as a colorless oil.

^{1}H NMR (401 MHz, $CDCl_3$, δ): 0.64–0.72 (m, 2H), 0.88 (t, J = 7.0 Hz, 3H), 0.99 (s, 9H), 1.20–1.46 (m, 12H), 3.51 (t, J = 4.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 7.73 (CH_2), 14.2 (CH_3), 15.8 (C), 22.8 (CH_2), 25.7 (CH_2), 28.0 (CH_3), 29.3 (CH_2), 29.4 (CH_2), 32.0 (CH_2), 33.2 (CH_2). HRMS-EI (m/z): $[M]^+$ calcd for $C_{12}H_{28}Si$, 200.1960; found 200.1954.

Preparation of 1d



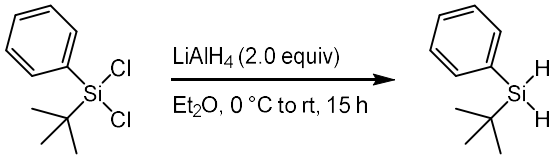
n-Butyllithium (1.57 M in hexane, 16.0 mL, 25.1 mmol, 1.00 equiv) was added dropwise to a hexane solution (250 mL) of cyclohexyltrimethoxysilane (5.13 g, 25.1 mmol) under nitrogen atmosphere. The reaction was stirred for 18 h at room temperature. After the reaction was quenched by saturated NH_4Cl aqueous solution, the resulting mixture was extracted by hexane three times. The combined organic layer was dried over $MgSO_4$, followed by filtration and evaporation. The residue was purified by Kugelrohr distillation under reduced pressure (66 Pa, bath temp. 110 °C) to afford butyl(cyclohexyl)dimethoxysilane (5.44 g, 23.6 mmol, 94% yield) as a colorless oil.

^{1}H NMR (401 MHz, $CDCl_3$, δ): 0.59–0.67 (m, 2H), 0.77–0.87 (m, 1H), 0.90 (t, J = 6.8 Hz, 3H), 1.13–1.28 (m, 5H), 1.31–1.43 (m, 4H), 1.64–1.81 (m, 5H), 3.54 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 10.2 (CH_2), 13.6 (CH), 24.4 (CH_3), 25.0 (CH_2), 26.5 (CH_2), 26.7 (CH_2), 26.8 (CH_2), 27.8 (CH_2), 50.4 (CH_3). HRMS-EI (m/z): $[M]^+$ calcd for $C_{12}H_{26}O_2Si$, 230.1702; found 230.1691.

Butyl(cyclohexyl)dimethoxysilane (4.60 g, 20.0 mmol) was added dropwise to a suspension of $LiAlH_4$ (0.762 g, 20.1 mmol, 1.00 equiv) in Et_2O (40.0 mL) under nitrogen atmosphere. The reaction mixture was stirred for 16 h at room temperature. After diluting with Et_2O, the reaction was quenched by MeOH. The resulting mixture was filtered through a celite pad, followed by evaporation. The residue was purified by Kugelrohr distillation under reduced pressure (60 Pa, bath temp. 100 °C) to afford the crude product. The crude product was passed through silica-gel column chromatography (hexane as eluent) to afford the corresponding silane **1d** (1.43 g, 8.39 mmol, 42% yield) as a colorless oil.

^{1}H NMR (401 MHz, $CDCl_3$, δ): 0.59–0.76 (m, 2H), 0.78–0.97 (m, 4H), 1.10–1.30 (m, 5H), 1.31–1.45 (m, 4H), 1.61–1.83 (m, 5H), 3.51 (quint, J = 3.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 7.5 (CH_2), 13.8 (CH), 21.3 (CH_3), 26.0 (CH_2), 26.8 (CH_2), 27.8 (CH_2), 27.9 (CH_2), 29.3 (CH_2). HRMS-EI (m/z): $[M]^+$ calcd for $C_{10}H_{22}Si$, 170.1491; found 170.1497.

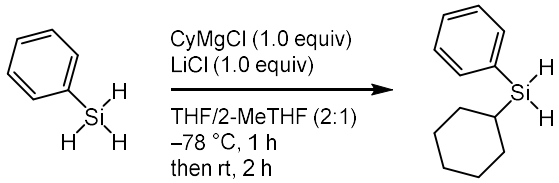
Preparation of 1e



1e
84% yield

The reaction was performed according to the literature procedure.[4] *tert*-Butyldichloro(phenyl)silane (1.02 g, 4.38 mmol) was added dropwise to a suspension of $LiAlH_4$ (0.334 g, 8.80 mmol, 2.0 equiv) in Et_2O (40.0 mL) under nitrogen atmosphere. The reaction mixture was stirred for 15 h at room temperature. After diluting with Et_2O, the reaction mixture was quenched by MeOH. After the resulting mixture was filtered through a celite pad, the filtrate was extracted by Et_2O three times. The combined organic layer was dried over $MgSO_4$, followed by filtration and evaporation. The residue was purified by silica-gel column chromatography (hexane as eluent) to afford the corresponding silane **1e** (0.607 g, 3.69 mmol, 84% yield) as a colorless oil. The NMR spectra of **1e** were in agreement with the literature.[4]

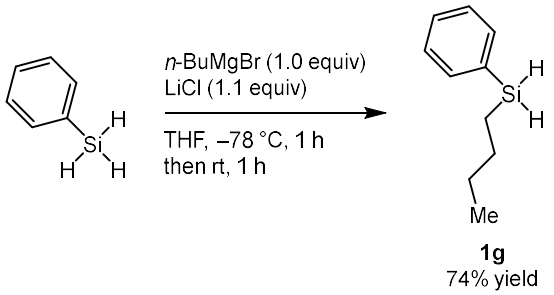
Preparation of 1f



1f
82% yield

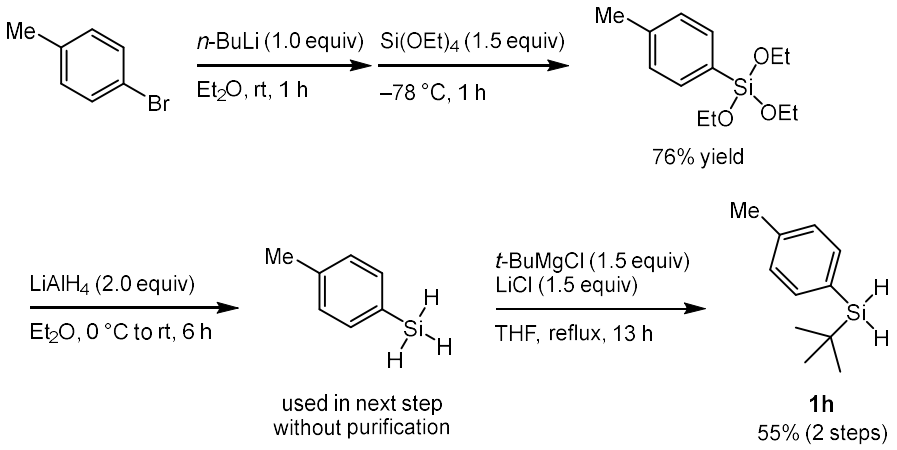
The reaction was performed according to the literature procedure.[5] Cyclohexylmagnesium chloride (1.0 M in 2-MeTHF, 10 mL, 1.0 equiv) was added dropwise to a solution of phenylsilane (1.09 g, 10.1 mmol) and lithium chloride (0.430 g, 10.2 mmol, 1.0 equiv) in THF (20.0 mL) at –78 °C under nitrogen atmosphere, and stirred for 1 h. Then, the reaction mixture was allowed to warm to room temperature slowly and stirred for 2 h. The reaction mixture was quenched by a saturated aqueous NH_4Cl. The resulting mixture was extracted by Et_2O three times. The combined organic layer was dried over $MgSO_4$, followed by filtration and evaporation. The residue was purified by silica-gel column chromatography (hexane as eluent) to afford the corresponding silane **1f** (1.58 g, 8.31 mmol, 82%) as a colorless oil. The NMR spectra of **1f** were in agreement with the literature.[6]

Preparation of 1g



The reaction was performed according to the literature procedure.[5] *n*-Butylmagnesium bromide (1.0 M in THF, 10.0 mL, 1.0 equiv) was added dropwise to a solution of phenylsilane (1.07 g, 9.92 mmol) and lithium chloride (0.443 g, 10.5 mmol, 1.1 equiv) in THF (20.0 mL) at –78 °C under nitrogen atmosphere, and stirred for 1 h. Then, the reaction mixture was allowed to warm to room temperature slowly and stirred for 1 h. The reaction mixture was quenched by a saturated aqueous NH_4Cl. The resulting mixture was extracted by Et_2O three times. The combined organic layer was dried over $MgSO_4$, followed by filtration and evaporation. The residue was purified by silica-gel column chromatography (hexane as eluent) to afford the corresponding silane **1g** (1.21 g, 7.37 mmol, 74%) as a colorless oil. The NMR spectra of **1g** were in agreement with the literature.[7]

Preparation of 1h



The reaction was performed according to the literature procedure.[8] *n*-Butyllithium (1.57 M, 6.4 mL, 1.0 equiv) was added dropwise to a solution of 4-bromotoluene (1.73 g, 10.1 mmol) in Et_2O (14.0 mL) at room temperature and stirred for 1 h. After cooling to –78 °C, the reaction mixture was added via cannula to the solution of tetraethyl orthosilicate (3.4 mL, 15.0 mmol, 1.5 equiv) in Et_2O (14.0 mL) at –78 °C. The reaction mixture was stirred for 1 h. After warming to room temperature, the reaction mixture was quenched by a saturated aqueous NH_4Cl. The resulting mixture was extracted by Et_2O three times. The combined organic layer was dried over $MgSO_4$, followed by filtration and evaporation. The residue was purified by Kugelrohr distillation under reduced pressure (50 Pa, bath temp. 125 °C)

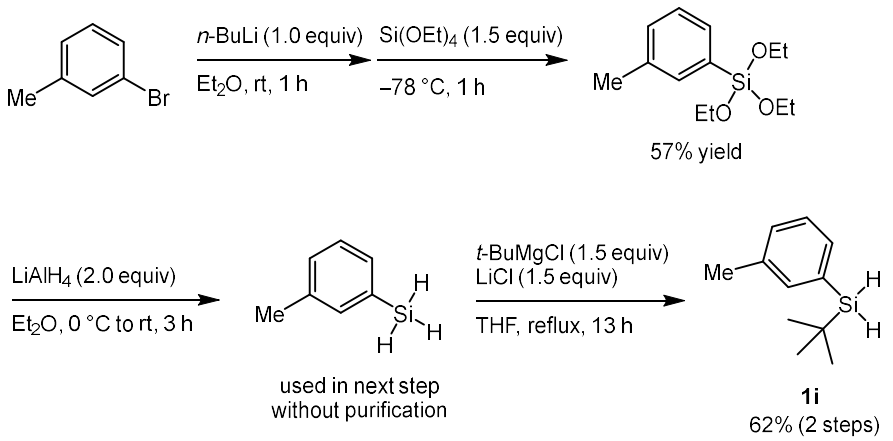
to afford triethoxy(*p*-tolyl)silane (1.93 g, 7.58 mmol, 76% yield) as a colorless oil.

The hydride reduction of triethoxy(*p*-tolyl)silane, followed by reaction with *t*-BuMgCl, were performed according to the literature procedure.[5,9] Triethoxy(*p*-tolyl)silane (1.29 g, 5.07 mmol) was added dropwise to a suspension of $LiAlH_4$ (0.377 g, 9.9 mmol, 2.0 equiv) in Et_2O (10.0 mL) under nitrogen atmosphere. The reaction mixture was stirred for 6 h at room temperature. After diluting with pentane (100 mL), the reaction mixture was filtered through a celite pad, followed by evaporation (150 hPa 0 °C). *Be careful with fires caused by the precipitated hydride species.* The residue was passed through a silica-gel column (Et_2O as an eluent), followed by evaporation (150 hPa, 0 °C). The crude mixture was employed for the next reaction without further purification.

The crude mixture of *p*-tolylsilane was added to the solution of lithium chloride (0.319 g, 7.5 mmol, 1.5 equiv) in THF (10.0 mL). After *tert*-butylmagnesium chloride (2.0 M, 3.8 mL, 7.6 mmol, 1.5 equiv) was added, the reaction mixture was warmed to 80 °C (reflux) and stirred for 13 h. After cooling to room temperature, the reaction mixture was quenched by a saturated aqueous NH_4Cl. The resulting mixture was extracted by Et_2O three times. The combined organic layer was dried over $MgSO_4$, followed by filtration and evaporation. The residue was purified by silica-gel column chromatography (hexane as eluent) to afford **1h** [0.495 g, 2.78 mmol, 55% (over two steps)] as a colorless oil.

^{1}H NMR (401 MHz, $CDCl_3$, δ): 1.00 (s, 9H), 2.36 (s, 3H), 4.12 (s, 2H), 7.18 (d, J = 6.8 Hz, 2H), 7.46 (d, J = 6.4 Hz, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 16.4 (*C*), 21.5 (CH_3), 27.4 (CH_3), 128.5 (*C*), 128.7 (*C*H), 135.9 (*C*H), 139.5 (*C*). HRMS-EI (m/z): $[M]^+$ calcd for $C_{11}H_{18}Si$, 178.1178; found 178.1185.

Preparation of 1i



The reaction was performed according to the literature procedure.[8] *n*-Butyllithium (1.57 M, 6.4 mL, 1.0 equiv) was added dropwise to a solution of 3-bromotoluene (1.72 g, 10.1 mmol) in Et_2O (14.0 mL) at room temperature and stirred for 1 h. After cooling to –78 °C, the reaction mixture was added via cannula to the solution of tetraethyl orthosilicate (3.4 mL, 15.0 mmol, 1.5 equiv) in Et_2O (14.0 mL) at

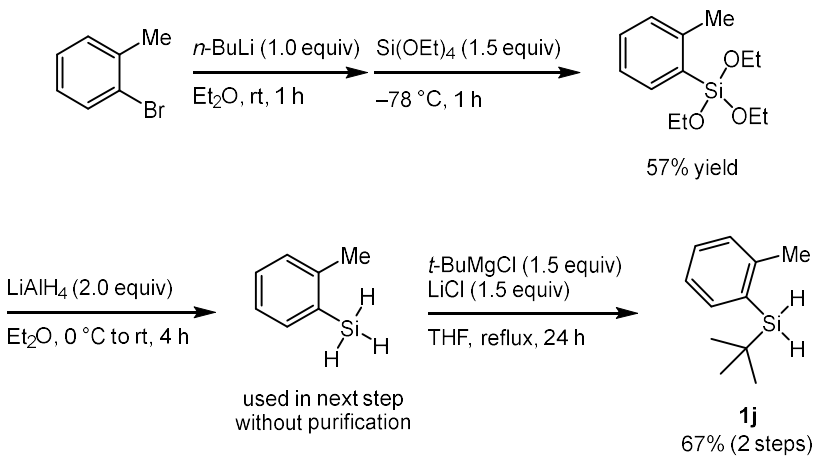
–78 °C. The reaction mixture was stirred for 1 h. After warming to room temperature, the reaction mixture was quenched by a saturated aqueous NH_4Cl. The resulting mixture was extracted by Et_2O three times. The combined organic layer was dried over $MgSO_4$, followed by filtration and evaporation. The residue was purified by Kugelrohr distillation under reduced pressure (31 Pa, bath temp. 160 °C) to afford triethoxy(*m*-tolyl)silane (1.46 g, 5.73 mmol, 57% yield) as a colorless oil.

The hydride reduction of triethoxy(*m*-tolyl)silane, followed by reaction with *t*-BuMgCl, were performed according to the literature procedure.[5,9] Triethoxy(*m*-tolyl)silane (1.26 g, 4.97 mmol) was added dropwise to a suspension of $LiAlH_4$ (0.381 g, 10.0 mmol, 2.0 equiv) in Et_2O (10.0 mL) under nitrogen atmosphere. The reaction mixture was stirred for 3 h at room temperature. After diluting with pentane (100 mL), the reaction mixture was filtered through a celite pad, followed by evaporation (150 hPa, 0 °C). *Be careful with fires caused by the precipitated hydride species.* The residue was passed through a silica-gel column (Et_2O as an eluent), followed by evaporation (150 hPa, 0 °C). The crude mixture was employed for the next reaction without further purification.

The crude mixture of *m*-tolylsilane was added to the solution of lithium chloride (0.335 g, 7.9 mmol, 1.6 equiv) in THF (10.0 mL). After *tert*-butylmagnesium chloride (2.0 M, 3.8 mL, 7.6 mmol, 1.5 equiv) was added, the reaction mixture was warmed to 80 °C (reflux) and stirred for 15 h. After cooling to room temperature, the reaction mixture was quenched by a saturated aqueous NH_4Cl. The resulting mixture was extracted by Et_2O three times. The combined organic layer was dried over $MgSO_4$, followed by filtration and evaporation. The residue was purified by silica-gel column chromatography (hexane as eluent) to afford **1i** [0.546 g, 3.06 mmol, 62% (over two steps)] as a colorless oil.

^{1}H NMR (399 MHz, $CDCl_3$, δ): 1.02 (s, 9H), 2.36 (s, 3H), 4.13 (s, 2H), 7.20–7.28 (m, 2H), 7.35 – 7.40 (m, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 16.4 (*C*), 21.5 (*C*H$_3$), 27.5 (*C*H$_3$), 127.7 (*C*H), 130.3 (*C*H), 132.0 (*C*), 132.9 (*C*H), 136.6 (*C*H), 137.1 (*C*). HRMS-EI (m/z): $[M]^+$ calcd for $C_{11}H_{18}Si$, 178.1178; found 178.1178.

Preparation of 1j



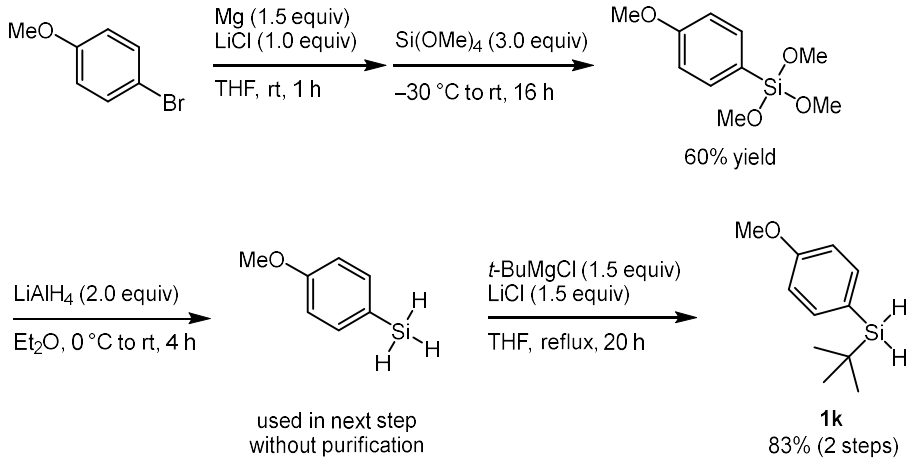
The reaction was performed according to the literature procedure.[8] *n*-Butyllithium (1.57 M, 6.4 mL, 1.0 equiv) was added dropwise to a solution of 2-bromotoluene (1.73 g, 10.1 mmol) in Et_2O (14.0 mL) at room temperature and stirred for 1 h. After cool to –78 °C, the reaction mixture was added via cannula to the solution of tetraethyl orthosilicate (3.4 mL, 15.0 mmol, 1.5 equiv) in Et_2O (14.0 mL) at –78 °C. The reaction mixture was stirred for 1 h. After warm to room temperature, the reaction mixture was quenched by a saturated aqueous NH_4Cl. The resulting mixture was extracted by Et_2O three times. The combined organic layer was dried over $MgSO_4$, followed by filtration and evaporation. The residue was purified by Kugelrohr distillation under reduced pressure (35 Pa, bath temp. 110 °C) to afford triethoxy(*o*-tolyl)silane (1.46 g, 5.74 mmol, 57% yield) as a colorless oil.

The hydride reduction of triethoxy(*o*-tolyl)silane, followed by reaction with *t*-BuMgCl, were performed according to the literature procedure.[5,9] Triethoxy(*o*-tolyl)silane (1.27 g, 5.00 mmol) was added dropwise to a suspension of $LiAlH_4$ (0.382 g, 10.1 mmol, 2.0 equiv) in Et_2O (10.0 mL) under nitrogen atmosphere. The reaction mixture was stirred for 4 h at room temperature. After dilut with pentane (100 mL), the reaction mixture was filtered through a celite pad, followed by evaporation (150 hPa, 0 °C). *Be careful with fires caused by the precipitated hydride species.* The residue was passed through a silica-gel column (Et_2O as an eluent), followed by evaporation (150 hPa, 0 °C). The crude mixture was employed for the next reaction without further purification.

The crude mixture of *o*-tolylsilane was added to the solution of lithium chloride (0.317 g, 7.5 mmol, 1.5 equiv) in THF (10.0 mL). After *tert*-butylmagnesium chloride (2.0 M, 3.8 mL, 7.6 mmol, 1.5 equiv) was added, the reaction mixture was warmed to 80 °C (reflux) and stirred for 24 h. After cool to room temperature, the reaction mixture was quenched by a saturated aqueous NH_4Cl. The resulting mixture was extracted by Et_2O three times. The combined organic layer was dried over $MgSO_4$, followed by filtration and evaporation. The residue was purified by silica-gel column chromatography (hexane as eluent) to afford **1j** [0.594 g, 3.33 mmol, 67% (over two steps)] as a colorless oil.

^{1}H NMR (401 MHz, $CDCl_3$, δ): 1.03 (s, 9H), 2.47 (s, 3H), 4.22 (s, 2H), 7.14–7.21 (m, 2H), 7.30 (td, J = 1.6, 7.5 Hz, 1H), 7.51 (dd = 1.4, 7.4 z, 1H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 17.2 (*C*), 23.4 (CH_3), 27.9 (CH_3), 124.8 (*C*H), 129.6 (*C*H), 130.0 (*C*H), 131.5 (*C*), 137.5 (*C*H), 144.1 (*C*). HRMS-EI (m/z): $[M]^+$ calcd for $C_{11}H_{18}Si$, 178.1178; found 178.1174.

Preparation of 1k



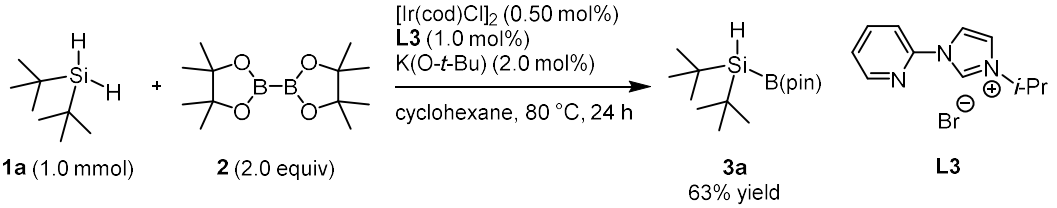
The reaction was performed according to the literature procedure.[9] 4-bromoanisole (3.65 g, 19.5 mmol) was added to a mixture of Mg (0.732 g, 30.1 mmol, 1.5 equiv), LiCl (0.850 g, 20.1 mmol, 1.0 equiv), and THF (20.0 mL) at room temperature. After stirr for 1 h, the solution of the Grignard reagent was added dropwise via cannula to the solution of tetramethyl orthosilicate (8.9 mL, 60 mmol, 3.0 equiv) in THF (20.0 mL) at –30 °C. Then, the reaction mixture was allowed to warm to room temperature and stirred for 16 h. The reaction mixture was quenched by a saturated aqueous NH_4Cl. The resulting mixture was extracted by Et_2O three times. The combined organic layer was dried over $MgSO_4$, followed by filtration and evaporation. The residue was purified by Kugelrohr distillation under reduced pressure (34 Pa, bath temp. 120 °C) to afford trimethoxy(4-methoxyphenyl)silane (2.67 g, 11.7 mmol, 60% yield) as a colorless oil.

The hydride reduction of triethoxy(*o*-tolyl)silane, followed by reaction with *t*-BuMgCl, were performed according to the literature procedure.[5,9] Trimethoxy(4-methoxyphenyl)silane (1.14 g, 4.99 mmol) was added dropwise to a suspension of $LiAlH_4$ (0.381 g, 10.0 mmol, 2.0 equiv) in Et_2O (10.0 mL) under nitrogen atmosphere. The reaction mixture was stirred for 4 h at room temperature. After diluting with pentane (100 mL), the reaction mixture was filtered through a celite pad, followed by evaporation (150 hPa, 0 °C). *Be careful with fires caused by the precipitated hydride species.* The residue was passed through a silica-gel column (Et_2O as an eluent), followed by evaporation (150 hPa, 0 °C). The crude mixture was employed for the next reaction without further purification.

The crude mixture of (4-methoxyphenyl)silane was added to the solution of lithium chloride (0.323 g, 7.6 mmol, 1.5 equiv) in THF (10.0 mL). After *tert*-butylmagnesium chloride (2.0 M, 3.8 mL, 7.6 mmol, 1.5 equiv) was added, the reaction mixture was warmed to 80 °C (reflux) and stirred for 20 h. After cooling to room temperature, the reaction mixture was quenched by a saturated aqueous NH_4Cl. The resulting mixture was extracted by Et_2O three times. The combined organic layer was dried over $MgSO_4$, followed by filtration and evaporation. The residue was purified by silica-gel column chromatography (hexane as eluent) to afford **1k** [0.804 g, 4.14 mmol, 83% (over two steps)] as a colorless oil.

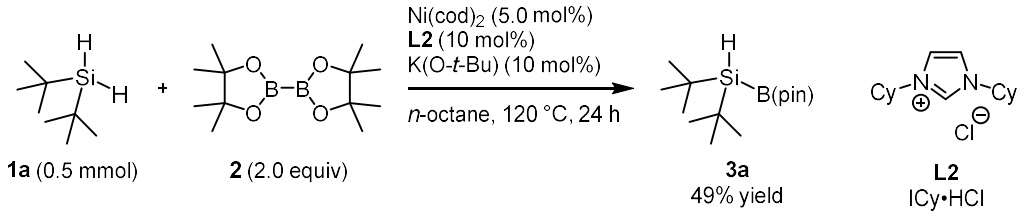
^{1}H NMR (401 MHz, $CDCl_3$, δ): 1.00 (s, 9H), 3.83 (s, 3H), 4.12 (s, 2H), 6.92 (dt, J = 2.1, 8.6 Hz, 2H), 7.50 (dt, J = 2.2, 8.8 Hz, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 16.4 (*C*), 27.4 (CH_3), 54.9 (CH_3), 113.6 (*C*H), 122.9 (*C*), 137.3 (*C*H), 160.8 (*C*). HRMS-EI (m/z): $[M]^+$ calcd for $C_{11}H_{18}OSi$, 194.1127; found 194.1127.

General Procedure for Iridium-Catalyzed Si–H Borylation of Dialkylsilanes: Procedure A



Bis(pinacolato)diboron **2** (507.1 mg, 2.00 mmol, 2.0 equiv) and **L3** (2.8 mg, 0.010 mmol, 1.0 mol%) were placed in a vial with a screw cap containing a Teflon®-coated rubber septum under air. The vial was placed in a glove box under an argon atmosphere, and then $[Ir(cod)Cl]_2$ (3.4 mg, 0.0051 mmol, 0.51 mol%) and K(O-*t*-Bu) (2.3 mg, 0.020 mmol, 2.0 mol%) were added to the vial. After the reaction vial was sealed with the screw cap, it was removed from the glove box. Then, cyclohexane (2.0 mL) was added to the vial via a syringe. The resulting mixture was allowed to warm at 80 °C and stirred for 1 h. Then, di-*tert*-butylsilane **1a** (144.5 mg, 1.00 mmol, 1.00 equiv) was added dropwise via a syringe. After the reaction mixture was stirred at 80 °C for 24 h, the reaction mixture was analyzed by GC to determine the product's GC yield (71%). The mixture was directly filtered through a silica-gel pad with pentane/Et_2O (9:1) as an eluent, and then the resulting solution was concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 98:2) as an eluent to afford the corresponding product **3a** (171.1 mg, 0.633 mmol, 63% yield) as a colorless oil.

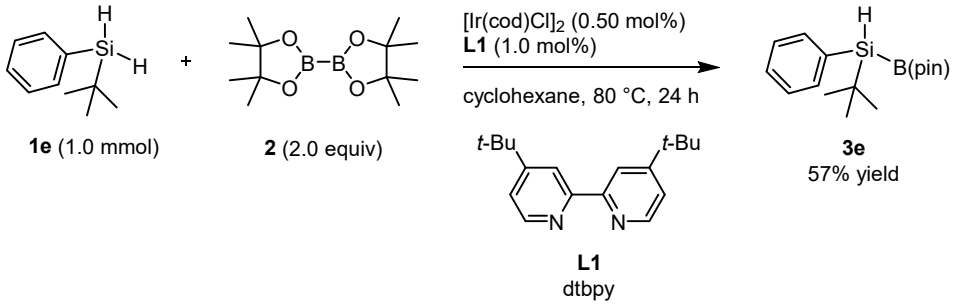
General Procedure for Nickel-Catalyzed Si–H Borylation: Procedure B



Bis(pinacolato)diboron **2** (254.5 mg, 1.00 mmol, 2.0 equiv) was placed in a vial with a screw cap containing a Teflon®-coated rubber septum under air. The vial was placed in a glove box under an argon atmosphere, and then $Ni(cod)_2$ (6.8 mg, 0.025 mmol, 5.0 mol%), **L2** (13.5 mg, 0.0502 mmol, 10.0 mol%), and K(O-*t*-Bu) (5.7 mg, 0.51 mmol, 10 mol%) were added to the vial. After the vial was sealed with the screw cap, it was removed from the glove box. Then, *n*-octane (1.0 mL) was added to

the vial via a syringe. The resulting mixture was allowed to warm at 120 °C and stirred for 1 h. Then, di-*tert*-butylsilane **1a** (72.1 mg, 0.500 mmol, 1.00 equiv) was added dropwise via a syringe. After the reaction mixture was stirred at 120 °C for 24 h, the reaction mixture was analyzed by GC to determine the product's GC yield (59%). The mixture was directly filtered through a silica-gel pad with pentane/Et_2O (9:1) as an eluent, and then the resulting solution was concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 98:2) as an eluent to afford the corresponding product **3a** (66.8 mg, 0.247 mmol, 49% yield) as a colorless oil.

General Procedure for Iridium-Catalyzed Si–H Borylation of Alkylarylsilanes: Procedure C

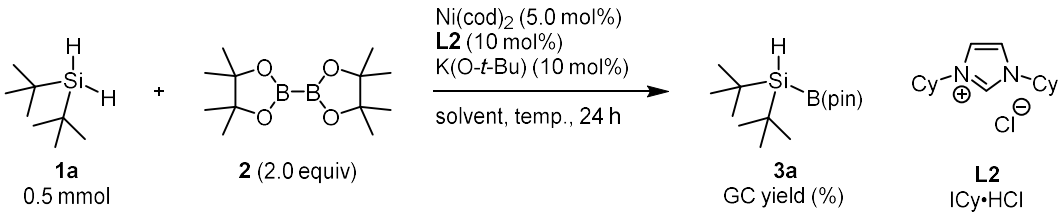


Bis(pinacolato)diboron **2** (255.7 mg, 1.01 mmol, 2.0 equiv) and **L1** (1.4 mg, 0.0052 mmol, 1.0 mol%) were placed in a vial with a screw cap containing a Teflon®-coated rubber septum under air. The vial was placed in a glove box under an argon atmosphere, and then $[Ir(cod)Cl]_2$ (1.8 mg, 0.0027 mmol, 0.5 mol%) was added to the vial. After the reaction vial was sealed with the screw cap, it was removed from the glove box. Then, cyclohexane (1.0 mL) was added to the vial via a syringe. The resulting mixture was allowed to warm at 80 °C and stirred for 1 h. Then, *tert*-butylphenylsilane **1e** (82.0 mg, 0.499 mmol, 1.00 equiv) was added dropwise via a syringe. After the reaction mixture was stirred at 80 °C for 24 h, the mixture was directly filtered through a silica-gel pad with pentane/Et_2O (9:1) as an eluent. The resulting solution was concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 97:3) as an eluent to afford the corresponding product **3e** (81.9 mg, 0.282 mmol, 57% yield) as a colorless oil.

Details of Optimization Study on Nickel-Catalyzed Si–H Borylation

The nickel-catalyzed borylation reaction in cyclohexane at 80 °C afforded **3a** in 50% yield (average of four runs, Table S1). However, the reproducibility of the reaction was unsatisfactory under these conditions. After an extensive screening of the reaction conditions, we found that when the reaction was carried out in *n*-octane at 120 °C, **3a** was obtained in 54% yield (average of four runs, Table S1) with better reproducibility.

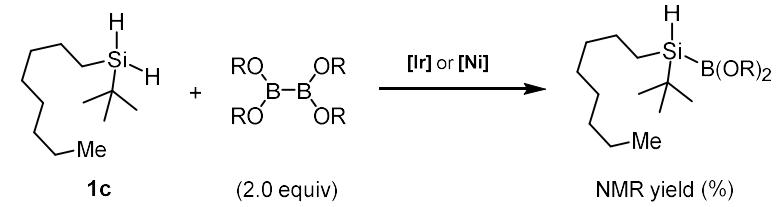
Table S1. Optimization on Reaction of 1a



conditions: cyclohexane, 80 °C	conditions: *n*-octane, 120 °C
1st run 55%	1st run 51%
2nd run 48%	2nd run 54%
3rd run 43%	3rd run 59%
4th run 55%	4th run 54%

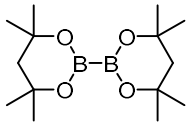
The borylations using more bulky diborons (**B1** and **B2**) were carried out to improve the yield (Table S2). Although the iridium-based catalyst produced the borylated product, the nickel-based catalyst did not work well. Unfortunately, the yield was not satisfactory when other boron sources were used.

Table S2. Investigation of other boron sources

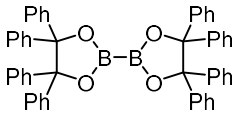


[Ir] : $[Ir(cod)Cl]_2$ (2.5 mol%), **L3** (5.0 mol%), K(O-*t*-Bu) (10 mol%), cyclohexane, 80°C, 24 h

[Ni] : $Ni(cod)_2$ (5.0 mol%), **L2** (10 mol%), K(O-*t*-Bu) (10 mol%), ^{n}octane, 120°C, 24 h



B1

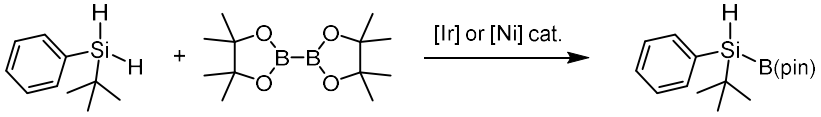


B2

entry	$B_2(OR)_4$	conditions	NMR yield (%)
1	**B1**	**[Ir]**	8
2	**B1**	**[Ni]**	trace
3	**B2**	**[Ir]**	11
4	**B2**	**[Ni]**	no reaction

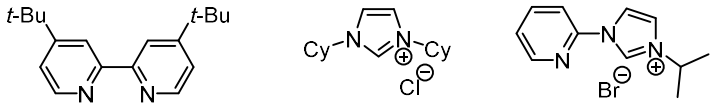
The monoborylation of **1e** was carried out under the developed conditions (Table S3). Although the Ir/**L3** catalytic system produced the desired product in low yield (11%, entry 1), the Ir/dtbpy (**L1**) catalytic system resulted in a good yield (57%, entry 2). The nickel-based catalyst also produced the borylated product (31%, entry 3).

Table S3. Investigation of the borylation of 1e



1e (0.5 mmol) **2** (2.0 equiv) **3e**

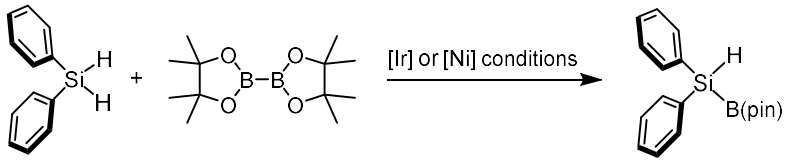
entry	conditions	isolated yield (%)
1	$[Ir(cod)Cl]_2$ (0.5 mol%) **L3** (1 mol%) K(O-*t*-Bu) (2 mol%) cyclohexane, 80 °C, 24 h	11
2	$[Ir(cod)Cl]_2$ (0.5 mol%) **L1** (1 mol%) cyclohexane, 80 °C, 24 h	57
3	$Ni(cod)_2$ (5 mol%) **L2** (1 mol%) K(O-*t*-Bu) (10 mol%) *n*-octane, 120 °C, 24 h	31



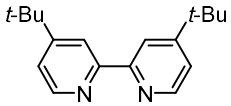
L1 dtbpy **L2** ICy•HCl **L3**

The borylation of diarylsilanes did not produce the desired silylboronates (Table S4). In the case of the iridium-based catalyst, dehydrogenative homo-coupling afforded oligosilanes. On the other hand, the reactions using the nickel-based catalyst resulted in the production of complex mixtures.

Table S4. Investigation of the borylation of diarylsilanes

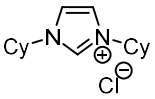


[Ir] conditions:
$[Ir(cod)Cl]_2$ (2.5 mol%)
L1 (5.0 mol%)
cyclohexane, 80°C, 24 h

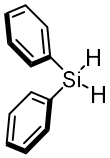
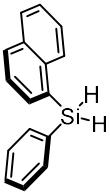
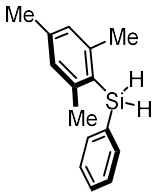


L1
dtbpy

[Ni] conditions:
$Ni(cod)_2$ (5.0 mol%)
L2 (10 mol%)
K(O-*t*-Bu) (10 mol%)
n-octane, 120°C, 24 h

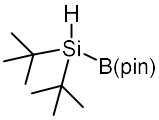


L2
ICy•HCl

entry	dihydrosilane	conditions	result
1		[Ir]	oligosilanes
		[Ni]	complex mixture
2		[Ir]	oligosilanes
		[Ni]	complex mixture
3		[Ir]	oligosilanes
		[Ni]	complex mixture

Characterization of Borylation Products 3a–3c, 3e, and 3h–3k

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



3a

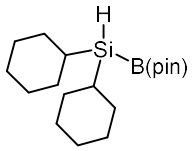
Procedure **A**: The reaction was performed with **1a** (144.5 mg, 1.00 mmol). The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 97:3) as an eluent to afford the corresponding silylboronate **3a** in 63% isolated yield (171.1 mg, 0.633 mmol) as a colorless oil.

Procedure **B**: The reaction was performed with **1a** (72.1 mg, 0.500 mmol). The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 97:3) as an eluent to afford

the corresponding silylboronate **3a** in 49% isolated yield (66.8 mg, 0.247 mmol) as a colorless oil.

^{1}H NMR (401 MHz, $CDCl_3$, δ): 1.06 (s, 18H), 1.25 (s, 12H), 3.25 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 18.4 (*C*), 24.9 (CH_3), 29.5 (CH_3), 83.1 (*C*). ^{11}B{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 34.5. ^{29}Si{^{1}H} NMR (119 MHz, $CDCl_3$, δ): –8.45 (brs). The broad signal of ^{29}Si was caused by the quadrupolar boron atom. HRMS-EI (m/z): $[M–Me]^+$ calcd for $C_{13}H_{28}{}^{11}BO_2Si$, 255.1951; found 255.1954.

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



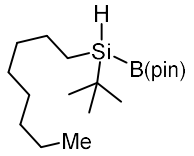
3b

Procedure **A**: The reaction was performed with **1b** (192.4 mg, 0.980 mmol). The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 97:3) as an eluent to afford the corresponding silylboronate **3b** in 24% GC yield.

Procedure **B**: The reaction was performed with **1b** (99.7 mg, 0.508 mmol). The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 97:3) as an eluent to afford the corresponding silylboronate **3b** in 29% isolated yield (48.0 mg, 0.149 mmol) as a colorless oil.

^{1}H NMR (401 MHz, $CDCl_3$, δ): 0.87–1.04 (m, 2H), 1.13–1.34 (m, 22H), 1.62–1.84 (m, 10H), 3.21 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 20.9 (*C*H), 25.0 (CH_3), 26.8 (CH_2), 28.0 (CH_2), 29.8 (CH_2), 30.1 (CH_2), 83.2 (*C*). ^{11}B{^{1}H} NMR (127 MHz, $CDCl_3$, δ): 34.6. The signal derived from the silicon directly attached to the boron atom was not detected by ^{29}Si{^{1}H} NMR, which is likely due to quadrupolar relaxation. HRMS-EI (m/z): $[M–Me]^+$ calcd for $C_{17}H_{32}{}^{11}BO_2Si$, 307.2273; found 307.2268.

***tert*-Butyl(octyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (3c).**



3c

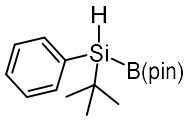
Procedure **A**: The reaction was performed with **1c** (200.7 mg, 1.00 mmol). The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 97:3) as an eluent to afford the corresponding silylboronate **3c** in 11% isolated yield (36.3 mg, 0.111 mmol) as a colorless oil.

Procedure **B**: The reaction was performed with **1c** (100.2 mg, 0.500 mmol). The crude product was

purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 97:3) as an eluent to afford the corresponding silylboronate **3c** in 43% isolated yield (69.9 mg, 0.214 mmol) as a colorless oil.

^{1}H NMR (396 MHz, $CDCl_3$, δ): 0.65–0.75 (m, 2H), 0.86 (t, J = 7.2 Hz, 3H), 0.99 (s, 9H), 1.20–1.45 (m, 24H), 3.35 (t, J = 4.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 8.04 (CH_2), 14.1 (CH_3), 16.4 (*C*), 22.7 (CH_2), 25.0 (CH_3), 26.1 (CH_2), 28.5 (CH_3), 29.2 (CH_2), 29.3 (CH_2), 31.9 (CH_2), 33.3 (CH_2), 83.2 (*C*). ^{11}B{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 34.7. ^{29}Si{^{1}H} NMR (119 MHz, $CDCl_3$, δ): –22.0 (brs). The broad signal of ^{29}Si was caused by the quadrupolar boron atom. HRMS-EI (m/z): $[M–Me]^+$ calcd for $C_{17}H_{36}{}^{11}BO_2Si$, 311.2582; found 311.2581.

***tert*-Butyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (3e).**



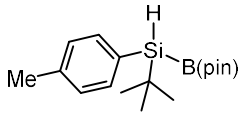
3e

Procedure **C**: The reaction was performed with **1e** (82.0 mg, 0.499 mmol). The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 97:3) as an eluent to afford the corresponding silylboronate **3e** in 57% isolated yield (81.9 mg, 0.282 mmol) as a colorless oil.

Procedure **B**: The reaction was performed with **1e** (82.0 mg, 0.499 mmol). The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 97:3) as an eluent to afford the corresponding silylboronate **3e** in 31% isolated yield (45.1 mg, 0.155 mmol) as a colorless oil.

^{1}H NMR (401 MHz, $CDCl_3$, δ): 1.00 (s, 9H), 1.28 (s, 12H), 3.98 (s, 1H), 7.29–7.39 (m, 3H), 7.60–7.69 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 17.1 (*C*), 25.0 (CH_3), 28.0 (CH_3), 83.6 (*C*), 127.5 (*C*H), 128.8 (*C*H), 133.8 (*C*), 136.4 (*C*H). ^{11}B{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 34.0. The signal derived from the silicon directly attached to the boron atom was not detected by ^{29}Si{^{1}H} NMR, which is likely due to quadrupolar relaxation. HRMS-EI (m/z): $[M–Me]^+$ calcd for $C_{15}H_{24}{}^{11}BO_2Si$, 275.1639; found 275.1632.

***tert*-Butyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(*p*-tolyl)silane (3h).**



3h

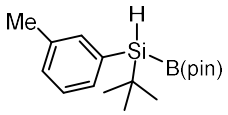
Procedure **C**: The reaction was performed with **1h** (89.7 mg, 0.503 mmol). The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 97:3) as an eluent to afford the corresponding silylboronate **3h** in 61% isolated yield (92.9 mg, 0.305 mmol) as a white solid.

Procedure **B**: The reaction was performed with **1h** (90.3 mg, 0.506 mmol). The crude product was

purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 97:3) as an eluent to afford the corresponding silylboronate **3h** in 29% isolated yield (45.1 mg, 0.148 mmol) as a white solid.

^{1}H NMR (401 MHz, $CDCl_3$, δ): 0.99 (s, 9H), 1.28 (s, 12H), 2.35 (s, 3H), 3.96 (s, 1H), 7.16 (d, J = 7.2 Hz, 2H), 7.53 (d, J = 7.2 Hz, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 17.1 (*C*), 21.5 (CH_3), 25.0 (CH_3), 28.0 (CH_3), 83.6 (*C*), 128.4 (*C*H), 130.1 (*C*), 136.4 (*C*H), 138.7 (*C*). ^{11}B{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 34.1. The signal derived from the silicon directly attached to the boron atom was not detected by ^{29}Si{^{1}H} NMR, which is likely due to quadrupolar relaxation. HRMS-EI (m/z): $[M–Me]^+$ calcd for $C_{16}H_{26}{}^{11}BO_2Si$, 289.1795; found 289.1786. mp 50–58 °C.

***tert*-Butyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(*m*-tolyl)silane (3i).**



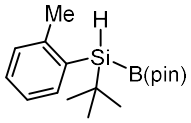
3i

Procedure **C**: The reaction was performed with **1i** (89.7 mg, 0.503 mmol). The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 97:3) as an eluent to afford the corresponding silylboronate **3i** in 58% isolated yield (88.5 mg, 0.291 mmol) as a white solid.

Procedure **B**: The reaction was performed with **1i** (89.2 mg, 0.500 mmol). The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 97:3) as an eluent to afford the corresponding silylboronate **3i** in 31% isolated yield (46.6 mg, 0.153 mmol) as a white solid.

^{1}H NMR (401 MHz, $CDCl_3$, δ): 1.00 (s, 9H), 1.278 (s, 6H), 1.282 (s, 6H), 2.34 (s, 3H), 3.96 (s, 1H), 7.15–7.19 (m, 1H), 7.23 (t, J = 7.6 Hz, 1H), 7.41–7.46 (m, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 17.1 (*C*), 21.5 (CH_3), 25.0 (CH_3), 28.0 (CH_3), 83.6 (*C*), 127.5 (*C*H), 130.0 (*C*H), 133.4 (*C*H), 133.6 (*C*), 136.7 (*C*), 137.1 (*C*H). ^{11}B{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 34.0. The signal derived from the silicon directly attached to the boron atom was not detected by ^{29}Si{^{1}H} NMR, which is likely due to quadrupolar relaxation. HRMS-EI (m/z): $[M–Me]^+$ calcd for $C_{16}H_{26}{}^{11}BO_2Si$, 289.1795; found 289.1796. mp 40–45 °C.

***tert*-Butyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(*o*-tolyl)silane (3j).**

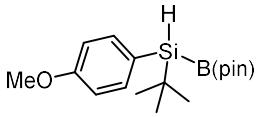


3j

Procedure **B**: The reaction was performed with **1j** (89.3 mg, 0.501 mmol). The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 97:3) as an eluent to afford the corresponding silylboronate **3j** in 59% isolated yield (89.7 mg, 0.295 mmol) as a colorless oil.

^{1}H NMR (401 MHz, $CDCl_3$, δ): 1.03 (s, 9H), 1.27 (s, 6H), 1.28 (s, 6H), 2.47 (s, 3H), 4.16 (s, 1H), 7.11–7.19 (m, 2H), 7.25 (td, J = 1.6, 7.5 Hz, 1H), 7.63 (d, J = 7.2 Hz, 1H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 18.0 (*C*), 23.8 (CH_3), 25.0 (CH_3), 28.4 (CH_3), 83.6 (*C*), 124.6 (*C*H), 129.2 (*C*H), 129.5 (*C*H), 132.9 (*C*), 137.9 (*C*H), 144.2 (*C*). ^{11}B{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 34.2. The signal derived from the silicon directly attached to the boron atom was not detected by ^{29}Si{^{1}H} NMR, which is likely due to quadrupolar relaxation. HRMS-EI (m/z): $[M–Me]^+$ calcd for $C_{16}H_{26}{}^{11}BO_2Si$, 289.1795; found 289.1794.

***tert*-Butyl(4-methoxyphenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (3k).**



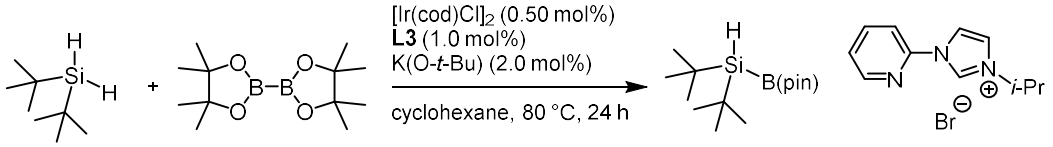
3k

Procedure **C**: The reaction was performed with **1k** (97.3 mg, 0.501 mmol). The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 97:3) as an eluent to afford the corresponding silylboronate **3k** in 71% isolated yield (113.1 mg, 0.353 mmol) as a white solid.

Procedure **B**: The reaction was performed with **1k** (97.2 mg, 0.500 mmol). The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 97:3) as an eluent to afford the corresponding silylboronate **3k** in 29% isolated yield (45.8 mg, 0.143 mmol) as a white solid.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.98 (s, 9H), 1.28 (s, 12H), 3.81 (s, 3H), 4.00 (s, 1H), 6.90 (dt, J = 2.1, 8.6 Hz, 2H), 7.57 (dt, J = 2.2, 8.6 Hz, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 17.2 (*C*), 25.0 (CH_3), 27.9 (CH_3), 54.9 (CH_3), 83.5 (*C*), 113.4 (*C*H), 124.5 (*C*), 137.8 (*C*H), 160.4 (*C*). ^{11}B{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 34.1. The signal derived from the silicon directly attached to the boron atom was not detected by ^{29}Si{^{1}H} NMR, which is likely due to quadrupolar relaxation. HRMS-EI (m/z): $[M–Me]^+$ calcd for $C_{16}H_{26}{}^{11}BO_3Si$, 305.1744; found 305.1747. mp 50–53 °C.

Procedure for Gram-Scale Synthesis of 3a



1a (7.0 mmol) **2** (2.0 equiv) **3a** 70% yield **L3**

Bis(pinacolato)diboron **2** (3.56 g, 14.0 mmol, 2.00 equiv) and **L3** (18.8 mg, 0.0701 mmol, 1.00 mol%) were placed in a vial with a screw cap containing a Teflon®-coated rubber septum under air. The vial was placed in a glove box under an argon atmosphere, and then $[Ir(cod)Cl]_2$ (23.5 mg, 0.0350 mmol, 0.500 mol%) and K(O-*t*-Bu) (15.7 mg, 0.140 mmol, 2.00 mol%) were added to the vial. After

the vial was sealed with the screw cap, it was removed from the glove box. Then, cyclohexane (7.0 mL) was added to the vial via a syringe. The resulting mixture was allowed to warm at 80 °C and stirred for 1 h. Then, di-*tert*-butylsilane **1a** (1.01 g, 7.01 mmol, 1.00 equiv) was added dropwise via a syringe. After the reaction mixture was stirred at 80 °C for 24 h, the reaction mixture was analyzed by GC to determined the GC yield of the product (73%). The mixture was directly filtered through a silica-gel pad with pentane/Et_2O (9:1) as an eluent, and then the resulting solution was concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 98:2) as an eluent to afford the corresponding product **3a** (1.33 g, 4.93 mmol, 70% yield) as a colorless oil.

Single Crystal X-ray Structural Analysis of 3a

The molecular structure of **3a** was confirmed by single-crystal X-ray diffraction analysis (Figure S1). Although several conformers of **3a** were observed in the disordered structure, the presence of a silicon-boron bond was confirmed unambiguously.

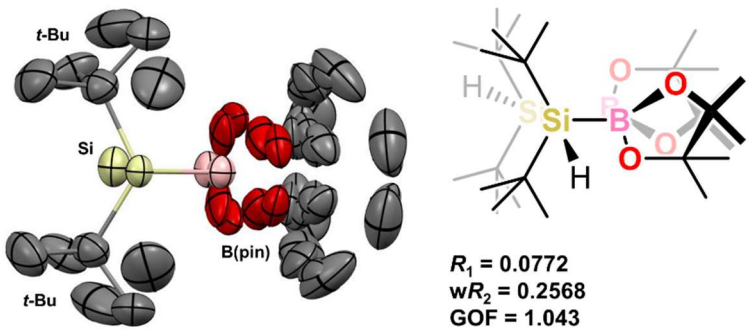


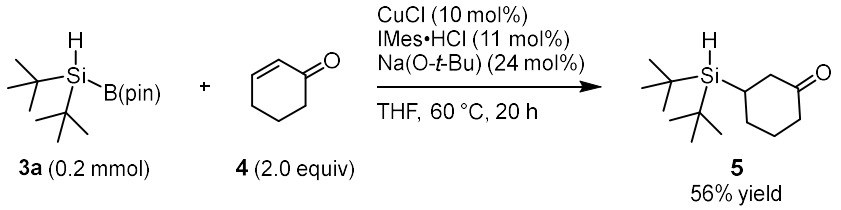
Figure S1. Molecular structure of **3a** with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity.

Table S5. Summary of X-ray crystallographic data for **3a**.

CCDC	2065033
Empirical formula	$C_{14}H_{31}BO_2Si$
Formula weight	270.29
Temperature/K	173
Crystal system	orthorhombic
Space group	Pnma
a / Å	12.7304(6)
b / Å	14.6636(6)
c / Å	9.7331(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1816.91(14)
Z	4
ρ_{calc} g/cm^3	0.988
μ/mm^{-1}	0.124
F(000)	600.0
Crystal size/mm^3	0.3×0.3×0.02
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	5.268 to 58.418
Index ranges	$-15 \leqq h \leqq 16$, $-19 \leqq k \leqq 19$, $-12 \leqq l \leqq 12$
Reflections collected	25184
Independent reflections	2333 [R_{int} = 0.0841, R_{sigma} = 0.0524]
Data/restraints/parameters	2333/449/236
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0772, wR_2 = 0.2346
Final R indexes [all data]	R_1 = 0.0948, wR_2 = 0.2568
Largest diff. peak/hole / e Å^{-3}	0.27/–0.59

Procedures for Organic Transformations of 3a

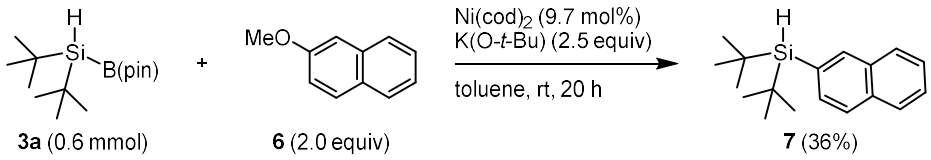
Copper-Catalyzed Conjugated Silylation



Copper(I) chloride (2.0 mg, 0.020 mmol, 10 mol %) and IMes·HCl (7.5 mg, 0.022 mmol, 11 mol %) were placed in a vial under air. The vial was placed in a glove box, and then Na(O-*t*-Bu) (4.5 mg, 0.048 mmol, 24 mol%) was added to the vial under an argon atmosphere. After the vial was sealed with a screw cap containing a Teflon®-coated rubber septum, it was removed from the glove box. Then, THF (1.0 mL) and **3a** (54.8 mg, 0.203 mmol) were added to the vial via syringes. The resulting mixture was stirred for 10 min at room temperature, and then 2-cyclohexen-1-one (**4**) (38.0 μL, 0.400 mmol, 2.00 equiv) and MeOH (16.0 μL, 0.400 mmol, 2.00 equiv) were added dropwise to the vial. After the resulting mixture was stirred at 60 °C for 20 h, the mixture was directly filtered through a silica-gel pad 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 (100:0 to 98:2) to give the corresponding product **5** (26.7 mg, 0.111 mmol, 56% yield) as a colorless oil.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.07 (s, 9H), 1.08 (s, 9H), 1.39–1.50 (m, 1H), 1.70 (qt, J = 4.1, 12.6 Hz, 1H), 1.82 (qd, J = 3.2, 12.9 Hz, 1H), 1.97–2.04 (m, 1H), 2.16–2.23 (m, 1H), 2.33 (td, J = 6.0, 13.3 Hz, 1H), 2.39–2.57 (m, 3H), 3.29 (s, 1H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 19.9 (*C*), 20.1 (*C*), 25.3 (*C*H), 28.9 (CH_2), 29.4 (CH_3), 29.5 (CH_3), 30.2 (CH_2), 42.0 (CH_2), 45.3 (CH_2), 211.9 (*C*). HRMS-EI (m/z): $[M–^tBu]^+$ calcd for $C_{10}H_{19}OSi$, 183.1205; found 183.1203.

Nickel-Catalyzed Silylation of Ether

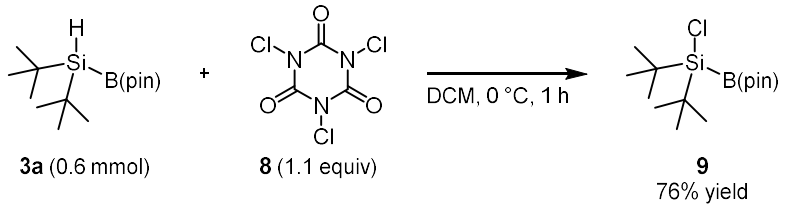


2-Methoxynaphthalene **6** (189.6 mg, 1.20 mmol, 2.00 equiv) was placed in a vial under air. The vial was placed in a glove box, and then $Ni(cod)_2$ (16.3 mg, 0.0593 mmol, 9.71 mol%) and K(O-*t*-Bu) (167.9 mg, 1.50 mmol, 2.45 equiv) were added to the vial under an argon atmosphere. After the vial was sealed with a screw cap containing a Teflon®-coated rubber septum, it was removed from the glove box. Then, toluene (3.0 mL) and **3a** (165.6 mg, 0.613 mmol) were added to the vial via syringes. After the resulting mixture was stirred for 20 h at room temperature, the mixture was directly filtered through a silica-gel pad 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 as eluent and GPC to give the corresponding product **7** (60.1 mg, 0.222 mmol, 36% yield) as a white solid

^{1}H NMR (401 MHz, $CDCl_3$, δ): 1.09 (s, 18H), 4.00 (s, 1H), 7.47–7.51 (m, 2H), 7.65 (dd, J = 1.2, 8.0 Hz, 1H), 7.78–7.87 (m, 3H), 8.09 (s, 1H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 19.2 (*C*), 29.0 (CH_3), 125.8 (*C*H), 126.3 (*C*H), 126.5 (*C*H), 127.7 (*C*H), 128.1 (*C*H), 131.8 (*C*H), 132.8 (*C*), 133.2 (*C*), 133.6 (*C*), 136.8 (*C*H). HRMS-EI (m/z): $[M]^+$ calcd for $C_{18}H_{26}Si$, 270.1804; found 270.1798. mp 50–53 °C.

Chlorination of Si–H Bond

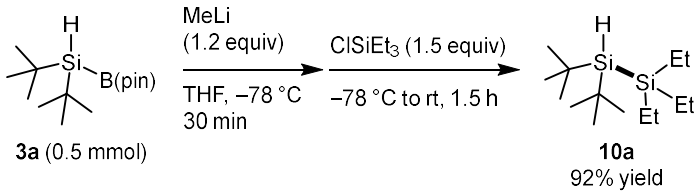


This reaction was performed according to the literature procedure.[10] Trichloroisocyanuric acid **8** (763.6 mg, 3.29 mmol, 1.10 equiv) was placed in a vial under air. After the vial was sealed with a screw cap containing a Teflon®-coated rubber septum, it was connected to a vacuum/nitrogen manifold through a needle. It was evacuated and then backfilled with nitrogen. This cycle was repeated three times. CH_2Cl_2 (15.0 mL) was added to the vial via a syringe and allowed to cool at 0 °C. Then, **3a** (809.1 mg, 2.99 mmol) was added dropwise to the mixture via a syringe. After the reaction mixture was stirred for 1 h at 0 °C, the solution was filtered under a nitrogen atmosphere and concentrated under reduced pressure. The crude product was purified by Kugelrohr distillation under reduced pressure (87 Pa, bath temp. 125 °C to 145 °C) to afford the corresponding product **9** (695.9 mg, 2.28 mmol, 76% yield) as a colorless oil.

^{1}H NMR (401 MHz, $CDCl_3$, δ): 1.09 (s, 18H), 1.27 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.6 (*C*), 24.9 (CH_3), 27.6 (CH_3), 84.0 (*C*). ^{11}B{^{1}H} NMR (127 MHz, $CDCl_3$, δ): 33.0. ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$, δ): 24.1 (brs). The broad signal of ^{29}Si was caused by the quadrupolar boron atom. HRMS-EI (m/z): $[M–Me]^+$ calcd for $C_{13}H_{27}{}^{11}BClO_2Si$, 289.1572; found 289.1565.

Procedure for Silicon-Silicon Coupling with 3a

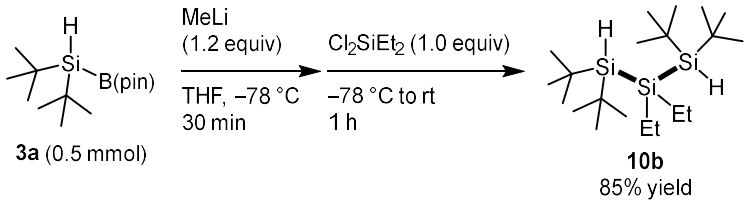
2,2-Di-*tert*-butyl-1,1,1-triethyldisilane (10a).



The vial was sealed with a screw cap containing a Teflon®-coated rubber septum and connected to a vacuum/nitrogen manifold through a needle. It was evacuated and then backfilled with nitrogen. This cycle was repeated three times. THF (2.0 mL) and **3a** (135.7 mg, 0.502 mmol) were added to the vial via syringes and allowed to cool at –78 °C. Then MeLi (1.16 M in Et_2O, 500 μL, 0.580 mmol, 1.16 equiv) was added dropwise to the mixture via a syringe. After the reaction mixture was stirred for 30 min at –78 °C, triethylchlorosilane (125.0 μL, 0.750 mmol, 1.50 equiv) was added to the reaction mixture and allowed to warm to room temperature slowly. After stirring for 1.5 h, the mixture was directly filtered through a silica-gel pad with pentane as an eluent. Then, the resultant solution was concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography with hexane as an eluent to afford the corresponding product **10a** (119.7 mg, 0.463 mmol, 92% yield) as a colorless oil.

^{1}H NMR (401 MHz, $CDCl_3$, δ): 0.76 (q, J = 7.6 Hz, 6H), 1.01 (t, J = 7.8 Hz, 9H), 1.09 (s, 18H), 3.43 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 5.47 (CH_2), 8.32 (CH_3), 20.5 (C), 30.9 (CH_3). ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$, δ): –7.96, –5.89. HRMS-EI (m/z): $[M]^+$ calcd for $C_{14}H_{34}Si_2$, 258.2199; found 258.2194.

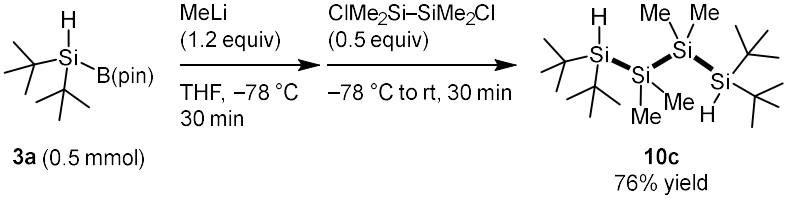
1,1,3,3-Tetra-*tert*-butyl-2,2-diethyltrisilane (10b).



The vial was sealed with a screw cap containing a Teflon®-coated rubber septum and connected to a vacuum/nitrogen manifold through a needle. It was evacuated and then backfilled with nitrogen. This cycle was repeated three times. THF (2.0 mL) and **3a** (135.7 mg, 0.502 mmol) were added to the vial via syringes and allowed to cool at –78 °C. Then MeLi (1.16 M in Et_2O, 500 μL, 0.580 mmol, 1.16 equiv) was added dropwise to the mixture via a syringe. After the reaction mixture was stirred for 30 min at –78 °C, diethyldichlorosilane (37.0 μL, 0.250 mmol, 0.500 equiv) was added to the reaction mixture and allowed to warm to room temperature slowly. After stirring for 1 h, the mixture was directly filtered through a silica-gel pad with pentane as an eluent. Then the resultant solution was concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography with hexane as an eluent to afford the corresponding product **10b** (79.8 mg, 0.214 mmol, 85% yield) as a white solid.

^{1}H NMR (401 MHz, $CDCl_3$, δ): 1.02–1.17 (m, 46H), 3.64 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 4.35 (CH_2), 10.5 (CH_3), 21.9 (C), 31.1 (CH_3). ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$, δ):–33.0, 3.74. HRMS-EI (m/z): $[M–^tBu]^+$ calcd for $C_{16}H_{39}Si_3$, 315.2360; found 315.2350. mp 102–103 °C.

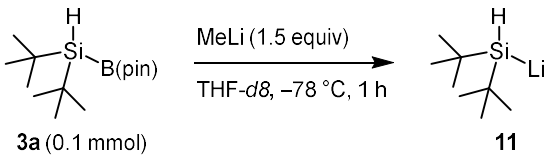
1,1,4,4-Tetra-*tert*-butyl-2,2,3,3-tetramethyltetrasilane (10c).



The vial was sealed with a screw cap containing a Teflon®-coated rubber septum and connected to a vacuum/nitrogen manifold through a needle. It was evacuated and then backfilled with nitrogen. This cycle was repeated three times. THF (2.0 mL) and **3a** (134.9 mg, 0.499 mmol) were added to the vial via syringes and allowed to cool at –78 °C. Then MeLi (1.16 M in Et_2O, 500 μL, 0.580 mmol, 1.16 equiv) was added dropwise to the mixture via a syringe. After the reaction mixture was stirred for 30 min at –78 °C, 1,2-dichloro-1,1,2,2-tetramethylsilane (46.0 μL, 0.250 mmol, 0.500 equiv) was added to the reaction mixture and allowed to warm to room temperature slowly. After stirring for 30 min, the mixture was directly filtered through a silica-gel pad with pentane as an eluent. Then the resultant solution was concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography with hexane as an eluent to afford the corresponding product **10c** (76.5 mg, 0.190 mmol, 76% yield) as a white solid.

^{1}H NMR (401 MHz, $CDCl_3$, δ): 0.33 (s, 12 H), 1.09 (s, 36H), 3.55 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): –1.38 (*C*H$_3$), 21.0 (*C*), 30.7 (*C*H$_3$). ^{29}Si{1H} NMR (79 MHz, $CDCl_3$, δ): –42.9, –1.58. HRMS-EI (m/z): [M–^{t}Bu]$^+$ calcd for $C_{16}H_{41}Si_4$, 345.2285; found 345.2279. mp 108–110 °C.

Details of ^{29}Si NMR Experiments



The vial was sealed with a screw cap containing a Teflon®-coated rubber septum and connected to a vacuum/nitrogen manifold through a needle. It was evacuated and then backfilled with nitrogen. This cycle was repeated three times. THF (500 μL) and **3a** (27.0 mg, 0.100 mmol) were added to the vial via syringes and allowed to cool at –78 °C. Then MeLi (1.16 M in Et_2O, 130 μL, 0.151 mmol, 1.51 equiv) was added dropwise to the mixture via a syringe. After the reaction mixture was stirred for 1 h at –78 °C and a further 1 h at room temperature, the resulting mixture was transferred to an NMR tube and analyzed by ^{29}Si{^{1}H} NMR spectroscopy (JEOL JNM-ECZ600R/S3) at room temperature.

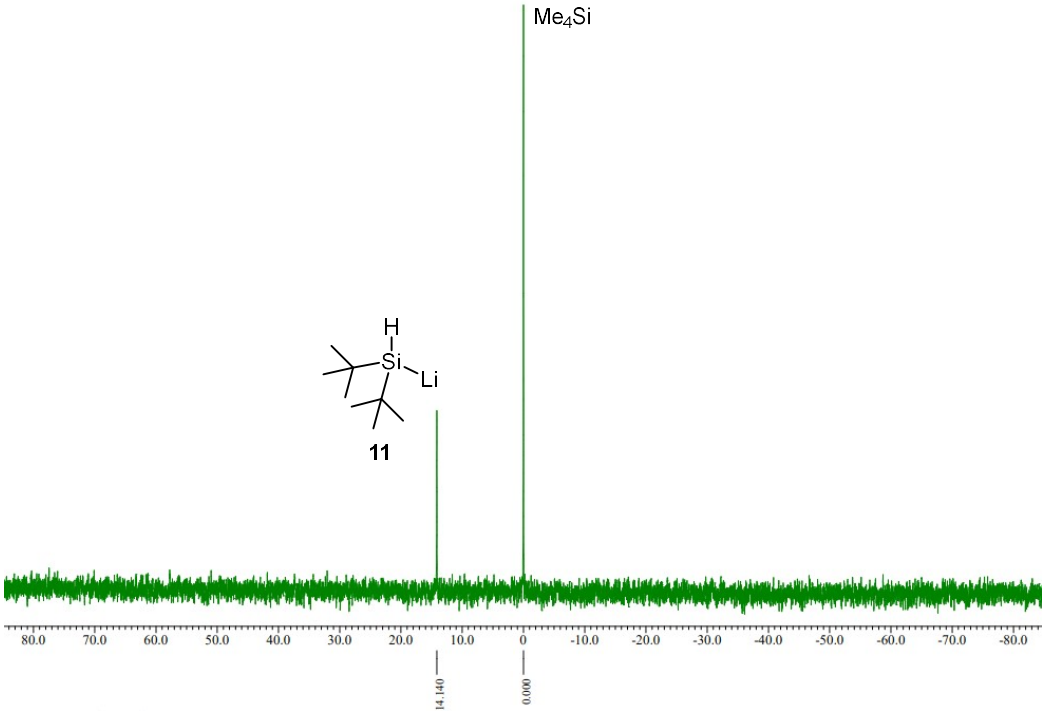


Figure S2. $^{29}Si\{^{1}H\}$ NMR spectra of (*t*-Bu)$_2$HSiLi (**11**) at room temperature.

The vial was sealed with a screw cap containing a Teflon®-coated rubber septum and connected to a vacuum/nitrogen manifold through a needle. It was evacuated and then backfilled with nitrogen. This cycle was repeated three times. THF (500 μL) and **3a** (26.7 mg, 0.0988 mmol) were added to the vial via syringes and allowed to cool at –78 °C. Then MeLi (1.16 M in Et_2O, 130 μL, 0.151 mmol, 1.53 equiv) was added dropwise to the mixture via a syringe. After the reaction mixture was stirred for 1 h at –78 °C, the resulting mixture was transferred to an NMR tube and analyzed by $^{29}Si\{^{1}H\}$ NMR spectroscopy (JEOL JNM-ECA600) at –95°C.

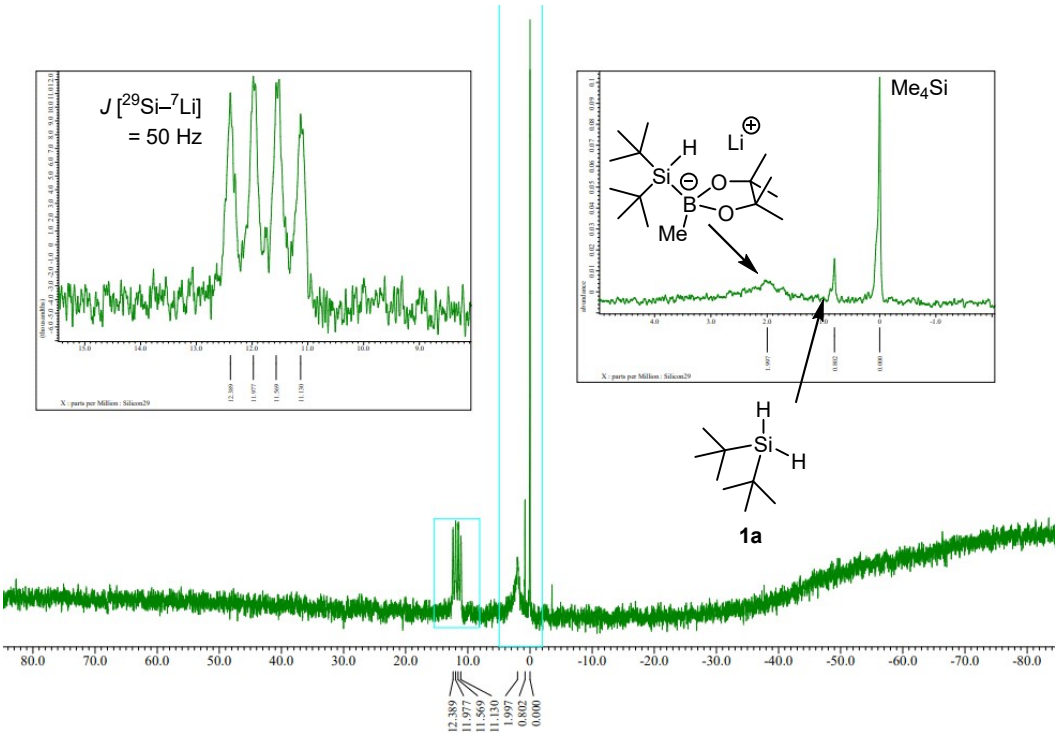


Figure S3. ^{29}Si{^{1}H} NMR spectra of (t-Bu)$_2$HSiLi (**11**) at –95°C.

^{29}Si{^{1}H} NMR analysis revealed that **11** was generated in the reaction mixture (Figure S2 and S3). Signals derived from the corresponding borate and hydrolyzed dihydrosilane **1a** were also observed at –95°C (Figure S3).

References

1) Gründemann, S.; Albrecht, M.; Kovacevic, A.; Faller, J. W.; Crabtree, R. H. *J. Chem. Soc., Dalton Trans.* **2002**, *10*, 2163.
2) Masaoka, S.; Banno, T.; Ishikawa, M. *J. Organomet. Chem.* **2006**, *691*, 182.
3) Iwanaga, K.; Tokuhisa, K. METHOD FOR PRODUCING TERTIARY ALKYLSILANE AND TERTIARY ALKOXYSILANE. Tosoh Corporation Patent JP 2016/138086, Aug 4, 2016.
4) Igawa, K.; Yoshihiro, D.; Ichikawa, N.; Kokan, N.; Tomooka, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 12745.
5) Hirone, N.; Sanjiki, H.; Tanaka, R.; Hata, T.; Urabe, H. *Angew. Chem., Int. Ed.* **2010**, *49*, 7762.
6) Zhu, J.; Chen, S.; He, C. *J. Am. Chem. Soc.* **2021**, *143*, 5301.
7) Shirakawa, E.; Ikeda, D.; Masui, S.; Yoshida, M.; Hayashi, T. *J. Am. Chem. Soc.* **2012**, *134*, 272.
8) Manoso, A. S.; Ahn, C.; Soheili, A.; Handy, C. J.; Correia, R.; Seganish, W. M.; DeShong, P. *J. Org. Chem.* **2004**, *69*, 8305.
9) Visco, M. D.; Wieting, J. M.; Mattson, A. E. *Org. Lett.* **2016**, *18*, 2883.

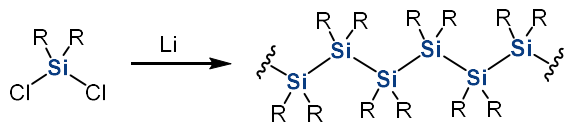
10) Varaprath, S.; Stutts, D. H. *J. Organomet. Chem.* **2007**, *692*, 1892.

III Iterative Synthesis of Oligosilanes Using Methoxyphenyl- or Hydrogen-Substituted Silylboronates as Building Blocks

2.1: Introduction

Organosilicon compounds[1-6] are interesting molecules in not only academic research but also industry. Due to the general reaction similarities between the group-14 elements carbon and silicon, organosilicon compounds have been synthesized by the same way as carbon-based organic compounds. However, while there are currently over 200 million registered structures for organic compounds, the number of known organosilicon compounds is less than ~1.4 million (<1%). This lack of diversity in organosilicon compounds is primarily due to the limited number of synthetic routes to organosilicon compounds compared to other organic compounds.[1-6]

Despite the large variety of carbon–carbon bond-formation reactions, Si–Si bond-formation reactions are far more limited. Wurtz-type coupling of dichlorosilanes using alkali metals has been used to form Si–Si bonds (Scheme 1).[1,2,4] In contrast, cross-Si–Si bond-forming reactions, which can give more complex structures, are difficult due to the requirement of silicon nucleophiles. While silyl electrophiles are easily prepared in many cases, silyl anions have been generated only for limited structures (phenyl or disilyl substitution on the silicon atom is usually required), and trialkylsilyl anions are relatively difficult to generate.[2i, 3] Although the synthesis of oligosilanes with simple repeating units can be synthesized by homocoupling reactions, more complicated organosilane consisting of different substituents with a defined sequence generally require customized synthetic procedures.[5, 6] General synthetic methods for various oligosilanes comparable to those used in carbon-based organic synthesis are thus strongly desirable for the development of advanced oligosilane-based materials.



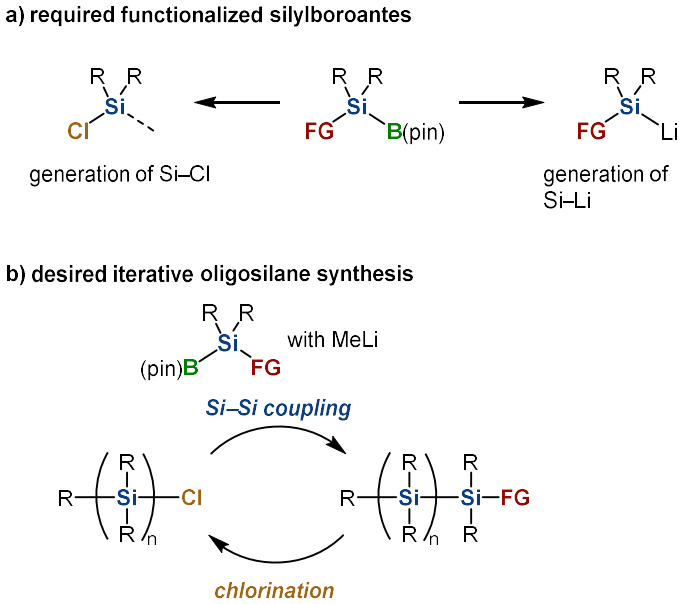
R = simple organic substituents (alkyl and Ph)
– Synthesis of designed oligosilanes is difficult.

Scheme 1. General synthetic method of oligosilanes.

Iterative synthetic methods are a powerful strategy to produce various structures of oligomer molecules.[7-9] In nature, enzyme-catalyzed iterative syntheses using building blocks such as amino acids, saccharides, and nucleosides are employed for the synthesis of complicated biopolymers with specific properties.[7,8] Moreover, chemists have inspired by such smart natural processes and developed laboratory-scale iterative syntheses of various natural and non-natural compounds.[9] However, the

iterative synthesis of organosilicon compounds has scarcely been studied.[10–13] In an early study, Kashimura reported in 2000 a pioneering iterative synthesis of oligosilanes using the electrochemical coupling of chlorohydrosilane building blocks.[10] However, this method was applicable only to a very limited range of structures. In 2012, Venkataraman and Nuckolls reported an iterative synthesis using $PhMe_2SiCl$ as the building block,[12] which was similar to the approach reported in 2007 by Tamao for the customized synthesis of structurally confined oligosilanes.[11] In these methods, Si–Si cross-coupling between silyl anions generated by the reduction of $PhMe_2SiCl$ with Li metal and the terminal chlorosilane moiety was used. And terminal Si–Ph moiety was chlorinated for the iteration of these two reactions. The power of this iterative synthetic method was successfully shown via studies on single-molecule conductance.[12] However, this Si–Si cross-coupling method is limited by the difficulty of generating silyl anions with more complicated structures ($PhSiR^1R^2Li$).[2i, 3, 14] Requirements for potential iterative syntheses of oligosilanes include: 1) effective Si–Si cross-bond formation with various classes of substituents on the silicon atom under mild conditions, 2) selective activation of the terminal position for the subsequent round of Si–Si bond formation, and 3) easy access to silane building blocks with various structures and high bench stability that can withstand purification techniques such as chromatography on silica gel.

Since the pioneering study of Suginome and Ito in 1996, silylboronates have been regarded as versatile silylation and borylation reagents in the presence of transition-metal catalysts.[15–17] In particular, activation of silylboronates by a base can generate silyl nucleophile species, allowing cross-Si–Si bond-forming reactions with chlorosilanes under mild conditions.[18] Although this reaction would seem to be suitable as the unit reaction for the Si–Si cross-bond formation in iterative oligosilane synthesis,[18] synthetic routes to silylboronates remain limited and are difficult to apply for the generation of silyl anions with various structures. However, Ito recently developed a general method for the synthesis of a variety of silylboronates via the Rh-, Pt-, and Ni-catalyzed borylation of hydrosilanes by modifying the Ir-based catalysis reported by Hartwig.[19–21] This new method enables the generation of silylboronates and silyl nucleophiles with a wide range of structures, which cannot be prepared using previous methods. Ito also reported that cross-Si–Si bond formation between various silylboranes activated by MeLi and chlorosilanes proceeded with high efficiency.[20–22] I anticipated that by using silylboronates of the type $(pin)B–SiR^1R^2PG$, which bear various R^1 and R^2 substituents and a protecting group (PG) that could be removed from the terminal Si atom to produce a Si electrophile that could react with the subsequent Si nucleophile, I could establish a general iterative synthesis for oligosilanes (Scheme 2).



Scheme 2. Envisioned iterative oligosilane synthesis

Here, I describe an iterative synthesis of oligosilanes using methoxyphenyl- or hydrogen-substituted silylboronates, which can be obtained from the transition-metal-catalyzed borylation of hydrosilanes.[20–21] These silylboronates are bench stable and can be purified by column chromatography on silica gel.[20–22] The reaction of these silylboronates with MeLi generates the corresponding silyl nucleophiles that engage in highly efficient cross-Si–Si bond-forming reactions with terminal chlorosilane moieties. An ensuing chlorination of the methoxyphenyl or hydride groups under mild conditions selectively reproduces a chlorosilane moiety at the terminal of the oligosilane,[23,24] allowing the next Si–Si cross-coupling. This method enables the rapid and convenient synthesis of various oligosilanes by changing the building block type and order of the Si–Si cross-couplings. To demonstrate the practical utility of this iterative synthesis, oligosilanes with different sequences were prepared by simply changing the order of the reaction of four different silicon units. As a further demonstration of target-oriented synthesis, a tree-shaped oligosilane was prepared. The structures of several of these oligosilanes were unambiguously confirmed using single-crystal X-ray diffraction analysis.

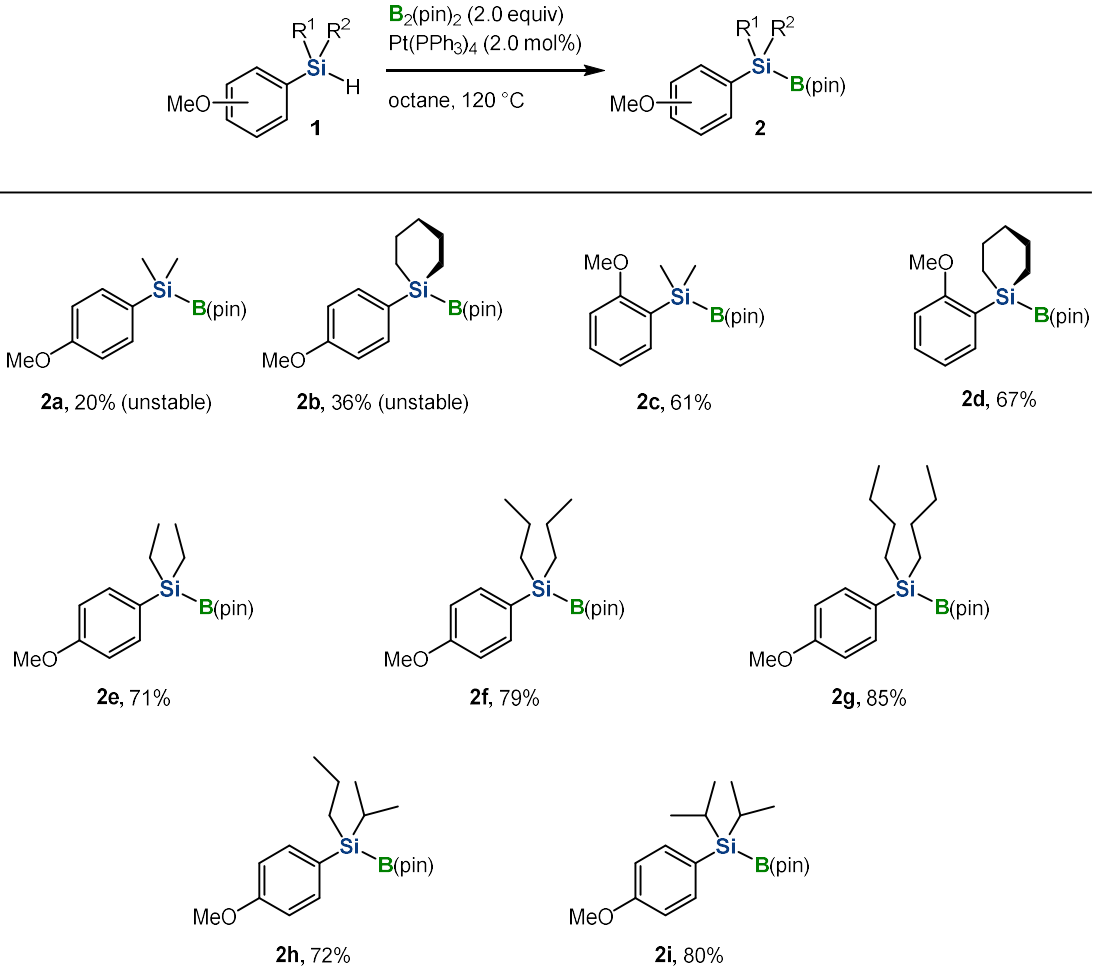
2.2: Results and Discussion

First, I thought about silylboronates building blocks for the envisioned iterative synthesis of oligosilanes. Of the three requirements I proposed above, I first searched for appropriate functional groups (FGs) that could potentially be converted to leaving groups for the nucleophilic substitution by silyl nucleophiles. In previous of silicon chemistry, the phenyl group has often been used as a parent group of chlorine; the phenyl group on the silicon atom can be removed by Brønsted or Lewis acids

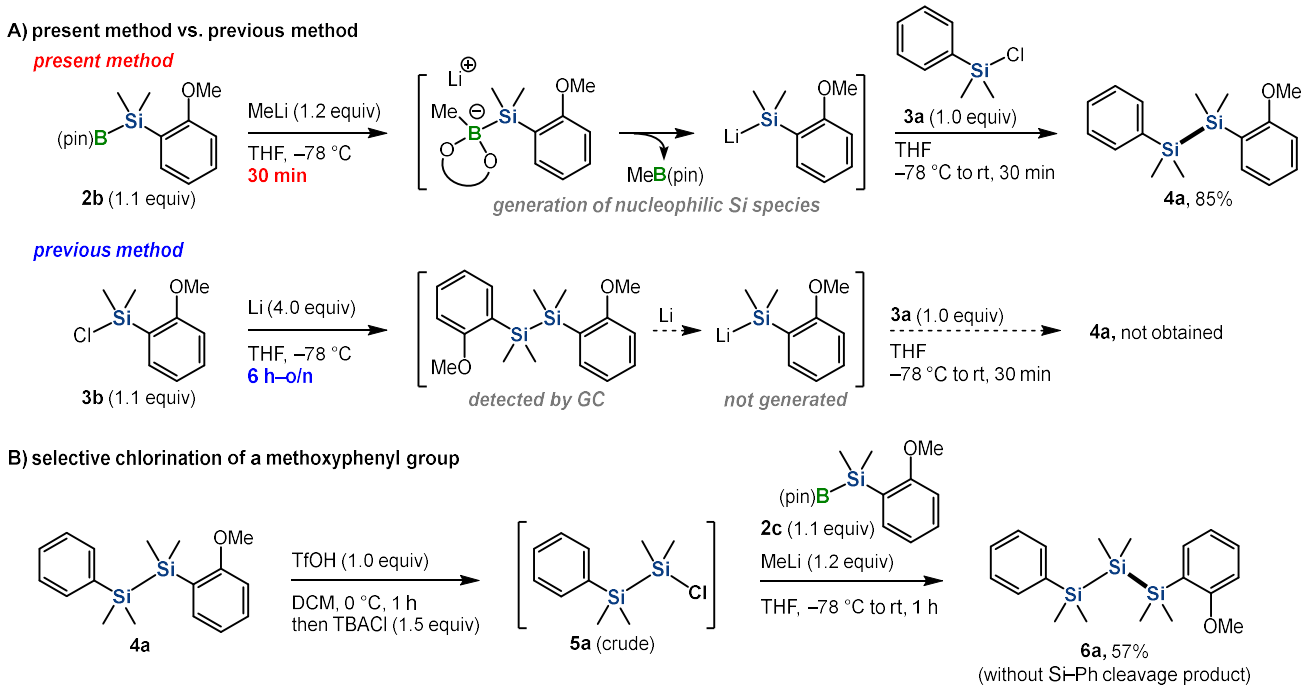
to form a Si–Cl moiety, which is reactive toward nucleophiles.[23a-c] However, such chlorination conditions lack selectivity to prepare oligosilanes with phenyl groups in other positions. In order to design a broadly applicable reaction, I used the more-electron-rich 4- and 2-methoxyphenyl groups, which are more reactive toward acid-catalyzed deprotection and chlorination than the phenyl group.[23] I also considered the hydride group, which would be suitable for the generation of silyl anions, as it is known to be easily chlorinated under mild conditions (chapter 2).[24] Chemical stability is also an important factor in the preparation of building blocks for iterative synthesis. $PhMe_2Si$–B(pin) is one of the most widely used silylboronates in organic synthesis, but sensitive to air and moisture.[15–17] Silylboronates with sterically more demanding silyl groups are stable toward air and moisture and can be isolated using chromatography on silica gel.[19–22] I have already reported that silylboronates with a hydride group are unstable when the steric demand of the other substituents is relatively low (R = *prim*-alkyl, Me), albeit that their stability improves with increasingly bulkier substituents (R = *iso*-Pr, *t*-Bu).[21] Silylboronates with a phenyl or a 4-methoxyphenyl group are unstable when the other substituents are relatively small (R = Me), albeit that 2-methoxyphenyl is expected to stabilize the silylboronates via steric shielding of the Si–B bond by the 2-methoxy group.

I investigated the synthesis of methoxyphenyl-substituted silylboronates via transition-metal-catalyzed Si–H borylations recently reported by Ito (table 1). By Pt-catalyzed Si–H borylation, desired methoxyphenyl-substituted silylboronates were obtained. Although (*p*-MeOPh)Me2Si–B(pin) **2a** was obtained in low yield (20%), (*o*-MeOPh)Me2Si–B(pin) 2b was obtained in high yield (61%) due to the enhanced stability by the steric bulkiness around the silicon center. *Sila*-cyclic silylboronates 2c and **2d** were obtained in a similar trend (36% and 71%, respectively). Et, Pr, and Bu disubstituted silylboronates **2e–g**, which are probably bulkier around the silicon center, were obtained in high yields (79%, 77%, and 79%, respectively), even with a less hindered *p*-methoxyphenyl group. Bulkier iPr substituted **2h** and **2i** were also obtained in high yields (both 80%).

Table 1. Synthesis of methoxyphenyl-substituted silylboronates.

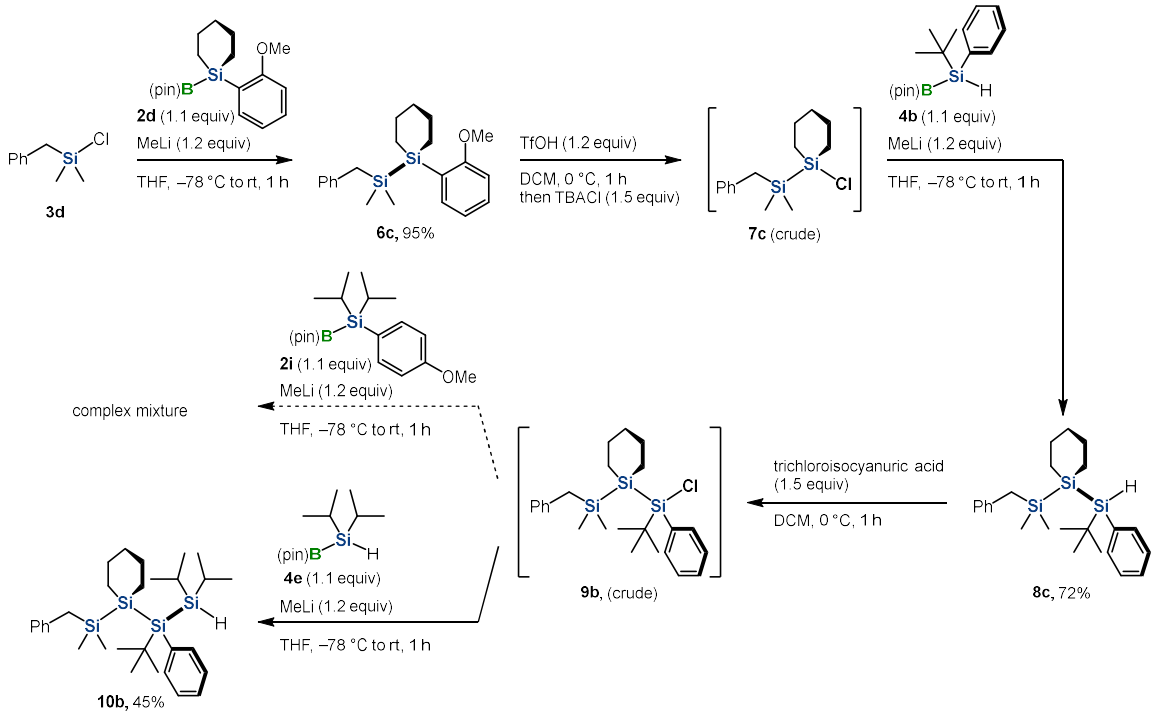


Next, I demonstrated the utility of methoxyphenyl-substituted silylboronates (Scheme 2). The activation of silylboronates **2c** with MeLi and subsequent addition of dimethyphenylsilylchloride **3a** afforded disilane **4a** in high yield (Scheme2a, 85%), which indicates the corresponding silicon nucleophile was generated. On the other hand, the classical reduction of methoxyphenyl-substituted chlorosilane **3b** and subsequent addition of **3a** did not produce **4a** (Scheme2a). In this reaction, disilane intermediate was observed by GC analysis in the first period and then a complex mixture was observed. [14] The further reduction of the disilane intermediate for the generation of silyllithium species would not work well, resulting in the decomposition of **6b**. [14] Next, the treatments of **4a** with TfOH and followed TBACl produced chlorodisilane **5a** (Scheme 3B). Although the phenyl group of **4a** is also active toward such reaction conditions, the methoxyphenyl group reacted preferentially to give **6a**. Additionally, **5a** was roughly isolated by filtration and used for the next Si–Si coupling with **2c**, and trisilane **6a** was obtained in moderate yield without the Si–Ph bond cleavage product (Scheme 3B, 57%). Thus, repeating Si–Si coupling and chlorination allows the iterative synthesis of oligosilanes.



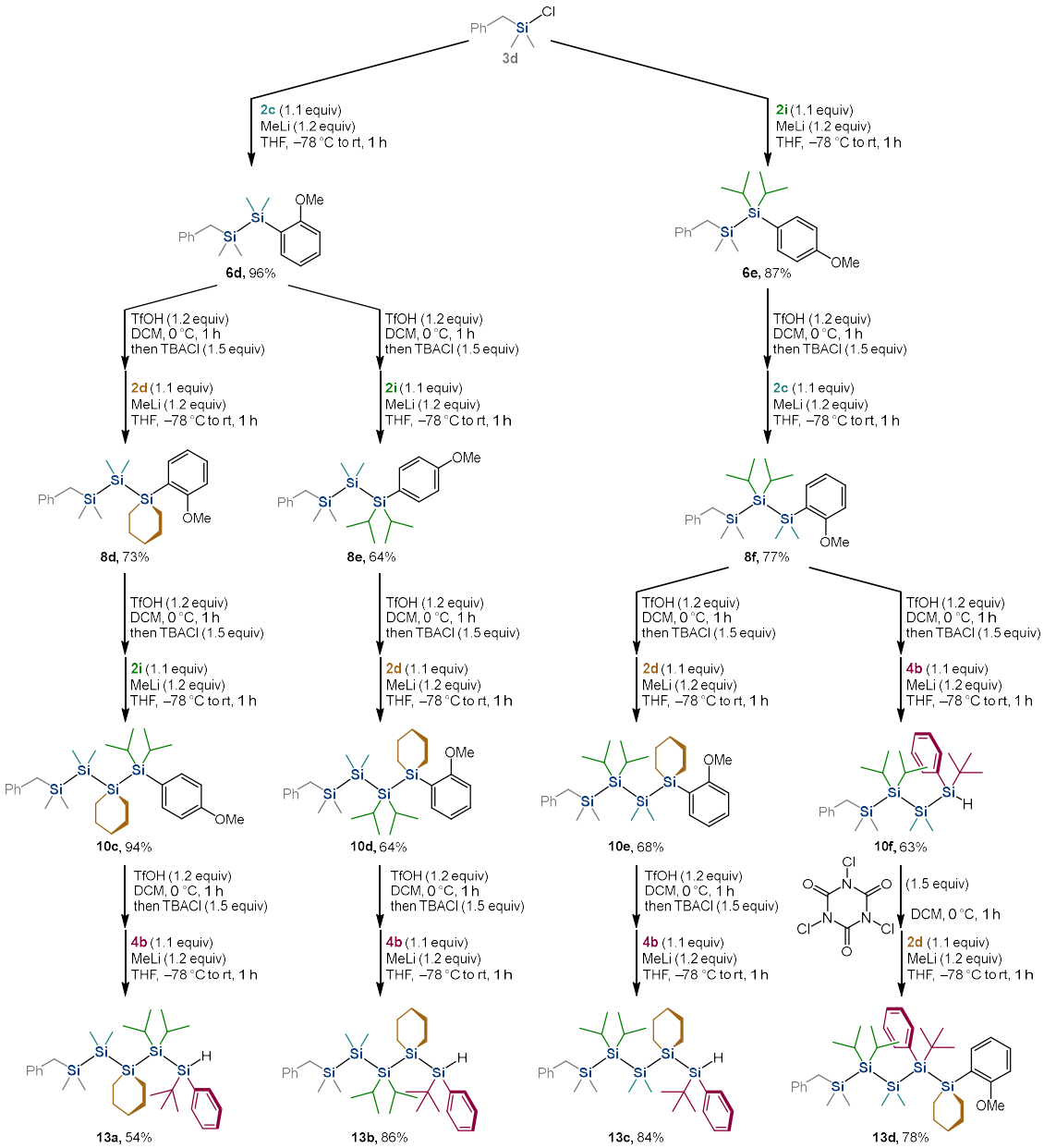
Scheme 3. (A) The generation of the silicon nucleophile bearing a methoxyphenyl group and (B) selective chlorination of the methoxy-phenyl group.

Next, I explain the iterative synthesis including hydrogen-substituted silylboronates **4** (Scheme 4). The Si–Si coupling between benzyldimethylsilylchloride **3d** and silylboronate **2d** produced disilane **6d** in high yield (95% yield). Then Si–Si coupling between **7c** produced by chlorination of **6c** and silylboroante **4b** afforded trisilane **8c** (72% yield). Then the chlorination of the hydrogen at the terminal of **8c** was performed by the treatment with trichloroisocyanuric acid, producing chlorotrisilane **9b**. **9b** was roughly isolated by filtration and used for the next Si–Si coupling without further purification. Next, I tried to introduce a di-*i*-propylsilyl unit to form tetrasilane. However, Si–Si coupling between **9b** and methoxyphenyl-substituted silylboronate **2i** produced a complex mixture without the desired tetrasilane. In contrast, Si–Si coupling with hydrogen-substituted silylboronate **4e** afforded the desired tetrasilane **10b** (45% yield). These results indicate that the steric repulsion between chlorotrisilane **9b** and the silyllithium specie was relieved by changing the methoxyphenyl group to a hydrogen atom. Therefore, hydrogen-substituted silylboronates **4** are preferable when performing cross-coupling between chlorooligosilane and silylboronates with high steric repulsion.



Scheme 4. Iterative synthesis including hydrogen-substituted silylboronates.

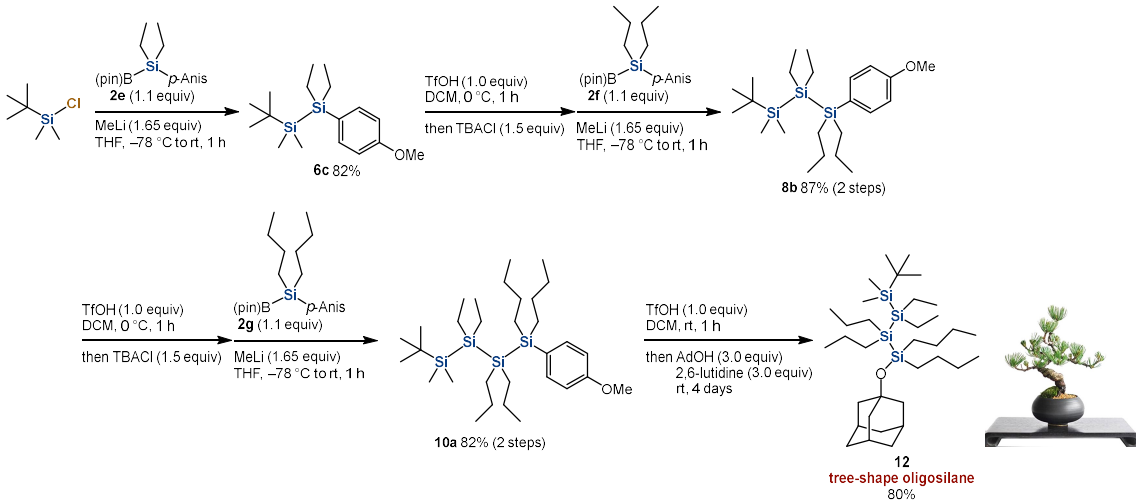
Iterative synthesis can easily form oligomers with different sequences by changing the order of the introduction of units. In this context, oligosilanes with different sequences were synthesized using the same set of silylboronates **2b**, **2d**, **2i**, and **4b** (Scheme 5). In the first step, two disilanes **6d** and **6e** were produced by the Si–Si coupling using silylboronates **2b** and **2i** (96% and 87% yields, respectively). Derived from disilane **6d**, two trisilanes **8d** and **8e** were afforded by the chlorination of the methoxyphenyl group and Si–Si coupling using silylboronates **2d** and **2i** (73% and 64% yields, respectively). The chlorination of the methoxyphenyl group of disilane **6e** and the followed Si–Si coupling using silylboronate **2i** afforded trisilane **8f** in 77% yield. Then, trisilane **8d** and **8e** were elongated by chlorination and Si–Si coupling using silylboronates **2i** and **2d**, respectively, and tetrasilane **10c** and **10d** were obtained in 94% and 64% yields, respectively. Trisilane **8f** was derived into tetrasilane **10e** and **10f** by the chlorination and Si–Si coupling using silylboronates **2d** and **4b**, respectively (68% and 63% yields, respectively). Eventually, tetrasilanes **10c**–**f** were elongated to form pentasilane **13a**–**d** (54%, 86%, 84%, and 78% yields, respectively). Such divergent synthesis is very useful because various oligosilanes can be prepared even from a limited set of silylboronates.



Scheme 5. Syntheses of multi-unit peptasilanes with different sequences.

Next, I tried the synthesis of the oligosilanes **12** designed to be a tree-shape structure (Scheme 3). The Si–Si coupling using silylboronate **2e** with tert-butyldimethylsilylchloride **3c** afforded disilane **6c** in high yield (82% yield). The chlorination of the methoxyphenyl group of 6c produced chlorodisilane **7b**, and subsequent Si–Si coupling using silylboronates **2f** produced trisilane **8b** in high yield (87% yield over 2 steps). Furthermore, chlorination yielding chlorotrisilane **9a** and subsequent Si–Si coupling using silylboronate **2g** yielded tetrasilane **10a** in high yield (82% yield over 2 steps). Finally, oligosilane **12** was obtained by Si–O coupling between 1-adamantanol and chlorotetrasilane **11a** produced by chlorination of **10**. The synthesis of oligosilane **12** is very difficult by previous iterative

synthetic methods because these methods involve the preparation and the reduction of unstable hydrogen or phenyl-substituted chlorosilanes.



Scheme 6. Synthesis of the tree-shaped oligosilane.

Finally, I tried to observe the iterative synthetic menner of the present method by SC-XRD analysis (figure 1). The oligosilanes synthesized in this study are generally liquids or viscous oils due to their flexible structures. In order to enhance the crystallization of oligosilanes for the SC-XRD analysis, I designed oligosilanes with symmetric and rigid structures. Trisilane **14** was obtained by two-fold Si–Si coupling of dichlorosilane **13** with silylboronate **2i** (65% yield). Unfortunately, trisilane **14** was an oily compound. Subsequent chlorination of **14** followed by Si–Si coupling using **2d** afforded pentasilane **15** in 67% yield as a crystalline solid. The molecular structure of **15** was unequivocally determined by SC-XRD analysis (Figure 1). Furthermore, heptasilane **16** was synthesized from pentasilane **15** through chlorination and Si–Si coupling using silylboronate **7a** (83% yield). Due to its highly rigid structure, heptasilane **16** is also a crystalline solid, and its molecular structure was unambiguously confirmed using SC-XRD (Figure 1). Most notably, in their crystals, **15** and **16** adopt an *all-anti*-conformation, which is similar to that reported by Tamao in their customized synthesis of oligosilanes.[5d,e] These obtained molecular XRD images clearly show the stepwise extension of the Si chain via the present iterative synthesis.

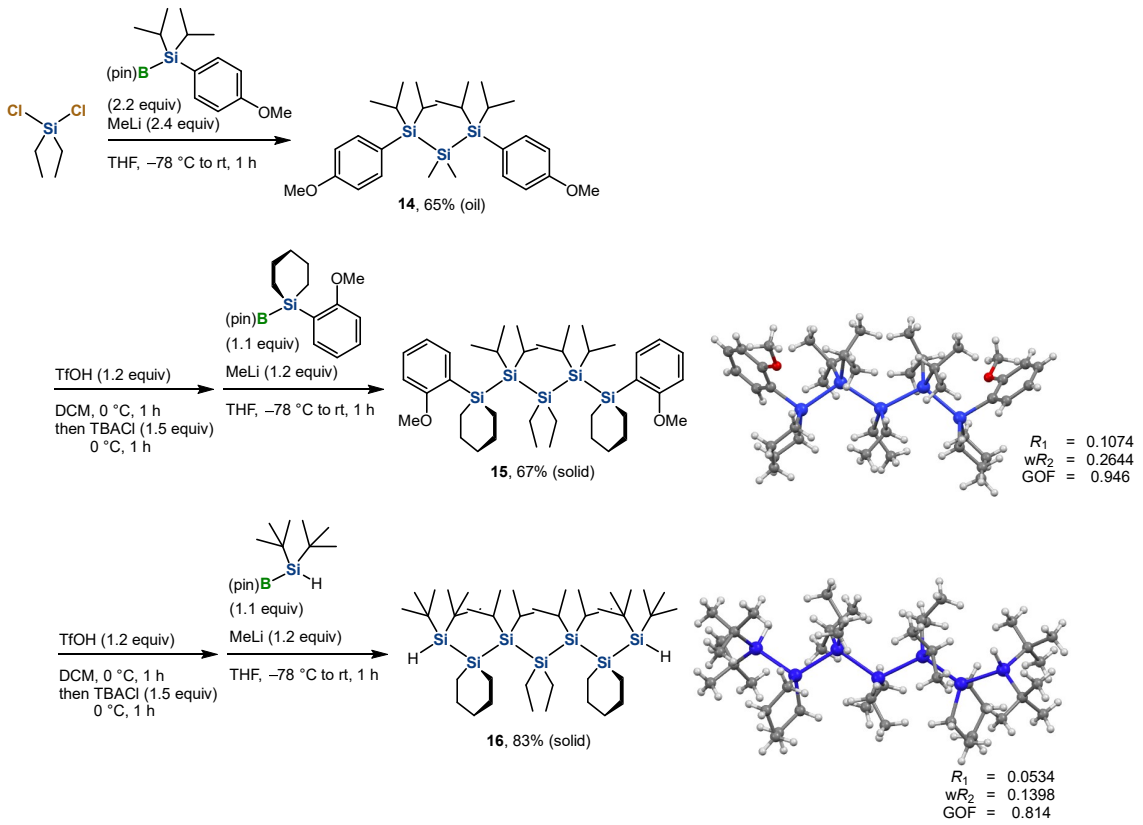


Figure 1. Iterative synthesis of crystalline oligosilanes and their structure in the solid state.

2.3: Conclusion

In summary, I developed the iterative synthesis of oli-gosilanes using methoxyphenyl- or hydrogen-substituted silyl-boronates. The corresponding silylluthium species were easily generated by the activation with MeLi, allowing the Si–Si coupling with chloro(oligo)silanes. The followed chlorination of a methoxyphenyl group or a hydrogen atom at the terminal of oligosilanes reproduced chlorosilane moiety for the next Si–Si coupling with silylboronates. By repeating these two reac-tions, various oligosilanes, including tree-shape oligosilanes and oligosilanes with different sequences, were easily ob-tained. The precise synthetic manner of the present iterative synthesis was clearly confirmed by single crystal X-ray diffraction analyses of oligosilanes.

2.4: References

(1) (a) Hiyama, T.; Oestreich, M. Organosilicon Chemistry: Novel Approaches and Reactions; John Wiley & Sons, 2020. (b) Scheschkewitz, D. *In Functional Molecular Silicon Compounds I, II*; Springer, 2014. (c) Brook M. A. Silicon in Organic, Organometallic, and Polymer Chemistry; Wiley-Interscience, 2000.

(2) For reviews on poly- and oligosilanes, see: (a) West, R. The Polysilane High Polymers. *J. Organomet. Chem.* **1986**, *300*, 327–346. (b) Miller, R. D.; Michl, J. Polysilane High Polymers. *Chem. Rev.* **1989**, *89*, 1359–1410. (c) Tsuji, H.; Michl, J.; Tamao, K. Recent Experimental and Theoretical Aspects of the Conformational Dependence of UV Absorption of Short Chain Peralkylated Oligosilanes. *J. Organomet. Chem.* **2003**, *685*, 9–14. (d) Karatsu, T. Photochemistry and Photophysics of Organomonosilane and Oligosilanes: Updating Their Studies on Conformation and Intramolecular Interactions. *J. Photochem. Photobiol., C* **2008**, *9*, 111–137. (e) Priegert, A. M.; Rawe, B. W.; Serin, S. C.; Gates, D. P. Polymers and the p-Block Elements. *Chem. Soc. Rev.* **2016**, *45*, 922–953. (f) Vidal, F.; Jäkle, F. Functional Polymeric Materials Based on Main-group Elements. *Angew. Chem., Int. Ed.* **2019**, *58*, 5846–5870. (g) Kumar, V. B.; Leitao, E. M. Properties and Applications of Polysilanes. *Appl. Organometal. Chem.* **2020**, *34*, e5402. (h) Marschner, C. Oligosilanes. In *Functional Molecular Silicon Compounds I: Regular Oxidation States*; Springer, 2014; pp 163–228. (i) Präsang, C.; Scheschkewitz, D. Silyl Anions, In *Functional Molecular Silicon Compounds II: Low Oxidation States*; Springer, 2014, pp 1–48.

(3) For reviews on silyl anions, see: (a) Lerner, H.-W. Silicon Derivatives of Group 1, 2, 11, 12 elements. *Coord. Chem. Rev.* **2005**, *249*, 781–798. (b) Sekiguchi, A.; Lee, V. Y.; Nanjo, M. Lithiosilanes and Their Application to the Synthesis of Polysilane Dendrimers. *Coord. Chem. Rev.* **2000**, *210*, 11–45. (c) Kawachi, A.; Tamao, K. Preparation and Reaction of Functionalized Silyllithiums. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 945–955.

(4) (a) Kipping, F. S.; Sands, J. E. XCIII.-Organic Derivatives of Silicon. Part XXV. Saturated and Unsaturated Silicohydrocarbons, Si_4Ph_8. *J. Chem. Soc., Trans.* **1921**, *119*, 830–847. (b) Kipping, F. S. CCCVIII.-Organic Derivatives of Silicon. Part XXX. Complex Silicohydrocarbons $[SiPh_2]_n$. *J. Chem. Soc., Trans.* **1924**, *125*, 2291–2297.

(5) For pioneering precise syntheses of designed oligosilanes reported by Tamao, see: (a) Kawachi, A.; Tamao, K. Mixed Reagent (aminosilyl)lithium/*i*-PrMgBr for the Synthesis of Functionalized Oligosilanes. *J. Organomet. Chem.* **2000**, *601*, 259–266. (b) Tamao, K.; Tsuji, H.; Terada, M.; Asahara, M.; Yamaguchi, S.; Toshimitsu, A. Conformation Control of Oligosilanes Based on Configurationally Constrained Bicyclic Disilane Units. *Angew. Chem., Int. Ed.* **2000**, *39*, 3287–3290. (c) Tsuji, H.; Terada, M.; Toshimitsu, A.; Tamao, K. σσ* Transition in *anti,cisoid* Alternating Oligosilanes: Clear-Cut Evidence for Suppression of Conjugation Effect by a *cisoid* Turn. *J. Am. Chem. Soc.* **2003**, *125*, 7486–7487. (d) Tsuji, H.; Fukazawa, A.; Yamaguchi, S.; Toshimitsu, A.; Tamao, K. *all-anti*-Pentasilane: Conformation Control of Oligosilanes Based on the Bis(tetramethylene)-Tethered Trisilane Unit. *Organometallics* **2004**, *23*, 3375–3377. (e) Fukazawa, A.; Tsuji, H.; Tamao, K. *all-anti*-Octasilane: Conformation Control of Silicon Chains Using the Bicyclic Trisilane as a Building Block. *J. Am. Chem. Soc.* **2006**, *128*, 6800–6801.

(6) For other reports on designed oligosilanes, see: (a) Marschner, C. Preparation and Reaction of Polysilanyl Anions and Dianions. *Organometallics* **2006**, *25*, 2110–2125. (b) Krempner, C.; Reinke, H. An Approach to Dendritic Oligosilanes: Controlling the Conformation through Ring Formation. *Organometallics* **2007**, *26*, 2053–2057. (c) Krempner, C.; Köckerling, M. Nanoscale Double-Core Oligosilane Dendrimers: Synthesis, Structure, and Electronic Properties. *Organometallics* **2008**, *27*, 346–352. (d) Wallner, A.; Wagner, H.; Baumgartner, J.; Marschner, C.; Rohm, H. W. Köckerling, M.; Krempner, C. Structure, Conformation and UV Absorption Behavior of Partially Trimethylsilylated Oligosilane Chains. *Organometallics* **2008**, *27*, 5221–5229. (e) Wallner, A.; Hlina, J.; Konopa, T.; Wagner, H.; Baumgartner, J.; Marschner, C.; Flörke, U. Cyclic and Bicyclic Methylpolysilanes and Some Oligosilanylene-Bridged Derivatives. *Organometallics* **2010**, *29*, 2660–2675. (f) Wallner, A.; Hlina, J.; Wagner, H.; Baumgartner, J.; Marschner, C. Conformational Control of Polysilanes: Use of CH_2 Spacer in the Silicon Backbone. *Organometallics* **2011**, *30*, 3930–3938. (g) Wagner, H.; Baumgartner, J.; Marschner, C.; Poelt, P. Rearrangement/Fragmentation Reactions of Oligosilanes with Aluminum Chloride. *Organometallics* **2011**, *30*, 3939–3954. (h) Iwamoto, T.; Tsushima, D.; Kwon, E.; Ishida, S.; Isobe, H. Persilastaffanes: design, synthesis, structure, and conjugation between silicon cages. *Angew. Chem., Int. Ed.* **2012**, *51*, 2340–2343. (i) Krempner, C. Polysilane Dendrimers. *Polymers* **2012**, *4*, 408–447. (j) Wallner, A.; Emanuelsson, R.; Baumgartner, J.; Marschner, C.; Ottosson, H. Coupling of Disilane and Trisilane Segments through Zero, One, Two, and Three Disilanyl Bridges in Cyclic and Bicyclic Saturated Carbosilanes. *Organometallics* **2013**, *32*, 396–405. k) Hlina, J.; Zitz, R.; Wagner, H.; Stella, F.; Baumgartner, J.; Marschner, C. σ-Bond Electron Delocalization of Branched Oligogermanes and Germanium Containing Oligosilanes. *Inorg. Chim. Acta* **2014**, *422*, 120–130. (l) Hlina, J.; Stella, F.; Meshgi, M. A.; Marschner, C.; Baumgartner, J. σ-Bond Electron Delocalization in Oligosilanes as Function of Substitution Pattern, Chain Length, and Spatial Orientation. *Molecules* **2016**, *21*, 1079–1103. (m) Press, E. M.; Marro, E. A.; Surampudi, S. K.; Siegler, M. A.; Tang, J. A.; Klausen, R. S. Synthesis of a Fragment of Crystalline Silicon: Poly(cyclosilane). *Angew. Chem., Int. Ed.* **2017**, *56*, 568–572. (n) Marro, E. A.; Press, E. M.; Siegler, M. A.; Klausen, R. S. Directional Building Blocks Determine Linear and Cyclic Silicon Architectures. *J. Am. Chem. Soc.* **2018**, *140*, 5976–5986. (o) Marro, E. A.; Folster, C. P.; Press, E. M.; Im, H.; Ferguson, J. T.; Siegler, M. A.; Klausen, R. S. Stereocontrolled Synthesis of Functionalized cis- and trans-Siladecalins. *J. Am. Chem. Soc.* **2019**, *141*, 17926–17936. (p) Marro, E. A.; Klausen, R. S. Conjugated Polymers Inspired by Crystalline Silicon. *Chem. Mater.* **2019**, *31*, 2202–2211. (q) Ballestero-Martínez, E.; Ferguson, J. T.; Siegler, M. A.; Klausen, R. S. Isolation of a Cyclopentasilane from Magnesium Reduction of a Linear Hexasilane. *Eur. J. Org. Chem.* **2021**, *2021*, 4641–4646.

(7) For reviews on iterative synthesis, see: (a) Feuerbacher, N.; Vögtle, F. Iterative Synthesis in Organic Chemistry. *Top. Curr. Chem.* Springer, **1998**, *197*. (b) Wang, C.; Glorius, F. Controlled Iterative Cross-Coupling: On the Way to the Automation of Organic Synthesis. *Angew. Chem., Int. Ed.*

2009, *48*, 5240–5244. (b) Lehmann, J. W.; Blair, D. J.; Burke, M. D. Toward the Generalized Iterative Synthesis of Small Molecules. *Nat. Rev. Chem.* **2018**, *2*, 0115.

(8) For iterative syntheses in nature, see: Garrett, R. H.; Grisham, C. M. Biochemistry. Saunders College Publishing, Philadelphia. **1995**.

(9) For selected examples of iterative synthesis in the laboratory, see: (a) Hanessian, S.; Yang, Y.; Giroux, S.; Mascitti, V.; Ma, J.; Raeppel, F. Application of Conformation Design in Acyclic Stereoselection: Total Synthesis of Borrelidin as the Crystalline Benzene Solvate. *J. Am. Chem. Soc.* **2003**, *125*, 13784–13792. (b) Hanessian, S.; Giroux, S.; Mascitti, V. The Iterative Synthesis of Acyclic Deoxypropionate Units and Their Implication in Polyketide-Derived Natural Products. *Synthesis* **2006**, 1057–1076. (c) ter Horst, B.; Feringa, B. L.; Minnaard, A. J. Catalytic Asymmetric Synthesis of Phthioceranic Acid, a Heptamethyl-Branched Acid from Mycobacterium Tuberculosis. *Org. Lett.* **2007**, *9*, 3013–3015. (d) ter Horst, B.; Feringa, B. L.; Minnaard, A. J. Iterative Strategies for the Synthesis of Deoxypropionates *Chem. Commun.* **2010**, *46*, 2535–2547. (e) Negishi, E.-i.; Tan, Z.; Liang, B.; Novak, T. An Efficient and General Route to Reduced Polypropionates via Zr-Catalyzed Asymmetric C–C Bond Formation *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 5782–5787. (f) Brand, G. J.; Studte, C.; Breit, B. Iterative Synthesis of (Oligo)deoxypropionates via Zinc-Catalyzed Enantiospecific sp^3–sp^3 Cross-Coupling *Org. Lett.* **2009**, *11*, 4668–4670. (g) Han, S. B.; Hassen, A.; Kim, I. S.; Krische, M. J. Total Synthesis of (+)-Roxaticin via C–C Bond Forming Transfer Hydrogenation: A Departure from Stoichiometric Chiral Reagents, Auxiliaries, and Premetalated Nucleophiles in Polyketide Construction. *J. Am. Chem. Soc.* **2010**, *132*, 15559–15561. (h) Gillis, E. P.; Burke, M. D. A Simple and Modular Strategy for Small Molecular Synthesis: Iterative Suzuki–Miyaura Coupling of B-Protected Haloboronic Acid Building Blocks. *J. Am. Chem. Soc.* **2007**, *129*, 6716–6717. (i) Lee, S. J.; Gray, K. C.; Peak, J. S.; Burke, M. D. Simple, Efficient, and Modular Synthesis of Polyene Natural Products via Iterative Cross-Coupling. *J. Am. Chem. Soc.* **2008**, *130*, 466–468. (j) Woerly, E. M.; Roy, J.; Burke, M. D. Synthesis of Most Polyene Natural Product Motifs Using Just 12 Building Blocks and One Coupling Reaction. *Nat. Chem.* **2014**, *6*, 484–491. (k) Balieu, S.; Hallett, G. E.; Burns, M.; Bootwicha, T.; Studley, J.; Aggarwal, V. K. Toward Ideality: The Synthesis of (+)-Kalkitoxin and (+)-Hydroxyphthioceranic Acid by Assembly-Line Synthesis. *J. Am. Chem. Soc.* **2015**, *137*, 4398–4403. (l) Xie, Q.; Dong, G. Programmable Ether Synthesis Enabled by Oxa-Matteson Reaction. *J. Am. Chem. Soc.* **2022**, *144*, 8498–8503.

(10) Ishifune, M.; Kashimura, S.; Kogai, Y.; Fukuhara, Y.; Kato, T.; Bu, H.-B.; Yamashita, N.; Murai, Y.; Murase, H.; Nishida, R. Electroreductive Synthesis of Oligosilanes and Polysilanes with Ordered Sequences. *J. Organomet. Chem.* **2000**, *611*, 26–31.

(11) Shibano, Y.; Sasaki, M.; Tsuji, H.; Araki, Y.; Ito, O, Tamao, K. Conformation Effect of Oligosilane Linker on Photoinduced Electron Transfer of Tetrasilane-Linked Zinc Porphyrin-[60]Fullerene Dyads. *J. Organomet. Chem.* **2007**, *692*, 356–367.

(12) (a) Klausen, R. S.; Widawsky, J. R.; Steigerwald, M. L.; Venkataraman, L.; Nuckolls, C. Conductive Molecular Silicon. *J. Am. Chem. Soc*. **2012**, *134*, 4541–4544. (b) Su, T. A.; Li, H.; Steigerwald, M. L.; Venkataraman, L.; Nuckolls, C. Stereoelectronic Switching in Single-Molecule Junctions. *Nat. Chem*. **2015**, *7*, 215–220.

(13) The iterative synthesis of siloxanes has already been reported; for details, see: Matsumoto, K.; Shimada, S.; Sato, K. Sequence-Controlled Catalytic One-Pot Synthesis of Siloxane Oligomers. *Chem. – Eur. J.* **2019**, *25* (4), 920–928.

(14) (a) Rahman, N. A.; Fleming, I; Zwicky, A. B. Failure in Several Attempts to Prepare Arylsilyl-lithium Reagents by the Gilman Cleavage of Disilanes with Lithium. *J. Chem. Res*., *Miniprint* **1992**, 2401–2409. (b) Lee, T. W. Corey, E. J. (2-Methoxyphenyl)dimethylsilyl Lithium and Cuprate Reagents Offer Unique Advantages in Multistep Synthesis. *Org. Lett*. **2001**, *3*, 3337–3339.

(15) (a) Suginome, M.; Nakamura, H.; Ito, Y. Regio- and Stereo-selective Silaboration of Alkynes catalyzed by Palladium and Platinum Complexes. *Chem. Commun*. **1996**, 2777–2778. (b) Suginome, M.; Matsuda, T.; Ito, Y. Convenient Preparation of Silylboranes. *Organometallics* **2000**, *19*, 4647–4649. (c) Ohmura, T.; Matsuda, K.; Furukawa, H.; Suginome, M. Synthesis of Silylboronic Esters Functionalized on Silicon. *Organometallics* **2007**, *26*, 1291–1294.

(16) (a) Hiyama, T.; Oestreich, M. Organosilicon Chemistry: Novel approaches and Reactions. Wiley-VCH, Weinheim, 2020. (b) Brook, M. A. Silicon in Organic Organometallics, and Polymer Chemistry. Wiley-Interscience Publication 2000. (c) Cuenca, A. B.; Shishido, R.; Ito, H.; Fernández, E. Transition-Metal-Free B–B and B–interelement reactions with Organic Molecules. *Chem. Soc. Rev*. **2017**, *46*, 415–430.

(17) (a) Oestreich, M.; Hartmann, E.; Mewald, M. Activation of the Si–B Interelement Bond: Mechanism, Catalysis, and Synthesis. *Chem. Rev.* **2013**, *113*, 402–441. (b) Ohmura, T.; Suginome, M. Silylboronates as New Tools in Organic Synthesis. *Bull. Chem. Soc. Jpn*. **2009**, *82*, 29–49. (c) Xue, W.; Oestreich, M. Beyond Carbon: Enantioselective and Enantiospecific Reactions with Catalytically Generated Boryl- and Silylcopper Intermediates. *ACS Cent. Sci*. **2020**, *6*, 1070–1081. (d) Feng, J.-J.; Mao, W.; Zhang, L.; Oestreich, M. Activation of the Si–B Interelement Bond Related to Catalysis. *Chem. Soc. Rev*. **2021**, *50*, 2010–2073.

(18) (a) Kawachi, A.; Minamimoto, T.; Tamao, K. Boron–Metal Exchange Reaction of Silylboranes with Organometallic Reagents: A New Route to Arylsilyl Anions. *Chem. Lett*. **2001**, *30*, 1216–1217. (b) Kajiwara, T.; Takeda, N.; Sasamori, T.; Tokitoh N. Synthesis of Alkali Metal Salts of Borylsilyl Anions Utilizing Highly Crowded Silylboranes and Their Properties. *Organometallics* **2008**, *27*, 880–893.

(19) Boebel, T. A.; Hartwig, J. F. Iridium-Catalyzed Preparation of Silylboranes by Silane Borylation and Their Use in the Catalytic Borylation of Arenes. *Organometallics* **2008**, *27*, 6013–6019.

(20) Shishido, R.; Uesugi, M.; Takahashi, R.; Mita, T.; Ishiyama, T.; Kubota, K.; Ito, H. General Synthesis of Trialkyl- and Dialkylarylsilylboranes: Versatile Silicon Nucleophiles in Organic Synthesis. *J. Am. Chem. Soc.* **2020**, *142*, 14125–14133.

(21) Takeuchi, T.; Shishido, R.; Kubota, K.; Ito, H. Synthesis of Hydrosilylboronates via the Monoborylation of a Dihydrosilane Si–H Bond and Their Application for the Generation of Dialkylhydrosilyl Anions. *Chem. Sci*. **2021**, *12*, 11799–11804.

(22) Yamamoto, E.; Shishido, R.; Seki, T.; Ito, H. Tris(trimethylsilyl)silylboronates Ester: Novel Bulky, Air-and Moisture-Stable Silylboronate Ester Reagents for Boryl Substitution Reactions. *Organometallics* **2017**, *36*, 3019–3022.

(23) (a) Gilman, H.; Marshall, F. J. Cleavage of Some Organosilanes by Hydrogen Chloride. *J. Am. Chem. Soc*. **1949**, *71*, 2066–2069. (b) Benkeser, R. A.; Krysiak, H. R. The Hydrogen Chloride Cleavage of Some Trimethylarylsilanes. *J. Am. Chem. Soc*. **1953**, *75*, 4528–4531. (c) Uhlig, W. Silyl Triflates – Valuable Synthetic Materials in Organosilicon Chemistry. *Chem. Ber*. **1996**, *129*, 733–739. (d) Popp, F.; Nätscher, J. B.; Daiss, J. O.; Burschka, C.; Tacke, R. The 2,4,6-Trimethoxyphenyl Unit as a Unique Protecting Group for Silicon in Synthesis and the Silylation Potential of (2,4,6-Trimethoxyphenyl)silanes. *Organometallics* **2007**, *26*, 6014–6028.

(24) (a) Voorhoeve, R. J. H. Organohalosilanes Precursors to Silicones. Elsevier Publishing Company, **1967**. (b) Uchida, H.; Kabe, Y.; Yoshino, K.; Kawamata, A.; Tsumuraya, T.; Masamune, S. General Strategy for the Systematic Synthesis of Oligosiloxanes. Shilicone Dendrimers. *J. Am. Chem. Soc*. **1990**, *112*, 7077–7079. (c) Esteruelas, M. A.; Herrero, J.; Oliván, M. Dehalogenation of Hexachlorocyclohexanes and Simultaneous Chlorination of Triethylsilane Catalyzed by Rhodium and Ruthenium Complexes. *Organometallics* **2004**, *23*, 389–3897. (d) Varaprath, S.; Stutts, D. H. Utility of Trichloroisocyanuric Acid in the Efficient Chlorination of Silicon Hydrides. *J. Organomet. Chem.* **2007**, *692*, 1892–1897.

(25) Chanteau, S. H.; Tour, J. M. Synthesis of Anthropomorphic Molecules: The NanoPutians. *J. Org. Chem.* **2003**, *68*, 8750–8766.

2.5: Experimental Details

Instrumentation and Chemicals

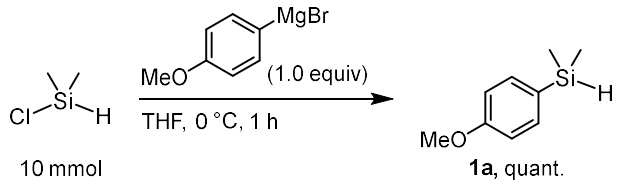
All reactions were performed in oven-dried glassware using conventional Schlenk techniques under a static pressure of nitrogen. Materials were obtained from commercial suppliers and used as received unless otherwise noted. Bis(pinacolato)diboron was recrystallized from pentane before use. Dry solvents for the reactions were purchased from commercial suppliers, degassed via three freeze-pump-thaw cycles, and dried over molecular sieves (MS4A) before use. Silica Gel 60 N (40–100 μm, spherical, neutral) purchased from Kanto Chemical Co. was used as received. GLC analyses were conducted with a Shimadzu GC-2014 or GC-2025 equipped with ULBON HR-1 glass capillary

column (Shinwa Chemical Industries) and an FID detector. Recycle preparative gel chromatography (GPC) was conducted with JAILC-9101 using $CHCl_3$ as an eluent. NMR spectra were recorded on JEOL JNM-ECX400P and ECS-400 (^{1}H: 400 MHz, ^{13}C: 100 MHz, ^{11}B: 126 MHz, ^{29}Si: 79.5 MHz) and JNM-ECA600 (^{1}H: 600 MHz, ^{13}C: 150 MHz, ^{29}Si: 119 MHz). $CDCl_3$ (δ = 7.26 ppm for ^{1}H-NMR and δ = 77.0 ppm for ^{13}C-NMR) and $SiMe_4$ (δ = 0.00 ppm for ^{29}Si-NMR) were employed as internal standards, respectively. $BF_3{\cdot}OEt_2$ (δ = 0.00 ppm for ^{11}B-NMR) was employed as an external standard. Multiplicity was reported as follows: s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, sext = sextet, and m = multiplet. High-resolution mass spectra were recorded at the Global Facility Center for Instrumental Analysis in Hokkaido University and GC-MS & NMR Lab., Research Faculty of Agriculture in Hokkaido University. Single crystal X-ray structural analyses were carried out on a Rigaku XtaLAB AFC11 (RCD3) and XtaLAB PRO MM007 diffractometer using graphite monochromated Mo-Kα or Cu- Kα 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.

Preparation of substrates

Grignard reagents were purchased from commercial suppliers (TCI and Sigma-Aldrich) or prepared by reaction between magnesium and the corresponding halides.[1]

Preparation of 1a

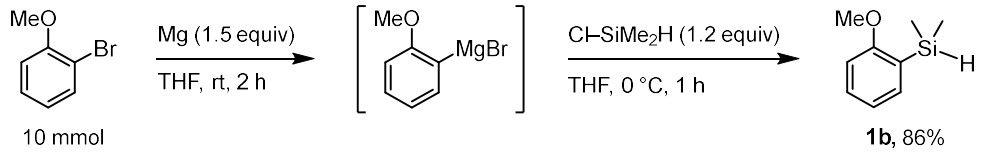


This reaction was performed according to the literature procedure.[2] 4-Methoxyphenylmagnesium bromide (1.0 M, 10 mL, 1.0 equiv) was added dropwise to dimethylchlorosilane (1.1 mL, 10.0 mmol) in THF (20 mL) at 0 °C under nitrogen atmosphere. After stirring for 1 hour, the reaction was quenched with water and extracted with hexane three times. The combined organic layer was washed with brine and dried over $MgSO_4$. Then, the resulting solution was filtered off and evaporated. The resulting crude oil was purified by silica-gel column chromatography with hexane/EtOAc (100:0 to 95:5) as an eluent to afford the corresponding product **1a** (1.67 g, 10.0 mmol, quantitative yield) as a colorless oil.

^{1}H NMR (399 MHz, $CDCl_3$, δ): 0.32 (d, J = 4.0 Hz, 6H), 3.82 (s, 3H), 4.40 (sept, J = 3.7 Hz, 1H), 6.92 (m, 2H), 7.47 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): –3.55 (CH_3), 55.0 (CH_3), 113.6 (*C*H), 128.2 (*C*), 135.4 (*C*H), 160.5 (*C*). HRMS-EI (m/z): $[M]^+$ calcd for $C_9H_{14}OSi$, 166.0814; found

166.0808.

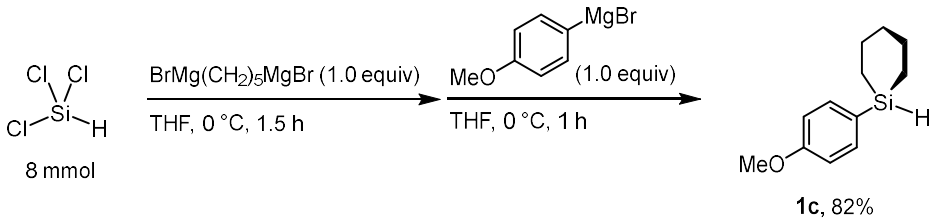
Preparation of 1b



2-Bromomethoxybenzene (1.90 g, 10 mmol) was added dropwise to magnesium (366 mg, 15 mmol, 1.5 equiv) in THF (10 mL) at room temperature under nitrogen atmosphere. After stirring for 2 hours, the Grignard reagent was added dropwise to the solution of chlorodimethylsilane (1.35 mL, 12 mmol, 1.2 equiv) in THF (10 mL) at 0 °C. After stirring for 1 hour, the reaction was quenched with water and extracted with hexane three times. The combined organic layer was washed with brine and dried over $MgSO_4$. Then, the resulting solution was filtered off and evaporated. The resulting crude oil was purified by silica-gel column chromatography with hexane/EtOAc (100:0 to 90:10) as an eluent to afford the corresponding product **1b** (1.45 g, 8.74 mmol, 86% yield) as a colorless oil.

^{1}H NMR (401 MHz, $CDCl_3$, δ): 0.33 (d, J = 3.6 Hz, 6H), 3.82 (s, 3H), 4.40 (sept, J = 3.7 Hz, 1H), 6.84 (d, J = 8.4 Hz, 1H), 6.96 (t, J = 8.4 Hz, 1H), 7.37 (td, J = 1.7, 7.8 Hz, 1H), 7.43 (dd, J = 1.8, 7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): –3.85 (CH_3), 55.1 (CH_3), 109.4 (*C*H), 120.5 (*C*H), 125.4 (*C*) 131.1 (*C*H), 135.7 (*C*H), 164.2 (*C*). HRMS-EI (m/z): $[M]^+$ calcd for $C_9H_{14}OSi$, 166.0814; found 166.0810.

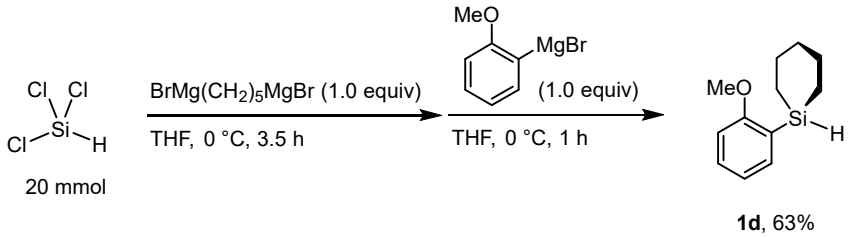
Preparation of 1c



This reaction was performed according to the literature procedure.[3] Pentamethylenebis(magnesiumbromide) (0.5 M, 16 mL, 1.0 equiv) was added dropwise to trichlorosilane (0.8 mL, 8.0 mmol) in THF (20 mL) at 0 °C under nitrogen atmosphere. After stirring for 1.5 hours, 4-methoxyphenylmagnesium bromide (1.0 M, 8.0 mL, 1.0 equiv) was added to the reaction mixture. After stirring for 1 h, the reaction was quenched with water and extracted with hexane three times. The combined organic layer was washed with brine and dried over $MgSO_4$. Then, the resulting solution was filtered off and evaporated. The resulting crude oil was purified by silica-gel column chromatography with hexane/EtOAc (100:0 to 90:10) as an eluent to afford the corresponding product **1c** (1.36 g, 6.57 mmol, 82% yield) as a colorless oil.

^{1}H NMR (399 MHz, $CDCl_3$, δ): 0.79–0.89 (m, 2H), 0.99–1.09 (m, 2H), 1.28–1.42 (m, 1H), 1.56–1.72 (m, 3H), 1.83–1.94 (m, 2H), 3.82 (s, 3H), 4.32 (t, J = 5.2 Hz, 1H), 6.92 (m, 2H), 7.49 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 10.8 (CH_2), 24.8 (CH_2), 29.8 (CH_2), 55.0 (CH_3), 113.7 (*C*H), 126.7 (*C*), 135.8 (*C*H), 160.6 (*C*). HRMS-EI (m/z): $[M]^+$ calcd for $C_{12}H_{18}OSi$, 206.1127; found 206.1120.

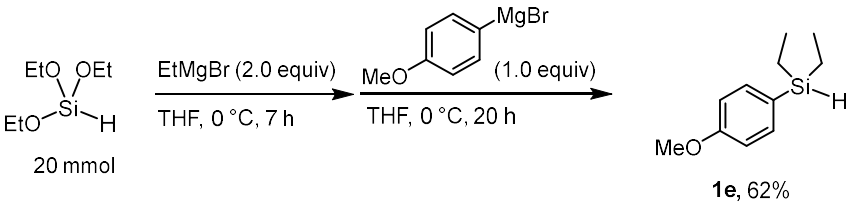
Preparation of 1d



This reaction was performed according to the literature procedure.[3] Pentamethylenebis(magnesiumbromide) (0.5 M, 40 mL, 1.0 equiv) was added dropwise to trichlorosilane (2.0 mL, 20 mmol) in THF (50 mL) at 0 °C under nitrogen atmosphere. After stirring for 3.5 hours, 2-methoxyphenylmagnesium bromide (1.0 M, 20 mL, 1.0 equiv) was added to the reaction mixture. After stirring for 1 h, the reaction was quenched with water and extracted with hexane three times. The combined organic layer was washed with brine and dried over $MgSO_4$. Then, the resulting solution was filtered off and evaporated. The resulting crude oil was purified by silica-gel column chromatography with hexane/EtOAc (100:0 to 98:2) as an eluent to afford the corresponding product **1d** (2.58 g, 12.5 mmol, 63% yield) as a colorless oil.

^{1}H NMR (399 MHz, $CDCl_3$, δ): 0.88–0.99 (m, 2H), 1.02–1.13 (m, 2H), 1.22–1.40 (m, 1H), 1.58–1.71 (m, 3H), 1.86–2.00 (m, 2H), 3.82 (s, 3H), 4.32 (tt, J = 1.2, 5.5 Hz, 1H), 6.84 (d, J = 8.4 Hz, 1H), 6.96 (t, J = 7.4 Hz, 1H), 7.36 (ddd, J = 1.7, 7.3, 8.1 Hz, 1H), 7.42 (dd, J = 2.0, 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 10.4 (CH_2), 25.1 (CH_2), 29.8 (CH_2), 55.2 (CH_3), 109.4 (*C*H), 120.5 (*C*H), 123.8 (*C*), 131.2 (*C*H), 136.0 (*C*H), 164.4 (*C*). HRMS-EI (m/z): $[M]^+$ calcd for $C_{12}H_{18}OSi$, 206.1127; found 206.1123.

Preparation of 1e

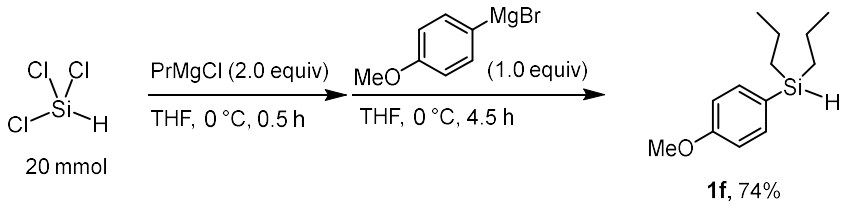


Ethylmagnesium bromide (3 M, 13.5 mL, 2.0 equiv) was added dropwise to triethoxysilane (3.38 mg, 20 mmol) in THF (40 mL) at 0 °C under nitrogen atmosphere. After stirring for 7 hours, 4-methoxyphenylmagnesium bromide (1.0 M, 20 mL, 1.0 equiv) was added to the reaction mixture.

After stirring for 20 h, the reaction was quenched with water and extracted with hexane three times. The combined organic layer was washed with brine and dried over $MgSO_4$. Then, the resulting solution was filtered off and evaporated. The resulting crude oil was purified by distillation (31 Pa, bath temp.: 90 °C) to afford the corresponding product **1e** (2.49 g, 12.8 mmol, 62% yield) as a colorless oil.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.78–0.87 (m, 4H), 1.01 (t, J = 7.8 Hz, 6H), 3.83 (s, 3H), 4.19 (quint, J = 3.3 Hz, 1H), 6.93 (d, J = 8.6 Hz, 2H), 7.47 (dt, J = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 3.62 (CH_2), 8.07 (CH_3), 54.8 (CH_3), 113.6 (*C*H), 126.1 (*C*), 136.0 (*C*H), 160.5 (*C*). HRMS-EI (m/z): $[M]^+$ calcd for $C_{11}H_{18}OSi$, 194.1127; found 194.1121.

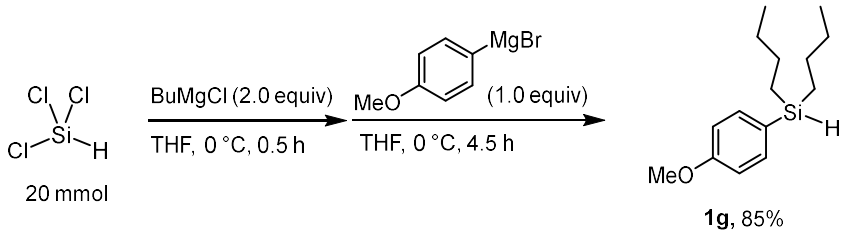
Preparation of 1f



Propylmagnesium chloride (2.0 M, 20 mL, 2.0 equiv) was added dropwise to trichlorosilane (2.0 mL, 20 mmol) in THF (40 mL) at 0 °C under nitrogen atmosphere. After stirring for 0.5 hours at room temperature, 4-methoxyphenylmagnesium bromide (1.0 M, 20 mL, 1.0 equiv) was added to the reaction mixture. After stirring for 4.5 hours at room temperature, the reaction was quenched with water and extracted with Et_2O three times. The combined organic layer was washed with brine and dried over $MgSO_4$. Then, the resulting solution was filtered off and evaporated. The resulting crude oil was purified by distillation (41 Pa, bath temp.: 140 °C) to afford the corresponding product **1f** (3.29 g, 14.8 mmol, 74% yield) as a colorless oil.

^{1}H NMR (401 MHz, $CDCl_3$, δ): 0.79–0.87 (m, 4H), 0.97 (t, J = 7.0 Hz, 6H), 1.42 (sext, J = 7.5 Hz, 4H), 3.82 (s, 3H), 4.23, (quint, J = 3.5 Hz, 1H), 6.92 (d, J = 8.8 Hz, 2H), 7.46 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 14.7 (CH_2), 17.9 (CH_3), 18.0 (CH_2), 55.0 (CH_3), 113.6 (*C*H), 126.7 (*C*), 136.0 (*C*H), 160.4 (*C*). HRMS-EI (m/z): $[M]^+$ calcd for $C_{13}H_{22}OSi$, 222.1440; found 222.1430.

Preparation of 1g

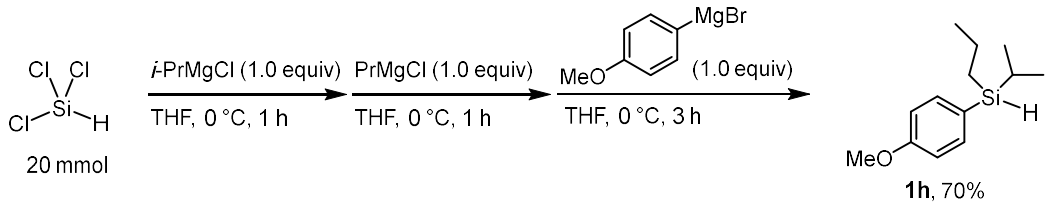


Butylmagnesium chloride (2.0 M, 20 mL, 2.0 equiv) was added dropwise to trichlorosilane (2.0 mL, 20 mmol) in THF (40 mL) at 0 °C under nitrogen atmosphere. After stirring for 0.5 hours at room

temperature, 4-methoxyphenylmagnesium bromide (1.0 M, 20 mL, 1.0 equiv) was added to the reaction mixture. After stirring for 4.5 hours at room temperature, the reaction was quenched with water and extracted with Et_2O three times. The combined organic layer was washed with brine and dried over $MgSO_4$. Then, the resulting solution was filtered off and evaporated. The resulting crude oil was purified by distillation (37 Pa, bath temp.: 135 °C) to afford the corresponding product **1g** (4.24 g, 16.9 mmol, 85% yield) as a colorless oil.

^{1}H NMR (401 MHz, $CDCl_3$, δ): 0.78–0.96 (m, 10H), 1.27–1.45 (m, 8H), 3.83 (s, 3H), 4.24 (quint, J = 3.4 Hz, 1H), 6.92 (d, J = 8.8 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 11.9 (CH_2), 13.8 (CH_3), 26.2 (CH_2), 26.7 (CH_2), 55.0 (CH_3), 113.6 (*C*H), 126.8 (*C*), 136.0 (*C*H), 160.4 (*C*). HRMS-EI (m/z): $[M]^+$ calcd for $C_{15}H_{26}OSi$, 250.1753; found 250.1745.

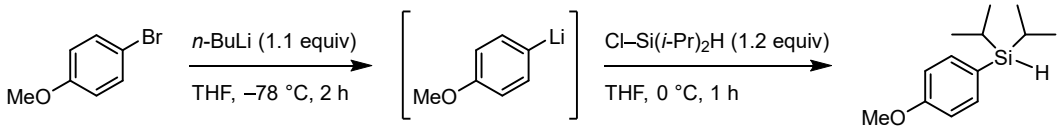
Preparation of 1h



2-Propylmagnesium chloride (2.0 M, 10 mL, 1.0 equiv) was added dropwise to trichlorosilane (2.0 mL, 20 mmol) in THF (40 mL) at 0 °C under nitrogen atmosphere. After stirring for 1 hour, propylmagnesium chloride (2.0 M, 10 mL, 1.0 equiv) was added dropwise at 0 °C. After stirring for 1 hour, 4-methoxyphenylmagnesium bromide (1.0 M, 20 mL, 1.0 equiv) was added to the reaction mixture. After stirring for 3 hours, the reaction was quenched with water and extracted with hexane three times. The combined organic layer was washed with brine and dried over $MgSO_4$. Then, the resulting solution was filtered off and evaporated. The resulting crude oil was purified by distillation (33 Pa, bath temp.: 140 °C) to afford the corresponding product **1h** (3.13 g, 14.1 mmol, 70% yield) as a colorless oil.

^{1}H NMR (401 MHz, $CDCl_3$, δ): 0.82–0.89 (m, 2H), 0.93–1.14 (m, 10H), 1.42 (sext, J = 7.5 Hz, 2H), 3.82 (s, 3H), 4.10 (q, J = 3.2 Hz, 1H), 6.92 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 12.0 (*C*H), 12.9 (CH_2), 17.9 (CH_3), 18.2 (CH_2), 18.31 (CH_3), 18.34 (CH_3), 54.9 (CH_3), 113.5 (*C*H), 125.8 (*C*), 136.4 (*C*H), 160.5 (*C*H). HRMS-EI (m/z): $[M]^+$ calcd for $C_9H_{14}OSi$, 222.1440; found 222.1433.

Preparation of 1i



10 mmol

1i, 89%

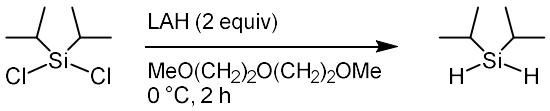
n-Butyllithium (1.6 M, 7.0 mL, 1.1 equiv) was added to the solution of 4-methoxyphenylbromide (1.82 g, 10 mmol) in THF (25 mL) at –78 °C under nitrogen atmosphere. After stirring for 2 hours, chlorodi(2-propyl)silane (2.2 mL, 1.3 equiv) was added dropwise. Then, the reaction mixture was allowed to warm to room temperature and stirred for 2 hours. The reaction was quenched with saturated NH_4Cl aqueous solution and extracted with Et_2O three times. The combined organic layer was washed with brine and dried over $MgSO_4$. Then, the resulting solution was filtered off and evaporated. The resulting crude oil was purified by silica-gel column chromatography with hexane/EtOAc (100:0 to 98:2) as an eluent to afford the corresponding product **1i** (1.93 g, 8.68 mmol, 89% yield) as a colorless oil.

^{1}H NMR (401 MHz, $CDCl_3$, δ): 0.98 (d, J = 7.2 Hz, 6H), 1.05 (d, J = 7.2 Hz, 6H), 1.20 (m, 2H), 3.82 (s, 3H), 3.91 (t, J = 3.2 Hz, 1H), 6.91 (d, J = 8.8 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 10.8 (*C*H), 18.4 (*C*H_3), 18.7 (*C*H_3), 54.9 (*C*H_3), 113.4 (*C*H), 124.8 (*C*), 136.8 (*C*H), 160.4 (*C*). HRMS-EI (m/z): $[M]^+$ calcd for $C_9H_{14}OSi$, 222.1440; found 222.1433.

Preparation of Dihydrosilanes

Dihydrosilanes for preparations of **7a**, **7b** and **7c** were prepared by the reported procedures.[4]

Preparation of S1



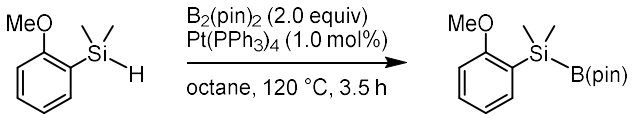
50 mmol

S1, 56%

Dichlorodi(2-propyl)silane (9 mL, 50 mmol) was added to the suspension of LAH (3.80 mg, 2 equiv) in diethyl glycol dimethyl ether (50 mL) at 0 °C under nitrogen atmosphere. After stirring for 2 hours, the corresponding product **S1** was directly distilled (24 hPa, bath temp.; 40 °C) from the reaction mixture (3.27 g, 28.1 mmol, 56%). The spectroscopic data of **S1** was consistent with literature values.[5]

Synthesis and Characterization of Silylboronates (2a–i and 7a–c)

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

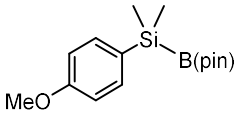


1b (1 mmol) **2b**, 61%

This reaction was performed according to our previous report.[6] Bis(pinacolato)diboron (513.5 mg, 2.0 mmol, 2.0 equiv) and tetrakis(triphenylphosphine)platinum (24.8 mg, 0.020 mmol, 2 mol%) were placed in a vial. After the vial was sealed with a screw cap containing a Teflon®-coated rubber septum, the vial was connected to a vacuum/nitrogen manifold through a needle. It was evacuated and then backfilled with nitrogen. This cycle was repeated three times. Then, *n*-octane (1.0 mL) and hydrosilane **1b** (166 mg, 1.0 mmol) were sequentially added to the vial via syringes. The resulting mixture was allowed to warm at 120 °C. After the reaction was completed, the mixture was directly filtered through a silica-gel pad with Et_2O as an eluent. Then, the resulting solution was concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography with hexane/EtOAc (100:0 to 96:4) as an eluent to afford the corresponding product **2b** (177.3 mg, 0.61 mmol, 61% yield) as a colorless oil. This compound is solidified in a freezer (–30 °C).

^{1}H NMR (396 MHz, $CDCl_3$, δ): 0.30 (s, 6H), 1.24 (s, 12H), 3.78 (s, 3H), 6.79 (d, J = 6.8 Hz, 1H), 6.94 (t, J = 7.1 Hz, 1H), 7.29–7.35 (m, 1H), 7.43 (dd, J = 1.6, 7.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): –3.64 (*C*H$_3$), 24.9 (*C*H$_3$), 54.9 (*C*H$_3$), 83.0 (*C*), 109.1 (*C*H), 120.4 (*C*H), 126.9 (*C*), 130.4 (*C*H), 135.3 (*C*H), 163.9 (*C*). ^{11}B{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 34.8 (brs). The signal derived from the silicon directly attached to the boron atom was not detected by ^{29}Si{^{1}H} NMR, which is likely due to quadrupolar relaxation. HRMS-EI (m/z): [M–Me]$^+$ calcd for $C_{14}H_{22}{}^{11}BO_3Si$, 277.1431; found 277.1434.

(4-Methoxyphenyl)dimethyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (2a).



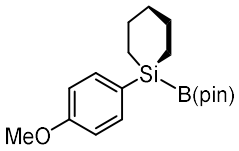
2a

The reaction was conducted with 167.4 mg (1.0 mmol) of **1a** according to the procedure for the synthesis of **2b**. The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 92:8) as an eluent to afford the corresponding silylboronate **2a** in 20% isolated yield (58.2 mg, 0.20 mmol) as a colorless oil.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.30 (s, 6H), 1.24 (s, 12H), 3.80 (s, 3H), 6.90 (d, J = 8.2 Hz, 2H), 7.50 (d, J = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): –2.91 (*C*H$_3$), 24.9 (*C*H$_3$), 54.8 (*C*H$_3$), 83.3 (*C*), 113.5 (*C*), 129.7 (*C*), 135.5 (*C*H), 160.1 (*C*). ^{11}B{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 34.4 (brs). The signal derived from the silicon directly attached to the boron atom was not detected by ^{29}Si{^{1}H} NMR, which is likely due to quadrupolar relaxation. HRMS-EI (m/z): [M–Me]$^+$ calcd for $C_{14}H_{22}{}^{11}BO_3Si$,

277.1431; found 277.1430.

1-(4-Methoxyphenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silinane (2c).

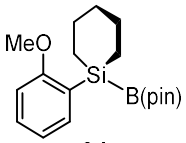


2c

The reaction was conducted with 208.3 mg (1.0 mmol) of **1c** according to the procedure for the synthesis of **2b**. The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 98:2) as an eluent to afford the corresponding silylboronate **2c** in 36% isolated yield (121.8 mg, 0.37 mmol) as a white solid.

^{1}H NMR (399 MHz, $CDCl_3$, δ): 0.83 (ddd, J = 4.1, 10.5, 13.5 Hz, 2H), 1.00–1.10 (m, 2H), 1.21–1.37 (m, 2H), 1.25 (s, 12H), 1.54–1.69 (m, 2H), 1.82–1.92 (m, 2H), 3.80 (s, 3H), 6.89 (dt, J = 2.2, 9.0 Hz, 2H), 7.50 (dt, J = 2.1, 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 11.4 (CH_2), 25.0 (CH_3), 25.04 (CH_2), 30.0 (CH_2), 55.0 (CH_3), 83.2 (C), 113.5 (CH), 128.2 (C), 135.9 (CH), 160.1 (C). ^{11}B{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 34.5 (brs). The signal derived from the silicon directly attached to the boron atom was not detected by ^{29}Si{^{1}H} NMR, which is likely due to quadrupolar relaxation. HRMS-EI (m/z): $[M–Me]^+$ calcd for $C_{17}H_{26}{}^{11}BO_3Si$, 317.1744; found 317.1739. mp: 54–58 °C.

1-(2-Methoxyphenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silinane (2d).

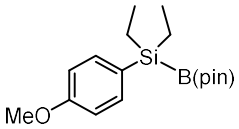


2d

The reaction was conducted with 206.4 mg (1.0 mmol) of **1d** according to the procedure for the synthesis of **2b**. The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 96:4) as an eluent to afford the corresponding silylboronate **2d** in 67% isolated yield (223.9 mg, 0.67 mmol) as a white solid.

^{1}H NMR (401 MHz, $CDCl_3$, δ): 0.90 (ddd, J = 4.1, 10.5, 13.5 Hz, 2H), 1.02–1.10 (m, 2H), 1.19–1.40 (m, 2H), 1.24 (s, 12H), 1.54–1.70 (m, 2H), 1.83–1.93 (m, 2H), 3.77 (s, 3H), 6.78 (d, J = 8.4 Hz, 1H), 6.93 (t, J = 7.4 Hz, 1H), 7.31 (td, J = 1.6, 7.8 Hz, 1H), 7.41 (dd, J = 2.0, 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 10.7 (CH_2), 24.9 (CH_3), 25.3 (CH_2), 30.1 (CH_2), 55.0 (CH_3), 83.0 (C), 109.1 (CH), 120.5 (CH), 125.4 (C), 130.4 (CH), 135.8 (CH), 164.1 (C). ^{11}B{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 34.8 (brs). The signal derived from the silicon directly attached to the boron atom was not detected by ^{29}Si{^{1}H} NMR, which is likely due to quadrupolar relaxation. HRMS-EI (m/z): $[M–Me]^+$ calcd for $C_{17}H_{26}{}^{11}BO_3Si$, 317.1744; found 317.1740. mp: 114–118 °C.

Diethyl(4-methoxyphenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (2e).

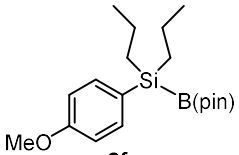


2e

The reaction was conducted with 198.8 mg (1.0 mmol) of **1e** according to the procedure for the synthesis of **2b**. The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 98:2) as an eluent to afford the corresponding silylboronate **2e** in 71% isolated yield (232.3 mg, 0.73 mmol) as a colorless oil.

^{1}H NMR (399 MHz, $CDCl_3$, δ): 0.83 (q, J = 8.0 Hz, 4H), 1.00 (t, J = 7.8 Hz, 6H), 1.27 (s, 12H), 3.81 (s, 3H), 6.91 (d, J = 8.8 Hz, 2H), 7.52 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 4.3 (CH_2), 8.3 (CH_3), 25.0 (CH_3), 54.9 (CH_3), 83.2 (*C*), 113.4 (*C*H), 127.7 (*C*), 136.2 (*C*H), 160.1 (*C*). ^{11}B{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 34.6 (brs). The signal derived from the silicon directly attached to the boron atom was not detected by ^{29}Si{^{1}H} NMR, which is likely due to quadrupolar relaxation. HRMS-EI (m/z): $[M–2Me]^+$ calcd for $C_{15}H_{24}{}^{11}BO_3Si$, 291.1588; found 291.1587.

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

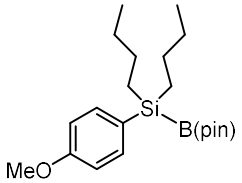


2f

The reaction was conducted with 222.1 mg (1.0 mmol) of **1f** according to the procedure for the synthesis of **2b**. The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 97:3) as an eluent to afford the corresponding silylboronate **2f** in 72% isolated yield (249.6 mg, 0.72 mmol) as a colorless oil.

^{1}H NMR (399 MHz, $CDCl_3$, δ): 0.79–0.86 (m, 4H), 0.94 (t, J = 7.0 Hz, 6H), 1.26 (s, 12H), 1.33–1.43 (m, 4H), 3.80 (s, 3H), 6.89 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 15.6 (CH_2), 18.2 (CH_2), 18.4 (CH_3), 25.0 (CH_3), 54.9 (CH_3), 83.2 (*C*), 113.4 (*C*H), 128.1 (*C*), 136.2 (*C*H), 160.0 (*C*). ^{11}B{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 34.6 (brs). The signal derived from the silicon directly attached to the boron atom was not detected by ^{29}Si{^{1}H} NMR, which is likely due to quadrupolar relaxation. HRMS-EI (m/z): $[M–Pr]^+$ calcd for $C_{16}H_{26}{}^{11}BO_3Si$, 305.1744; found 305.1739.

Dibutyl(4-methoxyphenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (2g).

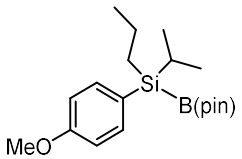


2g

The reaction was conducted with 249.7 mg (1.0 mmol) of **1g** according to the procedure for the synthesis of **2b**. The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 98:2) as an eluent to afford the corresponding silylboronate **2g** in 79% isolated yield (295.3 mg, 0.78 mmol) as a colorless oil.

^{1}H NMR (399 MHz, $CDCl_3$, δ): 0.78–0.91 (m, 10H), 1.26 (s, 12H), 1.28–1.38 (m, 8H), 3.80 (s, 3H), 6.89 (dt, *J* = 2.0, 8.5 Hz, 2H), 7.51 (dt, *J* = 2.3, 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 12.6 (*C*H_2), 13.8 (*C*H_3), 25.0 (*C*H_3), 26.6 (*C*H_2), 26.9 (*C*H_2), 54.9 (*C*H_3), 83.2 (*C*), 113.4 (*C*H), 128.2 (*C*), 136.2 (*C*H), 160.0 (*C*). ^{11}B{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 34.8 (brs). The signal derived from the silicon directly attached to the boron atom was not detected by ^{29}Si{^{1}H} NMR, which is likely due to quadrupolar relaxation. HRMS-EI (m/z): $[M–Me]^+$ calcd for $C_{20}H_{34}{}^{11}BO_3Si$, 361.2370; found 361.2366.

Isopropyl(4-methoxyphenyl)(propyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (2h).

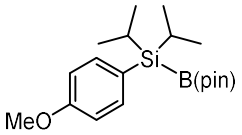


2h

The reaction was conducted with 222.7 mg (1.0 mmol) of **1h** according to the procedure for the synthesis of **2b**. The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 98:2) as an eluent to afford the corresponding silylboronate **2h** in 80% isolated yield (278.0 mg, 0.80 mmol) as a colorless oil.

^{1}H NMR (399 MHz, $CDCl_3$, δ): 0.83–0.91 (m, 2H), 0.93–0.99 (m, 6H), 0.99–1.13 (m, 4H), 1.28 (s, 12H), 1.34–1.46 (m, 2H), 3.81 (s, 3H), 6.90 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 12.7 (*C*H), 13.8 (*C*H_2), 18.3 (*C*H_2), 18.4 (*C*H_3), 18.6 (*C*H_3), 54.9 (*C*H_3), 83.1 (*C*), 113.3 (*C*H), 127.0 (*C*), 136.7 (*C*H), 160.0 (*C*). ^{11}B{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 34.7 (brs). The signal derived from the silicon directly attached to the boron atom was not detected by ^{29}Si{^{1}H} NMR, which is likely due to quadrupolar relaxation. HRMS-EI (m/z): $[M–Pr]^+$ calcd for $C_{16}H_{26}{}^{11}BO_3Si$, 305.1744; found 305.1733.

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

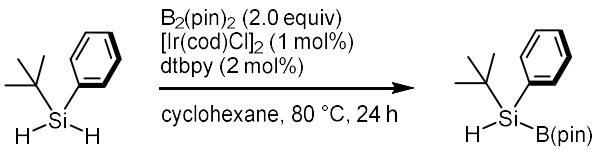


2i

The reaction was conducted with 224.4 mg (1.0 mmol) of **1i** according to the procedure for the synthesis of **2b**. The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 98:2) as an eluent to afford the corresponding silylboronate **2i** in 85% isolated yield (299.2 mg, 0.86 mmol) as a colorless oil.

^{1}H NMR (399 MHz, $CDCl_3$, δ): 0.96 (d, J = 7.2 Hz, 6H), 1.04 (d, J = 7.2 Hz, 6H), 1.22 (q, J = 7.4 Hz, 2H), 1.28 (s, 12H), 3.81 (s, 3H), 6.90 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 11.1 (*C*H), 18.5 (*C*H_3), 18.7 (*C*H_3), 25.1 (*C*H_3), 54.9 (*C*H_3), 83.1 (*C*), 113.3 (*C*H), 125.9 (*C*), 137.2 (*C*H), 160.0 (*C*). ^{11}B{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 34.7 (brs). The signal derived from the silicon directly attached to the boron atom was not detected by ^{29}Si{^{1}H} NMR, which is likely due to quadrupolar relaxation. HRMS-EI (m/z): $[M–Me]^+$ calcd for $C_{18}H_{30}{}^{11}BO_3Si$, 333.2057; found 333.2048.

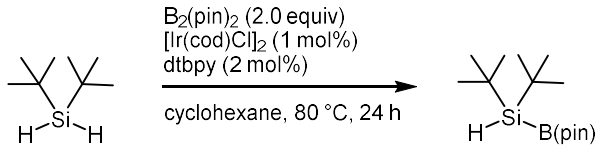
***tert*-Butyl(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (7b).**



S2 (1 mmol) **7b**, 49%

This reaction was performed according to our previous report.[4] Bis(pinacolato)diboron (513.8 mg, 2.0 mmol, 2.0 equiv), $[Ir(cod)Cl]_2$ (6.8 mg, 0.010 mmol, 1.0 mol%), and dtbpy (5.8 mg, 0.022 mmol, 2.2 mol%) were placed in a vial. After the vial was sealed with a screw cap containing a Teflon®-coated rubber septum, the vial was connected to a vacuum/nitrogen manifold through a needle. It was evacuated and then backfilled with nitrogen, and this cycle was repeated three times. Then, cyclohexane (1.0 mL) was added to the vial via a syringe. After stirring for 30 min at 80 °C, dihydrosilane **S2** (169.9 mg, 1.0 mmol) was added to the vial via a syringe. After the reaction was completed, the mixture was directly filtered through a silica-gel pad with Et_2O as an eluent. Then, the resulting solution was concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography with hexane/EtOAc (100:0 to 98:2) as an eluent to afford the corresponding product **7b** (146.8 mg, 0.51 mmol, 49% yield) as a colorless oil. The spectroscopic data of **7b** was consistent with literature values.[4]

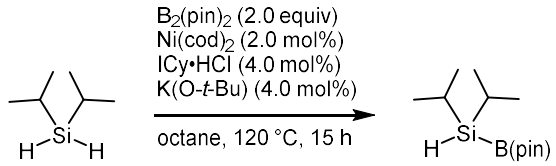
Di-*tert*-butyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (7a).



S3 (3 mmol) **7a**, 73%

The reaction was conducted with 431.9 mg (3.0 mmol) of **S3** according to the procedure for the synthesis of **7b**. The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 98:2) as an eluent to afford the corresponding silylboronates **7a** in 73% isolated yield (593.4 mg, 2.2 mmol) as a colorless oil. The spectroscopic data of **7a** was consistent with literature values.[4]

Diisopropyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (7c).



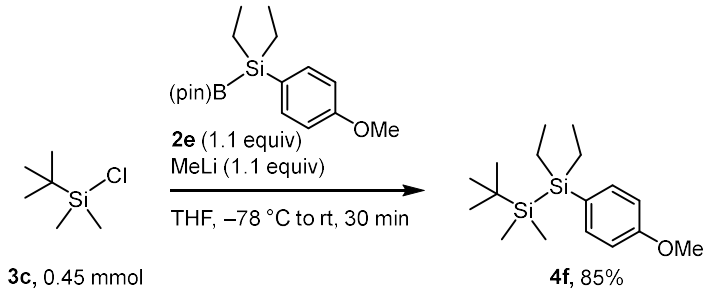
S1 (1 mmol) **7c**, 27%

This reaction was performed according to our previous report.[4] Bis(pinacolato)diboron (508.9 mg, 2.0 mmol, 2.0 equiv) was placed in a vial with a screw cap containing a Teflon®-coated rubber septum under air. The vial was placed in a glove box under an argon atmosphere, and then $Ni(cod)_2$ (5.6 mg, 0.020 mmol, 2.0 mol%), ICy·HCl (11.1 mg, 0.41 mmol, 4.1 mol%), and K(O-*t*-Bu) (4.6 mg, 0.041 mmol, 4.1 mol%) were added to the vial. After the vial was sealed with the screw cap, it was removed from the glove box. Then, *n*-octane (1.0 mL) was added to the vial via a syringe. After stirring for 1 hour at 120 °C, dihydrolsilane **S1** (120.3 mg, 1.0 mmol) was added dropwise via a syringe. After the reaction was completed, the mixture was directly filtered through a silica-gel pad with Et_2O as an eluent. Then, the resulting solution was concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography with hexane/EtOAc (100:0 to 98:2) as an eluent to afford the corresponding product **7c** (67.6 mg, 0.28 mmol, 27% yield) as a colorless oil.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.01–1.13 (m, 14H), 1.25 (s, 12H), 3.27 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 9.8 (*C*H), 19.7 (*C*H_3), 20.0 (*C*H_3), 25.0 (*C*H_3), 83.2 (*C*). ^{11}B{^{1}H} NMR (126 MHz, $CDCl_3$, δ): 34.5 (brs). The signal derived from the silicon directly attached to the boron atom was not detected by ^{29}Si{^{1}H} NMR, which is likely due to quadrupolar relaxation. HRMS-EI (m/z): $[M–H]^+$ calcd for $C_{12}H_{26}{}^{11}BO_2Si$, 241.1795; found 241.1793.

Procedures for the iterative oligosilane synthesis

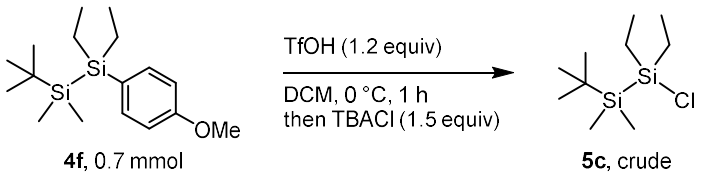
Typical procedure of the Si–Si coupling



This reaction was conducted according to previous reports.[7]

Silylboronate **2e** (354.7 mg, 1.1 mmol, 1.1 equiv) was placed in a vial. The vial was sealed with a screw cap containing a Teflon®-coated rubber septum and connected to a vacuum/nitrogen manifold through a needle. It was evacuated and then backfilled with nitrogen. This cycle was repeated three times. After THF (4.0 mL) was added to the vial via a syringe, the solution was allowed to cool at –78 °C. Then, MeLi (1.18 M in Et_2O, 940 μL, 1.1 mmol, 1.1 equiv) was added dropwise to the mixture via a syringe. After the reaction mixture was stirred for 1 h at –78 °C, chlorosilane **3c** (153.9 mg, 1.0 mmol) dissolved in THF (1.0 mL) was added to the reaction mixture and allowed to warm to room temperature slowly. After stirring for 0.5 h, the mixture was directly filtered through a silica-gel pad 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 (100:0 to 98.5:1.5) as an eluent to afford the corresponding product **4f** (257.5 mg, 0.83 mmol, 82% yield) as a colorless oil.

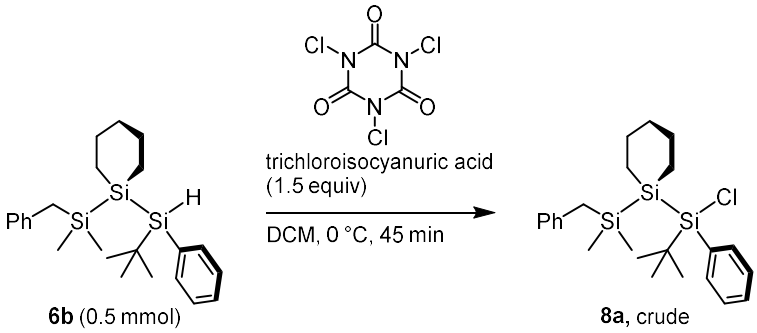
Typical procedure of the chlorination of methoxyphenyl group at the terminal of oligosilane



This reaction was conducted according to previous reports.[8] Disilane **4f** (216.2 mg, 0.7 mmol) was placed in a vial. The vial was sealed with a screw cap containing a Teflon®-coated rubber septum and connected to a vacuum/nitrogen manifold through a needle. It was evacuated and then backfilled with nitrogen. This cycle was repeated three times. After DCM (2.5 mL) was added to the vial via a syringe, the solution was allowed to cool at 0 °C. Then, TfOH (74 μL, 0.84 mmol, 1.2 equiv) was added dropwise to the mixture via a syringe. After the reaction mixture was stirred for 1 h at 0 °C, the DCM solution of tetrabutylammonium chloride (291.0 mg, 1.0 mmol, 1.5 equiv) was added to the reaction mixture. After stirring for a further 0.5 h, the mixture was concentrated under reduced

pressure. Then, the resulting residue was dissolved with hexane, resulting in precipitation. After filtering off precipitates, volatiles were removed in vacuo to afford the crude chlorodisilane **5c** as a colorless oil. This crude was employed for the next Si–Si coupling without further purification.

Typical procedure of the chlorination of hydride group at the terminal of oligosilanes



This reaction was conducted according to previous reports.[9] Trichloroisocyanuric acid (174.9 mg, 0.75 mmol, 1.5 equiv) was placed in a vial. The vial was sealed with a screw cap containing a Teflon®-coated rubber septum and connected to a vacuum/nitrogen manifold through a needle. It was evacuated and then backfilled with nitrogen. This cycle was repeated three times. After DCM (3.0 mL) was added to the vial via a syringe, the solution was allowed to cool at 0 °C. Then, trisilane **6b** (207.4 mg, 0.5 mmol) was added to the mixture via a syringe. After the reaction mixture was stirred for 45 min at 0 °C, the mixture was concentrated under reduced pressure. Then, the resulting residue was dissolved with hexane, resulting in precipitation. After filtering off precipitates, volatiles were removed in vacuo to afford the crude chlorotrisilane **8a** as a colorless oil. This crude was employed for the next Si–Si coupling without further purification.

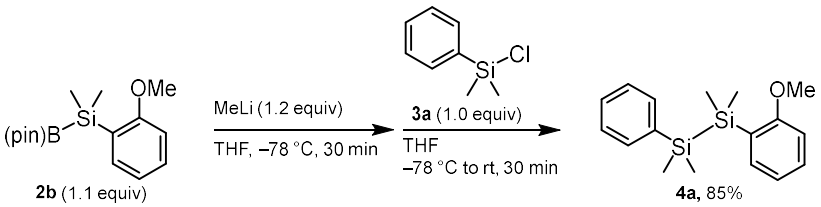
Notes for the iterative reactions:

1. In Si–Si coupling, if chloro(oligo)silanes were viscous oils or solids, they were added via a syringe after dissolving with THF.
2. In both chlorination, if oligosilanes were viscous oils or solids, they were added via a syringe after dissolving with DCM.
3. In both chlorination, the resulting solid byproducts should be almost completely excluded for the next Si–Si coupling. If necessary, the cycle of dissolving with hexane and filtration should be repeated several times.

Investigation of the generation of methoxyphenyl-substituted silyl nucleophiles and the selective chlorination of the methoxyphenyl group

Synthesis of 1-(2-methoxyphenyl)-1,1,2,2-tetramethyl-2-phenyldisilane (4a)

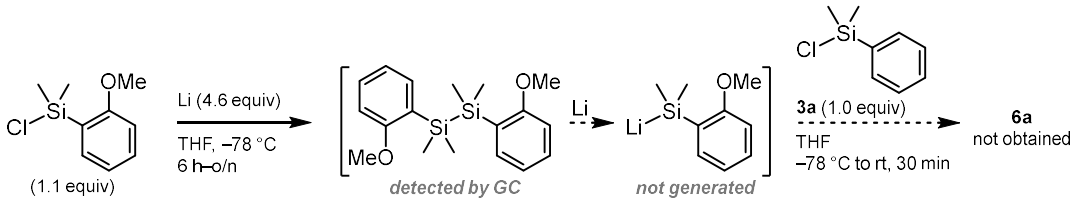
The activation of a silylboronate 2b with MeLi



This reaction was conducted with 76.2 mg (0.45 mmol) of chlorosilane **4a** according to the typical procedure for Si-Si coupling for **4f**. The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 98.5:1.5) as an eluent to afford the corresponding disilane **4a** in 85% isolated yield (114.2 mg, 0.38 mmol) as a colorless oil.

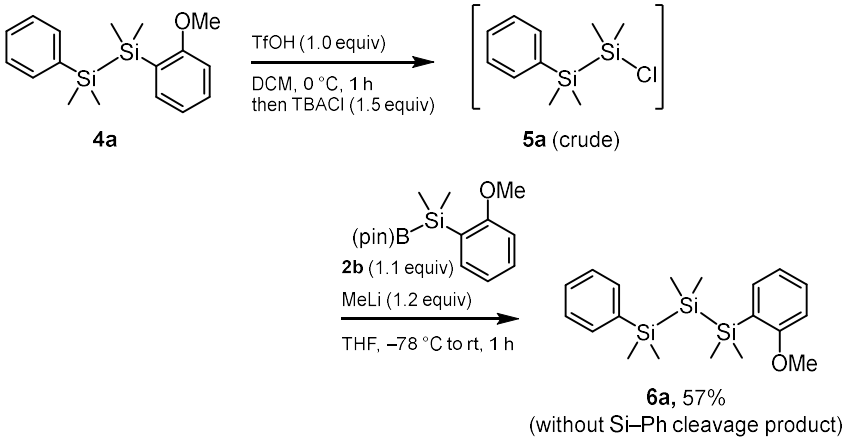
^{1}H NMR (396 MHz, $CDCl_3$, δ): 0.28 (s, 6H), 0.31 (s, 6H), 3.64 (s, 3H), 6.76 (d, J = 8.7 Hz, 1H), 6.93 (t, J = 7.3 Hz, 1H), 7.25–7.35 (m, 5H), 7.37–7.43 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): –3.5 (CH_3), –3.4 (CH_3), 54.4 (CH_3), 108.7 (*C*H), 120.4 (*C*H), 126.8 (*C*), 127.5 (*C*H), 128.0 (*C*H), 130.4 (*C*H), 133.8 (*C*H), 135.0 (*C*H), 140.2 (*C*), 163.6 (*C*). ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$, δ): –23.7, –20.8. HRMS-EI (m/z): $[M]^+$ calcd for $C_{17}H_{24}OSi_2$, 300.1366; found 300.1356.

The reduction of chlorosilane with Li



This reaction was conducted according to a previous report.[10] In a grove box under argon atmosphere, lithium (35.5 mg, 5.1 mmol, 5.1 equiv) was placed in a vial. After the reaction vial was sealed with a screw cap containing a Teflon®-coated rubber septum, it was removed from the glove box. After THF (2.0 mL) was added to the vial via a syringe, the solution was allowed to cool at 0 °C. Then, chloro(4-methoxyphenyl)dimethysilane (1.18 M in Et_2O, 75 μL, 1.2 equiv) was added dropwise to the mixture via a syringe. After the reaction mixture was stirred for 1 min at 0 °C, disilane intermediate was detected by GC analysis. However, after stirring for a further 5 h, disilane was fully consumed and the reaction mixture resulted in a complex mixture. Although dimethylphenylchlorosilane **3a** (168.1 mg, 0.98 mmol) was added, the desired cross-coupling product 6a was not detected. Fleming reported that this reduction resulted in failure.[11] This result indicates that methoxyphenyl-substituted silyl nucleophiles are accessible almost only to silylboronates.

Synthesis of 1-(2-methoxyphenyl)-1,1,2,2,3,3-hexamethyl-3-phenyltrisilane (6a)

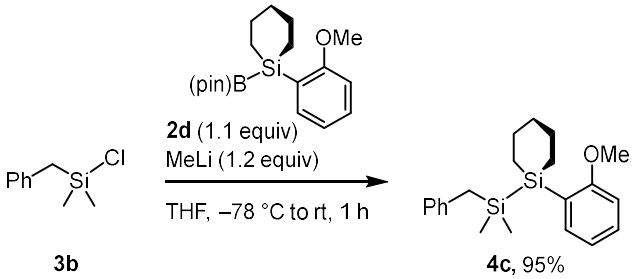


These reactions were conducted with 90.5 mg (0.3 mmol) of disilane **4a** according to the typical procedure for chlorination for **5c** and the typical procedure for Si–Si coupling for **4f**. The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 98.5:1.5) as an eluent to afford the corresponding trisilane **6a** in 57% isolated yield (61.4 mg, 0.17 mmol) as a colorless oil.

^{1}H NMR (399 MHz, $CDCl_3$, δ): 0.07 (s, 6H), 0.21 (s, 6H), 0.25 (s, 6H), 3.67 (s, 3H), 6.75 (d, J = 8.0 Hz, 1H), 6.94 (t, J = 7.2 Hz, 1H), 7.24–7.35 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): –6.0 (CH_3), –3.4 (CH_3), –2.9 (CH_3), 54.5 (CH_3), 108.8 (*C*H), 120.4 (*C*H), 127.3 (*C*), 127.5 (*C*H), 128.1 (*C*H), 130.3 (*C*H), 133.7 (*C*H), 134.9 (*C*H), 140.0 (*C*), 163.7 (*C*). ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$, δ): –47.1, –20.9, –18.2. HRMS-EI (m/z): $[M–Me]^+$ calcd for $C_{18}H_{27}OSi_3$, 343.1370; found 343.1359.

Iterative synthesis of tetrasilane 9a

1-(Benzyldimethylsilyl)-1-(2-methoxyphenyl)silane (4c).

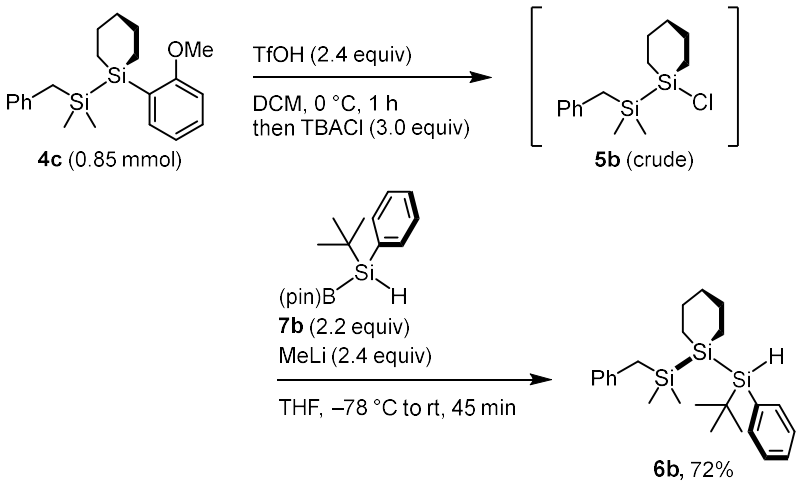


This reaction was conducted with 184.5 mg (1.0 mmol) of chlorosilane **3b** according to the typical procedure for Si–Si coupling for **4f**. The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 99:1) as an eluent to afford the corresponding disilane **4c** in 95% isolated yield (335.5 mg, 0.95 mmol) as a colorless oil.

^{1}H NMR (399 MHz, $CDCl_3$, δ): –0.03 (s, 6H), 0.90–1.10 (m, 4H), 1.37–1.50 (m, 2H), 1.65–1.80 (m, 4H), 2.07 (s, 2H), 3.78 (s, 3H) 6.81 (d, J = 18.4 Hz, 1H), 6.86 (d, J = 7.2 Hz, 2H), 7.00 (dt, J = 7.4, 20.0 Hz, 2H), 7.15 (t, J = 7.6 Hz, 2H), 7.31–7.37 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): –3.5 (CH_3), 10.7 (CH_2), 24.9 (CH_2), 24.9 (CH_2), 30.1 (CH_2), 54.6 (CH_3), 108.9 (*C*), 120.5 (*C*H), 123.6

(*C*H), 125.5 (*C*), 127.9 (*C*H), 128.2 (*C*H), 130.2 (*C*H), 135.4 (*C*H), 140.5 (*C*H), 163.9 (*C*). ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$, δ): –26.7, –17.6. HRMS-EI (m/z): $[M–Me]^+$ calcd for $C_{20}H_{27}OSi_2$, 339.1600; found 339.1609.

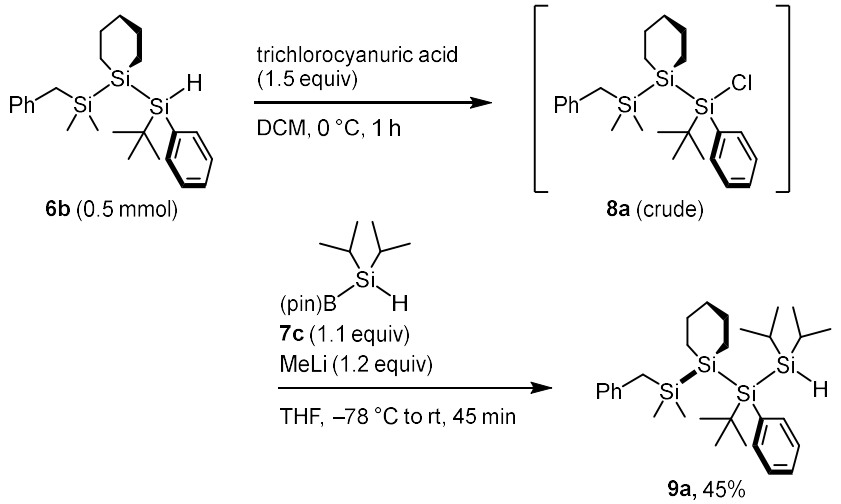
1-(Benzyldimethylsilyl)-1-[*tert*-butyl(phenyl)silyl]silinane (6b).



These reactions were conducted with 307.5 mg (0.85 mmol) of disilane **4c** according to the typical procedure for chlorination for **5c** and the typical procedure for Si–Si coupling for **4f**. The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 99:1) as an eluent to afford the corresponding trisilane **6b** in 72% isolated yield (256.9 mg, 0.63 mmol) as a colorless oil.

^{1}H NMR (399 MHz, $CDCl_3$, δ): –0.08 (s, 3H), 0.04 (s, 3H), 0.85–1.03 (m, 4H), 1.08 (s, 9H), 1.28–1.39 (m, 1H), 1.48–1.63 (m, 3H), 1.81–1.92 (m, 2H), 2.04 (s, 2H), 4.15 (s, 1H), 6.85 (d, J = 7.2 Hz, 2H), 7.03 (t, J = 7.2 Hz, 1H), 7.16 (t, J = 7.4 Hz, 2H), 7.29–7.36 (m, 3H), 7.52–7.56 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): –2.6 (CH_3), 9.4 (CH_2), 9.6 (CH_2), 19.4 (*C*), 25.4 (CH_2), 26.0 (CH_2), 29.2 (CH_3), 29.8 (CH_2), 123.8 (*C*H), 127.7 (*C*H), 128.0 (*C*H), 128.2 (*C*), 128.7 (*C*H), 135.6 (*C*), 136.2 (*C*H), 140.0 (*C*H). ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$, δ): –48.5, –14.8, –13.5. HRMS-EI (m/z): $[M–{}^{t}Bu]^+$ calcd for $C_{20}H_{29}Si_3$, 353.1577; found 353.1575.

1-(Benzyldimethylsilyl)-1-[1-(*tert*-butyl)-2,2-diisopropyl-1-phenyldisilaneyl]silinane (9a).

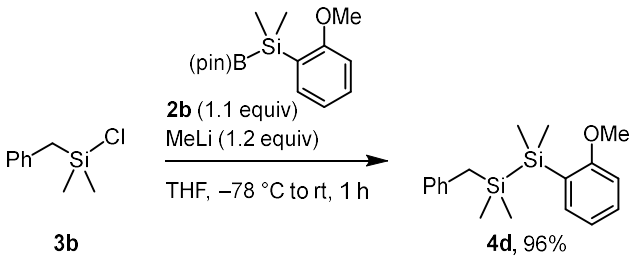


These reactions were conducted with 174.9 mg (0.5 mmol) of trisilane **6b** according to the typical procedure for chlorination for **8a** and the typical procedure for Si–Si coupling for **4f**. The crude product was purified by silica-gel column chromatography with hexane as an eluent and GPC to afford the corresponding tetrasilane **9a** in 45% isolated yield (119.8 mg, 0.23 mmol) as a colorless oil.

*Several rotamer signals were observed in ^{1}H NMR analysis. ^{1}H NMR (399 MHz, $CDCl_3$, δ): *[–0.154 (s) and –0.146 (s) (3H)], *[–0.134 and –0.130 (s, 3H)], 1.03 (dd, J = 3.3, 7.2 Hz, 3H), 1.06 – 1.31 (m, 25H), 1.32–1.59 (m, 2H), 1.66–1.78 (m, 1H), 1.89–2.10 (m, 4H), 3.84 (q, J = 2.9 Hz, 1H), 6.71 (d, J = 8.2 Hz, 1H), 6.81 (q, J = 7.1 Hz, 1H), 7.02 (t, J = 7.4 Hz, 1H), 7.10–7.19 (m, 2H), 7.27–7.32 (m, 3H), 7.58 (quint, J = 3.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): Aromatic carbon signals were complicated due to the restricted rotation of Si–Si bonds between bulky silicon units. –1.9 (CH_3), 11.4 (CH_2), 11.7 (CH_2), 12.6 (CH), 12.7 (CH), 20.5 (CH_3), 20.8 (CH_3), 21.3 (C), 22.4 (CH_3), 22.9 (CH_3), 25.4 (CH_2), 25.9 (CH_2), 26.2 (CH_2), 29.5 (CH_2), 31.1 (CH_3), 123.7 (CH), 127.57 (CH), 127.61 (CH), 127.87 (CH). 127.93 (CH), 128.0 (CH), 128.02 (CH), 128.2 (CH), 129.4 (CH), 136.3 (CH), 136.4 (CH), 137.7(C), 138.6 (C), 140.1 (C). ^{29}Si{^{1}H} NMR (78 MHz, $CDCl_3$, δ): Several signals were observed as doublet due to the restricted rotation of Si–Si bonds between bulky silicon units. (–44.3 and –44.2), (–22.0 and –21.8), (–14.6 and –14.5), –9.7. HRMS-FD (m/z): $[M]^+$ calcd for $C_{30}H_{52}Si_4$, 524.3146; found 524.3134.

Synthesis of multi-unit pentasilanes with different sequences

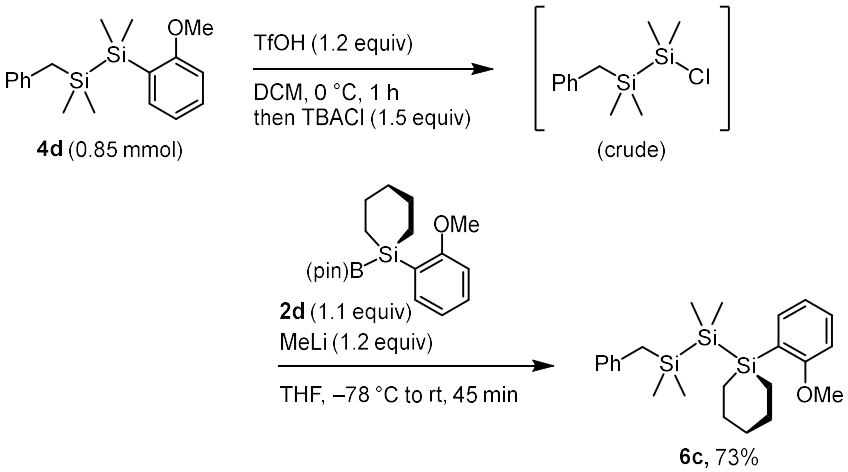
1-Benzyl-2-(2-methoxyphenyl)-1,1,2,2-tetramethyldisilane (4d).



This reaction was conducted with 184.1 mg (1.0 mmol) of chlorosilane **3b** according to the typical procedure for Si–Si coupling for **4f**. The crude product was purified by silica-gel column chromatography with hexane/EtOAc (100:0 to 99:1) as an eluent to afford the corresponding disilane **4d** in 96% isolated yield (300.2 mg, 0.95 mmol) as a colorless oil.

^{1}H NMR (399 MHz, $CDCl_3$, δ): –0.02 (s, 6H), 0.27 (s, 6H), 2.10 (s, 2H), 3.79 (s, 3H), 6.81 (d, J = 8.4 Hz, 1H), 6.86 (d, J = 7.6 Hz, 2H), 6.97 (t, J = 7.2 Hz, 1H), 7.02 (t, J = 7.4 Hz, 1H), 7.14 (t, J = 7.6 Hz, 2H), 7.30–7.38 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): –3.9 (CH_3), –3.5 (CH_3), 24.8 (CH_2), 54.6 (CH_3), 108.8 (*C*H), 120.5 (*C*H), 123.7 (*C*H), 127.0 (*C*), 127.9 (*C*H), 128.1 (*C*H), 135.0 (*C*H), 140.6 (*C*), 163.6 (*C*). ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$, δ): –23.8, –16.5. HRMS-EI (m/z): $[M–Me]^+$ calcd for $C_{17}H_{23}OSi_2$, 299.1287; found 299.1283.

1-(2-Benzyl-1,1,2,2-tetramethyldisilaneyl)-1-(2-methoxyphenyl)silinane (6c).

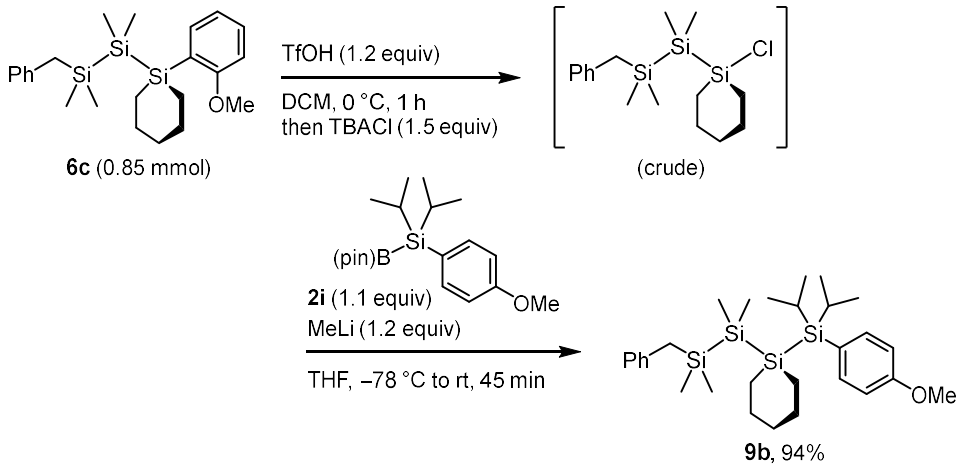


These reactions were conducted with 240.5 mg (0.75 mmol) of disilane **4d** according to the typical procedure for chlorination for **5c** and the typical procedure for Si–Si coupling for **4f**. The crude product was purified by silica-gel column chromatography with hexane/EtOAc (100:0 to 99:1) as an eluent to afford the corresponding trisilane **6c** in 73% isolated yield (229.9 mg, 0.56 mmol) as a colorless oil.

^{1}H NMR (399 MHz, $CDCl_3$, δ): –0.13 (s, 6H), 0.09 (s, 6H), 0.95–0.05 (m, 2H), 1.14–1.22 (m, 2H), 1.38–1.55 (m, 2H), 1.64–1.85 (m, 4H), 3.78 (s, 3H), 6.81 (d, J = 8.4 Hz, 1H), 6.86 (d, J = 7.6 Hz, 2H), 6.99 (t, J = 7.4 Hz, 2H), 7.04 (t, J = 7.4 Hz, 2H), 7.18 (t, J = 7.6 Hz, 2H), 7.31–7.41 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): –5.8 (CH_3), –4.0 (CH_3), 11.4 (CH_2), 24.9 (CH_2), 30.2 (CH_2), 54.6 (CH_3), 109.0 (*C*H), 120.5 (*C*H), 123.7 (*C*H), 125.7 (*C*), 128.0 (*C*H), 128.1 (*C*H), 130.2 (*C*H), 135.4 (*C*H), 140.5

(*C*), 164.1 (*C*). $^{29}Si\{^{1}H\}$ NMR (79 MHz, $CDCl_3$, δ): –48.1, –23.7, –13.4. HRMS-EI (m/z): $[M–Me]^+$ calcd for $C_{22}H_{33}OSi_3$, 397.1839; found 397.1831.

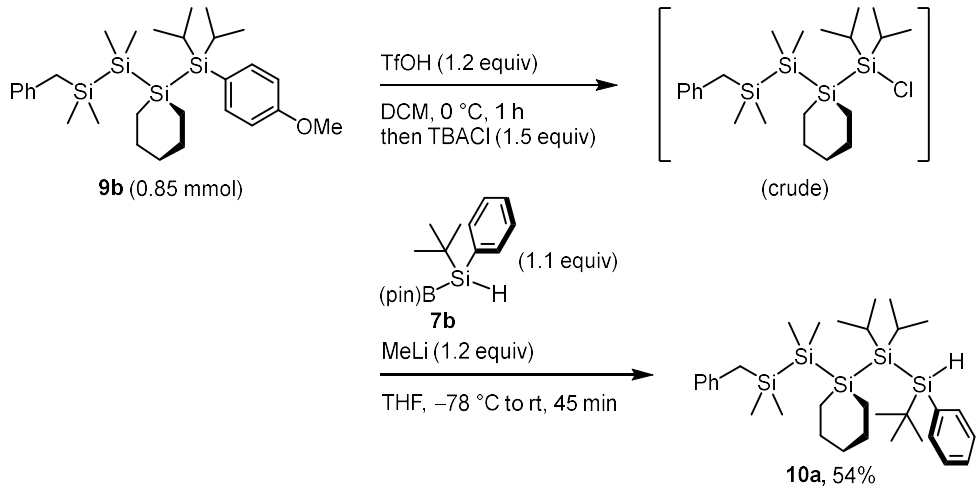
1-(2-Benzyl-1,1,2,2-tetramethyldisilaneyl)-1-[diisopropyl(4-methoxyphenyl)silyl]silinane (9b).



These reactions were conducted with 184.9 mg (0.45 mmol) of trisilane **6c** according to the typical procedure for chlorination for **5c** and the typical procedure for Si–Si coupling for **4f**. The crude product was purified by silica-gel column chromatography with hexane/EtOAc (100:0 to 98.5:1.5) as an eluent to afford the corresponding tetrasilane **9b** in 94% isolated yield (222.0 mg, 0.42 mmol) as a colorless oil.

^{1}H NMR (399 MHz, $CDCl_3$, δ): 0.02 (s, 6H), 0.4 (s, 6H), 0.94–1.13 (m, 2H), 1.15 (td, *J* =1.2, 5.3 Hz, 14H), 1.25–1.41 (m, 2H), 1.41–1.56 (m, 2H), 1.59–1.70 (m, 2H), 1.77–1.89 (m, 2H), 2.15 (s, 2H), 3.81 (s, 3H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 7.2 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (10 MHz, $CDCl_3$, δ): –4.2 (CH_3), –3.5 (CH_3), 11.2 (CH_2), 13.5 (*C*H), 19.7 (CH_3), 19.8 (CH_3), 25.0 (CH_2), 26.1 (CH_2), 26.9 (CH_2), 54.9 (CH_3), 113.4 (*C*H), 123.8 (*C*H), 127.6 (*C*), 128.0 (*C*H), 128.2 (*C*H), 136.5 (*C*H), 140.3 (*C*), 159.8 (*C*). $^{29}Si\{^{1}H\}$ NMR (79 MHz, $CDCl_3$, δ): –44.8. –44.2, –12.8, –6.6. HRMS-EI (m/z): $[M–Me]^+$ calcd for $C_{28}H_{47}OSi_4$, 511.2704; found 511.2687.

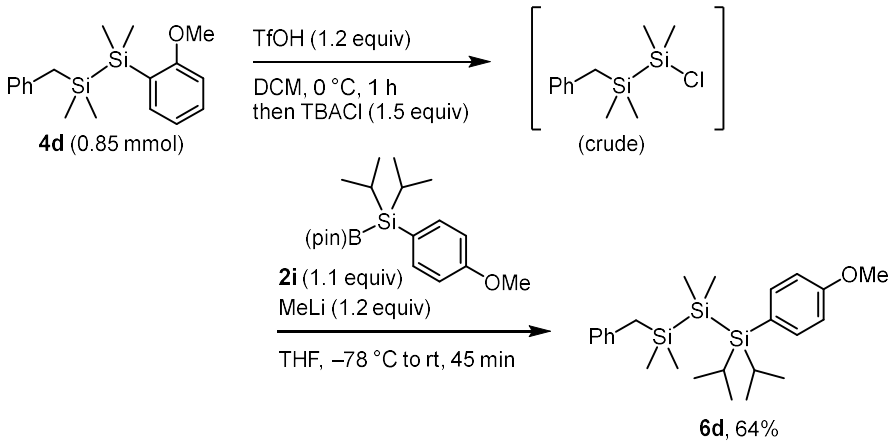
1-(2-Benzyl-1,1,2,2-tetramethyldisilaneyl)-1-(2-(*tert*-butyl)-1,1-diisopropyl-2-phenyldisilaneyl)silinane (10a).



These reactions were conducted with 160.4 mg (0.30 mmol) of tetrasilane **9b** according to the typical procedure for chlorination for **5c** and the typical procedure for Si–Si coupling for **4f**. The crude product was purified by silica-gel column chromatography with hexane/EtOAc (100:0 to 99:1) as an eluent to afford the corresponding pentasilane **10a** in 54% isolated yield (96.3 mg, 0.17 mmol) as a colorless oil.

^{1}H NMR (399 MHz, $CDCl_3$, δ): 0.07 (s, 6H), 0.23 (s, 6H), 0.80–1.62 (m, 31H), 1.81–2.02 (m, 2H), 2.23 (s, 2H), 4.37 (s, 1H), 7.01 (d, J = 7.6 Hz, 2H), 7.10 (t, J = 7.6 Hz, 1H), 7.24 (t, J = 7.4 Hz, 2H), 7.31–7.40 (m, 3H), 7.62–7.70 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, δ): –3.5 (CH_3), –3.4 (CH_3), 11.3 (CH_2), 11.6 (CH_2), 13.6 (*C*H), 13.7 (*C*H), 19.5 (*C*), 21.5 (CH_3), 21.67 (CH_3), 21.74 (CH_3), 24.9 (CH_2), 26.0 (CH_2), 26.1 (CH_2), 28.8 (CH_2), 30.0 (CH_3), 123.9 (*C*H), 127.6 (*C*H), 128.1 (*C*H), 128.2 (*C*H), 128.6 (*C*H), 136.3 (*C*), 136.8 (*C*H), 140.2 (*C*). ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$, δ): –44.3, –39.2, –15.5, –12.5, –11.8. HRMS-EI (m/z): $[M]^+$ calcd for $C_{32}H_{58}Si_5$, 582.3385; found 582.3377.

1-Benzyl-3,3-diisopropyl-3-(4-methoxyphenyl)-1,1,2,2-tetramethyltrisilane (6d).

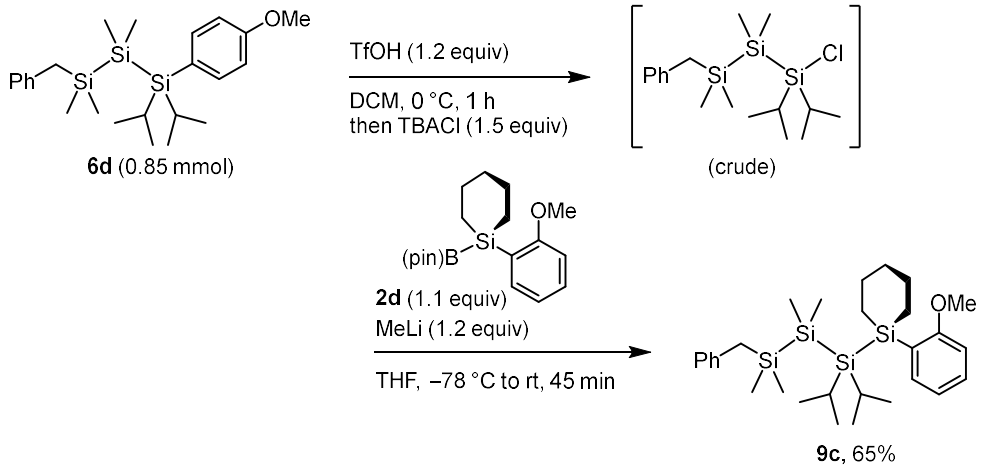


These reactions were conducted with 188.8 mg (0.6 mmol) of disilane **4d** according to the typical procedure for chlorination for **5c** and the typical procedure for Si–Si coupling for **4f**. The crude product

was purified by silica-gel column chromatography with hexane/EtOAc (100:0 to 99:1) as an eluent to afford the corresponding trisilane **6d** in 64% isolated yield (165.5 mg, 0.39 mmol) as a colorless oil.

^{1}H NMR (399 MHz, $CDCl_3$, δ): –0.07 (s, 6H), 0.26 (s, 6H), 1.14 (d, *J* = 7.2 Hz, 6H), 1.15 (d, *J* = 8.0 Hz, 6H), 1.44 (sept, *J* = 7.4 Hz, 2H), 2.07 (s, 2H), 3.82 (s, 3H), 6.88–6.94 (m, 4H), 7.05 (t, *J* = 7.2 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): –3.8 (CH_3), –3.6 (CH_3), 13.2 (*C*H), 19.5 (CH_3), 19.6 (CH_3), 24.8 (CH_2), 54.9 (CH_3), 113.5 (*C*H), 123.8 (*C*H), 127.3 (*C*), 128.0 (*C*H), 128.2 (*C*H), 136.5 (*C*H), 140.2 (*C*), 159.9 (*C*). ^{29}Si{^{1}H} NMR (119 MHz, $CDCl_3$, δ): –48.7, –14.0, –6.1. HRMS-EI (m/z): $[M]^+$ calcd for $C_{24}H_{40}OSi_3$, 428.2387; found 428.2366.

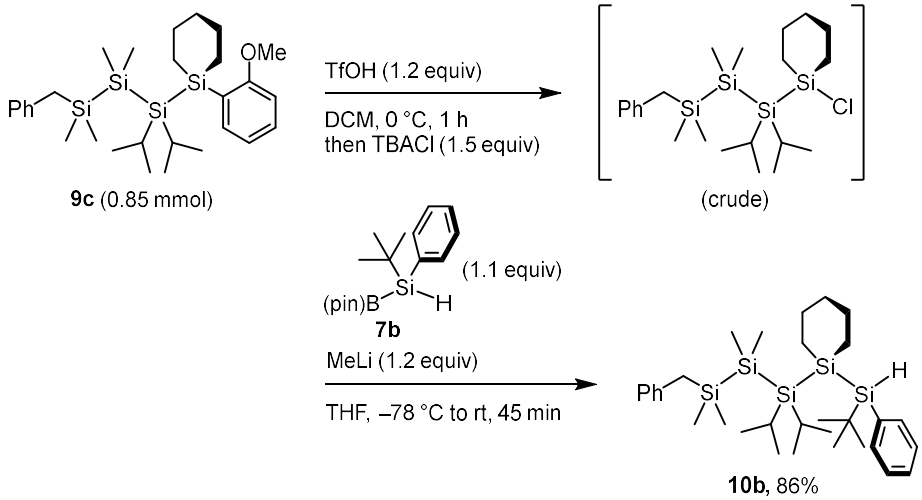
1-(3-Benzyl-1,1-diisopropyl-2,2,3,3-tetramethyltrisilaneyl)-1-(2-methoxyphenyl)silane (9c).



These reactions were conducted with 198.5 mg (0.46 mmol) of trisilane **6d** according to the typical procedure for chlorination for **5c** and the typical procedure for Si–Si coupling for **4f**. The crude product was purified by silica-gel column chromatography with hexane as an eluent to afford the corresponding tetrasilane **9c** in 65% isolated yield (158.8 mg, 0.31 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$, δ): –0.02 (s, 6H), 0.17 (s, 6H), 0.93 (td, *J* = 4.4, 14.0 Hz, 2H), 1.00 (dd, *J* = 7.5, 10.5 Hz, 2H), 1.06 (dd, *J* = 7.5, 14.7 Hz, 12H), 1.20–1.32 (m, 4H), 1.36–1.57 (m, 5H), 1.62–1.68 (m, 1H), 1.89–1.96 (m, 2H), 2.14 (s, 2H), 3.76 (s, 3H), 6.80 (d, *J* = 7.8 Hz, 1H), 6.94–6.99 (m, 3H), 7.06 (t, *J* = 7.2 Hz, 1H), 7.20 (t, *J* = 7.8 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 5.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): –3.3 (CH_3), –2.9 (CH_3), 13.2 (*C*H), 14.4 (CH_2), 21.2 (CH_3), 21.3 (CH_3), 24.7 (CH_2), 25.0 (CH_2), 30.5 (CH_2), 54.5 (CH_3), 109.4 (*C*H), 120.6 (*C*H), 123.9 (*C*H), 125.1 (*C*), 128.0 (*C*H), 128.4 (*C*H), 130.3 (*C*H), 136.6 (*C*H), 140.4 (*C*), 164.5 (*C*). ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$, δ): –45.3, –21.0 (two peaks overlap), –13.6. HRMS-EI (m/z): $[M–Me]^+$ calcd for $C_{28}H_{47}OSi_4$, 511.2704; found 511.2687.

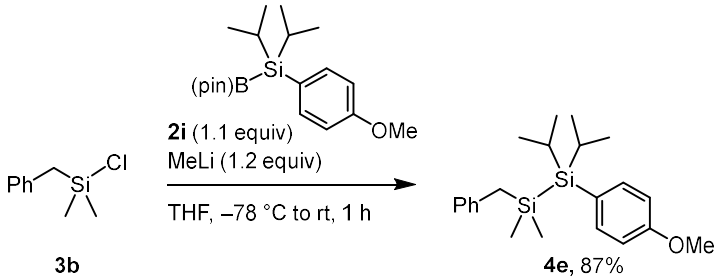
1-(3-Benzyl-1,1-diisopropyl-2,2,3,3-tetramethyltrisilaneyl)-1-[*tert*-butyl(phenyl)silyl]silane (10b).



These reactions were conducted with 105.5 mg (0.2 mmol) of tetrasilane **9c** according to the typical procedure for chlorination for **5c** and the typical procedure for Si–Si coupling for **4f**. The crude product was purified by silica-gel column chromatography with hexane/EtOAc (100:0 to 99.5:0.5) as an eluent to afford the corresponding pentasilane **10b** in 86% isolated yield (100.0 mg, 0.17 mmol) as a colorless oil.

^{1}H NMR (396 MHz, $CDCl_3$, δ): 0.03 (s, 6H), 0.31 (d, J = 6.7 Hz, 6H), 0.80 (d, J = 7.5 Hz, 3H), 0.87–1.16 (m, 22H), 1.16–1.47 (m, 4H), 1.50–1.85 (m, 2H), 2.02–2.17 (m, 2H), 2.19 (s, 2H), 4.30 (s, 1H), 6.98 (d, J = 7.5 Hz, 2H), 7.08 (t, J = 7.3 Hz, 1H), 7.22 (t, J = 7.5 Hz, 2H), 7.28–7.37 (m, 3H), 7.53–7.61 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): –3.2 (CH_3), –2.0 (CH_3), 11.5 (CH_2), 12.0 (CH_2), 13.5 (*C*H), 13.7 (*C*H), 19.9 (*C*), 21.2 (CH_3), 21.28 (CH_3), 21.32 (CH_3), 21.4 (CH_3), 24.9 (CH_3), 26.4 (CH_2), 26.4 (CH_2), 29.3 (CH_3), 29.5 (CH_2), 123.8 (*C*H), 127.5 (*C*H), 128.0 (*C*H), 128.3 (*C*H), 128.5 (*C*H), 135.7 (*C*), 136.5 (*C*H), 140.1 (*C*). ^{29}Si{^{1}H} NMR (78 MHz, $CDCl_3$, δ): –44.4, –41.8, –14.5, –13.5, –10.9. HRMS-EI (m/z): $[M]^+$ calcd for $C_{32}H_{58}Si_5$, 582.3385; found 582.3393.

1-Benzyl-2,2-diisopropyl-2-(4-methoxyphenyl)-1,1-dimethyldisilane (4e).

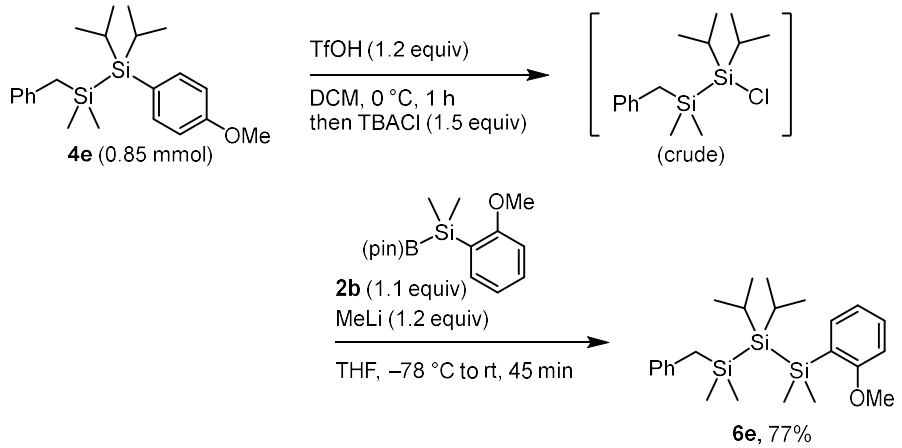


This reaction was conducted with 184.4 mg (1.0 mmol) of chlorosilane **3b** according to the typical procedure for Si–Si coupling for **4f**. The crude product was purified by silica-gel column chromatography with hexane/EtOAc (100:0 to 98.5:1.5) as an eluent and GPC to afford the corresponding disilane **4e** in 87% isolated yield (323.0 mg, 0.87 mmol) as a colorless oil.

^{1}H NMR (401 MHz, $CDCl_3$, δ): –0.10 (s, 6H), 1.10 (d, J = 7.2 Hz, 6H), 1.11 (d, J = 7.2 Hz, 6H),

1.40 (sept, J = 7.4 Hz, 2H), 2.25 (s, 2H), 3.83 (s, 3H), 6.89–6.97 (m, 4H), 7.06 (t, J = 7.2 Hz, 1H), 7.20 (t, J = 7.6 Hz, 2H), 7.41 (t, J = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): –1.7 (CH_3), 12.7 (CH), 19.3 (CH_3), 19.4 (CH_3), 26.1 (CH_2), 54.9 (CH_3), 113.5 (CH), 123.9 (CH), 126.6 (C), 128.0 (CH), 128.2 (CH), 136.6 (CH), 139.9 (C), 159.9 (C). ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$, δ): –18.0, –9.5. HRMS-EI (m/z): $[M]^+$ calcd for $C_{22}H_{34}OSi_2$, 370.2148; found 370.2137.

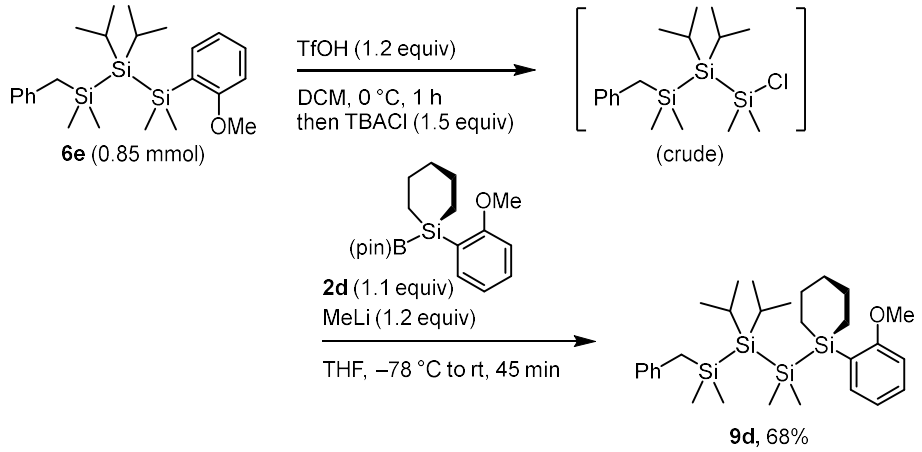
1-Benzyl-2,2-diisopropyl-3-(2-methoxyphenyl)-1,1,3,3-tetramethyltrisilane (6e).



These reactions were conducted with 277.7 mg (0.75 mmol) of disilane **4e** according to the typical procedure for chlorination for **5c** and the typical procedure for Si–Si coupling for **4f**. The crude product was purified by silica-gel column chromatography with hexane/EtOAc (100:0 to 99:1) as an eluent to afford the corresponding trisilane **6e** in 77% isolated yield (248.6 mg, 0.58 mmol) as a colorless oil.

^{1}H NMR (399 MHz, $CDCl_3$, δ): –0.07 (s, 6H), 0.50 (s, 6H), 1.11 (dd, J = 2.0, 7.6 Hz, 12H), 1.33 (sext, J = 7.4 Hz, 2H), 2.06 (s, 2H), 3.78 (s, 3H), 6.80 (d, J = 8.4 Hz, 1H), 6.83 (d, J = 6.8 Hz, 2H), 6.97 (td, J = 0.9, 7.3 Hz, 1H), 7.03 (t, J = 7.2 Hz, 1H), 7.17 (t, J = 7.6 Hz, 2H), 7.34 (td, J = 1.3, 7.9 Hz, 1H), 7.40 (dd, J = 1.8, 7.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, δ): –1.7 (CH_3), 0.4 (CH_3), 12.8 (CH), 21.1 (CH_3), 21.2 (CH_3), 26.2 (CH_2), 54.6 (CH_3), 109.1 (CH), 120.5 (CH), 123.7 (CH), 127.9 (CH), 128.2 (CH), 128.3 (C), 130.4 (CH), 135.3 (CH), 140.1 (C), 163.7 (C). ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$, δ): –26.9, –21.5, –15.0. HRMS-EI (m/z): $[M–Me]^+$ calcd for $C_{23}H_{37}OSi_3$, 413.2152; found 413.2142.

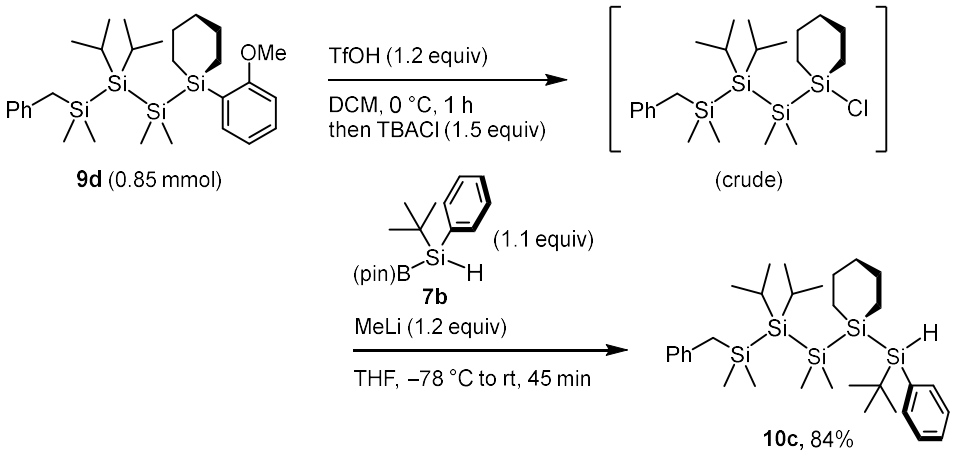
1-(3-Benzyl-2,2-diisopropyl-1,1,3,3-tetramethyltrisilaneyl)-1-(2-methoxyphenyl)silinane (9d).



These reactions were conducted with 198.7 mg (0.46 mmol) of trisilane **6e** according to the typical procedure for chlorination for **5c** and the typical procedure for Si–Si coupling for **4f**. The crude product was purified by silica-gel column chromatography with hexane/EtOAc (100:0 to 98:2) as an eluent to afford the corresponding tetrasilane **9d** in 68% isolated yield (166.0 mg, 0.32 mmol) as a colorless oil.

^{1}H NMR (399 MHz, $CDCl_3$, δ): 0.08 (s, 6H), 0.28 (s, 6H), 0.95 (td, J = 4.2, 13.5 Hz, 2H), 1.10 (dd, J = 7.3, 14.5 Hz, 12H), 1.21–1.46 (m, 5H), 1.47–1.62 (m, 2H), 1.62–1.74 (m, 1H), 1.91–2.03 (m, 2H), 2.27 (s, 2H), 3.80 (s, 3H), 6.84 (d, J = 7.9 Hz, 1H), 6.97–7.05 (m, 3H), 7.12 (t, J = 7.5 Hz, 1H), 7.22–7.31 (m, 2H), 7.37 (t, J = 7.7 Hz, 1H), 7.45 (d, J = 7.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): –2.2 (CH_3), –1.1 (CH_3), 11.7 (CH_2), 13.0 (CH), 21.2 (CH_3), 24.7 (CH_2), 26.9 (CH_2), 30.3 (CH_2), 54.4 (CH_3), 109.0 (CH), 120.5 (CH), 123.8 (CH), 124.7 (C), 128.0 (CH), 128.2 (CH), 130.1 (CH), 135.8 (CH), 140.0 (C), 164.3 (C). ^{29}Si{^{1}H} NMR (78 MHz, $CDCl_3$, δ): –45.4, –20.6, –20.4, –14.6. HRMS-EI (m/z): $[M–Me]^+$ calcd for $C_{28}H_{47}OSi_4$, 511.2704; found 511.2690.

1-(3-Benzyl-2,2-diisopropyl-1,1,3,3-tetramethyltrisilaneyl)-1-(*tert*-butyl(phenyl)silyl)silinane (10c).

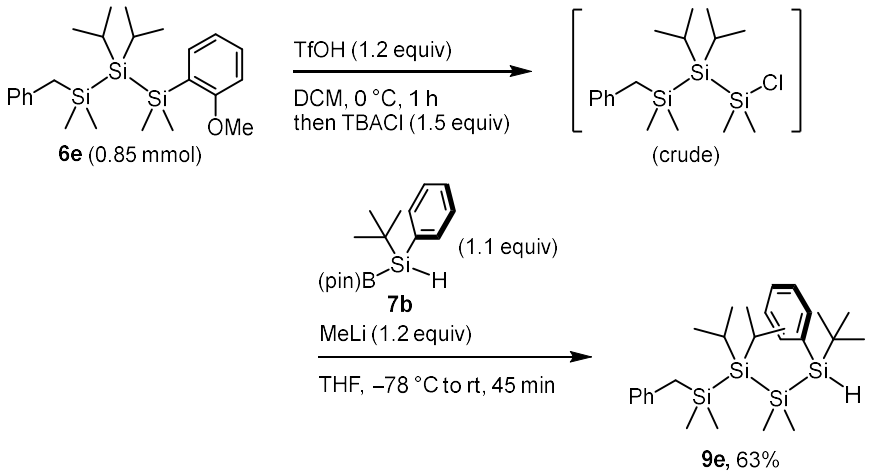


These reactions were conducted with 105.9 mg (0.2 mmol) of tetrasilane **9d** according to the typical

procedure for chlorination for **5c** and the typical procedure for Si–Si coupling for **4f**. The crude product was purified by silica-gel column chromatography with hexane/EtOAc (100:0 to 98:2) as an eluent to afford the corresponding pentasilane **10c** in 84% isolated yield (97.6 mg, 0.17 mmol) as a colorless oil.

^{1}H NMR (399 MHz, $CDCl_3$, δ): 0.09 (s, 6H), 0.24 (s, 3H), 0.30 (s, 3H), 0.94–1.21 (m, 25H), 1.26–1.44 (m, 3H), 1.56–1.74 (m, 2H), 1.76–1.97 (m, 3H), 2.29 (s, 2H), 4.29 (s, 1H), 6.98 (d, *J* = 7.5 Hz, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 2H), 7.29–7.39 (m, 3H), 7.54–7.62 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): –1.1 (*C*H_3), –0.8 (*C*H_3), 10.6 (*C*H_2), 10.8 (*C*H_2), 13.3 (*C*H), 19.5 (*C*), 21.4 (*C*H_3), 21.6 (*C*H_3), 25.8 (*C*H_2), 26.0 (*C*H_2), 27.1 (*C*H_2), 29.4 (*C*H_3), 29.7 (*C*H_2), 123.9 (*C*H), 127.6 (*C*H), 128.0 (*C*H), 128.3 (*C*H), 128.6 (*C*H), 135.8 (*C*), 136.3 (*C*H), 139.8 (*C*H). ^{29}Si{^{1}H} NMR (78 MHz, $CDCl_3$, δ): –42.3, –40.7, –19.1, –14.4, –13.7. HRMS-EI (m/z): $[M]^+$ calcd for $C_{32}H_{58}Si_5$, 582.3385; found 582.3383.

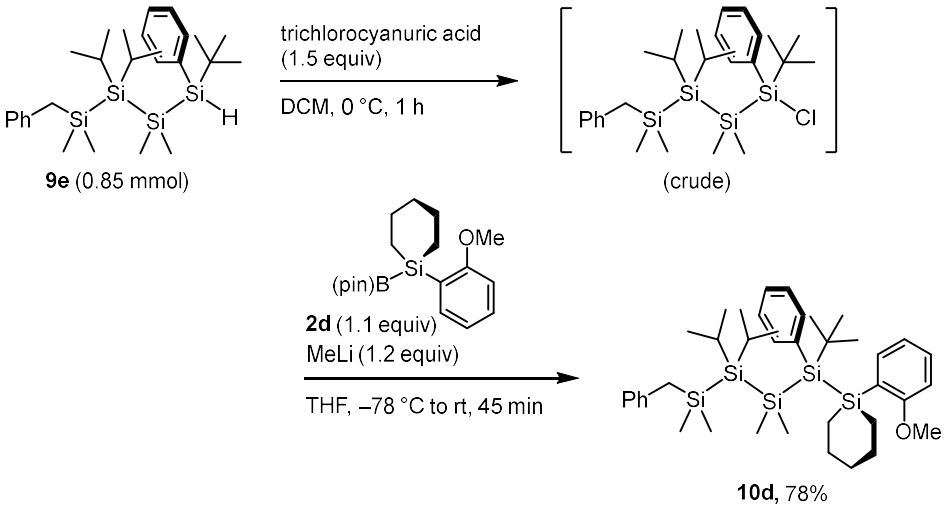
1-Benzyl-4-(*tert*-butyl)-2,2-diisopropyl-1,1,3,3-tetramethyl-4-phenyltetrasilane (9e).



These reactions were conducted with 192.0 mg (0.45 mmol) of trisilane **6e** according to the typical procedure for chlorination for **5c** and the typical procedure for Si–Si coupling for **4f**. The crude product was purified by silica-gel column chromatography with hexane/EtOAc (100:0 to 99:1) as an eluent to afford the corresponding tetrasilane **9e** in 63% isolated yield (137.7 mg, 0.28 mmol) as a colorless oil.

^{1}H NMR (399 MHz, $CDCl_3$, δ): 0.00 (s, 6H), 0.44 (s, 3H), 0.54 (s, 3H), 0.86 (d, *J* = 7.2 Hz, 3H), 1.01 (d, *J* = 7.6 Hz, 3H), 1.03–1.30 (m, 17H), 2.18 (s, 2H), 4.17 (s, 1H), 6.92 (d, *J* = 7.2 Hz, 2H), 7.06 (t, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 7.8 Hz, 2H), 7.27–7.34 (m, 3H) , 7.52–7.57 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, δ): –1.2 (*C*H_3), –1.1 (*C*H_3), –0.4 (*C*H_3), 12.9 (*C*H), 13.0 (*C*H), 20.4 (*C*), 21.0 (*C*H_3), 21.1 (*C*H_3), 21.16 (*C*H_3), 21.24 (*C*H_3), 26.8 (*C*H_2), 29.3 (*C*H_3), 123.9 (*C*H), 127.6 (*C*H), 128.0 (*C*H), 128.3 (*C*H), 128.7 (*C*H), 135.8 (*C*), 136.3 (*C*H), 139.8 (*C*). ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$, δ): –44.2, –22.1, –14.5, –12.4. HRMS-EI (m/z): $[M–^{i}Pr]^+$ calcd for $C_{24}H_{41}Si_4$, 441.2285; found 441.2275.

1-[4-Benzyl-1-(*tert*-butyl)-3,3-diisopropyl-2,2,4,4-tetramethyl-1-phenyltetrasilaneyl]-1-(2-methoxyphenyl)silinane (10d).

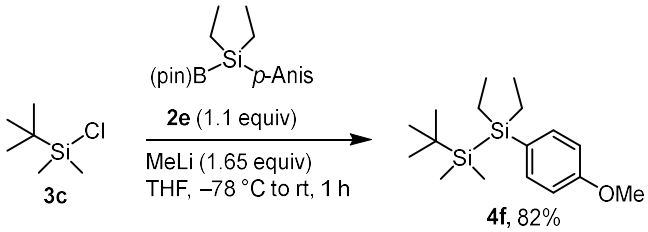


These reactions were conducted with 95.7 mg (0.2 mmol) of tetrasilane **9e** according to the typical procedure for chlorination for **8a** and the typical procedure for Si–Si coupling for **4f**. The crude product was purified by silica-gel column chromatography with hexane/EtOAc (100:0 to 99:1) as an eluent to afford the corresponding pentasilane **10d** in 78% isolated yield (105.7 mg, 0.15 mmol) as a colorless oil.

*Several rotamer signals were observed in ^{1}H, ^{13}C, and ^{29}Si NMR analysis. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 0.04–0.10 (m, 6H), 0.39 (d, J = 2.4 Hz, 3H), 0.51 (d, J = 4.2 Hz, 3H), 0.87–0.94 (m, 3H), 0.99–1.15 (m, 18H), 1.17–1.60 (m, 9H), 1.64–1.72 (m, 1H), 1.94–2.03 (m, 2H), *[2.25 (s) and 2.29 (s), (2H)], 3.20 (s, 3H), 6.67 (d, J = 8.4 Hz, 1H), *[6.88 (d, J = 9.0 Hz) and 6.94–7.00 (m), 3H], *[7.09 (t, J = 7.2 Hz) and 7.18–7.34 (m), 7H], 7.48 (d, J = 7.8 Hz, 1H), 7.58–7.63 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, δ): *[–0.18, –0.15, –0.11, and –0.08 (CH_3)], 0.94 (CH_3), 1.77 (CH_3), 13.6 (*C*H), 13.8 (*C*H), 14.4 (CH_2), 14.7 (CH_2), 21.3 (CH_3), 21.4 (CH_3), 21.68 (CH_3), 21.73 (*C*), 24.9 (CH_2), *[27.1 and 27.6 (CH_2)], 30.3 (CH_2), 31.0 (CH_3), 53.8 (CH_3), 109.3 (*C*H), 120.4 (*C*H), 124.0 (*C*H), *[124.8 and 124.9 (*C*)], 127.2 (*C*H), 127.6 (*C*H), *[128.1 and 128.2 (*C*H)], 128.5 (*C*H), 129.6 (*C*H), 130.4 (*C*H), *[136.5 and 136.7 (*C*H)], *[138.1 and 138.2 (*C*)], 138.5 and 140.0 (*C*)], 164.6 (*C*). ^{29}Si{^{1}H} NMR (119 MHz, $CDCl_3$, δ): –39.0, –20.4, *[–19.9 and –19.8], *[–17.96 and –18.02], *[–13.69 and –13.73]. HRMS-FD (m/z): $[M]^+$ calcd for $C_{39}H_{64}OSi_5$, 688.3804; found 688.3810.

Synthesis of the tree-shaped oligosilane

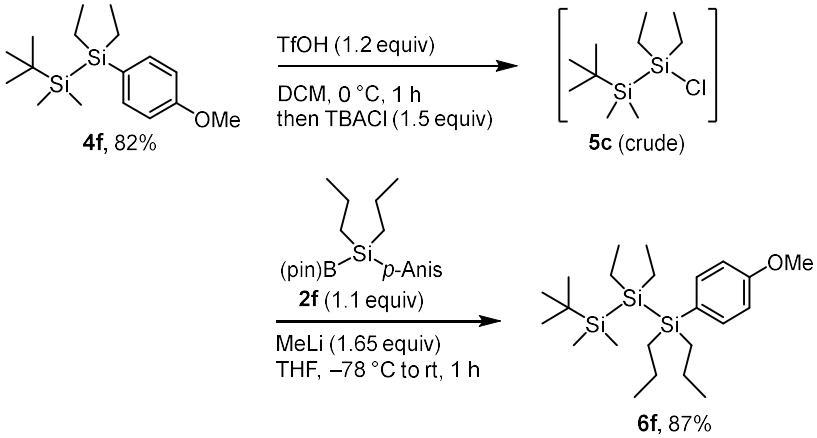
1-(*tert*-Butyl)-2,2-diethyl-2-(4-methoxyphenyl)-1,1-dimethyldisilane (4f).



This reaction was conducted with 153.9 mg (1.0 mmol) of chlorosilane **3c** according to the typical procedure for Si–Si coupling for **4f**. The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 97.5:1.5) as an eluent to afford the corresponding disilane **4f** in 82% isolated yield (257.5 mg, 0.83 mmol) as a colorless oil.

^{1}H NMR (401 MHz, $CDCl_3$, δ): 0.02 (s, 6H), 0.80 (s, 9H), 0.93–1.05 (m, 10H), 3.81 (s, 3H), 6.89 (d, J = 8.8 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): –4.9 (CH_3), 3.9 (CH_2), 8.1 (CH_3), 17.9 (*C*H), 27.6 (CH_3), 54.6 (CH_3), 113.5 (*C*H), 128.2 (*C*), 135.7 (*C*H), 159.8 (*C*). ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$, δ): –16.1, –8.8. HRMS-EI (m/z): $[M]^+$ calcd for $C_{17}H_{32}OSi_2$, 308.1992; found 308.1985.

1-(*tert*-Butyl)-2,2-diethyl-3-(4-methoxyphenyl)-1,1-dimethyl-3,3-dipropyltrisilane (6f).

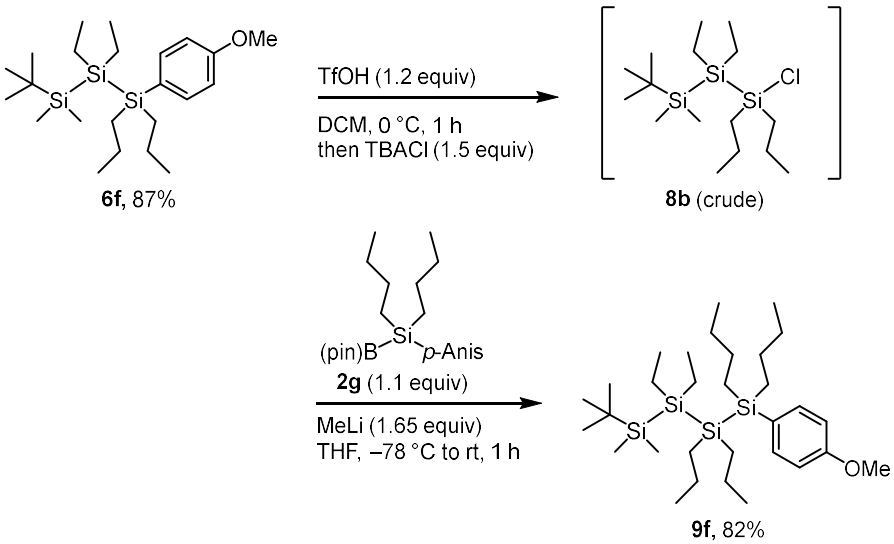


These reactions were conducted with 216.2 mg (0.7 mmol) of disilane **4f** according to the typical procedure for chlorination for **5c** and the typical procedure for Si–Si coupling for **4f**. The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 98.5:1.5) as an eluent to afford the corresponding trisilane **6f** in 87% isolated yield (258.6 mg, 0.61 mmol) as a colorless oil.

^{1}H NMR (392 MHz, $CDCl_3$, δ): –0.07 (s, 6H), 0.77–0.87 (m, 13H), 0.93–1.05 (m, 16H), 1.33–1.45 (m, 4H), 3.81 (s, 3H), 6.87 (d, J = 9.0 Hz, 2H), 7.36 (d, J = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): –3.7 (CH_3), 3.8 (CH_2), 10.3 (CH_3), 16.5 (CH_2), 18.3 (CH_2), 18.4 (*C*), 18.8 (CH_3), 27.8 (CH_3), 54.9 (CH_3), 113.4 (*C*H), 128.9 (*C*), 135.8 (*C*H), 159.7 (*C*). ^{29}Si{^{1}H} NMR (78 MHz, $CDCl_3$, δ): –37.3, –16.1, –4.5. HRMS-EI (m/z): $[M]^+$ calcd for $C_{23}H_{46}OSi_3$, 422.2856; found 422.2844.

4-(*tert*-Butyl)-1,1-dibutyl-3,3-diethyl-1-(4-methoxyphenyl)-4,4-dimethyl-2,2-dipropyltetrasilane

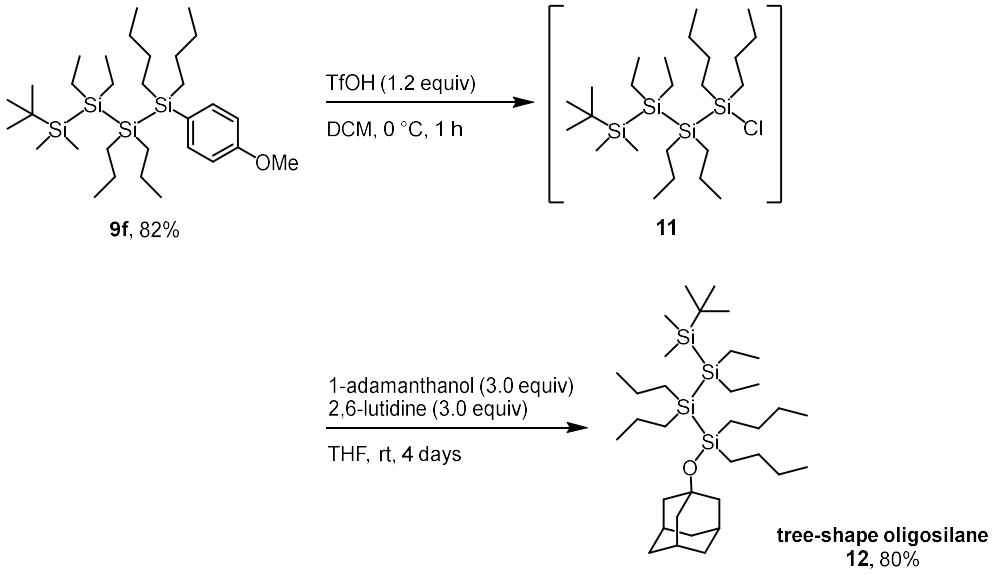
(9f).



These reactions were conducted with 189.6 mg (0.45 mmol) of trisilane **6f** according to the typical procedure for chlorination for **5c** and the typical procedure for Si–Si coupling for **4f**. The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 98.5:1.5) as an eluent to afford the corresponding tetrasilane **9f** in 82% isolated yield (207.5 mg, 0.37 mmol) as a colorless oil.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.02 (s, 6H), 0.65–0.82 (m, 8H), 0.83–1.06 (m, 31H), 1.24–1.42 (m, 12H), 3.81 (s, 3H), 6.88 (d, J = 9.0 Hz, 2H), 7.35 (d, J = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): –3.2 (CH_3), 4.8 (CH_2), 10.4 (CH_3), 13.3 (CH_3), 13.7 (CH_3), 15.8 (CH_2), 18.7 (*C*), 19.0 (CH_3), 20.5 (CH_2), 26.7 (CH_2), 27.0 (CH_2), 27.9 (CH_3), 54.9 (CH_3), 113.4 (*C*H), 129.0 (*C*), 135.8 (*C*H), 159.7 (*C*). ^{29}Si{^{1}H} NMR (78 MHz, $CDCl_3$, δ): –36.8, –31.4, –14.9, –4.3. HRMS-EI (m/z): $[M]^+$ calcd for $C_{31}H_{64}OSi_4$, 564.4034; found 564.4012.

{[(3s,5s,7s)-Adamantan-1-yl]oxy}-4-(*tert*-butyl)-1,1-dibutyl-3,3-diethyl-4,4-dimethyl-2,2-dipropyltetrasilane (12).

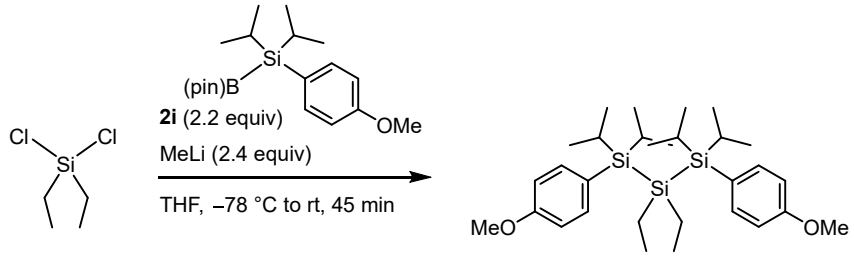


These reactions were conducted according to the typical procedure for chlorination for **5c** and a previous report.[12] Tetrasilane **9f** (56.8 mg, 0.1 mmol) was placed in a vial. The vial was sealed with a screw cap containing a Teflon®-coated rubber septum and connected to a vacuum/nitrogen manifold through a needle. It was evacuated and then backfilled with nitrogen. This cycle was repeated three times. After DCM (1.0 mL) was added to the vial via a syringe, the solution was allowed to cool at 0 °C. Then, TfOH (14 μL, 0.15 mmol, 1.5 equiv) was added dropwise to the mixture via a syringe. After the reaction mixture was stirred for 1 h at 0 °C, 1-adamantanol (46.7 mg, 0.30 mmol, 3.0 equiv) and 2,6-lutidine (35 μL, 0.30 mmol, 3.0 equiv) were added. After stirring for additional 4 days, the mixture was directly filtered through a silica-gel pad 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 (100:0 to 99:1) as an eluent to afford the corresponding product **12** (49.1 mg, 0.081 mmol, 80% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$, δ): 0.10 (s, 6H), 0.75–0.99 (m, 33H), 1.06 (t, J = 8.1 Hz, 6H), 1.23–1.46 (m, 12H), 1.59 (s, 6H), 1.74 (s, 6H), 2.09 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, δ): –3.0 (CH_3), 4.8 (CH_2), 10.6 (CH_3), 13.7 (CH_3), 16.1 (CH_2), 18.7 (C), 19.1 (CH_3), 20.3 (CH_2), 20.4 (CH_2), 26.4 (CH_2), 26.9 (CH_2), 28.0 (CH_3), 31.0 (CH), 36.3 (CH_2), 46.2 (CH_2), 72.3 (C). ^{29}Si{^{1}H} NMR (78 MHz, $CDCl_3$, δ): –38.5, –31.9, –4.2, 10.4. HRMS-FD (m/z): $[M]^+$ calcd for $C_{34}H_{72}OSi_4$, 608.4660; found 608.4681.

Iterative synthesis of heptasilane 16

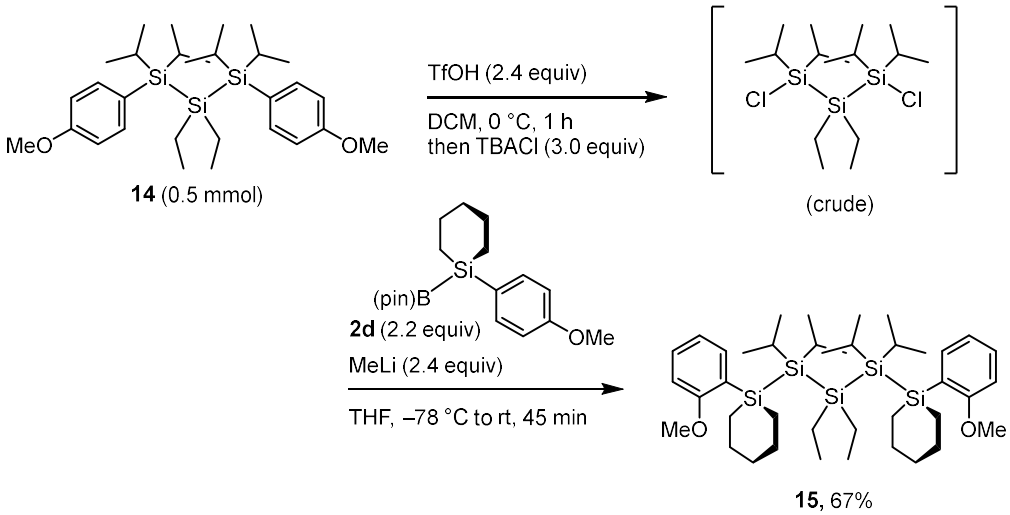
2,2-Diethyl-1,1,3,3-tetraisopropyl-1,3-bis(4-methoxyphenyl)trisilane (14).



This reaction was conducted according to the typical procedure for Si–Si coupling for **4f** with 155.9 mg (1.0 mmol) of dichlorosilane **13** and other reagents with double amounts. The crude product was purified by silica-gel column chromatography with hexane/EtOAc (100:0 to 99:1) as an eluent to afford the corresponding trisilane **14** in 65% isolated yield (343.3 mg, 0.65 mmol) as a colorless oil.

^{1}H NMR (399 MHz, $CDCl_3$, δ): 0.97–1.10 (m, 34H), 1.31 (sept, J = 7.4 Hz, 4H), 3.82 (s, 6H), 6.85 (d, J = 8.8 Hz, 4H), 7.28 (d, J = 8.8 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 4.9 (CH_2), 10.5 (CH_3), 14.0 (CH), 19.9 (CH_3), 20.2 (CH_3), 54.9 (CH_3), 113.2 (CH), 128.1 (C), 136.5 (CH), 159.6 (C). ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$, δ): –34.9, –8.1. HRMS-EI (m/z): $[M]^+$ calcd for $C_{30}H_{52}O_2Si_3$, 528.3275; found 528.3267.

1,1'-(2,2-Diethyl-1,1,3,3-tetraisopropyltrisilane-1,3-diyl)bis[1-(2-methoxyphenyl)silinane] (15).

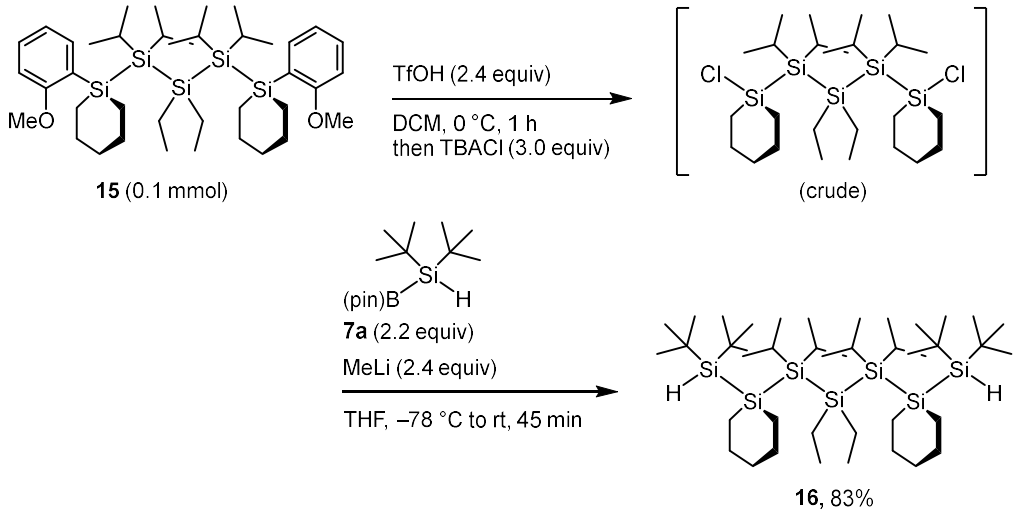


These reactions were conducted according to the typical procedure for chlorination for **5c** and the typical procedure for Si–Si coupling for **4f** with 261.8 mg (0.5 mmol) of trisilane **14** and other reagents with double amounts. The crude product was purified by silica-gel column chromatography with hexane/Et_2O (100:0 to 98.5:1.5) as an eluent to afford the corresponding pentasilane **15** in 67% isolated yield (240.2 mg, 0.33 mmol) as a crystalline solid.

^{1}H NMR (399 MHz, $CDCl_3$, δ): 0.81–0.99 (m, 14H), 1.02 (d, J = 7.2 Hz, 12H), 1.07 (d, J = 7.2 Hz, 12H), 1.14–1.40 (m, 10H), 1.46–1.64 (m, 6H), 1.84–1.94 (m, 4H), 3.74 (s, 6H), 6.78 (d, J = 7.6 Hz, 2H), 6.94 (t, J = 7.2 Hz, 2H), 7.31 (ddd, J = 1.9, 7.3, 8.0 Hz, 2H), 7.46 (dd, J = 1.8, 7.4 Hz, 2H). ^{13}C

NMR (100 MHz, $CDCl_3$, δ): 6.9 (CH_2), 11.1 (CH_3), 14.2 (*C*H), 15.3 (CH_2), 21.1 (CH_3), 21.4 (CH_3), 24.6 (CH_2), 30.2 (CH_2), 54.2 (CH_3), 109.2 (*C*H), 120.2 (*C*H), 125.4 (*C*), 130.1 (*C*H), 137.0 (*C*H), 164.4 (*C*). $^{29}Si\{^1H\}$ NMR (79 MHz, $CDCl_3$, δ): –22.9, –18.4, –16.6. HRMS-EI (m/z): $[M–^iPr]^+$ calcd for $C_{37}H_{65}O_2Si_5$, 681.3831; found 681.3815. mp: 129–131 °C.

1,1'-(2,2-Diethyl-1,1,3,3-tetraisopropyltrisilane-1,3-diyl)bis[1-(di-*tert*-butylsilyl)silinane] (16).



These reactions were conducted according to the typical procedure for chlorination for **5c** and the typical procedure for Si–Si coupling for **4f** with 72.6 mg (0.1 mmol) of pentasilane **15** and other reagents with double amounts. The crude product was purified by silica-gel column chromatography with hexane as an eluent to afford the corresponding heptasilane **16** in 83% isolated yield (66.3 mg, 0.083 mmol) as a crystalline solid.

^1H NMR (399 MHz, $CDCl_3$, δ): 1.06–1.37 (m, 80H), 1.49–1.66 (m, 8H), 1.72–1.82 (m, 2H), 2.01–2.11 (m, 4H), 3.84 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 8.19 (CH_2), 11.8 (*C*H), 14.3 (CH_2), 14.9 (CH_3), 22.0 (CH_3), 22.2 (CH_3), 22.4 (*C*), 26.7 (CH_2), 29.4 (CH_2), 31.6 (CH_3). $^{29}Si\{^1H\}$ NMR (119 MHz, $CDCl_3$, δ): –33.7, –18.0, –6.5, 0.1. HRMS-FD (m/z): $[M–H]^+$ calcd for $C_{42}H_{95}Si_7$, 795.5819; found 795.5820. mp: 175–178 °C.

SC-XRD analyses of 15 and 16

The molecular structures of **15** and **16** were confirmed by single-crystal X-ray diffraction analysis (Figures S1 and S2). X-Ray crystallographic data for **15** and **16** were summarized in Table S1 and S2.

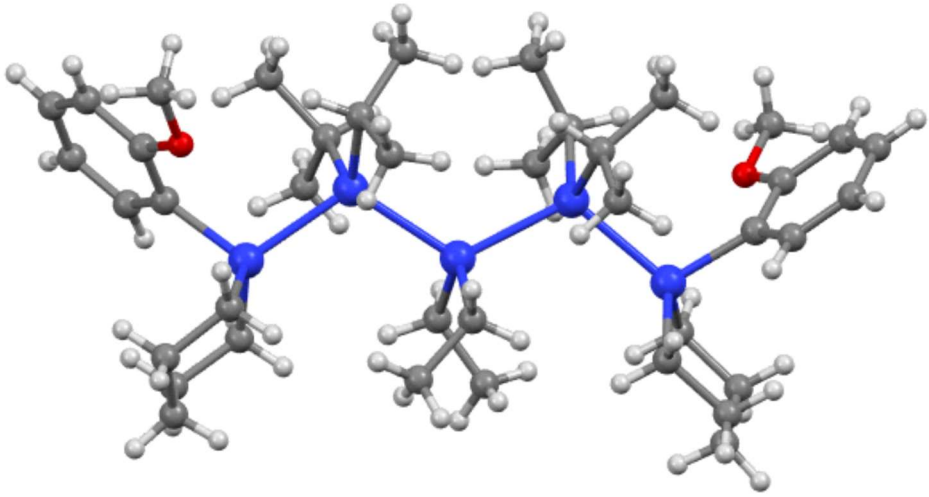


Figure S1. Molecular structure of **15** with thermal ellipsoids at 50% probability.

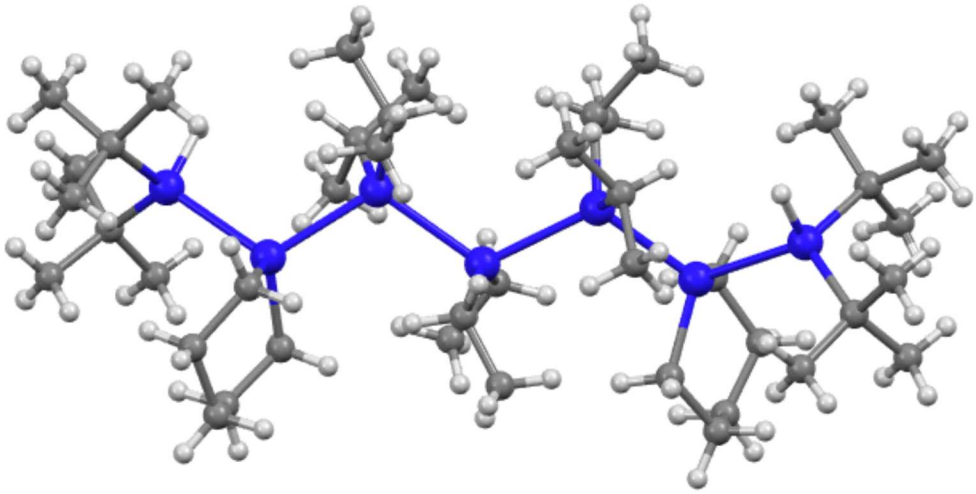


Figure S2. Molecular structure of **16** with thermal ellipsoids at 50% probability.

From these molecular images, the precise synthetic manner of the present iterative synthesis was clearly confirmed.

Table S1. Summary of X-ray crystallographic data for **15**.

CCDC	2202495
Empirical formula	$C_{40}H_{72}O_2Si_5$
Formula weight	725.43
Temperature/K	123
Crystal system	monoclinic
Space group	I2/a
a / Å	14.3510(17)
b / Å	9.4254(9)
c / Å	32.149(3)
α/°	90
β/°	101.529(10)
γ/°	90
Volume/Å^3	4260.8(8)
Z	4
ρ_{calc} g/cm^3	1.131
μ/mm^{-1}	1.793
F(000)	1592.0
Crystal size/mm^3	0.5×0.5×0.05
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	5.612 to 154.3
Index ranges	$-17 \leqq h \leqq 14$, $-11 \leqq k \leqq 11$, $-27 \leqq l \leqq 40$
Reflections collected	10984
Independent reflections	4269 [R_{int} = 0.0821, R_{sigma} = 0.0644]
Data/restraints/parameters	4269/75/280
Goodness-of-fit on F^2	1.072
Final R indexes [I>=2σ (I)]	R_1 = 0.1074, wR_2 = 0.2560
Final R indexes [all data]	R_1 = 0.1189, wR_2 = 0.2644
Largest diff. peak/hole / e Å^{-3}	0.84/–0.81

Table S2. Summary of X-ray crystallographic data for **16**.

CCDC	2202496
Empirical formula	$C_{42}H_{96}Si_7$
Formula weight	797.82
Temperature/K	123
Crystal system	Orthorhombic
Space group	Pbcn
a / Å	9.0346(4)
b / Å	15.7388(7)
c / Å	35.0171(18)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4979.2(4)
Z	8
ρ_{calc} g/cm^3	1.064
μ/mm^{-1}	0.218
F(000)	1784.0
Crystal size/mm^3	0.8×0.8×0.05
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.652 to 61.348
Index ranges	$-11 \leqq h \leqq 10$, $-22 \leqq k \leqq 18$, $-46 \leqq l \leqq 45$
Reflections collected	32703
Independent reflections	6279 [R_{int} = 0.0472, R_{sigma} = 0.0483]
Data/restraints/parameters	6279/0/260
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0534, wR_2 = 0.1301
Final R indexes [all data]	R_1 = 0.0728, wR_2 = 0.1398
Largest diff. peak/hole / e Å^{-3}	1.10/–0.35

References

1) Cullen, K. E.; Sharp. J. T. Reactions of diene-conjugated 1,3-dipolar intermediates: a versatile and efficient route to dibenz[c,e]azepines via benzonitrile o-arylbenzyl ylides. *J. Chem. Soc., Perkin Trans.* 1 **1993**, 2961–2967.

2) Franz, A. K.; DreyFuss, P. D.; Schreiber, S. L. Synthesis and Cellular Profiling of Diverse Organosilicon Small Molecules. *J. Am. Chem. Soc.* **2007**, *129*, 1020–1021.

3) West, R. Cyclic Organosilicon Compounds. I. Preparation of Cyclic Silanes. *J. Am. Chem. Soc.* **1954**, *76*, 6012–6014.

4) Takeuchi, T.; Shishido, R.; Kubota, K.; Ito, H. Synthesis of Hydrosilylboronates via the Monoborylation of a Dihydrosilane Si–H Bond and Their Application for the Generation of Dialkylhydrosilyl Anions. *Chem. Sci.* **2021**, *12*, 11799–11804.

5) Sturm, A. G.; Schweizer, J. I.; MeyerL.; Santowski, T.; Auner, N.; Holthausen, M. C. Lewis Base Catalyzed Selective Chlorination of Monosilanes. *Chem. Eur. J.* **2018**, *24*, 17796–17801.

6) Shishido, R.; Uesugi, M.; Takahashi, R.; Mita, T.; Ishiyama, T.; Kubota, K.; Ito, H. General Synthesis of Trialkyl- and Dialkylarylsilylboronates: Versatile Silicon Nucleophiles in Organic Synthesis. *J. Am. Chem. Soc.* **2020**, *142*, 14125–14133.

7) Kawachi, A.; Minamimoto, T.; Tamao, K. Boron-Metal Exchange Reaction of Silylboranes with Organometallic Reagents: A New Route to Arylsilyl Anions. *Chem. Lett.* **2001**, *30*, 1216–1217.

8) (a) Gilman, H.; Marshall, F. J. Cleavage of Some Organosilanes by Hydrogen Chloride. *J. Am. Chem. Soc.* **1949**, *71*, 2066–2069. (b) Benkeser, R. A.; Krysiak, H. R. The Hydrogen Chloride Cleavage of Some Trimethylarylsilanes. *J. Am. Chem. Soc.* **1953**, *75*, 4528–4531. (c) Uhlig, W. Silyl Triflates – Valuable Synthetic Materials in Organosilicon Chemistry. *Chem. Ber.* **1996**, *129*, 733–739. (d) Popp, F.; Nätscher, J. B.; Daiss, J. O.; Burschka, C.; Tacke, R. The 2,4,6-Trimethoxyphenyl Unit as a Unique Protecting Group for Silicon in Synthesis and the Silylation Potential of (2,4,6-Trimethoxyphenyl)silanes. *Organometallics* **2007**, *26*, 6014–6028.

9) (a) Voorhoeve,R. J. H. Organohalosilanes Precursors to Silicones. Elsevier Publishing Company, **1967**. (b) Uchida, H.; Kabe, Y.; Yoshino, K.; Kawamata, A.; Tsumuraya, T.; Masamune, S. General Strategy for the systematic Synthesis of Oligosiloxanes. Shilicone Dendrimers. *J. Am. Chem. Soc.* **1990**, *112*, 7077–7079. (c) Esteruelas, M. A.; Herrero, J.; Oliván, M. Dehalogenation of Hexachlorocyclohexanes and Simultaneous Chlorination of Triethylsilane Catalyzed by Rhodium and Ruthenium Complexes. *Organometallics* **2004**, *23*, 389–3897. (d) Varaprath, S.; Stutts, D. H. Utility of Trichloroisocyanuric Acid in the Efficient Chlorination of Silicon Hydrides. *J. Organomet. Chem.* **2007**, *692*, 1892–1897.

10) George M. V.; Peterson, D. J.; Gilman, H. Preparation of Silyl-and Germanylmetalic Compounds. *J. Am. Chem. Soc.* **1960**, *82*, 403–406.

11) (a) Rahman, N. A.; Fleming, I; Zwicky, A. B. Failure in Several Attempts to Prepare Arylsilyl-

lithium Reagents by the Gilman Cleavage of Disilanes with Lithium. *J. Chem. Res.*, *Miniprint* **1992**, 2401–2409. (b) Lee, T. W. Corey, E. J. (2-Methoxyphenyl)dimethylsilyl Lithium and Cuprate Reagents Offer Unique Advantages in Multistep Synthesis. *Org. Lett.* **2001**, *3*, 3337–3339.

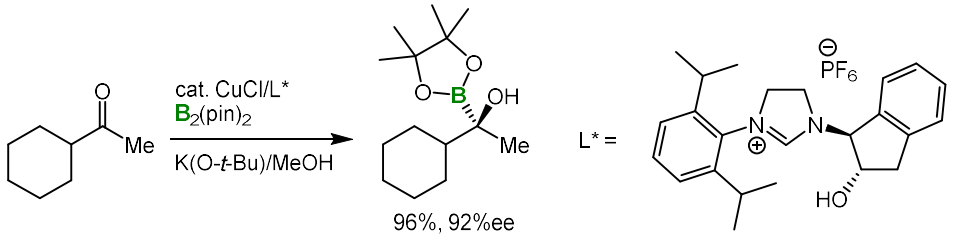
12) Matsubara, H.; Maegawa, T.; Kita, Y.; Yokoji, T.; Nomoto, A. Synthesis and Properties of Fluorous Benzoquinones and Their Application in Deprotection of Silyl Ethers. *Org. Biomol. Chem.* **2014**, *12*, 5442–5447.

IV Synthesis of α-Amino boronates via the Cu(I)-Catalyzed Enantioselective Hydroborylation of Ketimines

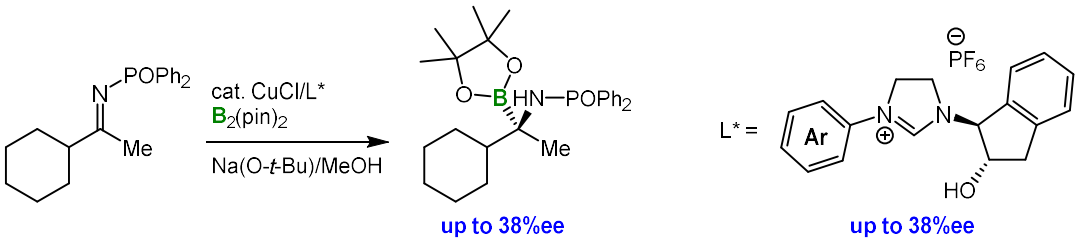
3.1: Introduction

α-Amino boronic acid derivatives are attracted as bioisosteres of α-amino acids in pharmaceutical area.[1,2] Due to the success of these organoboron compounds, preparation methods of them, especially enantioselective ones, are strongly required. In 1981, Matteson established a practical synthetic route to chiral α-amino boronic acids via a diastereoselective homologation of pinanediol-derived boronic esters with a subsequent stereospecific substitution using amine nucleophiles.[4] Recently, the asymmetric addition of a boron nucleophile to a C═N double bond is enthusiastically investigated as one of the most efficient method.[3] For example, Ellman and coworkers have reported that the copper(I)-catalyzed asymmetric borylation of aldimines and ketimines in the presence of a chiral auxiliary afford the corresponding chiral α-amino secondary and tertiary boronates with excellent stereoselectivity.[5] Although this pioneering study is remarkable, a stoichiometric amount of a chiral auxiliary is required in this approach, and only two ketimine substrates were investigated in this study. The development of a broadly applicable catalytic enantioselective method would thus be highly desirable. Fernández,[6] Lin,[7] Liao,[8] and Morken[9] have independently reported the catalytic enantioselective borylation of aldimines to afford the corresponding α-amino secondary boronates with high enantioselectivity. There have been many impressive advances in the development of enantioselective methods for the borylation of prochiral C═N double bonds. However, there are currently no catalytic methods available for the synthesis of chiral α-amino tertiary boronates from ketimines, and therefore, the development of an efficient method for the enantioselective nucleophilic borylation of ketimines would be highly attractive. Such a method can be expected to significantly facilitate the discovery of new pharmaceutically active α-amino tertiary boronic acid derivatives that are otherwise difficult to synthesize.[10–12] The main challenge in the development of such a method is that ketimines, especially dialkyl ketimines, exhibit relative to aldimines a much smaller degree of steric contrast between the substituents attached to their imino group. Indeed, there have only been a limited number of reports on the enantioselective addition of dialkyl ketimines.[13]

Ito have previously reported the first enantioselective borylation of dialkyl ketones catalyzed by Cu(I) complex (scheme 1).[14] Due to small differences between substituents compared to aldimines, achieving high enantioselectivity of enantioselective borylation of ketimines has been difficult. Ito overcame this problem with NHC ligand with alcohol moiety. Encouraged by this success, I started the investigation of the enantioselective borylation of dialkyl ketimines using a copper(I)/chiral NHC catalyst. However, NHC ligands with alcohol moiety resulted in no selectivity or low selecticvity (Scheme 2).



Scheme 1. Enantioselective borylations of ketones with the Cu(I)/chiral NHC catalyst reported by Ito.



Scheme 2. Enantioselective borylations of ketimines with the Cu(I)/chiral NHC catalyst reported by Ito.

In order to find a suitable ligand, I conducted computational analysis of transition states. I proposed the reason of enantioselectivity is the steric repulsion between bulky phosphoryl protecting group on the N atom and ligand. From this idea, I came up with NHC ligands with a large substituent to interact with protecting group of substrates. Pleasingly, a NHC ligand I expected resulted in excellent enantioselectivity (up to 99% ee). Furthermore, a boryl peptide was synthesized via simple condensation reaction between an obtained α-Amino boronate and L-alanine with perfect enantiospecificity.

3.2: Results and Discussion

I initially conducted computational study of the Cu(I)-catalyzed borylation with NHC ligand. I show the proposed catalytic cycle of this reaction (figure 1). In this reaction, boryl cuplation into C=N bond is the enantioselectivity-determining step. Thus, I analyzed this transition state with DFT calculation (figure 2). In the pathway to form *S* isomer, I found that the phosphoryl protecting group closed to a substituent of NHC ligand, while there is no such steric interaction in the pathway to *R*-isomer. As results, the pathway to *S*-isomer is more unstable than one of *R*-isomer (+9.5 kcal/mol). Notably, such energy difference should be excellent enantioselectivity, but no selectivity was observed in the real reaction. I guess the reason of this large energy difference is the over-estimate of the steric repulsion between substrate and K ion. From this result, I determined the ligand using NHC without alcohol moiety to exclude inonic interactions. Further, I focused on the steric repulsion between ligand and large phosphoryl protecting group. If this steric repulsion can be enhanced in minor pathway, the enantioselectivity would be improved. Therefore, I proposed a guideline of ligand for this reaction

(figure 3). For the stercic repulsion with protecting group, NHC ligands should have large substituents in first quadrant. To satisfied this requirement, I focused on NHCs with triazole-core because they have a large substituents to first quadrant.

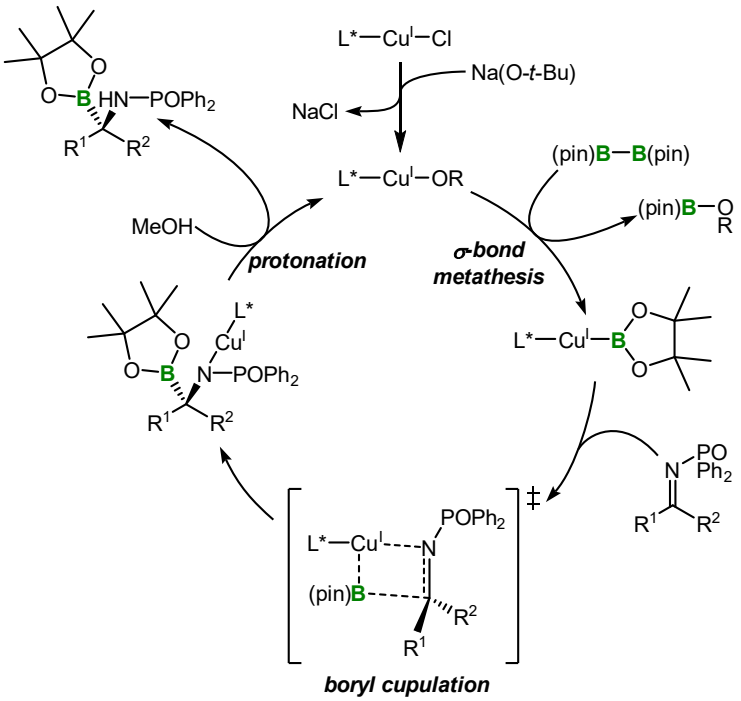


Figure 1. Proposed catalytic cycle of the Cu(I)-catalyzed borylation of ketimines.

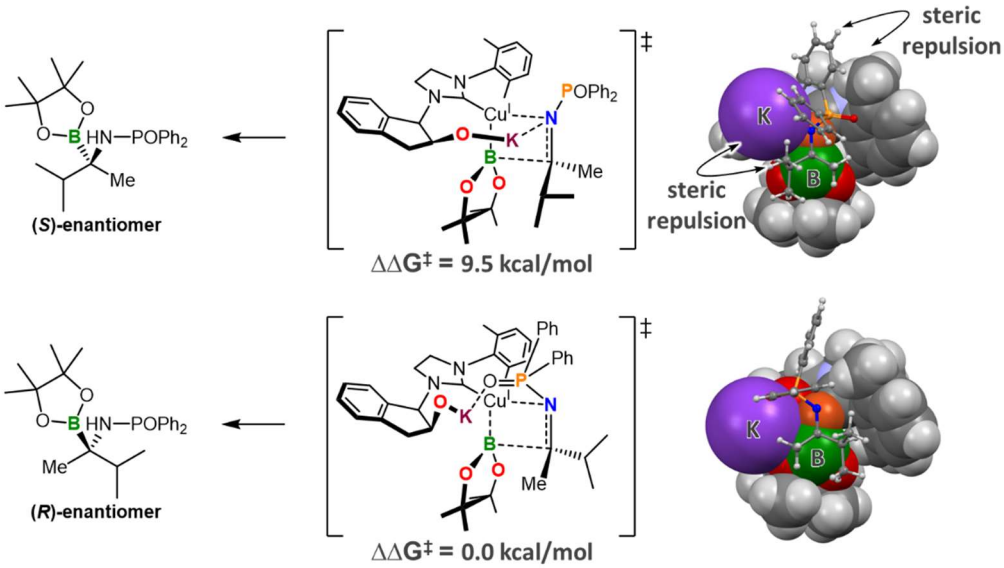


Figure 2. Results of DFT calculations of transition states.

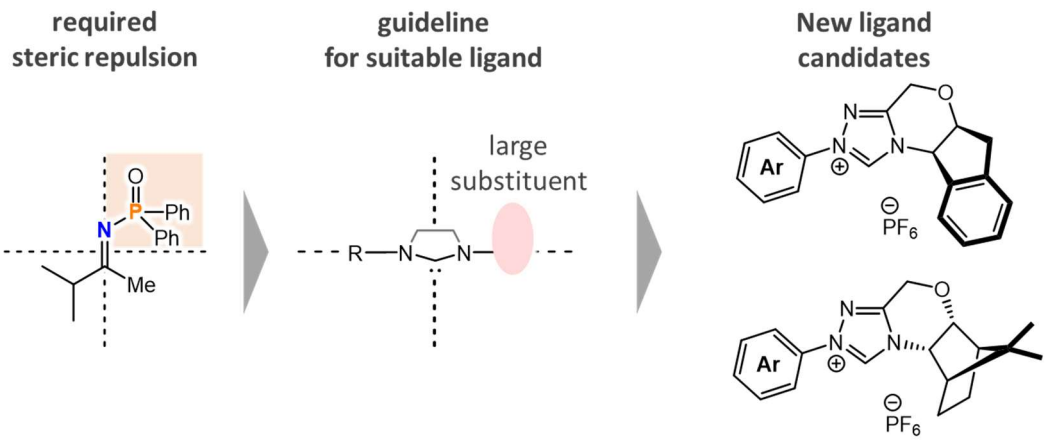
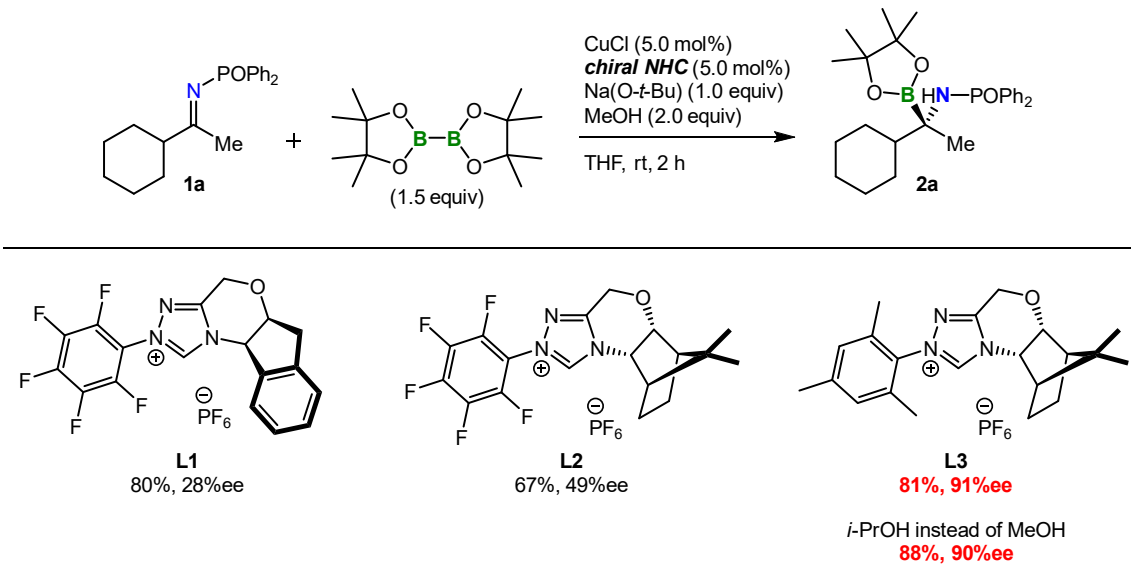


Figure 3. Guideline of NHC ligand for enantioselective borylation of ketim.

Next, I tested NHCs with triazole-cores (table 1). As expected, a triazole NHC **L3** with mestyl and camphor moiety resulted in high enantioselectivity (91%ee). Although Other NHCs **L2** and **L3** with pentafluorophenyl also gave product in good to high yields, enantioselectivities were low (28% amd 49%). Furthermore, the use of *i*-PrOH instead of MeOH as proton source improve the yield without significant reducing of enantioselectivity (88%, 99%ee).

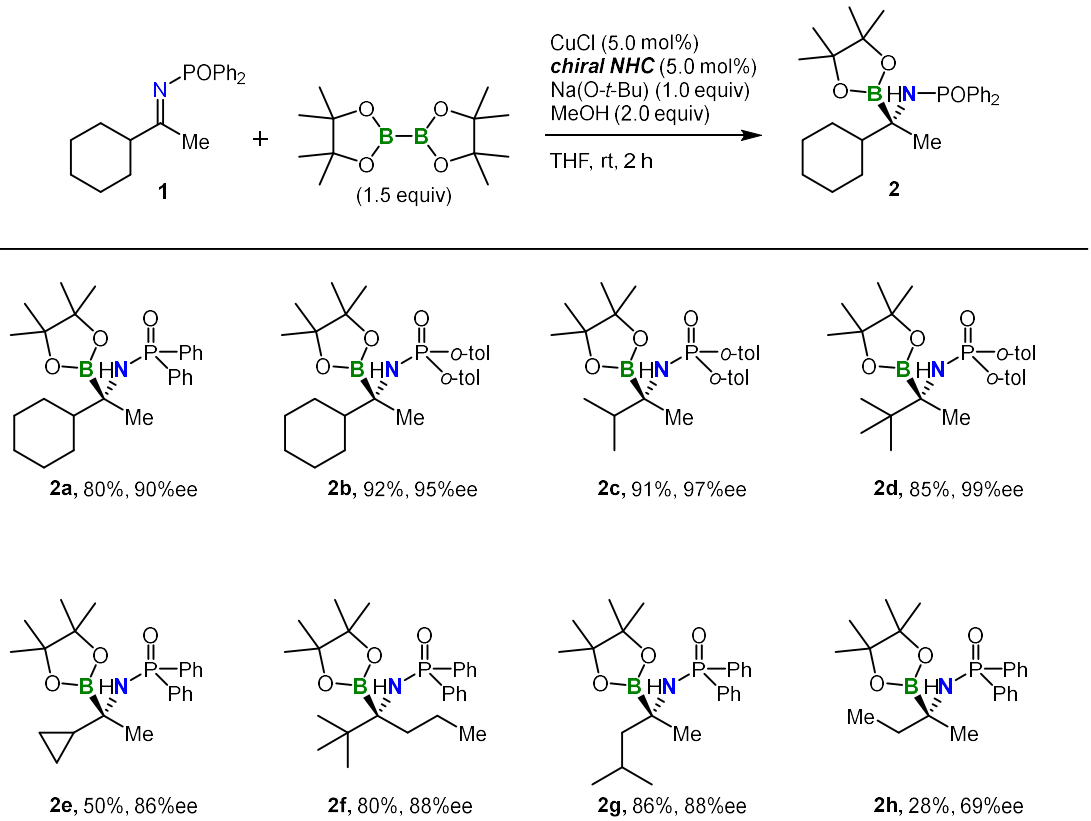
Table 1. Borylation with NHCs with triazole-core.



With the found NHC, I investigated the substrate scope of this borylation reaction (table 2). Larger protecting group (di-*o*-torylphosphoryl) improved enantioselectivity (**2b**, 92%, 95%ee), indicating the steric repulsion between protecting group and ligand expected by calsulation is one of the reason of enantioselectivity. *i*-Pr substituents also acceptable with high enantioselectivity (**2c**, 91%, 97%ee).

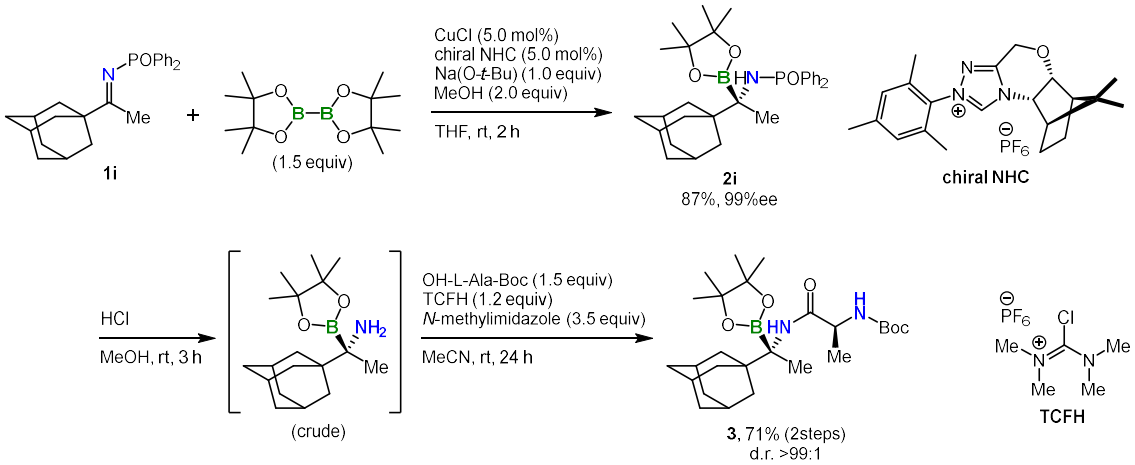
Bulky *t*-butyl group produced the product with almost perfect enantioselectivity (**2d**, 85%, 99%ee). Ketimines with low steric bias between substituents were tested. Small cyclopropyl substituent also gave the product with high selectivity (**2e**, 50%, 86%). Longer alkyl chain instead of Me afforded the product with high selectivity (**2f**, 80%, 88%ee). Ketimines with less steric substituents biases also resulted in good to high selectivities [(**2g**, 86%, 88%ee) and (**2h**, 28%, 69%ee)]. I also discovered that aromatic ketimine 1o was converted into the corresponding simple reduction product (62%) under the optimized conditions and the desired borylation product 3o was not detected. The reduction byproduct might be formed via the in situ protodeboration by i-PrOH.

Table 2. Substrate scope of enantioselective borylation of ketimines.



The enantioenriched α-amino tertiary boronates prepared in the present study can be employed for the synthesis of biologically active peptidyl boronic acid derivatives.[1] I conducted a preliminary investigation of amide-bond-forming condensations using the obtained chiral aminoboronates (Scheme 3). First, adamantly substituted ketimine was converted to the corresponding α-amino tertiary boronates by the present enantioselective borylation (**2i**, 87%, 99%ee). After the treatment with HCl to cleave the N-DPP protecting group, subsequent condensation with a Boc-protected alanine proceeded smoothly to form the corresponding peptidylboronic acid derivative in good yield (**3**, 71%,

d.r. > 99:1).[18] This method, which was recently developed by Beutner and coworkers, uses N,N,N',N'-tetramethylchloroformamidinium hexafluorophate (TCFH) and N-methylimidazole (NMI).[19] Other commonly used condensing reagents did not provide the desired product. Since several boryl substituted peptides have bioactivity and used as drugs,[1] this result supports the utility of the present asymmetric borylation.



Scheme 3. Synthesis of peptide boronic acids derivatives from obtained chiral α-amino boronates.

3.3: Conclusion

In summary, I have developed the enantioselective borylation of ketimines using a copper(I)/chiral NHC complex catalyst. The suitable chiral NHC ligand was found by the guideline proposed by computational analysis. Although acyclic dialkyl ketimines are generally difficult substrates for catalytic enantioselective reactions, this method provides facile access to corresponding chiral α-amino tertiary boronates with unprecedented enantioselectivity (up to 99% ee). The synthetic utility of this protocol was demonstrated by the synthesis of chiral peptidylboronic acid derivatives that bear bulky aliphatic substitutes, which are difficult to access by other means. I, therefore, expect that this work will provide a platform for the discovery of novel α-aminoboronic acid derivatives with unique biological activity.

3.4: References

(1) For selected reviews on medicinal applications of α-aminoboronates, see: (a) Diaz, D. B.; Yudin, A. K. The Versatility of Boron in Biological Target Engagement. *Nat. Chem.* **2017**, *9*, 731−742. (b) Touchet, S.; Carreaux, F.; Carboni, B.; Bouillon, A.; Boucher, J. L. Aminoboronic Acids and Esters: From Synthetic Challenges to the Discovery of Unique Classes of Enzyme Inhibitors. *Chem. Soc. Rev.* **2011**, *40*, 3895−3914. (c) Smoum, R.; Rubinstein, A.; Dembitsky, V. M.; Srebnik, M. Boron Containing Compounds as Protease Inhibitors. *Chem. Rev.* **2012**, *112*, 4156−4220. (d)

Dembitsky, V. M.; Srebnik, N. Synthesis and Biological Activity of α-Aminoboronic Acids, Amine-Carboxyboranes and Their Derivatives. *Tetrahedron* **2003**, *59*, 579−593.

(2) For selected reviews on biological applications of boroncontaining small molecules, see: (a) Adamczyk-Wozniak, A.; Borys, K. M.; Sporzynski, A. Recent Developments in the Chemistry and Biological Applications of Benzoxaboroles. *Chem. Rev.* **2015**, *115*, 5224−5247. (b) Baker, S. J.; Ding, C.; Akama, T.; Zhang, Y.; Hernandez, V.; Xia, Y. Therapeutic Potential of Boron-Containing Compounds. *Future Med. Chem.* **2009**, *1*, 1275−1288. (c) Trippier, P. C.; McGuigan, C. Boronic Acids in Medicinal Chemistry: Anticancer, Antibacterial and Antiviral Applications. *MedChemComm* **2010**, *1*, 183−198. (d) Baker, S.; Tomsho, J. W.; Benkovic, S. J. BoronContaining Inhibitors of Synthetases. *Chem. Soc. Rev.* **2011**, *40*, 4279−4285.

(3) For selected reviews on the synthesis of α-aminoboronates, see: (a) Andrés, P.; Ballano, G.; Calaza, M. I.; Cativiela, C. Synthesis of αAminoboronic Acids. *Chem. Soc. Rev.* **2016**, *45*, 2291−2307. (b) Š terman, A.; Sosic, I.; Gobec, S.; Casar, Z. Synthesis of Aminoboronic Acid Derivatives: An Update on Recent Advances. *Org. Chem. Front.* **2019**, *6*, 2991−2998.

(4) Matteson, D. S.; Sadhu, K. M.; Lienhard, G. E. R-1-Acetamido-2-phenylethaneboronic Acid. A Specific Transition-State Analog for Chymotrypsin. *J. Am. Chem. Soc.* **1981**, *103*, 5241−5242.

(5) (a) Buesking, A. W.; Bacauanu, V.; Cai, I.; Ellman, J. A. Asymmetric Synthesis of Protected α-Amino Boronic Acid Derivatives with an Air- and Moisture-Stable Cu(II) Catalyst. *J. Org. Chem.* **2014**, *79*, 3671−3677. (b) Beenen, M. A.; An, C.; Ellman, J. A. Asymmetric Copper-Catalyzed Synthesis of α-Amino Boronate Esters From N-*tert*-Butanesulfinyl Aldimines. *J. Am. Chem. Soc.* **2008**, *130*, 6910− 6911.

(6) Solé, C.; Gulyás, H.; Fernández, E. Asymmetric Synthesis of αAmino Boronate Esters via Organocatalytic Pinacolboryl Addition to Tosylaldimines. *Chem. Commun.* **2012**, *48*, 3769−3771.

(7) Zhang, S.-S.; Zhao, Y.-S.; Tian, P.; Lin, G.-Q. Chiral NHC/ Cu(I)-Catalyzed Asymmetric Hydroboration of Aldimines: Enantioselective Synthesis of α-Amido Boronic Esters. *Synlett* **2013**, *24*, 437− 442.

(8) Wang, D.; Cao, P.; Wang, B.; Jia, T.; Lou, Y.; Wang, M.; Liao, J. Copper(I)-Catalyzed Asymmetric Pinacolboryl Addition of N-BocImines Using a Chiral Sulfoxide−Phosphine Ligand. *Org. Lett.* **2015**, *17*, 2420−2423.

(9) Hong, K.; Morken, J. P. Catalytic Enantioselective One-Pot Amino-borylation of Aldehydes: A Strategy for Construction of Nonracemic α-Amino Boronates. *J. Am. Chem. Soc.* **2013**, *135*, 9252−9254.

(10) For the synthesis of chiral α-amino tertiary boronates via enantioselective hydroboration of enamides, see: (a) Hu, N.; Zhao, G.; Zhang, Y.; Liu, X.; Li, G.; Tang, W. Synthesis of Chiral α-Amino Tertiary Boronic Esters by Enantioselective Hydroboration of α-Arylenamides. *J. Am. Chem. Soc.* **2015**, *137*, 6746−6749. (b) Bai, X.- Y.; Zhao, W.; Sun, X.; Li, B. J. Rhodium-Catalyzed

Regiodivergent and Enantioselective Hydroboration of Enamides. *J. Am. Chem. Soc.* **2019**, *141*, 19870−19878.

(11) For the synthesis of chiral α-amino tertiary boronates via multicomponent coupling involving indolylboron ate complexes, see: (a) Panda, S.; Ready, J. M. Palladium Catalyzed Asymmetric ThreeComponent Coupling of Boronic Esters, Indoles, and Allylic Acetates. *J. Am. Chem. Soc.* **2017**, *139*, 6038−6041. (b) Das, S.; Daniliuc, C. G.; Studer, A. Lewis Acid Catalyzed Stereoselective Dearomative Coupling of Indolylboron Ate Complexes with Donor−Acceptor Cyclopropanes and Alkyl Halides. *Angew. Chem., Int. Ed.* **2018**, *57*, 4053−4057.

(12) For the synthesis of chiral α-amino tertiary boronates via enantiospecific electrophilic borylation, see: Qi, Q.; Yang, X.; Fu, X.; Xu, S.; Negishi, E. Highly Enantiospecific Borylation for Chiral αAmino Tertiary Boronic Esters. *Angew. Chem., Int. Ed.* **2018**, *57*, 15138−15142.

(13) For selected reviews on the enantioselective addition of dialkyl ketimines, see: (a) Riant, O.; Hannedouche, J. Asymmetric Catalysis for the Construction of Quaternary Carbon Centres: Nucleophilic Addition on Ketones and Ketimines. *Org. Biomol. Chem.* **2007**, *5*, 873−888. (b) Shibasaki, M.; Kanai, M. Asymmetric Synthesis of Tertiary Alcohols and α-Tertiary Amines via Cu-Catalyzed C−C Bond Formation to Ketones and Ketimines. *Chem. Rev.* **2008**, *108*, 2853−2873. (c) Kobayashi, S.; Mori, Y.; Fossey, J. S.; Salter, M. M. Catalytic Enantioselective Formation of C−C Bonds by Addition to Imines and Hydrazones: A Ten-Year Update. *Chem. Rev.* **2011**, *111*, 2626−2704. (d) Jia, T.; Cao, P.; Liao, J. Enantioselective Synthesis of Gem-Diarylalkanes by Transition Metal-Catalyzed Asymmetric Arylations (TMCAAr). *Chem. Sci.* **2018**, *9*, 546−559. (e) Quan, M.; Wu, L.; Yang, G.; Zhang, W. Pd(II), Ni(II) and Co(II)-Catalyzed Enantioselective Additions of Organoboron Reagents to Ketimines. *Chem. Commun.* **2018**, *54*, 10394−10404.

(14) Kubota, K.; Osaki, A.; Jin, M.; Ito, H. Copper(I)-Catalyzed Enantioselective Nucleophilic Borylation of Aliphatic Ketones: Synthesis of Enantioenriched Chiral Tertiary α-Hydroxyboronates. *Angew. Chem., Int. Ed.* **2017**, *56*, 6646−6650.

(15) The ligand (*S*,*S*)-**L4** was originally developed by Shintani, Hayashi, and co-workers: Shintani, R.; Takatsu, K.; Takeda, M.; Hayashi, T. Copper-Catalyzed Asymmetric Allylic Substitution of Allyl Phosphates with Aryl- and Alkenylboronates. *Angew. Chem., Int. Ed.* **2011**, *50*, 8656−8659.

(16) Kubota, K.; Yamamoto, E.; Ito, H. Copper(I)-Catalyzed Enantioselective Nucleophilic Borylation of Aldehydes: An Efficient Route to Enantiomerically Enriched α-Alkoxyorganoboronate Esters. *J. Am. Chem. Soc.* **2015**, *137*, 420−424.

(17) (a) Lee, K.-S.; Zhugralin, A. R.; Hoveyda, A. H. Efficient C−B Bond Formation Promoted by N-Heterocyclic Carbenes: Synthesis of Tertiary and Quaternary B-Substituted Carbons Through Metal-Free Catalytic Boron Conjugate Additions to Cyclic and Acyclic α,β-Unsaturated Carbonyls. *J. Am. Chem. Soc.* **2009**, *131*, 7253−7255. (b) Wu, H.; Radomkit, S.; O'Brien, J. M.; Hoveyda, A. H. Metal-Free Catalytic Enantioselective C−B Bond Formation: (Pinacolato)boron Conjugate

Additions to α,β-Unsaturated Ketones, Esters, Weinreb Amides, and Aldehydes Promoted by Chiral N-Heterocyclic Carbenes. *J. Am. Chem. Soc.* **2012**, *134*, 8277−8285.

(18) I attempted a deprotection of the pinacol ester of 4a by the treatment with NaIO4, which afforded the corresponding boroxine in high yield (70%). The corresponding boronic acid was not detected.

(19) Beutner, G. L.; Young, I. S.; Davies, M. L.; Hickey, M. R.; Park, H.; Stevens, J. M.; Ye, Q. TCFH−NMI: Direct Access to N-Acyl Imidazoliums for Challenging Amide Bond Formations. *Org. Lett.* **2018**, *20*, 4218−4222.

3.5: Experimental Details

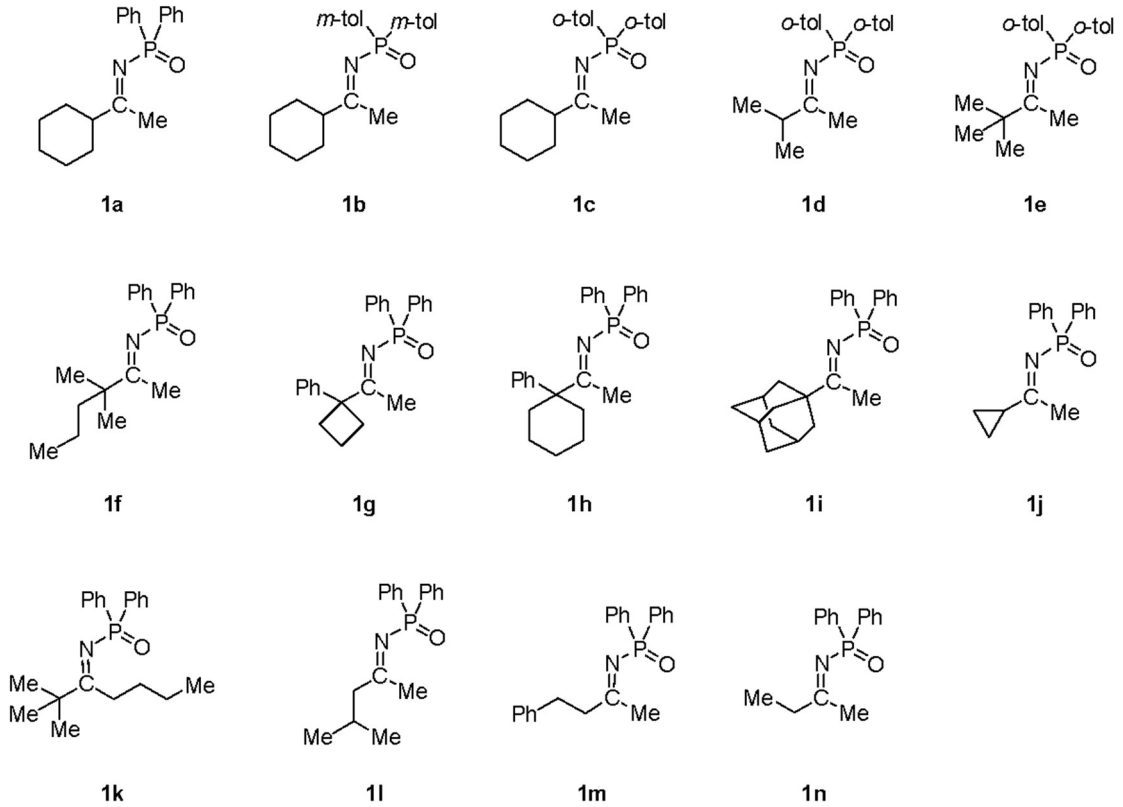
General and Materials

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 reactions were purchased from commercial suppliers, degassed via three freeze-pump-thaw cycles, and further dried over molecular sieves (MS4A) prior to use. 1,3-Dicyclohexylimidazolium chloride (ICy·HCl, >98.0%) and K(O-*t*-Bu) (>97.0%) purchased from Tokyo Chemical Industry Co. The chiral *N*-heterocyclic carbene (NHC) ligand precursors (*R*,*S*)-**L1,** (*R*,*S*)-**L2,** (*R*,*S*)-**L3** were purchased from Strem Chemicals, Inc. [(*S*,*S*)-**L4**-(*S*,*S*)-**L7**[1], (*S*,*S*)-**L8**[2], (*S*,*S*)-**L9**[2] and (*R*,*R*)-**L10**[3]] were synthesized according to the literature. (*R*)-DTBM-SEGPHOS [(*R*)-**L11**] was purchased from Tokyo Chemical Industry Co. (*R*,*R*)-Quinox P* [(*R*,*R*)-**L12**] was obtained from Nippon Chemical Industrial Co. 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 (^{1}H: 392 or 396 MHz, ^{13}C: 99 or 100 MHz), and JNM-ECA600 (^{13}C: 151 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. $BF_3 \cdot Et_2O$ was used as an external standard for ^{11}B NMR analysis. D_3PO_4 in D_2O was used as an external standard for ^{31}P NMR analysis. Multiplicity was reported as follows: s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, 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 an FID detector. Recycle preparative gel chromatography (GPC) was conducted with JAILC-9101 using $CHCl_3$ as an eluent. FTIR spectra were recorded on a JASCO FT IR 4700 spectrometer. Single crystal X-ray structural analyses were carried out on an XtaLAB PRO MM007 diffractometer using graphite monochromated 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.

Substrate Synthesis

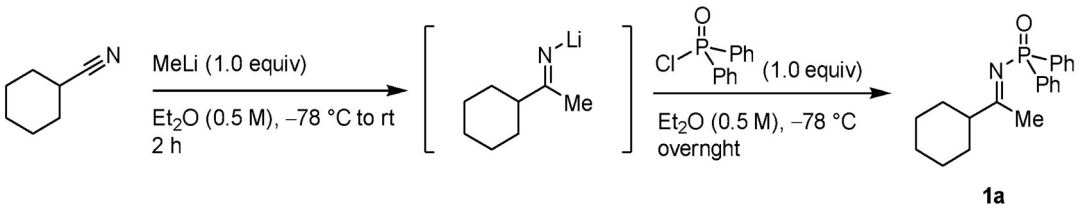
List of the substrate used in this study.



The spectroscopic data of **1a** and **1e** were consistent with literature values.[4,5] The *E*/*Z* configurations of other substrates were deduced relative to these compounds.

Procedure A.

(*E*)-*N*-(1-Cyclohexylethylidene)-*P*,*P*-diphenylphosphinic amide (1a).

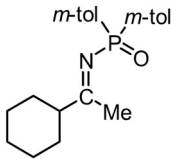


MeLi (Et_2O 1.1 M) (9.1 mL, 10 mmol, 1.0 equiv) was added dropwise to a suspension of cyclohexanecarbonitrile (1.2 mL, 10 mmol, 1.0 equiv) in Et_2O (20 mL) at −78 °C under nitrogen atmosphere. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. Then, the reaction mixture was cooled down to −78 °C, and diphenyl phosphinic chloride (1.91 mL, 10 mmol,

1.0 equiv) was added dropwise to the mixture. The reaction mixture was kept at −78 °C and stirred overnight. The mixture was directly filtered through a short silica-gel column with EtOAc as an eluent, and then the resultant solution was concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography with EtOAc/Hex eluent (100:0 to 30:70). Further purification was conducted by GPC to afford the corresponding ketimine **1a** (280.5 mg, 0.86 mmol, 9% yield) as a white solid. The spectroscopic data were matched in those reported.[4]

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.17–1.46 (m, 5H), 1.71–1.95 (m, 5H), 2.35–2.43 (m, 1H), 2.47 (d, *J* = 1.6 Hz, 3H), 7.39–7.47 (m, 6H), 7.89–7.94 (m, 4H). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{20}H_{24}NOP$, 325.1596; found, 325.1598.

(*E*)-*N*-(1-Cyclohexylethylidene)-*P*,*P*-di-*m*-tolylphosphinic amide (1b).

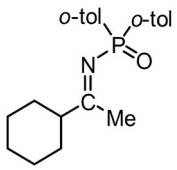


1b

1b was prepared from the corresponding nitrile according to procedure A. The product **1b** was obtained in 26% yield (373.7 mg, 1.1 mmol, yellow oil) from the corresponding nitrile (4.0 mmol).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.19–1.49 (m, 5H), 1.70–1.94 (m, 5H), 2.36 (s, 6H), 2.38–2.42 (m, 1H), 2.45 (d, *J* = 2.4 Hz, 3H), 7.24–1.34 (m, 4H), 767–7.76 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 21.5 (CH_3), 25.2 (d, *J* = 13.4 Hz, CH_3), 25.99 (CH_2), 26.04 (CH_2), 30.2 (CH_2), 52.1 (d, *J* = 20.1 Hz, *C*H), 128.2 (d, *J* = 13.4 Hz, *C*H), 128.7 (d, *J* = 8.6 Hz, *C*H), 132.0 (d, *J* = 5.8 Hz, *C*H), 132.1 (*C*H), 134.9 (d, *J* = 130.3 Hz, *C*), 138.1 (d, *J* = 13.4 Hz, *C*), 195.4 (d, *J* = 11.5 Hz, *C*). ^{31}P{^{1}H} NMR (159 MHz, $CDCl_3$, δ): 18.4. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{22}H_{28}NOP$, 353.1909; found, 353.1908. IR (neat, cm^{-1}): 1187(P=O), 1652(C=N).

(*E*)-*N*-(1-Cyclohexylethylidene)-*P*,*P*-di-*o*-tolylphosphinic amide (1c).



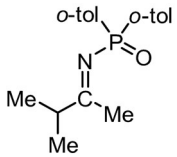
1c

1c was prepared from the corresponding nitrile according to procedure A. The product **1c** was obtained in 4% yield (187.4 mg, 0.50 mmol, white solid) from the corresponding nitrile (13.6 mmol).

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.22–1.39 (m, 5H), 1.70–1.94 (m, 5H), 2.30 (s, 6H), 2.34–2.39 (m, 1H), 2.41 (d, *J* = 1.8 Hz, 3H), 7.14–7.17 (m, 2H), 7.28–7.30 (m, 2H), 7.35–7.41 (m, 2H), 8.08 (ddd, *J*

= 1.0, 7.8, 15.7 Hz, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 21.7 (d, *J* = 2.9 Hz, *C*H$_3$), 25.3 (d, *J* = 14.2 Hz, *C*H$_3$), 26.1 (*C*H$_2$), 30.3 (*C*H$_2$), 52.6 (d, *J* = 20.8 Hz, *C*H), 125.4 (d, *J* = 12.3 Hz, *C*H), 131.4 (d, *J* = 12.3 Hz, *C*H), 131.6 (d, *J* = 1.9 Hz, *C*H), 132.6 (d, *J* = 123.8 Hz, *C*), 133.4 (d, *J* = 9.5 Hz, *C*H), 141.5 (d, *J* = 10.3 Hz, *C*), 196.3 (d, *J* = 11.3 Hz, *C*). ^{31}P{^{1}H} NMR (159 MHz, $CDCl_3$, δ): 20.3. HRMS-EI (*m*/*z*): [M]$^+$ calcd for $C_{22}H_{28}NOP$, 353.1909; found, 353.1903. mp 95–100 °C. IR (neat, cm^{-1}): 1186(P=O), 1652(C=N).

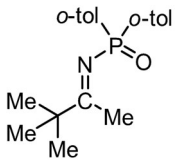
(*E*)-*N*-(3-Methylbutan-2-ylidene)-*P*,*P*-di-*o*-tolylphosphinic amide (1d).



1d

1d was prepared from the corresponding nitrile according to procedure A. The product **1d** was obtained in 9% yield (146.2 mg, 0.45 mmol, white solid) from the corresponding nitrile (5.0 mmol). ^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.17 (d, *J* = 6.7 Hz, 6H), 2.30 (s, 6H), 2.42 (d, *J* = 2.0 Hz, 3H), 2.72 (h, *J* = 6.9 Hz, 1H), 7.14–7.17 (m, 2H), 7.26–7.30 (m, 2H), 7.35–7.39 (m, 2H), 8.09 (ddd, *J* = 1.4, 5.9, 13.7 Hz, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 19.9 (*C*H$_3$), 21.6 (d, *J* = 3.8 Hz, *C*H$_3$), 24.9 (d, *J* = 14.2 Hz, *C*H$_3$), 42.4 (d, *J* = 20.8 Hz, *C*H), 125.4 (d, *J* = 11.3 Hz, *C*H), 131.4 (d, *J* = 12.3 Hz, *C*H), 131.6 (d, *J* = 1.9 Hz, *C*H), 132.5 (d, *J* = 124.6 Hz, *C*), 133.4 (d, *J* = 8.5 Hz, *C*H), 141.5 (d, *J* = 10.4 Hz, *C*), 196.9 (d, *J* = 11.4 Hz, *C*). ^{31}P{^{1}H} NMR (159 MHz, $CDCl_3$, δ): 20.4. HRMS-EI (*m*/*z*): [M]$^+$ calcd for $C_{19}H_{24}NOP$, 313.1596; found, 313.1593. mp 108–111 °C. IR (neat, cm^{-1}): 1188(P=O), 1658(C=N).

(*E*)-*N*-(3,3-Dimethylbutan-2-ylidene)-*P*,*P*-di-*o*-tolylphosphinic amide (1e).

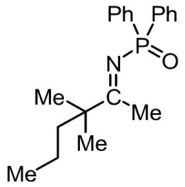


1e

1e was prepared from the corresponding nitrile according to procedure A. The product **1e** was obtained in 32% yield (414.6 mg, 1.27 mmol, white solid) from the corresponding nitrile (4.0 mmol). The spectroscopic data were matched in those reported.[5]

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.22 (s, 9H), 2.28 (s, 6H), 2.43 (d, *J* = 1.8 Hz, 3H), 7.13–7.17 (m, 2H), 7.26–7.30 (m, 2H), 7.35–7.39 (m, 2H), 8.09 (dd, *J* = 1.8, 7.6 Hz, 2H), 8.12 (dd, *J* = 1.4, 7.6 Hz, 2H). HRMS-EI (*m*/*z*): [M]$^+$ calcd for $C_{20}H_{26}NOP$, 325.1752; found, 327.1746.

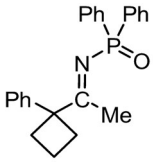
(*E*)-*N*-(3,3-Dimethylhexan-2-ylidene)-*P*,*P*-diphenylphosphinic amide (1f).



1f

1f was prepared from the corresponding nitrile according to procedure A. The product **1f** was obtained in 44% yield (579.3 mg, 1.77 mmol, white solid) from the corresponding nitrile (4.0 mmol).
^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.84 (t, *J* = 7.4 Hz, 3H), 1.09–1.18 (m, 2H), 1.20 (s, 6H), 1.54–1.58 (m, 2H), 2.46 (d, *J* = 1.6 Hz, 3H), 7.38–7.47 (m, 6H), 7.89–7.94 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 14.8 (CH_3), 18.1 (CH_2), 22.1 (d, *J* = 13.4 Hz, CH_3), 25.9 (CH_3), 43.5 (CH_2), 47.3 (d, *J* = 20.1 Hz, *C*), 128.4 (d, *J* = 12.5 Hz, *C*H), 131.3 (d, *J* = 2.9 Hz, *C*H), 131.6 (d, *J* = 9.6 Hz, *C*H), 135.1 (d, *J* = 131.2 Hz, *C*), 197.7 (d, *J* = 12.4 Hz, *C*). ^{31}P{^{1}H} NMR (159 MHz, $CDCl_3$, δ): 17.3. HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{20}H_{27}NOP$, 328.1825; found, 328.1823. mp 56–61 °C. IR (neat, cm^{-1}): 1203(P=O), 1650(C=N).

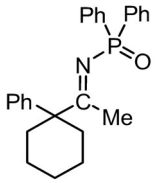
(*E*)-*P*,*P*-Diphenyl-*N*-[1-(1-phenylcyclobutyl)ethylidene]phosphinic amide (1g).



1g

1g was prepared from the corresponding nitrile according to procedure A. The product **1g** was obtained in 28% yield (416.6 mg, 1.12 mmol, white solid) from the corresponding nitrile (4.0 mmol).
^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.89 (quint, *J* = 13.2 Hz, 2H), 2.23 (d, *J* = 2.0 Hz, 3H), 2.50–2.57 (m, 2H), 2.83–2.90 (m, 2H), 7.17–7.31 (m, 5H), 7.42–7.50 (m, 6H), 7.96 (ddd, *J* = 1.5, 5.9, 9.8 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 15.9 (CH_2), 21.9 (d, *J* = 12.4 Hz, CH_3), 31.9 (CH_2), 59.1 (d, *J* = 22.1 Hz, *C*), 126.4 (*C*H), 126.8 (*C*H), 128.4 (*C*H), 128.6 (d, *J* = 8.6 Hz, *C*H), 131.5 (d, *J* = 2.8 Hz, *C*H), 131.6 (d, *J* = 8.6 Hz, *C*H), 134.9 (d, *J* = 130.3 Hz, *C*), 144.0 (*C*), 193.3 (d, *J* = 11.5 Hz, *C*). ^{31}P{^{1}H} NMR (159 MHz, $CDCl_3$, δ): 18.5. HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{24}H_{24}NOPNa$, 396.1488; found, 396.1486. mp 88–96 °C. IR (neat, cm^{-1}): 1204(P=O), 1655(C=N).

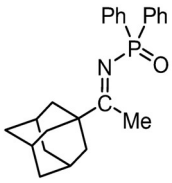
(*E*)-*P*,*P*-Diphenyl-*N*-[1-(1-phenylcyclohexyl)ethylidene]phosphinic amide (1h).



1h

1h was prepared from the corresponding nitrile according to procedure A. The product **1h** was obtained in 35% yield (567.9 mg, 1.41 mmol, white solid) from the corresponding nitrile (4.0 mmol).
^{1}H NMR (396 MHz, $CDCl_3$, δ): 1.37–1.58 (m, 6H), 2.01–2.08 (m, 2H), 2.24 (d, *J* = 2.4 Hz, 3H), 2.31–2.35 (m, 2H), 7.16–7.30 (m, 5H), 7.42–7.52 (m, 6H), 7.92–7.98 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 22.9 (d, *J* = 13.4 Hz, CH_3), 23.0 (CH_2), 26.1 (CH_2), 34.4 (CH_2), 54.9 (d, *J* = 20.1 Hz, *C*), 126.8 (*C*H), 126.9 (*C*H), 128.5 (d, *J* = 12.4 Hz, *C*H), 128.7 (*C*H), 131.5 (d, *J* = 2.9 Hz, *C*H), 131.7 (d, *J* = 9.6 Hz, *C*H), 134.6 (d, *J* = 130.3 Hz, *C*), 143.5 (*C*), 194.5 (d, *J* = 12.5 Hz, *C*). ^{31}P{^{1}H} NMR (159 MHz, $CDCl_3$, δ): 18.4. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{26}H_{28}NOP$, 401.1909; found, 401.1897. mp 103–106 °C. IR (neat, cm^{-1}): 1211(P=O), 1651(C=N).

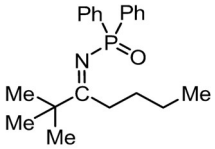
***N*-{(*E*)-1-[(3r,5r,7r)-Adamantan-1-yl]ethylidene}-*P*,*P*-diphenylphosphinic amide (1i).**



1i

1i was prepared from the corresponding nitrile according to procedure A. The product **1i** was obtained in 10% yield (157.0 mg, 0.42 mmol, white solid) from the corresponding nitrile (4.0 mmol).
^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.75 (q, *J* = 13.2 Hz, 6H), 1.88 (d, *J* = 2.7 Hz, 6H), 2.09 (s, 3H), 2.45 (d, *J* = 2.0 Hz, 3H), 7.38–7.47 (m, 6H), 7.90–7.96 (m, 4H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 21.2 (d, *J* = 13.3 Hz, CH_3), 28.3 (*C*H), 36.7 (CH_2), 39.5 (CH_2), 45.9 (d, *J* = 19.8 Hz, *C*), 128.4 (d, *J* = 12.3 Hz, *C*H), 131.2 (d, *J* = 2.8 Hz, CH_3), 131.6 (d, *J* = 9.4 Hz, CH_3), 135.3 (d, *J* = 130.3 Hz, *C*), 197.9 (d, *J* = 11.3 Hz, *C*). ^{31}P{^{1}H} NMR (159 MHz, $CDCl_3$, δ): 17.6. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{24}H_{28}NOP$, 377.1909; found, 377.1908. mp 170–172 °C. IR (neat, cm^{-1}): 1202(P=O), 1651(C=N).

(*E*)-*N*-(2,2-Dimethylheptan-3-ylidene)-*P*,*P*-diphenylphosphinic amide (1k).

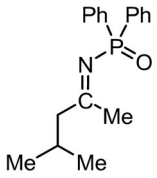


1k

1k was prepared from the corresponding nitrile according to the procedure A. The product **1k** was

obtained in 66% yield (905.7 mg, 2.65 mmol, white solid) from the corresponding nitrile (4.0 mmol). ^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.86 (t, *J* = 7.1 Hz, 3H), 1.26 (s, 9H), 1.38 (quint, *J* = 7.3 Hz, 2H), 1.45–1.53 (m, 2H), 2.80–2.84 (m, 2H), 7.37–7.46 (m, 6H), 7.91–7.96 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 13.7 (CH_3), 23.4 (CH_2), 28.0 (CH_3), 31.3 (CH_2), 35.3 (d, *J* = 11.5 Hz, CH_2), 44.2 (d, *J* = 21.1 Hz, *C*), 128.4 (d, *J* = 12.4 Hz, *C*H), 131.2 (d, *J* = 2.9 Hz, *C*H), 131.6 (d, *J* = 8.6 Hz, *C*H), 135.6 (d, *J* = 132.2 Hz, *C*), 200.8 (d, *J* = 12.4 Hz, *C*). ^{31}P{^{1}H} NMR (159 MHz, $CDCl_3$, δ): 15.6. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{21}H_{28}NOP$, 341.1909; found, 341.1912. mp 67–70 °C. IR (neat, cm^{-1}): 1199(P=O), 1650(C=N).

(*E*)-*N*-(4-Methylpentan-2-ylidene)-*P*,*P*-diphenylphosphinic amide (1l).

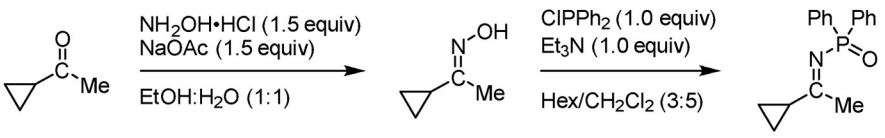


1l

1l was prepared from the corresponding nitrile according to procedure A. The product **1l** was obtained in 25% yield (302.0 mg, 1.0 mmol, white solid) from the corresponding nitrile (4.0 mmol).
^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.94 (d, *J* = 7.1 Hz, 6H), 2.17–2.31 (m, 1H), 2.43–2.45 (m, 5H), 7.39–7.48 (m, 6H), 7.89–7.95 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 22.7 (CH_3), 26.3 (*C*H), 27.6 (d, *J* = 15.4 Hz, CH_3), 53.2 (d, *J* = 28.1 Hz, CH_2), 128.4 (d, *J* = 12.4 Hz, *C*H), 131.4 (d, *J* = 2.0 Hz, *C*H), 131.7 (d, *J* = 9.5 Hz, *C*H), 134.9 (d, *J* = 130.3 Hz, *C*), 191.9 (d, *J* = 10.6 Hz, *C*). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, δ): 22.3. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{18}H_{22}NOP$, 299.1439; found, 299.1431. mp 166–168 °C. IR (neat, cm^{-1}): 1180(P=O), 1555(C=N).

Procedure B.

(*E*)-*N*-(1-Cyclopropylethylidene)-*P*,*P*-diphenylphosphinic amide (1j).



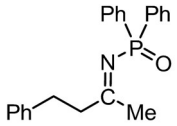
1j

1-Cyclopropylethan-1-one (841.0 mg, 10 mmol, 1.0 equiv) was added to a stirred solution of $NH_2OH \cdot HCl$ (1.04 g, 15 mmol, 1.5 equiv) and NaOAc (1.23 g, 15 mmol, 1.5 equiv) in EtOH/H_2O (1/1, 10 mL), and then heated to reflux. When the reaction was completed, the mixture was cooled down to ambient temperature. The reaction mixture was then diluted with Na_2CO_3 saturated aqueous solution and extracted with CH_2Cl_2 three times, and dried over $MgSO_4$. After filtration, the obtained oxime was

dried under vacuum overnight and used directly for the next process without purification. A solution of chlorodiphenylphosphine (1.04 mL, 6.0 mmol, 1.0 equiv) in CH_2Cl_2 (6 mL) was added to a stirred solution of the oxime (597.5 mg, 6.0 mmol, 1.0 equiv) and triethylamine (836 μL, 6.0 mmol, 1.0 equiv) in petroleum ether/CH_2Cl_2 (1:1, 9 mL) over 1 h at −45 °C. After the addition was finished, the cooling bath was removed, and the reaction temperature was gradually increased. The mixture was then allowed to stir overnight at ambient temperature. The mixture was directly filtered through a short silica-gel column with EtOAc as an eluent; then the resultant solution was concentrated under reduced pressure. The residue was purified by GPC to afford the corresponding ketimine **1j** (130.2 mg, 0.46 mmol, 8% yield) as a white solid.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.99–1.04 (m, 2H), 1.15–1.18 (m, 2H), 1.93–2.00 (m, 1H), 2.54 (d, *J* = 2.0 Hz, 3H), 7.38–7.45 (m, 6H), 7.83–7.89 (m, 4H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 12.3 (*C*H_2), 22.7 (d, *J* = 24.6 Hz, *C*H), 26.9 (d, *J* = 13.3 Hz, *C*H_3), 128.3 (d, *J* = 12.3 Hz, *C*H), 131.2 (d, *J* = 1.9 Hz, *C*H), 131.4 (d, *J* = 8.5 Hz, *C*H), 135.1 (d, *J* = 131.3 Hz, *C*), 194.1 (d, *J* = 7.5 Hz, *C*). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, δ): 18.4. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{17}H_{18}NOP$, 283.1126; found, 283.1120. mp 118–122 °C. IR (neat, cm^{-1}): 1194(P=O), 1652(C=N).

(*E*)-*P*,*P*-Diphenyl-*N*-(4-phenylbutan-2-ylidene)phosphinic amide (1m).

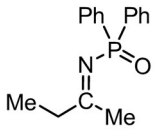


1m

1m was prepared from the corresponding ketone according to procedure B. The product **1m** was obtained in 7% yield (127.7 mg, 0.37 mmol, white solid) from the corresponding oxime (5.0 mmol). The spectroscopic data were matched in those reported[6].

^{1}H NMR (392 MHz, $CDCl_3$, δ): 2.47 (d, *J* = 1.6 Hz, 3H), 2.90 (t, *J* = 7.3 Hz, 2H), 3.04 (t, *J* = 7.4 Hz, 2H), 7.19–7.28 (m, 5H), 7.38–7.50 (m, 6H), 7.83–7.88 (m, 4H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 27.3 (d, *J* = 14.2 Hz, *C*H_3), 31.7 (*C*H_2), 45.1 (d, *J* = 20.7 Hz, *C*H_2), 126.2 (*C*H), 128.31 (*C*H), 128.33 (*C*H), 128.5 (d, *J* = 11.4 Hz, *C*H), 131.4 (d, *J* = 2.8 Hz, *C*H), 131.6 (d, *J* = 9.4 Hz, *C*H), 134.6 (d, *J* = 130.3 Hz, *C*), 140.1 (*C*), 190.8 (d, *J* = 10.3 Hz, *C*). HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{22}H_{22}NOP$, 347.1439; found, 347.1430.

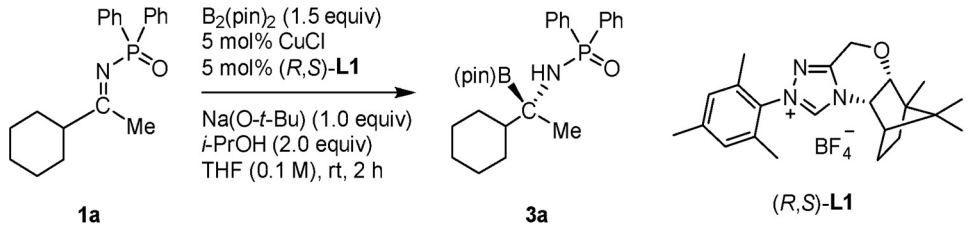
(*E*)-*N*-(Butan-2-ylidene)-*P*,*P*-diphenylphosphinic amide (1n).



1n

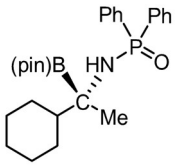
1n was prepared from the corresponding ketone according to procedure B. The product **1n** was obtained in 5% yield (102.8 mg, 0.38 mmol, white solid) from the corresponding oxime (8.0 mmol). ^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.20 (t, *J* = 7.3 Hz, 3H), 2.46 (d, *J* = 2.0 Hz, 3H), 2.58 (q, *J* = 7.3 Hz, 2H), 7.39–7.48 (m, 6H), 7.90–7.96 (m, 4H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 10.2 (CH_3), 26.9 (d, *J* = 14.2 Hz, CH_3), 37.4 (d, *J* = 20.8 Hz, CH_2), 128.5 (d, *J* = 12.3 Hz, *C*H), 131.4 (d, *J* = 2.9 Hz, *C*H), 131.7 (d, *J* = 9.5 Hz, *C*H), 135.0 (d, *J* = 131.3 Hz, *C*), 192.8 (d, *J* = 10.4 Hz, *C*). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, δ): 22.4. HRMS-EI (*m*/*z*): $[M]^+$ calcd for $C_{16}H_{18}NOP$, 271.1126; found, 271.1121. mp 161–168 °C. IR (neat, cm^{-1}): 1179(P=O), 1557(C=N).

General Experimental Procedures for Borylation of Ketimines



CuCl (1.0 mg, 0.01 mmol, 5 mol %), (*R*,*S*)-**L1** (4.4 mg, 0.01 mmol, 5 mol %), and bis(pinacolato)diboron (76.2 mg, 0.30 mmol, 1.5 equiv) were placed in a vial with a screw cap containing a Teflon®-coated rubber septum under air. The vial was put in a glove box, and then Na(O-*t*-Bu) (19.2 mg, 0.20 mmol, 1.0 equiv) was also added to the vial in the glove box under an argon atmosphere. After the reaction, the 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 room temperature, then a THF solution (1.4 mL) of ketimine **1a** (65.0 mg, 0.20 mmol, 1.0 equiv) was added dropwise to the vial. *i*-PrOH (31 μL, 0.40 mmol, 2.0 equiv) was added to the reaction mixture. After the resulting mixture was stirred at room temperature 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 EtOAc 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 40:60). After silica-gel column purification, the mixture was further purified by extraction with CH_2Cl_2 and H_2O three times to remove pinacol. The CH_2Cl_2 solution was dried over $MgSO_4$. After filtration, the corresponding product **3a** was obtained in 86% yield (78.0 mg, 0.17 mmol) as a colorless oil. The racemic sample was prepared using ICy·HCl for the ligand instead of (*R*,*S*)-**L1**.

(*R*)-*N*-[1-Cyclohexyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]-*P*,*P*-diphenylphosphinic amide [(*R*)-3a].

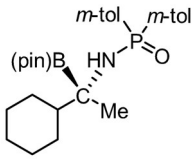


(*R*)-**3a**

The reaction was conducted with 65.1 mg (0.20 mmol) of **1a**. The product (*R*)-**3a** was purified by flash column chromatography (SiO_2, hexane/EtOAc, 100:0→40:60) and extracted with H_2O to remove pinacol, and dried over $MgSO_4$. After filtration, (*R*)-**3a** was obtained in 86% yield (78.0 mg, 0.17 mmol, colorless oil) with 89% ee.

^{1}H NMR (396 MHz, $CDCl_3$, δ): 1.01–1.26 (m, 5H), 1.17 (s, 3H), 1.29 (s, 6H) 1.30 (s, 6H), 1.44–1.50 (m, 1H), 1.64–1.89 (m, 5H), 3.04 (d, *J* = 7.9 Hz, 1H), 7.38–7.48 (m, 6H), 7.80–7.88 (m, 4H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 19.6 (d, *J* = 3.9 Hz, *C*H$_3$), 25.0 (*C*H$_3$), 25.1 (*C*H$_3$), 26.76 (*C*H$_2$), 26.81 (d, *J* = 1.9 Hz, *C*H$_2$), 28.5 (d, *J* = 42.6 Hz, *C*H$_2$), 47.5 (d, *J* = 4.4 Hz, *C*H), 49.5 (br, B-*C*), 84.2 (*C*), 128.2 (*C*H), 128.4 (*C*H), 131.3 (*C*H), 131.8 (d, *J* = 9.5 Hz, *C*H), 132.0 (d, *J* = 9.4 Hz, *C*H), 135.3 (d, *J* = 6.6 Hz, *C*), 136.6 (d, *J* = 5.7 Hz, *C*). ^{11}B{^{1}H} NMR (127 MHz, $CDCl_3$, δ): 33.1. ^{31}P{^{1}H} NMR (159 MHz, $CDCl_3$, δ): 21.9. HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{26}H_{37}{}^{11}BNO_3PNa$, 476.2501; found, 476.2496. $[\alpha]_D^{21.0}$ –6.59 (*c* 1.10 in $CHCl_3$, 89% ee). Daicel CHIRALPAK® OZ-3, 2-PrOH/Hexane = 10/90, 0.5 mL/min, 40 °C, *S* isomer: t_S = 11.97 min., *R* isomer: t_R = 15.01 min. IR (neat, cm^{-1}): 1200(P=O).

(*R*)-*N*-[1-Cyclohexyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]-*P*,*P*-di-*m*-tolylphosphinic amide [(*R*)-3b].



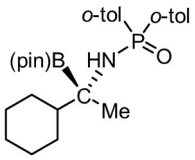
(*R*)-**3b**

The reaction was conducted with 71 mg (0.20 mmol) of **1b** for 2 h. The product (*R*)-**3b** was purified by flash column chromatography (SiO_2, hexane/EtOAc, 100:0→40:60) and extracted with H_2O to remove pinacol, and dried over $MgSO_4$. After filtration, (*R*)-**3b** was obtained in 74% yield (70.6 mg, 0.15 mmol, colorless oil) with 90% ee.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.01–1.24 (m, 5H), 1.17 (s, 3H), 1.29 (s, 6H), 1.31 (s, 6H), 1.43–1.50 (m, 1H), 1.56–1.94 (m, 5H), 2.36 (s, 6H), 3.02 (d, *J* = 7.8 Hz, 1H), 7.26–7.34 (m, 4H), 7.57–7.62 (m, 2H), 7.70 (dd, *J* = 4.5, 12.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 19.5 (d, *J* = 3.8 Hz, *C*H$_3$), 21.5 (*C*H$_3$), 25.0 (*C*H$_3$), 25.1 (*C*H$_3$), 26.76 (*C*H$_2$), 26.82 (d, *J* = 2.9 Hz, *C*H$_2$), 28.4 (d, *J* = 47.9 Hz, *C*H$_2$), 47.5 (d, *J* = 3.9 Hz, *C*H), 49.5 (br, B-*C*), 84.2 (*C*), 128.1 (d, *J* = 3.9 Hz, *C*H), 128.2 (d, *J* = 3.8 Hz, *C*H), 128.8 (d, *J* = 10.6 Hz, *C*H), 128.9 (d, *J* = 10.5 Hz, *C*H), 131.98 (d, *J* = 2.9 Hz, *C*H), 132.01 (d, *J* = 2.8 Hz, *C*H), 135.2 (d, *J* = 13.4 Hz, *C*), 136.5 (d, *J* = 11.5 Hz, *C*), 138.0 (d, *J* = 12.4 Hz, *C*). ^{11}B{^{1}H}

NMR (127 MHz, $CDCl_3$, δ): 33.5. $^{31}P\{^1H\}$ NMR (159 MHz, $CDCl_3$, δ): 22.3. HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{28}H_{41}{}^{11}BNO_3PNa$, 504.2814; found, 504.2814. $[\alpha]_D^{25.1}$ +1.24 (*c* 1.45 in $CHCl_3$, 90% ee). Daicel CHIRALPAK® OZ-3, 2-PrOH/Hexane = 10/90, 0.5 mL/min, 40 °C, *S* isomer: t_S = 10.21 min., *R* isomer: t_R = 11.23 min. IR (neat, cm^{-1}): 1193(P=O).

(*R*)-*N*-[1-Cyclohexyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]-*P*,*P*-di-*o*-tolylphosphinic amide [(*R*)-3c].

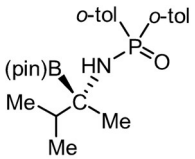


(*R*)-**3c**

The reaction was conducted with 69.2 mg (0.20 mmol) of **1c** for 3 h. The product (*R*)-**3a** was purified by flash column chromatography (SiO_2, CH_2Cl_2/Et_2O, 100:0→80:20) and obtained in 92% yield (86.3 mg, 0.18 mmol, colorless oil) with 95% ee.

^1H NMR (396 MHz, $CDCl_3$, δ): 1.03–1.24 (m, 5H), 1.26 (s, 6H), 1.28 (s, 6H), 1.34 (s, 3H), 1.60–1.91 (m, 6H), 2.44 (s, 3H), 2.57 (s, 3H), 2.80 (d, *J* = 11.5 Hz, 1H), 7.14–7.24 (m, 4H), 7.35 (q, *J* = 7.8 Hz, 2H), 7.53 (ddd, *J* = 1.0, 7.9, 11.9 Hz, 1H), 7.89 (ddd, *J* = 1.2, 7.9, 15.8 Hz, 1H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 20.0 (d, *J* = 2.9 Hz, CH_3), 21.7 (d, *J* = 3.8 Hz, CH_3), 22.0 (d, *J* = 3.8 Hz, CH_3), 25.0 (CH_3), 25.1 (CH_3), 26.76 (CH_2), 26.84 (CH_2), 28.7 (d, *J* = 64.3 Hz, CH_2), 48.1 (d, *J* = 3.8 Hz, *C*H), 49.6 (br, B-*C*), 84.1 (*C*), 124.9 (d, *J* = 12.3 Hz, *C*H), 125.1 (d, *J* = 12.3 Hz, *C*H), 131.19 (d, *J* = 2.8 Hz, *C*H), 131.23 (d, *J* = 2.9 Hz, *C*H), 131.5 (d, *J* = 12.3 Hz, *C*H), 131.7 (d, *J* = 11.3 Hz, *C*H), 132.9 (d, *J* = 11.3 Hz, *C*H), 133.61 (d, *J* = 29.2 Hz, *C*), 133.67 (d, *J* = 10.4 Hz, *C*H), 134.8 (d, *J* = 32.2 Hz, *C*), 142.0 (d, *J* = 9.4 Hz, *C*), 142.1 (d, *J* = 10.4 Hz, *C*). $^{11}B\{^1H\}$ NMR (127 MHz, $CDCl_3$, δ): 33.6. $^{31}P\{^1H\}$ NMR (159 MHz, $CDCl_3$, δ): 27.2. HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{28}H_{41}{}^{11}BNO_3PNa$, 504.2814; found, 504.2814. $[\alpha]_D^{23.6}$ –26.5 (*c* 0.26 in $CHCl_3$, 95% ee). Daicel CHIRALPAK® OZ-3, 2-PrOH/Hexane = 10/90, 0.5 mL/min, 40 °C, *S* isomer: t_S = 8.77 min., *R* isomer: t_R = 9.57 min. IR (neat, cm^{-1}): 1192(P=O).

(*R*)-*N*-[3-Methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl]-*P*,*P*-di-*o*-tolylphosphinic amide [(*R*)-3d].



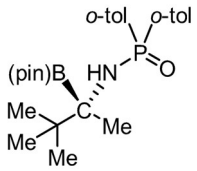
(*R*)-**3d**

The reaction was conducted with 63.7 mg (0.20 mmol) of **1d** for 2 h. The product (*R*)-**3d** was purified by flash column chromatography (SiO_2, CH_2Cl_2/Et_2O, 100:0→80:20) and extracted with H_2O to

remove pinacol, and dried over $MgSO_4$. After filtration, (*R*)-**3d** was obtained in 91% yield (81.8 mg, 0.19 mmol, colorless oil) with 97% ee.

^{1}H NMR (396 MHz, $CDCl_3$, δ): 0.98 (d, *J* = 6.7 Hz, 3H), 1.01 (d, *J* = 6.7 Hz, 3H), 1.25 (s, 6H), 1.27 (s, 6H), 1.32 (s, 3H), 1.93–2.02 (m, 1H), 2.43 (s, 3H), 2.56 (s, 3H), 2.75 (d, *J* = 10.7 Hz, 1H), 7.14–7.24 (m, 4H), 7.30–7.39 (m, 2H), 7.56 (ddd, *J* = 1.4, 7.9, 11.9 Hz, 1H), 7.91 (ddd, *J* = 1.2, 5.9, 13.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 18.3 (*C*H$_3$), 18.7 (*C*H$_3$), 19.7 (d, *J* = 2.9 Hz, *C*H$_3$), 21.8 (d, *J* = 3.9 Hz, *C*H$_3$), 22.0 (d, *J* = 3.8 Hz, *C*H$_3$), 25.0 (*C*H$_3$), 25.1 (*C*H$_3$), 37.6 (d, *J* = 4.8 Hz, *C*H), 49.8 (br, B-*C*), 84.1 (*C*), 124.9 (d, *J* = 13.4 Hz, *C*H), 125.1 (d, *J* = 13.5 Hz, *C*H), 131.2 (d, *J* = 2.9 Hz, *C*H), 131.3 (d, *J* = 2.0 Hz, *C*H), 131.5 (d, *J* = 11.5 Hz, *C*H), 131.7 (d, *J* = 11.5 Hz, *C*H), 132.9 (d, *J* = 11.5 Hz, *C*H), 133.6 (d, *J* = 25.9 Hz, *C*), 133.7 (d, *J* = 10.5 Hz, *C*H), 134.8 (d, *J* = 27.8 Hz, *C*), 141.9 (d, *J* = 9.6 Hz, *C*), 142.1 (d, *J* = 9.6 Hz, *C*). ^{11}B{^{1}H} NMR (127 MHz, $CDCl_3$, δ): 33.1. ^{31}P{^{1}H} NMR (159 MHz, $CDCl_3$, δ): 27.2. HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{25}H_{37}{}^{11}BNO_3PNa$, 464.2501; found, 464.2501. $[\alpha]_D^{27.4}$ +1.44 (*c* 1.08 in $CHCl_3$, 97% ee). Daicel CHIRALPAK® OZ-3, 2-PrOH/Hexane = 10/90, 0.5 mL/min, 40 °C, *S* isomer: t_S = 9.57 min., *R* isomer: t_R = 10.16 min. IR (neat, cm^{-1}): 1191(P=O).

(*R*)-*N*-[3,3-Dimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl]-*P*,*P*-di-*o*-tolylphosphinic amide [(*R*)-3e].



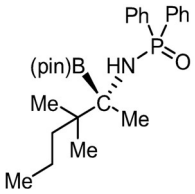
(*R*)-**3e**

The reaction was conducted with 63.6 mg (0.20 mmol) of **1e** for 20 h. The product (*R*)-**3e** was purified by flash column chromatography (SiO_2, CH_2Cl_2/Et_2O, 100:0→80:20) and obtained in 85% yield (74.9 mg, 0.16 mmol, white solid) with 99% ee.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.04 (s, 9H), 1.28 (s, 6H), 1.29 (s, 6H), 1.37 (s, 3H), 2.40 (s, 3H), 2.50 (s, 3H), 2.77 (d, *J* = 9.4 Hz, 1H), 7.15–7.24 (m, 4H), 7.34 (tq, *J* = 1.4, 7.8 Hz, 2H), 7.66 (ddd, *J* = 1.3, 7.8, 15.7 Hz, 1H), 7.94 (ddd, *J* = 1.4, 7.8, 11.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 18.0 (d, *J* = 2.9 Hz *C*H$_3$), 21.86 (d, *J* = 2.9 Hz, *C*H$_3$), 21.94 (d, *J* = 3.8 Hz, *C*H$_3$), 25.0 (*C*H$_3$), 25.2 (*C*H$_3$), 26.5 (*C*H$_3$), 37.2 (d, *J* = 4.7 Hz, *C*), 52.7 (br, B-*C*), 84.2 (*C*), 124.6 (d *J* = 12.5 Hz, *C*H), 125.1 (d, *J* = 13.4 Hz, *C*H), 131.1 (d, *J* = 2.9 Hz, *C*H), 131.2 (d, *J* = 2.9 Hz, *C*H), 131.5 (d, *J* = 7.7 Hz, *C*H), 131.6 (d, *J* = 7.7 Hz, *C*H), 132.9 (d, *J* = 10.5 Hz, *C*H), 133.5 (d, *J* = 10.5 Hz, *C*H), 133.9 (d, *J* = 28.8 Hz, *C*), 135.1 (d, *J* = 29.7 Hz, *C*), 141.5 (d, *J* = 9.5 Hz, *C*), 142.1 (d, *J* = 10.6 Hz, *C*). ^{11}B{^{1}H} NMR (127 MHz, $CDCl_3$, δ): 33.3. ^{31}P{^{1}H} NMR (159 MHz, $CDCl_3$, δ): 26.9. HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{26}H_{40}{}^{11}BNO_3P$, 456.2839; found, 456.2831. $[\alpha]_D^{23.3}$ −11.68 (*c* 1.01 in $CHCl_3$, 99% ee). Daicel

CHIRALPAK® IA-3, 2-PrOH/Hexane = 8/92, 0.5 mL/min, 40 °C, *S* isomer: t_S = 48.21 min., *R* isomer: t_R = 51.56 min. mp 114–120 °C. IR (neat, cm^{-1}): 1191(P=O).

(*R*)-*N*-[3,3-Dimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-yl]-*P*,*P*-diphenylphosphinic amide [(*R*)-3f].

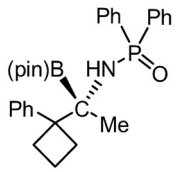


(*R*)-**3f**

The reaction was conducted with 64.8 mg (0.20 mmol) of **1f** for 3 h. The product (*R*)-**3f** was purified by flash column chromatography (SiO_2, hexane/EtOAc, 100:0→50:50) and extracted with H_2O to remove pinacol, and dried over $MgSO_4$. After filtration, (*R*)-**3f** was obtained in 82% yield (73.9 mg, 0.16 mmol, colorless oil) with 99% ee.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.91 (t, *J* = 6.9 Hz, 3H), 0.955 (s, 3H), 0.961 (s, 3H), 1.17 (s, 3H), 1.21–1.48 (m, 4H), 1.28 (s, 6H), 1.32 (s, 6H), 3.07 (d, *J* = 7.4 Hz, 1H), 7.38–7.48 (m, 6H), 7.79–7.89 (m, 4H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 15.3 (CH_3), 16.8 (d, *J* = 4.8 Hz CH_3), 17.7 (CH_2), 22.0 (d, *J* = 28.4 Hz, CH_3), 25.0 (CH_3), 25.1 (CH_3), 39.3 (d, *J* = 4.8 Hz, *C*), 39.9 (CH_2), 53.5 (br, B-*C*), 128.3 (*C*H), 128.4 (*C*H), 131.19 (d, *J* = 2.8 Hz, *C*H), 131.23 (d, *J* = 2.9 Hz, *C*H), 131.7 (d, *J* = 9.4 Hz, *C*H), 131.9 (d, *J* = 9.4 Hz, *C*H), 135.5 (*C*), 136.8 (d, *J* = 5.6 Hz, *C*). ^{11}B{^{1}H} NMR (127 MHz, $CDCl_3$, δ): 33.7. ^{31}P{^{1}H} NMR (159 MHz, $CDCl_3$, δ): 22.5. HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{26}H_{40}{}^{11}BNO_3P$, 456.2838; found, 456.2834. $[\alpha]_D^{27.9}$ +2.15 (*c* 0.93 in $CHCl_3$, 99% ee). Daicel CHIRALPAK® OZ-3, 2-PrOH/Hexane = 10/90, 0.5 mL/min, 40 °C, *S* isomer: t_S = 9.39 min., *R* isomer: t_R = 12.77 min. IR (neat, cm^{-1}): 1199(P=O).

(*R*)-*P*,*P*-Diphenyl-*N*-[1-(1-phenylcyclobutyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phosphinic amide [(*R*)-3g].

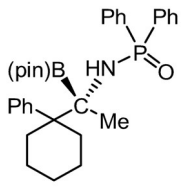


(*R*)-**3g**

The reaction was conducted with 74.2 mg (0.20 mmol) of **1g** for 2 h. The product (*R*)-**3g** was purified by flash column chromatography (SiO_2, hexane/EtOAc, 100:0→0:100) and extracted with H_2O to remove pinacol, and dried over $MgSO_4$. After filtration, (*R*)-**3g** was obtained in 74% yield (73.4 mg, 0.15 mmol, colorless oil) with 98% ee.

^{1}H NMR (396 MHz, $CDCl_3$, δ): 1.09 (s, 3H), 1.30 (s, 6H), 1.34 (s, 6H), 1.75–1.89 (m, 2H), 2.37–2.44 (m, 2H), 2.67–2.74 (m, 1H), 2.77–2.84 (m, 1H), 2.88 (d, *J* = 5.5 Hz, 1H), 7.20–7.48 (m, 13H), 7.78–7.83 (m, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 15.5 (*C*H_2), 17.7 (d, *J* = 3.8 Hz, *C*H_3), 25.3 (*C*H_3), 30.4 (d, *J* = 31.1 Hz, *C*H_2), 51.8 (br, B-*C*), 52.6 (d, *J* = 6.5 Hz, *C*), 84.3 (*C*), 125.9 (*C*H), 127.3 (*C*H), 128.1 (d, *J* = 12.3 Hz, *C*H), 128.3 (d, *J* = 13.3 Hz, *C*H), 128.9 (*C*H), 131.1 (d, *J* = 1.9 Hz, *C*H), 131.2 (d, *J* = 2.8 Hz, *C*H), 131.7 (d, *J* = 9.5 Hz, *C*H), 135.3 (d, *J* = 34.0 Hz, *C*), 136.6 (d, *J* = 28.3 Hz, *C*), 147.1 (*C*). ^{11}B{^{1}H} NMR (127 MHz, $CDCl_3$, δ): 32.7. ^{31}P{^{1}H} NMR (159 MHz, $CDCl_3$, δ): 22.4. HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{30}H_{37}{}^{11}BNO_3PNa$, 524.2502; found, 524.2501. $[\alpha]_D^{28.0}$ +1.67 (*c* 1.50 in $CHCl_3$, 98% ee). Daicel CHIRALPAK® OZ-3, 2-PrOH/Hexane = 10/90, 0.5 mL/min, 40 °C, *S* isomer: t_S = 10.85 min., *R* isomer: t_R = 15.55 min. IR (neat, cm^{-1}): 1200(P=O).

(*R*)-*P*,*P*-Diphenyl-*N*-[1-(1-phenylcyclohexyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]phosphinic amide [(*R*)-3h].

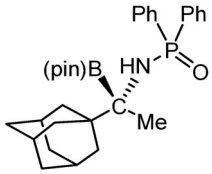


(*R*)-**3h**

The reaction was conducted with 79.4 mg (0.20 mmol) of **1h** for 3 h. The product (*R*)-**3h** was purified by flash column chromatography (SiO_2, CH_2Cl_2/EtOAc, 100:0→90:10 to SiO_2, EtOAc /MeOH, 100:0→50:50) and extracted with H_2O to remove pinacol, and dried over $MgSO_4$. . After filtration, (*R*)-**3h** was obtained in 72% yield (75.3 mg, 0.14 mmol, white solid) with 97% ee.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.06 (s, 3H), 1.13–1.26 (m, 3H), 1.30 (s, 6H), 1.33 (s, 6H), 1.50–1.60 (m, 4H), 1.73 (t, *J* = 13.1 Hz, 1H), 2.55 (t, *J* = 13.3 Hz, 2H), 2.93 (d, *J* = 3.9 Hz, 1H), 7.19 (td, *J* = 3.1, 7.6 Hz, 2H), 7.27–7.45 (m, 11H), 7.77 (ddd, *J* = 1.5, 7.8, 11.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 18.0 (d, *J* = 3.9 Hz, *C*H_3), 22.5 (d, *J* = 2.8 Hz, *C*H_2), 25.0 (*C*H_3), 25.2 (*C*H_3), 26.9 (*C*H_2), 31.5 (d, *J* = 70.9 Hz, *C*H_2), 48.8 (d, *J* = 6.7 Hz, *C*), 53.8 (br, B-*C*), 84.3 (*C*), 125.8 (*C*H), 127.8 (*C*H), 128.0 (d, *J* = 13.4 Hz, *C*H), 128.3 (d, *J* = 12.5 Hz, *C*H), 130.0 (*C*H), 130.9 (d, *J* = 1.9 Hz, *C*H), 131.1 (d, *J* = 1.9 Hz, *C*H), 131.5 (d, *J* = 9.6 Hz, *C*H), 131.7 (d, *J* = 9.6 Hz, *C*H), 135.5 (d, *J* = 38.3 Hz, *C*), 136.7 (d, *J* = 32.6 Hz, *C*), 140.7 (*C*). ^{11}B{^{1}H} NMR (127 MHz, $CDCl_3$, δ): 32.9. ^{31}P{^{1}H} NMR (159 MHz, $CDCl_3$, δ): 22.7. HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{32}H_{42}{}^{11}BNO_3P$, 530.2996; found, 530.2998. $[\alpha]_D^{27.9}$ +0.48 (*c* 1.05 in $CHCl_3$, 97% ee). Daicel CHIRALPAK® OZ-3, 2-PrOH/Hexane = 10/90, 0.5 mL/min, 40 °C, *S* isomer: t_S = 9.92 min., *R* isomer: t_R = 12.13 min. mp 79–81 °C. IR (neat, cm^{-1}): 1196(P=O).

***N*-{(*R*)-1-[(3*R*,5*R*,7*R*)-Adamantan-1-yl]-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl}-*P*,*P*-diphenylphosphinic amide [(*R*)-3i].**

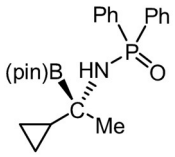


(*R*)-**3i**

The reaction was conducted with 74.2 mg (0.20 mmol) of **1i** for 5 h. The product (*R*)-**3i** was purified by flash column chromatography (SiO_2, hexane/EtOAc, 100:0→20:80) and extracted with H_2O to remove pinacol, and dried over $MgSO_4$. After filtration, (*R*)-**3i** was obtained in 87% yield (86.8 mg, 0.17 mmol, white solid) with 99% ee.

^{1}H NMR (396 MHz, $CDCl_3$, δ): 1.14 (s, 3H), 1.30 (s, 6H), 1.33 (s, 6H), 1.60–1.77 (m, 12H), 2.02 (s, 3H), 3.05 (d, *J* = 7.9 Hz, 1H), 7.38–7.48 (m, 6H), 7.80–7.88 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 15.5 (d, *J* = 4.8 Hz *C*H$_3$), 25.1 (*C*H$_3$), 25.2 (*C*H$_3$), 28.8 (*C*H), 37.35 (*C*H$_2$), 37.44 (*C*H$_2$), 38.3 (d, *J* = 4.8 Hz, *C*), 53.0 (br, B-*C*), 84.3 (*C*), 128.3 (d, *J* = 1.9 Hz, *C*H), 128.4 (d, *J* = 1.9 Hz, *C*H), 131.16 (d, *J* = 2.9 Hz, *C*H), 131.23 (d, *J* = 1.9 Hz, *C*H), 131.7 (d, *J* = 9.6 Hz, *C*H), 132.0 (d, *J* = 9.6 Hz, *C*H), 135.7 (d, *J* = 3.8 Hz, *C*H), 137.0 (*C*). ^{11}B{^{1}H} NMR (127 MHz, $CDCl_3$, δ): 33.7. ^{31}P{^{1}H} NMR (159 MHz, $CDCl_3$, δ): 22.6. HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{30}H_{42}{}^{11}BNO_3P$, 506.2995; found, 506.2989. $[\alpha]_D^{27.8}$ −1.34 (*c* 1.12 in $CHCl_3$, 99% ee). Daicel CHIRALPAK® OZ-3, 2-PrOH/Hexane = 10/90, 0.5 mL/min, 40 °C, *S* isomer: t_S = 11.28 min., *R* isomer: t_R = 13.47 min. mp 194–197 °C. IR (neat, cm^{-1}): 1202(P=O).

(*R*)-*N*-[1-Cyclopropyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]-*P*,*P*-diphenylphosphinic amide [(*R*)-3j].



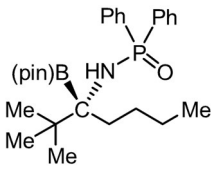
(*R*)-**3j**

The reaction was conducted with 56.3 mg (0.20 mmol) of **1j** for 2 h. The product (*R*)-**3j** was purified by flash column chromatography (SiO_2, hexane/EtOAc, 100:0→20:80) and extracted with H_2O to remove pinacol, and dried over $MgSO_4$. After filtration, (*R*)-**3j** was obtained in 50% yield (40.5 mg, 0.10 mmol, colorless oil) with 86% ee.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.29–0.32 (m, 2H), 0.34–0.46 (m, 2H), 1.04–1.14 (m, 1H), 1.24 (s, 3H), 1.25 (s, 6H), 1.26 (s, 6H), 3.08 (d, *J* = 8.6 Hz, 1H), 7.38–7.48 (m, 6H), 7.82–7.90 (m, 4H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 1.93 (*C*H$_2$), 2.56 (*C*H$_2$), 21.6 (d, *J* = 5.6 Hz, *C*H), 22.9 (d, *J* = 3.8 Hz, *C*H$_3$), 24.8 (*C*H$_3$), 24.9 (*C*H$_3$), 84.3 (*C*), 128.2 (d, *J* = 2.9 Hz, *C*H), 128.4 (d, *J* = 3.8 Hz, *C*H), 131.29 (*C*H), 131.31 (*C*H), 131.9 (d, *J* = 9.6 Hz, *C*H), 132.0 (d, *J* = 8.5 Hz, *C*H), 135.1 (*C*), 136.4 (*C*). The

carbon directly attached to the boron atom was not detected, likely because of quadrupolar relaxation. $^{11}B\{^1H\}$ NMR (127 MHz, $CDCl_3$, δ): 33.0. $^{31}P\{^1H\}$ NMR (159 MHz, $CDCl_3$, δ): 22.2. HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{23}H_{31}{}^{11}BNO_3PNa$, 434.2031; found, 434.2029. $[\alpha]_D^{25.2}$ −2.44 (*c* 1.17 in $CHCl_3$, 86% ee). Daicel CHIRALPAK® OZ-3, 2-PrOH/Hexane = 10/90, 0.5 mL/min, 40 °C, *S* isomer: t_S = 21.95 min., *R* isomer: t_R = 28.56 min. IR (neat, cm^{-1}): 1197(P=O).

(*R*)-*N*-[2,2-Dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptan-3-yl]-*P*,*P*-diphenylphosphinic amide [(*R*)-3k].

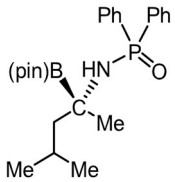


(*R*)-**3k**

The reaction was conducted with 67.2 mg (0.20 mmol) of **1k** for 2 h. The product (*R*)-**3k** was purified by flash column chromatography (SiO_2, hexane/EtOAc, 100:0→20:80) and extracted with H_2O to remove pinacol, and dried over $MgSO_4$. After filtration, (*R*)-**3k** was obtained in 80% yield (73.6 mg, 0.16 mmol, colorless oil) with 86% ee.

^1H NMR (392 MHz, $CDCl_3$, δ): 0.63 (t, *J* = 7.3 Hz, 3H), 0.84–1.21 (m, 4H), 1.03 (s, 9H), 1.25 (s, 6H), 1.26 (s, 6H), 1.62 (dt, *J* = 6.5, 18.8 Hz, 1H), 1.82–1.94 (m, 1H), 3.04 (d, *J* = 11.0 Hz, 1H), 7.37–7.46 (m, 6H), 7.73–7.79 (m, 2H), 7.86–7.91 (m, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 14.1 (CH_3), 23.5 (CH_2), 25.0 (CH_3), 25.2 (CH_3), 27.3 (CH_3), 29.7 (CH_2), 31.3 (d, *J* = 2.8 Hz, CH_2), 37.9 (*C*), 60.0 (br, B-*C*), 84.4 (*C*), 128.0 (d, *J* = 13.2 Hz, *C*H), 128.3 (d, *J* = 12.3 Hz, *C*H), 130.9 (d, *J* = 2.9 Hz, *C*H), 131.0 (d, *J* = 1.9 Hz, *C*H), 131.3 (d, *J* = 10.4 Hz, *C*H), 132.2 (d, *J* = 10.4 Hz, *C*H), 136.6 (d, *J* = 61.4 Hz, *C*), 137.9 (d, *J* = 59.5 Hz, *C*). $^{11}B\{^1H\}$ NMR (127 MHz, $CDCl_3$, δ): 33.0. $^{31}P\{^1H\}$ NMR (159 MHz, $CDCl_3$, δ): 22.2. HRMS-ESI (*m*/*z*): $[M+H]^+$ calcd for $C_{27}H_{42}{}^{11}BNO_3P$, 470.2995; found, 470.2989. $[\alpha]_D^{25.7}$ +1.40 (*c* 3.67 in $CHCl_3$, 88% ee). Daicel CHIRALPAK® OZ-3, 2-PrOH/Hexane = 10/90, 0.5 mL/min, 40 °C, *S* isomer: t_S = 9.49 min., *R* isomer: t_R = 12.08 min. IR (neat, cm^{-1}): 1204(P=O).

(*R*)-*N*-[4-Methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-2-yl]-*P*,*P*-diphenylphosphinic amide [(*R*)-3l].



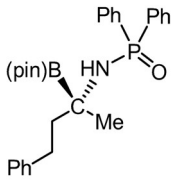
(*R*)-**3l**

The reaction was conducted with 60.2 mg (0.20 mmol) of **1i** for 2 h. The product (*R*)-**3i** was purified

by flash column chromatography (SiO_2, hexane/EtOAc, 100:0→40:60) and extracted with H_2O to remove pinacol, and dried over $MgSO_4$. After filtration, (*R*)-**3l** was obtained in 86% yield (73.5 mg, 0.17 mmol, colorless oil) with 88% ee.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.90 (d, *J* = 6.7, Hz, 3H), 0.93 (d, *J* = 6.7, Hz, 3H), 1.23 (s, 3H), 1.26 (s, 6H), 1.28 (s, 6H), 1.44 (dd, *J* = 7.6, 13.9 Hz, 1H), 1.68 (dd, *J* = 5.5, 13.3 Hz, 1H), 1.83–1.97 (m, 1H), 3.11 (d, *J* = 9.0 Hz, 1H), 7.39–7.50 (m, 6H), 7.77–7.83 (m, 2H), 7.87–7.93 (m, 2H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 23.7 (*C*H_3), 24.2 (*C*H_3), 24.6 (d, *J* = 4.8 Hz, *C*H_3), 25.0 (*C*H_3), 25.3 (*C*H), 45.7 (br, B-*C*), 50.6 (d, *J* = 2.9 Hz, *C*H_2), 84.4 (*C*), 128.3 (d, *J* = 3.8 Hz, *C*H), 128.4 (d, *J* = 3.8 Hz, *C*H), 131.3 (*C*H), 131.7 (d, *J* = 9.5 Hz, *C*H), 132.1 (d, *J* = 9.4 Hz, *C*H), 135.2 (*C*), 136.5 (*C*). ^{11}B{^{1}H} NMR (127 MHz, $CDCl_3$, δ): 33.8. ^{31}P{^{1}H} NMR (159 MHz, $CDCl_3$, δ): 21.9. HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{24}H_{35}{}^{11}BNO_3P$, 450.2344; found, 450.2340. $[\alpha]_D^{25.9}$ +1.34 (*c* 4.28 in $CHCl_3$, 88% ee). Daicel CHIRALPAK® OZ-3, 2-PrOH/Hexane = 10/90, 0.5 mL/min, 40 °C, *S* isomer: t_S = 13.73 min., *R* isomer: t_R = 17.52 min. IR (neat, cm^{-1}): 1198(P=O).

(*R*)-*P*,*P*-Diphenyl-*N*-[4-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl]phosphinic amide [(*R*)-3m].

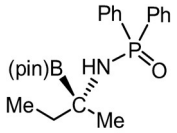


(*R*)-**3m**

The reaction was conducted with 69.1 mg (0.20 mmol) of **1m** for 6 h. The product (*R*)-**3m** was purified by flash column chromatography (SiO_2, hexane/EtOAc, 100:0→40:60) and extracted with H_2O to remove pinacol, and dried over $MgSO_4$. After filtration, (*R*)-**3m** was obtained in 44% yield (41.4 mg, 0.09 mmol, colorless oil) with 89% ee.

^{1}H NMR (392 MHz, $CDCl_3$, δ):1.285–1.294 (m, 15H), 1.82 (td, *J* = 4.3, 12.9 Hz, 1H), 2.00 (td, *J* = 5.0, 13.0 Hz, 1H), 2.57 (td, *J* = 4.7, 12.9 Hz, 1H), 2.87 (td, *J* = 4.8, 12.9 Hz, 1H), 3.21 (d, *J* = 8.6 Hz, 1H), 7.13–7.16 (m, 3H), 7.23–7.27 (m, 2H), 7.39–7.52 (m, 6H) , 7.83–7.92 (m, 4H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 24.2 (d, *J* = 3.8 Hz, *C*H_3), 24.9 (*C*H_3), 25.0 (*C*H_3), 32.3 (*C*H_2), 43.5 (d, *J* = 3.8 Hz, *C*H_2), 46.1 (br, B-*C*), 84.5 (*C*), 125.8 (*C*H), 128.3 (d, *J* = 2.9 Hz, *C*H), 128.40 (*C*H), 128.45 (d, *J* = 1.9 Hz, *C*H), 128.55 (*C*H), 135.0 (d, *J* = 5.7 Hz, *C*), 136.3 (d, *J* = 6.6 Hz, *C*), 142.7 (*C*). ^{11}B{^{1}H} NMR (127 MHz, $CDCl_3$, δ): 32.6. ^{31}P{^{1}H} NMR (159 MHz, $CDCl_3$, δ): 22.1. HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{28}H_{35}{}^{11}BNO_3PNa$, 498.2345; found, 498.2339. $[\alpha]_D^{22.0}$ –13.9 (*c* 0.85 in $CHCl_3$, 89% ee). Daicel CHIRALPAK® OZ-3, 2-PrOH/Hexane = 5/95, 0.5 mL/min, 40 °C, *S* isomer: t_S = 32.80 min., *R* isomer: t_R = 47.56 min. IR (neat, cm^{-1}): 1196(P=O).

(*R*)-*P*,*P*-Diphenyl-*N*-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl]phosphinic amide [(*R*)-3n].

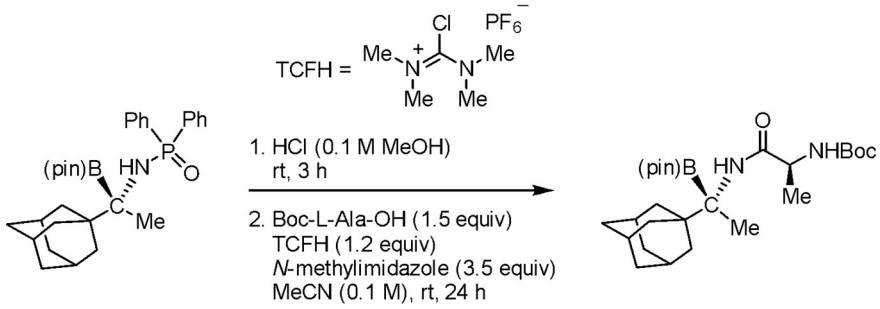


(*R*)-**3n**

The reaction was conducted with 53.8 mg (0.20 mmol) of **1n** for 1 h. The product (*R*)-**3n** was purified by flash column chromatography (SiO_2, hexane/EtOAc, 100:0→50:50) and extracted with H_2O to remove pinacol, and dried over $MgSO_4$. After filtration, (*R*)-**3n** was obtained in 28% yield (22.3 mg, 0.06 mmol, colorless oil) with 69% ee.

^{1}H NMR (392 MHz, $CDCl_3$, δ): 0.94 (t, *J* = 7.4 Hz, 3H), 1.23 (s, 3H), 1.26 (s, 6H), 1.27 (s, 6H), 1.57 (sxt, *J* = 7.2 Hz, 1H), 1.70 (sxt, *J* = 7.1 Hz, 1H), 3.11 (d, *J* = 9.0 Hz, 1H), 7.39–7.49 (m, 6H), 7.82–7.91 (m, 4H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 10.1 (CH_3), 23.6 (d, *J* = 3.8 Hz, CH_3), 24.9 (CH_3), 25.0 (CH_3), 34.2 (d, *J* = 3.8 Hz, CH_2), 46.7 (br, B-*C*), 84.3 (*C*), 128.2 (*C*H), 128.4 (*C*H), 131.3 (*C*H), 131.8 (d, *J* = 10.4 Hz, *C*H), 132.1 (d, *J* = 10.4 Hz, *C*H), 135.1 (*C*), 136.4 (*C*). ^{11}B{^{1}H} NMR (127 MHz, $CDCl_3$, δ): 32.5. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, δ): 22.0. HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{22}H_{31}{}^{11}BNO_3P$,422.2031; found, 422.2026. $[\alpha]_D^{25.0}$ +18.9 (*c* 0.12 in $CHCl_3$, 69% ee). Daicel CHIRALPAK® OZ-3, 2-PrOH/Hexane = 10/90, 0.5 mL/min, 40 °C, *S* isomer: t_S = 19.49 min., *R* isomer: t_R = 24.40 min. IR (neat, cm^{-1}): 1196(P=O).

Experimental Procedures for the Synthesis of Peptydilboronic Acid Derivatives



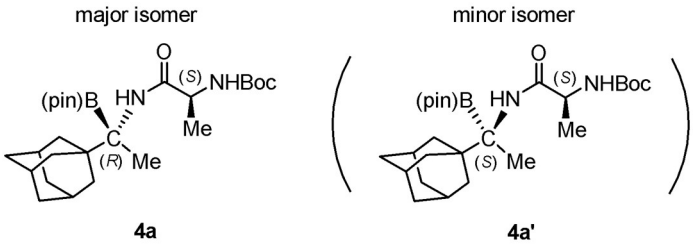
(*R*)-**3i**
99% ee

4a
d.r. >99:1

The borylation product (*R*)-**3i** (177 mg, 0.35 mmol, 1.0 equiv) was placed in a vial with a screw cap containing a Teflon®-coated rubber septum under air. A MeOH solution of HCl (0.1 M, 3.5 mL) was added to the vial via a syringe. The resulting mixture was stirred for 3 h at room temperature. The solvents are removed under reduced pressure to afford the deprotection product. The product was used in the next step without further purification. The condensation reaction was performed according to the literature.[7]. Boc-L-Ala-OH (85.9 mg, 0.46 mmol, 1.3 equiv) and TCFH (118 mg, 0.42 mmol, 1.2 equiv) were placed in a vial with a screw cap containing a Teflon®-coated rubber septum under air.

MeCN (100 μL) was added to the vial via a syringe. The resulting mixture was stirred for 5 min at room temperature. A THF solution (250 μL) of the deprotection product was then added dropwise to the vial. *N*-Metylimidazole (94 μL, 1.2 mmol, 3.5 equiv) was added dropwise to the vial. The reaction mixture was stirred for 24 h. The reaction mixture was analyzed by TLC to check the completeness of the reaction. The mixture was directly filtered through a short silica-gel column with EtOAc 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 40:60) to give the corresponding product **4a** in 71% yield (118.0 mg, 0.25 mmol) as white solid. The diastereomeric ratio was determined by HPLC analysis (d.r. >99:1).

***tert*-Butyl [(*S*)-1-({(*R*)-1-[(3*R*,5*R*,7*R*)-adamantan-1-yl]-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl}amino)-1-oxopropan-2-yl]carbamate (4a).**



NMR spectra for **4a** contains conformational isomers, which is caused by the restricted C−N bond rotation around the carbamate group. ^{1}H NMR (392 MHz, $CDCl_3$, δ): 1.14 (s, 3H), 1.23 (s, 6H), 1.24 (s, 6H), 1.35 (d, *J* = 7.4 Hz, 3H), 1.45 (s, 9H), 1.60–1.76 (m, 12H), 1.96 (s, 3H), 4.09–4.29 (m, 1H), 4.73–5.01 (m, 1H), 6.59–6.87 (m, 1H). ^{13}C NMR (99 MHz, $CDCl_3$, δ): 16.4 (CH_3), 24.9 (CH_3), 25.2 (CH_3), 25.5 (CH_3), 28.4 (CH_3), 28.7 (*C*H), 36.9 (CH_2), 37.2 (CH_2), 37.5 (*C*), 48.0 (*C*H), 51.1 (br, B-*C*), 75.1 and 80.5 (a pair of s, *C*), 81.9 (*C*), 155.8 (*C*), 173.8 (*C*). ^{11}B{^{1}H} NMR (127 MHz, $CDCl_3$, δ): 25.5. HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{26}H_{45}N_2O_5{}^{11}BNa$, 499.3319; found, 499.3313. $[\alpha]_D^{22.3}$ –25.3 (*c* 0.39 in $CHCl_3$). The diastereomeric ratio was determined by HPLC analysis (d.r. >99:1, right side in Figure S1) by comparison with a mixture of the diastereomers that was obtained by the reaction of racemic **3i** with Boc-L-Ala-OH (d.r. 80:20, left side in Figure S1). Daicel CHIRALPAK® ID-3, 2-PrOH/Hexane = 3/97, 0.5 mL/min, 40 °C, minor isomer = 11.88 min., major isomer = 15.07 min. mp

82–92 °C. IR (neat, cm^{-1}): 1699(C=O, amide).

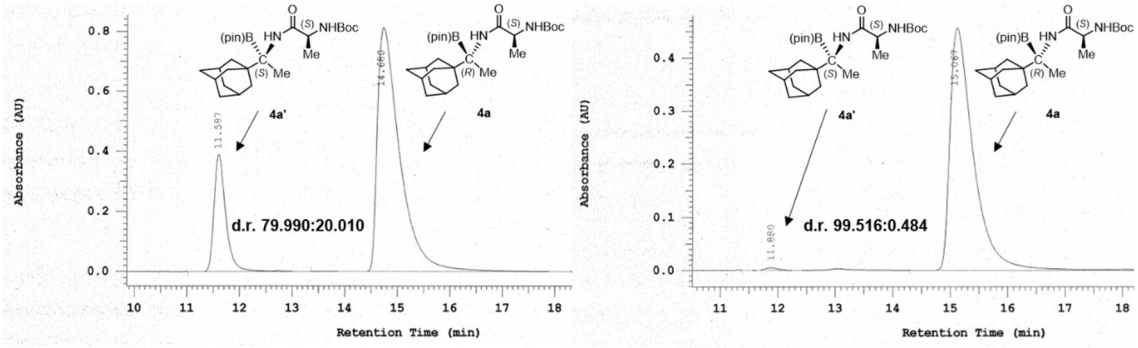
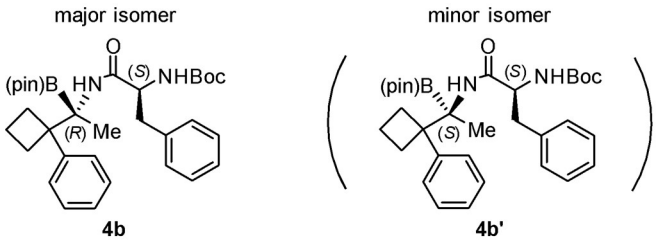


Figure S1. Determination of the diastereomeric ratio of **4a** by HPLC analysis.

***tert*-Butyl ((*S*)-1-oxo-3-phenyl-1-{[(*R*)-1-(1-phenylcyclobutyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]amino}propan-2-yl)carbamate (4b).**



4b was synthesized according to the procedure for the synthesis of **4a**. The reaction was conducted with 100.5 mg (0.20 mmol) of (*R*)-**3g** using Boc-L-Phe-OH (79.9 mg, 0.30 mmol, 1.5 equiv) and TCFH (78.2 mg, 0.28 mmol, 1.4 equiv). The product **4b** was purified by flash column chromatography (SiO_2, hexane/EtOAc, 100:0→70:30) to give the corresponding product **4b** in 62% yield (69.3 mg, 0.12 mmol) as white solid. The diastereomeric ratio was determined by HPLC analysis (d.r. >99:1). NMR spectra for **4b** contains conformational isomers, which is caused by the restricted C−N bond rotation around the carbamate group. ^{1}H NMR (396 MHz, $CDCl_3$, δ): 0.82 (brs, 3H), 1.29 (s, 6H), 1.35 (s, 6H), 1.35–1.39 (m, 9H), 1.66–1.85 (m, 2H), 2.16–2.23 (m, 1H), 2.34–2.42 (m, 1H), 2.50–2.58 (m, 1H), 2.72–2.84 (m, 1H), 2.94 (dd, *J* = 6.9, 13.7 Hz, 1H), 3.13 (dd, *J* = 6.1, 14.1 Hz, 1H), 4.23–4.33 (m, 1H), 4.88–4.97 (m, 1H), 5.75–5.86 (m, 1H), 7.12–7.31 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 15.3 (CH_2), 18.6 (CH_3), 25.4 (CH_3), 25.8 (CH_3), 28.3 (CH_3), 31.0 (CH_2), 38.2 (CH_2), 48.8 (br, B-*C*), 51.0 (*C*), 54.7 (*C*H), 80.2 (*C*), 82.9 (*C*), 126.0 (*C*H), 127.0 (*C*H), 127.6 (*C*H), 128.6 (*C*H), 128.7 (*C*H), 129.6 (*C*H), 136.4 (*C*), 145.9 (*C*), 155.2 (*C*), 171.8 (*C*). ^{11}B{^{1}H} NMR (127 MHz, $CDCl_3$, δ): 29.1. HRMS-ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{32}H_{45}N_2O_5{}^{11}BNa$, 571.3319; found, 571.3316. $[\alpha]_D^{22.0}$ –5.94 (*c* 1.10 in $CHCl_3$). The diastereomeric ratio was determined by HPLC analysis (d.r. >99:1). Daicel CHIRALPAK® ID-3, 2-PrOH/Hexane = 3/97, 0.5 mL/min, 40 °C, minor isomer = 8.65 min., major isomer = 12.01 min. mp 62–70 °C. IR (neat, cm^{-1}): 1708(C=O, amide).

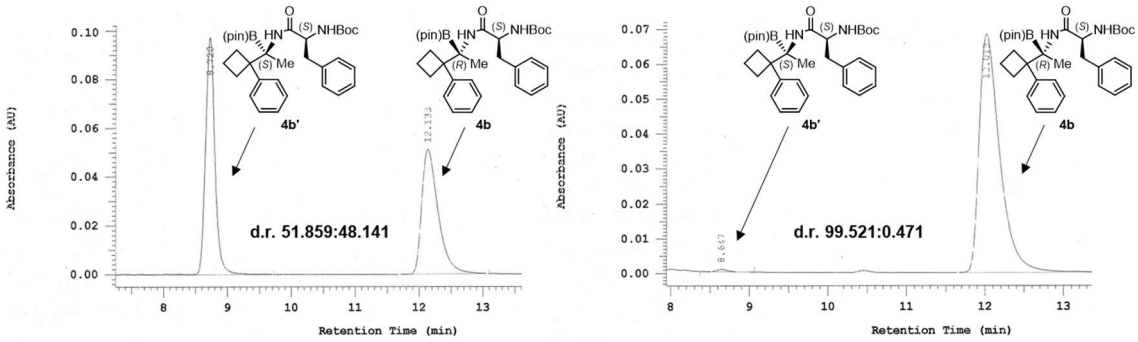
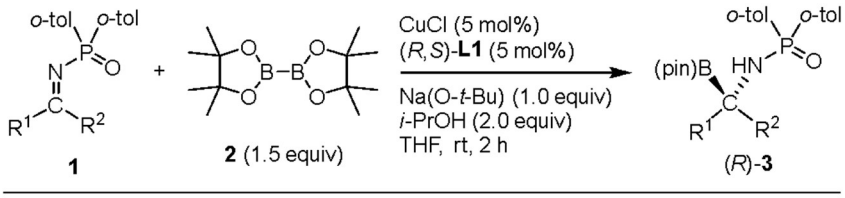
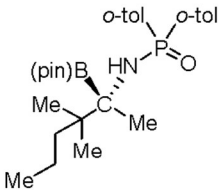


Figure S2. Determination of the diastereomeric ratio of **4b** by HPLC analysis.

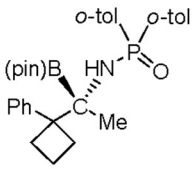
Additional Experimental Results

Unsuccessful examples of the borylation of ketimines with P(O)(*o*-tol)$_2$ as the protecting group

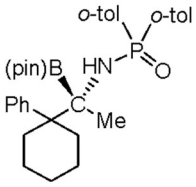




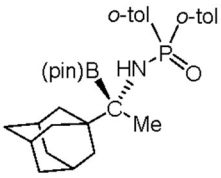
(*R*)-**3f'**
no reaction



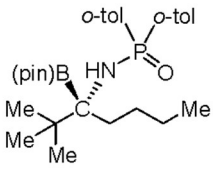
(*R*)-**3g'**
no reaction



(*R*)-**3h'**
no reaction

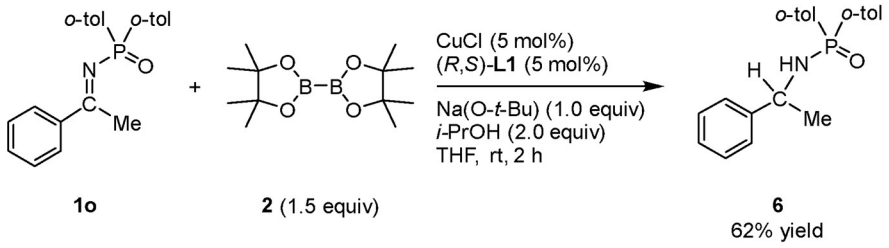


(*R*)-**3i'**
no reaction

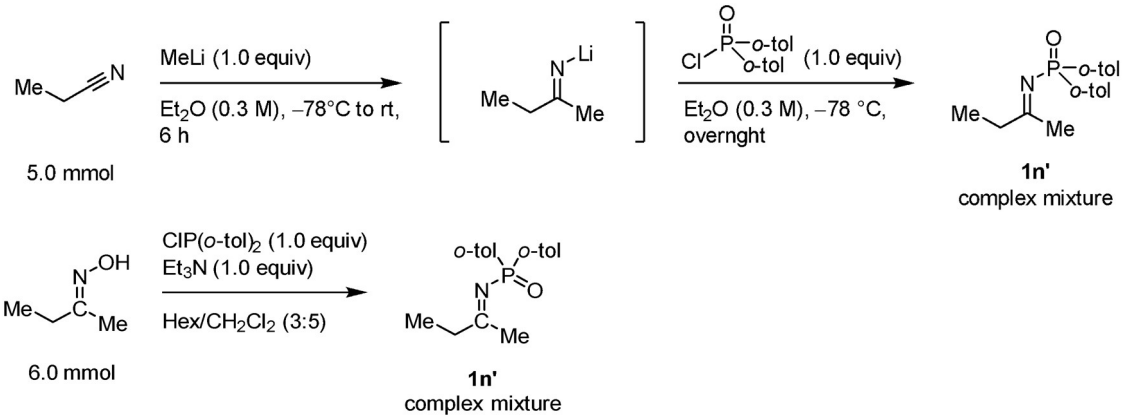


(*R*)-**3k'**
no reaction

An unsuccessful example of the borylation of aromatic ketimine 1o

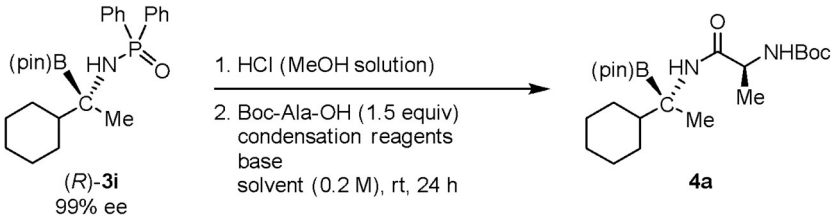


Unsuccessful synthesis of the substrate 1n'

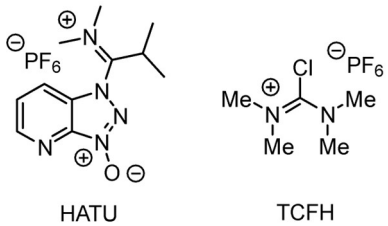


Neither procedure A nor B could synthesize the ketimine **1n'**.

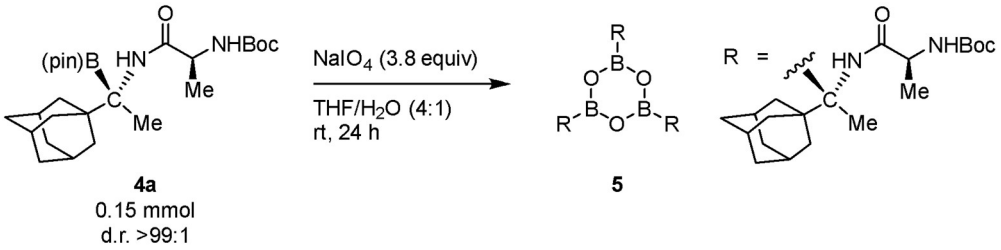
Condensation reactions with Boc-Ala-OH



entry	condensation reagents	base	solvent	yield (%)
1	HATU (3.0 equiv)	*i*-Pr_2EtN (3.0 equiv)	DCM	0
2	TCFH (1.2 equiv)	N-methylimidazole (3.5 equiv)	MeCN	74%



Hydrolysis of 4a with $NaIO_4$



4a (71.6 mg, 0.15 mmol, 1.0 equiv) and $NaIO_4$ (121.9 mg, 0.57 mmol, 3.8 equiv) were placed in a vial with a screw cap containing a Teflon®-coated rubber septum under air. THF (1.0 mL) and H_2O (250 μL) were added to the vial via a syringe. The resulting mixture was stirred for 24 h at room temperature. The reaction mixture was then diluted with brine and extracted with EtOAc three times, and dried over $MgSO_4$, and concentrated under reduced pressure. The combined mixture was washed cold pentane to give the boroxine **5** in 70% yield (41.3 mg, 0.105 mmol) as white solid. The corresponding boronic acid was not detected.

Determination of Absolute Configuration of Borylation Product

The absolute configuration of the product was determined based on X-ray crystallographic analysis of the compound (*R*)-**3e**. The absolute configurations of other borylation products were deduced by this product. The details were summarized in Figure S3 and Table S1.

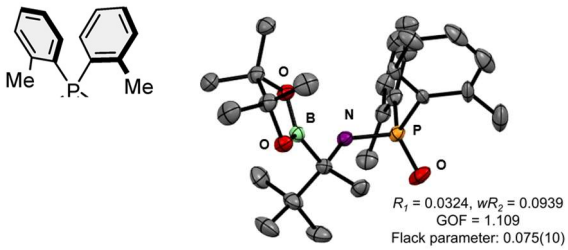


Figure S3. Molecular structure of (*R*)-**3e**. Thermal ellipsoids set at 50% probability; hydrogen atoms omitted for clarity.

Table S1. Summary of X-ray crystallographic data

CCDC Name	2052090
Empirical Formula	$C_{52}H_{78}B_2N_2O_6P_2$
Formula Weight	910.72
Crystal System	monoclinic
Crystal Size / mm^3	0.15 × 0.15 × 0.1
a / Å	7.83470(10)
b / Å	33.8529(3)
c / Å	10.56040(10)
β / °	111.6360(10)
V / Å3	2603.57(5)
Space Group	$P2_1$
Z value	2
*D*calc / g cm^{-3}	1.162
Temperature / K	123
$2\theta_{max}$ / °	147.536
μ(MoKα) /cm^{-1}	11.32
No. of Reflections Measured	Total: 12604 Unique: 7917 (R_{int} = 0.0223)
No. of Observations (All reflections)	7917
Residuals: R_1 (I > 2.00σ(I))	0.0324
Residuals: wR_2 (All reflections)	0.0939
Goodness of Fit Indicator (GOF)	1.109
Maximum Peak in Final Diff. Map / $Å^3$	0.23 e^-
Minimum Peak in Final Diff. Map / $Å^3$	–0.24 e^-
Flack Parameter	0.075(10)

Plausible Catalytic Cycle

Based on the theoretical and experimental results, I have proposed a plausible mechanism for the enantioselective borylation of aliphatic ketimines (Figure S4). First, CuCl, (*R*,*S*)-**L1** and Na(O-*t*-Bu) would react to form the copper(I)/NHC complex **A**, which would undergo sigma-bond metathesis with **2** to give borylcopper(I) **B**. The subsequent insertion to **1** would lead to the formation of the copper(I) intermediate **D**, which would be protonated in the presence of an alcohol to afford the borylated product **3**. This step would also result in the formation of copper alkoxide **A**.

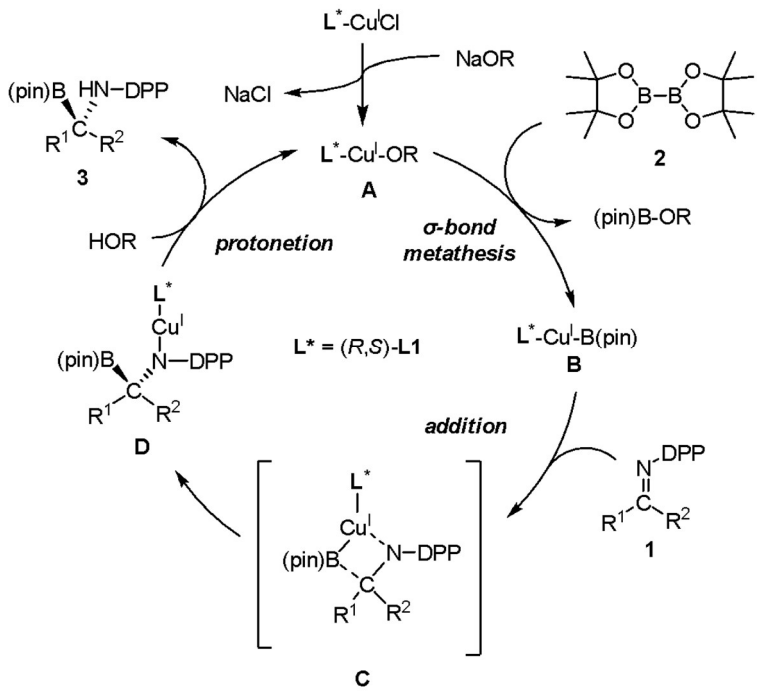


Figure S4. Proposed mechanism for the copper(I)-catalyzed enantioselective borylation of aliphatic ketimines.

DFT Calculations

All calculations were performed using the Gaussian 09W (revision C.01) program package.[8] Geometry optimizations and transition states (TS) calculations were performed with wB97XD/def2tzvp//wB97XD/Def2svp/THF(SMD). Molecular structures were drawn using the Mercury 3.5 program.[9] Frequency calculations were conducted on gas-phase optimized geometries to check all the stationary points as either minima or transition states. Intrinsic reaction coordinate (IRC) calculations were carried out to confirm the transition state connecting the correct reactant and product on the potential energy surface.

I conducted the DFT calculations on the addition of the (*R*,*S*)-**L3**/borylcopper(I) complex (**II**) to ketimine **1p** (**I**) to investigate the reaction mechanism and the origin of the enantioselectivity. The

copper(I)-catalyzed borylation of dialkyl ketimine **1p** proceeded to give (*R*)-**3p** in 74% yield with 90% ee. As shown in Figure S3, The energy of the transition state (**TS1**) in the *Si*-face addition is lower than that of the transition state (**TS3**) in the *Re*-face addition by 1.93 kcal/mol. This calculation result is in good agreement with the experimental result (calc. 92% ee versus exp. 90% ee).

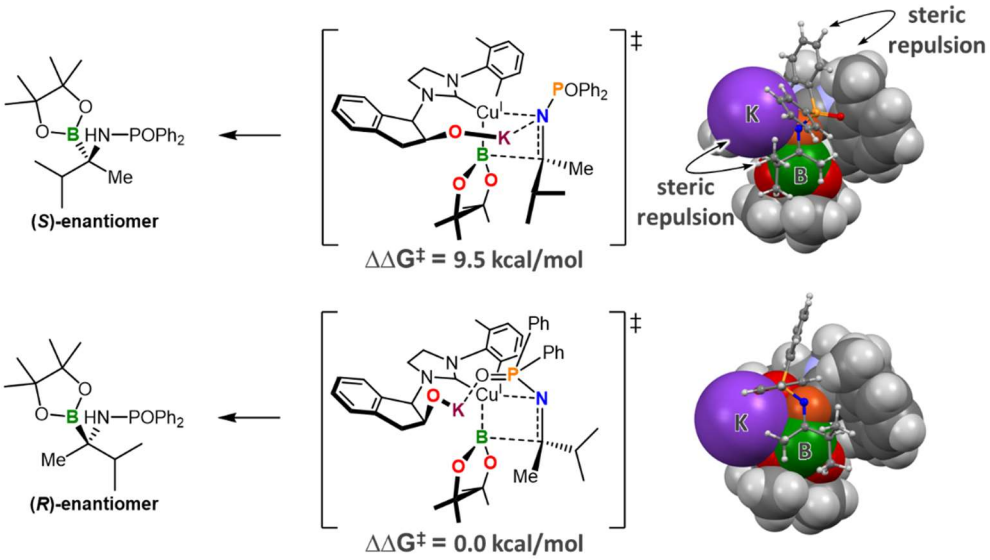


Figure S5. DFT calculation of TSs of boryl cuplation with a NHC bearing alcohol moiety.

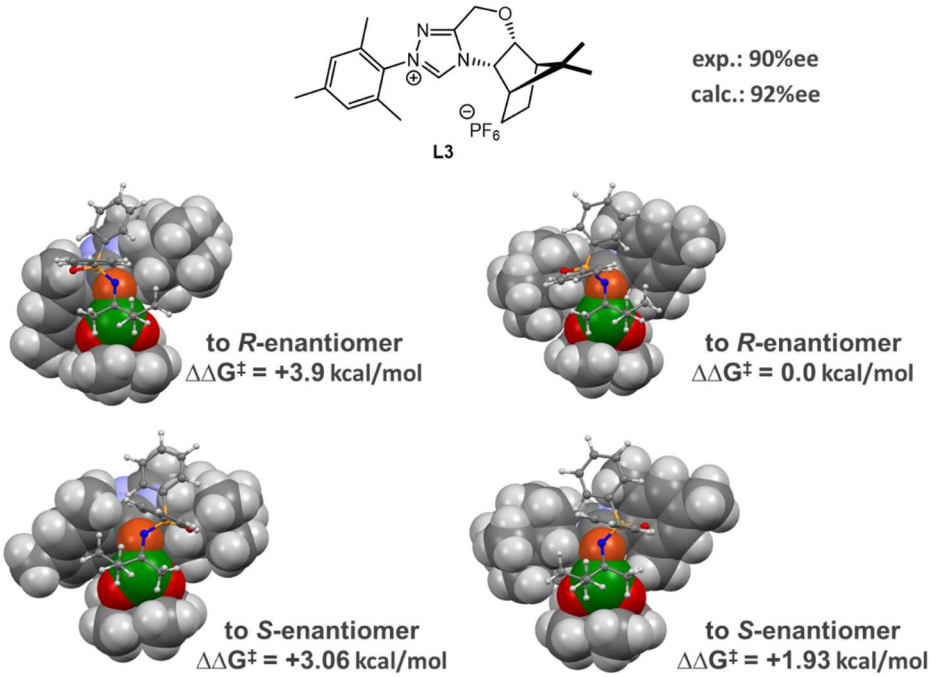


Figure S6. DFT calculation of TSs of boryl cuplation with L3.

Reference of SI

(1) Shintani, R.; Takatsu, K.; Takeda, M.; Hayashi, T. Copper-Catalyzed Asymmetric Allylic Substitution of Allyl Phosphates with Aryl- and Alkenylboronates. *Angew. Chem., Int. Ed*. **2011**, *50*, 8656–8659.

(2) Winn, C. L.; Guillen, F.; Pytkowicz, J.; Roland, S.; Mangeney, P.; Alexakis, A. Enantioselective copper catalysed 1,4-conjugate addition reactions using chiral N-heterocyclic carbenes. *J. Org. Met. Chem*. **2005**, *690*, 5672–5695.

(3) Harada, A.; Makida, Y.; Sato, T.; Ohmiya, H.; Sawamura, M. Copper-Catalyzed Enantioselective Allylic Alkylation of Terminal Alkyne Pronucleophiles. *J. Am. Chem. Soc*. **2014**, *136*, 13932–13939.

(4) Núñez, M. G.; Farley, A. J. M.; Dixon, D. J. Bifunctional Iminophosphorane Organocatalysts for Enantioselective Synthesis: Application to the Ketimine Nitro-Mannich Reaction. *J. Am. Chem. Soc.* **2013**, *135*, 16348–16351.

(5) Abell, J. P.; Yamamoto, H. Dual-Activation Asymmetric Strecker Reaction of Aldimines and Ketimines Catalyzed by a Tethered Bis(8-quinolinolato) Aluminum Complex. *J. Am. Chem. Soc.* **2009**, *131*, 15118–15119.

(6) Masumoto, S., Usuda, H., Suzuki, M., Kanai, M., & Shibasaki, M. Catalytic Enantioselective Strecker Reaction of Ketoimines. *J. Am. Chem. Soc.* **2003**, *125*, 5634–5635.

(7) Beutner, G. L.; Young, I. S.; Davies, M. L.; Hickey, M. R.; Park, H.; Stevens, J. M.; Ye, Q. TCFH–

NMI: Direct Access to N-Acyl Imidazoliums for Challenging Amide Bond Formations. *Org. Lett.* **2018**, *20*, 4218–4222.

(8) Gaussian 09, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; Gaussian, Inc., Wallingford CT, 2009.

(9) Mercury: http://www.ccdc.cam.ac.uk/Solutions/CSDSystem/Pages/Mercury.aspx

V Summary of This Thesis

Organoboron compounds and silylboranes are very useful synthetic reagent for organic synthesis. Furthermore, functionalized them, which have another functional group on carbon or silicon atom bearing a boryl group, are particularly important building blocks for synthesis of complex molecules. Additionally, the property of borylated compounds is also interesting for pharmaceutical and material science. If direct borylation is difficult due to the complexity of substrates, complex organoboron compounds can be prepared by derivatization of functionalized organoboron compounds. Thus, the efficient preparation methods of functionalized them is highly required. In this thesis, I focused on the synthesis of functionalized organoboron compounds and silylboranes. Moreover, I investigated their synthetic application to produce material silicon compounds and pharmaceutic peptide-motifs.

In Chapter 2, I developed iridium- or nickel-catalyzed monoborylation of dihydrosilanes to propduce hydrosilylboronates, which have a hydrogen atom on the silicon atom. Obtained hydrosilylboronates can be employed for reported transition-metal-catalyzed silylation reactions with retention of their Si–H bond. Additionally, Si–H bond of hydrosilylboronates can be transformed into Si–Cl bond with their Si–B bond intact. Importantly, the corresponding hydrosilyl lithium was generated by the treatment of hydrosilylboronate with MeLi. This generation of silyl anion species was confirmed by the Si–Si coupling with chlorosilanes and $^{29}Si\{^{1}H\}$ NMR measurements.

In chapter 3, I developed the iterative synthesis of oligosilanes using methoxyphenyl- and hydrogen-substituted silylboronates as building blocks. Methoxyphenyl- or hydrogen-substituted silylboronates were prepared by The corresponding silyl nucleophiles were generated by the treatment of these silylboronates with MeLi, allowing Si–Si coupling with chlorosilanes. Additionally, methoxyphenyl or hydrogen at the terminal was easily chlorinated by acid or chlorination reagent, allowing the next Si–Si coupling with silylboronates and iteration. Since the generation of silyl lithiums bearing methoxyphenyl was failed by the reduction of the chlorosilane with Li, this iterative synthesis was achieved by functionalized silylboronates. By this method, a designed oligosilane to be a tree-shape was easily synthesized. The most important feature of iterative synthetic methods is that various structures can be synthesized by the changing introduced units even from a limited set of building blocks. By the present method, I could diversely synthesize four oligosilanes with different sequences from a chlorosilane and 4 silylboronates. Additionally, from SC-XRD analysis of obtained oligosilanes, the iterative synthetic manner was confirmed. Compared to previous synthetic methods of oligosilanes, the present method has great potential to produce complex oligosilanes.

In Chapter 4, I developed the Cu(I)-catalyzed enantioselective borylation of ketimines to form chiral α-amino boronates. The suitable chiral NHC ligand was found by the computational-study-guided ligand design. Additionally, a boryl peptide was easily synthesized via simple condensation between obtained an α-amino boronate and an amino acid. As such boryl peptides are attracted as drug candidates, this catalytic asymmetric borylation would be useful method to produce the parent chiral

α-amino boronates.

Through this thesis, I developed synthetic methods of functionalized organoboron compounds including hydro- and methoxyphenyl-substituted silylboronates and chiral α-amino boronates via transition-metal-catalyzed borylation reactions. Further, I demonstrated that they can be used for the synthesis of oligosilanes, which are attracted as materials, and boryl peptides, which are regarded as bioisosteres of peptide-based drugs, respectively. Those useful synthetic applications would benefit further development of oligosilane-based materials and boron-contained pharmaceuticals.

VI List of Publications

Chapter II:

Synthesis of Hydrosilylboronates via the Monoborylation of a Dihydrosilane Si–H Bond and Their Application for the Generation of Dialkylhydrosilyl anions

Takumi Takeuchi, Ryosuke Shishido, Koji Kubota, and Hajime Ito

Chem. Sci. **2020**, *12*, 11799–11804.

Chapter III:

Iterative Synthesis of Oligosilanes Using Methoxyphenyl- or Hydrogen-Substituted Silylboronates as Building Blocks: General Synthetic Method for Complex Oligosilanes

Takumi Takeuchi, Avijit Roy, and Hajime Ito

under revision.

Chapter IV:

Synthesis of Chiral α-Amino Tertiary Boronates via the Catalytic Enantioselective Nucleophilic Borylation of Dialkyl Ketimines

Koji Kubota, Daiyo Miura, Takumi Takeuchi, Shun Osaki, and Hajime Ito

ACS Catal. **2021***, 11,* 6733–6740.

Other publication:

Concise Synthesis of Potassium Acyltrifluoroborates from Aldehydes through Copper(I)-Catalyzed Borylation/Oxidation

Jumpei Taguchi, Takumi Takeuchi, Rina Takahashi, Fabio Masero, and Hajime Ito

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