Synthetic Studies on the Chemistry of *gem*-Dimetalation with Inter-element Compounds

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Contents

Abbreviations

Ac	acetyl
Anal.	element analysis
aq.	aqueous
Bn	benzyl
Bpin	4,4,5,5-tetramethyl-1,3,2-dioxabolan-2-yl
brs	broad singlet (spectral)
Bu	butyl
calcd	calculated
cat.	catalytic
Cy	cyclohexyl
d	doublet (spectral)
dba	dibenzylideneacetone
DME	1,2-dimethoxyethane
DMF	N,N-dimethylformamide
δ	scale (NMR)
ed.	edition
ee	enantiomeric excess
Et	ethyl
FAB	fast atom bombardment
GC	gas chromatography
GPC	gel permeation chromatography
h	hour(s)
Hex	hexyl
HMPA	hexamethylphosphoramide
HPLC	high performance liquid chromatography
HRMS	high-resolution mass spectra
Hz	hertz
J	coupling constant in Hz
LDA	lithium diisopropylamide
m	multiplet (spectral)
M	mol per liter
Me	methyl
MEM	2-methoxyethoxymethyl
min	minute(s)
mL	mililiter
mp	melting point
Ms	mesyl
NMR	nuclear magnetic resonance
Pent	pentyl
Ph	phenyl
Pr	propyl
q	quartet (spectral)
r.t.	room temperature
R_f	relative mobility
s	singlet (spectral)
t	triplet (spectral)
temp	temperature
TBAF	tetrabutylammonium fluoride
Tf	trifluoromethanesulfonyl
THF	tetrahydrofuran
TLC	thin layer chromatography
TMP	2,2,6,6-tetramethylpiperide
TMS	trimethylsilyl

Chapter 1

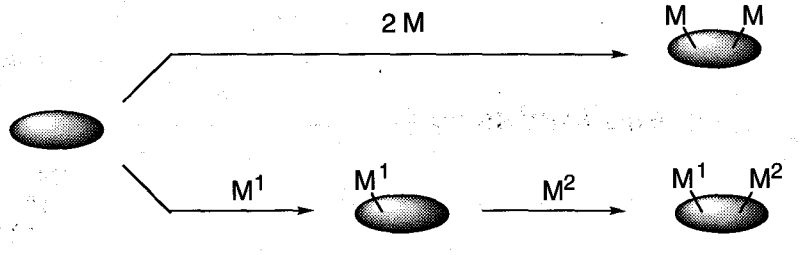
Introduction and General Summary

Modern Organic Synthesis

Over decades, organic chemistry has contributed to the prosperity of human beings by providing important chemicals such as pharmaceuticals, agrochemicals, and functional materials. To prepare such valuable target compounds, organic synthesis has played crucial roles and provided various kinds of synthetic reactions and reagents that exhibit high chemo-, regio- and stereoselectivities. Since Grignard succeeded in preparation of organomagnesium compounds in 1900, explosive use of such organometallic reagents as Zn, Mg, Li, Cu, Al, Sn, Si, and B have evolved as anion synthons in carbon–carbon bond formation or functionalization of target molecules.[1] Modern organic synthesis cannot be performed without organometallic reagents any more.

Organodimetallic Compounds

Recently, organodimetallic reagents containing two metals have attracted considerable attention as further versatile reagents in organic synthesis, because they behave as double nucleophile and accordingly allow successive double carbon–carbon bond formation to effect efficient construction of target molecules.[2] Moreover they often exhibit unique reactivities and selectivities that differ considerably from monofunctional organometallic reagents. Thus, organodimetallic reagents have been recognized decisively as novel and unique class of synthetic reagents. Although organodimetallic compounds are extremely versatile in organic synthesis, they have generally following drawbacks: (1) preparation of organodimetallics is not always straightforward, (2) dimetallic reagents with two different metals require stepwise procedures for preparation (Scheme 1), (3) organodimetallic compounds are usually unstable and thus generated *in situ* and used directly without purification.



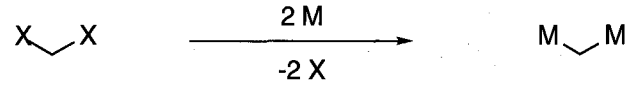
Scheme 1

Preparation of Organodimetallic Compounds

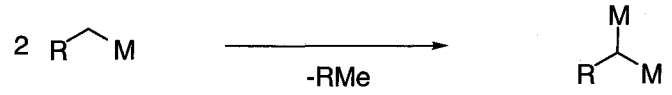
Preparative methods of organodimetallic compounds can be classified into following types (*vide infra*): (1) halogen–metal exchange of dihalo substrates, (2) disproportion of organometallic compounds, (3) metalation from organometallic compounds, (4) insertion of metal-substituted carbenoid into organometallic compounds, (5) hydrometalation to alkynes,

alkynyl- or alkenylmetals, (6) carbometalation to alkynyl- or allylmetals, (7) transmetalation of organodimetallic compounds, (8) double deprotonation of activated methyl or methylene compounds, and (9) metalative dimerization of alkenes. Typical and important examples are mentioned below principally in the order of substituted position of two metallic atoms.

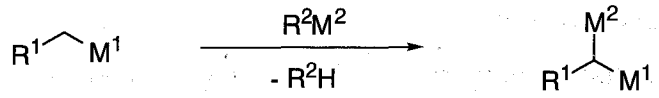
(1) Halogen–metal exchange



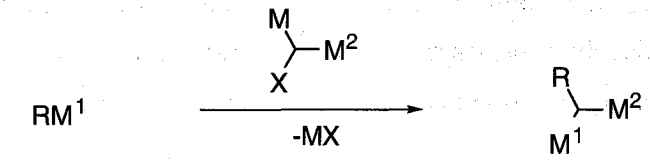
(2) Disproportion



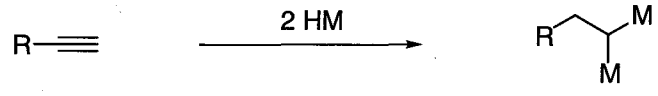
(3) Deprotonation



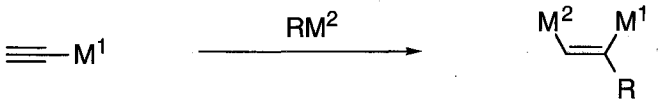
(4) Insertion



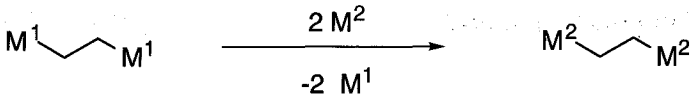
(5) Hydrometalation



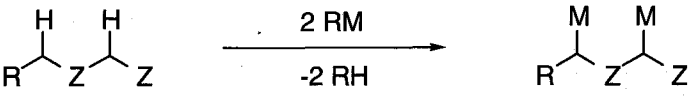
(6) Carbometalation



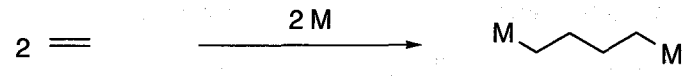
(7) Transmetalation



(8) Double deprotonation

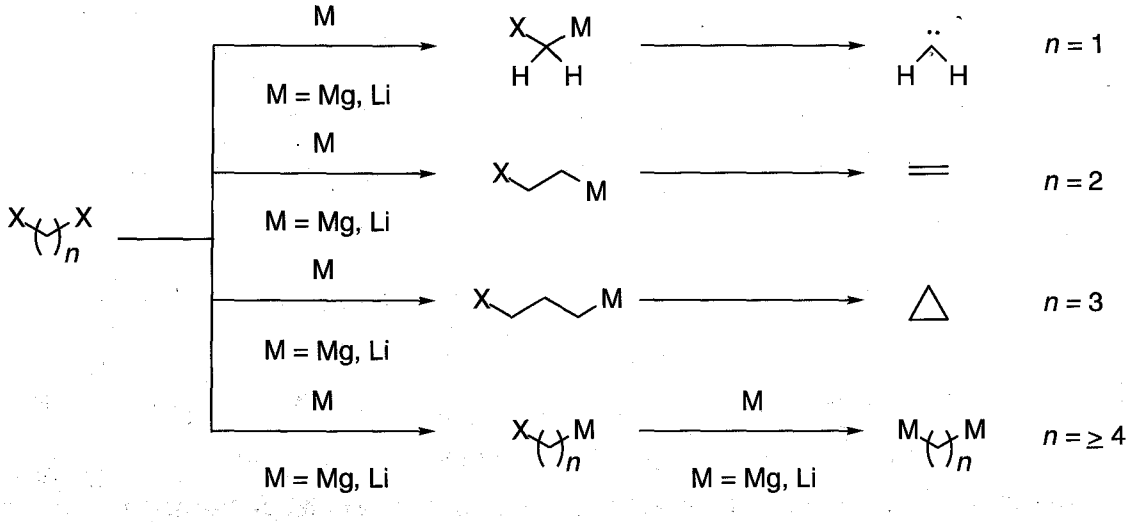


(9) Metalative dimerization



Direct replacement of a halogen atom in organic molecules with magnesium or lithium metal is the most powerful and widely used method for the synthesis of organometallic

reagents but is often of limited value for the synthesis of organodimetallic reagents due to rapid α-, β-, or γ- elimination of metal halide, yielding carbenes, ethenes, or cyclopropanes in cases that 1,*n*-dihalo compounds (*n*<4) are employed (Scheme 2). This type of reaction is applicable to only 1,*n*-dihalo compounds (*n*≥4) to give 1,*n*-organodimetallic compounds.[2h,3]

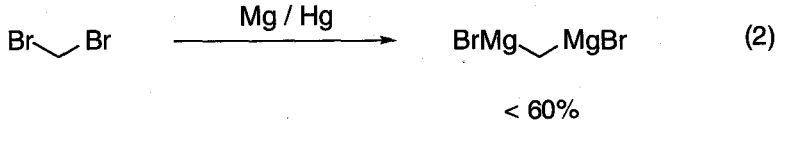


Scheme 2

The first synthetic route to dilithiomethane was recorded by Ziegler, who employed pyrolytic disproportion of methyllithium at high temperatures (eq 1).[2f] Although this method still represents the best procedure for dilithiomethane, delicate temperature control is necessary as dilithiomethane decomposes above 230 °C to give hydrogen, lithium hydride, and lithium carbide.

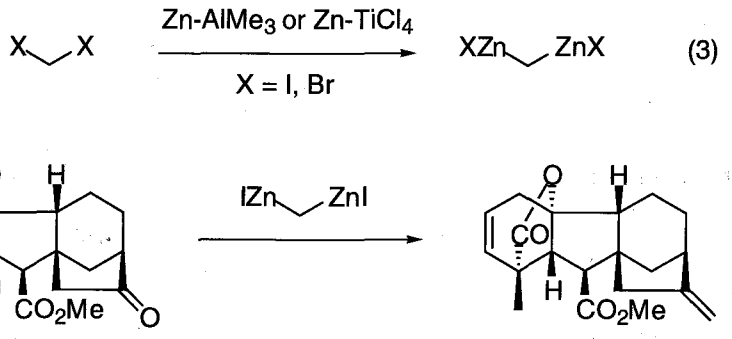
$$2CH_3Li \xrightarrow[225\ ^\circ C]{} CH_2Li_2 + CH_4 \qquad (1)$$

Bis(bromomagnesio)methane is prepared starting with dibromomethane and magnesium amalgam instead of metallic magnesium (eq 2). Yields of the di-Grignard reagent are, however, unreproducible and generally less than 60%.[4]

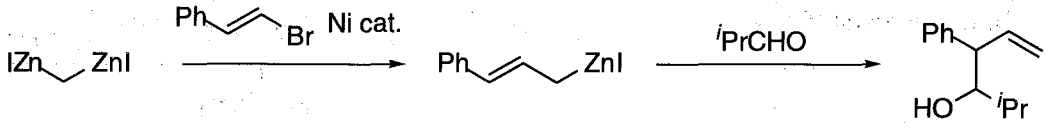


Bis(halozincio)methanes are synthesized by direct reduction of dihalomethane with zinc dust in the presence of organoaluminum or titanium tetrachloride (eq 3) and shown to be applicable to methylenation of carbonyl compounds under mild conditions by Nozaki,

Oshima, Takai and their coworker.[5] This methylenation reaction has advantages over the Wittig reaction particularly for easily enolizable ketones: neither isomerization of a chiral center nor undesired reactions of base-sensitive functionality in substrates take place.[19] For instance, nor-gibberellin that is very prone to enolization and is not pertinent to the Wittig methylenation gives the desired exo methylene product only with the reagent (eq 4).[6]

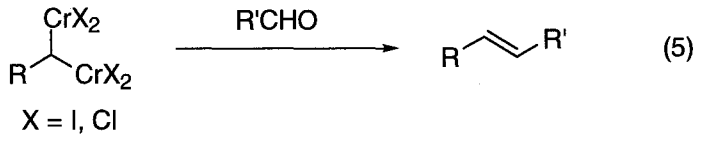


More recently, an excellent preparative method for *gem*-bis(halozincio)alkanes was disclosed by Utimoto, Matsubara and their coworker starting with *gem*-dihaloalkanes, zinc dust, and a catalytic amount of Pb.[2c,7a,7b] The *gem*-bis(halozincio)alkane is demonstrated to be a highly potential synthetic reagent. Its reaction with carbonyl compounds proceeds without epimerization of a chiral center. α,β-Unsaturated enals undergo 1,2-addition selectively to give conjugated dienes. Moreover sterically hindered or easily enolizable ketones are also converted into the corresponding alkenes in the presence of a stoichiometric amount of $TiCl_3$. A stepwise reaction of bis(iodozincio)methane with two different electrophiles is achieved by transition metal catalyzed cross coupling reaction followed by carbonyl addition (Scheme 3).



Scheme 3

gem-Dichromium reagents can also be prepared by reduction of *gem*-dihalomethanes with a divalent chromium reagent.[8] A general method for conversion of aldehydes to a 1,2-disubstituted olefins is disclosed by means of a *gem*-dichromium reagent and shown to have *E*-selectivity. The reaction is also considered to be a good alternative to the Wittig olefination.



(5)

Tebbe's reagent ($Cp_2TiCH_2AlClMe_3$) is one of the most famous *gem*-organodimetallic compounds and widely used in organic synthesis. The reagent is prepared by reaction of $AlMe_3$ with Cp_2TiCl_2 and is a versatile methylene transfer reagent for homologation of olefins and for conversion of ketones to terminal olefins (eq 6).[9,10]

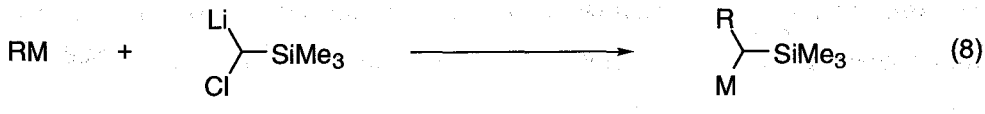
(6)

The rich chemistry of allylic metal reagents[11] has provided a variety of new synthetic reagents including *gem*-dimetallic reagents (eq 7).[2a,12] Regio- and stereo-chemical control is essential in the preparation of dimetallic reagents by deprotonation of allylic metals and in the reaction with electrophiles. Thus, preparation of requisite allylic metal reagents in an isomerically pure form is of great concern.

(7)

M = Si, Ge, B

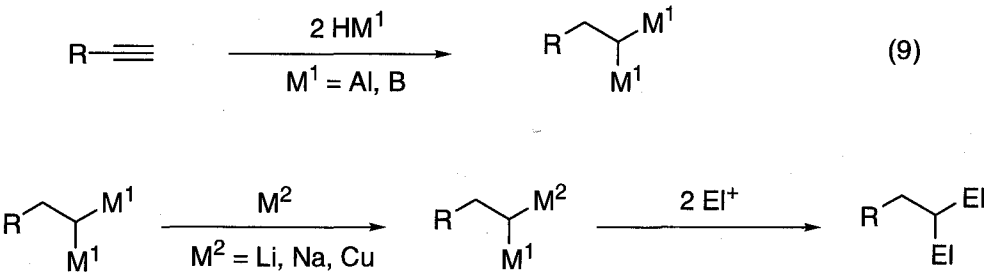
Insertion reaction of silyl substituted carbenoids into C–B bonds of organoborons affords *gem*-dimetallic compounds as disclosed by Matteson (eq 8).[13] Similarly, the silyl substituted carbenoids react with organoaluminum, organozirconium and organocopper compounds to give various kinds of *gem*-organodimetallic compounds.[14,15]



(8)

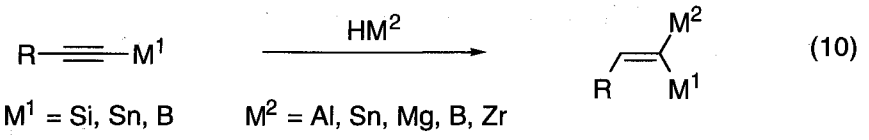
M = B, Al, Zr, Cu

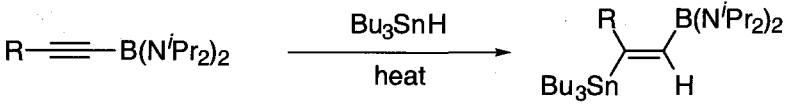
gem-Dialumino-alkanes and *gem*-diborylalkanes are readily accessible via double hydroalumination or hydroboration, respectively, to terminal acetylenes (eq 9).[2a] However, they have not been widely utilized for organic synthesis because of low nucleophilicity. In general, it is necessary that at least one of two metals is transmetalated to lithium, sodium or copper to attain enough nucleophilicity (Scheme 4).[4a,16]

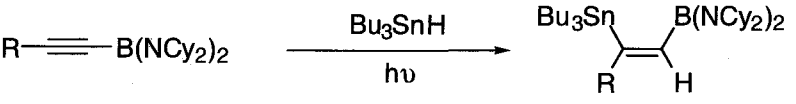


Scheme 4

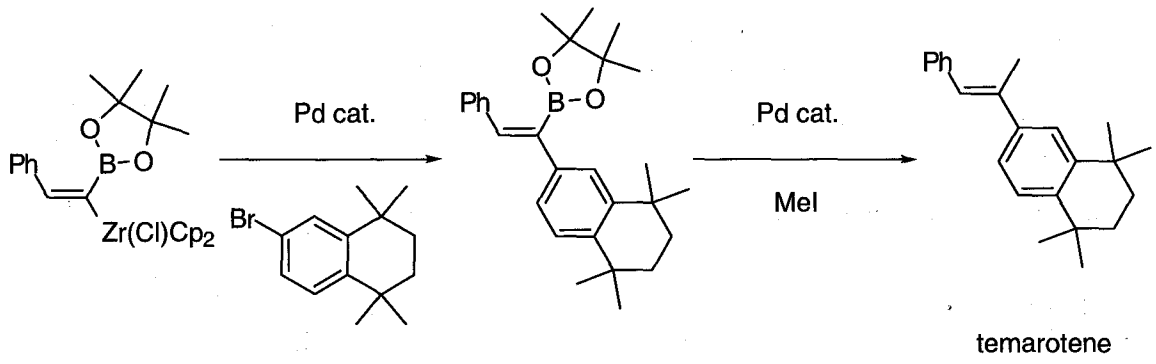
Hydrometalation to alkynylmetal is a straightforward route to *gem*-dimetalalkenes, although the requisite alkynylmetals should be separately prepared before (eq 10).[2a,17] Problems in this method are selectivity in regio- and stereochemistry. Regioselective addition of tributyltin hydride to alkynylborane is attained by a proper choice of boron substituents and experimental conditions (eqs 11 and 12), giving (*E*)- or (*Z*)-1-boryl-2-stannylalkenes.[17l]





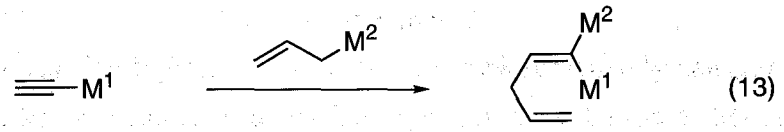


The synthetic utility of the *gem*-borylzircona-alkenes has been demonstrated by the total synthesis of temarotene, chokol A, and chokol G through a combination of sequential palladium-catalyzed cross coupling reactions (Scheme 5).[18]



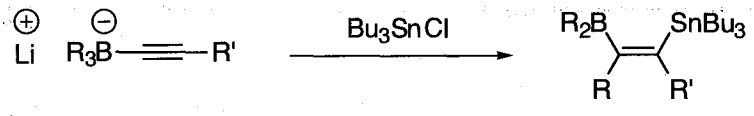
Scheme 5

Addition of allylzinc bromide to alkynylzinc bromide or alkynylmagnesium bromide also leads to geminal organodimetallic alkenes (eq 13).[2a,2b,19] In a similar way, various kinds of organodimetallic compounds including Zn, Mg, Al, Li, B, Si, Cu, and In were synthesized.



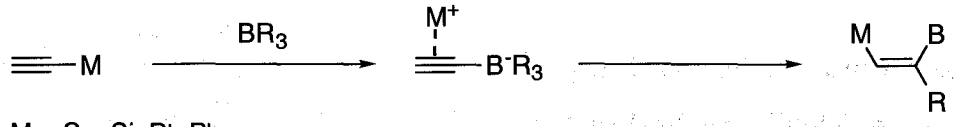
M^1, M^2 = Zn, Mg, Al, Li, B, Si, Cu, In (13)

An alkyl group in trialkyl(alkynyl)borates rearranges from boron to alkynyl carbon by reaction with variety of electrophiles. For example, treatment of trialkyl(alkynyl)borates with Bu_3SnCl specifically produces 1-boryl-2-stannylalkenes with *E*-configuration (eq 14).[20]



(14)

Similarly, alkynylmetals of Sn, Si, Pt and Pb react with trialkylboranes to give the corresponding 1-boryl-2-metalo-alkenes via rearrangement of an alkyl group in trialkyl(alkynyl)borate intermediates generated in situ (Scheme 6).[21]

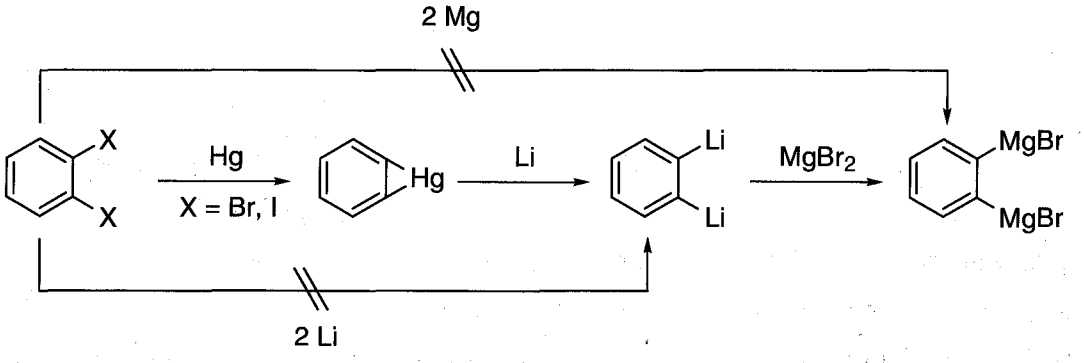


M = Sn, Si, Pt, Pb

Scheme 6

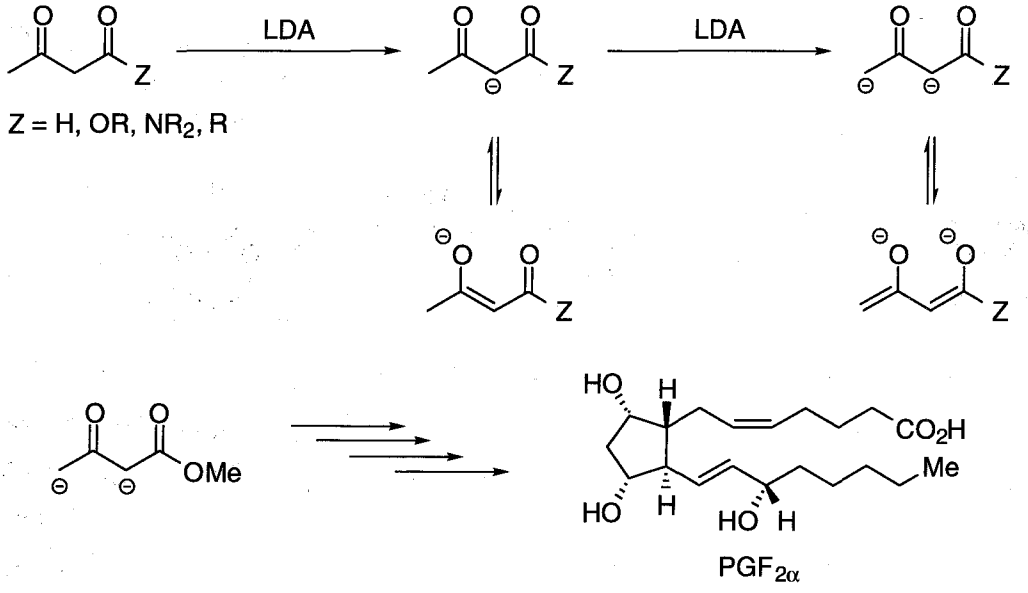
Wittig and Bickelhaupt were the first who applied mercury-lithium exchange of *o*-dimercuriobenzene to the synthesis of *o*-dilithiobenzene, that was unavailable by direct

halogen-lithium exchange reaction (Scheme 7).[2h,22] *o*-Di(bromomagnesio)benzene, inaccessible by direct halogen-metal exchange as well, can be obtained via *o*-dilithiobenzene. Although mercury-lithium exchange is effective for preparation of organodimetallic compounds that are inaccessible by halogen-metal exchange reaction, toxicity of mercury should be considered carefully.



Scheme 7

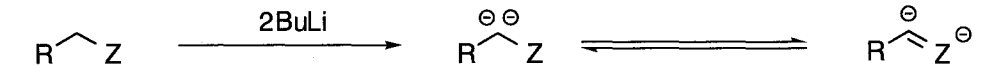
Dianions prepared by double deprotonation of acidic hydrogens, have been widely used in organic synthesis owing to their ready accessibility, predictable reactivity, and wide reaction repertoires.[2a,2b,2e,23] A typical example is 1,3-dianion reagents generated by double deprotonation of β-keto carbonyl compounds that are widely utilized in synthesis of such natural products as prostaglandin $F_{2\alpha}$, geraniol, vernolpin, and macrolides (Scheme 8).



Scheme 8

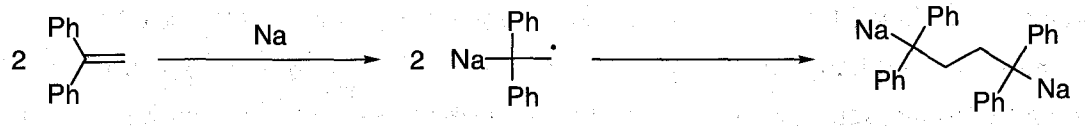
However, dianions can only be prepared from β-dicarbonyl compounds or heteroatom substituted methanes that possess acidic hydrogens and can stabilize the resulting dianions by

delocalization (Schemes 8 and 9).



Scheme 9

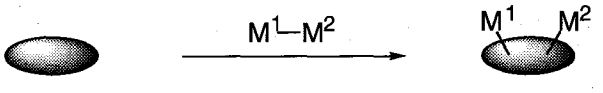
Metalative dimerization reaction of alkene with sodium metal affords disodiobutane. This is a novel route to 1,4-metalobutenes (Scheme 10), but practical applications for organic synthesis are limited.[24,25]



Scheme 10

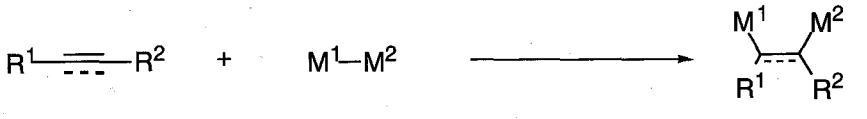
Dimetalation with Interelement Compounds

In recent decades, new synthetic strategies for synthesis of organodimetallic compounds have been developed which involves simultaneous introduction of two metals into organic molecules using interelement compounds M^1–M^2.[26] It is apparent that this approach, if feasible, is attractive and straightforward, especially for preparation of organodimetallic compounds bearing different kinds of metals (eq 15).



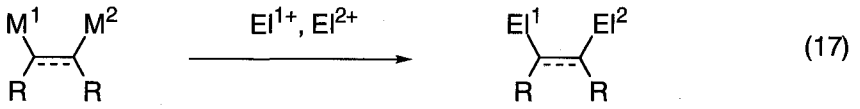
(15)

It is well documented that interelement compounds such as B-B, B-Si, B-Sn, Mg-Si, Mg-Zn, Mg-Sn, Al-Si, Si-Si, Si-Sn, Ge-Ge, Sn-Cu and Sn-Sn add to alkynes and or alkenes in the presence or absence of transition metal catalysts to give *vic*-dimetalated compounds (eq 16) which can be elaborated for extension of carbon framework (eq 17).[27]



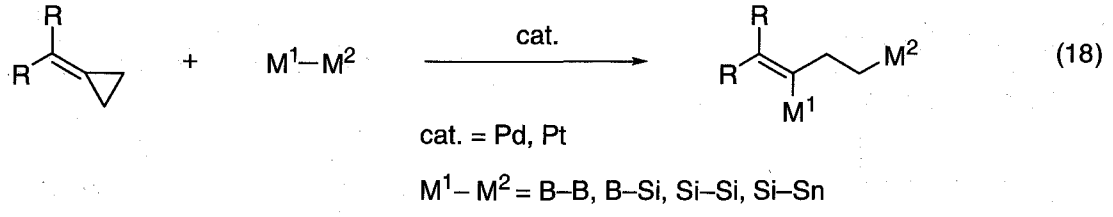
(16)

M^1– M^2 = B–B, B–Si, B–Sn, Si–Si, Si–Sn, Sn–Sn, Si–Mg, Si–Al, Zn–Mg,Sn–Zn, Ge–Ge, Sn–Cu



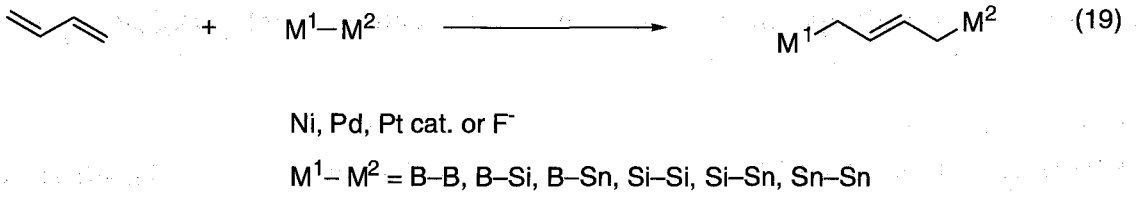
(17)

Methylenecyclopropanes can be employed for the reaction with B-B, B-Si, Si-Si, and Si-Sn in the presence of transition metal catalysts to give α,γ- dimetallic compounds (eq 18), as reported by Miyaura, Ito, and de Meijere independently.[28]



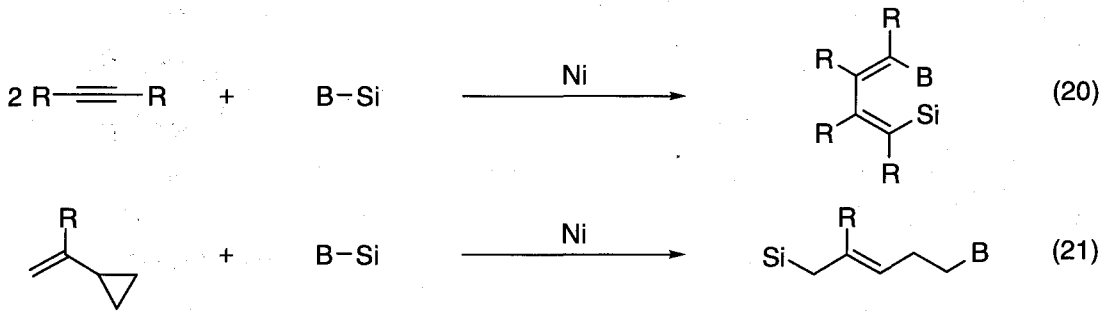
(18)

1,3-Butadienes also react with interelement compounds to give 1,4-organodimetallic compounds (eq 19).[29]



(19)

Dimetalation under dimerization of 1-alkynes is achieved by Ni catalysts to afford 1-silyl-4-boryl-1,3-butadienes in a regio- and stereoselective manner (eq 20)[30]. Similarly, vinylcyclopropanes undergo regio- and stereoselective reaction with silylborane in the presence of Ni catalyst, giving 5-boryl-1-silyl-2-pentenes (eq 21).[31]



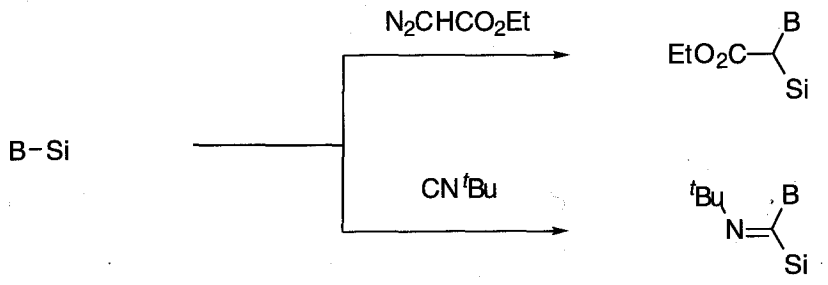
(20)

(21)

***gem*-Dimetalation with Interelement Compounds**

At the outset of the present study, examples of the *gem*-dimetalations with interelement compounds were limited only to the reaction of silylborane with ethyl diazoacetate (Buynak,

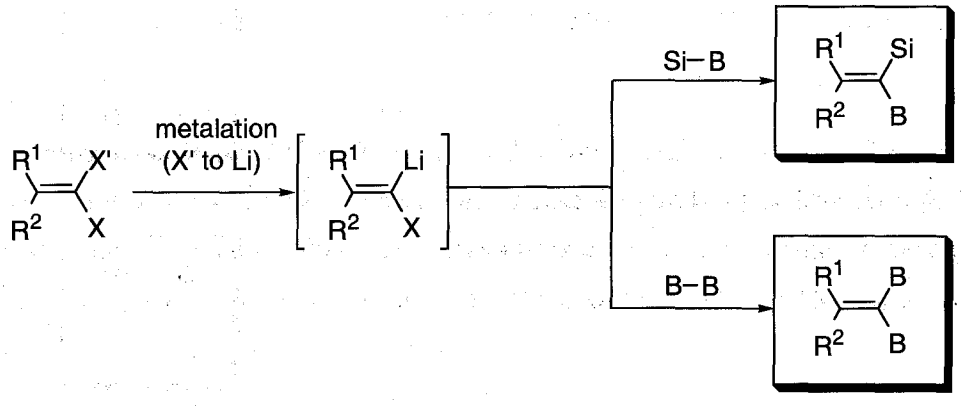
Ali)[32,33] or isonitriles (Suginome, Ito)[34] (Scheme 11).



Scheme 11

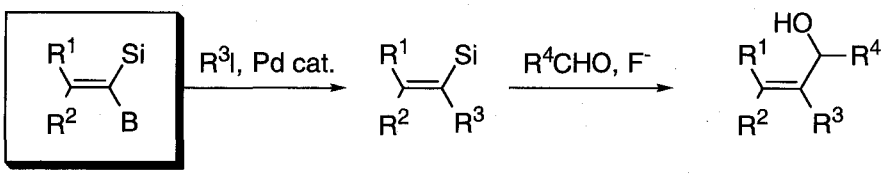
In view of growing interest in organodimetallic reagents, novel methods for efficient synthesis of *gem*-organodimetallics using interelement compounds should be of great significance. Among various kinds of interelement compounds, the author selected silylboranes and diborons, because the resulting dimetallic reagents are relatively stable, less toxic, compatible with many functional groups, and applicable to a variety of efficient transformations of organosilanes and organoboranes.

Chapter 2 describes the synthesis of 1-boryl-1-silyl-1-alkenes and 1,1-diboryl-1-alkenes. Alkenylidene-type carbenoids are demonstrated to react with the interelement compounds and to afford 1-boryl-1-silyl-1-alkenes and 1,1-diboryl-1-alkenes, respectively, through formation of ate complexes between lithium carbenoids and the interelement compounds (Scheme 12). The author discusses in detail the synthesis of these *gem*-dimetallic compounds.



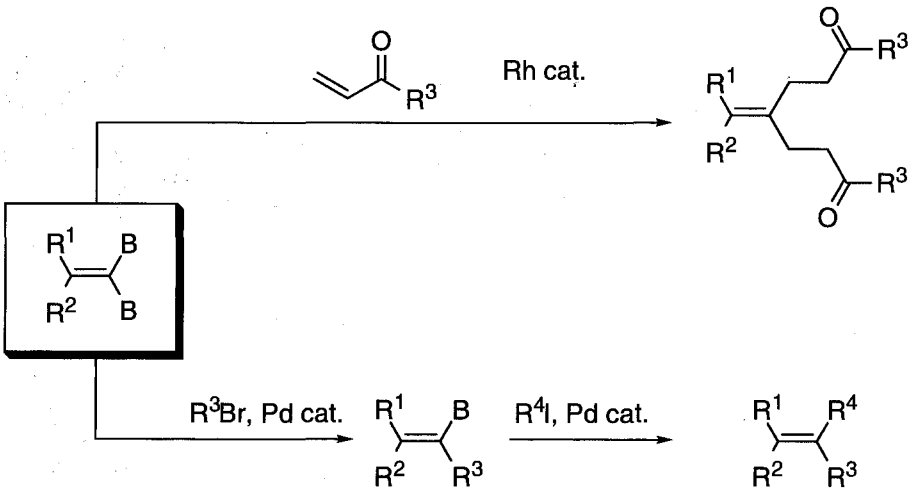
Scheme 12

In addition, synthetic utilities of the silylborylated and diborylated compounds are demonstrated by cross-coupling with aryl halides, giving rise to the corresponding 1-aryl-1-alkenylsilanes in good yields.[35] The coupled products are shown to further react smoothly with aldehydes in the presence of anhydrous fluoride ion (Scheme 13).[36,37]



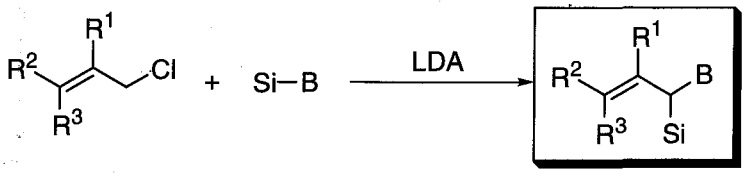
Scheme 13

Two C-B bonds in the diborylated products are also simultaneously employed for double C-C bond formation as exemplified by Rh-catalyzed Michael-type addition reaction or Pd-catalyzed cross-coupling reaction (Scheme 14).[38]



Scheme 14

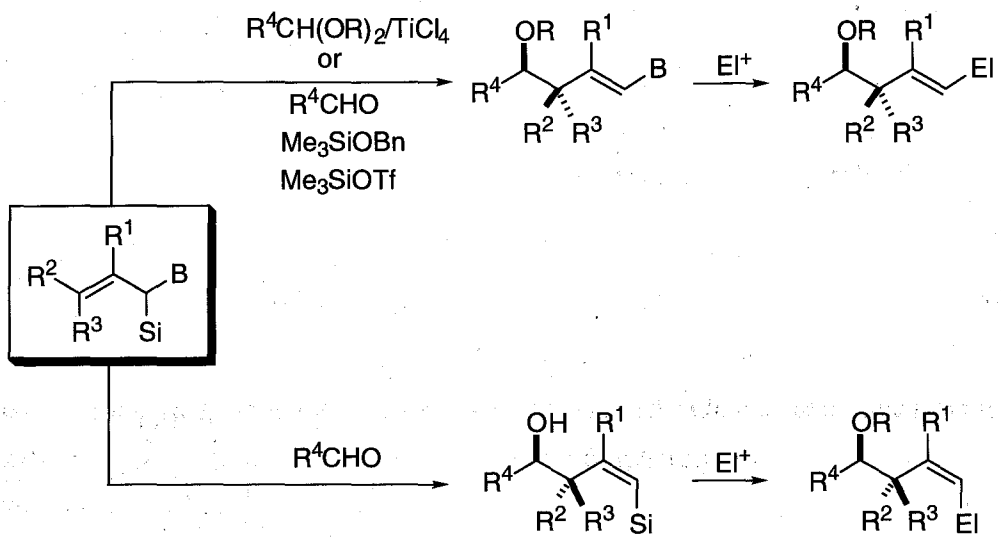
In Chapter 3, the author successively describes *gem*-silylborylation at an allylic sp^3 carbon. Thus, *gem*-silylborylation of α-chloroallyllithiums[39] with the silylborane was studied carefully and 1-boryl-1-silyl-2-alkenes were isolated with retention of configuration (eq 22).



(22)

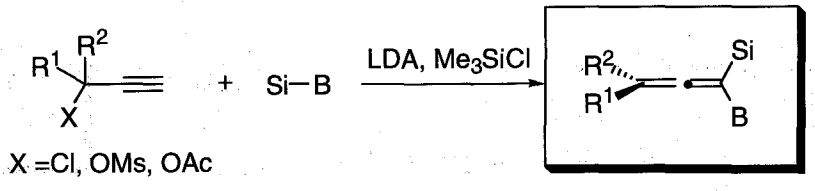
The resulting 1-boryl-1-silyl-2-alkenes are apparently versatile reagents in organic synthesis, because such compounds can be regarded as hybrids of allylic boranes[11a,40] and silanes,[11a,41] both of which are well-documented to readily allylate carbonyl compounds. In

the presence of Lewis acids, 1-boryl-1-silyl-2-alkenes react with acetals and aldehydes as an allylsilane reagent to produce (*E*)-4-alkoxyalkenylboronates in a stereospecific manner.[42] Upon heating with aldehydes, the reagents react as an allylborane reagent to afforded (*Z*)-4-hydroxy-1-alkenylsilanes stereospecifically. The allylated products can be further elaborated as alkenylmetals for extension of carbon frameworks (Scheme 15).



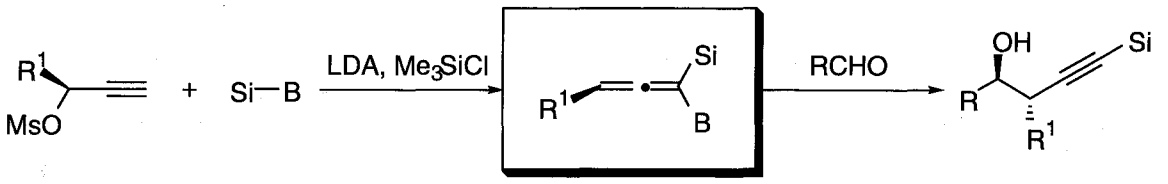
Scheme 15

Chapter 4 deals with *gem*-silylborylation at an *sp* carbon. The author has found that 1-boryl-1-silylallenes can be synthesized from 3-chloro-, 3-acetoxy- or 3-mesyloxyalkyn-1-yllithiums with the silylborane in moderate to good yields (eq 23).



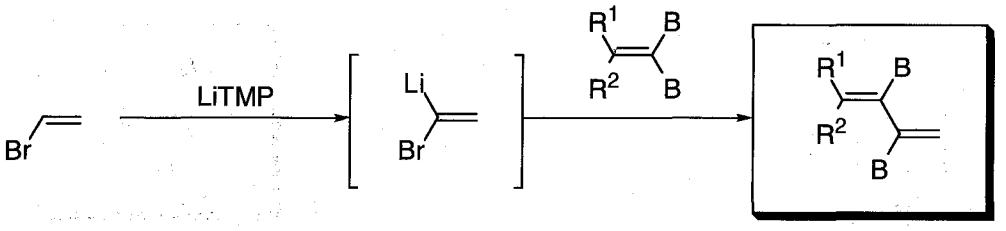
(23)

The reaction involves 1,2-migration of the silyl group from a negatively charged boron atom of an intermediate borate complex to the terminal acetylenic carbon. Worthy to note is that the reaction is accelerated by the addition of chlorotrimethylsilane in case that methanesulfonyloxy is employed for a leaving group. Furthermore, axially enantio-enriched products could be prepared from mesylates of optically active propargylic alcohols (Scheme 16). These results are the first demonstration of asymmetric *gem*-silylborylation of organolithium reagents. *gem*-Silylborylated allenes are shown to react with aldehydes as an allenylborane to yield the corresponding homopropargylic alcohols with high *anti* diastereoselectivity.



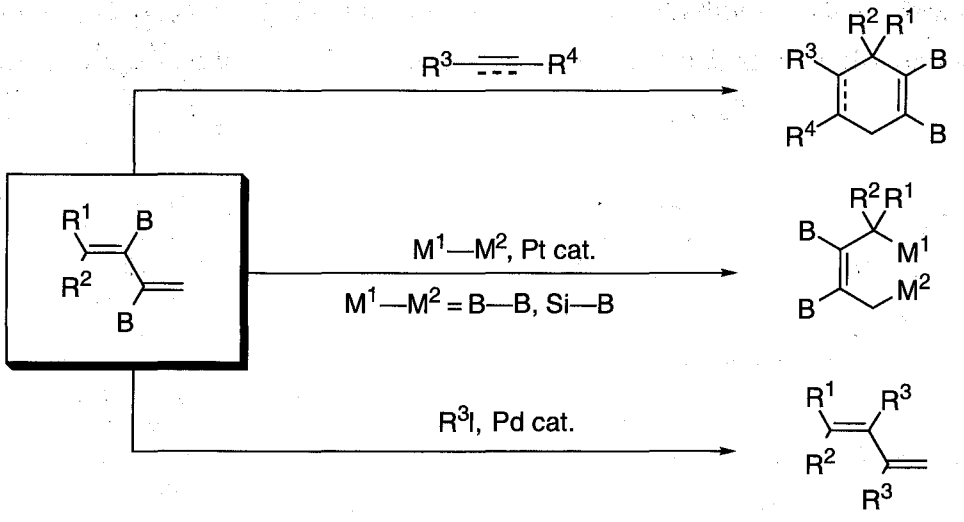
Scheme 16

During the study of *gem*-dimetalation reaction, he has found that treatment of 1,1-diborylethene with 1-bromo-1-lithioethene gave 2,3-bis[(pinacolato)boryl]-1,3-butadiene in moderate to good yields (Scheme 17).



Scheme 17

In addition, one-pot preparation is possible from diboron (B–B) and 1-bromo-1-lithioethene. Synthetic transformations of the 1,3-butadiene are also demonstrated. For example, Diels-Alder reaction with various dienophiles readily gives rise to 1,2-diborylated cyclohexenes; Pt-catalyzed 1,4-addition of diboron[29h,43] or silylborane[29j,44] produces (*Z*)-2-butenes having B or Si on each carbon; Pd catalyzed cross-coupling reaction[35] with organic halides gives 2,3-disubstituted-1,3-butadienes (Scheme 18).



Scheme 18

In summary, the present Thesis discusses how *gem*-silylborylated and *gem*-diborylated compounds are successfully synthesized through *gem*-dimetalation of lithium carbenoids with such interelement compound as silylboranes and diborons. Furthermore, the synthetic utility and versatility of the dimetalated products have been demonstrated. Chemistry described herein should provide a new family of organodimetallics and thus contribute to the development of not only organometallic chemistry and modern organic synthesis but also organic materials chemistry.

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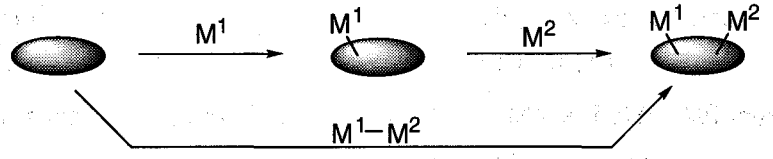
Chapter 2

Silylborylation and Diborylation of Alkylidene-type Carbenoids. Synthesis of 1-Boryl-1-silyl-1-alkenes and 1,1-Diboryl-1-alkenes

A novel and efficient method for *gem*-dimetalation of carbenoids has been demonstrated. Treatment of alkylidene-type lithium carbenoids with such an interelement compound as silylborane or diboron to generate the corresponding borate complex, followed by warming to room temperature, induced migration of the silyl or boryl group from a negatively charged boron atom to the carbenoid carbon to afford 1-boryl-1-silyl-1-alkenes or 1,1-diboryl-1-alkenes in good yields. Carbon-carbon bond forming transformations of the *gem*-dimetalated compounds mediated by boron or silicon is also described. Facile stereoselective synthesis of *Z* tamoxifen is also demonstrated.

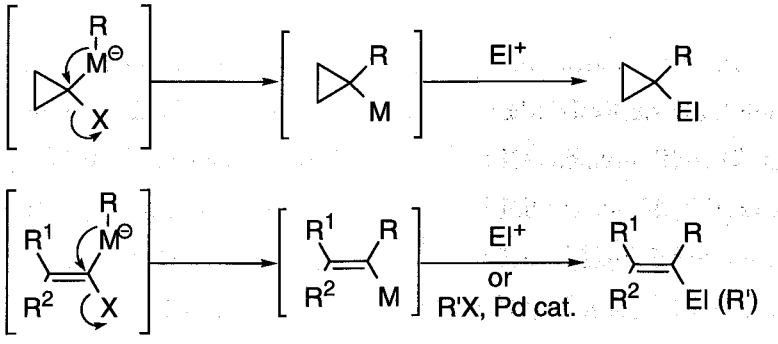
Introduction

As mentioned in Chapter 1, much attention has been paid on organodimetallic compounds in organic synthesis, because such bimetallic compounds serve as versatile intermediates or reagents for further elaborative transformations.[1] In view of synthetic methods for organodimetallic compounds, two strategies are conceptually possible (Scheme 1). One is a stepwise procedure involving initial preparation of an M^1-containing organometallic compound from an organic molecule and metal M^1, followed by introduction of another metal M^2. The other involves simultaneous introduction of two metals into an organic molecule using an interelement compound M^1-M^2.[2-5] It is apparent that the second approach, if feasible, is an attractive and straightforward method.



Scheme 1. Synthetic route to organodimetallic compounds.

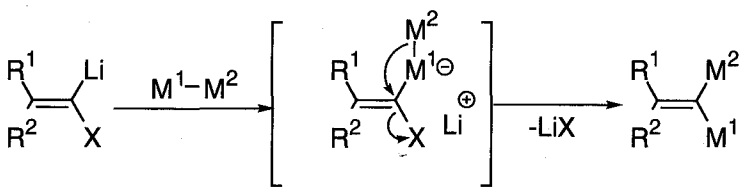
Ate-type carbenoids generated from *gem*-dihalo compounds by treatment with an ate complex or a combination of BuLi and an organometallic reagent undergo 1,2-migration of a carbonaceous substituent from the negatively charged metal to the carbenoid carbon with inversion of configuration, giving rise to homologated organometallic compounds which can then react with an electrophile, all operations being carried out in one pot (Scheme 2). Various kinds of organometallic reagents are applicable to this type of reaction.[6]



M = Li, B, Al, Mg, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Zr, Cd, Hf

Scheme 2. 1,2-Migration of a carbonaceous substituent in an ate complex.

The author envisioned that *gem*-dimetalation of carbenoids should be realized if an ate complex possessing metal M^2 as a migrating group could be generated when an interelement compound was applied to an alkylidene-type carbenoid reagent (Scheme 3).[7]



Scheme 3. Strategy for the synthesis of *gem*-dimetalated compounds from lithium carbenoids and interelement compounds.

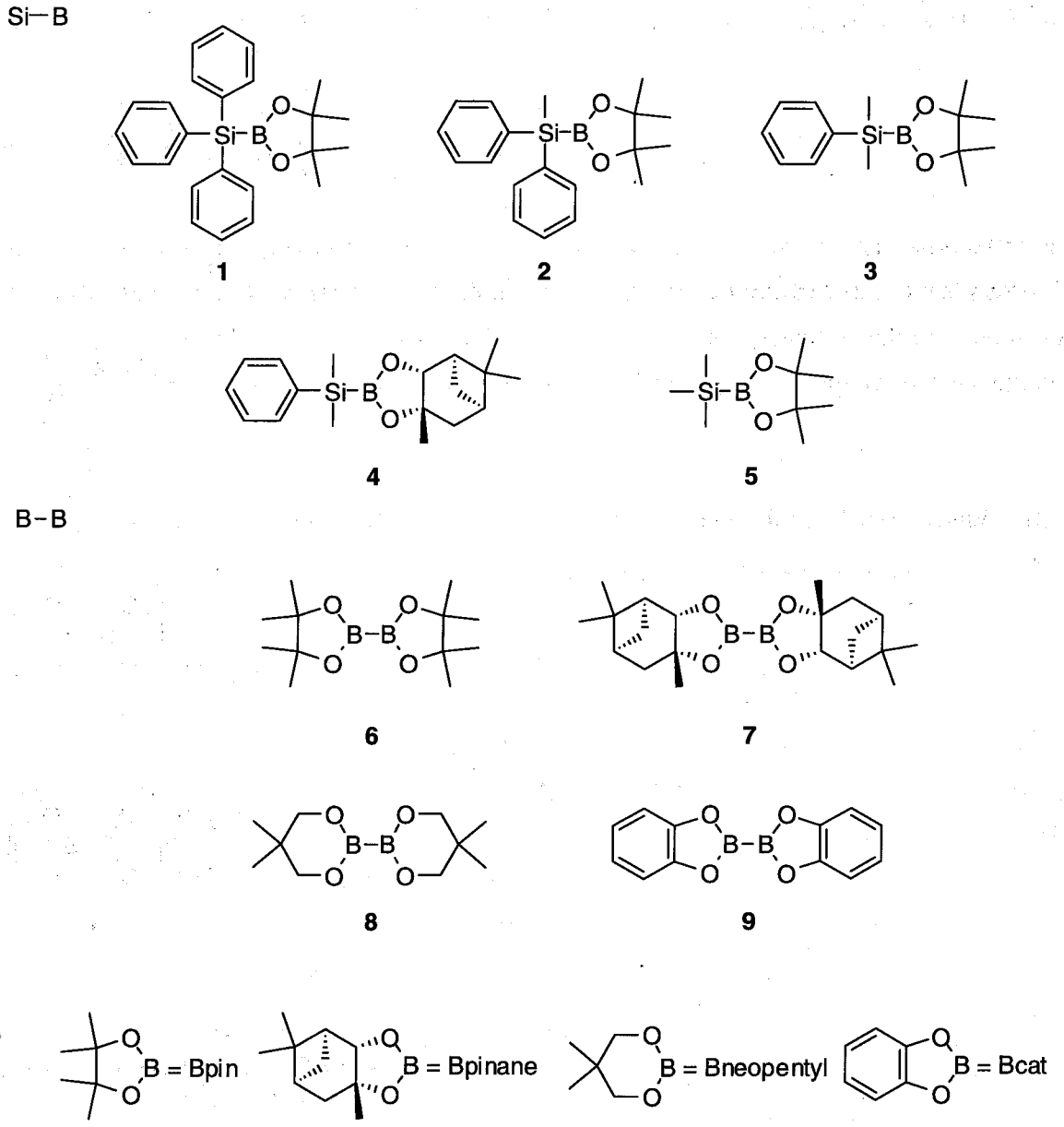


Figure 1. Silylboranes **1-5** and diborons **6-9**.

Silylboranes and diborons are chosen as the interelement compounds to be employed, because various kinds of those dimetallic compounds are commercially or readily available, stable, and easy to handle. Furthermore, the resulting products, 1-boryl-1-silyl-1-alkenes[8] or 1,1-diboryl-1-alkenes,[9] should be potentially valuable reagents for construction of complex carbon framework in view that a variety of efficient transformations using alkenylborane and -silane functionalities are available.[10,11] In this Chapter, the author describe novel synthesis of *gem*-dimetallic compounds by *gem*-silylborylation and *gem*-diborylation of alkylidene-type lithium carbenoids with silylboranes **1-5** and diborons **6-9**, respectively (Figure 1).[12] In addition, further transformations of the silylborylated and diborylated compounds are disclosed.

Results and Discussion

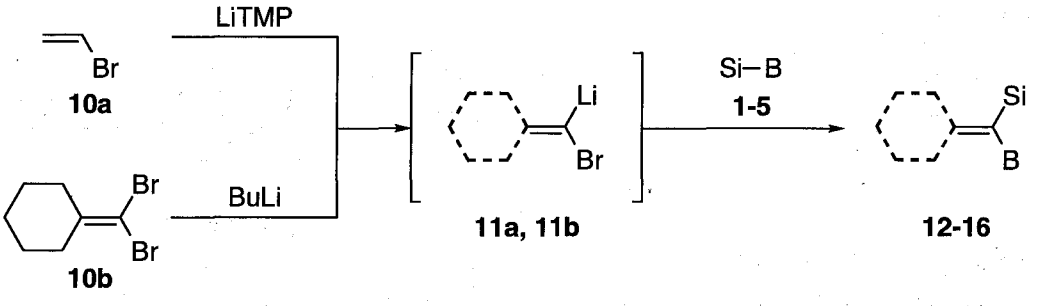
gem-Silylborylation of Alkylidene-type Carbenoids

Silylboranes **1-5** were obtained as follows: (triphenylsilyl)(pinacolato)borane (**1**) and (methyldiphenylsilyl)(pinacolato)borane (**2**), and (dimethylphenylsilyl)(pinacolato)borane (**3**) were prepared according to the procedure reported previously.[13] When the author applied the procedure to dimethylphenylsilyllithium and (+)-(pinanediolato)borane,[14] obtained (dimethylphenylsilyl)((+)-pinanediolato)borane (**4**) as a novel silylborane in 64% yield. Similarly, the author examined the preparation and isolation of (trimethylsilyl)(pinacolato)borane (**5**). Although the formation of **5** was reportedly suggested by GC-MS during the Pt-catalyzed diborylation of bis(trimethylsilyl)acetylene with **6**,[15] to his knowledge, no example involving the isolation and use of **5** as a reagent is available. Accordingly, the author treated trimethylsilyllithium, generated from hexamethyldisilane and methyllithium in HMPA,[16] with a THF solution of (pinacolato)borane to confirm the formation of **5** by GC-MS of the reaction mixture. However, attempted purification of **5** by distillation, silica gel column chromatography, or gel permeation chromatography resulted in the decomposition of **5**. Therefore, **5** was used as a THF/HMPA (5 : 1) solution without further purification.

Using 1-bromo-1-lithioethene (**11a**) and (1-bromo-1-lithiomethylene)cyclohexane (**11b**) as a typical alkylidene-type carbenoid, the author first investigated the scope of silylboranes on *gem*-silylborylation. Carbenoids **11a** and **11b** in THF were treated with silylboranes **1-5** at -110 °C, and the resulting mixture was warmed to room temperature. The results are summarized in Table 1. (Triphenylsilyl)borane **1** and (methyldiphenylsilyl)borane **2** reacted with unsubstituted carbenoid **11a** to give the corresponding products **12a** and **13a** in moderate yields (entries 1 and 3), whereas dimetalated products **12b** and **13b** were not obtained with 2,2-disubstiuted carbenoid **11b** (entries 2 and 4). In contrast, *gem*-silylborylation of **11a** and **11b** using (dimethylphenylsilyl)borane **3** or optically active silylborane **4** proceeded in good yields, respectively (entries 5-8). These results suggest that the relatively bulkier substiuent

on silicon induces repulsion with substituents in a carbenoid and probably prevents formation of a borate complex or 1,2-migration of a silicon atom. Indeed, (trimethylsilyl)borane **5** that is less bulkier than **3** is also applicable to this *gem*-silylborylation, although **16a** and **16b** slightly decompose during purification by silica gel column chromatography (entries 9 and 10). These results are the first demonstration that **5** can be utilized as a reagent for the synthesis of diorganometallics.

Table 1. Reaction of **11a** and **11b** with silylboranes **1-5**.[a]

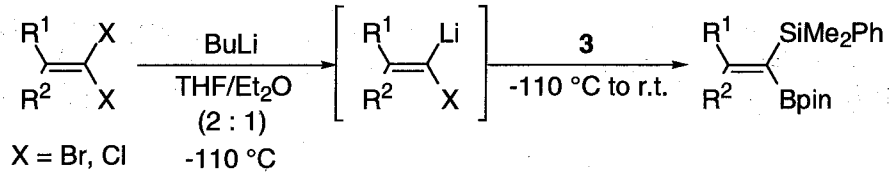


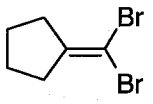
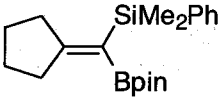
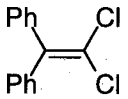
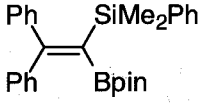
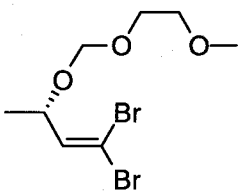
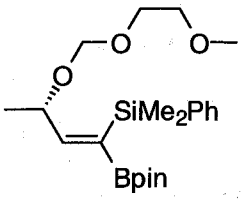
Entry	Silylborane	Carbenoid	Product	Yield (%)[b]
1	**1**	**11a**	**12a**	60
2	**1**	**11b**	**12b**	<1
3	**2**	**11a**	**13a**	62
4	**2**	**11b**	**13b**	<1
5	**3**	**11a**	**14a**	81
6	**3**	**11b**	**14b**	84
7	**4**	**11a**	**15a**	72
8	**4**	**11b**	**15b**	78
9	**5**[c]	**11a**	**16a**	45
10	**5**[c]	**11b**	**16b**	67

[a] A mixture of **10a** (0.50 mmol), THF (2 mL), and Et_2O (1 mL) was treated with LiTMP (0.50 mmol) and silylborane **1-5** (0.50 mmol) at -110 °C for 10 min, then gradually warmed to room temperature. Alternatively, a mixture of **10b** (0.53 mmol), THF (2 mL), and Et_2O (1 mL) was treated with BuLi (0.50 mmol) and silylborane **1-5** (0.50 mmol) at -110 °C for 10 min, then warmed to room temperature gradually. [b] Isolated yields based on silylborane **1-5** are given. [c] A 0.6 M solution in THF/HMPA (5 : 1) was used.

The best results obtained with **3** in hand, the author next applied the silylborylation to various kinds of carbenoids using **3**. The carbenoids were generated by halogen-lithium exchange, and results are shown in Table 2. 2,2-Disubstituted dibromoalkene **10c** and dichloroalkene **10d** afforded the corresponding products **17** and **18** in 84% and 60% yields, respectively (entries 1 and 2). Stereoselective *gem*-silylborylation is possible, when an unsymmetrical alkylidene-type carbenoid is generated stereoselectively. Thus, dibromoalkene **10e** containing a 2-methoxyethoxymethoxy group (MEM group) was treated with 0.95-0.98 molar amount of BuLi in Et_2O at −110 °C to produce a carbenoid stereoselectively with the MEMO group and lithium being cis.[17] The carbenoid selectively reacted with **3** to give **19** as a single diastereomer (entry 3). The stereochemical outcome clearly demonstrates that lithium is first replaced by boron and the subsequent anionic 1,2-migration induces inversion of configuration to finally give rise to **19** (*vide infra*).

Table 2. *gem*-Silylborylation of alkylidene-type carbenoids generated by halogen-lithium exchange.[a]

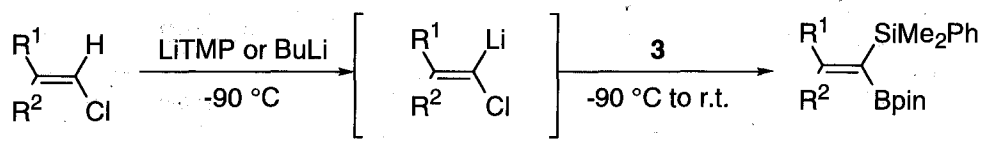


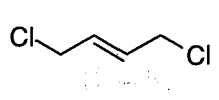
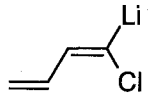
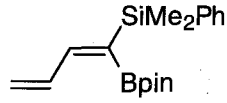
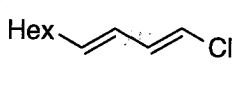
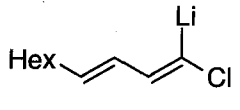
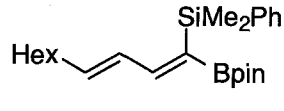
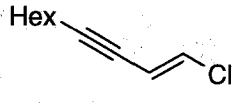
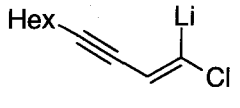
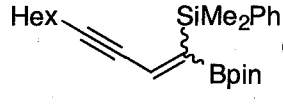
Entry	Dihaloalkene	Product	Yield (%)[b]
1	 **10c**	 **17**	84
2	 **10d**	 **18**	60
3[c]	 **10e**	 **19**	45

[a] A mixture of 1,1-dihaloalkene **10c-10e** (0.50 mmol), THF (2 mL), and Et_2O (1 mL) was treated with BuLi (0.50 mmol) and **3** (0.50 mmol) at -110 °C for 10 min, then gradually warmed to room temperature. [b] Isolated yields based on **3** are given. [c] Et_2O (2 mL) was used as a solvent.

Lithium carbenoids generated by deprotonation of chloroalkenes with lithium 2,2,6,6-tetramethylpiperidide (LiTMP) or BuLi could be also applied to the silylborylation (Table 3). As (*E*)-1,4-dihalo-2-butene is known to give predominantly (*Z*)-1-halobutadiene,[18] dichlorobutene **10f** was treated with two equivalents of LiTMP at -90 °C to give (*Z*)-1-chloro-1-lithio-1,3-butadiene (**11f**) stereoselectively, which was allowed to react with **3**, affording (*E*)-*gem*-silylborylated product **20** in a good yield (Table 3, entry 1). Conjugated carbenoids **11g** and **11h**, generated from **10g** and **10h**, respectively, were *gem*-silylborylated with **3** to give diene **21** and enyne **22** (entries 2 and 3). The stereochemistry of **21** was completely controlled to be *Z*, whereas **22** was isolated as a stereoisomeric mixture due probably to facile isomerization of carbenoid **11h**.

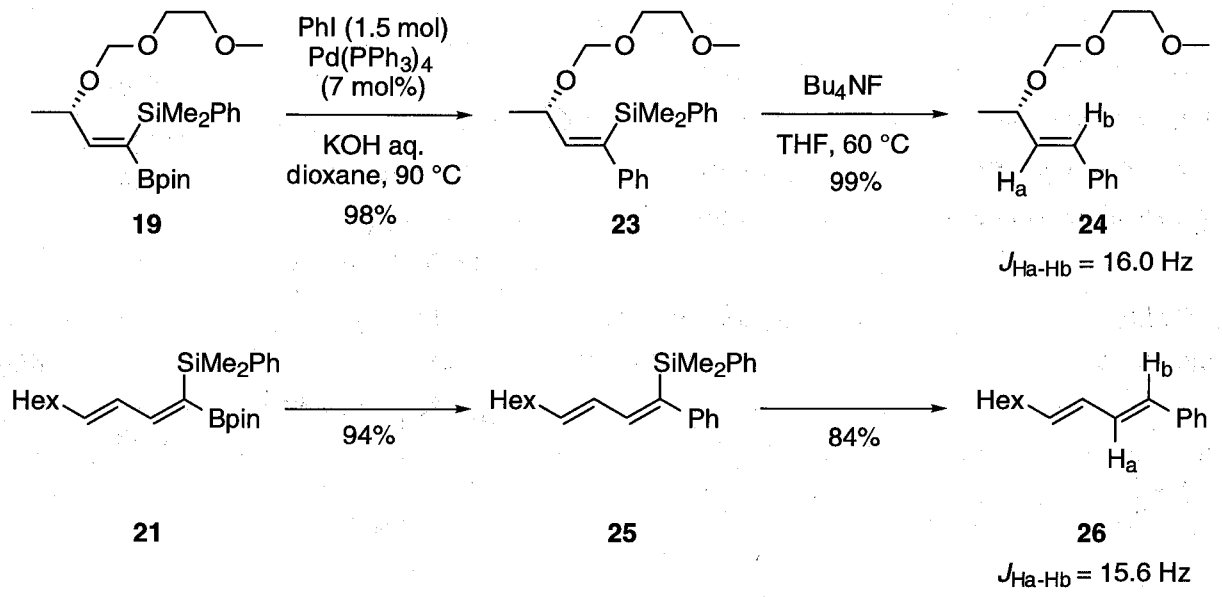
Table 3. *gem*-Silylborylation of alkylidene-type carbenoids generated by deprotonation.



Entry	Substrate	Carbenoid	Product	Yield (%)[a]
1	 **10f**[b]	 **11f**	 **20**	75 (*E* only)
2	 **10g**[c]	 **11g**	 **21**	89 (*Z* only)
3	 **10h**[d]	 **11h**	 **22**	49 (*E*:*Z* = 1 : 1)

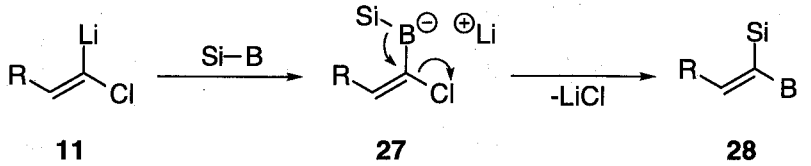
[a] Isolated yields based on **3** are given. [b] A solution of **10f** (0.50 mmol) in THF (2 mL) was treated with LiTMP (1.05 mmol) and **3** (0.50 mmol) at -90 °C for 15 min, then gradually warmed to room temperature. [c] A solution of **10g** (0.50 mmol) in THF (2 mL) was treated with BuLi (0.53 mmol) and **3** (0.50 mmol) at -90 °C for 15 min, then gradually warmed to room temperature. [d] A solution of **10h** (0.50 mmol) in THF (2 mL) was treated with LiTMP (0.53 mmol) and **3** (0.50 mmol) at -90 °C for 15 min, then gradually warmed to room temperature.

Stereochemistry of **19** and **21** was confirmed by the chemical transformations shown in Scheme 4: Pd-catalyzed cross-coupling reaction of **19** and **21** with iodobenzene with retention of configuration followed by protodesilylation with Bu_4NF (retention of configuration) gave **24** and **26,** whose configurations were assigned as *trans* by the *vic*-coupling constants of vinyl hydrogens in phenyl-substituted double bonds being 16.0 and 15.6 Hz, respectively. Thus, olefinic configuration in **19** and **21** was both assigned as *Z*.



Scheme 4. Stereochemical assignment of **19** and **21**.

Considering that the 1,2-migration of a carbonaceous substituent in an ate complex proceeds with inversion of configuration,[6] these stereochemical outcome clearly demonstrates that, at first, a borate complex **27** forms from carbenoid **11** and silylborane, and then silyl migration takes place, giving rise to **28** with inversion of configuration (Scheme 5). Monitoring the reaction by TLC (after quenching), the 1,2-migration of a silyl group is apparently taking place above -50 °C.

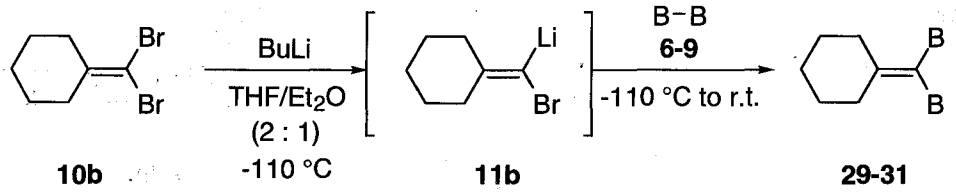


Scheme 5. Plausible Mechanism of *gem*-silylborylation of alkylidene-type carbenoids with silylborane.

gem-Diborylation of Alkylidene-type Carbenoids

The author next studied *gem*-diborylation of alkylidene-type carbenoids with diborons. Using **11b** as a typical carbenoid, commercially available diborons **6-9** were screened (Figure 1). The results are shown in Table 4. Bis(pinacolato)diboron (**6**)[19] and optically active bis((+)-pinanediolato)diboron (**7**) reacted with **11b** to give *gem*-diborylated compounds **29** and **30** in high yields (entries 1 and 2). In contrast, reaction with bis(neopentanediolato)diboron (**8**) resulted in low yield of **31** due probably to its low solubility under the reaction conditions (entry 3), while any desired diborylated compound was not obtained when bis(catecolato)diboron (**9**) was employed (entry 4).

Table 4. Reaction of **11b** with diboron **6-9**.[a]



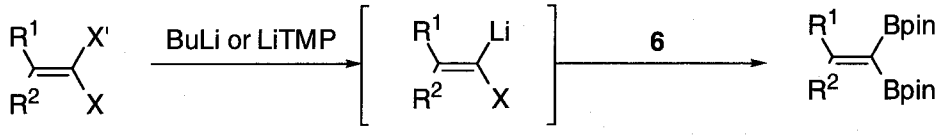
10b **11b** **29-31**

Entry	*B-B*	Product	Yield (%)[b]
1	**6**	**29**	93
2	**7**	**30**	>99
3	**8**	**31**	15
4	**9**	—	<1

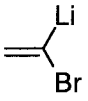
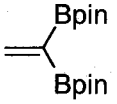
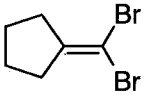
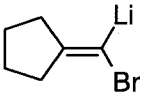
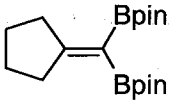
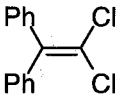
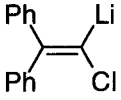
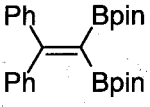
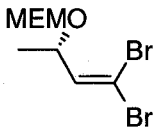
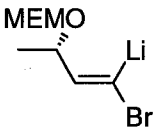
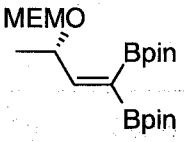
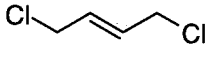
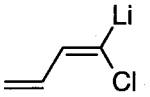
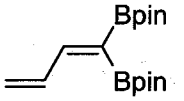
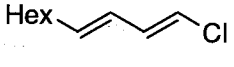
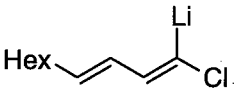
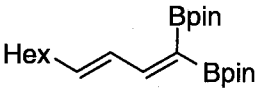
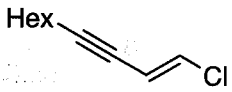
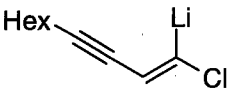
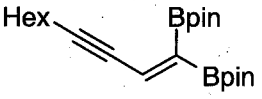
[a] A mixture of **10b** (0.53 mmol), THF (2 mL), and Et_2O (1 mL) was treated with BuLi (0.50 mmol) and diboron (0.50 mmol) at -110 °C for 10 min, then gradually warmed to room temperature. [b] Isolated yields based on diboron are given.

By use of **6**, various kinds of alkylidene-type carbenoids **11** were *gem*-diborylated as shown in Table 5. Unsubstituted and 2,2-disubstituted carbenoids **11a** and **11c** gave 1,1-diborylalkenes **32** and **33** in high yields (entries 1 and 2). Dichloroalkene **10d** could also be applied, which after chlorine-lithium exchange underwent *gem*-diborylation, giving rise to **34** in 54% yield (entry 3), while optically active 1,1-diborylalkene **35** was obtained from the corresponding dibromide **10e** in 65% yield (entry 4). Double deprotonation of **10f** generated **11f** which reacted with **6** to afford 1,1-diborylbutadiene **36** in 89% yield (entry 5). *gem*-Diborylation of lithium carbenoids **11g** and **11h** prepared from conjugated chloroalkenes **37** and **38** proceeded smoothly, producing conjugated compounds **37** and **38** bearing two boryl groups at the terminal positions (entries 6 and 7).

Table 5. *gem*-Diborylation of alkylidene-type carbenoid.



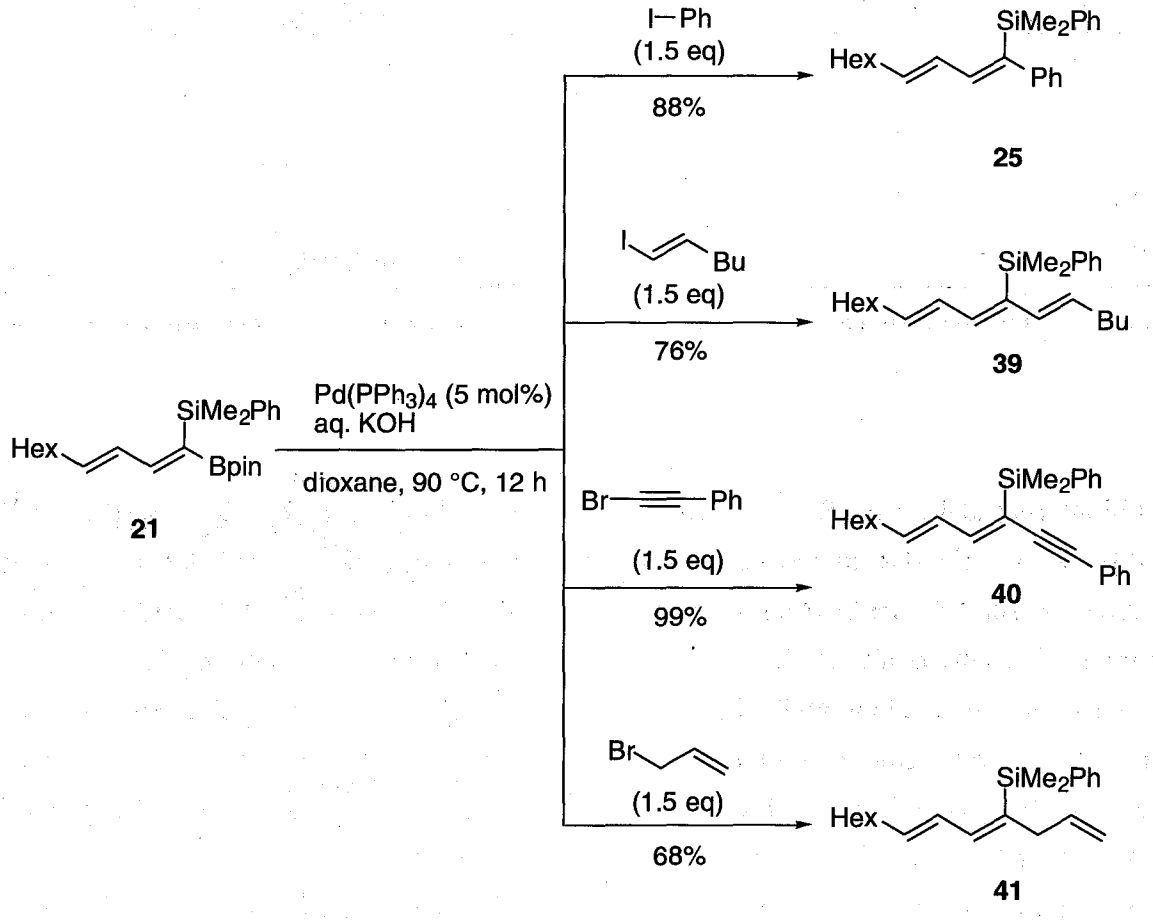
X = Br, Cl X' = Br, Cl, H

Entry	Substrate	Carbenoid	Product	Yield (%)[a]
1	 **10a**[b]	 **11a**	 **32**	91
2	 **10c**[c]	 **11c**	 **33**	96
3	 **10d**[c]	 **11d**	 **34**	54
4	 **10e**[c,d]	 **11e**	 **35**	65
5	 **10f**[e]	 **11f**	 **36**	89
6	 **10g**[f]	 **11g**	 **37**	82
7	 **10h**[g]	 **11h**	 **38**	48

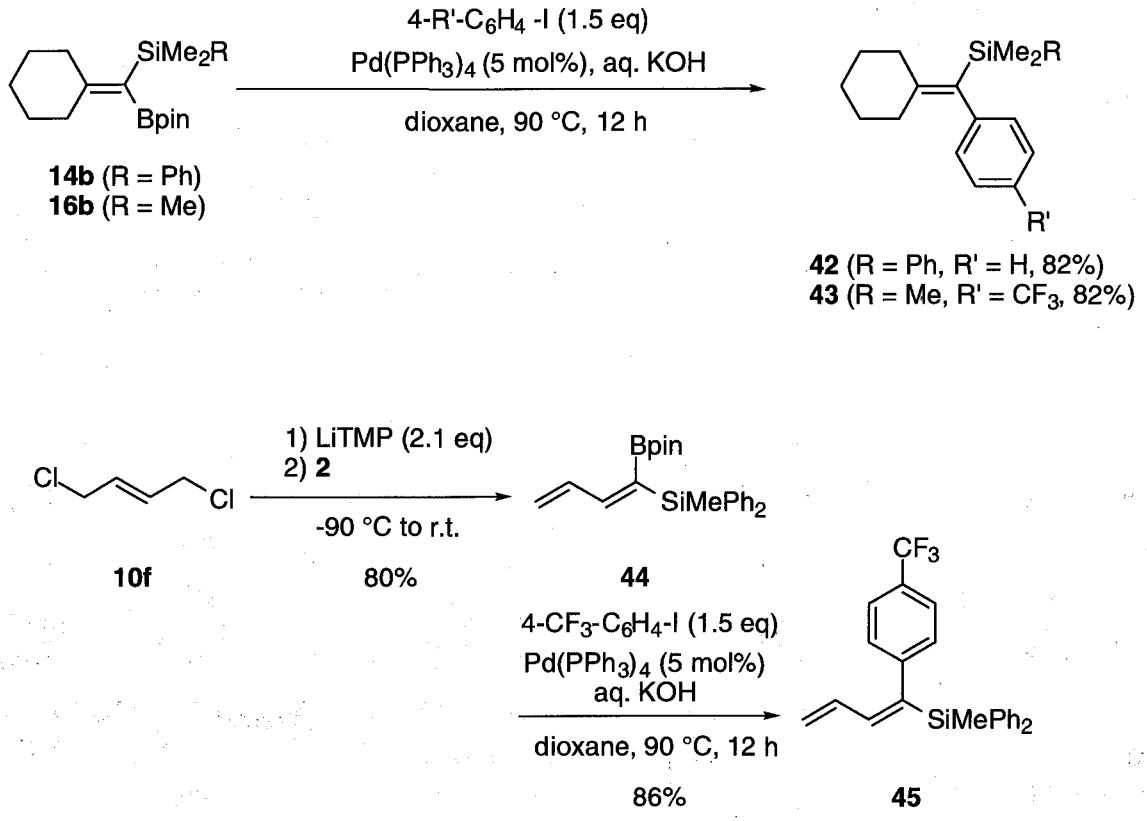
[a] Isolated yields based on **6** are given. [b] A mixture of **10a** (0.50 mmol), THF (2 mL), and Et_2O (1 mL) was treated with LiTMP (0.50 mmol) and **6** (0.50 mmol) at -110 °C for 10 min, then gradually warmed to room temperature. [c] A mixture of 1,1-dihaloalkene **10c-10e** (0.50 mmol), THF (2 mL), and Et_2O (1 mL) was treated with BuLi (0.50 mmol) and **6** (0.50 mmol) at -110 °C for 10 min, then gradually warmed to room temperature. [d] Et_2O (2 mL) was only used as a solvent. [e] A solution of **10f** (0.50 mmol) in THF (2 mL) was treated with LiTMP (1.05 mmol) and **6** (0.50 mmol) at -90 °C for 15 min, then gradually warmed to room temperature. [f] A solution of **10g** (0.50 mmol) in THF (2 mL) was treated with BuLi (0.53 mmol) and **6** (0.50 mmol) at -90 °C for 15 min, then gradually warmed to room temperature. [g] A solution of **10h** (0.50 mmol) in THF (2 mL) was treated with LiTMP (0.53 mmol) and **6** (0.50 mmol) at -90 °C for 15 min, then gradually warmed to room temperature.

Synthetic Applications of *gem*-Dimetallic Compounds

Since *gem*-silylborylation and -diborylation were established as a novel way to *gem*-diorganometallics, the author further studied the carbon-carbon bond extension of the *gem*-dimetalated compounds in order to demonstrate the synthetic utility of such bifunctional molecules. Some examples of Suzuki-Miyaura coupling reaction of **21** are firstly illustrated in Scheme 6.[20] (Dimethylphenylsilyl)borylated diene **21** reacted with iodobenzene to give alkenylsilane **25** in 88% yield. Under the same conditions, such an organic halide as (*E*)-1-iodo-1-hexene, bromophenylacetylene, or allyl bromide coupled with **21** to produce the corresponding alkenylsilanes **39**-**41** in good yields. In addition, the cross-coupling of 2,2-disubstituted alkenylboronate **14b** and **16b** with iodobenzene or 1-iodo-4-trifluoromethylbenzene also underwent smoothly giving rise to the corresponding 1-aryl-1-alkenylsilane **42** or **43** in good yields, respectively. Moreover, the methyldiphenylsilyl group in alkenylboronate **44**, prepared from **10f** with **2** in 80% yield, did not affect the Pd-catalyzed coupling reaction with 1-iodo-4-trifluoromethylbenzene as demonstrated at the bottom of Scheme 6. In all cases, any kinds of silyl groups including a trimethylsilyl group were not lost in spite of the basic conditions.

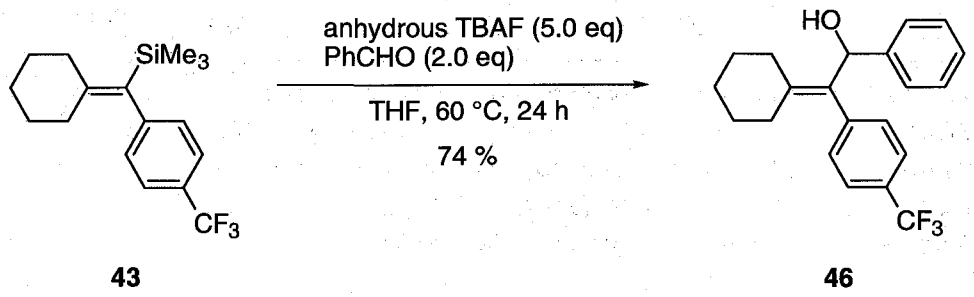


Scheme 6. Boron-mediated cross-coupling reaction of *gem*-silylborylated compounds.



Scheme 6 (continued). Boron-mediated cross-coupling reaction of *gem*-silylborylated compounds.

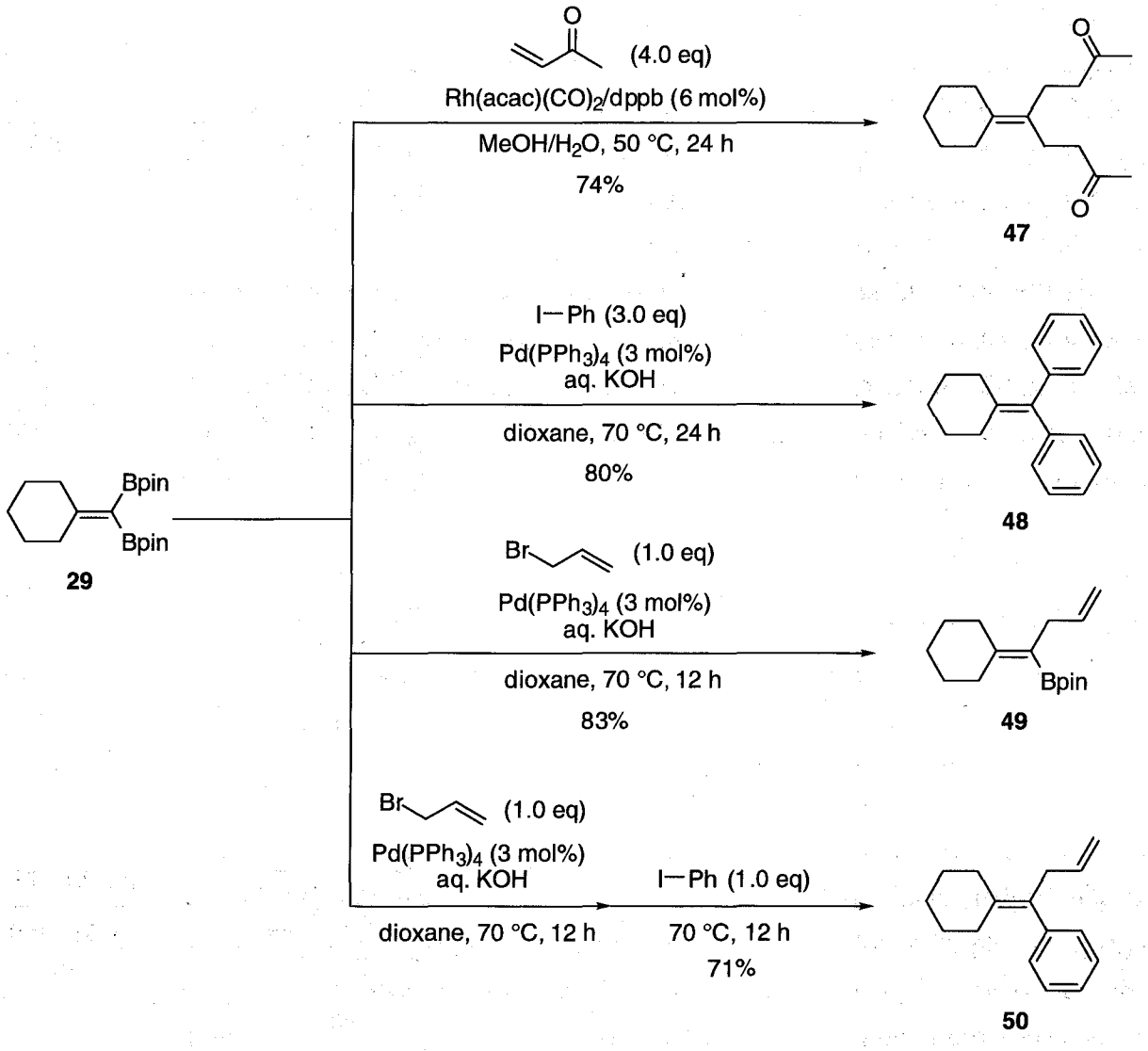
Further elaboration of the coupled products demonstrates the utility of the silicon functionality. Although the cross-coupling reaction of **45** with ethyl *p*-iodobenzoate[21,22] or fluoride-mediated reaction of **42** or **45** with benzaldehyde[23] resulted in protodesilylation, alkenyltrimethylsilane **43** was shown to react smoothly with benzaldehyde in THF at 60 °C in the presence of anhydrous Bu_4NF,[24] giving rise to **46** in 74% yield (Scheme 7).



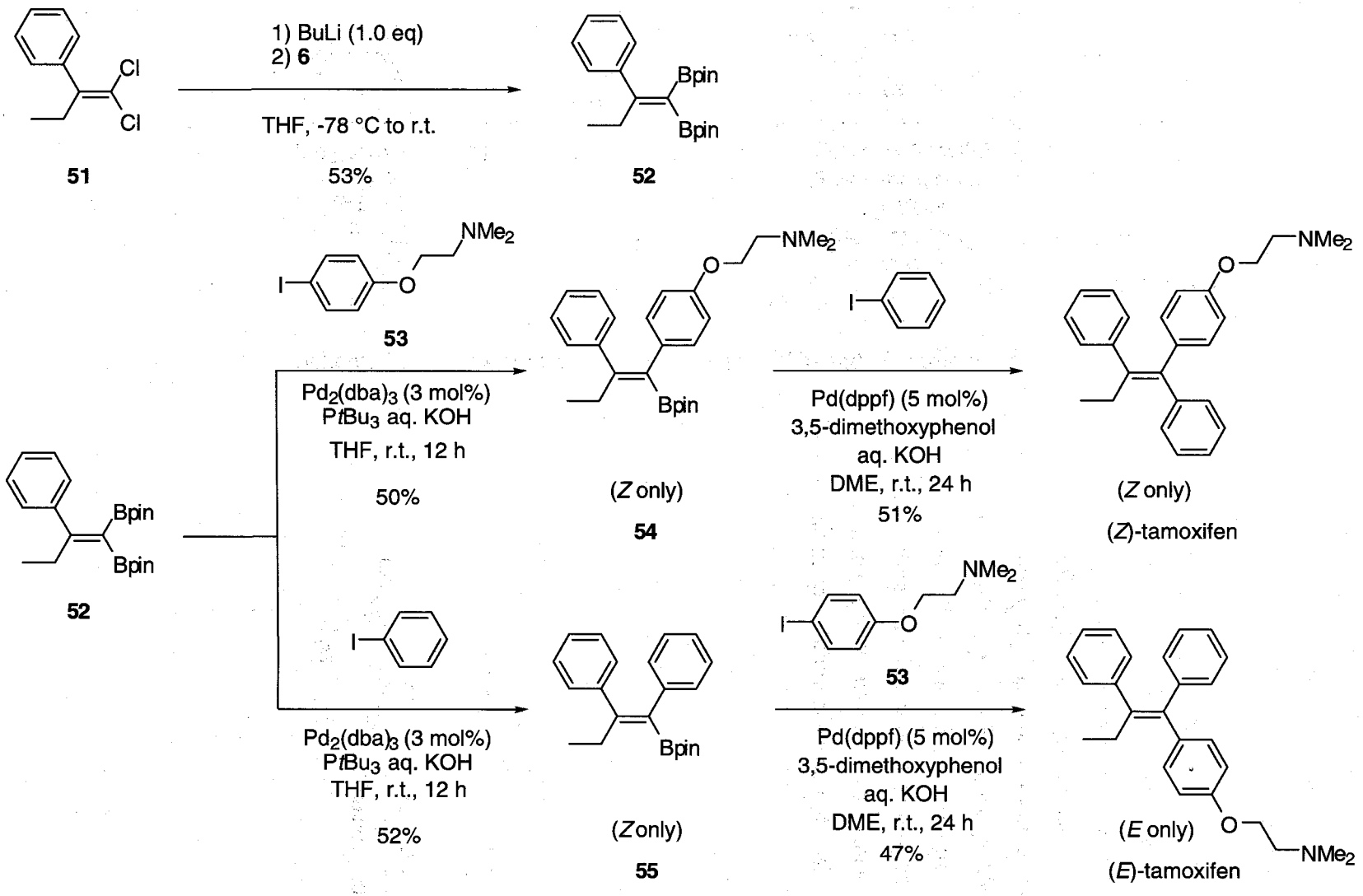
Scheme 7. Silicon-mediated coupling reaction.

Finally shown is the synthetic application of diborylated compound **29** (Scheme 8). Rh-catalyzed Michael-type addition reaction of **29** to methyl vinyl ketone proceeded smoothly to give diketone **47** in 74% yield.[25] Two C-B bonds in **29** were simultaneously

converted into two C-C bonds as exemplified by Pd-catalyzed cross-coupling reaction, with iodobenzene giving rise to **48**. When an equimolar amount of allyl bromide was used as the coupling partner, stepwise coupling was found possible. Thus, **29** was treated with allyl bromide in an equimolar amount to give allylated alkenylboronate **49**. Furthermore, the allylation followed by coupling with iodobenzene in one pot gave the corresponding bis-coupled product **50** in good overall yield.



Scheme 8. Synthetic applications of *gem*-diborylated compound.



Scheme 9. Facile stereoselective synthesis of (*Z*)- and (*E*)-tamoxifen.

Tamoxifen is a drug for treatment of hormone dependent breast cancer in clinic. For this purpose, only the *Z* isomer of this tetrasubstituted olefin has been required for the antiestrogenic activity.[26f] The *E* isomer is contrastingly estrogenic and consequently procedures for the stereoselective synthesis of tamoxifen are worthwhile. Thus, the author was stimulated to develop a facile stereospecific synthesis of tamoxifen by means of the double cross-coupling reaction of *gem*-diborylalkene **52** with two different aryl iodides. By use of **6**, *gem*-dichloroalkene **51** was *gem*-diborylated in 53% yield. Coupling reaction of **52** with [2-(4-iodo-phenoxy)ethyl]dimethylamine **53** gave **54** as a single *Z* isomer in a moderate yield. (Z)-Tamoxifen was obtained by the coupling reaction with **54** and iodobenzene as a single *Z* isomer in 51% yield. In the same manner, (*E*)-tamoxifen was also synthesized stereoselectively. This is the shortest and the most reliable method for the synthesis of the target molecular.[26]

Conclusion

In conclusion, the author have demonstrated that *gem*-dimetalation of carbenoids with interelement compounds provides a novel and highly efficient route to *gem*-dimetallic compounds. Thus, alkylidene-type lithium carbenoids react with silylboranes or diborons to stereoselectively afford 1-boryl-1-silyl-alkenes or 1,1-diboryl-1-alkenes respectively. The resulting *gem*-organodimetallic compounds are demonstrated to be applicable to ready extension of the olefinic carbon framework and thus are shown to be extremely versatile reagents in organic synthesis.

Experimental

General Remarks: All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a purified argon atmosphere (deoxygenated by passing through BASF-Catalyst R3-11 column at 80 °C). ^{1}H NMR spectra were measured on a Varian Mercury 200 (^{1}H, 200 MHz) spectrometer. Chemical shifts of ^{1}H NMR are expressed in parts per million downfield relative to an internal tetramethylsilane (δ = 0 ppm) or chloroform (δ = 7.26 ppm). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; brs, broad singlet. ^{13}C NMR spectra were measured on a Varian Mercury 200 (^{13}C, 50 MHz) spectrometer and JEOL JMN ECP-500 (^{13}C, 125 MHz) spectrometer with tetramethylsilane as an internal standard (δ = 0 ppm). ^{19}F NMR spectra were measured on a Varian Mercury 200 (^{19}F, 188 MHz) spectrometer with $CFCl_3$ as an internal standard (δ = 0 ppm). Infrared spectra (IR) were recorded on a Shimadzu FTIR-8400 spectrometer. GC-MS analyses were obtained with a JEOL JMS-700 spectrometer by electron ionization at 70 eV. Elemental analyses were carried out with a YANAKO MT2 CHN CORDER machine at Kyoto University Elemental Analysis Center. Melting points were determined using a YANAKO MP-500D. TLC analyses were performed by means of Merck Kieselgel 60 F_{254} and R_f values were given. Column chromatography was carried out using Wakogel C-200. Preparative recycling gel permeation chromatography (GPC) was performed with a JAI LC-908 chromatograph equipped with JAIGEL-1H and -2H columns (chloroform as an eluent). Cooling a reaction vessel at –110 °C, –98 °C, or –78 °C was effected using pentane with liquid nitrogen, methanol with liquid nitrogen, or methanol with dry ice, respectively.

Materials. Ethereal solvents like THF, 1,4-dioxane, and diethyl ether were distilled from benzophenone and sodium under an argon atmosphere. Butyllithium was purchased from Sigma-Aldrich Co. Inc., and titrated with *N*-pivaloyl-*o*-toluidine as an indicator. (Triphenylsilyl)(pinacolato)borane, (methyldiphenylsilyl)(pinacolato)borane, (dimethylphenylsilyl)(pinacolato)borane were synthesized by the reported procedure.[13] Bis(pinacolato)diboron, bis((+)-pinanediolato)diboron, bis(2,2-dimethyl-propane-1,3-diolato)diboron, and bis(catecolato)diboron were purchased from Sigma-Aldrich Chemical Co. Inc. and used as received.

Preparation of Silylborane 4 and 5. (Dimethylphenylsilyl)((+)-pinanediolato)borane (4). To a stirred solution of (+)-pinandiolatoborane (1.1 g, 6.0 mmol) in hexane (5 mL) was added dimethylphenylsilyllithium (ca. 2.5 mol/L in THF, 2 mL, 5.0 mmol) dropwise at 0 °C. The resulting solution was allowed to warm gradually to room temperature. Evaporation of the volatile materials afforded a yellow oil, which was redissolved in hexane to remove insoluble materials. After suction filtration, the filtrate was concentrated *in vacuo*. Purification of

the residue by column chromatography on silica gel gave **4** as a pale yellow oil (1.10 g, 64% yield). $[\alpha]_D^{25}$ 4.01° (*c* 0.92, $CHCl_3$). R_f 0.50 (hexane/ethyl acetate 10 : 1). ^1H NMR ($CDCl_3$) δ 0.36 (s, 6H), 0.85 (s, 3H), 1.02 (d, *J* = 11 Hz, 1H), 1.28 (s, 3H), 1.40 (s, 3H), 1.82-1.90 (m, 2H), 2.08 (t, *J* = 6.5 Hz, 1H), 2.14-2.20 (m, 1H), 2.29-2.34 (m, 1H), 4.25 (d, *J* = 8.9 Hz, 1H), 7.26-7.36 (m, 3H), 7.57-7.61 (m, 2H). ^{13}C NMR ($CDCl_3$) δ -3.0, 22.7, 26.7, 27.1, 28.9, 35.4, 38.0, 39.7, 51.5, 77.2, 77.7, 86.4, 127.6, 128.5, 132.9, 134.0. IR (neat) 2918, 1441, 1375, 1252, 1210, 1120, 837, 700 cm^{-1}. MS *m/z* 315 (M^++1, 3), 314 (M^+, 7), 313 (M^+-1, 2), 135 (57), 93 (100). HRMS Calcd for $C_{18}H_{27}BO_2Si$: M^+-Me, 299.1639. Found: *m/z* 299.1639.

(Trimethylsilyl)(pinacolato)borane (5). A solution of hexamethyldisilane (0.51 mL, 2.5 mmol) in anhydrous HMPA (2 mL) was cooled at 0 °C under an argon atmosphere. To the solution was added an ethereal solution of methyllithium (1.10 M, 1.91 mL, 2.0 mmol) dropwise, and the resulting deep red solution was stirred for 15 min at 0 °C. This was diluted with anhydrous THF (10 mL), and the resultant was immediately cooled to –78 °C. To the solution was added isopropoxy(pinacolato)borane (0.50 g, 2.2 mmol) dropwise at –78 °C. Formation of **7** was confirmed by GC-MS analyses of the crude product which was used without further purification. MS *m/z* 200 (M^+, 1), 185 (M^+-Me, 27), 143 (11), 101 (37), 84 (100), 69 (90). HRMS Calcd for $C_8H_{18}BO_2Si$: M^+-Me, 185.1169. Found: *m/z* 185.1166

Typical Procedure for *gem*-Silylborylation of Alkylidene-type Carbenoids Generated by Deprotonation. 1-Dimethylphenylsilyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (14a). To a solution of vinyl bromide **10a** (1.00 M, 0.50 mL, 0.50 mmol) in THF (2 mL) and diethyl ether (1 mL) was added a solution of LiTMP (0.50 mmol) in THF (1 mL) at –110 °C. To the resulting mixture was added **3** (0.13 mg, 0.50 mmol) dropwise at –110 °C. The reaction mixture was stirred for 10 min and then allowed to gradually warm to room temperature. After quenching with saturated aq. NH_4Cl (1 mL), the mixture was diluted with diethyl ether (20 mL), and then washed with water (10 mL). The organic layer was dried over anhydrous magnesium sulfate, and concentrated *in vacuo*. Purification by column chromatography on silica gel (hexane/ethyl acetate 9 : 1) afforded **14a** as a colorless oil (0.12 g, 81% yield). R_f 0.50 (hexane/ethyl acetate 9 : 1). ^1H NMR ($CDCl_3$) δ 0.40 (s, 6H), 1.21 (s, 12H), 6.20 (d, *J* = 5.5 Hz, 1H), 6.67 (d, *J* = 5.5 Hz, 1H), 7.29-7.36 (m, 2H), 7.51-7.59 (m, 3H). ^{13}C NMR ($CDCl_3$) δ -2.7, 24.8, 83.1, 127.5, 128.7, 134.1, 138.7, 145.1. IR (neat) 3050, 2975, 1580, 1420, 1375, 1320, 1300, 1275, 1240, 1215, 1140 cm^{-1}. MS *m/z* 288 (M^+, 56), 289 (M^++1, 13), 273 (100). Anal. Calcd for $C_{16}H_{25}BO_2Si$: C, 66.67; H, 8.74. Found: C, 66.39; H, 8.49.

Typical Procedure for *gem*-Silylborylation of Alkylidene-type Carbenoids Generated by

Halogen-lithium Exchange. [Dimethylphenylsilyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene]cyclohexane (14b). Butyllithium in hexane (1.56 M, 1.47 mL, 2.3 mmol) was added dropwise to a solution of 1,1-(dibromomethylene)cyclohexane (**10b**) (0.55 mg, 2.2 mmol) in THF (6 mL) and diethyl ether (3 mL) at –110 °C, and stirred at –110 °C for 15 min to prepare **11b**. The mixture was then treated with **3** (0.62 g, 2.4 mmol), warmed gradually to room temperature, and further stirred for 12 h at room temperature. After quenching with saturated aq. NH_4Cl (1 mL), the mixture was diluted with diethyl ether (20 mL) and then washed with water (10 mL). The organic layer was dried over anhydrous magnesium sulfate, and concentrated *in vacuo*. Purification by column chromatography on silica gel (hexane/ethyl acetate 9 : 1) afforded **14b** as a colorless oil (0.65 g, 84% yield). R_f 0.44 (hexane/ethyl acetate 9 : 1). ^{1}H NMR ($CDCl_3$) δ 0.34 (s, 6H), 1.21 (s, 12H), 1.36-1.72 (m, 6H), 2.13 (t, J = 5.8 Hz, 2H), 2.31 (t, J = 6.0 Hz, 2H), 7.25-7.65 (m, 5H). ^{13}C NMR ($CDCl_3$) δ -0.05, 25.1, 26.1, 28.1, 28.8, 37.7, 39.3, 83.0, 127.4, 128.4, 133.9, 140.8, 168.0. IR (neat) 2980, 2920, 2850, 1590, 1365, 1330, 1320, 1280, 1250, 1140, 1105, 850, 830, 820, 730, 700 cm^{-1}. MS *m/z* 358 (M^++2, 1.7), 357 (M^++1, 6), 356 (M^+, 21), 355 (M^+-1, 5), 196 (100). Anal. Calcd for $C_{21}H_{33}BO_2Si$: C, 70.77; H, 9.33. Found: C, 70.53; H, 9.61.

1-Triphenylsilyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (12a). Yield: 60%. Colorless needles. Mp, 97.6 °C. R_f 0.36 (hexane/ethyl acetate 10 : 1). ^{1}H NMR ($CDCl_3$) δ 1.12 (s, 12H), 6.27 (d, J = 5.6 Hz, 1H), 6.94 (d, J = 5.6 Hz, 1H), 7.30-7.67 (m, 15H). ^{13}C NMR ($CDCl_3$) δ 24.6, 83.3, 127.8, 129.1, 130.1, 134.7, 136.4, 150.0. IR (KBr) 2924, 2855, 1458, 1427, 1377, 1323, 1302, 1130, 1109, 700 cm^{-1}. MS *m/z* 413 (M^++1, 3), 412 (M^+, 9), 411 (M^+-1, 2), 329 (11), 259 (70), 181 (22), 84 (100). HRMS Calcd for $C_{26}H_{29}BO_2Si$: M^+, 412.2030. Found: *m/z* 412.2033.

1-Methyldiphenylsilyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (13a). Yield: 62%. Colorless oil. R_f 0.37 (hexane/ethyl acetate 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.69 (s, 3H), 1.15 (s, 12H), 6.19 (d, J = 5.4 Hz, 1H), 6.80 (d, J = 5.4 Hz, 1H), 7.30-7.55 (m, 10H). ^{13}C NMR ($CDCl_3$) δ -3.6, 24.6, 83.2, 127.5, 128.9, 133.9, 135.7, 136.6, 147.6. IR (neat) 3069, 2978, 1427, 1327, 1304, 1134, 1113, 851, 793, 735, 698 cm^{-1}. MS *m/z* 351 (M^++1, 2), 350 (M^+, 8), 349 (M^+-1, 2), 335 (6), 253 (24), 197 (50), 84 (100). Anal. Calcd for $C_{21}H_{27}BO_2Si$: C, 72.00; H, 7.77. Found: C,72.13; H,7.63.

1-Dimethylphenylsilyl-1-[(3a*S*,4*S*,6*S*,7a*R*)-hexahydro-3a,5,5-trimethyl-4,6-methano-1,3,2-benzodioxaborol-2-yl]ethene (15a). Yield: 72%. Colorless oil. $[\alpha]_D^{25}$ 2.65° (*c* 0.75, $CHCl_3$). R_f 0.41 (hexane/ethyl acetate 10 :1). ^{1}H NMR ($CDCl_3$) δ 0.41 (s, 6H), 0.83 (s, 3H), 1.02 (d, J = 11.0 Hz, 1H), 1.27 (s, 3H), 1.36 (s, 3H), 1.78-1.88 (m, 2H), 2.01-2.12 (m, 2H), 2.24-2.41 (m, 1H), 4.28 (dd, J = 8.9, 1.9 Hz, 1H), 6.22 (d, J = 5.7 Hz, 1H), 6.70 (d, J =

5.7 Hz, 1H), 7.31-7.33 (m, 3H), 7.53-7.56 (m, 2H). ^{13}C NMR ($CDCl_3$) δ -2.6, 24.1, 26.5, 27.2, 28.7, 35.6, 38.2, 39.6, 51.4, 77.2, 77.8, 85.4, 127.4, 128.6, 134.0, 138.6, 145.2. IR (neat) 2920, 1578, 1427, 1325, 1246, 1111, 1030, 818 cm^{-1}. MS *m/z* 340 (M^+, 1), 325 (M^+-Me, 8), 205 (9), 191 (17), 135 (100), 93 (64). HRMS (FAB). Calcd for $C_{20}H_{30}BO_2Si$: MH^+ 341.2108. Found: *m/z* 341.2109.

{Dimethylphenylsilyl[(3a*S*,4*S*,6*S*,7a*R*)-hexahydro-3a,5,5-trimethyl-4,6-methano-1,3,2-benzodioxaborol-2-yl]methylene}cyclohexane (15b). Yield: 78%. Pale yellow oil. $[\alpha]_D^{26}$ 3.84° (*c* 0.91, $CHCl_3$). R_f 0.46 (hexane/ethyl acetate 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.41 (s, 6H), 0.85 (s, 3H), 1.30 (s, 6H), 1.38-1.60 (m, 6H), 1.60-1.74 (m, 4H), 1.82-1.97 (m, 2H), 2.04-2.24 (m, 2H), 2.30-2.43 (m, 1H), 4.27 (d, *J* = 8.6 Hz, 1H), 7.30-7.36 (m, 3H), 7.57-7.62 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 24.1, 26.1, 26.6, 27.1, 28.1, 28.7, 28.9, 35.5, 37.8, 38.2, 39.5, 39.7, 51.2, 77.4, 77.6, 85.5, 127.5, 128.3, 133.9, 140.8, 168.5. IR (neat) 2926, 2855, 1589, 1448, 1364, 1325, 1309, 1248, 1211, 1111, 1032, 816 cm^{-1}. MS *m/z* 409 (M^++1, 2), 408 (M^+, 7), 407 (M^+, 2), 393 (4), 330 (5), 196 (21), 135 (100). HRMS Calcd for $C_{25}H_{37}BO_2Si$: M^+, 408.2656. Found: *m/z* 408.2639.

1-Trimethylsilyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (16a). Yield: 45%. Purified by GPC (flow rate 3.6 mL/min, T_R = 48 min). Colorless oil. R_f 0.40 (hexane/ethyl acetate 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.13 (s, 9H), 1.27 (s, 12H), 6.22 (d, *J* = 5.4 Hz, 1H), 6.58 (d, *J* = 5.4 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ -1.4, 24.8, 65.9, 83.0, 143.1. IR (neat) 2957, 2926, 1456, 1248, 964, 818, 700 cm^{-1}. MS *m/z* 211 (M^+-Me, 58), 129 (41), 83 (100). HRMS Calcd for $C_{10}H_{20}BO_2Si$: M^+-Me, 211.1326. Found: *m/z* 211.1331.

[Trimethylsilyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene]cyclohexane (16b). Yield: 67%. Purified by GPC (flow rate 3.6 mL/min, T_R = 46 min). Colorless oil. R_f 0.44 (hexane/ethyl acetate 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.16 (s, 9H), 1.29 (s, 12H), 1.51-1.62 (m, 6H), 2.20-2.36 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 1.0, 25.1, 26.2, 28.4, 28.8, 36.6, 37.1, 39.2, 82.9, 166.3. IR (neat) 2928, 1593, 1323, 1285, 1246, 1144, 839 cm^{-1}. MS *m/z* 295 (M^++1, 3), 294 (M^+, 12), 293 (M^+-1, 3), 279 (M^+-Me, 9), 197 (100), 179 (28), 83 (34). HRMS Calcd for $C_{16}H_{31}BO_2Si$: M^+, 294.2186. Found: *m/z* 294.2188.

[Dimethylphenylsilyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene]cyclopentane (17). Yield: 84%. Colorless oil. R_f 0.42 (hexane/ethyl acetate 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.39 (s, 6H), 1.20 (s, 12H), 1.45-1.80 (m, 4H), 2.13 (brs, 2H), 2.46 (brs, 2H), 7.25-7.70 (m, 5H). ^{13}C NMR ($CDCl_3$) δ -0.8, 24.9, 26.0, 26.6, 35.8, 36.7, 82.8, 127.5, 128.4, 134.0, 140.4, 173.8. IR (neat) 2976, 1593, 1427, 1369, 1325, 1303, 1271, 1143, 1109, 997, 852, 831, 700 cm^{-1}. MS *m/z* 344 (M^++2, 0.3), 343 (M^++1, 1.0), 342

(M^+, 3.3), 327 (12), 264 (16), 259 (18), 245 (100), 227 (21), 182 (51), 167 (24), 135 (37). HRMS Calcd for $C_{20}H_{31}BO_2Si$: M^+, 342.2186. Found: *m/z* 342.2193.

1-Dimethylphenylsilyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2-diphenylethene (18). Yield: 60%. Purified by GPC (flow rate 3.6 mL/min, T_R = 44.5 min). Colorless needles. Mp, 202 °C. R_f 0.31 (hexane/ethyl acetate 10 : 1). ^1H NMR ($CDCl_3$) δ 0.08 (s, 6H), 0.99 (s, 12H), 7.00-7.58 (m, 15H). ^{13}C NMR ($CDCl_3$) δ -0.6, 24.9, 83.3, 127.1, 127.2, 127.5, 127.6, 127.7, 128.4, 128.5, 128.8, 134.0, 140.9, 144.8, 146.1, 165.4. IR (Nujol) 1561, 1318, 1141, 1105, 840, 734, 700 cm^{-1}. MS *m/z* 442 (M^++2, 2.8), 441 (M^++1, 9.6), 440 (M^+, 28.6), 358 (12), 357 (43), 356 (100), 355 (25). Anal. Calcd for $C_{28}H_{33}BO_2Si$: C, 76.35; H, 7.55. Found: C, 76.10; H, 7.67.

(1*Z*,3*S*)-3-(2-Methoxyethoxy)methoxy-1-dimethylphenylsilyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-butene (19). Yield: 45%. Colorless oil. $[\alpha]_D^{25}$ -12.3° (*c* 0.62, $CHCl_3$). R_f 0.32 (hexane/ethyl acetate 3 : 1). ^1H NMR ($CDCl_3$) δ 0.45 (s, 6H), 1.00 (d, *J* = 6.2 Hz, 3H), 1.19 (s, 12H), 3.37 (s, 3H), 3.43-3.60 (brs, 4H), 4.26 (dq, *J* = 6.2, 8.6 Hz, 1H), 4.53 (s, 2H), 6.78 (d, *J* = 6.8 Hz, 1H), 7.26-7.62 (m, 5H). ^{13}C NMR ($CDCl_3$) δ -0.69, 0.23, 20.5, 24.6, 24.7, 58.9, 66.5, 71.7, 72.8, 83.1, 93.0, 127.6, 128.7, 133.9, 140.2, 161.3. IR (neat) 3060, 3050, 2970, 2950, 2900, 2800, 1600, 1440, 1420, 1370, 1320, 1300, 1270, 1250, 1220, 1140, 1110, 1020, 980, 940, 860, 840, 820 cm^{-1}. MS *m/z* 421 (M^++1,0.3), 420 (M^+, 0.5), 419 (M^+-1, 0.2), 135 (100). Anal. Calcd for $C_{22}H_{37}BO_5Si$: C, 62.85; H, 8.87. Found: C, 62.67; H, 8.93.

(1*E*)-1-Dimethylphenylsilyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3-butadiene (20). Yield: 75%. Colorless oil. R_f 0.45 (hexane/ethyl acetate 9 : 1). ^1H NMR ($CDCl_3$) δ 0.41 (s, 6H), 1.20 (s, 12H), 5.20-5.40 (m, 2H), 7.30-7.62 (m, 5H). ^{13}C NMR ($CDCl_3$) δ -2.0, 24.2, 83.0, 121.7, 128.5, 129.0, 134.0, 138.1, 138.2, 156.0. IR (neat) 3050, 3000, 2950, 2900, 2850, 1610, 1550, 1460, 1420, 1410, 1360, 1320, 1300, 1280, 1260, 1140, 1100, 1000, 980, 950, 920, 910, 860, 840, 820 cm^{-1}. MS *m/z* 314 (M^+, 8.3), 171 (100). Anal. Calcd for $C_{18}H_{27}BO_2Si$: C, 68.29; H, 8.66. Found: C, 68.13; H, 8.49.

(1*Z*,3*E*)-1-Dimethylphenylsilyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaboro-lan-2-yl)-1,3-decadiene (21). Yield: 89%. Colorless oil. R_f 0.50 (hexane/ethyl acetate 9 : 1). ^1H NMR ($CDCl_3$) δ 0.45 (s, 6H), 0.87 (t, *J* = 6.6 Hz, 3H), 1.20-1.36 (brs, 20H), 1.98 (m, 2H), 5.86 (dt, *J* = 14.8, 6.8 Hz, 1H), 6.15 (dd, *J* = 14.8 Hz, 11.0, 1H), 7.25-7.35 (m, 3H), 7.49 (d, *J* = 11.0 Hz, 1H), 7.54-7.60 (m, 2H). ^{13}C NMR ($CDCl_3$) δ -0.1, 14.1, 22.6, 24.7, 28.5, 31.6, 32.6, 82.8, 127.5, 128.4, 131.6, 133.9, 140.8, 142.1, 158.3. IR (neat) 2930, 1631, 1546, 1325, 1143 cm^{-1}. MS *m/z* 399 (M^++1, 3), 398 (M^+, 6), 397 (M^+-1, 3), 135 (100). HRMS

Calcd for $C_{24}H_{39}BO_2Si$: M^+, 398.2810. Found: *m/z* 398.2812.

(*E*) and (*Z*)-1-Dimethylphenylsilyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-decen-3-yne (22). Yield: 49% (*E* : *Z* = 1 : 1). Colorless oil. R_f 0.50 (hexane/ethyl acetate 9 : 1). ^{1}H NMR ($CDCl_3$) δ 0.41 (s, 6H), 0.92 (t, 3H), 1.21 (s, 12H), 1.20-1.31 (brs, 8H), 2.29 (dt, *J* = 6.5, 2.1 Hz, 2H), 6.21 (s, 1H), 7.30-7.61 (m, 5H). ^{13}C NMR ($CDCl_3$) δ -2.6, 14.0, 19.6, 22.5, 24.6, 28.5, 31.3, 83.1, 94.6, 127.2, 128.3, 133.9, 137.5. IR (neat) 2970, 2940, 2840, 2050, 1550, 1460, 1420, 1380, 1320, 1300, 1250, 1210, 1150, 1100, 1010, 980, 950 cm^{-1}. MS *m/z* 398 (M^++2, 1), 397 (M^++1, 2), 396 (M^+, 8), 395 (M^+-1, 2), 253 (100). HRMS Calcd for $C_{24}H_{37}BO_2Si$: M^+, 396.2654. Found: *m/z* 396.2656.

Cross-coupling/Protodesilylation of 19. A mixture of **19** (42 mg, 0.100 mmol), iodobenzene (30 mg, 0.15 mmol), $Pd(PPh_3)_4$ (3.5 mg, 3.0 μmol), and 3 M KOH aqueous solution (0.20 mL, 0.60 mmol) in dioxane (1 mL) was heated at 90 °C for 12 h. The reaction mixture was diluted with diethyl ether (10 mL), washed with water (3 mL). The organic layer was then separated, dried over anhydrous $MgSO_4$, and concentrated to give crude **23**. To a solution of crude **23** in THF (2 mL) was added 1 M solution of tetrabutylammonium fluoride in THF (1 mL), and the resulting solution was heated at 50 °C for 3 h. The mixture was diluted with diethyl ether (3 mL) and treated with water (3 mL). The organic layer was separated, dried over anhydrous $MgSO_4$, and concentrated. The crude product was purified by column chromatography on silica gel to give (*E*,3*S*)-3-(2-methoxyethoxy)methoxy-1-phenyl-1-butene (**24**) as a colorless oil (17 mg, 72% yield). $[\alpha]_D^{24}$ -6.18° (*c* 1.06, $CHCl_3$). R_f 0.32 (hexane/ethyl acetate 9 : 1). ^{1}H NMR ($CDCl_3$) δ 1.35 (d, *J* = 6.4 Hz, 1H), 3.38 (s, 3H), 3.52-3.87 (m, 4H), 4.40 (m, 1H), 4.78 (dd, *J* = 7.0, 23.1 Hz, 1H), 6.10 (dd, *J* = 7.4, 16.0 Hz, 1H), 6.56 (d, *J* = 16.0 Hz, 1H), 7.22-7.41 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 21.5, 59.0, 66.8, 71.8, 72.6, 92.7, 126.4, 127.6, 128.5, 130.7, 131.5, 136.5. IR (neat) 3050, 3000, 2950, 2900, 2850, 1610, 1550, 1460, 1420, 1410, 1360, 1320, 1300, 1280, 1260, 1140, 1100, 1000, 980, 950, 920, 910, 860, 840, 820 cm^{-1}. MS *m/z* 236 (M^+, 0.06), 129 (100). Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.36; H, 8.75.

(1*Z*, 3*E*)-1-Dimethylphenylsilyl-1-phenyl-1,3-decadiene (25). Yield: 94%. Colorless oil. R_f 0.41 (hexane). ^{1}H NMR ($CDCl_3$) δ 0.39 (s, 6H), 0.89 (t, *J* = 6.8 Hz, 3H), 1.24 (broad, 8H), 2.00 (m, 2H), 5.77 (dt, *J* = 14.4 Hz, 6.8, 1H), 6.24 (dd, *J* = 14.4, 11.4 Hz, 1H), 6.76 (d, *J* = 11.4 Hz, 1H), 7.07-7.65 (m, 10H). ^{13}C NMR ($CDCl_3$) δ -0.14, 14.1, 22.6, 28.7, 31.7, 32.6, 125.5, 127.5, 127.8, 127.9, 128.9, 129.6, 133.9, 138.8, 139.4, 140.5, 145.7, 146.7. IR (neat) 3060, 3050, 2950, 2920, 2850, 1640, 1600, 1480, 1420, 1250, 1100, 970, 830, 810, 780, 730, 700 cm^{-1}. MS *m/z* 350 (M^++2, 1), 349 (M^++1, 5), 348 (M^+, 16), 135 (100). Anal. Calcd for $C_{24}H_{32}Si$: C, 82.69; H, 9.25. Found: C, 82.93; H, 9.51.

(1*E*, 3*E*)-1-Phenyl-1,3-decadiene (26).[27] Yield: 84%. Colorless oil. R_f 0.80 (hexane/ethyl acetate 9 : 1). ^{1}H NMR ($CDCl_3$) δ 0.92 (t, *J* = 6.5 Hz, 3H), 1.21-1.62 (broad, 8H), 2.16 (m, 2H), 5.85 (dt, *J* = 7.1, 15.1 Hz, 1H), 6.23 (dd, *J* = 15.6, 10.2 Hz, 1H), 6.46 (d, *J* = 15.6 Hz, 1H), 6.78 (dd, *J* = 15.6, 10.2 Hz, 1H).

Typical Procedure for *gem*-Diborylation of Alkylidene-type Carbenoids. [Bis (4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene]cyclohexane (29). Butyllithium in hexane (1.50 M, 0.15 mL, 0.22 mmol) was added dropwise to a solution of 1,1-(dibromomethylene)cyclohexane (**1b**) (51 mg, 0.20 mmol) in THF (1 mL) and diethyl ether (0.5 mL) at –110 °C, and the resulting solution was stirred at –110 °C for 10 min. To the resulting solution of (bromolithiomethylene)cyclohexane was added dropwise a solution of bis(pinacolato)diboron (**6**) (56 mg, 0.22 mmol) in THF (1 mL). The mixture was gradually warmed to room temperature and stirred for 12 h. The reaction mixture was quenched with saturated aq. NH_4Cl (1 mL), diluted with diethyl ether (10 mL), and treated with water (3 mL). The organic layer was separated, dried over anhydrous magnesium sulfate, and concentrated to give a colorless solid, which was purified by column chromatography on silica gel (hexane/ethyl acetate 9 : 1) to give **29** as colorless plates (65 mg, 93% yield). Mp, 77 °C. R_f 0.31 (hexane/ethyl acetate 9 : 1). ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 24 H), 1.50-1.70 (m, 6 H), 2.30-2.45 (m, 4 H). ^{13}C NMR ($CDCl_3$) δ 24.7, 26.4, 28.7, 37.4, 82.7, 171.5. IR (Nujol) 1615, 1320, 1285, 1265, 1245, 1220, 1140, 1105, 1010, 985, 965, 890, 855, 670 cm^{-1}. MS *m/z* 350 (M^++2, 0.2), 349 (M^++1, 2), 348 (M^+, 8), 347 (M^+-1, 4), 333 (M^+-Me, 8), 291 (100). Anal. Calcd for $C_{19}H_{34}B_2O_4$: C, 65.56; H, 9.84%. Found: C, 65.31; H, 10.03%.

{Bis[(3a*S*,4*S*,6*S*,7a*R*)-hexahydro-3a,5,5-trimethyl-4,6-methano-1,3,2-benzodioxaborol-2-yl]methylene}cyclohexane (30). Yield: 99%. Colorless oil. $[\alpha]_D^{25}$ 8.21° (*c* 0.73, $CHCl_3$). R_f 0.51 (hexane/ethyl acetate 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.84 (s, 6H), 1.28 (s, 6H), 1.38 (s, 6H), 1.50-1.69 (m, 6H), 1.81-1.95 (m, 4H), 2.02-2.20 (m, 4H), 2.21-2.38 (m, 2H), 2.38-2.46 (m, 2H), 4.29 (dd, *J* = 2.2, 6.6 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 24.0, 26.4, 27.1, 28.7, 35.7, 37.6, 37.7, 38.1, 39.5, 51.4, 76.4, 77.4, 85.1, 171.5. IR (neat) 2926, 2868, 1618, 1448, 1375, 1327, 1310, 1273, 1215, 1123, 1078, 1034, 995, 756, 735 cm^{-1}. MS *m/z* 453 (M^++1, 4), 452 (M^+, 11), 451 (M^+-1, 5), 342 (3), 135 (100), 93 (56). HRMS Calcd for $C_{27}H_{42}B_2O_4$: M^+, 452.3269. Found: *m/z* 452.3284.

[Bis(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)methylene]cyclohexane (31). Yield: 15%. Colorless needles. Mp, 52.4 °C. R_f 0.10 (hexane/ethyl acetate 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.98 (s, 12H), 1.53-1.60 (m, 6H), 2.33 (m, 4H), 3.63 (s, 8H). ^{13}C NMR ($CDCl_3$) δ 21.9, 26.5, 28.9, 31.6, 37.2, 72.1, 165.5. IR (KBr) 2924, 2855, 1618, 1464, 1404, 1294, 1224,

1107 cm^{-1}. MS *m/z* 321 (M^++1, 13), 320 (M^+, 65), 319 (M^+-1, 32), 234 (66), 135 (42), 69 (100). HRMS Calcd for $C_{17}H_{30}B_2O_4$: M^+, 320.2330. Found: *m/z* 320.2356.

1,1-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (32). Yield: 91%. Colorless plates. Mp, 81.2 °C. R_f 0.25 (hexane/ethyl acetate 9 : 1). ^1H NMR ($CDCl_3$) δ 1.26 (s, 24H), 6.58 (s, 2H). ^{13}C NMR ($CDCl_3$) δ 24.7, 83.1, 147.9. IR (Nujol) 1590, 1385, 1305, 1280, 1200, 1150, 1110, 1100, 980, 855 cm^{-1}. MS *m/z* 280 (M^+, 56), 265 (M^+-Me,79), 84 (100). Anal. Calcd for $C_{14}H_{26}B_2O_4$: C, 60.06; H, 9.36%. Found: C, 60.09; H, 9.31%.

[Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-methylene]cyclopentane (33). Yield: 96%. Colorless plates. Mp, 73.5 °C. R_f 0.45 (hexane/ethyl acetate 4 : 1). ^1H NMR ($CDCl_3$) δ 1.24 (s, 24H), 1.59-1.67 (m, 4H), 2.44-2.52 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 24.8, 26.2, 36.0, 82.5, 178.8. IR (Nujol) 1620, 1320, 1140, 1010, 990, 855, 720 cm^{-1}. MS *m/z* 335 (M^++1, 1), 334 (M^+, 6), 333 (M^+-1, 2), 319 (M^+-Me, 9), 277 (100). Anal. Calcd for $C_{18}H_{32}B_4O_4$: C, 64.72; H, 9.65. Found: C, 64.46; H, 9.88.

1,1-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2-diphenylethene (34). Yield: 54%. Colorless needles. Mp, 182.8 °C. R_f 0.41 (hexane/ethyl acetate 4 : 1). ^1H NMR ($CDCl_3$) δ 1.14 (s, 12H), 7.24 (s, 10H). ^{13}C NMR ($CDCl_3$) δ 24.4, 83.0, 127.4, 127.6, 129.3, 144.4, 164.5. IR (Nujol) 2977, 1560, 1442, 1371, 1290, 1269, 1141, 1014, 848, 700 cm^{-1}. MS *m/z* 433 (M^++1, 5), 432 (M^+, 11), 431 (M^+-1, 4), 274 (100), 83 (24). Anal. Calcd for $C_{26}H_{34}B_2O_4$: C, 7.93; H, 72.26. Found: C, 7.99; H, 72.18.

(*S*)-3-(2-Methoxyethoxy)methoxy-1,1-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-butene (35). Yield: 65%. Colorless oil. $[\alpha]_D^{25}$ -48.4° (*c* 1.06, MeOH). R_f 0.42 (hexane/ethyl acetate 1 : 1). ^1H NMR ($CDCl_3$) δ 1.20-1.29 (m, 3H), 1.23 (s, 12H), 1.28 (s, 12H), 3.38 (s, 3H), 3.50-3.80 (m, 4H), 4.42 (t, *J* = 6.0 Hz, 1H), 4.69 (s, 2H), 6.76 (d, *J* = 5.1 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 20.7, 24.5, 24.7, 24.8, 58.9, 66.6, 71.7, 73.3, 82.9, 83.1, 93.4, 159.6. IR (neat) 2980, 2930, 2890, 2810, 1620, 1465, 1445, 1390, 1370, 1350, 1330, 1300, 1250, 1210, 1140, 1110, 1040, 985, 965, 920, 855, 750, 660 cm^{-1}. MS *m/z* 397 (M^+-Me, 0.4), 131 (100). Anal. Calcd for $C_{20}H_{38}B_2O_7$: C, 58.29; H, 9.29%. Found: C, 58.13; H, 9.02%.

1,1-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3-butadiene (36). Yield: 89%. Colorless oil. R_f 0.25 (hexane/ethyl acetate 9 : 1). ^1H NMR ($CDCl_3$) δ 1.24 (s, 12H), 1.29 (s, 12H), 5.35 (d, *J* = 10.9 Hz, 2H), 5.42 (d, *J* = 17.5 Hz, 1H), 6.79 (ddd, *J* = 17.5, 10.9, 10.4 Hz, 1H), 7.30 (d, *J* = 10.4 Hz, 1 H). ^{13}C NMR ($CDCl_3$) δ 24.7, 83.0, 83.2, 123.1, 138.0, 157.8. IR (Nujol) 1620, 1560, 1320, 1260, 1210, 1140, 1110, 1010, 990, 965, 910, 855 cm^{-1}. MS *m/z* 308 (M^++2, 2), 307 (M^++1, 11), 306 (M^+, 69), 305 (M^+-1, 31), 304 (M^+-2, 4), 291

(M^+-Me, 26), 206 (100). HRMS Calcd for $C_{16}H_{28}B_2O_4$: M^+, 306.2172. Found: *m/z* 306.2173.

(3*E*)-1,1-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3-decadiene (37). Yield: 82%. Colorless oil. R_f 0.29 (hexane/ethyl acetate 10 : 1). ^1H NMR ($CDCl_3$) δ 0.87 (t, *J* = 6.6 Hz, 3H), 1.23 (s, 12H), 1.30 (s, 12H), 1.20-1.38 (brs, 8H), 2.11 (m, 2H), 5.96 (dd, *J* = 15.1, 6.8 Hz, 1 H), 6.49 (dd, *J* = 15.1, 11.0 Hz, 1H), 7.32 (d, *J* = 11.0 Hz, 1 H). ^{13}C NMR ($CDCl_3$) δ 14.1, 22.6, 24.8, 28.7, 28.8, 31.7, 32.8, 82.8, 83.1, 131.8, 142.3, 158.6. IR (neat) 2980, 2930, 2855, 1740, 1630, 1570, 1460, 1400, 1365, 1350, 1290, 1265, 1210, 1140, 1105, 1010, 985, 910, 850, 730, 660 cm^{-1}. MS *m/z* 392 (M^++2, 1), 391 (M^++1, 9), 390 (M^+, 36), 389 (M^+-1, 18), 375 (M^+-Me, 10), 131 (100). Anal. Calcd for $C_{22}H_{40}B_2O_4$: C, 67.72; H, 10.33%. Found: C, 67.80; H, 10.53%.

1,1-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-decen-3-yne (38). Yield: 48%. Colorless oil. R_f 0.36 (hexane/ethyl acetate 10 : 1). ^1H NMR ($CDCl_3$) δ 0.88 (t, *J* = 6.5 Hz, 3H), 1.22 (s, 12H), 1.31 (s, 12H), 2.32 (dt, *J* = 2.2, 6.9 Hz, 2H), 6.71 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 14.0, 19.7, 22.5, 24.6, 24.7, 28.5, 31.3, 83.2, 83.4, 97.2, 136.0. IR (neat) 2980, 2930, 2860, 2200, 1560, 1460, 1400, 1340, 1250, 1210, 1140, 1105, 1010, 990, 960, 850, 830 cm^{-1}. MS *m/z* 389 (M^++1, 2), 388 (M^+, 7), 387 (M^+-1, 7), 373 (M^+-Me, 26), 84 (100). Anal. Calcd for $C_{22}H_{38}B_2O_4$: C, 68.07; H, 9.87%. Found: C, 68.15; H, 10.07%.

Cross-coupling of *gem*-Silylborylated Compounds. (5*E*, 7*Z*, 9*E*)-7-Dimethylphenylsilyl-hexadeca-5,7,9-triene (39). A mixture of **21** (0.100 mmol), (*E*)-1-iodo-1-hexene (32 mg, 0.15 mmol), $Pd(PPh_3)_4$ (3.5 mg, 3.0 μmol), and 3 M KOH aqueous solution (0.20 mL, 0.60 mmol) in dioxane (1 mL) was heated at 90 °C for 12 h. The reaction mixture was diluted with diethyl ether (10 mL) and washed with water (3 mL). The organic layer was then separated, dried over anhydrous $MgSO_4$, and concentrated. The resulting crude product was purified by column chromatography (silica gel) to give **39** as a colorless oil (27 mg, 76% yield). R_f 0.72 (hexane). ^1H NMR ($CDCl_3$) δ 0.39 (s, 6H), 0.83-0.95 (m, 6H), 1.14-1.46 (m, 12H), 1.94-2.21 (m, 4H), 5.52 (dt, *J* = 12.0, 7.4 Hz, 1H), 5.78 (dt, *J* = 14.8, 7.4 Hz, 1H), 6.37 (d, *J* = 10.8 Hz, 1H), 6.52 (d, *J* = 14.8 Hz, 1H), 6.62 (ddt, *J* = 14.8, 10.8, 1.4 Hz, 1H), 7.28-7.40 (m, 3H), 7.40-7.58 (m, 2H). ^{13}C NMR ($CDCl_3$) δ -1.8, 13.9, 14.1, 22.1, 22.6, 28.9, 29.3, 31.6, 31.7, 33.0, 33.3, 124.2, 126.4, 127.6, 128.2, 128.7, 134.0, 134.8, 135.6, 137.7, 139.4. IR (neat) 2957, 2926, 1684, 1558, 1248, 1111, 964 cm^{-1}. MS *m/z* 355 (M^++1, 4), 354 (M^+, 13), 297 (10), 135 (100). HRMS Calcd for $C_{24}H_{38}Si$: M^+, 354.2743. Found: *m/z* 354.2742.

(3*Z*, 5*E*)-3- Dimethylphenylsilyl-1-phenyl-dodeca-3,5-dien-1-yne (40). Yield: 99%.

Colorless oil. R_f 0.67 (hexane). ^{1}H NMR ($CDCl_3$) δ 0.51 (s, 6H), 0.87 (t, *J* = 6.8 Hz, 3H), 1.10-1.38 (m, 10H), 1.98 (q, *J* = 6.2 Hz, 2H), 5.81 (dt, *J* = 14.8, 6.8 Hz, 1H), 6.15 (ddt, *J* = 12.2, 7.2, 1.2 Hz, 1H), 7.20 (d, *J* = 12.2 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ -1.2, 14.1, 22.6, 28.5, 28.7, 31.6, 32.7, 93.5, 94.2, 120.1, 124.4, 127.5, 127.9, 128.2, 129.1, 129.5, 131.2, 133.9, 138.2, 140.7, 151.5. IR (neat) 3051, 2957, 2926, 2855, 1626, 1488, 1250, 106, 968, 818, 754, 700, 691 cm^{-1}. MS *m/z* 373 (M^++1, 12), 372 (M^+, 34), 371 (M^+-1, 7), 287 (66), 135 (100). HRMS Calcd for $C_{26}H_{32}Si$: M^+, 372.2273. Found: *m/z* 372.2260.

(4*Z*, 6*E*)-4-(Dimethylphenylsilyl)-trideca-1,4,6-triene (41). Yield: 68%. Colorless oil. R_f 0.50 (hexane/ethyl acetate 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.43 (s, 6H), 0.88 (t, *J* = 6.6 Hz, 3H), 1.22 (brs, 8H), 1.96 (q, *J* = 6.4 Hz, 2H), 2.92 (d, *J* = 6.2 Hz, 2H), 5.49 (d, *J* = 16 Hz, 1H), 5.00 (d, *J* = 11.6 Hz, H), 6.63 (d, *J* = 11.2 Hz, 1H), 7.28-7.42 (m, 3H), 7.48-7.60 (m, 2H). ^{13}C NMR ($CDCl_3$) δ -0.9, 14.1, 22.6, 28.7, 28.9, 31.7, 32.5, 42.1, 115.4, 127.8, 128.8, 129.6, 133.9, 136.3, 136.4, 138.1, 139.3, 143.7. IR (neat) 2957, 2926, 2855, 1638, 1572, 1427, 1248, 1111, 966, 910, 833, 916, 773, 729, 700 cm^{-1}. MS *m/z* 314 (M^++2, 1), 313 (M^++1, 16), 312 (M^+, 16), 295 (11), 227 (12), 135 (100). Anal. Calcd for $C_{21}H_{32}Si$: C, 80.70; H, 10.32. Found: C, 80.41; H, 10.59.

[(Dimethylphenylsilyl)phenylmethylene]cyclohexane (42). Yield: 82%. Colorless oil. R_f 0.47 (hexane). ^{1}H NMR ($CDCl_3$) δ 0.17 (s, 6H), 1.47 (brs, 6H), 1.97 (m, 2H), 2.18 (m, 2H), 6.91-7.00 (m, 1H), 7.08-7.20 (m, 1H), 7.21-7.29 (m, 2H), 7.29-7.40 (m, 3H), 7.56-7.66 (2H). ^{13}C NMR ($CDCl_3$) δ -0.2, 26.5, 28.3, 28.7, 33.3, 35.8, 124.8, 127.7, 127.9, 128.4, 128.5, 132.1, 133.7, 140.5, 145.0, 155.0. IR (neat) 2958, 2894, 1605, 1455, 1402, 1337, 1248, 1111, 937, 830, 707 cm^{-1}. MS *m/z* 308 (M^++2, 2), 307 (M^++1, 7), 306 (M^+, 20), 261 (15), 228 (100), 135 (85), 121 (24). Anal. Calcd for $C_{21}H_{36}Si$: C, 82.29; H, 8.55. Found: C, 82.54; H, 8.66.

[(Trimethylsilyl)(4-trifluoromethyphenyl)methylene]cyclohexane (43). Yield: 82%. Purified by GPC (flow rate 3.6 mL/min, T_R = 48 min). Colorless plates. Mp, 32.4 °C. R_f 0.51 (hexane). ^{1}H NMR ($CDCl_3$) δ 0.03 (s, 9H), 1.40-1.92 (m, 6H), 1.86 (t, *J* = 6.0 Hz, 2H), 2.38 (t, *J* = 6.6 Hz, 2H), 6.97 (d, *J* = 7.4 Hz, 2H), 7.50 (d, *J* = 7.4 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 0.76, 26.5, 28.7, 28.9, 33.4, 35.1, 35.2, 124.5 (q, *J* = 295 Hz), 124.7, 127.0 (q, *J* = 31 Hz), 133.8, 149.6, 154.0. ^{19}F NMR ($CDCl_3$) δ -62.5. IR (neat) 2953, 2920, 2897, 1605, 1448, 1402, 1323, 1248, 1153, 1124, 1101, 935, 837, 797 cm^{-1}. MS *m/z* 313 (M^++1, 17), 312 (M^+, 70), 311 (M^+-1, 1), 297 (98), 220 (68), 73 (100). Anal. Calcd for $C_{17}H_{23}F_3Si$: C, 65.35; H, 7.42. Found: C, 65.34; H, 7.50.

(1*E*)-1-Methyldiphenylsilyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3-

butadiene (44). Yield: 80%. Colorless oil. R_f 0.50 (hexane/ethyl acetate 10 : 1). ^1H NMR ($CDCl_3$) δ 0.70 (s, 3H), 1.13 (s, 12H), 5.32 (m, 2H), 6.91 (m, 2H), 7.30-7.60 (brs, 5H). ^{13}C NMR ($CDCl_3$) δ -3.2, 24.7, 83.2, 121.8, 127.5, 129.0, 135.3, 136.8, 138.3, 157.3. IR (neat) 3068, 2977, 2929, 1552, 1427, 1362, 1302, 1259, 1143, 1109, 999, 975, 856, 808, 700 cm^{-1}. MS *m/z* 376 (M^+, 9),197 (50), 105 (12), 84 (100). Anal. Calcd for $C_{23}H_{29}BO_2Si$: C, 73.40; H, 7.84. Found: C, 73.40; H, 7.77.

(1Z)-1-(4-Trifluoromethylphenyl)buta-1,3-diene (45). Yield: 85%. Colorless oil. R_f 0.67 (hexane/ethyl acetate 10 : 1). ^1H NMR ($CDCl_3$) δ 0.6 (s, 3H), 5.2 (m, 2H), 6.30 (m, 1H), 6.60 (d, J = 10.9 Hz, 1H), 7.00 (d, J = 7.9 Hz, 1H), 7.31-7.72 (m, 14H). ^{13}C NMR ($CDCl_3$) δ -4.0, 121.1. 124.9 (q, J = 3.8 Hz), 127.9, 128.2 (q, J = 246 Hz), 128.7, 129.6, 133.7, 134.9, 135.2, 141.9, 143.6, 145.6 ^{19}F NMR ($CDCl_3$) δ -62.8. IR (neat) 3068, 2960, 1614, 1564, 1429, 1408, 1325, 1167, 1119, 1068, 1018, 930, 795, 727, 740, 702, 669, 609 cm^{-1}. MS *m/z* 314 (M^++2, 1), 313 (M^++1, 16), 312 (M^+, 16), 295 (11), 227 (12), 135 (100). Anal. Calcd for $C_{24}H_{21}F_3Si$: C, 73.07; H, 5.37. Found: C, 73.24; H, 5.50.

Silicon Mediated Coupling Reaction. 2,2-Cyclohexylidene-1-phenyl-2-(4-trifluoromethylphenyl)ethanol (46). A THF solution of anhydrous Bu_4NF (1.00 M, 1.00 mL, 1.00 mmol) was added to **43** (62 mg, 0.20 mmol) and benzaldehyde (42 mg, 0.40 mmol) under an argon atmosphere. The resulting solution was stirred at 60 °C for 24 h. The reaction mixture was diluted with diethyl ether (10 mL) and washed with saturated aq. NH_4Cl (6 mL). The organic layer was then separated, dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography (silica gel) to give **46** as a colorless plates (51 mg, 74% yield). Mp, 44.1 °C. R_f 0.29 (hexane/ethyl acetate 4 : 1). ^1H NMR ($CDCl_3$) δ 1.61-1.92 (m, 8H), 2.50-2.64 (m, 2H), 2.65 (s, 1H), 6.05 (s, 1H), 7.19-7.58 (m, 9H). ^{13}C NMR ($CDCl_3$) δ 26.7, 28.2, 28.4, 30.6, 32.9, 36.8, 71.3, 124.3 (q, J = 273 Hz), 124.6 (q, J = 38 Hz), 125.7, 127.0, 128.1, 130.8, 133.1, 140.0, 142.4, 142.7. ^{19}F NMR ($CDCl_3$) δ -62.8. IR (neat) 3375, 2928, 2855, 1614, 1450, 1325, 1168, 1123, 1067, 1020, 843, 704 cm^{-1}. MS *m/z* 347 (M^++1, 5), 346 (M^+, 23), 345 (M^+-1, 1), 328 (100), 285 (52), 107 (57), 79 (35). HRMS Calcd for $C_{21}H_{21}F_3O$: M^+, 346.1544. Found: *m/z* 354.1545.

Boron Mediated Coupling Reaction of *gem*-Diborylated Compounds. 5,5-(Cyclohexylidene)nonan-2,8-dione (47). Methanol (1 mL) was added to a flask charged with $Rh(acac)(CO)_2$ (1.5 mg, 6.0 μmol), 1,3-bis(diphenylphosphino)propane (2.5 mg, 6.0 μmol), and **29** (35 mg, 0.100 mmol). After being stirred for 15 min at room temperature, the mixture was treated with water (0.20 mL) and methyl vinyl ketone (28 mg, 0.40 mmol). The resulting mixture was stirred at 50 °C for 24 h, diluted with diethyl ether (10 mL), and washed with water (3 mL). The organic layer was then separated, dried over $MgSO_4$, and concentrated.

The resulting crude product was purified by column chromatography on silica gel to give **47** as a colorless oil (17 mg, 74% yield). R_f 0.32 (hexane/ethyl acetate 9 : 1). ^1H NMR ($CDCl_3$) δ 1.51 (s, 8H), 2.05-2.31 (broad, 14H), 2.45 (t, J = 6.2 Hz, 4H). ^{13}C NMR ($CDCl_3$) δ 25.9, 26.8, 28.4, 30.0, 30.4, 43.3, 126.0, 135.9, 208.9. IR (neat) 3400, 2900, 1700, 1440, 1380, 1220, 1120, 1040, 940, 900, 840 cm^{-1}. MS *m/z* 237 (M^++1, 2), 236 (M^+, 100), 235 (M^+-1, 10). HRMS (FAB) Calcd for $C_{15}H_{24}O_2$: M^+, 236.1776. Found: *m/z* 236.1742.

1,1-Diphenylmethylenecyclohexane (48). A mixture of **29** (35 mg, 0.100 mmol), iodobenzene (61 mg, 0.30 mmol), $Pd(PPh_3)_4$ (3.5 mg, 3.0 μmol), and 3 M KOH aqueous solution (0.20 mL, 0.60 mmol) in dioxane (1 mL) was heated at 90 °C for 24 h. Workup followed by column chromatography on silica gel gave **48** as colorless plates (20 mg, 80% yield). Mp, 73.2 °C. R_f 0.70 (hexane/ethyl acetate 9 : 1). ^1H NMR ($CDCl_3$) δ 1.60 (m, 6H), 2.24 (m, 4H), 7.10-7.32 (m, 10H). ^{13}C NMR ($CDCl_3$) δ 26.8, 28.7, 32.4, 126.0, 127.8, 129.8, 134.5, 139.1, 143.1. IR (Nujol) 3400, 2900, 1700, 1440, 1380, 1220, 1120, 1040, 940, 900, 840 cm^{-1}. MS *m/z* 250 (M^++2, 2), 249 (M^++1, 21), 248 (M^+, 100). Anal. Calcd for $C_{19}H_{20}$: C, 91.88; H, 8.12. Found: C, 91.61; H, 8.28.

4,4-Cyclohexylidene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-butene (49). A mixture of **29** (35 mg, 0.100 mmol), allylbromide (12 mg, 0.100 mmol), $Pd(PPh_3)_4$ (3.5 mg, 3.0 μmol), and 3 M KOH aqueous solution (0.100 mL, 0.30 mmol) in dioxane (1 mL) was heated at 70 °C for 12 h. Workup followed by column chromatography on silica gel gave **49** as a colorless oil (22 mg, 83% yield). R_f 0.61 (hexane/ethyl acetate 3 : 1). ^1H NMR ($CDCl_3$) δ 1.25 (m, 12H), 1.55 (m, 6H), 2.18 (m, 2H), 2.44 (m, 2H), 2.88 (d, J = 6.0 Hz, 2H), 5.87 (m, 1H), 4.91 (d, J = 2.1 Hz, 1H), 4.93 (dd, J = 14.3, 2.1 Hz, 1H), 5.87 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 25.5, 27.6, 28.9, 29.6, 31.6, 35.0, 35.8, 83.5, 114.4, 138.9, 146.2, 156.4. IR (neat) 2976, 2926, 1624, 1359, 1329, 1225, 1148, 1107, 991, 964, 851 cm^{-1}. MS *m/z* 263 (M^++1, 8), 262 (M^+, 42), 261 (M^+-1, 9), 205 (52), 161 (50),101 (100), 84 (92). Anal. Calcd for $C_{16}H_{27}BO_2$: C, 73.29; H, 10.38. Found: C, 73.02; H, 10.29.

3,3-Cyclohexylidene-3-phenyl-1-butene (50). A mixture of **29** (35 mg, 0.100 mmol), allyl bromide (12 mg, 0.100 mmol), $Pd(PPh_3)_4$ (3.5 mg, 3.0 μmol), and 3 M KOH aqueous solution (0.20 mL, 0.60 mmol) in dioxane (1 mL) was heated at 70 °C for 12 h. Iodobenzene (20 mg, 0.100 mmol) was added to the reaction mixture. The resulting mixture was stirred at 70 °C for another 12 h. Workup followed by column chromatography on silica gel gave **50** as a colorless oil (15 mg, 71% yield). R_f 0.60 (hexane/ethyl acetate 9 : 1). ^1H NMR ($CDCl_3$) δ 1.56 (m, 6H), 2.00 (m, 2H), 2.28 (m, 2H), 3.09 (d, J = 6.1 Hz, 2H), 4.95 (dd, J = 9.9, 2.0 Hz, 1H), 5.02 (d, J = 2.0 Hz, 1H), 5.69 (m, 1H), 7.26-7.44 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 6.8, 28.4, 28.7, 30.7, 32.2, 38.5, 114.5, 125.7, 127.7, 128.8, 129.2, 136.4, 137.4, 143.8. IR (neat)

2924, 2853, 1489, 1443, 1234, 1070, 1026, 989, 908, 854, 700 cm^{-1}. MS *m/z* 213 (M^++1, 17), 212 (M^+, 83), 211 (M^+-1, 6), 135 (100), 129 (47). HRMS Calcd for $C_{16}H_{20}$: M^+, 212.1565. Found: *m/z* 212.1531.

Facile Stereoselective Synthesis of (Z)-Tamoxifen. 1,1-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-phenyl-1-butene (52). Butyllithium in hexane (1.56 M, 0.32 mL, 0.50 mmol), was added dropwise to a solution of 1,1-dichloro-2-phenyl-1-butene (**51**) (0.100 g, 0.50 mmol) in THF (2 mL) at –78 °C, and stirred at –78 °C for 10 min. The mixture was then treated with **6** (0.13 g, 0.50 mmol), warmed gradually to room temperature. After quenching with saturated aq. NH_4Cl (1 ml), the mixture was diluted with diethyl ether (20 mL) and washed with water (5 mL). The organic layer was dried over anhydrous magnesium sulfate, and concentrated *in vacuo*. Purification by column chromatography on silica gel (hexane/ethyl acetate 10 : 1) afforded **52** as a colorless solid (0.14 g, 0.37 mmol, 74% yield). Mp, 80.6 °C (dec). R_f 0.21 (hexane/ethyl acetate 10 : 1). ^1H NMR ($CDCl_3$) δ 0.92 (t, *J* = 7.6 Hz, 3H), 1.04 (s, 12H), 1.28 (s, 12H), 2.72 (q, *J* = 7.6 Hz, 2H), 7.28 (s, 5H). ^{13}C NMR ($CDCl_3$) δ 13.8, 24.4, 24.8, 32.1, 82.8, 82.9, 126.9, 127.6, 144.3, 170.8. IR (neat) 2970, 2930, 2872, 1595, 1458, 1440, 1371, 1354, 1321, 1291, 1143, 1107, 854 cm^{-1}. MS *m/z* 386 (M^++2, 3), 385 (M^++1, 22), 384 (M^+, 87), 369 (M^+-Me, 28), 327 (100), 202 (85), 84 (89). HRMS Calcd for $C_{22}H_{34}B_2O_4$: M^+, 384.2643. Found: *m/z* 384.2643.

(Z)-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1-4-(2-dimethylaminoethoxy)phenyl-2-phenyl-1-butene (54). A mixture of **52** (38 mg, 0.100 mmol), [2-(4-iodo-phenoxy)ethyl]dimethylamine **53** (29 mg, 0.100 mmol), $Pd_2(dba)_3$ (3.5 mg, 3.0 μmol), P*t*Bu_3 (3.1 mg, 1.5 μmol) and 3 M KOH aqueous solution (0.100 mL, 0.30 mmol) in THF (1 mL) was stirred at room temperature for 12 h. Workup followed by column chromatography on silica gel gave **54** as a colorless oil (17 mg, 0.05 mmol, 52% yield). R_f 0.30 (hexane/ethyl acetate 10 : 1). ^1H NMR ($CDCl_3$) δ 0.85 (t, *J* = 5.8 Hz, 3H), 1.00 (s, 12H), 2.42 (s, 6H), 2.43 (q, *J* = 5.8 Hz, 2H), 2.80 (t, *J* = 4.2 Hz, 2H), 4.11 (t, *J* = 4.2 Hz, 2H), 6.89 (d, *J* = 7.2 Hz, 2H), 7.14 (d, *J* = 7.2 Hz, 2H), 7.25-7.32 (m, 5H). ^{13}C NMR ($CDCl_3$) 13.4, 24.5, 27.1, 45.8, 58.2, 65.6, 83.2, 114.1, 126.8, 127.7, 128.3, 129.4, 133.9, 143.6, 153.2, 156.8. IR (neat) 2974, 2932, 2872, 2770, 1604, 1506, 1356, 1298, 1240, 1143, 1036, 978, 854. MS *m/z* 423 (M^++2, 3), 422 (M^++1, 15), 421 (M^+, 39), 58 (100). HRMS Calcd for $C_{26}H_{36}BNO_3$: M^+, 421.2788. Found: *m/z* 421.2786.

(Z)-Tamoxifen. A mixture of **54** (12 mg, 0.03 mmol), iodobenzene (11 mg, 0.05 mmol), 3,5-dimethoxyphenol (23 mg, 0.15 mmol), Pd(dppf) (2.1 mg, 0.60 μmol), and 6 M KOH aqueous solution (25 μmL, 0.15 mmol), in DME (1 mL) was stirred at room temperature for 24 h. Workup followed by purification with GPC gave (Z)-tamoxifen as a white solid (6.1

mg, 0.02 mmol, 51% yield). ^{1}H NMR ($CDCl_3$) δ 0.92 (t, J = 7.4 Hz, 3H), 2.36 (s, 3H), 2.45 (q, J = 7.4 Hz, 3H), 2.51 (s, 3H), 2.92 (t, J = 5.6 Hz, 2H), 3.92 (t, J = 5.6 Hz, 2H), 6.54 (d, J = 8.8 Hz, 2H), 6.78 (d, J = 8.8 Hz, 2H), 7.11-7.38 (m, 14H). ^{13}C NMR ($CDCl_3$) δ 13.6, 29.1, 45.8, 58.2, 113.4, 125.6, 126.1, 126.5, 127.3, 127.5, 127.8, 128.1, 128.2, 129.5, 129.7, 131.9, 141.3, 142.6, 143.9. IR (neat) 2929, 2870, 2770, 1604, 1500, 1242, 1032, 702 cm^{-1}. MS *m/z* 373 (M^++2, 8), 372 (M^++1, 22), 371 (M^+, 34), 300 (4), 58 (100). HRMS Calcd for $C_{26}H_{29}NO$: M^+, 371.2249. Found: *m/z* 371.2255. Lit.[26b] ^{1}H NMR ($CDCl_3$) δ 0.92 (t, J = 7.2 Hz, 3H), 2.36 (s, 3H), 2.47 (q, J = 7.2 Hz, 3H), 2.51 (s, 3H), 2.92 (t, J = 5.8 Hz, 2H), 3.92 (t, J = 5.8 Hz, 2H), 6.54 (d, J = 8.8 Hz, 2H), 6.77 (d, J = 8.8 Hz, 2H), 7.11-7.35 (m, 14H). ^{13}C NMR ($CDCl_3$) δ 13.6, 29.0, 45.8, 58.2, 113.4, 125.6, 126.0, 126.5, 127.3, 127.4, 127.8, 127.9, 128.1, 129.5, 129.7, 131.9, 141.3, 142.4, 143.8.

(*Z*)-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-diphenyl-1-butene (55). A mixture of **52** (38 mg, 0.100 mmol), iodobenzene (21 mg, 0.100 mmol), $Pd_2(dba)_3$ (3.5 mg, 3.0 μmol), and 3 M KOH aqueous solution (0.10 mL, 0.30 mmol) in THF (1 mL) was stirred at room temperature for 12 h. Workup followed by column chromatography on silica gel gave **55** as a colorless oil (17 mg, 0.05 mmol, 52% yield). R_f 0.32 (hexane/ethyl acetate 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.86 (t, J = 5.8 Hz, 3H), 1.00 (s, 12H), 2.41 (q, J = 5.8 Hz, 2H), 7.22-7.38 (m, 10H). ^{13}C NMR ($CDCl_3$) δ 13.4, 24.5, 27.2, 83.3, 125.8, 126.9, 127.8, 128.0, 128.4, 141.4, 143.5, 153.6. IR (neat) 2976, 2932, 2872, 1597, 1493, 1356, 1300, 1269, 1215, 1103, 1030, 978, 905, 854, 702, 771, 702. MS *m/z* 336 (M^++2, 8), 335 (M^++1, 22), 334 (M^+, 100), 319 (M^+-Me, 9), 227 (87), 234 91), 130 (52). HRMS Calcd for $C_{22}H_{27}BO_2$: M^+, 334.2104. Found: *m/z* 334.2105.

(*E*)-Tamoxifen. A mixture of **55** (11 mg, 0.03 mmol), [2-(4-Iodo-phenoxy)ethyl]dimethylamine **53** (26 mg, 0.05 mmol), 3,5-dimethoxyphenol (23 mg, 0.15 mmol), Pd(dppf) (2.1 mg, 0.60 μmol), and 6 M KOH aqueous solution (25 μmL, 0.15 mmol), in DME (1 mL) was stirred at room temperature for 24 h. Workup followed by purification with GPC gave (*E*)-tamoxifen as a white solid (6.1 mg, 0.02 mmol, 47% yield). ^{1}H NMR ($CDCl_3$) δ 0.92 (t, J = 7.4 Hz, 3H), 2.36 (s, 3H), 2.45 (q, J = 7.4 Hz, 3H), 2.51 (s, 3H), 2.92 (t, J = 5.2 Hz, 2H), 4.10 (t, J = 5.2 Hz, 2H), 6.54 (d, J = 8.8 Hz, 2H), 6.78 (d, J = 8.8 Hz, 2H), 7.11-7.35 (m, 14H). ^{13}C NMR ($CDCl_3$) δ 13.7, 29.1, 44.9, 57.5, 113.3, 125.2, 126.0, 126.5, 127.7, 128.0, 128.1, 128.9, 129.3, 129.6, 131.9, 141.5, 142.1, 143.5. IR (neat) 2931, 2870, 2772, 1604, 1508, 1242, 1032, 700 cm^{-1}. MS *m/z* 373 (M^++2, 8), 372 (M^++1, 22), 371 (M^+, 34), 300 (4), 58 (100). HRMS Calcd for $C_{26}H_{29}NO$: M^+, 371.2249. Found: *m/z* 371.2252.

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Chapter 3

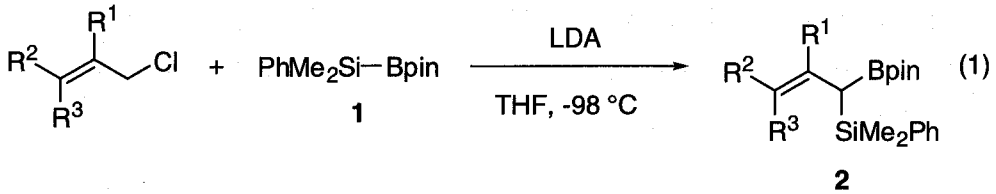
Stereospecific Silylborylation of α-Chloroallyllithiums. Synthesis and Reactions of Allylic *gem*-Silylborylated Reagents

Allyldimetallic reagents, 1-silyl-1-boryl-2-alkenes, were prepared efficiently by *gem*-silylborylation of α-chloroallyllithiums from silylborane with retention of the olefin configuration and were demonstrated to allylate acetals and aldehydes in the presence of Lewis acid to produce (*E*)-4-alkoxyalkenylboronates stereospecifically. Upon heating with aldehydes the reagents afforded (*Z*)-4-hydroxyalkenylsilanes in a stereospecific manner. The allylated products are used for further synthetic elaboration.

Introduction

Allylation of carbony compounds with allylmetal reagents is an important and powerful method to construct regio- and stereodefined carbon frameworks and can be regarded as a complementary approach to the aldol reaction for acyclic stereocontrol. Thus, allylmetal reagents have been widely used in organic synthesis.[1] Meanwhile, since Corriu reported the first α,α–allyldimetallic reagent, α-silylallylithium, which can be regarded as a hybrid of two allylmetal reagents and reacts as an ambident anions with electrophiles,[2] numerous allyldimetallic reagents including such metals as Li, Si, Sn, Al, B, Ti, and Zr, have been intensively investigated to explore possibilities of new synthetic transformations.[3] However, no example is available that demonstrates metal-selective reaction of α,α–allyldimetallic reagents. Since it is well documented that allylic boranes[4] react with carbonyl compounds through a cyclic 6-membered transition state, whereas allylic silanes[5] react with carbonyl compounds through an acyclic transition states in the presence of a Lewis acid, the author envisioned that metal dependent allylation of carbonyl compounds with stereospecific manner might be achieved under appropriate conditions using 1-silyl-1-boryl-2-alkenes, which can be regarded as a hybrid of allylic boranes and silanes, and thus should be highly versatile owing to their wide availability, high stability, and low toxicity as well as excellent chemo-, regio- and stereoselectivities. However, little attention has been paid on the dimetallic reagents. Yamamoto, Yatagai, and Maruyama prepared α-trimethylsilyl-substituted crotyl-9-BBN by deprotonation of crotyl-9-BBN followed by silylation with chlorotrimethylsilane.[6] Similar boronates were synthesized by Tsai and Matteson via homologation of alkenylboronates with [chloro(trimethylsilyl)methyl]lithium.[7] Both reagents were found to allylate aldehydes[8] in a manner similar to allylic boranes. Although this methodology is shown to be effective for acyclic stereocontrol, allylation as allylic silanes and stereospecificity in boron-selective allylation remained yet to be explored.

As discussed in Chapter 2, the reaction that introduces two metals simultaneously into an organic molecule by means of interelement compounds is apparently straightforward and highly efficient for preparation of such organodimetallic compounds. Thus, the author envisaged that the title *gem*-dimetallic reagents **2** might be prepared readily by the *gem*-silylborylation of vinyl-substituted carbenoids using **1** [Eq. (1)].[9-12]



(1)

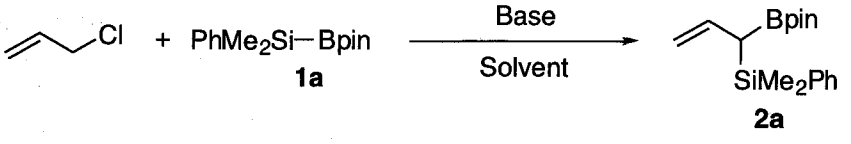
In this Chapter, the author describes novel stereocontrolled synthesis of 1-silyl-1-boryl-2-alkenes via *gem*-silylborylation of α-chloroallyllithiums and dual stereospecific allylation of aldehydes with the *gem*-dimetallic reagents under appropriate conditions. In addition, synthetic utilities of the resulting allylated products are also disclosed.

Results and Discussion

gem-Silylborylation of α-Chloroallyllithium-type Carbenoids

Using allyl chloride as a typical α-chloroallyllithium precursor, the author first screened and optimized the reaction conditions. α-Chloroallyllithium was generated *in situ* from allyl chloride and a base in the presence of (dimethylphenylsilyl)borane (**1a**) at –98 °C. The mixture was stirred for 10 min, and then warmed to room temperature. The results are summarized in Table 1. It was found that LDA was better than lithium dicyclohexylamide, or lithium 2,2,6,6-tetramethylpiperidide in yield of the desired product, whereas dimetalated product was not obtained when butyllithium was employed (entries 1-4). No significant difference was observed even if the reaction was carried out at –110 °C in a mixed solvent of THF and diethyl ether (entry 5). Accordingly, the best results were obtained when the reaction was carried out using LDA in THF at –98 °C and **2a** was given in 90%. Noteworthy is that 1-silyl-1-boryl-2-alkenes (**2**) was stable enough to purify by column chromatography on silica gel.

Table 1. Optimization of conditions for silylborylation of allyl chloride.[a]

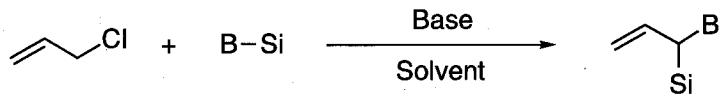


Entry	Base	Solvent	Temperature (°C)	Yield (%)[b]
1	LiN^iPr_2	THF	-98	90
2	$LiNCy_2$	THF	-98	77
3	LiTMP	THF	-98	75
4	BuLi	THF	-98	—
5	LiN^iPr_2	THF/Et_2O (2 : 1)	-110	88

[a] A mixture of allyl chloride (1.0 mol) and **1a** in a solvent was treated with a base at -98 °C or -110 °C for 10 min and then gradually warmed to room temperature. [b] Isolated yields are given.

The author next examined the scope and limitations of silylboranes available for this reaction. Results are summarized in Table 2. (Methyldiphenylsilyl)borane (**1b**) and (triphenylsilyl)borane (**1c**) also reacted with the carbenoid to give the corresponding products in moderate yields (entries 2 and 3).[13] Unexpectedly, however, dimetalated products were not obtained with (trimethylsilyl)borane (**1d**) (entry 4). [14]

Table 2. Reaction with variety of silylborane.[a]

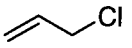
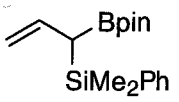
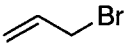
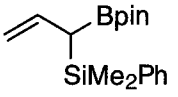
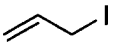
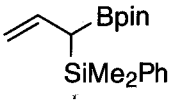
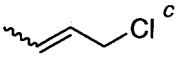
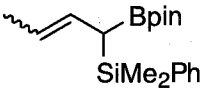
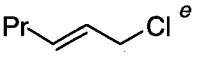
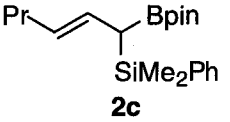
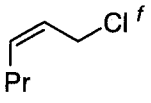
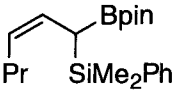
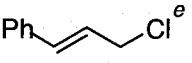
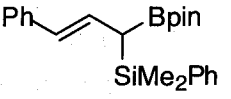
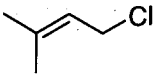
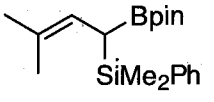
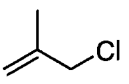
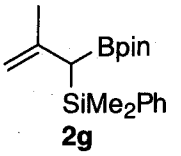


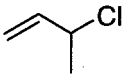
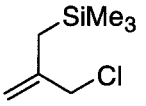
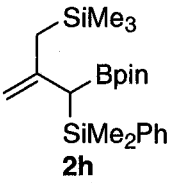
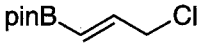
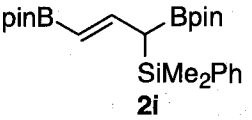
Entry	B–Si	Yield (%)[b]
1	$PhMe_2Si$–Bpin **1a**	90
2	Ph_2MeSi–Bpin **1b**	66
3	Ph_3Si–Bpin **1c**	65
4	Me_3Si–Bpin **1d**	—

[a] A mixture of allyl chloride (1.0 mol) and a silylborane (1.1 mol) in THF was treated with LDA (1.0 mol) at -98 °C for 10 min and then gradually warmed to room temperature. [b] Isolated yields are given.

With the best results of **1a** in hand, the author next applied the silylborylation to various kinds of carbenoids using **1a** (Table 3). *gem*-Silylborylation of allyl bromide and allyl iodide also proceeded in moderate yields (entries 2 and 3). Substituted allylic chlorides were also *gem*-silylborylated smoothly in good yields irrespective of the substitution pattern (entries 4-9, 11 and 12), except α-substituted one (entry 10). No trace of γ-silyl-α-boration via 1,4-migration of a silyl group was observed. Noteworthy is that olefinic configuration was perfectly retained in **2** (entries 4-7 and 12): stereochemically pure allylic chlorides gave single stereoisomers of **2** stereospecifically. β-(Trimethylsilyl)methyl substituted allyllic chloride was also *gem*-silylborylated smoothly in good yields to give a trimetalated allyllic compound (entry 11). When the procedure was applied to γ-boryl substituted allylic chlorides, an α-silyl-α,γ-diborylated product was obtained albeit in a low yield (entry 12).

Table 3. *gem*-Silylborylation of α-haloallyllithiums.[a]

Entry	Allylic chloride	Product	Yield (%)[b]
1		 **2a**	90
2		 **2a**	70
3		 **2a**	58
4		 **2b**	86[d]
5		 **2c**	75[e]
6		 **2d**	79[f]
7		 **2e**	75[e]
8		 **2f**	72
9		 **2g**	73

10		—	—
11		 **2h**	80
12		 **2i**	21[g]

[a] A mixture of allylic halide (1.0 mol) and **1a** (1.1 mol) in THF was treated with LDA (1.0 mol) at -98 °C for 10 min and then gradually warmed to room temperature. [b] Isolated yields are given. [c] *E*: *Z*= 85 : 15. [d] *E*: *Z* = 83 : 17. [e] *E* : *Z* = >99 : <1. [f] *E* : *Z* = <1 : >99. [g] 20% of allyl chloride and 12% of silylborane was recovered.

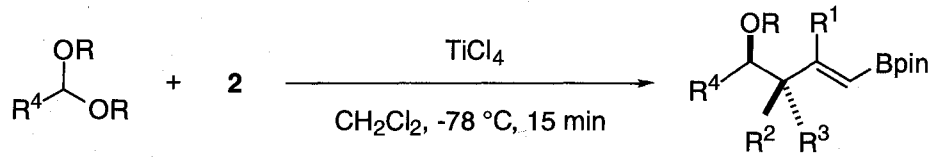
Although reactions involving lithium carbenoid often encounter reproducibility problems when carried out in a larger scale because of instability of lithium carbenoids, the present *gem*-silylborylation can be carried out in ten times larger scales also. For example, from 2.6 g of **1a** and 0.8 g of allyl chloride, 2.8 g of **2a** was isolated in 88% yield.

Metal Dependent Stereospecific Allylation of Carbonyl Compounds with 1-Silyl-1-boryl-2-alkenes

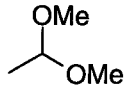
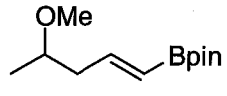
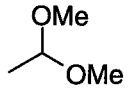
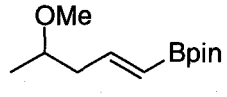
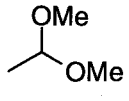
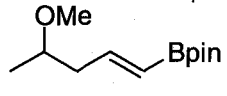
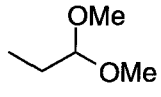
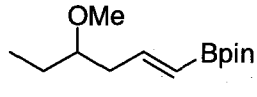
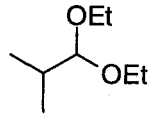
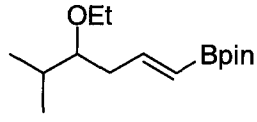
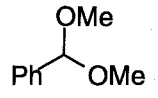
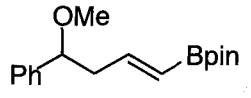
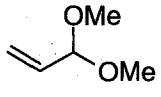
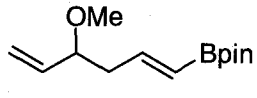
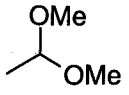
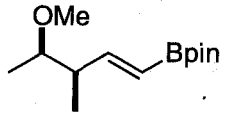
As *gem*-silylborylation of α-chloroallyllithiums straightforwardly gives α,α-allyldimetallic compounds, the author further studied allylation of **2**, taking advantage of the allylic silane or borane functionality by controlling reaction conditions.

After many attempts,[15] he has found that **2** reacts as an allylsilane to allylate acetals in the presence of a Lewis acid.[16,17] The results are summarized in Table 4. The reaction proceeded in good yields in the presence of titanium tetrachloride (entry 1), whereas yields were significantly reduced when boron trifluoride etherate or dichloromethylaluminum was employed (entries 2 and 3). Aliphatic, aromatic, and α,β-unsaturated acetals reacted with **2** to produce alkenylboronates **3a-f** in good yields with high (*E*)-selectivity (entries 1-6).

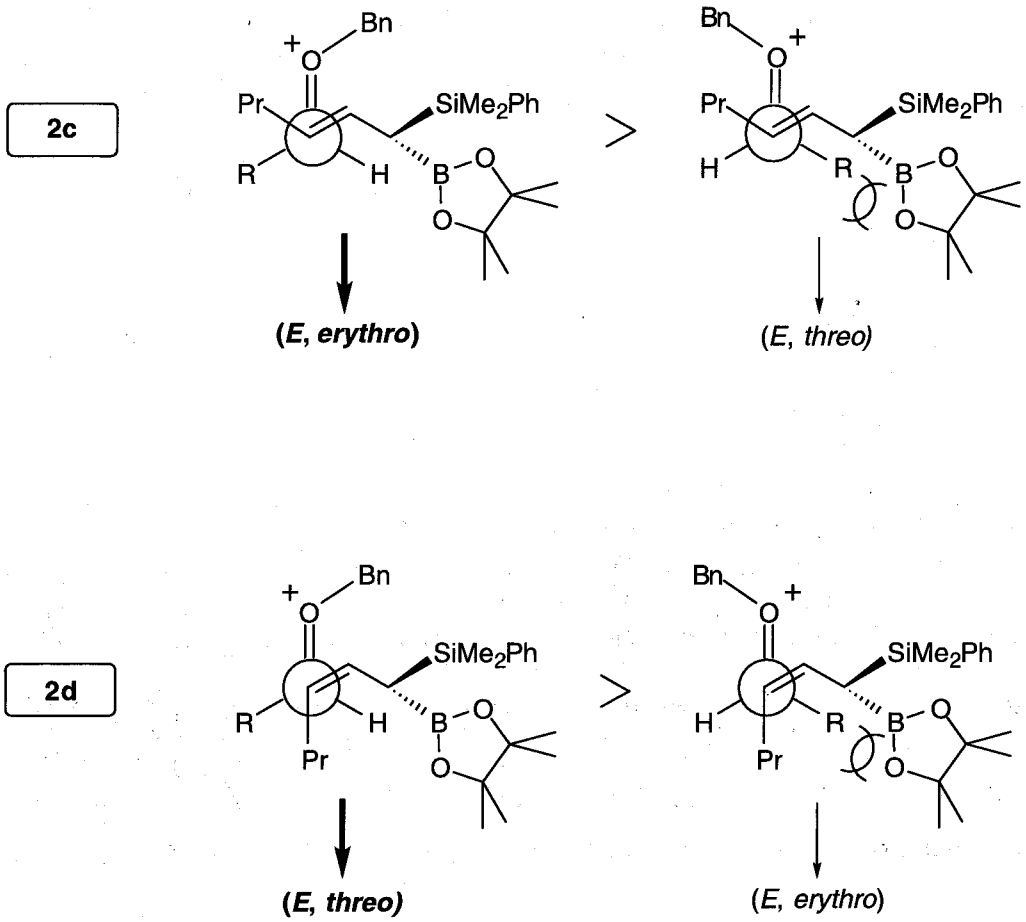
Table 4. Allylation of acetals with **2** as an allylic silane.[a]



3

Entry	**2**	Electrophile	Product	Yield (%)[b]	Isomer ratio[c]
1	**2a**		 **3a**	78	94 : 6[d]
2	**2a**		 **3a**	18[e]	–[f]
3	**2a**		 **3a**	5[g]	–[f]
4	**2a**		 **3b**	77	95 : 5[h]
5	**2a**		 **3c**	85	–[f]
6	**2a**		 **3d**	69	97 : 3[h]
7	**2a**		 **3e**	62	>95 : <5[h]
8	**2b**[i]		 **3f**	81	73 : 24 : 3[j]

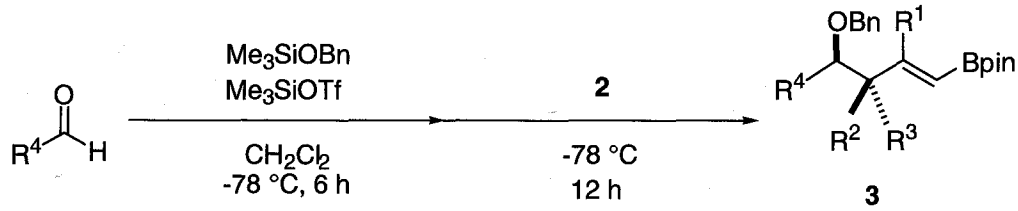
[a] A mixture of **2** (1.0 mol) and an acetal (2.0 mol) in CH_2Cl_2 was treated with $TiCl_4$ (1.5 mol) at -78 °C for 15 min. [b] Isolated yields are given. [c] Determined by ^1H NMR of a crude product mixture. [d] (*E*)-**3a**: 78% yield; (*Z*)-**3a**: 3% yield. [e] $BF_3{\cdot}Et_2O$ (1.5 mol) was used instead of $TiCl_4$. [f] Not determined. [g] $AlMeCl_2$ (1.5 mol) was used instead of $TiCl_4$. [h] A ratio of *E* : *Z*. [i] An *E*/*Z* mixture of **2b** was used (*E* : *Z* = 83 : 17). [j] A ratio of (*E, erythro*) : (*E, threo*) : others.

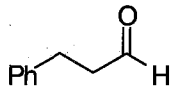
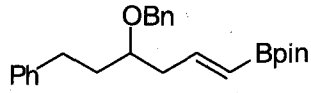
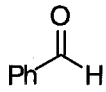
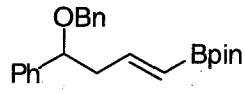
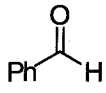
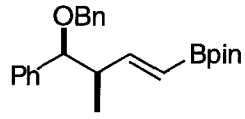
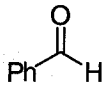
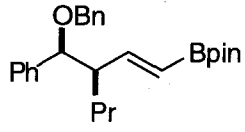
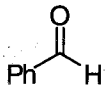
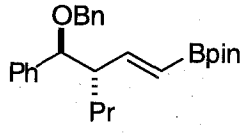
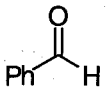
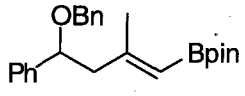


Scheme 2. Transition states for allylation of oxonium ions with **2** as an allylsilane.

Moreover, reagents **2** were shown to allylate oxonium ions *in situ* generated from aldehydes, Me_3SiOBn, and Me_3SiOTf, giving rise to the corresponding (*E*)-benzyl ethers **3g-3l** stereoselectively (Table 5).[18,19] High (*E*)-selectivity of **3** was observed irrespective of the olefinic geometry of **2** (entries 3, 4, and 5).[20] Markedly, allylation by 1-silyl-(*E*)- and -(*Z*)-2-hexenyl boronates **2c** and **2d** proceeded stereospecifically with high (*E*, *erythro*) and (*E*, *threo*) selectivities, respectively (entries 4 and 5).[21] *Erythro* selectivity using (*E*)-allylic silane **2c** may be understood by acyclic *antiperiplanar* transition states.[16d,18b] However, such model cannot rationalize *threo* selectivity from the (*Z*)-allylic silane **2d**. Although the reason for *threo* selectivity is not clear at present, acyclic *synclinal* transition states[5e] might be involved to minimize the steric effect of the boryl group as illustrated in Scheme 2. These results are the first demonstration of silicon-selective allylation over boron in **2**.[22,23]

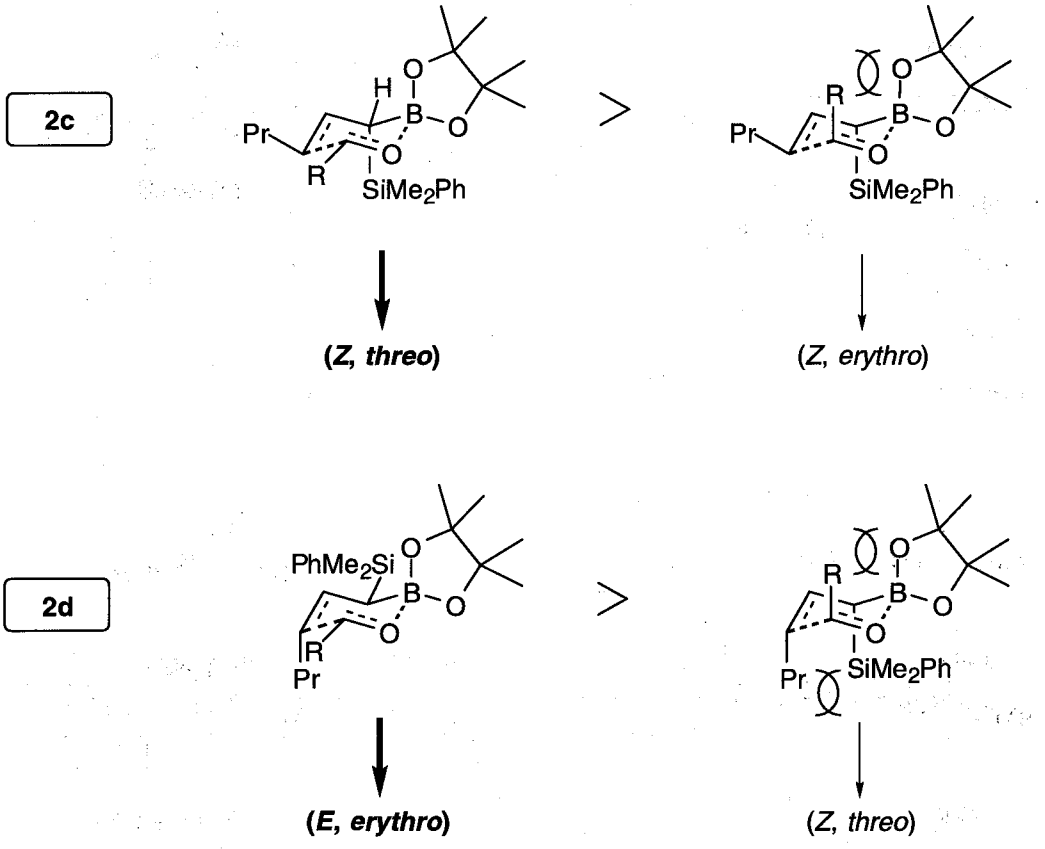
Table 5. Allylation of aldehydes with **2** as an allylic silane.[a]



Entry	2	Electrophile	Product	Yield (%)[b]	Isomer ratio[c]
1	**2a**		 **3g**	85	>95 : <5[d]
2	**2a**		 **3h**	88 (73)[f]	>95 : <5[d]
3	**2b**[e]		 **3i**	81	84 : 16[g]
4	**2c**		 **3j**	83	95 : 5[g]
5	**2d**		 **3k**	94	9 : 91[g]
6	**2g**		 **3l**	70	>95 : <5[d]

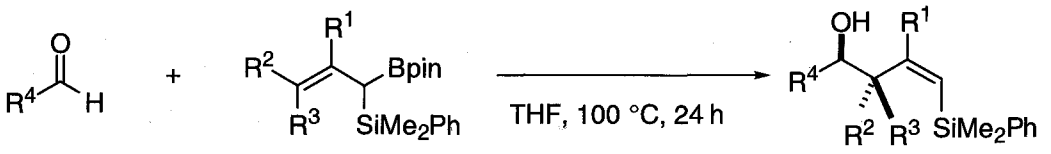
[a] A mixture of an aldehyde (1.0 mol), Me_3SiOBn (1.3 mol), and Me_3SiOTf (1.0 mol) was stired at -78 °C for 6 h and then **2** (1.0 mol) was added at -78 °C. It was stirred for another 15 min. [b] Isolated yields are given. [c] Determined by ^1H NMR of a crude product mixture. [d] A ratios of *E* : *Z*. [e] An *E*/*Z* mixture of **2b** was used (*E* : *Z* = 83 : 17). [f] 88% with Me_3SiOTf (1.0 mol); 73%with Me_3SiOTf (0.1 mol). [g] A ratio of (*E*, *erythro*) : (*E*, *threo*).

Allylation of aldehydes with allylic borane reagents **2a**, **2c** and **2d** was also examined. Results are summarized in Table 6. Both aliphatic and aromatic aldehydes were allylated by **2a** upon heating at 100 °C in the absence of any additive to yield the corresponding alkenylsilanes **4a** and **4b** in moderate to good yields with high *Z*-selectivity (entries 1 and 2).[24] Comparing with the results of pinacol α-trimethylsilyl allylboronate,[7] the selectivity slightly increased due probably to a bulkier dimethylphenylsilyl group. Stereochemically pure (*E*)-2-hexenyl boronate **2c** reacted with benzaldehyde to give **4c** in a (*E*, *threo*)/(*Z*, *threo*) ratio of 7 : 93 (entry 3), whereas (*E*, *erythro*) isomer **4d** was produced by using **2d** with 94% selectivity (entry 4). The stereospecific outcome is in accord with chair-like 6-membered transition states with R being equatorial (Scheme 3) as disclosed before.[6,7]

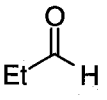
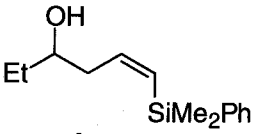
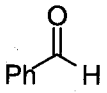
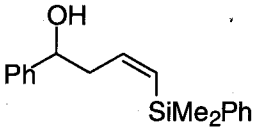
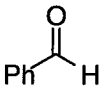
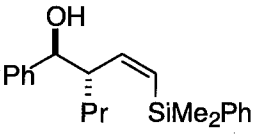
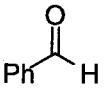
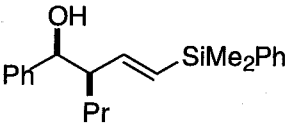


Scheme 3. Transition states for allylation of aldehydes with **2** as allylic boranes.

Table 6. Allylation of aldehydes with **2** as an allylic borane.[a]



2 **4**

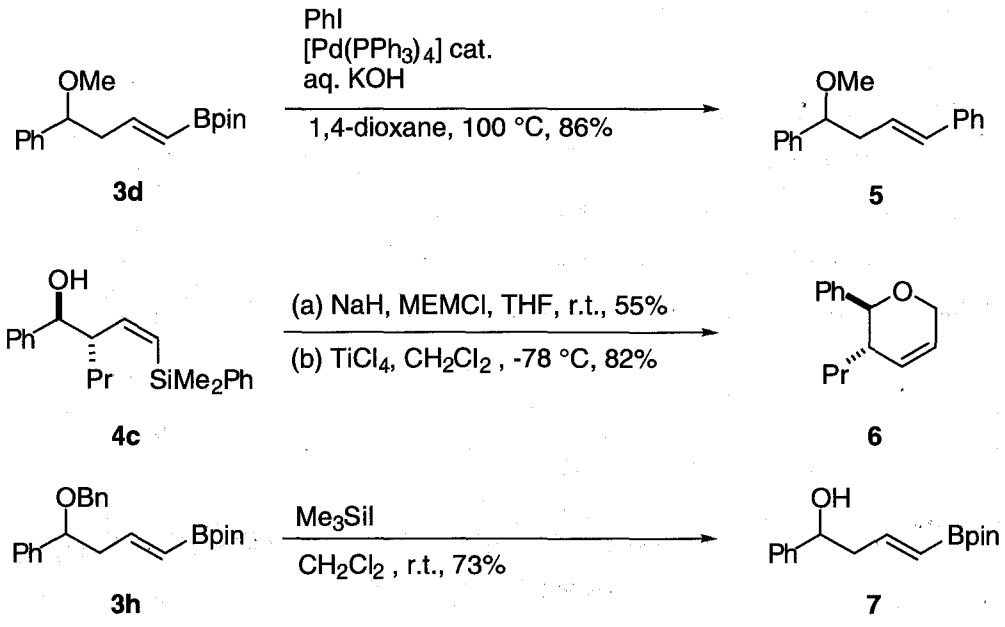
Entry	**2**	Aldehyde	Product	Yield (%)[b]	Isomer ratio[c]
1	**2a**		 **4a**	74 (17)	15 : 85[d]
2	**2a**		 **4b**	89 (0)	9 : 91[d]
3	**2c**		 **4c**	87 (10)	7 : 93[e]
4[f]	**2d**		 **4d**	46 (20)	94 : 6[g]

[a] A solution of **2** (1.0 mol), and an aldehyde (1.1 mol) in THF was stired at 100 °C for 24 h. [b] Isolated yields are given. The values in parentheses are recovery of **2**. [c] Determined by ^{1}H NMR. [d] Ratio of *E* : *Z*. [e] A ratio of (*E, threo*) : (*Z, threo*). [f] Benzaldehyde (3 molar equivalents) were reacted at 65 °C for 45 h. [g] A ratio of (*E, erythro*) : (*Z, threo*).

Further Synthetic Elaborations

Further synthetic elaboration of the allylated products with the aid of the remaining metal functionality in **3** and debenzylation of **3** are illustrated in Scheme 5. The Suzuki-Miyaura coupling[25] of **3d** with iodobenzene gave (*E*)-homoallylic ether **5**, while methylation of **4b** followed by attempted coupling[26] with iodobenzene resulted in protodesilylation to give 1-methoxy-1-phenyl-3-butene. Methoxyethoxymethylation of **4c** with 2-methoxyethoxymethyl chloride (MEMCl) followed by acetal-vinylsilane

cyclization mediated by titanium tetrachloride gave *trans*-6-phenyl-5-propyl-5,6-dihydro-2*H*-pyran (**7**).[27] Debenzylation of **3h** was achieved by treatment with Me_3SiI in good yield with retaining the (*E*)-alkenylboryl moiety.[28]



Scheme 5. Synthetic applications of alkenylmetal produced by allylation.

Conclusion

gem-Silylborylation of α-chloroallyllithiums derived from stereochemically defined allylic chloride using silylborane **1** is demonstrated to constitute a new method for the stereocontrolled synthesis of 1-silyl-1-boryl-2-alkenes **2**. Furthermore, metal selective and stereospecific allylation of aldehydes with **2** was achieved with either the silicon- or boron-functionality and was demonstrated that under appropriate conditions the corresponding adducts are readily converted into substituted (*E*)- or (*Z*)-homoallylic alcohols.

Experimental

Typical Procedure for *gem*-Silylborylation of Allylic Chlorides. 3-(Dimethylphenylsilyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propene (2a). To a solution of allyl chloride (80 μL, 1.00 mmol) and (dimethylphenylsilyl)(pinacolato)borane (**1**) (0.29 g, 1.10 mmol) in THF (3.0 mL) at –98 °C was added a solution of LDA (1.1 mmol) in THF (1 mL). The reaction mixture was stirred for 10 min at –98 °C and then allowed to gradually warm to room temperature. Stirring the solution overnight followed by usual workup gave the crude product. Purification by column chromatography on silica gel (hexane/ethyl acetate 9 : 1) afforded **2a** as a colorless oil (0.27 g, 90% yield). R_f 0.45 (hexane/ethyl acetate 9 : 1). ^{1}H NMR ($CDCl_3$) δ 0.34 (s, 3H), 0.35 (s, 3H), 1.13 (s, 6H), 1.16 (s, 6H), 1.79 (d, *J* = 10.5 Hz, 1H), 4.74 (ddd, *J* = 16.8, 2.2, 0.6 Hz, 1H), 4.78 (dd, *J* = 10.5, 2.2 Hz, 1H), 5.85 (ddd, *J* = 16.8, 10.5, 10.5 Hz, 1H), 7.28-7.38 (m, 3H), 7.48-7.60 (m, 2H). ^{13}C NMR ($CDCl_3$) δ -3.2, -3.2, 24.7, 24.8, 82.8, 112.2, 127.4, 128.8, 133.9, 135.3, 138.0. IR (neat) 2985, 1623, 1374, 1339, 1318, 1145, 839 cm^{-1}. MS *m/z* 303 (M^++1, 1), 302 (M^+, 5), 301 (M^+-1, 1), 284 (M^+-Me, 6), 245 (28), 235 (M^+-Ph, 13), 202 (32), 187 (32), 160 (49), 135 ($PhMe_2Si^+$, 100). Anal. Calcd for $C_{17}H_{27}BO_2Si$: C, 67.55; H, 9.00. Found: C, 67.29; H, 8.92.

3-(Methyldiphenylsilyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propene. Yield: 66%. Colorless oil. R_f 0.47 (hexane/ethyl acetate 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.66 (s, 3H), 1.03 (s, 6H), 1.10 (s, 6H), 2.19 (d, *J* = 10.4 Hz, 1H), 4.82 (dd, *J* = 17.6, 3.2 Hz, 1H), 4.87 (dd, *J* = 9.4, 3.2 Hz, 1H), 5.94 (ddd, *J* = 17.6, 10.4, 9.4 Hz, 1H), 7.33-7.54 (m, 6H), 7.55-7.65 (m, 4H). ^{13}C NMR ($CDCl_3$) δ -4.37, 24.6, 83.0, 113.2, 127.5, 129.1, 134.9, 135.0, 136.2, 136.5. IR (neat) 3049, 2978, 1618, 1427, 1371, 1142, 1116, 849, 698 cm^{-1}. MS *m/z* 365 (M^++1, 1), 364 (M^+, 4), 349 (M^+-Me, 3), 307 (30), 236 (47), 197 (100). HRMS (FAB) Calcd for $C_{22}H_{29}BO_2Si$: M^+ 364.2030. Found: *m/z* 364.2029.

3-Triphenylsilyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propene. Yield: 65%. White solid. Mp 101.4 °C~101.8 °C. R_f 0.54 (hexane/ethyl acetate 10 : 1). ^{1}H NMR ($CDCl_3$) δ 1.01 (s, 6H), 1.07 (s, 6H), 2.57 (d, *J* = 10.6 Hz, 1H), 4.88 (dd, *J* = 10.0, 2.0 Hz, 1H), 4.95 (dd, *J* = 17.6, 2.0 Hz, 1H), 6.02 (ddd, *J* = 17.6, 10.6, 10.0 Hz, 1H), 7.33-7.48 (m, 9H), 7.63-7.70 (m, 6H). ^{13}C NMR ($CDCl_3$) δ 24.6, 83.1, 113.7, 127.5, 129.3, 134.7, 135.3, 136.3. IR (neat) 3068, 2978, 1618, 1427, 1317, 1142, 1109, 849, 698. MS *m/z* 427 (M^++1, 1), 426 (M^+, 4), 411 (M^+-Me, 1), 259 (100), 181 (31). HRMS (FAB) Calcd for $C_{27}H_{31}BO_2Si$: M^+ 426.2186. Found: *m/z* 426.2185.

(*E*) and (*Z*)-1-(Dimethylphenylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-butene (2b). Yield: 86% (*E*/*Z* = 83/17). Colorless oil. R_f 0.44 (hexane/ethyl acetate 9 :

1). ^{1}H NMR ($CDCl_3$) (*E*-**2b**): δ 0.35 (s, 3H), 0.37 (s, 3H), 1.15 (s, 6H), 1.18 (s, 6H), 1.63 (dd, *J* = 6.3, 1.5 Hz, 3H), 1.70 (d, *J* = 10.0 Hz, 1H), 5.15 (dq, *J* = 15.1, 6.3 Hz, 1H), 5.51 (ddq, *J* = 15.1, 10.1, 1.5 Hz, 1H), 7.28-7.38 (m, 3H), 7.48-7.60 (m, 2H). (*Z*-**2b**) (assignable peaks): δ = 0.37 (s, 3H), 0.39 (s, 3H), 1.38 (dd, *J* = 6.6, 1.6 Hz, 3H), 2.05 (d, *J* = 11.4 Hz, 1H). ^{13}C NMR ($CDCl_3$) (*E*-**2b**): δ -3.1, -3.1, 18.1, 24.8, 82.7, 122.8, 126.9, 127.3, 128.7, 134.0, 138.5. IR (neat) 2978, 2989, 1655, 1641, 1589, 1371, 1348, 1313, 1252, 1144, 1113, 833, 793, 731, 698 cm^{-1}. MS *m/z* 317 (M^++1, 2.6), 316 (M^+, 9.8), 301 (M^+-Me, 4.3), 216 (89), 174 (100), 135 ($PhMe_2Si^+$, 87). Anal. Calcd for $C_{18}H_{29}BO_2Si$: C, 68.35; H, 9.24. Found: C, 68.60; H, 9.10. The isomer ratio was determined on the basis of integration of the following signals in ^{1}H NMR spectra : (*E*)-**2b**: δ 1.63 (dd, *J* = 6.3, 1.5 Hz); (*Z*)-**2b**: δ 1.38 (dd, *J* = 6.6, 1.6 Hz).

(*E*)-1-(Dimethylphenylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-hexene (2c). Yield: 75%. Colorless oil. R_f 0.45 (hexane/ethyl acetate 9 : 1). ^{1}H NMR ($CDCl_3$) δ 0.34 (s, 3H), 0.35 (s, 3H), 0.83 (t, *J* = 7.3 Hz, 3H), 1.14 (s, 6H), 1.17 (s, 6H), 1.30 (m, 2H), 1.69 (d, *J* = 10.2 Hz, 1H), 1.93 (q, *J* = 7.0 Hz, 2H), 5.12 (dt, *J* = 15.0, 6.8 Hz, 1H), 5.46 (ddt, *J* = 15.1, 10.1, 1.2 Hz, 1H), 7.28-7.40 (m, 3H), 7.48-7.60 (m, 2H). ^{13}C NMR ($CDCl_3$) δ -3.2, -3.0, 13.6, 23.1, 24.8, 24.9, 35.0, 82.8, 126.0, 127.4, 128.5, 128.8, 134.0, 138.5. IR (neat) 2980, 2960, 1650, 1379, 1372, 1356, 1316, 1248, 1143, 850, 837, 700 cm^{-1}. MS *m/z* 345 (M^++1, 3.0), 344 (M^+, 9.0), 244 (61), 202 (100), 135 ($PhMe_2Si^+$, 89). Anal. Calcd for $C_{20}H_{33}BO_2Si$: C, 69.75; H, 9.66. Found: C, 69.51; H, 9.80.

(*Z*)-1-(Dimethylphenylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-hexene (2d). Yield: 79%. Colorless oil. R_f 0.44 (hexane/ethyl acetate 9 : 1). ^{1}H NMR ($CDCl_3$) δ 0.34 (s, 3H), 0.35 (s, 3H), 0.80 (t, *J* = 7.3 Hz, 3H), 1.13 (s, 6H), 1.16 (s, 6H), 1.10-1.30 (m, 2H, overlap), 1.58-1.97 (m, 2H), 2.01 (d, *J* = 11.8 Hz, 1H), 5.20 (dt, *J* = 10.6, 7.2 Hz, 1H), 5.49 (ddt, *J* = 11.6, 10.8, 1.6 Hz, 1H), 7.28-7.42 (m, 3H), 7.48-7.62 (m, 2H). ^{13}C NMR ($CDCl_3$) δ -3.1, -3.0, 13.8, 22.6, 24.8, 29.1, 82.8, 125.6, 126.8, 127.4, 128.8, 133.9, 138.4. IR (neat) 2980, 2960, 1639, 1370, 1334, 1310, 1248, 1143, 1113, 850, 836, 699 cm^{-1}. MS *m/z* 345 (M^++1, 1.9), 344 (M^+, 6.7), 329 (M^+-Me, 4.2), 244 (56), 202 (97), 135 ($PhMe_2Si^+$, 100). Anal. Calcd for $C_{20}H_{33}BO_2Si$: C, 69.75; H, 9.66. Found: C, 69.81; H, 9.42.

(*E*)-3-(Dimethylphenylsilyl)-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propene (2e). Yield: 75%. White solid. Mp 74.5 °C~75.5 °C. R_f 0.36 (hexane/ethyl acetate 9 : 1). ^{1}H NMR ($CDCl_3$) δ 0.37 (s, 3H), 0.40 (s, 3H), 1.12 (s, 6H), 1.16 (s, 6H), 1.92 (d, *J* = 10.4 Hz, 1H), 6.08 (d, *J* = 15.8 Hz, 1H), 6.32 (dd, *J* = 15.7, 10.5 Hz, 1H), 7.04-7.17 (m, 1H), 7.17-7.27 (m, 4H), 7.27-7.38 (m, 3H), 7.46-7.60 (m, 2H). ^{13}C NMR ($CDCl_3$) δ -3.1, -3.0, 24.8, 24.9, 83.0, 125.5, 125.9, 127.5, 127.7, 128.3, 128.4, 129.0, 134.0, 137.9, 138.6. IR

(Nujol) 1637, 1598, 1350, 1318, 1302, 1265, 1249, 1139, 1111, 813 cm^{-1}. MS *m/z* 379 (M^++1, 1.2), 378 (M^+, 4.2), 236 (43), 200 (100), 135 ($PhMe_2Si^+$, 97). Anal. Calcd for $C_{23}H_{31}BO_2Si$: C, 73.01; H, 8.26. Found: C, 72.77; H, 8.18.

1-(Dimethylphenylsilyl)-3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-butene (2f). Yield: 72%. Colorless oil. R_f 0.45 (hexane/ethyl acetate 9 : 1). ^1H NMR ($CDCl_3$) δ 0.33 (s, 3H), 0.37 (s, 3H), 1.15 (s, 6H), 1.18 (s, 6H), 1.30 (d, *J* = 1.0 Hz, 3H), 1.67 (d, *J* = 1.2 Hz, 3H), 1.86 (d, *J* = 11.4 Hz, 1H), 5.27 (dt, *J* = 11.4, 1.1 Hz, 1H), 7.28-7.40 (m, 3H), 7.46-7.62 (m, 2H). ^{13}C NMR ($CDCl_3$) δ -3.0, -3.0, 24.8, 24.9, 25.8, 82.8, 120.0, 127.3, 128.1, 128.7, 134.0, 138.7. IR (neat) 2980, 1660, 1590, 1358, 1327, 1310, 1142, 1112, 837, 820, 699 cm^{-1}. MS *m/z* 331 (M^++1, 1.3), 330 (M^+, 4.3), 315 (M^+-Me, 2.5), 230 (61), 188 (100), 152 (16), 135 ($PhMe_2Si^+$, 48). Anal. Calcd for $C_{19}H_{31}BO_2Si$: C, 69.08; H, 9.46. Found: C, 69.26; H, 9.39.

3-(Dimethylphenylsilyl)-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propene (2g). Yield: 73%. Colorless oil. R_f 0.48 (hexane/ethyl acetate 9 : 1). ^1H NMR ($CDCl_3$) δ 0.37 (s, 3H), 0.39 (s, 3H), 1.14 (s, 6H), 1.18 (s, 6H), 1.61 (s, 3H), 4.64 (s, 2H), 7.28-7.42 (m, 3H), 7.50-7.62 (m, 2H). ^{13}C NMR ($CDCl_3$) δ -2.7, 24.7, 24.9, 26.5, 82.8, 109.2, 127.4, 128.8, 134.0, 138.9, 143.3. IR (neat) 2977, 1628, 1369, 1330, 1310, 1259, 1141, 1110, 699 cm^{-1}. MS *m/z* 317 (M^++1, 0.1), 316 (M^+, 0.4), 315 (M^+-1, 0.2), 301 (M^+-Me, 4.6), 259 (41), 225 (21), 216 (25), 201 (96), 174 (29), 159 (15), 135 ($PhMe_2Si^+$, 100). Anal. Calcd for $C_{18}H_{29}BO_2Si$: C, 68.35; H, 9.24. Found: C, 68.57; H, 9.36.

3-(Dimethylphenylsilyl)-2-(trimethylsilyl)methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propene (2h). Yield: 80%. Pale yellow oil. R_f 0.48 (hexane/ethyl acetate 9 : 1). ^1H NMR ($CDCl_3$) δ 0.0 (s, 9H), 0.36 (s, 3H), 0.38 (s, 3H), 1.04 (d, *J* = 13.4 Hz, 1H), 1.13 (s, 6H), 1.16 (s, 6H), 1.37 (s, 1H), 1.48 (d, *J* = 13.6 Hz, 1H), 4.50 (s, 1H), 4.67 (d, *J* = 2.0 Hz, 1H), 7.26-7.42 (m, 3H), 7.50-7.62 (m, 2H). ^{13}C NMR ($CDCl_3$) δ -3.0, -2.8, -1.2, 24.7, 24.9, 32.1, 82.8, 106.5, 127.4, 128.8, 134.0, 139.0, 143.9. IR (neat)2977, 2952, 1615, 1338, 1311, 1247, 1142, 1111, 852, 699 cm^{-1}. MS *m/z* 390 (M^++2, 0.5), 389 (M^++1, 1.1), 388 (M^+, 3.1), 373 (M^+-Me, 11), 331 (18), 297 (43), 273 (34), 200 (37), 135 ($PhMe_2Si^+$, 100), 84 (41). Anal. Calcd for $C_{21}H_{37}BO_2Si_2$: C, 64.92; H, 9.60. Found: C, 64.74; H, 9.34.

(*E*)-3-(Dimethylphenylsilyl)-1,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propene (2i). Yield: 21%. Colorless oil. R_f 0.33 (hexane/ethyl acetate 10 : 1). ^1H NMR ($CDCl_3$) δ 0.33 (s, 3H), 0.36 (s, 3H), 1.08 (s, 6H), 1.12 (s, 6H), 1.24 (s, 12H), 1.97 (d, *J* = 10.4 Hz, 1H), 5.16 (d, *J* = 17.8 Hz, 1H), 6.73 (dd, *J* = 10.4, 17.8 Hz, 1H) 7.27-7.34 (m, 3H), 7.47-7.53 (m, 2H). ^{13}C NMR ($CDCl_3$) δ -3.2, -3.0, 24.6, 24.8, 24.9, 82.5, 82.9, 127.4, 129.0,

134.0, 134.6, 137.8, 152.2. IR (neat) 2978, 1616, 1312, 1248, 1146, 1113, 1005, 970, 854, 841, 812, 698 cm^{-1}. MS *m/z* 413 (M^+-Me, 9), 328 (61), 250 (37), 168 (100) 135 ($PhMe_2Si^+$, 100). HRMS (FAB) Calcd for $C_{22}H_{35}B_2O_4Si$: M^+-Me 413.2491. Found: *m/z* 413.2495.

General Procedure for Allylation of Acetals with 2a and Titanium Tetrachloride. (*E*)-4-Methoxy-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-pentene (3a). To a solution of **2a** (0.172 g, 0.55 mmol) and acetaldehyde dimethylacetal (0.116 mL, 1.10 mmol) in CH_2Cl_2 (6 mL) was added a solution of $TiCl_4$ in CH_2Cl_2 (1.00 M, 0.82 mL, 0.82 mmol) at –78 °C. The solution was stirred for 15 min at –78 °C before quenching with water (0.50 mL) at –78 °C. The mixture was warmed up to room temperature, dried over anhydrous $MgSO_4$, and filtered. The filtrate was concentrated to give a crude product consisting of *E*/*Z* = 94 : 6 as revealed by ^1H NMR spectra. Purification by silica gel column chromatography (hexane/ethyl acetate = 2 : 1) afforded (*E*)-**3a** (97 mg, 78% yield) and (*Z*)-**3a** (4.1 mg, 3% yield). R_f 0.53 (hexane/ethyl acetate 2 : 1). ^1H NMR ($CDCl_3$) δ 1.15 (d, *J* = 6.0 Hz, 3H), 1.27 (s, 12H), 2.27 (ddt, *J* = 14.4, 6.7, 1.4 Hz, 1H), 2.44 (ddt, *J* = 14.4, 6.4, 1.5 Hz, 1H), 3.32 (s, 3H), 3.42 (m, 1H), 5.50 (dt, *J* = 18.2, 1.5 Hz, 1H), 6.60 (dt, *J* = 18.0, 6.6 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 19.1, 24.8, 42.6, 56.0, 75.9, 83.1, 150.3. IR (neat) 2980, 2935, 1640, 1362, 1321, 1146, 998, 972, 852 cm^{-1}. MS *m/z* 225 (M^+-1, 0.6), 211 (M^+-Me, 17), 111 (8.9), 101 (8.0), 95 (7.5), 59 (100). Anal. Calcd for $C_{12}H_{23}BO_3$: C, 63.74; H, 10.25. Found: C, 63.62; H, 10.41. Data for (*Z*)-**3a**: Yield: 3% R_f 0.58 (hexane/ethyl acetate 2 : 1). ^1H NMR ($CDCl_3$) δ 1.15 (d, *J* = 6.2 Hz, 3H), 1.27 (s, 12H), 2.46-2.78 (m, 2H), 3.35 (s, 3H), 3.38 (m, 1H), 5.46 (dt, *J* = 13.6, 1.3 Hz, 1H), 6.47 (dt, *J* = 13.8, 7.0 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 19.0, 24.8, 24.9, 38.1, 56.0, 76.9, 82.9, 150.6. MS *m/z* 226 (M^+, 0.03), 211 (M^+-Me, 1.0), 195 (M^+-OMe, 0.6), 110 (15), 95 (13), 59 ($MeCHOMe^+$, 100). The isomer ratio was determined from the integration ration of signals in ^1H NMR spectra of the crude product mixture: (*E*)-**3a** δ 3.32 (s, 3H); (*Z*)-**3a** δ 3.35 (s, 3H).

(*E*)-4-Methoxy-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-hexene (3b). Yield: 77%. Colorless oil. R_f 0.43 (hexane/ethyl acetate 4 : 1). ^1H NMR ($CDCl_3$) δ 0.90 (t, *J* = 7.3 Hz, 3H), 1.27 (s, 12H), 1.42-1.62 (m, 2H), 2.37 (m, 2H), 3.21 (m, 1H), 3.34 (s, 3H), 5.50 (dt, *J* = 18.0, 1.4 Hz, 1H), 6.62 (dt, *J* = 18.0, 6.9 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 9.3, 24.7, 25.9, 39.3, 56.4, 81.0, 83.0, 150.3. IR (neat) 2977, 2930, 1638, 1399, 1360, 1320, 1145, 1088, 1000, 971, 849 cm^{-1}. MS *m/z* 239 (M^+-1, 0.6), 225 (M^+-Me, 20), 211 (M^+-Et, 8.6), 111 (25), 101 (9.9), 83 (13), 73 ($EtCHOMe^+$, 100). Anal. Calcd for $C_{13}H_{25}BO_3$: C, 65.02; H, 10.49. Found: C, 64.74; H, 10.23. Data of (*Z*)-**3b**: Yield: 5%. R_f 0.49 (hexane/ethyl acetate 4 : 1). ^1H NMR ($CDCl_3$) δ 0.91 (t, *J* = 7.5 Hz, 3H), 1.27 (s, 12H), 1.51 (m, 2H), 2.64 (t, *J* = 6.6 Hz, 2H), 3.17 (m, 1H), 3.36 (s, 3H), 5.44 (d, *J* = 13.8 Hz, 1H), 6.49 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 9.5, 24.9, 26.1, 35.3, 56.5, 82.3, 82.9, 150.9. MS *m/z* 239 (M^+-1, 0.1), 225

(M^+-Me, 4.3), 211 (M^+-Et, 5.8), 193 (25), 124 (76), 111 (67), 101 (51), 95 (68), 83 (49), 73 ($EtCHOMe^+$, 100).

(*E*)-4-Ethoxy-5-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-hexene (3c). Yield: 85% (*E* only). Colorless oil. R_f 0.28 (hexane/ethyl acetate 9 : 1). ^1H NMR ($CDCl_3$) δ 0.88 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H), 1.26 (s, 12H), 1.78 (m, 1H), 2.35 (tt, *J* = 6.4, 1.4 Hz, 2H), 3.07 (q, *J* = 5.8 Hz, 1H), 3.43 (dq, *J* = 9.2, 7.0 Hz, 1H), 3.56 (dq, *J* = 9.2, 7.0 Hz, 1H), 5.49 (dt, *J* = 18.0, 1.4 Hz, 1H), 6.66 (dt, *J* = 17.8, 6.8 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 15.6, 18.0, 18.6, 24.8, 31.0, 37.7, 65.2, 83.0, 83.7, 151.3. IR (neat) 2980, 2935, 2872, 1639, 1400, 1361, 1321, 1265, 1147, 1111, 1002, 973, 850 cm^{-1}. MS *m/z* 267 (M^+-1, 0.4), 253 (M^+-Me, 15), 225 (M^+-$CHMe_2$, 25), 101 ($Me_2CHCHOEt^+$, 100), 73 (81). Anal. Calcd for $C_{15}H_{29}BO_3$: C, 67.17; H, 10.90. Found: C, 67.41; H, 11.20.

(*E*)-4-Methoxy-4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-butene (3d). 69% (*E* only). Colorless oil. R_f 0.43 (hexane/ethyl acetate 4 : 1). ^1H NMR ($CDCl_3$) δ 1.26 (s, 12H), 2.71 (dddd, *J* = 15.2, 6.4, 5.0, 1.6 Hz, 1H), 2.67 (dddd, *J* = 15.2, 8.3, 6.7, 1.7 Hz, 1H), 3.21 (s, 3H), 4.23 (dd, *J* = 8.2, 5.0 Hz, 1H), 5.50 (dt, *J* = 17.9, 1.6 Hz, 1H), 6.63 (dt, *J* = 18.0, 6.4 Hz, 1H), 7.25-7.40 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 24.8, 44.6, 56.7, 82.9, 83.1, 126.6, 127.6, 128.4, 141.73, 150.2. IR (neat) 2980, 2935, 2823, 1639, 1450, 1361, 1320, 1144, 1105, 971, 851, 759, 701 cm^{-1}. MS *m/z* 287 (M^+-1, 0.2), 273 (M^+-Me, 13), 122 (47), 121 ($PhCHOMe^+$, 100), 105 (12), 91 (24), 77 (29). Anal. Calcd for $C_{17}H_{25}BO_3$: C, 70.85; H, 8.74. Found: C, 70.99; H, 8.94. The isomer ratio was determined based on the integral value of the distinguishable signals in ^1H NMR spectra of the crude product mixture: (*E*)-**3d** δ 3.21 (s, 3H); (*Z*)-**3d** δ 3.24 (s, 3H).

(*E*)-4-Methoxy-(4,4,5,5-tetramethyl-1,3,2-dioxaborola-2-yl)-1,5-hexadiene (3e). Yield: 62%. Colorless oil. R_f 0.24 (hexane/ethyl acetate 9 : 1). ^1H NMR ($CDCl_3$) δ 1.25 (s, 12H), 2.41 (m, 2H), 3.27 (s, 3H), 3.61 (d, *J* = 6.8 Hz, 1H), 3.68 (d, *J* = 6.8 Hz, 1H), 5.17 (ddd, *J* = 4.2, 1.8, 0.8 Hz, 1H), 5.24 (dd, *J* = 2.0, 0.6 Hz, 1H), 5.49 (dt, *J* = 18.0, 1.4 Hz, 1H), 5.68 (dd, *J* = 18.0, 7.4 Hz, 1H), 6.59 (dt, *J* = 18.0, 6.8 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 24.7, 41.9, 56.1, 81.7, 83.1, 117.4, 117.4, 138.0, 149.7. IR (neat) 3209, 3080, 2980, 2928, 1639, 1398, 1364, 1146, 1101, 1043, 851 cm^{-1}. MS *m/z* 238 (M^+, 1.5), 223 (M^+-Me, 18), 71(100). Anal. Calcd for $C_{13}H_{23}BO_3$: C, 65.57; H, 9.74. Found: C, 65.70; H, 10.02.

(*E*)-4-Methoxy-3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-pentene (3f). Yield: 81% as a diastereomeric mixture (*E, erythro*/*E, threo*/others = 73 : 24 : 3). Colorless oil. R_f 0.38 (hexane/ethyl acetate 4 : 1). *(E, erythro) isomer*: ^1H NMR ($CDCl_3$) δ 1.03 (d, *J* = 6.8 Hz, 3H), 1.08 (d, *J* = 6.2 Hz, 3H), 1.27 (s, 12H), 2.41 (m, *J* = 6.6 Hz, 1H), 3.20 (m, *J* =

6.2 Hz, 1H), 3.33 (s, 3H), 5.46 (d, J = 18.2 Hz, 1H), 6.60 (dd, J = 18.2, 7.1 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 15.1, 16.1, 24.7, 44.2, 56.2, 80.0, 82.8, 155.5. *(E, threo) isomer* (assignable peaks): ^1H NMR ($CDCl_3$) δ 3.32 (s, 3H), 6.59 (dd, J = 18.1, 6.7 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 13.5, 15.2, 43.4, 79.7, 155.5. IR (neat) 2978, 2932, 1638, 1362, 1321, 1269, 1213, 1148, 1099, 1001, 970, 851 cm^{-1}. MS *m/z* 225 (M^+-Me, 7.3), 182 (2.2), 109 (3.7), 101 (6.7), 82 (16), 67 (6.4), 56 ($MeCHOMe^+$, 100). Anal. Calcd for $C_{17}H_{25}BO_3$: C, 65.02; H, 10.49. Found: C, 65.09; H, 10.71. The ratio of *E*- and *Z*-isomers was determined by ^1H NMR. The isomer ratio of *E*-isomers was determined by GC analysis (column: OV-1701 bonded 0.25 mmϕ x 25 m, column temperature: 120 °C constant): (*E, erythro*) R_t = 11.2 min; (*E, threo*) R_t = 10.8 min.

General Procedure for Allylation of Aldehyde with 2a, Trimethylsilyl trifluoromethanesulfonate, and Benzyl trimethylsilyl ether. (*E*)- 4-Benzyloxy-6-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-hexene (3g). To a solution of benzyl trimethylsilyl ether (47 μL, 0.24 mmol) and 3-phenylpropanal (25 μL, 0.192 mmol) in CH_2Cl_2 (2 mL) was added trimethylsilyl trifluoromethanesulfonate (TMSOTf) (34 μL, 0.193 mmol) at –78 °C. The solution was stirred at –78 °C for 6 h before the addition of **2a** (57 mg; 0.189 mmol) at –78 °C. The resulting mixture was stirred at –78 °C for 12 h and then quenched with water (0.5 mL) at –78 °C. The organic layer was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Purification by silica gel column chromatography (hexane/ethyl acetate = 10 : 1) afforded **3g** as a colorless oil (63 mg, 85% yield). R_f 0.30 (hexane/ethyl acetate 9 : 1). ^1H NMR ($CDCl_3$) δ 1.26 (s, 12H), 1.85 (m, 2H), 2.49 (m, 2H), 2.69 (m, 2H), 3.53 (m, 1H), 4.46 (d, J = 11.4 Hz, 1H), 4.60 (d, J = 11.4 Hz, 1H), 5.52 (dt, J = 18.0, 1.4 Hz, 1H), 6.64 (dt, J = 18.0, 7.0 Hz, 1H), 7.19-7.40 (m, 10H). ^{13}C NMR ($CDCl_3$) δ 24.8, 31.7, 35.8, 40.4, 70.8, 77.2, 83.1, 125.7, 126.1, 127.5, 127.8, 128.3, 128.4, 129.1, 138.7, 142.2, 150.1. IR (neat) 3062, 3027, 2929, 1638, 1362, 1143, 908, 698 cm^{-1}. MS *m/z* 377 (M^+-Me, 7.2), 117 (93), 91(100). Anal. Calcd for $C_{25}H_{33}BO_3$: C, 76.53; H, 8.48. Found: C, 76.78; H, 8.51.

(*E*)- 4-Benzyloxy-4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-butene (3h). Yield: 88%. Colorless oil. R_f 0.30 (hexane/ethyl acetate 9 : 1). ^1H NMR ($CDCl_3$) δ 1.26 (s, 12H), 2.62 (m, 2H), 4.27 (d, J = 11.8 Hz, 1H), 4.41 (dd, J = 8.0, 5.4 Hz, 1H), 4.45 (d, J = 11.8 Hz, 1H), 5.49 (dt, J = 18.0, 1.4 Hz, 1H), 6.64 (dt, J = 18.0, 6.6 Hz, 1H), 7.29-7.45 (m, 10H). ^{13}C NMR ($CDCl_3$) δ 24.7, 44.7, 70.2, 80.6, 83.0, 126.8, 127.4, 127.6, 127.7, 127.9, 128.2, 128.4, 138.5, 141.8, 150.3. IR (neat) 3062, 3028, 2978, 1638, 1495, 1362, 1323, 1143, 1094, 1070, 910, 700 cm^{-1}. MS *m/z* 349 (M^+-Me, 2.6), 197 (29), 91(100). Anal. Calcd for $C_{23}H_{29}BO_3$: C, 75.83; H, 8.02. Found: C, 75.59; H, 7.76.

(*E*)-4-Benzyloxy-3-methyl-4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-

butene (3i). Yield: 81% as a diastereomeric mixture (*E, erythro/ E, threo* = 84 : 16). Colorless oil. R_f 0.33 (hexane/ethyl acetate 9 : 1). *(E, erythro) isomer*: ^{1}H NMR ($CDCl_3$) δ 1.09 (d, *J* = 6.8 Hz, 3H), 1.24 (s, 12H), 2.62 (m, 1H), 4.25 (d, *J* = 12.2 Hz, 1H), 4.25 (d, *J* = 6.0 Hz, 1H), 4.50 (d, *J* = 12.2 Hz, 1H), 5.34 (d, *J* = 18.0 Hz, 1H), 6.57 (dd, *J* = 18.0, 6.0 Hz, 1H), 7.26-7.61 (m, 10H). ^{13}C NMR ($CDCl_3$) δ 14.6, 24.7, 46.4, 70.5, 82.9, 84.4, 127.3, 127.4, 127.5, 127.6, 127.7, 128.0, 128.2, 138.6, 140.5, 155.9. *(E, threo) isomer*: ^{1}H NMR ($CDCl_3$) δ 0.81 (d, *J* = 6.8 Hz, 3H), 1.29 (s, 12H), 2.84 (m, 1H), 4.12 (d, *J* = 7.8 Hz, 1H), 4.13 (d, *J* = 7.0 Hz, 1H), 4.20 (d, *J* = 7.8 Hz, 1H), 5.48 (d, *J* = 18.0 Hz, 1H), 6.77 (d, *J* = 18.0 Hz, 1H). 7.26-7.61 (m, 10H). ^{13}C NMR ($CDCl_3$) δ 16.0, 24.8, 46.1, 70.3, 77.2, 85.2, 126.3, 126.5, 126.7, 127.0,127.0, 128.3, 128.4, 139.2, 140.4, 156.8. IR (neat) 3063, 3028, 2976, 2930, 1638, 1360, 1321, 1146, 1067, 970, 700 cm^{-1}. MS *m/z* 363 (M^+-Me, 2.7), 197 (32), 91 (100). Anal. Calcd for $C_{24}H_{31}BO_3$: C, 76.20; H, 8.26. Found: C, 76.45; H, 8.08. The isomer ratio was determined by GC analysis (column: OV-1701 bonded 0.25 mmϕ x 25 m, column temperature: 200 °C constant): (*E, erythro*) R_t = 14.1 min; (*E, threo*) R_t = 14.6 min.

***erythro*-(*E*)-3-[Benzyloxy(phenyl)methyl]-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-hexene (3j).** Yield: 83%. Colorless oil. R_f 0.33 (hexane/ethyl acetate 9 : 1). ^{1}H NMR ($CDCl_3$) δ 0.81 (t, *J* = 7.2 Hz, 3H), 1.24 (s, 12H), 1.40 (m, 2H), 1.67 (m, 2H), 2.47 (m, 1H), 4.26 (d, *J* = 11.8 Hz, 1H), 4.28 (d, *J* = 6.4 Hz, 1H), 4.50 (d, *J* = 11.8 Hz, 1H), 5.25 (dd, *J* = 18.0, 0.8 Hz, 1H), 7.24-7.38 (m, 10H). ^{13}C NMR ($CDCl_3$) δ 14.1, 20.3, 24.6, 31.3, 53.0, 70.5, 82.9, 84.0, 127.3, 127.5, 127.6, 127.7, 127.9, 128.1, 128.2, 138.6, 140.6, 154.6. IR (neat) 3063, 3028, 2976, 2930, 2870, 1638, 1364, 1146, 1067, 897, 700 cm^{-1}. MS *m/z* 391 (M^+-Me, 2.0), 197 (33), 91 (100). The isomer ratio was determined by GC analysis (column: OV-1701 bonded 0.25 mmϕ x 25 m, column temperature: 220 °C constant): (*E, erythro*) R_t = 17.8 min; (*E, threo*) R_t = 18.4 min.

***threo*-(*E*)-3-[Benzyloxy(phenyl)methyl]-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-hexene (3k).** Yield: 94%. Colorless oil. R_f 0.27 (hexane/ethyl acetate 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.76 (t, *J* = 7.0 Hz, 3H), 1.18 (m, 4H), 1.27 (s, 12H), 2.51 (m, 1H), 4.21 (d, *J* = 12.2 Hz, 1H), 4.21 (d, *J* = 7.6 Hz, 1H), 4.47 (d, *J* = 12.2 Hz, 1H), 5.44 (dd, *J* = 18.8, 1.0 Hz, 1H), 6.54 (dd, *J* = 18.8, 8.8 Hz, 1H), 7.24-7.48 (m, 10H). ^{13}C NMR ($CDCl_3$) δ 13.9, 20.1, 24.8, 32.3, 52.7, 70.3, 82.9, 84.2, 127.2, 127.3, 127.6, 127.7, 127.9, 128.1, 128.1, 138.7, 140.6, 155.4. IR (neat) 3063, 3028, 2976, 2959, 2931, 2870, 1638, 1454, 1367, 1321, 1146, 1094, 999, 849, 700 cm^{-1}. MS *m/z* 391 (M^+-Me, 7.0), 197 (89), 91 (100). The isomer ratio was determined by GC analysis (column: OV-1701 bonded 0.25 mmϕ x 25 m, column temperature: 220 °C constant): (*E, erythro*) R_t = 17.8 min; (*E, threo*) R_t = 18.4 min.

(*E*)-4-Benzyloxy-2-methyl-4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-butene (3l). Yield: 70%. Colorless oil. R_f 0.33 (hexane/ethyl acetate 9 : 1). ^{1}H NMR ($CDCl_3$) δ 1.26 (s, 12H), 1.96 (s, 3H), 2.42 (dd, *J* = 14.4, 5.0 Hz, 1H), 2.68 (dd, *J* = 14.4, 8.4 Hz, 1H), 4.26 (d, *J* = 11.6 Hz, 1H), 4.44 (d, *J* =11.6 Hz, 1H), 4.51 (dd, *J* = 8.6, 4.8 Hz, 1H), 7.19-7.42 (m, 10H). ^{13}C NMR ($CDCl_3$) δ 21.8, 24.8, 50.9, 70.3, 80.5, 82.6, 126.0, 126.7, 127.6, 127.6, 127.6, 128.2, 128.4, 138.5, 142.3, 159.3. IR (neat) 3063, 3030, 2978, 2930, 1638, 1495, 1369, 1319, 1265, 1144, 1105, 1070, 853, 698 cm^{-1}. MS *m/z* 363 (M^+-Me, 1.4), 197 (27), 91 (100). Anal. Calcd for $C_{24}H_{31}BO_3$: C, 76.20; H, 8.26. Found: C, 76.08; H, 8.07.

General Procedure for Allylation of Aldehydes upon Heating. (*Z*)-4-(Dimethylphenylsilyl)-1-ethyl-3-buten-1-ol (4a). A solution of **2a** (0.130 g, 0.42 mmol) and propionaldehyde (33 μL, 0.46 mmol) in THF (4 mL) was stirred at 100 °C (oil bath) for 24 h. Ethanol amine (42 μL) was added to the reaction mixture at room temperature, and the resulting milky suspension was stirred for 30 min. Filtration of insoluble materials followed by concentration of the filtrate gave a crude product whose ^{1}H NMR spectra provided isomeric ratio of *E*/*Z* = 15 : 85. Purification by silica gel column chromatography (hexane/ethyl acetate 2 : 1) gave **4a** as a colorless oil (0.113 g, 74% yield, *E*/*Z* = 14/86). R_f 0.27 (hexane / ethyl acetate 4 : 1). ^{1}H NMR ($CDCl_3$) δ 0.42 (s, 3H), 0.43 (s, 3H), 0.88 (t, *J* = 7.4 Hz, 3H), 1.30-1.60 (m, 2H), 2.10-2.40 (m, 2H), 3.51 (tt, *J* = 7.0, 5.1 Hz, 1H), 5.85 (dt, *J* = 14.0, 1.3 Hz, 1H), 6.50 (dt, *J* = 14.0, 7.6 Hz, 1H), 7.30-7.50 (m, 3H), 7.50-7.70 (m, 2H). ^{13}C NMR ($CDCl_3$) δ -0.9, -0.9, 9.9, 29.7, 40.8, 72.6, 127.8, 128.9, 130.3, 133.7, 139.4, 146.3. IR (neat) 3350 (br), 2958, 1601, 1425, 1247, 1110, 810, 778, 728, 699 cm^{-1}. MS *m/z* 233 (M^+-1, 0.04), 219 (M^+-Me, 5.8), 201 (M^+-Me-H_2O, 8.7), 161 (29), 145 (17), 137 (45), 135 ($PhMe_2Si^+$, 100), 121 (23), 98 (41), 75 (28), 59 ($EtCHOH^+$, 29). Anal. Calcd for $C_{14}H_{22}OSi$: C, 71.73; H, 9.46. Found: C, 72.01; H, 9.67. The isomer ratio of the purified products was determined from the ^{1}H NMR spectra: *E* / *Z* = 15 /85, being obtained from the area ratio of δ 6.16 (ddd, *J* = 18.7, 7.1, 6.0 Hz),/ δ 6.50 (dt, *J* = 14.0, 7.6 Hz).

(*Z*)-4-(Dimethylphenylsilyl)-1-phenyl-3-buten-1-ol (4b). Yield: 89% (*E*/*Z* = 9/91). Colorless oil. R_f 0.31 (hexane/ethyl acetate 4 : 1). ^{1}H NMR ($CDCl_3$) δ 0.38 (s, 6H), 1.77 (brs, 1H), 2.35-2.65 (m, 2H), 4.64 (dd, *J* = 7.4, 5.6 Hz, 1H), 5.85 (dt, *J* = 13.9, 1.3 Hz, 1H), 6.46 (dt, *J* = 13.9, 7.4 Hz, 1H), 7.16-7.42 (m, 8H), 7.48-7.58 (m, 2H). ^{13}C NMR ($CDCl_3$) δ -1.0, 1.0, 43.0, 73.6, 125.7, 127.4, 127.8, 128.3, 128.9, 130.6, 133.7, 139.3, 143.8, 145.6. IR (neat) 3400 (br), 3070, 3035, 2965, 2900, 1608, 1428, 1250, 1114, 1053, 822 cm^{-1}. MS *m/z* 283 (M^++1, 0.3), 282 (M^+, 0.5), 281 (M^+-1, 1.9), 264 (M^+-H_2O, 13), 249 (M^+-H_2O-Me, 16), 241 (34), 173 (52), 145 (36), 135 ($PhMe_2Si^+$, 91), 121 (47), 107 ($PhCHOH^+$, 100). Anal. Calcd for $C_{18}H_{22}OSi$: C, 76.54; H, 7.85. Found: C, 76.82; H, 7.88. The isomer ratio was

determined from the integral value of the distinguishable signals in ^{1}H NMR spectra : (*E*)-**4b**: δ 6.08 (dt, *J* = 18.6, 6.4 Hz); (*Z*)-**4b** δ 6.46 (dt, *J* = 13.8, 7.3 Hz).

***threo*-(*Z*)-4-(Dimethylphenylsilyl)-1-phenyl-2-propyl-3-buten-1-ol (4c).** Yield: 87% (*E*/*Z* = 7 : 93). Colorless oil. R_f 0.44 (hexane/ethyl acetate 4 : 1). ^{1}H NMR ($CDCl_3$) δ 0.42 (s, 6H), 0.70 (t, *J* = 6.7 Hz, 3H), 0.80-1.30 (m, 4H), 1.99 (d, *J* = 2.2 Hz, 1H), 2.30-2.50 (m, 1H), 4.24 (dd, *J* = 8.2, 2.2 Hz, 1H), 5.95 (d, *J* = 14.0 Hz, 1H), 6.22 (dd, *J* = 14.3, 10.3 Hz, 1H), 7.08-7.20 (m, 2H), 7.20-7.31 (m, 3H), 7.30-7.42 (m, 3H), 7.50-7.63 (m, 2H). ^{13}C NMR ($CDCl_3$) δ -0.9, -0.8, 14.3, 20.4, 33.1, 51.1, 76.8, 127.1, 127.5, 127.9, 128.1, 129.0, 131.9, 133.8, 139.3, 142.3, 150.7. IR (neat) 3450 (br), 2962, 2938, 2878, 1607, 1457, 1430, 1250, 1113, 838, 822, 783, 735, 701 cm^{-1}. MS *m/z* 306 (M^+-H_2O, 0.8), 281 (M^+-Pr, 1.9), 241 (11), 218 (7.9), 135 ($PhMe_2Si^+$, 100), 121 (13), 107 ($PhCHOH^+$, 29). Anal. Calcd for $C_{21}H_{28}OSi$: C, 77.72; H, 8.70. Found: C, 77.43; H, 8.67. The isomer ratio was determined from the integral value of the distinguishable signals in ^{1}H NMR spectra: (*E*)-**4c** δ 4.45 (d, *J* = 7.4 Hz); (*Z*)-**4c** δ 4.24 (d, *J* = 8.2 Hz).

***erythro*-(*E*)-4-(Dimethylphenylsilyl)-1-phenyl-2-propyl-3-buten-1-ol (4d).** Yield: 46%. Colorless oil. R_f 0.36 (hexane/ethyl acetate = 4 : 1). ^{1}H NMR ($CDCl_3$) δ 0.23 (s, 3H), 0.25 (s, 3H), 0.87 (t, *J* = 6.9 Hz, 3H), 1.10-1.70 (m, 4H), 2.11 (d, *J* = 3.0 Hz, 1H), 2.38-2.58 (m, 1H), 4.55 (dd, *J* = 5.8, 2.2 Hz, 1H), 5.65 (d, *J* = 18.8 Hz, 1H), 5.71 (dd, *J* = 18.6, 7.8 Hz, 1H), 7.16-7.40 (m, 10H). ^{13}C NMR ($CDCl_3$) δ -2.5, 14.1, 20.5, 32.0, 54.2, 77.0, 126.7, 127.3, 127.6, 127.9, 128.8, 131.0, 133.7, 138.8, 142.7, 148.6. IR (neat) 3420 (br), 2965, 2880, 1617, 1458, 1430, 1251, 1117, 1030, 995, 846, 787, 763, 734, 702 cm^{-1}. MS *m/z* 323 (M^+-1, 0.8), 306 (M^+-H_2O, 4.1), 281 (M^+-Pr, 2.0), 241 (12), 218 (7.1), 215 (11), 170 (8.9), 135 ($PhMe_2Si^+$, 100), 121 (20), 107 ($PhCHOH^+$, 25), 105 (24). Anal. Calcd for $C_{21}H_{28}OSi$: C, 77.72; H, 8.70. Found: C, 77.51; H, 8.56. The isomer ratio was determined from the integral value of the distinguishable signals in ^{1}H NMR spectra: (*E*, *erythro*) δ 4.55 (dd, *J* = 5.8, 2.2 Hz, 1H); (*Z*, *threo*) δ 4.24 (dd, *J* = 8.2, 2.2 Hz, 1H).

Boron Mediated Coupling Reaction of 3d. 4-Methoxy-1,4-diphenyl-1-pentene (5). To a solution of **3d** (0.20 g, 0.88 mmol), iodobenzene (0.112 mL, 0.95 mmol), $Pd(PPh_3)_4$ (50 mg, 0.043 mmol) in dioxane (5 mL) was added an aqueous KOH solution (1.20 M, 2.2 mL), and the resulting mixture was stirred at 100 °C (bath) for 24 h. The solution was neutralized with a saturated NH_4Cl solution and the aqueous layer was extracted with ethyl acetate. The combined organic layer was dried over anhydrous $MgSO_4$, concentrated *in vacuo*, and purified by silica gel column chromatography (hexane/ethyl acetate 4 : 1) to give **5** as a colorless oil (0.13 g, 86% yield). Colorless oil. R_f 0.46 (hexane/ethyl acetate 4 : 1). ^{1}H NMR ($CDCl_3$) δ 1.19 (d, *J* = 6.2 Hz, 3H), 2.22-2.58 (m, 2H), 3.37 (s, 3H), 3.44 (m, 1H), 6.22

(dt, J = 15.8, 7.1 Hz, 1H), 6.44 (d, J = 15.8 Hz, 1H), 7.14-7.44 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 19.0, 39.7, 56.1, 76.6, 126.0, 126.7, 127.0, 128.4, 132.0, 137.6. IR (neat) 3025, 2970, 2927, 2820, 1598, 1493, 1448, 1373, 1135, 1092, 966, 742, 691 cm^{-1}. MS *m/z* 177 (M^++1, 1.5), 176 (M^+, 12), 145 (M^+-OMe, 3.1), 117 ($PhCH{=}CHCH_2^+$, 11), 115 (15), 91 ($PhCH_2^+$, 8.0), 77 (Ph^+, 2.6), 59 (CH_3CHOMe^+, 100). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.91; H, 9.34.

4-Methoxy-4-phenyl-1-butene. To a solution of **4b** (0.143 g, 0.50 mmol) in THF (5 mL) was added BuLi (0.35 ml, 0.55mmol) at –78 °C, and stirred for 15 min. Methyl iodide (0.06 mL, 0.60 mmol) was added to the mixture, and the resulting mixture was stirred for 2 h. Usual work-up and silica gel column chromatography (hexane/ethyl acetate 4: 1) afforded (*Z*)-4-methoxy-4-phenyl-1-dimethylphenylsilyl-1-butene as a colorless oil. (0.14 g, 96% yield). R_f 0.49 (hexane/ethyl acetate 4 : 1). ^{1}H NMR ($CDCl_3$) δ 0.63 (s, 6H), 2.40 (m, 2H), 3.12 (s, 3H), 3.95 (t, J = 6.6 Hz, 1H), 5.95 (d, J = 14 Hz, 1H), 6.58 (dt, J = 7.0, 14 Hz, 1H), 7.04-7.56 (m, 10H). ^{13}C NMR ($CDCl_3$) δ -2.0, 41.9, 56.5, 83.3, 126.6, 127.2, 127.5, 127.8, 128.3, 129.1, 134.6, 137.2, 137.4, 141.4, 147.8. IR (neat) 3067, 2903, 1603, 1427, 1107, 999, 793, 729, 700 cm^{-1}. MS *m/z* 281 (M^+-Me, 15), 197 (31), 121 (100), 105 (43). Anal. Calcd for $C_{19}H_{24}OSi$: C, 76.97; H, 8.16. Found: C, 76.91; H, 8.12. To a solution of the methyl ether (0.141 g, 0.48 mmol), iodobenzene (0.06 mL, 0.50 mmol), $Pd_2(dba)_3$ (11 mg, 0.0129 mmol), *t*-BuOK (0.112 g, 0.96 mmol), and 18-crown-6 (0.191 g, 0.72 mmol) in THF (5 mL) was added TBAF (1 M, 0.96 ml, 0.96 mmol), and the resulting mixture was stirred at room temperature for 1 h. The solution was neutralized with a saturated NH_4Cl solution and the aqueous layer was extracted with ethyl acetate. The combined organic layer was dried over anhydrous $MgSO_4$, concentrated *in vacuo*, and purified by silica gel column chromatography to give **6** as a major product (9.2 mg, 13% yield) instead of a coupling product, (*Z*)-4-methoxy-1,4-diphenyl-1-pentene. Colorless oil. R_f 0.56 (hexane/ethyl acetate 4 : 1). ^{1}H NMR ($CDCl_3$) δ 2.14-2.73 (m, 2H), 3.15 (s, 3H), 4.00 (t, J = 6.0 Hz, 1H), 4.80-6.10 (m, 3H), 7.20-7.34 (m, 5H), IR (neat) 3020, 1640, 1450, 1110, 915 cm^{-1}. MS *m/z* 121 (100), 91 (18), 77 (25), 51 (9).

Acetal-vinylsilane Cyclization Mediated by $TiCl_4$. *threo*-(Z)-1-Dimethylphenylsilyl-3-[(2-methoxyethoxy)phenylmethyl]-hex-1-ene. To a solution of **4c** (0.24 g, 0.74 mmol) in THF (5 mL) was added NaH (ca. 60wt%, 0.147 g), and stirred at room temperature for 2 h. 2-Methoxyethoxymethyl chloride (0.79 mL, 4.5 mmol) was added to the mixture, and the resulting mixture was stirred for 1 h. Usual work-up and silica gel column chromatography (hexane/ethyl acetate 6 : 1) afforded the corresponding MEM ether as a colorless oil. (0.172 g, 55% yield). R_f 0.44 (hexane/ethyl acetate 4 : 1). ^{1}H NMR ($CDCl_3$) δ 0.28 (s, 6H), 0.73 (t, J = 5.6 Hz, 3H), 0.90-1.40 (m, 4H), 2.49 (m, 1H), 3.34 (s, 3H), 3.36-3.55 (m, 3H), 3.65-3.90

(m, 1H), 4.44 (d, J = 6.4 Hz, 1H), 4.49 (d, J = 7.0 Hz, 1H), 4.55 (d, J = 7.0 Hz, 1H), 5.70 (d, J = 14.4 Hz, 1H), 6.22 (dd, J = 14.4, 10.4 Hz, 1H), 7.10-7.40 (m, 8H), 7.40-7.58 (m, 2H). ^{13}C NMR ($CDCl_3$) δ -1.0, -0.7, 14.3, 20.2, 33.6, 49.2, 59.0, 66.9, 71.7, 80.7, 93.2, 127.4, 127.6, 127.9, 127.9, 128.7, 128.8, 133.9, 139.8, 140.7, 150.8. IR (neat) 2955, 2932, 2874, 1611, 1454, 1427, 1246, 1111, 1042, 1024, 820, 781, 731, 700 cm^{-1}. MS *m/z* 367 (M^+-$MeOCH_2$, 0.13), 307 (M^+-MEMO, 1.7), 195 (27), 135 ($PhMe_2Si^+$, 41), 121 (16), 89 ($MeOCH_2CH_2OCH_2^+$, 100), 59 ($MeOCH_2CH_2^+$, 52). Anal. Calcd for $C_{25}H_{36}O_3Si$: C, 72.77; H, 8.79. Found: C, 72.81; H, 8.62.

***trans*-6-Phenyl-5-propyl-5,6-dihydro-2*H*-pyran (6).** To a solution of the MEM ether (0.112 g, 0.25 mmol) in CH_2Cl_2 (4 mL) was added a solution of $TiCl_4$ in CH_2Cl_2 (1.00 M, 0.75 mL, 0.75 mmol) at –78°C. The solution was stirred at –78 °C for 15 min before quenching by the addition of water (0.5 mL) at –78 °C. Warming up the mixture to room temperature, workup and purification by silica gel column chromatography (hexane/ethyl acetate 9 : 1) gave **7** (42 mg) in 82% yield as a colorless oil. R_f 0.36 (hexane/ethyl acetate 9 : 1). ^{1}H NMR ($CDCl_3$) δ 0.79 (t, J = 6.9 Hz, 3H), 0.94–1.54 (m, 4H), 2.32–2.54 (m, 1H), 4.11 (d, J = 9.2 Hz, 1H), 4.20–4.34 (m, 2H), 5.81 (dq, J = 10.2, 2.2 Hz, 1H), 5.90 (dt, J = 10.3, 1.7 Hz, 1H), 7.20–7.42 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 14.2, 19.1, 32.9, 40.3, 66.2, 81.6, 125.8, 127.5, 127.9, 128.3, 128.9, 141.2. IR (neat) 3025, 2955, 2923, 2864, 2806, 1451, 1133, 1091, 1022, 753, 697 cm^{-1}. MS *m/z* 202 (M^+, 0.37), 184 (0.18), 173 (M^+-Et, 0.32), 159 (M^+-Pr, 2.2), 96 (100), 81 (76), 67 (54), 54 (79). Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.04; H, 9.21.

Debenzylation of 3h. (*E*)-1-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-but-3-en-1-ol (7). To a solution of **3h** (15 mg, 0.04 mmol) in CH_2Cl_2 (1 mL) was added Me_3SiI (0.05 mmol) at room temperature. The solution was stirred at room temperature for 30 min before quenching with water (0.5 mL). Usual workup and purification by silica gel column chromatography (hexane/ethyl acetate = 9 : 1) gave **8** as a colorless oil (8.0 mg,73% yield). R_f 0.55 (hexane/ethyl acetate 4 : 1). ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 12H), 2.98-3.31 (m, 2H), 5.16 (t, J = 7.6 Hz, 1H), 5.53 (t, J = 18.0 Hz, 1H), 6.46 (dt, J = 18.0, 6.6 Hz, 1H), 7.22-7.48 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 24.7, 29.7, 47.1, 79.6, 127.1, 128.0, 128.4, 128.7, 139.7, 149.3. IR (neat) 3396 (br), 2926, 2855, 1456, 1371, 1142, 698 cm^{-1}. MS *m/z* 256 (M^+-H_2O, 75), 156 (100), 129 (89), 84 (87). HRMS (FAB) Calcd for $C_{16}H_{21}BO_2$: M^+- H_2O 256.1635. Found: *m/z* 265.1638.

Stereochemical Assignment of 3k [reference 21]. *threo*-3-[Benzyloxy(phenyl)methyl]-1-hexene. Protodeborylation of 3k. To a solution of **3k** (20 mg, 0.050 mmol) in THF (2 mL) was added butyllithium in hexane (1.56 M, 96 μL, 0.150 mmol) at 0 °C. The mixture

was stirred at 0 °C for 1 h before addition of a 6 M aqueous KOH solution. The resulting mixture was stirred for 2 h at 0 °C. Workup and purification by silica gel column chromatography (hexane/ethyl acetate 9 : 1) gave *threo*-3-[benzyloxy(phenyl)methyl]-1-hexene (8.0 mg) in 58% yield as a colorless oil.

Benzylation and protodesilylation of 4c. To a solution of **4c** (30 mg, 0.090 mmol) in THF (4 mL) was added benzyl bromide (0.45 mmol) and powder KOH (9.0 mmol). The reaction mixture was stirred at 100 °C for 36 h. Workup and purification by silica gel column chromatography (hexane/ethyl acetate 9 : 1) gave *threo*-3-[benzyloxy(phenyl)methyl]-1-hexene, which was identical with the stereoisomer obtained from **3k** (20 mg) in 77% yield as a colorless oil. R_f 0.41 (hexane/ethyl acetate 9 : 1). ^{1}H NMR ($CDCl_3$) δ 0.79 (t, J = 5.6 Hz, 3H), 1.06-1.21 (m, 4H), 2.35-2.47 (m, 1H), 4.22 (d, J = 12.6 Hz, 1H), 4.22 (s, 1H), 4.49 (d, J = 12.6 Hz, 1H), 4.93 (dd, J = 17.2, 2.0 Hz, 1H), 5.06 (dd, J = 10.2, 2.0 Hz, 1H), 5.67 (dt, J = 17.2, 7.0 Hz, 1H), 7.24-7.43 (m, 10H). ^{13}C NMR ($CDCl_3$) δ 14.0, 20.2, 32.8, 50.9, 70.4, 84.1, 116.2, 127.3, 127.4, 127.6, 127.6, 128.0, 128.2, 138.7, 139.4, 140.8. IR (neat) 3064, 3030, 2957, 2929, 2870, 1495, 1454, 1094, 1069, 1028, 912, 700 cm^{-1}. MS *m/z* 253 (M^+-C_2H_3, 1.3), 197 (4.5), 149 (100), 91 (21).

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(13) These results suggest that the relatively bulkier substiuent on silicon induces repulsion between substituents in a carbenoid and probably prevents 1,2-migration of a silicon atom.

(14) (Trimethylsilyl)borane was used as a THF/HMPA (5 : 1) solution. See also ref. 10c.

(15) For example, $TiCl_4$-promoted allylation of benzaldehyde with **2a** resulted in protodesilylation of **2a**, producing 1-propenylboronate as a major isomer in a low yield, while the same reaction mediated by Bu_4NF afforded a complex mixture.

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(17) Reaction of 1-silyl-1-stannyl-2-alkenes with acetals in the presence of BF_3•OEt_2 was reported in which a carbon-tin bond cleaved selectively over a carbon-silicon bond, giving rise to (*E*)-alkenylsilanes. See, ref. 3g.

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(19) Ketones such as cyclohexanone and acetophenone were not allylated even at elevated temperatures.

(20) (*E*)-Olefinic selectivity can be explained by *anti*-S_E2' transition states of allylsilanes. See, (a) Hayashi, T.; Konishi, M.; Ito, H.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 4962-4963. (b) Hayashi, T.; Konishi, M.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 4963-4965.

(21) Relative stereochemistry between benzyloxy and propyl groups of **3k** being *threo* was confirmed by protodeborylation of **3k** to give *threo*-3-[benzyloxy(phenyl)methyl]-1-hexene that was identical with the product obtained by benzylation and protodesilylation of **4c**.

(22) The author attemped to apply the diastereoselective reaction of **2** with chiral oxonium ion which was prepared from enantiopure chiral trimethylsilyl benzyl ether derivatives. However, when trimethylsilyl 1-phenylethyl ether, trimethylsilyl 1-trifluoromethyl-1-phenylmethyl ether, trimethylsilyl 1-methyl-1-naphthyl ether, and trimethylsilyl 1-indanyl ether were applied, neither allylation of an aldehyde nor kinetic resolution of **2** was observed, while at elevated reaction temperatures a complex mixture resulted. Steric repulsion between relatively bulky boryl substiuent on allyl silane at α-position and substituents in oxonium ion might prevent the reaction. (a) Mukaiyama, T.; Ohshima, M.; Miyoshi, N. *Chem. Lett* **1987**, 1121-1124. (b) Manju, K.; Trehan, S. *Chem. Comm* **1999**, 1929-1930. (c) Cossrow, J.; Rychnovsky, S. D. *Org. Lett.* **2002**, *4*, 147-150.

(23) It is known that allylsilanes function as effective three carbon components with α,β-enones or α,β-enals for the synthesis of five membered carbocycles and heterocycles in a related [3+2] annulation promoted by Lewis acid. Thus, the author treated **2** with such α,β-unsaturated carbonyl compounds as 1-acetylcyclohexene, methyl vinyl ketone, and methacrolein in the presence of titanium tetrachloride or boron trifluoride diethyl ether complex. However, neither [3+2] annulation nor 1,4-addition was observed, and a complex mixture of 1,2-adducts resulted in a low yield. (a) Knölker, H.-J.; Jones, P. G.; Pannek, J.-B. *Synlett* **1990**, 429-430. (b) Danheiser, R. L.; Dixon, B. R.; Gleason, R. W. *J. Org. Chem.* **1992**, *57*, 6094-6097. (c) Panek, J. S.; Jain, N. F. *J. Org. Chem.* **1993**, *58*, 2345-2348.

(24) In case that toluene was used as a solvent instead of THF, the diastereoselectivity increased slightly but yield was slightly lower. For example, allylation of benzaldehyde with **2a** upon heating at 100 °C in toluene for 12 h gave allylated product **4b** in 81% yield with high *Z*-selectivity (*E*/*Z* = >1 : <99).

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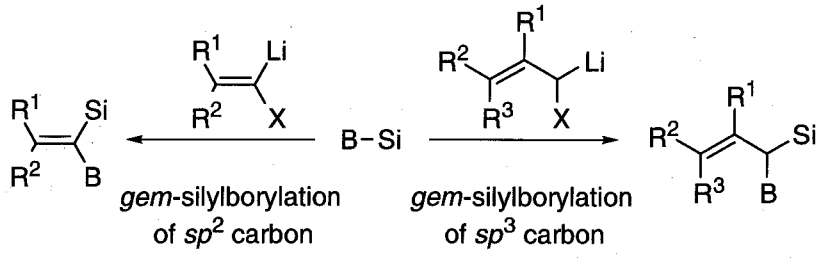
Chapter 4

Synthesis and Reactions of 1-Boryl-1-silylallenes

Treatment of 3-chloro-, 3-acetoxy-, or 3-mesyloxyalkyn-1-yllithiums with silyborane gives 1-boryl-1-silylallenes in moderate to good yields. The reaction is understood in terms of 1,2-migration of a silyl group from the negatively charged boron atom of an intermediate borate complex to a terminal acetylenic carbon and is accelerated by chloromethylsilane particularly when methanesulfonyloxy is employed for a leaving group. Furthermore, axially enantioenriched products could be prepared from mesylates of optically active propargylic alcohols.

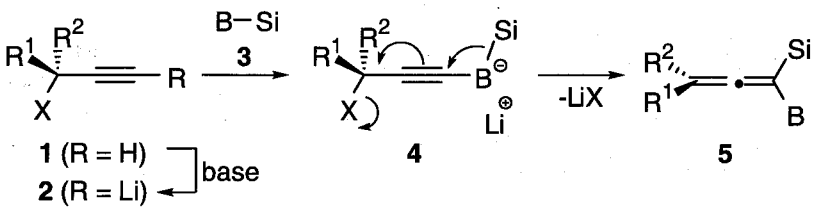
Introduction

As mentioned in Chapters 2 and 3, the author developed novel and efficient ways for the preparation of 1-boryl-1-silyl-1-alkenes and 1-boryl-1-silyl-2-alkenes via *gem*-silylborylation of alkylidene-type cabenoiods and α-chloroallyllithiums with silylboranes, respectively (Scheme 1). These reactions proceed through formation of ate complexes produced from a lithium carbenoid and a silylborane, followed by 1,2-migration of a silyl group from a negatively charged boron to the carbenoid carbon.



Scheme 1. *gem*-Silylborylation of lithium carbenoids.

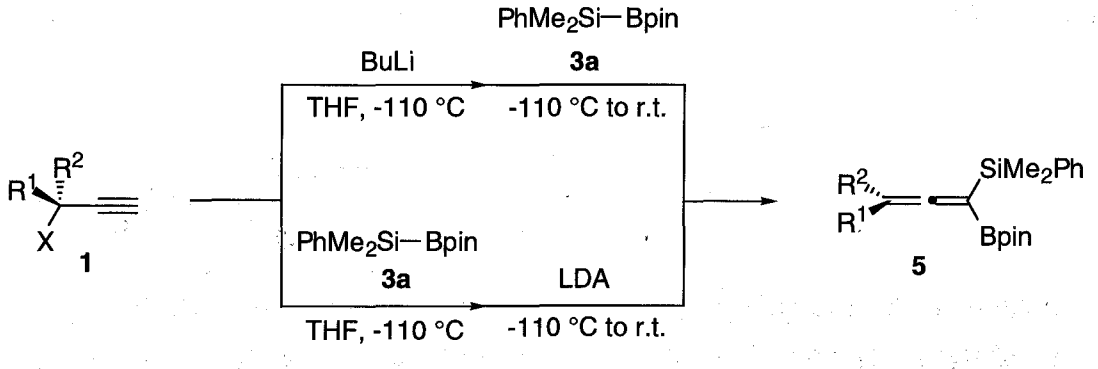
To further extend *gem*-dimetalation utilizing silylboranes, the author turned his attention to *gem*-silylborylation at an *sp* carbon of terminal acetylenes leading to allenyl organodimetallics.[1] Thus, he describes in this Chapter that treatment of 3-chloro-, 3-acetoxy-, or 3-mesyloxy-1-alkyne **1** (X = Cl, OAc or OMs) with a base generates the corresponding alkynyllithium **2** which reacts with silylborane (**3**) to produce 1-boryl-1-silyl-allenes **5** (Scheme 2).[2,3] This method should allow to prepare enantioenriched allenes **5** using optically active 3-mesyloxy-1-alkynes **1** (X = OMs). In addition, the resulting allenes are shown to undergo diastereoselective propargylation of aldehydes.



Scheme 2. Concept of*gem*-silylborylation at an acetylenic carbon.

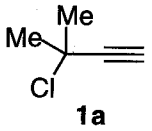
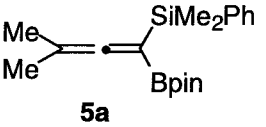
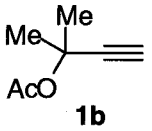
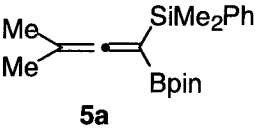
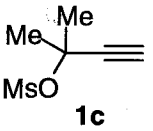
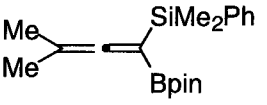
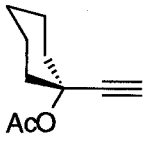
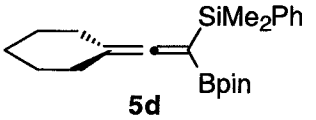
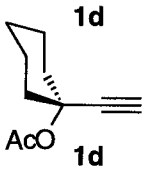
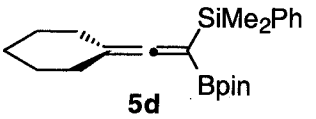
Results and Discussion

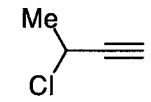
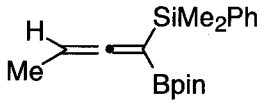
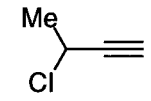
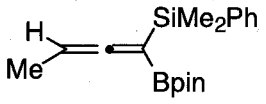
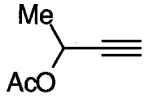
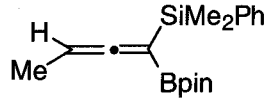
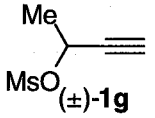
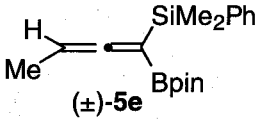
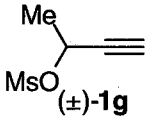
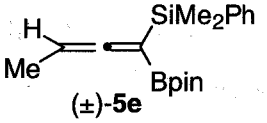
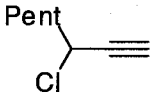
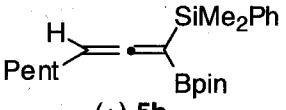
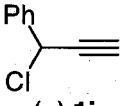
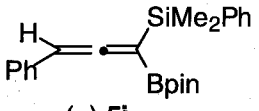
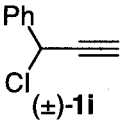
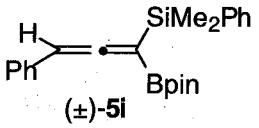
Treatment of **1** with BuLi in THF at −110 °C was followed by the addition of (dimethylphenylsilyl)(pinacolato)borane (**3a**) at −110 °C. Deprotonation of **1** was alternatively effected in the presence of **3a** at −110 °C using LDA as a base (Scheme 3).[4] In both cases, the resulting solution was allowed to warm to room temperature before quenching with sat. NH_4Cl aq. solution. Workup and purification by column chromatography on silica gel afforded **5** in moderate to good yields. The results are summarized in Table 1.



Scheme 3. Reaction procedure for the preparation of **5**.

Table 1. *gem*-Silylborylation of **1**.[a]

Entry	1	Base	5	Yield (%)[b]
1	 **1a**	BuLi	 **5a**	70
2	 **1b**	BuLi	 **5a**	77
3	 **1c**	BuLi	 **5a**	59
4	 **1d**	BuLi	 **5d**	53
5	 **1d**	LDA	 **5d**	60

6	 (±)-**1e**	BuLi	 (±)-**5e**	50
7	 (±)-**1e**	LDA	 (±)-**5e**	58
8	 (±)-**1f**	BuLi	 (±)-**5e**	50
9	 (±)-**1g**	BuLi	 (±)-**5e**	51
10	 (±)-**1g**	LDA	 (±)-**5e**	57
11	 (±)-**1h**	BuLi	 (±)-**5h**	83
12	 (±)-**1i**	BuLi	 (±)-**5i**	41
13	 (±)-**1i**	LDA	 (±)-**5i**	52

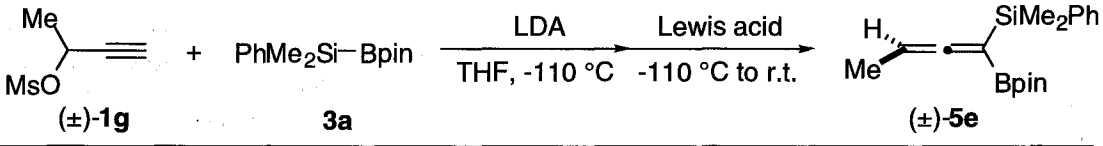
[a] BuLi: To a solution of **1** (0.50 mmol) in THF (3 mL) was added BuLi (0.50 mmol) at -110 °C. After stirring for 2 min, the mixture was treated with **3a** (0.50 mmol) and allowed to warm to room temperature before quenching with sat. aq. NH_4Cl (1 mL). LDA: To a solution of **1** (0.50 mmol) and **3a** (0.50 mmol) in THF (3 mL) was added LDA (0.50 mmol) at -110 °C. The resulting mixture was allowed to warm to room temperature. [b] Isolated yields are given.

Alkynyllithium **2a** prepared from 3-chloro-3-methyl-1-butyne (**1a**) and BuLi reacted with **3a** exactly as expected to give **5a** in 70% yield (entry 1). The yield of **5a** slightly increased by switching the leaving group from chloride to acetate (entry 2). Vinylidenecyclohexane **5d** was obtained from **1d** in 53% yield (entry 4). Racemic α-

monosubstituted propargylic chlorides **1e-i** were *gem*-silylborylated to give corresponding racemic allene **5e**, **5h**, or **5i** respectively in moderate to good yields (entries 6, 8, 9, 11, and 12). In general, better yields were obtained when LDA was used instead of BuLi (entries 5, 7, 10, and 13). Additionally, acetate and mesylate were better leaving groups for the present transformation. *gem*-Silylborylation of (±)-**1g** proceeded via deprotonation with BuLi or LDA, and warming the reaction mixture to room temperature gave rise to (±)-**5e** in 51 or 57% yield, respectively (entries 9 and 10). In all cases, no isomerization of **5** to propargylboranes was observed.[5]

It is noteworthy that the addition of chlorotrimethylsilane to the reaction mixture starting from **1g** accelerated the *gem*-silylborylation and enhanced the yield to 75% (Table 2, entry 1). In this case, the reaction went to completion below –78 °C, whereas without chlorotrimethylsilane it was essential to warm the reaction mixture to room temperature for complete consumption of **3**. Chlorotrimethylsilane is considered to play a role of a Lewis acid for promoting elimination of the mesyloxy group (Figure 1). Addition of trimethylsilyl trifluoromethanesulfonate or borontrifluoride etherate resulted in a lower yield or a complex mixture, respectively (entries 2 and 3).

Table 2. Acceleration of *gem*-silylborylation with Lewis acid.[a]



Entry	Lewis acid	Yield (%)[b]
1	Me_3SiCl	75
2	Me_3SiOTf	51
3	$BF_3{\cdot}Et_2O$	<1[c]

[a] To a solution of (±)-**1g** (0.50 mmol) and **3a** (0.50 mmol) in THF (3 mL) was added LDA (0.50 mmol) at -110 °C. Then Lewis acid (0.55 mmol) was added to the reaction mixture at -110 °C, and the resulting mixture was allowed to warm to room temperature. [b] Isolated yields are given. [c] A complex mixture with a trace amount of **5e**.

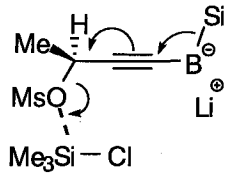
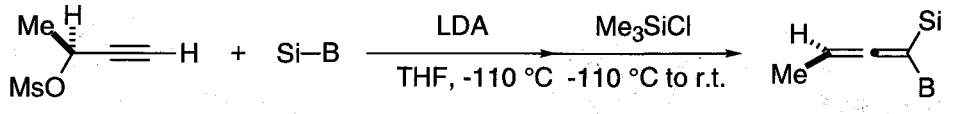
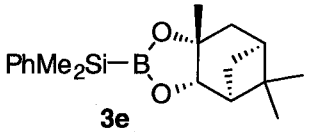


Figure 1.

The author next investigated the scope and limitations of available silylboranes, and results are shown in Table 3. Silylborane such as (methyldiphenylsilyl)(pinacolato)borane (**3b**) and (triphenylsily)(pinacolato)borane (**3c**) also reacted with (±)-**1g** under the optimized conditions to give the corresponding 1-boryl-1-silyl-allenes in moderate yields (entries 2 and 3), whereas the expected dimetalated product using (trimethylsilyl)(pinacolato)borane was not obtained (entry 4). Furthermore, for the *gem*-silylborylation of **1g** optically active silylborane **3e** also was applicable and a 60 : 40 diastereomeric mixture of the corresponding silylborane was isolated in 64% yield.

Table 3. Reaction of (±)-**1g** with various silylboranes **3**.[a]



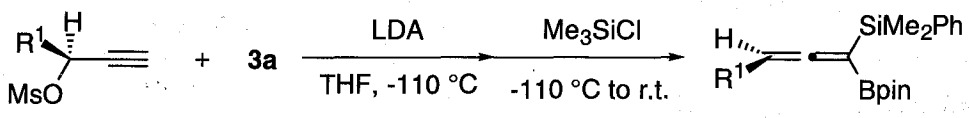
Entry	Si–B	Yield (%)[b]
1	$PhMe_2Si$–Bpin **3a**	75
2	Ph_2MeSi–Bpin **3b**	67
3	Ph_3Si–Bpin **3c**	56
4	Me_3Si–Bpin **3d**	—
5	$PhMe_2Si$–B  **3e**	64[c]

[a] To a solution of (±)-**1g** (0.50 mmol) and **3** (0.50 mmol) in THF (3 mL) was added LDA (0.50 mmol) at -110 °C. Chlorotrimethylsilane (0.55 mmol) was added to the reaction mixture at -110 °C, and then the resulting mixture was allowed to warm to room temperature. [b] Isolated yields are given. [c] A mixture of diastereomers of 60 : 40 as determined by ^{1}HNMR.

In order to explore possibility of asymmetric synthesis of 1-boryl-1-silylallenes, the author next carried out the *gem*-silylborylation starting with optically active mesylates (*S*)-**1g** and (*S*)-**1j**.[6] After several experiments,[7] he found that treatment of (*S*)-**1g** or (*S*)-**1j** with LDA in the presence of **3** at –110 °C followed by addition of chlorotrimethylsilane gave (*R*)-**5e** or (*R*)-**5f** in 75% or 67% yield with >74% ee (*vide infra*) or 70% ee, respectively (Table 4). The fact that *S* chirality of the stereogenetic center was transferred into axial *R* chirality of the

product allene can be reasonably explained by assuming that the 1,2-migration of the silyl accomplished by elimination of the mesyloxy group proceeds in *anti* S_N2' fashion as exemplified in Figure 1. These results are the first demonstration of asymmetric *gem*-silylborylation of this system.

Table 4. Asymmetric synthesis of (*R*)-**5e** and (*R*)-**5h** via *gem*-silylborylation of (*S*)-**1g** and (*S*)-**1j**.

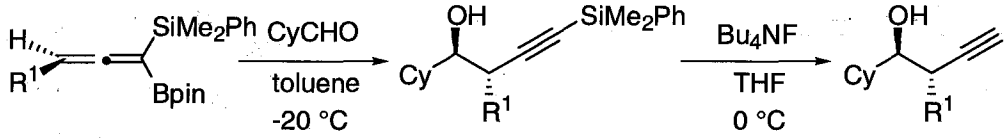


(*S*)-**1g** or **1j** (>99% ee) (*R*)-**5e** or **5h**

Entry	1	R^1	5	Yield (%)[a]	$[a]_D^{25}$	% ee
1	**1g**	Me	**5e**	75	-11.44 (*c* 3.20, $CHCl_3$)	>74[b]
2	**1j**	Pent	**5h**	67	-9.78 (*c* 3.22, $CHCl_3$)	70[c]

[a] Isolated yields are given. [b] Estimated by the results of propargylation of **5e** (*vide infra*). [c] Determined by HPLC analysis using Daicel AD column.

Table 5. Stereochemical assignment of (*R*)-**5e** and (*R*)-**5h.**



(*R*)-**5e** or **5h** **6e** or **6h** **7e** or **7h** (1*R*, 2*S*)

Entry	5		6	Yield (%)[a,c]	7	Yield (%)[b,c]
1	**5e**	Me	**6e**	92 (*anti* : *syn* = 93 : 7)	**7e**	80 (74% ee)[d]
2	**5h**	Pent	**6h**	67 (*anti* : *syn* = 89 : 11)	**7h**	82 (70% ee)[d]

[a] Propargylation: To a solution of **5e** or **5h** in toluene was added cyclohexanecarbaldehyde at -20 °C and stirred for 12 h. [b] Desilylation: A solution of **6e** or **6h** in THF was treated with TBAF at 0 °C and stirred for 4 h. [c] Isolated yields are given. [c] Determined by GC analysis using Chiral-DEX CB column.

Absolute configuration of **5e** and **5h** was deduced by chemical transformation to known alcohols **7e** and **7h**, respectively (Table 5).[6] Thus, both **5e** and **5h** reacted with cyclohexanecarbaldehyde in toluene at –20 °C to yield **6e** or **6f** with high *anti* diastereoselectivity, which was desilylated to give **7e** or **7h**, respectively. As specific rotations $[\alpha]_D$ of -1.78 (*c* 0.93, $CHCl_3$) for **7e** and -3.21 (*c* 1.37, $CHCl_3$) for **7h** correspond to (1*R*, 2*S*)-enantiomers,[8] absolute configuration of **5e** and **5h** was assigned both as *R*.[9] No loss of optical purity in the reaction of (*R*)-**5e** indicates that this propargylation is perfectly stereospecific. Hence, ee of **5e** was estimated to >74% as shown in Scheme 3.

Conclusion

In conclusion, the author has demonstrated that 1-boryl-1-silylallenes can be efficiently synthesized from readily available silylboranes and 3-chloro-, 3-acetoxy-, or 3-mesyloxyalkyn-1-yllithiums in moderate to good yields. In addition, the present reaction is demonstrated to be a straightforward methodology leading to enantioenriched 1-boryl-1-silylallenes.

Experimental

General Procedure for *gem*-Silylborylation of 3-Mesyloxy-1-alkyne. 3-Methyl-1-(dimethylphenylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)buta-1,2-diene (5a). Butyllithium in hexane (1.60 M, 0.32 mL, 0.50 mmol) was added dropwise at -110 °C to a solution of 3-chloro-3-methylbut-1-yne (**1a**) (50 mg, 0.50 mmol) in THF (3 mL). The resulting mixture was stirred at –110 °C for 2 min, then treated with (dimethylphenylsilyl)(pinacolato)borane (**3**) (0.131 g, 0.50 mmol) at –110 °C, and warmed up gradually to room temperature. After quenching with saturated aq. NH_4Cl (1 mL), the mixture was diluted with diethyl ether (30 mL) and then washed with water (10 mL). The organic layer was dried over anhydrous magnesium sulfate and concentrated *in vacuo*. Purification of the crude product by column chromatography on silica gel (hexane/ethyl acetate 9 : 1) afforded **5a** as a pale yellow oil (0.109 g, 70% yield). R_f 0.38 (hexane/ethyl acetate 9 : 1). ^1H NMR ($CDCl_3$) δ 0.37 (s, 6H), 1.18 (s, 12H), 1.60 (s, 6H), 7.26-7.39 (m, 3H), 7.51-7.61 (m, 2H). ^{13}C NMR ($CDCl_3$) δ -2.0, 18.8, 24.7, 83.0, 127.3, 128.5, 133.9, 139.7, 217.2. IR (neat) 2975, 2925, 1940, 1362, 1310, 1120, 1109, 856, 820, 698 cm^{-1}. MS *m/z* 328 (M^+, 3), 327 (M^+-1, 1), 313 (M^+-Me, 3), 135 (100). HRMS Calcd for $C_{19}H_{29}BO_2Si$: M^+, 328.2030. Found: *m/z* 328.2052.

2-[2-Cyclohexylidene-1-(dimethylphenylsilyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5d). Yield: 53% (BuLi); 60% (LDA). Pale yellow oil. R_f 0.45 (hexane/ethyl acetate 9 : 1). ^1H NMR ($CDCl_3$) δ 0.40 (s, 6H), 1.17 (s, 12H), 1.20-1.70 (m, 6H), 1.96-2.12 (m, 4H), 7.24-7.38 (m, 3H), 7.50-7.62 (m, 2H). ^{13}C NMR ($CDCl_3$) δ -1.8, 24.6, 26.2, 27.1, 29.8, 82.9, 89.7, 127.3, 128.5, 133.9, 139.7, 213.9. IR (neat) 2928, 2856, 1933, 1304, 1142, 1113, 980, 854, 731 cm^{-1}. MS *m/z* 369 (M^++1, 2), 368 (M^+, 10), 353 (M^+-Me, 3), 226 (100), 135 (48). HRMS Calcd for $C_{22}H_{33}BO_2Si$: M^+, 368.2343. Found: *m/z* 368.2333.

3-Phenyl-1-(dimethylphenylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propa-1,2-diene (5i). Yield: 41% (BuLi); 52% (LDA). Pale yellow oil. R_f 0.37 (hexane/ethyl acetate 9 : 1). ^1H NMR ($CDCl_3$) δ 0.42 (d, J = 18.8 Hz, 6H), 1.12 (d, J = 3.6 Hz, 12H), 5.74 (s, 1H), 7.03-7.28 (m, 8H), 7.51-7.56 (m, 2H). ^{13}C NMR ($CDCl_3$) δ -3.8, 23.0, 81.9, 123.7, 124.2, 125.8, 126.8, 127.2, 132.2, 132.9, 133.2, 136.7, 214.5. IR (neat) 2978, 1919, 1381, 1321, 1269, 1144, 1113, 852, 694 cm^{-1}. MS *m/z* 377 (M^++1, 2), 376 (M^+, 8), 234 (100), 135 (59). HRMS Calcd for $C_{23}H_{29}BO_2Si$: M^+, 376.2030. Found: *m/z* 376.2045.

(*R*)-(-)-1-(Dimethylphenylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)buta-1,2-diene (5e). To a solution of (*S*)-1-methylprop-2-ynyl methanesulfonate (**1g**) (71 mg, 0.50 mmol) and (dimethylphenylsilyl)(pinacolato)borane (**3**) (0.131 g, 0.50 mmol) in THF (3 mL)

was added LDA (0.50 mmol) in THF (1 mL) dropwise at -110 °C and stirred at –110 °C for 5 min. The mixture was then treated with chlorotrimethylsilane (59 mg, 0.55 mmol) and then warmed gradually to room temperature. After quenching with saturated aq. NH_4Cl (1 mL), the mixture was diluted with diethyl ether (30 mL) and then washed with water (10 mL). The organic layer was dried over anhydrous magnesium sulfate and concentrated *in vacuo*. Purification of the crude product by column chromatography on silica gel (hexane/ethyl acetate 10 : 1) afforded **5e** as pale yellow oil (0.122 g, 75% yield). $[\alpha]_D^{25}$ -11.44° (*c* 3.20, $CHCl_3$). R_f 0.42 (hexane/ethyl acetate 10 : 1). ^1H NMR ($CDCl_3$) δ 0.40 (s, 6H), 1.21 (s, 12H), 1.60 (d, *J* = 7.0 Hz, 3H), 4.61 (q, *J* = 7.0 Hz, 1H), 7.26-7.41 (m, 3H), 7.41-7.62 (m, 2H). ^{13}C NMR ($CDCl_3$) δ -2.2, 12.1, 73.3, 83.4, 127.6, 129.2, 134.1, 139.2, 217.6. IR (neat) 2978, 2895, 1933, 1381, 1319, 1142, 1110, 979, 813, 779, 700 cm^{-1}. MS *m/z* 315 (M^++1, 3), 314 (M^+, 5), 299 (M^+-Me, 10), 172 (100). HRMS (FAB) Calcd for $C_{18}H_{27}BO_2Si$: M^+, 314.1873. Found: *m/z* 314.1868.

(*R*)-(-)-1-(Dimethylphenylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octa-1,2-diene (5h). Yield: 83%. Pale yellow oil. $[\alpha]_D^{25}$ -9.78° (*c* 3.22, $CHCl_3$). R_f 0.52 (hexane/ethyl acetate 9 : 1). ^1H NMR ($CDCl_3$) δ 0.42, (s, 6H), 0.87 (t, *J* = 5.0 Hz, 3H), 1.14-1.35 (m, 18H), 1.95 (m, 2H), 4.68 (td, *J* = 7.0, 1.8 Hz, 1H), 7.29-7.33 (m, 3H), 7.56-7.60 (m, 2H). ^{13}C NMR ($CDCl_3$) δ -1.9, 14.2, 22.7, 24.6, 24.6, 24.7, 24.8, 24.9, 25.0, 26.9, 27.0, 29.6, 31.4, 78.9, 83.2, 127.3, 128.6, 133.9, 139.2, 216.7. IR (neat) 2928, 2856, 1933, 1427, 1389, 1304, 1269, 1142, 1113, 980, 854, 816, 779, 731, 700 cm^{-1}. MS *m/z* 371 (M^++1, 21), 370 (M^+, 60), 369 (M^+-1, 18), 355 (M^+-Me, 18), 192 (100). HRMS (FAB) Calcd for $C_{22}H_{35}BO_2Si$: M^+, 370.2499. Found: *m/z* 370.2508. Ee was determined to be 70% by HPLC (column: Daicel AD (0.46 cmϕ x 25 cm), eluent: hexane, flow rate: 0.5 mL/min): (*R*) R_t = 17.2 min; (*S*) R_t = 15.8 min.

1-Methyldiphenylsilyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)buta-1,2-diene. Yield: 67%. Pale yellow oil. R_f 0.45 (hexane/ethyl acetate 9 : 1). ^1H NMR ($CDCl_3$) δ 0.64 (s, 3H), 1.13 (s, 12H), 1.51 (d, *J* = 5.2 Hz, 3H), 4.59 (q, *J* = 5.2 Hz, 1H), 7.26-7.36 (m, 6H), 7.54-7.63 (m, 4H). ^{13}C NMR ($CDCl_3$) δ -2.9, 12.0, 24.7, 73.8, 83.3, 127.3, 127.7, 128.9, 129.4, 134.3, 134.9, 136.8, 136.9, 218.6. IR (neat) 3069, 2978, 2924, 1933, 1919, 1427, 1379, 1319, 1142, 1113, 793, 698 cm^{-1}. MS *m/z* 377 (M^++1, 3), 376 (M^+, 9), 361 (M^+-Me, 4), 294 (17), 197 (100). HRMS Calcd for $C_{23}H_{29}BO_2Si$: M^+, 376.2030. Found: *m/z* 376.2031.

1-Triphenylsilyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)buta-1,2-diene. Yield: 56%. Pale yellow oil. R_f 0.48 (hexane/ethyl acetate 9 : 1). ^1H NMR ($CDCl_3$) δ 1.12 (s, 12H), 1.43 (d, *J* = 7.5 Hz, 3H), 5.51 (q, *J* = 7.5 Hz, 1H), 7.19-7.45 (m, 9H), 7.52-7.64 (m, 6H).

^{13}C NMR ($CDCl_3$) δ 24.1, 74.4, 83.4, 127.3, 129.0, 134.8, 136.1, 217.0. IR (neat) 3047, 2978, 2164, 1933, 1427, 1317, 1302, 1142, 1109, 698 cm^{-1}. MS *m/z* 439 (M^++1, 2), 438 (M^+, 5), 429 (M^+-Me, 12), 259 (100), 207 (40). HRMS Calcd for $C_{28}H_{31}BO_2Si$: M^+, 438.2186. Found: *m/z* 438.2187.

1-Dimethylphenylsilyl-1-[(3a*S*,4*S*,6*S*,7a*R*)-hexahydro-3a,5,5-trimethyl-4,6-methano-1,3,2-benzodioxaborol-2-yl]buta-1,2-diene. Yield: 64% (mixture of diastereomers). Pale yellow oil. $[\alpha]_D^{25}$ -5.78° (*c* 3.54, $CHCl_3$). R_f 0.51 (hexane/ethyl acetate 9 : 1). ^{1}H NMR ($CDCl_3$) δ 0.40 (s, 6H), 0.80 (s, 3H), 1.02 (d, *J* = 10.4 Hz, 1H), 1.25 (s, 3H), 1.33 (s, 3H), 1.60 (d, *J* = 7.0 Hz, 3H), 1.75-2.33 (m, 5H), 4.25 (d, *J* = 8.8 Hz, 1H), 4.64 (q, *J* = 7.0 Hz, 1H), 7.29-7.46 (m, 3H), 7.55-7.59 (m, 2H). ^{13}C NMR ($CDCl_3$) δ -2.2, 12.1, 24.0, 26.3, 27.0, 28.5, 35.4, 38.0, 39.4, 51.2, 76.7, 77.3, 85.6, 127.4, 128.7, 133.9, 139.1, 217.9. IR (neat) 2911, 1942, 1365, 1261, 1114, 978, 818, 711 cm^{-1}. MS *m/z* 367 (M^++1, 2), 366 (M^+, 7), 365 (M^+-1, 1), 172 (62), 135 (100), 93 (45). HRMS Calcd for $C_{22}H_{31}BO_2Si$: M^+, 366.2186. Found: *m/z* 366.2193.

Stereochemical Assignment of 5e and 5h. Propargylation of Cyclohexanecarbaldehyde. A solution of **5e** (91 mg, 0.31 mmol) and cyclohexanecarbaldehyde (49 mg, 0.45 mmol) in toluene (2 mL) was stirred at -20 °C for 24 h. After quenching with water (1 mL), the mixture was diluted with diethyl ether (40 mL) and then washed with water (10 mL). The organic layer was dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The diastereomer ratio was determined from the integral value of the distinguishable signals in ^{1}H NMR spectra of the crude product: *anti*-**6e**: δ 3.10 (dd, *J* = 6.8, 4.4 Hz, 1H); *syn*-**6e**: δ 3.37 (dd, *J* = 6.0, 6.0 Hz, 1H). Each diastereomer was separated by column chromatography on silica gel (hexane/ethyl acetate 10 : 1).

***anti*-1-Cyclohexyl-4-(dimethylphenylsilyl)-2-methylbut-3-yn-1-ol (*anti*-6e).** Yield: 75 mg, 86%. Pale yellow oil. $[\alpha]_D^{25}$ -1.39° (*c* 3.51, $CHCl_3$). R_f 0.27 (hexane/ethyl acetate 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.40 (s, 6H), 1.00-1.81 (m, 14H), 1.92 (d, *J* = 11.4 Hz, 1H), 2.80 (m, 1H), 3.10 (dd, *J* = 6.8, 4.4 Hz, 1H), 7.31-7.50 (m, 3H), 7.56-7.70 (m, 2H). ^{13}C NMR ($CDCl_3$) δ -0.65, 26.0, 26.3, 28.1, 29.7, 31.2, 41.2, 78.5, 85.4, 109.6, 127.8, 129.3, 133.6, 137.3. IR (neat) 3441, 2926, 2853, 2164, 1448, 1427, 1248, 1114, 1049, 991, 974, 829, 779, 700 cm^{-1}. MS (FAB) *m/z* 301 (MH^+, 17), 223 (28), 135 (100). HRMS (FAB) Calcd for $C_{19}H_{29}OSi$: MH^+, 301.1988. Found: *m/z* 301.1991.

***syn*-1-Cyclohexyl-4-(dimethylphenylsilyl)-2-methylbut-3-yn-1-ol (*syn*-6e).** Yield: 5 mg, 6%. Pale yellow oil. $[\alpha]_D^{25}$ -3.58° (*c* 0.67, $CHCl_3$). R_f 0.20 (hexane/ethyl acetate 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.39 (s, 6H), 0.81-1.84 (m, 14H), 1.95 (m, 1H), 2.71 (m, 1H), 3.37 (dd, *J*

= 6.0, 6.0 Hz, 1H), 7.31-7.50 (m, 3H), 7.55-7.71 (m, 2H). ^{13}C NMR ($CDCl_3$) δ -0.5, 15.2, 26.1, 26.5, 27.7, 29.8, 31.3, 40.1, 78.1, 84.3, 111.3, 127.3, 129.2, 133.5, 137.3. IR (neat) 3385, 2928, 2853, 2164, 1450, 1427, 1249, 1117, 1067, 837, 700 cm^{-1}. MS (FAB) *m/z* 301 (MH^+, 15), 223 (26), 135 (100). HRMS (FAB) Calcd for $C_{19}H_{29}OSi$: MH^+, 301.1988. Found: *m/z* 301.1985.

***anti*-1-Cyclohexyl-4-(dimethylphenylsilyl)-2-pentylbut-3-yn-1-ol (*anti*-6h).** In a manner similar to the above procedure, **5h** was reacted with cyclohexanecarbaldehyde. The diastereomer ratio of product was determined based on integral ratio of following ^{1}H NMR signals of the crude products: *anti*-**6h**: δ 3.15 (m, 1H); *syn*-**6h**: δ 3.40 (m, 1H). Each was separated, and *anti*-**6h** was isolated in 70% yield as a colorless oil. $[\alpha]_D^{26}$ 16.91° (*c* 2.56, $CHCl_3$). R_f 0.38 (hexane/ethyl acetate 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.41 (s, 6H), 0.87-1.80 (m, 22H), 1.97 (d, *J* = 11.2 Hz, 1H), 2.68 (m, 1H), 3.15 (m, 1H), 7.26-7.41 (m, 3H), 7.59-7.66 (m,2H). ^{13}C NMR ($CDCl_3$) δ -0.6, 14.0, 22.6, 26.0, 26.3, 26.4, 27.2, 28.5, 29.6, 31.6, 32.1, 37.2, 42.2, 86.5, 108.7, 127.8, 129.3, 133.6, 137.4, 144.6. IR (neat) 3441, 3068, 2924, 2855, 2164, 1450, 1248, 1115, 837, 814, 731 cm^{-1}. MS (FAB) *m/z* 357 (MH^+, 15), 279 (18), 135 (100) 75 (51). HRMS (FAB) Calcd for $C_{23}H_{37}OSi$: MH^+, 357.2614. Found: *m/z* 357.2612.

***syn*-Cyclohexyl-4-(dimethylphenylsilyl)-2-pentylbut-3-yn-1-ol (*syn*-6h).** Yield: 9%. Colorless oil. $[\alpha]_D^{26}$ 8.03° (*c* 1.22, $CHCl_3$). R_f 0.38 (hexane/ethyl acetate 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.39 (s, 6H), 0.81-1.89 (m, 22H), 1.93 (d, *J* = 11.6 Hz, 1H), 2.61 (m, 1H), 3.40 (m, 1H), 7.26-7.39 (m, 3H), 7.60-7.65 (m, 2H). ^{13}C NMR ($CDCl_3$) δ -0.6, 14.0, 22.6, 26.0, 26.3, 27.1, 27.2, 29.8, 31.7, 37.2, 40.2, 85.5, 110.2, 127.8, 129.3, 133.6, 137.5, 139.0. IR (neat) 3385, 2926, 2855, 2166, 1448, 1248, 1115, 814, 779, 729, 698 cm^{-1}. MS (FAB) *m/z* 357 (MH^+, 13), 279 (41), 135 (100) 75 (77). HRMS (FAB) Calcd for $C_{23}H_{37}OSi$: MH^+, 357.2614. Found: *m/z* 357.2608.

Protodesilylation. *anti*-1-Cyclohexyl-2-methylbut-3-yn-1-ol (*anti*-7e). To a solution of *anti*-**6e** (81 mg, 0.25 mmol) in THF (2 mL) was added 1.00 M solution of TBAF in THF (0.25 mL, 0.25 mmol), and the resulting solution was stirred at 0 °C for 6 h. After quenching with water (1 mL), the mixture was diluted with diethyl ether (30 mL) and then washed with water (10 mL). The organic layer was dried over anhydrous magnesium sulfate and concentrated *in vacuo*. Purification by column chromatography on silica gel (hexane/ethyl acetate 10 : 1) afforded *anti*-**7e** as colorless oil (31 mg, 72% yield). $[\alpha]_D^{27}$ -3.21° (*c* 1.37, $CHCl_3$). R_f 0.21 (hexane/ethyl acetate 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.95-1.80 (m, 14H), 1.96 (d, *J* = 12.3 Hz, 1H), 2.20 (d, *J* = 2.4 Hz, 1H), 2.72 (m, 1H), 3.03 (m, 1H). Ee was determined to be 74% by GC (column: Chiral-DEX CB (0.25 mmϕ x 25 m), column temperature: 120 °C constant): (1*R*, 2*S*) R_t = 15.0 min; (1*S*, 2*R*) R_t = 13.9 min.

***anti*-1-Cyclohexyl-2-pentylbut-3-yn-1-ol (*anti*-7h).** Yield: 82% (70% ee). $[\alpha]_D^{27}$ 5.38° (*c* 1.20, $CHCl_3$). R_f 0.30 (hexane/ethyl acetate 10 : 1). ^1H NMR ($CDCl_3$) δ 0.89 (t, *J* = 6.6 Hz, 3H), 0.90-1.84 (m, 19H), 1.99 (m, 1H), 2.11 (d, *J* = 2.4 Hz, 1H), 2.56 (m, 1H), 3.13 (ddd, *J* = 8.1, 8.1, 3.3 Hz). The optical purity was determined by GC analysis (column: Chiral-DEX CB (0.25 mmϕ x 25 m), column temperature: 130 °C constant): (1*R*, 2*S*) R_t = 17.2 min; (1*S*, 2*R*) R_t = 16.5 min.

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(2) Preparations and reactions of 1-boryl-1-silyl-1,2-dienes: (a) Haruta, R.; Ishiguro, M.; Furuta, K.; Mori, A.; Ikeda, N.; Yamamoto, H. *Chem. Lett.* **1982**, 1093-1096. (b) Wang, K. K.; Nikam, S. S.; Ho, C. D. *J. Org. Chem.* **1983**, *48*, 5376-5377. (c) Yamamoto, Y.; Ito, W.; Maruyama, K. *J. Chem. Soc., Chem. Commun.* **1984**, 1004-1005. (d) Furuta, K.; Ishiguro, M.; Haruta, R.; Ikeda, N.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2768-2776. (e) Nikam, S. S.; Wang, K. K. *J. Org. Chem.* **1985**, *50*, 2193-2195. (f) Yamamoto, Y.; Maruyama, K.; Komatsu, T.; Ito, W. *J. Org. Chem.* **1986**, *51*, 886-891. (g) Wang, K. K.; Wang, Z.; Gu, Y. G. *Tetrahedron Lett.* **1993**, *34*, 8391-8394.

(3) Pioneering studies on the preparation of allenylboranes from propargylic chlorides or acetates and organoboranes: (a) Leung, T.; Zweifel, G. *J. Am. Chem. Soc.* **1974**, *96*, 5620-5621. (b) Midland, M. M. *J. Org. Chem.* **1977**, *42*, 2650-2651. Preparation of allenylzinc reagents via 1,2-migration of a carbonaceous substituents in alkylzincates was reported. (c) Harada, T.; Katsuhira, T.; Osada, A.; Iwazaki, K.; Maejima, K.; Oku, A. *J. Am. Chem. Soc.* **1996**, *118*, 11377-11390.

(4) Treatment of **1** with LDA followed by addition of **3** resulted in no production of **5** at all.

(5) Zweifel, G.; Backlund, S. J.; Leung, T. *J. Am. Chem. Soc.* **1978**, *100*, 5561-5562.

(6) Axially chiral allenylboranes and -silanes were reportedly prepared by asymmetric hydrometalation of but-1-en-3-ynes. (a) Matsumoto, Y.; Naito, M.; Uozumi, Y.; Hayashi, T. *J. Chem. Soc., Chem. Commun.* **1993**, 1468-1469. (b) Han, J. W.; Tokunaga, N.; Hayashi, T. *J. Am. Chem. Soc.* **2001**, *123*, 12915-12916.

(7) Reaction of (*S*)-**1g** and **3a** with Me_3SiCl in Et_2O resulted in the production of (*R*)-**5e** in 64% yield with 60% ee, while (*R*)-**5e** formed in THF without the addition of Me_3SiCl in 51% yield with 70% ee.

(8) Marshall, J. A.; Adams, N. D. *J. Org. Chem.* **1997**, *62*, 8976-8977.

(9) Propargylation of aldehydes with allenylboranes is assumed to proceed via 6-membered cyclic transition states. Haruta, R.; Ishiguro, M.; Ikeda, N.; Yamamoto, H. *J. Am. Chem. Soc.* **1982**, *104*, 7667-7669.

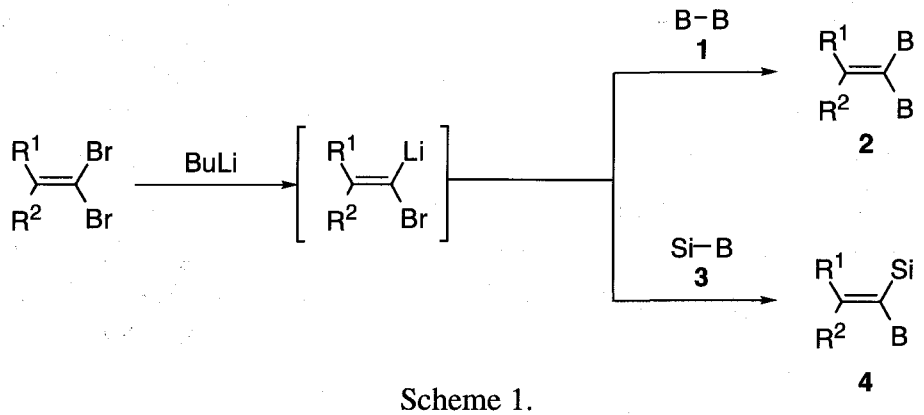
Chapter 5

Efficient Synthesis of 2,3-Bis[(pinacolato)boryl]-1,3-dienes and Synthetic Applications

Treatment of 1,1-[bis(pinacolato)boryl]alkenes with excess of 1-bromo-1-lithioethene gives 2,3-bis[(pinacolato)boryl]-1,3-dienes in moderate to good yields. Synthetic potentials of 2,3-[bis(pinacolato)boryl]-1,3-dienes are demonstrated by the Diels-Alder reaction, 1,4-dimetalation reactions, cross-coupling reactions, and facile synthesis of anolignan analogs.

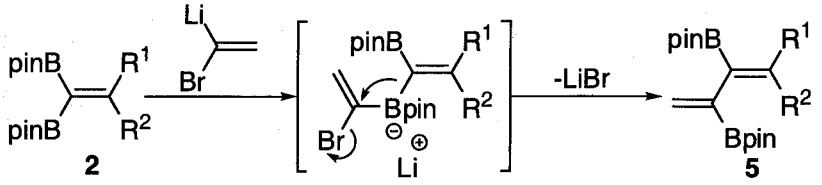
Introduction

Alkenylborons are readily accessible and extremely useful reagents in organic synthesis.[1] In contrast, bis(alkenylboron) compounds have attracted less attention, probably because of limited synthetic methods,[2] though such compounds could be employed for an efficient synthesis of polysubstituted olefins through double carbon–carbon bond formation with retention of configuration by a simple experimental operation. As discussed in Chapter 2, the author has found that treatment of diboron (**1**) and silylborane (**3**) with 1-halo-1-alkenyllithium gives the corresponding 1,1-diborylalkenes (**2**) or 1-silyl-1-borylalkenes (**4**), respectively (Scheme 1).[3]



Scheme 1.

During the course of the synthetic studies, the author eventually found that 2,3-diboryl-1,3-butadienes (**5a**) was produced when 1-bromo-1-lithioethene in excess was treated with diboron **1**. Formation of **5a** was ascribed to the reaction of 1,1-diborylethene (**2a**) with CH_2=CBrLi to give an alkenylborate intermediate, followed by 1,2-migration of an alkenyl group (Scheme 2). In this Chapter, the author describes that the synthesis of 2,3-diboryl-1,3-dienes is general,[4] and diborylated 1,3-dienes (**5**) serve as useful precursors for the synthesis of 1,3-dienes of complex structures.[5] In addition, introduction of two boryl groups into the 1,3-diene unit enhances the synthetic utility of the addition products.



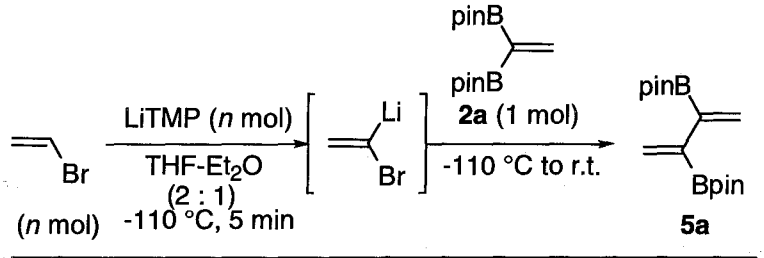
Scheme 2.

Results and Discussion

Synthesis of 2,3-Diboryl-1,3-dienes

To 1-bromo-1-lithioethene (1 mol) generated from vinyl bromide and lithium 2,2,6,6-tetramethylpiperidide (LiTMP) in THF-Et_2O (2 : 1) at –110 °C, was added 1,1-bis[(pinacolato)boryl]ethene (**2a**) (1 mol) at–110 °C to give 2,3-diboryl-1,3-butadiene (**5a**) only in 7% yield (Table 1, entry 1). In view that diboron **1** reacts with an equimolar amount of 1-bromo-1-lithioethene to give **2a** in 91% yield,[3] the low yield indicates that the reaction of the carbenoid with **2a** is slower than that with **1** and apparently competes with the decomposition of the lithium carbenoid. Then, the author increased the amount of the carbenoid reagent, and observed that 72% yield was achieved when 5 molar equivalents of vinyl bromide and LiTMP were employed (entry 3).[6] Noteworthy is that **5a** can be purified by column chromatography on silica gel in view that 2-boryl-1,3-diene is reported to be highly susceptible to dimerization.[7] Carbenoid generation carried out in the presence of **2a** gave **5a** in lower yield (59%), while reaction of 2-substituted 1-bromo-1-lithioethene with **2a** did not proceed at all.

Table 1. Synthesis of 2,3-diboryl-1,3-diene **5a**.[a]

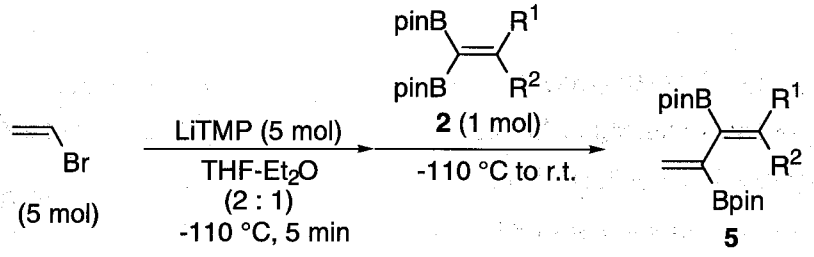


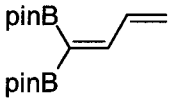
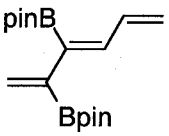
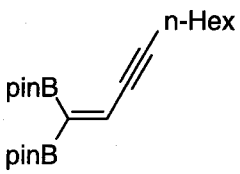
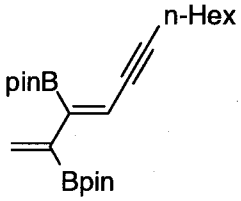
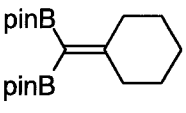
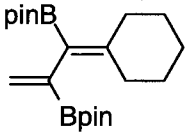
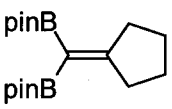
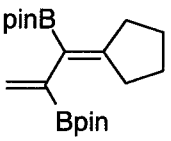
Entry	n (mol)	Yield (%)[b]
1	1	7
2	3	46
3	5	72
4	10	60

[a] A mixture of vinyl bromide (n mmol) , THF (2 mL), and Et_2O (1 mL) was treated with LiTMP (n mmol) and 1,1-bis[(pinacolato)boryl]ethene (**2a**) (0.50 mmol) at -110 °C for 5 min. The whole was then gradually warmed to room temperature. [b] Isolated yields based on **2a** are given.

The optimized conditions were applied to 2-monosubstituted diborylethenes **2b** and **2c**. From **2b** the corresponding conjugated triene **5b** formed as an *E*/*Z* mixture (80 : 20) in 80% yield, whereas (*E*)-dienyne **5c** was isolated as a single isomer in 38% yield (Table 2, entries 1 and 2). Stereochemistry of **5b** was assigned by ^{1}H NMR with 6-(dimethylphenylsilyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-nonene as a reference compound (Figure 1). As readily seen, the olefinic protons of *E*-isomers gives smaller chemical shifts than *Z*-isomers which are susceptible to deshielding by a boryl group.[8] The stereochemical outcome indicates that 1-bromo-1-lithioethene preferentially attacks sterically less hindered boron atom of **2**. This mechanism applies also to the formation of **5c**. Reaction of 2,2-disubstituted-1,1-diborylethenes **2d** and **2e** also took place smoothly, giving rise to **5d** and **5e** in good yields (entries 3 and 4).

Table 2. Synthesis of 2,3-diboryl-1,3-diene **5**.[a]



Entry	2	5	Yield (%)[b]
1	 **2b**	 **5b**	80 (*E* : *Z* = 80 : 20)
2	 **2c**	 **5c**	38 (*E* only)
3	 **2d**	 **5d**	85
4	 **2e**	 **5e**	74

[a] A mixture of vinyl bromide (2.5 mmol) , THF (2 mL), and Et_2O (1 mL) was treated with LiTMP (2.5 mmol) and **2** (0.50 mmol) at -110 °C for 5 min. The whole was then gradually warmed to room temperature. [b] Isolated yields based on **2** are given.

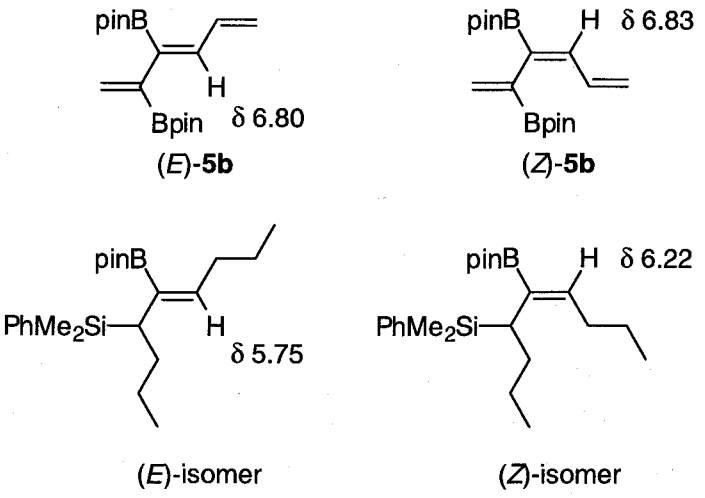
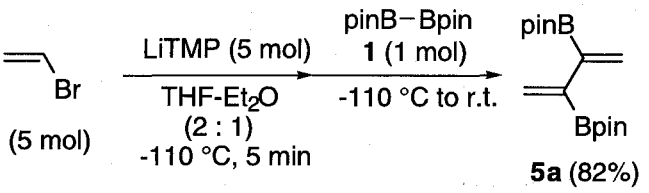


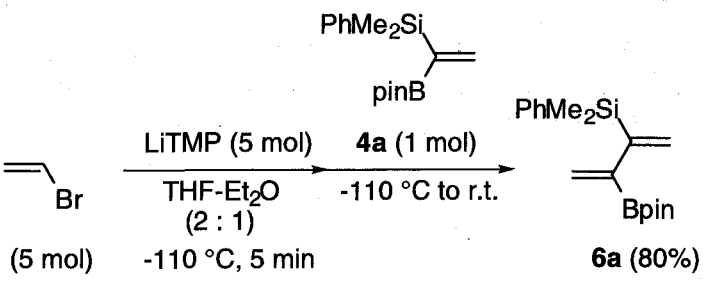
Figure 1.

One-pot synthesis of **5a** starting with **1** is also possible. As shown in Scheme 3, treatment of vinyl bromide (5 mol) with LiTMP (5 mol) followed by the addition of diboron **1** produced **5a** in 82% yield.



Scheme 3. One-pot synthesis of **5a** from **1**.

2-Silyl-3-boryl-1,3-butadiene (**6a**) can also be obtained by treatment of 5 molar equivalents of the same carbenoid reagent with 1-silyl-1-borylethene **4a** instead of 1,1-diborylethenes (Scheme 4). However, the reaction with 2-mono- or 2,2-disubstituted-1-silyl-1-borylethenes did not proceed to give the corresponding 1,3-dienes.

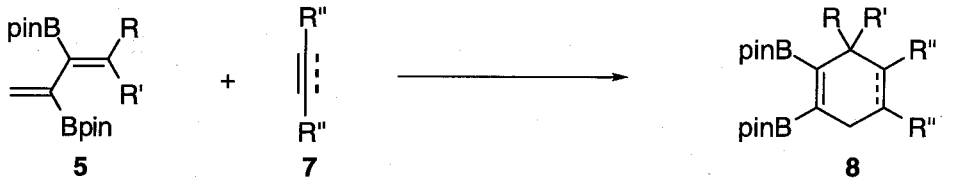


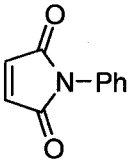
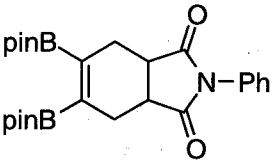
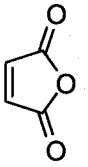
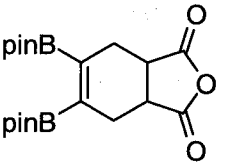
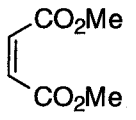
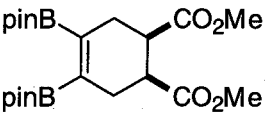
Scheme 4. Synthesis of 2-silyl-3-boryl-1,3-diene **6a**.

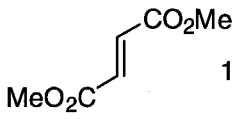
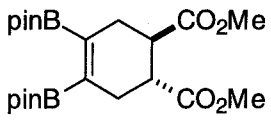
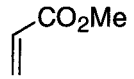
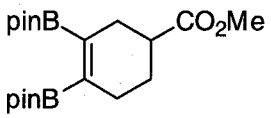
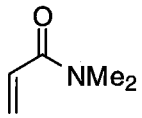
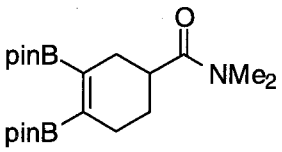
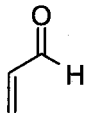
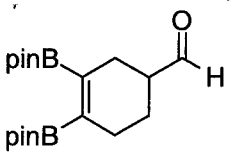
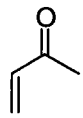
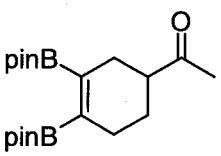
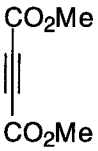
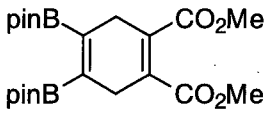
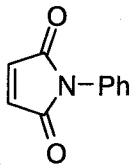
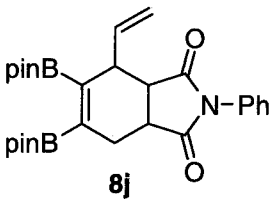
Synthetic Utility of 2,3-Diboryl-1,3-dienes

With 2,3-diboryl-1,3-dienes in hands, the author studied their synthetic applications. Some examples of the Diels-Alder reaction of **5** are illustrated in Table 3. It should be noted that the reaction is particularly accelerated by the two boryl groups and indeed proceeded with *N*-phenylmaleimide **7a** even at room temperature to give 1,2-diborylated cyclohexene **8a** in 99% yield (entry 1). The olefinic configuration of the dienophiles is preserved in the adduct. For example, reactions of **5a** with dimethyl maleate and dimethyl fumarate gave *cis*- and *trans*-dimethyl 4,5-diborylcyclohex-4-ene-1,2-dicarboxylate, respectively (entries 3 and 4). Dienophiles such as methyl acrylate, dimethyl acrylamide, acrolein, and methyl vinyl ketone also reacted with **5a** to give the corresponding 1,2-diborylated cyclohexenes in moderate to high yields (entries 5-8). Furthermore, **5a** reacted with dimethyl acetylenedicarboxylate to give a 1,2-diborylated 1,4-cyclohexadiene in good yield (entry 9). It is noteworthy that diborylated triene **5b** reacted with *N*-phenylmaleimide **7a** and 1,2-diboryl-3-vinyl-1-cyclohexene (**8j**) was produced with high regioselectivity.

Table 3. Diels-Alder reaction of 2,3-diboryl-1,3-dienes with various dienophiles.[a]



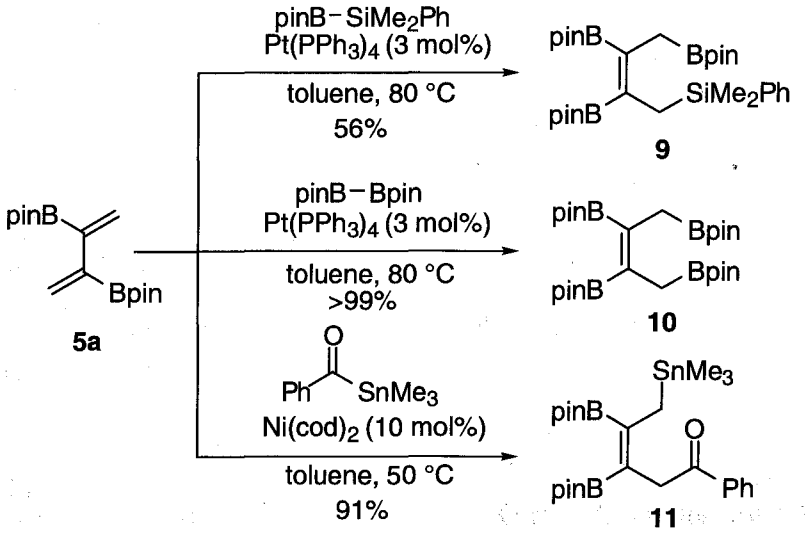
Entry	5	7 (eq)	Conditions	Product	Yield (%)[b]
1	**5a**	 **7a** (1.1)	r.t., 10 h	 **8a**	99
2	**5a**	 **7b** (1.1)	120 °C, 2.5 h	 **8b**	99
3	**5a**	 **7c** (1.1)	150 °C, 24 h	 **8c**	94

4	**5a**	 **7d** (2.0)	100 °C, 48 h	 **8d**	90
5	**5a**	 **7e** (4.0)	130 °C, 5.5 h	 **8e**	65
6	**5a**	 **7f** (4.0)	115 °C, 48 h	 **8f**	99
7	**5a**	 **7g** (12)	130 °C, 24 h	 **8g**	61
8	**5a**	 **7h** (15)	130 °C, 2.5 h	 **8h**	78
9	**5a**	 **7i** (1.1)	100 °C, 16 h	 **8i**	73
10	**5b**	 **7j** (1.1)	130 °C, 2 h	 **8j**	76

[a] A mixture of **5** (0.50 mmol) and **7** in toluene or xylene (2 ml) was heated and stirred under argon atmosphere. [b] Isolated yields based on **5** are given.

Pt-catalyzed 1,4-addition reaction of bis(pinacolato)diboron **1** or (dimethylphenylsilyl)(pinacolato)boron **3** towards **5a**, gave (Z)-1-silyl-2,3,4-tris(boryl)-2-butene **9** and (Z)-1,2,3,4-tetraboryl-2-butene **10** as sole isomers.[9,10] Nickel-catalyzed acylstannylation of **5a** also proceeded smoothly to give 1,4-difunctionalized product **11**.[11]

Highly metalated compounds **9**, **10**, and **11** contain both alkenyl- and allylmetal moieties and thus may serve as versatile synthetic reagents.

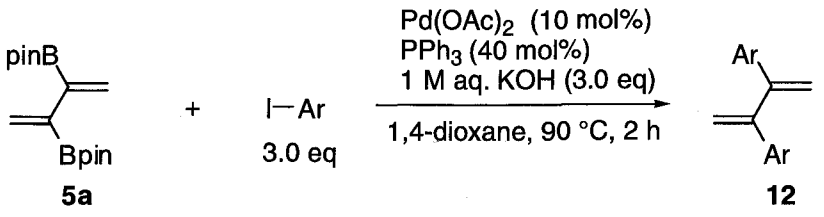


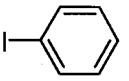
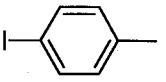
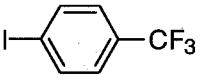
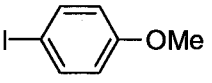
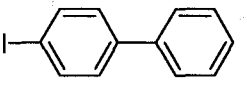
Scheme 6. Borylmetalation and acylstannylation of **5a**.

Double cross-coupling of **5a** with aryl iodides under the Suzuki-Miyaura conditions is summarized in Table 4.[12] 2,3-Diboryl-1,3-butadiene **5a** reacted with iodobenzene to give 2,3-diphenyl-1,3-butadiene[13a] **12a** in 75% yield. Under the same conditions, 4-methyliodobenzene,[13c] 4-trifluoromethyliodobenzene,[13e] and 4-methoxyiodobenzene[13b] coupled with **5a** to produce the corresponding 2,3-diaryl-1,3-butadienes **12b-12d** in good yields. In addition, the cross-coupling of **5a** with biphenyl iodide also underwent smoothly, giving rise to **12e**.[13e]

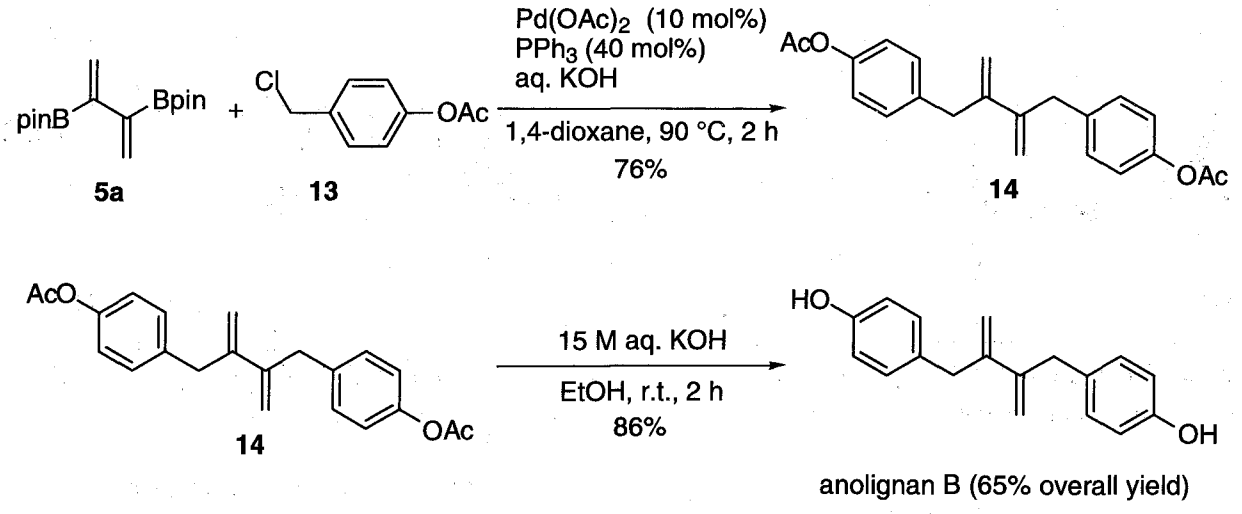
Cross-coupling of **5a** with benzylic halides should give 2,3-bisbenzyl-1,3-butadienes, a new class of lignans. For example, anolignan B were isolated from *Anogeissus acuminata* by bioassay-guided fractionation[14] and identified as the active HIV-1 reverse transcriptase inhibitory constituents of this plant. A structural feature of these is that they have a 1,3-diene moiety in common. Thus, the author was stimulated to develop a facile synthetic methodology for anolignan B by means of the cross-coupling reaction of **5a** with benzyl chloride derivatives. Under the optimized conditions, double coupling **5a** with **13** followed by alkaline hydrolysis gave anolignan B in 65% overall yield. This is the shortest and the most reliable method for the synthesis of the target molecular.[11b]

Table 4. Double cross-Coupling reaction of **5a** with various aryl halides.[a]



Entry	I—Ar	Product	Yield (%)[b]
1		**12a**	75
2		**12b**	75
3		**12c**	68
4		**12d**	81
5		**12d**	65

[a] To a mixture of **5a** (0.50 mmol), aryl iodide (1.5 mmol), Pd $(OAc)_2$ (10 mol%), PPh_3 (40 mol%) in 1,4-dioxane (2 ml) was added 1 M aq.KOH (1.5 ml). The resulting mixture was stirred at 90 °C for 2 h under an argon atmosphere. [b] Isolated yields based on **5a** are given.



Scheme 5. Facile total synthesis of anolignan B.

Conclusion

In conclusion, the author have established novel synthesis of 2,3-diboryl-1,3-dienes from 1-bromo-1-lithioethene and 1,1-diborylalkenes. 2,3-Diboryl-1,3-dienes can be transformed to various types of complex molecules using the boron functionality as a key element before or after typical reactions of the 1,3-diene moieties.

Experimental

Representative Procedure for Synthesis of 5. 2,3-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3-butadiene (5a). Butyllithium in hexane (1.56 M, 0.32 mL, 0.49 mmol) was added to a solution of 2,2,6,6-tetramethylpiperidine (0.084 mL, 0.50 mmol) in a mixture of THF (1 mL) and diethyl ether (0.5 mL) at 0 °C, and the resulting solution was stirred at 0 °C for 5 min. To this solution was added a THF solution of vinyl bromide (1.00 M, 0.50 mL, 0.50 mmol) at –110°C and 1,1-[bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)]ethene (**2a**) (25 mg, 0.10 mmol) in THF (0.1 mL) successively. The resulting mixture was allowed to gradually warm up to room temperature and stirred for 12 h. The reaction mixture was quenched with three drops of sat. aq.NH_4Cl, and diluted with diethyl ether (10 mL) and water (3 mL). The organic layer was separated, dried over anhydrous magnesium sulfate, and concentrated *in vacuo* to give a colorless solid, which was purified by column chromatography (200 mesh silica gel, hexane/ethyl acetate 10 : 1) to give **5a** (22 mg, 72% yield). Mp 140 °C (dec). R_f 0.33 (hexane/ethyl acetate 10 : 1). ^1H NMR ($CDCl_3$) δ 1.28 (s, 24H), 5.85 (d, J = 3.9 Hz, 2H), 5.96 (d, J =3.9 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 24.8, 83.5, 130.6; IR (Nujor) 1460, 1375, 1340, 1300, 1277, 1218, 1120, 1102, 959, 880, 847, 740, 682 cm^{-1}. MS *m/z* 307 (M^++1, 7.0), 306 (M^+, 40.0), 305 (M^+-1, 19.6), 291 (M^+-Me, 8.5), 165 (100). Anal. Calcd for $C_{16}H_{28}B_2O_4$: C, 62.80; H, 9.22. Found: C, 62.53; H, 9.42.

2,3-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-1,3-diene (5b). Yield: 80% (*E*/*Z* = 80/20). (*E*)-**5b** Colorless oil. R_f 0.57 (hexane/ethyl acetate 4 : 1). ^1H NMR ($CDCl_3$) δ 1.27 (s, 12H), 1.31 (s, 12H), 5.22 (dd, J = 10.0, 1.9 Hz, 1H), 5.33 (dd, J = 16.7, 1.9 Hz, 1H), 5.79 (s, 2H), 6.80 (d, J = 10.0 Hz, 1H), 7.01 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 24.0, 24.9, 83.4, 83.5, 119.7, 129.5, 136.8, 144.3. IR (neat) 1560, 1380, 1300, 1210, 1140, 980, 850, 660 cm^{-1}. MS *m/z* 333 (M^++1, 6), 332 (M^+, 25), 317 (M^+-Me, 8), 275 (82), 232 (51), 191 (60), 83 (100). HRMS (FAB) Calcd for $C_{18}H_{30}B_2O_4$: M^+ 323.2330. Found: *m/z* 323.2333. (*Z*)-**5b** Colorless oil. R_f 0.55 (hexane/ethyl acetate 4 : 1). ^1H NMR ($CDCl_3$) δ 1.24 (s, 24H), 5.20 (dd, J = 9.7, 2.2 Hz, 1H), 5.38 (dd, J = 16.5, 2.2 Hz, 1H), 5.60 (d, J = 3.9, 1H), 6.01 (d, J = 3.9, 1H), 6.68 (m, 1H), 6.83 (d, J = 11.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 22.6, 24.7, 83.4, 83.5, 120.3, 131.4, 134.4, 134.2, 141.6. IR (neat) 1560, 1380, 1300, 1210, 1140, 980, 850, 660 cm^{-1}. MS *m/z* 333 (M^++1, 2), 332 (M^+, 9), 317 (M^+-Me, 1), 231 (5), 191 (67), 84 (100). HRMS (FAB) Calcd for $C_{18}H_{30}B_2O_4$: M^+ 323.2330. Found: *m/z* 323.2332. The isomer ratio was determined based on ^1H NMR signals : (*E*)-**5b**: δ 5.79 (s, 2H); (*Z*)-**5b** δ 6.01 (d, J = 3.9, 1H).

2,3-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dodeca-1,3-dien-5-yne (5c). Yield: 38% (*E* only). Colorless oil. R_f 0.60 (hexane/ethyl acetate 4 : 1). ^1H NMR ($CDCl_3$) δ

0.91 (t, J = 10.0 Hz, 3H), 1.27 (m, 2H), 2.36 (t, J = 10.0 Hz, 2H), 5.70 (s, 1H), 5.79 (d, J = 3.0 Hz, 1H), 5.85 (d, J = 3.0 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 14.1, 19.9, 20.0, 24.8, 24.9, 28.8, 31.4, 83.4, 83.5, 95.3, 97.0, 109.0, 120.7, 131.3, 133.3. IR (neat) 1575, 1360, 1300, 1250, 1200, 1140, 960, 840 cm^{-1}. MS *m/z* 415 (M^++1, 4), 414 (M^+, 18), 399 (M^+-Me, 5), 357 (17), 273 (28), 83 (100). HRMS (FAB) Calcd for $C_{24}H_{40}B_2O_4$: M^+ 414.3113. Found: *m/z* 414.3116.

[1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allylidene]cyclohexane (5d). Yield: 85%. Colorless oil. R_f 0.52 (hexane/ethyl acetate 4 : 1). ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 24H), 1.44-1.64 (brs, 6H), 2.16 (m, 2H), 2.43 (m, 2H), 5.47 (d, J = 4.0 Hz, 1H), 5.88 (d, J = 4.0 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 24.7, 24.9, 26.8, 28.5, 28.8, 32.6, 35.0, 82.8, 83.3, 129.9, 154.1. IR (neat) 1600, 1440, 1370, 1300, 1220, 1140, 1100, 1010, 980, 860, 850 cm^{-1}. MS *m/z* 375 (M^++1, 5), 374 (M^+, 19), 359 (M^+-Me, 9), 83 (100). Anal. Calcd for $C_{21}H_{36}B_2O_4$: C, 67.42; H, 9.70. Found: C, 67.52; H, 9.90.

[1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allylidene]cyclopentane (5e). Yield: 74%. Colorless oil. R_f 0.57 (hexane/ethyl acetate 4 : 1). ^{1}H NMR ($CDCl_3$) δ1.25 (s, 12H), 1.26 (s, 12H), 1.67 (m, 4H), 2.30 (t, J = 6.0 Hz, 1H), 2.58 (t, J = 6.0 Hz, 1H), 5.55 (d, 4.0 Hz, 1H), 5.89 (d, J = 4.0 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 24.8, 24.9, 26.5, 29.7, 30.3, 33.4, 33.7, 82.7, 83.2, 129.6, 161.5.IR (neat) 1600, 1460, 1375, 1330, 1200, 1140, 1020, 980, 900, 875, 600 cm^{-1}. MS *m/z* 361 (M^++1, 9), 360 (M^+, 37), 345 (M^+-Me, 8), 203 (100). Anal. Calcd for $C_{20}H_{34}B_2O_4$: C, 66.71; H, 9.52. Found: C, 66.76; H, 9.31.

One-pot synthesis of 5a. Butyllithium in hexane (1.56 M, 0.32 mL, 0.49 mmol) was added to a solution of 2,2,6,6-tetramethylpiperidine (84 μL, 0.50 mmol) in THF (1 mL) and diethyl ether (0.5 mL) at 0 °C, and the resulting solution was stirred at 0 °C for 5 min. This solution was added to a THF solution of vinyl bromide (1.00 M, 0.50 mL, 0.50 mmol) at –110°C. Successively bis(pinacolato)diboron (**1**) (25 mg, 0.100 mmol) in THF (0.1 mL) was added. The resulting mixture was allowed to gradually warm up to room temperature and stirred for 12 h, quenched with 3 drops of sat. aq.NH_4Cl, and diluted with diethyl ether (10 mL) and water (3 mL). The organic layer was separated, dried over anhydrous magnesium sulfate, and concentrated in vacuo to give a colorless solid, which was purified by column chromatography (200 mesh silica gel, hexane/ethyl acetate 10 : 1) to give **5a** (25 mg, 82% yield).

2-Dimethylphenylsilyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)buta-1,3-diene (6a). Butyllithium in hexane (1.56 M, 0.32 mL, 0.49 mmol) was added to a solution of 2,2,6,6-tetramethylpiperidine (0.084 mL, 0.50 mmol) in a mixture of THF (1 mL) and diethyl ether

(0.5 mL) at 0 °C, and the resulting solution was stirred at 0 °C for 5 min. To this solution was added a THF solution of vinyl bromide (1.00 M, 0.50 mL, 0.50 mmol) at –110°C and 1-silyl-1-borylethene (**4a**) (29 mg, 0.100 mmol) in THF (0.1 mL) successively. The resulting mixture was allowed to gradually warm up to room temperature and stirred for 12 h. Work up as above followed by column chromatography (200 mesh silica gel, hexane/ethyl acetate 10 : 1) gave **6a** (25 mg, 80% yield). R_f 0.36 (hexane/ethyl acetate 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.40 (s, 6H), 1.23 (s, 12H), 5.51 (d, *J* = 3.2 Hz, 2H), 5.73 (d, *J* = 3.2 Hz, 1H), 5.90 (d, *J* = 3.2 Hz, 1H), 7.26-7.60 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 24.8, 83.5, 130.6 IR (neat) 1460, 1375, 1340, 1300, 1277, 1218, 1120, 1102, 959, 880, 847, 740, 682 cm^{-1}. MS *m/z* 307 (M^++1, 7.0), 306 (M^+, 40.0), 305 (M^+-1, 19.6), 291 (M^+-Me, 8.5), 165 (100). HRMS (FAB) Calcd for $C_{24}H_{40}B_2O_4$: M^+ 414.3113. Found: *m/z* 414.3116.

Diels-Alder Reaction of 2,3-Bis[(pinacolato)boryl]-1,3-dienes. 2-Phenyl-5,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3a,4,7,7a-tetrahydro-isoindole-1,3-dione (8a). A solution of **5a** (31 mg, 0.100 mmol) and *N*-phenyl maleimide (**7a**) (17 mg, 0.110 mmol) in toluene (2 mL) was stirred at room temperature for 10 h. Concentration of the reaction mixture followed by purification by GPC ($CHCl_3$) gave **8a** as a coloress solid (48 mg, 99% yield). Mp 152 °C. R_f 0.10 (hexane/ethyl acetate 4 : 1). ^{1}H NMR ($CDCl_3$) δ 1.27 (s, 24H), 2.44-2.69 (m, 4H), 3.02-3.11 (m, 2H), 7.30-7.54 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 24.8, 27.4, 39.2, 83.8, 126.9, 128.4, 128.9, 132.1, 178.7. IR (neat) 2923, 2854, 1701, 1460, 1377, 1340, 1311, 1144, 1115, 1024 cm^{-1}. MS *m/z* 480 (M^++1, 5), 479 (M^+, 17), 338 (100), 297 (51), 83 (47). HRMS (FAB) Calcd for $C_{26}H_{35}B_2NO_6$: M^+ 479.2650. Found: *m/z* 479.2651.

5,6-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3a,4,7,7a-tetrahydroisobenzofuran-1,3-dione (8b). Yield: 99%. Colorless oil. R_f 0.53 (hexane/ethyl acetate 1 : 1). ^{1}H NMR ($CDCl_3$) δ 1.28 (s, 24H), 2.50-2.53 (m, 4H), 3.15-3.25 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 24.9, 26.6, 39.4, 84.1, 173.6. IR (neat) 1780, 1450, 1344, 1317, 1143, 1110, 1033, 928, 854 cm^{-1}. MS *m/z* 389 (M^+-Me, 8.5), 346 (34), 263 (100), 149 (21), 83 (48). HRMS (FAB) Calcd for $C_{20}H_{30}B_2O_7$: M^+-Me 389.1943. Found: *m/z* 389.1942.

Dimethyl *cis*-4,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-4-ene-1,2-dicarboxylate (8c). Yield: 94%. Colorless oil. R_f 0.21 (hexane/ethyl acetate 4 : 1). ^{1}H NMR ($CDCl_3$) δ 1.28 (s, 24H), 2.44-2.93 (m, 4H), 2.94-3.00 (t, 6.5 Hz, 2H), 3.66 (s, 6H). ^{13}C NMR ($CDCl_3$) δ 24.9, 28.7, 39.1, 51.8, 83.6, 173.6. IR (neat) 2927, 2931, 1731, 1437, 1342, 1305, 1146, 856, 756, 667 cm^{-1}. MS *m/z* 451 (M^++1, 3), 450 (M^+, 9), 490 (M^+-1, 5), 350 (67), 83 (100). HRMS (FAB) Calcd for $C_{22}H_{36}B_2O_8$: M^+ 450.2596. Found: *m/z* 450.2600.

Dimethyl *trans*-4,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-4-ene-1,2-dicarboxylate (8d). Yield: 90%. Colorless oil. R_f 0.49 (hexane/ethyl acetate 1 : 1). ^1H NMR ($CDCl_3$) δ 1.28 (s, 24H), 2.14-2.34 (m, 2H), 3.67 (s, 6H). ^{13}C NMR ($CDCl_3$) δ 24.7, 31.5, 40.9, 51.7, 83.7, 175.5. IR (neat) 1735, 1624, 1458, 1438, 1377, 1344, 1307, 1145, 1114, 1028, 958, 856, 756 cm^{-1}. MS *m/z* 451 (M^++1, 3), 450 (M^+, 9), 490 (M^+-1, 5), 350 (67), 83 (100). Anal. Calcd for $C_{22}H_{36}B_2O_8$: C, 58.70; H, 8.06. Found: C, 58.40; H, 7.79.

Methyl 3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-3-enecarboxylate (8e). Yield: 65%. Colorless oil. R_f 0.21 (hexane/ethyl acetate 4 : 1). ^1H NMR ($CDCl_3$) δ 1.28 (s, 24H), 1.95-3.66 (m, 7H), 3.66 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 24.8, 24.9, 28.3, 30.6, 39.1, 51.1, 83.5, 76.4. IR (neat) 2978, 2932, 2839, 1732, 1622, 1147, 1020, 856, 665 cm^{-1}. MS *m/z* 393 (M^++1, 3), 392 (M^+, 12), 391 (M^+-1, 8), 292 (100), 83 (92). Anal. Calcd for $C_{20}H_{34}B_2O_6$: C, 59.45; H, 7.48. Found: C, 59.19; H, 7.34.

***N,N*-Dimethyl 3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-3-enecarboxyamide (8f).** Yield: 99%. Colorless oil. R_f 0.48 (ethyl acetate). ^1H NMR ($CDCl_3$) δ 1.27 (s, 24H), 2.24-2.96 (m, 6H), 2.97 (s, 6H). ^{13}C NMR ($CDCl_3$) δ 24.9, 25.1, 28.7, 31.2, 36.4, 83.5, 175.9. IR (neat) 2978, 2929, 1643, 1456, 1342, 1304, 1146, 1014, 854, 663 cm^{-1}. MS *m/z* 406 (M^++1, 23), 405 (M^+, 100), 350 (72), 205 (64), 83 (53). HRMS (FAB) Calcd for $C_{22}H_{36}B_2O_8$: M^+ 405.2858. Found: *m/z* 450.2852.

3,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-3-enecarbaldehyde (8g). Yield: 61%. Colorless oil. R_f 0.35 (hexane/ethyl acetate 4 : 1). ^1H NMR ($CDCl_3$) δ 1.29 (s, 24H), 1.97-2.02 (m, 1H), 2.19-2.47 (m, 6H), 9.67 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 21.9, 25.0, 27.5, 27.6, 46.0, 83.6, 204.5. IR (neat) 2978, 2925, 2856, 1726, 1620, 1306, 1146, 856, 665 cm^{-1}. MS *m/z* 364 (M^++2, 1), 363 (M^++1, 5), 362 (M^+, 21), 262 (100), 221 (71), 83 (83). HRMS (FAB) Calcd for $C_{22}H_{36}B_2O_8$: M^+ 362.2436. Found: *m/z* 362.2435.

1-[3,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-3-enyl]ethan-1-one (8h). Yield: 78%. Colorless oil. R_f 0.25 (hexane/ethyl acetate 4 : 1). ^1H NMR ($CDCl_3$) δ 1.28 (s, 24H), 1.35-1.55 (m, 1H), 1.85-2.00 (m, 2H), 2.10-2.20 (s, 3H), 2.20-2.60 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 24.2, 24.9, 28.1, 28.6, 30.1, 47.1, 83.5, 211.8. IR (neat) 2978, 2928, 1713, 1621, 1305, 1269, 1213, 1147, 1113, 856, 667 cm^{-1}. MS *m/z* 378 (M^++2, 1), 377 (M^++1, 4), 376 (M^+, 19), 318 (15), 276 (100), 83 (79). HRMS (FAB) Calcd for $C_{22}H_{36}B_2O_8$: M^+ 376.2592. Found: *m/z* 376.2592.

Dimethyl 4,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexa-1,4-diene-1,2-dicarboxylate (8i). Yield: 73%. Colorless oil. R_f 0.25 (hexane/ethyl acetate 4 : 1). ^1H

NMR ($CDCl_3$) δ 1.26 (s, 24H), 3.08 (s, 4H), 3.79 (s, 6H). ^{13}C NMR ($CDCl_3$) δ 24.8, 30.2, 52.1, 83.2, 132.1, 168.5. IR (neat) 2978, 2928, 1718, 1371, 1346, 1312, 1269, 1148, 856 cm^{-1}. MS *m/z* 449 (M^++1, 1), 448 (M^+, 4), 447 (M^+-1, 3), 289 (75), 275 (100), 83 (79). HRMS (FAB) Calcd for $C_{22}H_{34}B_2O_8$: M^+ 448.2440. Found: *m/z* 448.2440.

2-Phenyl-5,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-vinyl-3a,4,7,7a-tetrahydroisoindole-1,3-dione (8j). Yield: 76%. Colorless oil. R_f 0.40 (hexane/ethyl acetate 2 : 1). ^1H NMR ($CDCl_3$) δ 1.29, 248-2.88 (m, 2H), 3.06-3.26 (m, 2H), 3.69 (dd, *J* = 8.8, 5.8 Hz, 1H), 5.13 (t, *J* = 10.4 Hz, 1H), 5.26 (s, 1H), 5.73 (dt, *J* = 16.8, 7.2 Hz, 1H), 7.21-7.50 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 24.9, 25.4, 29.8, 38.4, 43.6, 83.9, 118.8, 126.5, 128.4, 129.0, 132.0, 132.1, 177.1, 179.0. IR (neat) 2978, 2926, 2855, 2341, 1774, 1713, 1599, 1502, 1385, 1344, 1311, 1145, 758, 692, 667 cm^{-1}. MS *m/z* 507 (M^++2, 4), 506 (M^++1, 2), 505 (M^+, 71), 405 (66), 364 (72), 347 (74), 323 (65), 221 (71), 83 (100). HRMS (FAB) Calcd for $C_{22}H_{36}B_2O_8$: M^+ 505.2807. Found: *m/z* 505.2805.

Metalation of 2,3-Bis[(pinacolato)boryl]-1,3-butadiene. 1-Dimethylphenylsilyl-2,3,4-tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-ene (9). A mixture of **5a** (31 mg, 0.100 mmol), (dimethylphenylsilyl)(pinacolato)borane (26 mg, 0.10 mmol), $Pt(PPh_3)_4$ (3.7 mg, 3.0 μmol) in toluene (2 mL) was heated at 80 °C for 12 h. The reaction mixture was diluted with diethyl ether (10 mL) and washed with water (3 mL). The organic layer was then separated, dried over anhydrous $MgSO_4$, and concentrated. The resulting crude product was purified by column chromatography (silica gel) to give **9** as a colorless oil (32 mg, 56% yield). R_f 0.40 (hexane/ethyl acetate 2 : 1). ^1H NMR ($CDCl_3$) δ 0.3 (s, 6H), 1.20 (s, 12H), 1.21 (s, 12H), 1.22 (s, 1.23), 1.80 (s, 2H), 2.03 (s, 2H). ^{13}C NMR ($CDCl_3$) δ 0.8, 7.5, 21.7, 30.4, 89.2, 125.1, 125.5, 128.6, 132.9, 137.4, 196.5. MS *m/z* 569 (M^++1, 4), 568 (M^+, 2), 567 (M^+-1 71), 405 (66), 364 (72), 347 (74), 323 (65), 221 (71), 83 (100). HRMS (FAB) Calcd for $C_{36}H_{51}B_3O_6Si$: M^+ 568.3734. Found: *m/z* 568.3730.

1,2,3,4-Tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-ene (10). A mixture of **5a** (31 mg, 0.100 mmol), bis(pinacolato)diboron (25 mg, 0.100 mmol), $Pt(PPh_3)_4$ (3.7 mg, 3.0 μmol) in toluene (2 mL) was heated at 80 °C for 12 h. Work up and column chromatography (silica gel) gave **10** as a colorless oil (55 mg, 99% yield). R_f 0.40 (hexane/ethyl acetate 2 : 1). ^1H NMR ($CDCl_3$) δ 1.20 (s, 24H), 1.25 (s, 24H), 1.83 (s, 4H). ^{13}C NMR ($CDCl_3$) δ 19.8 (brs), 24.7, 24.8, 82.8, 83.1, 126 (brs). MS *m/z* 561 (M^++1, 10), 560 (M^+, 11), 545 (M^+-Me, 5), 460 (23), 360 (26), 83 (100). HRMS (FAB) Calcd for $C_{28}H_{52}B_4O_8$: M^+ 560.4034. Found: *m/z* 560.4034.

1-Phenyl-3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trimethylstannanyl)pent-3-en-1-one (11). A mixture of **5a** (31 mg, 0.100 mmol), phenyl(trimethylstannanyl)methanone (27 mg, 0.100 mmol), $Ni(COD)_2$ (2.8 mg, 10 μmol) in toluene (2 mL) was heated at 50 °C for 12 h. The reaction mixture was diluted with diethyl ether (10 mL) and washed with water (3 mL). The organic layer was then separated, dried over anhydrous $MgSO_4$, and concentrated. The resulting crude product was purified by column chromatography (silica gel) to give **11** as a colorless oil (57 mg, 99% yield). R_f 0.40 (hexane/ethyl acetate 2 : 1). ^1H NMR ($CDCl_3$) δ 1.29, 248-2.88 (m, 2H), 3.06-3.26 (m, 2H), 3.69 (dd, *J* = 8.8, 5.8 Hz, 1H), 5.13 (t, *J* = 10.4 Hz, 1H), 5.26 (s, 1H), 5.73 (dt, *J* = 16.8, 7.2 Hz, 1H), 7.21-7.50 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 0.7, 7.8, 19.4, 21.6, 21.7, 88.9, 89.2, 124.2, 125.5, 127.8, 128.9, 133.4, 140.1. MS *m/z* 575 (M^++1, 15), 561 (M^+-Me, 35), 307 (36), 154 (100), 83 (39). HRMS (FAB) Calcd for $C_{26}H_{43}B_2O_5Sn$: MH^+ 577.2319. Found: *m/z* 577.2325.

Cross-coupling Reaction of 2,3-Bis[(pinacolato)boryl]-1,3-butadiene. 2,3-Diphenylbuta-1,3-diene (12a). A mixture of **5a** (31 mg, 0.100 mmol), iodobenzene (61 mg, 0.30 mmol), $Pd(OAc)_2$ (2.3 mg, 10.0 μmol), PPh_3 (11 mg, 40 μmol) and 1 M KOH aqueous solution (0.30 mL, 0.30 mmol) in dioxane (2 mL) was heated at 90 °C for 2 h. Work up and purification by column chromatography (silica gel) gave **12a** as a white solid (15 mg, 75% yield). R_f 0.43 (hexane). ^1H NMR ($CDCl_3$) δ 5.32 (d, *J* = 1.0 Hz, 2H), 5.55 (d, *J* = 1.0 Hz, 2H), 7.20-7.50 (m, 10H). ^{13}C NMR ($CDCl_3$) δ 105.3, 126.2, 127.7, 128.4, 134.9, 149.4. MS *m/z* 207 (M^++1, 3), 206 (M^+, 32), 205 (M^+-1, 94), 218 (100).

2,3-Bis(4-methylphenyl)buta-1,3-diene (12b). Yield: 75%. R_f 0.35 (hexane). ^1H NMR ($CDCl_3$) δ 2.33 (s, 6H), 5.29 (m, 2H), 5.54 (m, 2H), 7.06-7.12 (m, 4H), 7.27-7.34 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 21.2, 115.2, 127.2, 128.8, 137.1, 137.2, 149.6. MS *m/z* 235 (M^++1, 3), 234 (M^+, 32), 233 (M^+-1, 94), 218 (100).

2,3-Bis(4-trifluoromethylphenyl)buta-1,3-diene (12c). Yield: 68%. R_f 0.45 (hexane). ^1H NMR ($CDCl_3$) δ 5.43 (d, *J* = 1.1 Hz, 2H), 5.64 (d, *J* = 1.1 Hz, 2H), 7.52 (dd, *J* = 20.8, 8.1 Hz, 8H). ^{13}C NMR ($CDCl_3$) δ 118.6, 124.0 (q, *J* = 271 Hz), 125.3 (q, *J* = 3.3 Hz), 127.7, 129.8 (q, *J* = 32.3 Hz), 143.2, 148.1. MS *m/z* 343 (M^++1, 3), 342 (M^+, 13), 341 (M^+-1, 2), 253 (100).

2,3-Bis(4-methoxyphenyl)buta-1,3-diene (12d). Yield: 81%. R_f 0.32 (hexane). ^1H NMR ($CDCl_3$) δ 3.77 (s, 6H), 5.48 (d, *J* = 1.6 Hz, 2H), 6.85 (d, *J* = 1.6 Hz, 2H), 6.86 (m, 4H), 7.30 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 55.2, 113.5, 114.3, 128.4, 132.5, 149.2, 158.9. MS *m/z* 267 (M^++1, 42), 266 (M^+, 100), 265 (M^+-1, 47), 251 (49), 234 (77), 121 (52).

2,3-Bis(4-biphenyl)-1,3-butadiene (12e). Yield: 65%. R_f 0.46 (hexane). ^1H NMR ($CDCl_3$) δ 5.41 (d, *J* = 1.4 Hz, 2H), 5.68 (d, *J* = 1.4 Hz, 2H), 7.26-7.61 (m, 18H). ^{13}C NMR ($CDCl_3$) δ 116.2, 126.9, 129.2, 129.9, 128.6, 138.9, 140.2, 140.5, 149.1. MS *m/z* 233 (100), 218 (92), 190 (79), 106 (76), 91 (90), 63 (81).

Synthesis of Anolignans. Anolignan B. A mixture of **5a** (31 mg, 0.100 mmol), **13** (55 mg, 0.30 mmol), $Pd(OAc)_2$ (2.3 mg, 10 μmol), PPh_3 (11 mg, 40 μmol) and 1 M KOH aqueous solution (0.30 mL, 0.30 mmol) in dioxane (2 mL) was heated at 90 °C for 2 h, then diluted with diethyl ether (10 mL) and washed with water (3 mL). The organic layer was separated, dried over anhydrous $MgSO_4$, and concentrated. The resulting crude product **14** was purified by column chromatography (silica gel) to give coupled product as a colorless solid (27 mg, 76% yield). To an aqueous solution of KOH (15 M, 1 mL) was added the solution of the whole of the product in EtOH (3 mL) at room temperature and stirred for 2h. Work up and column chromatography (silica gel) gave anolignan B as a white solid (17 mg, 86%). R_f 0.21 (hexane/ethyl acetate 9 : 1). ^1H NMR (CD_3OD) δ 3.37 (s, 4H), 4.81 (s, 2H), 5.12 (s, 2H), 6.55 (d, *J* = 8.5 Hz, 4H), 6.83 (d, *J* = 8.5 Hz, 4H). ^{13}C NMR (CD_3OD) δ 40.9, 115.3, 130.6, 131.9, 147.8, 156.4. MS *m/z* 267 (M^++1, 5), 266 (M^+, 10), 159 (100). Lit.[14b] ^1H NMR (CD_3OD) δ 3.38 (s, 4H), 4.81 (s, 2H), 5.12 (s, 2H), 6.56 (d, *J* = 8.5 Hz, 4H), 6.83 (d, *J* = 8.5 Hz, 4H).

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List of Publications

I. Parts of the present Thesis have been, or are to be, published in the following journals.

Chapter 1

(1) Novel Bifunctional Synthetic Reagents: *gem*-Dimetallic Compounds Derived from Carbenoid Reagents and Interelement Compounds.
Shimizu, M.; Kurahashi, T.; Hiyama, T. *Yuki Gosei Kagaku Kyokai Shi* **2001**, *59*, 1062-1069.

Chapter 2

(2) Geminal Difunctionalization of Alkenylidene-Type Carbenoids by Using Interelement Compounds.
Hata, T.; Kitagawa, H.; Masai, H.; Kurahashi, T.; Shimizu, M.; Hiyama, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 790-792.

(3) Geminal Dimetalation of Alkylidene-Type Carbenoids with Silylboranes and Diborons.
Kurahashi, T.; Hata, T.; Masai, H.; Kitagawa, H.; Shimizu, M.; Hiyama, T. *Tetrahedron* **2002**, *58*, 6381-6395.

Chapter 3

(4) 1-Silyl-1-boryl-2-alkenes: Reagents for Stereodivergent Allylation Leading to 4-Oxy-(*E*)-1-alkenylboronates and 4-Oxy-(*Z*)-1-alkenylsilanes.
Shimizu, M.; Kitagawa, H.; Kurahashi, T.; Hiyama, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 4283-4286.

(5) Stereospecific Silylborylation of α-Chloroallyllithiums: Synthesis and Stereodivergent Allylation of 1-Silyl-1-boryl-2-alkenes.
Kurahashi, T.; Kitagawa, H.; Shimono, K; Shimizu, M.; Hiyama, T., to be submitted.

Chapter 4

(6) *gem*-Silylborylation of an *sp* Carbon: Novel Synthesis of 1-Boryl-1-silyl-2-allenes.
Shimizu, M.; Kurahashi, T.; Kitagawa, H.; Hiyama, T. *Org. Lett.*, to be submitted.

Chapter 5

(7) Novel Synthesis of 2,3-Bisboryl-1,3-dienes from 1-Bromo-1-lithioethene and 1,1-Bisborylalkenes.
Shimizu, M.; Kurahashi, T.; Hiyama, T. *Synlett* **2001**, 1006-1008.

(8) Novel Synthesis of 2,3-Bisboryl-1,3-dienes and Synthetic Applications.
Kurahashi, T.; Shimono, K; Masai, H.; Shimizu, M.; Hiyama, T., to be submitted.

II. Following publications are not included in this Thesis.

(9) Carbostannylation of Alkynes Catalyzed by an Iminophosphine-Palladium Complex.
Shirakawa, E.; Yoshida, H.; Kurahashi, T.; Nakao, Y.; Hiyama, T. *J. Am. Chem. Soc.* **1998**, *120*, 2975-2976.

(10) Diphenylphosphinophenolate: a ligand for the palladium-catalyzed silylation of aryl halides activating simultaneously both palladium and silicon.
Shirakawa, E.; Kurahashi, T.; Yoshida, H.; Hiyama, T. *Chem. Commun.* **2000**, 1895-1896.

(11) Palladium-Iminophosphine-Catalyzed Alkynylstannylation of Alkynes.
Yoshida, H.; Shirakawa, E.; Kurahashi, T.; Nakao, Y.; Hiyama, T. *Organometallics* **2000**, *19*, 5671-5678.

(12) Novel Synthesis of Polymetal-substituted Methanes.
Kurahashi, T.; Kitagawa, H.; Shimizu, M.; Hiyama, T., to be submitted.

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