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Geminal dimetalation of alkylidene-type carbenoids with silylboranes and diborons

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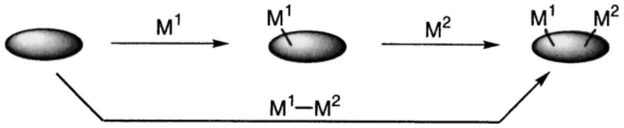
Dedicated to Professor Yoshito Kishi on the occasion of his receipt of the Tetrahedron Prize for Creativity in Organic Chemistry

Abstract—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. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

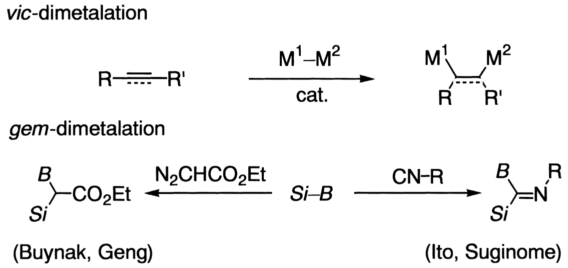
Much attention has been paid on organodimetallic compounds in organic synthesis, because such bimetallic compounds serve as versatile intermediates or reagents for further elaborative transformations.[1] In view of synthetic methods for organodimetallic compounds, two strategies are conceptually possible (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] It is apparent that the second approach, if feasible, is an attractive and straightforward method.

One of the examples categorized in the second approach is transition metal-catalyzed *vic*-dimetalation of a carbon–carbon unsaturated bond with such an interelement compound as B–B, B–Si, B–Sn, Mg–Si, Mg–Zn, Mg–Sn, Al–Si, Si–Si, Si–Sn, Ge–Ge, or Sn–Sn (Scheme 2).[3] In sharp contrast, *gem*-dimetalation with interelement compounds are limited to the reaction of silylborane with ethyl diazoacetate[4] or isonitriles.[5] In view of the growing interest in *gem*-organodimetallics,[1a,b] novel and efficient synthesis of *gem*-dimetallic compounds via *gem*-dimetalation with interelement compounds should be of great significance.

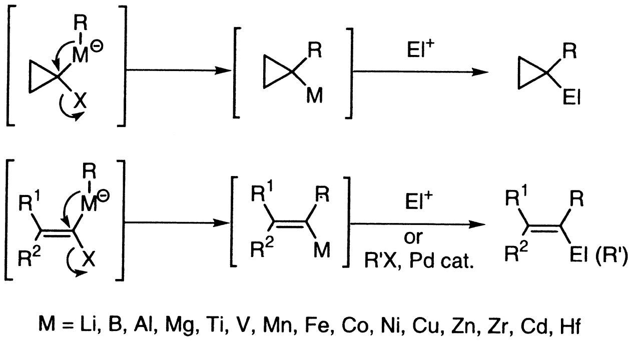


Scheme 1. Synthetic route to organodimetallic compounds.

Ate-type carbenoids generated from *gem*-dihalo compounds



Scheme 2. Examples of dimetalation with interelement compounds.



Scheme 3. 1,2-Migration of a carbonaceous substituent in an ate complex.

Keywords: boron; carbenoids; metalation; silicon.

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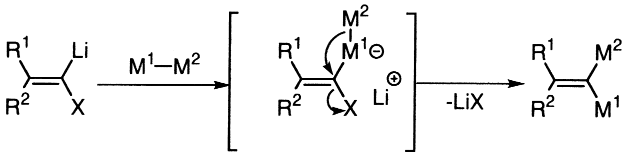


Scheme 4. Synthetic strategy for the synthesis of *gem*-dimetalated compounds from lithium carbenoids and interelement compounds.

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 3). Various kinds of organometallic reagents are applicable to this type of reaction.[6]

We 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 4).[7] We chose silylboranes and diborons 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] Herein we 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 (Fig. 1).[12] In addition, further transformations of the silylborylated and diborylated compounds are disclosed.

2. Results and discussion

2.1. *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 we applied the procedure to dimethylphenylsilyllithium and (+)-(pinanediolato)borane,[14] we obtained (dimethylphenylsilyl)((+)-pinanediolato)borane (**4**) as a novel silylborane in 64% yield.

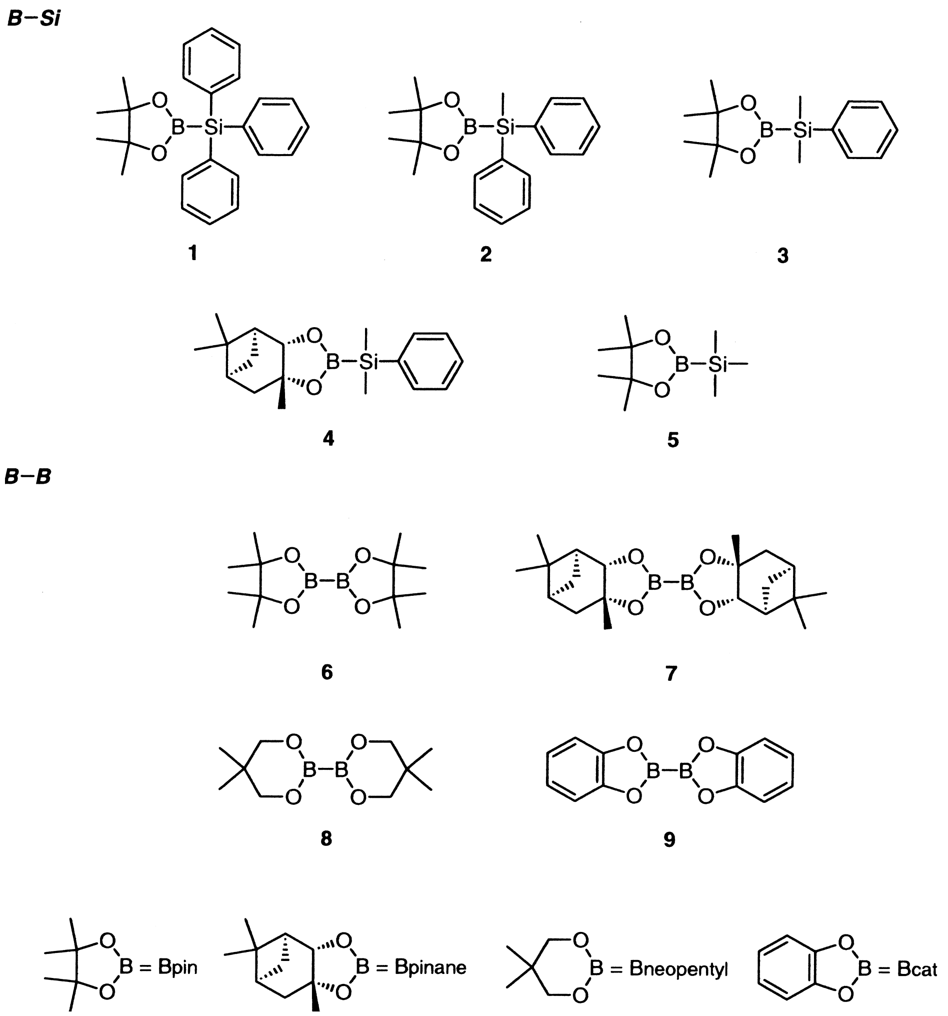
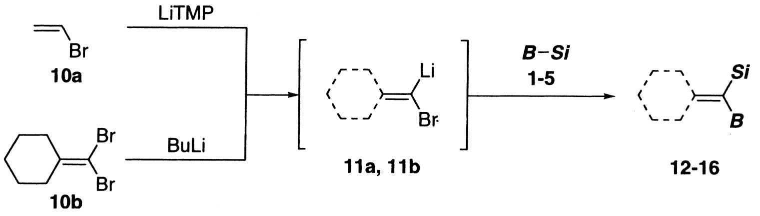


Figure 1. Silylboranes **1**–**5** and diborons **6**–**9**.

Table 1. Reaction of **11a** and **11b** with silylboranes **1–5**



Entry	Silylborane	Carbenoid	Product	Yield (%)[a]
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**[b]	**11a**	**16a**	45
10	**5**[b]	**11b**	**16b**	67

A mixture of **10a** (0.50 mmol), THF (2 mL), and Et$_2$O (1 mL) was treaed with LiTMP (0.50 mmol) and silylborane **1–5** (0.50 mmol) at −10°C for 10 min, then gradually warmed to room temperature. Alternatively, a mixture of **10b** (0.53 mmol), THF (2 mL), and Et$_2$O (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.

[a] Isolated yields based on silylborane **1–5** are given.

[b] A 0.6 M solution in THF/HMPA (5:1) was used.

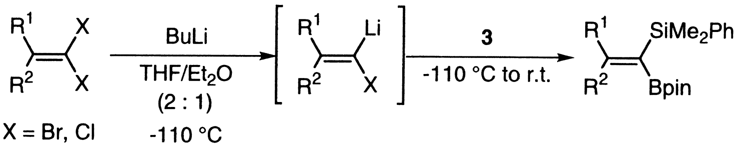
Similarly, we examined the preparation and isolation of (trimethylsilyl)(pinacolato)borane (**5**). Although the formation of **5** was reportedly suggested by GC–MS during the Pt-catalyzed diboration of bis(trimethylsilyl)acetylene with **6**,[15] to our knowledge, no example involving the isolation and use of **5** as a reagent is available. Accordingly, we 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.

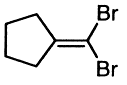
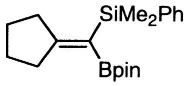
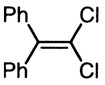
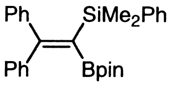
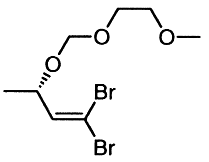
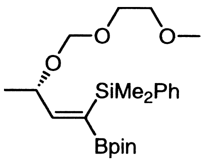
Using 1-bromo-1-lithioethene (**11a**) and (1-bromo-1-lithiomethylene)cyclohexane (**11b**) as a typical alkylidene-type carbenoid, we first investigated the scope of silylboranes on *gem*-silylborylation. Carbenoids **11a** and **11b** in THF were treated with silylboranes **1–5** at −110°C, and the 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 substituent 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.

The best results obtained with **3** in hand, we 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-(methoxyethoxy)methoxy group (MEMO group) was treated with 0.95–0.98 molar amount of BuLi in Et$_2$O 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).

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 2 equiv. 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). Conjugated carbenoids **11g** and **11h**, generated from **10g** and **10h**, respectively, were *gem*-silylborylated with **3** to give diene **21** and enyne **22**. The stereochemistry of **21** was completely controlled to be *Z*, whereas **22** was isolated as a

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



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

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.

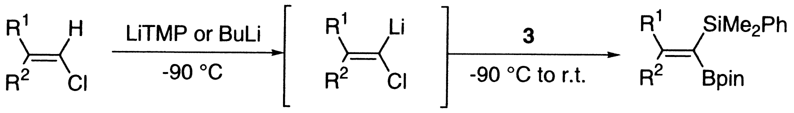
[a] Isolated yields based on **3** are given.

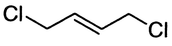
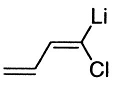
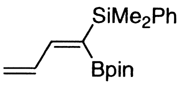
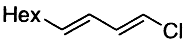
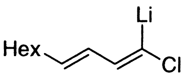
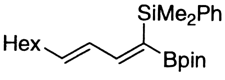
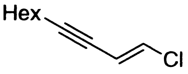
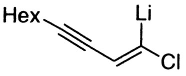
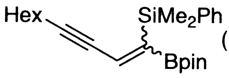
[b] Et_2O (2 mL) was used as a solvent.

stereoisomeric mixture due probably to facile isomerization of carbenoid **11h**.

Stereochemistry of **19** and **21** was confirmed by the chemical transformations shown in Scheme 5: 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**,

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



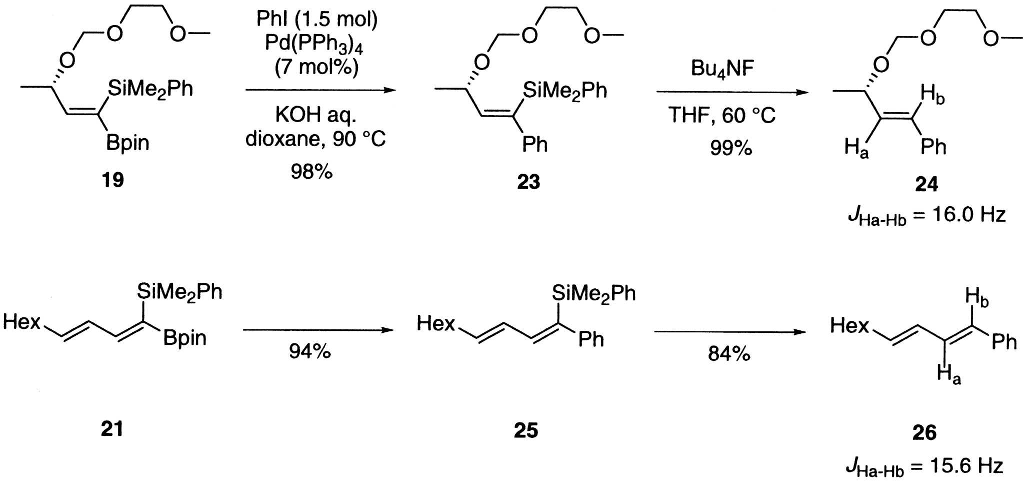
Substrate	Carbenoid	Product	Yield (%)[a]
 **10f**[b]	 **11f**	 **20**	75 (*E* only)
 **10g**[c]	 **11g**	 **21**	89 (*Z* only)
 **10h**[d]	 **11h**	 **22**	49 (*E*:*Z* = 1 : 1)

[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.



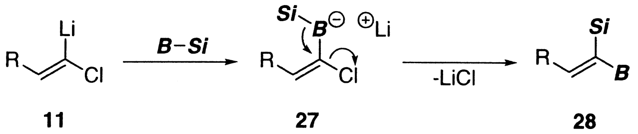
Scheme 5. Stereochemical assignment of **19** and **21**.

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*.

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 6). Monitoring the reaction by TLC (after quenching), the 1,2-migration of a silyl group is apparently taking place above −50°C.

2.2. *gem*-Diborylation of alkylidene-type carbenoids

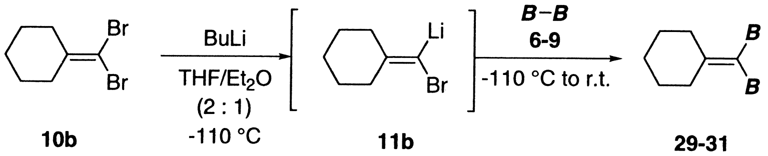
We next studied *gem*-diborylation of alkylidene-type carbenoids with diborons. Using **11b** as a typical carbenoid, commercially available diborons **6–9** were screened (Fig. 1). The results are shown in Table 4. Bis(pinacolato)diboron (**6**)[19] and optically active bis((+)-pinanediolato)diboron (**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).



Scheme 6. Plausible mechanism of *gem*-silylborylation of alkylidene-type carbenoids with silylborane.

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. Dichloroalkene **10d** could also be applied, which after chlorine–lithium exchange underwent *gem*-diborylation, giving rise to **34** in 40% yield, while optically active 1,1-diborylalkene **35** was obtained from the corresponding dibromide **10e** in 65% yield. Double deprotonation of **10f** generated **11f** which reacted with **6** to afford 1,1-diborylbutadiene **36** in 89% yield. *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.

Table 4. Reaction of **11b** with diboron **6–9**

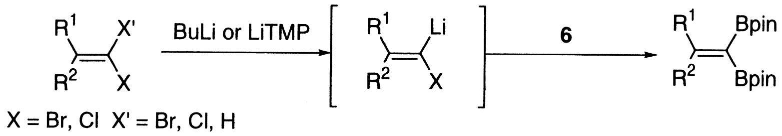


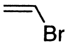
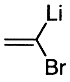
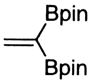
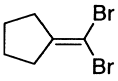
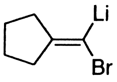
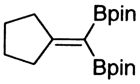
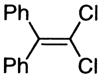
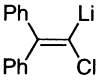
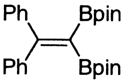
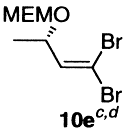
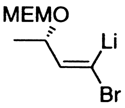
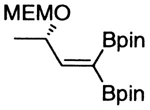
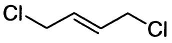
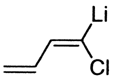
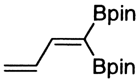
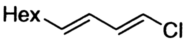
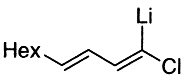
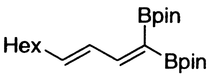
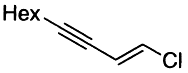
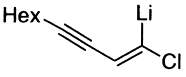
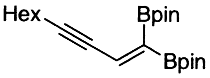
Entry	***B–B***	Product	Yield (%)[a]
1	**6**	**29**	93
2	**7**	**30**	>99
3	**8**	**31**	15
4	**9**	–	<1

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.

[a] Isolated yields based on diboron are given.

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



Substrate	Carbenoid	Product	Yield (%)[a]
 **10a**[b]	 **11a**	 **32**	91
 **10c**[c]	 **11c**	 **33**	96
 **10d**[c]	 **11d**	 **34**	40
 **10e**[c,d]	 **11e**	 **35**	65
 **10f**[e]	 **11f**	 **36**	89
 **10g**[f]	 **11g**	 **37**	82
 **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.

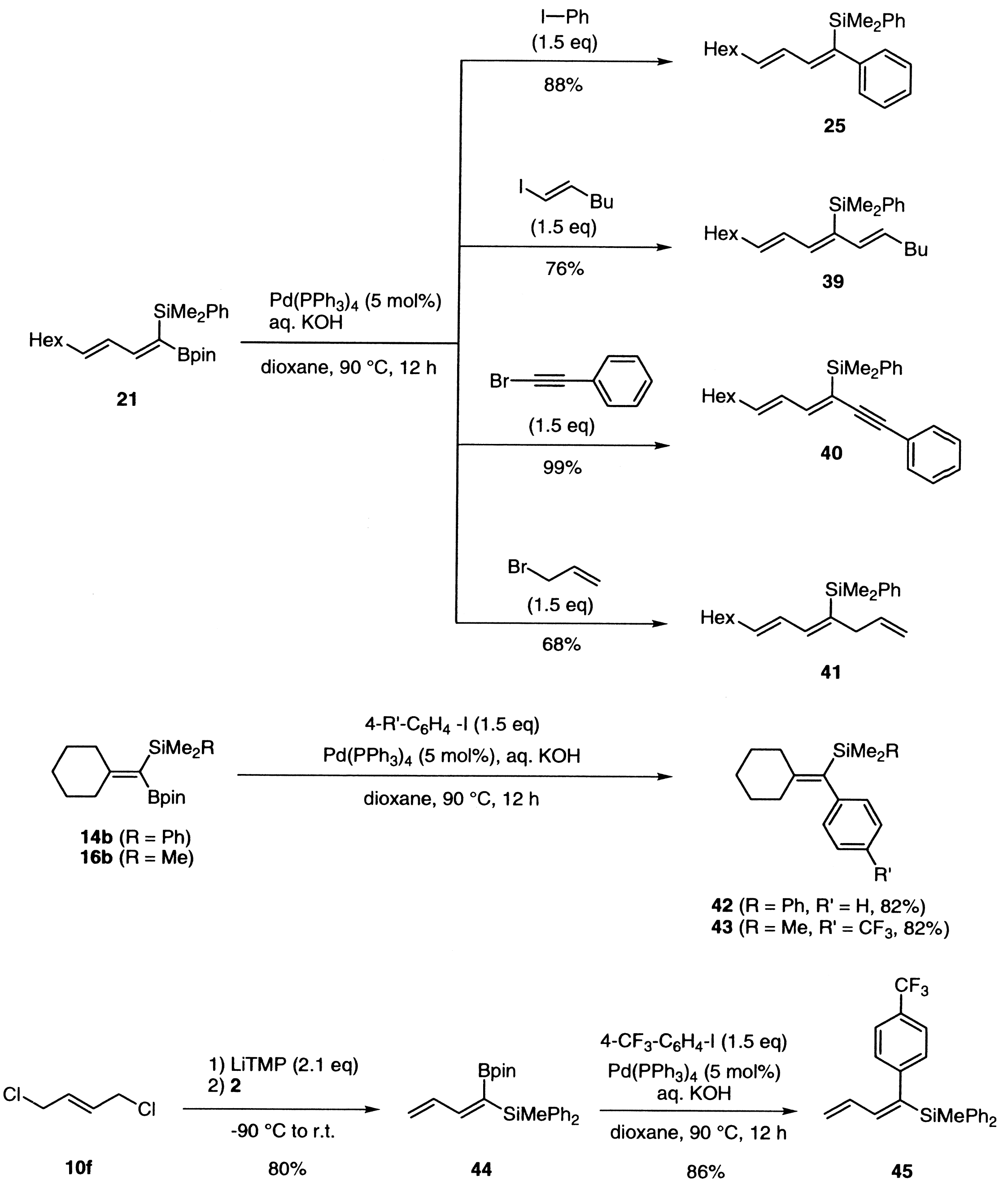
[e] A solution of **10f** (0.50 mmol) in THF (2 mL) was treated with LiTMP (1.05 mmol) and **6** (0.50 mmol) at −90°C for 15 min, then gradually warmed to room temperature.

[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.

2.3. Synthetic applications of *gem*-dimetallic compounds

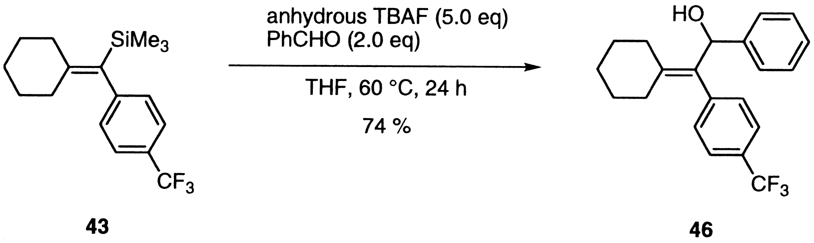
Since *gem*-silylborylation and -diborylation were established as a novel way to *gem*-diorganometallics, we further studied the carbon–carbon bond extension of the *gem*-dimetalated compounds in order to demonstrate the synthetic utility of such bifunctional molecules. Some examples of Suzuki–Miyaura coupling reaction of **21** are firstly illustrated in Scheme 7.[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



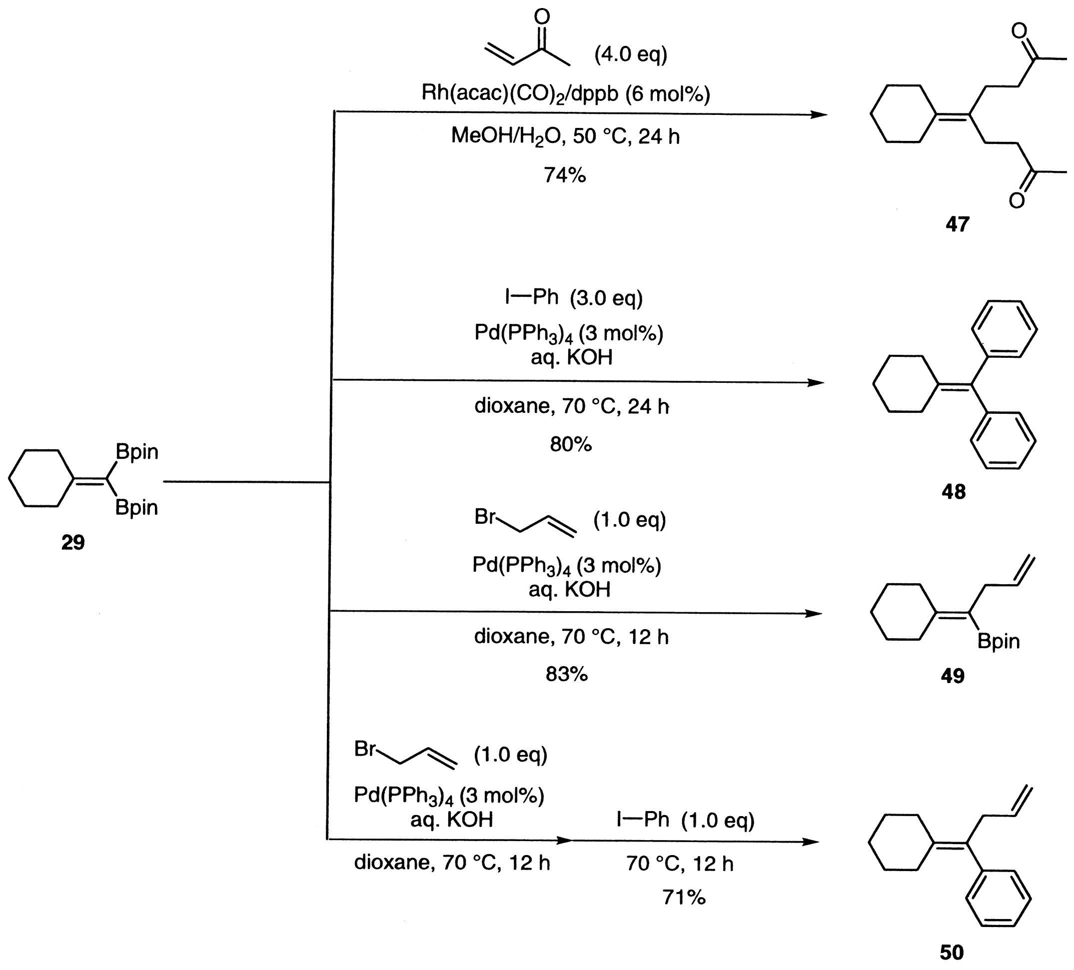
Scheme 7. Boron-mediated cross-coupling reaction of *gem*-silylborylated compounds.

80% yield, did not affect the Pd-catalyzed coupling reaction with 1-iodo-4-trifluoromethylbenzene as demonstrated at the bottom of Scheme 7. In all cases, any kinds of silyl groups including a trimethylsilyl group were not lost inspite of the basic conditions.

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



Scheme 8. Silicon-mediated coupling reaction.



Scheme 9. Synthetic applications of *gem*-diborylated compound.

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 8).

Finally shown is the synthetic application of diborylated compound **29** (Scheme 9). 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 a good overall yield.

3. Conclusion

In conclusion, we 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.

4. Experimental

4.1. 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). ^1H NMR spectra were measured on a Varian Mercury 200 (^1H, 200 MHz) spectrometer. Chemical shifts of ^1H NMR are expressed in parts per million downfield relative to an internal tetramethylsilane ($\delta=0$ ppm) or chloroform ($\delta=7.26$ 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 ($\delta=0$ ppm). ^{19}F NMR spectra were measured on a Varian Mercury 200 (^{19}F, 188 MHz) spectrometer with $CFCl_3$ as an internal standard ($\delta=0$ 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, −98, or −78°C was effected using pentane with liquid nitrogen, methanol with liquid nitrogen, or methanol with dry ice, respectively.

4.2. 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.

4.3. Preparation of silylborane 4 and 5

4.3.1. (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 (1.0 g, 64% yield). $[\alpha]_D^{25}=4.01°$ (*c* 0.92, $CHCl_3$). R_f 0.50 (hexane/ethyl acetate 10:1). ^{1}H 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.

4.3.2. (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 (1.1 M, 1.9 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 **5** 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.

4.4. Typical procedure for *gem*-silylborylation of alkylidene-type carbenoids generated by deprotonation

4.4.1. 1-Dimethylphenylsilyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (14a). To a solution of vinyl bromide **10a** (1.0 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). ^{1}H 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.

4.5. Typical procedure for *gem*-silylborylation of alkylidene-type carbenoids generated by halogen–lithium exchange

4.5.1. [Dimethylphenylsilyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene]cyclohexane (14b). Butyllithium in hexane (1.5 M, 1.5 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.

4.5.2. 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.

4.5.3. 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.

4.5.4. 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.

4.5.5. {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.

4.5.6. 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.

4.5.7. [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.

4.5.8. [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.

4.5.9. 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). ^{1}H 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.

4.5.10. (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). ^{1}H 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.

4.5.11. (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). ^{1}H 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.

4.5.12. (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). ^{1}H 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, 11.0 Hz, 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.

4.5.13. (*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.

4.5.14. Cross-coupling/protodesilylation of 19. A mixture of **19** (42 mg, 0.10 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.

4.5.15. (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, 6.8 Hz, 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.

4.5.16. (1*E*,3*E*)-1-Phenyl-1,3-decadiene (26). 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). The registry number for (**26**): [62060-09-7].[26]

4.6. Typical procedure for *gem*-diborylation of alkylidene-type carbenoids

4.6.1. [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$_4$Cl (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, 24H), 1.50–1.70 (m, 6H), 2.30–2.45 (m, 4H). ^{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%.

4.6.2. {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.

4.6.3. 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.

4.6.4. 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). ^{1}H 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%.

4.6.5. [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). ^{1}H 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.

4.6.6. 1,1-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2-diphenylethene (34). Yield: 40%. Colorless needles. Mp 182.8°C. R_f 0.41 (hexane/ethyl acetate 4:1). ^{1}H 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.

4.6.7. (*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). ^{1}H 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%.

4.6.8. 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). ^{1}H 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, 1H). ^{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.

4.6.9. (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). ^{1}H 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, 1H), 6.49 (dd, J=15.1, 11.0 Hz, 1H), 7.32 (d, J=11.0 Hz, 1H). ^{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%.

4.6.10. 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). ^{1}H 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%.

4.7. Cross-coupling of *gem*-silylborylated compounds

4.7.1. (5*E*,7*Z*,9*E*)-7-Dimethylphenylsilyl-hexadeca-5,7,9-triene (39). A mixture of **21** (0.10 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). ^{1}H 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.

4.7.2. (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.

4.7.3. (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.

4.7.4. [(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.

4.7.5. [(Trimethylsilyl)(4-trifluoromethyphenyl)metylene]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.

4.7.6. (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). ^{1}H 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.

4.7.7. (1*Z*)-1-(4-Trifluoromethylphenyl)buta-1,3-diene (45). Yield: 85%. Colorless oil. R_f 0.67 (hexane/ethyl acetate 10:1). ^{1}H 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.

4.8. Silicon mediated coupling reaction

4.8.1. 2,2-Cyclohexylidene-1-phenyl-2-(4-trifluoromethylphenyl)ethanol (46). A THF solution of anhydrous Bu_4NF (1.0 M, 1.0 mL, 1.0 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). ^{1}H 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.

4.9. Boron mediated coupling reaction of *gem*-diborylated compounds

4.9.1. 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, 0.10 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). ^{1}H 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.

4.9.2. 1,1-Diphenylmethylenecyclohexane (48). A mixture of **29** (35 mg, 0.10 mmol), iodobenzene (61 mg, 0.30 mmol), $Pd(PPh_3)_4$ (3.5 mg, 3 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). ^{1}H 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.

4.9.3. 4,4-Cyclohexylidene-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-butene (49). A mixture of **29** (35 mg, 0.10 mmol), allyl bromide (12 mg, 0.10 mmol), $Pd(PPh_3)_4$ (3.5 mg, 3.0 μmol), and 3 M KOH aqueous solution (0.10 mL, 0.30 mmol) in dioxane (1 mL) was heated at 70°C for 12 h. Workup followed by column chromatography on silica gel to give **49** as a colorless oil (22 mg, 83% yield). R_f 0.61 (hexane/ethyl acetate 3:1). ^{1}H 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.

4.9.4. 3,3-Cyclohexylidene-3-phenyl-1-butene (50). A mixture of **29** (35 mg, 0.10 mmol), allyl bromide (12 mg, 0.10 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, 0.10 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 to give **50** as a colorless oil (15 mg, 71% yield). R_f 0.60 (hexane/ethyl acetate 9:1). ^{1}H 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.

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