Pergamon

Tetrahedron 55 (1999) 8787–8800

TETRAHEDRON

Regio- and Stereoselective Synthesis of (Z)-β-Silylalkenylboranes by Silaboration of Alkynes Catalyzed by Palladium and Platinum Complexes

Michinori Suginome, Takanori Matsuda, Hiroshi Nakamura, and Yoshihiko Ito*

Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan

Received 19 February 1999; revised 30 March 1999; accepted 6 April 1999

Abstract: Addition of the silicon–boron bonds of (dimethylphenylsilyl)boranes having pinacol, catechol, and diethylamino groups on the boron across carbon–carbon triple bonds is effectively catalyzed by palladium complexes. The silaboration of a variety of terminal alkynes took place with almost complete regio- and stereoselectivity to afford (Z)-1-boryl-2-silylalkenes in high yields. The silaboration products were subjected to the palladium-catalyzed cross-coupling reaction with aryl iodide and rhodium-catalyzed conjugate addition to methyl vinyl ketone, giving β-silylstyrene derivatives and δ-silyl-γ,δ-unsaturated ketones, respectively, in high yields.

Introduction

Activation of boron-containing σ-bonds by transition metal catalysts has gained increasing interest in organic synthesis, providing new access to the synthetically useful organoborane derivatives.[1] Catalytic hydroboration of unsaturated organic molecules through B–H bond activation has found wide application to organic synthesis,[2] which includes asymmetric synthesis by means of enantioselective hydroboration reactions with appropriate optically active ligands on the transition metals.[3] Recently, it has been disclosed that boron–element bonds such as B–B[4] and B–Sn[5] are effectively activated by transition metal catalyst to undergo insertion reactions of unsaturated organic compounds. It is suggested that the reactions involve a mechanism quite similar to that of transition metal catalyzed bis-silylation reactions with Si–Si bonds, which have been investigated extensively.[6,7]

Based upon the new catalytic system for Si–Si bond activation, which enabled the bis-silylation reactions synthetically useful, our attention was directed to transition metal catalyzed activation of Si–B bond. In spite of the fact that compounds having Si–B bonds, i.e., silylboranes, were already prepared in early 1960s,[8–10] transition metal catalyzed reaction of the silylboranes has never been reported until our preliminary reports on the alkyne silaboration[11] and related reactions[12–14] appeared.[15] Buynak and Geng reported that no reaction took place at all in an attempted silaboration of alkenes in the presence of rhodium catalyst.[9]

Herein, we describe the full detail of palladium- and platinum-catalyzed addition reaction of silylboranes, i.e., silaboration reaction, with alkynes. Usefulness of the silaboration in organic synthesis

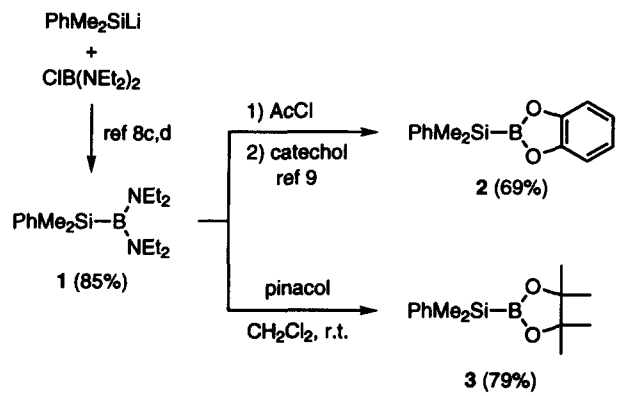
Dedicated to Professors Teruaki Mukaiyama and David A. Evans on the occasion of their receipt of the 1998 Tetrahedron Prize.

0040-4020/99/$ - see front matter
PII: S0040-4020(99)00444-5

is presented by new selective carbon–carbon bond formation with the silaboration products.

Results and Discussion

Synthesis of Silylboranes. According to the reported procedure,[8c,d,9] a silylborane **1** having two amino ligands on the boron atom was prepared by reaction of dimethylphenylsilyllithium with chlorobis(diethylamino)borane in good yield (Scheme 1). Catechol derivative **2** was prepared from **1** by substitution with catechol via deaminochlorination by acetyl chloride. We also prepared new silylborane derivative **3** having pinacol ligand on the boron by direct reaction of **1** with pinacol at room temperature.

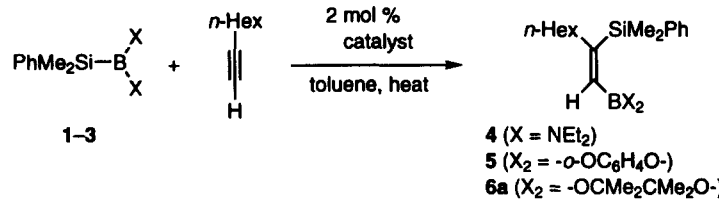


Scheme 1

Silylboranes **1–3** thus prepared were thermally stable and could be stored under inert atmosphere without significant decomposition. They can be handled in air during a short period, though prolonged exposure to the air resulted in gradual decomposition.

Silaboration of 1-Octyne: Optimization of Reaction Conditions. First of all, reactions of the silylboranes **1–3** with 1-octyne were examined in the presence of palladium complex catalysts. Our investigation on the bis-silylation of alkynes prompted us to use a palladium(0)–*tert*-alkyl isonitrile in situ generated for the silaboration.[16–18] Under reflux in toluene, addition of the Si–B bonds of **1–3** across the carbon–carbon triple bond of 1-octyne, i.e., silaboration, took place in the presence of the catalyst prepared from 2 mol % of $Pd(OAc)_2$and 30 mol % of 1,1,3,3-tetramethylbutyl isocyanide (*t*-OcNC) (Table 1). The silaboration products **4** and **6a** obtained from **1** and **3**, respectively, were isolated by distillation in high yields, whereas catechol derivative **5** was converted to pinacol derivative **6a** by ligand substitution prior to distillation due to its thermal instability (entries 1–3).

Table 1. Reaction of 1-Octyne with Silylborane **1–3** in the Presence of Transition Metal Catalysts[a]



1–3

4 (X = NEt_2)
5 (X_2 = -*o*-OC_6H_4O-)
6a (X_2 = -$OCMe_2CMe_2O$-)

entry	silylborane	catalyst	temp (°C)	time (h)	yield (%)	regioisomeric ratio
1	**1**	$Pd(OAc)_2$/*t*-OcNC	110	2	94	>99:1
2	**2**	$Pd(OAc)_2$/*t*-OcNC	110	2	78[b]	>99:1
3	**3**	$Pd(OAc)_2$/*t*-OcNC	110	1	94	>99:1
4	**3**	$Pd(OAc)_2$/*t*-OcNC	50	3	89	>99:1
5[c]	**3**	$Pd(OAc)_2$/*t*-OcNC	110	2	98	>99:1
6	**3**	$Pd(OAc)_2$/*c*-HexNC	110	4	95	>99:1
7	**3**	$Pd_2(dba)_3{\cdot}CHCl_3/P(OEt)_3$	110	4	99	>99:1
8	**3**	$PdCl_2(PPh_3)_2$	110	2	89	>99:1
9	**3**	$Pd(PPh_3)_4$	110	1	<20	>99:1
10	**3**	$Pt(PPh_3)_4$	110	1	80	90:10
11	**3**	$Pt(PPh_3)_4$	50	3	24	95:5
12	**3**	$RhCl(PPh_3)_3$	110	1	0	–

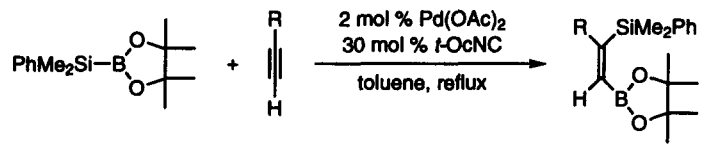
[a] Silylborane and 1-octyne (1.5 equiv) were reacted in toluene in the presence of 2 mol % of each catalyst unless otherwise noted (Pd/RNC = 1/15, $Pd/P(OEt)_3$ = 1/2). [b] Compound **6** was isolated after treatment of the reaction mixture with pinacol. See text. [c] 0.5 mol % of $Pd(OAc)_2$ and 4 mol % of *t*-OcNC were used.

It should be noted that the silaboration of 1-octyne with **1–3** proceeded not only in high yields but also in nearly complete regio- and stereoselectivities to give Z-alkenes **4**, **5**, and **6a** with the boryl groups attached to the terminal sp^2 carbon. In no case, the regio- and stereoisomers were detected by ^{1}NMR spectroscopy of the crude reaction mixtures.

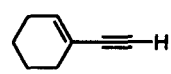
The silaboration reaction of 1-octyne with the pinacol derivative **3** proceeded in the presence of the palladium–isonitrile catalyst even at 50 °C to give **6a** in comparable yield (entry 4). The reaction also proceeded with 0.5 mol % of catalyst to give **6a** in nearly quantitative yield (entry 5). In addition to *tert*-alkyl isonitrile on palladium, which has been crucial for the high catalytic activity in the bis-silylation reactions reported so far,[16–18] a *sec*-alkyl isonitrile, e.g., cyclohexyl isonitrile, effectively worked as a spectator ligand on palladium to promote the silaboration of 1-octyne (entry 6). The silaboration reaction was successfully catalyzed also by palladium complexes with phosphorous ligands such as

$P(OEt)_3$ and PPh_3 (entries 7–9); however, use of $Pd(PPh_3)_4$ resulted in the formation of a complex mixture including the desired product of less than 20% (entry 9), while $PdCl_2(PPh_3)_2$ catalyzed the reaction in high yield (entry 8). A platinum complex also worked as an active catalyst for the silaboration of 1-octyne with **3** at 110 °C, although the regioisomeric silaboration product was accompanied as a by-product in low yield (entry 10). However, the platinum catalyst failed to promote the reaction at 50 °C effectively, resulting in the formation of the silaboration product only in 24% yield (entry 11). As previously reported by Buynak and Geng,[9] Wilkinson's complex was totally ineffective for the silaboration reaction with **3** at 110 °C (entry 12).

Table 2. Silaboration of Terminal Alkynes with **3** in the Presence of Palladium–Isonitrile Catalyst[a]



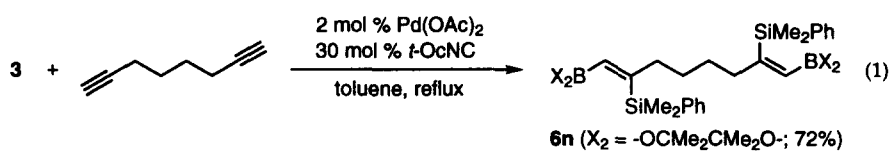
3 **6b–m**

entry	alkyne R—≡—H	product	yield (%)	regioisomeric ratio	stereoisomeric ratio
1	$Cl(CH_2)_3$—	**6b**	87	>99:1	>99:1
2	$NC(CH_2)_3$—	**6c**	77	>99:1	>99:1
3	$TBSOCH_2$—	**6d**	83	>99:1	>99:1
4	$THPO(CH_2)_2$—	**6e**	88	>99:1	>99:1
5	$MEMO(CH_2)_3$—	**6f**	85	>99:1	>99:1
6	$HO(CH_2)_2$—	**6g**	77	>99:1	>99:1
7	Ph—	**6h**	82	>99:1	>99:1
8		**6i**	94	>99:1	>99:1
9	EtO_2C—	**6j**	77	>99:1	>99:1
10	CH_3CO—	**6k**	88	>99:1	>99:1
11	Me_3Si—	**6l**	76	>99:1	96:4
12[b]	H—	**6m**	91	–	90:10

[a] Silylborane, alkyne (1.5 equiv), $Pd(OAc)_2$ (0.02 equiv), and *t*-OcNC (0.30 equiv) were heated in refluxing toluene. [b] Silylborane, $Pd(OAc)_2$ (0.02 equiv), and *t*-OcNC (0.30 equiv) were heated in refluxing toluene under acetylene atmosphere (1 atm).

Silaboration of Terminal Alkynes. With one of the most effective catalyst, the palladium–isonitrile catalyst, in hand, terminal alkynes with a variety of substituents were subjected to the silaboration with the silylborane **3** in refluxing toluene (Table 2). 5-Chloro- and 5-cyano-1-pentyne afforded the corresponding silaboration products **6b** and **6c** in high yields with high regio- and stereoselectivities (entries 1 and 2). Protected alkynols including a silyl-protected propargylic alcohol provided **6d–f** in high yields (entries 3–5). Furthermore, homopropargyl alcohol successfully underwent the silaboration with **3** to give **6g** with high regioselectivity (entry 6). Phenylacetylene and a conjugated enyne provided the corresponding silaboration products **6h** and **6i** in high yields (entries 7 and 8). In the latter case, no 1,4-addition reaction took place at all. Carbon–carbon triple bonds conjugated with ester and ketone groups similarly underwent the addition of the Si–B bond in a 1,2-fashion in high yields (entries 9 and 10). The reactions of these electronically deficient alkynes also proceeded with the regioselectivity identical to that for the other terminal alkynes to give α-silyl-β-boryl α,β-unsaturated carbonyl compounds **6j** and **6k** in high selectivity. Silaboration of trimethylsilylacetylene also proceeded with the same regiochemical preference; however, a small amount of the stereoisomer was formed (entry 11). The silylborane **3** reacted with ethyne under atmospheric pressure in the presence of the palladium–isonitrile catalyst to give 9:1 mixture of (*Z*)- and (*E*)-1-silyl-2-borylethene **6m** in high yield (entry 12). The minor formation of the (*E*)-**6m** can be attributed to palladium-catalyzed isomerization of the (Z)-**6m** under the reaction conditions. Indeed, prolonged reaction time resulted in increase in the *E*/*Z* ratio. It should be noted that the silaboration of ethyne did not take place at all by use of either $Pd_2(dba)_3{\cdot}CHCl_3$–$P(OEt)_3$ or $PdCl_2(PPh_3)_2$ under otherwise identical conditions.

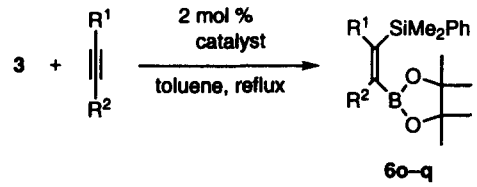
1,7-Octadiyne underwent double silaboration with two equivalents of **3** to give diene **6n**, which has two terminal boryl groups, in high selectivity (eq 1).



6n (X_2 = -$OCMe_2CMe_2O$-; 72%)

Silaboration of Internal Alkynes. Complete *cis*-addition of the Si–B bond of **3** across carbon–carbon triple bond of diphenylacetylene was effected by the palladium–isonitrile complex to furnish (*E*)-1-silyl-2-borylstilbene **6o** in 74% yield (Table 3, entry 1). Similarly, 1-phenyl-1-propyne reacted with **3** under the identical conditions to give the corresponding *cis*-product **6p** in which the silyl group is α to the phenyl group in high yield with good selectivity (entry 2). With this alkyne, use of the platinum catalyst also resulted in the predominant formation of **6p** in comparable yield but in slightly decreased regioselectivity (entry 3). In contrast to the advantage of palladium catalyst over platinum catalyst with respect to catalytic activity as well as selectivity in the silaboration reactions described thus far, the platinum catalyst exhibited superior catalytic activity toward silaboration of 5-decyne. The platinum catalyst afforded *cis*-silaboration product **6q** in 72% yield (entry 5), whereas the palladium–isonitrile catalyst provided **6q** only in low yield (entry 4).

Table 3. Palladium- and Platinum-Catalyzed Silaboration of Internal Alkynes[a]

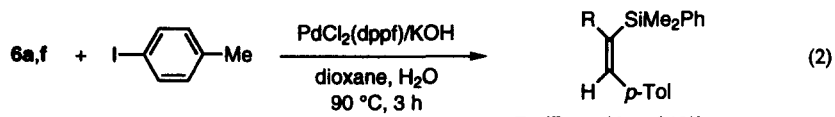


6o–q

entry	alkyne R¹—≡—R²	catalyst	product	yield (%)	regioisomeric ratio
1	Ph—≡—Ph	$Pd(OAc)_2$/*t*-OcNC	**6o**	74	–
2	Ph—≡—Me	$Pd(OAc)_2$/*t*-OcNC	**6p**	85	93:7
3	Ph—≡—Me	$Pt(PPh_3)_4$	**6p**	75	82:18
4	*n*-Bu—≡—Bu-*n*	$Pd(OAc)_2$/*t*-OcNC	**6q**	24	–
5	*n*-Bu—≡—Bu-*n*	$Pt(PPh_3)_4$	**6q**	72	–

[a] Silylborane and alkyne (1.5 equiv) were reacted in refluxing toluene in the presence of $Pt(PPh_3)_4$ (0.02 equiv) or $Pd(OAc)_2$ (0.02 equiv) and *t*-OcNC (0.30 equiv).

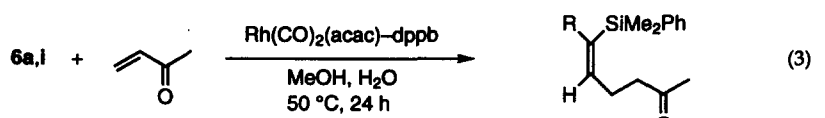
Synthetic Application of the Silaboration Reactions. Cross-coupling reaction of organic halides with alkenylboranes having silyl group *β* and *cis* to the boryl group may produce the corresponding vinylsilanes stereoselectively. The usefullness of the cross-coupling was exemplified by stereoselective coupling of **6a** and **6f** with *p*-iodotoluene under the reaction conditions for the Miyaura–Suzuki coupling using $PdCl_2$(dppf) with KOH (eq 2).[19]



(2)

7a (R = *n*-Hex; 81%)
7f (R = MEMO$(CH_2)_3$; 83%)

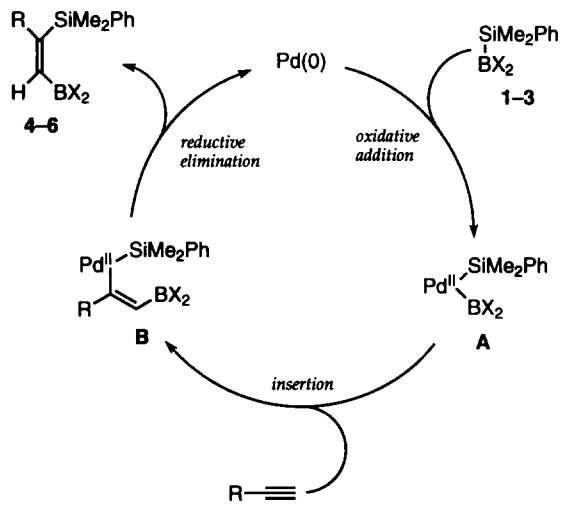
The *β*-silylalkenylboranes **6a** and **6i** also underwent conjugate addition to methyl vinyl ketone catalyzed by Rh complex to give **8a** and **8i**, respectively, in good yields (eq 3).[20]



(3)

8a (R = *n*-Hex; 83%)
8i (R = *c*-Hexen-1-yl; 78%)

Mechanistic Consideration. A possible catalytic cycle for the palladium-catalyzed silaboration of terminal alkynes involves an oxidative addition of the Si–B bond onto the transition metals, followed by regioselective insertion of the carbon–carbon triple bond and subsequent reductive elimination of the product, as illustrated in Scheme 2. It is notable that the (boryl)(silyl)palladium intermediate **A**, which is formed by oxidative addition of silylborane onto palladium, may undergo a regioselective and *cis*-insertion of alkyne at the B–Pd bond with regioselective B–C bond formation at the terminal *sp* carbon to give **B**.[21]



Scheme 2. Possible catalytic cycle for palladium-catalyzed silaboration of terminal alkynes (neutral ligands on the palladium atom are omitted).

Conclusion

Addition of the silicon–boron bond across the carbon–carbon triple bond was effectively catalyzed by palladium as well as platinum complex catalysts to afford *cis*-β-silylalkenylborane derivatives in high yields. The silaboration of terminal alkynes proceeded with the regioselective B–C bond formation at the terminal alkynyl carbon atoms. In most cases, palladium catalysts showed higher catalytic activity as well as regioselectivity than the platinum catalyst. However, in the silaboration of internal aliphatic alkyne, platinum catalysts gave higher yield than the palladium complexes.

Experimental

General. All reactions were carried out under a nitrogen atmosphere. All solvents were distilled under a nitrogen atmosphere in the presence of appropriate drying agents. The ^{1}H and ^{13}C NMR spectra were recorded on Varian VXR-200 and Varian Gemini 2000 equipped with 4.7 T and 7.0 T magnets, respectively. The ^{11}B and ^{29}Si NMR spectra were recorded on a JEOL JNM-A400 equipped with 9.3 T magnet. The boron and silicon chemical shifts were referenced to the external standards trimethoxyborane ($B(OMe)_3$) and tetramethylsilane ($SiMe_4$), respectively. Mass spectra were recorded on a JEOL JMS-HX110A. IR spectra were recorded on a Hitachi 270-30 spectrometer. Silylboranes **1** and **2** were prepared according to the literature procedure.[8c,d,9]

2-(Dimethylphenylsilyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3). To a solution of (dimethylphenylsilyl)bis(diethylamino)borane (**1**) (9.0 g, 31 mmol) in CH_2Cl_2 (30 mL) was added pinacol (3.7 g, 31 mmol) at room temperature; the mixture was stirred for 10 h. After evaporation of volatile materials, distillation (82-85 °C/0.1 mmHg) affrded **3** (6.4 g, 79%) as a colorless liquid. ^{1}H NMR ($CDCl_3$) δ 0.33 (s, 6H), 1.25 (s, 12H), 7.32-7.36 (m, 3H), 7.56-7.61 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –3.2, 25.0, 83.4, 127.7, 128.5, 134.2, 139.1; IR (neat) 2988, 1444, 1248, 1138 cm^{-1}. HRMS Calcd for $C_{13}H_{20}O_2BSi$ (M–CH_3): 247.1326. Found: 247.1324.

Typical Procedure for the Silaboration of Alkynes in the Presence of Palladium–Isonitrile Catalyst. To palladium(II) acetate (9.0 mg, 40 μmol) placed in a Schlenk-type tube under nitrogen was added 1,1,3,3-tetramethylbutyl isocyanide (84 mg, 0.60 mmol) with stirring at room temperature. Deep red color occurred immediately, indicating the formation of active palladium(0)–isonitrile catalyst. To the mixture were successively added toluene (0.5 mL), silylborane **1–3** (2.0 mmol), and alkyne (3.0 mmol) at room temperature. The mixture was heated under reflux for 1–4 h, cooled to room temperature, and then subjected to a short column on silica gel (ether). Bulb-to-bulb distillation of the crude mixture gave the silaboration products.

(*Z*)-1-[Bis(diethylamino)boryl]-2-(dimethylphenylsilyl)-1-octene (4). According to the typical procedure, **4** (133 mg, 94%) was prepared from **1** (102 mg, 0.35 mmol) and 1-octyne (57 mg, 0.52 mmol). **4**: ^{1}H NMR (C_6D_6) δ 0.48 (s, 6H), 0.82 (t, J = 6.9 Hz, 3H), 0.98 (t, J = 6.9 Hz, 12H), 1.12-1.27 (m, 6H), 1.37-1.48 (m, 2H), 2.24 (dt, J = 1.3, 7.7 Hz, 2H), 2.77-2.89 (m, 4H), 3.04-3.17 (m, 4H), 6.69 (s, 1H), 7.14-7.26 (m, 3H), 7.61-7.64 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –1.7, 14.1, 15.5, 23.0, 29.6, 30.3, 32.1, 39.9, 42.7, 127.9, 128.9, 134.4, 140.2, 146.8, 147.7 (br); IR (neat) 2972, 1582, 1430, 1266 cm^{-1}. HRMS Calcd for $C_{24}H_{45}BN_2Si$: 400.3445. Found: 400.3437.

(*Z*)-2-(Dimethylphenylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-octene (6a). According to the typical procedure, **6a** (274 mg, 94%) was prepared from **3** (206 mg, 0.79 mmol) and 1-octyne (126 mg, 1.1 mmol). **6a**: ^{1}H NMR ($CDCl_3$) δ 0.44 (s, 6H), 0.85 (t, J = 6.6 Hz, 3H), 1.07 (s, 12H), 1.14-1.38 (m, 10H), 2.18-2.25 (m, 2H), 6.18 (t, J = 1.3 Hz, 1H), 7.26-7.31 (m, 3H), 7.51-7.55 (m, 2H); ^{13}C NMR

($CDCl_3$) δ –0.9, 14.1, 22,5, 24.6, 29.1, 29.6, 31.7, 42.6, 83.0, 127.4, 128.3, 131.9 (br), 134.0, 140.5, 166.7; ^{11}B NMR ($CDCl_3$) δ 10.9 (br); ^{29}Si NMR ($CDCl_3$) δ –9.7; IR (neat) 2968, 1588, 1356, 1256, 1148 cm^{-1}. Anal. Calcd for $C_{22}H_{37}BO_2Si$: C, 70.95; H, 10.01. Found: C, 70.70; H, 10.25. For the minor regioisomer: ^1H NMR ($CDCl_3$) δ 0.39 (s, 6H), 0.88 (t, J = 6.5 Hz, 3H), 1.12 (s, 12H), 1.20-1.50 (m, 10H), 2.22-2.29 (m, 2H), 6.40 (s, 1H), 7.25-7.40 (m, 3H), 7.50-7.60 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –0.8, 14.0, 22.5, 24.7, 28.9, 29.4, 31.7, 41.3, 83.3, 127.5, 128.3, 133.9, 141.4, 143.9; IR (neat) 2968, 1584, 1314, 1244, 1146 cm^{-1}.

(*Z*)-5-Chloro-2-(dimethylphenylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-pentene (6b). According to the typical procedure, **6b** (248 mg, 87%) was prepared from **3** (204 mg, 0.78 mmol) and 5-chloro-1-pentyne (117 mg, 1.1 mmol). **6b**: ^1H NMR ($CDCl_3$) δ 0.46 (s, 6H), 1.08 (s, 12H), 1.73-1.88 (m, 2H), 2.31-2.39 (m, 2H), 3.43 (t, J = 6.7 Hz, 2H), 6.21 (t, J = 1.3 Hz, 1H), 7.28-7.34 (m, 3H), 4.49-7.54 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –1.1, 24.6, 32.1, 39.3, 44.5, 83.2, 127.5, 128.6, 133.8 (br), 134.0, 139.9, 164.3; IR (neat) 2984, 1588, 1342, 1250, 1144 cm^{-1}. Anal. Calcd for $C_{19}H_{30}BClO_2Si$: C, 62.56; H, 8.29. Found: C, 62.66; H, 8.51.

(*Z*)-5-Cyano-2-(dimethylphenylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-pentene (6c). According to the typical procedure, **6c** (217 mg, 77%) was prepared from **3** (208 mg, 0.79 mmol) and 5-cyano-1-pentyne (107 mg, 1.1 mmol). **6c**: ^1H NMR ($CDCl_3$) δ 0.47 (s, 6H), 1.11 (s, 12H), 1.67 (tt, J = 7.2, 7.6 Hz, 2H), 2.20 (t, J = 7.2 Hz, 2H), 2.34 (dt, J = 1.3, 7.6 Hz, 2H), 6.19 (t, J = 1.3 Hz, 1H), 7.29-7.35 (m, 3H), 7.49-7.54 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –1.3, 16.2, 24.5, 24.7, 40.8, 83.2, 119.4, 127.5, 128.6, 133.9, 134.1 (br), 139.4, 163.3; IR (neat) 2988, 2252, 1588, 1344, 1252, 1144 cm^{-1}. Anal. Calcd for $C_{20}H_{30}BNO_2Si$: C, 67.60; H, 8.51; N, 3.94. Found: C, 67.35; H, 8.61; N, 4.03.

(*Z*)-3-(*tert*-Butyldimethylsilyloxy)-2-(Dimethylphenylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-propene (6d). According to the typical procedure, **6d** (141 mg, 83%) was prepared from **3** (103 mg, 0.39 mmol) and 3-(*tert*-butyldimethylsilyloxy)-1-propyne (TBDMS ether of propargyl alcohol) (91 mg, 0.53 mmol). **6d**: ^1H NMR ($CDCl_3$) δ 0.02 (s, 6H), 0.45 (s, 6H), 0.89 (s, 9H), 1.08 (s, 12H), 4.21 (d, J = 2.2 Hz, 2H), 6.55 (t, J = 2.2 Hz, 1H), 7.28-7.31 (m, 3H), 7.50-7.54 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –5.5, –1.6, 18.4, 24.6, 25.9, 69.3, 83.0, 127.5, 128.0 (br), 128.5, 134.0, 139.7, 162.7; IR (neat) 2968, 1588, 1326, 1256, 1146, 1112 cm^{-1}. HRMS Calcd for $C_{23}H_{41}BO_3Si_2$: 432.2687. Found: 432.2673.

(*Z*)-2-(Dimethylphenylsilyl)-4-[(tetrahydropyran-2-yl)oxy]-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-butene (6e). According to the typical procedure, **6e** (140 mg, 88%) was prepared from **3** (100 mg, 0.38 mmol) and 4-[(tetrahydropyran-2-yl)oxy]-1-butyne (88 mg, 0.57 mmol). **6e**: ^1H NMR ($CDCl_3$) δ 0.45 (s, 6H), 1.05 (s, 12H), 1.42-1.87 (m, 6H), 2.52-2.57 (m, 2H), 3.36-3.48 (m, 2H), 3.69-3.83 (m, 2H), 4.94 (t, J = 3.6 Hz, 1H), 6.27 (t, J = 1.2 Hz, 1H), 7.27-7.30 (m, 3H), 7.51-7.54 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –1.01, –0.98, 19.4, 24.6, 25.4, 30.6, 411.8, 62.1, 67.5, 83.1, 98.7, 127.5, 128.5, 134.1, 140.2, 162.2; IR (neat) 2956, 1588, 1344, 1256, 1146 cm^{-1}. Anal. Calcd for $C_{23}H_{37}BO_4Si$: C, 66.34; H, 8.96. Found: C, 66.17; H, 9.04.

(Z)-2-(Dimethylphenylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6,8,11-trioxa-1-dodecene (6f). According to the typical procedure, **6f** (419 mg, 85%) was prepared from **3** (297 mg,1.1 mmol) and 6,8,11-trioxa-1-dodecene (MEM ether of 4-pentyn-1-ol) (296 mg, 1.7 mmol). **6f**: ^{1}H NMR ($CDCl_3$) δ 0.45 (s, 6H), 1.07 (s, 12H), 1.57-1.72 (m, 2H), 2.25-2.32 (m, 2H), 3.39 (s, 3H), 3.46 (t, J = 6.6 Hz, 2H), 3.51-3.56 (m, 2H), 3.62-3.67 (m, 2H), 4.65 (s, 2H), 6.20 (t, J = 1.4 Hz, 1H), 7.26-7.30 (m, 3H), 7.50-7.54 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –1.0, 24.6, 29.2, 38.8, 58.9, 66.5, 67.3, 71.8, 83.1, 95.3, 127.4, 128.4, 133.9, 140.1, 165.3; IR (neat) 2952, 1590, 1342, 1254, 1146 cm^{-1}. Anal. Calcd for $C_{23}H_{39}BO_5Si$: C, 63.95; H, 9.05. Found: C, 63.82; H, 9.12.

(Z)-3-(Dimethylphenylsilyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-buten-1-ol (6g). According to the typical procedure, **6g** (209 mg, 77%) was prepared from **3** (213 mg, 0.81 mmol) and 3-butyn-1-ol (81 mg, 1.1 mmol). **6g**: ^{1}H NMR ($CDCl_3$) δ 0.47 (s, 6H), 1.09 (s, 12H), 1.53 (br, 1H), 2.52 (dt, J = 1.2, 6.7 Hz, 2H), 3.60 (t, J = 6.7 Hz, 2H), 6.26 (t, J = 1.2 Hz, 1H), 7.28-7.34 (m, 3H), 7.51-7.55 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –1.1, 24.6, 45.2, 61.5, 83.3, 127.6, 128.6, 134.0, 135.7 (br), 139.7, 162.0; IR (neat) 3448, 2988, 1588, 1354, 1254, 1146 cm^{-1}. Anal. Calcd for $C_{18}H_{29}BO_3Si$: C, 65.06; H, 8.80. Found: C, 65.08; H, 8.45.

(Z)-1-(Dimethylphenylsilyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-phenylethene (6h). According to the typical procedure, **6h** (119 mg, 82%) was prepared from **3** (104 mg, 0.39 mmol) and phenylacetylene (58 mg, 0.57 mmol). **6h**: ^{1}H NMR ($CDCl_3$) δ 0.38 (s, 6H), 11.09 (s, 12H), 6.34 (s, 1H), 7.05-7.08 (m, 2H), 7.15-7.23 (m, 3H), 7.2-7.31 (m, 3H), 7.57-7.60 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 0.2, 24.7, 83.4, 126.0, 126.5, 127.5, 127.8, 128.5, 134.1, 140.1, 149.2, 165.9; IR (neat) 2988, 1582, 1340, 1256, 1144 cm^{-1}. Anal. Calcd for $C_{22}H_{29}BO_2Si$: C, 72.52; H, 8.02. Found: C, 72.24; H, 7.98.

(Z)-1-(Cyclohexen-1-yl)-1-(dimethylphenylsilyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (6i). According to the typical procedure, **6i** (275 mg, 94%) was prepared from **3** (209 mg, 0.80 mmol) and 1-ethynyl-1-cyclohexene (127 mg, 1.20 mmol). **6i**: ^{1}H NMR ($CDCl_3$) δ 0.43 (s, 6H), 1.08 (s, 12H), 1.44-1.50 (m, 4H), 1.91-1.99 (m, 4H), 5.27-5.31 (m, 1H), 6.12 (s, 1H), 7.26-7.30 (m, 3H), 7.52-7.56 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –0.5, 22.1, 22.7, 24.7, 25.2, 29.1, 83.2, 120.6, 127.3, 128.3, 134.0, 140.6, 145.9, 169.1; IR (neat) 2988, 1580, 1336, 1248, 1146 cm^{-1}. Anal. Calcd for $C_{22}H_{33}BO_2Si$: C, 71.73; H, 9.03. Found: C, 71.46; H, 9.12.

Ethyl (Z)-2-(Dimethylphenylsilyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propenoate (6j). According to the typical procedure, **6j** (219 mg, 77%) was prepared from **3** (208 mg, 0.79 mmol) and ethyl propiolate (112 mg, 1.1 mmol). **6j**: ^{1}H NMR ($CDCl_3$) δ 0.50 (s, 6H), 1.14 (s, 12H), 1.16 (t, J = 7.2 Hz, 3H), 4.05 (q, J = 7.2 Hz, 2H), 7.03 (s, 1H), 7.29-7.33 (m, 3H), 7.53-7.59 (m, 2H); ^{13}C NMR ($CDCl_3$) δ – 1.4, 14.0, 24.7, 60.5, 83.9, 127.5, 128.8, 134.0, 138.7, 143.0 (br), 154.8, 171.7; IR (neat) 2988, 1714, 1594, 1340, 1258, 1142 cm^{-1}. Anal. Calcd for $C_{19}H_{29}BO_4Si$: C, 63.33; H, 8.11. Found: C, 63.10; H, 8.24.

(Z)-3-(Dimethylphenylsilyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-buten-2-one (6k). According to the typical procedure, **6k** (232 mg, 88%) was prepared from **3** (211 mg, 0.80 mmol) and 3-

butyn-2-one (78 mg, 1.2 mmol). **6k**: ^{1}H NMR ($CDCl_3$) δ 0.48 (s, 6H), 1.12 (s, 12H), 2.22 (s, 3H), 6.63 (s, 1H), 7.27-7.34 (m, 3H), 7.51-7.59 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –1.2, 24.7, 27.8, 84.0, 127.6, 128.9, 134.1, 138.0 (br), 138.7, 166.3, 207.8; IR (neat) 2988, 1684, 1592, 1340, 1258, 1144 cm^{-1}. Anal. Calcd for $C_{18}H_{27}BO_3Si$: C, 65.45; H,8.24. Found: C, 65.28; H, 8.39.

(*Z*)-1-(Dimethylphenylsilyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(trimethylsilyl)ethene (6l). According to the typical procedure, **6l** (282 mg, 76%) was prepared as a 94:6 mixuture of the stereoisomers from **3** (268 mg, 1.0 mmol) and trimethylsilylacetylene (151 mg, 1.5 mmol). **6l**: ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 9H), 0.44 (s, 6H), 1.04 (s, 12H), 7.12 (s, 1H), 7.26-7.30 (m, 3H), 7.48-7.51 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –0.2, 0.4, 24.7, 83.4, 127.5, 128.4, 134.2, 141.3, 151.1 (br), 169.2; IR (neat) 2988, 1558, 1346, 1322, 1250, 1144 cm^{-1}. Anal. Calcd for $C_{19}H_{33}BO_2Si_2$: C, 63.31; H, 9.23. Found: C, 63.05; H, 9.44. For the minor (*E*)-isomer: ^{1}H NMR ($CDCl_3$) δ 0.04 (s, 9H), 0.35 (s, 6H), 1.31 (s, 12H), 7.06 (s, 1H), 7.25-7.35 (m, 3H), 7.40-7.48 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –1.6, 1.2, 25.0, 83.6, 127.6, 128.7, 134.1, 139.6, 151.0 (br), 170.2; IR (neat) 2988, 1552, 1348, 1322, 1256, 1144 cm^{-1}.

(*Z*)-1-(Dimethylphenylsilyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene (6m). A mixture of $Pd(OAc)_2$, 1,1,3,3-tetramethylbuthyl isocyanide, and **3** (153 mg, 0.58 mmol) was stirred under acetylene atmosphere at 110°C for 2 h. Short column on silica gel followed by bulb-to-bulb distillation gave **6m** as a 90:10 mixture of the stereoisomers (152 mg, 91%). **6m**: ^{1}H NMR ($CDCl_3$) δ 0.44 (s, 6H), 1.16 (s, 12H), 6.56 (d, J = 18.9 Hz, 1H), 7.00 (d, J = 18.9 Hz, 1H), 7.29-7.35 (m, 3H), 7.52-7.60 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –1.4, 24.7, 83.3, 127.6, 128.6, 133.9, 139.7 (br), 140.2, 155.3; IR (neat) 2988, 1588, 1386, 1338, 1262, 1146 cm^{-1}. Anal. Calcd for $C_{16}H_{25}BO_2Si$: C, 66.66; H, 8.74. Found: C, 66.91; H, 8.92. For the minor (*E*)-isomer: ^{1}H NMR ($CDCl_3$) δ 0.36 (s, 6H), 1.27 (s, 12H), 6.30 (d, J = 21.8 Hz, 1H), 7.22 (d, J = 21.8 Hz, 1H), 7.31-7.37 (m, 3H), 7.48-7.54 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –3.3, 24.7, 83.4, 127.8, 129.1, 134.0, 137.9, 138.6 (br), 155.3; IR (neat) 2984, 1596, 1374, 1330, 1146, 1018 cm^{-1}.

(Z,Z)-2,7-Bis(dimethylphenylsilyl)-1,8-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,7-octadiene (6n). According to the typical procedure, **6n** (221 mg, 72%) was prepared from **3** (290 mg, 1.1 mmol) and 1,7-octadiyne (52 mg, 0.49 mmol). **6n**: mp 79.0-81.0 °C; ^{1}H NMR ($CDCl_3$) δ 0.43 (s, 12H), 1.07 (s, 24H), 1.29 (m, 4H), 2.15 (m, 4H), 6.16 (s, 2H), 7.25-7.35 (m, 6H), 7.47-7.58 (m, 4H); ^{13}C NMR ($CDCl_3$) δ –1.0, 24.6, 29.4, 42.3, 83.0, 127.4, 128.4, 132.3 (br), 134.0, 140.5, 166.4; IR (KBr) 2998, 1584, 1430, 1254, 1112 cm^{-1}. HRMS Calcd for $C_{35}H_{53}B_2O_4Si_2$ (M–CH_3): 615.3668. Found: 615.3650.

(*E*)-1-(Dimethylphenylsilyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-diphenylethene (6o). According to the typical procedure, **6o** (126 mg, 74%) was prepared from **3** (101 mg, 0.39 mmol) and diphenylacetylene (102 mg, 0.57 mmol). **6o**: mp 87.8-88.1 °C; ^{1}H NMR ($CDCl_3$) δ 0.34 (s, 6H), 1.05 (s, 12H), 6.69-6.74 (m, 2H), 6.91-7.04 (m, 8H), 7.33-7.37 (m, 3H), 7.63-7.67 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –0.3, 24.8, 83.8, 124.7, 125.3, 127.1, 127.2, 127.6, 128.4, 128.7, 128.9, 134.3, 139.6, 142.7, 144.4, 154.9; IR (KBr) 3060, 2984, 1316, 1116, 698 cm^{-1}. Anal. Calcd for $C_{28}H_{33}BO_2Si$: C, 76.35; H, 7.55. Found: C, 76.22; H, 7.74.

(*E*)-1-(Dimethylphenylsilyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-phenyl-1-propene (6p). According to the typical procedure, **6p** (251 mg, 85%) was prepared from **3** (204 mg, 0.78 mmol) and 1-phenyl-1-propyne (133 mg, 1.1 mmol). **6p**: mp 69.0-71.0 °C; ^{1}H NMR ($CDCl_3$) δ 0.21 (s, 6H), 1.04 (s, 12H), 1.65 (s, 3H), 6.85-6.91 (m, 2H), 7.08-7.18 (m, 1H), 7.22-7.33 (m, 5H), 7.50-7.60 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –0.1, 20.4, 24.6, 83.4, 125.0, 127.1, 127.5, 128.1, 128.4, 134.1, 140.8, 145.8, 156.1; IR (KBr) 2988, 1566, 1310, 1114 cm^{-1}. Anal. Calcd for $C_{23}H_{31}BO_2Si$: C, 73.01; H, 8.26. Found: C, 72.72; H, 8.33.

(*E*)-5-(Dimethylphenylsilyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-decene (6q). To a solution of $Pt(PPh_3)_4$ (9.5 mg, 7.6 μmol) in toluene (0.1 mL) were added **3** (97 mg, 0.37 mmol) and 5-decyne (79 mg, 0.57 mmol) at room temperature under nitrogen. The mixture was heated under reflux for 4 h. Evaporation of volatile materials followed by bulb-to-bulb distillation gave **6q** (107 mg, 72%). **6q**: ^{1}H NMR ($CDCl_3$) δ 0.39 (s, 6H), 0.84 (t, J = 6.6 Hz, 3H), 0.91 (t, J = 7.1 Hz, 3H), 0.98 (s, 12H), 1.22-1.27 (m, 4H), 1.31-1.37 (m, 4H), 2.20-2.31 (m, 4H), 7.25-7.28 (m, 3H), 7.48-7.52 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 0.2, 13.8, 14.0, 23.0, 23.1, 24.7, 31.8, 32.3, 32.5, 32.6, 83.0, 127.4, 128.2, 134.1, 141.8, 151.4; IR (neat) 2968, 1566, 1344, 1248, 1144 cm^{-1}. Anal. Calcd for $C_{24}H_{41}BO_2Si$: C, 71.98; H, 10.32. Found: C, 72.04; H, 10.44.

(*Z*)-2-(Dimethylphenylsilyl)-1-(4-methylphenyl)-1-octene (7a). A mixture of $PdCl_2$(dppf) (4.7 mg, 6.5 μmol), **6a** (80 mg, 0.22 mmol), and 4-iodotoluene (70 mg, 0.32 mmol) in dioxane (1 mL) was heated at 90 °C for 3 h under nitrogen. Extractive workup with ether followed by preparative TLC on silica gel (hexane:ether = 200:1) gave **7a** (58 mg, 81%). **7a**: ^{1}H NMR ($CDCl_3$) δ 0.18 (s, 6H), 0.90 (t, J = 7.2 Hz, 3H), 1.20-1.40 (m, 6H), 1.41-1.58 (m, 2H), 2.22-2.30 (m, 2H), 2.30 (s, 3H), 6.92-7.04 (m, 4H), 7.26 (t, J = 1.8 Hz, 1H), 7.30-7.35 (m, 3H), 7.47-7.52 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –1.0, 14.0, 21.0, 22.6, 29.1, 30.4, 31.7, 39.2, 127.6, 128.3, 128.5, 128.6, 133.9, 136.3, 137.4, 140.3, 141.8, 143.3; IR (neat) 2936, 1432, 1110, 818 cm^{-1}. Anal. Calcd for $C_{23}H_{32}Si$: C, 82.07; H, 9.58. Found: C, 81.93; H, 9.47.

(*Z*)-2-(Dimethylphenylsilyl)-1-(4-methylphenyl)-6,8,11-trioxa-1-dodecene (7f). According to a procedure similar to that for the synthesis of **7a**, **7f** (191 mg, 83%, hexane:ether = 3:1) was prepared from **6f** (250 mg, 0.58 mmol). **7f**: ^{1}H NMR ($CDCl_3$) δ 0.16 (s, 6H), 1.67-1.81 (m, 2H), 2.28 (s, 3H), 2.28-2.36 (m, 2H), 3.38 (s, 3H), 3.51-3.57 (m, 4H), 3.64-3.70 (m, 2H), 6.98 (s, 4H), 7.26-7.34 (m, 4H), 7.44-7.50 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –1.0, 21.1, 30.3, 35.4, 58.9, 66.6, 67.4, 71.8, 95.4, 127.6, 128.5, 128.6, 133.8, 136.4, 137.0, 139.8, 140.7, 143.7; IR (neat) 2944, 1598, 1250, 820 cm^{-1}. Anal. Calcd for $C_{24}H_{34}O_3Si$: C, 72.32; H, 8.60. Found: C, 72.21; H, 8.81.

(*Z*)-6-(Dimethylphenylsilyl)-5-dodecen-2-one (8a). A mixture of **6a** (220 mg, 0.59 mmol), $Rh(CO)_2$(acac) (4.6 mg, 18 μmol), and 1,4-bis(diphenylphosphino)butane (7.7 mg, 18 μmol) in methanol (3.6 mL) was stirred at room temperature for 15 min. To the mixture was added methyl vinyl ketone (63 mg, 0.90 mmol) and H_2O (0.6 mL); the mixture was stirred at 50 °C for 24 h. After cooling to room temperature, the mixture was passed through a short column of silica gel (ether). Column chromatography on silica gel afforded **8a** (154 mg, 83%). **8a**: ^{1}H NMR ($CDCl_3$) δ 0.39 (s, 6H), 0.88 (t, J =

6.5 Hz, 3H), 1.10-1.45 (m, 8H), 1.94 (s, 3H), 2.02-2.24 (m, 6H), 5.89-6.05 (m, 1H), 7.31-7.33 (m, 3H), 7.50-7.54 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –1.2, 14.0, 22.5, 26.6, 29.0, 29.6, 30.7, 31.6, 38.4, 43.2, 127.8, 128.7, 133.8, 139.2, 139.9, 141.8, 208.3; IR (neat) 2936, 1724, 1614, 1432, 1366, 1252, 1112 cm^{-1}. Anal. Calcd for $C_{20}H_{32}OSi$: C, 75.88; H, 10.19. Found: C, 75.82; H, 10.20.

(Z)-6-(Cyclohexen-1-yl)-6-(dimethylphenylsilyl)-5-hexen-2-one (8i). According to a procedure similar to that for the synthesis of **8a**, **8i** (148 mg, 78%) was prepared from **6i** (225 mg, 0.61 mmol), methyl vinyl ketone (63 mg, 0.90 mmol), $Rh(CO)_2(acac)$ (4.6 mg, 18 μmol), and 1,4-bis(diphenylphosphino)butane (7.7 mg, 18 μmol) in methanol (3.6 mL) and H_2O (0.6 mL). **8i**: ^{1}H NMR ($CDCl_3$) δ 0.38 (s, 6H), 1.42-1.64 (m, 4H), 1.87-2.08 (m, 4H), 1.95 (s, 3H), 2.13-2.25 (m, 4H), 5.26-5.27 (m, 1H), 5.89-5.96 (m, 1H), 7.29-7.40 (m, 3H), 7.48-7.60 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –1.0, 22.1, 22.8, 25.2, 26.5, 29.6, 30.4, 43.0, 121.0, 127.7, 128.7, 133.8, 139.9, 141.6, 143.3, 144.8, 208.2; IR (neat) 2936, 1724, 1604, 1432, 1366, 1252, 1112 cm^{-1}. Anal. Calcd for $C_{20}H_{28}OSi$: C, 76.86; H, 9.03. Found: C, 76.72; H, 8.99.

References

1. For recent reviews for reactions involving boron–element bond activation, see: (a) Wadepohl. H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2441. (b) Braunschweig, H. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1786. (c) Irvine, G. J.; Lesley, M. J. G.; Marder, T. B.; Norman, N. C.; Rice, C. R.; Robins, E. G.; Roper, W. R.; Whittell, G. R.; Wright, L. J. *Chem. Rev.* **1998**, *98*, 2685.
2. Männig, D.; Nöth, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 878.
3. (a) Burgess, K.; Ohlmeyer, M. J. *J. Org. Chem.* **1988**, *53*, 5178. (b) Hayashi, T.; Matsumoto, Y.; Ito, Y. *J. Am. Chem. Soc.* **1989**, *111*, 3426. (c) Sato, M.; Miyaura, N.; Suzuki, A. *Tetrahedron Lett.* **1990**, *31*, 231. (d) Hayashi, T.; Matsumoto, Y.; Ito, Y. *Tetrahedron: Asymmetry* **1991**, *2*, 601. (e) Brown, J. M.; Hulmes, D. I.; Layzell, T. P. *J. Chem. Soc., Chem. Commun.* **1993**, 1673. (f) Schnyder, A.; Hintermann, L.; Togni, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 931.
4. (a) Ishiyama, T.; Matsuda, N.; Miyaura, N.; Suzuki, A. *J. Am. Chem. Soc.* **1993**, *115*, 11018. (b) Baker, R. T.; Nguyen, P.; Marder, T. B.; Westcott, S. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1336. (c) Ishiyama, T.; Matsuda, N.; Murata, M.; Ozawa, F.; Suzuki, A.; Miyaura, N. *Organometallics* **1996**, *15*, 713. (d) Ishiyama, T.; Yamamoto, M.; Miyaura, N. *Chem. Commun.* **1996**, 2073. (e) Ishiyama, T.; Yamamoto, M.; Miyaura, N. *Chem. Commun.* **1997**, 689. (f) Ishiyama, T.; Kitano, T.; Miyaura, N. *Tetrahedron Lett.* **1998**, *39*, 2357, and references therein.
5. (a) Onozawa, S.-y.; Hatanaka, Y.; Sakakura, T.; Shimada, S.; Tanaka, M. *Organometallics* **1996**, *15*, 5450. (b) Onozawa, S.-y.; Hatanaka, Y.; Choi, N.; Tanaka, M. *Organometallics* **1997**, *16*, 5389. (c) Onozawa, S.-y.; Hatanaka, Y.; Tanaka, M. *Tetrahedron Lett.* **1998**, *39*, 9043.
6. (a) Horn, K. A. *Chem. Rev.* **1995**, *95*, 1317. (b) Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, *95*, 1351.
7. Suginome, M.; Ito, Y. *J. Chem. Soc., Dalton Trans.* **1998**, 1925.
8. (a) Seyferth, D.; Kögler, H. P. *J. Inorg. Nucl. Chem.* **1960**, *15*, 99. (b) Cowley, A. H.; Sisler, H. H.;

Ryschkewitsch, G. E. *J. Am. Chem. Soc.* **1960**, *82*, 501. (c) Nöth, H.; Höllerer, G. *Chem. Ber.* **1966**, *99*, 2197. (d) Biffar, W.; Nöth, H.; Schwerthöffer, R. *Liebigs Ann. Chem.* **1981**, 2067.

9. Buynak, J. D.; Geng, B. *Organometallics* **1995**, *14*, 3112.
10. An addition of a borate complex, $PhMe_2SiBEt_3Li$ generated in situ to alkynes was reported. However, protodeboration of the (β-silylalkenyl)borate thus produced is requisite for completion of the reversible silaboration reaction, leading to the formation of alkenylsilane in high yields. Nozaki, K.; Wakamatsu, K.; Nonaka, T.; Tückmantel, W.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1986**, *27*, 2007.
11. Suginome, M.; Nakamura, H.; Ito, Y. *Chem. Commun.* **1996**, 2777.
12. Suginome, M.; Nakamura, H.; Ito, Y. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2516.
13. Suginome, M.; Nakamura, H.; Matsuda, T.; Ito, Y. *J. Am. Chem. Soc.* **1998**, 120, 4248.
14. Suginome, M.; Matsuda, T.; Ito, Y. *Organometallics* **1998**, *17*, 5233.
15. Onozawa, S.-y.; Hatanaka, Y.; Tanaka, M. *Chem. Commun.* **1997**, 1229.
16. For the use of the palladium–isonitrile catalyst in bis-silylation of alkynes, see: (a) Suginome M.; Takama, A.; Ito, Y. *J. Am. Chem. Soc.* **1998**, *120*, 1930. (b) Suginome, M.; Matsumoto, A.; Ito, Y. *J. Org. Chem.* **1996**, *61*, 4884. (c) Murakami, M.; Suginome, M.; Fujimoto, K.; Ito, Y. *Angew. Chem. Int. Ed. Engl.***1993**, *32*, 1473. (d) Murakami, M.; Oike, H.; Sugawara, M.; Suginome, M.; Ito, Y. *Tetrahedron* **1993**, *49*, 3933. (e) Ito, Y.; Suginome, M.; Murakami, M. *J. Org. Chem.* **1991**, *56*, 1948.
17. For the bis-silylation reactions using the palladium–isonitrile catalyst, see: (a) Suginome, M.; Iwanami, T.; Ito, Y. *J. Org. Chem.* **1998**, *63*, 6096. (b) Suginome, M.; Iwanami, T.; Ito, Y. *Tetrahedron: Asymmetry* **1997**, *8*, 859. (c) Suginome, M.; Nakamura, H.; Ito, Y. *Tetrahedron Lett.* **1997**, 38, 555. (d) Suginome, M.; Matsumoto, A.; Ito, Y. *J. Am. Chem. Soc.* **1996**, 118, 3061. (e) Suginome, M.; Matsunaga, S.; Iwanami, T.; Matsumoto, A.; Ito, Y. *Tetrahedron Lett.* **1996**, *37*, 8887. (f) Suginome, M.; Yamamoto, Y.; Fujii, K.; Ito, Y. *J. Am. Chem. Soc.* **1995**, *117*, 9608. (g) Suginome, M.; Matsumoto, A.; Nagata, K.; Ito, Y. *J. Organomet. Chem.* **1995**, *499*, C1. (h) Murakami, M.; Suginome, M.; Fujimoto, K.; Nakamura, H.; Andersson, P. G.; Ito, Y. *J. Am. Chem. Soc.* **1993**, *115*, 6487. (i) Murakami, M.; Andersson, P. G.; Suginome, M.; Ito, Y. *J. Am. Chem. Soc.* **1991**, *113*, 3987.
18. For other reactions using the palladium–isonitrile complexes, see: (a) Suginome, M.; Kato, Y.; Takeda, N.; Oike, H.; Ito, Y. *Organometallics* **1998**, *17*, 495. (b) Suginome, M.; Oike, H.; Shuff, P. H.; Ito, Y. *Organometallics* **1996**, *15*, 2170. (c) Suginome, M.; Oike, H.; Park, S.-S.; Ito, Y. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 289. (d) Suginome, M.; Oike, H.; Ito, Y. *J. Am. Chem. Soc.* **1995**, *117*, 1665. (e) Suginome, M.; Oike, H.; Ito, Y. *Organometallics* **1994**, *13*, 4148.
19. Miyaura, N., Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.
20. (a) Sakai, M.; Hayashi, H.; Miyaura, N. *Organometallics* **1997**, *16*, 4229. (b) Takaya, Y.; Ogasawara, M.; Hayashi, T.; Sakai, M.; Miyaura, N. *J. Am. Chem. Soc.* **1998**, *120*, 5579.
21. The proposed preference for the insertion at the B–Pd bond over that at the Si–Pd bond is based upon the regiochemical preference of palladium-catalyzed germaborative dimerization of alkynes. See ref 14.