

BCSJ Award Article

PSiP-Pincer Type Palladium-Catalyzed Dehydrogenative Borylation of Alkenes and 1,3-Dienes

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Dehydrogenative borylation of alkenes and 1,3-dienes was realized by carrying out the reaction in the presence of bis(pinacolato)diboron (B_2pin_2) and a catalytic amount of PSiP-pincer palladium complex. This protocol has the following notable features. 1) Monoanionic nature of the PSiP-pincer ligand prevents the formation of boryl(hydrido)- or dihydridopalladium species, enabling synthesis of various vinyl- or dienylboronic esters in good yield from a 1:1 mixture of B_2pin_2 and alkenes or 1,3-dienes without forming hydroboration or hydrogenation products. 2) Due to the strong trans influence of the silicon atom, PSiP-pincer palladium complex showed high activity toward migratory insertion. 3) Suppression of these side-reactions and the high reactivity of the PSiP-pincer palladium complex enabled an efficient, successive dehydrogenative borylation to give 1,1- or 1,2-diborylated products depending on the kind of substituent on alkenes by using more than 2 equivalents of B_2pin_2. Mechanistic study revealed that PSiP-pincer borylpalladium complex was generated from hydridopalladium complex and B_2pin_2, and this complex underwent alkene insertion followed by β-hydride elimination to give alkenylboronic ester with regeneration of the hydridopalladium complex.

Alkenyl boronic esters are an important class of compounds, which have been widely employed in the synthesis of natural products, functional molecules, and functional polymers as a component of metal-catalyzed cross-coupling reactions.[1] There have been reported various methods for the preparation of alkenylboronic esters, such as alkenylation of trialkylborate with alkenyllithium or magnesium reagents, Ishiyama–Miyaura borylation of alkenyl halides with diboron[2] or borane,[3] and hydroboration of alkynes.[4] However, these methods need pre-functionalization of the alkenyl group or are unsuitable for the synthesis of β,β-disubstituted or cyclic alkenylboronic esters. Transition-metal-catalyzed dehydrogenative borylation of alkenes is an alternative straightforward method for the synthesis of alkenylboronic esters, which could formally convert alkene C–H bonds to C–B bonds directly.[5] The reaction does not require the preparation of alkenyl halides and is expected to be applicable to the synthesis of β,β-disubstituted or cyclic alkenylboronic esters. However, previously reported reactions catalyzed by Rh(I),[6] Ir(I),[7] Ru(III),[8] Pd(II),[9] Pt(II),[10] or Ti(IV)[11] have several disadvantages; the reaction is often accompanied by hydrogenation and/or hydroboration of alkenes caused by boryl(hydrido)- or dihydrido complex intermediates, and thus an excess amount of alkenes is usually required.[12–14] Additionally, substrate scope of alkenes was rather poor in many of these reactions, and it is common that the reaction proceeded smoothly only with styrene derivatives. Therefore, to expand the utility of dehydrogenative borylation, development of a novel catalytic system which excludes the generation of boryl(hydrido)- or dihydrido complexes and shows high reactivity is highly desirable. Recently, NCN-pincer palladium-catalyzed dehydrogenative borylation was reported by Szabó et al.[15] This system involved a Pd(II)–Pd(IV) cycle which excluded the generation of boryl(hydrido)- or dihydrido complex, affording alkenylboronic esters without concomitant formation of hydroboration or hydrogenation products. However, this reaction still necessitated the use of an excess amount of alkenes along with two molar equivalents of $PhI(OAc)_2$ as oxidant.

We previously reported the synthesis of PSiP-pincer type palladium complex for the catalytic hydrocarboxylation reaction of allenes and 1,3-dienes.[16] We envisioned that PSiP-pincer ligand would prevent the formation of boryl(hydrido)- or dihydridopalladium species, because monoanionic character of the PSiP-pincer ligand permits the palladium(II) center to bind only one additional anionic ligand (Figure 1). Furthermore, the strong trans influence of the silicon atom would enhance the reactivity of the palladium complex toward migratory insertion. We expected that these features would enable development of a novel and efficient dehydrogenative borylation of alkenes. In this paper, we report detailed study of PSiP-pincer type palladium complex catalyzed dehydrogenative borylation, which allows synthesis of mono- and diborylalkenes or 1,3-dienes without accompanying hydroboration or hydrogenation.[17]

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Results and Discussion

Preparation of PSiP-Pincer Borylpalladium Complex. First, we examined the synthesis of PSiP-pincer borylpalladium complex, which was expected to be an active species of dehydrogenative borylation. We selected palladium triflate **1a** bearing Ph groups on phosphorus as a palladium complex and bis(pinacolato)diboron (B_2pin_2) or pinacolborane (HBpin) as a boron source. When palladium triflate **1a** was mixed with B_2pin_2 or HBpin in benzene-d_6, no formation of a new complex was observed by ^{31}P NMR spectra. However, after several attempts, it was found that the addition of 2 molar equivalents of $AlEt_3$, which was employed as a reductant in the hydrocarboxylation reaction, to a mixture of palladium triflate **1a** and 20 molar equivalents of B_2pin_2 afforded the desired borylpalladium complex **2a** in 62% yield (Scheme 1). A similar reaction of palladium triflate **1a** and $AlEt_3$ using HBpin instead of B_2pin_2 did not generate the complex **2a**.

Unfortunately, our attempt to isolate complex **2a** was unsuccessful due to decomposition during the process of removing solvent in the presence of aluminum reagent. After examination of other reductants, we found that addition of *n*-BuLi also generated the same complex **2a** cleanly, and isolation of borylpalladium complex **2a** was successfully achieved in 84% yield by the reaction of palladium chloride **3a**, B_2pin_2, and *n*-BuLi in a ratio of 1:4:2.4. The structure of **2a** was confirmed as the PSiP-pincer borylpalladium by X-ray analysis (Figure 2). Due to the strong trans influence of the silicon atom,[18] the Pd–B bond length elongated to 2.12 Å, which is the longest among the borylpalladium complexes ever reported.[19] Thus, high reactivity of this borylpalladium toward alkene insertion was expected.

Although the exact mechanism of the generation of borylpalladium **2a** is not clear, it is thought to be generated by the reaction of hydridopalladium and B_2pin_2, and hydridopalladium could be generated by transmetalation of palladium triflate with $AlEt_3$ followed by β-hydride elimination.[16a,16c] From these results, we expected that PSiP-pincer palladium-catalyzed dehydrogenative borylation would become possible according to the following successive reactions (Scheme 2). At first, borylpalladium **2** is generated from palladium triflate **1**, B_2pin_2, and $AlEt_3$ via formation of hydridopalladium **4**. Following insertion of alkene **5** to borylpalladium **2**, followed by β-hydride elimination would produce alkenylboronic ester **6** with regeneration of hydridopalladium **4**. This hydridopalladium **4** would react again with diboron to regenerate borylpalladium **2**. Importantly, this proposed catalytic cycle does not include boryl(hydrido)- or dihydridopalladium species, thus should prevent the formation of undesirable hydroboration or hydrogenation products.

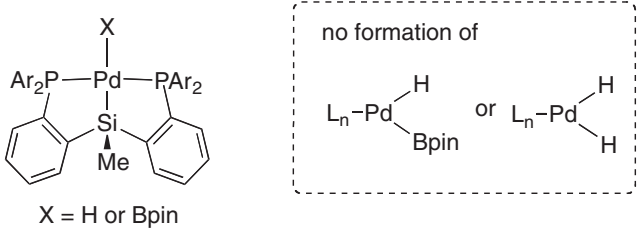


Figure 1. PSiP-pincer palladium complex.

Optimization of Reaction Conditions. At first, styrene **5a** and B_2pin_2 were selected as substrates for optimization of the catalytic dehydrogenative borylation. As expected, when 2 mol % each of PSiP-pincer palladium triflate **1a** bearing phenyl groups on phosphorus and $AlEt_3$ was used as catalyst, dehydrogenative borylation proceeded regio- and stereoselectively to afford desired (*E*)-styrylboronic ester **3a** in 24% yield after 6 h at 60 °C (Table 1, Entry 1). Notably, neither hydroboration nor hydrogenation products were observed in the crude reaction mixture. Addition of $AlEt_3$ was essential and no formation of the product was observed when palladium triflate **1a** was used alone (Entry 2). Employment of pinacolborane did not afford **3a** (Entry 3). Then, we examined other PSiP-pincer Pd complexes to improve catalytic activity of the reaction. When the reaction was carried out in the presence of palladium triflate **1b** bearing *p*-anisyl groups on phosphorus, the yield of **3a** was decreased (Entry 4). Sterically demanding *o*-tolyl-substituted complex **1c** did not show any catalytic activity (Entry 5). 2-Furyl-substituted complex **1d** did not show high activity either, but palladium complex **1e** bearing 4-$CF_3C_6H_4$ groups on phosphorus improved the yield dramatically (Entries 6 and 7). Furthermore, it was found that 3,5-$(CF_3)_2C_6H_3$-substituted complex **1f** was quite efficient for this reaction and **3a** was obtained in high yield as a single stereoisomer even at room temperature.

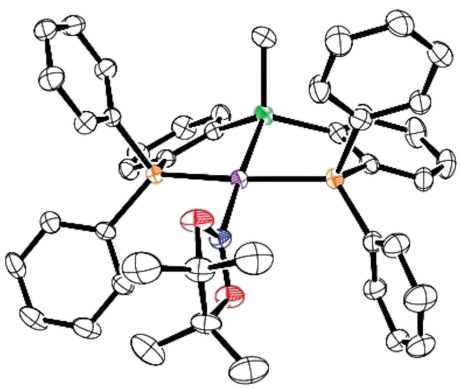
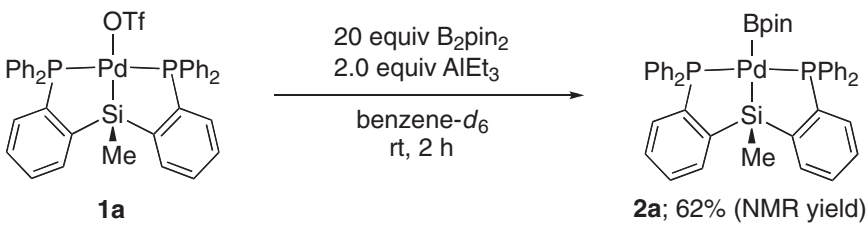
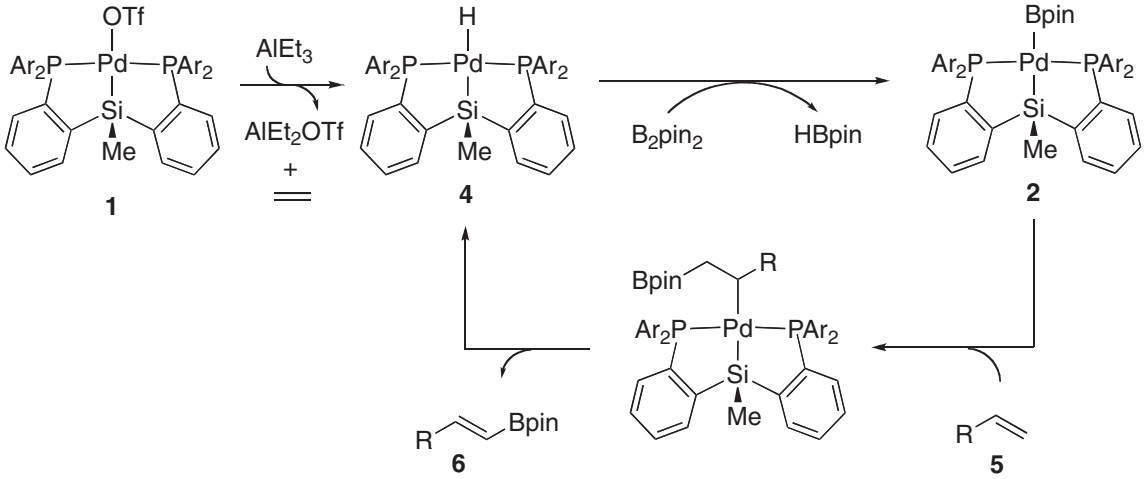


Figure 2. ORTEP plot of borylpalladium **2a**. Hydrogen atoms are omitted for clarity.

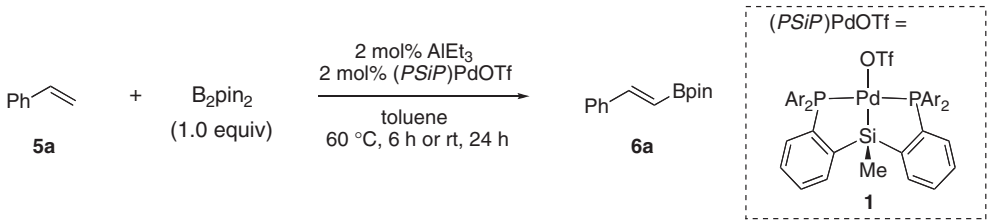


Scheme 1. Generation of borylpalladium **2a**.



Scheme 2. Strategy for PSiP-pincer palladium-catalyzed dehydrogenative borylation.

Table 1. Optimization of Reaction Conditions

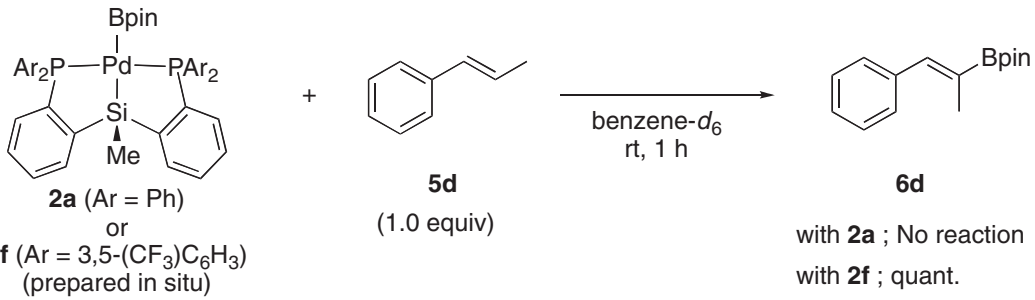


Entry	(PSiP)PdOTf (Ar on Phosphorus atom)	Reductant	Boron source	Temp/°C	Yield[a)]/%
1	**1a** (Ph)	$AlEt_3$	B_2pin_2	60	24
2	**1a** (Ph)	none	B_2pin_2	60	0
3	**1a** (Ph)	$AlEt_3$	HBpin	60	0
4	**1b** (4-$MeOC_6H_4$)	$AlEt_3$	B_2pin_2	60	7
5	**1c** (2-MeC_6H_4)	$AlEt_3$	B_2pin_2	60	0
6	**1d** (2-furyl)	$AlEt_3$	B_2pin_2	60	12[b)]
7	**1e** (4-$CF_3C_6H_4$)	$AlEt_3$	B_2pin_2	60	quant.
8	**1f** (3,5-$(CF_3)_2C_6H_3$)	$AlEt_3$	B_2pin_2	60	quant.
9	**1f** (3,5-$(CF_3)_2C_6H_3$)	$AlEt_3$	B_2pin_2	rt	quant. (92[c)])

a) NMR yield. b) (PSiP)PdCl was used. c) Isolated yield.

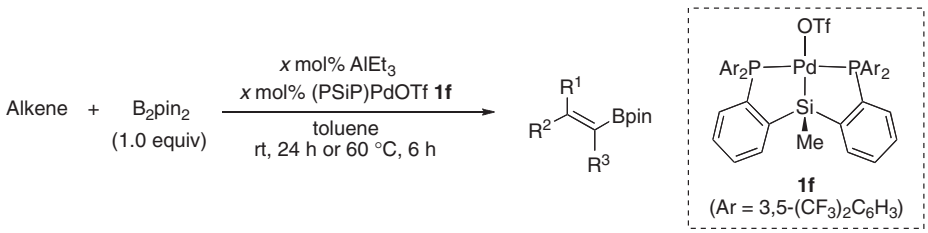
This higher catalytic activity of 3,5-$(CF_3)_2C_6H_3$-substituted complex **1f** was explicitly shown in the stoichiometric reaction of borylpalladium **2a** or **2f** and β-methylstyrene (**5d**) (Scheme 3). Borylpalladium **2f** was prepared in situ from the reaction of palladium chloride **3f**, 10 equivalents of B_2pin_2 and *n*-BuLi, because isolation of **2f** was unsuccessful due to its high solubility. While borylpalladium **2a** did not react with β-methylstyrene (**5d**) at room temperature, borylpalladium **2f** bearing 3,5-$(CF_3)_2C_6H_3$ moiety immediately reacted with β-methylstyrene (**5d**) at room temperature to give **6d** quantitatively as a single geometric isomer. Thus, by decreasing electron-donating ability of phosphorus atoms, migratory insertion was facilitated, leading to high catalytic activity. It should be noted that from (*E*)-β-methylstyrene (**5d**), (*Z*)-alkenylboronic ester **6d** was obtained selectively, suggesting that the reaction proceeded via *syn*-borylpalladation, followed by *syn*-β-hydride elimination.

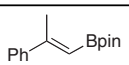
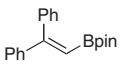
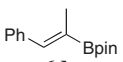
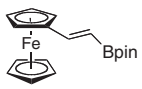
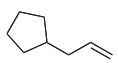
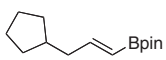
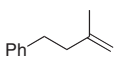
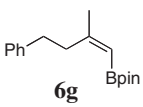
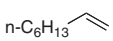
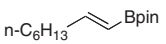
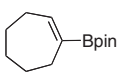
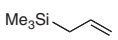
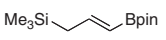
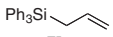
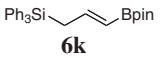
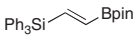
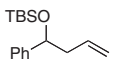
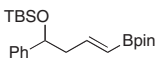
Scope and Limitation. Then, substrate scope of alkenes was examined by using 1 equivalent of B_2pin_2 in the presence of a catalytic amount of palladium triflate **1f** and $AlEt_3$ (Table 2). α- or β-Substituted styrenes **5b**–**5d** were applicable to this reaction and corresponding alkenylboronic esters were stereoselectively obtained in high yields even with 1 mol % catalyst loading at room temperature (Table 2, Entries 1–3). Importantly, 1,1-disubstituted alkenyl boronic ester **6b**, which cannot be synthesized by hydroboration of alkyne, was easily available by this method. Similarly, vinylferrocene (**5e**) could be employed although it required 5 mol % of **1f** and heating (Entry 4). Moreover, this selective synthesis of monoborylalkenes was also applicable to other simple terminal alkenes. The reaction of allylcyclopentane (**5f**) or 2-methyl-4-phenyl-1-butene (**5g**) afforded alkenylboronates **6f** or **6g** in good yields (Entries 5 and 6). This reaction was applicable to 1-octene (**5h**), a simple straight chain alkene, although use of 3 equivalents of alkene was necessary due to partial isomerization of the double bond of the starting material (Entry 7). We also examined the reaction of simple internal alkenes such as (*E*)- and (*Z*)-4-octene, however, the reaction did not give the desired alkenyl-



Scheme 3. Reaction of borylpalladium with (*E*)-β-methylstyrene.

Table 2. Dehydrogenative Borylation of Alkenes



Entry	Substrates	*x*	Temp/°C	Product	Yield/%	*E*:*Z*
1	 **5b**	1	rt	 **6b**	87	*E* only
2	 **5c**	1	rt	 **6c**	quant.	—
3	 **5d**	1	rt	 **6d**	89	*Z* only
4	 **5e**	5	60	 **6e**	93	*E* only
5	 **5f**	10	60	 **6f**	43[a)]	*E* only
6	 **5g**	5	rt	 **6g**	82	37:63
7	 **5h**	5	60	 **6h**	87[b),c)]	93:7
8	 **5i**	5	60	 **6i**	98	*Z* only
9	 **5j**	1	60	 **6j**	58[d)]	87:13
10	 **5k**	1	60	 **6k**	84[e)]	75:25
11	 **5l**	10	60	 **6l**	88[f)]	*E* only
12	 **5m**	10	60	 **6m**	62[a)]	88:12

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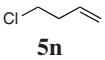
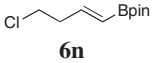
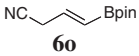
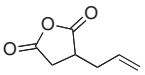
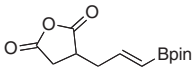
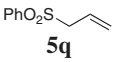
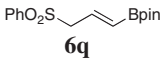
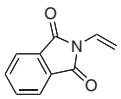
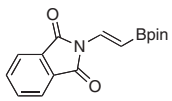
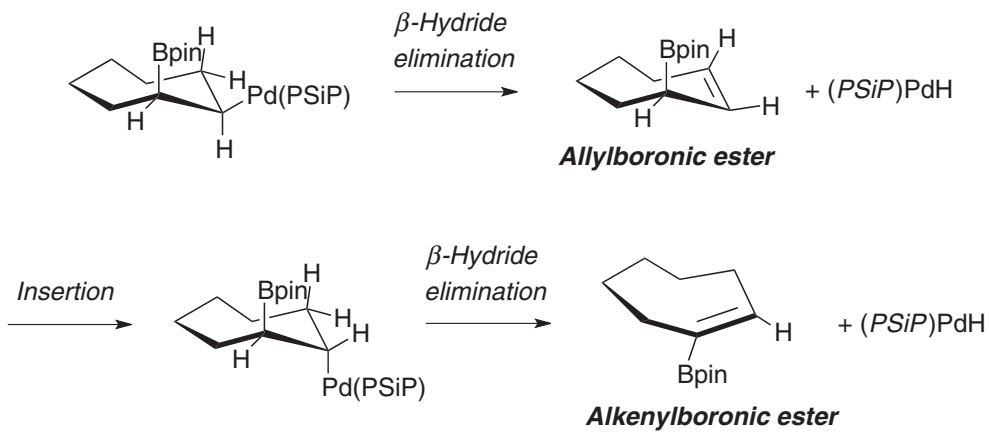
Entry	Substrates	*x*	Temp/°C	Product	Yield/%	*E*:*Z*
13	 **5n**	10	60	 **6n**	53[a)]	92:8
14	 **5o**	5	60	 **6o**	64[f),g)]	62:38
15	 **5p**	5	60	 **6p**	87[g)]	86:14
16	 **5q**	5	60	 **6q**	70	56:44
17	 **5r**	10	60	 **6r**	91	*E* only

a) 3–15% of diborylation product was obtained. b) 3 equivalents of 1-octene were used. c) The reaction was carried out in THF. d) Obtained as a mixture with 13% of **9j**. e) (*Z*)-Isomer was obtained as a mixture with a small amount of 1-propenyltriphenylsilane and some isomers. f) 2 equivalents of B_2pin_2 were used. g) NMR yield.



Scheme 4. Proposed mechanism of the generation of cycloheptenylboronic ester **6i**.

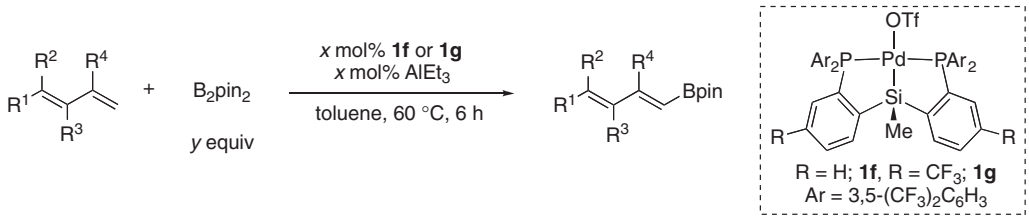
boronic esters in good yield.[20] This is a limitation of this protocol, however, selective synthesis of the above alkenylboronic ester **6h** was achieved successfully, because isomerized internal alkene did not react to afford internal alkenylboronic esters. Cycloheptenylboronic ester **6i**, which could not be synthesized by hydroboration of alkyne, was obtained in good yield (Entry 8).

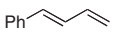
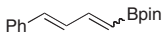
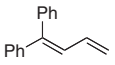
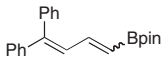
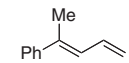
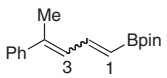
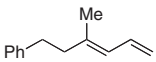
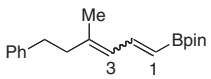
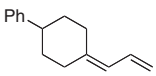
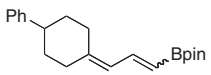
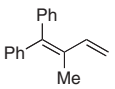
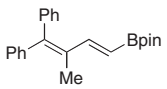
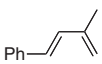
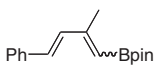
Then functional group compatibility of this reaction was examined next. Synthesis of functionalized boryl alkenes was hardly examined in previously reported dehydrogenative borylation reactions. Allyl- or vinylsilanes **5j**, **5k**, and **5l** were allowed to react with B_2pin_2, affording bifunctional compounds **6j**, **6k**, and **6l**, which could be utilized for further reactions of organoboron and silicon compounds (Entries 9–11). Alkenyl boronic esters **6m**–**6p** which contained silyl ether, chloro, cyano, and acid anhydride groups were obtained in reasonable yield without loss of these functional groups, although formation of a small amount of diborylated products was observed in some cases (Entries 12–15). Sulfone or imide functionality was also compatible under these reaction conditions (Entries 16 and 17).

In most cases, sterically less hindered (*E*)-alkenylboronic esters were obtained in good to high selectivity. This selectivity was thought to be realized at the stage of the β-hydride elimination from the alkylpalladium intermediate through the less sterically congested conformer, but in some case, there seems to be an equilibrium between (*E*)- and (*Z*)-alkenylboronic esters through a hydropalladation/β-hydride elimination sequence. Actually, we believe that cycloheptenylboronic ester **6i** was obtained through isomerization of initially produced allylboronic ester via hydropalladation followed by β-hydride elimination (Scheme 4). A similar mechanism was proposed in Rh-catalyzed dehydrogenative borylation of cyclic alkenes.[6g]

Next, we focused on the application of the current catalytic system toward the preparation of dienylboronic esters. Although dienyl boronic esters are a useful building block for synthesis of natural products and π-conjugated molecules,[21] only one example was reported for dehydrogenative borylation

Table 3. Dehydrogenative Borylation of 1,3-Diene



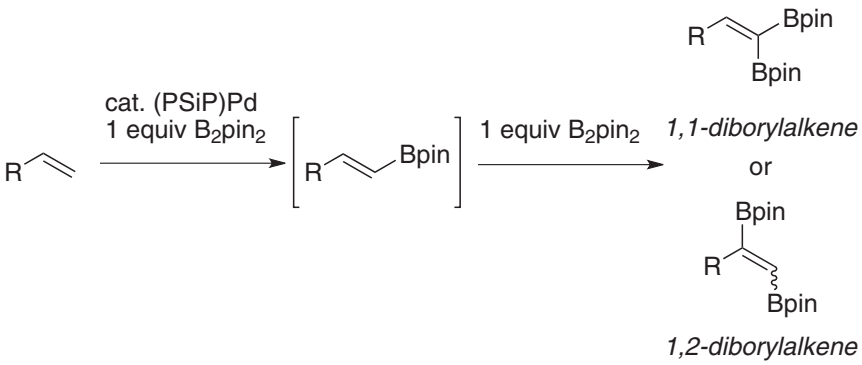
Entry	Substrates	x (**1f** or **1g**)	y	Product	Yield/%	E/Z
1	 **7a** (E only)	2.5 (**1g**)	2	 **8a**	80	58:42
2	 **7b**	2.5 (**1f**)	1	 **8b**	98	87:13
3	 **7c** (E:Z = 8:2)	2.5 (**1f**)	1	 **8c**	98[b]	86:14
4	 **7d** (E:Z = 7:3)	2.5 (**1f**)	1	 **8d**	93[b]	74:26
5	 **7e**	2.5 (**1f**)	1	 **8e**	91	85:15
6	 **7f**	2.5 (**1f**)	2	 **8f**	90	—
7	 **7g**	2.5 (**1g**)	2	 **8g**	46[a]	62:38

a) The reaction was carried out in THF. b) Contained ca. 5% of isomers (1Z, 3E/Z)-**8**.

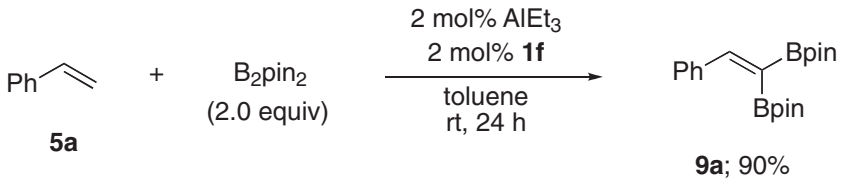
of 1,3-dienes using silylborane with Ni catalyst.[22] In this reaction, hydrosilylation of 1,3-diene also proceeded, and 2 molar equivalents of 1,3-diene were needed to obtain dienylboronic ester in good yield.

Unfortunately, the reaction of 1-phenyl-1,3-butadiene (**7a**) in the presence of 2.5 mol % palladium triflate **1f** and $AlEt_3$ afforded 4-phenylbutadienylboronic ester **8a** only in 11% yield even when 2 equivalents of B_2pin_2 were used. However we have succeeded in improving the yield by introducing CF_3 to the phenylene backbone of the pincer palladium complex. When 2.5 mol % of newly synthesized PSiP-pincer palladium triflate **1g** was used, dienylboronic ester **8a** was obtained in 80% yield (Table 3, Entry 1). Neither hydroboration- nor hydrogenation product was detected in the reaction mixture. Similarly, the reaction of 1,1-disubstituted dienes **7b**–**7e** also underwent dehydrogenative borylation, affording the corresponding dienyl boronic esters **8b**–**8e** in high yield by using palladium triflate **1f** or **1g** and 1 equivalent of B_2pin_2 (Entries 2–5). 1,1,2- or 1,3-substituted dienes **7f** and **7g** were also applicable for this reaction to give corresponding boronic esters in moderate to good yields. The geometry of the obtained dienylboronic esters was thought to be dependent on the steric environment. The stereoselectivity of the reaction of monosubstituted diene **7a** was low, but in contrast, the reaction of 1,1,2-trisubstituted diene **7f** gave **8f** as a single isomer probably due to steric repulsion between the Me group and boryl group.

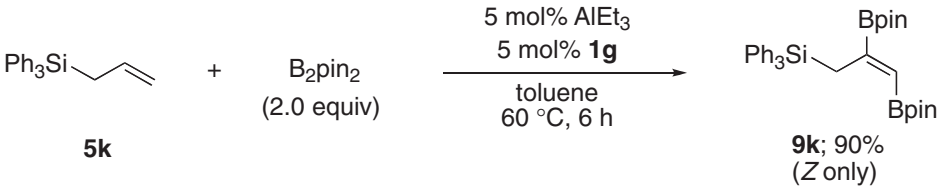
As summarized above, this protocol showed high activity and wide generality for dehydrogenative borylation, suppressing the hydroboration and hydrogenation completely. In most cases, monoborylalkenes were obtained from a 1:1 mixture of substrate and B_2pin_2. These notable features prompted us to examine the successive dehydrogenative borylation by using 2 equivalents of B_2pin_2. We expected that dehydrogenative borylation of monoborylalkenes would proceed to give 1,1-[23] or 1,2-diborylalkenes[8c,15,24] depending on the regioselectivity of the second borylation (Scheme 5). Such diborylalkenes are useful building blocks for the synthesis of π-conjugated material because two boryl groups could be utilized for successive cross-coupling reaction to afford various trisubstituted alkenes.[25] It should be noted that most reported dehydrogenative borylations necessitate the use of excess amounts of alkenes due to accompanying hydroboration or hydrogenation, which renders realization of successive dehydrogenative borylations difficult. Only one report describes the synthesis of diborylalkenes by a Rh-catalyzed successive reaction, in which only two examples were reported.[12b]



Scheme 5. Successive dehydrogenative borylation.



Scheme 6. Successive dehydrogenative borylation of styrene **5a**.



Scheme 7. Successive dehydrogenative borylation of triphenylallylsilane (**5k**).

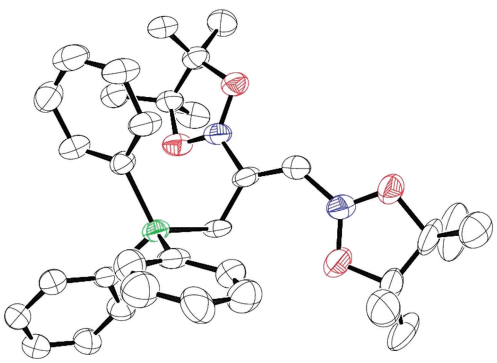
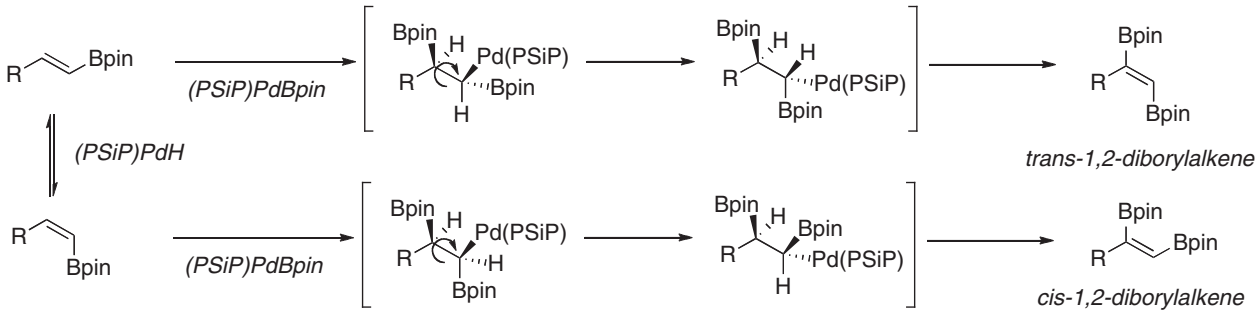


Figure 3. ORTEP plot of **9k**. Hydrogen atoms are omitted for clarity.

We then examined whether such successive dehydrogenative borylation was possible or not by using our protocol. When styrene **5a** and 2 equivalents of B_2pin_2 were treated with 2 mol % of palladium triflate **1f** and $AlEt_3$, the desired 1,1-diborylstyrene **9a** was obtained in high yield (Scheme 6). Interestingly, when triphenylallylsilane (**5k**) was employed under similar conditions, (*Z*)-1,2-diboryl alkene **9k**, the opposite regioisomer for the reaction of styrene, was obtained selectively (Scheme 7). Regio- and stereochemistry of compound **9k** was confirmed by X-ray analysis (Figure 3). As shown in Table 2, the intermediate monoborylalkene **6k** was obtained as a mixture of stereoisomers with *E*:*Z* = 75:25. We believe that (*Z*)-**9k** (*trans*-1,2-diborylated alkene in which two boryl groups located *trans*) was obtained mainly from (*E*)-monoborylalkene through *syn*-borylpalladation followed by *syn*-β-hydride elimination, and the remaining less reactive (*Z*)-monoborylalkene would have isomerized to (*E*)-monoborylalkene during the course of the reaction through a hydropalladation/β-hydride elimination sequence as described before, although the possibility of isomerization of 1,2-diborylated alkene product cannot be ruled out (Scheme 8).[26] Then we examined the substrate scope and the regioselectivity of successive dehydrogenative borylation reaction.

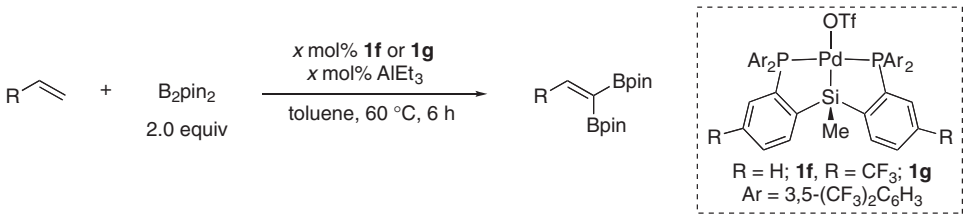
As a result, it was found that the reaction of terminal alkenes bearing a bulky substituent or a conjugated substituent such as an aryl and alkenyl group afforded 1,1-diborylated products selectively (Table 4). The reaction of vinylferrocene (**5e**) and *N*-vinylphthalimide (**5r**) gave 1,1-diborylalkenes **9e** and **9r** in high yield by using palladium complex **1g** (Table 4, Entries 1 and 2). While our attempt to synthesize diborylalkenes from other styrenes such as α-methylstyrene (**5b**) or β-methylstyrene (**5d**) was not successful, a 1:2 mixture of 1,1-disubstituted dienes **7b**–**7e** and B_2pin_2 also gave 1,1-diboryldienes **10b**–**10e** in high yield in the presence of 2.5 mol % of palladium triflate **1a** or **1g** and $AlEt_3$ (Table 3, Entries 3–6). These are the first diboryldiene synthesis by dehydrogenative borylation.[27] Although the reason is not obvious, diboryldiene synthesis from monosubstituted diene **7a**, 1,1,2- or 1,3-substituted diene **7f** or **7g** was not successful and monoboryldienes were obtained in these cases.

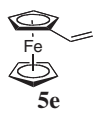
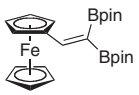
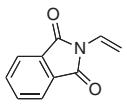
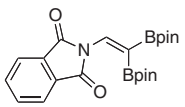
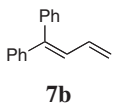
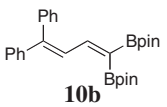
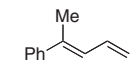
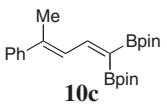
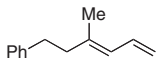
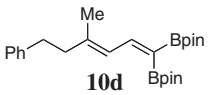
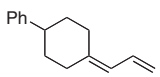
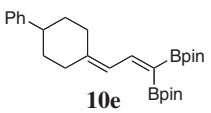
In contrast to these results, the reaction of sterically less demanding, unconjugated terminal alkenes such as allylcyclo-



Scheme 8. Proposed mechanism of the generation of (*E*)-1,2-diborylalkene **9k**.

Table 4. Dehydrogenative 1,1-Diborylation

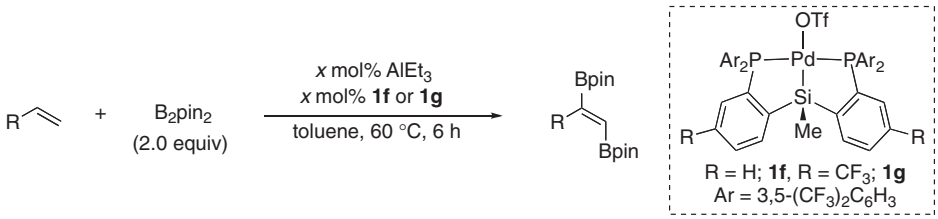


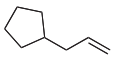
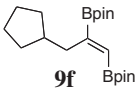
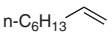
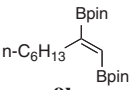
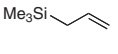
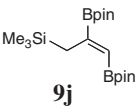
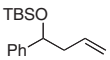
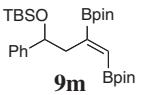
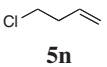
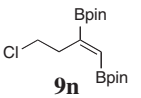
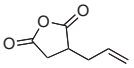
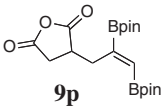
Entry	Substrates	*x* (**1f** or **1g**)	Product	Yield/%	*E*:*Z*	*di*:*mono*[b)]
1	 **5e**	5 (**1g**)	 **9e**	92	—	≧50:1
2	 **5r**	5 (**1g**)	 **9r**	94[a)]	—	≧50:1
3	 **7b**	2.5 (**1f**)	 **10b**	98	—	≧50:1
4	 **7c** (*E*:*Z* = 8:2)	2.5 (**1f**)	 **10c**	93	—	≧50:1
5	 **7d** (*E*:*Z* = 7:3)	2.5 (**1g**)	 **10d**	95	73:27	≧50:1
6	 **7e**	2.5 (**1g**)	 **10e**	89	—	≧50:1

a) 3.0 equivalents of B_2pin_2 were used. b) The ratio of diborylalkene and monoborylalkene was determined by crude NMR spectrum.

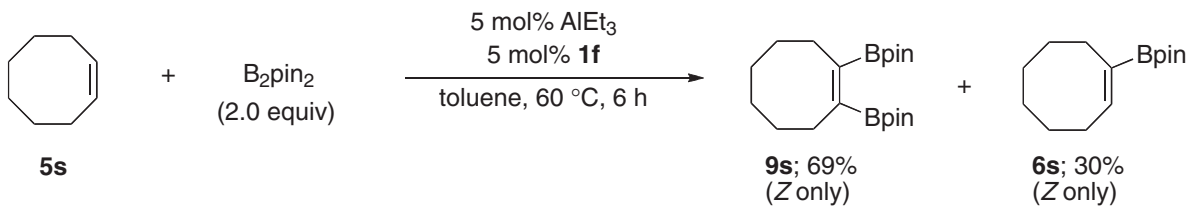
pentane (**5f**) and 1-octene (**5h**) gave *1,2-diboryl*alkenes with good *trans* selectivity (Table 5, Entries 1 and 2). This reaction also showed good compatibility of functional groups, and functionalized (*Z*)-1,2-diborylalkenes **9j**–**9p** (*trans*-1,2-diboryl) were obtained in moderate to good yield under appropriate conditions, suggesting our protocol is applicable to the synthesis of multifunctionalized compounds (Entries 3–6). These results clearly demonstrated that 1,2-selectivity was general for the reaction of electronically nonactivated alkenes. It should be noted that, in previously reported Rh-catalyzed successive dehydrogenative borylation, the reaction of 1-octene gave 1,1-diborylalkene and Pt-catalyzed diborylation of alkynes afforded *cis*-1,2-diborylalkenes.[28] Our protocol is the first general method for the synthesis of *trans*-1,2-diborylalkenes by successive dehydrogenative borylation. Moreover, the current protocol allowed the synthesis of 1,2-diborylcyclooctene **9s** which could not be synthesized by Pt-catalyzed diborylation of alkyne (Scheme 9). This compound was also thought to be generated by double bond migration as discussed in the monoborylation of cycloheptene (**5i**). However, successive dehydro-

Table 5. Dehydrogenative 1,2-Diborylation



Entry	Substrates	*x* (**1f** or **1g**)	Product	Yield/%	*E*:*Z*	*di*:*mono*[c)]
1	 **5f**	10 (**1f**)	 **9f**	85[a)]	22:78	≧50:1
2	 **5h**	10 (**1f**)	 **9h**	63[a),b)]	19:81	≧50:1
3	 **5j**	1 (**1g**)	 **9j**	82	4:96	≧50:1
4	 **5m**	10 (**1f**)	 **9m**	68	11:89	≧50:1
5	 **5n**	10 (**1f**)	 **9n**	49	11:89	≧50:1
6	 **5p**	10 (**1f**)	 **9p**	52	*Z* only	≧50:1

a) 3.0 equiv of B_2pin_2. b) The reaction was carried out in THF. c) The ratio of diborylalkene and monoborylalkene was determined by crude NMR spectrum.



Scheme 9. Successive dehydrogenative borylation of cyclooctene (**5s**).

genative borylation of cyclic alkenes showed poor generality, and the reaction of cycloheptene (**5i**) or cyclopentene gave several compounds including allylboronic esters probably due to isomerization of double bonds. Cyclohexene did not react at all although the reason was not obvious.

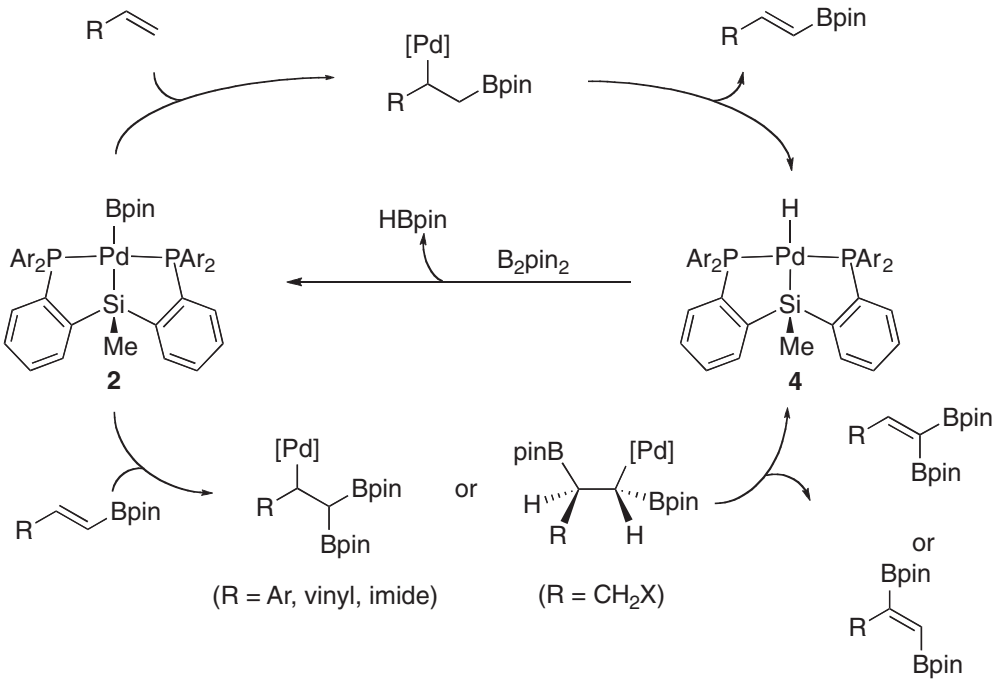
A proposed mechanism of this reaction is summarized in Scheme 10. At first, the palladium triflate complex **1** reacts with $AlEt_3$ in the presence of B_2pin_2 to give the monoborylpalladium complex **2** and HBpin. The borylpalladium **2** undergoes alkene insertion and β-hydride elimination to give the monoborylation product with generation of the palladium hydride **4**, which reacts with B_2pin_2 to regenerate the borylpalladium **2**. Second, borylation in the presence of excess B_2pin_2 gives the diborylation product with high regioselectivity depending on the substituent on the terminal alkenes. This catalytic cycle excludes formation of boryl(hydrido)- or dihydrido complex, thus selective synthesis of alkenyl- or dienylboronic ester could be realized.

Conclusion

In summary, we successfully developed PSiP-pincer type palladium-catalyzed dehydrogenative borylation. Various alkenes and 1,3-dienes are applicable to this reaction and synthetically useful mono- and diborylalkenes or dienes are obtained selectively without hydroboration or hydrogenation.

Experimental

General. All operations except workup and purification were performed under an argon atmosphere. ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX-500 (500 MHz for



Scheme 10. Proposed mechanism of PSiP-pincer palladium-catalyzed dehydrogenative borylation.

^{1}H, 125 MHz for ^{13}C) spectrometer, a JEOL ECX-500 (500 MHz for ^{1}H, 125 MHz for ^{13}C), a JEOL ECX-400 (400 MHz for ^{1}H, 100 MHz for ^{13}C), a JEOL Lambda-400 (400 MHz for H^1 and 100 MHz for ^{13}C), a JEOL AL-400 (400 MHz for H^1 and 100 MHz for ^{13}C) or a JEOL AL-300 (300 MHz for H^1 and 75 MHz for ^{13}C) spectrometer in $CDCl_3$ (99.8% atom enriched, Acros Co., Ltd.). Chemical shifts are expressed in parts per million (ppm) downfield from tetramethylsilane and are referenced to residual solvents (d_H 7.26 and d_C 77.0). IR spectra were recorded on an FT/IR-460 plus (JASCO Co., Ltd.). Silica Gel 60 (Kanto Chemical Co., Inc.) was used for flash column chromatography. Merck Kieselgel 60 F_{254} (0.25 mm thickness, coated on glass 20 × 20 cm^2) plate was used for analytical thin layer chromatography (TLC), and Wakogel B-5F coated on glass with a thickness of 0.9 mm was used for preparative TLC. Elemental analyses were performed on an Elementar Vario MICRO. THF and toluene were purified by Glass-Contour solvent purification system. $AlEt_3$ (0.95 M solution in toluene) was purchased from Kanto Chemicals. Bis(pinacolato)diboron was purchased from Aldrich and purified by recrystallization from hexane before use. Pd complexes **1a**,[16a] **1f**,[17] and **1g**,[17] were prepared according to a previously reported method. Alkenes **5m**[29] and **5n**[30] and 1,3-dienes **7a**,[31] **7b**,[32] **7c**,[33] **7d**,[16c] **7e**,[16c] **7f**,[34] and **7g**[35] were known compounds in literature and others were commercially available. The geometry of the obtained boronic esters was determined by coupling constants between two olefinic protons or by NOE measurement.

General Procedure for Dehydrogenative Monoborylation of Alkene. To a solution of bis(pinacolato)diboron (50.8 mg, 0.20 mmol) and palladium catalyst **1f** (2.7–27.3 mg, 0.002–0.02 mmol) in toluene (2.0 mL) were added $AlEt_3$ (0.95 M in toluene, 2.0–21.0 μL, 0.02–0.02 mmol) and an alkene **5** (0.20 mmol) at room temperature in a 30-mL two-necked flask equipped with a three-way stopcock. The mixture was stirred for 24 h at room temperature or for 6 h at 60 °C. After the solvent was removed under reduced pressure (*Caution! The reaction affords pinacolborane as a by-product, which produces hydrogen gas by reacting with water. This manipulation should be conducted carefully in a well-ventilated hood.*), the resulting crude product was purified by silica gel column chromatography (hexanes/AcOEt) to give alkenylboronic ester **6** (43%–93% yield). In most cases, column chromatography was carried out at low temperature by using a column fitted with an outer jacket (the column temperature was maintained below ca. −40 °C by filling dry ice/acetone in the outer jacket) since some alkenylboronic esters were unstable to protodeboration on the silica gel.

(*E*)-4,4,5,5-Tetramethyl-2-styryl-1,3,2-dioxaborolane (6a): 105.8 mg, 0.46 mmol from 0.50 mmol of **5a**. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.31 (12H, s), 6.16 (1H, d, J = 9.1 Hz), 7.27–7.35 (3H, m), 7.39 (1H, d, J = 9.1 Hz), 7.48 (2H, d, J = 7.9 Hz). Spectral data were in good agreement with literature values.[36]

(*E*)-4,4,5,5-Tetramethyl-2-(2-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane (6b): 106.6 mg, 0.437 mmol from 0.50 mmol of **5b**. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.32 (12H, s), 2.41 (3H, s), 5.76 (1H, s), 7.27–7.34 (3H, m), 7.48–7.52 (2H, m). Spectral data were in good agreement with literature values.[12b]

2-(2,2-Diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6c): 64.1 mg, 0.20 mmol from 0.20 mmol of **4d**. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.18 (12H, s), 6.03 (1H, s), 7.27–7.36 (10H, m). Spectral data were in good agreement with literature values.[37]

(*Z*)-4,4,5,5-Tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane (6d): 108.2 mg, 0.443 mmol from 0.50 mmol of **4f**. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.32 (12H, s), 1.99 (3H, s), 7.22–7.27 (2H, m), 7.32–7.40 (4H, m). Spectral data were in good agreement with literature values.[38]

(*E*)-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ferrocene (6e): 62.8 mg, 0.186 mmol from 0.20 mmol of **5e**. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.30 (12H, s), 4.11 (5H, s), 4.27 (2H, s), 4.43 (2H, s), 5.72 (1H, d, $J = 18.2$ Hz), 7.22 (1H, d, $J = 18.2$ Hz). Spectral data were in good agreement with literature values.[8a]

2-(3-Cyclopentylprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6f): *E*:*Z* = 93:7, 20.6 mg, 0.0872 mmol from 0.20 mmol of **5f**. IR (neat): 2951, 1637, 1362, 1318, 1145 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): (*E*)-isomer: δ 1.09–1.16 (2H, m), 1.26 (12H, m), 1.44–1.62 (4H, m), 1.70–1.78 (2H, m), 1.87–1.94 (1H, m), 2.16 (2H, td, $J = 6.9$, 1.5 Hz), 5.41 (1H, dt, $J = 17.9$, 1.5 Hz), 6.62 (1H, dt, $J = 17.9$, 6.9 Hz); characteristic resonances of the (*Z*)-isomer: 2.39 (1H, t, $J = 8.0$ Hz), 5.33 (1H, d, $J = 13.0$ Hz), 6.40–6.47 (1H, m); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 24.8, 25.1, 32.4, 39.0, 42.4, 83.0, 154.1 (the olefinic carbon atom connected to B is missing); Anal. Calcd for $C_{14}H_{25}BO_2$: C, 71.20; H, 10.67%. Found: C, 71.08; H, 10.40%.

4,4,5,5-Tetramethyl-2-(2-methyl-4-phenylbut-1-en-1-yl)-1,3,2-dioxaborolane (6g): *E*:*Z* = 37:63, 44.8 mg, 0.165 mmol from 0.20 mmol of **6g**. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.26 ((*Z*), 12H, s), 1.28 ((*E*), 12H, s), 1.91 ((*Z*), 3H, s), 2.04 ((*E*), 3H, s), 2.38–2.43 ((*E*), 2H, m), 2.66–2.75 ((*Z*), 4H, m), 2.75–2.79 ((*E*), 2H, m), 5.17 ((*Z*), 1H, s), 5.21 ((*E*), 1H, s), 7.15–7.20 (both isomers, 2H, m), 7.23–7.30 (both isomers, 3H, m). Spectral data were in good agreement with literature values.[39]

4,4,5,5-Tetramethyl-2-(oct-1-en-1-yl)-1,3,2-dioxaborolane (6h): *E*:*Z* = 93:7, 40.6 mg, 0.170 mmol from 0.20 mmol of **7h**. IR (neat): 2926, 1638, 1361, 1318, 1143 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): (*E*)-isomer: δ 0.82–0.92 (3H, m), 1.27 (12H, s), 1.22–1.34 (6H, m), 1.36–1.44 (2H, m), 2.14 (2H, q, $J = 8.1$ Hz), 5.43 (1H, d, $J = 18.8$ Hz), 6.62 (1H, dt, $J = 18.8$, 8.1 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 14.1, 22.6, 24.8, 28.2, 28.9, 31.7, 35.8, 83.0, 154.8 (the olefinic carbon atom connected to B is missing). Characteristic resonances of the (*Z*)-isomer: 2.33–2.42 (2H, m), 5.32 (1H, d, $J = 13.4$ Hz), 6.38–6.46 (1H, m). Spectral data of both isomers were in good agreement with literature values.[36,40]

2-(Cyclohept-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6i): 43.7 mg, 0.197 mmol from 0.20 mmol of **7i**. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.26 (12H, s), 1.43–1.50 (4H, m), 1.71–1.77 (2H, m), 2.20–2.28 (4H, m), 6.77 (1H, t, $J = 5.6$ Hz). Spectral data were in good agreement with literature values.[41]

Trimethyl[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl]silane (6j): *E*:*Z* = 87:13, obtained as a mixture with **9j** (**6j**:**9j** = 82:18), 37.5 mg, 0.117 mmol of **6j** from 0.20 mmol of **5j**. ^{1}H NMR ($CDCl_3$, 500 MHz): δ −0.02 ((*Z*), 9H, s), 0.02 ((*E*), 9H, s), 1.24 ((*Z*), 12H, s), 1.25 ((*E*), 12H, s), 1.69 ((*E*), 2H, d, $J = 8.2$ Hz), 2.04 ((*Z*), 2H, d, $J = 9.0$ Hz), 5.18 ((*Z*), 1H, d, $J = 12.2$ Hz), 5.23 ((*E*), 1H, dt, $J = 17.7$, 1.2 Hz), 6.48–6.55 ((*Z*), 1H, m), 6.66 ((*E*), 1H, dt, $J = 17.7$, 8.2 Hz). Spectral data were in good agreement with literature values.[15]

Triphenyl[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl]silane (6k): *E*:*Z* = 75:25, (*Z*)-isomer was obtained as a mixture with a small amount of 1-propenyltriphenylsilane and some isomers of alkenylboronic ester (less than 4%). (*E*)-**6k**: 53.5 mg, 0.126 mmol from 0.20 mmol of **5k**. IR (neat): 2975, 1622, 1427, 1358, 1325 cm^{-1}; (*E*)-isomer: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.22 (12H, s), 2.56 (2H, d, $J = 8.0$ Hz), 5.34 (1H, d, $J = 17.7$ Hz), 6.73 (1H, dt, $J = 17.7$, 8.0 Hz), 7.33–7.37 (6H, m), 7.39–7.43 (3H, m), 7.49–7.52 (6H, m); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 24.67, 24.79, 82.8, 127.8, 129.6, 134.3, 135.7, 150.0 (the olefinic carbon atom connected to B is missing); (*Z*)-isomer: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.14 (12H, s), 2.93 (2H, d, $J = 8.5$ Hz), 5.26 (1H, d, $J = 13.3$ Hz), 6.58 (1H, dt, $J = 13.3$, 8.5 Hz), 7.32–7.41 (9H, m), 7.51–7.56 (6H, m); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 21.5, 24.8, 82.6, 127.7, 129.4, 134.6, 135.9, 150.6 (the olefinic carbon atom connected to B is missing); Anal. Calcd for $C_{27}H_{31}BO_2Si$: C, 76.05; H, 7.33%. Found: C, 76.07; H, 7.09%.

(*E*)-Triphenyl[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl]silane (6l): 72.6 mg, 0.176 mmol from 0.20 mmol of **7k**. IR (neat): 3066, 2965, 1588, 1427, 1325, 1261 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.28 (12H, s), 6.38 (1H, d, $J = 21.7$ Hz), 7.33–7.37 (6H, m), 7.38–7.43 (3H, m), 7.51–7.54 (6H, m), 7.58 (1H, d, $J = 21.7$ Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 24.8, 83.5, 127.8, 129.5, 133.8, 136.1, 150.5 (the olefinic carbon atom connected to B is missing); Anal. Calcd for $C_{26}H_{29}BO_2Si$: C, 75.72; H, 7.09%. Found: C, 75.58; H, 6.93%.

***tert*-Butyldimethyl{[1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yl]oxy}silane (6m):** *E*:*Z* = 88:12, 48.4 mg, 0.125 mmol from 0.20 mmol of **5m**. IR (neat): 2957, 2929, 2857, 1638, 1361, 1321, 1257 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ −0.13 ((*E*), 3H, s), −0.11 ((*Z*), 3H, s), 0.01 ((*E*), 3H, s), 0.02 ((*Z*), 3H, s), 0.87 (both isomers, 9H, s), 1.25 (both isomers, 12H, s), 2.42–2.48 ((*E*), 1H, m), 2.52 ((*E*), 1H, dt, $J = 14.2$, 7.0 Hz), 2.72–2.87 ((*Z*), 2H, m), 4.70 ((*E*), 1H, dd, $J = 8.0$, 4.6 Hz), 4.72–4.75 ((*Z*), 1H, m), 5.41 ((*Z*), 1H, d, $J = 13.5$ Hz), 5.46 ((*E*), 1H, d, $J = 18.1$ Hz), 6.39–6.44 ((*Z*), 1H, m), 6.64 ((*E*), 1H, dt, $J = 18.1$, 7.0 Hz), 7.20–7.32 (both isomers, 5H, m); ^{13}C NMR ($CDCl_3$, 125 MHz): δ −4.9, −4.6, 18.3, 24.70, 24.74, 25.8, 47.7, 74.8, 83.0, 125.8, 127.0, 128.0, 145.2, 151.2 (the olefinic carbon atom connected to B is missing); Anal. Calcd for $C_{22}H_{37}BO_3Si$: C, 68.03; H, 9.60%. Found: C, 67.89; H, 9.31%.

2-(3-Chloroprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6n): *E*:*Z* = 92:8, 19.5 mg, 0.107 mmol from 0.20 mmol of **5n**. IR (neat): 2978, 1638, 1362, 1319, 1140 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): (*E*)-isomer: δ 1.27 (12H, s), 2.62 (2H, q, $J = 7.0$ Hz), 3.57 (2H, t, $J = 7.0$ Hz), 5.55 (1H, d, $J = 18.0$ Hz), 6.57 (1H, dt, $J = 18.0$, 7.0 Hz); characteristic resonances of the (*Z*)-isomer: 2.87 (2H, q, $J = 7.5$ Hz), 5.52 (1H, d, $J = 13.0$ Hz), 6.40–6.48 (1H, m); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 24.8, 38.6, 42.8, 83.3, 148.8 (the olefinic carbon atom connected to B is missing); Anal. Calcd for $C_{10}H_{18}BClO_2$: C, 55.47; H, 8.38%. Found: C, 55.23; H, 8.08%.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-enenitrile (6o): *E*:*Z* = 62:38. The (*E*)-isomer was roughly purified by silica gel column chromatography at low temperature, and its spectral data are shown below. On the other hand, the (*Z*)-isomer was not obtained after column chromatography probably due to its instability to silica gel. Therefore, the yield and the *E*:*Z* ratio of **6o** were determined by ^{1}H NMR of the crude mixture using tetrachloroethane as an internal standard. (*E*)-isomer: IR (neat): 2979, 1643, 1362, 1330, 1279, 1138 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.27 (12H, s), 3.19–

3.22 (2H, m), 5.87 (1H, d, $J = 17.8$ Hz), 6.42 (1H, dt, $J = 17.8$, 5.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 23.2, 24.7, 83.7, 116.5, 138.6 (the olefinic carbon atom connected to B is missing); (*Z*)-isomer: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.27 (12H, s), 3.54 (2H, dd, $J = 7.1$, 1.6 Hz), 5.65 (1H, brd, $J = 11.7$ Hz), 6.30–6.38 (1H, m).

3-[3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)allyl]-dihydrofuran-2,5-dione (6p): *E*:*Z* = 86:14. A part of the (*E*)-isomer was purified by silica gel column chromatography at low temperature, and its spectral data are shown below. Most of (*E*)- and (*Z*)-isomer were obtained as a mixture with some unidentified compounds derived from the Pd-complex after column chromatography, and therefore the yield and the *E*:*Z* ratio of **6p** were determined by ^{1}H NMR of the crude mixture using tetrachloroethane as an internal standard. (*E*)-isomer: IR (neat): 2979, 1861, 1774, 1364 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.27 (12H, s), 2.48–2.56 (1H, m), 2.70 (1H, dd, $J = 18.9$, 6.6 Hz), 2.77–2.93 (1H, m), 3.07 (1H, dd, $J = 18.9$, 9.9 Hz), 3.22–3.29 (1H, m), 5.57 (1H, d, $J = 17.9$ Hz), 6.47 (1H, dt, $J = 17.9$, 6.6 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 24.74, 24.77, 33.4, 36.4, 39.6, 83.5, 146.3, 169.6, 173.0 (the olefinic carbon atom connected to B is missing); Anal. Calcd for $C_{13}H_{19}BO_5$: C, 58.68; H, 7.20%. Found: C, 58.64; H, 6.90%. Characteristic resonances of (*Z*)-isomer: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.62 (1H, d, $J = 13.5$ Hz), 6.29–6.36 (1H, m).

4,4,5,5-Tetramethyl-2-[3-(phenylsulfonyl)prop-1-en-1-yl]-1,3,2-dioxaborolane (6q): *E*:*Z* = 56:44, 42.3 mg, 0.137 mmol from 0.20 mmol of **5q**. IR (neat): 2979, 1629, 1447, 1421, 1308, 1281, 1263 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.14 ((*Z*), 12H, s), 1.23 ((*E*), 12H, s), 3.88 ((*E*), 2H, d, $J = 7.5$ Hz), 4.34 ((*Z*), 2H, d, $J = 7.8$ Hz), 5.51 ((*E*), 1H, d, $J = 16.9$ Hz), 5.66 ((*Z*), 1H, d, $J = 13.4$ Hz), 6.36–6.43 ((*Z*), 1H, m), 6.49 ((*E*), 1H, dt, $J = 16.9$, 7.5 Hz), 7.49–7.65 (both isomers, 3H, m), 7.84–7.90 (both isomers, 2H, m); ^{13}C NMR ($CDCl_3$, 125 MHz): (*E*)-isomer: δ 24.7, 62.6, 83.6, 128.4, 129.0, 133.8, 137.3, 138.7 (the olefinic carbon atom connected to B is missing); (*Z*)-isomer: 24.7, 58.7, 83.4, 128.6, 128.8, 133.4, 136.6, 138.6 (the olefinic carbon atom connected to B is missing); Anal. Calcd for $C_{15}H_{21}BO_4S$: C, 58.46; H, 6.87; S, 10.40%. Found: C, 58.28; H, 6.59; S, 10.61%.

(*E*)-2-[2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-vinyl]isoindoline-1,3-dione (6r): 54.1 mg, 0.181 mmol from 0.20 mmol of **5r**. IR (neat): 2978, 1725, 1625, 1345, 1309 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.30 (12H, s), 6.45 (1H, d, $J = 16.9$ Hz), 7.47 (1H, d, $J = 16.9$ Hz), 7.74–7.78 (2H, m), 7.88–7.91 (2H, m); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 24.8, 83.4, 123.8, 131.6, 133.7, 134.7, 166.2 (the olefinic carbon atom connected to B is missing); Anal. Calcd for $C_{16}H_{18}BNO_4$: C, 64.24; H, 6.07; N, 4.68%. Found: C, 64.16; H, 5.80; N, 4.42%.

General Procedure for Dehydrogenative Monoborylation of 1,3-Diene. To a solution of bis(pinacolato)diboron (25.4 mg, 0.10 mmol) and palladium catalyst **1f** or **1g** (0.025 mmol) in toluene (1.0 mL) were added $AlEt_3$ (0.95 M in toluene, 2.6 µL, 0.025 mmol) and 1,3-diene **7** (0.10 mmol) at room temperature in a 30-mL flask. The mixture was stirred for 6 h at 60 °C. After the solvent was removed under reduced pressure, the resulting crude product was purified by silica gel column chromatography (hexanes/AcOEt) at low temperature to give dienylboronic.

4,4,5,5-Tetramethyl-2-(4-phenylbuta-1,3-dien-1-yl)-1,3,2-dioxaborolane (8a): (1*E*, 3*E*):(1*Z*, 3*E*) = 58:42, 20.6 mg, 0.080 mmol, 80%. IR (neat): 1584, 1453, 1424, 1372, 1335, 1255, 1135 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.30 ((*E*), 12H, s), 1.33 ((*Z*), 12H, s), 5.48 ((*Z*), 1H, d, $J = 13.3$ Hz), 5.68 ((*E*), 1H, d, $J = 17.8$ Hz), 6.65 ((*Z*), 1H, d, $J = 15.3$ Hz), 6.70 ((*E*), 1H, d, $J = 15.8$ Hz), 6.86 (1H, dd, $J = 10.3$, 15.8 Hz), 7.02 ((*Z*), 1H, dd, $J = 11.3$, 13.3 Hz), 7.18 ((*E*), 1H, dd, $J = 10.3$, 17.8 Hz), 7.22–7.51 (both isomers, 5H, m); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 24.7, 24.9, 83.1, 83.2, 126.8, 127.9, 128.1, 128.5, 128.6, 129.3, 130.5, 136.0, 136.3, 136.7, 137.1, 149.7, 150.3 (the olefinic carbon atom connected to B is missing); HRMS Calcd for $C_{16}H_{21}BO_2$, 256.1635, found 256.1624.

2-(4,4-Diphenylbuta-1,3-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8b): *E*:*Z* = 87:13, 26.5 mg, 0.098 mmol, 98%. IR (neat): 2974, 1605, 1445, 1378, 1371, 1326, 1254, 1142 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): *E*-isomer: δ 1.22 (12H, s), 5.75 (1H, d, $J = 17.7$ Hz), 6.74 (1H, d, $J = 11.1$ Hz), 7.09 (1H, dd, $J = 11.1$, 17.7 Hz), 7.20–7.39 (10H, m); characteristic resonances of the (*Z*)-isomer: δ 1.31 (12H, s), 5.41 (1H, d, $J = 13.8$ Hz), 6.93 (1H, dd, $J = 12.0$, 13.8 Hz), 7.63 (1H, d, $J = 12.0$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 24.7, 83.1, 127.6, 127.8, 127.9, 128.2, 130.1, 130.5, 139.4, 142.2, 145.9, 146.9 (the olefinic carbon atom connected to B is missing); HRMS Calcd for $C_{22}H_{25}BO_2$, M + H 333.2026, found 333.2024.

4,4,5,5-Tetramethyl-2-(4-phenylpenta-1,3-dien-1-yl)-1,3,2-dioxaborolane (8c): The geometry of the two isomers (1*E*, 3*E*)-**8c** and (1*E*, 3*Z*)-**8c** was determined by the observation of NOE between the methyl protons and the olefinic proton of 3-position or 2-position, (1*E*, 3*E*):(1*E*, 3*Z*) = 86:14. This compound contained small amounts of other stereoisomers (1*Z*, 3*E*/*Z*)-**8c** (ca. 5%), 26.5 mg, 0.098 mmol, 98%. IR (neat): 2981, 2360, 2343, 1617, 1592, 1355, 1336, 1259, 1137 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.22 ((*Z*), 12H, s), 1.30 ((*Z*), 12H, s), 2.15 ((*Z*), 3H, s), 2.26 ((*E*), 3H, d, $J = 1.1$ Hz), 5.54 ((*Z*), 1H, d, $J = 17.6$ Hz), 5.67 ((*E*), 1H, d, $J = 17.2$ Hz), 6.23 ((*Z*), 1H, d, $J = 10.9$ Hz), 6.55 ((*E*), 1H, d, $J = 10.9$ Hz), 7.05 ((*Z*), 1H, dd, $J = 10.9$, 17.6 Hz), 7.22–7.39 (both isomers, 3H, m), 7.45 ((*E*), 1H, dd, $J = 10.9$, 17.2 Hz), 7.43–7.53 (both isomers, 2H, m); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 16.3, 24.7, 83.2, 125.8, 127.6, 128.3, 129.1, 140.3, 142.6, 145.8 (the olefinic carbon atom connected to B is missing); HRMS Calcd for $C_{17}H_{23}BO_2$, 270.1791, found 270.1796.

4,4,5,5-Tetramethyl-2-(4-methyl-6-phenylhexa-1,3-dien-1-yl)-1,3,2-dioxaborolane (8d): The geometry of the two isomers (1*E*, 3*E*)-**8d** and (1*E*, 3*Z*)-**8d** was determined by the observation of NOE between the olefinic proton of 3-position and the methylene protons or the methyl protons, (1*E*, 3*E*):(1*E*, 3*Z*) = 74:26. This compound contained small amounts of other stereoisomers (1*Z*, 3*E*/*Z*)-**8d** (ca. 5%), 27.7 mg, 0.093 mmol, 93%. IR (neat): 2977, 1638, 1599, 1364, 1336, 1315, 1143 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.22 ((*Z*), 12H, s), 1.30 ((*Z*), 12H, s), 2.15 ((*Z*), 3H, s), 2.26 ((*E*), 3H, d, $J = 1.1$ Hz), 5.54 ((*Z*), 1H, d, $J = 17.6$ Hz), 5.67 ((*E*), 1H, d, $J = 17.2$ Hz), 6.23 ((*Z*), 1H, d, $J = 10.9$ Hz), 6.55 ((*E*), 1H, d, $J =$

10.9 Hz), 7.05 ((*Z*), 1H, dd, $J = 10.9$, 17.6 Hz), 7.22–7.39 (both isomers, 3H, m), 7.45 ((*E*), 1H, dd, $J = 10.9$, 17.2 Hz), 7.43–7.53 (both isomers, 2H, m); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 17.3, 24.7, 34.4, 41.9, 83.0, 125.8, 127.7, 128.3, 141.8, 143.2, 145.3, 145.9 (the olefinic carbon atom connected to B is missing); HRMS Calcd for $C_{19}H_{27}BO_2$, 298.2104, found 298.2084.

4,4,5,5-Tetramethyl-2-[3-(4-phenylcyclohexylidene)prop-1-en-1-yl]-1,3,2-dioxaborolane (8e): *E*:*Z* = 85:15, 28.6 mg, 0.091 mmol, 91%. IR (neat): 2974, 1640, 1599, 1380, 1343, 1317, 1141 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.34 ((*E*), 12H, s), 1.36 ((*Z*), 12H, s), 1.50–1.72 (both isomers, 2H, m), 2.00–2.12 (both isomers, 2H, m), 2.30–2.56 (both isomers, 2H, m), 2.72–2.84 (both isomers, 2H, m), 3.20–3.40 (both isomers, 1H, m), 5.37 ((*Z*), 1H, d, $J = 13.7$ Hz), 5.56 ((*E*), 1H, d, $J = 17.7$ Hz), 6.03 (1H, d, $J = 11.3$ Hz), 6.76 (1H, d, $J = 11.2$ Hz), 7.20–7.40 (both isomers, 5H, m), 7.32–7.36 (2H, m), 7.41 ((*E*), 1H, d, $J = 17.7$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 24.7, 29.3, 35.0, 35.6, 37.1, 44.5, 83.0, 125.2, 126.0, 126.8, 128.4, 145.3, 146.5, 146.9 (the olefinic carbon atom connected to B is missing); HRMS Calcd for $C_{21}H_{29}BO_2$, 324.2261, found 324.2241.

(*E*)-4,4,5,5-Tetramethyl-2-(3-methyl-4,4-diphenylbuta-1,3-dien-1-yl)-1,3,2-dioxaborolane (8f): 31.2 mg, 0.090, 90%. IR (neat): 3326, 2979, 1600, 1379, 1339, 1322, 1141, 1022 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.23 (12H, s), 1.93 (3H, s), 5.74 (1H, d, $J = 18.0$ Hz), 7.10–7.14 (4H, m), 7.20–7.34 (7H, m); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 16.7, 24.7, 83.0, 126.8, 127.0, 129.9, 130.8, 132.6, 141.8, 143.2, 145.3, 150.1 (the olefinic carbon atom connected to B is missing); HRMS Calcd for $C_{23}H_{27}BO_2$, 346.2104, found 346.2114.

4,4,5,5-Tetramethyl-2-(2-methyl-4-phenylbuta-1,3-dien-1-yl)-1,3,2-dioxaborolane (8g): The geometry of the two isomers (1*E*, 3*E*)-**8g** and (1*Z*, 3*E*)-**8g** was determined by the observation of NOE between the olefinic proton of 1-position and the olefinic proton of 3-position or the methyl protons, (1*E*, 3*E*):(1*Z*, 3*E*) = 62:38, 12.5 mg, 0.046 mmol, 46%. IR (neat): 2977, 1602, 1449, 1363, 1322, 1289, 1257, 1141 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): (*E*)-isomer: δ 1.30 ((*E*), 12H, s), 1.32 ((*Z*), 12H, s), 2.11 ((*Z*), 3H, s), 2.23 ((*E*), 3H, s), 5.41 ((*Z*), 1H, s), 5.47 ((*E*), 1H, s), 6.69 (both isomers, 1H, d, $J = 16.0$ Hz), 6.87 ((*E*), 1H, d, $J = 16.0$ Hz), 7.21–7.50 (both isomers, 10H, m), 7.87 ((*Z*), 1H, $J = 16.0$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 16.6, 24.8, 82.9, 126.7, 126.8, 127.8, 128.6, 130.6, 134.8, 155.3 (the olefinic carbon atom connected to B is missing); HRMS Calcd for $C_{17}H_{23}BO_2$, 270.1791, found 270.1795.

General Procedure for the Dehydrogenative Diborylation of Alkenes and 1,3-Dienes. To a solution of bis(pinacolato)-diboron (101.6 mg, 0.40 mmol) and the palladium catalyst **1f** (2.7–27.3 mg, 0.002–0.02 mmol) or **1g** (3.0–30.0 mg, 0.002–0.02 mmol) in toluene (2.0 mL) were added $AlEt_3$ (0.95 M in toluene, 2.0–21.0 μL, 0.02–0.02 mmol) and alkene **5** (0.20 mmol) or diene **7** (0.10 mmol) at room temperature in a 30-mL two-necked flask equipped with three-way stopcock. The mixture was stirred for 24 h at room temperature or 6 h at 60 °C. After the solvent was removed under reduced pressure, the resulting crude product was purified by silica gel column chromatography (hexanes/AcOEt) at low temperature to give diborylalkenes **9** or dienes **10** (48%–98% yield).

2,2′-(2-Phenylethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (9a): 161 mg, 0.451 mmol from 0.50 mmol of **5a**. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.28 (12H, s), 1.31 (12H, s), 7.25–7.31 (3H, m), 7.46–7.50 (2H, m), 7.71 (1H, s). Spectral data were in good agreement with literature values.[42]

2,2′-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)ferrocene (9e): 43.2 mg, 0.0923 mmol from 0.10 mmol of **5e**. IR (neat): 2977, 1597, 1460, 1409, 1389, 1370, 1346, 1313, 1286, 1262, 1236 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.27 (12H, s), 1.35 (12H, s), 4.14 (5H, s), 4.26 (2H, s), 4.51 (2H, s), 7.46 (2H, s); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 24.87, 24.88, 68.9, 69.4, 69.6, 82.9, 83.3, 84.1, 154.3 (the olefinic carbon atom connected to B is missing); Anal. Calcd for $C_{24}H_{34}B_2FeO_4$: C, 62.13; H, 73.9%. Found: C, 62.02; H, 7.09%.

2-[2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-vinyl]isoindoline-1,3-dione (9r): 73.1 mg, 0.172 mmol from 0.20 mmol of **5r**. IR (neat): 2973, 1728, 1628, 1329, 1306 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.27 (12H, s), 1.36 (12H, s), 7.53 (1H, s), 7.72–7.76 (2H, m), 7.85–7.89 (2H, m); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 24.8, 25.3, 83.3, 83.5, 123.8, 131.7, 134.5, 134.8, 166.2 (the olefinic carbon atom connected to B is missing); Anal. Calcd for $C_{22}H_{29}B_2NO_6$: C, 62.16; H, 6.88; N, 3.29%. Found: C, 62.01; H, 6.59; N, 2.99%.

2,2′-(4,4-Diphenylbuta-1,3-diene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (10b): 44.8 mg, 0.098 mmol, 98%. IR (neat): 2979, 1371, 1327, 1279, 1258, 1142 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.18 (12H, s), 1.36 (12H, s), 7.15 (1H, d, $J = 11.6$ Hz), 7.30–7.40 (11H, m); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 24.7, 24.8, 82.9, 83.3, 127.6, 127.8, 128.0, 128.1, 129.3, 130.8, 139.1, 142.6, 147.0, 154.0 (the olefinic carbon atom connected to B is missing); HRMS Calcd for $C_{28}H_{36}B_2O_4$, 458.2800, found 458.2794.

(*E*)-2,2′-(4-Phenylpenta-1,3-diene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (10c): The geometry of the product was determined by the observation of an NOE between the methyl protons and the olefinic proton of 2-position, 36.9 mg, 0.093 mmol, 93%. IR (neat): 2979, 1609, 1540, 1370, 1325, 1288, 1255, 1139 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.26 (12H, s), 1.34 (12H, s), 2.26 (3H, s), 6.95 (1H, d, $J = 11.6$ Hz), 7.23–7.45 (3H, m), 7.47 (2H, d, $J = 7.0$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 15.9, 24.7, 24.8, 82.9, 83.2, 125.9, 127.5, 128.2, 128.5, 141.4, 143.0, 152.9 (the olefinic carbon atom connected to B is missing); HRMS Calcd for $C_{23}H_{34}B_2O_4$, M + H 397.2721, found 397.2729.

2,2′-(4-Methyl-6-phenylhexa-1,3-diene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (10d): The geometry of the two isomers were determined by the observation of NOE between the methyl protons and the olefinic proton of 2- or 3-position, *E*:*Z* = 73:17, 40.3 mg, 0.095 mmol, 95%. IR (neat): 2977, 1559, 1370, 1321, 1140 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.24 ((*E*), 12H, s), 1.27 ((*Z*), 12H, s), 1.29 ((*E*), 12H, s), 1.31 ((*Z*), 12H, s), 2.36–2.41 ((*E*), 2H, m), 2.56–2.60 ((*Z*), 2H, m), 2.70–2.79 (both isomers, 2H, m), 6.29 ((*Z*), 1H, dd, $J = 1.4$, 11.8 Hz), 6.32 ((*E*), 1H, dd, $J = 1.3$, 11.4 Hz), 7.14–7.30 (both isomers, 5H, m), 7.58 ((*Z*), 1H, d, $J = 11.8$ Hz), 7.61 ((*Z*), 1H, d, $J = 11.4$ Hz); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 17.3, 24.7, 24.8, 34.0, 42.1, 82.8, 83.1, 125.8, 126.7, 128.2, 128.3, 142.0, 144.9, 153.1 (the olefinic carbon atom connected to B is missing); HRMS Calcd for $C_{25}H_{38}B_2O_4$, 424.2956, found 424.2967.

2,2′-[3-(4-Phenylcyclohexylidene)prop-1-ene-1,1-diyl]bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (10e): 39.8 mg, 0.089 mmol, 89%. IR (neat): 2977, 2928, 2360, 2341, 1559, 1370, 1320, 1140 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 1.31 (12H, s), 1.36 (12H, s), 1.52–1.78 (2H, m), 1.98–2.15 (2H, m), 2.30–2.52 (2H, m), 2.72–2.78 (2H, m), 3.16–3.30 (1H, m), 6.36 (1H, d, $J = 11.9$ Hz), 7.17–7.45 (5H, m), 7.74 (1H, d, $J = 11.9$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 24.7, 24.8, 28.9, 34.8, 35.5, 37.6, 44.6, 82.8, 83.1, 124.8, 126.0, 126.8, 128.3, 146.6, 148.4, 152.3 (the olefinic carbon atom connected to B is missing); HRMS Calcd for $C_{27}H_{40}B_2O_4$, 450.3113, found 450.3120.

(*Z*)-[2,3-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-allyl]triphenylsilane (9k): 88.8 mg, 0.161 mmol from 0.20 mmol of **5j**. IR (neat): 2980, 1604, 1427, 1338, 1313, 1249, 1134 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 0.97 (12H, s), 1.02 (12H, s), 3.12 (2H, s), 6.12 (1H, s), 7.27–7.37 (9H, m), 7.47–7.52 (6H, m); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 23.0, 24.5, 24.7, 82.5, 83.4, 127.3, 129.0, 135.2, 136.5 (the olefinic carbon atoms connected to B are missing); Anal. Calcd for $C_{33}H_{42}B_2O_4Si$: C, 71.75; H, 7.66%. Found: C, 71.65; H, 7.40%.

2,2′-(3-Cyclopentylprop-1-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (9f): *E*:*Z* = 22:78, the geometry of the minor product was confirmed to be *E* by the observation of an NOE between the methylene protons and the olefinic proton, 61.6 mg, 0.170 mmol from 0.20 mmol of **5f**. IR (neat): 2977, 2946, 1615, 1329, 1308, 1136 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 1.14–1.30 (both isomers, 2H, m), 1.237 ((*Z*), 12H, s), 1.242 ((*Z*), 12H, s), 1.26 ((*E*), 12H, s), 1.31 ((*E*), 12H, s), 1.42–1.76 (both isomers, 6H, m), 1.87–1.99 (both isomers, 1H, m), 2.23 ((*E*), 2H, d, $J = 7.4$ Hz), 2.47 ((*Z*), 2H, d, $J = 7.4$ Hz), 5.83 ((*E*), 1H, s), 6.24 ((*Z*), 1H, s); ^{13}C NMR ($CDCl_3$, 125 MHz): (*E*)-isomer: δ 24.87, 24.89, 24.98, 32.6, 39.0, 46.4, 83.2, 83.6 (the olefinic carbon atoms connected to B are missing); (*Z*)-isomer: 24.7, 24.8, 25.00, 32.1, 39.3, 40.8, 82.8, 83.4 (the olefinic carbon atoms connected to B are missing); Anal. Calcd for $C_{20}H_{36}B_2O_4$: C, 66.34; H, 10.02%. Found: C, 66.09; H, 9.73%.

2,2′-(Oct-1-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (9h): *E*:*Z* = 19:81, 46.1 mg, 0.127 mmol from 0.20 mmol of **7h**. IR (neat): 2977, 2927, 1323, 1141 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): (*Z*)-isomer: δ 0.82–0.92 (3H, m), 1.24 (24H, s), 1.20–1.44 (8H, m), 2.46 (2H, t, $J = 8.1$ Hz), 6.23 (1H, s); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 14.1, 22.5, 24.7, 24.8, 29.0, 30.5, 31.7, 33.6, 82.8, 83.4 (the olefinic carbon atoms connected to B are missing); HRMS Calcd for $C_{20}H_{39}B_2O_4$, M + H 365.3034, found 365.3011. Characteristic resonances of the (*E*)-isomer: ^1H NMR ($CDCl_3$, 500 MHz): δ 2.21 (2H, t, $J = 8.1$ Hz), 5.84 (1H, s). Spectral data of (*E*)-isomer were in good agreement with literature values.[28a]

[2,3-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-allyl]trimethylsilane (9j): *E*:*Z* = 4:96, the geometry of the minor product was confirmed to be *E* by the observation of an NOE between the methylene protons and the olefinic proton, 60.2 mg, 0.164 mmol from 0.20 mmol of **5j**. IR (neat): 2978, 1602, 1309, 1247 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): (*E*)-isomer: δ 0.02 (9H, s), 1.30 (24H, s), 1.79 (2H, s), 5.62 (1H, s); (*Z*)-isomer: −0.01 (9H, s), 1.24 (24H, s), 2.21 (2H, s), 6.07 (1H, s); ^{13}C NMR ($CDCl_3$, 125 MHz): (*Z*)-isomer: δ −1.30, 24.8, 24.9, 26.0, 82.6, 83.5 (the olefinic carbon atoms connected to B are missing); Anal. Calcd for $C_{18}H_{36}B_2O_4Si$: C, 59.04; H, 9.91%. Found: C, 59.01; H, 9.61%.

***tert*-Butyldimethyl{[1-phenyl-3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yl]oxy}silane (9m):** *E*:*Z* = 11:89, the geometry of the minor product was confirmed to be *E* by the observation of an NOE between the methylene protons and the olefinic proton, 69.9 mg, 0.136 mmol from 0.20 mmol of **5m**. IR (neat): 2979, 2925, 2855, 1616, 1471, 1346, 1328, 1311 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ −0.16 ((*E*), 3H, s), −0.15 ((*Z*), 3H, s), −0.01 ((*Z*), 3H, s), 0.01 ((*E*), 3H, s), 0.84 (both isomers, 9H, s), 1.20 ((*Z*), 12H, s), 1.23 ((*Z*), 12H, s), 1.25 ((*E*), 12H, s), 1.29 ((*E*), 12H, s), 2.48–2.58 ((*E*), 2H, m), 2.73 ((*Z*), 1H, dd, $J = 12.2$, 6.4 Hz), 3.00 ((*Z*), 1H, dd, $J = 12.2$, 7.6 Hz), 4.80 ((*E*), 1H, dd, $J = 7.6$, 5.6 Hz), 4.85–4.89 ((*Z*), 1H, m), 5.82 ((*E*), 1H, s), 6.34 ((*Z*), 1H, s), 7.14–7.18 (both isomers, 1H, m), 7.22–7.32 (both isomers, 4H, m); ^{13}C NMR ($CDCl_3$, 125 MHz): (*Z*)-isomer: δ −4.67, −4.57, 18.3, 24.7, 24.8, 24.9, 25.0, 26.0, 44.9, 75.5, 82.9, 83.4, 126.4, 126.5, 127.6, 145.8 (the olefinic carbon atoms connected to B are missing); Anal. Calcd for $C_{28}H_{48}B_2O_5Si$: C, 65.38; H, 9.41%. Found: C, 65.22; H, 9.14%.

2,2′-(3-Chloroprop-1-ene-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (9n): *E*:*Z* = 9:91, the geometry of the minor product was confirmed to be *E* by the observation of an NOE between the methylene protons and the olefinic proton. This compound was obtained as a mixture with **6n** and dechlorinated product, 37.2 mg, 0.097 mmol from 0.20 mmol of **5n**. IR (neat): 2979, 1610, 1371, 1313, 1138 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): (*E*)-isomer: δ 1.27 (24H, s), 2.66 (2H, t, $J = 7.5$ Hz), 3.56 (2H, t, $J = 7.5$ Hz), 6.01 (1H, s); (*Z*)-isomer: δ 1.24 (12H, s), 1.25 (12H, s), 2.92 (2H, t, $J = 7.3$ Hz), 3.59 (2H, t, $J = 7.3$ Hz), 6.42 (1H, s); ^{13}C NMR ($CDCl_3$, 125 MHz): (*Z*)-isomer: δ 24.7, 24.8, 36.3, 45.0, 83.2, 83.7 (the olefinic carbon atoms connected to B are missing); Anal. Calcd for $C_{16}H_{29}B_2ClO_4$: C, 56.11; H, 8.54%. Found: C, 56.03; H, 8.26%.

(*Z*)-3-[2,3-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl]dihydrofuran-2,5-dione (9p): 46.3 mg, 0.118 mmol from 0.20 mmol of **5p**. IR (neat): 2978, 1860, 1777, 1348, 1326, 1308, 1279, 1261 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 1.27 (24H, s), 2.81–2.93 (3H, m), 2.99 (1H, dd, $J = 12.7$, 5.3 Hz), 3.36–3.43 (1H, m), 6.48 (1H, s); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 24.68, 24.74, 24.78, 24.80, 33.3, 34.4, 40.7, 83.6, 84.1, 170.7, 173.6 (the olefinic carbon atoms connected to B are missing); Anal. Calcd for $C_{19}H_{30}B_2O_7$: C, 58.21; H, 7.71%. Found: C, 57.92; H, 7.45%.

(*Z*)-1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-cyclooct-1-ene (9s): 49.7 mg, 0.137 mmol from 0.20 mmol of **5s**. IR (neat): 2977, 2926, 1616, 1472, 1378, 1335, 1298 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 1.27 (24H, s), 1.40–1.45 (4H, m), 1.46–1.53 (4H, m), 2.29–2.34 (4H, m); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 24.8, 26.4, 28.8, 29.2, 83.1 (the olefinic carbon atoms connected to B are missing); Anal. Calcd for $C_{20}H_{36}B_2O_4$: C, 66.34; H, 10.02%. Found: C, 66.15; H, 9.74%.

(*Z*)-2-(Cyclooct-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6s): 17.2 mg, 0.0728 mmol from 0.20 mmol of **5s**. ^1H NMR ($CDCl_3$, 500 MHz): δ 1.25 (12H, s), 1.40–1.52 (8H, m), 2.18–2.30 (4H, m), 6.58 (1H, t, $J = 8.0$ Hz). Spectral data were in good agreement with literature values.[15]

Crystallographic data have been deposited with The Cambridge Crystallographic Data Centre: Deposition numbers CCDC-853574 and 853878 for compound **2a** and **9k**. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (or from The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; e-mail: data_request@ccdc.cam.ac.uk).

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Supporting Information

Synthesis of palladium complexes **1b**–**1e** and **2a** and spectral data of these compounds are provided. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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