

Rhodium- and Ruthenium-Catalyzed Dehydrogenative Borylation of Vinylarenes with Pinacolborane: Stereoselective Synthesis of Vinylboronates

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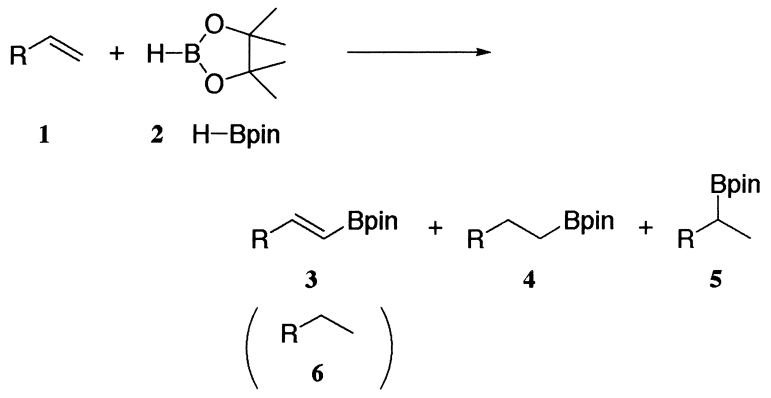
The treatment of pinacolborane (4,4,5,5-tetramethyl-1,3,2-dioxaborolane) with vinylarenes in the presence of a catalytic amount of phosphine-free di-μ-chlorobis(1,5-cyclooctadiene)dirhodium(I) [RhCl(cod)]$_2$, through dehydrogenative borylation, provides the corresponding regio- and stereodefined (*E*)-2-arylethenylboronates in high yields. Also, a ruthenium complex prepared in situ from (1,5-cyclooctadiene)(1,3,5-cyclooctatriene)ruthenium(0) [Ru(cod)(cot)] and P(4-$CF_3C_6H_4)_3$ showed considerable catalytic activity for dehydrogenative borylation.

Alkenylboronates are useful intermediates in organic synthesis, particularly with reactions involving carbon-carbon bond formation through a palladium-catalyzed Suzuki–Miyaura cross-coupling reaction.[1] They can be prepared by several methods, notably by uncatalyzed[2] or transition-metal-catalyzed[3] hydroboration of alkynes with 1,3,2-benzodioxaborole (catecholborane). Several authors have observed the formation of dehydrogenated vinylboronates in the catalytic hydroboration of alkenes, suggesting the potential application of that process for preparing alkenylboronates.[4,5]

On the other hand, the dehydrogenative silylation of organic compounds with hydrosilanes (silanes containing Si–H bond) is a useful method for synthesizing organosilicon compounds.[6] The process is effectively catalyzed by transition-metal complexes. The dehydrogenative silylation of alkenes is attractive as a useful alternative to the hydrosilylation of alkynes,[7] in which there are regio- and stereochemical problems. Although the dehydrogenative silylation of alkenes was competitive with the hydrosilylation of alkenes under the reaction conditions, Murai and co-workers have developed highly selective ruthenium-catalyzed dehydrogenative silylation.[8]

While dehydrogenative silylation has been well studied, selective dehydrogenative borylation is relatively unexplored. Brown and Lloyd–Jones have demonstrated a practical example of a rhodium-catalyzed dehydrogenative coupling reaction of vinylarenes using 3-isopropyl-1,3,2-oxazaborolidine.[9] To our knowledge, however, there has been no report concerning dehydrogenative borylation using dialkoxyborane to provide a direct procedure for preparing the corresponding vinylboronates from alkenes. In the present paper, the results of attempting the transition-metal-catalyzed dehydrogenative borylation of vinylarenes **1** by using 4,4,5,5-tetramethyl-1,3,2-dioxaborolane **2** (pinacolborane, HBpin) are described in detail (Scheme 1).[10] During the course of our study, a similar rhodium-catalyzed dehydrogenative borylation of vinyl ethers using **2** was reported by Westcott.[11]

Recently, pinacolborane **2** has been widely recognized as a potent borane reagent,[12] and has been utilized in the transition-metal-catalyzed hydroboration of alkynes or alkenes,[5,13] the borylation of organic halides,[14] and the dehydrogenative borylation of hydrocarbons.[15] Further, the resulting boronates (e.g., **3**) exhibit good reactivity for converting the boron functional-



Scheme 1.

ity to other atoms and excellent stability for an aqueous work-up and chromatography. Thus, pinacolborane **2** should be recognized as a synthetically useful borane reagent for dehydrogenative borylation.

Results and Discussion

Reaction Conditions. The reaction conditions were optimized using styrene **1a** (R = Ph) as a substrate (Table 1). The reaction of styrene **1a** (2 mmol) with pinacolborane **2** (1 mmol) in toluene (4 mL) at ambient temperature in the presence of a catalytic amount of chloro(1,5-cyclooctadiene)rhodium(I) dimer $[RhCl(cod)]_2$ (0.005 mmol) caused a dehydrogenative coupling to give (*E*)-2-phenylethenylboronate **3a** (94% GLC yield based on **2**) along with a small quantity of hydroboration products (2-phenylethylboronate **4a**, 3%; 1-phenylethylboronate **5a**, 3%) (entry 1). The present reaction proceeded regio- and stereoselectively; i.e., neither 1-phenylethenylboronate nor the (*Z*)-isomer was produced. This provides an alternative to the hydroboration of phenylacetylene using **2**, in which a small amount of the isomer (2–4%) was obtained as a by-product.[5,12,13a,d] Although hydrogen gas did not evolve, ethylbenzene **6a** was concurrently generated in 92% yield based on **2**, demonstrating that styrene **1a** acted as a hydrogen acceptor.[8] Five solvents, including toluene, benzene, CH_2ClCH_2Cl, THF, and dioxane, were tested; it was observed that these did not have a significant impact on the yields and the selectivity (entries 5–8).

It is interesting to note that dehydrogenative borylation by pinacolborane **2** in the presence of a phosphine-free rhodium catalyst proceeded predominantly over hydroboration (entries 1 and 2),[9,10] whereas, commonly, pinacolborane has been applied for the phosphine-containing rhodium-catalyzed hydroboration of alkenes, including vinylarenes.[5] It has hitherto been reported that other borane reagents usually used for catalytic hydroboration, such as catecholborane or 3-methyl-1,3,2-oxazaborolidine, were not suitable for selective dehydrogenative borylation, even in the absence of the phosphine ligands.[9]

With regard to catalysts, a variety of transition-metal complexes were examined. In comparison with $[RhCl(cod)]_2$, other phosphine-free complexes, such as $[Rh(cod)_2]BF_4$, $[Rh_4(CO)_{12}]$, and [Ru(cod)(cot)], were less effective (entries 3, 4, and 9). However, a triphenylphosphine-containing ruthenium complex showed some catalytic activity for dehydrogenative borylation at 50 °C (entry 12). We then examined the effect of phosphine ligands on a ruthenium-catalyzed reaction, and found that the product distribution was strongly dependent on the basicity of the phosphine. Thus, a treatment with weaker electron donors, such as $P(4\text{-}CF_3C_6H_4)_3$ and $P(3,4,5\text{-}F_3C_6H_2)_3$, increased the selectivity of dehydrogenative borylation (entries 10 and 11), and simple hydroboration proceeded selectively in the presence of strongly electron-donating $P(cyclo\text{-}C_6H_{11})_3$ (entry 14). To the best of our knowledge, these are the first examples of the ruthenium-catalyzed dehydrogenative borylation and hydroboration of alkenes.

Dehydrogenative Borylation of Representative Alkenes. The results obtained with representative alkenes are summarized in Table 2. As shown, the present reaction of vinylarenes proceeded regio- and stereoselectively, although **3** was contaminated with a small amount of hydroboration products **4** and **5** in each case (entries 1–8). The presence of functional groups, such as CO_2Me in the initial **1**, did not interfere with the outcome of the present reaction (entry 7), corroborating that **2** was inert to many functional groups. Furthermore, the application for vinylferrocene **1f**, which previously resulted in a low yield in the case of employing 1,3,2-oxazaborolidine,[9] also gave the corresponding **3** without significant difficulty

Table 1. Reaction of Styrene **1a** under Various Conditions[a)]

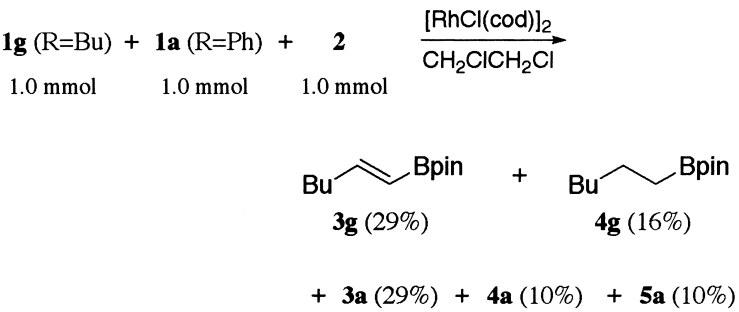
Entry	Catalyst system	Solvent	Yield/%[b)]		
			3a	**4a**	**5a**
1	$[RhCl(cod)]_2$	toluene	94	3	3
2	$[RhCl(cod)]_2/PPh_3$	toluene	8	2	15
3	$[Rh(cod)_2]BF_4$	benzene	6	23	64
4	$[Rh_4(CO)_{12}]$	toluene	5	0	2
5	$[RhCl(cod)]_2$	benzene	90	5	3
6	$[RhCl(cod)]_2$	dioxane	95	2	3
7	$[RhCl(cod)]_2$	THF	85	7	3
8	$[RhCl(cod)]_2$	CH_2ClCH_2Cl	95	2	3
9	[Ru(cod)(cot)]	toluene	4	8	1
10	$[Ru(cod)(cot)]/P(4\text{-}CF_3C_6H_4)_3$	toluene	78	15	7
11	$[Ru(cod)(cot)]/P(3,4,5\text{-}F_3C_6H_2)_3$	toluene	76	15	5
12	$[Ru(cod)(cot)]/PPh_3$	toluene	62	18	19
13	$[Ru(cod)(cot)]/P(4\text{-}MeOC_6H_4)_3$	toluene	50	22	9
14	$[Ru(cod)(cot)]/PCy_3$	toluene	3	52	0
15	$Ru_3(CO)_{12}/P(4\text{-}CF_3C_6H_4)_3$	toluene	3	1	0
16	$[RuCl_2(p\text{-cymene})]_2/P(4\text{-}CF_3C_6H_4)_3$	toluene	1	4	0

a) The rhodium-catalyzed reactions of **1a** (2.0 mmol) with **2** (1.0 mmol) were conducted at room temperature for 4 h in 4 mL of solvent using a catalyst (1 mol% of rhodium) (entries 1–8). The ruthenium-catalyzed reactions were carried out at 50 °C with 2 mol% of ruthenium (entries 9–16). Four equivalents of phosphine ligands per metal were used. b) GLC yields based on **2**.

Table 2. Reaction of Representative Alkenes **1**

Entry	**1**, R =	Method[a]	Yield /%[b]	Ratio/%[c]		
				3	**4**	**5**
1	4-$MeOC_6H_4$- (**1b**)	A	90	95	4	1
2		B	95	80	17	2
3	4-MeC_6H_4- (**1c**)	A	93	95	3	2
4		B	95	81	14	5
5	4-ClC_6H_4- (**1d**)	A	87	95	3	2
6		B	90	69	17	14
7	4-$MeO_2CC_6H_4$- (**1e**)	A	86	93	4	3
8	Ferrocenyl (**1f**)	A	85	85	14	1
9	*n*-Bu- (**1g**)	A	(99)	5	95	0
10	*t*-Bu- (**1h**)	A	(99)	0	100	0
11	CH_2=CH-$(CH_2)_2$- (**1i**)	A[d), e)]	(58)	0	62	38
12		A[d), f)]	(66)	0	30	70

a) All reactions were carried out in toluene (4 mL) for 4 h using **1** (2.0 mmol) and **2** (1.0 mmol), unless otherwise noted. Method A: $[RhCl(cod)]_2$ (0.005 mmol), at room temperature. Method B: [Ru(cod)(cot)] (0.02 mmol), P(4-$CF_3C_6H_4)_3$ (0.08 mmol), at 50 °C. b) Isolated yields of a mixture of **3**, **4**, and **5**, by Kugelrohr distillation and GLC yields in parentheses. c) Determined by GLC and GC–MS analysis of isolated products. d) Reactions were conducted in the presence of 4.0 mmol of **1i**. e) A mixture of $[RhCl(cod)]_2$ (0.005 mmol) and $AsPh_3$ (0.04 mmol) was used as a catalyst. f) PPh_3 (0.04 mmol) was used as a ligand in place of $AsPh_3$ in entry 11.



Scheme 2.

(entry 8). In addition, the differences in the yields and in the selectivity among vinylarenes having electron-donating or electron-withdrawing groups were not large (entries 1–7), but the selectivity decreased in the case of a ruthenium-catalyzed reaction of electron-deficient vinylarenes (entry 6).

On the other hand, all attempts at the present rhodium-catalyzed dehydrogenative borylation of other alkenes, except for vinylarenes, were unsuccessful (entries 9–12). In the case of aliphatic alkenes, such as 1-hexene **1g** and 3,3-dimethyl-1-butene **1h**, usual hydroboration proceeded only in the presence of a phosphine-free rhodium catalyst; trace amounts (less than 5%) of the vinylboronates could be detected by GLC (entry 9 and 10). Interestingly, however, the selectivity of the dehydrogenative borylation of 1-hexene **1g** increased in the presence of additional styrene **1a** (Scheme 2). The selectivity of the reaction of **1a** in such a case decreased to a similar extent to that of **1g**. Thus, vinylarene **1** would appear to play an important role in the dehydrogenative borylation as a ligand of a phosphine-free rhodium catalyst.

Also, the rhodium-catalyzed reaction of 1,5-hexadiene **1i** caused only hydroboration to give a mixture of Markovnikov-**5i** and *anti*-Markovnikov adduct **4i** (entry 11 and 12). In this case, the regioselectivity was affected by the ligands.

Reaction Mechanism. Generally, it is recognized that rhodium-catalyzed hydroboration involves a migratory insertion of alkene into the Rh–H bond of the boryl(hydrido)rhodium complex generated by the oxidative addition of borane.[3,16] However, the above dehydrogenative borylation should involve a migration of boron to alkenes opposite to that of hydride. Although there is no clear experimental evidence, we speculated that the reaction mechanism is as follows (Fig. 1). Initially, pinacolborane pinB–H **2** adds oxidatively to the transition-metal catalyst to give a boryl hydrido species, pinB–M–H, followed by the hydrometallation of alkene **1**, giving a monoalkyl complex. After that, the transfer of the pinB moiety to the coordinated alkene would produce a dialkyl complex. Then, β-hydride elimination would furnish the vinylboronate **3**, and a subsequent reductive elimination would lead to **6** along with regeneration of the catalyst. Hydroboration would occur in the case that the second insertion of the alkene was difficult, while

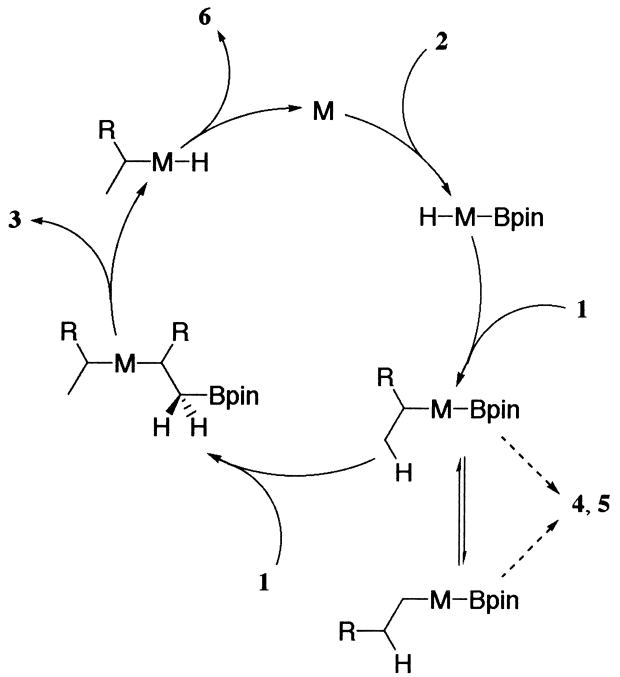


Fig. 1. Proposed catalytic cycle for dehydrogenative borylation (M = Rh, Ru).

both the phosphine-free rhodium complex and the ruthenium catalyst having a less electron-donating phosphine may be favorable for coordination of the second alkene. On the other hand, a catalyst having an electron-donating ligand, such as the phosphine (Table 1, entries 2 and 14) and the aliphatic alkene (Scheme 2), may be more favorable for the reductive elimination of **4** or **5** from the monoalkyl intermediate.

In the case of 1,5-hexadiene **1i**, the reaction gave **5i** predominantly in the presence of PPh_3 (Table 2, entry 12). Thus, the phosphine-containing rhodium catalysts also induced hydride migration. This regioselectivity was consistent with that of phosphinite- or amide-directed hydroboration.[16] On the other hand, the regioselectivity was more economically accommodated by a mechanism involving the migration of boron during the course of the phosphine-free rhodium-catalyzed hydroboration process (entry 11).

One-Pot Synthesis of Stilbenes. The potential versatility of the present borylation was demonstrated by a one-pot synthesis of stilbenes. Although the dehydrogenative borylation of **1** provided a mixture of the major alkenylboronates and a small amount of alkylboronates, the resulting solution could be used directly for the next Suzuki–Miyaura reaction, since alkylboronates, such as **4** and **5**, were not capable of palladium-catalyzed cross-coupling.[1,17] Thus, the cross-coupling of **3c** prepared from **1c** (3 mmol) with 4-fluoroiodobenzene (1.0 mmol) at 90 °C for 8 h in the presence of $[PdCl_2(dppf)]$ (0.03 mmol) and 3 M aq KOH (1 mL) provided the corresponding stilbene in a 79% isolated yield based on the iodoarene employed.

Experimental

Synthesis of Vinylboronates. Typical Procedure. A flask was charged with $[RhCl(cod)]_2$ (0.005 mmol) and toluene (4 mL) under an argon flow. Pinacolborane **1** (1.0 mmol) and vinylarenes **2** (2.0 mmol) were added successively, and the mixture was stirred at room temperature for 4 h. The reaction mixture was diluted with toluene, washed with water, and dried over $MgSO_4$. The solvent was evaporated, and the alkenylboronate **3** was isolated by distillation with Kugelrohr or by chromatography over silica gel.

The following compounds were prepared by the above procedure.

4,4,5,5-Tetramethyl-2-[(*E*)-styryl]-1,3,2-dioxaborolane (3a): ^{1}H NMR ($CDCl_3$) δ 1.32 (s, 12H), 6.16 (d, J = 18.5 Hz, 1H), 7.3–7.6 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 24.84, 83.35, 127.09, 128.55, 128.88, 137.59, 149.52; HRMS (*m/z*) for $C_{14}H_{19}BO_2$ calcd 230.1478, found 230.1477.

2-[(*E*)-2-(4-Methoxyphenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b): ^{1}H NMR ($CDCl_3$) δ 1.31 (s, 12H), 3.81 (s, 3H), 6.01 (d, J = 18.6 Hz, 1H), 6.87 (d, J = 8.5 Hz, 2H), 7.35 (d, J = 18.6 Hz, 1H), 7.44 (d, J = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 24.81, 55.28, 83.23, 113.97, 128.48, 130.43, 149.07, 160.30; HRMS (*m/z*) for $C_{15}H_{21}BO_3$ calcd 260.1583, found 260.1584.

4,4,5,5-Tetramethyl-2-[(*E*)-2-*p*-tolylethenyl]-1,3,2-dioxaborolane (3c): ^{1}H NMR ($CDCl_3$) δ 1.31 (s, 12H), 2.34 (s, 3H), 6.11 (d, J = 18.6 Hz, 1H), 7.14 (d, J = 7.9 Hz, 2H), 7.37 (d, J = 18.6 Hz, 1H), 7.38 (d, J = 7.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.33, 24.82, 83.28, 127.03, 129.29, 134.81, 138.96, 149.48; HRMS (*m/z*) for $C_{15}H_{21}BO_2$ calcd 2441635, found 244.1638.

2-[(*E*)-2-(4-Chlorophenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c): ^{1}H NMR ($CDCl_3$) δ 1.31 (s, 12H), 6.13 (d, J = 18.6 Hz, 1H), 7.30 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 18.6 Hz, 1H), 7.41 (d, J = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 24.82, 83.47, 128.24, 128.81, 134.63, 135.99, 148.03; HRMS (*m/z*) for $C_{14}H_{18}B^{35}ClO_2$ calcd 264.1088, found 264.1113.

Methyl 4-[(*E*)-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-ethenyl]benzoate (3d): ^{1}H NMR ($CDCl_3$) δ 1.32 (s, 12H), 3.91 (s, 3H), 6.28 (d, J = 18.5 Hz, 1H), 7.41 (d, J = 18.5 Hz, 1H), 7.53 (d, J = 8.4 Hz, 2H), 8.01 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 24.82, 52.13, 83.58, 126.91, 129.92, 130.15, 141.73, 148.14, 166.80; HRMS (*m/z*) for $C_{16}H_{21}BO_4$ calcd 288.1533, found 288.1513.

[(*E*)-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethenyl]ferrocene (3f): ^{1}H NMR ($CDCl_3$) δ 1.30 (s, 12H), 4.10 (s, 5H), 4.27 (t, J = 1.8 Hz, 2H), 4.42 (t, J = 1.8 Hz, 2H), 7.53 (d, J = 18.2 Hz, 1H), 8.01 (d, J = 18.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 24.81, 67.58, 69.44, 69.60, 83.07, 149.44; HRMS for $C_{18}H_{23}BFeO_2$ calcd 338.1141, found 338.1139.

Olefin-Directed Hydroboration of 1,5-Hexadiene. To a mixture of $[RhCl(cod)]_2$ (0.005 mmol) and a ligand (0.04 mmol) in toluene (4 mL), pinacolborane **2** (1.0 mmol) and 1,5-hexadiene **1i** (4.0 mmol) were added; the resulting solution was stirred for 4 h at room temperature. Two regio isomers were separated by column chromatography on silica gel; the spectral data are described below.

2-(5-Hexenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4i): ^{1}H NMR ($CDCl_3$) δ 0.78 (t, J = 7.3 Hz, 2H), 1.24 (s, 12H), 1.4–1.5 (m, 4H), 2.04 (dt, J = 6.1, 7.3 Hz, 2H), 4.92 (dd, J = 1.5, 9.8 Hz, 1H), 4.99 (dd, J = 1.5, 17.1 Hz, 1H), 5.81 (ddt, J = 6.1, 9.8, 17.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 23.55, 24.80, 31.66, 33.57, 82.86, 114.03, 139.19; HRMS (*m/z*) for $C_{12}H_{23}BO_2$ calcd 210.1792, found 210.1799.

4,4,5,5-Tetramethyl-2-(1-methyl-4-pentenyl)-1,3,2-dioxaborolane (5i): ^{1}H NMR ($CDCl_3$) δ 0.97 (d, J = 6.7 Hz, 3H), 1.04 (tq, J = 6.7, 7.9 Hz, 1H), 1.24 (s 12H), 1.38 (dt, J = 7.3, 7.9

Hz, 1H), 1.55 (dt, J = 7.3, 7.9 Hz, 1H), 2.07 (dt, J = 6.7, 7.3 Hz, 2H), 4.92 (dd, J = 1.2 10.4 Hz, 1H), 5.00 (dd, J = 1.2, 17.1 Hz, 1H), 5.82 (ddt, J = 6.7, 10.4, 17.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 15.36, 23.55, 24.75, 32.43, 33.14, 82.82, 114.16, 139.27; HRMS (m/z) for $C_{12}H_{23}BO_2$ calcd 210.1791, found 219.1804.

Cross-Coupling of Vinylboronate with Iodoarene. To the solution of **3c**, prepared in situ from **2c** (3 mmol), 4-fluoroiodobenzene (218 mg, 0.98 mmol) was added. Aqueous 3 M KOH (1 mL, 3 mmol) and [$PdCl_2$(dppf)] (22 mg, 0.03 mmol) were added successively, and the mixture was stirred at 90 °C for 8 h. The mixture was diluted with ether, washed with water, and dried ($MgSO_4$). The coupling product, 4-fluoro-4′-metylstilbene, was isolated by column chromatography on silica gel to give a 79% yield (166 mg): ^{1}H NMR ($CDCl_3$) δ 2.36 (s, 3H), 7.00 (d, J = 4.0 Hz, 2H), 7.03 (t, J = 8.7 Hz, 2H), 7.16 (d, J = 7.8 Hz, 2H), 7.39 (d, J = 7.8 Hz, 2H), 7.46 (dd, J = 5.4, 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.24, 115.55 (d, J = 21.7 Hz), 126.33, 126.46, 127.81 (d, J = 8.3 Hz), 128.38, 129.41, 133.68, 134.36, 137.57, 162.19 (d, J = 247.2 Hz); HRMS (m/z) for $C_{15}H_{13}F$ calcd 212.1001, found 212.1006.

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