有机化学 DOI: 10.6023/cjoc202210006 研究论文
Chinese Journal of Organic Chemistry ARTICLE

联吡啶配体促进铬催化炔烃的顺式硼氢化反应

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摘要 报道了金属铬催化炔烃的硼氢化反应. 廉价易得的三氯化铬在 4,4'-二叔丁基-2,2'-联吡啶配体及单质镁的还原作用下表现出高反应活性, 催化实现了频哪醇硼烷与炔烃加成的硼氢化反应, 为室温条件下制备烯基硼化合物提供了一条有效的合成策略.

关键词 铬催化; 硼氢化反应; 加成反应

Bipyridine Ligand-Promoted *cis*-Selective Hydroboration of Alkynes with Chromium Catalysis

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Abstract The chromium-catalyzed hydroboration of alkynes under mild conditions was reported. Low-cost chromium(III) chloride combined with 4,4'-di-*tert*-butyl 2,2'-bipyridine as the ligand and magnesium as the reductant shows high reactivity, which can catalyze and promote the hydroboration of alkynes with pinacolborane, thereby providing a strategy to form borylated olefins at ambient temperature.

Keywords chromium catalysis; hydroboration; addition reaction

1 Introduction

Organoboron compounds are synthetically valuable structure motifs that are widespread used as versatile building blocks in synthetic chemistry.[1] The hydroboration reaction, by the addition of B—H bonds to unsaturated bonds, provides an avenue to the formation of olefinated boron motifs in the atom-economic manner.[2] In the past years, advances in the development of effective hydroboration strategies have been achieved by transition metal catalysis.[3-4] In the context, late transition metal of copper shows ubiquitous reactivity toward the activation of pinacolborane for the catalytic hydroboration of alkynes.[5] Recent reports demonstrated that other first-row transition metals, such as iron,[6] cobalt,[7a-7b] and even main-group metals of magnesium[7c-7d] and aluminum,[7e-7f] could be used as catalysts to promote the hydroboration in the creation of vinylated organoboron structures. Given the synthetically importance of vinylboranes as feedstocks in accessing pharmaceuticals, agrochemicals and materials, catalytic techniques of hydroboration using low-cost metal catalysts such as early transition metal of chromium would be of value to the efficiently formation of these appealing motifs.[8-11]

Because of the feature of earth abundance, the use of first-row transition metals of nickel, iron, cobalt, and even manganese in developing cost-effective synthetic approaches has attracted immense interest of chemists. Compared with the great achievements with nickel, iron and cobalt catalysis, the catalytic properties of group 6 metal chromium still have rarely been explored, especially for hydrofunctionalization reactions,[12-13] although the chromium-hydide complexes that are proposed to be reactive intermediates for hydrofunctionalization have been synthesized and characterized by the group of Hou.[14] We recently disclosed that the *in-situ* formed low-valent Cr species shows the ability in promoting the borylation of aryl and vinyl esters by reaction with pinacolborane.[15] It is anticipated that the addition of pinacolborane to alkynes may occur with Cr catalysis by initially insertion of H—Bpin bond and followed by addition across triple bonds in affording vinylboronate esters. Herein, we report the hydroboration of alkynes that could be catalyzed chromium by using catalytic amount of metallic magnesium as reductant for the *in-situ* generation of reactive species,

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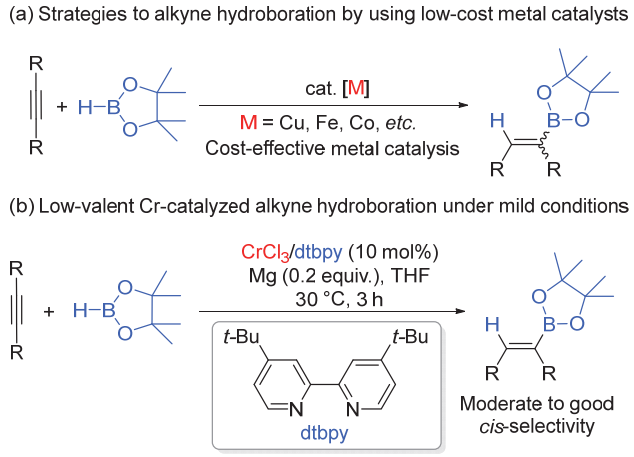
Received May 20, 2023; revised June 6, 2023; published online June 13, 2023.
Project supported by the National Natural Science Foundation of China (Nos. 21971168, 22125107).
国家自然科学基金(Nos. 21971168, 22125107)资助项目.

providing a strategy to access to olefinated boronate esters at ambient temperature (Scheme 1b).



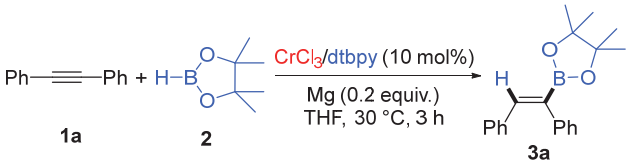
Scheme 1 Non-precious metal-catalyzed hydroboration of alkynes

2 Results and discussion

Our studies were commenced by exploring the reactivity of chromium in the reaction of 1,2-diphenylethyne with pinacolborane. Using commercially available $CrCl_3$ salt as the precatalyst and metallic magnesium as the reductant without ligand, we disclosed that the hydroboration did not occur at 30 °C (Table 1, Entry 3). It was pleased to see that 2,2'-bipyridine (**L1**) serving as ligand showed the ability to promote the hydroboration of alkyne with Cr catalysis, giving the olefinated boronate ester motif **3a** in 63% yield and 95∶5 *Z*/*E*-selectivity (Entry 5). The reaction with 4,4'-di-*tert*-butyl 2,2'-bipyridine (dtbpy) as the ligand allowed us to the synthesis of **3a** in good yield and slightly decreased *cis*-selectivity (Entry 1). In contrast, bidentate nitrogen ligands of 4,4'-dimethoxy-2,2'-bipyridine (**L2**), 1,10-phenanthroline (**L3**), 4,7-dimethoxy-1,10-phenanthroline (**L4**) and 5,6-dimethyl-1,10-phenanthroline (**L5**) were almost inefficient in promoting the Cr-catalyzed alkyne hydroboration (Entries 6～9). It was disclosed that catalytic amount of Mg (0.2 equiv) was required for the conversion, which reduced the $CrCl_3$ salt to generate reactive low-valent species in responsibility for the hydroboration (Entry 4). Other first-row metal salts such as $FeCl_2$, $NiCl_2$ and $CoCl_2$ almost showed no efficiency in promoting the reaction under present conditions (Entries 12～14).

The scope of the hydroboration of alkynes by chromium catalysis was examined for the synthesis of diverse substituted and *cis*-selective olefinated boronate esters (Table 2). Diarylethynes that contain the *ortho*-, *meta*- and *para*-methyl substituents on aryl scaffolds underwent the stereoselective hydroboration smoothly, forming *Z*-vinylated boronate esters as major products (**3b**～**3d**). Comparatively, the hydroboration with *ortho*-substituted diarylalkyne delivered high *cis*-selectivity, presumably causing from the steric hindrance of *ortho*-substituents in impeding the stereoisomerization of alkene motifs. The incorporation of functional groups such as methoxy, fluoride and chloride into the arenes did not greatly influence the hydroboration, providing access to olefinated boronate esters **3e**～**3l** in good *cis*-selectivity. The hydroboration using aryl alkyl alkyne occured smoothly, only giving regioselective alkenyl boronate ester **3m** in good yield and excellent *cis*-selectivity. Silylated alkynes could be hydroborated effectively with Cr catalysis, resulting in the formation of boronated (*E*)-styrylsilane **3n** in 70% yield. The variation of substituents on aryl and silyl scaffolds did not affect the regioselectivity of hydroboration, providing a strategy to the synthesis of silylated alkenyl boronate ester derivatives **3o**～**3s** at ambient temperature. Moreover, the Cr-catalyzed hydroboration with benzodioxolyl- and thiophenyl-substituted alkynes occured in the regioselective manner, giving heterocycle-containing alkenyl boronate

Table 1 Optimization of reaction parameters in the catalytic *cis*-selective hydroboration of alkyne[a]



Entry	Deviation from standard conditions	Yield/%
1	None	75 (87:13)[b]
2	Without $CrCl_3$	Nd[c]
3	Without dtbpy	Nd[c]
4	Without Mg	Nd[c]
5	**L1** instead of dtbpy	63 (95:5)[b]
6	**L2** instead of dtbpy	5[d]
7	**L3** instead of dtbpy	<2[d]
8	**L4** instead of dtbpy	<2[d]
9	**L5** instead of dtbpy	<2[d]
10	$CrCl_2$ instead of $CrCl_3$	62 (83:17)[b]
11	$Cr(acac)_3$ instead of $CrCl_3$	<2[d]
12	$FeCl_2$ instead of $CrCl_3$	<2[d]
13	$CoCl_2$ instead of $CrCl_3$	<2[d]
14	$NiCl_2$ instead of $CrCl_3$	<2[d]

[a] Reaction conditions: **1a** (0.4 mmol), **2** (0.8 mmol), metal salt (0.04 mmol), ligand (0.04 mmol), magnesium (0.08 mmol), THF, 30 °C, 3 h. Isolated yields are given. [b] The stereoisomer ratio (*Z*/*E*) was determined by GC analysis before purification. [c] Not detected. [d] Yields were determined by GC analysis.

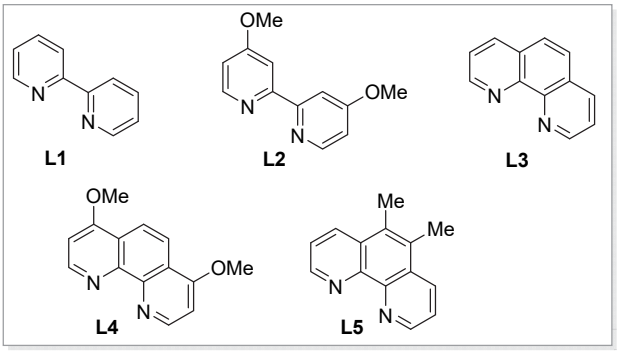
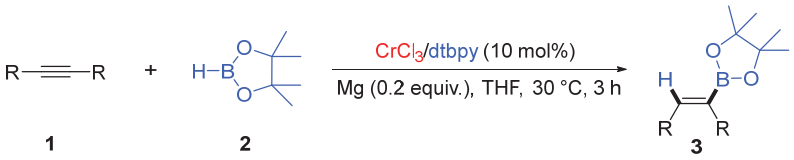
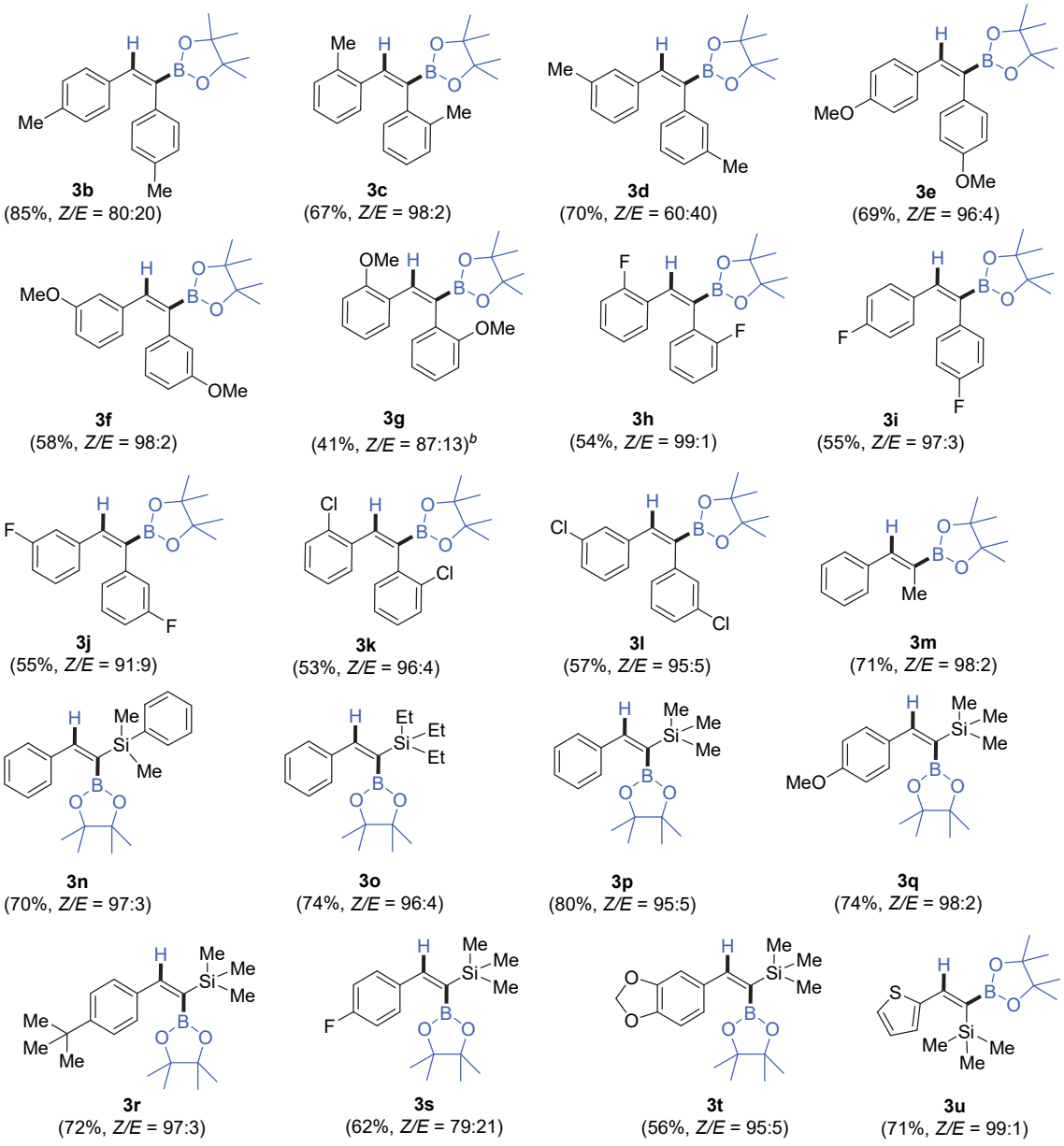


Table 2 Cr-catalyzed *cis*-selective hydroboration of alkynes for the synthesis of olefinated boronate esters

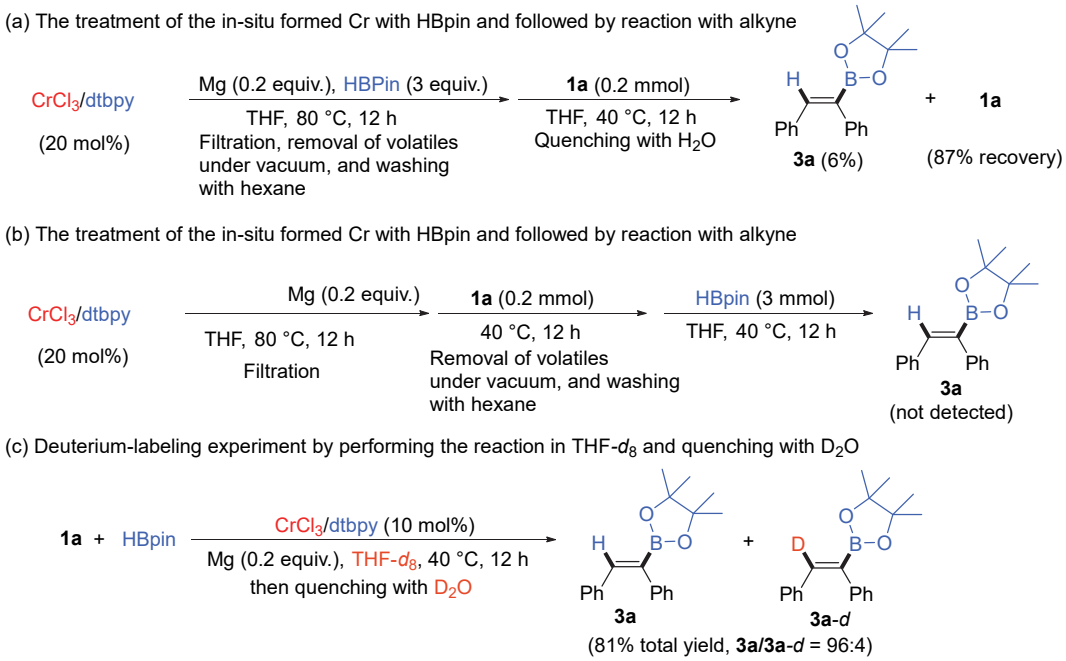




[a] Reaction conditions: internal alkyne **1** (0.4 mmol), **2** (0.8 mmol), $CrCl_3$ (0.04 mmol), dtbpy (0.04 mmol), magnesium (0.08 mmol), THF, 30 °C, 3 h. Isolated yields are given.

esters **3t** and **3u** in excellent *cis*-selectivity.[16]

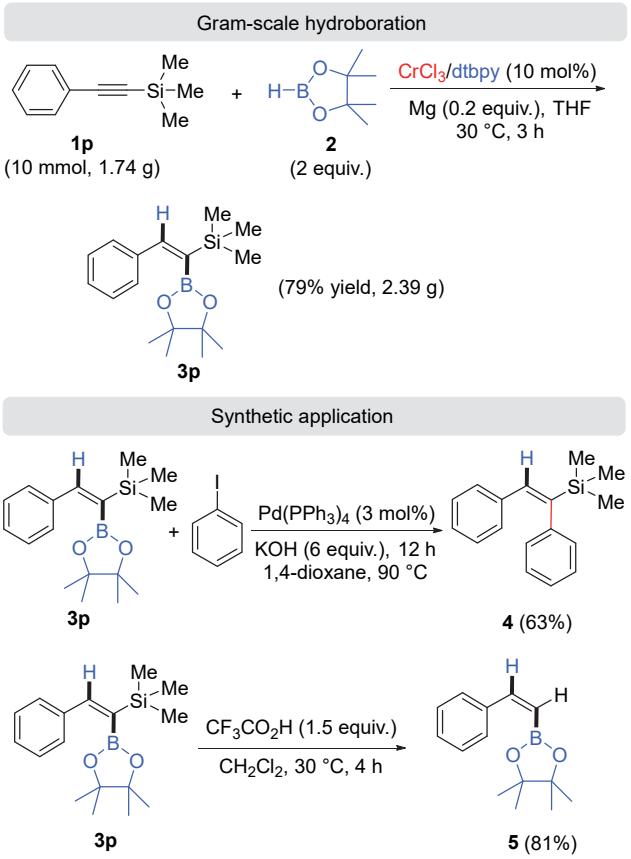
To study whether the activation of pinacolborane by low-valent Cr is involved in the transformation, we conducted the reaction of $CrCl_3$/dtbpy with Mg and HBpin at 80 °C (Scheme 2a). After filtration, removal of volatiles under vacuum and washing with hexane, the resulting residue was treated with alkyne in THF. It was disclosed that the hydroboration product **3a** could be formed. It indicates that the *in-situ* formed reactive Cr might initial react with HBpin via process of oxidative addition, giving L_nCr-(Bpin) species in the coordination and addition to alkyne, while an inner-sphere mechanism involving in the Cr-catalyzed hydroboration of alkynes may be considered. By contrast, the initially treatment of reactive Cr with alkyne and reaction with HBpin after the removal of alkyne cannot give the hydroborated product (Scheme 2b). The deuterium experiment by conducting the hydroboration in THF-d_8 and quenching with D_2O suggested that the hy-



Scheme 2 Preliminary mechanistic studies

dride of vinylated boronate ester mainly delivers from pinacolborane (Scheme 2c).

The scalability of the Cr-catalyzed alkyne hydroboration was investigated. As shown in Scheme 3, the reaction using 1,2-diphenylethyne can be conducted on gram scale without loss of the efficiency. The resulting vinylated boronate ester **3p** can be facilely functionalized by transformation of boron scaffold with Pd-catalyzed Suzuki coupling reaction, providing access to arylated derivative (**4**). The desilylation of the silicon-containing hydroborated alkene occurs smoothly with enabling the synthesis of (*E*)-styrylboronate ester **5**.



Scheme 3 Gram-scale hydroboration and synthetic applications

3 Conclusion

In conclusion, we developed the first hydroboration of alkynes that was catalyzed by low-cost group 6 metal chromium, providing an avenue to the *cis*-selective formation of olefinated boronate esters under mild conditions. It demonstrates that the bipyridine ligand of dtbpy plays an important role in enhancement of the reactivity of Cr in the reaction, probably the activation of pinacolborane by an inner-sphere mechanism in achieving the addition to alkyne. The hydroborated olefin compounds can be facilely functionalized by the coupling of boronate ester group. Further studies to understand the mechanism and characterization of intermediates are under way in our laboratory.

4 Experimental section

4.1 General information

All reactions dealing with air- or moisture-sensitive compounds were carried out in a dried and sealed Schlenk tube under an atmosphere of nitrogen. Analytical thin-layer chromatography was performed on glass plates coated with 0.25 mm 230～400 mesh silica gel containing a fluorescent indicator (Merck). Flash silica gel column chromatography was performed on silica gel 60N (spherical and neutral, 140～325 mesh) as described by Still. NMR spectra were measured on a Bruker AV-400 spectrometer. ^{1}H NMR spectra were recorded at 400 MHz in $CDCl_3$ and refer-

enced internally to tetramethylsilane as a standard, and ^{13}C NMR spectra were recorded at 100 MHz and referenced to the solvent resonance. Analytical gas chromatography (GC) was carried out on a Thermo Trace 1300 gas chromatograph, equipped with a flame ionization detector. Mass spectra (GC-MS) were taken at a Thermo Trace 1300 gas chromatograph mass spectrometer. High resolution mass spectra (HRMS) were recorded on a Exactive Mass Spectrometer (Thermo Scientific, USA) equipped with ESI ionization source. Melting points were determined with a Hanon MP-300.

4.2 General procedure for the hydroboration of alkyne with pinacolborane

A dried Schlenk tube was charged with alkyne (0.4 mmol), $CrCl_3$ (10 mol%), dtbpy (10 mol%), and Mg (0.08 mmol), followed by adding HBpin (0.8mmol) and a freshly distilled THF (1 mL) by syringe under atmosphere of nitrogen. The reaction mixture was stirred at 30 °C for 3 h. After quenched by aqueous ethyl acetate (2 mL), the crude product was extracted with ethyl acetate (3×10 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified by flash chromatography on silica gel (gradient eluent of EtOAc in petroleum ether) to give the desired product.

4.3 Procedure for the gram-scale hydroboration of alkyne

A dried Schlenk tube was charged with alkyne **1p** (1.74 g, 10 mmol), $CrCl_3$ (10 mol%), dtbpy (10 mol%), and Mg (2 mmol), followed by adding HBpin (20 mmol) and a freshly distilled THF (10 mL) by syringe under atmosphere of nitrogen. The reaction mixture was stirred at 30 °C for 3 h. After quenched by aqueous ethyl acetate (2 mL), the crude product was extracted with ethyl acetate (3×10 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified by flash chromatography on silica gel (gradient eluent of EtOAc in petroleum ether) to give the target product **3p** in 79% yield.

(*Z*)-2-(1,2-Diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3a**):[16c] Brown oil. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.46 (t, J=6.6 Hz, 2H), 7.38～7.30 (m, 2H), 7.27～7.23 (m, 2H), 7.22～7.15 (m, 2H), 7.13～7.07 (m, 2H), 7.05 (dt, J=4.8, 3.3 Hz, 1H), 1.30 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.3, 140.5, 137.0, 130.0, 128.9, 128.3, 127.9, 127.7, 126.3, 83.8, 24.8; ^{11}B NMR (128 MHz, $CDCl_3$) δ: 32.1; GC-MS (EI) calcd for $C_{20}H_{23}BO_2$ 306.2, found 306.1.

(*Z*)-2-(1,2-Di-*p*-tolylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3b**):[16c] Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.32 (s, 1H), 7.08 (s, 4H),7.01～6.92 (m, 4H), 2.34 (s, 3H), 2.26 (s, 3H), 1.31 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.0, 137.7, 137.6, 135.8, 134.4, 130.1, 129.5, 129.2, 128.8, 128.7, 83.8, 24.9, 21.43, 21.39; ^{11}B NMR (128 MHz, $CDCl_3$) δ: 30.4; GC-MS (EI) calcd for $C_{22}H_{27}BO_2$ 334.2, found 334.3.

(*Z*)-2-(1,2-Di-*o*-tolylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3c**):[16d] Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.48 (s, 1H), 7.04～6.98 (m, 3H), 6.92 (t, J=7.3 Hz, 2H), 6.81～6.76 (m, 1H), 6.71～6.63 (m, 1H), 6.53 (d, J=7.6 Hz, 1H), 2.29 (s, 3H), 2.06 (s, 3H), 1.22 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.5, 140.3, 136.7, 136.6, 135.5, 129.9, 129.9, 129.2, 129.1, 127.5, 126.4, 125.7, 125.2, 83.8, 24.9, 20.13, 20.10; ^{11}B NMR (128 MHz, $CDCl_3$) δ: 30.5; GC-MS (EI) calcd for $C_{22}H_{27}BO_2$ 334.2, found 334.3.

(*Z*)-2-(1,2-Di-*m*-tolylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3d**):[16c] Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.22～7.19 (m, 1H),7.14～7.09 (m, 1H), 7.02 (t, J=3.2 Hz, 1H), 6.99～6.94 (m, 1H), 6.93～6.85 (m, 4H), 6.77 (d, J=7.5 Hz, 1H), 2.23 (s, 3H), 2.12 (s, 3H), 1.25 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.2, 140.5, 137.6, 137.3, 136.9, 131.0, 129.4, 128.6, 128.4, 128.1, 127.7, 127.1, 127.0, 125.8, 83.7, 24.8, 21.6, 21.3; ^{11}B NMR (128 MHz, $CDCl_3$) δ: 29.5; GC-MS (EI) calcd for $C_{22}H_{27}BO_2$ 334.2, found 334.3.

(*Z*)-2-(1,2-Bis(4-methoxyphenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3e**):[16b] Brown oil. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.28 (s, 1H), 7.15～7.11 (m, 2H), 7.07～7.03 (m, 2H), 6.87～6.83 (m, 2H), 6.70～6.66 (m, 2H), 3.82 (s, 3H), 3.76 (s, 3H), 1.32 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.1, 158.1, 142.5, 133.1, 131.5, 131.1, 130.1, 129.9, 129.1, 114.6, 114.2, 114.0, 113.9, 113.4, 83.7, 55.4, 55.2, 24.9; ^{11}B NMR (128 MHz, $CDCl_3$) δ: 30.4; GC-MS (EI) calcd for $C_{22}H_{27}BO_4$ 366.2, found 366.2.

(*Z*)-2-(1,2-Bis(3-methoxyphenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3f**):[16d] Brown oil. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.33 (s, 1H), 7.20 (t, J=7.8 Hz, 1H), 7.06 (t, J=7.9 Hz, 1H), 6.79～6.67 (m, 5H), 6.62～6.59 (m, 1H), 3.72 (s, 3H), 3.51 (s, 3H), 1.31 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.6, 159.0, 143.2, 142.1, 138.2, 129.4, 129.0, 123.0, 121.4, 114.7, 114.2, 114.1, 112.2, 83.9, 55.2, 54.9, 24.9; ^{11}B NMR (128 MHz, $CDCl_3$) δ: 32.0; GC-MS (EI) calcd for $C_{22}H_{27}BO_4$ 366.2, found 366.1.

(*Z*)-2-(1,2-Bis(2-methoxyphenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3g**): Brown oil. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.54 (s, 1H), 7.20～7.14 (m, 1H), 7.13～7.07 (m, 1H), 6.93～6.85 (m, 2H), 6.83～6.72 (m, 3H), 6.61～6.54 (m, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 1.31 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.6, 157.0, 137.8, 130.5, 130.3, 130.1, 128.7, 127.8, 126.5, 120.7, 119.8, 110.5, 110.3, 83.5, 55.5, 55.3, 24.9; ^{11}B NMR (128 MHz, $CDCl_3$) δ: 31.2, 22.5; HR-MS (ESI) calcd for $C_{22}H_{27}BO_4Na$ $[M+Na]^+$: 389.1895, found 389.1896.

(*Z*)-2-(1,2-Bis(2-fluorophenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3h**): Brown oil. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.50 (s, 1H), 7.12～7.04 (m, 2H), 6.97～6.88 (m, 4H), 6.78～6.67 (m, 2H), 1.24 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.0 (d, J=248.0 Hz), 160.0 (d, J=243.0 Hz), 137.2 (d, J=4.4 Hz), 130.9 (d, J=3.9 Hz),

130.3 (d, J=3.0 Hz), 129.7 (d, J=8.4 Hz), 128.6 (d, J=8.0 Hz), 125.0 (d, J=12.9 Hz), 124.1 (d, J=3.5 Hz), 123.4 (d, J=3.6 Hz), 115.7 (d, J=12.3 Hz), 115.4 (d, J=12.3 Hz), 84.2, 24.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −113.9, −114.9; ^{11}B NMR (128 MHz, $CDCl_3$) δ: 30.9, 22.5; HR-MS (ESI) calcd for $C_{20}H_{21}BF_2O_2Na$ $[M+Na]^+$: 365.1500, found 365.1495.

(*Z*)-2-(1,2-Bis(4-fluorophenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3i**):[16c] Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49～7.39 (m, 3H), 7.22～7.15 (m, 2H), 7.09～7.06 (m, 2H), 7.01 (t, J=8.8 Hz, 1H), 6.86 (t, J=8.7 Hz, 1H), 1.36 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.5 (d, J=245.5 Hz), 162.3 (d, J=244.4 Hz), 140.0, 138.6, 135.0, 130.1 (d, J=8.0 Hz), 128.6 (d, J=8.0 Hz), 115.4 (d, J=21.0 Hz), 115.2 (d, J=23.0 Hz), 84.3, 25.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −114.3, −115.9; ^{11}B NMR (128 MHz, $CDCl_3$) δ: 30.3; GC-MS (EI) calcd for $C_{20}H_{21}BF_2O_2$ 342.2, found 342.2.

(*Z*)-2-(1,2-Bis(3-fluorophenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3j**): Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36～7.31(m, 1H), 7.30～7.27 (m, 1H), 7.25～7.20 (m, 4H), 7.18～7.17 (m, 1H), 7.03～6.99 (m, 2H), 1.34 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.0 (d, J=243.7 Hz), 162.7 (d, J=244.0 Hz), 144.5 (d, J=7.4 Hz), 140.6, 140.2, 129.9 (d, J=8.0 Hz), 129.7 (d, J=8.0 Hz), 124.3, 122.7, 114.9, 114.6 (d, J=12.7 Hz), 114.1, 113.8 (d, J=18.7 Hz), 84.4, 24.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −113.4 (major), −113.9 (major), −113.5 (minor), −113.7 (minor); ^{11}B NMR (128 MHz, $CDCl_3$) δ: 31.2; HR-MS (ESI) calcd for $C_{20}H_{21}BF_2O_2Na$ $[M+Na]^+$ 365.1495, found 365.1494.

(*Z*)-2-(1,2-Bis(2-chlorophenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3k**):[16c] Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (s, 1H), 7.39～7.35 (m, 1H), 7.33～7.30 (m, 1H), 7.15～7.10 (m, 1H), 7.08～7.00 (m, 2H), 6.91～6.82 (m, 2H), 6.73～6.69 (m, 1H), 1.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.9, 139.1, 135.3, 133.9, 133.4, 130.6, 130.5, 129.1, 129.0, 128.7, 127.9, 126.7, 125.9, 84.0, 24.7; ^{11}B NMR (128 MHz, $CDCl_3$) δ: 30.2; HR-MS (ESI) calcd for $C_{20}H_{21}BCl_2O_2Na$ $[M+Na]^+$: 397.0903, found 397.0904.

(*Z*)-2-(1,2-Bis(3-chlorophenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3l**):[16c] Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 (s, 1H), 7.36 (s, 1H), 7.22～7.17 (m, 6H), 7.11 (s, 1H), 1.24 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.5, 140.7, 140.6, 134.9, 134.6, 130.1, 130.04, 129.95, 128.3, 128.2, 127.6, 127.5, 127.3, 125.6, 84.9, 25.4.; ^{11}B NMR (128 MHz, $CDCl_3$) δ: 30.6; GC-MS (EI) calcd for $C_{20}H_{21}BCl_2O_2$ 374.1, found 374.2.

(*Z*)-4,4,5,5-Tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane (**3m**):[16a] Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37 (q, J=7.4 Hz, 3H), 7.21 (d, J=7.7 Hz, 2H), 6.78 (d, J=7.0 Hz, 1H), 1.81 (d, J=6.9 Hz, 3H), 1.31 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.1, 128.2, 127.8, 126.8, 126.5, 125.8, 82.3, 23.6, 14.6; ^{11}B NMR (128 MHz, $CDCl_3$) δ: 30.6; GC-MS (EI) calcd for $C_{15}H_{21}BO_2$ 244.2, found 244.2.

(*E*)-Dimethyl(phenyl)(2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (**3n**): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62～7.57 (m, 2H), 7.40 (d, J=7.6 Hz, 2H), 7.37～7.31 (m, 3H), 7.25 (m, 4H), 1.14 (s, 12H), 0.51～0.43 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.2, 140.3, 138.5, 134.6, 129.1, 128.11, 128.05, 127.8, 83.6, 25.0, −1.9; ^{11}B NMR (128 MHz, $CDCl_3$) δ: 30.0; HR-MS (ESI) calcd for $C_{22}H_{29}BO_2SiNa$ $[M+Na]^+$: 387.1922, found 387.1922.

(*E*)-Triethyl(2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (**3o**): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51～7.40 (m, 2H), 7.35～7.21 (m, 4H), 1.30 (s, 12H), 1.02 (t, J=7.8 Hz, 9H), 0.75 (d, J=7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.6, 143.0, 130.4, 130.2, 130.1, 85.8, 27.5, 9.8, 6.0; ^{11}B NMR (128 MHz, $CDCl_3$) δ: 30.2; HR-MS (ESI) calcd for $C_{20}H_{33}BO_2SiNa$ $[M+Na]^+$: 367.2222, found 367.2235.

(*E*)-Trimethyl(2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silan (**3p**):[16e] Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45～7.37 (m, 2H), 7.32～7.18 (m, 4H), 1.29 (s, 12H), 0.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.2, 140.6, 128.1, 127.9, 127.9, 83.6, 25.2, −0.7; ^{11}B NMR (128 MHz, $CDCl_3$) δ: 32.2; GC-MS (EI) calcd for $C_{17}H_{27}BO_2Si$ 302.2, found 302.3.

(*E*)-(2-(4-Methoxyphenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)trimethylsilane (**3q**):[16e] Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.18 (d, J=8.5 Hz, 2H), 7.01 (s, 1H), 6.62 (d, J=8.6 Hz, 2H), 3.60 (s, 3H), 1.11 (s, 12H), 0.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.5, 149.8, 133.5, 129.4, 113.5, 83.5, 55.4, 25.2, −0.7; ^{11}B NMR (128 MHz, $CDCl_3$) δ: 32.5; HR-MS (ESI) calcd for $C_{18}H_{29}BO_3SiNa$ $[M+Na]^+$: 355.1874, found 355.1871.

(*E*)-(2-(4-(*tert*-Butyl)phenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)trimethylsilane (**3r**): Yellow solid, m.p. 76～78 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.19～7.13 (m, 2H), 7.13～7.08 (m, 2H), 7.05 (s, 1H), 1.11 (s, 21H), 0.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.0, 150.1, 137.7, 127.7, 125.0, 83.5, 34.7, 31.4, 25.2, −0.7; ^{11}B NMR (128 MHz, $CDCl_3$) δ: 30.9; HR-MS (ESI) calcd for $C_{21}H_{35}BO_2SiNa$ $[M+Na]^+$: 381.2392, found 381.2392.

(*E*)-(2-(4-Fluorophenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)trimethylsilane (**3s**): Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39 (d, J=3.1 Hz, 2H), 7.21 (s, 1H), 6.98 (d, J=8.7 Hz, 2H), 1.28 (s, 12H), 0.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.6 (d, J=246.9 Hz), 148.9, 136.9, 129.6 (d, J=8.1 Hz), 128.0 (d, J=18.1 Hz), 115.0 (d, J=21.3 Hz), 83.7, 25.2, −0.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −114.4; ^{11}B NMR (128 MHz, $CDCl_3$) δ: 30.7; HR-MS (ESI) calcd for $C_{17}H_{26}BFO_2SiNa$ $[M+Na]^+$: 343.1668, found 343.1671.

(*E*)-(2-(Benzo[*d*][1,3]dioxol-5-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)trimethylsilane (**3t**): Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.16 (s, 1H), 7.02 (s, 1H), 6.89 (s, 1H), 6.76 (s, 1H), 5.95 (s, 2H), 1.32 (s, 12H), 0.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.2, 148.4, 148.1, 135.9, 123.2, 108.7, 108.5, 101.8, 84.3, 25.9,

0.0; ^{11}B NMR (128 MHz, $CDCl_3$) δ: 31.3; HR-MS (ESI) calcd for $C_{18}H_{27}BO_4SiNa$ $[M+Na]^+$: 369.1665, found 369.1664.

(*Z*)-Dimethyl(phenyl)(2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (**3u**):[16e] Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73 (s, 1H), 7.17～7.09 (m, 1H), 6.90～6.78 (m, 2H), 1.14 (s, 12H), 0.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.8, 143.9, 128.6, 127.0, 126.8, 83.4, 25.0, 0.8; ^{11}B NMR (128 MHz, $CDCl_3$) δ: 30.7; HR-MS (ESI) calcd for $C_{15}H_{25}BO_2SSiNa$ $[M+Na]^+$: 331.1335, found 331.1330.

(*E*)-(1,2-Diphenylvinyl)trimethylsilane (**4**):[16f] White solid, m.p. 54～56 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76 (t, J=7.6 Hz, 2H), 7.71～7.65 (m, 3H), 7.55～7.52 (m, 2H), 7.47～7.39 (m, 4H), 0.59 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.3, 142.9, 137.5, 129.6, 129.0, 128.7, 128.0, 127.5, 127.1, 125.7, −1.5; GC-MS (EI) calcd for $C_{17}H_{20}Si$ 252.1, found 252.1.

(*Z*)-4,4,5,5-Tetramethyl-2-styryl-1,3,2-dioxaborolane (**5**):[16g] Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47 (d, J=7.0 Hz, 2H), 7.27～7.16 (m, 4H), 5.53 (d, J=14.9 Hz, 1H), 1.23 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.3, 138.6, 128.7, 128.14, 128.05, 127.2, 83.6, 24.9; GC-MS (EI) calcd for $C_{14}H_{19}BO_2$ 230.1, found 230.1.

Supporting Information ^{1}H NMR, ^{13}C NMR, ^{11}B NMR and ^{19}F NMR spectra of compounds **3**～**5**. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn/.

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