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无催化剂、无溶剂条件下炔烃和烯烃与儿茶酚硼烷的硼氢化反应

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摘要 报道了无催化剂和无溶剂条件下炔烃和烯烃与儿茶酚硼烷的硼氢化反应, 各种芳香族和脂肪族炔烃和烯烃底物分别以高产率和高区域/立体选择性成功地转化为相应的反马氏烯基和烷基硼酸酯产物. 克级硼氢化和多用途转化反应显示了其在实际应用中的巨大潜力. 在相应密度泛函理论(DFT)计算的基础上, 提出了一种可能的反应机理.
关键词 绿色化学; 硼氢化; 无催化剂; 炔烃; 烯烃

Catalyst-Free and Solvent-Free Hydroboration of Alkynes and Alkenes with Catecholborane

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Abstract A catalyst-free and solvent hydroboration of alkynes and alkenes with catecholborane was reported. Various alkynes and alkenes including aromatic and aliphatic groups were smoothly converted into the corresponding anti-Markovnikov alkenyl and alkyl boronate esters in high yields and high regio/stereoselectivity at room temperature and 50 ℃, respectively. The gram-scale hydroboration and further versatile conversions demonstrated great potential in the practical application. A plausible reaction mechanism was proposed based on the corresponding density function theory (DFT) calculations.
Keywords green chemistry; hydroboration; catalyst-free; alkyne; alkene

1 Introduction

The development of green and sustainable synthetic methods is always the high priority of modern synthetic chemistry. A range of convenient, efficient synthetic methods were improved due to the influences of environmental and economic aspects. Organoboronates are very important precursors in the organic chemistry, which are widely applied in various transformations, such as Suzuki-Miyaura cross-coupling reaction.[1] Hydroboration of unsaturated substrates is simple, straightforward and efficient method to produce the organoboron compounds.[2] Amongst the unsaturated compounds, the C—C unsaturated compounds, namely C=C double bond and C≡C triplet bond, are usually more stable than those compounds including C=O, C=N or C≡N unsaturated bonds. Hence hydroboration of alkynes and alkenes is more difficult and challenging than those of the corresponding carbonyl compounds, imines and nitrile, *etc*.[3-13] Because the resultant alkyl and alkenyl boronic esters are very useful intermediates in many organic syntheses, the considerable progress on the hydroboration of alkynes and alkenes has been achieved using various catalysts including transition metals, main group metals and other non-metal compounds (Scheme 1).[14-37] However, most of catalysts are prepared by complicated synthesis. Meanwhile they have inherent drawbacks of high cost, environmental pollution of heavy metals, and removal or recover of catalyst isolation *etc*. These disadvantages are against the principles of green chemistry. In this regard, the development of sustainable and green process for the hydroboration of alkynes and alkenes from requiring catalyst, especially metal catalyst, to catalyst-free is highly desirable.

Recently, catalyst-free strategy has received increasing attention. In contrast to the extensive investigation on the metal-catalyzed hydroboration, the corresponding catalyst-free hydroboration example is relatively few.[38-41] The pyridyl directed catalyst-free *trans*-hydroboration of internal alkynes with 9-borabicyclo[3.3.1]nonane (9-BBN) has been reported by Wang *et al*.[42] recently. The directing pyridyl group was found to play a key role in the highly

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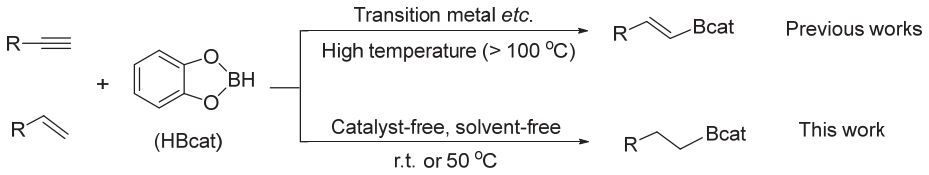


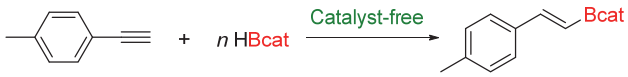
Scheme 1 Hydroboration of alkynes and alkenes with HBcat

stereo- and regioselective *trans*-hydroboration of internal alkynes, however, the alkyne substrate scope was limited. Meanwhile, in most cases high reaction temperature was essential for full conversion. For example, catalyst-free hydroboration of aldehyde with HBpin could be completed at room temperature or 60 ℃,[43] however, catalyst-free hydroboration of more sterically hindered ketones with excessive HBpin (2 equiv.) must be finished by increasing the reaction temperature to 80 or 140 ℃.[44] Because the parent borane (BH_3 or B_2H_6) is too reactive to easy handle, the relatively stable borane reductants such as pinacolborane (HBpin) or catecholborane (HBcat) are often used in the hydroboration. Compared to HBpin, HBcat is relatively more reactive because it has a higher Lewis acidity than HBpin. We wonder whether the hydroboration of C—C unsaturated bonds could be achieved at room temperature without any catalyst. To our delight, this protocol could be realized with HBcat as a reducing reagent. Herein, we report an efficient and green catalyst-free and solvent-free hydroboration of various alkynes and alkenes with HBcat in high yield and high selectivity at room temperature and lower reaction temperature, respectively.

2 Results and discussion

The investigation was started by performing the hydroboration of 4-ethynyltoluene as a model substrate with HBcat in catalyst-free manner (Table 1). Initially, the hydroboration of 4-ethynyltoluene with 1.1 equiv. of HBcat was carried out under catalyst-free condition in trace amounts of $CDCl_3$ solvent (20 μL) at room temperature, the corresponding boronate ester was obtained in 70% yield after 12 h (Entry 1). When the amount of HBcat was increased to 1.2 equiv., 76% yield was obtained within half reaction time (6 h) in solvent-free condition at room temperature, and quantitative conversion was observed in 12 h (Entries 2, 3). To our delight, full conversion was also achieved even in the presence of trace of solvent (Entry 4). While the reaction temperature was elevated to 40 ℃, the yield was only slightly improved and 12 h was required for full conversion under the same conditions by ^{1}H NMR spectroscopy analysis (Entries 5, 6). Furthermore, we envisioned that the reaction may proceed via dihydroboration. Therefore, the corresponding reaction between 4-ethynyltoluene and 3 equiv. of HBcat was conducted at room temperature or high temperature (110 ℃). However, only monohydroboration product was generated and no dihydroboration proceeded (Entries 7, 8). In contrast, when other borane derivative such as HBpin was tested in the hydroboration of 4-ethynyltoluene, however, the corresponding hydroboration product could not be observed at room temperature under the same reaction conditions.

Table 1 Optimization of reaction conditions for 4-ethynyltoluene with HBcat



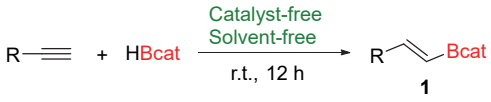
Entry	*n*	Temp./℃	Time/h	Solvent	Conv.[a]/%
1	1.1	r.t.	12	$CDCl_3$	70
2	1.2	r.t.	6		76
3	1.2	r.t.	12		99
4	1.2	r.t.	12	$CDCl_3$	99
5	1.2	40	6		80
6	1.2	40	12		99
7	3.0	r.t.	12		99
8	3.0	110	12	$CDCl_3$	99

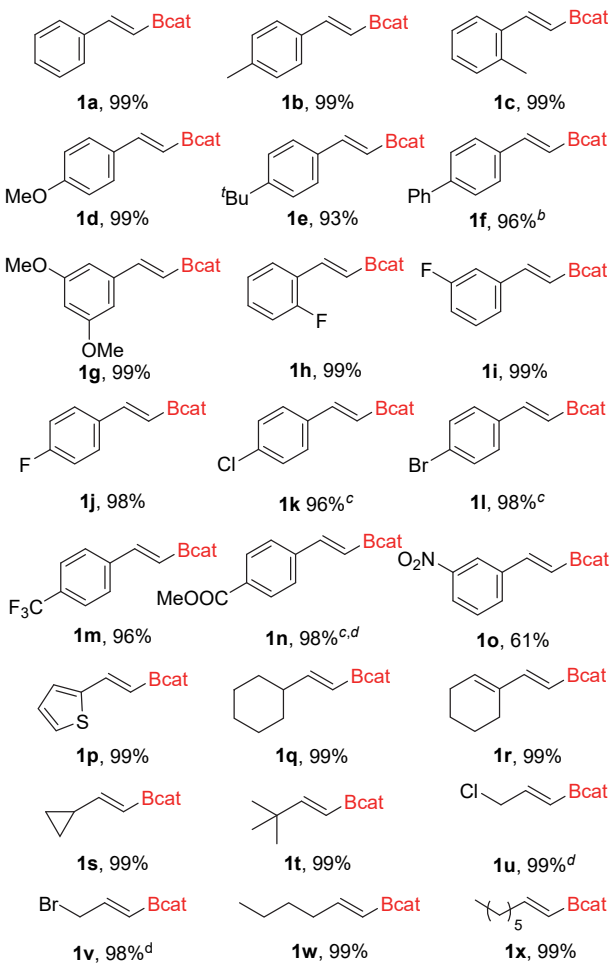
[a] Conversion was determined by ^{1}H NMR analysis.

With the optimized conditions of hydroboration of alkynes with HBcat in hand, the scope of alkyne substrates including various aromatic, aliphatic and heterocyclic alkynes was explored (Table 2). The hydroboration of all tested alkyne substrates proceeded smoothly under catalyst-free condition. It is noteworthy that in most cases, the hydroboration reaction was completed within 12 h in quantitative yields at room temperature. As for some solid substrates such as 4-chlorophenylacetylene and 4-bromophenylacetylene, microliter solvent was required to promote the corresponding hydroboration reaction. Aromatic alkyne substrates bearing electron-donating group [Me (*o*, *p*), OMe, ^{t}Bu, Ph] and electron-withdrawing group [F (*o*, *m*, *p*), Cl, Br, CF_3, COOMe] all exclusively afforded the corresponding alkenyl boronate esters in excellent yields (**1a**～**1f**, **1h**～**1n**). The position of substituents on the phenyl ring (*o*, *m*, *p*) had no effect on the final yield of hydroboration (**1b**, **1c**, **1h**～**1j**). The hydroboration of disubstituted alkyne such as 3,5-dimethoxyphenyl acetylene could also generate the corresponding product in full conversion at room temperature (**1g**). 3-Nitrophenyl-acetylene with strong electron-withdrawing nitro group gave a moderate yield (**1o**). Furthermore, the present protocol was also applied to aliphatic and heterocyclic alkyne substrates which showed the generality of the protocol. For example, heterocyclic substrate such as 2-ethynylthiophene was also hydroborated with HBcat in full conversion (**1p**). A range of aliphatic alkyne substrates with different cycloalkyl group such as cyclohexyl and cyclopropyl, bulky steric

hindrance group such as ^{t}Bu, or electron-withdrawing group such as Cl and Br, were found to be compatible and all furnished the corresponding boronate esters in quantitative yields under the standard conditions (**1q**～**1x**). To our delight, only the C≡C triple bond of 1-cyclohexenylacetylene proceeded the hydroboration to generate the corresponding boryldiene, and the C=C double bond of enyne remained intact demonstrating good chemoselectivity in the reaction (**1r**).

Table 2 Hydroboration of various alkynes with HBcat[a]

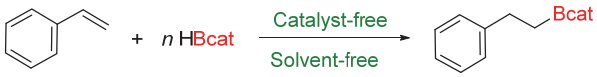




[a] Reaction conditions: alkynes (0.20 mmol), HBcat (0.24 mmol), r.t., 12 h. Conversion was determined by ^{1}H NMR analysis. [b] 20 μL of $CDCl_3$. [c] 50 μL of $CDCl_3$. [d] 24 h.

Encouraged by the above successful alkyne hydroboration with HBcat at room temperature, we proceeded to explore the hydroboration of more stable alkenes with HBcat. Initially, the hydroboration of styrene as a model substrate with 1.2 equiv. of HBcat was carried out under catalyst-free and solvent-free conditions at room temperature, however, only 12% yield of hydroboration was obtained in 12 h (Table 3, Entry 1). Subsequently, the reaction temperature was slightly elevated to 50 ℃, 81% yield of hydroboration was generated in 20 h (Entries 2, 3). Finally, when the amount of HBcat was increased to 1.5 equiv., a quantitative yield was achieved in 20 h (Entry 4).

Table 3 Optimization of reaction conditions for styrene with HBcat

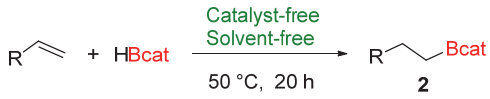


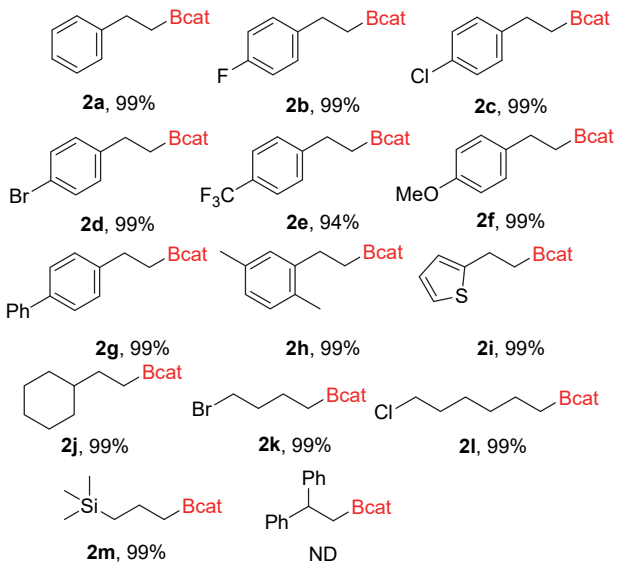
Entry	*n*	Temp./℃	Time/h	Conv.[a]/%
1	1.2	rt	12	12
2	1.2	50	12	76
3	1.2	50	20	81
4	1.5	50	20	99

[a] Conversion was determined by ^{1}H NMR analysis.

With the optimal reaction conditions of catalyst-free and solvent-free alkene hydroboration established, namely 1.5 equiv. of HBcat, 50 ℃, 20 h, we embarked to explore the alkene substrate scope. As summarized in Table 4, various alkylboronate esters were successfully prepared in quantitative yields. The hydroboration of aromatic alkenes with electron-withdrawing group such as F, Cl, Br, CF_3, or electron-donating group such as OMe, Ph, Me, all gave high yields under the standard reaction conditions (**2b**～**2h**). Similarly, heterocyclic alkene 2-ethenylthiophene also afforded the corresponding boronate ester in 99% yield (**2i**). To our delight, aliphatic alkenes with cyclohexyl, halogens (Br, Cl) and trimethylsilyl group were also hykylboronate products in quantitative yields (**2j**～**2m**). It should be noted that in some cases the yields of several

Table 4 Hydroboration of various alkenes with HBcat[a]

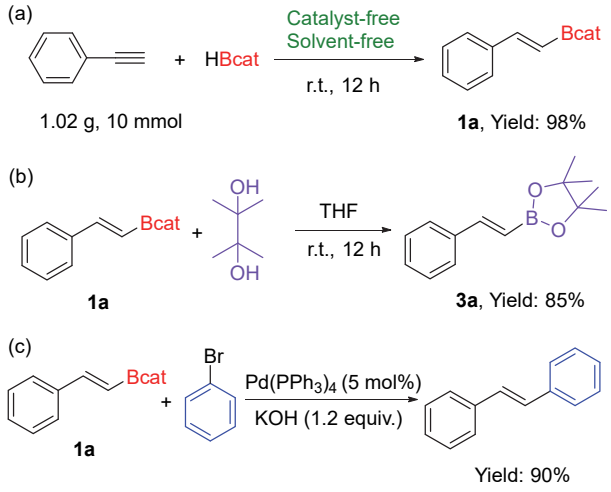




[a] Reaction conditions: alkenes (0.20 mmol), HBcat (0.30 mmol), 50 ℃, 20 h. Conversion was determined by ^{1}H NMR analysis. ND: No detected.

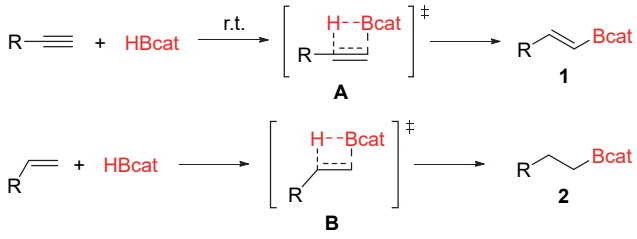
substrates were indeed better than those previously reported Fe- or Ir-catalyzed system.[16,25] Unfortunately, the hydrodroborated with HBcat to produce the corresponding alboration of bulky sterically 1,1-diphenylethylene with HBcat could not be proceeded under the same reaction conditions.

It is well known that stilbene derivatives have many useful applications in various fields such as biochemistry, pharmaceutical medicine and material science.[45-47] Hence, the boronate esters which were obtained via catalyst-free hydroboration of alkynes with HBcat could be furtherly applied to synthesize these important stilbene derivatives. To demonstrate the practical utility of this protocol, a gram-scale hydroboration of phenylacetylene (10 mmol) with HBcat was performed under optimized conditions and the corresponding boronate ester was produced as an orange solid in 98% yield (Scheme 2, a). Moreover, the boronate ester **1a** was transformed to more stable boronic ester derivative **3a** using pinacol which could be separated in 85% isolated yield via one-pot method (Scheme 2, b). Additionally, the boronate ester **1a** was applied to the Suzuki-coupling reaction with bromobenzene under the palladium-catalyzed conditions[1] and generated (*E*)-stilbene compound in 90% yield (Scheme 2, c).



Scheme 2 (a) Scale-up hydroboration of phenylacetylene, (b) transformation of **1a** to more stable **3a** and (c) Suzuki-coupling reaction of **1a**

According to the previously reported literatures[41] and the corresponding density function theory (DFT) theoretical calculations, a plausible mechanism for this catalyst-free process was proposed. As depicted in Scheme 3, the alkyne and alkene were firstly reacted with HBcat to produce the corresponding B-H-C-C four-membered ring transition state, respectively. Subsequently, the intermediates **A** and **B** were rapidly converted into the alkenyl boronate ester **1** and alkyl boronate ester **2**, respectively.[48] Furthermore, the corresponding DFT calculations were carried out to compare the activation barrier energy of the hydroboration of phenylacetylene with HBcat or HBpin, respectively (Figure 1, a). The activation energy barrier of the hydroboration of phenylacetylene with HBcat was lower than that of HBpin (39.91 kcal/mol vs 42.11 kcal/mol). This is also consistent with the experimental results we obtained that the catalyst-free hydroboration of phenylacetylene with HBcat proceeded smoothly at room temperature and the corresponding hydroboration of phenylacetylene with HBpin was unsuccessful at room temperature, which is similar to previously reported results.[49-50] Similarly, the activation energy barrier of the hydroboration of styrene with HBcat was slightly lower than that of HBpin (42.50 kcal/mol vs 42.72 kcal/mol, Figure 1, b). In addition, DFT calculations showed that the activation barrier of the hydroboration of styrene with HBcat was higher than that of phenylacetylene (42.50 kcal/mol vs 39.91 kcal/mol). These results were in accordance



Scheme 3 Proposed mechanism for the hydroboration of alkynes and alkenes

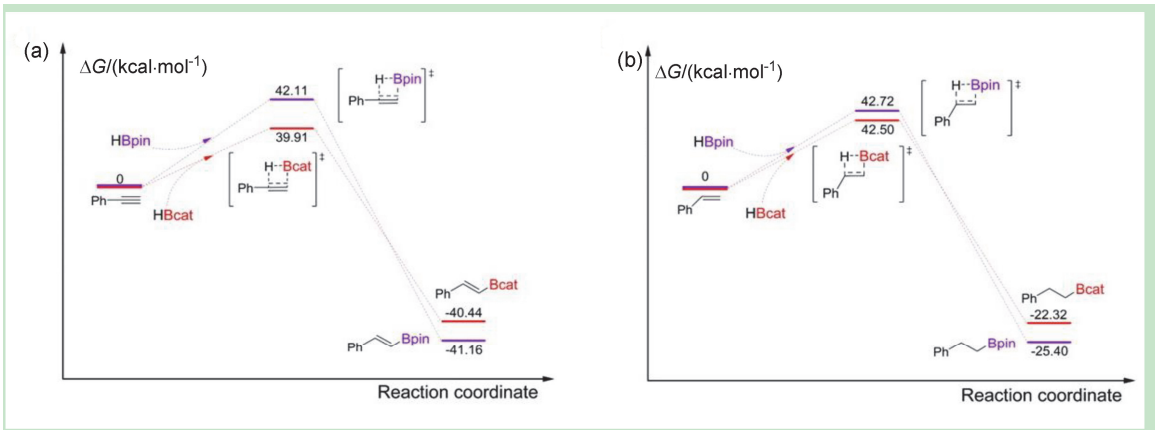


Figure 1 DFT calculations for the hydroboration of phenylacetylene (a, 298.15 K) and styrene (b, 323.15 K)

with experimental phenomena that alkyne reacted with HBcat only at room temperature while the reaction of alkene proceeded at slightly higher temperature (50 ℃).

3 Conclusions

In conclusion, a green and facile protocol for the catalyst-free and solvent-free hydroboration of various alkynes and alkenes with HBcat was developed. The resultant anti-Markovnikov products alkenyl and alkyl boronate esters were obtained in high yields and high regio/stereoselectivity at room temperature or relatively low temperature, respectively. It exhibited good functional group tolerance. The corresponding scale-up and Suzuki-coupling reaction demonstrated the practical utility of the protocol. A plausible reaction mechanism was proposed based on the corresponding DFT calculations. This is a good alternative strategy for the metal catalyzed-hydroboration of various alkynes and alkenes to afford very useful alkenyl and alkyl boronate esters.

4 Experimental section

4.1 General information

All reactions were performed under an atmosphere of nitrogen using glove box technique. ^{1}H NMR, ^{13}C NMR, and ^{11}B NMR spectra were monitored at 25 ℃ on a Bruker Avance III 600 MHz spectrometer in deuterated solvents and were referenced to the resonances of the solvent used. Chemicals were purchased from Sigma-Aldrich, Alfa Aesar, Energy Chemical and TCL which were used without further purification.

4.2 General procedure for hydroboration of alkynes and alkenes

The mixture of alkynes (0.20 mmol) and HBcat (0.24 mmol) was stirred at 25 ℃ for 12 h. Similarly, the mixture of alkenes (0.20 mmol) and HBcat (0.30 mmol) was stirred at 50 ℃ for 20 h. The progress of the reaction was monitored by ^{1}H NMR, ^{13}C NMR, and ^{11}B NMR. Conversion was determined by ^{1}H NMR analysis based on consumption of starting material.

Scale-up reaction: HBcat (12 mmol) was added dropwise to phenylacetylene (10 mmol, 1.02 g) at 0 ℃. Subsequently, the mixture was warmed to room temperature and stirred for 12 h to produce an orange solid in 98% yield.

(*E*)-2-(2'-Phenylethenyl)-1,3,2-benzodioxaborole (**1a**):[51] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.77 (d, ^{3}J=18.5 Hz, 1H, =CH), 7.60～7.59 (m, 2H, Ar-H), 7.41～7.39 (m, 2H, Ar-H), 7.38～7.35 (m, 1H, Ar-H), 7.27～7.25 (m, 2H, Ar-H), 7.11～7.09 (m, 2H, Ar-H), 6.50 (d, ^{3}J=18.5 Hz, 1H, =CH); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 152.06, 148.31, 136.94, 129.68, 128.78, 127.43, 122.70, 112.40; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 31.75.

(*E*)-2-(4-Methylstyryl)-1,3,2-benzodioxaborole (**1b**):[52] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.74 (d, ^{3}J=18.5 Hz, 1H, =CH), 7.49 (d, ^{3}J=8.0 Hz, 2H, Ar-H), 7.26～7.24 (m, 2H, Ar-H), 7.21 (d, ^{3}J=8.0 Hz, 2H, Ar-H), 7.10～7.08 (m, 2H, Ar-H), 6.43 (d, ^{3}J=18.5 Hz, 1H, =CH), 2.38 (s, 3H, CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 152.03, 148.34, 139.94, 134.28, 129.49, 127.40, 122.63, 112.34, 21.42; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 32.10.

(*E*)-2-(2-Methylstyryl)-1,3,2-benzodioxaborole (**1c**):[52] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.05 (d, ^{3}J=18.3 Hz, 1H, =CH), 7.68～7.67 (m, 1H, Ar-H), 7.27～7.25 (m, 4H, Ar-H), 7.21～7.19 (m, 1H, Ar-H), 7.11～7.09 (m, 2H, Ar-H), 6.42 (d, ^{3}J=18.3 Hz, 1H, =CH), 2.49 (s, 3H, CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 149.61, 148.33, 136.77, 136.08, 130.66, 129.38, 126.31, 125.83, 122.69, 112.39, 19.78; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 31.74.

(*E*)-2-(4-Methoxystyryl)-1,3,2-benzodioxaborole (**1d**):[53] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.72 (d, ^{3}J=18.4 Hz, 1H, =CH), 7.55 (d, ^{3}J=8.7 Hz, 2H, Ar-H), 7.25～7.24 (m, 2H, Ar-H), 7.10～7.08 (m, 2H, Ar-H), 6.92 (d, ^{3}J=8.7 Hz, 2H, Ar-H), 6.33 (d, ^{3}J=18.4 Hz, 1H, =CH), 3.85 (s, 3H, CH_3O); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 160.92, 151.61, 148.38, 129.90, 128.96, 122.60, 114.18, 112.32, 55.39; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 31.86.

(*E*)-2-(4-(*tert*-Butyl)styryl)-1,3,2-benzodioxaborole (**1e**):[27] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.76 (d, ^{3}J=18.4 Hz, 1H, =CH), 7.54 (d, ^{3}J=7.8 Hz, 2H, Ar-H), 7.43 (d, ^{3}J=7.5 Hz, 2H, Ar-H), 7.26～7.25 (m, 2H, Ar-H), 7.10～7.08 (m, 2H, Ar-H), 6.45 (d, ^{3}J=18.4 Hz, 1H, =CH), 1.34 (s, 9H, ^{t}Bu); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 153.12, 151.94, 148.34, 134.26, 127.24, 125.74, 122.65, 112.35, 34.84, 31.24; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 32.14.

(*E*)-2-(2-((1,1'-Biphenyl)-4-yl)ethenyl)-1,3,2-benzodioxaborole (**1f**):[54] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.81 (d, ^{3}J=18.4 Hz, 1H, =CH), 7.68～7.67 (m, 2H, Ar-H), 7.65～7.62 (m, 4H, Ar-H), 7.47～7.45 (m, 2H, Ar-H), 7.36～7.36 (m, 1H, Ar-H), 7.28～7.25 (m, 2H, Ar-H), 7.12～7.10 (m, 2H, Ar-H), 6.53 (d, ^{3}J=18.4 Hz, 1H, =CH); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 151.51, 148.33, 142.43, 140.41, 135.92, 128.88, 127.90, 127.68, 127.45, 127.06, 122.71, 112.40; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 32.08.

(*E*)-2-(3,5-Dimethoxystyryl)-1,3,2-benzodioxaborole (**1g**):[53] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.69 (d, ^{3}J=18.4 Hz, 1H, =CH), 7.26～7.25 (m, 2H, Ar-H), 7.10～7.09 (m, 2H, Ar-H), 6.75～6.74 (m, 2H, Ar-H), 6.49 (brs, 1H, Ar-H), 6.45 (d, ^{3}J=18.4 Hz, 1H, =CH), 3.83 (s, 6H, CH_3O); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 161.00, 151.92, 148.29, 138.93, 122.72, 112.40, 105.39, 101.98, 55.44; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 31.66.

(*E*)-2-(2-Fluorostyryl)-1,3,2-benzodioxaborole (**1h**):[55] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.96 (d, ^{3}J=18.6 Hz, 1H, =CH), 7.69～7.66 (m, 1H, Ar-H), 7.35～7.32 (m, 1H, Ar-H), 7.27～7.25 (m, 2H, Ar-H), 7.19～7.16 (m, 1H, Ar-H), 7.11～7.10 (m, 2H, Ar-H), 6.89～6.81 (m, 1H, Ar-H), 6.57 (d, ^{3}J=18.6 Hz, 1H, =CH); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 160.95 (d, J=253.7 Hz), 148.27, 143.87, 131.01 (d, J=9.1 Hz), 127.63 (d, J=3.0 Hz), 124.30 (d, J=4.5 Hz), 122.76, 116.05 (d, J=22.7 Hz), 112.45; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 31.49.

(*E*)-2-(3-Fluorostyryl)-1,3,2-benzodioxaborole (**1i**):[55] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.72 (d, ^3J=18.4 Hz, 1H, =CH), 7.37～7.34 (m, 2H, Ar-H), 7.27～7.25 (m, 3H, Ar-H), 7.12～7.10 (m, 2H, Ar-H), 7.07～7.49 (m, 1H, Ar-H), 6.49 (d, ^3J=18.4 Hz, 1H, =CH); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 163.15 (d, J=246.1 Hz), 150.54, 148.24, 130.27 (d, J=7.6 Hz), 123.40 (d, J=3.0 Hz), 122.80, 116.47 (d, J=21.1 Hz), 113.61 (d, J=21.1 Hz), 112.45; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 31.50.

(*E*)-2-(4-Fluorostyryl)-1,3,2-benzodioxaborole (**1j**):[54] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.72 (d, ^3J=18.5 Hz, 1H, =CH), 7.59～7.55 (m, 2H, Ar-H), 7.26～7.25 (m, 2H, Ar-H), 7.11～7.10 (m, 2H, Ar-H), 7.08～7.06 (m, 2H, Ar-H), 6.40 (d, ^3J=18.5 Hz, 1H, =CH); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 163.60 (d, J=250.7 Hz), 150.65, 148.27, 133.22, 129.17 (d, J=9.1 Hz), 122.72, 115.82 (d, J=21.1 Hz), 112.39; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 31.82.

(*E*)-2-(4-Chlorostyryl)-1,3,2-benzodioxaborole (**1k**):[41] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.71 (d, ^3J=18.4 Hz, 1H, =CH), 7.52 (d, ^3J=8.4 Hz, 2H, Ar-H), 7.37 (d, ^3J=8.4 Hz, 2H, Ar-H), 7.27～7.25 (m, 2H, Ar-H), 7.12～7.10 (m, 2H, Ar-H), 6.46 (d, ^3J=18.4 Hz, 1H, =CH); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 150.48, 148.25, 135.47, 135.41, 129.01, 128.58, 122.77, 112.42; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 31.65.

(*E*)-2-(4-Bromostyryl)-1,3,2-benzodioxaborole (**1l**):[41] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.69 (d, ^3J=18.4 Hz, 1H, =CH), 7.53 (d, ^3J=8.0 Hz, 2H, Ar-H), 7.45 (d, ^3J=8.0 Hz, 2H, Ar-H), 7.27～7.25 (m, 2H, Ar-H), 7.12～7.10 (m, 2H, Ar-H), 6.48 (d, ^3J=18.4 Hz, 1H, =CH); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 150.55, 148.25, 135.83, 131.98, 128.83, 123.80, 122.78, 112.43; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 31.78.

(*E*)-2-(4-(Trifluoromethyl)styryl)-1,3,2-benzodioxaborole (**1m**):[19] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.78 (d, ^3J=18.5 Hz, 1H, =CH), 7.70～7.65 (m, 4H, Ar-H), 7.28～7.25 (m, 2H, Ar-H), 7.12～7.11 (m, 2H, Ar-H), 6.59 (d, ^3J=18.5 Hz, 1H, =CH); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 150.09, 148.20, 140.17, 127.52, 126.39, 125.77, 122.88, 112.50; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 31.43.

(*E*)-4-(2-(1,3,2-Benzodioxaborol-2-yl)ethenyl)-benzoate (**1n**):[19] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.07 (d, ^3J=8.3 Hz, 2H, Ar-H), 7.78 (d, ^3J=18.5 Hz, 1H, =CH), 7.65 (d, ^3J=8.3 Hz, 2H, Ar-H), 7.28～7.26 (m, 2H, Ar-H), 7.12～7.11 (m, 2H, Ar-H), 6.60 (d, ^3J=18.5 Hz, 1H, =CH), 3.94 (s, 3H, CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 166.76, 150.55, 148.22, 141.08, 130.76, 130.07, 127.26, 122.84, 112.48, 52.27; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 32.10.

(*E*)-2-(3-Nitrostyryl)-1,3,2-benzodioxaborole (**1o**):[56] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.44 (s, 1H, Ar-H), 8.22～8.19 (m, 1H, Ar-H), 7.89 (d, ^3J=18.4 Hz, 1H, =CH), 7.81～7.78 (m, 1H, Ar-H), 7.60～7.58 (m, 1H, Ar-H), 7.29～7.27 (m, 2H, Ar-H), 7.14～7.12 (m, 2H, Ar-H), 6.64 (d, ^3J=18.4 Hz, 1H, =CH); ^{11}B NMR (193 MHz, $CDCl_3$) δ: 31.41.

(*E*)-2-(2-(Thiophen-2-yl)ethenyl)-1,3,2-benzodioxaborole (**1p**):[41] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.84 (d, ^3J=18.1 Hz, 1H, =CH), 7.34 (d, ^3J=5.0 Hz, 1H, C_4H_3S), 7.25～7.23 (m, 2H, Ar-H), 7.22 (d, ^3J=3.5 Hz, 1H, C_4H_3S), 7.10～7.08 (m, 2H, Ar-H), 7.05 (dd, ^3J=5.0 Hz, ^3J=3.6 Hz, 1H, C_4H_3S), 6.22 (d, ^3J=18.1 Hz, 1H, =CH); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 148.30, 144.08, 143.36, 128.96, 127.92, 127.40, 122.68, 112.37; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 31.62.

(*E*)-2-(2-Cyclohexylethenyl)-1,3,2-benzodioxaborole (**1q**):[41] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.21～7.19 (m, 2H, Ar-H), 7.08～7.05 (m, 2H, Ar-H), 6.99 (dd, ^3J=18.2 Hz, ^3J=6.4 Hz, 1H, =CH), 5.74 (d, ^3J=18.2 Hz, 1H, =CH), 2.20～2.14 (m, 1H, C_6H_{11}), 1.79～1.75 (m, 2H, C_6H_{11}), 1.71～1.66 (m, 2H, C_6H_{11}), 1.36～1.38 (m, 2H, C_6H_{11}), 1.24～1.15 (m, 4H, C_6H_{11}); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 163.02, 148.28, 122.48, 112.24, 43.54, 31.81, 26.11, 25.85; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 31.18.

(*E*)-2-(2-(Cyclohex-1-en-1-yl)ethenyl)-1,3,2-benzodioxaborole (**1r**):[41] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.38 (d, ^3J=18.2 Hz, 1H, =CH), 7.25～7.21 (m, 2H, Ar-H), 7.07～7.06 (m, 2H, Ar-H), 6.12 (s, 1H, =CH), 5.74 (d, ^3J=18.2 Hz, 1H, =CH), 2.25～2.22 (m, 4H, C_6H_9), 1.73～1.70 (m, 2H, C_6H_9), 1.66～1.63 (m, 2H, C_6H_9); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 155.73, 148.38, 137.21, 136.36, 122.46, 112.23, 26.32, 23.78, 22.30, 22.24; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 31.94.

(*E*)-2-(2-Cyclopropylvinyl)-1,3,2-benzodioxaborole (**1s**):[36] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.20～7.18 (m, 2H, Ar-H), 7.06～7.04 (m, 2H, Ar-H), 6.46 (dd, ^3J=17.8 Hz, ^3J=9.4 Hz, 1H, =CH), 5.84 (d, ^3J=17.8 Hz, 1H, =CH), 1.69～1.63 (m, 1H, C_3H_5), 0.94～0.91 (m, 2H, C_3H_5), 0.66～0.63 (m, 2H, C_3H_5); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 161.97, 148.28, 122.44, 112.19, 17.52, 8.50; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 31.30.

(*E*)-2-(3,3-Dimethylbut-1-en-1-yl)-1,3,2-benzodioxaborole (**1t**):[36] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.22～7.20 (m, 2H, Ar-H), 7.07～7.05 (m, 2H, Ar-H), 7.05 (d, ^3J=18.4 Hz, 1H, =CH), 5.71 (d, ^3J=18.4 Hz, 1H, =CH), 1.11 (s, 9H, CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 167.66, 148.28, 122.49, 112.24, 35.47, 28.62; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 31.73.

(*E*)-2-(3-Chloroprop-1-en-1-yl)-1,3,2-benzodioxaborole (**1u**):[36] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.25～7.23 (m, 2H, Ar-H), 7.11～7.09 (m, 2H, Ar-H), 7.03 (dt, ^3J=17.7 Hz, ^3J=5.8 Hz, 1H, =CH), 6.13 (d, ^3J=17.7 Hz, 1H, =CH), 4.23 (d, ^3J=5.8 Hz, 2H, CH_2); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 149.28, 148.08, 122.85, 112.50, 45.76. ^{11}B NMR (193 MHz, $CDCl_3$) δ: 30.56.

(*E*)-2-(3-Bromoprop-1-en-1-yl)-1,3,2-benzodioxaborole (**1v**):[36] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.26～7.23 (m, 2H, Ar-H), 7.11～7.09 (m, 2H, Ar-H), 7.07～7.03 (m, 1H, =CH), 6.05 (d, ^3J=17.6 Hz, 1H, =CH), 4.09 (d, ^3J=7.0 Hz, 2H, CH_2); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 149.37, 148.06, 122.93, 112.69, 33.06; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 30.76.

(*E*)-2-(1-Hexenyl)-1,3,2-benzodioxaborole (**1w**):[55] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.21～7.19 (m, 2H, Ar-H), 7.07～7.05 (m, 2H, Ar-H), 7.04～7.01 (m, 1H, =CH),

5.79 (d, ^3J=18.0 Hz, 1H, =CH), 2.31～2.27 (m, 2H, C_4H_9), 1.50～1.46 (m, 2H, C_4H_9), 1.40～1.34 (m, 2H, C_4H_9), 0.93 (t, ^3J=7.3 Hz, 3H, CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 158.06, 148.27, 122.48, 112.24, 35.77, 30.29, 22.24, 13.90; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 31.21.

(*E*)-2-(1-Octenyl)-1,3,2-benzodioxaborole (**1x**):[41] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.21～7.20 (m, 2H, Ar-H), 7.07～7.05 (m, 2H, Ar-H), 7.04～7.01 (m, 1H, =CH), 5.79 (d, ^3J=18.0 Hz, 1H, =CH), 2.30～2.26 (m, 2H, C_6H_{13}), 1.51～1.46 (m, 2H, C_6H_{13}), 1.36～1.28 (m, 6H, C_6H_{13}), 0.89 (t, ^3J=6.7 Hz, 3H, CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 158.11, 148.27, 122.49, 112.25, 36.10, 31.71, 28.87, 28.14, 22.61, 14.10; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 31.34.

2-Phenethyl-benzo-1,3,2-dioxaborole (**2a**):[17] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.30～7.25 (m, 4H, Ar-H), 7.22～7.20 (m, 2H, Ar-H), 7.20～7.17 (m, 1H, Ar-H), 7.09～7.06 (m, 2H, Ar-H), 2.98 (t, ^3J=8.3 Hz, 2H, CH_2), 1.67 (t, ^3J=8.3 Hz, 2H, CH_2); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 148.19, 143.62, 128.45, 127.91, 125.87, 122.58, 112.30, 29.66; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 35.27.

2-(4-Fluorophenethyl)-benzo-1,3,2-dioxaborole (**2b**):[17] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.22～7.19 (m, 4H, Ar-H), 7.08～7.06 (m, 2H, Ar-H), 6.98～6.95 (m, 2H, Ar-H), 2.95 (t, ^3J=8.2 Hz, 2H, CH_2), 1.64 (t, ^3J=8.2 Hz, 2H, CH_2); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 161.28 (d, J=243.1 Hz), 148.14, 139.16, 129.26 (d, J=7.6 Hz), 122.63, 115.15 (d, J=21.1 Hz), 112.31, 28.89; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 35.54.

2-(4-Chlorophenethyl)-benzo-1,3,2-dioxaborole (**2c**):[35] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.24 (d, ^3J=8.4 Hz, 2H, Ar-H), 7.22～7.20 (m, 2H, Ar-H), 7.18 (d, ^3J=8.4 Hz, 2H, Ar-H), 7.08～7.06 (m, 2H, Ar-H), 2.95 (t, ^3J=8.2 Hz, 2H, CH_2), 1.63 (t, ^3J=8.2 Hz, 2H, CH_2); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 148.13, 141.99, 131.59, 129.30, 128.53, 122.65, 112.33, 29.06; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 35.51.

2-(4-Bromophenethyl)-benzo-1,3,2-dioxaborole (**2d**):[17] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.39 (d, ^3J=8.4 Hz, 2H, Ar-H), 7.22～7.20 (m, 2H, Ar-H), 7.13 (d, ^3J=8.4 Hz, 2H, Ar-H), 7.08～7.07 (m, 2H, Ar-H), 2.93 (t, ^3J=8.2 Hz, 2H, CH_2), 1.63 (t, ^3J=8.2 Hz, 2H, CH_2); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 148.12, 142.51, 131.49, 129.72, 122.65, 119.60, 112.33, 29.12; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 35.49.

2-(2-(4-(Trifluoromethyl)phenyl)ethyl)-benzo-1,3,2-dioxaborole (**2e**):[17] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.54 (d, ^3J=8.1 Hz, 2H, Ar-H), 7.37 (d, ^3J=8.0 Hz, 2H, Ar-H), 7.22～7.21 (m, 2H, Ar-H), 7.09～7.07 (m, 2H, Ar-H), 3.04 (t, ^3J=8.2 Hz, 2H, CH_2), 1.68 (t, ^3J=8.2 Hz, 2H, CH_2); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 148.10, 128.25, 125.41, 125.38, 122.70, 112.35, 29.53; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 35.31.

2-(2-(4-Methoxyphenyl)ethyl)-benzo-1,3,2-dioxaborole (**2f**):[17] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.22～7.20 (m, 2H, Ar-H), 7.17 (d, ^3J=8.6 Hz, 2H, Ar-H), 7.07～7.06 (m, 2H, Ar-H), 6.83 (d, ^3J=8.6 Hz, 2H, Ar-H), 3.78 (s, 3H, CH_3), 2.92 (t, ^3J=8.2 Hz, 2H, CH_2), 1.63 (t, ^3J=8.2 Hz, 2H, CH_2); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 157.78, 148.20, 135.75, 128.81, 122.55, 113.86, 112.29, 55.27, 28.78; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 35.59.

2-(2-((1,1'-Biphenyl)-4-yl)ethyl)-benzo-1,3,2-dioxaborole (**2g**):[35] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.58～7.56 (m, 2H, Ar-H), 7.53～7.51 (m, 2H, Ar-H), 7.43～7.41 (m, 3H, Ar-H), 7.34～7.31 (m, 2H, Ar-H), 7.23～7.21 (m, 2H, Ar-H), 7.08～7.07 (m, 2H, Ar-H), 3.03 (t, ^3J=8.3 Hz, 2H, CH_2), 1.71 (t, ^3J=8.3 Hz, 2H, CH_2); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 148.20, 142.73, 141.09, 138.87, 128.71, 128.34, 127.21, 127.02, 122.61, 112.33, 29.31; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 35.66.

2-(2-(2,5-Dimethylphen)ethyl))-benzo-1,3,2-dioxaborole (**2h**):[58] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.23～7.21 (m, 2H, Ar-H), 7.08～7.07 (m, 2H, Ar-H), 7.04～7.03 (m, 2H, Ar-H), 6.93～6.91 (m, 1H, Ar-H), 2.91 (t, ^3J=8.4 Hz, 2H, CH_2), 2.31 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 1.61 (t, ^3J=8.4 Hz, 2H, CH_2); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 148.22, 141.58, 135.51, 132.53, 130.12, 128.80, 126.64, 122.59, 112.30, 26.96, 21.02, 18.77.; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 35.69.

2-(2-(Thiophen-2-yl)ethyl)-benzo-1,3,2-dioxaborole (**2i**):[59] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.22～7.20 (m, 2H, Ar-H), 7.11～7.09 (m, 1H, C_4H_3S), 7.08～7.07 (m, 2H, Ar-H), 6.91～6.90 (m, 1H, C_4H_3S), 6.86～6.85 (m, 1H, C_4H_3S), 3.20 (t, ^3J=8.0 Hz, 2H, CH_2), 1.75 (t, ^3J=8.0 Hz, 2H, CH_2); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 148.16, 146.77, 126.79, 123.73, 123.02, 122.63, 112.35, 24.07; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 35.22.

2-((2-Cyclohexyl)ethyl)-benzo-1,3,2-dioxaborole (**2j**):[60] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.20～7.19 (m, 2H, Ar-H), 7.06～7.05 (m, 2H, Ar-H), 1.78～1.75 (m, 2H, C_6H_{11}), 1.70 (dt, ^3J=13.0 Hz, ^3J=3.4 Hz, 2H, CH_2), 1.66～1.63 (m, 1H, C_6H_{11}), 1.55～1.51 (m, 2H, C_6H_{11}), 1.28 (t, ^3J=8.4 Hz, 2H, CH_2), 1.25～1.11 (m, 4H, C_6H_{11}), 0.93～0.89 (m, 2H, C_6H_{11}); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 148.25, 122.44, 112.20, 39.66, 32.97, 31.16, 26.70, 26.36; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 35.98.

2-(4-Bromobutyl)-benzo-1,3,2-dioxaborole (**2k**):[60] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.21～7.20 (m, 2H, Ar-H), 7.08～7.06 (m, 2H, Ar-H), 3.46 (t, ^3J=6.9 Hz, 2H, CH_2), 2.01～1.96 (m, 2H, CH_2), 1.82～1.77 (m, 2H, CH_2), 1.34 (t, ^3J=7.8 Hz, 2H, CH_2); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 148.15, 122.60, 112.29, 34.94, 33.39, 22.40; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 35.36.

2-(6-Chlorohexyl)-benzo-1,3,2-dioxaborole (**2l**):[60] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.22～7.19 (m, 2H, Ar-H), 7.08～7.05 (m, 2H, Ar-H), 3.55 (t, ^3J=6.6 Hz, 2H, CH_2), 1.82～1.77 (m, 2H, CH_2), 1.68～1.63 (m, 2H, CH_2), 1.51～1.46 (m, 2H, CH_2), 1.45～1.40 (m, 2H, CH_2), 1.31 (t, ^3J=7.8 Hz, 2H, CH_2); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 148.21, 122.50, 112.23, 45.11, 32.49, 31.43, 26.65, 23.57; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 35.72.

[3-(Benzo-1,3,2-dioxaborol-2-yl)propyl]trimethylsilane (**2m**):[60] ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.22～7.20 (m, 2H, Ar-H), 7.07～7.06 (m, 2H, Ar-H), 1.70～1.64 (m, 2H, CH_2), 1.36 (t, ^3J=7.8 Hz, 2H, CH_2), 0.65～0.62 (m, 2H, CH_2), 0.01 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR (151 MHz, $CDCl_3$)

δ: 148.24, 122.44, 112.22, 20.04, 18.45, −1.66; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 35.56.

4.3 General procedure for reaction of **1a** with pinacol

To the boronic ester **1a** (0.30 mmol, 66.6 mg) was added dropwise with the solution of pinacol (0.45 mmol, 53.2 mg) in THF (0.3 mL) at 0 ℃, and stirred for 12 h at room temperature. The solvent was removed, and the residue was dissolved in chloroform. Then organic layers were washed by water and dried over anhydrous Na_2SO_4. The boronic ester **3a**[41] was purified by silica column chromatography as yellow oil in 85% isolated yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.49～7.48 (m, 2H, Ar-H), 7.40 (d, ^3J= 18.4 Hz, 1H, =CH), 7.35～7.32 (m, 2H, Ar-H), 7.30～7.28 (m, 1H, Ar-H), 6.17 (d, ^3J=18.4 Hz, 1H, =CH), 1.32 (s, 12H, CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ: 149.54, 137.48, 128.91, 128.58, 127.07, 83.37, 24.82; ^{11}B NMR (193 MHz, $CDCl_3$) δ: 30.15.

4.4 General procedure for Suzuki-coupling reaction

The mixture of **1a** (0.50 mmol, 111.0 mg), bromobenzene (0.60 mmol, 94.2 mg), $Pd(PPh_3)_4$ (5 mol%) and KOH (1.2 equiv.) in 1,4-dioxane (3.0 mL) was stirred for 15 h at 110 ℃. The solvent was removed and the residual was added with water (20 mL). The reaction mixture was extracted with chloroform (20 mL×3). Then the organic layers were dried over anhydrous $MgSO_4$. Finally, (*E*)-stilbene[56] was purified by silica column chromatography with ethyl acetate/hexane (V∶V=0.5∶99.5) as yellow solid in 90% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.52 (d, ^3J=7.2 Hz, 4H, Ar-H), 7.36 (t, ^3J=7.5 Hz, 4H, Ar-H), 7.26 (t, ^3J=7.4 Hz, 2H, Ar-H), 7.11 (s, 2H, =CH).

Supporting Information NMR spectroscopic spectra and computational studies. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

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