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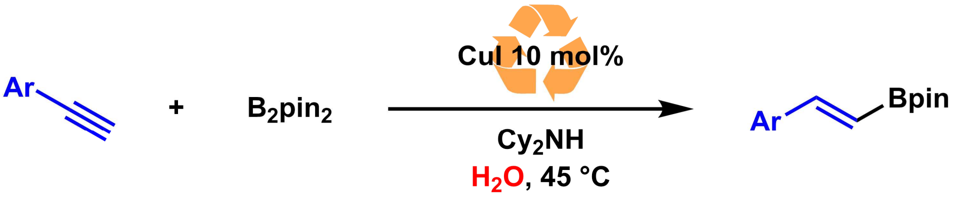

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ABSTRACT

In this paper, we established copper catalyzed reductive borylation of terminal alkynes and diboron on water in the presence of amine. Moderate conditions enabled selective borylations of vinyl-substituted phenylacetylenes to undergo the borylation at a C-C triple bond. The Cu catalyst can be recycled for seven times.

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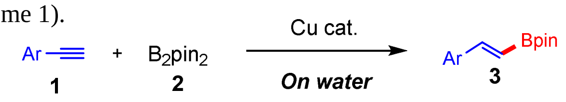
1. Introduction

1-Alkenylboron compounds are very useful and important reagents for organic synthesis [1,2]. In particular, 1-alkenylborons are an important coupling partner for Suzuki-Miyaura couplings [2]. Several synthetic utilities have been developed, whereas their synthetic approaches have also been well-studied, including reaction of alkenyl metal species (Mg or Li) with $B(OR)_3$[3], metal catalyzed hydroborations of alkynes with HBpin (pinacolborane) [4], olefin metathesis [5] and boron Heck reaction [6].

Several approaches mentioned above realized useful synthetic methodologies, the reactions under sustainable conditions are still problematic. In this context, reductive borylations are one of the promising reactions to accomplish sustainable borylations. Reductive borylation reaction provides a simple protocol to synthesize 1-alkenylborons, in which terminal alkyne, diboron and protic solvent require to carry out the reaction [7,8,9]. Although some reports enabled various reductive borylation reactions, borylation with recycling a catalyst on water has not yet been established. Water is one of the most attractive medium for organic synthesis because of safety, economics, and environmental compatibilities[10]. In this report, we established copper-catalyzed reductive borylation on water, in which the copper catalyst embedded in water can be recycled several times (Scheme 1).



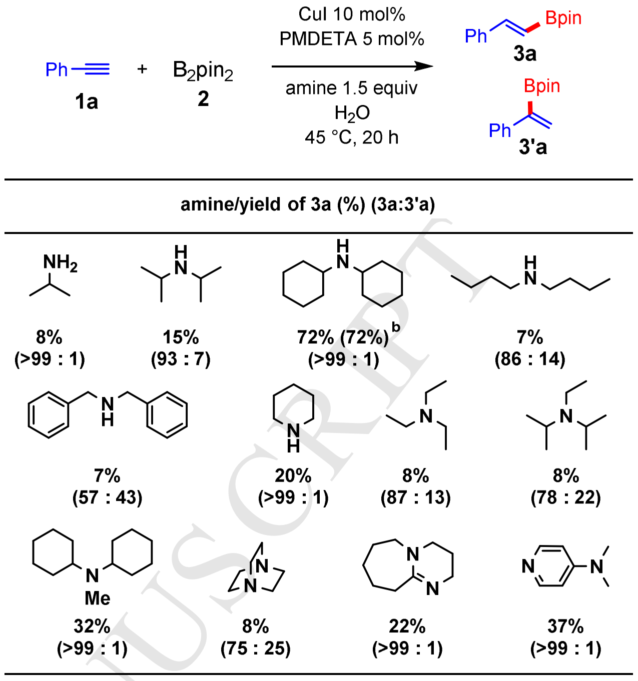
Scheme 1. Reductive borylation on water.

2. Results and discussion

Our initial screening shown in Table 1 employed the reaction of phenylacetylene (**1a**), bis(pinacolate)diboron (B_2pin_2), CuI, PMDETA (*N*,*N*,*N′*,*N″*,*N″*-pentamethyldiethylenetriamine), and amine in water at 45 °C. In reductive borylation chemistry, inorganic bases are effective but the reaction in water required an organic base, such as amine, rather than inorganic bases. Primary- and tertiary-amines did not gave satisfied yield of **3a**. On the other hand, secondary-amine, especially dicyclohexylamine, gave 72% of **3a** in water. Other amines were also examined but the yields and selectivities were problematic. The reason for amine effects were not clear. PMDETA ligand was not important in this reaction and good yield was obtained without the ligand. We also screened various copper salts, and ligands but CuI without a ligand was found to be the best catalyst system in water medium. Recently, Lipshutz reported the metal-catalyzed reactions in water in the presence of various surfactants but surfactants were not effective for current reductive borylation.

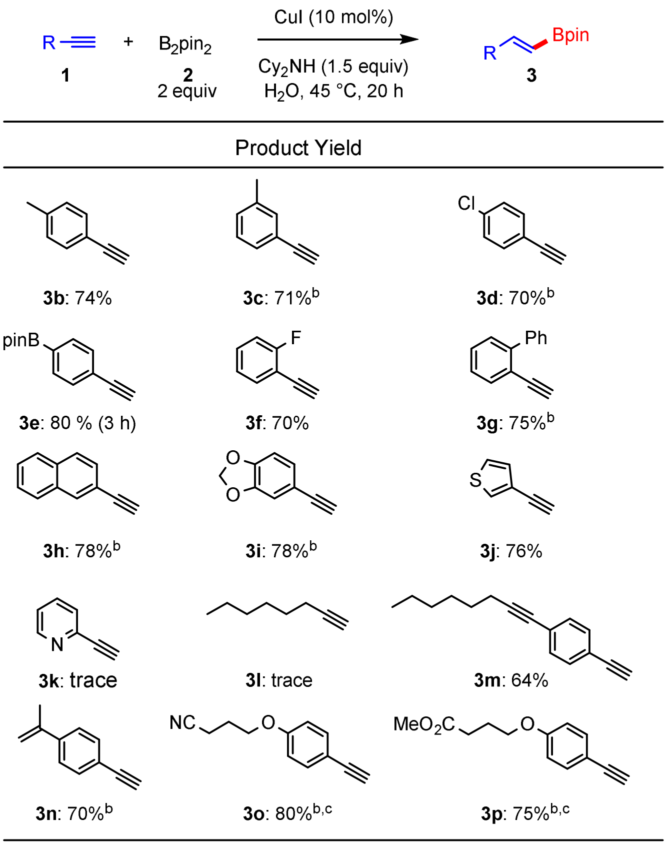
Under optimal conditions, we evaluated the reactivities of alkynes **1** possessing various structures for reductive borylations in water (Table 2). Generally, reactivities are moderate in water but fundamental functional groups including methyl, halogen, and aryl groups resulted in good yields in the presence of 2 or 3 equivalents of diboron (**3b-3d**, **3f-3h**). Interestingly, borylated substrate gave **3e** without loss of the boron moiety. Heteroaromatic alkynes (**3i** and **3j**) reacted smoothly with diboron but pyridine substituted alkyne was not effective (**3k**). Arylalkynes showed

Table 1 Amine effects



[a] All reactions were carried out on water at 45 °C for 20 h with CuI (10 mol%), PMDETA (5 mol%), amine (1.5 equiv), **1a** (1.0 equiv.) and **2** (2.0 equiv.). Yields were isolated. [b] Without PMDETA.

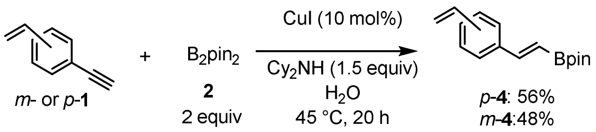
Table 2 Substrate scope



[a]All reactions were carried out on water at 45 ºC for 20 h with CuI (10 mol%), Cy_2NH (1.5 equiv), **1a** (1.0 equiv.) and **2** (2.0 equiv.). Yields were isolated. [b] 3 equiv of B_2pin_2 was used. [c] Brij (4wt%aq.) was used as a solvent.

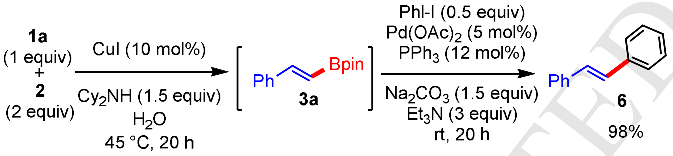
nice reactivities, whereas aliphatic alkynes, such as 1-octyne, did not give **3l**. In this reaction, an internal alkyne or alkene were not reactive and the corresponding products (**3m** and **3n**) were obtained in 64% and 70% yield without loss of C-C unsaturated bonds, respectively. The substrates having CN or ester (**3o** and **3p**) were not reactive on water, because of the solubility problem. But the reactions in the presence of surfactant such as Brij 35 (Polyoxyethyleneglycol dodecyl ether) gave good yields of the products.

Overall, our borylation reactivities were moderate but this moderate reactivities were effective to undergo the selective borylation with vinyl substituted alkynes (*m*-**1** and *p*-**1** in Scheme 2)[11]. Under the optimal conditions, borylations occurred selectively at C-C triple bond in each substrates.



Scheme 2. Selective borylations.

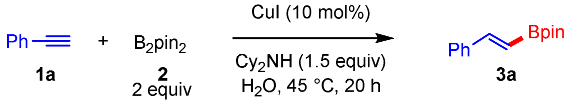
Our protocol on water is useful to carry out one-pot reaction and recycling of catalyst. 1-Alkenylboron is a good Suzuki coupling pater. After the first borylation to form **3a**, second Suzuki coupling reaction smoothly occurred to produce **6** in 98% yield (Scheme 3).



Scheme 3. One-pot process.

Our final goal is to establish catalyst recycling system on water (Table 3). Our recycling is very simple. After the borylation reaction, the product **3a** was extracted with ethyl acetate. After that, substrates (**1** and **2**) were added to the water. We tested the reaction for seven times but the yields were gradually dropped at each reaction. Especially, the yield was dramatically decreased at 6th reaction. The problem for recycling of catalyst is extraction process. After the reaction, the product was extracted with ethyl acetate, but the surface was not clear due to the generation boronic acid-related salts. Therefore, a part of catalyst in water was extracted.

Table 3. Recycling of catalyst.



Cycle	1	2	3	4	5	6	7
Yield (%)	74	73	74	60	55	39	30

3. Conclusion

In conclusion, we have established the Cu-catalyzed reductive borylation on water. Various substrates were able to be applied to the reaction system. The reactivities were moderate but this was effective to carry out selective borylation of alkynes having unsaturated C-C bonds. Recycling of the catalyst was also possible on water.

4. Experimental section

4.1 General

All reactions were carried out under nitrogen (99.95%) atmosphere. For TLC analyses precoated Kieselgel 60 F254 plates (Merck, 0.25 mm thick) were used; for column chromatography Silica *Flash*® P60 (SiliCycle, 40-63 µm) was used. Visualization was accomplished by UV light (254 nm), ^1H and ^{13}C NMR spectra were obtained using a JEOL 400 MHz NMR spectrometer. Chemical shifts for ^1H NMR were described in parts per million (chloroform as an internal standard δ = 7.26) in $CDCl_3$, unless otherwise noted. Chemical shifts for ^{13}C NMR were expressed in parts per million in $CDCl_3$ as an internal standard (δ = 77.16), unless otherwise noted. High resolution mass analyses were obtained using an ACQUITY UPLC/ TOF-MS for ESI.

4.2 General procedure for the reductive borylations

CuI (10 mol%), **1** (1 equiv, 0.5 mmol), and **2** (2 equiv, 1.0 mmol) were sequentially added under air to a dram vial equipped with a stir bar. Amine (1.5 equiv, 0.75 mmol), and distilled water (1.0 mL) were added by syringe, and the resulting mixture was vigorously stirred under nitrogen atmosphere [charged by general N_2 (99.95%) gas flow] for 20 h at the temperature, as shown in the tables. After this time, the contents of the flask were extracted with ethyl acetate and then concentrated by rotary evaporation. The residue was purified by flash chromatography, eluting with hexane/EtOAc to afford the product **3**.

*4.2.1. (E)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (**3a**)*[12]

Following the general procedure above, using **1a** (0.5 mmol), B_2Pin_2 (254 mg, 1.0 mmol), CuI (9.5 mg, 0.05 mmol), and Cy_2NH (136 mg, 0.75 mmol), and H_2O (1.0 mL) at 45 °C for 20 h, yielded the product **3a** (72%); Yellow oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 1.31 (s, 12H), 6.17 (d, *J* = 18.5 Hz, 1H), 7.28 (dd, *J* = 1.3 and 8.2 Hz, 1H), 7.33 (dd, *J* = 1.3 and 8.2 Hz, 2H), 7.40 (d, *J* = 18.5 Hz, 1H), 7.49 (dd, *J* = 1.3 and 7.3 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ: 24.86, 83.43, 127.20, 128.71, 129.05, 137.60, 149.68.

*4.2.2.(E)-4,4,5,5-tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (**3b**)*[12]

Following the general procedure above, using **1b** (0.5 mmol), B_2Pin_2 (254 mg, 1.0 mmol), CuI (9.5 mg, 0.05 mmol), and Cy_2NH (136 mg, 0.75 mmol), and H_2O (1.0 mL) at 45 °C for 20 h, yielded the product **3b** (74%); Yellow solid; m.p. 55-56ºC; ^1H NMR (500 MHz, $CDCl_3$) δ: 1.31 (s, 12H), 2.34 (s, 3H), 6.11 (d, *J* = 18.5 Hz, 1H), 7.14 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 18.5 Hz, 1H), 7.39 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 21.39, 24.88, 83.38, 127.18, 129.45, 134.95, 139.12, 149.66.

4.2.3. (E)-4,4,5,5-tetramethyl-2-(3-methylstyryl)-1,3,2-dioxaborolane (3c)

Yellow oil; IR (neat) ν 2976, 1623, 1378 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ: 1.31 (s, 12H), 2.34 (s, 3H), 6.15 (d, *J* = 18.5 Hz, 1H), 7.11 (d, *J* = 7.0 Hz, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 6.8 Hz, 2H), 7.37 (d, *J* = 18.5 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ: 21.41, 24.84, 83.36, 124.36, 127.90, 128.59, 129.85, 137.59, 138.19, 149.84; HREIMS calcd. for $C_{15}H_{22}BO_2$ (M+H$^+$): 245.1712; found 245.1713.

*4.2.4. (E)-2-(4-chlorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaboro-lane (**3d**)*[6]

Yellow solid; m.p. 90-91ºC; ^{1}H NMR (500 MHz, CDCl$_3$) δ: 1.31 (s, 12H), 6.14 (d, *J* = 18.3 Hz, 1H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 18.3 Hz, 1H), 7.41 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ: 24.90, 83.61, 128.42, 128.98, 134.80, 136.14, 148.23.

*4.2.5. (E)-4,4,5,5-tetramethyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)styryl)-1,3,2-dioxaborolane (**3e**)*

Colorless solid; m.p. 210-211ºC; IR (neat) ν 2978, 1622, 961 cm^{-1};^{1}H NMR (500 MHz, CDCl$_3$) δ: 1.31 (s, 12H), 1.33 (s, 12H), 6.23 (d, *J* = 18.5 Hz, 1H), 7.40 (d, *J* = 18.5 Hz, 1H), 7.48 (d, *J* = 18.5 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.77 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ: 24.89, 24.94, 83.51, 83.94, 126.48, 135.19, 140.18, 149.56; HREIMS calcd. for $C_{20}H_{31}B_2O_4$ (M+H$^+$): 357.2408; found 357.2403.

*4.2.6. (E)-2-(2-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3f**)*[13]

Yellow oil; ^{1}H NMR (500 MHz, CDCl$_3$) δ: 1.31 (s, 12H), 6.24 (d, *J* = 18.0 Hz, 1H), 7.02 (dd, *J* = 1.2 and 8.3 Hz, 1H), 7.11 (dd, *J* = 0.8 and 7.5 Hz, 1H), 7.25 (m, 1H), 7.57 (dd, *J* = 1.8 and 7.5 Hz, 1H), 7.60 (d, *J* = 18.0 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ: 24.88, 83.57, 116 (d, *J* = 22.1 Hz), 124 (d, *J* = 3.6 Hz), 125 (d, *J* = 11.8 Hz), 127 (d, *J* = 3.3 Hz), 130 (d, *J* = 8.6 Hz), 141 (d, *J* = 4.1 Hz), 160 (d, *J* = 251 Hz).

*4.2.7. (E)-2-(2-([1,1'-biphenyl]-2-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3g**)*

Yellow oil; IR (neat) ν 3058, 2975, 1616 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ: 1.25 (s, 12H), 6.12 (d, *J* = 18.2 Hz, 1H), 7.31 (d, *J* = 4.5 Hz, 1H), 7.30-7.31 (m, 1H), 7.34-7.43 (m, 9H); ^{13}C NMR (125 MHz, CDCl$_3$) δ: 24.84, 83.34, 126.67, 127.28, 127.64, 128.22, 128.68, 130.13, 130.47, 136.20, 140.75, 141.66, 148.78; HREIMS calcd. for $C_{20}H_{24}BO_2$ (M+H$^+$): 307.1869; found 307.1871.

*4.2.8. (E)-4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)vinyl)-1,3,2-dioxaborolane (**3h**)*

Yellow oil; IR (neat) ν 3056, 2974, 1615 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ: 1.33 (s, 12H), 6.29 (d, *J* = 18.4 Hz, 1H), 7.45-7.48 (m, 2H), 7.57 (d, *J* = 18.4 Hz, 1H), 7.70 (dd, *J* = 8.9 Hz, *J* = 1.7 Hz, 1H), 7.79-7.84 (m, 4H); ^{13}C NMR (125 MHz, CDCl$_3$) δ: 24.92, 83.53, 123.57, 126.46, 126.58, 127.87, 128.21, 128.43, 128.60, 133.62, 133.91, 135.17, 149.71; HREIMS calcd. for $C_{18}H_{22}BO_2$ (M+H$^+$): 281.1712; found 281.1711.

*4.2.9. (E)-2-(2-(benzo[d][1,3]dioxol-5-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3i**)*[6]

Yellow solid; m.p. 77-78ºC; ^{1}H NMR (500 MHz, CDCl$_3$) δ: 1.30 (s, 12H), 5.95 (d, *J* = 18.5 Hz, 1H), 5.97 (s, 2H), 6.77 (d, *J* = 8.1 Hz, 1H), 6.94 (dd, *J* = 1.6 and 8.1 Hz, 1H), 7.03 (d, *J* = 1.6 Hz, 1H), 7.29 (d, *J* = 18.5 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ: 24.87, 83.40, 101.34, 106.01, 108.40, 122.83, 132.34, 148.26, 148.55, 149.20.

*4.2.10. (E)-4,4,5,5-tetramethyl-2-(2-(thiophen-3-yl)vinyl)-1,3,2-d-ioxaborolane (**3j**)* [12]

Yellow oil; ^{1}H NMR (500 MHz, CDCl$_3$) δ: 1.30 (s, 12H), 5.94 (d, *J* = 18.3 Hz, 1H), 7.27 (dd, *J* = 0.5 and 2.8 Hz, 1H), 7.29 (d, *J* = 1.3 Hz, 1H), 7.31 (dd, *J* = 1.4 and 2.8 Hz, 1H) 7.38 (d, *J* = 18.3 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ: 24.85, 83.40, 125.02, 125.16, 126.27, 141.37, 143.32.

*4.2.11. (E)-4,4,5,5-tetramethyl-2-(4-(oct-1-yn-1-yl)styryl)-1,3,2-dioxaborolane (**3m**)*

Yellow oil; IR (neat) ν 3289, 2976, 2105, 1620 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ: 0.90 (t, *J* = 7.4 Hz, 3H), 1.26-1.36 (m, 4H), 1.31 (s, 12H), 1.41-1.47 (s, 2H) 1.56-1.62 (m, 2H), 2.40 (t, *J* = 7.4 Hz, 3H), 6.14 (d, *J* = 18.5 Hz, 1H), 7.33-7.40 (m, 4H); 7.37 (d, *J* = 18.5 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ: 14.15, 19.59, 22.65, 24.89, 28.70, 28.78, 31.46, 80.69, 83.52, 92.06, 124.78, 127.04, 131.93, 136.69, 148.97; HREIMS calcd. for $C_{22}H_{32}BO_2$ (M+H$^+$): 339.2495; found 339.2495.

*4.2.12. (E)-4,4,5,5-tetramethyl-2-(4-(prop-1-en-2-yl)styryl)-1,3,2-dioxaborolane (**3n**)*

Yellow oil; IR (neat) ν 3084, 2975, 1602 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ: 1.31 (s, 12H), 2.15 (s, 3H), 5.09 (s, 1H), 5.41 (s, 1H), 6.16(d, *J* = 18.4 Hz, 1H), 7.39 (d, *J* = 18.4 Hz, 1H), 7.45 (s, 4H); ^{13}C NMR (125 MHz, CDCl$_3$) δ: 21.74, 24.89, 83.46, 112.95, 125.82, 127.14, 136.76, 136.76, 141.77, 149.23; HREIMS calcd. for $C_{17}H_{24}BO_2$ (M+H$^+$): 271.1869; found 271.1865.

*4.2.13. (E)-4-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-vinyl)phenyl)butanenitrile (**3o**)*

Colorless solid; m.p. 98-99ºC; IR (neat) ν 2984, 2945, 2249 1602 cm^{-1};^{1}H NMR (500 MHz, CDCl$_3$) δ: 1.31 (s, 12H), 2.14 (m, 2H), 2.09 (t, *J* = 7.1 Hz, 2H), 4.08 (t, *J* = 5.7 Hz, 2H), 6.02 (d, *J* = 18.4 Hz,1H), 6.85 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 18.4 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ: 14.22, 24.86, 25.48, 65.33, 83.30, 114.55, 119.20, 128.57, 130.95, 148.90, 159.06; HREIMS calcd. for $C_{18}H_{25}BNO_2$ (M+H$^+$): 298.1978; found 298.1979.

*4.2.14. Methyl (E)-4-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)butanoate (**3p**)*

Yellow solid; m.p. 66-67ºC; IR (neat) ν 2978, 1730, 1617, 1511, 1354, 1140, 996, 805 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ: 1.30 (s, 12H), 2.10 (pent, *J* = 7.0 Hz, 2H), 2.52 (t, *J* = 7.2 Hz, 2H), 3.68 (s, 3H), 4.01 (t, *J* = 6.1 Hz, 2H), 6.00 (d, *J* = 18.3 Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 2H), 7.33 (d, *J* = 18.4 Hz, 1H), 7.41 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ: 24.65, 24.88, 30.57, 51.69, 66.75, 83.27, 114.56, 128.53, 130.54, 149.12, 159.61, 173.66; HREIMS calcd. for $C_{19}H_{28}BO_4$ (M+H$^+$): 331.2080; found 331.2083.

*4.2.15. (E)-4,4,5,5-tetramethyl-2-(4-vinylstyryl)-1,3,2-dioxaborolane (**p-4**)*

Yellow oil; IR (neat) ν 2980, 1625 cm^{-1};^{1}H NMR (500 MHz, CDCl$_3$) δ: 1.31 (s, 12H), 5.26 (dd, *J* = 0.6 and 11.0 Hz, 1H), 5.77 (dd, *J* = 0.7 and 17.7 Hz, 1H), 6.16 (d, *J* = 18.4 Hz, 1H), 6.70 (dd, *J* = 10.9 and 17.7 Hz, 1H) , 7.37 (d, *J* = 18.4 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ: 24.90, 83.50, 114.46, 126.62, 127.47, 136.58, 137.17, 138.31, 149.20; HREIMS calcd. for $C_{16}H_{22}BO_2$ (M+H$^+$): 257.1712; found 257.1713.

*4.2.16. (E)-4,4,5,5-tetramethyl-2-(3-vinylstyryl)-1,3,2-dioxaborolane (**m-4**)*

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.31 (s, 12H), 5.26 (d, J = 11.0 Hz, 1H), 5.76 (d, J = 17.5 Hz, 1H), 6.19 (d, J = 18.5 Hz, 1H), 6.70 (dd, J = 11.0 and 17.5 Hz, 1H), 7.31 (d, J = 7.2 Hz, 1H), 7.34 (s, 1H), 7.36 (d, J = 18.5 Hz, 1H), 7.41 (d, J = 9.2 Hz, 1H), 7.52 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 24.90, 83.52, 114.35, 125.21, 126.59, 126.87, 128.93, 136.78, 137.90, 137.99, 149.52; HREIMS calcd. for $C_{16}H_{22}BO_2$ ($M+H^+$): 257.1712; found 257.1712.

*4.2.17. Biphenyl (**6**)*[14]

White solid; m.p. 123ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.12 (s, 2H), 7.27 (t, J = 7.4 Hz, 2H), 7.37 (t, J = 7.4 Hz, 4H), 7.53 (dd, J = 1.4 and 8.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 127.4, 128.5, 129.5, 138.22.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/j.tet.2017.03.074.

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