Borane-Catalysed Hydroboration of Alkynes and Alkenes

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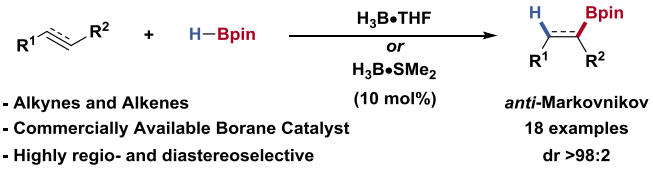

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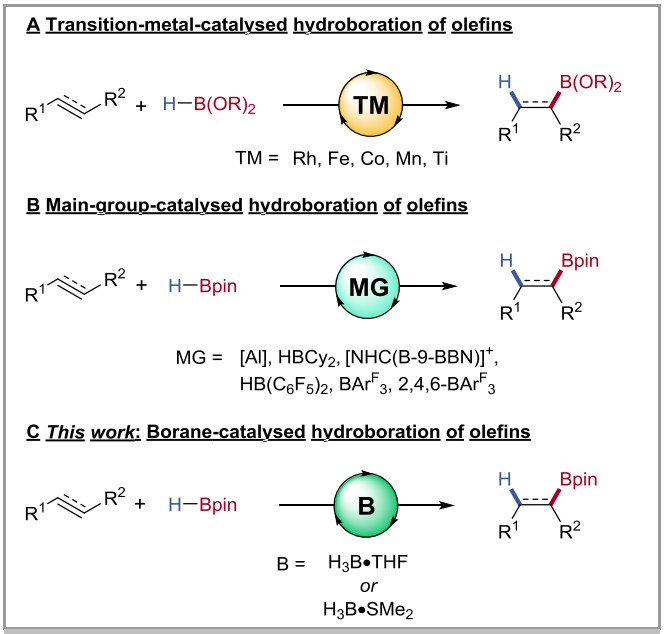
Abstract Simple, commercially available borane adducts, $H_3B•THF$ and $H_3B•SMe_2$, have been used to catalyse the hydroboration of alkynes and alkenes with pinacolborane to give the alkenyl- and alkyl boronic esters, respectively. Alkynes and terminal alkenes underwent highly regioselective hydroboration to give the linear boronic ester products. Good functional group tolerance was observed for substrates bearing ester, amine, ether and halide substituents. This catalytic process shows comparable reactivity to transition metal-catalysed hydroboration protocols.

Key words borane, hydroboration, alkynes, alkenes, main-group, catalysis

Boronic esters are powerful synthetic intermediates which have found widespread use and act as precursors for an array of transformations.[1,2] The hydroboration of alkynes and alkenes offers the simplest route to boronic esters, however, and unlike boranes, boronic esters do not readily undergo olefin hydroboration. Most commonly a 2nd- or 3rd-row transition metal catalyst is needed for the direct hydroboration of olefins with boronic esters.[3] However, the increasing need for sustainable chemical processes has led to a drive for 1st-row transition metal[4–7] (Scheme 1, A) and main-group catalyst alternatives (Scheme 1, B).[8-17] Although alkyne hydroboration has been achieved using boron-derived catalysts,[9-15] there is only a single report of a boron-catalysed alkene hydroboration.[12] Oestreich and co-workers used the highly Lewis acid tris(3-5-trifluoromethylphenyl)borane, BAr^F_3, to catalyse the direct addition of pinacol borane, HBpin, to alkenes.[12] Here the active catalyst was generated by ligand metathesis between BAr^F_3 and HBpin to generate a borane which underwent alkene hydroboration and another ligand metathesis with HBpin to give the product boronic ester and regenerate the borane catalyst. A catalytic role for boranes in olefin hydroboration has also been proposed in the titanium- and calcium-catalysed addition of catechol borane to alkynes.[18,19] However, and to the best of our knowledge, a simple borane has not used to catalyse the hydroboration of alkynes or alkenes. Herein we report the direct hydroboration of alkynes and alkenes with HBpin using either of the commercially available borane adducts, $H_3B•THF$ or $H_3B•SMe_2$, as the catalyst (Scheme 1, C).

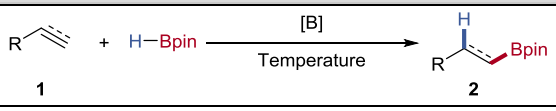


Scheme 1 (A) Transition-metal-catalysed hydroboration of olefins. (B) Main-group-catalysed hydroboration of olefins. (C) *This work*: borane-catalysed hydroboration of olefins.

Our investigations began by testing commercially available solutions of $H_3B•THF$ (1.0 M in THF) and $H_3B•SMe_2$ (ca. 10 M in SMe_2) for catalytic competency in the hydroboration of phenylacetylene and 4-*tert*-butylstyrene with HBpin (Table 1). Borane dimethyl sulphide showed low catalytic activity at room temperature (Table 1, Entry 1 and 4). Increasing the reaction temperature to 60 °C led to successful catalysis by both borane adducts in only 30 minutes for the hydroboration of phenylacetylene which gave the linear alkenyl boronic ester **2a** in good yield, regio- and diastereoselectivity (Entries 2 and 3).

Significantly, both borane adducts successfully catalysed the hydroboration of 4-*tert*-butylstyrene to give the alkyl boronic ester in good yield and regioselectivity (Entries 5 and 6). During the preparation of this manuscript Wu, Liu, Zhao and co-workers reported the hydroxide-catalysed hydroboration of olefins and proposed a catalytically active borohydride intermediate.[20] Thus, we trialled hydridic boron reagents as catalysts,[21,22] but decreased reactivity was observed in all cases (Entries 7-10). Importantly, in the absence of borane catalyst only trace hydroboration was observed for both the alkyne and alkene substrates (Entries 11-12).

Table 1 Catalyst identification[a]



1 2

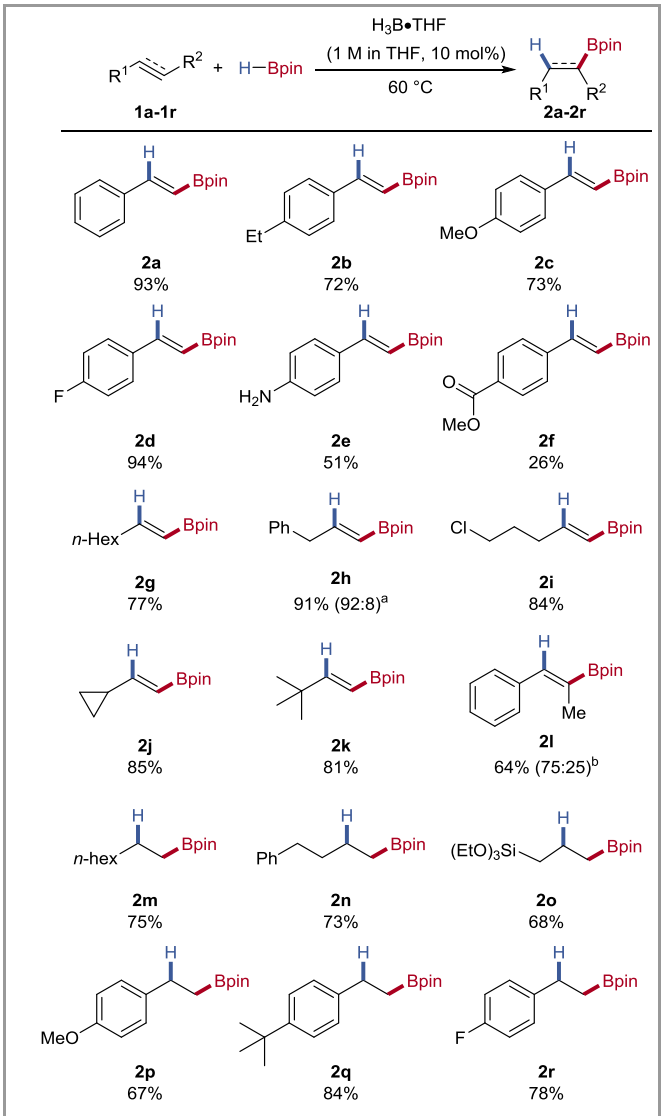
Entry	Cat (10 mol%)	Substrate	*T* (°C)	Yield (%)[b]
1	$H_3B•SMe_2$	Phenylacetylene	25	19[c]
2	$H_3B•THF$	Phenylacetylene	60	76
3	$H_3B•SMe_2$	Phenylacetylene	60	75
4	$H_3B•SMe_2$	4-*tert*-Butylstyrene	25	5[c]
5	$H_3B•THF$	4-*tert*-Butylstyrene	60	84
6	$H_3B•SMe_2$	4-*tert*-Butylstyrene	60	83
7	$NaHBEt_3$	Phenylacetylene	60	45
8	$Na(CH_3COO)_3BH$	Phenylacetylene	60	50
9	$NaHBEt_3$	4-*tert*-Butylstyrene	60	40
10	$Na(CH_3COO)_3BH$	4-*tert*-Butylstyrene	60	17
11	-	Phenylacetylene	60	-
12	-	4-*tert*-Butylstyrene	60	-

[a]Reaction conditions: olefin (1 equiv.), catalyst (10 mol%), pinacolborane (1.25 equiv.), *t* = 30 mins (alkyne) or 18 hours (alkene). [b]Yield was determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. [c]Reaction mixtures were stirred for 18 hours at 25 °C.

Using optimised reaction conditions[23] of $H_3B•THF$ (1.0 M in THF, 10 mol%) and HBpin (1.1 equivalents) at 60 °C in no additional solvent for 1 hour we investigated the substrate scope of this hydroboration (Scheme 2). Terminal alkynes underwent hydroboration to give the linear (*E*)-alkenyl boronic esters with excellent control of regioselectivity and diastereoselectivity (**2a-k**). Aryl substituted alkynes bearing electron-donating alkyl **2b** or ether **2c** groups and an electron-withdrawing fluoro-substituent **2d** all underwent successful hydroboration in good yield and without loss of regioselectivity. A free amine **2e** and even an ester substituent **2f** were tolerated without the observation of detrimental side reactions, albeit with decreased product yields, presumably by coordination and inhibition of the borane catalyst.

Alkyl substituted alkynes were also successful substrates in this hydroboration again giving the linear (*E*)-alkenyl boronic esters with excellent control of regioselectivity and diastereoselectivity (**2g-k**). Primary **2g-i**, secondary **2j** and tertiary **2k** alkyl substitution had little effect on catalyst activity and regioselectivity, with only the benzyl substituted alkyne **2h** showing a slight decrease in regiocontrol. Even an internal alkyne underwent hydroboration to give the (*Z*)-alkenyl boronic ester **2l** with moderate regioselectivity for addition of the boron group at the least sterically encumbered carbon.

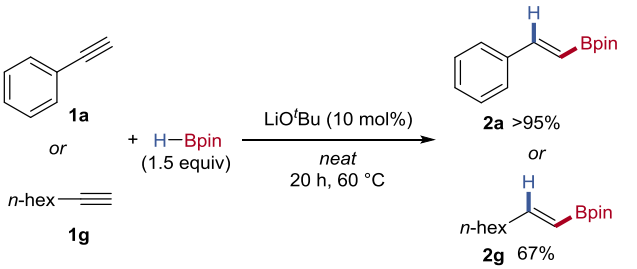
We next turned out attention to terminal alkenes (Scheme 2, **2m-r**). Although a longer reaction time (18 hours) was required for this substrate class compared to alkynes, alkyl- **2m-o** and aryl-substituted **2p-r** alkenes all successfully underwent hydroboration with complete control of the regioselectivity of addition to give the linear boronic esters. Once again, electron-donating **2p,q** and electron-withdrawing **2r** aryl substituents gave equal reactivity.



Scheme 2 Substrate scope for the $H_3B•THF$-catalysed hydroboration of alkynes and alkenes. Reaction conditions: Olefin (1 equiv.), $H_3B•THF$ (1.0 M in THF, 10 mol%), HBpin (1.1 equiv.) at 60 °C for 1 hour (alkynes) or 18 hours (alkenes). Yields are reported as isolated yield. Regio- and diastereoselectivity >98:2. [a]As a mixture of regioisomers (*E*/*Z* 92:8). [b]A mixture of regioisomers were obtained with (linear/branched 75:25).

Given that BH_3 was capable of catalysing the hydroboration of olefins, we questioned whether nucleophile promoted decomposition of HBpin[22,24] would facilitate this same olefin hydroboration reaction. Therefore we trialled using alkoxide salts as reagents to generate BH_3 *in situ*, from HBPin, that would subsequently undergo hydroboration with the present olefin. The use of LiO^tBu as an initiative catalyst in combination with HBpin and alkynes **1a** or **1g** at 60 °C successfully gave the alkyne hydroboration products **2a** and **2g** in excellent yields and with

complete control of diastereoselectivity and regioselectivity (>95% and 67%, Scheme 3).



Scheme 3 Use of an alkoxide salt as an initiative catalyst for alkyne hydroboration. Yields were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

In summary, we have developed a BH_3-catalysed hydroboration of alkynes and alkenes with pinacolborane to give alkenyl- and alkyl pinacol boronic esters in good yield and with excellent control of regio- and diastereoselectivity. Using commercially available borane adducts, H_3B•THF and H_3B•SMe_2, terminal alkynes and alkenes underwent the direct hydroboration with HBpin to give the boronic ester products in synthetically useful yield. Detailed mechanistic studies are ongoing and will be reported in due course.

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All manipulations were carried out under an argon atmosphere using Schlenk techniques or in an inert atmosphere glovebox. All reaction apparatus including flasks, if not otherwise specified, were evacuated, heated with a heatgun and purged with argon three times. Liquid reagents were added with septum and single use plastic syringes. These syringes were flushed prior to use. In addition, all glassware was cleaned in a base bath (KOH/^{i}PrOH) and acid (HCl (aq.)) bath; rinsed with acetone and dried in an oven at 180°C.

All the borane sources were commercially available and used without further purification. Solvents were dried over sodium/benzophenone and distilled under pure argon atmosphere. C_6D_6 and d_8-toluene were dried over potassium and distilled under argon atmosphere. NMR Spectra were recorded on Bruker PRO 500 MHz (^{1}H 500.2 MHz, ^{11}B 160.5 MHz, ^{13}C 125.8 MHz, ^{19}F NMR 471 MHz, ^{29}Si NMR 99 MHz) AVA 500 (^{1}H 500.1 MHz, ^{2}H 500.2 MHz, ^{13}C 125.8 MHz) or AVA 600 (^{1}H 600.8 MHz, ^{13}C 151.1 MHz) spectrometers. ^{1}H and ^{13}C were referenced to residual solvent signals ^{1}H NMR: δ (ppm) = 7.26 ($CDCl_3$), 7.15 (C_6D_6), 7.09 (toluene-d_8), 5.32 (CD_2Cl_2), 1.72 (THF-d_8), ^{13}C NMR: δ (ppm) = 53.84 (CD_2Cl_2), 67.21 (THF-d_8), 77.16 ($CDCl_3$), 128.06 (C_6D_6), 137.48 (toluene-d_8).

Flash Column Chromatography was performed on silica gel (Merck Kielselgel 60, 40-63 μm) and product spots were visualised by UV light at 254 nm or by oxidising with $KMnO_4$. Short columns were prepared using a Braun Injekt 10 mL syringe of diameter 0.6 inches with a Luer Lock.

Pinalcolborane **3** (HBpin) Cat N 010818 was purchased from Fluorochem.

All other reagents were purchased from Sigma-Aldrich, Alfa Aesar, Acros Organics, Tokyo Chemical Industries UK and Fluorochem, and were used without further purification. Specifically, the borane sources, H_3B•THF; H_3B•SMe_2; H-B-9-BBN; $NaBH_4$, $NaHBEt_3$ were obtained from Sigma-Aldrich and $Na(CH_3COO)_3BH$ was obtained from Acros Organics.

(*E*)-4,4,5,5-Tetramethyl-2-(phenyl-1-enyl)-1,3,2-dioxaborolane (2a)

General Procedure A

Phenylacetylene (1.00 mmol, 0.110 mL), pinacolborane (1.10 mmol, 0.160 mL) and H_3B•THF (0.100 mmol, 1M, 0.100 mL) were added sequentially to a sealed reaction vial flushed with an argon atmosphere. The reaction mixture was stirred for 1 hour at 60 °C. The reaction was then quenched by filtration through a short silica plug (5 cm) with CH_2Cl_2. The solvents were removed under reduced pressure and the residue purified by flash column chromatography (SiO_2; hexane/ethyl acetate 98:2), to give the boronic ester **2a** (215.1 mg, 0.93 mmol, 93%) as a colourless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 2H), 7.41 (d, *J* = 18.4 Hz, 1H), 7.36 – 7.27 (m, 3H), 6.18 (d, *J* = 18.4 Hz, 1H), 1.32 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 137.6, 129.0, 128.7, 127.2, 116.4 (br, *C-B*), 83.5, 25.0.

^{11}B NMR (160 MHz, $CDCl_3$) δ 29.87.

Procedure for alkoxide-initiated hydroboration of Alkynes

Phenylacetylene (1.00 mmol, 0.110 mL) or 1-octyne (1.00 mmol, 0.148 mL), pinacolborane (1.50 mmol, 0.218 mL) and LiO^{t}Bu (0.100 mmol, 8.00 mg) was added sequentially into a sealed reaction vial flushed with nitrogen. The reaction mixture was stirred for 20 hours at 60 °C. The reaction was cooled to room temperature. Et_2O (2.00 mL) and distilled H_2O (1.00 mL) was added and the organic layer was extracted. The yield was determined by adding 1,3,5-trimethoxybenzene (0.10 mmol, 16.8 mg) as internal standard.

(*E*)-4,4,5,5-Tetramethyl-2-(4-ethylphenyl-1-enyl)-1,3,2-dioxaborolane (2b)

According to general procedure A, 4-ethylphenylacetylene (1.00 mmol, 0.140 mL), pinacolborane (1.10 mmol, 0.160 mL), H_3B•THF (0.100 mmol, 1 M, 0.100 mL) were reacted for 1 hour. The residue was purified by flash column chromatography (SiO_2; hexane/ethyl acetate 98:2), to give the boronic ester **2b** (184.7 mg, 0.720 mmol, 72%) as a colourless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.41 (m, 2H), 7.39 (d, *J* = 18.2 Hz, 1H), 7.18 – 7.16 (m, 2H), 6.12 (d, *J* = 18.4 Hz, 1H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.32 (s, 12H), 1.23 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 145.4, 135.2, 128.2, 127.2, 115.4 (br *C-B*), 83.4, 28.8, 25.0, 15.5.

^{11}B NMR (160 MHz, $CDCl_3$) δ 29.93.

(*E*)-4,4,5,5-Tetramethyl-2-(4-methoxyphenyl-1-enyl)-1,3,2-dioxaborolane (2c)

According to general procedure A, 4-ethylnylanisole (1.00 mmol, 0.130 mL), pinacolborane (1.10 mmol, 0.160 mL), H_3B•THF (0.100 mmol, 1 M, 0.100 mL) were reacted for 1 hour. The residue was purified with flash column chromatography (SiO_2; hexane/ethyl acetate 98:2), to give the boronic ester **2c** (188.5 mg, 0.730 mmol, 73%) as a colourless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.41 (m, 2H), 7.39 (d, *J* = 18.2 Hz, 1H), 7.18 – 7.16 (m, 2H), 6.12 (d, *J* = 18.4 Hz, 1H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.32 (s, 12H), 1.23 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.64, 145.43, 135.20, 128.22, 127.24, 115.43 (br *C-B*) 83.41, 28.84, 24.97, 15.54.

^{11}B NMR (160 MHz, $CDCl_3$) δ 29.93.

(*E*)-4,4,5,5-Tetramethyl-2-(4-fluorophenyl-1-enyl)-1,3,2-dioxaborolane (2d)

According to general procedure A, 4-fluorophenylacetylene (1.00 mmol, 0.115 mL), pinacolborane (1.10 mmol, 0.160 mL), H_3B•THF (0.100 mmol, 1 M, 0.100 mL) were reacted for 1 hour. The residue was purified by flash column chromatography (SiO_2; hexane/ethyl acetate 98:2), to give the boronic ester **2d** (232.5 mg, 0.940 mmol, 94%) as colourless needles. Melting point (hexane/ethyl acetate) 63.5 - 65.3 °C, Lit. 62-63 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.42 (m, 2H), 7.35 (d, *J* = 18.4 Hz, 1H), 7.06 – 6.98 (m, 2H), 6.07 (d, *J* = 18.5 Hz, 1H), 1.31 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.3 (d, $J_{C\text{-}F}$ = 248.6 Hz), 148.3, 133.9 (d, *J* = 3.3 Hz), 128.9 (d, *J* = 8.4 Hz), 115.7 (d, *J* = 21.7 Hz), 83.5, 25.0.

^{11}B NMR (160 MHz, $CDCl_3$) δ 29.80.

^{19}F NMR (471 MHz, $CDCl_3$) δ -112.46 (m).

(*E*)-4,4,5,5-Tetramethyl-2-(4-aminophenyl-1-enyl)-1,3,2-dioxaborolane (2e)

According to general procedure A, 4-aminophenylacetylene (1.00 mmol, 0.117 g), pinacolborane (1.10 mmol, 0.160 mL), H_3B•THF (0.100 mmol, 1 M, 0.100 mL) were reacted for 1 hour. The residue was purified by flash

column chromatography (SiO_2; dichloromethane/methanol 99:1), to give the boronic ester **2e** (124.2 mg, 0.510 mmol, 51%) as yellow prisms.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 3H), 6.67 – 6.57 (m, 2H), 5.93 (d, *J* = 18.3 Hz, 1H), 3.78 (s, 2H), 1.30 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.7, 147.5, 128.7, 128.4, 115.0, 111.8 (br *C*-*B*), 83.2, 25.0.

^{11}B NMR (160 MHz, $CDCl_3$) δ 29.91.

Methyl 4-[(*E*)-2-(4,4,5,5-tetramethyl -2-yl)-ethenyl]benzoate-1,3,2-dioxaborolane (2f)

According to general procedure A, methyl 4-ethynylbenzoate (1.00 mmol, 0.160 g), pinacolborane (1.10 mmol, 0.160 mL), H_3B•THF (0.100 mmol, 1 M, 0.100 mL) were reacted for 1 hour. The residue was purified by flash column chromatography (SiO_2; hexane/ethyl acetate 98:2), to give the boronic ester **2f** (74.7 mg, 0.260 mmol, 26%) as an amorphous pale yellow powder. Melting point (hexane/ethyl acetate) 95.6 - 97.4 °C, Lit. 90-91 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 – 7.90 (m, 2H), 7.55 – 7.52 (m, 2H), 7.41 (d, *J* = 18.4 Hz, 1H), 6.27 (d, *J* = 18.4 Hz, 1H), 3.91 (s, 3H), 1.32 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 148.3, 141.9, 130.1, 129.7, 127.0, 119.5 (br *C*-*B*), 83.7, 52.3, 25.0.

^{11}B NMR (160 MHz, $CDCl_3$) δ 29.68.

(*E*)-4,4,5,5-Tetramethyl-2-(oct-1-enyl)-1,3,2-dioxaborolane (2g)

According to general procedure A, 1-octyne (1.00 mmol, 0.148 mL), pinacolborane (1.10 mmol, 0.160 mL), H_3B•THF (0.100 mmol, 1 M, 0.100 mL) were reacted for 1 hour. The residue was purified by flash column chromatography (SiO_2; hexane/ethyl acetate 98:2), to give the boronic ester **2g** (183.3 mg, 0.770 mmol, 77%) as a colourless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.63 (dt, *J* = 17.9, 6.4 Hz, 1H), 5.42 (dt, *J* = 18.0, 1.6 Hz, 1H), 2.14 (td, *J* = 7.9, 1.6 Hz, 2H), 1.46 – 1.36 (m, 3H), 1.33 – 1.20 (m, 14H), 0.91 – 0.85 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.0, 118.8 (br *C*-*B*), 83.1, 36.0, 31.9, 29.1, 28.4, 24.9, 22.7, 14.2.

^{11}B NMR (160 MHz, $CDCl_3$) δ 29.69.

(*E*)-4,4,5,5-Tetramethyl-2-(3-phenylpropy-1-enyl)-1,3,2-dioxaborolane (2h)

According to general procedure A, 3-phenyl-1-propyne (1.00 mmol, 0.124 mL), pinacolborane (1.10 mmol, 0.160 mL), H_3B•THF (0.100 mmol, 1 M, 0.100 mL) were reacted for 1 hour. The residue was purified with flash column chromatography (SiO_2;hexane/ethyl acetate 98:2), to give the boronic ester **2h** [223.2 mg, 0.910 mmol, 91% (92^a+8^b)] as a colourless oil. The product was isolated as a mixture of regioisomers (*a*+*b*).

^{1}H NMR of major isomer (500 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.24 – 7.16 (m, 3H), 6.79 (dt, *J* = 17.9, 6.3 Hz, 1H), 5.47 (d, *J* = 17.9, 1H), 3.50 (d, *J* = 6.4, 2H), 1.27 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.6, 139.2, 129.1, 128.6, 126.3, 120.0 (br *C*-*B*), 83.2, 42.4, 24.9.

^{11}B NMR (160 MHz, $CDCl_3$) δ 29.49.

(*E*)-4,4,5,5-Tetramethyl-2-(5-chloropent-1-enyl)-1,3,2-dioxaborolane (2i)

According to general procedure A, 5-chloro-1-pentyne (1.00 mmol, 0.106 mL), pinacolborane (1.10 mmol, 0.160 mL), H_3B•THF (0.100 mmol, 1 M, 0.100 mL) were reacted for 1 hour. The residue was purified by flash column chromatography (SiO_2; hexane/ethyl acetate 98:2), to give the boronic ester **2i** (193.3 mg, 0.840 mmol, 84%) as a colourless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.58 (dt, *J* = 18.0, 6.4 Hz, 1H), 5.48 (dt, *J* = 18.0, 1.6 Hz, 1H), 3.53 (t, *J* = 6.7 Hz, 2H), 2.33 – 2.27 (m, 2H), 1.93 – 1.86 (m, 2H), 1.26 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.2, 120.2 (br *C*-*B*), 83.3, 44.5, 32.9, 31.2, 24.9.

^{11}B NMR (160 MHz, $CDCl_3$) δ 29.39.

(*E*)-4,4,5,5-Tetramethyl-2-(cyclopropyl-1-enyl)-1,3,2-dioxaborolane (2j)

According to general procedure A, cyclopropylacetylene (1.00 mmol, 0.085 mL), pinacolborane (1.10 mmol, 0.160 mL), H_3B•THF (0.100 mmol, 1 M, 0.100 mL) were reacted for 1 hour. The residue was purified by flash column chromatography (SiO_2; hexane/ethyl acetate 98:2), to give the boronic ester **2j** (164.3 mg, 0.850 mmol, 85%) as a colourless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.09 (ddd, *J* = 17.8, 9.3, 1.1 Hz, 1H), 5.50 (d, *J* = 17.8, 1H), 1.58 – 1.49 (m, 1H), 1.27 (s, 12H), 0.84 – 0.79 (m, 2H), 0.57 – 0.52 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.7, 115.4 (br *C*-*B*), 83.1, 25.0, 17.1, 8.0.

^{11}B NMR (160 MHz, $CDCl_3$) δ 29.51.

(*E*)-4,4,5,5-Tetramethyl-2-(3,3-dimethyl-but-1-enyl)-1,3,2-dioxaborolane (2k)

According to general procedure A, 3,3-dimethyl-1-butyne (1.00 mmol, 0.122 mL), pinacolborane (1.10 mmol, 0.160 mL), H_3B•THF (0.100 mmol, 1 M, 0.100 mL) were reacted for 1 hour. The residue was purified by flash column chromatography (SiO_2; hexane/ethyl acetate 98:2), to give the boronic ester **2k** (170.5 mg, 0.810 mmol, 81%) as a viscous colourless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.64 (d, *J* = 18.3 Hz, 1H), 5.35 (d, *J* = 18.3 Hz, 1H), 1.27 (s, 12H), 1.02 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.6, 112.5 (br *C*-*B*), 83.1, 35.2, 29.0, 25.0.

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.23.

(*Z*)-4,4,5,5-Tetramethyl-2-(1-phenyl(prop-1-en)-2-yl)-1,3,2-dioxaborolane (2l)

According to general procedure A, 1-phenyl-1-propyne (1.00 mmol, 0.125 mL), pinacolborane (1.10 mmol, 0.160 mL), H_3B•THF (0.100 mmol, 1 M, 0.100 mL) were reacted for 1 hour. The residue was purified by flash column chromatography (SiO_2; hexane/ethyl acetate 98:2), to give the boronic ester **2l** (156.2 mg, 0.640 mmol, 64% (75^a+25^b)) as a colourless oil. The product was isolated as a mixture of regioisomers (*a*+*b*).

^{1}H NMR of major isomer (500 MHz, $CDCl_3$) δ 7.41 – 7.30 (m, 4H), 7.27 – 7.14 (m, 2H), 2.00 (d, *J* = 1.7 Hz, 3H), 1.77 (m, 3H), 1.32 (s, 12H), 1.27 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.8, 142.5, 140.0, 138.1, 129.5, 129.2, 128.2, 127.9, 127.2, 126.0, 83.7, 25.0, 24.9, 16.1, 16.0.

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.23.

4,4,5,5-Tetramethyl-2-(octyl)-1,3,2-dioxaborolane (2m)

According to general procedure A, 1-octene (1.00 mmol, 0.157 mL), pinacolborane (1.10 mmol, 0.160 mL), H_3B•THF (0.100 mmol, 1 M, 0.100 mL) were reacted for 18 hours. The residue was purified by flash column chromatography (SiO_2;hexane/ethyl acetate 98:2), to give the boronic ester **2m** (180.2 mg, 0.750 mmol, 75%) as a colourless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.45 – 1.38 (m, 2H), 1.32 – 1.25 (m, 10H), 1.24 (s, 12H), 0.87 (t, *J* = 6.9 Hz, 3H), 0.76 (t, *J* = 7.8 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 83.0, 32.6, 32.1, 29.5, 29.4, 25.0, 24.2, 22.8, 14.3, 11.1 (br *C*-*B*).

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.96.

4,4,5,5-Tetramethyl-2-(4-phenyl-1-butyl)-1,3,2-dioxaborolane (2n)

According to general procedure A, 4-phenyl-1-butene (1.00 mmol, 0.150 mL), pinacolborane (1.10 mmol, 0.160 mL), H_3B•THF (0.100 mmol, 1 M, 0.100 mL) were reacted for 18 hours. The residue was purified by flash column chromatography (SiO_2; hexane/ethyl acetate 98:2), to give the boronic ester **2n** (188.7 mg, 0.730 mmol, 73%) as a colourless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 2H), 7.20 – 7.14 (m, 3H), 2.63 – 2.58 (m, 2H), 1.68 – 1.59 (m, 2H), 1.53 – 1.44 (m, 2H), 1.25 (s, 12H), 0.82 (t, *J* = 7.8 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.1, 128.5, 128.3, 125.6, 83.0, 35.9, 34.3, 25.0, 23.9, 11.3 (br *C*-*B*).

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.94.

4,4,5,5-Tetramethyl-2-(3-(triethoxysilyl)-propyl)-1,3,2-dioxaborolane (2o)

According to general procedure A, allyltriethoxysilane (1.00 mmol, 0.226 mL), pinacolborane (1.10 mmol, 0.160 mL), H_3B•THF (0.100 mmol, 1 M, 0.100 mL) were reacted for 18 hours. The residue was purified by flash column chromatography (SiO_2; hexane/ethyl acetate 98:2), to give the boronic ester **2o** (215.2 mg, 0.680 mmol, 68%) as a colourless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.80 (q, *J* = 7.0 Hz, 6H), 1.59 – 1.50 (m, 2H), 1.24 – 1.19 (m, 21H), 0.85 (t, *J* = 7.6 Hz, 2H), 0.70 – 0.64 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 83.0, 58.4, 25.0, 18.4, 17.6, 15.3 (br *C*-*B*), 13.5.

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.83.

^{29}Si NMR (99 MHz, $CDCl_3$) δ -45.02.

4,4,5,5-Tetramethyl-2-(4-methoxyphenyl-1-ethyl)-1,3,2-dioxaborolane (2p)

According to general procedure A, 4-methoxystyrene (1.00 mmol, 0.133 mL), pinacolborane (1.10 mmol, 0.160 mL), H_3B•THF (0.100 mmol, 1 M, 0.100 mL) were reacted for 18 hours. The residue was purified by flash column chromatography (SiO_2; hexane/ethyl acetate 98:2), to give the boronic ester **2p** (175.3 mg, 0.670 mmol, 67%) as a colourless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 – 7.10 (m, 2H), 6.84 – 6.77 (m, 2H), 3.78 (s, 3H), 2.73 – 2.66 (m, 2H), 1.22 (s, 12H), 1.15 – 1.08 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.7, 136.7, 129.0, 113.7, 83.2, 55.4, 29.2, 25.0, 13.3 (br *C*-*B*).

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.64.

4,4,5,5-Tetramethyl-2-(4-tert-Butylphenyl-1-ethyl)-1,3,2-dioxaborolane (2q)

According to general procedure A, 4-*tert*-butyl-styrene (1.00 mmol, 0.183 mL), pinacolborane (1.10 mmol, 0.160 mL), H_3B•THF (0.100 mmol, 1 M, 0.100 mL) were reacted for 18 hours. The residue was purified by flash column chromatography (SiO_2; hexane/ethyl acetate 98:2), to give the boronic ester **2q** (195.3 mg, 0.840 mmol, 84%) as a colourless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 2H), 7.17 – 7.13 (m, 2H), 2.76 – 2.67 (m, 2H), 1.30 (s, 9H), 1.22 (s, 12H), 1.17 – 1.11 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.4, 141.5, 127.8, 125.2, 83.2, 34.5, 31.6, 29.5, 25.0, 13.1 (br *C*-*B*).

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.66.

4,4,5,5-Tetramethyl-2-(4-fluorophenyl-1-ethyl)-1,3,2-dioxaborolane (2r)

According to general procedure A, 4-fluorostyrene (1.00 mmol, 0.119 mL), pinacolborane (1.10 mmol, 0.160 mL), H_3B•THF (0.100 mmol, 1 M, 0.100 mL) were reacted for 18 hours. The residue was purified by flash column chromatography (SiO_2; hexane/ethyl acetate 98:2), to give the boronic ester **2r** (193.7 mg, 0.780 mmol, 78%) as a colourless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 – 7.11 (m, 2H), 6.99 – 6.87 (m, 2H), 2.72 (t, *J* = 8.1 Hz, 2H), 1.21 (s, 12H), 1.15 – 1.09 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.2 (d, $J_{C\text{-}F}$ = 242.5 Hz), 140.1 (d, *J* = 3.1 Hz), 129.5 (d, *J* = 7.6 Hz), 115.0 (d, *J* = 21.0 Hz), 83.3, 29.3, 25.0, 13.34 (br *C*-*B*).

^{11}B NMR (160 MHz, $CDCl_3$) δ 33.48.

^{19}F NMR (471 MHz, $CDCl_3$) δ -118.43 (tt, *J* = 9.5, 4.0 Hz).

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Supporting Information

YES (this text will be updated with links prior to publication)

Primary Data

NO (this text will be deleted prior to publication)

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