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Hydroboration and Diboration of Internal Alkynes Catalyzed by a Well-Defined Low-Valent Cobalt Catalyst

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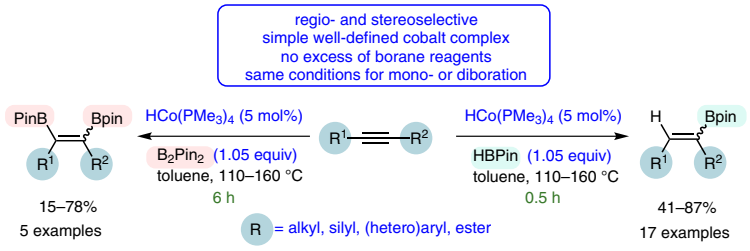
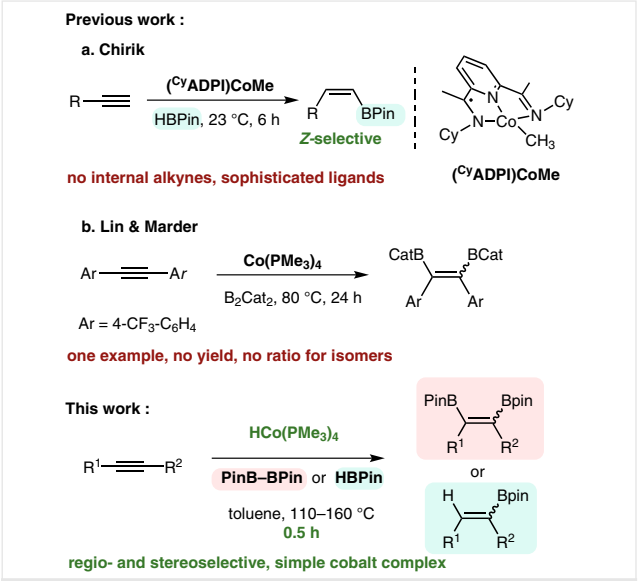
Abstract The use of a simple well-defined low-valent cobalt(I) catalyst [$HCo(PMe_3)_4$] capable of performing the regio- and stereoselective hydroboration of internal alkynes is reported. Extension to the diboration of internal alkynes is also related using the same reaction conditions.

Key words cobalt, hydroboration, diboration, regioselectivity, low-valent



Transition-metal-catalyzed hydroboration and diboration of alkynes represent one of the most straightforward methods to obtain valuable alkenyl organoboron compounds.[1] There have been several reports on group 10-catalyzed hydroboration and diboration of alkynes using expensive metals such as Pd and Pt.[2] Over the last decades reports on copper-catalyzed borylation of alkynes had seen an exponential increase. Significant levels of control in both the stereo- and regioselectivity have been obtained, however, this often requires the use of expensive ligands such as N-heterocycle carbenes.[3] In comparison, catalysis using other earth abundant metals such as Fe[4] and Co remains rare. Chirik has reported the stereo- and regioselective hydroboration of terminal alkynes using a cobalt complex bearing a functionalized, non-innocent, bis(imino)pyridine ligand (Scheme 1, a).[5,6] In 2006, Lin and Marder studied the reactivity of cobalt boryl complexes, and reported the only example of cobalt-catalyzed diboration of alkynes, however, no yield was reported (Scheme 1, b).[7]

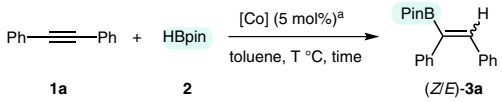
Our group has been interested in the application of two well-defined simple low-valent cobalt complexes, $HCo(PMe_3)_4$ and $Co(PMe_3)_4$ toward cycloaddition[8] and C–H functionalization.[9] Recently, we reported that $HCo(PMe_3)_4$ was an efficient catalyst for the highly regio- and stereoselective hydrosilylation of unsymmetrical alkynes through a hydrocobaltation mechanism.[10] Herein we report, the diboration and hydroboration of internal alkynes using a well-defined cobalt catalyst. The present study is notable for a number of features: (i) good to high regio- and stereoselectivities have been obtained for unsymmetrical alkynes, (ii) regioselectivities are opposite compare to our previously reported hydrosilylation reaction, (iii) diboration is accessible using the same catalyst and reaction conditions, and (iv) the catalyst is inexpensive and can be synthesized in one step on gram scale.



Scheme 1 Cobalt-catalyzed hydroboration of alkynes

To begin this study, the ability of complexes $Co(PMe_3)_4$ and $HCo(PMe_3)_4$ to perform the hydroboration of diphenylacetylene (**1a**) in the presence of HBpin (pinacolborane) was first examined. The results are shown in Table 1. Both complexes are capable of catalyzing the reaction with a loading of 5 mol% in the presence of a slight excess of HBpin (1.05 equiv). The reaction can be performed either at 110 °C in 18 hours (Table 1, entries 1 and 2) or at 160 °C in 30 minutes (entries 3 and 4) to give the desired alkenyl borane in good yields. Blank reactions without catalyst in thermal conditions (entry 5) or in the presence of 20 mol% of PMe_3 (entry 6) were carried out in order to show the necessity of the cobalt catalyst. Based on our previous studies the use of microwave conditions was also explored, but no significant increases in the yield were observed (entries 7 and 8). Due to its easy synthesis and its usefulness in mechanism interpretation $HCo(PMe_3)_4$ was chosen as catalyst for the following study.

Table 1 Optimization of the Hydroboration Reaction



1a **2** (*Z*/*E*)-**3a**

Entry	[Co]	Temp (°C)	Time (h)	Yield (%)[b] *Z*/*E*[c]
1	$HCo(PMe_3)_4$	110	18	78
2	$Co(PMe_3)_4$	110	18	87
3	$HCo(PMe_3)_4$	160	0.5	85
4	$Co(PMe_3)_4$	160	0.5	78
5	–	160	0.5	n.r.
6	PMe_3 (20 mol%)	160	0.5	n.r.
7	$HCo(PMe_3)_4$	160 (MW)[d]	0.5	85
8	$Co(PMe_3)_4$	160 (MW)[d]	0.5	82

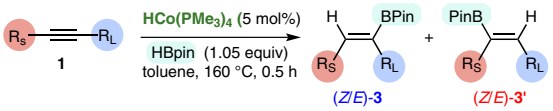
[a] Diphenylacetylene (0.5 mmol), HBPin (1.05 equiv, 0.52 mmol).
[b] Isolated yields; n.r. = no reaction.
[c] *Z*/*E* ratio determined by ^{1}H NMR analysis was always around 85:15.
[d] MW = microwave.

Our attention was then turned to the more challenging hydroboration of unsymmetrical internal alkynes (Table 2). These alkynes were substituted by functional groups with different degrees of steric hindrance, described as $\mathbf{R_S}$ (smaller group) and $\mathbf{R_L}$ (larger group). Using less reactive alkynes such as alkyne **1b** the desired product was not obtained at 110 °C. Thus, the optimal reaction conditions were established at 160 °C for 0.5 hour in toluene to give 55% yield of the alkenyl borane **3b** (Table 2, entry 1). Products from the hydroboration of 1-arylhex-1-ynes were isolated in 46% and 73% yield, respectively, for the 4-MeO- and 4-F_3C-substituted aryls (entries 2 and 3). The *syn*-adducts **3c** and **3d** (product of type **3** with the boron atom positioned close to the larger substituent) are the major isomers. Variation of the electronics on the phenyl moiety seems to have an effect on the yield, but only a slight effect on the regioselectivity, which was observed to be lower in the presence of an electron-withdrawing group (entries 2 and 3). Next, the reactivity of TMS-protected alkynes **1e–k** was examined. Previous reports on the hydroboration of similar alkynes indicated that both regioisomers **3** and **3′** could be selectively obtained. Under our reaction conditions, the hydroboration of TMS-protected arylacetylenes **1e–i** (entries 4–8) led in good yields and complete regioselectivity toward the adduct of type **3**, that is, with the boron atom close to the larger group. The catalytic system also allowed the use of heteroatoms with TMS-protected pyridylalkynes **1j** and **1k**, providing only the products of type **3** in moderate to good yields (entries 9 and 10). Surprisingly, compound **3j** and **3k** have the opposite stereochemistry, with the *cis*- or *Z*-isomer for the 3-pyridyl group and the *trans*- or *E*-isomer for the 2-pyridyl group. The position of the nitrogen in the newly-formed alkenyl boronate **3k** would be favorable for a chelation of the cobalt complex that could catalyze a post-isomerization pathway. The reaction of non-sterically differentiated unsymmetrical alkynes but bearing electronically distinct substituents (**1l** and **1m**) gave, respectively, a 57:43 and 40:60 mixtures of vinylboranes of type **3** and **3′** (entries 11–12). These latter results imply that the regio- and stereocontrol of the reaction are predominantly governed by steric factors of the starting substrates, while electronic factors have no significant effect on the outcome of the reaction. On the other hand, adding two methyl groups in the *ortho*-position on a phenyl ring generates a steric bulk on one side of the alkyne, which counter intuitively directs the addition of the boron atom to the sterically hindered carbon to give product **3n** (entry 13). This result suggests that the mechanism is not going through a hydrocobaltation pathway that should give obviously the other regioisomer. Finally, the use of ester-substituted substrates **1o**, **1p**, and **1q** in the hydroboration with HBpin yields solely the product of type **3**, presumably due to the chelating effect of the ester, which appears to overcome the steric control (entries 14–16).[11] Previous reports have shown that phosphines can be used as organocatalysts for the silaboration or diboration of alkynoates.[12] In order to establish if the phosphine presumably liberated from our complex was the catalyst of the non-described hydroboration of alkynoates, the reactions were reproduced without cobalt using 20 mol% of trimethylphosphine as potential organocatalyst. For **1o** the yield, the regio- and stereoselectivities are identical suggesting that the cobalt catalyst is not involved in this special case. However, for the two other alkynoates **1p** and **1q**, $HCo(PMe_3)_4$ allows better reactivity with an increase of the yields.

It is worth noting that the regioselectivity observed in the hydroboration reaction is opposite to the one we previously reported for the hydrosilylation using the exact same reaction conditions (catalyst, temperature, and solvent).

This in combination with the result observed from entry 13 in Table 2 strongly suggests that the mechanism is different and does not involve a hydrocobaltation pathway.[13]

Table 2 Hydroboration of Unsymmetrical Alkynes



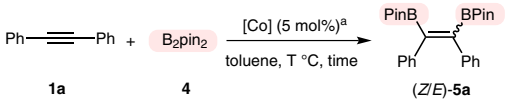
Entry	1	R_S	R_L	Yield (%)[a]	(Z/E)-3/(Z/E)-3'[b]
1	**1b**	*n*-Pr	*n*-Pr	55	100 (*Z*):0
2	**1c**	4-MeOC$_6$H$_4$	*n*-Bu	46	85 (*Z*):15 (*Z*)
3	**1d**	4-F$_3$CC$_6$H$_4$	*n*-Bu	73	65 (*Z*):35 (*Z*)
4[c]	**1e**	Ph	TMS	71	100 (*Z*):0[d]
5	**1f**	4-MeOC$_6$H$_4$	TMS	57	100 (*Z*):0[d]
6	**1g**	4-F$_3$CC$_6$H$_4$	TMS	85	100 (*Z*):0
7	**1h**	3,5-(MeO)$_2$C$_6$H$_3$	TMS	66	100 (*Z*):0
8	**1i**	6-methoxynaphthyl	TMS	75	100 (*Z*):0
9	**1j**	3-pyridyl	TMS	41	100 (*Z*):0
10	**1k**	2-pyridyl	TMS	68	100 (*E*):0
11	**1l**	Ph	4-F$_3$CC$_6$H$_4$	58	57 (*Z*):43
12	**1m**	Ph	4-MeOC$_6$H$_4$	68	40:60 (*Z*)
13	**1n**	Ph	2,4,6-Me$_3$C$_6$H$_2$	69	87 (*Z*):13
14[e]	**1o**	CO_2Me	*n*-Bu	63	100 (38/62):0
15[f]	**1p**	CO_2Et	TMS	61	100 (*E*):0
16[g]	**1q**	CO_2Et	Ph	47	100 (*E*)/0

[a] Isolated yields.
[b] Regio- and stereoselectivities were determined by ^{1}H and NOESY NMR analyses (see SI).
[c] Blank reaction without catalyst gives no conversion.
[d] Stereochemistry of **1e** and **1f** was confirmed after protodesilylation to produce **6e** and **6f**.
[e] Reaction with 20% of PMe$_3$ as catalyst gives the same yield and ratio.
[f] Reaction with 20% of PMe$_3$ as catalyst gives only traces of the desired compound.
[g] Reaction with 20% of PMe$_3$ as catalyst gives a lower yield of 30%.

We next decided to study the diboration of alkynes as initiated by Lin and Marder using Co(PMe$_3$)$_4$.[7b] Indeed, although diboration is well described using expensive metal (Pt or Pd),[14] this process using more accessible metals such as Cu,[15] Fe[16] and Co[7b] remains sparse with only one example for each metal.

We first screened the reaction conditions using both catalysts with different temperatures and reaction times (Table 3). It appears that HCo(PMe$_3$)$_4$ was the most efficient in the diboration process compared to Co(PMe$_3$)$_4$ (Table 3, entries 1, 3 vs entries 2, 4). It is important to note that the diboration process is slower than the hydroboration and a time of 6 hours at 160 °C is necessary to reach decent yields (entry 5). The reaction does not provide the desired compound without catalyst (entry 6). Finally, using trimethylphosphine as organocatalyst, no conversion occurred (entry 7).

Table 3 Optimization of the Diboration Reaction

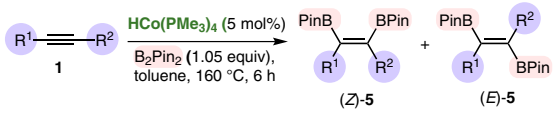


Entry	[Co] or catalyst	Temp (°C)	Time (h)	Yield (%)[b,c]
1	HCo(PMe$_3$)$_4$	110	18	50
2	Co(PMe$_3$)$_4$	110	18	37
3	HCo(PMe$_3$)$_4$	160	0.5	30
4	Co(PMe$_3$)$_4$	160	0.5	31
5	HCo(PMe$_3$)$_4$	160	6	52
6	–	160	6	n.r.
7	PMe$_3$	160	6	n.r.

[a] Diphenylacetylene (0.5 mmol), B$_2$Pin$_2$ (1.05 equiv, 0.52 mmol).
[b] Isolated yields; n.r. = no reaction.
[c] *Z*/*E* ratio was not determined in the optimization study.

Next our attention turned to the diboration of various alkynes and we studied the *Z*/*E* ratio of the alkenyl diborane compounds **5** (Table 4). Symmetrical alkyne **1a** and unsymmetrical alkynes **1e** and **1g** gave the desired compounds **5a**, **5e**, and **5g** in moderate to good yields with a stereoselectivity around 70:30 in favor of the *syn* addition of the diboron moiety (Table 4, entries 1–3). For alkynes **1c** and **1d** bearing an alkyl group, yields decreased to 29% and 15% and only *Z*-isomers are isolated (entries 4 and 5). Alkyne **1b** did not deliver the desired product under our reaction conditions, rather complete degradation of the starting material was observed. Generally, when alkynes are less reactive, due to the high temperature and the longer reaction times neces-

Table 4 Diboration of Internal Alkynes



Entry	Alkyne	R^1	R^2	Yield (%)[a]	5 (*Z*)/5 (*E*)[b]
1	**1a**	Ph	Ph	52	75:25
2	**1e**	Ph	TMS	70	65:35
3	**1g**	4-CF$_3$C$_6$H$_4$	TMS	58	68:32
4	**1c**	4-MeOC$_6$H$_4$	*n*-Bu	29	100:0
5	**1d**	4-CF$_3$C$_6$H$_4$	*n*-Bu	15	100:0
6	**1b**	*n*-Pr	*n*-Pr	n.r.	–

[a] Isolated yields; n.r. = no reaction.
[b] *Z*/*E* ratio determined by ^{1}H NMR analysis.

sary for the diboration reaction, degradation of the alkynes is observed and lower yields are obtained. The moderate selectivity observed above is disappointing, due to the fact that *trans*-diborylations are rare in the literature and often reported as traces.[17] In order to establish, if the *trans*-isomers were obtained during the process or via post-isomerization, compound (*Z*)-**5a** was reintroduced in the reaction conditions, in the presence and absence of $HCo(PMe_3)_4$ and B_2Pin_2. In both cases, no traces of (*E*)-**5a** were observed suggesting that the *trans*-isomer was obtained during the diboration pathway.

In summary, we have demonstrated that a simple well-defined low valent cobalt species $HCo(PMe_3)_4$ is an efficient catalyst to access a wide variety of synthetically useful vinyl boranes. We have reported the regio- and stereoselective hydroboration of a variety of internal alkynes, and also successfully managed to extend this methodology to the diboration of internal alkynes. The observed regioselectivity seems to suggest the reaction does not proceed via a hydrocobaltation pathway as we previously reported for the hydrosilylation of alkynes using the same catalytic system. This curiosity will be further explored in our future studies with a full mechanistic investigation.

Unless otherwise mentioned, all reactions were carried out in oven-dried glassware under argon atmosphere with magnetic stirring, and all commercially available compounds were used as received. Toluene was purified by mean of distillation under dry nitrogen atmosphere on sodium benzophenone ketyl and degassed by sparging argon. Chromatographic purification of products were accomplished using force-flow chromatography on neutral Davisil 60 Å (40–63 µm; pH 7.3) silica gel according to the method of Still.[18] TLC was performed on Merck 60 F254 silica gel plates. TLC visualization was performed by fluorescence quenching (λ = 254 nm), dipping in $KMnO_4$, or *p*-anisaldehyde stains. Filtration through Celite were performed using Hyflo Super Cel from Fluka. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. ^{1}H NMR spectra were recorded on a Bruker 400 Avance or 300 Avance (400 and 300 MHz, respectively) and are referenced relative to residual $CDCl_3$ protons signals at δ 7.26 ppm. ^{13}C NMR spectra were recorded on a Bruker 400 Avance or 300 Avance (100 and 75 MHz respectively) and are referenced relative to $CDCl_3$ at δ = 77.16. ^{11}B and ^{19}F NMR spectra were recorded on a Bruker 400 Avance (400 MHz) using pinacolborane (δ = 28.1) and trifluorotoluene (δ = –63.7), respectively, as external reference. Data are reported as follows: chemical shift (δ ppm), multiplicity (standard abbreviations), coupling constant (*J*, Hz), and integration. IR spectra were recorded on a Bruker Tensor 27 (ATR diamond) and are reported in terms of frequency of absorption (cm^{-1}). Melting points were measured on a Kofler bench. High-resolution mass spectrometry (HRMS) analyses were performed at the IPCM on a Bruker MicroTof mass spectrometer.

The preparation and full characterization of compounds **1c–q** were reported previously.[10]

Hydroboration of Alkynes with Pinacolborane; General Procedure A

In a glove box, a microwave reaction vial (0.5–2 mL) was charged with $HCo(PMe_3)_4$ (18.2 mg, 0.05 mmol, 5 mol%) and then sealed. Next, a degassed mixture of the corresponding alkyne (1.00 mmol, 1 equiv) and pinacolborane (97%, 157 µL 1.05 mmol, 1.05 equiv) in toluene (1 mL) was added via syringe. The reaction mixture was heated in an oil bath at 160 °C for 30 min. The mixture was diluted with petroleum ether (2 mL), filtered through a plug of silica gel, and washed with Et_2O (3 × 10 mL). The crude product was purified by silica gel chromatography (mixtures of pentane/Et_2O as eluents) to afford the final products.

Diboration of Alkynes with Bis(pinacolato)diboron; General Procedure B

In a glove boxe, a microwave reaction vial (0.5–2 mL) was charged with $HCo(PMe_3)_4$ (18.2 mg, 0.05 mmol, 5 mol%) and then sealed. Next, a degassed mixture of the corresponding alkyne (1.00 mmol, 1 equiv) and bis(pinacolato)diboron (97%, 266.6 mg, 1.05 mmol, 1.05 equiv) in toluene (1 mL) was added via syringe. The reaction was heated in an oil bath at 160 °C for 6 h. The reaction mixture was diluted with petroleum ether (2 mL), filtered through a plug of silica gel and washed with Et_2O (3 × 10 ml). The crude product was purified by silica gel chromatography (mixtures of pentane/Et_2O as eluents) to afford the final products.

(*Z*)-2-(1,2-Diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3a)[19]

The general procedure A was applied to diphenylacetylene (**1a**; 180.0 mg, 1.00 mmol, 1 equiv) and the reaction mixture was heated in an oil bath at 160 °C for 30 min. Purification by silica gel flash chromatography (pentane/Et_2O 99:1 to 98:2) afforded the title compound as a white solid (261.0 mg, 85%) and as an 87:13 mixture of *Z*/*E*-isomers. The major product, the *Z*-isomer **3a** was isolated by flash chromatography for characterization; mp 91–98 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (s, 1 H), 7.32–7.27 (m, 2 H), 7.26–7.20 (m, 3 H), 7.16–7.08 (m, 5 H), 1.35 (s, 12 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.3, 140.6, 137.1, 130.1 (2 C), 129.0 (2 C), 128.4 (2 C), 128.0 (2 C), 127.7, 126.4, 83.9 (2 C), 24.9 (4 C). The carbon directly attached to the boron atom was not detected due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 30.6.

(*Z*)-4,4,5,5-Tetramethyl-2-(oct-4-en-4-yl)-1,3,2-dioxaborolane (3b)[20]

The general procedure A was applied to oct-4-yne (**1b**; 147 µL, 1.00 mmol, 1 equiv) and the reaction mixture was heated in an oil bath at 160 °C for 30 min. Purification by silica gel flash chromatography (pentane/Et_2O 100:0 to 98:2) afforded the title compound **3b** as a colorless oil (130.2 mg, 55%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.29 (t, *J* = 7.1 Hz, 1 H), 2.13–2.08 (m, 4 H), 1.44–1.33 (m, 4 H), 1.25 (s, 12 H), 0.93–0.88 (m, 6 H)

^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.1, 83.1 (2 C), 30.8, 30.7, 24.9 (4 C), 23.5, 22.6, 14.2, 14.2. The carbon directly attached to the boron atom was not detected due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 30.4.

(*Z*)-2-[1-(4-Methoxyphenyl)hex-1-en-2-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c) and (*Z*)-2-[1-(4-Methoxyphenyl)hex-1-en-1-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3′c)

The general procedure A was applied to 1-(hex-1-yn-1-yl)-4-methoxybenzene (**1c**; 188.3 mg, 1.00 mmol, 1 equiv) and the reaction mixture was heated in an oil bath at 160 °C for 30 min. Purification by silica gel flash chromatography (pentane/Et_2O 99:1 to 97:3) afforded an 85:15 mixture of the title compounds **3c**/**3′c** as a colorless oil (147.0 mg, 46%). The two products were isolated by an additional flash chromatography for characterization.

3c

IR (ATR): 2976, 2930, 1607, 1508, 1347, 1246, 829 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.29 (m, 2 H), 7.15 (s, 1 H), 6.89–6.85 (m, 2 H), 3.81 (s, 3 H), 2.40 (m, 2 H), 1.52–1.44 (m, 2 H), 1.41–1.30 (m, 2 H), 1.30 (s, 12 H), 0.91 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.8, 141.3, 130.8, 130.6 (2 C), 113.6 (2 C), 83.4 (2 C), 55.3, 32.3, 29.3, 24.9 (4 C), 23.0, 14.2. The carbon directly attached to the boron atom was not detected due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 30.8.

HRMS (ESI): *m*/*z* calcd for $C_{19}H_{29}BO_3Na$ [M + Na]$^+$: 339.2105; found: 329.2106.

3′c

IR (ATR): 2923, 1604, 1511, 1244, 830 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.09–7.07 (m, 2 H), 6.87–6.84 (m, 2 H), 6.53 (t, *J* = 7.3 Hz, 1 H), 3.80 (s, 3 H), 2.16 (q, *J* = 7.3 Hz, 2 H), 1.43–1.27 (m, 4 H), 1.27 (s, 12 H), 0.84 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.9, 148.1, 132.7, 130.2 (2 C), 113.3 (2 C), 83.5 (2 C), 55.3, 31.7, 29.8, 24.9 (4 C), 22.7, 14.1. The carbon directly attached to the boron atom was not detected due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 30.2.

HRMS (ESI): *m*/*z* calcd for $C_{19}H_{29}BO_3Na$ [M + Na]$^+$: 339.2105; found: 329.2114.

(*Z*)-4,4,5,5-Tetramethyl-2-{1-[4-(trifluoromethyl)phenyl]hex-1-en-2-yl}-1,3,2-dioxaborolane (3d) and (*Z*)-4,4,5,5-Tetramethyl-2-{1-[4-(trifluoromethyl)phenyl]hex-1-en-1-yl}-1,3,2-dioxaborolane (3′d)

The general procedure A was applied to 1-(hex-1-yn-1-yl)-4-(trifluoromethyl)benzene (**1d**; 226.2 mg, 1.00 mmol, 1 equiv) and the reaction mixture was heated in an oil bath at 160 °C for 30 min. Purification by silica gel flash chromatography (pentane/Et_2O 99:1 to 98:2) afforded an inseparable 65:35 mixture of the title compounds **3d**/**3′d** as a colorless oil (259.7 mg, 73%).

3d

^1H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8.3 Hz, 2 H), 7.39 (d, *J* = 8.3 Hz, 2 H), 7.20 (s, 1 H), 2.34 (m, 2 H), 1.49–1.24 (m, 4 H), 1.31 (s, 12 H), 0.88 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.0, 140.1, 129.2 (2 C), 125.2 (q, *J* = 3.8 Hz, 2 C), 83.7 (2 C), 32.2, 29.4, 24.9 (4 C), 22.9, 14.1. The carbon directly attached to the boron atom was not detected due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 32.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –63.4.

3′d

^1H NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 10.0 Hz, 2 H), 7.23 (d, *J* = 8.0 Hz, 2 H), 6.65 (t, *J* = 7.4 Hz, 1 H), 2.11 (q, *J* = 7.4 Hz, 2 H), 1.49–1.24 (m, 4 H), 1.27 (s, 12 H), 0.84 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.4, 141.7, 129.4 (2 C), 124.9 (q, *J* = 3.8 Hz, 2 C), 83.8 (2 C), 31.5, 29.8, 24.9 (4 C), 22.6, 14.0. The carbon directly attached to the boron atom was not detected due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 32.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –63.2.

(*Z*)-Trimethyl[2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl]silane (3e)

The general procedure A was applied to 1-phenyl-2-(trimethylsilyl)acetylene (**1e**; 199 µL, 1.00 mmol, 1 equiv) and the reaction mixture was heated in an oil bath at 160 °C for 30 min. Purification by silica gel flash chromatography (pentane/Et_2O 98:2) afforded the title compound **3e** as a yellowish oil (213.6 mg, 71%).

IR (ATR): 2981, 1569, 1446, 1319, 1246, 1142, 845 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.02 (s, 1 H), 7.31–7.21 (m, 5 H), 1.30 (s, 12 H), 0.00 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.2, 141.6, 128.4 (2 C), 127.8 (2 C), 127.6, 83.4 (2 C), 25.0 (4 C), 1.1 (3 C). The carbon directly attached to the boron atom was not detected due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 32.4.

HRMS (ESI): *m*/*z* calcd for $C_{17}H_{27}BO_2SiLi$ [M + Li]$^+$: 309.2032; found: 309.2021.

(*Z*)-[2-(4-Methoxyphenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl]trimethylsilane (3f)

The general procedure **A** was applied to [(4-methoxyphenyl)ethynyl]trimethylsilane (**1f**; 204.3 mg, 1.00 mmol, 1 equiv) and the reaction mixture was heated in an oil bath at 160 °C for 30 min. Purification by silica gel flash chromatography (pentane/Et_2O 98:2) afforded the title compound **3f** as a white solid (189.4 mg, 57%); mp 85 °C.

IR (ATR): 2985, 1606, 1557, 1504, 1466, 1308, 1241, 1139, 837, 760 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.95 (s, 1 H), 7.22–7.20 (m, 2 H), 6.84–6.82 (m, 2 H), 3.81 (s, 3 H), 1.29 (s, 12 H), 0.04 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.4, 156.9, 134.0, 130.0 (2 C), 113.2 (2 C), 83.3 (2 C), 55.4, 25.0 (4 C), 1.2 (3 C). The carbon directly attached to the boron atom was not detected due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 31.5.

HRMS (ESI): *m*/*z* calcd for $C_{18}H_{29}BO_3SiLi$ [M + Li]$^+$: 339.2137; found: 339.2131.

(*Z*)-Trimethyl{1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-[(4-(trifluoromethyl)phenyl]vinyl}silane (3g)

The general procedure A was applied to trimethyl{[4-(trifluoromethyl)phenyl]ethynyl}silane (**1g**; 242.3 mg, 1.00 mmol, 1 equiv) and the reaction mixture was heated in an oil bath at 160 °C for 30 min. Purification by silica gel flash chromatography (pentane/EtOAc 98:2) afforded the title compound **3g** as a white solid (314.0 mg, 85%); mp 81 °C.

IR (ATR): 2982, 1577, 1312, 1156, 1109, 1057, 833, 759 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (s, 1 H), 7.55 (d, *J* = 8.1 Hz, 2 H), 7.34 (d, *J* = 8.5 Hz, 2 H), 1.31 (s, 12 H), –0.01 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.1, 145.1, 129.6 (q, *J* = 32.4 Hz), 128.6 (2 C), 124.8 (q, *J* = 3.7 Hz, 2 C), 124.4 (q, *J* = 270 MHz), 83.6 (2 C), 25.0 (4 C), 1.0 (3 C). The carbon directly attached to the boron atom was not detected due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 32.6.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –63.4.

HRMS (ESI): *m*/*z* calcd for $C_{18}H_{26}BF_3O_2SiNa$ [M + Na]$^+$: 393.1643; found: 393.1641.

(*Z*)-[2-(3,5-Dimethoxyphenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl]trimethylsilane (3h)

The general procedure A was applied to [(3,5-dimethoxyphenyl)ethynyl]trimethylsilane (**1h**; 234.4 mg, 1.00 mmol, 1 equiv) and the reaction mixture was heated in an oil bath at 160 °C for 30 min. Purification by silica gel flash chromatography (pentane/Et_2O 97:3) afforded the title compound **3h** as a colorless oil (240.0 mg, 66%).

IR (ATR): 2982, 1598, 1459, 1317, 1302, 1243, 1147, 840 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (s, 1 H), 6.42 (m, 2 H), 6.37 (t, *J* = 2.3 Hz, 1 H), 3.77 (s, 6 H), 1.30 (s, 12 H), 0.04 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.3 (2 C), 156.9, 143.6, 106.3 (2 C), 100.2, 83.4 (2 C), 55.5 (2 C), 25.0 (4 C), 1.0 (3 C). The carbon directly attached to the boron atom was not detected due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 31.4.

HRMS (ESI): *m*/*z* calcd for $C_{19}H_{31}BO_4SiNa$ [M + Na]$^+$: 385.1981; found: 385.1983.

(*Z*)-[2-(6-Methoxynaphthalen-2-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl]trimethylsilane (3i)

The general procedure A was applied to [(6-methoxynaphthalen-2-yl)ethynyl]trimethylsilane (**1i**; 254.4 mg, 1.00 mmol, 1 equiv) and the reaction mixture was heated in an oil bath at 160 °C for 30 min. Purification by silica gel flash chromatography (pentane/Et_2O 98:2 to 95:5) afforded the title compound **3i** as a white solid (285.5 mg, 75%); mp 102–103 °C.

IR (ATR): 2972, 1571, 1313, 1262, 1138, 838 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (s, 1 H), 7.72–7.67 (m, 3 H), 7.39 (dd, *J* = 8.5, 1.5 Hz, 1 H), 7.16–7.12 (m, 2 H), 3.92 (s, 3 H), 1.33 (s, 12 H), 0.05 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.0, 157.3, 136.8, 134.1, 129.8, 128.5, 127.5, 127.3, 126.2, 119.1, 105.9, 83.4 (2 C), 55.4, 25.0 (4 C), 1.2 (3 C). The carbon directly attached to the boron atom was not detected due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 31.5.

HRMS (ESI): *m*/*z* calcd for $C_{22}H_{31}BO_3SiNa$ [M + Na]$^+$: 405.2032; found: 405.2043.

(*Z*)-3-[2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)vinyl]pyridine (3j)

The general procedure A was applied to 3-[(trimethylsilyl)ethynyl]pyridine (**1j**; 175.3 mg, 1.00 mmol, 1 equiv) and the reaction mixture was heated in an oil bath at 160 °C for 30 min. Purification by silica gel flash chromatography (pentane/Et_2O 80:20 to 70:30) afforded the title compound **3j** as a colorless oil (125.4 mg, 41%).

IR (ATR): 2980, 1590, 1470, 1325, 1311, 1247, 1141, 836 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51 (m, 2 H), 7.91 (s, 1 H), 7.55–7.52 (m, 1 H), 7.22 (dd, *J* = 7.7, 4.8 Hz, 1 H), 1.30 (s, 12 H), 0.00 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.7, 149.3, 148.7, 137.0, 135.4, 122.8, 83.6 (2 C), 25.0 (4 C), 1.0 (3 C). The carbon directly attached to the boron atom was not detected due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 32.2.

HRMS (ESI): *m*/*z* calcd for $C_{16}H_{27}BNO_2Si$ [M + H]$^+$: 304.1902; found: 304.1900.

(*E*)-2-[1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)vinyl]pyridine (3k)

The general procedure A was applied to 2-[(trimethylsilyl)ethynyl]pyridine (**1k**; 175.3 mg, 1.00 mmol, 1 equiv) and the reaction mixture was heated in an oil bath at 160 °C for 30 min. Purification by silica gel flash chromatography (pentane/Et_2O 80:20 to 70:30) afforded the title compound **3k** as a brown oil (205.8 mg, 68%).

IR (ATR): 2974, 1582, 1473, 1289, 1244, 1140, 833 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49 (d, *J* = 4.9 Hz, 1 H), 7.66 (td, *J* = 7.6, 1.7 Hz, 1 H), 7.16–7.11 (m, 2 H), 7.03 (s, 1 H), 1.39 (s, 12 H), 0.22 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.4, 146.6, 143.7, 138.3, 122.2, 122.1, 82.5 (2 C), 26.2 (4 C), –0.8 (3 C). The carbon directly attached to the boron atom was not detected due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 27.0.

HRMS (ESI): *m*/*z* calcd for $C_{16}H_{27}BNO_2Si$ [M + H]$^+$: 304.1902; found: 304.1911.

(*Z*)-4,4,5,5-Tetramethyl-2-{2-phenyl-1-[4-(trifluoromethyl)phenyl]vinyl}-1,3,2-dioxaborolane (3l) and 4,4,5,5-Tetramethyl-2-{1-phenyl-2-[4-(trifluoromethyl)phenyl]vinyl}-1,3,2-dioxaborolane (3′l)

The general procedure A was applied to 1-(phenylethynyl)-4-(trifluoromethyl)benzene (**1l**; 246.2 mg, 1.00 mmol, 1 equiv) and the reaction mixture was heated in an oil bath at 160 °C for 30 min. Purification by silica gel flash chromatography (pentane/Et_2O 97:3) afforded a 57:43 mixture of the title compounds **3l**/**3′l** as a pale yellow solid (216.7 mg, 58%). The major product was isolated by flash chromatography for characterization.

3l

Mp 112 °C.

IR (ATR): 2985, 1610, 1322, 1168, 1117, 1062, 850, 751, 694 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 8.0 Hz, 2 H), 7.45 (s, 1 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 7.15–7.11 (m, 3 H), 7.04–7.02 (m, 2 H), 1.32 (s, 12 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.5, 136.5, 136.4, 129.9 (2 C), 129.3 (2 C), 128.0 (2 C), 128.0, 125.2 (q, *J* = 3.9 Hz, 2 C), 84.0 (2 C), 24.8 (4 C). The carbon directly attached to the boron atom was not detected due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 31.8.

HRMS (ESI): *m*/*z* calcd for $C_{21}H_{22}BF_3O_2Na$ [M + Na]$^+$: 397.1561; found: 397.1566.

2-[1-(4-Methoxyphenyl)-2-phenylvinyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3m) and (*Z*)-2-[2-(4-Methoxyphenyl)-1-phenylvinyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3′m)

The general procedure A was applied to 1-methoxy-4-(phenylethynyl)benzene (**1m**; 208.3 mg, 1.00 mmol, 1 equiv) and the reaction mixture was heated in an oil bath at 160 °C for 30 min. Purification by silica gel flash chromatography (pentane/Et_2O 93:7) afforded an inseparable 40:60 mixture of the title compounds **3m**/**3′m** as a white solid (228.2 mg, 68%).

3m

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (s, 1 H), 7.30–7.29 (m, 2 H), 7.23–7.21 (m, 2 H), 6.83–6.80 (m, 2 H), 3.80 (s, 3 H), 1.32 (s, 12 H); other signals are overlapped with the major product.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.1, 140.9, 137.2, 132.5, 130.1, 129.6, 127.8, 126.1, 113.7, 83.7; other signals are overlapped with the major product. The stereoselectivity could not be assigned by NMR analysis.

3′m

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (s, 1 H), 7.20–7.17 (m, 2 H), 7.14–7.08 (m, 3 H), 7.02–6.99 (m, 2 H), 6.67–6.63 (m, 2 H), 3.74 (s, 3 H), 1.30 (s, 12 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 142.7, 142.7, 131.5, 129.9, 128.8, 128.3, 127.4, 113.3, 83.6, 55.1, 24.8. The carbon directly attached to the boron atom was not detected due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 31.8.

(*Z*)-2-(1-Mesityl-2-phenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3n) and 2-(2-Mesityl-1-phenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3′n)

The general procedure A was applied to 1,3,5-trimethyl-2-(phenylethynyl)benzene (**1n**; 220.3 mg, 1.00 mmol, 1 equiv) and the reaction mixture was heated in an oil bath at 160 °C for 30 min. Purification by silica gel flash chromatography (pentane/Et_2O 93:7) afforded an inseparable 87:13 mixture of the title compounds **3n**/**3′n** as a white solid (240.8 mg, 69%).

3n

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (s, 1 H), 7.16–7.11 (m, 3 H), 7.04–6.99 (m, 2 H), 6.90 (s, 2 H), 2.34 (s, 3 H), 2.08 (s, 6 H), 1.31 (s, 12 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.0, 137.5, 136.7, 135.3, 134.3, 129.1, 128.4, 128.1, 127.9, 83.5, 24.6, 21.2, 20.1. The carbon directly attached to the boron atom was not detected due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 31.4.

3′n

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.75 (s, 2 H), 2.25 (s, 3 H), 2.03 (s, 6 H), 1.38 (s, 12 H); other signals are overlapped with the major product.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.4, 140.2, 136.1, 135.2, 134.2, 128.7, 127.9, 127.5, 126.1, 83.7, 24.8, 21.0, 20.2. The carbon directly attached to the boron atom was not detected due to quadrupolar relaxation. The stereoselectivity could not be assigned by NMR analysis.

Methyl 3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oct-2-enoate (3o)

The general procedure A was applied to methyl oct-2-ynoate (**1o**; 168 µL, 1.00 mmol, 1 equiv) and the reaction mixture was heated in an oil bath at 160 °C for 30 min. Purification by silica gel flash chromatography (pentane/Et_2O 95:5) afforded the title compound **3o** as a colorless oil (178.1 mg, 63%) and as a 38:62 mixture of *Z*/*E*-isomers. The two isomers were separated by flash chromatography for characterization.

(*Z*)-3o

IR (ATR): 2987, 2925, 1724, 1330, 1264, 1133 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.39 (s, 1 H), 3.70 (s, 3 H), 2.66 (m, 2 H), 1.45–1.38 (m, 2 H), 1.32–1.28 (m, 4 H), 1.26 (s, 12 H), 0.88 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 129.3, 84.2 (2 C), 51.1, 32.0, 30.2, 29.4, 24.8 (4 C), 22.7, 14.1. The carbon directly attached to the boron atom was not detected due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 30.0.

HRMS (ESI): *m*/*z* calcd for $C_{15}H_{27}BO_4Na$ [M + Na]$^+$: 305.1897; found: 305.1888.

(*E*)-3o

IR (ATR): 2986, 2926, 1715, 1305, 1137 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.00 (s, 1 H), 3.71 (s, 3 H), 2.27 (m, 2 H), 1.51–1.45 (m, 2 H), 1.35 (s, 12 H), 1.31–1.25 (m, 4 H), 0.88 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.3, 125.6, 84.1 (2 C), 51.7, 35.9, 31.6, 27.8, 25.0 (4 C), 22.5, 14.1. The carbon directly attached to the boron atom was not detected due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 30.3.

HRMS (ESI): *m*/*z* calcd for $C_{15}H_{27}BO_4Li$ [M + Li]$^+$: 289.2160; found: 289.2150.

Ethyl (*E*)-3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trimethylsilyl)acrylate (3p)

The general procedure A was applied to ethyl 3-(trimethylsilyl)propiolate (**1p**; 170.3 mg, 1.00 mmol, 1 equiv) and the reaction mixture was heated in an oil bath at 160 °C for 30 min. Purification by silica gel flash chromatography (pentane/Et_2O 94:6) afforded the title compound **3p** as a pale yellow oil (181.9 mg, 61%).

IR (ATR): 2983, 1716, 1598, 1345, 1299, 1251, 1190, 1139, 842, 757 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.39 (s, 1 H), 4.19 (q, *J* = 7.1 Hz, 2 H), 1.36 (s, 12 H), 1.27 (t, *J* = 7.1 Hz, 3 H), 0.16 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 137.0, 84.0 (2 C), 60.8, 25.3 (4 C), 14.4, –1.4 (3 C). The carbon directly attached to the boron atom was not detected due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 31.7.

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{27}BO_4SiNa$ [M + Na]$^+$: 321.1667; found: 321.1672.

Ethyl (*E*)-3-Phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (3q)[21]

The general procedure A was applied to ethyl 3-phenylpropiolate **1q** (168 µL, 1.00 mmol, 1 equiv) and the reaction mixture was heated in an oil bath at 160 °C for 30 min. Purification by silica gel flash chromatography (pentane/Et_2O 90:10) afforded the title compound **3q** as a yellowish oil (140.7 mg, 47%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.48 (m, 2 H), 7.38–7.32 (m, 3 H), 6.43 (s, 1 H), 4.26 (q, *J* = 7.1 Hz, 2 H), 1.42 (s, 12 H), 1.31 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.2, 138.8, 129.2, 128.8 (2 C), 127.3 (2 C), 126.2, 84.5 (2 C), 60.9, 25.2 (4 C), 14.4. The carbon directly attached to the boron atom was not detected due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 30.1.

(*Z*)-1,2-Diphenyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethane and (*E*)-1,2-Diphenyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethane [(*Z*/*E*)-5a]

The general procedure B was applied to diphenylacetylene (**1a**; 180.0 mg, 1.00 mmol, 1 equiv) and the reaction mixture was heated in an oil bath at 160 °C for 6 h. Purification by recrystallization from hexane afforded the title compound (*Z*/*E*)-**5a** as a white solid (224.0 mg, 52%) and as a 75:25 mixture of *Z*/*E*-isomers. The two isomers were separated by flash chromatography (pentane/Et_2O 90:10) for characterization.

(*Z*)-5a[22]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.09–7.00 (m, 6 H), 6.96–6.93 (m, 4 H), 1.32 (s, 24 H).

^{13}C NMR (100 MHz, $CDCl_3$): 141.4 (2 C), 129.5 (4 C), 127.6 (4 C), 125.9 (2 C), 84.2 (4 C), 25.0 (8 C). The carbons directly attached to the boron atoms were not detected due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 30.2.

(*E*)-5a

Mp 172–173 °C.

IR (ATR): 2923, 1317, 1263, 1134, 845 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.34 (m, 4 H), 7.30–7.26 (m, 4 H), 7.24–7.20 (m, 2 H), 1.08 (s, 24 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.3 (2 C), 128.2 (4 C), 128.1 (4 C), 126.8 (2 C), 83.7 (4 C), 24.7 (8 C). The carbons directly attached to the boron atoms were not detected due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 30.1.

HRMS (ESI): *m*/*z* calcd for $C_{26}H_{34}B_2O_4Na$ [M + Na]$^+$: 455.2544; found: 455.2557.

(*Z*)-2,2′-[1-(4-Methoxyphenyl)hex-1-ene-1,2-diyl]bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5c)

The general procedure B was applied to 1-(hex-1-yn-1-yl)-4-methoxybenzene (**1c**; 188.3 mg, 1.00 mmol, 1 equiv) and the reaction mixture was heated in an oil bath at 160 °C for 6 h. Purification by silica gel flash chromatography (pentane/Et_2O 100:0 to 90:10) afforded the title compound **5c** as a colorless oil (129.0 mg, 29%).

IR (ATR): 2983, 2924, 1604, 1508, 1337, 1242, 1145, 1129, 845 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.04–7.01 (m, 2 H), 6.84–6.81 (m, 2 H), 3.79 (s, 3 H), 2.12–2.08 (m, 2 H), 1.33 (s, 12 H), 1.29–1.15 (m, 4 H), 1.24 (s, 12 H), 0.77 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.8, 134.2, 129.4 (2 C), 129.2, 128.4, 113.3 (2 C), 83.7 (2 C), 83.7 (2 C), 55.2, 32.2, 32.1, 25.1 (4 C), 24.9 (4 C), 23.0, 14.1.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 31.1.

HRMS (ESI): *m*/*z* calcd for $C_{25}H_{40}B_2O_5Na$ [M + Na]$^+$: 465.2962; found: 465.2977.

(*Z*)-2,2′-{1-[4-(Trifluoromethyl)phenyl]hex-1-ene-1,2-diyl}bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5d)

The general procedure **B** was applied to 1-(hex-1-yn-1-yl)-4-(trifluoromethyl)benzene (**1d**; 226.2 mg, 1.00 mmol, 1 equiv) and the reaction mixture was heated in an oil bath at 160 °C for 6 h. Purification by silica gel flash chromatography (pentane/Et_2O 100:0 to 90:10) afforded the title compound **5d** as a white solid (72.8 mg, 15%); mp 97–98 °C.

IR (ATR): 2986, 2927, 1602, 1466, 1321, 1267, 1119, 847 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 8.0 Hz, 2 H), 7.19 (d, *J* = 7.9 Hz, 2 H), 2.04 (m, 2 H), 1.35 (s, 12 H), 1.33–1.30 (m, 2 H), 1.24 (s, 12 H), 1.20–1.13 (m, 2 H), 0.75 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.1, 128.7 (2 C), 128.0 (q, *J* = 32.2 Hz), 124.9 (q, *J* = 3.7 Hz, 2 C), 124.7 (q, *J* = 270 MHz), 84.0 (4 C), 32.5, 31.9, 25.2 (4 C), 24.9 (4 C), 22.9, 14.0. The carbons directly attached to the boron atoms were not detected due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 29.9.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –63.2.

HRMS (ESI): *m*/*z* calcd for $C_{25}H_{37}B_2F_3O_4Na$ [M + Na]$^+$: 503.2731; found: 503.2736.

Trimethyl[2-phenyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl]silane (5e)

The general procedure B was applied to 1-phenyl-2-(trimethylsilyl)acetylene (**1e**; 199 µL, 1.00 mmol, 1 equiv) and the reaction mixture was heated in an oil bath at 160 °C for 6 h. Purification by flash chromatography (pentane/Et_2O 95:5) afforded the title compound **5e** as a white solid (300.1 mg, 70%) as a 65:35 mixture of *Z*/*E*-isomers. The two isomers were separated by an additional flash chromatography for characterization.

(*Z*)-Trimethyl[2-phenyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl]silane[23]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27–7.17 (m, 3 H), 7.14–7.11 (m, 2 H), 1.38 (s, 12 H), 1.24 (s, 12 H), –0.17 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.0, 127.9 (2 C), 127.6 (2 C), 126.3, 84.0 (2 C), 83.8 (2 C), 25.7 (4 C), 24.9 (4 C), 1.0 (3 C). The carbons directly attached to the boron atoms were not detected due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 30.3.

(*E*)-Trimethyl[2-phenyl-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl]silane

Mp 171–174 °C.

IR (ATR): 2982, 1305, 1255, 1138, 843 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22–7.20 (m, 4 H), 7.19–7.14 (m, 1 H), 1.23 (s, 12 H), 0.99 (s, 12 H), 0.25 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.1, 127.9 (2 C), 127.5 (2 C), 126.1, 83.7 (2 C), 83.2 (2 C), 25.2 (4 C), 24.9 (4 C), 0.9 (3 C). The carbons directly attached to the boron atoms were not detected due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 30.

HRMS (ESI): *m*/*z* calcd for $C_{23}H_{38}B_2O_4SiNa$ [M + Na]$^+$: 451.2626; found: 451.2627.

{1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-[4-(trifluoromethyl)phenyl]vinyl}trimethylsilane (5g)

The general procedure B was applied to trimethyl{[4-(trifluoromethyl)phenyl]ethynyl}silane (**1g**; 242.3 mg, 1.00 mmol, 1 equiv) and the reaction mixture was heated in an oil bath at 160 °C for 6 h. Purification by flash chromatography (pentane/Et_2O 97:3 to 95:5) afforded the title compound **5g** as a white solid (290.4 mg, 58%) and as an inseparable 68:32 mixture of *Z*/*E*-isomers.

(*Z*)-{1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-[4-(trifluoromethyl)phenyl]vinyl}trimethylsilane[23]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.48 (m, 2 H), 7.22 (d, *J* = 8.0 Hz, 2 H), 1.38 (s, 12 H), 1.22 (s, 12 H), –0.18 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.8, 128.5 (q, *J* = 32 MHz), 128.3 (2 C), 124.7 (q, *J* = 238 Hz), 124.6 (q, *J* = 3.8 Hz, 2 C), 84.3 (2 C), 84.0 (2 C), 25.7 (4 C), 24.9 (4 C), 0.99 (3 C). The carbons directly attached to the boron atoms were not detected due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 28.8.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –63.1.

(*E*)-{1,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-[4-(trifluoromethyl)phenyl]vinyl}trimethylsilane

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.48 (m, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 1.22 (s, 12 H), 0.97 (s, 12 H), 0.26 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.0, 128.5 (q, *J* = 32 MHz), 128.4 (2 C), 124.7 (q, *J* = 238 Hz), 124.6 (q, *J* = 3.8 Hz, 2 C), 84.1 (2 C), 83.6 (2 C), 25.2 (4 C), 25.0 (4 C), 0.99 (3 C). The carbons directly attached to the boron atoms were not detected due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 28.8.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –63.2.

(*E*)-4,4,5,5-Tetramethyl-2-styryl-1,3,2-dioxaborolane (6e)[24]

To a solution of (*Z*)-trimethyl[2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl]silane (**3e**; 100.0 mg, 0.33 mmol, 1 equiv) in CH_2Cl_2 (4 mL) was added trifluoroacetic acid (38 µL, 0.50 mmol, 1.5 equiv). After stirring for 4 h at r.t., the reaction mixture was concentrated under reduced pressure. Purification by silica gel flash chromatography (pentane/Et_2O 97:3) afforded the title compound **6e** as a colorless oil (51.1 mg, 67%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50–7.48 (m, 2 H), 7.40 (d, *J* = 18.4 Hz, 1 H), 7.36–7.27 (m, 3 H), 6.17 (d, *J* = 18.4 Hz, 1 H), 1.32 (s, 12 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.6, 137.6, 129.0, 128.7 (2 C), 127.2 (2 C), 83.5 (2 C), 25.0 (4 C). The carbon directly attached to the boron atom was not detected due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 29.7.

(*E*)-2-(4-Methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6f)[24]

To a solution of (*Z*)-[2-(4-methoxyphenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl]trimethylsilane (**3f**; 50.0 mg, 0.15 mmol, 1 equiv) in CH_2Cl_2 (2 mL) was added trifluoroacetic acid (17 µL, 0.23 mmol, 1.5 equiv). After stirring for 4 h at r.t., the reaction mixture was concentrated under reduced pressure. Purification by silica gel flash chromatography (pentane/Et_2O 95:5) afforded the title compound **6f** as a colorless oil (30.2 mg, 87%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.42 (m, 2 H), 7.35 (d, *J* = 18.4 Hz, 1 H), 6.88–6.85 (m, 2 H), 6.01 (d, *J* = 18.4 Hz, 1 H), 3.81 (s, 3 H), 1.31 (s, 12 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.4, 149.2, 130.6, 128.6 (2 C), 114.1 (2 C), 83.4 (2 C), 55.4, 25.0 (4 C). The carbon directly attached to the boron atom was not detected due to quadrupolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 30.0.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0036-1588996.

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