Supporting Information

Metal Free Direct Hydroboration of Alkynes with Pinacol Borane via Lewis Acid Catalysis

Mirco Fleige, Juri Möbus, Thorsten vom Stein, Frank Glorius, Douglas W. Stephan

These authors contributed equally to this work

Table of Content

1 Materials and Methods .............................................................................................................2
2 Synthesis and Spectroscopic Data .........................................................................................4
  2.1 Preparation of compound 24 ...............................................................................................4
  2.2 Preparation of compound 27 ...............................................................................................5
  2.3 Preparation of compound 25 ...............................................................................................7
  2.4 Preparation of compound 28 ...............................................................................................8
3 Stoichiometric studies ...........................................................................................................11
  3.1 Control reactions ...............................................................................................................11
    Formation of compound 25 from compound 2 ...................................................................11
    Formation of compound 25 from compound 2 ...................................................................12
    Reaction between B(C₆F₅)₃ and pinacol borane ...............................................................13
    Reaction between HB(C₆F₅)₂ and pinacol borane ............................................................15
    Reaction between MeB(C₆F₅)₂ and pinacol borane ...........................................................16
    Reaction between ClB(C₆F₅)₂ and pinacol borane ............................................................17
    Non-equilibrium nature between compounds 2 and 24 ....................................................19
    Non-equilibrium nature between compounds 6 and 27 .....................................................20
  3.2 Cross-over experiments ....................................................................................................20
    Reaction between compound 25 and p-CF₃-C₆H₄-C≡C-H ..................................................20
    Reaction between compound 25 and Ph-C≡C-H ...............................................................21
    Reaction between compound 28 and Ph-C≡C-H ...............................................................22
  3.3 Reaction of compound 25 with t-butylisocyanide .............................................................23
4 Variable temperature NMR studies .......................................................................................25
  4.1 VT NMR study of compound 25 .......................................................................................25
4.2 VT NMR study of the reaction of compound 25 and HBPin ..............................................26
4.3 VT NMR study of the reaction of B(C₆F₅)₃ and HBPin.......................................................27
4.4 VT NMR study of the reaction of HB(C₆F₅)₂ and HBPin ....................................................28

5 Catalytic Reactions.................................................................................................................30

5.1 Optimization of the reaction conditions and catalyst screening.........................................30
5.2 General procedure.............................................................................................................33
5.3 Product data......................................................................................................................33

(1) (E)-4,4,5,5-tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane ........................................33
(2) (E)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane........................................................34
(3) (E)-2-(2-([1,1′-biphenyl]-4-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ...................35
(4) (E)-2-(4-(tert-butyl)styryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ................................36
(5) (E)-2-(4-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.....................................38
(6) (E)-4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)styryl)-1,3,2-dioxaborolane .........................39
(7) Methyl (E)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzoate ..................40
(8) (E)-2-(3,5-difluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ....................................41
(9) (E)-4,4,5,5-tetramethyl-2-(2,4,6-trimethylstyryl)-1,3,2-dioxaborolane .............................42
(10) (E)-4,4,5,5-tetramethyl-2-(2-(thiophen-3-yl)vinyl)-1,3,2-dioxaborolane .......................43
(11) (E)-2-(2-(cyclohex-1-en-1-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane .................44
(12) (E)-2-(6-chlorohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane .........................45
(13) (1E,7E)-1,8-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octa-1,7-diene ....................46
(14) (E)-2-(6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-en-1-yl)isoindoline-1,3-dione 47
(15) (E)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-ene-nitrile ...............................48
(16) (E)-trimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane ...................49
(17) (Z)-4,4,5,5-tetramethyl-2-(1-phenylhex-1-en-2-yl)-1,3,2-dioxaborolane .......................50
(18) (Z)-trimethyl(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(thiophen-2-yl)vinyl) silane 51
(19) (Z)-2-(1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ...............................52
(20) (Z)-2-(1,2-bis(4-bromophenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ...............53
(21) (Z)-4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane ......................55
(22) (Z)-4,4,5,5-tetramethyl-2-(oct-4-en-4-yl)-1,3,2-dioxaborolane .......................................56
(23) (Z)-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene-1,2-diyli)silane(trimethylsilane) 57
1 Materials and Methods

All manipulations were performed in a Glove box MB Unilab produced by MBraun or using standard Schlenk techniques\[^{S1}\] under an inert atmosphere of anhydrous N\(_2\). Dry, oxygen-free solvents (CH\(_2\)Cl\(_2\), \(n\)-pentane) were prepared using an Innovative Technologies solvent purification system. Deuterated solvents chloroform (CDCl\(_3\)), dichloromethane (CD\(_2\)Cl\(_2\)), benzene (C\(_6\)D\(_6\)), toluene (C\(_7\)D\(_8\)) and bromobenzene (C\(_6\)D\(_5\)Br) were purchased from Cambridge Isotope Laboratories Inc. and stored over activated molecular sieves (3 Å) for at least two days and filtered over dried, activated Al\(_2\)O\(_3\) and/or silica gel (SiO\(_2\)) prior to use. If not stated otherwise commercial reagents were used as received without further purification. Liquid alkyne starting materials were dried over molecular sieves (3 Å) and routinely filtered over dried silica gel. Pinacol borane was purchased from Alfa Chemicals and used without additional purification. [CPh\(_3\)][B(C\(_6\)F\(_5\))\(_4\)] was purchased from Boulder Scientific and used without further purification. B(C\(_6\)F\(_5\))\(_3\) was purchased from Boulder Scientific and purified by sublimation prior to use.

All glassware was oven-dried at temperatures above 180\(^\circ\)C prior to use. NMR spectra were measured on a Bruker AVANCE 400 \(^1\)H (400.03 MHz), \(^{13}\)C (100.59 MHz), \(^{19}\)F (376.49 MHz), \(^{31}\)P (161.94 MHz), \(^{29}\)Si (79.49 MHz), \(^{11}\)B (128.37 MHz) or on an Agilent DD2 600 \(^1\)H (600.03 MHz), \(^{13}\)C (150.90 MHz), \(^{19}\)F (564.69 MHz), \(^{31}\)P (242.94 MHz), \(^{29}\)Si (119.23 MHz), \(^{11}\)B (192.46 MHz) at 26 \(^\circ\)C. All \(^{13}\)C NMR spectra were exclusively recorded with composite pile decoupling. Assignments of the carbon atoms in the \(^{13}\)C spectra were performed via indirect deduction from the cross-peaks in 2D correlation experiments (HMBC; HSQC). Chemical shifts were referenced to \(\delta\) (TMS) = 0.00 ppm (\(^1\)H, \(^{13}\)C) and \(\delta\) H\(_3\)PO\(_4\)(85%) = 0.00 ppm (\(^{31}\)P, externally). Chemical shifts (\(\delta\)) are reported in ppm, multiplicity is reported as follows (s = singlet, d = doublet, t = triplet, quart. = quartet, m = multiplet) and coupling constants (J) are reported in Hz. Assignments of individual resonances were done using 2D techniques (HMBC, HSQC, HH-COSY) when necessary. Yields of products in solution were determined by integration of all resonances observed in the respective NMR spectra if not stated otherwise. High-resolution mass spectra (HRMS) were obtained on a micro mass 70S-250 spectrometer (EI), an ABI/Sciex QStar Mass Spectrometer (DART), or on a JOEL AccuTOF-DART (DART).

2 Synthesis and Spectroscopic Data

2.1 Preparation of compound 24

![Chemical Structure]

Compound 24 was prepared according to modified literature procedures.\textsuperscript{[S7],[S8]} Phenylacetylene (30 mg, 0.29 mmol) was dissolved in CH\textsubscript{2}Cl\textsubscript{2} (3 ml), cooled to -35 °C and HB(C\textsubscript{6}F\textsubscript{5})\textsubscript{2} (91.5 mg, 0.26 mmol) was added in portions. The resulting suspension was stirred for 30 min at -35 °C, then allowed to warm to room temperature and stirred another 2 h at r.t. Trace insolubles were filtered off over Celite and washed with CH\textsubscript{2}Cl\textsubscript{2} (1 ml) twice. The combined liquors were evaporated to dryness and the orange residue taken up in pentane (1 ml) and cooled to -35 °C. The supernatant was removed by decantation and the residue washed with pentane (0.5 ml) at -35 °C twice. Compound 24 was obtained as pale yellow solid (105 mg, 0.23 mmol, 89%).

\textsuperscript{1}H NMR (400 MHz, 298 K, CD\textsubscript{2}Cl\textsubscript{2}): δ\textsuperscript{1}H: 7.70 (m, 2H, o-Ph), 7.62 (m, 2H, =CH-Ph and =CH-B), 7.49 (m, 1H, p-Ph)\textsuperscript{a}, 7.48 (m, 2H, m-Ph)\textsuperscript{a}. \textsuperscript{a} from ghsqc

\textsuperscript{13}C\textsuperscript{1}{\textsuperscript{1}H} NMR (126 MHz, 298 K, CD\textsubscript{2}Cl\textsubscript{2}): δ\textsuperscript{13}C: 163.7 (=CH-Ph), 136.3 (i-Ph)\textsuperscript{b}, 132.6 (p-Ph), 129.8 (o-Ph), 129.5 (m-Ph). N.o. =CH-B, C\textsubscript{6}F\textsubscript{5}.

\textsuperscript{1}H,\textsuperscript{13}C GHSQC (500 MHz / 126 MHz, 298 K, CD\textsubscript{2}Cl\textsubscript{2}): δ\textsuperscript{1}H / δ\textsuperscript{13}C: 7.70 / 129.8 (o-Ph), 7.62 / 163.7 (=CH-Ph), 7.49 / 132.6 (p-Ph), 7.48 / 129.5 (m-Ph). N.o. =CH-B

\textsuperscript{11}B NMR (128 MHz, 298 K, CD\textsubscript{2}Cl\textsubscript{2}): δ\textsuperscript{11}B: 58.5 (\nu\textsubscript{1/2} ≈ 700 Hz).

\textsuperscript{19}F NMR (376 MHz, 298 K, CD\textsubscript{2}Cl\textsubscript{2}): δ\textsuperscript{19}F: -129.7 (m, 2F, o-C\textsubscript{6}F\textsubscript{5}), -149.8 (t, \nu\textsubscript{3}J\textsubscript{FF} = 19.5 Hz, 1F, p-C\textsubscript{6}F\textsubscript{5}), -162.2 (m, 2F, m-C\textsubscript{6}F\textsubscript{5}).

\textsuperscript{1965}, 3933-3939.


1H NMR (400 MHz, 298 K, CD$_2$Cl$_2$) spectrum of compound 24.

13C{1H} NMR (126 MHz, 298 K, CD$_2$Cl$_2$) spectrum of compound 24.

11B{1H} NMR (128 MHz, 298 K, CD$_2$Cl$_2$) and 19F NMR (470 MHz, 298 K, CD$_2$Cl$_2$) NMR spectra of compound 24.

2.2 Preparation of compound 27

4-Ethynyl-α,α,α-trifluorotoluene (40 mg, 0.23 mmol) was dissolved in CH$_2$Cl$_2$ (2 ml), at r.t and HB(C$_6$F$_5$)$_2$ (73.2 mg, 0.21 mmol, 0.9 eq.) was added in portions. The resulting suspension was stirred for 4 h at r.t. Trace insolubles were filtered off over Celite and washed with CH$_2$Cl$_2$ (0.5 ml) twice. The combined liquors were evaporated to dryness and the light yellow residue was taken up
in pentane (2 ml) at r.t. The supernatant was removed by decantation at r.t. and the residue was washed with pentane (1 ml) twice. Compound 27 was obtained as pale yellow solid (70 mg, 0.16 mmol, 74%). A second precipitation at -35 °C yielded another 19 mg (0.04 mmol, 20%) of product of equal purity.

**Elemental analysis:** Calcd.: C: 48.88, H: 1.17; Found: C: 48.88, H: 0.93.

**1H NMR** (700 MHz, 300 K, CD$_2$Cl$_2$): $\delta^{1}H$: 7.81 (d, $^3J_{HH} = 8.5$ Hz, 2H, o-Ar), 7.72 (d, $^3J_{HH} = 8.5$ Hz, 2H, m-Ar), 7.71 (d, $^3J_{HH} = 17.8$ Hz, 1H, =CH(1)), 7.58 (d, $^3J_{HH} = 17.8$ Hz, 1H, =CH(2)).

**13C{1H} NMR** (176 MHz, 300 K, CD$_2$Cl$_2$): $\delta^{13}C$: 160.6 (=CH(2)), 148.1 (dm, $^1J_{FC} = 248$ Hz, o-C$_6$F$_5$)$_2$, 143.8 (dm, $^1J_{FC} = 257$ Hz, p-C$_6$F$_5$)$_2$, 139.7 (i-Ar), 138.0 (dm, $^1J_{FC} = 252$ Hz, m-C$_6$F$_5$)$_2$, 134.2 (br, =CH(1)), 133.1 (q, $^2J_{FC} = 32.4$ Hz, p-Ar), 129.8 (o-Ar), 126.3 (q, $^3J_{FC} = 3.8$ Hz, m-Ar), 124.3 (q, $^1J_{FC} = 272.1$ Hz, CF$_3$), 114.1 (br, i-C$_6$F$_5$).

**1H,13C GHSQC** (700 MHz / 176 MHz, 300 K, CD$_2$Cl$_2$): $\delta^{1}H / \delta^{13}C$: 7.72 / 129.8 (o-Ar), 7.72 / 126.3 (m-Ar), 7.71 / 134.2 (=CH(1)), 7.58 / 160.6 (=CH(2)).

**11B NMR** (128 MHz, 298 K, CD$_2$Cl$_2$): $\delta^{11}B$: 59.4 ($\nu_{1/2} \approx 800$ Hz).

**19F NMR** (376 MHz, 298 K, CD$_2$Cl$_2$): $\delta^{19}F$: -63.3 (s, 3F, CF$_3$), -129.2 (m, 4F, o-C$_6$F$_5$), -148.7 (l, $^3J_{FF} = 20.4$ Hz, 2F, p-C$_6$F$_5$), -161.8 (m, 4F, m-C$_6$F$_5$).

1H NMR (700 MHz, 300 K, CD$_2$Cl$_2$) spectrum of compound 27.

13C{1H} NMR (176 MHz, 300 K, CD$_2$Cl$_2$) spectrum of compound 27.
2.3 Preparation of compound 25

Compound 24 (40 mg, 0.058 mmol, 1 eq.) was suspended in pentane (2 ml) at r.t and pinacol borane (8.2 mg, 0.064 mmol, 1.1 eq.) was added to the stirred suspension. The resulting suspension was stirred for 2 h at r.t., the suspension turned clear after ca. 30 min. Trace insolubles were filtered off over Celite and washed with pentane (0.5 ml) twice. The combined pentane solutions were concentrated to ca. 0.5 ml and cooled to -35 °C for precipitation. The supernatant was removed by decantation at -35 °C and the residue dried in vacuum. Compound 25 was obtained as colorless, crystalline solid (40 mg, 0.048 mmol, 86%).

Elemental analysis: Calcd.: C: 54.21, H: 3.50; Found: C: 54.62, H: 3.58.

\( ^1H \) NMR (700 MHz, 300 K, CD\(_2\)Cl\(_2\)): \( \delta \)H: 7.17 (m, 2H, m-Ph), 7.10 (m, 1H, p-Ph), 6.99 (m, 2H, o-Ph), 3.26 (dd, \( ^2J_{HH} = 15.0 \) Hz, \( ^3J_{HH} = 5.7 \) Hz, 1H, CH\(_{2,a}\)), 3.17 (dd, \( ^2J_{HH} = 15.0 \) Hz, \( ^3J_{HH} = 9.2 \) Hz, 1H, CH), 3.00 (dd, \( ^2J_{HH} = 15.0 \) Hz, \( ^3J_{HH} = 9.2 \) Hz, 1H, CH\(_{2,b}\)), 1.20 (s, 6H, CMe\(_{2,a}\)), 1.16 (s, 6H, CMe\(_{2,b}\)).

\( ^{13}C\{^1H\} \) NMR (176 MHz, 300 K, CD\(_2\)Cl\(_2\)): \( \delta \)C: 146.2 (dm, \( ^1J_{FC} = 245 \) Hz, o-C\(_6\)F\(_5\)), 143.9 (i-Ph), 143.1 (dm, \( ^1J_{FC} = 255 \) Hz, p-C\(_6\)F\(_5\)), 137.7 (dm, \( ^1J_{FC} = 251 \) Hz, m-C\(_6\)F\(_5\)), 128.6 (m-Ph), 128.2 (p-Ph), 126.1 (p-Ph), 115.3 (br, i-C\(_6\)F\(_5\)), 84.6 (OCMe\(_2\)), 38.3 (br, CH), 33.3 (CH\(_2\)), 25.1 (CH\(_{3,a}\)), 24.7 (CH\(_{3,b}\)).

\( ^1H\),\(^{13}C\) GHSQC (500 MHz / 126 MHz, 298 K, CD\(_2\)Cl\(_2\)): \( \delta \)\(^1H\) / \( \delta ^{13}C\): 7.17 / 128.6 (m-Ph), 7.10 / 126.1 (p-Ph), 6.99 / 128.2 (o-Ph), 3.26, 3.00 / 33.3 (CH\(_2\)), 3.17 / 38.3 (br, CH), 1.20 / 24.7 (CH\(_{3,a}\)), 1.16 / 25.1 (CH\(_{3,b}\)).

\( ^{11}B \) NMR (128 MHz, 298 K, CD\(_2\)Cl\(_2\)): \( \delta ^{11}B \): 75.2 (\( \nu_{1/2} \approx 1000 \) Hz), 31.8 (\( \nu_{1/2} \approx 400 \) Hz).

\( ^{19}F \) NMR (376 MHz, 298 K, CD\(_2\)Cl\(_2\)): \( \delta ^{19}F \): -131.2 (m, 2F, o-C\(_6\)F\(_5\)), -150.6 (tt, \( ^3J_{FF} = 20.3 \) Hz, \( ^4J_{FF} = 3.5 \) Hz, 1F, p-C\(_6\)F\(_5\)), -162.5 (m, 4F, m-C\(_6\)F\(_5\)).
$^1$H NMR (700 MHz, 300 K, CD$_2$Cl$_2$) spectrum of compound 25.

$^{13}$C($^1$H) NMR (176 MHz, 300 K, CD$_2$Cl$_2$) spectrum of compound 25.

$^{11}$B($^1$H) and $^{19}$F NMR spectra of compound 25.
2.4 Preparation of compound 28

Compound 27 (30 mg, 0.058 mmol, 1 eq.) was suspended in pentane (2 ml) at r.t and pinacol borane (8.2 mg, 0.064 mmol, 1.1 eq.) was added to the stirred suspension. The resulting suspension was stirred for 2 h at r.t., the suspension turned clear after ca. 30 min. Trace insolubles were filtered off over Celite and washed with pentane (0.5 ml) twice. The combined pentane solutions were concentrated to ca. 0.5 ml and cooled to -35 °C for precipitation. The supernatant was removed by decantation at r.t. and the residue was washed with pentane (0.5 ml) at -35 °C and dried in vacuum. Compound 28 was obtained as colorless, crystalline solid (31 mg, 0.048 mmol, 92%).

Elemental analysis: Calcd.: C: 50.35, H: 2.97; Found: C: 49.67, H: 2.80.

$^1$H NMR (700 MHz, 300 K, CD$_2$Cl$_2$): $\delta$^1H: 7.46 (d, $^3$J$_{HH}$ = 8.1 Hz, 2H, m-Ar), 7.17 (d, $^3$J$_{HH}$ = 8.1 Hz, 2H, o-Ar), 3.32 (dd, $^2$J$_{HH}$ = 15.1 Hz, 6J$_{HH}$ = 6.1 Hz, 1H, CH$_2$), 3.15 (dd, $^4$J$_{HH}$ = 8.6 Hz, $^3$J$_{HH}$ = 6.1 Hz, 1H, CH), 3.07 (dd, $^2$J$_{HH}$ = 15.1 Hz, $^3$J$_{HH}$ = 8.6 Hz, 1H, CH$_2$), 1.19 (s, 6H, CMe$_2$), 1.15 (s, 6H, CMe$_2$).

$^{13}$C{$^1$H} NMR (176 MHz, 300 K, CD$_2$Cl$_2$): $\delta^{13}$C: 148.1 (i-Ar), 146.3 (dm, $^1$J$_{FC}$ = 244 Hz, o-C$_6$F$_5$), 143.3 (dm, $^1$J$_{FC}$ = 258 Hz, p-C$_6$F$_5$), 137.8 (dm, $^1$J$_{FC}$ = 247 Hz, m-C$_6$F$_5$), 128.7 (o-Ar), 128.4 (q, $^2$J$_{FC}$ = 31.8 Hz, p-Ar), 125.5 (q, $^3$J$_{FC}$ = 3.6 Hz, m-Ar), 124.8 (q, $^1$J$_{FC}$ = 272.6 Hz, CF$_3$), 115.1 (br, i-C$_6$F$_5$), 84.8 (OCMe$_2$), 37.8 (br, CH), 33.1 (CH$_2$), 25.1 (CH$_3$), 24.7 (CH$_3$).

$^1$H, $^{13}$C GHMBC (700 MHz / 176 MHz, 300 K, CD$_2$Cl$_2$) [selected traces]: $\delta^1$H / $\delta^{13}$C: 7.46 / 125.5 (m-Ar), 7.17 / 128.7 (o-Ar), 3.32, 3.07 / 33.1 (CH$_2$), 3.15 / 37.8 (CH), 1.19 / 24.7 (CH$_3$), 1.15 / 25.1 (CH$_3$).

$^1$H, $^{13}$C GHSQC (700 MHz / 176 MHz, 300 K, CD$_2$Cl$_2$): $\delta^1$H / $\delta^{13}$C: 7.46 / 125.5 (m-Ar), 7.17 / 128.7 (o-Ar), 3.32, 3.07 / 33.1 (CH$_2$), 3.15 / 37.8 (CH), 1.19 / 24.7 (CH$_3$), 1.15 / 25.1 (CH$_3$).

$^{11}$B NMR (128 MHz, 298 K, CD$_2$Cl$_2$): $\delta^{11}$B: 74.7 ($\nu_{1/2}$ ≈ 1300 Hz), 31.7 ($\nu_{1/2}$ ≈ 400 Hz).

$^{19}$F NMR (376 MHz, 298 K, CD$_2$Cl$_2$): $\delta^{19}$F: -62.8 (s, 3F, CF$_3$), -131.2 (m, 4F, o-C$_6$F$_5$), -150.0 (tt, $^3$J$_{FF}$ = 20.5 Hz, $^4$J$_{FF}$ = 4.0 Hz, 2F, p-C$_6$F$_5$), -162.2 (m, 4F, m-C$_6$F$_5$).
$^1$H NMR (700 MHz, 300 K, CD$_2$Cl$_2$) spectrum of compound 28.

$^{13}$C{$^1$H} NMR (176 MHz, 300 K, CD$_2$Cl$_2$) spectrum of compound 28.

$^{11}$B{$^1$H} NMR (128 MHz, 298 K, CD$_2$Cl$_2$) and $^{19}$F NMR (470 MHz, 298 K, CD$_2$Cl$_2$) NMR spectra of compound 28.
$^{1}H,^{13}C$ GHSQC (700 MHz / 176 MHz, 300 K, CD$_2$Cl$_2$) spectra of compound 28.

Excerpt from the $^{1}H,^{13}C$ GHMBC (700 MHz / 176 MHz, 300 K, CD$_2$Cl$_2$) of compound 28.
3 Stoichiometric studies

3.1 Control reactions

Formation of compound 25 from compound 2

Compound 2 (8.0 mg, 0.035 mmol, 1 eq) was taken up in CD$_2$Cl$_2$ (0.25 ml) at r.t. in a glovebox and HB(C$_6$F$_5$)$_2$ (12.0 mg, 0.035 mmol, 1 eq) added. The resulting solution was transferred to a 3 mm NMR tube and left to stand for 15 min at r.t. before acquisition of the NMR spectra.

$^1$H NMR (500 MHz, 298 K, CD$_2$Cl$_2$) spectra of the isolated compound 25 (top) and the reaction mixture between compound 2 and HB(C$_6$F$_5$)$_2$ after 15 min at r.t. (bottom).

$^{19}$F (470 MHz, 298 K, CD$_2$Cl$_2$) spectra of the isolated compound 25 (top) and the reaction mixture between compound 2 and HB(C$_6$F$_5$)$_2$ after 15 min at r.t. (bottom, ca. 15% residual HB(C$_6$F$_5$)$_2$ as impurity).
Formation of compound 25 from compound 2

![Reaction Scheme](image)

Compound 9 (8.0 mg, 0.035 mmol, 1 eq) was taken up in CD$_2$Cl$_2$ (0.25 ml) at r.t. in a glovebox and HB(C$_6$F$_5$)$_2$ (12.0 mg, 0.035 mmol, 1 eq) added. The resulting solution was transferred to a 3 mm NMR tube and left to stand for 30 min at r.t. before acquisition of the NMR spectra.

**$^1$H NMR** (500 MHz, 298 K, CD$_2$Cl$_2$) spectrum of reaction between compound 9 and HB(C$_6$F$_5$)$_2$ after 30 min at r.t.

**$^{19}$F** (470 MHz, 298 K, CD$_2$Cl$_2$) spectrum of the reaction mixture between compound 9 and HB(C$_6$F$_5$)$_2$ after 30 min at r.t. (ca. 25% residual HB(C$_6$F$_5$)$_2$ as impurity).
Reaction between $\text{B(C}_6\text{F}_5)_3$ and pinacol borane

\[
\text{B(C}_6\text{F}_5)_3 + \text{HBPin} \rightarrow \text{CD}_2\text{Cl}_2
\]

In a glovebox, $\text{B(C}_6\text{F}_5)_3$ (12.6 mg, 0.025 mmol, 1 eq) and pinacol borane (3.2 mg, 0.025 mmol, 1 eq) were mixed in CD$_2$Cl$_2$ (0.25 ml) at r.t. and the resulting solution transferred to a 3 mm NMR tube. The reaction was monitored by $^1\text{H}$, $^{19}\text{F}$ and $^{11}\text{B}$ NMR spectroscopy.

$^1\text{H}$ NMR (400 MHz, 298 K, CD$_2$Cl$_2$) spectrum of the reaction of $\text{B(C}_6\text{F}_5)_3$ with HBPin after 1 h at r.t. (top) and $^1\text{H}$ NMR (600 MHz, 298 K, CD$_2$Cl$_2$) after 18 h at r.t. (bottom).

$^{19}\text{F}$ NMR (376 MHz, 298 K, CD$_2$Cl$_2$) spectrum of the reaction of $\text{B(C}_6\text{F}_5)_3$ with HBPin after 1 h at r.t. (top) and $^{19}\text{F}$ NMR (564 MHz, 298 K, CD$_2$Cl$_2$) after 18 h at r.t. (bottom).
Reaction between HB(C₆F₅)₂ and pinacol borane

\[
\text{HB(C}_6\text{F}_5)_2 + \text{HB} \rightarrow \text{CD}_2\text{Cl}_2
\]

In a glovebox, HB(C₆F₅)₂ (13.5 mg, 0.039 mmol, 1 eq) and pinacol borane (5.0 mg, 0.039 mmol, 1 eq) were mixed in CD₂Cl₂ (0.25 ml) at r.t. and the resulting solution transferred to a 3 mm NMR tube. The reaction was monitored by \(^1\text{H}, \ ^{19}\text{F}\) and \(^{11}\text{B}\) NMR spectroscopy.

\(^{11}\text{B}\) NMR (128 MHz, 298 K, CD₂Cl₂) spectrum of the reaction of B(C₆F₅)₃ with HBPin after 1 h at r.t. (top) and \(^{11}\text{B}\) NMR (192 MHz, 298 K, CD₂Cl₂) after 18 h at r.t. (bottom).

\(^{1}\text{H}\) NMR (400 MHz, 298 K, CD₂Cl₂) spectrum of the reaction of HB(C₆F₅)₂ with HBPin after 1 h at r.t. (top) and after 18 h at r.t. (bottom).
Reaction between MeB(C₆F₅)₂ and pinacol borane

![19F NMR spectrum](image)

$^{19}$F NMR (376 MHz, 298 K, CD₂Cl₂) spectrum of the reaction of HB(C₆F₅)₂ with HBPin after 1 h at r.t. (top) and after 18 h at r.t. (bottom).

![11B NMR spectrum](image)

$^{11}$B NMR (128 MHz, 298 K, CD₂Cl₂) spectrum of the reaction of HB(C₆F₅)₂ with HBPin after 1 h at r.t. (top) and after 18 h at r.t. (bottom).

In a glovebox, MeB(C₆F₅)₂ (7.0 mg, 0.020 mmol, 1 eq) and pinacol borane (2.5 mg, 0.020 mmol, 1 eq) were mixed in CD₂Cl₂ (0.25 ml) at r.t. and the resulting solution transferred to a 3 mm NMR tube. The reaction was monitored by $^1$H, $^{19}$F and $^{11}$B NMR spectroscopy.
Reaction between ClB(C₆F₅)₂ and pinacol borane

\[
\text{ClB(C}_{6}\text{F}_{5})_{2} + \text{HB(O)O} \rightarrow \text{CD}_{2}\text{Cl}_{2}
\]

In a glovebox, ClB(C₆F₅)₂ (7.4 mg, 0.020 mmol, 1 eq) and pinacol borane (2.5 mg, 0.020 mmol, 1 eq) were mixed in CD₂Cl₂ (0.25 ml) at r.t. and the resulting solution transferred to a 3 mm NMR tube. The reaction was monitored by \(^1\text{H}, \, ^{19}\text{F}\) and \(^{11}\text{B}\) NMR spectroscopy.
$^1$H NMR (600 MHz, 298 K, CD$_2$Cl$_2$) spectrum of the reaction of MeB(C$_6$F$_5$)$_2$ with HBPin after 18 h at r.t.

$^{19}$F NMR (564 MHz, 298 K, CD$_2$Cl$_2$) spectrum of the reaction of MeB(C$_6$F$_5$)$_2$ with HBPin after 18 h at r.t.

$^{11}$B NMR (192 MHz, 298 K, CD$_2$Cl$_2$, top) and $^{11}$B/$^1$H NMR (bottom) spectra of the reaction of MeB(C$_6$F$_5$)$_2$ with HBPin after 18 h at r.t.
Non-equilibrium nature between compounds 2 and 24

\[
\begin{align*}
\text{Ph} & \quad \text{O} \quad \text{B(O)} & \quad \text{Ph} \\
\text{Ph} & \quad \text{B}(\text{C}_6\text{F}_5)_2 & \quad \text{Ph} \\
+ & \quad \text{Ph} & \quad \text{B}(\text{C}_6\text{F}_5)_2 & \xrightarrow{\text{CD}_2\text{Cl}_2} & \quad \text{Ph} & \quad \text{B}(\text{C}_6\text{F}_5)_2 \\
& & & & \quad \text{BPin} & \quad \text{Ph} = \text{H}
\end{align*}
\]

\[^1\text{H}\
\]

\[^{19}\text{F}\
\]

\[^1\text{H} \text{ NMR (500 MHz, 298 K, CD}_2\text{Cl}_2) \text{ and } ^{19}\text{F} \text{ (376 MHz, 298 K, CD}_2\text{Cl}_2) \text{ spectra of the reaction between compounds 24 and 2 after 24 h at r.t.}\
\]
Non-equilibrium nature between compounds 6 and 27

\[
\begin{align*}
\text{B(C}_6\text{F}_5)_2 + \text{BPin} & \rightarrow \text{B(C}_6\text{F}_5)_2 + \text{BPin} \\
6 & \quad + \quad 27 & \rightarrow & \quad 28 & \quad + \quad 27
\end{align*}
\]

\[\Delta H\]

\[\Delta F\]

\[\Delta B\]

1H NMR (500 MHz, 298 K, CD$_2$Cl$_2$) and 19F (376 MHz, 298 K, CD$_2$Cl$_2$) spectra of the reaction between compounds 6 and 27 after 24 h at r.t.

3.2 Cross-over experiments

Reaction between compound 25 and p-CF$_3$C$_6$H$_4$-C≡C-H

\[
\begin{align*}
\text{B(O)} & \quad \text{B(O)} \\
\text{Ph} & \quad \text{Ph} \\
25 & \quad \rightarrow & \quad 27 & \quad \text{B(C}_6\text{F}_5)_2 \\
\end{align*}
\]

In a glovebox, compound 25 (8.0 mg, 0.014 mmol, 1 eq) and p-CF$_3$C$_6$H$_4$-C≡C-H (2.4 mg, 0.014 mmol, 1 eq) were mixed in CD$_2$Cl$_2$ (0.25 ml) at r.t. and the resulting solution transferred to a 3 mm NMR tube. The reaction was monitored by 1H, 19F and 11B NMR spectroscopy.
In a glovebox, compound 25 (8.0 mg, 0.014 mmol, 1 eq) and Ph-C≡C-H (1.4 mg, 0.014 mmol, 1 eq) were mixed in CD$_2$Cl$_2$ (0.25 ml) at r.t. and the resulting solution transferred to a 3 mm NMR tube. The reaction was monitored by $^1$H, $^{19}$F and $^{11}$B NMR spectroscopy. After 18 h at r.t. the conversion of 25 was determined to be ca 71% and the product ratio to be 1:1:1.17 (2/24/SP) by $^1$H NMR integration. The tentative assignment of the side product as the 1,1-carboboration product was based on the broad multiplet resonance at $\delta^1$H 2.55, a set of diastereotopic $^1$H NMR resonances of a CH$_2$ group ($\delta^1$H 3.16) and diastereotopic pinacolate-methyl resonances ($\delta^1$H 1.08).
In a glovebox, compound 28 (5.5 mg, 0.009 mmol, 1 eq) and Ph-C≡C-H (1.7 mg, 0.017 mmol, 1 eq) were mixed in CD₂Cl₂ (0.25 ml) at r.t. and the resulting solution transferred to a 3 mm NMR tube. The reaction was monitored by ¹H, ¹⁹F and ¹¹B NMR spectroscopy. After 18 h at r.t. the conversion of 28 was determined to be ca. 45% and the product ratio to be 1:1:8.7 (6/24/29) by ¹H NMR integration. With an excess of alkyne (5 eq, 4 h, r.t.) full conversion of 28 was observed. The tentative assignment of 29 was based on the broad multiplet resonance at δ¹H 2.59, a multiplet resonances of a CH₂ group (δ¹H 3.24) and diastereotopic pinacolate-methyl resonances (δ¹H 1.09). The product could not be isolated.
3.3 Reaction of compound 25 with t-butylisocyanide

In a glovebox, compound 25 (5.5 mg, 0.010 mmol, 1 eq) and t-Bu-NC (1.6 mg, 0.020 mmol, 2 eq) were mixed in CD$_2$Cl$_2$ (0.25 ml) at r.t. and the resulting solution transferred to a 3 mm NMR tube. The product was not isolated.

$^1$H NMR (600 MHz, 298 K, CD$_2$Cl$_2$) spectra of the reaction between compound 25 and t-Bu-NC after 1 h at r.t.
Single crystals of compound 26 were obtained by slow diffusion of a dilute pentane solution of t-Bu-NC into a concentrate CD₂Cl₂ solution of compound 25 at -40 °C.

See CCDC 1484364.
4 Variable temperature NMR studies

4.1 VT NMR study of compound 25

In a glovebox, compound 25 (11 mg, 0.020 mmol, 1 eq) was dissolved in CD$_2$Cl$_2$ (0.25 ml) at r.t. and the resulting solution transferred to a 3 mm NMR tube.

$^1$H NMR (600 MHz, C$_2$D$_2$Cl$_4$) spectra (top) and $^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectra (bottom) compound 25 at variable temperatures.
19F NMR (564 MHz, C$_2$D$_2$Cl$_2$) spectra (top) and 19F NMR (564 MHz, CD$_2$Cl$_2$) spectra (bottom) compound 25 at variable temperatures.

4.2 VT NMR study of the reaction of compound 25 and HBPin

\[
\begin{align*}
\text{Ph} & \quad \text{B(C}_6\text{F}_5)_2 \\
25 & + \quad \text{HBPin} \\
\rightarrow & \quad \text{CD}_2\text{Cl}_2
\end{align*}
\]

In a glovebox, compound 25 (9.5 mg, 0.016 mmol, 1 eq) and pinacol borane (2.1 mg, 0.016 mmol, 1 eq) were mixed in CD$_2$Cl$_2$ (0.25 ml) at r.t. and the resulting solution transferred to a 3 mm NMR tube.
4.3 VT NMR study of the reaction of $\text{B(C}_6\text{F}_5)_3$ and HBPin

$$\text{B(C}_6\text{F}_5)_3 + \text{HBPin} \rightarrow \text{CD}_2\text{Cl}_2$$

In a glovebox, $\text{B(C}_6\text{F}_5)_3$ (9.5 mg, 0.016 mmol, 1 eq) and pinacol borane (2.1 mg, 0.016 mmol, 1 eq) were mixed in $\text{CD}_2\text{Cl}_2$ (0.25 ml) at r.t. and the resulting solution transferred to a 3 mm NMR tube.
1H NMR (600 MHz, CD₂Cl₂) spectra of a 1:1 mixture of B(C₆F₅)₃ and HBPin at variable temperatures.

19F NMR (564 MHz, CD₂Cl₂) spectra of a 1:1 mixture of B(C₆F₅)₃ and HBPin at variable temperatures.

4.4 VT NMR study of the reaction of HB(C₆F₅)₂ and HBPin

In a glovebox, B(C₆F₅)₃ (13.5 mg, 0.04 mmol, 1 eq) and pinacol borane (5.0 mg, 0.04 mmol, 1 eq) were dissolved separately in CD₂Cl₂ (0.25 ml total) at r.t. and layered in a 3 mm NMR tube. The tube was shaken vigorously just before inserting it into the NMR spectrometer, which was precooled to 0 °C.
$^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectra of a 1:1 mixture of HB(C$_6$F$_5$)$_2$ and HBPin at variable temperatures.

$^{19}$F NMR (564 MHz, CD$_2$Cl$_2$) spectra of a 1:1 mixture of HB(C$_6$F$_5$)$_2$ and HBPin at variable temperatures.
5 Catalytic Reactions

5.1 Optimization of the reaction conditions and catalyst screening

Reaction were carried out in NMR tubes and the yield was determined by conversion of starting material from the crude spectra. As a model reaction the hydroboration of 4-ethynyltoluene was chosen (Scheme 1). Under the optimized conditions (Entry 21) the scope reactions were performed for 5 h and 1.2 eq. of pinacol borane to ensure full conversion of alkyne.

It is worth noting that the reaction time can be significantly decreased by heating and/or increased catalyst loading (Entry 9). Lowering catalyst to 1 mol% leads to no (Entry 14) or insufficient (Entry 27) conversion, presumably due to trace water content in the reaction mixture.

\[
\text{\begin{align*}
\text{Reaction} & \quad \text{conditions} \\
\text{Product} & \quad \text{1}
\end{align*}}
\]

Model reaction for optimization studies.

\[\text{Model reaction for optimization studies.}\]

Representative crude $^1H$ NMR spectrum of the reaction in CD$_2$Cl$_2$ (50% conversion of starting material).
<table>
<thead>
<tr>
<th>No</th>
<th>Alkyne</th>
<th>HBpin</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>T</th>
<th>time</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1 mmol</td>
<td>0.1 mmol</td>
<td>-</td>
<td>CDCl₃ (0.5 ml)</td>
<td>60°C</td>
<td>15 h</td>
<td>0%</td>
</tr>
<tr>
<td>2</td>
<td>0.1 mmol</td>
<td>0.1 mmol</td>
<td>-</td>
<td>CD₂Cl₂ (0.5 ml)</td>
<td>50°C</td>
<td>18 h</td>
<td>0%</td>
</tr>
<tr>
<td>3</td>
<td>0.1 mmol</td>
<td>0.1 mmol</td>
<td>-</td>
<td>CD₂Cl₂ (0.5 ml)</td>
<td>60°C</td>
<td>18 h</td>
<td>0%</td>
</tr>
<tr>
<td>4</td>
<td>0.1 mmol</td>
<td>0.1 mmol</td>
<td>5 mol% [Ph₃PF]⁺</td>
<td>CD₂Cl₂ (0.5 ml)</td>
<td>50°C</td>
<td>48 h</td>
<td>0%</td>
</tr>
<tr>
<td>5</td>
<td>0.1 mmol</td>
<td>0.1 mmol</td>
<td>5 mol% [Ph₃PF(C₆H₅)₂]⁺</td>
<td>CDCl₃ (0.5 ml)</td>
<td>60°C</td>
<td>15 h</td>
<td>55%</td>
</tr>
<tr>
<td>6</td>
<td>0.1 mmol</td>
<td>0.1 mmol</td>
<td>5 mol% [MeOC₆H₄CPh₂]⁺</td>
<td>CDCl₃ (0.5 ml)</td>
<td>60°C</td>
<td>15 h</td>
<td>38%</td>
</tr>
<tr>
<td>7</td>
<td>0.1 mmol</td>
<td>0.1 mmol</td>
<td>[Ph₃C][B(C₆F₅)₃]</td>
<td>CDCl₃ (0.5 ml)</td>
<td>60°C</td>
<td>15 h</td>
<td>0%</td>
</tr>
<tr>
<td>8</td>
<td>0.1 mmol</td>
<td>0.1 mmol</td>
<td>5 mol% B(C₆F₅)₃</td>
<td>CDCl₃ (0.5 ml)</td>
<td>60°C</td>
<td>18 h</td>
<td>86%</td>
</tr>
<tr>
<td>9</td>
<td>0.1 mmol</td>
<td>0.1 mmol</td>
<td>10 mol% B(C₆F₅)₃</td>
<td>CDCl₃ (0.5 ml)</td>
<td>r.t.</td>
<td>2 h</td>
<td>74%</td>
</tr>
<tr>
<td>10</td>
<td>0.1 mmol</td>
<td>0.1 mmol</td>
<td>10 mol% B(C₆F₅)₃</td>
<td>CD₂Cl₂ (0.5 ml)</td>
<td>r.t.</td>
<td>2 h</td>
<td>98%</td>
</tr>
<tr>
<td>11</td>
<td>0.1 mmol</td>
<td>0.1 mmol</td>
<td>10 mol% B(C₆F₅)₃</td>
<td>CD₂Cl₂ (0.5 ml)</td>
<td>r.t.</td>
<td>2 h</td>
<td>80%</td>
</tr>
<tr>
<td>12</td>
<td>0.05 mmol</td>
<td>0.055 mmol</td>
<td>5 mol% B(C₆F₅)₃</td>
<td>CD₂Cl₂ (0.25 ml)</td>
<td>r.t.</td>
<td>3.5 h</td>
<td>56%</td>
</tr>
<tr>
<td>13</td>
<td>0.05 mmol</td>
<td>0.055 mmol</td>
<td>2.5 mol% B(C₆F₅)₃</td>
<td>CD₂Cl₂ (0.25 ml)</td>
<td>r.t.</td>
<td>3.5 h</td>
<td>35%</td>
</tr>
<tr>
<td>14</td>
<td>0.05 mmol</td>
<td>0.055 mmol</td>
<td>1.0 mol% B(C₆F₅)₃</td>
<td>CD₂Cl₂ (0.25 ml)</td>
<td>r.t.</td>
<td>2 d</td>
<td>1%</td>
</tr>
<tr>
<td>15</td>
<td>0.1 mmol</td>
<td>0.11 mmol</td>
<td>5 mol% B(C₆F₅)₃</td>
<td>CD₂Cl₂ (0.5 ml)</td>
<td>r.t.</td>
<td>3 h</td>
<td>75%</td>
</tr>
<tr>
<td>16</td>
<td>0.1 mmol</td>
<td>0.11 mmol</td>
<td>5 mol% B(C₆F₅)₃</td>
<td>CD₂Cl₂ (0.5 ml)</td>
<td>r.t.</td>
<td>4 h</td>
<td>81%</td>
</tr>
<tr>
<td>17</td>
<td>0.1 mmol</td>
<td>0.11 mmol</td>
<td>5 mol% B(C₆F₅)₃</td>
<td>CD₂Cl₂ (0.5 ml)</td>
<td>r.t.</td>
<td>16 h</td>
<td>99%</td>
</tr>
<tr>
<td>18</td>
<td>0.1 mmol</td>
<td>0.1 mmol</td>
<td>5 mol% PhCH=CD₂Cl₂</td>
<td>CD₂Cl₂ (0.5 ml)</td>
<td>r.t.</td>
<td>2 h</td>
<td>30%</td>
</tr>
<tr>
<td>19</td>
<td>0.1 mmol</td>
<td>0.1 mmol</td>
<td>MeB(C₆F₅)₂</td>
<td>CD₂Cl₂ (0.5 ml)</td>
<td>r.t.</td>
<td>2 h</td>
<td>57%</td>
</tr>
<tr>
<td>20</td>
<td>0.1 mmol</td>
<td>0.1 mmol</td>
<td>ClB(C₆F₅)₂</td>
<td>CD₂Cl₂ (0.5 ml)</td>
<td>r.t.</td>
<td>2 h</td>
<td>99%</td>
</tr>
<tr>
<td>21</td>
<td>0.05 mmol</td>
<td>0.055 mmol</td>
<td>5 mol% HB(C₆F₅)₂</td>
<td>CD₂Cl₂ (0.25 ml)</td>
<td>r.t.</td>
<td>30 min</td>
<td>99%</td>
</tr>
<tr>
<td>22</td>
<td>0.05 mmol</td>
<td>0.055 mmol</td>
<td>2.5 mol% HB(C₆F₅)₂</td>
<td>CD₂Cl₂ (0.25 ml)</td>
<td>r.t.</td>
<td>30 min</td>
<td>89%</td>
</tr>
<tr>
<td>23</td>
<td>0.05 mmol</td>
<td>0.055 mmol</td>
<td>2.5 mol% HB(C₆F₅)₂</td>
<td>CD₂Cl₂ (0.25 ml)</td>
<td>r.t.</td>
<td>2 h</td>
<td>96%</td>
</tr>
<tr>
<td>24</td>
<td>0.05 mmol</td>
<td>0.055 mmol</td>
<td>1.0 mol% HB(C₆F₅)₂</td>
<td>CD₂Cl₂ (0.25 ml)</td>
<td>r.t.</td>
<td>30 min</td>
<td>34%</td>
</tr>
<tr>
<td>25</td>
<td>0.05 mmol</td>
<td>0.055 mmol</td>
<td>1.0 mol% HB(C₆F₅)₂</td>
<td>CD₂Cl₂ (0.25 ml)</td>
<td>r.t.</td>
<td>2 h</td>
<td>44%</td>
</tr>
<tr>
<td>26</td>
<td>0.05 mmol</td>
<td>0.055 mmol</td>
<td>1.0 mol% HB(C₆F₅)₂</td>
<td>CD₂Cl₂ (0.25 ml)</td>
<td>r.t.</td>
<td>5 h</td>
<td>47%</td>
</tr>
<tr>
<td>27</td>
<td>0.05 mmol</td>
<td>0.055 mmol</td>
<td>1.0 mol% HB(C₆F₅)₂</td>
<td>CD₂Cl₂ (0.25 ml)</td>
<td>r.t.</td>
<td>24 h</td>
<td>51%</td>
</tr>
</tbody>
</table>

Conversion determined by ¹H NMR integration of characteristic resonances.

¹⁹F NMR spectra of selected optimization reactions with different catalysts illustrating the decomposition/transformation of the added catalyst.
$^{19}$F (470 MHz, 298 K, CD$_2$Cl$_2$) spectra of the model reaction with different catalysts during the reaction: B(C$_6$F$_5$)$_3$.

MeB(C$_6$F$_5$)$_2$, ClB(C$_6$F$_5$)$_2$, HB(C$_6$F$_5$)$_2$ (top to bottom).

Stacked $^1$H-NMR (600 MHz, CD$_2$Cl$_2$) spectra of the reaction solutions from the catalytic hydroboration of phenylacetylene employing [o-Ph$_2$PF(Ph)BCy$_3$][B(C$_6$F$_5$)$_4$] (top) and [Ph$_3$PF][B(C$_6$F$_5$)$_4$] (bottom).
5.2 General procedure

General procedure for the synthesis of alkenyl boranes: All work was performed in a glove box with a dry nitrogen atmosphere. CH\textsubscript{2}Cl\textsubscript{2} and the respective alkyne were filtered through a short pad of silica before used for catalysis. In a screw cap vial pinacol borane (1.2 eq) and alkyne (1.0 eq.) were dissolved in 2.5 ml of CH\textsubscript{2}Cl\textsubscript{2} before addition of a catalytic amount of HB(C\textsubscript{6}F\textsubscript{5})\textsubscript{2} (5 mol\%). After sealing the tube with a screw cap and electrical tape the reaction was standing in the glove box (in case of heating outside of the glove box) without stirring. After the indicated time an aliquot of the reaction was taken by dipping a pipette into the reaction solution. This aliquot was diluted with CDCl\textsubscript{3} and subjected to \textsuperscript{1}H NMR analysis to determine the ratio of isomers.

The crude reaction mixture was filtered through a short pad of silica and was flushed with CH\textsubscript{2}Cl\textsubscript{2} and the combined solutions evaporated to dryness. The respective alkenyl boranes were obtained without further purification.

5.3 Product data

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

According to the general procedure 4-ethylnyltoluene (58 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and HB(C\textsubscript{6}F\textsubscript{5})\textsubscript{2} (9 mg, 5 mol\%) were dissolved in CH\textsubscript{2}Cl\textsubscript{2} (2.5 ml) and reacted for 5 h at rt. Crude NMR studies showed greater 99\% conversion and alkenyl borane \textsuperscript{1} was isolated in 99\% (119 mg, 0.49 mmol) yield as a pale yellow oil. The NMR data was consistent with the literature.$^{50}$
Rf (hexanes/ether; 90/10) = 0.40.

$^1$H NMR (400 MHz, 298 K, CDCl$_3$): $\delta^1$H: 7.39 (d, $^3$$J_{HH}$ = 8.0 Hz, 2H), 7.38 (d, $^3$$J_{HH}$ = 18.5 Hz, 1H), 7.14 (d, $^3$$J_{HH}$ = 8.0 Hz, 2H), 6.11 (d, $^3$$J_{HH}$ = 18.5 Hz, 1H), 2.35 (s, 3H), 1.31 (s, 12H).

$^{13}$C($^1$H) NMR (126 MHz, 298 K, CDCl$_3$): $\delta^{13}$C: 149.5, 138.9, 134.8, 129.3, 127.0, 115.1 (br s), 83.3, 24.8, 21.3.

$^{11}$B NMR (128 MHz, CDCl$_3$): $\delta^{11}$B: 30.1 ($\nu_{1/2}$ ≈ 380 Hz).

HRMS (DART-TOF+): mass [M+H] calcd. for C$_{15}$H$_{22}$B$_1$O$_2$ 245.17128 Da, found: 245.17134 Da.

$^1$H NMR (400 MHz, 298 K, CDCl$_3$) and $^{11}$B (128 MHz, 298 K, CDCl$_3$) spectra of compound 1.

$^{13}$C($^1$H) NMR (126 MHz, 298 K, CDCl$_3$) spectrum of compound 1.

(2) (E)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane

According to the general procedure phenylacetylene (51 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and HBCF (9 mg, 5 mol%) were dissolved in CH$_2$Cl$_2$ (2.5 ml) and reacted for 5 h at rt. Crude NMR studies showed greater 99% conversion and alkenyl borane 2 was isolated in 90% (104 mg, 0.45 mmol) yield as a pale yellow oil. The $^1$H NMR data was consistent with the literature.[S10]


\( R_f \) (hexanes/ether; 90/10) = 0.52.

\(^1\text{H NMR}\) (500 MHz, 298 K, CDCl\(_3\)): \( \delta^1\text{H} \): 7.49 (m, 2H), 7.40 (d, \( ^3J_{\text{HH}} = 18.5 \text{ Hz}, 1\text{H} \)), 7.33 (m, 2H), 7.31 (m, 1H), 6.17 (d, \( ^3J_{\text{HH}} = 18.4 \text{ Hz}, 1\text{H} \)), 1.32 (s, 12H).

\(^{13}\text{C}\{^1\text{H}\} \text{ NMR}\) (126 MHz, 298 K, CDCl\(_3\)): \( \delta^{13}\text{C} \): 149.5, 137.4, 128.9, 128.5, 127.0, 116.3, 83.3, 24.8.

\(^{11}\text{B NMR}\) (128 MHz, CDCl\(_3\)): \( \delta^{11}\text{B} \): 30.2 (\( \nu_{1/2} \approx 380 \text{ Hz} \)).

\( \text{HRMS (DART-TOF+)} \): mass [M+H] calcd. for C\(_{14}\)H\(_{20}\)B\(_1\)O\(_2\) 231.15563 Da, found: 231.15530 Da.

\(^1\text{H NMR}\) (500 MHz, 298 K, CDCl\(_3\)) and \(^{11}\text{B}\) (128 MHz, 298 K, CDCl\(_3\)) spectra of compound 2.

\(^{13}\text{C}\{^1\text{H}\} \text{ NMR}\) (126 MHz, 298 K, CDCl\(_3\)) spectrum of compound 2.

(3) (\( E \))-2-(2-([1,1'-biphenyl]-4-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

According to the general procedure 4-ethynyl-1,1'-biphenyl (89 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and HB(C\(_6\)F\(_5\))\(_2\) (9 mg, 5 mol%) were dissolved in CH\(_2\)Cl\(_2\) (2.5 ml) and reacted for 5 h at rt. Crude NMR studies showed greater 99\% conversion and alkenyl borane 3 was isolated in 97\% (149 mg, 0.49 mmol) yield as a yellow solid. The NMR data was consistent with the one previously reported.\(^{[1]}\)

---

2551.
R_f (hexanes/ether; 90/10) = 0.35.

1H NMR (500 MHz, 298 K, CDCl_3): \( \delta^1H: 7.62 - 7.54 \) (m, 6H), 7.47 - 7.41 (m, 3H), 7.37 - 7.32 (m, 1H), 6.21 (d, \( 3J_{HH} = 18.4 \) Hz, 1H), 1.33 (s, 12H).

13C{^1H} NMR (126 MHz, 298 K, CDCl_3): \( \delta^{13C}: 149.0, 141.6, 140.6, 136.5, 128.8, 127.5, 127.4, 127.3, 127.0, 116.3 \) (br, =CH\(^B\)), 83.4, 24.8.

11B NMR (128 MHz, CDCl_3): \( \delta^{11B}: 30.1 \) (\( v_{1/2} = 400 \) Hz).

HRMS (DART-TOF+): mass [M+H] calcd. for \( C_{20}H_{24}B_1O_2 \) 307.18693 Da, found: 307.18622 Da.

1H NMR (500 MHz, 298 K, CDCl_3) and 11B NMR (128 MHz, 298 K, CDCl_3) spectra of compound 3.

\( ^{13}C{^1H} \) NMR (126 MHz, 298 K, CDCl_3) spectrum of compound 3.

(4) \((E)-2-(4-(tert-butyl)styryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane\)

According to the general procedure 1-(tert-butyl)-4-ethynylbenzene (79 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and HB(C_6F_5)_2 (9 mg, 5 mol%) were dissolved in CH_2Cl_2 (2.5 ml) and reacted for 5 h at rt. Crude NMR studies showed greater 99% conversion and alkenyl borane 4 was isolated in 87% (129 mg, 0.45 mmol) yield as a yellow solid.

R_f (hexanes/ether; 90/10) = 0.51.

1H NMR (500 MHz, 298 K, CDCl_3): \( \delta^1H: 7.43 \) (m, 2H, o-Ar), 7.38 (d, \( 3J_{HH} = 18.4 \) Hz, =CH\(^A\)), 7.36 (m, 2H, m-Ar) 6.12 (d, \( 3J_{HH} = 18.4 \) Hz, 1H, =CH\(^B\)), 1.314 (s, 9H, t-Bu\(^1\)), 1.313 (s, 12H, CH\(^3\))\(^1\) tentatively
assigned.

\[ ^{13}\text{C}\{^1\text{H}\} \text{NMR} (126 \text{ MHz}, 298 \text{ K, CDCl}_3): \delta^{13}\text{C}: 152.1 (p-\text{Ar}), 149.4 (=\text{CH}^\alpha), 134.8 (i-\text{Ar}), 126.8 (o-\text{Ar}), 125.5 (m-\text{Ar}), 83.3 (\text{OCH}_2), 34.7 (t-\text{Bu}^C), 31.2 (t-\text{Bu}^{CH_3}), 24.8 (\text{CH}_3). \text{ I tentatively assigned. N.o. =CH}^B \]

\[ ^1\text{H},^{13}\text{C} \text{ GHSQC} (700 \text{ MHz} / 176 \text{ MHz}, 300 \text{ K, CDCl}_3): \delta^1\text{H} / \delta^{13}\text{C}: 7.43 / 126.8 (o-\text{Ar}), 7.38 / 149.4 (=\text{CH}^\alpha), 7.36 / 125.5 (m-\text{Ar}), 1.31 / 31.2, 24.8 (t-\text{Bu}^{CH_3} \text{ and } \text{CH}_3). \text{ N. o. =CH}^B \]

\[ ^1\text{H},^{13}\text{C} \text{ GHMBC} (700 \text{ MHz} / 176 \text{ MHz}, 300 \text{ K, CDCl}_3) \text{ [selected traces]: } \delta^1\text{H} / \delta^{13}\text{C}: 7.43 / 152.1, 149.4, 126.8 (o-\text{Ar} / p-\text{Ar}, =\text{CH}^\alpha, o-\text{Ar}), 7.38 / 126.8 (=\text{CH}^\alpha / o-\text{Ar}), 7.36 / 134.8, 125.5, 31.2 (m-\text{Ar} / i-\text{Ar}, m-\text{Ar}, t-\text{Bu}^C). \]

\[ ^{11}\text{B} \text{ NMR} (128 \text{ MHz, CDCl}_3): \delta^{11}\text{B}: 29.6 (\nu_{1/2} = 380 \text{ Hz}). \]

HRMS (DART-TOF+): mass [M+H] calcd. for C_{18}H_{28}B_{1}O_{2} 287.21823 Da, found: 287.21879 Da.

(5) \((E)-2-(4\text{-methoxystyryl})-4,4,5,5\text{-tetramethyl-1,3,2-dioxaborolane}\)

\[ \text{According to the general procedure 1-ethynyl-4-methoxybenzene (51 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and HB(C_6F_5)_2 (9 mg, 5 mol%) were dissolved in CH}_2Cl_2 (2.5 ml) and reacted for 5 h at rt. Crude NMR studies showed greater 99\% conversion and} \]
alkenyl borane 5 was isolated in 80% (105 mg, 0.47 mmol) yield as light purple solid. The obtained NMR data is consistent with the values reported in the literature.\textsuperscript{[S11]}

\( R_f \) (hexanes/ether; 90/10) = 0.27.

\( ^1H \) NMR (500 MHz, 298 K, CDCl\(_3\)): \( \delta^1H: 7.43 \) (m, 2H), 7.35 (d, \( ^3J_{HH} = 18.4 \) Hz, 1H), 6.86 (m, 2H), 6.01 (d, \( ^3J_{HH} = 18.4 \) Hz, 1H), 3.81 (s, 3H), 1.31 (s, 12H).

\( ^{13}C\{^1H\} \) NMR (126 MHz, 298 K, CDCl\(_3\)): \( \delta^{13}C: 160.3, 149.0, 130.4, 128.5, 114.0, 113.6 \) (br, =CH\(_B\)), 83.2, 55.3, 24.6.

\( ^{11}B \) NMR (128 MHz, 298 K, CDCl\(_3\)): \( \delta^{11}B: 30.1 \) (\( \nu_{1/2} \approx 380 \) Hz).

HRMS (DART-TOF+): mass [M+H] calcd. for C\(_{15}\)H\(_{22}\)B\(_1\)O\(_3\) 261.16620 Da, found: 261.16643 Da.

(6) (E)-4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)styryl)-1,3,2-dioxaborolane

\[
\text{According to the general procedure 4-ethynyltrifluorotoluene (51 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and HBCF (9 mg, 5 mol%) were dissolved in CH}_2\text{Cl}_2 \text{ (2.5 ml)}
\]

and reacted for 5 h at rt. Crude NMR studies showed greater 99% conversion and alkenyl borane 6 was isolated in 94% (139 mg, 0.47 mmol) yield as a yellow solid. The NMR data was consistent with the literature.\[^{S12}\]

\[
R_f\text{ (hexanes/ether; 90/10) = 0.36.}
\]

\(^1H\text{ NMR (500 MHz, 298 K, CDCl}_3\text{): }\delta^1H: 7.58 \text{ (m, 4H), } 7.40 \text{ (d, } ^3J_{HH} = 18.4 \text{ Hz, 1H), } 6.26 \text{ (d, } ^3J_{HH} = 18.4 \text{ Hz, 1H), } 1.32 \text{ (s, 12H).}
\]

\(^{13}C\{^1H\}\text{ NMR (126 MHz, 298 K, CDCl}_3\text{): }\delta^{13}C: 147.6, 140.8, 130.4 \text{ (q, } ^2J_{FC} = 32.4 \text{ Hz), } 127.1, 125.5 \text{ (q, } ^3J_{FC} = 3.8 \text{ Hz), } 124.1 \text{ (q, } ^1J_{FC} = 272.0 \text{ Hz), } 119.4 \text{ (br), } 83.6, 24.8.
\]

\(^{11}B\text{ NMR (128 MHz, CDCl}_3\text{): }\delta^{11}B: 30.0 \text{ ( } \nu_{1/2} = 300 \text{ Hz).}
\]

\(^{19}F\text{ NMR (377 MHz, CDCl}_3\text{): }\delta^{19}F: -62.6.
\]

HRMS (DART-TOF\(+\)): mass [M+H] calcd. for C\(_{15}\)H\(_{19}\)B\(_{1}\)F\(_{3}\)O\(_{2}\) 299.14302 Da, found: 299.14273 Da.

---

(7) Methyl (E)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzoate

According to the general procedure methyl 4-ethynylbenzoate (80 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and HB(C₆F₅)₂ (9 mg, 5 mol%) were dissolved in CH₂Cl₂ (2.5 ml) and reacted for 5 h at rt. Crude NMR studies showed greater 99% conversion and the alkenyl borane 7 was isolated in 86% (125 mg, 0.43 mmol) yield as a pale yellow solid. The NMR data was consistent with the one previously reported.¹¹³

Rᵣ (hexanes/ether; 90/10) = 0.15.

¹¹H NMR (500 MHz, 298 K, CDCl₃): δ¹¹H: 8.00 (m, 2H), 7.53 (m, 2H), 7.41 (d, ³JHH = 18.4 Hz, 1H), 6.27 (d, ³JHH = 18.4 Hz, 1H), 3.91 (s, 3H), 1.32 (s, 12H).

¹³C{'¹H} NMR (126 MHz, 298 K, CDCl₃): δ¹³C: 166.8, 148.1, 141.7, 130.1, 129.9, 126.9, 83.6, 52.1, 24.8. N.o. =C'B

¹¹B NMR (128 MHz, CDCl₃): δ¹¹B: 30.2 (ν₁/₂ ≈ 380 Hz).


¹¹H NMR (500 MHz, 298 K, CDCl₃) and ¹¹B (128 MHz, 298 K, CDCl₃) spectra of compound 7.

¹³C{'¹H} NMR (126 MHz, 298 K, CDCl₃) spectrum of compound 7.

(8) (E)-2-(3,5-difluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

According to the general procedure 1-ethynyl-3,5-difluorobenzene (69 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and HB(C\textsubscript{6}F\textsubscript{5})\textsubscript{2} (9 mg, 5 mol%) were dissolved in CH\textsubscript{2}Cl\textsubscript{2} (2.5 ml) and reacted for 5 h at rt. Crude NMR studies showed greater 99% conversion and alkenyl borane 8 was isolated in 96% (127 mg, 0.48 mmol) yield as a colorless oil.

R\textsubscript{f} (hexanes/ether; 90/10) = 0.62.

\textit{\textsuperscript{1}H NMR} (500 MHz, 298 K, CDCl\textsubscript{3}): \textsuperscript{\delta}\textsuperscript{1}H: 7.26 (d, \textsuperscript{3}J\textsubscript{HH} = 18.3 Hz, 1H, =CH\textsubscript{Ar}), 6.97 (m, 2H, o-Ar), 6.15 (d, \textsuperscript{3}J\textsubscript{HH} = 18.3 Hz, 1H, =CH\textsuperscript{B}), 1.31 (s, 12H, CH\textsubscript{3}).

\textit{\textsuperscript{13}C{\textsuperscript{1}H}} NMR (126 MHz, 298 K, CDCl\textsubscript{3}): \textsuperscript{\delta}\textsuperscript{13}C: 163.1 (dd, \textsuperscript{1}J\textsubscript{FC} = 248.1 Hz, \textsuperscript{3}J\textsubscript{FC} = 12.9 Hz, m-Ar), 146.8 (t, \textsuperscript{4}J\textsubscript{FC} = 2.7 Hz, =CH\textsuperscript{Ar}), 140.9 (t, \textsuperscript{3}J\textsubscript{FC} = 9.2 Hz, i-Ar), 119.3 (br, =CH\textsuperscript{B}), 109.6 (dd, \textsuperscript{2}J\textsubscript{FC} = 19.4 Hz, \textsuperscript{4}J\textsubscript{FC} = 5.8 Hz, o-Ar), 103.9 (t, \textsuperscript{2}J\textsubscript{FC} = 25.7 Hz, p-Ar), 83.6 (s, OCMe\textsubscript{2}), 24.8 (s, CH\textsubscript{3}).

\textit{\textsuperscript{1}H,\textsuperscript{13}C GHSQC} (700 MHz / 176 MHz, 300 K, CDCl\textsubscript{3}): \textsuperscript{\delta}\textsuperscript{1}H / \textsuperscript{\delta}\textsuperscript{13}C: 7.26 / 146.8 (=CH\textsuperscript{Ar}), 6.97 / 109.6 (o-Ar), 6.73 / 103.9 (p-Ar), 1.31 / 24.8 (CH\textsubscript{3}). N. o. =CH\textsuperscript{B}

\textit{\textsuperscript{1}H,\textsuperscript{13}C GHMBC} (700 MHz / 176 MHz, 300 K, CDCl\textsubscript{3}) [selected traces]: \textsuperscript{\delta}\textsuperscript{1}H / \textsuperscript{\delta}\textsuperscript{13}C: 7.26 / 140.9, 109.6 (=CH\textsuperscript{Ar} / i-Ar, o-Ar), 6.97 / 163.1, 146.8, 109.6 (o-Ar / m-Ar, =CH\textsuperscript{Ar}, o-Ar), 6.15 / 146.8, 140.9 (=CH\textsuperscript{B} / =CH\textsuperscript{Ar}, i-Ar).

\textit{\textsuperscript{19}F NMR} (377 MHz, CDCl\textsubscript{3}): \textsuperscript{\delta}\textsuperscript{19}F: -110.1 (t, \textsuperscript{3}J\textsubscript{FH} = 8.8 Hz).

\textit{\textsuperscript{11}B NMR} (128 MHz, CDCl\textsubscript{3}): \textsuperscript{\delta}\textsuperscript{11}B: 29.9 (\nu_{1/2} = 340 Hz).

\textit{HRMS} (DART-TOF\textsuperscript{+}): mass [M+H] calcd. for C\textsubscript{14}H\textsubscript{18}B\textsubscript{1}F\textsubscript{2}O\textsubscript{2} 267.13679 Da, found: 267.13714 Da.

\textsuperscript{1}H NMR (500 MHz, 298 K, CDCl\textsubscript{3}), \textsuperscript{11}B (128 MHz, 298 K, CDCl\textsubscript{3}) and \textsuperscript{19}F (376 MHz, 298 K, CDCl\textsubscript{3}) spectra of compound 8.
(9) (E)-4,4,5,5-tetramethyl-2-(2,4,6-trimethylstyryl)-1,3,2-dioxaborolane

According to the general procedure 2-ethynyl-1,3,5-trimethylbenzene (72 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and HB(C\(_6\)F\(_5\))\(_2\) (9 mg, 5 mol%) were dissolved in CH\(_2\)Cl\(_2\) (2.5 ml) and reacted for 5 h at rt. Crude NMR studies showed greater 99% conversion and alkenyl borane 9 was isolated in 94% (128 mg, 0.47 mmol) yield as orange solid.

R\(_f\) (hexanes/ether; 90/10) = 0.54.

**\(^1\)H NMR** (500 MHz, 298 K, CDCl\(_3\)): \(\delta\)\(^1\)H: 7.44 (d, \(J = 18.8\) Hz, 1H), 6.86 (s, 2H), 5.68 (d, \(J = 18.8\) Hz, 1H), 2.30 (s, 6H), 2.27 (s, 3H), 1.32 (s, 12H).

**\(^{13}\)C\(^{1}\)H NMR** (126 MHz, 298 K, CDCl\(_3\)): \(\delta^{13}\)C: 148.5, 136.7, 135.9, 135.1, 128.7, 83.2, 24.8, 21.0, 20.9. N.o. =CH\(^8\)

**\(^{11}\)B NMR** (128 MHz, CDCl\(_3\)): \(\delta^{11}\)B: 29.8 (\(\nu_{1/2} \approx 390\) Hz).


**\(^1\)H NMR (500 MHz, 298 K, CDCl\(_3\)) and \(^{11}\)B NMR (128 MHz, 298 K, CDCl\(_3\)) spectra of compound 9.**
According to the general procedure 3-ethynylthiophene (54 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and HB(C₆F₅)₂ (9 mg, 5 mol%) were dissolved in CH₂Cl₂ (2.5 ml) and reacted for 5 h at rt. Crude NMR studies showed greater 99% conversion and alkenyl borane 10 was isolated in 98% (117 mg, 0.49 mmol) yield as a pale yellow oil. The NMR data was consistent with the values reported in the literature.¹⁴

Rᶠ (hexanes/ether; 90/10) = 0.43.

¹H NMR (500 MHz, 298 K, CDCl₃): ²ⁱH: 7.38 (d, ³J_HH = 18.3 Hz, 1H), 7.31 (m, 1H), 7.29 (m, 1H), 7.26 (m, 1H), 5.94 (d, ³J_HH = 18.3 Hz, 1H), 1.30 (s, 12H).

¹³C{¹H} NMR (126 MHz, 298 K, CDCl₃): δ¹³C: 143.1, 141.2, 126.1, 125.0, 124.8, 116.1 (br, =CHB), 83.3, 24.8.

¹¹B NMR (128 MHz, 298 K, CDCl₃): δ¹¹B: 30.2 (ν₁₂ = 300 Hz).


According to the general procedure 1-ethynylcyclohex-1-ene (53 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and HB(C₆F₅)₂ (9 mg, 5 mol%) were dissolved in CH₂Cl₂ (2.5 ml) and reacted for 5 h at rt. Crude NMR studies showed greater 99% conversion and alkenyl borane 11 was isolated in 94% (109 mg, 0.49 mmol) yield as a yellow oil. The NMR data was consistent with the values reported in the literature.[S12]

Rᵣ (hexanes/ether; 90/10) = 0.62.

**¹H NMR** (500 MHz, 298 K, CDCl₃): δ¹H: 7.02 (d, ³J_HH = 18.3 Hz, 1H), 5.95 (m, 1H), 5.42 (dd, ³J_HH = 18.3, ⁴J_HH = 0.6 Hz, 1H), 2.14 (m, 4H), 1.65 (m, 2H), 1.59 (m, 2H), 1.27 (s, 12H).

**¹³C{¹H} NMR** (126 MHz, 298 K, CDCl₃): δ¹³C: 153.2, 137.1, 134.3, 111.9 (br, =CHBO), 83.0, 26.2, 24.8, 23.7, 22.4, 22.3.

**¹¹B NMR** (128 MHz, 298 K, CDCl₃): δ¹¹B: 30.3 (ν₁/₂ = 300 Hz).

**HRMS (EI-TOF+):** mass [M+H] calcd. for C₁₄H₂₃B₂O₂ 234.1791 Da, found: 234.1797 Da.
1H NMR (500 MHz, 298 K, CDCl₃) and ¹¹B NMR (128 MHz, 298 K, CDCl₃) spectra of compound 11.

¹³C{¹H} NMR (126 MHz, 298 K, CDCl₃) spectrum of compound 11.

(12) (E)-2-(6-chlorohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

According to the general procedure 6-chlorohex-1-yne (58 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and HB(C₆F₅)₂ (9 mg, 5 mol%) were dissolved in CH₂Cl₂ (2.5 ml) and reacted for 5 h at rt. Crude NMR studies showed greater 99% conversion and alkenyl borane 12 was isolated in 90% (109 mg, 0.45 mmol) yield as a colorless oil. The NMR data was consistent with literature reported values.[S15]

Rᵣ (hexanes/ether; 90/10) = 0.38.

¹¹B NMR (128 MHz, CDCl₃): δ¹¹B: 29.7 (ν₁/₂ ≈ 300 Hz).

HRMS (DART-TOF+): mass [M+H] calcd. for C₁₂H₂₃B₁Cl₁O₂ 245.14796 Da, found: 245.114759 Da.

(13) (1E,7E)-1,8-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octa-1,7-diene

According to the general procedure octa-1,7-diyne (53 mg, 0.50 mmol, 1.0 eq.), pinacol borane (154 mg, 1.20 mmol, 2.4 eq.) and HB(C₅F₅)₂ (17 mg, 10 mol%) were dissolved in CH₂Cl₂ (2.5 ml) and reacted for 18 h at rt. Crude NMR studies showed greater 99% conversion and alkenyl boronic ester 13 was isolated in 99% (180 mg, 0.50 mmol) yield as a colorless solid. The NMR data was consistent with the values reported in the literature.\textsuperscript{[S15]}

\[ R_f \ (n\text{-pentane/ether; 97/3}) = 0.12. \]

\textbf{1H NMR} (500 MHz, 298 K, CDCl₃): δ\textsuperscript{1}H: 6.60 (dt, \( ^3J_{HH} = 17.9 \) Hz, \( ^3J_{HH} = 6.5 \) Hz, 1H), 5.41 (dt, \( ^3J_{HH} = 17.9 \) Hz, \( ^4J_{HH} = 1.6 \) Hz, 1H), 2.15 (m, 2H), 1.43 (m, 2H), 1.26 (s, 12H).

\textbf{13C\textsuperscript{1H} NMR} (126 MHz, 298 K, CDCl₃): δ\textsuperscript{13}C: 154.4, 118.6 (br, =CH\textsuperscript{B}), 83.0, 35.6, 27.8, 24.8.

\textbf{11B NMR} (128 MHz, 298 K, CDCl₃): δ\textsuperscript{11}B: 29.5 (\( \nu_{1/2} = 380 \) Hz).

\textbf{HRMS (DART-TOF+)}: mass [M+NH\textsubscript{4}] calcd. for C\textsubscript{20}H\textsubscript{38}B\textsubscript{2}N\textsubscript{4}O\textsubscript{4} 380.31434 Da, found: 380.31542 Da.
According to the general procedure 2-(hex-5-yne-1-yl)isoindoline-1,3-dione (114 mg, 0.50 mmol, 1.0 eq.), pinacolborane (77 mg, 0.55 mmol, 1.2 eq.) and HBCF (9 mg, 5 mol%) were dissolved in CH₂Cl₂ (2.5 ml) and reacted for 18 h at rt. Crude NMR studies showed greater 99% conversion and alkenyl borane 14 was isolated in 96% (170 mg, 0.48 mmol) yield as a colorless oil.

**Rf** (hexanes/ether; 80/20) = 0.14.

**¹H NMR** (500 MHz, 298 K, CDCl₃): δ¹H: 7.83 (m, 2H), 7.71 (m, 2H), 6.58 (dt, ³JHH = 17.9 Hz, ⁴JHH = 6.5 Hz, 1H), 5.42 (dt, ³JHH = 17.9 Hz, ⁴JHH = 1.6 Hz, 1H), 3.68 (t, ³JHH = 7.2 Hz, 2H), 2.19 (m, 2H), 1.69 (m, 2H), 1.47 (m, 2H), 1.25 (s, 12H).

**¹³C{¹H} NMR** (126 MHz, 298 K, CDCl₃): δ¹³C: 168.4, 153.6, 133.8, 132.1, 123.2, 119.0 (br, =CHₓ), 83.0, 37.8, 35.3, 28.2, 25.5, 24.8.

**¹¹B NMR** (128 MHz, 298 K, CDCl₃): δ¹¹B: 29.5 (ν₁/₂ = 400 Hz).

H NMR (500 MHz, 298 K, CDCl$_3$) and $^{11}$B NMR (128 MHz, 298 K, CDCl$_3$) spectra of compound 14.

$^{13}$C{$_1^H$} NMR (126 MHz, 298 K, CDCl$_3$) spectrum of compound 14.

(15) (E)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-ene-nitrile

According to the general procedure hex-5-ynenitrile (47 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and HB(C$_6$F$_5$)$_2$ (17 mg, 10 mol%) were dissolved in CH$_2$Cl$_2$ (2.5 ml) and reacted for 18 h at 50 °C. Crude NMR studies showed greater 99% conversion and alkenyl boronic ester 15 was isolated in 99% (110 mg, 0.50 mmol) yield as a yellow oil. The NMR data was consistent with the values reported in the literature.$^{[S16]}$

R$_f$ (n-pentane/ether; 85/15) = 0.19.

$^{1}$H NMR (500 MHz, 298 K, CDCl$_3$): $\delta^1$H: 6.53 (dt, $^3$J$_{HH}$ = 18.0 Hz, $^3$J$_{HH}$ = 6.5 Hz, 1H), 5.49 (dt, $^3$J$_{HH}$ = 18.0 Hz, $^4$J$_{HH}$ = 1.6 Hz, 1H), 2.34 (t, $^3$J$_{HH}$ = 7.2 Hz, 2H), 2.30 (m, 2H), 1.79 (p, $^3$J$_{HH}$ = 7.3 Hz, 2H), 1.26 (s, 12H).

$^{13}$C{$_1^H$} NMR (126 MHz, 298 K, CDCl$_3$): $\delta^{13}$C: 150.8, 120.8 (br, =CH$_B$), 119.4, 83.2, 34.2, 24.7, 23.9, 16.5.

$^{11}$B NMR (128 MHz, 298 K, CDCl$_3$): $\delta^{11}$B: 29.5 ($\nu_{1/2} = 330$ Hz).

HRMS (DART-TOF+): mass [M+H] calcd. for C$_{12}$H$_{21}$B$_1$N$_1$O$_2$ 222.16653 Da, found: 222.16641 Da.

$^1$H NMR (500 MHz, 298 K, CDCl$_3$) and $^{11}$B NMR (128 MHz, 298 K, CDCl$_3$) spectra of compound 15.

$^{13}$C($^1$H) NMR (126 MHz, 298 K, CDCl$_3$) spectrum of compound 15.

(16) (E)-trimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane

According to the general procedure ethynyltrimethylsilane (49 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and HB(C$_6$F$_5$)$_2$ (9 mg, 5 mol%) were dissolved in CH$_2$Cl$_2$ (2.5 ml) and reacted for 18 h at rt. Crude NMR studies showed greater 79% conversion and alkenyl borane 16 was isolated in 76% (86 mg, 0.38 mmol) yield as a pale yellow oil. The NMR data was consistent values reported in the literature.$^{[S17]}$

R$_f$ (n-pentane/ether; 97/3) = 0.67.

$^1$H NMR (500 MHz, 298 K, CDCl$_3$): $\delta^{1}$H: 7.11 (d, $^3$J$_{HH} = 21.8$ Hz, 1H), 6.24 (d, $^3$J$_{HH} = 21.8$ Hz, 1H), 1.27 (s, 12H), 0.07 (s, 9H).

$^{13}$C($^1$H) NMR (126 MHz, 298 K, CDCl$_3$): $\delta^{13}$C: 157.9, 136.7 (br, =CH$_{B}$), 83.4, 24.8, −1.9.

$^{11}$B NMR (128 MHz, 298 K, CDCl$_3$): $\delta^{11}$B: 28.9 ($v_{1/2} = 300$ Hz).

$^{29}$Si-dept (80 MHz, 298 K, CDCl$_3$): $\delta^{29}$Si: −6.7.

HRMS (DART-TOF+): mass [M+H] calcd. for C$_{11}$H$_{24}$B$_1$O$_2$Si$_1$, 227.16386 Da, found: 227.16352 Da.

(17) (Z)-4,4,5,5-tetramethyl-2-(1-phenylhex-1-en-2-yl)-1,3,2-dioxaborolane

According to the general procedure hex-1-yn-1-ylbenzene (79 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and HB(C₆F₅)₂ (9 mg, 5 mol%) were dissolved in CH₂Cl₂ (2.5 ml) and reacted for 18 h at 50 °C. Crude NMR studies showed greater 99% conversion and a ratio of 78:12 of isomers. Both isomers were isolated in 93% (133 mg, 0.47 mmol) yield as a pale yellow oil. The NMR data was consistent with the values reported in the literature.⁵¹⁸

(Data of the major isomer)

Rᵣ (n-pentane/ether; 90/3) = 0.62.

¹H NMR (500 MHz, 298 K, CDCl₃): δ¹H: 7.36 – 7.28 (m, 4H), 7.25 – 7.18 (m, 2H), 2.41 – 2.36 (m, 2H), 1.51 – 1.43 (m, 2H), 1.41 – 1.29 (m, 14H), 0.89 (t, J = 7.3 Hz, 3H).

¹³C{¹H} NMR (126 MHz, 298 K, CDCl₃): δ¹³C: 141.6, 138.0, 129.0, 128.0, 126.9, 83.3, 32.2, 29.2, 24.8, 22.8, 14.0. N.o. =C⁸

$^{11}$B NMR (128 MHz, 298 K, CDCl$_3$): $\delta^{11}$B: 30.6 ($\nu_{1/2} = 430$ Hz).

HRMS (DART-TOF+): mass [M+NH$_4$] calcd. for C$_{18}$H$_{31}$B$_1$N$_1$O$_2$ 304.24478 Da, found: 304.24401 Da.

$^1$H NMR (500 MHz, 298 K, CDCl$_3$) and $^{11}$B NMR (128 MHz, 298 K, CDCl$_3$) spectra of compound 17.

$^{13}$C{^1}H NMR (126 MHz, 298 K, CDCl$_3$) spectrum of compound 17.

(18) (Z)-trimethyl(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(thiophen-2-yl)vinyl) silane

According to the general procedure trimethyl(thiophen-2-ylethynyl)-silane (90 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and HBCF (17 mg, 10 mol%) were dissolved in CH$_2$Cl$_2$ (2.5 ml) and reacted for 18 h at 50 °C. Crude NMR studies showed greater 60% conversion. The crude product was purified by column chromatography (n-pentane/ether 98/2) and alkenyl borane 18 was isolated in 50% (76 mg, 0.25 mmol) yield as colorless oil.

$R_f$ (n-pentane/ether; 97/3) = 0.69.

$^1$H NMR (400 MHz, 298 K, CDCl$_3$): $\delta^1$H: 7.88 (s, 1H), 7.28 (dd, $J = 5.0, 1.2$ Hz, 1H), 7.02 (dt, $J = 3.6, 1.1$ Hz, 1H), 6.98 – 6.95 (m, 1H), 1.29 (s, 12H), 0.15 (s, 9H).

$^{13}$C{^1}H NMR (126 MHz, 298 K, CDCl$_3$): $\delta^{13}$C: 147.6, 143.7, 127.9, 126.9, 126.4, 83.3, 24.8, 0.7. N.o. =C$^8$. 
$^{11}$B NMR (128 MHz, 298 K, CDCl$_3$): $\delta^{11}$B: 31.5 ($\nu_{1/2} = 290$ Hz).

$^{29}$Si NMR (80 MHz, 298 K, CDCl$_3$): $\delta^{29}$Si: −8.4.

HRMS (DART-TOF+): mass [M+H] calcd. for C$_{15}$H$_{26}$B$_1$O$_2$S$_1$Si$_1$ 309.15158 Da, found: 309.15129 Da.

$^1$H NMR (500 MHz, 298 K, CDCl$_3$), $^{11}$B NMR (128 MHz, 298 K, CDCl$_3$) and $^{29}$Si NMR (80 MHz, 298 K, CDCl$_3$) spectra of compound 18.

(19) (Z)-2-(1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

According to the general procedure 1,2-diphenylethyne (89 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and HB(C$_6$F$_5$)$_2$ (9 mg, 5 mol%) were dissolved in CH$_2$Cl$_2$ (2.5 ml) and reacted for 18 h at 50 °C. Crude NMR studies showed greater 99% conversion and alkenyl borane 19 was isolated in 98% (150 mg, 0.49 mmol) yield as an off white solid. The NMR data was consistent with the values reported in the literature.$^{[S12]}$

$R_f$ (hexanes/ether; 90/10) = 0.67.

$^1$H NMR (500 MHz, 298 K, CDCl$_3$): $\delta^1$H: 7.36 (br s, 1H), 7.26 (m, 2H), 7.20 (m, 1H), 7.16 (m, 2H), 7.11 (m, 3H), 7.05 (m, 2H), 1.31 (s, 12H).
\[ ^{13}C\{^1H\} \text{ NMR (126 MHz, 298 K, CDCl}_3\}; \delta^{13}C: 143.1, 140.4, 137.0, 129.9, 128.2, 127.8, 127.5, 126.2, 83.8, 24.8. \text{ N.o. } = \text{C}^9. \]

\[ ^{11}B \text{ NMR (128 MHz, 298 K, CDCl}_3\}; \delta^{11}B: 30.3 (\nu_{1/2} \approx 380 \text{ Hz}). \]

\[ \text{HRMS (DART-TOF+): mass [M+H] calcd. for } C_{20}H_{24}B_1O_2 \text{ 307.18693 Da, found: 307.18587 Da.} \]

\[ {^1}H \text{ NMR (500 MHz, 298 K, CDCl}_3\) and } ^{11}B \text{ NMR (128 MHz, 298 K, CDCl}_3\) spectra of compound 19. \]

\[ {^{13}C\{^1H\} \text{ NMR (126 MHz, 298 K, CDCl}_3\) spectrum of compound 19.} \]

(20) (Z)-2-(1,2-bis(4-bromophenyl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

According to the general procedure 1,2-bis(4-bromophenyl)ethyne (168 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and HB(C\(_6\)F\(_5\)\(_2\) (9 mg, 5 mol%) were dissolved in CH\(_2\)Cl\(_2\) (2.5 mL) and reacted for 18 h at 50 °C. Crude NMR studies showed greater 99% conversion and alkenyl borane 20 was isolated in 98% (228 mg, 0.49 mmol) yield as a white solid. The NMR data was consistent with the values reported in the literature.[S\(^{19}\)]\(^1\)
**R** \textsubscript{f} \text{(hexanes/ether; 90/10)} = 0.55.

\textbf{\textsuperscript{1}H NMR} (500 MHz, 298 K, CDCl\textsubscript{3}): δ\textsuperscript{1}H: 7.41 – 7.37 (m, 2H), 7.29 (br s, 1H), 7.28 – 7.26 (m, 2H), 7.03 – 7.00 (m, 2H), 6.93 – 6.90 (m, 2H), 1.30 (s, 12H).

\textbf{\textsuperscript{13}C NMR} (126 MHz, 298 K, CDCl\textsubscript{3}): δ\textsuperscript{13}C: 142.3, 138.8, 135.5, 131.5, 131.3, 131.2, 130.6, 121.9, 120.5, 84.0, 24.8. N.o. =C\textsuperscript{6}.

\textbf{\textsuperscript{11}B NMR} (128 MHz, 298 K, CDCl\textsubscript{3}): δ\textsuperscript{11}B: 30.2 (\textit{\nu}_{1/2} \approx 380 \text{ Hz}).

\textbf{HRMS (DART-TOF+)}: mass [M+H] calcd. for C\textsubscript{20}H\textsubscript{22}B\textsubscript{1}Br\textsubscript{2}O\textsubscript{2} 463.00796 Da, measured 463.00663 Da.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{compound20_spectra.png}
\caption{\textsuperscript{1}H NMR (500 MHz, 298 K, CDCl\textsubscript{3}) and \textsuperscript{11}B NMR (128 MHz, 298 K, CDCl\textsubscript{3}) spectra of compound 20.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{compound20_spec.png}
\caption{\textsuperscript{13}C\{\textsuperscript{1}H\} NMR (126 MHz, 298 K, CDCl\textsubscript{3}) spectrum of compound 20.}
\end{figure}

(21) \textit{(Z)-4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{compound21.png}
\caption{Structure of compound 21.}
\end{figure}

According to the general procedure prop-1-yn-1-ylbenzene (58 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and HB(C\textsubscript{6}F\textsubscript{5})\textsubscript{2} (9 mg, 5 mol\%) were dissolved in CH\textsubscript{2}Cl\textsubscript{2} (2.5 ml) and reacted for 5 h at rt. Crude NMR studies showed greater 99% conversion and a ratio

of 88:12 of isomers. Both isomers were isolated in 94% (115 mg, 0.47 mmol) yield as a colorless oil. The NMR data was consistent with literature reported values.\[^{520}\]

(Data of the main isomer)

\(R_f\) (hexanes/ether; 90/10) = 0.54.

\(^1\text{H NMR}\) (500 MHz, 298 K, CDCl\(_3\)): \(\delta^1\text{H}: 7.41 – 7.30\) (m, 4H), 7.26 – 7.14 (m, 2H), 2.00 (d, \(J_{\text{HH}} = 1.7\) Hz, 3H), 1.32 (s, 12H).

\(^{13}\text{C}\{^1\text{H}\}\) NMR (126 MHz, 298 K, CDCl\(_3\)): \(\delta^{13}\text{C}: 142.3, 137.9, 129.4, 128.0, 127.1, 83.5, 24.8, 15.9\). N.o. = C\(^\circ\).

\(^{11}\text{B NMR}\) (128 MHz, CDCl\(_3\)): \(\delta^{11}\text{B}: 30.7\) (\(\nu_{1/2} \approx 320\) Hz).


---

(22) (Z)-4,4,5,5-tetramethyl-2-(oct-4-en-4-yl)-1,3,2-dioxaborolane

According to the general procedure 4-octyne (55 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and HB(C_6F_5)_2 (9 mg, 5 mol%) were dissolved in CH_2Cl_2 (2.5 ml) and reacted for 18 h at rt. Crude NMR studies showed greater 99% conversion and alkenyl borane 22 was isolated in 98% (118 mg, 0.49 mmol) yield as a colorless liquid.

R_f (hexanes/ether; 99/1) = 0.11.

^1H NMR (500 MHz, 298 K, CDCl_3): δ^1H: 6.29 (t, ^3J_{HH} = 7.1 Hz, 1H), 2.10 (m, 4H), 1.41 (m, 2H), 1.35 (m, 2H), 1.25 (s, 12H), 0.91 (t, ^3J_{HH} = 7.4 Hz, 3H), 0.88 (t, ^3J_{HH} = 7.4 Hz, 3H).

^13C(^1H) NMR (126 MHz, 298 K, CDCl_3): δ^13C: 146.0, 82.9, 30.7, 30.6, 24.7, 23.3, 22.4, 14.10, 14.06. N.o. =C^6.

^11B NMR (128 MHz, CDCl_3): δ^11B: 30.5 (\(v_{1/2}\) ≈ 290 Hz).

HRMS (DART-TOF+): mass [M+H] calcd. for C_{14}H_{28}B_{1}O_{2} 239.21823 Da, found: 239.21842 Da.

^1H NMR (500 MHz, 298 K, CDCl_3) and ^11B NMR (128 MHz, 298 K, CDCl_3) spectra of compound 22.

^13C(^1H) NMR (126 MHz, 298 K, CDCl_3) spectrum of compound 22.
(23) (Z)-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene-1,2-diyl)bis(trimethylsilane)

According to the general procedure 1,2-bis(trimethylsilyl)ethyne (85 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and HB(C\(_6\)F\(_5\))\(_2\) (9 mg, 5 mol%) were dissolved in CH\(_2\)Cl\(_2\) (2.5 ml) and reacted for 18 h at r.t. Crude NMR studies showed greater 99% conversion and alkenyl borane 23 was isolated in 99% (148 mg, 0.50 mmol) yield as colorless oil.

R\(_f\) (hexanes/ether; 99/1) = 0.14.

\(^1\)H NMR (500 MHz, 298 K, CDCl\(_3\)): \(\delta^1\)H: 6.95 (s, 1H), 1.29 (s, 12H), 0.18 (s, 9H), 0.10 (s, 9H).

\(^{13}\)C\({^1}\)H NMR (126 MHz, 298 K, CDCl\(_3\)): \(\delta^{13}\)C: 172.1, 148.4, 83.5, 25.1, 1.3, -0.2.

\(^{11}\)B NMR (128 MHz, 298 K, CDCl\(_3\)): \(\delta^{11}\)B: 29.0 (\(\nu_{1/2} \approx 300\) Hz).

\(^{29}\)Si-dept (80 MHz, 298 K, CDCl\(_3\)): \(\delta^{29}\)Si: -0.2, -7.2.

HRMS (DART-TOF+): mass [M+NH\(_4\)] calcd. for C\(_{14}\)H\(_{35}\)B\(_1\)N\(_1\)O\(_2\)Si\(_2\) 316.2994 Da, found: 316.23037 Da.

\(^1\)H NMR (500 MHz, 298 K, CDCl\(_3\)), \(^{11}\)B NMR (128 MHz, 298 K, CDCl\(_3\)) and \(^{29}\)Si-dept (80 MHz, 298 K, CDCl\(_3\)) spectra of compound 23.

\(^{13}\)C\({^1}\)H NMR (126 MHz, 298 K, CDCl\(_3\)) spectrum of compound 23.