Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

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

Mirco Fleige[ϕ], Juri Möbus[ϕ], Thorsten vom Stein, Frank Glorius, Douglas W. Stephan*

[ϕ] *These authors contributed equally to this work*

Table of Content

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_2Cl_2, *n*-pentane) were prepared using an Innovative Technologies solvent purification system. Deuterated solvents chloroform ($CDCl_3$), dichloromethane (CD_2Cl_2), benzene (C_6D_6), toluene (C_7D_8) and bromobenzene (C_6D_5Br) 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_2O_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. $[CPh_3][B(C_6F_5)]_4$ was purchased from Boulder Scientific and used without further purification. $B(C_6F_5)_3$ was purchased from Boulder Scientific and purified by sublimation prior to use.

All glassware was oven-dried at temperatures above 180°C prior to use. NMR spectra were measured on a Bruker AVANCE 400 ^1H (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 a Agilent DD2 600 ^1H (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 °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 δ **(**TMS) = 0.00 ppm (^1H, ^{13}C) and δ H_3PO_4(85%) = 0.00 ppm (^{31}P, externally). Chemical shifts (δ) 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).

$[FPPh_3][B(C_6F_5)]_4$ [S1],[S2], $[Ph_2PF(C_6H_4BCy_2)][B(C_6F_5)_4]$,[S1] $[MeOC_6H_4CPh_2][B(C_6F_5)_4]$[S3], $MeB(C_6F_5)_2$ [S4], $ClB(C_6F_5)_2$ [S5] and $HB(C_6F_5)_2$ [S6],[S7] were prepared according to literature procedures.

[S1] J. Möbus, T. vom Stein, D. W. Stephan, *Chem. Commun.* **2016**, *52*, 6387-6390.

[S2] C. B. Caputo, D. Winkelhaus, R. Dobrovetsky, L. J. Hounjet and D. W. Stephan, *Dalton Trans.* **2015**, *44*, 12256-12264.

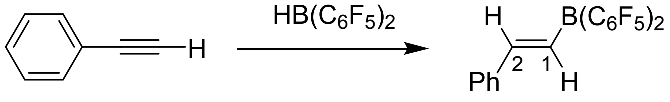
[S3] M. Horn, H. Mayr, *Chem. Eur. J.* **2010**, *16*, 7469-7477.

[S4] C. Chen, G. Kehr, R. Fröhlich, G. Erker, *J. Am. Chem. Soc.* **2010**, *132*, 13594-13595; R. E. v. Spence, W. E. Piers, Y. Sun, M. Parvez, L. R. MacGillivray, M. J. Zaworotko, *Organometallics* **1998**, *17*, 2459-2469.

[S5] I. Peuser, R. C. Neu, X. X. Zhao, M. Ulrich, B. Schirmer, J. A. Tannert, G. Kehr, R. Fröhlich, S. Grimme, G. Erker, D. W. Stephan, *Chem. Eur. J.* **2011**, *17*, 9640-9650; R. D. Chambers, T. Chivers, *J. Chem. Soc.*

2 Synthesis and Spectroscopic Data

2.1 Preparation of compound 24



24

Compound **24** was prepared according to modified literature procedures.[S7],[S8]

Phenylacetylene (30 mg, 0.29 mmol) was dissolved in CH_2Cl_2 (3 ml), cooled to -35 °C and $HB(C_6F_5)_2$ (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_2Cl_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%).

^{1}H NMR (400 MHz, 298 K, CD_2Cl_2): δ^1H: 7.70 (m, 2H, *o*-Ph), 7.62 (m, 2H, =CH-Ph and =CH-B), 7.49 (m, 1H, *p*-Ph)[a], 7.48 (m, 2H, *m*-Ph)[a]. [a] from ghsqc

^{13}C{^{1}H} NMR (126 MHz, 298 K, CD_2Cl_2): δ^{13}C: 163.7 (=CH-Ph), 136.3 (*i*-Ph)[t], 132.6 (*p*-Ph), 129.8 (*o*-Ph), 129.5 (*m*-Ph). N.o. =CH-B, C_6F_5.

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 298 K, CD_2Cl_2): δ^1H / δ^{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

^{11}B NMR (128 MHz, 298 K, CD_2Cl_2): δ^{11}B: 58.5 ($\nu_{1/2} \approx$ 700 Hz).

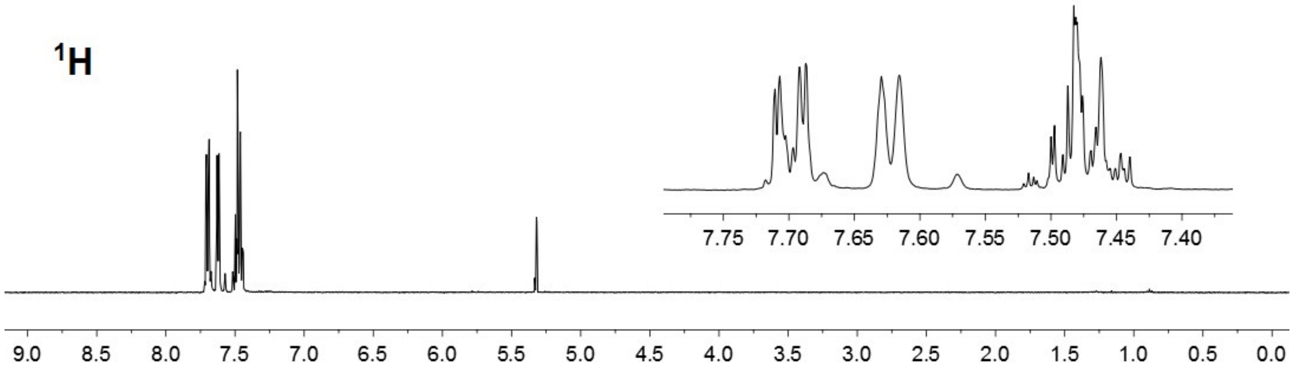
^{19}F NMR (376 MHz, 298 K, CD_2Cl_2): δ^{19}F: -129.7 (m, 2F, *o*-C_6F_5), -149.8 (t, $^3J_{FF}$ = 19.5 Hz, 1F, *p*-C_6F_5), -162.2 (m, 2F, *m*-C_6F_5).

1965, 3933-3939.

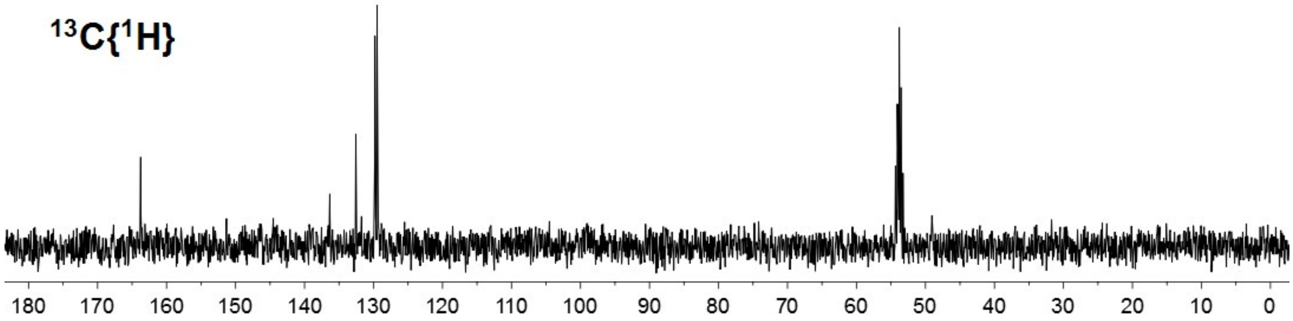
[S6] D. J. Parks, W. E. Piers, G. P. A. Yap, *Organometallics* **1998**, *17*, 5492-5503.

[S7] D. J. Parks, R. E. v. Spence, W. E. Piers, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 809-811.

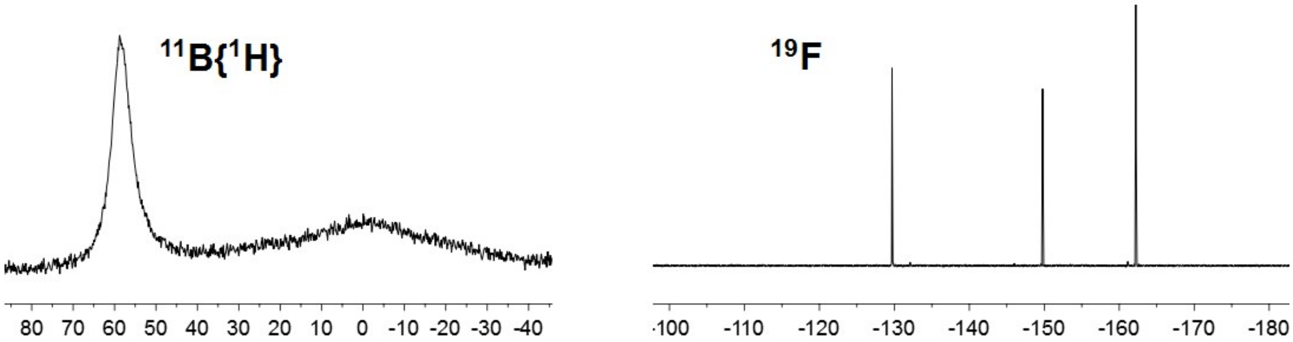
[S8] O. Ekkert, O. Tuschewitzki, C. G. Daniliuc, G. Kehr, G. Erker, *Chem. Commun.* **2013**, *49*, 6992-6994.



^1H NMR (400 MHz, 298 K, CD_2Cl_2) spectrum of compound ***24****.*

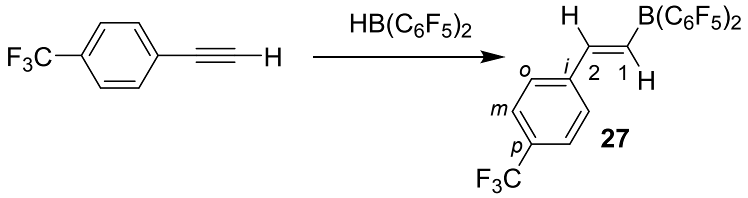


$^{13}C\{^1H\}$ NMR (126 MHz, 298 K, CD_2Cl_2) spectrum of compound ***24****.*



$^{11}B\{^1H\}$ NMR (128 MHz, 298 K, CD_2Cl_2) and ^{19}F NMR (470 MHz, 298 K, CD_2Cl_2) NMR spectra of compound ***24****.*

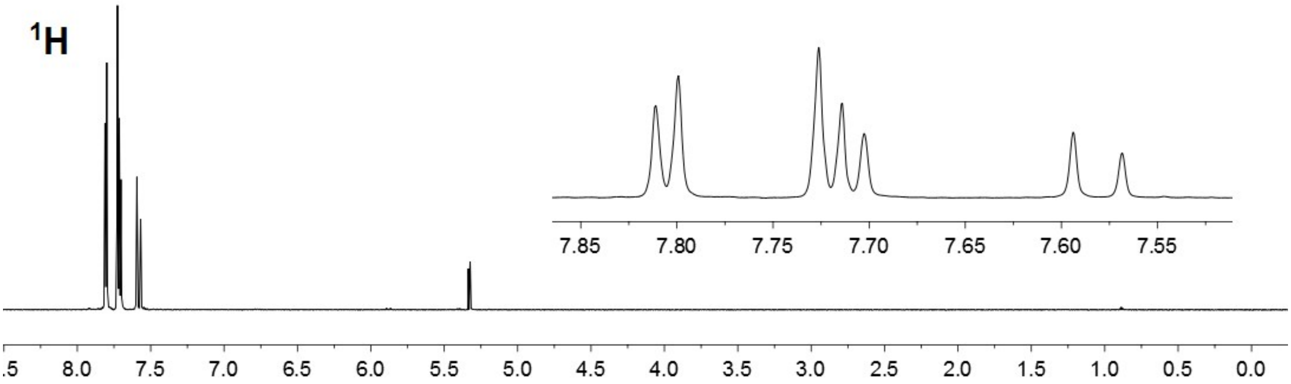
2.2 Preparation of compound 27



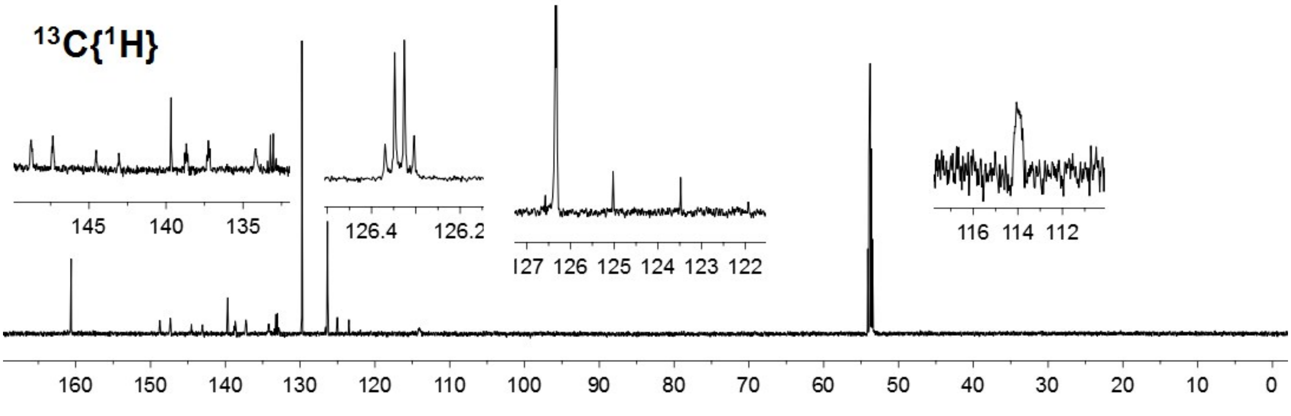
27

4-Ethynyl-α,α,α-trifluorotoluene (40 mg, 0.23 mmol) was dissolved in CH_2Cl_2 (2 ml), at r.t and $HB(C_6F_5)_2$ (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_2Cl_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.

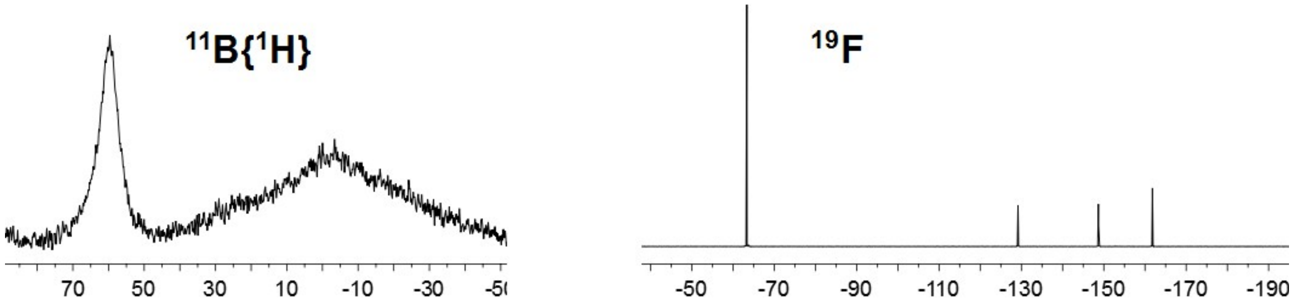
Elemental analysis: Calcd.: C: 48.88, H: 1.17; Found: C: 48.88, H: 0.93.
^{1}H NMR (700 MHz, 300 K, CD_2Cl_2): δ^{1}H: 7.81 (d, $^3J_{HH}$ = 8.5 Hz, 2H, *o*-Ar), 7.72 (d, $^3J_{HH}$ = 8.5 Hz, 2H, *m*-Ar), 7.71 (d, $^3J_{HH}$ = 17.8 Hz, 1H, =CH(1)), 7.58 (d, $^3J_{HH}$ = 17.8 Hz, 1H, =CH(2)).
^{13}C{^{1}H} NMR (176 MHz, 300 K, CD_2Cl_2): δ^{13}C: 160.6 (=CH(2)), 148.1 (dm, $^1J_{FC}$ ≈ 248 Hz, *o*-C_6F_5)^t, 143.8 (dm, $^1J_{FC}$ ≈ 257 Hz, *p*-C_6F_5)^t, 139.7 (*i*-Ar), 138.0 (dm, $^1J_{FC}$ ≈ 252 Hz, *m*-C_6F_5)^t, 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_6F_5).
^{1}H,^{13}C GHSQC (700 MHz / 176 MHz, 300 K, CD_2Cl_2): δ^{1}H / δ^{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)).
^{11}B NMR (128 MHz, 298 K, CD_2Cl_2): δ^{11}B: 59.4 ($\nu_{1/2}$ ≈ 800 Hz).
^{19}F NMR (376 MHz, 298 K, CD_2Cl_2): δ^{19}F: -63.3 (s, 3F, CF_3), -129.2 (m, 4F, *o*-C_6F_5), -148.7 (t, $^3J_{FF}$ = 20.4 Hz, 2F, *p*-C_6F_5), -161.8 (m, 4F, *m*-C_6F_5).



^{1}H NMR (700 MHz, 300 K, CD_2Cl_2) spectrum of compound **27**.

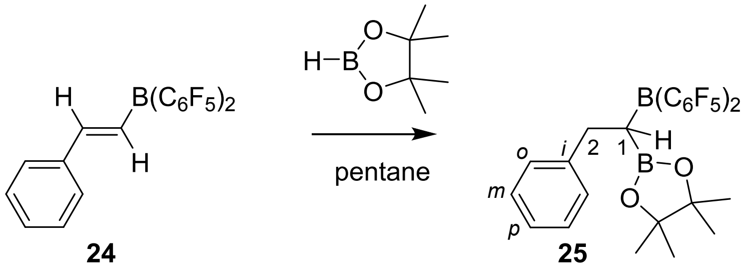


^{13}C{^{1}H} NMR (176 MHz, 300 K, CD_2Cl_2) spectrum of compound **27**.



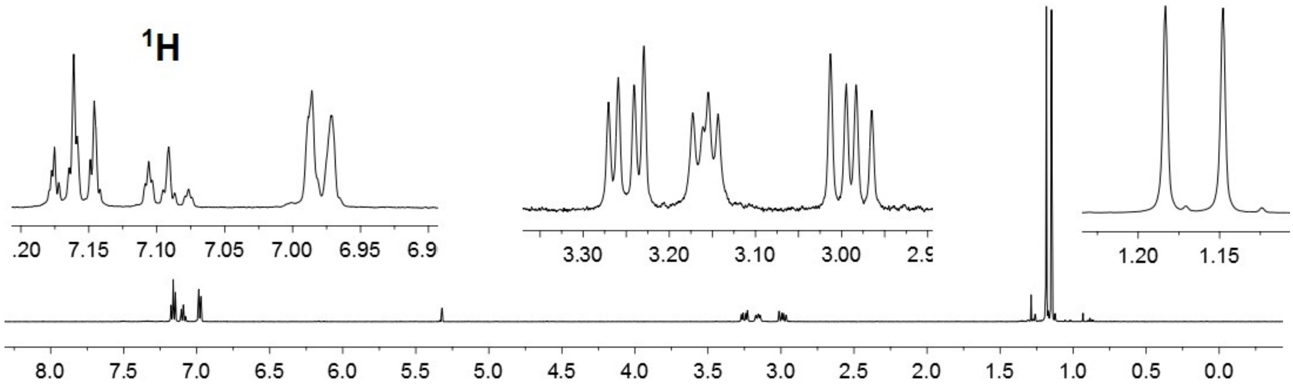
$^{11}B\{^1H\}$ NMR (128 MHz, 298 K, CD_2Cl_2) and ^{19}F NMR (470 MHz, 298 K, CD_2Cl_2) NMR spectra of compound **27**.

2.3 Preparation of compound 25

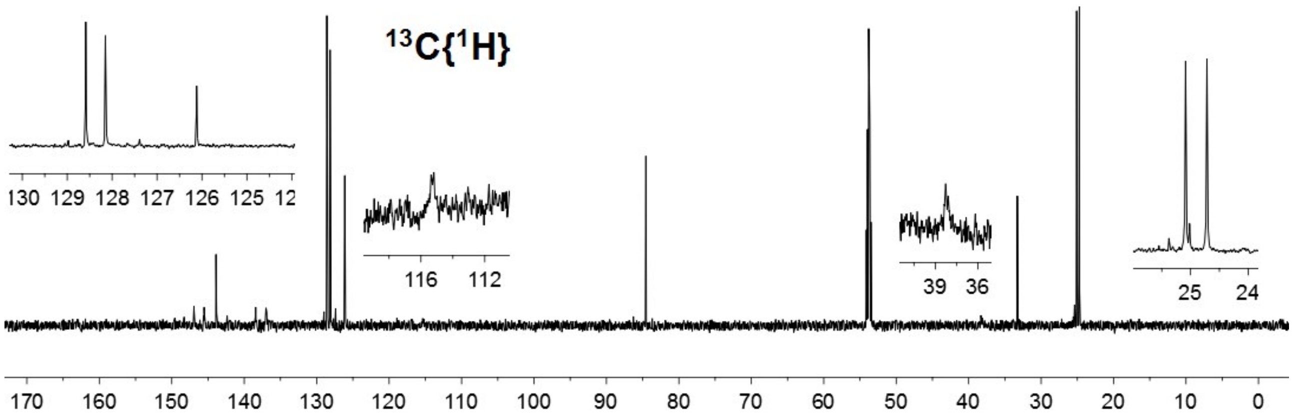


Compound **24** (40 mg, 0.058 mmol, 1 eq.) was suspended in pentane (2 ml) at r.t and pinacol borane (8.2 mg, 0.064 mmol, 1.1 eq.) was added to the stirred suspension. The resulting suspension was stirred for 2 h at r.t., the suspension turned clear after ca. 30 min. Trace insolubles were filtered off 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%).

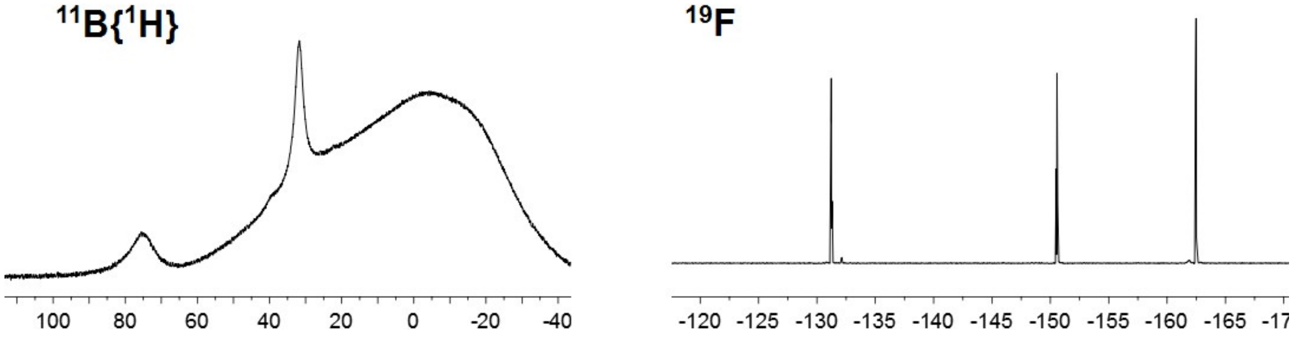
Elemental analysis: Calcd.: C: 54.21, H: 3.50; Found: C: 54.62, H: 3.58.
^{1}H NMR (700 MHz, 300 K, CD_2Cl_2): δ^1H: 7.17 (m, 2H, *m*-Ph), 7.10 (m, 1H, *p*-Ph), 6.99 (m, 2H, *o*-Ph), 3.26 (dd, $^2J_{HH}$ = 15.0 Hz, $^3J_{HH}$ = 5.7 Hz, 1H, $CH_{2,a}$), 3.17 (dd, $^3J_{HH}$ = 9.2 Hz, $^3J_{HH}$ = 5.7 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{^{1}H} NMR (176 MHz, 300 K, CD_2Cl_2): $\delta^{13}C$: 146.2 (dm, $^1J_{FC} \approx 245$ Hz, *o*-C_6F_5)^t, 143.9 (*i*-Ph), 143.1 (dm, $^1J_{FC} \approx 255$ Hz, *p*-C_6F_5)^t, 137.7 (dm, $^1J_{FC} \approx 251$ Hz, *m*-C_6F_5)^t, 128.6 (*m*-Ph), 128.2 (*o*-Ph), 126.1 (*p*-Ph), 115.3 (br, *i*-C_6F_5), 84.6 ($OCMe_2$), 38.3 (br, CH), 33.3 (CH_2), 25.1 ($CH_{3,b}$), 24.7 ($CH_{3,a}$).
^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 298 K, CD_2Cl_2): δ^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_2Cl_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_2Cl_2): $\delta^{19}F$: -131.2 (m, 2F, *o*-C_6F_5), -150.6 (tt, $^3J_{FF}$ = 20.3 Hz, $^4J_{FF}$ = 3.5 Hz, 1F, *p*-C_6F_5), -162.5 (m, 4F, *m*-C_6F_5).



^{1}H NMR (700 MHz, 300 K, CD_2Cl_2) spectrum of compound **25**.

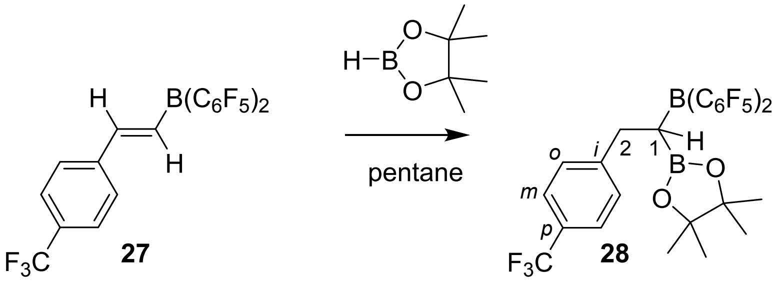


^{13}C{^{1}H} NMR (176 MHz, 300 K, CD_2Cl_2) spectrum of compound **25**.



^{11}B NMR (128 MHz, 298 K, CD_2Cl_2) and ^{19}F NMR (376 MHz, 298 K, CD_2Cl_2) 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_2Cl_2): δ^{1}H: 7.46 (d, $^3J_{HH}$ = 8.1 Hz, 2H, *m*-Ar), 7.17 (d, $^3J_{HH}$ = 8.1 Hz, 2H, *o*-Ar), 3.32 (dd, $^2J_{HH}$ = 15.1 Hz, $^3J_{HH}$ = 6.1 Hz, 1H, $CH_{2,a}$), 3.15 (dd, $^3J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 6.1 Hz, 1H, CH), 3.07 (dd, $^2J_{HH}$ = 15.1 Hz, $^3J_{HH}$ = 8.6 Hz, 1H, $CH_{2,b}$), 1.19 (s, 6H, $CMe_{2,a}$), 1.15 (s, 6H, $CMe_{2,b}$).

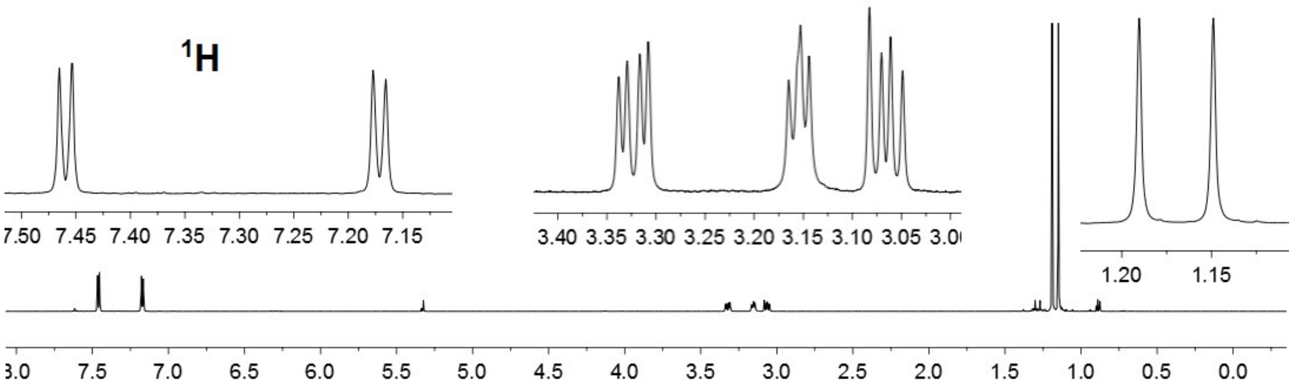
^{13}C{^{1}H} NMR (176 MHz, 300 K, CD_2Cl_2): δ^{13}C: 148.2 (*i*-Ar), 146.3 (dm, $^1J_{FC}$ ≈ 244 Hz, *o*-C_6F_5)^t, 143.3 (dm, $^1J_{FC}$ ≈ 258 Hz, *p*-C_6F_5)^t, 137.8 (dm, $^1J_{FC}$ ≈ 247 Hz, *m*-C_6F_5)^t, 128.7 (*o*-Ar), 128.4 (q, $^2J_{FC}$ = 31.8 Hz, *p*-Ar), 125.5 (q, $^3J_{FC}$ = 3.6 Hz, *m*-Ar), 124.8 (q, $^1J_{FC}$ = 272.6 Hz, CF_3), 115.1 (br, *i*-C_6F_5), 84.8 ($OCMe_2$), 37.8 (br, CH), 33.1 (CH_2), 25.1 ($CH_{3,b}$), 24.7 ($CH_{3,a}$).

^{1}H,^{13}C GHSQC (700 MHz / 176 MHz, 300 K, CD_2Cl_2): δ^{1}H / δ^{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 ($CH_{3,a}$), 1.15 / 25.1 ($CH_{3,b}$).

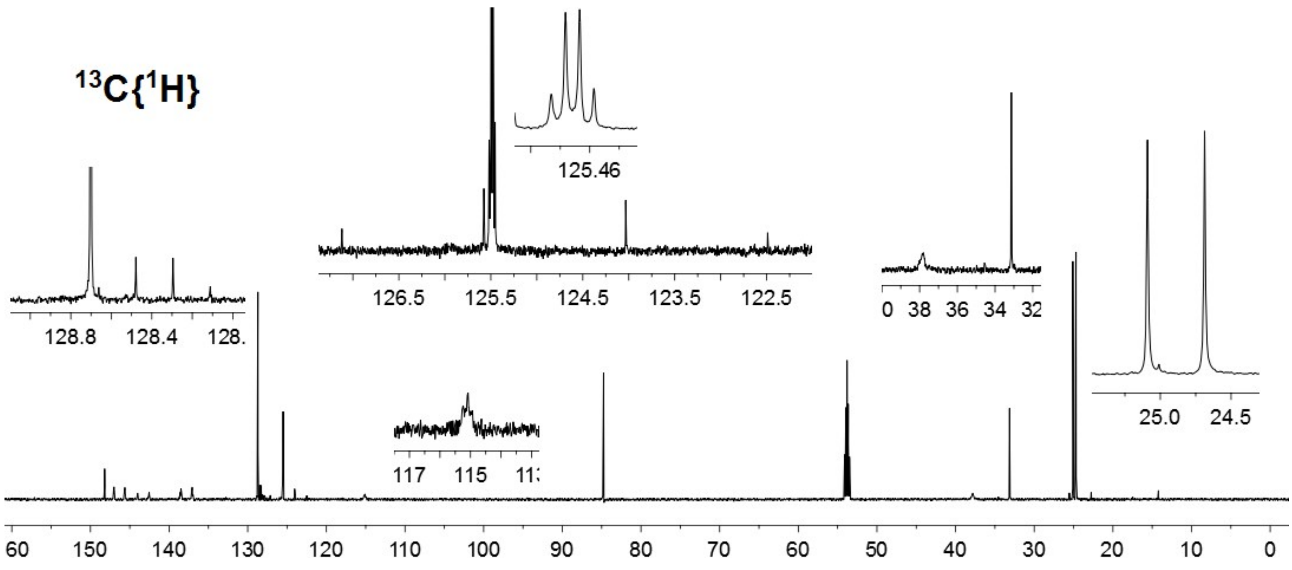
^{1}H,^{13}C GHMBC (700 MHz / 176 MHz, 300 K, CD_2Cl_2) [selected traces]: δ^{1}H / δ^{13}C: 7.46 / 148.2, 125.5 (*m*-Ar / *i*-Ar, *m*-Ar), 7.17 / 128.7, 33.1 (*o*-Ar / *o*-Ar, CH_2), 3.32 / 148.1, 128.7, 37.8 (CH_2 / *i*-Ar, *o*-Ar, CH), 3.15 / 148.1, 115.1, (CH / *i*-Ar, *i*-C_6F_5, CH), 1.19 / 84.8, 25.1 ($CH_{3,a}$ / $OCMe_2$, $CH_{3,b}$), 1.15 / 84.8, 24.7 ($CH_{3,b}$ / $OCMe_2$, $CH_{3,a}$).

^{11}B NMR (128 MHz, 298 K, CD_2Cl_2): δ^{11}B: 74.7 ($\nu_{1/2}$ ≈ 1300 Hz), 31.7 ($\nu_{1/2}$ ≈ 400 Hz).

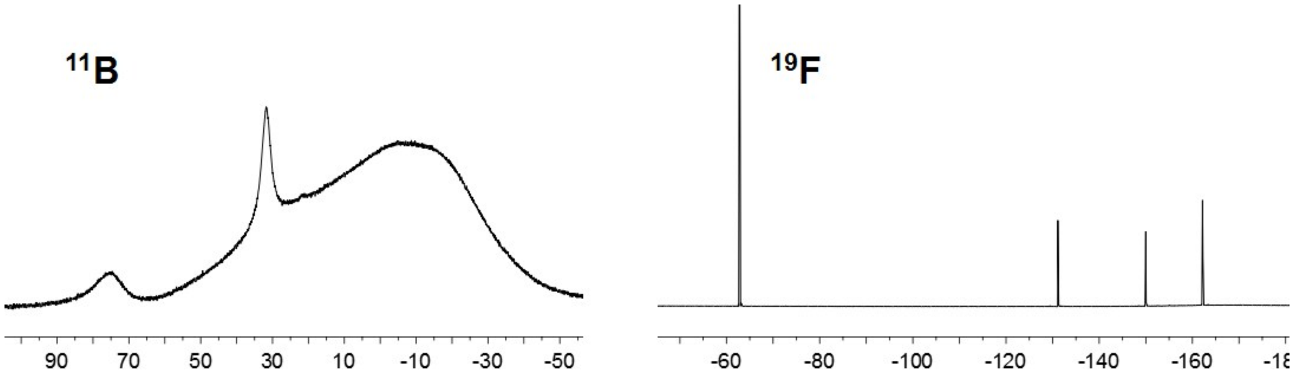
^{19}F NMR (376 MHz, 298 K, CD_2Cl_2): δ^{19}F: -62.8 (s, 3F, CF_3), -131.2 (m, 4F, *o*-C_6F_5), -150.0 (tt, $^3J_{FF}$ = 20.5 Hz, $^4J_{FF}$ = 4.0 Hz, 2F, *p*-C_6F_5), -162.2 (m, 4F, *m*-C_6F_5).



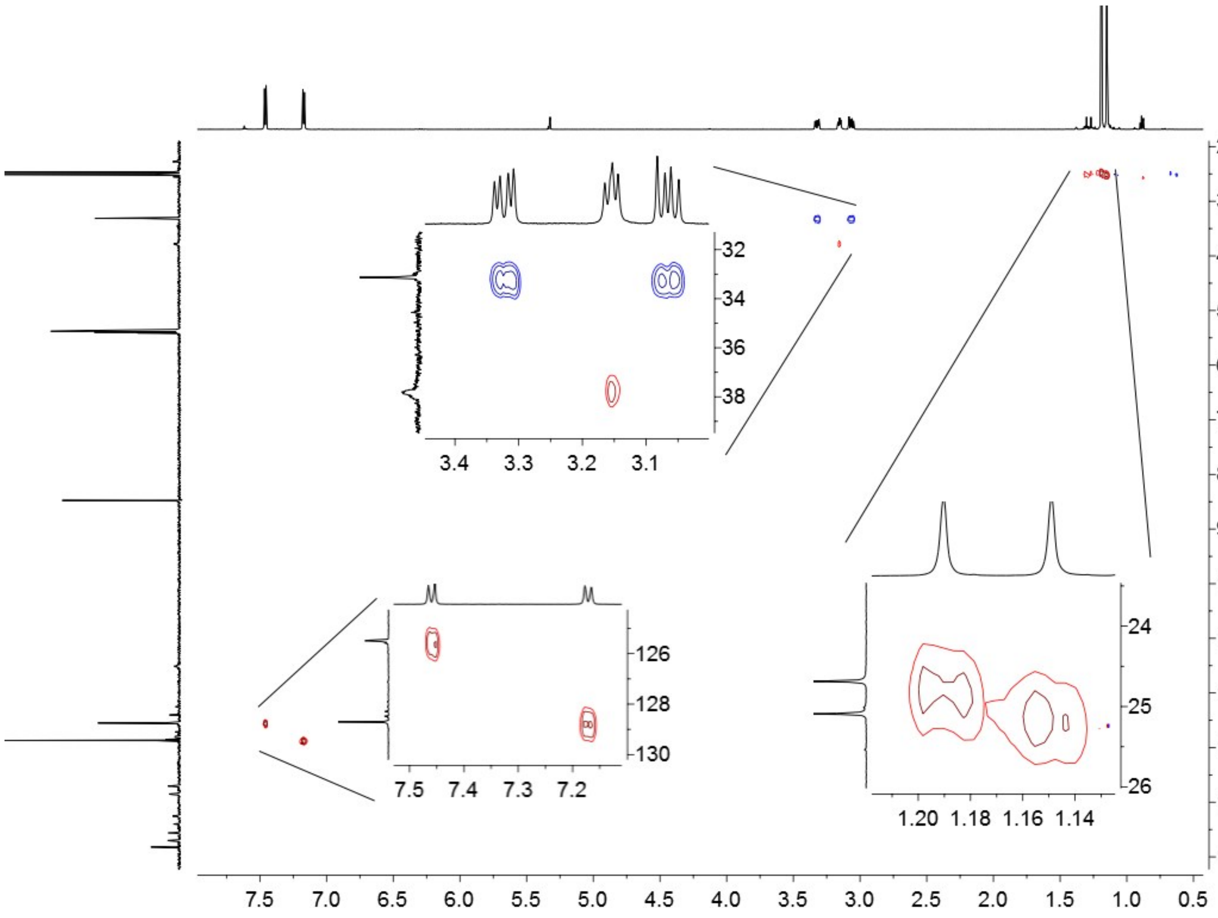
^{1}H NMR (700 MHz, 300 K, CD_2Cl_2) spectrum of compound ***28****.*



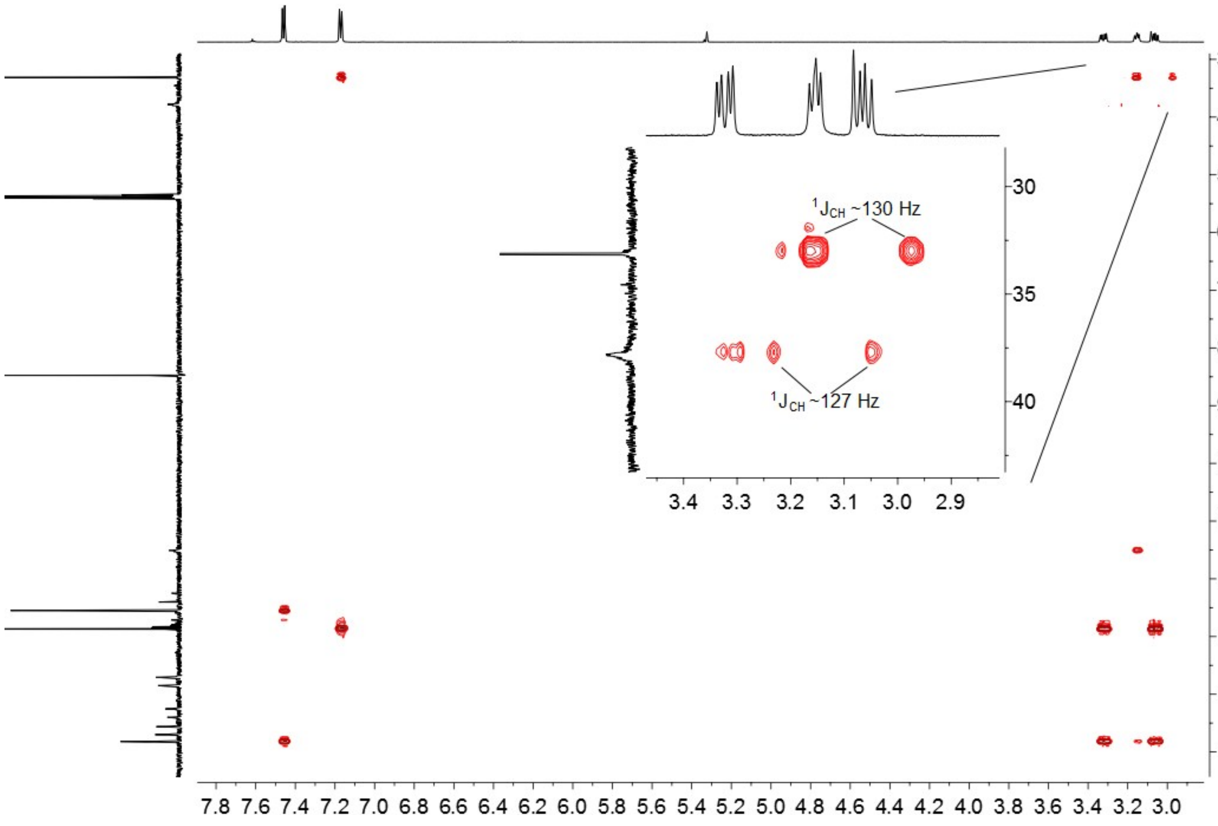
^{13}C{^{1}H} NMR (176 MHz, 300 K, CD_2Cl_2) spectrum of compound ***28****.*



^{11}B{^{1}H} NMR (128 MHz, 298 K, CD_2Cl_2) and ^{19}F NMR (470 MHz, 298 K, CD_2Cl_2) NMR spectra of compound ***28****.*



$^1H,^{13}C$ *GHSQC (700 MHz / 176 MHz, 300 K,* CD_2Cl_2*) spectra of compound* ***28****.*

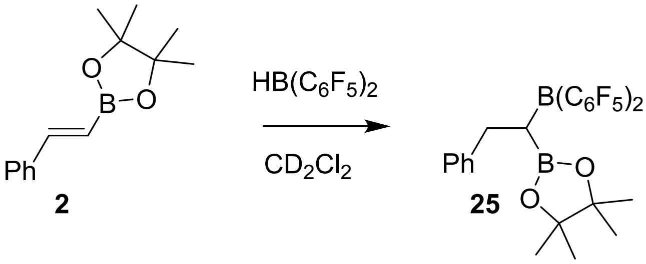


Excerpt from the $^1H,^{13}C$ *GHMBC (700 MHz / 176 MHz, 300 K,* CD_2Cl_2*) of compound* ***28****.*

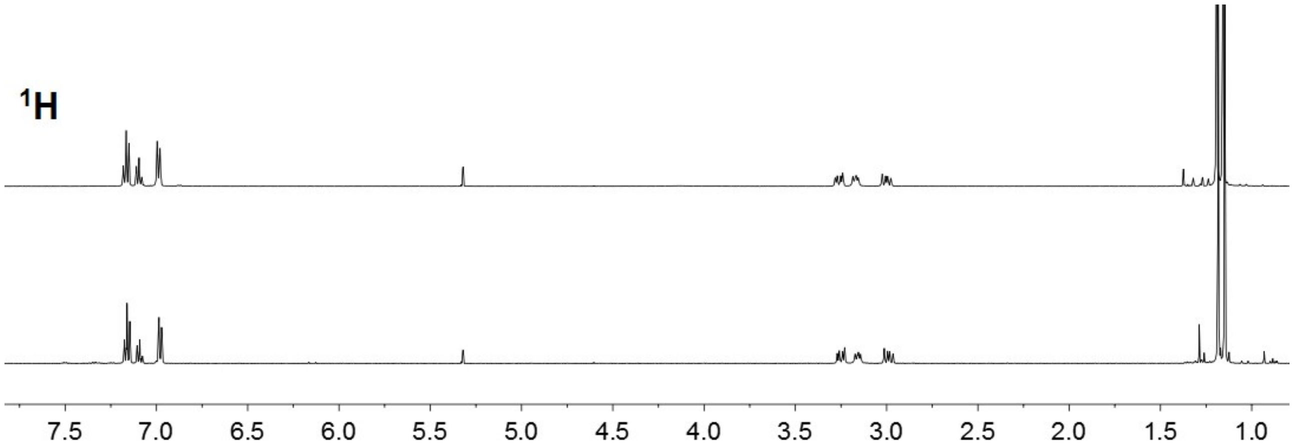
3 Stoichiometric studies

3.1 Control reactions

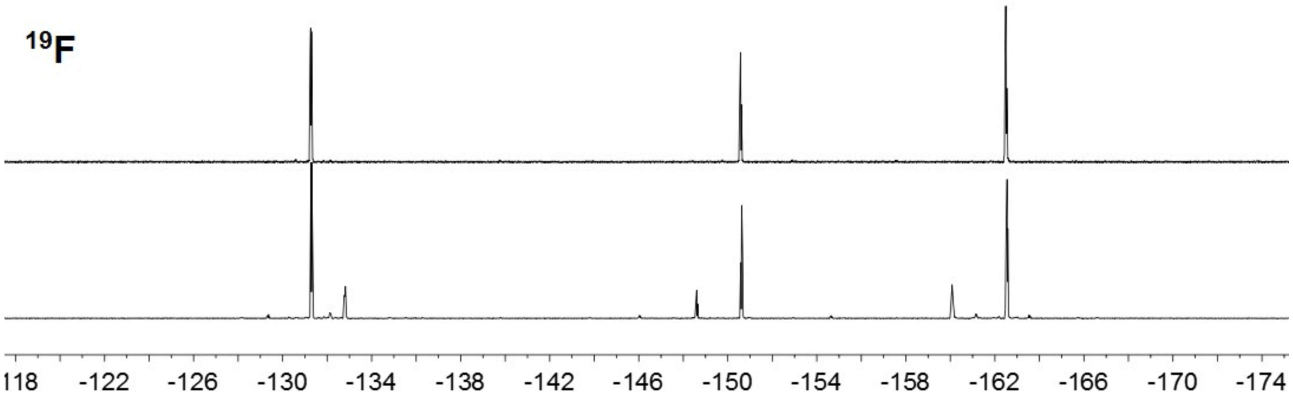
Formation of compound 25 from compound 2



Compound **2** (8.0 mg, 0.035 mmol, 1 eq) was taken up in CD_2Cl_2 (0.25 ml) at r.t. in a glovebox and $HB(C_6F_5)_2$ (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.

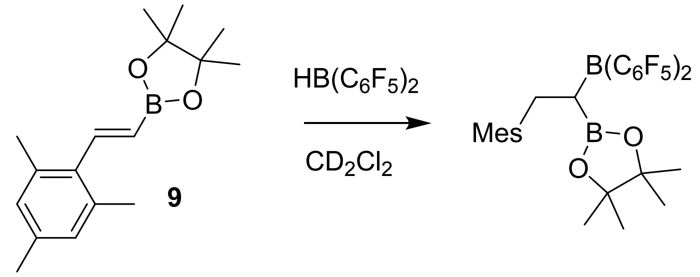


^{1}H NMR (500 MHz, 298 K, CD_2Cl_2) spectra of the isolated compound ***25*** *(top) and the reaction mixture between compound* ***2*** *and $HB(C_6F_5)_2$ after 15 min at r.t. (bottom).*

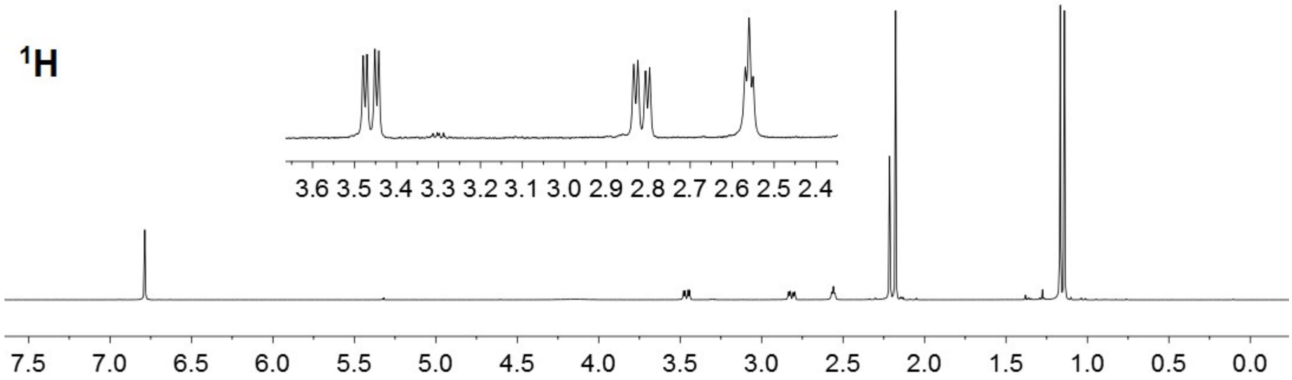


^{19}F (470 MHz, 298 K, CD_2Cl_2) spectra of the isolated compound ***25*** *(top) and the reaction mixture between compound* ***2*** *and $HB(C_6F_5)_2$ after 15 min at r.t. (bottom, ca. 15% residual $HB(C_6F_5)_2$ as impurity).*

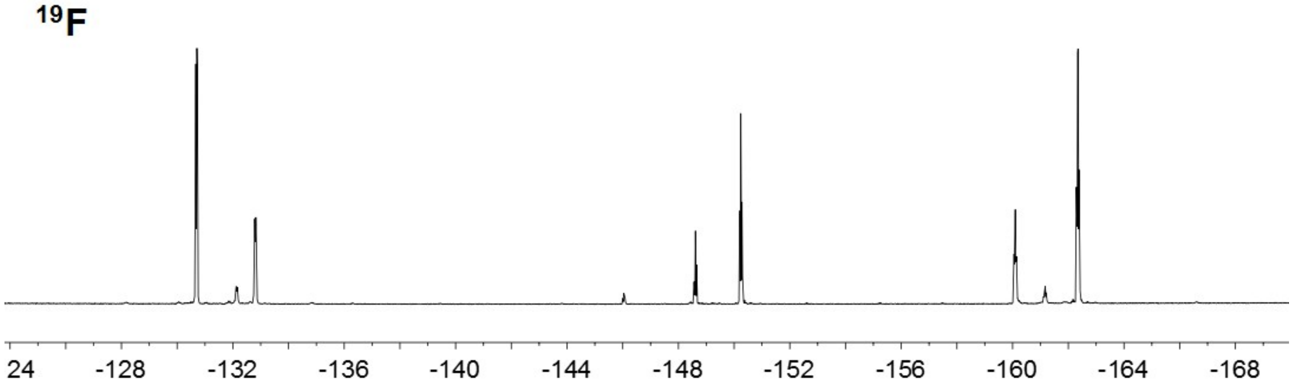
Formation of compound 25 from compound 2



Compound **9** (8.0 mg, 0.035 mmol, 1 eq) was taken up in CD_2Cl_2 (0.25 ml) at r.t. in a glovebox and $HB(C_6F_5)_2$ (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.

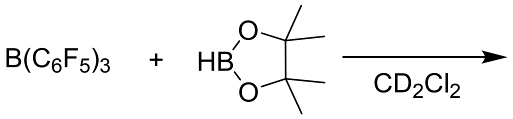


^1H NMR (500 MHz, 298 K, CD_2Cl_2) spectrum of reaction between compound **9** *and $HB(C_6F_5)_2$ after 30 min at r.t.*

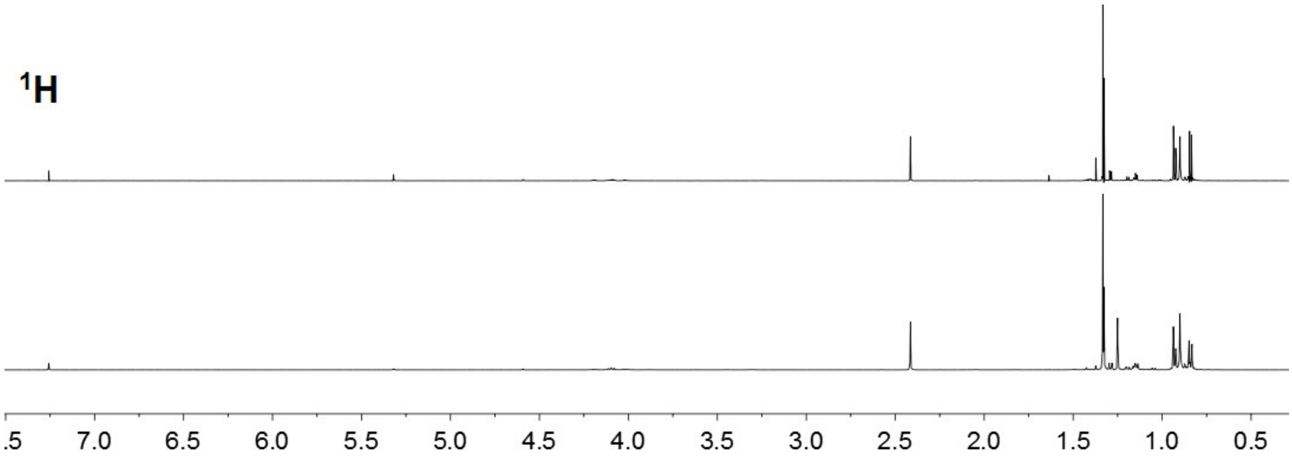


^{19}F (470 MHz, 298 K, CD_2Cl_2) spectrum of the reaction mixture between compound **9** *and $HB(C_6F_5)_2$ after 30 min at r.t. (ca. 25% residual $HB(C_6F_5)_2$ as impurity).*

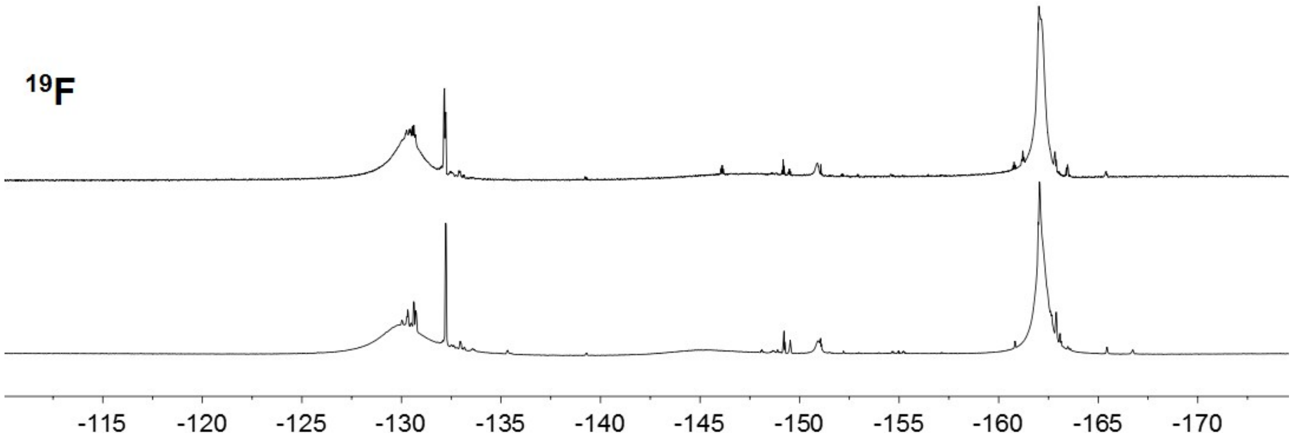
Reaction between $B(C_6F_5)_3$ and pinacol borane



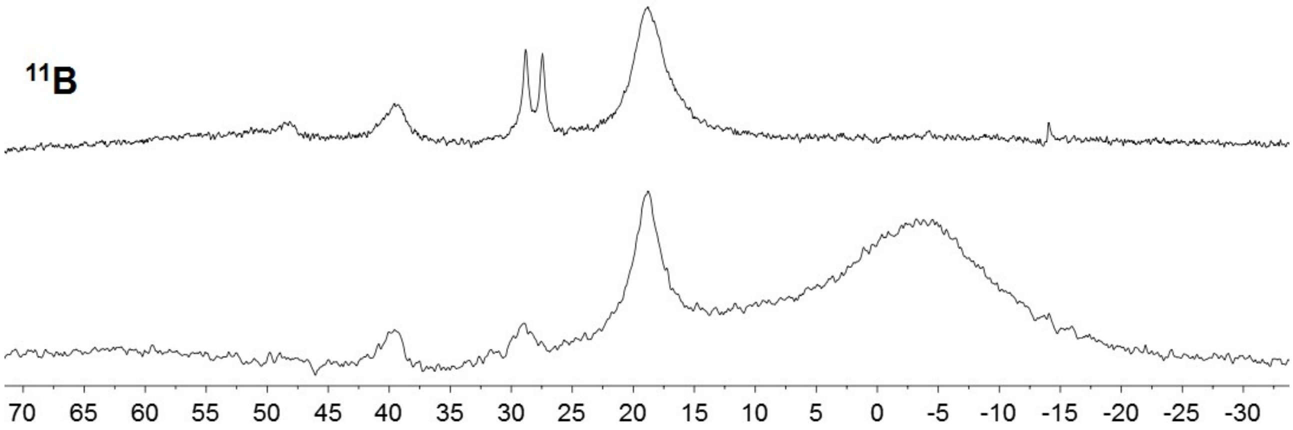
In a glovebox, $B(C_6F_5)_3$ (12.6 mg, 0.025 mmol, 1 eq) and pinacol borane (3.2 mg, 0.025 mmol, 1 eq) were mixed in CD_2Cl_2 (0.25 ml) at r.t. and the resulting solution transferred to a 3 mm NMR tube. The reaction was monitored by ^1H, ^{19}F and ^{11}B NMR spectroscopy.



^1H NMR (400 MHz, 298 K, CD_2Cl_2) spectrum of the reaction of $B(C_6F_5)_3$ with HBPin after 1 h at r.t. (top) and
^1H NMR (600 MHz, 298 K, CD_2Cl_2) after 18 h at r.t. (bottom).

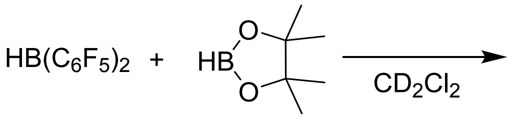


^{19}F NMR (376 MHz, 298 K, CD_2Cl_2) spectrum of the reaction of $B(C_6F_5)_3$ with HBPin after 1 h at r.t. (top) and
^{19}F NMR (564 MHz, 298 K, CD_2Cl_2) after 18 h at r.t. (bottom).

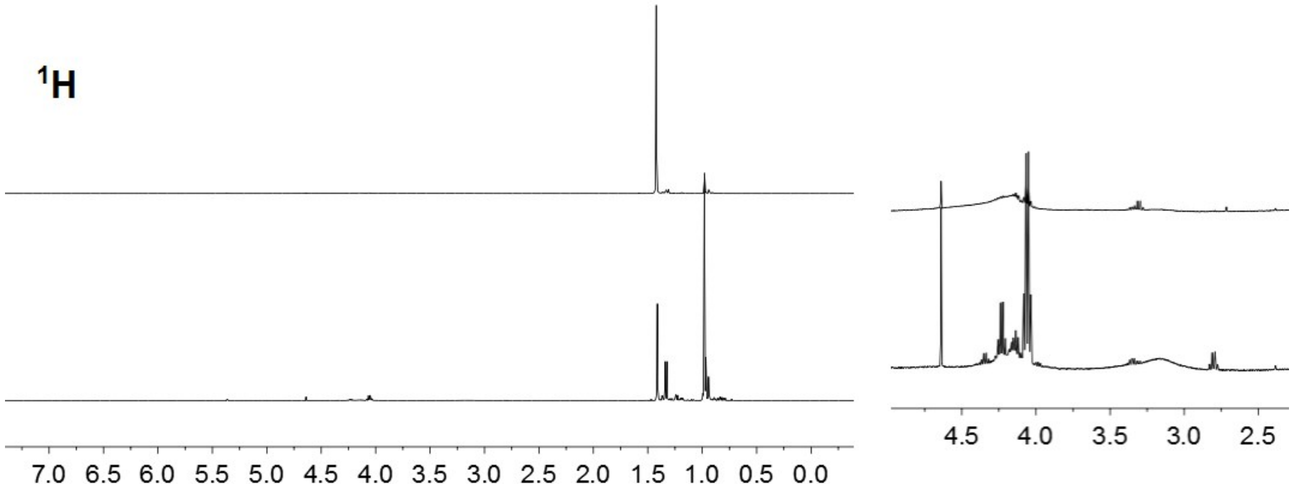


^{11}B NMR (128 MHz, 298 K, CD_2Cl_2) spectrum of the reaction of $B(C_6F_5)_3$ with HBPin after 1 h at r.t. (top) and ^{11}B NMR (192 MHz, 298 K, CD_2Cl_2) after 18 h at r.t. (bottom).

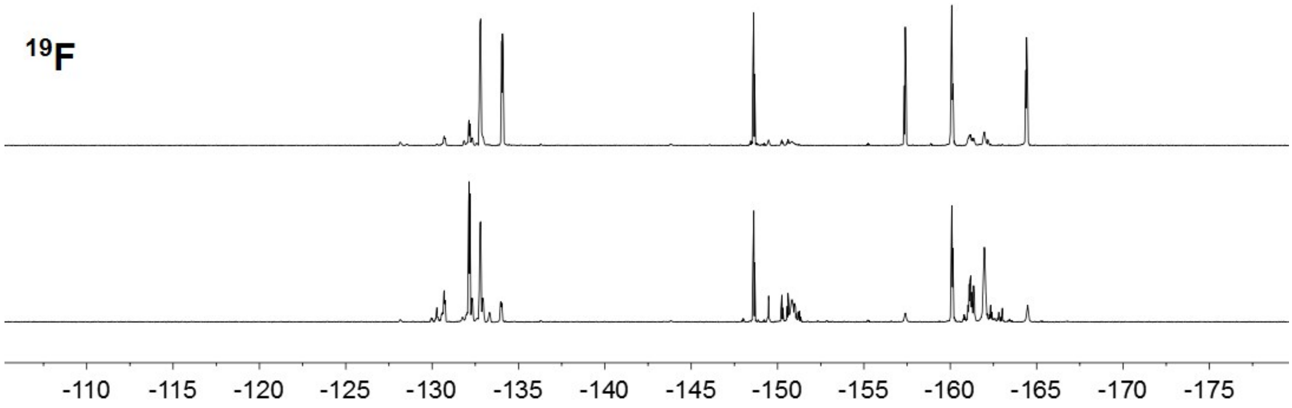
Reaction between $HB(C_6F_5)_2$ and pinacol borane



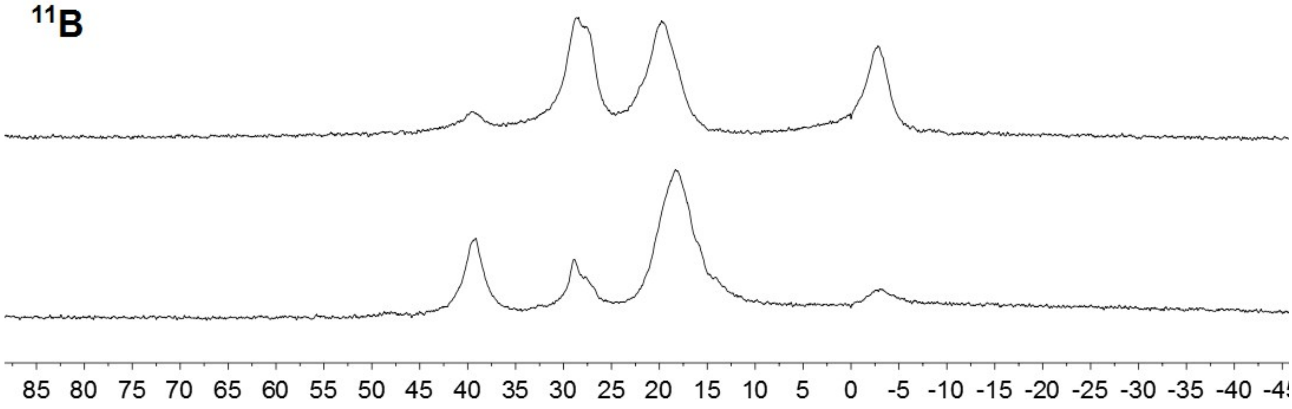
In a glovebox, $HB(C_6F_5)_2$ (13.5 mg, 0.039 mmol, 1 eq) and pinacol borane (5.0 mg, 0.039 mmol, 1 eq) were mixed in CD_2Cl_2 (0.25 ml) at r.t. and the resulting solution transferred to a 3 mm NMR tube. The reaction was monitored by ^1H, ^{19}F and ^{11}B NMR spectroscopy.



^1H NMR (400 MHz, 298 K, CD_2Cl_2) spectrum of the reaction of $HB(C_6F_5)_2$ with HBPin after 1 h at r.t. (top) and after 18 h at r.t. (bottom).

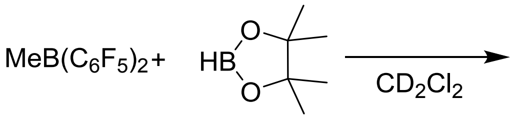


^{19}F NMR (376 MHz, 298 K, CD_2Cl_2) spectrum of the reaction of $HB(C_6F_5)_2$ with HBPin after 1 h at r.t. (top) and after 18 h at r.t. (bottom).

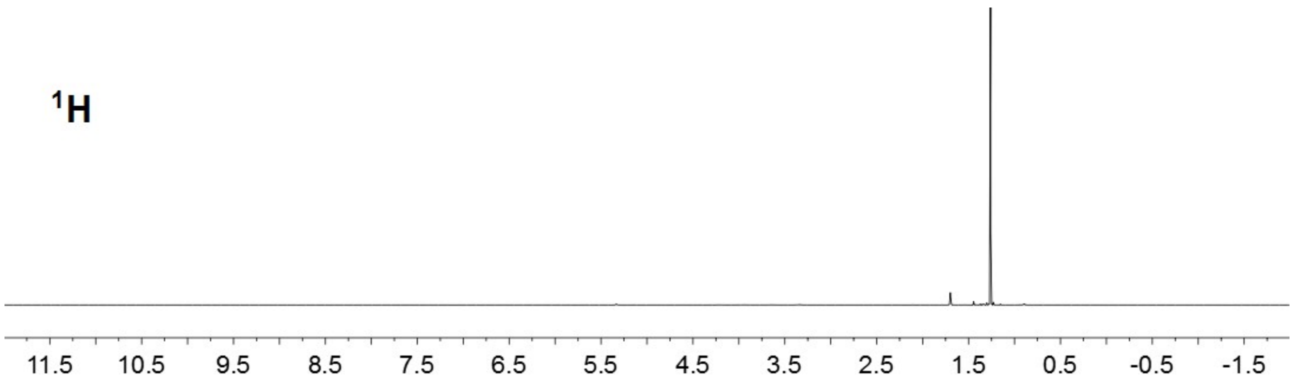


^{11}B NMR (128 MHz, 298 K, CD_2Cl_2) spectrum of the reaction of $HB(C_6F_5)_2$ with HBPin after 1 h at r.t. (top) and after 18 h at r.t. (bottom).

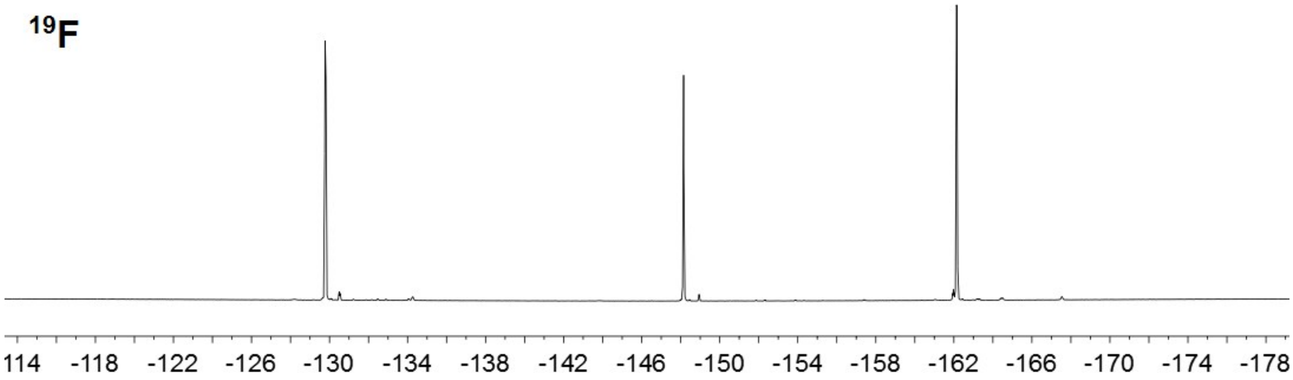
Reaction between $MeB(C_6F_5)_2$ and pinacol borane



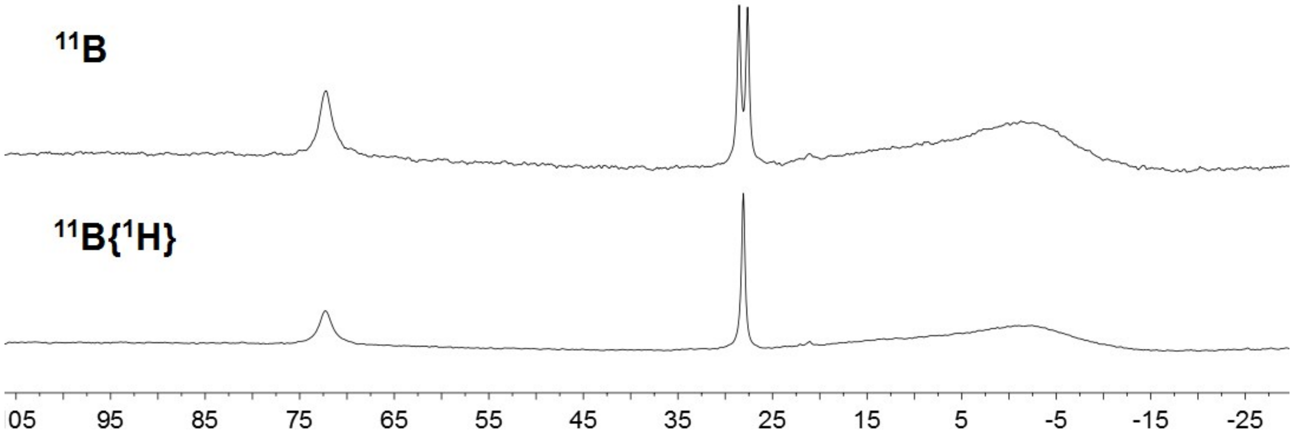
In a glovebox, $MeB(C_6F_5)_2$ (7.0 mg, 0.020 mmol, 1 eq) and pinacol borane (2.5 mg, 0.020 mmol, 1 eq) were mixed in CD_2Cl_2 (0.25 ml) at r.t. and the resulting solution transferred to a 3 mm NMR tube. The reaction was monitored by ^1H, ^{19}F and ^{11}B NMR spectroscopy.



^1H NMR (600 MHz, 298 K, CD_2Cl_2) spectrum of the reaction of $MeB(C_6F_5)_2$ with HBPin after 18 h at r.t.

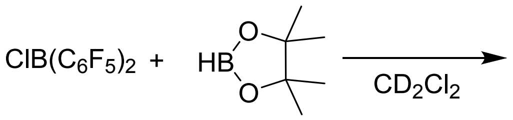


^{19}F NMR (564 MHz, 298 K, CD_2Cl_2) spectrum of the reaction of $MeB(C_6F_5)_2$ with HBPin after 18 h at r.t.

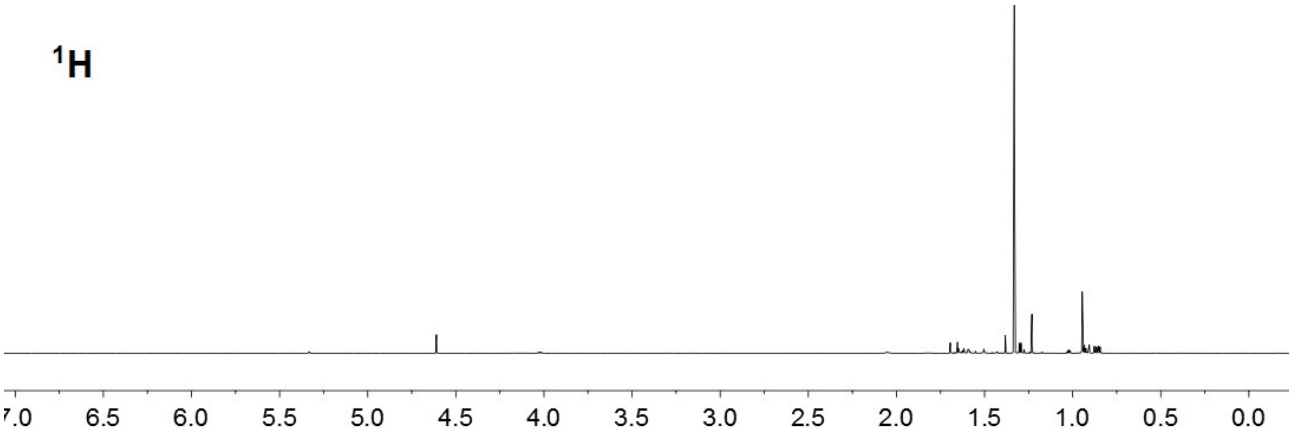


^{11}B NMR (192 MHz, 298 K, CD_2Cl_2, top) and $^{11}B\{^1H\}$ NMR (bottom) spectra of the reaction of $MeB(C_6F_5)_2$ with HBPin after 18 h at r.t.

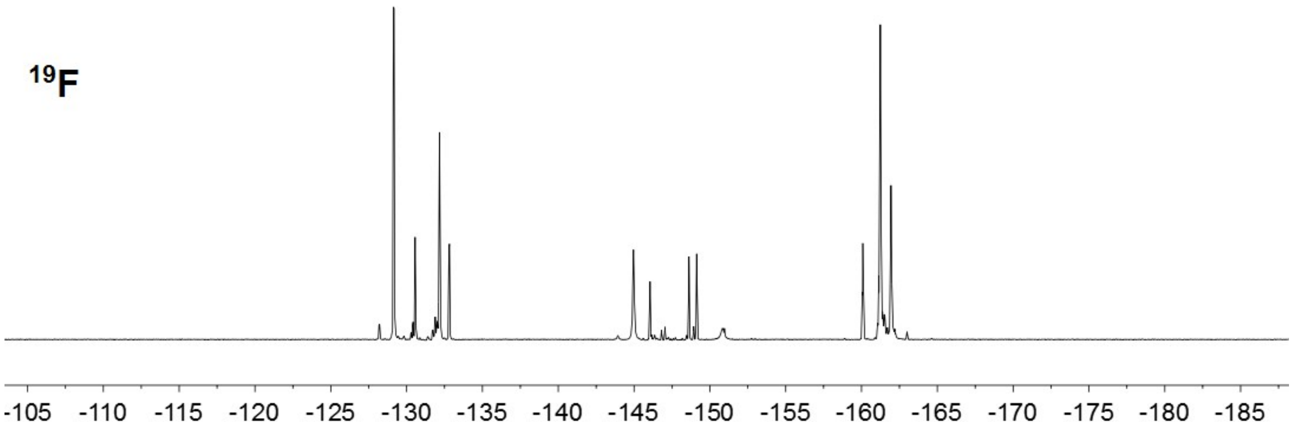
Reaction between $ClB(C_6F_5)_2$ and pinacol borane



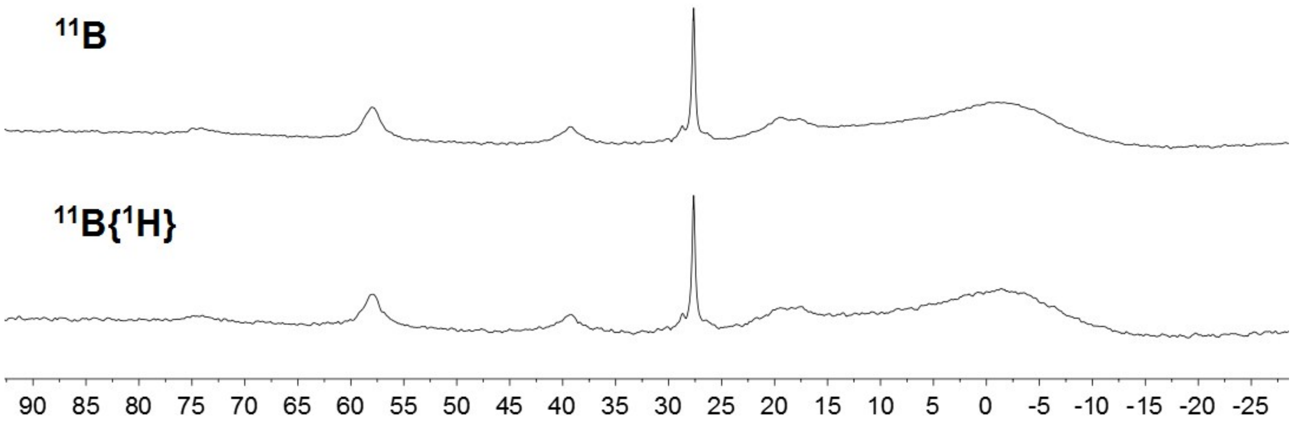
In a glovebox, $ClB(C_6F_5)_2$ (7.4 mg, 0.020 mmol, 1 eq) and pinacol borane (2.5 mg, 0.020 mmol, 1 eq) were mixed in CD_2Cl_2 (0.25 ml) at r.t. and the resulting solution transferred to a 3 mm NMR tube. The reaction was monitored by ^1H, ^{19}F and ^{11}B NMR spectroscopy.



^{1}H NMR (600 MHz, 298 K, CD_2Cl_2) spectrum of the reaction of $MeB(C_6F_5)_2$ with HBPin after 18 h at r.t.

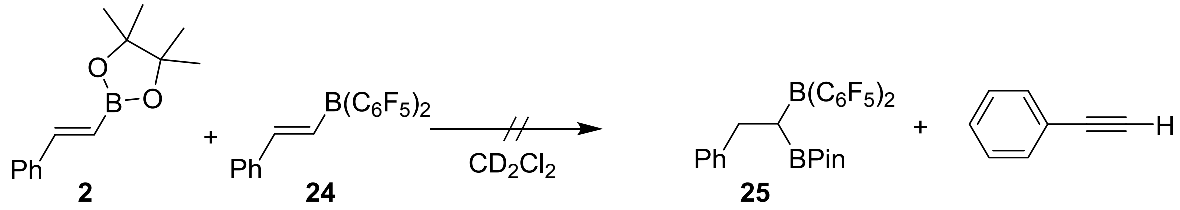


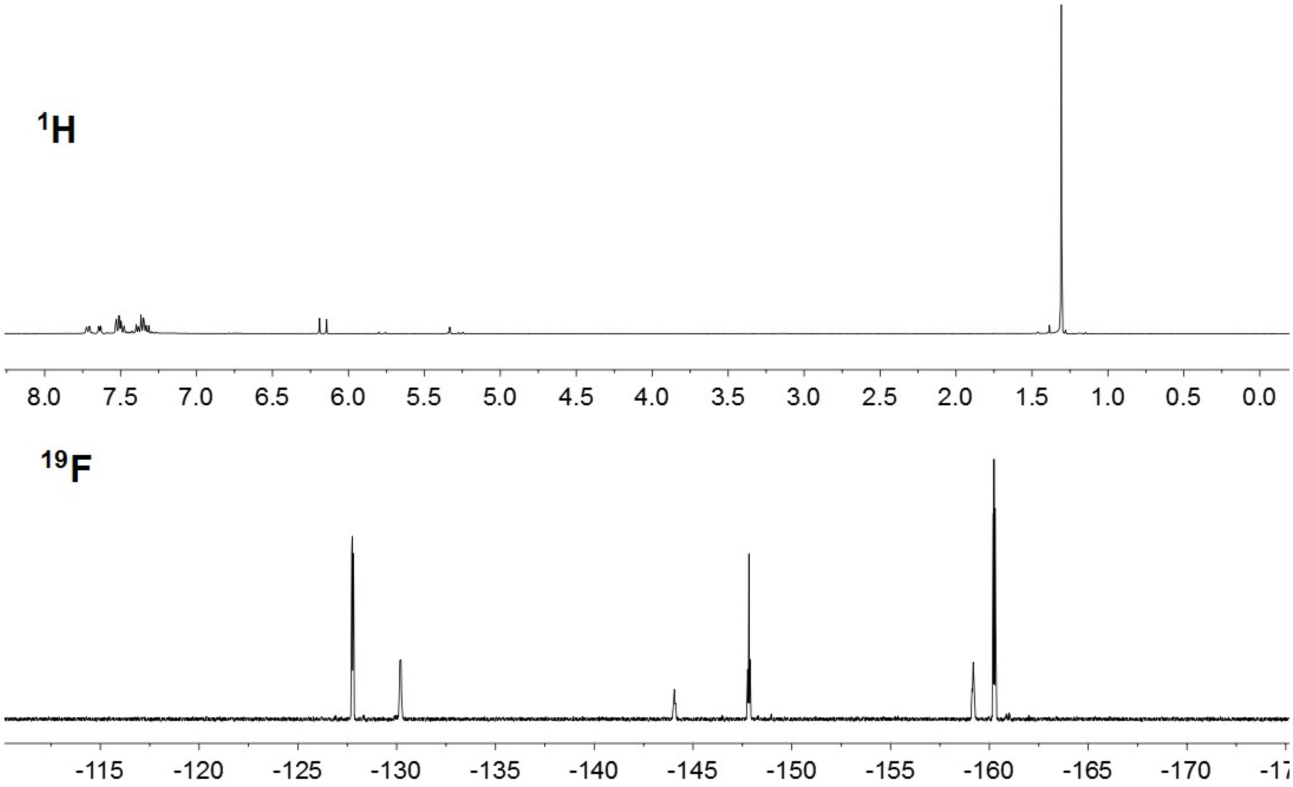
^{19}F NMR (564 MHz, 298 K, CD_2Cl_2) spectrum of the reaction of $MeB(C_6F_5)_2$ with HBPin after 18 h at r.t.



^{11}B NMR (192 MHz, 298 K, CD_2Cl_2, top) and ^{11}B{^{1}H} NMR (bottom) spectra of the reaction of $MeB(C_6F_5)_2$ with HBPin after 18 h at r.t.

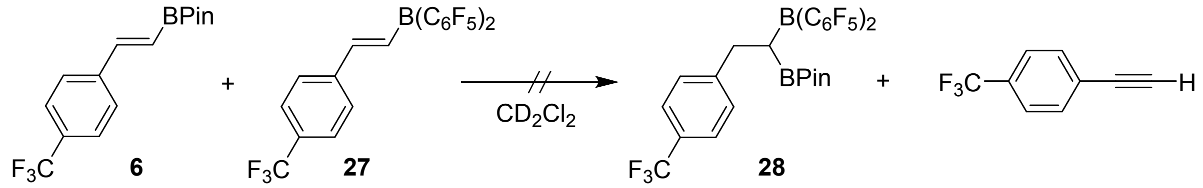
Non-equilibrium nature between compounds 2 and 24

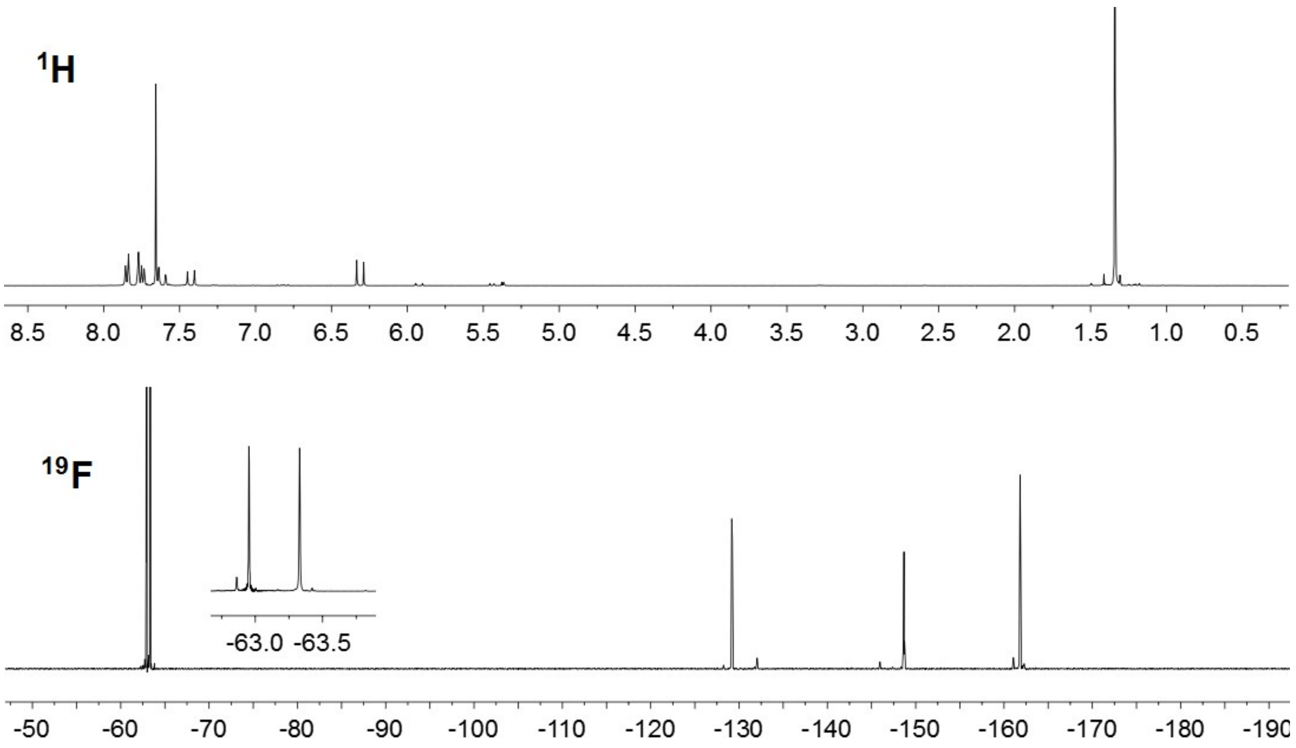




*^{1}H NMR (500 MHz, 298 K, CD_2Cl_2) and ^{19}F (376 MHz, 298 K, CD_2Cl_2) spectra of the reaction between compounds **24** and **2** after 24 h at r.t.*

Non-equilibrium nature between compounds 6 and 27

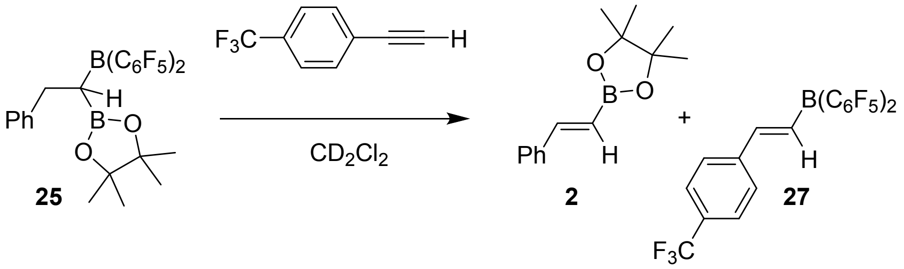




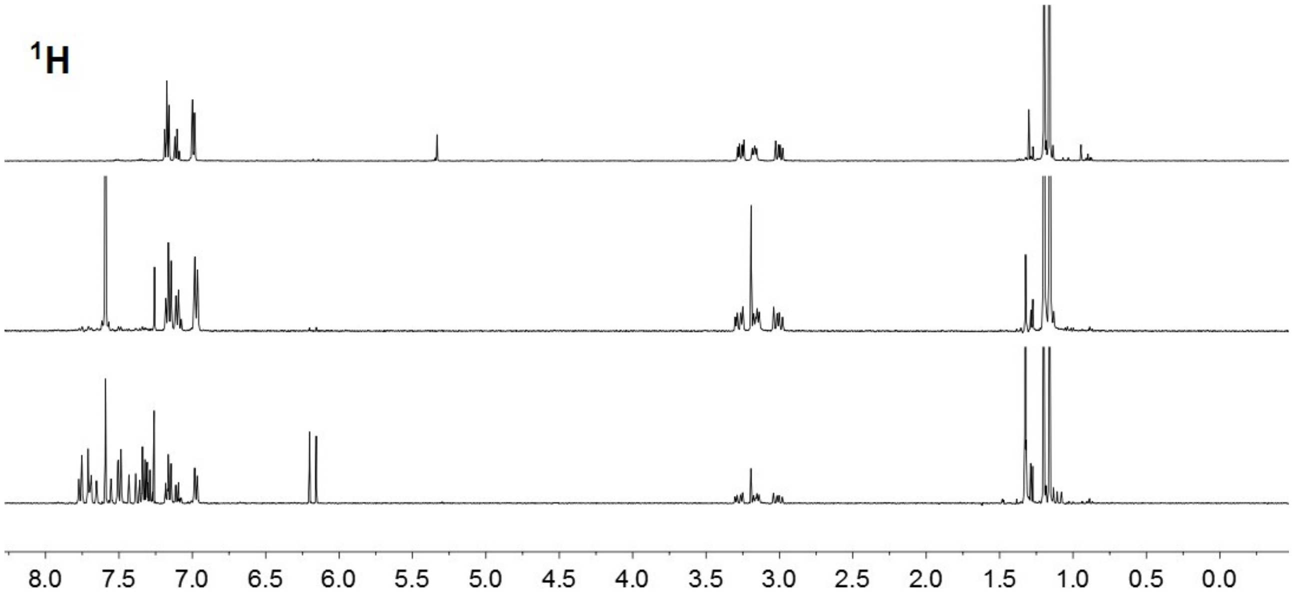
*^{1}H NMR (500 MHz, 298 K, CD_2Cl_2) and ^{19}F (376 MHz, 298 K, CD_2Cl_2) spectra of the reaction between compounds **6** and **27** after 24 h at r.t.*

3.2 Cross-over experiments

Reaction between compound 25 and *p*-CF_3-C_6H_4-C≡C-H

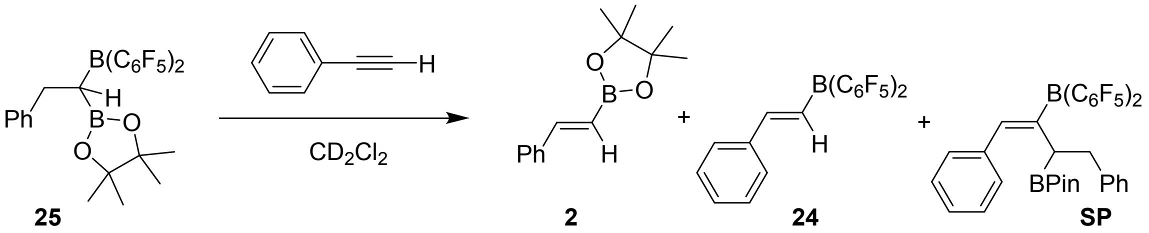


In a glovebox, compound **25** (8.0 mg, 0.014 mmol, 1 eq) and *p*-CF_3-C_6H_4-C≡C-H (2.4 mg, 0.014 mmol, 1 eq) were mixed in CD_2Cl_2 (0.25 ml) at r.t. and the resulting solution transferred to a 3 mm NMR tube. The reaction was monitored by ^{1}H, ^{19}F and ^{11}B NMR spectroscopy.

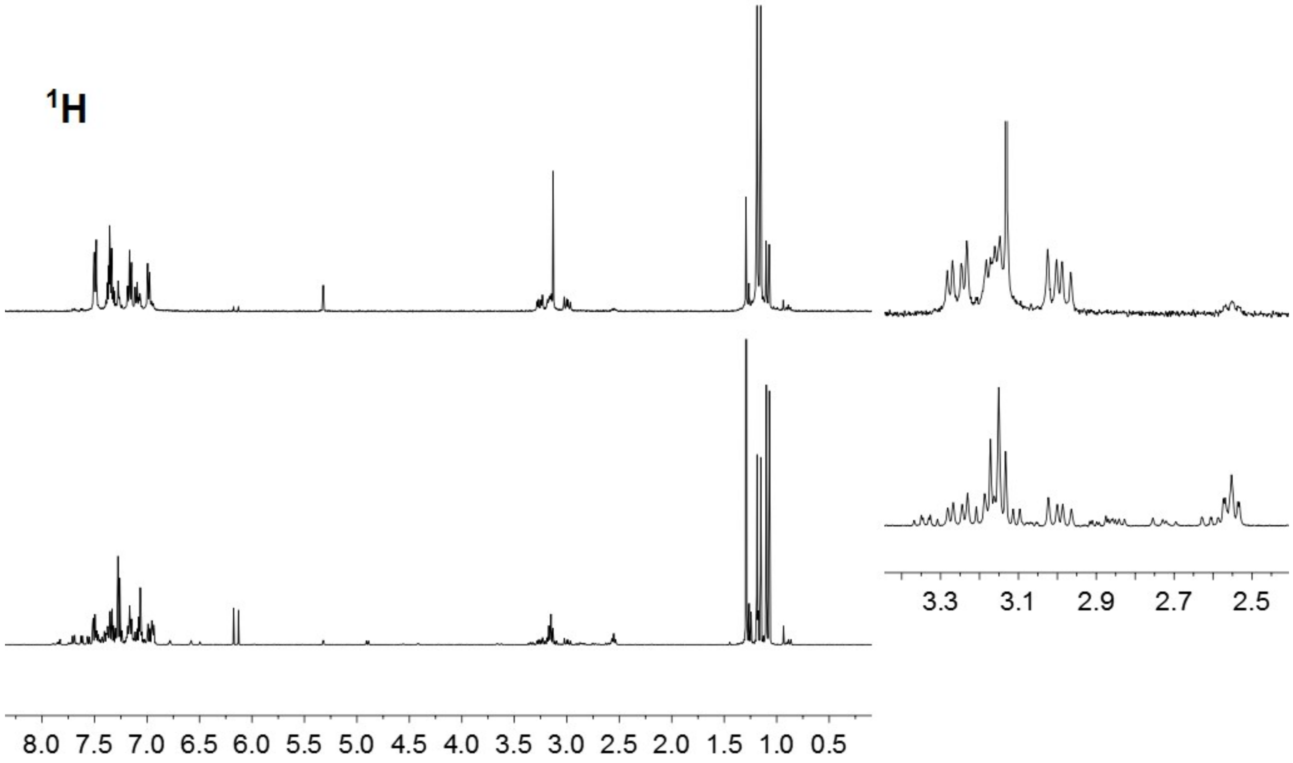


^{1}H NMR (600 MHz, 298 K, CD_2Cl_2) spectra of compound ***25*** *(top) and of the reaction between compound* ***25*** *and p-CF_3-C_6H_4-C≡C-H after 10 min at r.t. (middle) and after 18 h at r.t. (bottom).*

Reaction between compound 25 and Ph-C≡C-H

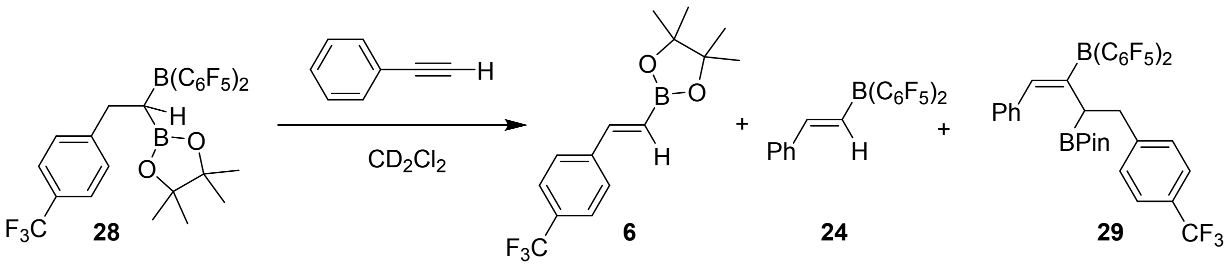


In a glovebox, compound **25** (8.0 mg, 0.014 mmol, 1 eq) and Ph-C≡C-H (1.4 mg, 0.014 mmol, 1 eq) were mixed in CD_2Cl_2 (0.25 ml) at r.t. and the resulting solution transferred to a 3 mm NMR tube. The reaction was monitored by ^{1}H, ^{19}F and ^{11}B NMR spectroscopy. After 18 h at r.t. the conversion 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 δ^{1}H 2.55, a set of diastereotopic ^{1}H NMR resonances of a CH_2 group (δ^{1}H 3.16) and diastereotopic pinacolate-methyl resonances (δ^{1}H 1.08).

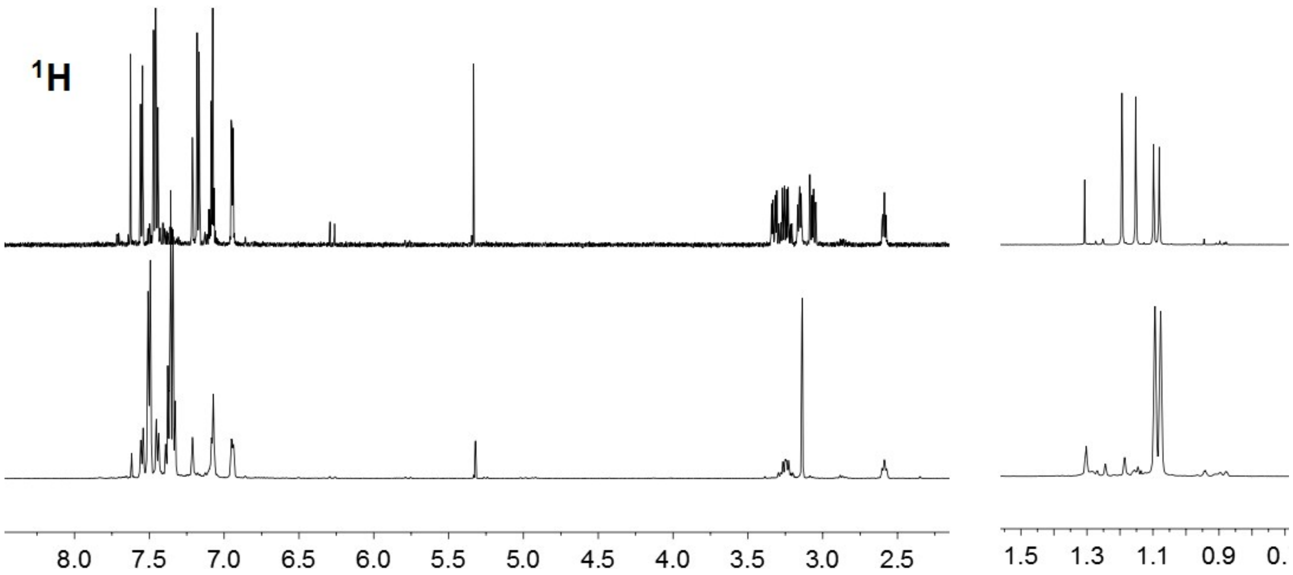


^{1}H NMR (400 MHz, 298 K, CD_2Cl_2) spectra of the reaction between compound ***25*** *and Ph-C≡C-H after 1 h at r.t. (top) and after 18 h at r.t. (bottom).*

Reaction between compound 28 and Ph-C≡C-H

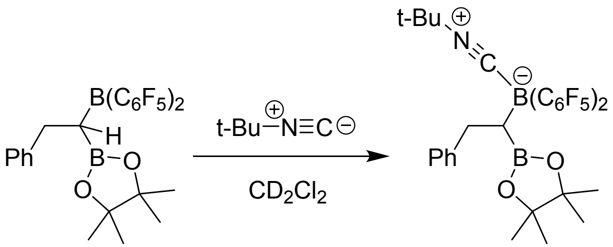


In a glovebox, compound **28** (5.5 mg, 0.009 mmol, 1 eq) and Ph-C≡C-H (1.7 mg, 0.017 mmol, 1 eq) were mixed in CD_2Cl_2 (0.25 ml) at r.t. and the resulting solution transferred to a 3 mm NMR tube. The reaction was monitored by ^{1}H, ^{19}F and ^{11}B NMR spectroscopy. After 18 h at r.t. the conversion of **28** was determined to be ca. 45% and the product ratio to be 1:1:8.7 (**6**/**24**/**29**) by ^{1}H 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 δ^{1}H 2.59, a multiplet resonances of a CH_2 group (δ^{1}H 3.24) and diastereotopic pinacolate-methyl resonances (δ^{1}H 1.09). The product could not be isolated.



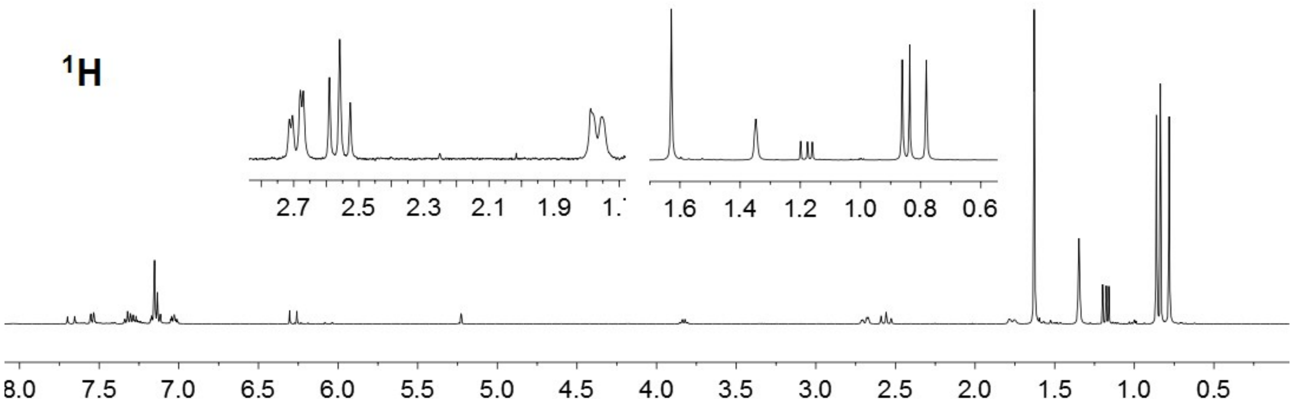
^{1}H NMR (600 MHz, 298 K, CD_2Cl_2) spectra of the reaction between compound **28** *and Ph-C≡C-H after 18 h at r.t. (top) and after addition of 5 eq Ph-C≡C-H after 4 h at r.t. (bottom).*

3.3 Reaction of compound 25 with *t*-butylisocyanide

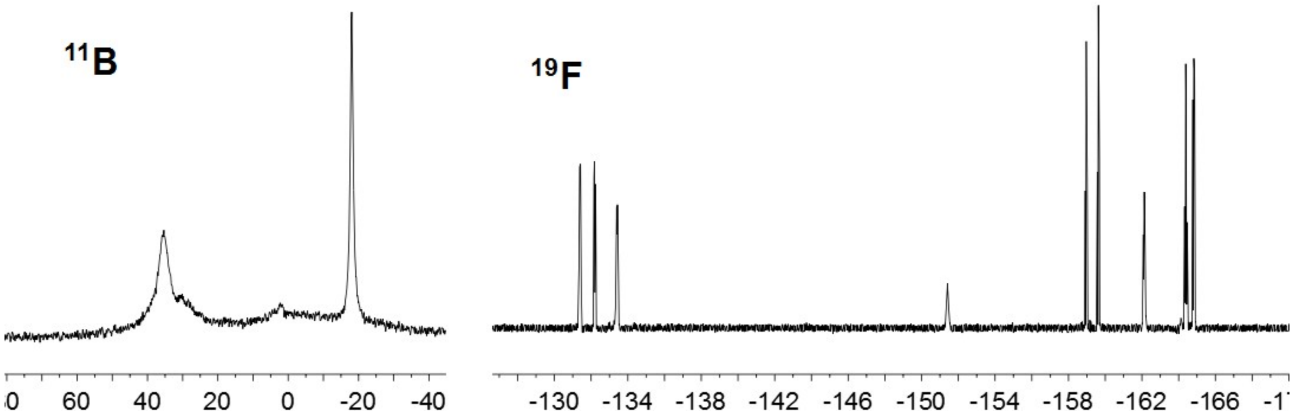


25 **26**

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_2Cl_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_2Cl_2) spectra of the reaction between compound **25** *and* t*-Bu-NC after 1 h at r.t.*



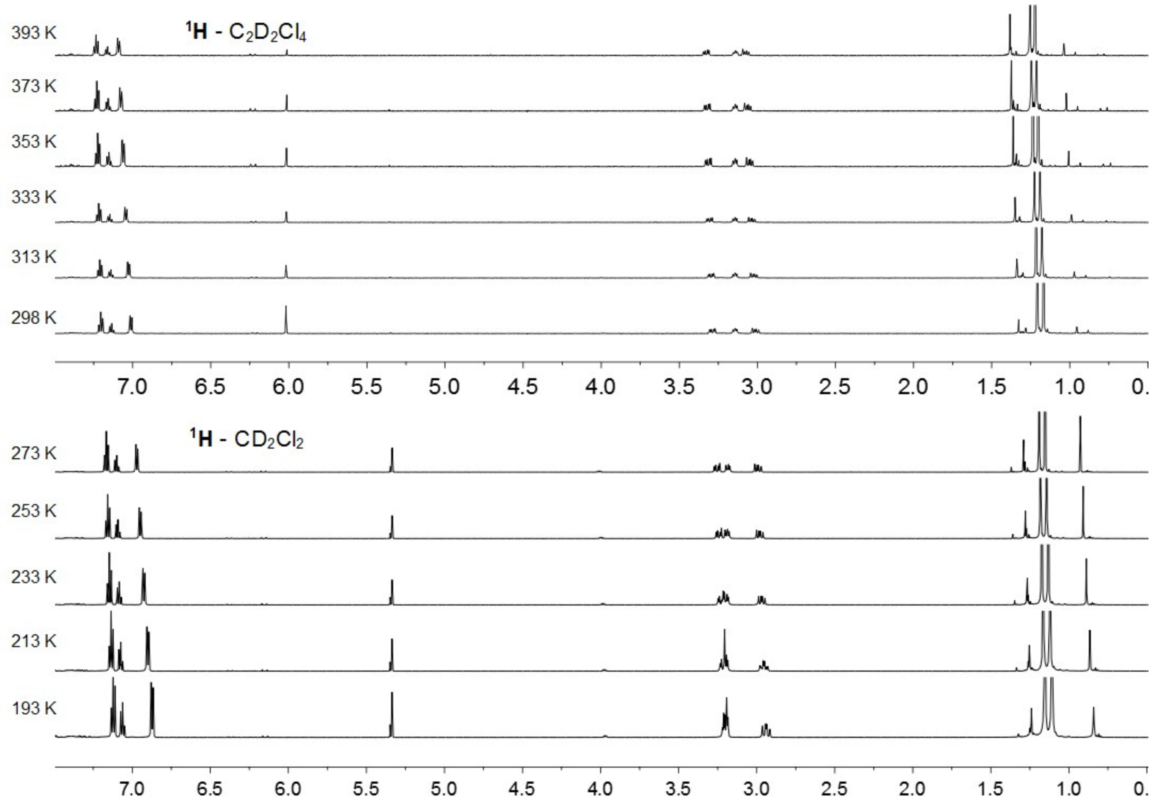
^{11}B NMR (192 MHz, 298 K, CD_2Cl_2) and ^{19}F NMR (564 MHz, 298 K, CD_2Cl_2) spectra of the reaction between compound **25** *and t-Bu-NC after 1 h at r.t.*

Single crystals of compound **26** were obtained by slow diffusion of a dilute pentane solution of *t*-Bu-NC into a concentrate CD_2Cl_2 solution of compound **25** at -40 °C.
See CCDC 1484364.

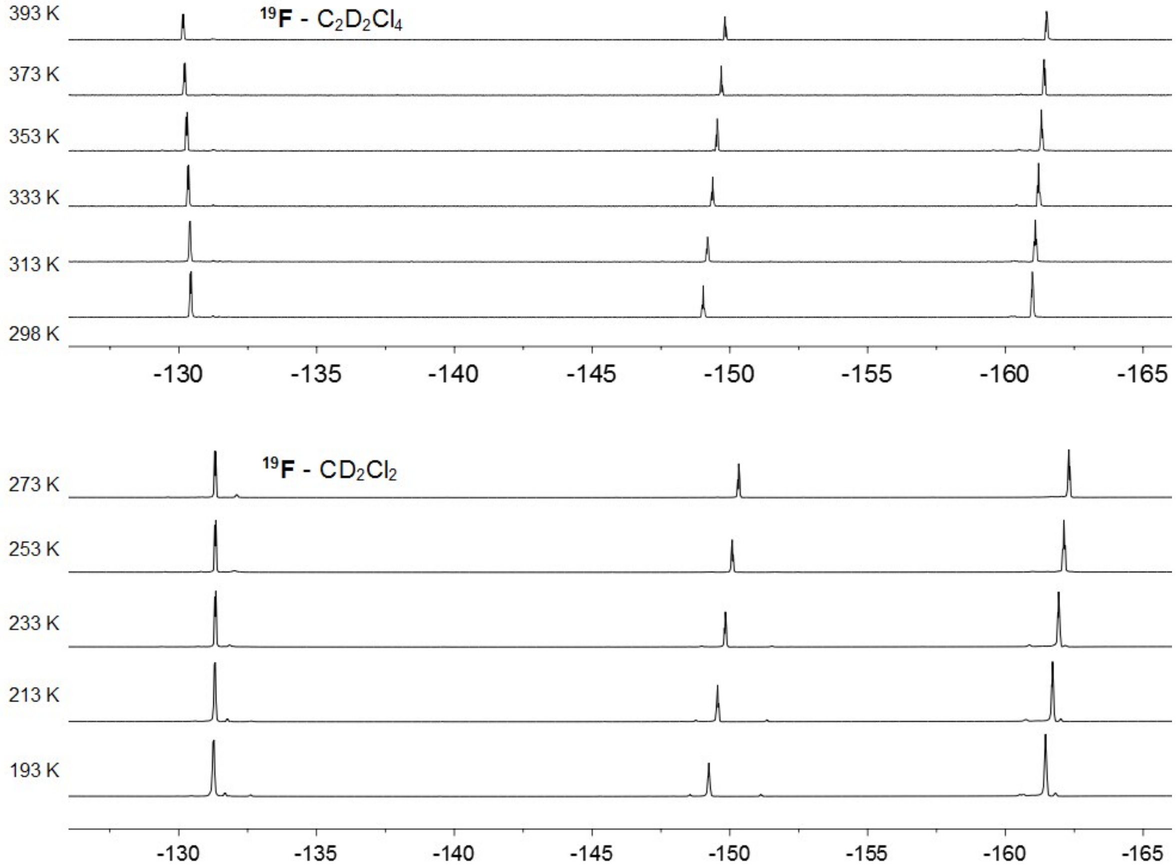
4 Variable temperature NMR studies

4.1 VT NMR study of compound 25

In a glovebox, compound **25** (11 mg, 0.020 mmol, 1 eq) was dissolved in CD_2Cl_2 (0.25 ml) at r.t. and the resulting solution transferred to a 3 mm NMR tube.

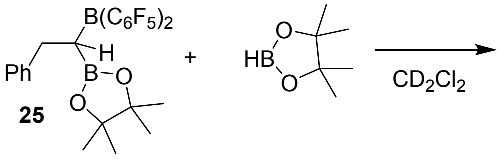


*^{1}H NMR (600 MHz, $C_2D_2Cl_4$) spectra (top) and ^{1}H NMR (600 MHz, CD_2Cl_2) spectra (bottom) compound **25** at variable temperatures.*

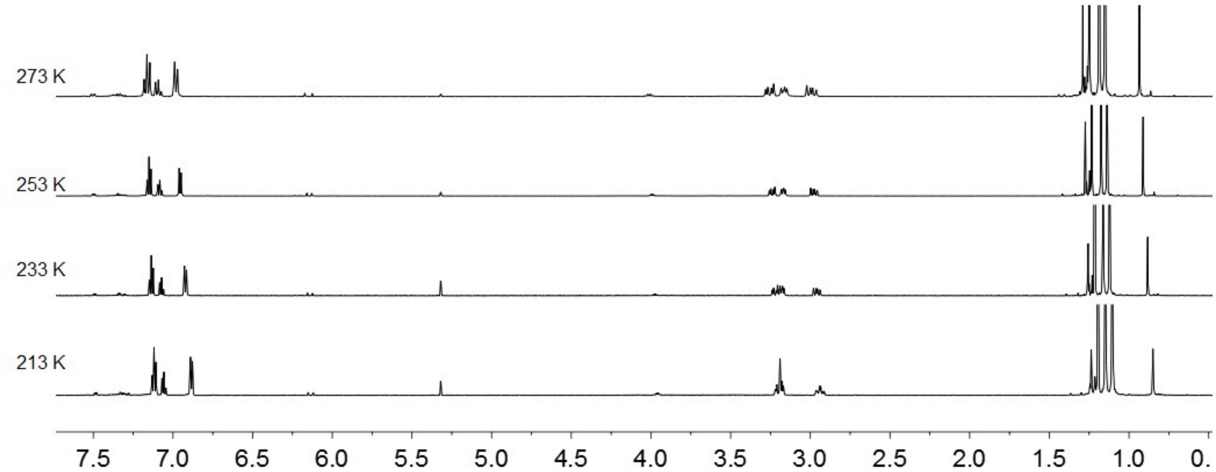


^{19}F NMR (564 MHz, $C_2D_2Cl_4$) spectra (top) and ^{19}F NMR (564 MHz, CD_2Cl_2) spectra (bottom) compound ***25*** *at variable temperatures.*

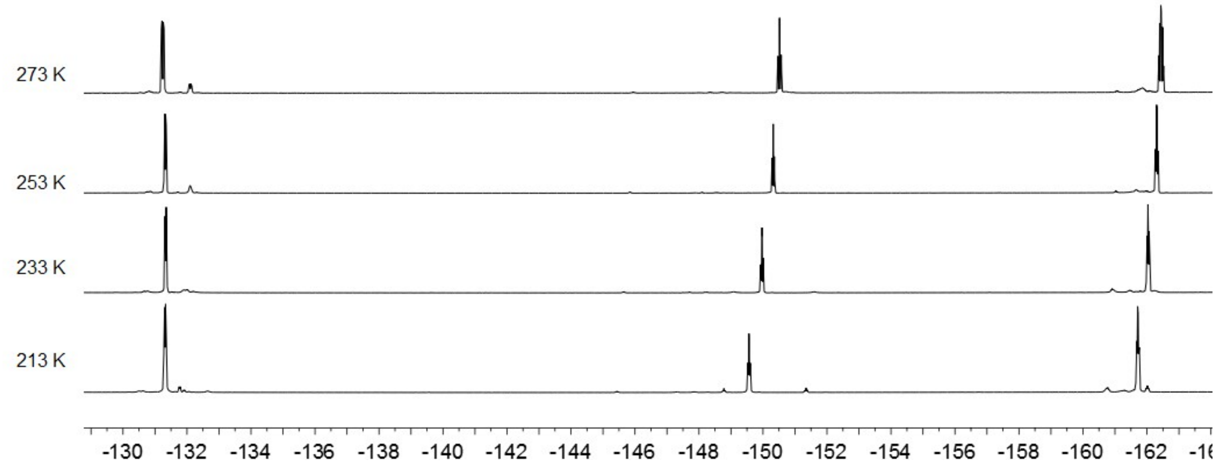
4.2 VT NMR study of the reaction of compound 25 and HBPin



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_2Cl_2 (0.25 ml) at r.t. and the resulting solution transferred to a 3 mm NMR tube.

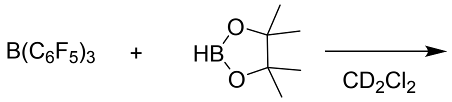


^1H NMR (600 MHz, CD_2Cl_2) spectra of a 1:1 mixture of compound ***25*** *and HBPin at variable temperatures.*

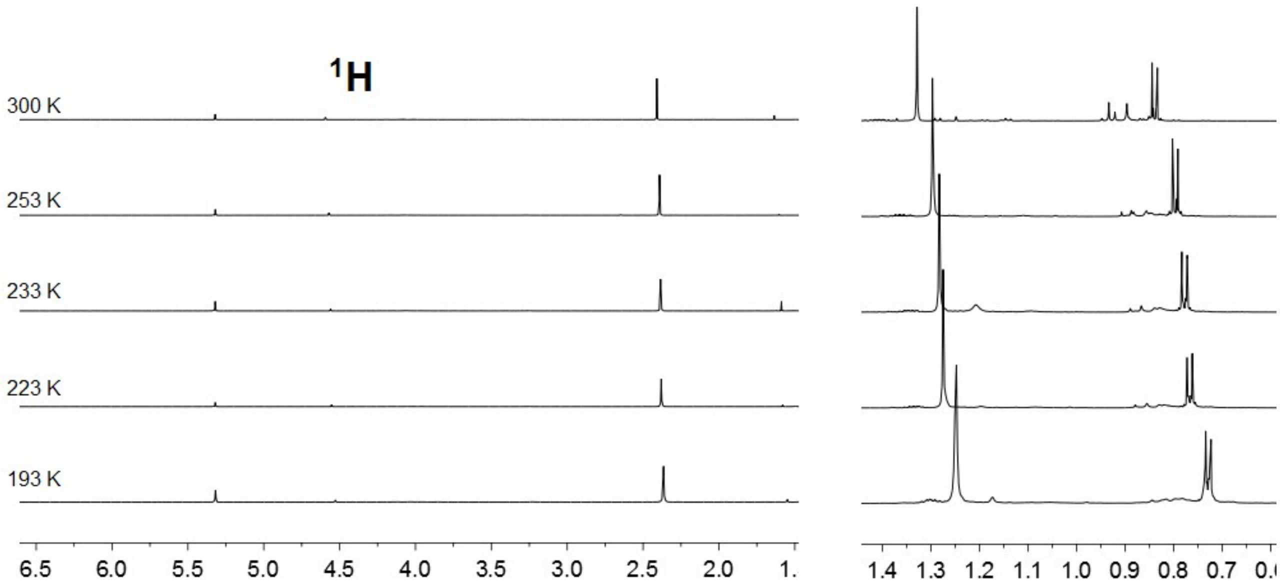


^{19}F NMR (564 MHz, CD_2Cl_2) spectra of a 1:1 mixture of compound ***25*** *and HBPin at variable temperatures.*

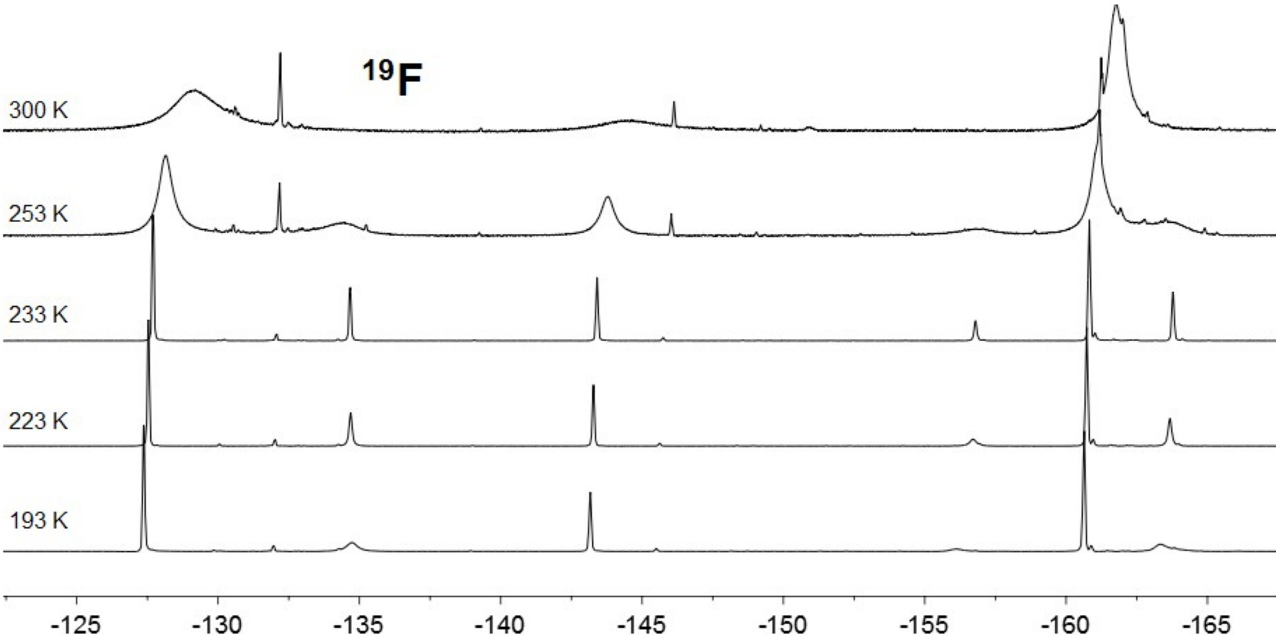
4.3 VT NMR study of the reaction of $B(C_6F_5)_3$ and HBPin



In a glovebox, $B(C_6F_5)_3$ (9.5 mg, 0.016 mmol, 1 eq) and pinacol borane (2.1 mg, 0.016 mmol, 1 eq) were mixed in CD_2Cl_2 (0.25 ml) at r.t. and the resulting solution transferred to a 3 mm NMR tube.

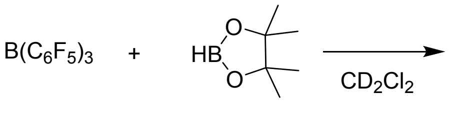


^1H NMR (600 MHz, CD_2Cl_2) spectra of a 1:1 mixture of $B(C_6F_5)_3$ and HBPin at variable temperatures.

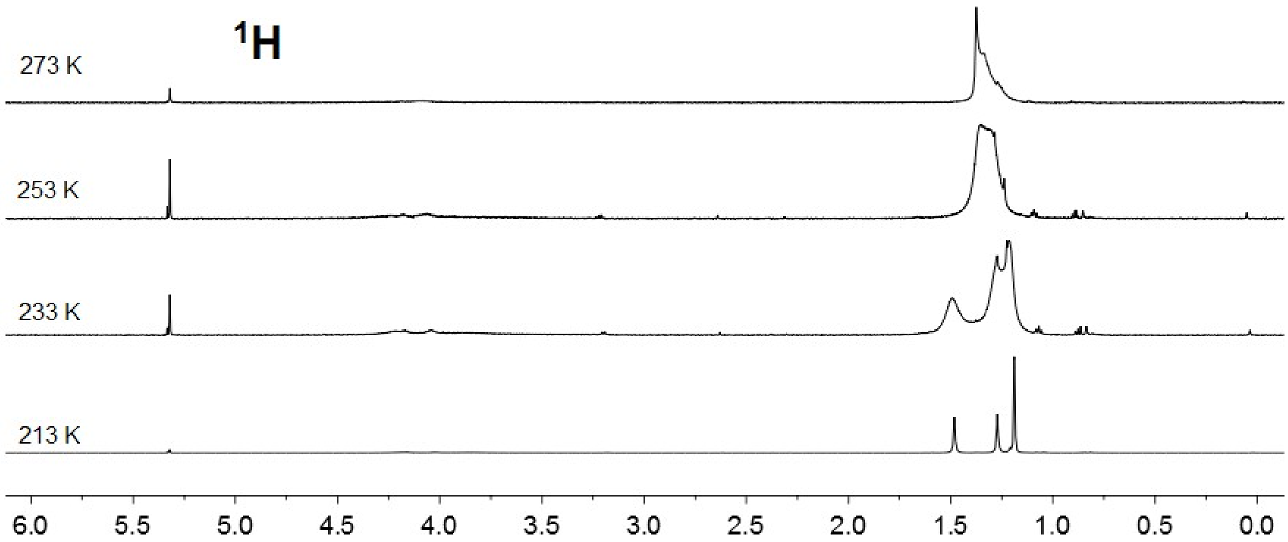


^{19}F NMR (564 MHz, CD_2Cl_2) spectra of a 1:1 mixture of $B(C_6F_5)_3$ and HBPin at variable temperatures.

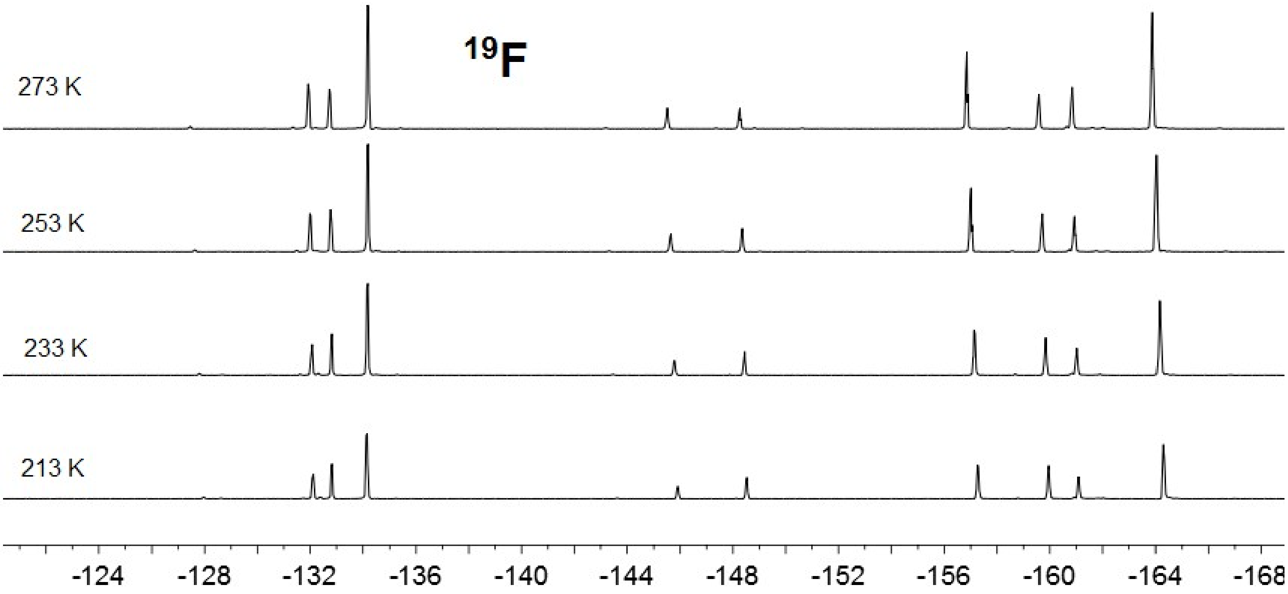
4.4 VT NMR study of the reaction of $HB(C_6F_5)_2$ and HBPin



In a glovebox, $B(C_6F_5)_3$ (13.5 mg, 0.04 mmol, 1 eq) and pinacol borane (5.0 mg, 0.04 mmol, 1 eq) were dissolved separately in CD_2Cl_2 (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_2Cl_2) spectra of a 1:1 mixture of $HB(C_6F_5)_2$ and HBPin at variable temperatures.



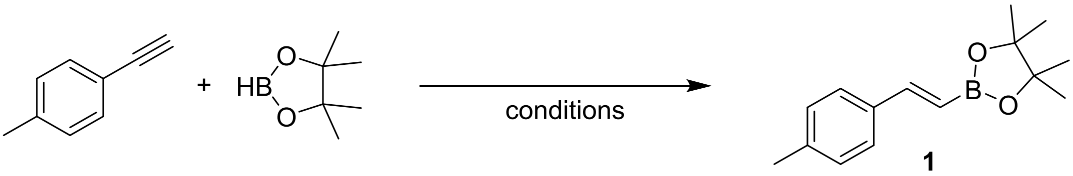
^{19}F NMR (564 MHz, CD_2Cl_2) spectra of a 1:1 mixture of $HB(C_6F_5)_2$ and HBPin at variable temperatures.

5 Catalytic Reactions

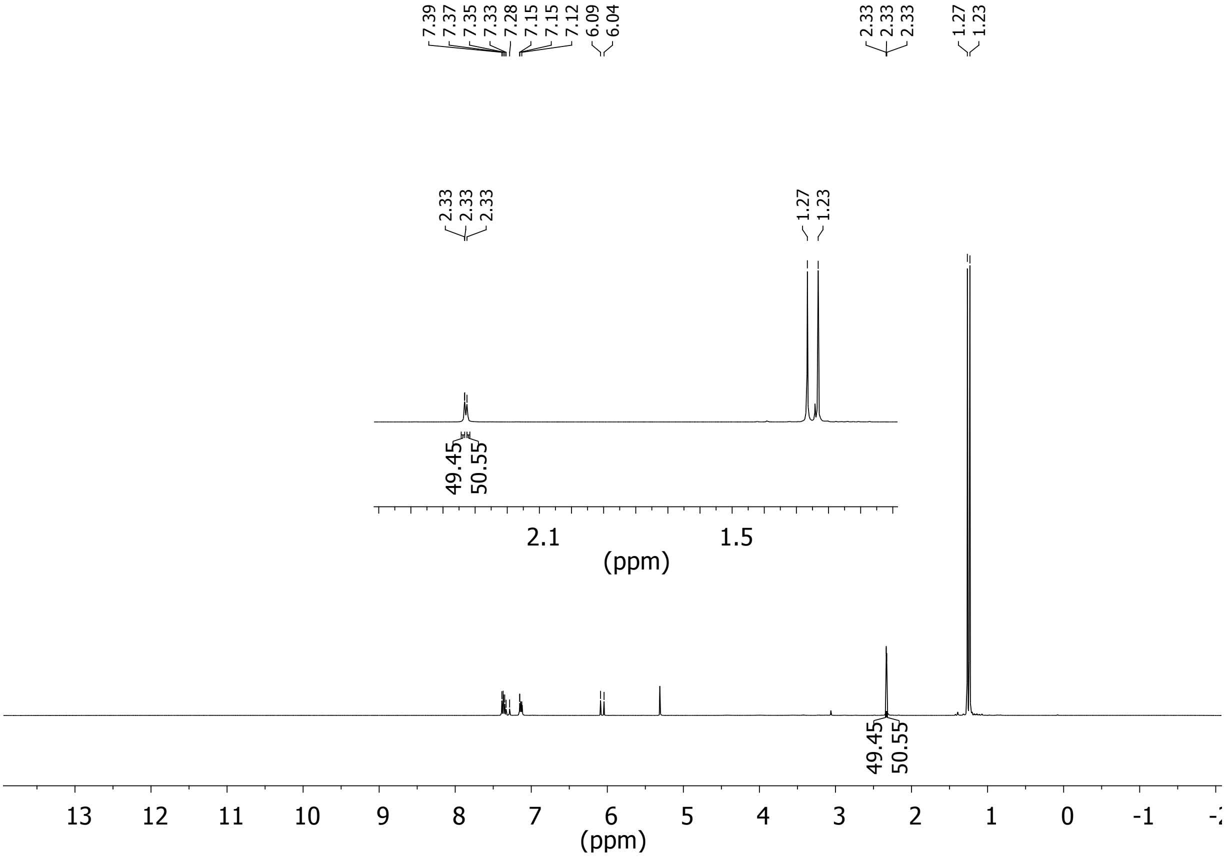
5.1 Optimization of the reaction conditions and catalyst screening

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.



Model reaction for optimization studies.

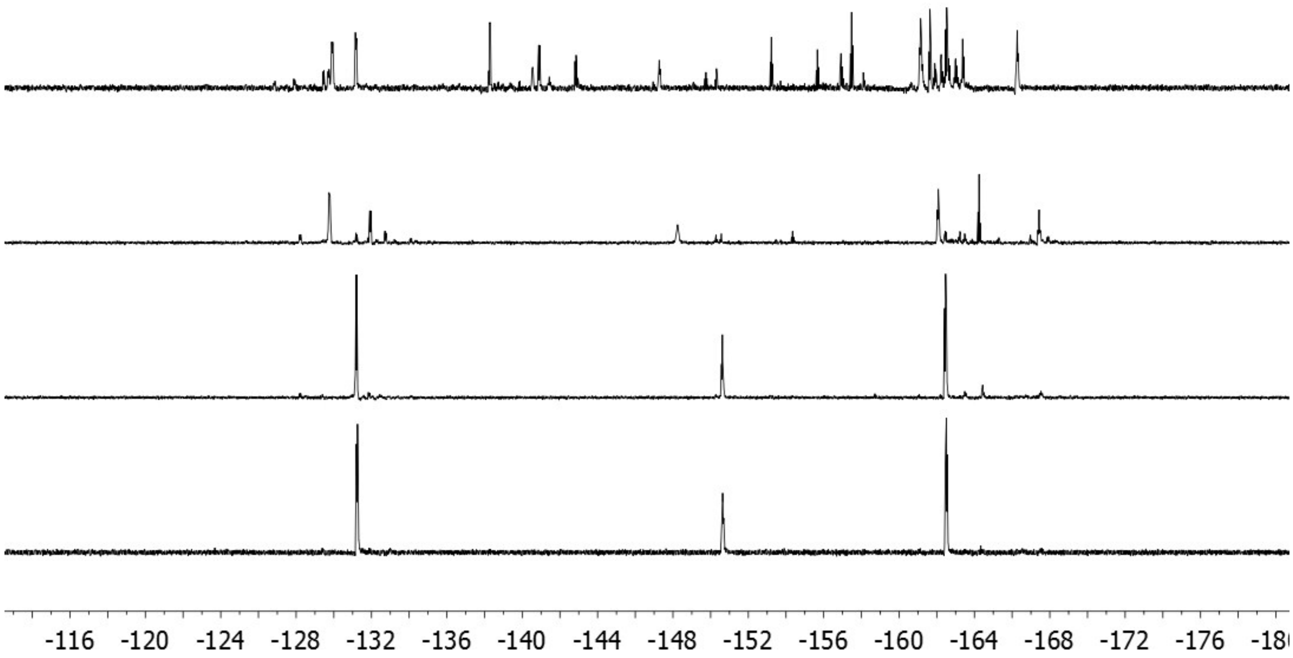


Representative crude ^1H NMR spectrum of the reaction in CD_2Cl_2 (50% conversion of starting material).

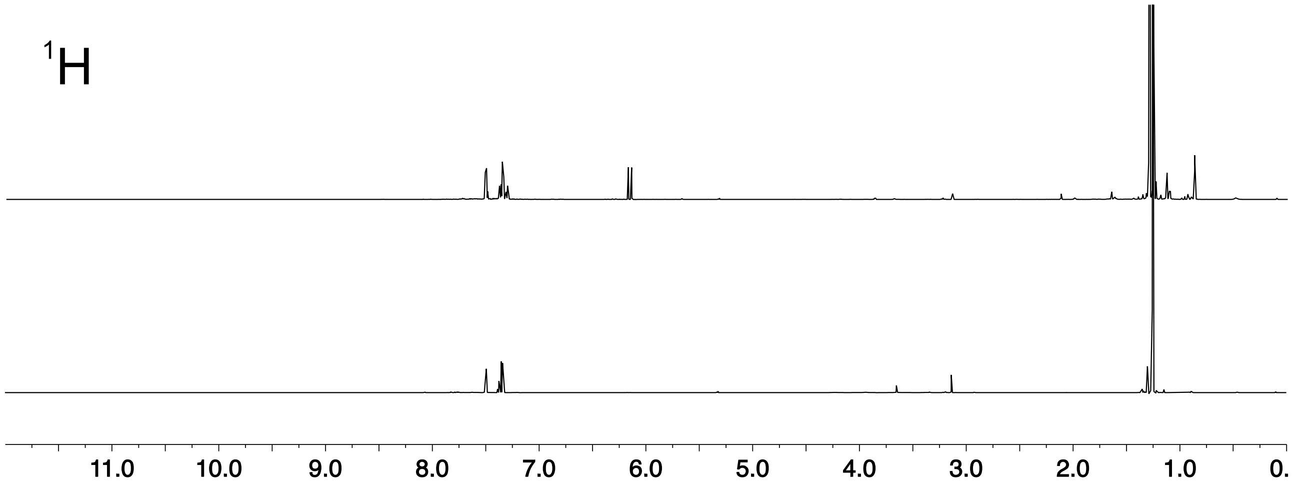
No	Alkyne	HBpin	Catalyst	Solvent	T	time	Yield
1	0.1 mmol	0.1 mmol	-	$CDCl_3$ (0.5 ml)	60°C	15 h	0%
2	0.1 mmol	0.1 mmol	-	CD_2Cl_2 (0.5 ml)	50°C	18 h	0%
3	0.1 mmol	0.1 mmol	-	C_6D_5Br (0.5 ml)	60°C	18 h	0%
4	0.1 mmol	0.1 mmol	5 mol% $[Ph_3PF]^+$	CD_2Cl_2 (0.5 ml)	50°C	48 h	0%
5	0.1 mmol	0.1 mmol	5 mol% $[Ph_2PF(C_6H_4BCy_2)]^+$	$CDCl_3$ (0.5 ml)	60°C	15 h	55%
6	0.1 mmol	0.1 mmol	5 mol% $[MeOC_6H_4CPh_2]^+$	$CDCl_3$ (0.5 ml)	60°C	15 h	38%
7	0.1 mmol	0.1 mmol	$[Ph_3C][B(C_6F_5)_4]$	$CDCl_3$ (0.5 ml)	60°C	15 h	0%
8	0.1 mmol	0.1 mmol	5 mol% $B(C_6F_5)_3$	$CDCl_3$ (0.5 ml)	60°C	18 h	86%
9	0.1 mmol	0.1 mmol	10 mol% $B(C_6F_5)_3$	$CDCl_3$ (0.5 ml)	r.t.	2 h	74%
10	0.1 mmol	0.1 mmol	10 mol% $B(C_6F_5)_3$	CD_2Cl_2 (0.5 ml)	r.t.	2 h	98%
11	0.1 mmol	0.1 mmol	10 mol% $B(C_6F_5)_3$	C_6D_5Br (0.5 ml)	r.t.	2 h	80%
12	0.05 mmol	0.055 mmol	5 mol% $B(C_6F_5)_3$	CD_2Cl_2 (0.25 ml)	r.t.	3.5 h	56%
13	0.05 mmol	0.055 mmol	2.5 mol% $B(C_6F_5)_3$	CD_2Cl_2 (0.25 ml)	r.t.	3.5 h	35%
14	0.05 mmol	0.055 mmol	1.0 mol% $B(C_6F_5)_3$	CD_2Cl_2 (0.25 ml)	r.t.	2 d	1%
15	0.1 mmol	0.11 mmol	5 mol% $B(C_6F_5)_3$	CD_2Cl_2 (0.5 ml)	r.t.	3 h	75%
16	0.1 mmol	0.11 mmol	5 mol% $B(C_6F_5)_3$	CD_2Cl_2 (0.5 ml)	r.t.	4 h	81%
17	0.1 mmol	0.11 mmol	5 mol% $B(C_6F_5)_3$	CD_2Cl_2 (0.5 ml)	r.t.	16 h	99%
18	0.1 mmol	0.1 mmol	5 mol% $PhCH{=}(C_6F_5)(B(C_6F_5)_2)$	CD_2Cl_2 (0.5 ml)	r.t.	2 h	30%
19	0.1 mmol	0.1 mmol	$MeB(C_6F_5)_2$	CD_2Cl_2 (0.5 ml)	r.t.	2 h	57%
20	0.1 mmol	0.1 mmol	$ClB(C_6F_5)_2$	CD_2Cl_2 (0.5 ml)	r.t.	2 h	99%
21	0.05 mmol	0.055 mmol	5 mol% $HB(C_6F_5)_2$	CD_2Cl_2 (0.25 ml)	r.t.	30 min	99%
22	0.05 mmol	0.055 mmol	2.5 mol% $HB(C_6F_5)_2$	CD_2Cl_2 (0.25 ml)	r.t.	30 min	89%
23	0.05 mmol	0.055 mmol	2.5 mol% $HB(C_6F_5)_2$	CD_2Cl_2 (0.25 ml)	r.t.	2 h	96%
24	0.05 mmol	0.055 mmol	1.0 mol% $HB(C_6F_5)_2$	CD_2Cl_2 (0.25 ml)	r.t.	30min	34%
25	0.05 mmol	0.055 mmol	1.0 mol% $HB(C_6F_5)_2$	CD_2Cl_2 (0.25 ml)	r.t.	2 h	44%
26	0.05 mmol	0.055 mmol	1.0 mol% $HB(C_6F_5)_2$	CD_2Cl_2 (0.25 ml)	r.t.	5 h	47%
27	0.05 mmol	0.055 mmol	1.0 mol% $HB(C_6F_5)_2$	CD_2Cl_2 (0.25 ml)	r.t.	24 h	51%

Conversion determined by ^1H NMR integration of characteristic resonances.

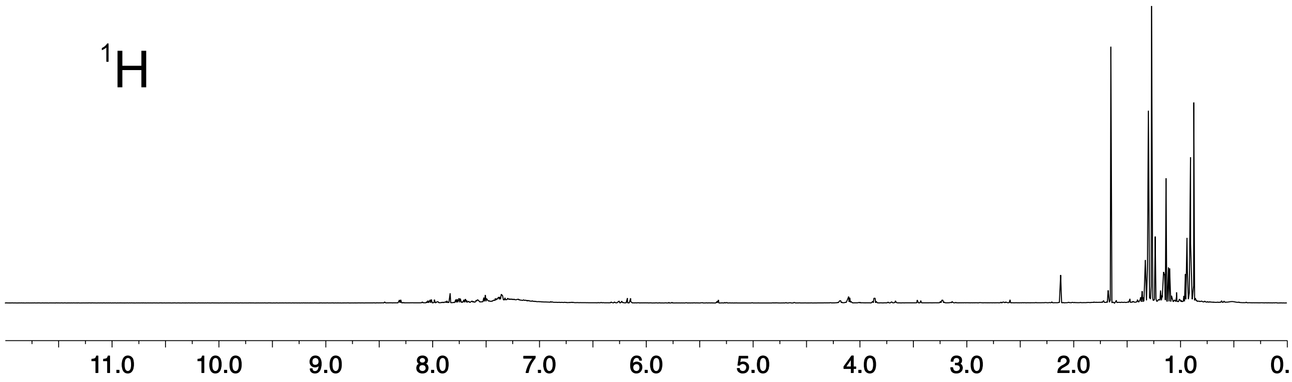
^{19}F NMR spectra of selected optimization reactions with different catalysts illustrating the decomposition/transformation of the added catalyst.



^{19}F (470 MHz, 298 K, CD_2Cl_2) spectra of the model reaction with different catalysts during the reaction: $B(C_6F_5)_3$. $MeB(C_6F_5)_2$, $ClB(C_6F_5)_2$, $HB(C_6F_5)_2$ *(top to bottom).*



Stacked ^1H-NMR (600 MHz, CD_2Cl_2) spectra of the reaction solutions from the catalytic hydroboration of phenylacetylene employing [o-$Ph_2PF(Ph)BCy_2$][$B(C_6F_5)_4$] (top) and [Ph_3PF][$B(C_6F_5)_4$] (bottom).



^{1}H-NMR (600 MHz, CD_2Cl_2) spectra of the reaction solution from the catalytic hydroboration of phenylacetylene employing $[(C_6F_5)_3PF][B(C_6F_5)_4]$.

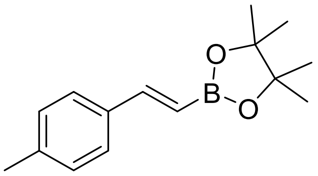
5.2 General procedure

General procedure for the synthesis of alkenyl boranes: All work was performed in a glove box with a dry nitrogen atmosphere. CH_2Cl_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_2Cl_2 before addition of a catalytic amount of $HB(C_6F_5)_2$ (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 $CDCl_3$ and subjected to ^{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_2Cl_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-ethynyltoluene (58 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 **1** was isolated in 99% (119 mg, 0.49 mmol) yield as a pale yellow oil. The NMR data was consistent with the literature.[S9]

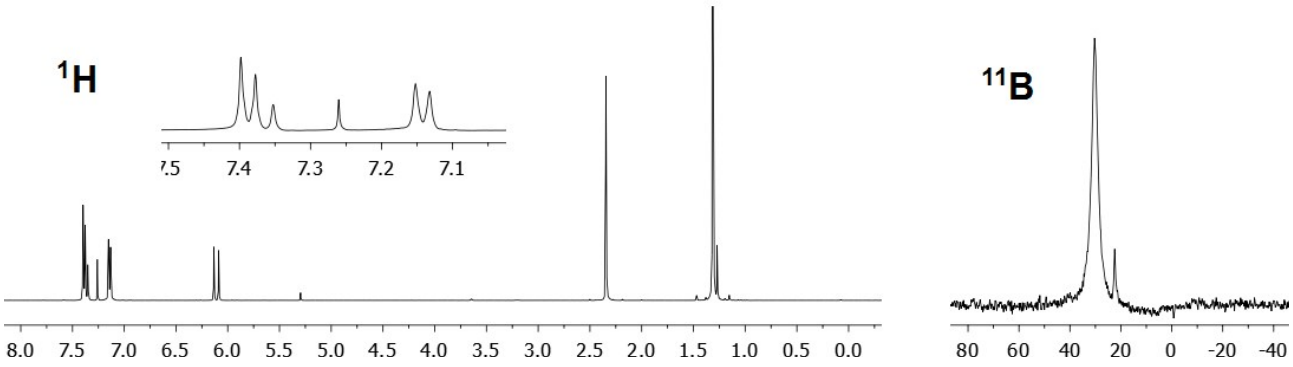
R$_f$ (hexanes/ether; 90/10) = 0.40.

^{1}H NMR (400 MHz, 298 K, CDCl$_3$): δ^{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).

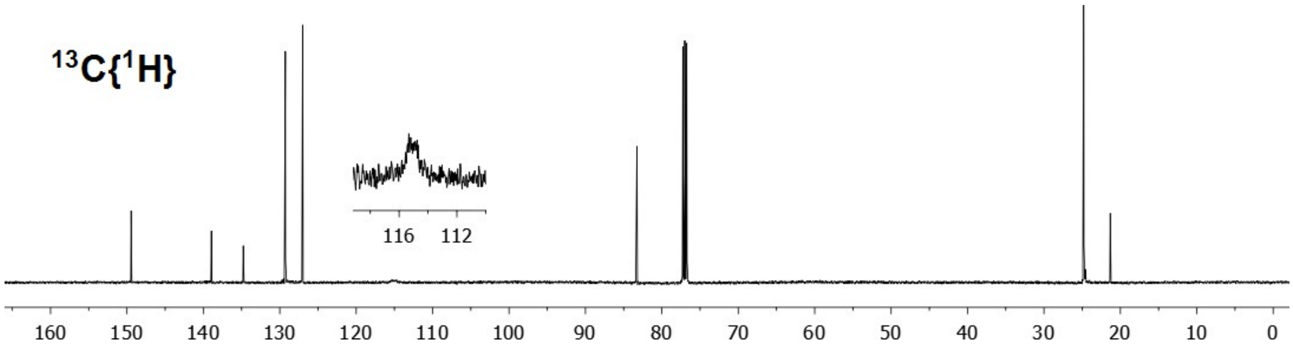
^{13}C{^{1}H} NMR (126 MHz, 298 K, CDCl$_3$): δ^{13}C: 149.5, 138.9, 134.8, 129.3, 127.0, 115.1 (br s), 83.3, 24.8, 21.3.

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

HRMS (DART-TOF+): mass [M+H] calcd. for $C_{15}H_{22}B_1O_2$ 245.17128 *Da*, found: 245.17134 *Da*.

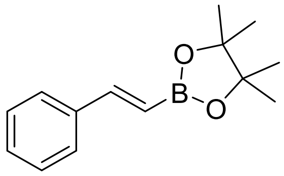


^{1}H NMR (400 MHz, 298 K, CDCl$_3$) and ^{11}B (128 MHz, 298 K, CDCl$_3$) spectra of compound **1**.



^{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_2Cl_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]

[S9] R. Hemelaere, F. Caijo, M. Mauduit, F. Carreaux, B. Carboni, *Eur. J. Org. Chem.* **2014**, *2014*, 3328-3333.

[S10] Z. Yang, M. Zhong, X. Ma, K. Nijesh, S. De, P. Parameswaran, H. W. Roesky, *J. Am. Chem. Soc.* **2016**, *138*, 2548-

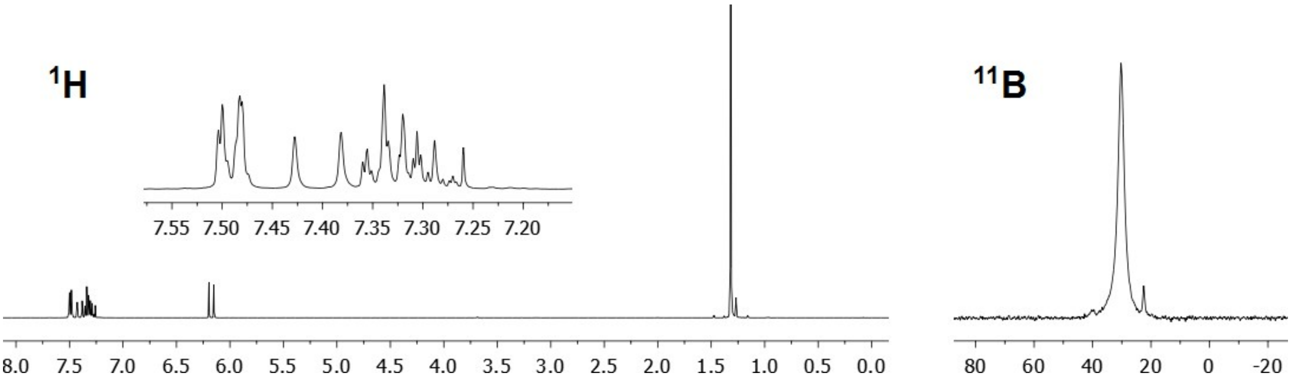
R$_f$ (hexanes/ether; 90/10) = 0.52.

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

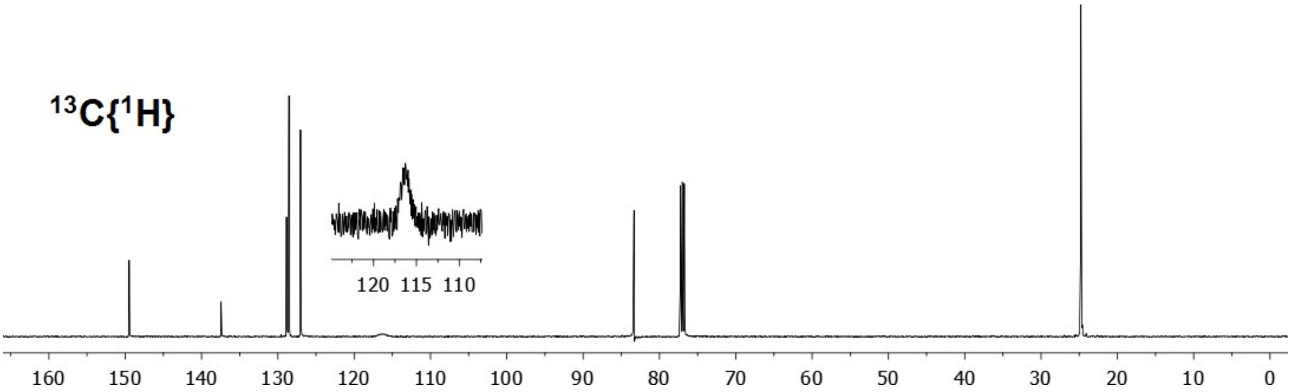
^{13}C{^{1}H} NMR (126 MHz, 298 K, CDCl$_3$): δ^{13}C: 149.5, 137.4, 128.9, 128.5, 127.0, 116.3, 83.3, 24.8.

^{11}B NMR (128 MHz, CDCl$_3$): δ^{11}B: 30.2 ($\nu_{1/2}$ ≈ 380 Hz).

HRMS (DART-TOF+): mass [M+H] calcd. for $C_{14}H_{20}B_1O_2$ 231.15563 *Da*, found: 231.15530 *Da*.

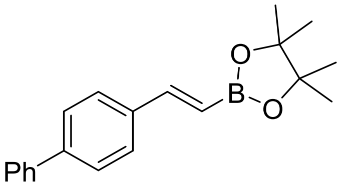


^{1}H NMR (500 MHz, 298 K, CDCl$_3$) and ^{11}B (128 MHz, 298 K, CDCl$_3$) spectra of compound **2**.



^{13}C{^{1}H} 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_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 **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.

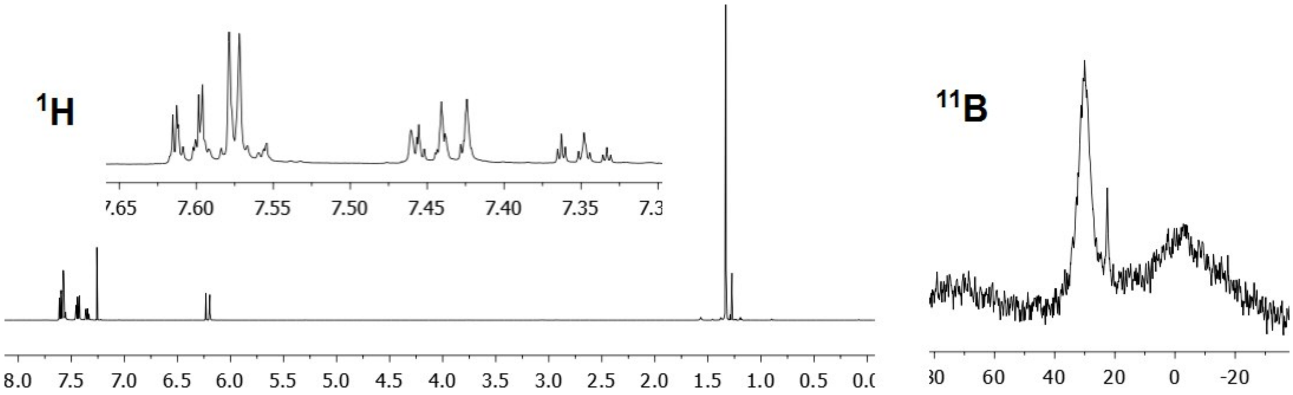
R$_f$ (hexanes/ether; 90/10) = 0.35.

^{1}H NMR (500 MHz, 298 K, CDCl$_3$): δ^{1}H: 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).

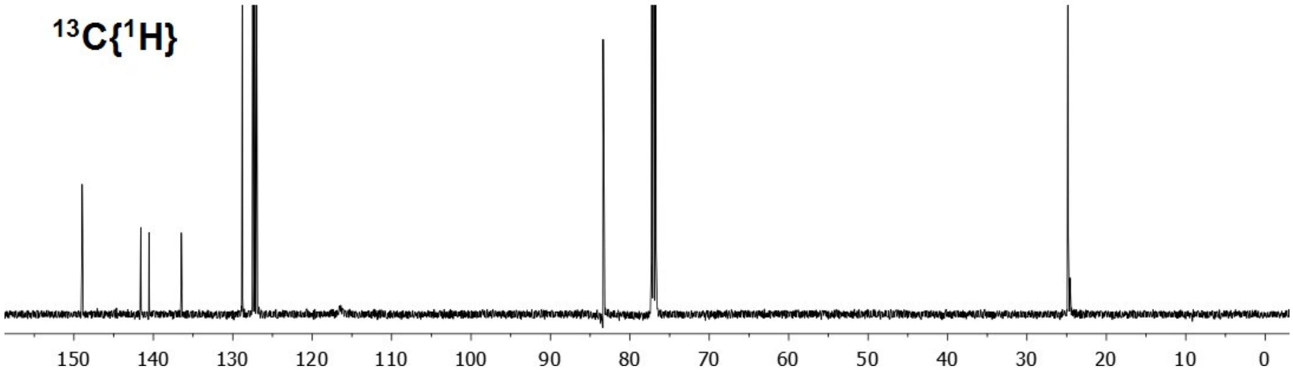
^{13}C{^{1}H} NMR (126 MHz, 298 K, CDCl$_3$): δ^{13}C: 149.0, 141.6, 140.6, 136.5, 128.8, 127.5, 127.4, 127.3, 127.0, 116.3 (br, =CH^B), 83.4, 24.8.

^{11}B NMR (128 MHz, CDCl$_3$): δ^{11}B: 30.1 ($\nu_{1/2}$ ≈ 400 Hz).

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

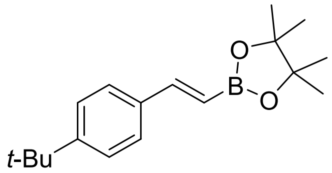


^{1}H NMR (500 MHz, 298 K, CDCl$_3$) and ^{11}B NMR (128 MHz, 298 K, CDCl$_3$) spectra of compound **3**.



^{13}C{^{1}H} 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$_6$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 **4** was isolated in 87% (129 mg, 0.45 mmol) yield as a yellow solid.

R$_f$ (hexanes/ether; 90/10) = 0.51.

^{1}H NMR (500 MHz, 298 K, CDCl$_3$): δ^{1}H: 7.43 (m, 2H, *o*-Ar), 7.38 (d, $^3J_{HH}$ = 18.4 Hz, =CH^{Ar}), 7.36 (m, 2H, *m*-Ar) 6.12 (d, $^3J_{HH}$ = 18.4 Hz, 18.4 Hz, 1H, =CH^B), 1.314 (s, 9H, *t*-Bu)^t 1.313 (s, 12H, CH$_3$)^t. ^{t} tentatively assigned.

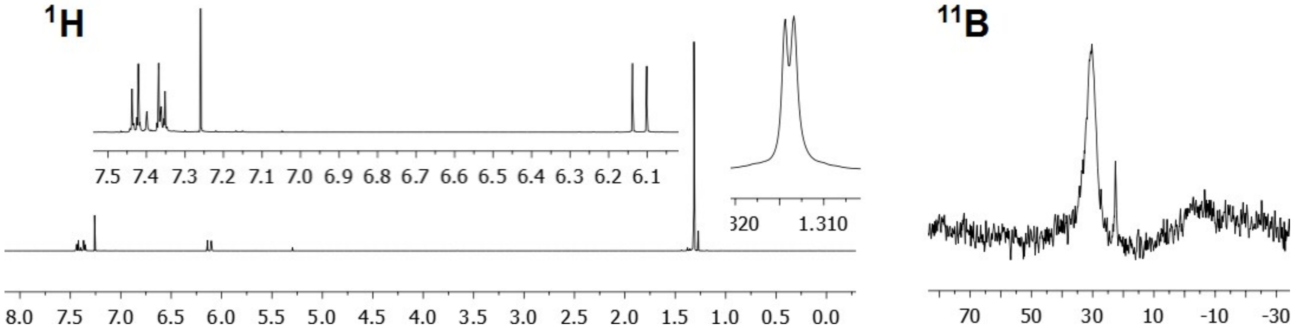
$^{13}C\{^1H\}$ NMR (126 MHz, 298 K, $CDCl_3$): $\delta^{13}C$: 152.1 (*p*-Ar), 149.4 (=CH^{Ar}), 134.8 (*i*-Ar), 126.8 (*o*-Ar), 125.5 (*m*-Ar), 83.3 ($OCMe_2$), 34.7 (*t*-Bu^C), 31.2 (*t*-Bu^{CH3})^t, 24.8 (CH_3)^t. ^{t} tentatively assigned. N.o. =CH^B

^1H,^{13}C GHSQC (700 MHz / 176 MHz, 300 K, $CDCl_3$): δ^1H / $\delta^{13}C$: 7.43 / 126.8 (*o*-Ar), 7.38 / 149.4 (=CH^{Ar}), 7.36 / 125.5 (*m*-Ar), 1.31 / 31.2, 24.8 (*t*-Bu^{CH3} and CH_3). N. o. =CH^B

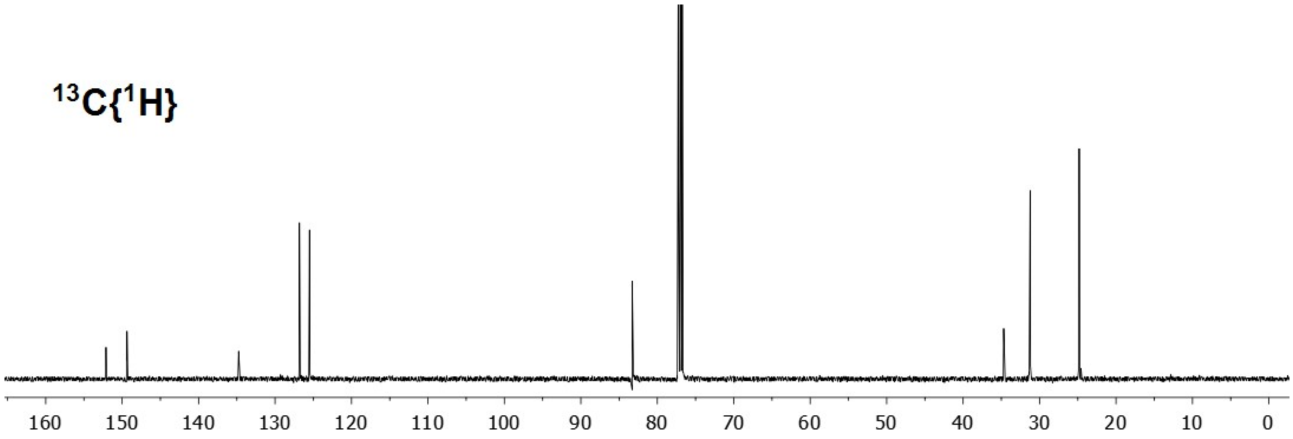
^1H,^{13}C GHMBC (700 MHz / 176 MHz, 300 K, $CDCl_3$) [selected traces]: δ^1H / $\delta^{13}C$: 7.43 / 152.1, 149.4, 126.8 (*o*-Ar / *p*-Ar, =CH^{Ar}, *o*-Ar), 7.38 / 126.8 (=CH^{Ar} / *o*-Ar), 7.36 / 134.8, 125.5, 31.2 (*m*-Ar / *i*-Ar, *m*-Ar, *t*-Bu^C).

^{11}B NMR (128 MHz, $CDCl_3$): $\delta^{11}B$: 29.6 ($\nu_{1/2} \approx$ 380 Hz).

HRMS (DART-TOF+): mass [M+H] calcd. for $C_{18}H_{28}B_1O_2$ 287.21823 *Da*, found: 287.21879 *Da*.

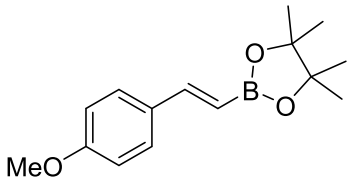


^1H NMR (500 MHz, 298 K, $CDCl_3$) and ^{11}B NMR (128 MHz, 298 K, $CDCl_3$) spectra of compound **4**.



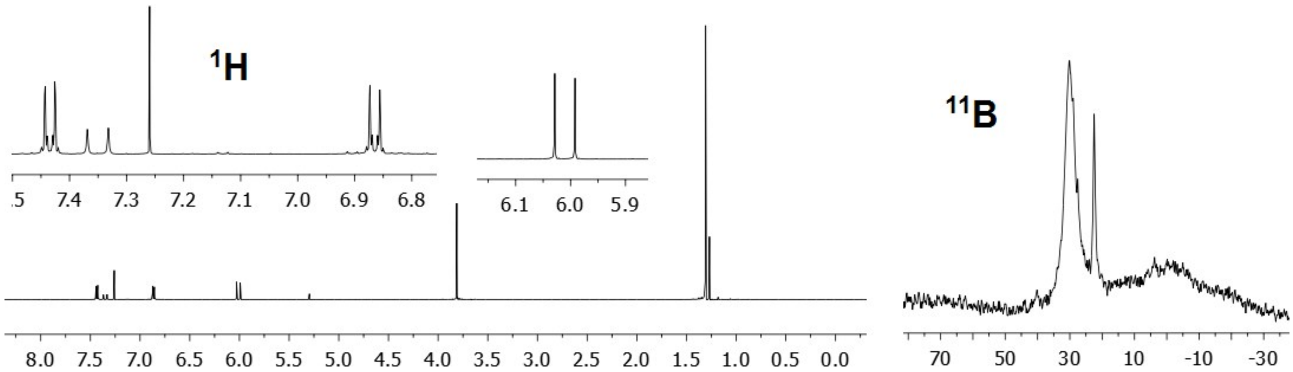
$^{13}C\{^1H\}$ NMR (126 MHz, 298 K, $CDCl_3$) spectrum of compound **4**.

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

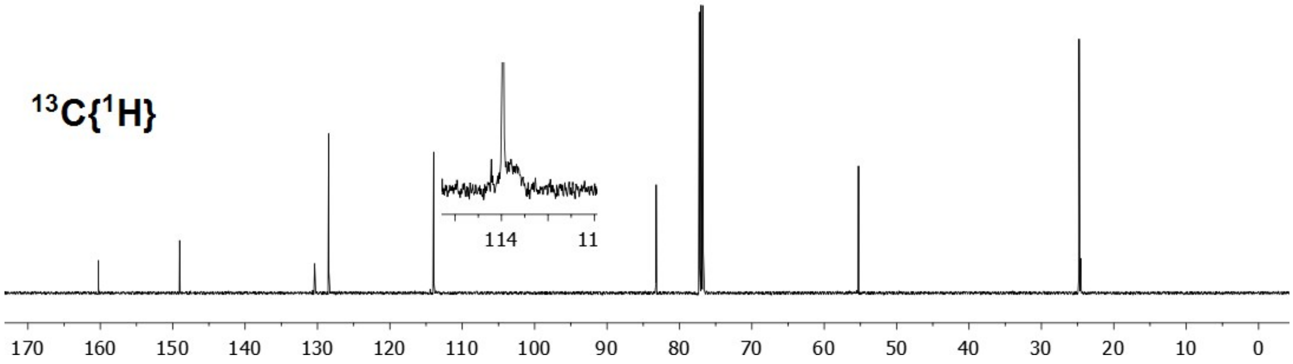


According to the general procedure 1-ethynyl-4-methoxybenzene (51 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and $HB(C_6F_5)_2$ (9 mg, 5 mol%) were dissolved in CH_2Cl_2 (2.5 ml) and reacted for 5 h at rt. Crude NMR studies showed greater 99% conversion and alkenyl borane **5** 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.[S11]

R*f* (hexanes/ether; 90/10) = 0.27.
^{1}H NMR (500 MHz, 298 K, $CDCl_3$): δ^{1}H: 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{^{1}H} NMR (126 MHz, 298 K, $CDCl_3$): δ^{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, $CDCl_3$): δ^{11}B: 30.1 ($\nu_{1/2}$ ≈ 380 Hz).
HRMS (DART-TOF+): mass [M+H] calcd. for $C_{15}H_{22}B_1O_3$ 261.16620 *Da*, found: 261.16643 *Da*.

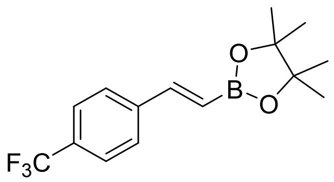


^{1}H NMR (500 MHz, 298 K, $CDCl_3$) and ^{11}B NMR (128 MHz, 298 K, $CDCl_3$) spectra of compound ***5****.*



^{13}C{^{1}H} NMR (126 MHz, 298 K, $CDCl_3$) spectrum of compound ***5****.*

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

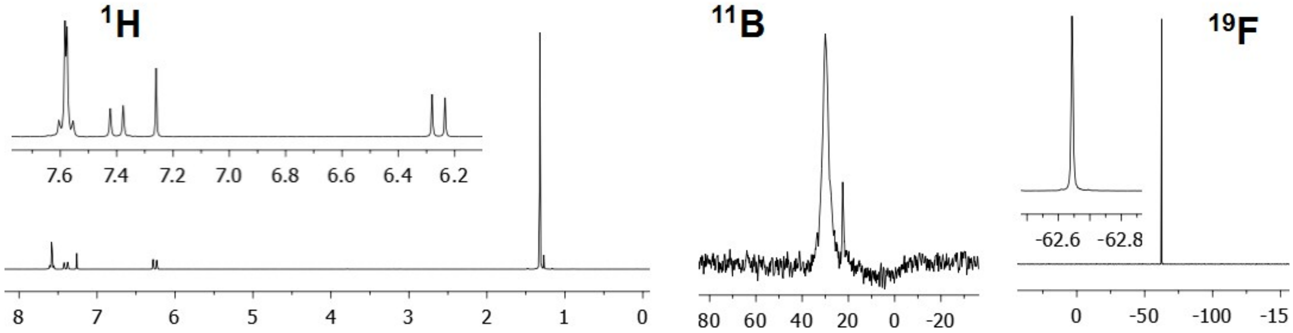


According to the general procedure 4-ethynyltrifluorotoluene (51 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and HBCF (9 mg, 5 mol%) were dissolved in CH_2Cl_2 (2.5 ml)

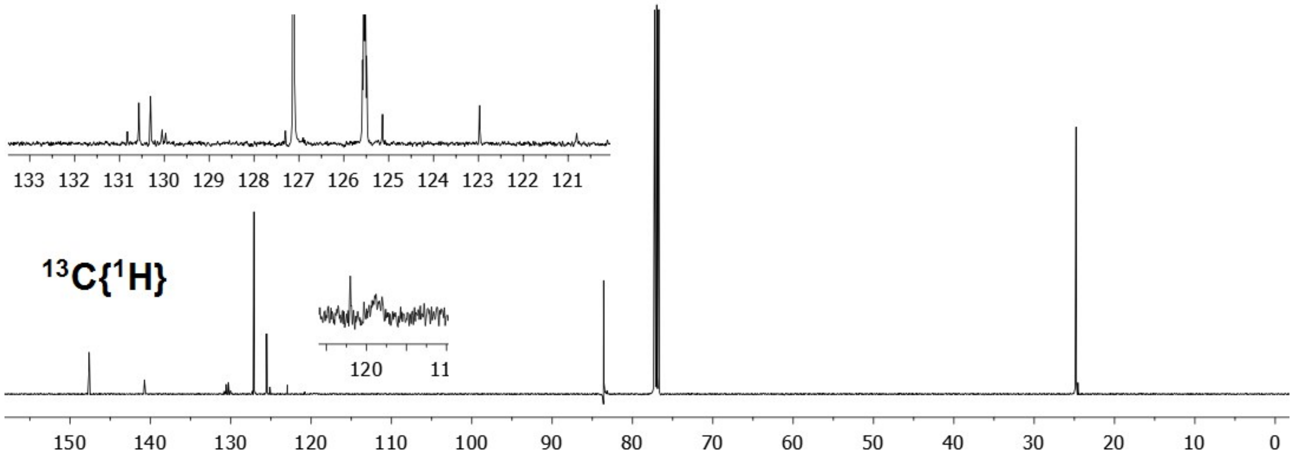
[S11] W. B. Reid, J. J. Spillane, S. B. Krause, D. A. Watson, *J. Am. Chem. Soc.* **2016**, *138*, 5539-5542.

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 (hexanes/ether; 90/10) = 0.36.
^{1}H NMR (500 MHz, 298 K, $CDCl_3$): δ^{1}H: 7.58 (m, 4H), 7.40 (d, $^3J_{HH}$ = 18.4 Hz, 1H), 6.26 (d, $^3J_{HH}$ = 18.4 Hz, 1H), 1.32 (s, 12H).
^{13}C{^{1}H} NMR (126 MHz, 298 K, $CDCl_3$): δ^{13}C: 147.6, 140.8, 130.4 (q, $^2J_{FC}$ = 32.4 Hz), 127.1, 125.5 (q, $^3J_{FC}$ = 3.8 Hz), 124.1 (q, $^1J_{FC}$ = 272.0 Hz), 119.4 (br), 83.6, 24.8.
^{11}B NMR (128 MHz, $CDCl_3$): δ^{11}B: 30.0 ($\nu_{1/2}$ ≈ 300 Hz).
^{19}F NMR (377 MHz, $CDCl_3$): δ^{19}F: -62.6.
HRMS (DART-TOF+): mass [M+H] calcd. for $C_{15}H_{19}B_1F_3O_2$ 299.14302 *Da*, found: 299.14273 *Da*.



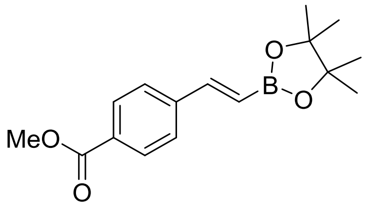
^{1}H NMR (500 MHz, 298 K, $CDCl_3$), ^{11}B (128 MHz, 298 K, $CDCl_3$) and ^{19}F (376 MHz, 298 K, $CDCl_3$) spectra of compound ***6****.*



^{13}C{^{1}H} NMR (126 MHz, 298 K, $CDCl_3$) spectrum of compound ***6****.*

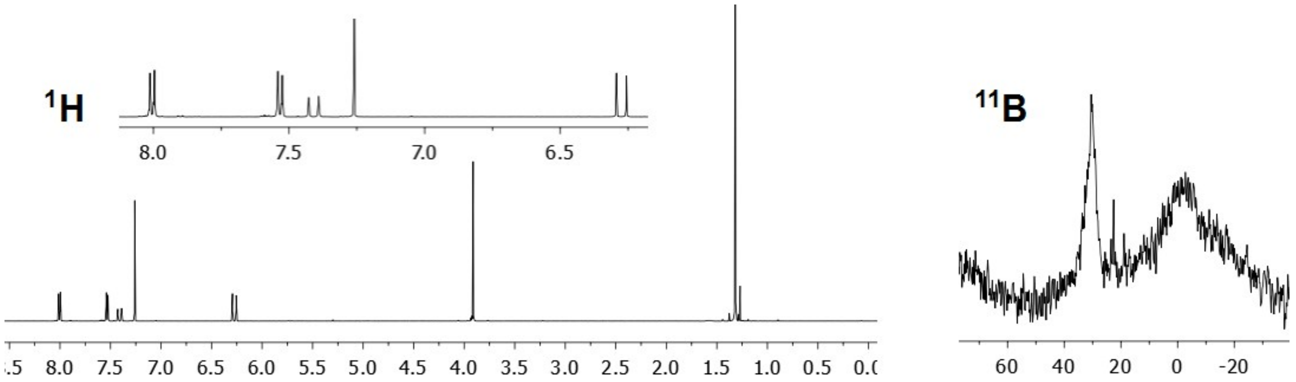
[S12] H. Jang, A. R. Zhugralin, Y. Lee, A. H. Hoveyda, *J. Am. Chem. Soc.* **2011**, *133*, 7859-7871.

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

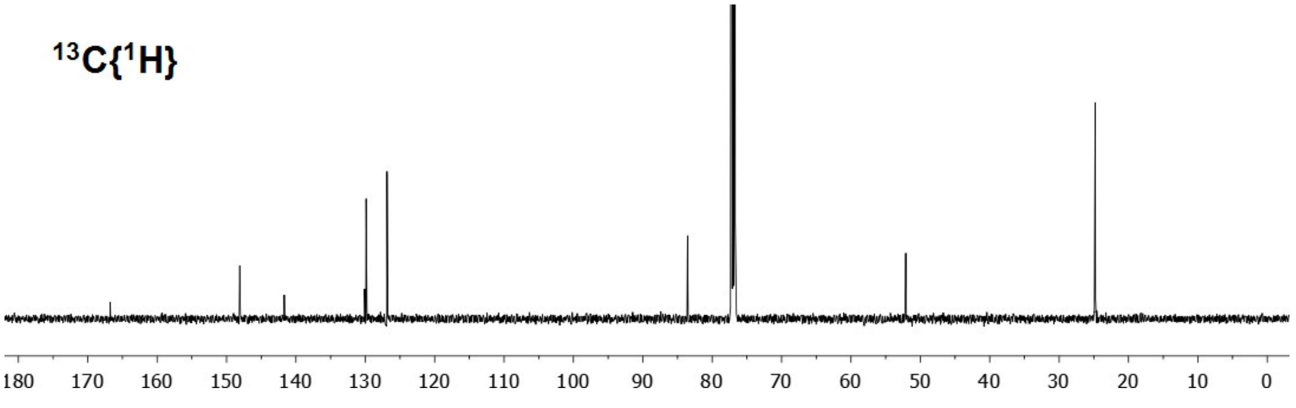


According to the general procedure methyl 4-ethynylbenzoate (80 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and $HB(C_6F_5)_2$ (9 mg, 5 mol%) were dissolved in CH_2Cl_2 (2.5 ml) and reacted for 5 h at rt. Crude NMR studies showed greater 99% conversion and the alkenyl borane **7** 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.[S13]

R*f* (hexanes/ether; 90/10) = 0.15.
^{1}H NMR (500 MHz, 298 K, $CDCl_3$): δ^{1}H: 8.00 (m, 2H), 7.53 (m, 2H), 7.41 (d, $^3J_{HH}$ = 18.4 Hz, 1H), 6.27 (d, $^3J_{HH}$ = 18.4 Hz, 1H), 3.91 (s, 3H), 1.32 (s, 12H).
^{13}C{^{1}H} NMR (126 MHz, 298 K, $CDCl_3$): δ^{13}C: 166.8, 148.1, 141.7, 130.1, 129.9, 126.9, 83.6, 52.1, 24.8. N.o. =C^B
^{11}B NMR (128 MHz, $CDCl_3$): δ^{11}B: 30.2 ($\nu_{1/2}$ ≈ 380 Hz).
HRMS (DART-TOF+): mass [M+H] calcd. for $C_{16}H_{22}B_1O_4$ 289.16111 *Da*, found: 289.16079 *Da*.



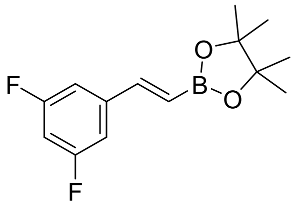
^{1}H NMR (500 MHz, 298 K, $CDCl_3$) and ^{11}B (128 MHz, 298 K, $CDCl_3$) spectra of compound **7**.



^{13}C{^{1}H} NMR (126 MHz, 298 K, $CDCl_3$) spectrum of compound **7**.

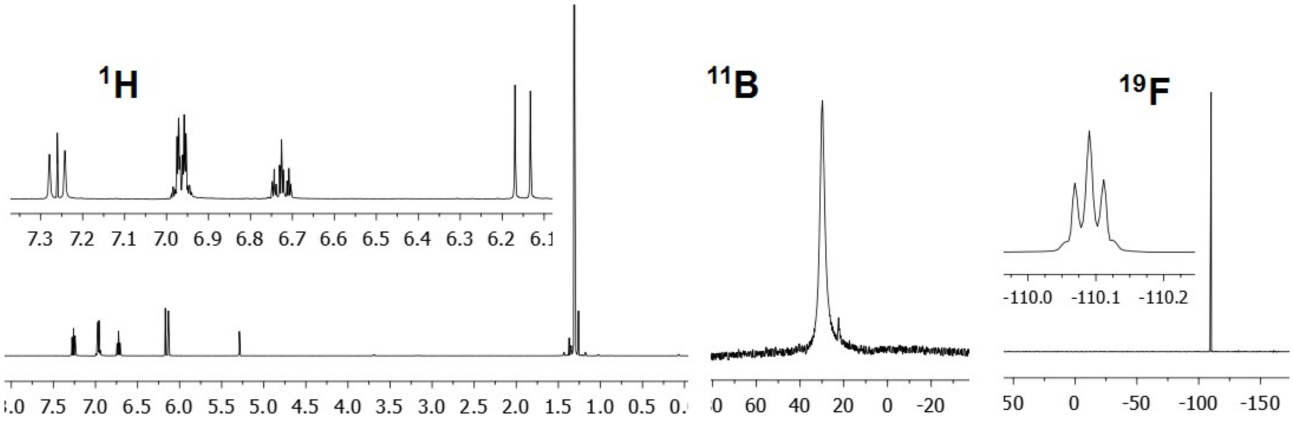
[S13] H. E. Ho, N. Asao, Y. Yamamoto, T. Jin, *Org. Lett.* **2014**, *16*, 4670-4673.

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

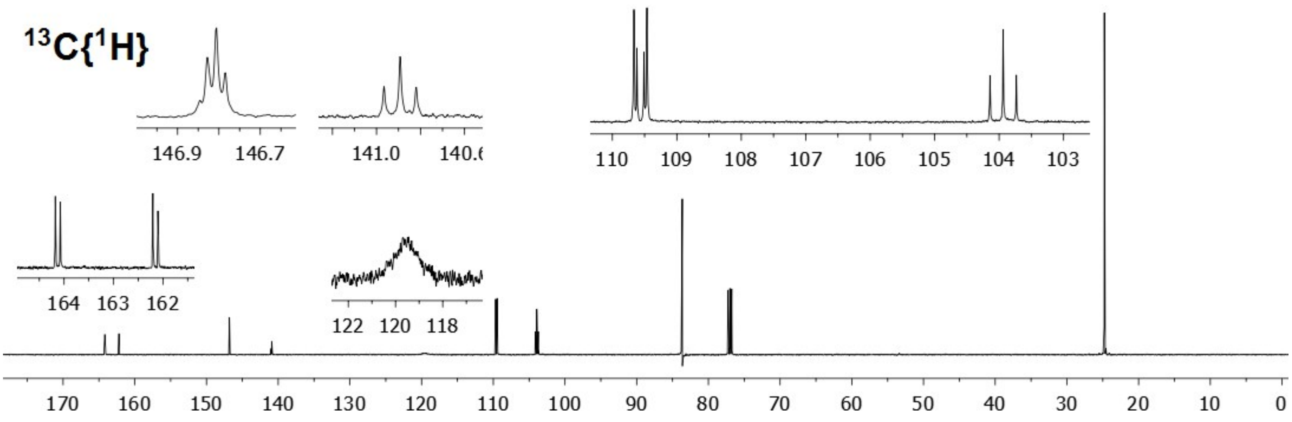


According to the general procedure 1-ethynyl-3,5-difluorobenzene (69 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and $HB(C_6F_5)_2$ (9 mg, 5 mol%) were dissolved in CH_2Cl_2 (2.5 ml) and reacted for 5 h at rt. Crude NMR studies showed greater 99% conversion and alkenyl borane **8** was isolated in 96% (127 mg, 0.48 mmol) yield as a colorless oil.

$\mathbf{R}_f$ (hexanes/ether; 90/10) = 0.62.
^{1}H NMR (500 MHz, 298 K, $CDCl_3$): δ^1H: 7.26 (d, $^3J_{HH}$ = 18.3 Hz, 1H, =CH^{Ar}), 6.97 (m, 2H, *o*-Ar), 6.73 (tt, $^3J_{FH}$ = 8.8 Hz, $^4J_{HH}$ = 2.3 Hz, 1H, *p*-Ar), 6.15 (d, $^3J_{HH}$ = 18.3 Hz, 1H, =CH^B), 1.31 (s, 12H, CH_3).
^{13}C{^{1}H} NMR (126 MHz, 298 K, $CDCl_3$): δ^{13}C: 163.1 (dd, $^1J_{FC}$ = 248.1 Hz, $^3J_{FC}$ = 12.9 Hz, *m*-Ar), 146.8 (t, $^4J_{FC}$ = 2.7 Hz, =CH^{Ar}), 140.9 (t, $^3J_{FC}$ = 9.2 Hz, *i*-Ar), 119.3 (br, =CH^B), 109.6 (dd, $^2J_{FC}$ = 19.4 Hz, $^4J_{FC}$ = 5.8 Hz, *o*-Ar), 103.9 (t, $^2J_{FC}$ = 25.7 Hz, *p*-Ar), 83.6 (s, $OCMe_2$), 24.8 (s, CH_3).
^{1}H,^{13}C GHSQC (700 MHz / 176 MHz, 300 K, $CDCl_3$): δ^1H / δ^{13}C: 7.26 / 146.8 (=CH^{Ar}), 6.97 / 109.6 (*o*-Ar), 6.73 / 103.9 (*p*-Ar), 1.31 / 24.8 (CH_3). N. o. =CH^B
^{1}H,^{13}C GHMBC (700 MHz / 176 MHz, 300 K, $CDCl_3$) [selected traces]: δ^1H / δ^{13}C: 7.26 / 140.9, 109.6 (=CH^{Ar} / *i*-Ar, *o*-Ar), 6.97 / 163.1, 146.8, 109.6 (*o*-Ar / *m*-Ar, =CH^{Ar}, *o*-Ar), 6.15 / 146.8, 140.9 (=CH^B / =CH^{Ar}, *i*-Ar).
^{19}F NMR (377 MHz, $CDCl_3$): δ^{19}F: −110.1 (t, $^3J_{FH}$ = 8.8 Hz).
^{11}B NMR (128 MHz, $CDCl_3$): δ^{11}B: 29.9 ($\nu_{1/2} \approx$ 340 Hz).
HRMS (DART-TOF+): mass [M+H] calcd. for $C_{14}H_{18}B_1F_2O_2$ 267.13679 *Da*, found: 267.13714 *Da*.

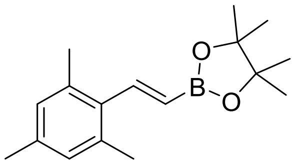


*^{1}H NMR (500 MHz, 298 K, $CDCl_3$), ^{11}B (128 MHz, 298 K, $CDCl_3$) and ^{19}F (376 MHz, 298 K, $CDCl_3$) spectra of compound **8**.*



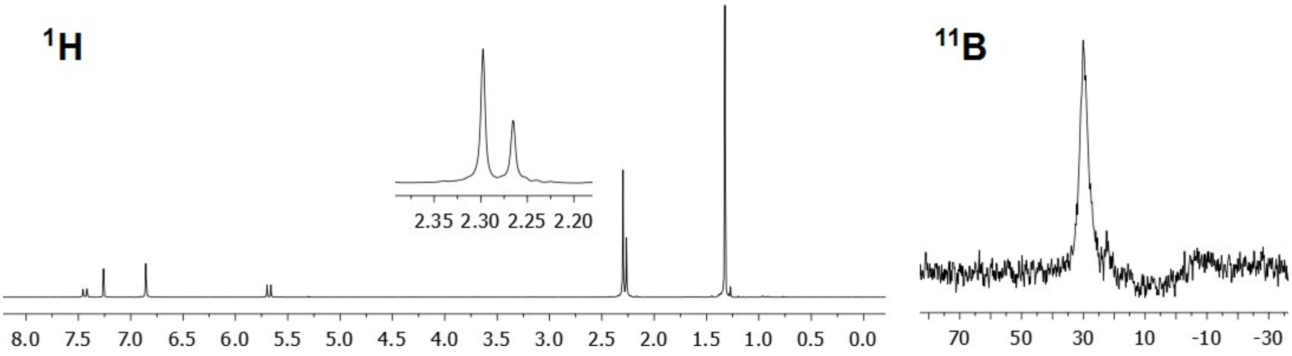
$^{13}C\{^1H\}$ NMR (126 MHz, 298 K, $CDCl_3$) spectrum of compound **8**.

(9) (*E*)-4,4,5,5-tetramethyl-2-(2,4,6-trimethylstyryl)-1,3,2-dioxaborolane

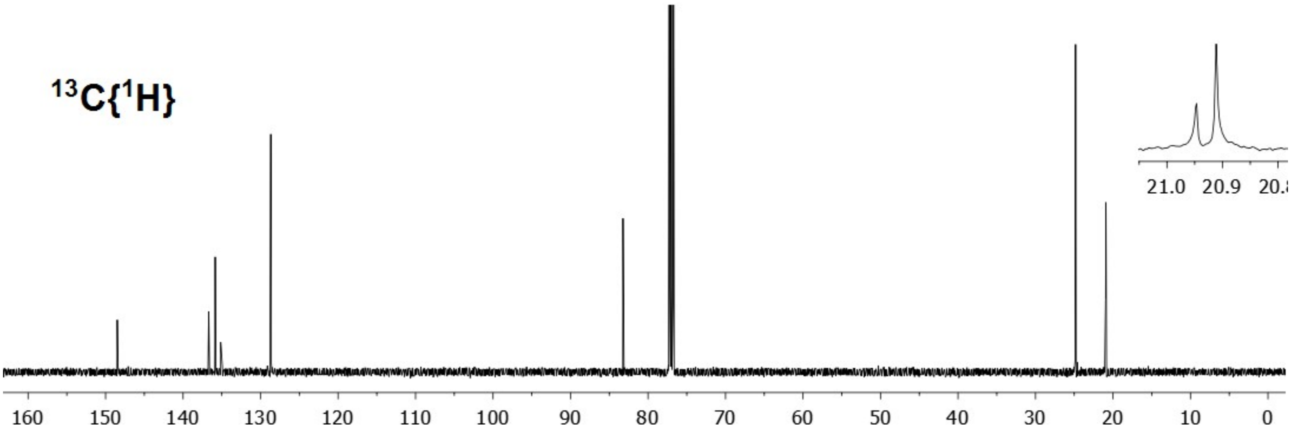


According to the general procedure 2-ethynyl-1,3,5-trimethylbenzene (72 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and $HB(C_6F_5)_2$ (9 mg, 5 mol%) were dissolved in CH_2Cl_2 (2.5 ml) and reacted for 5 h at rt. Crude NMR studies showed greater 99% conversion and alkenyl borane **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, $CDCl_3$): δ^1H: 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).
$^{13}C\{^1H\}$ NMR (126 MHz, 298 K, $CDCl_3$): δ^{13}C: 148.5, 136.7, 135.9, 135.1, 128.7, 83.2, 24.8, 21.0, 20.9. N.o. $=CH^B$
^{11}B NMR (128 MHz, $CDCl_3$): δ^{11}B: 29.8 ($\nu_{1/2} \approx 390$ Hz).
HRMS (DART-TOF+): mass [M+H] calcd. for $C_{17}H_{26}B_1O_2$ 273.20258 *Da*, found: 273.20334 *Da*.

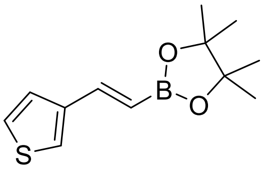


^1H NMR (500 MHz, 298 K, $CDCl_3$) and ^{11}B NMR (128 MHz, 298 K, $CDCl_3$) spectra of compound **9**.



$^{13}C\{^1H\}$ NMR (126 MHz, 298 K, $CDCl_3$) spectrum of compound **9**.

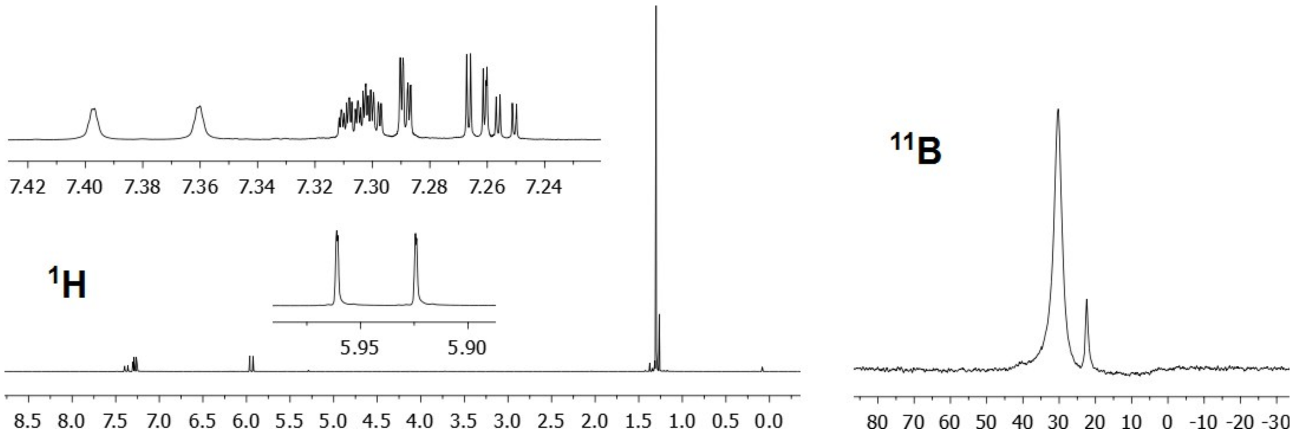
(10) (*E*)-4,4,5,5-tetramethyl-2-(2-(thiophen-3-yl)vinyl)-1,3,2-dioxaborolane



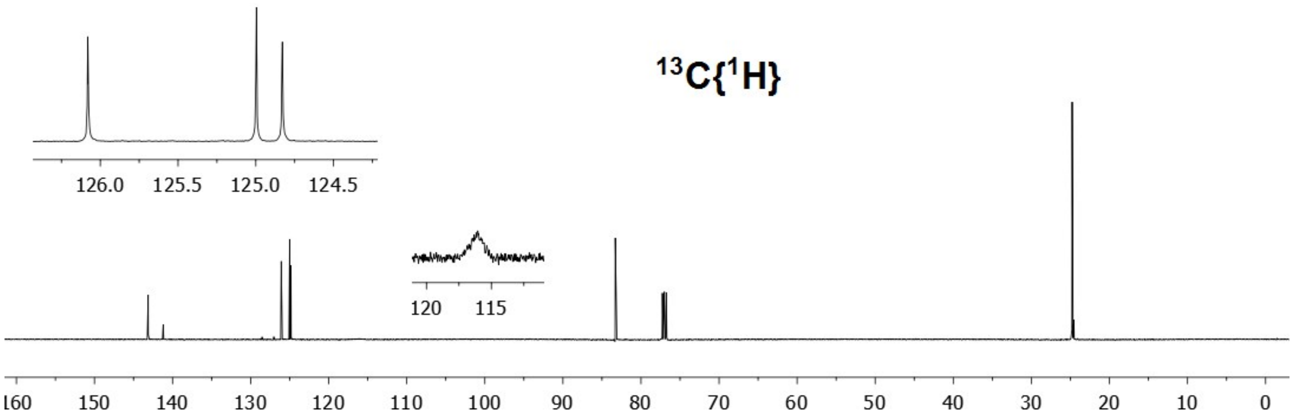
According to the general procedure 3-ethynylthiophene (54 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and $HB(C_6F_5)_2$ (9 mg, 5 mol%) were dissolved in CH_2Cl_2 (2.5 ml) and reacted for 5 h at rt. Crude NMR studies showed greater 99% conversion and alkenyl borane **10** was 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.[S14]

R_f (hexanes/ether; 90/10) = 0.43.
^{1}H NMR (500 MHz, 298 K, $CDCl_3$): δ^1H: 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).
^{13}C{^{1}H} NMR (126 MHz, 298 K, $CDCl_3$): δ^{13}C: 143.1, 141.2, 126.1, 125.0, 124.8, 116.1 (br, =CH^B), 83.3, 24.8.
^{11}B NMR (128 MHz, 298 K, $CDCl_3$): δ^{11}B: 30.2 ($\nu_{1/2} \approx$ 300 Hz).
HRMS (DART-TOF+): mass [M+H] calcd. for $C_{12}H_{18}B_1O_2S_1$ 237.11206 *Da*, found: 237.11190 *Da*.

[S14] J. Zhao, Z. Niu, H. Fu, Y. Li, *Chem. Commun.* **2014**, *50*, 2058-2060.

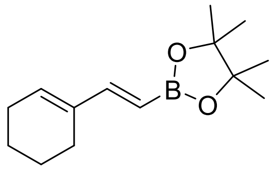


^1H NMR (500 MHz, 298 K, $CDCl_3$) and ^{11}B NMR (128 MHz, 298 K, $CDCl_3$) spectra of compound **10**.



$^{13}C\{^1H\}$ NMR (126 MHz, 298 K, $CDCl_3$) spectrum of compound **10**.

(11) (*E*)-2-(2-(cyclohex-1-en-1-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



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 $HB(C_6F_5)_2$ (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 **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]

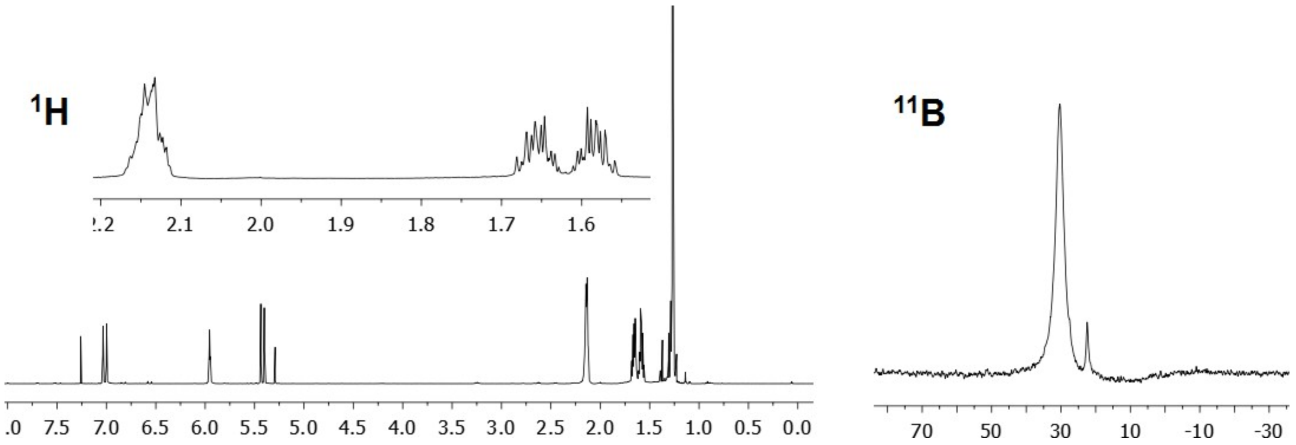
R_f (hexanes/ether; 90/10) = 0.62.

^{1}H NMR (500 MHz, 298 K, $CDCl_3$): δ^1H: 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).

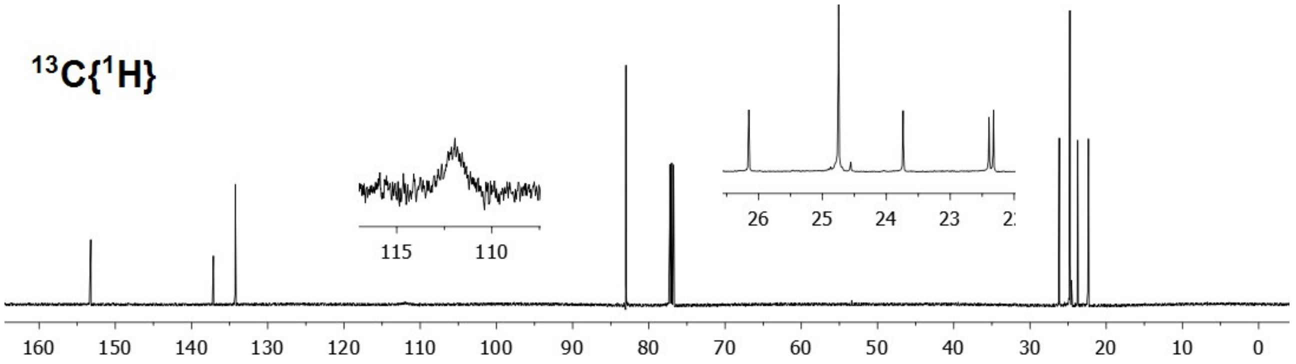
^{13}C{^{1}H} NMR (126 MHz, 298 K, $CDCl_3$): δ^{13}C: 153.2, 137.1, 134.3, 111.9 (br, =CH^B), 83.0, 26.2, 24.8, 23.7, 22.4, 22.3.

^{11}B NMR (128 MHz, 298 K, $CDCl_3$): δ^{11}B: 30.3 ($\nu_{1/2} \approx$ 300 Hz).

HRMS (EI-TOF+): mass [M+H] calcd. for $C_{14}H_{23}B_1O_2$ 234.1791 *Da*, found: 234.1797 *Da*.

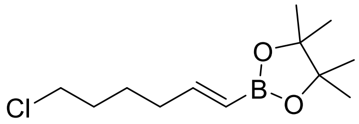


^1H NMR (500 MHz, 298 K, $CDCl_3$) and ^{11}B NMR (128 MHz, 298 K, $CDCl_3$) spectra of compound **11**.



$^{13}C\{^1H\}$ NMR (126 MHz, 298 K, $CDCl_3$) spectrum of compound **11**.

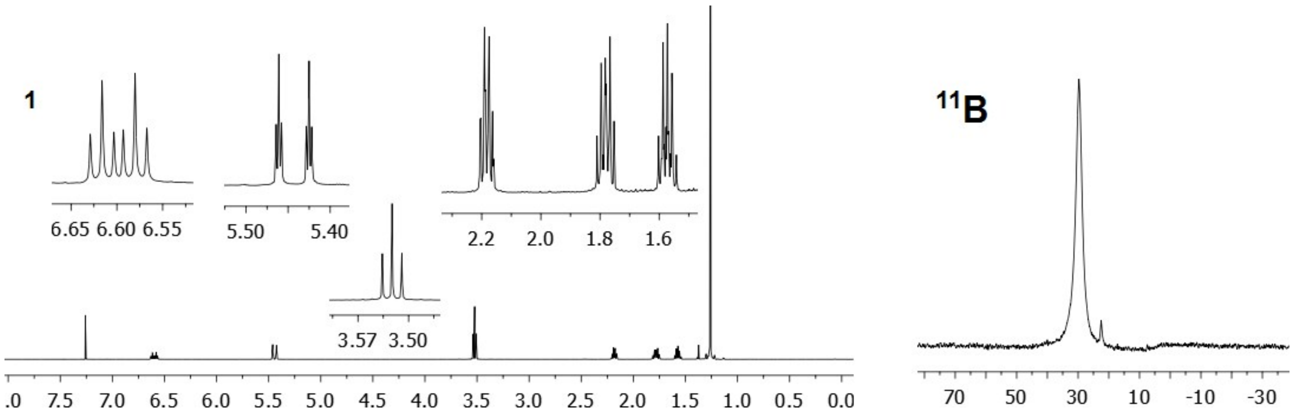
(12) (*E*)-2-(6-chlorohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



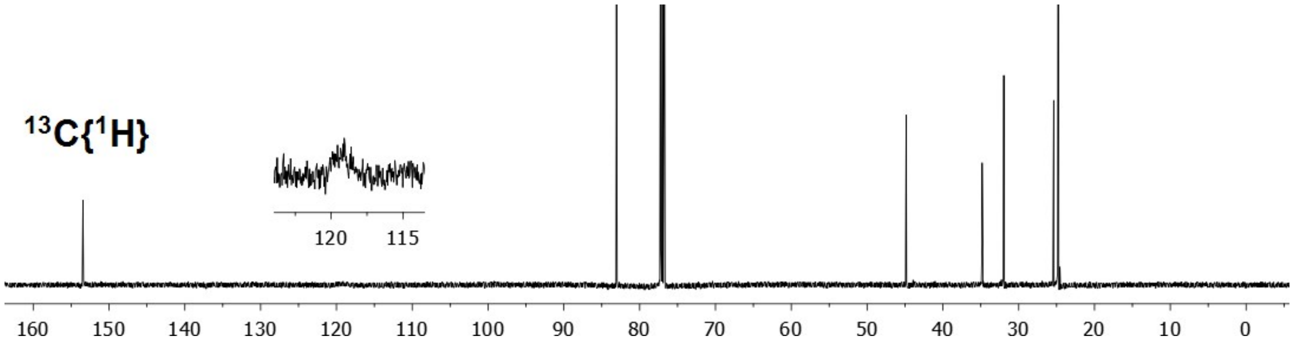
According to the general procedure 6-chlorohex-1-yne (58 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and $HB(C_6F_5)_2$ (9 mg, 5 mol%) were dissolved in CH_2Cl_2 (2.5 ml) and reacted for 5 h at rt. Crude NMR studies showed greater 99% conversion and alkenyl borane **12** was isolated in 90% (109 mg, 0.45 mmol) yield as a colorless oil. The NMR data was consistent with literature reported values.[S15]

R_f (hexanes/ether; 90/10) = 0.38.
^{1}H NMR (500 MHz, 298 K, $CDCl_3$): δ^1H: 6.60 (dt, *J* = 18.0, 6.4 Hz, 1H), 5.44 (dt, *J* = 18.0, 1.6 Hz, 1H), 3.52 (t, *J* = 6.7 Hz, 2H), 2.21 – 2.16 (m, 2H), 1.82 – 1.75 (m, 2H), 1.61 – 1.53 (m, 2H), 1.26 (s, 12H).
^{13}C{^{1}H} NMR (126 MHz, 298 K, $CDCl_3$): δ^{13}C: 153.4, 83.1, 44.8, 34.8, 32.0, 25.4, 24.8. N.o. =CH^B
^{11}B NMR (128 MHz, $CDCl_3$): δ^{11}B: 29.7 ($\nu_{1/2} \approx 300$ Hz).
HRMS (DART-TOF+): mass [M+H] calcd. for $C_{12}H_{23}B_1Cl_1O_2$ 245.14796 *Da*, found: 245.114759 *Da*.

[S15] Z.-J. Yao, S. Hong, W. Zhang, M. Liu, W. Deng, *Tetrahedron Lett.* **2016**, *57*, 910-913.

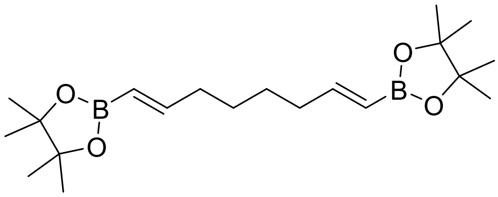


^1H NMR (500 MHz, 298 K, $CDCl_3$) and ^{11}B NMR (128 MHz, 298 K, $CDCl_3$) spectra of compound ***12****.*



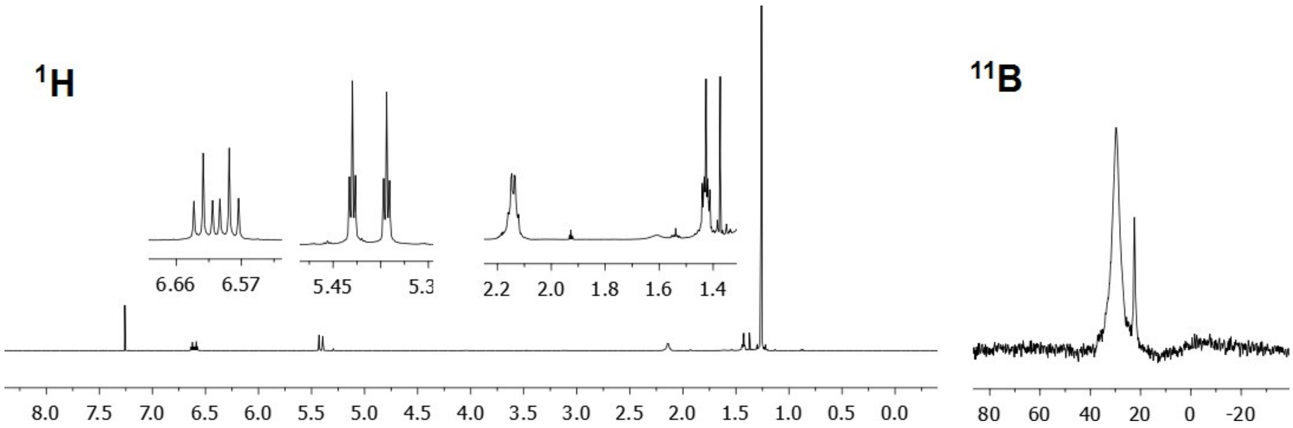
$^{13}C\{^1H\}$ NMR (126 MHz, 298 K, $CDCl_3$) spectrum of compound ***12****.*

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

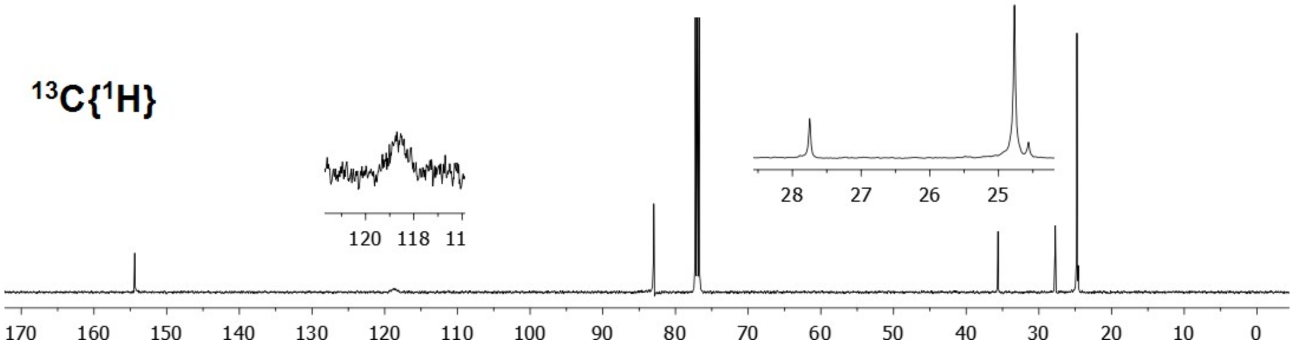


According to the general procedure octa-1,7-diyne (53 mg, 0.50 mmol, 1.0 eq.), pinacol borane (154 mg, 1.20 mmol, 2.4 eq.) and $HB(C_6F_5)_2$ (17 mg, 10 mol%) were dissolved in CH_2Cl_2 (2.5 ml) and reacted for 18 h at rt. Crude NMR studies showed greater 99% conversion and alkenyl boronic ester **13** 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.[S15]

R_f (*n*-pentane/ether; 97/3) = 0.12.
^{1}H NMR (500 MHz, 298 K, $CDCl_3$): δ^1H: 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).
^{13}C{^{1}H} NMR (126 MHz, 298 K, $CDCl_3$): δ^{13}C: 154.4, 118.6 (br, =CH^B), 83.0, 35.6, 27.8, 24.8.
^{11}B NMR (128 MHz, 298 K, $CDCl_3$): δ^{11}B: 29.5 ($\nu_{1/2} \approx$ 380 Hz).
HRMS (DART-TOF+): mass [M+NH$_4$] calcd. for $C_{20}H_{36}B_2N_1O_4$ 380.31434 *Da*, found: 380.31542 *Da*.

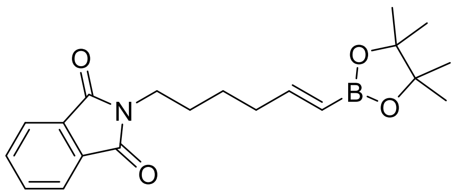


^{1}H NMR (500 MHz, 298 K, $CDCl_3$) and ^{11}B NMR (128 MHz, 298 K, $CDCl_3$) spectra of compound **13**.



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

(14) (*E*)-2-(6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-en-1-yl)isoindoline-1,3-dione



According to the general procedure 2-(hex-5-yn-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 CH_2Cl_2 (2.5 ml) and reacted for 18h 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.

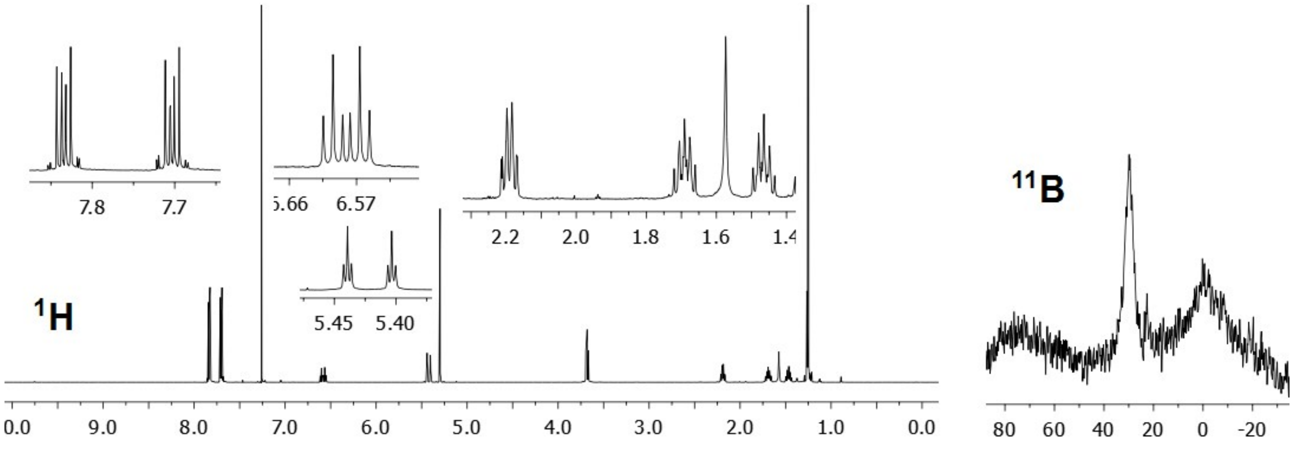
R$_f$ (hexanes/ether; 80/20) = 0.14.

^{1}H NMR (500 MHz, 298 K, $CDCl_3$): δ^{1}H: 7.83 (m, 2H), 7.71 (m, 2H), 6.58 (dt, $^3J_{HH}$ = 17.9 Hz, $^3J_{HH}$ = 6.5 Hz, 1H), 5.42 (dt, $^3J_{HH}$ = 17.9 Hz, $^4J_{HH}$ = 1.6 Hz, 1H), 3.68 (t, $^3J_{HH}$ = 7.2 Hz, 2H), 2.19 (m, 2H), 1.69 (m, 2H), 1.47 (m, 2H), 1.25 (s, 12H).

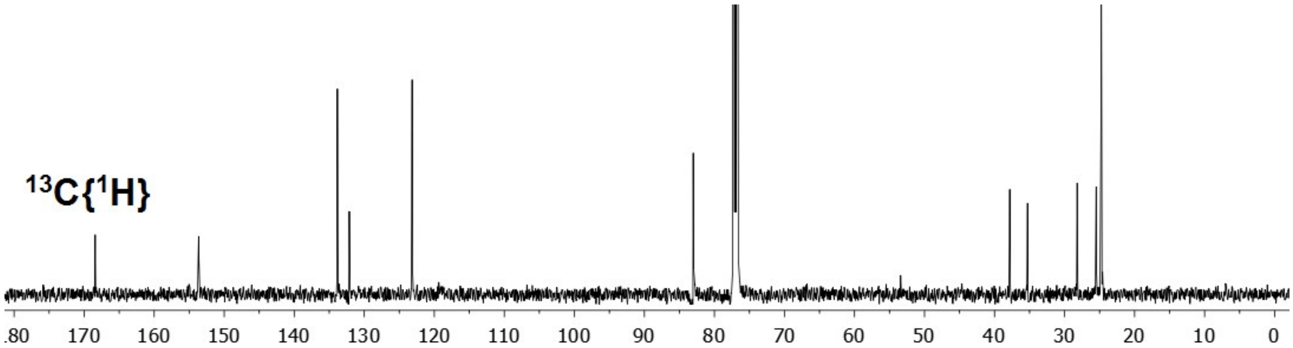
^{13}C{^{1}H} NMR (126 MHz, 298 K, $CDCl_3$): δ^{13}C: 168.4, 153.6, 133.8, 132.1, 123.2, 119.0 (br, =CH^B), 83.0, 37.8, 35.3, 28.2, 25.5, 24.8.

^{11}B NMR (128 MHz, 298 K, $CDCl_3$): δ^{11}B: 29.5 ($\nu_{1/2}$ ≈ 400 Hz).

HRMS (DART-TOF+): mass [M+H] calcd. for $C_{20}H_{27}B_1N_1O_4$ 356.20331 *Da*, found: 356.20346 *Da*.

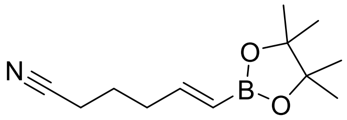


^{1}H NMR (500 MHz, 298 K, $CDCl_3$) and ^{11}B NMR (128 MHz, 298 K, $CDCl_3$) spectra of compound **14**.



^{13}C{^{1}H} NMR (126 MHz, 298 K, $CDCl_3$) spectrum of compound **14**.

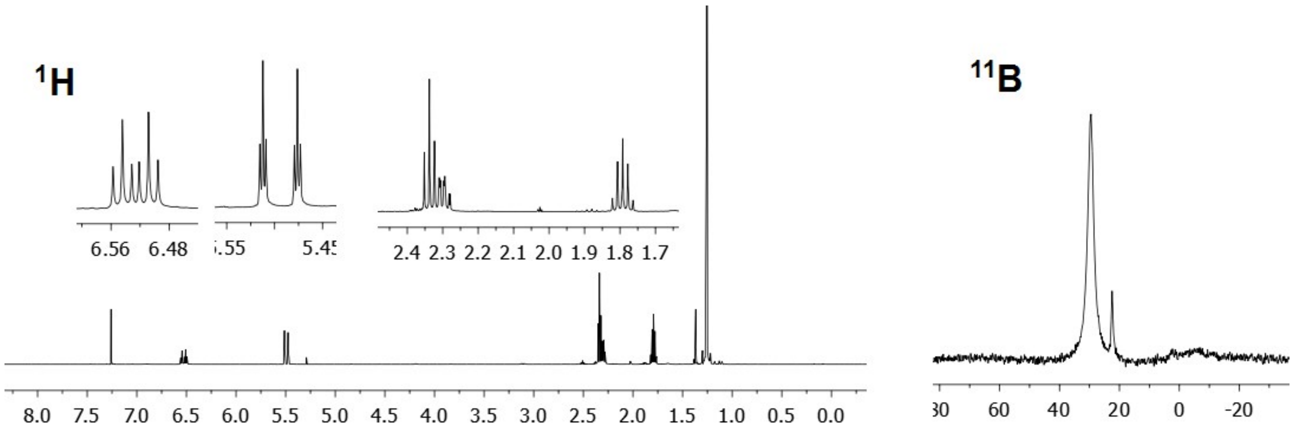
(15) (*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-ene-nitrile



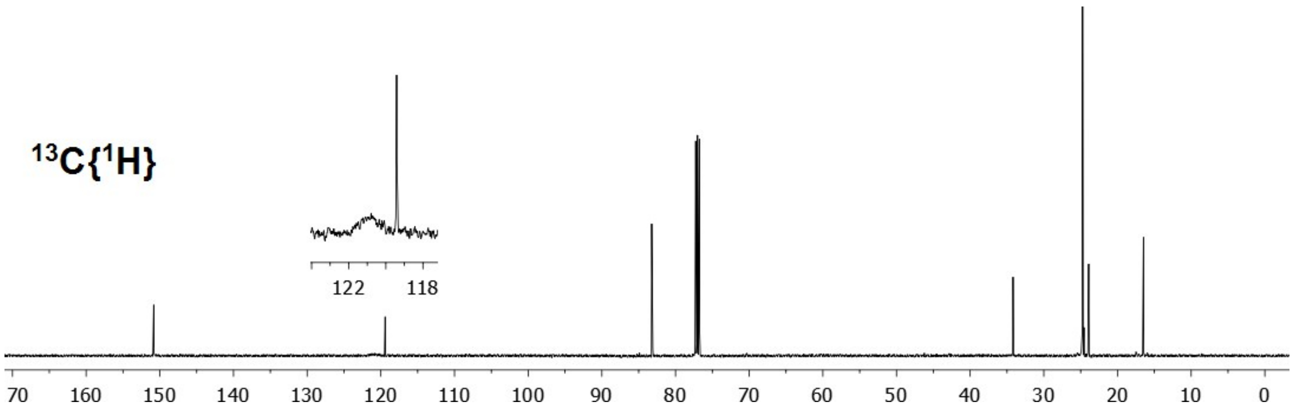
According to the general procedure hex-5-ynenitrile (47 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and $HB(C_6F_5)_2$ (17 mg, 10 mol%) were dissolved in CH_2Cl_2 (2.5 ml) and reacted for 18 h at 50 °C. Crude NMR studies showed greater 99% conversion and alkenyl boronic ester **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, $CDCl_3$): δ^{1}H: 6.53 (dt, $^3J_{HH}$ = 18.0 Hz, $^3J_{HH}$ = 6.5 Hz, 1H), 5.49 (dt, $^3J_{HH}$ = 18.0 Hz, $^4J_{HH}$ = 1.6 Hz, 1H), 2.34 (t, $^3J_{HH}$ = 7.2 Hz, 2H), 2.30 (m, 2H), 1.79 (p, $^3J_{HH}$ = 7.3 Hz, 2H), 1.26 (s, 12H).
^{13}C{^{1}H} NMR (126 MHz, 298 K, $CDCl_3$): δ^{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, $CDCl_3$): δ^{11}B: 29.5 ($\nu_{1/2} \approx$ 330 Hz).
HRMS (DART-TOF+): mass [M+H] calcd. for $C_{12}H_{21}B_1N_1O_2$ 222.16653 *Da*, found: 222.16641 *Da*.

[S16] C. E. Tucker, J. Davidson, P. Knochel, *J. Org.Chem.* **1992**, *57*, 3482-3485.

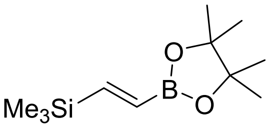


^1H NMR (500 MHz, 298 K, $CDCl_3$) and ^{11}B NMR (128 MHz, 298 K, $CDCl_3$) spectra of compound **15**.



$^{13}C\{^1H\}$ NMR (126 MHz, 298 K, $CDCl_3$) spectrum of compound **15**.

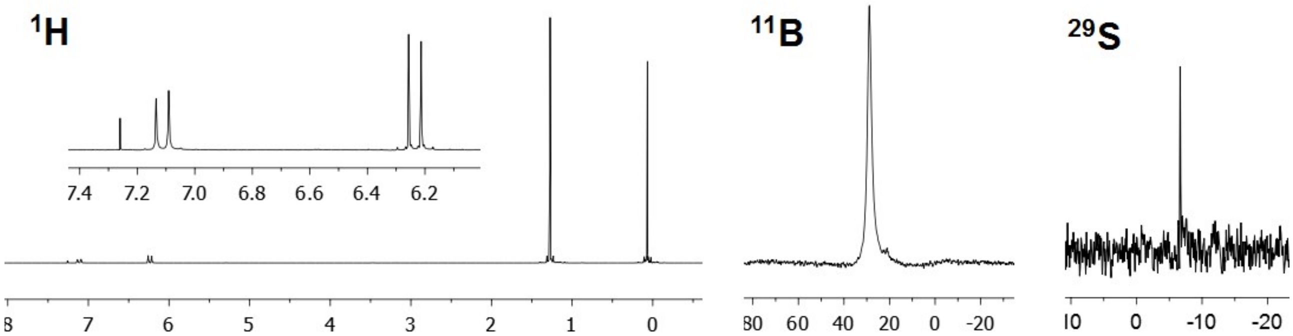
(16) (*E*)-trimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane



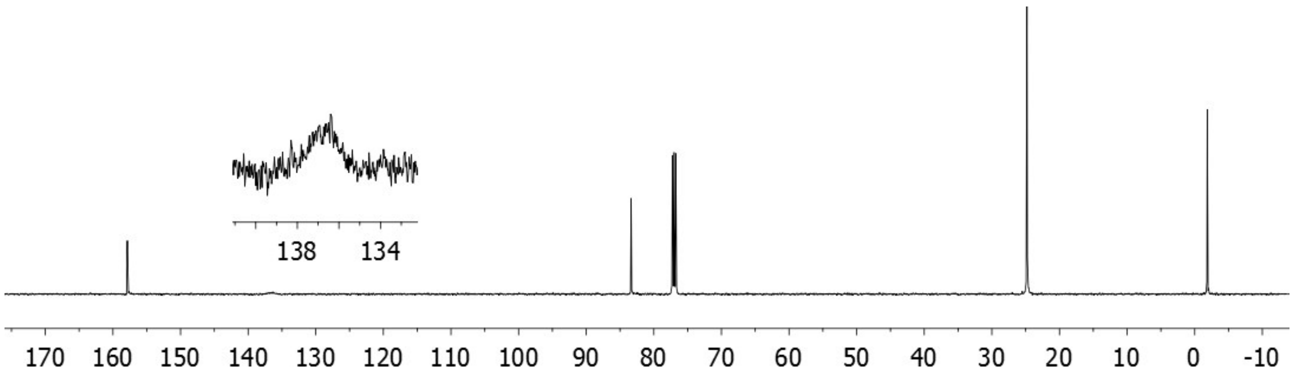
According to the general procedure ethynyltrimethylsilane (49 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and $HB(C_6F_5)_2$ (9 mg, 5 mol%) were dissolved in CH_2Cl_2 (2.5 ml) and reacted for 18 h at rt. Crude NMR studies showed greater 79% conversion and alkenyl borane **16** 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, $CDCl_3$): δ^1H: 7.11 (d, $^3J_{HH}$ = 21.8 Hz, 1H), 6.24 (d, $^3J_{HH}$ = 21.8 Hz, 1H), 1.27 (s, 12H), 0.07 (s, 9H).
^{13}C{^{1}H} NMR (126 MHz, 298 K, $CDCl_3$): δ^{13}C: 157.9, 136.7 (br, $=CH^B$), 83.4, 24.8, −1.9.
^{11}B NMR (128 MHz, 298 K, $CDCl_3$): δ^{11}B: 28.9 ($\nu_{1/2} \approx$ 300 Hz).
^{29}Si-dept (80 MHz, 298 K, $CDCl_3$): δ^{29}Si: −6.7.
HRMS (DART-TOF+): mass [M+H] calcd. for $C_{11}H_{24}B_1O_2Si_1$ 227.16386 *Da*, found: 227.16352 *Da*.

[S17] S. Pereira, M. Srebnik, *Organometallics* **1995**, *14*, 3127-3128.

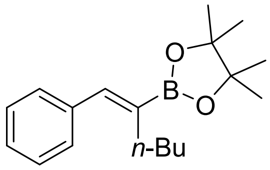


^1H NMR (500 MHz, 298 K, $CDCl_3$), ^{11}B NMR (128 MHz, 298 K, $CDCl_3$) and ^{29}Si-dept (80 MHz, 298 K, $CDCl_3$) spectra of compound **16**.



$^{13}C\{^1H\}$ NMR (126 MHz, 298 K, $CDCl_3$) spectrum of compound **16**.

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



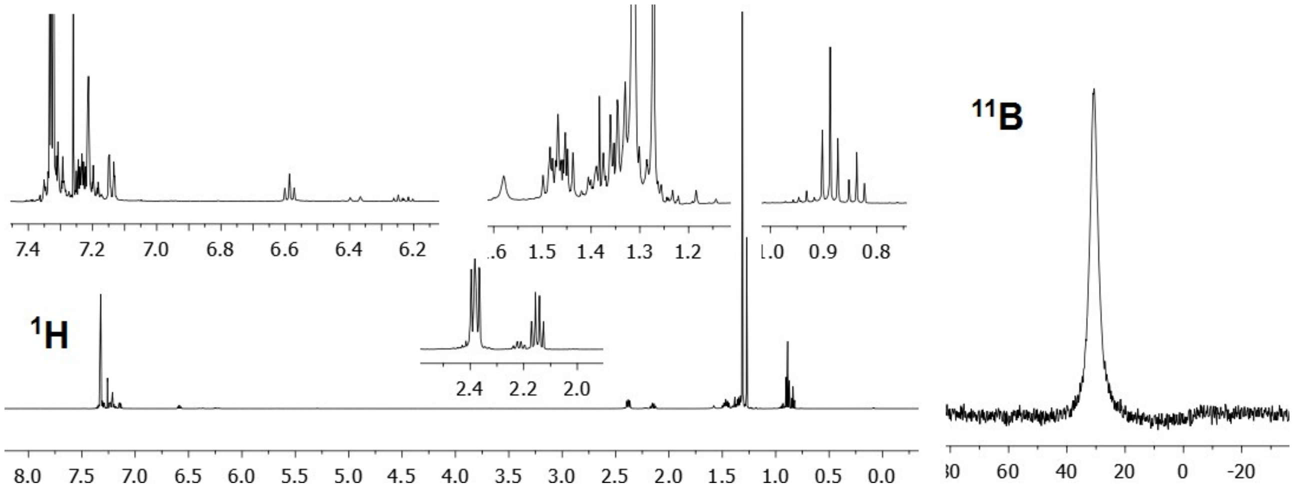
According to the general procedure hex-1-yn-1-ylbenzene (79 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and $HB(C_6F_5)_2$ (9 mg, 5 mol%) were dissolved in CH_2Cl_2 (2.5 ml) and reacted for 18 h at 50 °C. Crude NMR studies showed greater 99% conversion and a ratio of 78:12 of 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.[S18]

(Data of the major isomer)
R_f (*n*-pentane/ether; 90/3) = 0.62.
^{1}H NMR (500 MHz, 298 K, $CDCl_3$): δ^{1}H: 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).
^{13}C{^{1}H} NMR (126 MHz, 298 K, $CDCl_3$): δ^{13}C: 141.6, 138.0, 129.0, 128.0, 126.9, 83.3, 32.2, 29.2, 24.8, 22.8, 14.0. N.o. =C^B

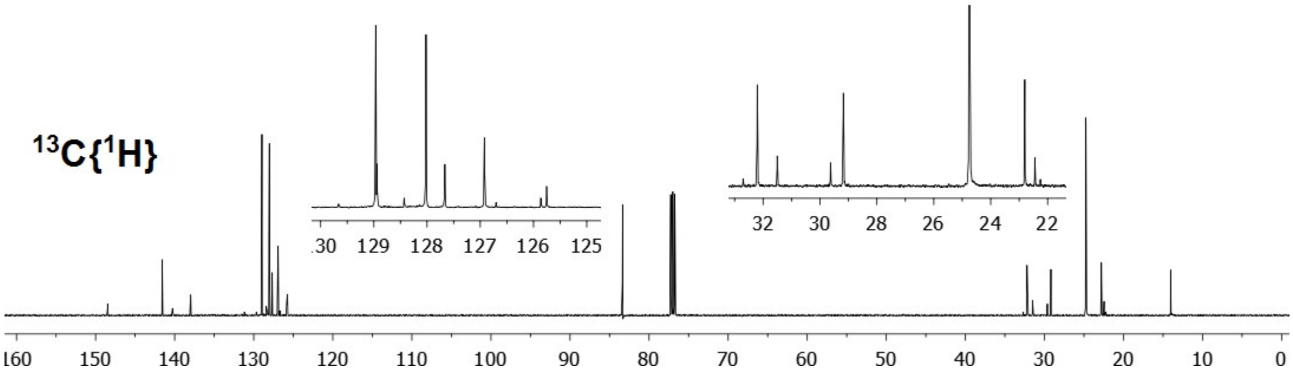
[S18] W. Yuan, S. Ma, *Org. Biomol. Chem.* **2012**, *10*, 7266-7268.

^{11}B NMR (128 MHz, 298 K, $CDCl_3$): δ^{11}B: 30.6 ($\nu_{1/2}$ ≈ 430 Hz).

HRMS (DART-TOF+): mass [M+NH$_4$] calcd. for $C_{18}H_{31}B_1N_1O_2$ 304.24478 *Da*, found: 304.24401 *Da*.

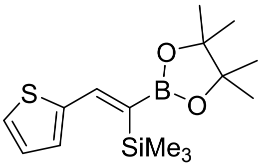


^{1}H NMR (500 MHz, 298 K, $CDCl_3$) and ^{11}B NMR (128 MHz, 298 K, $CDCl_3$) spectra of compound **17**.



^{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_2Cl_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.

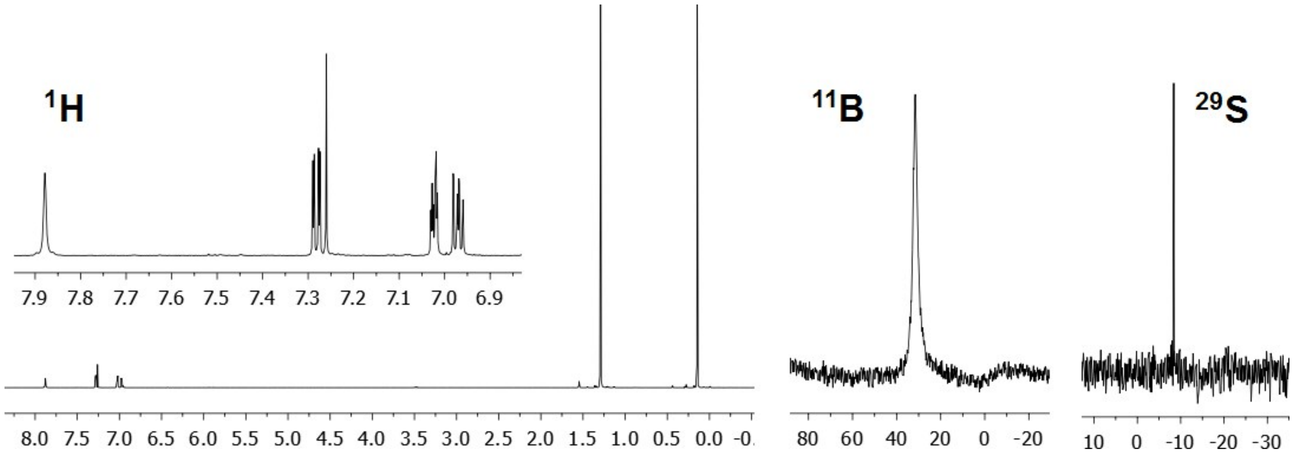
^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ^{1}H: 7.88 (s, 1H), 7.28 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.02 (dt, *J* = 3.6, 1.1 Hz, 1H), 6.98 – 6.95 (m, 1H), 1.29 (s, 12H), 0.15 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, 298 K, $CDCl_3$): δ^{13}C: 147.6, 143.7, 127.9, 126.9, 126.4, 83.3, 24.8, 0.7. N.o. =C^B.

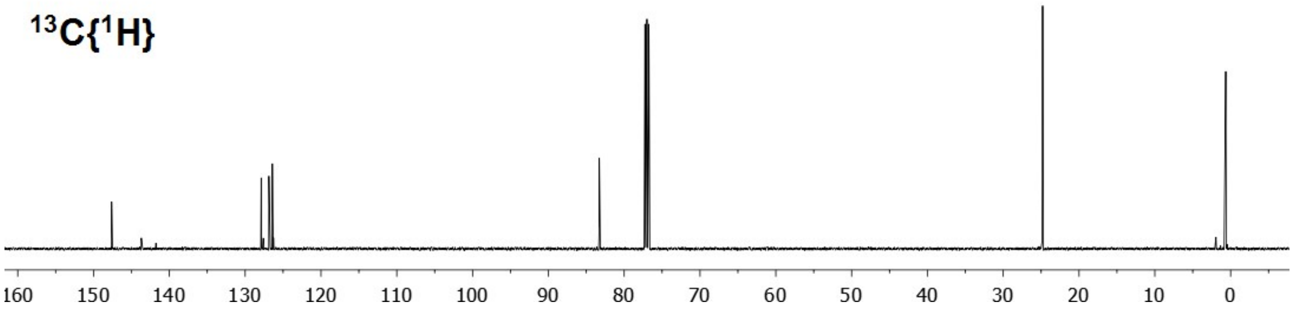
^{11}B NMR (128 MHz, 298 K, $CDCl_3$): δ^{11}B: 31.5 ($\nu_{1/2}$ ≈ 290 Hz).

^{29}Si NMR (80 MHz, 298 K, $CDCl_3$): δ^{29}Si: −8.4.

HRMS (DART-TOF+): mass [M+H] calcd. for $C_{15}H_{26}B_1O_2S_1Si_1$ 309.15158 *Da*, found: 309.15129 *Da*.

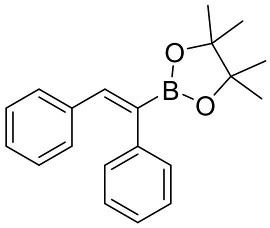


^{1}H NMR (500 MHz, 298 K, $CDCl_3$), ^{11}B NMR (128 MHz, 298 K, $CDCl_3$) and ^{29}Si NMR (80 MHz, 298 K, $CDCl_3$) spectra of compound **18**.



^{13}C{^{1}H} NMR (126 MHz, 298 K, $CDCl_3$) spectrum 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 $HB(C_6F_5)_2$ (9 mg, 5 mol%) were dissolved in CH_2Cl_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]

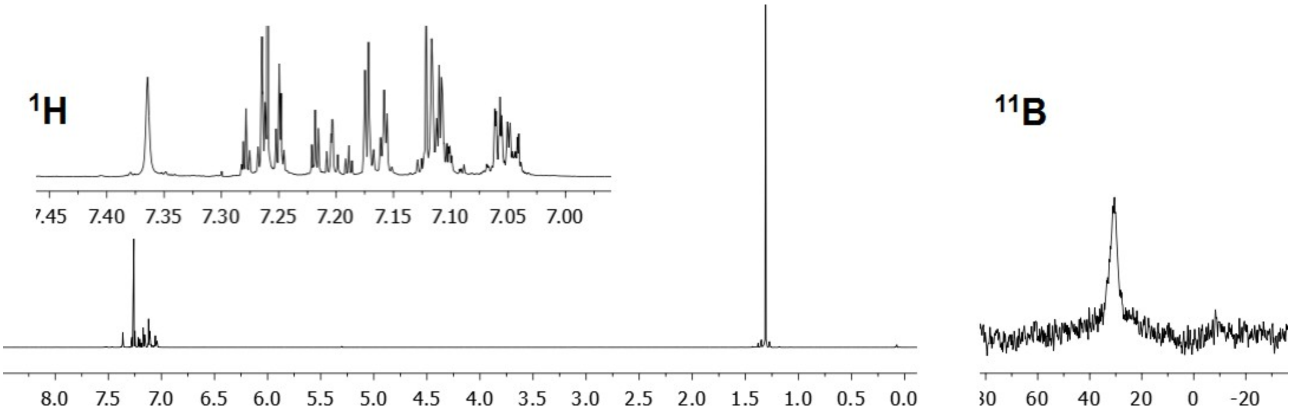
R*f* (hexanes/ether; 90/10) = 0.67.

^{1}H NMR (500 MHz, 298 K, $CDCl_3$): δ^{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).

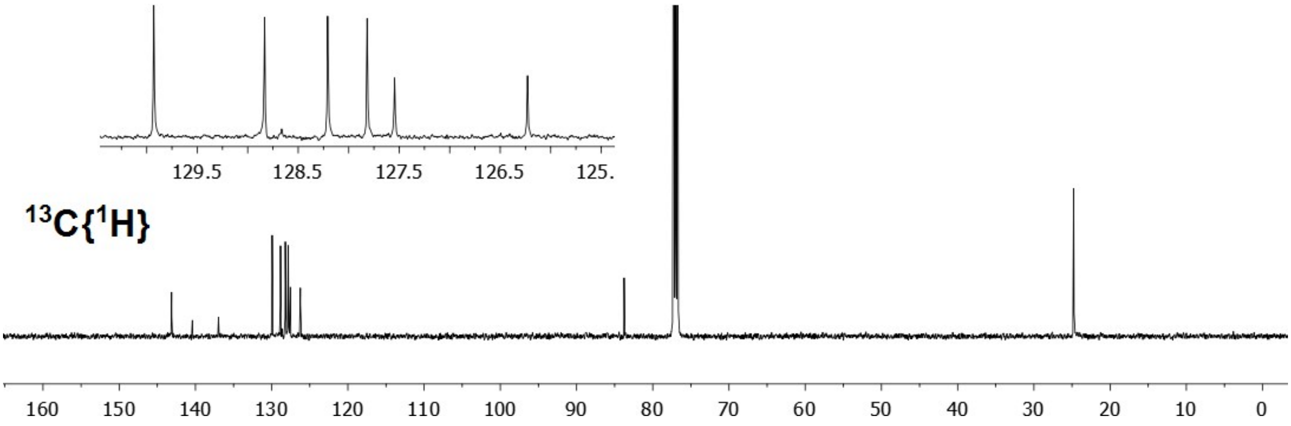
$^{13}C\{^1H\}$ NMR (126 MHz, 298 K, $CDCl_3$): $\delta^{13}C$: 143.1, 140.4, 137.0, 129.9, 128.8, 128.2, 127.8, 127.5, 126.2, 83.8, 24.8. N.o. $=C^B$.

^{11}B NMR (128 MHz, 298 K, $CDCl_3$): $\delta^{11}B$: 30.3 ($\nu_{1/2} \approx 380$ Hz).

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

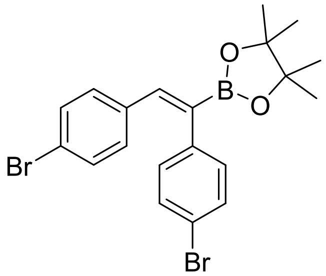


^1H NMR (500 MHz, 298 K, $CDCl_3$) and ^{11}B NMR (128 MHz, 298 K, $CDCl_3$) spectra of compound **19**.



$^{13}C\{^1H\}$ 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 $HB(C_6F_5)_2$ (9 mg, 5 mol%) were dissolved in CH_2Cl_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.[S19][1]

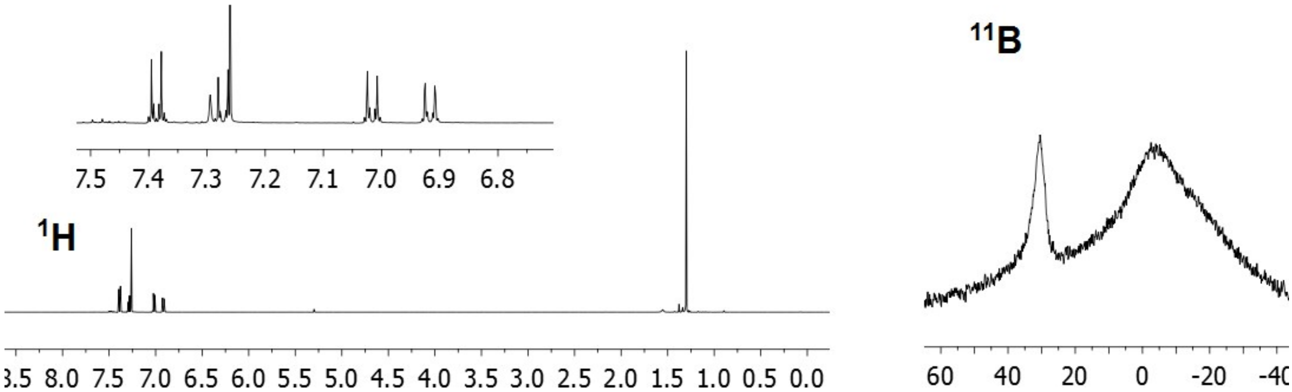
R_f (hexanes/ether; 90/10) = 0.55.

^{1}H NMR (500 MHz, 298 K, $CDCl_3$): δ^{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).

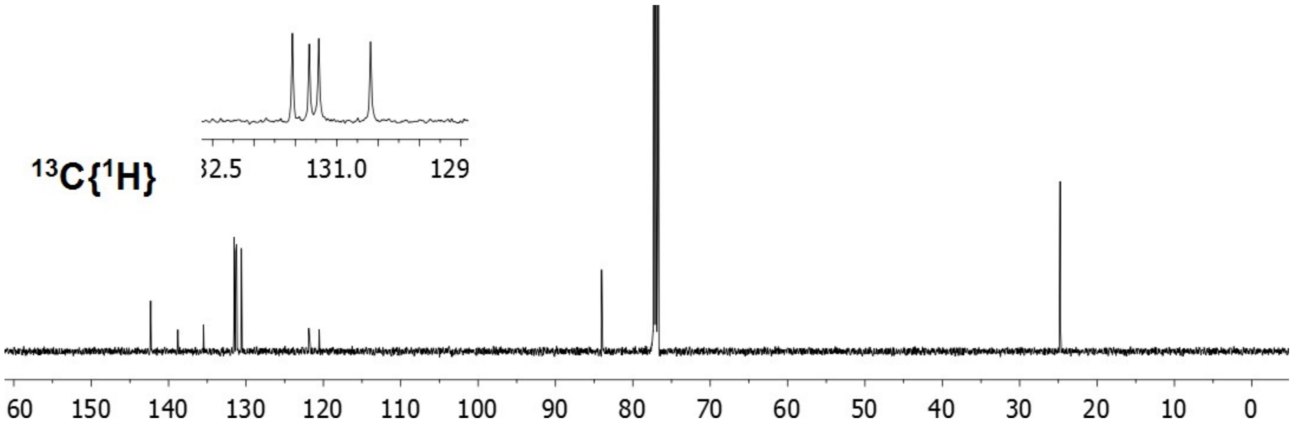
^{13}C NMR (126 MHz, 298 K, $CDCl_3$): δ^{13}C: 142.3, 138.8, 135.5, 131.5, 131.3, 131.2, 130.6, 121.9, 120.5, 84.0, 24.8. N.o. =C^B.

^{11}B NMR (128 MHz, 298 K, $CDCl_3$): δ^{11}B: 30.2 ($\nu_{1/2}$ ≈ 380 Hz).

HRMS (DART-TOF+): mass [M+H] calcd. for $C_{20}H_{22}B_1Br_2O_2$ 463.00796 *Da*, measured 463.00663 *Da*.

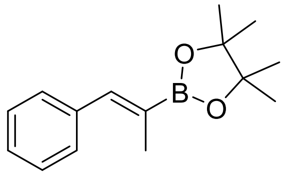


^{1}H NMR (500 MHz, 298 K, $CDCl_3$) and ^{11}B NMR (128 MHz, 298 K, $CDCl_3$) spectra of compound **20**.



^{13}C{^{1}H} NMR (126 MHz, 298 K, $CDCl_3$) spectrum of compound **20**.

(21) (*Z*)-4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane



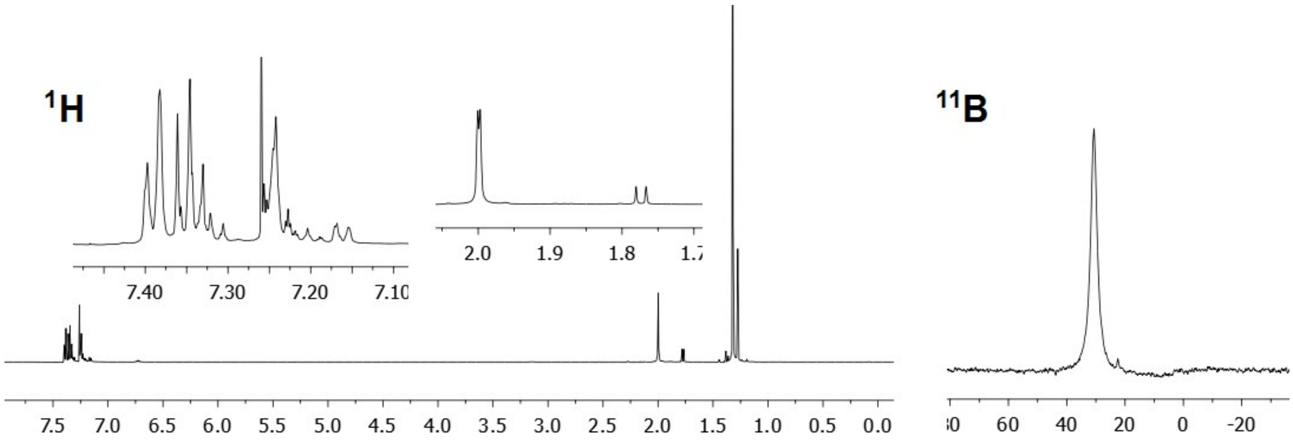
According to the general procedure prop-1-yn-1-ylbenzene (58 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and $HB(C_6F_5)_2$ (9 mg, 5 mol%) were dissolved in CH_2Cl_2 (2.5 ml) and reacted for 5 h at rt. Crude NMR studies showed greater 99% conversion and a ratio

---

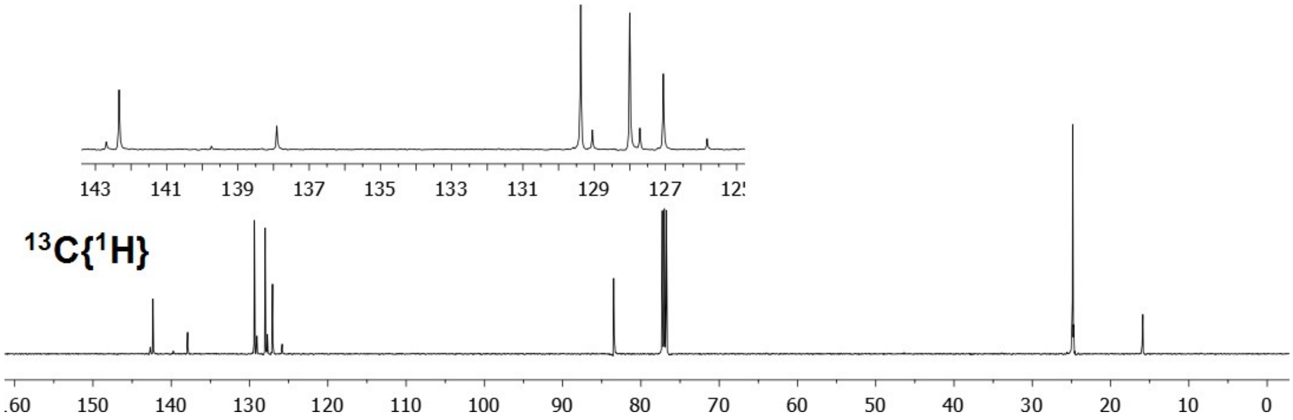
[19] C.-C. Tai, M.-S. Yu, Y.-L. Chen, W.-H. Chuang, T.-H. Lin, G. P. A. Yap, T.-G. Ong, *Chem. Commun.* **2014**, *50*, 4344-4346.

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.[S20]

(Data of the main isomer)
R_f (hexanes/ether; 90/10) = 0.54.
^{1}H NMR (500 MHz, 298 K, $CDCl_3$): δ^1H: 7.41 – 7.30 (m, 4H), 7.26 – 7.14 (m, 2H), 2.00 (d, $^4J_{HH}$ = 1.7 Hz, 3H), 1.32 (s, 12H).
^{13}C{^{1}H} NMR (126 MHz, 298 K, $CDCl_3$): δ^{13}C: 142.3, 137.9, 129.4, 128.0, 127.1, 83.5, 24.8, 15.9. N.o. =C^B.
^{11}B NMR (128 MHz, $CDCl_3$): δ^{11}B: 30.7 ($\nu_{1/2} \approx$ 320 Hz).
HRMS (DART-TOF+): mass [M+H] calcd. for $C_{15}H_{22}B_1O_2$ 245.17128 *Da*, found: 245.17127 *Da*.



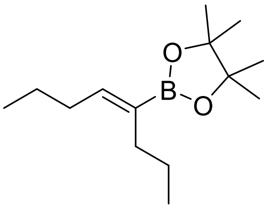
^{1}H NMR (500 MHz, 298 K, $CDCl_3$) and ^{11}B NMR (128 MHz, 298 K, $CDCl_3$) spectra of compound **21**.



^{13}C{^{1}H} NMR (126 MHz, 298 K, $CDCl_3$) spectrum of compound **21**.

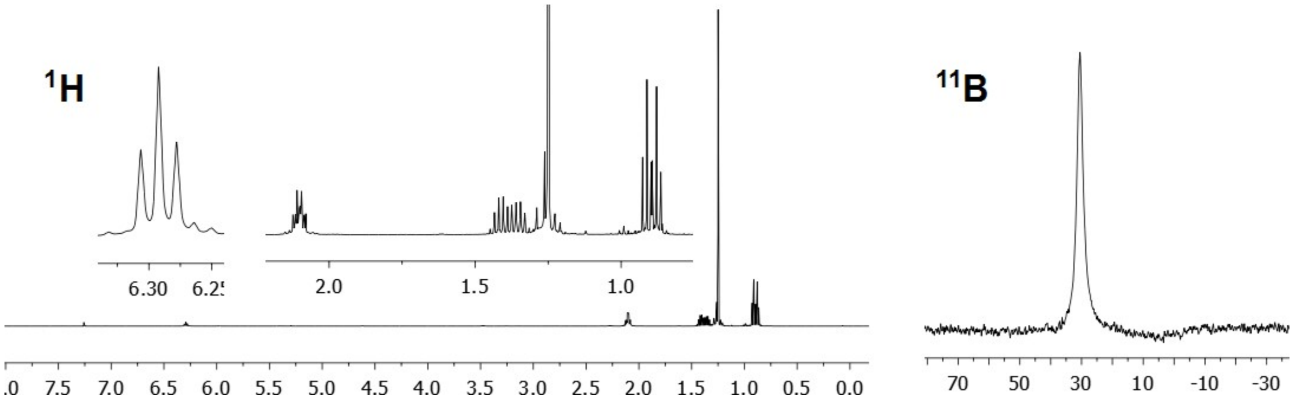
[S20] D. Janssen-Müller, M. Schedler, M. Fleige, C. G. Daniliuc, F. Glorius, *Angew. Chem. Int. Ed.* **2015**, *54*, 12492-12496.

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

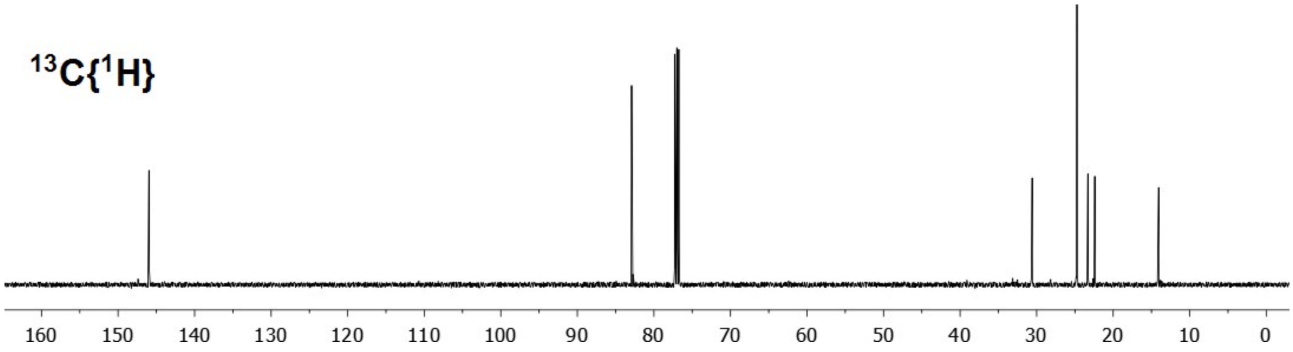


According to the general procedure 4-octyne (55 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and $HB(C_6F_5)_2$ (9 mg, 5 mol%) were dissolved in CH_2Cl_2 (2.5 ml) and reacted for 18 h at rt. Crude NMR studies showed greater 99% conversion and alkenyl borane **22** was isolated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

R*f* (hexanes/ether; 99/1) = 0.11.
^{1}H NMR (500 MHz, 298 K, $CDCl_3$): δ^{1}H: 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).
^{13}C{^{1}H} NMR (126 MHz, 298 K, $CDCl_3$): δ^{13}C: 146.0, 82.9, 30.7, 30.6, 24.7, 23.3, 22.4, 14.10, 14.06. N.o. =C^B.
^{11}B NMR (128 MHz, $CDCl_3$): δ^{11}B: 30.5 ($\nu_{1/2}$ ≈ 290 Hz).
HRMS (DART-TOF+): mass [M+H] calcd. for $C_{14}H_{28}B_1O_2$ 239.21823 *Da*, found: 239.21842 *Da*.

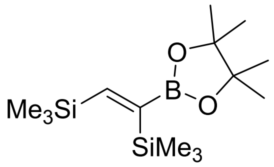


^{1}H NMR (500 MHz, 298 K, $CDCl_3$) and ^{11}B NMR (128 MHz, 298 K, $CDCl_3$) spectra of compound ***22***.



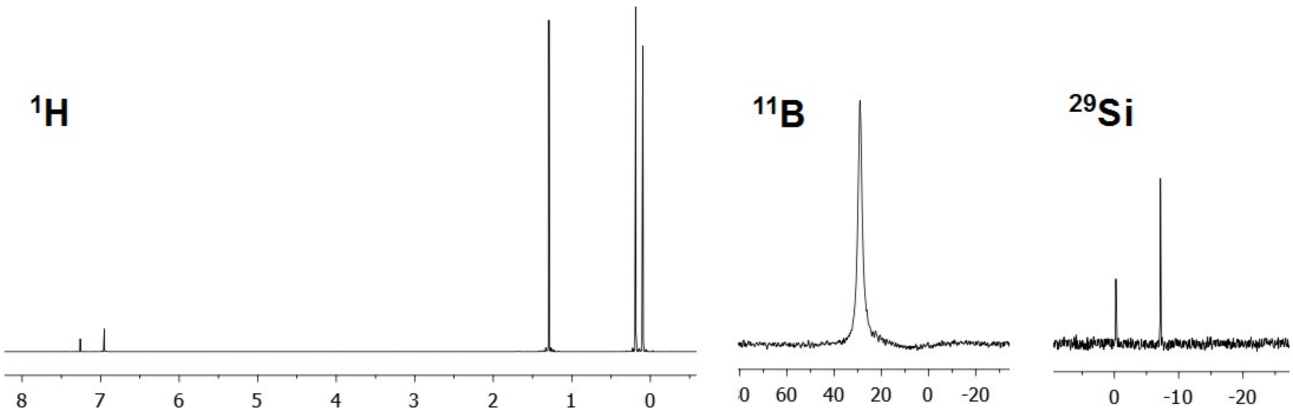
^{13}C{^{1}H} NMR (126 MHz, 298 K, $CDCl_3$) spectrum of compound ***22***.

(23) (*Z*)-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethene-1,2-diyl)bis(trimethylsilane)

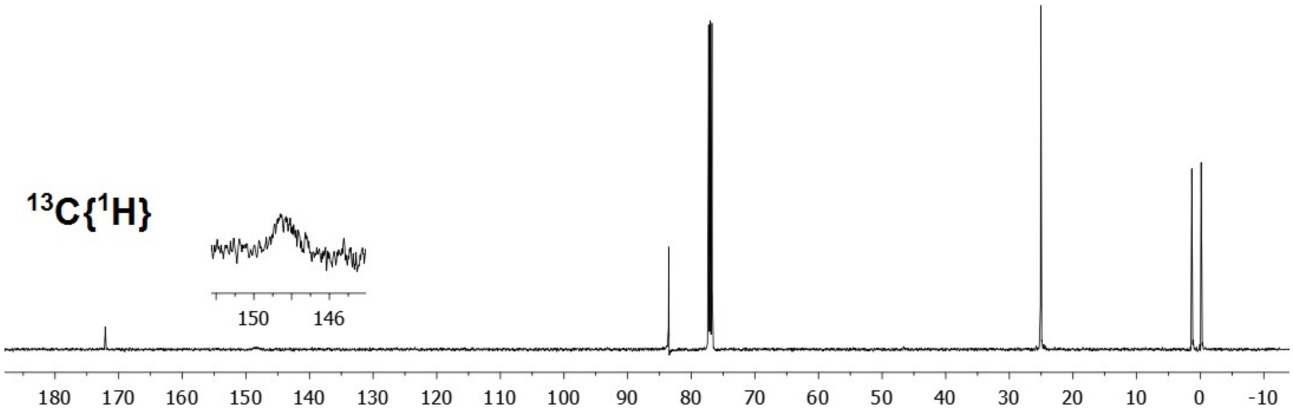


According to the general procedure 1,2-bis(trimethylsilyl)ethyne (85 mg, 0.50 mmol, 1.0 eq.), pinacol borane (77 mg, 0.55 mmol, 1.2 eq.) and $HB(C_6F_5)_2$ (9 mg, 5 mol%) were dissolved in CH_2Cl_2 (2.5 ml) and reacted for 18 h at r.t. Crude NMR studies showed greater 99% conversion and alkenyl borane **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, $CDCl_3$): δ^1H: 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, $CDCl_3$): δ^{13}C: 172.1, 148.4, 83.5, 25.1, 1.3, −0.2.
^{11}B NMR (128 MHz, 298 K, $CDCl_3$): δ^{11}B: 29.0 ($\nu_{1/2} \approx$ 300 Hz).
^{29}Si-dept (80 MHz, 298 K, $CDCl_3$): δ^{29}Si: −0.2, −7.2.
HRMS (DART-TOF+): mass [M+NH$_4$] calcd. for $C_{14}H_{35}B_1N_1O_2Si_2$ 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****.*