Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Formation of a Dihydroborole by Catalytic Isomerization of a Divinylborane

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$ X-Ray structure analyses

§ DFT calculations

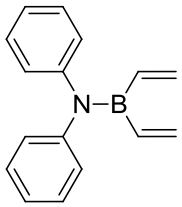
General remarks

All reactions were carried out under argon using Schlenk-type glassware or in a glovebox. Solvents were dried or distilled under argon prior to use. For the removal of volatiles and concentration of solutions a vacuum of ca 10^{-1} mbar (oil pump) was used, unless otherwise stated. The following instruments were used for characterization of the compounds. Differential scanning calorimetry (DSC): *DSC Q 20 (TA INSTRUMENT)*. Elemental analyses: ELEMENTAR *Vario El III*. ESI mass spectra: Bruker Daltonics MicroTof. IR spectra were recorded on a *Varian* 3100 FT-IR (Excalibur Series). NMR: *Agilent* DD2 600 NMR spectrometer (^{1}H, 600 MHz; ^{13}C, 151 MHz; ^{19}F, 564 MHz; ^{11}B, 192 MHz), *Agilent* VNMRS 500 spectrometer (^{1}H, 500 MHz; ^{13}C, 126 MHz; ^{19}F, 470 MHz; ^{11}B, 160 MHz), *Bruker* AV 300 (^{1}H, 300 MHz; ^{13}C, 76 MHz; ^{19}F, 282 MHz; ^{11}B, 96 MHz), *Bruker* AC 200 P-FT (^{1}H, 200 MHz; ^{11}B, 64 MHz). ^{1}H NMR and ^{13}C NMR, chemical shift δ is given relative to TMS (δ ^{1}H = 0, δ ^{13}C = 0) and referenced to the solvent signal; ^{19}F NMR, chemical shift δ is given relative to $CFCl_3$ (external reference, δ ^{19}F = 0); ^{11}B NMR, chemical shift δ is given relative to $BF_3{\cdot}Et_2O$ (external reference, δ ^{11}B = 0). Assignments of the resonances were supported by 2D experiments. Dichloro(diisopropylamino)borane and Dichloro(diphenylamino)borane were prepared by literature known procedures (M. Baudler, A. Marx, *Z. anorg. allg. Chem*. **1981**, *474*, 18 – 30). Comercially available reagents were purchased from *Sigma-Adlrich*, *TCI Chemicals*, *Acros* or *Merck* and used without further purification.

X-Ray diffraction: Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT (Nonius B.V., 1998); data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307-326); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr*. **2003**, *A59*, 228-234); structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr*. **1990**, *A46*, 467-473); structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr*. **2008**, *A64*, 112-122) and graphics, XP (BrukerAXS, 2000). Thermal ellipsoids are shown with 30% probability, *R*-values are given for observed reflections, and wR^2 values are given for all reflections. *Exceptions and special features*: Compound **1a** crystallized with two molecules in the asymmetric unit. For compound **11** one and half benzene molecule were found in the asymmetric unit. CCDC deposition numbers are 982551 to 982553 and 983316.

Synthesis of compounds

Preparation of (Diphenylamino)divinylborane (1a).



A solution of vinylmagnesium bromide (1 M in THF, 12.5 mL, 2.5 eq., 12.5 mmol) was added to a solution of dichloro(diphenylamino)borane (1245 mg, 5 mmol) in diethylether (30 mL) at -78 °C. After the obtained suspension was stirred for 4 days at room temperature it was concentrated in vacuum. Subsequently the residue was taken up in pentane (30 mL) and the resulting suspension was stirred for overnight. Then the suspension was filtered and the residue was washed with pentane (3 x 15 mL). The organic phases were combined and all volatiles were removed in vacuum. The product was obtained as a colorless oil which completely crystallizes after some minutes (880 mg, 76%).

Crystals suitable for the X-ray single crystal structure analysis were obtained by slow evaporation of a pentane solution at -32 °C.

^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ = 7.29 (m, 2H, *m*-Ph), 7.17 (m, 1H, *p*-Ph), 7.09 (m, 2H, *o*-Ph), 6.02 (dd, $^{3}J_{HH}$ = 18.8 Hz, $^{3}J_{HH}$ = 14.1 Hz, 1H, =CH), 5.87 (dd, $^{3}J_{HH}$ = 14.1 Hz, $^{2}J_{HH}$ = 4.7 Hz, 1H, $=CH_2^{E}$), 5.85 (dd, $^{3}J_{HH}$ = 18.8 Hz, $^{2}J_{HH}$ = 4.7 Hz, 1H, $=CH_2^{Z}$).

^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K): δ = 148.9 (*i*-Ph), 139.0 (br, =CH),134.1 ($=CH_2$), 129.1 (*m*-Ph), 128.2 (*o*-Ph), 125.6 (*p*-Ph).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, CD_2Cl_2, 298 K): δ ^{1}H / δ ^{13}C = 7.29 / 129.1 (*m*-Ph), 7.17 / 125.6 (*p*-Ph), 7.09 / 128.2 (*o*-Ph), 6.02 / 139.0 (=CH), 5.87 / 134.1 ($=CH_2^{E}$), 5.85 / 134.1 ($=CH_2^{Z}$).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz,CD_2Cl_2, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.29 / 148.9, 129.1, 128.2 (*m*-Ph / *i*-Ph, *m*-Ph, *o*-Ph), 7.17 / 148.9, 129.1, 128.2 (*p*-Ph / *i*-Ph, *m*-Ph, *o*-Ph), 7.09 / 148.9, 129.1, 128.2, 125.6 (*o*-Ph / *i*-Ph, *m*-Ph, *o*-Ph, *p*-Ph).

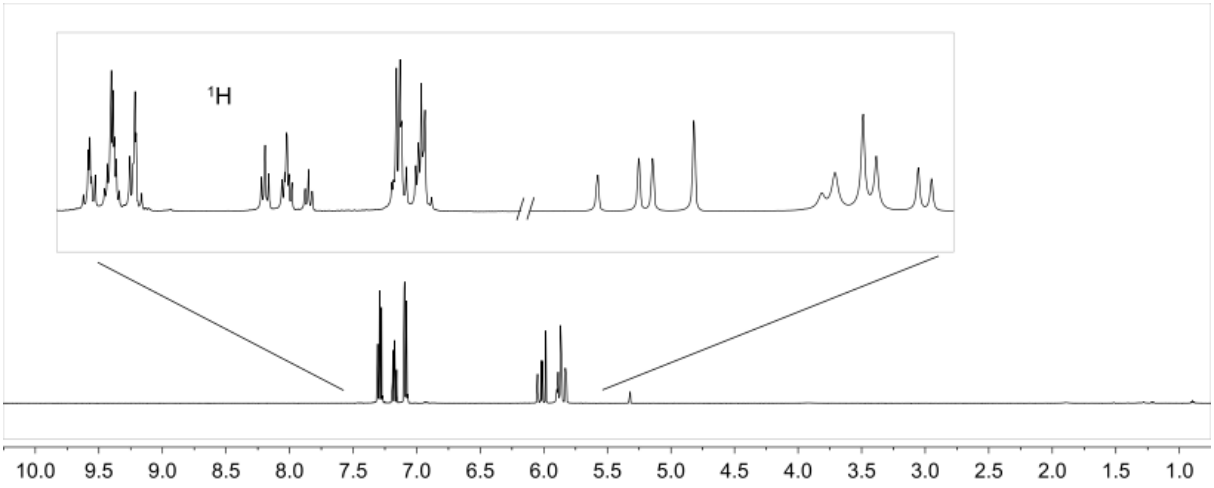
^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 298 K): δ = 39.0 ($\nu_{1/2}$ ~ 250 Hz).

IR (KBr): Wavenumber / cm^{-1} = 3060 (w, br), 2953 (w, br), 2338 (w), 1929 (w), 1795 (w), 1950 (w), 1596 (m), 1494 (m), 1431 (m), 1356 (w), 1280 (w), 1017 (w), 957 (w), 834 (w), 764 (s), 698 (w), 540 (w), 474 (w).

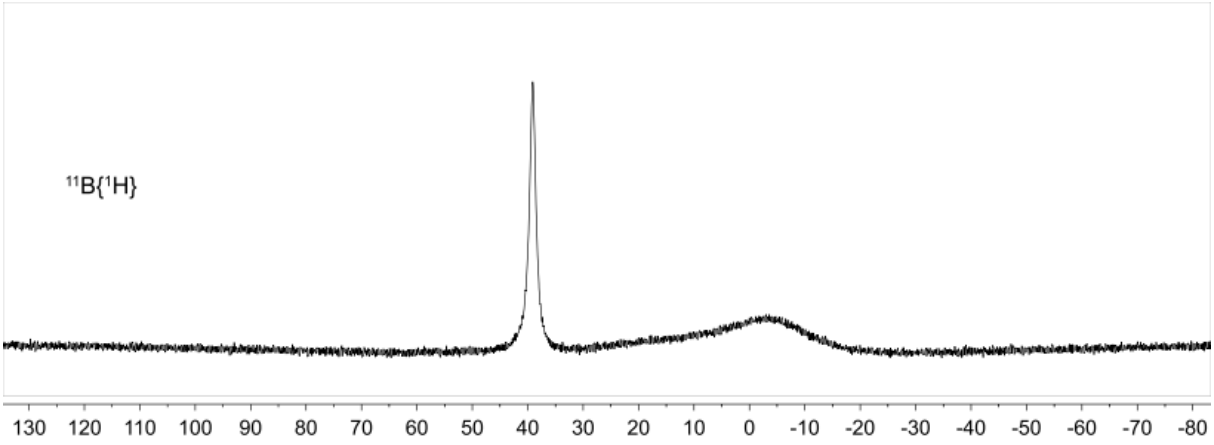
Melting Point (DSC): 57 °C.

Decomposition (DSC): 307 °C.

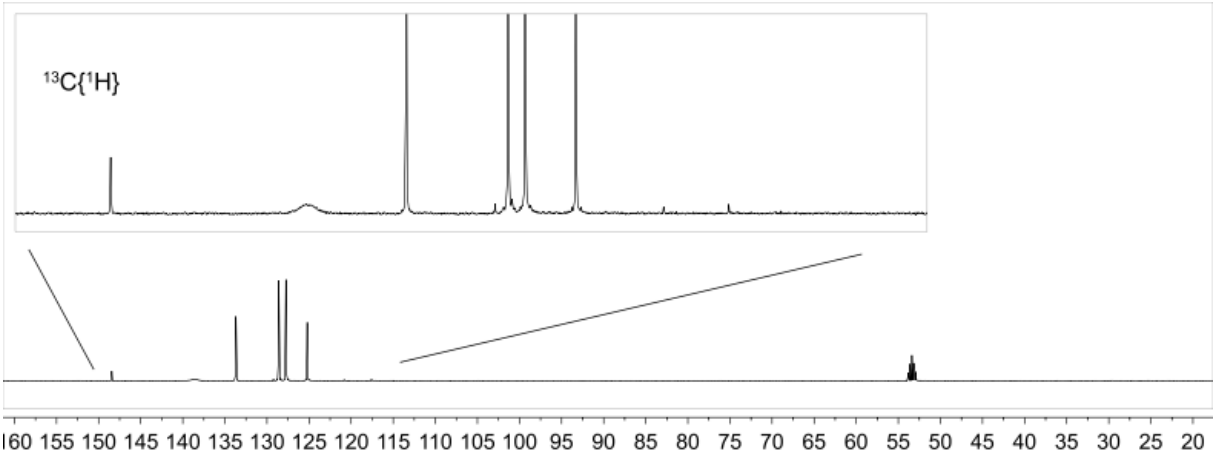
Elemental Analysis: Calcd. for $C_{16}H_{16}BN$: C, 82.44; H, 6.92; N, 6.01. Found: C, 82.32; H, 6.89; N, 5.91.



^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) spectrum of (diphenylamino)divinylborane (**1a**).



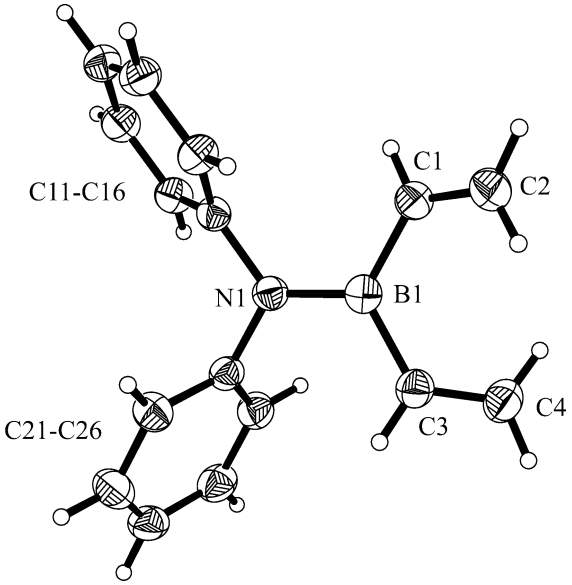
^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 298 K) spectrum of (diphenylamino)divinylborane (**1a**).



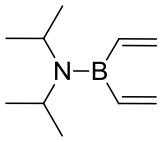
^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K) spectrum of (diphenylamino)divinylborane (**1a**).

X-ray crystal structure analysis of compound 1a: formula $C_{16}H_{16}BN$, M = 233.11, colourless crystal, 0.26 x 0.12 x 0.07 mm, a = 8.7384(3), b = 16.7458(6), c = 18.9805(7) Å, β = 96.163(2)°, V = 2761.4(2) Å^3, ρ_{calc} = 1.121 gcm^{-3}, μ = 0.482 mm^{-1}, empirical absorption correction (0.884 ≤ T ≤ 0.967), Z = 8, monoclinic, space group $P2_1/n$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 24587 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 4809 independent (R_{int} = 0.056) and 3697

observed reflections [$I>2\sigma(I)$], 325 refined parameters, R = 0.042, wR^2 = 0.118, max. (min.) residual electron density 0.09 (-0.14) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.



Preparation of (diisopropylamino)divinylborane (1b).



Dichloro(diisopropylamino)borane (909 mg, 10 mmol) was dissolved in diethyl ether (30 mL) and the obtained solution was cooled to -78 °C. Then vinylmagnesium bromide solution (1 M in THF, 14 mL, 2.8 eq., 14 mmol) was added and the resulting pale yellow suspension was stirred for 5 days at room temperature. Subsequently all volatiles were removed in vacuum and the residue was taken up in pentane (30 mL). After the suspension was stirred overnight it was filtered. The obtained solid was washed with pentane (3 x 10 mL). The filtrate and the pentane phases were combined and the solvent was removed in vacuum to give compound **1b** as a colorless oil (350 mg, 43%).

^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ = 6.45 (dd, $^3J_{HH}$ = 19.5 Hz, $^3J_{HH}$ = 14.0 Hz, 1H, =CH), 5.75 (br dd, $^3J_{HH}$ = 14.0 Hz, $^2J_{HH}$ = 4.4 Hz, 1H, $=CH_2^E$), 5.52 (dd, $^3J_{HH}$ = 19.5 Hz, $^2J_{HH}$ = 4.4 Hz, 1H, $=CH_2^Z$), 3.72 (br m, 1H, CH), 1.20 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH_3).

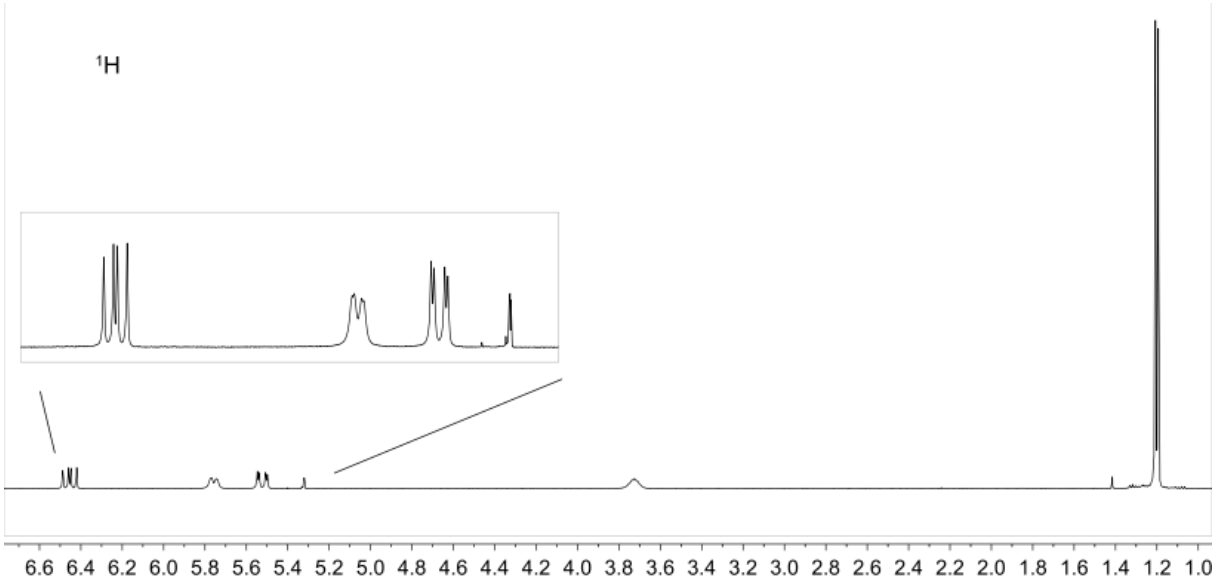
^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K): δ = 141.1 (br, =CH), 129.9 ($=CH_2$), 48.2 (CH), 23.6 (CH_3).

^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 298 K): δ = 37.7 ($\nu_{1/2}$ ~ 100 Hz).

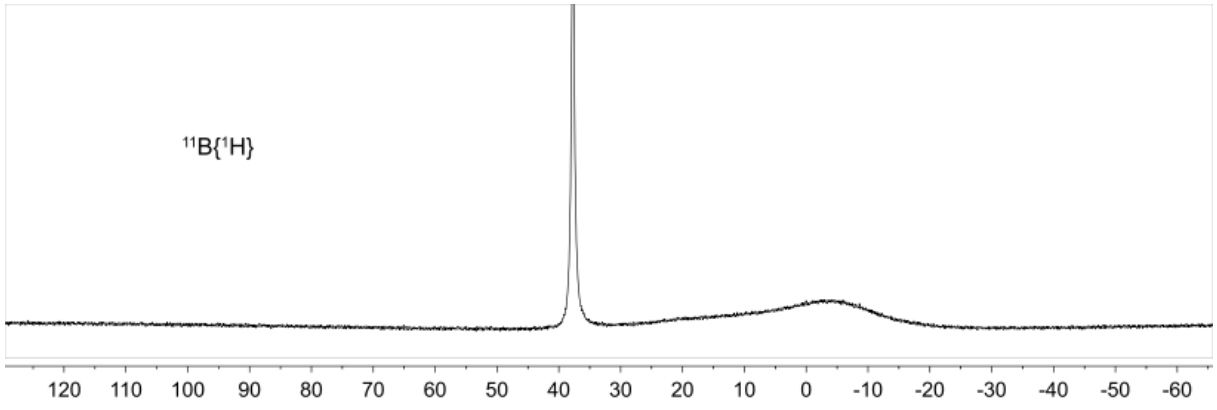
IR (KBr): Wavenumber / cm^{-1} = 3058 (w), 2969 (s), 2933 (m), 2873 (w), 1603 (m), 1449 (s), 1410 (w), 1368 (m), 1322 (s), 1284 (w), 1198 (s), 1159 (m), 1136 (m), 1016 (w), 949 (br, m), 810 (w), 717 (m), 597 (w), 506 (w).

HRMS: Calcd. for $[C_{10}H_{20}BN]H^+$: 166.176. Found: 166.175; Calcd. for $[C_{10}H_{20}BN]OH^-$: 182.171. Found: 182.170.

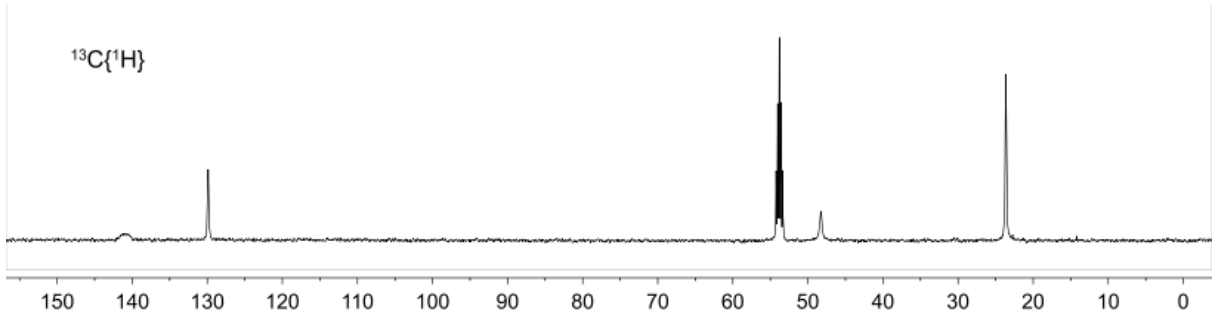
Elemental Analysis: Calcd for $C_{10}H_{20}BN$: C, 72.76; H, 12.21; N, 8.48. Found: C, 71.96; H, 11.94; N, 8.16.



^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) spectrum of (diisopropylamino)divinylborane (**1b**).

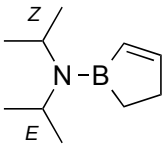


^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 298 K) spectrum of (diisopropylamino)divinylborane (**1b**).



^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K) spectrum of (diisopropylamino)divinylborane (**1b**).

Preparation of 1-(diisopropylamino)-2,3-dihydroborole (3b).



a) Generation of compound 3b: 8 mol% bis(pentafluorophenyl)borane as catalyst at 200 °C. (Diisopropylamino)divinylborane (**1b**) (350 mg, 2.12 mmol) was dissolved in toluene (8 mL) using an ampule. Then bis(pentafluorophenyl)borane (60 mg, 0.17 mmol, 0.08 eq.) was added to the solution. After stirring for 15 minutes the ampule was sealed and taken into an autoclave. Subsequently the autoclave was heated for 36 h at 200 °C. Then, at room temperature, all volatiles were carefully removed in vacuum. The product **3b** was condensed from the obtained yellow residue at 8 × 10^{-3} mbar and 100 °C as a colorless oil (218 mg, 62%).

^{1}H NMR (500 MHz, [D_8]-toluene, 298 K): δ = 7.13 (br dm, $^{3}J_{HH}$ = 8.1 Hz, 1H, =CH), 6.27 (dm, $^{3}J_{HH}$ = 8.1 Hz, 1H, BCH), 3.48 (hept, $^{3}J_{HH}$ = 6.8 Hz, 1H CH^{E}), 3.24 (br hept, $^{3}J_{HH}$ = 6.9 Hz, 1H, CH^{Z}), 2.29 (m, 2H, CH_2), 1.11 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H, CH_3^{Z}), 1.03 (m, 2H, BCH_2), 0.96 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, CH_3^{E}).

^{13}C{^{1}H} NMR (126 MHz, [D_8]-toluene, 298 K): δ = 162.0 (=CH), 135.4 (br, BCH), 50.5 (CH^{E}), 46.4 (CH^{Z}), 32.6 (CH_2), 24.7 (CH_3^{Z}), 22.4 (CH_3^{E}), 15.2 (br, BCH_2).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, [D_8]-toluene, 298 K): δ ^{1}H / δ ^{13}C = 7.13 / 162.0 (=CH), 6.27 / 135.4 (BCH), 3.48 / 50.5 (CH^{E}), 3.24 / 46.4 (CH^{Z}), 2.29 / 32.6 (CH_2), 1.11 / 24.7 (CH_3^{Z}), 1.03 / 15.2 (BCH_2), 0.96 / 22.4 (CH_3^{E}).

^{1}H{^{1}H} 1D-TOCSY (500 MHz, [D_8]-toluene, 298 K) [selected experiments]: δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 3.48 / 0.96 (CH^{E} / CH_3^{E}), 3.24 / 1.11 (CH^{Z} / CH_3^{c}), 2.29 / 7.13, 6.27, 1.03 (CH_2 / =CH, BCH, BCH_2).

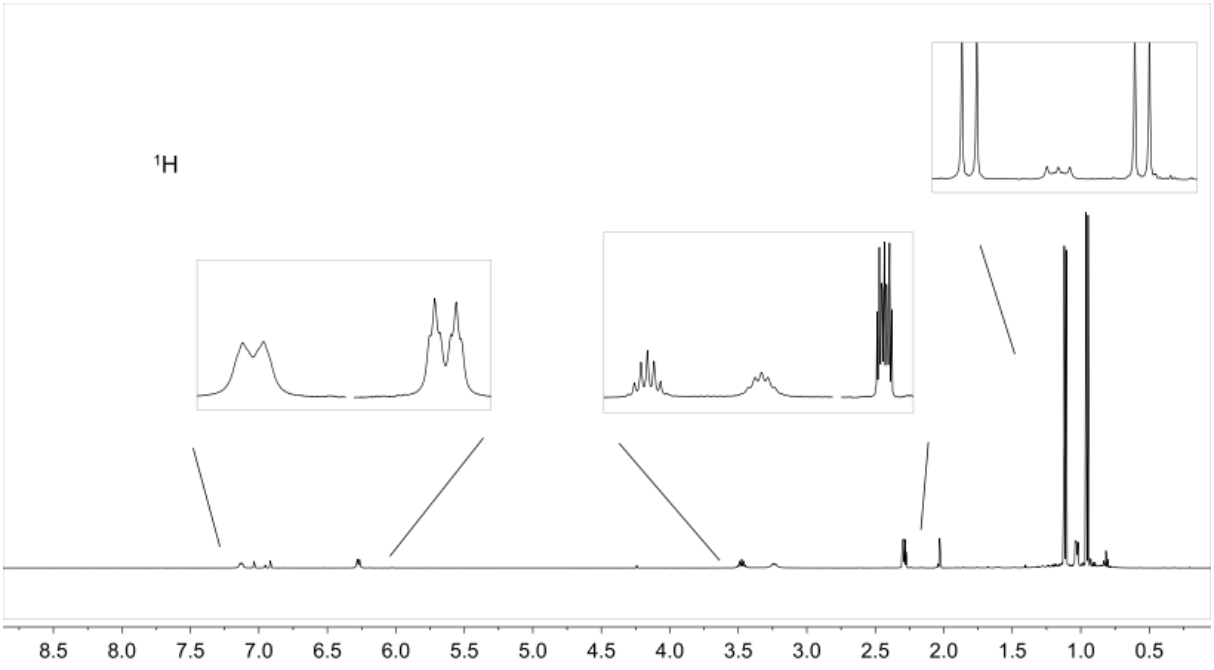
^{1}H{^{1}H} NOEDIF (500 MHz, [D_8]-toluene, 298 K) [selected experiments]: δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 1.11 / 6.27 (CH_3^{Z} / BCH).

^{11}B{^{1}H} NMR (160 MHz, [D_8]-toluene, 298 K): δ = 46.6 ($\nu_{1/2}$ ~ 150 Hz).

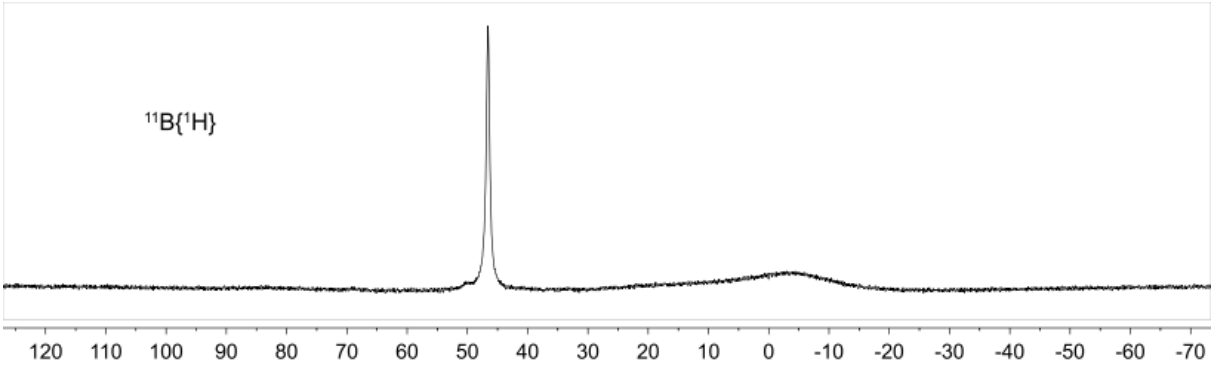
IR (KBr): Wavenumber / cm^{-1} = 2930 (w, br), 1646 (w), 1566 (w), 1451 (m, br), 1368 (m), 1260 (w), 1196 (w), 1099 (w), 1022 (w), 971 (w), 805 (w), 711 (w), 562 (w), 505 (w).

HRMS: Calcd. for $[C_{10}H_{20}BN]H^{+}$: 166.176. Found: 166.176.

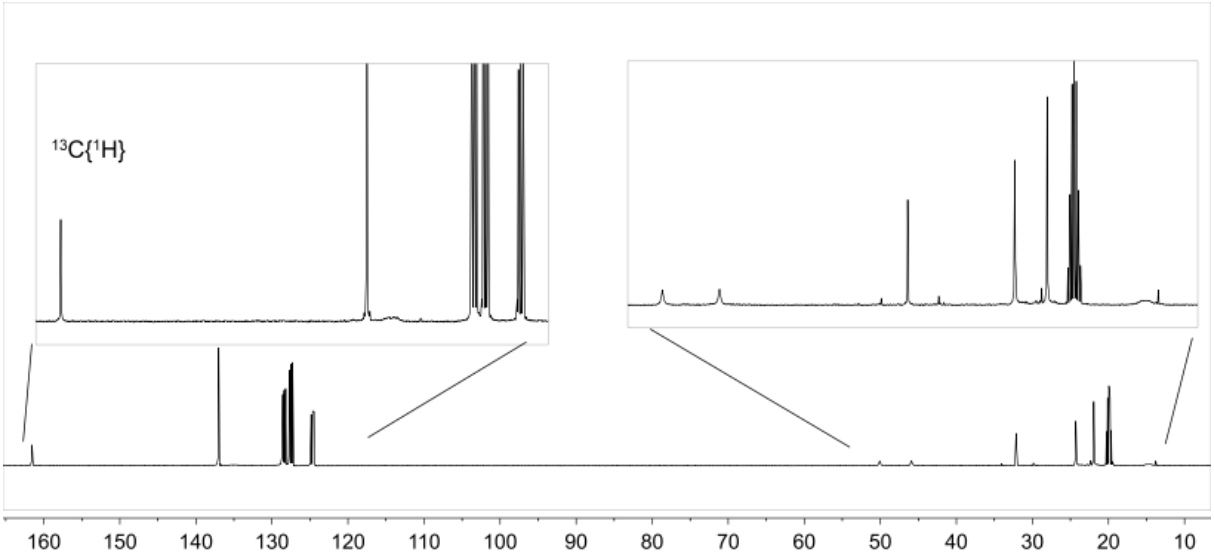
Elemental Analysis: Calcd. for $C_{10}H_{20}BN$: C, 72.76; H, 12.21; N, 8.48. Found: C, 72.79; H, 12.19; N, 8.66.



^{1}H NMR (500 MHz, [D_8]-toluene, 298 K) spectrum of 1-(diisopropylamino)-2,3-dihydroborole (**3b**) (method a).



^{11}B{^{1}H} (160 MHz, [D_8]-toluene, 298 K) spectrum of 1-(diisopropylamino)-2,3-dihydroborole (**3b**) (method a).



^{13}C{^{1}H} NMR (126 MHz, [D_8]-toluene, 298 K) spectrum of 1-(diisopropylamino)-2,3-dihydroborole (**3b**) (method a).

b) Generation of compound 3b: 15 mol% bis(pentafluorophenyl)borane as catalyst at 100 °C.

(Diisopropylamino)divinylborane (**1b**) (150 mg, 0.9 mmol) was dissolved in toluene (5 mL) in a Schlenk flask. Then bis(pentafluorophenyl)borane (47 mg, 0.13 mmol, 0.15 eq.) was added and the obtained solution was stirred for 1 h at 100 °C. Subsequently all volatiles were removed slowly in vacuum at room temperature. Finally the product was condensed from the obtained yellow residue at 8×10^{-3} mbar and 100 °C to give compound **3b** (90 mg, 60%).

c) Solvent dependency.

The reactions were carried out in the respective solvent (1mL) with (diisopropylamino)divinylborane (16.5 mg, 0.1 mmol) and bis(pentafluorophenyl)borane (3.5 mg, 0.01 mmol, 10 mol%) in a sealed NMR tube and heated in an autoclave. The conversion was determined by $^{11}B\{^1H\}$ NMR measurements.

Table 1: Conversion of (diisopropylamino)divinylborane (**1b**) in different solvents.

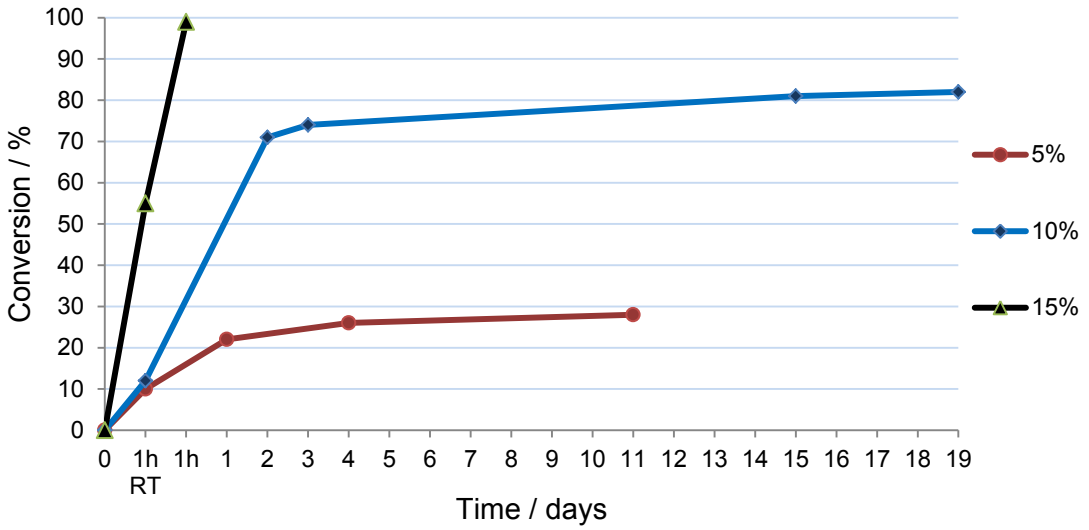
Solvent	**Total time (h) / % Prod.**					
	25 °C			200 °C		
Tol	0.5 / 35	10 / 64	35 / 71	5 / 99	16 / 100	24 / 100
THF	0.5 / 0	10 / 0	35 / 0	5 / 78	16 / 95	24 / 96
DCM	0.5 / 39	10 / 57	35 / 61	5 / 83	16 / 93	24 / 95
Pentane	0.5 / 15	10 / 40	35 / 45	5 / 57	16 / 68	24 / 73
Et_2O	0.5 / 19	10 / 52	35 / 58	5 / 79	16 / 89	24 / 95

d) Catalyst concentration dependency at 100 °C.

The reactions were carried out in $[D_8]$-toluene (1 mL) with (diisopropylamino)divinylborane (16.5 mg, 0.1 mmol) using different amounts of bis(pentafluorophenyl)borane (1.7 mg: 5 mol%; 3.5 mg: 10 mol%; 5.2 mg: 15 mol%) in sealed NMR tubes at 100 °C. The conversion was determined by $^{11}B\{^1H\}$ NMR measurements.

Table 2: Catalytic conversion of (diisopropylamino)divinylborane (**1b**) in $[D_8]$-toluene with different amounts of bis(pentafluorophenyl)borane.

$HB(C_6F_5)_2$ / mol%	**Temperature / °C**	**Time h (d)**	**Conversion %**
5	RT	1	10
5	100°C	24 (1)	22
5	100°C	96 (4)	26
5	100°C	264 (11)	28
10	RT	1	12
10	100°C	48 (2)	71
10	100°C	72 (3)	74
10	100°C	360 (15)	81
10	100°C	456 (19)	82
15	RT	1	55
15	100°C	1	99



Catalytic conversion of (diisopropylamino)divinylborane (**1b**) at 100 °C in [D_8]-toluene with different amounts of bis(pentafluorophenyl)borane. $1h^{RT}$: after 1 h at room temperature; 1h: after 1 h at 100°C.

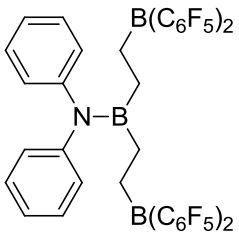
Comment: Full conversion of (diisopropylamino)divinylborane (**1b**) was achieved in toluene after 1 h at 100 °C with 15% bis(pentafluorophenyl)borane (black). Alternatively full conversion was also achieved at room temperature after 4 days [(diisopropylamino)divinylborane (**1b**) (16.5 mg, 0.1 mmol) with 15% bis(pentafluorophenyl)borane (5.2 mg: 15 mol%)].

Control experiments:

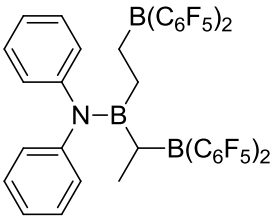
a) (Diisopropylamino)divinylborane (**1b**) (16.5 mg, 0.1 mmol) in [D_8]-toluene (1 mL) in a sealed NMR tube was heated at 200 °C in an autoclave for 3 days: no product formation was detected.

b) (Diisopropylamino)divinylborane (**1b**) (16.5 mg, 0.1 mmol) in [D_8]-toluene (1 mL) in a sealed NMR tube was irradiated with a water cooled Hg-high pressure lamp (Philips HPK 125 W), equipped with a quartz glass filter for 72 h at room temperature: no product formation was detected.

Preparation of compound 8.



8 (79%)



8' (21%)

Divinyl(diphenylamino)borane (**1a**) (70 mg, 0.3 mmol) was added to a suspension of bis(pentafluorophenyl)borane (208 mg, 0.6 mmol, 2 eq.) in toluene (2 mL) and the reaction mixture was stirred for 20 minutes. Then the suspension was filtered and the filtrate was concentrated to 1 mL. Subsequently pentane (0.5 mL) was added and the solution was stored for 2 days at -32 °C. The product crystalized as long colorless needles (144 mg, 52%). The obtained crystals were suitable for the X-ray single crystal structure analysis.

IR (KBr): Wavenumber / cm^{-1} = 3648 (s), 3236 (s), 2913 (s), 2822 (m), 2359 (w), 1960 (w), 1740 (w), 1647 (m), 1309 (m), 1199 (m), 1079 (s), 989 (m), 875 (m), 741 (m), 609 (s) 554 (s).

Melting point (DSC): 79 °C

Decomposition (DSC): 239 °C.

Elemental Analysis: Calcd. for $C_{40}H_{18}B_3F_{20}N$: C, 51.94; H, 1.96; N, 1.51. Found: C, 51.89; H, 1.85; N, 1.43.

Comment: In CD_2Cl_2 solution a mixture of 2 compounds was detected (ratio ca. 79 : 21). The major compound was assigned to compound **8**, the minor compound was tentatively assigned to its isomer **8'**.

*Major isomer **8**:* **^{1}H NMR** (500 MHz, CD_2Cl_2, 298 K): δ = 7.22 (m, 2H, *m*-Ph) 7.12 (m, 1H, *p*-Ph), 7.02 (m, 2H, *o*-Ph), 1.97 (m, 2H, CH_2B), 0.95 (m, 2H, $NBCH_2$).

^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K): δ = 148.3 (*i*-Ph),147.5 (dm, $^1J_{FC}$ ~ 248 Hz, C_6F_5) 143.6 (dm, $^1J_{FC}$ ~ 257 Hz, C_6F_5), 137.7 (dm, $^1J_{FC}$ ~ 251 Hz, C_6F_5) ,129.2 (*m*-Ph), 127.9 (*o*-Ph), 126.0 (*p*-Ph), 114.3 (br m, *i*-C_6F_5), 25.8 (br, CH_2B), 11.7 (br, $NBCH_2$).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, CD_2Cl_2, 298 K): δ ^{1}H / δ ^{13}C = 7.22 / 129.2 (*m*-Ph), 7.12 / 126.0 (*p*-Ph), 7.02 / 127.9 (*o*-Ph), 1.97 / 25.8 (CH_2B), 0.95 / 11.7 ($NBCH_2$).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, CD_2Cl_2, 298 K) [selected traces]: δ ^{1}H / δ ^{13}C = 7.22 / 148.3, 129.2, 127.9 (*m*-Ph / *i*-Ph, *m*-Ph, *o*-Ph) , 7.12 / 148.3, 129.2, 127.9 (*p*-Ph / *i*-Ph, *m*-Ph, *o*-Ph), 7.02 / 148.3, 127.9, 126.0 (*o*-Ph / *i*-Ph, *o*-Ph, *p*-Ph), 1.97 / 114.3, 11.7 (CH_2B / *i*-C_6F_5, $NBCH_2$), 0.95 / 25.8, 11.7 ($NBCH_2$ / CH_2B, $NBCH_2$).

^{1}H{^{1}H} NOEDIF (500 MHz, CD_2Cl_2, 298 K) [selected experiments]: δ $^1H_{irr}$ / δ $^1H_{res}$ = 7.02 / 0.95 (*o*-Ph / $NBCH_2$).

^{19}F NMR (470 MHz, CD_2Cl_2, 298 K): δ = –130.3 (m, 2F, *o*-C_6F_5), –149.2 (t, $^3J_{FF}$ = 20 Hz,1F, *p*-C_6F_5), -162.2 (m, 2F, *m*-C_6F_5), [Δδ $^{19}F_{p\text{-}m}$ = 13.0].

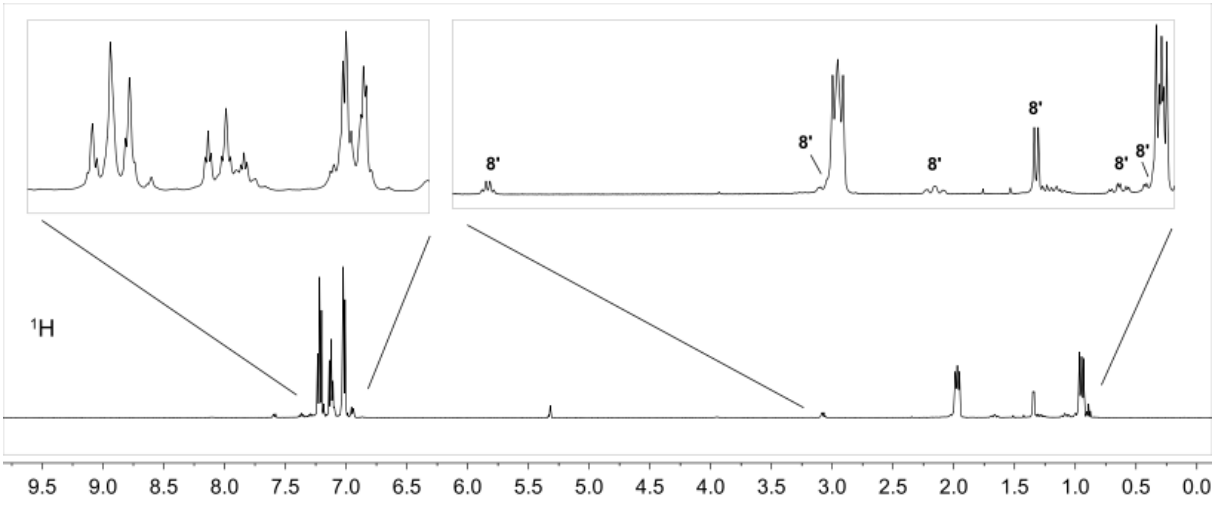
^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 298 K): δ = 70.7 ($\nu_{1/2}$ ~ 1200 Hz, B), 47.5 ($\nu_{1/2}$ ~ 900 Hz, BN).

*Minor isomer **8'**:* **^{1}H NMR** (500 MHz, CD_2Cl_2, 298 K)[selected resonances]: δ = 3.08 (q, $^3J_{HH}$ = 6.4 Hz, 1H, CH), 2.00 / 1.66 (each m, each 1H, CH_2B)^t, 1.08 / 0.97 (each m, each 1H, $NBCH_2$)^t, 1.34 (d, $^3J_{HH}$ = 6.4 Hz, 3H, CH_3), [tentatively assigned].

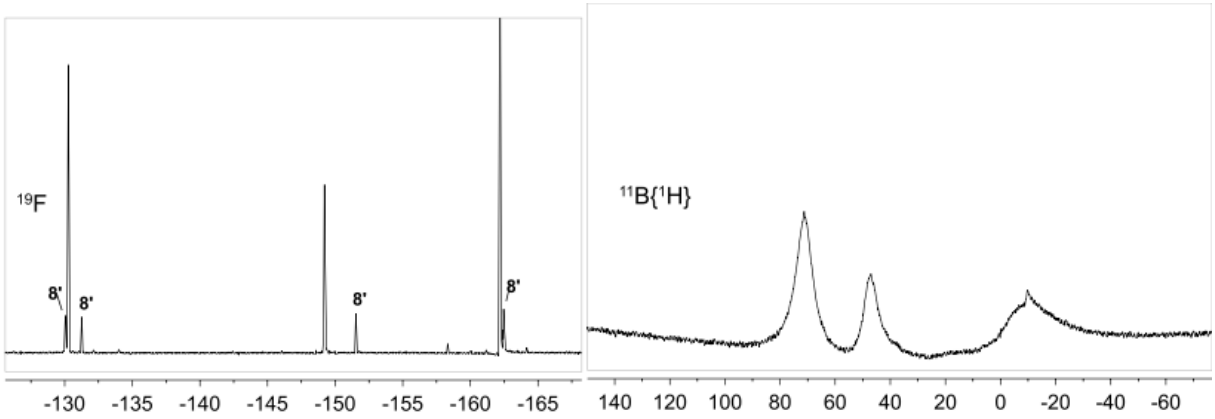
$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 298 K)[selected resonances]: δ = 148.8, 148.4 (*i*-Ph), 129.41, 129.35 (*m*-Ph), 128.1, 127.7 (*o*-Ph), 126.31, 126.25 (*p*-Ph), 37.0 (br, CH), 24.5 (br, $CH_2B)^t$, 10.8 (br, $NBCH_2)^t$, 12.2 (CH_3), [tentatively assigned].

^{19}F NMR (470 MHz, CD_2Cl_2, 298 K): δ = –130.1, -131.3 (each m, each 2F, *o*-C_6F_5), –149.2^t, -151.5 (each t, $^3J_{FF}$ = 20.0 Hz, each 1F, *p*-C_6F_5), -162.1, -162.5 (each m, each 2F, *m*-C_6F_5), [$\Delta\delta\ ^{19}F_{p\text{-}m}$ = 13.0].

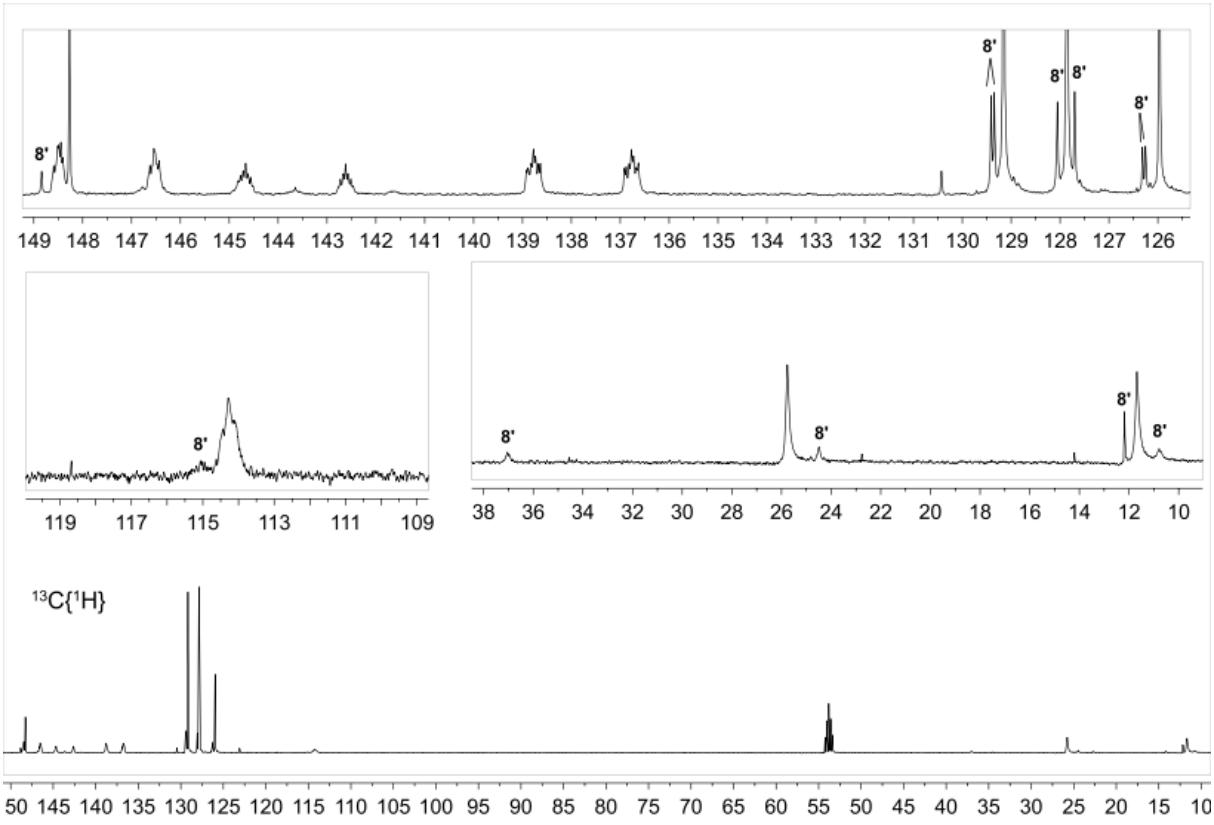
$^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 298 K): δ = 70.7 ($\nu_{1/2}$ ~ 1200 Hz, B), 47.5 ($\nu_{1/2}$ ~ 900 Hz, BN).



^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) spectrum of compound **8** and **8'**.

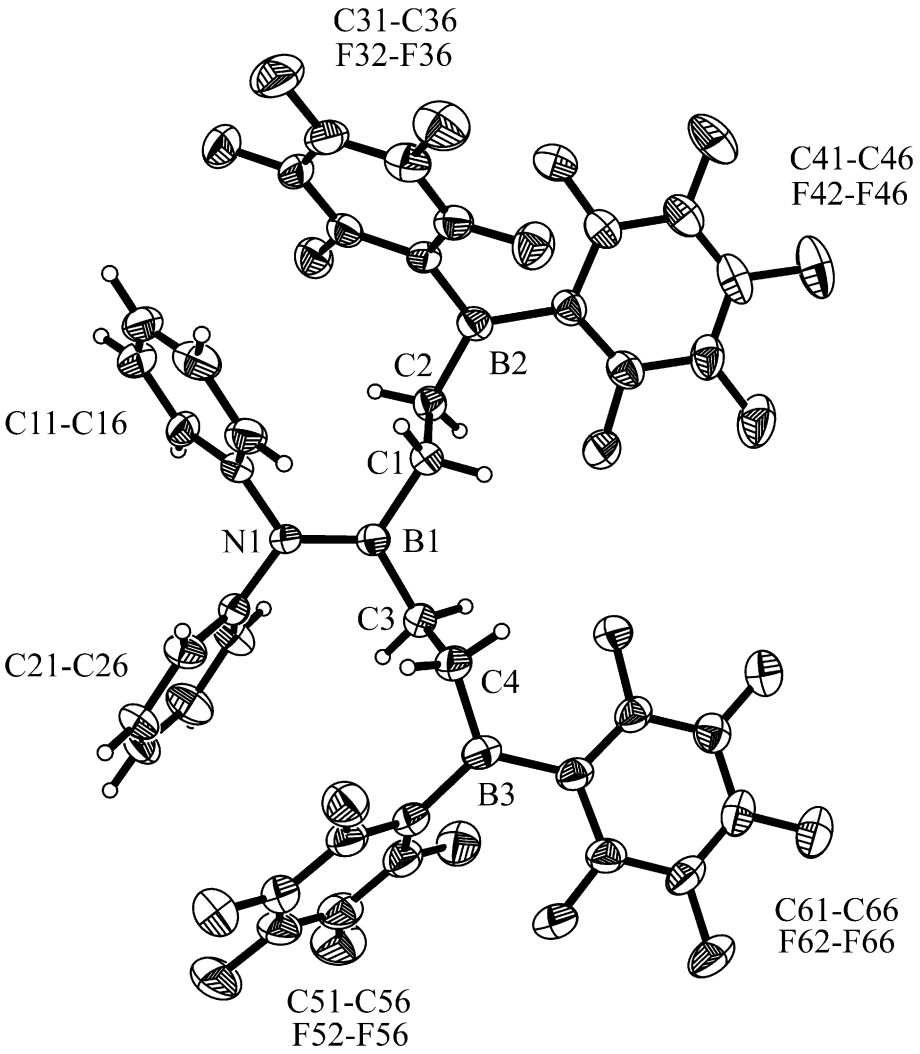


^{19}F NMR (470 MHz) and $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 298 K) spectra of compound **8** and **8'**.

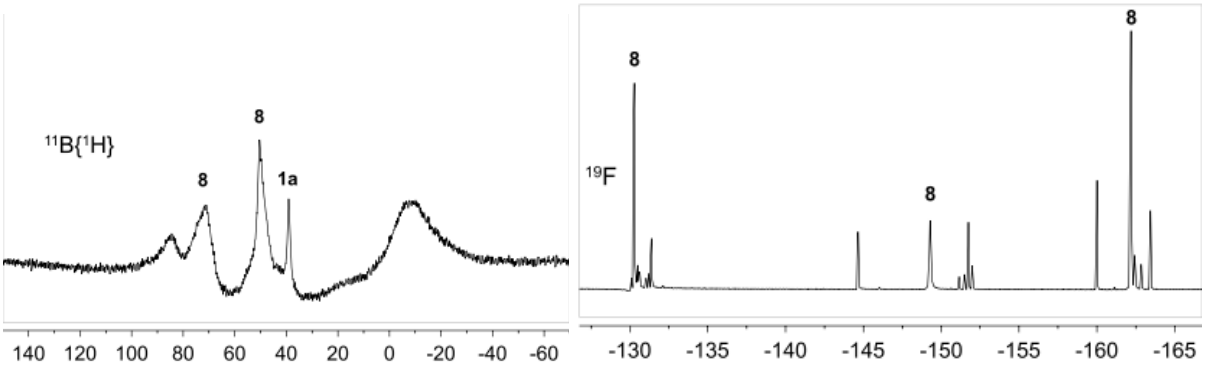


$^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 298 K) spectrum of compound **8** and **8'**.

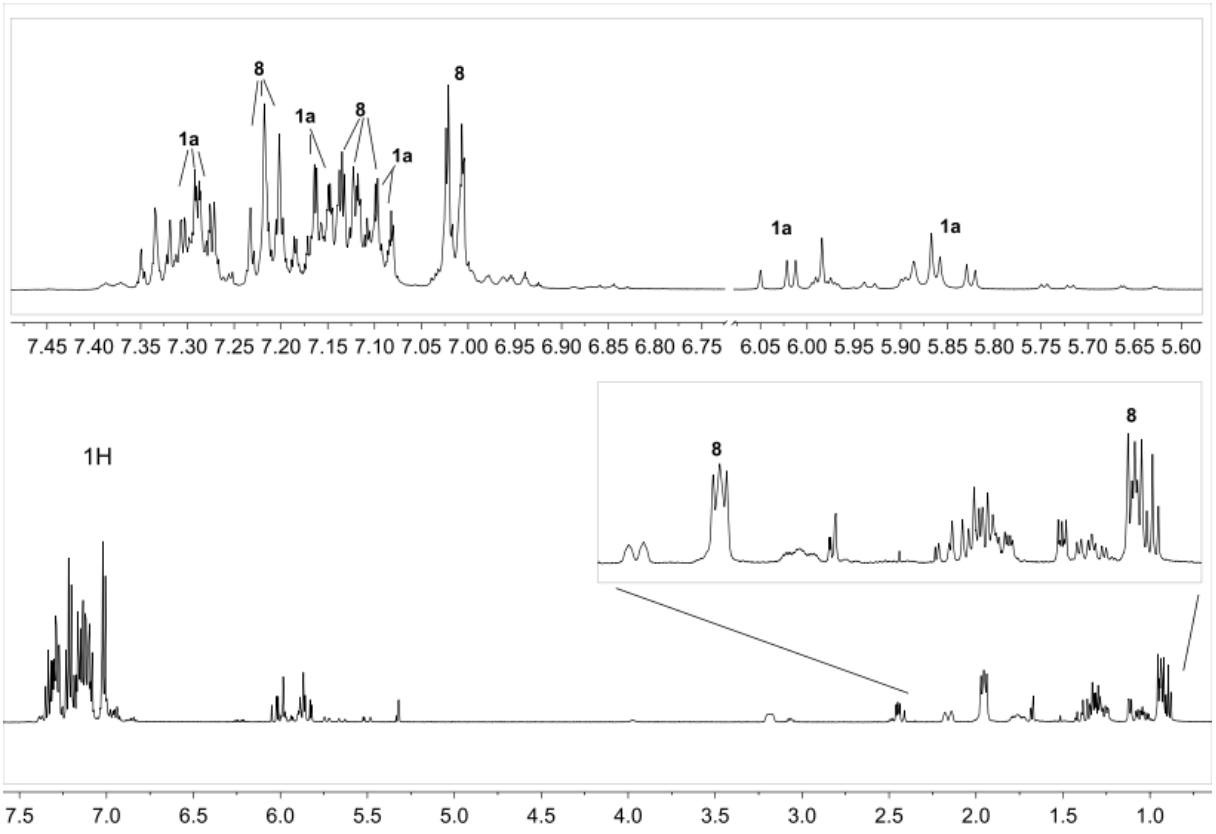
X-ray crystal structure analysis of compound 8: formula $C_{40}H_{18}B_3F_{20}N$, M = 924.98, colourless crystal, 0.16 x 0.08 x 0.03 mm, a = 19.6734(4), b = 6.2270(2), c = 31.1173(8) Å, β = 94.093(2)°, V = 3802.3(2) Å^3, ρ_{calc} = 1.616 gcm^{-3}, μ = 0.162 mm^{-1}, empirical absorption correction (0.974 ≤ T ≤ 0.995), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 22625 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.59 Å^{-1}, 6453 independent (R_{int} = 0.059) and 3882 observed reflections [I>2σ(I)], 577 refined parameters, R = 0.075, wR^2 = 0.149, max. (min.) residual electron density 0.22 (-0.19) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.



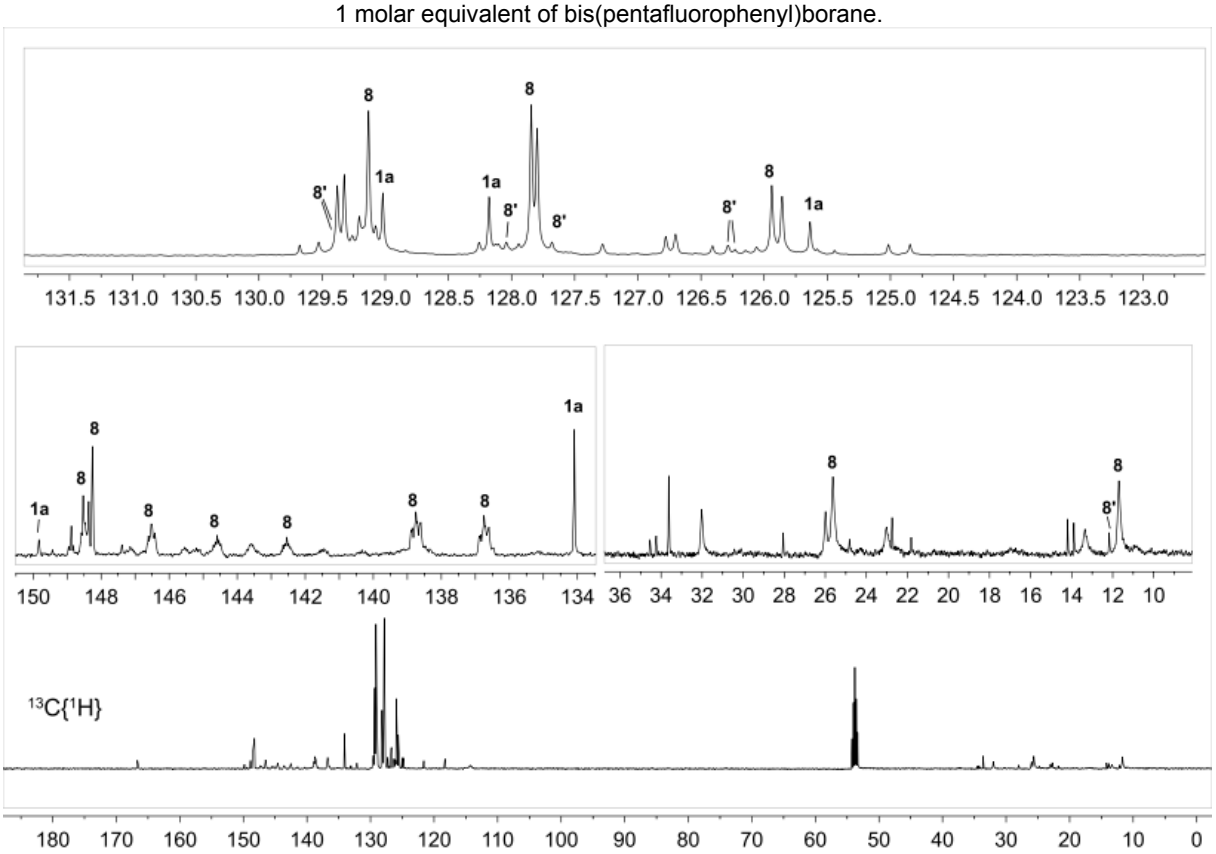
Comment: **1a** + 1 $HB(C_6F_5)_2$: compound **1a** (23.3 mg, 0.1 mmol) was added to a suspension of bis(pentafluorophenyl)borane (34.5 mg, 0.1 mmol, 1 eq.) in CD_2Cl_2 (1 mL) at room temperature and stirred for 10 min. Then the obtained reaction mixture was transferred to an NMR tube and characterized by NMR spectroscopy. The obtained reaction mixture contained compound **8**, **1a** and several not identified compounds.



$^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 298 K) and ^{19}F NMR (470 MHz, CD_2Cl_2, 298 K) spectra of the reaction mixture from (diphenylamino)divinylborane (**1a**) with 1 molar equivalent of bis(pentafluorophenyl)borane.

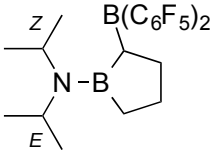


^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) spectrum of the reaction mixture from (diphenylamino)divinylborane (**1a**) with 1 molar equivalent of bis(pentafluorophenyl)borane.



$^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 298 K) spectrum of the reaction mixture from (diphenylamino)divinylborane (**1a**) with 1 molar equivalent of bis(pentafluorophenyl)borane.

Generation of compound 10.



a) Using (diisopropylamino)divinylborane (1b) and bispentafluorophenyl borane. Bis(pentafluorophenyl)borane (69 mg, 0.2 mmol) was stirred in dichloromethane (1 mL) and (diisopropylamino)divinylborane (33 mg, 0.2 mmol) was added. After stirring for 15 minutes at room temperature all volatiles were removed in vacuum and a colorless oil was obtained (94.8 mg, 93 %).

^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ = 3.36 (hept, $^{3}J_{HH}$ = 6.7 Hz, 1H, CH^{Z}), 3.28 (hept, $^{3}J_{HH}$= 7.0 Hz, 1H, CH^{E}), 2.70 (t, $^{3}J_{HH}$ = 6.8 Hz, 1H, BCH), 1.95, 1.74 (each m, each 1H, $CH_2{}^{CH}$), 1.52 (m, 2H, CH_2), 1.28, 1.11 (each m, each 1H, BCH_2), 1.24, 1.23 (each d, $^{3}J_{HH}$ = 7.0 Hz, 3H, $CH_3{}^{E}$), 0.95, 0.87 (each d $^{3}J_{HH}$ = 6.7 Hz, each 3H, $CH_3{}^{Z}$).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K): δ = 146.4 (dm, $^{1}J_{FC}$ ~ 248 Hz, C_6F_5), 142.7 (dm, $^{1}J_{FC}$ ~ 255 Hz, C_6F_5), 137.7 (dm, $^{1}J_{FC}$ ~ 252 Hz, C_6F_5), 116.3 (br, *i*-C_6F_5), 56.5 (CH^{Z}), 46.5 (br, BCH), 45.6 (CH^{E}), 31.9 ($CH_2{}^{CH}$), 27.9 (CH_2), 24.2, 24.1 ($CH_3{}^{E}$), 22.0, 21.5 ($CH_3{}^{Z}$), 21.2 (br, BCH_2).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, CD_2Cl_2, 298 K): δ ^{1}H / δ ^{13}C = 3.36 / 56.5 (CH^{Z}), 3.28 / 45.6 (CH^{E}), 2.70 / 46.5 (BCH), 1.95, 1.74 / 31.9 ($CH_2{}^{CH}$), 1.52 / 27.9 (CH_2), 1.28, 1.11 / 21.2 (BCH_2), 1.24 / 24.1 ($CH_3{}^{E}$), 1.23 / 24.2 ($CH_3{}^{E}$), 0.95 / 22.0 ($CH_3{}^{Z}$), 0.87 / 21.5 ($CH_3{}^{Z}$).

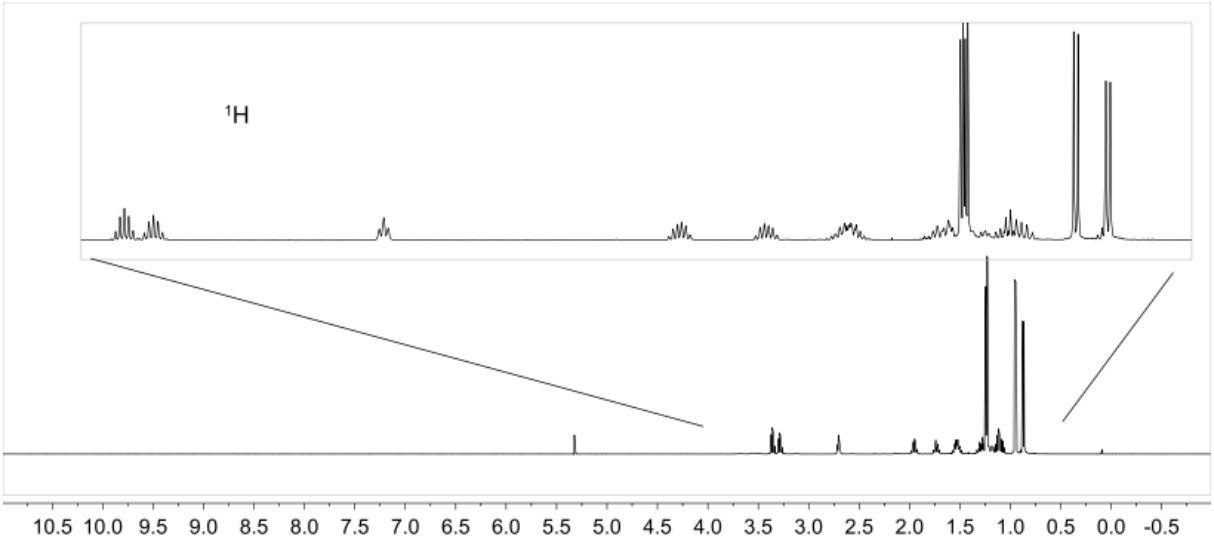
^{1}H,^{13}C GHMBC (600 MHz / 151 MHz,CD_2Cl_2, 298 K) [selected trace]: δ ^{1}H / δ ^{13}C = 2.70 / 116.3, 31.9, 27.9 (BCH / *i*-C_6F_5, $CH_2{}^{CH}$, CH_2).

^{1}H{^{1}H} 1D-TOCSY (600 MHz, CD_2Cl_2, 298 K) [selected experiments]: δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 3.36 / 0.95, 0.87 (CH^{Z} / $CH_3{}^{Z}$), 3.28 / 1.24, 1.23 (CH^{E} / $CH_3{}^{E}$), 2.70 / 1.95, 1.74, 1.52, 1.28, 1.11 (BCH / $CH_2{}^{CH}$, CH_2, BCH_2).

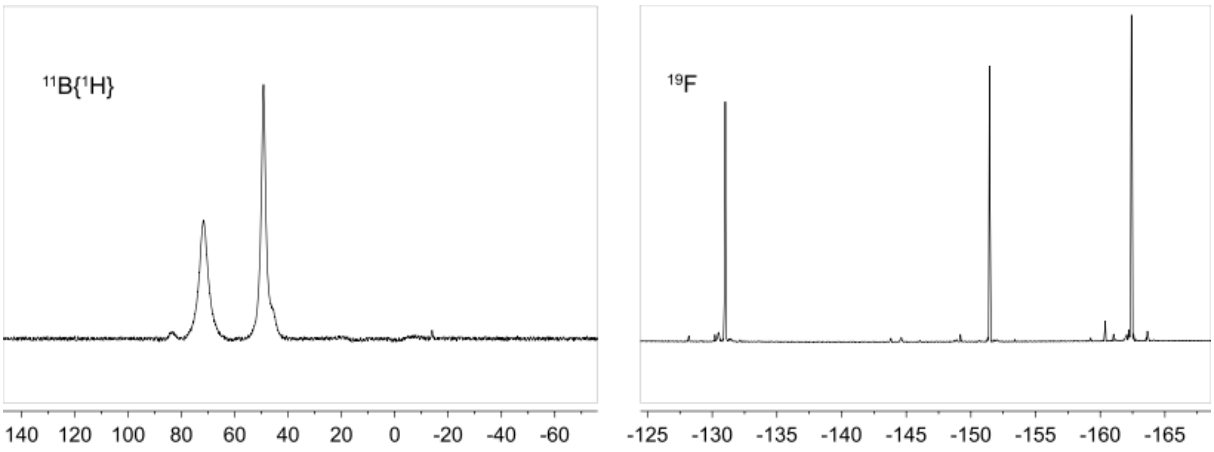
^{1}H{^{1}H} NOEDIF (600 MHz, CD_2Cl_2, 298 K) [selected experiment]: δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 2.70 / 3.36, 1.95, 1.24, 1.23, 0.95, 0.87. (BCH / CH^{Z}, $CH_2{}^{CH}$, $CH_3{}^{E}$, $CH_3{}^{Z}$).

^{19}F NMR (564 MHz, CD_2Cl_2, 298 K): δ = -131.0 (m, 2F, *o*-C_6F_5), -151.4 (tm, $^{3}J_{FF}$ = 20 Hz, 1F, *p*-C_6F_5), -162.4 (m, 2F, *m*-C_6F_5), [Δδ $^{19}F_{p\text{-}m}$ = 11.0].

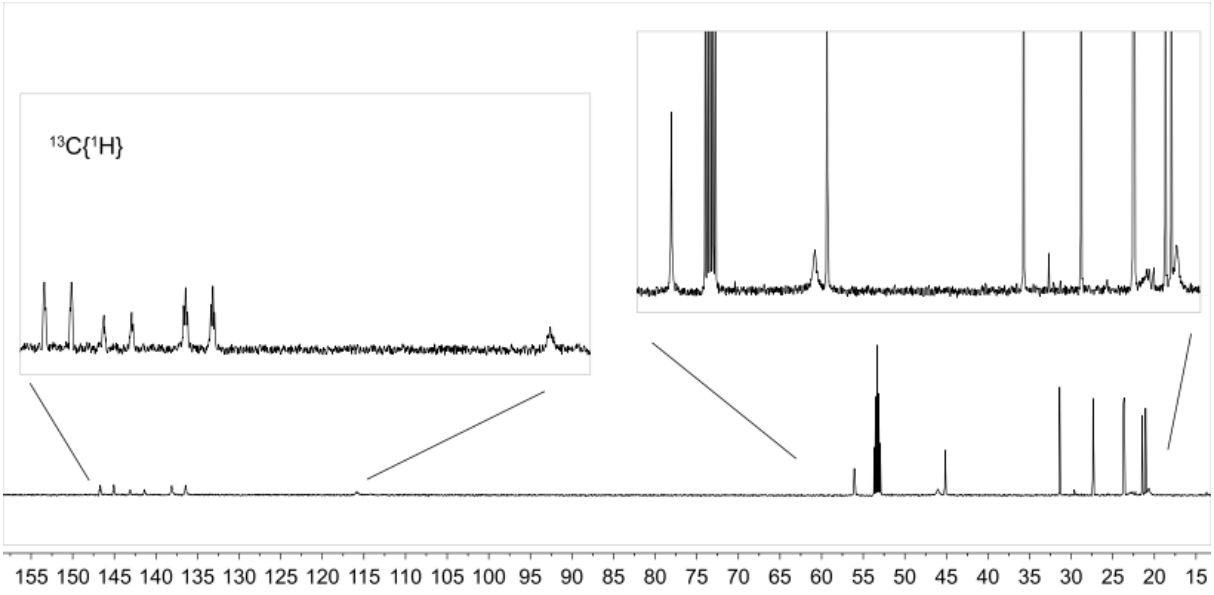
^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 298 K): δ = 71.7 ($\nu_{1/2}$ ~ 700 Hz, $B(C_6F_5)_2$), 49.2 ($\nu_{1/2}$ ~ 400 Hz, BN).



^{1}H NMR (600 MHz, CD_2Cl_2, 298 K) spectrum of compound **10** (method a).



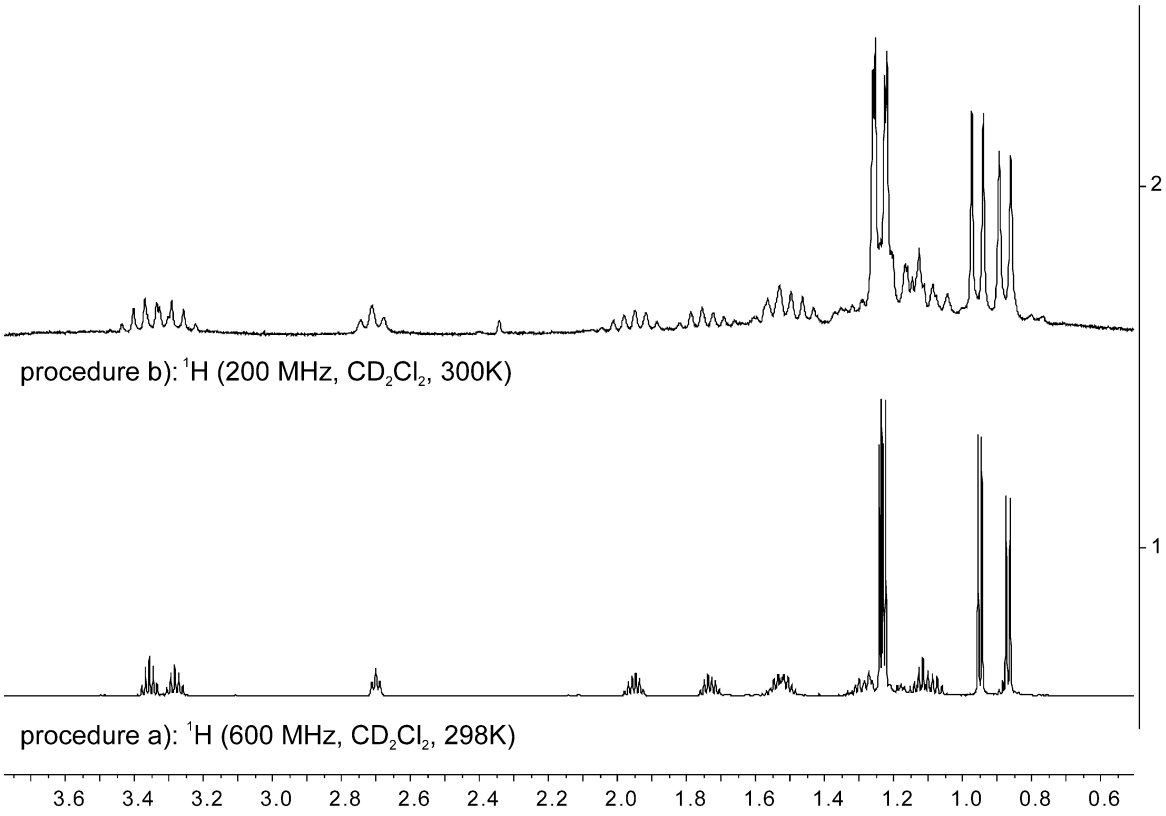
$^{11}B\{^1H\}$ NMR (192 MHz, CD_2Cl_2, 298 K) and ^{19}F NMR (564 MHz) spectra of compound **10** (method a).



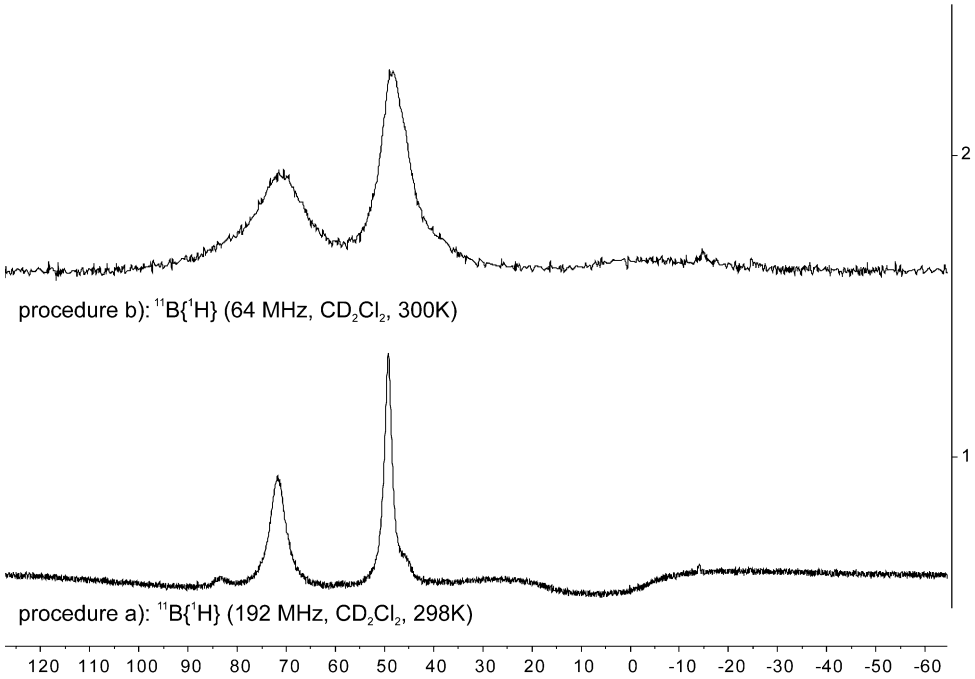
$^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, 298 K) spectrum of compound **10** (method a).

b) Using 1-(diisopropylamino)-2,3-dihydroborole and bis(pentafluorophenyl)borane.

1-(Diisopropylamino)-2,3-dihydroborole (**3b**) (33 mg, 0.2 mmol) was added to a solution of bis(pentafluorophenyl)borane (69 mg, 0.2 mmol) in dichloromethane (1 mL). After stirring for 15 minutes all volatiles were removed in vacuum and a colorless oil was obtained. (98.1 mg, 96 %).



^{1}H NMR spectra of compound **10** synthesized by procedure **a** (1) and by procedure **b** (2).

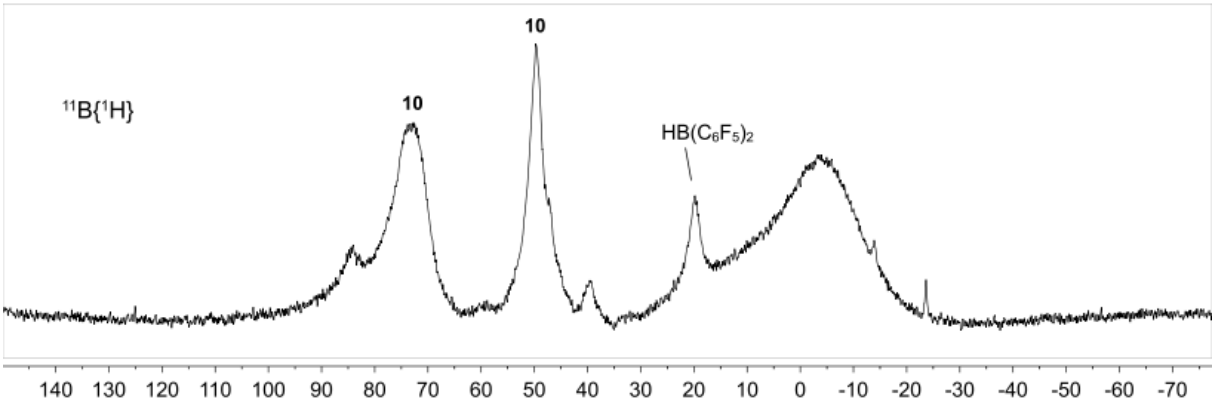


^{11}B{^{1}H} NMR spectra of compound **10** synthesized by procedure **a** (1) and by procedure **b** (2).

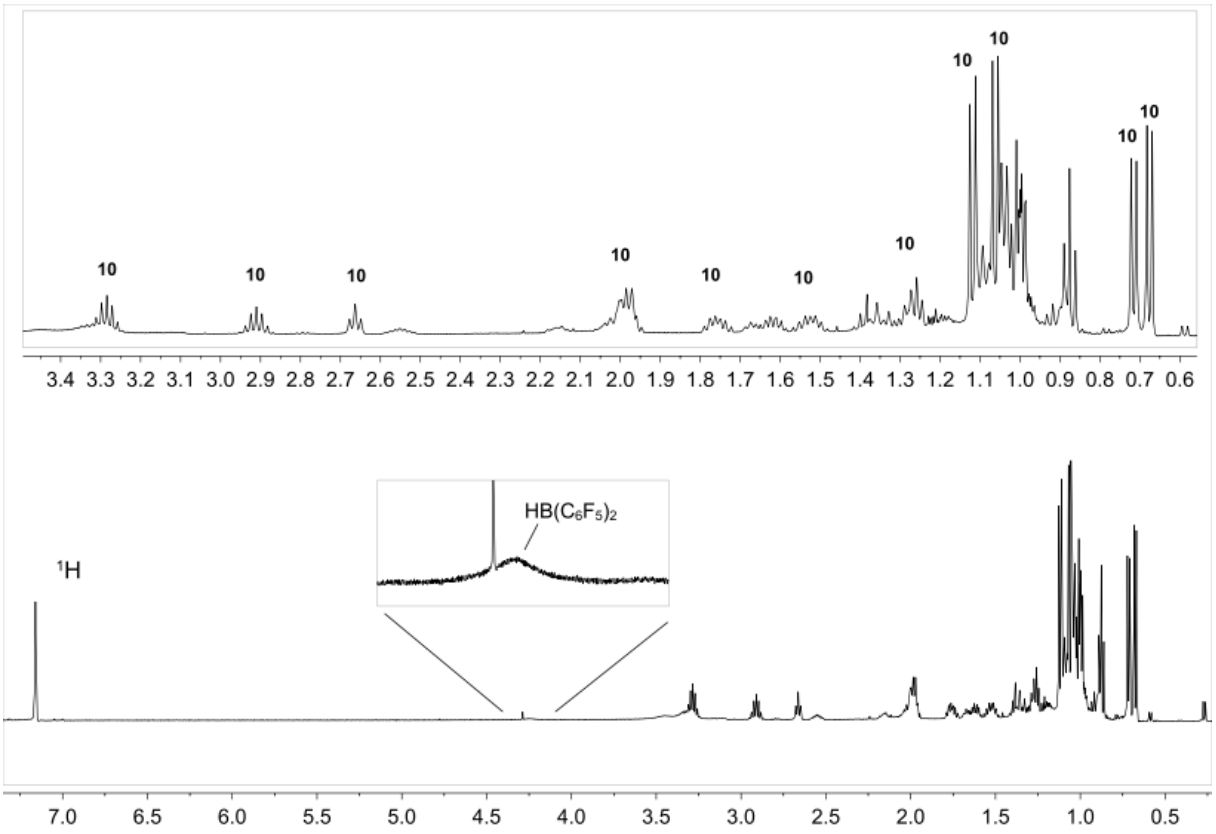
Comments:

a) Isolation and purification, respectively, of compound **10** by e.g. crystallization from dichloromethane at -70 °C or distillation, was not successful.

b) **1b** + 2 $HB(C_6F_5)_2$: (diisopropylamino)divinylborane (13.2 mg, 0.08 mmol) was added to a suspension of bis(pentafluorophenyl)borane (55.4 mg, 0.16 mmol, 2 eq.) in C_6D_6 (1 mL) at room temperature and stirred for 10 min. The obtained reaction mixture contained compound **10** as the main component, admixed with bis(pentafluorophenyl)borane and other not identified compounds.

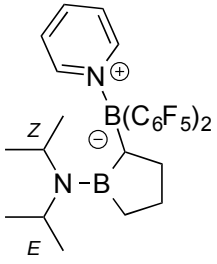


$^{11}B\{^1H\}$ NMR (160 MHz, C_6D_6, 298 K) spectrum of the reaction mixture.



^1H NMR (500 MHz, C_6D_6, 298 K) spectrum of the reaction mixture.

Preparation of compound 11.



Compound **10** was generated in situ by reaction of (diisopropylamino)divinylborane (**1b**) (33 mg, 0.2 mmol) and bis(pentafluorophenyl)borane (69 mg, 0.2 mmol) in dichloromethane (2 mL). After stirring the solution for 15 minutes pyridine (16 µL, 0.2 mmol) was added. The solution was stirred for 10 minutes and then concentrated in vacuum to less than 0.5 mL. Subsequently pentane (4 mL) was added and the mixture was stored at -32 °C for one day. The product precipitates as a white solid which was collected, washed with cold pentane (2 x 1 mL) and dried in vacuum to give compound **11** as a colorless solid (82 mg, 70%).

Crystals suitable for the X-ray single crystal structure analysis were obtained from a benzene/pentane solution of **11** at -32 °C.

^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ = 8.72 (br, 2H *o*-py), 8.08 (m, 1H, *p*-py), 7.59 (m, 2H, *m*-py), 3.78 (hept, $^{3}J_{HH}$ = 6.7 Hz, 1H, CH^{Z}), 3.23 (hept, $^{3}J_{HH}$ = 7.0 Hz, 1H, CH^{E}), 1.91 (br, 1H, BCH), 1.91, 1.44 (each br m, each 1H, CH_2^{CH}), 1.23, 0.25 (each m, each 1H, CH_2), 1.17, 1.15 (each d, $^{3}J_{HH}$ = 7.0 Hz, each 3H, CH_3^{E}), 1.02, 0.44 (each d, $^{3}J_{HH}$ = 6.7 Hz, each 3H, CH_3^{Z}), 0.87, 0.24 (each br m, each 1H, BCH_2).

^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K): δ = 147.2 (*o*-py), 141.8 (*p*-py), 125.4 (*m*-py), 52.6 (CH^{Z}), 45.0 (CH^{E}), 31.6 (CH_2^{CH}), 25.3 (CH_2), 24.4, 24.2 (CH_3^{E}), 23.1 (br, BCH), 22.5, 20.2 (CH_3^{Z}), 21.1 (br, BCH_2). [C_6F_5 not listed].

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, CD_2Cl_2, 298 K): δ ^{1}H / δ ^{13}C = 8.72 / 147.2 (*o*-py), 8.08 / 141.8 (*p*-py), 7.59 / 125,4 (*o*-py), 3.78 / 52.6 (CH^{Z}), 3.23 / 45.0 (CH^{E}), 1.91 / 23.1 (BCH), 1.91, 1.44 / 31.6 (CH_2^{CH}), 1.23, 0.25 / 25.3 (CH_2), 1.17 / 24.4 (CH_3^{E}), 1.15 / 24.2 (CH_3^{E}), 1.02 / 22.5 (CH_3^{Z}), 0.87, 0.24 / 21.1 (BCH_2), 0.44 / 20.2 (CH_3^{Z}).

^{1}H{^{1}H} 1D-TOCSY (500 MHz, CD_2Cl_2, 298 K) [selected experiments]: δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 8.72 / 8.08, 7.59 (*o-py / p-py, m*-py), 3.78 / 1.02, 0.44 (CH_3^{Z}), 3.23 / 1.17, 1.15 (CH_3^{E}), 0.87 / 1.91, 1.91, 1.44, 1.23, 0.25, 0.24 (BCH_2 / BCH, CH_2^{CH}, CH_2^{CH}, CH_2, CH_2, BCH_2).

^{19}F NMR (470 MHz, CD_2Cl_2, 298 K): δ = -129.1, -130.0 (each br, each 2F, *o*-C_6F_5), -159.4, -160.4 (each br, each 1F, *p*-C_6F_5), -164.5, -165.4 (each br, each 2F, *m*-C_6F_5), [$\Delta\delta\ ^{19}F_{p\text{-}m}$ = 5.1, 5.0].

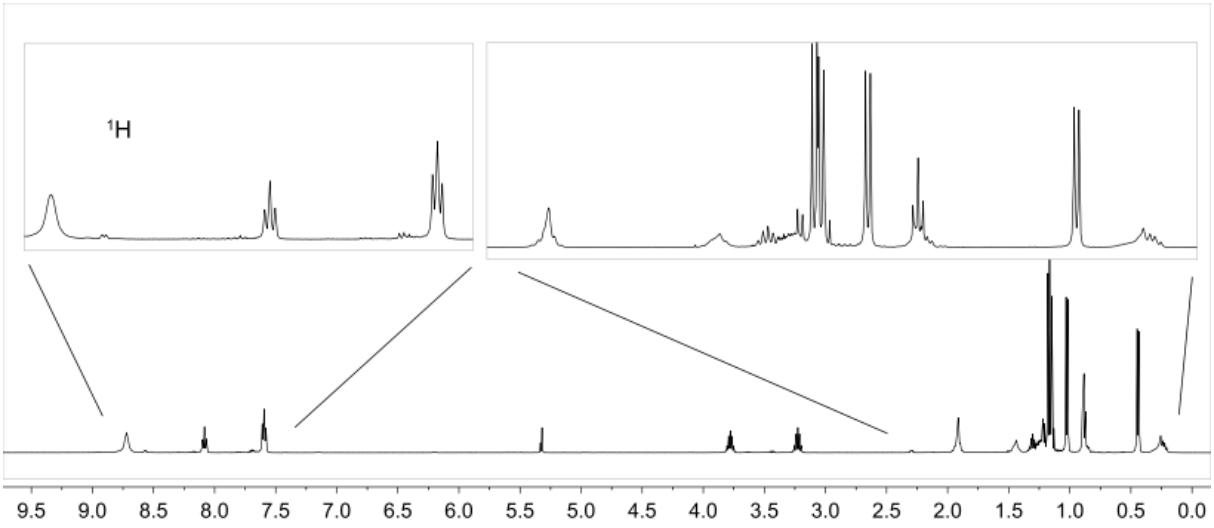
^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 298 K): δ = 52.0 ($\nu_{1/2}$ ~ 550 Hz, BN), 1.9 ($\nu_{1/2}$ ~ 250 Hz, py-B).

IR (KBr): Wavenumber / cm^{-1} = 3675 (w, br), 3286 (w), 3132 (w), 2921 (s, br), 2439 (m), 2214 (w), 1936 (w), 1851 (w), 1647 (m), 1440 (m, br), 1283 (w), 1086 (m, br), 954 (s), 920 (s), 767 (s), 741 (s), 691 (s), 483 (m).

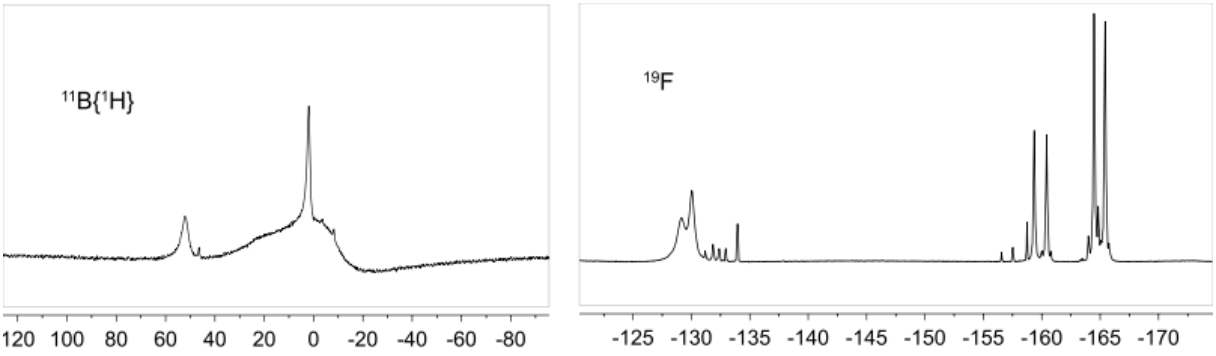
Melting point (DSC): 120 °C.

Decomposition (DSC): ~240 °C.

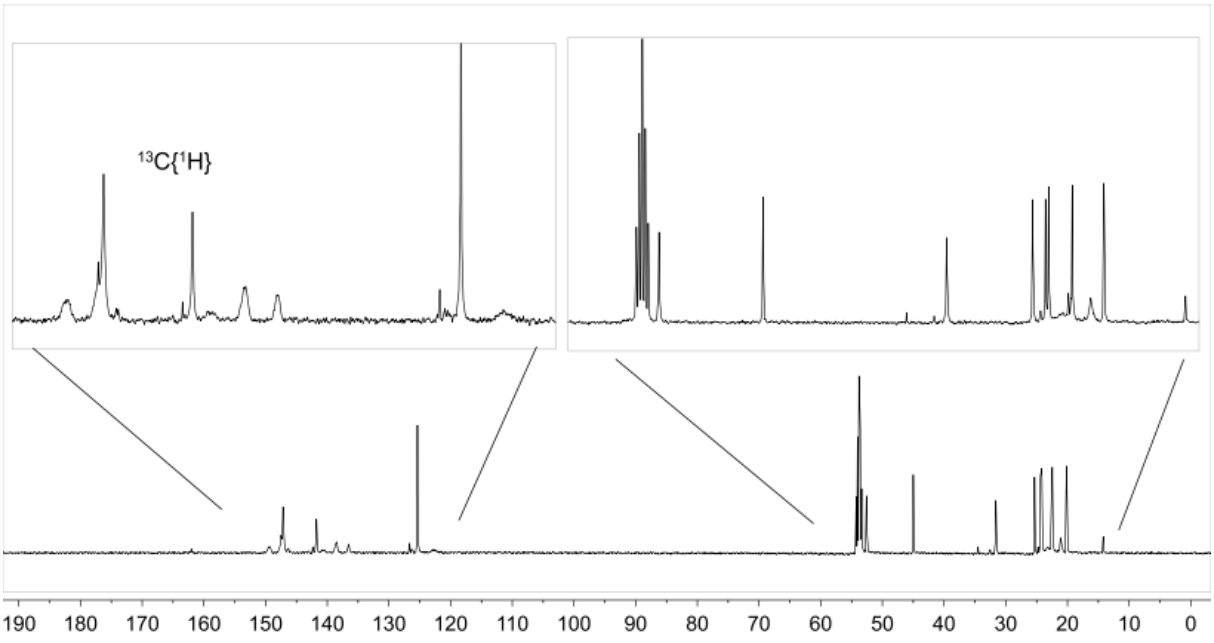
Elemental Analysis: Calcd. for $C_{27}H_{26}B_2F_{10}N_2$: C, 54.95; H, 4.44; N, 4.75. Found: C, 54.20; H, 4.21; N, 4.49.



^{1}H, ^{11}B{^{1}H}, ^{19}F and ^{13}C{^{1}H} NMR spectrum of compound **11**.

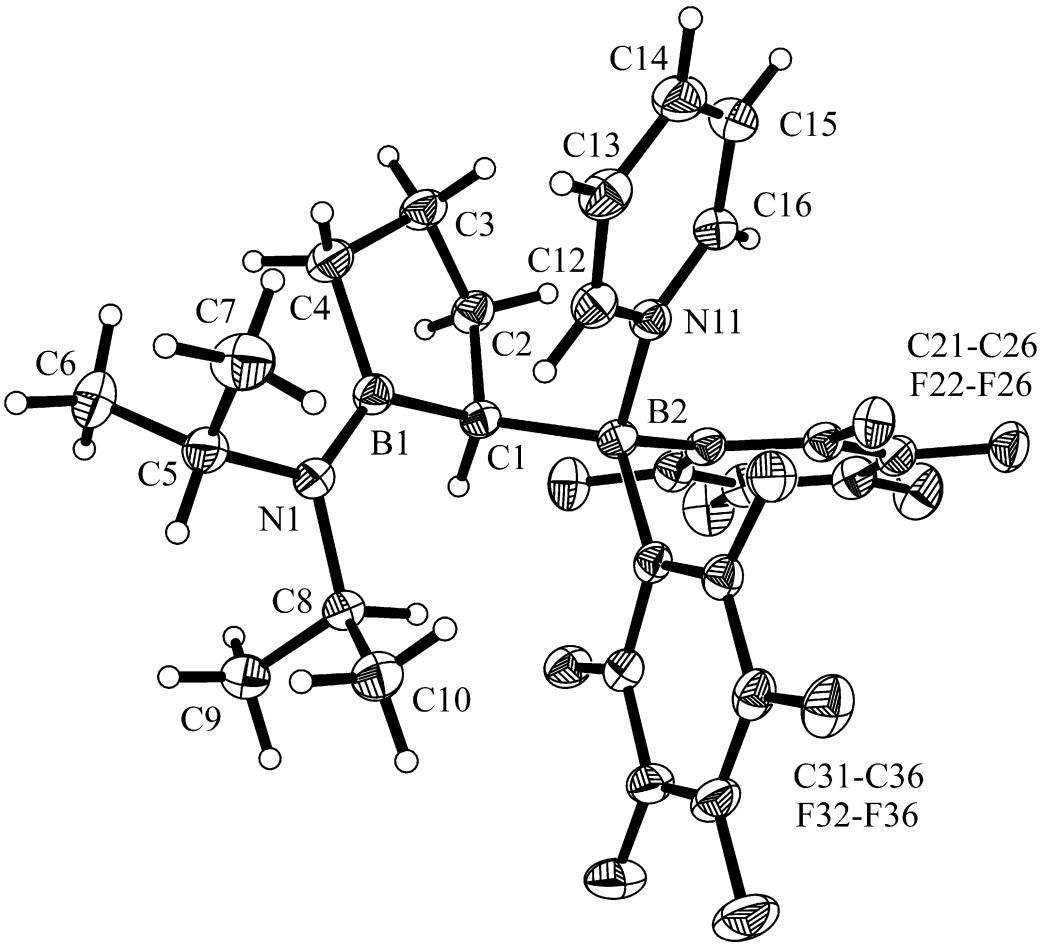


^{1}H, ^{11}B{^{1}H}, ^{19}F and ^{13}C{^{1}H} NMR spectrum of compound **11**.



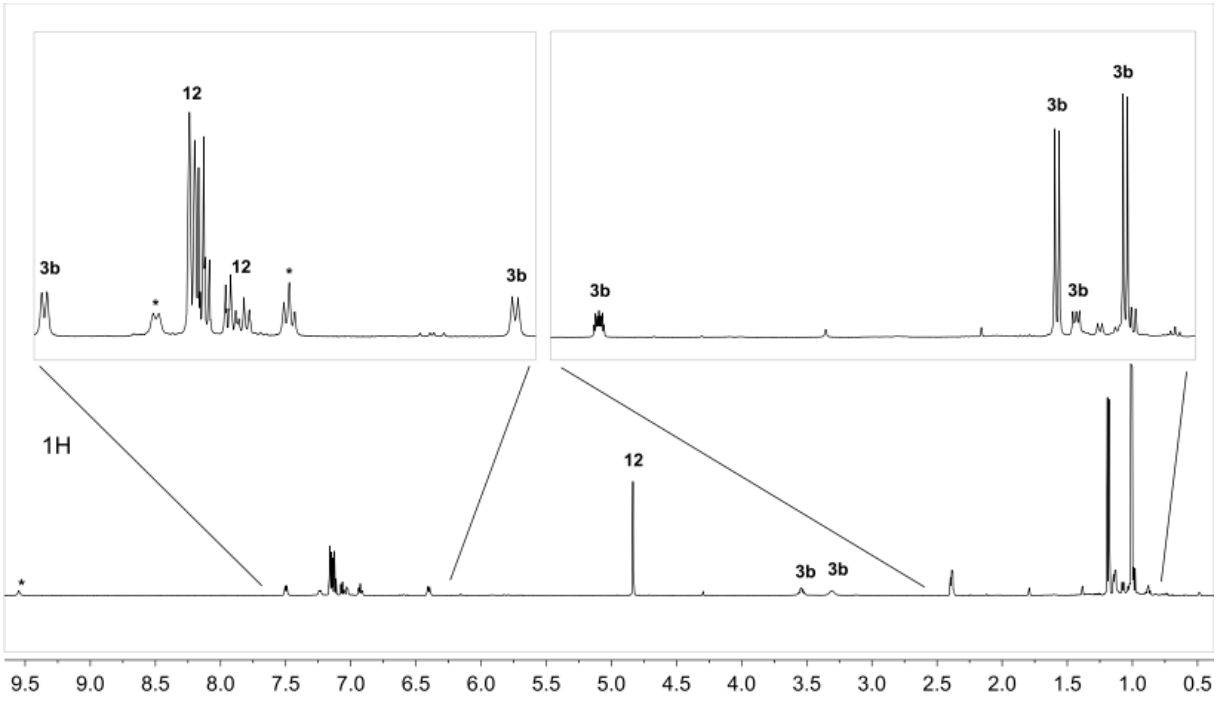
^{1}H, ^{11}B{^{1}H}, ^{19}F and ^{13}C{^{1}H} NMR spectrum of compound **11**.

X-ray crystal structure analysis of compound 11: formula $C_{27}H_{26}B_2F_{10}N_2 \cdot 1.5 \times C_6H_6$, M = 707.28, colourless crystal, 0.27 x 0.15 x 0.10 mm, a = 10.0640(4), b = 12.5390(5), c = 14.4570(6) Å, α = 95.573(2), β = 101.176(2), γ = 104.130(2)°, V = 1715.5(1) Å^3, ρ_{calc} = 1.369 gcm^{-3}, μ = 1.011 mm^{-1}, empirical absorption correction (0.772 ≤ T ≤ 0.905), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 18481 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 5829 independent (R_{int} = 0.034) and 5364 observed reflections [I>2σ(I)], 455 refined parameters, R = 0.039, wR^2 = 0.103, max. (min.) residual electron density 0.23 (-0.19) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

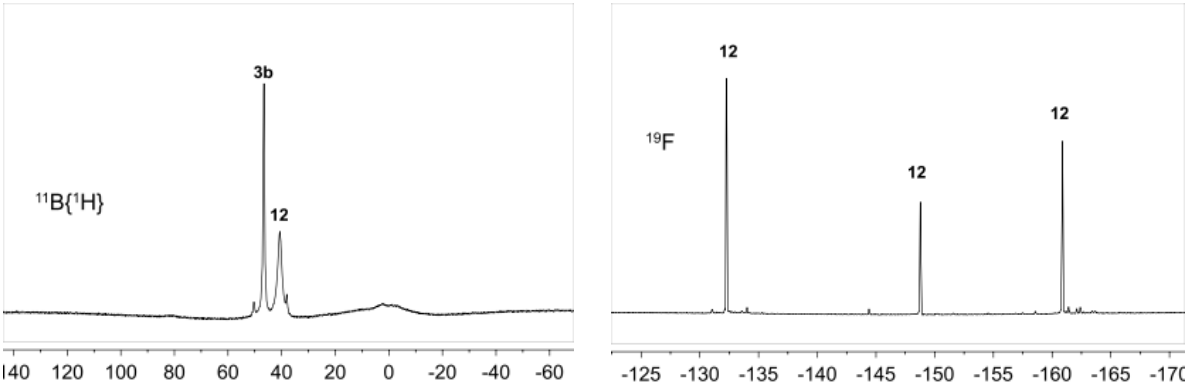


Reaction of compound 10 with benzaldehyde: generation of compound 12 and 3b

Compound **10** was generated in situ from (diisopropylamino)divinylborane (16.5 mg, 0.1 mmol) and bis(pentafluorophenyl)borane (34.5 mg, 0.1 mmol) in [D_6]-benzene (1 mL). The solution was stirred for 15 minutes and then benzaldehyde (10.1 μL, 0.1 mmol) was added. After some seconds a suspension containing a mixture of compound **3b** and **12** was obtained.

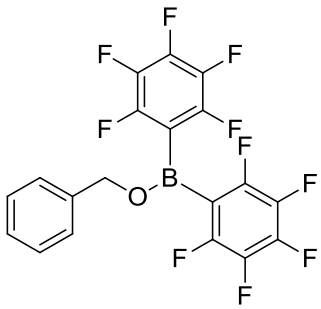


^{1}H NMR (500 MHz, C_6D_6, 298 K) spectrum of the reaction mixture of compound **10** and benzaldehyde (*).



^{11}B{^{1}H} (160 MHz, C_6D_6, 298 K) and ^{19}F NMR (470 MHz, C_6D_6, 298 K) spectra of the reaction mixture of compound **10** and benzaldehyde (*).

Control experiment: **Preparation of compound 12.**



A solution of benzaldehyde (40.4 μL, 0.4 mmol) in dichloromethane (1 mL) was added to a suspension of bis(pentafluorophenyl)borane (138 mg, 0.4 mmol) in dichloromethane (2 mL) and then stirred for 20 minutes. The obtained suspension was filtered and the collected solid material was washed with cold dichloromethane (2 x 1 mL). Then the solid was dried in vacuum and the product was obtained as a white powder (146 mg, 81%). Crystals suitable for the X-ray single crystal structure analysis were obtained by slow evaporation of a concentrated solution of 12 in dichloromethane at room temperature.

^{1}H NMR (500 MHz, C_6D_6, 298 K): δ = 7.14 (m, 2H, *o*-Ph), 7.11 (m, 2H, *m*-Ph), 7.05 (m, 1H, *p*-Ph), 4.81 (s, 2H, CH_2).

$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 298 K): δ = 147.7 (dm, $^1J_{FC}$ ~ 246 Hz, C_6F_5), 143.2 (dm, $^1J_{FC}$ ~ 257 Hz, C_6F_5), 137.6 (dm, $^1J_{FC}$ ~ 253 Hz, C_6F_5),136.8 (*i*-Ph), 128.9 (*m*-Ph), 128.7 (*p*-Ph), 127.0 (*o*-Ph), 109.0 (br m, *i*-C_6F_5), 72.2 (CH_2).

$^1H,^{13}C$ GHSQC (500 MHz / 126 MHz, C_6D_6, 298 K): δ ^1H / δ ^{13}C = 7.14 / 127.0 (*o*-Ph), 7.11 / 128.9 (*m*-Ph), 7.05 / 128.7 (*p*-Ph), 4.82 / 72.2 (CH_2).

$^1H,^{13}C$ GHMBC (500 MHz / 126 MHz, C_6D_6, 298 K) [selected trace]: δ ^1H / δ ^{13}C = 4.81 / 136.8, 127.0 (CH_2 / *i*-Ph, *o*-Ph).

^{19}F NMR (470 MHz, C_6D_6, 298 K): δ = –132.2 (br m, 2F, *o*-C_6F_5), –148.7 (br m, 1F, *p*-C_6F_5), –160.8 (br m, 2F, *m*-C_6F_5), [$\Delta\delta\ ^{19}F_{p\text{-}m}$ = 12.1].

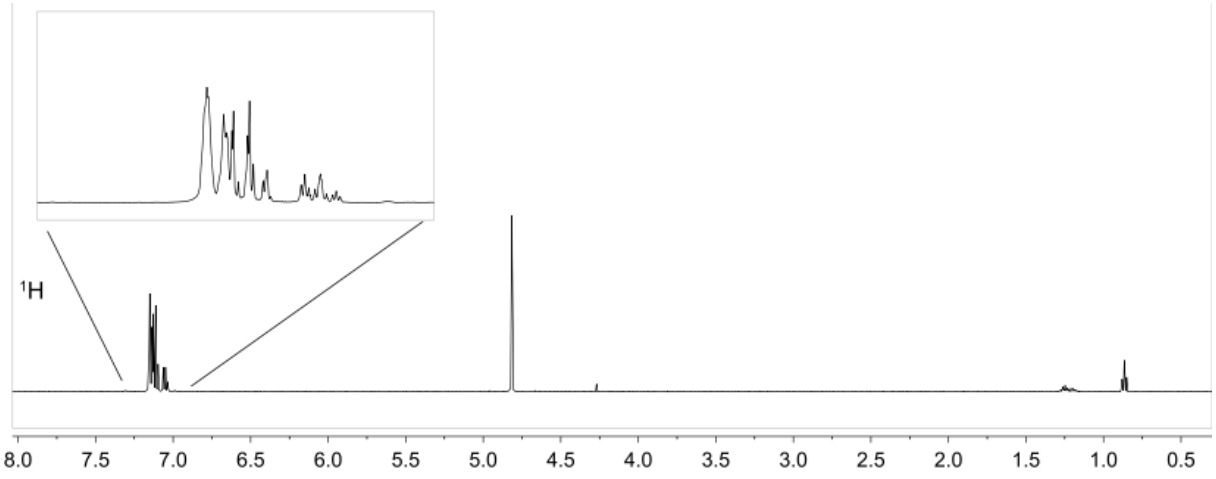
$^{11}B\{^1H\}$ NMR (160 MHz, C_6D_6, 298 K): δ = 40.7 ($\nu_{1/2}$ ~ 350 Hz).

IR (KBr): Wavenumber / cm^{-1} = 3064 (m), 2369 (w), 1878 (w), 1831 (w), 1655 (s), 1527 (m), 1260 (m), 1170 (s), 964 (s), 848 (s), 787 (s), 732 (s), 697 (s), 644 (s), 579 (m) 547 (s), 463 (s).

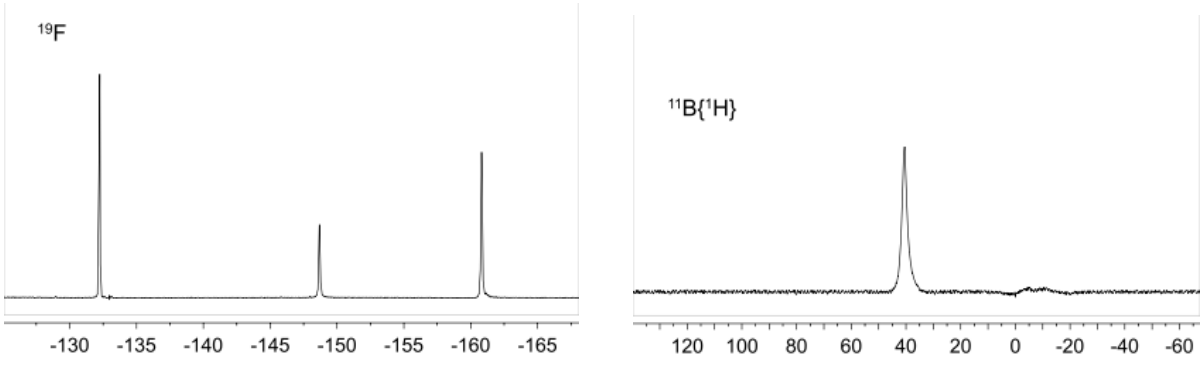
Melting point (DSC): 145 °C.

Decomposition (DSC): 200 °C.

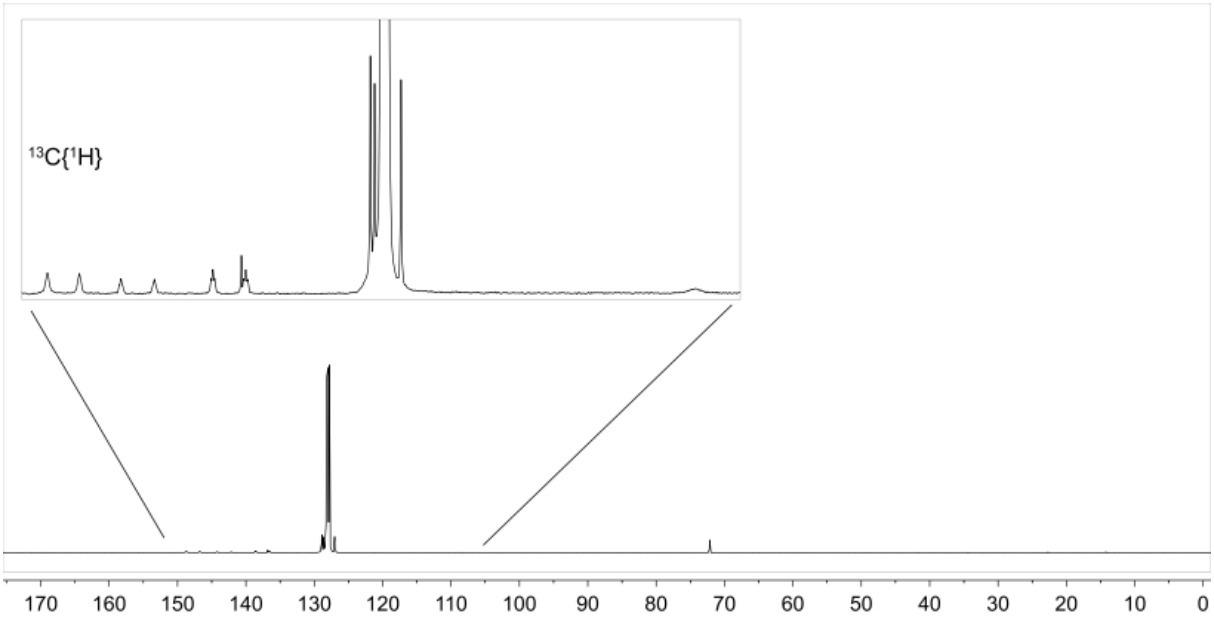
Elemental Analysis: Calcd. for $C_{19}H_7BF_{10}O$: C, 50.48; H, 1.56. Found: C, 50.44; H, 1.16.



^1H NMR (500 MHz, C_6D_6, 298 K) spectrum of compound **12**.

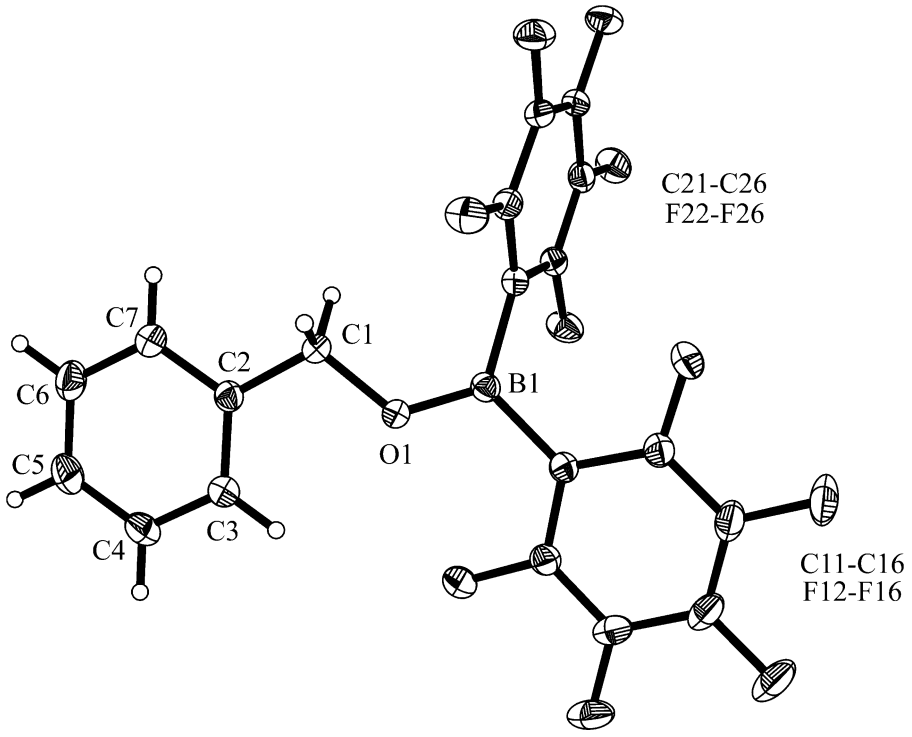


^{19}F NMR (470 MHz, C_6D_6, 298 K) and $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 298 K) spectra of compound **12**



$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 298 K) spectrum of compound **12**.

X-ray crystal structure analysis of compound 12: formula $C_{19}H_7BF_{10}O$, M = 452.06, colourless crystal, 0.32 x 0.24 x 0.10 mm, a = 7.5636(2), b = 11.1442(5), c = 11.3520(6) Å, α = 117.035(3), β = 93.834(3), γ = 95.053(2)°, V = 842.8(1) Å^3, ρ_{calc} = 1.781 gcm^{-3}, μ = 1.670 mm^{-1}, empirical absorption correction (0.617 ≤ T ≤ 0.850), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 9196 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 2852 independent (R_{int} = 0.036) and 2721 observed reflections [I>2σ(I)], 280 refined parameters, R = 0.037, wR^2 = 0.099, max. (min.) residual electron density 0.24 (-0.24) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.



Collection of calculated thermodynamical data and computational details

All calculations have been performed with the TURBOMOLE 6.3[1] and 6.5[2] suites of programs. The structures have been optimized with the *meta*-GGA functional TPSS[3] applying the new D3-dispersion correction with Becke-Johnson damping (denoted as (BJ)).[4,5] Subsequent single point calculations have been carried out with the more accurate double hybrid density functional B2PLYP-D3(BJ) level.[6,7] For both calculations the large Gaussian-AO basis set def2-TZVP[8] and the RI approximation[9,10] have been used. The final level of theory can therefore be abbreviated as B2PLYP-D3(BJ)/def2-TZVP//TPSS-D3(BJ)/def2-TZVP and has an estimated accuracy of about 1-2 kcal/mol.
The thermodynamic corrections are based on harmonic vibrational frequencies calculated at TPSS-D3/def2-TZVP level with strict convergence criteria and the numerical quadrature grid *m5*. Low-lying frequencies (effectively those below 100 cm^{-1}) are treated in a quasi-free-rotor approximation in order to avoid errors in the entropy calculation.[11] These (free) enthalpy values are denoted ΔH(G), ΔE marks electronic energies (i.e., not including ZPVE).
For a more detailed description of solvent effects and the accurate treatment of thermodynamic corrections in solvent - here (free) enthalpies of solvation - the COSMO-RS program[12–16] in the parametrization for dichloromethane has been used. All values are given in kcal/mol.

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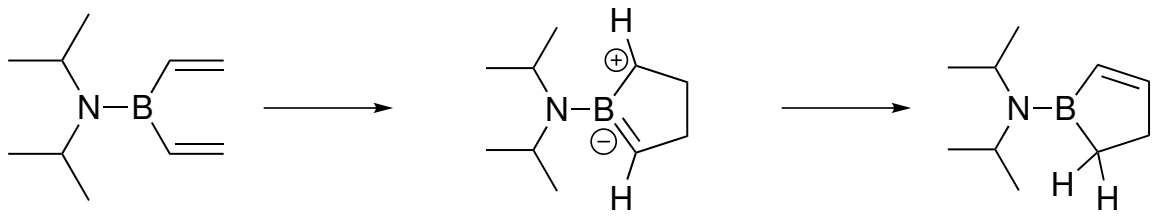

1b **2b** **3b**

Tab. 1: Electronic reaction energies.

	TPSS-D3	B2PLYP-D3
1b → **2b**	24.84	27.66
2b → **3b**	−45.86	−49.22
1b → **3b**	−21.02	−21.56

Tab. 2: Thermodynamic corrections and reaction (free) enthalpies for the reactions in the gas phase at 298.15K

	corrections		final B2PLYP-D3(BJ)	
	ΔH	ΔG	ΔH_{gas}	ΔG_{gas}
1b → **2b**	−0.92	−0.09	26.74	27.57
2b → **3b**	1.58	2.08	−47.64	−47.14
1b → **3b**	0.66	1.99	−20.90	−19.57

Tab. 3: Solvent corrections and reaction (free) enthalpies in the solvent dichloromethane at 298.15K.

	corrections		final B2PLYP-D3(BJ)	
	ΔH_{solv}	ΔG_{solv}	$\Delta H_{solution}$	$\Delta G_{solution}$
1b → **2b**	−0.70	−0.68	26.04	26.89
2b → **3b**	0.43	0.26	−47.21	−46.88
1b → **3b**	−0.26	−0.42	−21.16	−19.99