Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Consecutive intermolecular 1,1-carboboration reactions of Me_3Si-substituted alkynes with the halogeno-$B(C_6F_5)_2$ reagents

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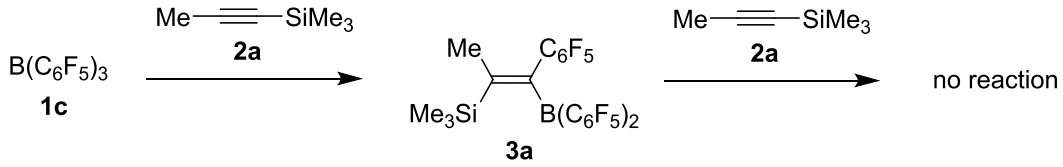
General Information:

All experiments were carried out under a dry argon atmosphere using standard Schlenk-type glassware and/or in a glove box. Solvents were dried and stored under an argon atmosphere. NMR spectra were recorded on a Varian UNITY plus 600 MHz spectrometer (^{1}H 600 MHz, ^{13}C 151 MHz, ^{11}B 192 MHz, ^{19}F 564 MHz, ^{29}Si 119 Hz) or Varian Inova 500 (^{1}H 500 MHz, ^{13}C 126 MHz, ^{11}B 160 MHz, ^{19}F 471 MHz, ^{29}Si 99 Hz). ^{1}H NMR and ^{13}C NMR chemical shifts δ are given relative to TMS and referenced to the solvent signal. ^{19}F NMR chemical shifts δ are given relative to $CFCl_3$ (external reference). ^{11}B NMR shifts δ are given relative to $BF_3{\cdot}Et_2O$ (external reference). ^{29}Si NMR shifts δ are given relative to TMS (external reference). NMR assignments were decided by additional 2D-NMR and ^{19}F decoupled experiments. HRMS was recorded on GTC Waters Micromass (Manchester, UK) and melting points were measures on TA-instruments DSC-20. Elemental analyses were performed on a Foss-Heraeus CHNO-Rapid. IR spectra were recorded on a Varian 3100 TF-IR (Excalibur Series).

Materials: Commercially available chemicals supplied by Sigma-Aldrich, TCI and ABCR were used as received unless stated otherwise. $B(C_6F_5)_3$ was obtained from Boulder Scientific Co. Deuterated solvents and pyridine were dried over CaH_2, distilled under reduced pressure and stored over molecular sieves in argon atmosphere. $ClB(C_6F_5)_2$, $BrB(C_6F_5)_2$ and trimethylsilylethynylcyclohexane were prepared according the previously described procedures. (J. Li, C.G. Daniliuc, G. Kehr and G. Erker, *Chem. Commun* 2018, **54**, 6344; A. Ueno, J. Li, C.G. Daniliuc, G. Kehr and G. Erker, *Chem. Eur*., 2018, **24**, 10044; S. Kim, J. Rojas-Martin and F.D. Toste, *Chem. Sci.*, 2016, **7**, 85).

X-Ray diffraction: Data sets for compounds **1a·pyr**, **3d·pyr**, **3g·pyr**, **4e**, **4e·pyr**, **6·pyr** and **9** were collected with a Bruker D8 Venture CMOS diffractometer. For compounds **3a**, **3c·pyr** and **4f** data sets were collected with a Bruker APEX II CCD diffractometer. Programs used: data collection: APEX3 V2016.1-0 (Bruker AXS Inc., **2016**); cell refinement: SAINT V8.37A (Bruker AXS Inc., **2015**); data reduction: SAINT V8.37A (Bruker AXS Inc., **2015**); absorption correction, SADABS V2014/7 (Bruker AXS Inc., **2014**); structure solution SHELXT-2015 (Sheldrick, **2015**); structure refinement SHELXL-2015 (Sheldrick, **2015**). For compounds **1d**, **3c·pyr**, **4g·pyr** and **5·pyr** data sets were collected with a Nonius Kappa CCD diffractometer. Programs used: data collection, COLLECT (R. W. W. Hooft, Bruker AXS, **2008**, Delft, The Netherlands); 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-2015 (Sheldrick, **2015**) and graphics, XP (Bruker AXS Inc., **2000**). *R*-values are given for observed reflections, and wR^2 values are given for all reflections. *Exceptions and special features*: For compound **3g·pyr** one phenyl group and one $SiMe_3$ group, for compound **4g·pyr** one phenyl group and for compounds **5·pyr** and **6·pyr** one $SiMe_3$ group were found disordered over two positions in the asymmetric unit. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. For compounds **3a** and **3c·pyr** a half pentane molecule, for compound **3d·pyr** two dichloromethane molecules and for compound **4g·pyr** a mixture of pentane and dichloromethane molecules were found badly disordered in the asymmetrical unit. For compound **3g·pyr** one dichloromethane molecule disordered over three positions was found in the asymmetrical unit and could not be satisfactorily refined. The program SQUEEZE (Spek, A.L. (**2015**). Acta Cryst. C71, 9-18) was therefore used to remove mathematically the effect of the solvent. The quoted formula and derived parameters are not included the squeezed solvent molecules.

Generation of compound 3a

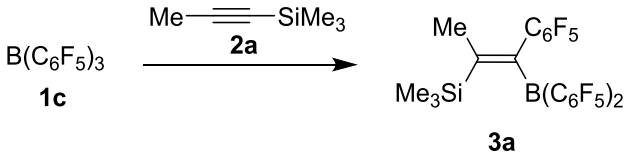


Scheme S1

A solution of MeC≡CSiMe$_3$ (11.2 mg, 0.1 mmol) in CD_2Cl_2 (0.2 ml) was added at r.t. to a suspension of $B(C_6F_5)_3$ (51.2 mg, 0.1 mmol) in CD_2Cl_2 (0.3 ml). The mixture was shaken vigorously, transferred to a Young NMR tube and ca. 10 minutes later characterized by NMR experiments. These showed nearly complete conversion to compound **3a** alongside with a small amount of unidentified compounds.

Addition of a second equivalent of MeC≡CSiMe$_3$ (11.2 mg, 0.1 mmol) in CD_2Cl_2 (0.2 mmol) to the obtained reaction mixture at r.t. did not result in any significant new product formation.

Preparation of compound 3a



Scheme S2

$B(C_6F_5)_3$ (102.4 mg, 0.2 mmol) was suspended in CH_2Cl_2 (2 ml) and a solution of MeC≡CSiMe$_3$ (22.4 mg, 0.2 mmol) in CH_2Cl_2 (2 ml) was added. The homogenous pale yellow solution was stirred for one hour at room temperature, then all volatilities were removed in vacuo. The pale yellow sticky residue was dissolved in pentane (1 ml), filtered and placed in the freezer at -35°C. Colorless crystals were formed during three days. The product was isolated by decantation and dried in vacuo. 73.3 mg of product **3a** was obtained (0.12 mmol, 64% yield) as colorless crystals. The material contained ca. 10% of an unknown impurity (potentially the Z-isomer) as judged by the NMR spectra.

Elementary analysis for $C_{24}H_{12}BF_{15}Si$ (624.2): calculated C 46.17, H 1.94; found C 46.00, H 1.99.

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 2.01 (t, J_{FH} = 2.4 Hz, 3H, Me), 0.03 (s, $^2J_{SiH}$ = 6.7 Hz, 9H, SiMe$_3$)

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = 174.0 (Si*C*=), 148.9 (dm, $^1J_{FC}$ ≈ 251 Hz, 4C, *o*-$C_6F_5^B$), 144.7 (dm, $^1J_{FC}$ ≈ 258 Hz, 2C, *p*-$C_6F_5^B$), 143.9 (dm, $^1J_{FC}$ ≈ 240 Hz, 2C, *o*-$C_6F_5^C$), 140.8 (dm, $^1J_{FC}$ ≈ 251 Hz 1C, *p*-$C_6F_5^C$), 140.0 (br, *C*-C_6F_5), 137.9 (dm, $^1J_{FC}$ ≈ 255 Hz, 2C, *m*-$C_6F_5^C$), 137.8 (dm, $^1J_{FC}$ ≈ 255 Hz, 4C, *m*-$C_6F_5^B$), 117.0 (tm, $^2J_{FC}$ ≈ 21 Hz 1C, *i*-$C_6F_5^C$), 114.4 (br, 2C, *i*-$C_6F_5^B$), 24.5 (t, J_{FC} = 2.5 Hz, Me), 0.3 ($^1J_{SiC}$ = 52.7 Hz, SiMe$_3$).

$^{13}C\{^{19}F,^{1}H\}$ NMR (151 MHz, CD_2Cl_2, 299 K):[selected resonances] δ = 148.9 (4C, *o*-$C_6F_5^B$), 144.7 (2C, *p*-$C_6F_5^B$), 143.9 (2C, *o*-$C_6F_5^C$), 140.8 (1C, *p*-$C_6F_5^C$), 137.9 (2C, *m*-$C_6F_5^C$), 137.8 (4C, *m*-$C_6F_5^B$), 117.0 (1C, *i*-$C_6F_5^C$), 114.4 (br, 2C, *i*-$C_6F_5^B$).

$^{11}B\{^{1}H\}$ NMR (192 MHz, CD_2Cl_2, 299 K): δ = 60.9 ($\nu_{1/2} \approx 860$ Hz).

^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = [-127.1 (m, 4F, *o*), -145.6 (tt, J_{FF} = 20 Hz, 6 Hz, 2F, *p*), -161.3 (m, 4F, *m*)] (B-C_6F_5, [$\Delta\delta^{19}F_{m,p}$ = 15.7]), [-137.9 (m, 2F, *o*), -155.6 (t, J_{FF} = 21 Hz, 1F, *p*), -162.5 (m, 2F, *m*)] (C-C_6F_5, [$\Delta\delta^{19}F_{m,p}$ = 6.9]).

$^{29}Si\{^{1}H\}$ DEPT (119 Hz, CD_2Cl_2, 299 K): δ = -2.5 ($\nu_{1/2} \approx 1$ Hz).

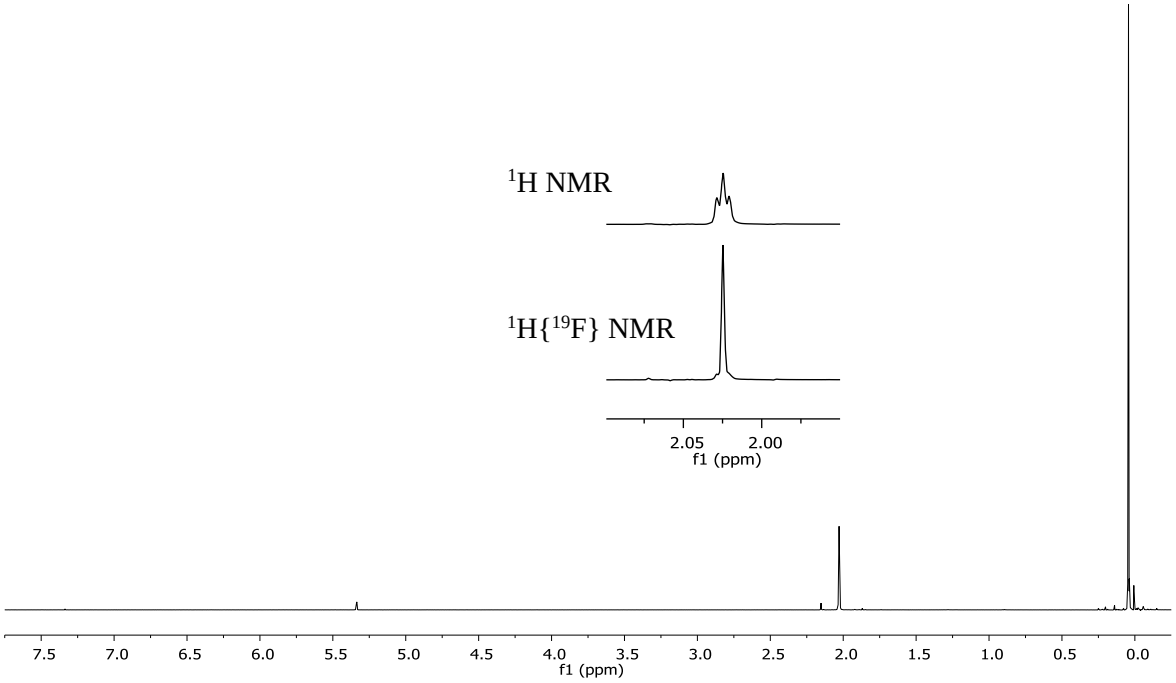


Figure S1: **^{1}H NMR** (600 MHz, CD_2Cl_2, 299K) and excerpt from **$^{1}H\{^{19}F\}$ NMR** (600 MHz, CD_2Cl_2, 299K) spectrum of compound **3a.**

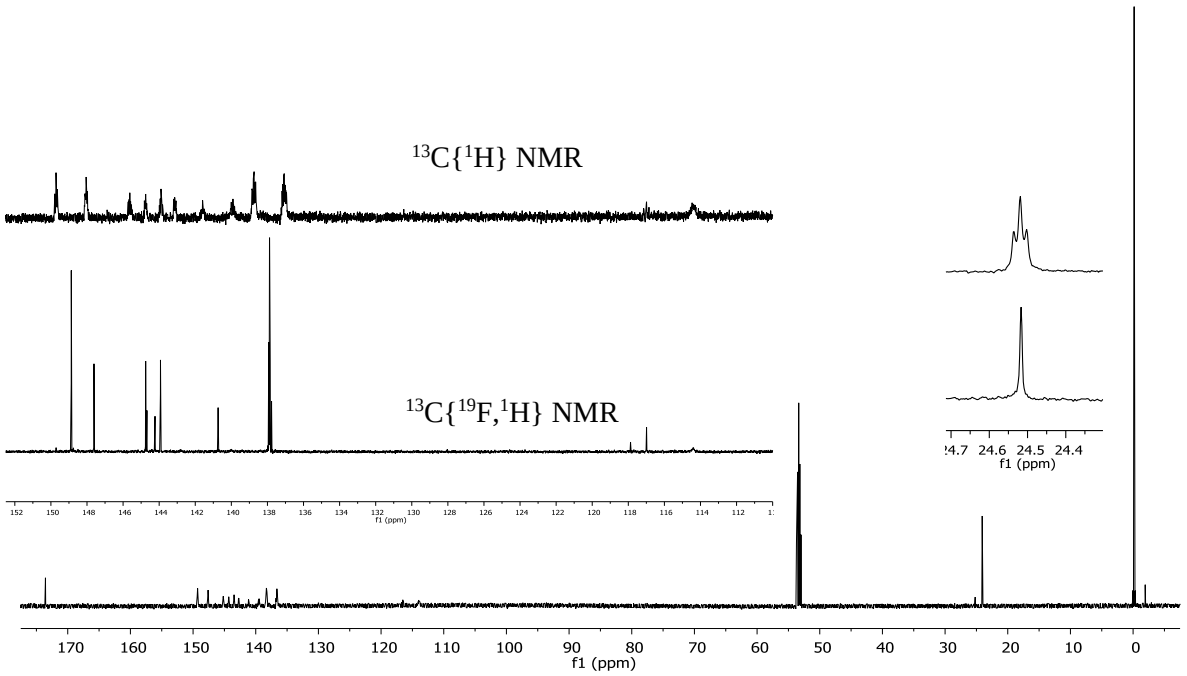


Figure S2: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, CD_2Cl_2, 299K) spectrum and detailed overview of aromatic singals with excerpt from **$^{13}C\{^{19}F,^{1}H\}$ NMR** (151 MHz, CD_2Cl_2, 299K) spectrum of compound **3a**.

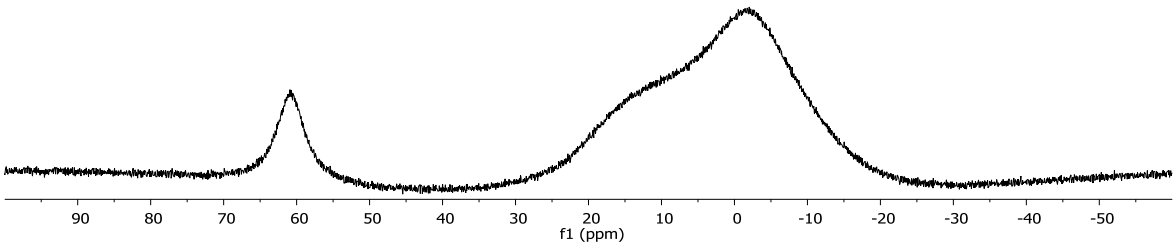


Figure S3: **$^{11}B\{^{1}H\}$ NMR** (192 MHz, CD_2Cl_2, 299K) spectrum of compound **3a**.

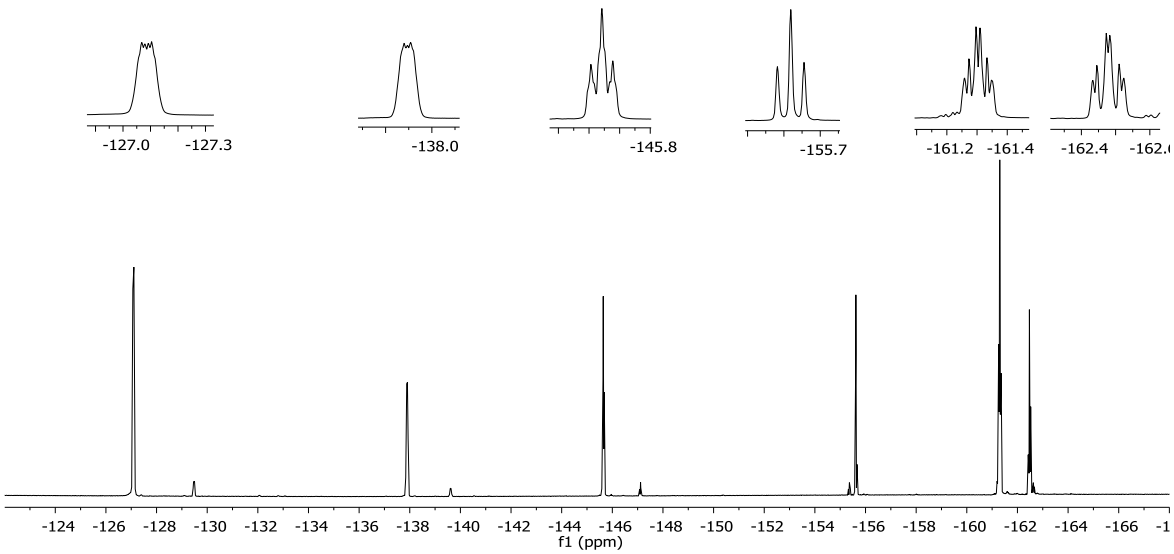


Figure S4: **^{19}F NMR** (564 MHz, CD_2Cl_2, 299 K) spectrum of compound **3a**.

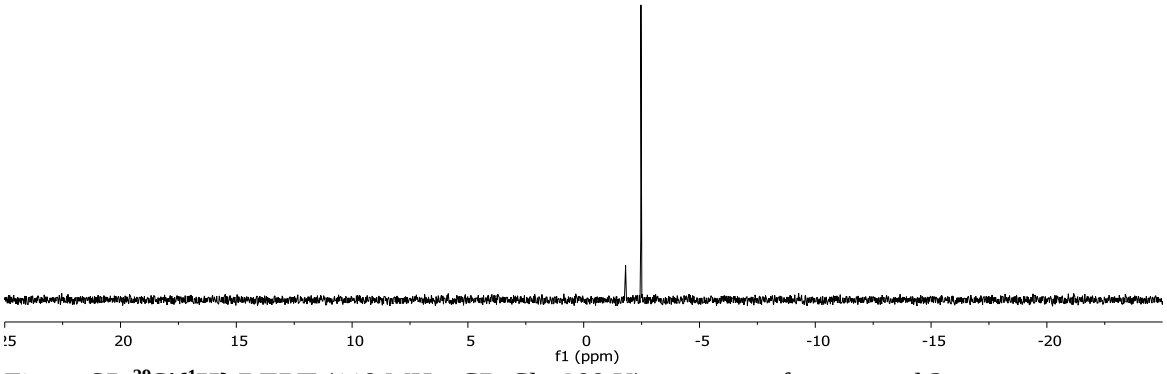


Figure S5: **^{29}Si{^{1}H} DEPT** (119 MHz, CD_2Cl_2, 299 K) spectrum of compound **3a**.

Crystals suitable for the X-ray crystal structure analysis were taken from the reaction batch (pentane, -35 °C).

X-ray crystal structure analysis of compound 3a (erk9332): A colorless prism-like specimen of $C_{24}H_{12}BF_{15}Si$, approximate dimensions 0.130 mm x 0.190 mm x 0.220 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1772 frames were collected. The total exposure time was 35.74 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 24177 reflections to a maximum θ angle of 66.76° (0.84 Å resolution), of which 4821 were independent (average redundancy 5.015, completeness = 98.9%, R_{int} = 4.38%, R_{sig} = 3.16%) and 4056 (84.13%) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.6491(3) Å, b = 11.8975(3) Å, c = 12.2730(3) Å, α = 101.4760(10)°, β = 96.2830(10)°, γ = 92.6620(10)°, volume = 1369.11(6) $Å^3$, are based upon the refinement of the XYZ-centroids of 9450 reflections above 20 σ(I) with 7.404° < 2θ < 133.4°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.805. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6870 and 0.7950. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P*-1, with Z = 2 for the formula unit, $C_{24}H_{12}BF_{15}Si$. The final anisotropic full-matrix least-squares refinement on F^2 with 374 variables converged at R1 = 3.26%, for the observed data and wR2 = 8.46% for all data. The goodness-of-fit was 1.044. The largest peak in the final difference electron density synthesis was 0.259 $e^-/Å^3$ and the largest hole was -0.238 $e^-/Å^3$ with an RMS deviation of 0.046 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.514 g/cm^3 and F(000), 620 e^-. CCDC Nr.: 1892606.

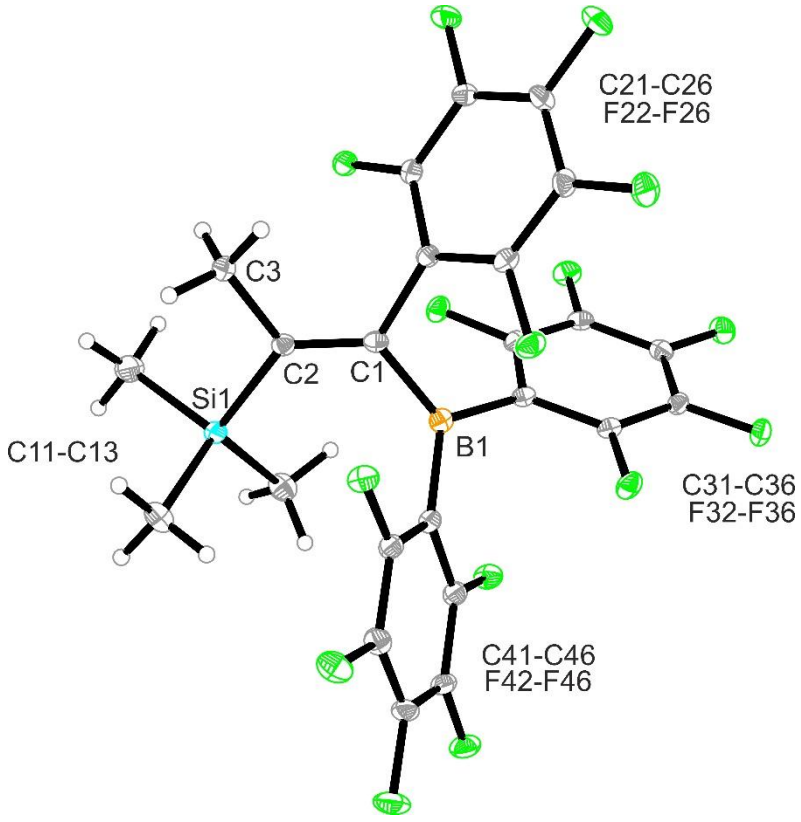
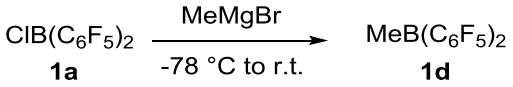


Figure S6: Crystal structure of compound **3a** (thermal ellipsoids: 30% probability).

Preparation of compound $MeB(C_6F_5)_2$ (1d)



Scheme S3

A solution of $ClB(C_6F_5)$ (1.90 g, 5.0 mmol) in toluene (20 ml) and cooled to -78 °C. Then a MeMgBr solution (1.67 ml; 3M in Et_2O, 5.0 mmol) was added dropwise and the mixture was allowed to react for one hour while cooling and subsequently for two hours at room temperature. The cloudy mixture was dried in vacuo, the remaining residue suspended in toluene, vigorously stirred for 10 minutes and dried in vacuo again. Then the obtained white solid was extracted with pentane (3x20 ml). Drying of the combined pentane extracts in vacuo gave product **1d** as a white solid (1.26 g, 3.5 mmol, 70% yield).

NMR spectra are in accordance with those reported in the literature (in C_6D_6) [C. Chen, G. Kehr, R. Fröhlich and G. Erker, *J.Am. Chem. Soc.*, 2010, **132**, 13594]

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 1.68 (quint, *J* =1.7 Hz, 3H, Me).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = 148.1 (dm, $^1J_{FC} \approx$ 250 Hz, C_6F_5), 144.1 (dm, $^1J_{FC} \approx$ 260 Hz, *p*-C_6F_5), 138.0 (dm, $^1J_{FC} \approx$ 250 Hz, C_6F_5), 115.2 (br, *i*-C_6F_5), 16.8 (br, Me).

^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = 72.2 ($\nu_{1/2} \approx$ 245 Hz).

^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = -129.8 (m, 2F, *o*-C_6F_5), -148.2 (tm, $^3J_{FF} \approx$ 19 Hz, 1F, *p*-C_6F_5), -162.2 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{m,p}$ = 14.0].

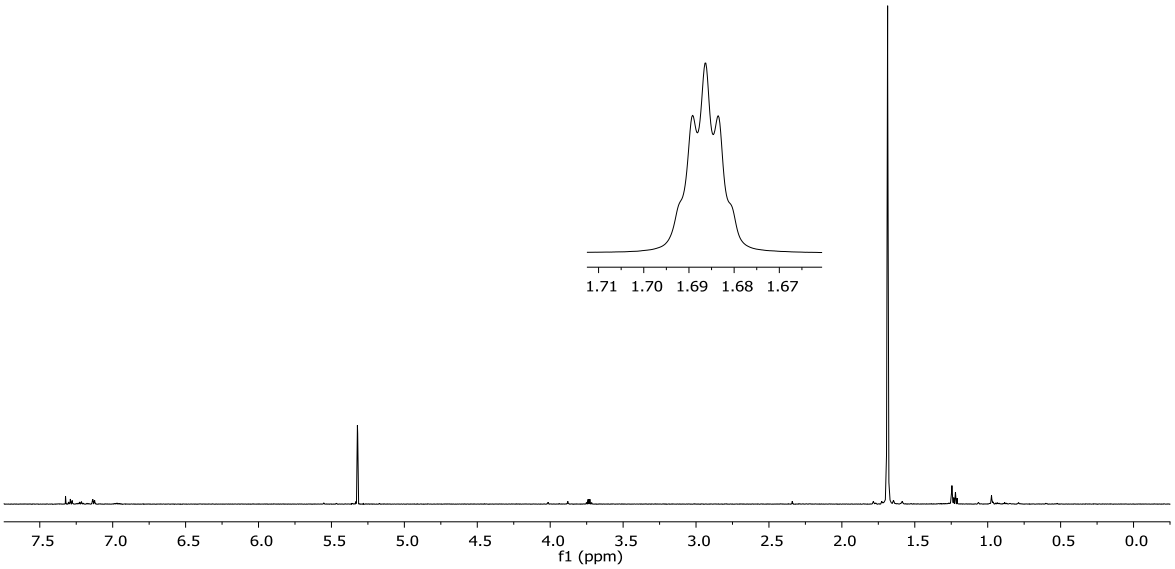


Figure S7: **^{1}H NMR** (600 MHz, CD_2Cl_2, 299K) spectrum of compound **1d**.

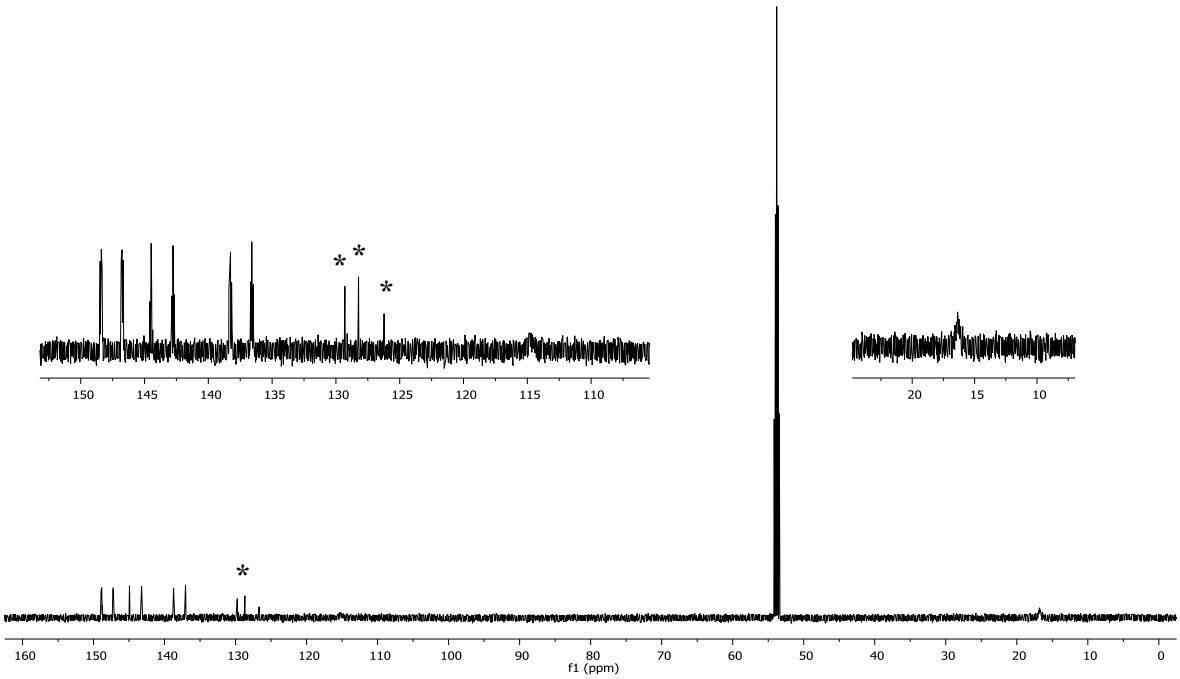


Figure S8: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, CD_2Cl_2, 299K) spectrum of compound **1d**; asterisk denotes unindetified impuirity.

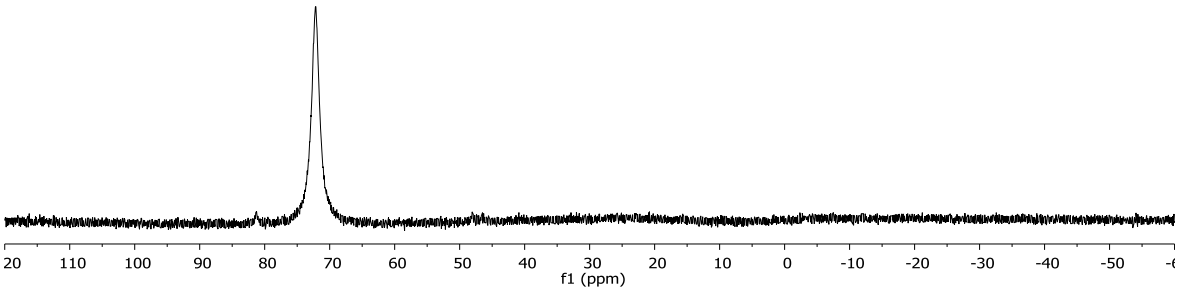


Figure S9: **$^{11}B\{^{1}H\}$ NMR** (192 MHz, CD_2Cl_2, 299K) spectrum of compound **1d**.

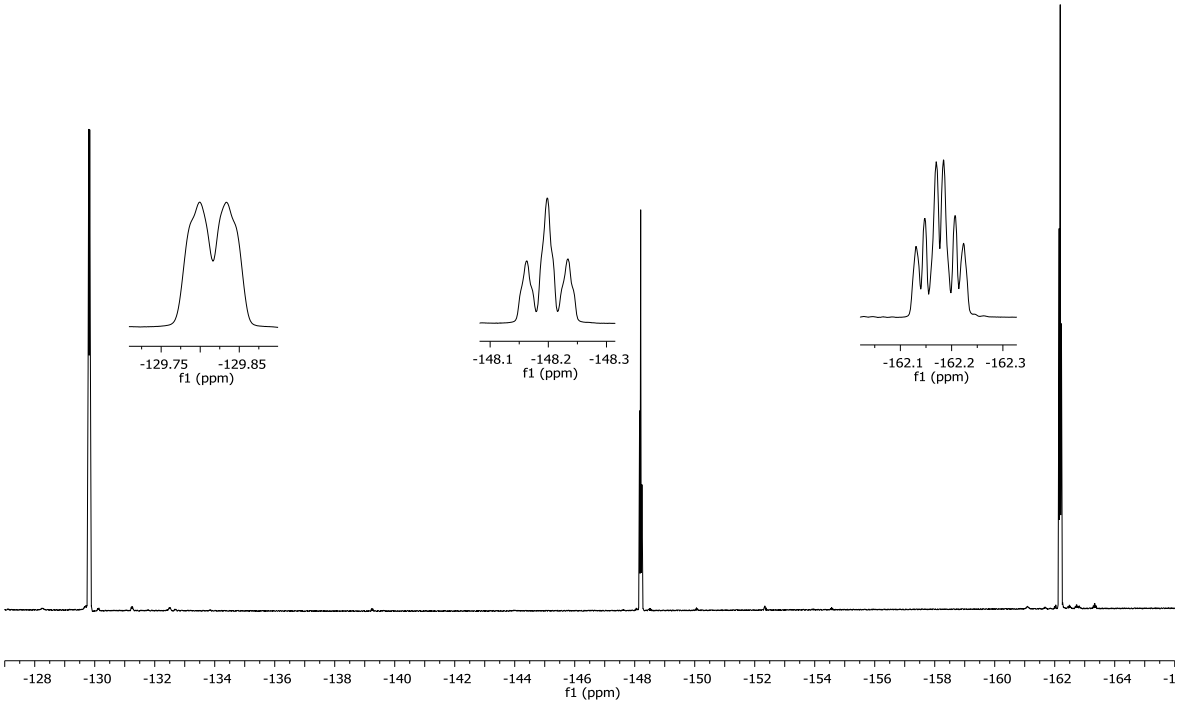


Figure S10: **^{19}F NMR** (564 MHz, CD_2Cl_2, 299 K) spectrum of compound **1d**.

Crystals suitable for the X-ray crystal structure analysis were obtained from a saturated pentane solution of compound **1d** at -20°C.

X-ray crystal structure analysis of compound 1d (erk9124): A colorless plate-like specimen of $C_{13}H_3BF_{10}$, approximate dimensions 0.030 mm x 0.100 mm x 0.160 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using a monoclinic unit cell yielded a total of 2290 reflections to a maximum θ angle of 25.00° (0.84 Å resolution), of which 2290 were independent (average redundancy 1.000, completeness = 99.0%, R_{sig} = 2.45%) and 1800 (78.60%) were greater than $2\sigma(F^2)$. The final cell constants of a = 5.2909(4) Å, b = 9.4999(11) Å, c = 26.104(3) Å, β = 90.161(8)°, volume = 1312.1(2) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9680 and 0.9940. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/c$, with Z = 4 for the formula unit, $C_{13}H_3BF_{10}$. The final anisotropic full-matrix least-squares refinement on F^2 with 218 variables converged at R1 = 4.70%, for the observed data and wR2 = 12.69% for all data. The goodness-of-fit was 1.080. The largest peak in the final difference electron density synthesis was 0.184 $e^-/Å^3$ and the largest hole was -0.171 $e^-/Å^3$ with an RMS deviation of 0.042 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.822 g/cm^3 and F(000), 704 e^-. CCDC Nr.: 1892605.

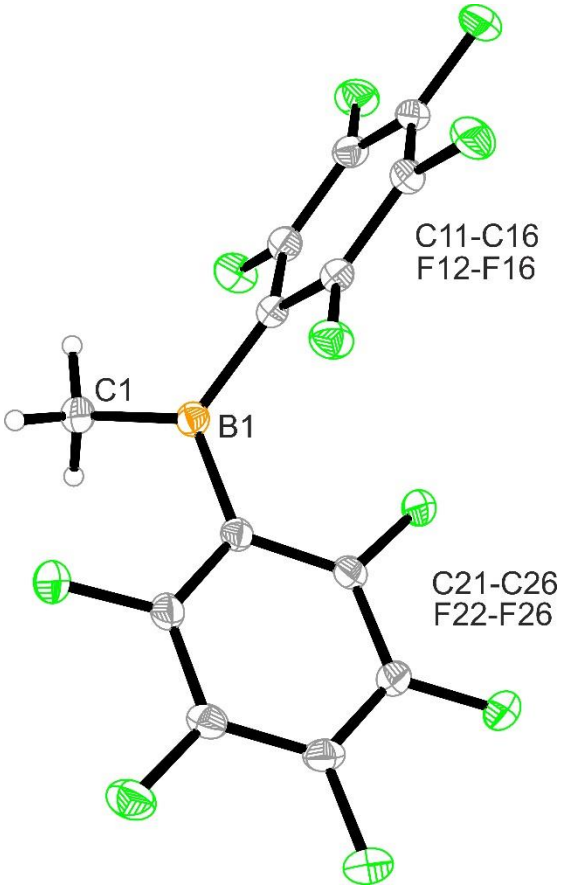
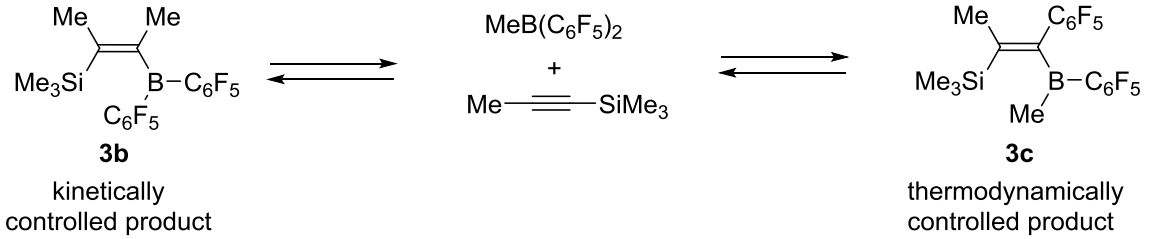


Figure S11: Crystal structure of compound **1d** (thermal ellipsoids: 15% probability).

Process of the reaction of $MeB(C_6F_5)_2$ (1d) with $MeC{\equiv}CSiMe_3$ (2a)



Scheme S4

To a solution of $MeB(C_6F_5)_2$ (**1d**) (36.0 mg, 0.1 mmol) in CD_2Cl_2 (0.2 ml) a solution of $MeC{\equiv}CSiMe_3$ (**2a**) (11.2 mg, 0.1 mmol) in CD_2Cl_2 (0.3 ml) was added. The mixture was shaken vigorously and then placed in a Young-NMR tube. Immediate characterization by NMR experiments (ca. 10 minutes after mixing) revealed formation of a mixture of the isomers **3b** and **3c** in a ca. 70:30 ratio (^{1}H NMR) The reaction mixture was stored at room temperature while its composition was monitored by ^{1}H and ^{19}F NMR measurements (vide infra). After 24 h, almost complete conversion (ca. 95 mol%, ^{1}H) to the isomer **3c** was observed.

Addition of a second equivalent of $MeC{\equiv}CSiMe_3$ to the reaction mixture (after 24 hours) and characterization of the mixture after one day at r.t. by NMR experiments did not show further reactions.

Kinetically controlled product (3b)

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 1.86 (q, J_{HH} = 1.0 Hz, 3H, Me), 1.76 (q, J_{HH} = 1.0 Hz, 3H, Me), -0.09 (s, $^2J_{SiH}$ = 6.5 Hz, 9H, $SiMe_3$).

^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = 61.2 ($\nu_{1/2} \approx 630$ Hz).

^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = -127.7 (m, 2F, *o*-C_6F_5), -147.1 (tt, J_{FF} = 20 Hz, 6 Hz, 1F, *p*-C_6F_5), -162.2 (m, 2F, *m*-C_6F_5) ($\Delta\delta^{19}F_{m,p}$ = 15.1).

Thermodynamically controlled product (3c)

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 1.77 (t, *J* =1.7 Hz, 3H, Me-C), 1.45 (br, $\nu_{1/2} \approx 5.6$ Hz, 3H, Me-B), 0.18 (s, $^2J_{SiH}$ = 6.6 Hz, 9H, $SiMe_3$).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = 156.4 (SiC=), 148.8 (dm, $^1J_{FC} \approx 250$ Hz, C_6F_5), 143.8 (dm, $^1J_{FC} \approx 245$ Hz, C_6F_5), 143.8 (dm, $^1J_{FC} \approx 247$ Hz, C_6F_5), 142.2 (br, Me-C=*C*-B), 140.5 (dm, $^1J_{FC} \approx 252$ Hz, C_6F_5), 138.1 (dm, $^1J_{FC} \approx 252$ Hz, C_6F_5), 137.8 (dm, $^1J_{FC} \approx 255$ Hz, C_6F_5), 115.2 (tm, $^2J_{FC} \approx 22$ Hz, *i*-$C_6F_5^C$), 114.1 (br, *i*-$C_6F_5^B$), 21.4 (*Me*-C), 18.3 (br, *Me*-B), -0.3 ($^1J_{SiC}$ = 52.6 Hz).

^{13}C{^{19}F,^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): [selected resonances] δ = 148.8 (2C, C_6F_5), 143.8 (1C, *p*- C_6F_5), 143.8 (2C, C_6F_5), 140.5 (1C, *p*-C_6F_5), 138.1 (2C, C_6F_5), 137.8 (2C, C_6F_5), 115.2 (1C, *i*-$C_6F_5^C$), 114.1 (br, *i*-$C_6F_5^B$).

^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = 72.4 ($\nu_{1/2} \approx 520$ Hz).

^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = [-127.3 (m, 2F, *o*), -149.0 (tt, J_{FF} = 20 Hz, 5 Hz, 1F, *p*), -162.6 (m, 2F, *m*)] (B-C_6F_5, [$\Delta\delta^{19}F_{m,p}$ = 13.6]), [-138.9 (m, 2F, *o*), -156.8 (t, J_{FF} = 21 Hz, 1F, *p*), -162.9 (m, 2F, *m*)] (C-C_6F_5, [$\Delta\delta^{19}F_{m,p}$ = 6.1]).

^{29}Si{^{1}H} DEPT (119 Hz, CD_2Cl_2, 299 K): δ = -2.8 ($\nu_{1/2} \approx 1$ Hz).

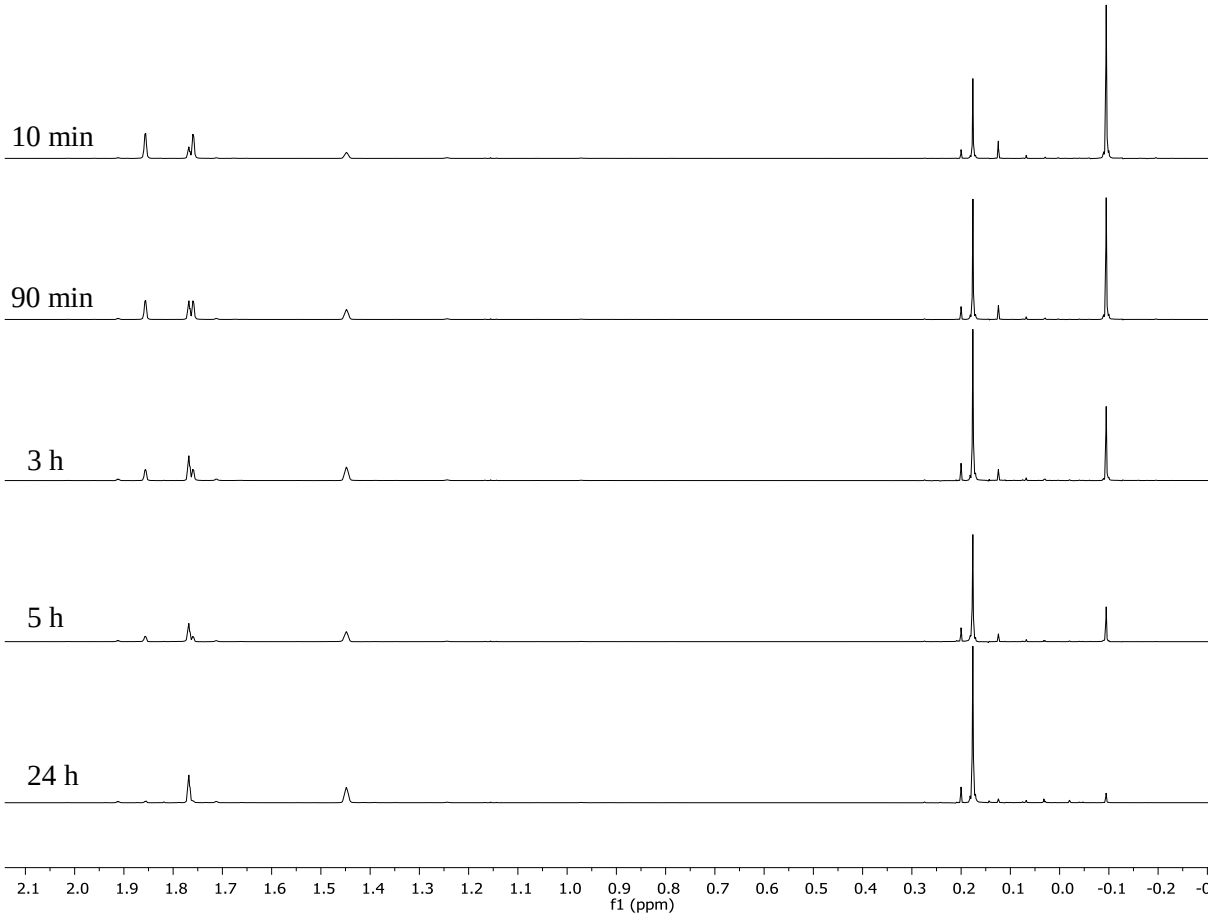


Figure S12: Time dependancy of the **^{1}H NMR** (600 MHz, CD_2Cl_2, 299K) spectra during the reaction of $MeB(C_6F_5)_2$ with $MeC{\equiv}CSiMe_3$, formation of the isomers **3b** and **3c**.

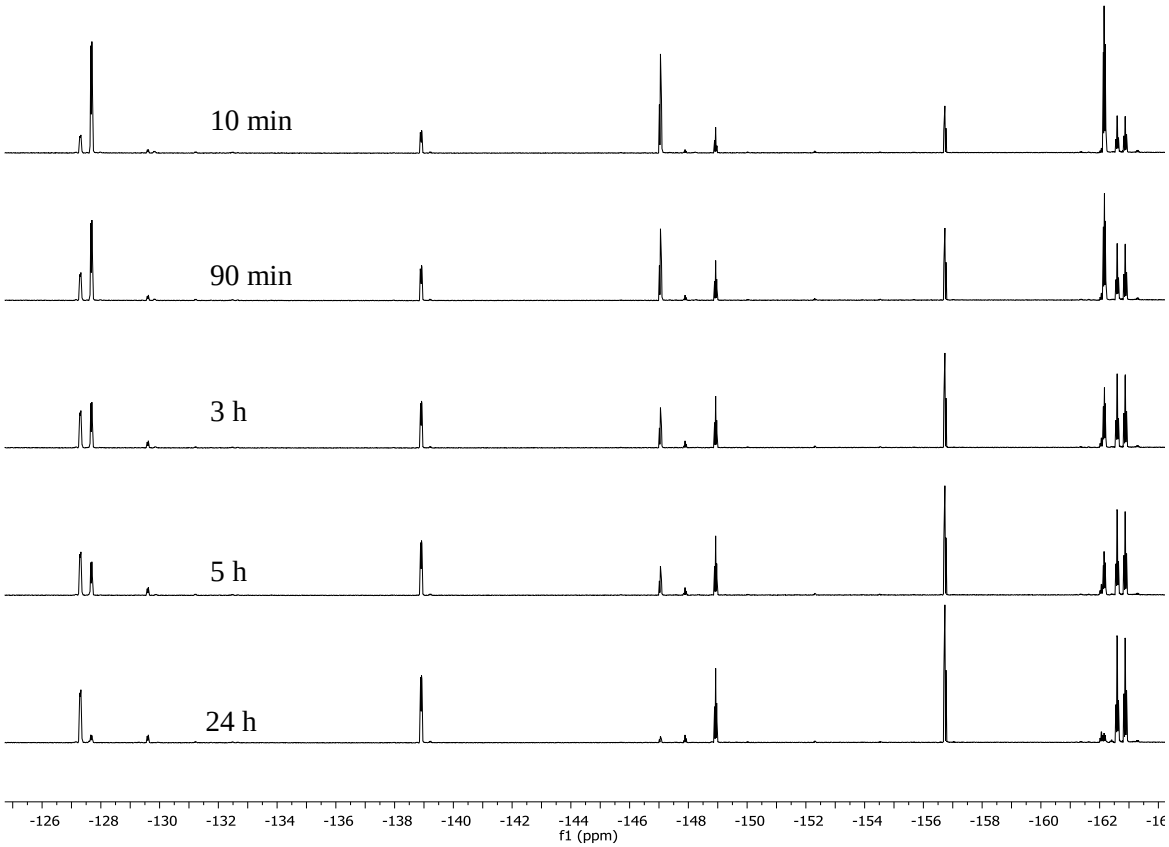


Figure S13: Time dependancy of the **^{19}F NMR** (564 MHz, CD_2Cl_2, 299K) spectra during the reaction of $MeB(C_6F_5)_2$ with $MeC{\equiv}CSiMe_3$: formation of the isomers **3b** and **3c**.

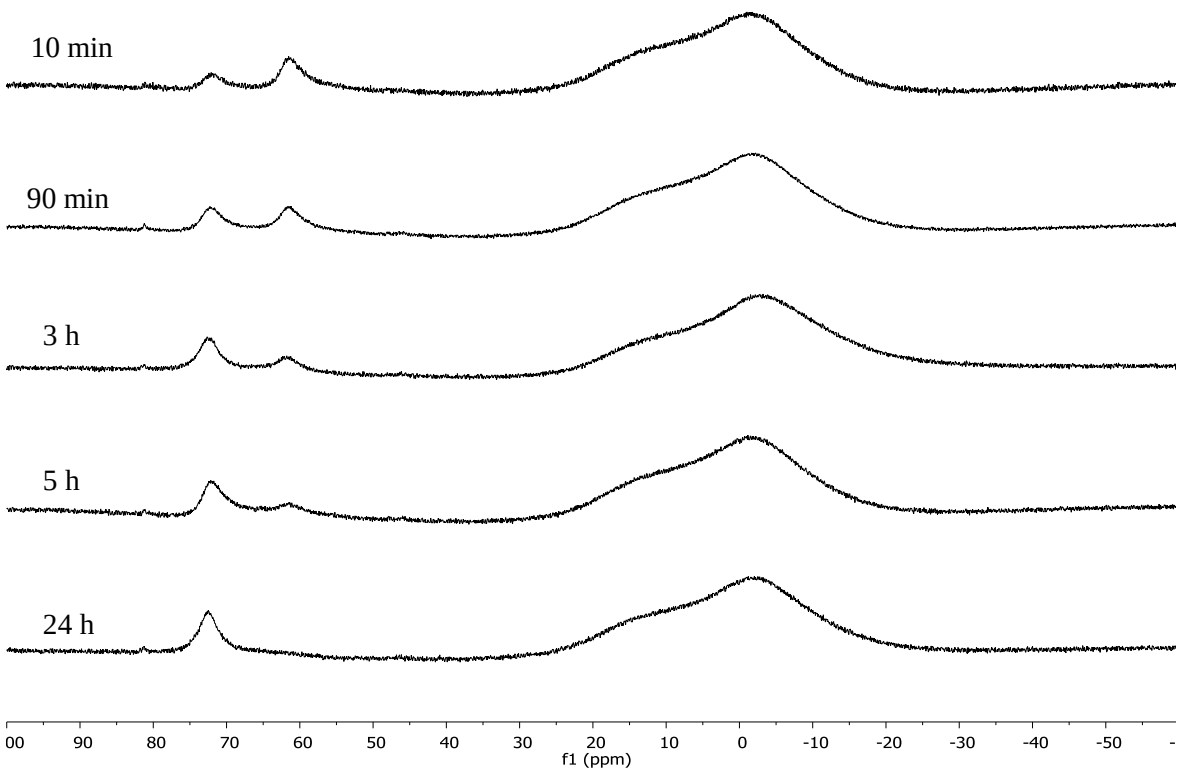


Figure S14: Time dependancy of the **$^{11}B\{^{1}H\}$ NMR** (564 MHz, CD_2Cl_2, 299K) spectra during the reaction of $MeB(C_6F_5)_2$ with $MeC{\equiv}CSiMe_3$: formation of the isomers **3b** and **3c**.

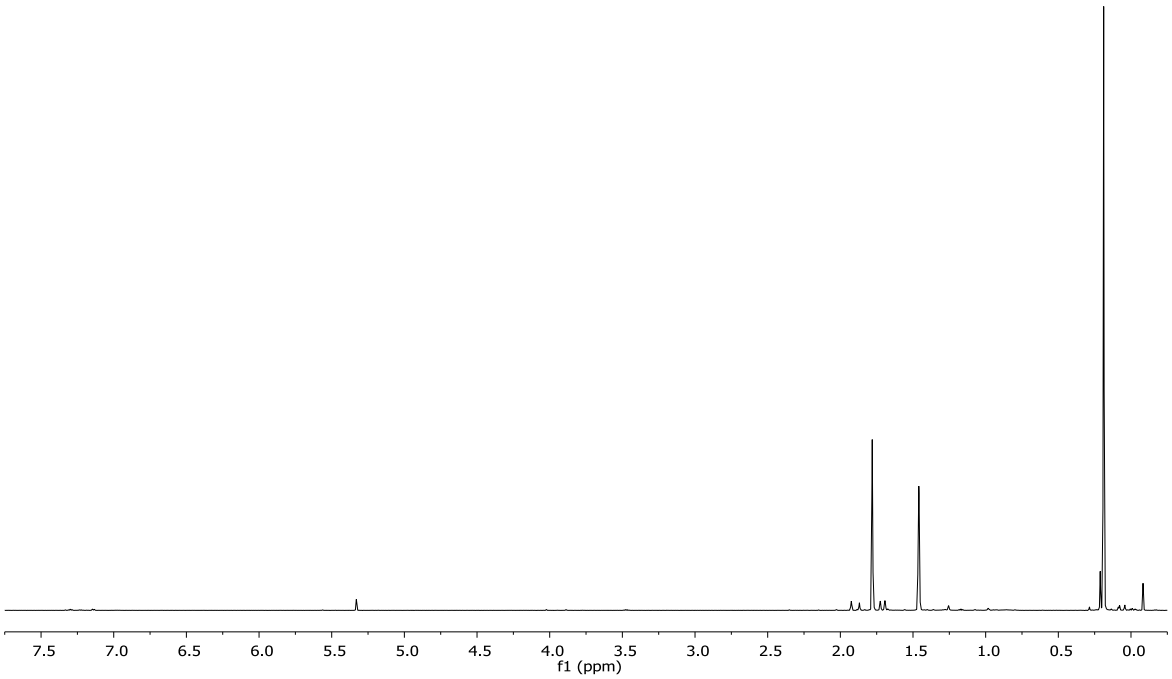


Figure S15: **^{1}H NMR** (600 MHz, CD_2Cl_2, 299K) spectrum of compound **3c**.

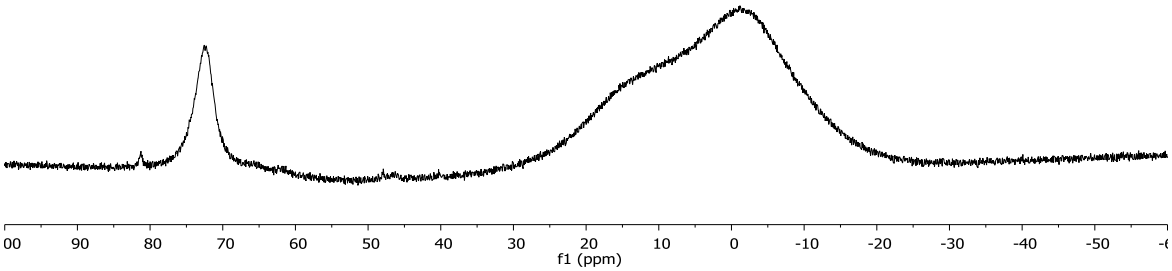


Figure S16: **^{11}B{^{1}H} NMR** (192 MHz, CD_2Cl_2, 299K) spectrum of compound **3c**.

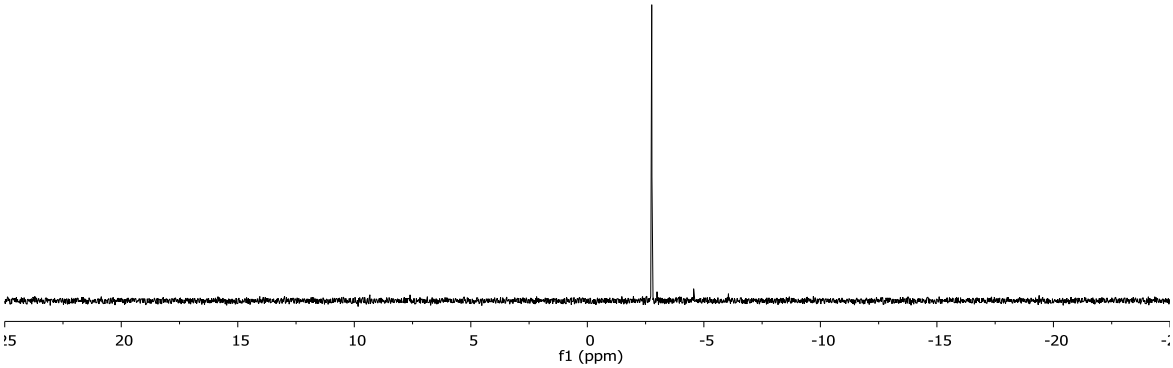


Figure S17: **^{29}Si{^{1}H} DEPT** (119 MHz, CD_2Cl_2, 299 K) spectrum of compound **3c**.

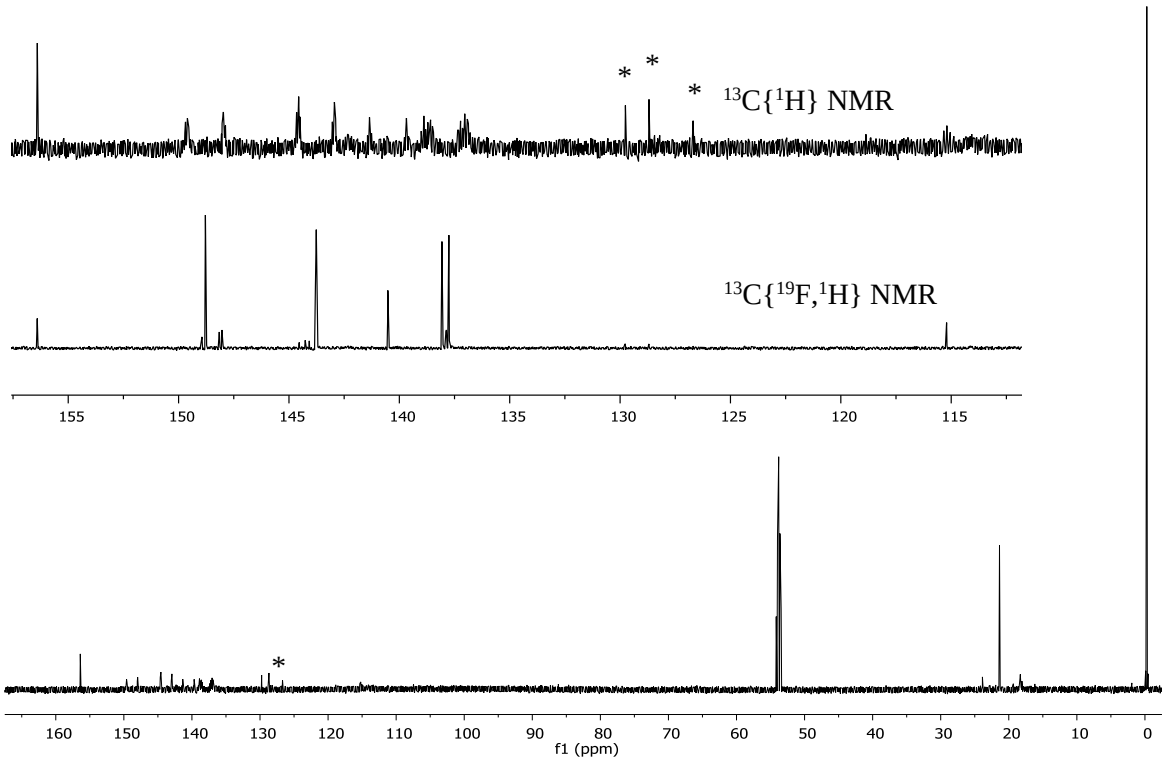


Figure S18: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, CD_2Cl_2, 299K) spectrum and detailed overview of aromatic signals with excerpt from **$^{13}C\{^{19}F,^{1}H\}$ NMR** (151 MHz, CD_2Cl_2, 299K) spectrum of compound **3c**, asterisks denote unidentified impuirities.

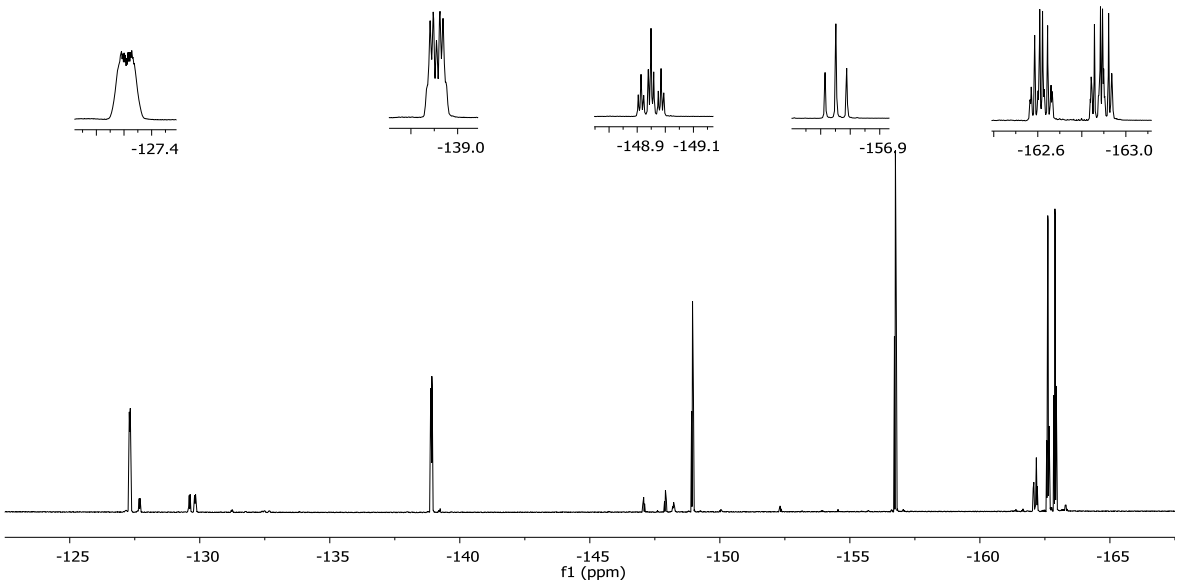
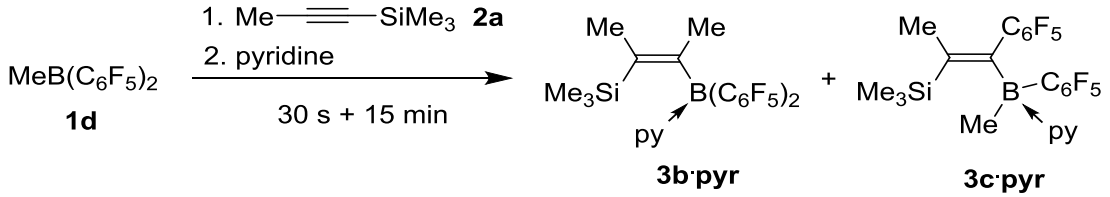


Figure S19: **^{19}F NMR** (564 MHz, CD_2Cl_2, 299 K) spectrum of compound **3c**.

Trapping the products of the reaction of 1d + 2a with pyridine



Scheme S5

A solution of MeC≡CSiMe$_3$ (56.1 mg, 0.5 mmol) in CH_2Cl_2 (3 ml) was added to a solution of MeB(C_6F_5)$_2$ (180 mg, 0.5 mmol) in CH_2Cl_2 (3 ml). The colorless mixture was stirred for thirty seconds at room temperature, then a solution of pyridine (60 mg, 0.75 mmol) in CH_2Cl_2 (2 ml) was added and after 15 minutes stirring at room temperature all volatilities were evaporated in vacuo to yield a colorless semi-solid residue. NMR analysis revealed complete conversion to **3b·pyr** and **3c·pyr** in approximate 70:30 ratio. Attempts to separate these by column chromatography or crystallization were not successful.

3b·pyr isomer:

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 8.80 (br d, J ≈ 6 Hz, 2H, 2,6-py), 8.08 (m, 1H, 4-py), 7.59 (m, 2H, 3,5-py), 1.84 (q, *J* = 1.1 Hz, 3H, Me), 1.70 (br, 3H, Me), -0.27 (s, 9H, $^2J_{SiH}$ = 6.3 Hz, $SiMe_3$).

^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = -1.0 ($\nu_{1/2}$ ≈ 160 Hz).

^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = -127.9 (m, 2F, *o*-C_6F_5), -157.4 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), -163.0 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 5.6]).

3c·pyr isomer (for complete characterization see below):

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 8.93 (br, 2H, 2,6-py), 8.08 (m, 1H, 4-py), 7.63 (m, 2H, 3,5-py), 1.67 (s, 3H, Me-C), 0.75 (br, 3H, Me-B), -0.08 (s, 9H, $^2J_{SiH}$ = 6.4 Hz, $SiMe_3$).

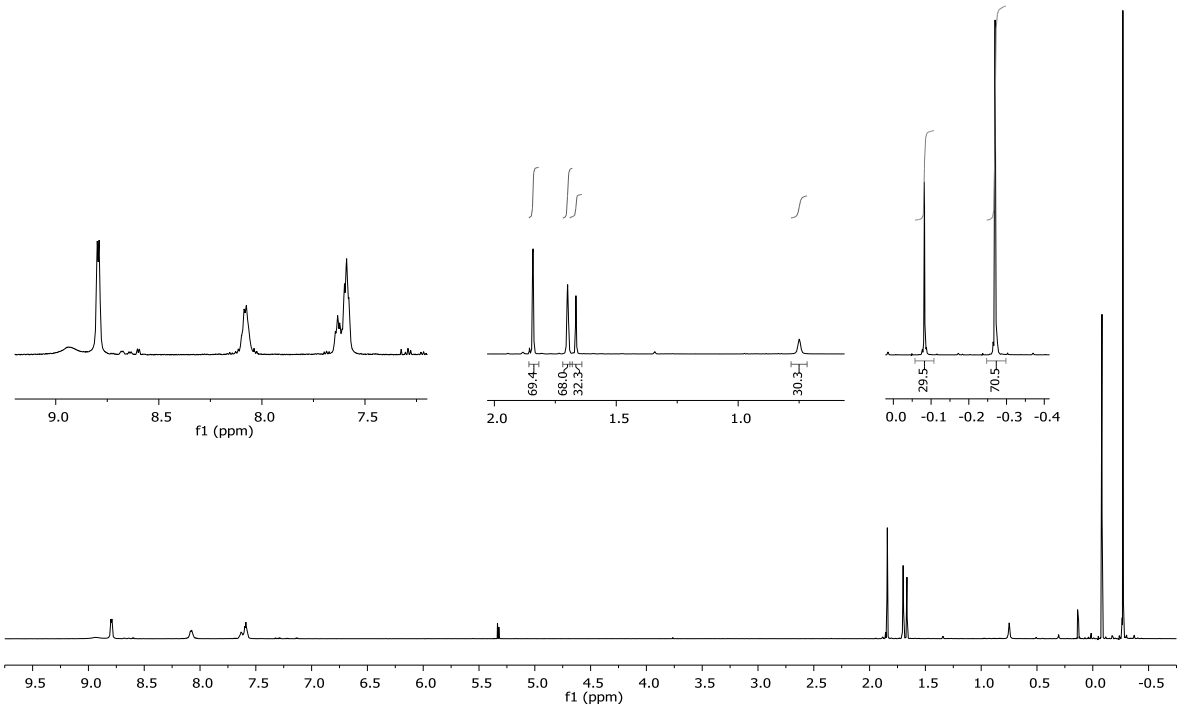


Figure S20: **^{1}H NMR** (600 MHz, CD_2Cl_2, 299K) spectrum of the mixture **3b·pyr** and **3c·pyr**.

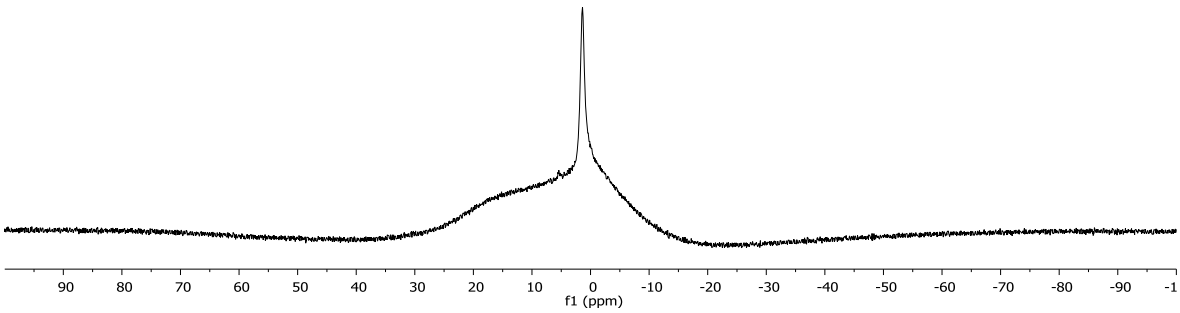


Figure S21: **^{11}B{^{1}H} NMR** (192 MHz, CD_2Cl_2, 299K) spectrum of the mixture **3b·pyr** and **3c·pyr**.

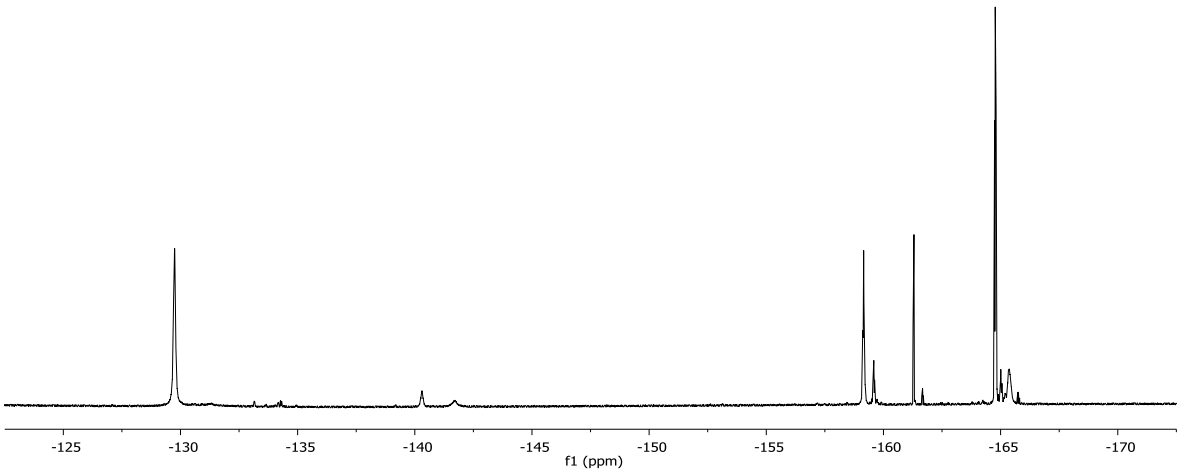
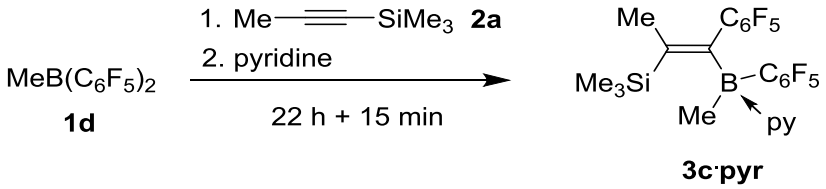


Figure S22: **^{19}F NMR** (564 MHz, CD_2Cl_2, 299K) spectrum of the mixture **3b·pyr** and **3c·pyr.**

Preparation of compound 3c·pyr



Scheme S6

A solution of $MeC{\equiv}CSiMe_3$ (22.7 mg, 0.2 mmol) in CH_2Cl_2 (3 ml) was added to a solution of $MeB(C_6F_5)_2$ (72.3 mg, 0.2 mmol) in CH_2Cl_2 (3 ml). The colorless mixture was allowed to react for 22 h at room temperature, then a solution of pyridine (24 mg, 0.3 mmol) in CH_2Cl_2 (2 ml) was added and after 15 minutes stirring at room temperature all volatilities were evaporated in vacuo to yield a colorless semi-solid. This was dissolved in CH_2Cl_2 (1 ml), transferred to a crystallization tube and layered with pentane (2 ml). After several days at -35°C, colorless prismatic crystals were formed. After isolation by decantation, washing with cold pentane and drying in vacuo compound **3c·pyr** was isolated as a white crystalline solid (63.6 mg, as shown by NMR **3c·pyr** crystallizes with 0.5 molar equiv. of pentane; 0.107 mmol, 54 % yield).

Melting point: 138.6 °C.

Elementary analysis for $C_{24}H_{20}BF_{10}NSi\cdot 0.5\ C_5H_{12}$ (587.4): calculated C 54.18, H 4.46, N 2.39; found C 54.02, H 4.45, N 2.18.

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 8.93 (br, 2H, 2,6-py), 8.08 (t, J_{HH} = 7.6 Hz, 1H, 4-py), 7.63 (m, 2H, 3,5-py), 1.66 (s, 3H, Me-C), 0.75 (br, 3H, Me-B), -0.08 (s, 9H, $^2J_{SiH}$ = 6.4 Hz, $SiMe_3$).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = 149.1 (br, *C*-C_6F_5), 148.6 (br, SiC=), 148.6 (dm, $^1J_{FC}$ ≈ 251 Hz, C_6F_5), 142.4 (dm, $^1J_{FC}$ ≈ 240 Hz, C_6F_5), 142.3 (dm, $^1J_{FC}$ ≈ 240 Hz, C_6F_5), 147.5 (br, 2,6-py), 141.8 (4-py), 139.2 (dm, $^1J_{FC}$ ≈ 250 Hz, C_6F_5), 138.5 (dm, $^1J_{FC}$ ≈ 250 Hz, C_6F_5), 137.5 (dm, $^1J_{FC}$ ≈ 250 Hz, C_6F_5), 137.3 (dm, $^1J_{FC}$ ≈ 250 Hz, C_6F_5), 137.1 (dm, $^1J_{FC}$ ≈ 250 Hz, C_6F_5), 125.9 (3,5-py), 124.8 (br, *i*-$C_6F_5^B$), 124.0 (tm, $^2J_{FF}$ ≈ 23 Hz, *i*-$C_6F_5^C$), 23.8 (*Me*-C), 12.6 (br, Me-B), 0.82 ($^1J_{SiC}$ = 52.5 Hz, $SiMe_3$).

^{13}C{^{19}F,^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): selected resonances δ = [148.6, 142.4, 142.3, 139.2, 138.5, 137.5, 137.3, 137.1] (C_6F_5), 124.0 (s, *i*-C_6F_5).

^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = -0.2 ($\nu_{1/2}$ ≈ 130 Hz).

^{19}F NMR (564 MHz, CD_2Cl_2, 213 K): δ = [-130.5 (*o*), -139.9 (*o*), -160.3 (*p*), -164.3 (*m*), 164.6 (*m*)] (each m, each 1F, C_6F_5, [$\Delta\delta^{19}F_{m,p}$ = 4.0, 4.3]), [-132.8 (*o*), -142.7 (*o*), -158.5 (*p*), -164.3 (*m*), -165.2 (*m*)] (each m, each 1F, C_6F_5 [$\Delta\delta^{19}F_{m,p}$ = 5.8, 6.7]).

^{29}Si{^{1}H} DEPT (119 Hz, CD_2Cl_2, 299 K): δ = 6.2 ($\nu_{1/2}$ ≈ 1 Hz).

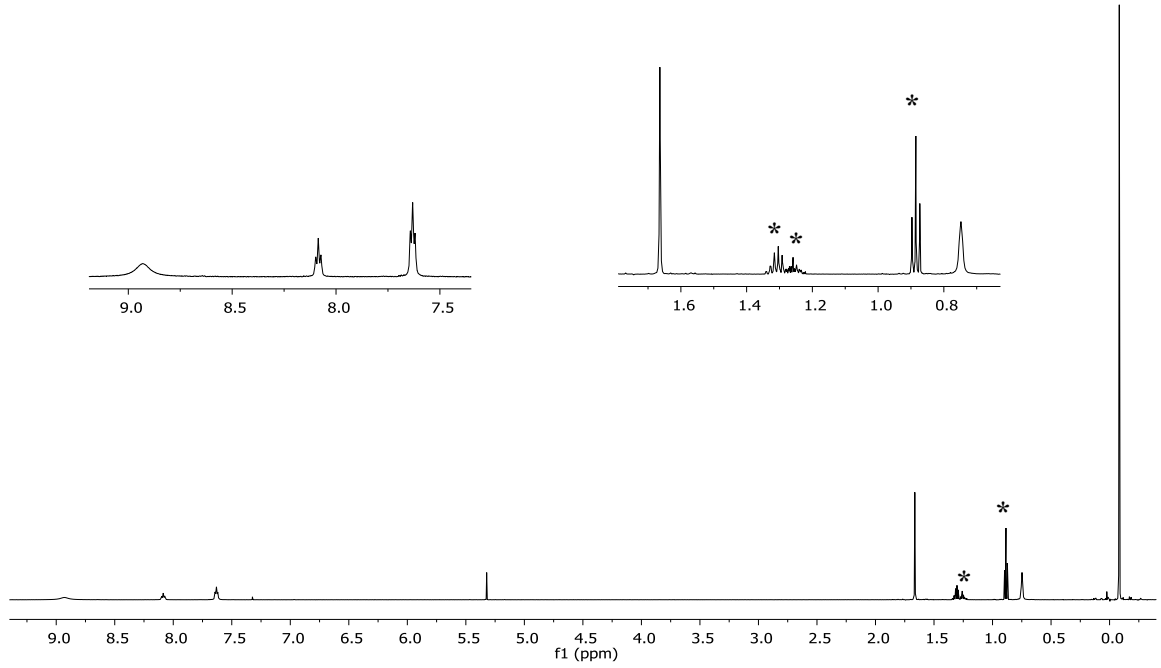


Figure S23: **^{1}H NMR** (600 MHz, CD_2Cl_2, 299K) spectrum of compound **3c·pyr**, asterisk denotes signals due to residual pentane.

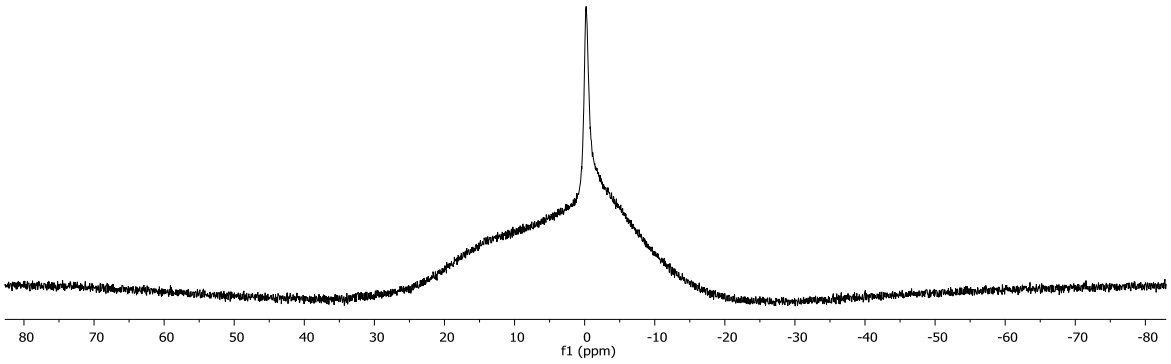


Figure S24: **^{11}B{^{1}H} NMR** (192 MHz, CD_2Cl_2, 299K) spectrum of compound **3c·pyr**.

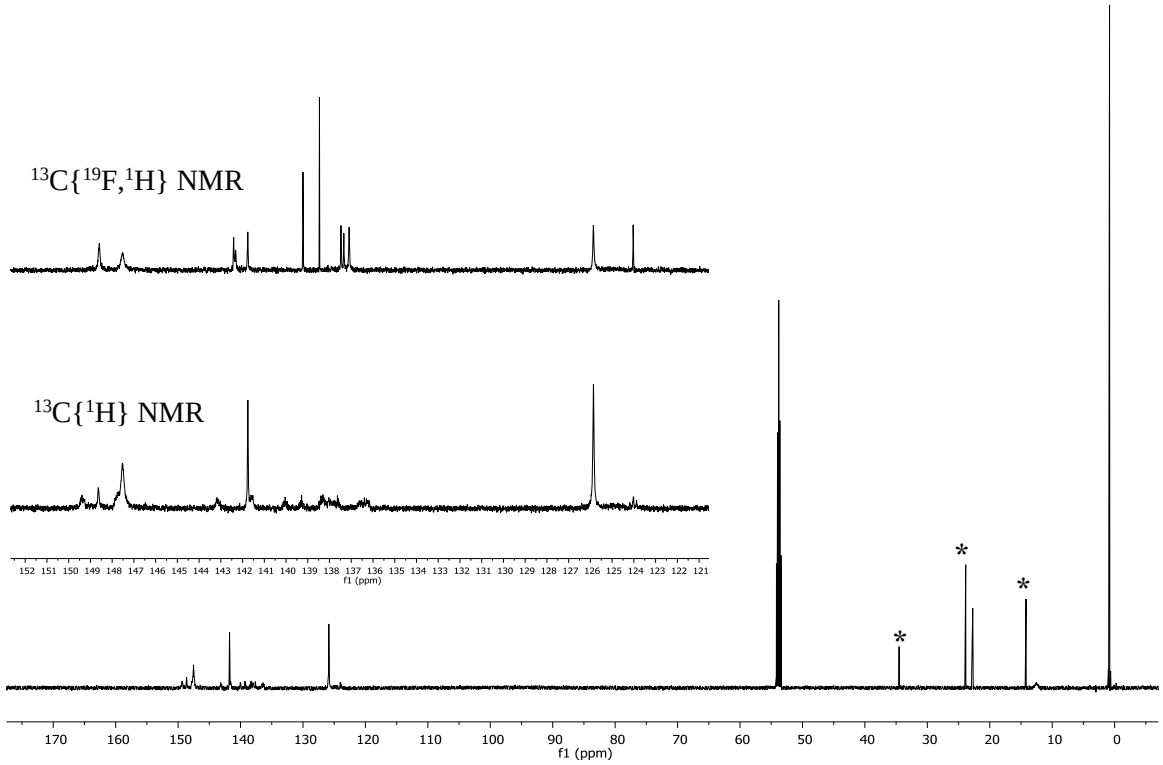


Figure S25: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, CD_2Cl_2, 299K) spectrum and detailed overview of aromatic singals with excerpt from **$^{13}C\{^{19}F,^{1}H\}$ NMR** (151 MHz, CD_2Cl_2, 299K) spectrum of compound **3c·pyr**, asterisks denote signals due to residual pentane.

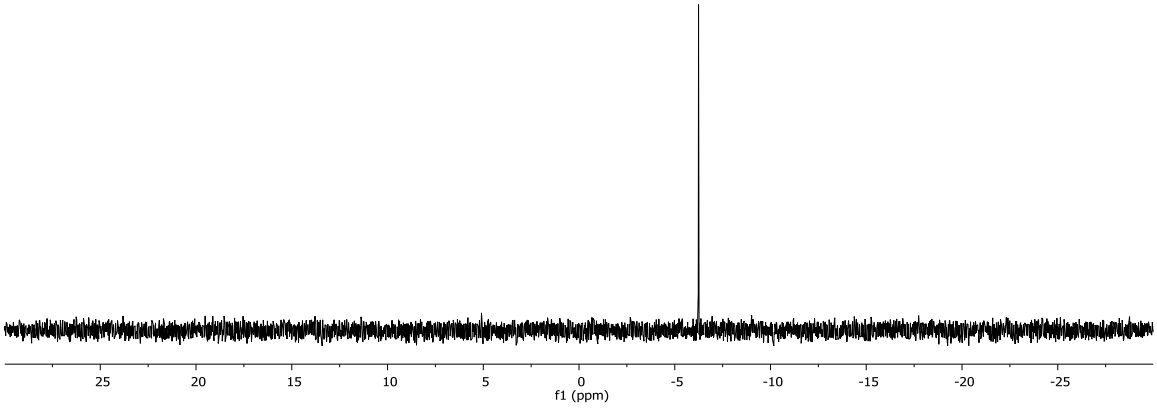


Figure S26: **$^{29}Si\{^{1}H\}$ DEPT** (119 MHz, CD_2Cl_2, 299 K) spectrum of compound **3c·pyr**.

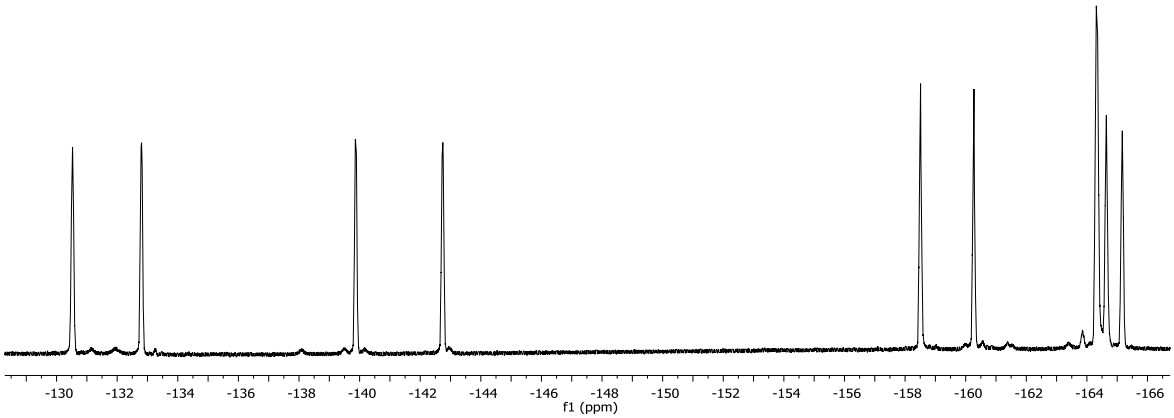


Figure S27: **^{19}F NMR** (564 MHz, CD_2Cl_2, 213K) spectrum of compound **3c·pyr**.

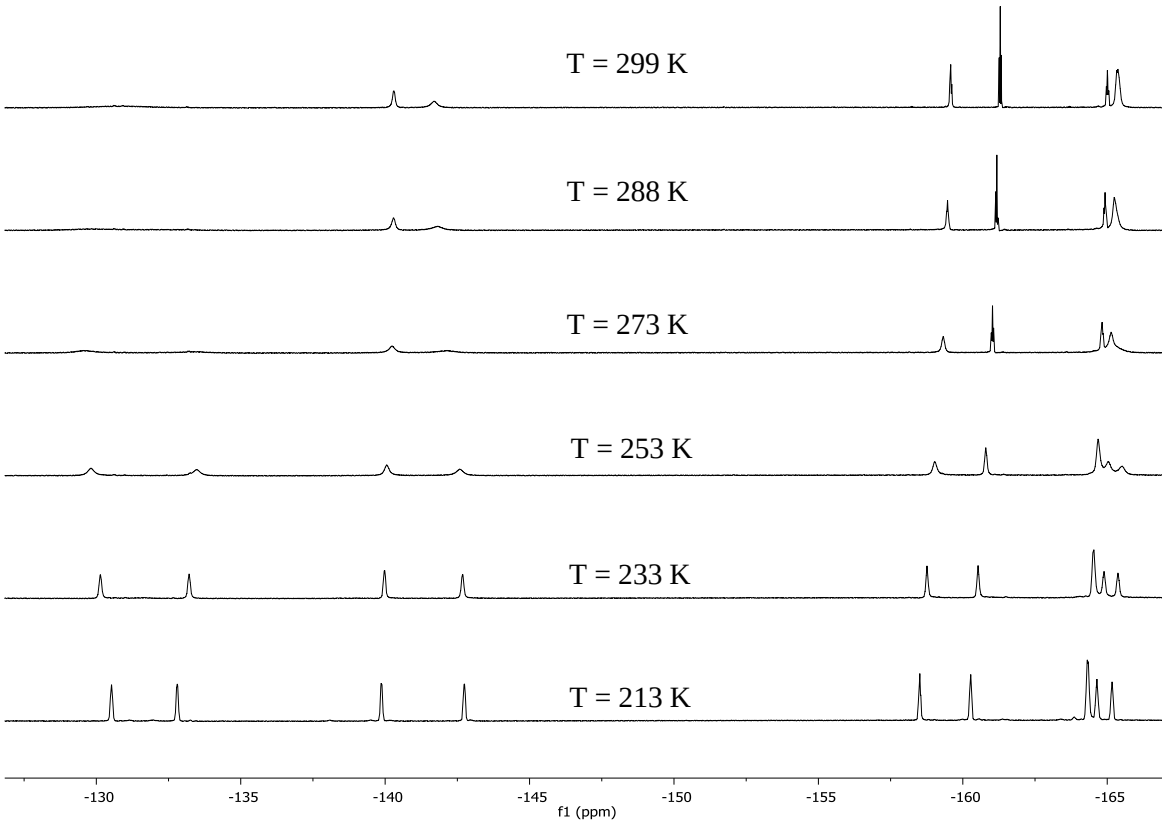


Figure S28: **^{19}F NMR** (564 MHz, CD_2Cl_2) spectrum of compound **3c·pyr** measured at various temperatures.

Crystals suitable for the X-ray crystal structure analysis were obtained from a pentane solution of **3c·pyr** at -35° C.

X-ray crystal structure analysis of compound 3c·pyr (erk9266): A colorless prism-like specimen of $C_{24}H_{20}BF_{10}NSi$, approximate dimensions 0.080 mm x 0.100 mm x 0.110 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using a triclinic unit cell yielded a total of 6682 reflections to a maximum θ angle of 25.00° (0.84 Å resolution), of which 4562 were independent (average redundancy 1.465, completeness = 94.9%, R_{int} = 3.86%, R_{sig} = 5.14%) and 3553 (77.88%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.7974(3) Å, b = 11.4497(4) Å, c = 13.2136(6) Å, α = 81.3890(10)°, β = 70.4050(10)°, γ = 62.300(2)°, volume = 1362.54(9) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9820 and 0.9870. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P*-1, with Z = 2 for the formula unit, $C_{24}H_{20}BF_{10}NSi$. The final anisotropic full-matrix least-squares refinement on F^2 with 339 variables converged at R1 = 5.87%, for the observed data and wR2 = 13.31% for all data. The goodness-of-fit was 1.072. The largest peak in the final difference electron density synthesis was 0.248 $e^-/Å^3$ and the largest hole was -0.220 $e^-/Å^3$ with an RMS deviation of 0.050 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.344 g/cm^3 and F(000), 560 e^-. CCDC Nr.: 1892607.

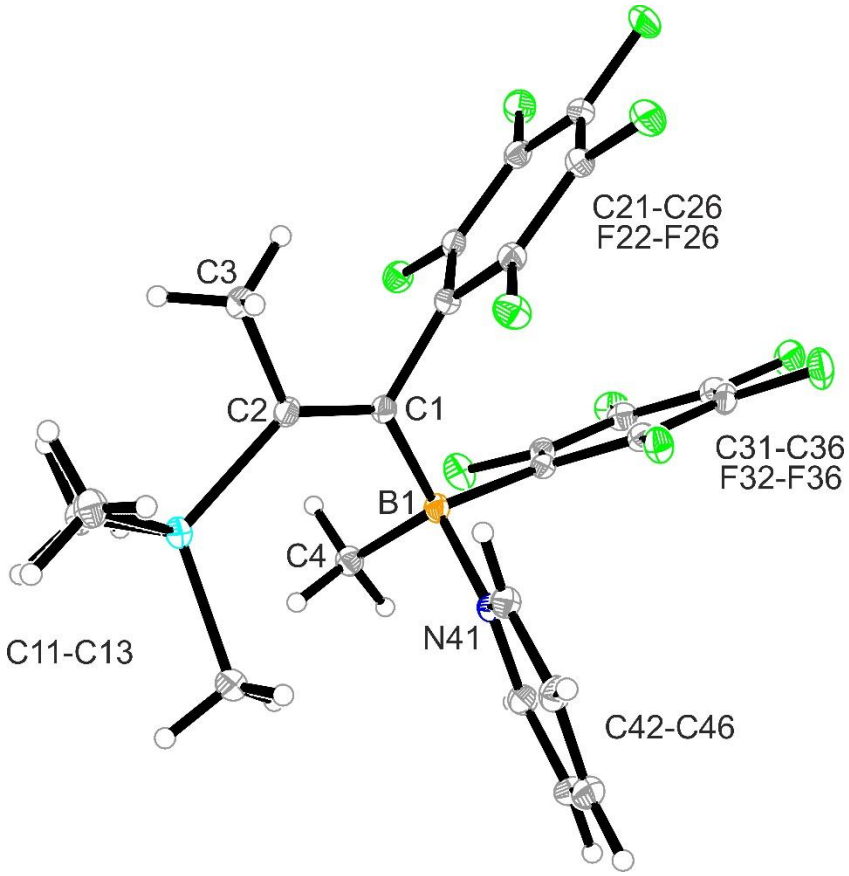
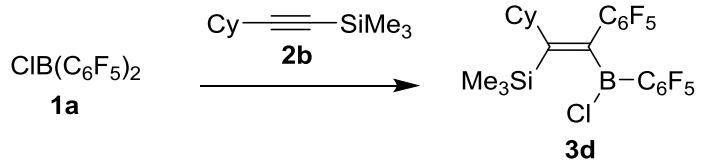


Figure S29: Crystal structure of compound **3c·pyr** (thermal ellipsoids: 15% probability).

Generation of compound 3d



Scheme S7

Solutions of CyC≡CSiMe$_3$ (**2b**) (18.0 mg, 0.1 mmol) in CD_2Cl_2 (0.3 ml) and ClB(C_6F_5)$_2$ (**1a**) (38.0 mg, 0.1 mmol) in CD_2Cl_2 (0.3 ml) were combined at room temperature and vigorously stirred for five minutes. The solution was transferred to a NMR tube, which was flame-sealed. Mesurement of ^{1}H and ^{19}F NMR spectra after one hour (stored at room temperature) revealed complete conversion to compound **3d**, which was in situ analyzed by NMR spectroscopy.

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 2.13 (tt, $^3J_{HH}$ = 12.2 Hz, 3.4 Hz, 1H, Cy), 1.72 (m, 2H, Cy), 1.60 (m, 2H, Cy), 1.43 (m, 3H, Cy), 1.08 (m, 3H, Cy), 0.30 (s, $^2J_{SiH}$ = 6.4 Hz, 9H, SiMe$_3$).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = 166.8 (SiC=), 149.7 (dm, $^1J_{FC}$ ≈ 256 Hz, 2C, *o*-$C_6F_5^B$), 148.7 (br, B*C*=), 145.0 (dm, $^1J_{FC}$ ≈ 255 Hz, 1C, *p*-$C_6F_5^B$), 143.9 (dm, $^1J_{FC}$ ≈ 256 Hz, 2C, *o*-$C_6F_5^C$), 141.1 (dm, $^1J_{FC}$ ≈ 254 Hz, 1C, *p*-$C_6F_5^C$), 138.0 (dm, $^1J_{FC}$ ≈ 254 Hz, 2C, *m*-$C_6F_5^C$), 137.9 (dm, $^1J_{FC}$ ≈ 252 Hz, 2C, *m*-$C_6F_5^B$), 113.3 (tm, $^2J_{FC}$ ≈ 23 Hz, *i*-$C_6F_5^C$), 110.9 (*i*-$C_6F_5^B$), 48.7 (1C, Cy), 31.8 (2C, Cy), 27.0 (2C, Cy), 26.3 (1C, Cy), 2.6 ($^1J_{SiC}$ = 52.2 Hz, SiMe$_3$).

^{13}C{^{19}F,^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): [selected resonances] δ = 149.7 (2C), 148.8 (1C), 145.0 (1C), 143.9 (2C), 141.1 (1C), 138.2 (2C), 137.9 (1C) (all C_6F_5).

^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = 58.4 ($\nu_{1/2}$ ≈ 540 Hz).

^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = [-125.1 (m, 2F, *o*-$C_6F_5^B$), -145.2 (tt, J_{FF} = 20 Hz, 7 Hz, 1F, *p*-$C_6F_5^B$), -161.8 (m, 2F, *m*-$C_6F_5^B$)] ($\Delta\delta^{19}F_{m,p}$ = 16.6), [-136.7 (m, 2F, *o*-$C_6F_5^C$), -154.7 (t, J_{FF} = 21 Hz, 1F, *p*-$C_6F_5^C$), -161.7 (m, 2F, *m*-$C_6F_5^C$)] ($\Delta\delta^{19}F_{m,p}$ = 7.0).

^{29}Si{^{1}H} DEPT (119 Hz, CD_2Cl_2, 299 K): δ = -2.5 ($\nu_{1/2}$ ≈ 1 Hz).

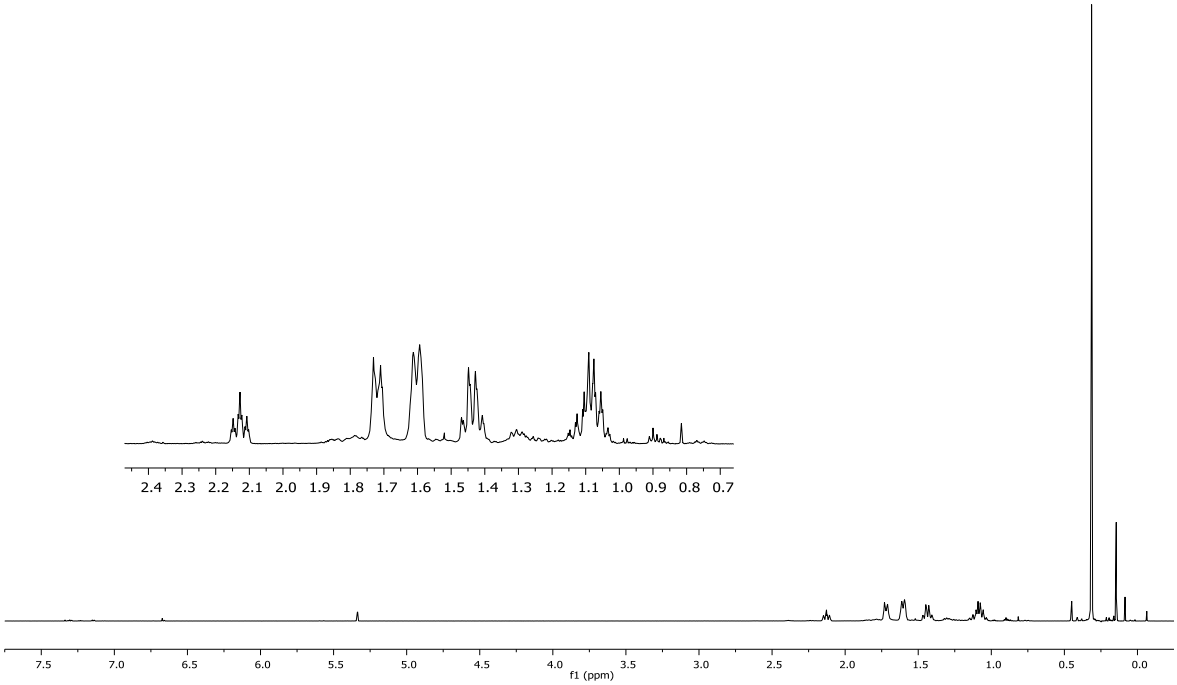


Figure S30: **^{1}H NMR** (600 MHz, CD_2Cl_2, 299K) spectrum of compound **3d**.

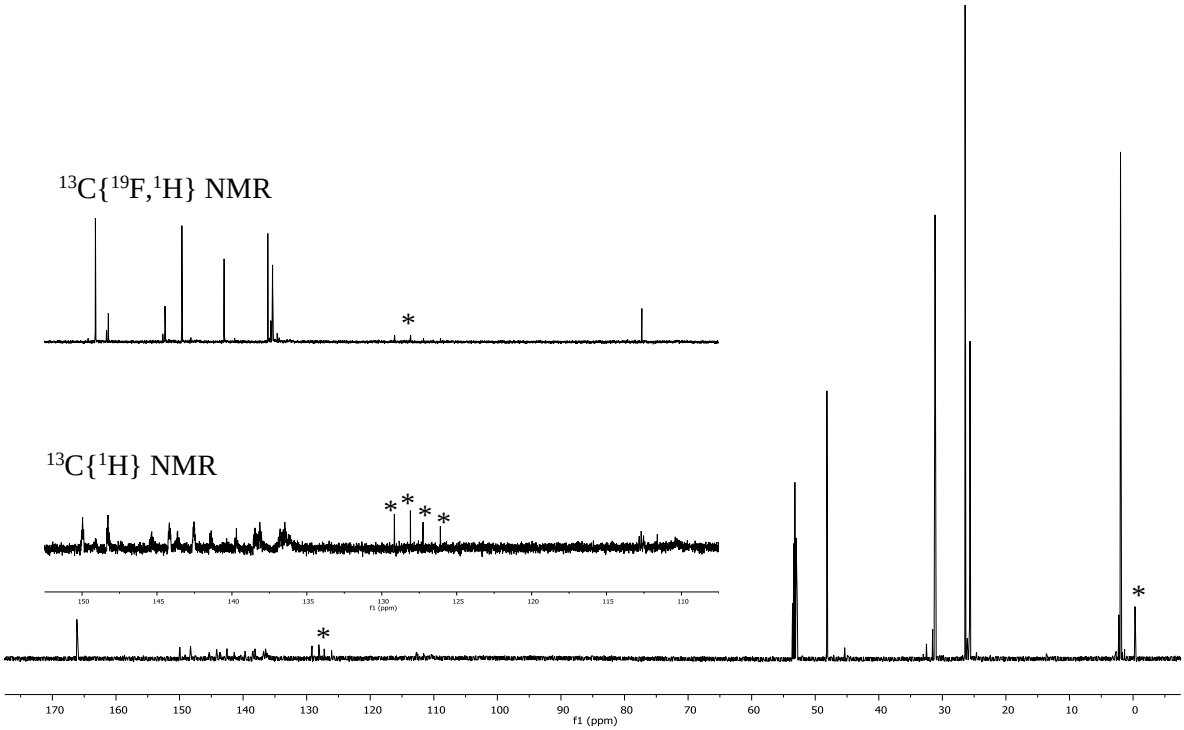


Figure S31: **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2, 299K) spectrum and detailed overview of aromatic signals with excerpt from **^{13}C{^{19}F,^{1}H} NMR** (151 MHz, CD_2Cl_2, 299K) spectrum of compound **3d**, asterisks denote some unidentified impurity.

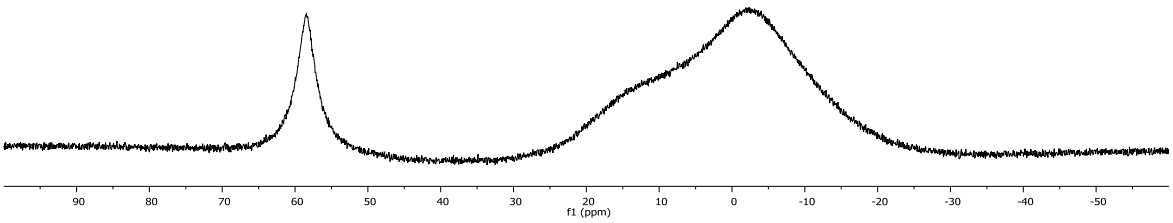


Figure S32: **^{11}B{^{1}H} NMR** (192 MHz, CD_2Cl_2, 299K) spectrum of compound **3d**.

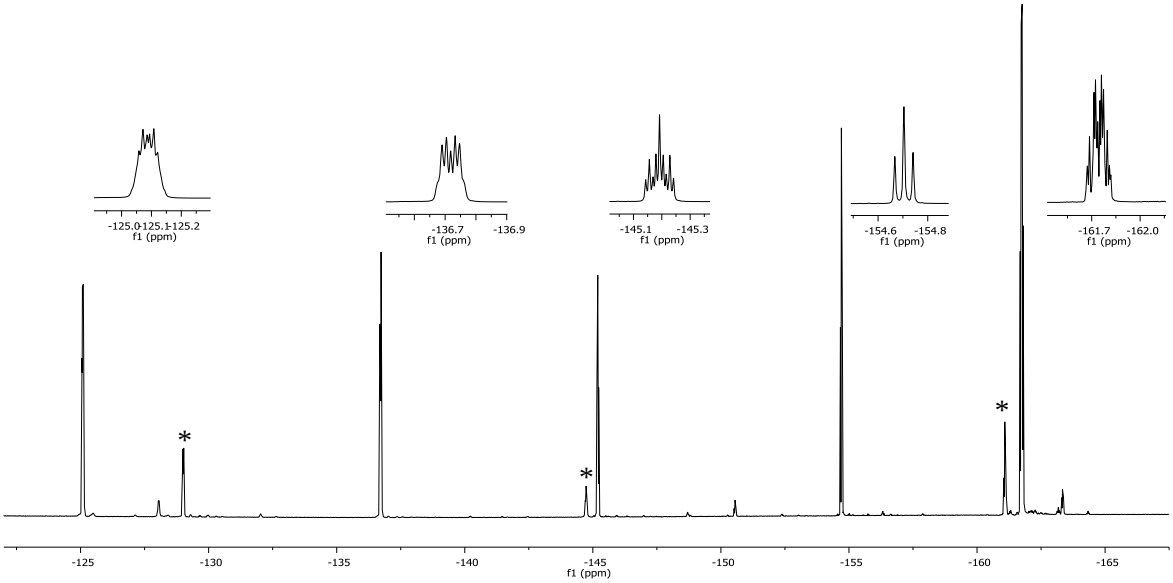


Figure S33: **^{19}F NMR** (564 MHz, CD_2Cl_2, 299 K) spectrum of compound **3d**, asterisks denote some unidentified impurity.

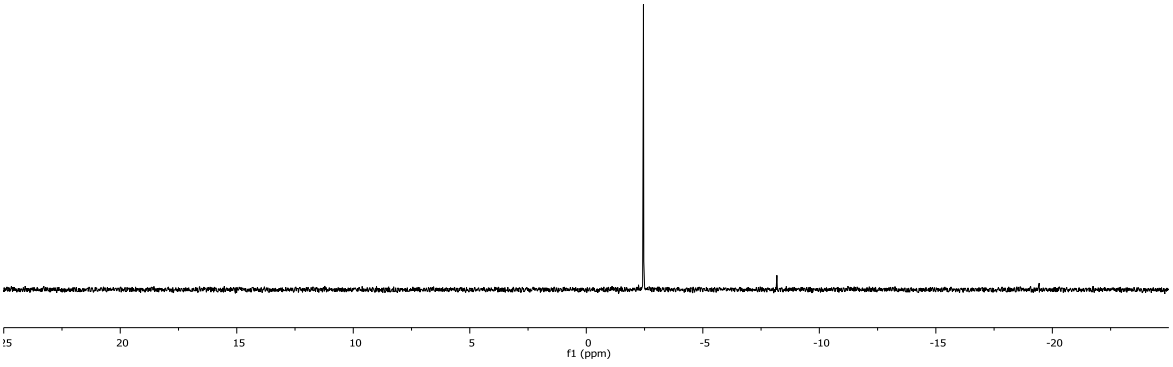
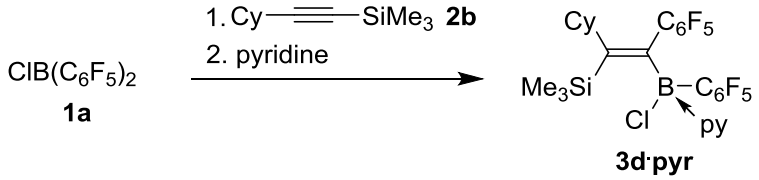


Figure S34: **^{29}Si{^{1}H} DEPT** (119 MHz, CD_2Cl_2, 299 K) spectrum of compound **3d**.

Preparation of compound 3d·pyr



Scheme S8

Solutions of CyC≡CSiMe$_3$ (**2b**) (90 mg, 0.5 mmol) in CH_2Cl_2 (3 ml) and ClB(C_6F_5)$_2$ (**1a**) (190 mg, 0.5 mmol) in CH_2Cl_2 (2 ml) were combined at room temperature. The reaction mixture turned yellow immediately and was allowed to stir at room temperature for one hour. Subsequently a solution of pyridine (48 mg, 0.6 mmol) was added (the color faded out immediately) and the mixture was stirred for 10 minutes at room temperature. All volatilities were removed in vacuo, the residue was taken up in a small amount of dichlormethane (ca 1 ml), layered with pentane (ca 3 ml) and placed in the freezer (-35°C). Over several days, colorless cystals of product appeared. They were isolated by decantation, washed with cold pentane and dried in vacuo. Product **3d·pyr** was isolated as 157 mg of white solid (0.245 mmol, 49% yield). [According to the obtained NMR spectra the product contained ca 10% of ClB(C_6F_5)$_2$·pyr (**1a·pyr**)]

Melting point: 149.3 °C.

Elementary analysis for $C_{28}H_{25}BClF_{10}NSi$ (639.8): calculated C 55.56, H 3.94, N 1.69; found C 55.33, H 3.75, N 2.05.

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 9.15 (br, 2H, 2,6-py), 8.19 (t, $^3J_{HH}$ = 8 Hz, 1H, 4-py), 7.70 (br, 2H, 3,5-py), [2.28 (br), 1.83-1.45 (br m), 1.01 (br)] (Cy), 0.11 (br, $SiMe_3$).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): [selected resonances] δ = 165.5 (br, SiC=), 147.3 (br, 2,6-py), 143.5 (4-py), 126.0 (br, 3,5-py), 123.3 (tm, $^2J_{FC}$ ≈ 21 Hz, *i*-$C_6F_5^C$), 120.8 (br, *i*-$C_6F_5^B$), 31.4 (br, Cy), 30.9 (br, Cy), 27.6 (br, Cy), 26.2 (br, Cy), 4.8 (br, $SiMe_3$).

^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = 3.2 ($\nu_{1/2}$ ≈ 220 Hz).

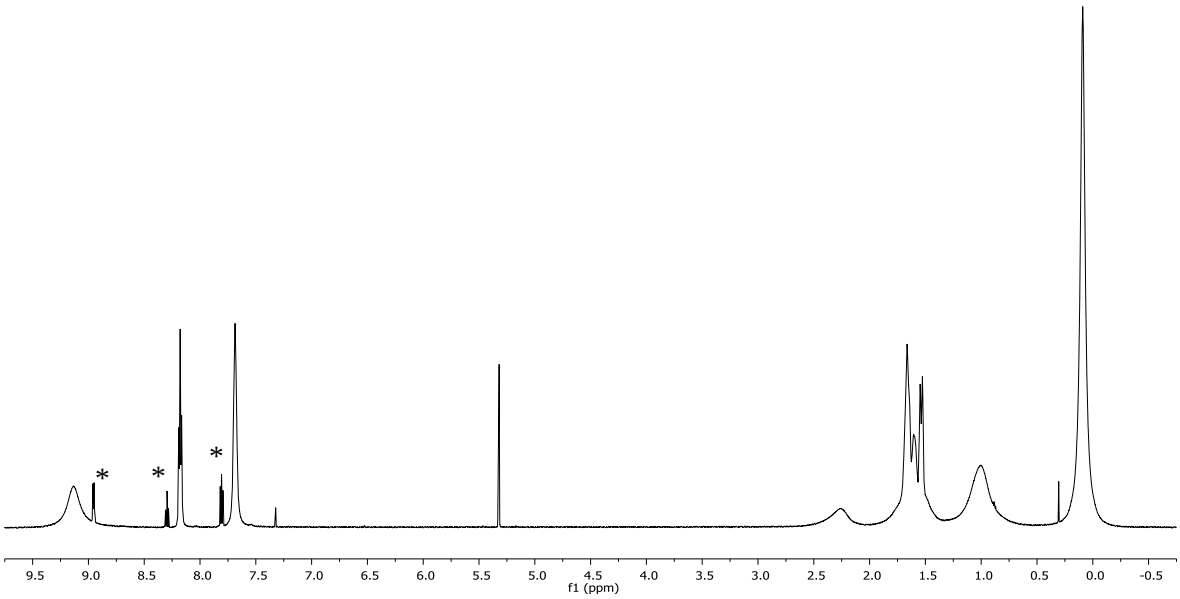


Figure S35: **^{1}H NMR** (600 MHz, CD_2Cl_2, 299K) spectrum of compound **3d·pyr**, asterisks denote signals due to $ClB(C_6F_5)_2$·pyr (**1a·pyr**).

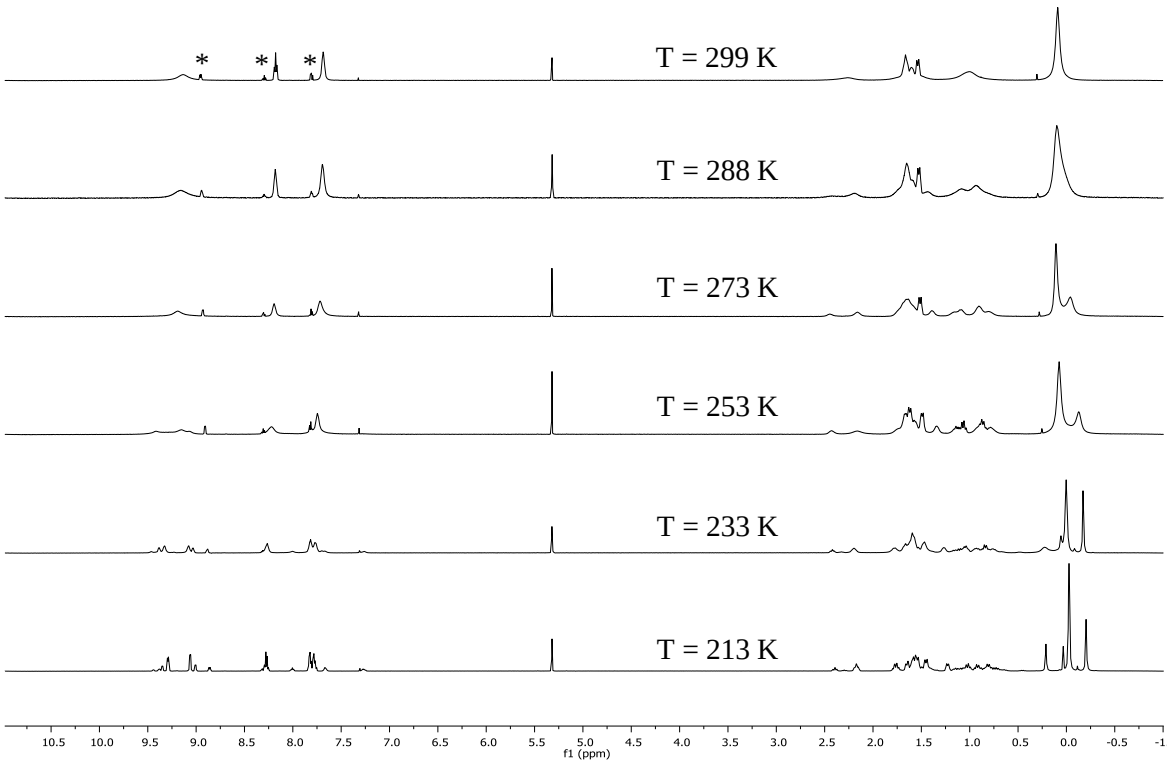


Figure S36: **^{1}H NMR** (600 MHz, CD_2Cl_2) spectrum of compound **3d·pyr** measured at various temperatures; asterisks denote signals due to $ClB(C_6F_5)_2$·pyr (**1a·pyr**).

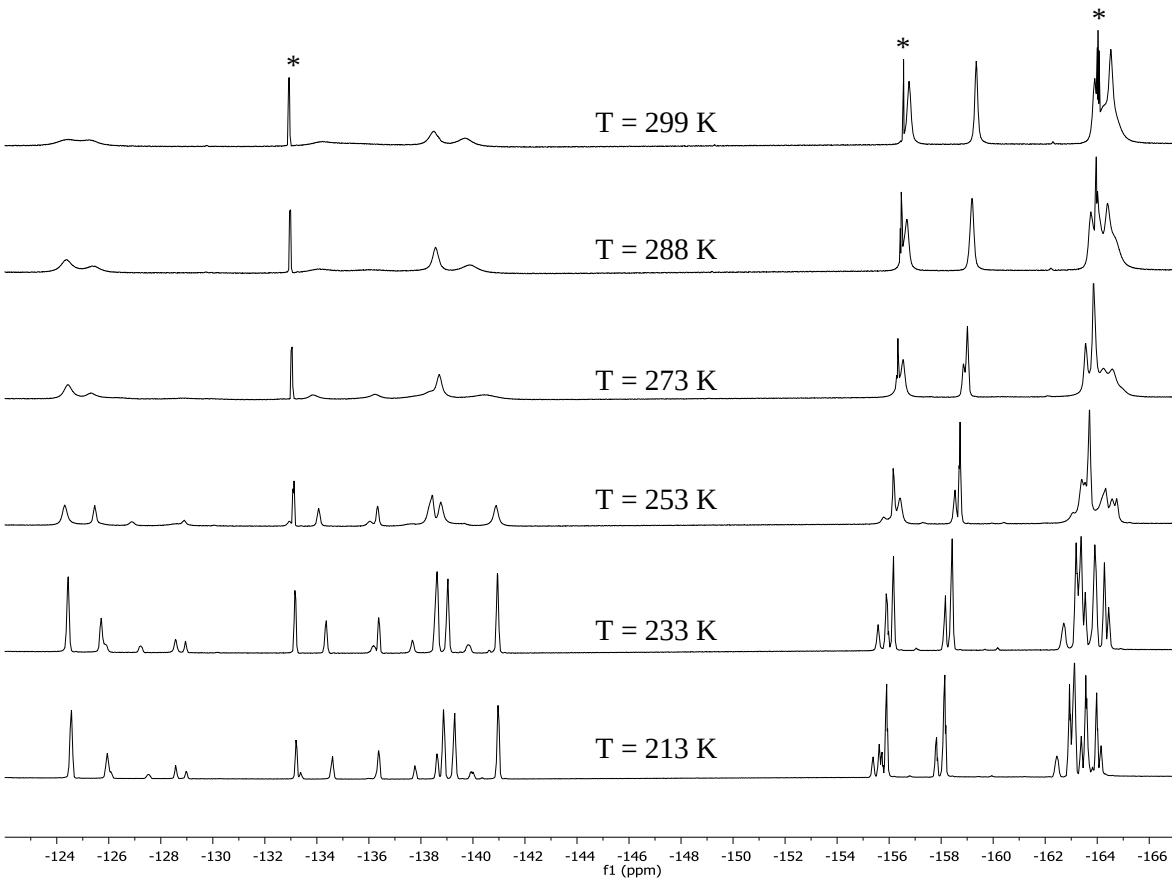


Figure S37: **^{19}F NMR** (564 MHz, CD_2Cl_2) spectrum of compound **3d·pyr** measured at various temperatures; asterisks denote signals due to $ClB(C_6F_5)_2$·pyr (**1a·pyr**).

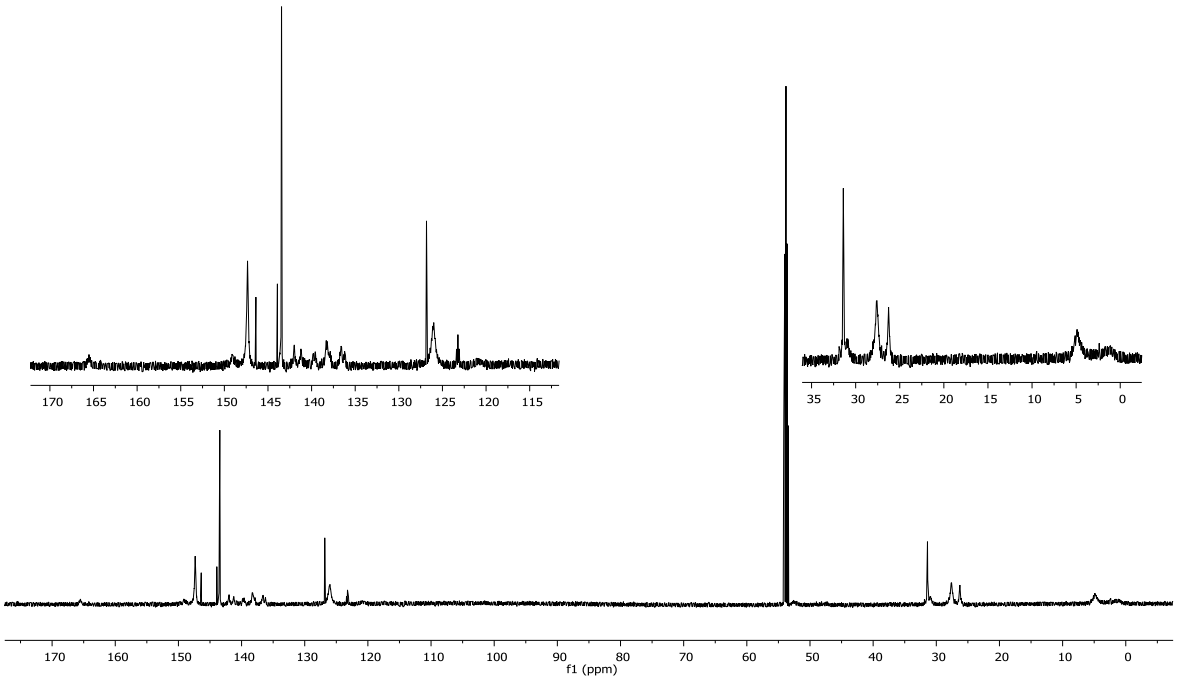


Figure S38: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, CD_2Cl_2, 299K) spectrum of compound **3d·pyr**.

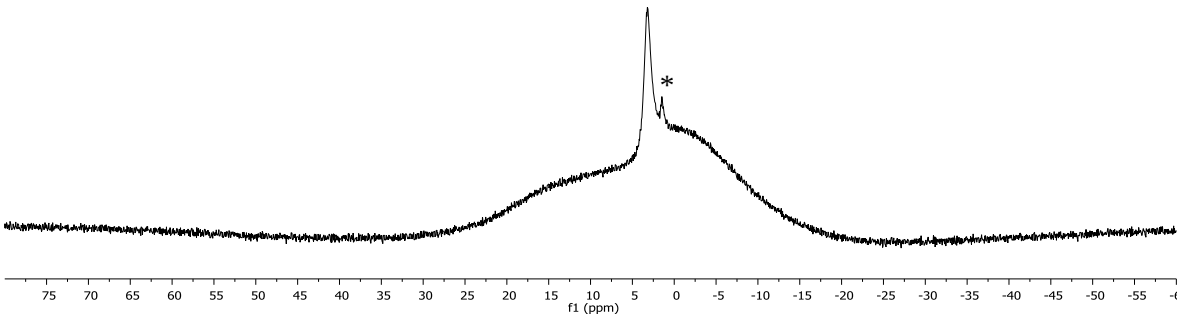


Figure S39: **$^{11}B\{^{1}H\}$ NMR** (192 MHz, CD_2Cl_2, 299K) spectrum of compound **3d·pyr,** asterisk denotes signals due to to $ClB(C_6F_5)_2$·pyr (**1a·pyr**).

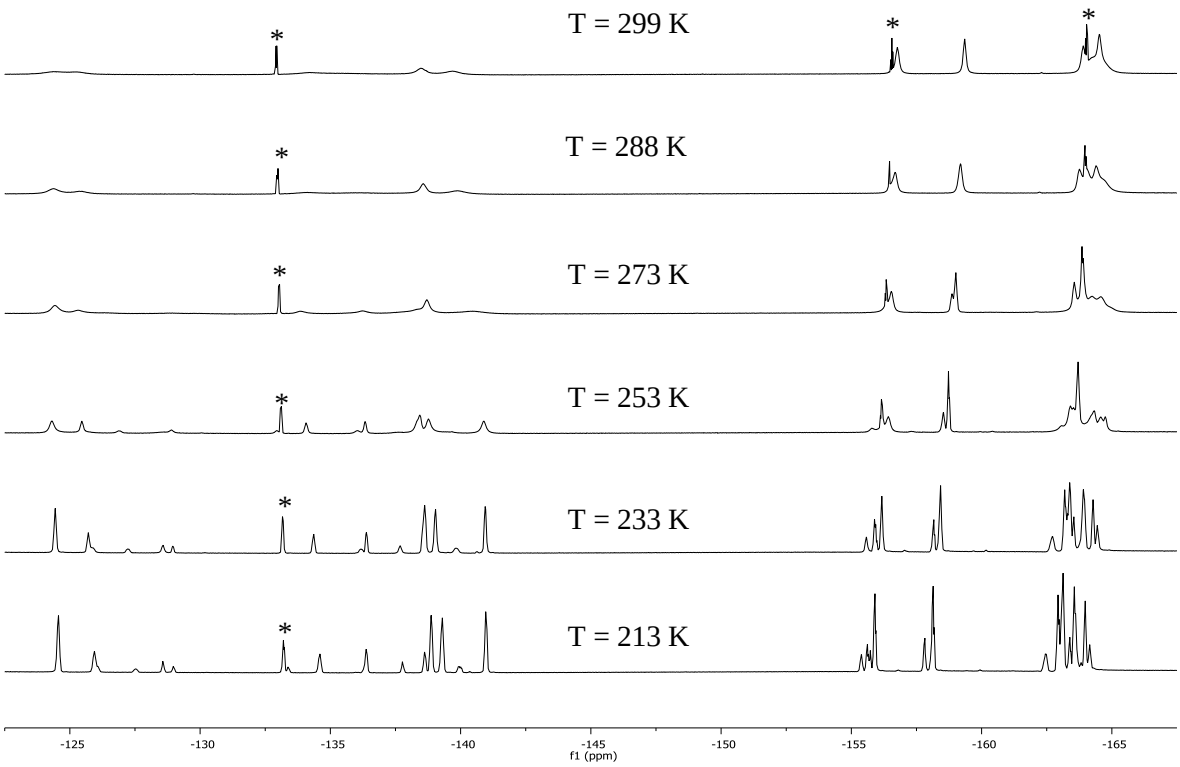


Figure S40: **^{19}F NMR** (564 MHz, CD_2Cl_2) spectrum of compound **3d·pyr,** measured at various temperatures; asterisks denote signals due to $ClB(C_6F_5)_2$·pyr (**1a·pyr**).

Crystals suitable for the X-ray crystal structure analysis were grown by slow diffusion of pentane into solution of **3d·pyr** in CH_2Cl_2 at -35°C.

X-ray crystal structure analysis of compound 3d·pyr (erk9208): A colorless prism-like specimen of $C_{28}H_{25}BClF_{10}NSi$, approximate dimensions 0.084 mm x 0.101 mm x 0.251 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 466 frames were collected. The total exposure time was 4.14 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 57071 reflections to a maximum θ angle of 26.37° (0.80 Å resolution), of which 13577 were independent (average redundancy 4.204, completeness = 99.8%, R_{int} = 7.35%, R_{sig} = 5.71%) and 9853 (72.57%) were greater than $2\sigma(F^2)$. The final cell constants of a = 12.1069(5) Å, b = 16.3988(6) Å, c = 19.2005(8) Å, α = 113.6920(10)°, β = 98.198(2)°, γ = 100.8220(10)°, volume = 3326.4(2) $Å^3$, are based upon the refinement of the XYZ-centroids of 9884 reflections above 20 σ(I) with 4.776° < 2θ < 53.99°. Data were corrected for absorption effects using the ♣-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.951. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9460 and 0.9810. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P*-1, with Z = 4 for the formula unit, $C_{28}H_{25}BClF_{10}NSi$. The final anisotropic full-matrix least-squares refinement on F^2 with 763 variables converged at R1 = 4.37%, for the observed data and wR2 = 9.83% for all data. The goodness-of-fit was 1.021. The largest peak in the final difference electron density synthesis was 0.421 $e^-/Å^3$ and the largest hole was -0.312 $e^-/Å^3$ with an RMS deviation of 0.058 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.278 g/cm^3 and F(000), 1304 e^-. CCDC Nr.: 1892608.

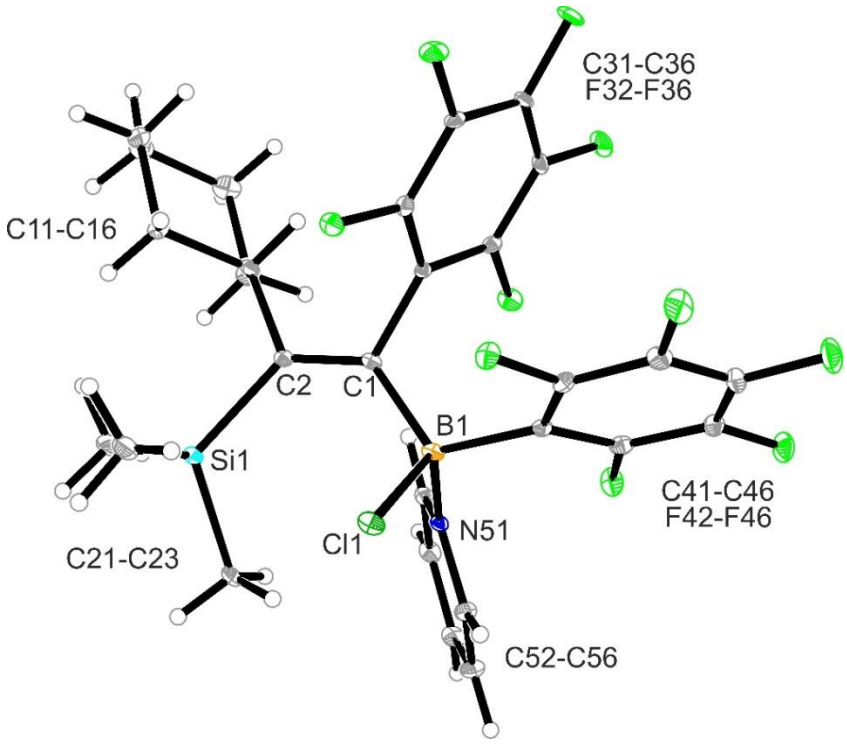
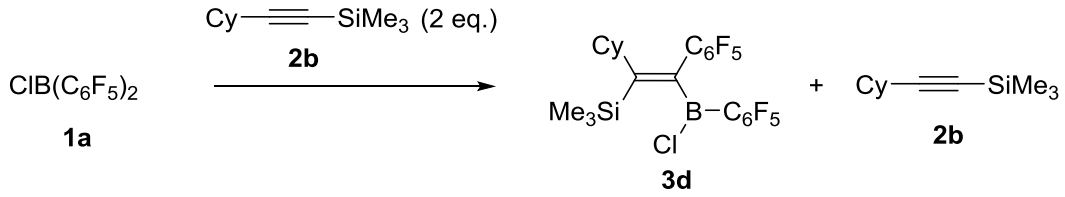


Figure S41: Crystal structure of compound **3d·pyr**, only one molecule ("A") of two found in the asymmetric unit is shown (thermal ellipsoids: 30% probability.)

Reaction of $ClB(C_6F_5)_2$ (1a) with two equivalents of $CyC{\equiv}CSiMe_3$ (2b)



Scheme S9

Solutions of $CyC{\equiv}CSiMe_3$ (36.0 mg, 0.2 mmol) in CD_2Cl_2 (0.3 ml) and $ClB(C_6F_5)_2$ (38.0 mg, 0.1 mmol) in CD_2Cl_2 (0.3 ml) were combined at room temperature and vigorously stirred for five minutes. The solution was transferred to a NMR tube, which was flame-sealed. Mesurement of ^{1}H and ^{19}F NMR spectra after 24 hours (stored at room temperature) revealed complete conversion to compound **3d** alongside with presence of one equivalent of unreacted $CyC{\equiv}CSiMe_3$.

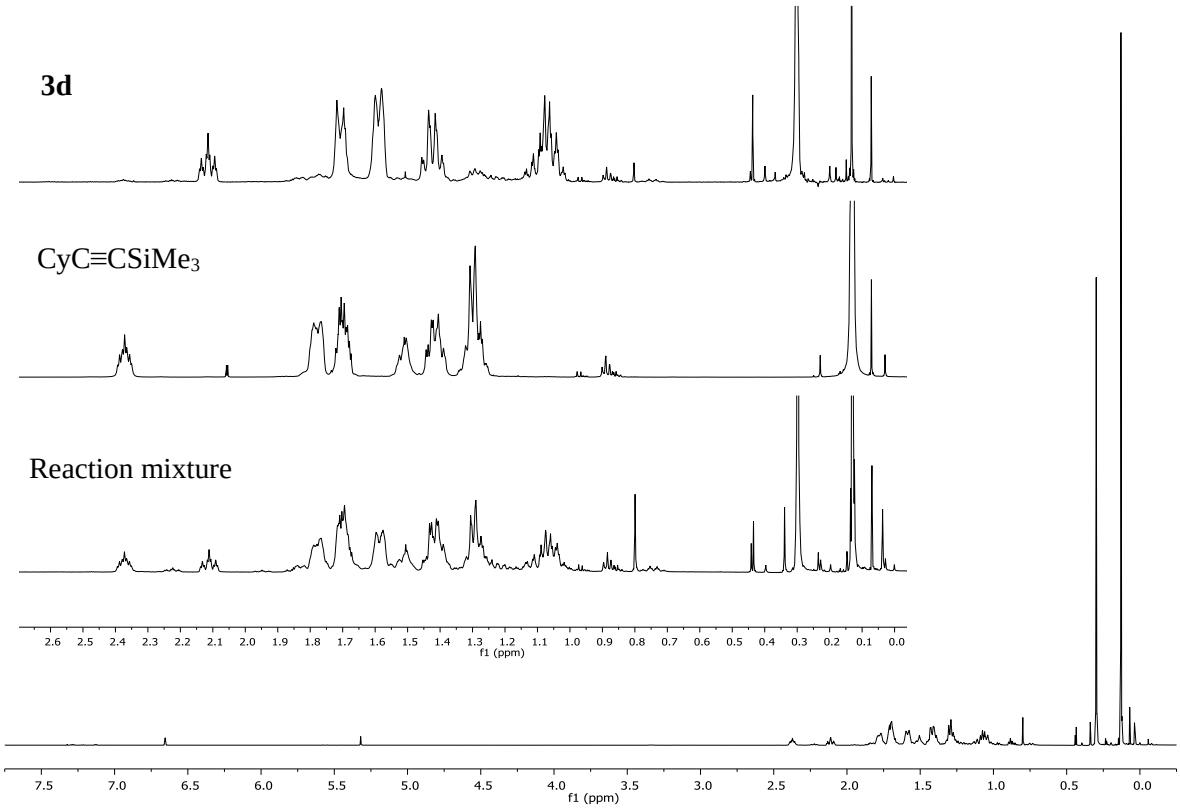
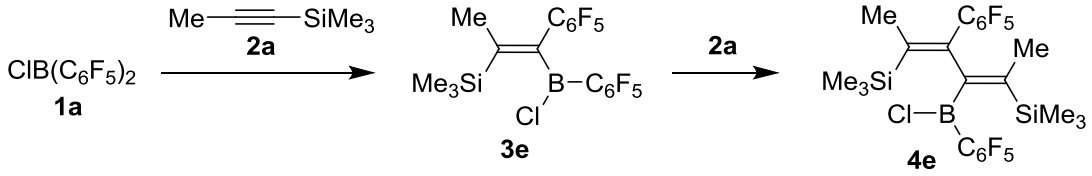


Figure S42: **^{1}H NMR** (600 MHz, CD_2Cl_2, 299K) spectrum of compound reaction mixture and detailed overview on the aliphatic region of compound **3d**, $CyC{\equiv}CSiMe_3$ and the reaction mixture.

Titration reaction of $ClB(C_6F_5)_2$ with $MeC{\equiv}CSiMe_3$



Scheme S10

Solutions of $ClB(C_6F_5)_2$ (38.0 mg, 0.1 mmol) in CD_2Cl_2 (0.3 ml) and $MeC{\equiv}CSiMe_3$ (11.2 mg, 0.1 mmol) in CD_2Cl_2 (0.2 mL) were combined in a NMR Young tube and shaken vigorously. Measurement of ^1H NMR spectra revealed complete conversion to the carboboration product within 10 minutes. The Young tube was taken back into the glovebox, and a solution of additional $MeC{\equiv}CSiMe_3$ (11.2 mg, 0.1 mmol) CD_2Cl_2 (in 0.3 mL) was added. The mixture was again shaken vigorously, stored at room temperature and the reaction progress was monitored by measurement of ^1H and ^{19}F NMR spectra (see below). After completion of the reaction (24 h, r.t.), an additional equivalent of $MeC{\equiv}CSiMe_3$ (11.2 mg, 0.1 mmol) in CD_2Cl_2 (0.3 mL) was added. No further reaction was observed even after heating to 60 °C for 24 h.

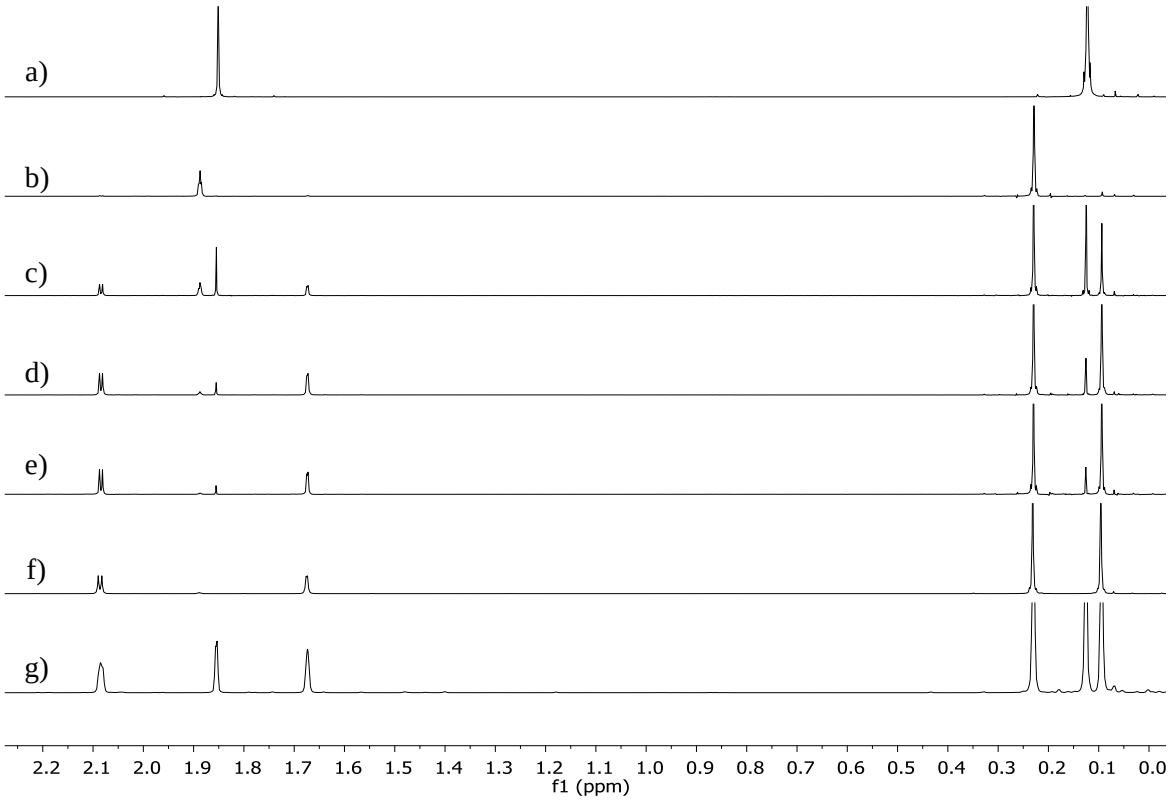


Figure S43: Monitoring of the reaction of $ClB(C_6F_5)_2$ with $MeC{\equiv}CSiMe_3$ by **^1H NMR** (600 MHz, CD_2Cl_2, 299 K) spectroscopy; a) $MeC{\equiv}CSiMe_3$; b) $MeC{\equiv}CSiMe_3$ + 1 equiv. $ClB(C_6F_5)_2$, reaction time ca 10 minutes (r.t); c) to previous mixture additional 1 equiv. of $MeC{\equiv}CSiMe_3$ added (reaction time ca 10 minutes at r.t), d) reaction time one hour (r.t), e) reaction time 3 hours (r.t), f) reaction time 24 hours (r.t), g) to previous mixture additional 1 equiv. of $MeC{\equiv}CSiMe_3$ was added and the mixture was heated to 60 °C for 24 hours.

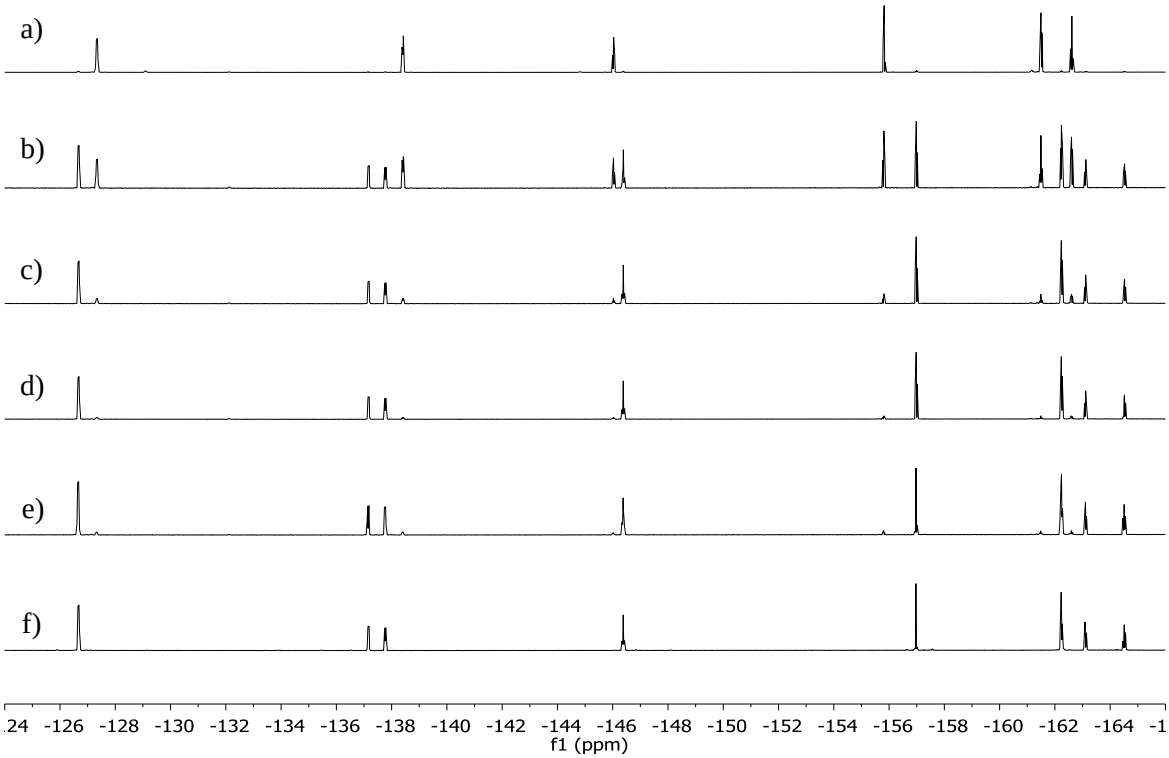
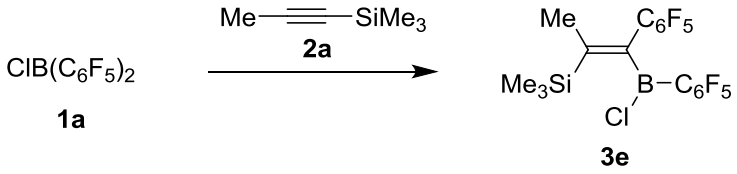


Figure S44: Monitoring of the reaction of $ClB(C_6F_5)_2$ and $MeC{\equiv}CSiMe_3$ by **^{19}F NMR** (564 MHz, CD_2Cl_2, 299K) spectroscopy; a) $MeC{\equiv}CSiMe_3$ + 1 equiv. $ClB(C_6F_5)_2$, reaction time ca 10 minutes (r.t); b) to previous mixture plus additional 1 equiv. of $MeC{\equiv}CSiMe_3$ added (reaction time ca 10 minutes at r.t.), c) reaction time one hour (r.t), d) reaction time 3 hours (r.t), e) reaction time 24 hours (r.t), f) to previous mixture additional 1 equiv. of $MeC{\equiv}CSiMe_3$ was added and the mixture was heated to 60°C for 24 hours.

Generation of compound 3e



Scheme S11

Solutions of $ClB(C_6F_5)_2$ (**1a**) (38.0 mg, 0.1 mmol) in CD_2Cl_2 (0.3 mL) and $MeC{\equiv}CSiMe_3$ (**2a**) (11.2 mg, 0.1 mmol) in CD_2Cl_2 (0.3 mL) were combined and stirred for 30 minutes at room temperature, then transferred to a NMR tube, which was flame-sealed. Following NMR measurement revealed complete conversion to product **3e**.

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 1.89 (t, J_{FH} = 1.6 Hz, 3H, Me), 0.23 (s, $^{2}J_{SiH}$ = 6.7 Hz, 9H, $SiMe_3$).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = 169.7 (SiC=), 149.0 (dm, $^{1}J_{FC}$ ≈ 252 Hz, *o*-$C_6F_5^B$), 144.8 (dm, $^{1}J_{FC}$ ≈ 260 Hz, *p*-$C_6F_5^B$), 143.9 (dm, $^{1}J_{FC}$ ≈ 248 Hz, *o*-$C_6F_5^C$), 140.9 (dm, $^{1}J_{FC}$ ≈ 255 Hz, *p*- $C_6F_5^C$), 138.5 (br, *C*C_6F_5), 138.1 (dm, $^{1}J_{FC}$ ≈ 250 Hz, *m*-$C_6F_5^C$), 137.9 (dm, $^{1}J_{FC}$ ≈ 250 Hz, *m*-$C_6F_5^B$), 115.4 (tm, $^{2}J_{FC}$ ≈ 24 Hz, *i*-*C*$_6F_5^C$), 112.1 (br, *i*-$C_6F_5^B$), 23.5 (Me), 0.4 ($^{1}J_{SiC}$ = 52.7 Hz, $SiMe_3$).

^{13}C{^{19}F,^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): selected resonances δ = 149.0 (*o*-$C_6F_5^B$), 144.8 (*p*-$C_6F_5^B$), 143.9 (*o*-$C_6F_5^C$), 140.9 (*p*-$C_6F_5^C$), 138.1 (*m*-$C_6F_5^C$), 137.9 (*m*-$C_6F_5^B$), 115.4 (*i*-$C_6F_5^C$).

^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = 59.5 ($\nu_{1/2}$ ≈ 500 Hz).

^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = [-127.3 (m, 2F, *o*), -146.0 (tt, $^{3}J_{FF}$ = 20 Hz, $^{4}J_{FF}$ = 6 Hz, 1F, *p*), -161.5 (m, 2F, *m*)]($C_6F_5^B$, [$\Delta\delta^{19}F_{m,p}$ = 15.5]), [-138.4 (m, 2F, *o*), -155.8 (t, J_{FF} = 21 Hz, 1F, *p*), -162.6 (m, 2F, *m*)](C-C_6F_5, [$\Delta\delta^{19}F_{m,p}$ = 6.8]).

^{29}Si{^{1}H} DEPT (119 Hz, CD_2Cl_2, 299 K): δ = -1.9 ($\nu_{1/2}$ ≈ 1 Hz).

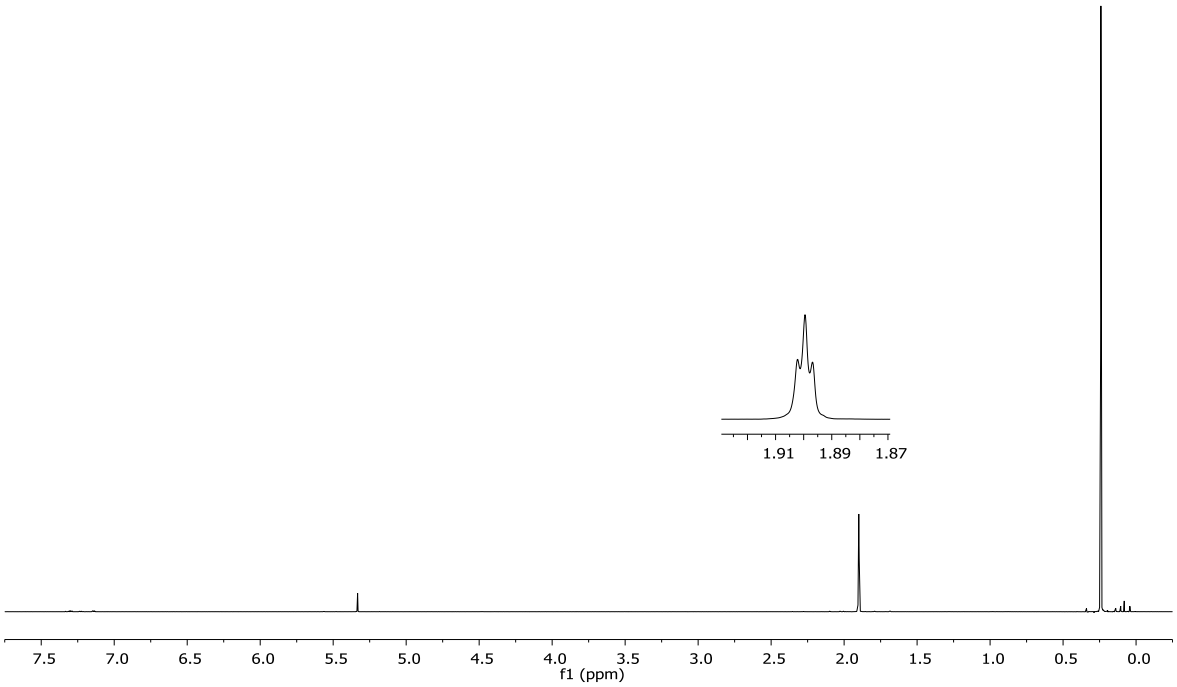


Figure S45: **^{1}H NMR** (600 MHz, CD_2Cl_2, 299 K) spectrum of compound **3e**.

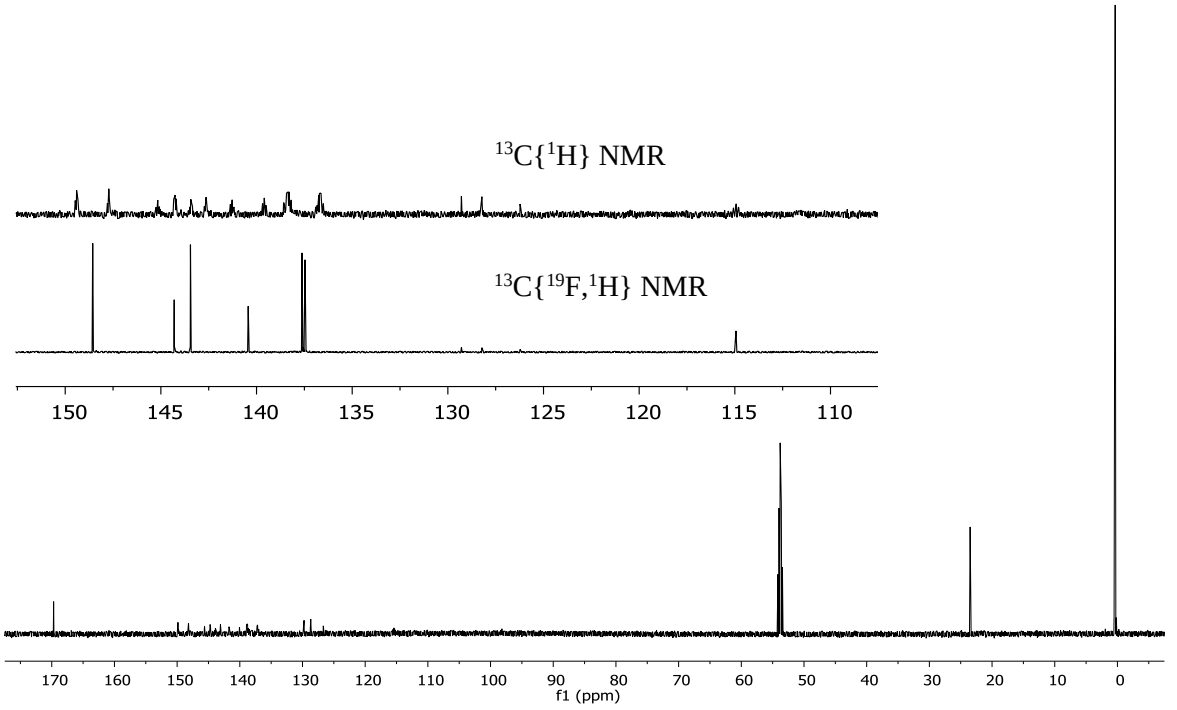


Figure S46: **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2, 299 K) spectrum and detailed overview of the aromatic signals with excerpt from **^{13}C{^{19}F,^{1}H} NMR** (151 MHz, CD_2Cl_2, 299 K) spectrum of compound **3e**.

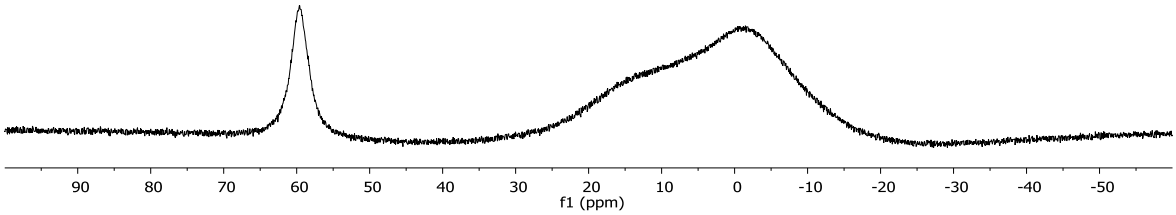


Figure S47: **$^{11}B\{^{1}H\}$ NMR** (192 MHz, CD_2Cl_2, 299 K) spectrum of compound **3e**.

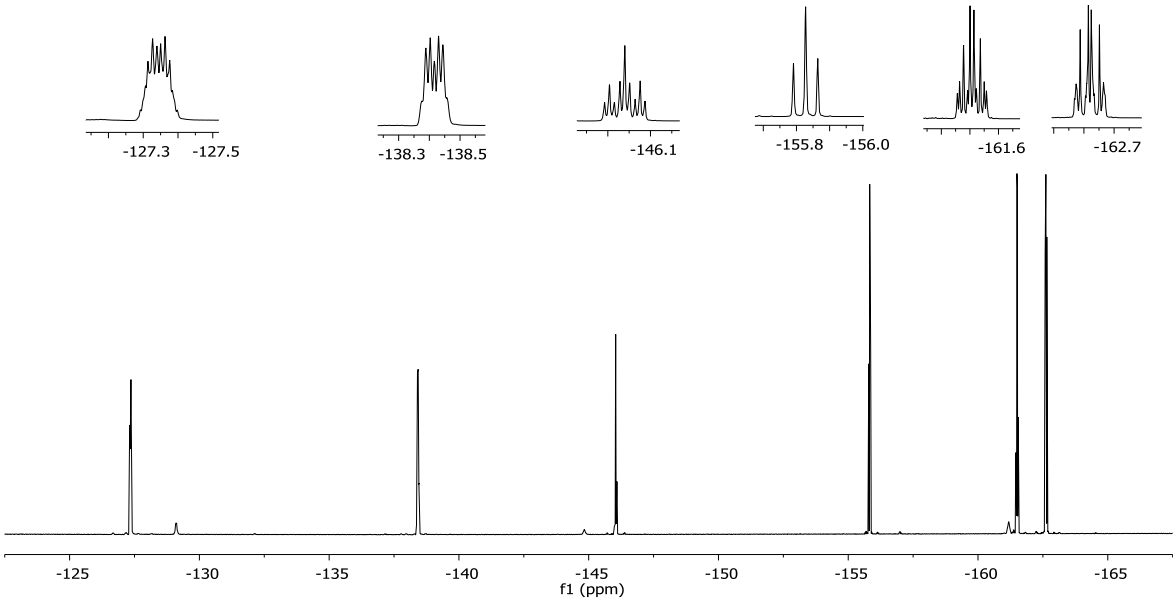


Figure S48: **^{19}F NMR** (564 MHz, CD_2Cl_2, 299 K) spectrum of compound **3e**.

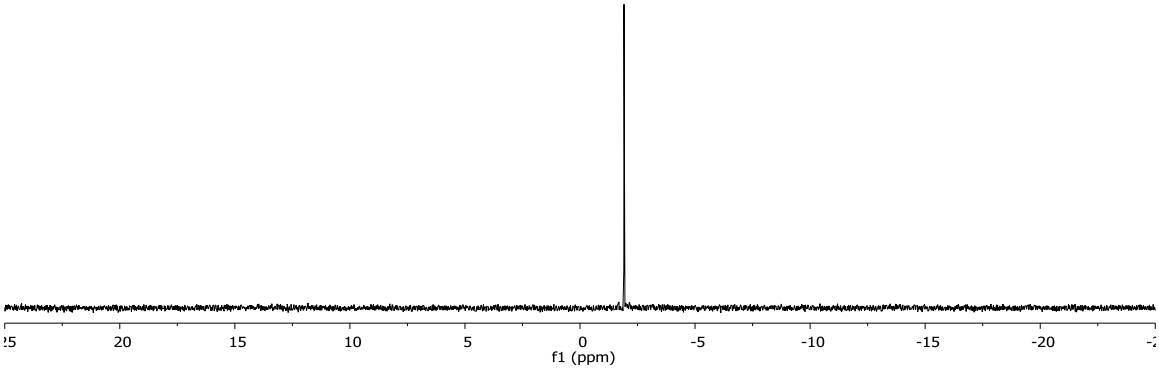
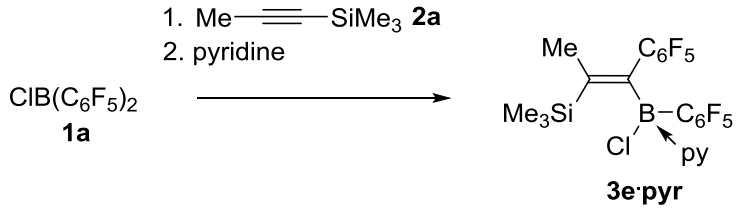


Figure S49: **$^{29}Si\{^{1}H\}$ DEPT** (119 MHz, CD_2Cl_2, 299 K) spectrum of compound **3e**.

Preparation of compound 3e·pyr



Scheme S12

Solutions of $ClB(C_6F_5)_2$ (76.2 mg, 0.2 mmol) in CH_2Cl_2 (2 ml) and $MeC{\equiv}CSiMe_3$ (22.9 mg, 0.2 mmol) in CH_2Cl_2 (2 ml) were combined and stirred for 2.5 hours at room temperature. Subsequently a solution of pyridine (23.7 mg, 0.3 mmol) in CH_2Cl_2 (1 ml) was added. The resulting colorless mixture was stirred for 15 minutes at temperature, then volatilities were removed in vacuo, the residue washed with a small amount of pentane (2x 1 ml) and dried in vacuo. Product **3e·pyr** was isolated as a white solid (62.7 mg, 0.11 mmol, yield 55%).

Melting point: 190.6 °C.

HRMS for $C_{23}H_{17}BClF_{10}NNaSi$ [$(M + Na)^+$]: calculated 594.0650; found 594.0647.

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 9.19 (br, 2H, 2,6-py), 8.21 (tt, $^3J_{HH}$= 7.7 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, 4-py), 7.73 (m, 2H, 3,5-py), 1.73 (s, 3H, Me), -0.02 (s, $^2J_{SiH}$ = 6.5 Hz, 9H, $SiMe_3$).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ [seleced resonances] = 156.4 (br, SiC=), 147.6 (2,6-py), 143.5 (4-py), 142.3 (br, =*C*C_6F_5), 125.7 (3,5-py), 24.0 (Me), 0.7 ($^1J_{SiC}$ = 52.7 Hz, $SiMe_3$).

^{13}C{^{19}F,^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): [selected resonances] δ = 148.0 (br, 2C, C_6F_5), 142.8 (1C, C_6F_5), 142.7 (1C, C_6F_5), 140.3 (1C, C_6F_5), 139.0 (1C, C_6F_5), 137.7 (1C, C_6F_5), 137.3 (br, 2C, C_6F_5), 137.2 (1C, C_6F_5), 121.9 (1C, *i*-$C_6F_5^C$), *i*-$C_6F_5^B$ not observed.

^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = 3.1 ($\nu_{1/2} \approx 140$ Hz).

^{19}F NMR (564 MHz, CD_2Cl_2, 213 K): δ = [-125.3 (m, 1F, *o*-C_6F_5), -139.9 (m, 1F, *o*-C_6F_5), -156.0 (t, J_{FF} = 21 Hz, 1F, *p*-C_6F_5), -163.2 (m, 1F, *m*-C_6F_5), -164.1 (m, 1F, *m*-C_6F_5)] ($\Delta\delta^{19}F_{m,p}$ = 7.2, 8.1), [-139.2 (m, 1F, *o*-C_6F_5), -141.3 (m, 1F, *o*-C_6F_5), -158.3 (t, J_{FF} = 22 Hz, 1F, *p*-C_6F_5), -163.2 (m, 1F, *m*-C_6F_5), -164.0 (m, 1F, *m*-C_6F_5)] ($\Delta\delta^{19}F_{m,p}$ = 4.9, 5.7).

^{29}Si{^{1}H} DEPT (119 Hz, CD_2Cl_2, 299 K): δ = -4.7 ($\nu_{1/2} \approx 2$ Hz).

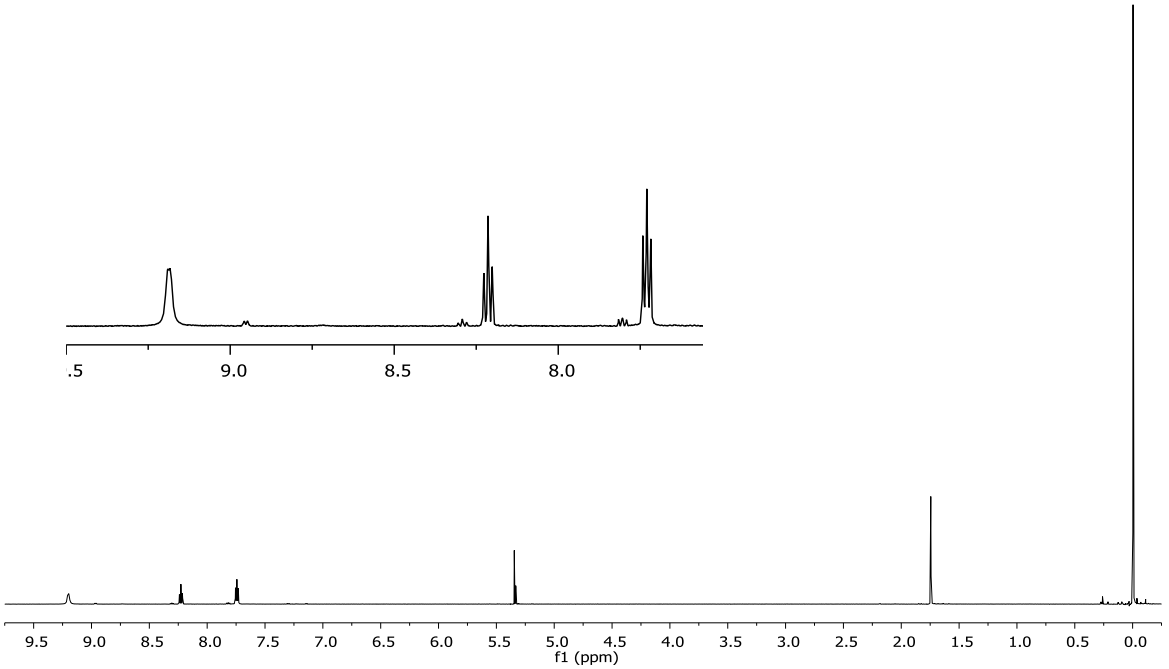


Figure S50: **^{1}H NMR** (600 MHz, CD_2Cl_2, 299K) spectrum of compound **3e·pyr**

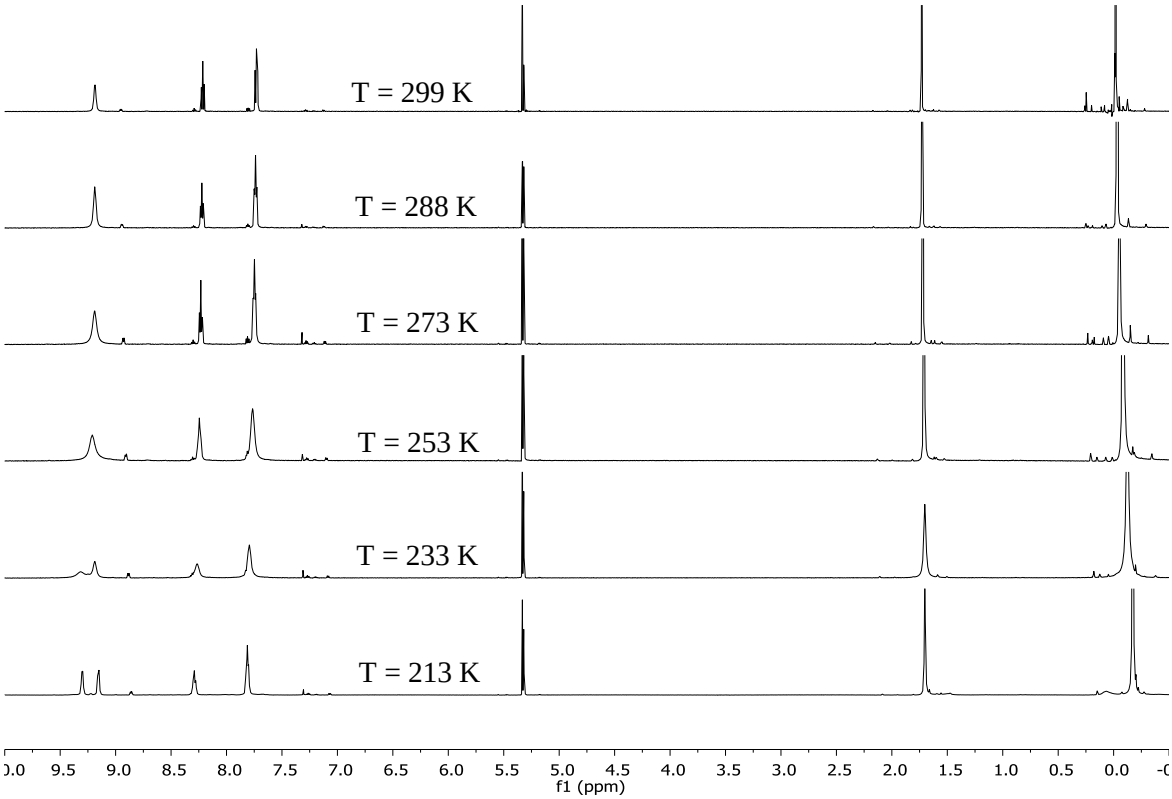


Figure S51: **^{1}H NMR** (600 MHz, CD_2Cl_2) spectra of compound **3e·pyr** measured at various temperatures.

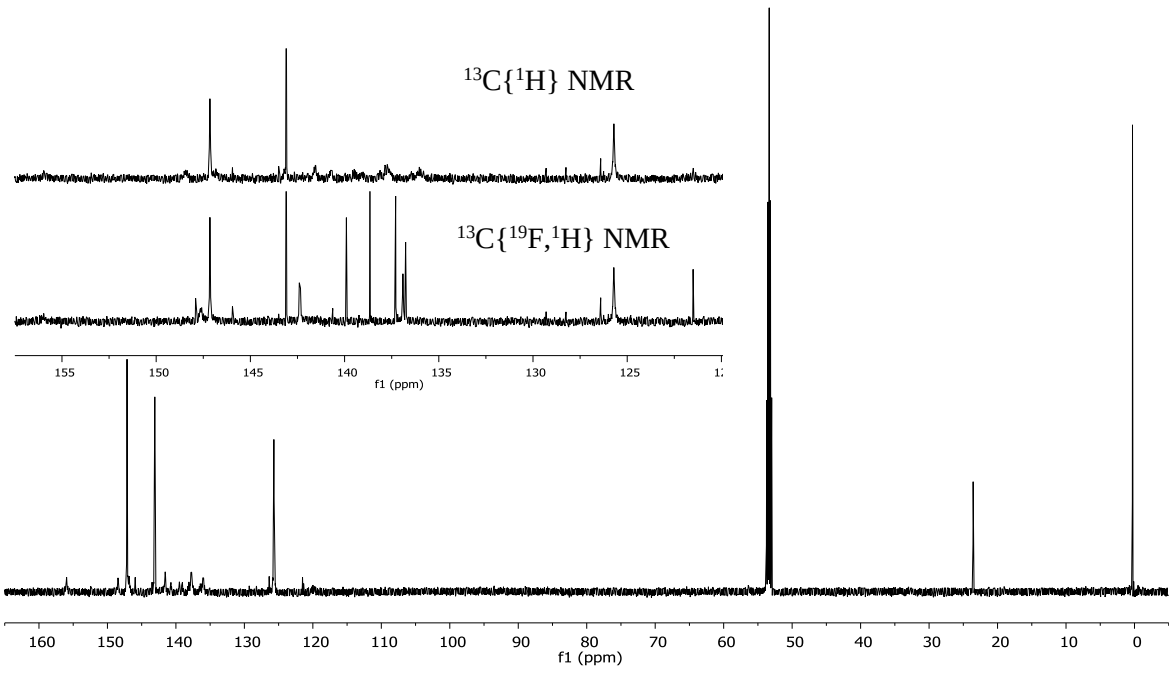


Figure S52: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, CD_2Cl_2, 299K) spectrum and detailed overview of the aromatic signals with excerpt from **$^{13}C\{^{19}F,^{1}H\}$ NMR** (151 MHz, CD_2Cl_2, 299K) spectrum of compound **3e·pyr**.

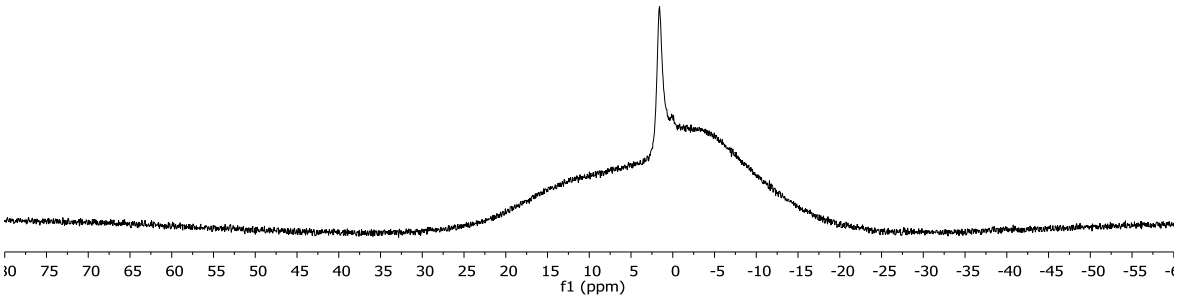


Figure S53: **$^{11}B\{^{1}H\}$ NMR** (192 MHz, CD_2Cl_2, 299 K) spectrum of compound **3e·pyr**.

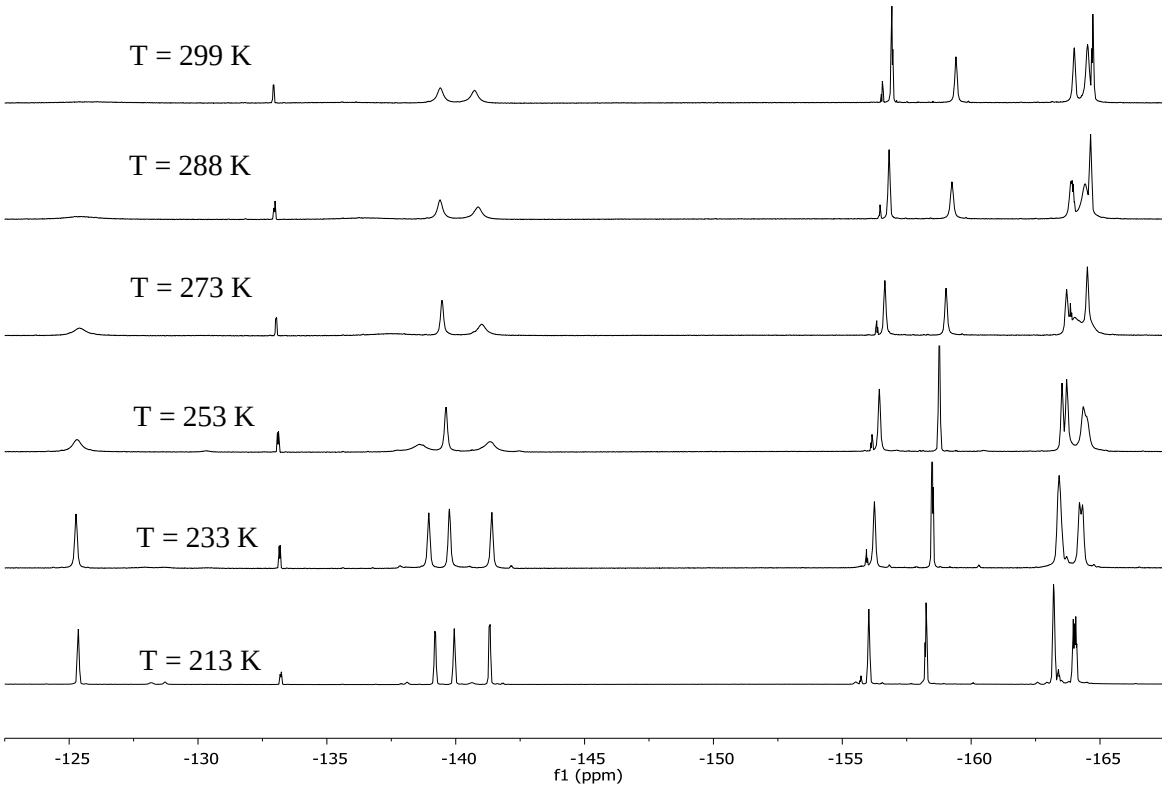


Figure S54: **^{19}F NMR** (564 MHz, CD_2Cl_2) spectra of compound **3e·pyr**, measured at various temperatures.

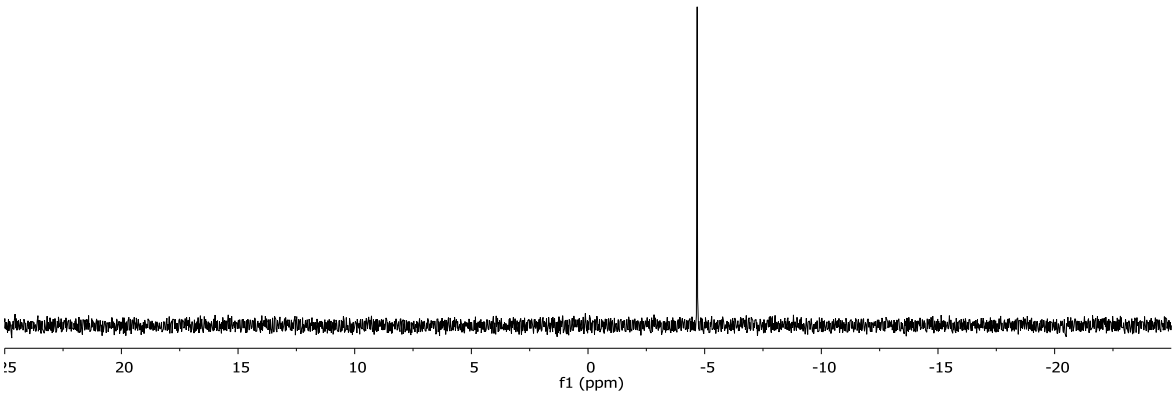


Figure S55: **^{29}Si{^{1}H} DEPT** (119 MHz, CD_2Cl_2, 299 K) spectrum of compound **3e·pyr**.

Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane into a solution of **3e·pyr** in dichlormethane at room temperature.

X-ray crystal structure analysis of compound 3e·pyr (erk9234): A colorless plate-like specimen of $C_{23}H_{17}BClF_{10}NSi$, approximate dimensions 0.060 mm x 0.100 mm x 0.200 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1527 frames were collected. The total exposure time was 19.61 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 26439 reflections to a maximum θ angle of 66.76° (0.84 Å resolution), of which 4292 were independent (average redundancy 6.160, completeness = 98.5%, R_{int} = 4.91%, R_{sig} = 3.11%) and 3736 (87.05%) were greater than $2\sigma(F^2)$. The final cell constants of a = 27.7237(7) Å, b = 8.5787(2) Å, c = 21.3851(6) Å, β = 105.2940(10)°, volume = 4906.0(2) $Å^3$, are based upon the refinement of the XYZ-centroids of 9191 reflections above 20 σ(I) with 8.573° < 2θ < 133.0°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.793. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6150 and 0.8550. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *C*2/*c*, with Z = 8 for the formula unit, $C_{23}H_{17}BClF_{10}NSi$. The final anisotropic full-matrix least-squares refinement on F^2 with 338 variables converged at R1 = 3.34%, for the observed data and wR2 = 8.61% for all data. The goodness-of-fit was 1.059. The largest peak in the final difference electron density synthesis was 0.267 $e^-/Å^3$ and the largest hole was -0.296 $e^-/Å^3$ with an RMS deviation of 0.053 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.548 g/cm^3 and F(000), 2304 e^-. CCDC Nr.: 1892609.

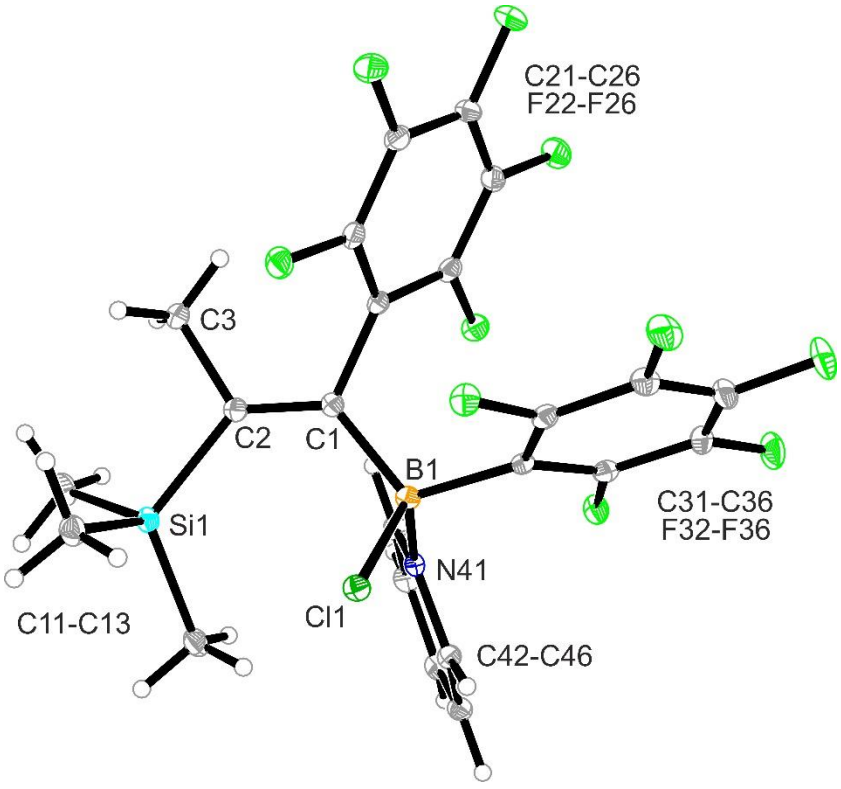
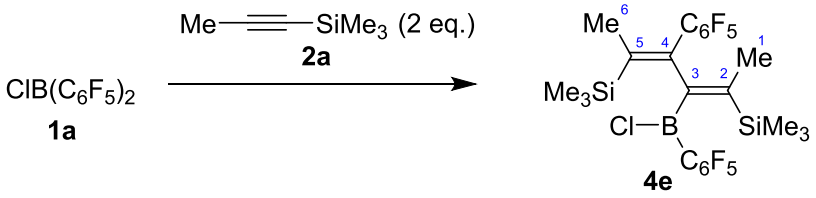


Figure S56: Crystal structure of compound **3e·pyr** (thermal ellipsoids: 30% probability).

Generation / preparation of compound 4e



Scheme S13

In situ experiment: Solutions of $ClB(C_6F_5)_2$ (38.0 mg, 0.1 mmol) in CD_2Cl_2 (0.3 mL) and $MeC{\equiv}CSiMe_3$ (22.4 mg, 0.2 mmol) in CD_2Cl_2 (0.2 mL) were combined, vigorously shaken and then placed in a NMR tube which was flame sealed. The mixture was stored for 20 hours at room temperature, consequently NMR spectra were measured revealing complete conversion to product **4e**.

Preparative experiment: Solutions of $ClB(C_6F_5)_2$ (380 mg, 1.0 mmol) in CH_2Cl_2 (3 mL) and $MeC{\equiv}CSiMe_3$ (224 mg, 2.0 mmol) in CH_2Cl_2 (3 mL) were combined and allowed to stir overnight (18 h) at room temperature. Subsequently, all volatilities were evaporated *in vacuo*, the residue was taken up in pentane (ca 3 mL), filtered and stored at -35 °C. Over several days, colorless crystals of product appeared. Product **4e** was isolated by decantation and drying *in vacuo* as a white solid (322 mg, 0.53 mmol, 53% isolated yield).

NMR data of material obtained thereof were the same as for in situ generated sample.

Melting point: 68.7 °C

Elementary analysis for $C_{24}H_{24}BClF_{10}NSi_2$ (604.8): calculated C 47.65, H 4.00; found C 47.69, H 3.80

NMR characterisation for in situ generated sample:

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 2.09 (d, J_{FH} = 3.6 Hz, 3H, Me1), 1.67 (d, J_{FH} = 3.6 Hz, 3H, Me^6), 0.23 (s, $^{2}J_{SiH}$ = 6.6 Hz, 9H, $SiMe_3$), 0.10 (s, $^{2}J_{SiH}$ = 6.5 Hz, 9H, $SiMe_3$).

^{1}H{^{19}F} NMR (600 MHz, CD_2Cl_2, 299 K): [selected resonances] δ = 2.09 (s, 3H, Me^1), 1.67 (s, 3H, Me^6).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = 156.5 (C^2), 152.6 (br, C^3), 149.3 (C^5), 148.9 (dm, $^{1}J_{FC}$ ≈ 260 Hz, *o*-$C_6F_5^B$), 145.0 (dm, $^{1}J_{FC}$ ≈ 240 Hz, *o*-$C_6F_5^C$), 144.4 (dm, $^{1}J_{FC}$ ≈ 260 Hz, *p*-$C_6F_5^B$), 143.5 (dm, $^{1}J_{FC}$ ≈ 240 Hz, *o*-$C_6F_5^C$), 140.5 (dm, $^{1}J_{FC}$ ≈ 255 Hz, *p*-$C_6F_5^C$), 138.1 (dm, $^{1}J_{FC}$ ≈ 250 Hz, *m*-$C_6F_5^B$), 137.6 (dm, $^{1}J_{FC}$ ≈ 252 Hz, *m*-$C_6F_5^C$), 137.3 (dm, $^{1}J_{FC}$ ≈ 252 Hz, *m*-$C_6F_5^C$), 130.8 (C^4), 116.1 (tm, $^{2}J_{FC}$ ≈ 21 Hz, *i*-$C_6F_5^C$), 113.2 (br, *i*-$C_6F_5^B$), 21.3 (d, J_{FC} = 8 Hz, Me^1), 20.5 (Me^6), 0.1 ($^{1}J_{SiC}$ = 52.8 Hz, $C^5Si\mathit{Me}_3$), -0.2 ($^{1}J_{SiC}$ = 53.1 Hz, $C^2Si\mathit{Me}_3$).

^{13}C{^{19}F,^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): [selected resonances] δ = 148.9 (*o*-$C_6F_5^B$), 145.0 (*o*-$C_6F_5^C$), 144.4 (*p*-$C_6F_5^B$), 143.5 (*o*-$C_6F_5^C$), 140.5 (*p*-$C_6F_5^C$), 138.1 (*m*-$C_6F_5^B$), 137.6 (*m*-$C_6F_5^C$), 137.3 (*m*-$C_6F_5^C$), 116.1 (*i*-$C_6F_5^C$), 21.3 (Me^1).

^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = 60.1 ($\nu_{1/2}$ ≈ 680 Hz).

^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = [-126.7 (m, 2F, *o*), -146.4 (tt, $^3J_{FF}$ = 21 Hz, $^4J_{FF}$ = 6 Hz, 1F, *p*), -162.2 (m, 2F, *m*)](B-C_6F_5, [$\Delta\delta^{19}F_{m,p}$ = 15.8]), [-137.2 (m, 1F, *o*), -137.8 (m, 1F, *o*), -157.0 (t, J_{FF} = 21 Hz, 1F, *p*), -163.1 (m, 1F, *m*), -164.5 (m, 1F, *m*)](C-C_6F_5, [$\Delta\delta^{19}F_{m,p}$ = 6.1, 7.5]).

^{29}Si{^{1}H} DEPT (99 Hz, CD_2Cl_2, 299 K): δ = -3.6 ($\nu_{1/2}$ ≈ 1 Hz, $^2SiMe_3$), -3.6 ($\nu_{1/2}$ ≈ 1 Hz, $^5SiMe_3$).

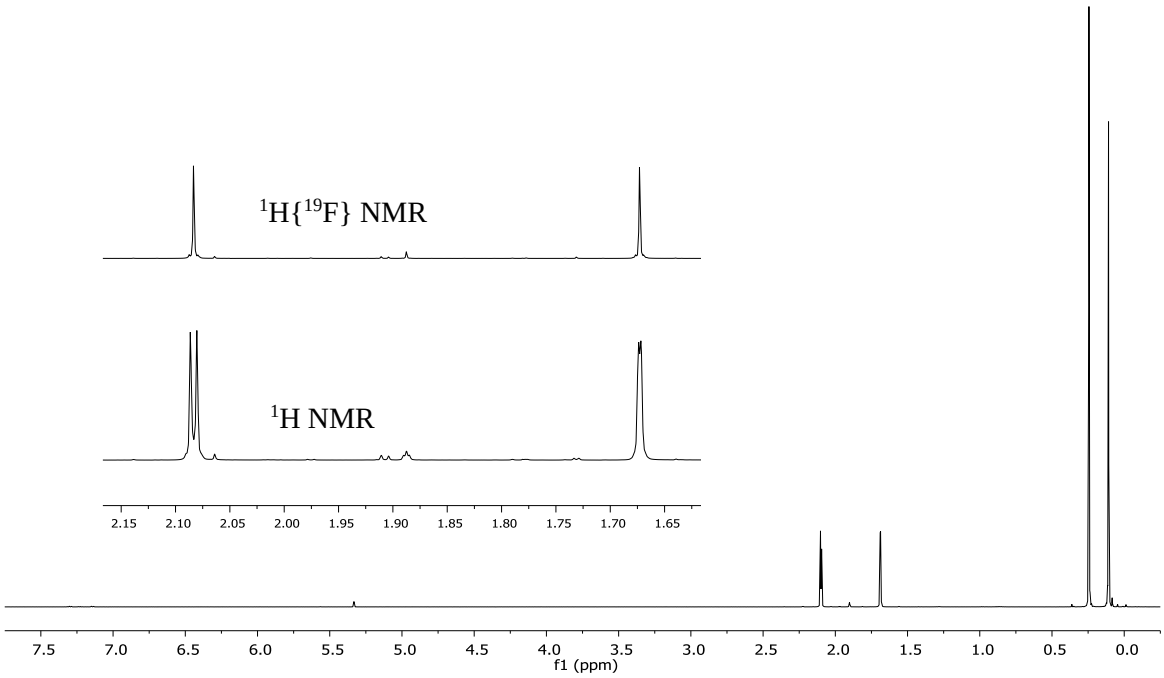


Figure S57: **^{1}H NMR** (600 MHz, CD_2Cl_2, 299 K) spectrum and excerpt from **^{1}H{^{19}F} NMR** (600 MHz, CD_2Cl_2, 299K) spectrum of compound **4e**.

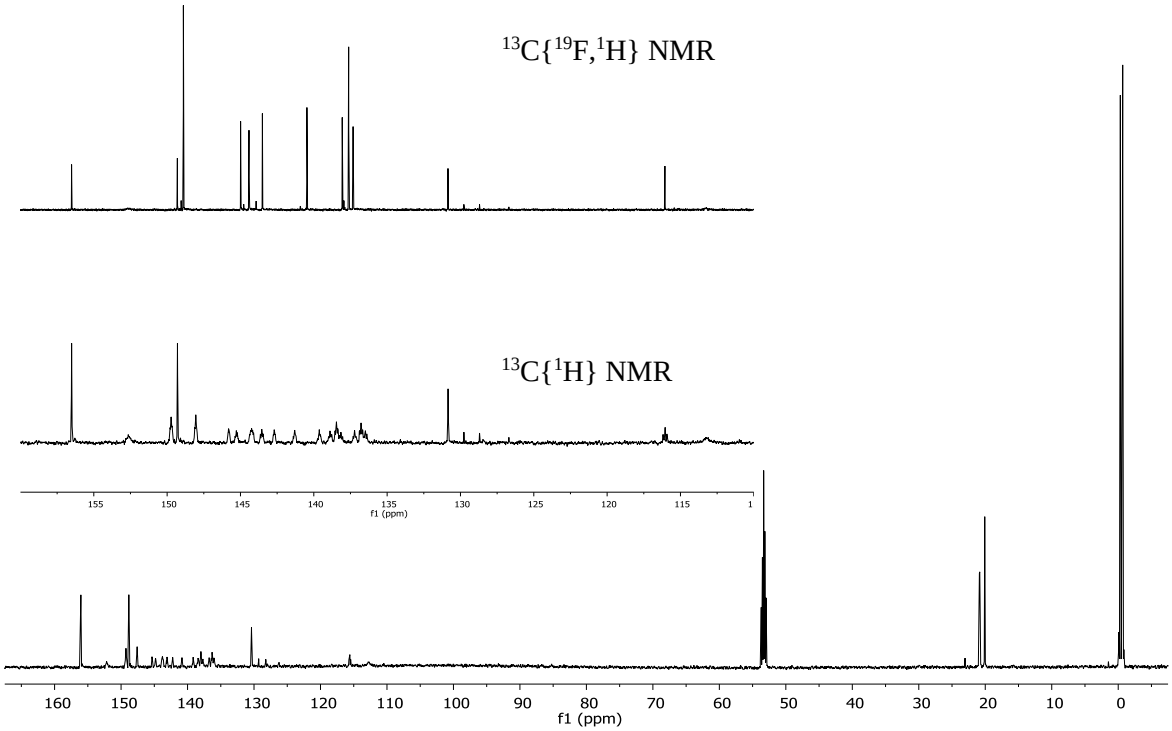


Figure S58: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, CD_2Cl_2, 299 K) spectrum and detailed overview of aromatic signals with excerpt from **$^{13}C\{^{19}F,^{1}H\}$ NMR** (151 MHz, CD_2Cl_2, 299 K) spectrum of compound **4e**.

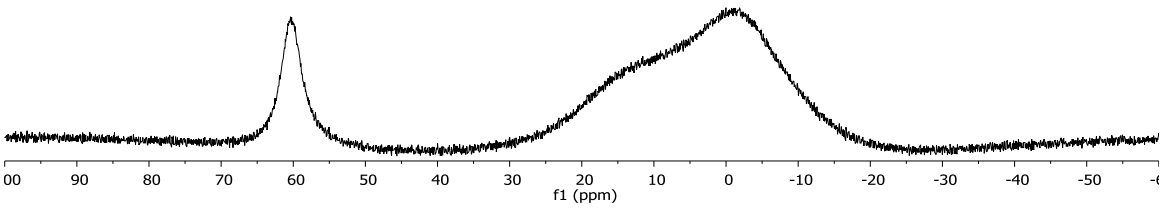


Figure S59: **$^{11}B\{^{1}H\}$ NMR** (192 MHz, CD_2Cl_2, 299K) spectrum of compound **4e**.

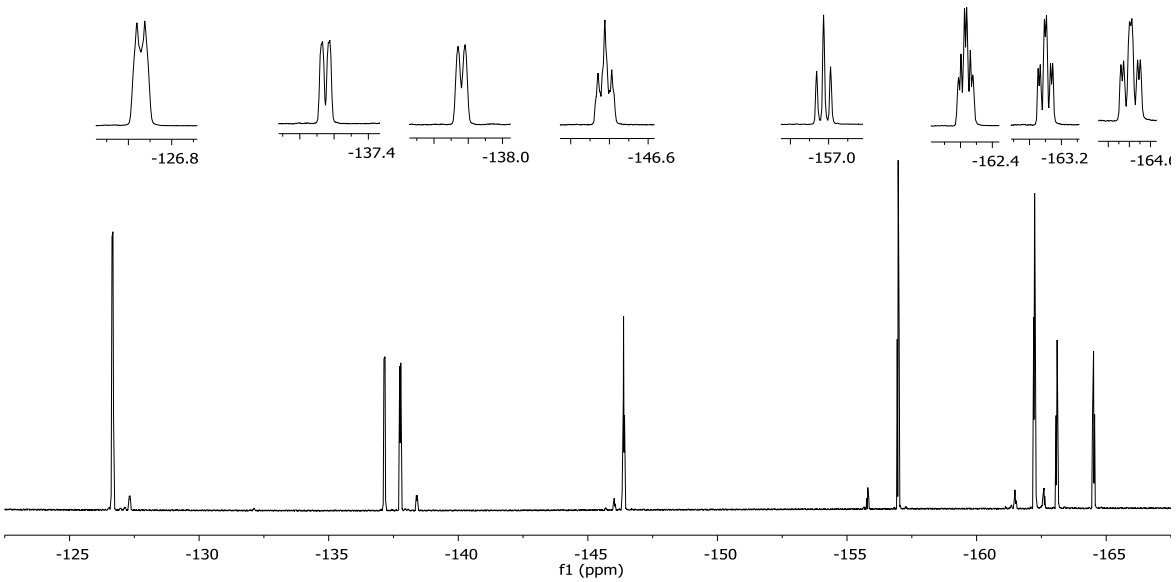


Figure S60: **^{19}F NMR** (564 MHz, CD_2Cl_2, 299 K) spectrum of compound **4e**.

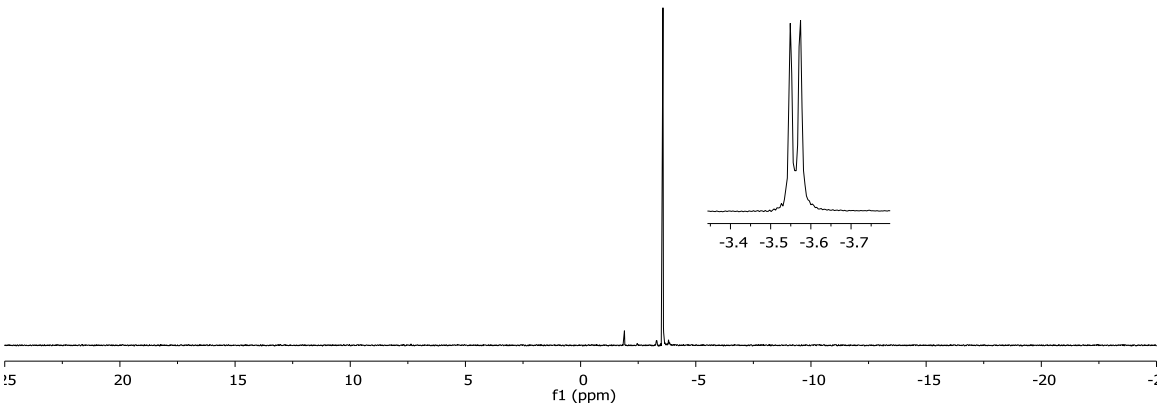


Figure S61: **^{29}Si{^{1}H} NMR** (99 MHz, CD_2Cl_2, 299 K) spectrum of compound **4e**.

Crystals suitable for the X-ray crystal structure analysis were obtained by slow evaporation of pentane solution of **4e** at -35°C.

X-ray crystal structure analysis of compound 4e (erk9392): A colorless prism-like specimen of $C_{24}H_{24}BClF_{10}Si_2$, approximate dimensions 0.092 mm x 0.245 mm x 0.281 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1638 frames were collected. The total exposure time was 19.13 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 42366 reflections to a maximum θ angle of 70.13° (0.82 Å resolution), of which 5168 were independent (average redundancy 8.198, completeness = 99.6%, R_{int} = 4.10%, R_{sig} = 2.47%) and 4996 (96.67%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.4024(5) Å, b = 30.1347(15) Å, c = 9.5483(5) Å, β = 114.5760(10)°, volume = 2722.0(2) $Å^3$, are based upon the refinement of the XYZ-centroids of 9804 reflections above 20 σ(I) with 9.799° < 2θ < 140.1°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.767. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.5020 and 0.7800. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/c$, with Z = 4 for the formula unit, $C_{24}H_{24}BClF_{10}Si_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 351 variables converged at R1 = 3.54%, for the observed data and wR2 = 9.07% for all data. The goodness-of-fit was 1.083. The largest peak in the final difference electron density synthesis was 0.370 $e^-/Å^3$ and the largest hole was -0.299 $e^-/Å^3$ with an RMS deviation of 0.053 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.476 g/cm^3 and F(000), 1232 e^-. CCDC Nr.: 1892611.

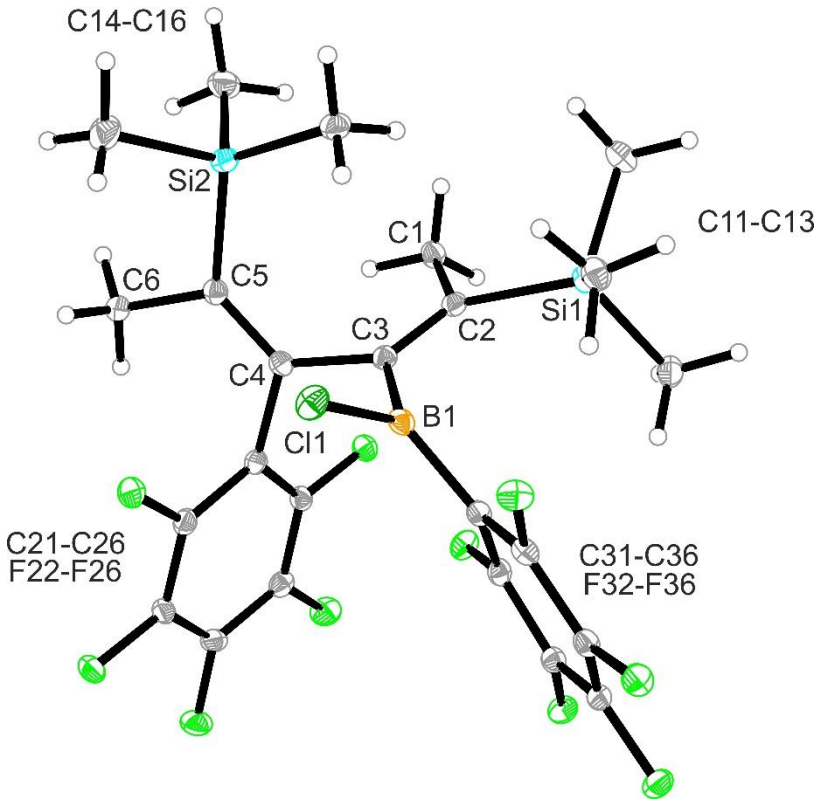
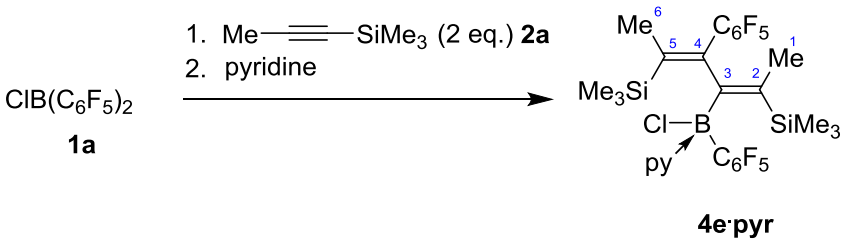


Figure S62: Crystal structure of compound **4e** (thermal ellipsoids: 30% probability).

Preparation of compound 4e·pyr



Scheme S14

Solutions of $ClB(C_6F_5)_2$ (76.2 mg, 0.2 mmol) in CH_2Cl_2 (2 mL) and of $MeC{\equiv}CSiMe_3$ (45.8 mg, 0.4 mmol) in CH_2Cl_2 (2 mL) were combined and stirred for 24 hours at room temperature. Subsequently, a solution of pyridine (23.7 mg, 0.3 mmol) in CH_2Cl_2 (1 mL) was added. The resulting colorless mixture was stirred for 15 minutes at room temperature, subsequently all volatilities were removed *in vacuo*. The semi-solid residue was washed twice with 1 mL of cold pentane, and then dried in vacuo. Product **4e·pyr** was obtained as a white solid (98.5 mg, 0.144 mmol, yield 72%).

Melting point: 191.0 °C.

HRMS for $C_{29}H_{29}BF_{10}NSi_2$ [(M - Cl)$^+$]: calculated 648.1768; found 648.1772.

Elementary analysis for $C_{29}H_{29}BClF_{10}NSi_2$ (684.0): calculated C 50.93, H 4.27, N 2.07; found C 50.63, H 4.09, N 2.06.

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 8.97 (br, 2H, 2,6-py), 8.15 (tt, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, 4-py), 7.64 (m, 2H, 3,5-py), 2.17 (d, J_{FH} = 3.5 Hz, 3H, Me^1), 1.57 (d, J_{FH} = 3.5 Hz, 3H, Me^6), 0.26 (s, $^2J_{SiH}$ = 6.7 Hz, 9H, C^5SiMe_3), -0.13 (s, $^2J_{SiH}$ = 6.5 Hz, 9H, C^2SiMe_3)

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = 153.7 (C^2), 152.8 (br, C^3)^t, 147.7 (br, 2,6-py), 144.7 (dm, $^1J_{FC}$ ≈ 253 Hz, 2C, C_6F_5), 144.4 (dm, $^1J_{FC}$ ≈ 250 Hz, 2C, C_6F_5), 144.1 (C^5), 143.4 (4-py), 140.5 (dm, $^1J_{FC}$ ≈ 252 Hz, 2C, C_6F_5), 140.1 (dm, $^1J_{FC}$ ≈ 250 Hz, 2C, C_6F_5), 137.8 (dm, $^1J_{FC}$ ≈ 255 Hz, 1C, *p*-C_6F_5), 137.8 (dm, $^1J_{FC}$ ≈ 255 Hz, 1C, *p*-C_6F_5), 137.5 (tm, $^3J_{FC}$ ≈ 2 Hz, C^4), 126.2 (br, 3,5-py), 115.7 (tm, $^2J_{FC}$ ≈ 20 Hz, *i*-$C_6F_5^C$), 24.1 (d, J_{FC} = 10 Hz, Me^1), 20.1 (d, J_{FC} = 6 Hz, Me^6), 1.6 ($^1J_{SiC}$ = 52.5 Hz, $C^2Si\mathit{Me}_3$), -0.3 ($^1J_{SiC}$ = 51.9 Hz, $C^5Si\mathit{Me}_3$). Signal *i*-$C_6F_5^B$ was not observed.

^{13}C{^{19}F,^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): [selected resonances] δ = 144.7 (2C, C_6F_5), 144.4 (2C, C_6F_5), 140.5 (2C, C_6F_5), 140.1 (2C, C_6F_5), 137.8 (1C, *p*-C_6F_5), 137.8 (1C, *p*-C_6F_5), 137.5(C(4)), 115.8 (*i*-$C_6F_5^C$), 24.1 (Me^1), 20.1 (Me^6).

^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = 3.2 ($\nu_{1/2}$ ≈ 200 Hz).

^{19}F NMR (564 MHz, CD_2Cl_2, 233 K): δ = [-119.8 (m, 1F, *o*-$C_6F_5^B$), -140.9 (m, 1F, *o*-$C_6F_5^B$), -157.5 (t, $^3J_{FF}$ = 21 Hz, 1F, *p*-$C_6F_5^B$), -164.0 (m, 1F, *m*-$C_6F_5^B$), -166.1 (m, 1F, *m*-$C_6F_5^B$)]($\Delta\delta^{19}F_{m,p}$ = 6.5, 8.6), [-136.4 (m, 1F, *o*-$C_6F_5^C$), -138.3 (m, 1F, *o*-$C_6F_5^C$), -155.9 (t, $^3J_{FF}$ = 21 Hz, 1F, *p*-$C_6F_5^C$), -163.3 (m, 1F, *m*-$C_6F_5^C$), -163.8 (m, 1F, *m*-$C_6F_5^C$)]($\Delta\delta^{19}F_{m,p}$ = 7.4, 7.9).

^{29}Si{^{1}H} DEPT (119 Hz, CD_2Cl_2, 299 K): δ = -4.1 ($\nu_{1/2}$ ≈ 3 Hz, $^5SiMe_3$), -6.7 ($\nu_{1/2}$ ≈ 1 Hz, $^2SiMe_3$).

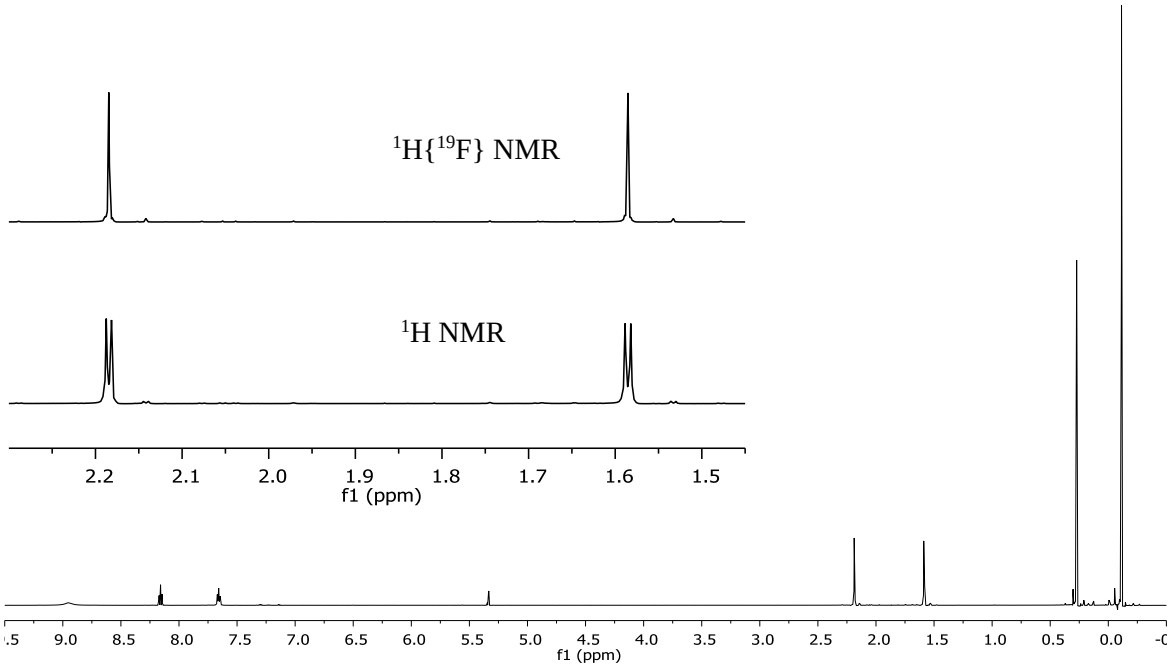


Figure S63: **^{1}H NMR** (600 MHz, CD_2Cl_2, 299 K) spectrum and excerpt from **^{1}H{^{19}F} NMR** (600 MHz, CD_2Cl_2, 299K) spectrum of compound **4e·pyr**.

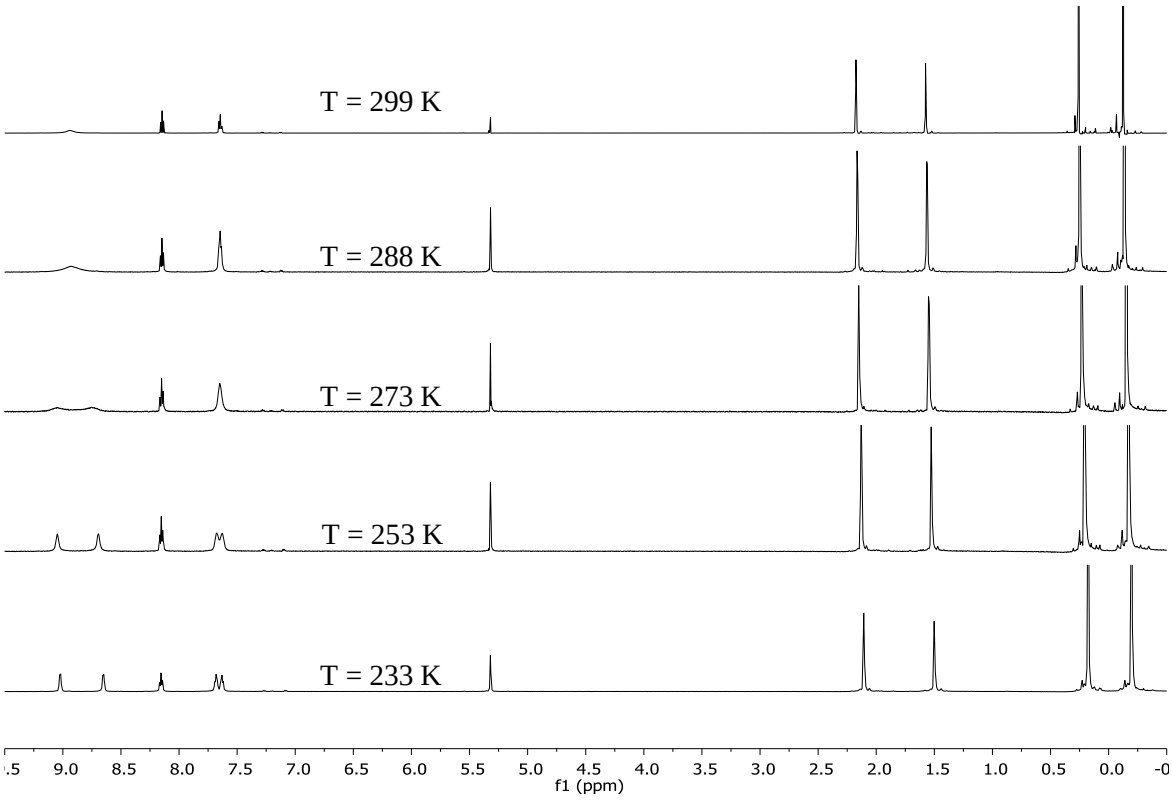


Figure S64: **^{1}H NMR** (600 MHz, CD_2Cl_2) spectrum of compound **4e·pyr** measured at various temperatures.

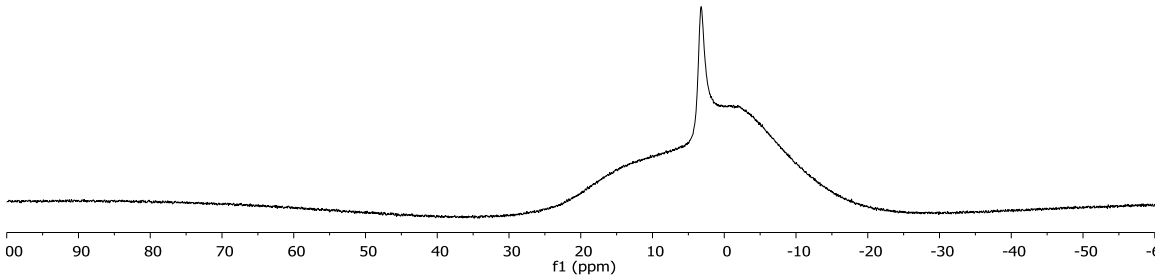


Figure S65: **^{11}B{^{1}H} NMR** (192 MHz, CD_2Cl_2, 299K) spectrum of compound **4e·pyr**.

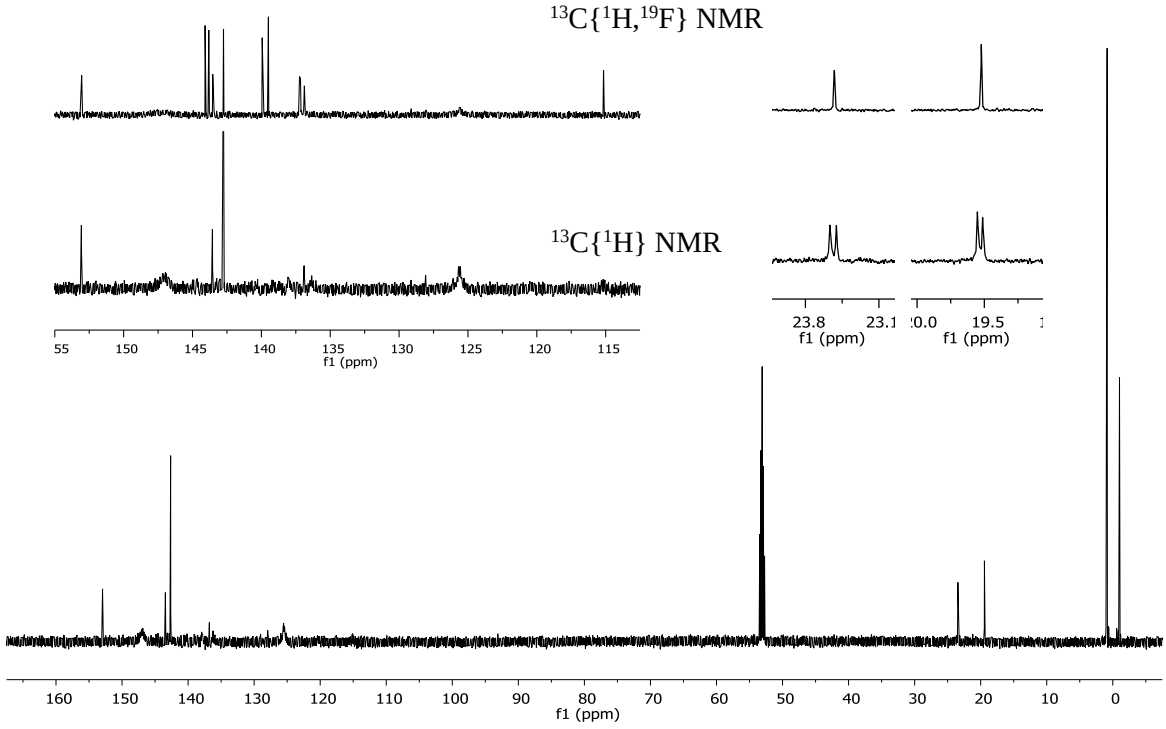


Figure S66: **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2, 299 K) spectrum and excerpt from **^{13}C{^{19}F,^{1}H} NMR** (151 MHz, CD_2Cl_2, 299K) spectrum of compound **4e·pyr**.

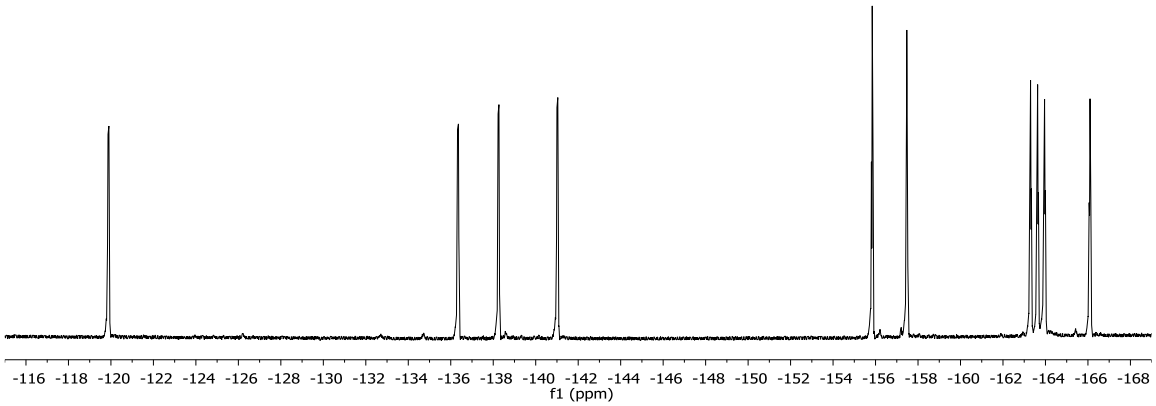


Figure S67: **^{19}F NMR** (600 MHz, CD_2Cl_2, 233 K) spectrum of compound **4e·pyr**.

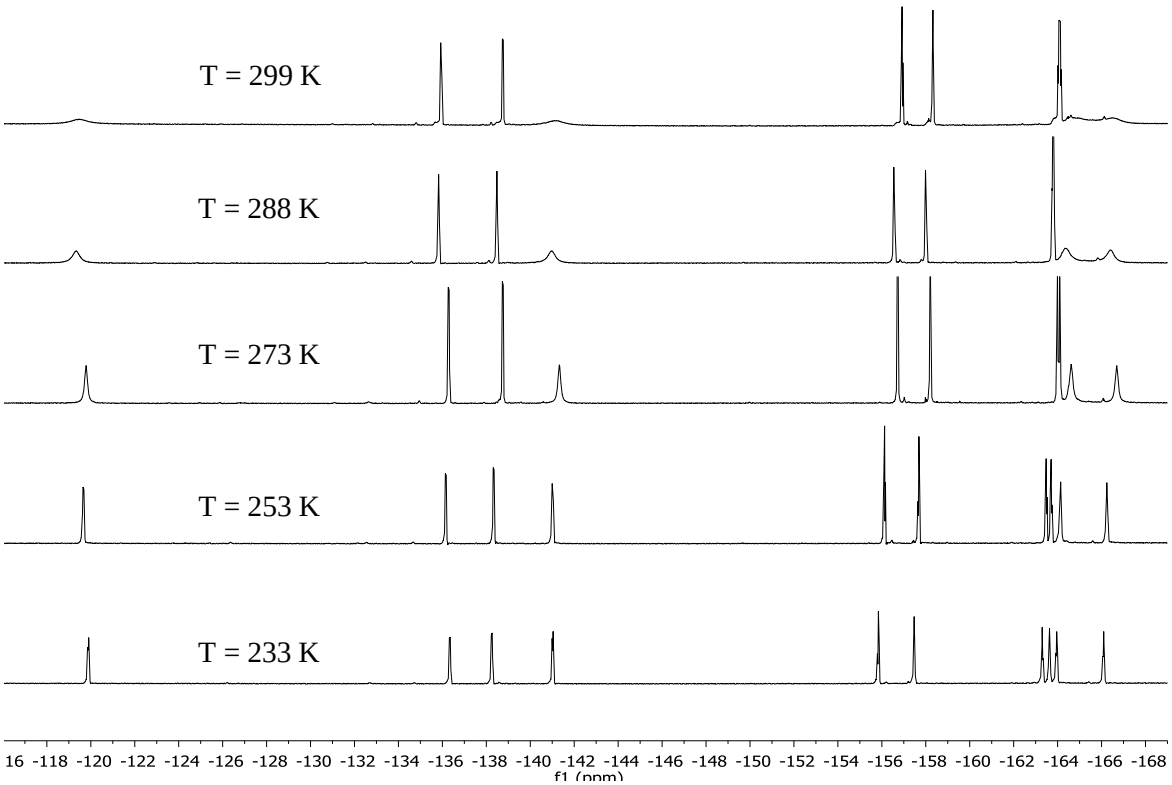


Figure S68: **^{19}F NMR** (564 MHz, CD_2Cl_2) spectrum of compound **4e·pyr** measured at various temperatures.

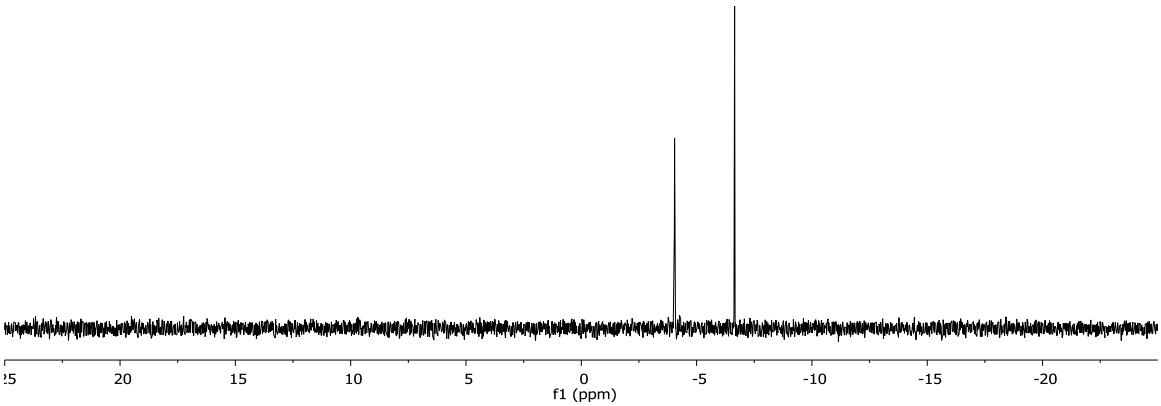


Figure S69: **^{29}Si{^{1}H} DEPT** (119 MHz, CD_2Cl_2, 299 K) spectrum of compound **4e·pyr**.

Crystals suitable for the X-ray crystal structure analysis were grown from pentane solution of **4e·pyr** at -35°C.

X-ray crystal structure analysis of compound 4e·pyr (erk9250): A colorless prism-like specimen of $C_{29}H_{29}BClF_{10}NSi_2$, approximate dimensions 0.058 mm x 0.095 mm x 0.165 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 956 frames were collected. The total exposure time was 15.93 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 58227 reflections to a maximum θ angle of 25.38° (0.83 Å resolution), of which 5779 were independent (average redundancy 10.076, completeness = 99.9%, R_{int} = 5.73%, R_{sig} = 2.45%) and 4854 (83.99%) were greater than $2\sigma(F^2)$. The final cell constants of a = 16.5070(5) Å, b = 11.0553(4) Å, c = 17.9516(6) Å, β = 106.1000(10)°, volume = 3147.50(18) $Å^3$, are based upon the refinement of the XYZ-centroids of 9990 reflections above 20 σ(I) with 4.723° < 2θ < 50.73°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.953. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9550 and 0.9840. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/n$, with Z = 4 for the formula unit, $C_{29}H_{29}BClF_{10}NSi_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 405 variables converged at R1 = 3.25%, for the observed data and wR2 = 7.65% for all data. The goodness-of-fit was 1.049. The largest peak in the final difference electron density synthesis was 0.324 $e^-/Å^3$ and the largest hole was -0.256 $e^-/Å^3$ with an RMS deviation of 0.051 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.443 g/cm^3 and F(000), 1400 e^-. CCDC Nr.: 1892612.

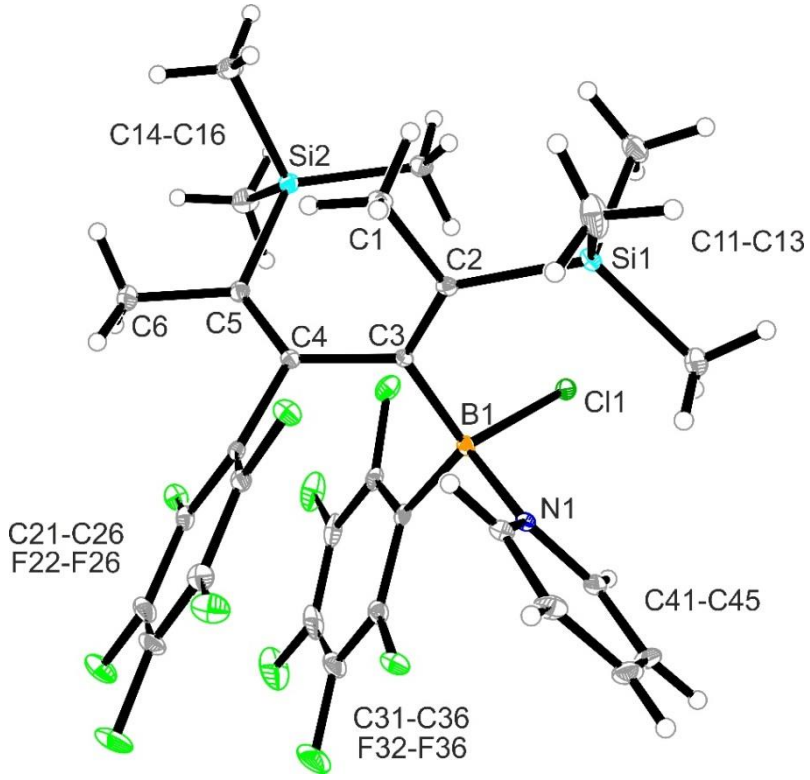
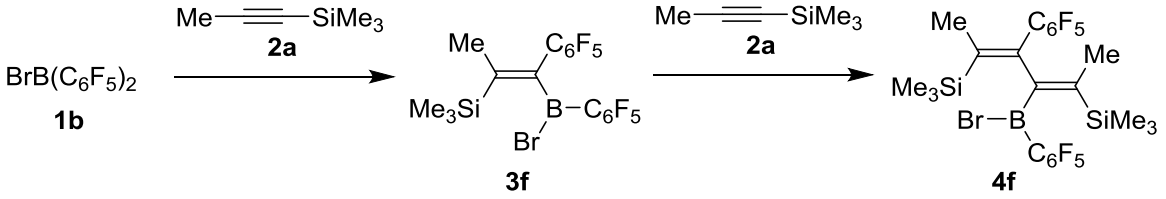


Figure S70: Crystal structure of compound **4e·pyr** (thermal ellipsoids: 30% probability).

Process of the reaction of $BrB(C_6F_5)_2$ (1b) with $MeC{\equiv}CSiMe_3$ (2a)



Scheme S15

Solutions of of $BrB(C_6F_5)_2$ (42.4 mg, 0.1 mmol) in CD_2Cl_2 (0.3 mL) and $MeC{\equiv}CSiMe_3$ (11.2 mg, 0.1 mmol) in CD_2Cl_2 (0.3 ml) were combined at room temperature, transfered to a Young NMR tube, vigorously shaken and after 10 minutes the resulting yellow solution was analyzed by NMR spectroscopy revealing complete conversion to the carboboration product **3f**. Subsequently, an additional equivalent of $MeC{\equiv}CSiMe_3$ was added (11.2 mg, 0.1 mmol in CD_2Cl_2, 0.3 mL). The mixture was vigorously shaken and the reaction progress was monitored by NMR spectroscopy while the tube was stored at room temperature. Complete conversion to compound **4f** was observed within three hours. Addition of a third equivalent of $MeC{\equiv}CSiMe_3$ did not show any further reaction even after heating for 18 h at 60°C.

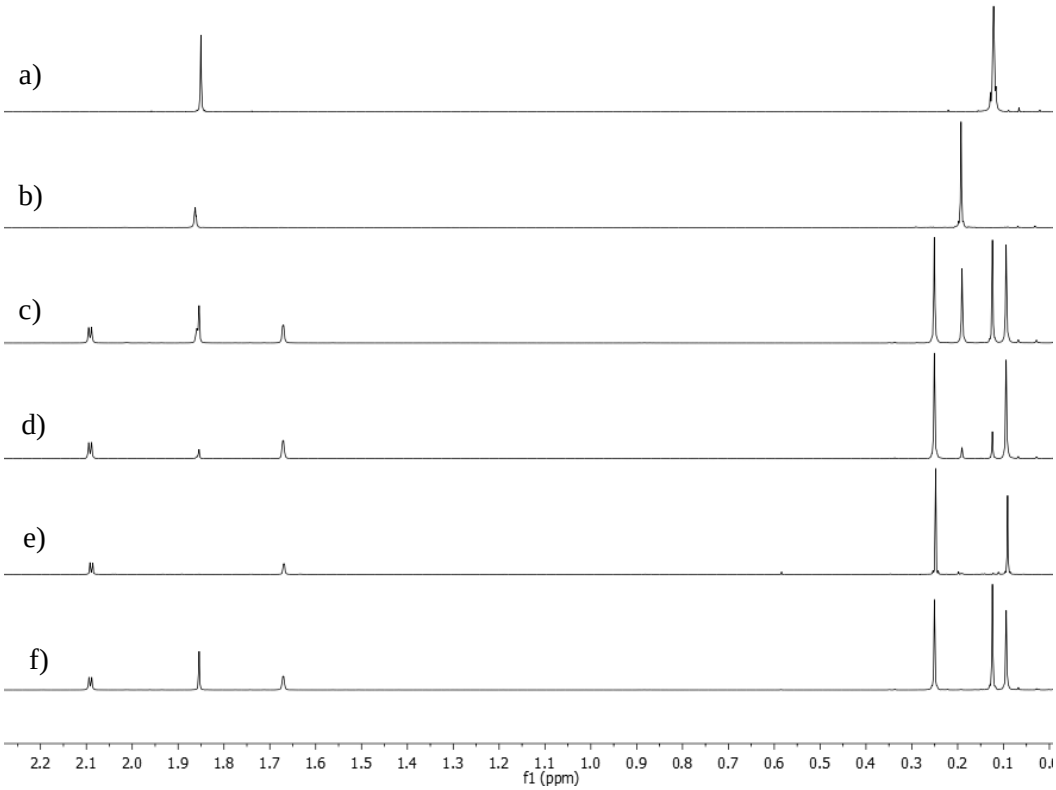
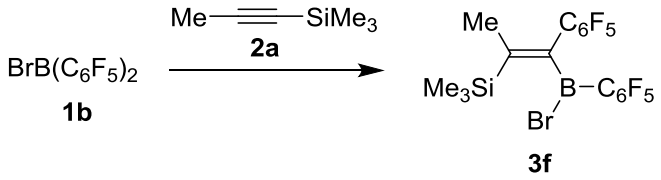


Figure S71: Monitoring of the reaction of $BrB(C_6F_5)_2$ with $MeC{\equiv}CSiMe_3$ by **^{1}H NMR** (600 MHz, CD_2Cl_2, 299 K) spectroscopy; a) $MeC{\equiv}CSiMe_3$; b) $MeC{\equiv}CSiMe_3$ + 1 equiv. $BrB(C_6F_5)_2$, reaction time ca 10 minutes (r.t); c) to previous mixture additional 1 equiv. of $MeC{\equiv}CSiMe_3$ added (reaction time ca 10 minutes at r.t), d) reaction time one hour (r.t), e) reaction time 3 hours (r.t), f) to previous mixture additional 1 equiv. of $MeC{\equiv}CSiMe_3$ was added and the mixture was heated to 60 °C for 18 hours.

Generation of compound 3f



Scheme S16

Solutions of of $BrB(C_6F_5)_2$ (42.4 mg, 0.1 mmol) in CD_2Cl_2 (0.3 ml) and $MeC{\equiv}CSiMe_3$ (11.2 mg, 0.1 mmol) in CD_2Cl_2 (0.3 mL) were combined at room temperature, transfered to an NMR tube, and vigorously shaken. The tube was flame sealed. The resulting yellow solution was within 10 minutes analyzed by NMR spectroscopy revealing complete conversion to the carboboration product **3f**.

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 1.86 (t, J_{FH} = 1.3 Hz, 3H, Me), 0.19 (s, $^{2}J_{SiH}$ = 6.6 Hz, 9H, $SiMe_3$).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = 168.4 (Me-*C*), 148.5 (dm, $^{1}J_{FC} \approx 254$ Hz, *o*- $C_6F_5^B$), 144.8 (dm, $^{1}J_{FC} \approx 260$ Hz, *p*- $C_6F_5^B$), 143.9 (dm, $^{1}J_{FC} \approx 247$ Hz, *o*-$C_6F_5^C$), 140.9 (dm, $^{1}J_{FC} \approx 252$ Hz, *p*-$C_6F_5^C$), 140.2 (br, *C*C_6F_5), 138.2 (dm, $^{1}J_{FC} \approx 250$ Hz, *m*-$C_6F_5^C$), 138.1 (dm, $^{1}J_{FC} \approx 253$ Hz, *m*-$C_6F_5^B$), 115.4 (tm, $^{2}J_{FC} \approx 22$ Hz, *i*-$C_6F_5^C$), 114.2 (br, *i*-$C_6F_5^B$), 23.6 (CH_3), 0.43 ($^{1}J_{SiC}$ = 53.0 Hz, $SiMe_3$).

^{13}C{^{19}F,^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): selected resonances δ = 148.5 (2C, *o*-$C_6F_5^B$), 144.8 (1C, *p*-$C_6F_5^B$), 143.9 (2C, *o*-$C_6F_5^C$), 140.9 (1C, *p*-$C_6F_5^C$), 138.2 (2C, *m*-$C_6F_5^C$), 138.1 (2C, *m*-$C_6F_5^B$), 115.4 (*i*-$C_6F_5^C$), 114.3 (*i*-$C_6F_5^B$).

^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = 61.7 ($\nu_{1/2} \approx 520$ Hz).

^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = [-125.6 (m, 2F, *o*), -145.6 (tt, J_{FF} = 20 Hz, 7 Hz, 1F, *p*), -161.5 (m, 2F, *m*)]($C_6F_5^B$, [$\Delta\delta^{19}F_{m,p}$ = 15.9]), [-138.3 (m, 2F, *o*), -155.7 (t, J_{FF} = 20 Hz, 1F, *p*), -162.6 (m, 2F, *m*)](C-C_6F_5, [$\Delta\delta^{19}F_{m,p}$ = 6.9]).

^{29}Si{^{1}H} DEPT (119 Hz, CD_2Cl_2, 299 K): δ = -2.0 ($\nu_{1/2} \approx 1$ Hz).

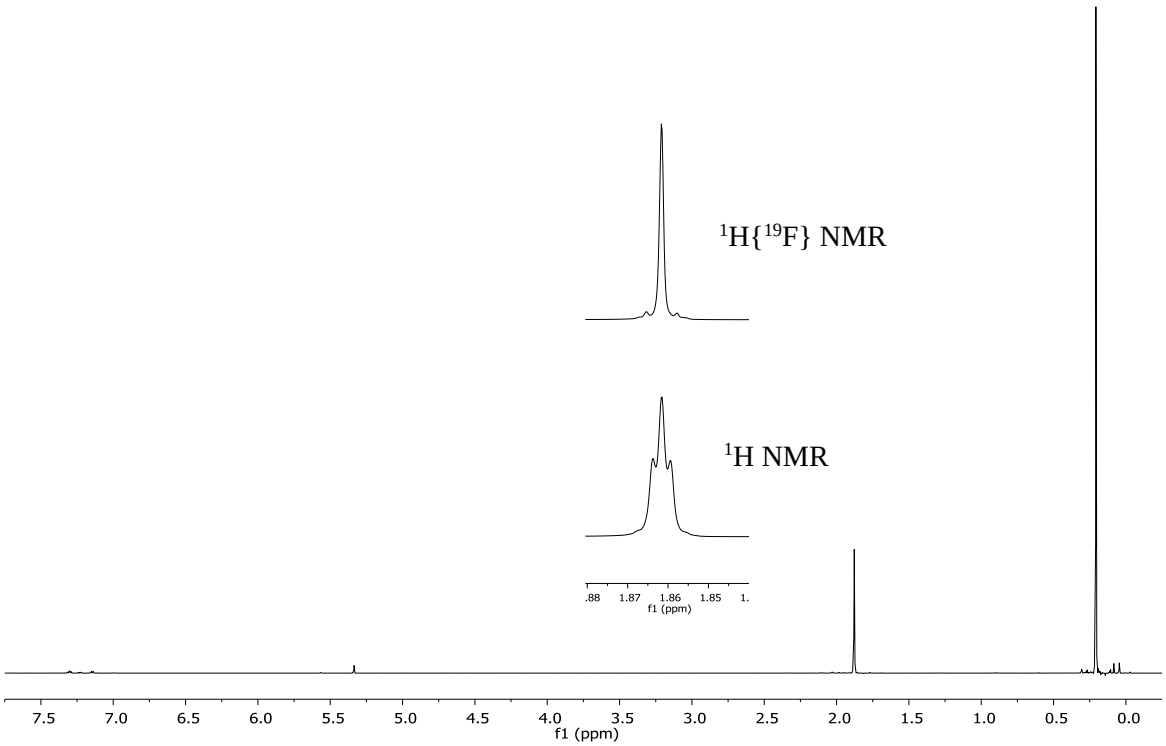


Figure S72: **^{1}H NMR** (600 MHz, CD_2Cl_2, 299K) spectrum and excerpt from **$^{1}H\{^{19}F\}$ NMR** (600 MHz, CD_2Cl_2, 299K) spectrum of compound **3f**.

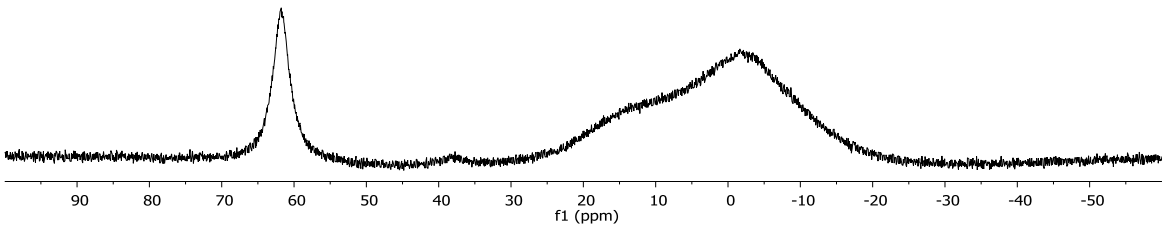


Figure S73: **$^{11}B\{^{1}H\}$ NMR** (192 MHz, CD_2Cl_2, 299K) spectrum of compound **3f**.

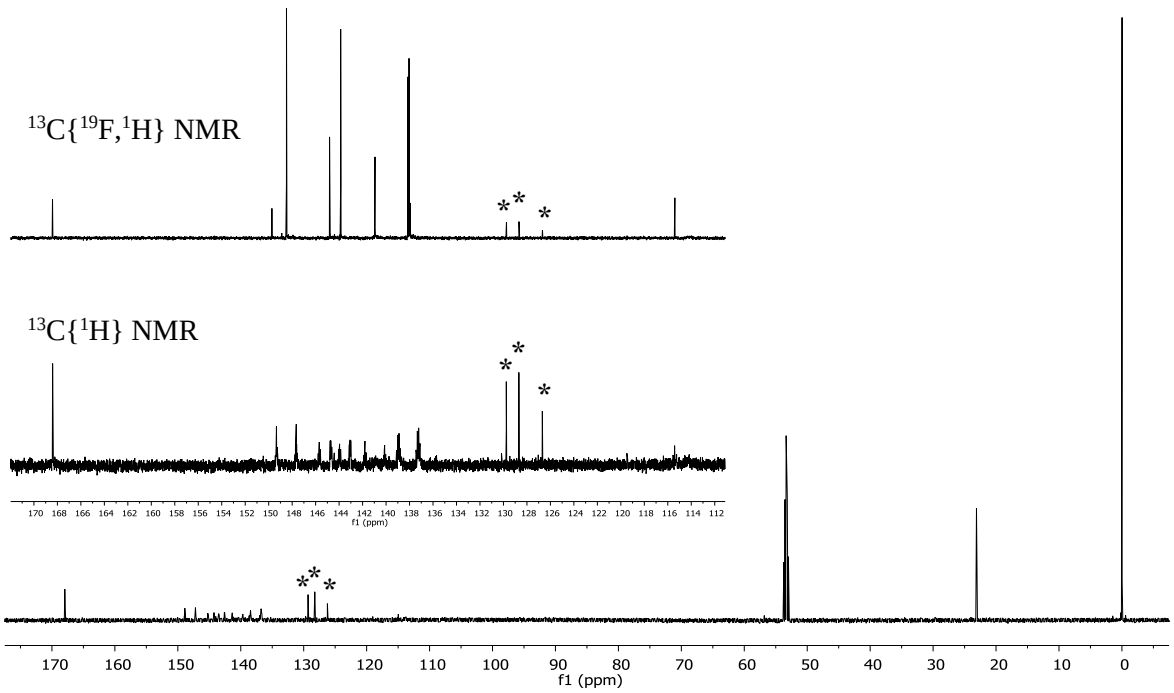


Figure S74: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, CD_2Cl_2, 299K) spectrum and detailed overview of aromatic signals with excerpt from **$^{13}C\{^{19}F,^{1}H\}$ NMR** (151 MHz, CD_2Cl_2, 299K) spectrum of compound **3f,** asterisks denots signals of an unindentified impurity originating from the preparation of $BrB(C_6F_5)_2$.

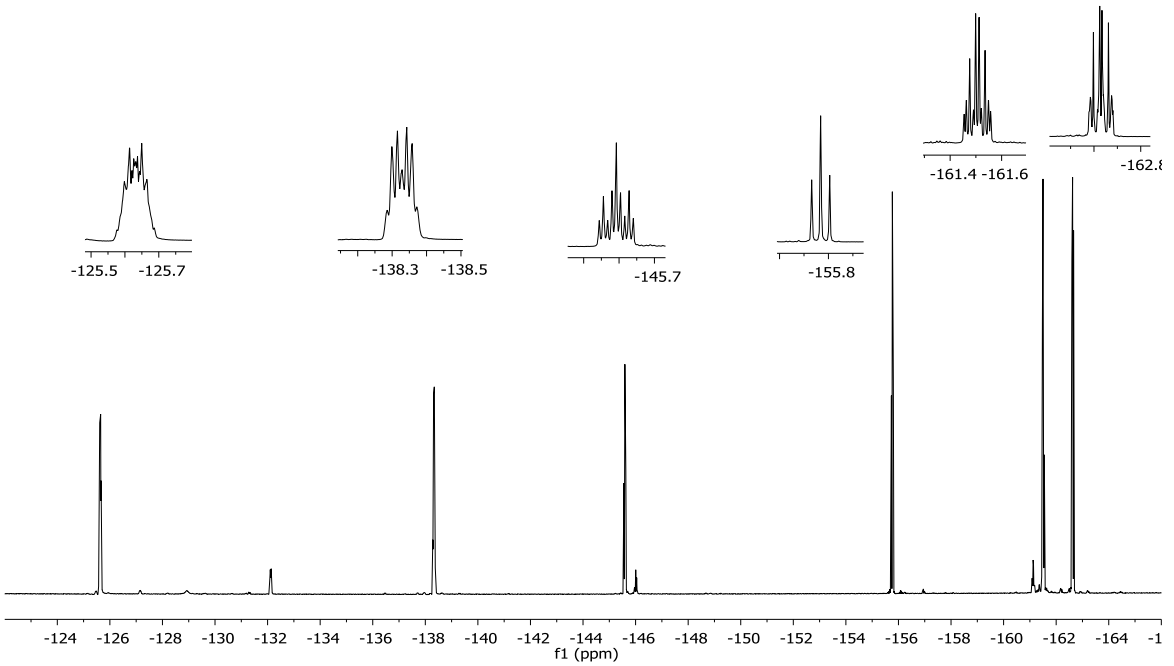


Figure S75: **^{19}F NMR** (564 MHz, CD_2Cl_2, 299K) spectrum of compound **3f**.

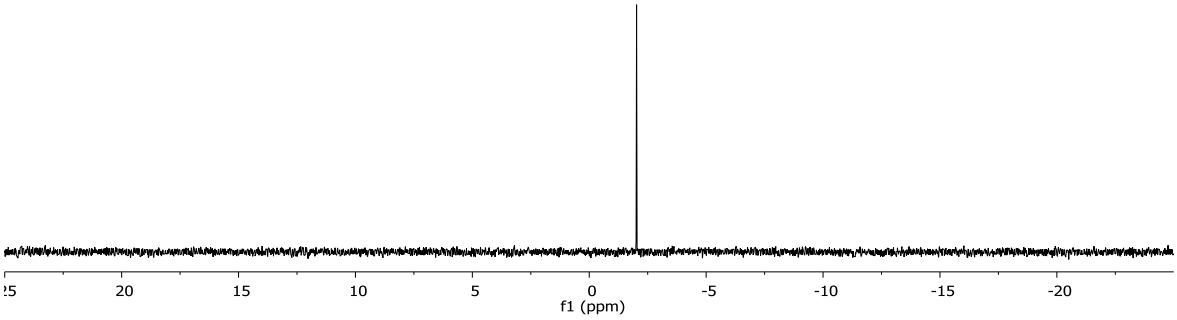
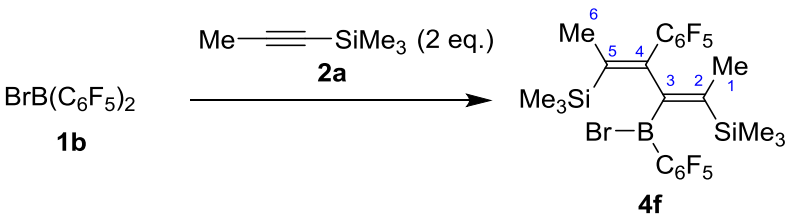


Figure S76: **^{29}Si{^{1}H} DEPT** (119 MHz, CD_2Cl_2, 299 K) spectrum of compound **3f**.

Preparation of compound 4f



Scheme S17

Solutions of of $BrB(C_6F_5)_2$ (212 mg, 0.5 mmol) in 3 ml of CH_2Cl_2 and of $MeC{\equiv}CSiMe_3$ (124 mg , 1.1 mmol) in of CH_2Cl_2 (2 ml) were combined and allowed to stir overnight at room temperature. All volatilities were removed in vacuo to yield a beige solid, which was taken up in 3 ml of pentane and stored at -35 °C. Over several days, colorless prism-shaped crystals of **4f** appeared. They were isolated by decantation and dried in vacuo. 156.2 mg of product were isolated as a white solid (0.24 mmol, 48 % yield).

Melting point: 79.2 °C.

Elementary analysis for $C_{24}H_{24}BBrF_{10}Si_2$ (649.3): calculated C 44.39, H 3.73; found C 44.56, H 3.70.

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 2.09 (d, J_{FH} = 3.7 Hz, 3H, Me^1), 1.67 (d, J_{FH} = 1.2 Hz, 3H, Me^6), 0.25 (s, $^2J_{SiH}$ = 6.6 Hz, 9H, C^5SiMe_3), 0.09 (s, $^2J_{SiH}$ = 6.4 Hz, 9H, C^2SiMe_3).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = 156.2 (C^2), 154.5 (br, C^3), 149.7 (br, C^5), 148.3 (dm, $^1J_{FF}$ ≈ 252 Hz, 2C, *o*-$C_6F_5^B$), 145.0 (dm, $^1J_{FF}$ ≈ 245 Hz, 1C, *o*-$C_6F_5^C$), 144.4 (dm, $^1J_{FF}$ ≈ 260 Hz, 1C, *p*-$C_6F_5^B$), 143.5 (dm, $^1J_{FF}$ ≈ 246 Hz, 1C, *o*-$C_6F_5^C$), 140.4 (dm, $^1J_{FF}$ ≈ 255 Hz, 1C, *p*-$C_6F_5^C$), 138.0 (dm, $^1J_{FF}$ ≈ 252 Hz, 1C, *m*-$C_6F_5^C$), 137.7 (dm, $^1J_{FF}$ ≈ 255 Hz, 2C, *m*-$C_6F_5^B$), 137.3 (dm, $^1J_{FF}$ ≈ 253 Hz, 1C, *m*- $C_6F_5^C$), 130.4 (C^4), 116.0 (tm, $^2J_{FF}$ ≈ 1 Hz, *i*-$C_6F_5^C$), 115.3 (br, *i*-$C_6F_5^B$), 21.7 (d, J_{FC} = 9 Hz, Me^1), 20.6 (d, J_{FC} = 2 Hz, Me^6), 0.4 ($^1J_{SiC}$ = 52.4 Hz, C^2SiMe_3), -0.1 ($^1J_{SiC}$ = 52.5 Hz, C^5SiMe_3).

$^{13}C\{^{19}F,^{1}H\}$ NMR (151 MHz, CD_2Cl_2, 299 K): selected resonances δ = 148.3 (2C, *o*-$C_6F_5^B$), 145.0 (1C, *o*- $C_6F_5^C$), 144.4 (1C, *p*-$C_6F_5^B$), 143.5 (1C, *o*-$C_6F_5^C$), 140.4 (1C, *p*-$C_6F_5^C$), 138.0 (1C, *m*-$C_6F_5^C$), 137.7 (2C, *m*-$C_6F_5^B$), 137.3 (1C, *m*-$C_6F_5^C$), 116.0 (*i*-$C_6F_5^C$).

$^{11}B\{^{1}H\}$ NMR (192 MHz, CD_2Cl_2, 299 K): δ = 62.6 ($\nu_{1/2} \approx 590$ Hz).

^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = [-125.4 (m, 2F, *o*), -146.0 (tt, $^3J_{FF}$ = 20 Hz, $^4J_{FF}$ = 7 Hz, 1F, *p*), -162.1 (m, 2F, *m*)](B-C_6F_5, [$\Delta\delta^{19}F_{m,p}$ = 16.1]), [-136.4 (m, 1F, *o*), -137.6 (m, 1F, *o*), -156.9 (t, J_{FF} = 21 Hz, 1F, *p*), -163.1 (m, 1F, *m*), -164.4 (m, 1F, *m*)](C-C_6F_5, [$\Delta\delta^{19}F_{m,p}$ = 6.2, 7.5])

$^{29}Si\{^{1}H\}$ DEPT (119 Hz, CD_2Cl_2, 299 K): δ = -3.6 ($\nu_{1/2} \approx 1$ Hz, $^2SiMe_3$), -3.6 ($\nu_{1/2} \approx 1$ Hz, $^5SiMe_3$).

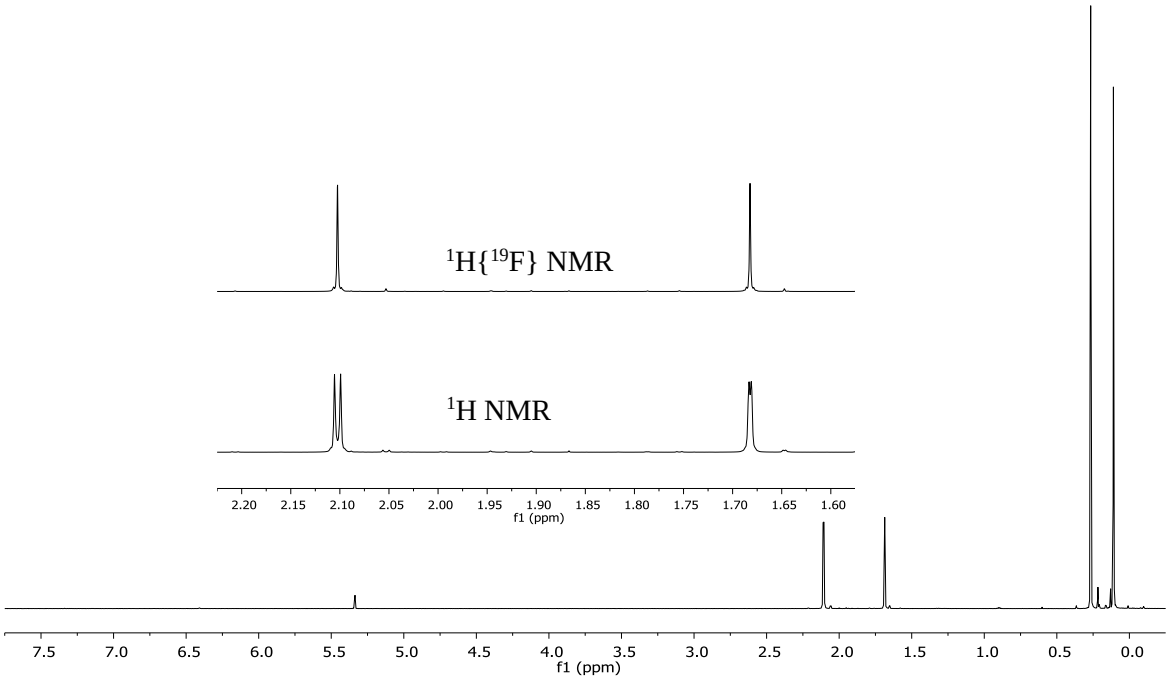


Figure S77: **^1H NMR** (600 MHz, CD_2Cl_2, 299K) spectrum and excerpt from **$^1H\{^{19}F\}$ NMR** (600 MHz, CD_2Cl_2, 299K) spectrum of compound **4f**.

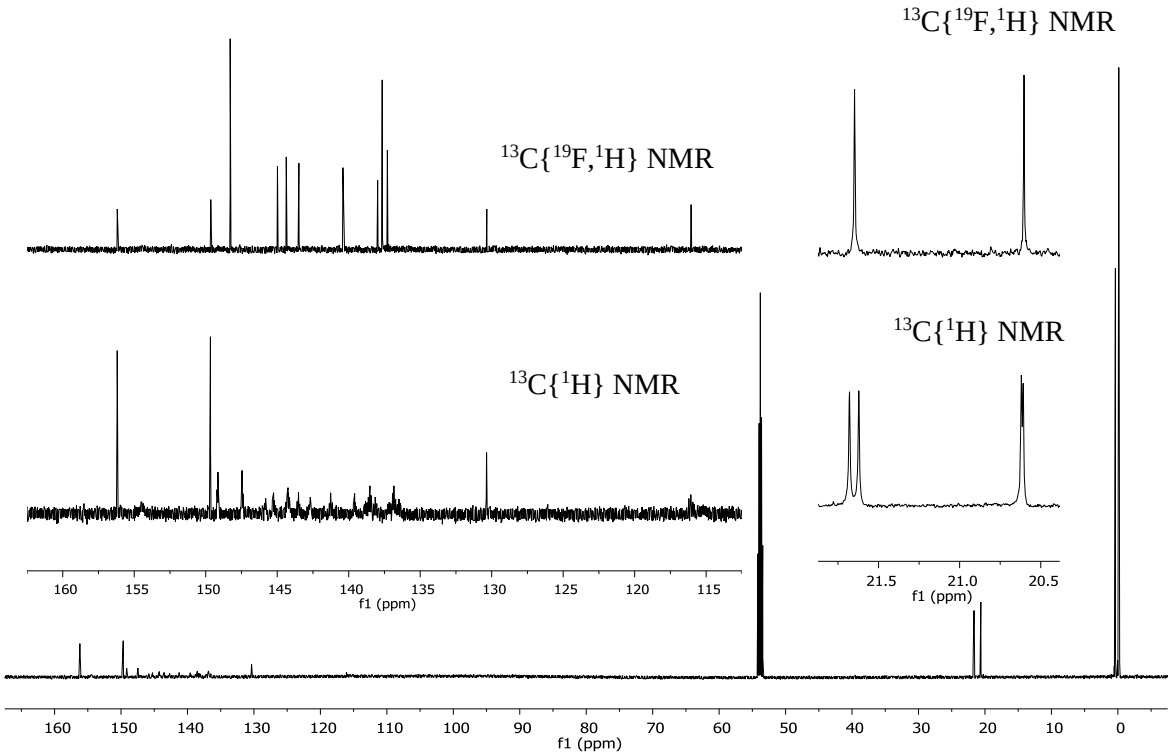


Figure S78: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, CD_2Cl_2, 299K) spectrum and detailed overview of aromatic and methyl signals with excerpt from **$^{13}C\{^{19}F,^{1}H\}$ NMR** (151 MHz, CD_2Cl_2, 299K) spectrum of compound **4f**.

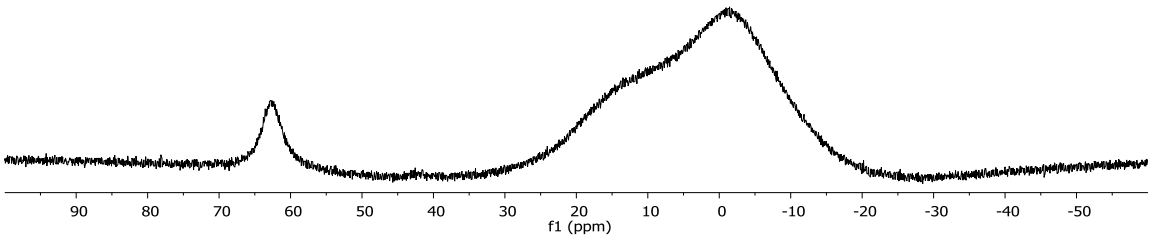


Figure S79: **$^{11}B\{^{1}H\}$ NMR** (192 MHz, CD_2Cl_2, 299K) spectrum of compound **4f**.

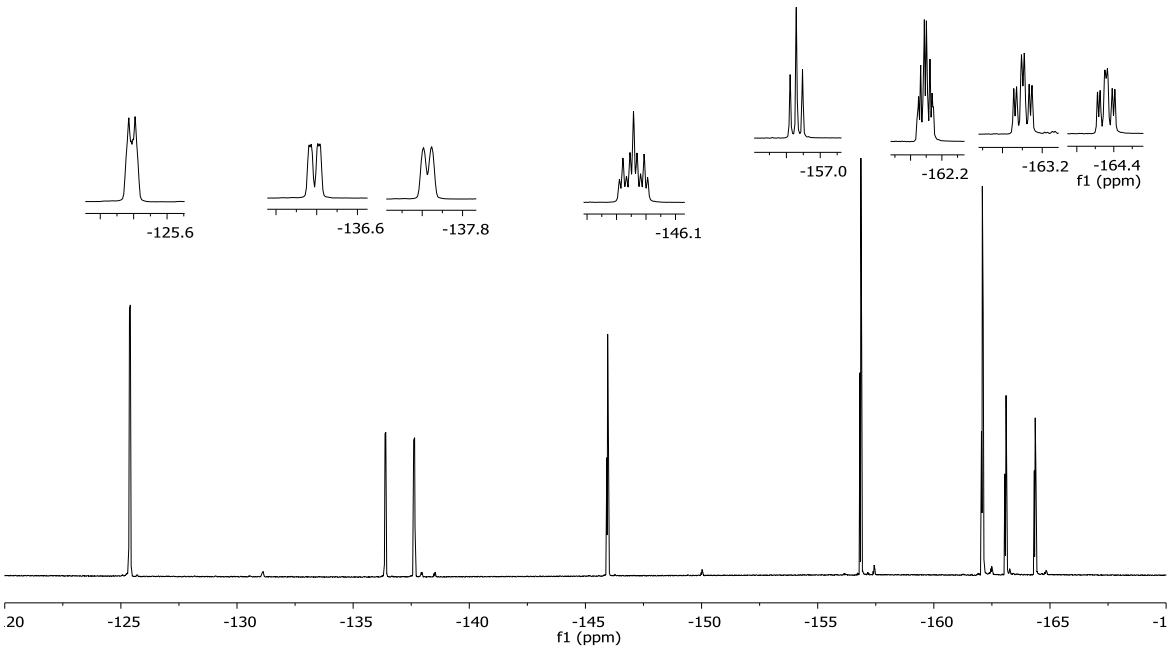


Figure S80: **^{19}F NMR** (564 MHz, CD_2Cl_2, 299 K) spectrum of compound **4f**.

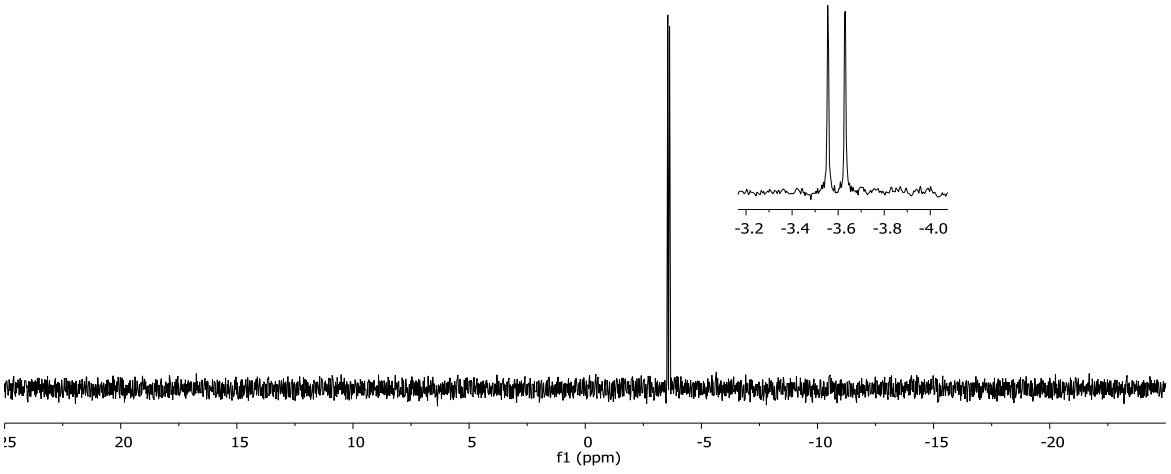


Figure S81: **^{29}Si{^{1}H} NMR** (119 MHz, CD_2Cl_2, 299 K) spectrum of compound **4f**.

Crystals suitable for the X-ray crystal structure analysis were taken from the reaction batch (pentane -35°C).

X-ray crystal structure analysis of compound 4f (erk9374): A colorless plate-like specimen of $C_{24}H_{24}BBrF_{10}Si_2$, approximate dimensions 0.020 mm x 0.100 mm x 0.120 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1530 frames were collected. The total exposure time was 19.41 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 32996 reflections to a maximum θ angle of 66.75° (0.84 Å resolution), of which 4848 were independent (average redundancy 6.806, completeness = 99.8%, R_{int} = 6.58%, R_{sig} = 4.04%) and 4054 (83.62%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.4154(4) Å, b = 30.5675(10) Å, c = 9.4626(3) Å, β = 114.686(2)°, volume = 2737.31(17) $Å^3$, are based upon the refinement of the XYZ-centroids of 7034 reflections above 20 σ(I) with 9.345° < 2θ < 133.5°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.795. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6690 and 0.9310. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/c$, with Z = 4 for the formula unit, $C_{24}H_{24}BBrF_{10}Si_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 351 variables converged at R1 = 3.54%, for the observed data and wR2 = 9.05% for all data. The goodness-of-fit was 1.035. The largest peak in the final difference electron density synthesis was 0.456 $e^-/Å^3$ and the largest hole was -0.337 $e^-/Å^3$ with an RMS deviation of 0.072 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.576 g/cm^3 and F(000), 1304 e^-. CCDC Nr.: 1892613.

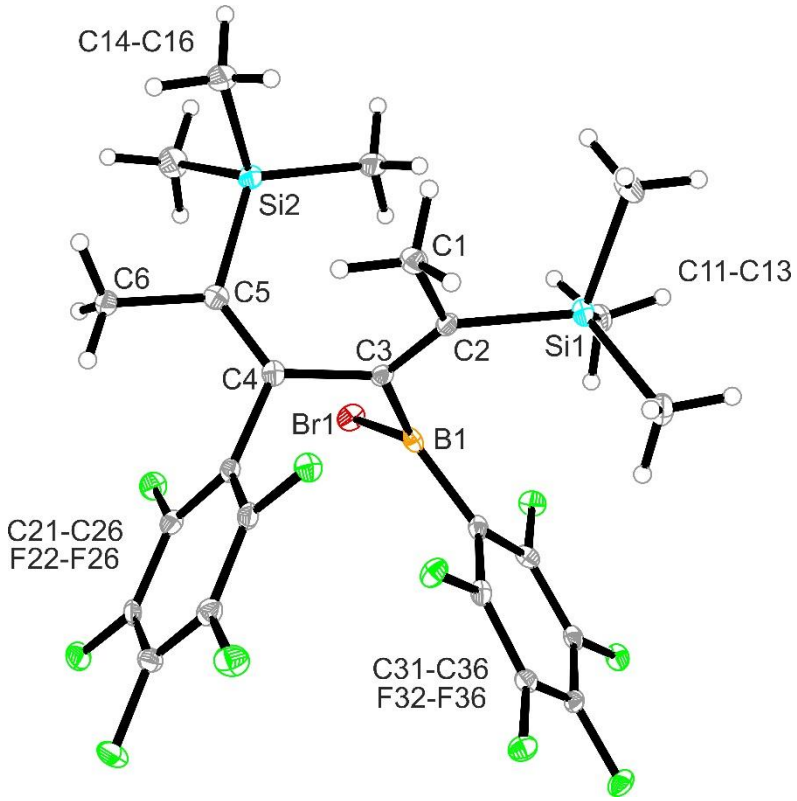
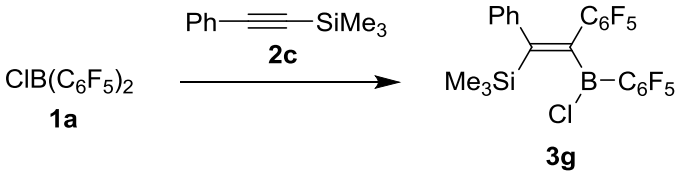


Figure S82: Crystal structure of compound **4f** (thermal ellipsoids: 30% probability).

Generation of compound 3g



Scheme S18

Solutions of of $ClB(C_6F_5)_2$ (**1a**) (38.0 mg, 0.1 mmol) in CD_2Cl_2 (0.3 ml) and $PhC{\equiv}CSiMe_3$ (**2c**) (17.4 mg, 0.1 mmol) in CD_2Cl_2 (0.2 ml) were combined. The resulting colorless solution was stirred for 2 hours at room temperature, then transferred to a NMR tube, which was flame-sealed. The reaction mixture was analyzed by NMR spectroscopy revealing complete conversion to product **3g.**

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 7.18 (m, 2H, *m*-Ph), 7.10 (m, 1H, *p*-Ph), 6.91 (m, 2H, *o*-Ph), 0.16 (s, $^{2}J_{SiH}$ = 7 Hz , 9H, $SiMe_3$).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = 168.1 (Me_3SiC=), 149.4 (dm, $^{1}J_{FC}$ ≈ 255 Hz, *o*-$C_6F_5^B$), 145.2 (dm, $^{1}J_{FC}$ ≈ 253 Hz, *p*-$C_6F_5^B$), 143.4 (dm, $^{1}J_{FC}$ ≈ 245 Hz, *o*-$C_6F_5^C$), 143.3 (*i*-Ph), 140.7 (dm, $^{1}J_{FC}$ ≈ 255 Hz, *p*-$C_6F_5^C$), [139.6, 111.4](each br, =*C*C_6F, *i*-$C_6F_5^B$), 138.0 (dm, $^{1}J_{FC}$ ≈ 255 Hz, *m*-$C_6F_5^B$), 137.8 (dm, $^{1}J_{FC}$ ≈ 250 Hz, *m*-$C_6F_5^C$), 128.3 (*m*-Ph), 126.9 (*p*-Ph), 126.0 (*o*-Ph), 114.5 (tm, $^{2}J_{FC}$ ≈ 21 Hz, *i*-$C_6F_5^C$), 0.1 ($^{1}J_{SiC}$ = 53.1 Hz, $SiMe_3$).

^{13}C{^{19}F,^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): [selected resonances] δ = 149.4 (2C, *o*-$C_6F_5^B$), 145.2 (1C, *p*-$C_6F_5^B$), 143.4 (2C, *o*-$C_6F_5^C$), 140.7 (1C, *p*-$C_6F_5^C$), 138.0 (2C, *m*-$C_6F_5^B$), 137.8 (2C, *m*-$C_6F_5^C$), 114.5 (1C, *i*-$C_6F_5^C$), 111.4 (br, 1C, *i*-$C_6F_5^B$).

^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = 60.0 ($\nu_{1/2}$ ≈ 670 Hz).

^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = [-125.9 (m, 2F, *o*), -145.0 (tt, J_{FF} = 21 Hz, 7 Hz, 1F, *p*), -161.4 (m, 2F, *m*)](B-C_6F_5, [$\Delta\delta^{19}F_{m,p}$ = 16.4]), [-137.2 (m, 2F, *o*), -155.5 (t, J_{FF} = 21 Hz, 1F, *p*), -162.9 (m, 2F, *m*)](C-C_6F_5, [$\Delta\delta^{19}F_{m,p}$ = 7.4]).

^{29}Si{^{1}H} DEPT (99 Hz, CD_2Cl_2, 299 K): δ = -3.0 ($\nu_{1/2}$ ≈ 1 Hz).

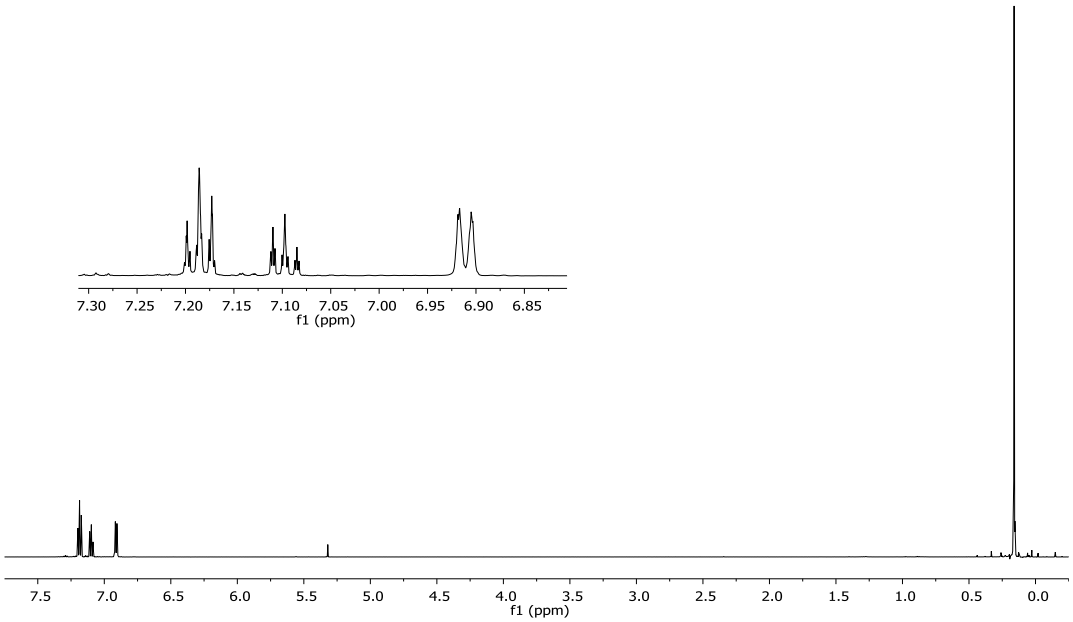


Figure S83: **^{1}H NMR** (600 MHz, CD_2Cl_2, 299K) spectrum of compound **3g**.

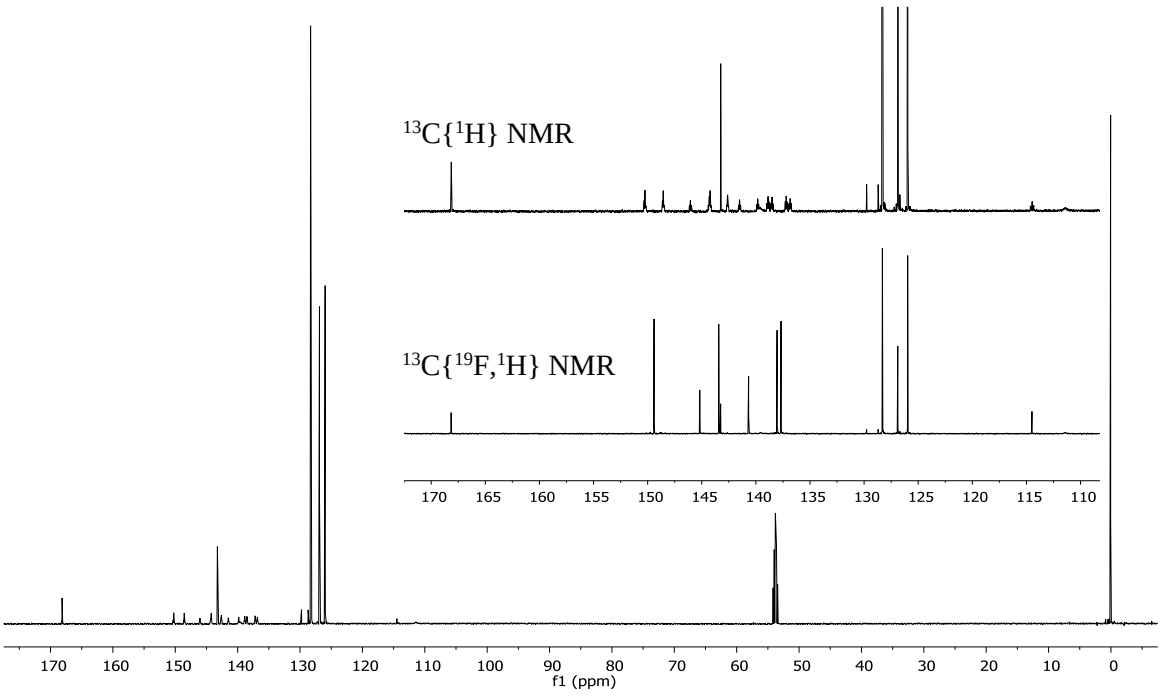


Figure S84: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, CD_2Cl_2, 299K) spectrum and detailed overview of aromatic signals with excerpt from **$^{13}C\{^{19}F,^{1}H\}$ NMR** (151 MHz, CD_2Cl_2, 299K) spectrum of compound **3g**.

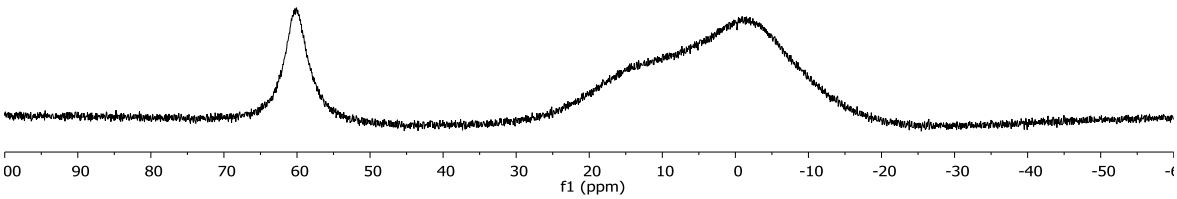


Figure S85: **$^{11}B\{^{1}H\}$ NMR** (192 MHz, CD_2Cl_2, 299K) spectrum of compound **3g**.

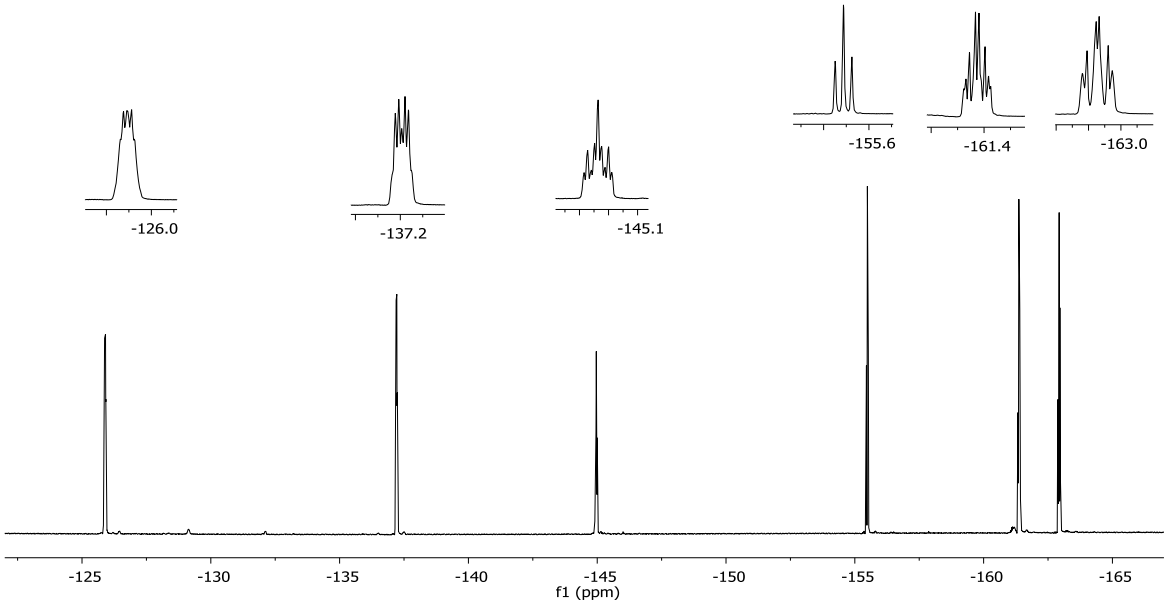


Figure S86: **^{19}F NMR** (564 MHz, CD_2Cl_2, 299 K) spectrum of compound **3g**.

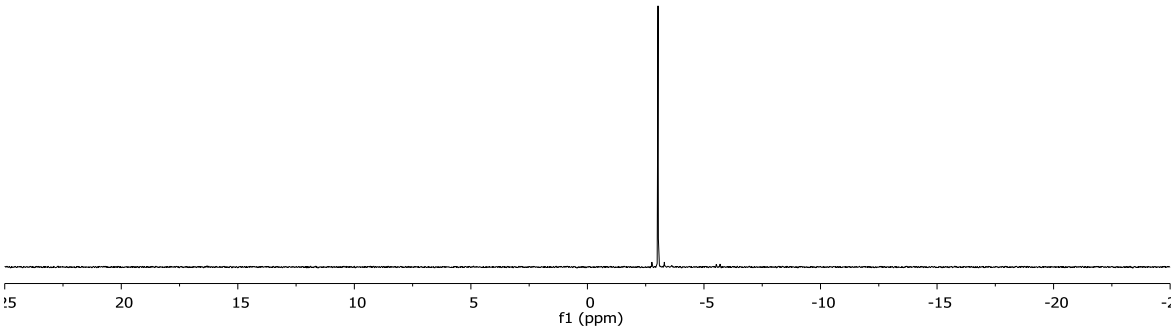
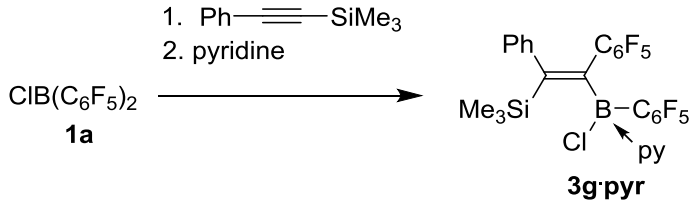


Figure S87: **$^{29}Si\{^{1}H\}$ DEPT** (99 MHz, CD_2Cl_2, 299 K) spectrum of compound **3g**.

Preparation of compound 3g·pyr



Scheme S19

A solution of $PhC{\equiv}CSiMe_3$ (174.3 mg, 0.5 mmol) in CH_2Cl_2 (2 ml) was added to a solution of $ClB(C_6F_5)_2$ (190 mg, 0.5 mmol) in CH_2Cl_2 (2 ml). The mixture was stirred for 3 hours at room temperature, subsequently a solution of pyridine (60 mg, 0.75 mmol) in CH_2Cl_2 (1 ml) was added. The pale yellow color faded out immediately. The resulting mixture was stirred for 25 minutes at room temperature, then all volatilies were removed. The residual white semi-solid was washed with a small amount of pentane and thoroughly dried in vacuo. Product **3g·pyr** was obtained as a colorless solid (306 mg, 0.48 mmol, 96 % yield).

Melting point: 92.1 °C.

HRMS for $C_{28}H_{19}BClF_{10}NNaSi$ [$(M + Na)^+$]: calculated 656.0801, found 656.0808

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 9.14 (br, 2H, 2,6-py), 8.17 (tt, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, 4-py), 7.70 (m, 2H, 3,5-py), 7.10 (m, 1H, *m*-Ph), 7.08 (m, 1H, *m*-Ph), 6.98 (m, 1H, *p*-Ph), 6.91 (m, 1H, *o*-Ph), 6.86 (m, 1H, *o*-Ph), -0.07 (s, $^2J_{SiH}$ = 6.7 Hz, 9H, $SiMe_3$).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = 163.9 (Me_3SiC=), 148.5 (dm, $^1J_{FC}$ ≈ 240 Hz, 2C, C_6F_5), 147.6 (*i*-Ph), 146.9 (2,6-py), 144.5 (br, CC_6F_5)^t, 143.6 (4-py), 142.0 (dm, $^1J_{FC}$ ≈ 242 Hz, 2C, C_6F_5), 140.7 (dm, $^1J_{FC}$ ≈ 250 Hz, 1C, C_6F_5), 138.8 (dm, $^1J_{FC}$ ≈ 250 Hz, 1C, C_6F_5), 137.7 (dm, $^1J_{FC}$ ≈ 250 Hz, 1C, C_6F_5), 137.6 (dm, $^1J_{FC}$ ≈ 250 Hz, 1C, C_6F_5), 136.8 (dm, $^1J_{FC}$ ≈ 253 Hz, 1C, C_6F_5), 136.7 (dm, $^1J_{FC}$ ≈ 251 Hz, 1C, C_6F_5), 127.9 (*m*-Ph), 127.8 (*m*-Ph), 126.4 (*o*-Ph), 126.2 (3,5-py), 126.1 (*o*-Ph), 125.9 (*p*-Ph), 122.7 (tm, $^2J_{FC}$ ≈ 24 Hz, *i*-$C_6F_5^C$), 119.5 (br, *i*-$C_6F_5^B$),^{t} 1.21 (s, $^1J_{SiC}$ = 53.6 Hz, $SiMe_3$), ^{t} tentatively assigned.

^{13}C{^{19}F,^{1}H } NMR (151 MHz, CD_2Cl_2, 299 K): selected resonances δ = 148.5 (2C, C_6F_5), 142.0 (2C, C_6F_5), 140.7 (1C, C_6F_5), 138.8 (1C, C_6F_5), 137.7 (1C, C_6F_5), 137.6 (1C, C_6F_5), 136.8 (1C, C_6F_5), 136.7 (1C, C_6F_5), 122.6 (1C, *i*-C_6F_5).

^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = 3.2 ($\nu_{1/2}$ ≈ 190 Hz).

^{19}F NMR (564 MHz, CD_2Cl_2, 213 K): δ = [-126.0, -136.1, -138.5, -140.6](each br, each 1F, *o*-C_6F_5), [-155.8 (br), -157.9 (t, $^3J_{FF}$ = 21 Hz)](each 1F, *p*-C_6F_5), [-163.0, -163.4, -163.9, -164.5](each br, each 1F, *m*-C_6F_5).

^{29}Si{^{1}H} DEPT (119 Hz, CD_2Cl_2, 299 K): δ = -6.4 ($\nu_{1/2}$ ≈ 3 Hz).

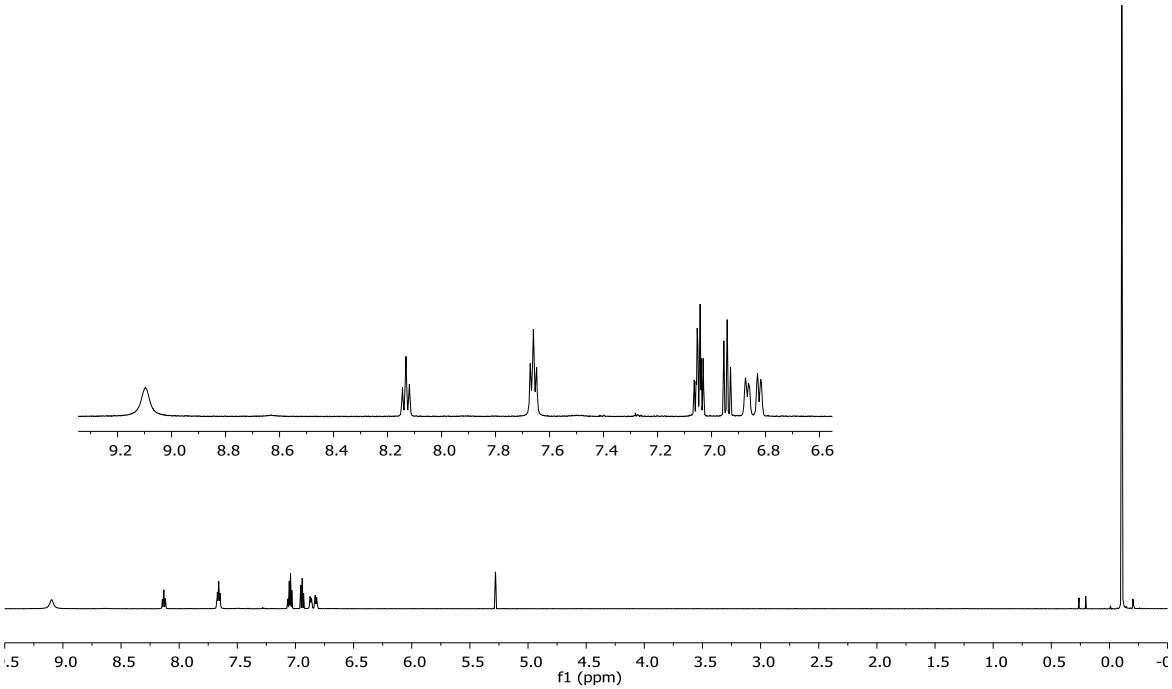


Figure S88: **^{1}H NMR** (600 MHz, CD_2Cl_2, 299K) spectrum of compound **3g·pyr**.

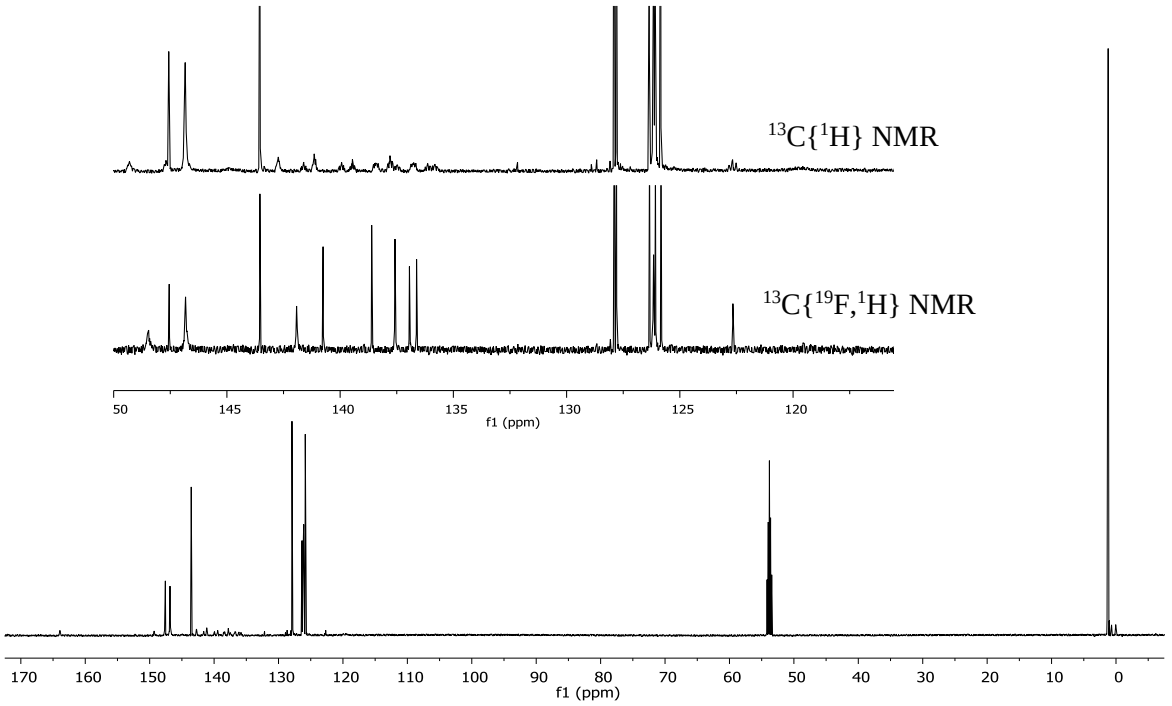


Figure S89: **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2, 299K) spectrum and detailed overview of aromatic signals with excerpt from **^{13}C{^{19}F,^{1}H} NMR** (151 MHz, CD_2Cl_2, 299K) spectrum of compound **3g·pyr**.

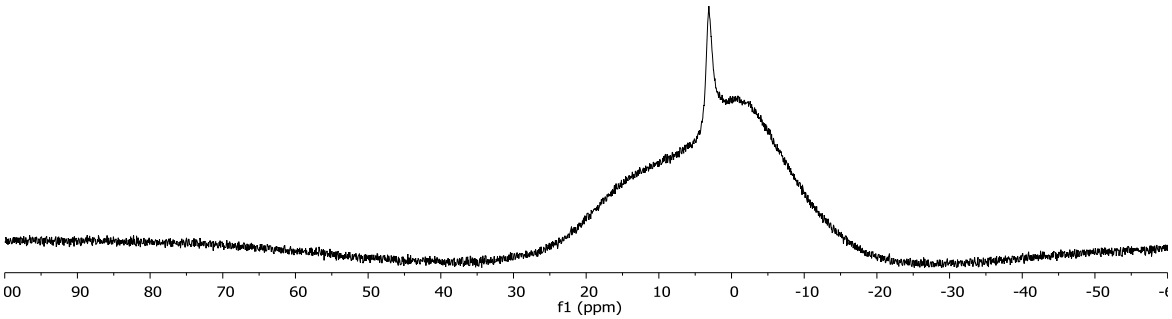


Figure S90: **^{11}B{^{1}H} NMR** (192 MHz, CD_2Cl_2, 299K) spectrum of compound **3g·pyr**.

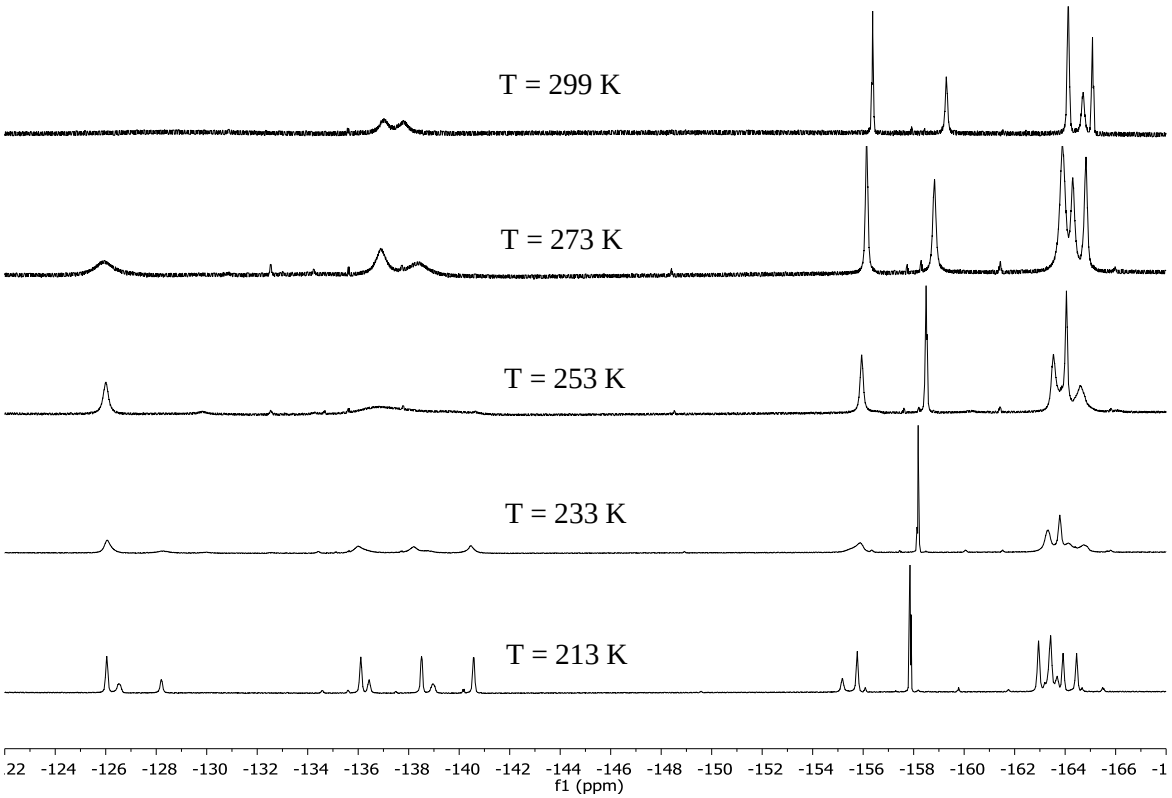


Figure S91: **^{19}F NMR** (564 MHz, CD_2Cl_2) spectrum of compound **3g·pyr** measured at various temperatures.

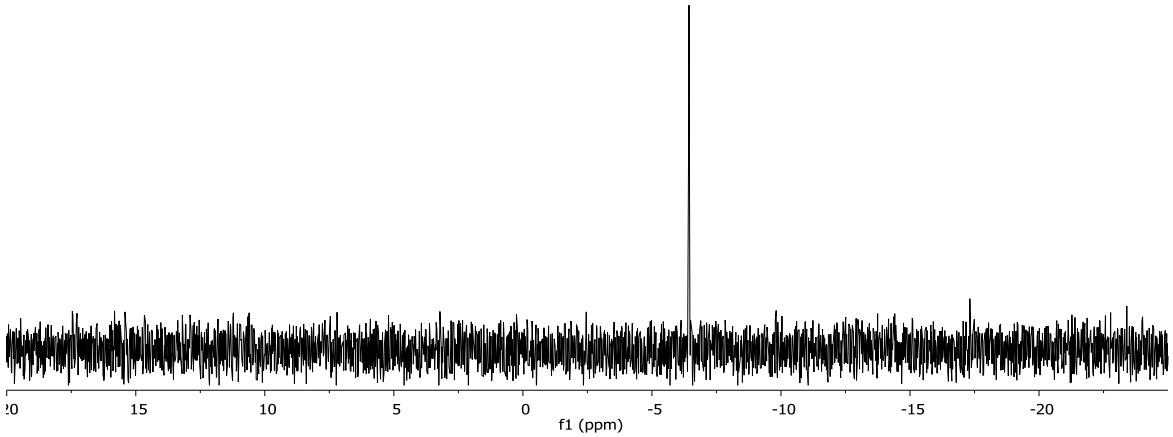


Figure S92: **^{29}Si{^{1}H} DEPT** (119 MHz, CD_2Cl_2, 299 K) spectrum of compound **3g·pyr**.

Crystals suitable for the X-ray structure analysis were grown by slow diffusion of pentane into solution of **3g·pyr** in CH_2Cl_2 at -35°C.

X-ray crystal structure analysis of compound 3g·pyr (erk9193): A colorless prism-like specimen of $C_{28}H_{19}BClF_{10}NSi$, approximate dimensions 0.083 mm x 0.097 mm x 0.107 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1624 frames were collected. The total exposure time was 24.95 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 42382 reflections to a maximum θ angle of 68.47° (0.83 Å resolution), of which 5575 were independent (average redundancy 7.602, completeness = 99.7%, R_{int} = 6.08%, R_{sig} = 3.16%) and 4518 (81.04%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.8003(2) Å, b = 21.9160(5) Å, c = 13.1037(3) Å, β = 101.6580(10)°, volume = 3037.65(11) $Å^3$, are based upon the refinement of the XYZ-centroids of 9316 reflections above 20 σ(I) with 7.983° < 2θ < 136.6°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.838. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7960 and 0.8370. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/n$, with Z = 4 for the formula unit, $C_{28}H_{19}BClF_{10}NSi$. The final anisotropic full-matrix least-squares refinement on F^2 with 477 variables converged at R1 = 4.10%, for the observed data and wR2 = 10.12% for all data. The goodness-of-fit was 1.051. The largest peak in the final difference electron density synthesis was 0.332 $e^-/Å^3$ and the largest hole was -0.422 $e^-/Å^3$ with an RMS deviation of 0.047 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.386 g/cm^3 and F(000), 1280 e^-. CCDC Nr.: 1892610.

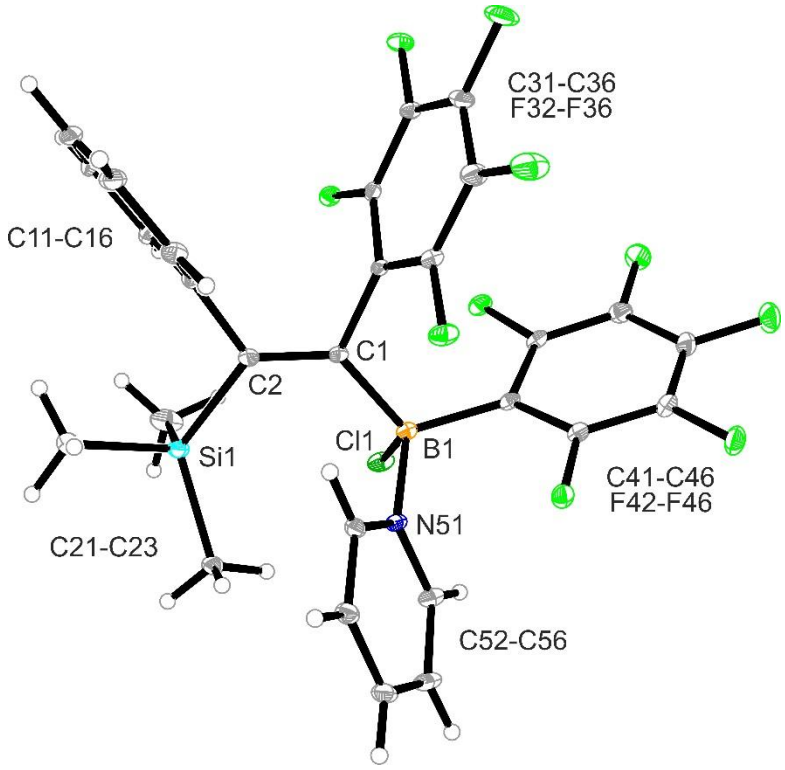
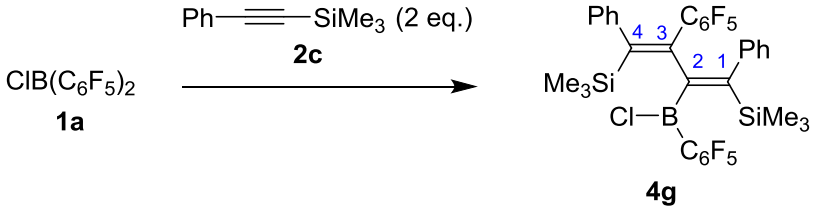


Figure S93: Crystal structure of compound **3g·pyr** (thermal ellipsoids 15% probability).

Generation of compound 4g



Scheme S20

Solutions of 38.0 mg $ClB(C_6F_5)_2$ (0.1 mmol) in CD_2Cl_2 (0.3 ml) and 34.9 mg PhC≡CSiMe$_3$ (0.2 mmol) in CD_2Cl_2 (0.2 ml) were combined, stirred for 2 hours at room temperature, then transfered to a NMR tube, which was flame-sealed. Measurement of ^{1}H and ^{19}F NMR spectra after 22 hours (stored at room temperature) revealed complete conversion to product **4g**, which was *in situ* characterized by NMR spectroscopy.

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = [7.36 (m, 2H, *m*), 7.29 (m, 1H, *p*), 6.89 (m, 2H, *o*)](Ph), [7.06 (br, 2H), 7.00 (m, 1H, *p*), 6.87 (br, 1H), 6.68 (br, 1H)](Ph), 0.34 (s, $^2J_{SiH}$ = 6.7 Hz, 9H, SiMe$_3$), -0.15 (s, $^2J_{SiH}$ = 6.6 Hz, 9H, SiMe$_3$).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = [168.5, 154.3](C^{1,4}), [153.6 (br), 135.1 (br)]C^{2,3}), [149.8 (dm, $^1J_{CF}$ ≈ 254 Hz, 2C), 144.9 (dm, $^1J_{CF}$ ≈ 260 Hz, 1C), 144.5 (dm, $^1J_{CF}$ ≈ 240 Hz, 1C), 142.2 (dm, $^1J_{CF}$ ≈ 255 Hz, 1C), 140.0 (dm, $^1J_{CF}$ ≈ 262 Hz, 1C), 138.2 (dm, $^1J_{CF}$ ≈ 250 Hz, 2C), 137.5 (dm, $^1J_{FF}$ ≈ 250 Hz, 1C), 136.6 (dm, $^1J_{CF}$ ≈ 250 Hz, 1C), 117.5 (tm, $^2J_{CF}$ ≈ 20 Hz), 114.4 (br)](C_6F_5), [143.5 (*i*), 128.3 (*m*), 126.8 (*p*), 126.4 (br, *o*),](Ph), [142.8 (*i*), 127.9 (br), 127.3 (br), 126.5 (*p*)](Ph), 0.9 ($^1J_{SiH}$ = 53.9 Hz, SiMe$_3$), 0.5 ($^1J_{SiH}$ = 53.2 Hz, SiMe$_3$).

^{13}C{^{19}F,^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): [selected resonances] δ = [149.8 (2C), 144.9 (1C), 144.5 (br, 1C), 142.2 (br, 1C), 140.0 (1C), 138.2 (2C), 137.5 (br, 1C), 136.6 (br, 1C)] (10x C_6F_5), 135.1 (C^3), 117.5 (*i*-$C_6F_5^C$).

^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = 60.0 ($\nu_{1/2}$ ≈ 1000 Hz).

^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = [-125.7 (m, 2F, *o*-$C_6F_5^B$), -145.4 (tt, J_{FF} = 20 Hz, 7 Hz, 1F, *p*-$C_6F_5^B$), -161.4 (m, 2F, *m*-$C_6F_5^B$)]($\Delta\delta^{19}F_{m,p}$ = 16.0), [-137.2, -135.9 (each m, each 1F, *o*-$C_6F_5^C$), -157.8 (t, J_{FF} = 21 Hz, 1F, *p*-$C_6F_5^C$), -164.2, 166.0 (each m, each 1F, *m*-$C_6F_5^C$)]($\Delta\delta^{19}F_{m,p}$ = 6.4, 8.2).

^{29}Si{^{1}H} DEPT (99 Hz, CD_2Cl_2, 299 K): δ = -5.5 ($\nu_{1/2}$ ≈ 1 Hz, SiMe$_3$), -5.7 ($\nu_{1/2}$ ≈ 1 Hz, SiMe$_3$).

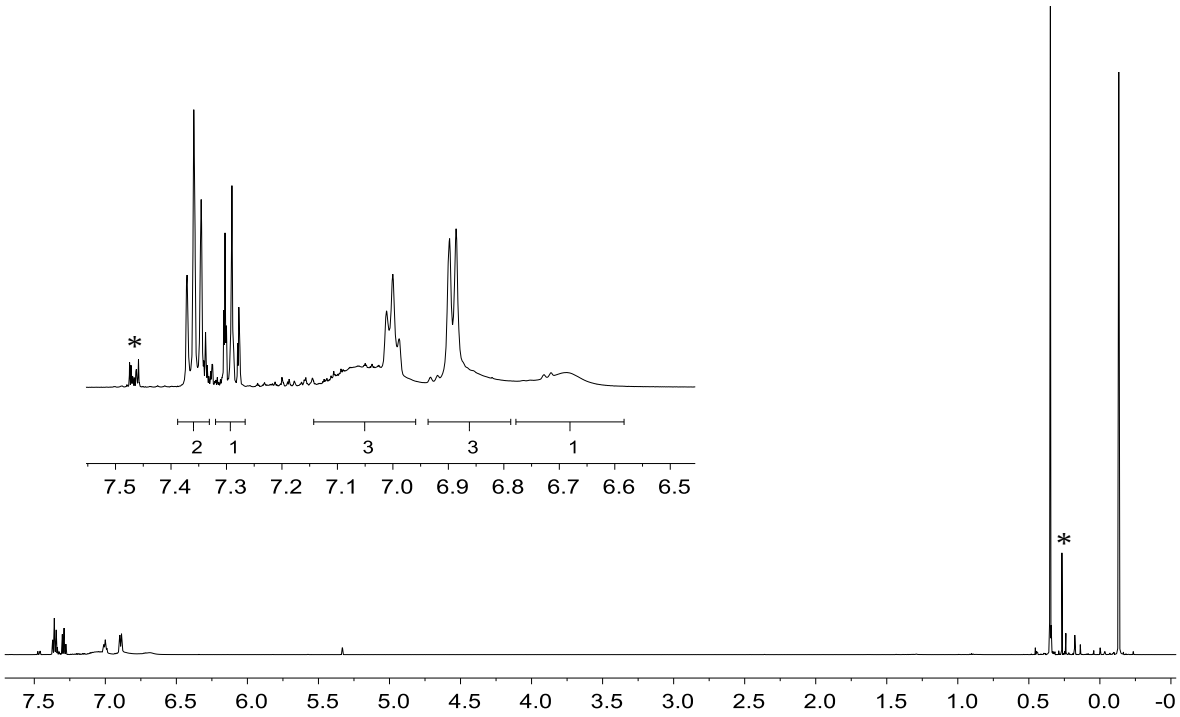


Figure S94: **^{1}H NMR** (600 MHz, CD_2Cl_2, 299K) spectrum of compound **4g**, asterisks denote signals due to unreacted PhC≡CSiMe$_3$.

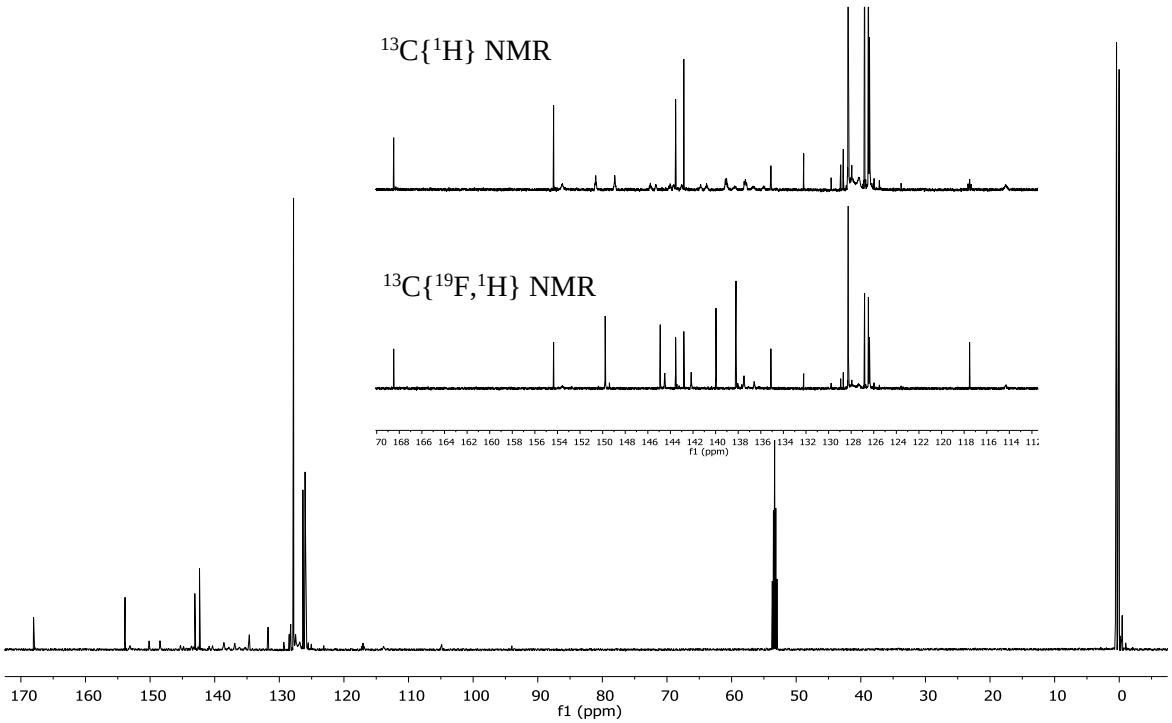


Figure S95: **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2, 299K) spectrum and detailed overview of aromatic signals with excerpt from **^{13}C{^{19}F,^{1}H} NMR** (151 MHz, CD_2Cl_2, 299K) spectrum of compound **4g**.

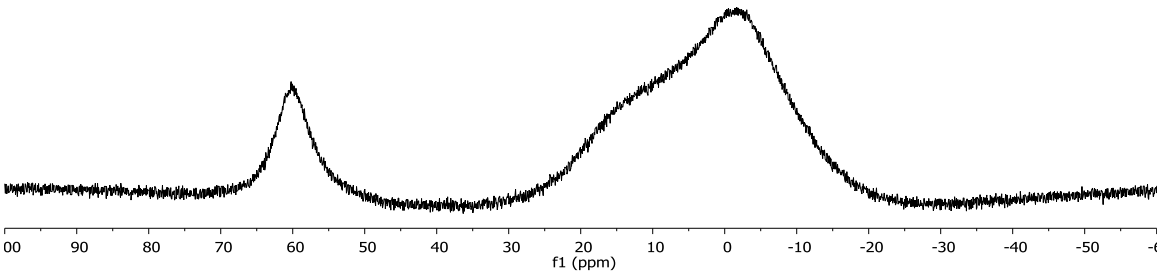


Figure S96: **$^{11}B\{^{1}H\}$ NMR** (192 MHz, CD_2Cl_2, 299K) spectrum of compound **4g**.

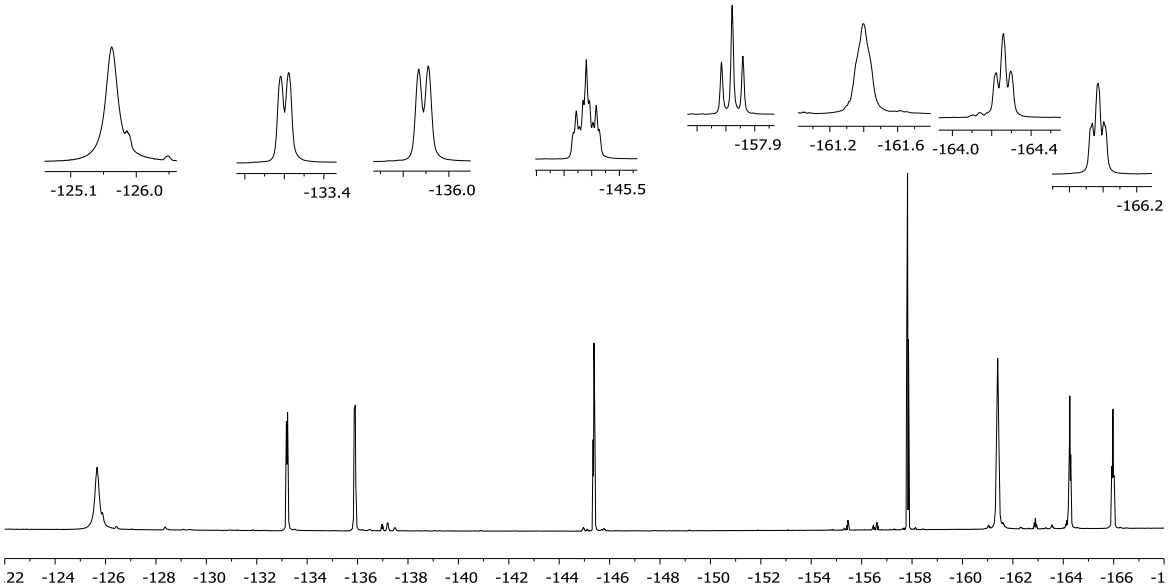


Figure S97: **^{19}F NMR** (564 MHz, CD_2Cl_2, 299 K) spectrum of compound **4g**.

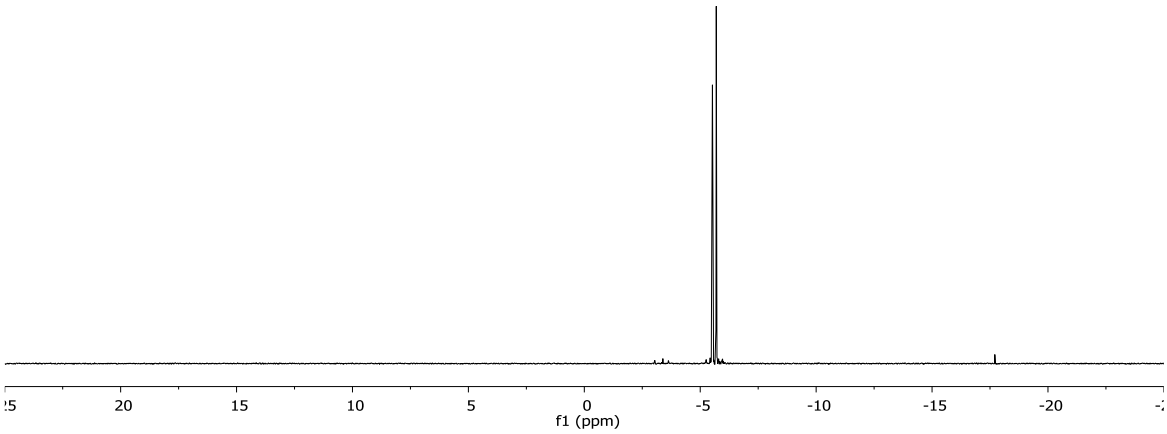
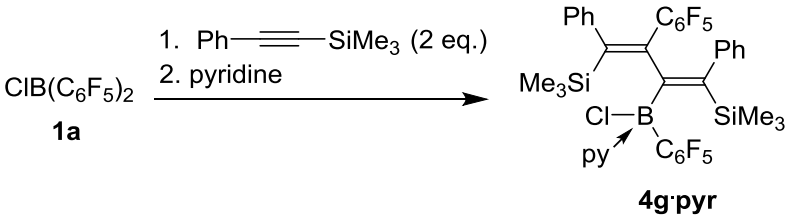


Figure S98: **^{29}Si{^{1}H} DEPT** (99 MHz, CD_2Cl_2, 299 K) spectrum of compound **4g**.

Preparation of compound 4g·pyr



Scheme S21

A solution of PhC≡CSiMe$_3$ (69.6 mg, 0.4 mmol) in CH_2Cl_2 (2 ml) was added to a solution of $ClB(C_6F_5)_2$ (75.9 mg, 0.2 mmol) in CH_2Cl_2 (2 ml). The solution was stirred for 24 hours at room temperature, subsequently a solution of pyridine (40 mg, 0.5 mmol) in CH_2Cl_2 (1 ml) was added. The pale yellow color faded out immediately. The resulting mixture was stirred for 15 minutes at room temperature, then all volatilies were removed. The residual white semi-solid was washed with a small amount of pentane, and thoroughly dried in vacuo. The product was taken up with 1 ml of CH_2Cl_2 and layered with 4 ml of pentane. The mixture was placed in the freezer (-35°C) for 5 days. After several days, white crystals of product appeared. They were isolated by decantation, washing with cold pentane and dried in vacuo. Product **4g·pyr** was isolated as 1:1 pentane adduct (according to NMR) as 162 mg of white crystalline solid (1.77 mmol, yield 88 %).

Melting point: 166.1 °C.

HRMS for $C_{39}H_{33}BCl_2F_{10}NSi_2$ [(M + Cl)$^-$]: calculated 842.1475, found 842.1473

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 9.30 (br, 2H, 2,6-py), 8.22 (tt, $^{3}J_{HH}$ = 7.6 Hz, $^{4}J_{HH}$ = 1.4 Hz, 1H, 4-py), 7.76 (m, 2H, 3,5-py), [7.47 (t, J_{HH} = 6.5 Hz, 1H, *o*), 7.41 (t, J_{HH} = 7.5 Hz, 1H, *m*), 7.39 (d, J_{HH} = 8.5 Hz, 1H, *o*), 7.25 (t, J_{HH} = 7.5 Hz, 1H, *m*), 7.18 (tt, J_{HH} = 7.4 Hz, 1.4 Hz, 1H, *p*)](Ph), 7.09 (t, J_{HH} = 6.7 Hz, 1H, *o*), 6.94 (t, J_{HH} = 7.7 Hz, 1H, *m*), 6.85 (tt, J_{HH} = 7.4 Hz, 1.3 Hz,

1H, *p*), 6.67 (t, J_{HH} = 7.6 Hz, 1H, *m*), 5.48 (d, J_{HH} = 7.8 Hz, 1H, *o*)](Ph), 0.31 (br, $\nu_{1/2} \approx$ 20 Hz, 9H, $SiMe_3$), -0.24 (s, $^2J_{SiH}$ = 6.6 Hz, $SiMe_3$).

$^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, 299 K): δ = 163.1 (*C*Ph^A), 157.8 (*C*Ph^B), 155.2 (br, *C*BC_6F_5), [147.8 (2,6-py), 143.6 (4-py), 126.3 (3,5-py)], [146.1 (*i*), 130.5 (*o*-Ph^A), 130.1 (*o*-Ph^A), 127.9 (*m*-Ph^A), 127.4 (*m*-Ph^A), 125.5 (*p*-Ph^A)](Ph), [145.8 (*i*-Ph^B), 129.9 (*o*-Ph^B), 127.8 (*m*-Ph^B), 127.5 (*o*-Ph^B), 126.8 (*m*-Ph^B), 126.2 (*p*-Ph^B)],[145.4 (dm, $^1J_{FC} \approx$ 240 Hz, 1C, C_6F_5), 143.9 (dm, $^1J_{FC} \approx$ 250 Hz, 1C, C_6F_5), 140.7 (dm, $^1J_{FC} \approx$ 250 Hz, 1C, C_6F_5), 140.0 (dm, $^1J_{FC} \approx$ 250 Hz, 1C, C_6F_5), 137.3 (dm, $^1J_{FC} \approx$ 250 Hz, 1C, C_6F_5), 137.1 (dm, $^1J_{FC} \approx$ 240 Hz, 1C, C_6F_5), 120.8 (br, *i*-$C_6F_5{}^B$), 118.6 (tm, $^2J_{FC} \approx$ 19 Hz, *i*-$C_6F_5{}^C$)], 139.8 (*C*C_6F_5), 2.36 ($^1J_{SiC}$ = 53.5 Hz, $SiMe_3{}^A$), 2.21 (br, $\nu_{1/2} \approx$ 10 Hz, $SiMe_3{}^B$) three C_6F_5 signals were not observed presumably due to broadening.

$^{13}C\{^{19}F,^1H\}$ NMR (151 MHz, CD_2Cl_2, 299 K): [selected resonances] δ = 145.4, 143.9, 140.7, 140.0, 137.3, 137.1, 120.8 (br), 118.6 (all C_6F_5).

$^{11}B\{^1H\}$ NMR (192 MHz, CD_2Cl_2, 299 K): δ = 3.3 ($\nu_{1/2} \approx$ 240 Hz).

^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = [-118.7 (br, 1F, *o*-C_6F_5), -140.2 (br, 1F, *o*-C_6F_5), -157.7 (t, $^3J_{FF}$ = 20 Hz, 1F, *p*-C_6F_5), -164.4 (br, 1F, *m*-C_6F_5), -166.6 (br, 1F, *m*-C_6F_5)]($\Delta\delta^{19}F_{m,p}$ = 6.7, 8.9), [-129.5 (m, 1F, *o*-C_6F_5), -135.4 (m, 1F, *o*-C_6F_5), -156.3 (t, $^3J_{FF}$ = 21 Hz, 1F, *p*-C_6F_5), -164.4 (m, 1F, *m*-C_6F_5), -165.0 (m, 1F, *m*-C_6F_5)]($\Delta\delta^{19}F_{m,p}$ = 8.1, 8.7).

$^{29}Si\{^1H\}$ NMR (99 Hz, CD_2Cl_2, 299 K): δ = -4.9 ($\nu_{1/2} \approx$ 1 Hz, $SiMe_3{}^B$), -7.1 ($\nu_{1/2} \approx$ 1 Hz, $SiMe_3{}^A$).

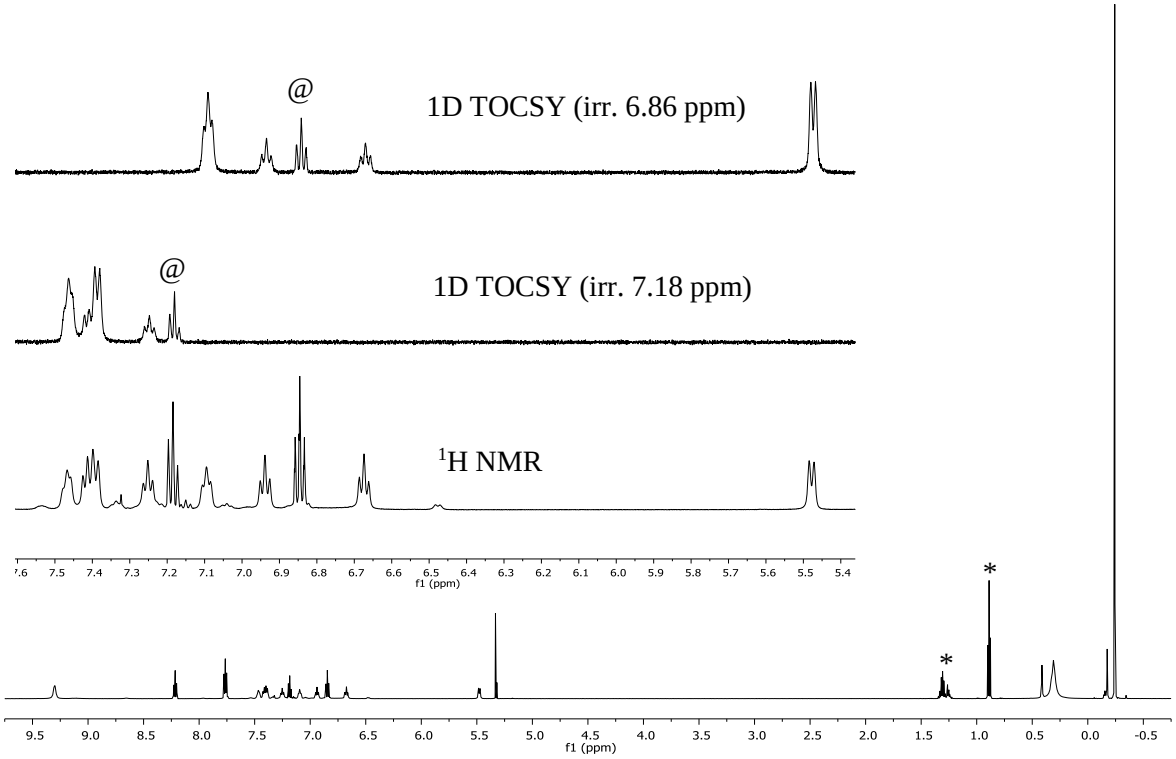


Figure S99: **^{1}H NMR** (600 MHz, CD_2Cl_2, 299K) and excerpts from **1D TOCSY** (600 MHz, CD_2Cl_2, 299K) spectra of compound **4g·pyr** with selected irradiation peaks (@), asterisks denote signals due to residual pentane.

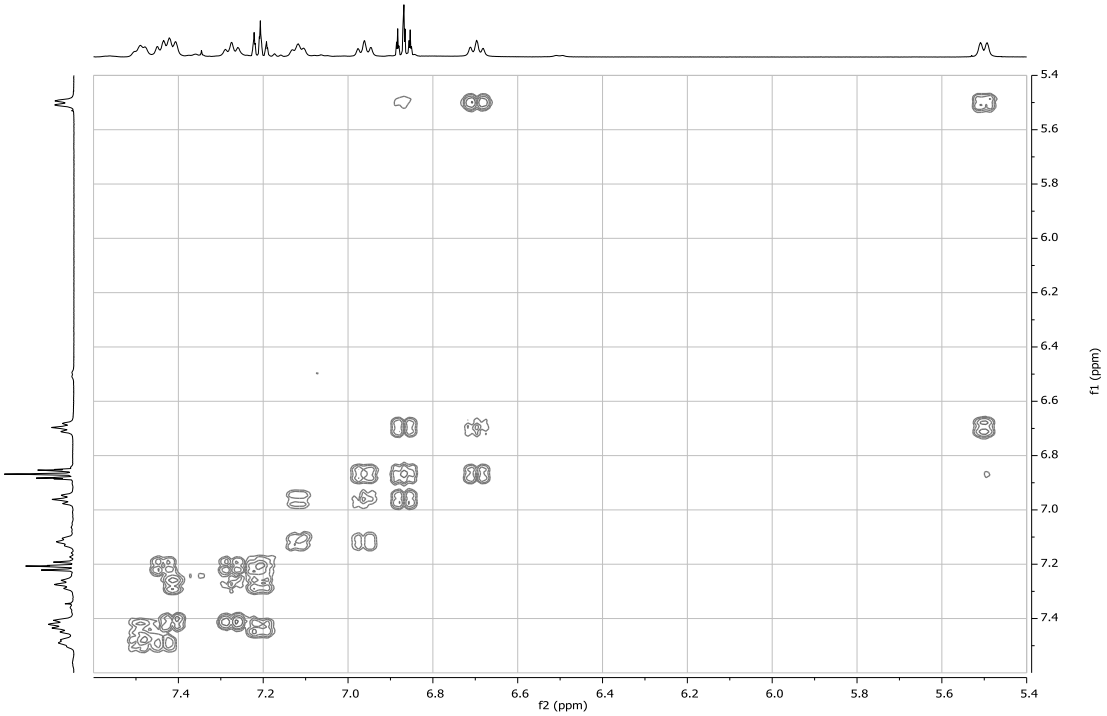


Figure S100: **^{1}H,^{1}H COSY** (600 MHz, CD_2Cl_2, 299K) spectra of compound **4g·pyr**.

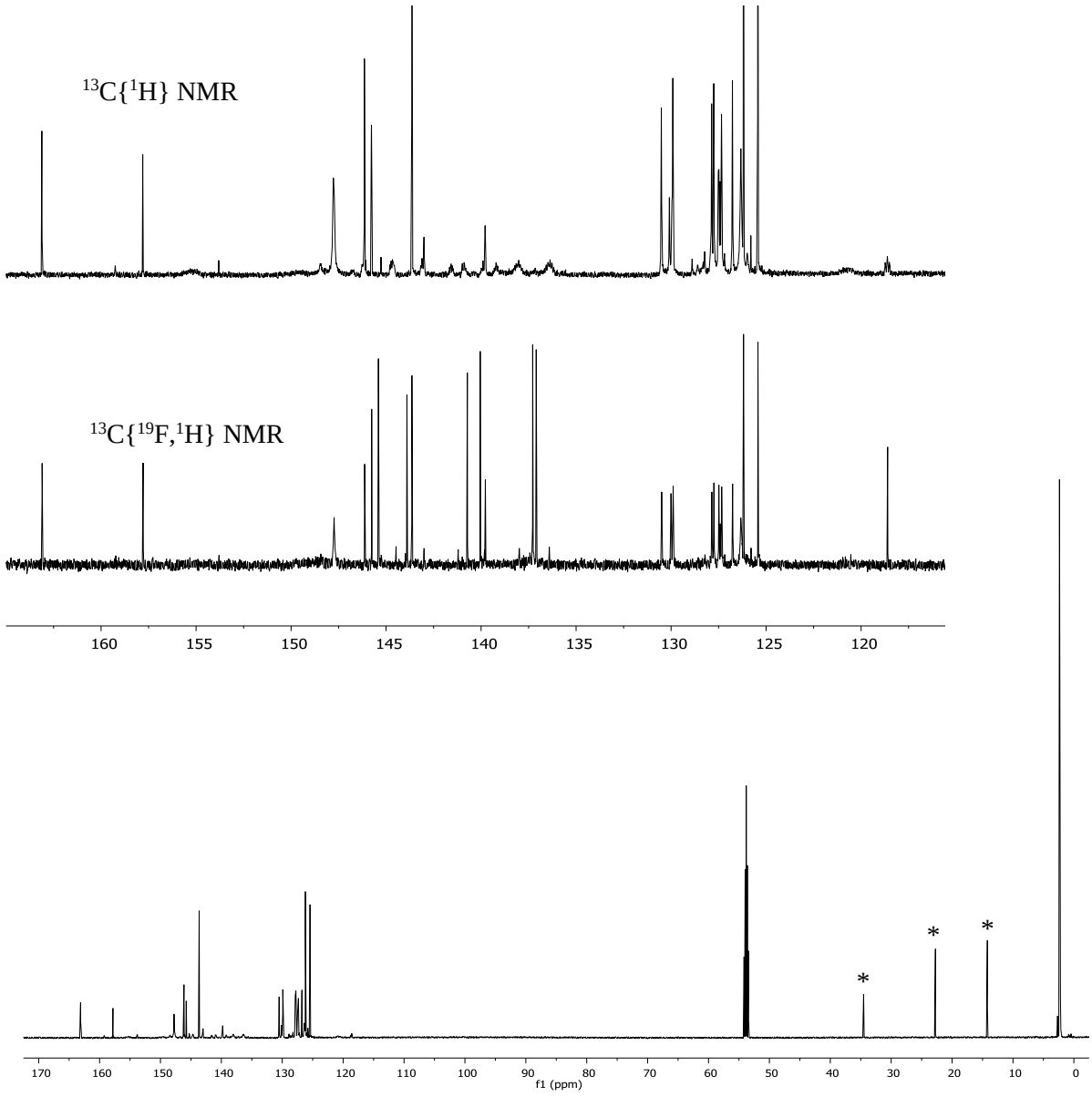


Figure S101: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, CD_2Cl_2, 299K) spectrum with detailed view of $SiMe_3$ region and aromatic signals with excerpt from **$^{13}C\{^{19}F,^{1}H\}$ NMR** (151 MHz, CD_2Cl_2, 299K) spectrum of compound **4g·pyr**, asterisks denote signals due to residual pentane.

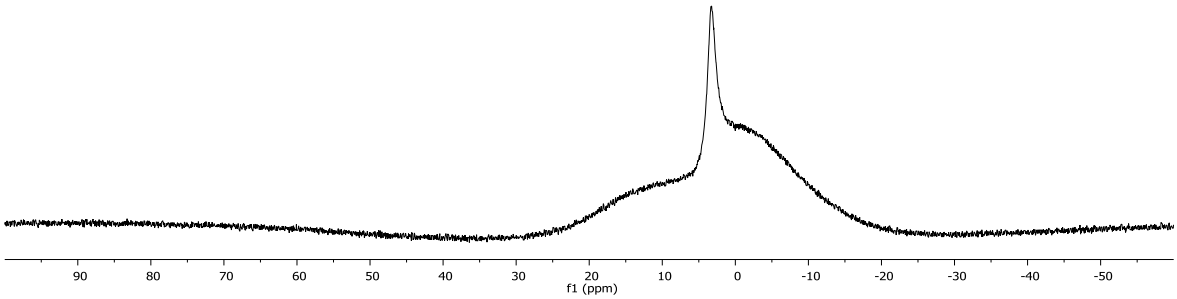


Figure S102: **^{11}B{^{1}H} NMR** (192 MHz, CD_2Cl_2, 299K) spectrum of compound **4g·pyr**.

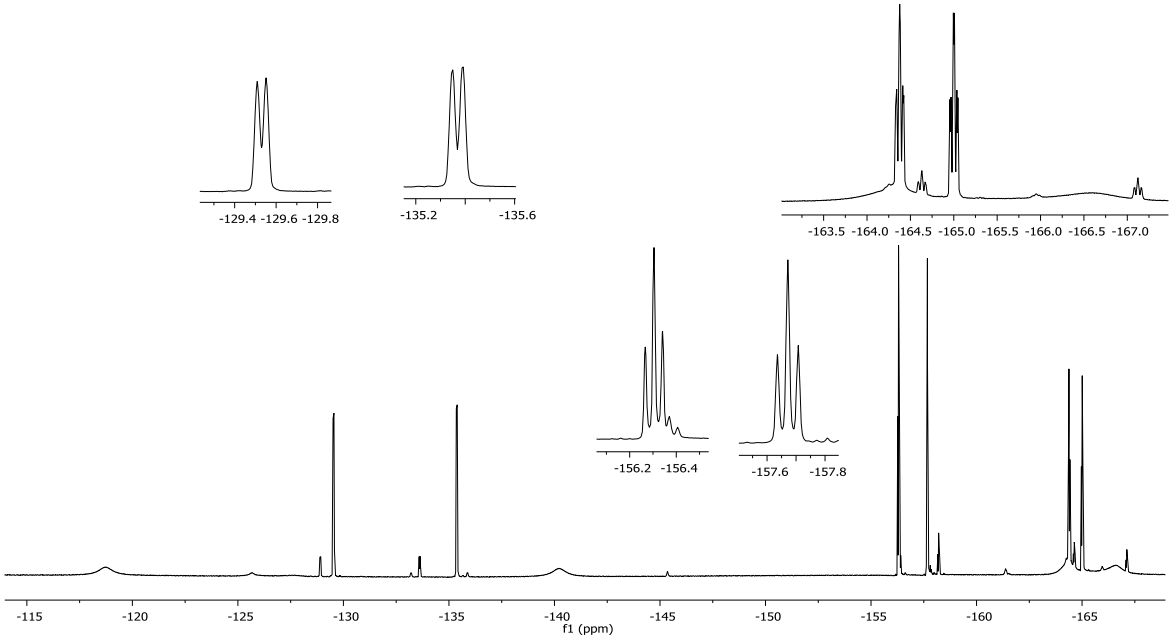


Figure S103: **^{19}F NMR** (564 MHz, CD_2Cl_2, 299 K) spectrum of compound **4g·pyr**.

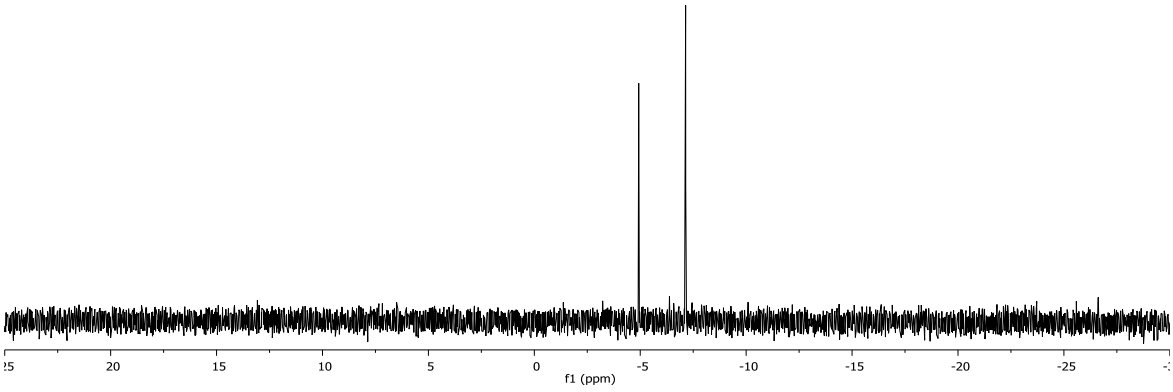


Figure S104: **^{29}Si{^{1}H} NMR** (99 MHz, CD_2Cl_2, 299 K) spectrum of compound **4g·pyr**.

Crystals suitable for the X-ray crystal structure analysis were grown by slow diffusion of pentane into a solution of **4g·pyr** in CH_2Cl_2 at -35°C.

X-ray crystal structure analysis of compound 4g·pyr (erk9186): A colorless prism-like specimen of $C_{39}H_{33}BClF_{10}NSi_2$, approximate dimensions 0.060 mm x 0.100 mm x 0.120 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using a monoclinic unit cell yielded a total of 13600 reflections to a maximum θ angle of 25.00° (0.84 Å resolution), of which 7539 were independent (average redundancy 1.804, completeness = 98.7%, R_{int} = 3.79%, R_{sig} = 4.39%) and 5831 (77.34%) were greater than $2\sigma(F^2)$. The final cell constants of a = 11.9125(2) Å, b = 19.3305(3) Å, c = 19.4412(4) Å, β = 103.855(7)°, volume = 4346.56(18) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9750 and 0.9870. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/n$, with Z = 4 for the formula unit, $C_{39}H_{33}BClF_{10}NSi_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 548 variables converged at R1 = 5.25%, for the observed data and wR2 = 11.55% for all data. The goodness-of-fit was 1.043. The largest peak in the final difference electron density synthesis was 0.230 $e^-/Å^3$ and the largest hole was -0.245 $e^-/Å^3$ with an RMS deviation of 0.045 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.235 g/cm^3 and F(000), 1656 e^-. CCDC Nr.: 1892614.

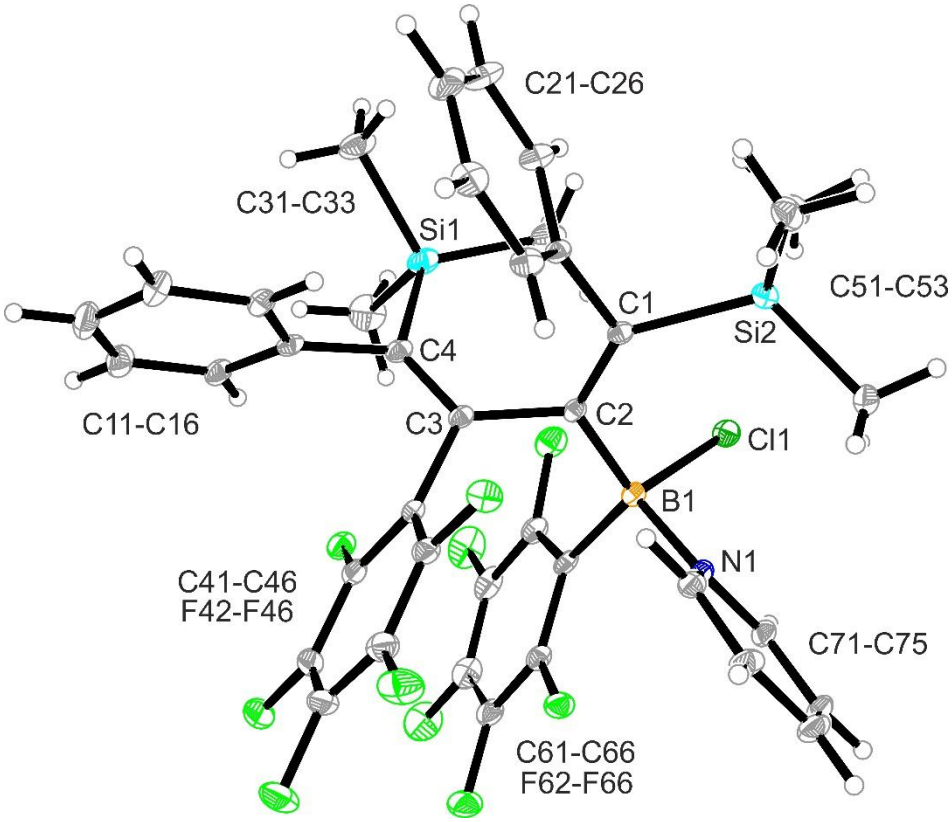


Figure S105: Crystal structure of compound **4g·pyr** (thermal ellipsoids: 15% probability).

Reaction of $ClB(C_6F_5)_2$ with three equivalents of $PhC{\equiv}CSiMe_3$

Solutions of 38.0 mg of $ClB(C_6F_5)_2$ (0.1 mmol) in toluene (1 ml) and $PhC{\equiv}CSiMe_3$ (52.2 mg, 0.3 mmol) in toluene (2 ml) were combined and heated to 100°C for 48 hours. Then all volatilities were removed in vacuo and the resulting orange oil was characterized by NMR experiments (CD_2Cl_2, 299K) revealing the presence of compound **4g** and alkyne **2c**.

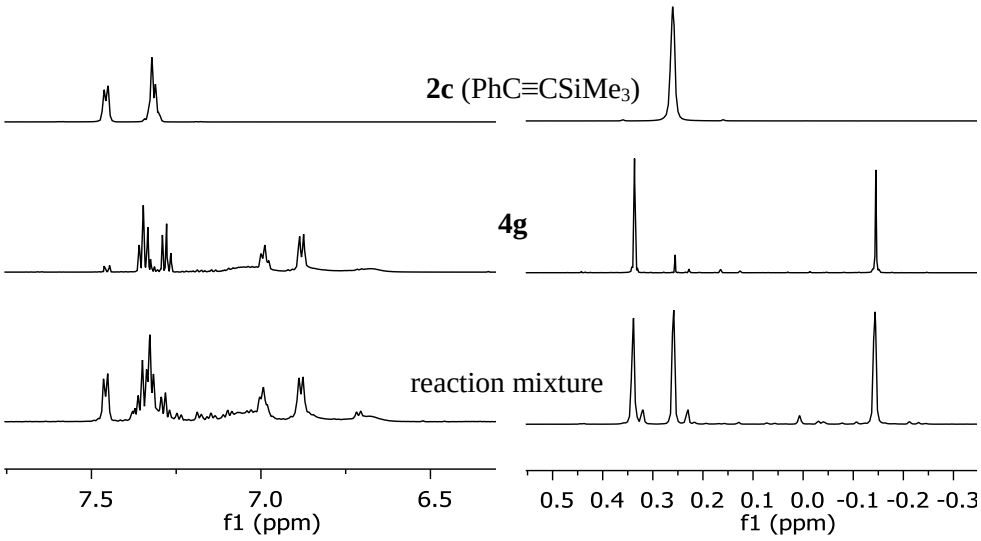


Figure S106: Comparison of **^{1}H NMR** (600 MHz, CD_2Cl_2, 299K) spectra of alkyne **2c**, compound **4g** and the mixture of the reaction of three equivalents of $PhC{\equiv}CSiMe_3$ (**2c**) with $ClB(C_6F_5)$.

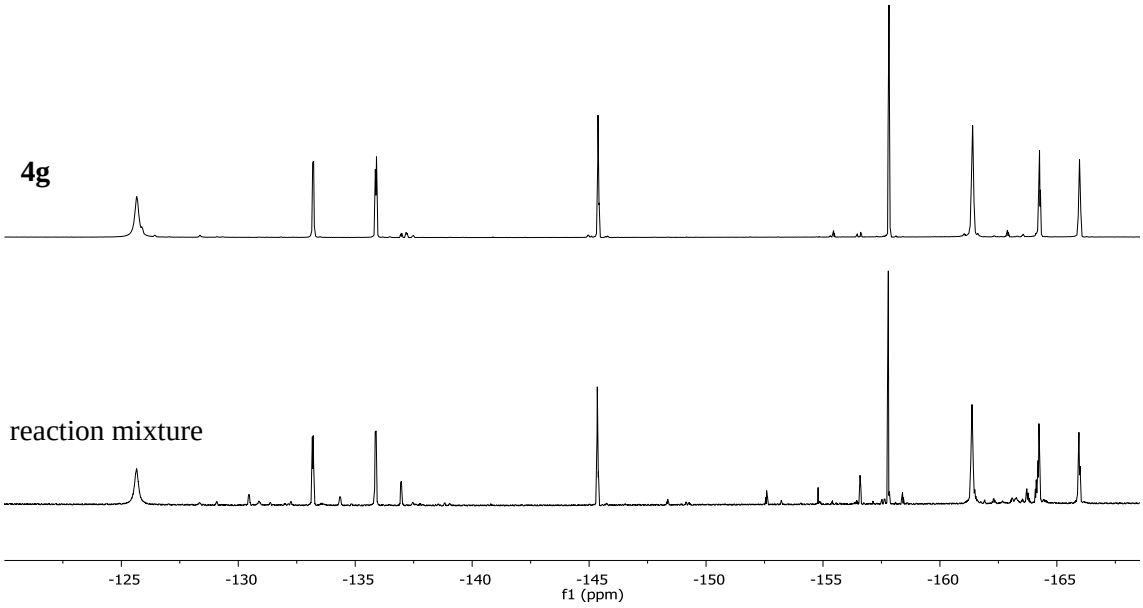
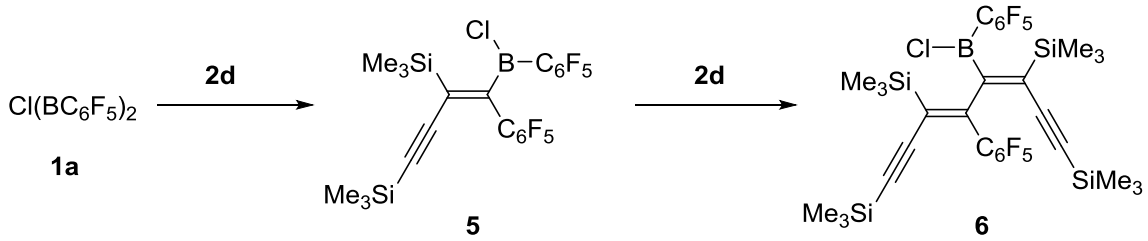


Figure S107: Comparison of **^{19}F NMR** (564 MHz, CD_2Cl_2, 299K) spectra of compound **4g** and the mixture of the reaction of three equivalents of $PhC{\equiv}CSiMe_3$ (**2c**) with $ClB(C_6F_5)$.

Titration reaction of $ClB(C_6F_5)_2$ (1a) with bis(trimethylsilyl)butadiyne (2d)



Scheme S22

A solution of 1,4-bis(trimethylsilyl)butadiyne (**2d**) (19.4 mg, 0.01 mmol) in CD_2Cl_2 (0.2 ml) was added to a solutio of $ClB(C_6F_5)_2$ (**1a**) (38.0 mg, 0.01 mmol) in CD_2Cl_2 (0.3 ml). The mixture was transferred to a NMR Young tube and the reaction progress was monitored by ^1H and ^{19}F NMR spectroscopy. After 3 hours at room temperature, complete conversion to the carboboration product **5** was observed. Subsequently, an additional equivalent of 1,4-bis(trimethylsilyl)butadiyne (**2d**) (19.4 mg, 0.01 mmol, solution in 0.2 ml of CD_2Cl_2) was added. The reaction mixture turned gradually dark and monitoring by ^1H and ^{19}F NMR spectroscopy revealed complete conversion to the dimerization product **6** after 24 hours at r.t.

NOTE: two equivalents of $ClB(C_6F_5)_2$ with bis(trimethylsilyl)butadiyne (**2d**) reacted to product **5** alongside with unreacted $ClB(C_6F_5)_2$ even after 20h heating to 60°C.

Generation of compound 5

$ClB(C_6F_5)_2$ (38.0 mg, 0.1 mmol) was dissolved in CD_2Cl_2 (0.3 ml) and a solution of 1,4-bis(trimethylsilyl)butadiyne (19.4 mg, 0.1 mmol) in CD_2Cl_2 (0.2 ml) was added. The yellow reaction mixture was transferred to a NMR tube, which was flame sealed. After 3 hours at room temperature the product was *in situ* analyzed by NMR spectroscopy revealing complete conversion to compound **5** (a small amount of the double addition product **6** originated from broken stoichiometry due to incorrect weighting).

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 0.30 (s, $^2J_{SiH}$ = 6.8 Hz, 9H, =CSiMe_3), 0.10 (s, $^2J_{SiH}$ = 7.2 Hz, 9H, ≡CSiMe_3).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = 154.4 (=*C*SiMe_3), 149.1 (dm, $^1J_{FC}$ ≈ 254 Hz, 2C, C_6F_5), 147.2 (br, *C*C_6F_5)^t, 145.1 (dm, $^1J_{FC}$ ≈ 260 Hz, 1C, C_6F_5)), 144.2 (dm, $^1J_{FC}$ ≈ 250 Hz, 2C, C_6F_5), 141.1 (dm, $^1J_{FC}$ ≈ 253 Hz, 1C, C_6F_5), 138.1 (dm, $^1J_{FC}$ ≈ 250 Hz, 2C, C_6F_5), 138.0 (dm, $^1J_{FC}$ ≈ 250 Hz, 2C, C_6F_5), 117.1 (tm, $^2J_{FC}$ ≈ 22 Hz, *i*-$C_6F_5^C$), 115.7 (*i*-$C_6F_5^B$),^{t} 106.5 (*C*≡CSiMe_3), 0.6 ($^1J_{SiC}$ = 54.6 Hz, =CSi*Me*$_3$), -0.6 ($^1J_{SiC}$ = 56.7 Hz, ≡CSi*Me*$_3$). ^{t}- tentative assigment

^{13}C{^{19}F,^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): [selected resonances] δ = 149.1 (2C), 145.1 (1C), 144.2 (2C), 141.1 (1C), 138.1 (2C), 138.0 (2C) (all C_6F_5).

^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = 59.5 ($\nu_{1/2}$ ~ 730 Hz).

^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = [-127.5 (m, 2F, *o*-$C_6F_5^B$), -145.2 (tt, J_{FF} = 20 Hz, 7 Hz, 1F, *p*-$C_6F_5^B$), -161.1 (m, 2F, *m*-$C_6F_5^B$)]($\Delta\delta^{19}F_{m,p}$ = 16.1), [-137.0 (m, 2F, *o*-$C_6F_5^C$), -155.9 (t, J_{FF} = 21 Hz, 1F, *p*-$C_6F_5^C$), -163.3 (m, 2F, *m*-$C_6F_5^C$)]($\Delta\delta^{19}F_{m,p}$ = 7.4).

^{29}Si{^{1}H} DEPT (119 Hz, CD_2Cl_2, 299 K): δ = -1.4 ($\nu_{1/2}$ ≈ 1 Hz, =CSiMe_3), -17.0 ($\nu_{1/2}$ ≈ 1 Hz, ≡CSiMe_3).

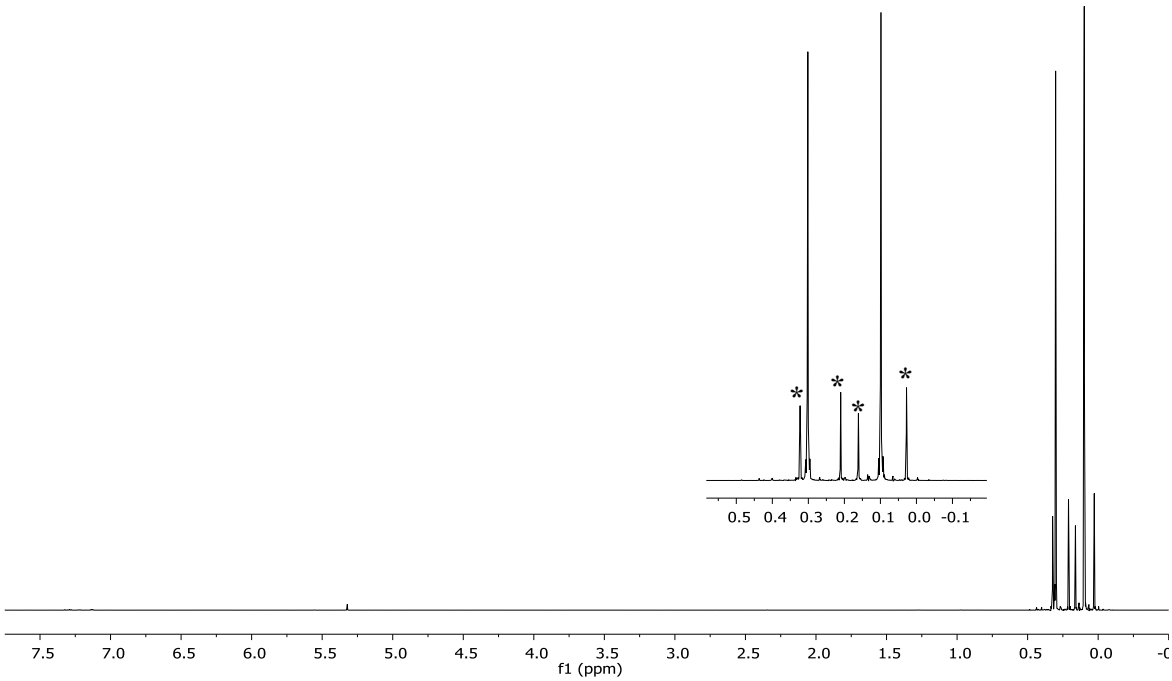


Figure S108: **^{1}H NMR** (600 MHz, CD_2Cl_2, 299K) spectrum of compound **5**, asterisks denote signals due to compound **6**.

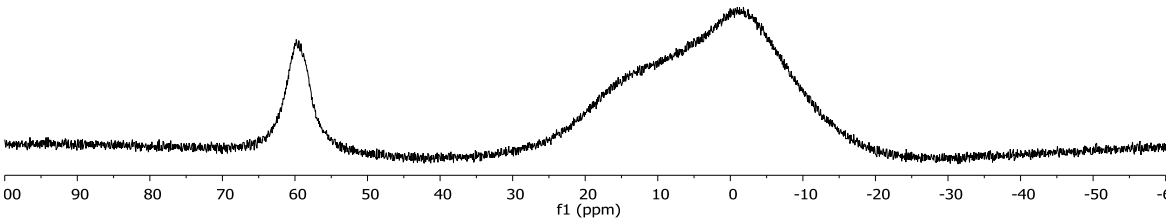


Figure S109: **^{11}B{^{1}H} NMR** (192 MHz, CD_2Cl_2, 299K) spectrum of compound **5**.

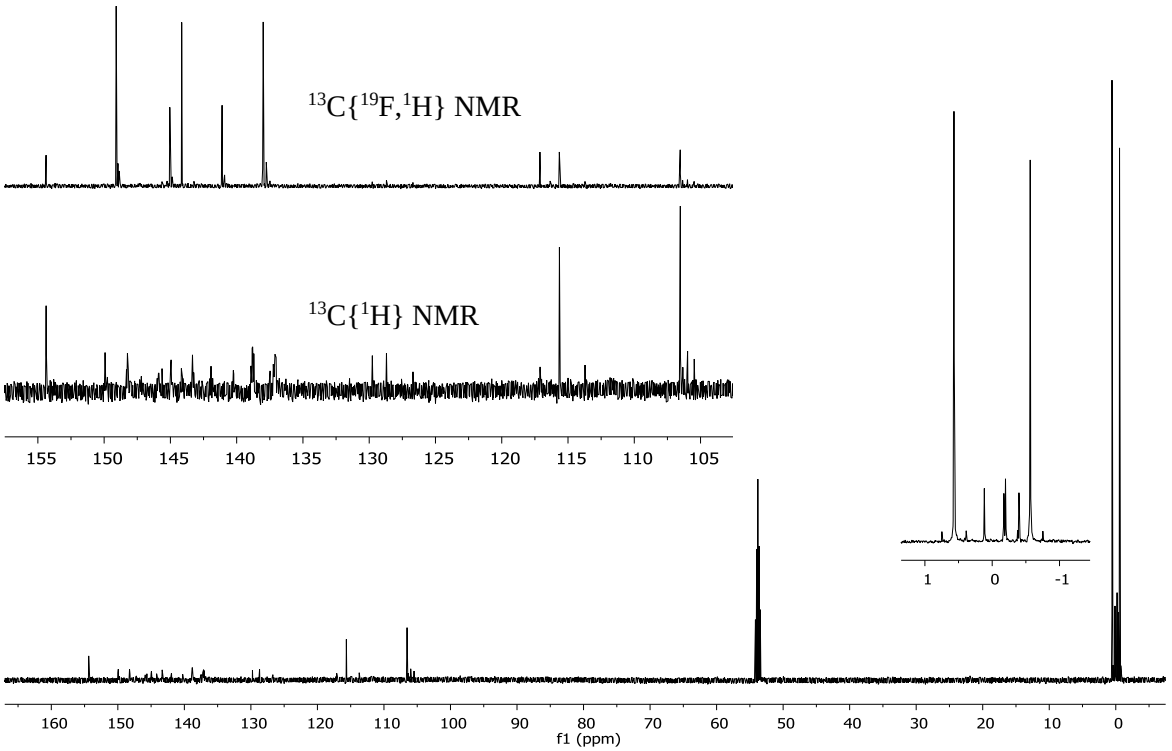


Figure S110: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, CD_2Cl_2, 299K) spectrum with detailed view of $SiMe_3$ region and aromatic signals with excerpt from **$^{13}C\{^{19}F,^{1}H\}$ NMR** (151 MHz, CD_2Cl_2, 299K) spectrum of compound **5.**

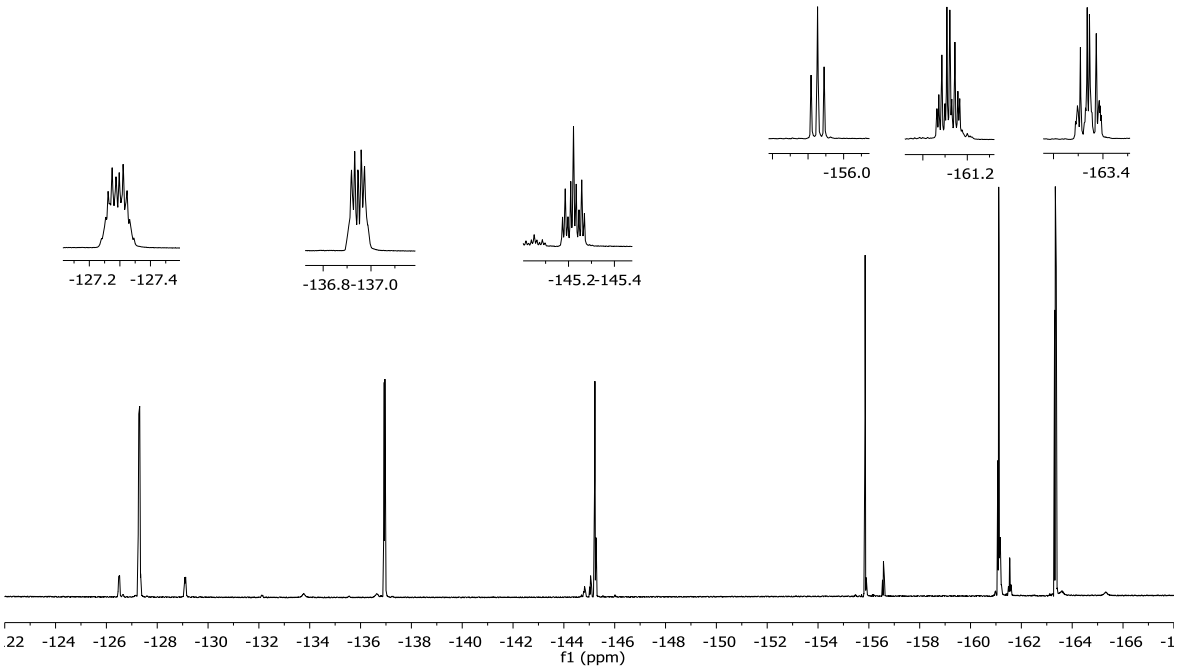


Figure S111: **^{19}F NMR** (564 MHz, CD_2Cl_2, 299K) spectrum of compound **5**.

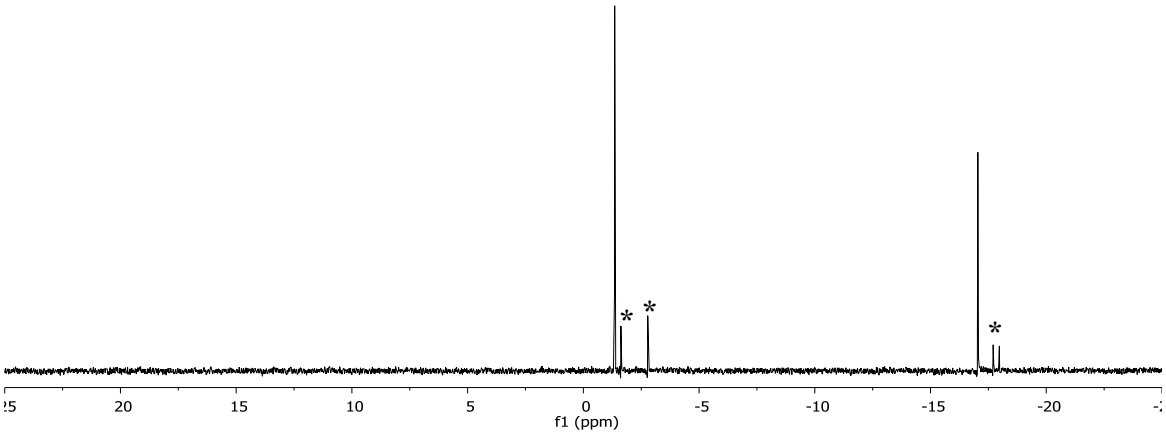
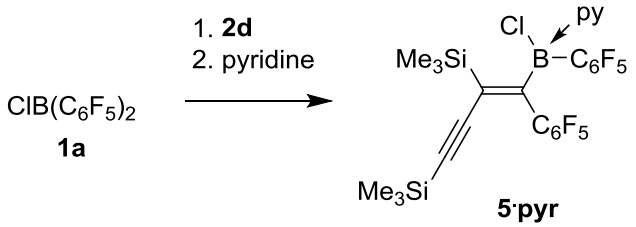


Figure S112: **^{29}Si{^{1}H} DEPT** (119 MHz, CD_2Cl_2, 299K) spectrum of compound **6,** asterisks denote signals due to compound **6**.

Preparation of compound 5·pyr



Scheme S23

Solutions of 1,4-bis(trimethylsilyl)butadiyne (**2d**) (38.8 mg, 0.2 mmol) in 2 ml of CH_2Cl_2 and $ClB(C_6F_5)_2$ (**1a**) (76.0 mg, 0.2 mmol) in CH_2Cl_2 (2 ml) were combined and allowed to stir at room temperature for 3 hours. Subsequently, a solution of pyridine (19.7 mg, 0.25 mmol) in CH_2Cl_2 (1 ml) was added. The mixture was stirred for 15 mintues at room temperature, subsequently all volatilities were removed in vacuo. The white residue was taken up with dichlormethane (1 ml) and layered with pentane (3 ml). The mixture was placed in a freezer (-35 °C). Over several days, colorless needle-shaped crystals appeared. They were isolated by decantation, washed with a small amount of cold pentane and dried in vacuo. Product **5·pyr** was obtained as a white solid (96.1 mg, 0.147 mmol, 74% yield).

Melting point: 123.1 °C.

Elementary analysis for $C_{27}H_{23}BClF_{10}NSi_2$ (653.1): calculated C 49.59, H 3.55, N 2.14; found C 49.26, H 3.33, N 2.10.

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 9.10 (m, 2H, 2,6-py), 8.22 (d, $^3J_{HH}$ = 7.8 Hz, 1.6 Hz, 1H, 4-py), 7.73 (m, 2H, 3,5-py), 0.08 (s, $^2J_{SiH}$ = 6.6 Hz, 9H, =CSiMe_3), 0.01 (s, $^2J_{SiH}$ = 7.0 Hz, 9H, ≡CSiMe_3).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = 155.5 (br, *C*C_6F_5)^t, 148.2 (dm, $^1J_{FC}$ ≈ 253 Hz, 2C, C_6F_5), 147.2 (2,6-py), 143.9 (br, SiC=), 143.8 (4-py), 143.3 (dm, $^1J_{FC}$ ≈ 245 Hz, 1C, C_6F_5), 142.8 (dm, $^1J_{FC}$ ≈ 240 Hz, 1C, C_6F_5), 140.7 (dm, $^1J_{FC}$ ≈ 254 Hz, 1C, C_6F_5), 139.4 (dm, $^1J_{FC}$ ≈ 252 Hz, 1C, C_6F_5), 137.6 (dm, $^1J_{FC}$ ≈ 260 Hz, 1C, C_6F_5), 137.4 (dm, $^1J_{FC}$ ≈ 250 Hz, 2C, C_6F_5), 137.1 (dm, $^1J_{FC}$ ≈ 251 Hz, 1C, C_6F_5), 126.4 (3,5-py), 123.0 (tm, $^2J_{FC}$ ≈ 21 Hz, *i*-$C_6F_5^C$), 119.5 (br, *i*-$C_6F_5^B$)^t, 108.3 (≡C), 106.0 (≡C), 0.5 ($^1J_{SiC}$ = 54.2 Hz, =CSi*Me*$_3$), -0.4 ($^1J_{SiC}$ = 56.4 Hz, ≡CSi*Me*$_3$), ^{t}-tentative assigment.

^{13}C{^{19}F,^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): [selected resonances] δ = 148.2 (2C), 143.3 (1C), 142.8 (1C), 140.7 (1C), 139.4 (1C), 137.6 (1C), 137.4 (2C), 137.1 (1C) (all C_6F_5)

^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = 2.8 ($\nu_{1/2}$ ≈ 200 Hz)

^{19}F NMR (564 MHz, CD_2Cl_2, 213 K): δ = [-125.3 (br, 1F, *o*-C_6F_5), -140.0 (br, 1F, *o*-C_6F_5), -155.7 (br, 1F, *p*-C_6F_5), -163.0 (br, 1F, *m*-C_6F_5), -163.9 (br, 1F, *m*-C_6F_5)]($\Delta\delta^{19}F_{m,p}$ = 7.3, 8.2), [-138.4 (br, 1F, *o*-C_6F_5), -141.2 (br, 1F, *o*-C_6F_5), -158.0 (br, 1F, *p*-C_6F_5), -163.9 (br, 1F, *m*-C_6F_5), -164.4 (br, 1F, *m*-C_6F_5)]($\Delta\delta^{19}F_{m,p}$ = 5.9, 6.4).

^{29}Si{^{1}H} DEPT (119 Hz, CD_2Cl_2, 299 K): δ = -4.1 ($\nu_{1/2}$ ≈ 1 Hz, =CSiMe_3), -18.5 ($\nu_{1/2}$ ≈ 1 Hz, ≡CSiMe_3).

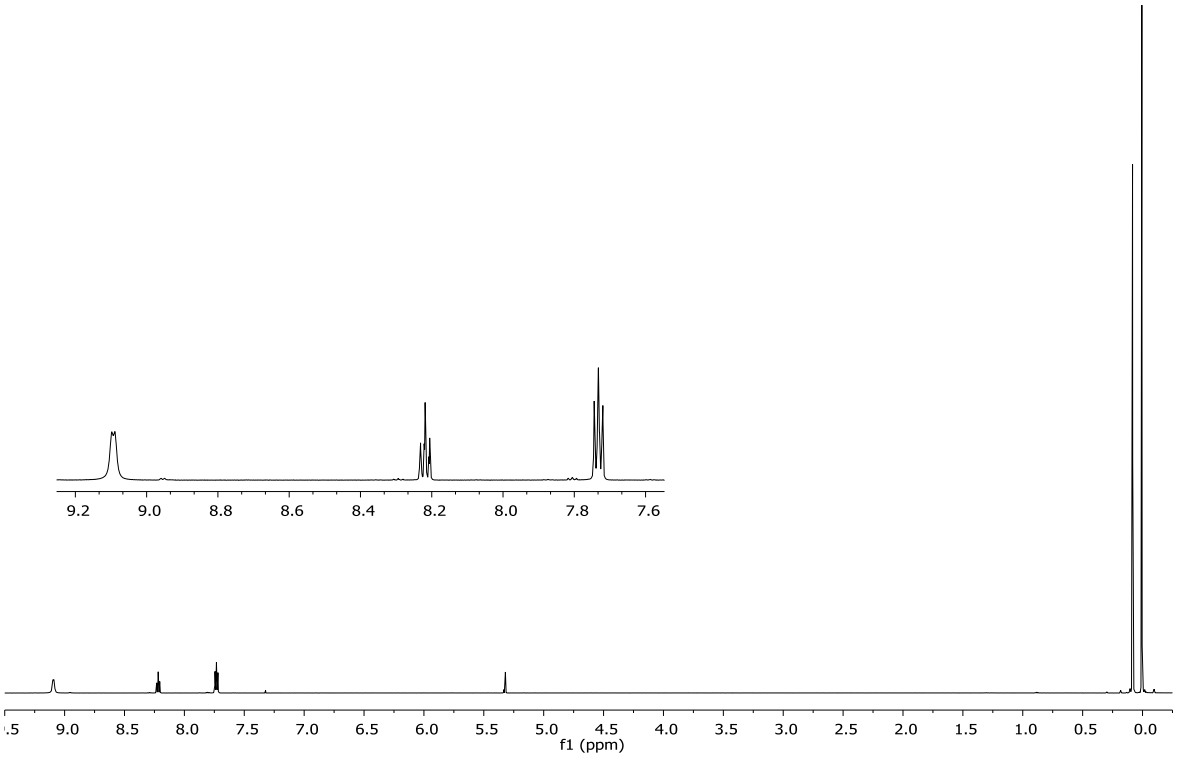


Figure S113: **^{1}H NMR** (600 MHz, CD_2Cl_2, 299K) spectrum of compound **5·pyr**.

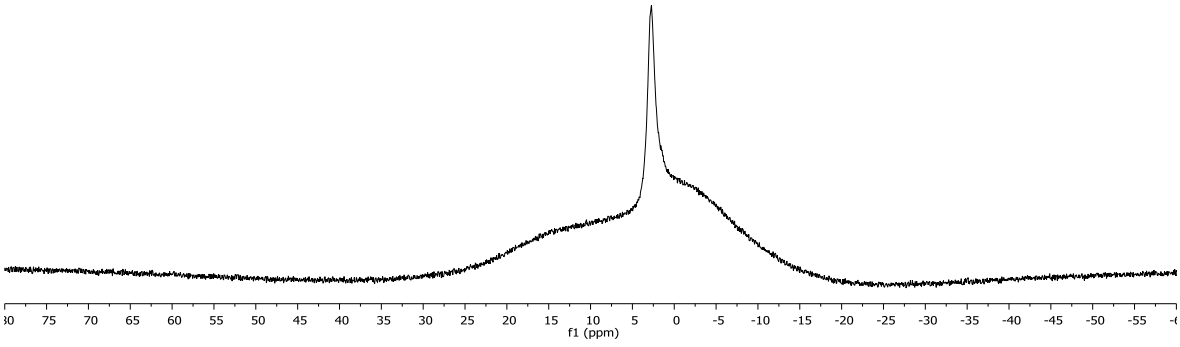


Figure S114: **^{11}B{^{1}H} NMR** (192 MHz, CD_2Cl_2, 299K) spectrum of compound **5·pyr**.

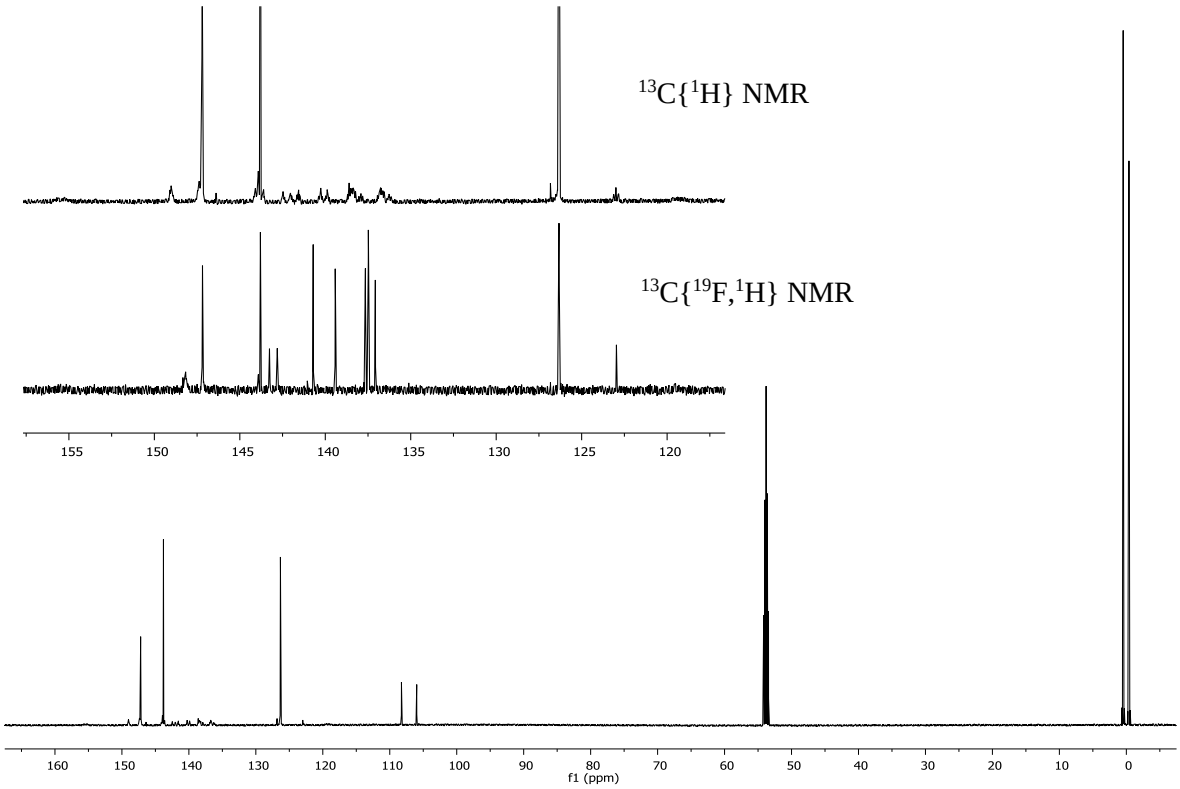


Figure S115: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, CD_2Cl_2, 299K) spectrum and detailed overview of aromatic signals with excerpt from **$^{13}C\{^{19}F,^{1}H\}$ NMR** (151 MHz, CD_2Cl_2, 299K) spectrum of compound **5·pyr**.

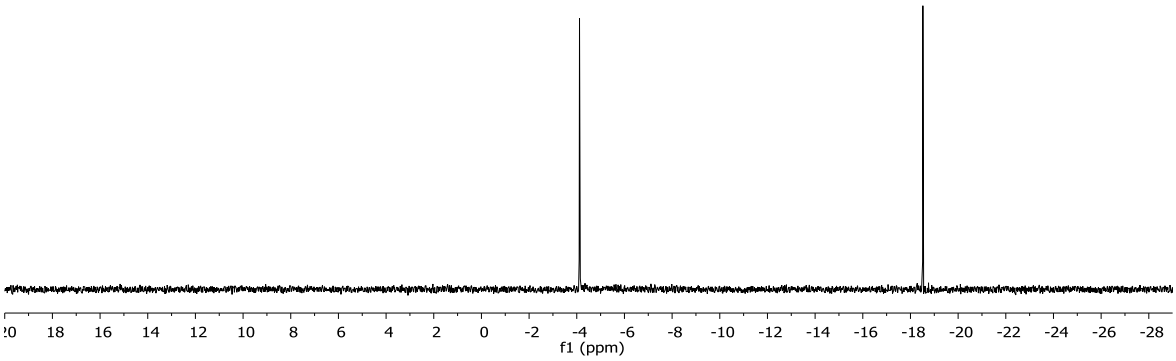


Figure S116: **$^{29}Si\{^{1}H\}$ DEPT** (119 MHz, CD_2Cl_2, 299K) spectrum of compound **5·pyr**.

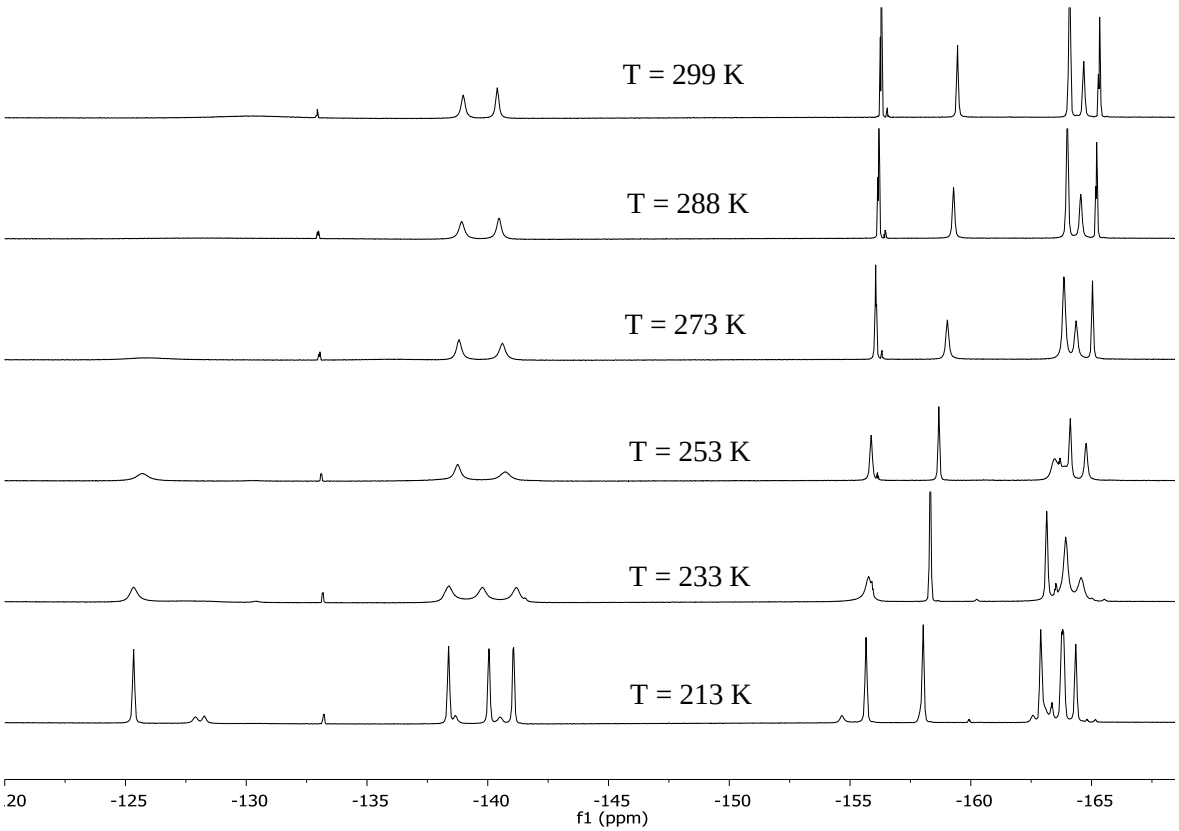


Figure S117: **^{19}F NMR** (564 MHz, CD_2Cl_2) spectrum of compound **5·pyr** measured at various temperatures.

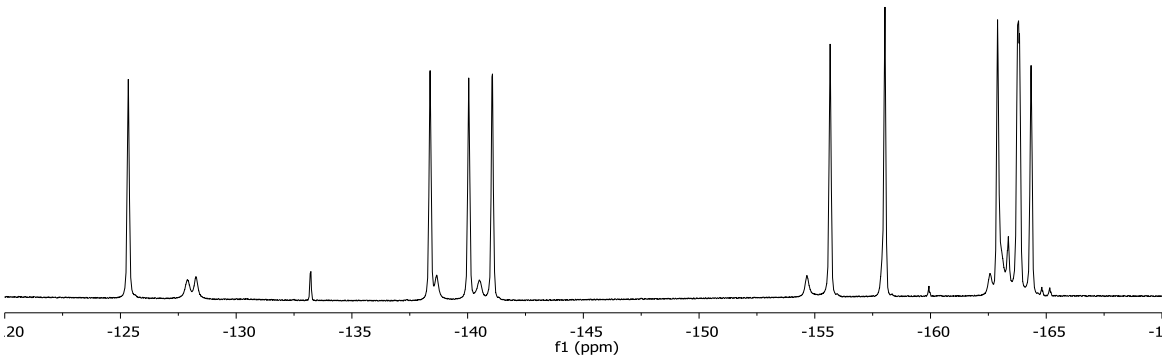


Figure S118: **^{19}F NMR** (564 MHz, CD_2Cl_2, 213 K) spectrum of compound **5·pyr**.

Crystals suitable for the X-ray crystal structure analysis were grown by slow evaporation of a solution of **5·pyr** in CH_2Cl_2/pentane at room temperature.

X-ray crystal structure analysis of compound 5·pyr (erk9180): A colorless plate-like specimen of $C_{27}H_{23}BClF_{10}NSi_2$, approximate dimensions 0.040 mm x 0.100 mm x 0.130 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using a monoclinic unit cell yielded a total of 9452 reflections to a maximum θ angle of 25.00° (0.84 Å resolution), of which 5268 were independent (average redundancy 1.794, completeness = 98.5%, R_{int} = 3.43%, R_{sig} = 4.28%) and 4285 (81.34%) were greater than $2\sigma(F^2)$. The final cell constants of a = 11.9676(2) Å, b = 18.7450(3) Å, c = 27.0581(5) Å, β = 90.8900(10)°, volume = 6069.28(18) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9640 and 0.9890. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *C*2/*c*, with Z = 8 for the formula unit, $C_{27}H_{23}BClF_{10}NSi_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 416 variables converged at R1 = 4.68%, for the observed data and wR2 = 9.78% for all data. The goodness-of-fit was 1.084. The largest peak in the final difference electron density synthesis was 0.315 $e^-/Å^3$ and the largest hole was -0.343 $e^-/Å^3$ with an RMS deviation of 0.052 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.431 g/cm^3 and F(000), 2656 e^-. CCDC Nr.: 1892615.

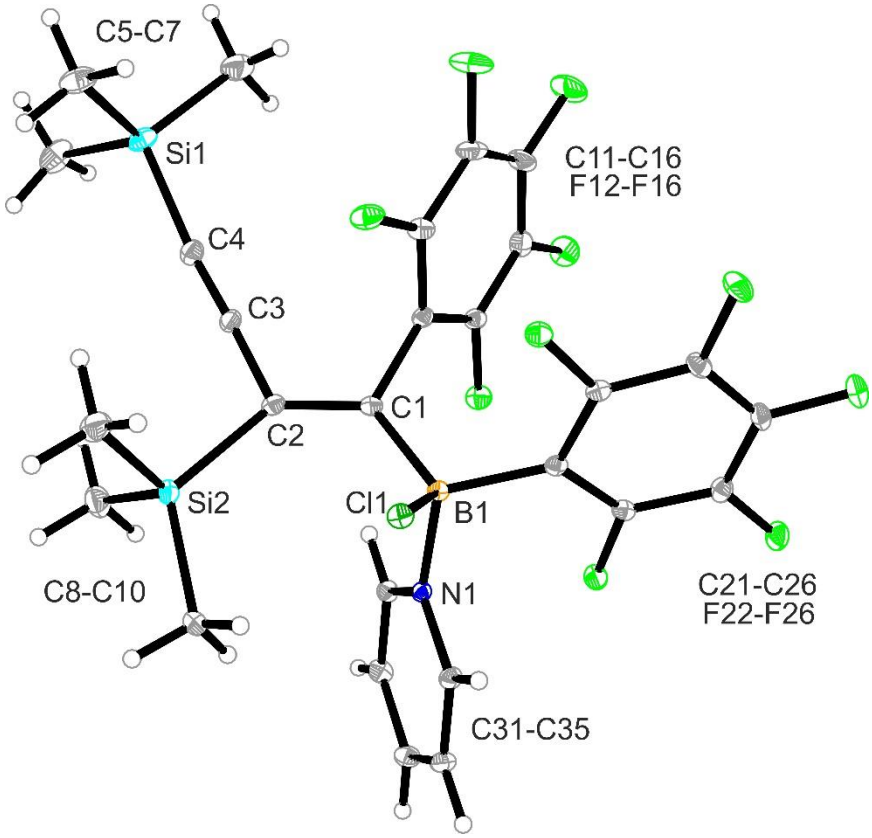
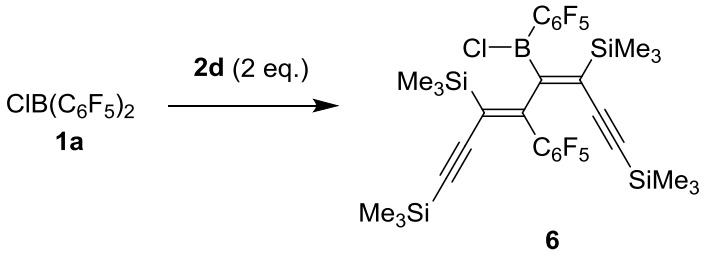


Figure S119: Crystal structure of compound **5·pyr** (thermal ellipsoids: 15% probability).

Generation of compound 6



Scheme S24

$ClB(C_6F_5)_2$ (**1a**) (38.0 mg, 0.1 mmol) was dissolved in CD_2Cl_2 (0.3 ml) and a solution of 1,4-bis(trimethylsilyl)butadiyne (**2d**) (38.8 mg, 0.2 mmol) in CD_2Cl_2 (0.2 ml) was added. The reaction mixture was vigorously shaken, transferred to a NMR tube, which was flame sealed and stored at room temperature. NMR measurements after 24 hours revealed complete conversion to compound **6**. Product **6** was in situ characterized by NMR spectroscopy.

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 0.33 (s, $^{2}J_{SiH}$ = 6.9 Hz, 9H, =CSiMe_3), 0.22 (s, $^{2}J_{SiH}$ = 7.1 Hz, 9H, ≡CSiMe_3), 0.17 (s, $^{2}J_{SiH}$ = 6.9 Hz, 9H, =CSiMe_3), 0.04 (s, $^{2}J_{SiH}$ = 7.1 Hz, 9H, ≡CSiMe_3)

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = 159.5 (=C), 145.6 (=CSi), 143.2 (=C),), 137.5 (=CSi), [149.0 (dm, $^{1}J_{FC}$ ≈ 254 Hz, 2C, *o*), 144.9 (dm, $^{1}J_{FC}$ ≈ 250 Hz, 1C, *p*), 137.8 ($^{1}J_{FC}$ ≈ 251 Hz, 2C, *m*), 112.6 (br, *i*)]($C_6F_5^B$), [140.9 (dm, $^{1}J_{FC}$ ≈ 253 Hz, 1C, *p*), 116.4 (tm, $^{2}J_{FC}$ ≈ 21 Hz, *i*)]($C_6F_5^C$), 113.7 (≡CSi), 106.4 (≡*C*-C), 106.0 (≡*C*-C), 105.5 (≡CSi), 0.1 ($^{1}J_{SiC}$ = 53.5 Hz, =CSi*Me*$_3$), -0.2 ($^{1}J_{SiC}$ = 56.3 Hz, =CSi*Me*$_3$), -0.2 ($^{1}J_{SiC}$ = 54.6 Hz, ≡CSi*Me*$_3$), -0.4 (≡CSi*Me*$_3$), signals of *o*- and *m*-$C_6F_5^C$ are broad and therefore lost in the noise),

^{13}C{^{19}F,^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): [selected resonances] δ = 149.0 (2C, *o*-$C_6F_5^B$), 144.9 (1C, *p*-$C_6F_5^B$), 140.9 (2C, *p*-$C_6F_5^C$), 137.8 (2C, *p*-$C_6F_5^B$), signals of *o*- and *m*-C_6F_5C are broad and therefore lost in the noise

^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = 59.8 ($\nu_{1/2}$ ≈ 950 Hz)

^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = [-126.5 (m, 2F, *o*-$C_6F_5^B$), -145.0 (tt, J_{FF} = 20 Hz, 7 Hz, 1F, *p*-$C_6F_5^B$), -161.5 (m, 2F, *m*-$C_6F_5^B$)]($\Delta\delta^{19}F_{m,p}$ = 16.5), [-133.8 (br, 1F, *o*-$C_6F_5^C$), -136.6 (br, 1F, *o*-$C_6F_5^C$), -156.5 (t, J_{FF} = 21 Hz, 1F, *p*-$C_6F_5^C$), -163.6 (br, 1F, *m*-$C_6F_5^C$), -165.3 (br, 1F, *m*-$C_6F_5^C$)]($\Delta\delta^{19}F_{m,p}$ = 5.0, 6.7).

^{29}Si{^{1}H} DEPT (119 Hz, CD_2Cl_2, 299 K): δ = -1.6 ($\nu_{1/2}$ ≈ 1 Hz, =CSiMe_3), -2.8 ($\nu_{1/2}$ ≈ 1 Hz, =CSiMe_3), -17.7 ($\nu_{1/2}$ ≈ 1 Hz, ≡CSiMe_3), -18.0 ($\nu_{1/2}$ ≈ 1 Hz, ≡CSiMe_3).

characterization at low temperature:

^{1}H NMR (600 MHz, CD_2Cl_2, 253 K): δ = 0.27 (s, $^{2}J_{SiH}$ = 6.6 Hz, 9H, SiMe_3), 0.18 (s, $^{2}J_{SiH}$ = 7.1 Hz, 9H, SiMe_3), 0.07 (s, $^{2}J_{SiH}$ = 6.5 Hz, 9H, SiMe_3), 0.01 (s, $^{2}J_{SiH}$ = 7.0 Hz, 9H, SiMe_3).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 253 K): δ = 159.4 (=C), 145.2 (=CSi), 143.5 (=C), 136.1 (=CSi), [148.8 (dm, $^{1}J_{FC}$ ≈ 254 Hz, 2C, *o*), 144.6 (dm, $^{1}J_{FC}$ ≈ 258 Hz, 1C, *p*), 137.4 (dm, $^{1}J_{FC}$ ≈ 252 Hz, 2C, *m*), 112.1 (br, *i*)]($C_6F_5^B$). [144.4 (dm, $^{1}J_{FC}$ ≈ 258 Hz, 1C, *o*), 143.6 (dm, $^{1}J_{FC}$ ≈ 252 Hz, 1C, *o*), 140.4 (dm, $^{1}J_{FC}$ ≈ 256 Hz, 1C, *p*), 137.7 (dm, $^{1}J_{FC}$ ≈ 252 Hz, 1C, *m*), 136.7 (dm, $^{1}J_{FC}$ ≈ 249 Hz,

1C, *m*), 115.8 (tm, $^{2}J_{FC} \approx 18$ Hz, *i*)]($C_6F_5^C$), 113.8 (≡CSi), 105.5 (≡*C*C), 105.3 (≡*C*C), 104.7 (≡CSi), 0.13 ($SiMe_3$), -0.48 ($SiMe_3$), -0.54 ($SiMe_3$), -0.66 ($SiMe_3$).

$^{13}C\{^{19}F,^{1}H\}$ NMR (151 MHz, CD_2Cl_2, 253 K): [selected resonances] δ = [148.8 (2C, *o*), 144.6 (1C, *p*), 137.4 (2C, *m*), 112.1 (*i*)]($C_6F_5^B$). [144.4 (1C, *o*), 143.6 (1C, *o*), 140.4 (1C, *p*), 137.7 (1C, *m*), 136.7 (1C, *m*), 115.8 (*i*)]($C_6F_5^C$).

^{19}F NMR (564 MHz, CD_2Cl_2, 253 K): δ = [-126.4 (m, 2F, *o*), -144.2 (t, J_{FF} = 18 Hz, 1F, *p*), -161.0 (m, 1F, *m*)]($C_6F_5^B$, [$\Delta\delta^{19}F_{m,p}$ = 16.8]), [-132.7 (m, 1F, *o*), -136.7 (m, 1F, *o*), -158.2 (t, J_{FF} = 21 Hz, 1F, *p*), -163.1 (m, 1F, *m*), -164.8 (m, 1F, *m*)]($C_6F_5^C$ [$\Delta\delta^{19}F_{m,p}$ = 4.9, 6.6]).

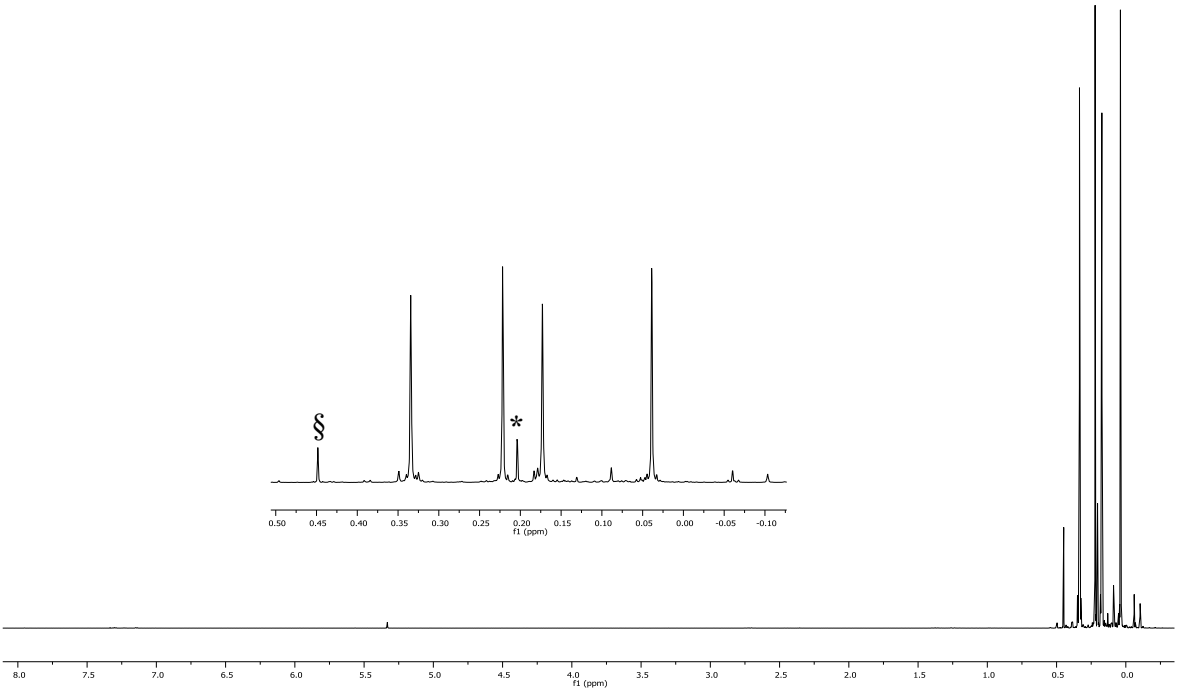


Figure S120: **^{1}H NMR** (600 MHz, CD_2Cl_2, 299K) spectrum of compound **6**, asterisk denotes the signal due to unreacted 1,4-bis(trimethylsilyl)butadiene (**2d**), § denotes some impurity.

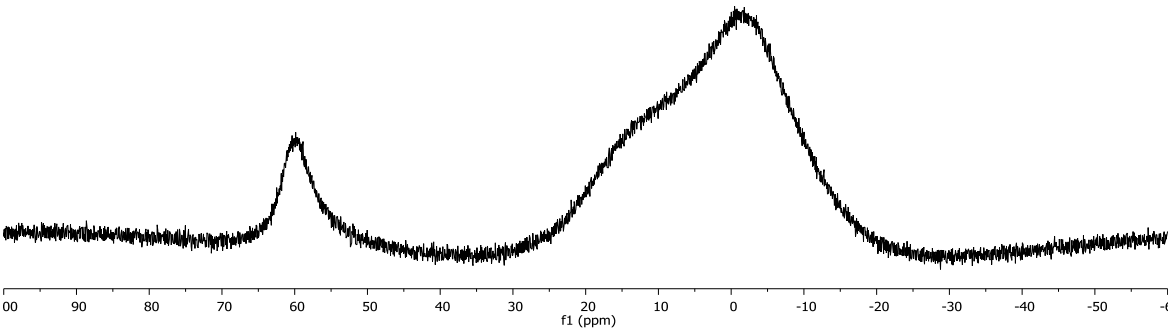


Figure S121: **$^{11}B\{^{1}H\}$ NMR** (192 MHz, CD_2Cl_2, 299K) spectrum of compound **6**.

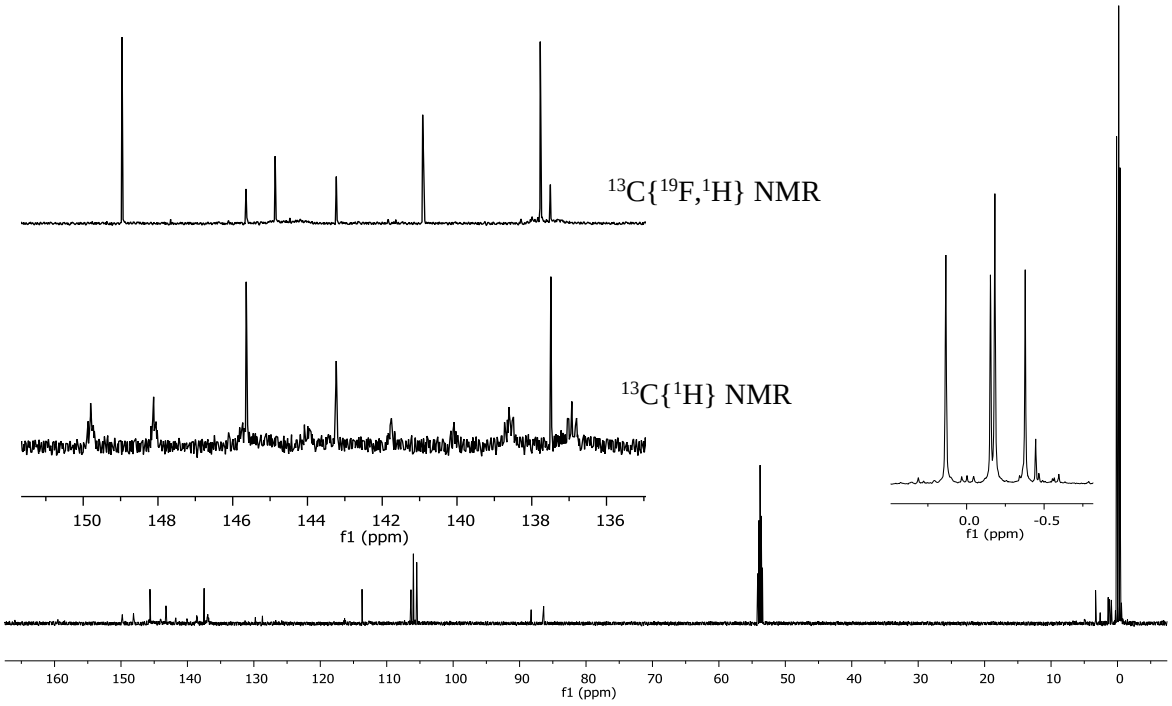


Figure S122: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, CD_2Cl_2, 299K) spectrum and detailed overview of C_6F_5 and $SiMe_3$ region with excerpt from **$^{13}C\{^{19}F,^{1}H\}$ NMR** (151 MHz, CD_2Cl_2, 299K) spectrum of compound **6**.

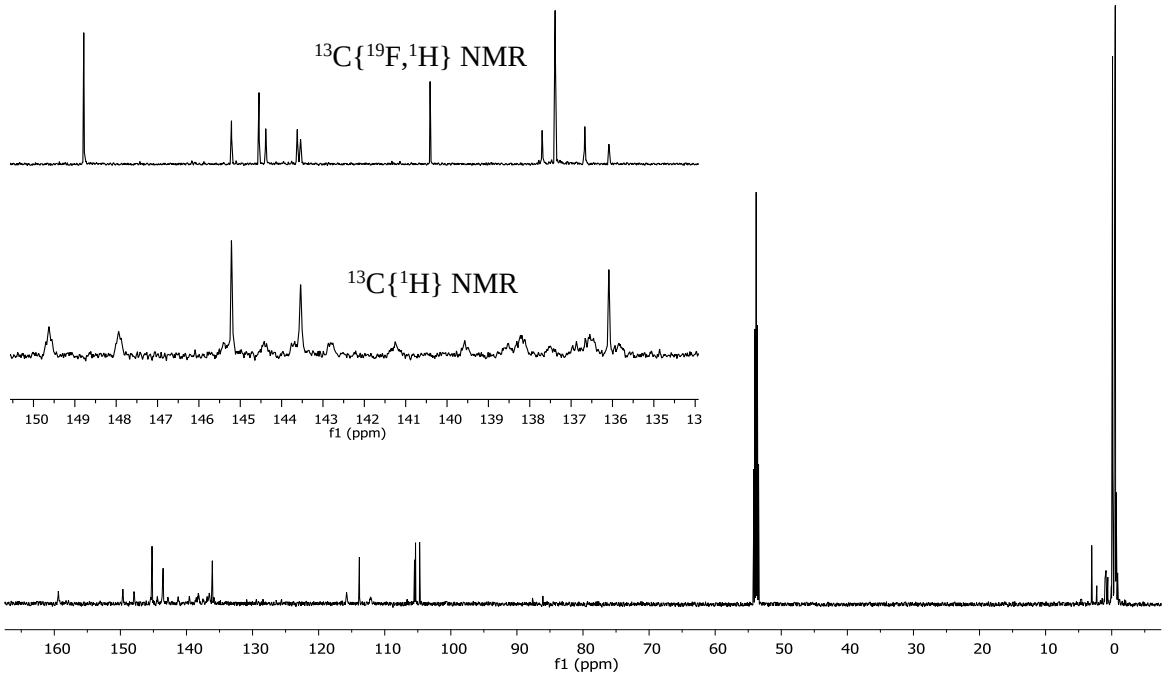


Figure S123: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, CD_2Cl_2, 253K) spectrum and detailed overview of C_6F_5 region with excerpt from **$^{13}C\{^{19}F,^{1}H\}$ NMR** (151 MHz, CD_2Cl_2, 253K) spectrum of compound **6**.

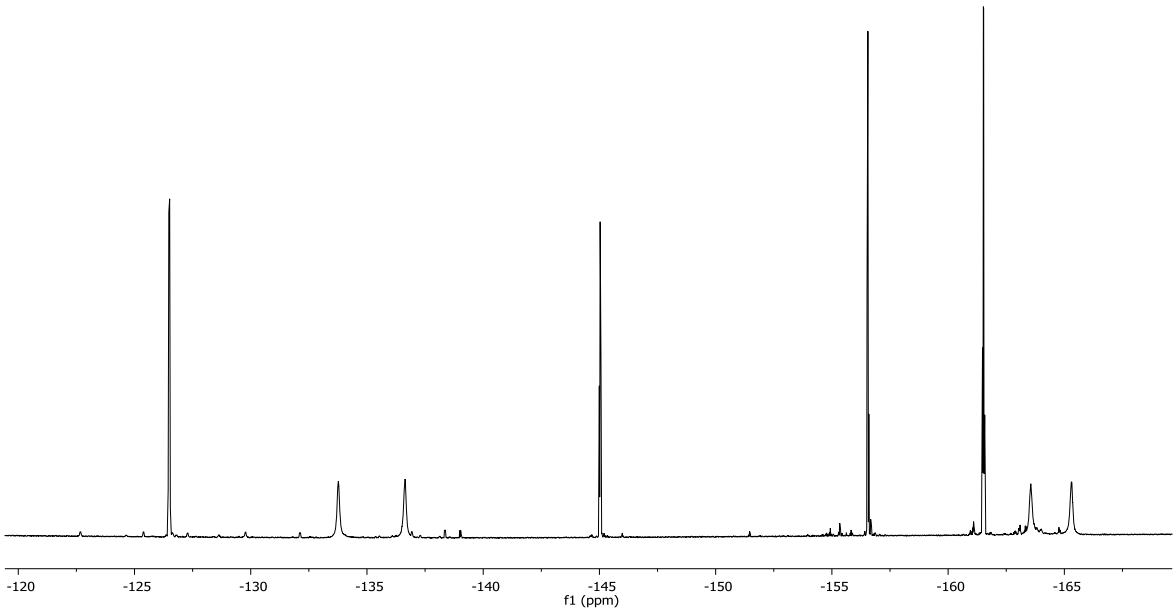


Figure S124: **^{19}F NMR** (564 MHz, CD_2Cl_2, 299K) spectrum of compound **6**.

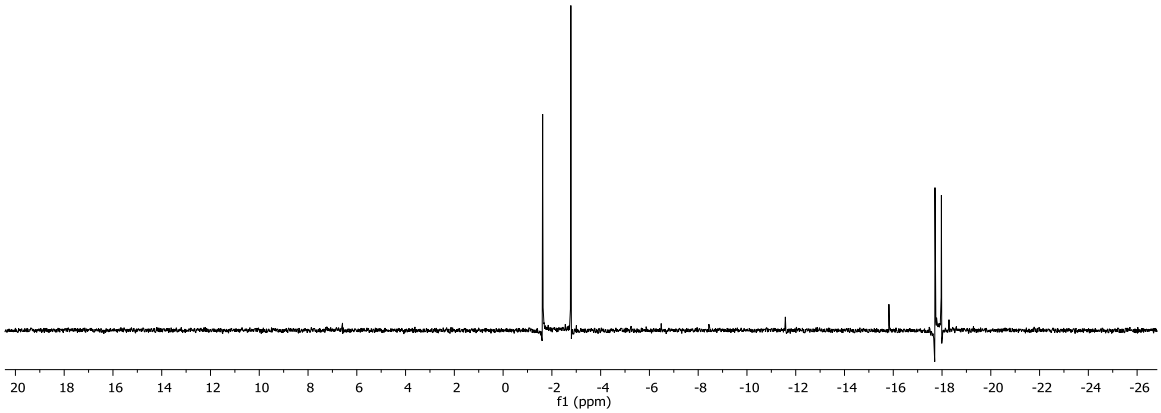
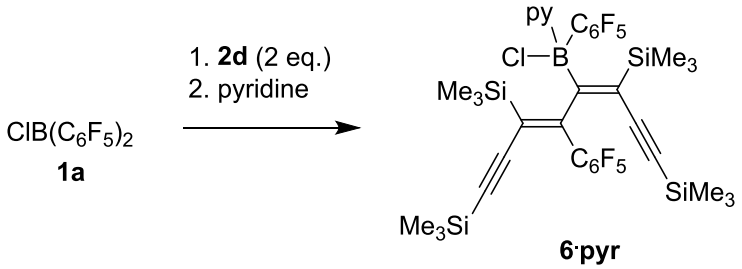


Figure S125: **^{29}Si{^{1}H} DEPT** (119 MHz, CD_2Cl_2, 299K) spectrum of compound **6**.

Preparation of compound 6·pyr



Scheme S25

Solutions of $ClB(C_6F_5)_2$ (**1a**) (76.0 mg, 0.2 mmol) in CH_2Cl_2 (2 ml) and of 1,4-bis(trimethylsilyl)butadiyne (**2d**) (77.6 mg, 0.4 mmol) in CH_2Cl_2 (2 ml) were combined and allowed to stir at room temperature for 24 hours. The reaction mixture turned gradually dark. To the resulting deep-brown mixture a solution of pyridine (19.5 mg, 0.25 mmol) in CH_2Cl_2 (1 ml) was added. The deep brown color faded out immediately. The resulting orange-red solution was stirred for 5 minutes at room temperature, subsequently all volatilities were removed in vacuo. The residue was washed with cold pentane (3 x 1ml) and dried in vacuo. Product **6·pyr** was isolated as an off-white solid (115 mg, 0.136 mmol, 68 % yield).

Melting point: 187.5 °C.

Elementary analysis for $C_{37}H_{41}BClF_{10}NSi_4$ (848.3): calculated C 52.38, H 4.87, N 1.65; found C 52.35, H 4.61, N 1.58.

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 8.92 (br, 2H, 2,6-py), 8.19 (d, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, 4-py), 7.70 (m, 2H, 3,5-py), 0.36 (s, $^2J_{SiH}$ = 6.7 Hz, 9H, =CSiMe_3), 0.16 (s, $^2J_{SiH}$ = 6.8 Hz, 9H, ≡CSiMe_3), -0.01 (s, $^2J_{SiH}$ = 6.7 Hz, 9H, =CSiMe_3), -0.03 (s, $^2J_{SiH}$ = 7.0 Hz, 9H, ≡CSiMe_3),

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = 163.1 (br, =*C*BC_6F_5)^t, 149.2 (=*C*C_6F_5)^t, 143.4 (=*C*SiMe_3), 134.9 (=*C*SiMe_3), [147.4 (br, 2,6-py), 143.7 (4-py), 126.5 (3,5-py)], [148.4 (br dm, $^1J_{FC}$ ≈ 260 Hz), 145.5 (dm, $^1J_{FC}$ ≈ 250 Hz), 144.3 (dm, $^1J_{FC}$ ≈ 245 Hz), 140.8 (dm, $^1J_{FC}$ ≈ 250 Hz), 140.6 (dm, $^1J_{FC}$ ≈ 248 Hz), 137.8 (dm, $^1J_{FC}$ ≈ 250 Hz), 137.7 (br dm, $^1J_{FC}$ ≈ 255 Hz), 137.6 (dm, $^1J_{FC}$ ≈ 255 Hz), 119.8 (br, *i*)^t, 116.3 (tm, $^2J_{FC}$ ≈ 20 Hz, *i*)](C_6F_5), 110.2 (d, J_{FC} ≈ 4 Hz, *C*≡CSi), 107.6 (≡CSi), 107.4 (d, J_{FC} = 2 Hz, *C*≡CSi), 102.6 (≡CSi), 1.1 ($^1J_{SiC}$ = 54.2 Hz, =CSiMe_3), 0.11 ($^1J_{SiC}$ = 55.9 Hz, =CSiMe_3), -0.33 ($^1J_{SiC}$ = 56.1 Hz, ≡CSiMe_3), -0.45 (br, =CSiMe_3) ^{t} tentative assigment

^{13}C{^{19}F,^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): [selected resonances] δ = 148.4 (br), 145.5, 144.3, 140.8, 140.6, 137.8, 137.6 (br), 137.6 (all C_6F_5), 110.2 (*C*≡CSi), 107.4 (*C*≡CSi)

^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = 2.6 ($\nu_{1/2}$ ≈ 240 Hz).

^{19}F NMR (564 MHz, CD_2Cl_2, 233 K): δ = [-120.9 (m, 1F, *o*-C_6F_5), -141.1 (m, 1F, *o*-C_6F_5), -156.5 (d, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), -163.5 (m, 1F, *m*-C_6F_5), -166.0 (m, 1F, *m*-C_6F_5)]($\Delta\delta^{19}F_{m,p}$ = 7.0, 9.5), [-135.1 (m, 1F, *o*-C_6F_5), -137.6 (m, 1F, *o*-C_6F_5), -155.4 (d, $^3J_{FF}$ = 22 Hz, *p*-C_6F_5), -163.0 (m, 1F, *m*-C_6F_5), -164.8 (m, 1F, *m*-C_6F_5)]($\Delta\delta^{19}F_{m,p}$ = 7.6, 9.4)

^{29}Si{^{1}H} DEPT (119 Hz, CD_2Cl_2, 299 K): δ = -1.8 ($\nu_{1/2}$ ≈ 1 Hz, =CSiMe_3), -5.5 ($\nu_{1/2}$ ≈ 1 Hz, =CSiMe_3), -18.8 ($\nu_{1/2}$ ≈ 1 Hz, ≡CSiMe_3), -18.9 ($\nu_{1/2}$ ≈ 1 Hz, ≡CSiMe_3).

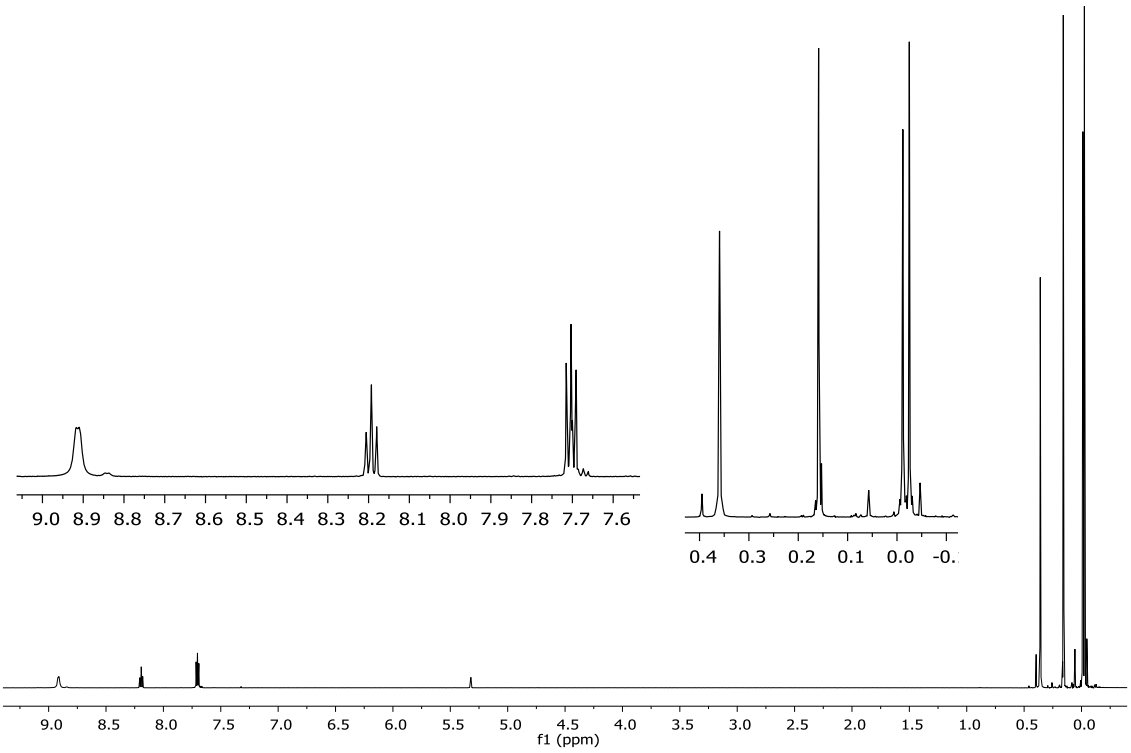


Figure S126: **^{1}H NMR** (600 MHz, CD_2Cl_2, 299K) spectrum of compound **6·pyr**.

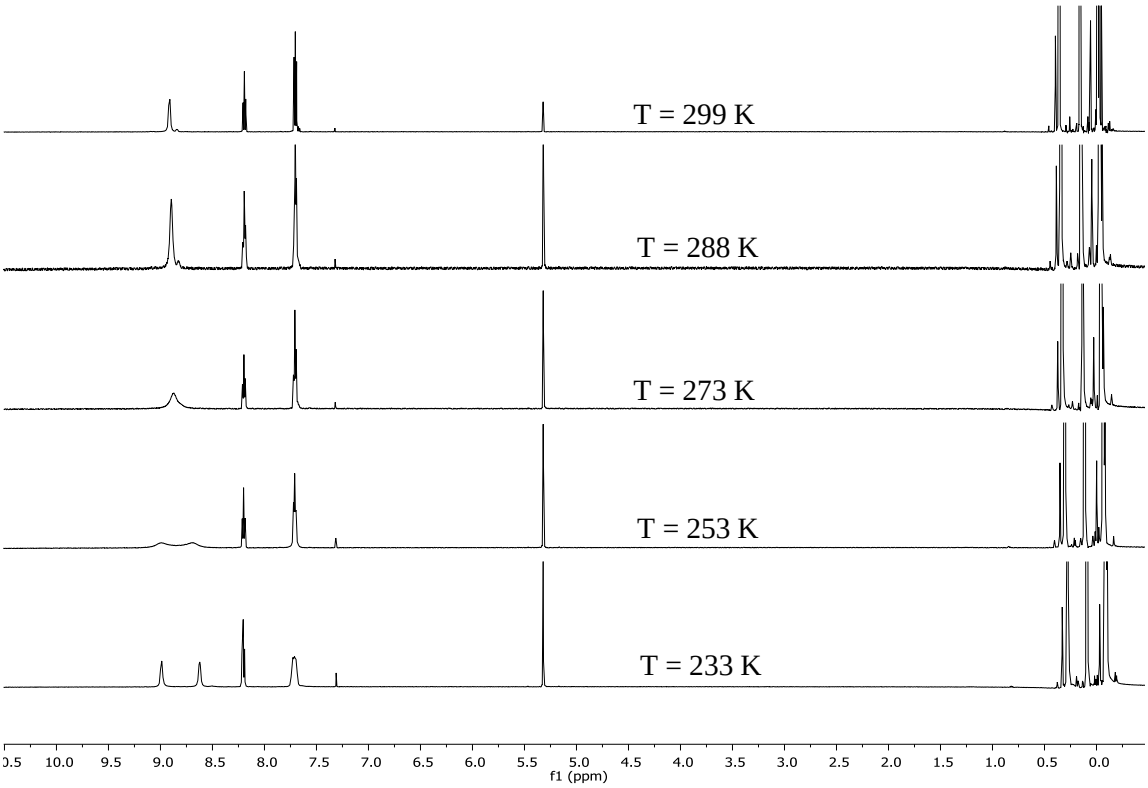


Figure S127: **^{1}H NMR** (600 MHz, CD_2Cl_2, 299K) spectrum of compound **6·pyr** measured at various temperatures.

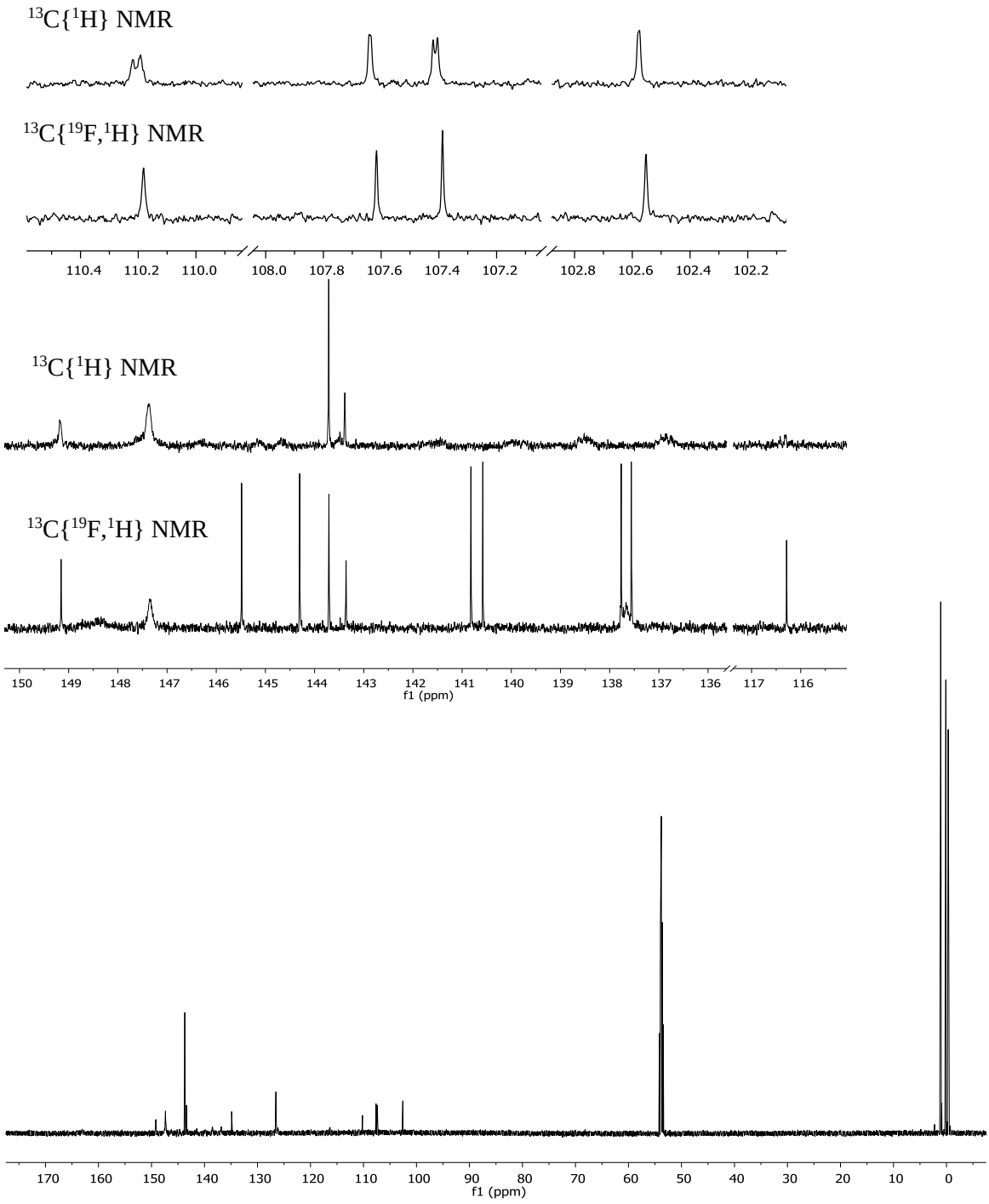


Figure S128: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, CD_2Cl_2, 299K) spectrum and detailed overview of triple bond region and olefinic and aromatic signals with excerpt from **$^{13}C\{^{19}F,^{1}H\}$ NMR** (151 MHz, CD_2Cl_2, 299K) spectrum of compound **6·pyr.**

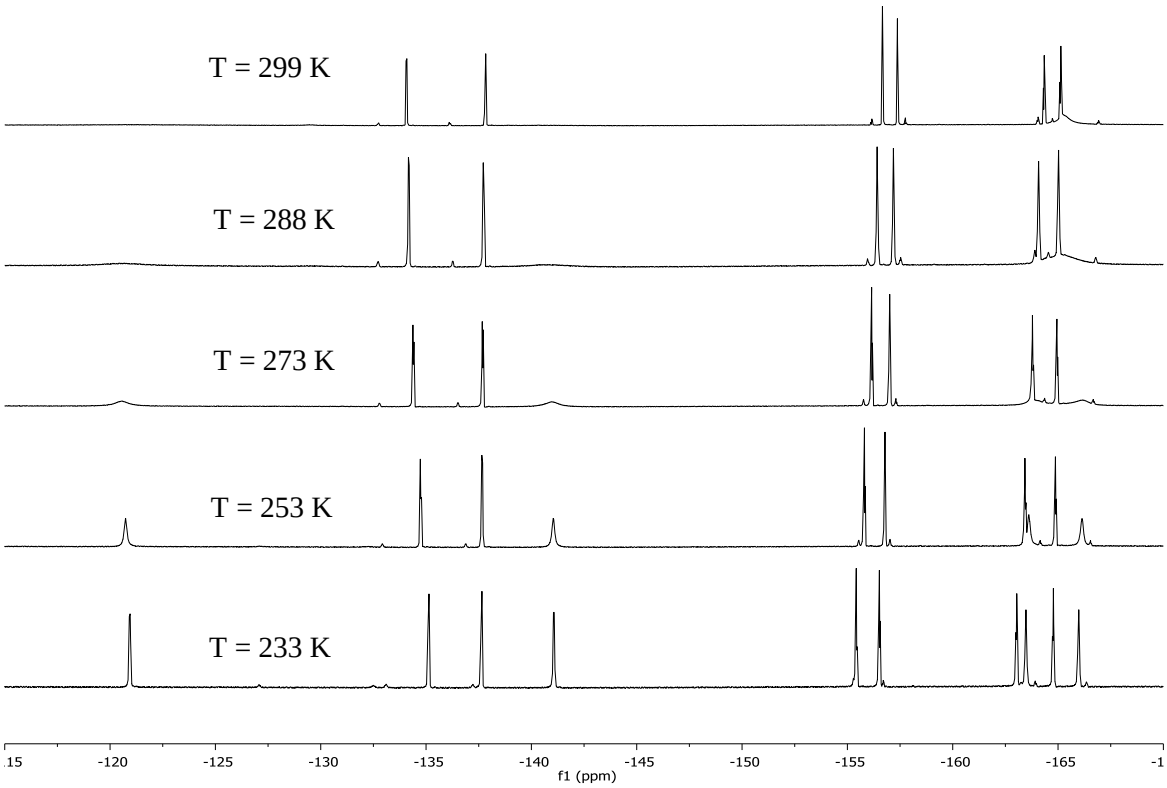


Figure S129: **^{19}F NMR** (564 MHz, CD_2Cl_2, 299K) spectrum of compound **6·pyr** measured at various temperatures.

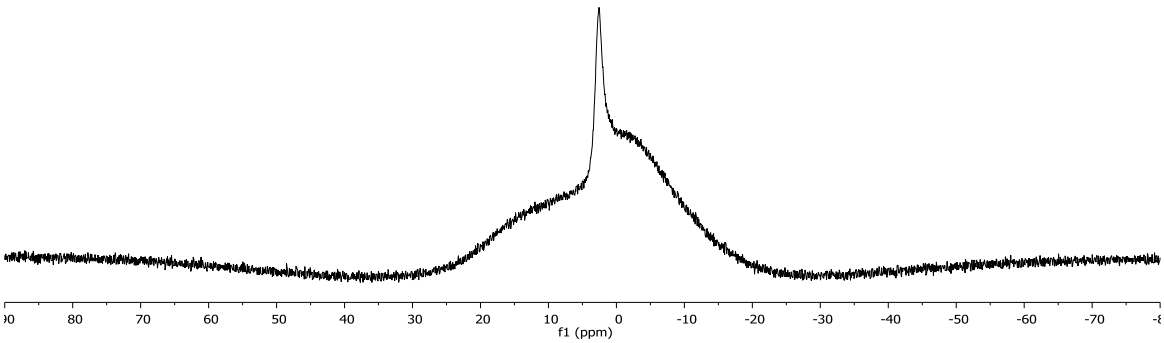


Figure S130: **^{11}B{^{1}H} NMR** (192 MHz, CD_2Cl_2, 299K) spectrum of compound **6·pyr**.

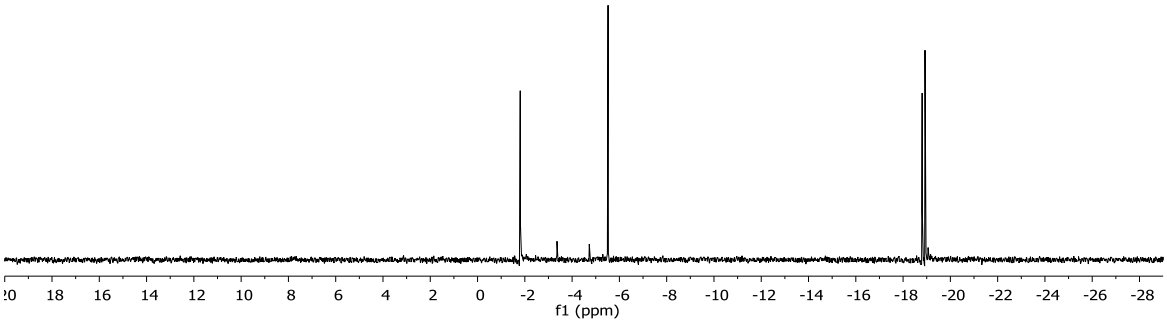


Figure S131: **^{29}Si{^{1}H} DEPT** (119 MHz, CD_2Cl_2, 299K) spectrum of compound **6·pyr**.

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **6·pyr** in a CH_2Cl_2/pentane (ca. 1:1) at room temperature.

X-ray crystal structure analysis of compound 6·pyr (erk9185): A colorless plate-like specimen of $C_{37}H_{41}BClF_{10}NSi_4$, approximate dimensions 0.053 mm x 0.159 mm x 0.212 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 472 frames were collected. The total exposure time was 5.90 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 59062 reflections to a maximum θ angle of 25.35° (0.83 Å resolution), of which 7703 were independent (average redundancy 7.667, completeness = 99.7%, R_{int} = 12.55%, R_{sig} = 7.11%) and 5777 (75.00%) were greater than $2\sigma(F^2)$. The final cell constants of a = 19.7064(18) Å, b = 11.2666(9) Å, c = 20.838(2) Å, β = 114.308(3)°, volume = 4216.4(7) $Å^3$, are based upon the refinement of the XYZ-centroids of 9878 reflections above 20 σ(I) with 5.179° < 2θ < 50.73°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.912. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9440 and 0.9860. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/n$, with Z = 4 for the formula unit, $C_{37}H_{41}BClF_{10}NSi_4$. The final anisotropic full-matrix least-squares refinement on F^2 with 524 variables converged at R1 = 7.33%, for the observed data and wR2 = 15.86% for all data. The goodness-of-fit was 1.162. The largest peak in the final difference electron density synthesis was 0.379 $e^-/Å^3$ and the largest hole was -0.428 $e^-/Å^3$ with an RMS deviation of 0.088 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.336 g/cm^3 and F(000), 1752 e^-. CCDC Nr.: 1892616.

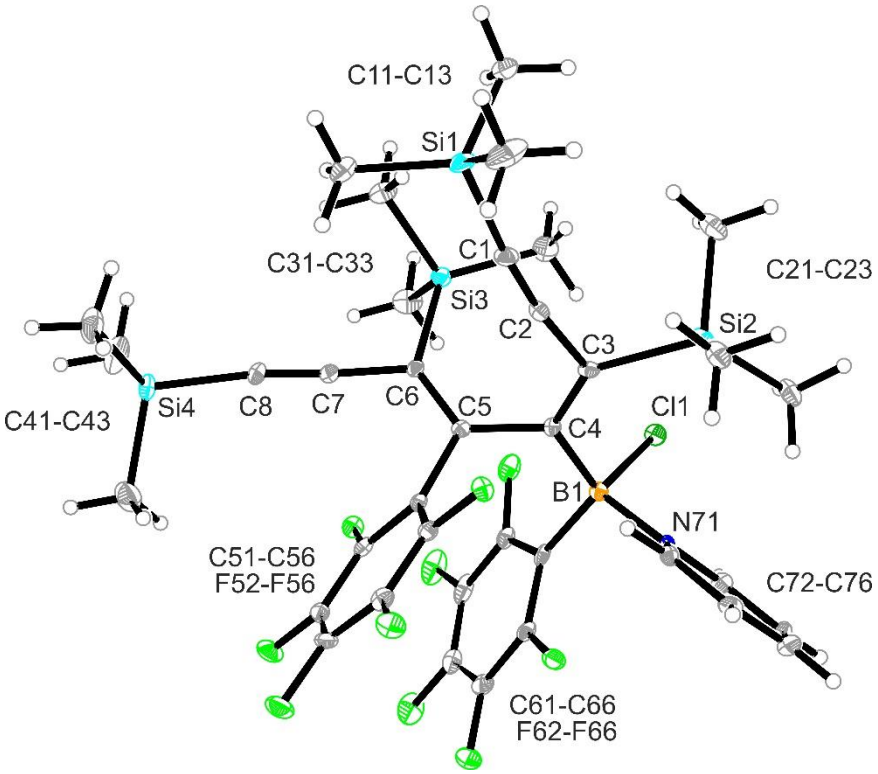
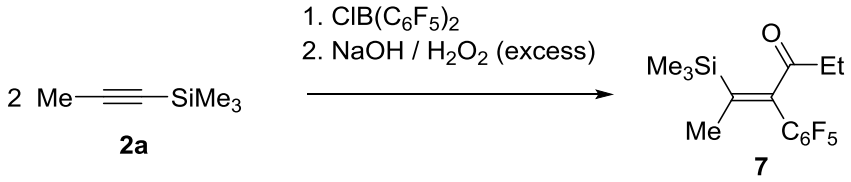


Figure S132: Crystal structure of compound **6·pyr** (thermal ellipsoids: 30% probability).

Preparation of compound 7



Scheme S26

MeC≡CSiMe$_3$ (56.2 mg, 0.5 mmol) and ClB(C_6F_5)$_2$ (95.0 mg, 0.25 mmol) were dissolved in ml CH_2Cl_2 (3 ml) and stirred for 3 hours at room temperature. The pale yellow homogenous mixture was evaporated to yield a thick yellow oil. The residue was dissolved in dry THF (3 ml) to which subsequently 0.2 ml of 30% aq. H_2O_2 and 0.2 ml of 3M aq. NaOH was added (a little effervescence was observed). The mixture was allowed to react for 2 hours at room temperature, finally quenched with saturated aqueous NH_4Cl solution. The mixture was diluted with Et_2O (5 ml) and the phases were separated. The aqueous phase was extracted with Et_2O, twice, and the combined organic phases were washed with brine, dried over $MgSO_4$ and after filtration finally purified over a short silica column (mobile phase pentane: CH_2Cl_2 1:1). Product **7** was isolated as a colorless oil (70 mg, 0.21 mmol, 83 % yield).

HRMS: *m*/*z* calc. for $C_{15}H_{17}OF_2SiNa$ [Na^+]: 359.0861, found 359.0865.

IR (ATR) ν (cm^{-1}) = 2948 (w), 2904 (w), 1696 (m), 1517 (s), 1491 (s), 1373 (w), 1347 (w), 1313 (w), 1248 (m), 1204 (m), 1134 (m), 1025 (w), 980 (s), 929 (m), 842 (s), 753 (m), 678 (m), 644 (m)

^{1}H NMR (500 MHz, 299 K, $CDCl_3$) δ = 2.24 (q, $^3J_{HH}$ = 7.2 Hz, 2H, CH_2), 1.74 (d, J_{FH} = 1.0 Hz, 3H, CH_3-C=), 1.01 (t, $^3J_{HH}$ = 7.2 Hz, 3H, CH_2CH_3), 0.22 (s, $^2J_{SiH}$ = 6.7 Hz, 9H, $SiMe_3$).

^{13}C{^{1}H} NMR (126 MHz, 299 K, $CDCl_3$) δ = 199.1 (CO), 164.2 (CH_3-*C*=), 143.6 (dm, $^1J_{FC}$ = 246 Hz, *o*-C_6F_5), 140.9 (dm, $^1J_{FC}$ = 255 Hz, *p*-C_6F_5), 137.7 (dm, $^1J_{FC}$ = 252 Hz, *m*-C_6F_5), 133.6 (m, *C*-C_6F_5), 113.4 (td, $^2J_{FC}$ = 21 Hz, $^3J_{FC}$ = 4 Hz, *i*-C_6F_5), 34.1 (CH_2), 22.3 (*C*H_3-C=), 7.7 (*C*H_3CH_2), -0.2 ($^1J_{SiH}$ = 54.8 Hz, $SiMe_3$).

^{19}F NMR (470 MHz, 299 K, $CDCl_3$) δ = -139.3 (m, 2F, *o*-C_6F_5), -153.8 (t, $^3J_{FF}$ = 20 Hz, 1F, *p*-C_6F_5), -161.2 (m, 2F, *m*-C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 7.4].

^{29}Si{^{1}H} NMR (99 Hz, $CDCl_3$, 299 K): δ = -3.3 ($\nu_{1/2} \approx 1$ Hz).

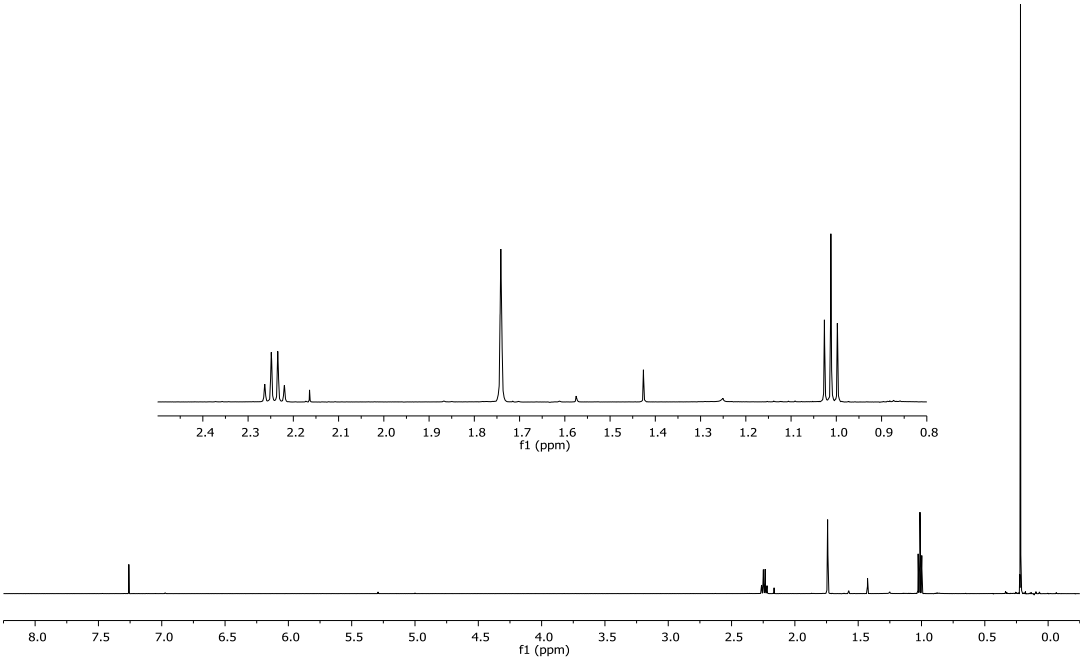


Figure S133: **^{1}H NMR** (600 MHz, $CDCl_3$, 299K) spectrum of compound **7**.

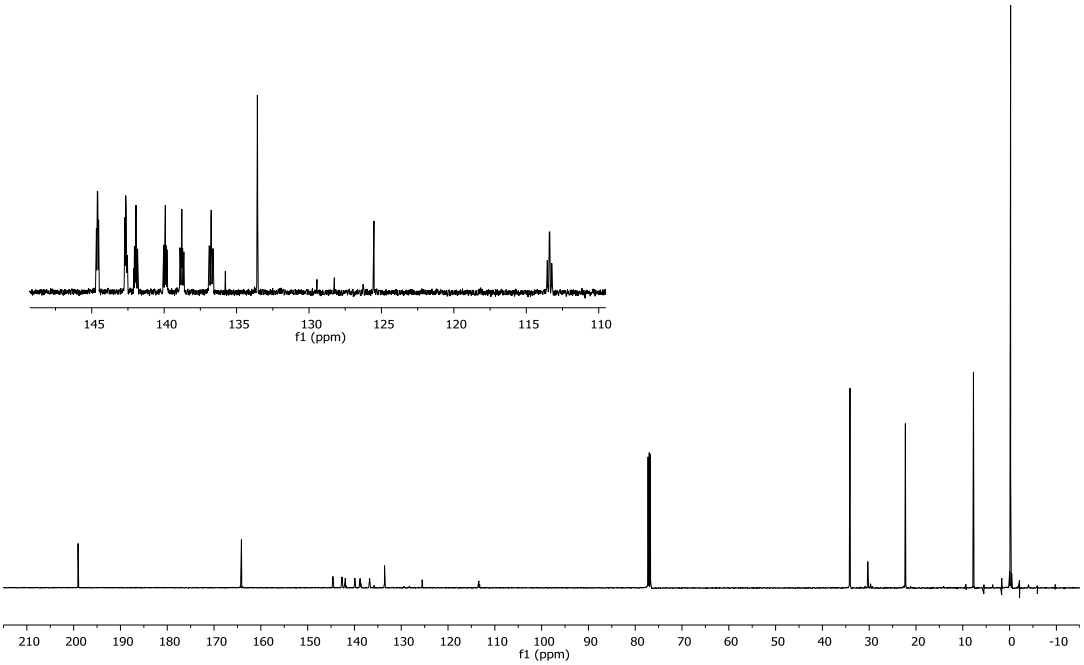


Figure S134: **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 299K) spectrum of compound **7**.

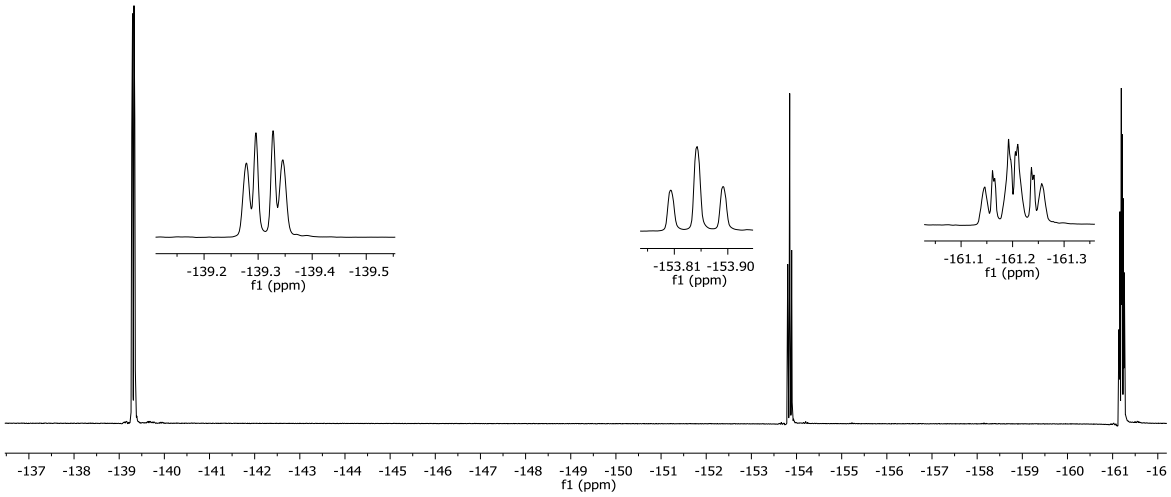


Figure S135: **^{19}F NMR** (470 MHz, $CDCl_3$, 299K) spectrum of compound **7**.

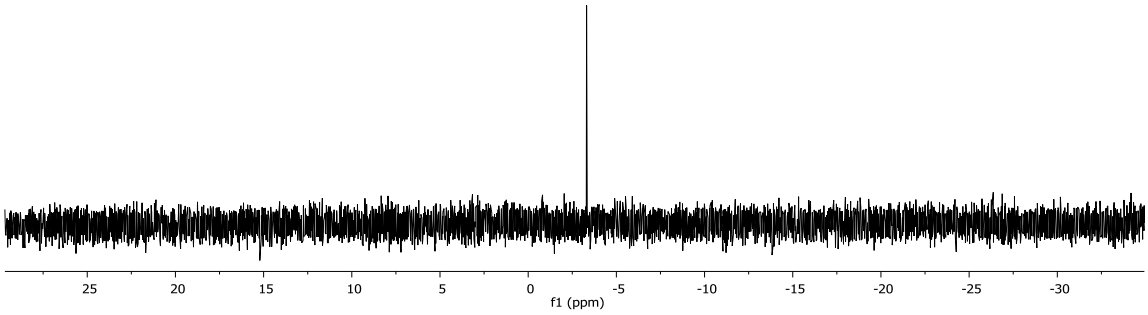
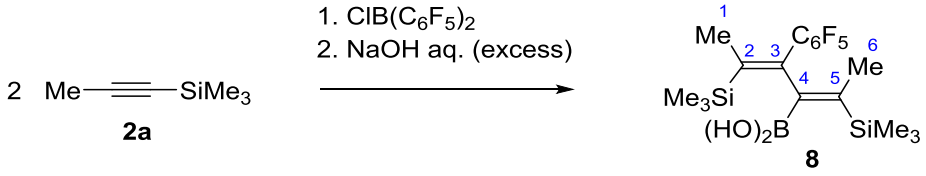


Figure S136: **^{29}Si{^{1}H} NMR** (99 MHz, $CDCl_3$, 299K) spectrum of compound **7**.

Preparation of compound 8



Scheme S27

$MeC{\equiv}CSiMe_3$ (112 mg, 1.0 mmol) and $ClB(C_6F_5)_2$ (190.0 mg, 0.50 mmol) were dissolved in CH_2Cl_2 (5 ml) and stirred overnight at room temperature. The pale yellow homogenous mixture was evaporated to yield a thick yellow oil. It was dissolved in dry THF (3 ml), then 3 ml of 3M aq. NaOH were added (the off-yellow color faded out immediately). The mixture was vigorously stirred for one hour at room temperature, and finally diluted with 5 ml of water and 5 ml of Et_2O. In a separatory funnel phases were separated and the aqueous phase was extracted with Et_2O twice. The combined organic phases were washed with brine, dried over $MgSO_4$ and after filtration finally purified over a short silica column (mobile phase pentane: CH_2Cl_2 1:1). Product **8** was isolated as a colorless oil (195 mg, 0.45 mmol, 90 % yield).

HRMS: *m/z* calc. for $C_{18}H_{25}BF_5O_2Si_2$ $[M - H]^-$: 435.1415; found 435.1409, and $C_{18}H_{26}BClF_5O_2Si_2$ $[M + Cl]^-$: 471.1176; found 471.1182.

IR (KBr) ν (cm^{-1}) = 3411 (br m), 2958 (m), 2902 (w), 1518 (s), 1486 (s), 1414 (s), 1304 (s), 1247 (s), 1196 (w), 1113 (m), 1054 (s), 986 (s), 911 (m), 840 (s), 755 (s), 678 (m), 608 (w), 547 (m)

^{1}H NMR (600 MHz, 299 K, $CDCl_3$) δ = 4.46 (m, 2H, $B(OH)_2$), 1.86 (d, J_{FH} = 2.6 Hz, 3H, Me^6), 1.68 (t, J_{FH} = 1.2 Hz, 3H, Me^1), 0.15 (s, $^2J_{SiH}$ = 6.7 Hz, 9H, $SiMe_3$), 0.15 (s, $^2J_{SiH}$ = 6.5 Hz, 9H, $SiMe_3$).

^{13}C{^{1}H} NMR (151 MHz, 299 K, $CDCl_3$) δ = 154.9 (C^5), 146.9 (br, C^4), 143.8 (dm, $^1J_{FC}$ ≈ 249 Hz, C_6F_5), 143.2 (dm, $^1J_{FC}$ ≈ 245 Hz, C_6F_5), 143.3 (C^2), 140.1 (dm, $^1J_{FC}$ ≈ 253 Hz, C_6F_5), 137.6 (dm, $^1J_{FC}$ ≈ 253 Hz, C_6F_5), 137.5 (dm, $^1J_{FC}$ ≈ 250 Hz, C_6F_5), 136.5 (C^3), 116.1 (tm, $^2J_{FC}$ ≈ 20 Hz, *i*-C_6F_5), 21.4 (d, J_{FC} = 6.9 Hz, Me^6), 20.1 (Me^1), -0.2 ($^1J_{SiH}$ = 52.4 Hz, $SiMe_3$), -0.3 ($^1J_{SiH}$ = 52.3 Hz, $SiMe_3$).

^{19}F NMR (564 MHz, 299 K, $CDCl_3$) δ = -137.6 (m, 1F, *o*-C_6F_5), -138.6 (m, 1F, *o*-C_6F_5), -153.3 (t, $^3J_{FF}$ = 21 Hz, 1F, *p*-C_6F_5), -162.2 (m, 1F, *m*-C_6F_5), -162.4 (m, 1F, *m*-C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 8.9, 9.1])

^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$, 299 K): δ = 28.4 ($\nu_{1/2}$ ≈ 340 Hz).

^{29}Si{^{1}H} DEPT (119 Hz, $CDCl_3$, 299 K): δ = -4.1 ($\nu_{1/2}$ ≈ 1 Hz, $^2SiMe_3$), -4.4 ($\nu_{1/2}$ ≈ 1 Hz, $^5SiMe_3$).

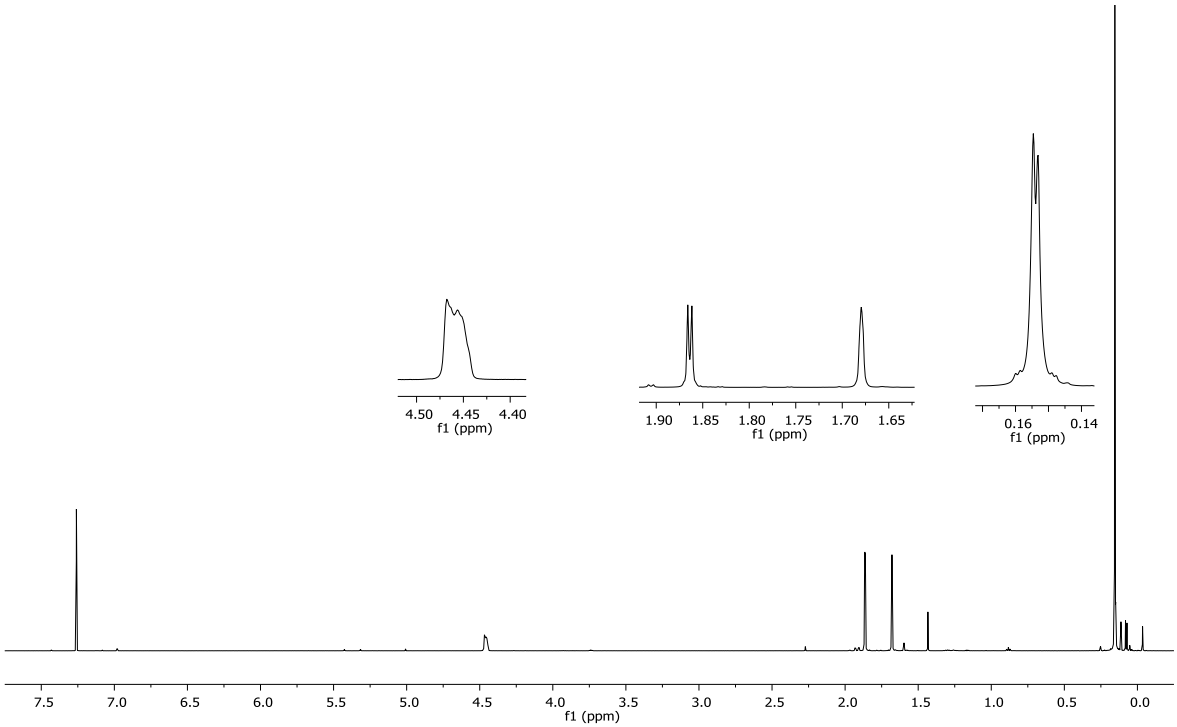


Figure S137: **^{1}H NMR** (600 MHz, $CDCl_3$, 299 K) spectrum of compound **8**.

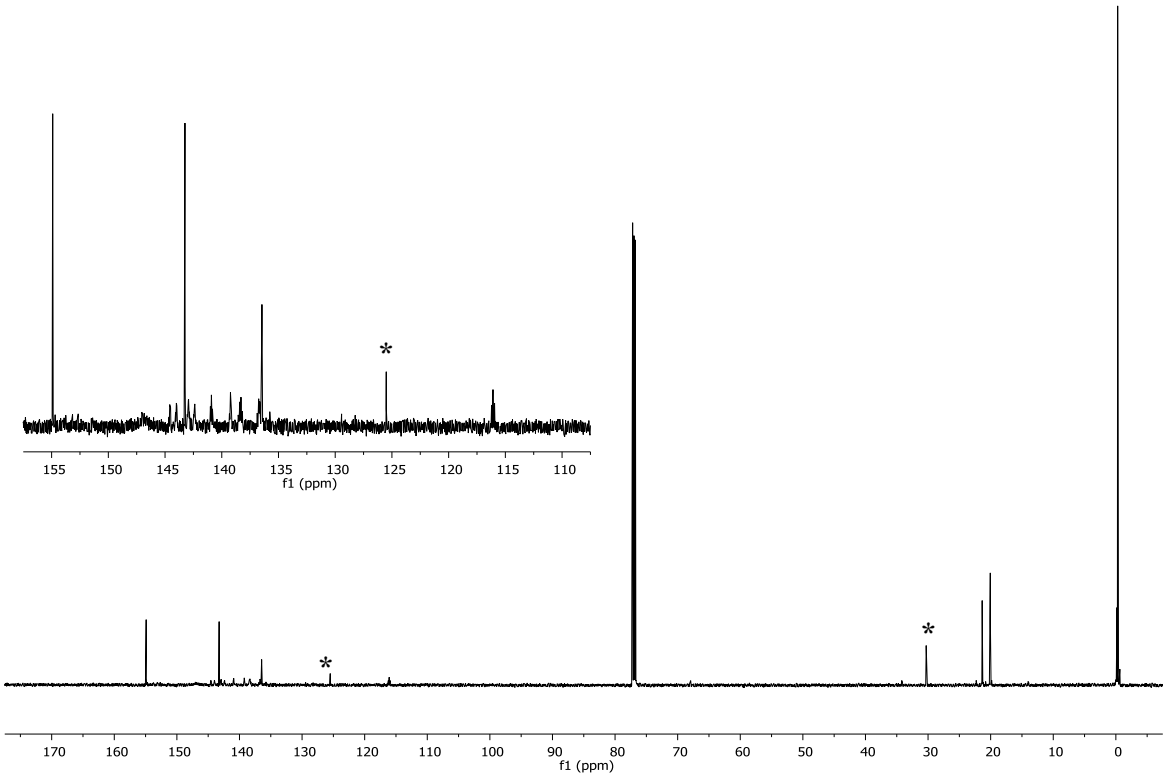


Figure S138: **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 299K) spectrum of compound **8**, asterisks denote signals due to unidentified impurity.

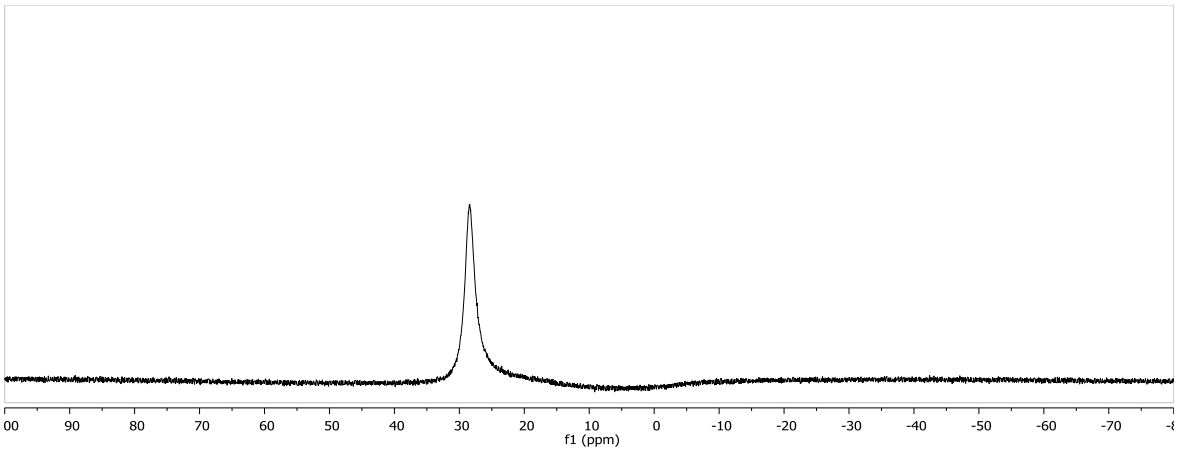


Figure S139: **$^{11}B\{^{1}H\}$ NMR** (192 MHz, $CDCl_3$, 299K) spectrum of compound **8**.

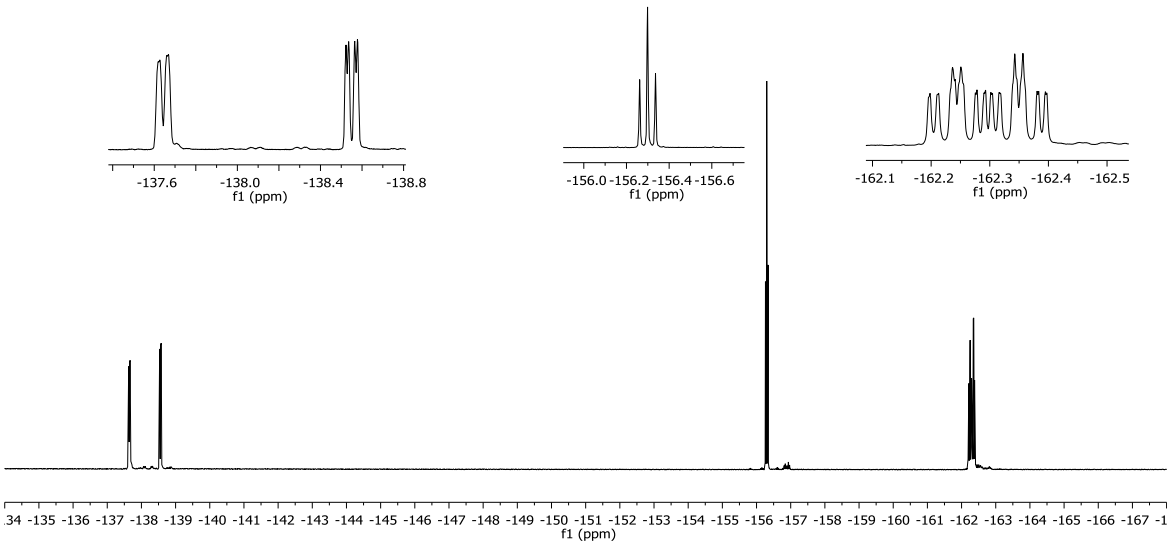


Figure S140: **^{19}F NMR** (564 MHz, $CDCl_3$, 299K) spectrum of compound **8**.

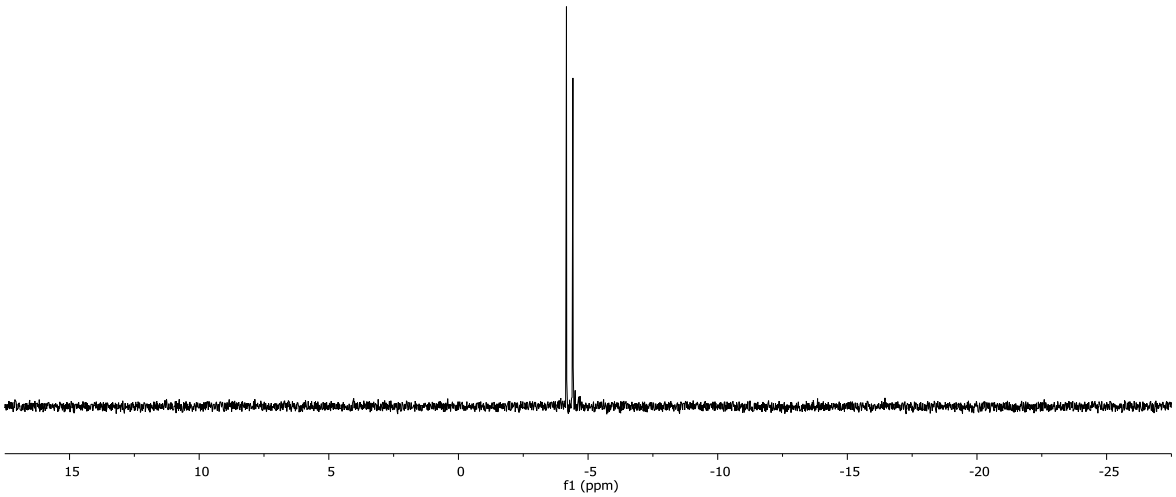


Figure S141: **^{29}Si{^{1}H} DEPT** (119 MHz, $CDCl_3$, 299K) spectrum of compound **8**.

The oily compound **8** was dissolved in heptane and stored at -20°C. Over several days, crystals of the anhydride **9** suitable for the X-ray crystal structure analysis were formed.

X-ray crystal structure analysis of compound 9 (erk9307): A colorless prism-like specimen of $C_{36}H_{50}B_2F_{10}O_3Si_4$, approximate dimensions 0.102 mm x 0.122 mm x 0.149 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1402 frames were collected. The total exposure time was 20.38 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 24599 reflections to a maximum θ angle of 66.75° (0.84 Å resolution), of which 3642 were independent (average redundancy 6.754, completeness = 99.5%, R_{int} = 4.17%, R_{sig} = 2.53%) and 3235 (88.82%) were greater than $2\sigma(F^2)$. The final cell constants of $\underline{a}$ = 23.7133(5) Å, $\underline{b}$ = 7.5887(2) Å, $\underline{c}$ = 25.2856(6) Å, β = 114.8340(10)°, volume = 4129.46(17) $Å^3$, are based upon the refinement of the XYZ-centroids of 9971 reflections above 20 σ(I) with 7.705° < 2θ < 133.5°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.917. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7500 and 0.8180. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *C*2/*c*, with Z = 4 for the formula unit, $C_{36}H_{50}B_2F_{10}O_3Si_4$.The final anisotropic full-matrix least-squares refinement on F^2 with 258 variables converged at R1 = 3.30%, for the observed data and wR2 = 8.30% for all data. The goodness-of-fit was 1.051. The largest peak in the final difference electron density synthesis was 0.300 $e^-/Å^3$ and the largest hole was -0.309 $e^-/Å^3$ with an RMS deviation of 0.048 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.375 g/cm^3 and F(000), 1784 e^-. CCDC Nr.: 1892617.

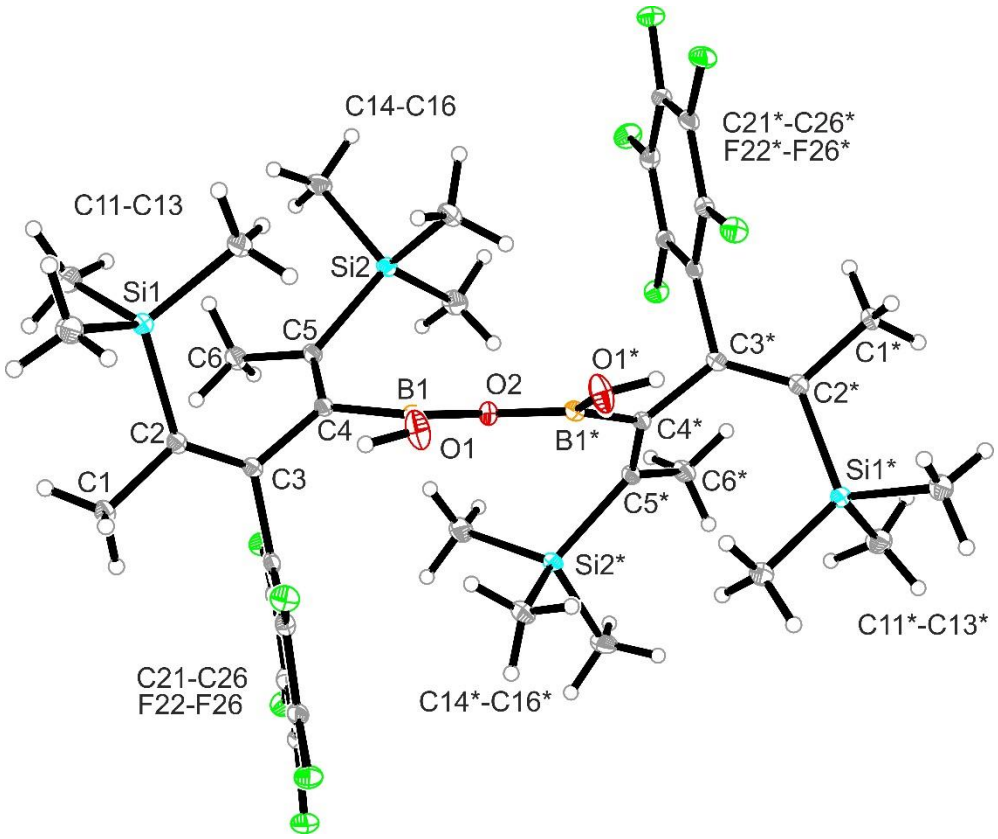


Figure S142: Crystal structure of compound **9** (thermal ellipsoids: 30% probability).

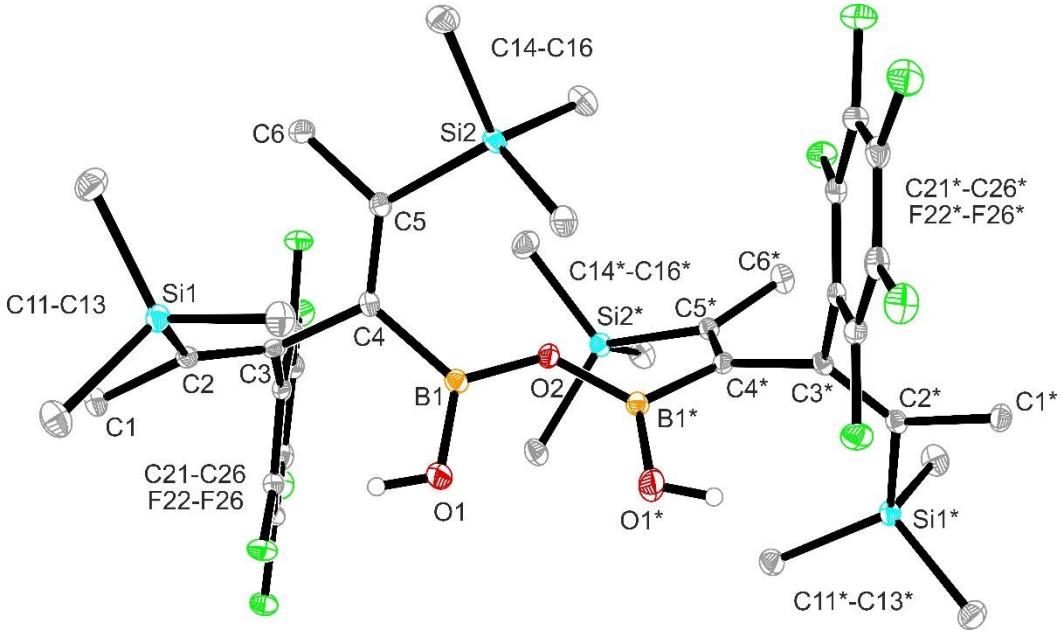
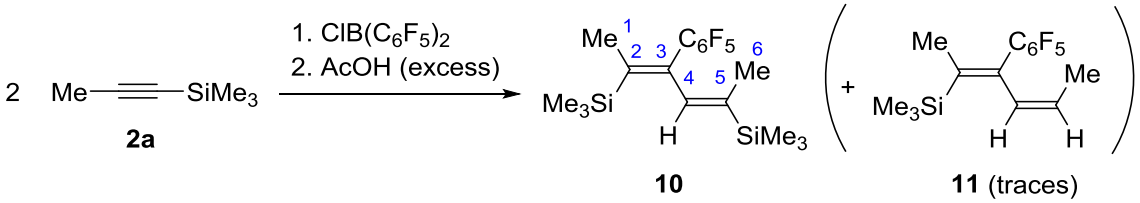


Figure S143: Crystal structure of compound **9**, hydrogen atoms are omitted for clarity (thermal ellipsoids: 30% probability).

Preparation of compound 10



Scheme S28

$MeC{\equiv}CSiMe_3$ (112 mg, 1.0 mmol) and $ClB(C_6F_5)_2$ (190.0 mg, 0.50 mmol) were dissolved in CH_2Cl_2 (5 ml) and stirred overnight (18h) at room temperature. Subsequently glacial acetic acid (0.1 ml) was added. The pale yellow color of reaction mixture faded out immediately. The mixture was stirred for 30 minutes at room temperature, followed by quenching with saturated aqueous $NaHCO_3$ solution (some effervescence occurred). The organic phase was separated and the aqueous phase 3x extracted with 5 ml of diethylether. The combined organic fractions were washed with brine and dried over $MgSO_4$. After filtration and removal of the volatilities in vacuo, the crude product was purified by short column chromatography (SiO_2, mobile phase 100% pentane, Rf = 0.9). Product **10** was isolated as a colourless oil (182 mg, 92%). NMR measurement revealed the presence of ca 6 % of partially desilylated product **11**.

HRMS: *m/z* calc. for $C_{18}H_{24}F_5Si_2$ [$(M\text{-}H)^-$]: 391.1331, found 391.1343.

^{1}H NMR (600 MHz, 299 K, $CDCl_3$) δ = 6.53 (sept J = 1.5 Hz, 1H, CH^4), 1.64 (d, J = 1.0 Hz, 3H, Me^1), 1.47 (d, J = 1.5 Hz, 3H, Me^6), 0.19 (s, $^2J_{SiH}$ = 6.6 Hz, 9H, $^2SiMe_3$), 0.06 (s, $^2J_{SiH}$ = 6.6 Hz, 9H, $^5SiMe_3$).

^{13}C{^{1}H} NMR (151 MHz, 299 K, $CDCl_3$) δ = 144.7 (C^2), 143.3 (dm, $^1J_{FC}$ ≈ 245 Hz, C_6F_5), 141.2 (C^5), 140.0 (dm, $^1J_{FC}$ ≈ 254 Hz, *p*-C_6F_5), 137.5 (dm, $^1J_{FC}$ ≈ 253 Hz, C_6F_5), 137.5 (CH^4), 132.8 (C^3), 116.6 (tm, $^2J_{FC}$ ≈ 21 Hz, *i*-C_6F_5), 19.9 (Me^1), 15.3 (Me^6), -0.4 ($^1J_{SiC}$ = 52.3 Hz, $^2Si\mathit{Me}_3$), -2.3 ($^1J_{SiC}$ = 51.9 Hz, $^5Si\mathit{Me}_3$).

^{19}F NMR (564 MHz, 299 K, $CDCl_3$) δ = -139.4 (m, 2F, *o*-C_6F_5), -157.1 (m, 1F, *p*-C_6F_5), -162.8 (m, 2F, *m*-C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 5.7]

^{29}Si{^{1}H} DEPT (119 Hz, $CDCl_3$, 299 K): δ = -2.6 ($\nu_{1/2}$ ≈ 1 Hz, $^5SiMe_3$), -4.4 ($\nu_{1/2}$ ≈ 1 Hz, $^2SiMe_3$).

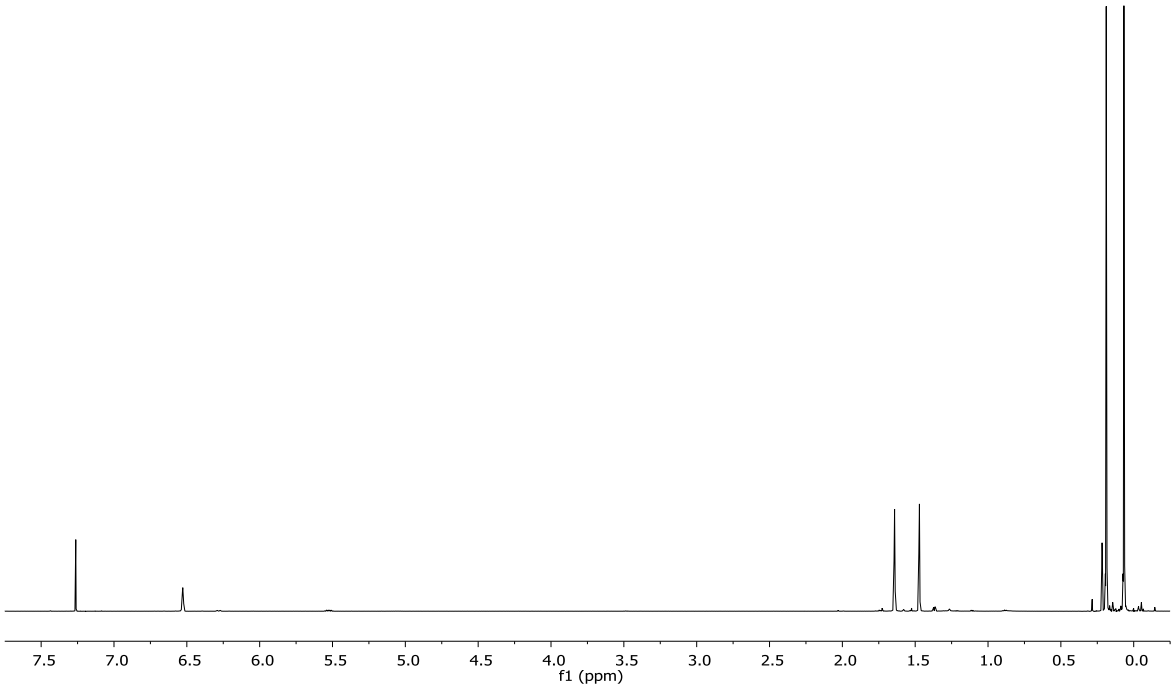


Figure S144: **^{1}H NMR** (600 MHz, $CDCl_3$, 299K) spectrum of compound **10**.

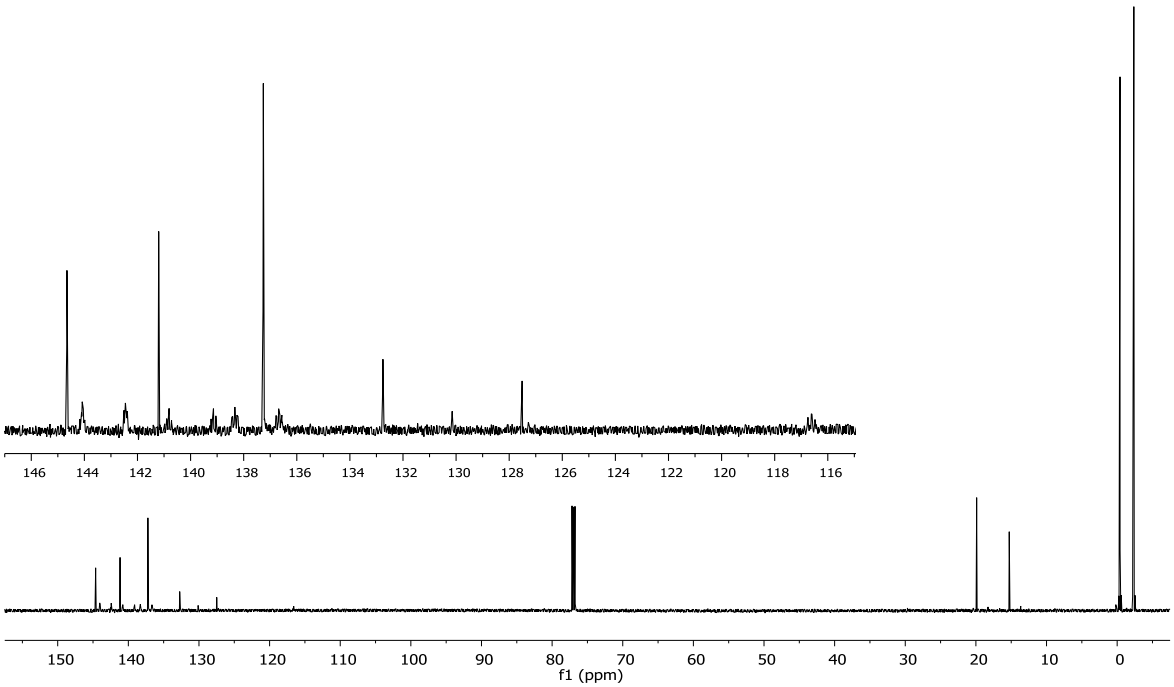


Figure S145: **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 299K) spectrum of compound **10**.

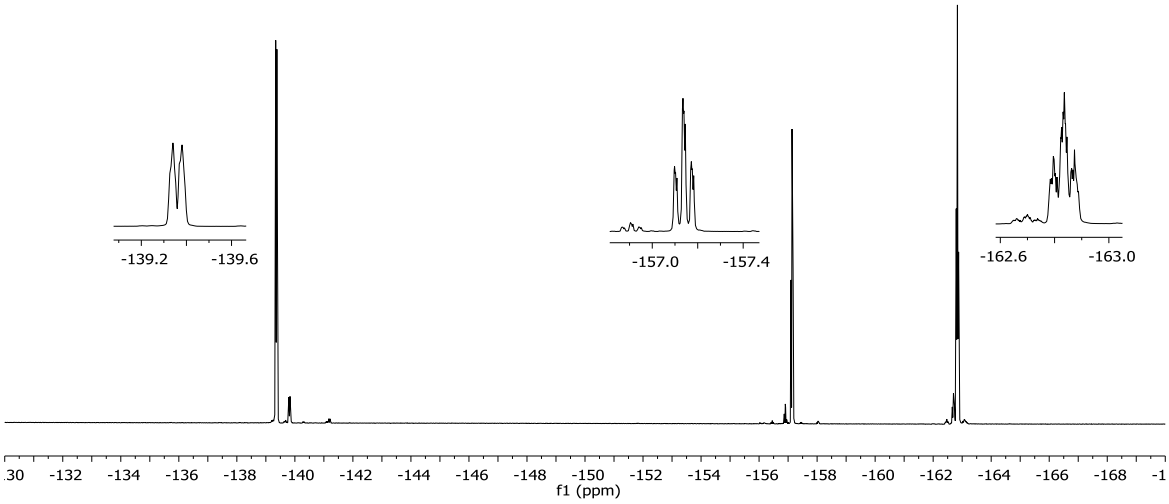


Figure S146: **^{19}F NMR** (564 MHz, $CDCl_3$, 299K) spectrum of compound **10**.

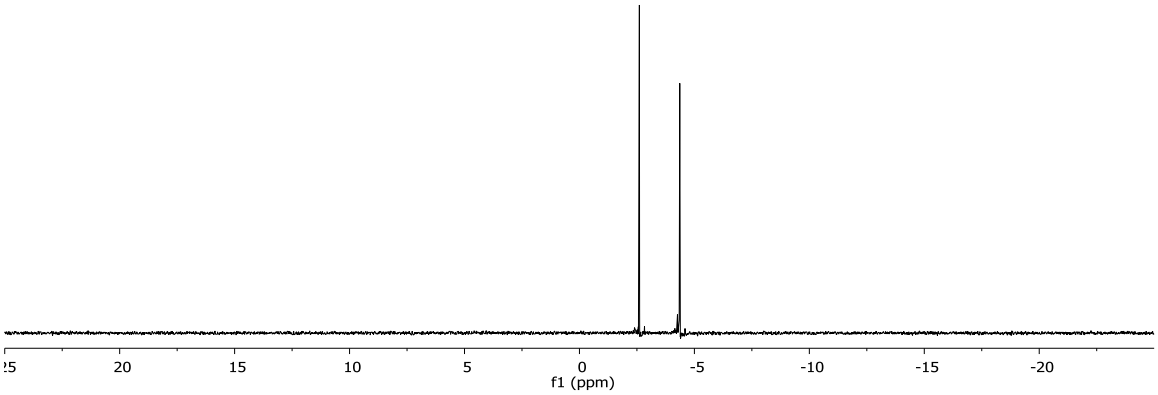
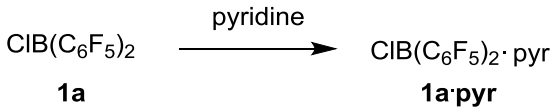


Figure S147: **^{29}Si{^{1}H} DEPT** (119 MHz, $CDCl_3$, 299K) spectrum of compound **10**.

Preparation of compound 1a·pyr as a reference



Scheme 29

Solutions of $ClB(C_6F_5)_2$ (190 mg, 0.5 mmol) in CH_2Cl_2 (2 ml) and pyridine (44 mg, 0.6 mmol) in CH_2Cl_2 (2 ml) were combined and stirred for 15 minutes at room temperature. Subsequently, all volatilities was removed in vacuo and residue was twice washed with pentane. **1a·pyr** was isolated as 213 mg of white solid (0.46 mmol, 92% yield).

Melting point: 130.0 °C.

HRMS: *m/z* calc. for $C_{17}H_5BF_{10}N$ [(M-Cl)$^-$]: 424.0346, found 424.0350.

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ = 8.95 (br d, $^3J_{HH}$ = 5.6 Hz, 2H, 2,6-py), 8.29 (tt, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, 4-py), 7.81 (m, 2H, 3,5-py).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ = 148.3 (dm, $^1J_{FC}$ ≈ 244 Hz, 4C, C_6F_5), 146.4 (2C, py), 143.9 (1C, 4-py), 141.0 (dm, $^1J_{FC}$ ≈ 252 Hz, 4C, C_6F_5), 137.7 (dm, $^1J_{FC}$ ≈ 254 Hz, 4C, C_6F_5), 126.8 (2C, py), 117.8 (br, *i*-C_6F_5)

^{13}C{^{1}H,^{19}F} NMR (151 MHz, 299 K, CD_2Cl_2): [selected resonances] δ = 148.3 (4C, *o*-C_6F_5), 141.0 (2C, *p*-C_6F_5), 137.7 (4C, *m*-C_6F_5)

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) δ = -132.9 (m, 2F, *o*-C_6F_5), -156.6 (t, $^3J_{FF}$ = 20 Hz, 1F, *p*-C_6F_5), -164.0 (m, 2F, *m*-C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 7.4].

^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = 1.5 ($\nu_{1/2}$ ~ 100 Hz).

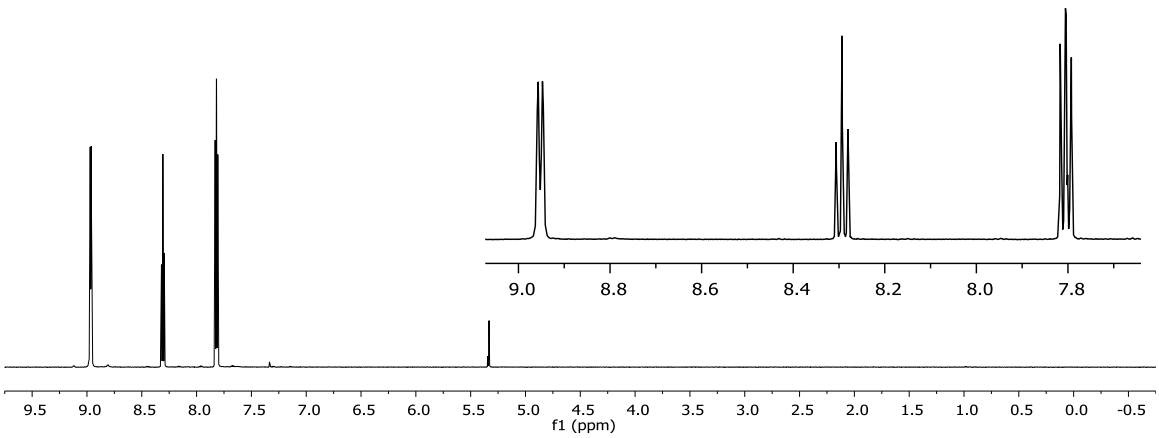


Figure S148: **^{1}H NMR** (600 MHz, $CDCl_3$, 299K) spectrum of compound **1a·pyr**.

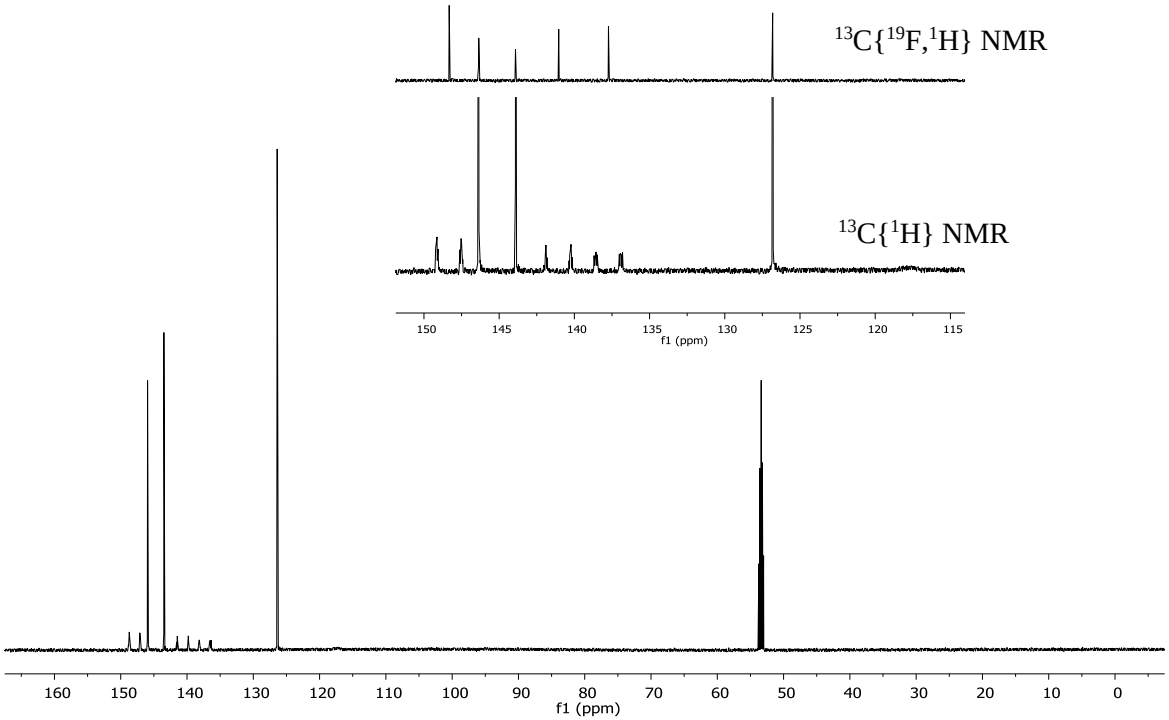


Figure S149: **$^{13}C\{^{1}H\}$ NMR** (151 MHz, CD_2Cl_2, 299K) spectrum and detailed overview of aromatic signals with excerpt from **$^{13}C\{^{19}F,^{1}H\}$ NMR** (151 MHz, CD_2Cl_2, 299K) spectrum of compound **1a·pyr**.

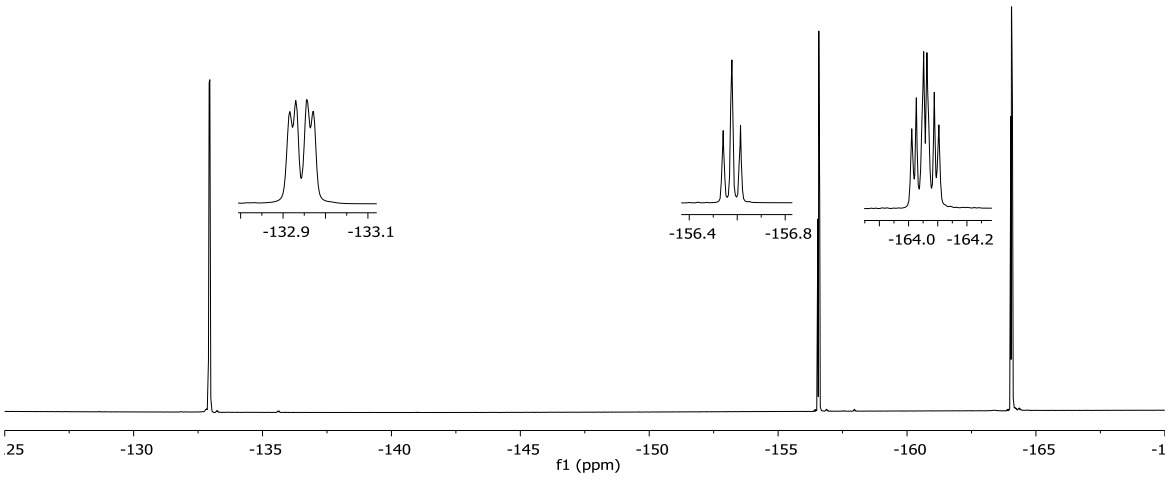


Figure S150: **^{19}F NMR** (470 MHz, $CDCl_3$, 299K) spectrum of compound **1a·pyr**.

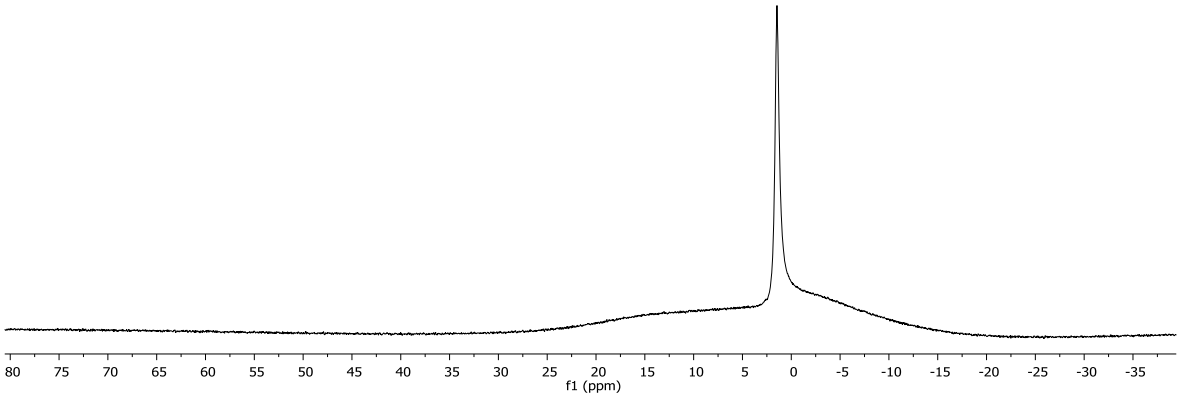


Figure S151: **$^{11}B\{^{1}H\}$ NMR** (192 MHz, CD_2Cl_2, 299K) spectrum of compound **1a·pyr**.

Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane into a solution of **1a·pyr** in dichlormethane at room temperature.

X-ray crystal structure analysis of compound 1a·pyr (erk9233): A colorless prism-like specimen of $C_{17}H_5BClF_{10}N$, approximate dimensions 0.062 mm x 0.131 mm x 0.181 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1367 frames were collected. The total exposure time was 22.78 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 102801 reflections to a maximum θ angle of 25.40° (0.83 Å resolution), of which 12363 were independent (average redundancy 8.315, completeness = 99.8%, R_{int} = 6.97%, R_{sig} = 3.63%) and 11006 (89.02%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.3540(7) Å, b = 17.9612(12) Å, c = 18.0990(11) Å, β = 90.255(2)°, volume = 3365.8(4) $Å^3$, are based upon the refinement of the XYZ-centroids of 9946 reflections above 20 σ(I) with 4.523° < 2θ < 50.68°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.933. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9420 and 0.9790. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1$, with Z = 8 for the formula unit, $C_{17}H_5BClF_{10}N$. The final anisotropic full-matrix least-squares refinement on F^2 with 1082 variables converged at R1 = 3.58%, for the observed data and wR2 = 7.60% for all data. The goodness-of-fit was 1.069. The largest peak in the final difference electron density synthesis was 0.372 $e^-/Å^3$ and the largest hole was -0.258 $e^-/Å^3$ with an RMS deviation of 0.056 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.813 g/cm^3 and F(000), 1808 e^-. CCDC Nr.: 1892604.

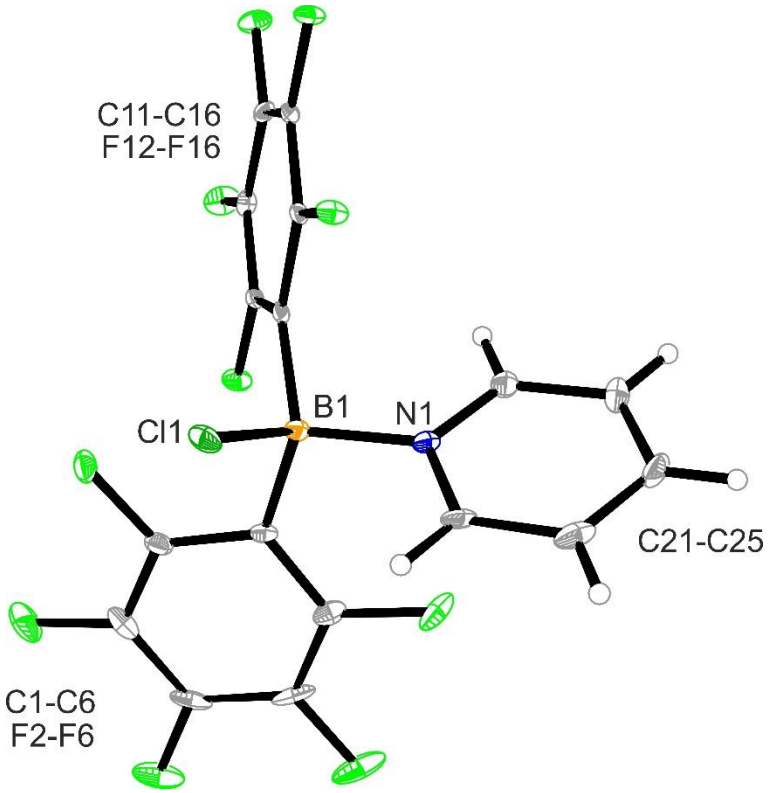


Figure S1: Crystal structure of compound **1a·pyr**, only one molecule ("A") of four found in the asymmetric unit is shown (thermal ellipsoids: 30% probability).