Using the FpXylBH$_2$ SMe$_2$ Reagent for the Regioselective Synthesis of Cyclic Bis(alkenyl)boranes

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Supporting Information

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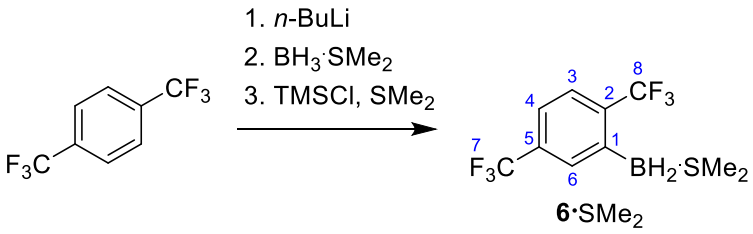
General Information

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 tetramethylsilane and referenced to the solvent signal. ^{31}P NMR: chemical shifts δ are given relative to H_3PO_4 (85% in D_2O) (external reference, $\delta^{31}P = 0$). ^{11}B NMR: chemical shifts δ are given relative to $BF_3{\cdot}OEt_2$) (external reference, $\delta^{11}B = 0$). ^{19}F NMR: chemical shifts δ are given relative to $CFCl_3$) (external reference, $\delta^{19}F = 0$). ^{29}Si NMR shifts δ are given relative to TMS (external reference, $\delta^{29}Si = 0$). NMR assignments were supported by additional 2D-NMR experiments and ^{19}F or ^{31}P decoupled experiments. HRMS was recorded on GTC Waters Micromass (Manchester, UK) and melting points were measures on TA-instruments DSC-2010. Elemental analyses were performed on a Foss-Heraeus CHNO-Rapid. IR spectra were recorded on aVarian 3100 TF-IR (Excalibur Series).
X-Ray diffraction: Data sets for compounds **10**, **13a**, **13b**, **17·pyr**, and **SI-1** were collected with a Bruker D8 Venture CMOS diffractometer. For compounds (**6**)$_2$, **15·pyr** and **SI-2** 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, G. M. *Acta Cryst.*, 2015, *A71*, 3-8); structure refinement *SHELXL-2015* (Sheldrick, G. M. *Acta Cryst.*, 2015, **C71** (1), 3-8) and graphics, *XP* (Version 5.1, Bruker AXS Inc., Madison, Wisconsin, USA, 1998). *R*-values are given for observed reflections, and wR^2 values are given for all reflections. *Exceptions and special features*: For compound **10** one CF_3 group and for compound **13a** two CF_3 groups were found disordered over two positions in the asymmetric unit. For compound **SI-1** the OH group was found disordered over two positions in the asymmetric unit. For compound **SI-2** one CF_3 group was found disordered over three positions in the asymmetric unit. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability.

Unless otherwise noted, all chemicals were purchased from commercially available sources (Sigma-Aldrich, TCI, ABCR, Alfa-Aesar, Fluorochem) and used as received unless stated otherwise. Deuterated solvents were dried over CaH_2, distilled under reduced pressure and stored over molecular sieves in argon atmosphere. FpXyl abbreviates 2,5-bis(trifluoromethyl)phenyl, Fmes abbreviates 2,4,6-tris(trifluoromethyl)phenyl. **Warning**: Many isonitriles are toxic reagents, they should be handled with due care.

Synthesis of compound 6·SMe_2



Scheme S1

1,4-Bis(trifluoromethyl)benzene (3.4 mL, 22 mmol) was dissolved in diethyl ether (60 mL) and the mixture was cooled with dry ice. Then a solution of *n*-BuLi (12.5 mL, 1.6 M in hexane, 20 mmol) was added portion wise and the mixture was allowed to react one hour while cooling and additional two hours at room temperature. The resulting pale yellow solution was cooled again with a dry-ice/isopropanol bath and a solution of BH_3·SMe_2 was added (10 ml, 2 M in toluene, 10 mL). The cooling bath was removed and the mixture was allowed to react overnight at room temperature. On the following day, all volatiles were removed in vacuo and the resulting yellow highly viscous (honey-like) oil was suspended in pentane (60 mL). Trimethylsilyl chloride (3.8 mL, 30 mmol) and dimethylsulfide (2.2 mL, 30 mmol) were added consecutively and the mixture was stirred for 30 minutes at room temperature. Then the stirring was stopped so that formed LiCl could settle and the mixture left standing undisturbed for two hours at room temperature. Subsequently, the mixture was carefully filtered via cannula and the filtrate was concentrated in vacuo to yield compound **6**·SMe_2 as a yellow oil (4.78 g, 16.6 mmol, 83 % yield).

Elemental analysis calculated for $C_{10}H_{11}BF_6S$ (496.4): C 41.69, H 3.85; found: C 41.43, H 3.51.

[Ar: 2,5-bis(trifluoromethyl)phenyl]

^{1}H NMR (500 MHz, CD_2Cl_2, 299 K): δ = 7.86 (s, 1H, 6-CH^{Ar}), 7.74 (d, $^3J_{HH}$ = 8.2 Hz, 1H, 3-CH^{Ar}), 7.54 (d, $^3J_{HH}$ = 8.2 Hz, 1H, 4-CH^{Ar}), 2.73 (broad 1:1:1:1 q, $^1J_{BH}$ ~ 115 Hz, 2H, BH_2), 2.23 (s, $^1J_{CH}$ = 142.3 Hz, 6H, SMe_2).

^{1}H{^{19}F} NMR (500 MHz, CD_2Cl_2, 299 K): δ = 7.86 (d, $^4J_{HH}$ = 2.0 Hz, 1H, 6-CH^{Ar}), 7.74 (d, $^3J_{HH}$ = 8.2 Hz, 1H, 3-CH^{Ar}), 7.54 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 2.0 Hz, 1H, 4-CH^{Ar}), 2.73 (broad 1:1:1:1 q, $^1J_{BH}$ ~ 115 Hz, 2H, BH_2), 2.23 (s, $^1J_{CH}$ = 142.3 Hz, 6H, SMe_2).

^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 299 K): δ = 145.9 (br, 1-C^{Ar}), 138.2 (q, $^2J_{FC}$ = 29.3 Hz, 2-C^{Ar}), 135.7 (q, $^3J_{FC}$ = 3.7 Hz, 6-CH^{Ar}), 132.2 (d, $^2J_{FC}$ = 31.6 Hz, 5-C^{Ar}), 126.1 (q, $^3J_{FC}$ = 5.9 Hz, 3-CH^{Ar}), 125.1 (q, $^1J_{FC}$ = 274.5 Hz, 8-CF_3), 124.6 (q, $^1J_{FC}$ = 272.5 Hz, 7-CF_3), 123.5 (q, $^3J_{FC}$ = 3.9 Hz, 4-CH^{Ar}), 24.0 (SMe_2)

^{13}C{^{19}F, ^{1}H} NMR (126 MHz, CD_2Cl_2, 299 K): δ = 145.80 (br, 1-C), 138.2 (2-C^{Ar}), 135.7 (6-CH^{Ar}), 132.24 (5-C), 126.1 (3-CH^{Ar}), 125.1 (8-CF_3), 124.6 (7-CF_3), 123.5 (4-CH^{Ar}), 24.0 (SMe_2)

^{11}B NMR (192 MHz, CD_2Cl_2, 299 K): δ = -9.8 (t, $^1J_{BH}$ ~ 110 Hz)

^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = -9.8 ($\nu_{1/2}$ ≈ 70 Hz)

^{19}F NMR (470 MHz, CD_2Cl_2, 299 K): δ = -59.5 (t, J_{FH} = 4.4 Hz, 1F, *o*-CF_3), -63.3 (quint., J_{FF} ~ J_{FH} = 0.9 Hz, 1F, *p*-CF_3^{FMes}).

^{19}F{^{1}H} NMR (564 MHz, CD_2Cl_2, 299 K): δ = -59.5 (q, J_{FF} = 0.9 Hz, 1F, *o*-CF_3), -63.3 (q, J_{FF} = 0.9 Hz, 1F, *p*-CF_3).

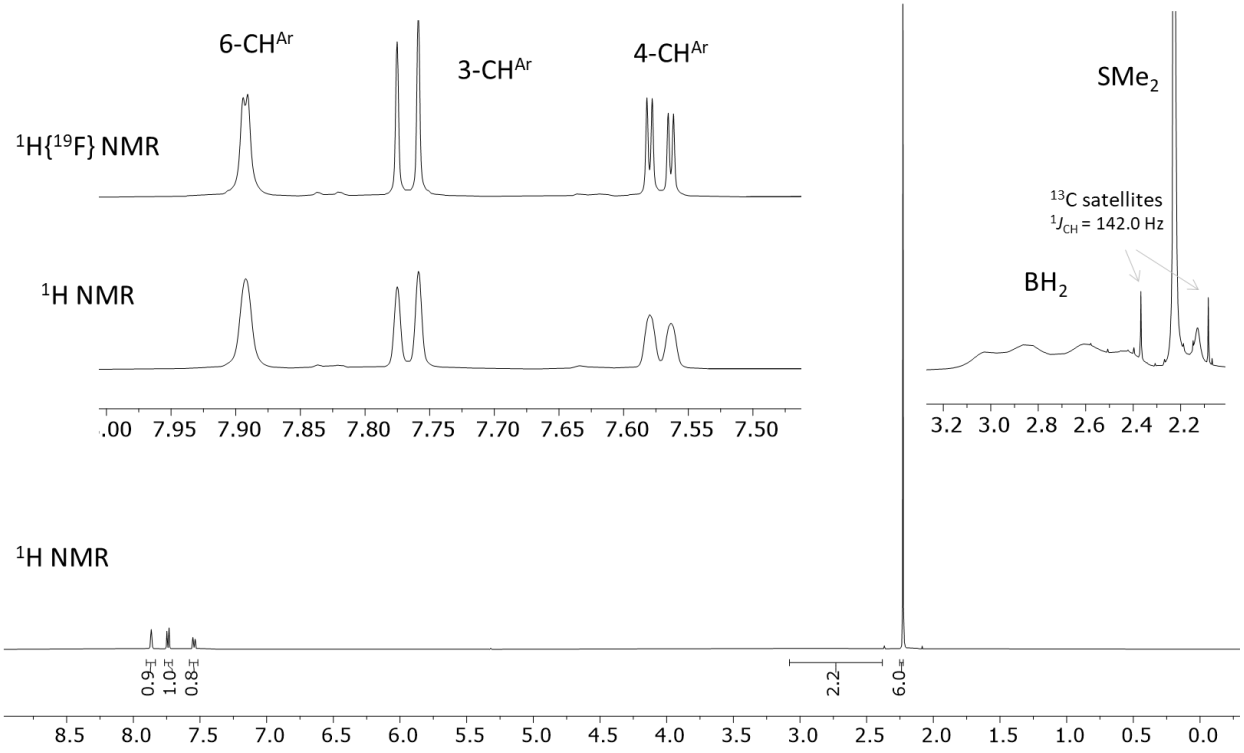


Figure S1: ^{1}H NMR (500 MHz, CD_2Cl_2, 299 K) and excerpt from **^{1}H{^{19}F} NMR** (500 MHz, CD_2Cl_2, 299 K) spectra of compound **6**·SMe_2.

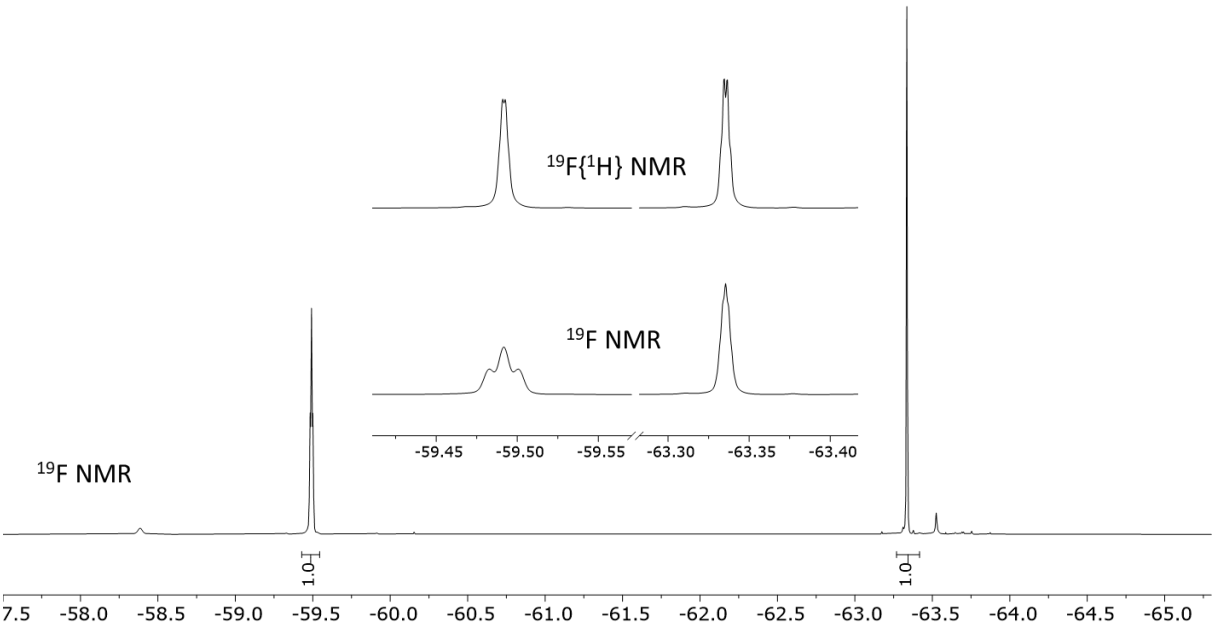


Figure S2: ^{19}F NMR (470 MHz, CD_2Cl_2, 299 K) spectra and excerpt from **^{19}F{^{1}H} NMR** (470 MHz, CD_2Cl_2, 299 K) spectrum of compound **6**·SMe_2.

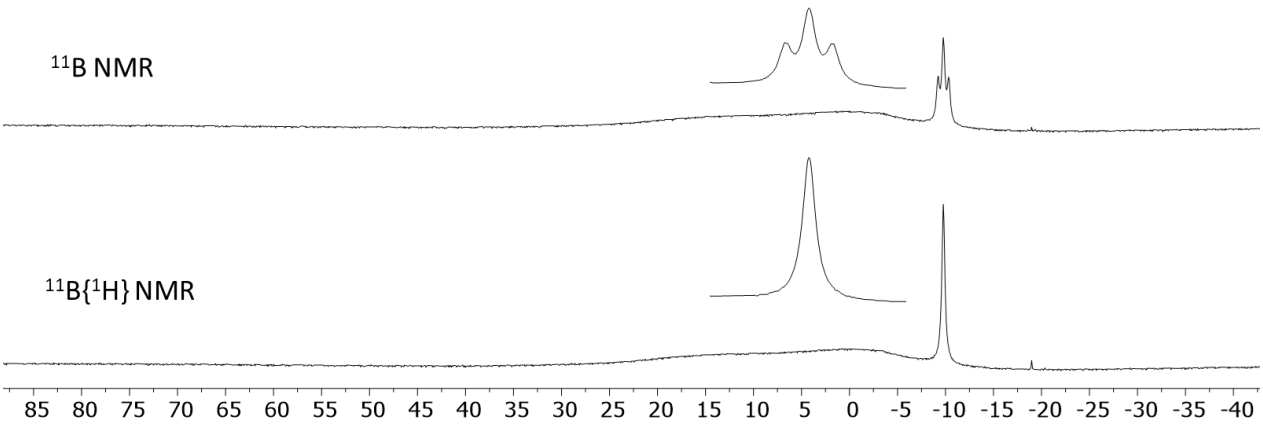


Figure S3: ^{11}B NMR and **^{11}B{^{1}H} NMR** (192 MHz, CD_2Cl_2, 299 K) spectra of compound **6**·SMe_2.

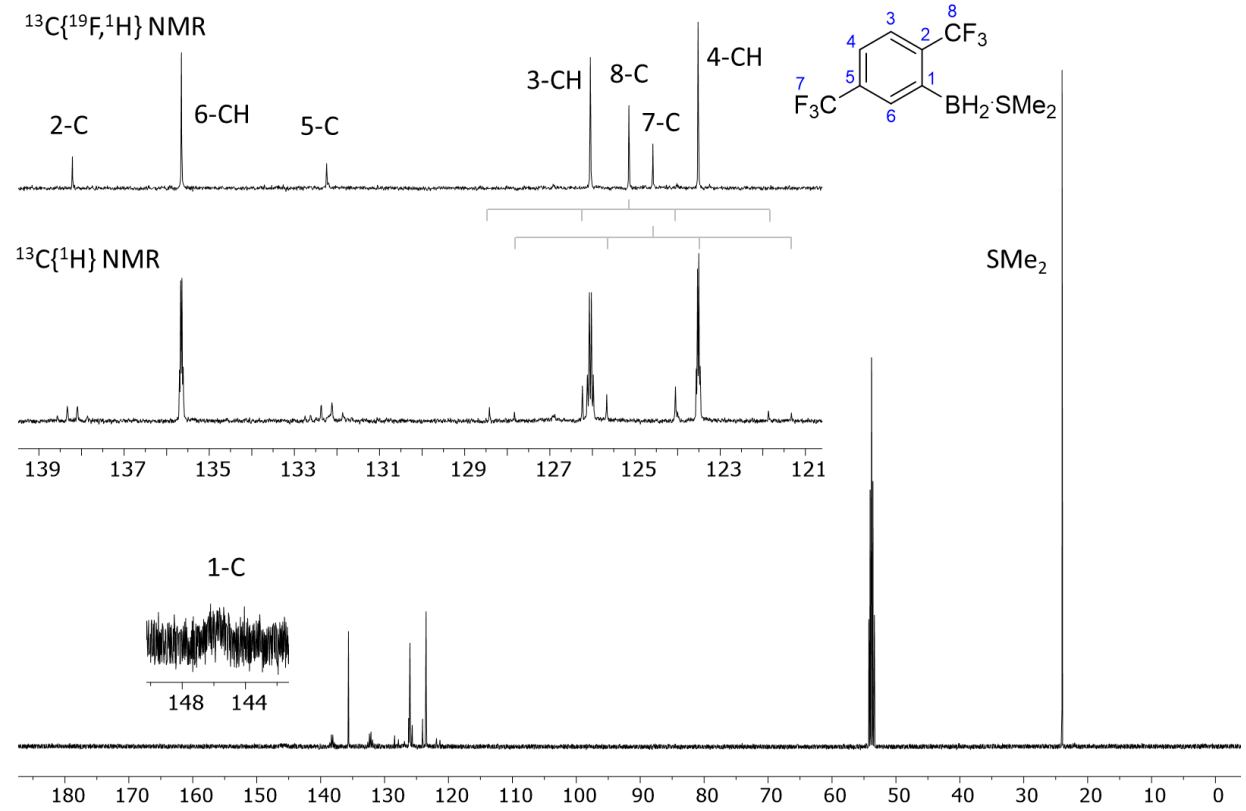


Figure S4: ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 299 K) spectrum and excerpt from **^{13}C{^{19}F,^{1}H} NMR** (126 MHz, CD_2Cl_2, 299 K) spectrum of compound **6**·SMe_2.

Generation of crystalline FpXylBH$_2$ dimer (6)$_2$ (SMe$_2$-free):

Neat borane **6**·SMe$_2$ was (0.5 g) distilled at 50 °C in vacuum (10 mbar). The initially beige oil turned to a semi-solid and the condensed fraction of SMe$_2$ was discarded. The temperature was increased to 80°C and an additional fraction of condensate was isolated as a white suspension. The NMR analysis revealed the presence of dimer (**6**)$_2$ and borane **6**·SMe$_2$ alongside with some impurities. The solid was washed with a small amount of pentane and dried in vacuo to give a crude material (ca 100 mg) which was dissolved in a small amount of dichloromethane (ca. 1 ml) and layered with pentane (ca 3 mL). Upon standing at room temperature for a several days, the mixture provided a few crystals of the dimer (**6**)$_2$ suitable for the X-ray crystal structure analysis.

X-ray crystal structure analysis of compound (6)$_2$ (erk9658): A colorless needle-like specimen of $C_{16}H_{10}B_2F_{12}$, approximate dimensions 0.030 mm x 0.060 mm x 0.200 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1488 frames were collected. The total exposure time was 22.02 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 11415 reflections to a maximum θ angle of 66.78° (0.84 Å resolution), of which 1519 were independent (average redundancy 7.515, completeness = 99.4%, R_{int} = 9.81%, R_{sig} = 4.41%) and 1264 (83.21%) were greater than 2σ(F^2). The final cell constants of a = 7.5560(3) Å, b = 8.4678(3) Å, c = 13.5930(5) Å, β = 96.564(2)°, volume = 864.02(6) Å^3, are based upon the refinement of the XYZ-centroids of 3836 reflections above 20 σ(I) with 13.11° < 2θ < 133.4°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.799. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7230 and 0.9500. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P*2$_1$/*n*, with Z = 2 for the formula unit, $C_{16}H_{10}B_2F_{12}$. The final anisotropic full-matrix least-squares refinement on F^2 with 144 variables converged at R1 = 4.38%, for the observed data and wR2 = 10.00% for all data. The goodness-of-fit was 1.049. The largest peak in the final difference electron density synthesis was 0.203 e$^-$/Å^3 and the largest hole was -0.309 e$^-$/Å^3 with an RMS deviation of 0.059 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.737 g/cm^3 and F(000), 448 e$^-$. The hydrogens at B1 atom were refined freely. CCDC number: 2016810.

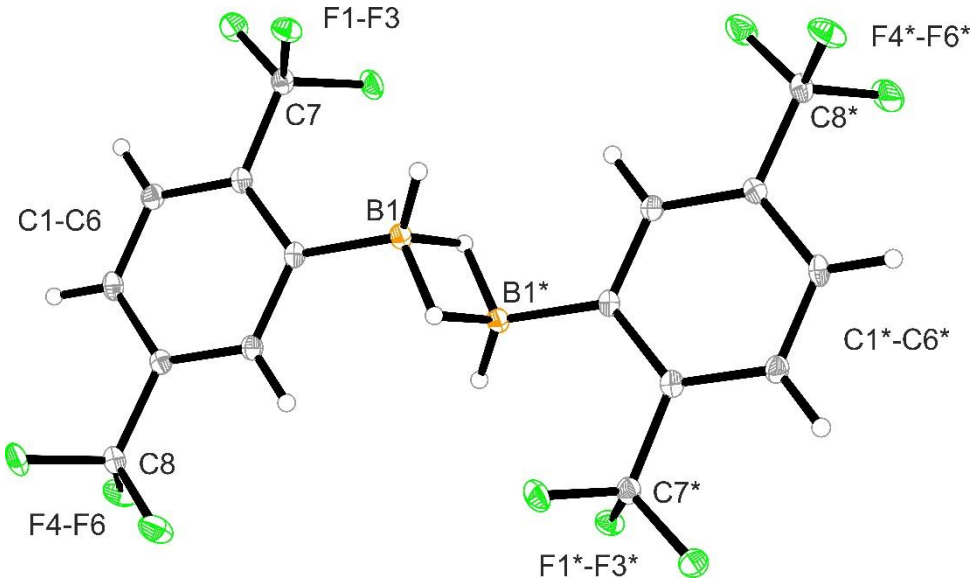
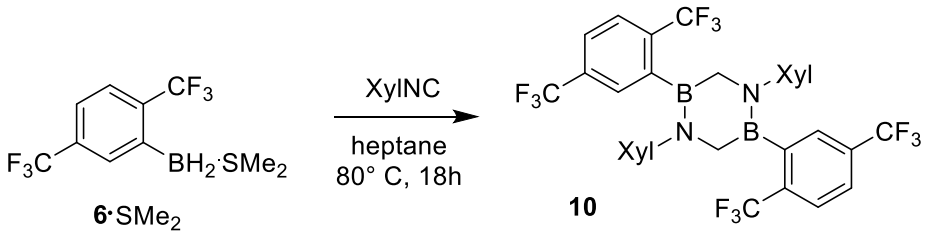


Figure S5: Crystal structure of compound (**6**)$_2$. Thermal ellipsoids are set at 30% probability.

Synthesis of compound 10.



Scheme S2

A solution of compound **6**·SMe_2 (288 mg, 1.0 mmol) in heptane (5 ml) was added to a solution of XylNC (131 mg, 1.0 mmol) in heptane (10 ml). The mixture was heated to 80°C overnight, subsequently stirring was stopped and the mixture was allowed to cool slowly to room temperature. Then the reaction mixture was placed in a freezer (-20°C), where precipitation of the product occurred. The obtained solid was isolated by decantation and washed with cold pentane to give compound **10** as an off-white solid (126 mg, 0.196 mmol, 39% yield).

Melting point: 274.2 °C.

Elemental analysis calculated for $C_{34}H_{28}B_2F_{12}N_2$ (496.4): C 57.17, H 3.95, N 3.92; found: C 56.99, H 3.98, N 3.78.

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = [7.61 (d, $^3J_{HH}$ = 8.3 Hz), 7.51 (d, $^3J_{HH}$ = 8.3 Hz), 7.47 (s)](each 1H, FpXyl), [6.95 (br, 2H), 6.91 (t, $^3J_{HH}$ = 7.3 Hz, 1H)](Xyl), 3.34 (br, 2H, CH_2), [2.48, 2.27](each br, each 3H, Me).

^{19}F NMR (564 MHz CD_2Cl_2, 299 K): δ = -57.7 (br, 1F, CF_3), -63.8 (s, 1F, CF_3).

^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = 40.4 ($\nu_{1/2} \approx 500$ Hz).

At low temperature (253 K) a mixture of two conformers ca. 54 : 46 (^{19}F) [ca. 53 : 47 (^{1}H)]was observed

^{1}H NMR (600 MHz, CD_2Cl_2, 253 K): **major** δ = [7.60 (d, $^3J_{HH}$ = 8.2 Hz), 7.51 (d, $^3J_{HH}$ = 8.2 Hz), 7.40 (s)](each 1H, FpXyl), [7.01 (d, $^3J_{HH}$ = 7.4 Hz), 6.90 (t, $^3J_{HH}$ = 7.4 Hz), 6.86 (d, $^3J_{HH}$ = 7.4 Hz](each 1H, Xyl), [3.28, 3.24] (each d, $^2J_{HH}$ = 18.5 Hz, each 1H, CH_2), [2.53, 2.17](each s, 3H, Me); **minor** δ = [7.60 (d, $^3J_{HH}$ = 8.2 Hz), 7.51 (d, $^3J_{HH}$ = 8.2 Hz), 7.43 (s)](each 1H, FpXyl), [7.05 (d, $^3J_{HH}$ = 7.4 Hz), 6.90 (t, $^3J_{HH}$ = 7.4 Hz), 6.83 (d, $^3J_{HH}$ = 7.4 Hz](each 1H, Xyl), [3.37, 3.21](each d, $^2J_{HH}$ = 18.8 Hz, each 1H, CH_2), [2.57, 2.13](each s, 3H, Me)

^{19}F NMR (564 MHz, CD_2Cl_2, 253 K): **major** δ = -57.5 (s, 1F, CF_3), -63.6 (s, 1F, CF_3); **minor** δ = -57.4 (s, 1F, CF_3), -63.6 (s, 1F, CF_3)

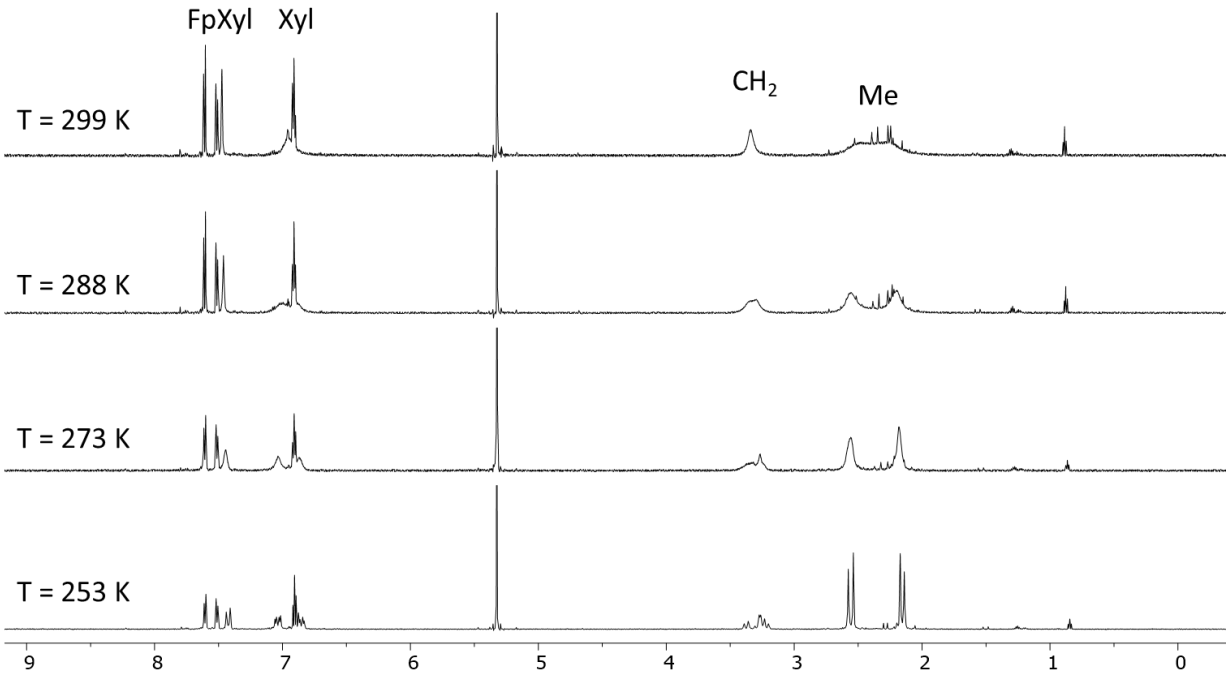


Figure S6: ^{1}H NMR (600 MHz, CD_2Cl_2) spectra of compound **10** measured at various temperatures.

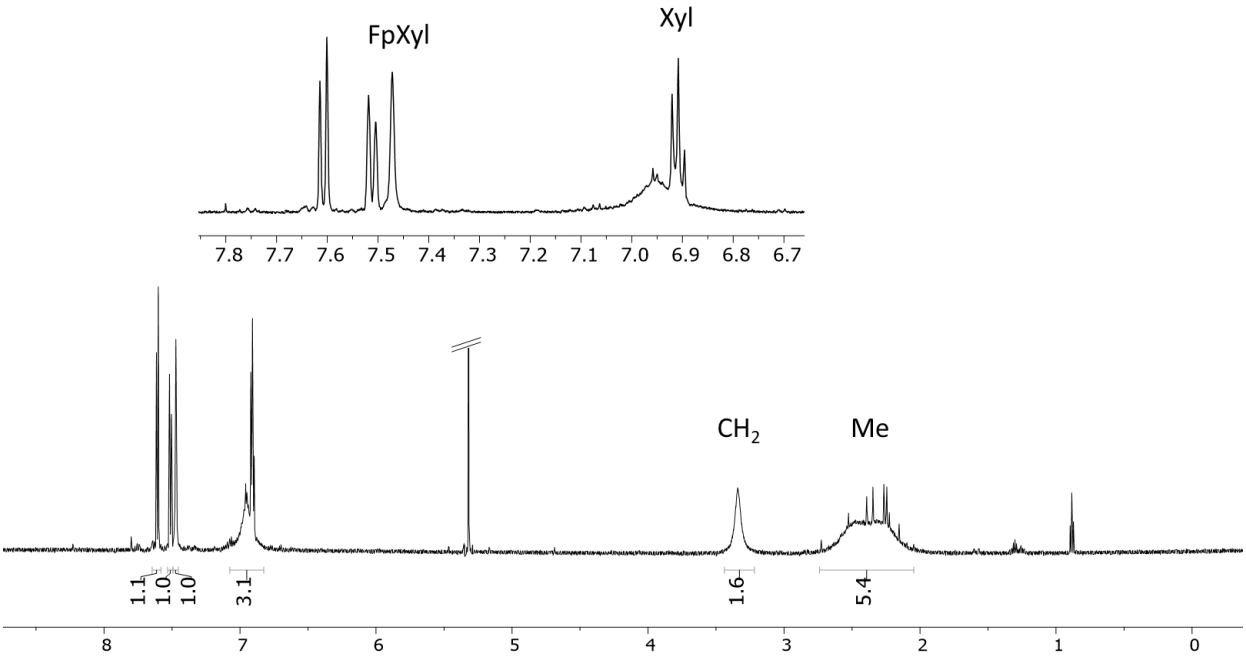


Figure S7: ^{1}H NMR (600 MHz, CD_2Cl_2, 299 K) spectrum of compound **10**.

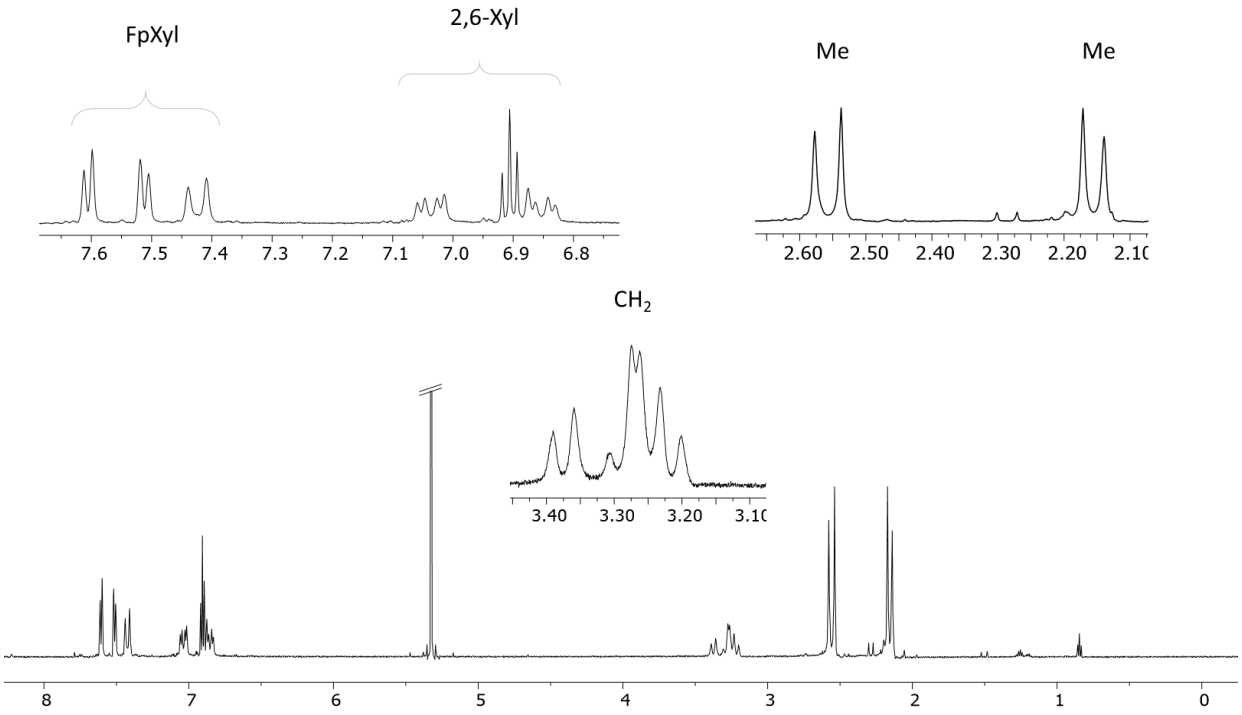


Figure S8: ^{1}H NMR (600 MHz, CD_2Cl_2, 253 K) spectrum of compound **10**.

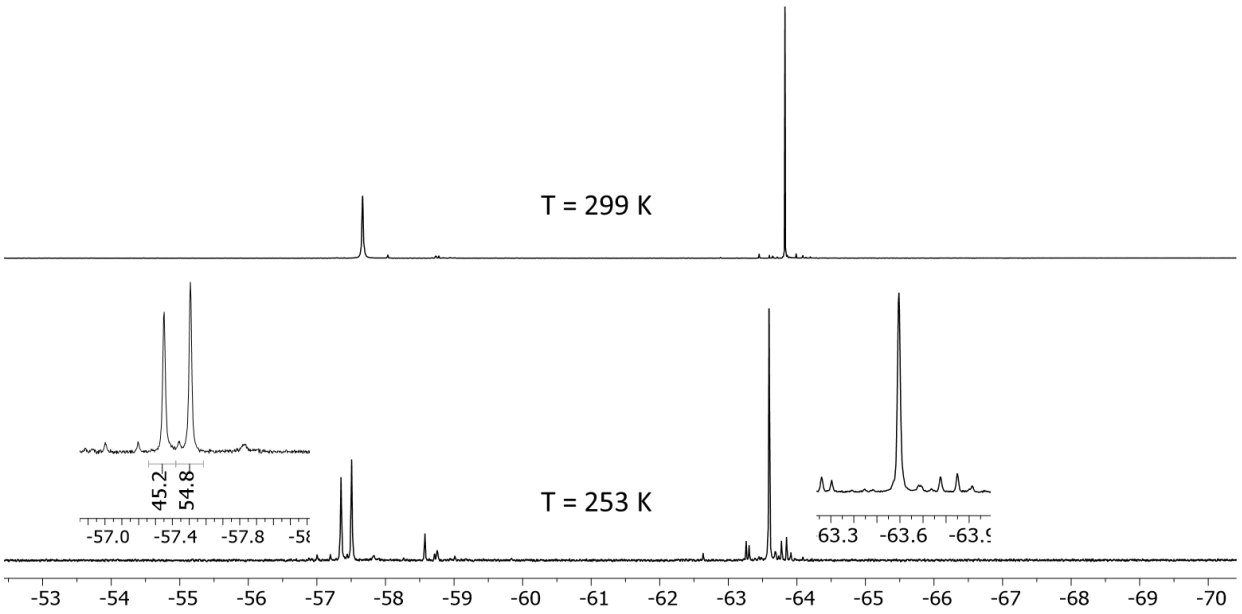


Figure S9: ^{19}F NMR (564 MHz, CD_2Cl_2) spectra of compound **10** measured at various temperatures.

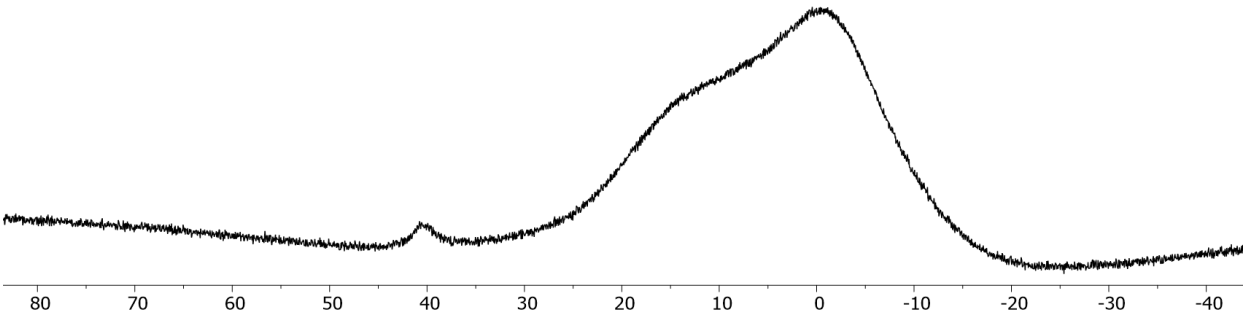


Figure S10: $^{11}B\{^{1}H\}$ NMR (192 MHz, CD_2Cl_2, 299 K) spectrum of compound **10**.

Crystals suitable for the X-ray crystal structure analysis were obtained by diffusion of pentane into a saturated solution of compound **10** in dichloromethane at room temperature.

X-ray crystal structure analysis of compound 10 (erk9686): A colorless plate-like specimen of $C_{34}H_{28}B_2F_{12}N_2$, approximate dimensions 0.046 mm x 0.088 mm x 0.154 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 515 frames were collected. The total exposure time was 6.44 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 15605 reflections to a maximum θ angle of 26.82° (0.79 Å resolution), of which 3526 were independent (average redundancy 4.426, completeness = 99.2%, R_{int} = 6.25%, R_{sig} = 4.65%) and 2639 (74.84%) were greater than $2\sigma(F^2)$. The final cell constants of a = 8.7742(5) Å, b = 9.5777(6) Å, c = 11.1573(7) Å, α = 98.124(2)°, β = 99.074(2)°, γ = 113.422(2)°, volume = 827.78(9) $Å^3$, are based upon the refinement of the XYZ-centroids of 2911 reflections above 20 σ(I) with 4.757° < 2θ < 53.42°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.939. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9800 and 0.9940. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P*-1, with Z = 1 for the formula unit, $C_{34}H_{28}B_2F_{12}N_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 256 variables converged at R1 = 6.24%, for the observed data and wR2 = 13.88% for all data. The goodness-of-fit was 1.065. The largest peak in the final difference electron density synthesis was 0.324 $e^-/Å^3$ and the largest hole was -0.262 $e^-/Å^3$ with an RMS deviation of 0.055 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.433 g/cm^3 and F(000), 364 e^-. CCDC number: 2016811.

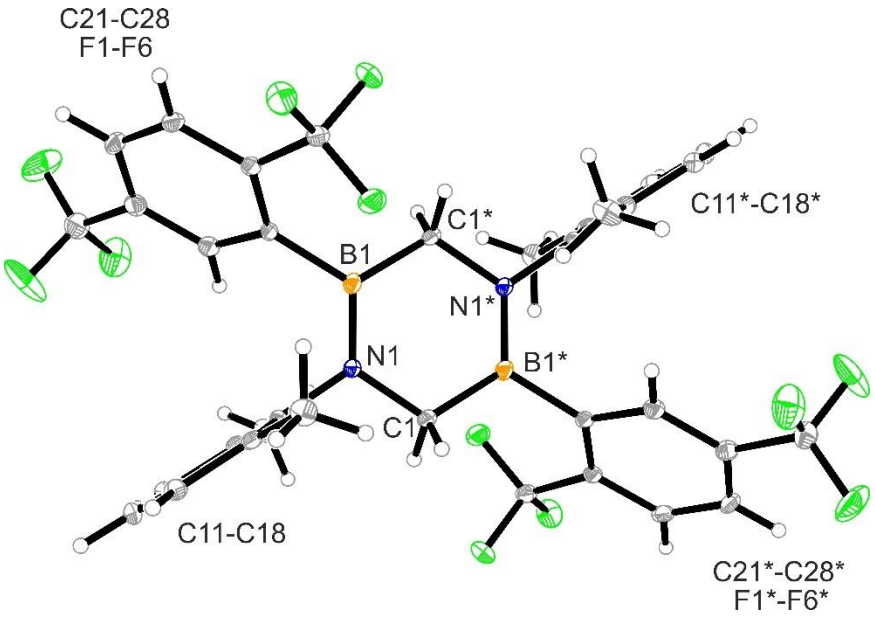
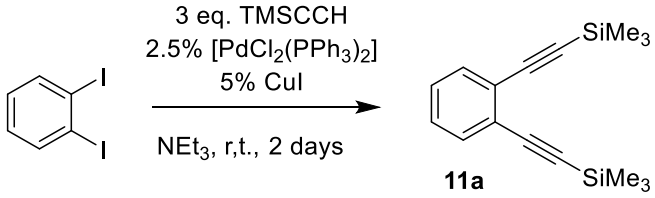


Figure S11: Crystal structure of compound **10**. Thermal ellipsoids are set at 30% probability.

Synthesis of bis-acetylene 11a [S1]



Scheme S3

1,2-Diiodobenzene (2.6 mL, 20 mmol), CuI (188 mg, 1 mmol, 0.05 eq.) and $[PdCl_2(PPh_3)_2]$ (700 mg, 1 mmol, 0.05 eq.) were suspended in triethylamine (60 mL). Then trimethylsilylacetylene (8.4 mL, 60 mmol, 3 eq.) was added dropwise. The mixture spontaneously darkened and warmed up. The resulting brown-black suspension was stirred for two days at room temperature. Subsequently all volatiles were removed in vacuo. The residue was taken up in diethyl ether and passed through a Celite plug. The obtained red solution was concentrated in vacuo and purified by flash chromatography on silica gel using pentane as eluent. Small amount of impurities was eluted first followed by the product, which was obtained as a yellow oil which readily crystallized to give product **11a** as a yellow crystalline solid (5.21 g, 19.2 mmol, 96% yield).

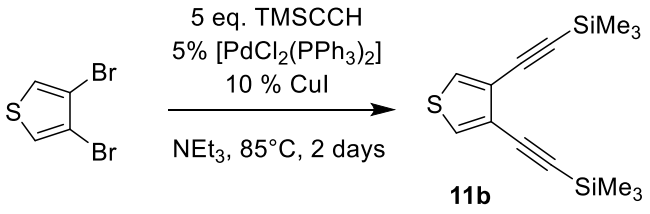
^{1}H NMR (600 MHz, $CDCl_3$, 299 K): δ = [7.45, 7.23](each m, each 1H, CH^{Ar}), 0.27 (s, $^{2}J_{SiH}$ = 7.1 Hz, 9H, $SiMe_3$).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 299 K): δ = [132.3, 128.0](CH^{Ar}), 125.8 (C^{Ar}), [103.3, 98.5](C≡C), 0.0 ($^{1}J_{SiC}$ = 57.0 Hz, $SiMe_3$)

^{29}Si{^{1}H} DEPT (119 MHz, $CDCl_3$, 299 K): δ = -17.6 ($\nu_{1/2}$ ~ 1 Hz).

Obtained data correspond to those reported in literature.[S1,2]

Synthesis of the bis-acetylene 11b [S1]



Scheme S4

3,4-Dibromothiophene (1.1 mL, 10 mmol), CuI (188 mg, 1 mmol, 0.1 eq.) and $[PdCl_2(PPh_3)_2]$ (350 mg, 0.5 mmol, 0.05 eq.) were suspended in triethylamine (40 mL). Then trimethylsilylacetylene (7.1 mL, 50 mmol, 5 eq.) was added dropwise. The mixture spontaneously darkened. The resulting brown-black suspension was stirred for two days at 85°C. Subsequently all volatiles were removed in vacuo. Then the residue was taken up in diethyl ether and passed through a Celite plug. The obtained orange solution was concentrated in vacuo and purified by chromatography on silica gel using pentane as eluent. Small amounts of impurities were eluted first followed by the product **11b**, which was obtained as a red oil (1.39 g, 5.03 mmol, 50% yield).

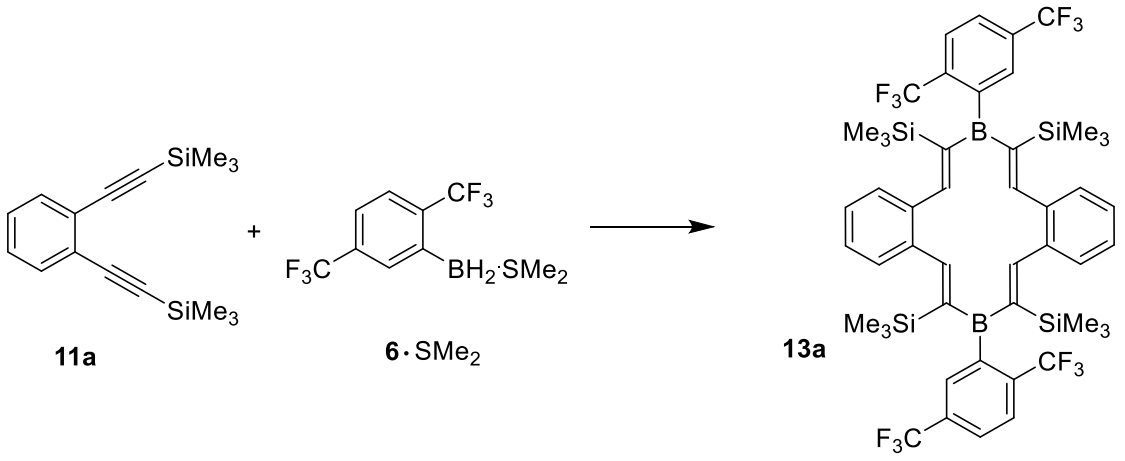
^{1}H NMR (600 MHz, $CDCl_3$, 299 K): δ = 7.39 (s, 1H, CH), 0.26 (s, $^{2}J_{SiH}$ = 7.0 Hz, 9H, $SiMe_3$)

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 299 K): δ = 128.8 (CH), 125.2 (C), [98.1, 96.7](C≡C), 0.0 ($^{1}J_{SiC}$ = 56.5 Hz, $SiMe_3$)

^{29}Si{^{1}H} DEPT (119 MHz, $CDCl_3$, 299 K): δ = -17.5 ($\nu_{1/2}$ ~ 1 Hz).

The obtained data correspond to those reported in literature[S3]

Synthesis of compound 13a.



Scheme S5

Solutions of compound **11a** (270 mg, 1.0 mmol) in CH_2Cl_2 (ca 4 mL) and compound **6**·SMe_2 (288 mg, 1.0 mmol) in CH_2Cl_2 (ca 4 mL) were combined and stirred for 60 minutes at room temperature to give an orange solution. Subsequently all volatiles were removed in vacuo and the solid residue was taken up in pentane (ca 5 mL) and the solution was placed in a freezer (-35°C). Over several days a white solid precipitated, which was subsequently separated by decantation, then carefully washed with a small amount cold pentane and dried in vacuo. Compound **13a** was isolated as an off-white solid (238 mg, 0.48 mmol, 48% yield).

Melting point: 101.5 °C.

Elemental analysis calculated for $C_{48}H_{54}B_2F_{12}Si_4$ (998.9): C 58.06, H 5.48; found: C 59.97, H 5.64.

HRMS for $C_{48}H_{55}B_2F_{12}OSi_4$ [$(M + OH)^-$]: calculated 1009.3325; found 1009.3324.

^{1}H NMR (600 MHz, C_6D_6, 299 K): δ = 8.28 ($\nu_{1/2}$ ≈ 120 Hz, 2H, =CH), [7.95 (s), 7.35 (d, $^3J_{HH}$ = 8.3 Hz), 7.23 (d, $^3J_{HH}$ = 8.3 Hz)](each 1H, FpXyl), [7.40 ($\nu_{1/2}$ ≈ 22 Hz), 7.04 (m)](each 2H, C_6H_4), -0.18 (s, 18H, $SiMe_3$).

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 8.03 ($\nu_{1/2}$ ≈ 80 Hz, 2H, =CH), [7.89 (d, $^3J_{HH}$ = 8.3 Hz), 7.83 (d, $^3J_{HH}$ = 8.3 Hz), 7.72 (s)](each 1H, FpXyl), [7.36 (m), 7.32 (br m)](each 2H, C_6H_4), -0.30 (s, 18H, $SiMe_3$).

^{1}H NMR (600 MHz, CD_2Cl_2, 233 K): δ = [8.43, 7.63](each s, 1H, =CH), [7.88 (d, $^3J_{HH}$ = 8.3 Hz), 7.83 (d, $^3J_{HH}$ = 8.3 Hz), 7.67 (s)](each 1H, FpXyl), [7.37, 7.36, 7.36, 7.24](each m, 1H, C_6H_4), [-0.30, -0.45](each s, 9H, $SiMe_3$).

^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 233 K): δ = [169.1, 151.4](=CH), [156.7, 153.6](=CB), [144.9 (B-C), 134.7 (q, $^2J_{FC}$ = 31.1 Hz, *C*-CF_3), 131.6 (q, $^2J_{FC}$ = 32.6 Hz, *C*-CF_3), 128.7 (br q, $^3J_{FC}$ = 3.4 Hz, CH), 126.5 (br q, $^3J_{FC}$ = 4.6 Hz, CH), 125.7 (br q, $^3J_{FC}$ = 3.2 Hz, CH), 124.1 (q, $^1J_{FC}$ = 275.6 Hz, CF_3), 123.6 (q, $^1J_{FC}$ = 272.8 Hz, CF_3)](FpXyl), [140.6 (C), 140.1 (C), 128.6 (CH), 128.5 (CH), 127.9 (CH), 127.4 (CH)](C_6H_4), [1.2, 0.4]($SiMe_3$)

^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = 71.2 ($\nu_{1/2}$ ≈ 2000 Hz)

^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = -55.4 ($\nu_{1/2}$ ≈ 30 Hz, 1F, CF_3), -63.6 (s, 1F, CF_3).

^{19}F NMR (564 MHz, CD_2Cl_2, 213 K): δ = -55.1 ($\nu_{1/2}$ ≈ 6 Hz, 1F, CF_3), -63.1 (s, 1F, CF_3).

^{1}H,^{29}Si{^{1}H} gHMBC (599 MHz / 119 MHz, CD_2Cl_2, 299 K): δ ^{1}H / ^{29}Si = -0.30 / -7.9

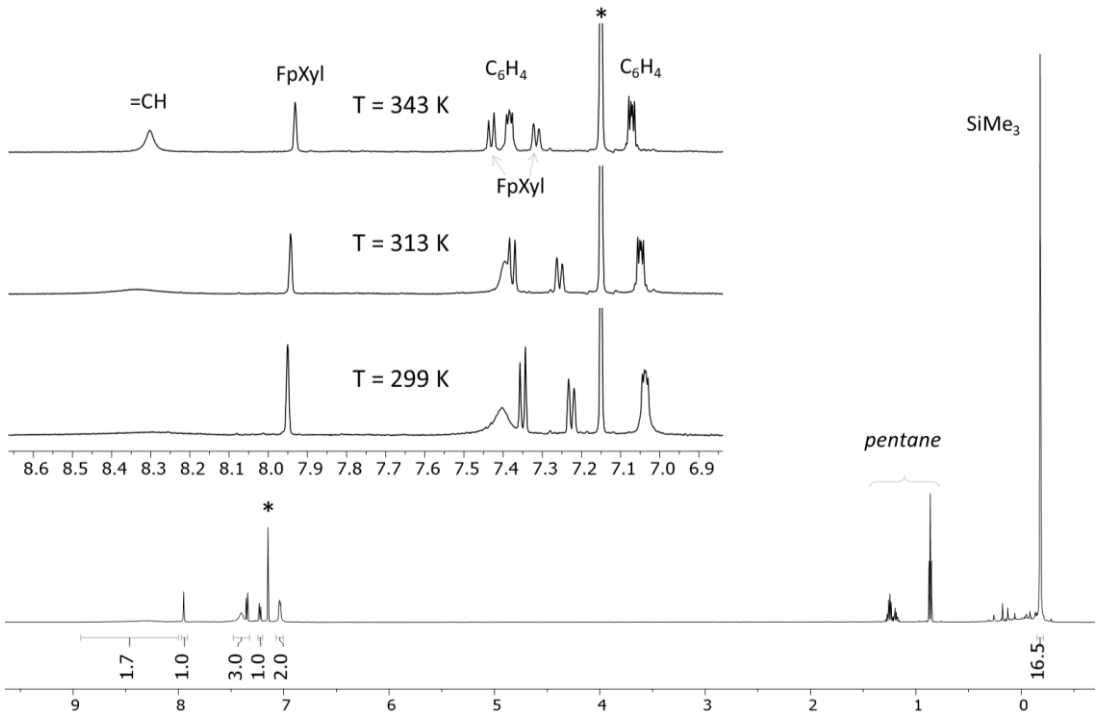


Figure S12: ^{1}H NMR (600 MHz, C_6D_6, 299 K) spectrum of compound **13a** with overview of the aromatic region measured at elevated temperatures.

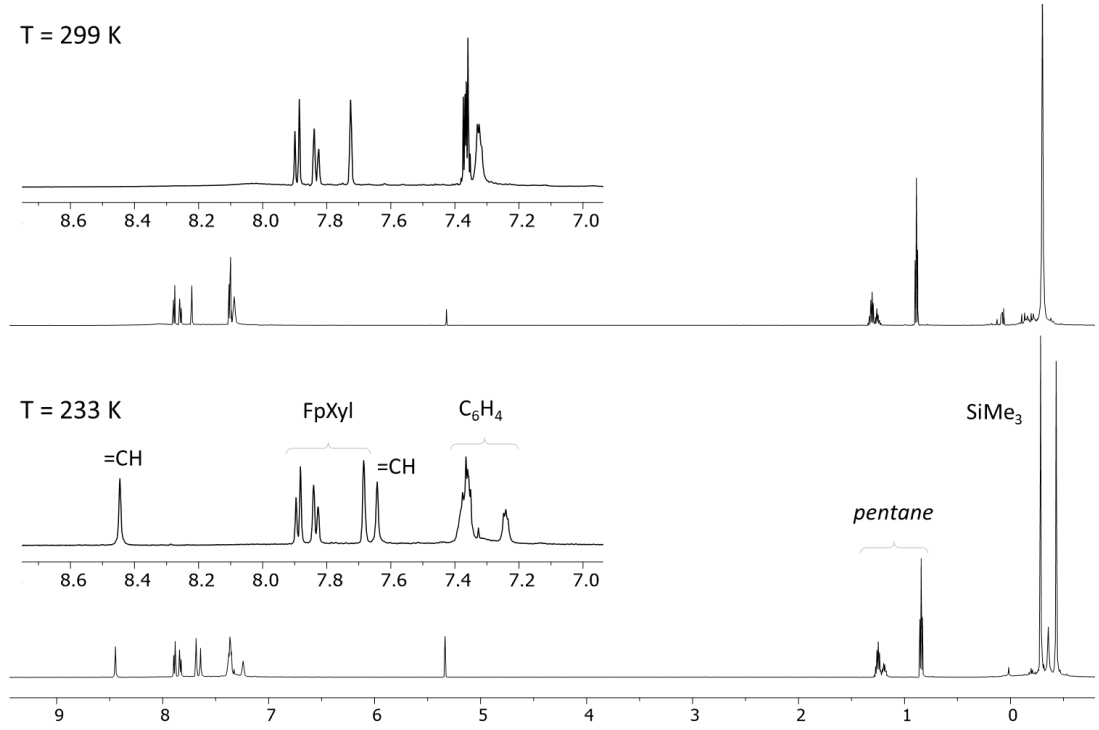


Figure S13: ^{1}H NMR (600 MHz, CD_2Cl_2) spectra of compound **13a** measured at 299 K and 233 K.

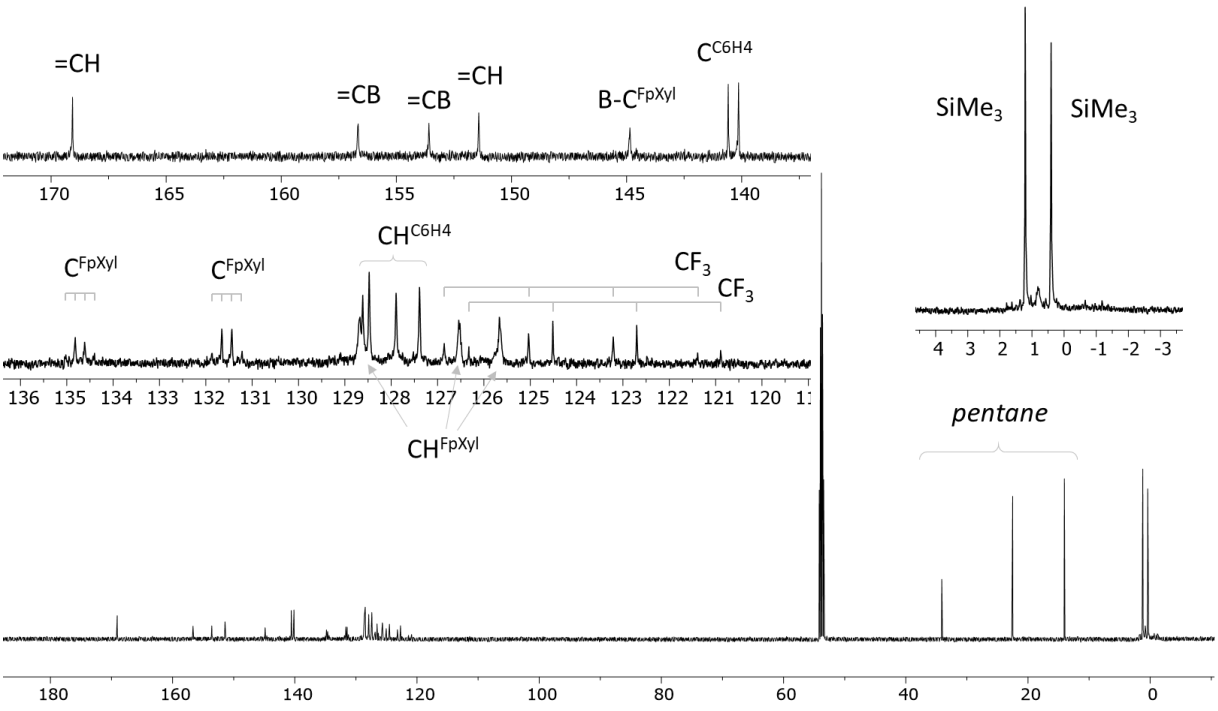


Figure S14: $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2, 233 K) spectrum of compound **13a**.

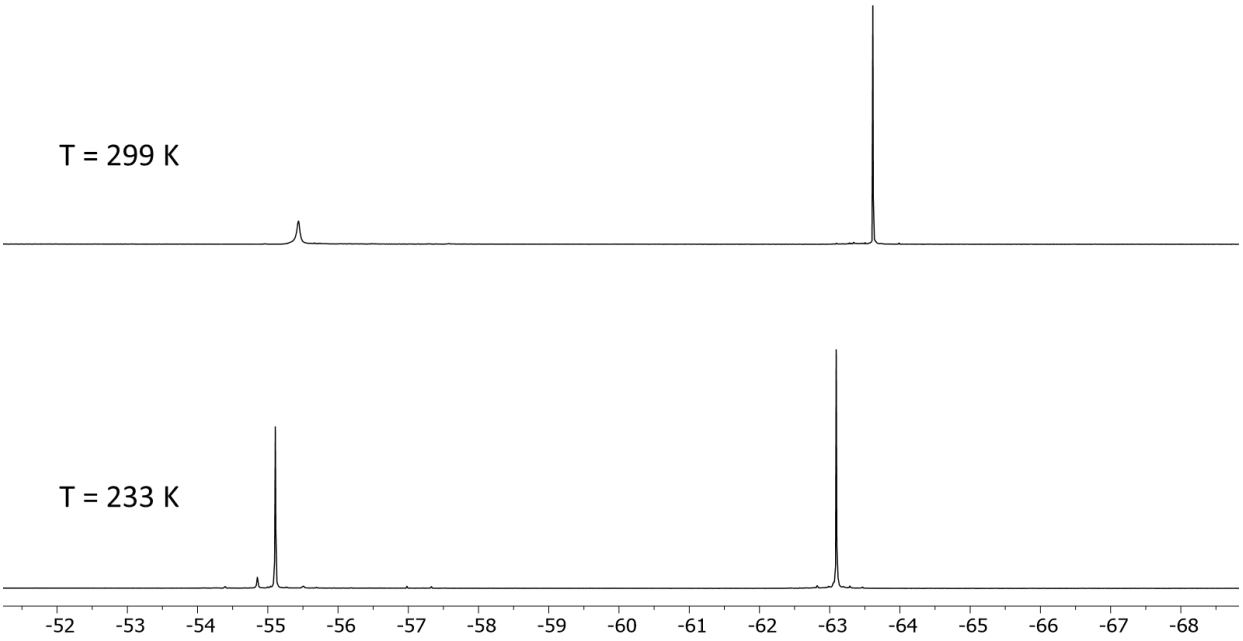


Figure S15: ^{19}F NMR (564 MHz, CD_2Cl_2) spectrum of compound **13a** measured at 299 K and 233 K.

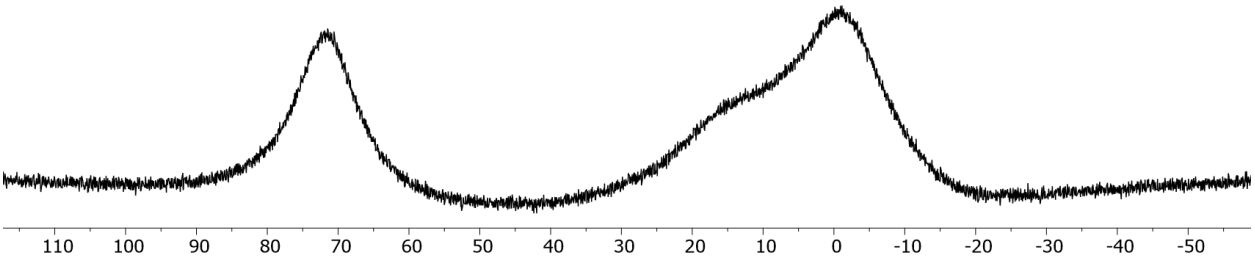


Figure S16: $^{11}B\{^{1}H\}$ NMR (192 MHz, CD_2Cl_2, 299 K) spectrum of compound **13a**.

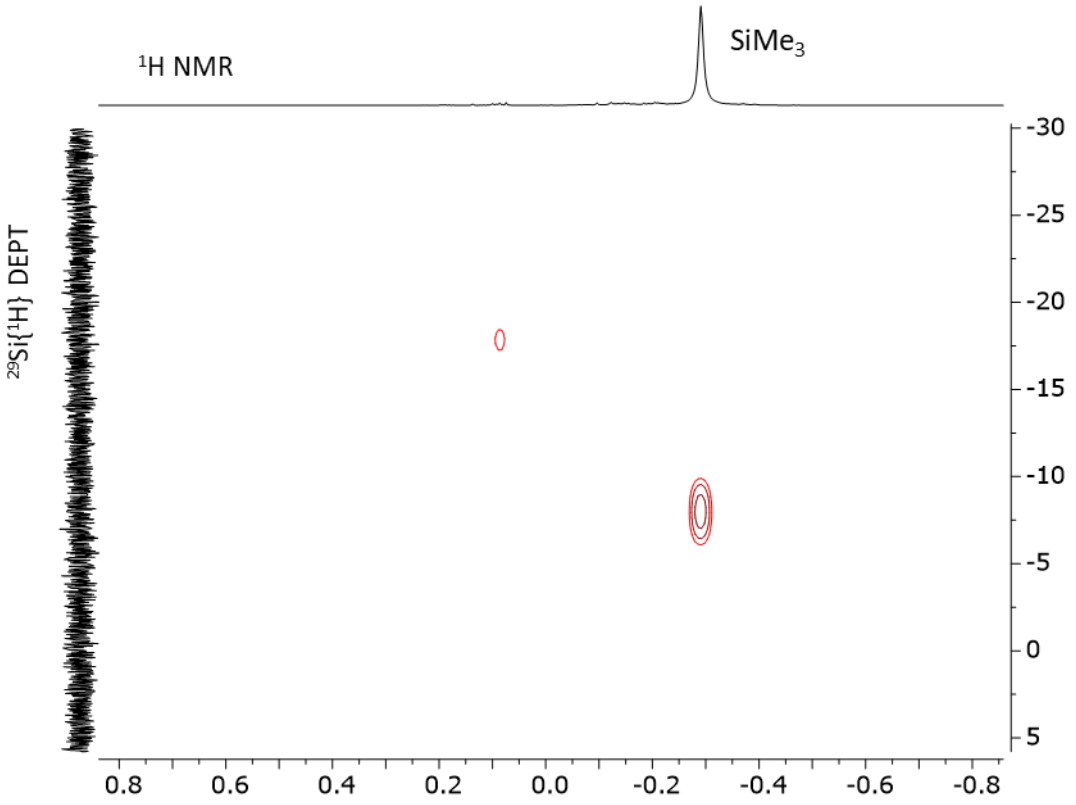


Figure 17: $^{1}H,^{29}Si\{^{1}H\}$ gHMBC (599 MHz / 119 MHz, CD_2Cl_2, 299 K) of compound **13a** [projections for F2: **^{1}H NMR** (600 MHz, CD_2Cl_2, 299 K) spectrum and F1: **$^{29}Si\{^{1}H\}$ DEPT** (119 MHz, CD_2Cl_2, 299 K) spectrum].

Crystals suitable for the X-ray crystal structure analysis were obtained from a saturated solution of compound **13a** in pentane at room temperature.

X-ray crystal structure analysis of compound 13a (erk9783): A colorless plate-like specimen of $C_{48}H_{54}B_2F_{12}Si_4$, approximate dimensions 0.060 mm x 0.128 mm x 0.147 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture PHOTON III Diffractometer system equipped with a micro focus tube Mo ImS (MoK_α, λ = 0.71073 Å) and a MX mirror monochromator. A total of 408 frames were collected. The total exposure time was 4.53 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 35372 reflections to a maximum θ angle of 25.35° (0.83 Å resolution), of which 9559 were independent (average redundancy 3.700, completeness = 99.9%, R_{int} = 11.45%, R_{sig} = 14.05%) and 5662 (59.23%) were greater than $2\sigma(F^2)$. The final cell constants of a = 13.3784(11) Å, b = 14.4310(13) Å, c = 16.3141(14) Å, α = 65.319(2)°, β = 66.050(2)°, γ = 78.620(2)°, volume = 2614.0(4) $Å^3$, are based upon the refinement of the XYZ-centroids of 2445 reflections above 20 σ(I) with 4.633° < 2θ < 42.14°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.916. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9730 and 0.9890. 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, $C_{48}H_{54}B_2F_{12}Si_4$. The final anisotropic full-matrix least-squares refinement on F^2 with 672 variables converged at R1 = 6.01%, for the observed data and wR2 = 17.39% for all data. The goodness-of-fit was 1.027. The largest peak in the final difference electron density synthesis was 0.354 $e^-/Å^3$ and the largest hole was -0.413 $e^-/Å^3$ with an RMS deviation of 0.070 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.261 g/cm^3 and F(000), 1032 e^-. CCDC number: 2016812.

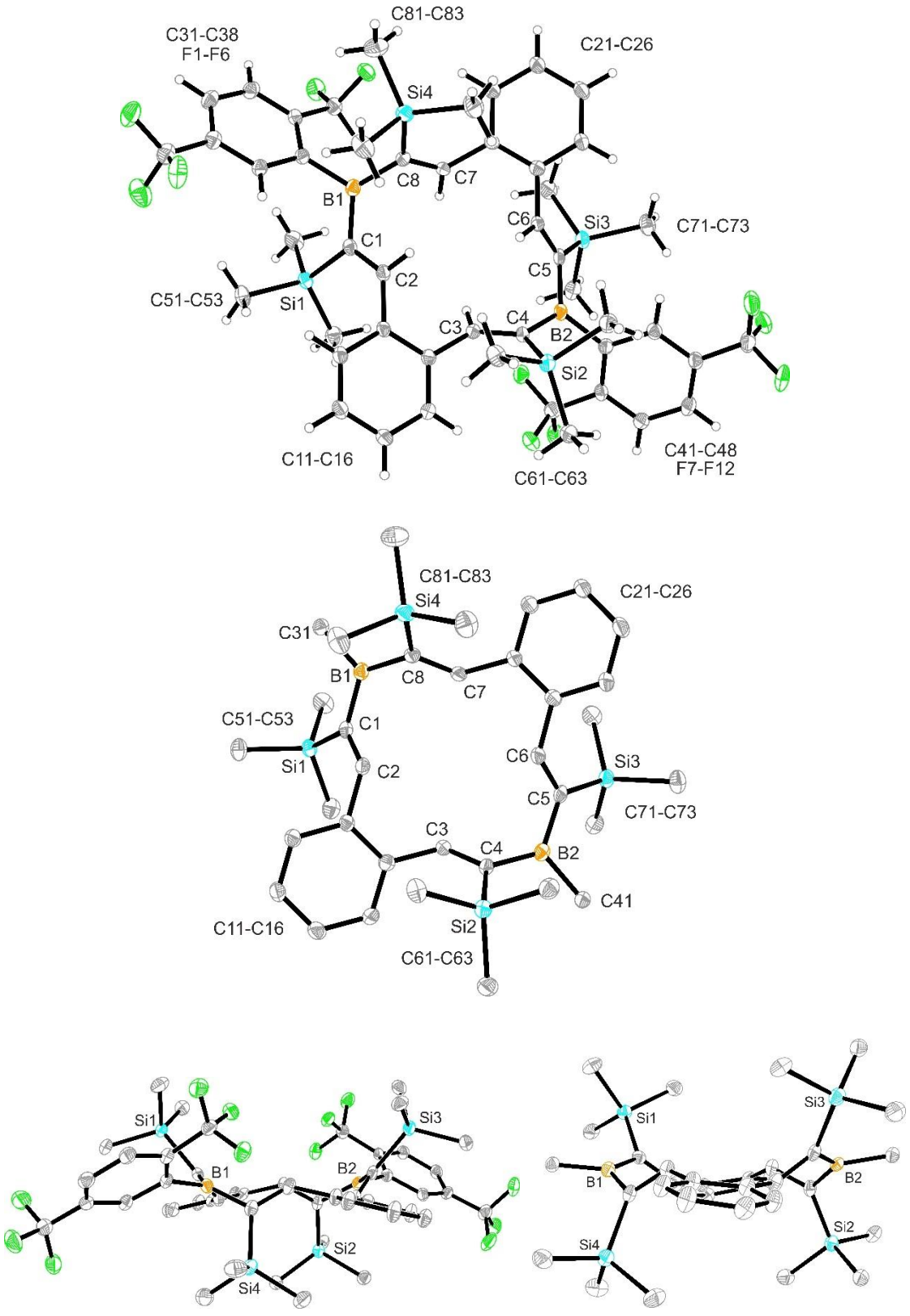
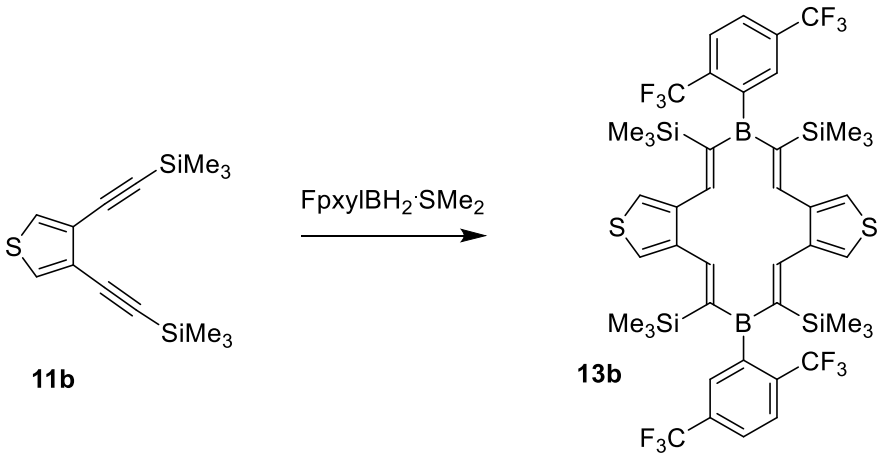


Figure S18: Crystal structure of compound **13a**. Thermal ellipsoids are set at 30% probability.

Synthesis of compound 13b.



Scheme S6

Solutions of compound **11b** (276 mg, 1.0 mmol) in CH_2Cl_2 (ca 3 mL) and compound **6**·SMe_2 (288 mg, 1.0 mmol) in CH_2Cl_2 (ca 3 mL) were combined and stirred for 60 minutes at room temperature to give a yellow solution. Subsequently all volatiles were removed in vacuo and the orange oily residue was taken up in pentane (3 mL) and the solution was stored at -35°C. Over several days a white solid was formed. It was isolated by decantation, carefully washed with cold pentane (2 x 1 mL) and dried in vacuo. Compound **13b** was obtained as an off white solid (isolated yield 301 mg, 0.30 mmol, 60 % yield).

Melting point: 120.3 °C.

Elemental analysis calculated for $C_{44}H_{50}B_2F_{12}S_2Si_4$ (1004.9): C 52.58, H 5.02; found: C 53.02, H 5.18.

HRMS for $C_{44}H_{50}B_2F_{12}S_2Si_4$ [M^+]: calculated 1004.2425; found 1004.2421.

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = [7.88 (d, $^3J_{HH}$ = 8.3 Hz), 7.81 (d, $^3J_{HH}$ = 8.3 Hz), 7.68 (s)](each 1H, FpXyl), 7.71 ($\nu_{1/2} \approx$ 100 Hz, =CH), 7.27 (s, 2H, C_4H_2S), -0.21 (s, 18H, $SiMe_3$)

^{1}H NMR (600 MHz, CD_2Cl_2, 213 K): δ = [8.11, 7.23](each s, each 1H, =CH), [7.85 (d, $^3J_{HH}$ = 8.3 Hz), 7.79 (br d, $^3J_{HH}$ = 8.1 Hz), 7.64 (s)](each 1H, FpXyl), [7.39, 7.06](each m, each 1H, C_4H_2S), [-0.23, -0.45](each s, 9H, $SiMe_3$)

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 213 K): δ = [164.0, 145.8](=CH), [158.3, 152.2](=CB), [144.7 (br, B-C), 134.3 (q, $^2J_{FC}$ = 31.0 Hz, *C*-CF_3), 131.2 (q, $^2J_{FC}$ = 32.4 Hz, *C*-CF_3), 128.1 (br, CH), 126.1 (br, CH), 125.4 (br, CH), 123.8 (q, $^1J_{FC}$ = 274.3 Hz, CF_3), 123.3 (q, $^1J_{FC}$ = 274.3 Hz, CF_3)](FpXyl), [143.2 (C), 140.8 (C), 124.5 (CH), 122.7 (CH)](C_4H_2S), [1.0, 0.0]($SiMe_3$).

^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ ≈ 70.0 ($\nu_{1/2} \approx$ 2200 Hz)

^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = -55.5 (s, 1F, CF_3), -63.6 (s, 1F, CF_3).

^{19}F NMR (564 MHz, CD_2Cl_2, 213 K): δ = -55.2 (s, 1F, CF_3), -63.0 (s, 1F, CF_3)

^{1}H,^{29}Si gHSQC (600 MHz/119 MHz, CD_2Cl_2, 299 K): δ ^{1}H / δ ^{29}Si = -0.21 / -8.2

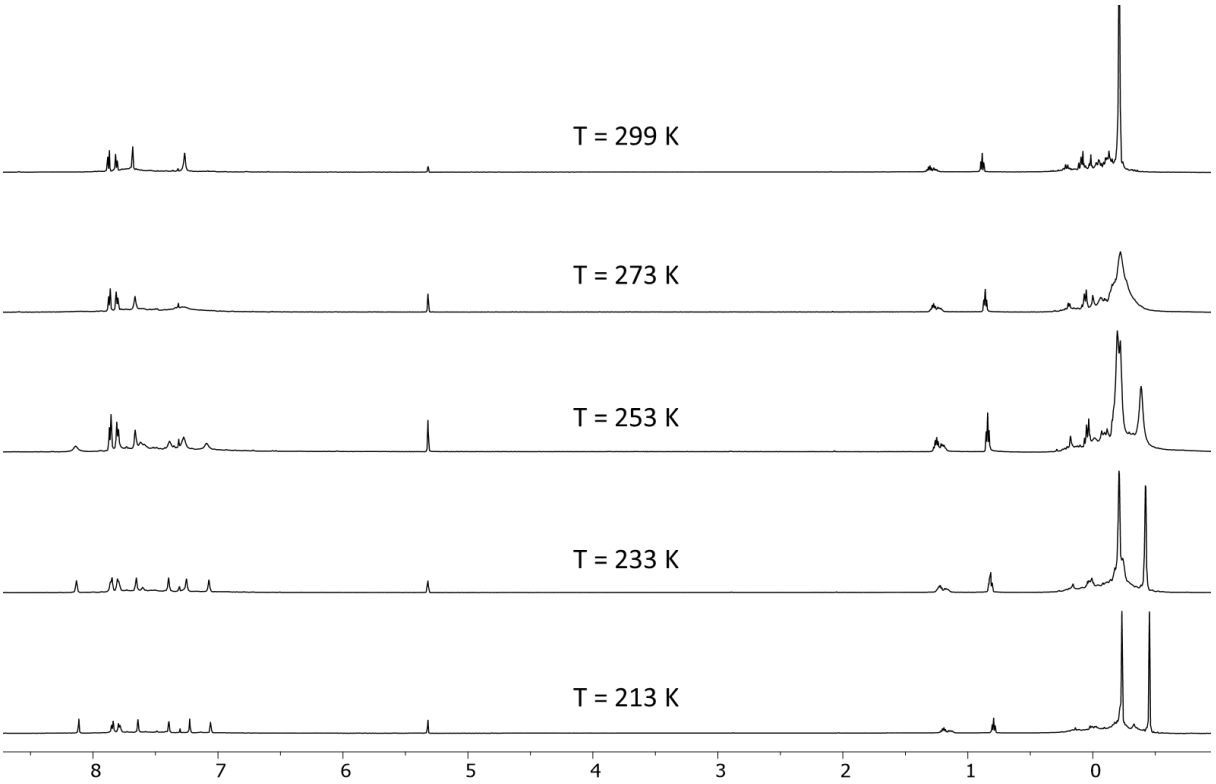


Figure S19: ^{1}H NMR (600 MHz, CD_2Cl_2) spectra of compound **13b** measured at various temperatures.

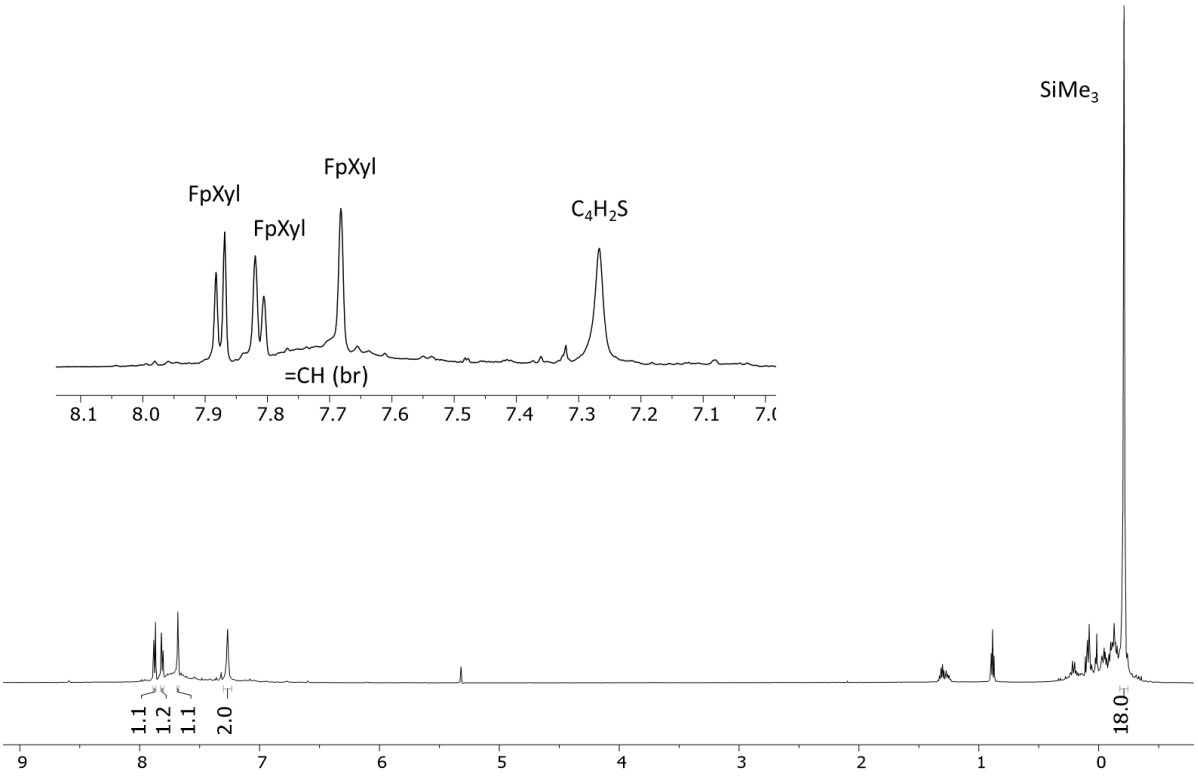


Figure S20: ^{1}H NMR (600 MHz, CD_2Cl_2, 299 K) spectrum of compound **13b**.

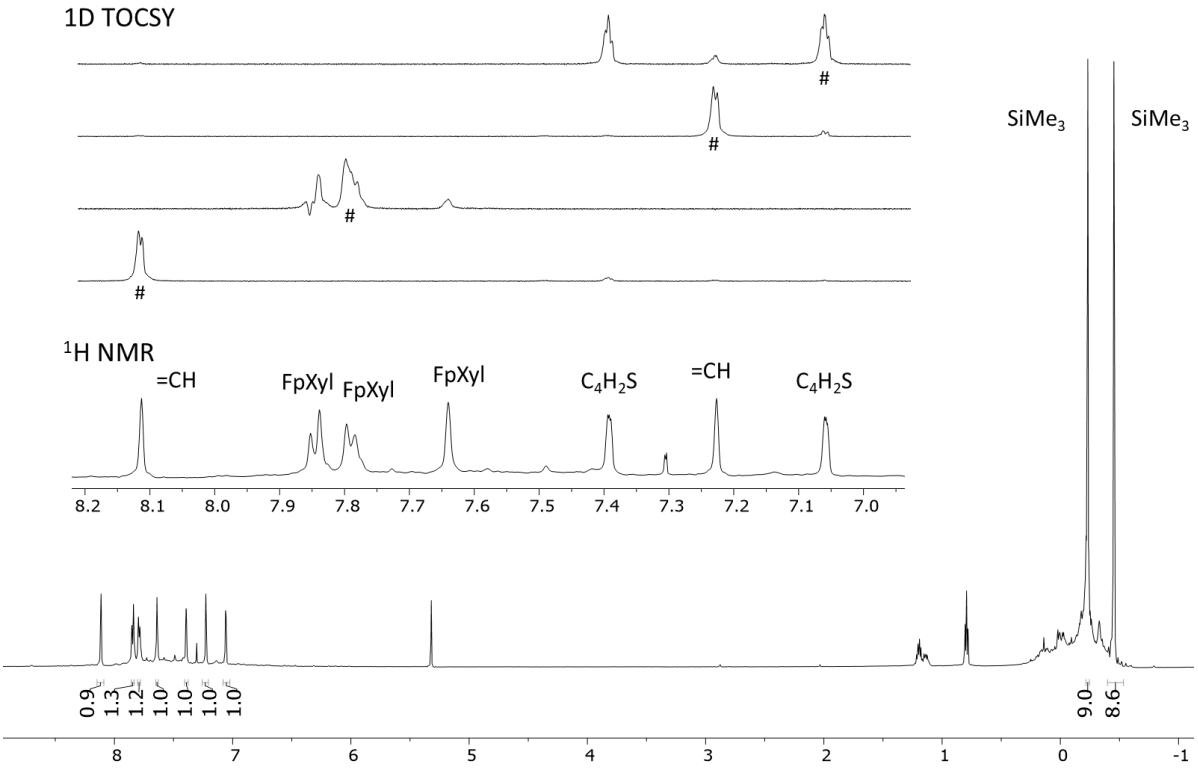


Figure S21: ^{1}H NMR (600 MHz, CD_2Cl_2, 213 K) spectrum of compound **13b** with excerpts from **1D TOCSY** (600 MHz, CD_2Cl_2, 213 K) spectra (# irradiation points).

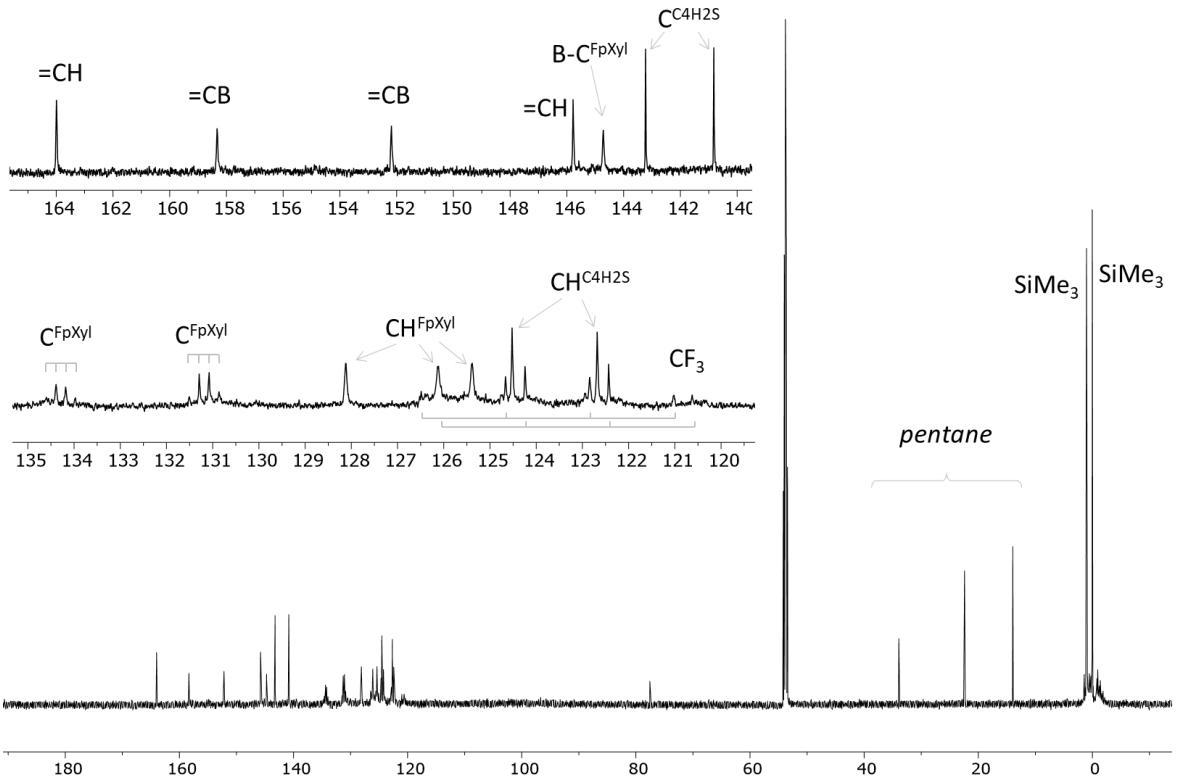


Figure S22: ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 213 K) spectrum of compound **13b**.

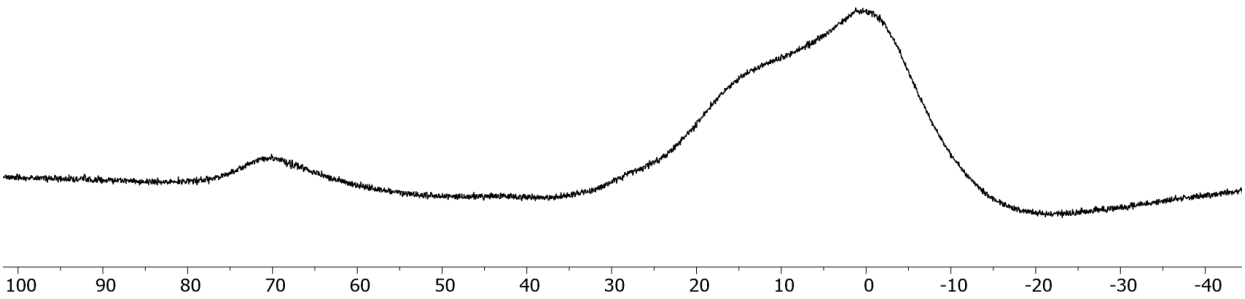


Figure S23: $^{11}B\{^{1}H\}$ NMR (192 MHz, CD_2Cl_2, 299 K) spectrum of compound **13b**.

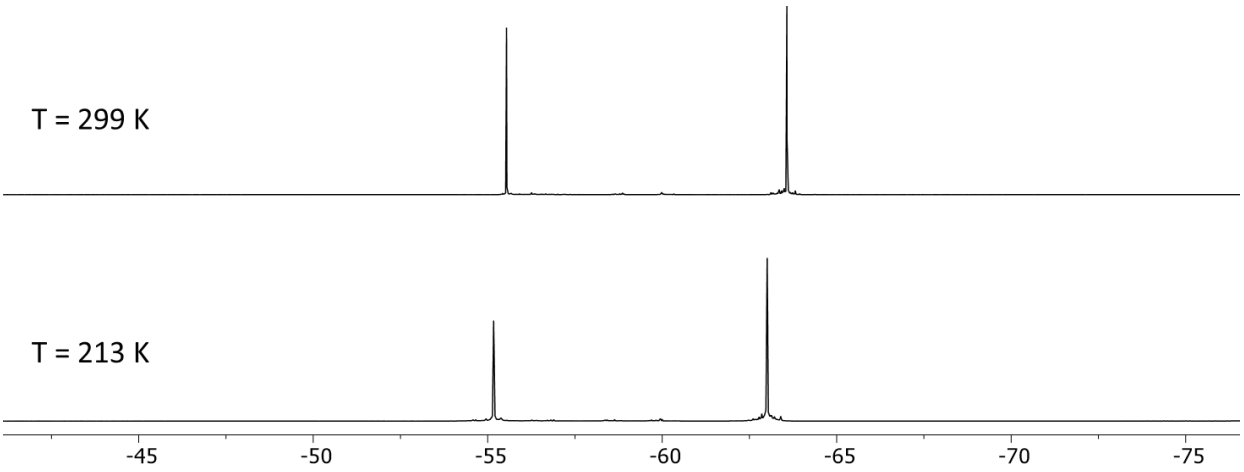


Figure S24: ^{19}F NMR (564 MHz, CD_2Cl_2) spectrum of compound **13b** measured at 299 K and 213 K.

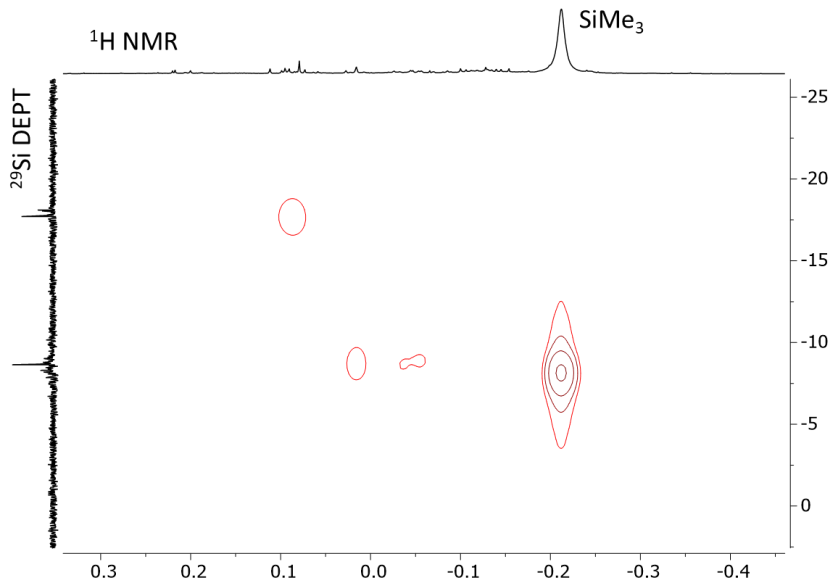
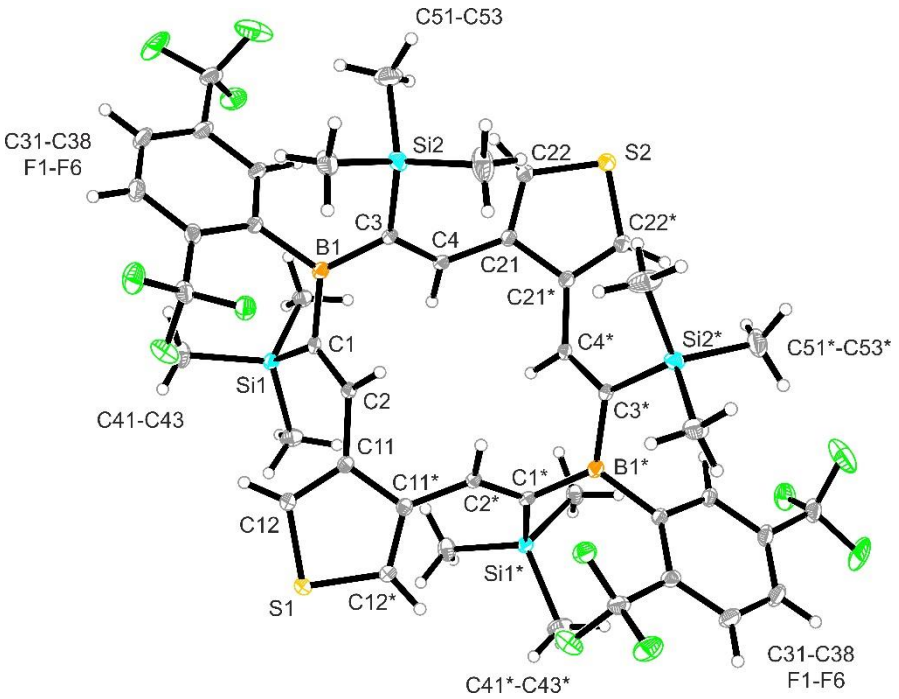


Figure S25: $^{1}H,^{29}Si$ gHSQC (600 MHz/119 MHz, CD_2Cl_2, 299 K) of compound **13b** [projections for F2: **^{1}H NMR** (600 MHz, CD_2Cl_2, 299 K) spectrum and F1: **$^{29}Si\{^{1}H\}$ DEPT** (119 MHz, CD_2Cl_2, 299 K) spectrum.

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **13b** in dichlormethane covered with heptane at room temperature.

X-ray crystal structure analysis of compound 13b (erk9869): A colorless needle-like specimen of $C_{44}H_{50}B_2F_{12}S_2Si_4$, approximate dimensions 0.048 mm x 0.053 mm x 0.118 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture PHOTON III Diffractometer system equipped with a micro focus tube Cu Ims (CuK_α, λ = 1.54178 Å) and a MX mirror monochromator. A total of 1123 frames were collected. The total exposure time was 15.55 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 48355 reflections to a maximum θ angle of 68.40° (0.83 Å resolution), of which 4557 were independent (average redundancy 10.611, completeness = 99.6%, R_{int} = 7.94%, R_{sig} = 3.54%) and 3785 (83.06%) were greater than $2\sigma(F^2)$. The final cell constants of a = 13.3555(3) Å, b = 31.1720(7) Å, c = 11.7335(3) Å, volume = 4884.9(2) $Å^3$, are based upon the refinement of the XYZ-centroids of 9970 reflections above 20 σ(I) with 5.670° < 2θ < 136.5°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.904. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7480 and 0.8850. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *Pnma*, with Z = 4 for the formula unit, $C_{44}H_{50}B_2F_{12}S_2Si_4$. The final anisotropic full-matrix least-squares refinement on F^2 with 298 variables converged at R1 = 4.13%, for the observed data and wR2 = 10.35% for all data. The goodness-of-fit was 1.056. The largest peak in the final difference electron density synthesis was 0.507 $e^-/Å^3$ and the largest hole was -0.336 $e^-/Å^3$ with an RMS deviation of 0.058 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.366 g/cm^3 and F(000), 2080 e^-. CCDC number: 2016813.



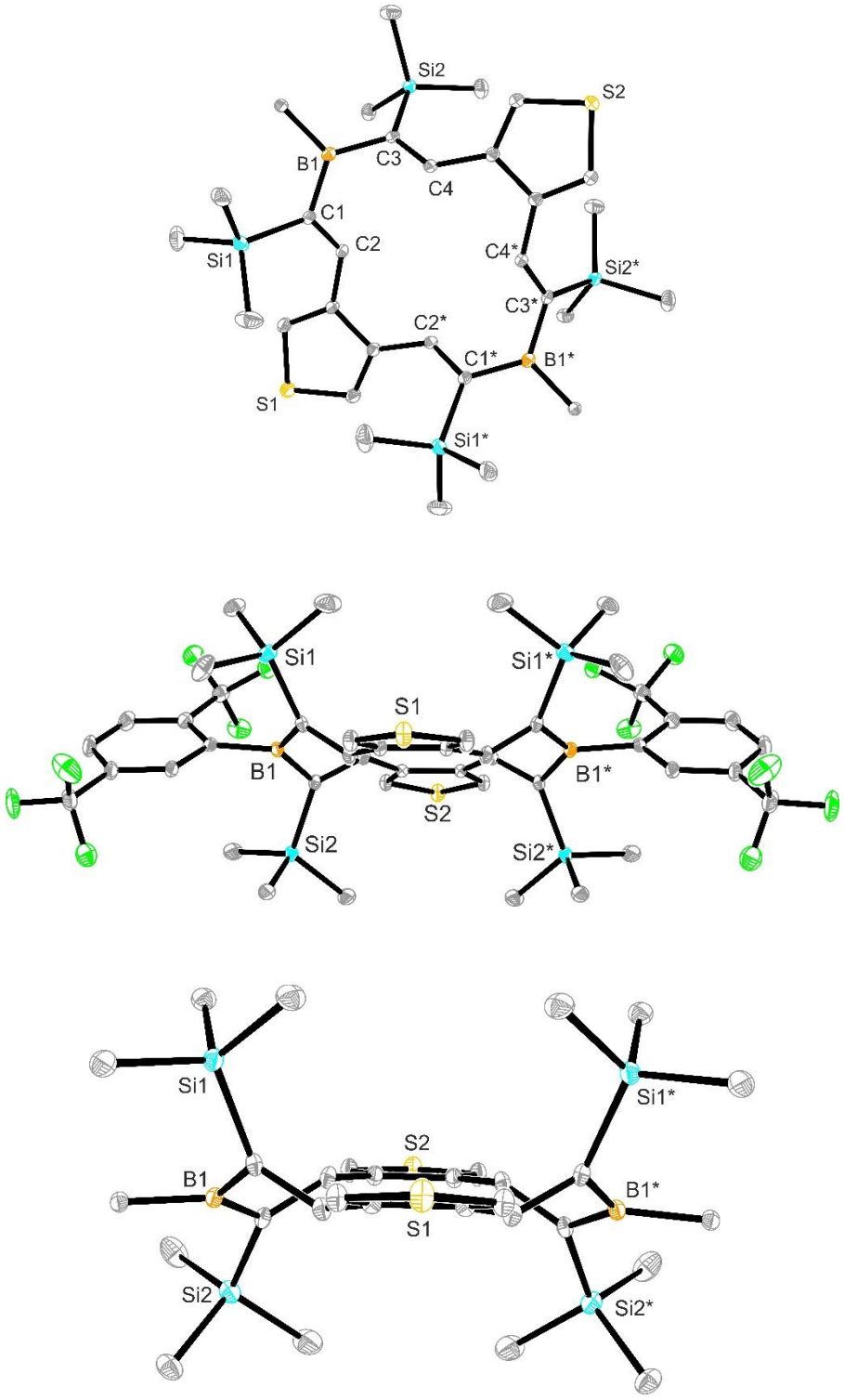
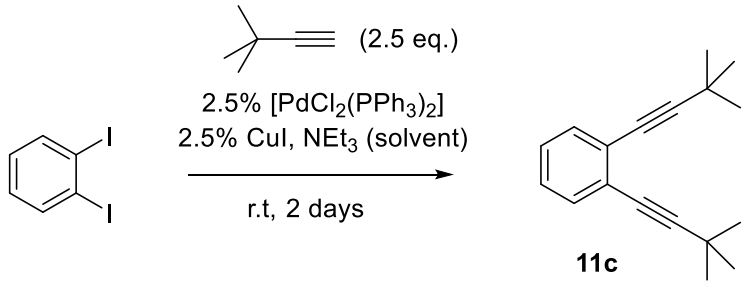


Figure S26: Crystal structure of compound **13b**. Thermal ellipsoids are set at 30% probability.

Synthesis of compound 11c [S1]



Scheme S7

1,2-Diiodobenzene (2.6 mL, 20 mmol), copper(I) iodide (188 mg, 1.0 mmol, 0.05 eq.) and $[PdCl_2(PPh_3)_2]$ (350 mg, 0.5 mmol, 0.025 eq.) were suspended in triethylamine (100 mL). Then the resulting yellow mixture was treated with 3,3-dimethylbut-1-yne (6.4 mL, 50 mmol, 2.5 eq.), which turned brown almost immediately and spontaneously warmed up itself after a few minutes. The mixture was allowed to react for 2 days at room temperature to give a deep brown suspension. Subsequently all volatiles were removed in vacuo and the obtained brown black solid was consecutively extracted with Et_2O (ca 200 mL in total). The combined extracts were passed through a short Celite pad. Then all volatiles were removed in vacuo to give a brown-yellow oil, which was purified by short column chromatography on silica using pentane as eluent. Compound **11c** was obtained as a yellow liquid (4.48 g, 18.8 mmol, 94% yield).

HRMS for $C_{18}H_{22}$ [M^+]: calculated 238.1716; found 238.1717.

^{1}H NMR (600 MHz, $CDCl_3$, 299 K): δ = [7.36, 7.15](each m, each 1H, CH^{Ar}), 1.35 (s, 9H, CMe_3).

^{1}H NMR (600 MHz, d_8-toluene, 299 K): δ = 7.25 (m, 1H, CH^{Ar}), 6.74 (m, 1H, CH^{Ar}), 1.27 (s, 9H, CMe_3).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 299 K): δ = 131.9 (CH^{Ar}), 127.0 (CH^{Ar}), 126.1 (C^{Ar}), 101.9 (≡*C*-CMe_3), 78.1 (*C*≡), 31.1 (C*Me*$_3$), 28.1 (*C*Me_3)

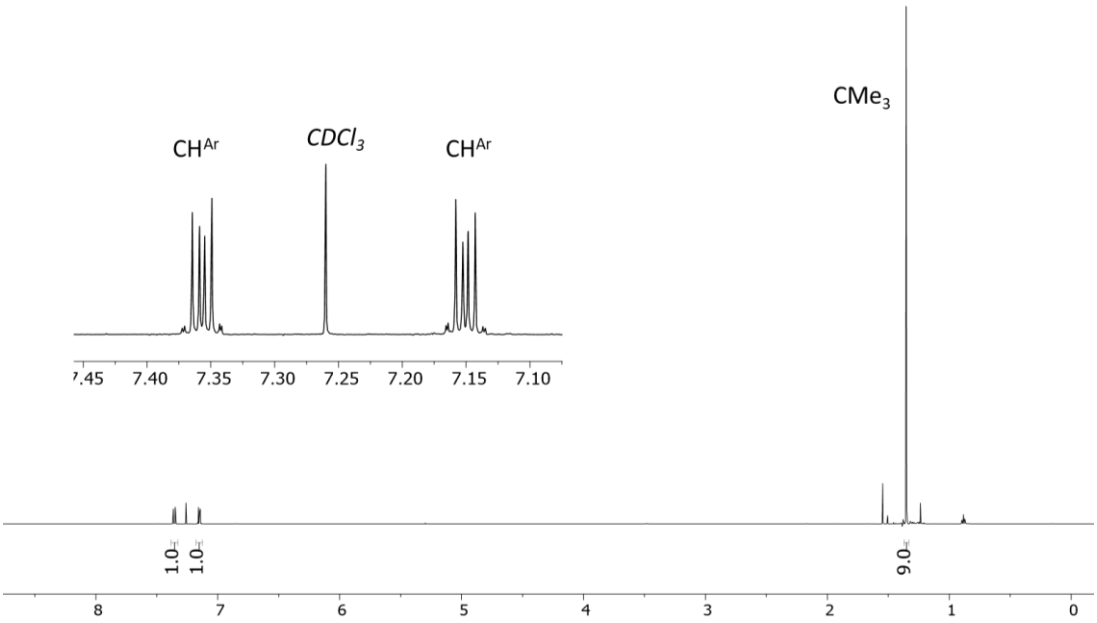


Figure S27: ^{1}H NMR (600 MHz, $CDCl_3$, 299 K) spectrum of compound **11c**.

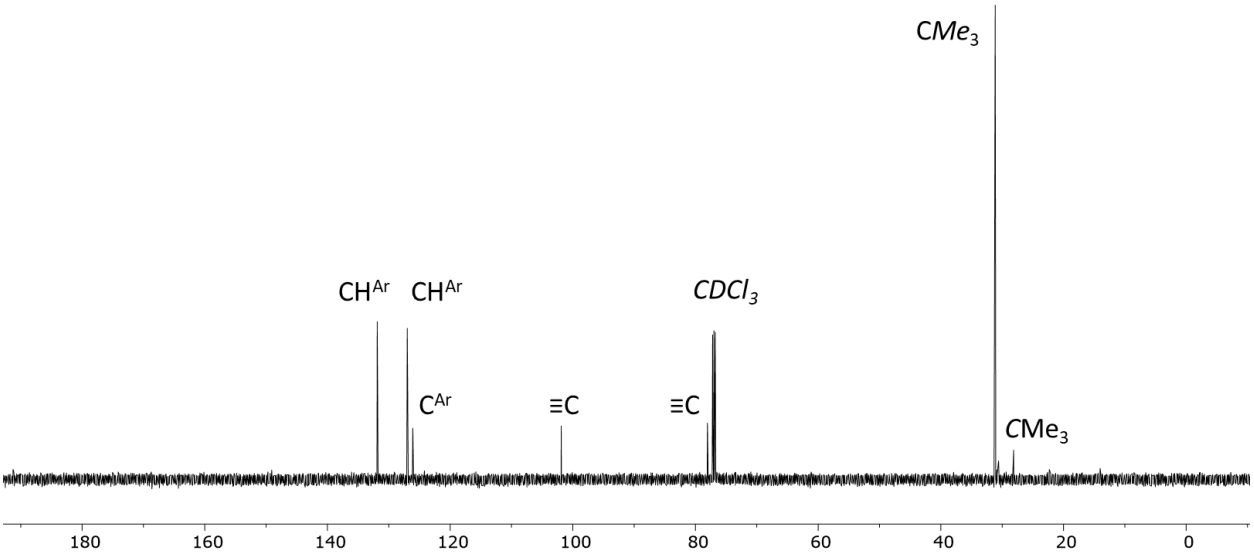
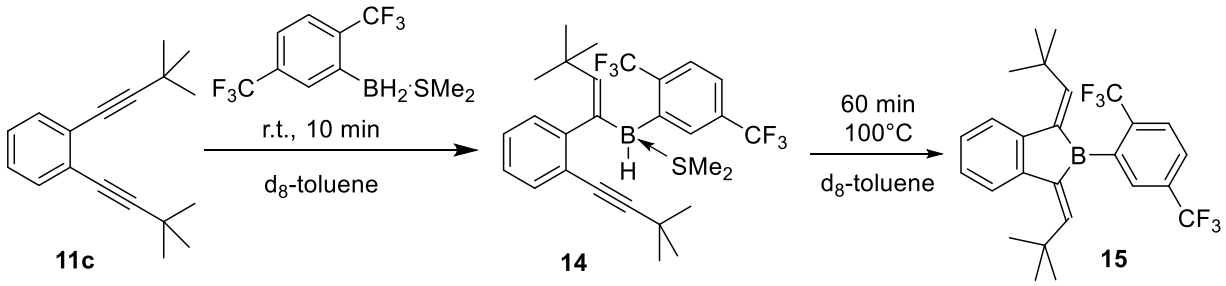


Figure S28: $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2, 299 K) spectrum of compound **11c**.

In situ monitoring of the generation of compounds 14 and 15 (NMR scale)



Scheme S8

Bis-acetylene **11c** (23.8 mg, 0.1 mmol) and borane **6**·SMe_2 (28.8 mg, 0.1 mmol) were combined in d_8-toluene (0.6 mL) and the mixture was placed in a NMR Young tube. After 10 minutes NMR experiments were recorded, revealing complete consumption of the starting material and formation of compound **14** with some unidentified impurities (Step 1). Attempts to isolate **14** were not successful, therefore compound **14** was characterized by in situ NMR experiments (see below, Step 1). Subsequently, the NMR tube was placed in an oil bath preheated to 100 °C. After 60 minutes the reaction was characterized by NMR experiments (Step 2).

Characterization of compound **14** (Step 1).

^{1}H NMR (600 MHz, d_8-toluene, 299 K): δ = [7.43 (d, $^{3}J_{HH}$ = 8.3 Hz), 7.34 (s), 7.12 (d, $^{3}J_{HH}$ = 8.3 Hz)] (each 1H, FpXyl), [7.28, 6.83, 6.81, 6.64](each m, each 1H, C_6H_4), 5.72 (s, 1H, =CH), 3.45 ($\nu_{1/2} \approx 140$ Hz, 1H, BH), 1.35 ($\nu_{1/2} \approx 4$ Hz, 6H, SMe_2), 1.19 (s, 9H, ≡C-CMe_3), 0.94 (s, 9H, =CH-CMe_3)

^{13}C{^{1}H} NMR (151 MHz, d_8-toluene, 299 K): δ = [148.1 (br, B-C), 138.5 (q, $^{2}J_{FC}$ = 29.7 Hz, *C*-CF_3), 132.4 (q, $^{3}J_{FC}$ = 3.7 Hz, CH), 131.9 (q, $^{2}J_{FC}$ = 31.6 Hz, *C*-CF_3), 125.6 (q, $^{3}J_{FC}$ = 5.8 Hz, CH), 122.8 (q, $^{3}J_{FC}$ = 4.0 Hz, CH), n.o. (CF_3)](FpXyl), [148.2 (C^{C6H4}), 133.0 (CH^{C6H4}), 129.2 (CH^{C6H4}), 126.7 (CH^{C6H4}), 125.1 (CH^{C6H4}), 123.5 (C^{C6H4})], [148.6 (=CH), 142.6 (br, =C-B), 36.0 (=CH-*C*Me_3), 31.0 (=CH-C*Me*$_3$)], [100.4 (≡*C*-CMe_3), 80.8 (*C*≡), 31.16 (≡C-C*Me*$_3$), 28.2 (≡C-*C*Me_3)], 20.7 (br, SMe_2).

^{11}B NMR (192 MHz, d_8-toluene, 299 K): δ = 3.4 ($\nu_{1/2} \approx 400$ Hz)

^{11}B{^{1}H} NMR (192 MHz, d_8-toluene, 299 K): δ = 3.4 ($\nu_{1/2} \approx 400$ Hz)

^{19}F NMR (564 MHz, d_8-toluene, 299 K): δ = -57.6 (d, *J* = 8.2 Hz, 1F), -62.7 (s, 1F)

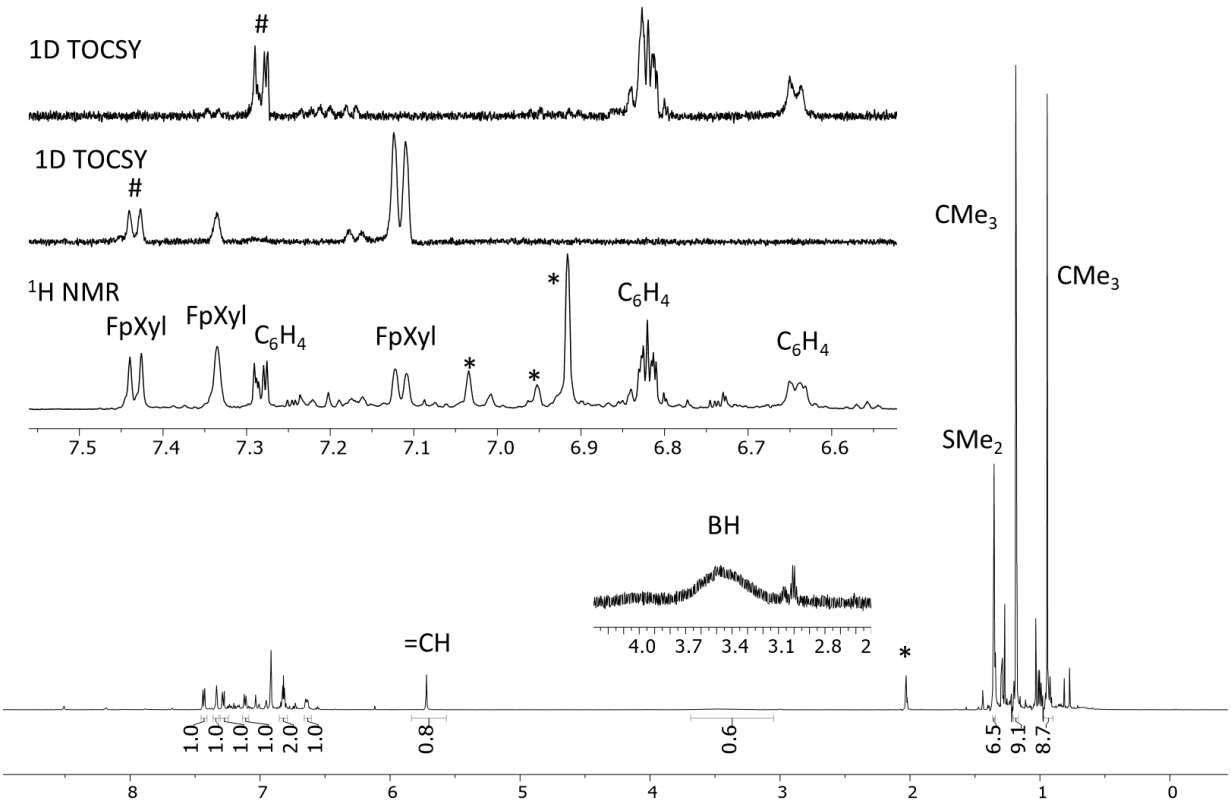


Figure S29: ^{1}H NMR (600 MHz, d_8-toluene*, 299 K) spectrum and excerpts from **1D TOCSY** (600 MHz, d_8-toluene, 299 K) of the reaction mixture (Step 1) (# irradiation points).

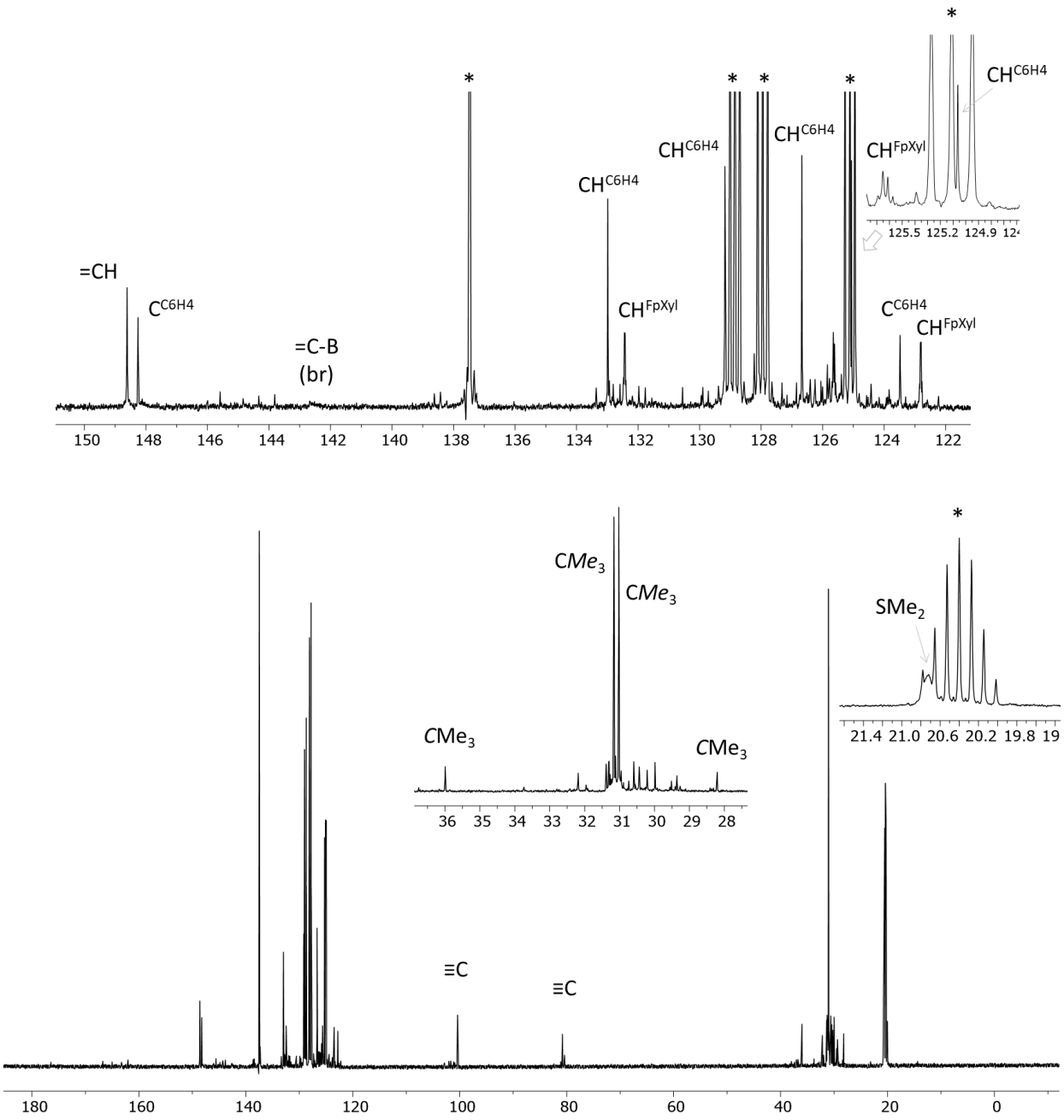


Figure S30: $^{13}C\{^1H\}$ NMR (151 MHz, d_8-toluene*, 299 K) spectrum of reaction mixture (Step 1).

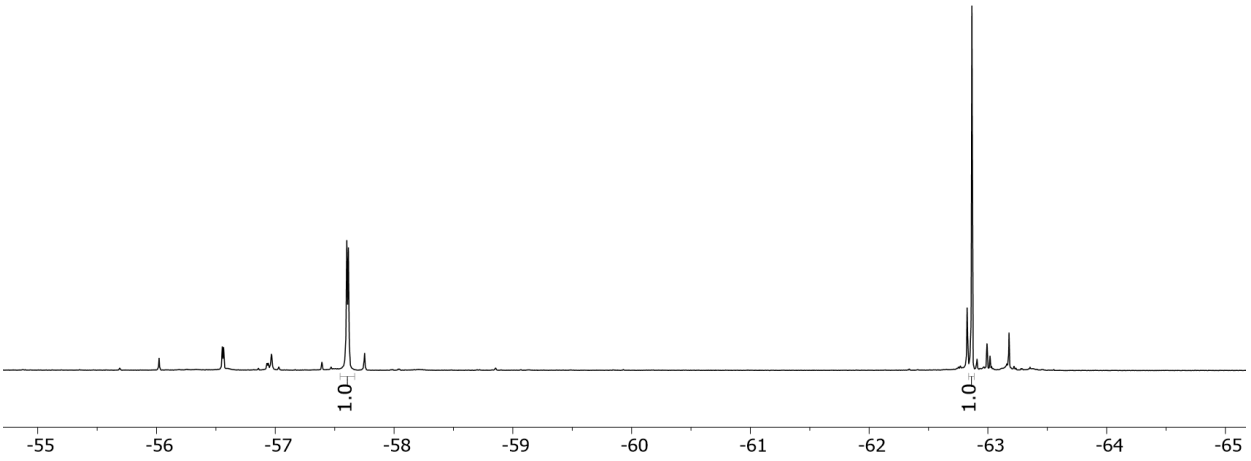


Figure S31: ^{19}F NMR (564 MHz, d_8-toluene, 299 K) spectrum of reaction mixture (Step 1).

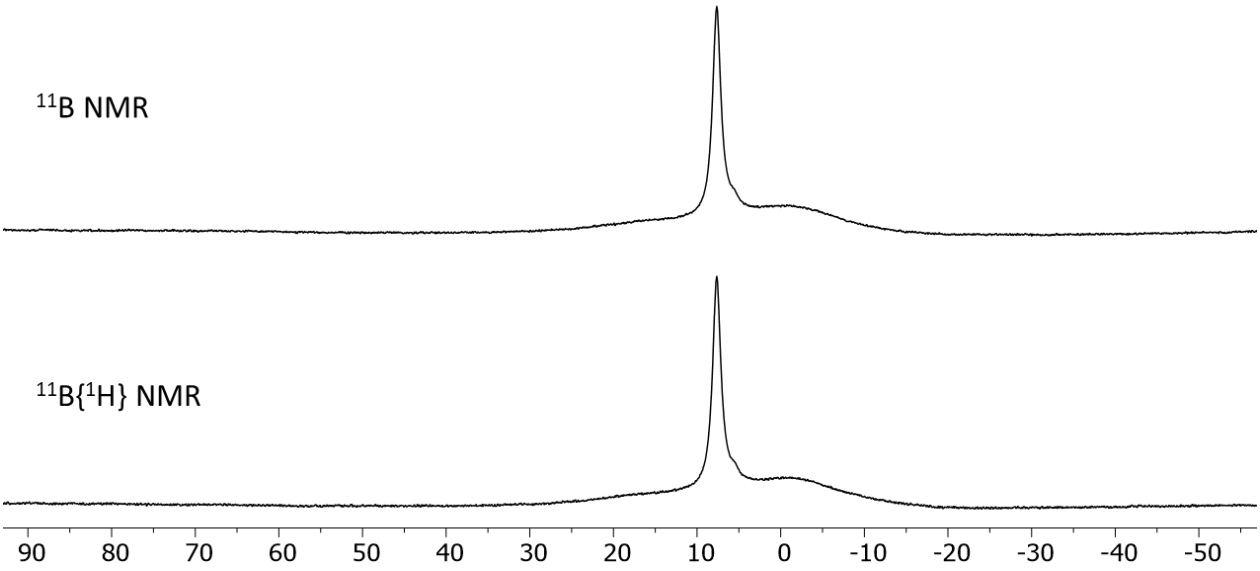


Figure S32: ^{11}B{^{1}H} and **^{11}B NMR** (192 MHz, d_8-toluene, 299 K) spectra of the reaction mixture (Step 1).

Characterization of compound **15** (Step 2)

^{1}H NMR (600 MHz, d_8-toluene, 299 K): δ = [7.83, 7.08](each m, 2H, C_6H_4), [7.53 (s), 7.27 (d, $^{3}J_{HH}$= 8.4 Hz), 7.14 (d, $^{3}J_{HH}$= 8.4 Hz)](each 1H, FpXyl), 6.42 (s, 2H, =CH), 1.11 (s, 18H, CMe_3)

^{13}C{^{1}H} NMR (151 MHz, d_8-toluene, 299 K): δ = [162.1 (=CH), 145.9 (br, =CB), 34.1 (CMe_3), 29.3 (CMe_3)], [144.7 (C),128.7 (CH), 127.3 (CH)](C_6H_4), [140.3 (br, B-C), 135.9 (qm, $^{2}J_{FC}$ ~ 31 Hz, C-CF_3), 132.3 (qm, $^{2}J_{FC}$ ~ 33 Hz, C-CF_3), n.o. (CF_3), 128.1 (q, $^{3}J_{FC}$ = 3.7 Hz, CH), 126.4 (q, $^{3}J_{FC}$ = 4.0 Hz, CH), 125.1 (q, $^{3}J_{FC}$ = 3.7 Hz, CH)](FpXyl),

^{11}B{^{1}H} NMR (192 MHz, d_8-toluene, 299 K): δ = 68.7 ($\nu_{1/2}$ ≈ 1500 Hz)

^{11}B NMR (192 MHz, d_8-toluene, 299 K): δ = 68.7 ($\nu_{1/2}$ ≈ 1500 Hz)

^{19}F NMR (564 MHz, d_8-toluene, 299 K): δ = -57.5 (s, 1F, CF_3), -63.0 (s, 1F, CF_3)

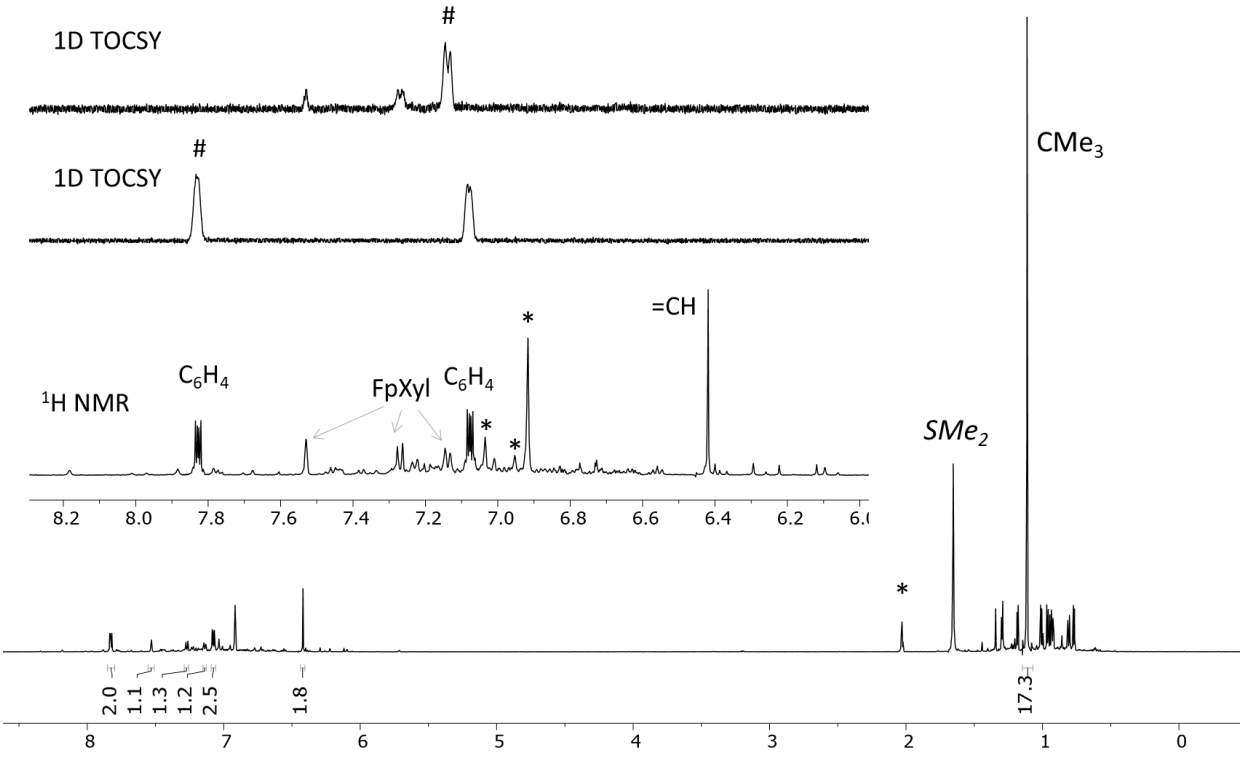


Figure S33: ^{1}H NMR (600 MHz, d_8-toluene*, 299 K) spectrum and excerpts from **1D TOCSY** (600 MHz, d_8-toluene, 299 K) spectra of the reaction mixture after 60 minutes of heating at 100°C (Step 2). # TOCSY irradiation points.

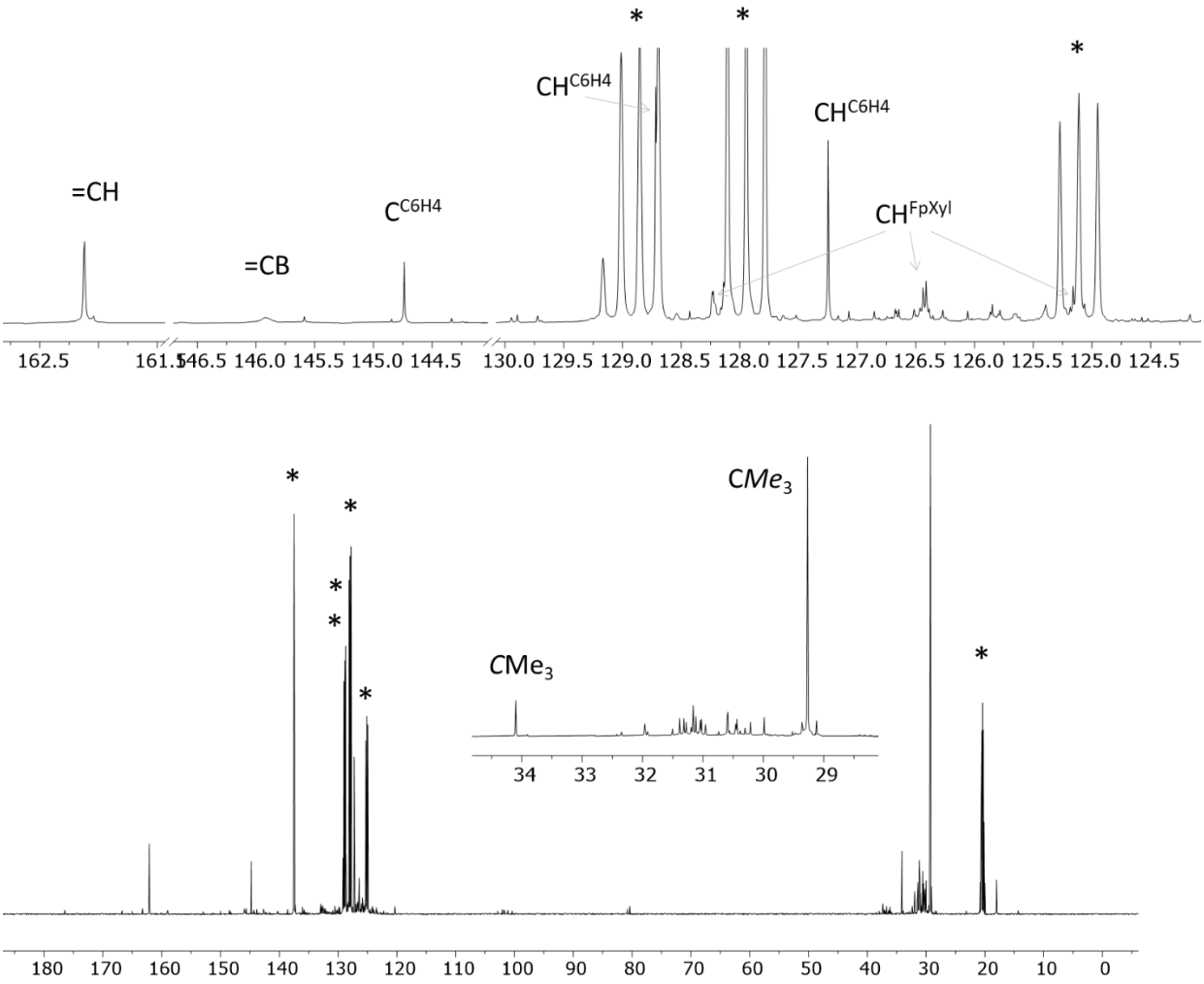


Figure S34: $^{13}C\{^{1}H\}$ NMR (151 MHz, d_8-toluene*, 299 K) spectrum of the reaction mixture after 60 minutes of heating at 100°C (Step 2).

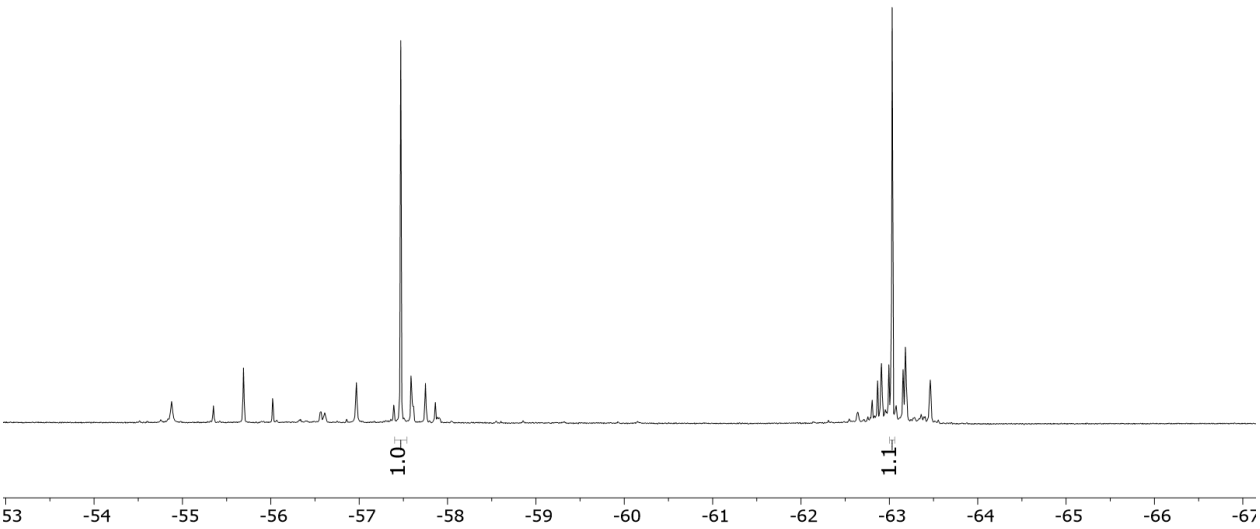


Figure S35: ^{19}F NMR (564 MHz, d_8-toluene, 299 K) spectrum of the reaction mixture after 60 minutes of heating at 100°C (Step 2).

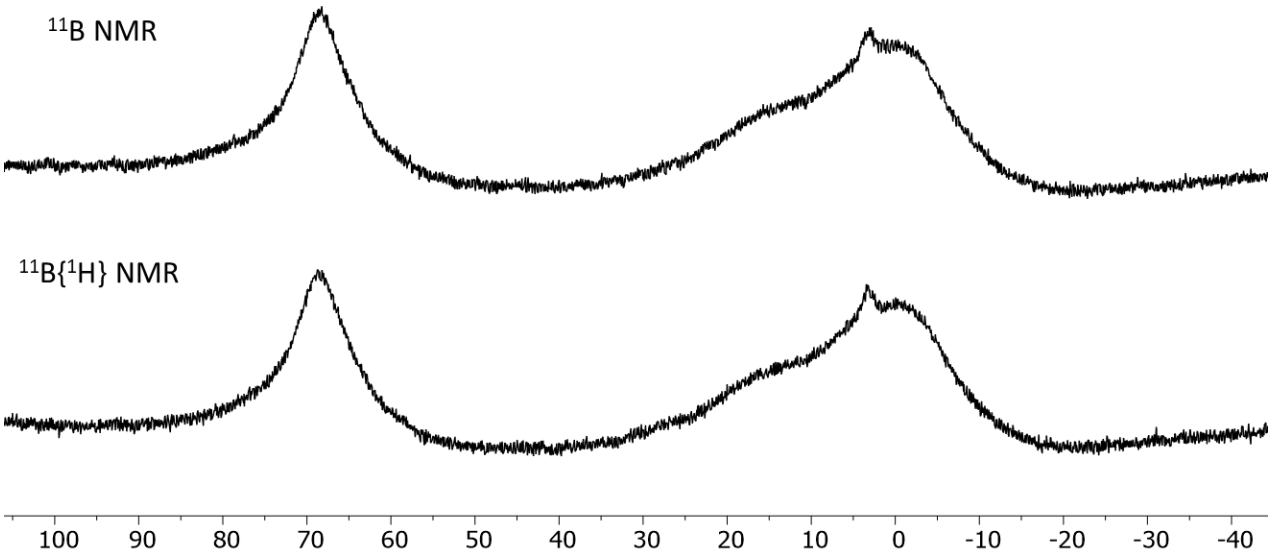
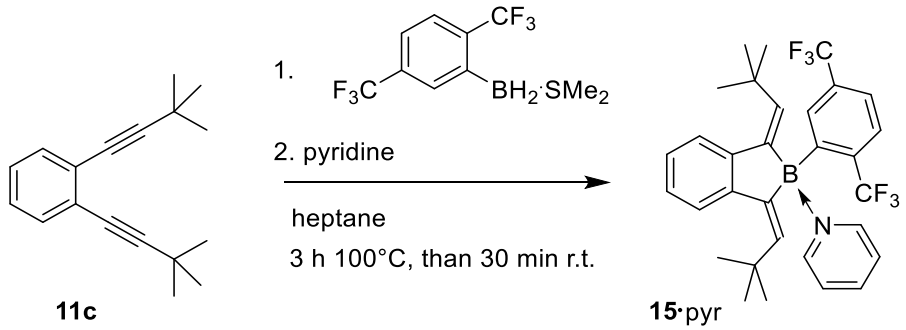


Figure S36: ^{11}B{^{1}H} and **^{11}B NMR** (192 MHz, d_8-toluene, 299 K) spectra of the reaction mixture after 60 minutes of heating at 100°C (Step 2).

Synthesis of the adduct 15·pyr



Scheme S9

Bis-acetylene **11c** (119 mg, 0.5 mmol) and borane **6**·SMe_2 (144 mg, 0.5 mmol) were combined in toluene (5 mL). Then the flask was sealed and placed in an oil bath preheated to 100 °C. After one hour of stirring, the reaction mixture was cooled to room temperature and a solution of pyridine (44 mg, 0.55 mmol) in toluene (2 mL) was added. The mixture was stirred for 15 minutes at room temperature and subsequently all volatiles were removed in vacuo. The residue was washed with cold pentane (3x 3 mL) and dried in vacuo. Compound **15**·pyr was obtained as a white solid (222 mg, 0.42 mmol, 84% yield).

Melting point: 137.6 °C

HRMS for $C_{26}H_{28}BF_6O$ [$(M - py + OH)^-$]: calculated 481.2137; found 481.2136.

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = [8.81 (br, 2H, *o*), 8.01 (m, 1H, *p*), 7.53 (m, 2H, *m*)](py), [7.71 (d, $^3J_{HH}$ = 8.3 Hz), 7.49 (d, $^3J_{HH}$ = 8.3 Hz), 7.24 (s)](each 1H, FpXyl), [7.50 (m), 6.98 (m)](each 2H, C_6H_4), 5.22 (s, 2H, =CH), 1.21 (s, 18H, CMe_3).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = [147.4 (*o*), 141.42 (*p*), 125.3 (*m*)](py), [150.8 (br, B-C), 137.9 (q, $^2J_{FC}$ = 30.0 Hz, *C*-CF_3), 133.3 (q, $^3J_{FC}$ = 3.9 Hz, CH), 131.4 (q, $^3J_{FC}$ = 31.1 Hz, *C*-CF_3), 127.4 (q, $^3J_{FC}$ = 5.6 Hz, CH), 125.3 (q, $^1J_{FC}$ = 275.8 Hz, CF_3), 124.7 (q, $^1J_{FC}$ = 272.8 Hz, CF_3), 122.8 (q, $^3J_{FC}$ = 3.7 Hz, CH)](FpXyl), [146.8 (C), 128.2 (CH), 125.5 (CH)](C_6H_4), [152.8 (br, =CB), 141.36 (=CH), 33.8 (*C*Me_3), 30.8 (C*Me*$_3$)]

^{11}B NMR (192 MHz, CD_2Cl_2, 299 K): δ = 7.7 ($\nu_{1/2} \approx 250$ Hz)

^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = 7.7 ($\nu_{1/2} \approx 250$ Hz)

^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = -55.5 (s, 1F, CF_3), -63.5 (s, 1F, CF_3)

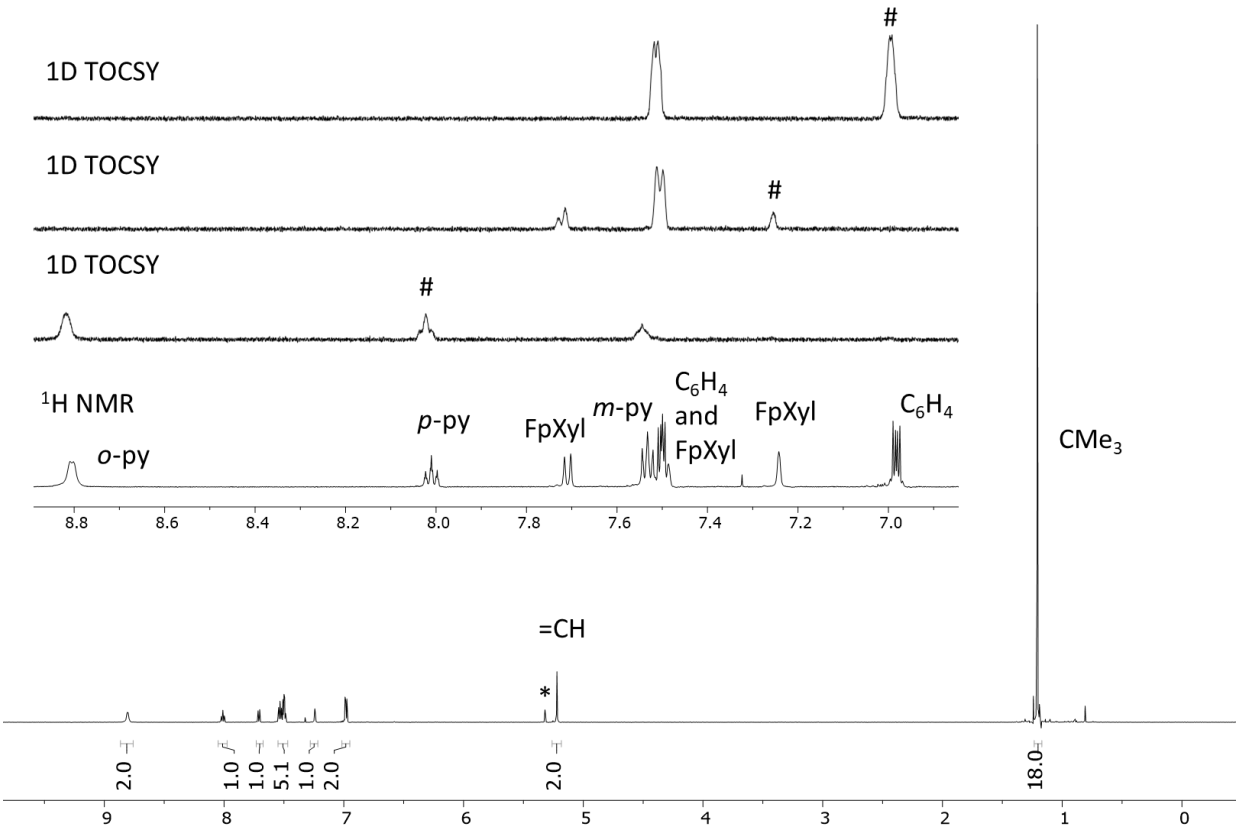


Figure S37: ^{1}H NMR (600 MHz, CD_2Cl_2*, 299 K) spectrum and excerpts from **1D TOCSY** (600 MHz, CD_2Cl_2, 299 K) of compound **15**·pyr. # TOCSY irradiation points.

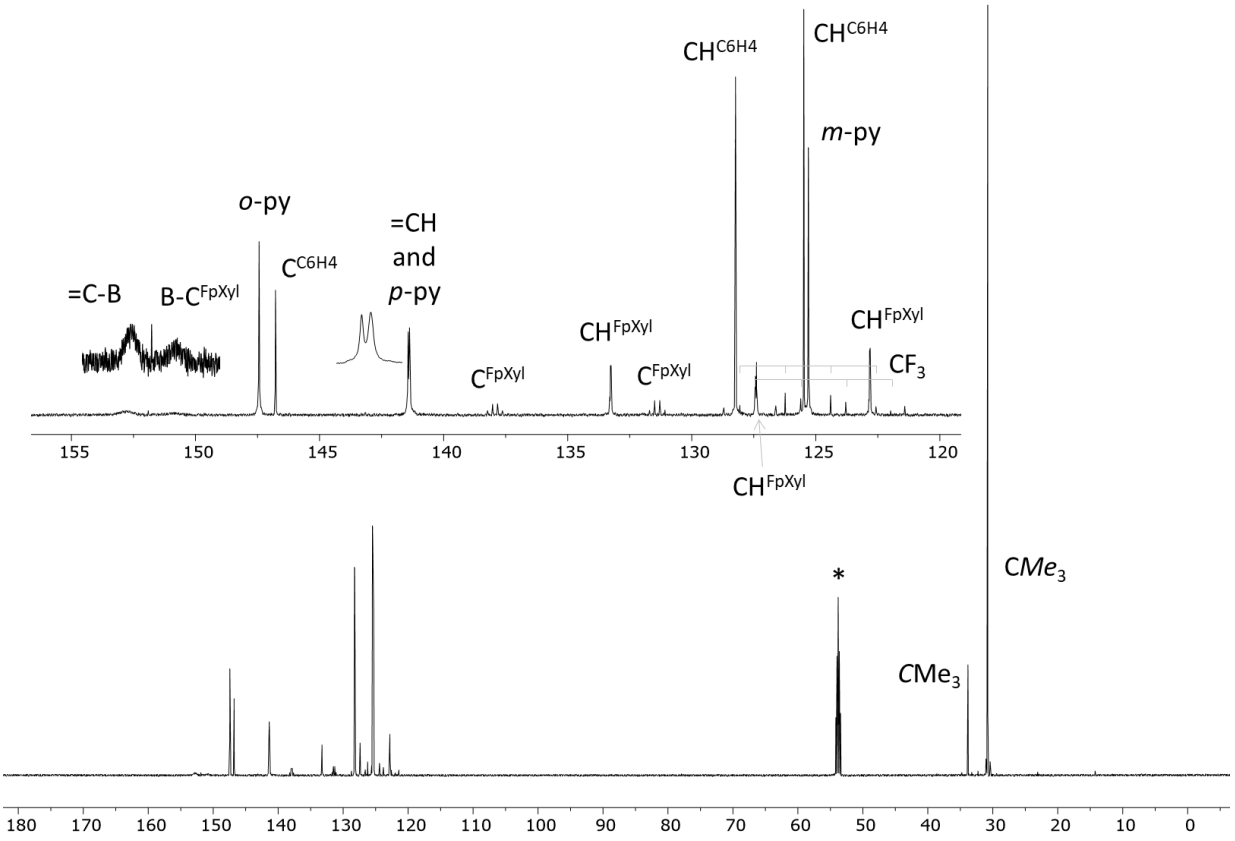


Figure S38: $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2*, 299 K) spectrum of compound **15**·pyr.

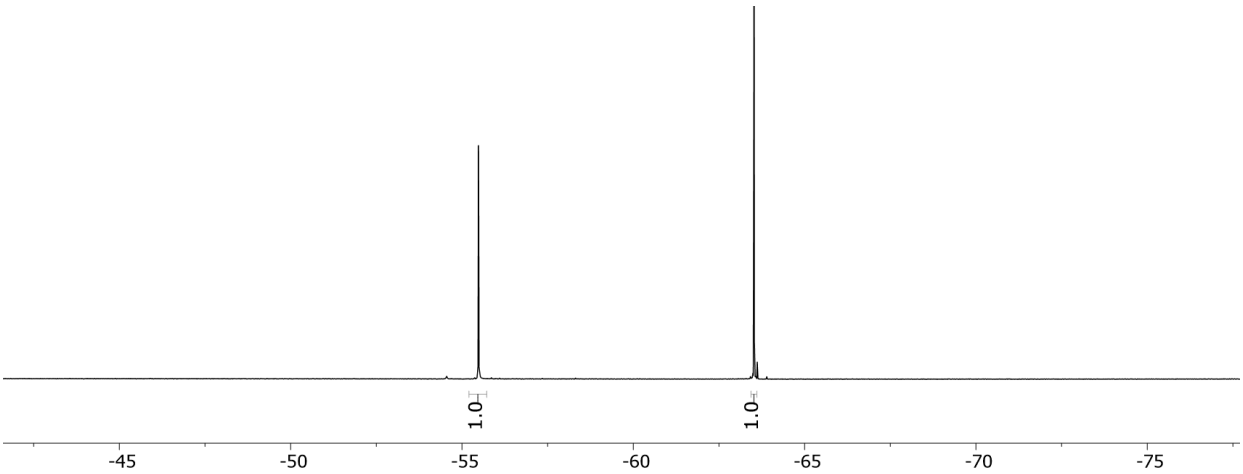


Figure S39: ^{19}F NMR (564 MHz, CD_2Cl_2, 299 K) spectrum of compound **15**·pyr.

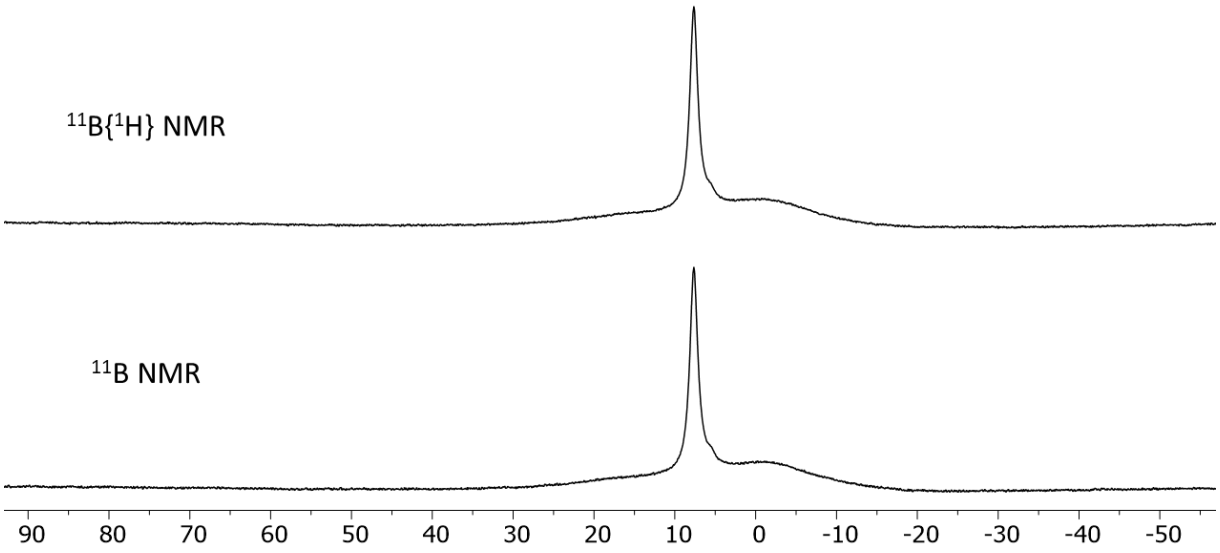


Figure S40: $^{11}B\{^{1}H\}$ and **^{11}B NMR** (192 MHz, CD_2Cl_2, 299 K) spectra of compound **15**·pyr.

Crystals suitable for the X-ray crystal structure analysis were obtained from by slow diffusion of pentane into a solution of compound **15**·pyr in dichloromethane at room temperature.

X-ray crystal structure analysis of compound 15·pyr (erk9814): A colorless plate-like specimen of $C_{31}H_{32}BF_6N$, approximate dimensions 0.060 mm x 0.120 mm x 0.140 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker APEX II diffractometer system equipped with a fine-focus sealed tube Cu sealed tube (CuKα, λ = 1.54178 Å) and a graphite monochromator. A total of 1639 frames were collected. The total exposure time was 18.86 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 36782 reflections to a maximum θ angle of 66.68° (0.84 Å resolution), of which 4778 were independent (average redundancy 7.698, completeness = 98.7%, R_{int} = 13.20%, R_{sig} = 8.37%) and 3239 (67.79%) were greater than $2\sigma(F^2)$. The final cell constants of a = 8.7063(4) Å, b = 17.2992(10) Å, c = 18.1817(9) Å, β = 93.565(3)°, volume = 2733.1(2) $Å^3$, are based upon the refinement of the XYZ-centroids of 3782 reflections above 20 σ(I) with 7.059° < 2θ < 133.1°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.806. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8870 and 0.9490. 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, $C_{31}H_{32}BF_6N$. The final anisotropic full-matrix least-squares refinement on F^2 with 359 variables converged at R1 = 6.30%, for the observed data and wR2 = 15.99% for all data. The goodness-of-fit was 1.033. The largest peak in the final difference electron density synthesis was 0.477 $e^-/Å^3$ and the largest hole was -0.247 $e^-/Å^3$ with an RMS deviation of 0.068 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.321 g/cm^3 and F(000), 1136 e^-. CCDC number: 2016814.

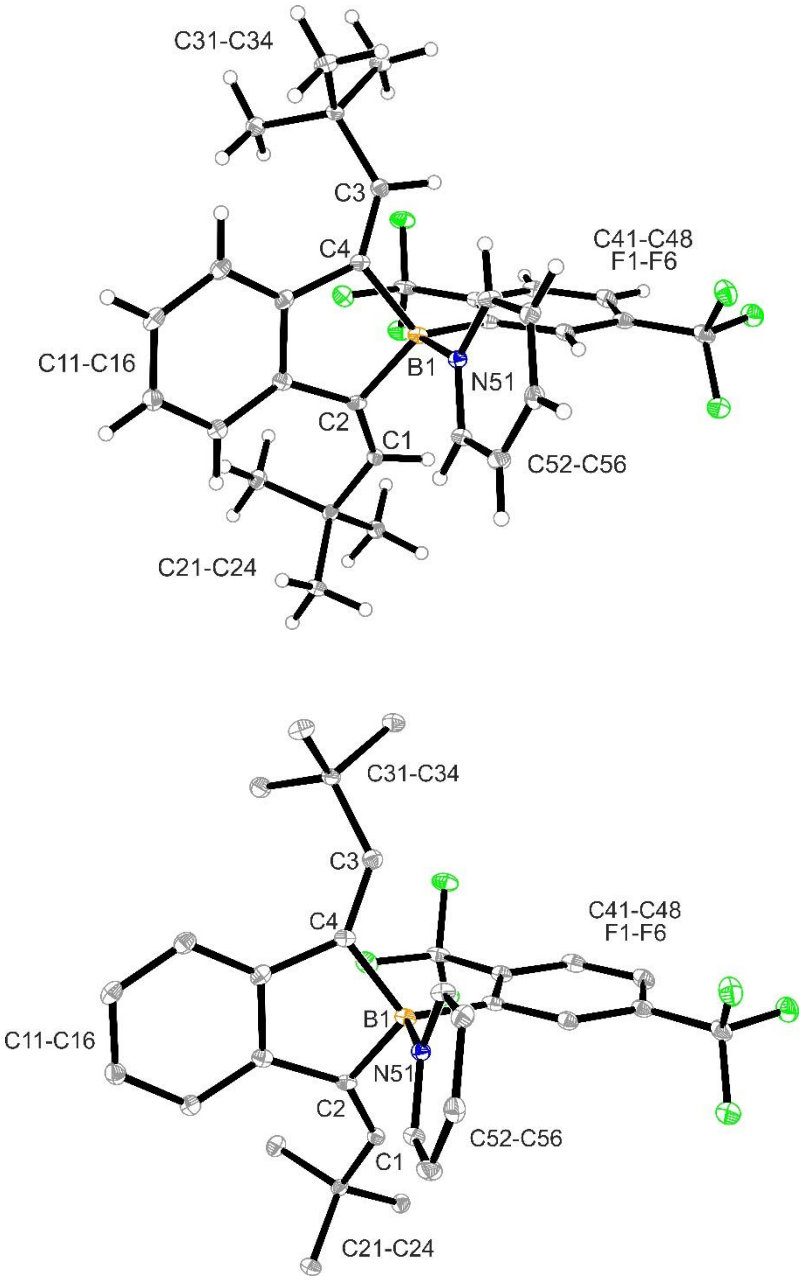
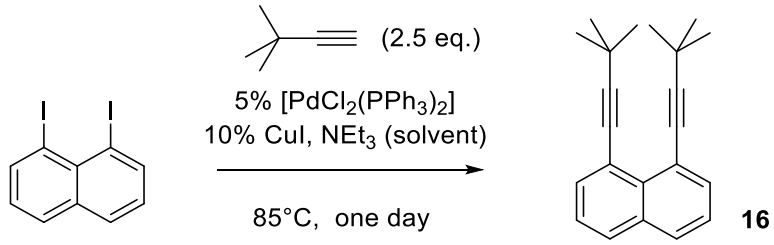


Figure S41: Crystal structure of compound **15**·pyr. Thermal ellipsoids are set at 15% probability.

Synthesis of the bis-acetylene 16



Scheme S10

1,8-Diiodonaphthalene (3.80 g, 10 mmol), copper(I) iodide (188 mg, 1.0 mmol, 0.10 eq.) and $[PdCl_2(PPh_3)_2]$ (350 mg, 0.5 mmol, 0.05 eq.) were suspended in triethylamine (50 mL). The resulting yellow mixture was treated with 3,3-dimethylbut-1-yne (3.1 mL, 25 mmol, 2.5 eq.). The mixture gradually turned brown. The mixture was allowed to react for one day at 85°C to give a dark green-brown suspension. After all volatiles were removed in vacuo, the residue was consecutively extracted with Et_2O (ca 150 mL in total) and the extracts were passed through a short Celite pad. Then all volatiles were removed in vacuo to give a dark brown oil which was purified by column chromatography on silica using pentane as eluent. An orange band was eluted first containing mainly 1-iodo-8-(3,3-dimethylbut-1-ynyl)naphthalene followed by a deep purple band containing unidentified compounds. After increasing polarity to pentane/CH_2Cl_2 mixture (10/1), the deep orange band corresponding to compound **16** was obtained. Removal of all volatiles provided a brown oil (1.10 g, 3.8 mmol, 38 % yield).

HRMS for $C_{22}H_{24}$ [M^+]: calculated 288.1872; found 288.1873

^{1}H NMR (600 MHz, $CDCl_3$, 299 K): δ = 7.71 (d, $^3J_{HH}$ = 7.6 Hz, 2H, CH^{Ar}), 7.35 (t, $^3J_{HH}$ = 7.6 Hz, 1H, CH^{Ar}), 1.44 (s, 9H, CMe_3).

^{1}H NMR (600 MHz, d_8-toluene, 299 K): δ = 7.62 (dd, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, CH^{Ar}), 7.30 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, CH^{Ar}), 6.96 (dd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 7.2 Hz, 1H, CH^{Ar}), 1.35 (s, 9H, CMe_3).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 299 K): δ = [135.8, 128.6, 125.2](CH^{Ar}), [134.2, 130.8, 121.8](C^{Ar}), 106.1 (≡CtBu), 80.2 (≡C), 31.0 (C*Me*$_3$), 28.7 (*C*Me_3)

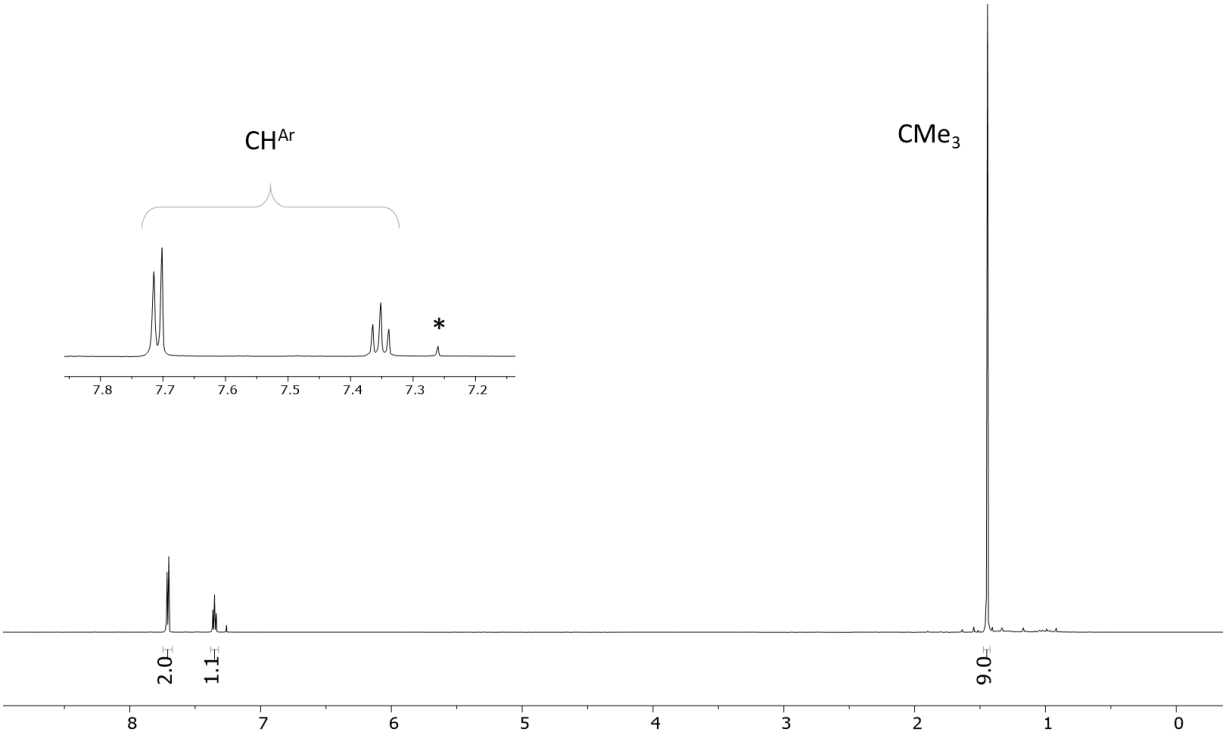


Figure S42: ^{1}H NMR (600 MHz, $CDCl_3$*, 299 K) spectrum of compound **16**.

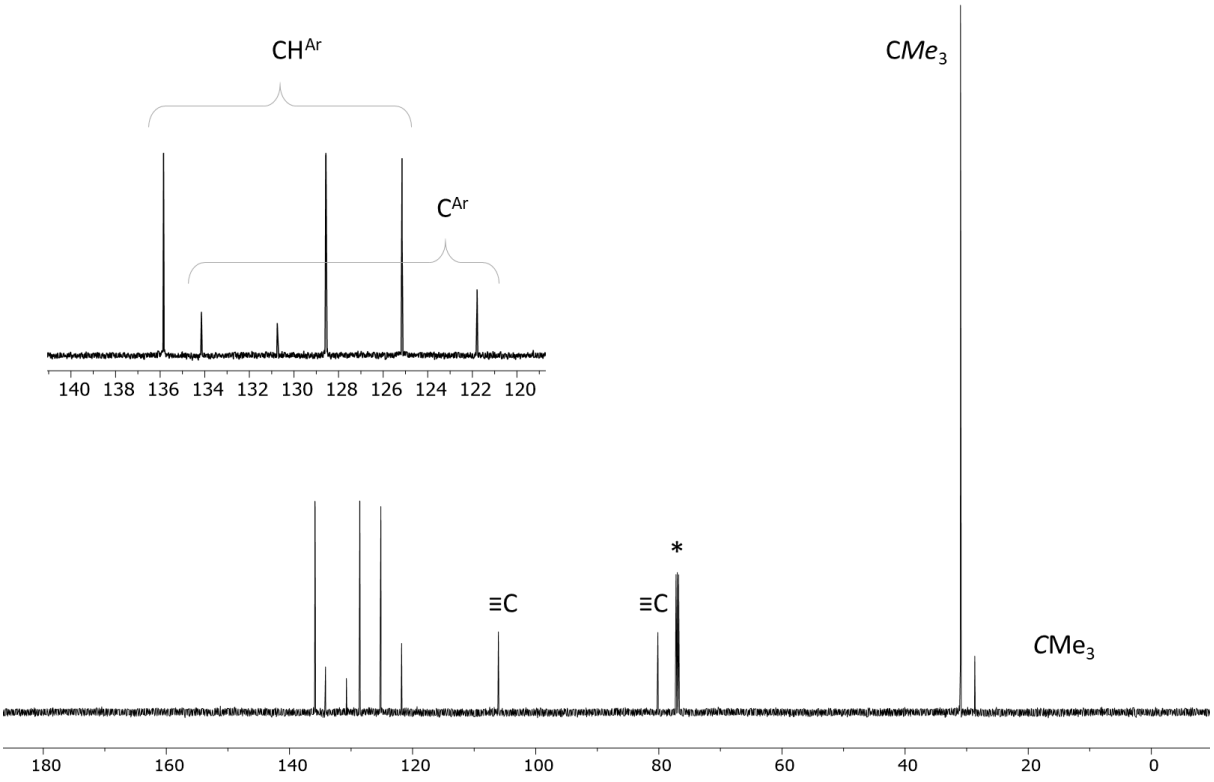
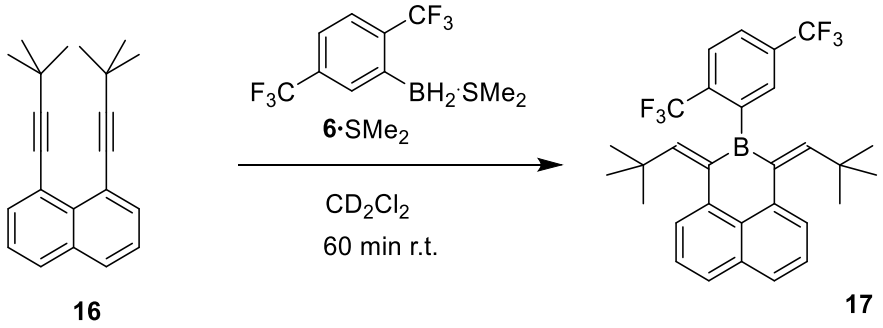


Figure S43: ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$*, 299 K) spectrum of compound **16**.

In situ generation of compound 17 (NMR scale)



Scheme S11

Bis-acetylene **16** (28.8 mg, 0.1 mmol) and borane **6**·SMe_2 (28.8 mg, 0.1 mmol) were combined in CD_2Cl_2 (0.6 mL) and the mixture was placed in a NMR Young tube which was vigorously shaken. The reaction progress was monitored by NMR experiments. After 60 minutes (at room temperature) complete consumption of the starting material was observed. Attempts to isolate compound **17** were not successful.

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = [7.87 (dm, $^3J_{HH}$ = 8.2 Hz), 7.81 (dm, $^3J_{HH}$ = 8.2 Hz), 7.77 (m)](each 1H, FpXyl), [7.79 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.2 Hz), 7.56 (dd, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.2 Hz), 7.47 (dd, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 7.2 Hz)](each 2H, $C_{10}H_6$), 6.18 (s, 2H, =CH), 1.04 (s, 18H, CMe_3).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = [164.2 (=CH), 145.0 (br, =CB), 36.1 (*C*Me_3), 30.7 (C*Me*$_3$)], [134.3 (C), 133.4 (C), 130.9 (C), 127.7 (CH), 127.6 (CH), 124.8 (CH)]($C_{10}H_6$), [142.6 (br, B-C), 135.6 (q, $^2J_{FC}$ = 30.8 Hz, *C*-CF_3), 132.1 (q, $^2J_{FC}$ = 32.0 Hz, *C*-CF_3), 129.6 (q, $^3J_{FC}$ = 3:8 Hz, CH), 126.6 (q, $^3J_{FC}$ = 4.0 Hz, CH), 125.0 (q, $^3J_{FC}$ = 3.9 Hz, CH), n.o. (CF_3)](FpXyl).

^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = 60.2 ($\nu_{1/2} \approx 1000$ Hz)

^{11}B NMR (192 MHz, CD_2Cl_2, 299 K): δ = 60.2 ($\nu_{1/2} \approx 1000$ Hz)

^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = -58.5 (s, 1F, CF_3), -63.5 (s, 1F, CF_3)

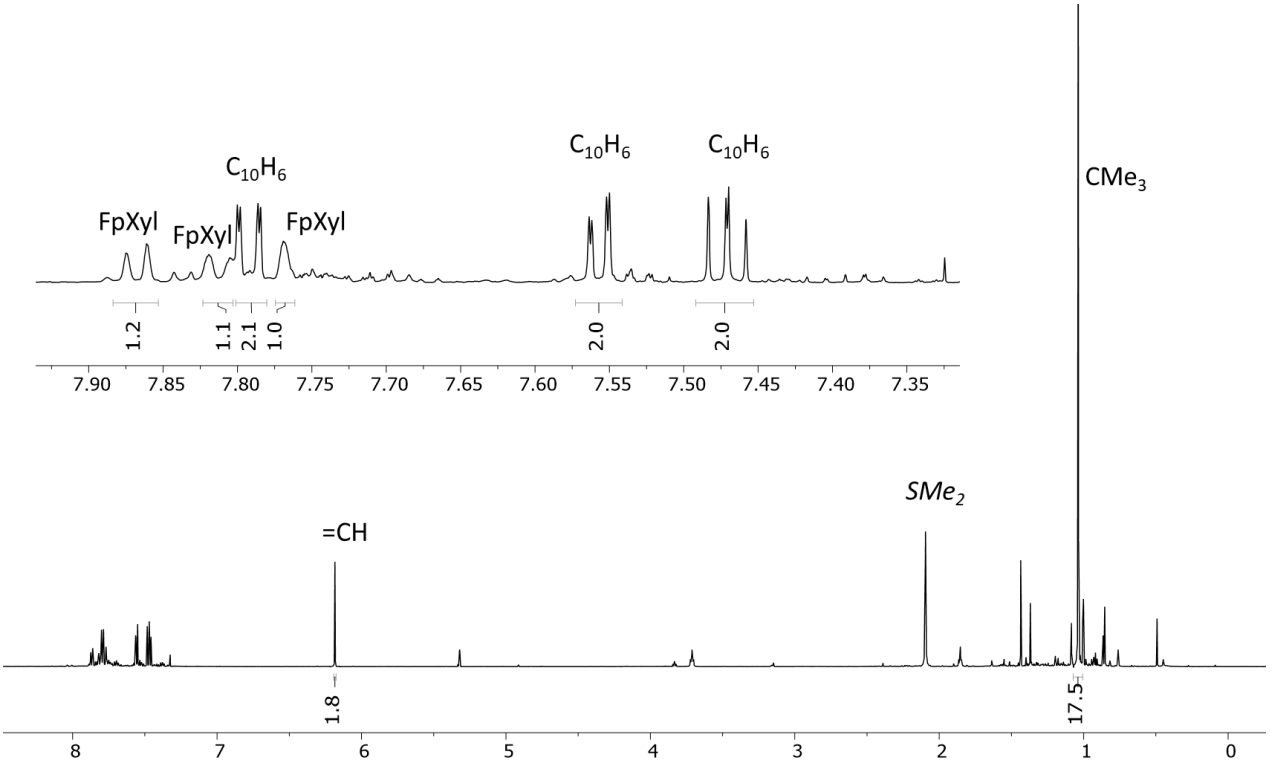


Figure S44: ^{1}H NMR (600 MHz, CD_2Cl_2, 299 K) spectrum of the reaction mixture.

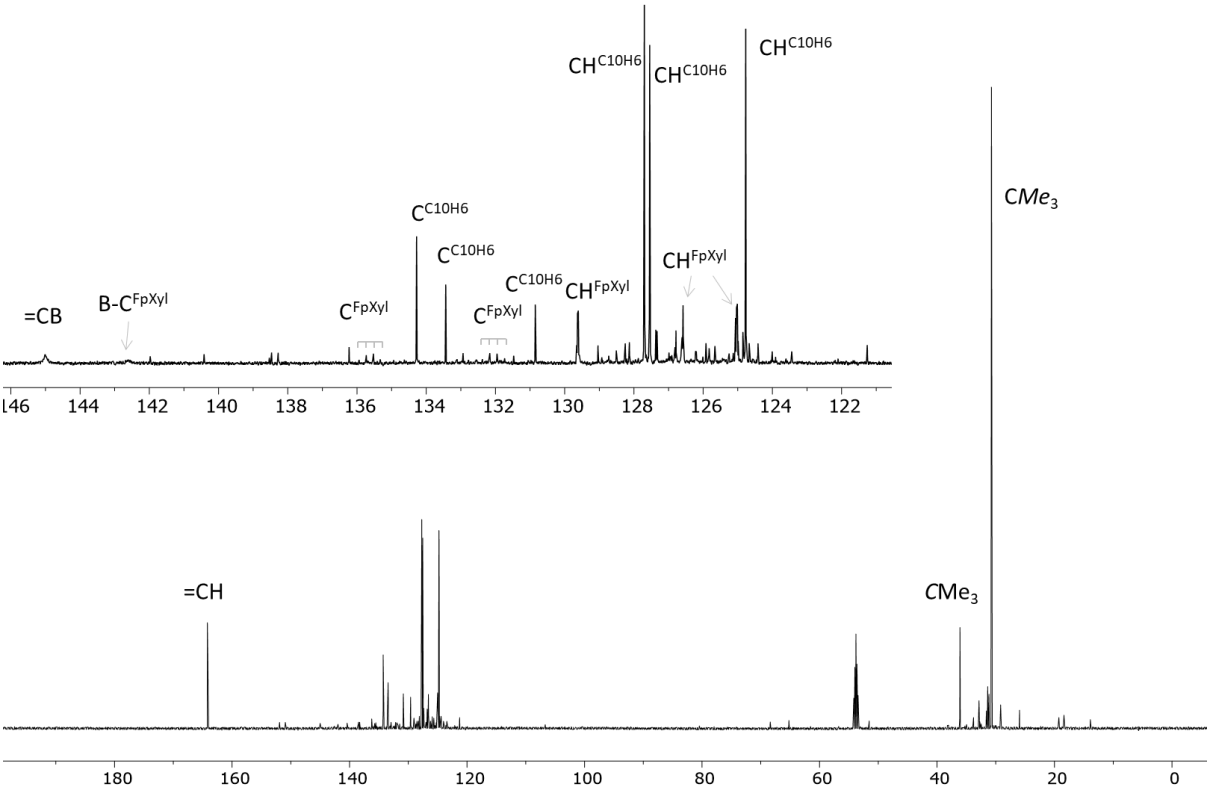


Figure S45: ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K) spectrum of the reaction mixture.

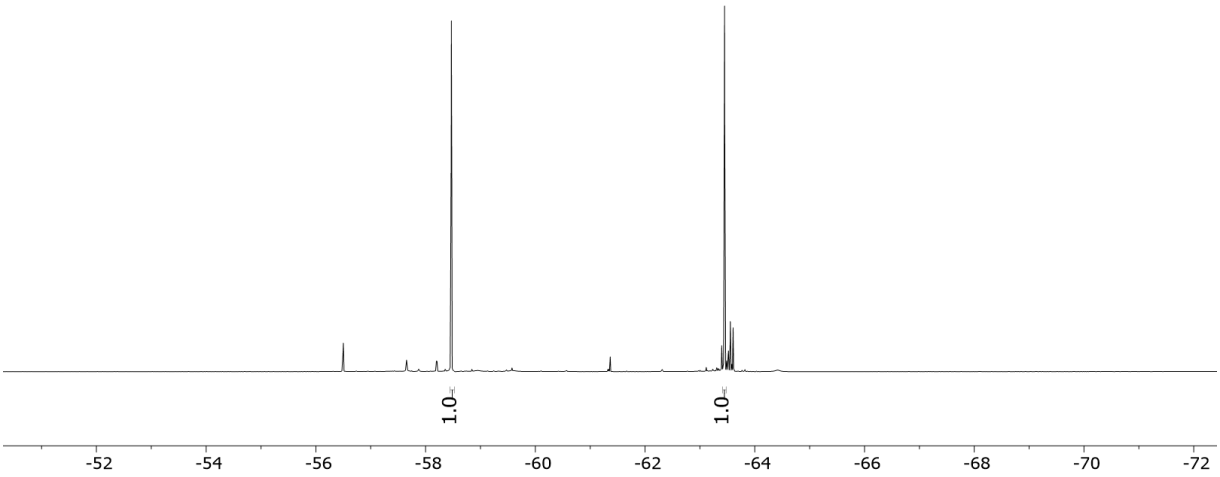


Figure S46: ^{19}F NMR (564 MHz, CD_2Cl_2, 299 K) spectrum of the reaction mixture.

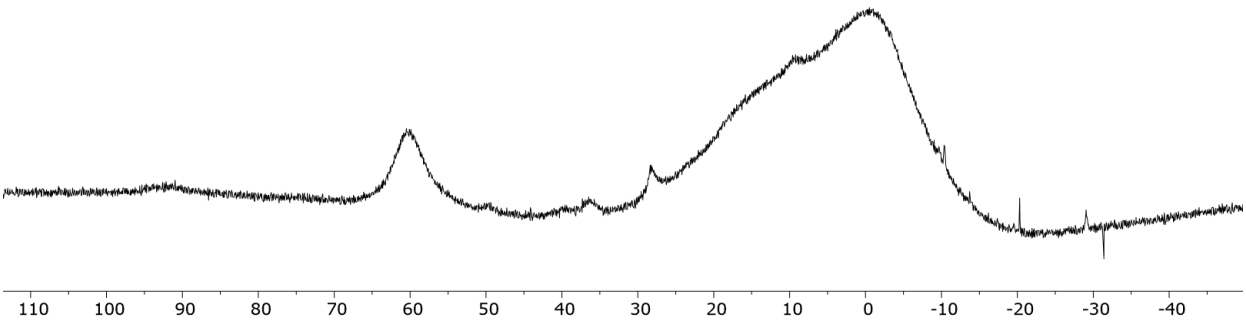
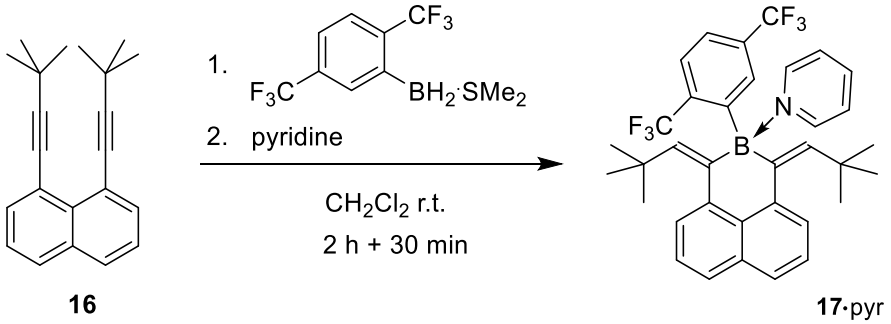


Figure S47: ^{11}B{^{1}H} (192 MHz, CD_2Cl_2, 299 K) spectrum of the reaction mixture.

Synthesis of the adduct 17·pyr



Scheme S12

Bis-acetylene **16** (72.1 mg, 0.25 mmol) and borane **6**·SMe_2 (72.0 mg, 0.25 mmol) were combined in dichloromethane (3 mL) and the mixture was stirred for two hours at room temperature. Subsequently, a solution of pyridine (21.3 mg, 0.27 mmol) in dichloromethane (1 mL) was added and the mixture was stirred for 30 minutes at room temperature. Then all volatiles were removed in vacuo and the brown glassy residue was treated with pentane (ca 3 mL). The mixture was stirred vigorously for 15 minutes at room temperature. The formed solid was separated by decantation and washed with pentane (2x 1 mL). After drying in vacuo, compound **17**·pyr was obtained as a yellow solid (114 mg, 0.19 mmol, 76 % yield).

Melting point: 120.3 °C

Elemental analysis calculated for $C_{35}H_{34}BF_6N$ (593.4): C 70.83, H 5.78, N 2.36; found: C 70.63, H 5.65, N 2.23.

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = [8.37 (br, 2H, *o*), 7.97 (br, 1H, *p*), 7.45 (br, 2H, *m*)](py), [7.98 (br), 7.57 (d, $^3J_{HH}$ = 8.3 Hz), 7.36 (d, $^3J_{HH}$ = 8.3 Hz)](each 1H, FpXyl), [7.47 (d, $^3J_{HH}$ = 8.1 Hz), 7.39 (d, $^3J_{HH}$ = 7.3 Hz), 7.23 (dd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 7.3 Hz)](each 2H, $C_{10}H_6$), 4.97 (br, 2H, =CH), 1.13 (s, 18H, CMe_3).

^{1}H NMR (600 MHz, CD_2Cl_2, 213 K): δ = [8.74 (br d, $J \approx 5$ Hz), 8.03 (t, $^3J_{HH}$ = 7.8 Hz), 7.65 (br t, $J \approx 7$ Hz), 7.61 (br d, $J \approx 5$ Hz), 7.34 (br m)](each 1H, py), [7.86 (s), 7.49 (d, $^3J_{HH}$ = 8.3 Hz), 7.26 (br m)] (FpXyl), [{7.46 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 0.9 Hz), 7.40 (dd, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 0.9 Hz), 7.24 (dd, $^3J_{HH}$ = 8.1 Hz, 7.3 Hz)}, {7.44 (dd, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 0.9 Hz), 7.26 (br m), 7.18 (dd, $^3J_{HH}$ = 7.9 Hz, 7.3 Hz)}](each 1H, $C_{10}H_6$), [5.03, 4.40](each s, each 1H, =CH), [1.09, 1.04](each s, each 9H, CMe_3)

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K)[selected resonances]: δ = [149.9 (*o*), 141.1 (*p*), 124.0 (*m*)](py), 140.7 (br, =CH), [139.8 (br, C), 133.3 (C), 131.1 (C), 127.9 (CH), 126.4 (CH), 124.3 (CH)]($C_{10}H_6$), [137.8 (br q, $^2J_{FC}$ = 32.4 Hz, C-CF_3), 137.3 (br, CH), 131.2 (br q, $^2J_{FC} \approx 30.5$ Hz, *C*-CF_3), 126.6 (br q, $^3J_{FC}$ = 6.2 Hz, CH), 125.0 (q, $^1J_{FC}$ = 275.2 Hz, CF_3), 124.6 (q, $^1J_{FC}$ = 272.7 Hz, CF_3), 123.2 (br, CH)](FpXyl), 35.6 (*C*Me_3), 32.0 (C*Me*$_3$).

^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = 2.7 ($\nu_{1/2} \approx 350$ Hz)

^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 213 K): δ = 0.9 (br)

^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = -57.3 (s, 1F, CF_3), -63.5 (s, 1F, CF_3)

^{19}F NMR (564 MHz, CD_2Cl_2, 213 K): δ = -57.7 (s, 1F, CF_3), -63.3 (s, 1F, CF_3)

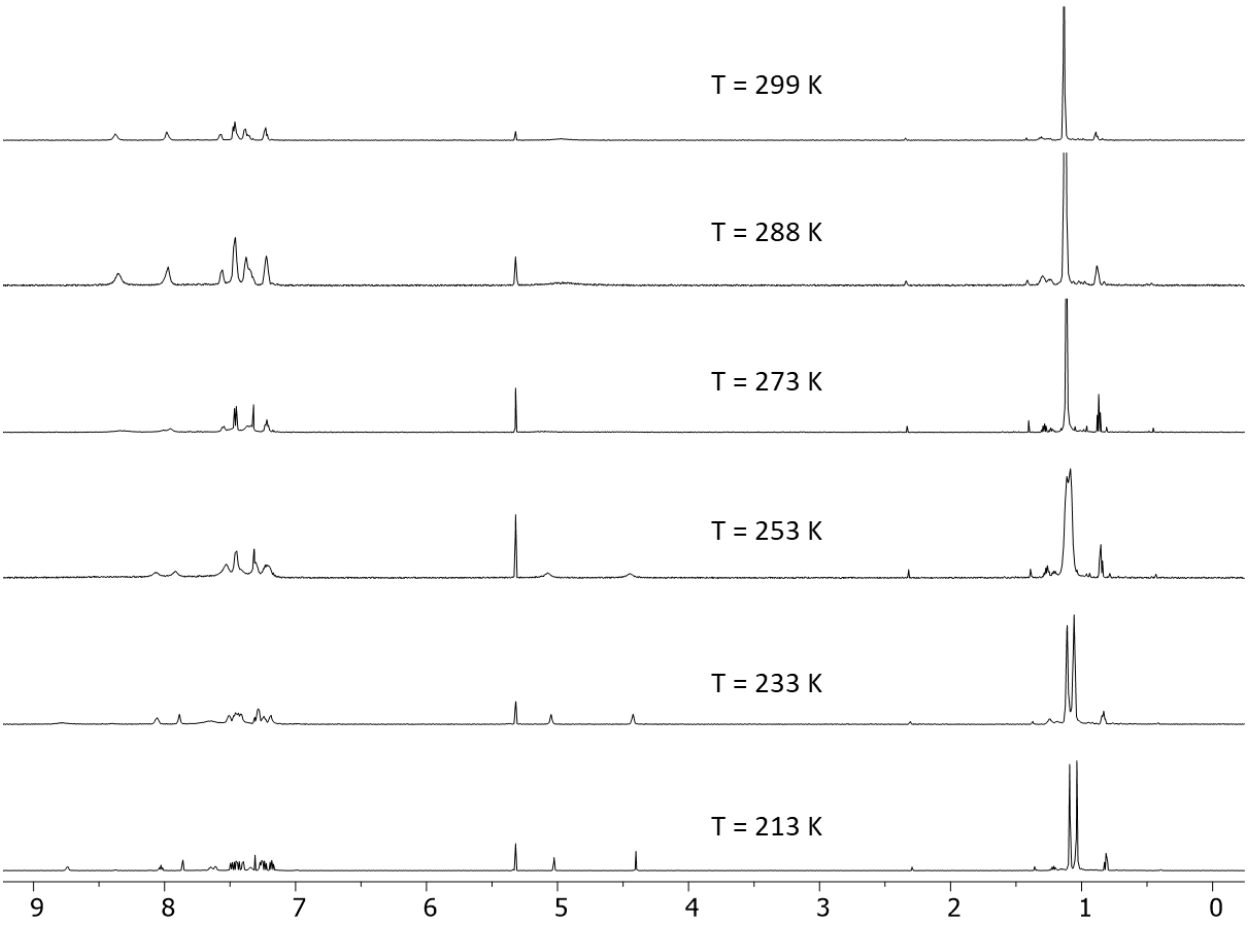


Figure S48: **^{1}H NMR** (600 MHz, CD_2Cl_2) spectra of compound **17**·pyr measured at various temperatures.

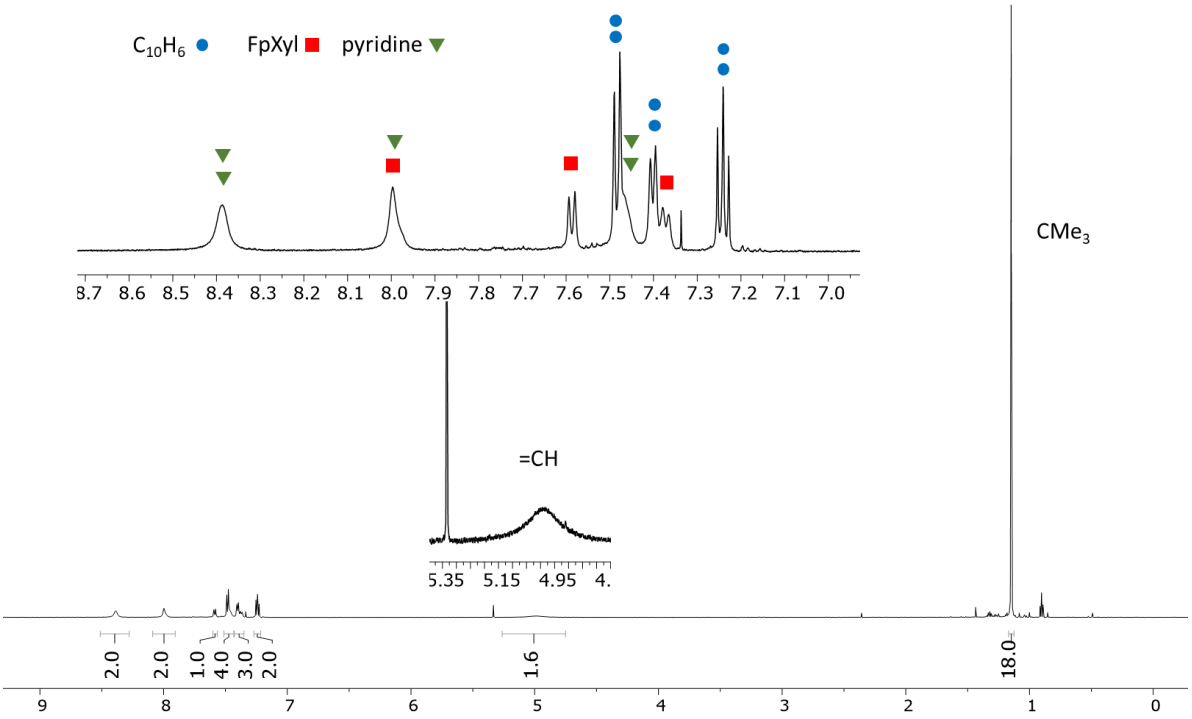


Figure S49: **^{1}H NMR** (600 MHz, CD_2Cl_2, 299 K) spectrum of compound **17**·pyr.

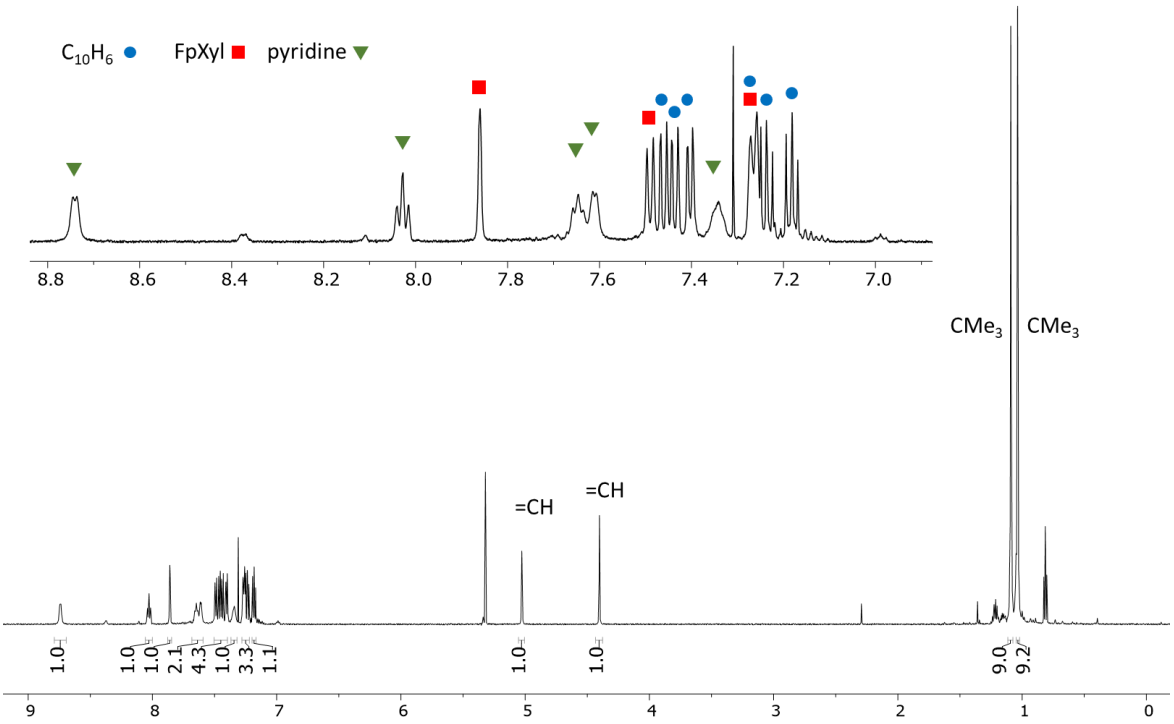


Figure S50: ^{1}H NMR (600 MHz, CD_2Cl_2, 213 K) spectrum of compound **17**·pyr.

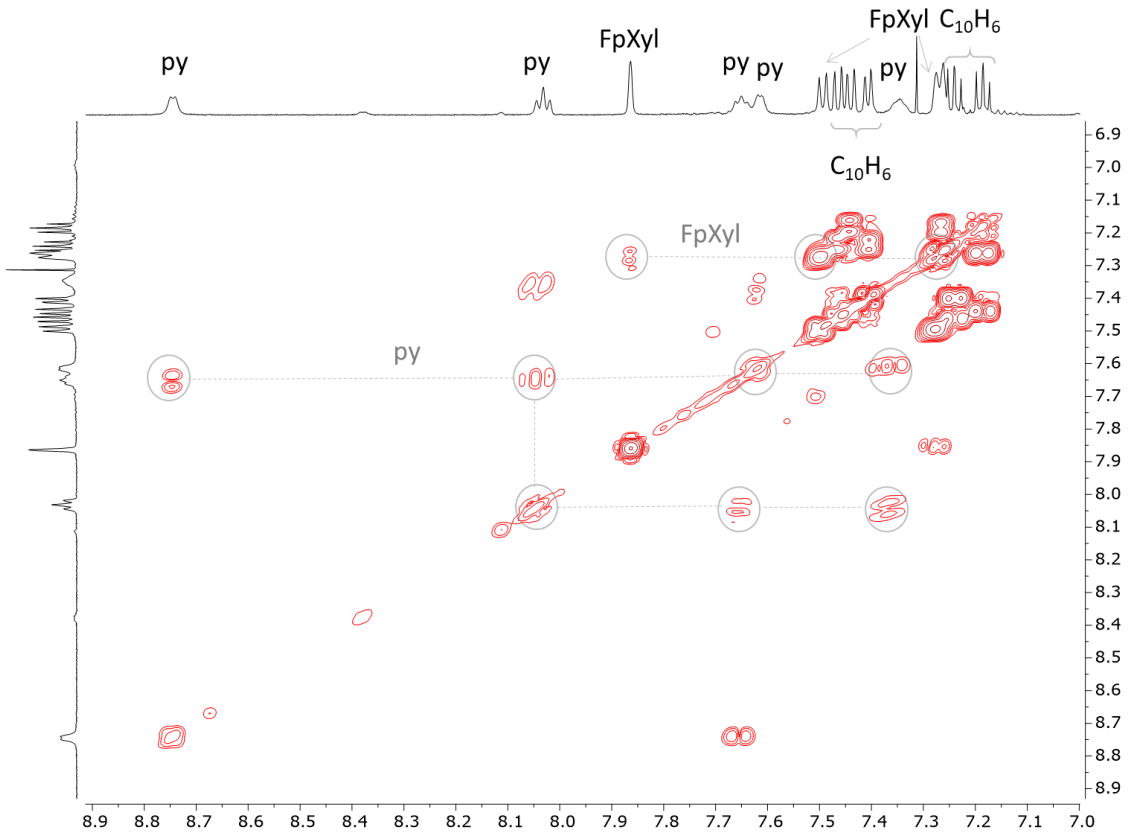


Figure S51: ^{1}H,^{1}H gCOSY NMR (600 MHz, CD_2Cl_2, 213 K) of compound **17**·pyr.

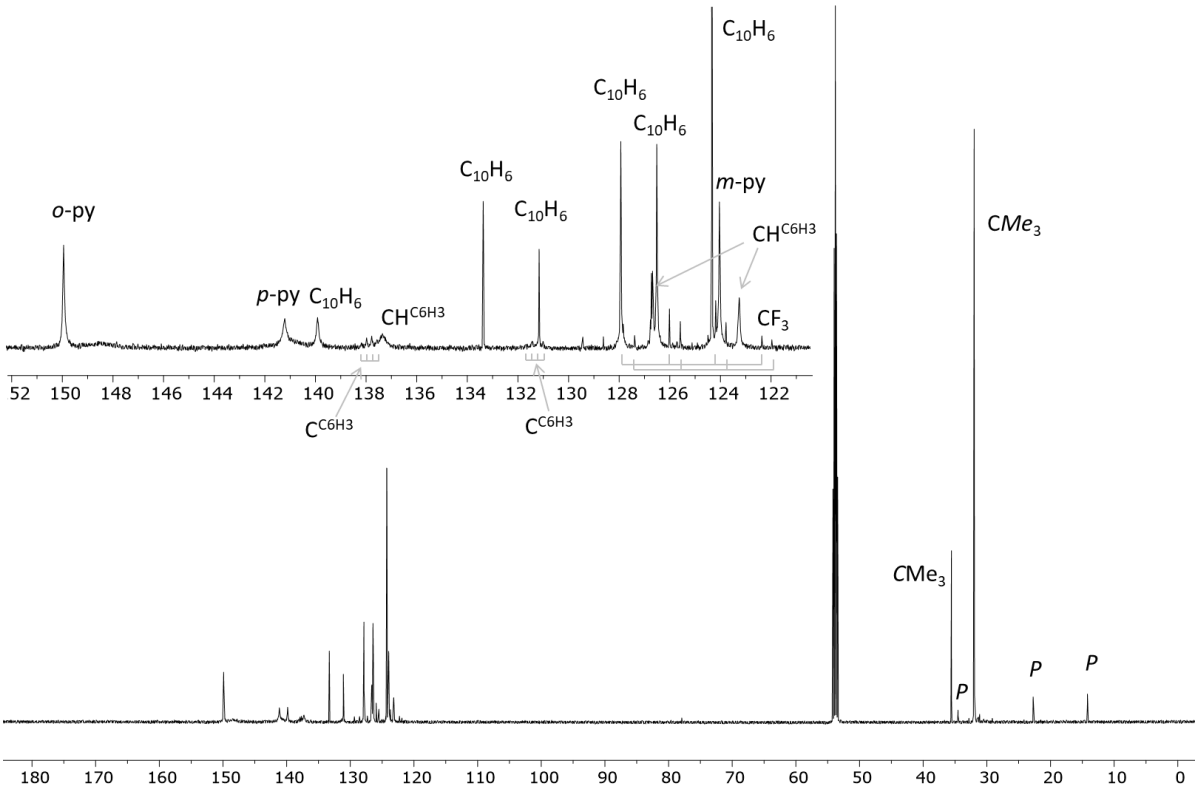


Figure S52: $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2, 299 K) spectrum of compound **17**·pyr (P: pentane).

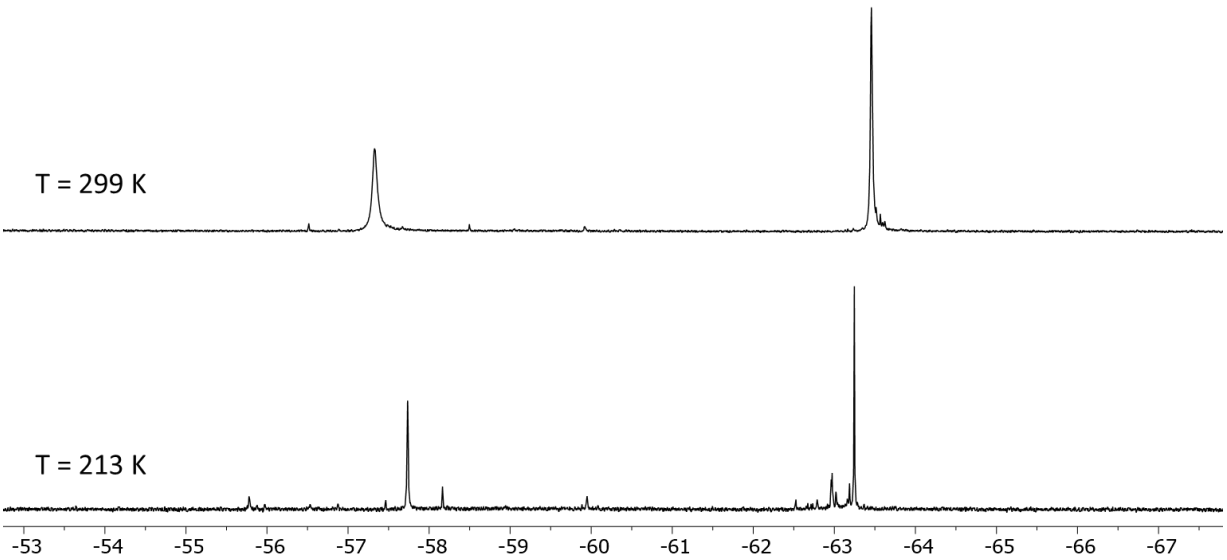


Figure S53: ^{19}F NMR (564 MHz, CD_2Cl_2) spectrum of compound **17**·pyr measured at 299 K and 213 K

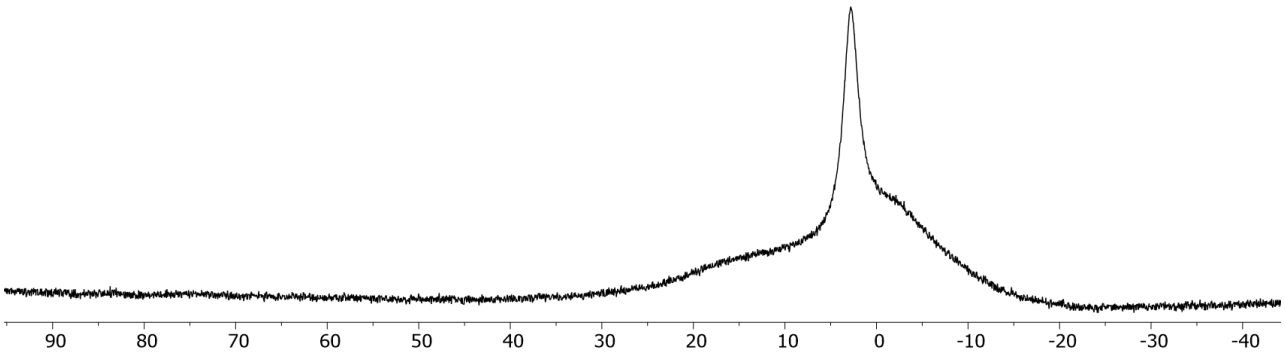


Figure S54: $^{11}B\{^{1}H\}$ NMR (192 MHz, CD_2Cl_2, 299 K) spectrum of compound **17**·pyr.

Crystals suitable for the X-ray crystal structure analysis were obtained from by slow diffusion of pentane into a solution of compound **17**·pyr in dichloromethane at room temperature.

X-ray crystal structure analysis of compound 17·pyr (erk9862): A colorless prism-like specimen of $C_{35}H_{34}BF_6N$, approximate dimensions 0.084 mm x 0.157 mm x 0.278 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture PHOTON III Diffractometer system equipped with a micro focus tube Mo Ims (MoK_α, $\lambda = 0.71073$ Å) and a MX mirror monochromator. A total of 1460 frames were collected. The total exposure time was 12.17 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 55787 reflections to a maximum θ angle of 26.74° (0.79 Å resolution), of which 6498 were independent (average redundancy 8.585, completeness = 99.6%, R_{int} = 4.08%, R_{sig} = 2.05%) and 5553 (85.46%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.3110(3) Å, b = 14.3855(5) Å, c = 21.2243(7) Å, β = 103.1290(10)°, volume = 3065.89(17) $Å^3$, are based upon the refinement of the XYZ-centroids of 9547 reflections above 20 σ(I) with 4.853° < 2θ < 53.46°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.922. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9730 and 0.9920. 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, $C_{35}H_{34}BF_6N$. The final anisotropic full-matrix least-squares refinement on F^2 with 394 variables converged at R1 = 3.93%, for the observed data and wR2 = 10.91% for all data. The goodness-of-fit was 1.045. The largest peak in the final difference electron density synthesis was 0.347 $e^-/Å^3$ and the largest hole was -0.213 $e^-/Å^3$ with an RMS deviation of 0.045 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.286 g/cm^3 and F(000), 1240 e^-. CCDC number: 2016815.

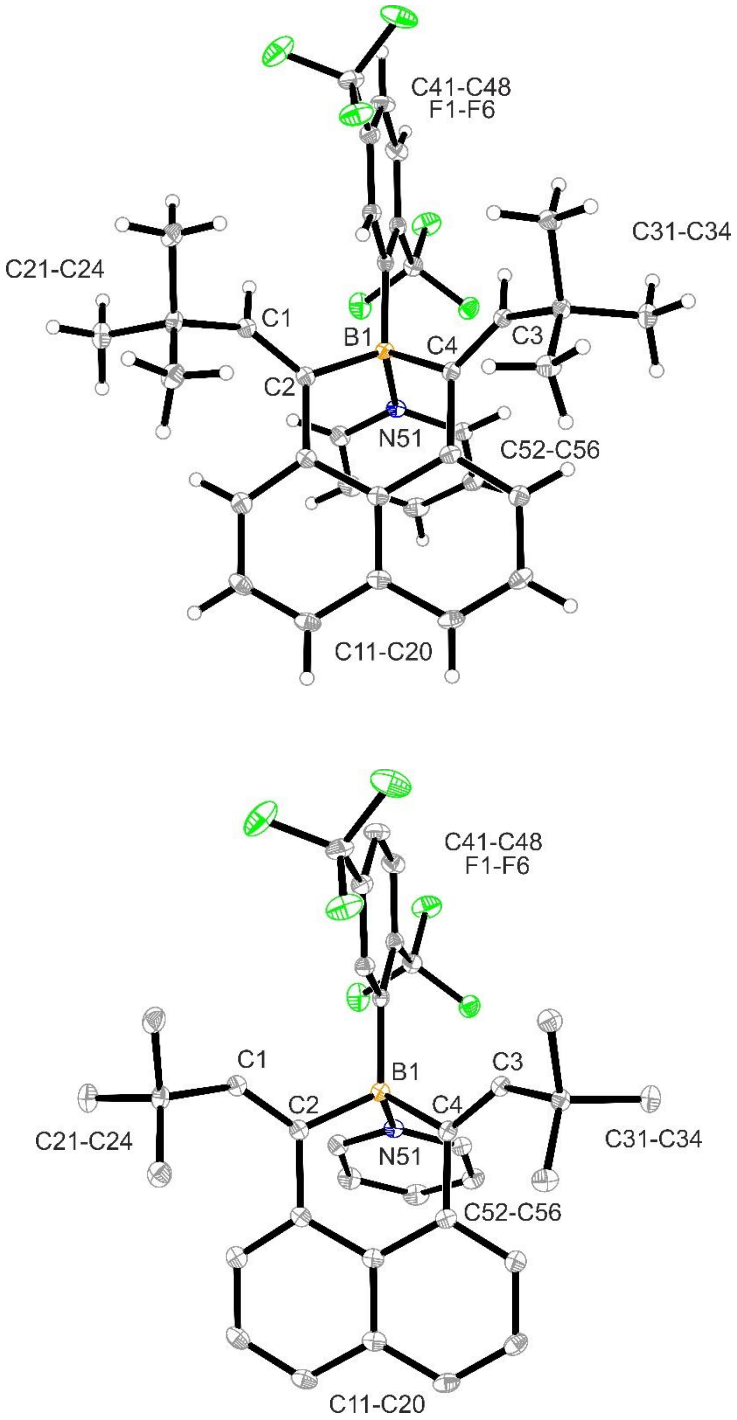
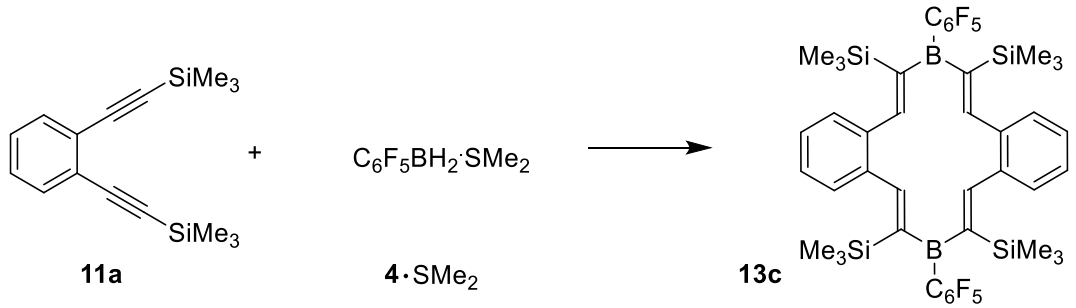


Figure S55: Crystal structure of compound **17**·pyr. Thermal ellipsoids are set at 30% probability.

Control reactions:

Reaction of bis-acetylene 11a with borane 4·SMe$_2$: preparation of cycle 13c



Scheme S13

Bis-acetylene **11a** (541 mg, 2.0 mmol) and borane **4**·SMe$_2$ (484 mg, 2.0 mmol) were combined in CH_2Cl_2 (ca 10 mL) and stirred for 60 minutes at room temperature to give an orange solution. Subsequently all volatiles were removed in vacuo. Then the residue was washed with pentane (3x2 mL). Drying the residue in vacuo provided the first fraction of product **13c** as a white amorphous solid. Cooling the combined pentane extracts to -35°C for 2 days provided an additional fraction of product **13c** as a white flaky solid, which was isolated by decantation and washed with a small amount of cold pentane (combined isolated yield 653 mg, 0.73 mmol, 73%).

Melting point: 113.2 °C

HRMS for $C_{44}H_{48}B_2ClF_{10}Si_4$ [(M + Cl)$^-$]: calculated 935.2537; found 935.2559.

Elemental analysis calculated for $C_{22}H_{24}BF_5Si_2$ (450.4): C 58.66, H 5.37; found: C 58.64, H 5.30.

^{1}H NMR (600 MHz, C_6D_6, 299 K): δ = 8.21 (s, 1H, =CH), 7.32 (m, 1H, CH^{Ar}), 7.04 (m, 1H, CH^{Ar}), -0.12 (s, 9H, $SiMe_3$).

^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 299 K): δ = 159.7 (br, =CB), 158.8 (=CH), 146.4 (dm, $^1J_{FC} \approx 243$ Hz, C_6F_5), 142.5 (dm, $^1J_{FC} \approx 257$ Hz, C_6F_5), 140.8 (C^{Ar}), 137.9 (dm, $^1J_{FC} \approx 253$ Hz, C_6F_5), 128.7 (CH^{Ar}), 128.6 (CH^{Ar}), 117.2 (tm, $^2J_{FC} \approx 27$ Hz, C_6F_5), 0.9 (s, $^1J_{SiC} = 52.1$ Hz, $SiMe_3$)

^{11}B NMR (192 MHz, C_6D_6, 299 K): δ = 68.6 ($\nu_{1/2} \approx 2200$ Hz)

^{11}B{^{1}H} NMR (192 MHz, C_6D_6, 299 K): δ = 68.6 ($\nu_{1/2} \approx 2000$ Hz)

^{19}F NMR (564 MHz, C_6D_6, 299 K): δ = -127.8 (m, 2F, *o*-), -149.9 (m, 1F, *p*-), -161.5 (m, 2F, *m*-) [C_6F_5, $\Delta\delta^{19}F_{m,p}$ = 11.6 ppm]

^{29}Si{^{1}H} DEPT (119 MHz, C_6D_6, 299 K): δ = -8.5 ($\nu_{1/2} \approx 1$ Hz)

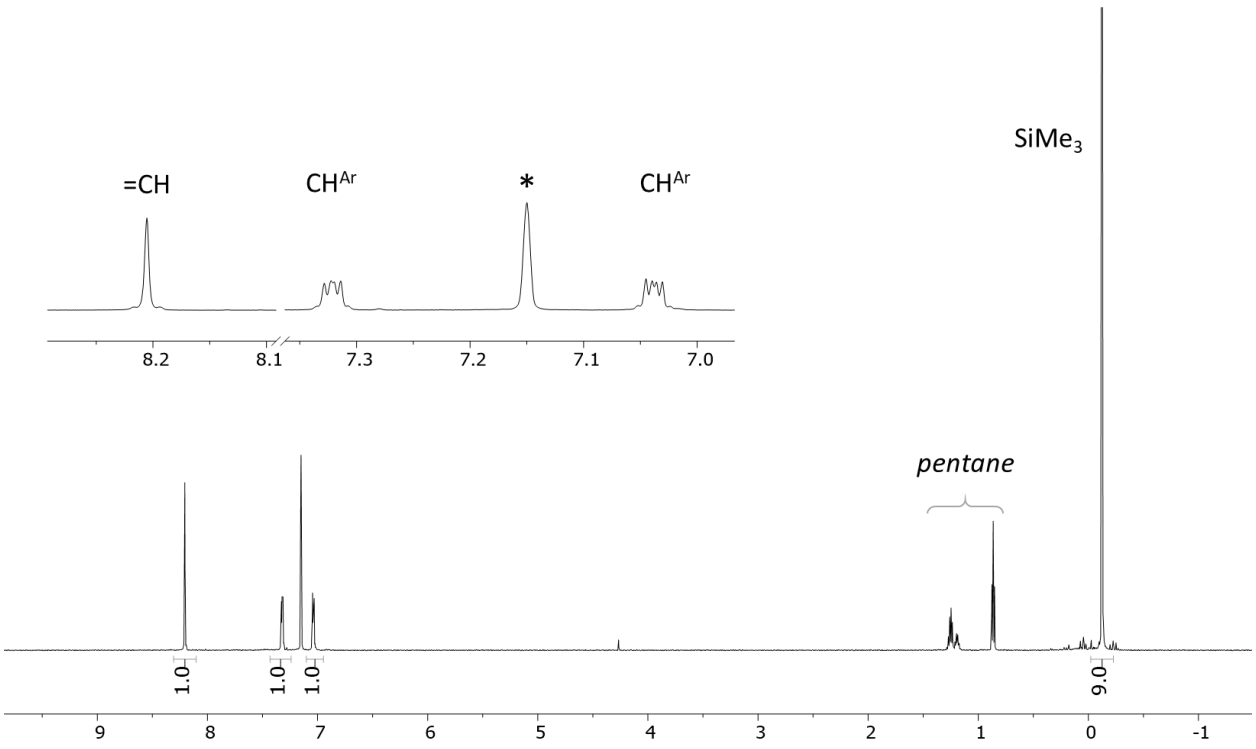


Figure S56: ^{1}H NMR (600 MHz, C_6D_6*, 299 K) spectrum of compound **13c**.

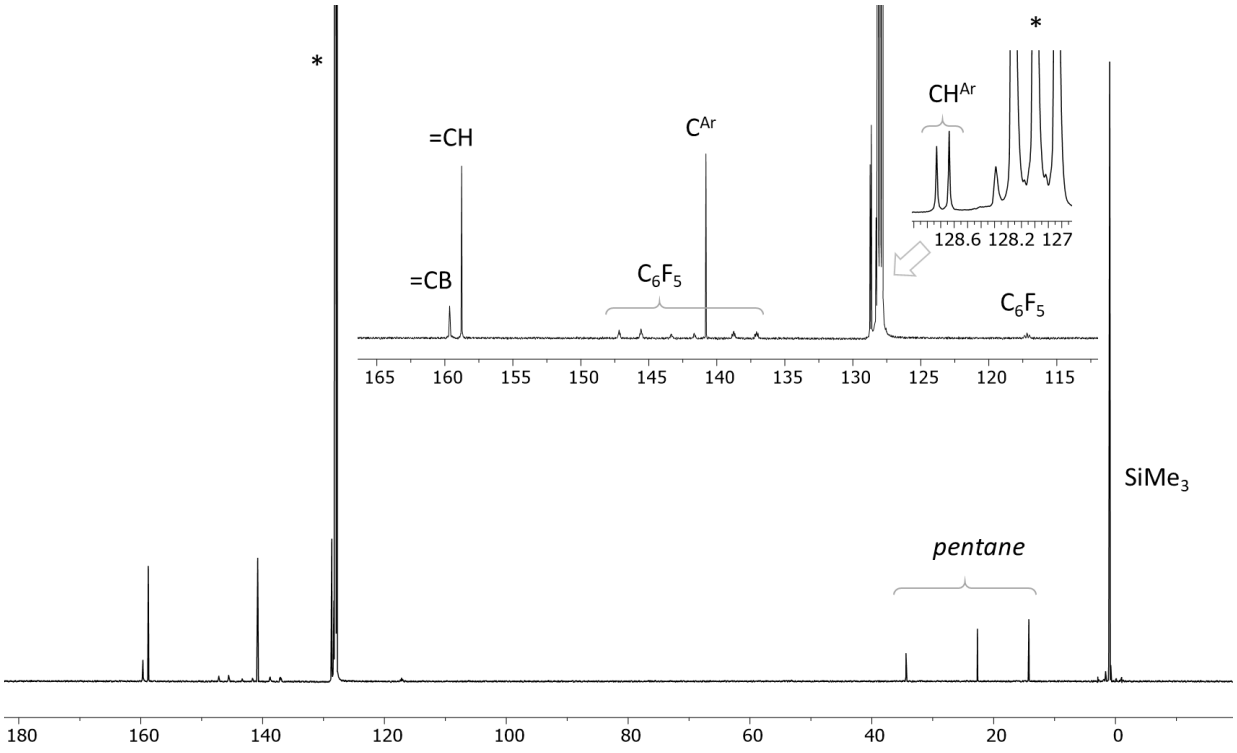


Figure S57: ^{13}C{^{1}H} NMR (151 MHz, C_6D_6*, 299 K) spectrum of compound **13c**.

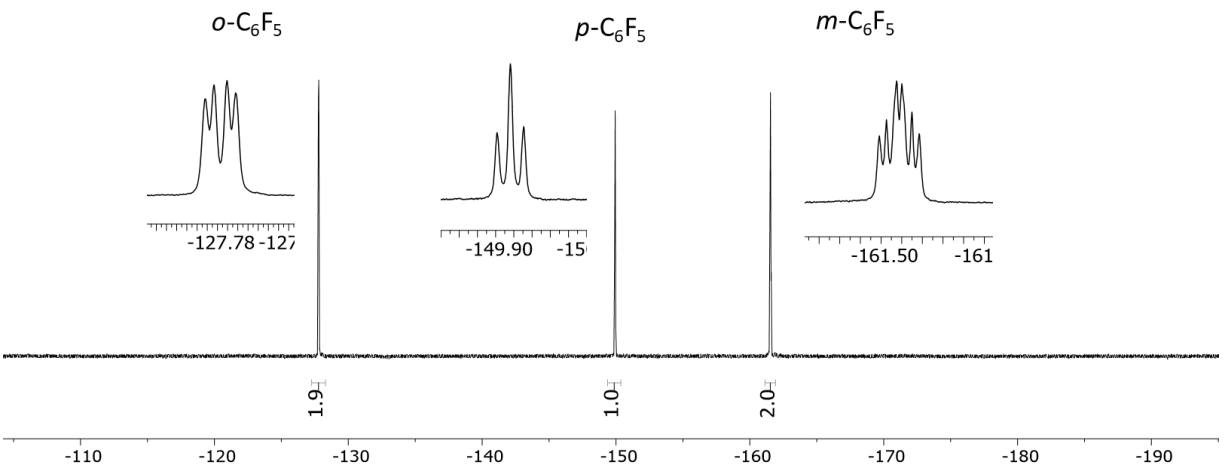


Figure S58: ^{19}F NMR (564 MHz, C_6D_6, 299 K) spectrum of compound **13c**.

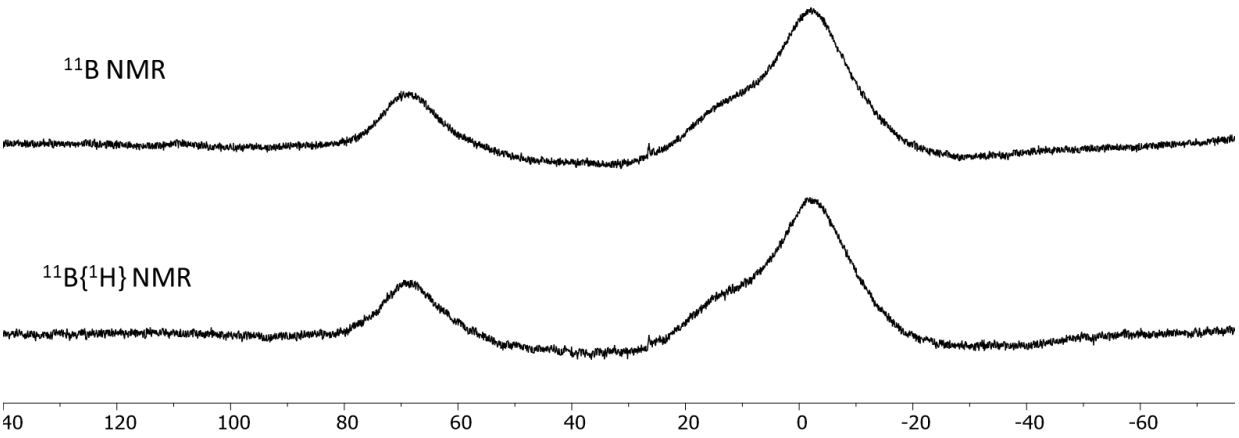


Figure S59: ^{11}B{^{1}H} and **^{11}B NMR** (192 MHz, C_6D_6, 299 K) spectra of compound **13c**.

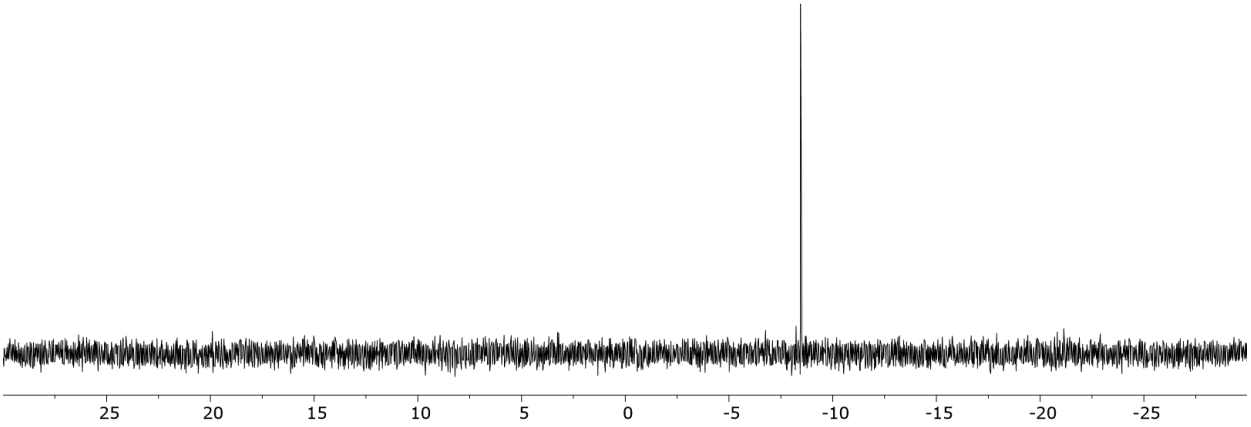
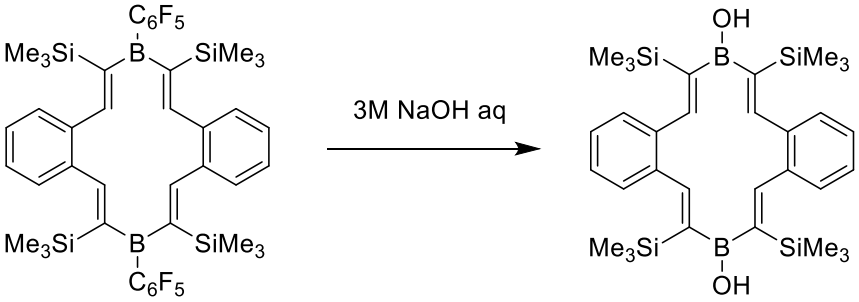


Figure S60: ^{29}Si{^{1}H} DEPT (119 Hz, C_6D_6, 299 K) spectrum of compound **13c**.

Hydrolysis of compound 13c: preparation of cycle SI-1



13c **SI-1**

Scheme S14

Cycle **13c** (90 mg, 0.10 mmol) was dissolved in THF (3 mL) and a solution of $NaOH_{aqu}$ was added (3 mL of 3M aqueous solution). The biphasic mixture was vigorously stirred for 60 minutes at room temperature. Subsequently several drops of hydrochloric acid (1M of aqueous HCl) were added until the mixture was acidic. The obtained emulsion was extracted with diethyl ether (3x 5mL). The combined extracts were washed with brine, dried over $MgSO_4$, filtered and then all volatiles were removed under reduced pressure. The residue was purified by flash column chromatography (mixture pentane: Et_2O 5:1 was used as eluent) to give product **SI-1** as a colourless oil which readily crystallized (54 mg, 0.090 mmol, 90% yield).

HRMS for $C_{32}H_{49}B_2O_2Si_4$ [$(M - H)^-$]: calculated 599.2996; found 599.2997.

Elemental analysis calculated for $C_{32}H_{50}B_2O_2Si_4$ (600.7): C 63.98, H 8.39; found: C 64.10, H 8.34.

^{1}H NMR (600 MHz, $CDCl_3$, 299 K): δ = 7.76 (s, 2H, =CH), 7.26 (m, 2H, CH^{Ar}), 7.17 (m, 2H, CH^{Ar}), 4.98 (s, 1H, OH), 0.01 (s, $^2J_{SiH}$ = 6.6 Hz, 18H, $SiMe_3$)

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 299 K): δ = 156.9 (=CH), 148.7 (br, $\nu_{1/2} \approx 15$ Hz, =CB), 140.31 (C^{Ar}), 128.5 (CH^{Ar}), 127.4 (CH^{Ar}), 1.23 (s, $^1J_{SiC}$ = 51.6 Hz, $SiMe_3$)

^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$, 299 K): δ = 49.1 ($\nu_{1/2} \approx 1200$ Hz)

^{29}Si{^{1}H} DEPT (119 MHz, $CDCl_3$, 299 K): δ = -8.4 ($\nu_{1/2} \approx 1$ Hz)

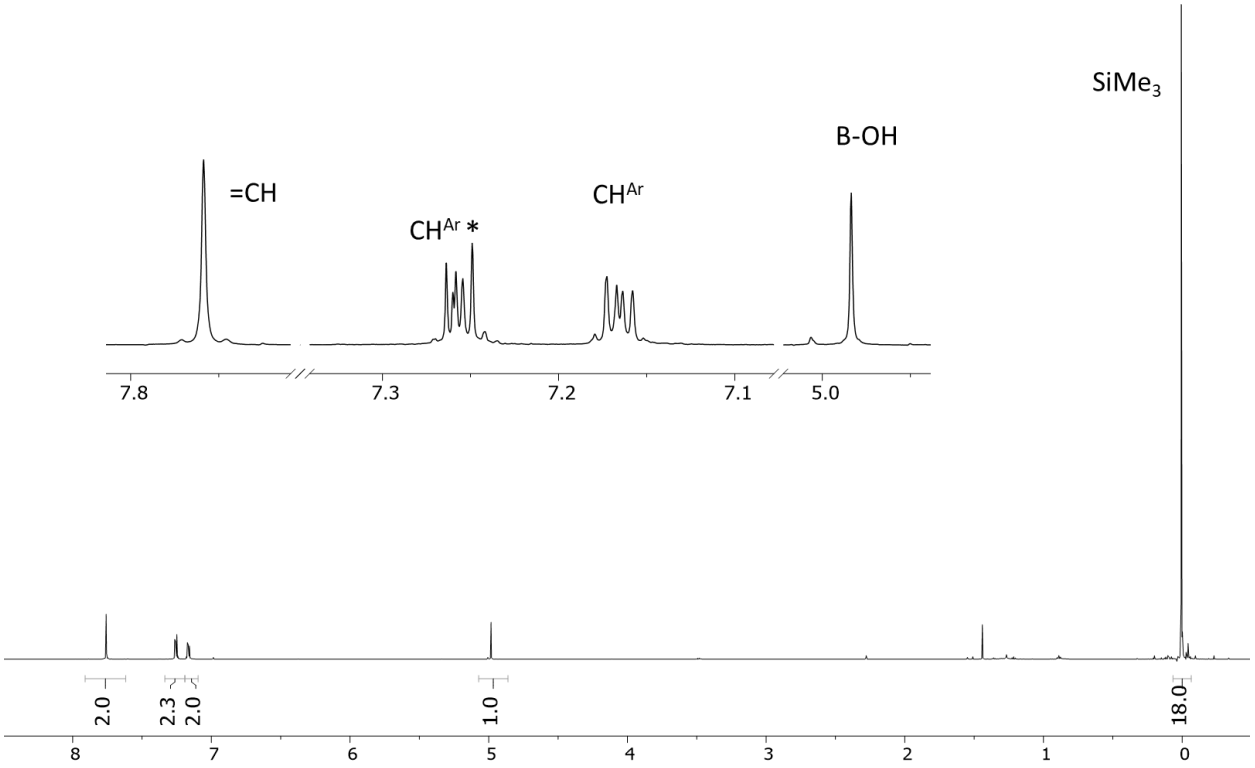


Figure S61: ^{1}H NMR (600 MHz, $CDCl_3$*, 299 K) spectrum of compound **SI-1**.

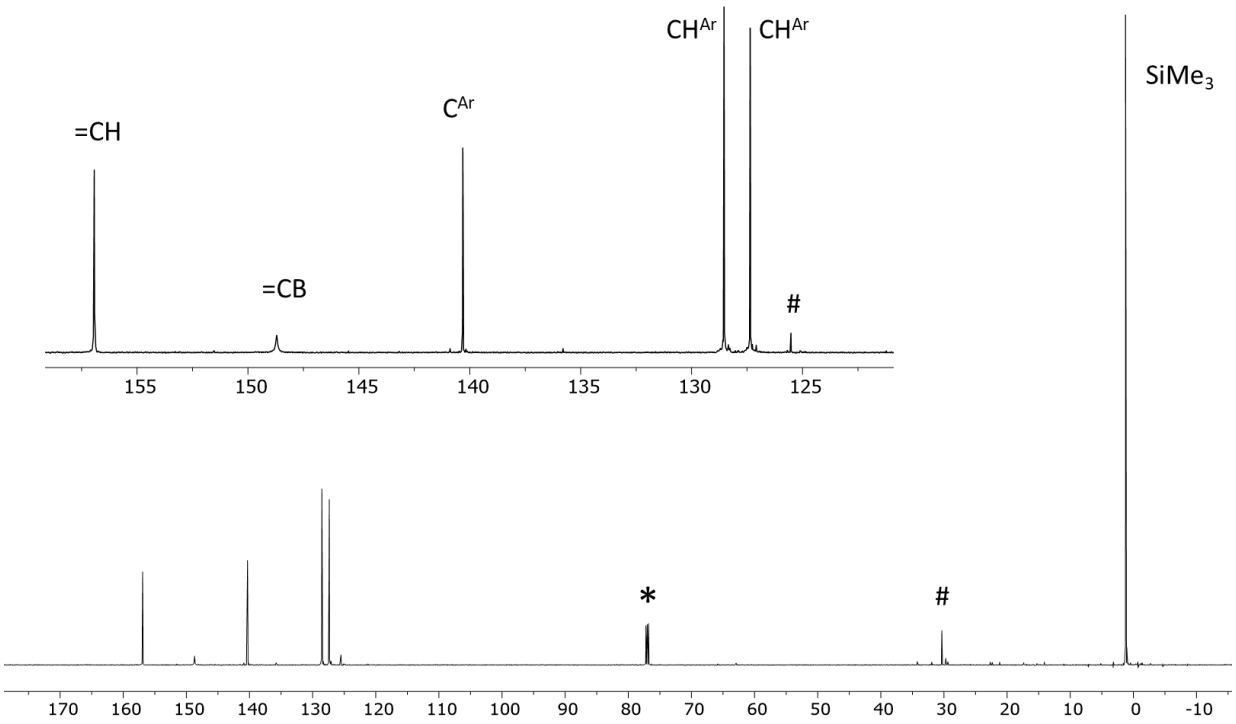


Figure S62: ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$*, 299 K) spectrum of compound **SI-1**, (# impurity).

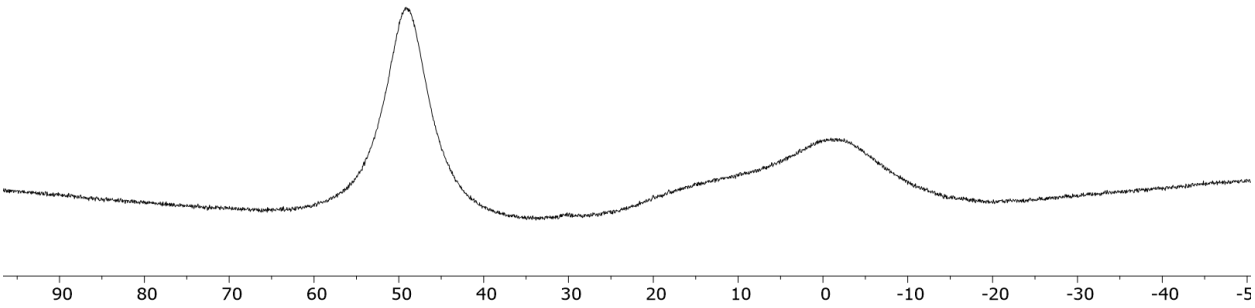


Figure S63: $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$, 299 K) spectrum of compound **SI-1**.

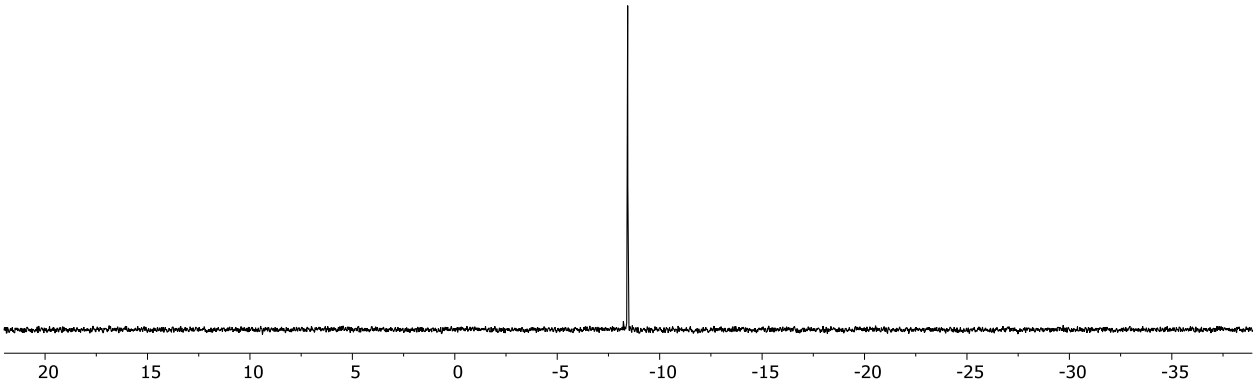


Figure S64: $^{29}Si\{^1H\}$ DEPT (119 MHz, $CDCl_3$, 299 K) spectrum of compound **SI-1**.

Crystals suitable for the X-ray crystal structure analysis were obtained from a heptane solution of compound **SI-1** under ambient conditions.

X-ray crystal structure analysis of compound SI-1 (erk9861): A colorless prism-like specimen of $C_{32}H_{50}B_2O_2Si_4$, approximate dimensions 0.105 mm x 0.143 mm x 0.280 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture PHOTON III Diffractometer system equipped with a micro focus tube Mo Ims (MoK_α, λ = 0.71073 Å) and a MX mirror monochromator. A total of 621 frames were collected. The total exposure time was 3.97 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 33285 reflections to a maximum θ angle of 26.73° (0.79 Å resolution), of which 3994 were independent (average redundancy 8.334, completeness = 99.7%, R_{int} = 6.23%, R_{sig} = 2.99%) and 3695 (92.51%) were greater than $2\sigma(F^2)$. The final cell constants of a = 18.4614(6) Å, b = 34.6525(10) Å, c = 11.8617(4) Å, volume = 7588.3(4) $Å^3$, are based upon the refinement of the XYZ-centroids of 9971 reflections above 20 σ(I) with 5.000° < 2θ < 53.28°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.909. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9510 and 0.9810. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *Fdd*2, with Z = 8 for the formula unit, $C_{32}H_{50}B_2O_2Si_4$. The final anisotropic full-matrix least-squares refinement on F^2 with 191 variables converged at R1 = 3.32%, for the observed data and wR2 = 8.28% for all data. The goodness-of-fit was 1.059. The largest peak in the final difference electron density synthesis was 0.271 $e^-/Å^3$ and the largest hole was -0.137 $e^-/Å^3$ with an RMS deviation of 0.037 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.052 g/cm^3 and F(000), 2592 e^-. CCDC number: 2026639.

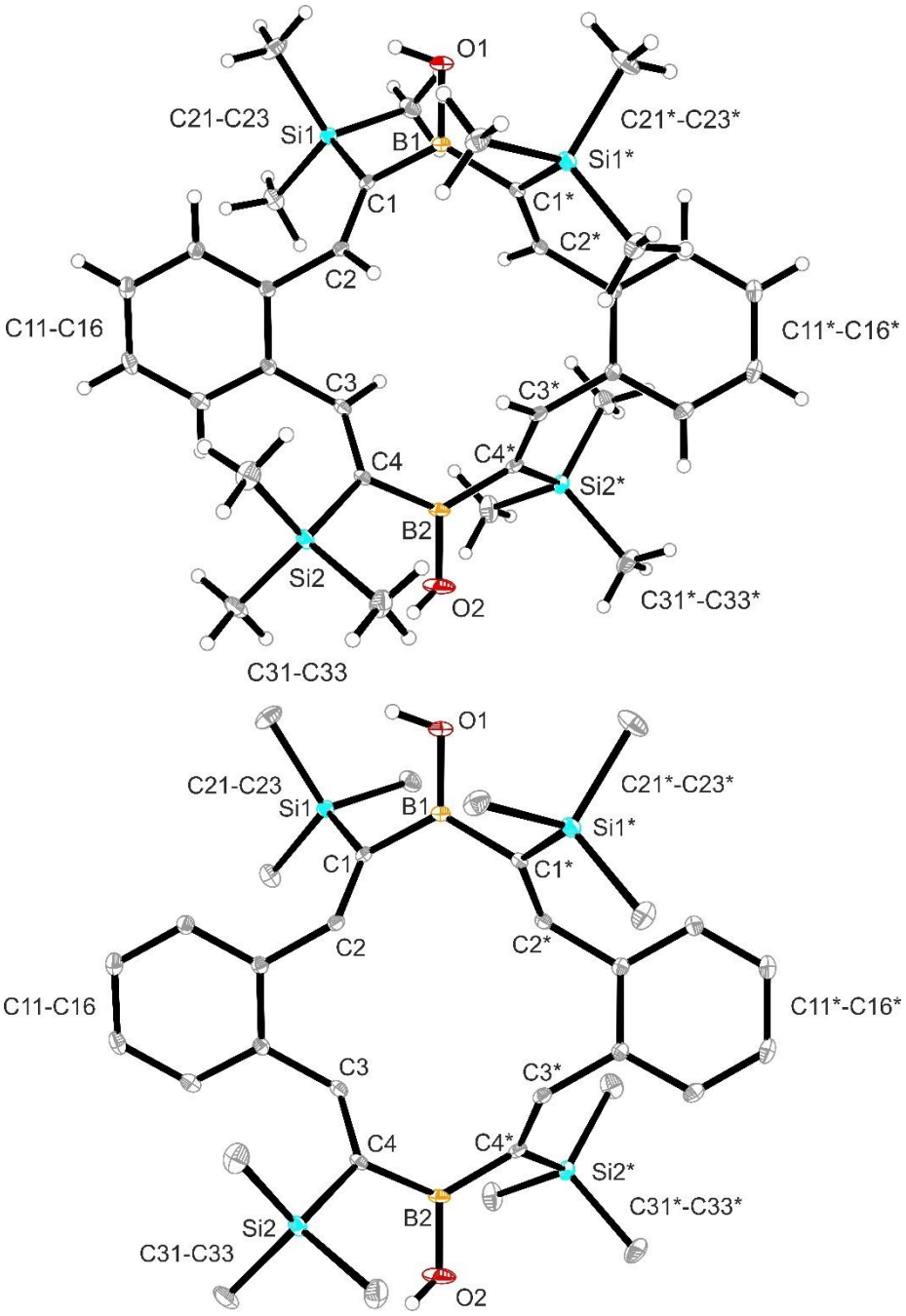
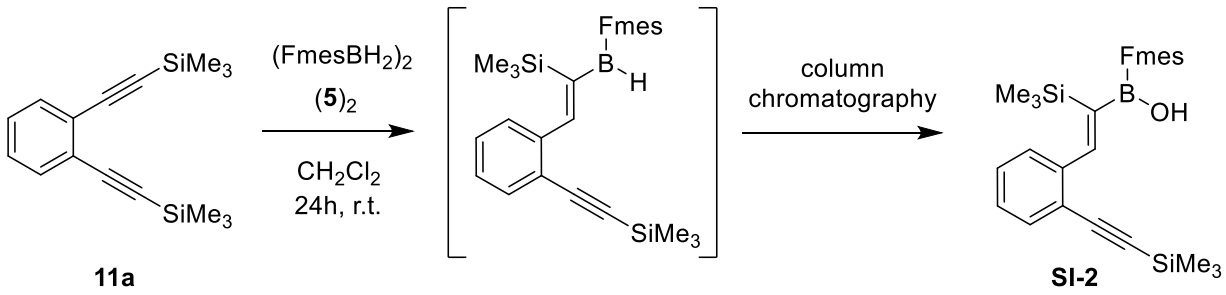


Figure S65: Crystal structure of compound **SI-1**. Thermal ellipsoids are set at 15% probability.

Reaction of bis-acetylene 11a with diborane $(5)_2$ followed by hydrolysis: preparation of compound SI-2



Scheme S15

Bis-acetylene **11a** (270 mg, 1.0 mmol) and borane dimer $(\mathbf{5})_2$ (294 mg, 0.5 mmol) were combined in CH_2Cl_2 (10 mL) and stirred for 24 h at room temperature. Subsequently all volatiles were removed in vacuo and the residue was placed on the top of a chromatography column which was eluted with a mixture of pentane : dichloromethane (5 : 1). Minor bands containing impurities and unreacted starting material were eluted first, followed by a major band of the product **SI-2**. Its evaporation provided a readily crystallizing pale yellow solid (315 mg, 0.54 mmol, 54% yield).

Elemental analysis calculated for $C_{25}H_{26}BF_9OSi_2$ (580.4): C 51.73, H 4.52; found: C 51.87, H 4.58.

^{1}H NMR (600 MHz, $CDCl_3$, 299 K): δ = 8.09 (s, 2H, Fmes), 7.47 (s, 1H, =CH), [7.40 (dm, $^3J_{HH} \approx 7.5$ Hz), 7.23 (tm, $^3J_{HH} \approx 7.5$ Hz), 7.20 (tm, $^3J_{HH} \approx 7.5$ Hz), 7.07 (dm, $^3J_{HH} \approx 7.5$ Hz)](each 1H, C_6H_4), 5.80 (s, 1H, OH), 0.14 (s, $^2J_{SiH} = 7.1$ Hz, 9H, ≡CSiMe_3), 0.03 (s, $^2J_{SiH} = 7.1$ Hz, 9H, =CSiMe_3)

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 299 K): δ = 164.3 (=CH), 145.2 (br, =CB), [143.3 (C), 132.8 (CH), 128.4 (CH), 127.7 (CH), 127.7 (CH), 121.5 (C)](C_6H_4), [142.0 (br, B-C), 134.7 (q, $^2J_{FC} = 32.2$ Hz, *o*-C), 131.8 (q, $^2J_{FC} = 34.3$ Hz, *p*-C), 125.7 (m, CH), 123.5 (q, $^1J_{FC} = 274.8$ Hz, *o*-CF_3), 122.7 (q, $^1J_{FC} = 272.6$ Hz, *p*-CF_3)](Fmes), 102.9 (≡C^{C6H4}), 98.8 (≡CSi), 0.95 (s, $^1J_{SiC} = 52.0$ Hz, ≡CSiMe_3), -0.24 (s, $^1J_{SiC} = 52.0$ Hz, =CSiMe_3).

^{11}B{^{1}H} NMR (192 MHz, $CDCl_3$, 299 K): δ = 46.2 ($\nu_{1/2} \approx 750$ Hz)

^{19}F NMR (564 MHz, $CDCl_3$, 299 K): δ = -57.5 (s, 2F), -63.3 (s, 1F)

^{29}Si{^{1}H} DEPT (99 MHz, $CDCl_3$, 299 K): δ = -5.7 (=CSiMe_3), -17.8 (≡CSiMe_3)

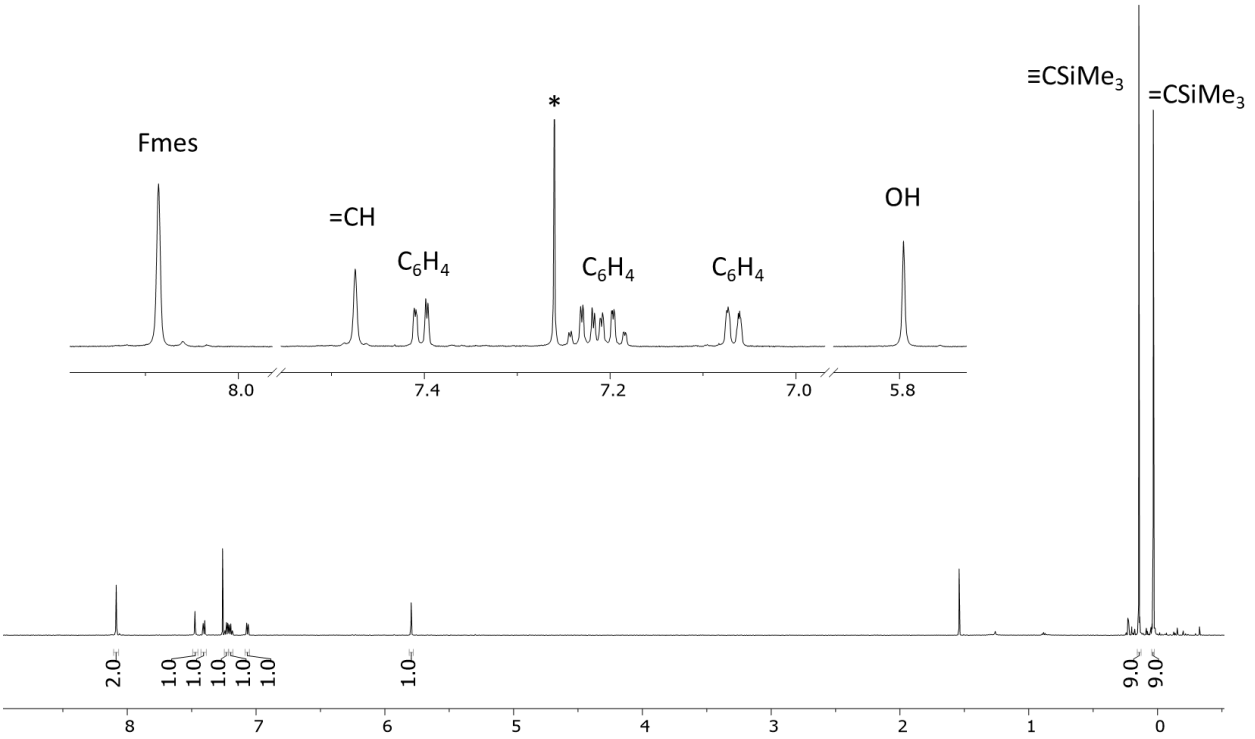


Figure S66: ^{1}H NMR (600 MHz, $CDCl_3$*, 299 K) spectrum of compound **SI-2**.

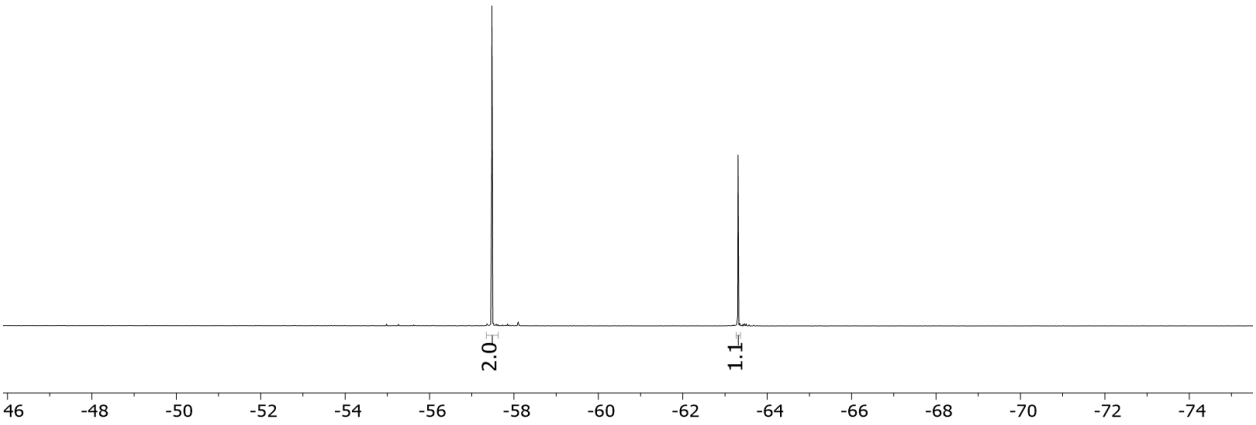


Figure S67: ^{19}F NMR (564 MHz, $CDCl_3$, 299 K) spectrum of compound **SI-2**.

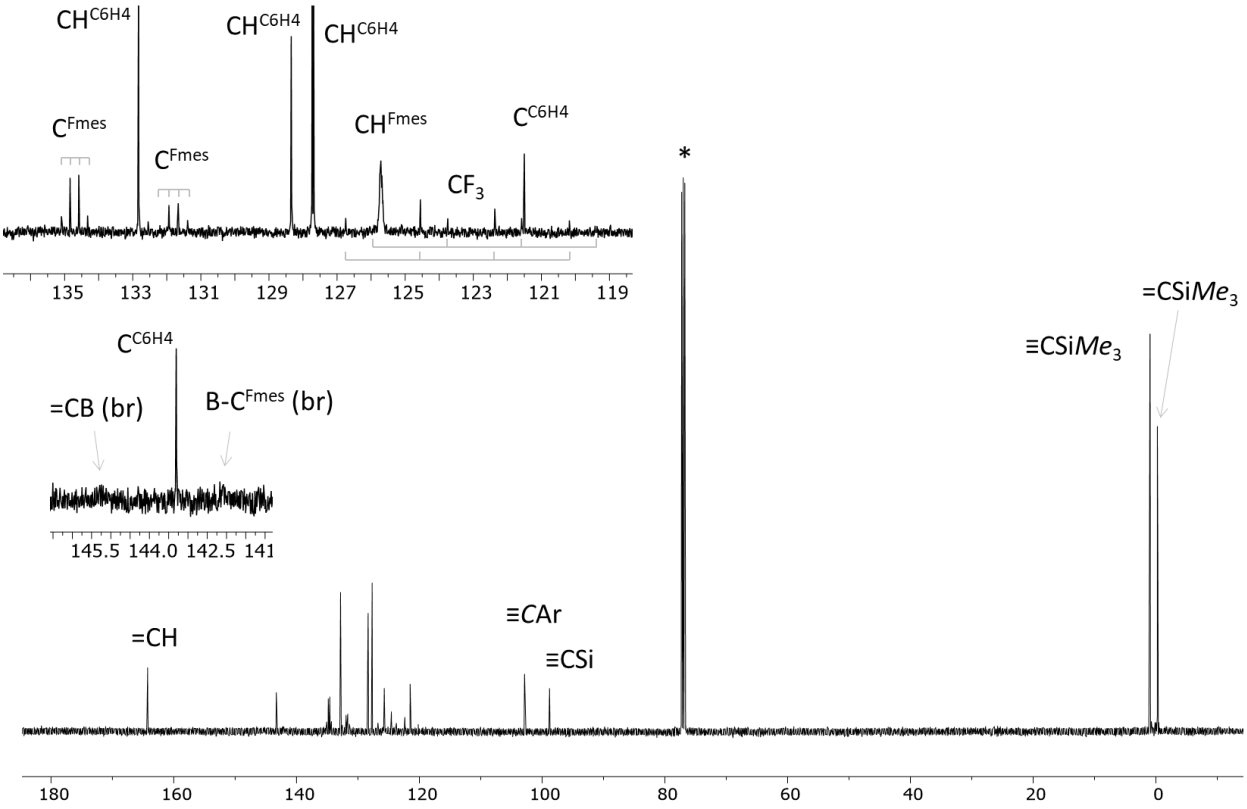


Figure S68: $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$*, 299 K) spectrum of compound **SI-2**.

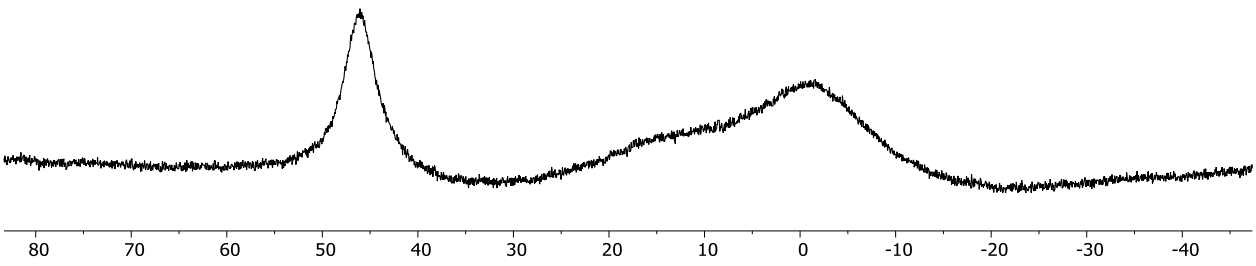


Figure S69: $^{11}B\{^1H\}$ NMR (192 MHz, $CDCl_3$, 299 K) spectrum of compound **SI-2**.

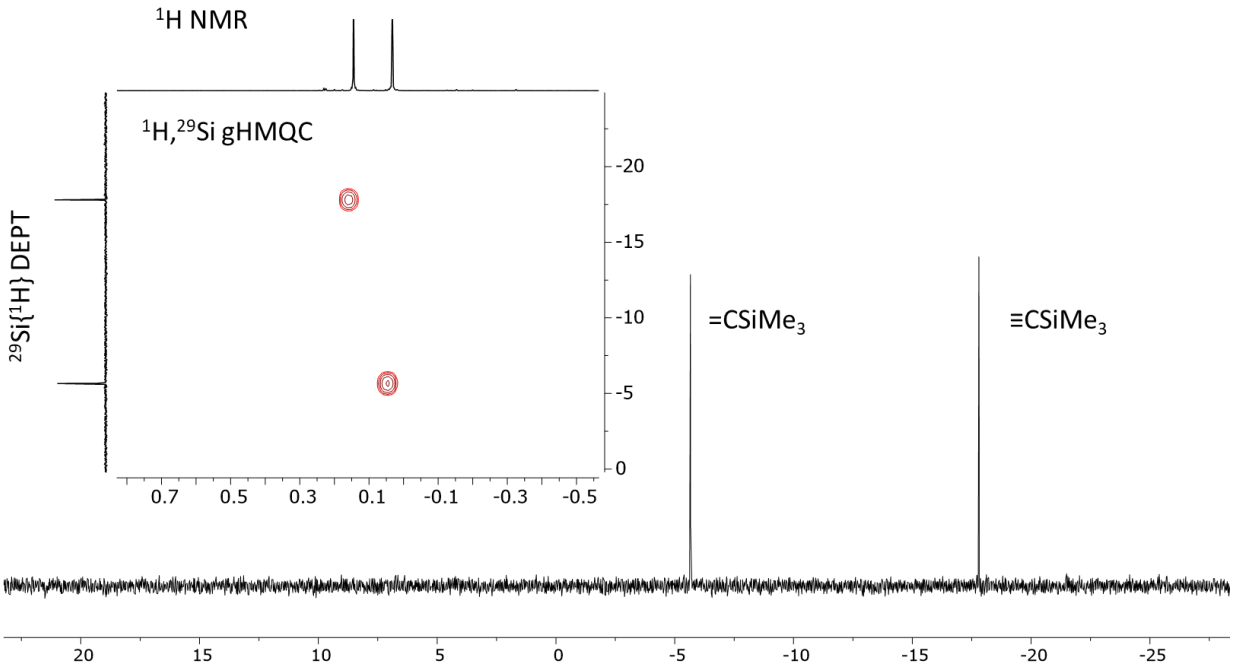


Figure S70: ^{29}Si{^{1}H} DEPT (99 MHz, CD_2Cl_2, 299 K) spectrum and excerpt from **^{1}H,^{29}Si gHMQC** (500 MHz / 99 MHz, $CDCl_3$, 299 K) [projections for F2: **^{1}H NMR** (500 MHz, CD_2Cl_2, 299 K) spectrum and F1: **^{29}Si{^{1}H} DEPT** (99 MHz, CD_2Cl_2, 299 K) spectrum] of compound **SI-2**.

Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of heptane into a solution of compound **SI-2** in diethyl ether at room temperature.

X-ray crystal structure analysis of compound SI-2 (erk9800): A prism-like specimen of $C_{25}H_{26}BF_9OSi_2$, approximate dimensions 0.100 mm x 0.180 mm x 0.200 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker APEX II diffractometer system equipped with a fine-focus sealed tube Cu sealed tube (CuKα, λ = 1.54178 Å) and a graphite monochromator. A total of 1292 frames were collected. The total exposure time was 18.53 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 36267 reflections to a maximum θ angle of 66.69° (0.84 Å resolution), of which 5028 were independent (average redundancy 7.213, completeness = 100.0%, R_{int} = 5.02%, R_{sig} = 2.83%) and 4797 (95.41%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.9779(3) Å, b = 13.7265(3) Å, c = 18.8688(4) Å, volume = 2843.30(12) $Å^3$, are based upon the refinement of the XYZ-centroids of 9937 reflections above 20 σ(I) with 7.965° < 2θ < 133.1°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.884. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7110 and 0.8380. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_12_12_1$, with Z = 4 for the formula unit, $C_{25}H_{26}BF_9OSi_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 407 variables converged at R1 = 2.91%, for the observed data and wR2 = 7.50% for all data. The goodness-of-fit was 1.064. The largest peak in the final difference electron density synthesis was 0.344 $e^-/Å^3$ and the largest hole was -0.175 $e^-/Å^3$ with an RMS deviation of 0.037 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.356 g/cm^3 and F(000), 1192 e^-. CCDC number: 2024709.

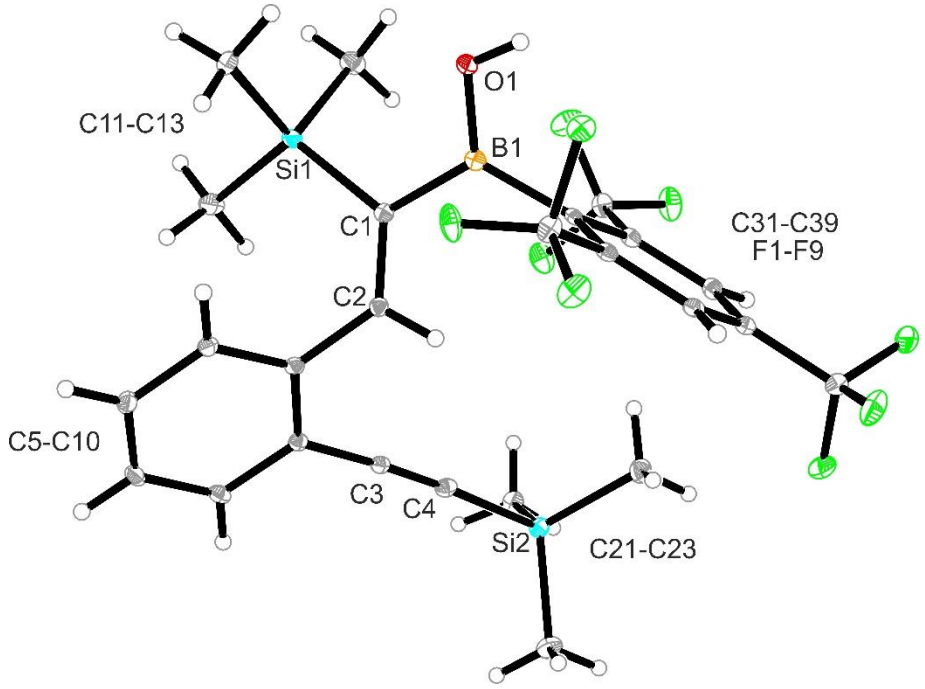


Figure S71: Crystal structure of compound **SI-2**. Thermal ellipsoids are set at 15% probability.

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