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Supplementary Information

Formation of Borata-alkene/Iminium Zwitterions by Ynamine Hydroboration

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General Information:

All syntheses involving air- and moisture sensitive compounds were carried out using standard Schlenk-type glassware (or in a glove box) under an atmosphere of argon. Toluene, CH_2Cl_2, Et_2O, pentane and THF were dried using a Grubbs-type solvent purification system with alumina spheres as the drying agent. All solvents were stored under an argon atmosphere. NMR spectra were recorded on a *Varian* Inova 500 (^{1}H: 500 MHz, ^{13}C: 126 MHz, ^{31}P: 202 MHz, ^{19}F: 470 MHz, ^{11}B: 160 MHz) or a *Varian* Inova 600 (^{1}H: 600 MHz, ^{13}C: 151 MHz, ^{31}P: 243 MHz, ^{19}F: 564 MHz, ^{11}B: 192 MHz, ^{29}Si: 119 MHz). ^{1}H NMR and ^{13}C NMR: chemical shifts δ are given relative to TMS and referenced to the solvent signal. ^{31}P NMR: chemical shifts δ are given relative to H_3PO_4 (external reference), ^{19}F NMR: chemical shifts δ are given relative to $CFCl_3$ (external reference), ^{11}B NMR: chemical shifts δ are given relative to $BF_3{\cdot}Et_2O$ (external reference), ^{29}Si NMR: chemical shifts δ are given relative to TMS (external reference). NMR assignments were supported by additional 1D (NOESY and TOCSY) and 2D (gCOSY, gHSQC and gHMBC) NMR experiments. Elemental analysis data was recorded on Foss-Heraeus CHNO-Rapid. Melting points were measured on TA-instruments DSC Q-20.

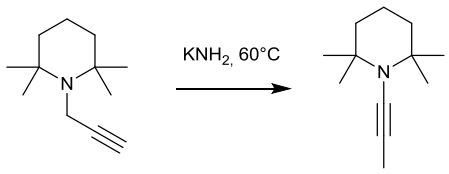
X-Ray diffraction: Data sets for compounds **8a** were collected with a D8 Venture CMOS diffractometer. For compounds **8b**, **10a**, **10b**, **10c** and ***Z*-13** data sets were collected with a Bruker APEX II CCD diffractometer. Programs used: data collection: APEX3 V2016.1-0 (Bruker AXS Inc., **2016**); 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 **5**, **6**, **7** and **10b** 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-97 (G. M. Sheldrick, *Acta Crystallogr*. **2008**, *A64*, 112-122) 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 **6** one C_6F_5 group, for compound **7** one phenyl group and for compound **10b** one N(*i*Pr)$_2$ 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 compound **6** one disordered solvent molecule (probably a mixture of dichloromethane and pentane) was found in the asymmetrical unit and could not be satisfactorily refined. The program SQUEEZE (A. L. Spek (**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 molecule. The CCDC numbers of the compounds are 1843575-1843584

Materials: Compound **4** was prepared according to the known procedure.[1] Compound **9** was synthesized according to the similar known procedure.[2] Bis(pentafluorophenyl)-borane ($HB(C_6F_5)_2$)[3,4] was prepared according to the literature procedure. All other reagents were commercially available and used as received. Trityl tetrakis(pentafluoro-phenyl)borate $[Ph_3C][B(C_6F_5)_4]$ was obtained from ABCR company and used as

received. [(1) E. J. Corey and D. E. Cane, *J. Org. Chem.*, 1970, **35**, 3405-3409. (2) (a) R. B. King, R. M. Murray, R. E. Davis and P. K. Ross, *J. Organomet. Chem.*, 1987, **330**, 115-132; (b) G. Himbert, H. Naßhan and O. Gerulat, *Synthesis*, 1997, 293-294; (c) T. Holtrichter-Rößmann, C. Rösener, J. Hellmann, W. Uhl, E.-U. Würthwein, R. Fröhlich and B. Wibbeling, *Organometallics*, 2012, **31**, 3272-3283. (3) D. J. Parks, R. E. von H. Spence and W. E. Piers, *Angew. Chem. Int. Ed. Engl.*, 1995, **34**, 809-811. (4) D. J. Parks, W. E. Piers and G. P. A. Yap, *Organometallics*, 1998, **17**, 5492-5503.

Synthesis of compound 4

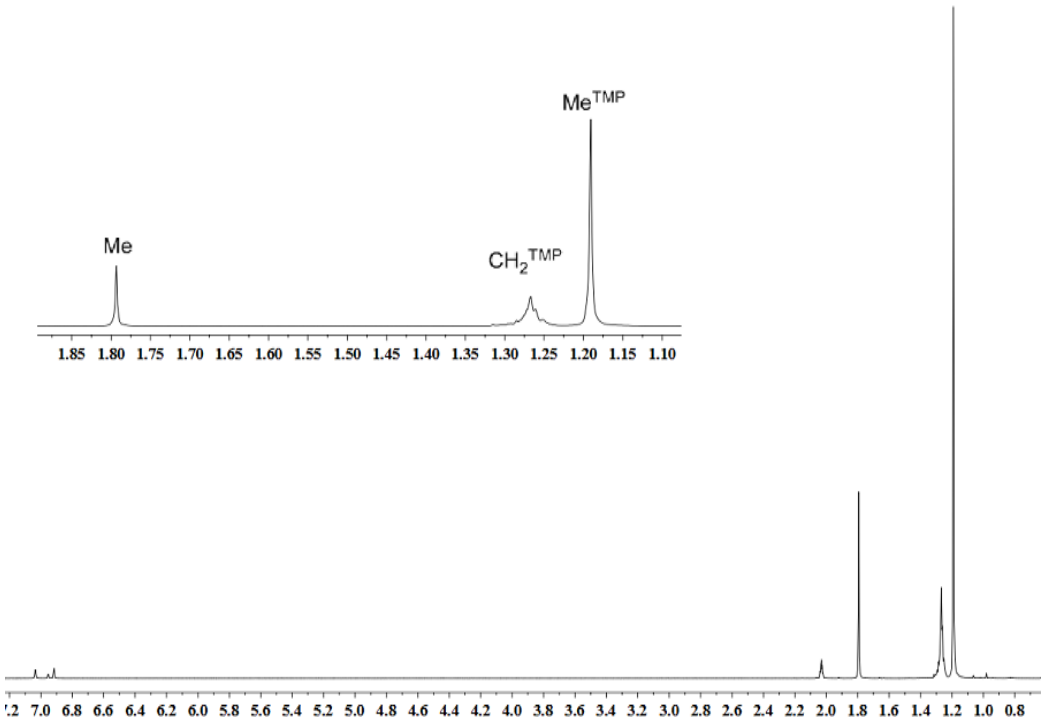


4

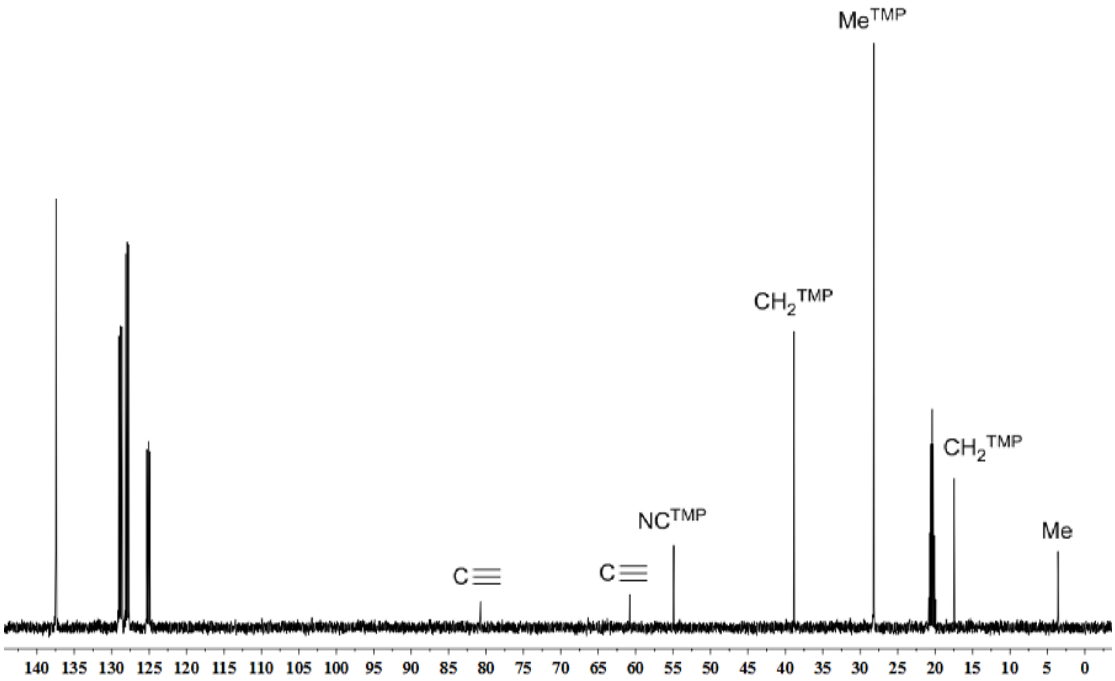
Compound **4** was synthesized by the reported literature procedure (E. J. Corey and D. E. Cane, *J. Org. Chem.*, 1970, **35**, 3405-3409.) It was obtained as a colorless oil after purification by vacuum distillation (yield: 4.50 g, 0.025 mmol, 63%).

^{1}H NMR (600 MHz, 299 K, toluene-d_8) δ = 1.79 (s, 3H, Me), 1.27 (m, 2H, CH_2^{TMP}), 1.26 (m, 4H, CH_2^{TMP}), 1.19 (s, 12H, Me^{TMP}).

^{13}C{^{1}H} NMR (151 MHz, 299 K, toluene-d_8) δ = [80.7, 60.8](C≡), 54.9 (NC^{TMP}), 38.9 (CH_2^{TMP}), 28.2 (Me^{TMP}), 17.5 (CH_2^{TMP}), 3.6 (Me).

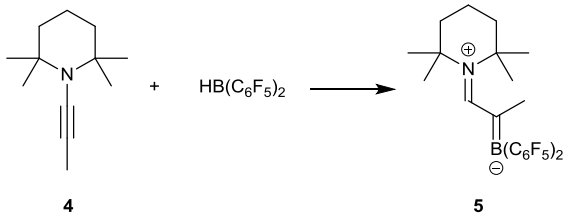


^{1}H NMR (600 MHz, 299 K, toluene-d_8) of compound **4**



$^{13}C\{^1H\}$ NMR (151 MHz, 299 K, toluene-d_8) of compound **4**

Synthesis of compound 5



4 **5**

A mixture of ynamine **4** (17.9 mg, 0.1 mmol) and $HB(C_6F_5)_2$ (34.6 mg, 0.1 mmol) in dichloromethane-d_2 (1 mL) was kept for 10 min at r.t. to give a yellow solution of compound **5**, which was characterized by NMR experiments (see below). Then all volatiles were removed in vacuo to give compound **5** as a yellow solid (52.0 mg, 0.099 mmol, 99 %).

HRMS: m/z calc. for $C_{24}H_{22}BF_{10}N+[H^+]$ 526.1758; found 526.1763.

Melting point: 113 °C

NMR data from the *in situ* generated yellow solution in dichloromethane-d_2:

^{1}H NMR (600 MHz, 299 K, dichloromethane-d_2) δ = 7.56 (br, 1H, N=CH), 2.00 (s, 3H, Me), 1.78 (m, 6H, CH_2^{TMP}), 1.34 (s, 12H, Me^{TMP}).

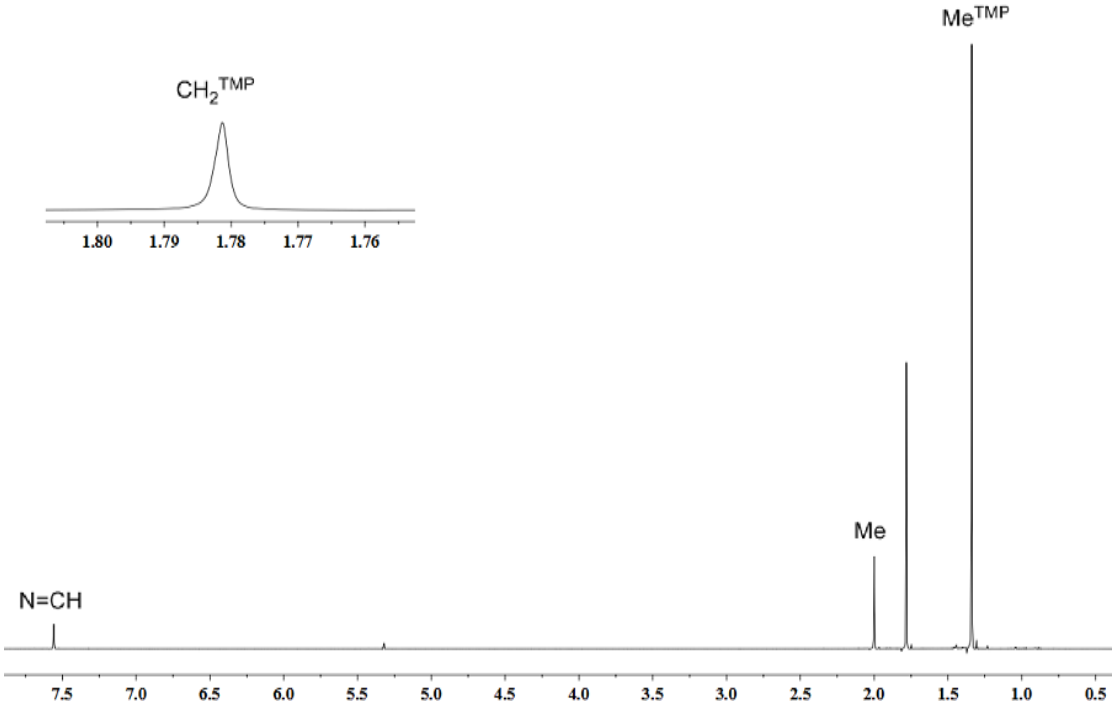
$^{13}C\{^1H\}$ NMR (151 MHz, 299 K, dichloromethane-d_2) δ = 166.6 (N=CH), 145.7 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 141.2 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 137.6 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5),

119.4 (br, C=B), 117.0 (br, *i*-C_6F_5), 59.2 (NC^{TMP}), 36.9 (CH_2^{TMP}), 30.5 (Me^{TMP}), 19.9 (Me), 14.8 (CH_2^{TMP}).

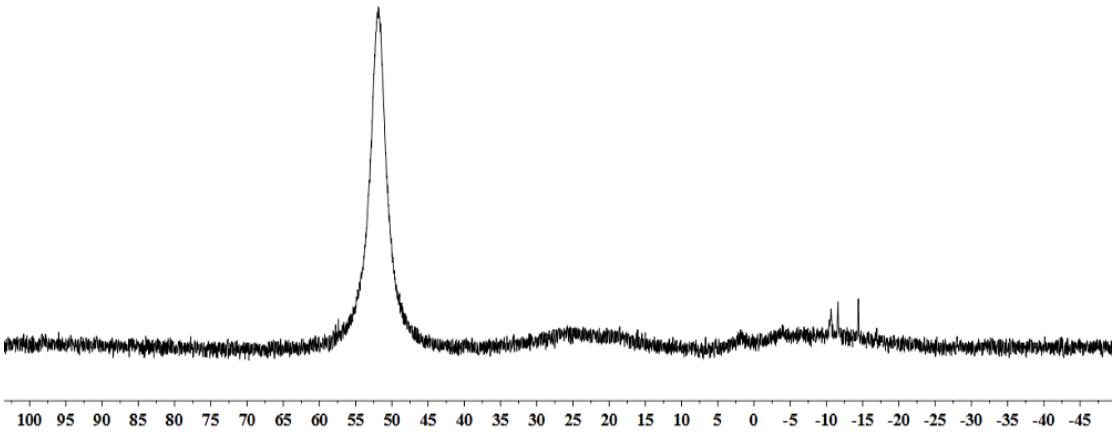
$^{11}B\{^1H\}$ NMR (192 MHz, 299 K, dichloromethane-d_2) δ = 51.9 ($\nu_{1/2}$ ~ 500 Hz).

^{19}F NMR (564 MHz, 299 K, dichloromethane-d_2) δ = -132.2 (m, 2F, *o*-C_6F_5), -155.9 (t, $^3J_{FF}$ = 19.9 Hz, 1F, *p*-C_6F_5), -163.6 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 7.7].

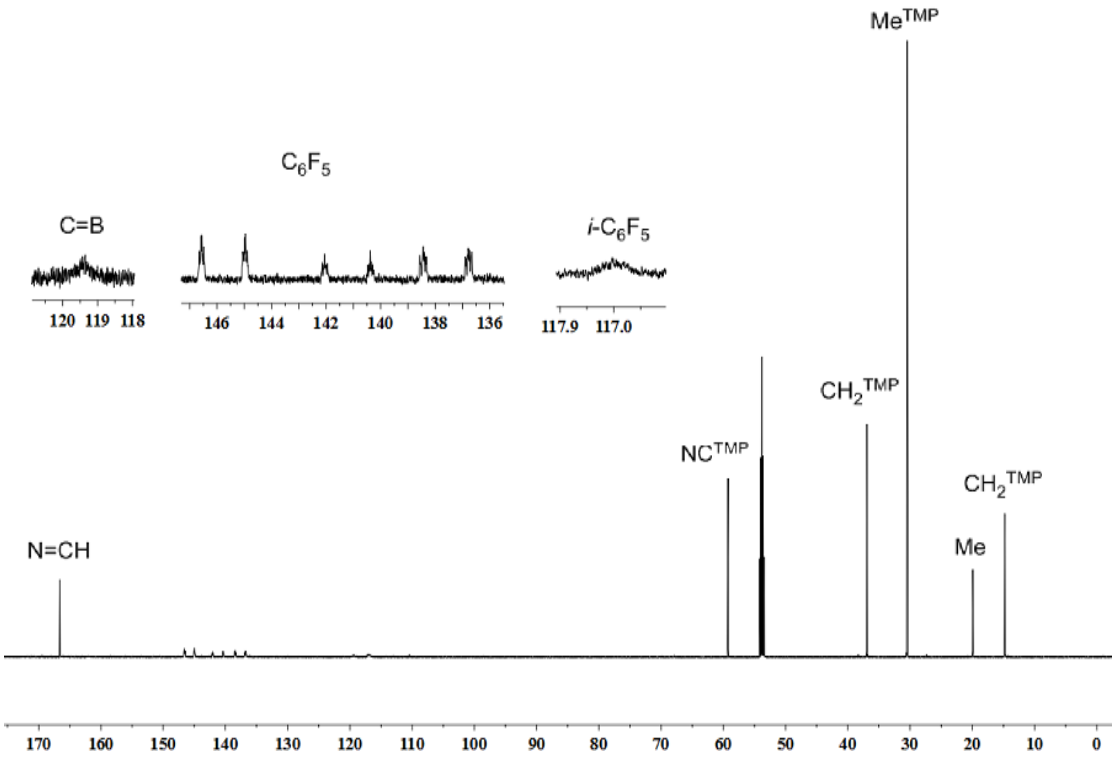
^{19}F NMR (564 MHz, 213 K, dichloromethane-d_2) δ = -131.8 (m, 2F, *o*-C_6F_5), -155.2 (t, $^3J_{FF}$ = 20.8 Hz, 1F, *p*-C_6F_5), -162.8 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{m,p}$ = 7.6]; -132.9 (m, 2F, *o*-C_6F_5), -155.6 (t, $^3J_{FF}$ = 20.6 Hz, 1F, *p*-C_6F_5), -163.2 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{m,p}$ = 7.6].



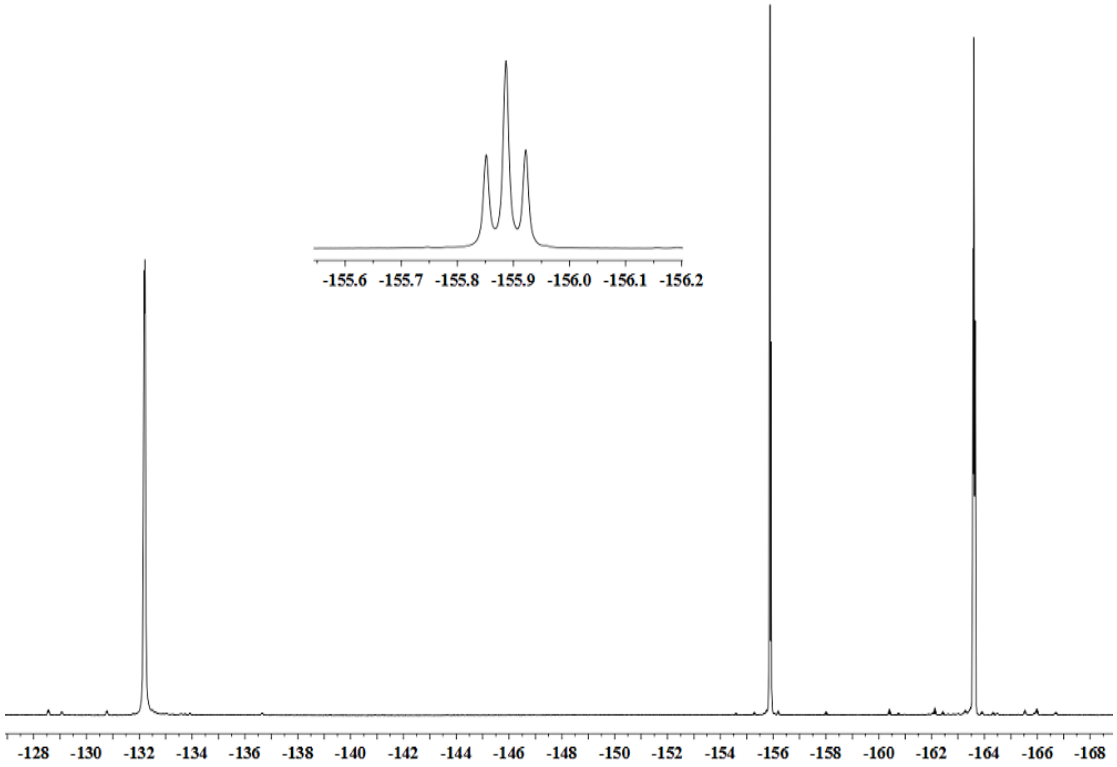
^1H NMR (600 MHz, 299 K, dichloromethane-d_2) spectrum of compound **5**



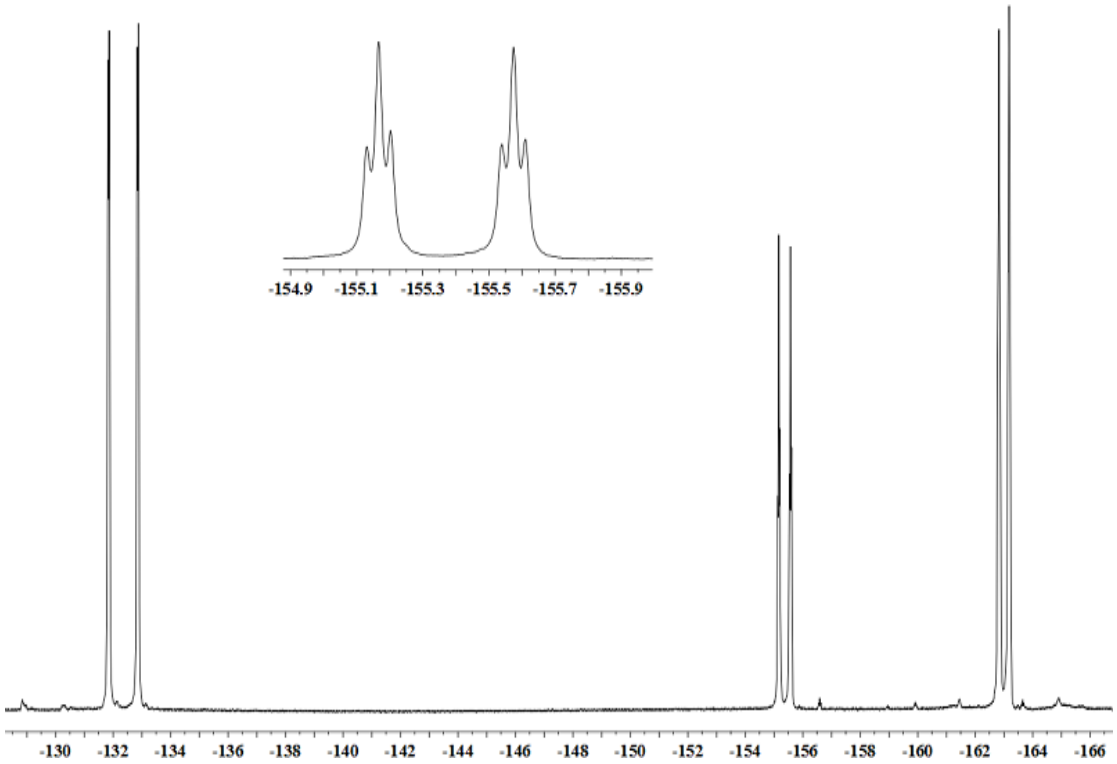
$^{11}B\{^1H\}$ NMR (192 MHz, 299 K, dichloromethane-d_2) spectrum of compound **5**



$^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, dichloromethane-d_2) spectrum of compound **5**



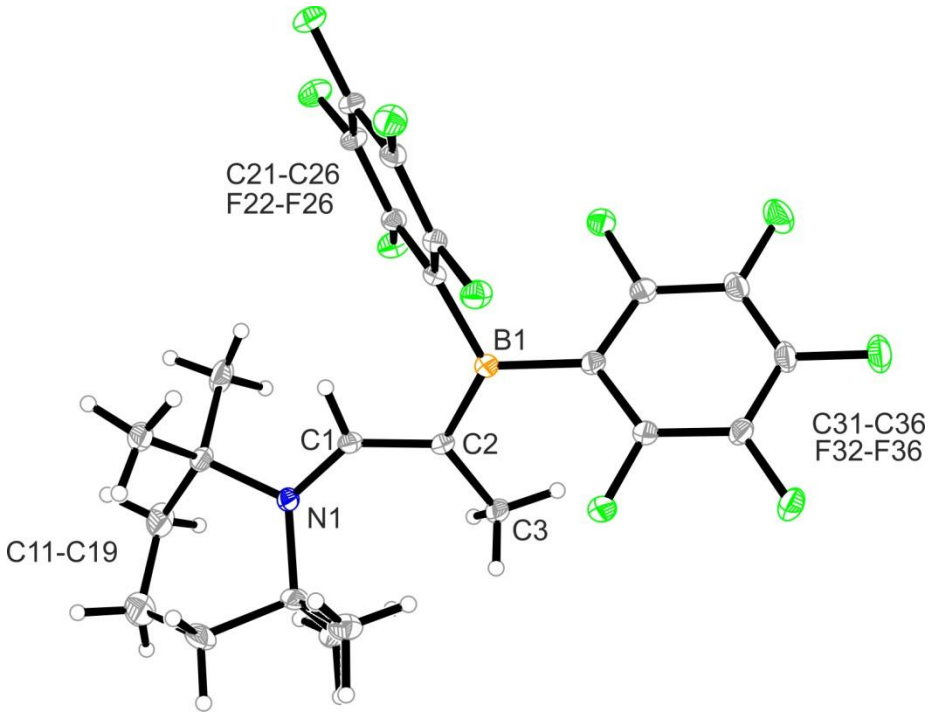
^{19}F NMR (564 MHz, 299 K, dichloromethane-d_2) spectrum of compound **5**



^{19}F NMR (564 MHz, 213 K, dichloromethane-d_2) spectrum of compound **5**

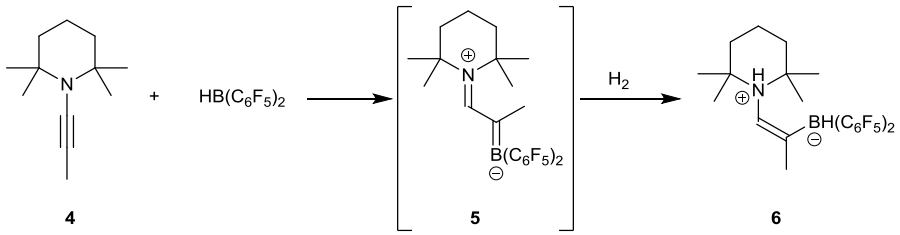
Crystals of compound **5** suitable for the X-ray crystal structure analysis were obtained by slow solvent evaporation from a solution of the yellow solid in benzene at room temperature.

X-ray crystal structure analysis of compound 5 (erk8479): formula $C_{24}H_{22}BF_{10}N$, M = 525.24, yellow crystal, 0.08 x 0.06 x 0.03 mm, a = 13.7333(3), b = 13.9943(3), c = 14.2142(5) Å, α = 75.894(1), β = 88.553(1), γ = 64.471(2)°, V = 2380.8(1) Å^3, ρ_{calc} = 1.465 gcm^{-3}, μ = 0.140 mm^{-1}, empirical absorption correction (0.988 ≤ T ≤ 0.995), Z = 4, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 173(2) K, ω and φ scans, 24670 reflections collected (±h, ±k, ±l), 8215 independent (R_{int} = 0.070) and 5157 observed reflections [I>2σ(I)], 659 refined parameters, R = 0.085, wR^2 = 0.172, max. (min.) residual electron density 0.23 (-0.24) e.Å^{-3}, the position of the hydrogen were calculated and refined as riding atoms.



X-ray crystal structure of compound **5**. Thermal ellipsoids are shown at 15 % probability.

Synthesis of compound 6



A mixture of ynamine **4** (35.9 mg, 0.2 mmol) and $HB(C_6F_5)_2$ (69.2 mg, 0.2 mmol) in dichloromethane-d_2 (1 mL) were stirred for 10 min to give a yellow solution. The yellow solution was filled in a *J*-Young NMR tube, carefully degassed in vacuo and exposed to a H_2 atmosphere (1.5 bar). After 10 min, a colorless solution of compound **6** was obtained and characterized by NMR experiments.
Then all volatiles were removed in vacuo to give compound **6** as a white solid (104.4 mg, 0.198 mmol, 99 %).

HRMS: m/z calc. for $C_{24}H_{24}BF_{10}N+[Na^+]$ 550.1734; found 550.1739.

Melting point: 167 °C

NMR data from the *in situ* generated colorless solution in dichloromethane-d_2:

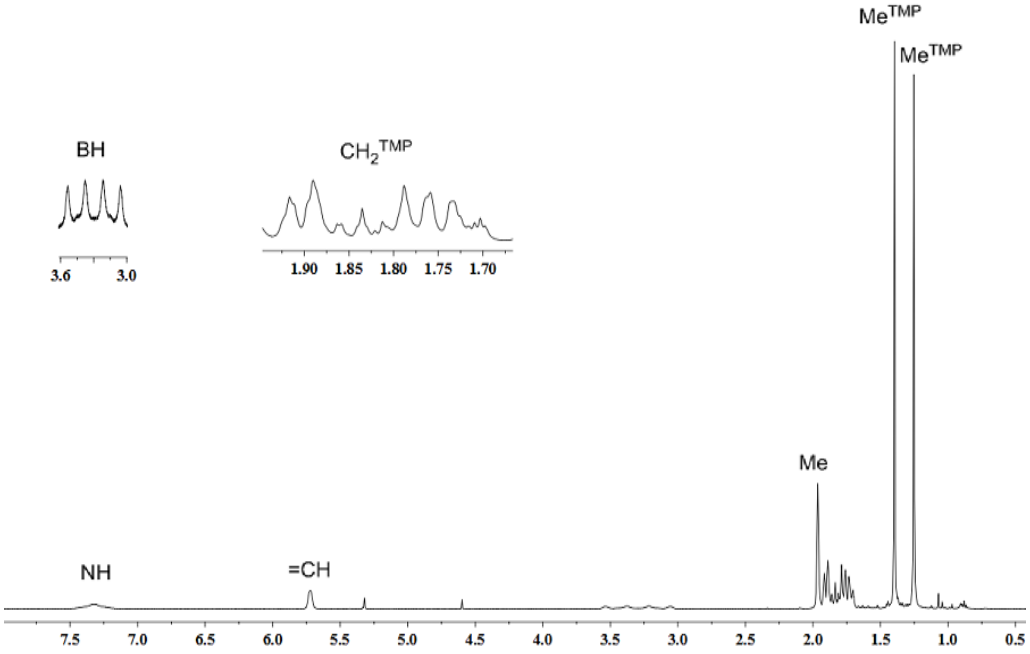
^{1}H NMR (500 MHz, 299 K, dichloromethane-d_2) δ = 7.33 (br, 1H, NH), 5.72 (br, =CH), 3.30 (1:1:1:1 q, $^1J_{BH}$ = 79.3 Hz, BH), 1.96 (s, 3H, Me), [1.90/1.77 (each 2H), 1.82/1.72 (each 1H)](each m, CH_2^{TMP}), [1.40, 1.25](each s, each 6H, Me^{TMP}).

$^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, dichloromethane-d_2) δ = 159.1 (br 1:1:1:1 q, $^{1}J_{BC}$ = 53.0 Hz, BC=), 148.2 (dm, $^{1}J_{FC}$ ~ 240 Hz, C_6F_5), 138.5 (dm, $^{1}J_{FC}$ ~ 245 Hz, C_6F_5), 137.1 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 124.1 (br, *i*-C_6F_5), 116.7 (=CH), 66.6 (NC^{TMP}), 39.3 (CH_2^{TMP}), 30.4 (t, *J* = 3.0 Hz, Me^{TMP}), 23.6 (quint, *J* = 4.0 Hz, Me), 21.6 (Me^{TMP}), 16.3 (CH_2^{TMP}).

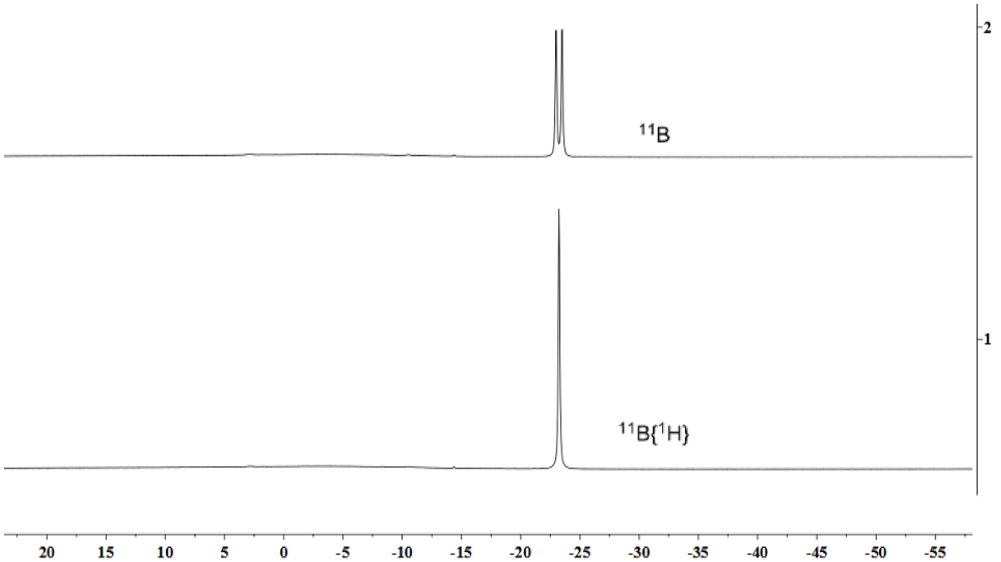
$^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, dichloromethane-d_2) δ = -23.2 ($\nu_{1/2}$ ~ 24 Hz).

^{11}B NMR (160 MHz, 299 K, dichloromethane-d_2) δ = -23.2 (d, $^{1}J_{BH}$ = 79.3 Hz).

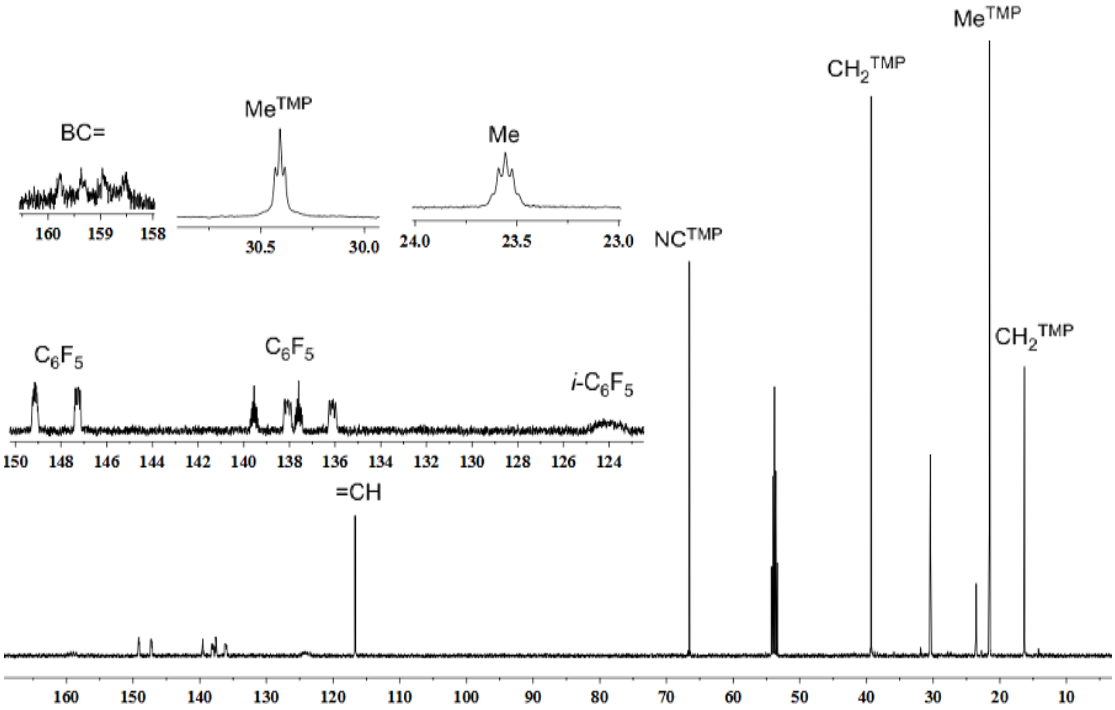
^{19}F NMR (470 MHz, 299 K, dichloromethane-d_2) δ = -131.6 (m, 2F, *o*-C_6F_5), -162.9 (t, $^{3}J_{FF}$ = 20.1 Hz, 1F, *p*-C_6F_5), -166.4 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 3.5].



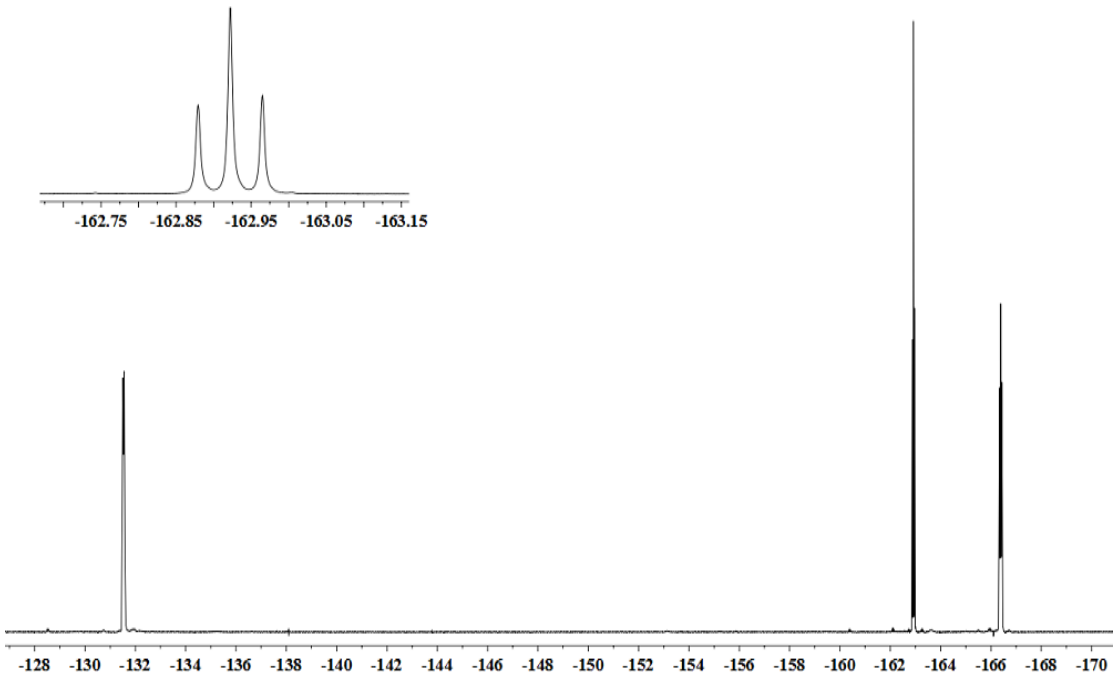
^{1}H NMR (500 MHz, 299 K, dichloromethane-d_2) spectrum of compound **6**



(1) **$^{11}B\{^{1}H\}$ NMR** and (2) **^{11}B NMR** (160 MHz, 299 K, dichloromethane-d_2) spectra of compound **6**



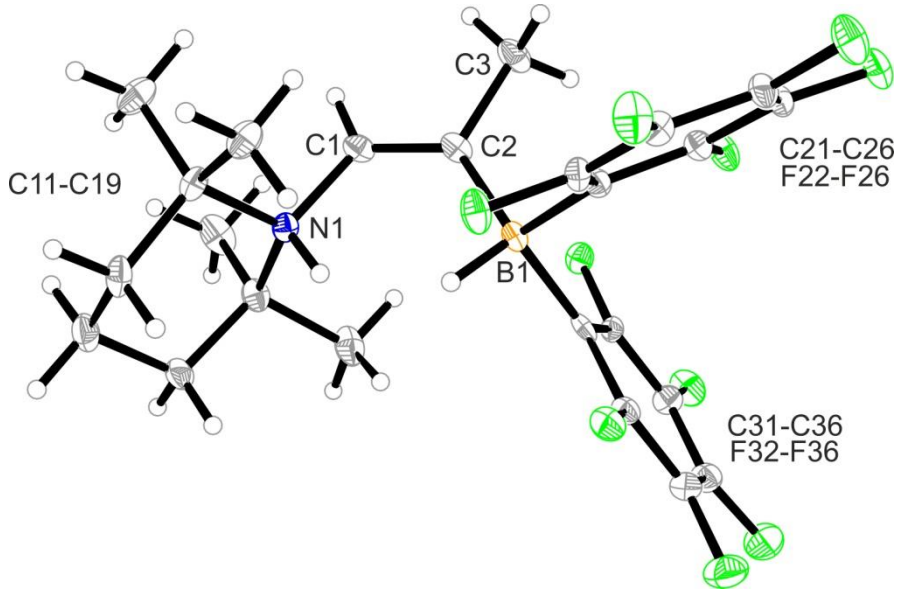
^{13}C{^{1}H} NMR (126 MHz, 299 K, dichloromethane-d_2) spectrum of compound **6**



^{19}F NMR (470 MHz, 299 K, dichloromethane-d_2) spectrum of compound **6**

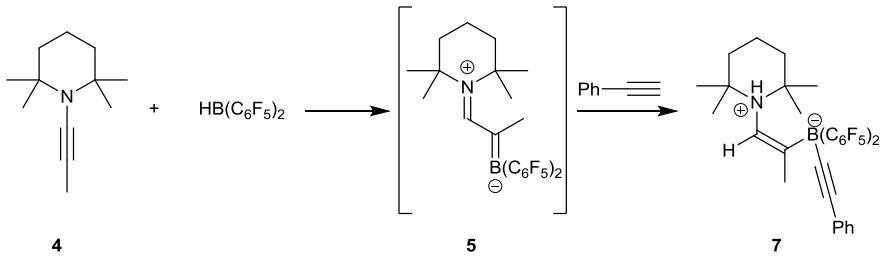
Crystals of compound **6** suitable for the X-ray crystal structure analysis were obtained from slow diffusion of pentane to a solution of the white solid in dichloromethane at -36 °C.

X-ray crystal structure analysis of compound 6 (erk8359): formula $C_{24}H_{24}BF_{10}N$, M = 527.25, colourless crystal, 0.13 x 0.07 x 0.03 mm, a = 12.8034(2), b = 11.3378(2), c = 18.2647(4) Å, β = 105.982(1)°, V = 2548.9(1) Å^3, ρ_{calc} = 1.374 gcm^{-3}, μ = 0.131 mm^{-1}, empirical absorption correction ($0.983 \leq T \leq 0.996$), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 173(2) K, ω and φ scans, 17860 reflections collected ($\pm h$, $\pm k$, $\pm l$), 4421 independent (R_{int} = 0.053) and 2961 observed reflections [$I > 2\sigma(I)$], 438 refined parameters, R = 0.060, wR^2 = 0.126, max. (min.) residual electron density 0.20 (-0.22) e.Å^{-3}, the hydrogen atoms at N1 and B1 were refined freely; others were calculated and refined as riding atoms.



Crystal structure of compound **6**. Thermal ellipsoids are shown at 15 % probability.

Synthesis of compound 7



A mixture of ynamine **4** (53.8 mg, 0.3 mmol) and $HB(C_6F_5)_2$ (103.8 mg, 0.3 mmol) in dichloromethane (2 mL) was stirred for 10 min at r.t. to give a yellow solution. Then phenyl acetylene (30.7 mg, 0.3 mmol) was added and the reaction mixture stirred for 12 h at r.t. All volatiles were removed in vacuo to give a pink solid. The pink solid was washed with cold pentane (1 mL × 3) and dried in vacuo to give compound **7** as a white solid (167.5 mg, 0.267 mmol, 89 %).

HRMS: m/z calc. for $C_{32}H_{28}BF_{10}N$+[Na^+] 650.2047; found 650.2053.

Melting point: 193 ^oC

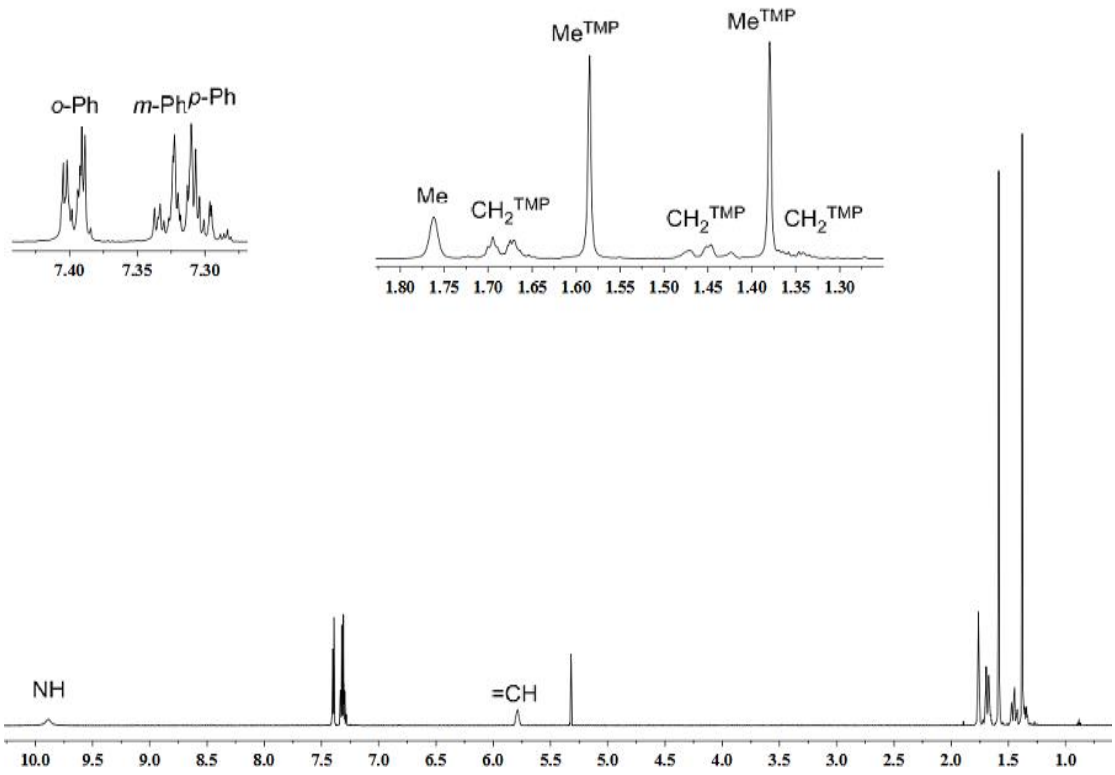
NMR data from a solution of the white solid in dichloromethane-d_2:

^{1}H NMR (600 MHz, 299 K, dichloromethane-d_2) δ = 9.89 (br, 1H, NH), 7.40 (m, 2H, *o*-Ph), 7.32 (m, 2H, *m*-Ph), 7.31 (m, 1H, *p*-Ph), 5.79 (br m, 1H, =CH), 1.76 (s, 3H, Me), [1.69/1.35 (each 1H), 1.68/1.45 (each 2H)](each m, CH_2^{TMP}), [1.58, 1.38](each s, each 6H, Me^{TMP}).

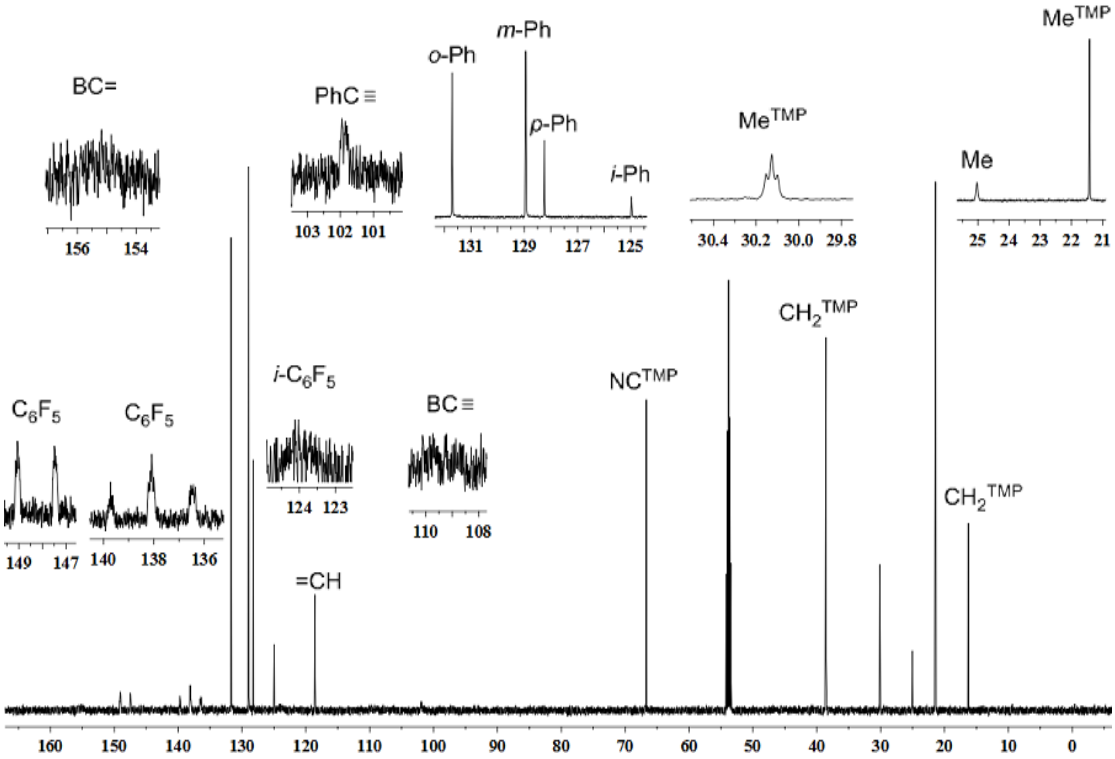
^{13}C{^{1}H} NMR (151 MHz, 299 K, dichloromethane-d_2) δ = 155.3 (br, BC=), 148.3 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 138.9 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 137.3 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 131.7 (*o*-Ph), 128.9 (*m*-Ph), 128.2 (*p*-Ph), 125.0 (*i*-Ph), 124.0 (br, *i*-C_6F_5), 118.6 (=CH), 109.5 (br, BC≡), 101.9 (br, PhC≡), 66.7 (NC^{TMP}), 38.6 (CH_2^{TMP}), 30.1 (t, *J* = 4.1 Hz, Me^{TMP}), 25.0 (br, Me), 21.4 (Me^{TMP}), 16.3 (CH_2^{TMP}). [C_6F_5 not listed,]

^{11}B{^{1}H} NMR (192 MHz, 299 K, dichloromethane-d_2) δ = -19.7 ($\nu_{1/2}$ ~ 20 Hz).

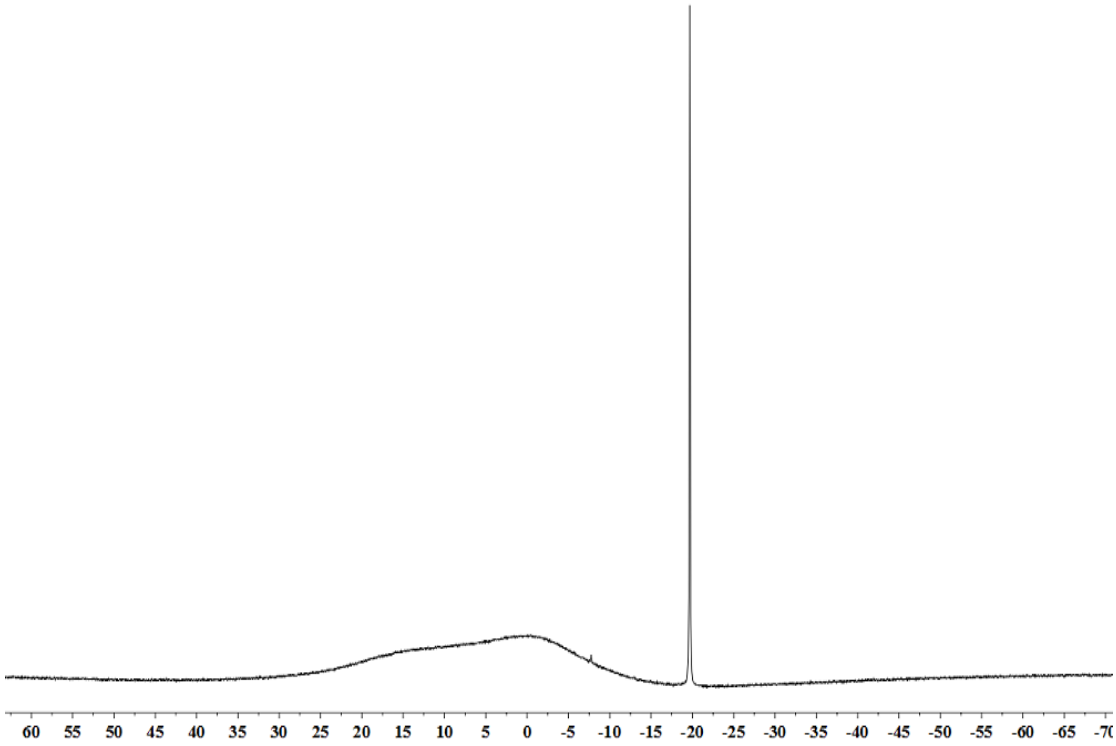
^{19}F NMR (564 MHz, 299 K, dichloromethane-d_2) δ = -130.3 (m, 2F, *o*-C_6F_5), -162.3 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), -166.2 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 3.9].



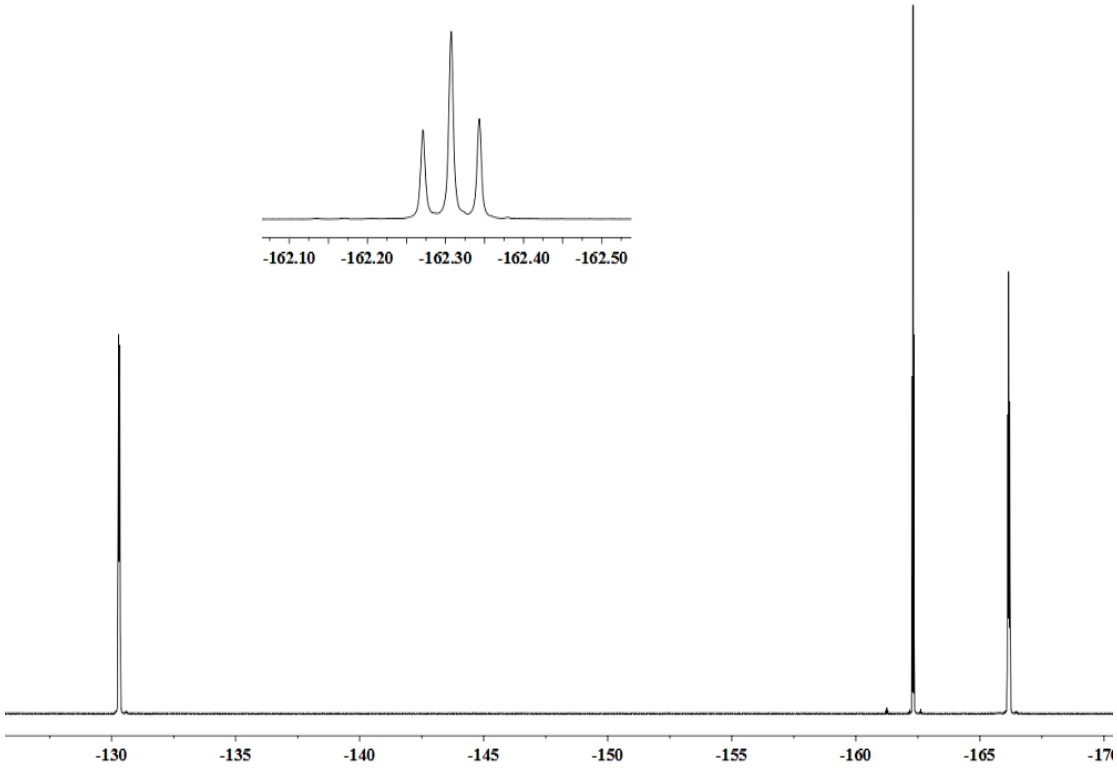
^{1}H NMR (600 MHz, 299 K, dichloromethane-d_2) spectrum of compound **7**



$^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, dichloromethane-d_2) spectrum of compound **7**



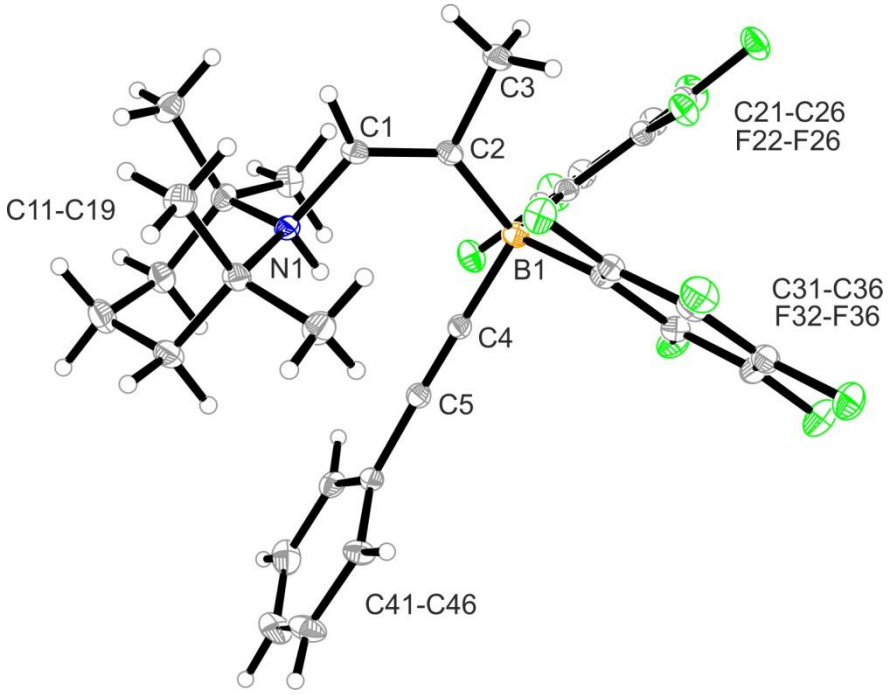
$^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, dichloromethane-d_2) spectrum of compound **7**



^{19}F NMR (564 MHz, 299 K, dichloromethane-d_2) spectrum of compound **7**

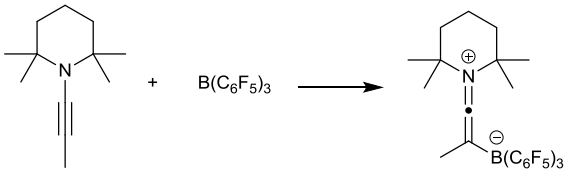
Crystals of compound **7** suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a solution of the white solid in dichloromethane at -36 ^{o}C.

X-ray crystal structure analysis of compound 7 (erk8394): formula $C_{32}H_{28}BF_{10}N$, M = 627.36, colourless crystal, 0.08 x 0.05 x 0.05 mm, a = 8.6741(3), b = 11.6278(3), c = 14.9181(5) Å, α = 83.155(1), β = 85.939(1), γ = 77.609(1)°, V = 1457.5(1) Å^3, ρ_{calc} = 1.429 gcm^{-3}, μ = 0.127 mm^{-1}, empirical absorption correction (0.989 ≤ T ≤ 0.993), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 13670 reflections collected (±h, ±k, ±l), 5035 independent (R_{int} = 0.048) and 3685 observed reflections [I>2σ(I)], 461 refined parameters, R = 0.072, wR^2 = 0.145, max. (min.) residual electron density 0.21 (-0.23) e.Å^{-3}, the hydrogen atom at N1 was refined freely; others positions of the hydrogen atoms were calculated and refined as riding atoms.



Crystal structure of compound **7**. Thermal ellipsoids are shown at 15 % probability.

Synthesis of compound 8a



4 **8a**

A mixture of ynamine **4** (89.7 mg, 0.5 mmol) and $B(C_6F_5)_3$ (256.0 mg, 0.5 mmol) in dichloromethane (2 mL) was stirred for 10 min to give a colorless solution. Then all volatiles were removed in vacuo to give a white solid, which was washed with cold pentane (1 mL × 2) and dried in vacuo to give compound **8a** as a white solid (321.5 mg, 0.465 mmol, 93 %).

HRMS: m/z calc. for $C_{30}H_{21}BF_{15}N+[Na^+]$ 714.1420; found 714.1425.

Decomp.: 222 °C

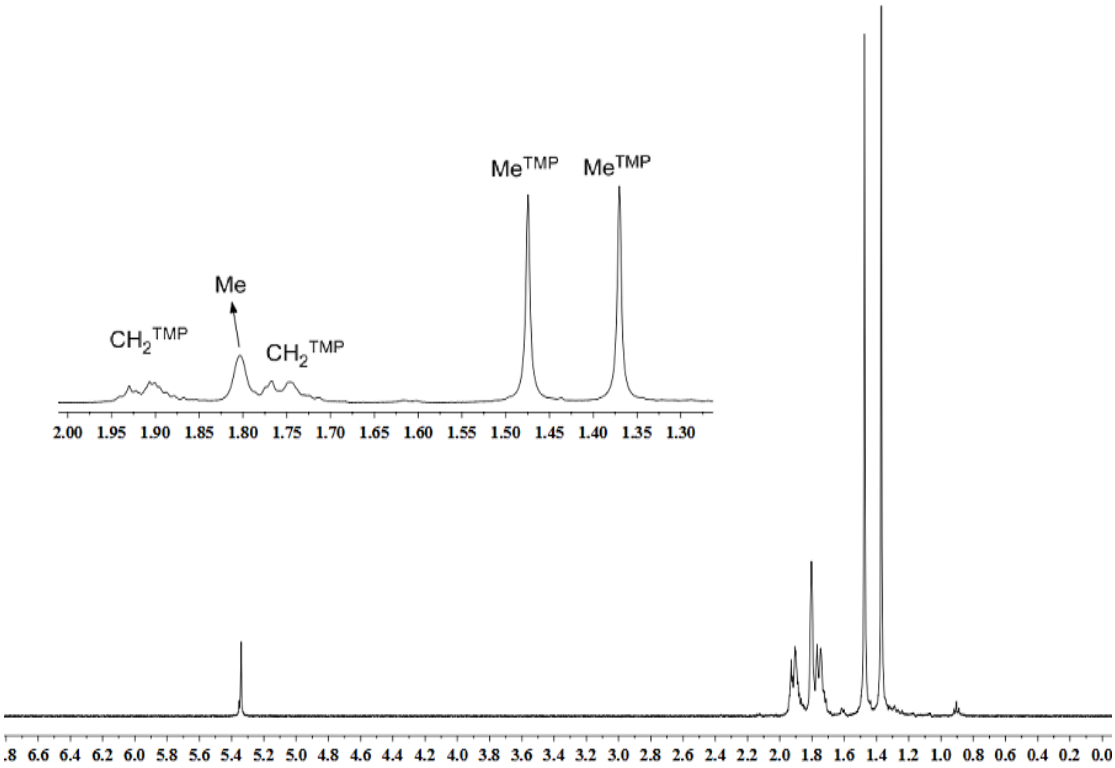
NMR data from a solution of the white solid in dichloromethane-d_2:

^{1}H NMR (500 MHz, 299 K, dichloromethane-d_2) δ = [1.89/1.73 (each 2H), 1.88/1.74 (each 1H)](each m, CH_2^{TMP}), 1.78 (s, 3H, Me), [1.45, 1.35](each s, each 6H, Me^{TMP}).

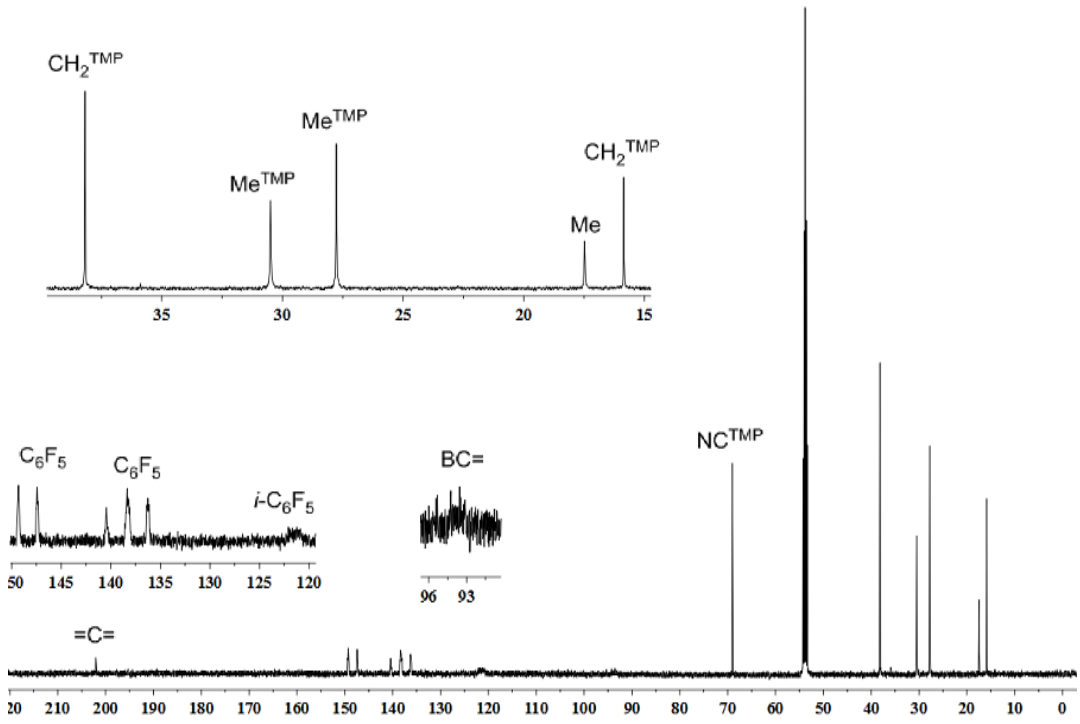
^{13}C{^{1}H} NMR (126 MHz, 299 K, dichloromethane-d_2) δ = 202.1 (=C=), 148.4 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 139.3 (dm, $^1J_{FC}$ ~ 260 Hz, C_6F_5), 137.2 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 121.5 (br, *i*-C_6F_5), 93.5 (br, BC=), 69.0 (NC^{TMP}), 38.2 (CH_2^{TMP}), 30.5 (Me^{TMP}), 27.8 (Me^{TMP}), 17.5 (Me), 15.9 (CH_2^{TMP}).

$^{11}B\{^1H\}$ NMR (160 MHz, 299 K, dichloromethane-d_2) δ = -14.4 ($\nu_{1/2}$ ~ 20 Hz).

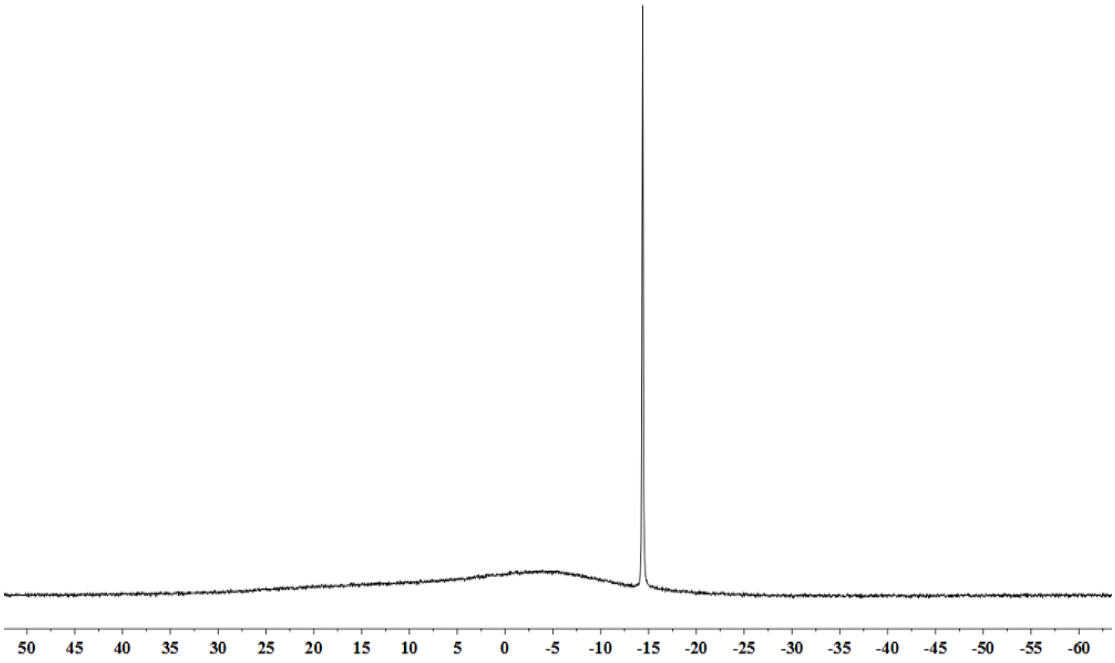
^{19}F NMR (470 MHz, 299 K, dichloromethane-d_2) δ = -130.8 (m, 2F, *o*-C_6F_5), -160.4 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), -165.5 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 5.1].



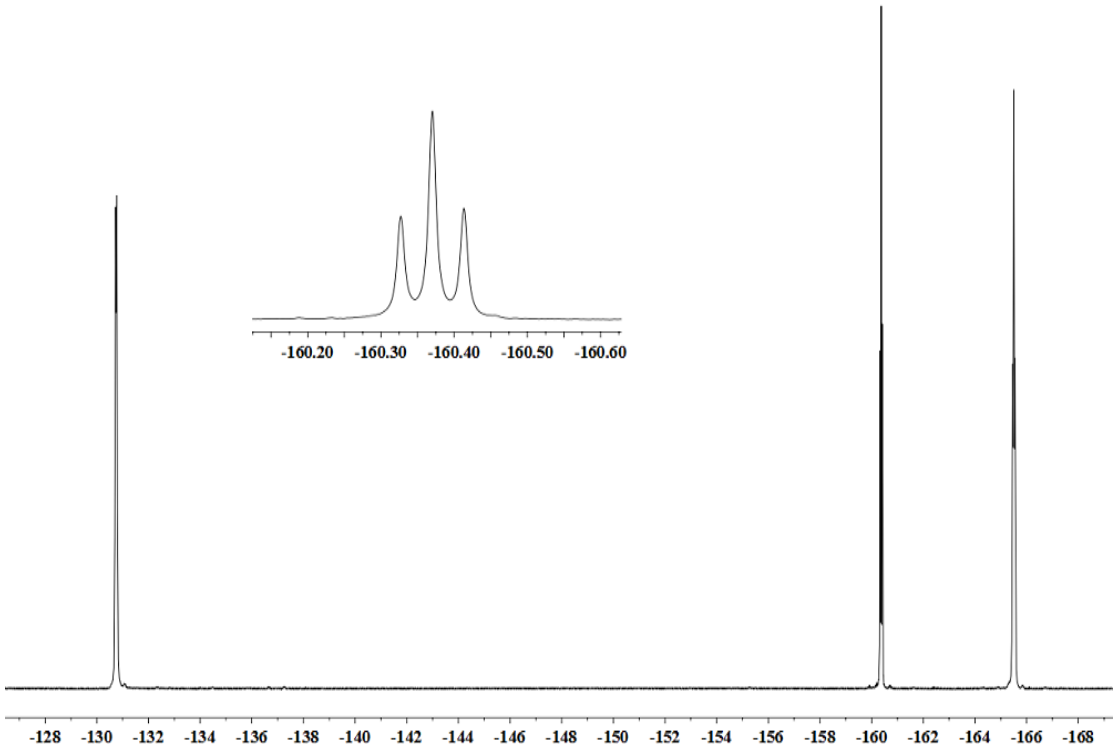
^1H NMR (500 MHz, 299 K, dichloromethane-d_2) spectrum of compound **8a**



$^{13}C\{^1H\}$ NMR (126 MHz, 299 K, dichloromethane-d_2) spectrum of compound **8a**



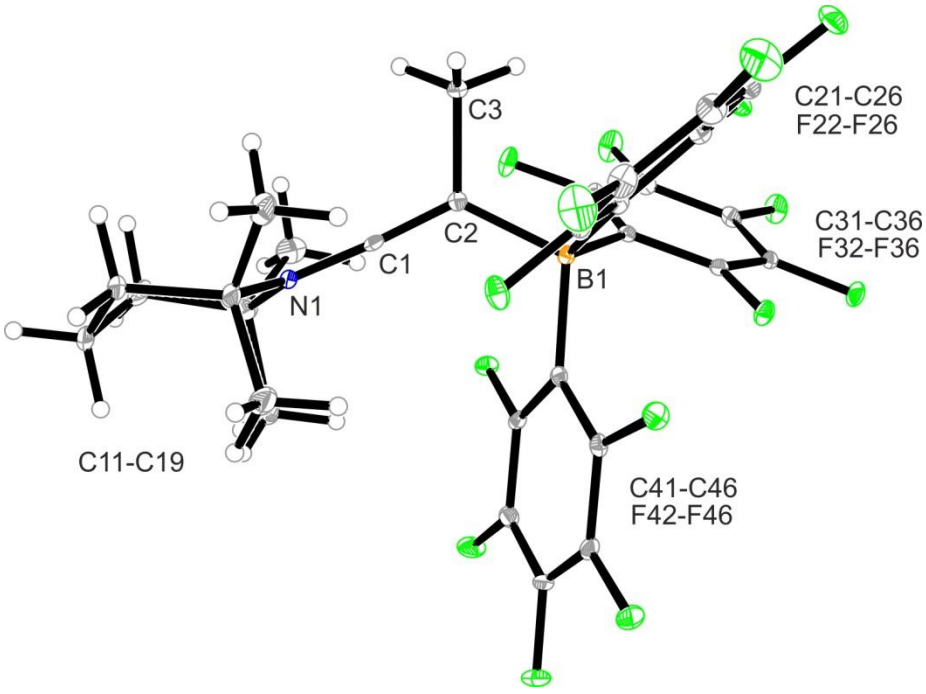
$^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, dichloromethane-d_2) spectrum of compound **8a**



^{19}F NMR (470 MHz, 299 K, dichloromethane-d_2) spectrum of compound **8a**

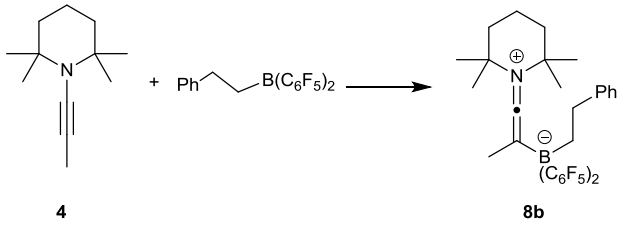
Crystals of compound **8a** suitable for the X-ray crystal structure analysis were obtained by diffusion of pentane to a solution of the white solid in dichloromethane at -36 °C.

X-ray crystal structure analysis of compound 8a (erk8383): A colorless prism-like specimen of $C_{30}H_{21}BF_{15}N$, approximate dimensions 0.104 mm x 0.123 mm x 0.320 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1554 frames were collected. The total exposure time was 15.11 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 77832 reflections to a maximum θ angle of 27.57° (0.77 Å resolution), of which 6574 were independent (average redundancy 11.839, completeness = 99.7%, R_{int} = 3.90%, R_{sig} = 1.80%) and 5555 (84.50%) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.0404(3) Å, b = 16.5379(6) Å, c = 19.3560(7) Å, β = 99.7720(10)°, volume = 2851.91(17) $Å^3$, are based upon the refinement of the XYZ-centroids of 9886 reflections above 20 σ(I) with 4.706° < 2θ < 55.13°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.966. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9500 and 0.9830. 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, $C_{30}H_{21}BF_{15}N$. The final anisotropic full-matrix least-squares refinement on F^2 with 429 variables converged at R1 = 3.51%, for the observed data and wR2 = 8.82% for all data. The goodness-of-fit was 1.044. The largest peak in the final difference electron density synthesis was 0.343 $e^-/Å^3$ and the largest hole was -0.270 $e^-/Å^3$ with an RMS deviation of 0.052 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.610 g/cm^3 and F(000), 1392 e^-.



Crystal structure of compound **8a**.Thermal ellipsoids are shown at 30 % probability.

Synthesis of compound 8b



4 **8b**

A mixture of ynamine **4** (35.9 mg, 0.2 mmol) and $PhCH_2CH_2B(C_6F_5)_2$ (90.0 mg, 0.2 mmol) in dichloromethane (2 mL) was stirred for 10 min to give a pale yellow solution. Then all volatiles were removed in vacuo to give a pale yellow solid. The pale yellow solid was washed with cold pentane (1 mL × 2) and dried in vacuo to give compound **8b** as a white solid (117.0 mg, 0.186 mmol, 93 %).

HRMS: m/z calc. for $C_{32}H_{30}BF_{10}N+[Na^+]$ 652.2204; found 652.2209.

Melting point: 174 ^oC

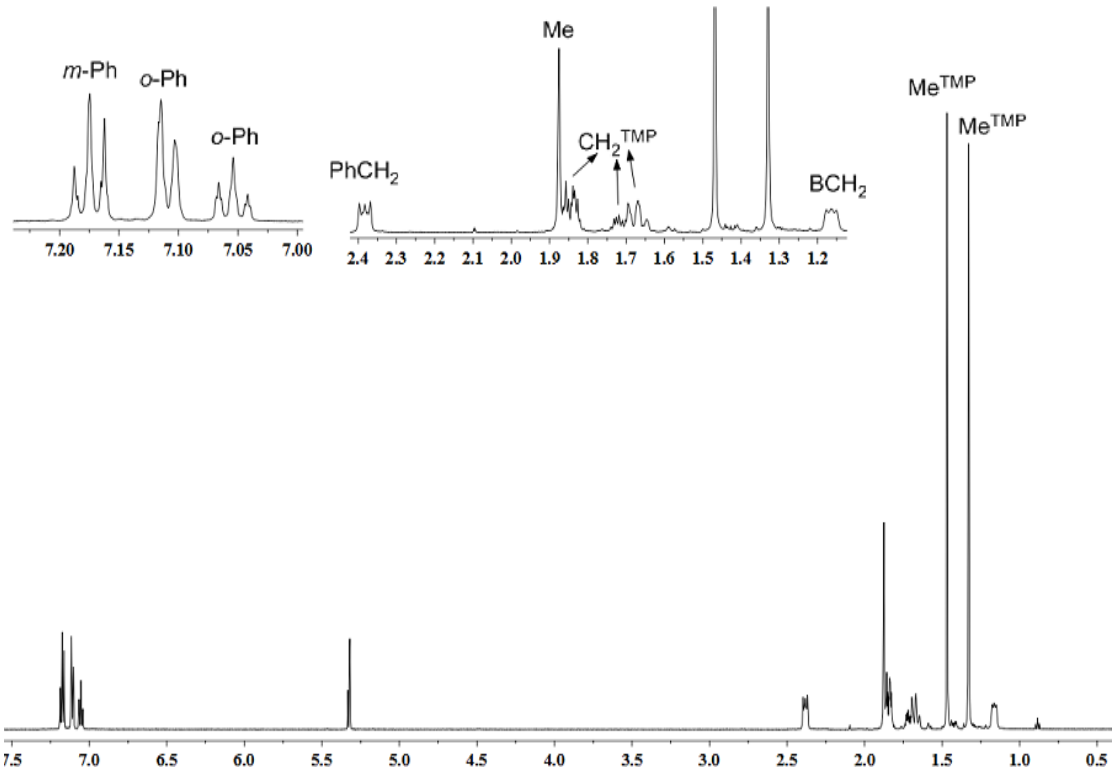
NMR data from a solution of the white solid in dichloromethane-d_2:

^{1}H NMR (600 MHz, 299 K, dichloromethane-d_2) δ = 7.17 (m, 2H, *m*-Ph), 7.11 (m, 2H, *o*-Ph), 7.05 (m, 1H, *p*-Ph), 2.38 (m, 2H, $PhCH_2$), 1.88 (s, 3H, Me), [1.85/1.71 (each 1H), 1.84/1.67 (each 2H)](each m, CH_2^{TMP}), [1.47, 1.33](each s, each 6H, Me^{TMP}), 1.16 (m, 2H, BCH_2).

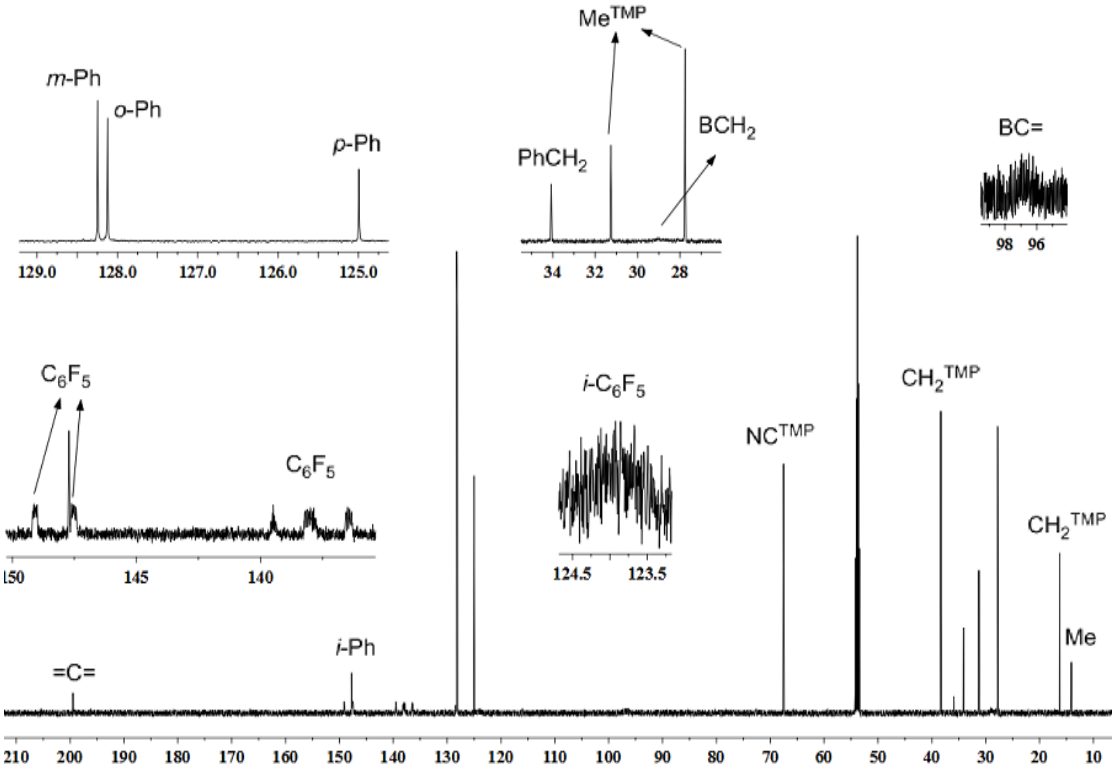
^{13}C{^{1}H} NMR (151 MHz, 299 K, dichloromethane-d_2) δ = 199.5 (=C=), 148.3 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 147.7 (*i*-Ph), 138.7 (dm, $^1J_{FC}$ ~ 245 Hz, C_6F_5), 137.3 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 128.3 (*m*-Ph), 128.1 (*o*-Ph), 125.0 (*p*-Ph), 123.9 (br, *i*-C_6F_5), 96.8 (br, BC=), 67.5 (NC^{TMP}), 38.3 (CH_2^{TMP}), 34.1 ($PhCH_2$), 31.3 (Me^{TMP}), 28.9 (br, BCH_2), 27.8 (Me^{TMP}), 16.2 (CH_2^{TMP}), 14.1 (Me).

^{11}B{^{1}H} NMR (192 MHz, 299 K, dichloromethane-d_2) δ = -11.7 ($\nu_{1/2}$ ~ 70 Hz).

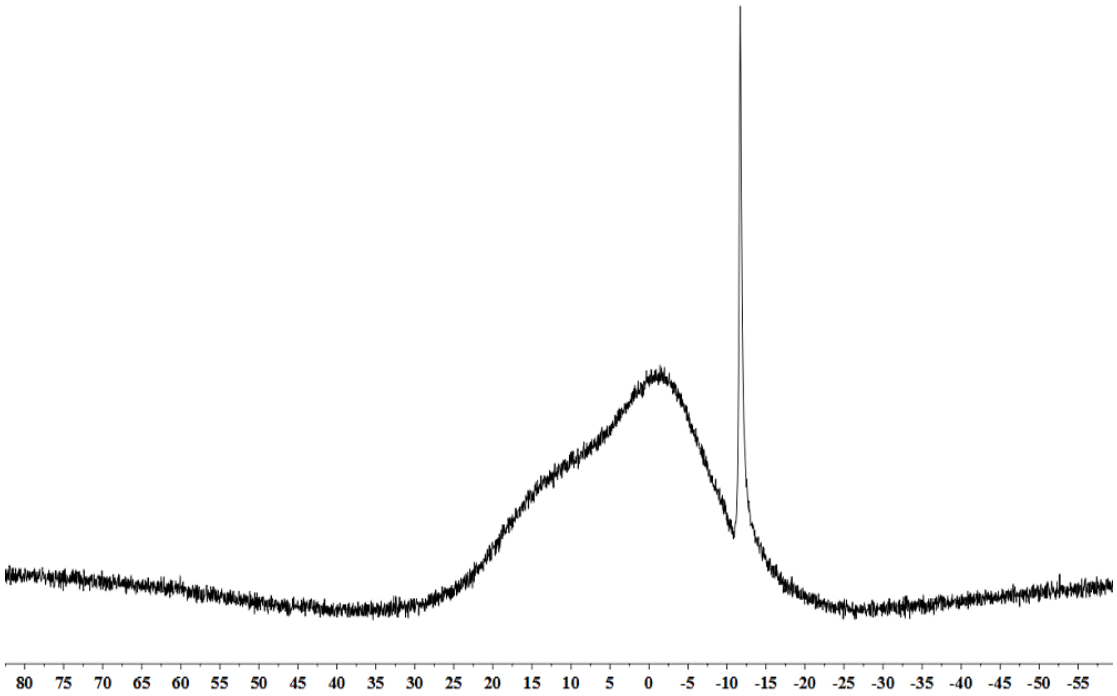
^{19}F NMR (564 MHz, 299 K, dichloromethane-d_2) δ = -131.9 (m, 2F, *o*-C_6F_5), -162.1 (t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), -165.6 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 3.5].



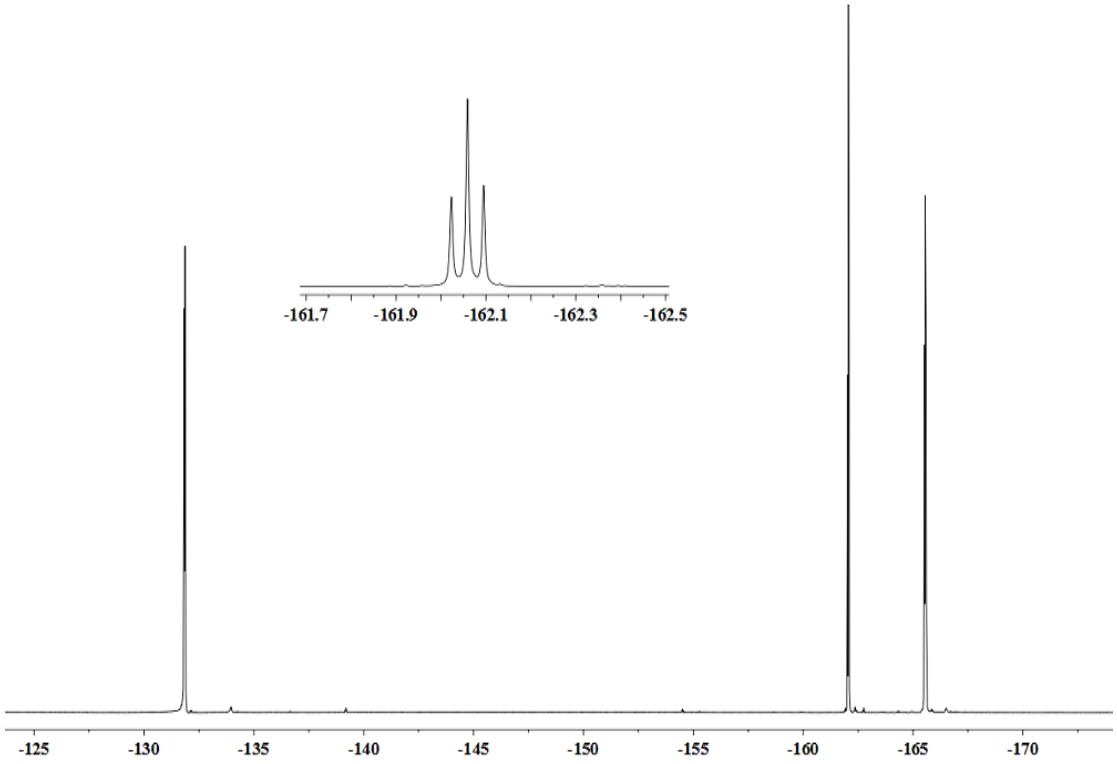
^{1}H NMR (600 MHz, 299 K, dichloromethane-d_2) spectrum of compound **8b**



^{13}C{^{1}H} NMR (151 MHz, 299 K, dichloromethane-d_2) spectrum of compound **8b**



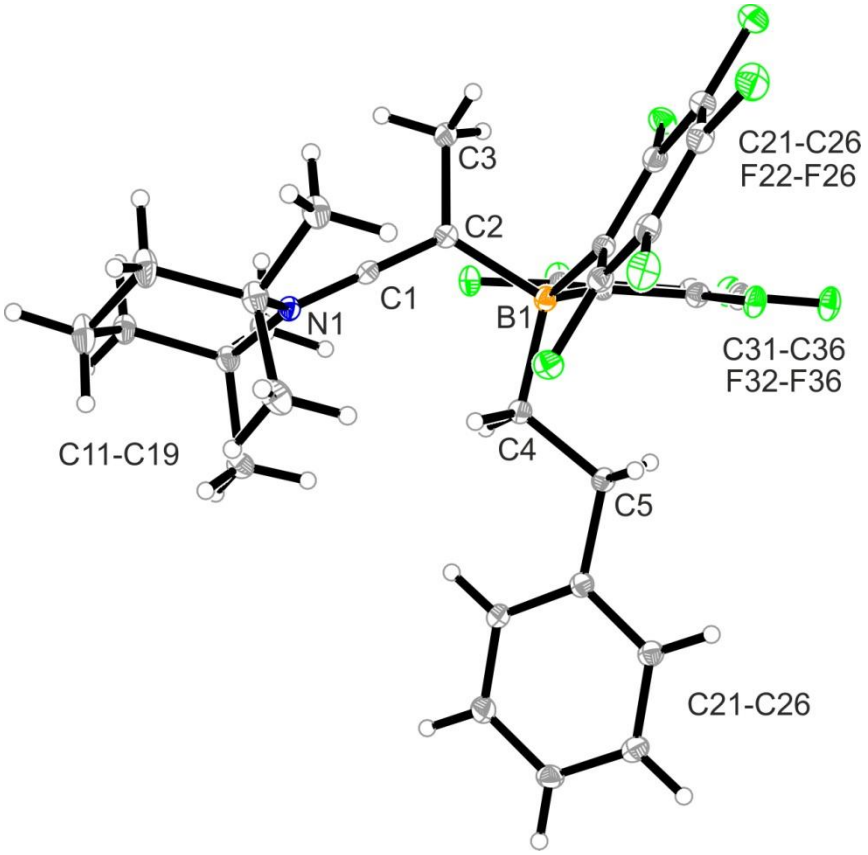
$^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, dichloromethane-d_2) spectrum of compound **8b**



^{19}F NMR (564 MHz, 299 K, dichloromethane-d_2) spectrum of compound **8b**

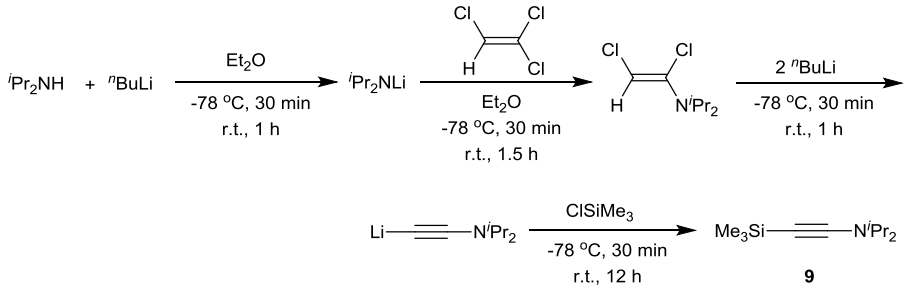
Crystals of compound **8b** suitable for the X-ray crystal structure analysis were obtained by diffusion of pentane to a solution of the white solid in dichloromethane at -36 °C.

X-ray crystal structure analysis of compound 8b (erk8875): A colorless plate-like specimen of $C_{32}H_{30}BF_{10}N$, approximate dimensions 0.020 mm x 0.120 mm x 0.140 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 36674 reflections to a maximum θ angle of 66.79° (0.84 Å resolution), of which 5166 were independent (average redundancy 7.099, completeness = 99.7%, R_{int} = 10.40%, R_{sig} = 7.78%) and 3527 (68.27%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.5438(16)Å, b = 14.550(2) Å, c = 19.382(3) Å, β = 101.141(11)°, volume = 2917.4(8) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8600 and 0.9780. 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, $C_{32}H_{30}BF_{10}N$. The final anisotropic full-matrix least-squares refinement on F^2 with 402 variables converged at R1 = 5.64%, for the observed data and wR2 =16.20% for all data. The goodness-of-fit was 1.017. The largest peak in the final difference electron density synthesis was 0.256 $e^-/Å^3$ and the largest hole was -0.285 $e^-/Å^3$ with an RMS deviation of 0.060 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.433 g/cm^3 and F(000), 1296 e^-.



Crystal structure of compound **8b**. Thermal ellipsoids are shown at 15 % probability.

Synthesis of compound 9

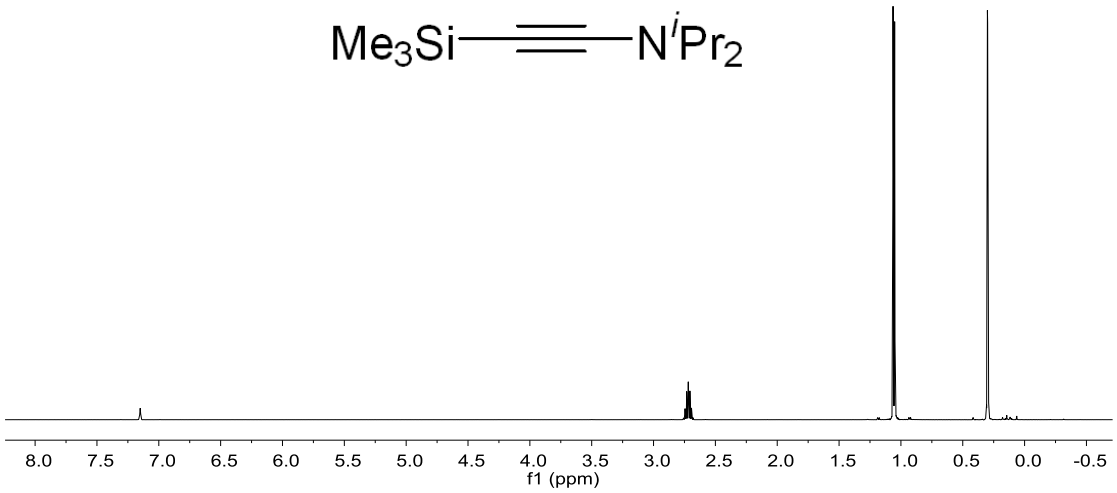


The synthesis of compound **9** was carried out according to the literature [(a) R. B. King, R. M. Murray, R. E. Davis and P. K. Ross, *J. Organomet. Chem.*, 1987, **330**, 115-132; (b) G. Himbert, H. Naßhan and O. Gerulat, *Synthesis*, 1997, 293-294; (c) T. Holtrichter-Rößmann, C. Rösener, J. Hellmann, W. Uhl, E.-U. Würthwein, R. Fröhlich and B. Wibbeling, *Organometallics*, 2012, **31**, 3272-3283.] In an Argon atmosphere, one equiv. of ^{n}BuLi was slowly added to the Et_2O solution (50 mL) of diisopropylamine (7 mL, 50 mmol) at −78 °C, and then the solution was allowed to warm to room temperature and stirred for 1 h. The solution formed was slowly added to a solution of one equiv. of trichloroethylene (6.6 g, 50 mmol) in 50 mL of Et_2O at −78 °C, and then the solution was allowed to warm to room temperature and stirred for 1.5 h. The solution obtained was again cooled to −78 °C, and two equiv. of ^{n}BuLi was slowly added. After stirring at room temperature for 1 h and cooling to −78 °C, one equiv. of chlorotrimethylsilane (6.4 mL, 50 mmol) was added to the black suspension at −78 °C, and then stirred for further 12 h. The solvent was removed under vacuum, and the resulting mixture was directly distilled under vacuum (34 °C/0.5 mbar) to yield the colorless liquid product **9** (2 g, 20 %). The ynamine product is air and moisture sensitive and should be stored in glovebox at −35 °C.

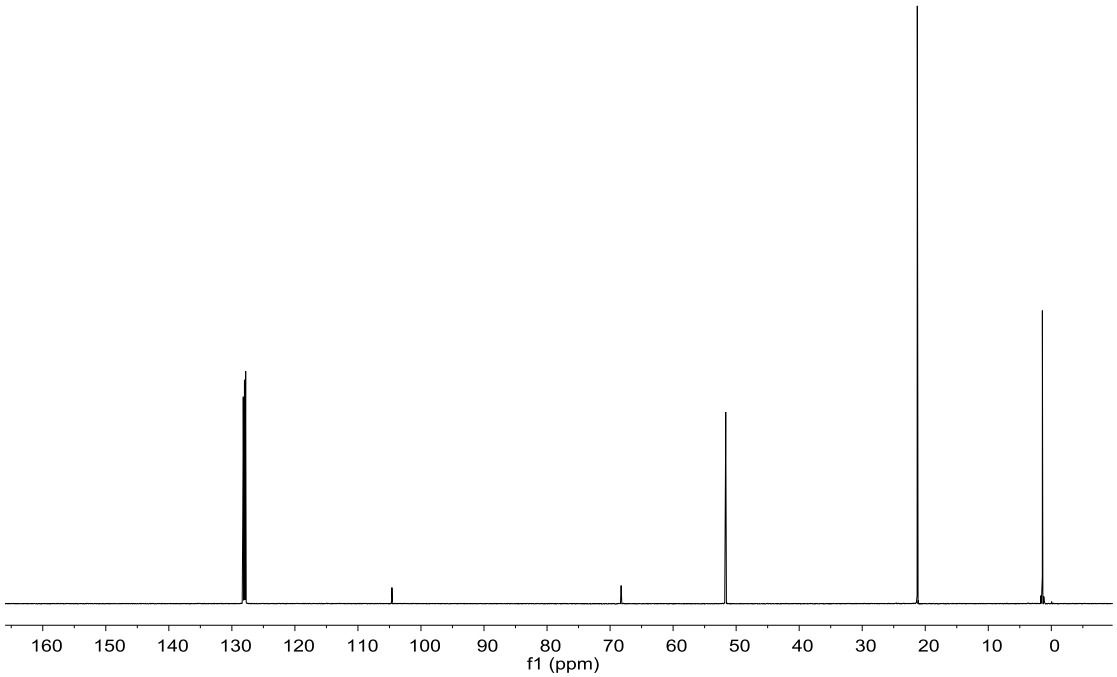
^{1}H NMR (500 MHz, 299 K, C_6D_6, 7.15 ppm): δ = 2.72 (sept, $^{3}J_{HH}$ = 6.6 Hz, 2H, C*H*$(CH_3)_2$), 1.06 (d, $^{3}J_{HH}$ = 6.6 Hz, 12H, CH(C*H*$_3)_2$), 0.30 (s, 9H, Si(C*H*$_3)_3$).

^{13}C{^{1}H} NMR (126 MHz, 299 K, C_6D_6, 128.0 ppm): δ = 104.6 (≡*C*N), 68.3 (*C*≡), 51.7 (*C*H$(CH_3)_2$), 21.3 (CH(*C*H$_3)_2$), 1.4 (Si(*C*H$_3)_3$).

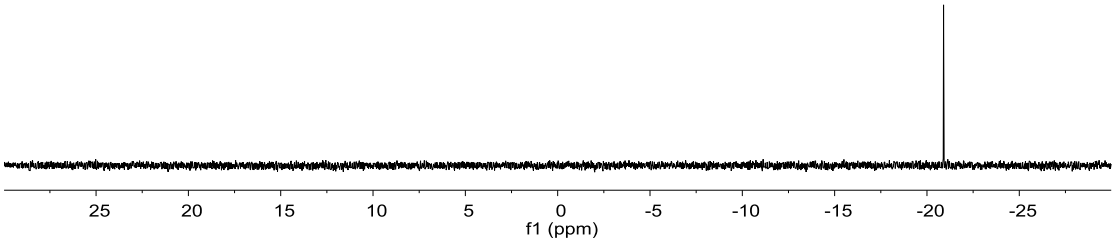
^{29}Si{^{1}H} dept NMR (119 MHz, 299 K, C_6D_6): δ = −20.9 (s).



^{1}H NMR (500 MHz, 299 K, C_6D_6) spectrum of compound **9**.

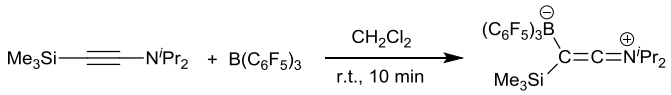


^{13}C{^{1}H} NMR (126 MHz, 299 K, C_6D_6) spectrum of compound **9**.



^{29}Si{^{1}H} dept NMR (119 MHz, 299 K, C_6D_6) spectrum of compound **9**.

Synthesis of compound 10a



9 **10a**

Compound **9** (99 mg, 0.5 mmol) and $B(C_6F_5)_3$ (256 mg, 0.5 mmol) were mixed in CH_2Cl_2 (3 mL) at room temperature. After stirring for 1 h, pentane (3 mL) was added to the clear pale yellow solution. The resulting clear solution was stored at −35 °C to give colorless crystals. Yield: 284 mg, 80 %.

Elemental analysis: calc. for $C_{29}H_{23}BNSiF_{15}$ (709.4 g mol^{-1}): C, 49.10; H, 3.27; N, 1.97. Found: C, 48.69; H, 3.12; N, 2.13.

Decomp. Temp.: 223 °C.

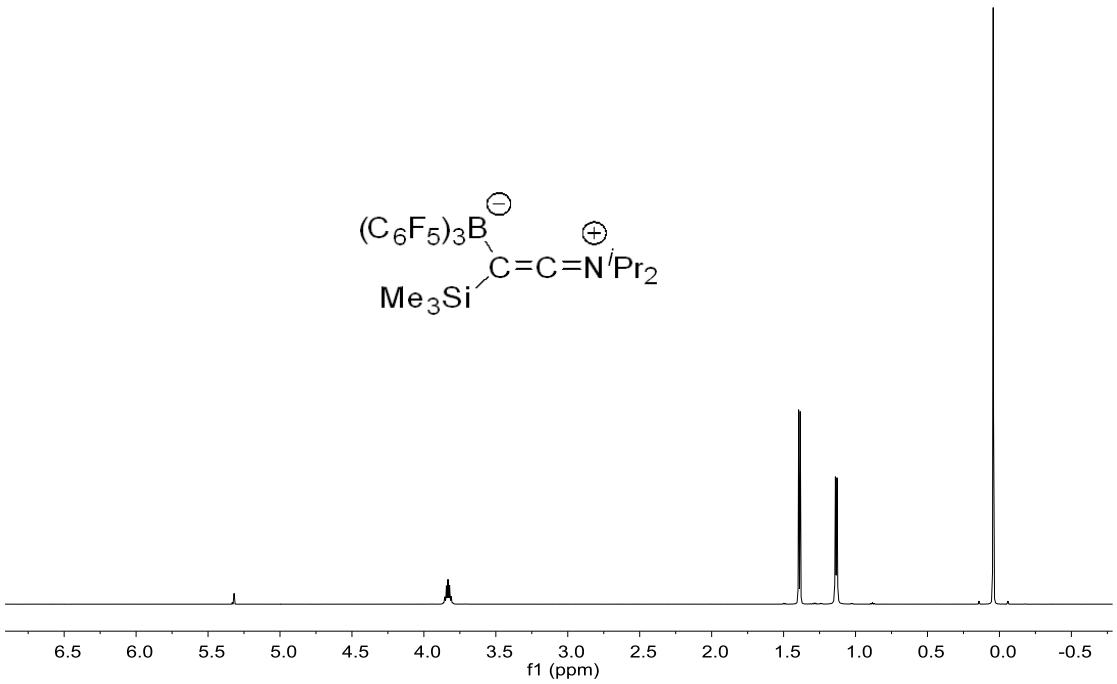
^{1}H NMR (600 MHz, 299 K, CD_2Cl_2, 5.32 ppm): δ = 3.83 (sept, $^{3}J_{HH}$ = 6.6 Hz, 2H, C*H*$(CH_3)_2$), 1.39 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3)_2$), 1.13 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3)_2$), 0.04 (s, 9H, Si(C*H*$_3)_3$).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2, 53.8 ppm): δ = 183.8 (=*C*=), 148.5 (dm, $^{1}J_{FC}$ ~ 240 Hz, C_6F_5), 139.7 (dm, $^{1}J_{FC}$ ~ 248 Hz, C_6F_5), 137.2 (dm, $^{1}J_{FC}$ ~ 252 Hz, C_6F_5), 121.6 (br, *i*-C_6F_5), 84.1 (br, B*C*=), 57.7 (*C*H$(CH_3)_2$), 21.8 (CH(*C*H$_3)_2$), 21.4 (CH(*C*H$_3)_2$), 0.8 (Si(*C*H$_3)_3$).

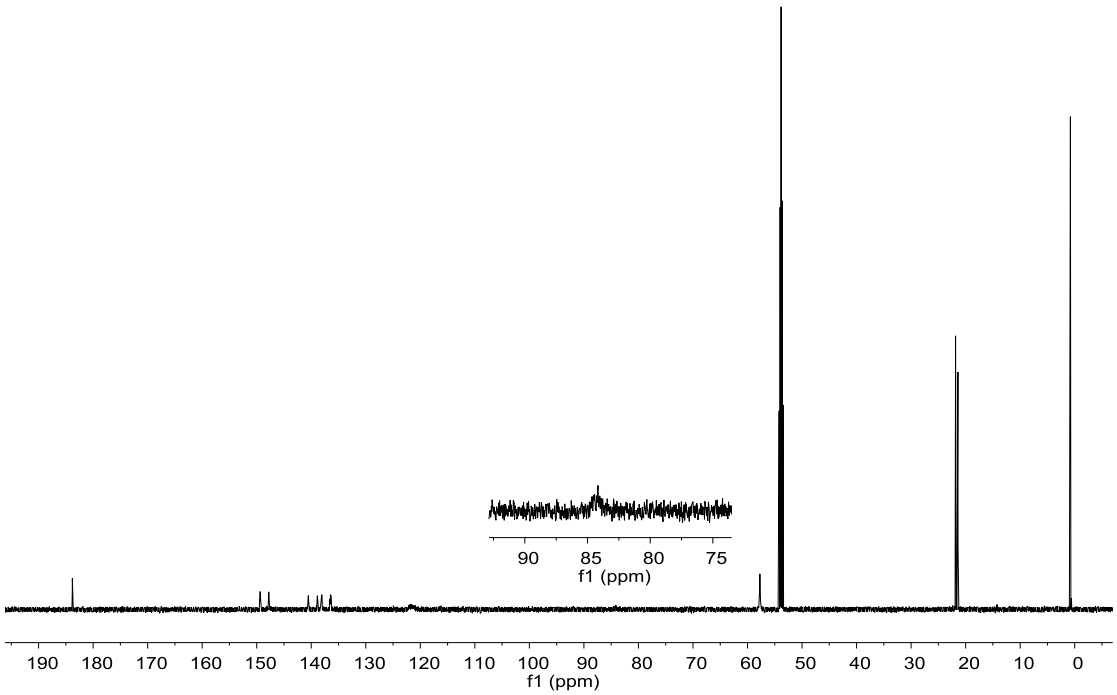
^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ = −14.4 ($\nu_{1/2}$ ~ 28 Hz).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = −131.1 (br, 2F, *o*-C_6F_5), −160.0 (t, $^{3}J_{FF}$ = 18.0 Hz, 1F, *p*-C_6F_5), −165.5 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 5.5].

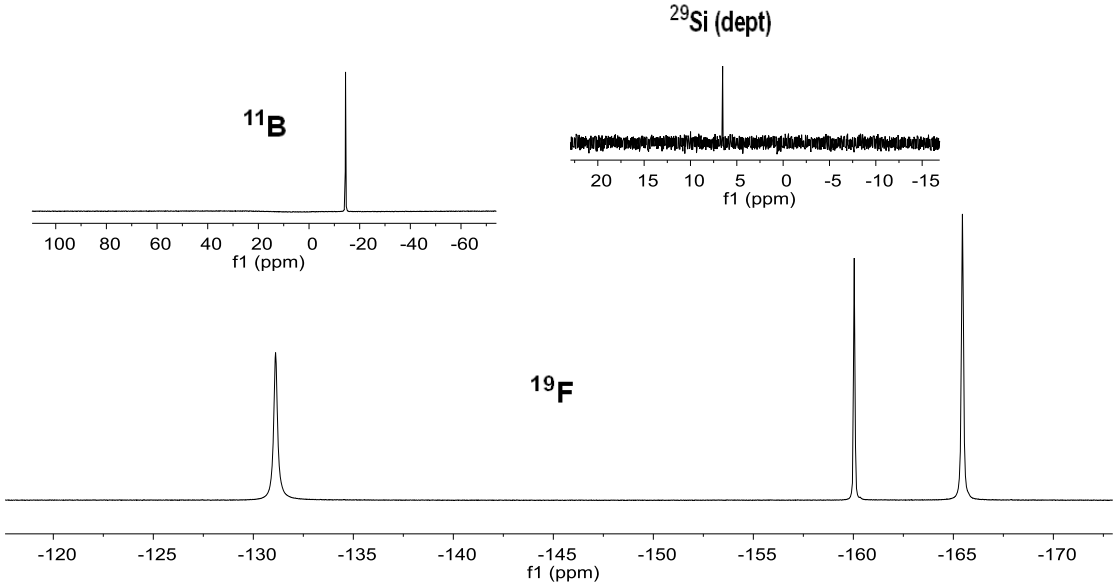
^{29}Si{^{1}H} dept NMR (119 MHz, 299 K, CD_2Cl_2): δ = 6.5 (s).



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



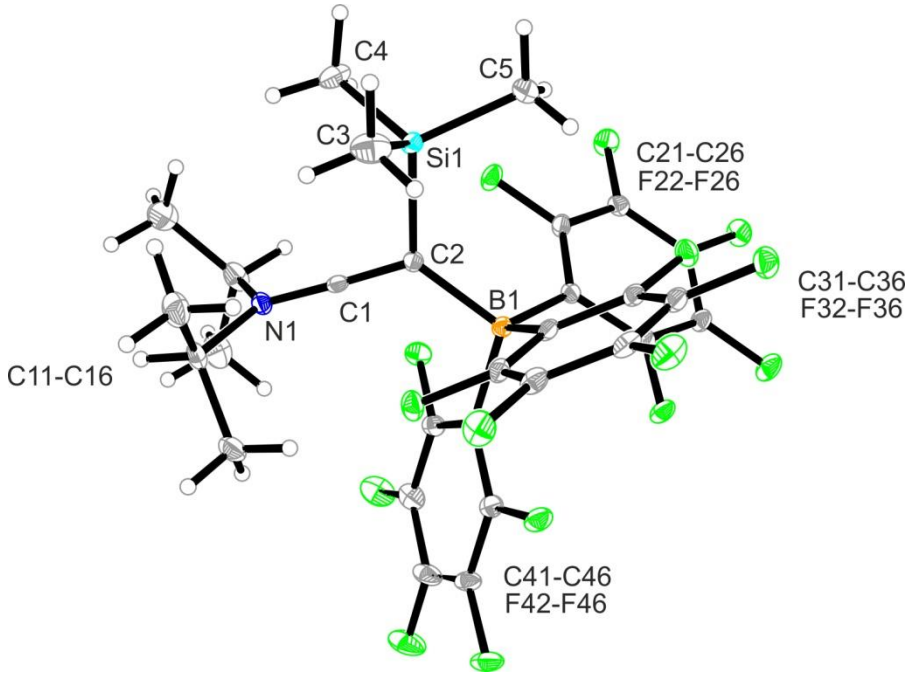
^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of compound **10a**.



^{19}F (564 MHz, 299 K, CD_2Cl_2), **^{11}B{^{1}H}** (192 MHz, 299 K, CD_2Cl_2), and **^{29}Si{^{1}H} dept NMR** (119 MHz, 299 K, CD_2Cl_2) spectra of compound **10a**.

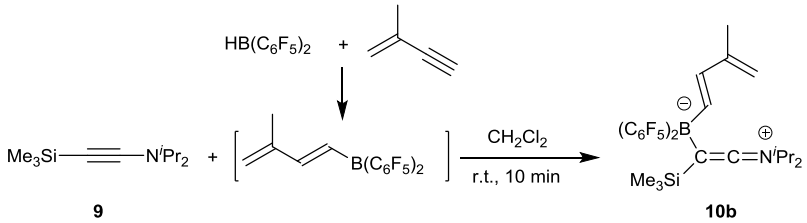
Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **10a** in CH_2Cl_2 and pentane at −35 °C.

X-ray crystal structure analysis of compound 10a (erk8313): A colorless plate-like specimen of $C_{29}H_{23}BF_{15}NSi$, approximate dimensions 0.040 mm x 0.200 mm x 0.200 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 72474 reflections to a maximum θ angle of 68.07° (0.83 Å resolution), of which 5523 were independent (average redundancy 13.122, completeness = 98.8%, R_{int} = 4.73%, R_{sig} = 1.87%) and 4965 (89.90%) were greater than $2\sigma(F^2)$. The final cell constants of a = 12.6697(4) Å, b = 17.9299(6) Å, c = 13.6897(4) Å, β = 100.9250(10)°, volume = 3053.48(17) Å^3, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7220 and 0.9340. 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, $C_{29}H_{23}BF_{15}NSi$. The final anisotropic full-matrix least-squares refinement on F^2 with 431 variables converged at R1 = 3.01%, for the observed data and wR2 = 7.46% for all data. The goodness-of-fit was 1.036. The largest peak in the final difference electron density synthesis was 0.245 e$^-$/Å^3 and the largest hole was -0.258 e$^-$/Å^3 with an RMS deviation of 0.041 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.543 g/cm^3 and F(000), 1432 e$^-$.



Crystal structure of compound **10a**.Thermal ellipsoids are shown at 30 % probability.

Synthesis of compound 10b



2-Methylbut-1-en-3-yne (33 mg, 0.5 mmol) and $HB(C_6F_5)_2$ (173 mg, 0.5 mmol) were mixed in CH_2Cl_2 (3 mL) at room temperature. After stirring for 30 min, one equiv. of compound **9** (99 mg, 0.5 mmol) was added to the clear yellow solution. After stirring for 10 min, the solvent was removed in vacuo. The residue was crystallized in toluene and pentane at −35 °C to give a white solid. Yield: 238 mg, 78 %.

Elemental analysis: calc. for $C_{28}H_{30}BNSiF_{10}$ (609.4 g mol^{-1}): C, 55.18; H, 4.96; N, 2.30. Found: C, 55.18; H, 4.78; N, 2.22.

Melting point: 127 °C.

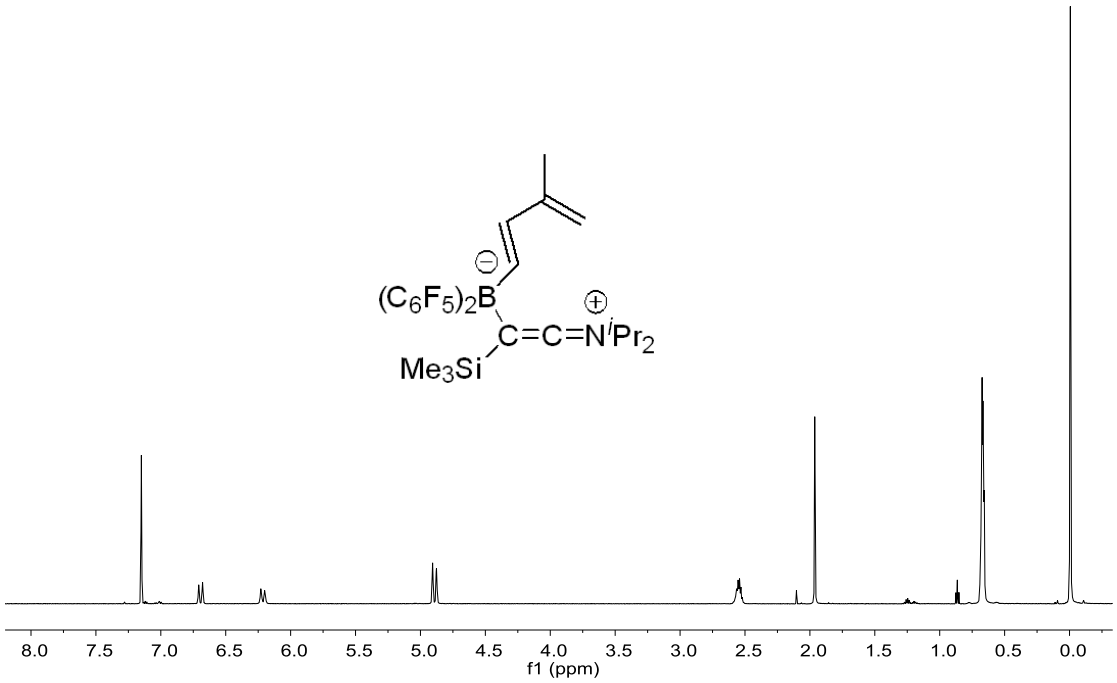
^{1}H NMR (600 MHz, 299 K, C_6D_6, 7.15 ppm): δ = 6.69 (d, $^3J_{HH}$ = 18.0 Hz, 1H, BC*H*=), 6.21 (d, $^3J_{HH}$ = 18.0 Hz, 1H, =C*H*), 4.89 (m, 2H, =CH_2), 2.54 (m, 2H, C*H*$(CH_3)_2$), 1.96 (s, 3H, CH_3), 0.67 (m, 12H, CH(CH_3)$_2$), 0.00 (s, 9H, Si(CH_3)$_3$).

^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6, 128.0 ppm): δ = 180.8 (=*C*=), 144.3 (*C*=), 141.6 (br, B*C*H=), 138.1 (=*C*H), 113.5 (=*C*H_2), 89.5 (br, B*C*=), 56.9 (*C*H$(CH_3)_2$), 20.94 (CH(*C*H_3)$_2$), 20.90 (CH(*C*H_3)$_2$), 19.1 (*C*H_3), 0.5 (Si(*C*H_3)$_3$), [C_6F_5 not listed].

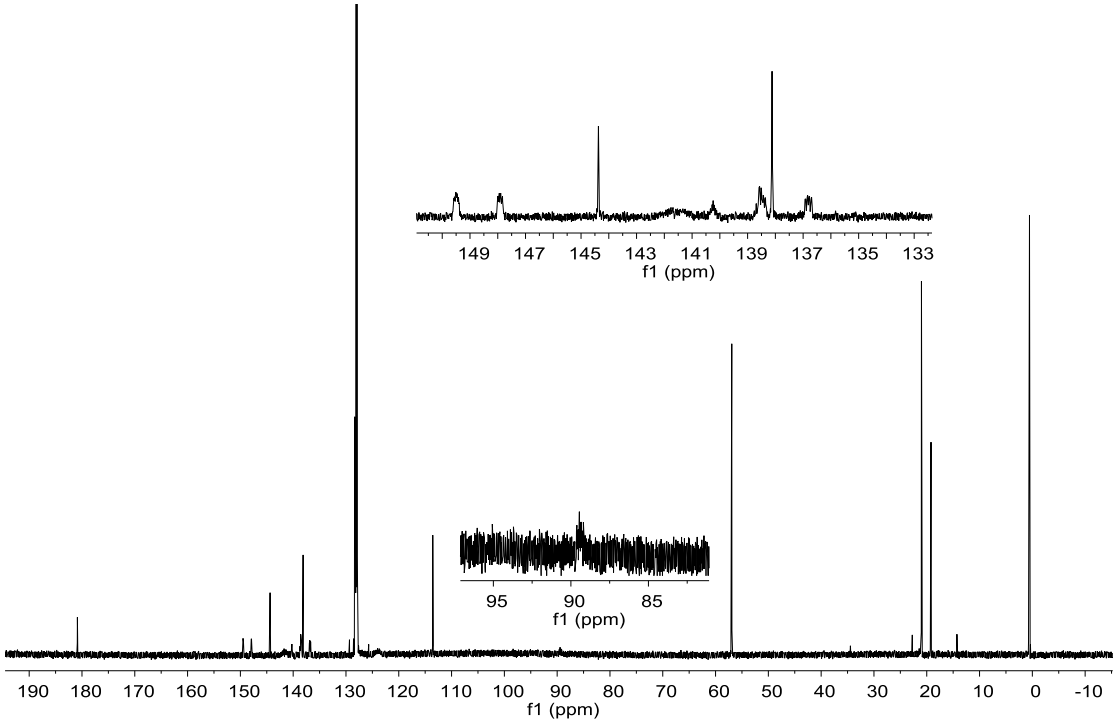
^{11}B{^{1}H} NMR (192 MHz, 299 K, C_6D_6): δ = −11.9 ($\nu_{1/2}$ ~ 107 Hz).

^{19}F NMR (564 MHz, 299 K, C_6D_6): δ = [−129.20, -129.22](each m, each 2F, *o*-C_6F_5), [−159.7 (t, $^3J_{FF}$ = 20.2 Hz), −159.8 (br, 1F)](*p*-C_6F_5), −164.7 (m, 4F, *m*-C_6F_5).

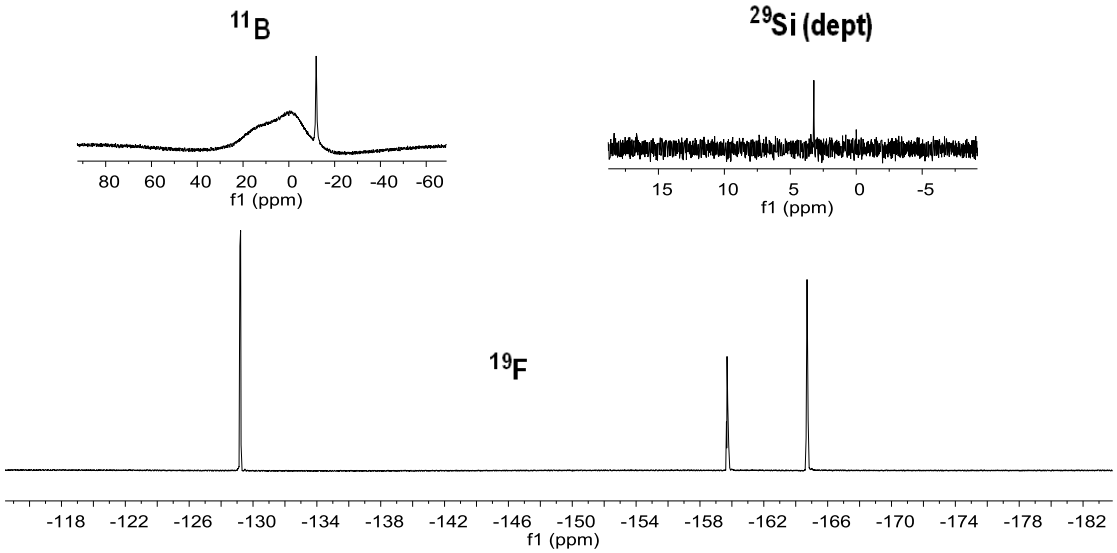
^{29}Si{^{1}H} dept NMR (119 MHz, 299 K, C_6D_6): δ = 3.2 (s).



^{1}H NMR (600 MHz, 299 K, C_6D_6) spectrum of compound **10b**.



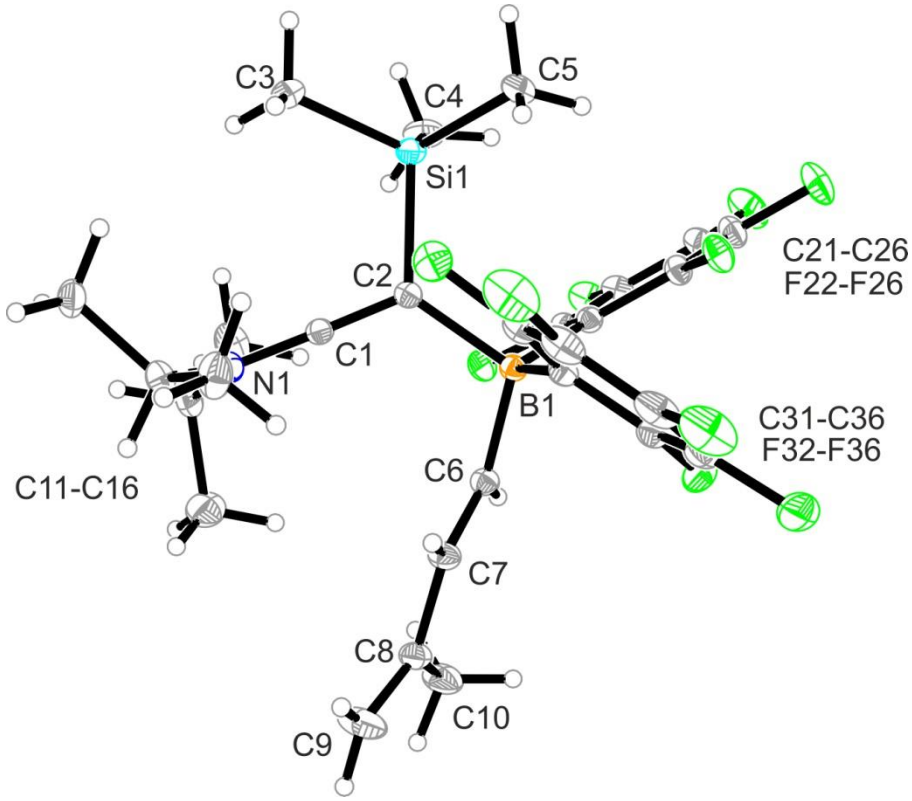
^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6) spectrum of compound **10b**.



^{29}Si{^{1}H} dept (119 MHz, 299 K, C_6D_6), **^{19}F** (564 MHz, 299 K, C_6D_6), and **^{11}B{^{1}H} NMR** (192 MHz, 299 K, C_6D_6) spectra of compound **10b**.

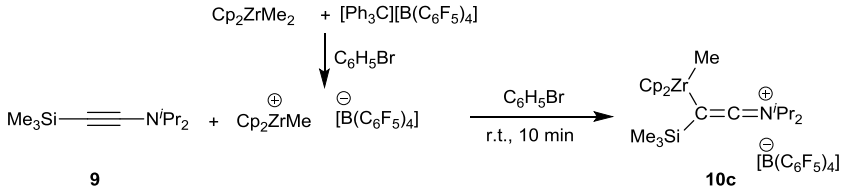
Crystals of compound **10b** suitable for the X-ray crystal structure analysis were obtained from a solution of the white solid in toluene and pentane at −35 °C.

X-ray crystal structure analysis of compound 10b (erk8404): formula $C_{28}H_{30}BF_{10}NSi$, M = 609.43, colourless crystal, 0.22 x 0.20 x 0.16 mm, a = 10.0190(2), b = 19.0596(3), c = 15.5129(3) Å, β = 94.422(1)°, V = 2953.5(1) Å^3, ρ_{calc} = 1.371 gcm^{-3}, μ = 0.161 mm^{-1}, empirical absorption correction (0.965 ≤ T ≤ 0.974), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 20730 reflections collected (±h, ±k, ±l), 7211 independent (R_{int} = 0.032) and 5743 observed reflections [I>2σ(I)], 437 refined parameters, R = 0.054, wR^2 = 0.132, max. (min.) residual electron density 0.23 (-0.22) e.Å^{-3}, the hydrogen atoms were calculated and refined as riding atoms.



Crystal structure of compound **10b**. Thermal ellipsoids are shown at 15 % probability.

Synthesis of compound 10c



Cp_2ZrMe_2 (126 mg, 0.5 mmol) and $[Ph_3C][B(C_6F_5)_4]$ (461 mg, 0.5 mmol) were mixed in bromobenzene (5 mL) at room temperature. After stirring for 5 min, compound **9** (99 mg, 0.5 mmol) was added to the clear solution. After standing for 12 h, yellow crystals were precipitated from the solution. The resulting crystals were filtered and washed twice with pentane to give the yellow product. Yield: 500 mg, 90 %.

Elemental analysis: calc. for $C_{46}H_{36}BNSiF_{20}Zr$ (1112.9 g mol^{-1}): C, 49.65; H, 3.26; N, 1.26. Found: C, 49.31; H, 3.07; N, 1.46.

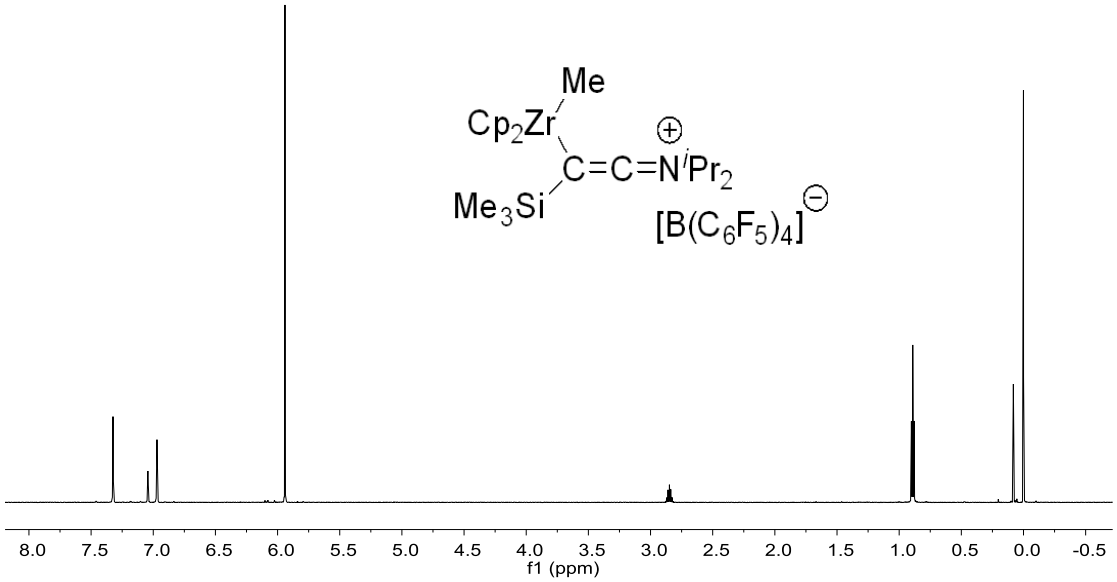
^{1}H NMR (600 MHz, 299 K, C_6D_5Br, 6.97 ppm): δ = 5.94 (s, 10H, Cp), 2.85 (sept, $^3J_{HH}$ = 6.6 Hz, 2H, C*H*$(CH_3)_2$), 0.89 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3)_2$), 0.88 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3)_2$), 0.08 (s, 3H, Zr-*Me*), 0.00 (s, 9H, Si(C*H*$_3)_3$).

^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_5Br, 122.3 ppm): δ = 146.7 (=*C*=), 112.7 (Cp), 95.5 (Zr*C*=), 55.0 (*C*H$(CH_3)_2$), 45.9 (Zr-*Me*), 21.3 (CH(*C*H$_3)_2$), 20.8 (CH(*C*H$_3)_2$), 1.6 (Si(*C*H$_3)_3$), [C_6F_5 not listed].

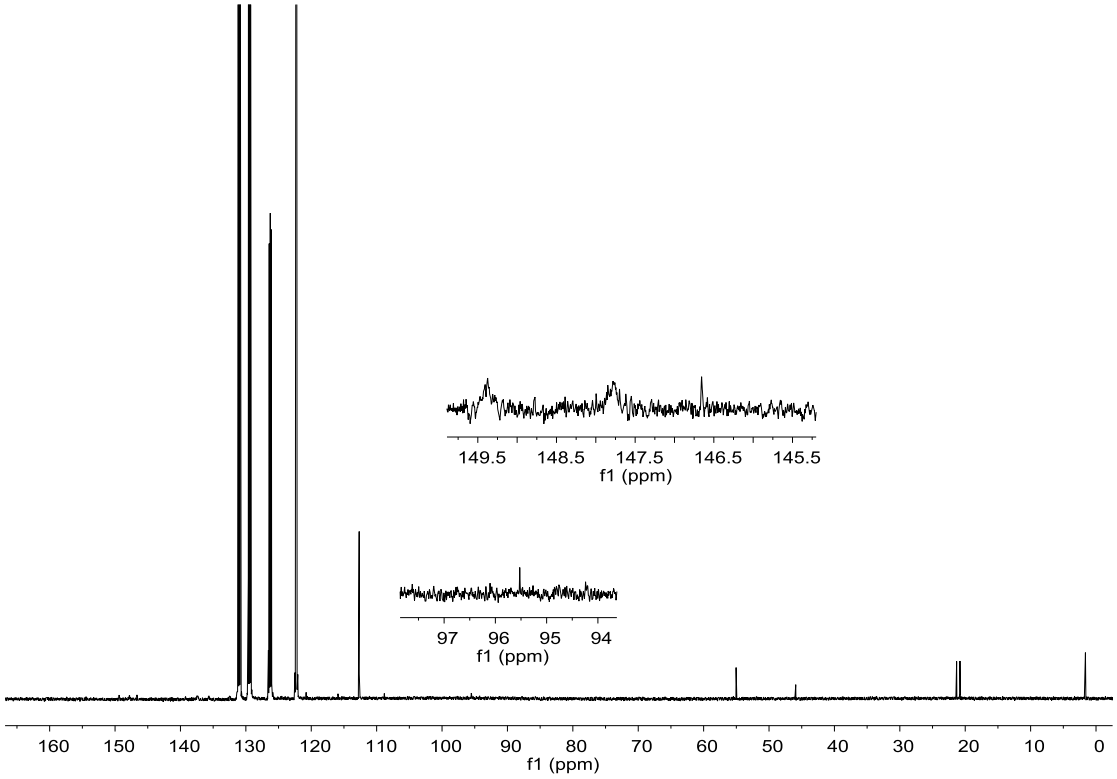
^{11}B{^{1}H} NMR (192 MHz, 299 K, C_6D_5Br): δ = −16.1 ($\nu_{1/2}$ ~ 22 Hz).

^{19}F NMR (564 MHz, 299 K, C_6D_5Br): δ = −131.6 (br, 2F, *o*-C_6F_5), −162.0 (t, $^{3}J_{FF}$ = 21.4 Hz, 1F, *p*-C_6F_5), −165.8 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 3.8].

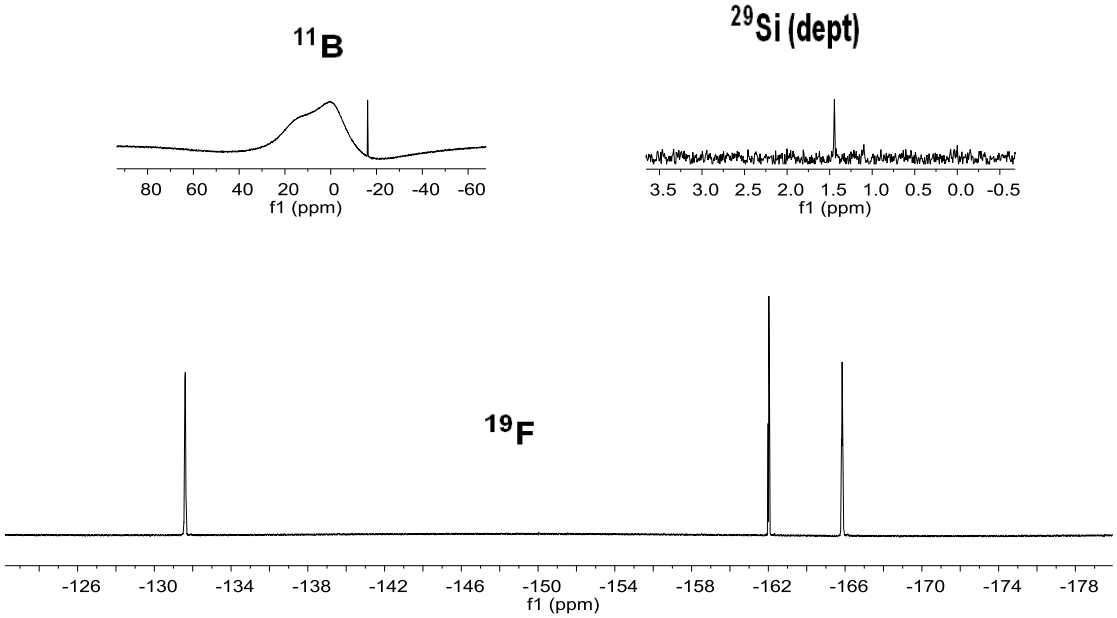
^{29}Si{^{1}H} dept NMR (119 MHz, 299 K, C_6D_5Br): δ = 1.4 (s).



^{1}H NMR (600 MHz, 299 K, C_6D_5Br) spectrum of compound **10c**.



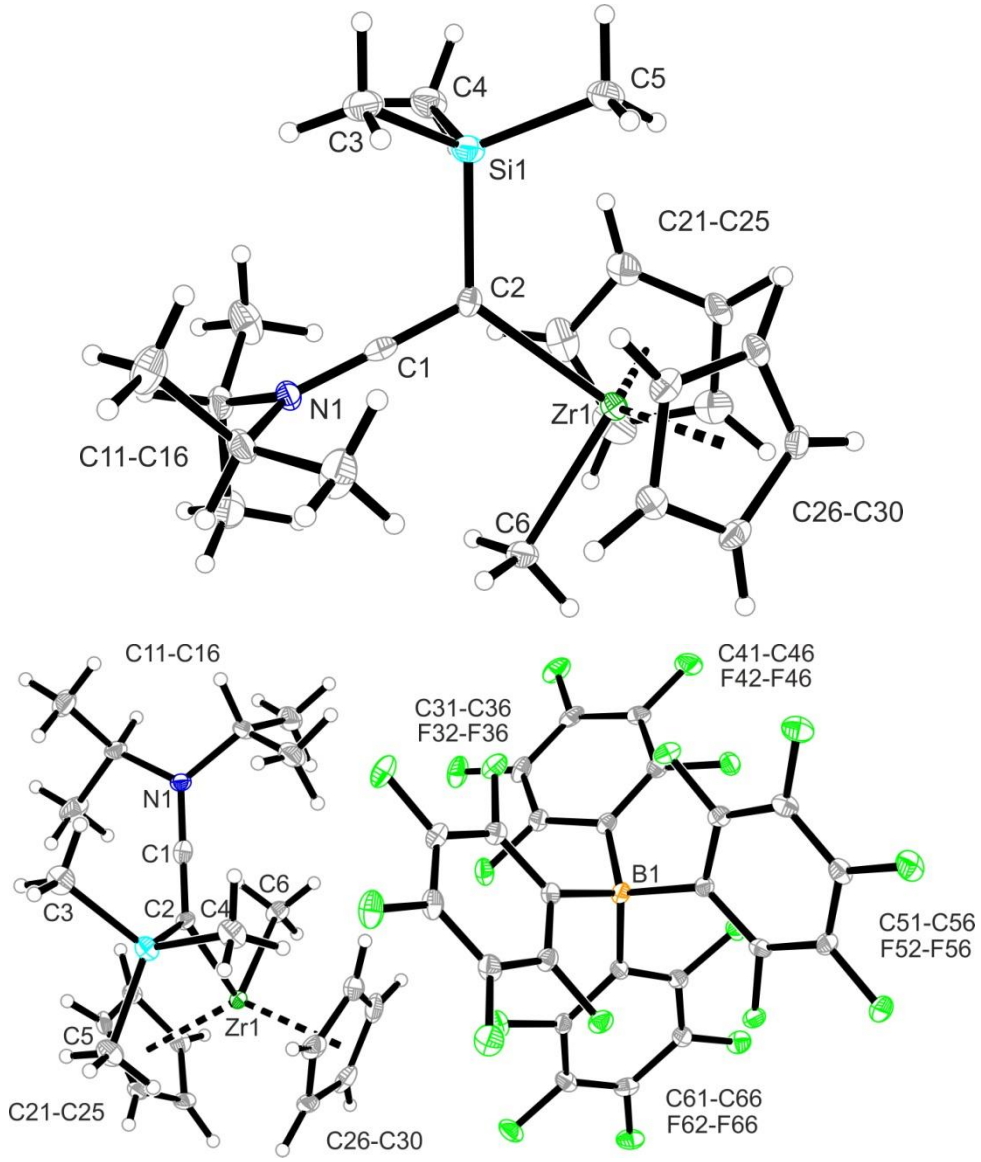
^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_5Br) spectrum of compound **10c**.



^{19}F (564 MHz, 299 K, C_6D_5Br), **^{11}B{^{1}H}** (192 MHz, 299 K, C_6D_5Br), and **^{29}Si{^{1}H} dept NMR** (119 MHz, 299 K, C_6D_5Br) spectra of compound **10c**.

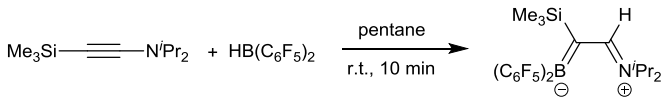
Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **10c** in bromobenzene at room temperature.

X-ray crystal structure analysis of compound 10c (erk8204): A pale yellow plate-like specimen of $C_{46}H_{36}BF_{20}NSiZr$, approximate dimensions 0.020 mm x 0.060 mm x 0.120 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The total exposure time was 20.40 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 35784 reflections to a maximum θ angle of 66.72° (0.84 Å resolution), of which 7704 were independent (average redundancy 4.645, completeness = 97.5%, R_{int} = 6.32%, R_{sig} = 4.96%) and 6445 (83.66%) were greater than $2\sigma(F^2)$. The final cell constants of a = 11.1163(6) Å, b = 13.9216(8) Å, c = 14.4781(8) Å, α = 88.616(3)°, β = 88.273(3)°, γ = 84.773(2)°, volume = 2229.7(2) Å^3, are based upon the refinement of the XYZ-centroids of 9984 reflections above 20 σ(I) with 6.108° < 2θ < 133.1°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.813. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6880 and 0.9360. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P\bar{1}$, with Z = 2 for the formula unit, $C_{46}H_{36}BF_{20}NSiZr$. The final anisotropic full-matrix least-squares refinement on F^2 with 639 variables converged at R1 = 4.37%, for the observed data and wR2 = 9.91% for all data. The goodness-of-fit was 1.079. The largest peak in the final difference electron density synthesis was 0.750 e$^-$/Å^3 and the largest hole was -0.573 e$^-$/Å^3 with an RMS deviation of 0.089 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.658 g/cm^3 and F(000), 1116 e$^-$.



Crystal structure of compound **10c**. Thermal ellipsoids are shown at 30 % probability.

Synthesis of compound 11



9 **11**

Compound **9** (99 mg, 0.5 mmol) and $HB(C_6F_5)_2$ (173 mg, 0.5 mmol) were mixed in pentane (3 mL) at room temperature. After stirring for 10 min, the pentane solution was stored at −35 °C to precipitate yellow crystals. Yield: 223 mg, 82 %.

Elemental analysis: calc. for $C_{23}H_{24}BNSiF_{10}$ (543.3 g mol^{-1}): C, 50.84; H, 4.45; N, 2.58. Found: C, 50.35; H, 4.10; N, 2.75.

Melting point: 97 °C.

^{1}H NMR (600 MHz, 299 K, C_6D_6, 7.15 ppm): δ = 7.82 (s, 1H, *H*C=), 4.59 (br, 1H, C*H*$(CH_3)_2$), 2.71 (br, 1H, C*H*$(CH_3)_2$), 0.60 (br, 6H, CH(C*H*$_3)_2$), 0.33 (br, 6H, CH(C*H*$_3)_2$), 0.07 (s, 9H, Si(C*H*$_3)_3$).

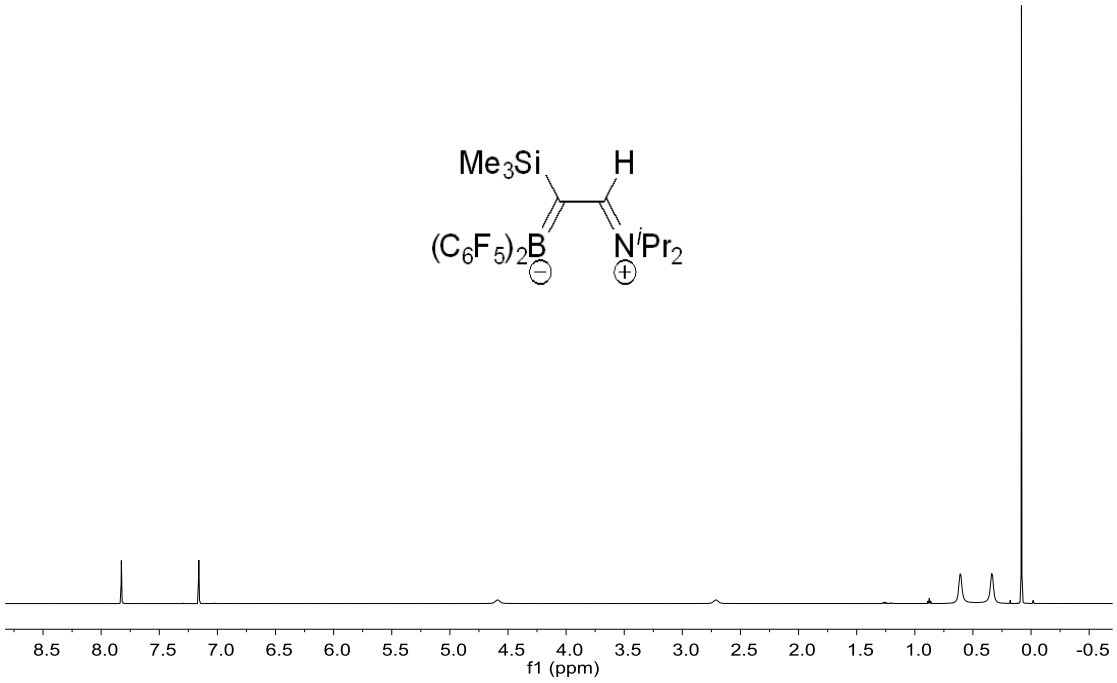
^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6, 128.0 ppm): δ = 170.6 (*C*H=), 146.5 (dm, $^{1}J_{FC}$ ~ 240 Hz, C_6F_5), 141.2 (dm, $^{1}J_{FC}$ ~ 252 Hz, C_6F_5), 137.8 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 118.8 (br, *i*-C_6F_5), 110.5 (br, *C*=B), 51.9 (*C*H$(CH_3)_2$), 47.7 (*C*H$(CH_3)_2$), 23.2 (CH(*C*H$_3)_2$), 18.4 (CH(*C*H$_3)_2$), 1.9 (Si(*C*H$_3)_3$).

^{11}B{^{1}H} NMR (192 MHz, 299 K, C_6D_6): δ = 42.0 ($\nu_{1/2}$ ~ 540 Hz).

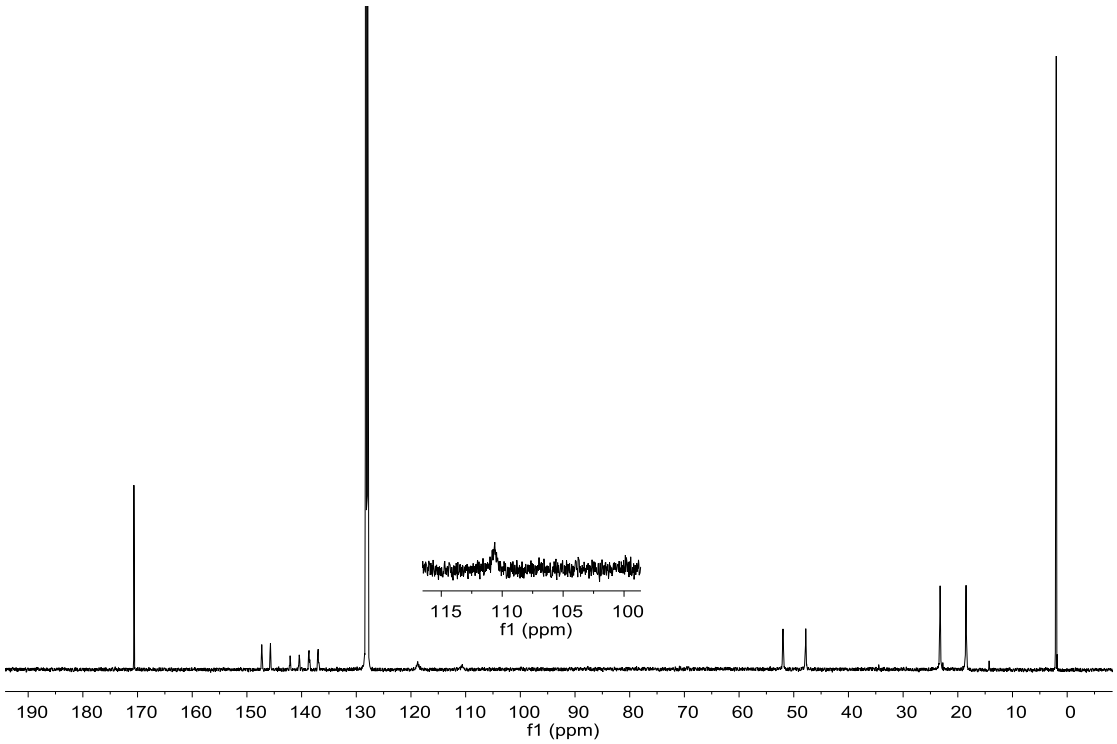
^{19}F NMR (564 MHz, 299 K, C_6D_6) δ = −132.2 (br, 2F, *o*-C_6F_5), −154.9 (t, $^{3}J_{FF}$ = 20.0 Hz, 1F, *p*-C_6F_5), −162.9 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 8.0].

^{19}F NMR (564 MHz, 233 K, dichloromethane-d_2) δ = -132.2 (m, 2F, *o*-C_6F_5), -156.7 (t, $^{3}J_{FF}$ = 20.5 Hz, 1F, *p*-C_6F_5), -163.8 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 7.1]; -133.5 (m, 2F, *o*-C_6F_5), -155.9 (t, $^{3}J_{FF}$ = 20.6 Hz, 1F, *p*-C_6F_5), -163.0 ((m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 7.1].

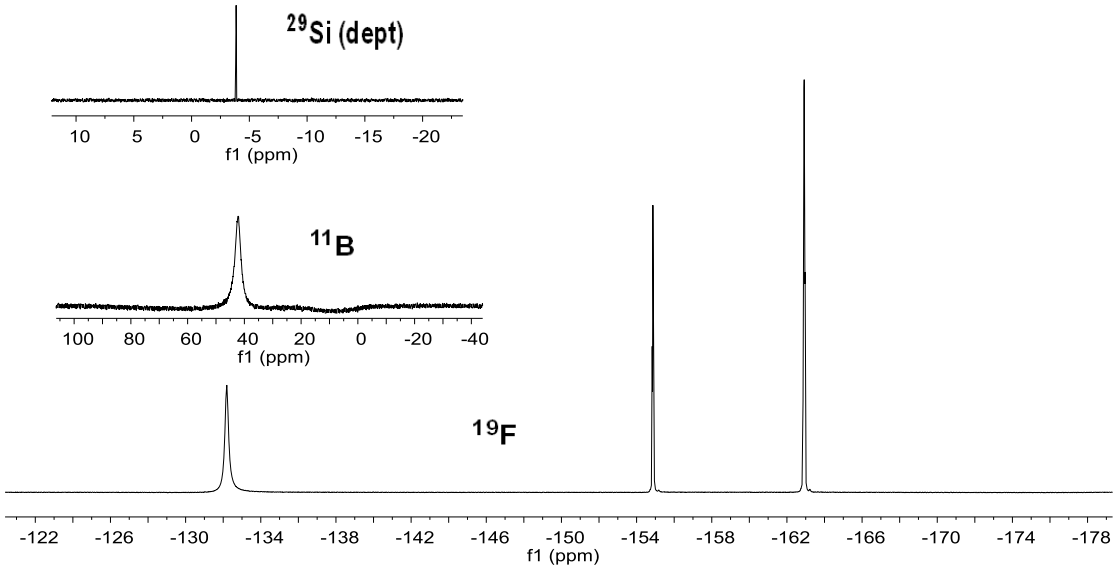
^{29}Si{^{1}H} dept NMR (119 MHz, 299 K, C_6D_6): δ = −3.9 (s).



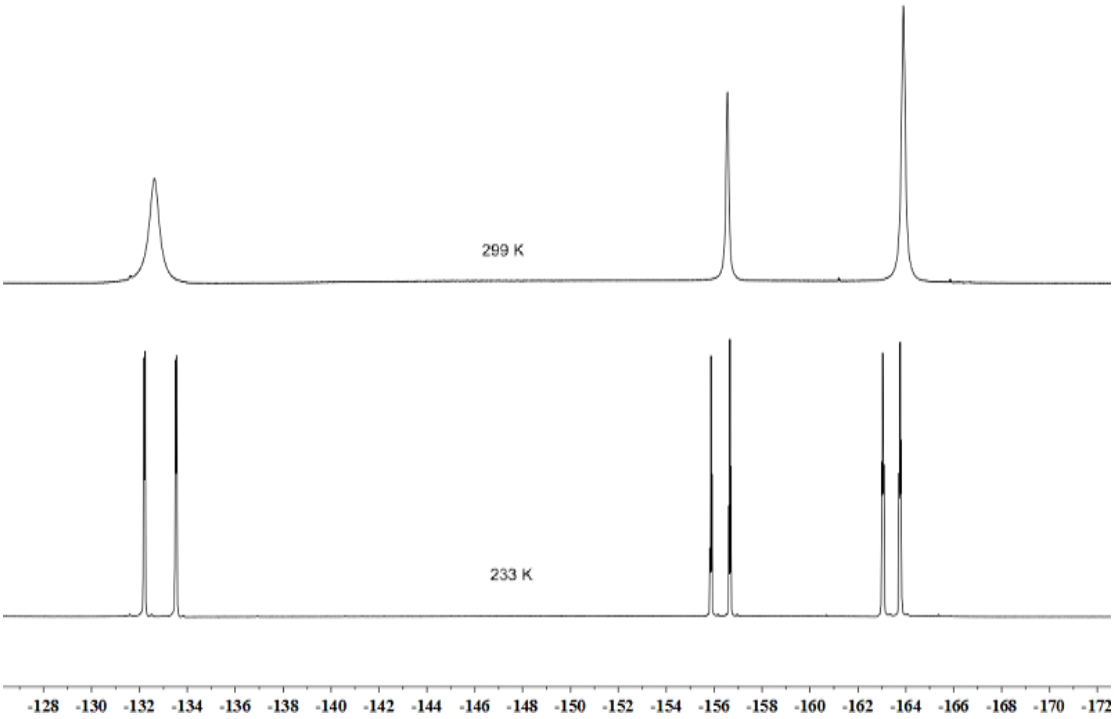
^{1}H NMR (600 MHz, 299 K, C_6D_6) spectrum of compound **11**.



^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6) spectrum of compound **11**.



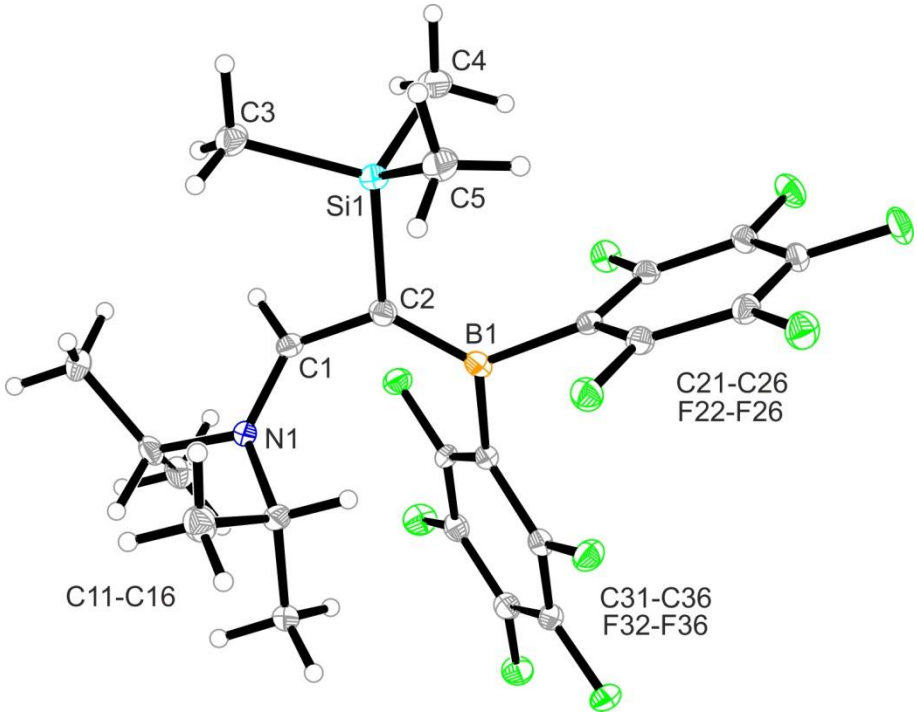
^{29}Si{^{1}H} dept (119 MHz, 299 K, C_6D_6), **^{19}F** (564 MHz, 299 K, C_6D_6), and **^{11}B{^{1}H} NMR** (192 MHz, 299 K, C_6D_6) spectra of compound **11**.



^{19}F NMR (564 MHz, dichloromethane-d_2) spectra of compound **11** at 299 K and 233 K.

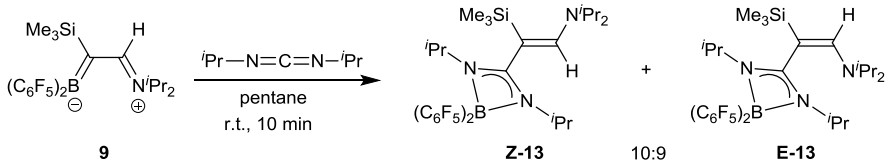
Crystals of compound **11** suitable for the X-ray crystal structure analysis were obtained from a solution of compound **11** in pentane at −35 °C.

X-ray crystal structure analysis of compound 11 (erk8302): A pale yellow plate-like specimen of $C_{23}H_{24}BF_{10}NSi$, approximate dimensions 0.030 mm x 0.070 mm x 0.080 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 36240 reflections to a maximum θ angle of 66.61° (0.84 Å resolution), of which 4428 were independent (average redundancy 8.184, completeness = 99.4%, R_{int} = 10.84%, R_{sig} = 5.82%) and 3082 (69.60%) were greater than $2\sigma(F^2)$. The final cell constants of a = 13.3272(5) Å, b = 12.2348(5) Å, c = 15.6178(6) Å, β = 98.650(2)°, volume = 2517.60(17) Å^3, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8810 and 0.9530. 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, $C_{23}H_{24}BF_{10}NSi$. The final anisotropic full-matrix least-squares refinement on F^2 with 332 variables converged at R1 = 4.68%, for the observed data and wR2 = 11.96% for all data. The goodness-of-fit was 1.036. The largest peak in the final difference electron density synthesis was 0.237 e^-/Å^3 and the largest hole was -0.365 e^-/Å^3 with an RMS deviation of 0.063 e^-/Å^3. On the basis of the final model, the calculated density was 1.433 g/cm^3 and F(000), 1112 e^-.



Crystal structure of compound **11**. Thermal ellipsoids are shown at 30 % probability.

Synthesis of compounds 13 (Z-/E-13)



Compound **9** (99 mg, 0.5 mmol) and $HB(C_6F_5)_2$ (173 mg, 0.5 mmol) were mixed in pentane (3 mL) at room temperature. After stirring for 10 min, one equiv. of *N*,*N*′-diisopropyl carbodiimide (63 mg, 0.5 mmol) was added to the pentane solution and stirred for another 10 min. The solvent was removed in vacuo and the residue was crystallized at −35 °C to give white crystals. Yield: 254 mg, 76 %.

Elemental analysis: calc. for $C_{30}H_{38}BN_3SiF_{10}$ (669.5 g mol^{-1}): C, 53.82; H, 5.72; N, 6.28. Found: C, 53.82; H, 5.58; N, 6.28.

Melting point: 131 °C.

Z-13: **^{1}H NMR** (600 MHz, 238 K, CD_2Cl_2, 5.32 ppm): δ = 6.82 (s, 1H, =C*H*), 4.09 (m, 1H, C*H*$(CH_3)_2$), 3.71 (m, 2H, BNC*H*$(CH_3)_2$), 3.48 (m, 1H, C*H*$(CH_3)_2$), 1.17 (d, $^3J_{HH}$ = 6.6 Hz, 12H, CH(C*H*$_3)_2$), 0.85 (d, $^3J_{HH}$ = 6.6 Hz, 6H, B−N−CH(C*H*$_3)_2$), 0.83 (d, $^3J_{HH}$ = 6.9 Hz, 6H, BNCH(C*H*$_3)_2$), 0.19 (s, 9H, Si(C*H*$_3)_3$).

E-13: **^{1}H NMR** (600 MHz, 238 K, CD_2Cl_2, 5.32 ppm): δ = 6.35 (s, 1H, =C*H*), 4.12 (m, 1H, C*H*$(CH_3)_2$), 3.71 (m, 2H, BNC*H*$(CH_3)_2$), 3.47 (m, 1H, C*H*$(CH_3)_2$), 1.15 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3)_2$), 1.07 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3)_2$), 0.93 (d, $^3J_{HH}$ = 7.2 Hz, 6H, B−N−CH(C*H*$_3)_2$), 0.92 (d, $^3J_{HH}$ = 7.2 Hz, 6H, B−N−CH(C*H*$_3)_2$), 0.14 (s, 9H, Si(C*H*$_3)_3$).

Z-13: **^{13}C{^{1}H} NMR** (151 MHz, 238 K, CD_2Cl_2, 53.8 ppm): δ = 181.1 (N*C*N), 148.7 (=*C*H), 82.3 (Si*C*=), 49.7 (br, *C*H(CH_3)$_2$), 45.7 (BN*C*H(CH_3)$_2$), 45.4 (br, *C*H(CH_3)$_2$), 23.4 (br, CH(*C*H_3)$_2$), 21.9 (BNCH(*C*H_3)$_2$), 21.3 (BNCH(*C*H_3)$_2$), 19.9 (br, CH(*C*H_3)$_2$), 0.8 (Si(*C*H_3)$_3$), [C_6F_5 not listed].

E-13: **^{13}C{^{1}H} NMR** (151 MHz, 238 K, CD_2Cl_2, 53.8 ppm): δ = 177.1 (N*C*N), 144.1 (=*C*H), 81.9 (Si*C*=), 48.1 (*C*H(CH_3)$_2$), 46.5 (BN*C*H(CH_3)$_2$), 45.6 (*C*H(CH_3)$_2$), 23.6 (CH(*C*H_3)$_2$), 22.5 (BNCH(*C*H_3)$_2$), 22.4 (BNCH(*C*H_3)$_2$), 20.8 (CH(*C*H_3)$_2$), 0.8 (Si(*C*H_3)$_3$), [C_6F_5 not listed].

^{11}B{^{1}H} NMR (192 MHz, 238 K, CD_2Cl_2): δ = 0.2, −0.4

Z-13: **^{19}F NMR** (564 MHz, 238 K, CD_2Cl_2): δ = [−130.2 , −132.1](each br, each 2F, *o*-C_6F_5), [−159.1 (t, $^3J_{FF}$ = 21.0 Hz), −159.3 (t, $^3J_{FF}$ = 20.6 Hz)](each 1F, *p*-C_6F_5), [−164.4, −164.6](each m, each 2F, *m*-C_6F_5).

E-13: **^{19}F NMR** (564 MHz, 238 K, CD_2Cl_2): δ = [−129.7, −131.0](each m, each 2F, *o*-C_6F_5), [−158.7 (t, $^3J_{FF}$ = 21.2 Hz), −159.0 (t, $^3J_{FF}$ = 20.6 Hz)](each 1F, *p*-C_6F_5), [−164.4, −164.6](each m, each 2F, *m*-C_6F_5).

Z-13: **^{29}Si{^{1}H} dept NMR** (119 MHz, 299 K, CD_2Cl_2): δ = −12.5 (s).

E-13: **^{29}Si{^{1}H} dept NMR** (119 MHz, 299 K, CD_2Cl_2): δ = 0.8 (s).

Z-13: **^{1}H, ^{1}H gCOSY** (600 MHz/600 MHz, 238 K, CD_2Cl_2) [selected traces]: δ^1H / δ^1H = 4.09 and 3.48 / 1.17 (C*H*(CH_3)$_2$ / CH(C*H*$_3$)$_2$), 3.71 / 0.85 and 0.83 (BNC*H*(CH_3)$_2$ / BNCH(C*H*$_3$)$_2$).

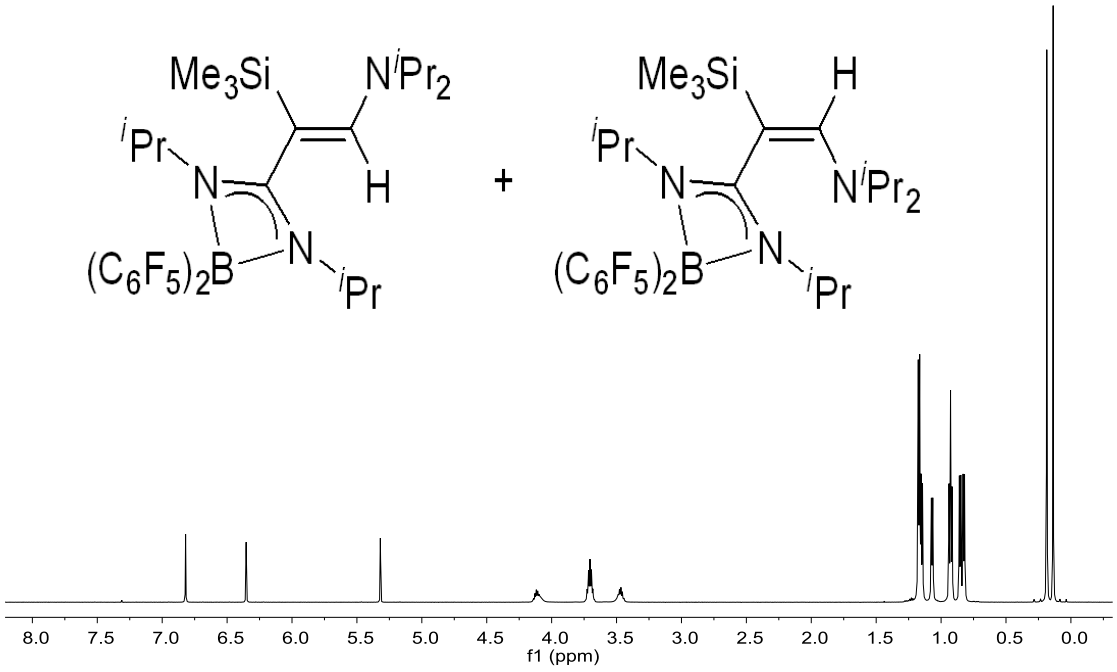
E-13: **^{1}H, ^{1}H gCOSY** (600 MHz/600 MHz, 238 K, CD_2Cl_2) [selected traces]: δ^1H / δ^1H = 4.12 / 1.07 (C*H*(CH_3)$_2$ / CH(C*H*$_3$)$_2$), 3.47 / 1.15 (C*H*(CH_3)$_2$ / CH(C*H*$_3$)$_2$), 3.71 / 0.93 and 0.92 (BNC*H*(CH_3)$_2$ / BNCH(C*H*$_3$)$_2$).

Z-13: **^{1}H, ^{13}C gHSQC** (600 MHz/151 MHz, 238 K, CD_2Cl_2) [selected traces]: δ^1H / δ^{13}C = 6.82 / 148.7 (=C*H*), 4.09 / 49.7 (C*H*(CH_3)$_2$), 3.71 / 45.7 (BNC*H*(CH_3)$_2$), 3.47 / 45.4 (C*H*(CH_3)$_2$), 1.17 / 23.4 and 19.9 (CH(C*H*$_3$)$_2$), 0.85 / 21.9 (BNCH(C*H*$_3$)$_2$), 0.83 / 21.3 (BNCH(C*H*$_3$)$_2$), 0.19 / 0.8 (Si(C*H*$_3$)$_3$).

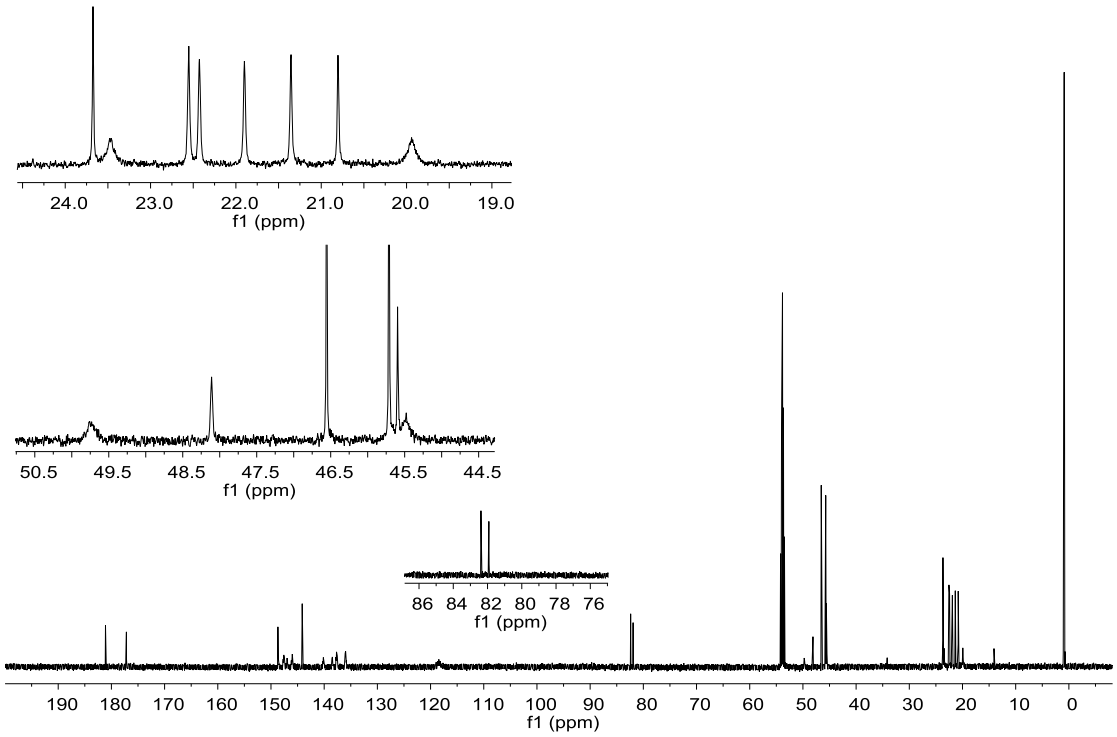
E-13: **^{1}H, ^{13}C gHSQC** (600 MHz/151 MHz, 238 K, CD_2Cl_2) [selected traces]: δ^1H / δ^{13}C = 6.35 / 144.1 (=C*H*), 4.12 / 48.1 (C*H*(CH_3)$_2$), 3.71 / 46.5 (BNC*H*(CH_3)$_2$), 3.47 / 45.6 (C*H*(CH_3)$_2$), 1.15 / 23.6 (CH(C*H*$_3$)$_2$), 1.07 / 20.8 (CH(C*H*$_3$)$_2$), 0.93 / 22.5 (B−N−CH(C*H*$_3$)$_2$), 0.92 / 22.4 (BNCH(C*H*$_3$)$_2$), 0.14 / 0.8 (Si(C*H*$_3$)$_3$).

Z-13: **^{1}H, ^{13}C gHMBC** (600 MHz/151 MHz, 238 K, CD_2Cl_2) [selected traces]: δ^1H / δ^{13}C = 6.82 / 181.1 and 82.3 (=C*H* / N*C*N and Si*C*=).

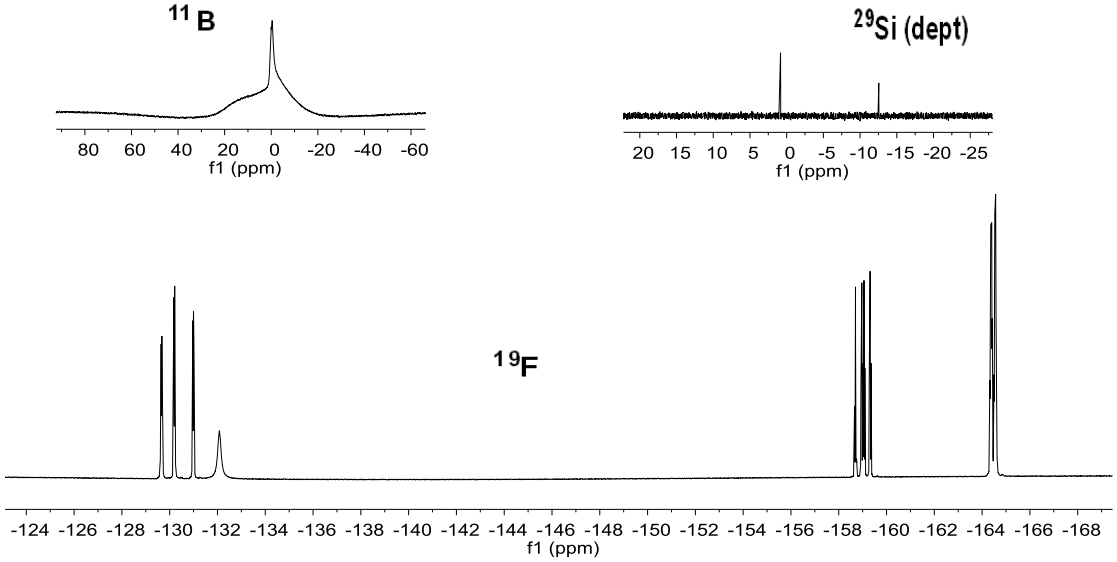
E-13: **^{1}H, ^{13}C gHMBC** (600 MHz/151 MHz, 238 K, CD_2Cl_2) [selected traces]: δ^1H / δ^{13}C = 6.35 / 177.1 and 81.9 (=C*H* / N*C*N and Si*C*=).



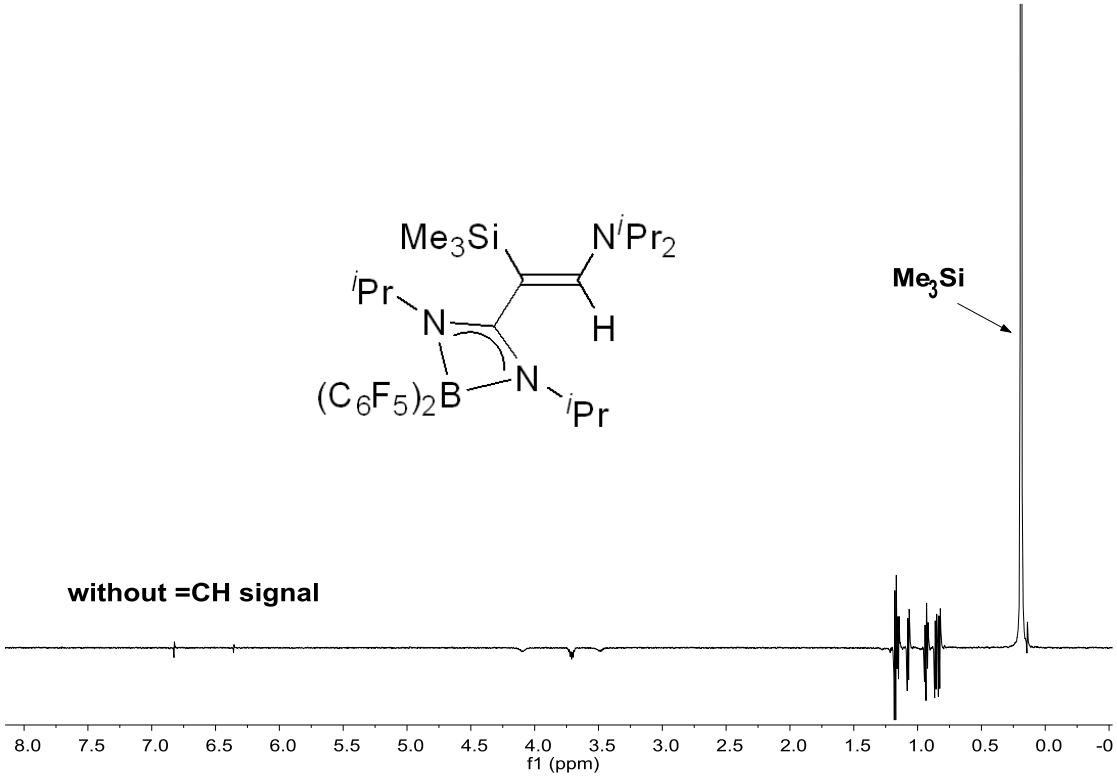
^{1}H NMR (600 MHz, 238 K, CD_2Cl_2) spectrum of compounds **Z-13** and **E-13**.



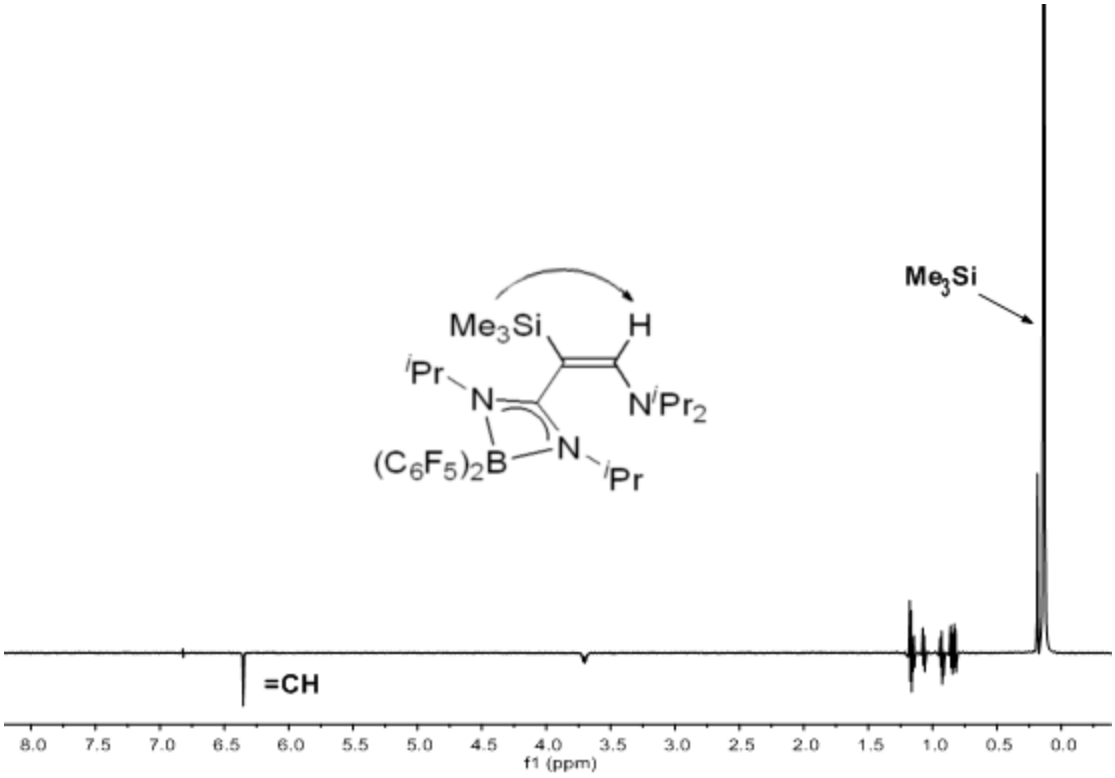
^{13}C{^{1}H} NMR (151 MHz, 238 K, CD_2Cl_2) spectrum of compounds **Z-13** and **E-13**.



^{29}Si{^{1}H} dept NMR (119 MHz, 299 K, CD_2Cl_2), **^{19}F** (564 MHz, 238 K, CD_2Cl_2), and **^{11}B{^{1}H} NMR** (192 MHz, 238 K, CD_2Cl_2) spectra of compounds **Z-13** and **E-13**.



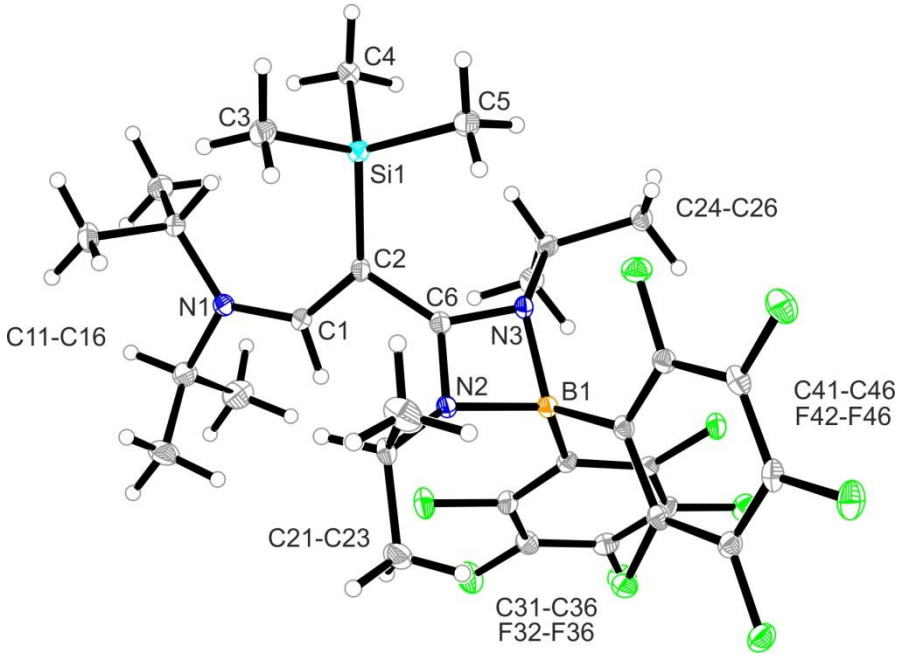
1D NOESY (600 MHz, 238 K, CD_2Cl_2) spectrum of compound **Z-13**.



1D NOESY (600 MHz, 238 K, CD_2Cl_2) spectrum of compound **E-13**.

Crystals of compound **Z-13** suitable for the X-ray crystal structure analysis were obtained from a solution of compounds **13** (**Z-13/E-13)** in toluene and pentane at −35 °C.

X-ray crystal structure analysis of compound *Z*-13 (erk8286): A colorless plate-like specimen of $C_{30}H_{38}BF_{10}N_3Si$, approximate dimensions 0.040 mm x 0.160 mm x 0.200 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 58309 reflections to a maximum θ angle of 66.59° (0.84 Å resolution), of which 5922 were independent (average redundancy 9.846, completeness = 99.8%, R_{int} = 8.46%, R_{sig} = 3.69%) and 4690 (79.20%) were greater than $2\sigma(F^2)$. The final cell constants of a = 13.5304(5) Å, b = 17.4187(6) Å, c = 14.8740(5) Å, β = 106.5560(10)°, volume = 3360.2(2) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7760 and 0.9480. 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, $C_{30}H_{38}BF_{10}N_3Si$. The final anisotropic full-matrix least-squares refinement on F^2 with 417 variables converged at R1 = 3.69%, for the observed data and wR2 = 8.95% for all data. The goodness-of-fit was 1.050. The largest peak in the final difference electron density synthesis was 0.247 $e^-/Å^3$ and the largest hole was -0.287 $e^-/Å^3$ with an RMS deviation of 0.045 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.323 g/cm^3 and F(000), 1392 e^-.



Crystal structure of compound ***Z*-13**. Thermal ellipsoids are shown at 30 % probability.