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$_2$Cl$_2$, Et$_2$O, 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 (H: 500 MHz, $^{13}$C: 126 MHz, $^{31}$P: 202 MHz, $^{19}$F: 470 MHz, $^{11}$B: 160 MHz) or a Varian Inova 600 (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 $\delta$ are given relative to TMS and referenced to the solvent signal. $^{31}$P NMR: chemical shifts $\delta$ are given relative to H$_3$PO$_4$ (external reference), $^{19}$F NMR: chemical shifts $\delta$ are given relative to CFCl$_3$ (external reference), $^{11}$B NMR: chemical shifts $\delta$ are given relative to BF$_3$Et$_2$O (external reference), $^{29}$Si NMR: chemical shifts $\delta$ 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. H. 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$_5$F$_5$ 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. Compound 9 was synthesized according to the similar known procedure. Bis(pentafluoro phenyl)borane (HB(C$_6$F$_5$)$_2$)$_3$ was prepared according to the literature procedure. All other reagents were commercially available and used as received. Trityl tetrakis(pentafluorophenyl)borate [Ph$_3$C][B(C$_6$F$_5$)$_4$] was obtained from ABCR company and used as
Synthesis of compound 4

\[
\begin{array}{c}
\text{KOH}  \rightarrow  \text{N} \\
\text{60°C} \\
\end{array}
\]

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\(_8\))** \(\delta = 1.79\) (s, 3H, Me), 1.27 (m, 2H, CH\(_2\)\(_{\text{TMP}}\)), 1.26 (m, 4H, CH\(_2\)\(_{\text{TMP}}\)), 1.19 (s, 12H, Me\(_{\text{TMP}}\)).

**\(^{13}\)C{\(^1\)H} NMR (151 MHz, 299 K, toluene-d\(_8\))** \(\delta = [80.7, 60.8](C\equiv), 54.9\) (NC\(_{\text{TMP}}\)), 38.9 (CH\(_2\)\(_{\text{TMP}}\)), 28.2 (Me\(_{\text{TMP}}\)), 17.5 (CH\(_2\)\(_{\text{TMP}}\)), 3.6 (Me).

\(^1\)H NMR (600 MHz, 299 K, toluene-d\(_8\)) of compound 4
Synthesis of compound 5

A mixture of ynamine 4 (17.9 mg, 0.1 mmol) and HB(C₆F₅)₂ (34.6 mg, 0.1 mmol) in dichloromethane-d₂ (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 C₂₄H₂₂BF₁₀N+[H⁺] 526.1758; found 526.1763.

**Melting point:** 113 °C

NMR data from the *in situ* generated yellow solution in dichloromethane-d₂:

**¹H NMR** (600 MHz, 299 K, dichloromethane-d₂) δ = 7.56 (br, 1H, N=CH), 2.00 (s, 3H, Me), 1.78 (m, 6H, CH₂ TMP), 1.34 (s, 12H, MeTMP).

**¹³C{¹H} NMR** (151 MHz, 299 K, dichloromethane-d₂) δ = 166.6 (N=CH), 145.7 (dm, J₉C ~ 240 Hz, C₆F₅), 141.2 (dm, J₉C ~ 250 Hz, C₆F₅), 137.6 (dm, J₉C ~ 250 Hz, C₆F₅), 131.2 (dm, J₉C ~ 250 Hz, C₆F₅), 127.6 (s, 6C, C₆F₅), 119.8 (s, 6C, C₆F₅), 114.1 (s, 6C, C₆F₅), 51.1 (t, J₉C ~ 250 Hz, CH₂ TMP), 43.6 (t, J₉C ~ 250 Hz, CH₂ TMP), 31.9 (t, J₉C ~ 250 Hz, CH₂ TMP), 28.3 (t, J₉C ~ 250 Hz, CH₂ TMP), 14.2 (s, 6C, MeTMP), 13.0 (s, 6C, MeTMP), 12.8 (s, 6C, MeTMP), 12.7 (s, 6C, MeTMP).
$^{11}$B{\textsuperscript{1}H} NMR (192 MHz, 299 K, dichloromethane-d$_2$) $\delta = 51.9$ ($\nu_{1/2} \sim 500$ Hz).

$^{19}$F NMR (564 MHz, 299 K, dichloromethane-d$_2$) $\delta = -132.2$ (m, 2F, o-C$_6$F$_5$), -155.9 (t, $^3J_{FF} = 19.9$ Hz, 1F, p-C$_6$F$_5$), -163.6 (m, 2F, m-C$_6$F$_5$) [$\Delta \delta ^{19}$F$_{m,p} = 7.7$].

$^{19}$F NMR (564 MHz, 213 K, dichloromethane-d$_2$) $\delta = -131.8$ (m, 2F, o-C$_6$F$_5$), -155.2 (t, $^3J_{FF} = 20.8$ Hz, 1F, p-C$_6$F$_5$), -162.8 (m, 2F, m-C$_6$F$_5$) [$\Delta \delta ^{19}$F$_{m,p} = 7.6$]; -132.9 (m, 2F, o-C$_6$F$_5$), -155.6 (t, $^3J_{FF} = 20.6$ Hz, 1F, p-C$_6$F$_5$), -163.2 (m, 2F, m-C$_6$F$_5$) [$\Delta \delta ^{19}$F$_{m,p} = 7.6$].

$^1$H NMR (600 MHz, 299 K, dichloromethane-d$_2$) spectrum of compound 5

$^{11}$B{\textsuperscript{1}H} 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
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\(^3\), \( ρ_{\text{calc}} = 1.465 \) 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 (\( R_{\text{int}} = 0.070 \)) 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**

\[
\begin{align*}
\text{Cyclic yamine} & \quad + \quad \text{HB}(\text{C}_6\text{F}_5)_2 \\
\text{5} & \quad \xrightarrow{\text{H}_2} \quad \text{6}
\end{align*}
\]

A mixture of yamine 4 (35.9 mg, 0.2 mmol) and HB(C\text{6}F\text{5})\text{2} (69.2 mg, 0.2 mmol) in dichloromethane-d\text{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\text{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\text{24}H\text{24}BF\text{10}N+[Na\text{+}] 550.1734; found 550.1739.

**Melting point:** 167 °C

NMR data from the *in situ* generated colorless solution in dichloromethane-d\text{2}:

\[^1\text{H NMR}\] (500 MHz, 299 K, dichloromethane-d\text{2}) \(\delta = 7.33\) (br, 1H, NH), 5.72 (br, =CH), 3.30 (1:1:1:1 q, \(^1J_{\text{BH}} = 79.3\) Hz, BH), 1.96 (s, 3H, Me), [1.90/1.77 (each 2H), 1.82/1.72 (each 1H)](each m, CH\text{2}\text{TMP}), [1.40, 1.25](each s, each 6H, Me\text{TMP}).
$^{13}$C{$^1$H} NMR (126 MHz, 299 K, dichloromethane-d$_2$) δ = 159.1 (br 1:1:1:1 q, $^1J_{BC}$ = 53.0 Hz, BC=), 148.2 (dm, $^1J_{FC}$ ~ 240 Hz, C$_6$F$_5$), 138.5 (dm, $^1J_{FC}$ ~ 245 Hz, C$_6$F$_5$), 137.1 (dm, $^1J_{FC}$ ~ 250 Hz, C$_6$F$_5$), 124.1 (br, $i$-C$_6$F$_5$), 116.7 (=CH), 66.6 (NC$_{\text{TMP}}$), 39.3 (CH$_2$$_{\text{TMP}}$), 30.4 (t, $J$ = 3.0 Hz, Me$_{\text{TMP}}$), 23.6 (quint, $J$ = 4.0 Hz, Me), 21.6 (Me$_{\text{TMP}}$), 16.3 (CH$_2$$_{\text{TMP}}$).

$^{11}$B{$^1$H} NMR (160 MHz, 299 K, dichloromethane-d$_2$) δ = -23.2 (ν$_{1/2}$ ~ 24 Hz).

$^{11}$B NMR (160 MHz, 299 K, dichloromethane-d$_2$) δ = -23.2 (d, $^1J_{BH}$ = 79.3 Hz).

$^{19}$F NMR (470 MHz, 299 K, dichloromethane-d$_2$) δ = -131.6 (m, 2F, $o$-C$_6$F$_5$), -162.9 (t, $^3J_{FF}$ = 20.1 Hz, 1F, $p$-C$_6$F$_5$), -166.4 (m, 2F, $m$-C$_6$F$_5$) [$\Delta\delta^{19}$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\{\textsuperscript{1}H\} NMR (126 MHz, 299 K, dichloromethane-d\textsubscript{2}) spectrum of compound 6

$^{19}$F NMR (470 MHz, 299 K, dichloromethane-d\textsubscript{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, \( \beta = 105.982(1) \)°, \( V = 2548.9(1) \) Å\(^3\), \( \rho_{\text{calc}} = 1.374 \) gcm\(^{-3}\), \( \mu = 0.131 \) mm\(^{-1}\), empirical absorption correction (0.983 ≤ T ≤ 0.996), Z = 4, monoclinic, space group \( P2_1/c \) (No. 14), \( \lambda = 0.71073 \) Å, \( T = 173(2) \) K, \( \omega \) and \( \varphi \) scans, 17860 reflections collected (±h, ±k, ±l), 4421 independent (\( R_{\text{int}} = 0.053 \)) 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_{6}F_{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\textsubscript{32}H\textsubscript{28}BF\textsubscript{10}N\textsuperscript{+}[Na\textsuperscript{+}] 650.2047; found 650.2053.

Melting point: 193 °C

NMR data from a solution of the white solid in dichloromethane-d\textsubscript{2}:

\textsuperscript{1}H NMR (600 MHz, 299 K, dichloromethane-d\textsubscript{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\textsubscript{2}\textsuperscript{TMP}), [1.58, 1.38](each s, each 6H, Me\textsuperscript{TMP}).

\textsuperscript{13}C\{\textsuperscript{1}H\} NMR (151 MHz, 299 K, dichloromethane-d\textsubscript{2}) δ = 155.3 (br, BC=), 148.3 (dm, \textsuperscript{1}J\textsubscript{FC} \sim 240 Hz, C\textsubscript{6}F\textsubscript{5}), 138.9 (dm, \textsuperscript{1}J\textsubscript{FC} \sim 250 Hz, C\textsubscript{6}F\textsubscript{5}), 137.3 (dm, \textsuperscript{1}J\textsubscript{FC} \sim 250 Hz, C\textsubscript{6}F\textsubscript{5}), 131.7 (o-Ph), 128.9 (m-Ph), 128.2 (p-Ph), 125.0 (i-Ph), 124.0 (br, i-C\textsubscript{6}F\textsubscript{5}), 118.6 (=CH), 109.5 (br, BC=), 101.9 (br, PhC=), 66.7 (NC\textsuperscript{TMP}), 38.6 (CH\textsubscript{2}\textsuperscript{TMP}), 30.1 (t, J = 4.1 Hz, Me\textsuperscript{TMP}), 25.0 (br, Me), 21.4 (Me\textsuperscript{TMP}), 16.3 (CH\textsubscript{2}\textsuperscript{TMP}). [C\textsubscript{6}F\textsubscript{5} not listed,]

\textsuperscript{11}B\{\textsuperscript{1}H\} NMR (192 MHz, 299 K, dichloromethane-d\textsubscript{2}) δ = -19.7 (ν\textsubscript{1/2} \sim 20 Hz).

\textsuperscript{19}F NMR (564 MHz, 299 K, dichloromethane-d\textsubscript{2}) δ = -130.3 (m, 2F, o-C\textsubscript{6}F\textsubscript{5}), -162.3 (t, \textsuperscript{3}J\textsubscript{FF} = 20.3 Hz, 1F, p-C\textsubscript{6}F\textsubscript{5}), -166.2 (m, 2F, m-C\textsubscript{6}F\textsubscript{5}) [Δδ\textsuperscript{19}F\textsubscript{m,p} = 3.9].

\textsuperscript{1}H NMR (600 MHz, 299 K, dichloromethane-d\textsubscript{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
$^{19}\text{F NMR}$ (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 °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, $\alpha = 83.155(1)$, $\beta = 85.939(1)$, $\gamma = 77.609(1)^\circ$, $V = 1457.5(1)$ Å$^3$, $\rho_{\text{calc}} = 1.429$ g cm$^{-3}$, $\mu = 0.127$ mm$^{-1}$, empirical absorption correction (0.989 ≤ $T$ ≤ 0.993), $Z = 2$, triclinic, space group $P\overline{1}$ (No. 2), $\lambda = 0.71073$ Å, $T = 223(2)$ K, $\omega$ and $\varphi$ scans, 13670 reflections collected ($\pm h$, $\pm k$, $\pm l$), 5035 independent ($R_{\text{int}} = 0.048$) and 3685 observed reflections [$I > 2\sigma(I)$], 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**

![Synthesis reaction](image)

A mixture of ynamine 4 (89.7 mg, 0.5 mmol) and B(C₆F₅)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 C₃₀H₂₁BF₁₅N+[Na⁺] 714.1420; found 714.1425.

**Decomp.:** 222 °C

NMR data from a solution of the white solid in dichloromethane-d₂:

**¹H NMR** (500 MHz, 299 K, dichloromethane-d₂) δ = [1.89/1.73 (each 2H), 1.88/1.74 (each 1H)](each m, CH₂TMP), 1.78 (s, 3H, Me), [1.45, 1.35](each s, each 6H, Me₃Me).

**¹³C{¹H} NMR** (126 MHz, 299 K, dichloromethane-d₂) δ = 202.1 (C=), 148.4 (dm, ¹J.FC ~ 240 Hz, C₆F₅), 139.3 (dm, ¹J.FC ~ 260 Hz, C₆F₅), 137.2 (dm, ¹J.FC ~ 250 Hz, C₆F₅), 121.5 (br, i-C₆F₅), 93.5 (br, BC=), 69.0 (NCTMP), 38.2 (CH₂TMP), 30.5 (Me₃Me), 27.8 (Me₃Me), 17.5 (Me), 15.9 (CH₂TMP).
$^{11}$B{$^1$H} NMR (160 MHz, 299 K, dichloromethane-$d_2$) $\delta = -14.4$ ($\nu_{1/2} \sim 20$ Hz).

$^{19}$F NMR (470 MHz, 299 K, dichloromethane-$d_2$) $\delta = -130.8$ (m, 2F, o-C$_6$F$_5$), -160.4 (t, $^3J_{FF} = 20.3$ Hz, 1F, p-C$_6$F$_5$), -165.5 (m, 2F, m-C$_6$F$_5$) [$\Delta \delta^{19}$F$_{m,p} = 5.1$].

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

$^{13}$C{$^1$H} NMR (126 MHz, 299 K, dichloromethane-$d_2$) spectrum of compound 8a
$^{11}\text{B}^{[\text{H}]} \text{NMR}$ (160 MHz, 299 K, dichloromethane-\(d_2\)) spectrum of compound 8a

$^{19}\text{F} \text{NMR}$ (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 2σ(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

\[
\text{Ynmine 4 (35.9 mg, 0.2 mmol) and PhCH}_2\text{CH}_2\text{B(C}_6\text{F}_5)_2\text{ (90.0 mg, 0.2 mmol) in dichloromethane (2 mL) was stirred for 10 min to give a pale yellow solution. Then all volatiles were removed in vacuo to give a pale yellow solid. The pale yellow solid was washed with cold pentane (1 mL × 2) and dried in vacuo to give compound 8b as a white solid (117.0 mg, 0.186 mmol, 93 %).}
\]

HRMS: m/z calc. for C\text{32}H\text{30}BF\text{10}N\text{+[Na+]} 652.2204; found 652.2209.

Melting point: 174 °C

NMR data from a solution of the white solid in dichloromethane-d\text{2}:

\textbf{1H NMR} (600 MHz, 299 K, dichloromethane-d\text{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\text{2}), 1.88 (s, 3H, Me), [1.85/1.71 (each 1H), 1.84/1.67 (each 2H)] (each m, CH\text{2TMP}), [1.47, 1.33] (each s, each 6H, Me\text{TMP}), 1.16 (m, 2H, BCH\text{2}).

\textbf{13C\{1H\} NMR} (151 MHz, 299 K, dichloromethane-d\text{2}) δ = 199.5 (=C=), 148.3 (dm, \text{J}_{FC} \sim 240 \text{ Hz, C}_6\text{F}_5), 147.7 (i-Ph), 138.7 (dm, \text{J}_{FC} \sim 245 \text{ Hz, C}_6\text{F}_5), 137.3 (dm, \text{J}_{FC} \sim 250 \text{ Hz, C}_6\text{F}_5), 128.3 (m-Ph), 128.1 (o-Ph), 125.0 (p-Ph), 123.9 (br, i-C\text{6F}_5), 96.8 (br, BC=), 67.5 (NC\text{TMP}), 38.3 (CH\text{2TMP}), 34.1 (PhCH\text{2}), 31.3 (Me\text{TMP}), 28.9 (br, BCH\text{2}), 27.8 (Me\text{TMP}), 16.2 (CH\text{2TMP}), 14.1 (Me).

\textbf{11B\{1H\} NMR} (192 MHz, 299 K, dichloromethane-d\text{2}) δ = -11.7 (\nu_{1/2} \sim 70 \text{ Hz}).

\textbf{19F NMR} (564 MHz, 299 K, dichloromethane-d\text{2}) δ = -131.9 (m, 2F, o-C\text{6F}_5), -162.1 (t, \text{J}_{FF} = 20.3 \text{ Hz, 1F, p-C}_6\text{F}_5), -165.6 (m, 2F, m-C\text{6F}_5) [\Delta \delta^{19F}_{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 2σ(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 $P_2_1/n$, 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.](image-url)
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 nBuLi was slowly added to the Et₂O 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 Et₂O 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 nBuLi 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.

^1H NMR (500 MHz, 299 K, C₆D₆, 7.15 ppm): δ = 2.72 (sept, ^3J_HH = 6.6 Hz, 2H, CH(CH₃)₂), 1.06 (d, ^3J_HH = 6.6 Hz, 12H, CH(CH₃)₂), 0.30 (s, 9H, Si(CH₃)₃).

^13C{^1H} NMR (126 MHz, 299 K, C₆D₆, 128.0 ppm): δ = 104.6 (≡CN), 68.3 (C≡), 51.7 (CH(CH₃)₂), 21.3 (CH(CH₃)₂), 1.4 (Si(CH₃)₃).

^29Si{^1H} dept NMR (119 MHz, 299 K, C₆D₆): δ = −20.9 (s).
\( ^1H \text{ NMR} \) (500 MHz, 299 K, C\(_6\)D\(_6\)) spectrum of compound 9.

\( ^{13}C\{^1H\} \text{ NMR} \) (126 MHz, 299 K, C\(_6\)D\(_6\)) spectrum of compound 9.
Synthesis of compound 10a

Compound 9 (99 mg, 0.5 mmol) and B(C₆F₅)₃ (256 mg, 0.5 mmol) were mixed in CH₂Cl₂ (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 C₂₉H₂₃BNSiF₁₅ (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.

¹H NMR (600 MHz, 299 K, CD₂Cl₂, 5.32 ppm): δ = 3.83 (sept, ³JHH = 6.6 Hz, 2H, CH(CH₃)₂), 1.39 (d, ³JHH = 6.6 Hz, 6H, CH(CH₃)₂), 1.13 (d, ³JHH = 6.6 Hz, 6H, CH(CH₃)₂), 0.04 (s, 9H, Si(CH₃)₃).

¹³C{¹H} NMR (151 MHz, 299 K, CD₂Cl₂, 53.8 ppm): δ = 183.8 (=C=), 148.5 (dm, ¹JFC ~ 240 Hz, C₆F₅), 139.7 (dm, ¹JFC ~ 248 Hz, C₆F₅), 137.2 (dm, ¹JFC ~ 252 Hz, C₆F₅), 121.6 (br, i-C₆F₅), 84.1 (br, BC=), 57.7 (CH(CH₃)₂), 21.8 (CH(CH₃)₂), 21.4 (CH(CH₃)₂), 0.8 (Si(CH₃)₃).

¹¹B{¹H} NMR (192 MHz, 299 K, CD₂Cl₂): δ = −14.4 (ν₁/₂ ~ 28 Hz).

¹⁹F NMR (564 MHz, 299 K, CD₂Cl₂): δ = −131.1 (br, 2F, o-C₆F₅), −160.0 (t, ³JFF = 18.0 Hz, 1F, p-C₆F₅), −165.5 (m, 2F, m-C₆F₅) [Δδ¹⁹Fₘₙₚ = 5.5].

²⁹Si{¹H} dept NMR (119 MHz, 299 K, CD₂Cl₂): δ = 6.5 (s).
$^1$H NMR (600 MHz, 299 K, CD$_2$Cl$_2$) spectrum of compound 10a.

$^{13}$C($^1$H) NMR (151 MHz, 299 K, CD$_2$Cl$_2$) spectrum of compound 10a.
19F (564 MHz, 299 K, CD2Cl2), 11B{1H} (192 MHz, 299 K, CD2Cl2), and 29Si{1H} dept NMR (119 MHz, 299 K, CD2Cl2) spectra of compound 10a.

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound 10a in CH2Cl2 and pentane at −35 °C.

X-ray crystal structure analysis of compound 10a (erk8313): A colorless plate-like specimen of C29H23BF15NSi, 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%, Rint = 4.73%, Rsig = 1.87%) and 4965 (89.90%) were greater than 2σ(F2). 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) Å³, 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 P21/n, with Z = 4 for the formula unit, C29H23BF15NSi. The final anisotropic full-matrix least-squares refinement on F2 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/Å³ and the largest hole was -0.258 e/Å³ with an RMS deviation of 0.041 e/Å³. On the basis of the final model, the calculated density was 1.543 g/cm³ 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(C6F5)2 (173 mg, 0.5 mmol) were mixed in CH2Cl2 (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 C28H30BNSiF10 (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.

**1H NMR** (600 MHz, 299 K, C6D6, 7.15 ppm): δ = 6.69 (d, 3JHH = 18.0 Hz, 1H, BCH=), 6.21 (d, 3JHH = 18.0 Hz, 1H, =CH), 4.89 (m, 2H, =CH2), 2.54 (m, 2H, CH(CH3)2), 1.96 (s, 3H, CH3), 0.67 (m, 12H, CH(C6H3)2), 0.00 (s, 9H, Si(CH3)3).

**13C[1H] NMR** (151 MHz, 299 K, C6D6, 128.0 ppm): δ = 180.8 (=C=), 144.3 (C=), 141.6 (br, BCH=), 138.1 (=CH), 113.5 (=CH2), 89.5 (br, BC=), 56.9 (CH(CH3)2), 20.94 (CH(CH3)2), 20.90 (CH(CH3)2), 19.1 (CH3), 0.5 (Si(CH3)3), [C6F5 not listed].

**11B[1H] NMR** (192 MHz, 299 K, C6D6): δ = −11.9 (v1/2 ~ 107 Hz).
$^{19}$F NMR (564 MHz, 299 K, C$_6$D$_6$): $\delta = [-129.20, -129.22]$ (each m, each 2F, $\alpha$-C$_6$F$_5$), $[-159.7$ (t, $^3J_{FF} = 20.2$ Hz), $-159.8$ (br, 1F)]($\rho$-C$_6$F$_5$), $-164.7$ (m, 4F, $m$-C$_6$F$_5$).

$^{29}$Si($^1$H) dept NMR (119 MHz, 299 K, C$_6$D$_6$): $\delta = 3.2$ (s).

$^1$H NMR (600 MHz, 299 K, C$_6$D$_6$) spectrum of compound 10b.

$^{13}$C($^1$H) NMR (151 MHz, 299 K, C$_6$D$_6$) spectrum 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, $\beta = 94.422(1)^\circ$, $V = 2953.5(1)$ Å$^3$, $\rho_{\text{calc}} = 1.371$ g cm$^{-3}$, $\mu = 0.161$ mm$^{-1}$, empirical absorption correction ($0.965 \leq T \leq 0.974$), $Z = 4$, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 0.71073$ Å, $T = 223(2)$ K, $\omega$ and $\phi$ scans, 20730 reflections collected ($\pm h$, $\pm k$, $\pm l$), 7211 independent ($R_{\text{int}} = 0.032$) and 5743 observed reflections [$I > 2\sigma(I)$], 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**

\[ \text{Cp}_2\text{ZrMe}_2 + [\text{Ph}_2\text{C}]\text{[B(C}_6\text{F}_5)_4] \rightarrow \text{Me}_2\text{Si} \text{NPr}_2 \text{Me}_3\text{Si} \text{C} = \text{C=NPr}_2 \]

Cp₂ZrMe₂ (126 mg, 0.5 mmol) and [Ph₂C][B(C₆F₅)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 C₄₆H₃₆BNSiF₂₀Zr (1112.9 g mol⁻¹): C, 49.65; H, 3.26; N, 1.26. Found: C, 49.31; H, 3.07; N, 1.46.

¹H NMR (600 MHz, 299 K, C₆D₅Br, 6.97 ppm): δ = 5.94 (s, 10H, Cp), 2.85 (sept, ³J_HH = 6.6 Hz, 2H, CH(CH₃)₂), 0.89 (d, ³J_HH = 6.6 Hz, 6H, CH(CH₃)₂), 0.88 (d, ³J_HH = 6.6 Hz, 6H, CH(CH₃)₂), 0.08 (s, 3H, Zr-Me), 0.00 (s, 9H, Si(CH₃)₃).

¹³C[¹H] NMR (151 MHz, 299 K, C₆D₅Br, 122.3 ppm): δ = 146.7 (=C=), 112.7 (Cp), 95.5 (ZrC=), 55.0 (CH(CH₃)₂), 45.9 (Zr-Me), 21.3 (CH(CH₃)₂), 20.8 (CH(CH₃)₂), 1.6 (Si(CH₃)₃), [C₆F₅ not listed].
$^{11}$B{¹H} NMR (192 MHz, 299 K, C₆D₅Br): δ = −16.1 (ν₁/₂ ~ 22 Hz).

$^{19}$F NMR (564 MHz, 299 K, C₆D₅Br): δ = −131.6 (br, 2F, o-C₆F₅), −162.0 (t, $^3J_{FF}$ = 21.4 Hz, 1F, p-C₆F₅), −165.8 (m, 2F, m-C₆F₅) [$Δδ^{19}F_{m,p} = 3.8$].

$^{29}$Si{¹H} depta NMR (119 MHz, 299 K, C₆D₅Br): δ = 1.4 (s).

$^1$H NMR (600 MHz, 299 K, C₆D₅Br) spectrum of compound 10c.

$^{13}$C{¹H} NMR (151 MHz, 299 K, C₆D₅Br) spectrum of compound 10c.
\(^{19}\text{F}\) (564 MHz, 299 K, C\(_6\)D\(_3\)Br), \(^{11}\text{B}\{^{1}\text{H}\}\) (192 MHz, 299 K, C\(_6\)D\(_3\)Br), and \(^{29}\text{Si}\{^{1}\text{H}\}\) dept NMR (119 MHz, 299 K, C\(_6\)D\(_3\)Br) 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 \(\theta\) angle of 66.72° (0.84 Å resolution), of which 7704 were independent (average redundancy 4.645, completeness = 97.5\%, \(R_{\text{int}} = 6.32\%\), \(R_{\text{sig}} = 4.96\%\)) 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, \(\alpha = 88.616(3)^\circ\), \(\beta = 88.273(3)^\circ\), \(\gamma = 84.773(2)^\circ\), volume = 2229.7(2) Å\(^3\), are based upon the refinement of the XYZ-centroids of 9984 reflections above 2\(\sigma(I)\) with 6.108° < 2\(\theta\) < 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 \(P^1\), 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 \(R_1 = 4.37\%\), 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 \(F(000) = 1116\ e^\circ\).
Crystal structure of compound 10c. Thermal ellipsoids are shown at 30 % probability.

**Synthesis of compound 11**

[Chemical reaction]

Compound 9 (99 mg, 0.5 mmol) and HB(C₆F₅)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 C₂₃H₂₄BNSi₁₀ (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$_6$D$_6$, 7.15 ppm): $\delta = 7.82$ (s, 1H, $HC=$), 4.59 (br, 1H, $CH(CH_3)_2$), 2.71 (br, 1H, $CH(CH_3)_2$), 0.60 (br, 6H, $CH(CH_3)_2$), 0.33 (br, 6H, $CH(CH_3)_2$), 0.07 (s, 9H, Si(CH$_3)_3$).

$^{13}$C($^1$H) NMR (151 MHz, 299 K, C$_6$D$_6$, 128.0 ppm): $\delta = 170.6$ ($C$H=$), 146.5 (dm, $^1$J$_{FC} \sim 240$ Hz, C$_6$F$_5$), 141.2 (dm, $^1$J$_{FC} \sim 252$ Hz, C$_6$F$_5$), 137.8 (dm, $^1$J$_{FC} \sim 250$ Hz, C$_6$F$_5$), 118.8 (br, $i$-C$_6$F$_5$), 110.5 (br, $C$=B), 51.9 ($CH(CH_3)_2$), 47.7 ($CH(CH_3)_2$), 23.2 ($CH(CH_3)_2$), 18.4 ($CH(CH_3)_2$), 1.9 (Si(CH$_3)_3$).

$^{11}$B($^1$H) NMR (192 MHz, 299 K, C$_6$D$_6$): $\delta = 42.0$ ($\nu_{1/2} \sim 540$ Hz).

$^{19}$F NMR (564 MHz, 299 K, C$_6$D$_6$) $\delta = -132.2$ (br, 2F, $o$-C$_6$F$_5$), -154.9 (t, $^3$J$_{FF} = 20.0$ Hz, 1F, $p$-C$_6$F$_5$), -162.9 (m, 2F, $m$-C$_6$F$_5$) [$\Delta \delta^{19}$F$_{m,p} = 8.0$].

$^{19}$F NMR (564 MHz, 233 K, dichloromethane-d$_2$) $\delta = -132.2$ (m, 2F, $o$-C$_6$F$_5$), -156.7 (t, $^3$J$_{FF} = 20.5$ Hz, 1F, $p$-C$_6$F$_5$), -163.8 (m, 2F, $m$-C$_6$F$_5$) [$\Delta \delta^{19}$F$_{m,p} = 7.1$]; -133.5 (m, 2F, $o$-C$_6$F$_5$), -155.9 (t, $^3$J$_{FF} = 20.6$ Hz, 1F, $p$-C$_6$F$_5$), -163.0 (m, 2F, $m$-C$_6$F$_5$) [$\Delta \delta^{19}$F$_{m,p} = 7.1$].

$^{29}$Si($^1$H) dept NMR (119 MHz, 299 K, C$_6$D$_6$): $\delta = -3.9$ (s).

$^1$H NMR (600 MHz, 299 K, C$_6$D$_6$) spectrum of compound 11.
$^{13}\text{C}^{[1\text{H}]}\text{NMR}$ (151 MHz, 299 K, C$_6$D$_6$) spectrum of compound 11.

$^{29}\text{Si}^{[1\text{H}]}(\text{dept})$ (119 MHz, 299 K, C$_6$D$_6$), $^{19}\text{F}$ (564 MHz, 299 K, C$_6$D$_6$), and $^{11}\text{B}^{[1\text{H}]}\text{NMR}$ (192 MHz, 299 K, C$_6$D$_6$) spectra of compound 11.
\[ ^{19}\text{F NMR} \text{ (564 MHz, dichloromethane-d}_2\text{)} \text{ spectra of compound 11 at 299 K and 233 K.} \]

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 \( \theta \) 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, \( \beta = 98.650(2)\)°, volume = 2517.60(17) Å\(^3\), are based upon the refinement of the XYZ-centroids of reflections above 20 \( \sigma \)(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(C₆F₅)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 C₃₀H₃₈BN₃SiF₁₀ (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: **¹H NMR** (600 MHz, 238 K, CD₂Cl₂, 5.32 ppm): δ = 6.82 (s, 1H, =CH), 4.09 (m, 1H, CH(CH₃)₂), 3.71 (m, 2H, BNCH(CH₃)₂), 3.48 (m, 1H, CH(CH₃)₂), 1.17 (d, 3J_HH = 6.6 Hz, 12H, CH(CH₃)₂), 0.85 (d, 3J_HH = 6.6 Hz, 6H, B−N−CH(CH₃)₂), 0.83 (d, 3J_HH = 6.9 Hz, 6H, BNCH(CH₃)₂), 0.19 (s, 9H, Si(CH₃)₃).

E-13: **¹H NMR** (600 MHz, 238 K, CD₂Cl₂, 5.32 ppm): δ = 6.35 (s, 1H, =CH), 4.12 (m, 1H, CH(CH₃)₂), 3.71 (m, 2H, BNCH(CH₃)₂), 3.47 (m, 1H, CH(CH₃)₂), 1.15 (d, 3J_HH = 6.6 Hz, 6H, CH(CH₃)₂), 1.07 (d, 3J_HH = 6.6 Hz, 6H, CH(CH₃)₂), 0.93 (d, 3J_HH = 7.2 Hz, 6H, B−N−CH(CH₃)₂), 0.92 (d, 3J_HH = 7.2 Hz, 6H, B−N−CH(CH₃)₂), 0.14 (s, 9H, Si(CH₃)₃).
Z-13: $^{13}$C$^{1}$H NMR (151 MHz, 238 K, CD$_2$Cl$_2$, 53.8 ppm): $\delta = 181.1$ (NCN), 148.7 (=CH), 82.3 (SiC=), 49.7 (br, CH(CH$_3$)$_2$), 45.7 (BNCH(CH$_3$)$_2$), 45.4 (br, CH(CH$_3$)$_2$), 23.4 (br, CH(CH$_3$)$_2$), 21.9 (BNCH(CH$_3$)$_2$), 21.3 (BNCH(CH$_3$)$_2$), 19.9 (br, CH(CH$_3$)$_2$), 0.8 (Si(CH$_3$)$_3$), [C$_6$F$_5$ not listed].

E-13: $^{13}$C$^{1}$H NMR (151 MHz, 238 K, CD$_2$Cl$_2$, 53.8 ppm): $\delta = 177.1$ (NCN), 144.1 (=CH), 81.9 (SiC=), 48.1 (CH(CH$_3$)$_2$), 46.5 (BNCH(CH$_3$)$_2$), 45.6 (CH(CH$_3$)$_2$), 23.6 (CH(CH$_3$)$_2$), 22.5 (BNCH(CH$_3$)$_2$), 22.4 (BNCH(CH$_3$)$_2$), 20.8 (CH(CH$_3$)$_2$), 0.8 (Si(CH$_3$)$_3$), [C$_6$F$_5$ not listed].

$^{11}$B$^{1}$H NMR (192 MHz, 238 K, CD$_2$Cl$_2$): $\delta = 0.2$, −0.4

Z-13: $^{19}$F NMR (564 MHz, 238 K, CD$_2$Cl$_2$): $\delta = [-130.2, -132.1]$ (each m, each 2F, o-C$_6$F$_5$), $[-159.1$ (t, $^3$J$_{FF} = 21.0$ Hz), $-159.3$ (t, $^3$J$_{FF} = 20.6$ Hz)] (each 1F, p-C$_6$F$_5$), $[-164.4$, $-164.6]$ (each m, each 2F, m-C$_6$F$_5$).

E-13: $^{19}$F NMR (564 MHz, 238 K, CD$_2$Cl$_2$): $\delta = [-129.7, -131.0]$ (each m, each 2F, o-C$_6$F$_5$), $[-158.7$ (t, $^3$J$_{FF} = 21.2$ Hz), $-159.0$ (t, $^3$J$_{FF} = 20.6$ Hz)] (each 1F, p-C$_6$F$_5$), $[-164.4$, $-164.6]$ (each m, each 2F, m-C$_6$F$_5$).

Z-13: $^{29}$Si$^{1}$H dept NMR (119 MHz, 299 K, CD$_2$Cl$_2$): $\delta = -12.5$ (s).

E-13: $^{29}$Si$^{1}$H dept NMR (119 MHz, 299 K, CD$_2$Cl$_2$): $\delta = 0.8$ (s).

Z-13: $^1$H, $^1$H gCOSY (600 MHz/600 MHz, 238 K, CD$_2$Cl$_2$) [selected traces]: $\delta^1$H / $\delta^1$H = 4.09 and 3.48 / 1.17 (CH(CH$_3$)$_2$ / CH(CH$_3$)$_2$), 3.71 / 0.85 and 0.83 (BNCH(CH$_3$)$_2$ / BNCH(CH$_3$)$_2$).

E-13: $^1$H, $^1$H gCOSY (600 MHz/600 MHz, 238 K, CD$_2$Cl$_2$) [selected traces]: $\delta^1$H / $\delta^1$H = 4.12 / 1.07 (CH(CH$_3$)$_2$ / CH(CH$_3$)$_2$), 3.47 / 1.15 (CH(CH$_3$)$_2$ / CH(CH$_3$)$_2$), 3.71 / 0.93 and 0.92 (BNCH(CH$_3$)$_2$ / BNCH(CH$_3$)$_2$).

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

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

Z-13: $^1$H, $^{13}$C gHMBC (600 MHz/151 MHz, 238 K, CD$_2$Cl$_2$) [selected traces]: $\delta^1$H / $\delta^{13}$C = 6.82 / 181.1 and 82.3 (=CH / NCN and SiC=).

E-13: $^1$H, $^{13}$C gHMBC (600 MHz/151 MHz, 238 K, CD$_2$Cl$_2$) [selected traces]: $\delta^1$H / $\delta^{13}$C = 6.35 / 177.1 and 81.9 (=CH / NCN and SiC=).
$^1$H NMR (600 MHz, 238 K, CD$_2$Cl$_2$) spectrum of compounds Z-13 and E-13.

$^{13}$C($^1$H) NMR (151 MHz, 238 K, CD$_2$Cl$_2$) spectrum of compounds Z-13 and E-13.
$^{29}\text{Si}^{[1\text{H}]}$ dept NMR (119 MHz, 299 K, CD$_2$Cl$_2$), $^{19}\text{F}$ (564 MHz, 238 K, CD$_2$Cl$_2$), and $^{11}\text{B}^{[1\text{H}]}$ NMR (192 MHz, 238 K, CD$_2$Cl$_2$) spectra of compounds Z-13 and E-13.

1D NOESY (600 MHz, 238 K, CD$_2$Cl$_2$) spectrum of compound Z-13.
1D NOESY (600 MHz, 238 K, CD₂Cl₂) 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 C₃₀H₃₈BF₁₀N₃Si, 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 2σ(F²). 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) Å³, 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 \( P2₁/n \), with \( Z = 4 \) for the formula unit, C₃₀H₃₈BF₁₀N₃Si. The final anisotropic full-matrix least-squares refinement on F² 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/Å³ and the largest hole was -0.287 e/Å³ with an RMS deviation of 0.045 e/Å³. On the basis of the final model, the calculated density was 1.323 g/cm³ and F(000), 1392 e⁻.
Crystal structure of compound Z-13. Thermal ellipsoids are shown at 30% probability.