Supplementary Data for:

Frustrated Lewis Pair Behavior of Intermolecular Amine/$B(C_6F_5)_3$ Pairs

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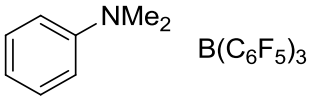
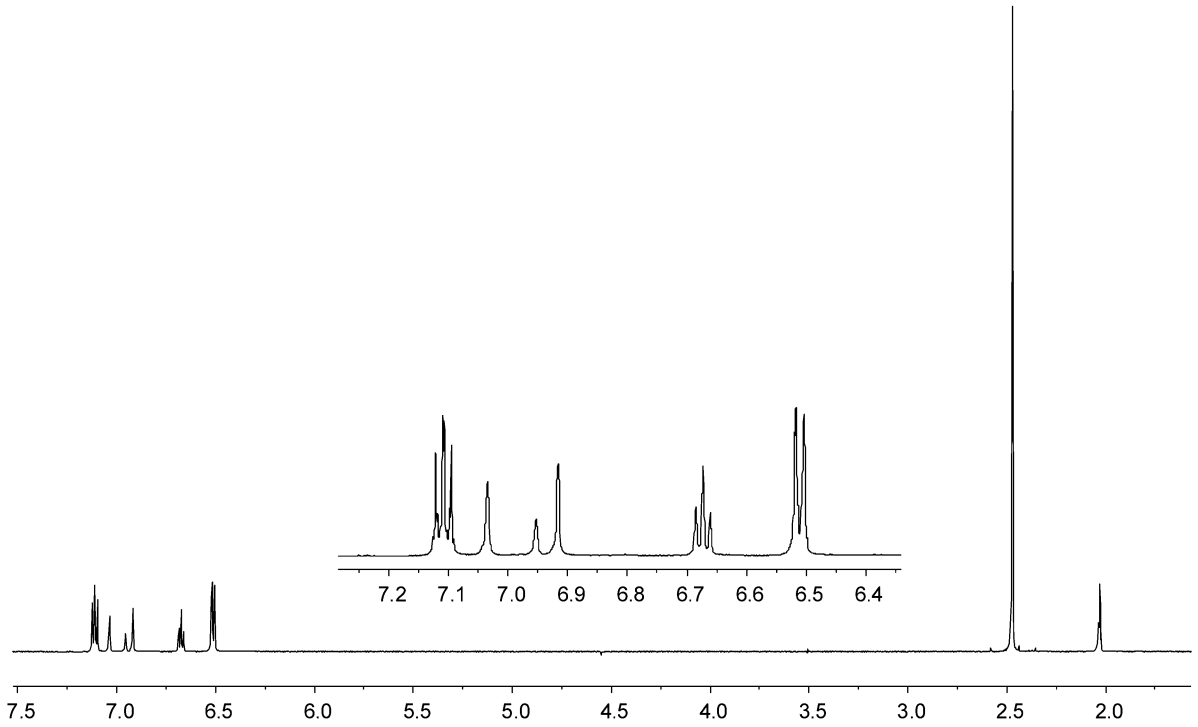
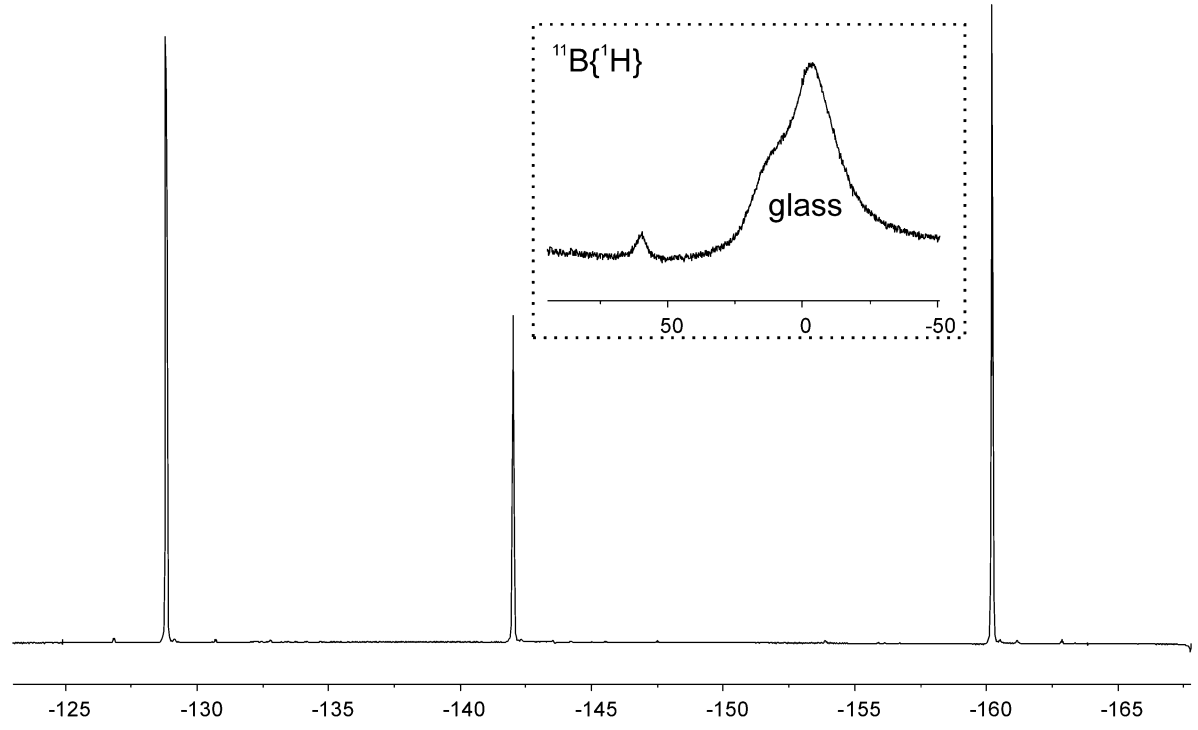
Reaction of $PhNMe_2$ and $B(C_6F_5)_3$. *N,N*-dimethylaniline (10.0 mg, 0.083 mmol) and $B(C_6F_5)_3$ (42.2 mg, 0.083 mmol) were dissolved in C_7D_8 (0.5 mL) each and mixed to yield a reaction solution which was characterized by NMR-spectroscopy.



^{1}H NMR (600 MHz, C_7D_8, 298K): δ 7.11 (m, 2H, *m*-C_6H_5); 6.67 (m, 1H, *p*-C_6H_5); 6.51 (m, 2H, *o*-C_6H_4); 2.47 (s, 6H, NMe_2). ^{19}F NMR (564 MHz, C_7D_8, 298K): δ −128.8 (m, 2F, *o*-C_6F_5); −142.0 (m, 1F, *p*-C_6F_5); −160.2 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{p,m}$ = 18.2]. $^{11}B\{^1H\}$ NMR (192 MHz, C_7D_8, 298K): δ 59.9 (br, $\nu_{1/2}$ ~ 950 Hz).

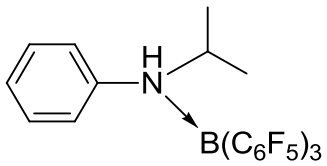


^{1}H NMR (600 MHz, C_7D_8, 298K)



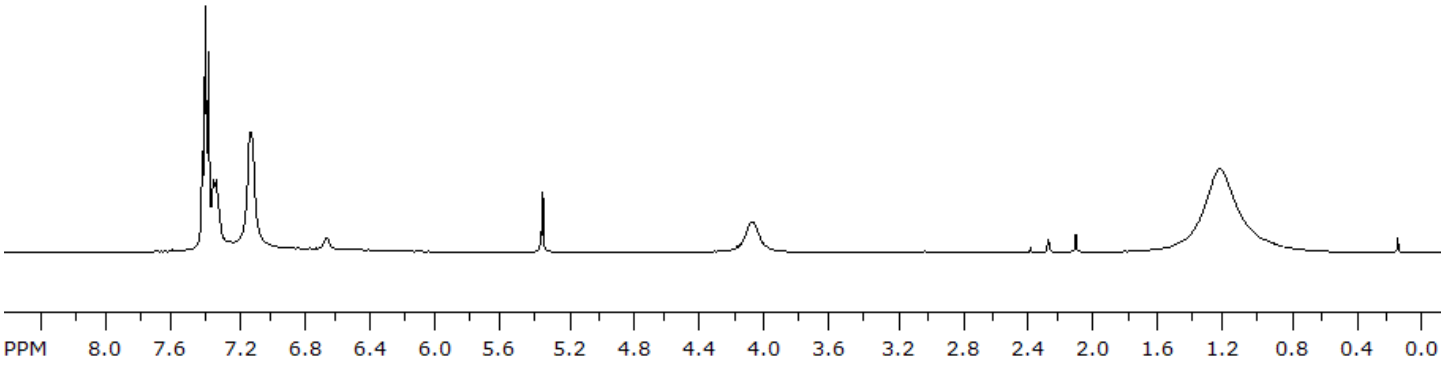
^{19}F NMR (564 MHz, C_7D_8, 298K) and ^{11}B{^{1}H} NMR (192 MHz, C_7D_8, 298K)

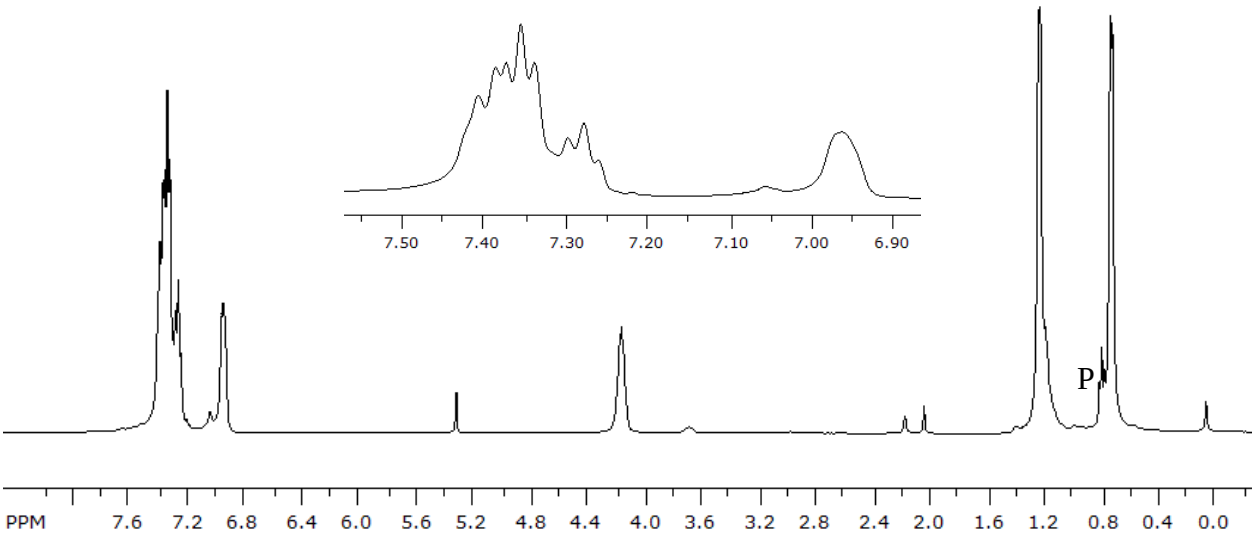
Synthesis of PhNH(*i*Pr)(B(C_6F_5)$_3$) (1). In a glovebox, a 20 mL dram vial equipped with a magnetic stir bar was charged with B(C_6F_5)$_3$ (176 mg, 0.344 mmol) and *N*-isopropylaniline (46.5 mg, 0.344 mmol) in toluene (4 mL). All volatiles were removed and the crude oil was washed with hexanes (2 mL). The hexanes portion was reduced in volume and placed in a – 40 ºC freezer. Colorless crystals of (**1**) were obtained (122 mg, 0.192 mmol, 55 %).



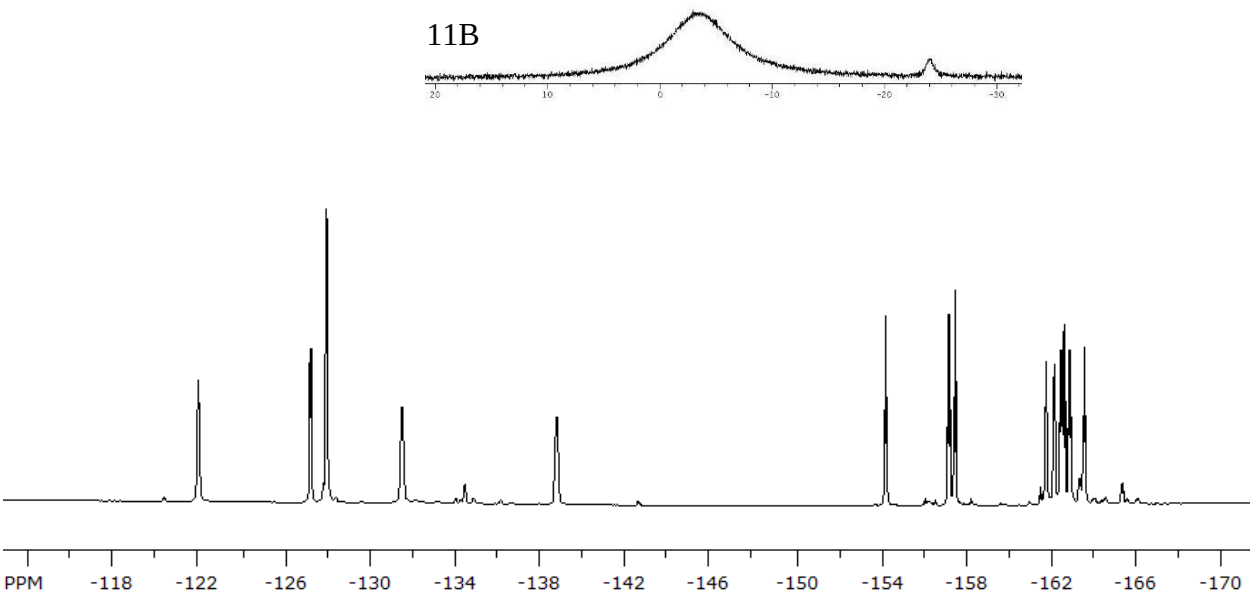
1: ^{1}H NMR (400 MHz, CD_2Cl_2, 193K): δ 7.40-7.26 (m, 5H, Ar), 6.96 (br, 1H, NH), 4.16 (br m, 1H, C*H*(CH_3)$_2$), 1.23 (br, 3H, CH_3), 0.72 (br, 3H, CH_3); ^{19}F NMR (367 MHz, CD_2Cl_2, 193K): δ -121.9 (m, 1F, *o*-C_6F_5), -127.2 (m, 1F, *o*-C_6F_5), -127.9 (m, 2F, *o*-C_6F_5), -131.5 (m, 1F, *o*-C_6F_5), -138.8 (m, 1F, *o*-C_6F_5), -154.3 (t, 1F, $^3J_{F\text{-}F}$ = 21 Hz, *p*-C_6F_5), -157.3 (t, 1F, $^3J_{F\text{-}F}$ = 21 Hz, *p*-C_6F_5), -157.5 (t, 1F, $^3J_{F\text{-}F}$ = 21 Hz, *p*-C_6F_5), -161.8 (m, 1F, *m*-C_6F_5), -162.2 (m, 1F, *m*-C_6F_5), -162.5 (m, 1F, *m*-C_6F_5), -162.7 (m, 1F, *m*-C_6F_5), -162.9 (m, 1F, *m*-C_6F_5), -163.6 (m, 1F, *m*-C_6F_5); ^{11}B NMR (128 MHz, CD_2Cl_2, 193K): δ -3.23; ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 298K): δ 147.8 (dm, $^1J_{C\text{-}F}$ ≈ 246 Hz, C_6F_5), 139.0 (dm, $^1J_{C\text{-}F}$ ≈ 242 Hz, C_6F_5), 136.5 (dm, $^1J_{C\text{-}F}$ ≈ 236 Hz, C_6F_5), 132.8 (*i*-Ar), 130.1 (*o*-Ar), 129.5 (*p*-Ar), 122.7 (*m*-Ar), 55.6 (*C*H(CH_3)$_2$), 19.5 (CH(*C*H_3)$_2$).

^{1}H NMR at 298 K.





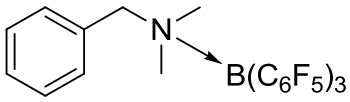
^{1}H NMR (400 MHz, CD_2Cl_2, 193K) (P: Pentane)



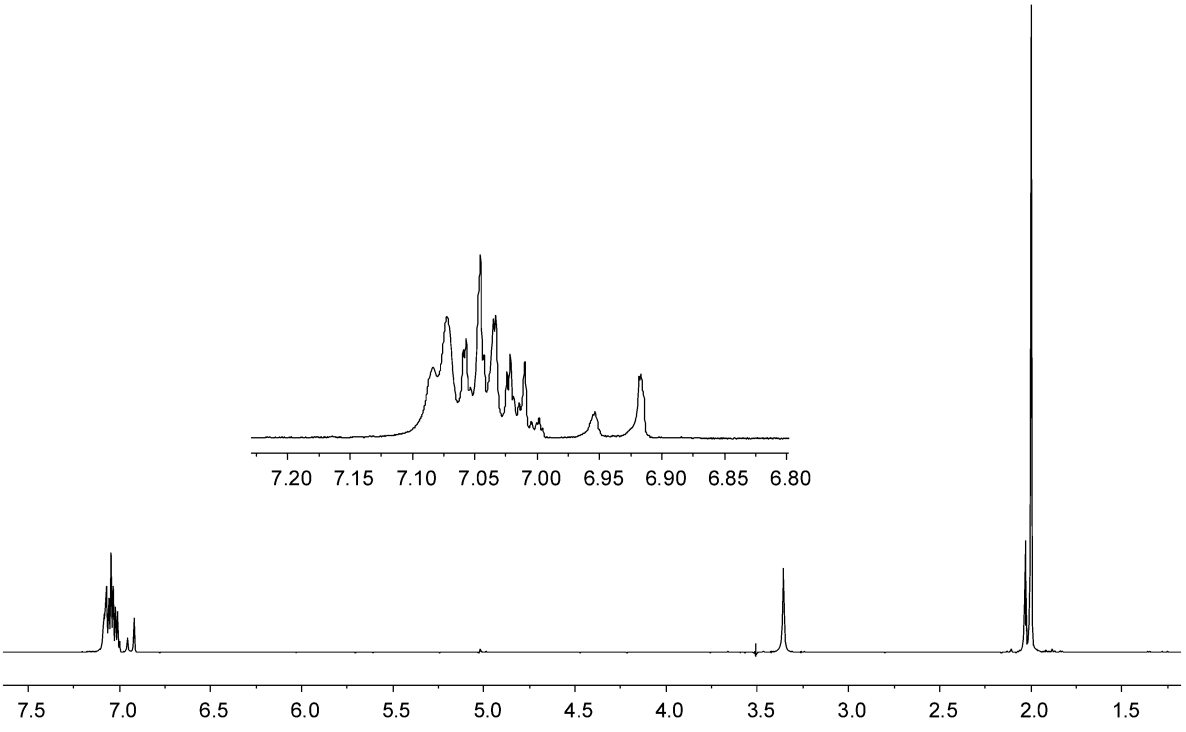
^{19}F NMR (367 MHz, CD_2Cl_2, 193K) and ^{11}B NMR (128 MHz, CD_2Cl_2, 193K)

Elem. Anal. $C_{27}H_{13}BF_{15}N$ calcd: C 50.11, H 2.02, N 2.16; found: C 49.61, H 2.46, N 2.09. X-ray: $C_{27}H_{13}BF_{15}N$, M = 647.19, a = 11.6228(4), b = 18.1284(7), c = 23.6578(9) Å, V = 4984.8(3) Å^3, Z = 8, orthorhombic, $P2_12_12_1$, Data (λ = 0.71069 Å, T = 150 K), 8773 (R_{int} = 0.030), 7798 [$I \geq 2\ \sigma(I)$], 798 parameters, R = 0.032, wR^2 = 0.076, GOF = 1.021.

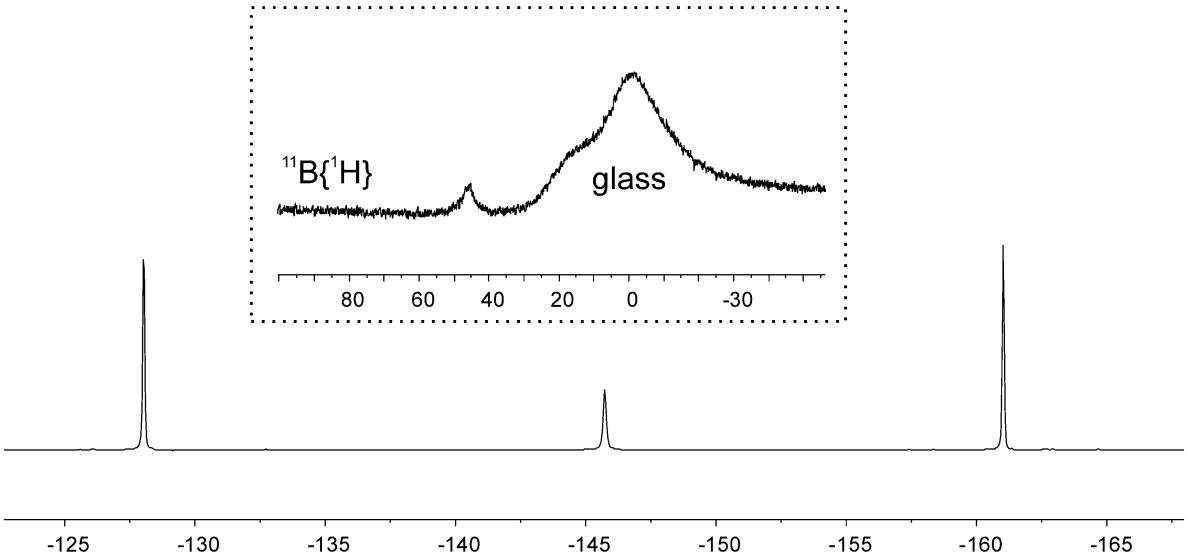
Synthesis of [$PhCH_2NMe_2(B(C_6F_5)_3)$] (2). *N*,*N*-dimethylbenzylamine (10.0 mg, 0.074 mmol) and $B(C_6F_5)_3$ (38.2 mg, 0.074 mmol) were dissolved in C_6D_5Br (0.5 mL) and C_7D_8 (0.5 mL) each, respectively, and mixed to yield a solution which was characterized by NMR-spectroscopy.



2: ^{1}H NMR (400 MHz, C_6D_5Br, 298K): δ 7.19 (m, 5H, C_6H_5); 3.63 (br s, 2H, CH_2N); 2.21 (s, 6H, NCH_3). ^{1}H NMR (600 MHz, C_7D_8, 298K): δ 7.08, 7.04, 7.02 (m, Σ 5H, C_6H_5); 3.36 (br s, 2H, CH_2N); 2.00 (s, 6H, NCH_3). ^{19}F NMR (377 MHz, C_6D_5Br, 298K): δ −126.3 (br, 2F, *o*-C_6F_5); −147.9 (br, 1F, *p*-C_6F_5); −160.6 (br, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{p,m}$ = 12.7]. ^{19}F NMR (564 MHz, C_7D_8, 298K): δ −128.0 (br, 2F, *o*-C_6F_5); −145.7 (br, 1F, *p*-C_6F_5); −161.0 (br, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{p,m}$ = 15.3]. $^{11}B\{^1H\}$ NMR (128 MHz, C_6D_5Br, 298K): δ 30.3 ($\nu_{1/2}$ ~ 1200 Hz). $^{11}B\{^1H\}$ NMR (192 MHz, C_7D_8, 298K): δ 46.3 ($\nu_{1/2}$ ~ 800 Hz).



^{1}H NMR (600 MHz, C_7D_8, 298K)

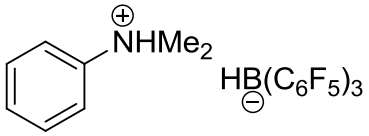


^{19}F NMR (564 MHz, C_7D_8, 298K) and ^{11}B{^{1}H} NMR (192 MHz, C_7D_8, 298K)

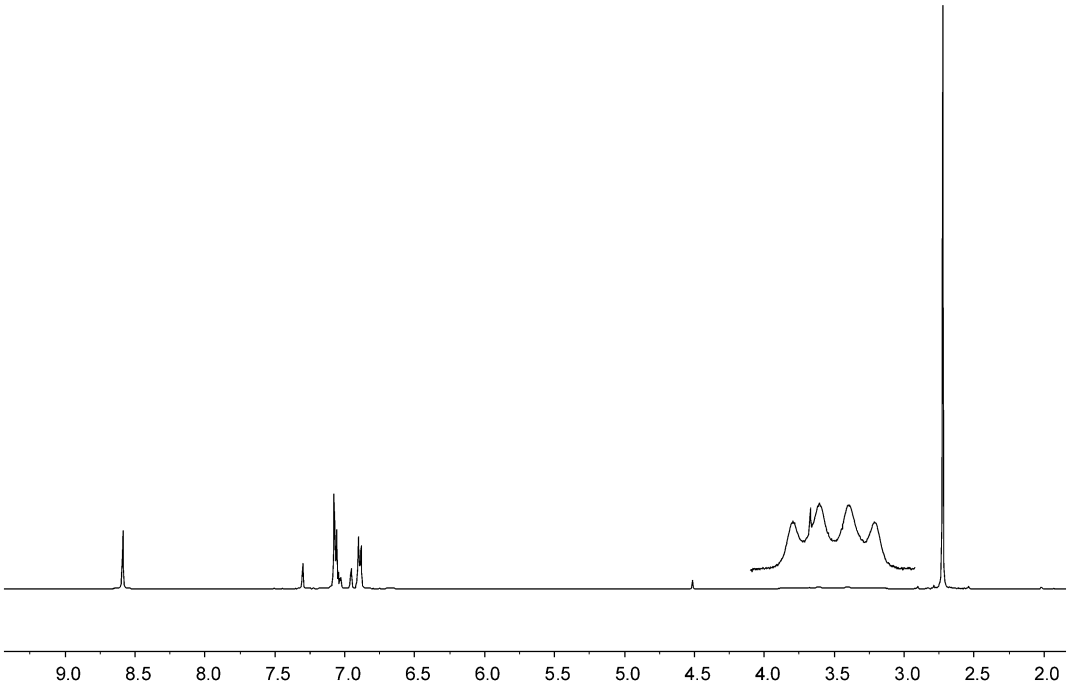
X-ray crystal structure analysis of **2**: formula $C_{27}H_{13}BF_{15}N$ * CH_2Cl_2, M = 732.12, colorless crystal 0.20 x 0.18 x 0.12 mm, a = 9.9870(5), b = 10.6730(5), c = 14.3150(7) Å, α = 70.935(2), β = 80.851(2), γ = 81.259(2)°, V = 1415.61(12) Å^3, ρ_{calc} = 1.718 g cm^{-3}, μ = 3.206 cm^{-1}, empirical absorption correction (0.567 $\leq$ T $\leq$ 0.700), Z = 2, triclinic, space group P1bar (No. 2), λ= 1.54178 Å, T = 223 K, ω and φ scans, 16585 reflections collected (± h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 4870 independent (R_{int} = 0.040) and 4419 observed reflections [$I \geq 2\ \sigma(I)$], 426 refined parameters, R = 0.047, wR^2 = 0.126, max. residual electron density 0.87 (-0.72) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Synthesis of [PhNMe$_2$H][HB(C$_6$F$_5$)$_3$] (3) and [PhNMe$_2$D][DB(C$_6$F$_5$)$_3$] (3-d$_2$). These compounds were prepared in similar fashions: A solution of B(C$_6$F$_5$)$_3$ (42.2 mg, 0.083 mmol) and *N*,*N*-dimethylaniline (10.0 mg, 0.083 mmol) in C$_6$D$_5$Br (2 mL) was subjected to three freeze-pump-thaw cycles and backfilled with H$_2$ (~ 4 atm) at -196 ºC. The solution was stored overnight at 25 ºC and all volatiles were removed *in vacuo*. Upon

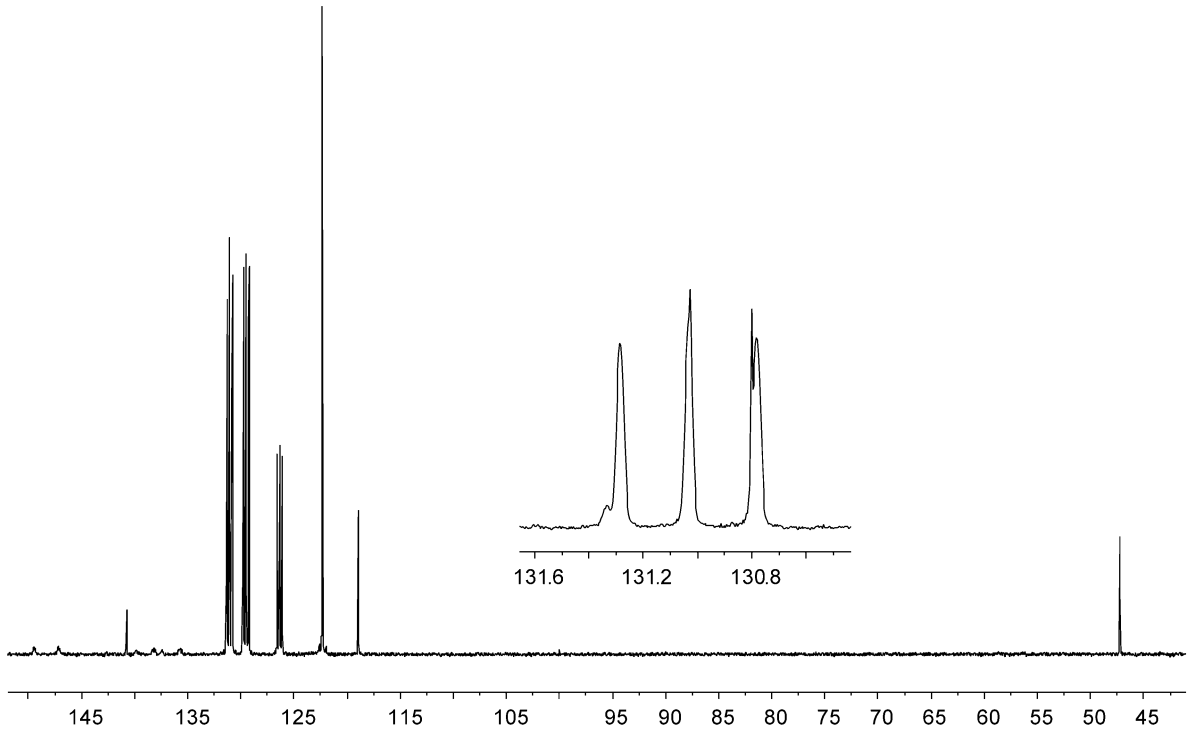
addition of dichloromethane (0.5 mL) and pentane (5 mL), a white precipitate was formed which was collected and dried to finally get the ammonium salt **3** (48.0 mg, 0.076 mmol, 92%).



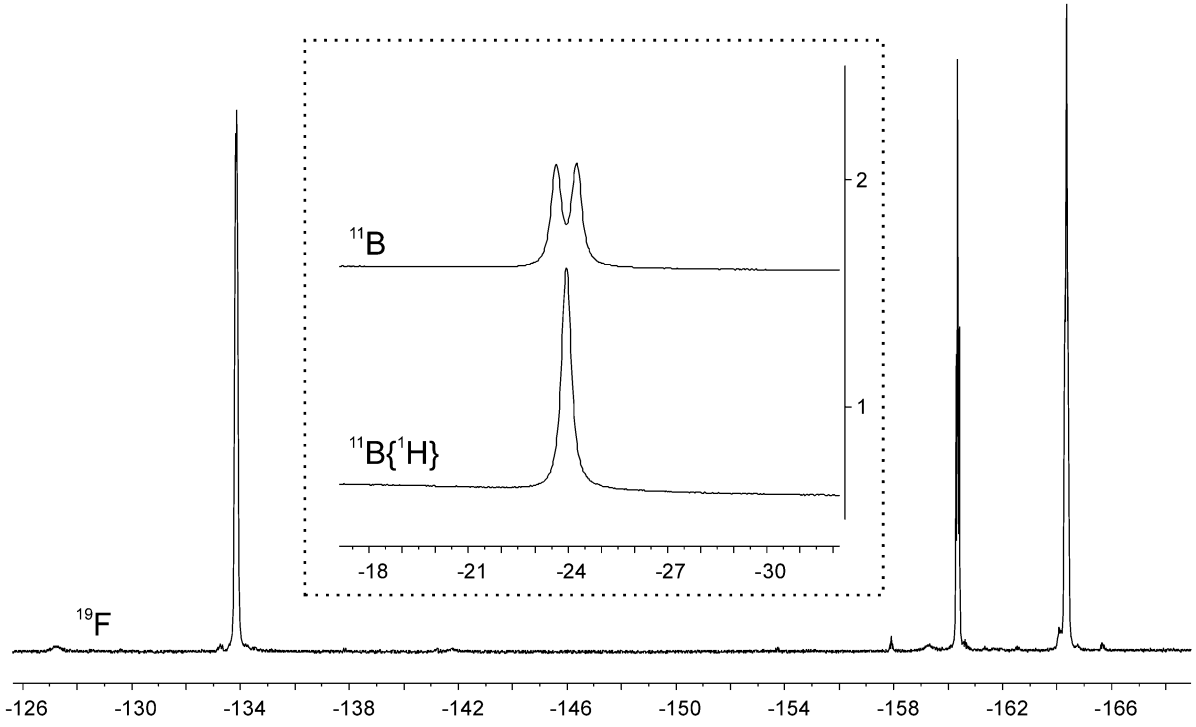
3: ^{1}H NMR (400 MHz, C_6D_5Br, 298K): δ 8.60 (s, 1H, NH); 7.07 (m, 3H, C_6H_5); 6.89 (m, 2H, C_6H_5); 3.50 (br, 1:1:1:1 q, $^{1}J_{BH}$ ~ 80 Hz, 1H, BH); 2.72 (s, 6H, NCH_3). ^{1}H NMR (500 MHz, CD_2Cl_2, 298K): δ 8.88 (s, 1H, NH); 7.56 (m, 3H, C_6H_5); 7.37 (m, 2H, C_6H_5); 3.46 (br, 1:1:1:1 q, $^{1}J_{BH}$ ~ 78 Hz, 1H, BH); 3.39 (s, 6H, NCH_3). $^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_5Br, 298K): δ 148.3 (dm, $^{1}J_{CF} \approx 230$ Hz, C_6F_5); 140.7 (*i*-C_6H_5); 138.7 (dm, $^{1}J_{CF} \approx 251$ Hz, C_6F_5); 136.8 (dm, $^{1}J_{CF} \approx 247$ Hz, C_6F_5); 131.0, 130.8, 118.9 (C_6H_5); 47.2 (NCH_3); n.o. (*i*-C_6F_5). ^{19}F NMR (377 MHz, C_6D_5Br, 298K): δ −133.9 (m, 2F, *o*-C_6F_5); −160.4 (m, 1F, *p*-C_6F_5); −164.3 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{p,m}$ = 4.1]. ^{11}B NMR (128 MHz, C_6D_5Br, 298K): δ −24.0 (d, $^{1}J_{BH}$ ~ 80 Hz). $^{11}B\{^{1}H\}$ NMR (128 MHz, C_6D_5Br, 298K): −24.0 (s, $\nu_{1/2}$ ~ 50 Hz). Elem. Anal. $C_{26}H_{13}BF_{15}N$ Calc.: C: 49.16, H: 2.06, N: 2.21; found C: 49.24, H: 2.25, N: 2.11.



^{1}H NMR (400 MHz, C_6D_5Br, 298K)



$^{13}C\{^{1}H\}$ NMR (101 MHz, C_6D_5Br, 298K)

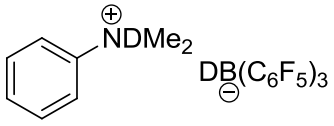


^{19}F NMR (377 MHz, C_6D_5Br, 298K) and

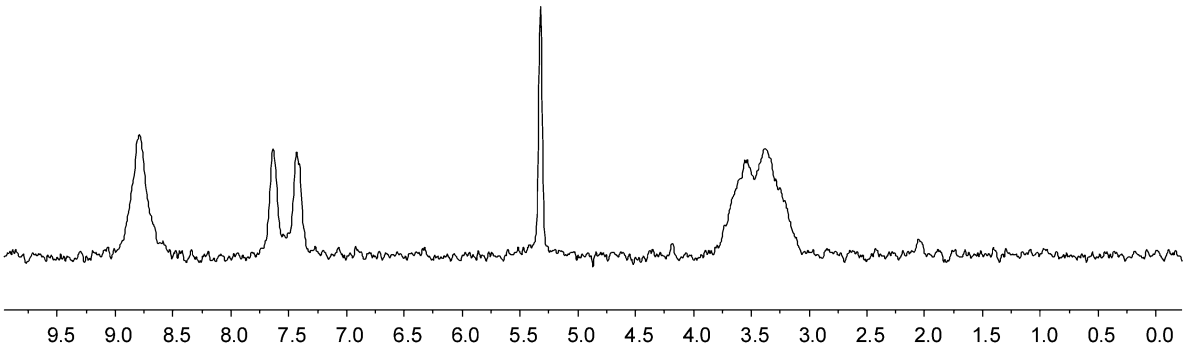
(1) $^{11}B\{^{1}H\}$ NMR (128 MHz, CD_2Cl_2, 298K) and (2) ^{11}B NMR (128 MHz, CD_2Cl_2, 298K)

X-ray crystal structure analysis of **3**: formula $C_{27}H_{15}BF_{15}N$, M = 635.18, colorless crystal 0.35 x 0.10 x 0.07 mm, a = 9.9101(4), b = 16.3709(14), c = 15.6368(10) Å, β = 94.644(4)°, V = 2528.5(3) Å^3, ρ_{calc} = 1.669 g cm^{-3}, μ = 1.587 cm^{-1}, empirical absorption correction ($0.607 \leq T \leq 0.897$), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ= 1.54178 Å, T = 223 K, ω and φ scans, 16926 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.60 Å^{-1}, 4294 independent (R_{int} = 0.058) and 3080 observed reflections [$I \geq 2\ \sigma(I)$], 396 refined parameters, R = 0.049, wR^2 = 0.128, max. residual electron density 0.29 (-0.21) e Å^{-3}, hydrogen atoms at N and B from difference fourier calculations, others calculated and refined as riding atoms.

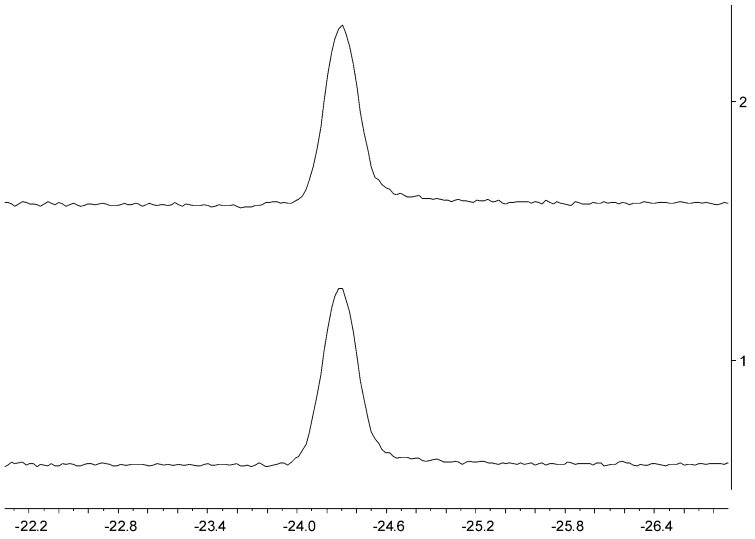
Synthesis of [PhNMe$_2$D][DB(C$_6$F$_5$)$_3$] (3-d$_2$). *N*,*N*-dimethylaniline (40.0 mg, 0.330 mmol) and B(C$_6$F$_5$)$_3$ (169 mg, 0.330 mmol) were dissolved in pentane (8 mL) and the solution degassed by two freeze-pump-thaw cycles. Afterwards, the reaction mixture was subjected to D_2 (1.5 bar) and stirred at room temperature over night. A white solid precipitated which was isolated *via* canula filtration and dried *in vacuo* to yield the deuterium-activated species **3-d$_2$** (166 mg, 0.261 mmol, 79%).



3-d$_2$: ^{2}H NMR (77 MHz, CD_2Cl_2, 298K): δ 8.81 (br s, ND); 7.63, 7.41 (each br, C_6H_4D); 3.45 (br m, BD). $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 298K): δ −24.3 (s, $\nu_{1/2}$ ~ 60 Hz). ^{11}B NMR (160 MHz, CD_2Cl_2, 298K): −24.3 (s, $\nu_{1/2}$ ~ 50 Hz).

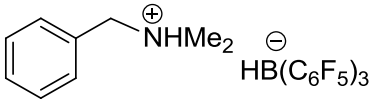


^{2}H NMR (77 MHz, CD_2Cl_2, 298K)

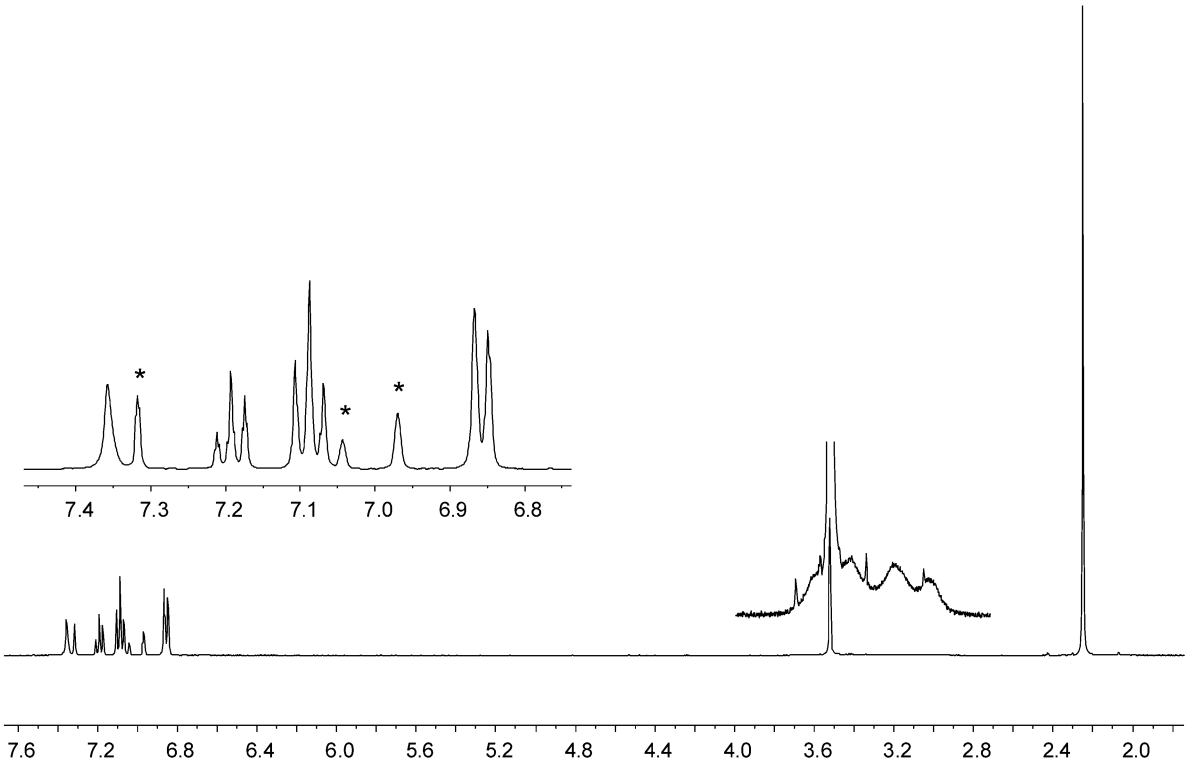


(1) $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 298K) and (2) ^{11}B NMR (160 MHz, CD_2Cl_2, 298K)

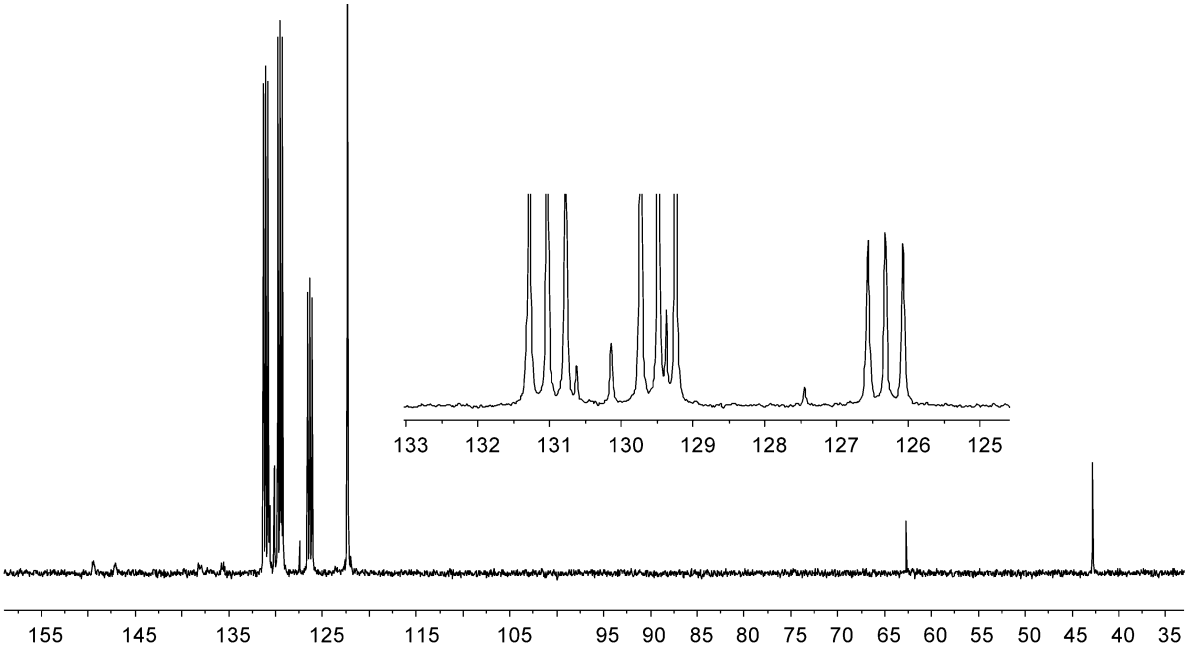
Synthesis of [PhCH$_2$NMe$_2$H][HB(C$_6$F$_5$)$_3$] (4). A solution of $B(C_6F_5)_3$ (37.9 mg, 0.074 mmol) and *N*,*N*-dimethylbenzylamine (10.0 mg, 0.074 mmol) in C_6D_5Br (1 mL) was subjected to three freeze-pump-thaw cycles and backfilled with H_2 at -196 ºC (~ 4 atm). After stirring at 25 ºC for 30 minutes, dichloromethane (0.1 mL) was added and the resulting solution was layered with hexane (5 mL). Storing at 25 ºC for 3 days yielded white crystals (42.4 mg, 0.065 mmol, 88%).



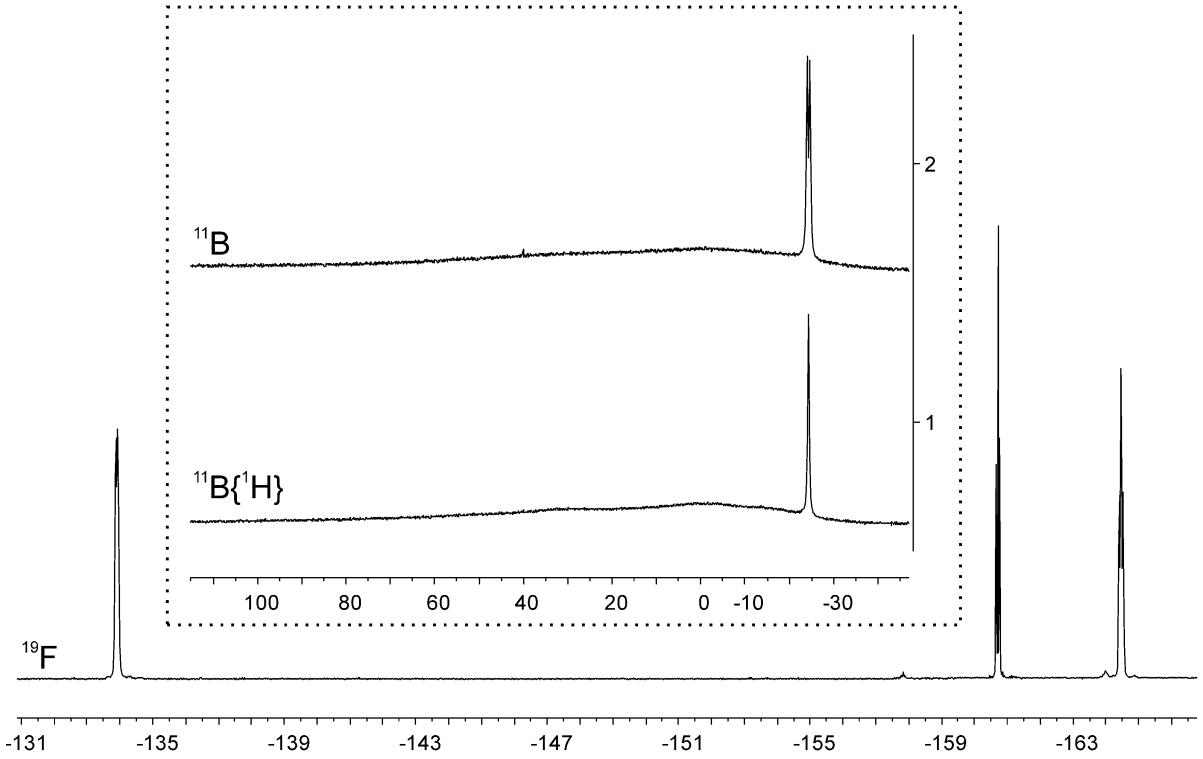
4: ^{1}H NMR (400 MHz, C_6D_5Br, 295K): δ 7.36 (NH), 7.19 (m, 1H, *p*-C_6H_5); 7.09 (m, 2H, *m*-C_6H_5); 6.86 (m, 2H, *o*-C_6H_5); 3.52 (s, 2H, CH_2N); 3.31 (br q, $^1J_{HB}$ ~ 83 Hz, BH); 2.25 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_5Br, 297K): δ 130.6 (*p*-C_6H_5); 130.1 (*o*-C_6H_5); 129.4 (*m*-C_6H_5); 127.5 (*i*-C_6H_5); 62.7 (CH_2N); 42.8 (NCH_3), [C_6F_5 not listed]. ^{19}F NMR (377 MHz, C_6D_5Br, 295K): δ −133.9 (m, 2F, *o*-C_6F_5); −160.7 (t, $^3J_{FF}$ = 20.1 Hz, 1F, *p*-C_6F_5); −164.5 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{p,m}$ = 3.8]. ^{11}B NMR (128 MHz, C_6D_5Br, 295K): δ −24.3 (d, $^1J_{BH}$ ~ 84 Hz). $^{11}B\{^1H\}$ NMR (128 MHz, C_6D_5Br, 295K): −24.3 (s, $\nu_{1/2}$ ~ 60 Hz). Elem. Anal. $C_{27}H_{15}BF_{15}N$ Calc.: C: 49.95, H: 2.33, N: 2.16; found C: 49.79, H: 2.39, N: 2.20.



^{1}H NMR (400 MHz, C_6D_5Br*, 295K)



^{13}C{^{1}H} NMR (101 MHz, C_6D_5Br, 297K)

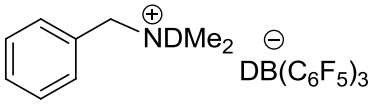


^{19}F NMR (377 MHz, C_6D_5Br, 295K),

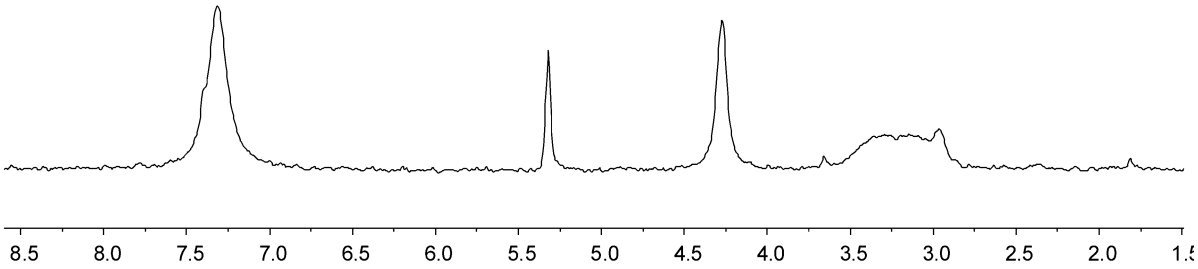
(1) $^{11}B\{^1H\}$ NMR (128 MHz, C_6D_5Br, 295K), and (2) ^{11}B NMR (128 MHz, C_6D_5Br, 295K):

X-ray crystal structure analysis of **4**: formula $C_{27}H_{15}BF_{15}N$, M = 649.21, colorless crystal 0.35 x 0.20 x 0.10 mm, a = 10.1853(3), b = 13.3147(8), c = 21.7805(7) Å, α = 86.615(4), β = 73.671(3), γ = 68.525(3)°, V = 2634.6(2) Å^3, ρ_{calc} = 1.637 g cm^{-3}, μ = 1.537 cm^{-1}, empirical absorption correction (0.615 $\leq T \leq$ 0.862), Z = 4, triclinic, space group P1bar (No. 2), λ= 1.54178 Å, T = 223 K, ω and φ scans, 36924 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.60 Å^{-1}, 9134 independent (R_{int} = 0.042) and 7448 observed reflections [$I \geq 2\ \sigma(I)$], 810 refined parameters, R = 0.056, wR^2 = 0.150, max. residual electron density 0.22 (-0.22) e Å^{-3}, hydrogen atoms at N and B from difference fourier calculations, others calculated and refined as riding atoms.

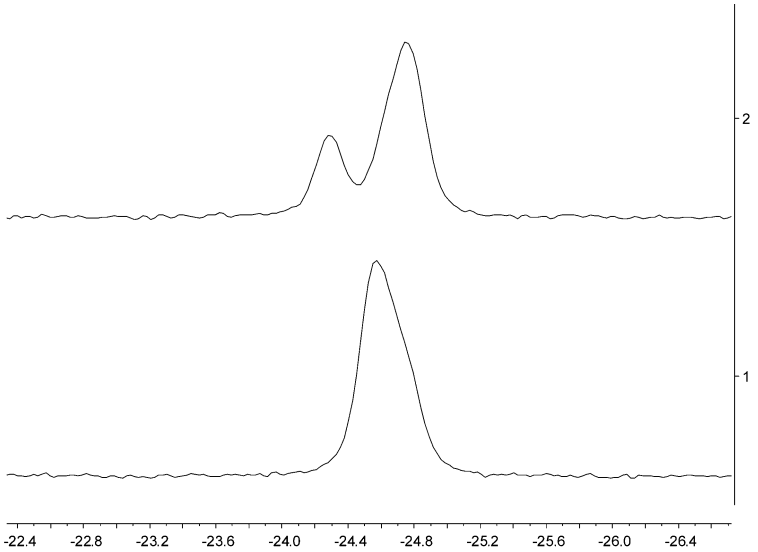
Synthesis of $[PhCH_2NMe_2D][DB(C_6F_5)_3]$ (4-d$_2$). *N*,*N*-dimethylbenzylamine (40.0 mg, 0.296 mmol) and $B(C_6F_5)_3$ (151.6 mg, 0.296 mmol) were dissolved in pentane (8 mL) and the solution degassed by two freeze-pump-thaw cycles. Afterwards the reaction mixture was subjected to D_2 (1.5 bar) and stirred at roomtemperature over night. A white solid precipitated that was isolated *via* canula filtration and dried *in vacuo* to yield of the deuterated species **4-d$_2$** (160.0 mg, 0.246 mmol, 83%; containing ca. 50% of the H_2-activated compound **4**).



4-d$_2$: ^{2}H NMR (77 MHz, CD_2Cl_2, 298K): δ 7.35 (br, C_6H_5D); 4.27 (br, CHDN); 3.23 (br, BD). ^{11}B NMR (160 MHz, CD_2Cl_2, 298K): δ −24.6 (ca. 50%, br d, $^1J_{BH}$ ~ 88 Hz, BH); −24.8 (ca. 50%, br, BD). ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 298K): −24.6 (BH); −24.8 (br, BD).

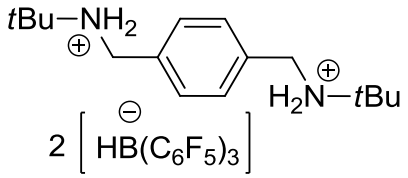


^{2}H NMR (77 MHz, CD_2Cl_2, 298K)

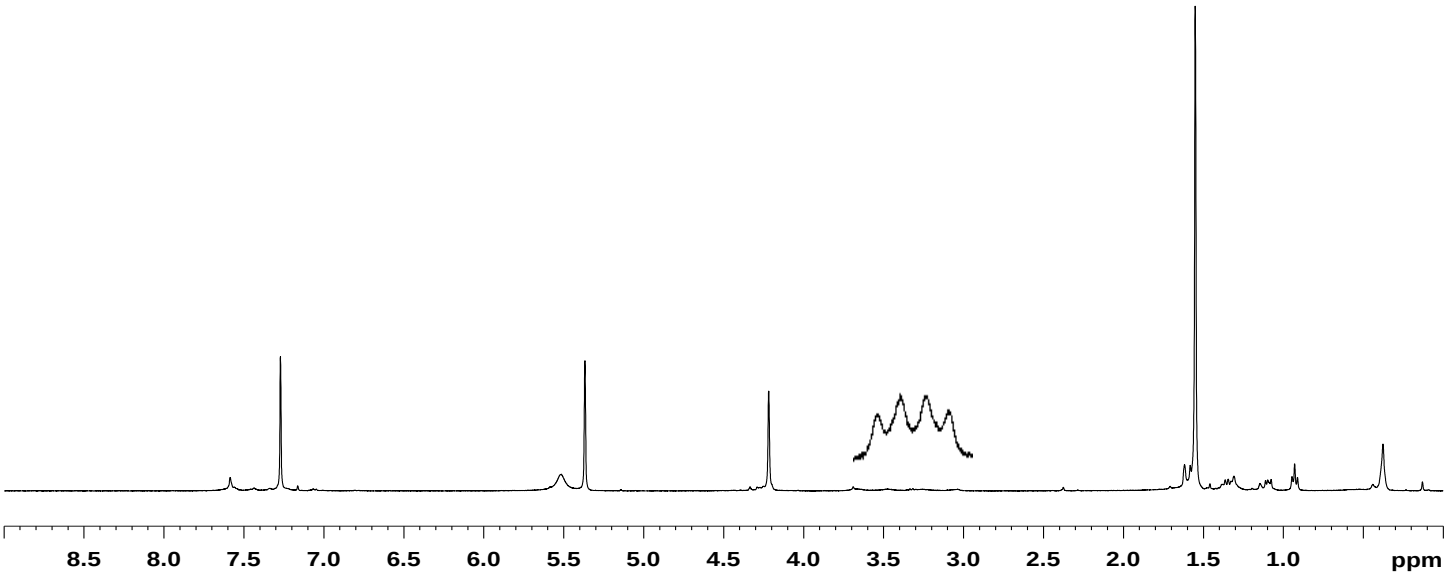


(1) ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 298K) and (2) ^{11}B NMR (160 MHz, CD_2Cl_2, 298K)

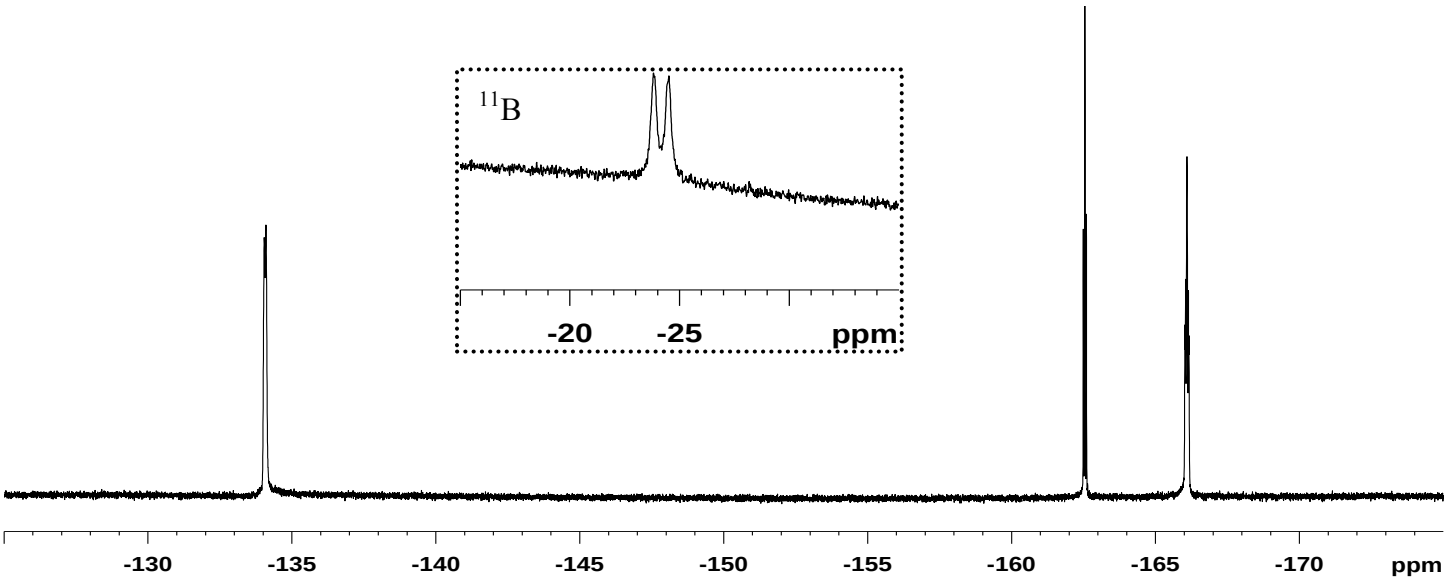
Synthesis of $[C_6H_4(CH_2NH_2tBu)_2][HB(C_6F_5)_3]_2$ (5). In a glovebox, a 100 mL glass bomb equipped with a magnetic stir bar and Teflon screw tap was charged with a solution of $B(C_6F_5)_3$ (304 mg, 0.594 mmol) and $C_6H_4(CH_2NHtBu)_2$ (72.5 mg, 0.297 mmol) in toluene (4 mL). The reaction was degassed three times through a freeze-pump-thaw cycle on the vacuum/H_2 line. The reaction flask was cooled to -196 ºC and filled with H_2 (4 atm). At 25 ^{o}C, immediate precipitation of a white solid was observed. The reaction mixture was stirred overnight at 70 ºC. Pentane (10 mL) was added, after which the supernatant was decanted. The residue was washed with pentane (2 x 2 mL) and dried *in vacuo* to afford (**5**) as a white powder (374 mg, 0.297 mmol, 100 %). Crystals suitable for X-ray crystal structure analyses were obtained by recrystallization from a concentrated solution in C_6D_5Br at 25 ^{o}C.



5: ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 7.27 (s, 4H, Ar), 5.95 (br s, 4H, N*H*$_2$), 4.38 (s, 4H, C*H*$_2$), 3.39 (br 1:1:1:1 q, $^{1}J_{H\text{-}B}$ = 83.7 Hz, B*H*), 1.62 (s, 18H, C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (101 MHz, d$_8$-THF, 298K): δ 149.3 (dm, $^{1}J_{C\text{-}F}$ ≈ 236 Hz, C_6F_5), 146.1 (*i*-Ar), 138.5 (dm, $^{1}J_{C\text{-}F}$ ≈ 243 Hz, C_6F_5), 137.4 (dm, $^{1}J_{C\text{-}F}$ ≈ 246 Hz, C_6F_5), 134.5 (br, *i*-C_6F_5), 131.4 (Ar), 59.5 (*C*(CH$_3$)$_3$) 46.1 (CH$_2$), 25.9 (C(*C*H$_3$)$_3$). ^{19}F NMR (377 MHz, CD_2Cl_2, 298 K): δ -134.9 (m, 2F, *o*-C_6F_5), -163.5 (t, 1F, $^{3}J_{F\text{-}F}$ = 20 Hz, *p*-C_6F_5), -167.0 (m, 2F, *m*-C_6F_5). ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K): δ -24.3 (d, $^{1}J_{B\text{-}H}$ = 83.7 Hz, BH).



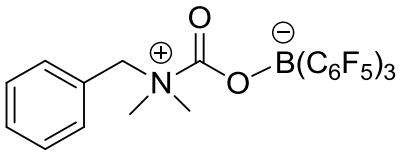
^{1}H NMR (400 MHz, CD_2Cl_2, 298K)



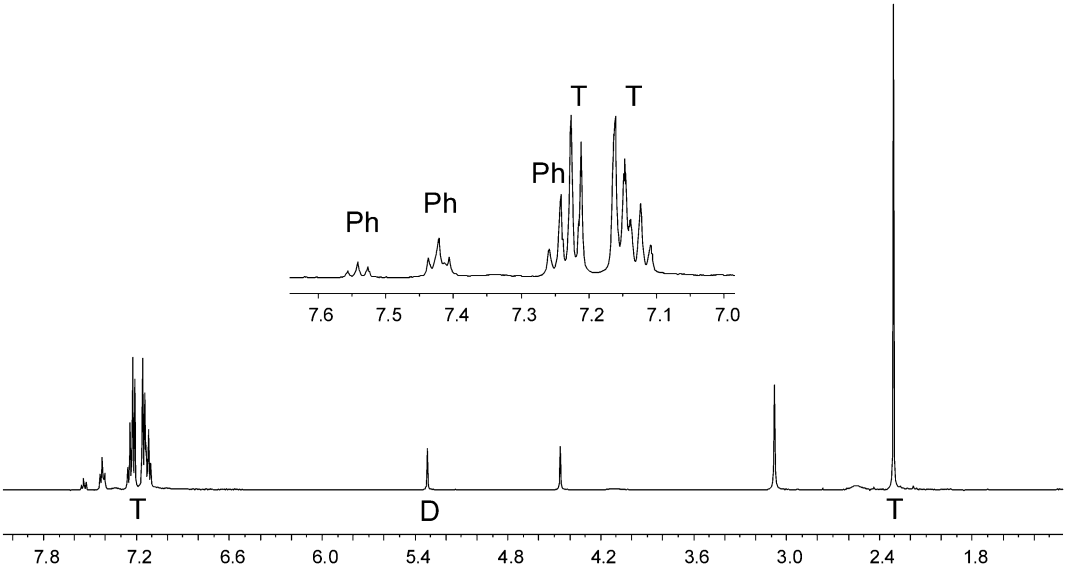
^{19}F NMR (377 MHz, CD_2Cl_2, 298K) and ^{11}B NMR (128 MHz, CD_2Cl_2, 298K)

Elem. Anal. $C_{52}H_{32}B_2F_{30}N_2$ Calc.: C 48.93, H 2.53, N 2.19; found: C 48.82, H 2.69, N 2.52. X-ray: $C_{52}H_{32}B_2F_{30}N_2$•C_6H_5Br M = 1432.42, a = 9.3616(18), b = 11.479(2), c = 15.046(3) Å, α = 73.474(9), β = 85.102(9), γ = 67.335(6)°, V = 1429.9(5) Å^3, Z = 1, triclinic, *P-1,* Data (λ = 0.71069 Å, T = 150 K), 4780 (R_{int} = 0.059), 2984 [$I \geq 2\ \sigma(I)$], 424 parameters, R = 0.060, wR^2 = 0.163, GOF = 1.081.

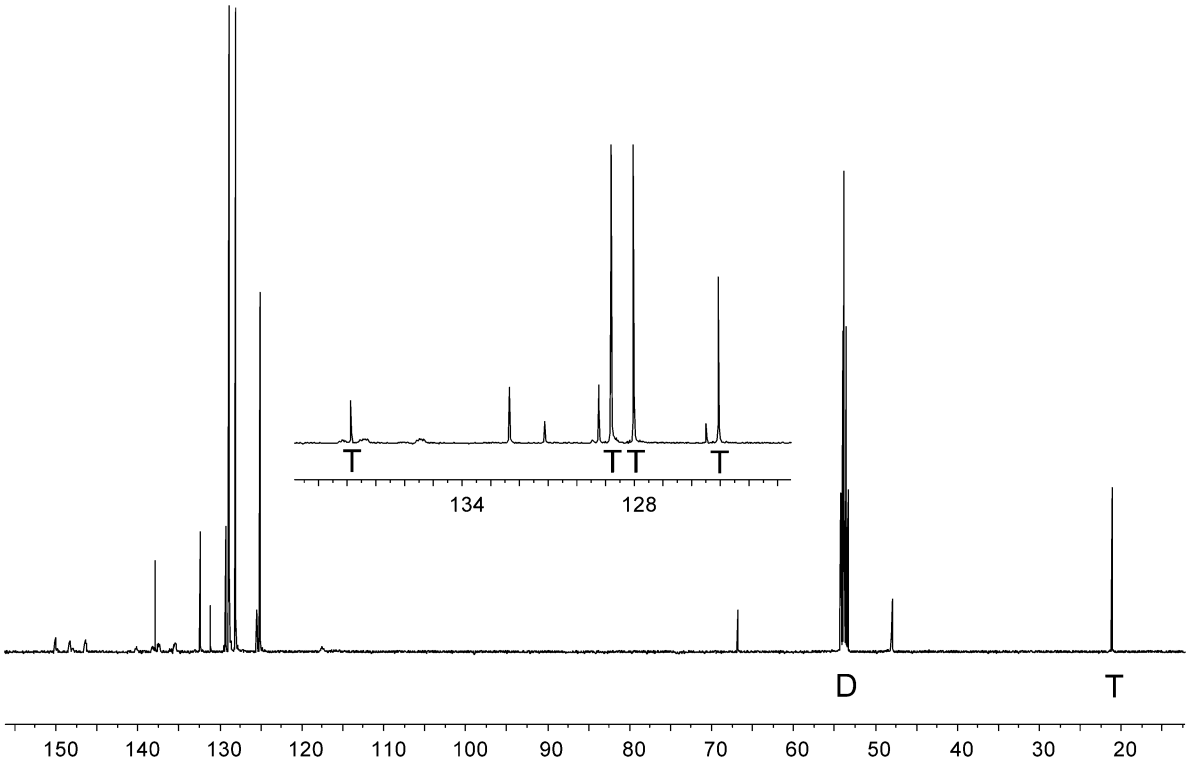
Synthesis of [$PhCH_2NMe_2CO_2B(C_6F_5)_3$] (6). *N*,*N*-dimethylbenzylamine (150 mg, 1.11 mmol) and $B(C_6F_5)_3$ (570 mg, 1.11 mmol) were dissolved in C_6H_5Br (10 mL) and the solution was subjected to two freeze-pump-thaw cycles. At 25 ºC the reaction flask was filled with an atmosphere of CO_2 and left at -32 °C for 12 hours. Then pentane (10 mL) were added, the resulting white precipitate was filtered off and dried *in vacuo* at -10 °C to yield 390 mg (54%, 0.600 mmol) of the carbon dioxide containing compound. Crystals suitable for diffraction were grown from a C_6H_5Br solution that was stored under an atmosphere of CO_2 at -32 °C for several days.



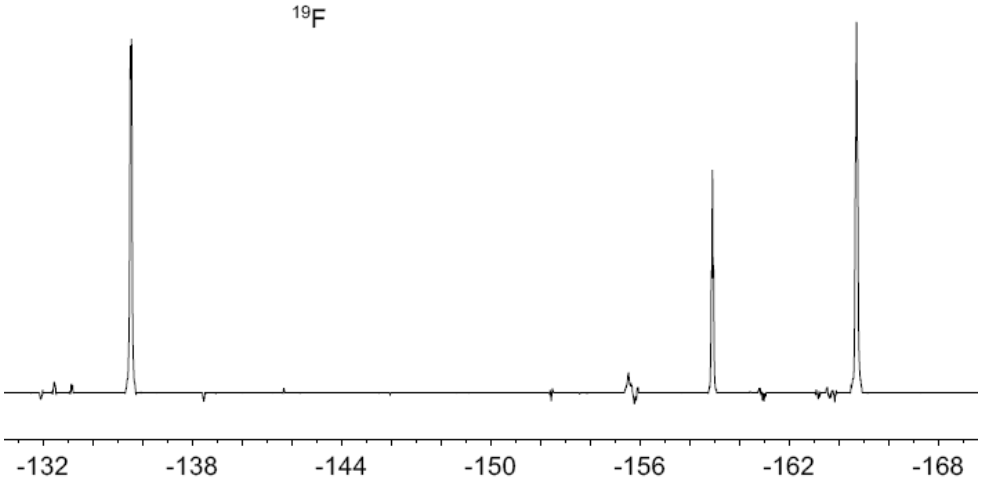
6: ^{1}H NMR (500 MHz, CD_2Cl_2, 218 K): δ 7.54 (m, 1H, *p*-C_6H_5); 7.42 (m, 2H, *m*-C_6H_5); 7.25 (m, 2H, *o*-C_6H_5); 4.46 (s, 2H, CH_2N); 3.08 (s, 6H, NCH_3). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 218 K): δ 150.1 (CO); 147.4 (dm, $^1J_{CF}$ ~ 238 Hz, C_6F_5); 139.1 (dm, $^1J_{CF}$ ~ 246 Hz, C_6F_5); 136.2 (dm, $^1J_{CF}$ ~ 246 Hz, C_6F_5); 132.4 (*o*-C_6H_5); 131.1 (*p*-C_6H_5); 129.3 (*m*-C_6H_5); 125.5 (*i*-C_6H_5); 117.5 (br, *i*-C_6F_5); 66.8 (CH_2N); 48.0 (NCH_3). ^{19}F NMR (470 MHz, CD_2Cl_2, 218 K): δ −135.6 (m, 2F, *o*-C_6F_5); −158.9 (br t, $^3J_{FF}$ ~ 20 Hz, 1F, *p*-C_6F_5); −164.7 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{p,m}$ = 5.8]. IR: ν (KBr / cm^{-1}): 1822 (s). Elem. Anal.: $C_{28}H_{13}BF_{15}NO_2$: Calc.: C: 48.65, H: 1.90, N: 2.03, found C: 48.52, H: 1.99, N: 1.97.



^{1}H NMR (500 MHz, 218 K, CD_2Cl_2) (D: CD_2Cl_2; T: toluene)



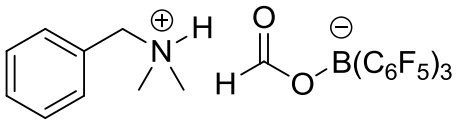
$^{13}C\{^{1}H\}$ NMR (126 MHz, 218 K, CD_2Cl_2) (D: CD_2Cl_2; T: toluene)



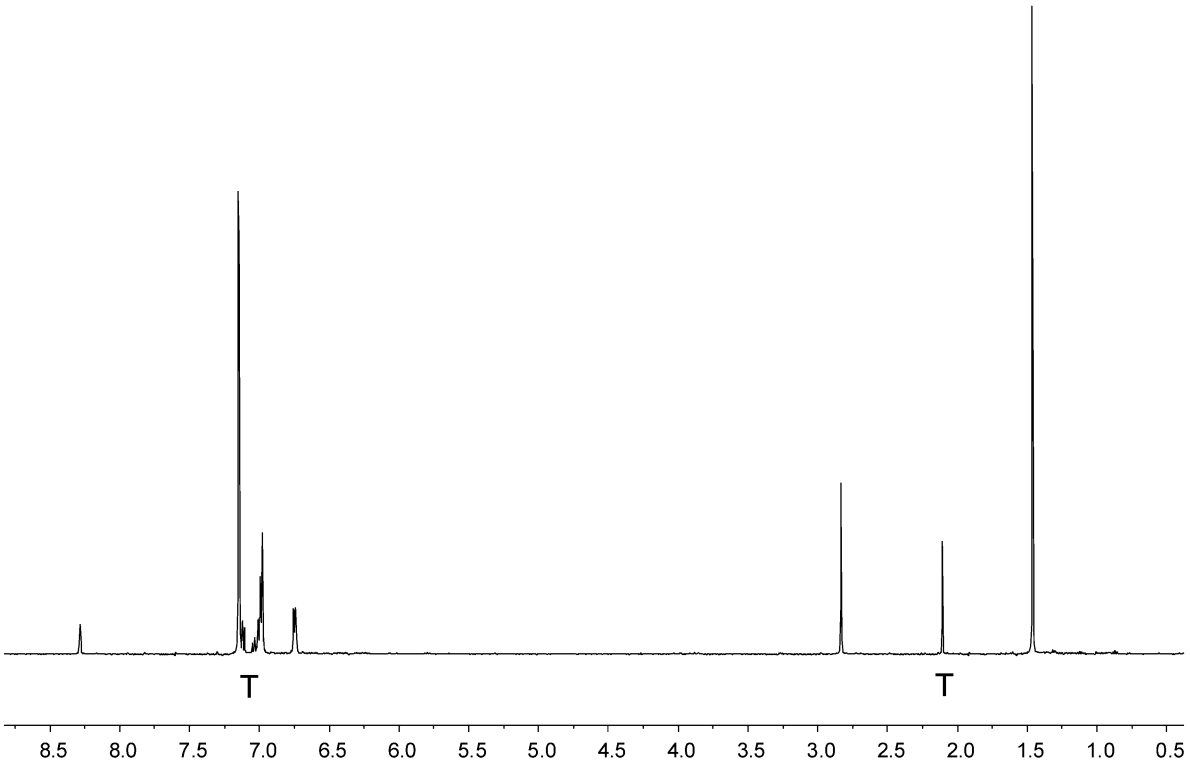
^{19}F NMR (470 MHz, 218 K, CD_2Cl_2)

X-ray crystal structure analysis: $C_{28}H_{13}BF_{15}NO_2$, M = 691.20, a = 14.309(3), b = 12.160(2), c = 15.471(3) Å, β = 92.833(7)°, V = 2688.6(9) Å^3, Z = 4, monoclinic, $P2_1/n$, Data (λ = 0.71069 Å, T = 150 K), 6176 (R_{int} = 0.036), 4293 [$I \geq 2\ \sigma(I)$], 424 parameters, R = 0.045, wR^2 = 0.115, GOF = 1016.

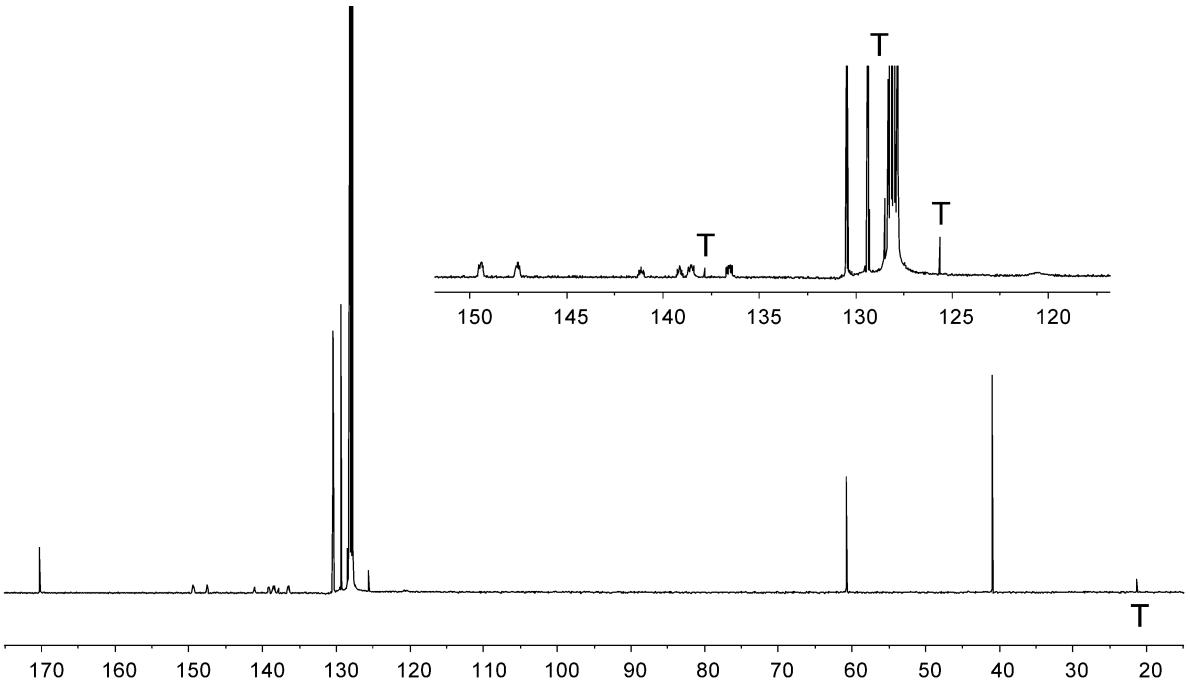
Synthesis of [$PhCH_2NHMe_2$][$HCO_2B(C_6F_5)_3$] (7). Compound **4** (100 mg, 0.154 mmol) was dissolved in toluene (4 mL). After two freeze-pump-thaw cycles, the solution was pressurized with CO_2 (1.5 atm) and then heated to 80 °C overnight. The solvent was removed under reduced pressure and pentane (10 mL) was added. Drying *in vacuo* yielded 96.0 mg (0.139 mmol, 90%) of the formic acid adduct **7**.



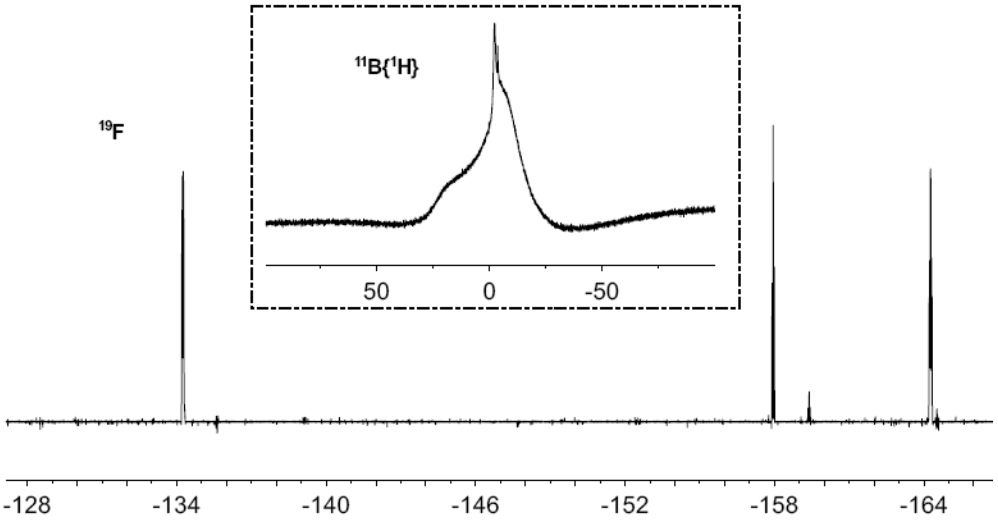
7: ^{1}H NMR (500 MHz, C_6D_6, 298K): δ 8.29 (s, 1H, CHO); 6.98 (m, 3H, *m,p*-C_6H_5); 6.75 (m, 2H, *o*-C_6H_5); 2.84 (s, 2H, CH_2N); 1.46 (s, 6H, NCH_3), n.o. (NH). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 298K): δ 170.2 (CHO); 148.6 (dm, $^1J_{CF}$ ~ 243 Hz, C_6F_5); 140.2 (dm, $^1J_{CF}$ ~ 247 Hz, C_6F_5); 137.6 (dm, $^1J_{CF}$ ~ 251 Hz, C_6F_5); 130.5 (*p*-C_6H_5), 130.4 (*o*-C_6H_5); 129.4 (*m*-C_6H_5); 128.0 (*i*-C_6H_5); 120.6 (br, *i*-C_6F_5); 60.8 (CH_2N); 40.9 (NCH_3). ^{19}F NMR (470 MHz, C_6D_6, 298K): δ −134.2 (m, 2F, *o*-C_6F_5); −157.9 (t, 1F, $^3J_{FF}$ ~ 21 Hz, *p*-C_6F_5); −164.3 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{p,m}$ = 6.4]. $^{11}B\{^1H\}$ NMR (160 MHz, C_6D_6, 298K): δ −2.2 ($\nu_{1/2}$ ~ 200 Hz). IR: ν(KBr / cm^{-1}) 1621 (m). Elem. Anal.: $C_{28}H_{15}BF_{15}NO_2$ Calc. C: 48.51, H: 2.18, N: 2.02; found: C: 48.33, H: 2.49, N: 2.36.



^{1}H NMR (500 MHz, 298 K, C_6D_6) (T: toluene)



$^{13}C\{^1H\}$ NMR (126 MHz, 298 K, C_6D_6) (T: toluene)

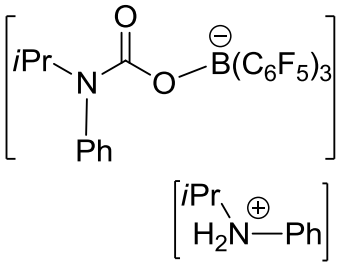


^{19}F NMR (470 MHz, 298 K, C_6D_6) and $^{11}B\{^1H\}$ NMR (160 MHz, 298 K, C_6D_6)

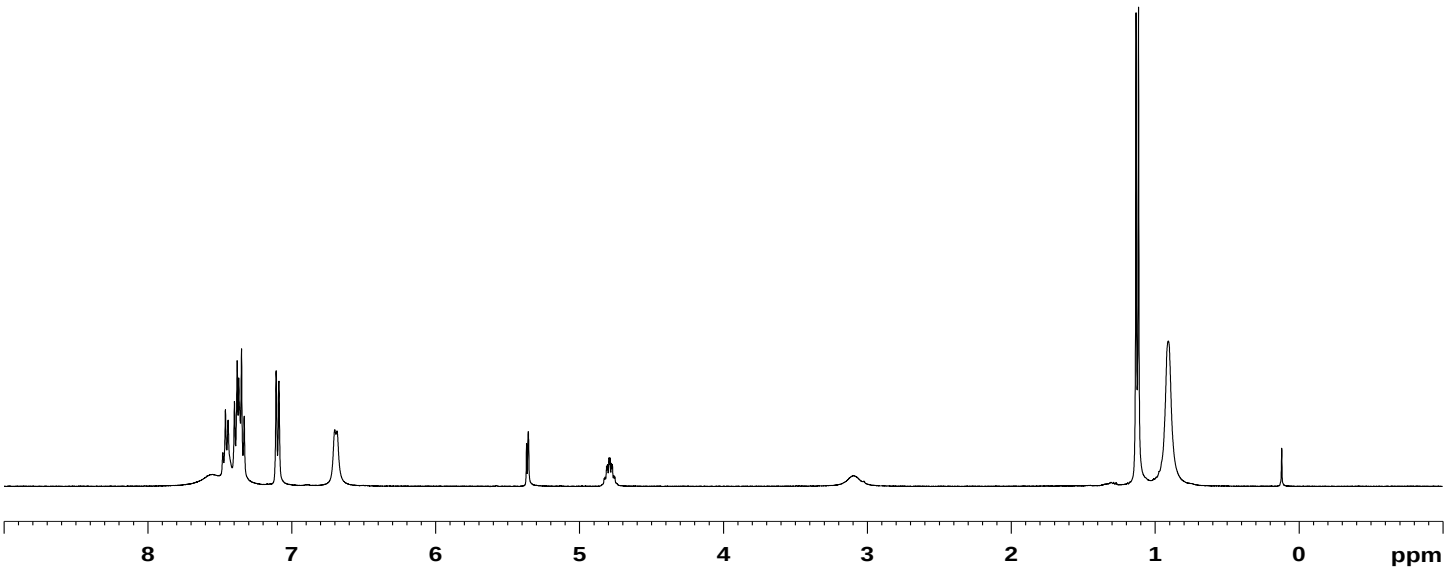
X-ray crystal structure analysis of **7**: formula $C_{28}H_{15}BF_{15}NO_2$, M = 693.22, colorless crystal 0.40 x 0.05 x 0.05 mm, a = 7.5203(3), b = 18.6531(8), c = 19.9816(10) Å, V = 2803.0(2) Å^3, ρ_{calc} = 1.643 g cm^{-3}, μ = 1.544 cm^{-1}, empirical absorption correction ($0.577 \leq T \leq 0.927$), Z = 4, orthorhombic, space group $P2_12_12_1$ (No. 19), λ= 1.54178 Å, T = 223 K, ω and φ scans, 15160 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.60 Å^{-1}, 4454

independent (R_{int} = 0.064) and 3270 observed reflections [$I \geq 2\ \sigma(I)$], 432 refined parameters, R = 0.043, wR^2 = 0.102, Flack parameter -0.09(17), max. residual electron density 0.16 (-0.17) e Å^{-3}, hydrogen atom at N from difference fourier calculations, others calculated and refined as riding atoms.

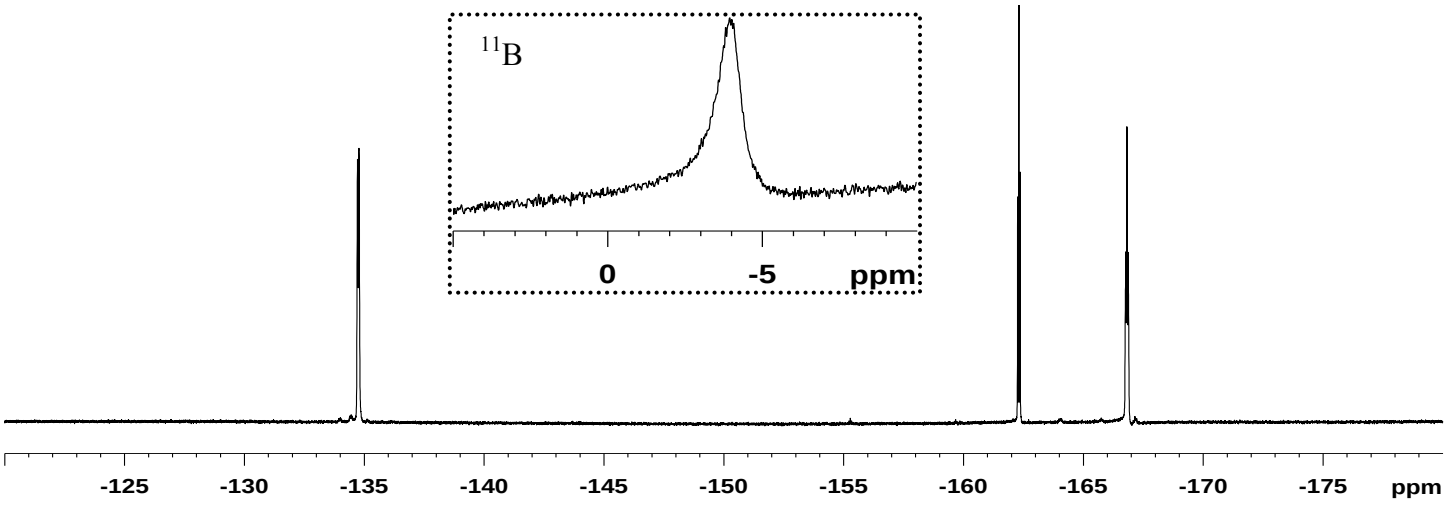
Synthesis of [PhN*i*PrH$_2$][PhN*i*PrCO$_2$B(C$_6$F$_5$)$_3$] (8). In a glovebox, a 50 mL glass bomb equipped with a magnetic stir bar and Teflon screw tap was charged with a solution of B(C$_6$F$_5$)$_3$ (500 mg, 0.978 mmol) and *N*-isopropylaniline (264 mg, 1.95 mmol) in toluene (7 mL). The reaction was degassed three times through a freeze-pump-thaw cycle on the vacuum/CO$_2$ line. The reaction flask was cooled to -196 ºC and filled with ^{13}CO$_2$ (1 atm). The reaction mixture was allowed to stir at 25 ºC for 2 days. All volatiles were then removed *in vacuo*; the residue was dissolved in minimum dichloromethane and the product was precipitated as a white powder using hexanes. The product was washed with hexanes (2 x 2 mL) and dried *in vacuo* to yield (**8**) (769 mg, 0.930 mmol, 95 %).



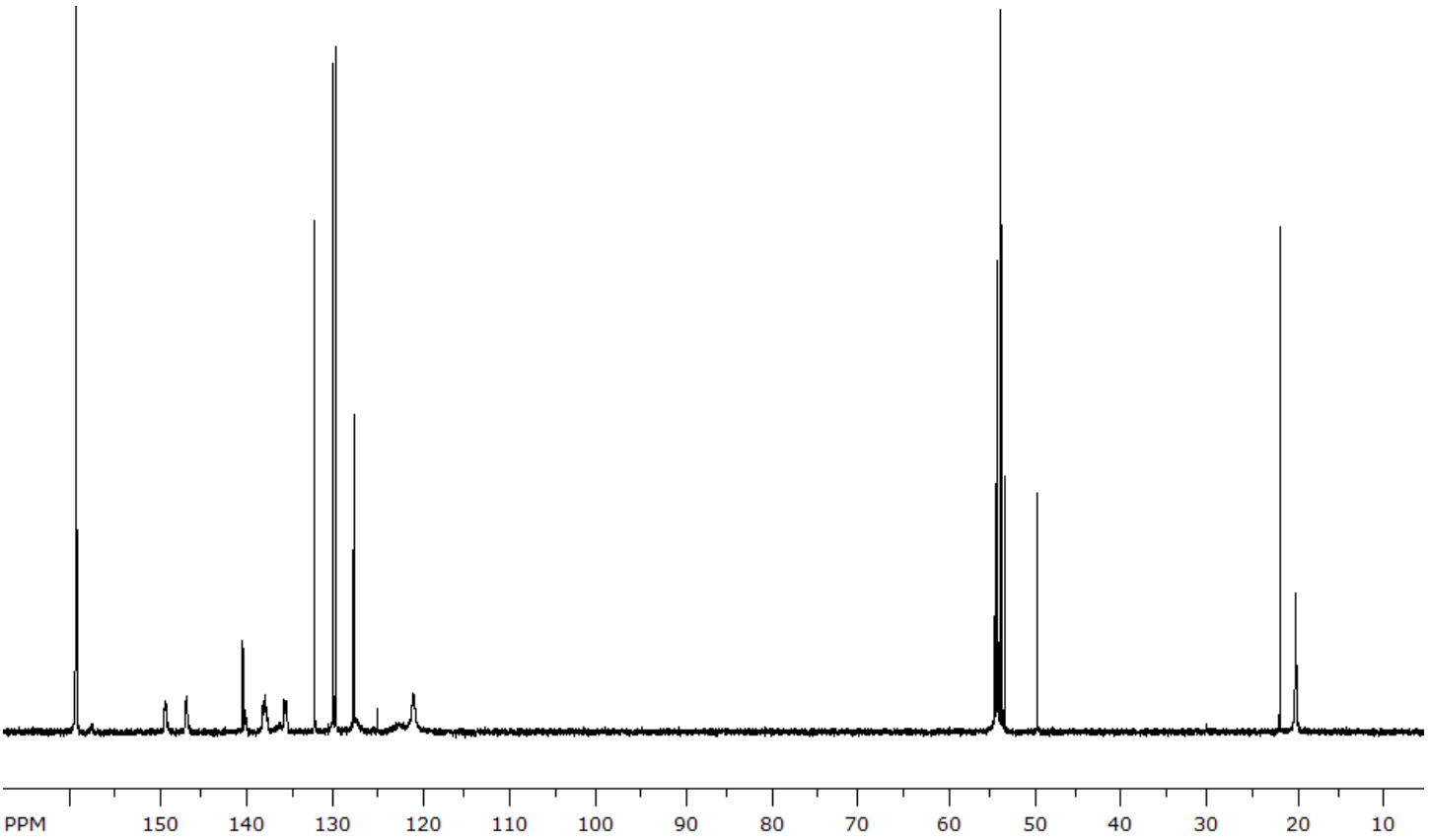
8: ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 298K): δ 7.55 (br s, NH_2), 7.48 – 7.33 (m, 6H, *m*,*p*-Ar), 7.10 (d, 2H, $^3J_{H\text{-}H}$ = 7.3 Hz, *o*-Ar), 6.68 (br d, 2H, $^3J_{H\text{-}H}$ = 7.8 Hz, *o*-Ar), 4.78 (m, 1H, $^3J_{H\text{-}H}$ = 6.6 Hz, C*H*(CH$_3$)$_2$), 3.09 (br m, 1H, C*H*(CH$_3$)$_2$), 1.12 (d, 6H, $^3J_{H\text{-}H}$ = 6.6 Hz, CH(C*H*$_3$)$_2$), 0.91 (br, 6H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (101 MHz, CD$_2$Cl$_2$, 298K): δ 159.4 (NCO$_2$), 147.9 (dm, $^1J_{C\text{-}F} \approx$ 240 Hz, C$_6$F$_5$) , 140.3 (*i*-Ar), 138.7 (dm, $^1J_{C\text{-}F} \approx$ 243 Hz, C$_6$F$_5$), 136.5 (dm, $^1J_{C\text{-}F} \approx$ 239 Hz, C$_6$F$_5$), 132.1 (*o*-Ar), 130.3 (*m*-Ar), 129.8 (Ar), 127.9 (*p*-Ar), 127.7 (br, Ar), 125.3 (Ar),122.2 (br, *o*-Ar), 120.8 (br, *i*-C$_6$F$_5$), 54.1 (*C*H(CH$_3$)$_2$), 49.0 (*C*H(CH$_3$)$_2$), 21.2 (CH(*C*H$_3$)$_2$), 19.2 (br, CH(*C*H$_3$)$_2$).^{19}F NMR (377 MHz, CD$_2$Cl$_2$, 298K): δ -134.7 (m, 2F, *o*-C$_6$F$_5$), -162.3 (t, 1F, $^3J_{F\text{-}F}$ = 20 Hz, *p*-C$_6$F$_5$), -166.8 (m, 2F, *m*-C$_6$F$_5$), [$\Delta\delta^{19}F_{p,m}$ = 4.5]. ^{11}B NMR (128 MHz, CD$_2$Cl$_2$, 298K): δ -4.0 (s).



^{1}H NMR (400 MHz, CD_2Cl_2, 298 K)



^{19}F NMR (377 MHz, CD_2Cl_2, 298 K) and ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K)

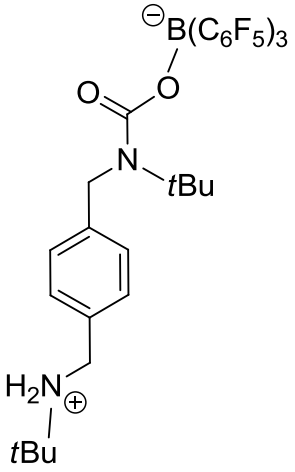


$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2, 298 K)

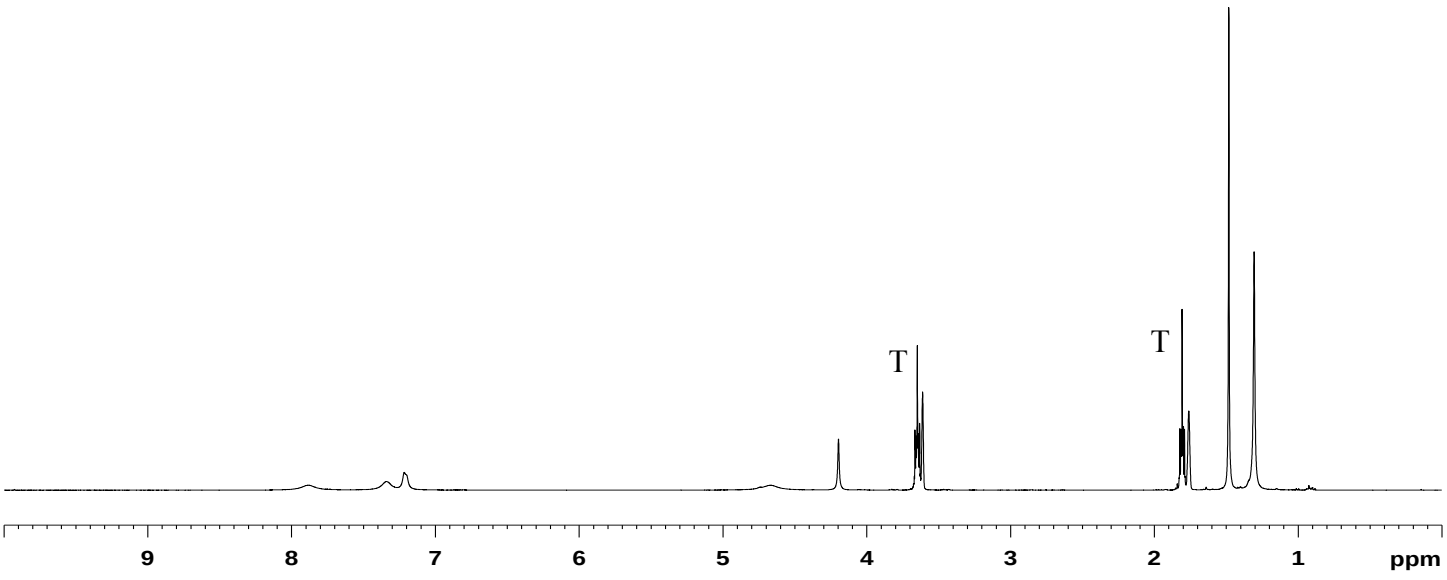
IR (KBr): ν = 1646 cm^{-1} (vs, C=O). Elem.Anal. $C_{75}H_{50}B_2Cl_2F_{30}N_4O_4$ Calc.: C 51.96, H 2.91, N 3.23; found: C 51.63, H 3.28, N 3.29. X-ray: $C_{37}H_{24}BF_{15}N_2O_2$•½$CH_2Cl_2$, M = 866.86, a = 11.2336(4), b = 14.9889(6), c = 44.3937(16) Å, β = 90.618(2)°, V = 7474.5(5) $Å^3$, Z = 8, monoclinic, $P2_1/c$, Data (λ = 0.71069 Å, T = 150 K), 13157 (R_{int} = 0.048), 10517 [$I \geq 2\ \sigma(I)$], 1072 parameters, R = 0.053, wR^2 = 0.127, GOF = 1.051.

Synthesis of [$C_6H_4(CH_2NH_2tBu)(CH_2NtBuCO_2B(C_6F_5)_3$] (9). In a glovebox, a 50 mL glass bomb equipped with a magnetic stir bar and Teflon screw tap was charged with a solution of $B(C_6F_5)_3$ (154 mg, 0.300 mmol) and *N*,*N*'-(1,4-phenylenebis(methylene))bis(*t*-butylamine) (73.3 mg, 0.300 mmol) in toluene (5 mL). The reaction was degassed three times through a freeze-pump-thaw cycle on the vacuum/CO_2 line. The reaction flask was cooled to -196 ºC and filled with $^{13}CO_2$ (1 atm). Upon warming to room temperature, precipitate was

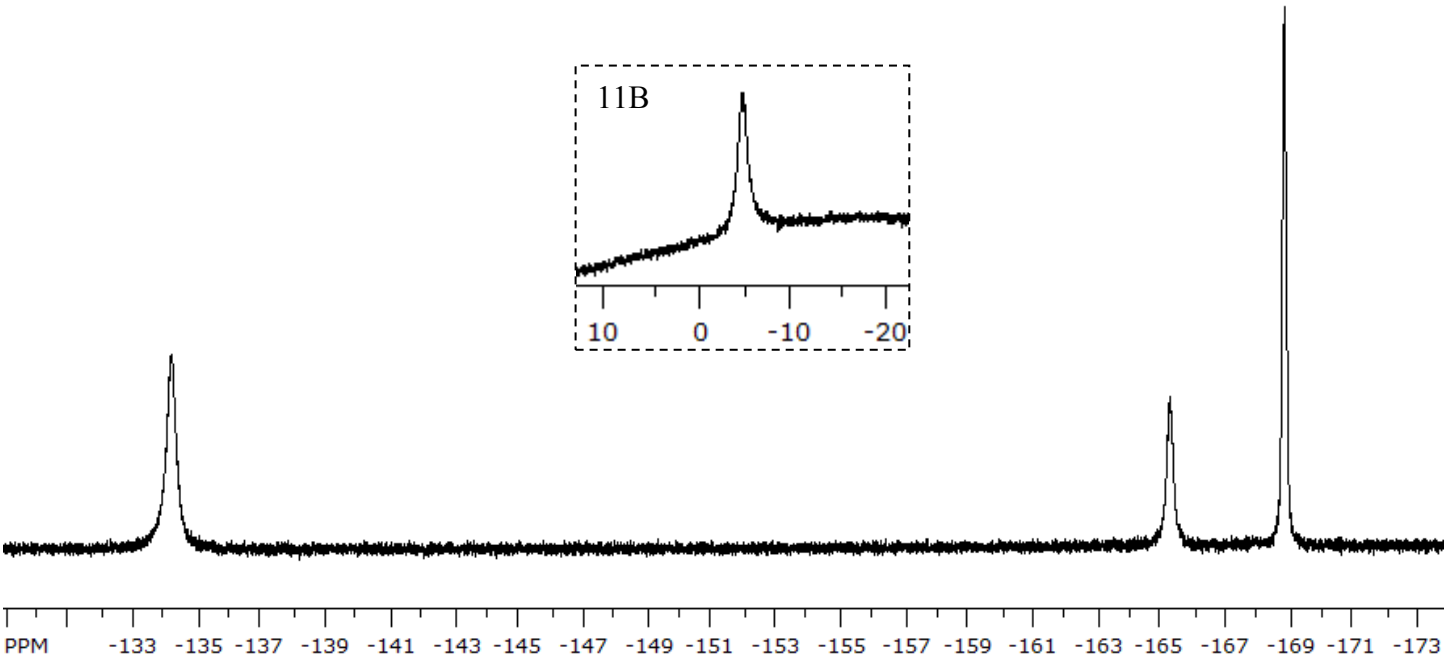
observed in the reaction flask. The mixture was allowed to stir overnight at 50 ºC. Pentane (3 mL) was added, after which the supernatant was decanted. The product was washed with pentane (3 x 2 mL) and dried *in vacuo* to afford (**9**) as a white powder (212 mg, 0.263 mmol, 88 %). Crystals suitable for X-ray crystal structure analyses were obtained by recrystallization from a standing solution in C_6H_5Br at 25 ^oC.



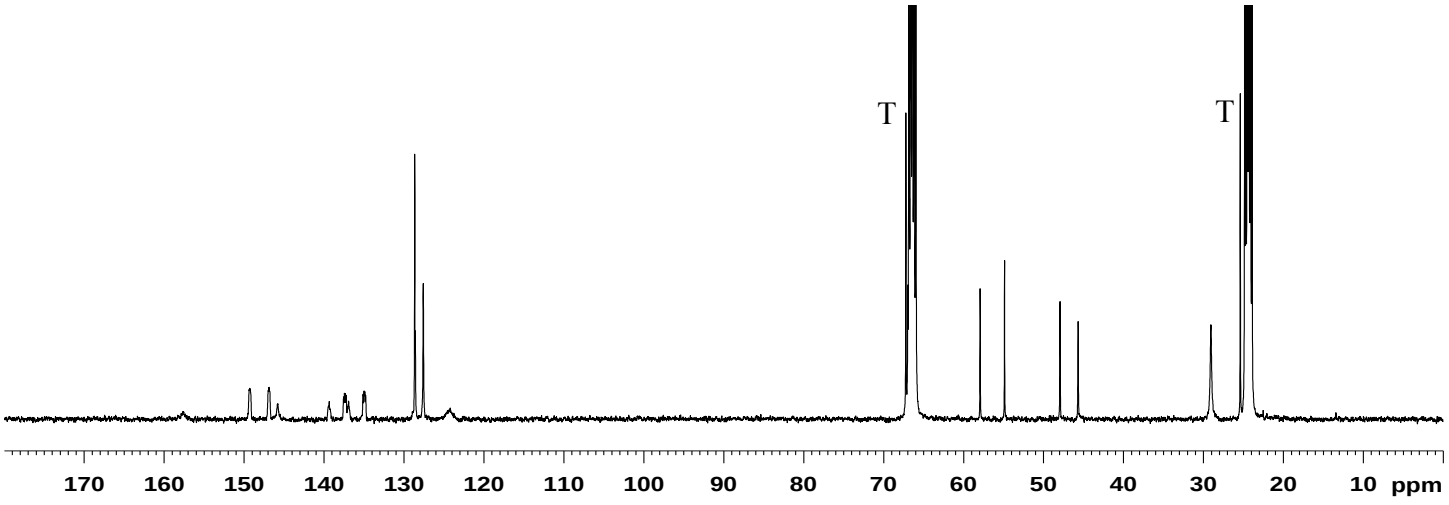
9: ^{1}H NMR (400 MHz, d_8-THF, 298K): δ 7.88 (br, 2H, NH_2), 7.34 (br, 2H, Ar), 7.21 (br d, 2H, $^3J_{H-H}$ = 6.4 Hz, Ar), 4.67 (br , 2H, CH_2), 4.20 (br m, 2H, NH_2CH_2), 1.48 (s, 9H, CH_3), 1.30 ppm (br, 9H, CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, d_8-THF, 298K): δ 157.6 (NCO_2), 148.1 (dm, $^1J_{C-F}$ ≈ 246 Hz, C_6F_5) , 145.7 (*i*-Ar), 138.1 (dm, $^1J_{C-F}$ ≈ 246 Hz, C_6F_5), 136.0 (dm, $^1J_{C-F}$ ≈ 242 Hz, C_6F_5), 128.7 (Ar), 128.6 (*i*-Ar), 127.6 (Ar), 124.3 (br, *i*-C_6F_5), 57.9 ($C(CH_3)_3$), 54.9 ($C(CH_3)_3$), 47.9 (CH_2), 45.7 (CH_2), 29.0 (br, $C(CH_3)_3$), 25.4 ($C(CH_3)_3$) ^{19}F NMR (377 MHz, d_8-THF, 298K): δ -134.1 (br, 2F, *o*-C_6F_5), -165.3 (br, 1F, *p*-C_6F_5), -168.8 (br, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{p,m}$ = 3.5]. ^{11}B NMR (128 MHz, d_8-THF, 298K): δ -4.8 (s).



^{1}H NMR (400 MHz, d_8-THF, 298 K) (T: THF)



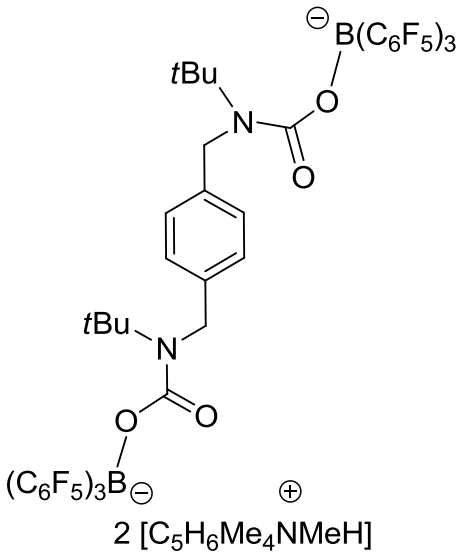
^{19}F NMR (377 MHz, d_8-THF, 298 K) and ^{11}B NMR (128 MHz, d_8-THF, 298 K)



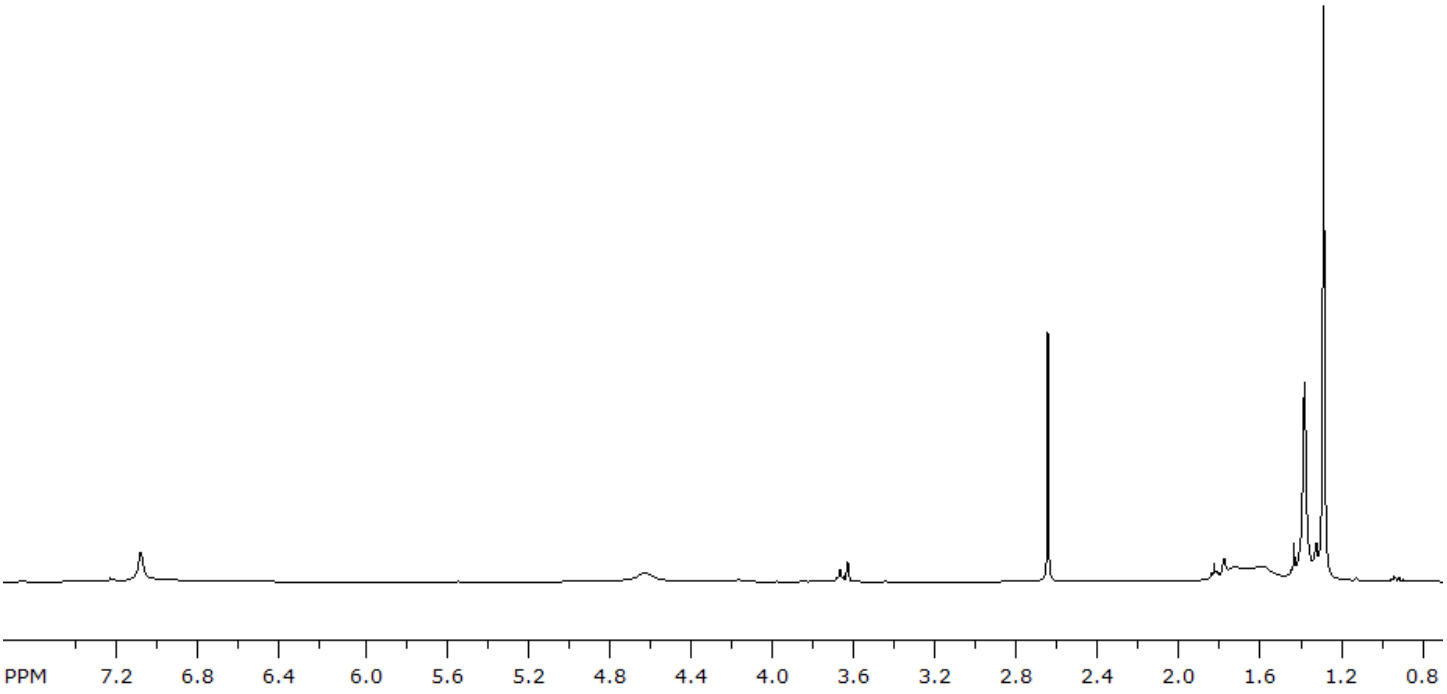
^{13}C{^{1}H} NMR (101 MHz, d_8-THF, 298 K) (T: THF)

IR (KBr): ν = 1645 cm^{-1} (vs, C=O). Elem. Anal. $C_{35}H_{28}BF_{15}N_2O_2$•THF Calc: C 53.44, H 4.14, N 320; found: C 53.89, H 4.63, N 3.16. X-ray: $C_{35}H_{28}BF_{15}N_2O_2$•$CH_2Cl_2$•THF, M = 961.43, a = 11.8169(9), b = 14.2528(10), c = 25.8313(18)Å, α = 92.291(4), β = 101.983(4), γ = 94.629(4)°, V = 4234.7(5) Å^3, Z = 4, triclinic, P-1, Data (λ = 0.71069 Å, T = 150 K), 14788 (R_{int} = 0.043), 8568 [$I \geq 2\ \sigma(I)$], 1135 parameters, R = 0.085, wR^2 = 0.271, GOF = 1.031.

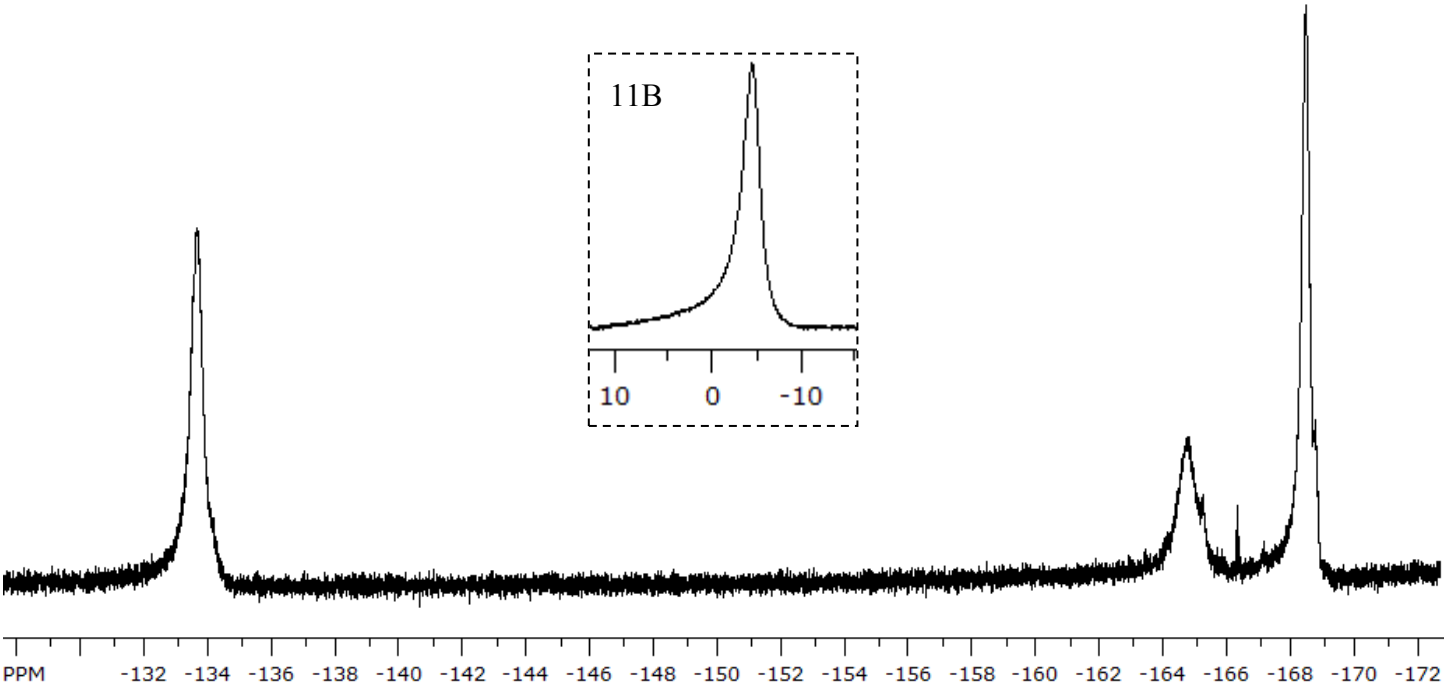
Synthesis of 2 **[$C_5H_6Me_4NMeH$] [$C_6H_4(CH_2N\mathit{t}BuCO_2B(C_6F_5)_3)_2$] (10).** In a glovebox, a 50 mL glass bomb equipped with a magnetic stir bar was charged with $B(C_6F_5)_3$ (206 mg, 0.402 mmol), *N,N'*-(1,4-phenylenebis-(methylene))bis(*t*-butylamine) (50.0 mg, 0.201 mmol), and 1,2,2,6,6-pentamethylpiperidine (62.4 mg, 0.402 mmol) in toluene (5 mL). The reaction was degassed three times through a freeze-pump-thaw cycle on the vacuum/CO_2 line. The reaction flask was cooled to -196 ºC and filled with CO_2 (1 atm). The reaction mixture was allowed to stir at 25 ºC overnight. Over this reaction time precipitate was observed in the reaction vessel. Pentane (3 mL) was added, after which the supernatant was decanted. The product was washed with pentane (3 x 2 mL) and dried *in vacuo* to afford the product as a white crystalline material (153 mg, mmol, 46 %). Colourless crystals suitable for X-ray crystal structure analyses were obtained by recrystallization from a THF solution layered with hexanes in a -40 ºC freezer.



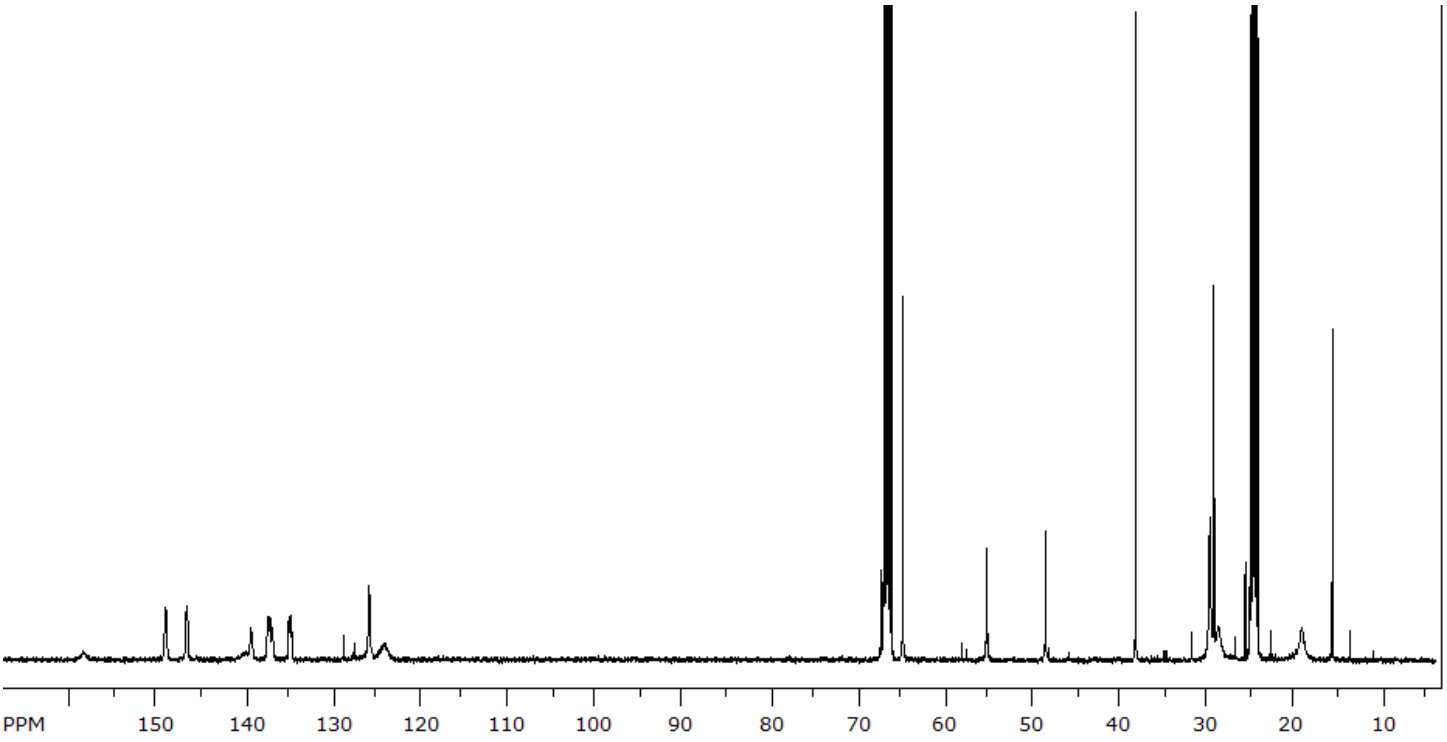
10: ^{1}H NMR (400 MHz, d_8-THF, 298K): δ 7.07 (s, 4H, Ar), 7.04 (br, 2H, NH), 4.61 (br, 4H, CH_2), 2.63 (s, 6H, NCH_3), 1.72 – 1.58 (br m, 12H, PMP-CH_2), 1.37 (br, 18H, 2 $C(CH_3)_3$), 1.28 (s, 24H, PMP-CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, d_8-THF, 298K): δ 158.7 (NCO_2), 148.0 (dm, $^1J_{C\text{-}F} \approx 240$ Hz, C_6F_5), 140.1 (*i*-Ar), 138.2 (dm, $^1J_{C\text{-}F} \approx 246$ Hz, C_6F_5), 136.2 (dm, $^1J_{C\text{-}F} \approx 246$ Hz, C_6F_5), 125.9 (Ar), 124.2 (*i*-C_6F_5), 64.8 (PMP-*C*(CH_3)), 54.9 (*C*(CH_3)$_3$), 48.3 (diamine-CH_2), 38.1 (PMP-CH_2), 29.5 (C(*C*H_3)$_3$), 29.0 (NCH_3), 28.5 (PMP-CH_3), 18.8 (PMP-CH_3), 15.4 (PMP-CH_2). ^{19}F NMR (377 MHz, d_8-THF, 298K): δ -133.6 (br, 2F, *o*-C_6F_5), -164.8 (br, 1F, *p*-C_6F_5), -168.6 (br, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{p,m} = 3.8$]. ^{11}B NMR (128 MHz, d_8-THF, 298K): δ -4.70 (s).



^{1}H NMR (400 MHz, d_8-THF, 298 K)



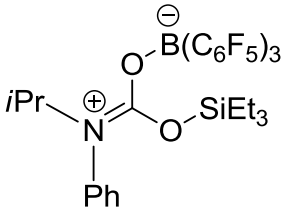
^{19}F NMR (377 MHz, d_8-THF, 298 K) and ^{11}B NMR (128 MHz, d_8-THF, 298 K)



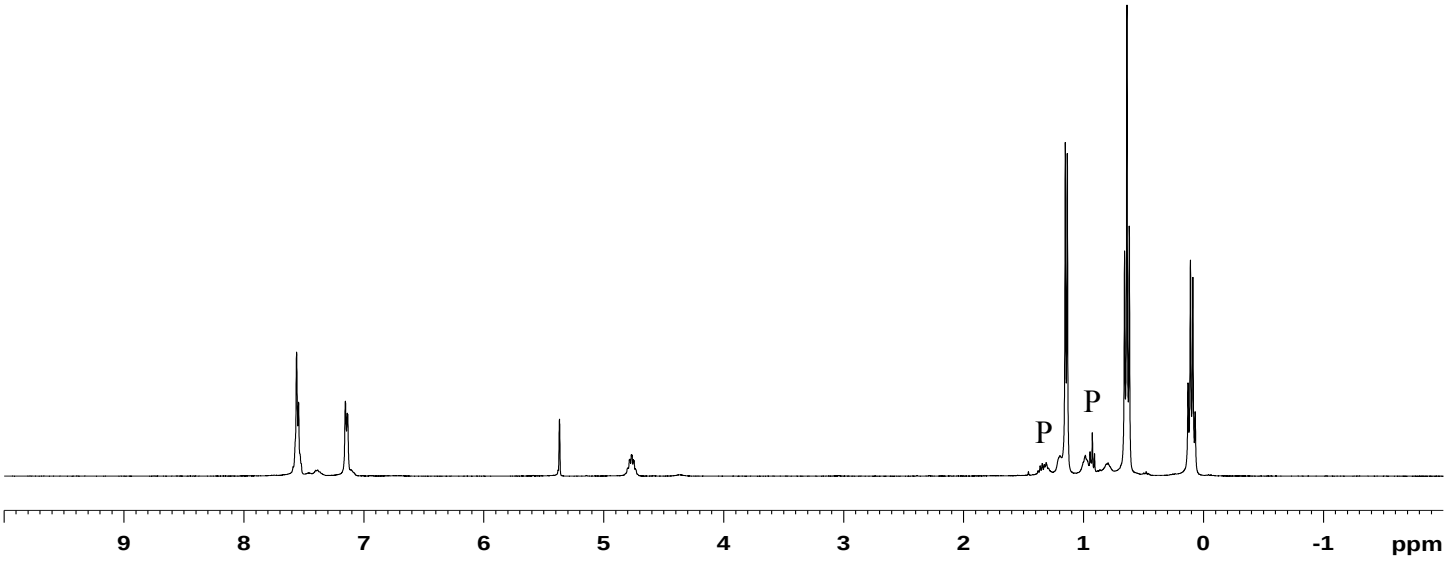
$^{13}C\{^{1}H\}$ NMR (101 MHz, d_8-THF, 298 K)

IR (KBr): ν = 1693 cm^{-1} (vs, C=O). Elem. Anal. $C_{74}H_{70}B_2F_{30}N_4O_4$ Calc.: C 53.19, H 4.22, N 3.35; found: C 53.03, H 4.38, N 3.39. X-ray: $C_{37}H_{35}BF_{15}N_2O_2$, M = 835.48, a = 15.0642(17), b = 12.3370(14), c = 21.279(2) Å, β = 109.498(7)°, V = 3727.8(7) $Å^3$, Z = 4, monoclinic, $P2_1/c$, Data (λ = 0.71069 Å, T = 150 K), 8566 (R_{int} = 0.129), 3321 [$I \geq 2\ \sigma(I)$], 526 parameters, R = 0.068, wR^2 = 0.221, GOF = 0.965.

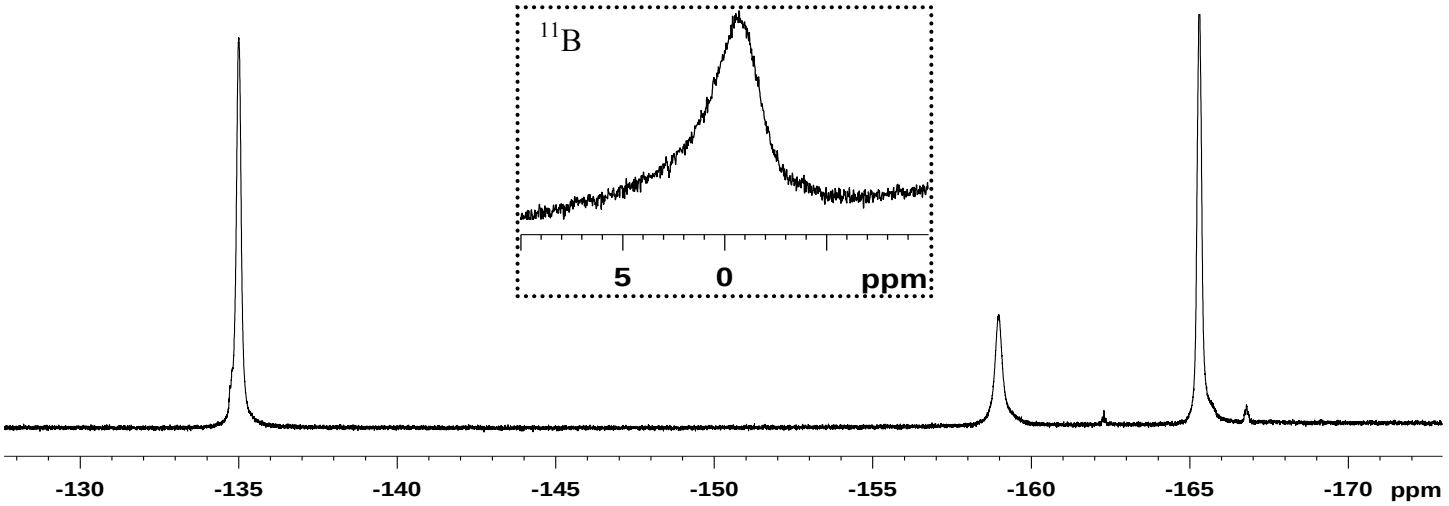
Synthesis of **[PhN*i*PrC(OSiEt$_3$)OB(C$_6$F$_5$)$_3$] (11).** In a glovebox, compound **8** (68.4 mg, 0.0827 mmol) was weighed into a 20 mL dram vial and dissolved in toluene (3 mL). To this solution, $HSiEt_3$ (13.3 µL, 0.0835 mmol) was added via syringe. The reaction mixture was allowed to mix overnight at 25 ^{o}C. All volatiles were removed and the crude oil was dissolved in minimum pentane and placed in -40 ^{o}C freezer overnight. Colorless crystals of **11** were obtained (42.6 mg, 0.0529 mmol, 64 %).



11: ^{1}H NMR (400 MHz, CD_2Cl_2, 298K): δ 7.56 (m, 3H, *m*,*p*-Ar), 7.15 (m, 2H, *o*-Ar), 4.77 (m, 1H, $^{3}J_{H\text{-}H}$ = 6.6 Hz, C*H*$(CH_3)_2$), 1.15 (d, 6H, $^{3}J_{H\text{-}H}$ = 6.6 Hz, CH(C*H*$_3)_2$), 0.64 (t, 9H, $^{3}J_{H\text{-}H}$ = 8.0 Hz, Si(CH_2C*H*$_3)_3$, 0.10 (q, 6H, $^{3}J_{H\text{-}H}$ = 8.0 Hz, Si(C*H*$_2CH_3)_3$. ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 298K): δ 156.4 (NCO_2), 148.3 (dm, $^{1}J_{C\text{-}F}$ ≈ 249 Hz, C_6F_5) , 137.5 (dm, $^{1}J_{C\text{-}F}$ ≈ 250 Hz, C_6F_5), 136.5 (dm, $^{1}J_{C\text{-}F}$ ≈ 242 Hz, *m*-C_6F_5), 134.8 (*i*-Ar), 130.7 (*p*-Ar), 130.2 (*m*-Ar), 130.1 (*o*-Ar), 129.4 (br, *i*-C_6F_5), 53.7 (*C*H$(CH_3)_2$), 20.7 (CH(*C*H$_3)_2$), 6.07 (Si(CH_2*C*H$_3)_3$), 4.31 (Si(*C*H$_2CH_3)_3$). ^{19}F NMR (377 MHz, CD_2Cl_2, 298K): δ -135.0 (br, 2F, *o*-C_6F_5), -159.0 (br, 1F, *p*-C_6F_5), -165.3 (br, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{p,m}$ = 6.3]. ^{11}B NMR (128 MHz, CD_2Cl_2, 298K): δ -0.4 (s).



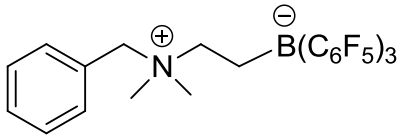
^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) (P: pentane)



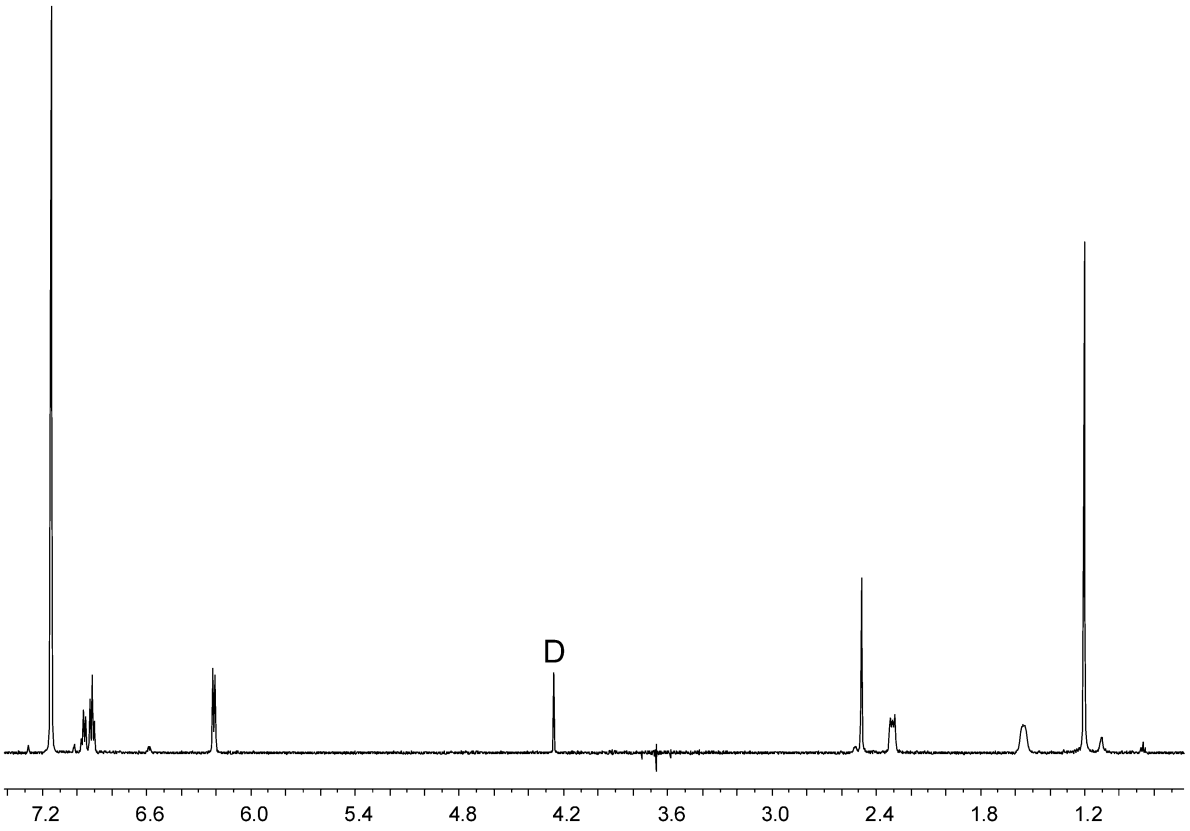
^{19}F NMR (377 MHz, CD_2Cl_2, 298 K) and ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K)

Elem. Anal. $C_{34}H_{27}BF_{15}NO_2Si$ Calc.: C 50.70, H 3.38, N 1.74; found: C 50.85, H 3.54, N 1.84. X-ray: $C_{34}H_{27}BF_{15}NO_2Si$, M = 805.47, a = 10.0980(8), b = 11.9201(9), c = 15.5418(13) Å, α = 88.808(4), β = 80.396(5), γ = 69.131(4)°, V = 1722.0(2)Å^3, Z = 2, triclinic, P-1, Data (λ = 0.71069 Å, T = 150 K), 6044 (R_{int} = 0.053), 4109 [I ≥ 2 σ(I)], 487 parameters, R = 0.042, wR^2 = 0.108, GOF = 1.012.

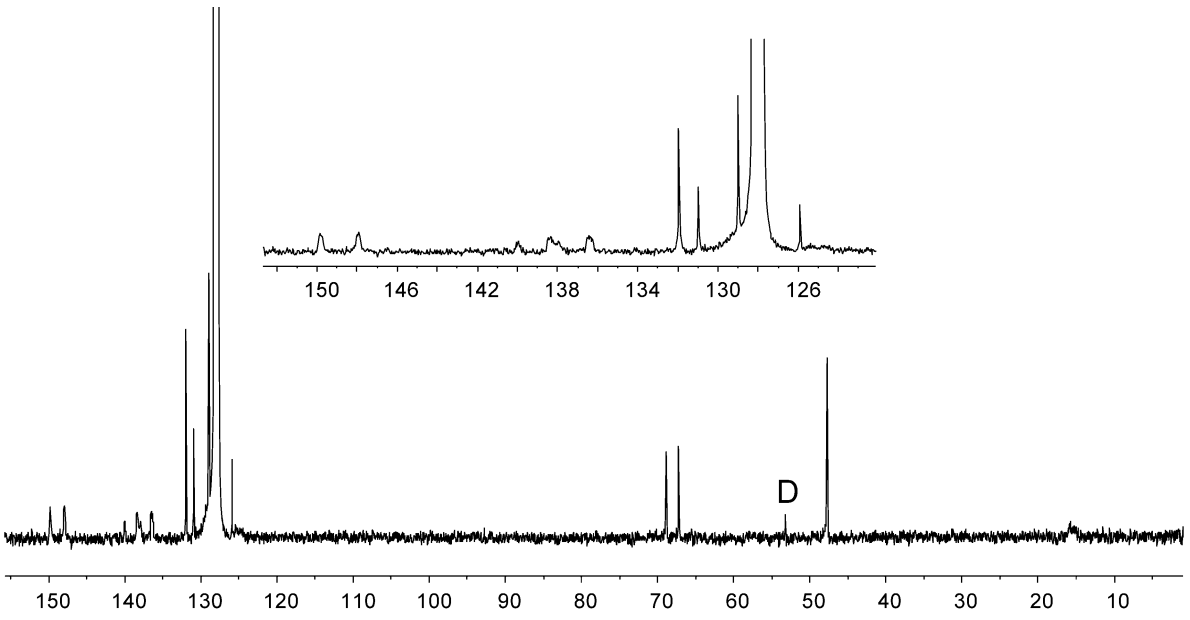
Synthesis of $PhCH_2NMe_2CH_2CH_2B(C_6F_5)_3$ (12). A solution of *N*,*N*-dimethylbenzylamine (30.0 mg, 0.222 mmol) and $B(C_6F_5)_3$ (114 mg, 0.222 mmol) in pentane (5 mL) was degassed carefully and pressurized with ethylene (2 atm), upon which a white solid started to precipitate. Stirring was continued for 2 days and then the precipitate was filtered off. After crystallization of the solid from dichloromethane / pentane at -32 °C, the product was obtained (57%, 85.6 mg, 0.126 mmol).



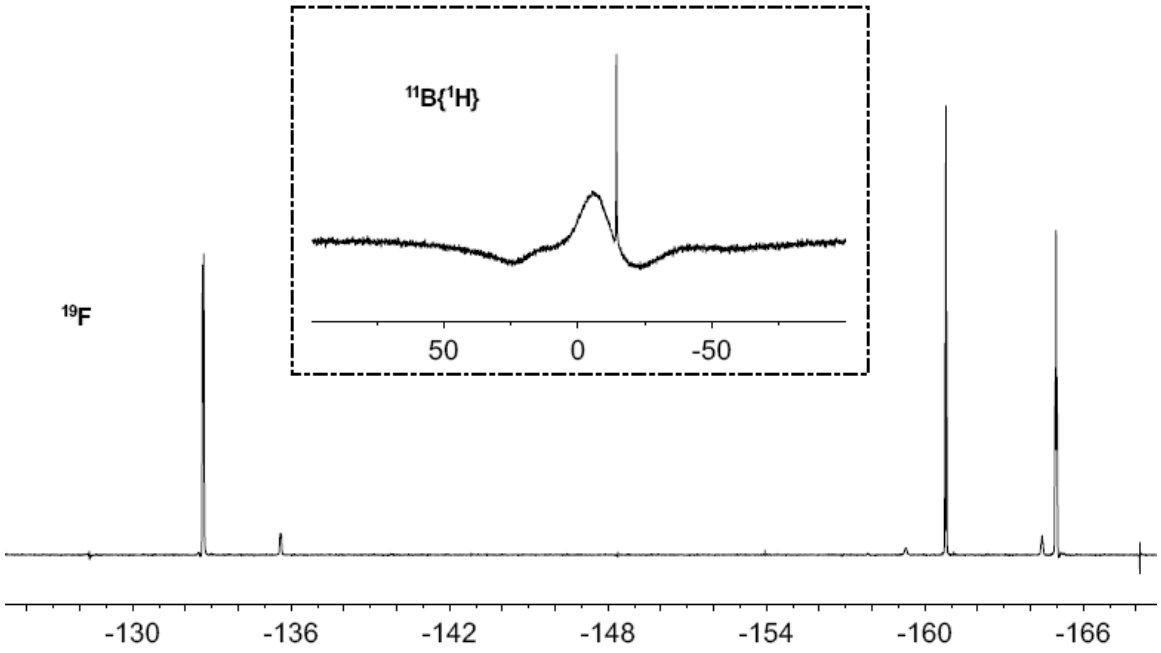
12: ^{1}H NMR (600 MHz, C_6D_6, 298K): δ 6.96 (m, 1H, *p*-C_6H_5); 6.91 (m, 2H, *m*-C_6H_5); 6.21 (m, 2H, *o*-C_6H_5); 2.48 (s, 2H, $^{Ph}CH_2N$); 2.31 (m, 2H, NCH_2); 1.55 (br, 2H, CH_2B); 1.20 (s, 6H, NCH_3). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 298K): δ 148.9 (dm, $^1J_{CF}$ ~ 241 Hz, C_6F_5); 139.0 (dm, $^1J_{CF}$ ~ 253 Hz, C_6F_5); 137.4 (dm, $^1J_{CF}$ ~ 239 Hz, C_6F_5); 132.0 (*o*-C_6H_5); 131.0 (*p*-C_6H_5); 129.0 (*m*-C_6H_5); 125.9 (*i*-C_6H_5); n.o. (*i*-C_6F_5); 68.9 (NCH_2); 67.2 ($^{Ph}CH_2N$); 47.8 (NCH_3); 15.6 (br, CH_2B). ^{19}F NMR (564 MHz, C_6D_6, 298K): δ −132.7 (m, 2F, *o*-C_6F_5); −160.8 (t, ^3J = 20.2 Hz, 1F, *p*-C_6F_5); −165.0 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{p,m}$ = 4.2]. $^{11}B\{^1H\}$ NMR (160 MHz, C_6D_6, 298K): δ −14.4 ($\nu_{1/2}$ ~ 30 Hz). Elem Anal.: $C_{29}H_{17}BF_{15}N*0.3CH_2Cl_2$ Calc.: C: 50.20; H: 2.51; N: 2.00; found C: 50.06; H: 2.17; N: 1.90.



^{1}H NMR (600 MHz, 298 K, C_6D_6) (D: CH_2Cl_2)



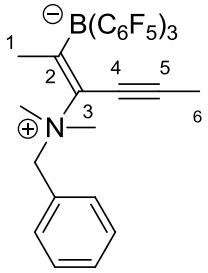
^{13}C{^{1}H} NMR (126 MHz, 298 K, C_6D_6) (D: CH_2Cl_2)



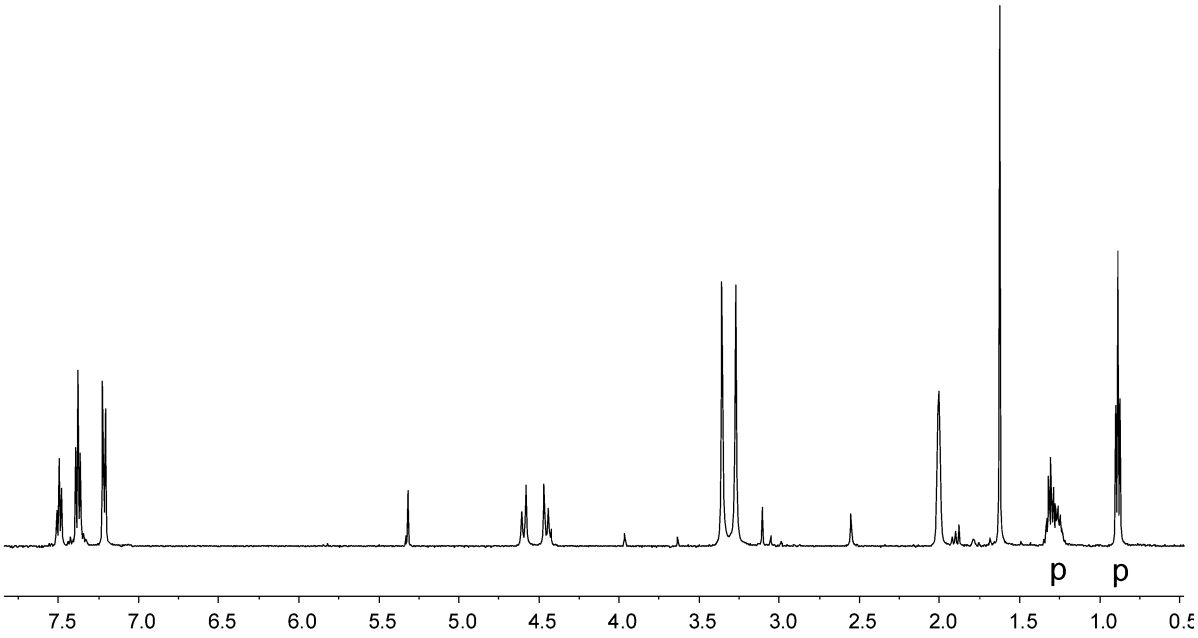
$^{11}B\{^1H\}$ NMR (160 MHz, 298 K, C_6D_6) and ^{19}F NMR (564 MHz, 298 K, C_6D_6)

X-ray crystal structure analysis of **12**: formula $C_{29}H_{17}BF_{15}N$ * ½ CH_2Cl_2, M = 717.71, colorless crystal 0.30 x 0.15 x 0.10 mm, a = 13.2426(3), b = 13.7868(3), c = 18.2798(5) Å, α = 111.590(2), β = 99.707(2), γ = 101.426(1)°, V = 2933.02(12) Å^3, ρ_{calc} = 1.625 g cm^{-3}, μ = 2.262 cm^{-1}, empirical absorption correction (0.550 $\leq$ T $\leq$ 0.805), Z = 4, triclinic, space group P1bar (No. 2), λ= 1.54178 Å, T = 223 K, ω and φ scans, 39408 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.60 Å^{-1}, 10000 independent (R_{int} = 0.052) and 7942 observed reflections [$I \geq 2\ \sigma(I)$], 872 refined parameters, R = 0.048, wR^2 = 0.124, max. residual electron density 0.27 (-0.45) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

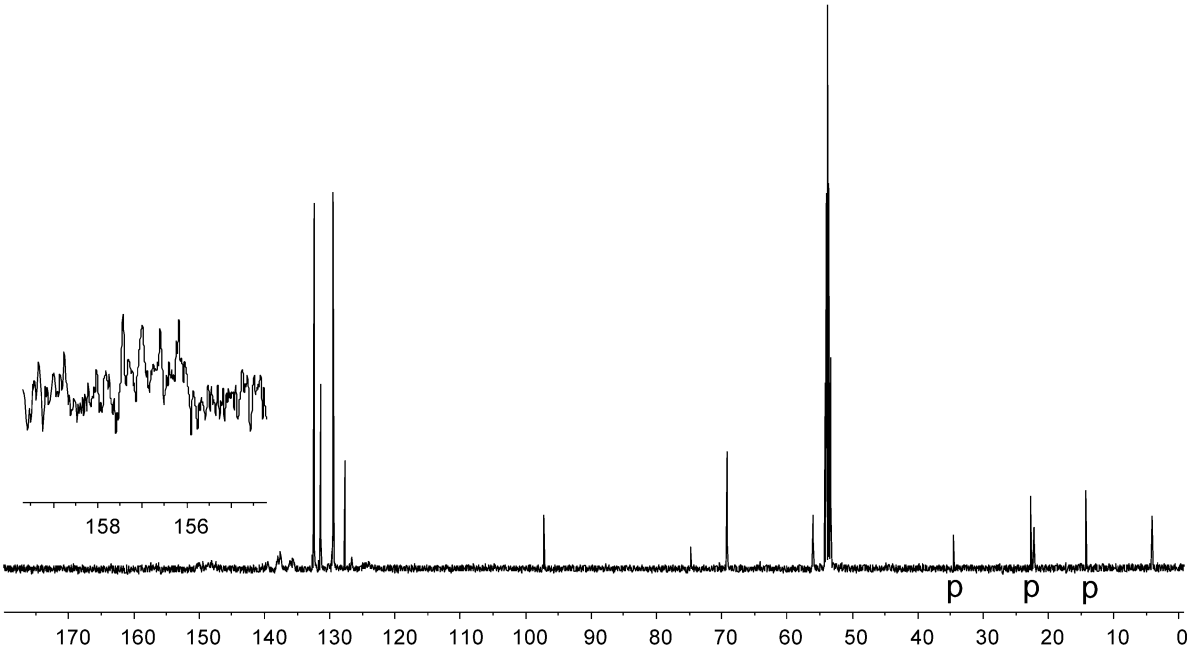
Synthesis of $PhCH_2NMe_2C(CCMe)=CMeB(C_6F_5)_3$ (13). 2,4-Hexadiyne (11.5 mg, 0.148 mmol) were added to a solution of *N*,*N*-dimethylbenzylamine (20.0 mg, 0.148 mmol) and $B(C_6F_5)_3$ (75.8 mg, 0.148 mmol) in pentane (5 mL). After stirring at 25 °C for overnight the obtained precipitate was filtered off and dried under reduced pressure to yield the product **13** (52%, 55.8 mg, 0.077 mmol).



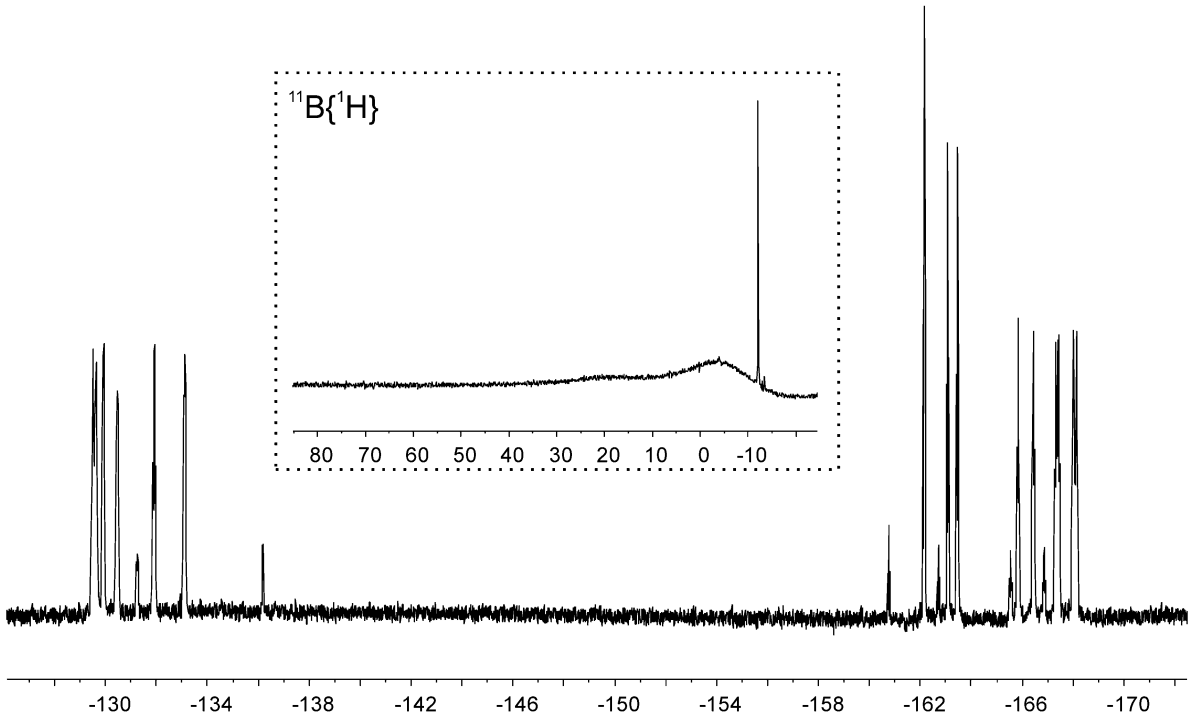
13: ^{1}H NMR (500 MHz, CD_2Cl_2, 298K): δ 7.50 (m, 1H, *p*-C_6H_5); 7.38 (m, 2H, *m*-C_6H_5); 7.22 (m, 2H, *o*-C_6H_5); 4.59 (d, $^2J_{HH}$ = 13.1 Hz, 1H, CH_2N); 4.46 (d, $^2J_{HH}$ = 13.1 Hz, 1H, CH_2N); 3.36 (s, 3H, NCH_3); 3.27 (s, 3H, NCH_3); 2.00 (br s, 3H, 1-H); 1.63 (s, 3H, 6-H). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 298K): δ 156.6 (1:1:1:1 q, $^1J_{CB}$ ~ 52 Hz, C-2); 132.4 (*o*-C_6H_5); 131.4 (*p*-C_6H_5); 129.5 (*m*-C_6H_5); 127.7 (*i*-C_6H_5); 126.7 (br, C-3); 97.2 (C-5); 74.7 (br, C-4); 69.2 (CH_2N); 56.0, 53.3 (NCH_3); 22.2 (br, C-1); 4.1 (C-6); [C_6F_5 not listed]. ^{19}F NMR (470 MHz, CD_2Cl_2, 298K): δ −129.5 (m, 1F, *o*-$C_6F_5^A$); −129.6 (m, 1F, *o*-$C_6F_5^C$); −129.9 (m, 1F, *o*-$C_6F_5^C$); −130.5 (m, 1F, *o*-$C_6F_5^B$); −131.9 (m, 1F, *o*-$C_6F_5^B$); −133.1 (m, 1F, *o*-$C_6F_5^A$); −162.2 (t, ^3J = 20.5 Hz, 1F, *p*-$C_6F_5^A$); −163.1 (t, ^3J = 21.6 Hz, 1F, *p*-$C_6F_5^C$); −163.5 (t, ^3J = 20.6 Hz, 1F, *p*-$C_6F_5^B$); −165.9 (m, 1F, *m*-$C_6F_5^A$); −166.5 (m, 1F, *m*-$C_6F_5^A$); −167.3 (m, 2F, *m*-$C_6F_5^C$); −167.4 (m, 2F, *m*-$C_6F_5^B$); −168.0 (m, 1F, *m*-$C_6F_5^C$); −168.2 (m, 1F, *m*-$C_6F_5^B$). $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 298K): δ −12.1 ($\nu_{1/2}$ ~ 20 Hz). Elem Anal. $C_{33}H_{19}BF_{15}N$: Calc.: C: 54.65, H: 2.64, N: 1.93; found C: 54.69, H: 3.00, N: 1.93.



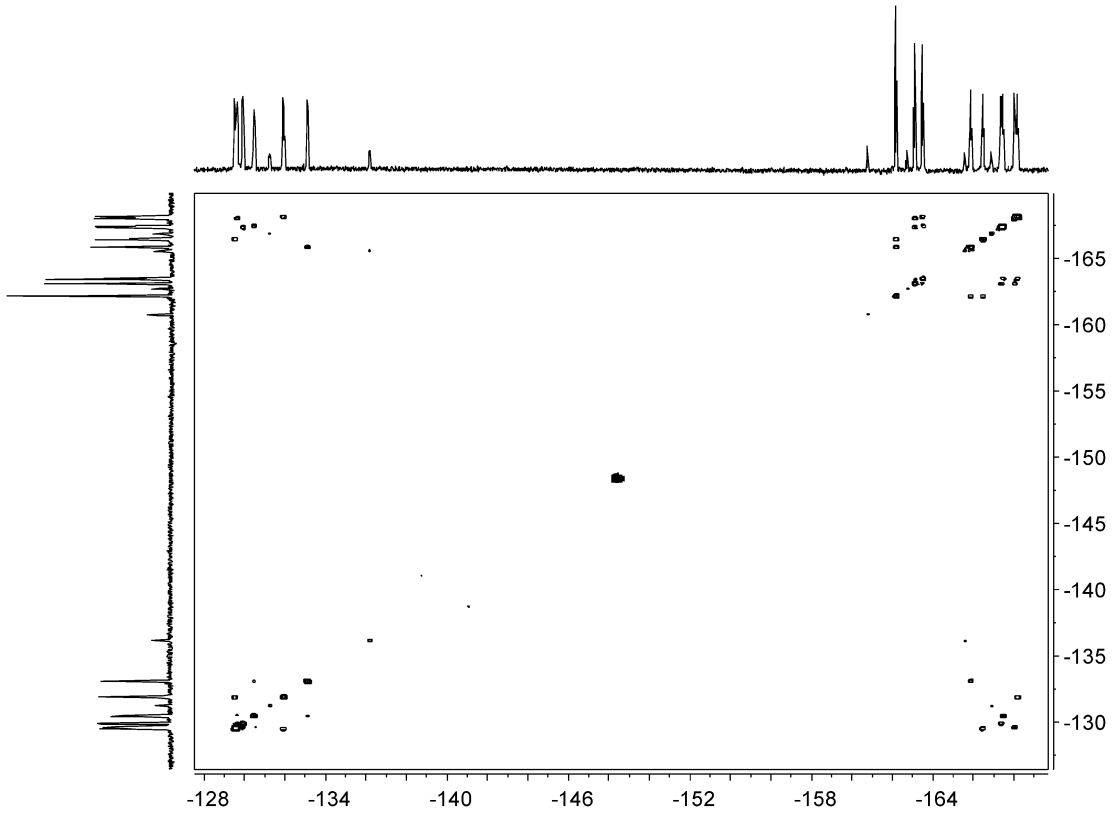
^{1}H NMR (500 MHz, 298 K, CD_2Cl_2) (p: pentane)



^{13}C{^{1}H} NMR (126 MHz, 298 K, CD_2Cl_2) (p: pentane)



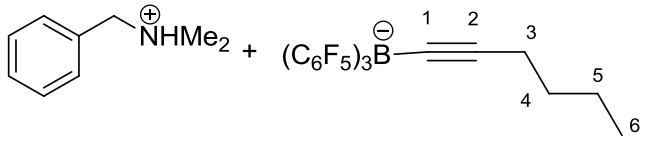
^{19}F NMR (470 MHz, 298 K, CD_2Cl_2) and $^{11}B\{^{1}H\}$ NMR (160 MHz, 298 K, CD_2Cl_2)



^{19}F,^{19}F cosy NMR (470/470 MHz, 298 K, CD_2Cl_2)

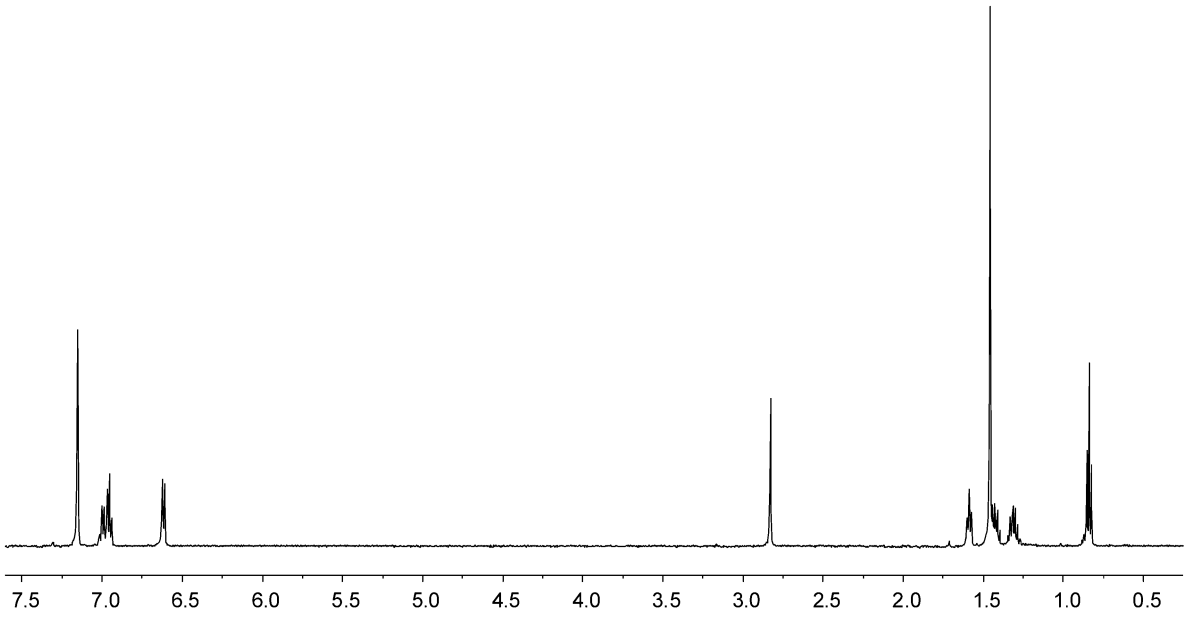
X-ray crystal structure analysis of **13**: formula $C_{33}H_{19}BF_{15}N$ * ½ C_5H_{12}, M = 761.38, colorless crystal 0.35 x 0.16 x 0.15 mm, a = 10.3487(3), b = 13.2156(8), c = 13.9427(10) Å, α = 97.316(3), β = 107.850(5), γ = 109.846(3)°, V = 1649.26(14) Å^3, ρ_{calc} = 1.533 g cm^{-3}, μ = 1.321 cm^{-1}, empirical absorption correction (0.655 ≤ T ≤ 0.827), Z = 2, triclinic, space group P1bar (No. 2), λ= 1.54178 Å, T = 223 K, ω and φ scans, 21550 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 5717 independent (R_{int} = 0.042) and 4943 observed reflections [$I \geq 2\ \sigma(I)$], 471 refined parameters, R = 0.058, wR^2 = 0.175, max. residual electron density 1.13 (-0.49) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Synthesis of [PhCH$_2$NMe$_2$H][RC≡CB(C$_6$F$_5$)$_3$] (R = *n*-Bu **14a**, Ph **14b**, *t*Bu **14c**, SiMe$_3$ **14d**) These compounds were prepared in a general way. A representative example: A solution of *N*,*N*-dimethylbenzylamine (50.0 mg, 0.370 mmol) and B(C$_6$F$_5$)$_3$ (190 mg, 0.370 mmol) in pentane (10 mL) was treated with 1-hexyne (30.5 mg, 0.370 mmol) and the reaction mixture was stirred vigorously overnight. The resulting white solid was filtered off, washed with pentane and dried *in vacuo* to yield the zwitterionic compound **14a** (190 mg, 0.26 mmol, 70%).

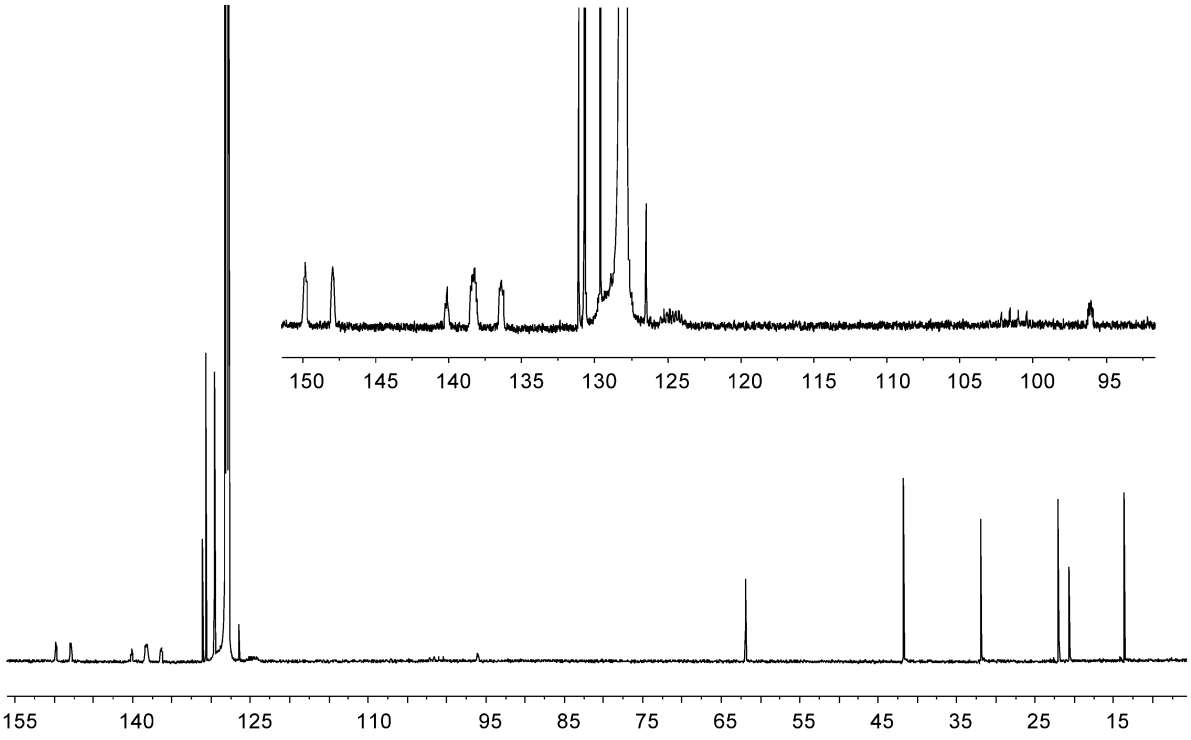


14a: ^{1}H NMR (500 MHz, C$_6$D$_6$, 298K): δ 7.00 (m, 1H, *p*-C$_6$H$_5$); 6.95 (m, 2H, *m*-C$_6$H$_5$); 6.62 (m, 2H, *o*-C$_6$H$_5$); 2.83 (s, 2H, CH$_2$N); 1.59 (m, 2H, 3-H); 1.46 (s, 6H, NCH$_3$); 1.43 (m, 2H, 4-H); 1.31 (m, 2H, 5-H); 0.84 (t, $^3J_{HH}$ = 7.3 Hz, 3H, 6-H); n.o. (NH). ^{13}C{^{1}H} NMR (126 MHz, C$_6$D$_6$, 298K): δ 148.9 (dm, $^1J_{CF}$ ~ 238 Hz, C$_6$F$_5$); 139.3 (dm, $^1J_{CF}$ ≈ 245 Hz, C$_6$F$_5$); 137.3 (dm, $^1J_{CF}$ ≈ 249 Hz, C$_6$F$_5$); 131.1 (*p*-C$_6$H$_5$); 130.7 (*o*-C$_6$H$_5$); 129.6 (*m*-C$_6$H$_5$); 126.5 (*i*-C$_6$H$_5$); 124.6 (br m, *i*-C$_6$F$_5$); 101.3 (1:1:1:1 q, $^1J_{CB}$ = 71.1 Hz, C-1); 96.1 (1:1:1:1 q, $^2J_{CB}$ = 14.4 Hz, C-2); 61.9 (CH$_2$N); 41.8 (NCH$_3$); 31.9 (C-4); 22.0 (C-5); 20.7 (C-3); 13.6 (C-6). ^{19}F NMR (470 MHz,

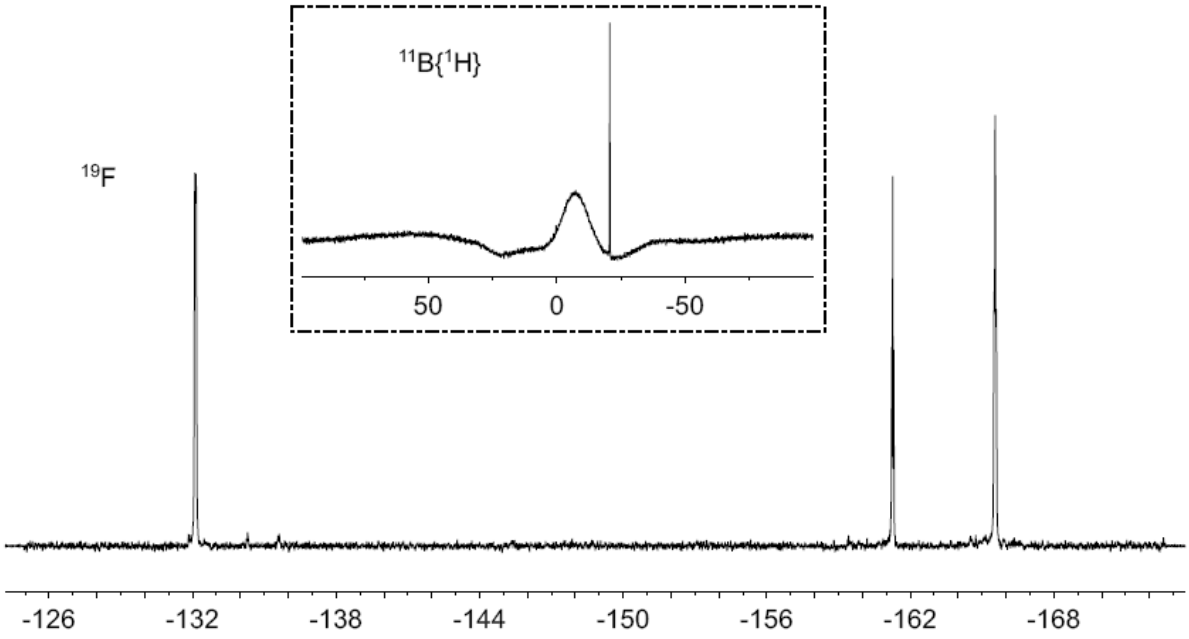
C_6D_6, 298K): δ −132.1 (m, 2F, *o*-C_6F_5); −161.3 (t, ^3J = 22.2 Hz, 1F, *p*-C_6F_5); −165.6 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{p,m}$ = 4.3]. $^{11}B\{^1H\}$ NMR (160 MHz, C_6D_6, 298K): δ −20.6 (s, $\nu_{1/2}$ ~ 20 Hz). Elem. Anal.: $C_{33}H_{23}BF_{15}N$ Calc.: C: 54.34, H: 3.18, N: 1.92; found: C: 53.84, H: 3.13, N: 2.07.



^1H NMR (500 MHz, 298 K, C_6D_6)

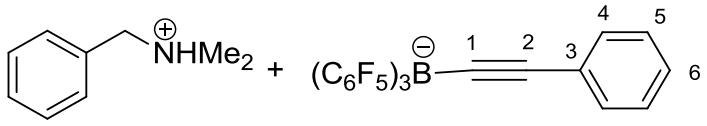


$^{13}C\{^1H\}$ NMR (126 MHz, 298 K, C_6D_6)



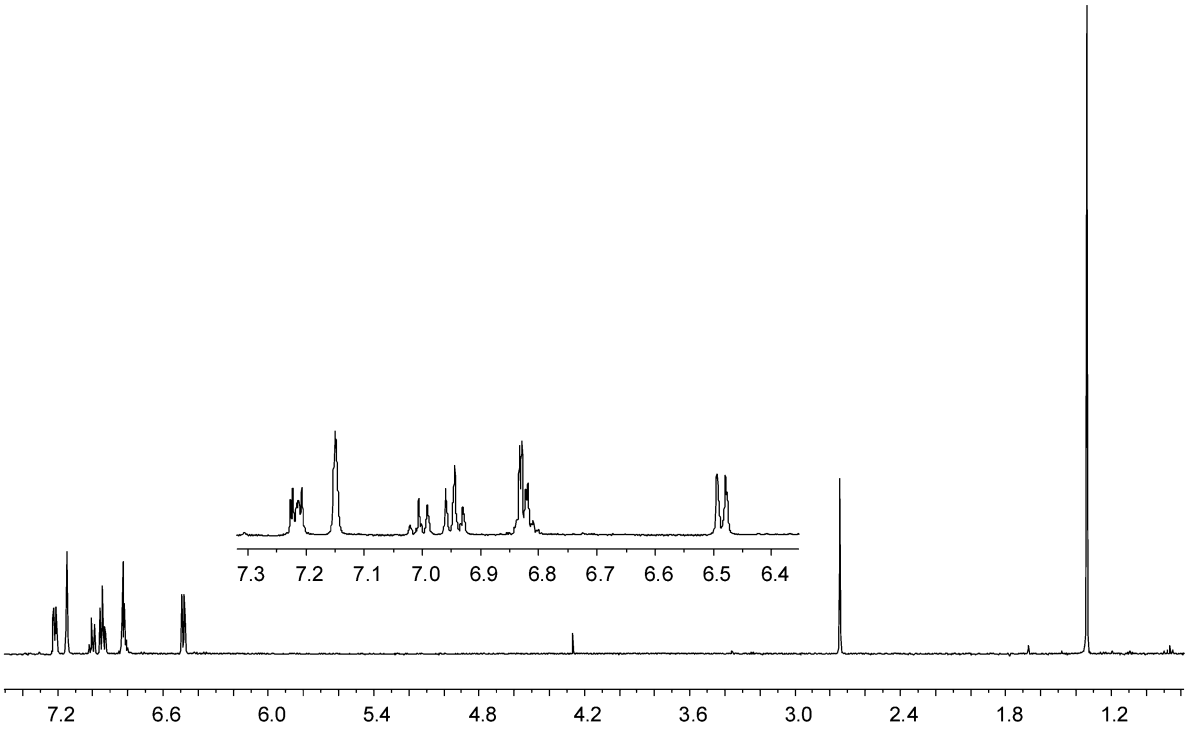
^{19}F NMR (470 MHz, 298 K, C_6D_6) and $^{11}B\{^1H\}$ NMR (160 MHz, 298 K, C_6D_6)

X-ray crystal structure analysis of **14a**: formula $C_{33}H_{23}BF_{15}N$, M = 729.33, colorless crystal 0.20 x 0.18 x 0.16 mm, a = 10.0966(4), b = 10.4671(6), c = 16.6994(5) Å, α = 73.407(4), β = 73.953(2), γ = 72.449(6)°, V = 1577.24(12) Å^3, ρ_{calc} = 1.536 g cm^{-3}, μ = 1.353 cm^{-1}, empirical absorption correction ($0.774 \leq T \leq 0.813$), Z = 2, triclinic, space group P1bar (No. 2), λ= 1.54178 Å, T = 223 K, ω and φ scans, 19952 reflections collected ($\pm h, \pm k, \pm l$), [(sinθ)/λ] = 0.60 Å^{-1}, 5412 independent (R_{int} = 0.040) and 4657 observed reflections [$I \geq 2\ \sigma(I)$], 471 refined parameters, R = 0.053, wR^2 = 0.151, max. residual electron density 0.64 (-0.38) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

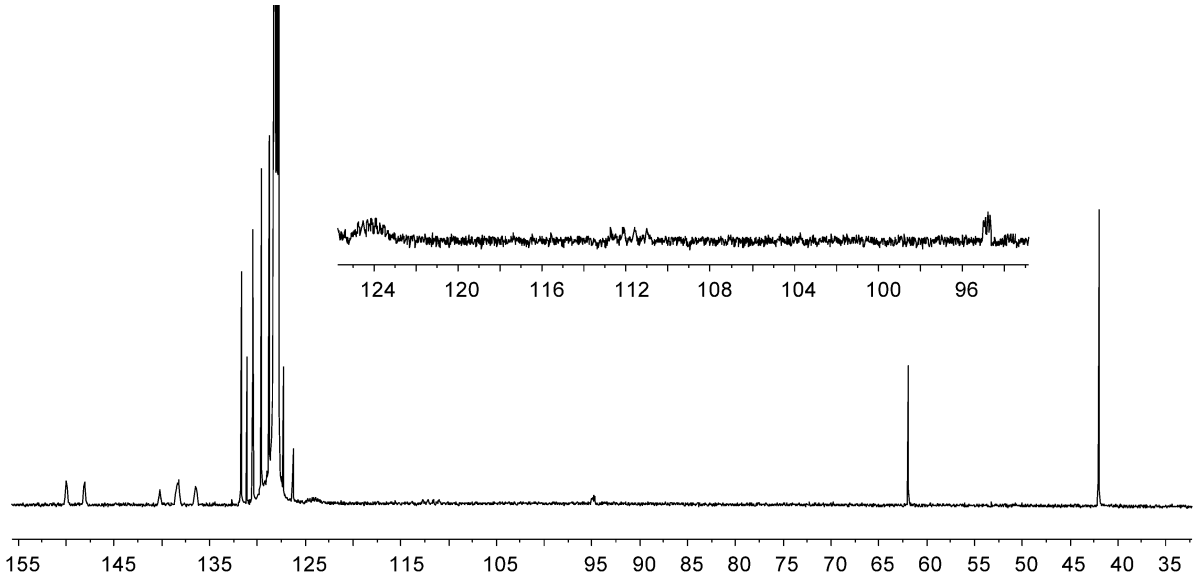


14b: ^1H NMR (500 MHz, C_6D_6, 298K): δ 7.22 (m, 2H, 4-H); 7.01 (m, 1H, p-C_6H_5); 6.94 (m, 2H,

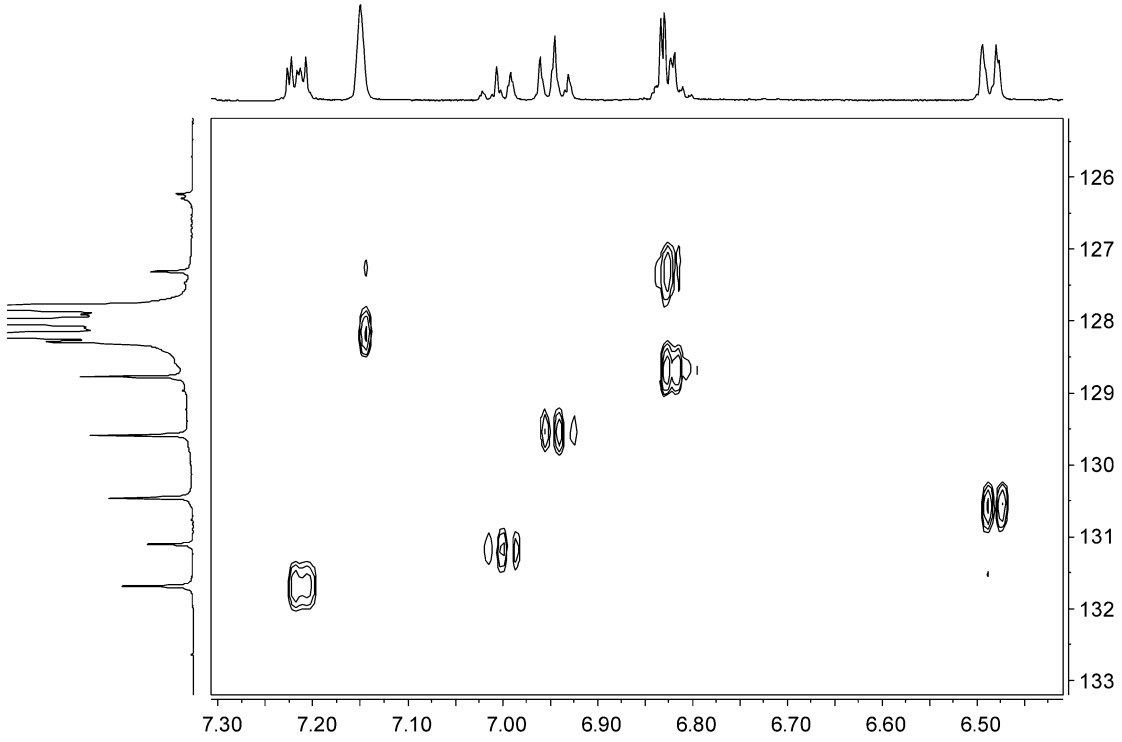
m-C_6H_5); 6.83 (m, 3H, 5,6-H); 6.49 (m, 2H, *o*-C_6H_5); 2.75 (s, 2H, CH_2N); 1.34 (s, 2H, NCH_3). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 298K): δ 149.0 (dm, $^1J_{CF}$ ~ 239 Hz, C_6F_5); 139.2 (dm, $^1J_{CF}$ ~ 221 Hz, C_6F_5); 137.3 (dm, $^1J_{CF}$ ~ 226 Hz, C_6F_5); 131.7 (C-4); 131.1 (*p*-C_6H_5); 130.5 (*o*-C_6H_5); 129.6 (*m*-C_6H_5); 128.8 (C-5); 127.3 (C-6); 126.3 (C-3); 126.2 (*i*-C_6H_5); 124.1 (br m, *i*-C_6F_5); 111.9 (1:1:1:1 q, $^1J_{CB}$ ~ 70 Hz, C-1); 94.9 (1:1:1:1 q, $^2J_{CB}$ ~ 15 Hz,, C-2); 61.9 (CH_2N); 42.0 (NCH_3). ^{19}F NMR (470 MHz, C_6D_6, 298K): δ −132.3 (m, 2F, *o*-C_6F_5); −161.2 (t, $^3J_{FF}$ = 21.1 Hz, 1F, *p*-C_6F_5); −165.5 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{p,m}$ = 4.3]. $^{11}B\{^1H\}$ NMR (160 MHz, C_6D_6, 298K): δ −20.3 ($\nu_{1/2}$ ~ 20 Hz). Elem. Anal. $C_{35}H_{19}BF_{15}N$ Calc.: C: 56.10, H: 2.56, N: 1.87; found C: 55.24, H: 2.56, N: 2.17.



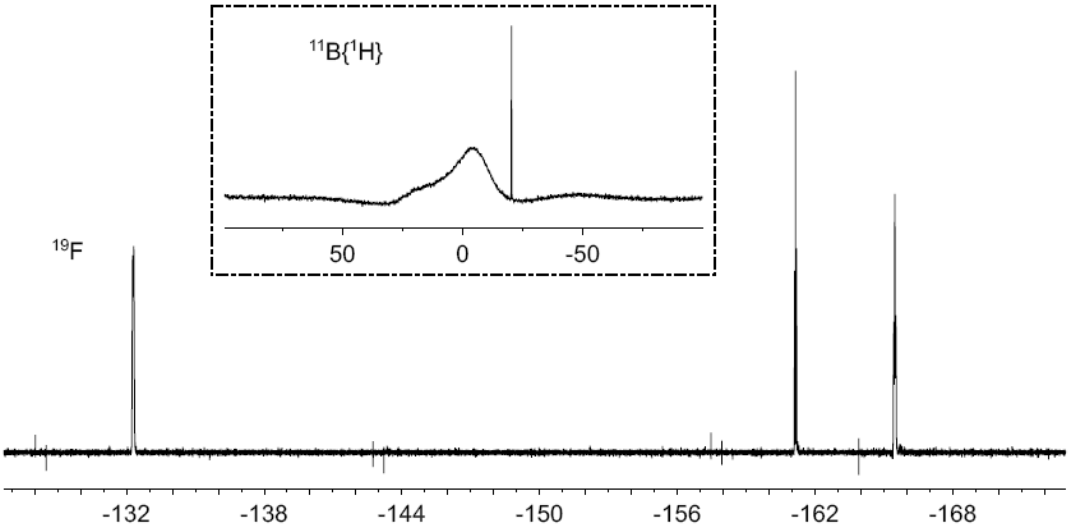
^1H NMR (500 MHz, 298 K, C_6D_6)



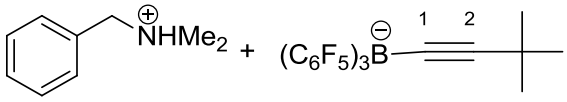
$^{13}C\{^{1}H\}$ NMR (126 MHz, 298 K, C_6D_6)



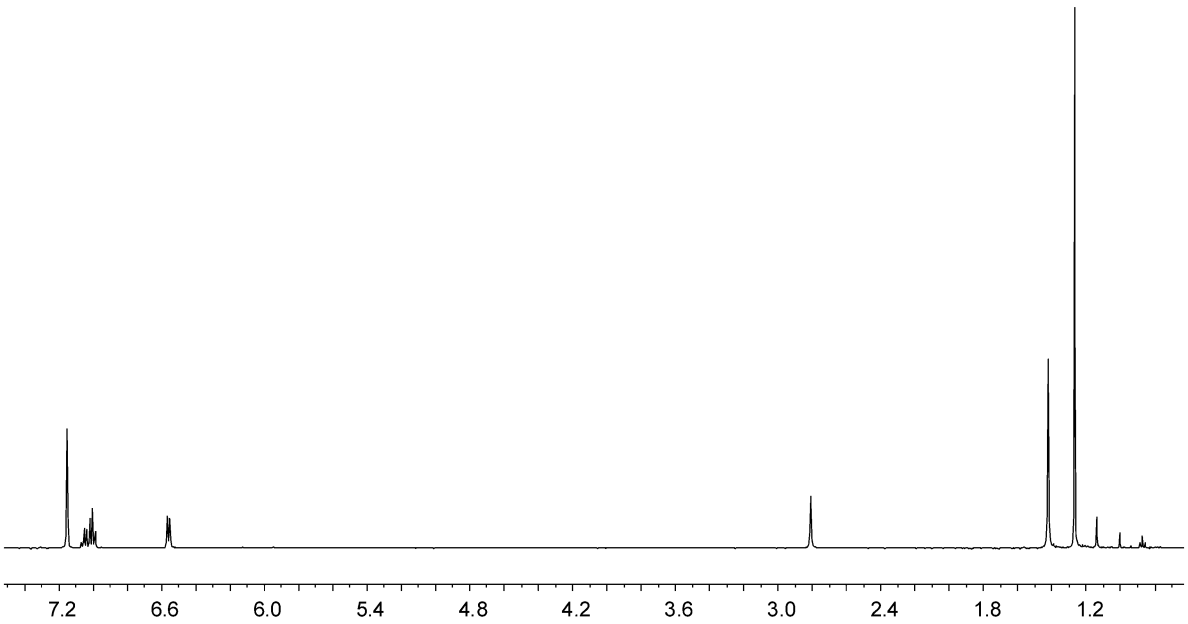
$^{1}H,^{13}C$ ghsqc (500/126 MHz, 298 K, C_6D_6)



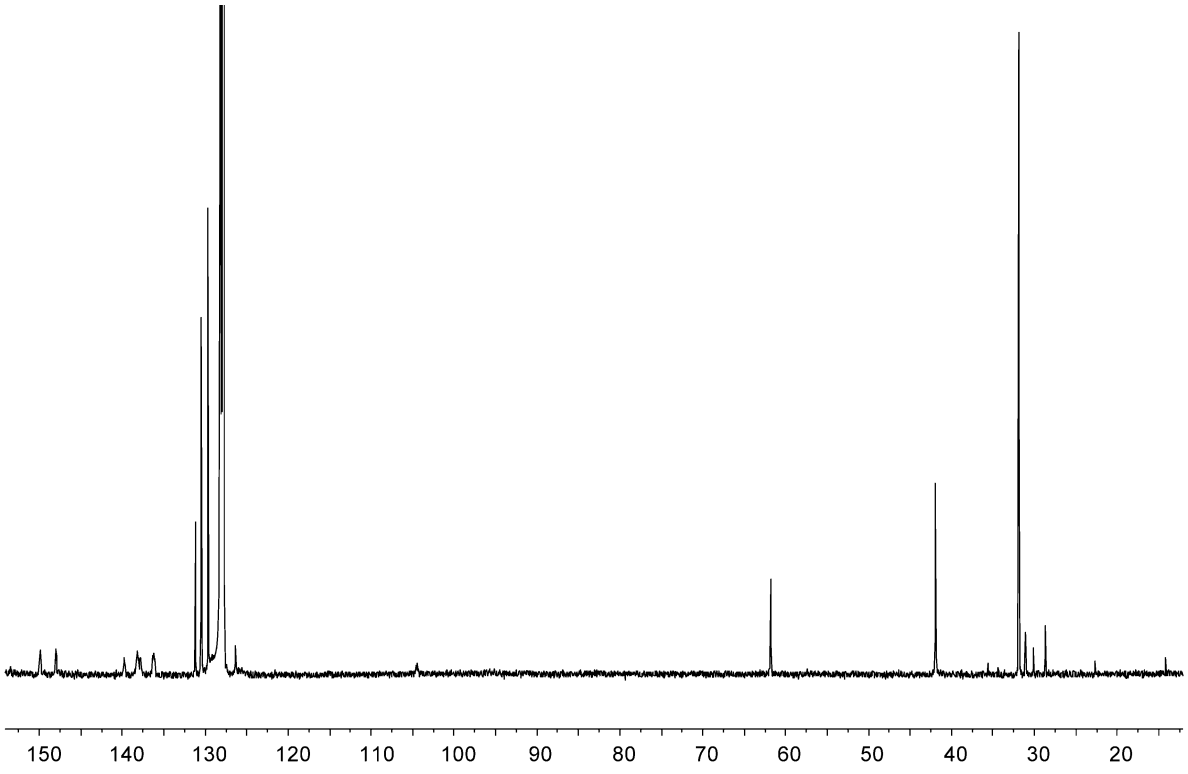
^{19}F NMR (470 MHz, 298 K, C_6D_6) and $^{11}B\{^1H\}$ NMR (160 MHz, 298 K, C_6D_6)



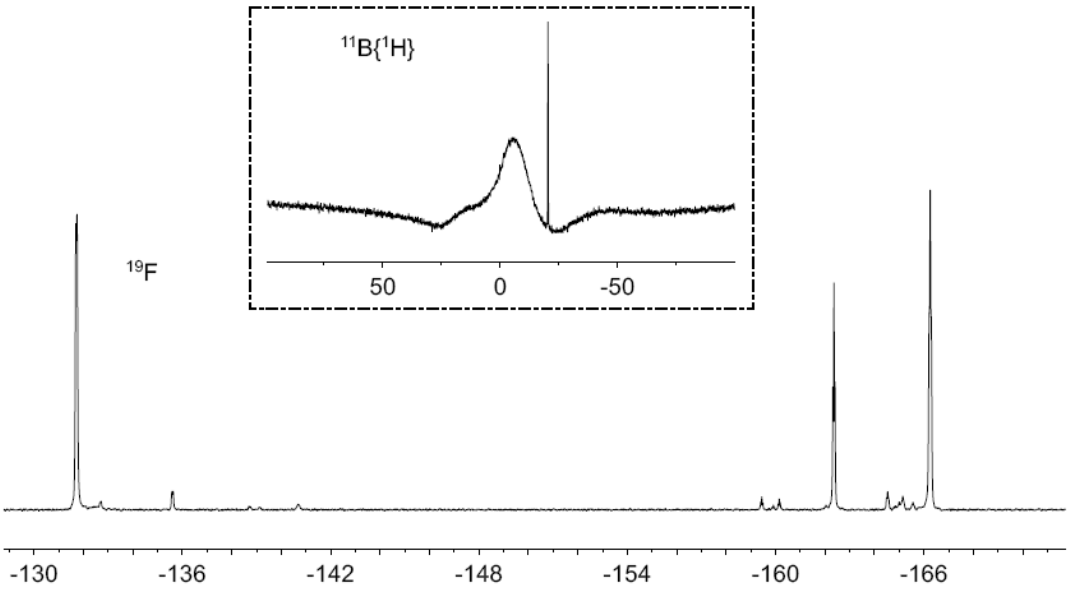
14c: ^1H NMR (500 MHz, C_6D_6, 298K): δ 7.05 (m, 1H, *p*-C_6H_5); 7.00 (m, 2H, *m*-C_6H_5); 6.56 (m, 2H, *o*-C_6H_5); 2.81 (s, 2H, CH_2N); 1.42 (s, 6H, NCH_3); 1.27 (s, 9H, *t*Bu). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 298K): δ 149.0 (dm, $^1J_{CF}$ ~ 240 Hz, C_6F_5); 138.8 (dm, $^1J_{CF}$ ~ 243 Hz, C_6F_5); 137.3 (dm, $^1J_{CF}$ ~ 247 Hz, C_6F_5); 131.2 (*p*-C_6H_5); 130.5 (*o*-C_6H_5); 129.7 (*m*-C_6H_5); 126.4 (*i*-C_6H_5); 104.4 (br, C-2); 61.8 (CH_2N); 42.0 (NCH_3); 31.9 (*t*Bu); 28.7 (*t*Bu), n.o. (*i*-C_6F_5); n.o. (C-1). ^{19}F NMR (470 MHz, C_6D_6, 298K): δ −131.7 (m, 2F, *o*-C_6F_5); −162.4 (t, $^3J_{FF}$ = 20.4 Hz, 1F, *p*-C_6F_5); −166.3 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{p,m}$ = 3.9]. $^{11}B\{^1H\}$ NMR (160 MHz, C_6D_6, 298K): δ −20.3 ($\nu_{1/2}$ ~ 25 Hz). Elem. Anal. $C_{33}H_{23}BF_{15}N$ Calc.: C: 54.34, H: 3.18, N: 1.92; found C: 54.62, H: 3.21, N: 1.89.



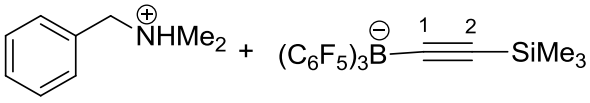
^{1}H NMR (500 MHz, 298 K, C_6D_6)



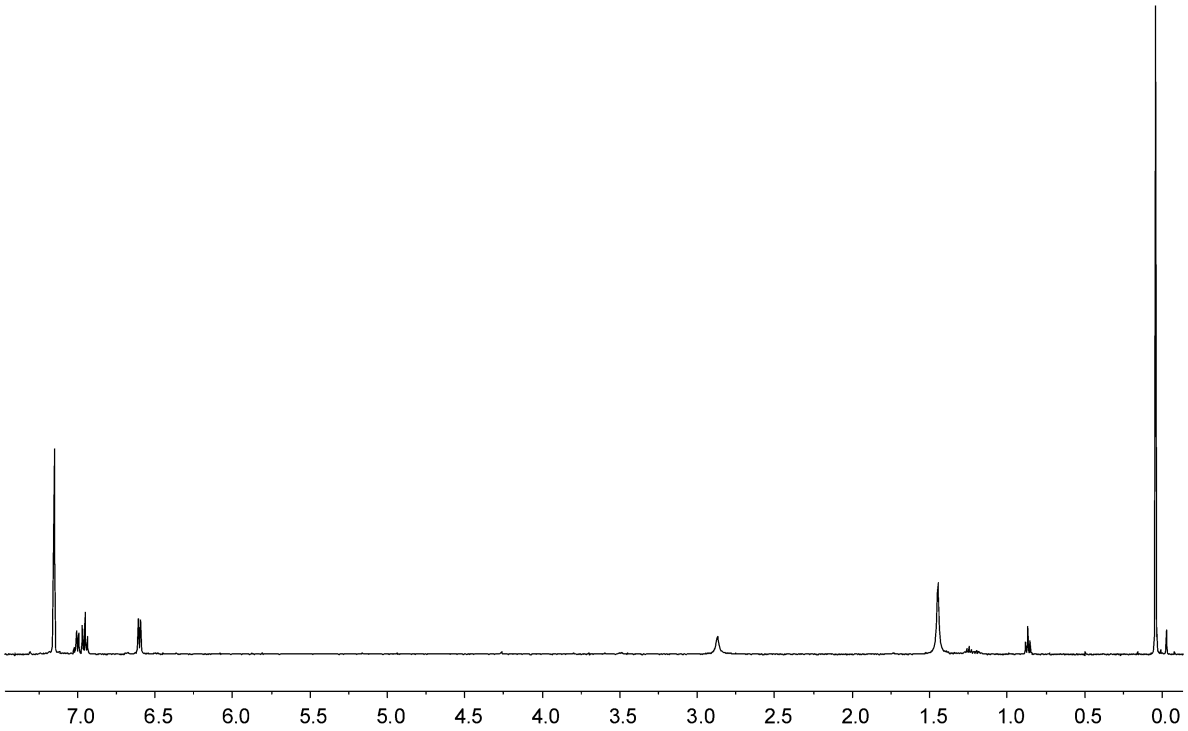
^{13}C{^{1}H} NMR (126 MHz, 298 K, C_6D_6)



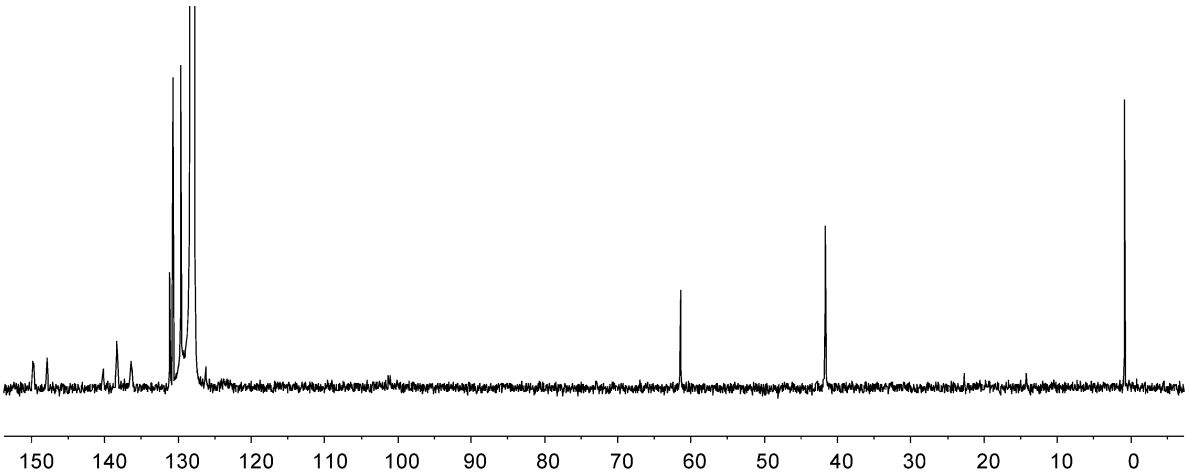
^{19}F NMR (470 MHz, 298 K, C_6D_6) and $^{11}B\{^1H\}$ NMR (160 MHz, 298 K, C_6D_6)



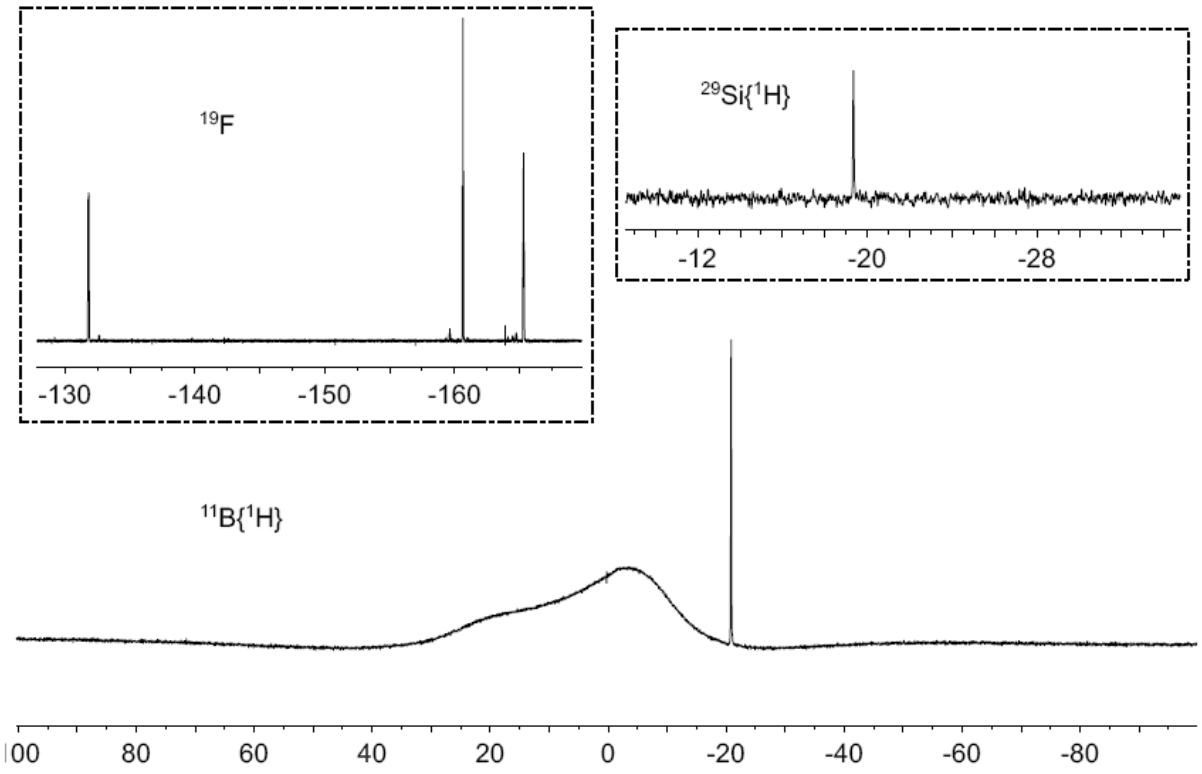
14d: ^1H NMR (500 MHz, C_6D_6, 298K): δ 7.01 (m, 1H, *p*-C_6H_5); 6.95 (m, 2H, *m*-C_6H_5); 6.60 (m, 2H, *o*-C_6H_5); 2.87 (br s, 2H, CH_2N); 1.45 (br s, 6H, NCH_3); 0.04 (s, $^2J_{SiH}$ = 6.9 Hz, 9H, $SiCH_3$). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 298K): δ 148.9 (dm, $^1J_{CF} \approx 244$ Hz, C_6F_5); 139.4 (dm, $^1J_{CF} \approx 235$ Hz, C_6F_5); 137.4 (dm, $^1J_{CF} \approx 245$ Hz, C_6F_5); 131.1 (*p*-C_6H_5); 130.7 (*o*-C_6H_5); 129.6 (*m*-C_6H_5); 126.3 (*i*-C_6H_5); 101.2 (m, C-2); 61.4 (CH_2N); 41.6 (NCH_3); 0.78 ($SiCH_3$), n.o. (*i*-C_6F_5); n.o. (C-1). ^{19}F NMR (470 MHz, C_6D_6, 298K): δ −131.8 (m, 2F, *o*-C_6F_5); −160.6 (t, ^3J = 21.1 Hz, 1F, *p*-C_6F_5); −165.3 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{p,m}$ = 4.7]. $^{11}B\{^1H\}$ NMR (160 MHz, C_6D_6, 298K): δ −20.9 ($\nu_{1/2}$ ~ 20 Hz). ^{29}Si dept NMR (99 MHz, C_6D_6, 298K): δ −19.3 ($\nu_{1/2}$ ~ 5 Hz). Elem. Anal. $C_{32}H_{23}BF_{15}NSi$ Calc.: C: 51.56, H: 3.11, N: 1.88; found C: 51.27, H: 3.29, N: 1.91.



^{1}H NMR (500 MHz, 298 K, C_6D_6)

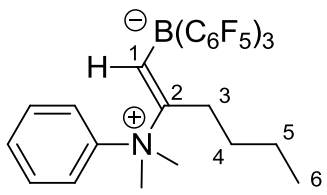


^{13}C{^{1}H} NMR (126 MHz, 298 K, C_6D_6)



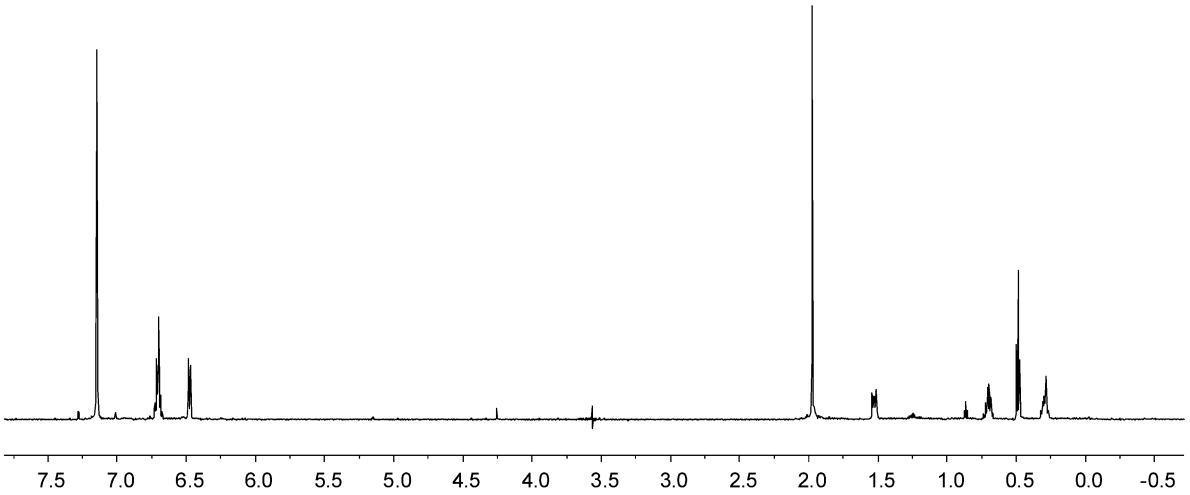
$^{11}B\{^1H\}$ NMR (160 MHz, 298 K, C_6D_6), ^{19}F NMR (470 MHz), and ^{29}Si dept NMR (99 MHz)

Synthesis of [PhNMe$_2$C(C$_4$H$_9$)=CH(B(C$_6$F$_5$)$_3$] 15: A solution of *N*,*N*-dimethylaniline (40.0 mg, 0.330 mmol), $B(C_6F_5)_3$ (170 mg, 0.332 mmol) and 1-hexyne (27.1 mg, 0.330 mmol) were dissolved in pentane (5 mL) and stirred at 25 °C overnight. The solvent was removed under reduced pressure to yield a yellow oil, that was purified by fractional crystallization from dichloromethane/pentane at -32 °C. Compound **15** was isolated in 50% yield (118 mg, 0.165 mmol).

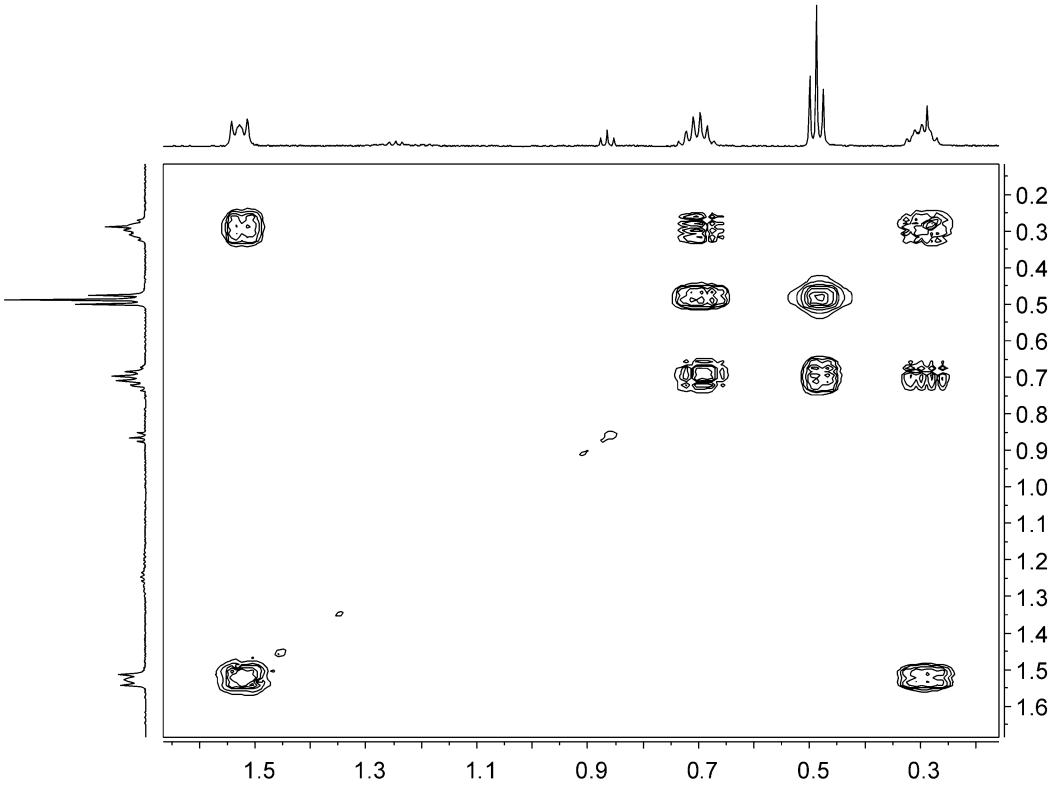


15: ^1H NMR (600 MHz, C_6D_6, 298K): δ 6.71 (m, 3H, *m*-,*p*-Ph); 6.70 (m, 1H, 1-H); 6.48 (m, 2H, *o*-Ph); 1.98 (s, 6H, NCH_3); 1.53 (m, 2H, 3-H); 0.70 (m, 2H, 5-H); 0.49 (t, $^3J_{HH}$ = 7.1 Hz, 3H, 6-H); 0.30 (m, 2H, 4-H). $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6, 298K): δ 146.4 (C-2); 141.1 (br, C-1); 130.1 (*p*-Ph); 129.9 (*m*-Ph), 120.1 (*o*-Ph); n.o. (*i*-Ph); 53.7

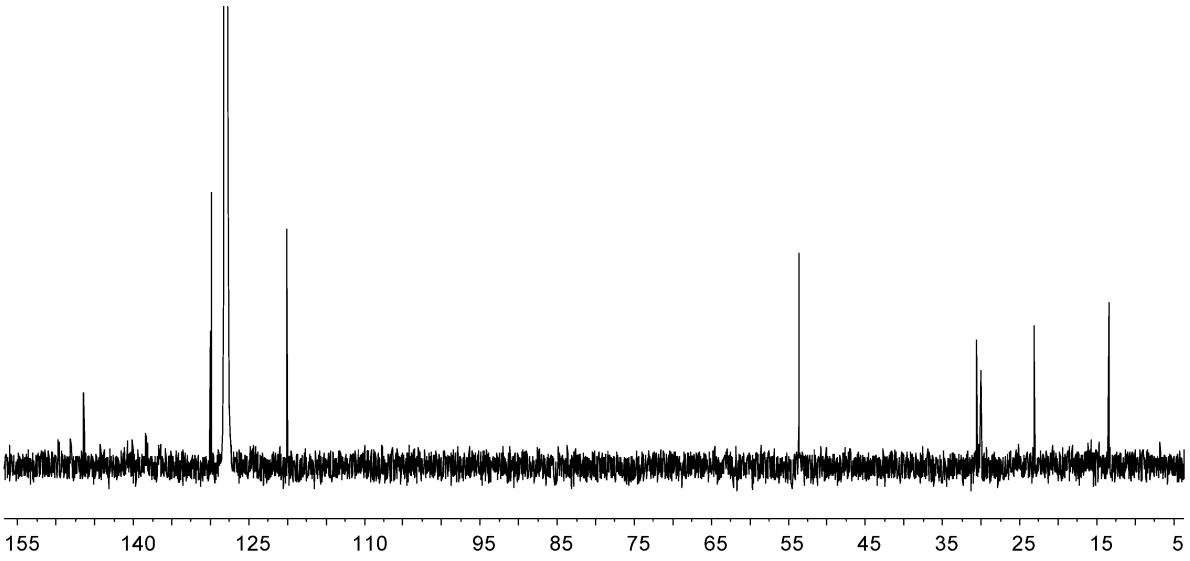
(NCH_3); 30.6 (C-4); 30.0 (C-3); 23.1 (C-5); 13.4 (C-6), [C_6F_5 not listed]. ^{19}F NMR (564 MHz, C_6D_6, 298K): δ −132.2 (m, 2F, *o*-C_6F_5); −160.6 (t, ^3J = 20.4 Hz, 1F, *p*-C_6F_5); −165.2 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{p,m}$ = 4.6]. ^{11}B{^{1}H} NMR (192 MHz, C_6D_6, 298K): δ −16.3 ($\nu_{1/2}$ ~ 20 Hz). Elem. Anal. $C_{33}H_{19}BF_{15}N$*0.25CH_2Cl_2 Calc.: C: 53.50, H: 2.61, N: 1.87; found C: 53.22, H: 2.97, N: 2.28.



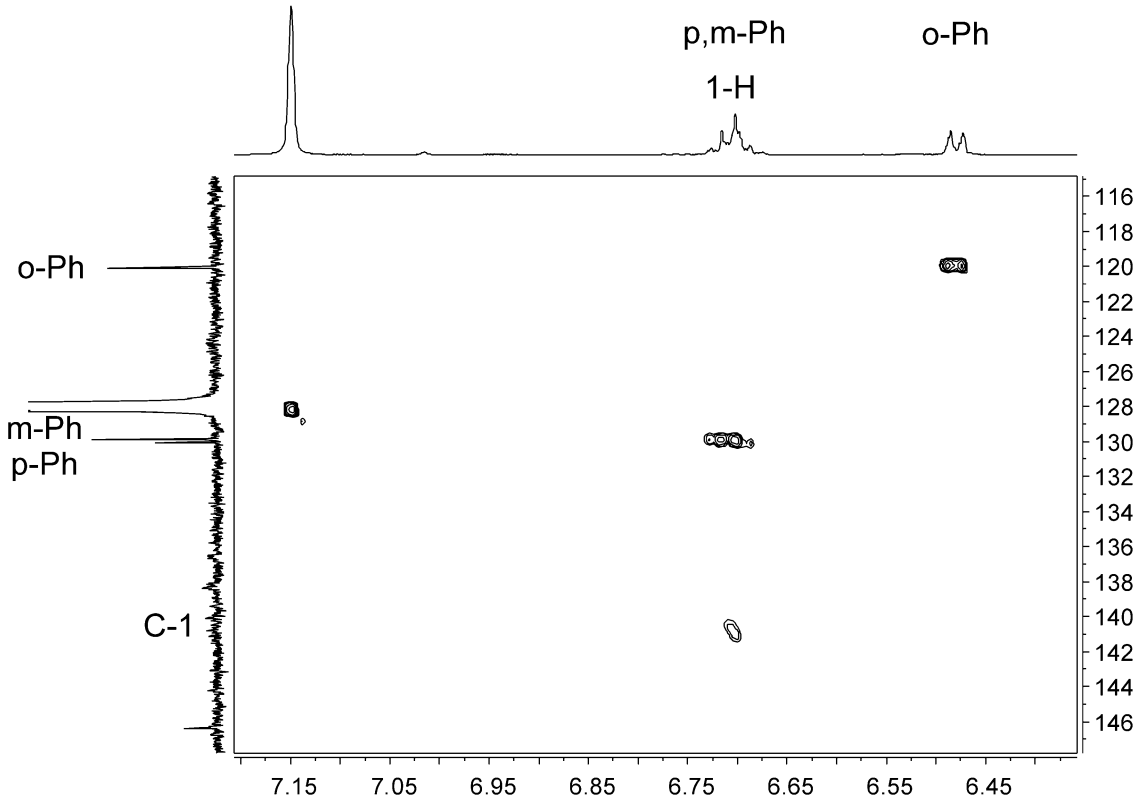
^{1}H NMR (600 MHz, 298 K, C_6D_6)



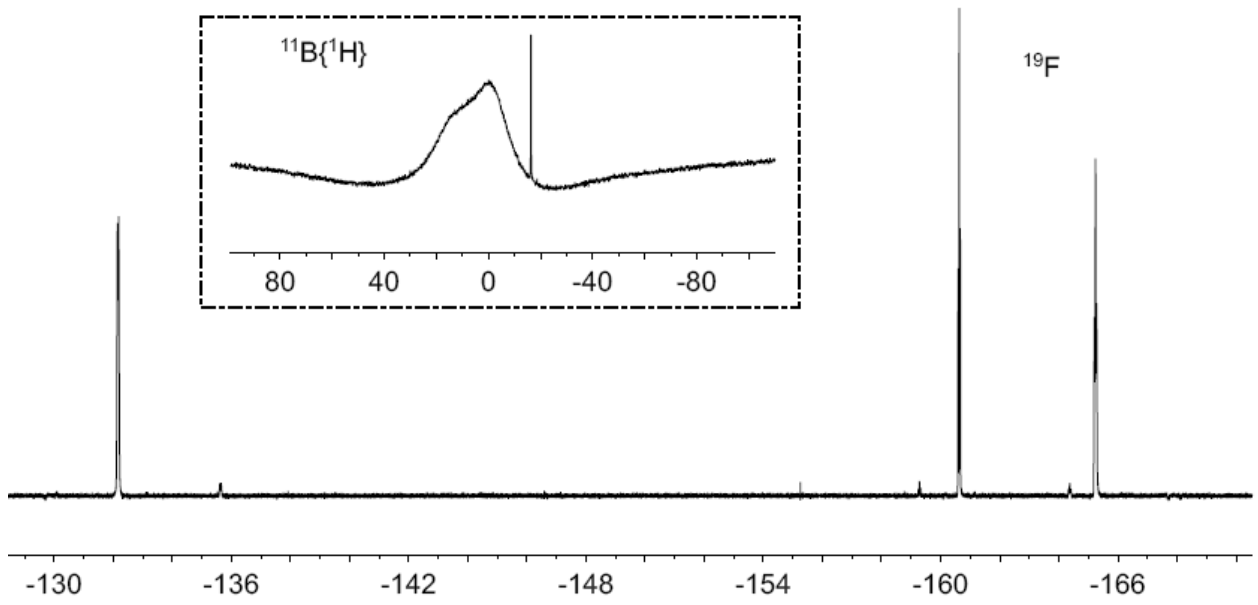
^{1}H,^{1}H gcosy (600/600 MHz, 298 K, C_6D_6)



$^{13}C\{^{1}H\}$ NMR (151 MHz, 298 K, C_6D_6)



$^{1}H,^{13}C$ ghsqc (600/151 MHz, 298 K, C_6D_6)



^{19}F NMR (564 MHz, 298 K, C_6D_6) and $^{11}B\{^1H\}$ NMR (192 MHz, 298 K, C_6D_6)

X-ray crystal structure analysis of **15**: formula $C_{32}H_{21}BF_{15}N * CH_2Cl_2$, M = 800.23, colorless crystal 0.30 x 0.25 x 0.03 mm, a = 9.5086(6), b = 11.9158(7), c = 15.6879(10) Å, α = 94.247(5), β = 97.456(4), γ = 106.783(3)°, V = 1675.69(18) Å^3, ρ_{calc} = 1.586 g cm^{-3}, μ = 2.763 cm^{-1}, empirical absorption correction (0.491 $\leq$ T $\leq$ 0.922), Z = 2, triclinic, space group P1bar (No. 2), λ= 1.54178 Å, T = 223 K, ω and φ scans, 19316 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.60 Å^{-1}, 5741 independent (R_{int} = 0.058) and 4440 observed reflections [$I \geq 2\ \sigma(I)$], 472 refined parameters, R = 0.068, wR^2 = 0.192, max. residual electron density 1.08 (-0.77) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.