Supporting Information for: Reactions of 1,1- and 1,2-bis-boranes with a Protic Diamine and Hydrazine

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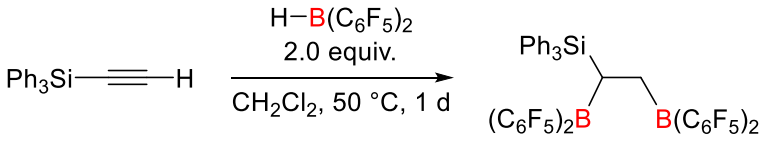
1.1 General Information

All preparative procedures were performed in an inert atmosphere of nitrogen using glovebox techniques or standard Schlenk line techniques. Dichloromethane (DCM, CH_2Cl_2), *n*-pentane, and *n*-hexane purchased from Sigma Aldrich were dried using a Grubbs-type Innovative Technologies solvent purification system. Benzene, and deuterated solvents ($CDCl_3$, C_6D_6, CD_2Cl_2) were purchased from Sigma Aldrich and dried by distillation from sodium-benzophenone or calcium hydride, CaH_2, prior to use. All solvents were stored over activated 4 Ă molecular sieves. Phenylacetylene and trimethylsilylacetylene were purchased from Sigma-Aldrich and distilled from molecular sieves prior to use. O-phenylenediamine (OPD) was purchased from Sigma-Aldrich and recrystallized from toluene prior to use. Hydrazine solution (1.0 M in THF) was purchased from Sigma-Aldrich and used without further purification. Bis(pentafluorophenyl)borane was prepared using literature procedures.[1] Plastic syringes and disposable needles were used to dispense solvents. Prior to use inside the glovebox, plastic syringes and disposable needles were placed under vacuum inside the antechamber of the glovebox overnight. All NMR spectra were collected at 298 K on Bruker Avance III 400 MHz, Bruker Avance NEO 400 MHz or Agilent DD2-500 MHz spectrometers in 3- or 5-mm diameter NMR tubes. ^{1}H chemical shifts are reported relative to proteo-solvent signals[2] ($CDCl_3$ δ = 7.26 ppm, C_6D_6 δ = 7.16 ppm and CD_2Cl_2 δ = 5.32 ppm). Data are reported as: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, hept = heptet, m = multiplet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, br = broad), coupling constants (Hz), integration and *assignment*. $^{13}C\{^{1}H\}$ chemical shifts are reported relative to proteo-solvent signals ($CDCl_3$ δ = 77.16 ppm, C_6D_6 δ = 128.06 ppm and CD_2Cl_2 δ = 53.84 ppm), while ^{11}B, ^{19}F and ^{31}P NMR chemical shifts are reported relative to $(Et_2O)\cdot BF_3$, $CFCl_3$ and 85% H_3PO_4 external standards, respectively. Departmental facilities were used for mass spectrometry (DART+/-: JEOL AccTOF or ESI: Agilent 6538 Q-TOF).

1.2 Spectra of $Ph_3SiCH(B(C_6F_5)_2)CH_2B(C_6F_5)_2$, 3



3

^{1}H NMR (400 MHz, C_6D_6, 298 K) δ: 7.64 (m, 6H, Ar-*H*), 7.07 (m, 9H, Ar-H), 4.17 (br d, $^3J_{HH}$ = 8 Hz, 1H, C*H*), 3.37 (dd, $^2J_{HH}$ = 19 Hz, $^3J_{HH}$ = 9 Hz, 1H, CH_2), 2.58 (br d, $^2J_{HH}$ = 18 Hz, 1H, CH_2).

^{11}B NMR (128 MHz, C_6D_6, 298 K) δ: 74.0.

^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 298 K) δ: 146.8 (dm, $^1J_{CF}$ = 244 Hz, *o*-C_6F_5), 146.4 (dm, $^1J_{CF}$ = 247 Hz, *o*-C_6F_5), 143.8 (dm, $^1J_{CF}$ = 264 Hz, *m/p*-C_6F_5), 143.2 (dm, $^1J_{CF}$ = 260 Hz, *m/p*-C_6F_5), 137.9 (dm, $^1J_{CF}$ = 255 Hz, *m/p*-C_6F_5), 137.7 (dm, $^1J_{CF}$ = 255 Hz, *m/p*-C_6F_5), 136.3 (s, *o*-C_6H_5), 132.9 (s, *p*-C_6H_5), 130.5 (s, *m*-C_6H_5), 115.1 (m, *i*-C_6F_5), 113.2 (m, *i*-C_6F_5), 37.2 (*C*H_2), 33.7 (*C*H).

^{19}F NMR (377 MHz, C_6D_6, 298 K) δ: -128.9 (br, 4F, *o*-C_6F_5), -130.1 (d, $^3J_{FF}$ = 19 Hz, 4F, *o*-C_6F_5), -146.2 (t, $^3J_{FF}$ = 21 Hz, 2F, *p*-C_6F_5), -147.9 (t, $^3J_{FF}$ = 20 Hz, 2F, *p*-C_6F_5), -160.1 (m, 4F, *m*-C_6F_5), -160.8 (m, 4F, *m*-C_6F_5).

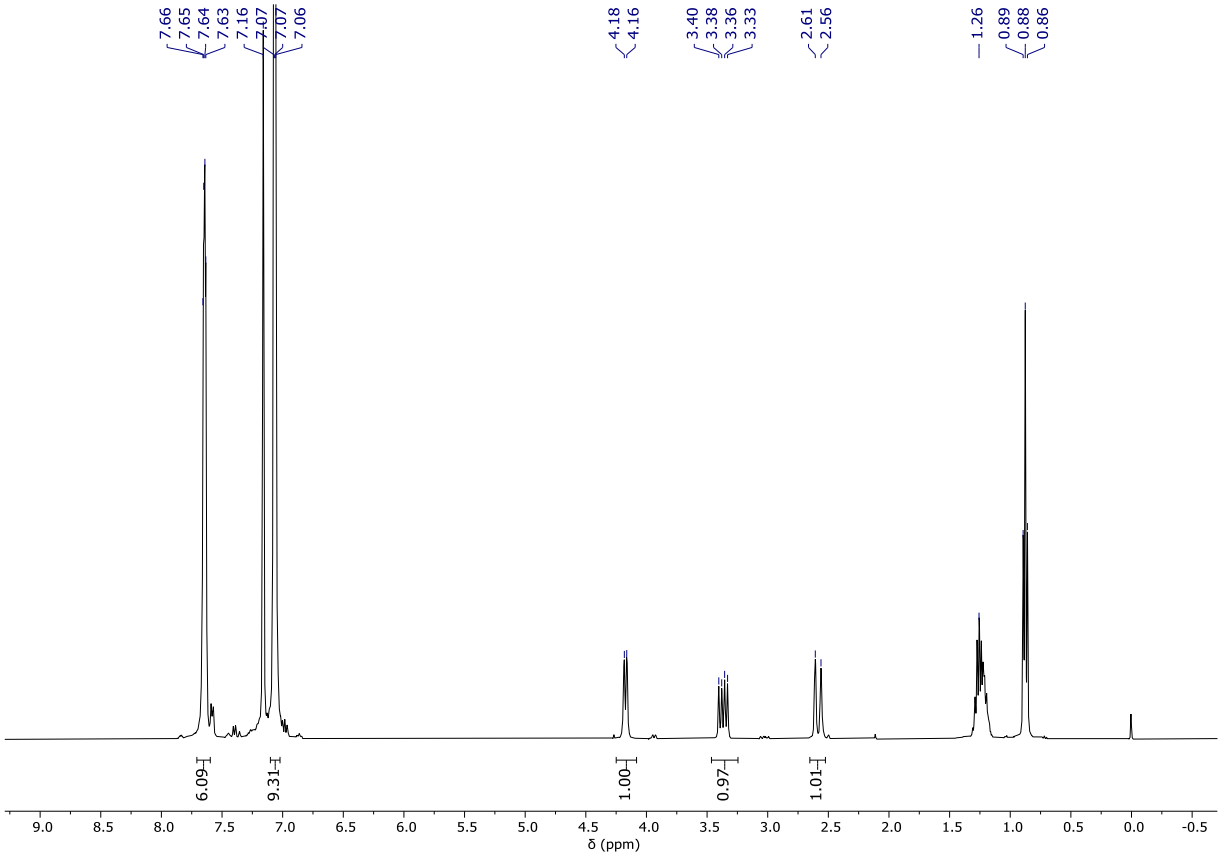


Figure S 1. ^{1}H NMR (400 MHz, C_6D_6, 298 K) spectrum of *bis*-borane **3**.

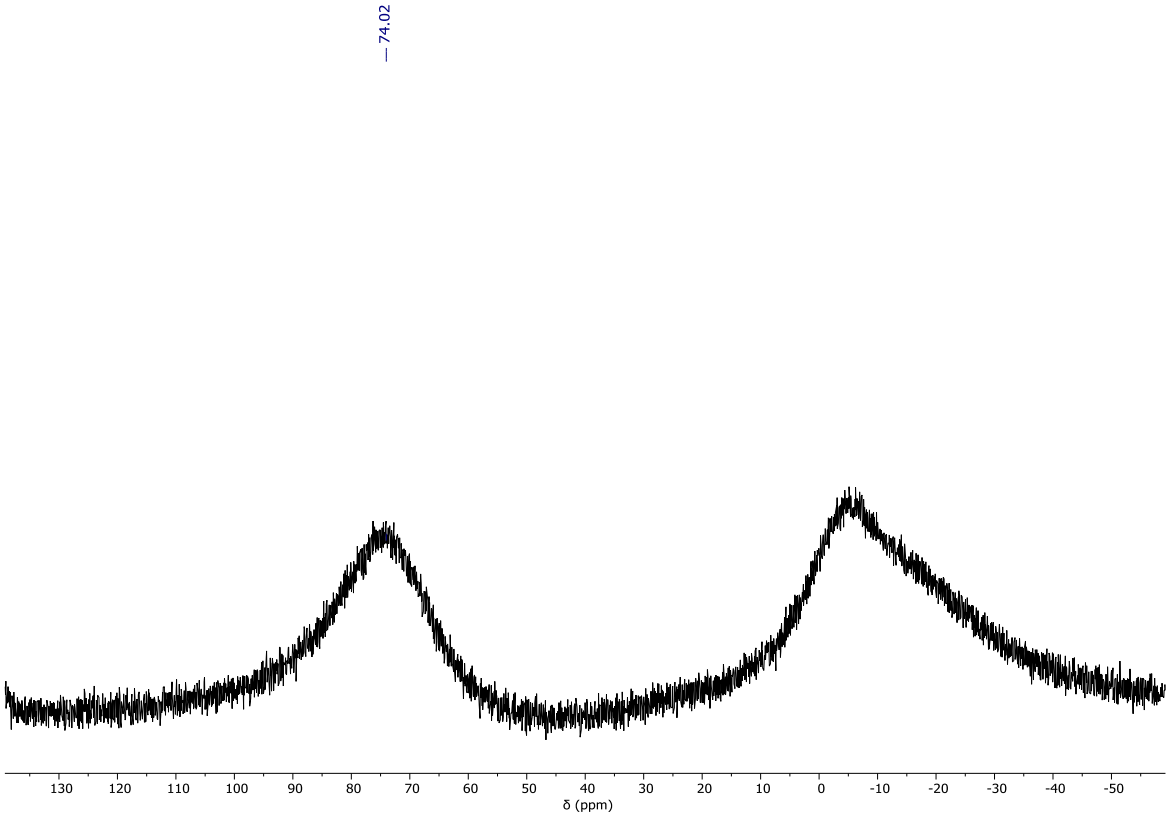


Figure S 2. ^{11}B NMR (128 MHz, C_6D_6, 298 K) spectrum of *bis*-borane **3**.

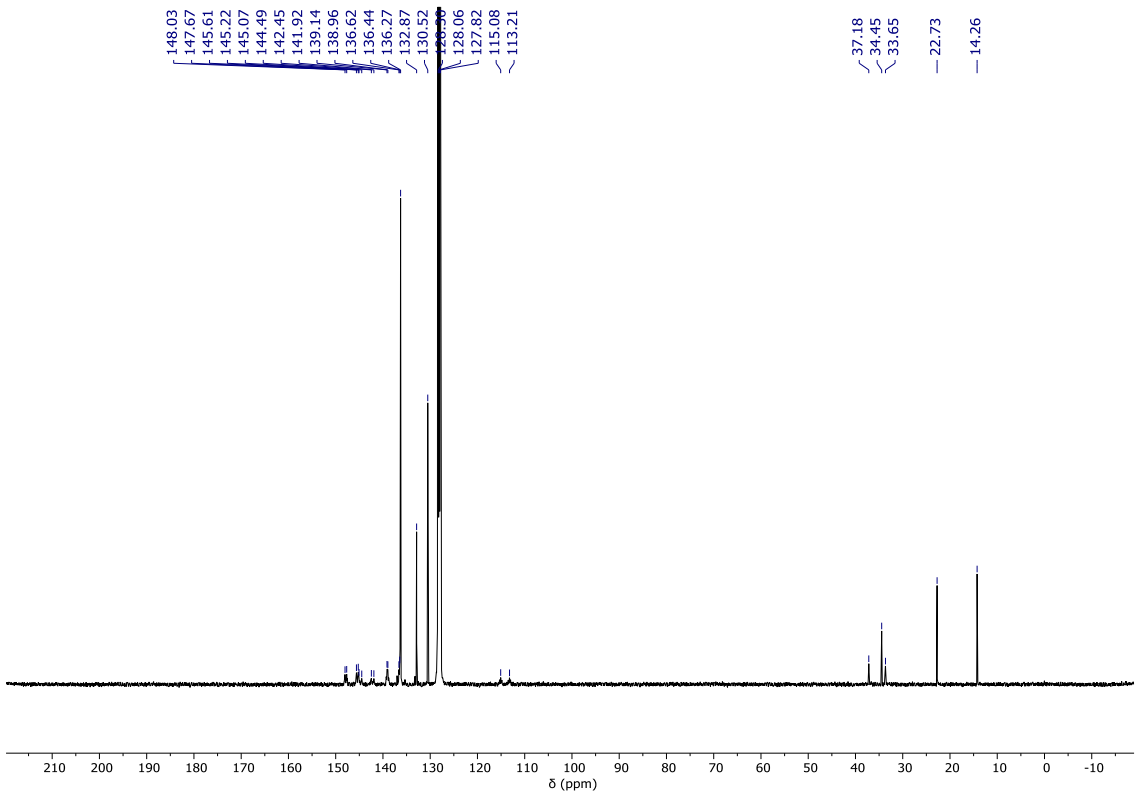


Figure S 3. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K) spectrum of *bis*-borane **3**.

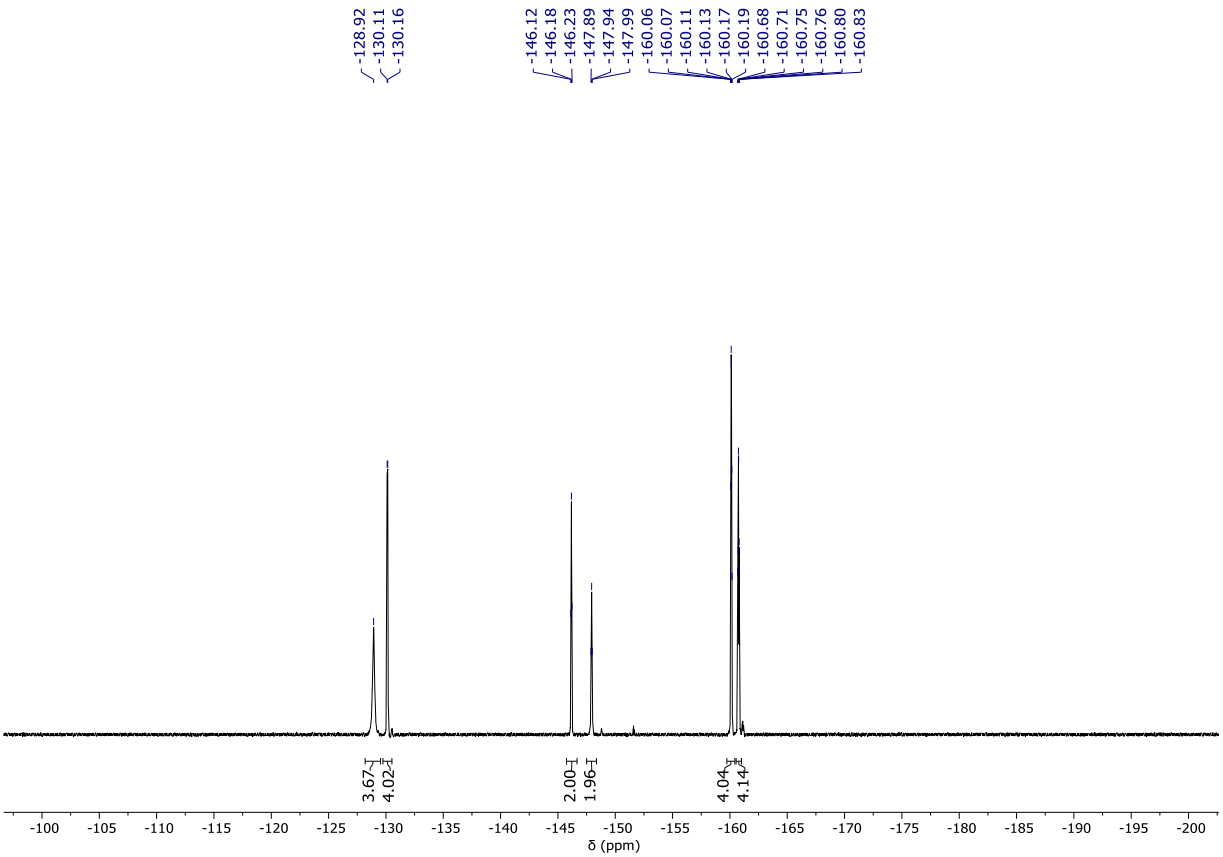
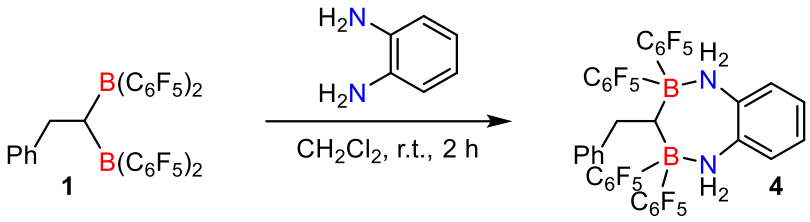


Figure S 4. ^{19}F NMR (377 MHz, C_6D_6, 298 K) spectrum of *bis*-borane **3**.

1.3 Spectra of $PhCH_2CH(B(C_6F_5)_2(NH_2))_2C_6H_4$, 4



^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) δ: 7.36 (dd, $^{3}J_{HH}$ = 5.9, 3.4 Hz, 2H, *H*$_{Ar}$), 7.24 (dd, $^{3}J_{HH}$ = 5.9, 3.5 Hz, 2H, *H*$_{Ar}$), 7.01 – 6.88 (m, 3H, Ph-*H*$_{Ar}$), 6.76 (s, 4H, N*H*$_2$), 6.52 (d, $^{3}J_{HH}$ = 6.2 Hz, 2H, Ph-*H*$_{Ar}$), 2.74 (br d, $^{3}J_{HH}$ = 4.8 Hz, 2H, C*H*$_2$), 2.44 (t, $^{3}J_{HH}$ = 5.9 Hz, 1H, *H*C(B(C$_6$F$_5$)$_2$)$_2$).

^{11}B NMR (128 MHz, CD_2Cl_2, 298 K) δ: 0.7.

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 298 K) δ: 147.8 (dm, $^{1}J_{CF}$ = 237 Hz, *o*-C$_6$F$_5$), 145.2 (*i*-Ph), 140.4 (dm, $^{1}J_{CF}$ = 237 Hz, *p*-C$_6$F$_5$), 137.8 (dm, $^{1}J_{CF}$ = 236 Hz, *m*-C$_6$F$_5$), 131.1 (OPD-*C*$_{Ar}$), 129.1 (*i*-OPD), 128.0 (*m/p*-Ph), 127.8 (OPD-*C*$_{Ar}$), 127.7 (*o*-Ph), 125.2 (m/*p*-Ph), 121.1 (br, *i*-C$_6$F$_5$), 119.8 (br, *i*-C$_6$F$_5$), 35.8 (br, *C*H(B(C$_6$F$_5$)$_2$)$_2$), 22.7 (br, PhCH$_2$).

^{13}C{^{1}H} DEPT-135 NMR (101 MHz, CD_2Cl_2, 298 K) δ: 131.1 (OPD-*C*$_{Ar}$), 128.0 (*m/p*-Ph), 127.8 (OPD-*C*$_{Ar}$), 127.7 (*o*-Ph), 125.2 (m/*p*-Ph), 35.8 (br, *C*H(B(C$_6$F$_5$)$_2$)$_2$).

^{19}F NMR (377 MHz, CD_2Cl_2, 298 K) δ: -130.2 (br, 2F, *o*-C$_6$F$_5$), -133.9 (br, 2F, *o*-C$_6$F$_5$), -156.5 (br, 2F, *p*-C$_6$F$_5$), -162.1 (br, 4F, *m*-C$_6$F$_5$). *Note: integrations are inaccurate due to broadening.*

^{1}H, ^{13}C gHMBC (400 MHz / 101 MHz, CD_2Cl_2, 298 K) δ ^{1}H / δ ^{13}C: 7.3/ 131.2, 7.3/ 129.1, 7.0/ 145.4, 7.0/ 127.7, 6.6/ 128.0, 6.6/ 125.2, 2.8/ 145.2, 2.8/ 22.4, 2.5/ 145.2, 2.5/ 35.7.

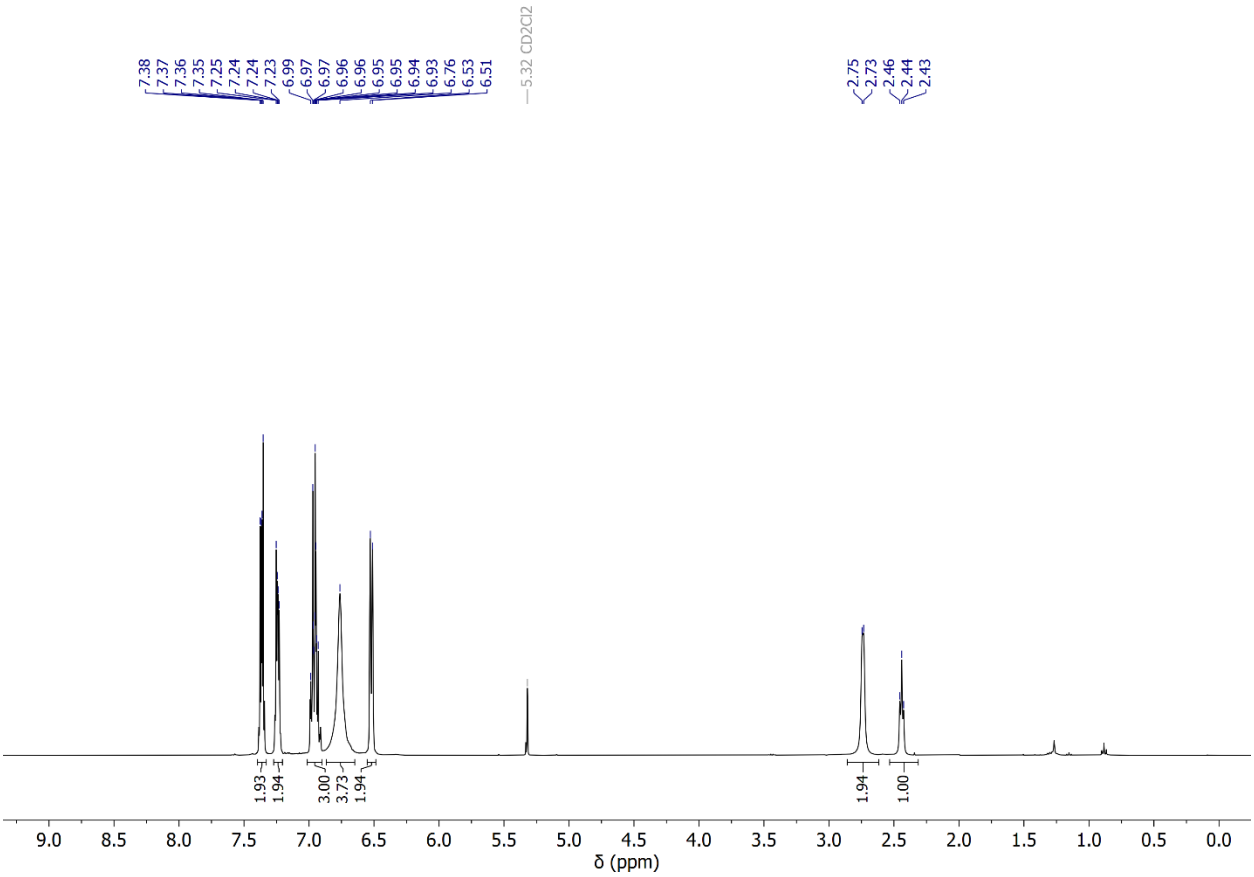


Figure S 5. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) spectrum of compound **4**.

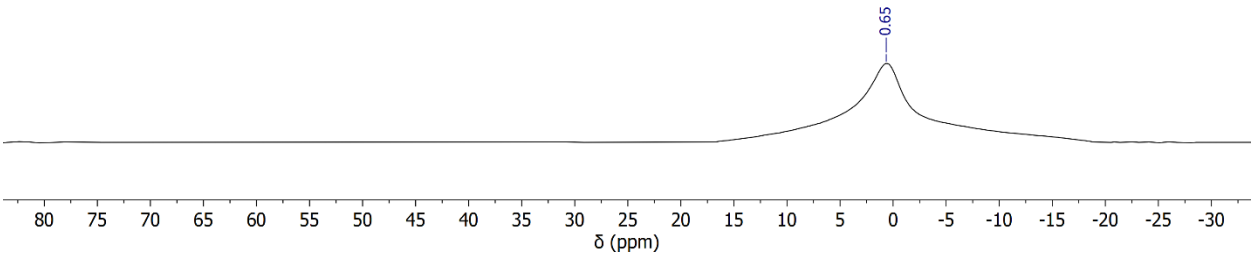


Figure S 6. ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K) spectrum of compound **4**.

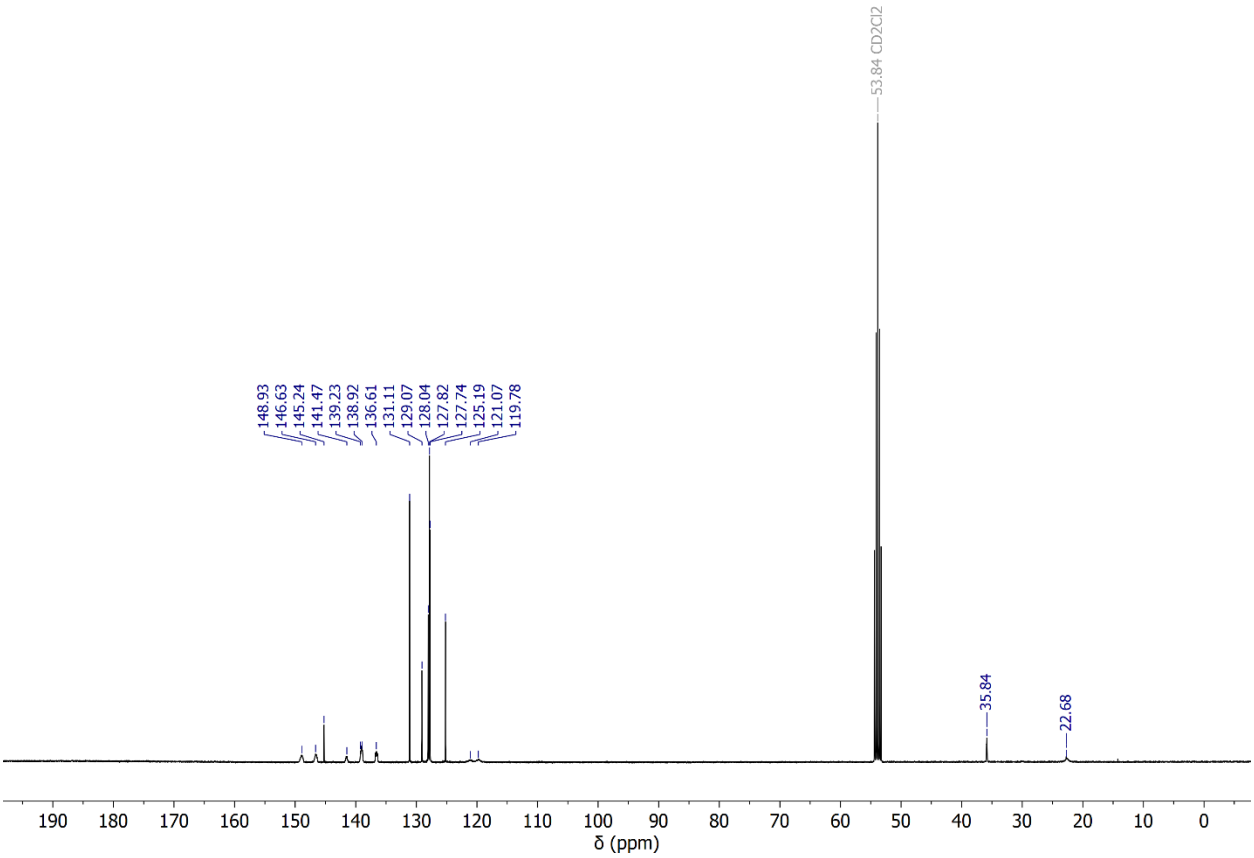


Figure S 7. $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2, 298 K) spectrum of compound **4**.

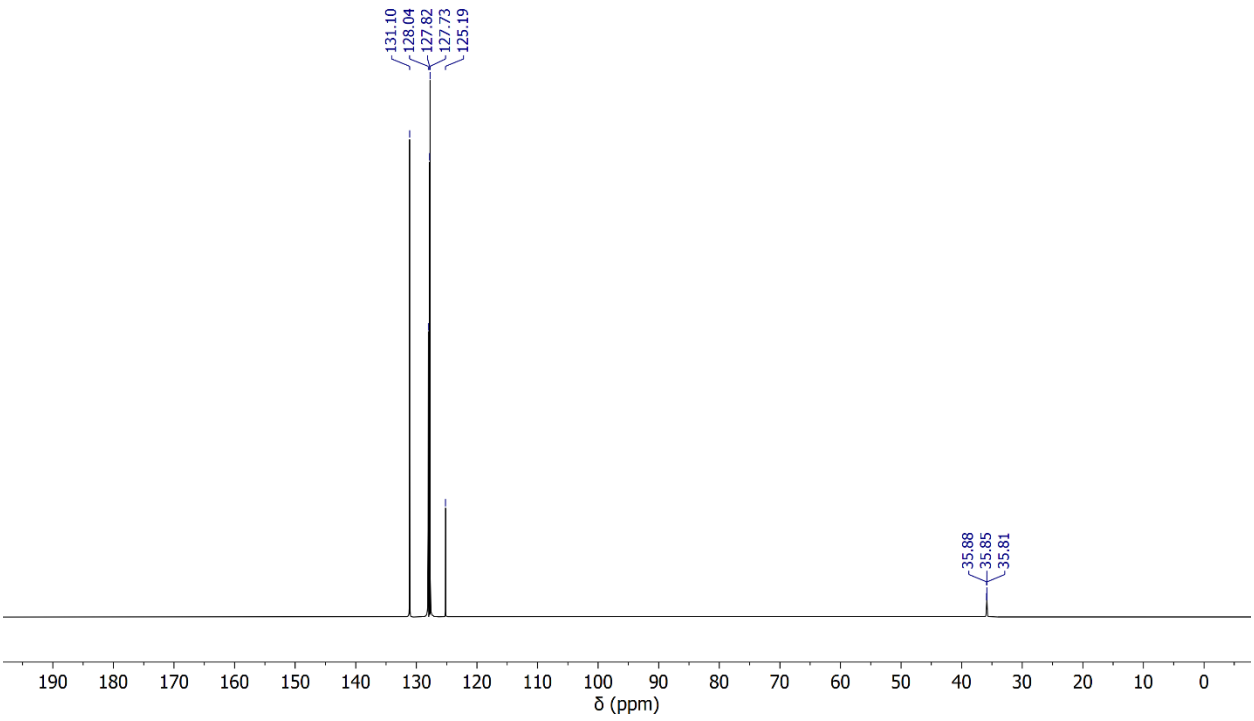


Figure S 8. $^{13}C\{^{1}H\}$ DEPT-135 NMR (101 MHz, CD_2Cl_2, 298 K) spectrum of compound **4**.

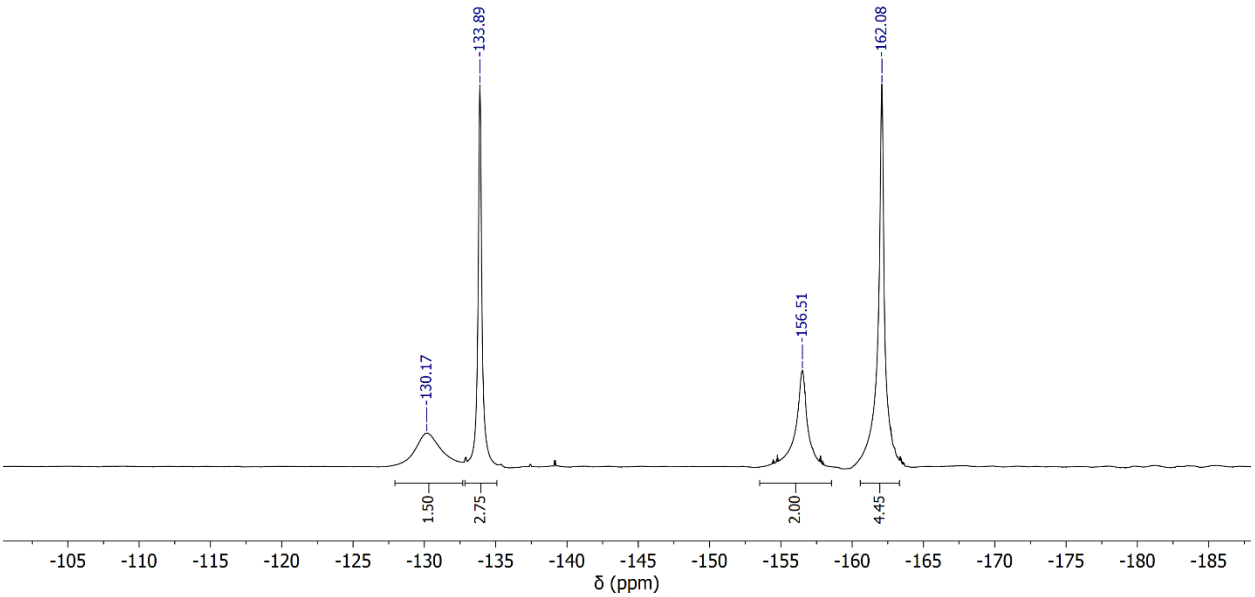


Figure S 9. ^{19}F NMR (377 MHz, $CDCl_3$, 298 K) spectrum of compound **4**.

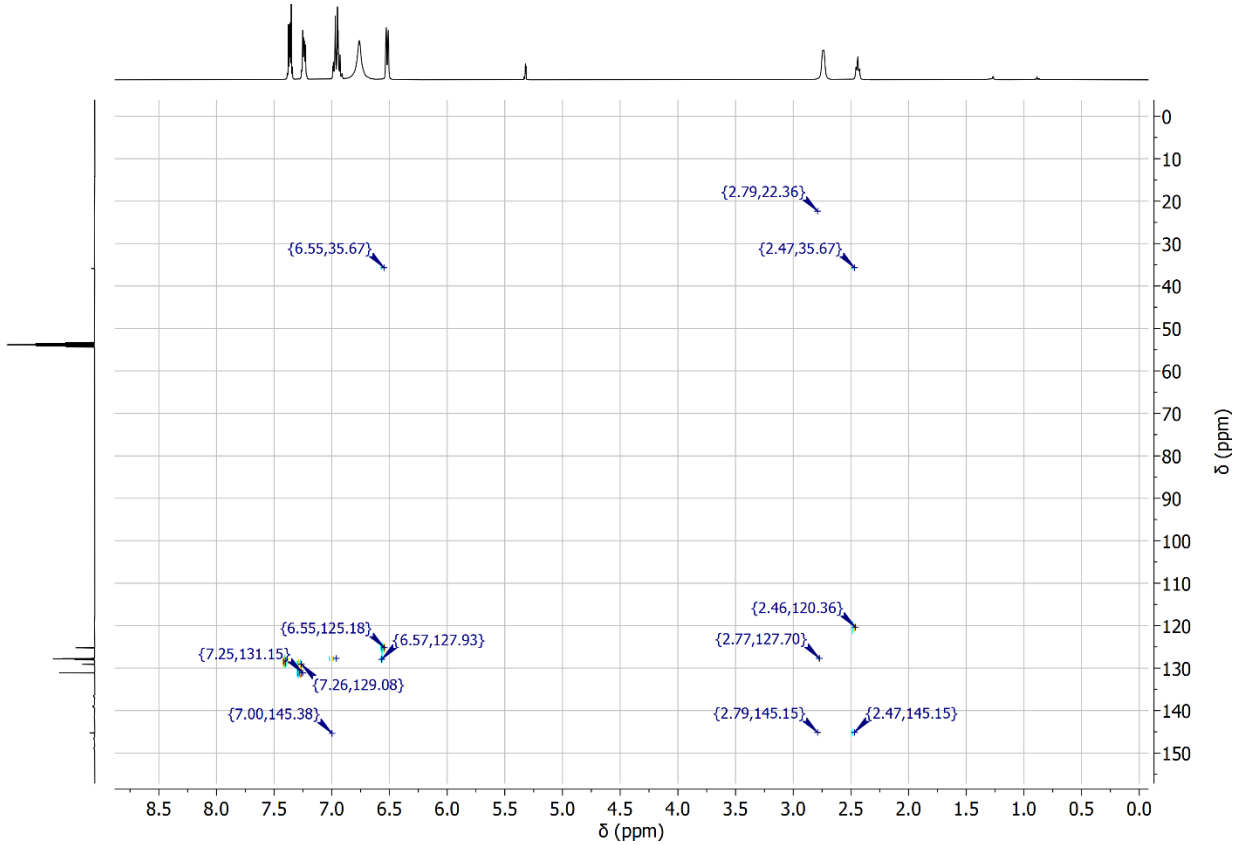
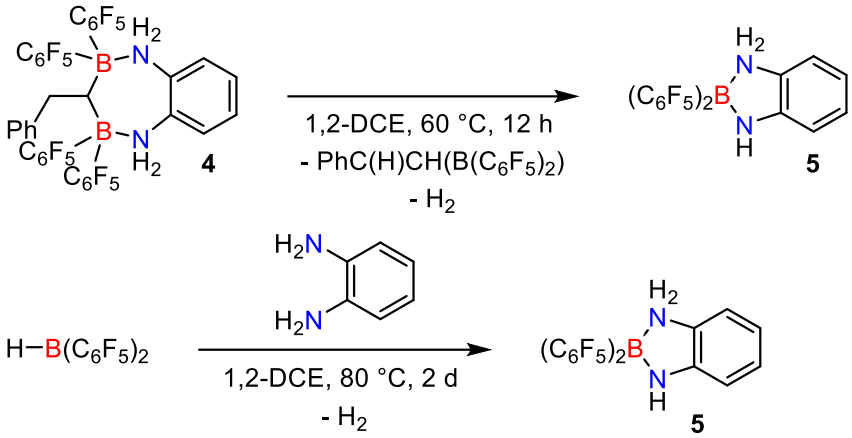


Figure S 10. ^{1}H, ^{13}C gHMBC (400 MHz / 101 MHz, CD_2Cl_2, 298 K) spectrum of compound **4**.

1.4 Spectra of $(C_6F_5)_2B(NH)(NH_2)C_6H_4$, 5



^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) δ: 6.93 (br d, 2H, H_{Ar}), 6.83 (s, 2H, H_{Ar}), 5.67 (br, 3H, N*H*).

^{11}B NMR (128 MHz, CD_2Cl_2, 298 K) δ: 1.2.

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 298 K) δ: 147.8 (dm, $^1J_{CF}$ = 237 Hz, *o*-C_6F_5), 140.6 (dm, $^1J_{CF}$ = 251 Hz, *p*-C_6F_5), 136.5 (dm, $^1J_{CF}$ = 253 Hz, *m*-C_6F_5), 123.8 (br, *i*-C_6F_5), 120.5 (C_{Ar}H), 116.7 (br, *i*-Ph), 112.1 (C_{Ar}H).

^{19}F NMR (377 MHz, CD_2Cl_2, 298 K) δ: -137.4 (m, 2F, *o*-C_6F_5), -157.2 (t, 1F, $^3J_{FF}$ = 20 Hz, *p*-C_6F_5), -163.2 (m, 2F, *m*-C_6F_5).

HRMS (ESI+ Ionization, *m/z*): Calcd. for $C_{18}H_8BF_{10}N_2^+$ ([M+H]$^+$): 453.06261; Found: 453.06221.

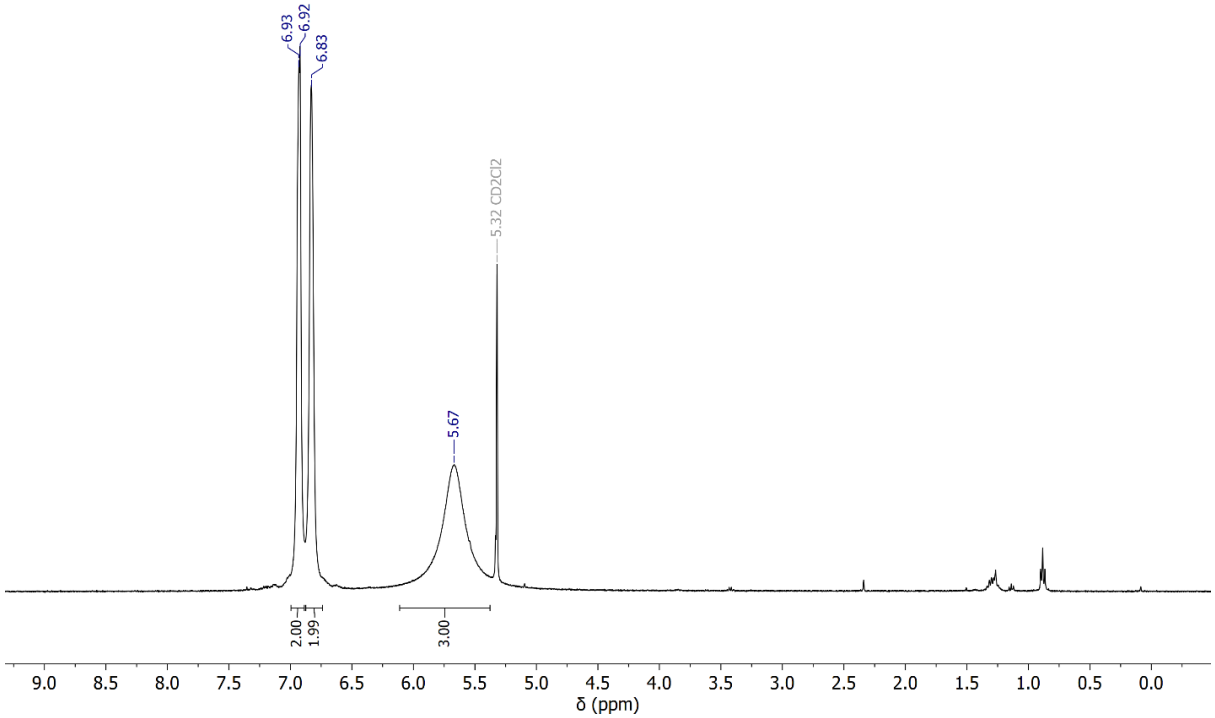


Figure S 11. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) spectrum of compound **5**.

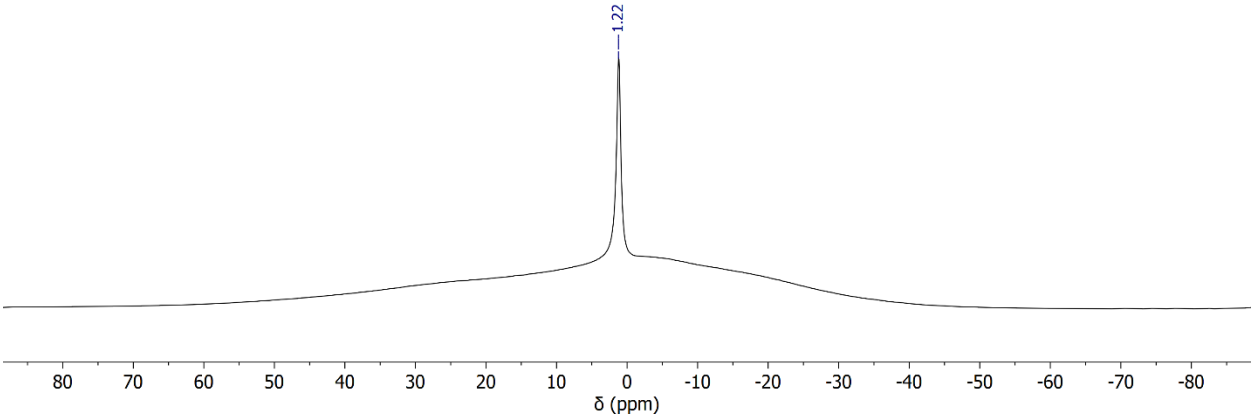


Figure S 12. ^{11}B NMR (128 MHz, CD_2Cl_2, 298 K) spectrum of compound **5**.

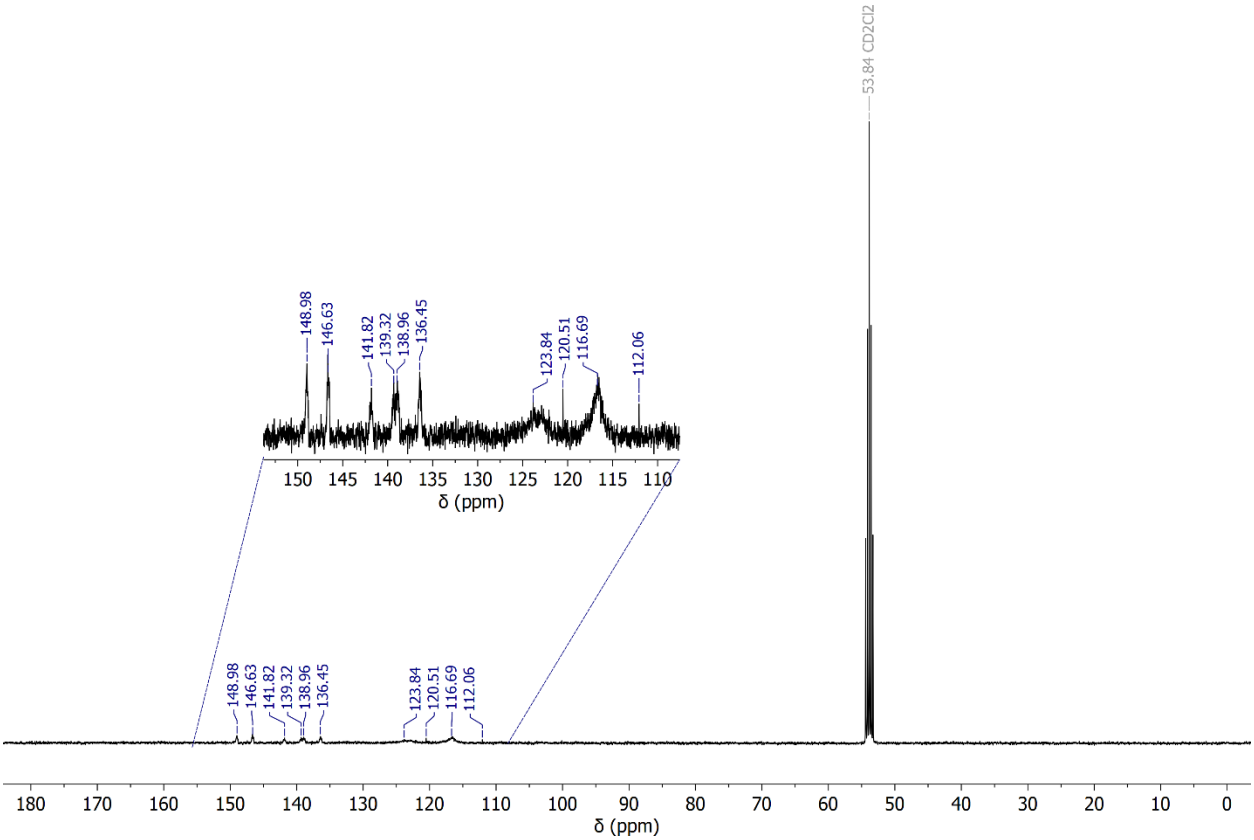


Figure S 13. $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 298 K) spectrum of compound **5**.

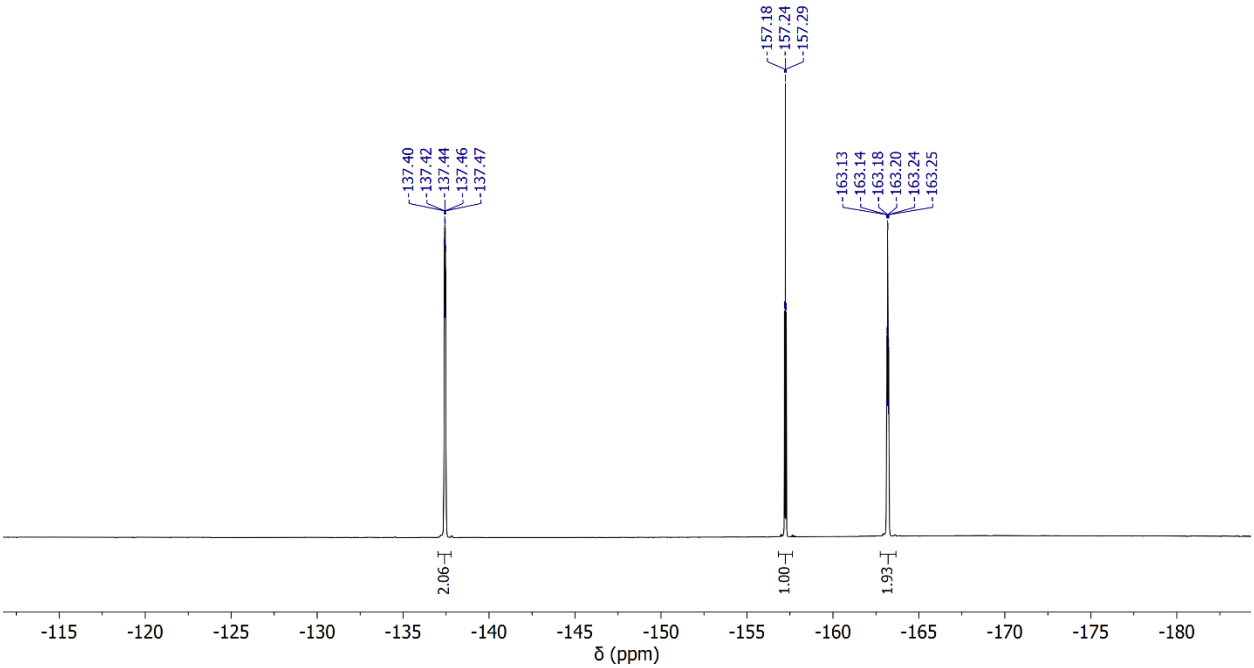
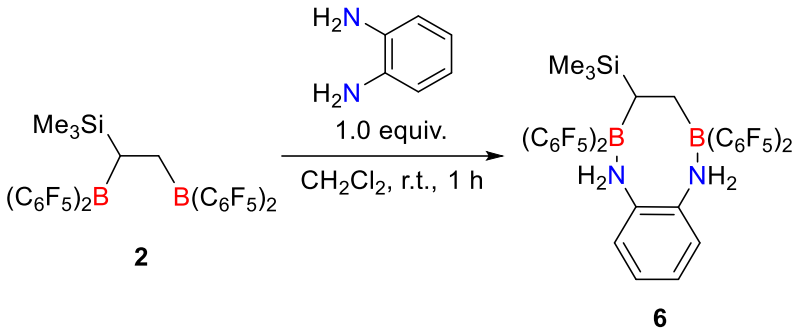


Figure S 14. ^{19}F NMR (377 MHz, CD_2Cl_2, 298 K) spectrum of compound **5**.

1.5 Spectra of $Me_3SiCH(B(C_6F_5)_2)CH_2B(C_6F_5)_2(H_2N)_2C_6H_4$, 6



^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.25 (m, 1H, Ar-*H*), 7.10 (m, 1H, Ar-*H*), 6.95 (m, 1H, Ar-*H*), 6.75 (br s, 1H, N*H*), 6.39 (m, 2H, overlapping Ar-*H* and N*H*), 6.04 (br s, 1H, N*H*), 5.11 (br s, 1H, N*H*), 1.69 (br d, $^{2}J_{HH}$ = 18 Hz, 1H, CH_2), 0.93 (br s, 1H, overlapping CH_2), 0.75 (br s, 1H, C*H*), -0.49 (s, 9H, Si-CH_3).

^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ: 8.7 (br s), 0.8 (br s).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K) δ: 129.9 (s, Ar*C*), 129.8 (s, Ar*C*), 128.6 (s, Ar*C*), 127.2 (s, Ar*C*), 124.0 (s, Ar*C*), 123.9 (s, Ar*C*), 17.6 (br s, *C*H_2), 16.3 (br s, *C*H), 0.4 (s, Si-*C*H_3).

^{19}F NMR (377 MHz, $CDCl_3$, 298 K) δ: -129.8 (br s, *o*-C_6F_5), -133.0 (br s, *o*-C_6F_5), -153.4 (t, $^{3}J_{FF}$ = 19 Hz, 1F, *p*-C_6F_5), -153.8 (t, $^{3}J_{FF}$ = 18 Hz, 1F, *p*-C_6F_5), -154.7 (t, $^{3}J_{FF}$ = 20 Hz, 1F, *p*-C_6F_5), -156.4 (t, $^{3}J_{FF}$ = 19 Hz, 1F, *p*-C_6F_5), -160.4 (m, 3F, *m*-C_6F_5), -161.8 (m, 5F, *m*-C_6F_5).

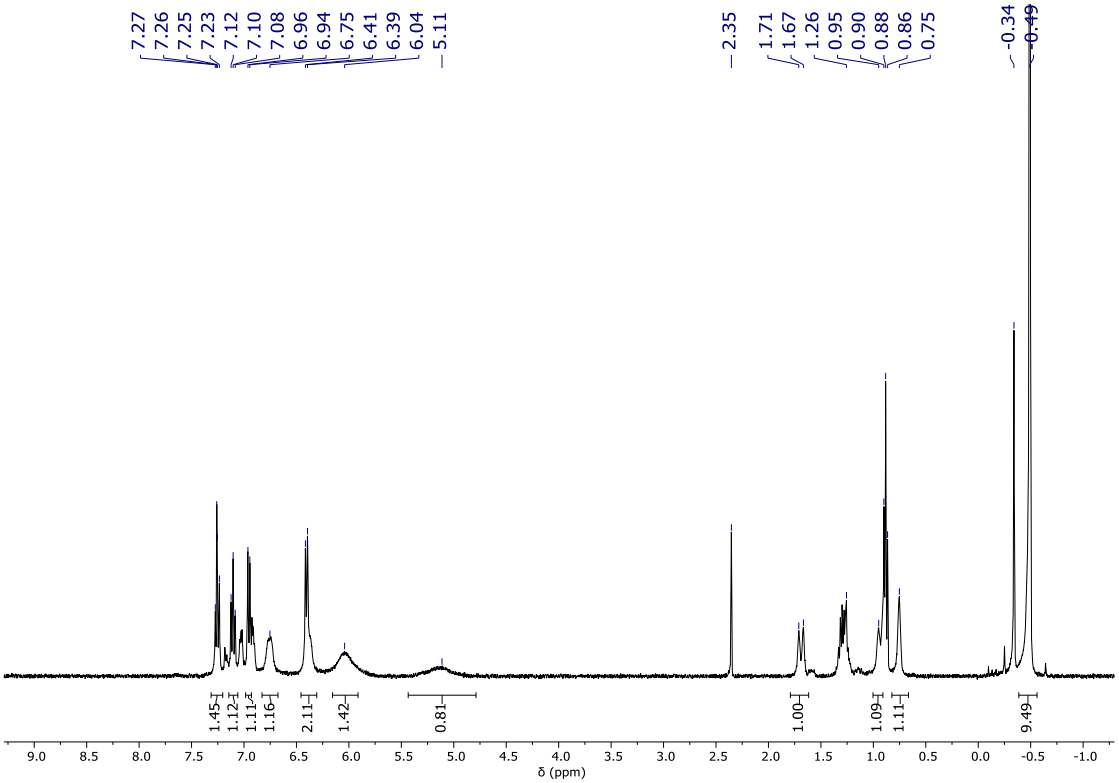


Figure S 15. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **6**.

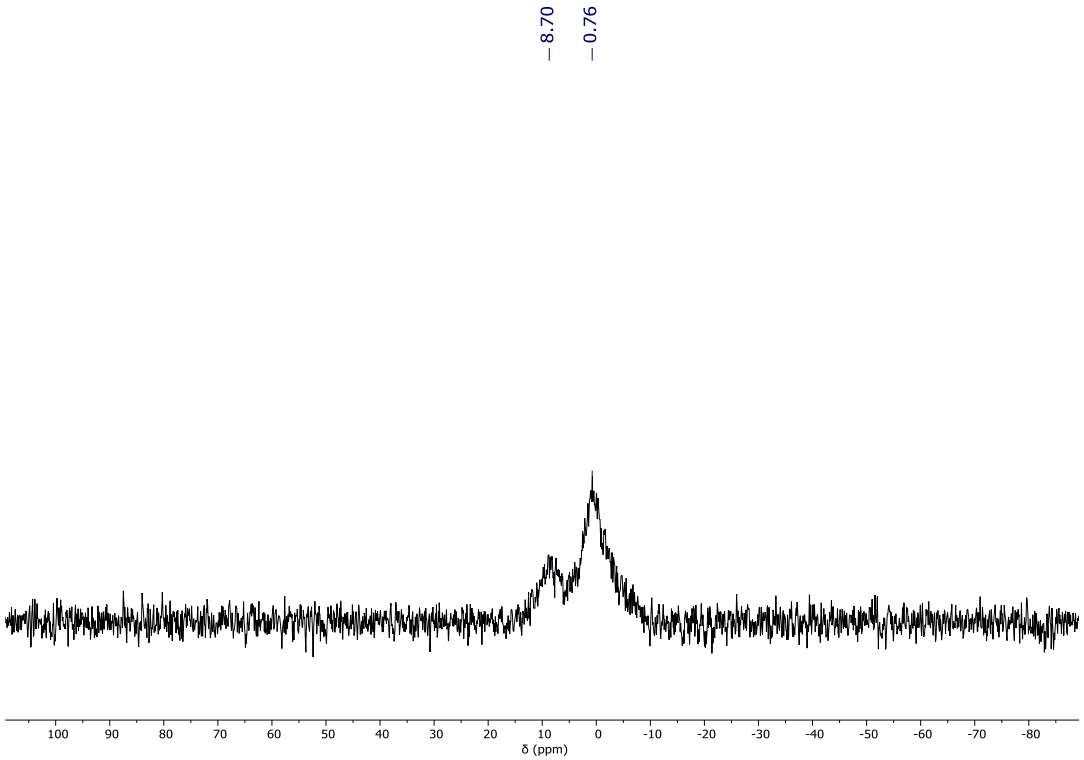


Figure S 16. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of compound **6**.

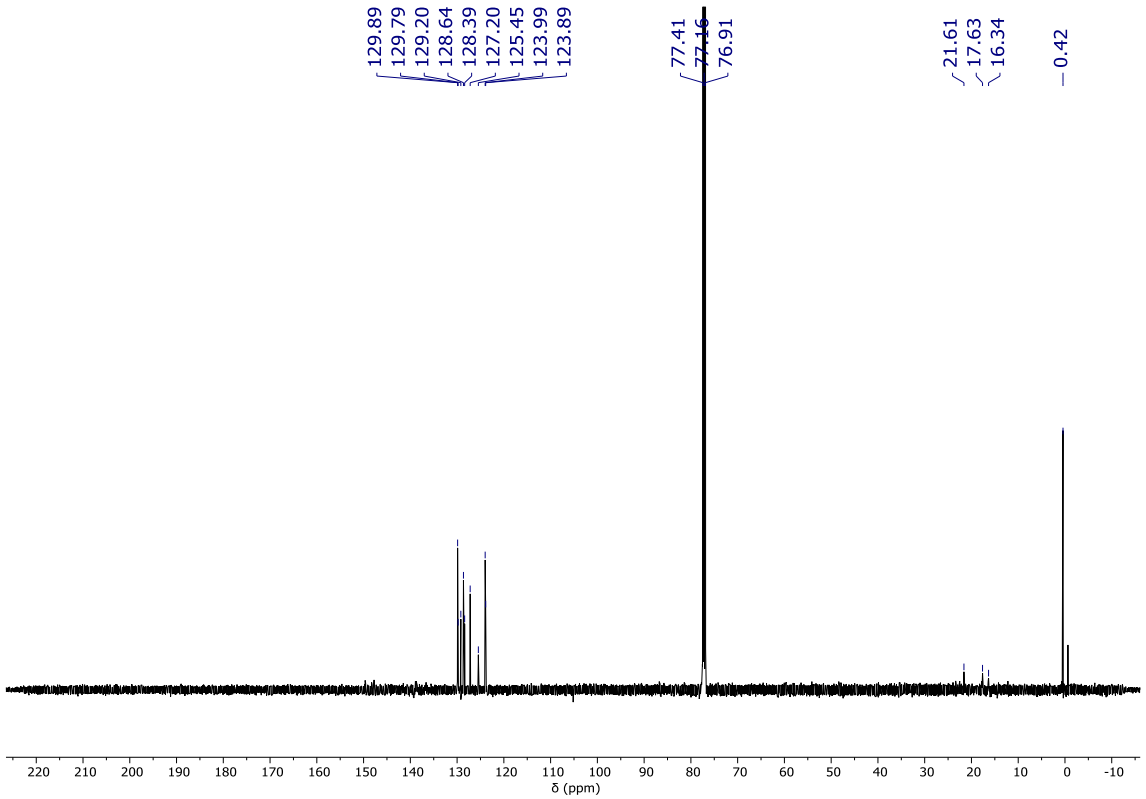


Figure S 17. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of compound **6**.

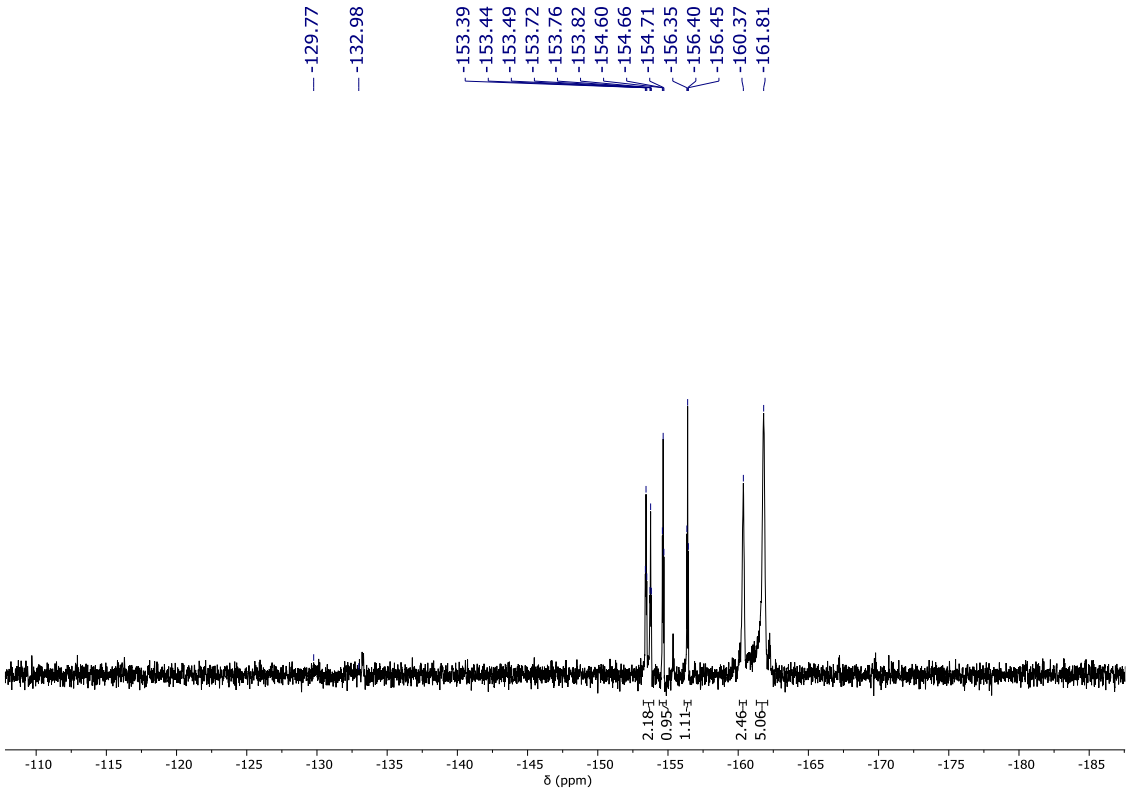
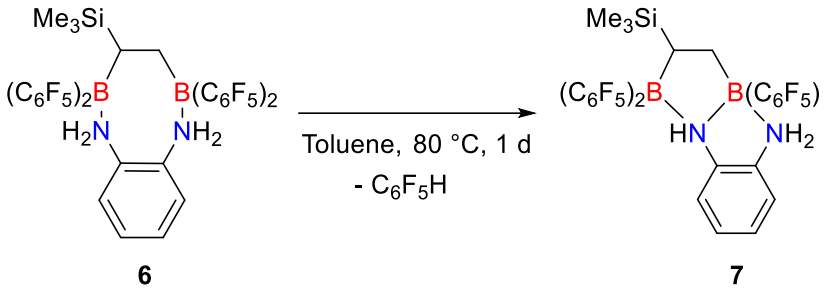


Figure S 18. ^{19}F NMR (377 MHz, $CDCl_3$, 298 K) spectrum of compound **6**.

1.6 Spectra of $Me_3SiCH(B(C_6F_5)_2)CH_2(B(C_6F_5)(NH_2)(NH)C_6H_4$, 7



6 **7**

^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ: 7.16 (m, 3H, Ar*H*), 6.91 (m, 1H, Ar*H*), 6.43 (br s, 1H, N*H*), 6.09 (br d, $^{2}J_{HH}$ = 13 Hz, 1H, NH_2), 5.32 (br d, $^{2}J_{HH}$ = 13 Hz, 1H, NH_2), 1.42 (br s, 1H, C*H*), 1.11 (br s, 2H, CH_2), -0.25 (s, 9H, Si-CH_3).

^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ: 8.8 (br s), 2.9 (br s).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K) δ: 142.1 (s, Ar*C*), 130.4 (s, Ar*C*), 128.6 (s, Ar*C*), 127.7 (s, Ar*C*), 123.2 (s, Ar*C*), 122.0 (s, Ar*C*), 19.7 (br, CH_2), 19.3 (br, C*H*), -1.3 (Si-*C*H_3).

^{19}F NMR (377 MHz, $CDCl_3$, 298 K) δ: -125.1 (br, 1F, *o*-C_6F_5), -125.8 (br, 1F, *o*-C_6F_5), -132.5 (br, 1F, *o*-C_6F_5), -134.5 (br, 2F, *o*-C_6F_5), -136.4 (br, 1F, *o*-C_6F_5), -153.8 (br m, 1F, *p*-C_6F_5), -156.9 (br m, 1F, *p*-C_6F_5), -158.7 (br m, 1F, *p*-C_6F_5), -160.9 (br m, 2F, *m*-C_6F_5), -163.4 (br m, 4F, *m*-C_6F_5).

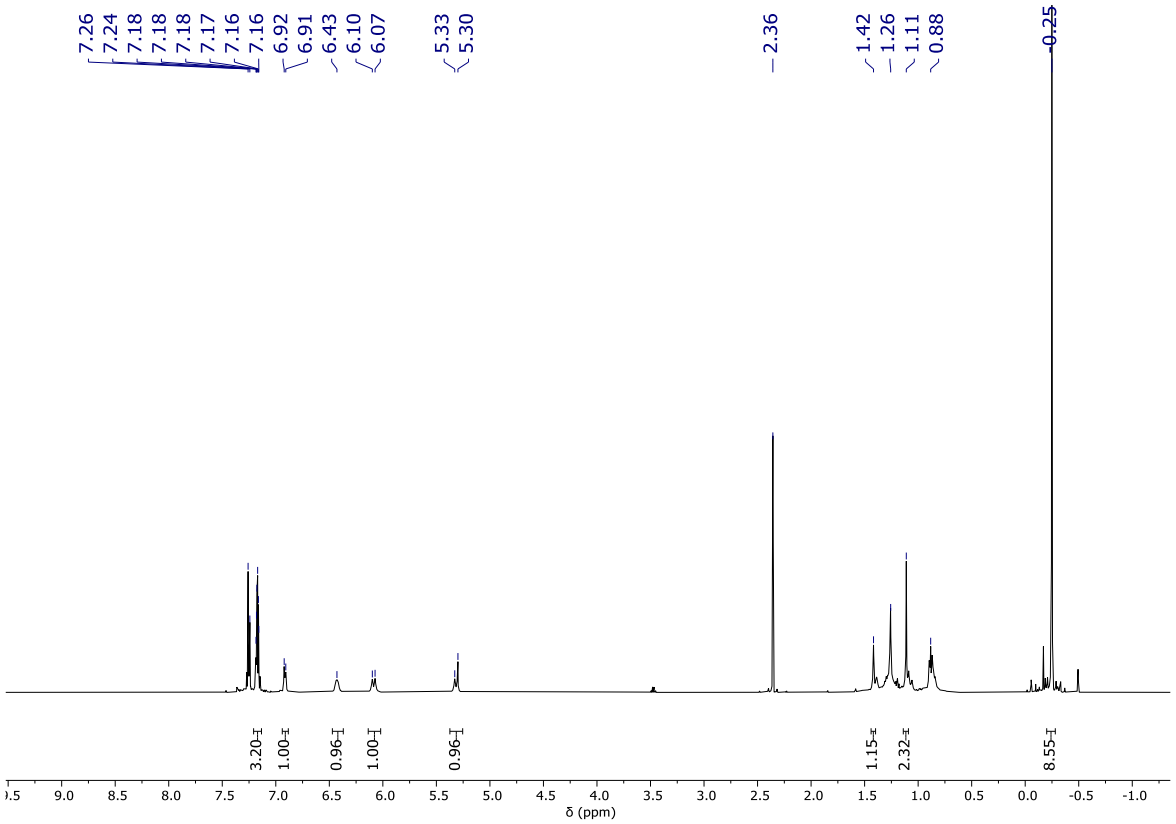


Figure S 19. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of compound **7**.

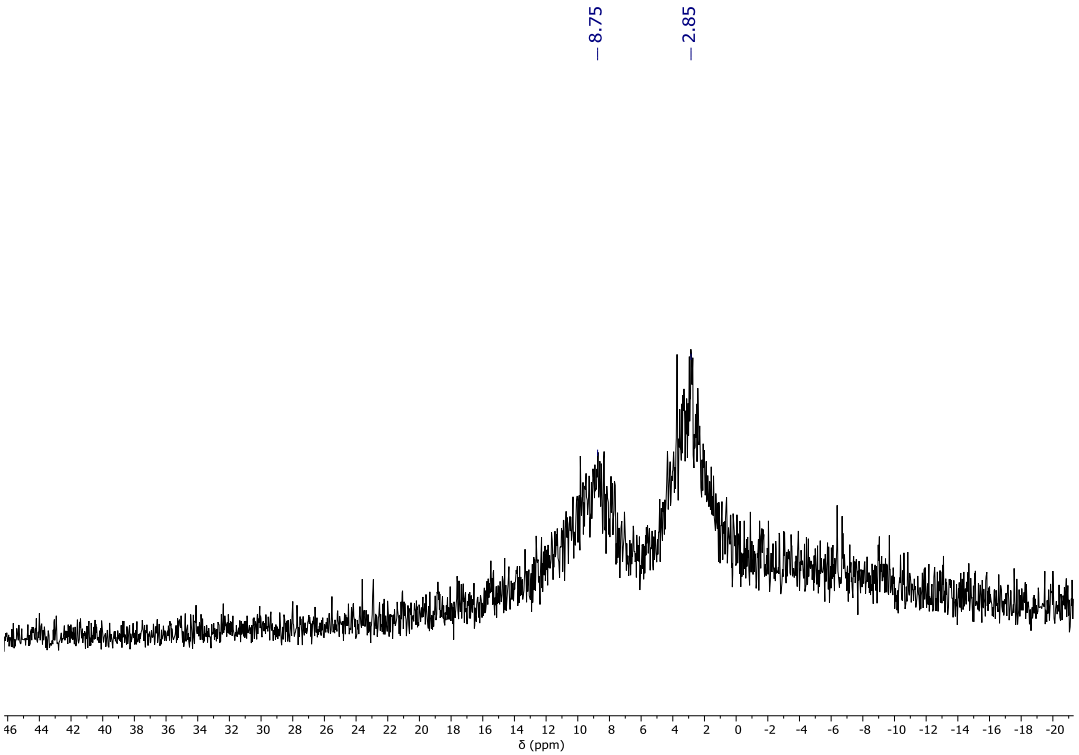


Figure S 20. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of compound **7**.

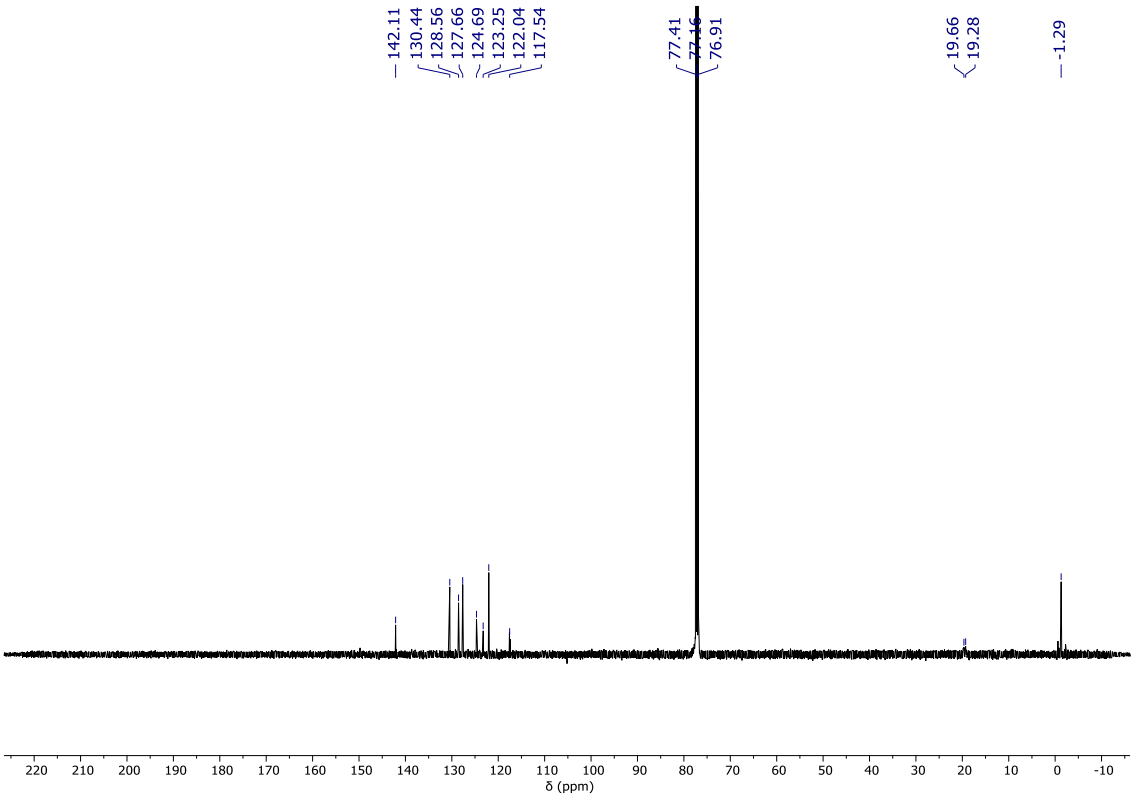


Figure S 21. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of compound **7**.

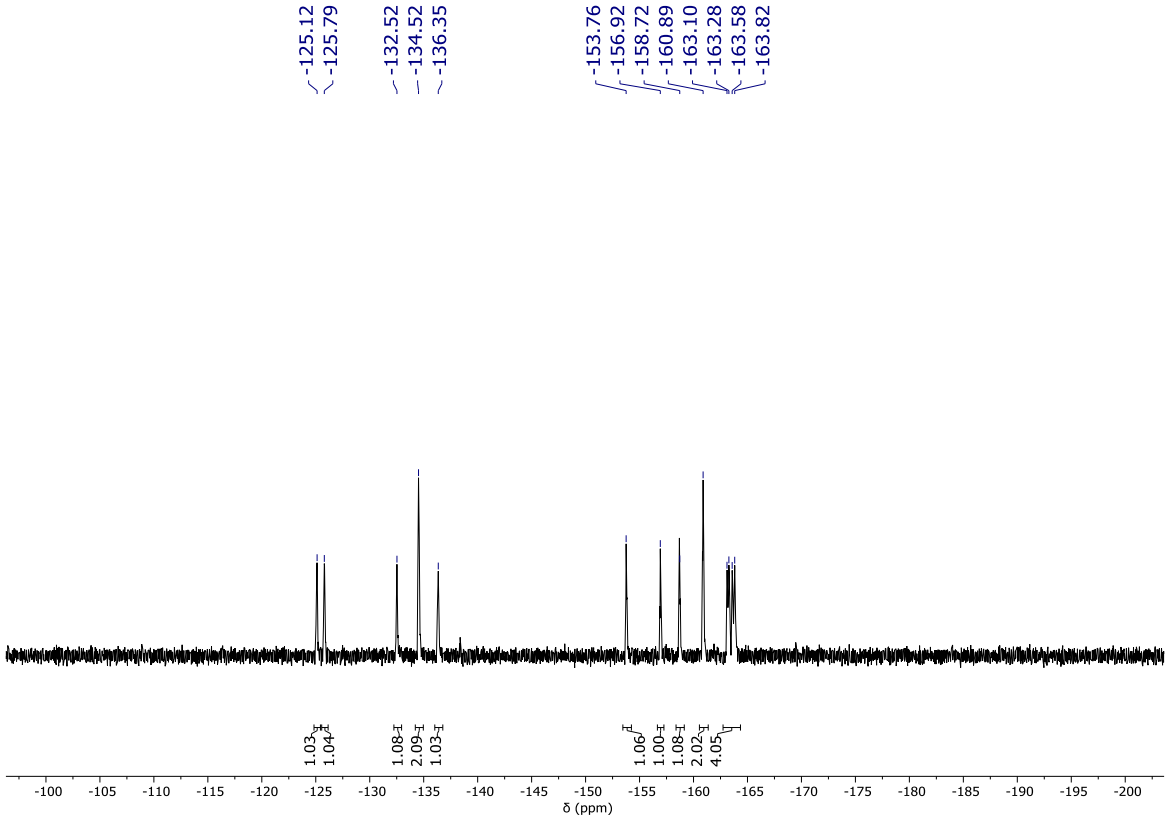
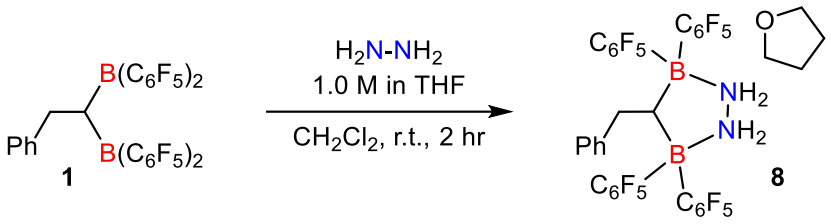


Figure S 22. ^{19}F NMR (377 MHz, $CDCl_3$, 298 K) spectrum of compound **7**.

1.7 Spectra of $PhCH_2CH(B(C_6F_5)_2(NH_2))_2)\cdot THF$, 8



8·THF:

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.87 (br, 2H, NH_2), 7.19 (br, 2H, NH_2), 7.06 (m, 3H, H_{Ar}), 6.86 (d, $^{3}J_{HH}$ = 6.4 Hz, 2H, H_{Ar}), 3.73 (t, $^{3}J_{HH}$ = 6.3 Hz, 4H, THF), 2.81 (t, $^{3}J_{HH}$ = 7.2 Hz, 1H, $HC(B(C_6F_5)_2)_2$), 2.45 (d, $^{3}J_{HH}$ = 7.1 Hz, 2H, PhCH_2), 1.92 (m, 4H, THF).

^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ: 2.3.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 298 K) δ: 148.2 (dm, $^{1}J_{CF}$ = ~242 Hz), 146.9 (dm, $^{1}J_{CF}$ = ~244 Hz), 143.1 (*i*-C_{Ar}), 141.2 (dm, $^{1}J_{CF}$ = ~244 Hz), 136.0 (dm, $^{1}J_{CF}$ = ~259 Hz), 128.0 (*o/m*-C_{Ar}), 127.8 (*o/m*-C_{Ar}), 125.7 (*p*-C_{Ar}), 69.2 (OCH_2CH_2), 38.0 ($CH(B(C_6F_5)_2)_2$), 25.7 (OCH_2CH_2), 20.0 ($PhCH_2$).

^{19}F NMR (377 MHz, $CDCl_3$, 298 K) δ: -133.8 (br, 4F, *o*-C_6F_5), -155.2 (t, $^{3}J_{FF}$ = 20 Hz, *p*-C_6F_5), -156.0 (t, $^{3}J_{FF}$ = 20 Hz, *p*-C_6F_5), -161.9 (br m, 4F, *m*-C_6F_5).

^{1}H, ^{13}C gHSQC (400 MHz / 101 MHz, $CDCl_3$, 298 K) δ ^{1}H / δ ^{13}C: 7.06/ 127.9, 6.88/ 127.7, 3.78/ 69.0, 2.50/ 37.8, 1.94/25.4.

*A single crystal sample of compound **8** without coordinated THF was isolated and the NMR is included here. However, this did not seem reproducible on bulk scale.* **8:**

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 6.98 (m, 3H, H_{Ar}), 6.87 (br, 2H, NH_2), 6.74 (br, 2H, NH_2), 6.67 – 6.60 (m, 2H, H_{Ar}), 2.83 (t, $^{3}J_{HH}$ = 7.0 Hz, 1H, $HC(B(C_6F_5)_2)_2$), 2.51 (d, $^{3}J_{HH}$ = 6.9 Hz, 2H, PhCH_2).

^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ: 3.8.

^{19}F NMR (377 MHz, $CDCl_3$, 298 K) δ: -134.0 (br, 4F, *o*-C_6F_5), -154.4 (t, $^{3}J_{FF}$ = 20 Hz, *p*-C_6F_5), -155.1 (t, $^{3}J_{FF}$ = 20 Hz, *p*-C_6F_5), -161.2 (br m, 4F, *m*-C_6F_5).

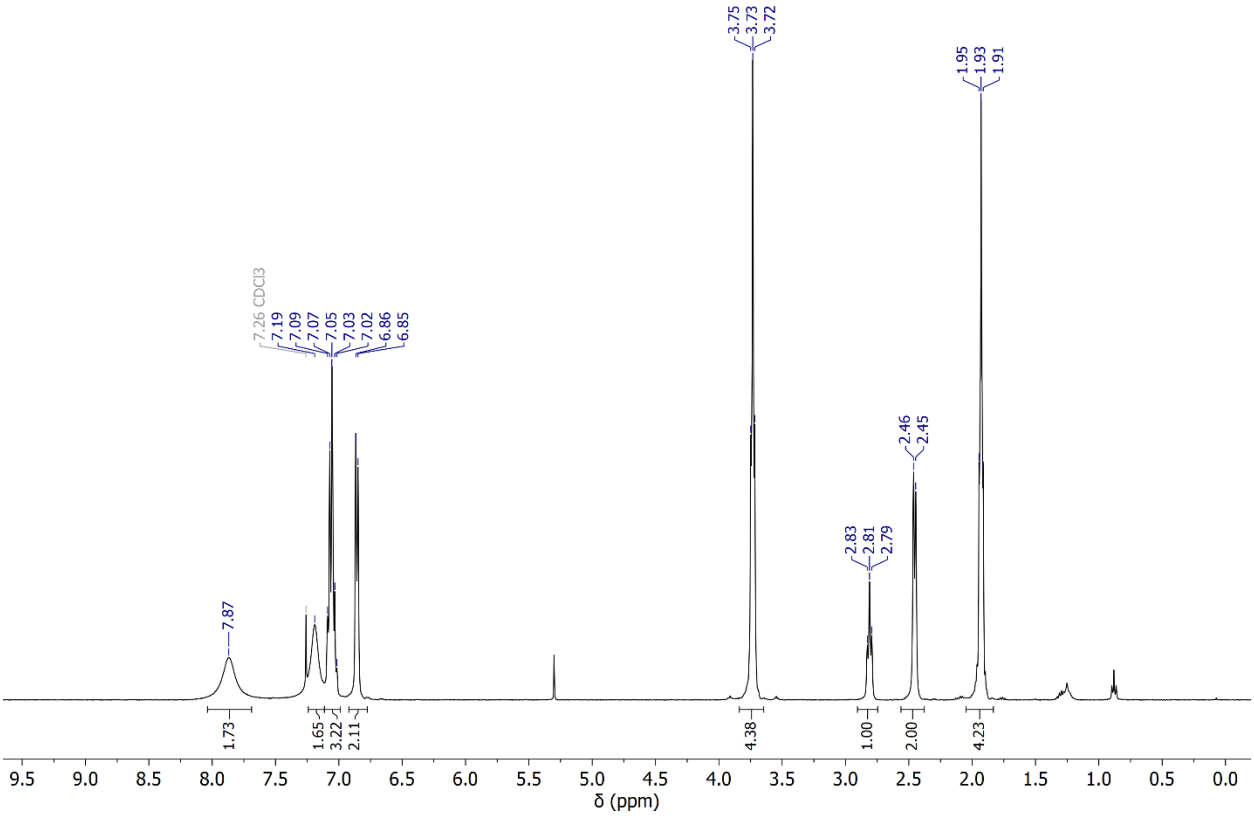


Figure S 23. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **8·THF**.

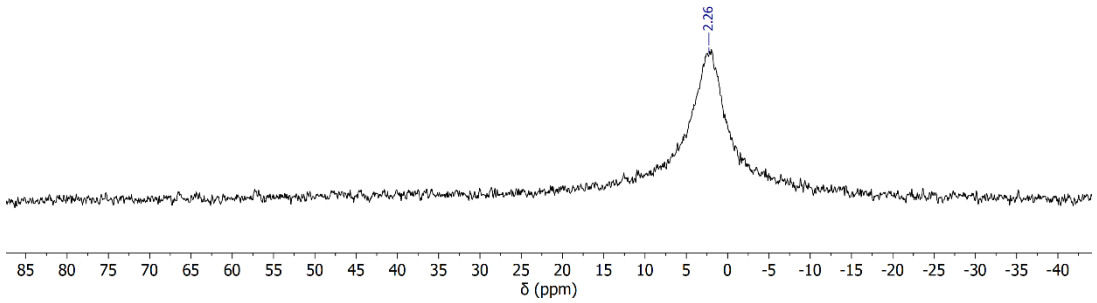


Figure S 24. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of **8·THF**.

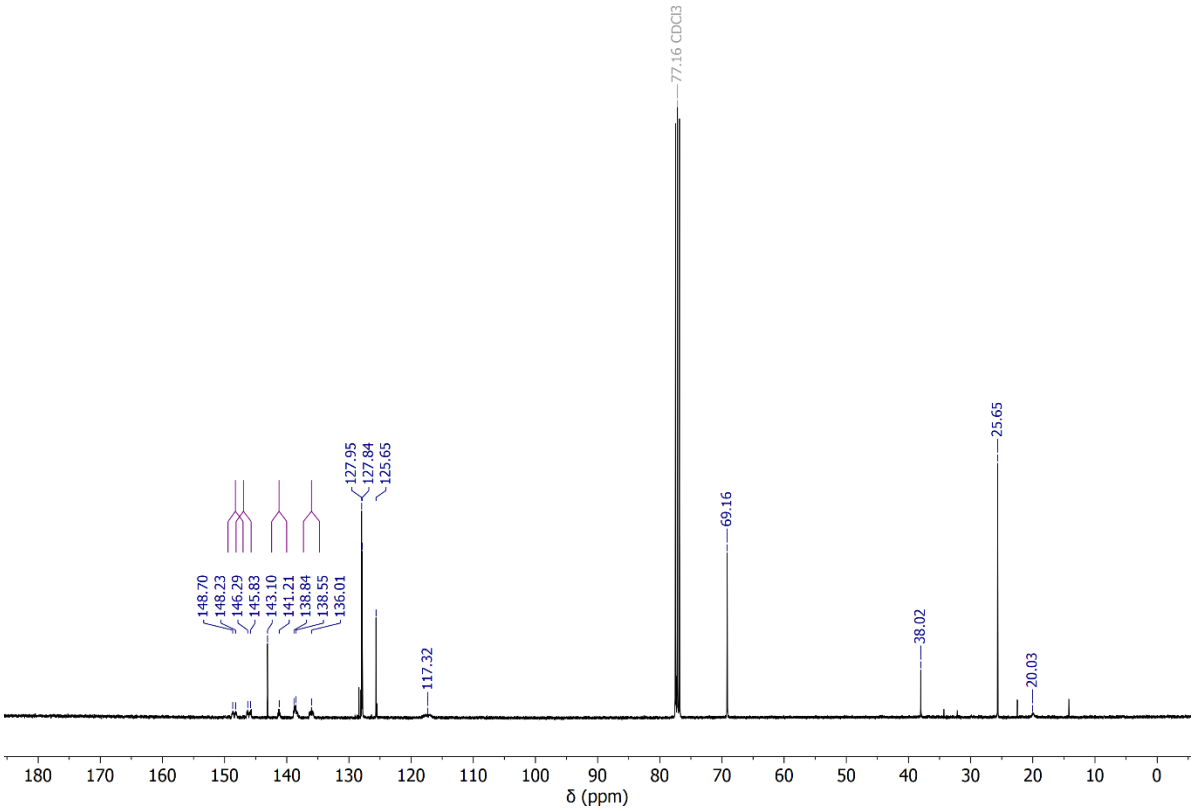


Figure S 25. ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum of **8·THF**.

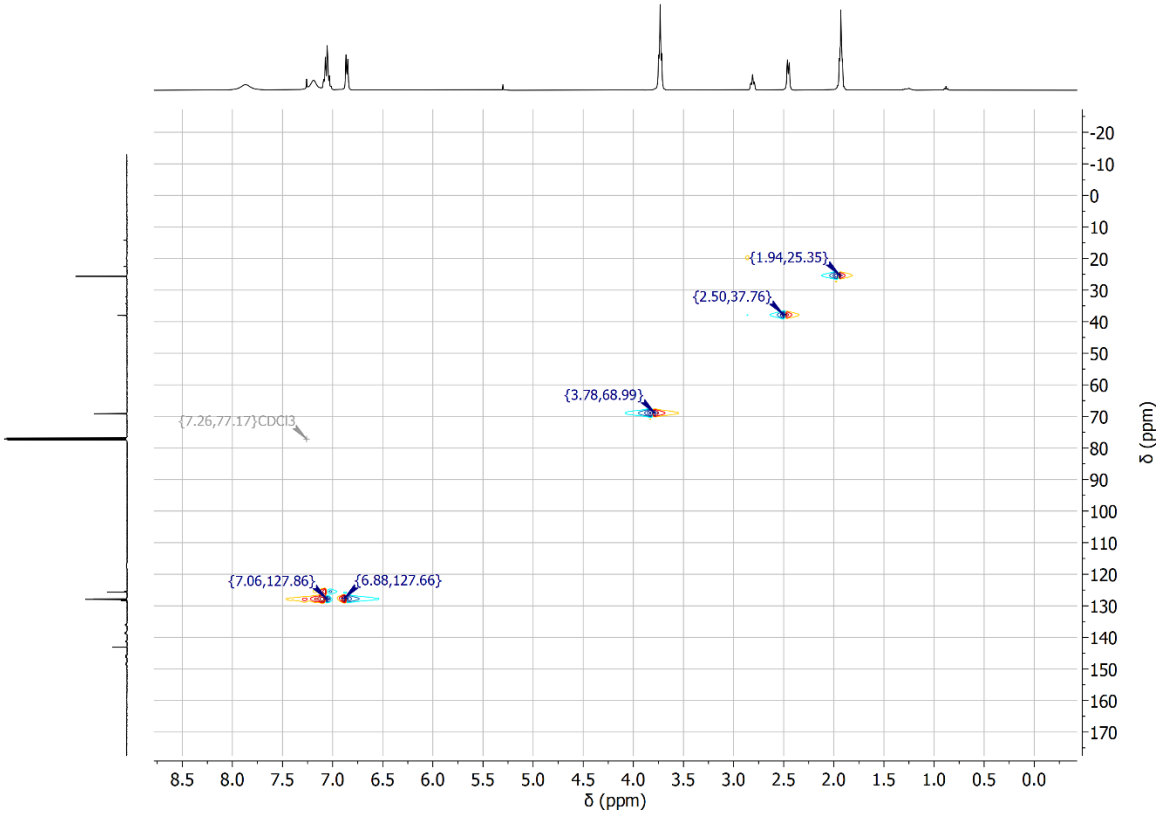


Figure S 26. ^{1}H, ^{13}C gHSQC (400 MHz / 101 MHz, $CDCl_3$, 298 K) spectrum of **8·THF**.

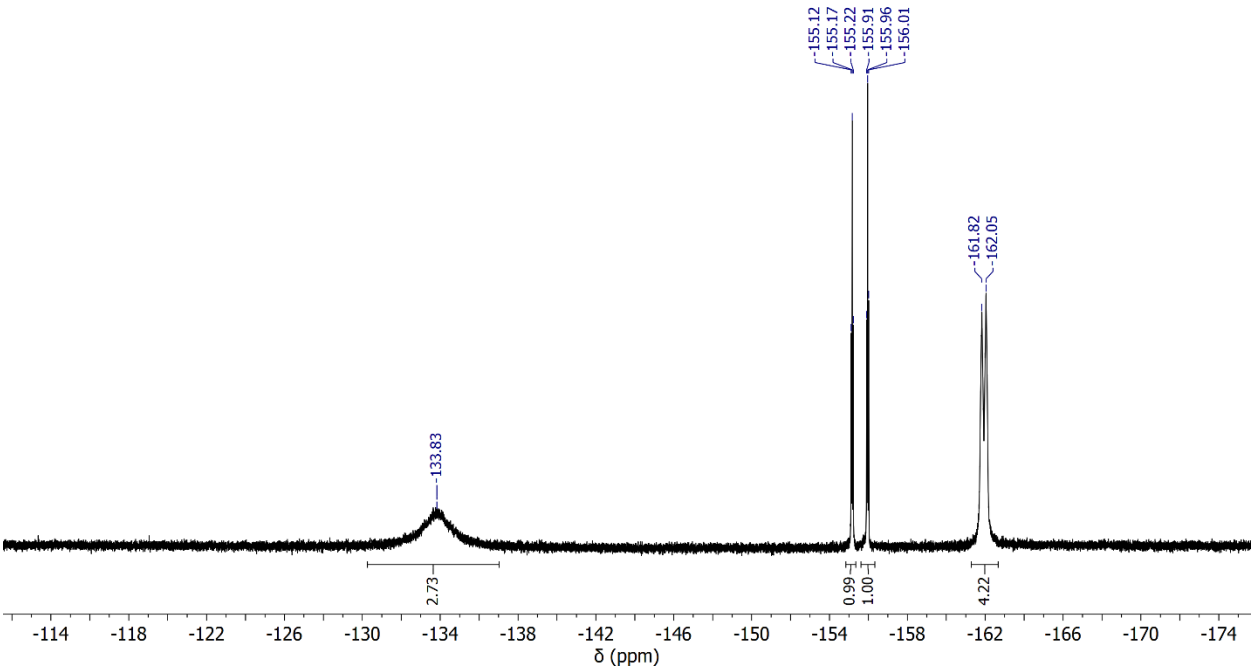


Figure S 27. ^{19}F NMR (377 MHz, $CDCl_3$, 298 K) spectrum of **8·THF**.

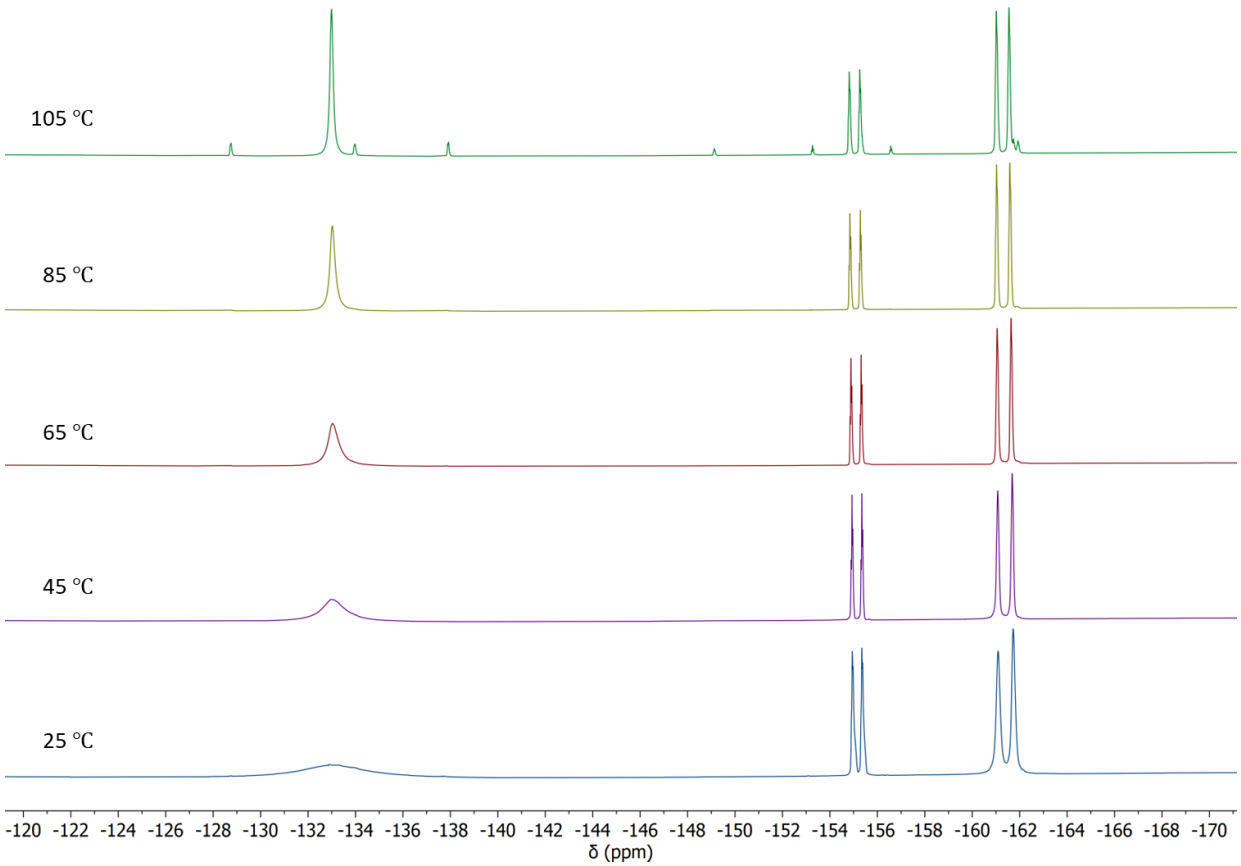


Figure S 28. Variable-temperature ^{19}F NMR (564 MHz, C_6D_5Br, 298-378 K) spectra of **8·THF**.

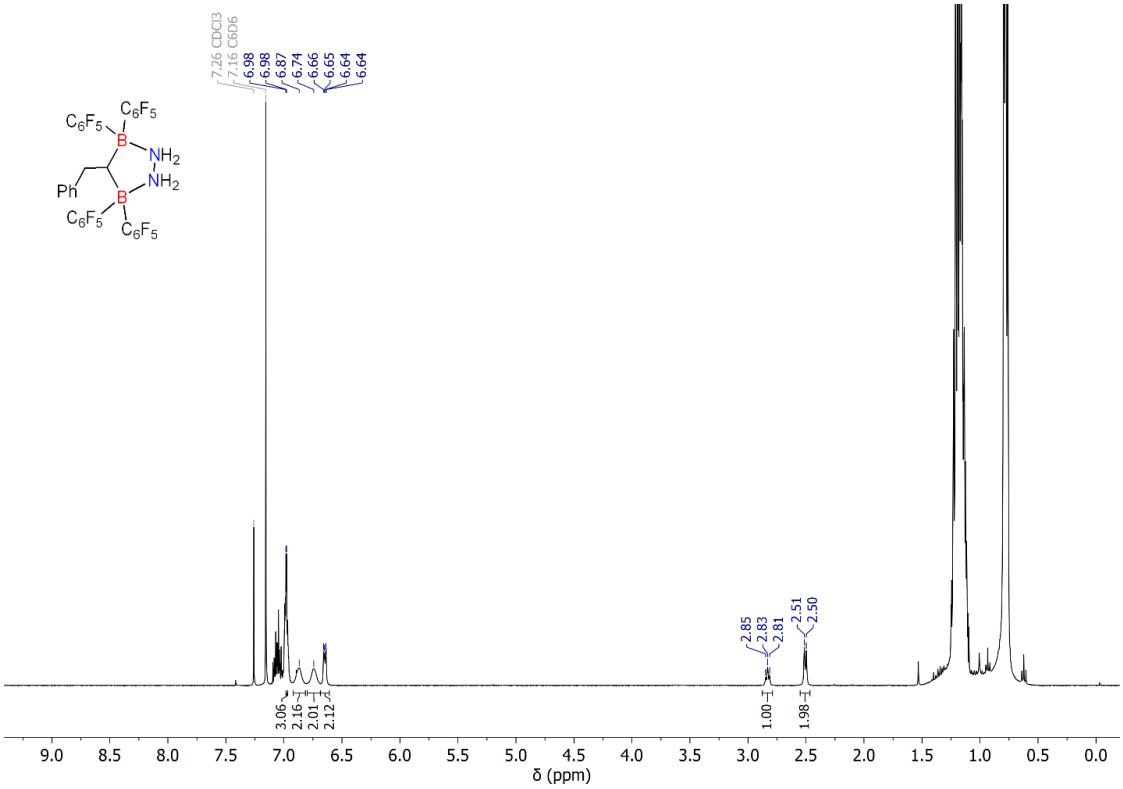


Figure S 29. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of compound **8**.

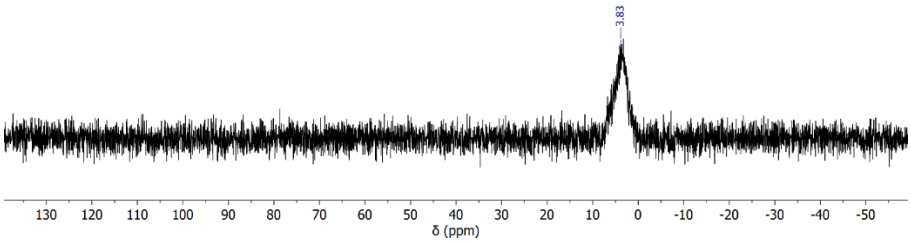


Figure S 30. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of compound **8**.

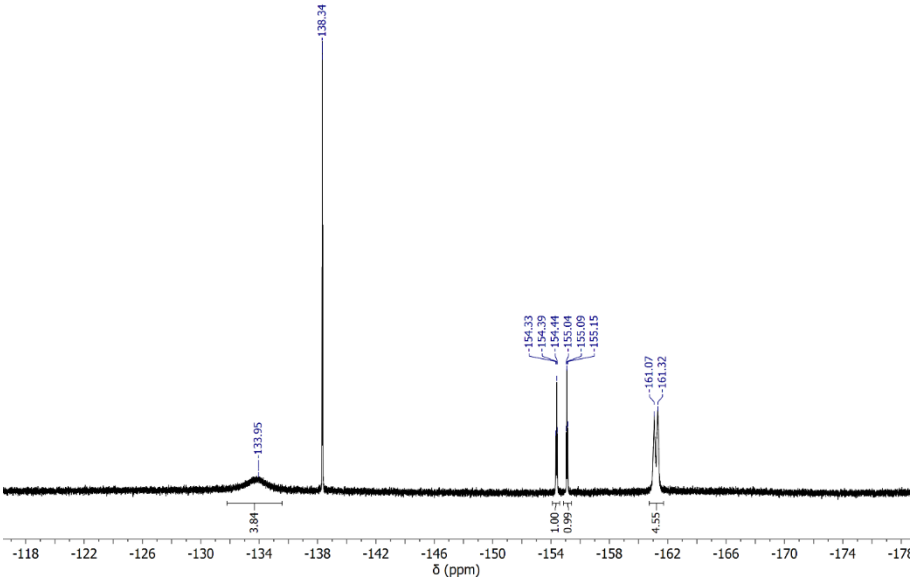
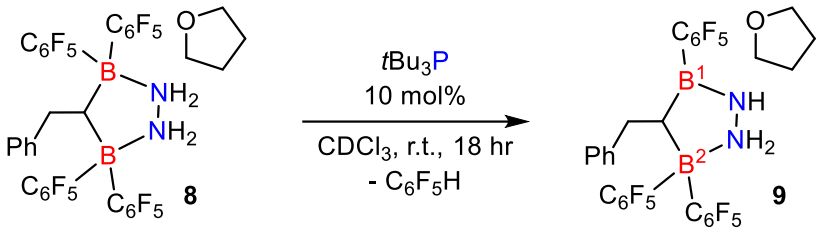


Figure S 31. ^{19}F NMR (377 MHz, $CDCl_3$, 298 K) spectrum of compound **8**.

1.8 Generation of $PhCH_2CH(B(C_6F_5)_2NH_2)(B(C_6F_5)NH)\cdot THF$, 9



***in-situ* NMR Analysis**

^{1}H NMR (400 MHz, $CDCl_3$, 298 K, *partial*) δ: 7.06 (m, 3H, H_{Ar}), 6.92 (m, 1H, C_6F_5H), 6.78 (m, 2H, H_{Ar}), 6.44 (br, 2H, N*H*), 3.71 (m, 2H, THF), 2.87 (dd, $^3J_{HH}$ = 13.4, 6.0 Hz, 1H, PhCH_2), 2.54 (d, $^3J_{HH}$ = 8.1 Hz, 1H, *H*C(B(C-$_6F_5)_2)_2$), 2.43 (dd, $^3J_{HH}$ = 13.3, 8.2 Hz, 1H, PhCH_2), 1.86 (m, 2H, THF).

^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ: 45.2 (B^1), -0.1 (B^2).

^{19}F NMR (377 MHz, $CDCl_3$, 298 K) δ: -129.5 (br, 2F, B^1 *o*-C_6F_5), -133.8 (br, 2F, B^2 *o*-C_6F_5), -134.7 (br, 2F, B^2 *o*-C_6F_5), -138.4 (m, 2F, *o*-C_6F_5), -149.0 (br, 1F, B^1 *p*-C_6F_5), -153.3 (t, $^3J_{FF}$ = 20 Hz, 1F, *p*-C_6F_5), -156.0 (t, $^3J_{FF}$ = 20 Hz, 1F, B^2 *p*-C_6F_5), -157.2 (t, $^3J_{FF}$ = 20 Hz, 1F, B^2 *p*-C_6F_5), -161.4 (m, , 2F, B^1 *m*-C_6F_5), -161.7 (m, 2F, *p*-C_6F_5), -162.4 (m, 4F, B^2 *m*-C_6F_5).

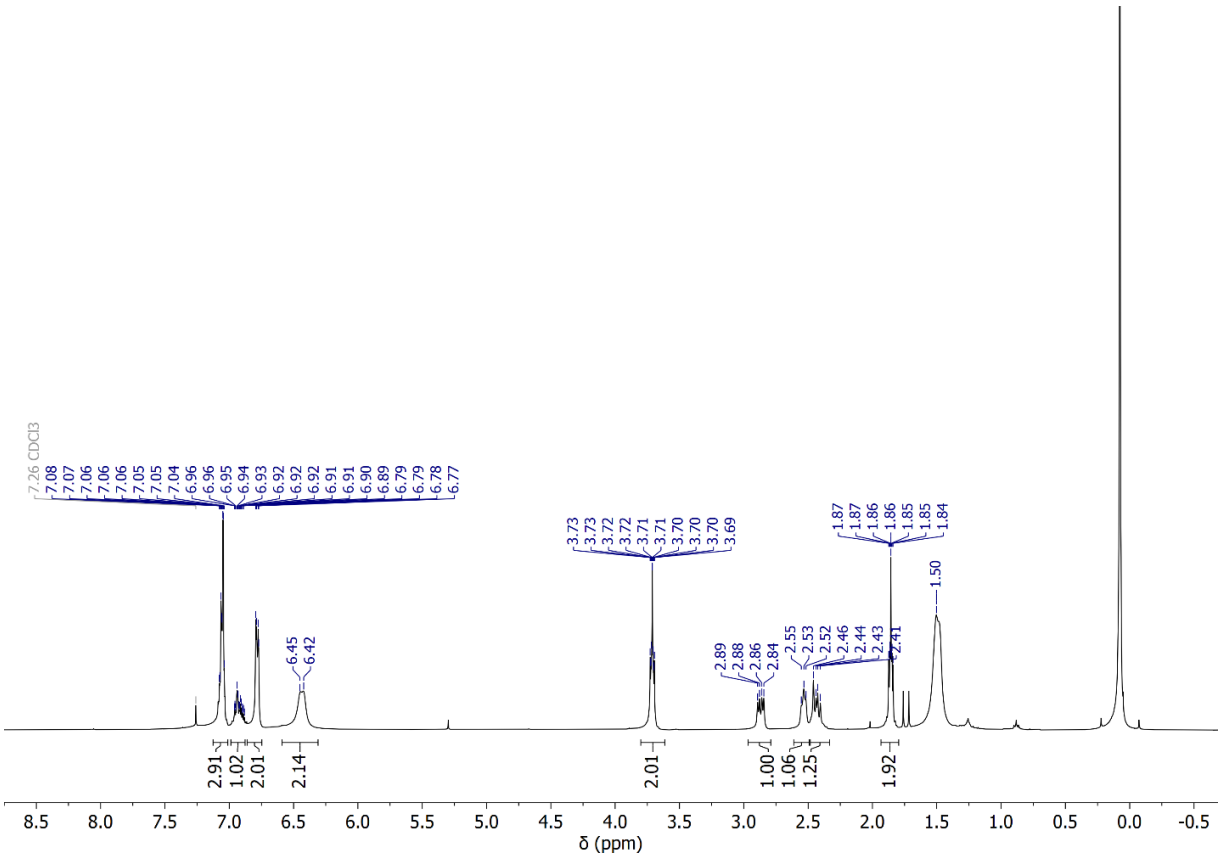


Figure S 32. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of the protonolysis of **$BCBN_2H_4\cdot THF$ 8** with *t*Bu_3P.

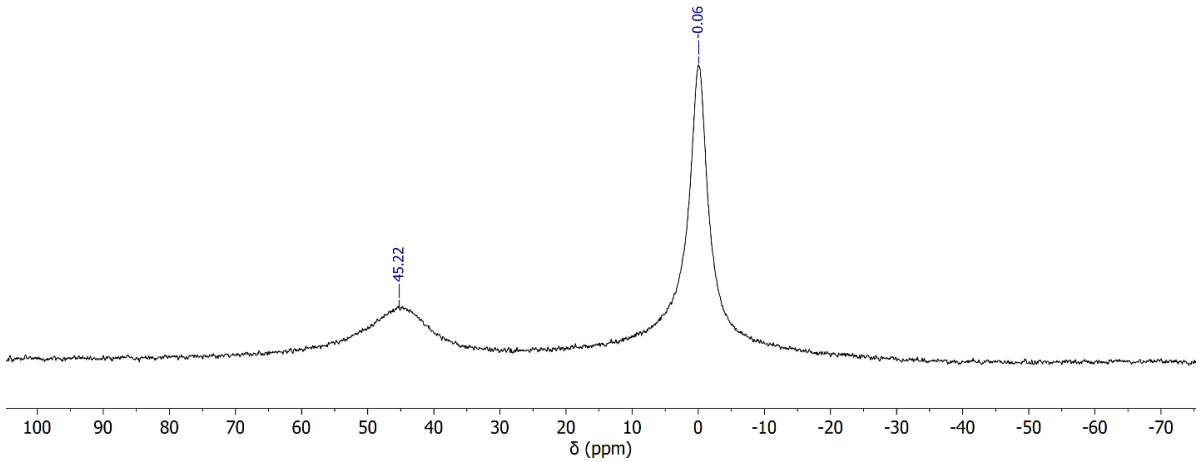


Figure S 33. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of the protonolysis of **$BCBN_2H_4$·THF 8** with *t*Bu_3P.

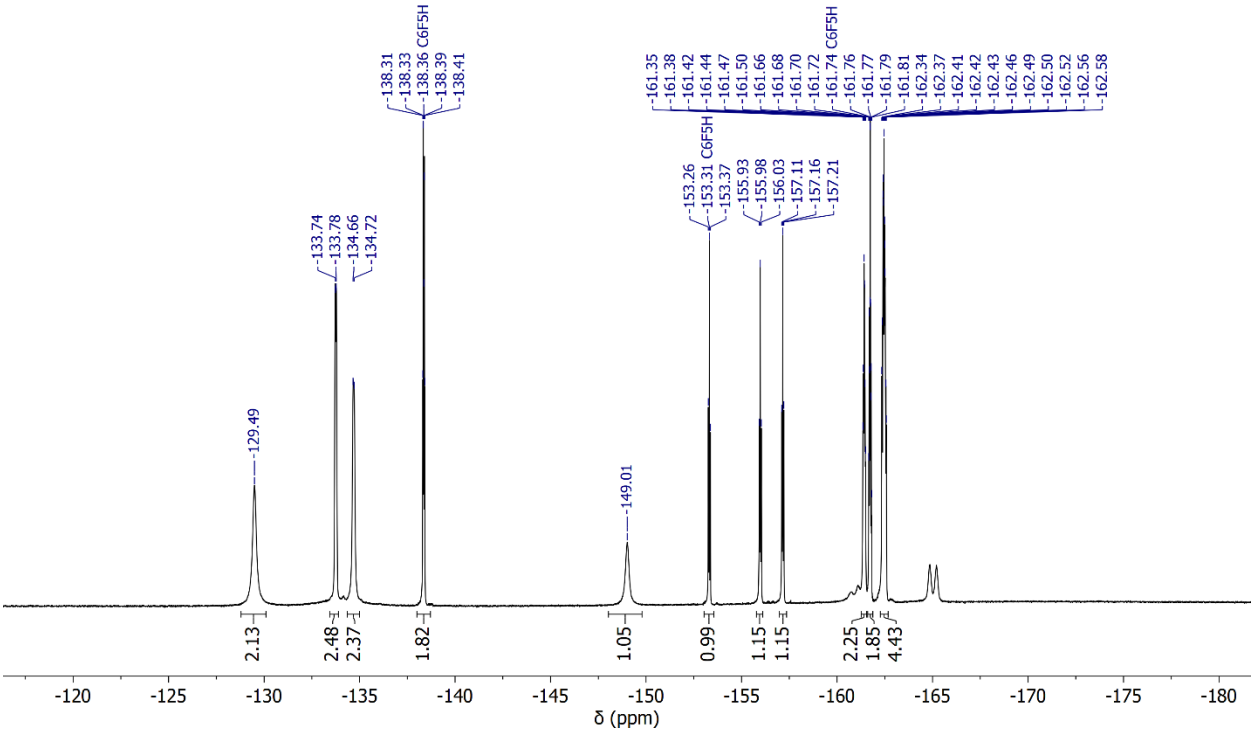
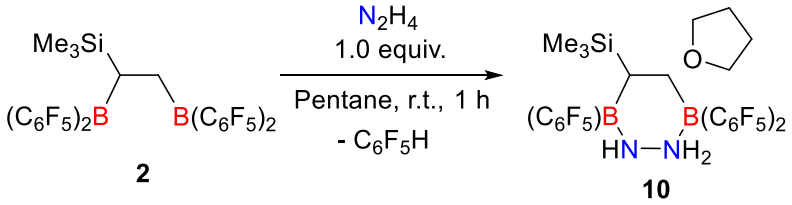


Figure S 34. ^{19}F NMR (377 MHz, $CDCl_3$, 298 K) spectrum the protonolysis of **$BCBN_2H_4$·THF 8** with *t*Bu_3P.

1.9 Spectra of $Me_3SiCH(B(C_6F_5)_2)CHB(C_6F_5)(N_2H_3)\cdot THF$, 10



^{1}H NMR (400 MHz, C_6D_6, 298 K) δ: 6.05 (br s, 1H, N*H*), 5.21 (d, $^2J_{HH}$ = 12 Hz, 1H, N*H*), 4.78 (d, $^3J_{HH}$ = 5 Hz, 1H, N*H*), 3.63 (m, 4H, O-CH_2), 2.03 (dd, $^2J_{HH}$ = 15 Hz, $^3J_{HH}$ = 8 Hz, 1H, CH_2), 1.40 (m, 4H, O-CH$_2$-CH_2), 1.05 (dd, $^3J_{HH}$ = 10 Hz, $^3J_{HH}$ = 8 Hz, 1H, C*H*), 0.58 (dd, $^2J_{HH}$ = 15 Hz, $^3J_{HH}$ = 10 Hz, 1H, CH_2), -0.14 (s, 9H, Si-CH_3).

^{11}B NMR (128 MHz, $CDCl_3$, 298 K) δ: 44.0 (br s, *B*(C_6F_5)), -4.4 (br s, *B*(C_6F_5)$_2$).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K) δ: 148.7 (d, $^2J_{CF}$ = 236 Hz, *C*$_6$F$_5$), 147.5 (d, $^2J_{CF}$ = 242 Hz, *C*$_6$F$_5$), 146.3 (d, $^2J_{CF}$ = 247 Hz, *C*$_6$F$_5$), 141.8 (d, $^2J_{CF}$ = 247 Hz, *C*$_6$F$_5$), 139.8 (d, $^2J_{CF}$ = 253 Hz, *C*$_6$F$_5$), 137.4 (d, $^2J_{CF}$ = 247 Hz, *C*$_6$F$_5$), 118.5, (br s, *i*-C$_6$F$_5$), 116.4 (br s, *i*-C$_6$F$_5$), 110.9 (br s, *i*-C$_6$F$_5$), 68.2 (s, O-*C*H$_2$), 25.7 (s, O-CH$_2$-*C*H$_2$), 18.7 (br s, *C*H$_2$), 15.9 (br s, *C*H), -1.5 (s, Si-C*H*$_3$).

^{19}F NMR (377 MHz, $CDCl_3$, 298 K) δ: -132.4 (m, 2F, *o*-C$_6$*F*$_5$), -134.9 (br d, $^3J_{FF}$ = 23 Hz, 2F, *o*-C$_6$*F*$_5$), -136.4 (br s, 2F, *o*-C$_6$*F*$_5$), -151.8 (t, $^3J_{FF}$ = 19 Hz, 1F, *p*-C$_6$*F*$_5$), -156.8 (t, $^3J_{FF}$ = 19 Hz, 1F, *p*-C$_6$*F*$_5$), -156.9 (t, $^3J_{FF}$ = 19 Hz, 1F, *p*-C$_6$*F*$_5$), -160.7 (m, 2F, *m*-C$_6$*F*$_5$), -162.3 (m, 2F, *m*-C$_6$*F*$_5$), -162.8 (m, 2F, *m*-C$_6$*F*$_5$).

HRMS (DART- ionization, m/z): Calcd. for $C_{23}H_{11}B_2N_2F_{15}Si^-$ ([M-H]$^-$): 653.0878; Found: 653.0889.

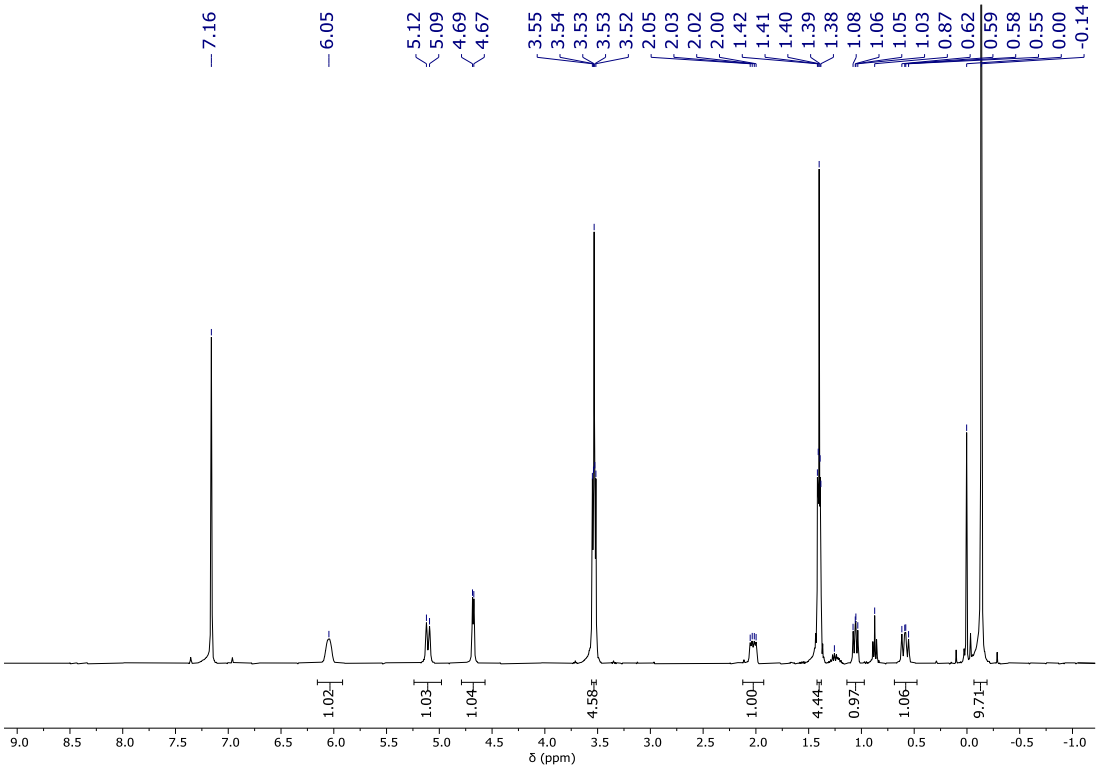


Figure S 35. ^{1}H NMR (400 MHz, C_6D_6, 298 K) spectrum of **10**.

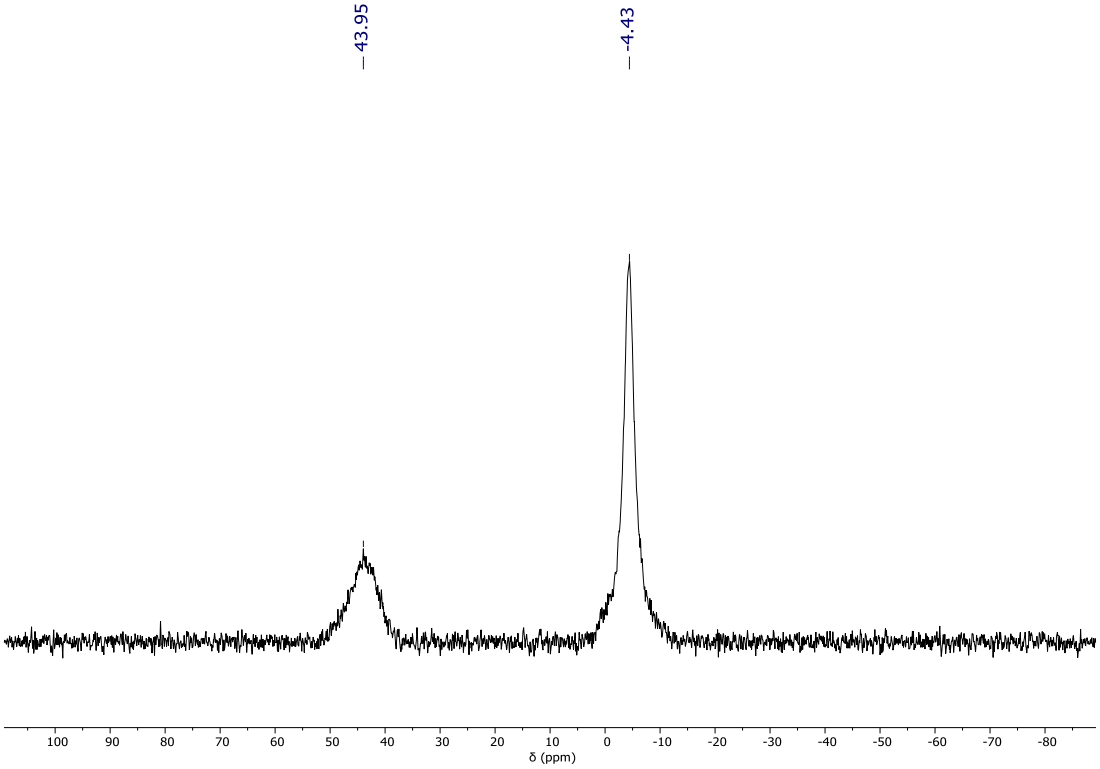


Figure S 36. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K) spectrum of **10**.

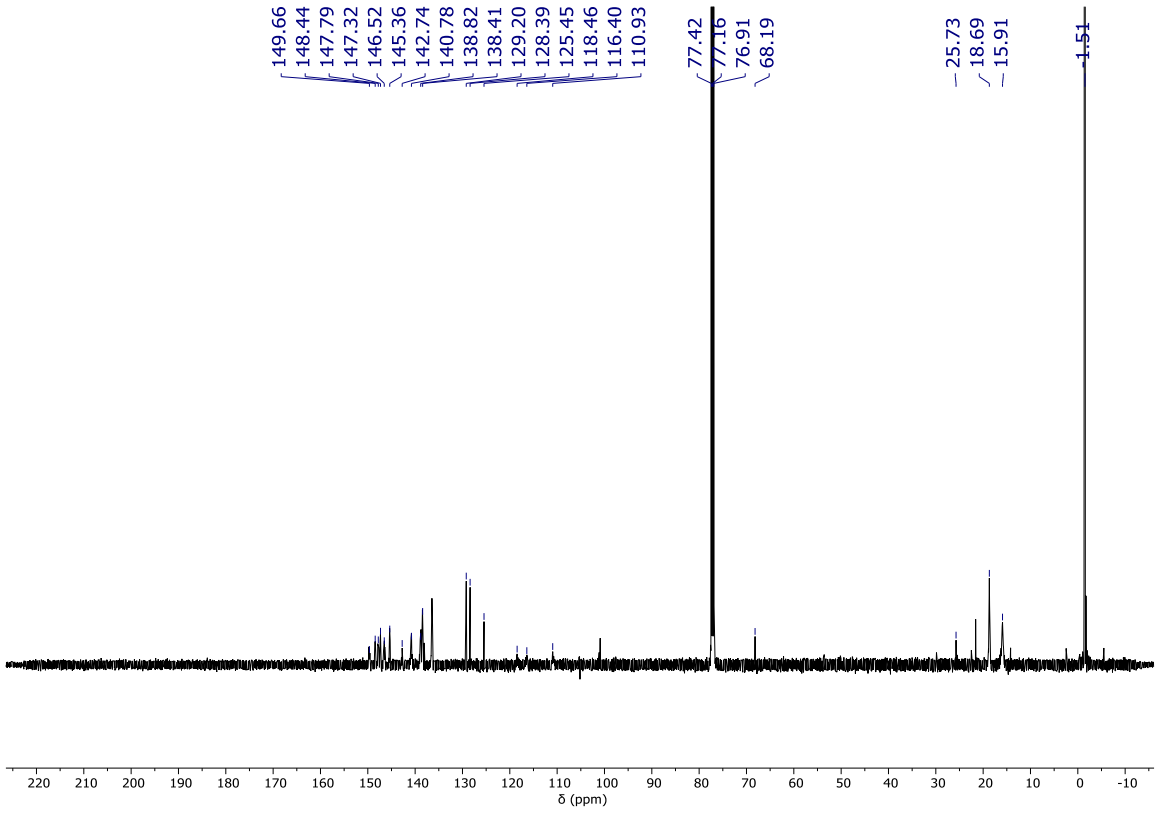


Figure S 37. ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) spectrum of **10**.

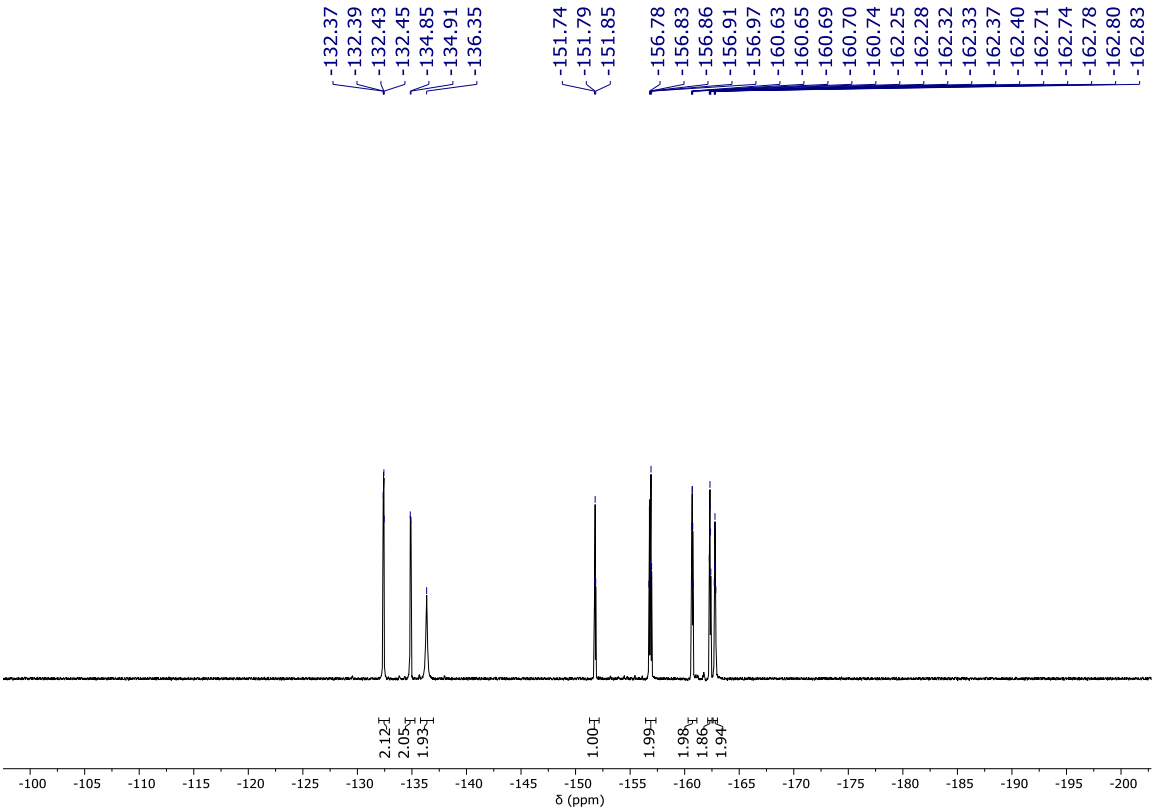


Figure S 38. ^{19}F NMR (377 MHz, $CDCl_3$, 298 K) spectrum of **10**.

1.10 References

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(2) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, *29* (9), 2176–2179.

(3) Parks, D. J.; von H. Spence, R. E.; Piers, W. E. Bis(Pentafluorophenyl)Borane: Synthesis, Properties, and Hydroboration Chemistry of a Highly Electrophilic Borane Reagent. *Angew. Chem. Int. Ed.* **1995**, *34* (7), 809–811.

(4) Liu, Y.-L.; Kehr, G.; Daniliuc, C. G.; Erker, G. Geminal Bis-Borane Formation by Borane Lewis Acid Induced Cyclopropyl Rearrangement and Its Frustrated Lewis Pair Reaction with Carbon Dioxide. *Chem. Sci.* **2017**, *8* (2), 1097–1104.