Electronic Supplementary Material (ESI) for Chemical Communications.

SUPPORTING INFORMATION

Highly Lewis Acidic Cationic Alkaline Earth Metal Complexes

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1. Supporting Experimental Data

1.1. General Experimental Procedures

All experiments were conducted under an inert nitrogen atmosphere using standard Schlenk and glovebox techniques (MBraun, Labmaster SP). Toluene, *n*-hexane and benzene were degassed with nitrogen, dried over activated aluminium oxide (Solvent Purification System: Pure Solv 400−4−MD, Innovative Technology) and stored over 3Å molecular sieves. Fluorobenzene, chlorobenzene and bromobenzene were dried over calcium hydride, distilled under N_2 atmosphere and stored over molecular sieves 3Å. C_6D_6 and C_6D_5Br (99.6% D, Sigma Aldrich) were dried over 3Å molecular sieves. Et_3PO (Acros Organics), *n*PrMgCl in Et_2O (2M, Sigma Aldrich), and $[Ph_3C^+][(C_6F_5)_4B^-]$ (Boulder Scientific) were used as received. BDI-H (BDI = HC{(Me)CN(2,6-*i*$Pr_2C_6H_3$)}$_2$),[S1] BDI-Li,[S1] bis[p-*t*Bu-benzyl]calcium,[S2] $[H(OEt_2)_2][BAr^F]$,[S3] $[(AM)CaH]_2$[S4] were synthesized according to a literature procedure. NMR spectra were recorded with a Bruker Avance III HD 400 MHz or a Bruker Avance III HD 600MHz spectrometer. The spectra were referenced to the respective residual signals of the deuterated solvents. Elemental analysis was performed with a Euro EA 3000 (Euro Vector) analyzer. All crystal structures have been measured on a SuperNova (Agilent) diffractometer with dual Cu and Mo microfocus sources and an Atlas S2 detector.

1.2. Synthesis

Synthesis of [(BDI)Mg(*n*Pr)]$_2$

(BDI)Li (3.0120 g, 7.0937 mmol) was dissolved in toluene (20 ml) and a 2M solution of *n*PrMgCl in Et_2O (3.55 ml, 2.00 mol/l, 7.10 mmol) was added over the course of 5 min while cooling with a water bath. After 2 hours all volatiles were removed *in vacuo* resulting in a white solid which was extracted with toluene (4 x 5 ml) using a filter cannula. The extract was evaporated to dryness yielding the desired product as a white powder (2.738 g, 5.645 mmol, 80%). Crystals suitable for X-ray diffraction analysis (Supporting Information) were grown at -30°C from a saturated hexane solution. ^{1}H NMR (600 MHz, C_6D_6, 298K) δ 7.14 – 7.09 (m, 6H, Ar*H*), 4.94 (s, 1H, CC*H*C), 3.17 (hept, $^3J_{HH}$ = 6.9 Hz, 4H, C*H*Me_2), 1.67 (s, 6H, CCH_3), 1.44 (m, 2H, $CH_2CH_2CH_3$), 1.27 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH(CH_3))$_2$, 1.16 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH(CH_3)$_2$), 0.78 (t, $^3J_{HH}$ = 7.2 Hz, 3H, CH_2CH_3), -0.15 – -0.26 (m, 2H, MgCH_2) ppm. ^{13}C

NMR (151 MHz, C_6D_6, 298K) δ 168.9 (s, N*C*(CH_3)), 143.5 (s, Ar*C*), 141.5 (s, Ar*C*), 125.6 (s, Ar*C*), 123.7 (s, Ar*C*), 95.0 (s, C*C*HC), 28.3 (s, *C*HMe_2), 24.3 (s, CH*C*H_3), 23.2 (s, NC(*C*H_3)), 23.1 (s, CH*C*H_3), 22.2 (s, CH_2*C*H_3), 21.7 (s, CH_2*C*H_2CH_3), 8.8 (s, Mg*C*H_2) ppm. Anal. Calcd for $C_{64}H_{96}Mg_2N_4$ (M = 970.12 g/mol): C, 79.24; H, 9.97; N, 5.78. Found: C, 79.43; H, 9.87; N, 5.68.

Synthesis of [(BDI)Mg^+][$B(C_6F_5)_4^-$]

[(BDI)Mg(*n*Pr)]$_2$ (0.168 g, 0.347 mmol) and [Ph_3C^+][$B(C_6F_5)_4^-$] (0.304 g, 0.330 mmol) were dissolved in chlorobenzene (2 ml) and stirred until the solution became almost colorless (1 min). All volatiles were removed under reduced pressure resulting in a sticky orange oil. After addition of hexane (4 ml) the biphasic system was allowed to stand at room temperature overnight, resulting in the formation of colorless crystals embedded in a sticky orange material which complicates work-up and lowers the yield. The crystals were successively washed with bromobenzene (1 x 0.2 ml + 1 x 0.1 ml) and hexane (1 ml) and dried under vacuum. Yield: 12%, 0.043 g, 0.038 mmol. ^{1}H NMR (600 MHz, C_6D_5Br, 298K) δ 7.18 (t, $^3J_{HH}$ = 7.7 Hz, 2H, Ar*H*), 7.06 (d, $^3J_{HH}$ = 7.7 Hz, 4H, Ar*H*), 4.97 (s, 1H, CC*H*C), 2.77 (hept, $^3J_{HH}$ = 6.9 Hz, 4H, C*H*Me_2), 1.59 (s, 6H, CCH_3), 1.06 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CHCH_3), 0.91 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CHCH_3) ppm. ^{13}C NMR (151 MHz, C_6D_5Br, 298K) δ 173.7 (s, N*C*(CH_3)), 149.1 (br d, $^1J_{CF}$ = 240 Hz, B(C_6F_5)$_4$), 142.4 (s, Ar*C*), 141.8 (s, Ar*C*), 138.1 (br t, $^1J_{CF}$ = 237 Hz, B(C_6F_5)$_4$), 127.7 (s, Ar*C*H), 125.1 (s, Ar*C*H), 97.1 (s, C*C*HC), 29.1 (s, *C*HMe_2), 24.6 (s, CH*C*H_3), 24.5 (s, NC(*C*H_3)), 24.5 (s, CH*C*H_3) ppm. ^{19}F NMR (565 MHz, C_6D_5Br, 298K) δ -131.4 (d, $^3J_{FF}$ = 21 Hz, 8F, *o*-C*F*), -159.7 (t, $^3J_{FF}$ = 21 Hz, 4F, *p*-C*F*), -164.9 (t, $^3J_{FF}$ = 21 Hz, 8F, *m*-C*F*) ppm. ^{11}B NMR (193 MHz, C_6D_5Br, 298K) δ -15.7 (s, *B*(C_6F_5)$_4$) ppm. Anal. Calcd for $C_{53}H_{41}MgN_2BF_{20}$ (M = 1121.01 g/mol): C, 56.79; H, 3.69; N, 2.50. Found: C, 56.94; H, 3.68; N, 2.55.

Synthesis of [(BDI)Mg^+·C_6H_6][$B(C_6F_5)_4^-$]

[(BDI)Mg(*n*Pr)]$_2$ (0.6286 g, 0.6480 mmol) and [Ph_3C^+][$B(C_6F_5)_4^-$] (1.010 g, 1.095 mmol) were dissolved in a mixture of chlorobenzene (9 ml) and benzene (1 ml). The brownish solution was stirred until colorless (1 min). Subsequently all volatiles were removed under reduced pressure and the material was washed with a 1:1 mixture of benzene and hexane (7 x 5 ml). The resulting white powder was dried *in vacuo* yielding 1.231g (94%) of the desired product. Suitable crystals for X-ray diffraction were obtained by slowly cooling a saturated chlorobenzene/benzene (2:1) solution from 60°C to room temperature. ^{1}H NMR (600 MHz, C_6D_5Br, 298K) δ 7.20 (t, $^3J_{HH}$ = 7.7 Hz, 2H, Ar*H*), 7.16 (s, 6H, C_6H_6), 7.08 (d, $^3J_{HH}$ = 7.7 Hz, 4H, Ar*H*), 4.89 (s, 1H, CC*H*C), 2.69 (hept, $^3J_{HH}$ = 6.9 Hz, 4H, C*H*Me_2), 1.55 (s, 6H, CCH_3), 1.02 (d, $^3J_{HH}$

= 6.9 Hz, 12H, CHCH_3), 1.00 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CHCH_3) ppm. ^{13}C NMR (151 MHz, C_6D_5Br, 298K) δ 173.1 (s, N*C*(CH_3)), 148.8 (br d, $^1J_{CF}$ = 242 Hz, B(C_6F_5)$_4$), 142.0 (s, Ar*C*), 141.6 (s, Ar*C*), 137.8 (br t, $^1J_{CF}$ = 243 Hz, B(C_6F_5)$_4$), 128.9 (s, Ar*C*H), 127.4 (s, Ar*C*H), 124.8 (s, C_6H_6), 96.6 (s, C*C*HC), 28.7 (s, *C*HMe_2), 24.3 (s, CH*C*H_3), 24.3 (s, NC(*C*H_3)), 24.0 (s, CH*C*H_3) ppm. ^{19}F NMR (565 MHz, C_6D_5Br, 298K) δ -131.4 (d, $^3J_{FF}$ = 19 Hz, 8F, *o*-C*F*), -160.6 (t, $^3J_{FF}$ = 21 Hz, 4F, *p*-C*F*), -165.6 (t, $^3J_{FF}$ = 21 Hz, 8F, *m*-C*F*) ppm. ^{11}B NMR (193 MHz, C_6D_5Br, 298K) δ -16.0 (s, *B*(C_6F_5)$_4$) ppm. Anal. Calcd for $C_{59}H_{47}MgN_2BF_{20}$ (M = 1199.12 g/mol): C, 59.10; H, 3.95; N, 2.34. Found: C, 59.04; H, 3.60; N, 2.09.

Synthesis of [(BDI)Mg$^+$·(OPEt$_3$)$_2$][B(C$_6$F$_5$)$_4^-$]

[(BDI)Mg$^+$·C_6H_6][B(C_6F_5)$_4^-$] (0.0381 g, 0.0318 mmol) and OPEt$_3$ (0.0095 g, 0.0708 mmol) were dissolved in chlorobenzene (0.5 ml) and layered with hexane (1 ml) in a vial in the glovebox. The crystalline product was isolated after 2 days as colorless crystalline blocks. Yield: 71%, 0.0315 g, 0.0227 mmol. ^{1}H NMR (600 MHz, C_6D_5Br, 298K) δ 7.13 – 7.05 (m, 6H, Ar*H*), 4.76 (s, 1H, CC*H*C), 2.98 (hept, $^3J_{HH}$ = 6.9 Hz, 4H, C*H*Me_2), 1.57 (s, 6H, CCH_3), 1.28 – 1.20 (m, 12H, PC$H_2$$CH_3$), 1.13 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CHCH_3), 1.07 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CHCH_3), 0.65 – 0.52 (m, 18H, PCH_2CH_3) ppm. ^{13}C NMR (151 MHz, C_6D_5Br, 298K) δ 170.2 (s, N*C*(CH_3)), 149.2 (br d, $^1J_{CF}$ = 242.9 Hz, B(C_6F_5)$_4$), 145.0 (s, Ar*C*), 142.0 (s, Ar*C*), 140.4 – 135.6 (m, B(C_6F_5)$_4$), 125.9 (s, Ar*C*H), 124.6 (s, Ar*C*H), 95.2 (s, C*C*HC), 28.0 (s, *C*HMe_2), 25.9 (s, CH*C*H_3), 24.8 (s, CH*C*H_3), 24.7 (s, NC(*C*H_3)), 18.7 (d, $^1J_{CP}$ = 67.6 Hz, PCH_2CH_3), 5.1 (d, $^2J_{CP}$ = 4.6 Hz, PCH_2*C*H_3) ppm. ^{31}P{^{1}H} NMR (243 MHz, C_6D_5Br, 298K) δ 66.3 ppm. ^{19}F NMR (565 MHz, C_6D_5Br, 298K) δ -130.6 – -131.5 (m, 8F, *o*-C*F*), -161.6 (t, $^3J_{FF}$ = 21.0 Hz, 4F, *p*-C*F*), -165.4 (t, $^3J_{FF}$ = 19.6 Hz, 8F, *m*-C*F*) ppm. ^{11}B NMR (193 MHz, C_6D_5Br, 298K) δ -15.6 (s, *B*(C_6F_5)$_4$) ppm. Anal. Calcd for $C_{65}H_{71}MgN_2P_2O_2BF_{20}$ (M = 1389.33 g/mol): C, 56.19; H, 5.15; N, 2.02. Found: C, 56,51; H, 5.13; N, 1.94.

Synthesis of [(BDI)Mg$^+$·(OPEt$_3$)(PhF)][B(C$_6$F$_5$)$_4^-$]

[(BDI)Mg$^+$·C_6H_6][B(C_6F_5)$_4^-$] (0.1763 g, 0.1470 mmol) and OPEt$_3$ (0.0176 g, 0.131 mmol) were dissolved in fluorobenzene (0.5 ml) and heated to 80°C for 2.5 days. The solution was allowed to cool to room temperature and was layered with hexane (0.7 ml). After 24h the glass wall of the reaction vessel was scratched with a spatula initiating crystallization of the biphasic system. After 1h the supernatant was decanted from the colorless crystals. The crystals were washed with hexane (0.5 ml) and dried *in vacuo*. Yield: 82%, 0.1444 g, 0.1069 mmol. ^{1}H NMR (600 MHz, C_6D_5Br, 298K) δ 7.14 – 7.07 (m, 4H, Ar*H*), 7.04 – 7.01 (m, 4H, Ar*H*),

6.98 – 6.89 (m, 3H, Ar*H*), 4.93 (s, 1H, CC*H*C), 2.88 (hept, $^{3}J_{HH}$ = 6.8 Hz, 4H, C*H*Me$_2$), 1.57 (s, 6H, CC*H*$_3$), 1.10 – 1.00 (m, 18H, PC*H*$_2$CH$_3$, CHC*H*$_3$), 0.95 (d, $^{3}J_{HH}$ = 6.8 Hz, 12H, CHC*H*$_3$), 0.25 (dt, $^{3}J_{PH}$ = 18.0, $^{3}J_{HH}$ 7.7 Hz, 9H, PCH$_2$C*H*$_3$) ppm. ^{13}C NMR (151 MHz, C$_6$D$_5$Br, 298K) δ 172.2 (s, N*C*(CH$_3$)), 163.4 (d, $^{1}J_{CF}$ = 242 Hz, *Ph*F), 149.1 (br d, $^{1}J_{CF}$ = 239 Hz, B(*C*$_6$F$_5$)$_4$), 142.7 (s, Ar*C*), 142.2 (s, Ar*C*), 138.1 (pseudo t, $^{1}J_{CF}$ = 252 Hz, B(*C*$_6$F$_5$)$_4$), 130.7 (d, $^{3}J_{CF}$ = 8 Hz, *Ph*F), 127.0 (s, Ar*C*), 125.10 (d, $^{4}J_{CF}$ = 2.7 Hz, *Ph*F), 124.7 (s, Ar*C*), 115.6 (d, $^{2}J_{CF}$ = 21 Hz, *Ph*F), 96.2 (s, C*C*HC), 28.6 (s, *C*HMe$_2$), 25.2 (s, CH*C*H$_3$), 24.3 (s, NC(*C*H$_3$)) , 24.0 (s, CH*C*H$_3$), 18.1 (d, $^{1}J_{PC}$ = 67 Hz, P*C*H$_2$CH$_3$), 4.4 (d, $^{2}J_{PC}$ = 5 Hz, PCH$_2$*C*H$_3$) ppm. ^{31}P NMR (243 MHz, C$_6$D$_5$Br, 298K) δ 72.8 (*P*OEt$_3$) ppm. ^{19}F NMR (565 MHz, C$_6$D$_5$Br, 298K) δ -113.7 (s, 1F, Ph*F*), -130.8 (d, $^{3}J_{FF}$ = 8.0 Hz, 8F, *o*-C*F*), -161.1 (t, $^{3}J_{FF}$ = 20 Hz, 4F, *p*-C*F*), -165.9 (t, $^{3}J_{FF}$ = 20 Hz, 8F, *m*-C*F*) ppm. ^{11}B NMR (193 MHz, C$_6$D$_5$Br, 298K) δ -15.6 (s, *B*(C$_6$F$_5$)$_4$) ppm. Anal. Calcd for $C_{65}H_{61}MgOPN_2BF_{21}$ (M = 1351.27 g/mol): C, 57.78; H, 4.55; N, 2.07. Found: C, 58.69; H, 4.54; N, 2.00.

[(BDI)Mg^{+}·EtC≡CEt][B(C$_6$F$_5$)$_4^{-}$]

[(BDI)Mg(*n*Pr)]$_2$ (0.0825 g, 0.0850 mmol) and [Ph$_3$C^{+}][B(C$_6$F$_5$)$_4^{-}$] (0.1501 g, 0.1627 mmol) were dissolved in chlorobenzene (1.9 ml). The brownish solution was stirred until it became colorless (1 min) and 3-hexyne (0.1 ml) was added. After 18 h all volatiles were removed under reduced pressure resulting in a sticky oil. The material was layered with *n*-hexane (2 ml) and left at room temperature for 30 days. The product was isolated as colorless crystals in a yield of 46% (0.0903 g, 0.0741 mmol). ^{1}H NMR (600 MHz, C$_6$D$_5$Br, 298K) δ 7.13 (t, $^{3}J_{HH}$ = 7.7 Hz, 2H, Ar*H*), 7.03 (d, $^{3}J_{HH}$ = 7.7 Hz, 4H, Ar*H*), 4.98 (s, 1H, CC*H*C), 2.83 (hept, $^{3}J_{HH}$ = 6.8 Hz, 4H, C*H*Me$_2$), 1.60 (s, 6H, CC*H*$_3$), 1.42 (br, 4H, CC*H*$_2$CH$_3$), 1.05 (d, $^{3}J_{HH}$ = 6.9 Hz, 12H, CHC*H*$_3$), 0.97 (d, $^{3}J_{HH}$ = 6.9 Hz, 12H, CHC*H*$_3$), 0.76 (br , 6H, C*H*$_2$CH$_3$) ppm. ^{13}C NMR (151 MHz, C$_6$D$_5$Br, 298K) δ 173.5 (s, N*C*(CH$_3$)), 149.1 (br d, $^{1}J_{CF}$ = 244 Hz, B(*C*$_6$F$_5$)$_4$), 142.5 (s, Ar*C*), 142.4 (s, Ar*C*), 138.1 (pseudo t, $^{1}J_{CF}$ = 243 Hz, B(*C*$_6$F$_5$)$_4$), 127.7 (s, Ar*C*), 125.2 (s, Ar*C*), 97.0 (s, C*C*HC), 28.9 (s, *C*HMe$_2$), 24.6 (s, CH*C*H$_3$), 24.6 (s, CH*C*H$_3$), 24.5 (s, NC(*C*H$_3$)), 14.5 (s, C*C*H$_2$CH$_3$), 12.9 (s, CH$_2$*C*H$_3$) ppm. The quaternary acetylene carbon atom could not be observed; also not at 333K. ^{19}F NMR (565 MHz, C$_6$D$_5$Br, 298K) δ -130.8 (d, $^{3}J_{FF}$ = 19 Hz, 8F, *o*-C*F*), -160.7 (t, $^{3}J_{FF}$ = 21 Hz, 4F, *p*-C*F*), -165.6 (t, $^{3}J_{FF}$ = 21 Hz, 8F, *m*-C*F*) ppm. ^{11}B NMR (193 MHz, C$_6$D$_5$Br, 298K) δ -15.6 (s, *B*(C$_6$F$_5$)$_4$). Anal. Calcd. for $C_{59}H_{51}MgBF_{20}N_2$ (M=1203.15 g/mol): C 58.90, H 4.27, N 2.33; found: C 58.30, H 4.20, N 2.25. Although the C value is outside the range viewed as establishing analytical purity, it is provided to illustrate the best value obtained to date.

Synthesis of $[(BDI)H_2^+][B(C_6F_5)_4^-]$

A mixture of $[H(OEt_2)_2^+][B(C_6F_5)_4^-]$ (1.0556 g, 1.2744 mmol) and BDI-H (0.5869 g, 1.4018 mmol) was dissolved in chlorobenzene (4 ml) and the resulting colorless solution was stirred over night at room temperature. All volatiles were removed *in vacuo*. The resulting white sticky solid was triturated with hexane (2x2 ml). Drying *in vacuo* afforded $[(BDI)H_2^+][B(C_6F_5)_4^-]$ as a fine white solid in quantitative yield (1.3658 g, 1.2431 mmol).

^{1}H NMR (600 MHz, C_6D_5Br, 298K): δ major isomer: 7.10 (t, $^3J_{HH}$ = 8 Hz, 2H, Ar*H*), 6.93 (s, 2H, N*H*), 6.85 (d, $^3J_{HH}$ = 8 Hz, 4H, Ar*H*), 4.39 (s, 1H, C*H*), 2.37 (hept, $^3J_{HH}$ = 7 Hz, 4H, C*H*Me$_2$), 2.10 (s, 6H, C*Me*), 0.92 (d, $^3J_{HH}$ = 7 Hz, 12H, CH*Me$_2$*), 0.72 (d, $^3J_{HH}$ = 7 Hz, 12H, CH*Me$_2$*). Minor isomer: 7.20 (t, $^3J_{HH}$ = 8 Hz, 1H, Ar*H*), 7.14 (d, $^3J_{HH}$ = 8 Hz, 2H, Ar*H*), 6.98 (d, $^3J_{HH}$ = 8 Hz, 2H, Ar*H*), 5.05 (bs, 1H, C*H*), 2.69 (hept, $^3J_{HH}$ = 7 Hz, 2H, C*H*Me$_2$), ~2.37 (omitted by major isomer, 2H, C*H*Me$_2$), 2.15 (bs, 3H, C*Me*), 1.77 (bs, 3H, C*Me*), 1.10 (d, $^3J_{HH}$ = 7 Hz, 6H, CH*Me$_2$*), 1.09 (d, $^3J_{HH}$ = 7 Hz, 6H, CH*Me$_2$*), 0.96 (d, $^3J_{HH}$ = 7 Hz, 6H, CH*Me$_2$*), 0.89 (d, $^3J_{HH}$ = 7 Hz, 6H, CH*Me$_2$*) ppm. Both NH signals and one ArH signal could not be observed. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_5Br, 298K): δ 172.31 (2x *C*(CMe$_3$)=NAr), 148.9 (d, $^1J_{CF}$ = 245 Hz, $[B(C_6F_5)_4^-]$), 144.89 (2x *C*-Ar), 136.8 (d, $^1J_{CF}$ = 245 Hz, $[B(C_6F_5)_4^-]$), 131.0 (2x *C*H-Ar), 124.74 (4x *C*H-Ar), 92.50 (*C*H), 28.81 (4x *C*HMe$_2$), 24.27 (4x CH*Me$_2$*), 22.88 (2x CMe$_2$), 22.70 (4xCH*Me$_2$*) ppm. $^{19}F\{^1H\}$ NMR (565 MHz, C_6D_5Br, 298K): δ -131.6 (m, 8F, *o*-C*F,* $[B(C_6F_5)_4^-]$), -161.9 (t, $^3J_{FF}$ = 21 Hz, 4F, *p*-C*F,* $[B(C_6F_5)_4^-]$), -165.8 (m, 8F, *m*-C*F,* $[B(C_6F_5)_4^-]$) ppm. $^{11}B\{^1H\}$ NMR (193 MHz, C_6D_5Br, 298K): δ -16.1 (s, $[B(C_6F_5)_4^-]$). ppm. Anal. Calcd. for $C_{53}H_{43}BF_{20}N_2$ (M=1098.72 g/mol): C, 57.94; H, 3.94; N, 2.55. Found: C, 58.22; H, 3.80; N, 2.46.

Synthesis of $[(BDI)Ca^+{\cdot}C_6H_6][B(C_6F_5)_4^-]$

A solution of *bis*[*p-t*Bu-benzyl]calcium (85.4 mg, 0.255 mmol) in chlorobenzene (2 ml) was added to a stirred solution of $[(BDI)H_2^+][B(C_6F_5)_4^-]$ (192.4 mg, 0.232 mmol) in chlorobenzene (1 ml). A yellow slime formed, which dissolved again after the mixture was heated to 65°C over night. All volatiles were removed *in vacuo*. The resulting yellow-brown foam was dissolved in benzene (0.5 mL) and layered with hexane (0.6 ml). Upon storage at room temperature small crystals growed, which were washed with a mixture of benzene/hexane (1:1) and dried *in vacuo*. Yield: 23%, 64.9 mg, 0.053 mmol. ^{1}H NMR (600 MHz, C_6D_6, 298K): δ 7.16 (s, 6H, benzene), 7.09 (t, $^3J_{HH}$ = 8 Hz, 2H, Ar*H*), 7.01 (d, $^3J_{HH}$ = 8 Hz, 4H, Ar*H*), 4.68 (s, 1H, C*H*), 2.51 (hept, $^3J_{HH}$ = 7 Hz, 4H, C*H*Me$_2$), 1.40 (s, 6H, C*Me*), 1.02 (d, $^3J_{HH}$ = 7 Hz, 12H, CH*Me$_2$*), 0.95 (d, $^3J_{HH}$ = 7 Hz, 12H, CH*Me$_2$*) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 298K): δ 167.7 (2x

C(CMe)=NAr), 149.1 (d, $^{1}J_{CF}$ = 245 Hz, [B(C_6F_5)$_4^-$]), 144.3 (2x *C*-Ar), 141.2 (4x *C*-Ar), 137.3 (d, $^{1}J_{CF}$ = 244 Hz, [B(C_6F_5)$_4^-$]), 128.6 (benzene), 126.3 (2x *C*H-Ar), 124.4 (4x *C*H-Ar), 94.0 (*C*H), 28.8 (4x *C*HMe$_2$), 24.4 (4x CH*Me$_2$*), 24.1 (2x CMe$_2$), 24.0 (4xCH*Me$_2$*) ppm. ^{19}F{^{1}H} NMR (565 MHz, C_6D_6, 298K): δ -131.4 (m, 8F, *o*-C*F*, [B(C_6F_5)$_4^-$]), -161.0 (t, $^{3}J_{FF}$ = 21 Hz, 4F, *p*-C*F*, [B(C_6F_5)$_4^-$]), -165.7 (m, 8F, *m*-C*F*, [B(C_6F_5)$_4^-$]) ppm. ^{11}B{^{1}H} NMR (193 MHz, C_6D_6, 298K): δ -16.0 (s, , [*B*(C_6F_5)$_4^-$]) ppm. Anal. Calcd. for $C_{59}H_{47}BCaF_{20}N_2$ (M=1214.90 g/mol): C, 58.33; H, 3.90; N, 2.31. Found: C, 56.61; H, 3.86; N, 2.01. Although the C value is outside the range viewed as establishing analytical purity, it is provided to illustrate the best value obtained to date.

1.3. NMR Spectra of Synthesized Compounds

1.3.1. Spectra of [(BDI)Mg(nPr)]$_2$

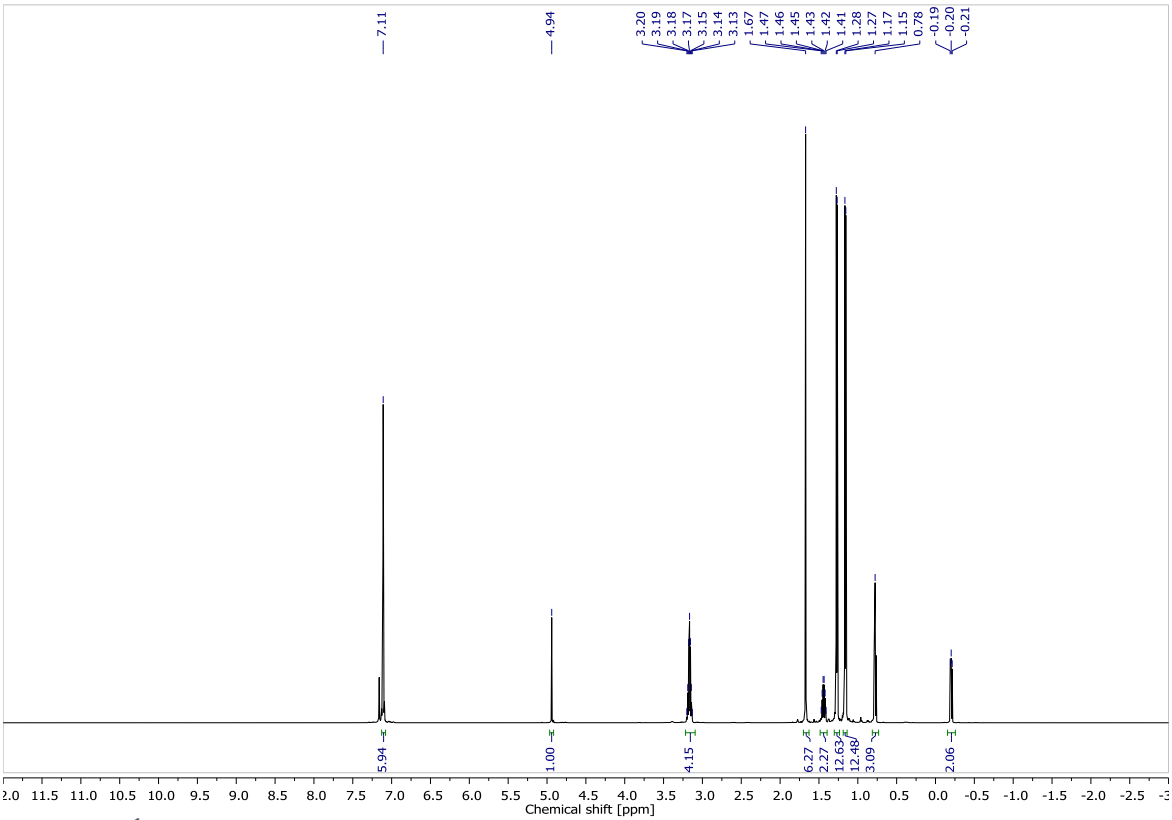


Figure S1: ^{1}H NMR spectrum of [(BDI)Mg(*n*Pr)]$_2$ in C_6D_6

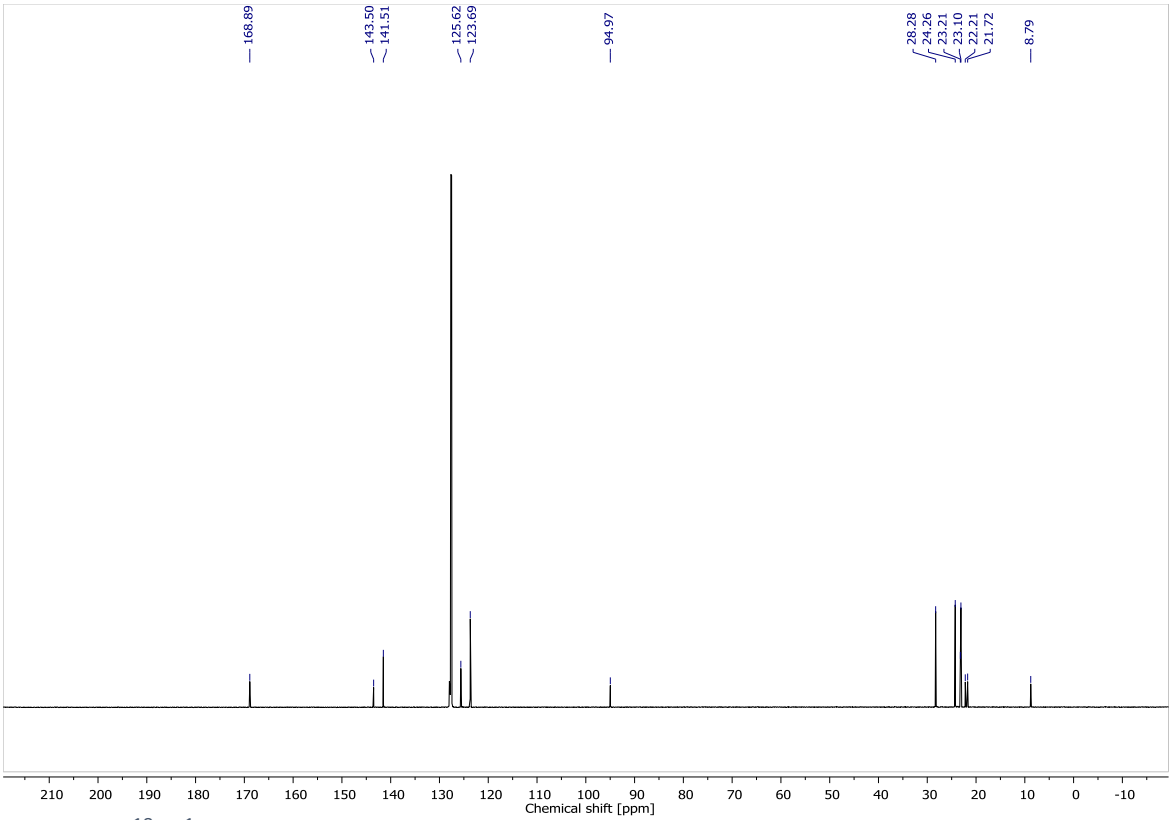


Figure S2: ^{13}C{^{1}H} NMR spectrum of [(BDI)Mg(*n*Pr)]$_2$ in C_6D_6

1.3.2. Spectra of $[(BDI)Mg^{+}][B(C_6F_5)_4^{-}]$

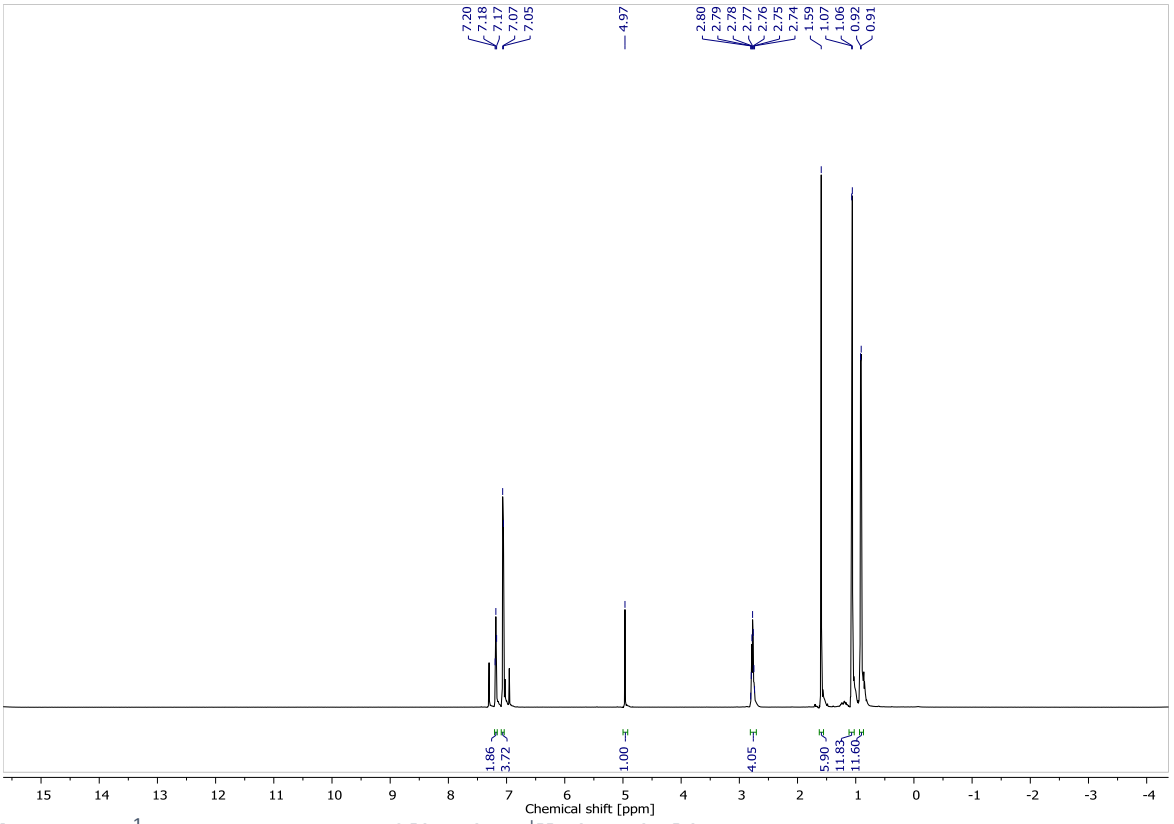


Figure S3: ^{1}H NMR spectrum of $[(BDI)Mg^{+}][B(C_6F_5)_4^{-}]$ in C_6D_5Br

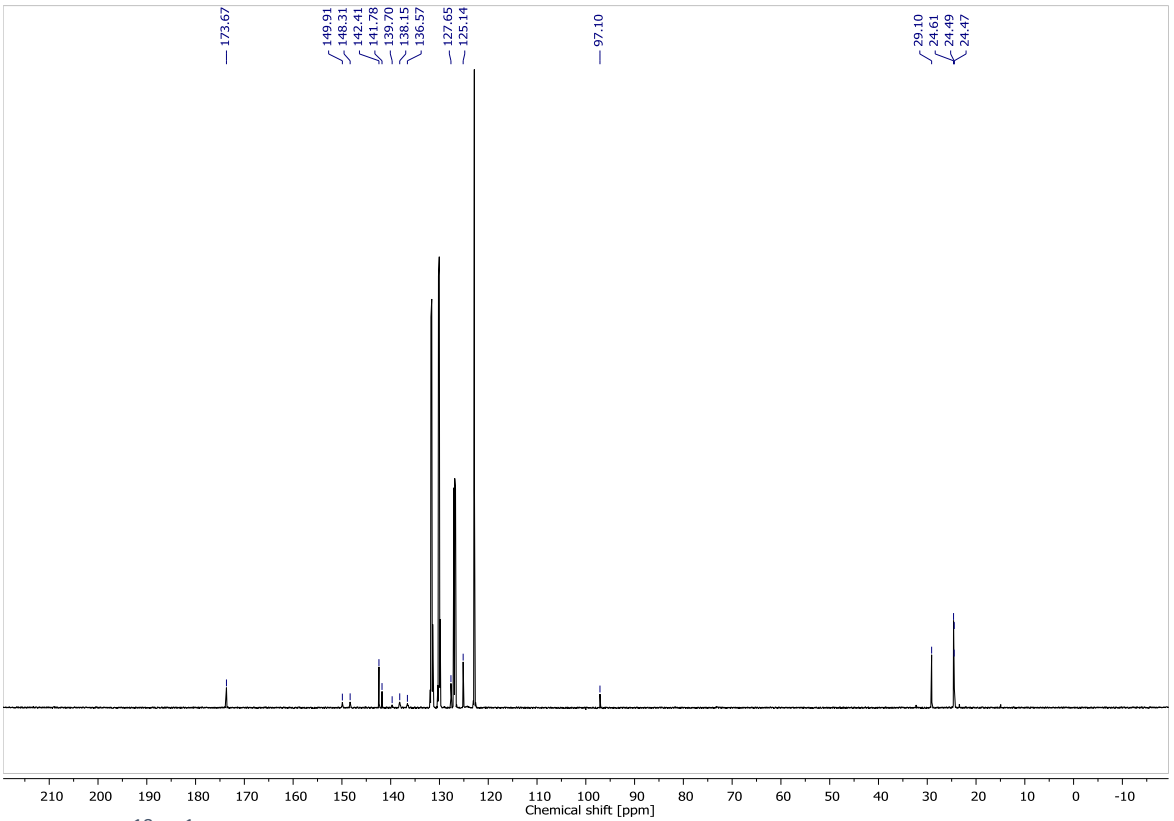


Figure S4: $^{13}C\{^{1}H\}$ NMR spectrum of $[(BDI)Mg^{+}][B(C_6F_5)_4^{-}]$ in C_6D_5Br

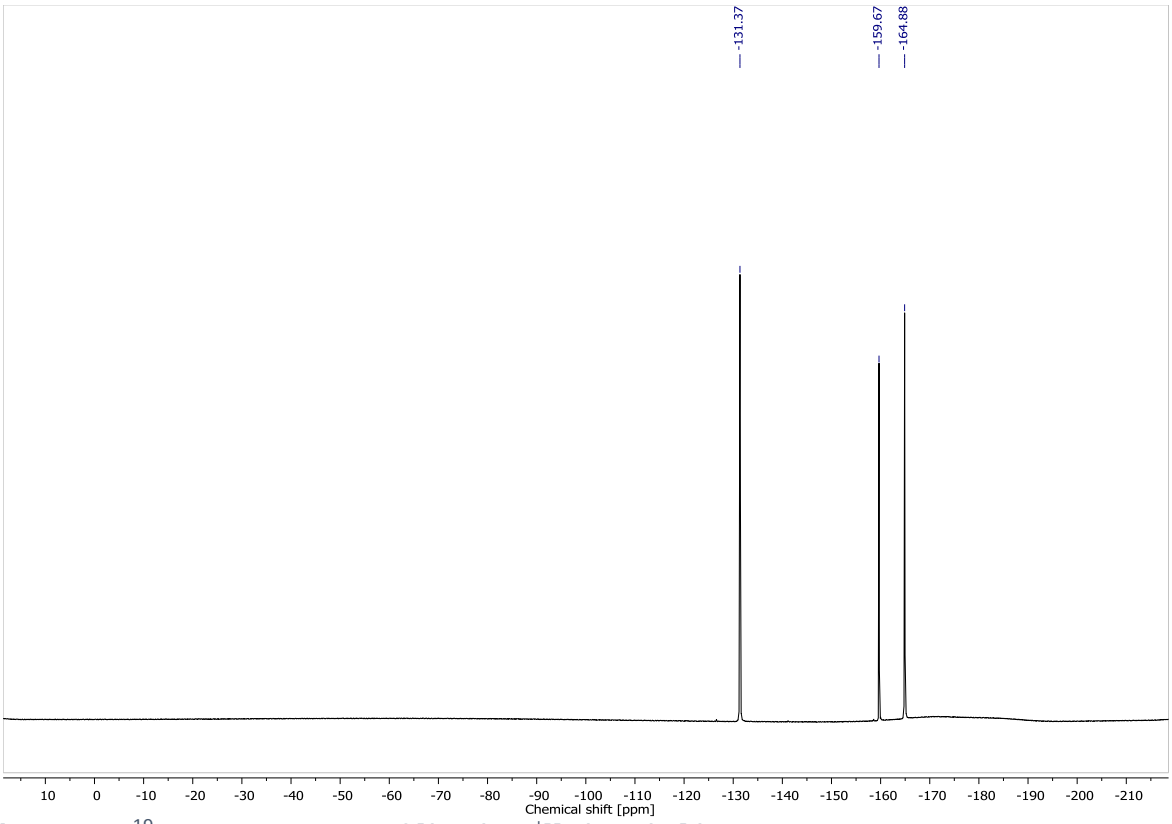


Figure S5: ^{19}F NMR spectrum of $[(BDI)Mg^{+}][B(C_6F_5)_4^{-}]$ in C_6D_5Br

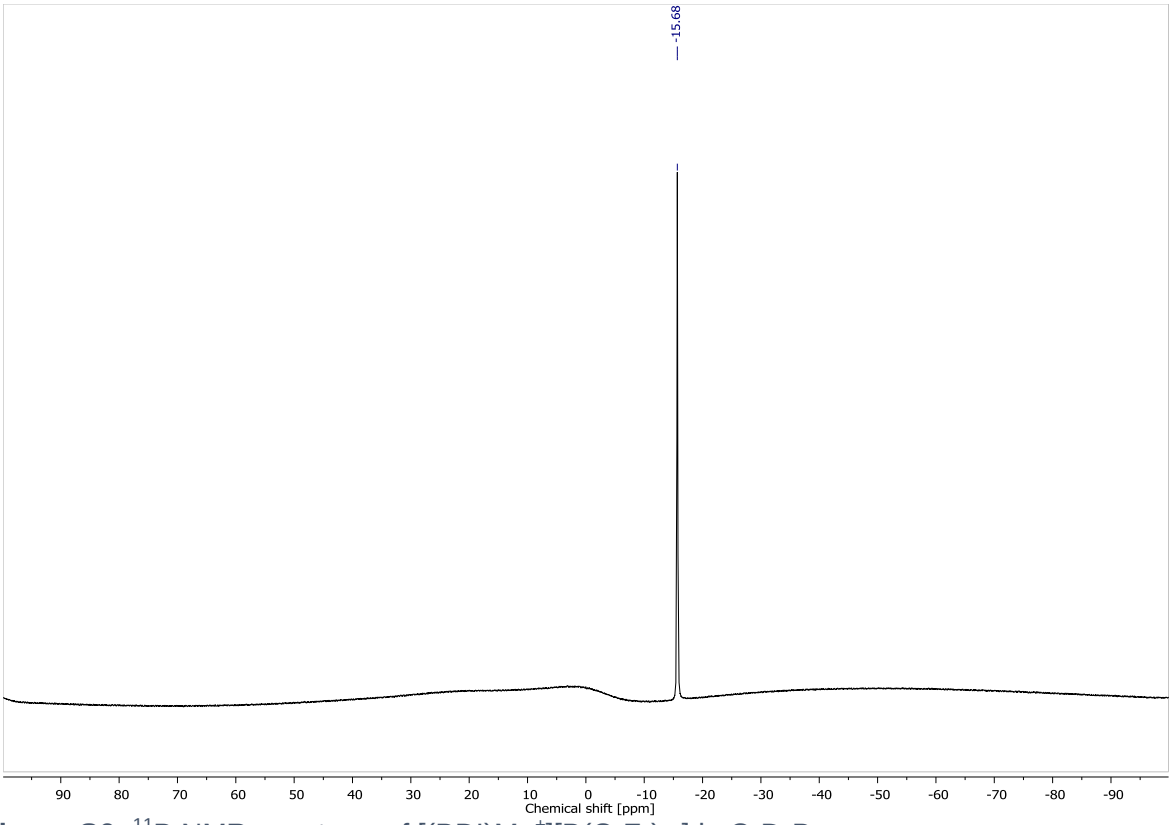


Figure S6: ^{11}B NMR spectrum of $[(BDI)Mg^{+}][B(C_6F_5)_4^{-}]$ in C_6D_5Br

1.3.3. Spectra of $[(BDI)Mg^{+}\cdot C_6H_6][B(C_6F_5)_4^{-}]$

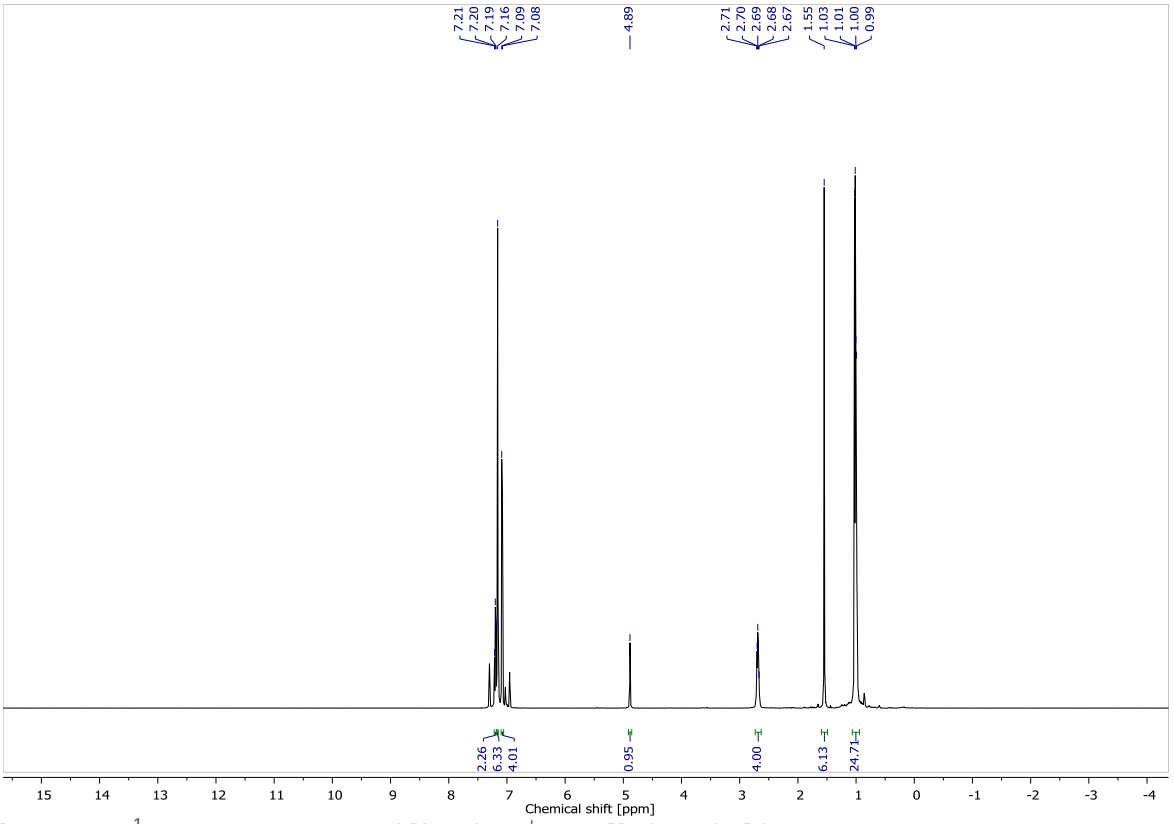


Figure S7: ^{1}H NMR spectrum of $[(BDI)Mg^{+}\cdot C_6H_6][B(C_6F_5)_4^{-}]$ in C_6D_5Br

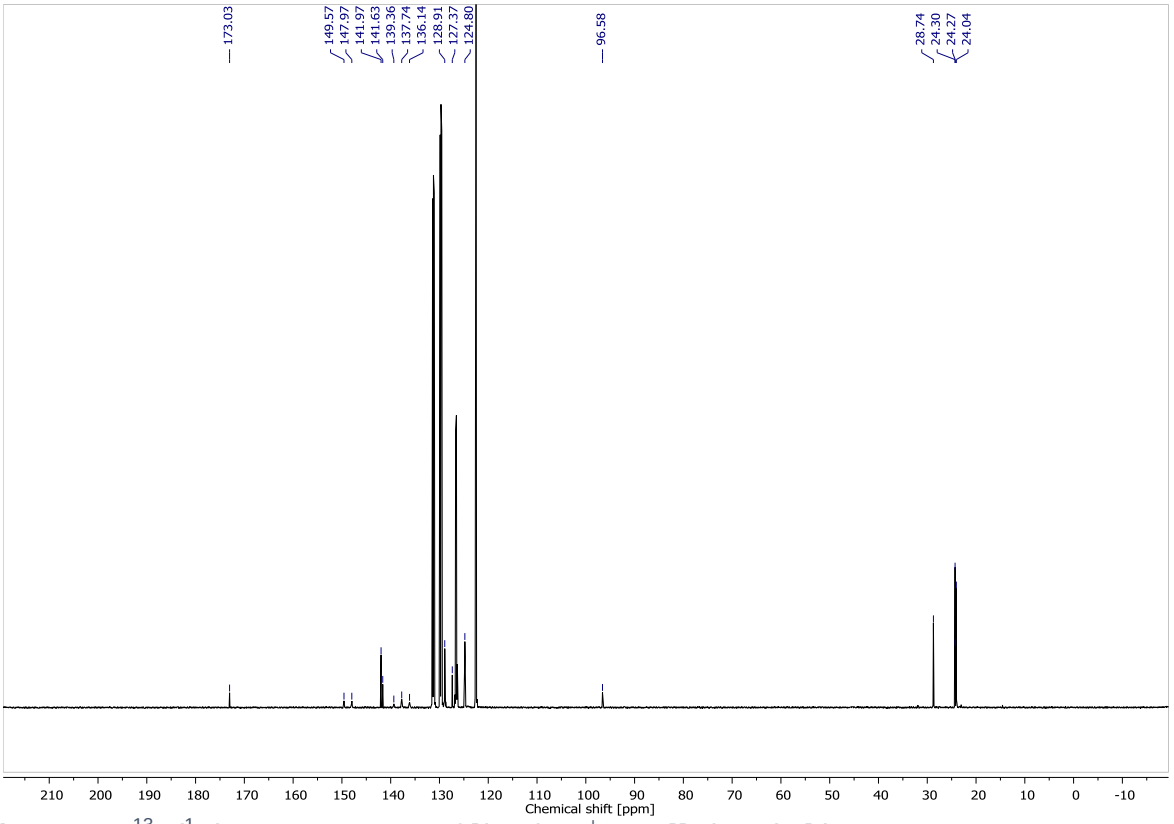


Figure S8: $^{13}C\{^{1}H\}$ NMR spectrum of $[(BDI)Mg^{+}\cdot C_6H_6][B(C_6F_5)_4^{-}]$ in C_6D_5Br

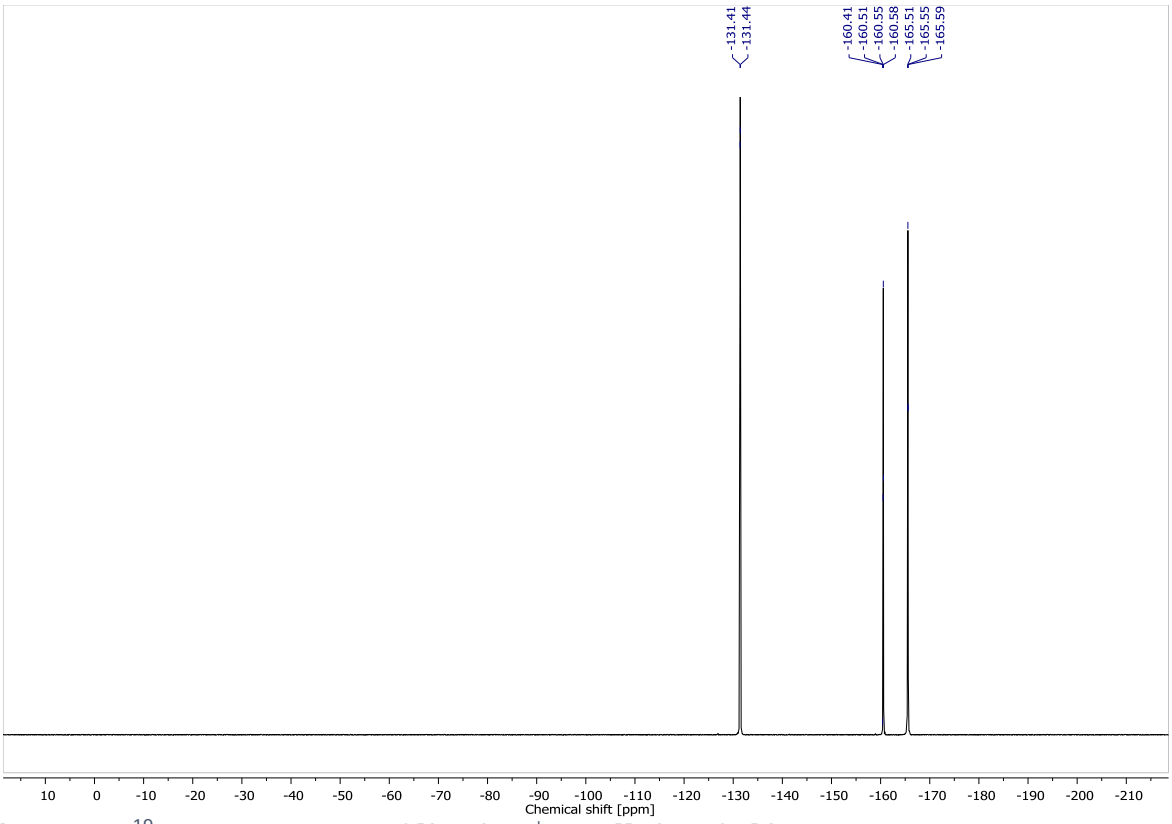


Figure S9: ^{19}F NMR spectrum of $[(BDI)Mg^{+}\cdot C_6H_6][B(C_6F_5)_4^{-}]$ in C_6D_5Br

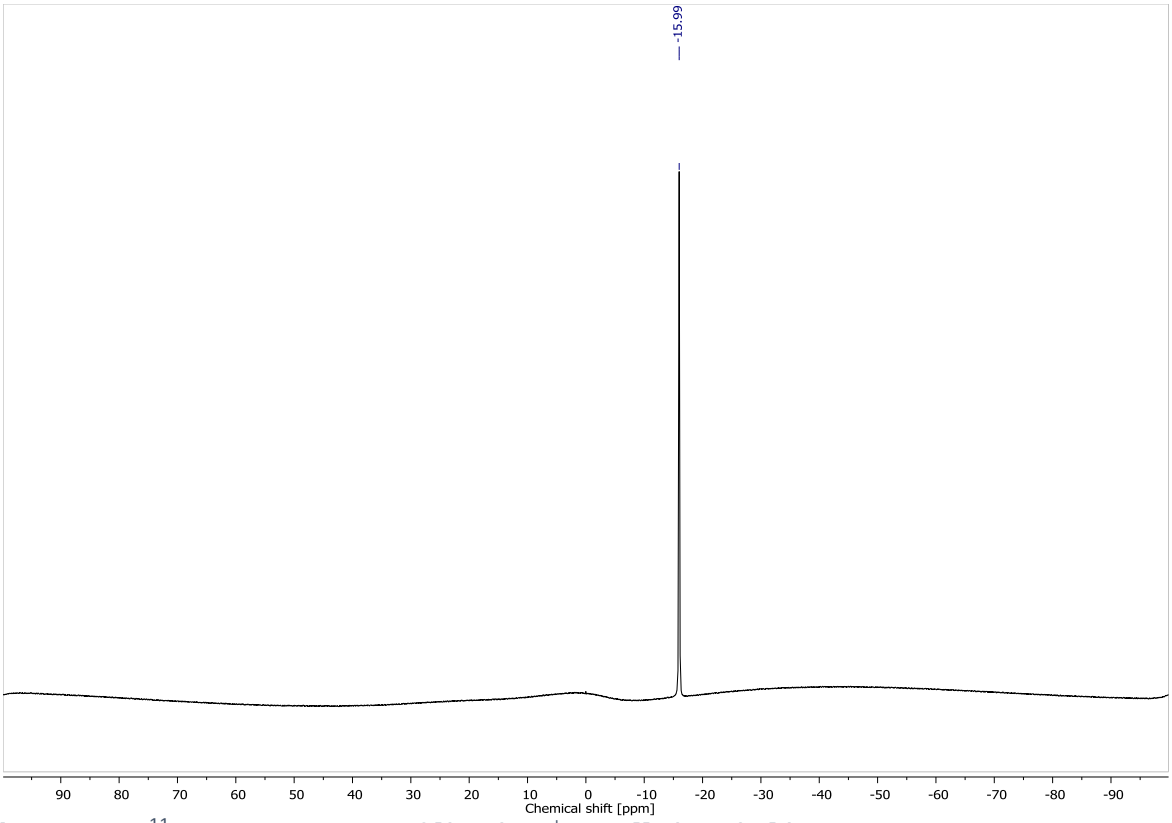


Figure S10: ^{11}B NMR spectrum of $[(BDI)Mg^{+}\cdot C_6H_6][B(C_6F_5)_4^{-}]$ in C_6D_5Br

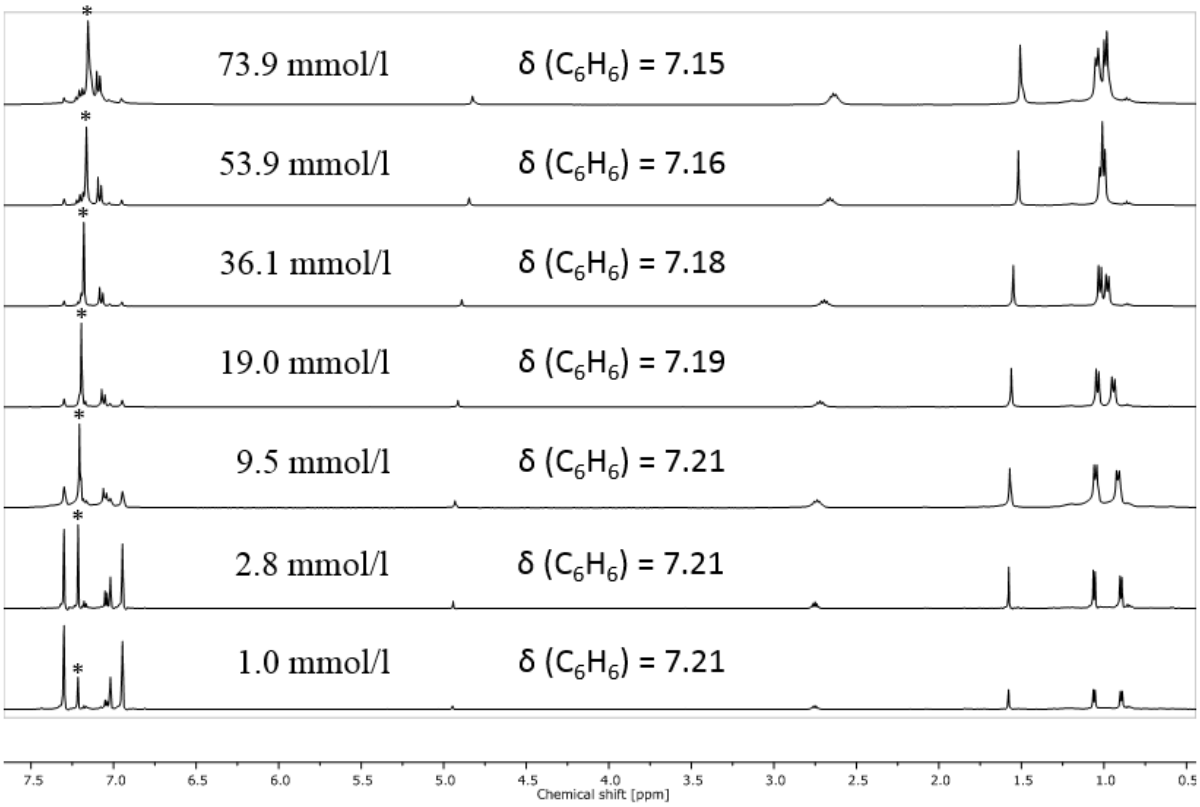


Figure S11: ^{1}H NMR spectra of [(BDI)Mg^{+}·C_6H_6][B(C_6F_5)$_4^{-}$] in C_6D_5Br with varying concentrations. The C_6H_6 signal is marked by *. Note that also the signals of the CH_3 groups belonging to the *iPr* (doublets around 1 ppm) change upon dilution.

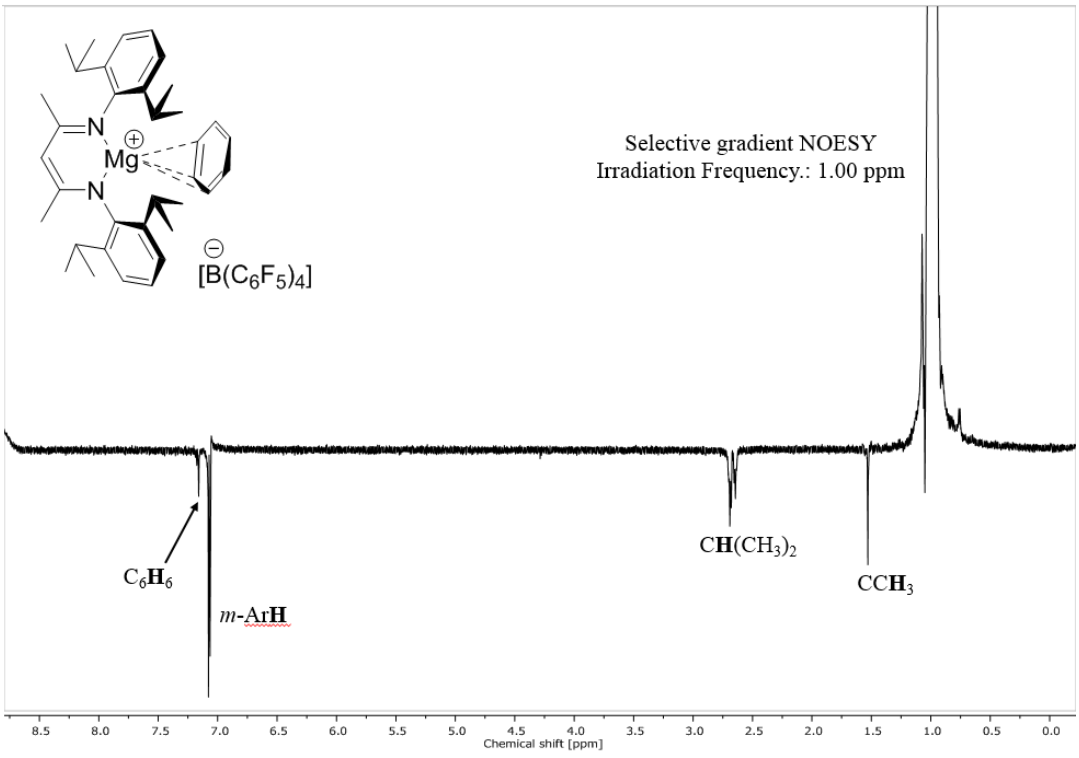


Figure S12: Selective NOESY spectrum (irradiation frequency: 1.00 ppm; *i*Pr-Me signal) of [(BDI)Mg^{+}·C_6H_6][B(C_6F_5)$_4^{-}$] in C_6D_5Br

1.3.4. Spectra of $[(BDI)Mg^{+}\cdot(OPEt_3)(PhF)][B(C_6F_5)_4^{-}]$

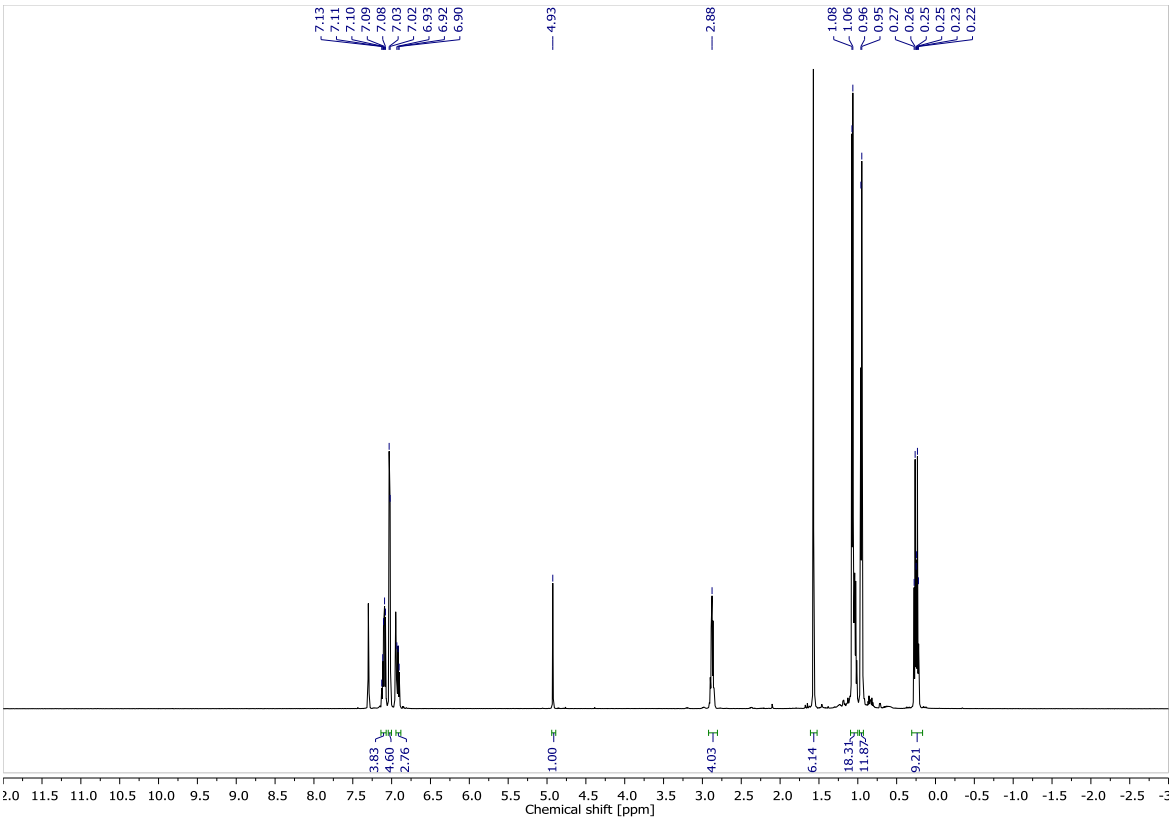


Figure S13: ^{1}H NMR spectrum of $[(BDI)Mg^{+}\cdot(OPEt_3)(PhF)][B(C_6F_5)_4^{-}]$ in C_6D_5Br

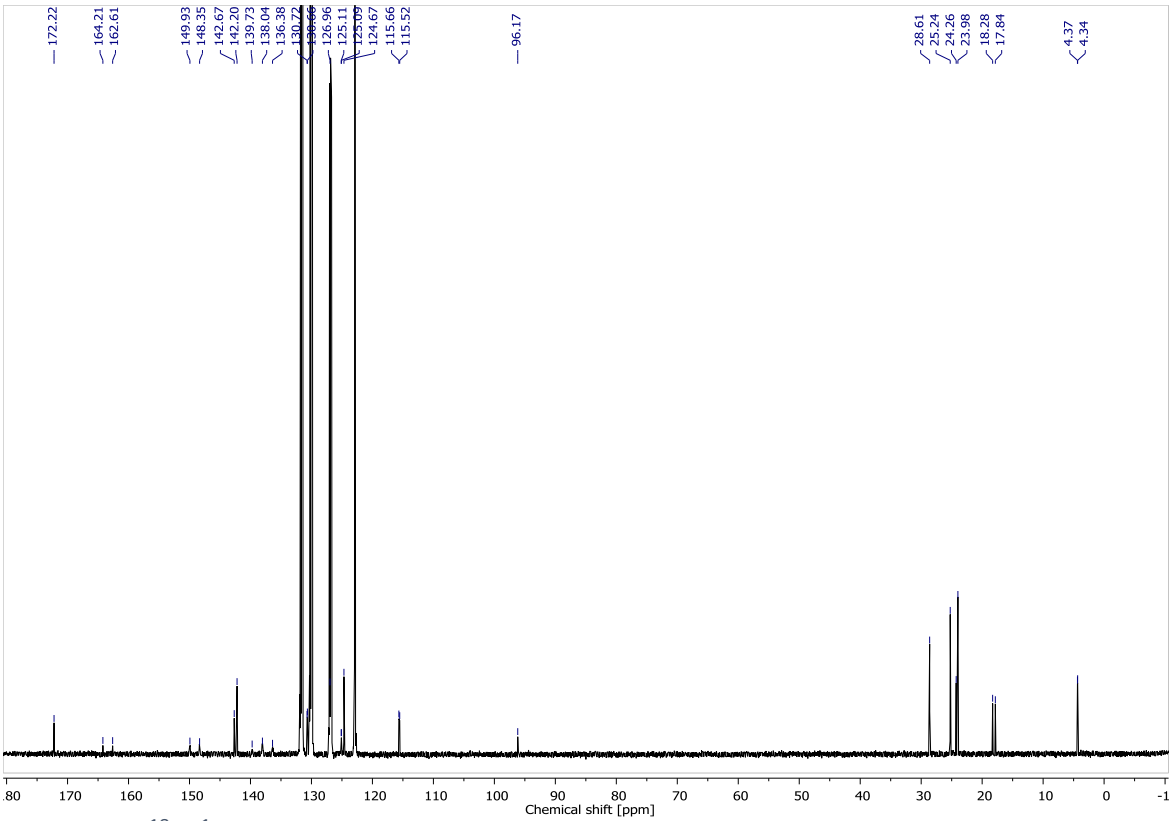


Figure S14: $^{13}C\{^{1}H\}$ NMR spectrum of $[(BDI)Mg^{+}\cdot(OPEt_3)(PhF)][B(C_6F_5)_4^{-}]$ in C_6D_5Br

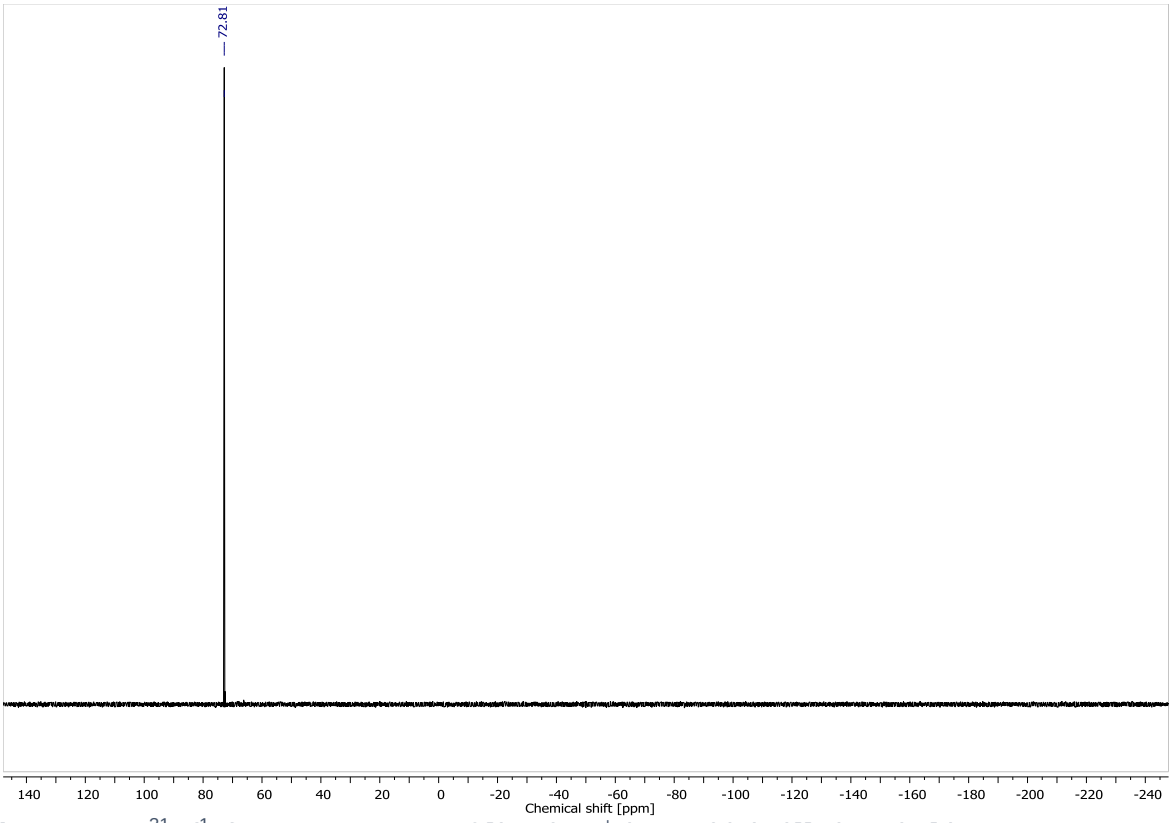


Figure S15: $^{31}P\{^{1}H\}$ NMR spectrum of $[(BDI)Mg^{+}\cdot(OPEt_3)(PhF)][B(C_6F_5)_4^{-}]$ in C_6D_5Br

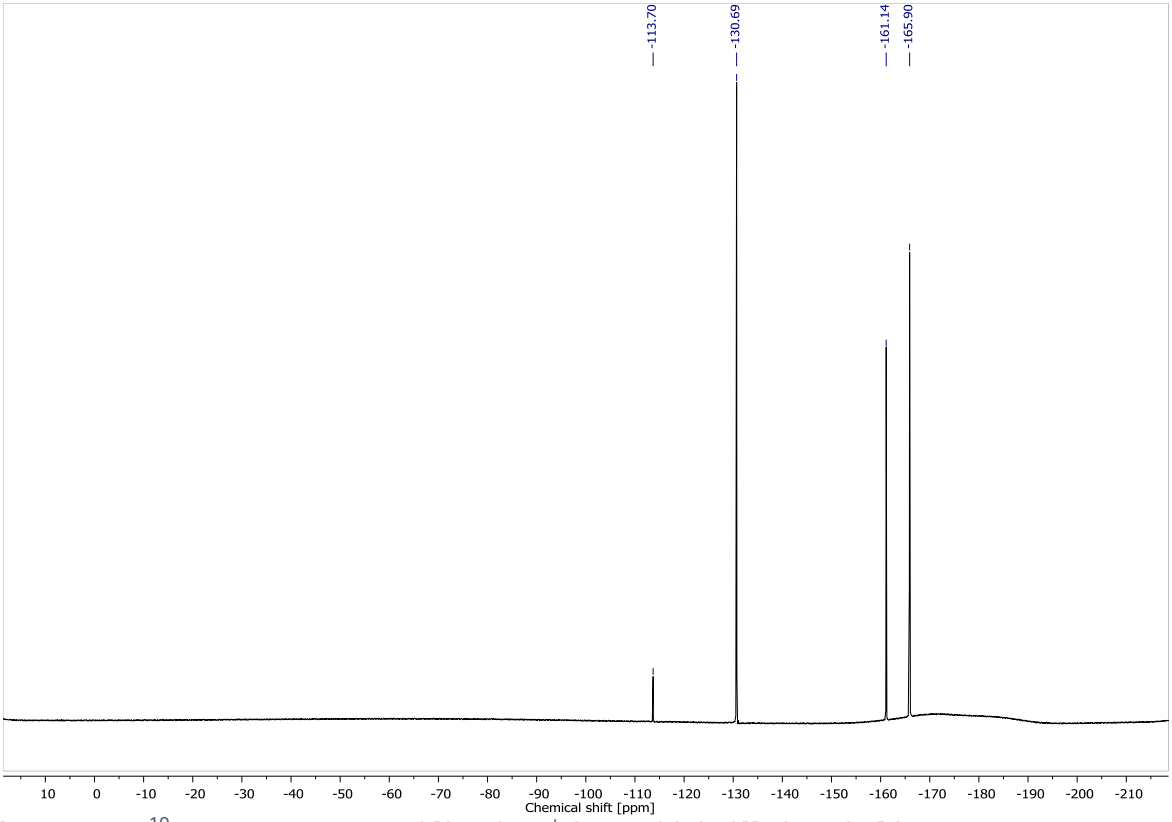


Figure S16: ^{19}F NMR spectrum of $[(BDI)Mg^{+}\cdot(OPEt_3)(PhF)][B(C_6F_5)_4^{-}]$ in C_6D_5Br

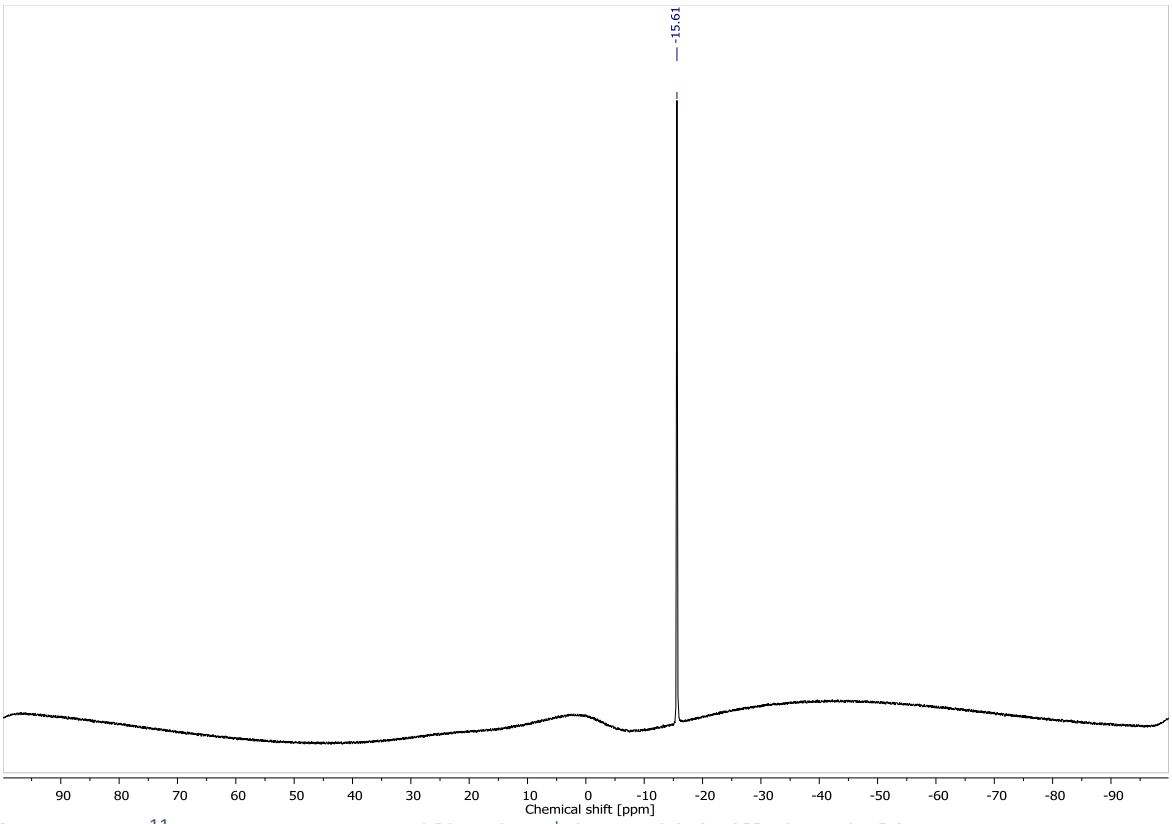


Figure S17: ^{11}B NMR spectrum of [(BDI)Mg^{+}·(OPEt$_3$)(PhF)][B(C$_6$F$_5$)$_4^-$] in C$_6$D$_5$Br

1.3.5. Spectra of [(BDI)Mg^{+}·(OPEt$_3$)$_2$][B(C$_6$F$_5$)$_4^-$]

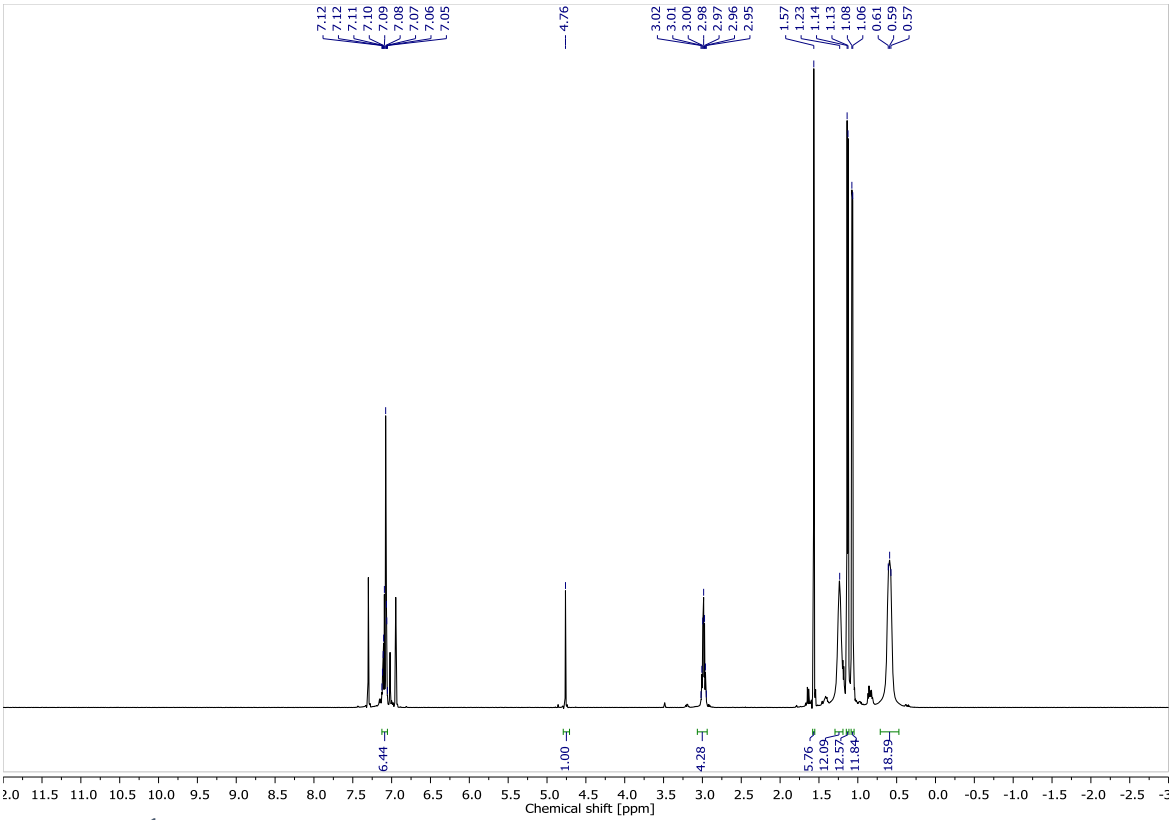


Figure S18: ^{1}H NMR spectrum of [(BDI)Mg^{+}·(OPEt$_3$)$_2$][B(C$_6$F$_5$)$_4^-$] in C$_6$D$_5$Br

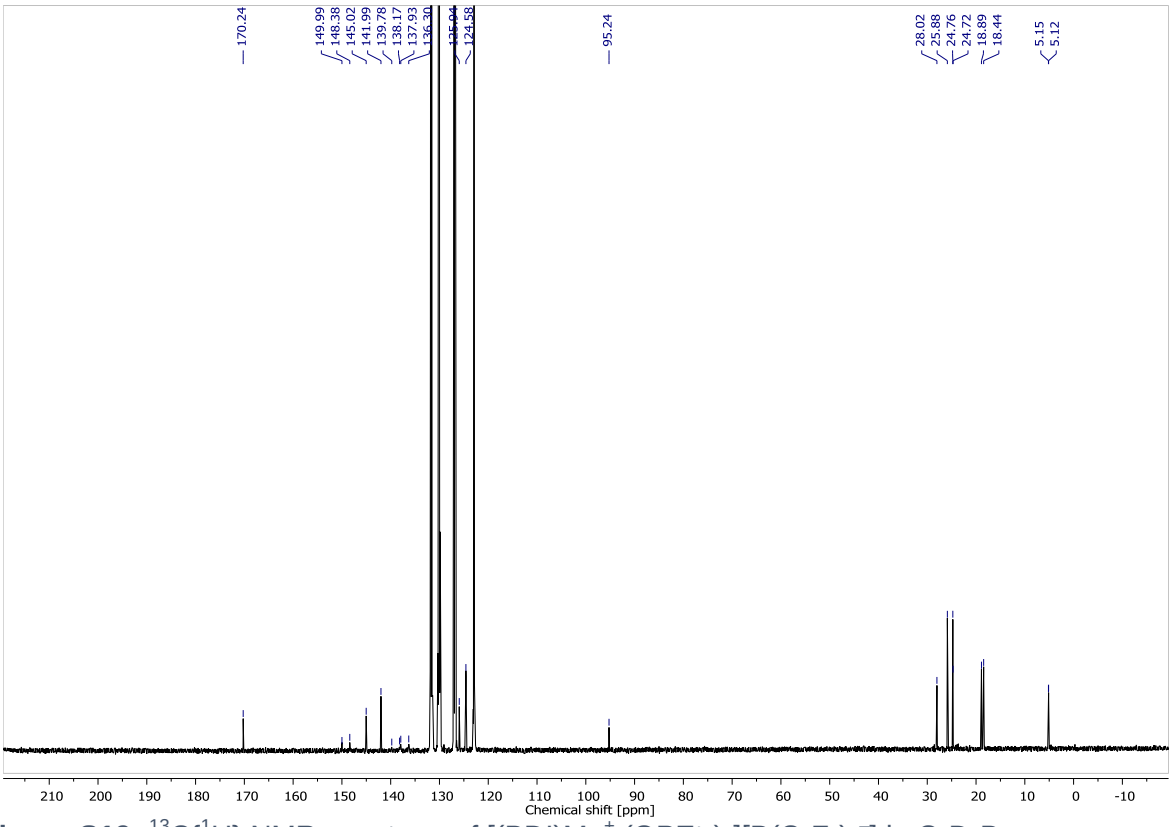


Figure S19: $^{13}C\{^{1}H\}$ NMR spectrum of $[(BDI)Mg^{+}\cdot(OPEt_3)_2][B(C_6F_5)_4^{-}]$ in C_6D_5Br

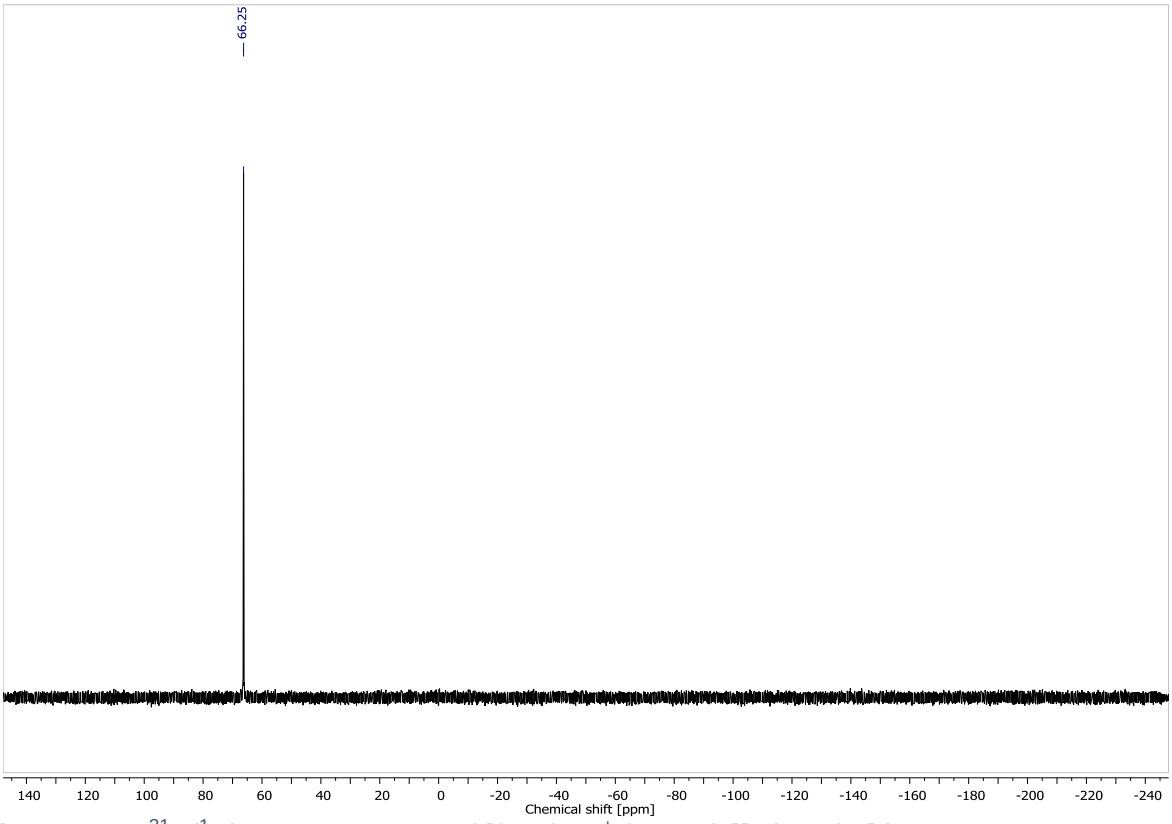


Figure S20: $^{31}P\{^{1}H\}$ NMR spectrum of $[(BDI)Mg^{+}\cdot(OPEt_3)_2][B(C_6F_5)_4^{-}]$ in C_6D_5Br

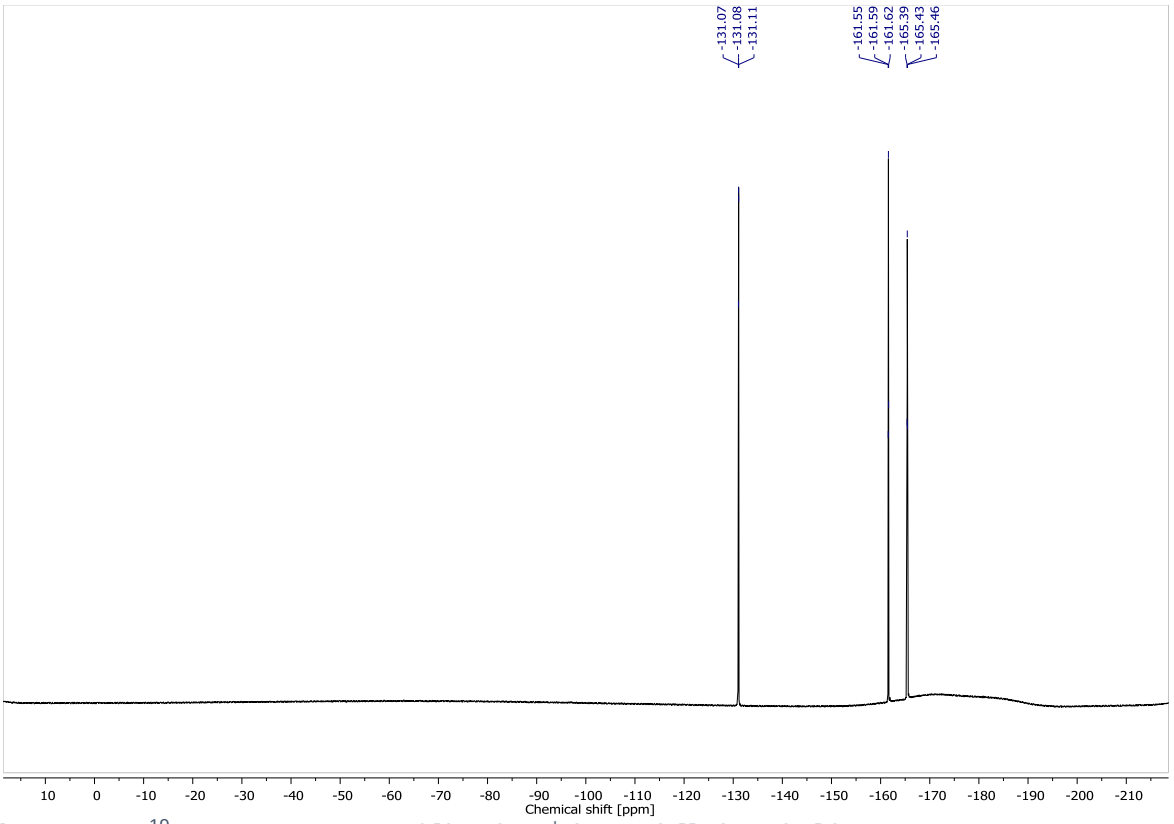


Figure S21: ^{19}F NMR spectrum of $[(BDI)Mg^{+}\cdot(OPEt_3)_2][B(C_6F_5)_4^{-}]$ in C_6D_5Br

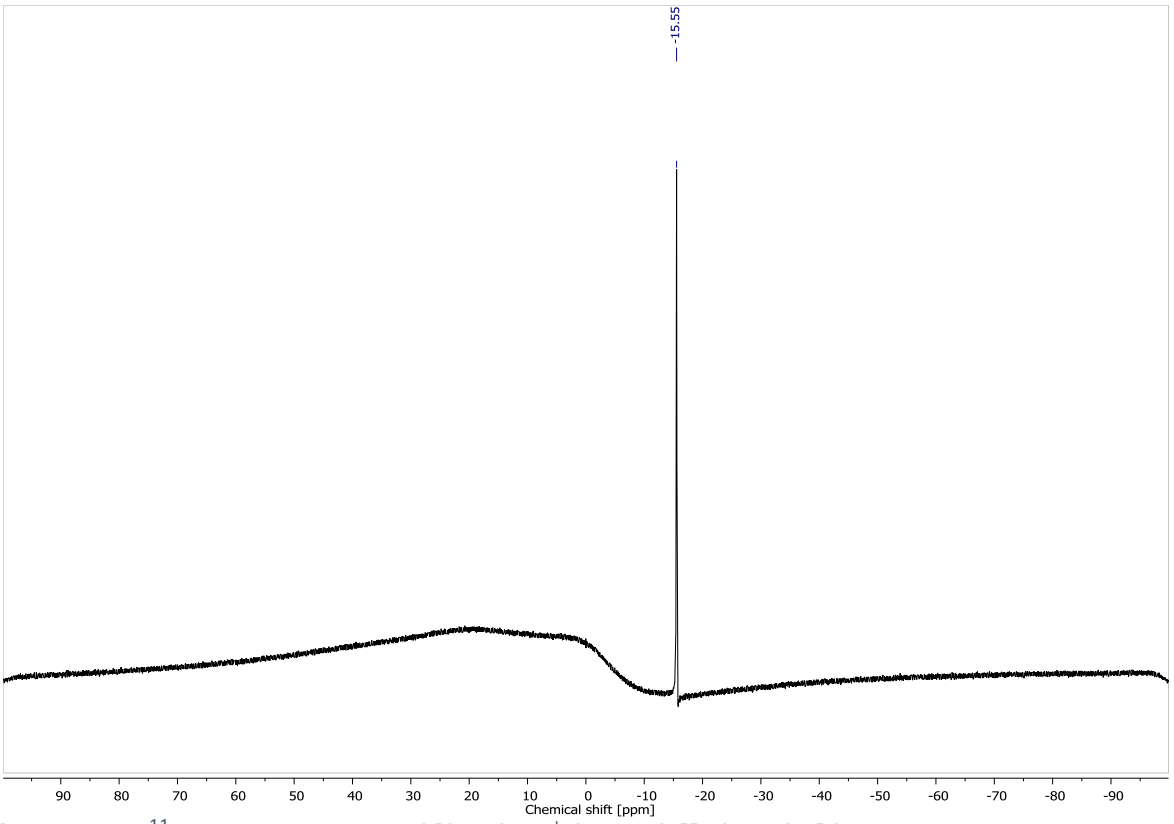


Figure S22: ^{11}B NMR spectrum of $[(BDI)Mg^{+}\cdot(OPEt_3)_2][B(C_6F_5)_4^{-}]$ in C_6D_5Br

1.3.6. Synthesis of [(BDI)Mg$^+$·EtC≡CEt][B(C$_6$F$_5$)$_4^-$]

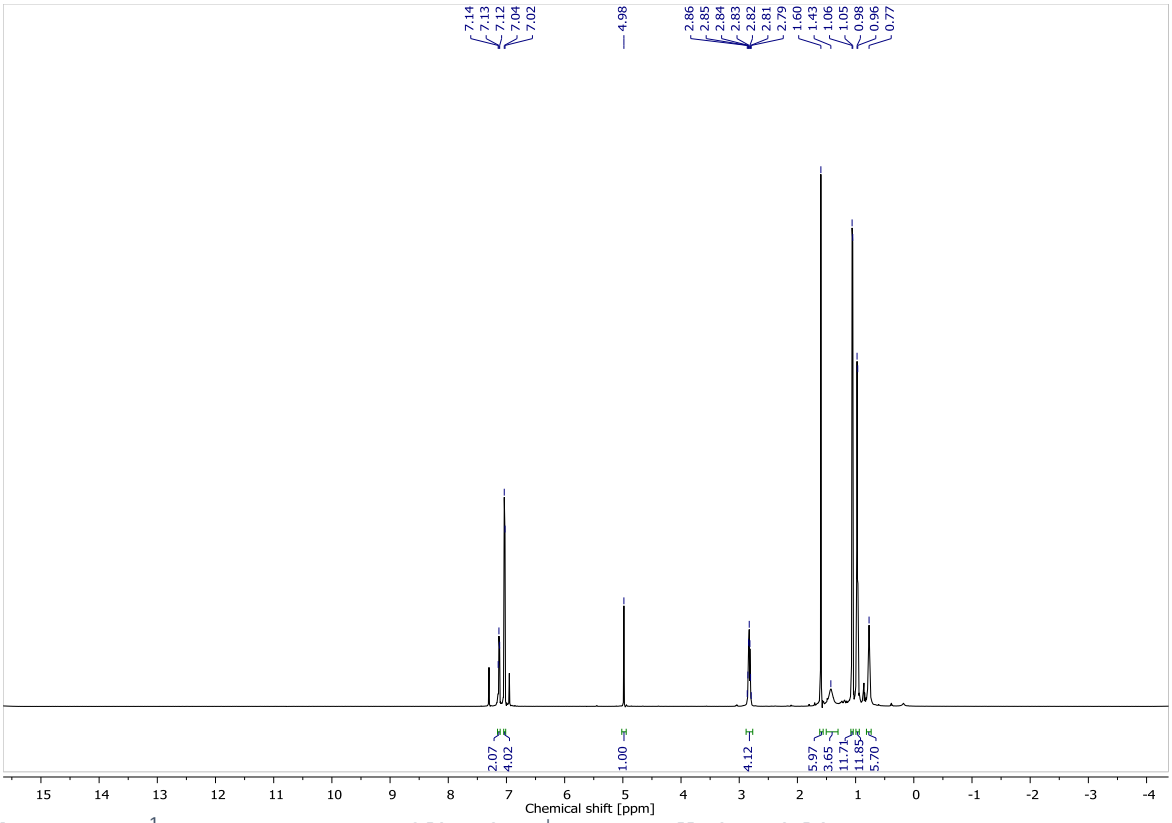


Figure S23: ^{1}H NMR spectrum of [(BDI)Mg$^+$·EtC≡CEt][B(C$_6$F$_5$)$_4$] in C$_6$D$_5$Br

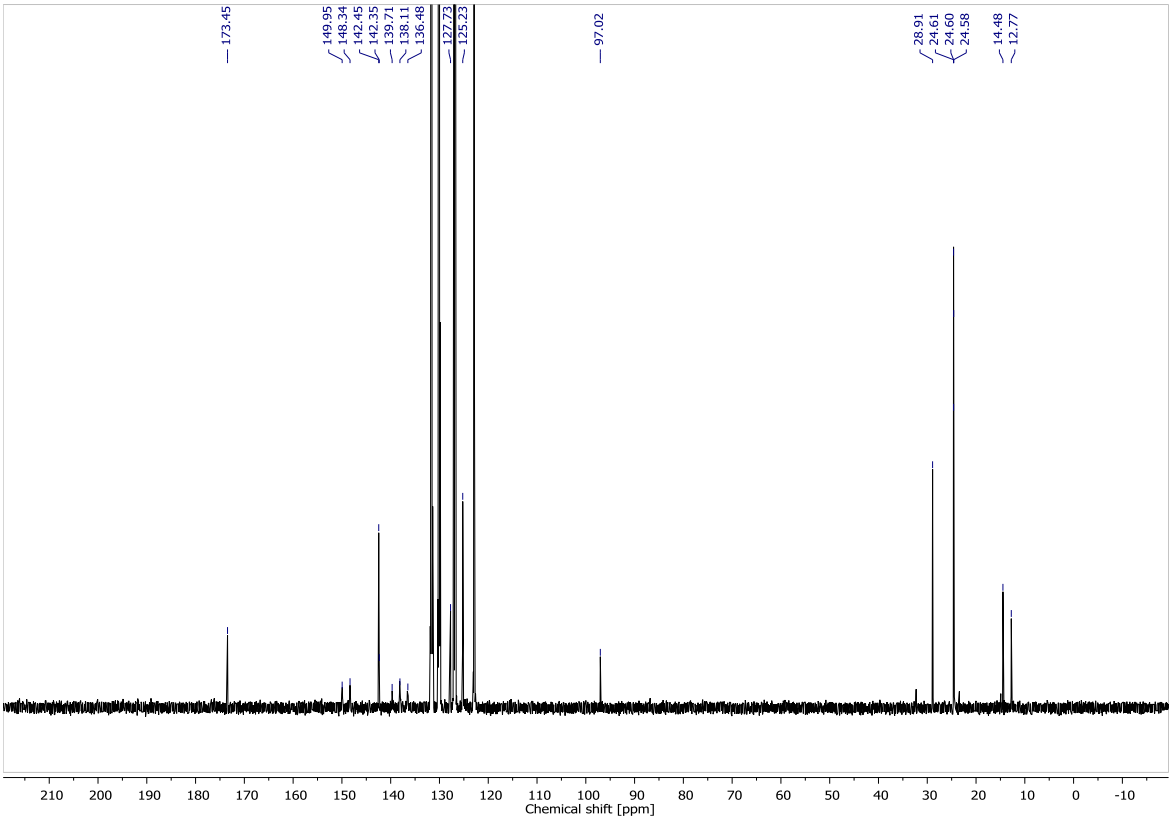


Figure S24: ^{13}C{^{1}H} NMR spectrum of [(BDI)Mg$^+$·EtC≡CEt][B(C$_6$F$_5$)$_4$] in C$_6$D$_5$Br

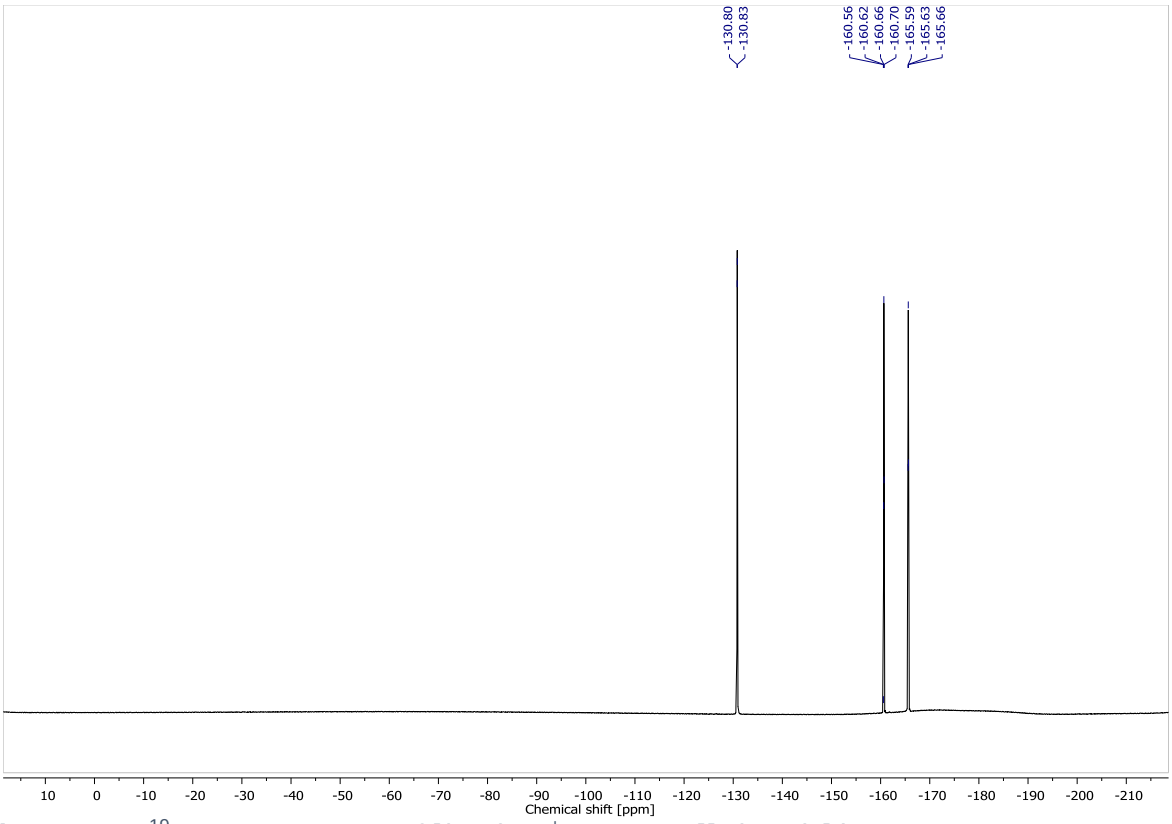


Figure S25: ^{19}F NMR spectrum of [(BDI)Mg^{+}· EtC≡CEt][$B(C_6F_5)_4$] in C_6D_5Br

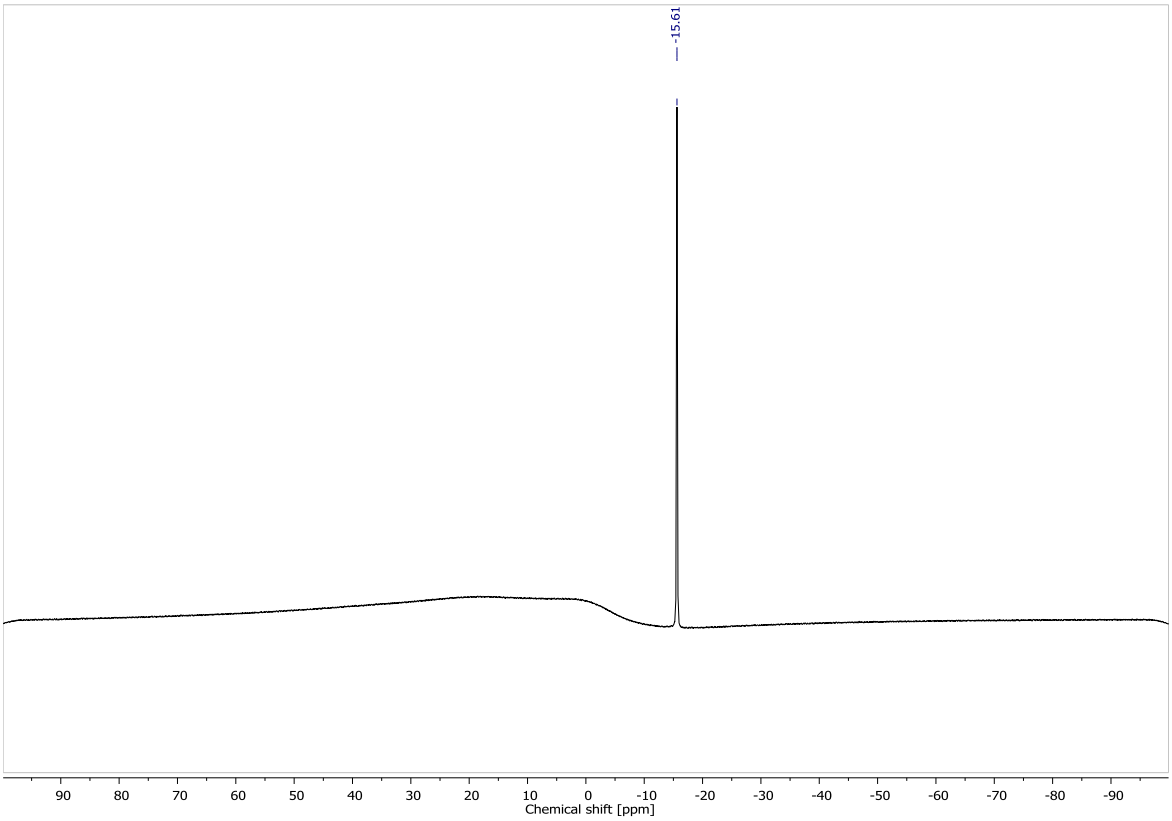


Figure S26: ^{11}B NMR spectrum of [(BDI)Mg^{+}· EtC≡CEt][$B(C_6F_5)_4$] in C_6D_5Br

1.3.7. Spectra of $[(BDI)H_2^+][B(C_6F_5)_4^-]$

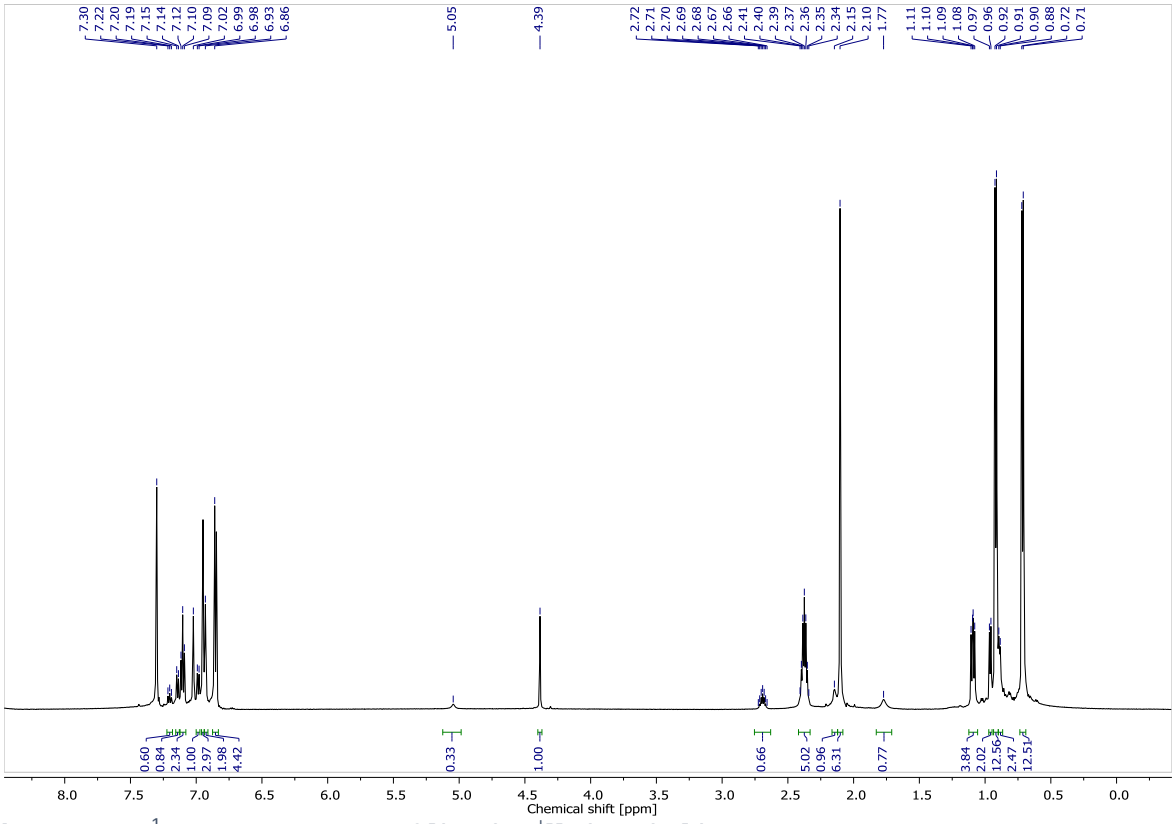


Figure S27: ^{1}H NMR spectrum of $[(BDI)H_2^+][B(C_6F_5)_4^-]$ in C_6D_5Br

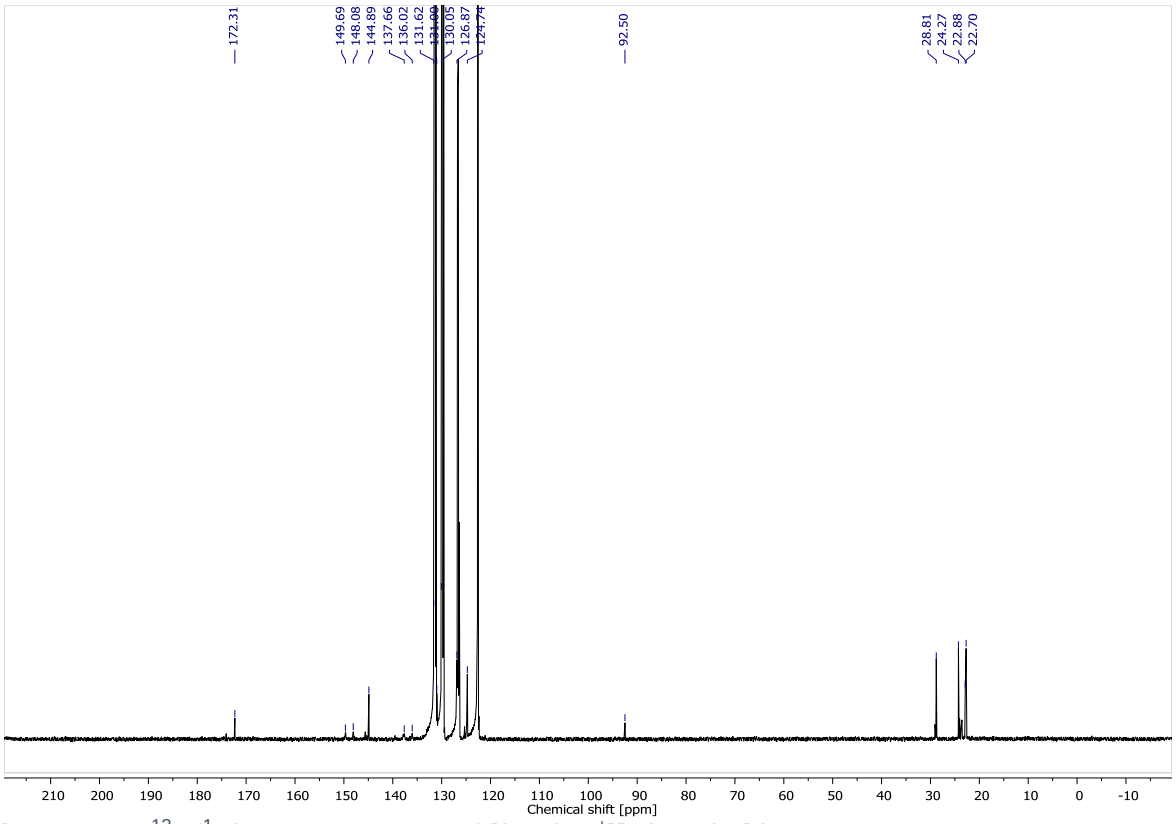


Figure S28: $^{13}C\{^1H\}$ NMR spectrum of $[(BDI)H_2^+][B(C_6F_5)_4^-]$ in C_6D_5Br

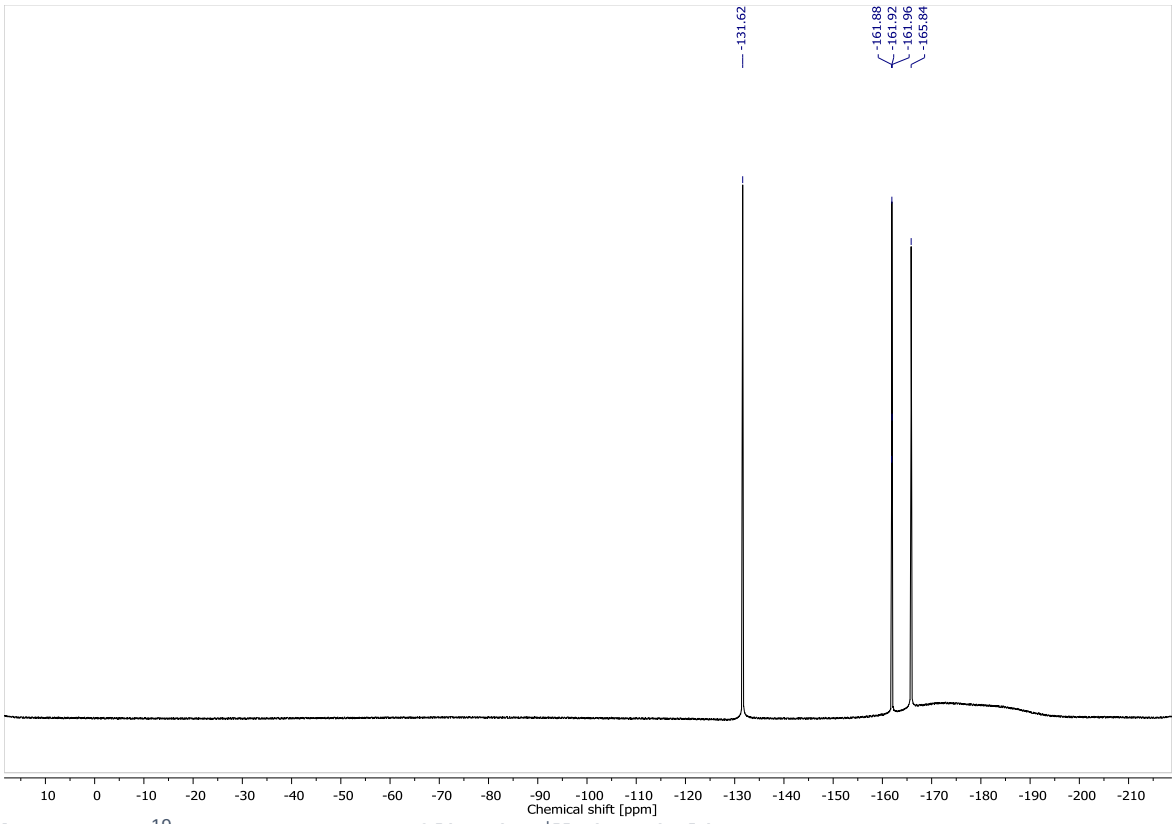


Figure S29: ^{19}F NMR spectrum of $[(BDI)H_2^+][B(C_6F_5)_4^-]$ in C_6D_5Br

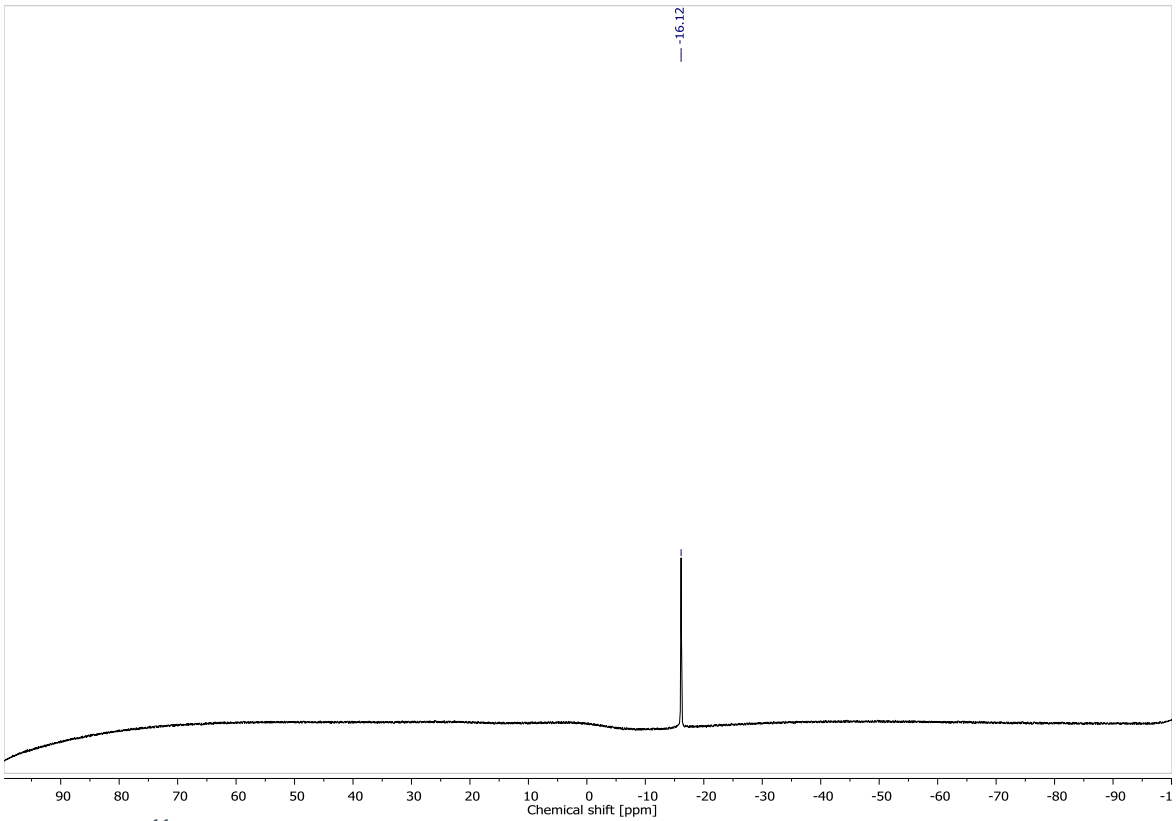


Figure S30: ^{11}B NMR spectrum of $[(BDI)H_2^+][B(C_6F_5)_4^-]$ in C_6D_5Br

1.3.8. Spectra of [(BDI)Ca^{+}·C$_6$H$_6$][B(C$_6$F$_5$)$_4^{-}$]

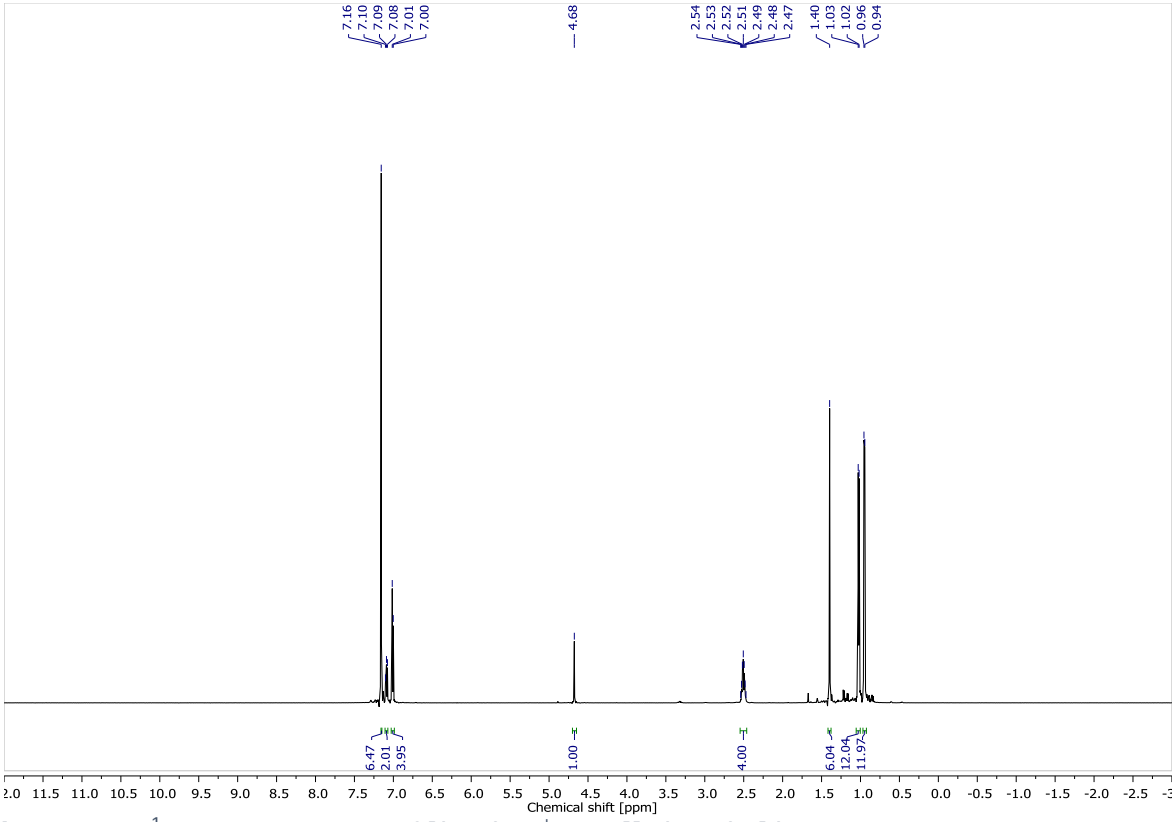


Figure S31: ^{1}H NMR spectrum of [(BDI)Ca^{+}·C$_6$H$_6$][B(C$_6$F$_5$)$_4^{-}$] in C$_6$D$_6$

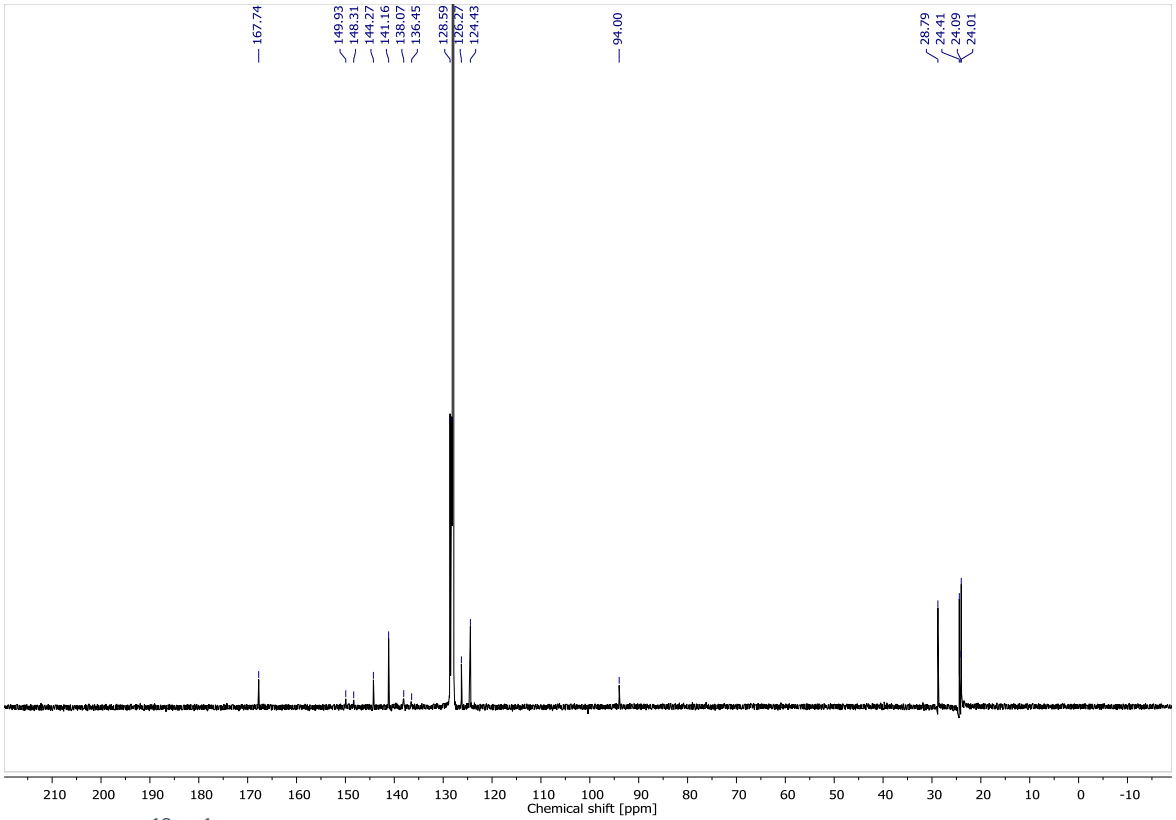


Figure S32: ^{13}C{^{1}H} NMR spectrum of [(BDI)Ca^{+}·C$_6$H$_6$][B(C$_6$F$_5$)$_4^{-}$] in C$_6$D$_6$

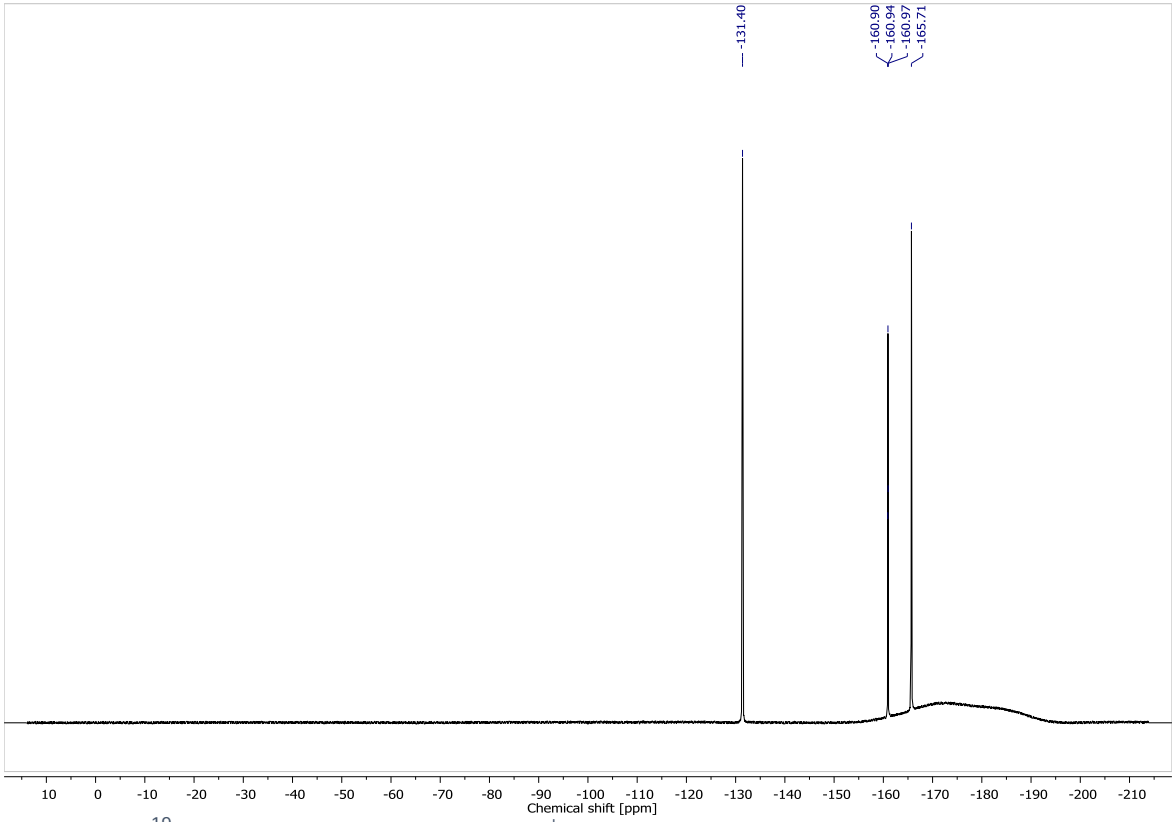


Figure S33: ^{19}F NMR spectrum of [(BDI)Ca^{+}·C_6H_6][B(C_6F_5)$_4^-$] in C_6D_6

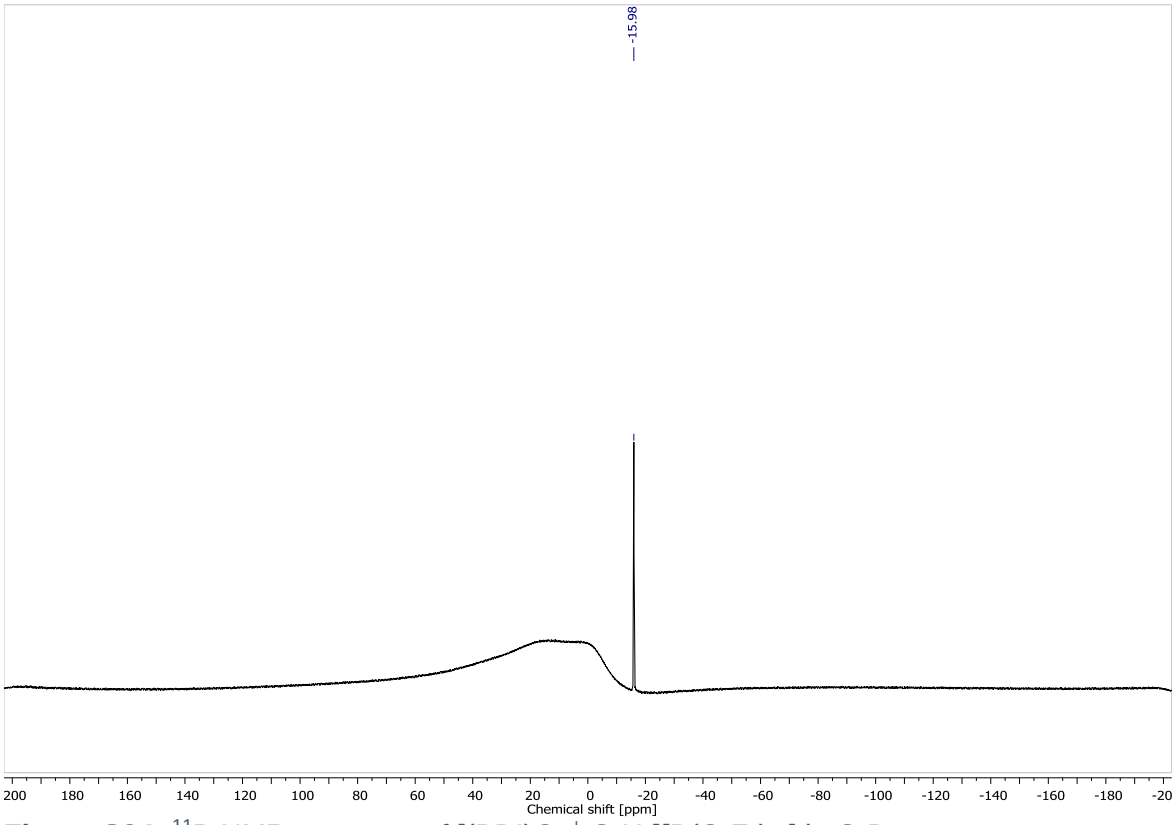


Figure S34: ^{11}B NMR spectrum of [(BDI)Ca^{+}·C_6H_6][B(C_6F_5)$_4^-$] in C_6D_6

1.4 Single Crystal X-Ray Diffraction

Single crystal X–ray diffraction data for all compounds were collected on a SuperNova diffractometer (Rigaku Oxford diffraction) with Atlas S2 detector using a CuK_α microfocus source. All crystals were maintained at 100 K during data collection. Using Olex2,[S5] the structures were solved by Direct Methods (ShelXT)[S6] and refined with ShelXL[S7] using Least Squares minimization. The hydrogen atoms have been placed on calculated positions and were refined isotropically in a riding model unless noted otherwise. The asymmetric unit of $[(BDI)Mg(n\text{Pr})]_2$ contains half a dimer and the two hydrogen atoms at the α-carbon of the *n*-propyl group were localized and refined isotropically. Complex $[(BDI)Mg^+][B(C_6F_5)_4^-]$ crystallizes with two separate molecules in the asymmetric unit with similar geometric parameter. No higher symmetry could be detected. Complex $[(BDI)Mg^+\cdot C_6H_6][B(C_6F_5)_4^-]$ crystallizes with one free benzene molecule in the asymmetric unit which has been refined anisotropically. Complex $[(BDI)Mg^+\cdot(OPEt_3)(PhF)]$ $[B(C_6F_5)_4^-]$ and $[(BDI)Mg^+\cdot(OPEt_3)_2][B(C_6F_5)_4^-]$ crystallize with one complete ion pair in their respective asymmetric units; cocrystallized solvent molecules were not found. In complex $[(BDI)Mg^+\cdot(OPEt_3)_2][B(C_6F_5)_4^-]$, two of the three Et groups of one of the $OPEt_3$ ligands were disordered and refined over two positions with an approximate ratio of 80:20. The C-C bond length of one Et group was idealized (SADI) and refined with Rigid Bond Restraints (RIGU).[S8]

Crystal structure data for the complexes (BDI)Mg(nPr) 1822418, $[(BDI)Mg^+][B(C_6F_5)_4^-]$ 1822419, $[(BDI)Mg^+\cdot C_6H_6][B(C_6F_5)_4^-]$ 1822420, $[(BDI)Mg^+\cdot(OPEt_3)(C_6H_5F)][B(C_6F_5)_4^-]$ 1822422, $[(BDI)Mg^+\cdot(OPEt_3)_2][B(C_6F_5)_4^-]$ 1822423, $[(BDI)Ca^+\cdot C_6H_6][B(C_6F_5)_4^-]$ 1844572, $[(BDI)Mg^+\cdot EtC{\equiv}CEt][B(C_6F_5)_4^-]$ 1844571 and $[(BDI)H_2^+][B(C_6F_5)_4^-]$ 1847903 have been deposited with the Cambridge Crystallographic Data Centre.

Table S1. Crystal data.

Identification code	[(BDI)Mg(*n*Pr)]$_2$	[(BDI)Mg$^+$][B(C$_6$F$_5$)$_4^-$]	[(BDI)Mg$^+$·C$_6$H$_6$] [B(C$_6$F$_5$)$_4^-$]
Empirical formula	$C_{64}H_{96}Mg_2N_4$	$C_{53}H_{41}BF_{20}MgN_2$	$C_{65}H_{53}BF_{20}MgN_2$
Formula weight	970.06	1121.00	1277.21
Temperature/K	100.00(10)	100.01(10)	100
Crystal system	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1
a/Å	11.6151(6)	15.0751(3)	12.6783(4)
b/Å	12.8269(9)	18.2135(4)	13.1414(4)
c/Å	13.1163(9)	19.1996(4)	19.5127(5)
α/°	76.087(6)	79.2972(18)	100.801(2)
β/°	74.884(5)	86.7245(15)	101.644(2)
γ/°	67.493(6)	72.6916(18)	110.656(3)
Volume/Å^3	1721.0(2)	4945.35(18)	2858.37(14)
Z	1	4	2
ρ_{calc}g/cm^3	0.936	1.506	1.484
μ/mm^{-1}	0.565	1.355	1.248
F(000)	532.0	2280.0	1308.0
Crystal size/mm^3	0.23 × 0.14 × 0.11	0.29 × 0.19 × 0.13	0.28 × 0.17 × 0.08
Crystal color	colorless	colorless	colorless
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.07 to 147.434	6.14 to 147.708	7.494 to 136.232
Index ranges	-14 ≤ h ≤ 13, -14 ≤ k ≤ 15, -16 ≤ l ≤ 15	-18 ≤ h ≤ 18, -22 ≤ k ≤ 20, -22 ≤ l ≤ 23	-14 ≤ h ≤ 15, -15 ≤ k ≤ 15, -21 ≤ l ≤ 23
Reflections collected	10517	43018	17441
Independent reflections	6601 [R_{int} = 0.0339, R_{sigma} = 0.0535]	18997 [R_{int} = 0.0425, R_{sigma} = 0.0474]	10342 [R_{int} = 0.0235, R_{sigma} = 0.0335]
Data/restraints/parameters	6601/0/335	18997/0/1407	10342/0/836
Goodness-of-fit on F^2	1.037	1.036	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0511, wR_2 = 0.1388	R_1 = 0.0415, wR_2 = 0.1058	R_1 = 0.0365, wR_2 = 0.0931
Final R indexes [all data]	R_1 = 0.0598, wR_2 = 0.1459	R_1 = 0.0522, wR_2 = 0.1125	R_1 = 0.0401, wR_2 = 0.0963
Largest diff. peak/hole / e Å^{-3}	0.38/-0.40	0.40/-0.31	0.78/-0.29

Table S2. Crystal data (continued).

Identification code	[(BDI)Mg^+·($OPEt_3$)(PhF)][$B(C_6F_5)_4^-$]	[(BDI)Mg^+·($OPEt_3$)$_2$][$B(C_6F_5)_4^-$]	[(BDI)Mg^+·EtCCEt][$B(C_6F_5)_4^-$]
Empirical formula	$C_{65}H_{61}BF_{21}MgN_2OP$	$C_{65}H_{71}BF_{20}MgN_2O_2P_2$	$C_{59}H_{51}BF_{20}MgN_2$
Formula weight	1351.24	1389.29	1203.14
Temperature/K	100.01(10)	100.00(10)	99.99(10)
Crystal system	triclinic	triclinic	monoclinic
Space group	P-1	P-1	$P2_1/c$
a/Å	12.6579(4)	12.9094(5)	14.3528(6)
b/Å	15.3343(5)	15.1447(6)	20.1560(9)
c/Å	17.5503(6)	16.9144(7)	19.2715(8)
α/°	92.793(3)	94.761(3)	90
β/°	107.979(3)	92.981(3)	100.557(4)
γ/°	99.369(2)	96.921(3)	90
Volume/$Å^3$	3179.12(19)	3265.1(2)	5480.8(4)
Z	2	2	4
ρ_{calc}g/cm^3	1.412	1.413	1.458
μ/mm^{-1}	1.417	1.606	0.142
F(000)	1388.0	1436.0	2464.0
Crystal size/mm^3	0.38 × 0.29 × 0.10	0.28 × 0.22 × 0.20	0.347 × 0.187 × 0.073
Crystal color	colorless	colorless	colorless
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.474 to 147.298	5.902 to 147.362	5.956 to 59.682
Index ranges	-15 ≤ h ≤ 15, -19 ≤ k ≤ 14, -21 ≤ l ≤ 21	-13 ≤ h ≤ 15, -18 ≤ k ≤ 18, -15 ≤ l ≤ 20	-13 ≤ h ≤ 19, -24 ≤ k ≤ 27, -25 ≤ l ≤ 26
Reflections collected	26083	20397	33685
Independent reflections	12436 [R_{int} = 0.0219, R_{sigma} = 0.0288]	12574 [R_{int} = 0.0287, R_{sigma} = 0.0392]	13472 [R_{int} = 0.0258, R_{sigma} = 0.0372]
Data/restraints/parameters	12436/0/842	12574/29/894	13472/0/760
Goodness-of-fit on F^2	1.025	1.016	1.017
Final R indexes [I>=2σ (I)]	R_1 = 0.0343, wR_2 = 0.0879	R_1 = 0.0439, wR_2 = 0.1146	R_1 = 0.0413, wR_2 = 0.0907
Final R indexes [all data]	R_1 = 0.0376, wR_2 = 0.0906	R_1 = 0.0503, wR_2 = 0.1208	R_1 = 0.0600, wR_2 = 0.1001
Largest diff. peak/hole / e $Å^{-3}$	0.56/-0.44	0.64/-0.40	0.31/-0.30

Table S3. Crystal data (continued).

Identification code	$[(BDI)H_2^+][B(C_6F_5)_4^-]$	$[(BDI)Ca^+{\cdot}C_6H_6][B(C_6F_5)_4^-]$
Empirical formula	$C_{53}H_{43}BF_{20}N_2$	$C_{65}H_{53}BCaF_{20}N_2$
Formula weight	1098.70	1292.98
Temperature/K	100.0(2)	100.0(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a/Å	10.73722(14)	15.4894(2)
b/Å	32.4655(4)	16.6388(2)
c/Å	14.61307(20)	22.8557(3)
α/°	90	90
β/°	100.9705(13)	94.3470(10)
γ/°	90	90
Volume/Å^3	5000.86(12)	5873.54(13)
Z	4	4
ρ_{calc}g/cm^3	1.459	1.462
μ/mm^{-1}	1.211	1.875
F(000)	2240.0	2648.0
Crystal size/mm^3	0.3596 × 0.1036 × 0.0656	0.278 × 0.209 × 0.088
Crystal color	colorless	colorless
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.736 to 136.234	6.578 to 146.282
Index ranges	-9 ≤ h ≤ 12, -38 ≤ k ≤ 38, -15 ≤ l ≤ 17	-18 ≤ h ≤ 16, -14 ≤ k ≤ 20, -25 ≤ l ≤ 28
Reflections collected	17824	20692
Independent reflections	9060 [R_{int} = 0.0409, R_{sigma} = 0.0524]	11345 [R_{int} = 0.0376, R_{sigma} = 0.0503]
Data/restraints/parameters	9060/0/703	11345/0/812
Goodness-of-fit on F^2	1.050	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0438, wR_2 = 0.1113	R_1 = 0.0447, wR_2 = 0.1178
Final R indexes [all data]	R_1 = 0.0504, wR_2 = 0.1179	R_1 = 0.0493, wR_2 = 0.1239
Largest diff. peak/hole / e Å^{-3}	0.36/-0.29	0.60/-0.38

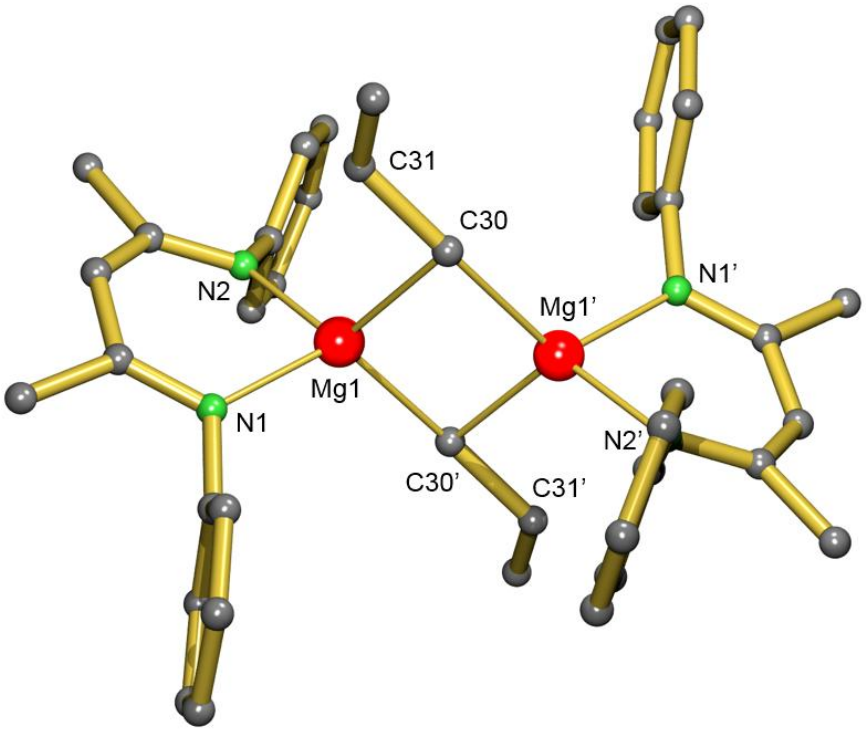


Figure S35: Crystal structure of [(BDI)Mg(*n*Pr)]$_2$. Hydrogen atoms and *iso*-propyl groups were omitted for clarity. Selected bond lengths (Å) and angles (°): Mg1-N1 2.1017(12), Mg1-N2 2.0943(12), Mg1-C30 2.2558(16), Mg1-C30' 2.2853(16), Mg1-C31 2.779(2), N2-Mg1-N1 92.77(5), Mg1-C30-Mg1' 77.09(5).

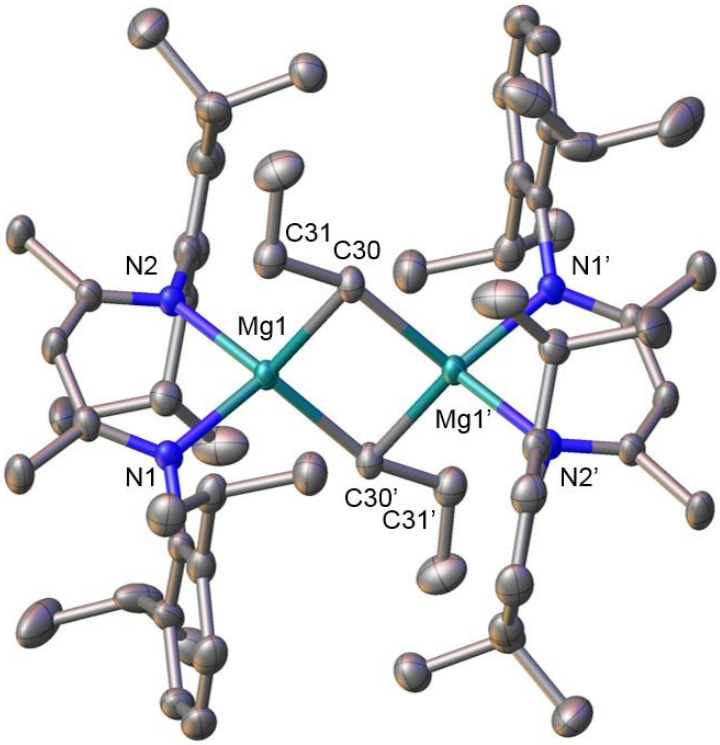


Figure S36: ORTEP representation of [(BDI)Mg(*n*Pr)]$_2$ (probability level 50%). Hydrogen atoms were omitted for clarity.

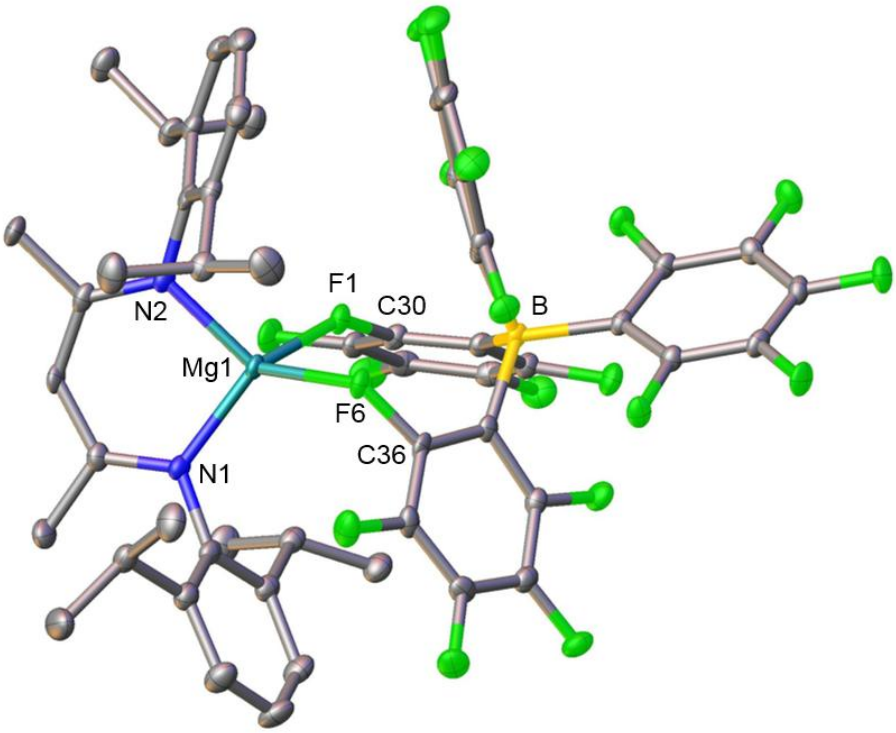


Figure S37: ORTEP representation of $[(BDI)Mg^{+}][B(C_6F_5)_4^{-}]$ (probability level 50%). Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Mg1-N1 1.9878(16), Mg1-N2 1.9836(15), Mg1-F1 2.0290(12), Mg1-F6 2.0560(10), F1-C30 1.406(2), F6-C36 1.4161(18), N2-Mg1-N1 97.13(6), F1-Mg1-F6 84.36(4). These values relate to one of the two molecules in the asymmetric unit. The other molecule shows similar geometric parameter.

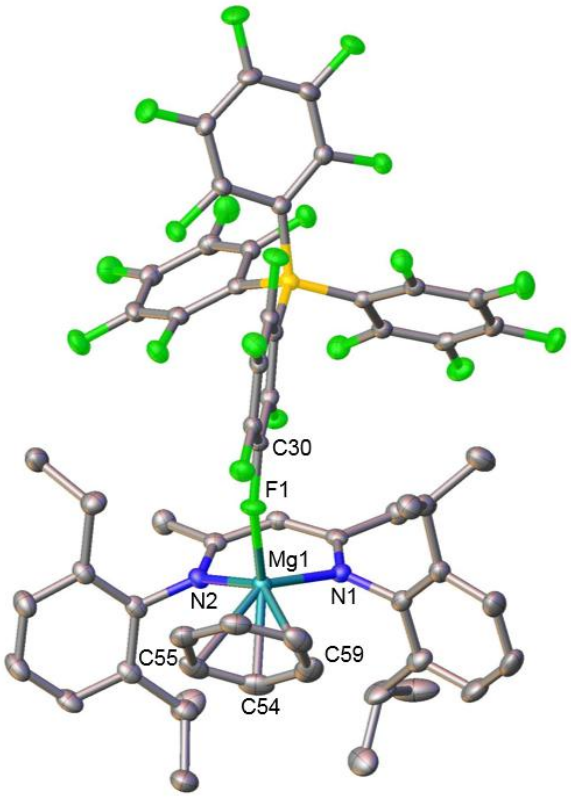


Figure S38: ORTEP representation of $[(BDI)Mg^{+}\cdot C_6H_6][B(C_6F_5)_4^{-}]$ (probability level 50%). Hydrogen atoms and a cocrystallized C_6H_6 molecule were omitted for clarity. Selected bond lengths (Å) and angles (°): Mg1-N1 1.9852(13), Mg1-N2 1.9943(13), Mg1-F1 2.0463(9), Mg1-C54 2.3673(17), Mg1-C55 2.6858(18), Mg1-C59 2.8101(19), F1-C30 1.3861(16), N1- Mg1-N2 97.13(6)

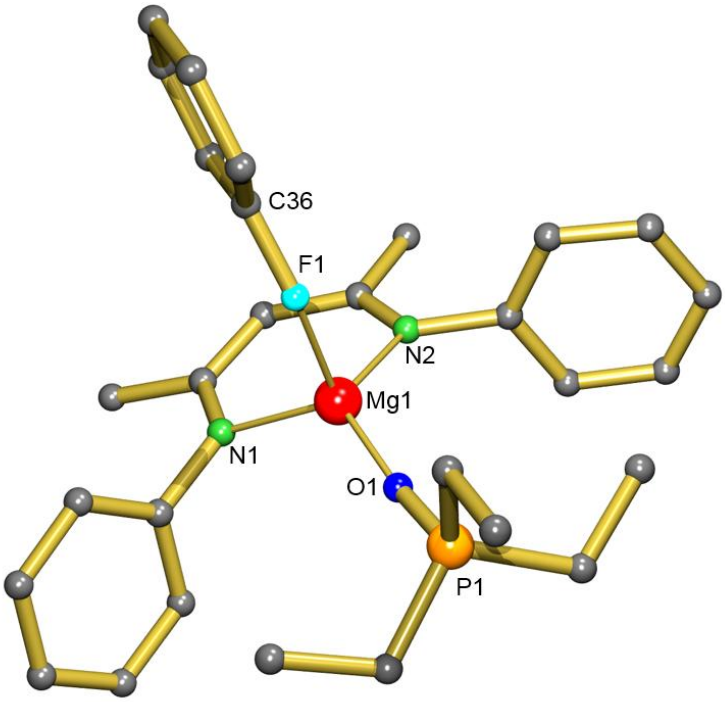


Figure S39: Solid state structure of [(BDI)Mg^{+}·(OEt_3)(PhF)][$B(C_6F_5)_4^{-}$]. Hydrogen atoms, *iso*-propyl groups and [$B(C_6F_5)_4^{-}$] were omitted for clarity. Selected bond lengths (Å) and angles (°): Mg1-N1 1.9941(11), Mg1-N2 2.0001(11), Mg1-O1 1.8695(10), Mg1-F1 2.0502(9), F1-C36 1.4025(16), N1-Mg1-N2 96.62(5)

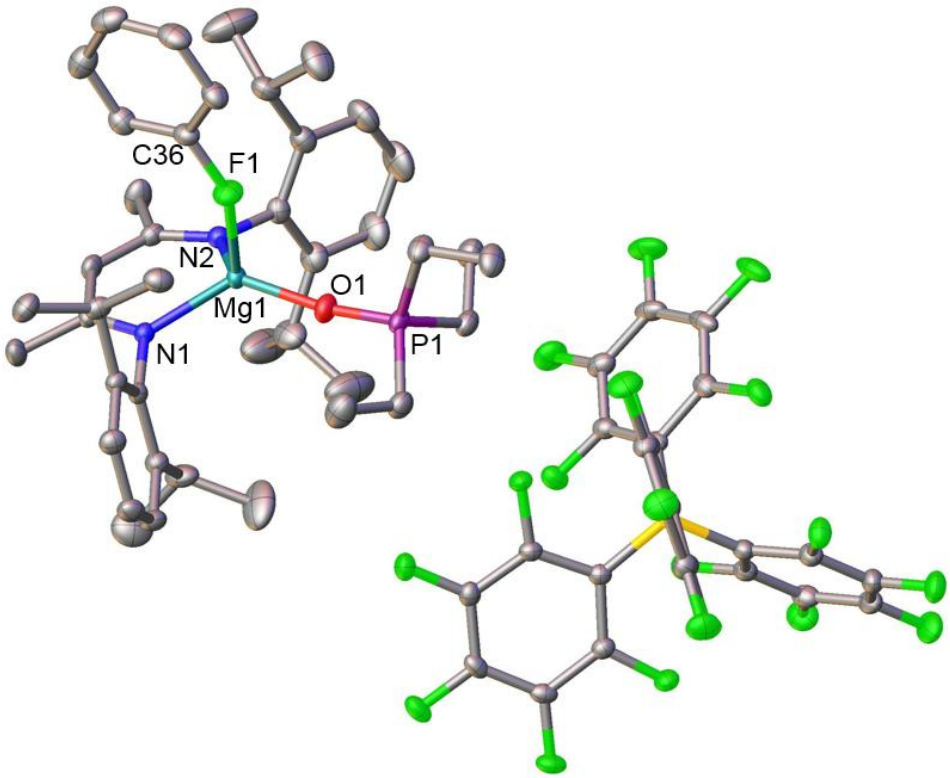


Figure S40: ORTEP representation of [(BDI)Mg^{+}·(OEt_3)(PhF)][$B(C_6F_5)_4^{-}$] (probability level 50%). Hydrogen atoms were omitted for clarity.

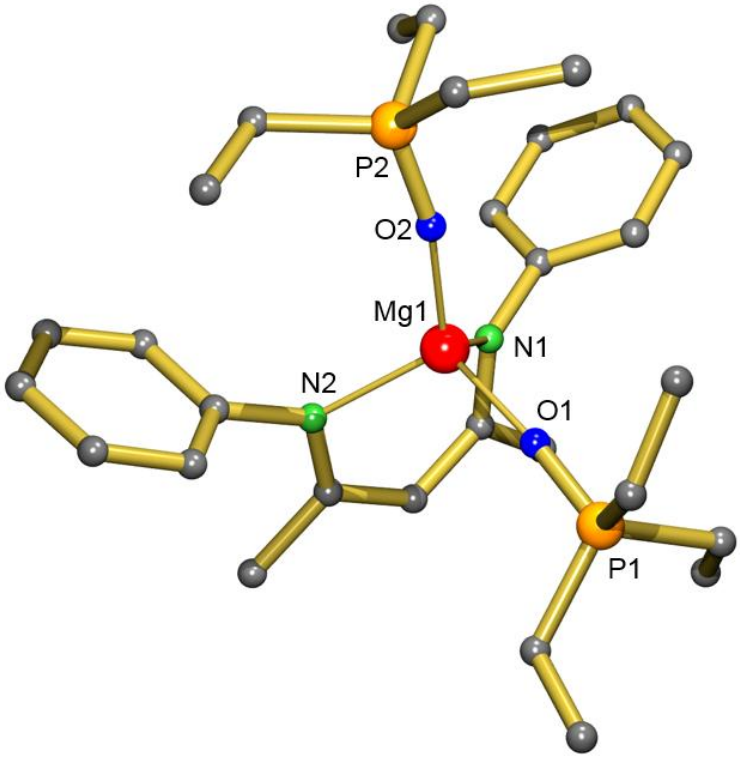


Figure S41: Solid state structure of $[(BDI)Mg^{+}\cdot(OPEt_3)_2][B(C_6F_5)_4^{-}]$. Hydrogen atoms, *iso*-propyl groups and $[B(C_6F_5)_4^{-}]$ were omitted for clarity. Selected bond lengths (Å) and angles (°): Mg1-N1 2.0415(15), Mg1-N2 2.0457(16), Mg1-O1 1.9418(14), Mg1-O2 1.9112(15), N1-Mg1-N2 93.66(6)

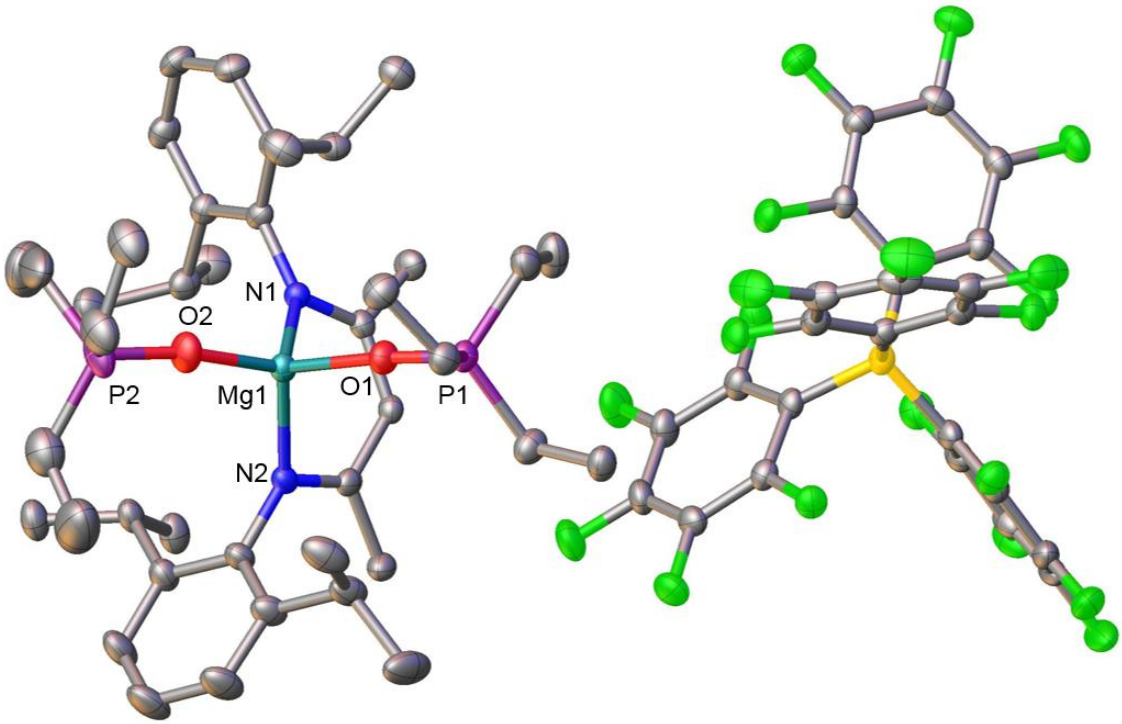


Figure S42: ORTEP representation of $[(BDI)Mg^{+}\cdot(OPEt_3)_2][B(C_6F_5)_4^{-}]$ (probability level 50%). Hydrogen atoms were omitted for clarity.

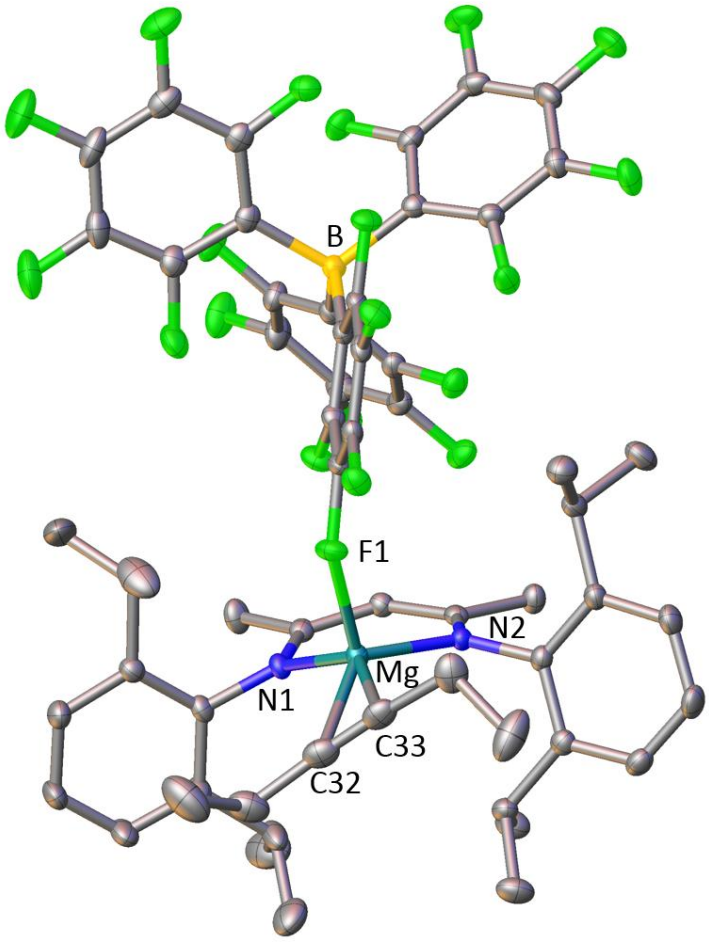


Figure S43: ORTEP representation of $[(BDI)Mg^{+}\cdot CH_3CH_2CCCH_2CH_3][B(C_6F_5)_4]$ (probability level 50%). Hydrogen atoms were omitted for clarity.

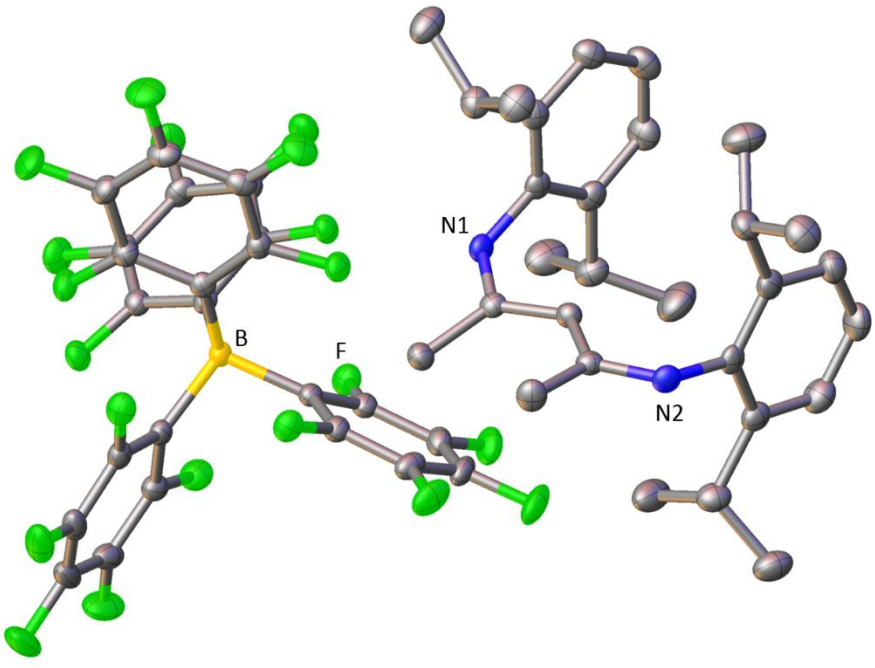


Figure S44: ORTEP representation of $[(BDI)H_2^{+}][B(C_6F_5)_4^{-}]$ (probability level 50%). Hydrogen atoms were omitted for clarity.

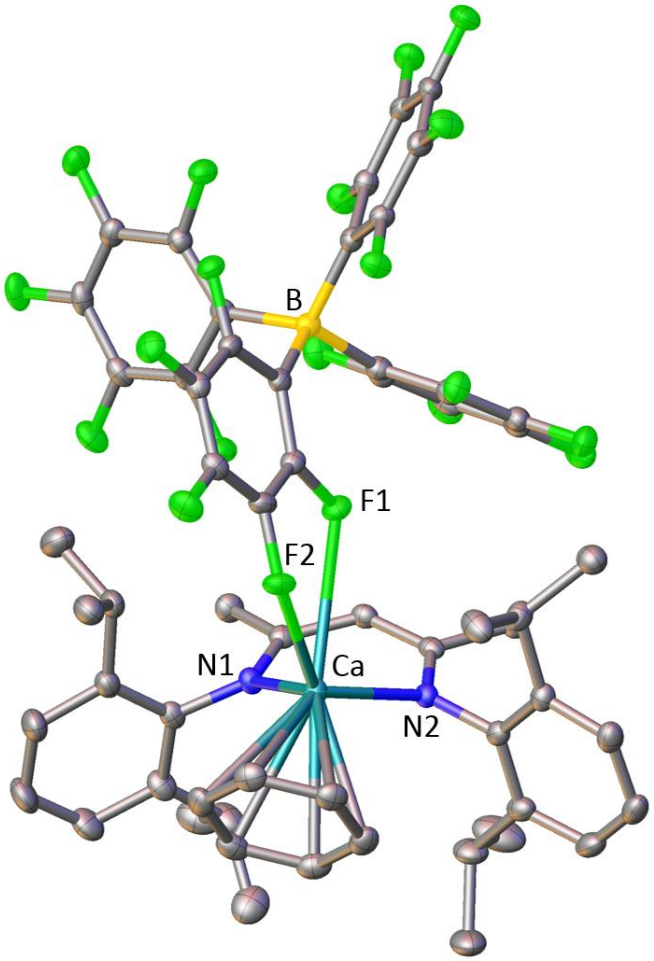


Figure S45: ORTEP representation of $[(BDI)Ca^{+}\cdot C_6H_6][B(C_6F_5)_4^{-}]$ (probability level 50%). Hydrogen atoms and a cocrystallized C_6H_6 molecule were omitted for clarity.

1.5 Lewis acidity quantification of (BDI)Mg^+ by the Gutmann-Beckett method

The direct synthesis of [(BDI)Mg^+·($OPEt_3$)(PhF)][$B(C_6F_5)_4^-$] and [(BDI)Mg^+·($OPEt_3$)$_2$] [$B(C_6F_5)_4^-$] with the respective ^{31}P NMR chemical shifts can be found in the experimental section 1.2. The resulting acceptor numbers are 70.3 for [(BDI)Mg^+·($OPEt_3$)(PhF)][$B(C_6F_5)_4^-$] and 56.0 for [(BDI)Mg^+·($OPEt_3$)$_2$][$B(C_6F_5)_4^-$].

Competition experiments

[(BDI)Mg^+·C_6H_6][$B(C_6F_5)_4^-$] (0.0189 g, 0.0157 mmol) and $(C_6F_5)_3B$·$OPEt_3$ (0.0101 g, 0.0156 mmol) were dissolved in C_6D_5Br (0.5 ml). The ^{31}P NMR spectrum showed only one resonance at 76.0 ppm indicating that the Et_3PO ligand is fully bound to $B(C_6F_5)_3$. After heating the sample to 60°C (one day) the ^{31}P NMR signal shifted to 72.9 ppm. This chemical shift is almost equal to that for [(BDI)Mg^+·($OPEt_3$)(PhF)][$B(C_6F_5)_4^-$] in C_6D_5Br (72.8 ppm), indicating full transfer of the Et_3PO ligand from B to Mg. Subsequent addition of a second equivalent of $(C_6F_5)_3B$·$OPEt_3$ (0.0103 g) and heating the sample to 60°C (one day) resulted in a single ^{31}P NMR signal at 66.3 ppm which is equal to that for the *bis*-adduct [(BDI)Mg^+·($OPEt_3$)$_2$][$B(C_6F_5)_4^-$] in C_6D_5Br. This suggests that despite their low acceptor numbers both, (BDI)Mg^+ (AN = 70.3) and even (BDI)Mg^+·($OPEt_3$) (AN = 56.0), can compete with the strong Lewis acid $B(C_6F_5)_3$ (AN = 77.1).

Similar, one Et_3PO ligand could be transferred from [(BDI)Mg^+·($OPEt_3$)$_2$][$B(C_6F_5)_4^-$] to [(BDI)$AlMe^+$][$B(C_6F_5)_4^-$] giving a mixture of (BDI)Mg^+·$OPEt_3$ and [(BDI)$AlMe^+$·$OPEt_3$] [$B(C_6F_5)_4^-$]. Transfer of Et_3PO from (BDI)Mg^+·$OPEt_3$ to (BDI)$AlMe^+$ was not observed (also not at 100°C). As also the reverse ligand transfer from [(BDI)$AlMe^+$·$OPEt_3$][$B(C_6F_5)_4^-$] to (BDI)Mg^+ does not proceed, this seems kinetically restricted. In order to evaluate the kinetic Lewis acidity differences, a sub-stoichiometric quantity of Et_3PO was added to a vigorously stirred equimolar solution of [(BDI)Mg^+·C_6H_6][$B(C_6F_5)_4^-$] and [(BDI)$AlMe^+$][$B(C_6F_5)_4^-$] in C_6D_5Br at room temperature. The ^{31}P NMR signals at 81.6 and 66.3 ppm (ratio ~ 40/60) are assigned to [(BDI)Mg^+·($OPEt_3$)$_2$][$B(C_6F_5)_4^-$] and [(BDI)$AlMe^+$·$OPEt_3$][$B(C_6F_5)_4^-$], respectively. It is noteworthy that despite a large difference in acceptor numbers between (BDI)$AlMe^+$ (AN = 89.7) and (BDI)Mg^+ (AN = 70.3) or (BDI)Mg^+·($OPEt_3$) (AN = 56.0), most of the Et_3PO (nearly 60%) is bound to Mg. The cationic Mg complex (BDI)Mg^+ is therefore slightly more Lewis acidic than (BDI)$AlMe^+$.

2. Computational Details

General

All calculations were carried out using Gaussian 16 A.[S9] All methods were used as implemented. All structures were fully optimized on a ωB97XD/6-31+G** level of theory. In order to determine zero point energies and to characterize the structures as minima frequency analysis has been applied.[S10-13] Energies were calculated on ωB97XD/6-311+G** level of theory. Charges were calculated via NBO analysis.[S14] Molecules were drawn and evaluated using Molecule V2.3.[S15] Topological analyses were carried out using AIMAll V17 using the wavefunctions of the geometry optimizations.[S16-17]

Charges

Molecule	**Atom or part**	**NPA Charge**
(BDI)Mg(C_6H_6)$^{(+)}$	Mg	+1.820
	BDI	-0.870
	C_6H_6	+0.051
(BDI)Ca(C_6H_6)$^{(+)}$	Ca	+1.786
	BDI	-0.828
	C_6H_6	+0.041
(BDI)Mg($CH_3CH_2C{\equiv}CCH_2CH_3$)$^{(+)}$	Mg	+1.826
	BDI	-0.865
	3-Hexyne	+0.042

Coordination Energies

(BDI)$M^{(+)}$ + C_6H_6 → (BDI)$Mg^{(+)}$ --- C_6H_6

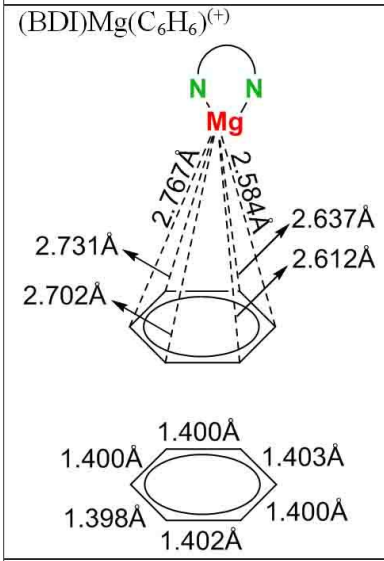
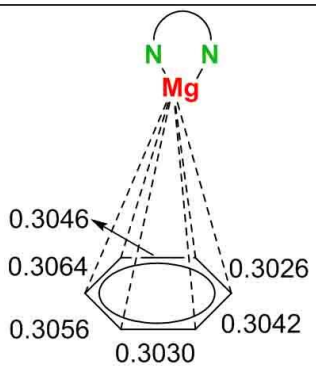
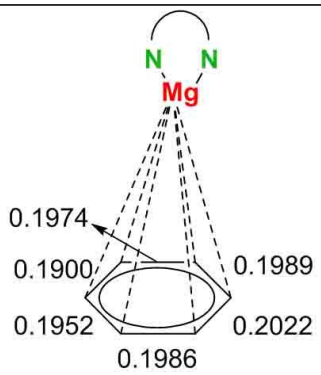
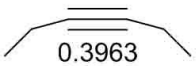
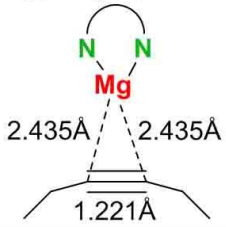
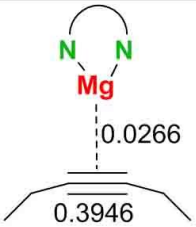
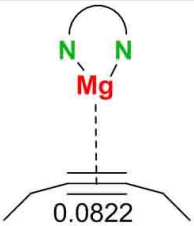
Metal	ΔE [kcal/mol]
(BDI)$Mg^{(+)}$	-36.1
(BDI)$Ca^{(+)}$	-34.3

(BDI)$M^{(+)}$ + Hexyne → (BDI)$Mg^{(+)}$ --- Hexyne

Metal	ΔE [kcal/mol]
(BDI)$Mg^{(+)}$	-43.1

AIM

Calculated bond distances, electron densities in the BCP at the C-C bonds and the bond ellipticities of the C-C bonds in free benzene (or alkyne) are compared with those in Mg-bound benzene (or alkyne).

Bond distance (Å)	Electron density ρ (a.u.)	Bond ellipticity ε (au)
Benzene C-C 1.394Å	0.3084	0.2044
(BDI)Mg(C_6H_6)$^{(+)}$ 		
Hexyne 		
(BDI)Mg(Hexyne)$^{(+)}$ 		

XYZ Coordinates

73

(BDI)Mg
(+)

Mg	-0.000045	-0.001639	-0.704801
N	-1.505358	-0.136778	0.545784
N	1.505619	0.134208	0.545425
C	-2.817446	-0.362181	0.019409
C	-1.257923	-0.247343	1.856981
C	3.820618	-0.614135	0.145177
C	0.000397	-0.002095	2.443017
H	0.000589	-0.002501	3.525692
C	1.258436	0.244147	1.856715
C	2.817149	0.362156	0.018733
C	-3.818941	0.616115	0.146238
C	5.071712	-0.338780	-0.412314
H	5.872285	-1.064410	-0.318189
C	-3.032620	-1.540120	-0.725067
C	3.029844	1.540643	-0.725606
C	1.849155	2.466409	-0.985334
H	1.245415	2.490690	-0.071348
C	-3.512778	1.969045	0.774762
H	-2.747504	1.830759	1.543398
C	4.292233	1.774497	-1.267388
H	4.487610	2.683745	-1.825554
C	5.314214	0.846898	-1.095396
H	6.297194	1.040966	-1.511221
C	3.517138	-1.967977	0.772993
H	2.750939	-1.831730	1.541075
C	-2.906132	2.898615	-0.288840
H	-1.992827	2.462107	-0.713193
H	-2.643144	3.868423	0.144441
H	-3.611222	3.066963	-1.109195
C	-5.070617	0.343455	-0.411274
H	-5.869735	1.070650	-0.316915
C	2.378630	0.653969	2.782493
H	3.148919	-0.119433	2.848626
H	2.004243	0.854832	3.785616
H	2.868689	1.554335	2.399798
C	-4.295525	-1.771253	-1.266825
H	-4.492860	-2.680008	-1.825095
C	-1.853948	-2.468557	-0.984463
H	-1.251238	-2.495150	-0.069900
C	-2.378213	-0.656757	2.782812
H	-3.148370	0.116787	2.848738
H	-2.003934	-0.857551	3.785988
H	-2.868420	-1.557094	2.400213
C	0.973567	1.879517	-2.130575

H	1.262835	2.292440	-3.101160
H	-0.097989	2.116259	-2.024816
H	1.154401	0.796721	-2.300483
C	-5.315554	-0.841550	-1.094661
H	-6.298942	-1.033495	-1.510508
C	2.214393	3.915557	-1.310480
H	2.829833	4.346079	-0.516852
H	1.308601	4.521997	-1.403053
H	2.763464	3.998853	-2.253334
C	4.724112	-2.625542	1.447684
H	5.476286	-2.947568	0.720667
H	4.404214	-3.516229	1.995602
H	5.206650	-1.945933	2.156508
C	-4.718718	2.629171	1.448815
H	-5.469535	2.953351	0.721352
H	-4.397118	3.518822	1.997421
H	-5.203439	1.950382	2.156932
C	-0.975348	-1.882879	-2.128135
H	-1.261292	-2.297340	-3.099041
H	0.096034	-2.119187	-2.018989
H	-1.156320	-0.800425	-2.299789
C	2.913443	-2.898422	-0.291537
H	1.999766	-2.463528	-0.716763
H	2.651937	-3.868894	0.141147
H	3.619723	-3.065100	-1.111205
C	-2.222593	-3.916462	-1.311327
H	-2.839968	-4.346162	-0.518753
H	-1.318270	-4.525152	-1.403490
H	-2.770869	-3.997465	-2.254846

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(BDI)Mg(C6H6)(+)

C	-1.421359	-0.878093	-2.721556
Mg	0.050330	-0.191623	-0.481621
N	1.559817	0.083817	0.793263
N	-1.417792	0.117088	0.829316
C	2.565351	0.652989	2.969590
C	-2.331854	0.525702	3.081900
C	1.378343	0.371585	2.079416
C	-1.175727	0.343118	2.124372
C	0.109802	0.457116	2.684970
C	2.852530	-0.116109	0.216009
C	-2.754823	0.080746	0.322740
C	3.576429	0.981846	-0.288862
C	-3.447352	1.280278	0.071135
C	4.727211	0.732262	-1.041880
C	-4.697433	1.203034	-0.549441
C	5.160831	-0.563997	-1.282994
C	-5.254720	-0.018986	-0.899804

C	3.307468	-1.440560	0.029808
C	-3.303080	-1.170769	-0.035038
C	4.462620	-1.633890	-0.733233
C	-4.561452	-1.196251	-0.637447
H	-2.422567	-1.290803	-2.682116
H	2.402881	0.256494	3.973519
H	-2.579013	1.589352	3.163564
H	0.125812	0.666078	3.748136
H	2.689291	1.737604	3.059819
H	-3.229534	0.004066	2.746757
H	3.491531	0.240503	2.567592
H	-2.062986	0.172410	4.078443
C	3.170550	2.420496	0.001954
C	-2.878698	2.644692	0.441963
H	5.297881	1.566875	-1.439124
H	-5.248404	2.115575	-0.756763
H	6.053232	-0.741599	-1.873998
H	-6.230887	-0.057319	-1.371972
C	2.698579	-2.677950	0.695006
C	-2.533448	-2.459224	0.228922
H	4.831233	-2.644818	-0.886251
H	-5.010736	-2.144221	-0.913065
C	-0.305016	-1.719289	-2.681578
C	0.987563	-1.176681	-2.711357
C	1.160980	0.211001	-2.779135
C	-1.250295	0.507913	-2.778996
C	0.038974	1.052383	-2.807067
H	-0.442336	-2.794169	-2.620924
H	1.858499	-1.821815	-2.664897
H	2.163458	0.625982	-2.783850
H	-2.120458	1.154969	-2.779977
H	0.169106	2.128637	-2.853902
C	-2.415170	3.420913	-0.798982
C	-3.877874	3.478200	1.256859
H	-1.994453	2.491556	1.065303
C	-2.941972	-3.629384	-0.670909
H	-1.473122	-2.259066	0.018315
C	-2.607964	-2.880730	1.703781
C	2.871702	3.221916	-1.271847
H	2.253069	2.401117	0.597369
C	4.252806	3.129995	0.831253
H	3.173907	-3.529052	0.193625
C	3.094628	-2.763429	2.177371
C	1.185646	-2.898821	0.553772
H	2.589269	4.248089	-1.018714
H	3.743857	3.271424	-1.931623
H	2.046900	2.782585	-1.840047
H	3.907397	4.120618	1.142332
H	4.511186	2.558733	1.726768

H	5.170319	3.265214	0.249491
H	2.831360	-3.745306	2.582991
H	4.170041	-2.617391	2.308602
H	2.569295	-2.010352	2.771058
H	0.934765	-3.923088	0.846645
H	0.605991	-2.236446	1.204888
H	0.855161	-2.792043	-0.486425
H	-2.061064	-3.815600	1.861731
H	-2.177063	-2.126572	2.365243
H	-3.649308	-3.041500	2.000299
H	-2.236714	-4.456138	-0.543529
H	-3.933453	-4.013100	-0.411805
H	-2.959117	-3.357206	-1.731691
H	-3.393613	4.382449	1.637295
H	-4.731209	3.795528	0.649352
H	-4.269488	2.913933	2.108190
H	-2.056693	4.415690	-0.517601
H	-1.592188	2.904786	-1.303990
H	-3.231834	3.548342	-1.517823

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(BDI)Ca(C6H6)(+)

Ca	0.094425	0.028334	0.599626
N	-1.371437	-0.110816	-1.205465
N	1.430911	-0.204867	-1.290597
C	-0.029985	-0.454076	-3.164834
H	-0.070729	-0.610063	-4.236492
C	-1.273034	-0.316785	-2.508984
C	-2.573003	0.116440	-0.494447
C	1.253576	-0.386022	-2.588955
C	2.660196	-0.196833	-0.598694
C	-3.325588	-0.964994	0.014650
C	-2.862622	1.446449	-0.092861
C	-2.521735	-0.455214	-3.350428
H	-2.780892	-1.516469	-3.439935
H	-2.367096	-0.067727	-4.359084
H	-3.375258	0.053775	-2.896617
C	-0.107371	-1.127548	3.310467
H	-0.227603	-2.201465	3.413109
C	-1.236888	-0.306727	3.213879
H	-2.232752	-0.738373	3.220143
C	-1.082426	1.079720	3.097549
H	-1.961141	1.711285	3.020332
C	2.459885	-0.483605	-3.492965
H	2.943784	0.497260	-3.564932
H	2.190057	-0.806086	-4.499017
H	3.203982	-1.175113	-3.086247
C	-2.996064	-2.400506	-0.363947
H	-2.195012	-2.373782	-1.108169

C	3.138149	-1.408721	-0.035302
C	3.241870	1.041380	-0.243917
C	-4.675115	0.604665	1.285702
H	-5.499774	0.793811	1.965268
C	1.330531	0.817267	3.148472
H	2.326375	1.246340	3.106327
C	1.176356	-0.567416	3.273170
H	2.054558	-1.202138	3.332882
C	-4.372668	-0.695720	0.899188
H	-4.966543	-1.517533	1.290080
C	0.199792	1.640381	3.067967
H	0.319518	2.715593	2.980253
C	-3.923564	1.664544	0.788147
H	-4.174075	2.677023	1.089343
C	2.528988	-2.743903	-0.463175
H	2.394028	-2.703098	-1.549632
C	-4.195542	-3.115133	-0.999279
H	-5.016554	-3.238103	-0.285542
H	-3.905989	-4.111650	-1.346039
H	-4.578844	-2.552574	-1.855227
C	4.269980	1.055428	0.703072
H	4.729619	1.999272	0.983111
C	1.130121	-2.977097	0.140374
H	1.134762	-2.803867	1.225421
H	0.807324	-4.011215	-0.010406
H	0.372450	-2.358813	-0.357868
C	-2.468353	-3.182717	0.847541
H	-1.578506	-2.704886	1.277661
H	-2.187928	-4.200969	0.561577
H	-3.222646	-3.249946	1.638952
C	4.169974	-1.341600	0.902684
H	4.562595	-2.253413	1.339891
C	-2.059118	2.610755	-0.660176
H	-1.061953	2.231051	-0.925476
C	4.724508	-0.121456	1.283701
H	5.528220	-0.095418	2.012487
C	2.750246	2.334782	-0.879445
H	2.118220	2.063556	-1.729647
C	-1.875066	3.774445	0.319216
H	-2.813541	4.303175	0.510951
H	-1.174969	4.504618	-0.096959
H	-1.477871	3.441199	1.285046
C	1.881303	3.147675	0.091238
H	0.960330	2.617083	0.376344
H	1.556613	4.087324	-0.365344
H	2.425387	3.384910	1.012142
C	3.428383	-3.946039	-0.162232
H	4.440510	-3.798889	-0.548790
H	3.016209	-4.842240	-0.633854

H	3.497915	-4.147814	0.912550
C	3.903369	3.193896	-1.413255
H	4.525074	3.594468	-0.606112
H	3.510919	4.044584	-1.978098
H	4.548852	2.612165	-2.076835
C	-2.682453	3.105493	-1.974624
H	-2.724645	2.306581	-2.718639
H	-2.095198	3.928045	-2.394132
H	-3.702423	3.464406	-1.801855

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(BDI)Ca(+) charges

Ca	-0.000217	-0.001274	-1.109229
N	-1.418716	0.084754	0.706456
N	1.418583	-0.084673	0.706358
C	-2.678457	0.102447	0.054388
C	-1.261324	0.119001	2.023085
C	3.115988	-1.295771	-0.561448
C	-0.000002	0.000389	2.641423
H	0.000042	0.000589	3.724433
C	1.261273	-0.118331	2.023028
C	2.678318	-0.102301	0.054270
C	-3.116077	1.295892	-0.561408
C	4.260344	-1.261800	-1.365134
H	4.614240	-2.174731	-1.835842
C	-3.375215	-1.115146	-0.155911
C	3.375039	1.115293	-0.156130
C	2.856680	2.413686	0.455791
H	2.531779	2.196618	1.478832
C	-2.355302	2.600494	-0.369845
H	-1.577980	2.425478	0.380996
C	4.515866	1.094950	-0.957609
H	5.076157	2.008726	-1.121130
C	4.959495	-0.080509	-1.559724
H	5.850765	-0.069392	-2.178106
C	2.355466	-2.600478	-0.369537
H	1.577956	-2.425332	0.381089
C	-1.671976	3.039227	-1.674867
H	-1.004577	2.263198	-2.097663
H	-1.055791	3.930354	-1.526563
H	-2.405151	3.249948	-2.459075
C	-4.260465	1.261908	-1.365036
H	-4.614318	2.174812	-1.835824
C	2.471290	-0.319932	2.904614
H	2.884944	-1.319773	2.731692
H	2.222198	-0.228554	3.961824
H	3.264429	0.394587	2.665865
C	-4.516062	-1.094817	-0.957376
H	-5.076409	-2.008567	-1.120834

C	-2.857003	-2.413491	0.456284
H	-2.533075	-2.196432	1.479645
C	-2.471247	0.321156	2.904663
H	-2.884499	1.321148	2.731645
H	-2.222179	0.229801	3.961881
H	-3.264673	-0.393067	2.665988
C	1.616812	2.926228	-0.299958
H	1.803163	2.974338	-1.380637
H	1.343146	3.932847	0.030283
H	0.743772	2.298050	-0.080749
C	-4.959666	0.080626	-1.559529
H	-5.850958	0.069506	-2.177881
C	3.911001	3.520698	0.539355
H	4.823440	3.170211	1.029560
H	3.519194	4.359877	1.120536
H	4.179732	3.907629	-0.449423
C	3.249471	-3.727563	0.163793
H	4.024549	-4.006243	-0.556798
H	2.654070	-4.620774	0.374853
H	3.746200	-3.422012	1.088236
C	-3.249154	3.728054	0.162720
H	-4.023913	4.006690	-0.558229
H	-2.653546	4.621170	0.373597
H	-3.746276	3.423050	1.087136
C	-1.616290	-2.925721	-0.298365
H	-1.801208	-2.972592	-1.379371
H	-1.343542	-3.932868	0.031013
H	-0.743267	-2.298256	-0.077066
C	1.672562	-3.040075	-1.674501
H	1.005224	-2.264404	-2.098081
H	1.056491	-3.931224	-1.525860
H	2.405991	-3.251142	-2.458378
C	-3.911093	-3.520798	0.538804
H	-4.824000	-3.170661	1.028382
H	-3.519516	-4.359981	1.120131
H	-4.178952	-3.907591	-0.450266

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C6H6

C	0.690191	-1.211131	-0.000101
H	1.227152	-2.154877	0.000158
C	1.394109	-0.007696	0.000026
H	2.479878	-0.013907	0.000510
C	-0.703746	-1.203303	-0.000103
H	-1.251278	-2.140956	0.000152
C	0.703871	1.203208	-0.000009
H	1.251636	2.140716	-0.000157
C	-0.690316	1.211038	-0.000010
H	-1.227520	2.154637	-0.000157

C	-1.394107	0.007959	0.000028
H	-2.479877	0.013929	0.000508

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(BDI)MgHexyne(+)

Mg	-0.000078	0.000371	0.245846
N	1.485928	0.031908	-1.073232
N	-1.486003	-0.031737	-1.073306
C	1.273326	0.023002	-2.393027
C	2.826485	0.068555	-0.569437
C	0.000003	-0.000048	-2.989100
H	0.000030	-0.000125	-4.071145
C	-1.273351	-0.023055	-2.393090
C	-2.826554	-0.068512	-0.569504
C	3.476087	-1.141110	-0.260974
C	3.416783	1.315080	-0.288013
C	2.467197	0.038908	-3.315887
H	3.079891	0.928033	-3.136909
H	2.161952	0.028290	-4.361480
H	3.108280	-0.827975	-3.127241
C	2.808265	-2.478528	-0.544167
H	2.061954	-2.321458	-1.328728
C	-3.476257	1.141106	-0.261051
C	2.687534	2.610938	-0.612581
H	1.984760	2.405107	-1.425710
C	-4.721617	1.079808	0.367959
H	-5.242649	1.997214	0.622178
C	4.662650	1.327641	0.341279
H	5.139784	2.274209	0.573455
C	4.721516	-1.079896	0.367911
H	5.242473	-1.997342	0.622142
C	0.608492	0.050478	2.603532
C	-3.416704	-1.315079	-0.287967
C	-2.808545	2.478560	-0.544333
H	-2.062533	2.321585	-1.329199
C	-2.467187	-0.039206	-3.315989
H	-3.079684	-0.928475	-3.137049
H	-2.161911	-0.028508	-4.361573
H	-3.108470	0.827527	-3.127343
C	5.308756	0.142289	0.674958
H	6.277208	0.171376	1.163539
C	-0.608422	-0.050593	2.603496
C	1.863672	3.081817	0.595026
H	1.147151	2.319506	0.931514
H	1.290613	3.982253	0.354856
H	2.514478	3.306440	1.446811
C	3.618984	3.729305	-1.091750
H	4.267525	4.097171	-0.290428
H	3.030118	4.579776	-1.447205

H	4.256338	3.389859	-1.913126
C	2.065750	-2.977571	0.704589
H	2.767393	-3.156998	1.526237
H	1.530962	-3.909901	0.500555
H	1.328156	-2.248672	1.068937
C	-4.662505	-1.327723	0.341458
H	-5.139519	-2.274326	0.573738
C	-5.308696	-0.142420	0.675144
H	-6.277093	-0.171580	1.163832
C	3.781806	-3.547300	-1.052299
H	4.359637	-3.182907	-1.906383
H	3.229460	-4.436566	-1.369517
H	4.487443	-3.863412	-0.277634
C	2.062624	0.129912	2.837443
H	2.304583	1.167350	3.089325
H	2.614812	-0.101688	1.923065
C	-2.062583	-0.129850	2.837311
H	-2.304755	-1.167302	3.088926
H	-2.614681	0.102063	1.922956
C	-2.687405	-2.610909	-0.612549
H	-1.984644	-2.405059	-1.425682
C	-1.863506	-3.081775	0.595035
H	-1.146854	-2.319527	0.931358
H	-1.290573	-3.982297	0.354884
H	-2.514265	-3.306266	1.446891
C	2.496349	-0.824183	3.957733
H	2.271185	-1.860526	3.694935
H	1.994341	-0.586893	4.898385
H	3.574592	-0.732605	4.105374
C	-2.065562	2.977427	0.704218
H	-2.766927	3.156916	1.526088
H	-1.530670	3.909674	0.500080
H	-1.327973	2.248406	1.068357
C	-3.618836	-3.729290	-1.091724
H	-4.267338	-4.097204	-0.290394
H	-3.029952	-4.579731	-1.447224
H	-4.256231	-3.389845	-1.913069
C	-3.782244	3.547447	-1.051912
H	-4.360469	3.183207	-1.905791
H	-3.229982	4.436720	-1.369255
H	-4.487520	3.863505	-0.276895
C	-2.496202	0.824074	3.957790
H	-3.574471	0.732663	4.105342
H	-2.270822	1.860440	3.695254
H	-1.994298	0.586476	4.898419

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Hexyne

C	-0.582043	-0.360622	0.164117

C	0.582064	-0.361047	-0.163524
C	-2.000784	-0.347866	0.533902
H	-2.095511	-0.013901	1.573660
H	-2.387004	-1.373299	0.502752
C	2.000850	-0.348999	-0.533157
H	2.095655	-0.017208	-1.573604
H	2.387153	-1.374329	-0.499831
C	-2.846650	0.551479	-0.377323
H	-2.788237	0.214858	-1.415901
H	-2.493848	1.585515	-0.336271
H	-3.895191	0.531232	-0.065738
C	2.846570	0.552312	0.376252
H	3.895209	0.531164	0.065050
H	2.787770	0.218113	1.415585
H	2.493959	1.586312	0.332689

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