Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

For

Reactivity of a quasi-four-coordinate butylmagnesium cation

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1. Experimental Methods

All reactions were performed under an argon atmosphere by using standard Schlenk technique or in a glove box under an atmosphere of argon. Glassware was dried at 200 °C prior to use. Solvents were dried, distilled and degassed by using standard methods.[1] $[HNEt_3][B\{C_6H_3(CF_3)_2\}_4]$ was synthesized according the reported literature procedure.[2] PMDTA and $PhSiH_3$ were purchased from TCI chemicals and distilled before use. HBpin was purchased from Sigma-Aldrich and was used as such. The gasses were passed through a column of molecular sieves dried overnight under vacuum at 200 °C. ^{1}H, ^{13}C, ^{11}B, and ^{19}F NMR spectra were recorded on a Bruker Avance 500 MHz spectrometer. Chemical shifts (δ in ppm) in the ^{1}H and^{13}C NMR spectra were referenced to the residual signals of the deuterated solvents. ^{11}B NMR spectra were referenced to $NaBH_4$ signal in D_2O. ^{19}F spectra were referenced to $CFCl_3$ signal. Abbreviations for NMR spectra: s (singlet), d (doublet), t (triplet), q (quartet), quin (quintuplet), sext (sextet), sep (septet), br (broad), m (multiplet). Elemental analyses were performed on an *Elemental Vario Micro Cube* machine. GC-Agilent 7890B series (Mass detector G7077B series, EI-70 eV, quadrupole ion detector) with silica capillary column (9091S-433UI, HP-5MSUI, with 30 m x 0.25 mm dimension) was used for mass analysis.

2. Synthetic Procedure and Characterization

<u>Synthesis of Compound 1a</u>

PMDTA (0.066 mL, 0.311 mmol) was added to $[NEt_3H][B\{C_6H_3(CF_3)_2\}_4]$ (0.300 g, 0.311 mmol) in 3 mL of dry Et_2O inside the glove box which formed a clear colorless solution. To the solution *n*-Bu_2Mg (0.31 mL, 1M in heptane, 0.310 mmol) was added slowly. [(pmdta)Mg-*n*-Bu][$B\{C_6H_3(CF_3)_2\}_4$] was precipitated by adding 1 mL pentane in the reaction mixture and keeping the reaction mixture at -30 C in glove box for 1 hour. (Yield: 0.302 g, 87 %).

Elemental analysis for $C_{45}H_{44}N_3BF_{24}Mg$: C, 48.35; H, 3.97; N, 3.76. Found: C, 48.29; H, 3.95; N, 3.79

^{1}H NMR [500 MHz, 300K, THF(D8)]: δ - 0.59 (sext, 2H, $^{3}J_{HH}$ = 4.7 Hz, Mg-*CH_2*-$CH_2CH_2CH_3$), 0.85 (t, 3H, $^{3}J_{HH}$ = 7.34 Hz, Mg-$(CH_2)_3$*CH_3*), 1.27 (sext, 2H, $^{3}J_{HH}$ = 7.20 Hz, Mg-$(CH_2)_2$*CH_2*CH_3), 1.48 (quin, 2H, $^{3}J_{HH}$ = 7.79 Hz, Mg-CH_2-*CH_2*-CH_2CH_3), 2.42 (s, 15H, pmdta *(Me)*N(CH_2CH_2N*Me_2*)$_2$), 2.65 (s, 4H, pmdta (Me)N(CH_2*CH_2*NMe_2)$_2$), 2.86 (s, 4H, pmdta (Me)N(*CH_2*CH_2NMe_2)$_2$), 7.57 (s, 4H, p-*CH*), 7.78 (s, 8H, o-*CH*))

^{13}C{^{1}H} NMR [125.74 MHz, 300K, THF(D8)]: 9.2 (Mg-*CH_2*-$CH_2CH_2CH_3$), 14.1 (Mg-$(CH_2)_3$*CH_3*)), 33.2 (Mg-$(CH_2)_2$*CH_2*CH_3), 34.6 (CH_2-*CH_2*-CH_2CH_3), 46.2 (pmdta *(Me)*N(CH_2CH_2N*Me_2*)$_2$), 55.9 (pmdta (Me)N(CH_2*CH_2*NMe_2)$_2$), 58.4 (pmdta (Me)N(*CH_2*CH_2NMe_2)$_2$), 118.2 (b sept, $^{3}J_{CF}$ = 3.87 Hz, *p*-C), 125.5 (q, $^{1}J_{CF}$ = 271.64 Hz, CF_3), 130.0 [qq, ($^{3}J_{CB}$ = 3.05 Hz, $^{2}J_{CF}$ = 31.57 Hz) *m*-C), 135.6 (*o*-C), 162.8 (q, $^{1}J_{BC}$ = 49.65 Hz, *ipso*-C)

^{11}B [160 MHz, 300K,THF(D8)]: δ -6.50 (s, $B\{C_6H_3(CF_3)_2\}_4$)

^{19}F [470.58 MHz, 300K, THF(D8)]: δ -63.3 (s, CF_3)

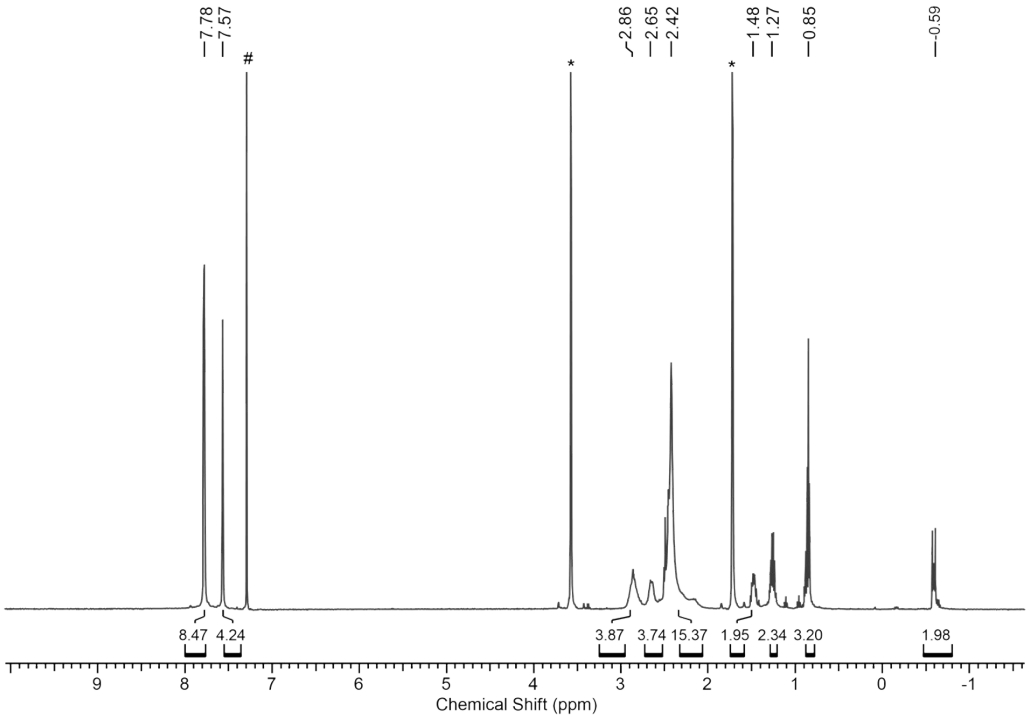


Figure S1: ^{1}H NMR spectrum of compound 1a in THF(D8). * THF(D8) peaks, # C6H6 impurity in THF(D8).

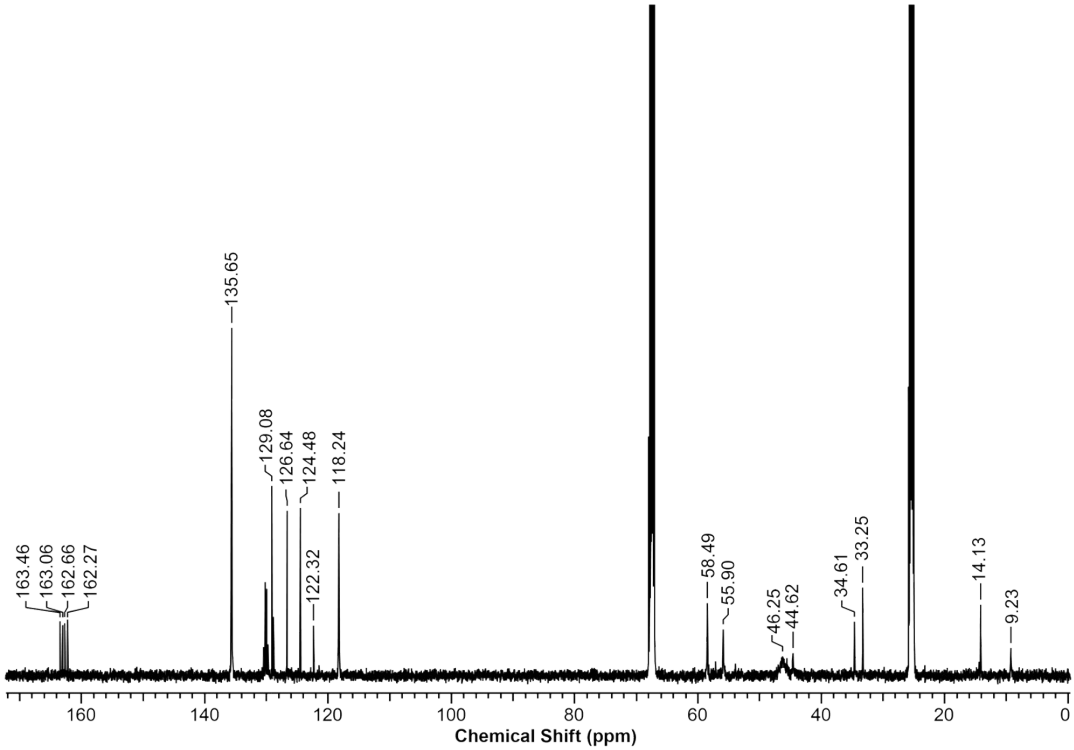


Figure S2: ^{13}C{^{1}H} NMR of compound 1a in THF(D8).

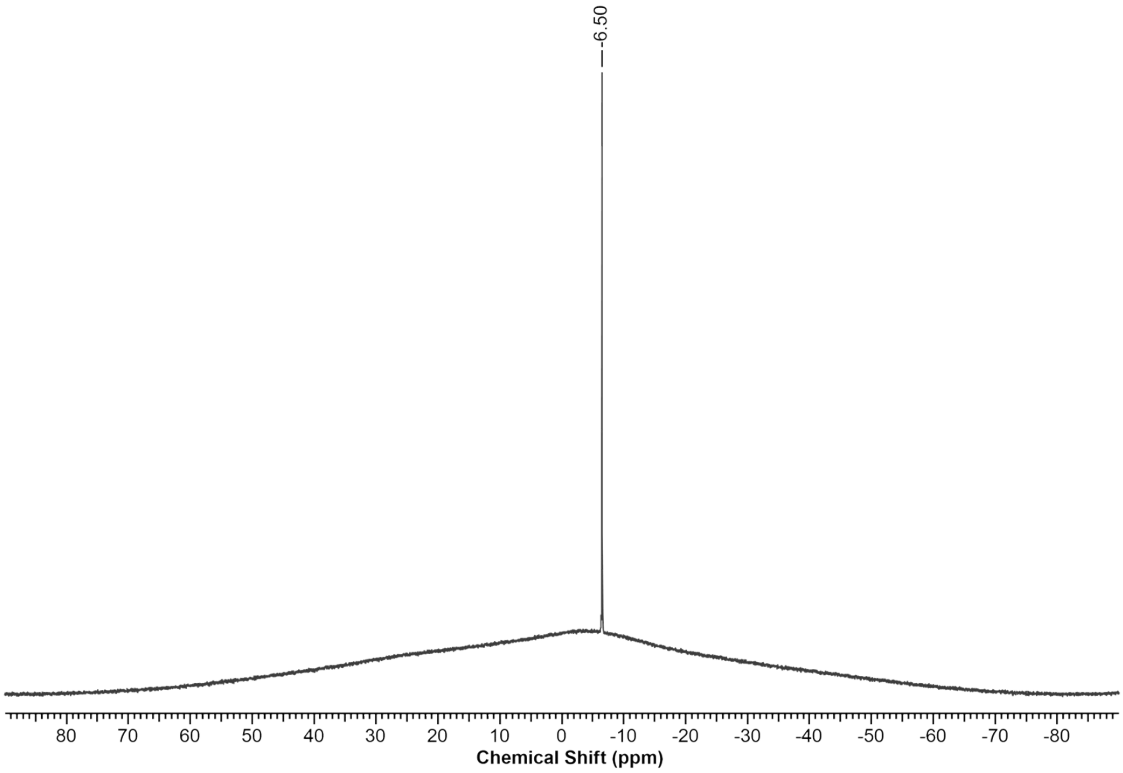


Figure S3: ^{11}B NMR spectrum of compound 1a in THF(D8).

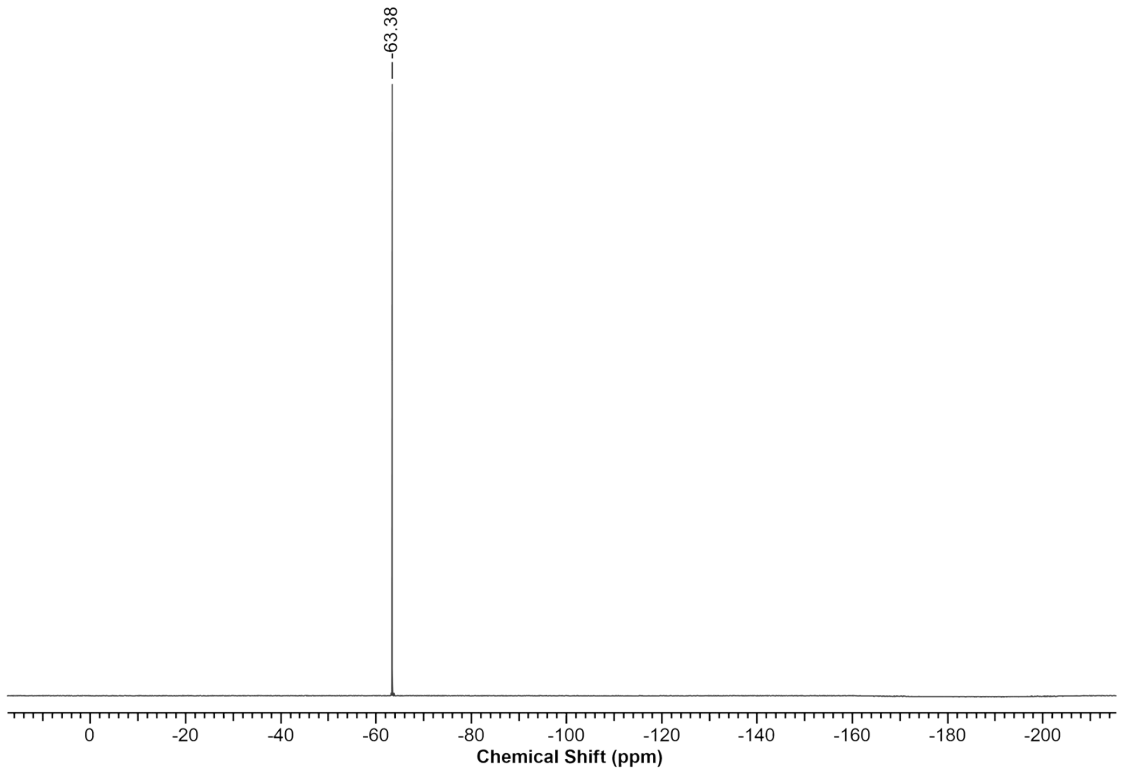


Figure S4: ^{19}F NMR spectrum of compound 1a in THF(D8).

Synthesis of Compound 1b

PMDTA (0.080 mL, 0.384 mmol) was added to $[NEt_3H][B(C_6F_5)_4]$ (0.300 g, 0.384 mmol) in 3 mL of dry Et_2O inside the glove box which formed a clear colorless solution. To the solution *n*-Bu_2Mg (0.39 mL, 1M in heptane, 0.390 mmol) was added slowly. Colorless crystals of [(pmdta)Mg-*n*-Bu][$B\{C_6H_3(CF_3)_2\}_4$] were obtained after layering the solution with 1 mL pentane at -25 °C after 24 hours. (Yield: 0.272 g, 76 %)

Elemental analysis for $C_{37}H_{32}N_3BF_{20}Mg$: C, 47.59; H, 3.45; N, 4.50. Found: C, 47.61; H, 3.42; N, 4.47;

^{1}H NMR [500 MHz, 300K, THF(D8)]: δ -0.59 (sext, 2H, $^3J_{HH}$ = 4.78 Hz, Mg-*CH_2*-$CH_2CH_2CH_3$), 0.85 (t, 3H, $^3J_{HH}$ = 7.32 Hz, Mg-$(CH_2)_3$*CH_3*), 1.25 (sext, 2H, $^3J_{HH}$ = 7.24 Hz, Mg-$(CH_2)_2$*CH_2*CH_3), 1.48 (quin, 2H, $^3J_{HH}$ = 7.80, Mg-CH_2-*CH_2*-CH_2CH_3), 2.42 (s, 15H, pmdta *(Me)*$N(CH_2CH_2N$*Me_2*$)_2$), 2.65 (s, 4H, pmdta (Me)$N(CH_2$*CH_2*$NMe_2)_2$), 2.86 (s, 4H, pmdta (Me)$N($*CH_2*$CH_2NMe_2)_2$)

^{13}C{^{1}H} NMR [125.74 MHz, 300K, THF(D8)]: δ 9.2 (Mg-*CH_2*-$CH_2CH_2CH_3$), 14.1 (Mg-$(CH_2)_3$*CH_3*)), 33.2 (Mg-$(CH_2)_2$*CH_2*CH_3), 34.6 (CH_2-*CH_2*-CH_2CH_3), 46.1 (pmdta *(Me)*$N(CH_2CH_2N$*Me_2*$)_2$), 55.9 (pmdta (Me)$N(CH_2$*CH_2*$NMe_2)_2$), 58.5 (pmdta (Me)$N($*CH_2*$CH_2NMe_2)_2$), 136.0 (ipso-C), 138.1 (p-CF), 148.2 (m-CF), 150.1 (o-CF)

^{11}B [160 MHz, 300K,THF(D8)]: δ -16.5 (s, $B(C_6F_5)_4$)

^{19}F [470.58 MHz, 300K, THF(D8)]: δ -132.7 (d, $^3J_{FF}$ = 9.1 Hz, *o*-CF), -164.94 (t, $^3J_{FF}$ = 20.5 Hz, *p*-CF), -168.44 (t, $^3J_{FF}$ = 17.3 Hz, *m*-CF).

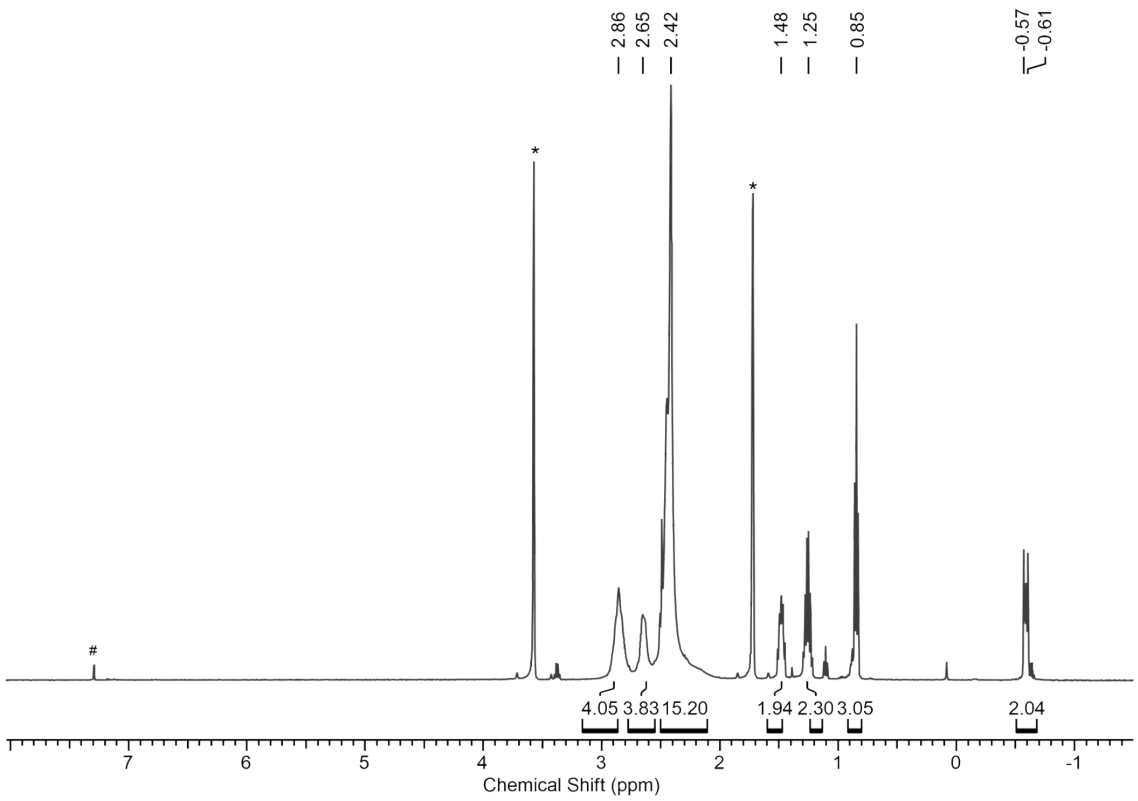


Figure S5: ^{1}H NMR spectrum of compound 1b in THF(D8). * THF(D8) peaks, # C6H6 impurity in THF(D8).

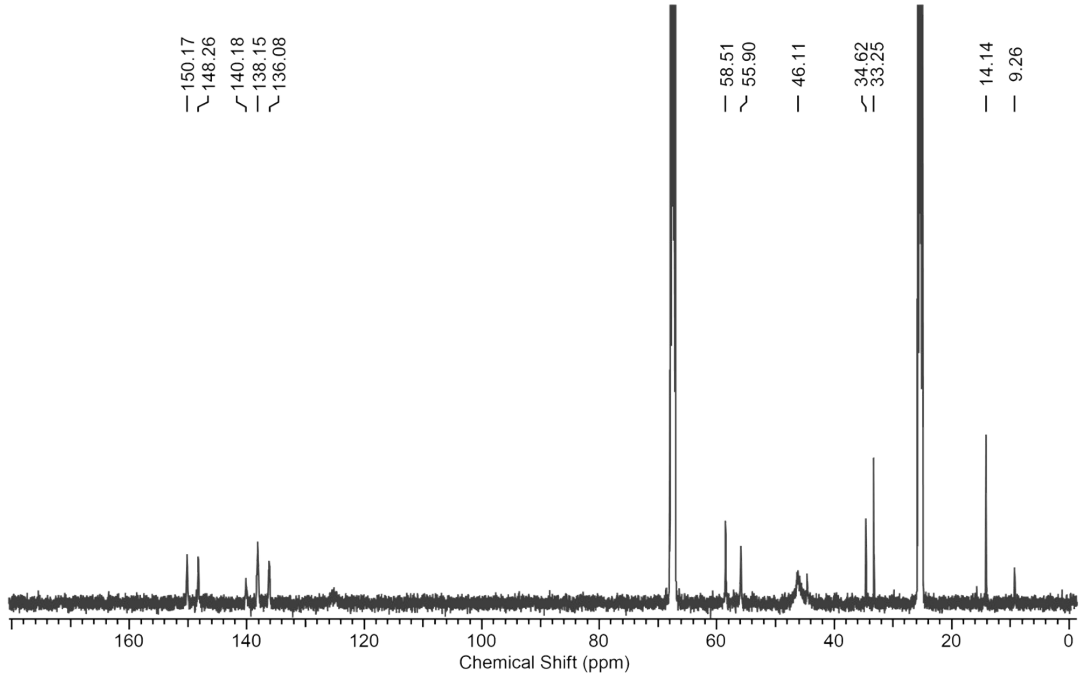


Figure S6: ^{13}C{^{1}H} NMR of compound 1b in THF(D8).

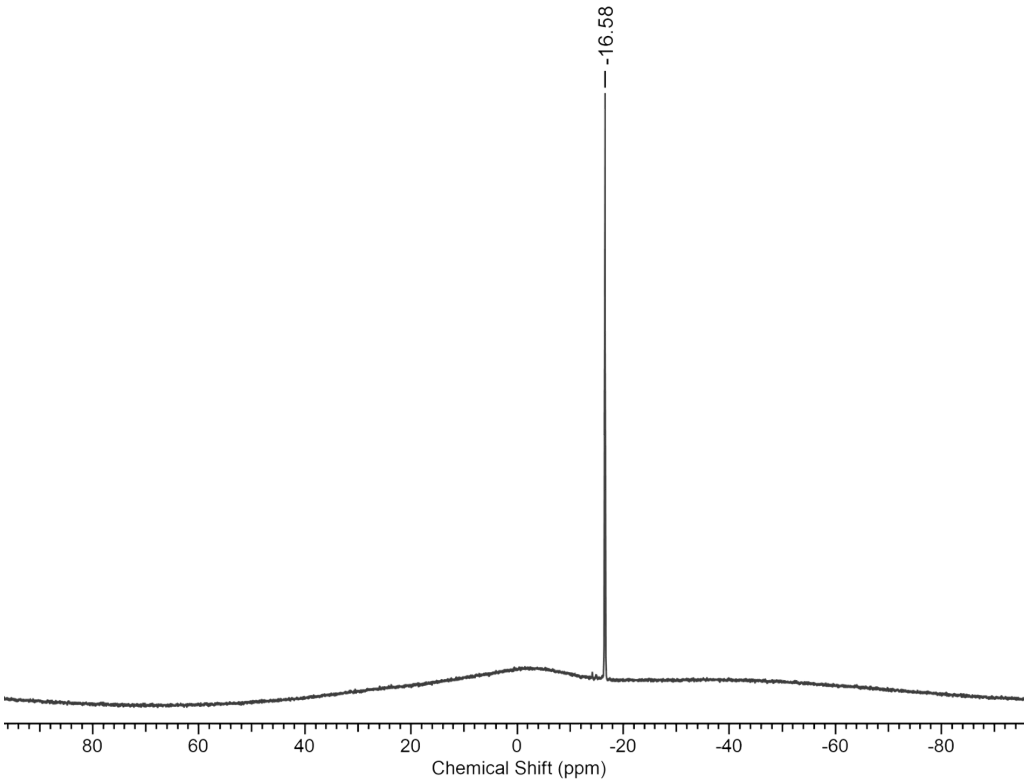


Figure S7: ^{11}B NMR spectrum of compound 1b in THF(D8).

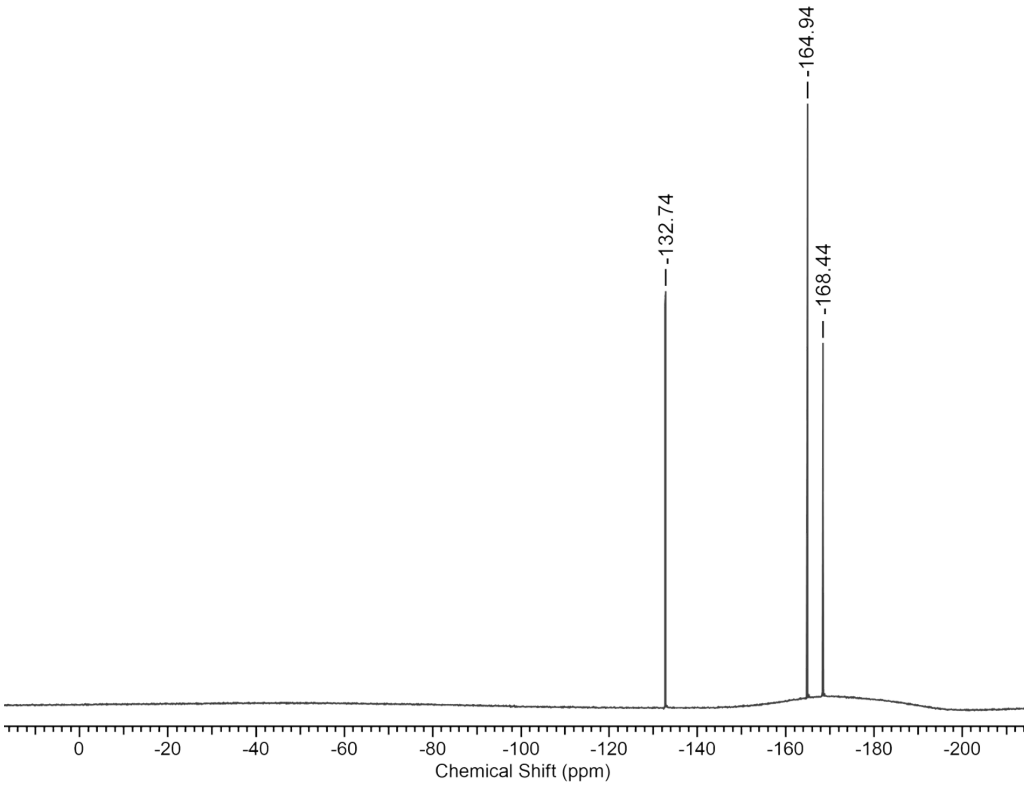


Figure S8: ^{19}F NMR spectrum of compound 1b in THF(D8).

NMR reaction of 1a with benzophenone in C_6D_5Br

Crystals of **1a** [(pmdta)Mg-*n*-Bu][B{$C_6H_3(CF_3)_2$}$_4$] (0.01 g, 0.009 mmol) and 1 equivalent of Ph_2CO (0.0016 g, 0.009 mmol) was added in a J Young NMR tube inside the glove box. 0.5 mL of dry C_6D_5Br was added to the NMR tube and proton NMR was recorded immediately in less than five minutes.

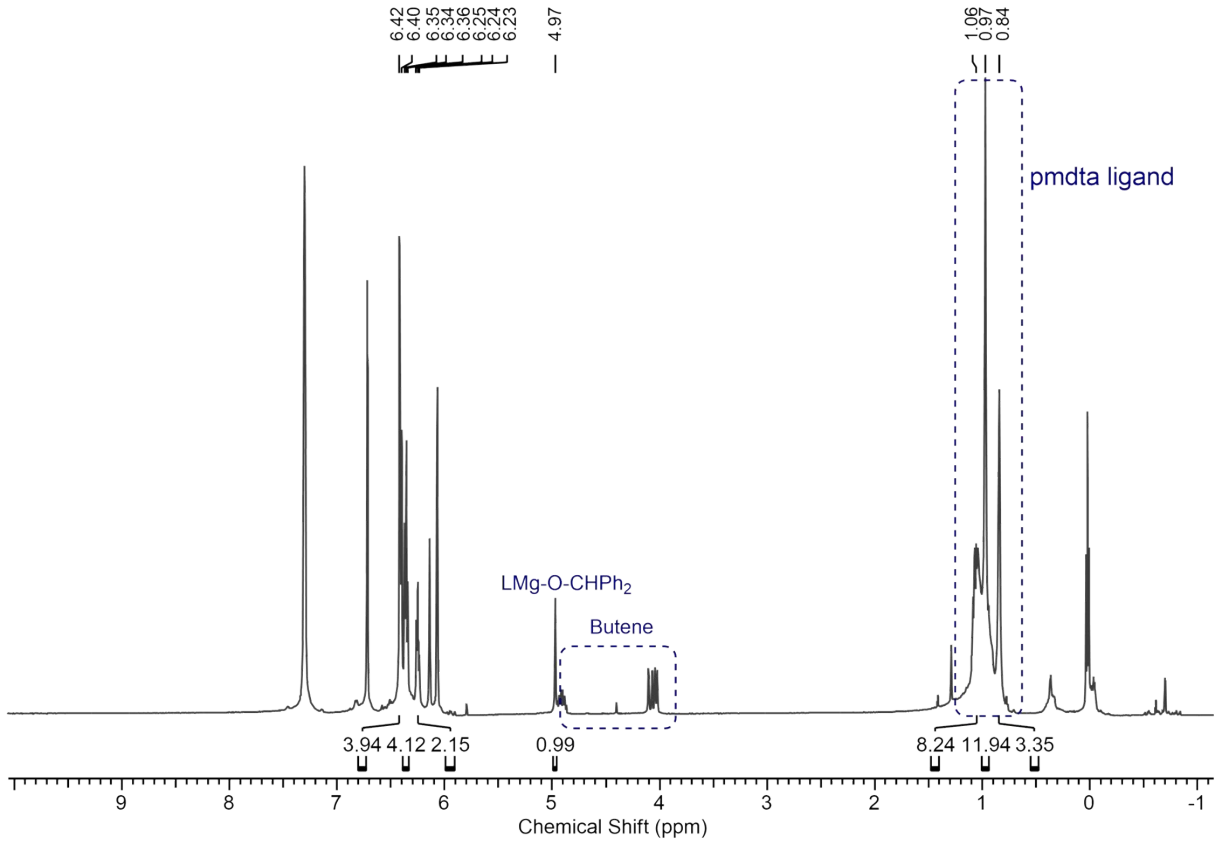


Figure S9: ^{1}H NMR spectrum of reaction between compound 1a and benzophenone in C_6D_5Br.

Synthesis of Compound 2a

Crystals of **1a** [(pmdta)Mg-*n*-Bu][B{$C_6H_3(CF_3)_2$}$_4$] (0.100 g, 0.089 mmol) and benzophenone (0.089 mmol, 0.016 g) was added to a vial in glove box and to the solid mixture 5 mL toluene was added. The reaction mixture was stirred for 30 minutes and toluene was removed under vacuum. Dry 5 mL Et_2O was added to the residual solid and layered with 2 mL of pentane. Colourless crystals of **2a** were obtained after 24 hours at room temperature. (Due to the presence of 0.79 equivalent Et_2O bound to Mg centre of the vacuum dried **2a**, the ^{1}H NMR spectrum exhibits two sets of peaks for protons) (Yield: 0.079 g, 71 %).

Elemental analysis for $C_{54}H_{54}N_3BOF_{24}Mg$. O.79$(CH_2CH_3)_2O$: C, 52.70; H, 4.18; N, 3.22. Found: C, 52.65; H, 4.24; N, 3.23;

^{1}H NMR [500 MHz, 300K, THF(D8)]: δ 1.11 (t, 6H, $^{3}J_{HH}$ = 7.03 Hz, (CH_3CH_2)$_2$O), 2.34 (s, 3H, pmdta *(Me)*N($CH_2CH_2NMe_2$)$_2$), 2.41 (s, 12H, pmdta (Me)N($CH_2CH_2NMe_2$)$_2$), 2.60 (d, 2H, $^{3}J_{HH}$ = 3.6 Hz, pmdta (Me)N($CH_2CH_2NMe_2$)($CH_2CH_2NMe_2$)), 2.68 (m, 2H, pmdta (Me)N($CH_2CH_2NMe_2$)($CH_2CH_2NMe_2$)), 2.79 (m, 2H, pmdta (Me)N($CH_2CH_2NMe_2$)($CH_2CH_2NMe_2$)), 2.86 (m, 2H, pmdta (Me)N($CH_2CH_2NMe_2$)($CH_2CH_2NMe_2$)), 3.38 (q, 4H, $^{3}J_{HH}$ = 6.9 Hz, (CH_3CH_2)$_2$O), 5.88 (s, MgO*CH*Ph$_2$) 7.13 (t, 4H, $^{3}J_{HH}$ = 6.9 Hz, *m*-CH(Mg-OC(H)Ph$_2$)), 7.36 (b,4H, *o*-CH(Mg-OC(H)Ph$_2$) 7.65 (b, 2H, *p*-CH(Mg-OC(H)Ph$_2$), 7.58 (s, 4H, p-*CH*(B{$C_6H_3(CF_3)_2$}$_4$)), 7.79 (s, 8H, o-*CH*(B{$C_6H_3(CF_3)_2$}$_4$))

^{13}C{^{1}H} NMR [125.74 MHz, 300K, THF(D8)]: δ 15.7 (CH_3CH_2)$_2$O), 43.7 (pmdta *(Me)*N($CH_2CH_2NMe_2$)$_2$), 45.2 (pmdta (Me)N($CH_2CH_2NMe_2$)$_2$), 53.9 (pmdta (Me)N($CH_2CH_2NMe_2$)($CH_2CH_2NMe_2$)), 55.6 (pmdta (Me)N($CH_2CH_2NMe_2$)($CH_2CH_2NMe_2$)), 57.1 (pmdta (Me)N($CH_2CH_2NMe_2$)($CH_2CH_2NMe_2$)), 58.2 (pmdta (Me)N($CH_2CH_2NMe_2$)($CH_2CH_2NMe_2$)), 66.3 (CH_3CH_2)$_2$O), 80.1 (MgO*CH*Ph$_2$), 122.3 (*m*-CH(Mg-OC(H)Ph$_2$)), 128.8, (*o*-CH(Mg-OC(H)Ph$_2$), 130.2, (*p*-CH(Mg-OC(H)Ph$_2$), 118.2 (b sept, $^{3}J_{CF}$ = 3.8 Hz, *p*-CH(B{$C_6H_3(CF_3)_2$}$_4$)), 125.5 (q, $^{1}J_{CF}$ = 271.6 Hz, CF_3-(B{$C_6H_3(CF_3)_2$}$_4$)), 130.0 [qq, ($^{3}J_{CB}$ = 3.05 Hz, $^{2}J_{CF}$ = 31.5 Hz) *m*-C(B{$C_6H_3(CF_3)_2$}$_4$))], 135.6 (*o*-C(B{$C_6H_3(CF_3)_2$}$_4$)), 162.8 (q, $^{1}J_{BC}$ = 49.6 Hz, *ipso*-C(B{$C_6H_3(CF_3)_2$}$_4$))

^{11}B [160 MHz, 300K,THF(D8)]: δ - 6.52 ppm (s, B{$C_6H_3(CF_3)_2$}$_4$)

^{19}F [470.58 MHz, 300K, THF(D8)]: δ -63.38 (s, CF_3)

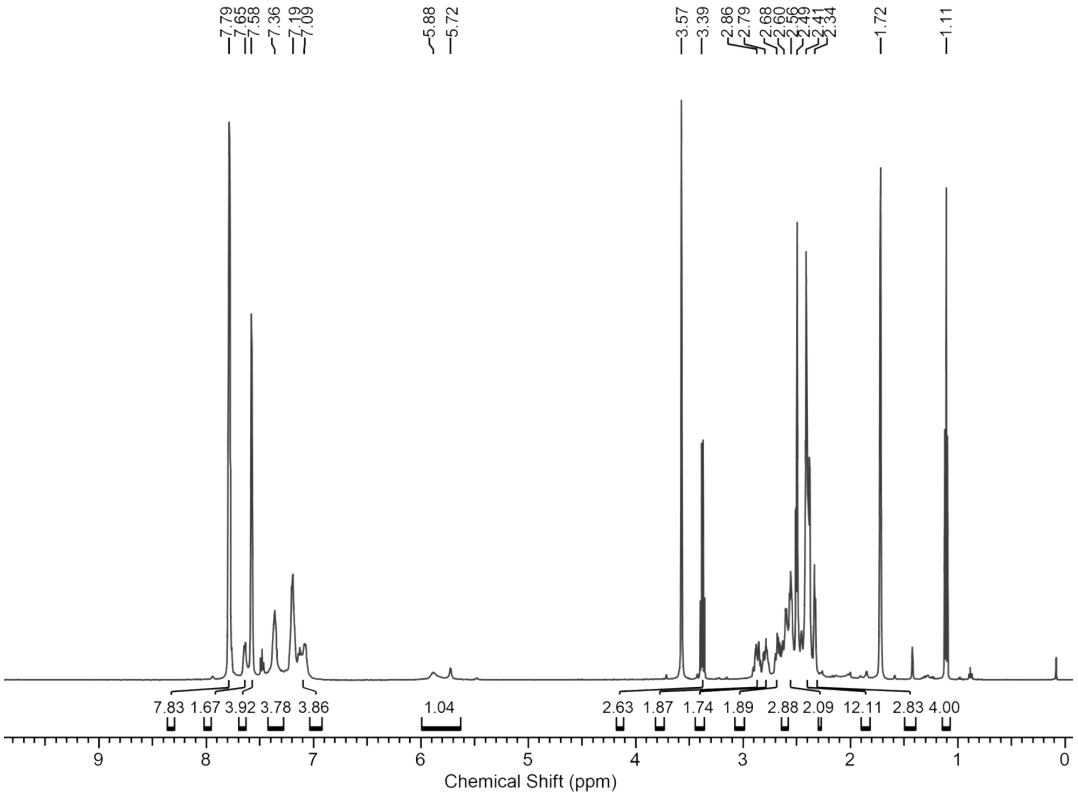


Figure S10: ^{1}H NMR spectrum of compound 2a in THF(D8).

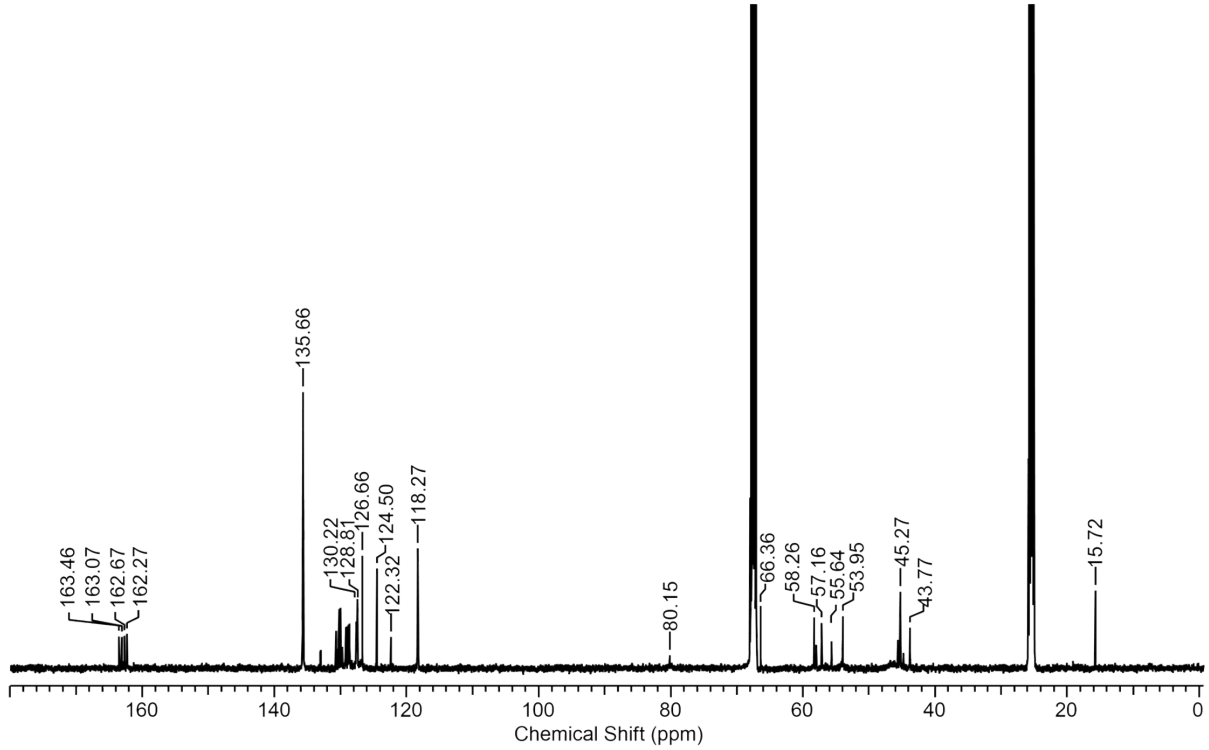


Figure S11: $^{13}C\{^{1}H\}$ NMR of compound 2a in THF(D8).

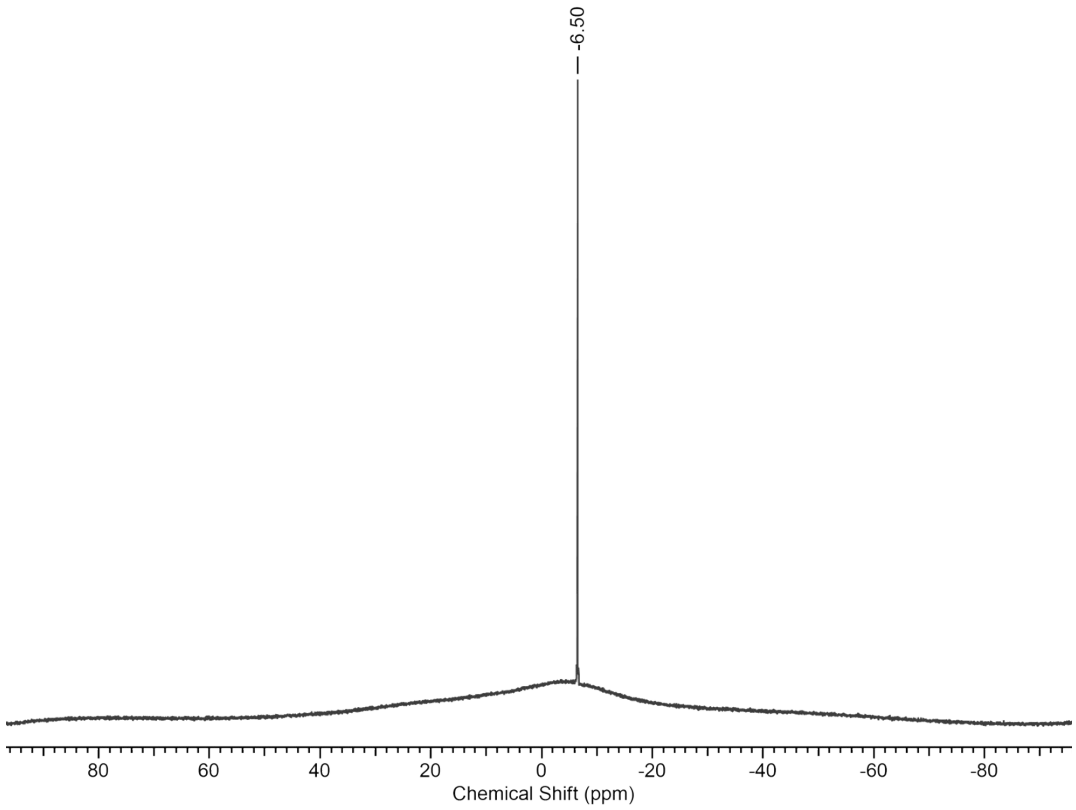


Figure S12: ^{11}B NMR spectrum of compound 2a in THF(D8).

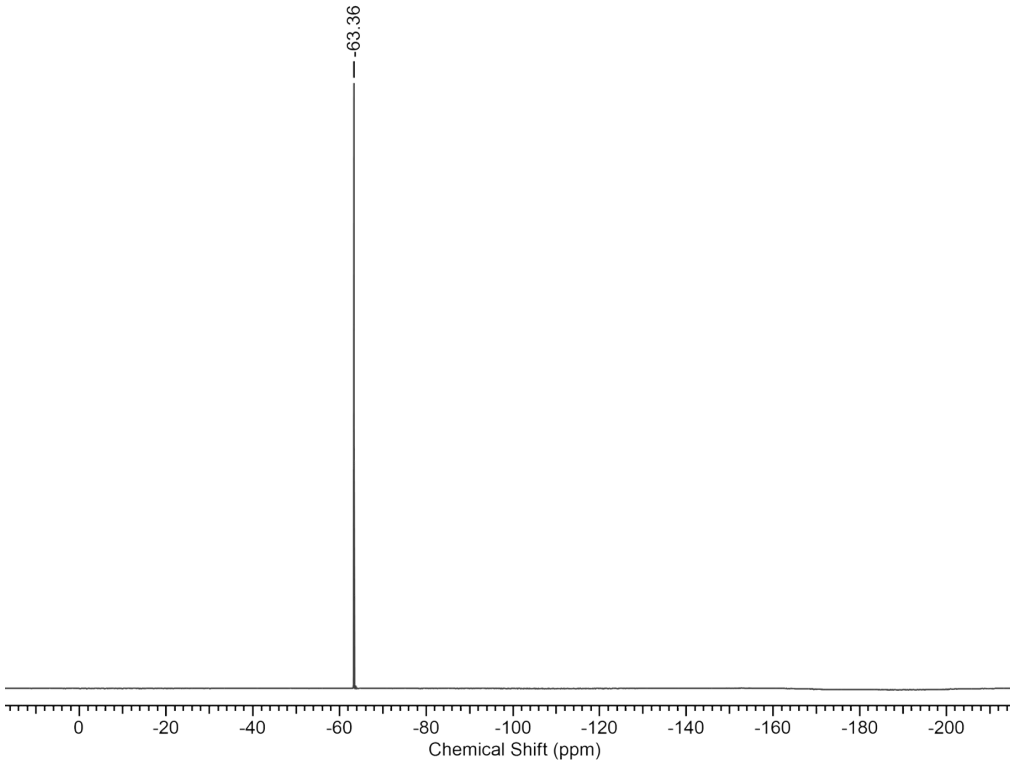


Figure S13: ^{19}F NMR spectrum of compound 2a in THF(D8).

Synthesis of Compound 3a

Method 1: Compound **2a** (0.100 g, 0.076 mmol) was dissolved in THF and was layered with pentane and kept at -30 °C in freezer. Colourless crystals were obtained of compound **3a** in 12 hours. (Yield: 0.068 g, 81 %).

Method 2: Compound **5a** (0.100 g, 0.047 mmol) was dissolved in THF and layered with pentane and kept at room temperature. Colourless crystals were obtained of compound **3a** in 12 hours. (Yield: 0.98 g ,96 %)

Elemental analysis for $C_{88}H_{72}B_2O_6F_{48}Mg$: C, 48.41; H, 3.32. Found: C, 48.38; H, 3.33

^{1}H NMR [500 MHz, 300K, THF(D8)]: δ 1.77 (quin, 4H, $^{3}J_{HH}$ = 3.3 Hz, THF, *m*-CH_2), 3.61 (t, 4H, $^{3}J_{HH}$ = 6.5 Hz, THF, o-CH_2) 7.57 (s, 4H, p-*CH*), 7.78 (s, 8H, o-*CH*)

^{13}C{^{1}H} NMR [125.74 MHz, 300K, THF(D8)]: δ 26.4 (THF, *m*-C), 68.2 (THF, *o*-C), 118.27 (b sept, $^{3}J_{CF}$ = 3.8 Hz, *p*-C), 125.5 (q, $^{1}J_{CF}$ = 271.6 Hz, CF_3), 130.0 [qq,($^{3}J_{CB}$ = 3.0 Hz, $^{2}J_{CF}$ = 31.5 Hz) *m*-C], 135.6 (*o*-C), 162.8 (q, $^{1}J_{BC}$ = 49.6 Hz, *ipso*-C)

^{11}B [160 MHz, 300K,THF(D8)]: δ - 6.50 (s, B{$C_6H_3(CF_3)_2$}$_4$)

^{19}F [470.58 MHz, 300K, THF(D8)]: δ -63.36 (s, CF_3)

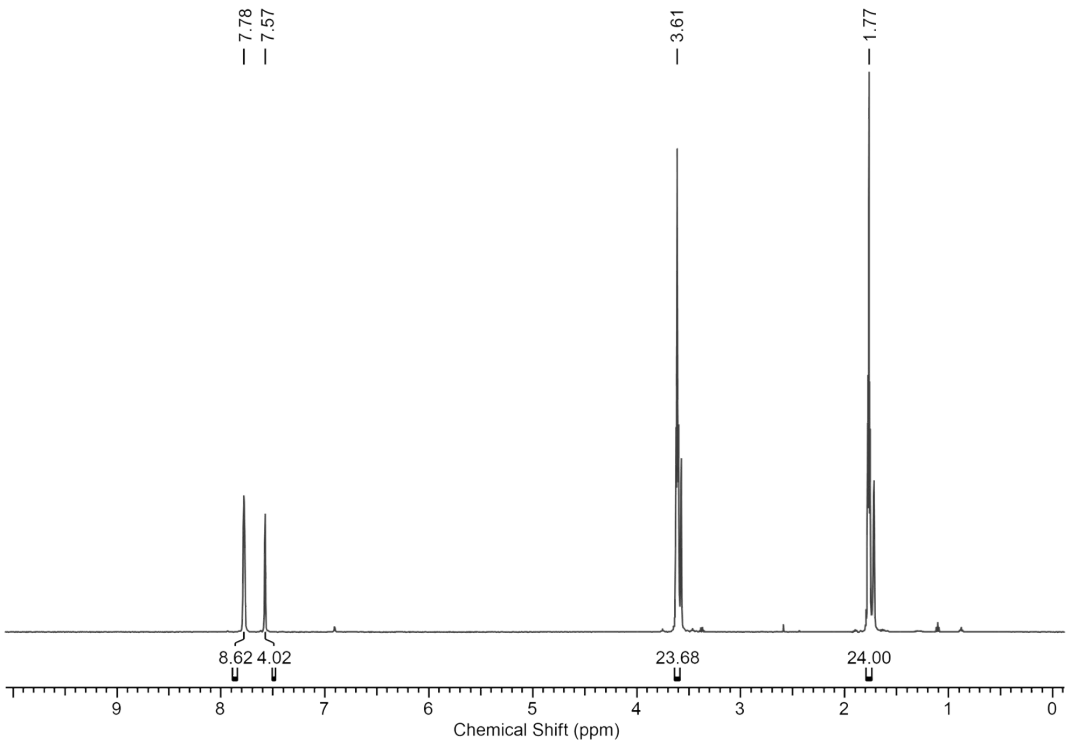


Figure S14: ^{1}H NMR spectrum of compound 3a in THF(D8).

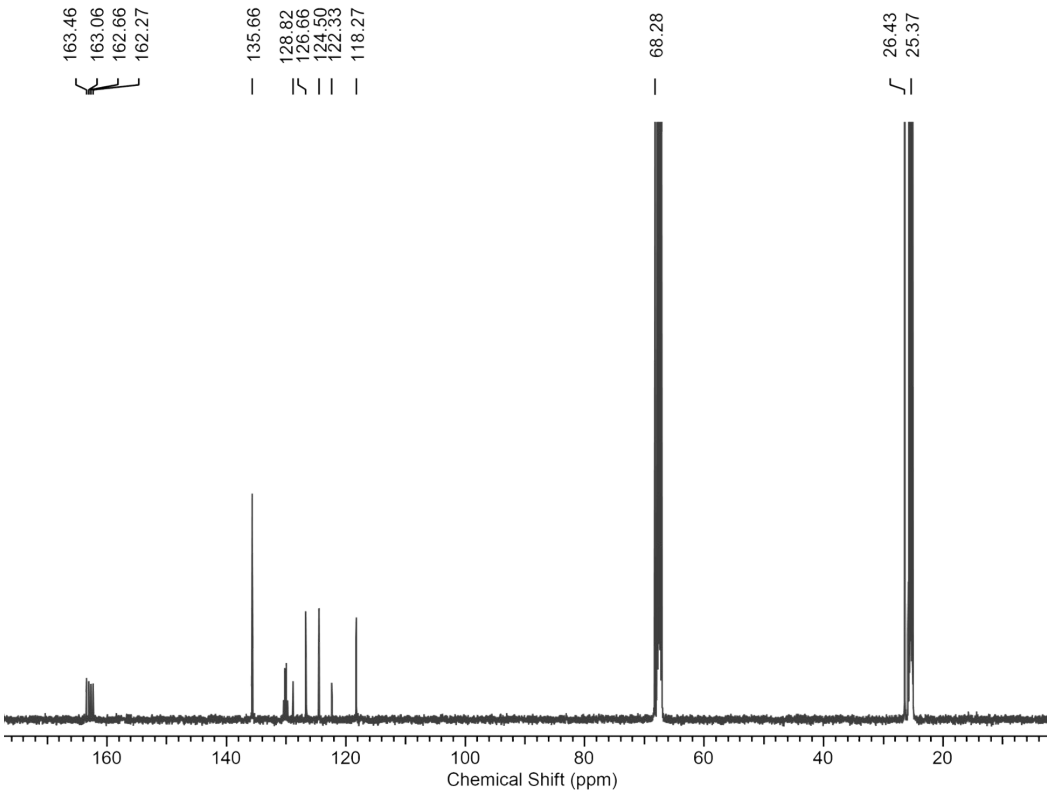


Figure S15: ^{13}C{^{1}H} NMR of compound 3a in THF(D8).

Figure S16: ^{11}B NMR spectrum of compound 3a in THF(D8).

Figure S17: ^{19}F NMR spectrum of compound 3a in THF(D8).

Reaction of 1a with phenylbenzoate

Crystals of **1a** [(pmdta)Mg-*n*-Bu][B{$C_6H_3(CF_3)_2$}$_4$] (0.100 g, 0.089 mmol) and phenylbenzoate (0.009 g, 0.045 mmol) was added to a vial in glove box and to the solid mixture 5 mL toluene was added. The reaction mixture was stirred for 12 hours and toluene was removed under vacuum. THF was added to the residual solid and layered with pentane. After 2 hours crystals of $Mg(THF)_6^{2+}$ was obtained and the residual solution was decanted. The decanted solution was removed under vacuum and NMR spectrum of the residual solid was recorded in C_6D_6. (Yield: 0.039 g, 79 %)

Thereafter, the product was extracted in diethyl ether and washed with 2M HCl solution. Volatiles were evaporated under reduced pressure and crude sample was obtained as yellow oil. Product formation was confirmed using GC-MS analysis.

^{1}H NMR [500 MHz, 300K, THF(D8)]: δ 0.76 ppm, (t, 6H, $^3J_{HH}$ = 7.3 Hz, $OCHCH_2CH_2CH_2\mathit{CH_3}$), 0.79 (sext, 4H, $^3J_{HH}$ = 4.7 Hz, $OCHCH_2CH_2\mathit{CH_2}CH_3$), 1.64 (m, 4H, $OCHCH_2\mathit{CH_2}CH_2CH_3$), 1.76 (m, 4H, $OCH\mathit{CH_2}CH_2CH_2CH_3$), 1.97 (m, 4H, $OCH\mathit{CH_2}CH_2CH_2CH_3$), 6.16 (t, 2H, $^3J_{HH}$ = 7.2 Hz, $O\mathit{CH}CH_2CH_2CH_2CH_3$), 7.03 (t, 2H, $^3J_{HH}$ = 1.3 Hz, PhO^-, *p*-CH), 7.05 (t, 4H, $^3J_{HH}$ = 1.29 Hz, PhO^-, *m*-CH), 7.08 (t, 2H, $^3J_{HH}$ = 1.45 Hz, *p*-CH), 7.12 (t, 4H, $^3J_{HH}$ = 1.3 Hz, *m*-CH), 7.36 (d, 4H, $^3J_{HH}$ = 7.2 Hz, PhO^-, *o*-CH), 8.19 (d, 4H, $^3J_{HH}$ = 7.0 Hz, *o*-CH)

^{13}C{^{1}H} NMR [125.74 MHz, 300K, THF(D8)]: δ 14.2 ($OCHCH_2CH_2CH_2\mathit{CH_3}$), 22.8 ($OCHCH_2CH_2\mathit{CH_2}CH_3$), 28.0 ($OCHCH_2\mathit{CH_2}CH_2CH_3$), 36.6 ($OCH\mathit{CH_2}CH_2CH_2CH_3$), 76.8 ($O\mathit{CH}CH_2CH_2CH_2CH_3$), 122.1 ($PhO^-$, *o*-CH), 125.8 ($PhO^-$, *p*-CH), 126.9 (*p*-CH), 128.5 (*o*-CH), 129.9 (PhO^-, *m*-CH), 132.8 (*i*-CH), 141.5 (PhO^-, *i*-CH)

EI-MS (m/z): mass calculated $[M]^+$ for $C_{16}H_{16}O$: 164.12; m/z found, 164.06. Literature reference[3]

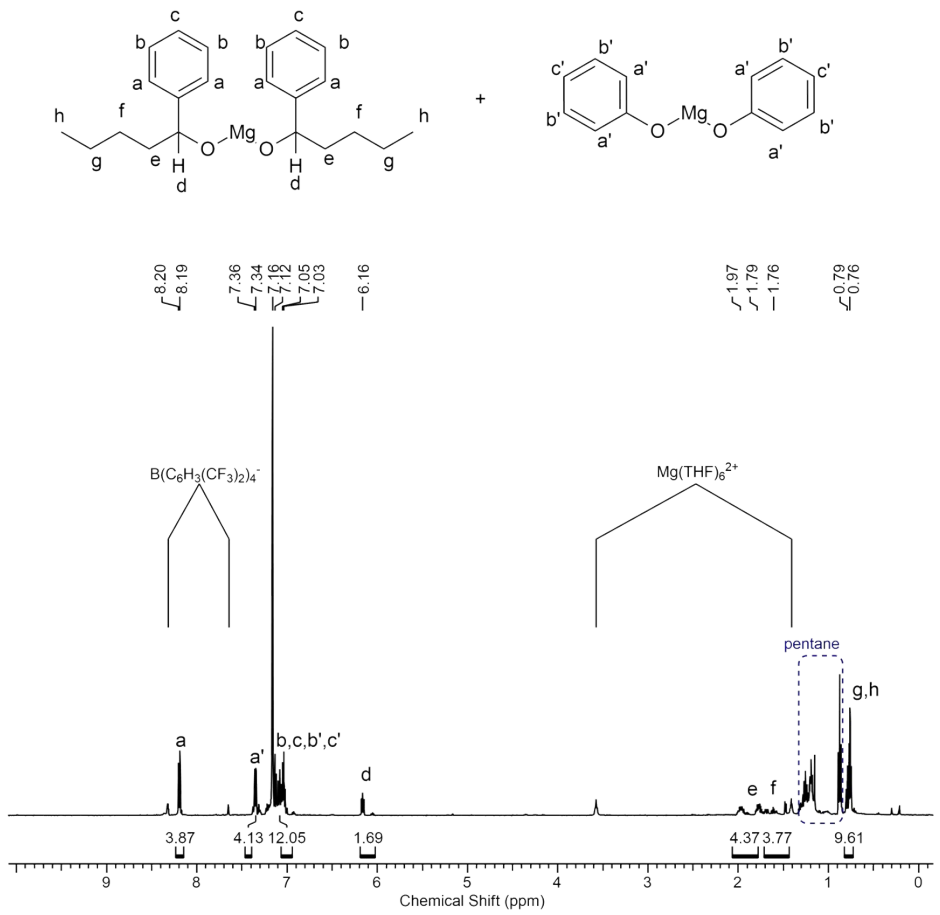


Figure S18: ^{1}H NMR spectrum of reaction between 1a and phenylbenzoate in C_6D_6.

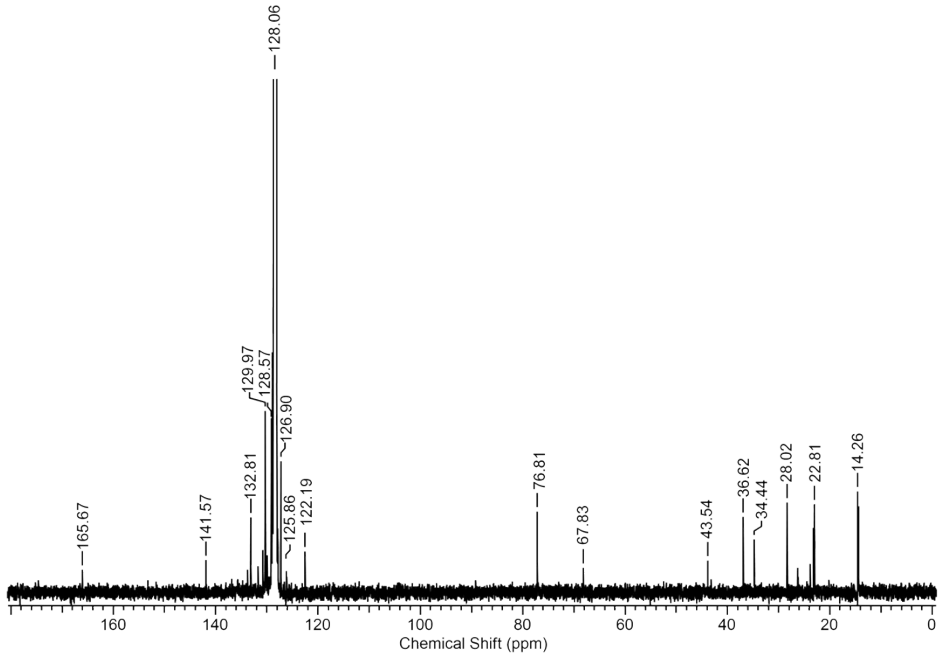


Figure S19: ^{13}C{^{1}H} NMR spectrum of reaction between 1a and phenylbenzoate in C_6D_6.

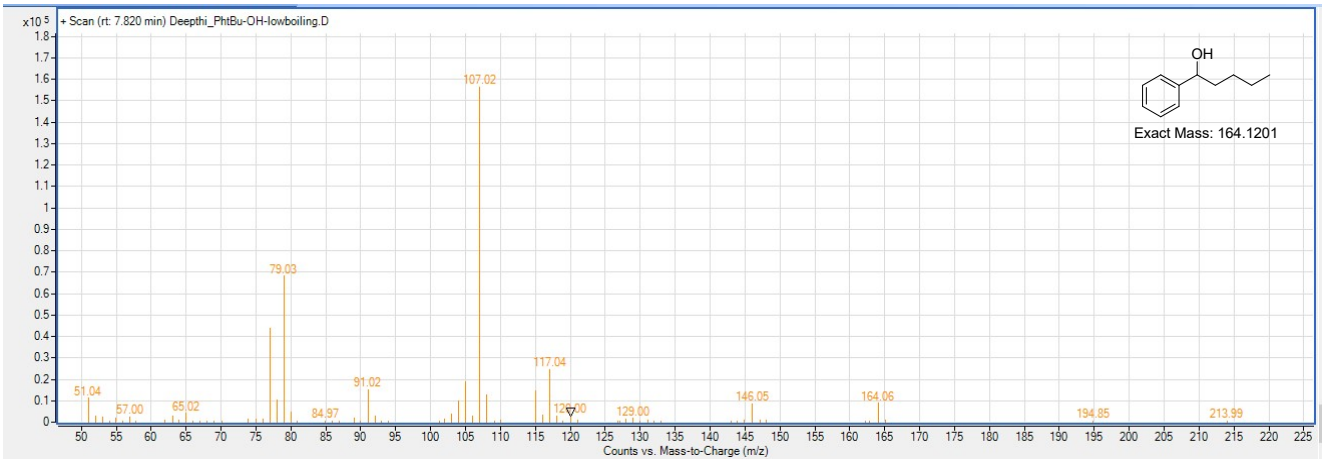


Figure S20: GC-MS spectrum of the product obtained. Literature reference[3]

Synthesis of Compound 4a

Crystals of **1a** [(pmdta)Mg-*n*-Bu][B{$C_6H_3(CF_3)_2$}$_4$] (0.100 g, 0.089 mmol) was dissolved in 3 mL of dry THF inside the glove box and HBpin (0.013 mL, 0.089 mmol) was added to the solution. Cooling the reaction mixture to -25 °C led to the isolation of **3a**. Colourless crystals of **4a** were obtained after layering with pentane and keeping the solution at room temperature for 24 hours. (Exact yield of **4a** cannot be determined because of impurity of **3a**)

^{1}H NMR [500 MHz, 300K, THF(D8)]: δ 1.18 (s, 24H, Mg-(O_2C_2*(CH$_3$)*$_4$), 2.44 (s, 6H, pmdta *(Me)*N($CH_2CH_2NMe_2$)$_2$), 2.58 (s, 24H, pmdta (Me)N($CH_2CH_2NMe_2$)$_2$), 2.65 (t, 8H, $^3J_{HH}$ = 5.3 Hz, pmdta (Me)N($CH_2CH_2NMe_2$)$_2$), 2.80 (s, 8H, $^3J_{HH}$ = 5.9 Hz, pmdta (Me)N($CH_2CH_2NMe_2$)$_2$), 4.53 (s, 2H, Mg_2(μ-H_2)), 7.57 (s, 8H, p-*CH*), 7.78 (s, 16H, o-*CH*)

^{13}C{^{1}H} NMR [125.74 MHz, 300K, THF(D8)]: δ (14.41 ppm, Mg-(O_2C_2*(CH$_3$)*$_4$), δ 23.2 (Mg-(O_2C_2(CH_3)$_4$), 43.4 (pmdta *(Me)*N($CH_2CH_2NMe_2$)$_2$), 46.2 (pmdta (Me)N($CH_2CH_2NMe_2$)$_2$), 57.5 (pmdta (Me)N($CH_2CH_2NMe_2$)$_2$), 58.9 (pmdta (Me)N($CH_2CH_2NMe_2$)$_2$), 118.2 (b sept, $^3J_{CF}$ = 3.8 Hz, *p*-C), 125.5 (q, $^1J_{CF}$ = 271.6 Hz, CF_3), 130.0 [qq, ($^3J_{CB}$ = 3.5 Hz, $^2J_{CF}$ = 31.5 Hz) *m*-C)], 135.6(*o*-C), 162.8 (q, $^1J_{BC}$ = 49.6 Hz, *ipso*-C)

^{11}B [160 MHz, 300K,THF(D8)]: δ - 6.52 (s, B{$C_6H_3(CF_3)_2$}$_4$), - 15.4 (s, BH_3^-)

^{19}F [470.58 MHz, 300K, THF(D8)]: δ -63.3(s, CF_3)

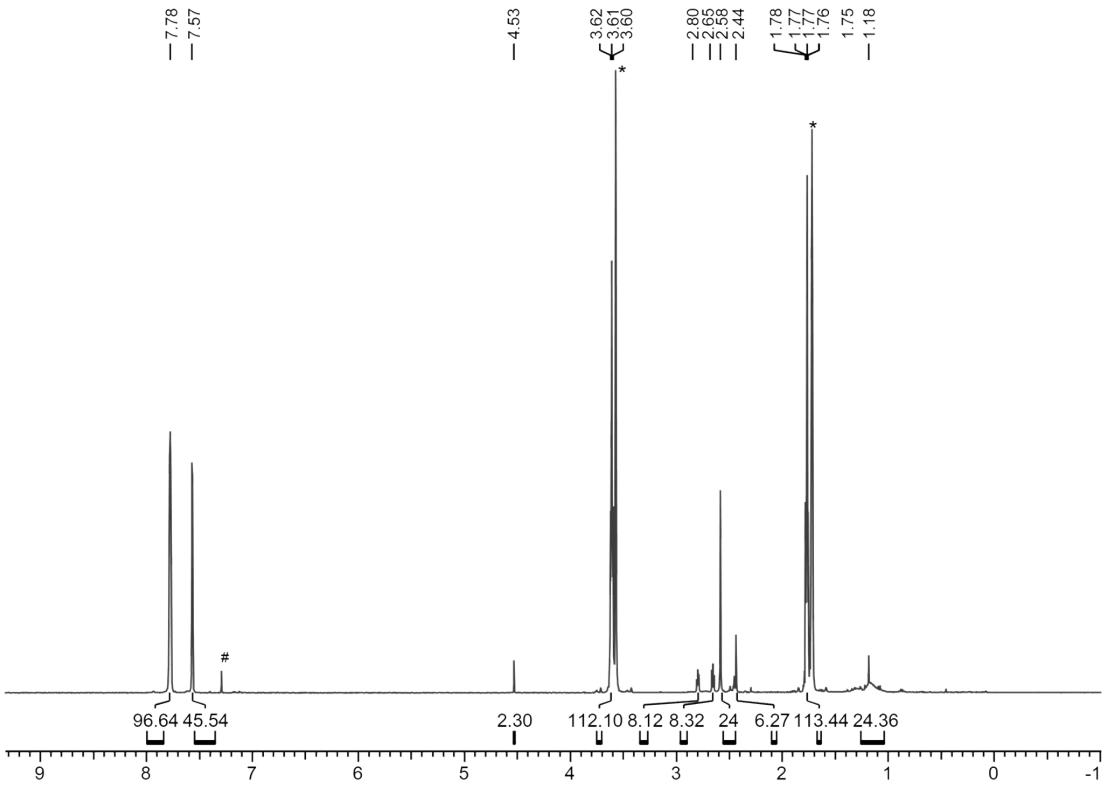


Figure S21: ^{1}H NMR spectrum of compound 4a in THF(D8). * THF(D8) peaks, # C_6H_6 impurity in THF(D8).

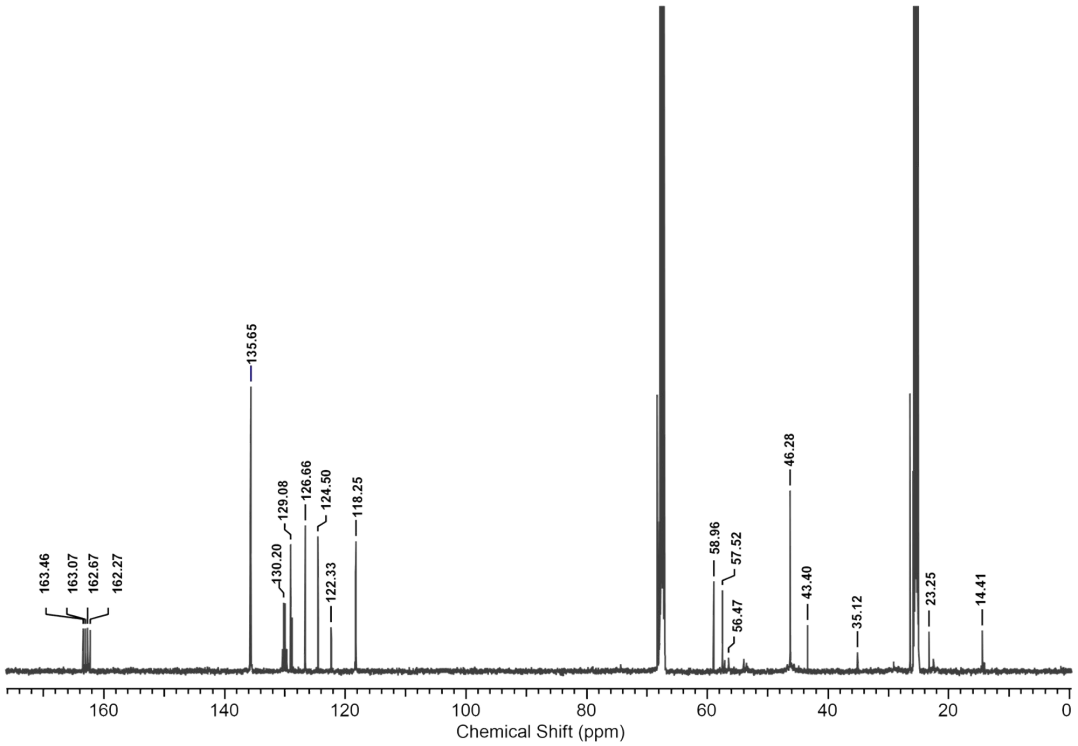


Figure S22: ^{13}C{^{1}H} NMR of compound 4a in THF(D8).

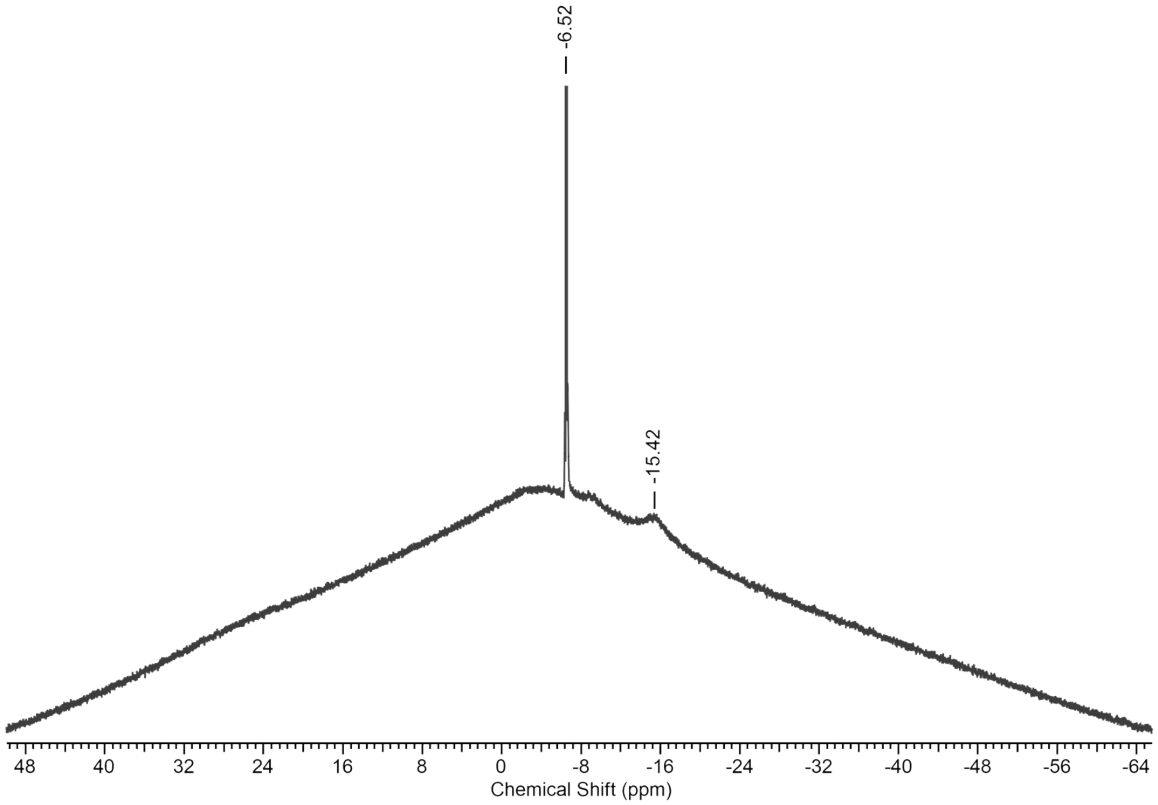


Figure S23: ^{11}B NMR spectrum of compound 4a in THF(D8).

Figure S24: ^{19}F NMR spectrum of compound 4a in THF(D8).

Synthesis of compound 5a

Method 1: Crystals of **1a** [(pmdta)Mg-*n*-Bu][B{$C_6H_3(CF_3)_2$}$_4$] (0.100 g, 0.089 mmol) was dissolved in dry Et_2O and HBpin (0.012 mL, 0.089 mmol) was added drop wise into the solution and instant precipitation of compound **5a** was observed. (Yield: 0.087 g, 92 %).

Method 2: Crystals of **1a** [(pmdta)Mg-*n*-Bu][B{$C_6H_3(CF_3)_2$}$_4$] (0.100 g, 0.089 mmol) was dissolved in dry Et_2O and five-fold excess of $PhSiH_3$ (0.054 mL, 0.445 mmol) was added in to the solution and the solution was stirred for 48 hours leading to the precipitation of **5a.** Crystals of **5a** was grown by keeping the solution of $PhSiH_3$ and 1a for 48 hours at -30 °C for 24 hours. (Yield: 0.079 g, 84 %).

Elemental analysis for $Mg_2N_6C_{82}H_{72}B_2F_{48}$: C, 46.38; H, 3.42; N, 3.96. Found: C, 46.36; H, 3.45; N, 3.93

^{1}H NMR [500 MHz, 300K, THF(D8)]: δ 2.15 (s, 24H, pmdta (Me)N(CH_2CH_2N*Me_2)$_2$), 2.19 (s, 6H, pmdta *(Me)*N($CH_2CH_2NMe_2$)$_2$), 2.30 (t, 8H, $^3J_{HH}$ = 6.8 Hz, pmdta (Me)N(CH_2*CH_2*NMe_2)$_2$), 2.41 (s, 8H, $^3J_{HH}$ = 6.5 Hz, pmdta (Me)N(*CH_2*CH_2NMe_2)$_2$), 4.53 (s, 2H, $Mg_2(\mu\text{-}H_2)$), 7.57 (s, 8H, p-*CH*), 7.78 (s, 16H, o-*CH*))

^{11}B [160 MHz, 300K,THF(D8)]: δ -6.5 (s, B{$C_6H_3(CF_3)_2$}$_4$)

^{19}F [470.58 MHz, 300K, THF(D8)]: δ -63.3 (s, CF_3)

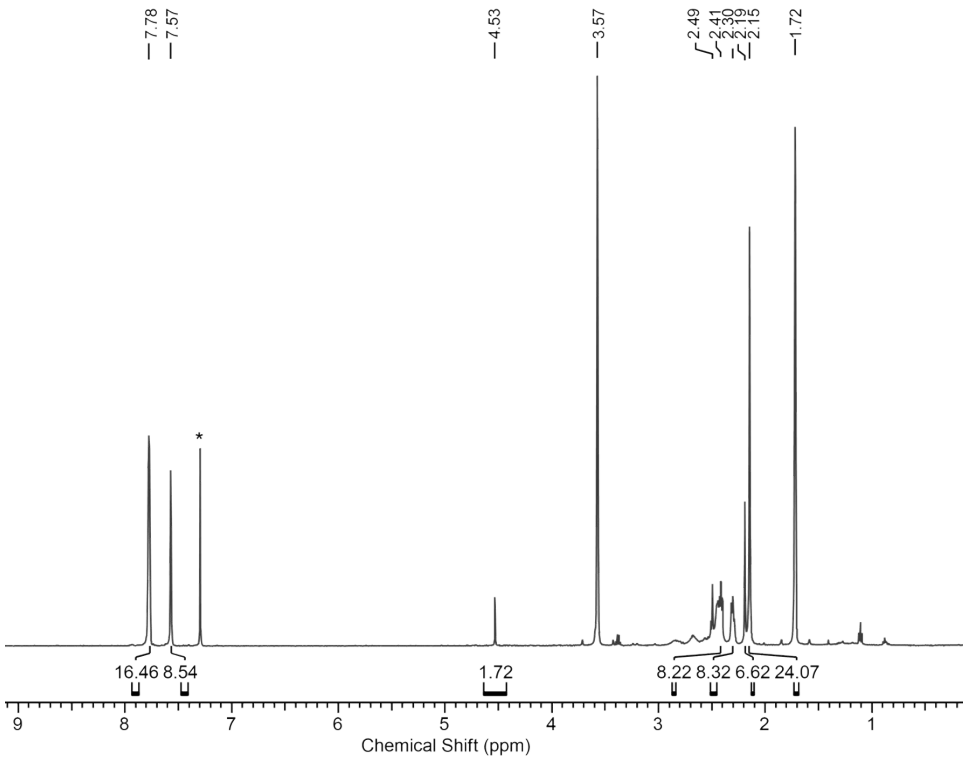


Figure S25: ^{1}H NMR spectrum of compound 5a in THF(D8).

Reaction of 5a with carbon monoxide

Crystals of **5a** [(pmdta)Mg-H]$_2$[B{$C_6H_3(CF_3)_2$}$_4$]$_2$ (0.100 g, 0.047 mmol) was added in a solvent tube fitted with J Young tap and dry Et_2O was added making a suspension of **5a**. The solvent tube was degassed twice and 1 atm of carbon monoxide was purged into the solvent tube. The reaction mixture was stirred for 12 hours and all the solvent was removed under vacuum. NMR of the obtained solid was recorded in dry THF(D8).

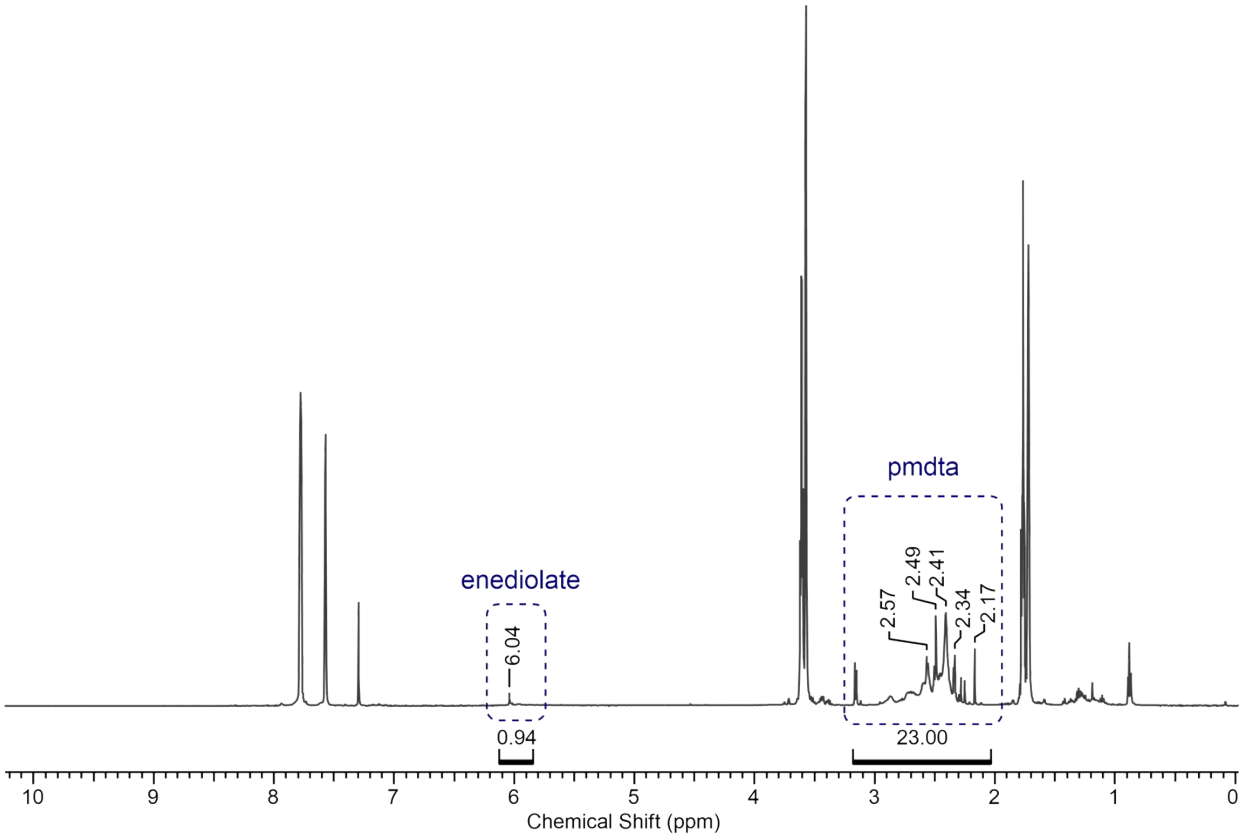


Figure S26: ^{1}H NMR spectrum of reaction between compound 5a and carbon monoxide.

3. Crystallographic Data

Crystals were layered with Paratone oil before mounting on diffractometer. Single-crystal X-ray crystallography for structural analysis was performed on a Bruker Kappa APEX II CCD Diffractometer, using Mo-Kα radiation, having a wavelength of 0.71073 Å, equipped with a CCD detector by using the APEX software package.[4] A matrix scan was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorenz and polarization effects and background using SAINT.[5] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS.[6] Space group assignments were based upon systematic absences, E statistics, and successful refinement of the structures. The structures were solved by SHELXT (version 2018/2) and refined by SHELXTL (version 2018/3) software package installed in the platform WinGX.[7,8] All non-hydrogen atoms, including those in disordered molecules, were refined anisotropically. Hydrogen atoms are placed at calculated positions and refined using a riding model. Crystallographic data, details of data collection and structure refinement parameters for compound **1b, 2a, 3a, 4a** and **5a** are presented below:

Table S1. Crystal data and structure refinement for **1b.**

Identification code	**1b**	
CCDC Number	2216372	
Empirical formula	$C_{37}H_{32}BF_{20}MgN_3$	
Formula weight	933.77	
Temperature	140(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 14.9256(14) Å	a= 90°.
	b = 20.6814(18) Å	b= 109.490(3)°.
	c = 13.6544(12) Å	g = 90°.
Volume	3973.4(6) $Å^3$	
Z	4	
Density (calculated)	1.561 Mg/m^3	
Absorption coefficient	0.172 mm^{-1}	
F(000)	1888	
Crystal size	0.170 x 0.120 x 0.080 mm^3	
Theta range for data collection	2.444 to 24.998°.	
Index ranges	-17<=h<=17, -24<=k<=24, -16<=l<=16	
Reflections collected	55572	
Independent reflections	6997 [R(int) = 0.0414]	
Completeness to theta = 24.998°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.986 and 0.971	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6997 / 102 / 615	
Goodness-of-fit on F^2	1.042	
Final R indices [I>2sigma(I)]	R1 = 0.0426, wR2 = 0.1062	
R indices (all data)	R1 = 0.0786, wR2 = 0.1321	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.429 and -0.193 $e.Å^{-3}$	

Table S2. Crystal data and structure refinement for **2a.**

Identification code	**2a**	
CCDC Number	2216373	
Empirical formula	$C_{58}H_{56}BF_{24}MgN_3O_2$	
Formula weight	1318.17	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 54.944(5) Å	a= 90°.
	b = 17.9070(14) Å	b= 106.948(5)°.
	c = 20.1401(16) Å	g = 90°.
Volume	18955(3) $Å^3$	
Z	12	
Density (calculated)	1.386 Mg/m^3	
Absorption coefficient	0.141 mm^{-1}	
F(000)	8088	
Crystal size	0.105 x 0.095 x 0.085 mm^3	
Theta range for data collection	2.029 to 25.000°.	
Index ranges	-65<=h<=65, -21<=k<=21, -23<=l<=23	
Reflections collected	246170	
Independent reflections	16669 [R(int) = 0.1182]	
Completeness to theta = 25.000°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.94 and 0.88	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	16669 / 5595 / 1708	
Goodness-of-fit on F^2	1.104	
Final R indices [I>2sigma(I)]	R1 = 0.0722, wR2 = 0.1264	
R indices (all data)	R1 = 0.1606, wR2 = 0.1749	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.288 and -0.259 $e.Å^{-3}$	

Table S3. Crystal data and structure refinement for **3a.**

Identification code	**3a**	
CCDC Number	2216374	
Empirical formula	$C_{100}H_{96}B_2F_{48}MgO_9$	
Formula weight	2399.69	
Temperature	142(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 29.124(2) Å	a= 90°.
	b = 17.614(2) Å	b= 123.418(5)°.
	c = 24.717(3) Å	g = 90°.
Volume	10583.1(19) $Å^3$	
Z	4	
Density (calculated)	1.506 Mg/m^3	
Absorption coefficient	0.157 mm^{-1}	
F(000)	4888	
Crystal size	0.085 x 0.085 x 0.045 mm^3	
Theta range for data collection	1.750 to 24.999°.	
Index ranges	-34<=h<=30, -20<=k<=20, -27<=l<=29	
Reflections collected	51561	
Independent reflections	9322 [R(int) = 0.0635]	
Completeness to theta = 24.999°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.993 and 0.987	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9322 / 246 / 873	
Goodness-of-fit on F^2	1.019	
Final R indices [I>2sigma(I)]	R1 = 0.0763, wR2 = 0.1787	
R indices (all data)	R1 = 0.1287, wR2 = 0.2166	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.926 and -0.501 $e.Å^{-3}$	

Table S4. Crystal data and structure refinement for **4a.**

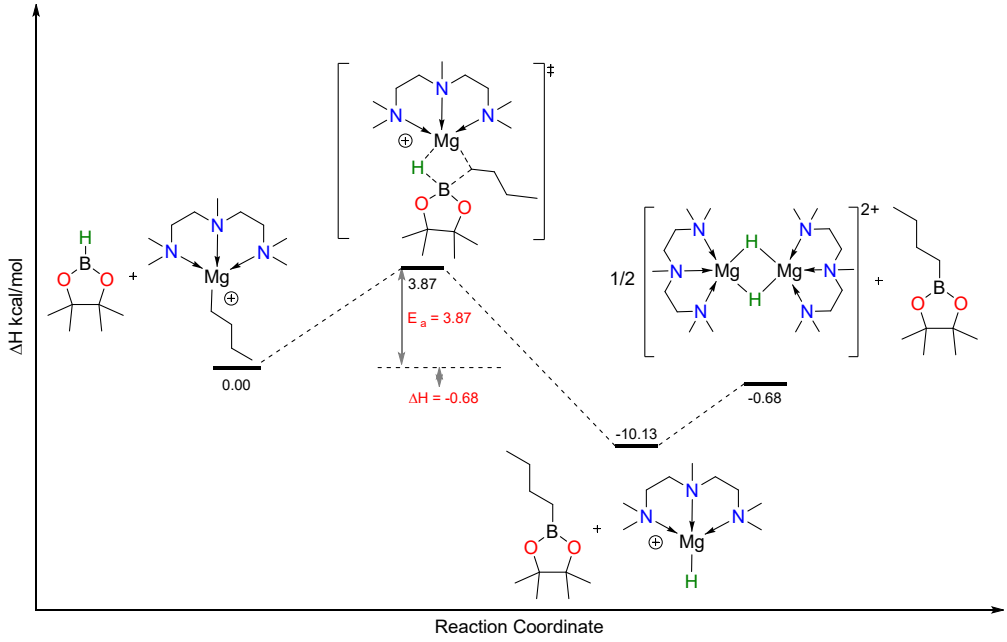
Identification code	**4a**	
CCDC Number	2216375	
Empirical formula	$C_{126}H_{166}B_4F_{48}Mg_4N_6O_{12}$	
Formula weight	3009.12	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.0441(13) Å	a= 104.003(4)°.
	b = 16.924(2) Å	b= 102.788(3)°.
	c = 19.3835(17) Å	g = 112.038(3)°.
Volume	3609.3(7) $Å^3$	
Z	1	
Density (calculated)	1.384 Mg/m^3	
Absorption coefficient	0.145 mm^{-1}	
F(000)	1560	
Crystal size	0.110 x 0.078 x 0.038 mm^3	
Theta range for data collection	1.702 to 24.998°.	
Index ranges	-15<=h<=15, -20<=k<=20, -23<=l<=23	
Reflections collected	86138	
Independent reflections	12719 [R(int) = 0.1088]	
Completeness to theta = 24.998°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.96 and 0.92	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12719 / 1122 / 1157	
Goodness-of-fit on F^2	1.017	
Final R indices [I>2sigma(I)]	R1 = 0.0707, wR2 = 0.1710	
R indices (all data)	R1 = 0.1367, wR2 = 0.2136	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.829 and -0.495 $e.Å^{-3}$	

Table S5. Crystal data and structure refinement for **5a.**

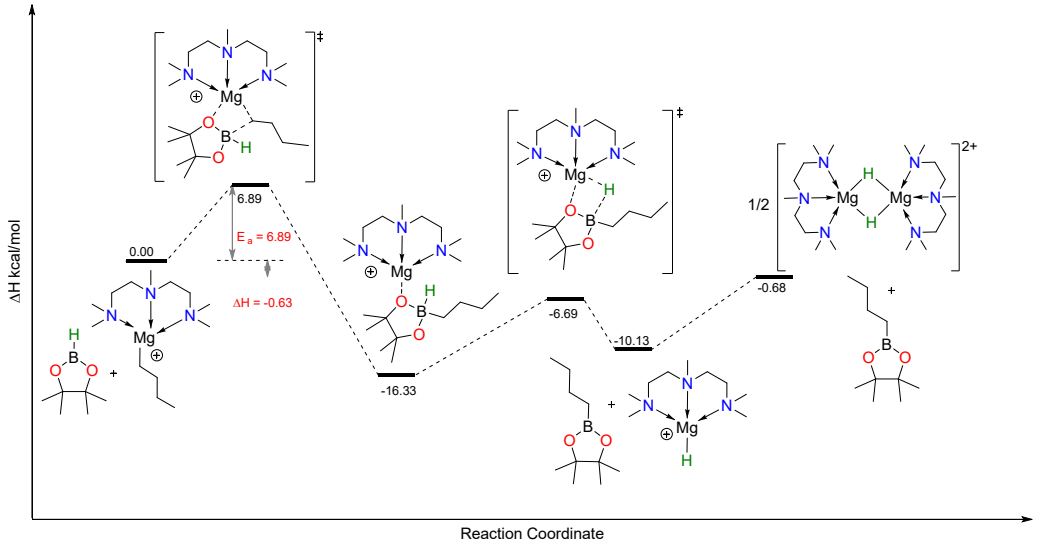
Identification code	**5a**	
CCDC Number	2216376	
Empirical formula	$C_{41}H_{36}BF_{24}MgN_3$	
Formula weight	1061.85	
Temperature	140(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 12.79(3) Å	a= 94.01(5)°.
	b = 13.69(3) Å	b= 99.53(5)°.
	c = 14.16(3) Å	g = 96.29(5)°.
Volume	2419(8) $Å^3$	
Z	2	
Density (calculated)	1.458 Mg/m^3	
Absorption coefficient	0.162 mm^{-1}	
F(000)	1072	
Crystal size	0.075 x 0.048 x 0.038 mm^3	
Theta range for data collection	1.990 to 24.997°.	
Index ranges	-15<=h<=15, -16<=k<=16, -16<=l<=16	
Reflections collected	43978	
Independent reflections	5511 [R(int) = 0.1354]	
Completeness to theta = 24.997°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.997 and 0.989	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8511 / 293 / 830	
Goodness-of-fit on F^2	1.003	
Final R indices [I>2sigma(I)]	R1 = 0.0840, wR2 = 0.2141	
R indices (all data)	R1 = 0.2178, wR2 = 0.3082	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.500 and -0.317 $e.Å^{-3}$	

4. Computational Details

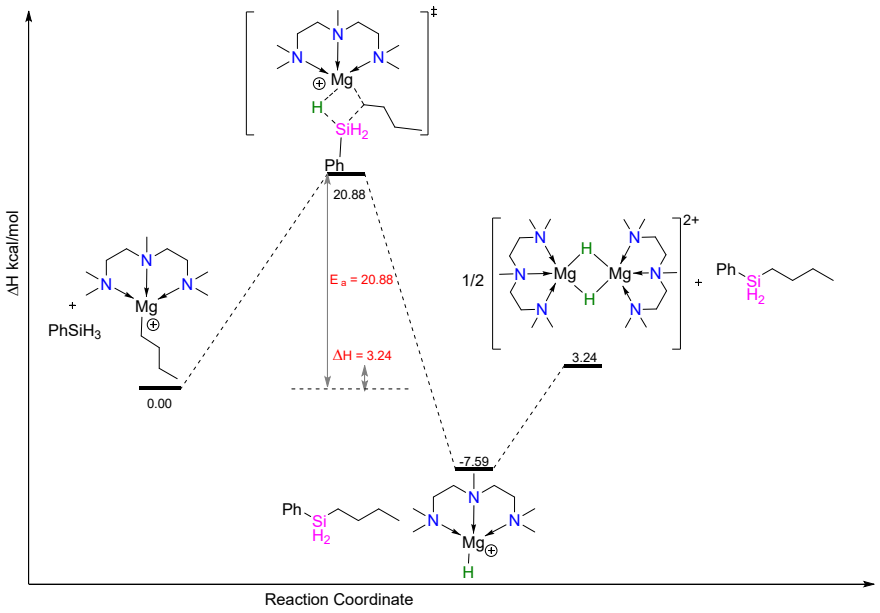
Geometry optimizations were performed using Gaussian16 suite of programs[9] using the Becke's 3-parameter hybrid functional,[10] combined with the non-local correlation functional provided by Perdew/Wang.[11] The 6-311+G(d) all-electron basis set was used for the magnesium atoms and the 6-311G(d,p) for the remaining atoms.[12] All stationary points have been identified for minimum (Nimag=0) or transition states (Nimag=1). Intrinsic Reaction Paths (IRPs)[13] were traced from the various transition structures to obtain the connected intermediates.



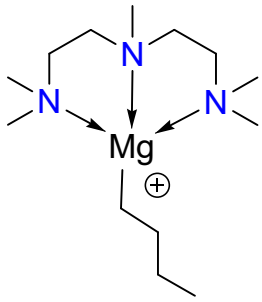
Scheme S1: Computed energy profile at room temperature for the formation of compound 5a (Pathway - I) via reaction between compound 1a and HBpin.



Scheme S2: Computed energy profile at room temperature for the formation of compound 5a (Pathway - II) via reaction between compound 1a and HBpin.



Scheme S3: Computed energy profile at room temperature for the formation of compound 5a via reaction between compound 1a and $PhSiH_3$.



C	2.782443000	0.961262000	-0.464039000
H	3.192943000	0.554180000	0.462671000
H	3.641060000	1.239263000	-1.088621000
C	1.946643000	2.197948000	-0.161338000
H	1.535472000	2.604370000	-1.089787000
H	2.582751000	2.981783000	0.271596000
C	2.493493000	-1.447439000	-0.839624000
H	2.090249000	-2.121784000	-1.598633000

H	3.586367000	-1.484070000	-0.941668000
C	2.099747000	-1.929619000	0.552068000
H	2.585482000	-1.317608000	1.317839000
H	2.467741000	-2.955342000	0.694357000
C	1.931677000	0.138750000	-2.588646000
H	1.566142000	1.144361000	-2.801836000
H	1.245601000	-0.570065000	-3.055629000
H	2.925279000	0.025731000	-3.040156000
C	-0.213425000	2.956812000	0.638402000
H	-1.043380000	2.730919000	1.309557000
H	-0.603642000	3.006764000	-0.379344000
H	0.205881000	3.932736000	0.913280000
C	1.258081000	1.792725000	2.137913000
H	1.671282000	2.747671000	2.487691000
H	2.027964000	1.027161000	2.247934000
H	0.413820000	1.529873000	2.778149000
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H	-0.728520000	-1.925656000	2.388390000
H	0.851433000	-1.226020000	2.795482000
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C	-0.068165000	-2.924424000	0.044738000
H	0.097686000	-2.830617000	-1.029576000
H	-1.140810000	-2.837610000	0.221645000
H	0.270558000	-3.916573000	0.369432000
C	-1.939415000	0.103640000	-1.079089000
H	-2.025327000	1.012707000	-1.694853000
H	-2.026758000	-0.718989000	-1.806348000
C	-3.148872000	0.043699000	-0.129123000
H	-3.112647000	-0.871856000	0.481613000
H	-3.109433000	0.871880000	0.594767000

N	1.975396000	-0.090336000	-1.130045000
N	0.807900000	1.890673000	0.737207000
N	0.640324000	-1.857190000	0.785415000
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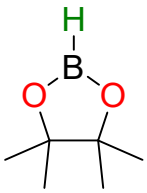
H	-4.565007000	1.007863000	-1.429348000
H	-4.567085000	-0.739492000	-1.544415000
C	-5.694985000	0.029272000	0.129307000
H	-5.682119000	0.868218000	0.833121000
H	-6.646861000	0.065727000	-0.407091000
H	-5.684474000	-0.894734000	0.717153000
Mg	-0.031411000	0.033730000	-0.177889000



C	0.784308000	-0.191382000	-0.048186000
C	-0.784260000	-0.191543000	0.048169000
O	-1.074700000	1.192148000	0.388091000
O	1.074485000	1.192315000	-0.388255000
B	-0.000227000	1.936653000	-0.000095000
H	-0.000469000	3.124666000	-0.000135000
C	-1.471443000	-0.461990000	-1.288369000
H	-1.364713000	-1.506051000	-1.593753000
H	-2.535890000	-0.238579000	-1.187689000
H	-1.066800000	0.175552000	-2.078110000
C	-1.365215000	-1.086257000	1.130353000
H	-2.453618000	-0.991517000	1.134843000
H	-1.116552000	-2.135088000	0.943547000
H	-0.999249000	-0.810039000	2.119562000
C	1.365472000	-1.086218000	-1.130205000

H	2.453840000	-0.991106000	-1.134854000
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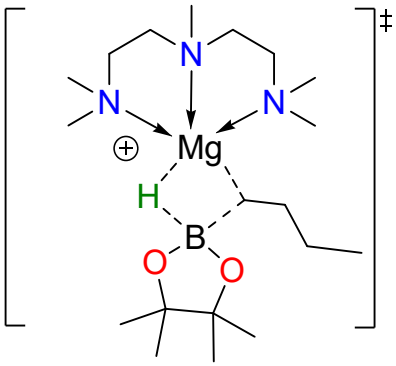

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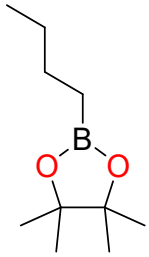

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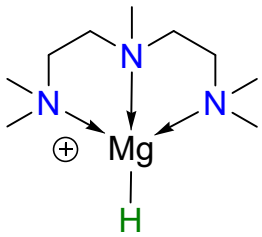

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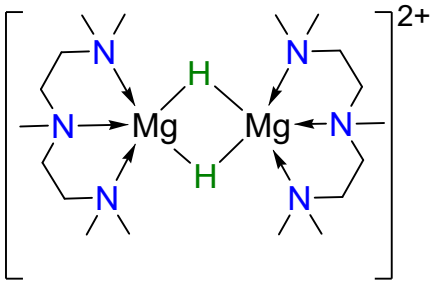

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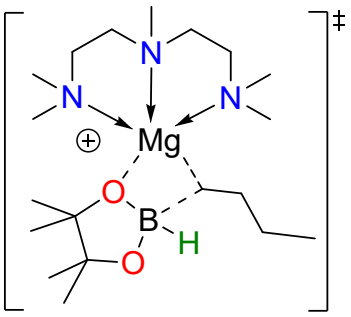

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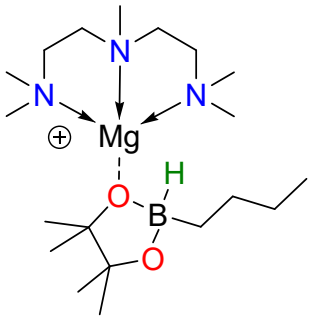

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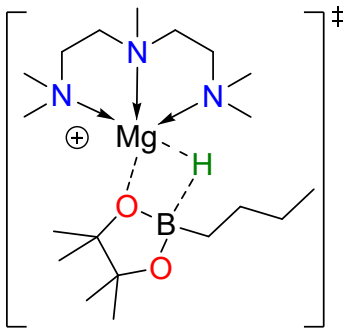

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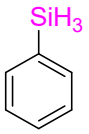

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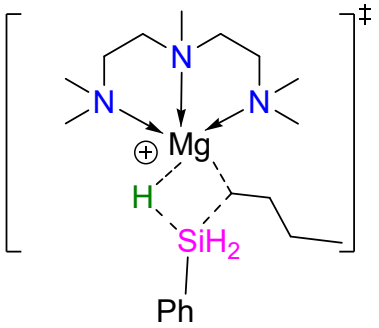

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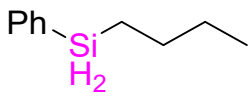

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