Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Disguised hydride in a butylmagnesium cation

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Experimental Methods

All reactions were performed under argon atmosphere using standard Schlenk techniques or in a glovebox under argon atmosphere. Prior to use, glassware was dried at 200 °C and solvents were dried, distilled and degassed using standard methods.[1] Tris(2-aminoethyl)amine (Me_6TREN) was synthesised according to the literature procedure.[2] N-dimethylanilinium tetrkis(pentaflurophenyl) borate ($[PhNMe_2H][B(C_6F_5)_4]$) and Tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) were purchased from Acros Organics and Sigma-Aldrich respectively. Tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) was further sublimed prior to use. CO_2 (99.990% purity) was purchased from Bhuruka Gases Limited, Bangalore and passed through a column of molecular sieves dried overnight at 200 ^oC. ^1H, ^{13}C, ^{11}B, and ^{19}F NMR spectra were recorded on a Bruker 500 MHz spectrometer at ambient temperature. Chemical shifts (δ in ppm) in the ^1H 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). Elemental analyses were performed on an *Elemental Vario Micro Cube* machine. Crystals were layered with paratone oil before mounting on the X-Ray diffractometer. X-ray diffraction data were collected on a Bruker Kappa Apex-II CCD diffractometer at 150 K and with Mo-Kα irradiation (λ = 0.71073 Å). The structures were solved by direct methods with SIR-92, SHELXS-97 or SHELX-2013.

Synthetic Procedures and Characterization

NMR reaction of n-Bu_2Mg and $B(C_6F_5)_3$: n-Bu_2Mg (8 µL, 1M in n-heptane, 0.039 mmol) was taken in a NMR tube inside the glove box at room temperature. After evaporating the solvent through applied vacuum, an equivalent amount of tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (0.020 g, 0.039 mmol) was added to it. THF(D8) stored over Na/K alloy was condensed onto the above mixture and ^1H and ^{11}B NMR spectra were recorded at room temperature.

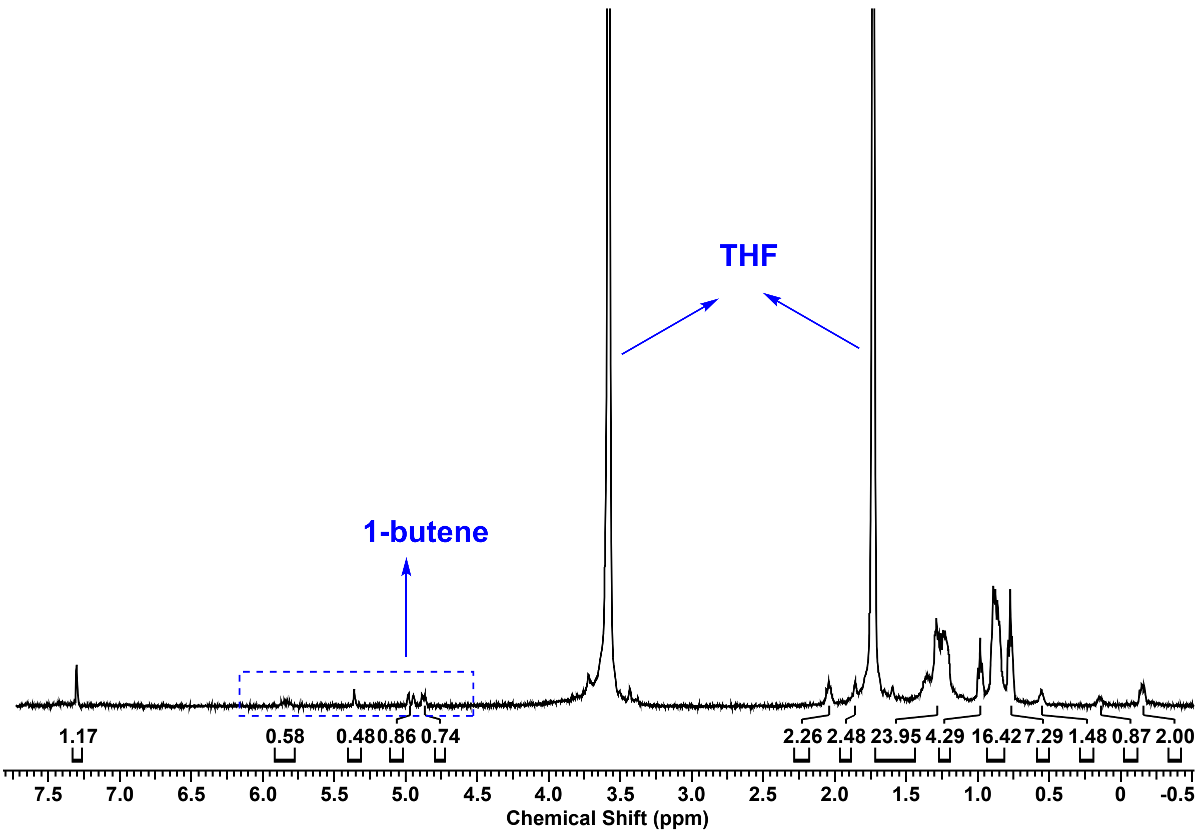


Figure S1. ^{1}H NMR spectrum of reaction between n-Bu_2Mg and $B(C_6F_5)_3$ in THF(D8)

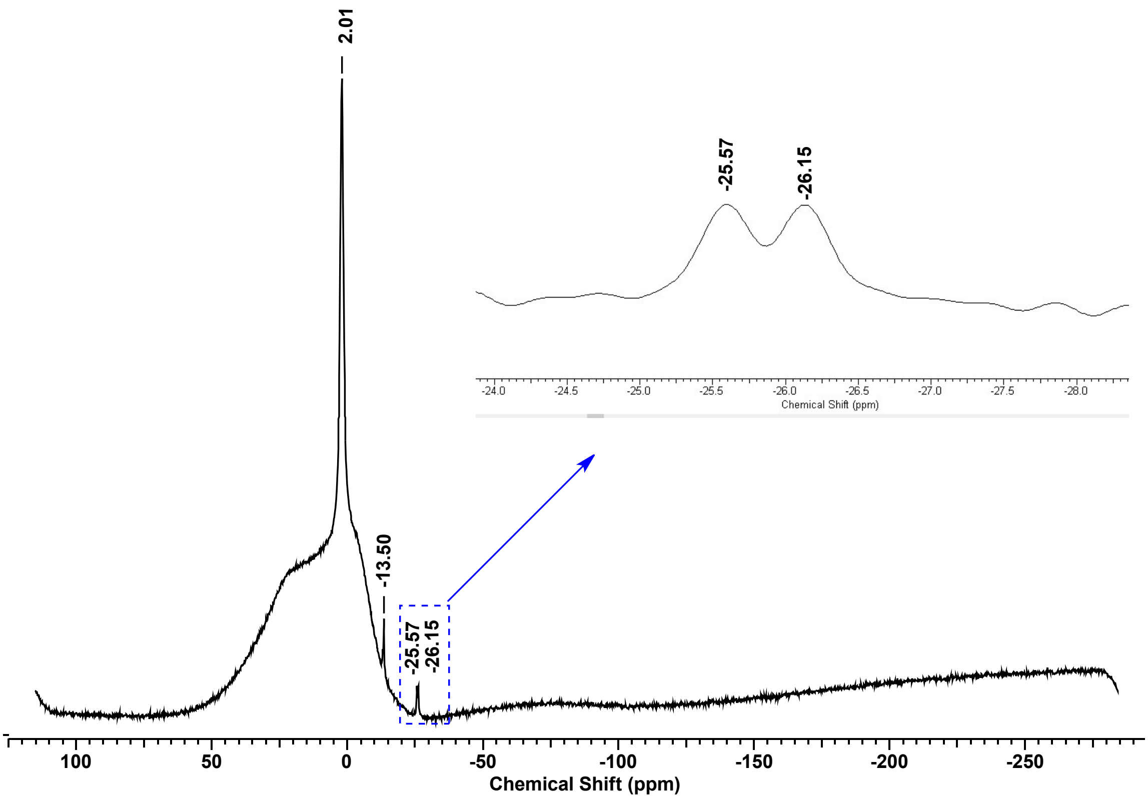


Figure S2. ^{11}B NMR spectrum of reaction between n-Bu_2Mg and $B(C_6F_5)_3$ in THF(D8)

Synthesis of 1 [Me$_6$TREN-Mg-n-Bu][B(C$_6$F$_5$)$_4$]: Me$_6$TREN (0.1 mL, 0.36 mmol) was added to [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] (0.288 g, 0.36 mmol) in 1 mL of dry diethyl ether inside the glove box to form a clear colourless solution. The solution was cooled to less than 10 ^{o}C and to it a cool solution of n-Bu$_2$Mg (0.36 mL, 1M in heptane, 0.36 mmol) in 1mL of diethyl ether was added slowly. Colourless crystals of [Me$_6$TREN-Mg-n-Bu][B(C$_6$F$_5$)$_4$] were obtained immediately. Anal. Calc. for Mg1B1O1N4F20C44H41 (%): C- 49.62, H- 4.60, N- 5.26 Anal. found: (%): C- 49.54, H- 4.47, N- 5.12; ^{1}H NMR [500 MHz, 300K, THF(D8)]: δ (sext, -0.59 ppm, 2H, Mg-CH_2-CH$_2$CH$_2$CH$_3$), δ (t, 0.86 ppm, 3H, Mg-(CH$_2$)$_3$CH_3), δ (sext, 1.27 ppm, 2H, Mg-(CH$_2$)$_2$CH_2CH$_3$), δ (quin, 1.5 ppm, 2H, Mg-CH$_2$-CH_2-CH$_2$CH$_3$), δ (s, 2.44 ppm, 18H, Me$_6$TREN- N(CH$_2$CH$_2$NMe_2)$_3$), δ (s, 2.70 ppm, 6H, Me$_6$TREN- N(CH$_2$CH_2NMe$_2$)$_3$), δ (s, 2.78 ppm, 6H, Me$_6$TREN- N(CH_2CH$_2$NMe$_2$)$_3$); ^{11}B [160 MHz, 300K, THF(D8)]: δ (s, -13.50 ppm, B(C$_6$F$_5$)$_4$); ^{13}C NMR [125.74 MHz, 300K, THF(D8)]: δ (6.09 ppm, Mg-(CH$_2$)$_3$CH_3), δ (32.43 ppm, Mg-(CH$_2$)$_2$CH_2CH$_3$), δ (34.32 ppm, Mg-CH$_2$-CH_2-CH$_2$CH$_3$), δ (6.09 ppm, Mg-CH_2-CH$_2$CH$_2$CH$_3$), δ (44.53 ppm, Me$_6$TREN- N(CH$_2$CH$_2$NMe_2)$_3$), δ (55.32 ppm, Me$_6$TREN-N(CH$_2$CH_2NMe$_2$)$_3$), δ (49.75 ppm, Me$_6$TREN-N(CH_2CH$_2$NMe$_2$)$_3$), δ (65.30 ppm, residual Et$_2$O), δ (14.68 ppm, residual Et$_2$O), δ (135.19 ppm, *ipso*-C), δ (149.14 ppm, *o*-CF), δ (147.24 ppm, *m*-CF), δ (137.11 ppm, *p*-CF); ^{19}F [470.58 MHz, 300K, THF(D8)]: δ (-132.74 ppm, *o*-C*F*), δ (-168.45 ppm, *m*-C*F*),δ (-164.96 ppm, *p*-C*F*).

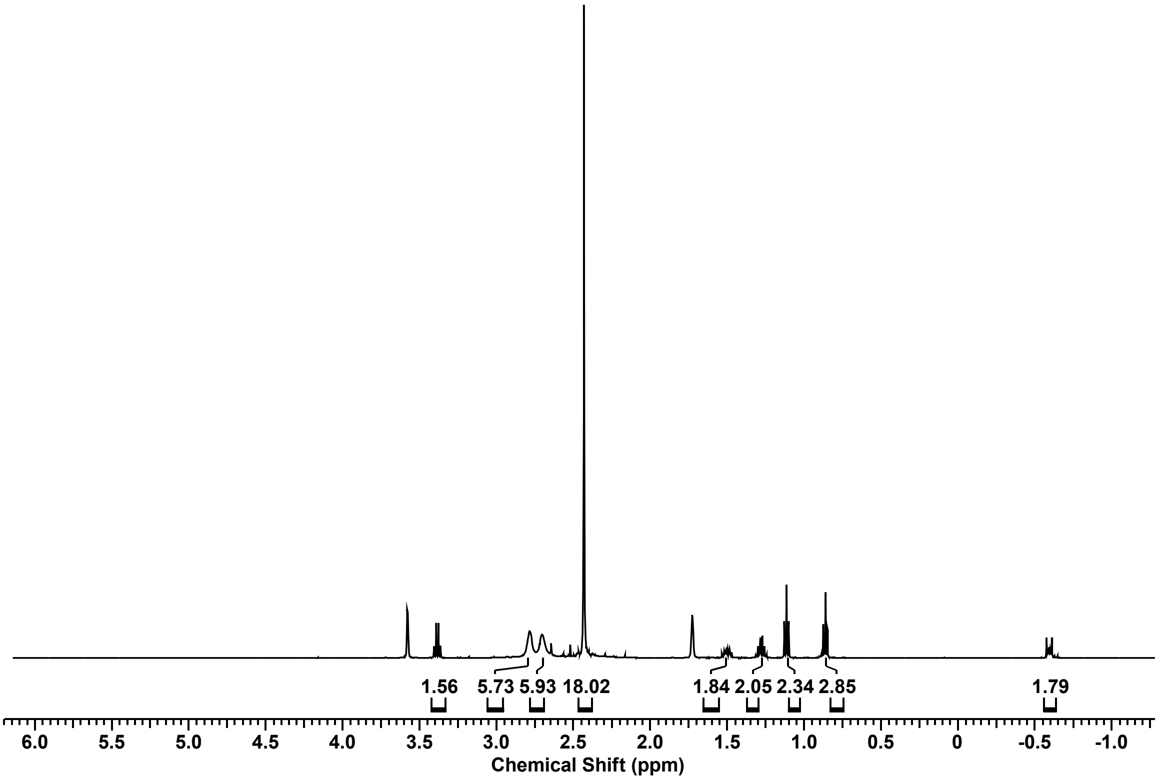


Figure S3. ^{1}H NMR spectrum of [Me$_6$TREN-Mg-n-Bu][B(C$_6$F$_5$)$_4$] (1) in THF(D8)

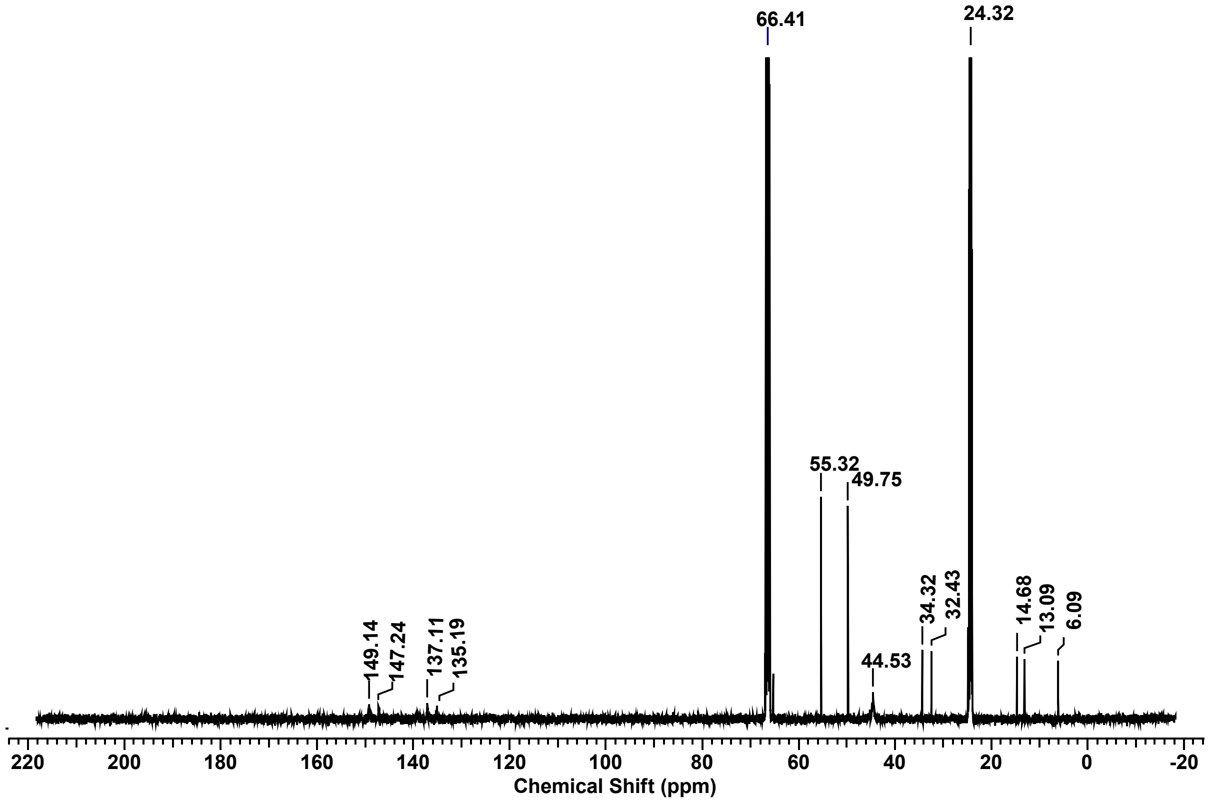


Figure S4. ^{13}C NMR spectrum of [Me$_6$TREN-Mg-n-Bu][B(C$_6$F$_5$)$_4$] (1) in THF(D8)

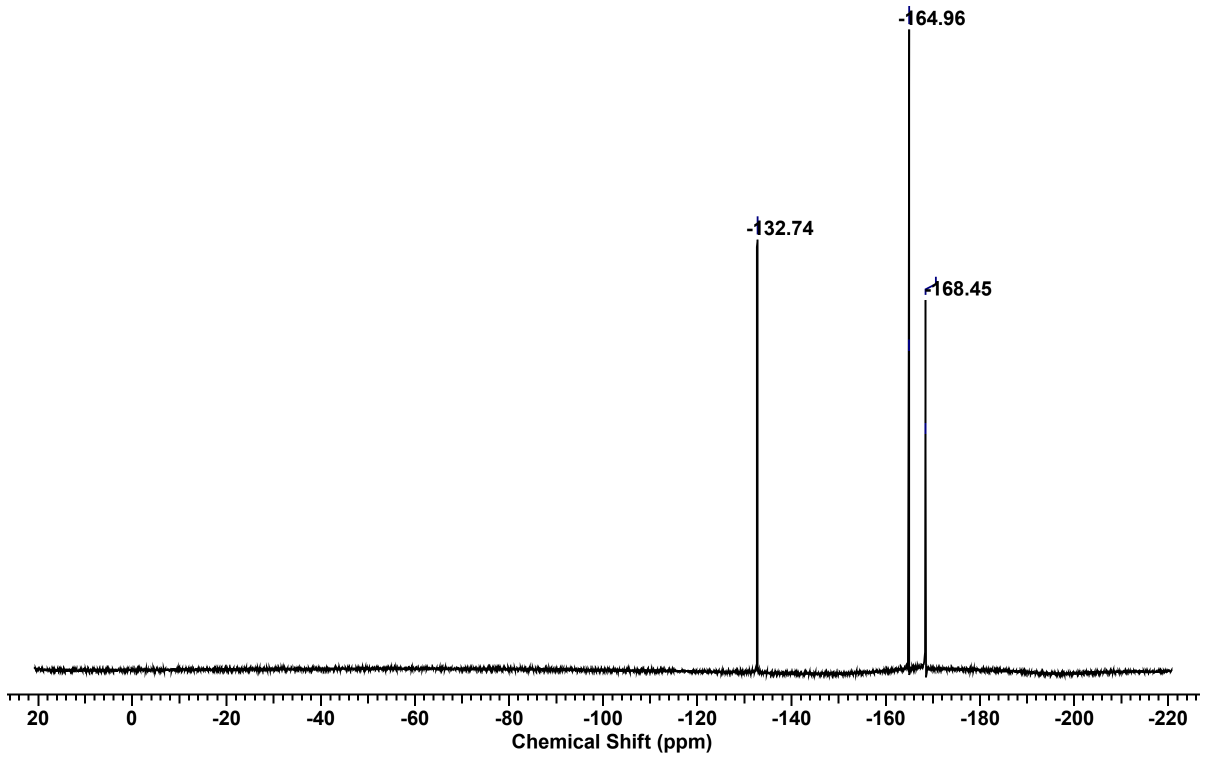


Figure S5. ^{19}F NMR spectrum of [Me$_6$TREN-Mg-n-Bu][B(C$_6$F$_5$)$_4$] (1) in THF(D8)

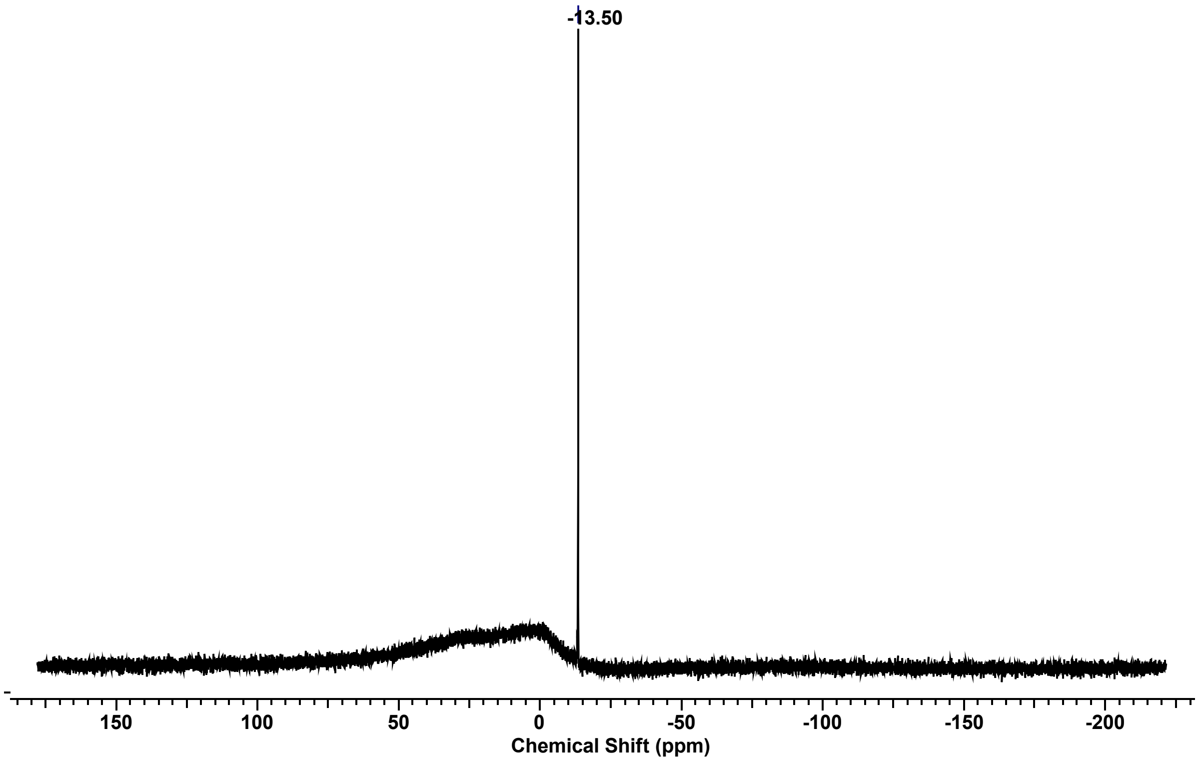
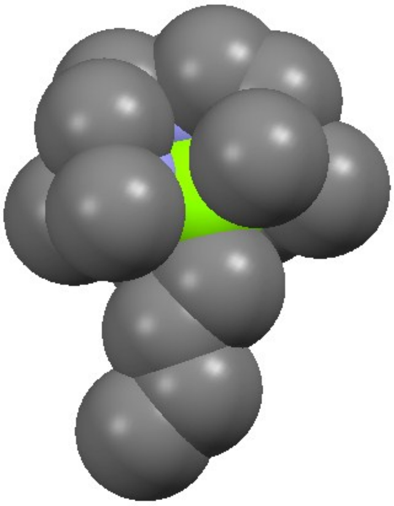


Figure S6. ^{11}**B NMR spectrum of** $[Me_6TREN\text{-}Mg\text{-}n\text{-}Bu][B(C_6F_5)_4]$ **(1) in THF(D8)**



🟩 - Mg atom, 🟦 - N atom, ⬛ - C atom

Figure S7. Space filling model of $[Me_6TREN\text{-}Mg\text{-}n\text{-}Bu][B(C_6F_5)_4]$ **(1) indicating that the metal centre is completely encapsulated by methyl groups on the** Me_6TREN **ligand (Hydrogen atoms have been hidden for clarity)**

Synthesis of 2 $[Me_6TREN\text{-}Mg\text{-}O_2C(n\text{-}Bu)]_2[B(C_6F_5)_4]_2$**:** Crystals of **1** $[Me_6TREN\text{-}Mg\text{-}(n)Bu][B(C_6F_5)_4]$ were dissolved in THF in a reaction flask and pressurised with carbon dioxide (1 atm) at -40 °C which was slowly raised to room temperature. The solution was allowed to stir for 12 hours. Upon layering the THF solution with pentane and storage at -25 °C colourless crystals were obtained with quantitative yield. Anal. Calc. for Mg1B1O3N4F20C45H49 (%): C- 48.74, H- 4.42, N- 5.05 Anal. found: (%): C- 48.60, H- 4.31, N- 4.99; ^{1}H NMR [500 MHz, 300K, THF(D8)]: δ (t, 2.23 ppm, 3H, $MgO_2C(C\mathit{H}_2\text{-}CH_2CH_2CH_3)$), δ (t, 0.9 ppm, 3H, $MgO_2C((CH_2)_3C\mathit{H}_3)$, δ (sext, 1.36 ppm, 2H, $MgO_2C((CH_2)_2C\mathit{H}_2CH_3))$, δ (quin, 1.59 ppm, 2H, $MgO_2C(CH_2\text{-}C\mathit{H}_2\text{-}CH_2CH_3))$, δ (s, 2.42 ppm, 18H, Me_6TREN- $N(CH_2CH_2N\mathit{Me_2})_3)$, δ (t, 2.68 ppm, 6H, Me_6TREN- $N(CH_2C\mathit{H}_2NMe_2)_3)$, δ (t, 2.89 ppm, 6H, Me_6TREN- $N(C\mathit{H}_2CH_2NMe_2)_3)$, δ (t, 1.09 ppm, residual Et_2O), δ (q, 3.36 ppm, residual Et_2O); ^{11}B [160 MHz, 300K, THF(D8)]: δ (s, -13.50 ppm, $B(C_6F_5)_4$); ^{13}C NMR [125.74 MHz, 300K, THF(D8)]: δ (124.89 ppm, $MgO_2\mathit{C}$(n-Bu)), δ (13.24 ppm, $MgO_2C((CH_2)_3C\mathit{H}_3))$, δ (35.06 ppm, $MgO_2C((CH_2)_2C\mathit{H}_2CH_3))$, δ (28.01 ppm, $MgO_2C(CH_2\text{-}C\mathit{H}_2\text{-}CH_2CH_3))$, δ (22.63 ppm, $MgO_2C(C\mathit{H}_2\text{-}CH_2CH_2CH_3))$, δ (45.27 ppm, Me_6TREN- $N(CH_2CH_2N\mathit{Me_2})_3)$, δ (52.20 ppm, Me_6TREN-$N(CH_2C\mathit{H}_2NMe_2)_3)$, δ (56.04 ppm, Me_6TREN- $N(C\mathit{H}_2CH_2NMe_2)_3)$, δ (65.29 ppm, residual Et_2O), δ (14.67 ppm, residual Et_2O), δ (135.17 ppm, *ipso*-C), δ (149.14 ppm, *o*-CF), δ (147.20 ppm, *m*-CF), δ (137.14 ppm, *p*-CF); ^{19}F [470.58 MHz, 300K, THF(D8)]: δ (-132.75 ppm, *o*-C*F*), δ (-168.46 ppm, *m*-C*F*), δ (-164.97 ppm, *p*-C*F*).

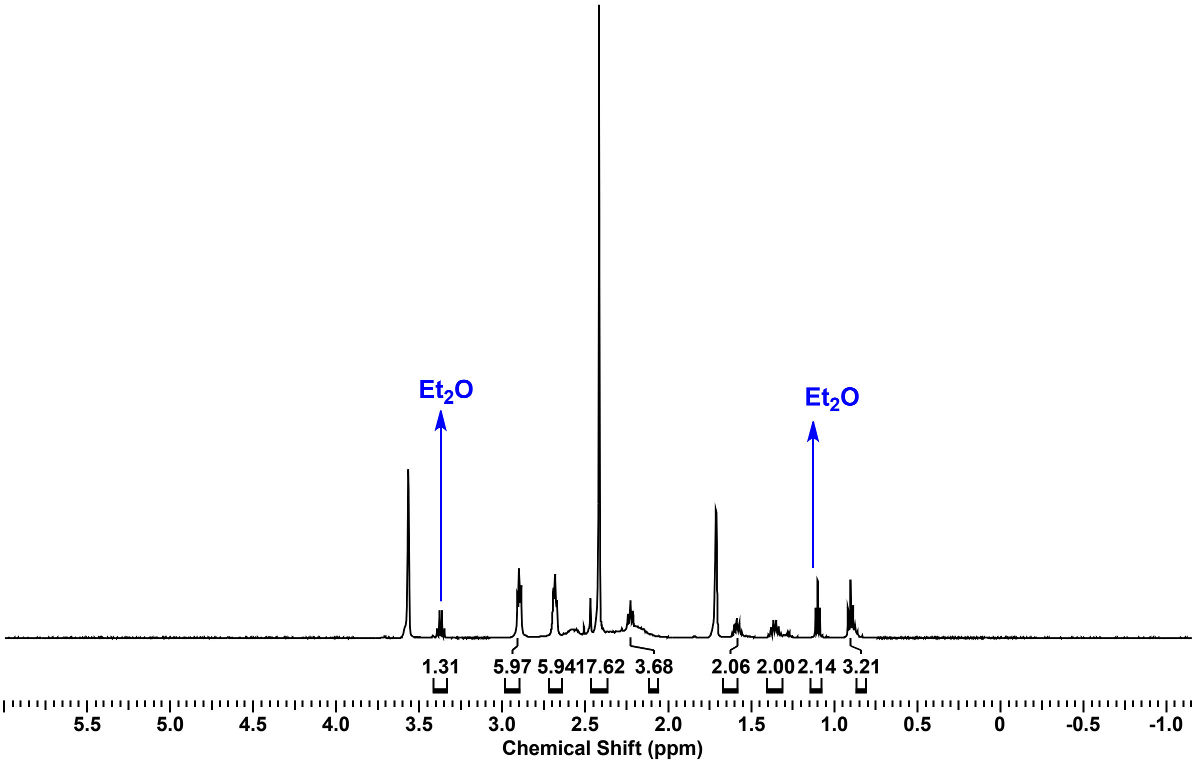


Figure S8. ^1H NMR spectrum of $[Me_6TREN\text{-}Mg\text{-}O_2C(n\text{-}Bu)]_22[B(C_6F_5)_4]$ (2) in THF(D8). Origin of Et_2O signals in the spectrum is due to the presence of traces of solvent in 1.

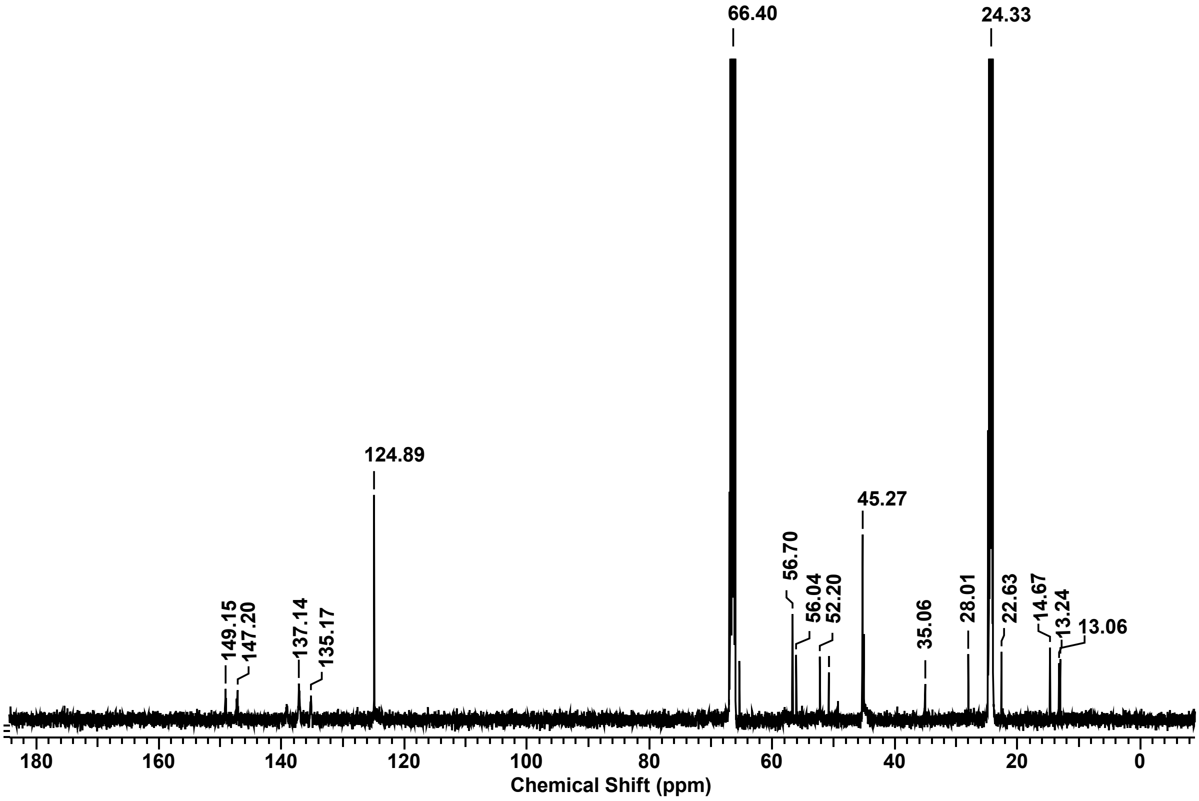


Figure S9. ^{1}H NMR spectrum of [Me$_6$TREN-Mg-O$_2$C(n-Bu)]$_2$2[B(C$_6$F$_5$)$_4$] (2) in THF(D8)

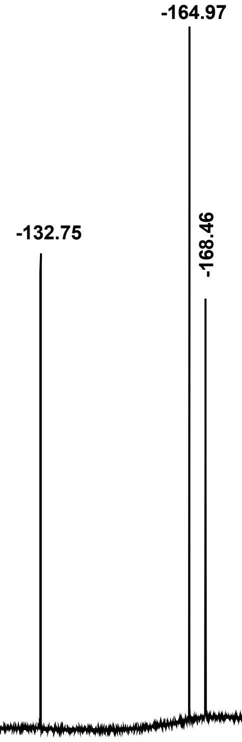


Figure S10. ^{19}F NMR spectrum of [Me$_6$TREN-Mg-O$_2$C(n-Bu)]$_2$2[B(C$_6$F$_5$)$_4$] (2) in THF(D8)

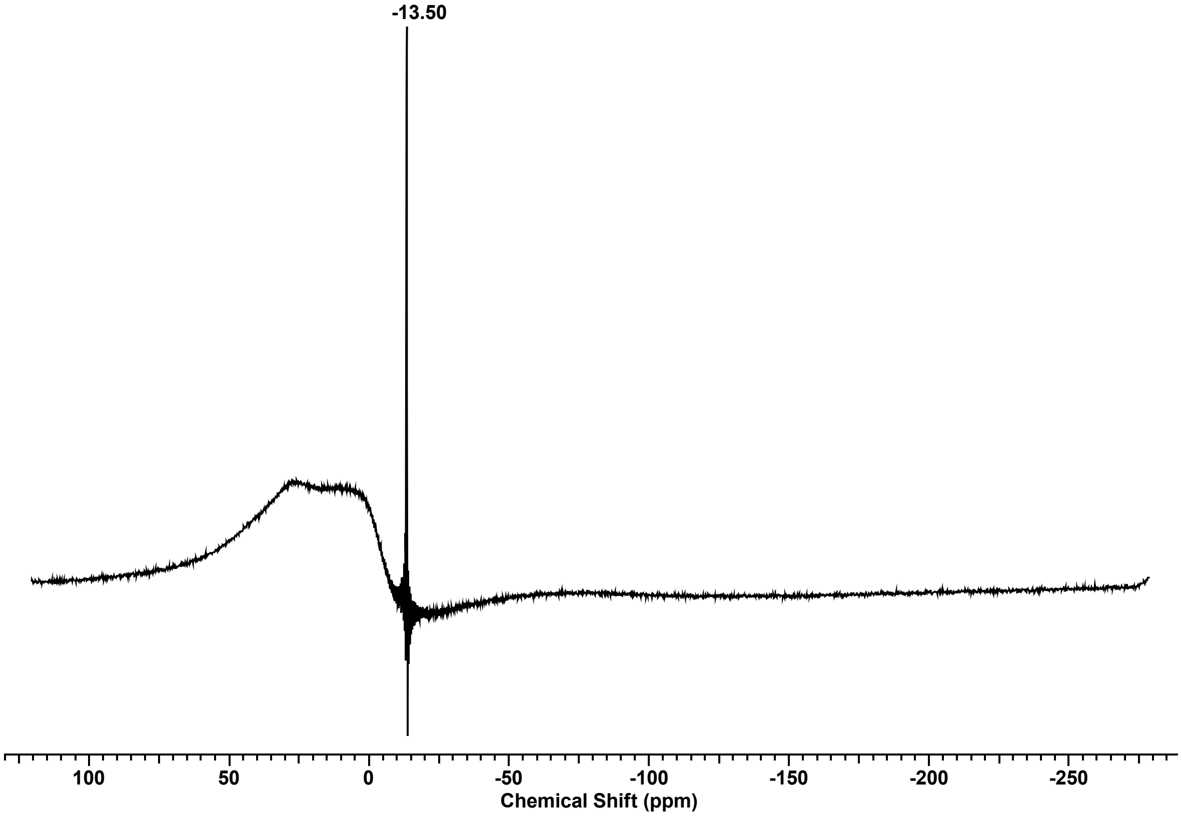


Figure S11. ^{11}B NMR spectrum of [Me$_6$TREN-Mg-O$_2$C(n-Bu)]$_2$2[B(C$_6$F$_5$)$_4$] (2) in THF(D8)

Synthesis of 4 [Me$_6$TREN-Mg-O-C(H)Ph$_2$][B(C$_6$F$_5$)$_4$]: Crystals of **1** [Me$_6$TREN-Mg-n-Bu][B(C$_6$F$_5$)$_4$](0.356 g, 0.36 mmol) were added to 1 equivalent of benzophenone(0.065 g, 0.36 mmol) in a reaction flask inside the glove box. Toluene was added to the solid mixture and the solution was heated to 60 ^{o}C for 12 hours. The solvent was evacuated and the resultant gel was washed multiple times with n-pentane till it turned into a solid powder. The solid was crystallised using THF/pentane at -30 ^{o}C. Colourless crystals were obtained from the yellow solution after 2 days. Anal. Calc. for Mg1B1O1N4F20C49H41 (%): C- 53.53, H- 4.12, N- 4.71 Anal. found: (%): C- 53.35, H- 4.01, N- 4.59; ^{1}H NMR [500 MHz, 300K, THF(D8)]: δ (s, 2.42 ppm, 18H, Me$_6$TREN- N(CH$_2$CH$_2$N*Me$_2$*)$_3$), δ (s, 2.69 ppm, 6H, Me$_6$TREN- N(CH$_2$C*H$_2$*NMe$_2$)$_3$), δ (s, 2.78 ppm, 6H, Me$_6$TREN- N(C*H$_2$*CH$_2$NMe$_2$)$_3$) δ (s, 6.01 ppm, Mg-OC(*H*)Ph$_2$), δ (t, 7.02 ppm, *m*-C*H*(Mg-OC(H)*Ph$_2$*)), δ (t, 7.16 ppm, *p*-C*H*(Mg-OC(H)*Ph$_2$*)), δ (d, 7.46 ppm, *o*-C*H*(Mg-OC(H)*Ph$_2$*)); ^{13}C NMR [125.74 MHz, 300K, THF(D8)]: δ (44.83 ppm, Me$_6$TREN- N(CH$_2$CH$_2$N*Me$_2$*)$_3$), δ (55.31 ppm, Me$_6$TREN-N(CH$_2$C*H$_2$*NMe$_2$)$_3$), δ (49.33 ppm, Me$_6$TREN- N(C*H$_2$*CH$_2$NMe$_2$)$_3$), δ (80.05 ppm, *ipso*-C(Mg-OC(H)*Ph$_2$*)), δ (127.49 ppm, *o*-C(Mg-OC(H)*Ph$_2$*)), δ (125.90 ppm, *m*-C(Mg-OC(H)*Ph$_2$*)), δ (125.36 ppm, *p*-C(Mg-OC(H)*Ph$_2$*)); δ (135.19 ppm, *ipso*-C), δ (149.16 ppm, *o*-CF), δ (147.22 ppm, *m*-CF), δ (137.19 ppm, *p*-CF)

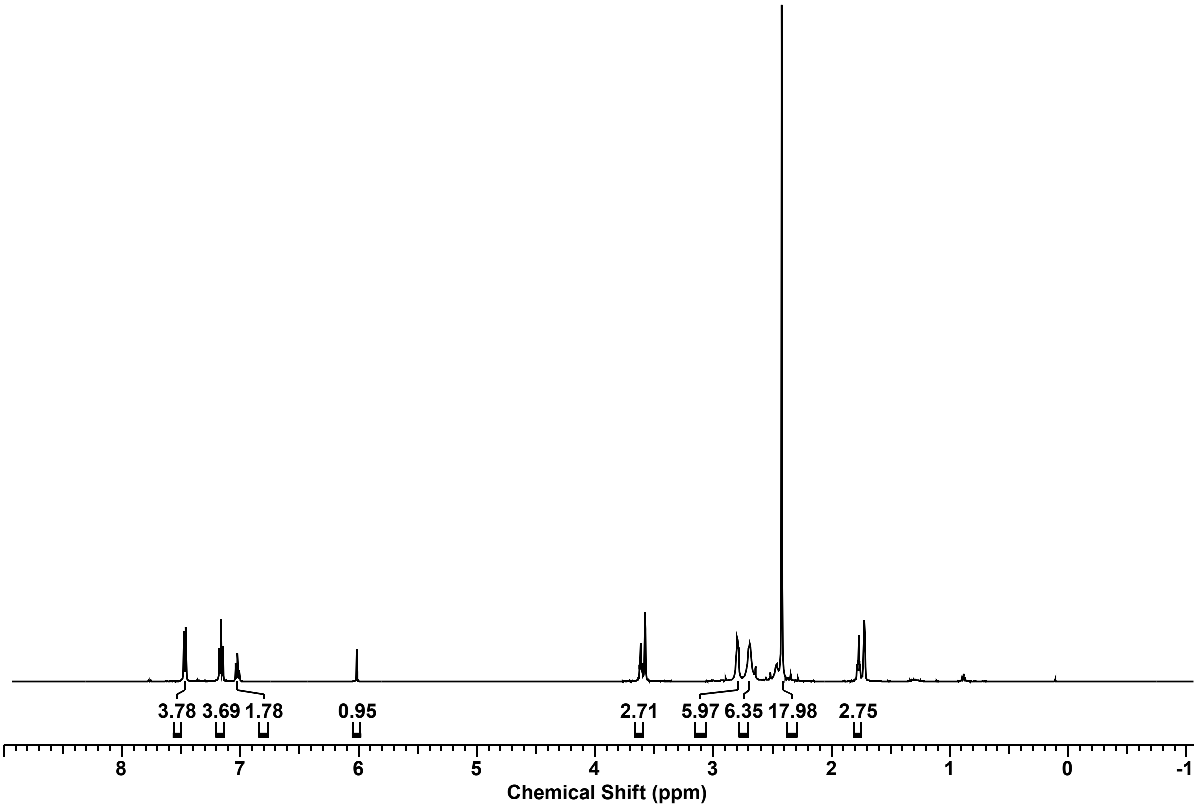


Figure S12. ^{1}H NMR spectrum of [Me$_6$TREN-Mg-O-C(H)Ph$_2$][B(C$_6$F$_5$)$_4$] 4 in THF(D8)

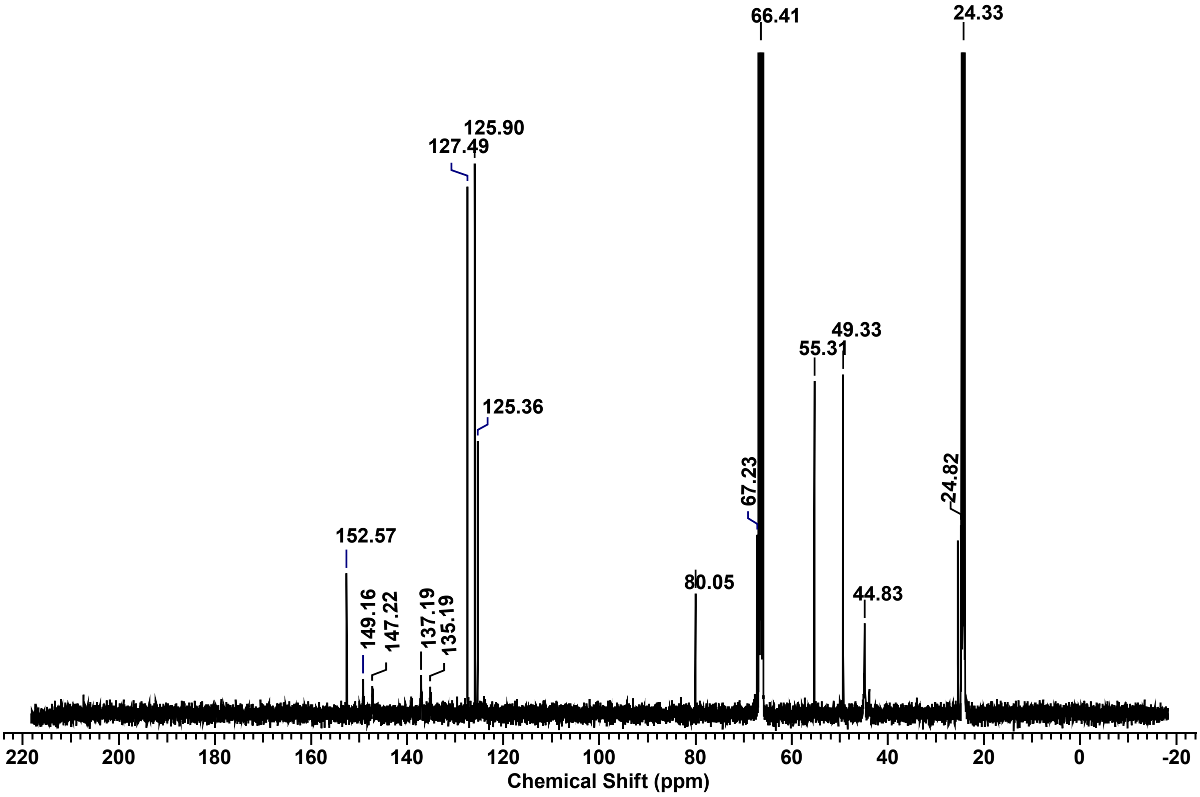


Figure S13. ^{13}C NMR spectrum of [Me$_6$TREN-Mg-O-C(H)Ph$_2$][B(C$_6$F$_5$)$_4$] 4 in THF(D8)

NMR reaction of [Me_6TREN-Mg-n-Bu][B(C_6F_5)$_4$] (1) with Benzophenone in THF(D8): Crystals of **1** [Me_6TREN-Mg-n-Bu][B(C_6F_5)$_4$](0.10 g, 0.10 mmol) were added to 1 equivalent of benzophenone(0.02 g, 0.10 mmol) in a J Young NMR tube inside the glove box. THF(D8) was condensed to the solid mixture and the solution was heated to 60 °C for 12 hours. ^{1}H NMR spectrum was recorded at room temperature.

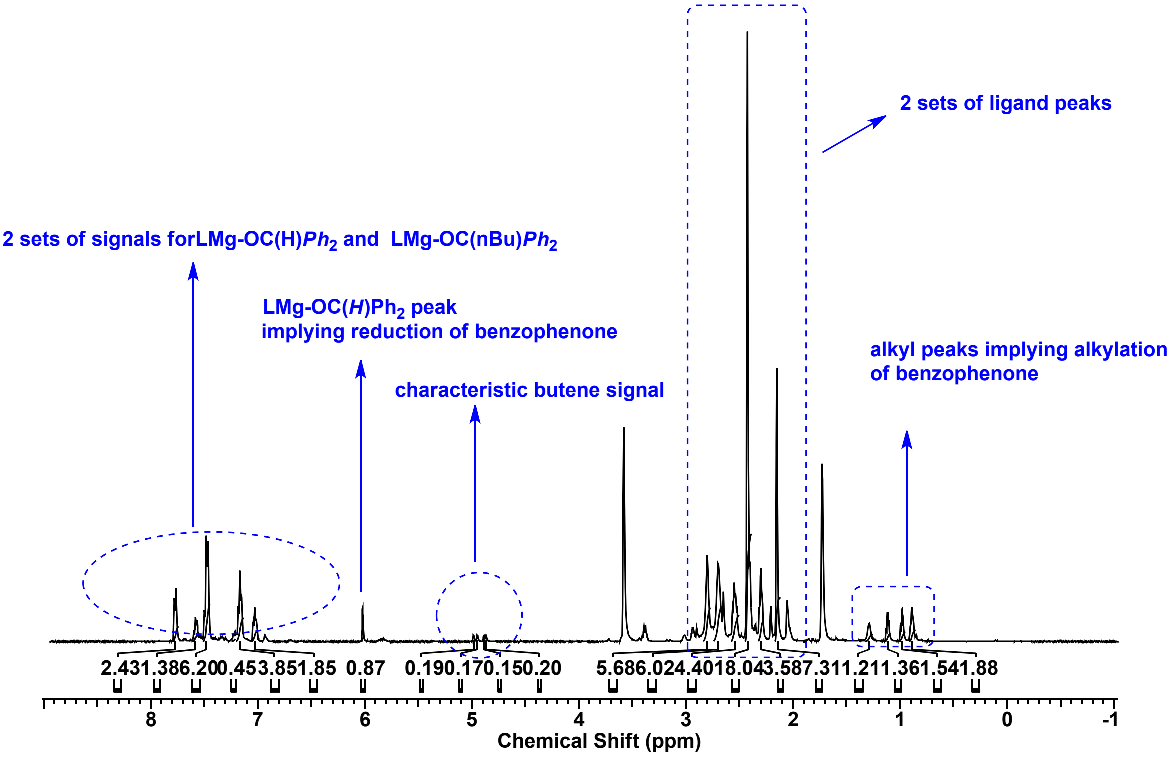


Figure S14. ^{1}H NMR spectrum of the reaction between [Me_6TREN-Mg-(n)Bu][B(C_6F_5)$_4$] (1) and benzophenone in THF(D8) depicting the formation of two distinct products

Synthesis of [Me_6TREN-Mg-][HB(C_6F_5)$_3$[B(C_6F_5)$_4$]: Crystals of **1** Me_6TREN-Mg-n-Bu][B(C_6F_5)$_4$] (0.356 g, 0.36 mmol) and an equivalent amount of tris(pentafluorophenyl)borane B(C_6F_5)$_3$ (0.18 g, 0.36 mmol) was added to a reaction flask followed by addition of 1 mL of toluene inside the glove box. The mixture was stirred for over 12 hours at 80 °C. Evacuated the solvent and washed the resultant gel with n-pentane till the formation of white powder. The white powder was redissolved in THF(D8) and analysed using NMR spectrometer. ^{1}H NMR [500 MHz, 300K, THF(D8)]: δ (s, 2.64 ppm, 18H, Me_6TREN-N(CH_2CH_2N*Me_2*)$_3$), δ (s, 2.92 ppm, 6H, Me_6TREN- N(CH_2C*H_2*NMe_2)$_3$), δ (t, 3.01 ppm, 6H, Me_6TREN- N(C*H_2*CH_2NMe_2)$_3$), δ (t, 1.11 ppm, residual Et_2O), δ (q, 3.38 ppm, residual Et_2O), δ (s, 2.30 ppm, residual toluene), δ (m, 7.06 - 7.19 ppm, residual toluene) ; ^{11}B [160 MHz, 300K, THF(D8)]: δ (s, -13.50 ppm, B(C_6F_5)$_4$), δ (d, J = 90.2 Hz, -22.28 ppm, *H*-B(C_6F_5)$_3$); ^{19}F [470.58 MHz, 300K, THF(D8)]: δ (-132.73 ppm, *o*-C*F*(B(C_6F_5)$_4$)), (-168.42 ppm, *m*-C*F*(B(C_6F_5)$_4$)), (-164.82 ppm, *p*-C*F*(B(C_6F_5)$_4$)), δ (-133.57 ppm, *o*-C*F*(HB(C_6F_5)$_3$)), δ (-168.60 ppm, *m*-C*F*(HB(C_6F_5)$_3$)), δ (-164.86 ppm, *o*-C*F*(HB(C_6F_5)$_3$)).

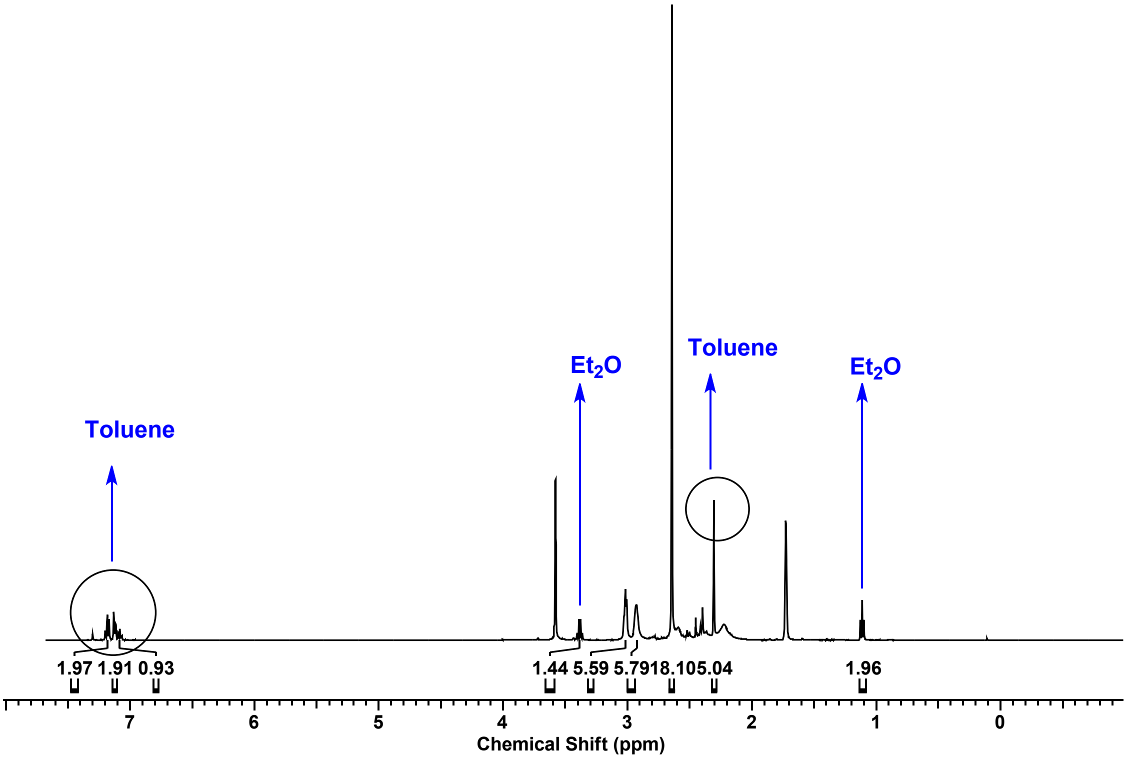


Figure S15. ^{1}H NMR spectrum of [Me$_6$TREN-Mg-][HB(C$_6$F$_5$)$_3$[B(C$_6$F$_5$)$_4$] in THF(D8). Origin of Et$_2$O signals in the spectrum is due to the presence of traces of solvent in 1.

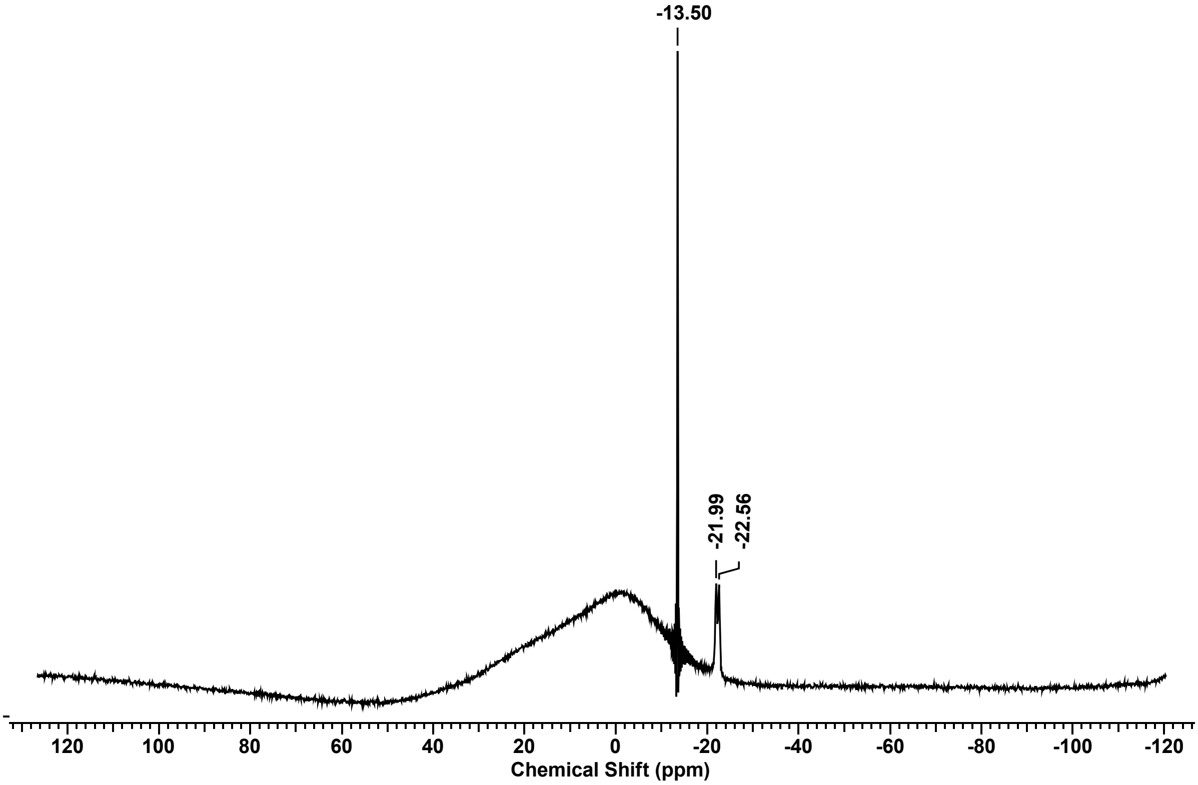


Figure S16. ^{11}B NMR spectrum of [Me$_6$TREN-Mg-][HB(C$_6$F$_5$)$_3$[B(C$_6$F$_5$)$_4$] in THF(D8)

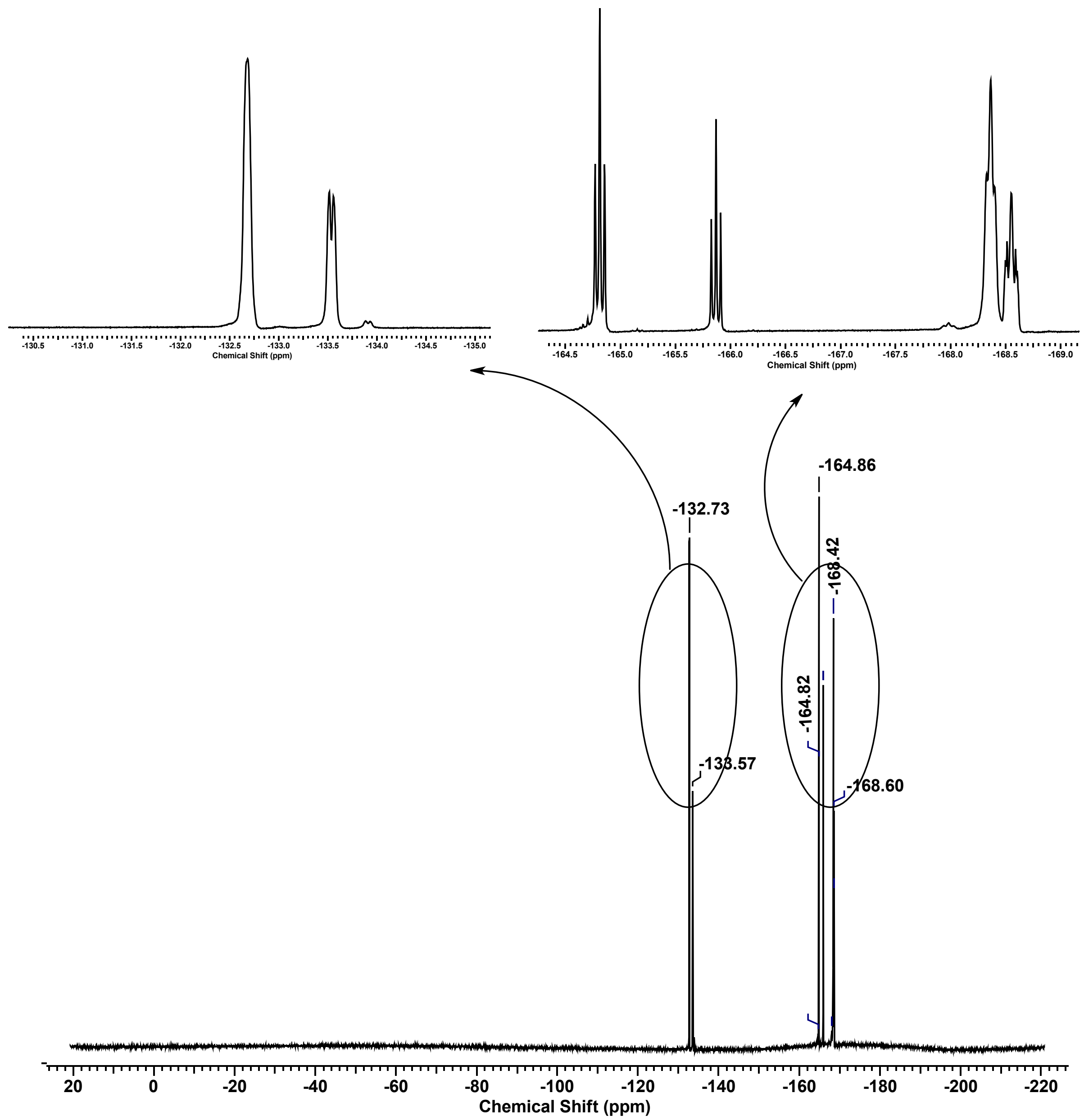


Figure S17. ^{19}**F NMR spectrum of [Me$_6$TREN-Mg-][HB(C$_6$F$_5$)$_3$[B(C$_6$F$_5$)$_4$] in THF(D8)**

NMR reaction of [Me$_6$TREN-Mg-n-Bu][B(C$_6$F$_5$)$_4$] (1) with B(C$_6$F$_5$)$_3$ in THF(D8): Crystals of **1** [Me$_6$TREN-Mg-n-Bu][B(C$_6$F$_5$)$_4$] (0.10 g, 0.10 mmol) were added to 1 equivalent of tris(pentafluorophenyl) borate (0.05 g, 0.10 mmol) in a J Young NMR tube inside the glove box. THF(D8) was condensed to the solid mixture and the solution was heated to 80 ^{o}C for 12 hours. ^{11}B and ^{19}F NMR spectra were recorded at room temperature.

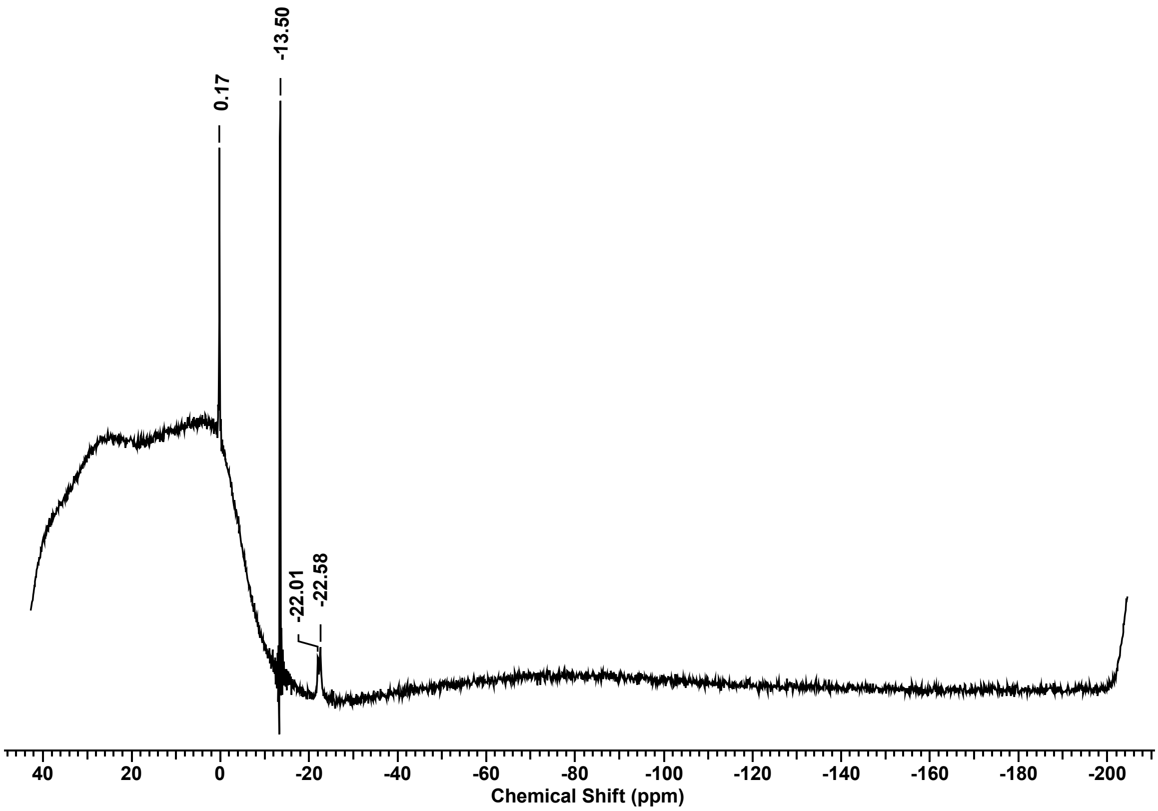


Figure S18. ^{11}B **NMR spectrum of the reaction between [Me$_6$TREN-Mg-n-Bu][B(C$_6$F$_5$)$_4$] (1) and B(C$_6$F$_5$)$_3$ in THF(D8) depicting the formation of two distinct products (alkyl transfer and β-hydride abstraction)**

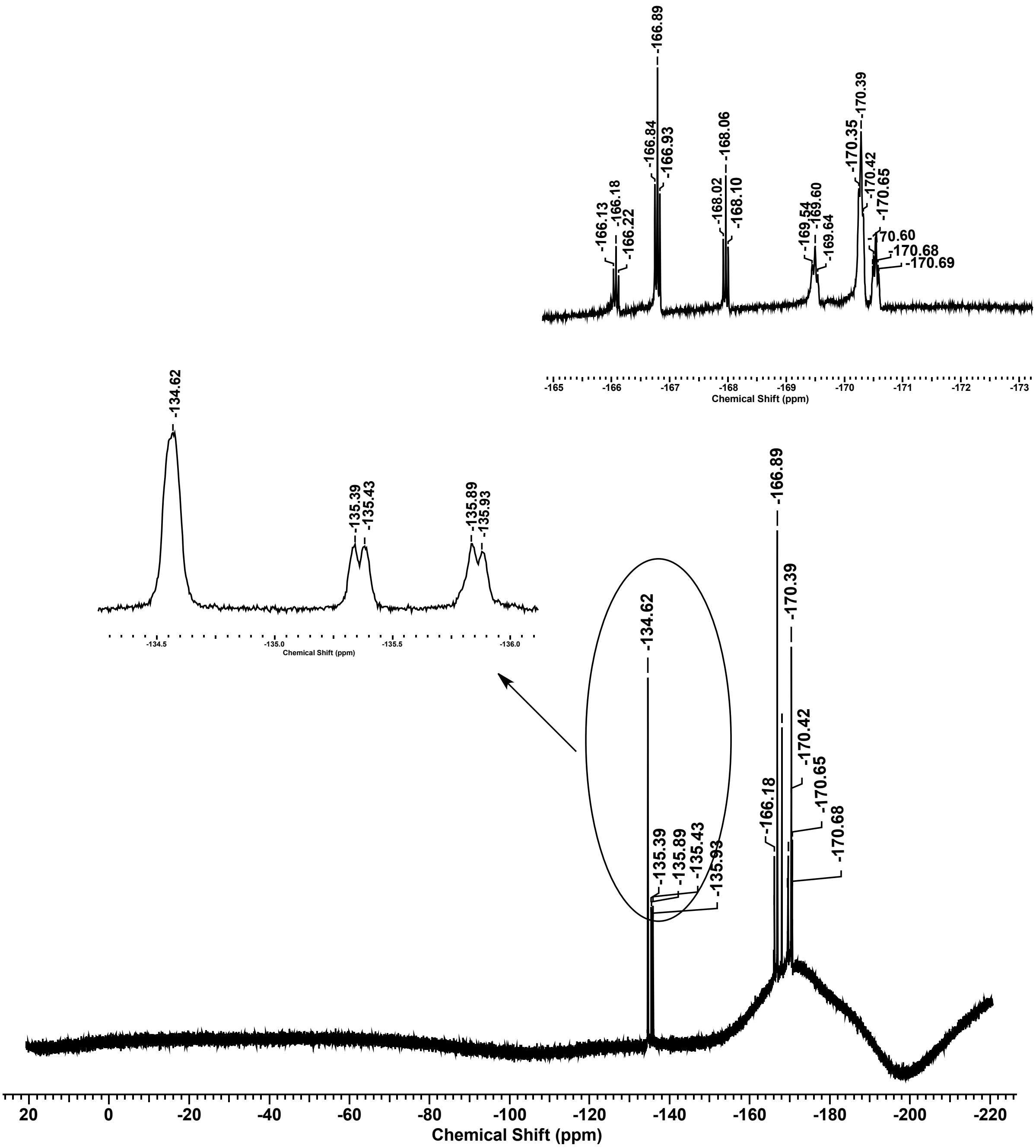


Figure S19. ^{19}F NMR spectrum of the reaction between [Me$_6$TREN-Mg-n-Bu][B(C$_6$F$_5$)$_4$] (1) and B(C$_6$F$_5$)$_3$ in THF(D8) depicting the formation of two distinct products

Reaction with [Me$_6$TREN-Mg-n-Bu][B(C$_6$F$_5$)$_4$] (1) with BPh$_3$ in toluene: Crystals of **1** Me$_6$TREN-Mg-n-Bu][B(C$_6$F$_5$)$_4$] (0.356 g, 0.36 mmol) and an equivalent amount of tris(pentafluorophenyl)borane B(C$_6$F$_5$)$_3$ (0.18 g, 0.36 mmol) were added in a reaction flask followed by addition of 1 mL of toluene inside the glove box. The mixture was stirred for over 12 hours at 80 °C. Evacuated the solvent and washed the resultant gel with n-pentane till the formation of white powder. The white powder was redissolved in THF(D8) and analysed using NMR spectrometer.

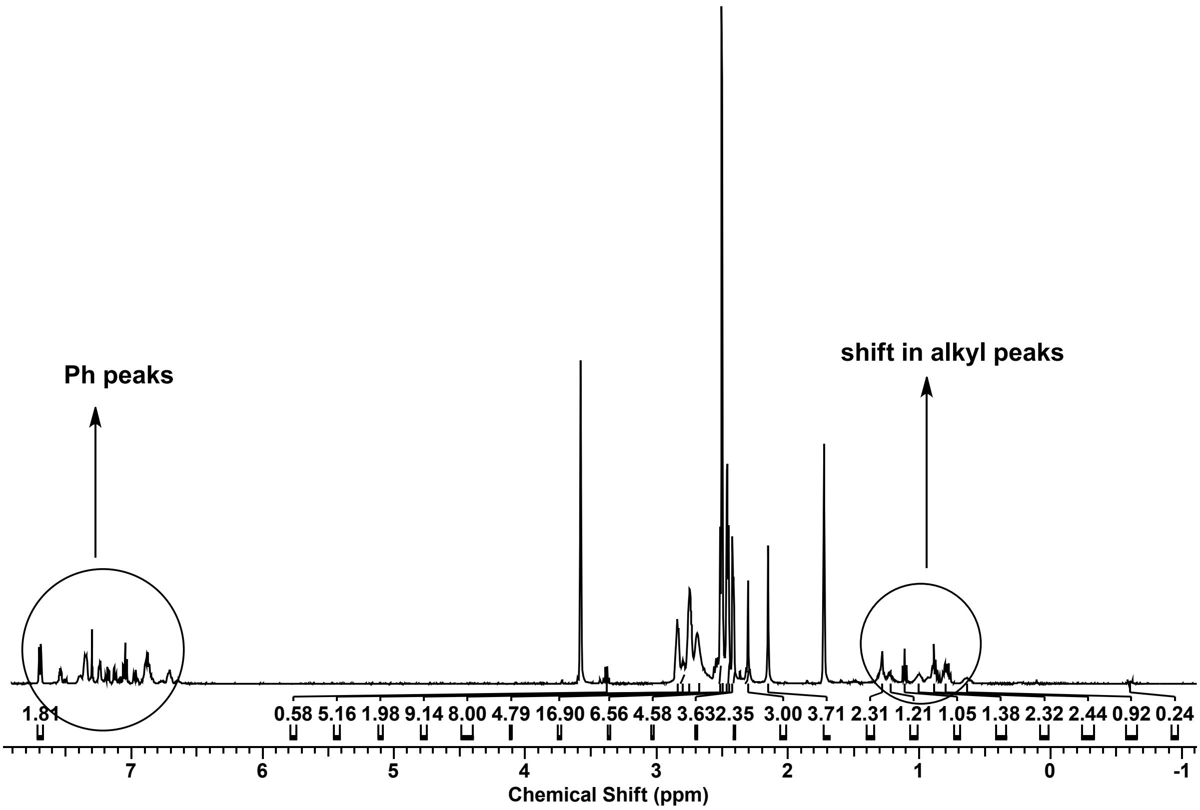


Figure S20. ^1H NMR spectrum of the reaction between $[Me_6TREN\text{-}Mg\text{-}n\text{-}Bu][B(C_6F_5)_4]$ (1) and BPh_3

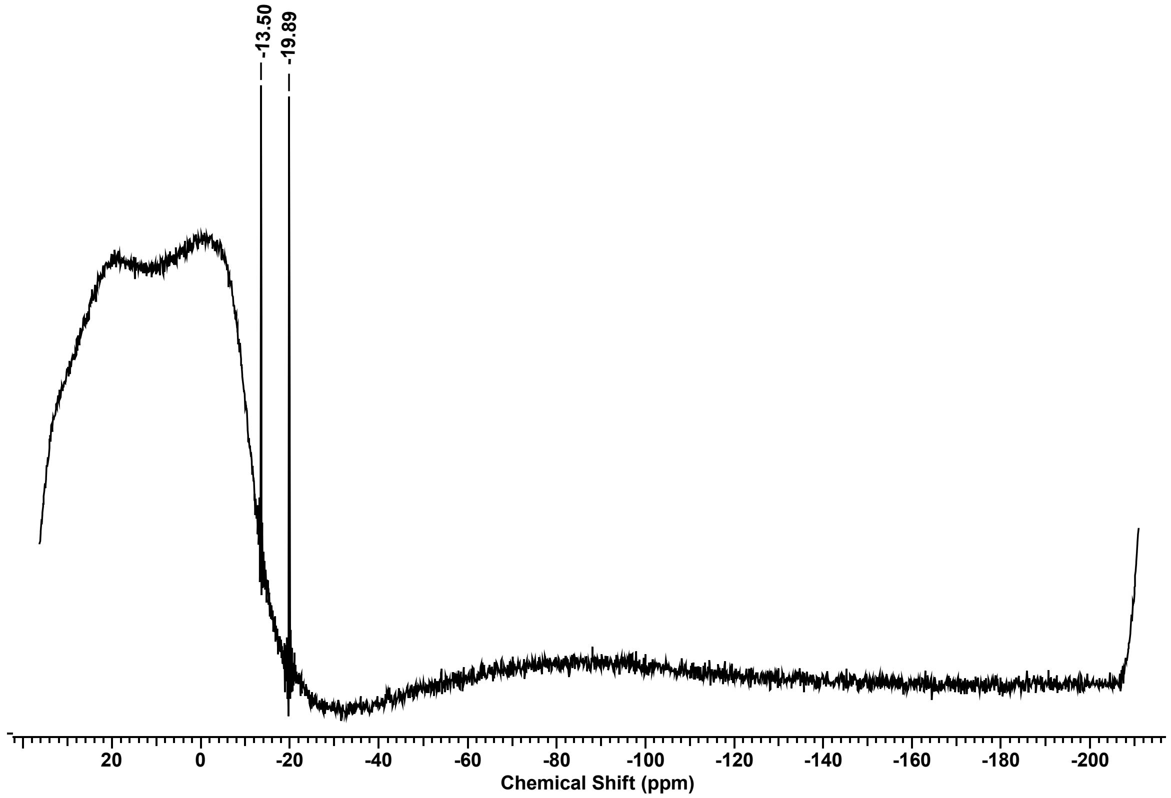


Figure S21. ^{11}B NMR spectrum of the reaction between $[Me_6TREN\text{-}Mg\text{-}n\text{-}Bu][B(C_6F_5)_4]$ (1) and BPh_3

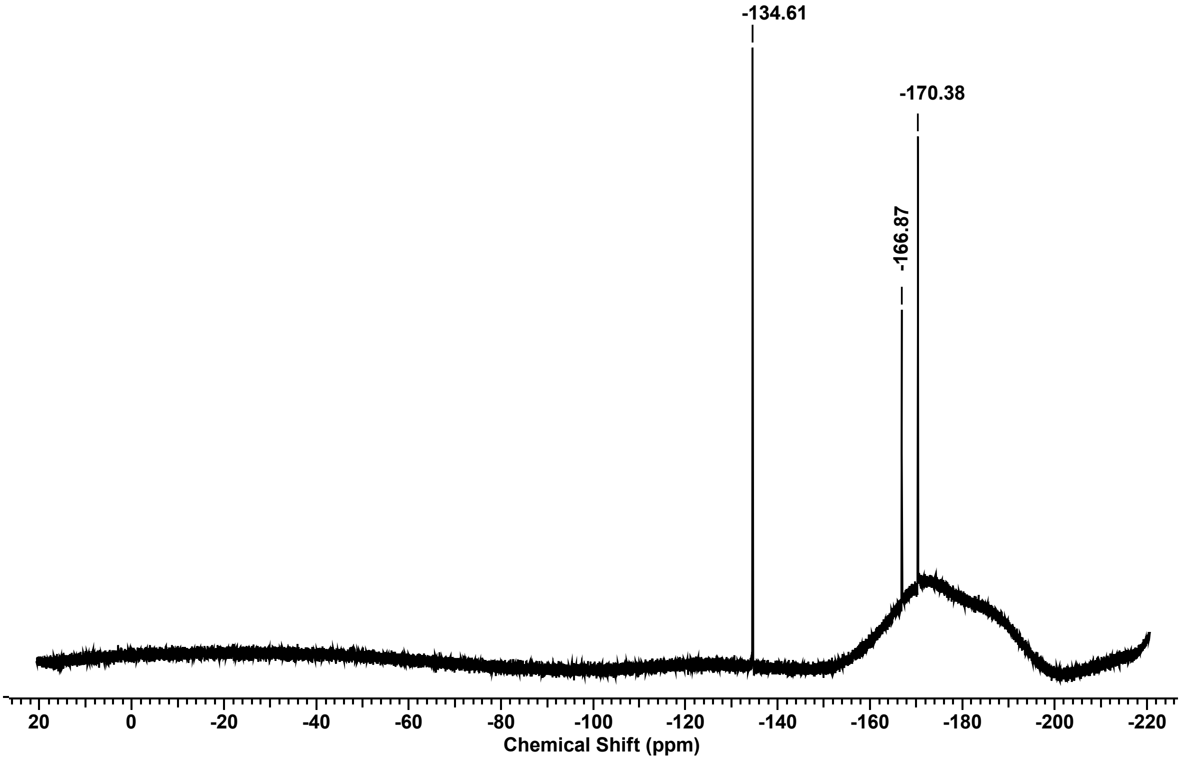


Figure S22. ^{19}F NMR spectrum of the reaction between [Me$_6$TREN-Mg-n-Bu][B(C$_6$F$_5$)$_4$] (1) and BPh$_3$

References

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