A Series of Neutral Alkaline Earth Metal Hydride Complexes Supported by a Bulky, Unsymmetrical β-Diketiminate Ligand, [{($^{Dip/TCHP}$Nacnac)M(μ-H)}$_2$] (M = Mg, Ca, Sr or Ba)

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Electronic Supplementary Information (47 pages)

Contents

1. Syntheses and Spectra

General Considerations

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. Pentane and diethyl ether were distilled over Na/K alloy (50:50), while hexane, cyclohexane, methylcyclohexane, toluene and THF were distilled over molten potassium. ^{1}H, ^{13}C{^{1}H} and ^{29}Si{^{1}H} NMR spectra were recorded on either Bruker AvanceIII 600 or Bruker AvanceIII 400 spectrometers at room temperature and were referenced to the resonances of the solvent used or $SiMe_4$. FTIR spectra were collected for solid samples or Nujol mulls on an Agilent Cary 630 attenuated total reflectance (ATR) spectrometer. Microanalyses were carried out at by the Elemental Analysis Service at London Metropolitan University. Melting points were determined in sealed glass capillaries under dinitrogen and are uncorrected. $^{Dip/TCHP}$NacnacH,[1] $Mg(CH_2SiMe_3)_2$,[2] $M\{N(SiMe_3)_2\}_2$ (M = Sr or Ba),[3,4] and $M\{N(SiMe_3)_2\}_2(THF)_2$ (M = Ca, Sr or Ba)[4,5] were prepared according to literature procedures. Unless otherwise stated, chemicals were purchased from Sigma-Aldrich and used as received. N.B. 1.0 M solutions of $MgBu^n_2$ in hexanes purchased from Sigma-Aldrich (with different batch numbers) were found to be consistently, and frustratingly, contaminated with significant amounts of THF. Hence, this reagent behaves as its THF adduct, $MgBu^n_2(THF)_x$, in this study.

Preparation of [Mg($^{Dip/TCHP}$Nacnac)(CH_2SiMe_3)] (1).

$^{Dip/TCHP}$NacnacH (300 mg, 0.52 mmol) and $Mg(CH_2SiMe_3)_2$ (123 mg, 0.62 mmol) were transferred to a *J* Young's ampoule and dissolved in toluene (~5 mL). The resulting mixture was heated to 100 °C and stirred for 1 hour. The solution was then filtered *via* cannula and volatiles removed *in vacuo*. The oily residue was suspended in hexane (~2 mL) and stored at –30 °C overnight to yield colourless crystals of **1**. Yield 104 mg, 29 %. **M.p.** 205–207 °C. **^{1}H NMR** (400 MHz, C_6D_6): δ -1.44 (s, 2H, CH_2Si(CH_3)$_3$), -0.15 (s, 9H, CH_2Si(CH_3)$_3$), 1.25 (d, J = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.28 – 1.37 (m, 5H, Cy–*H*), 1.39 (d, J = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.44 – 1.65 (m, 15H, Cy–*H*), 1.67 (s, 3H, NCCH_3), 1.74 (s, 3H, NCCH_3), 1.80 – 2.16 (m, 10H, Cy–*H*), 2.48 – 2.60 (m, 1H, Cy–*H*), 2.75 – 2.90 (m, 2H, Cy–*H*), 3.22 (hept, J = 6.8 Hz, 2H, C*H*(CH_3)$_2$), 4.95 (s, 1H, NCC*H*), 7.18 (s, 2H, $_{TCHP}$Ar–*H*), 7.19 – 7.20 (m, 3H, $_{Dip}$Ar–*H*). **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6) δ -9.5 (*C*H_2Si(CH_3)$_2$), 3.5 (CH_2Si(*C*H_3)$_2$), 23.6 (CH(*C*H_3)$_2$), 23.7, 23.8 (NC*C*H_3), 24.8 (CH(*C*H_3)$_2$), 26.7, 27.4, 27.7, 27.8 (Cy–*C*), 28.9 (*C*H(CH_3)$_2$), 34.0, 35.2, 35.9, 40.4, 45.2 (Cy–*C*), 95.3 (NC*C*H), 123.3, 124.1, 126.1, 140.4, 141.8, 142.1, 144.2, 145.2 ($_{Dip/TCHP}$Ar–*C*), 169.5, 169.9 (N*C*). **IR ν/cm^{-1}** (solid): 697 (w), 723 (w), 749 (w), 794 (w), 816 (w), 857 (s), 999 (w), 1021 (w), 1103 (w), 1144 (w), 1178 (m), 1249 (m), 1275 (w), 1312 (w), 1360 (w), 1405 (m), 1442 (m), 1491 (w), 1524 (w), 1547 (s), 1621 (m), 2848 (s), 2922 (s), 2952 (w). **Anal. Calcd.** for $C_{45}H_{70}MgN_2Si$ (691.46): C, 78.17; H, 10.20; N, 4.05 %. Found: C, 77.53; H, 10.47; N, 3.31 %.

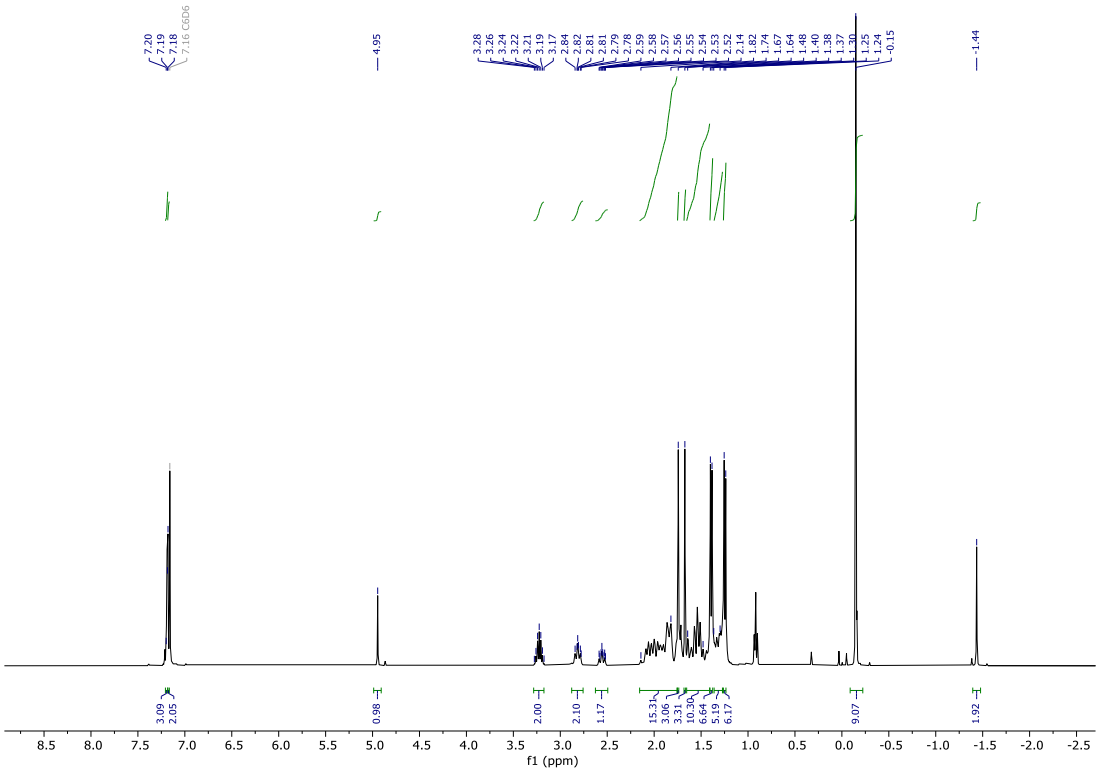

Figure S1: ^{1}H NMR spectrum (600 MHz, 298 K, C_6D_6) of [Mg($^{Dip/TCHP}$Nacnac)(CH_2SiMe_3)] (**1**).

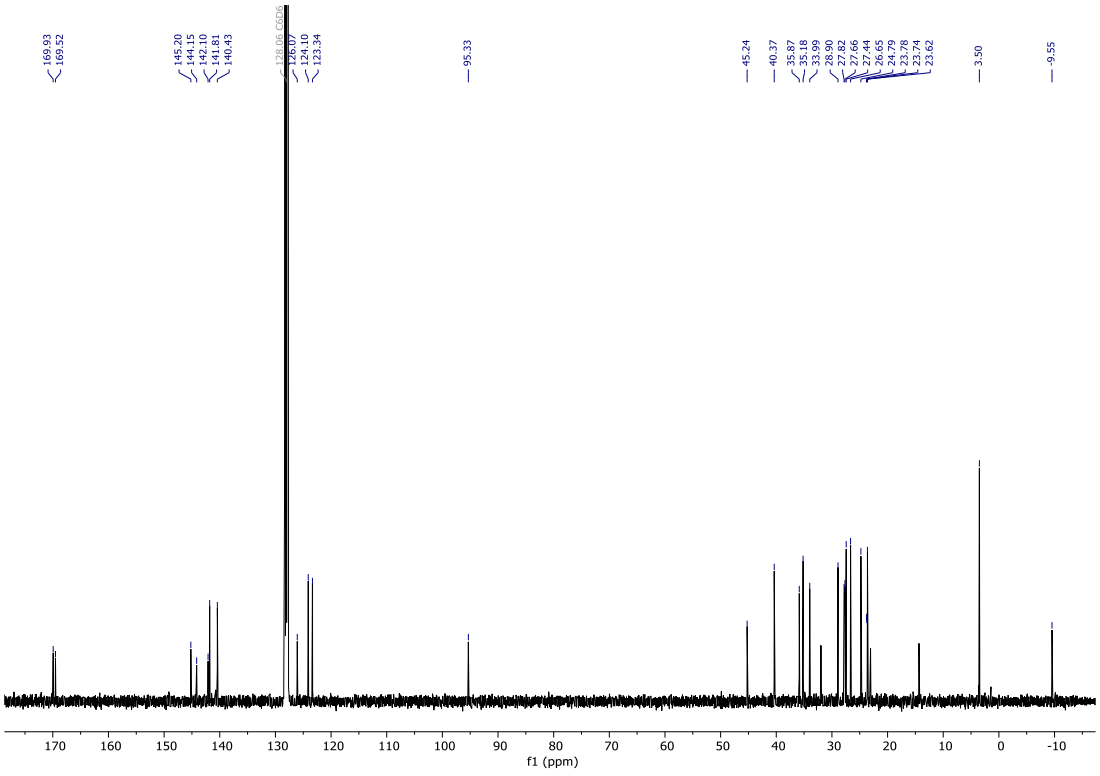

Figure S2: ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K, C_6D_6) of [Mg($^{Dip/TCHP}$Nacnac)(CH_2SiMe_3)] (**1**).

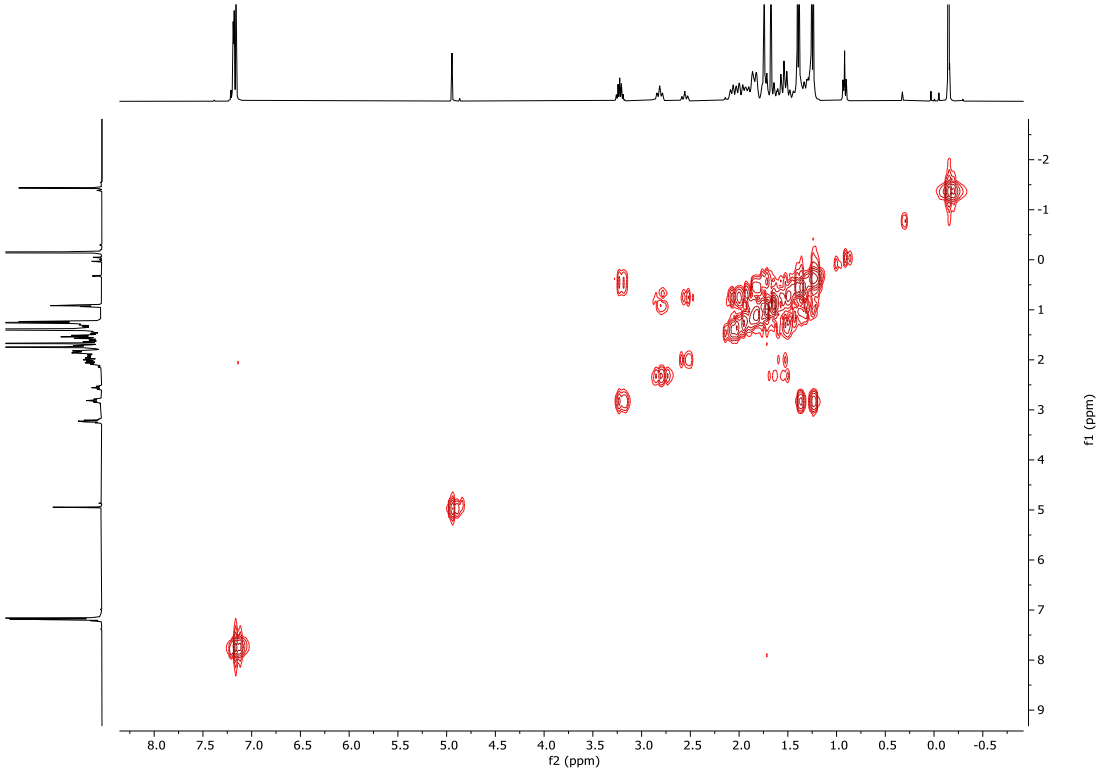

Figure S3: COSY NMR spectrum (400 MHz, 298 K, C_6D_6) of [Mg($^{Dip/TCHP}$Nacnac)(CH_2SiMe_3)] (**1**).

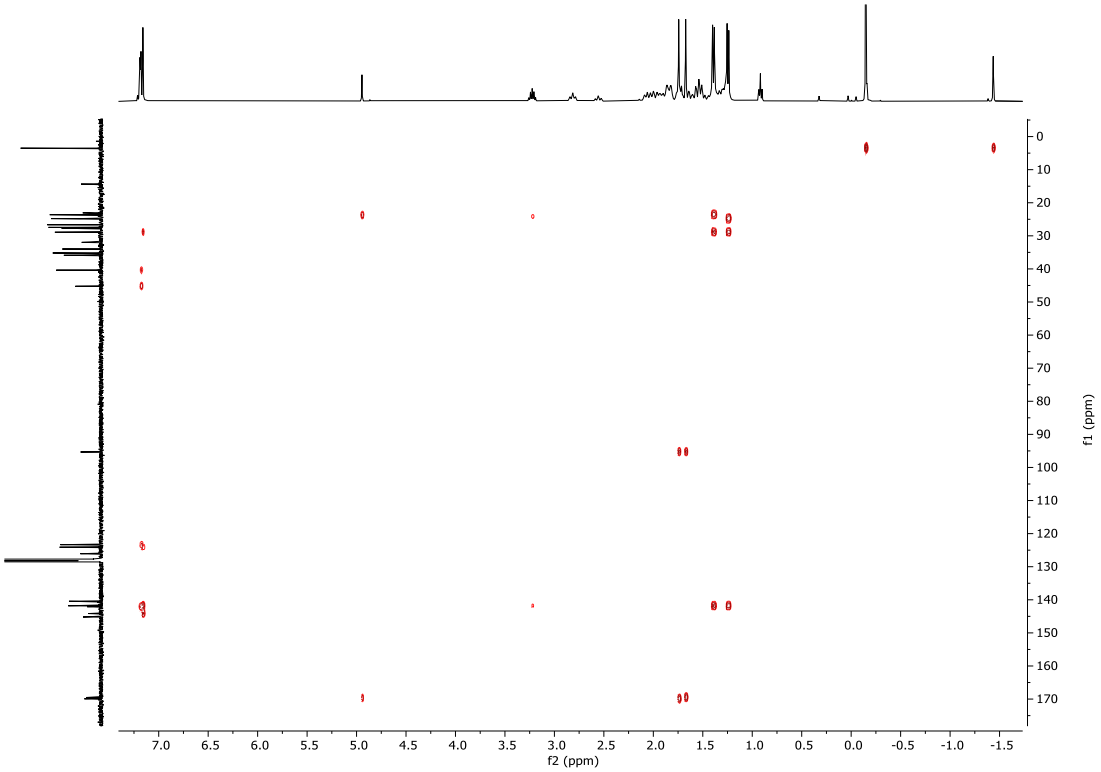

Figure S4: HMBC NMR spectrum (^{1}H: 400 MHz; ^{13}C: 101 MHz, 298 K, C_6D_6) of [Mg($^{Dip/TCHP}$Nacnac)(CH_2SiMe_3)] (**1**).

Preparation of [Mg($^{Dip/TCHP}$Nacnac)(Bu^{n})(THF)] (2).

$^{Dip/TCHP}$NacnacH (310 mg, 0.54 mmol) was transferred to a *J* Young's ampoule and dissolved in toluene (~10 mL). A solution of Mg^{n}Bu$_2$(THF)$_x$ (1M in hexane, 0.54 mmol, 0.54 mL) was added dropwise at room temperature. The reaction mixture was stirred for 30 minutes at room temperature, sealed, and then heated at 80 °C for 16 hours. Volatiles were then removed *in vacuo* and the residue dissolved in hexane (~2 mL). Colourless crystals were obtained by storage at –30 °C for 4 days. Yield 175 mg, 45 %. **M.p.** 118–120 °C. **^{1}H NMR** (400 MHz, C_6D_6) δ -0.30 – -0.22 (m, 2H, MgC*H*$_2$), 0.92 (t, *J* = 7.7 Hz, 3H, Mg(CH$_2$)$_3$C*H*$_3$), 1.14 – 1.24 (m, 2H, MgCH$_2$C*H*$_2$), 1.26 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.30 – 1.34 (m, 4H, THF), 1.35 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.39 – 1.65 (m, 16H, Mg(CH$_2$)$_2$C*H*$_2$, Cy–*H*), 1.68 (s, 3H, NCC*H*$_3$), 1.75 (s, 3H, NCC*H*$_3$), 1.77 – 2.12 (m, 16H, Cy–*H*), 2.48 – 2.59 (m, 1H, Cy–*H*), 2.86 – 2.98 (m, 2H, Cy–*H*), 3.31 (hept, *J* = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.55 (s, 4H, THF), 4.85 (s, 1H, NCC*H*), 7.16 – 7.18 (m, 3H, $_{Dip}$Ar–*H*), 7.19 (s, 2H, $_{TCHP}$Ar–*H*). **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6) δ 6.2 (Mg*C*H$_2$), 14.6 (Mg(CH$_2$)$_3$*C*H$_3$), 24.1 (2xNC*C*H$_3$), 24.3, 25.0 (CH(*C*H$_3$)$_2$), 25.5 (THF), 26.6, 26.7, 27.4, 27.6, 27.6 (Cy–*C*), 28.4 (*C*H(CH$_3$)$_2$), 31.7 (MgCH$_2$*C*H$_2$), 32.2 (Mg(CH$_2$)$_2$*C*H$_2$), 34.9, 35.0, 35.2, 35.2, 35.2, 39.5, 45.0 (Cy–*C*), 68.7 (THF), 94.6 (NC*C*H), 123.3, 124.1, 125.6, 141.0, 142.4, 143.1, 144.3, 145.3 ($_{Dip/TCHP}$Ar–*C*), 168.6, 169.1 (N*C*). **IR ν/cm^{-1}** (solid): 745 (w), 760 (w), 794 (m), 861 (m), 1021 (m),

1055 (w), 1100 (w), 1178 (m), 1260 (m), 1316 (w), 1360 (w), 1405 (s), 1442 (s), 1547 (s), 1621 (s), 2851 (s), 2922 (s), 2956 (w). **Anal. Calcd.** for $C_{49}H_{76}MgN_2O$ (733.46): C, 80.24; H, 10.44; N, 3.82 %. Found: C, 79.91; H, 10.39; N, 3.21 %.

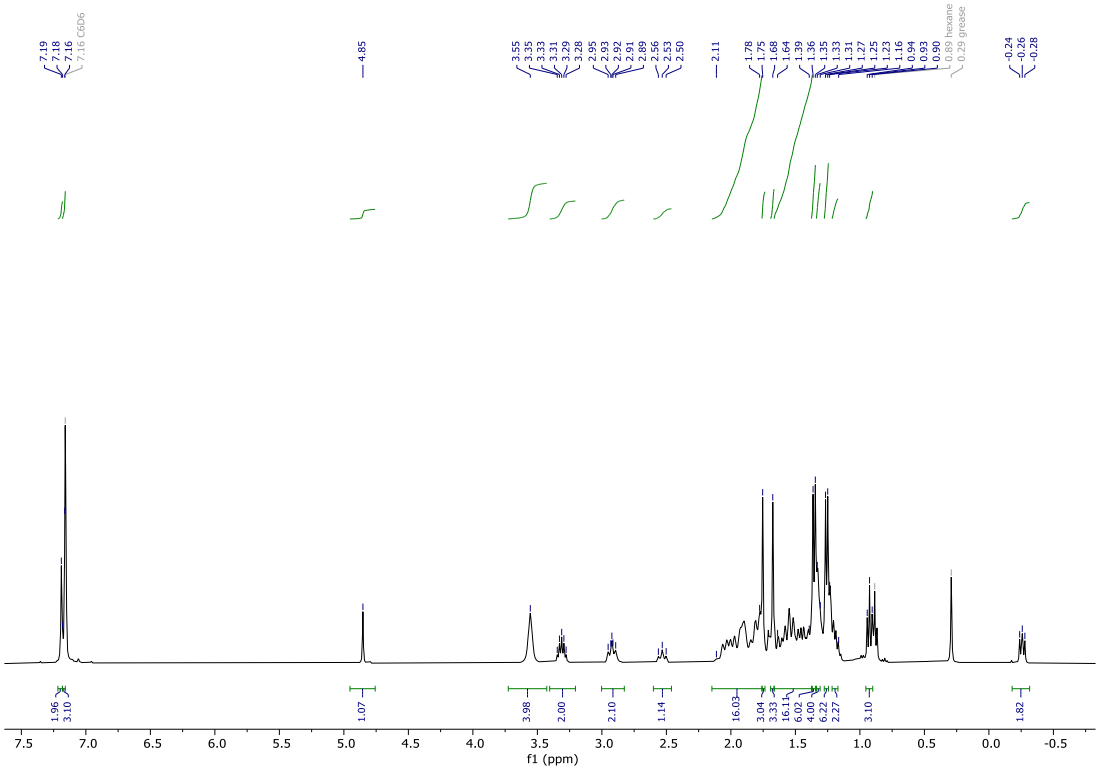

Figure S5: ^{1}H NMR spectrum (600 MHz, 298 K, C_6D_6) of [Mg($^{Dip/TCHP}$Nacnac)(Bu^n)(THF)] (**2**).

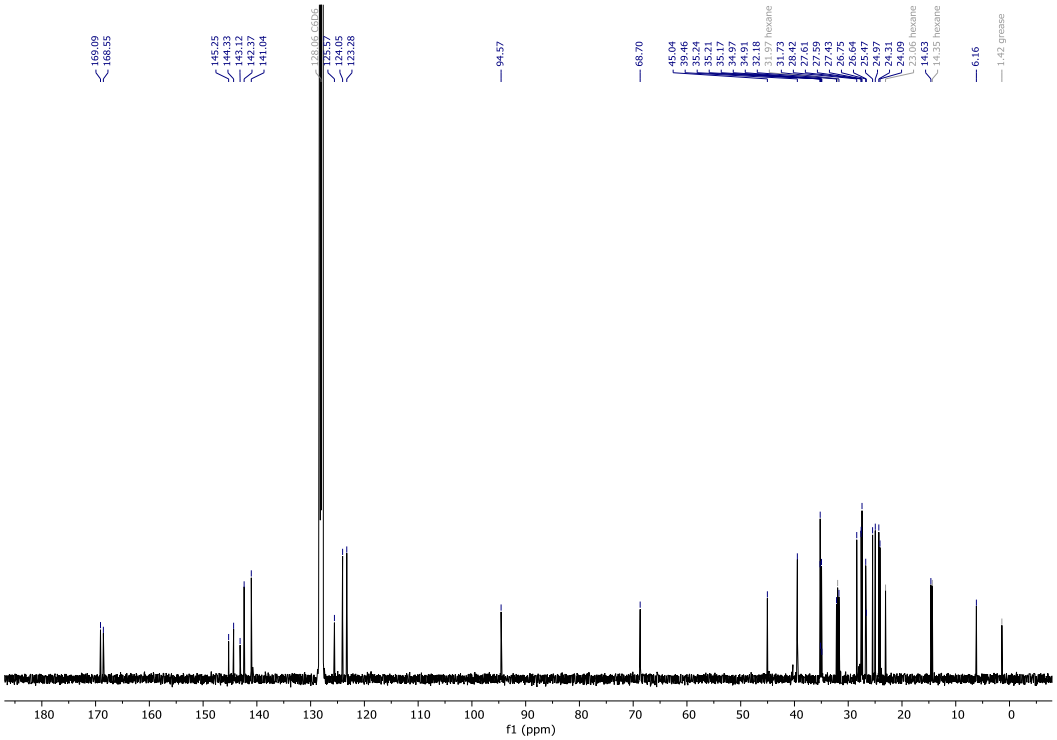

Figure S6: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K, C_6D_6) of [Mg($^{Dip/TCHP}$Nacnac)(Bu^{n})(THF)] (**2**).

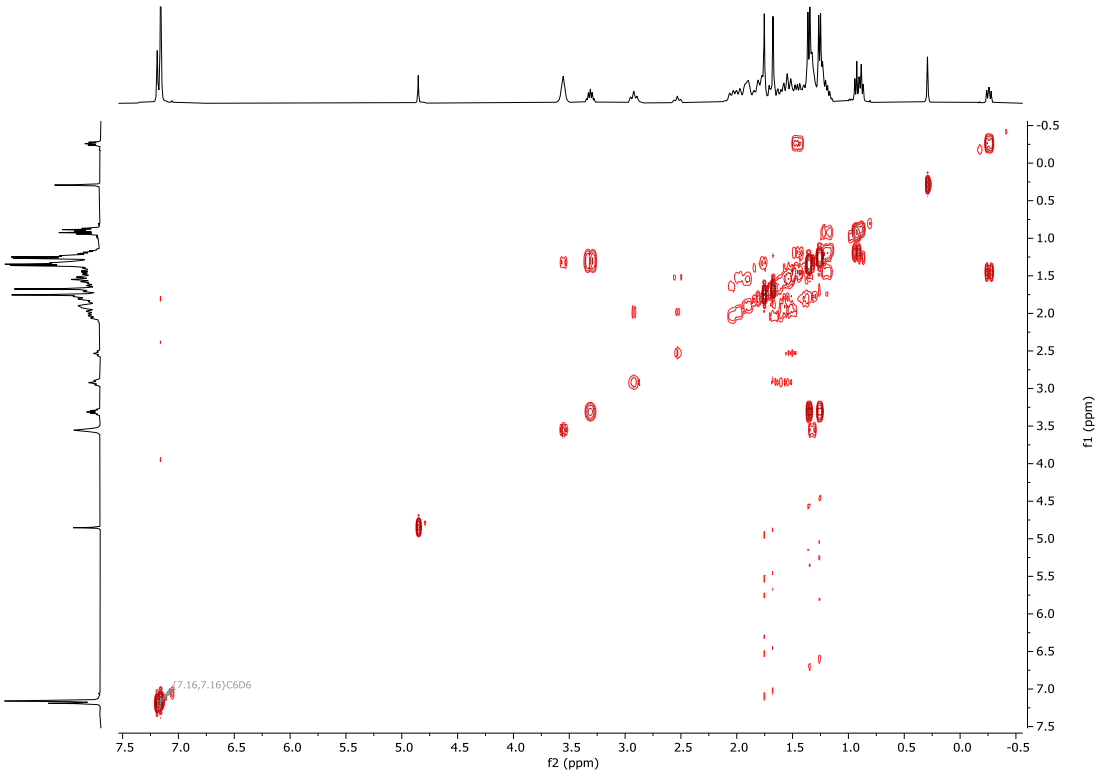

Figure S7: COSY NMR spectrum (400 MHz, 298 K, C_6D_6) of [Mg($^{Dip/TCHP}$Nacnac)(Bu^{n})(THF)] (**2**).

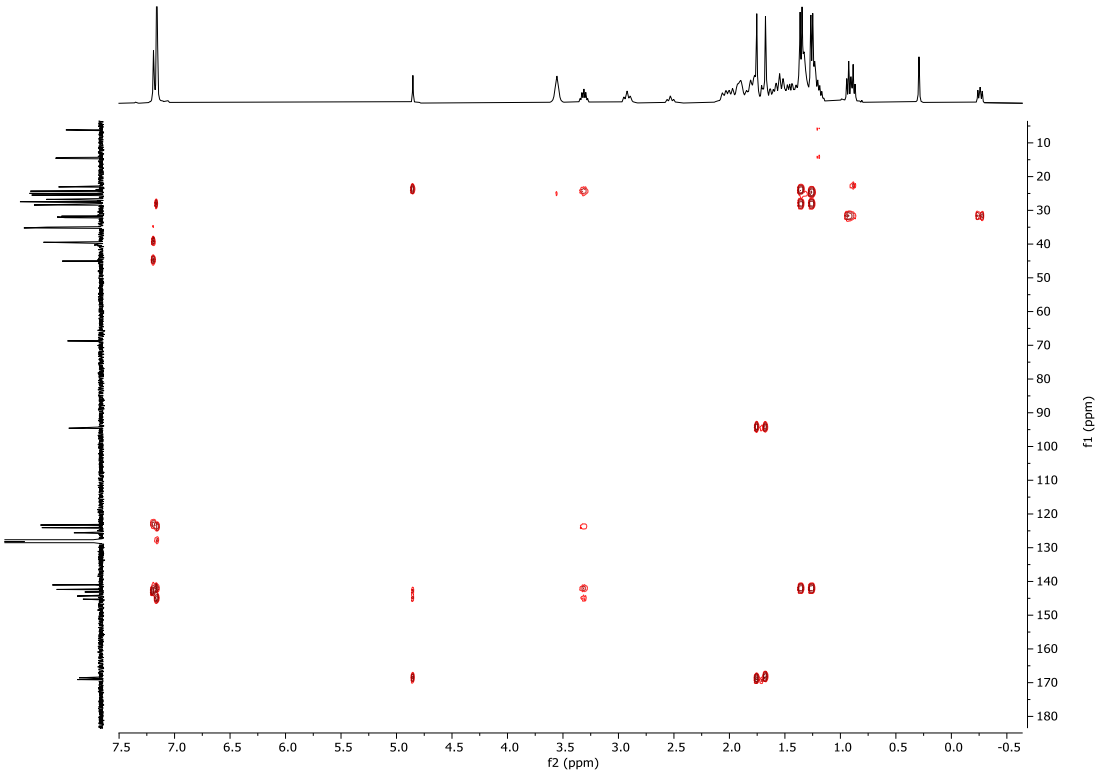

Figure S8: HMBC NMR spectrum (^{1}H: 400 MHz; ^{13}C: 101 MHz, 298 K, C_6D_6) of [Mg($^{Dip/TCHP}$Nacnac)(Bu^{n})(THF)] (**2**).

Preparation of [Sr($^{Dip/TCHP}$Nacnac){N(SiMe$_3$)$_2$}] (3)

$^{Dip/TCHP}$NacnacH (200 mg, 0.34 mmol) and Sr{N(SiMe$_3$)$_2$}$_2$ (140 mg, 0.34 mmol) were transferred to a J Young's ampoule and dissolved in toluene (~10 mL). The flask was sealed and heated at 120 °C for 3 days until no $^{Dip/TCHP}$NacnacH starting material remained (as determined by ^{1}H NMR spectroscopy). All volatiles were then removed *in vacuo* to afford the title compound as a spectroscopically near pure off-white waxy solid. Yield 369 mg, 89 %. **M.p.** 161–164 °C. **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ -0.13 (s, 18H, Si(C*H*$_3$)$_3$), 1.16 (d, J = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.31 (d, J = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.33 – 1.69 (m, 20H, Cy–*H*), 1.75 (s, 3H, NCC*H*$_3$), 1.78 (s, 3H, NCC*H*$_3$), 1.80 – 1.94 (m, 10H, Cy–*H*), 2.48 – 2.59 (m, 1H, Cy–*H*), 2.70 (m, 2H, Cy–*H*), 3.04 (hept, J = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 4.86 (s, 1H, NCC*H*), 7.00 – 7.08 (m, 3H, Ar–*H*), 7.10 – 7.12 (s, 2H, Ar–*H*). **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6, 298 K): δ 5.6 (Si(*C*H$_3$)$_3$), 23.5, 23.5 (NC*C*H$_3$), 24.3, 24.5 (CH(*C*H$_3$)$_2$), 26.5, 26.7, 27.4, 27.6, 27.9 (Cy–*C*), 28.8 (*C*H(CH$_3$)$_2$), 34.8, 35.3, 35.7, 40.2, 45.2 (Cy–*C*), 94.9 (NC*C*H), 124.8, 124.8, 125.6, 139.2, 140.1, 142.2, 144.1, 144.8 ($_{Dip/TCHP}$Ar–*C*), 163.9, 164.1 (N*C*). **^{29}Si{^{1}H} NMR** (79 MHz, C_6D_6, 298 K): δ -17.3 (*Si*Me$_3$). **IR ν/cm^{-1}** (solid): 2940 (s), 2848 (m), 1625 (m), 1557 (s), 1455 (s), 1400 (m), 1308 (s), 1248 (s), 1159 (m), 1117 (m), 1051 (s), 938 (m), 844 (s), 811 (s), 711 (w), 608 (w), 600 (w). **Anal. Calcd.** for $C_{47}H_{77}SrN_3Si_2$: C 68.18, H 9.37, N 5.08 %. Found: C 69.01, H 9.41, N 5.34 %.

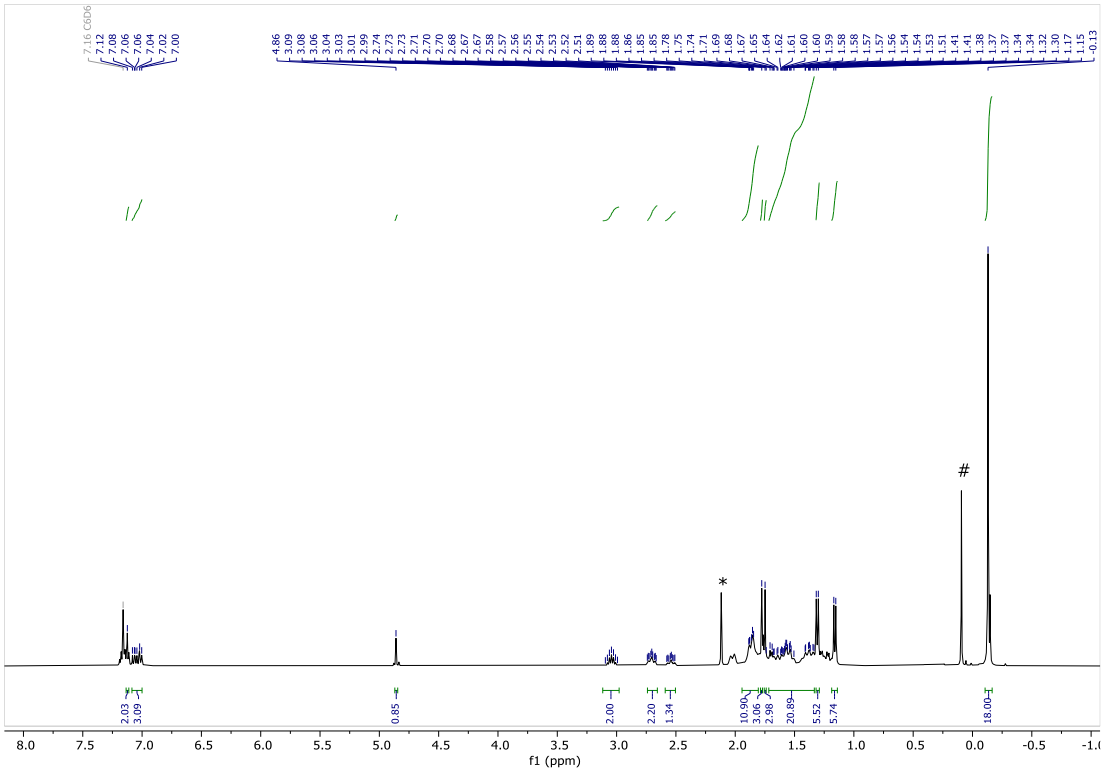

Figure S9: ^{1}H NMR spectrum (600 MHz, 298 K, C_6D_6) of [Sr($^{Dip/TCHP}$Nacnac){N(SiMe$_3$)$_2$}] (**3**) (* = toluene, # = HN(SiMe$_3$)$_2$).

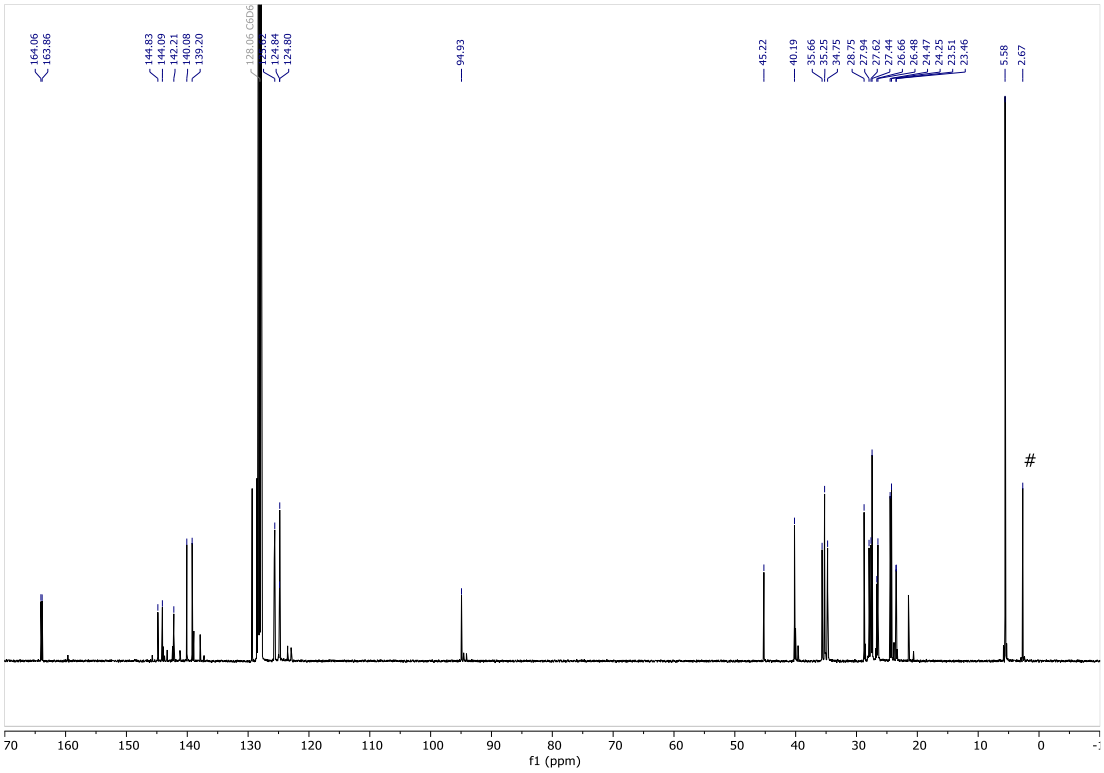

Figure S10: ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K, C_6D_6) of [Sr($^{Dip/TCHP}$Nacnac){N(SiMe$_3$)$_2$}] (**3**) (# = HN(SiMe$_3$)$_2$).

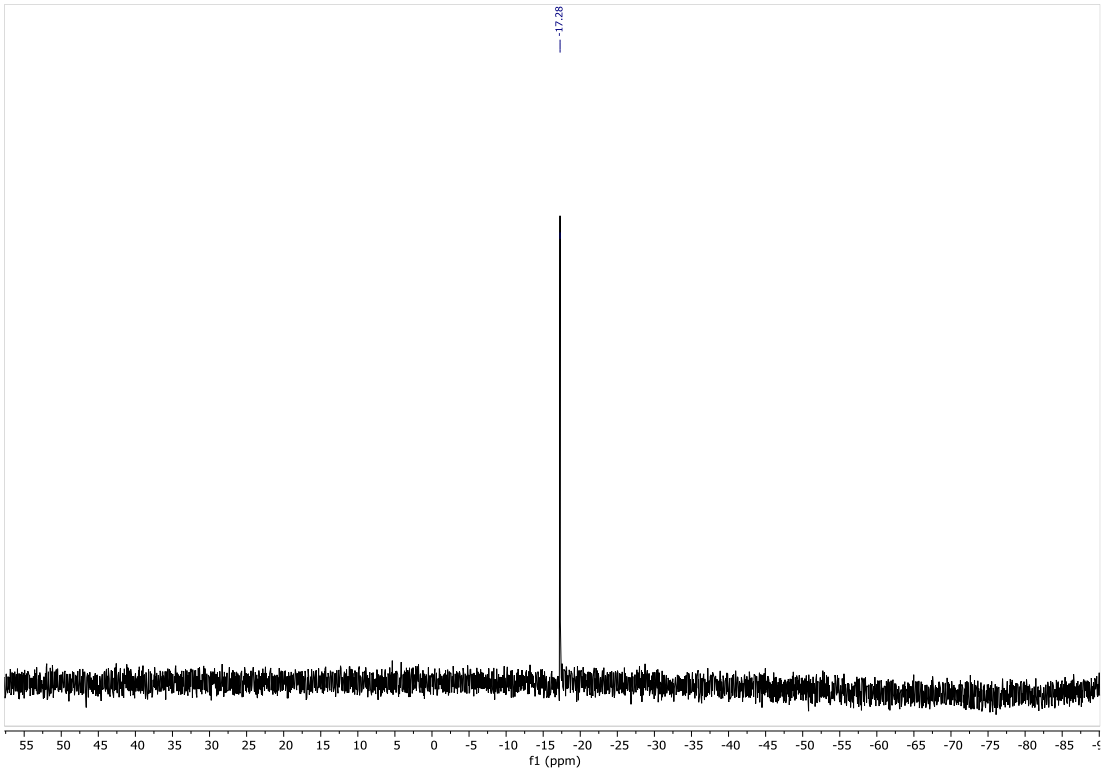

Figure S11: $^{29}Si\{^{1}H\}$ NMR spectrum (79 MHz, 298 K, C_6D_6) of [Sr($^{Dip/TCHP}$Nacnac){N(SiMe$_3$)$_2$}] (**3**).

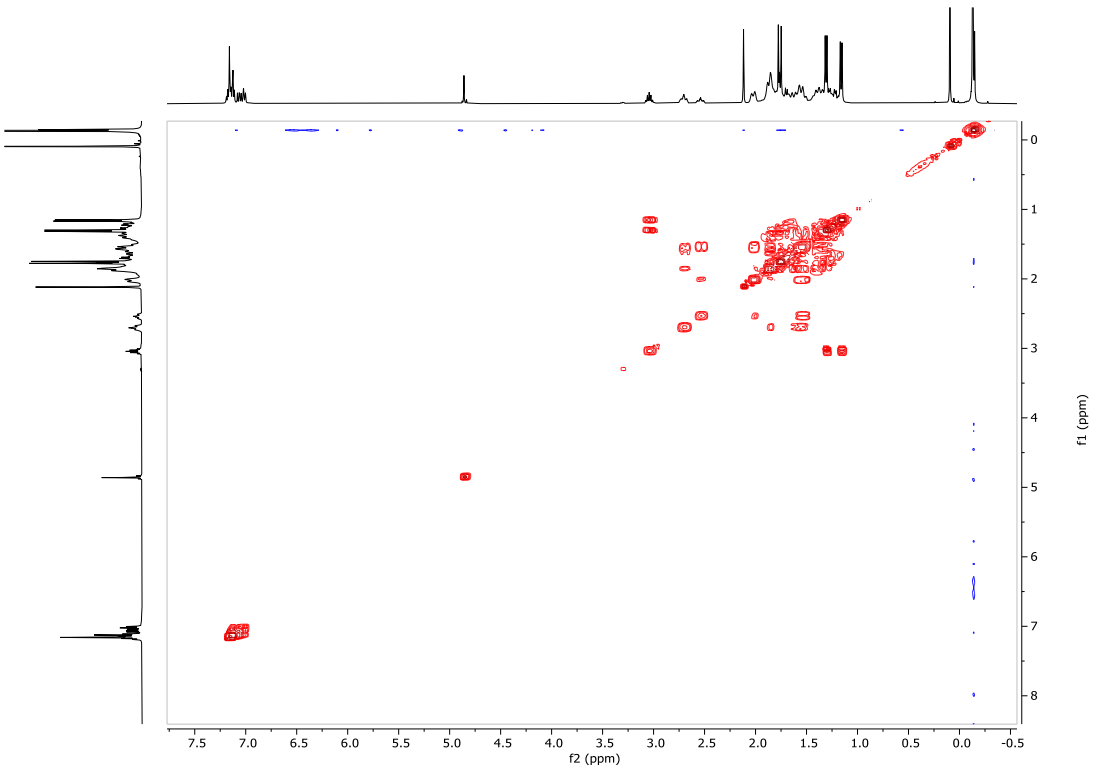

Figure S12: COSY NMR spectrum (400 MHz, 298 K, C_6D_6) of [Sr($^{Dip/TCHP}$Nacnac){N(SiMe$_3$)$_2$}] (**3**).

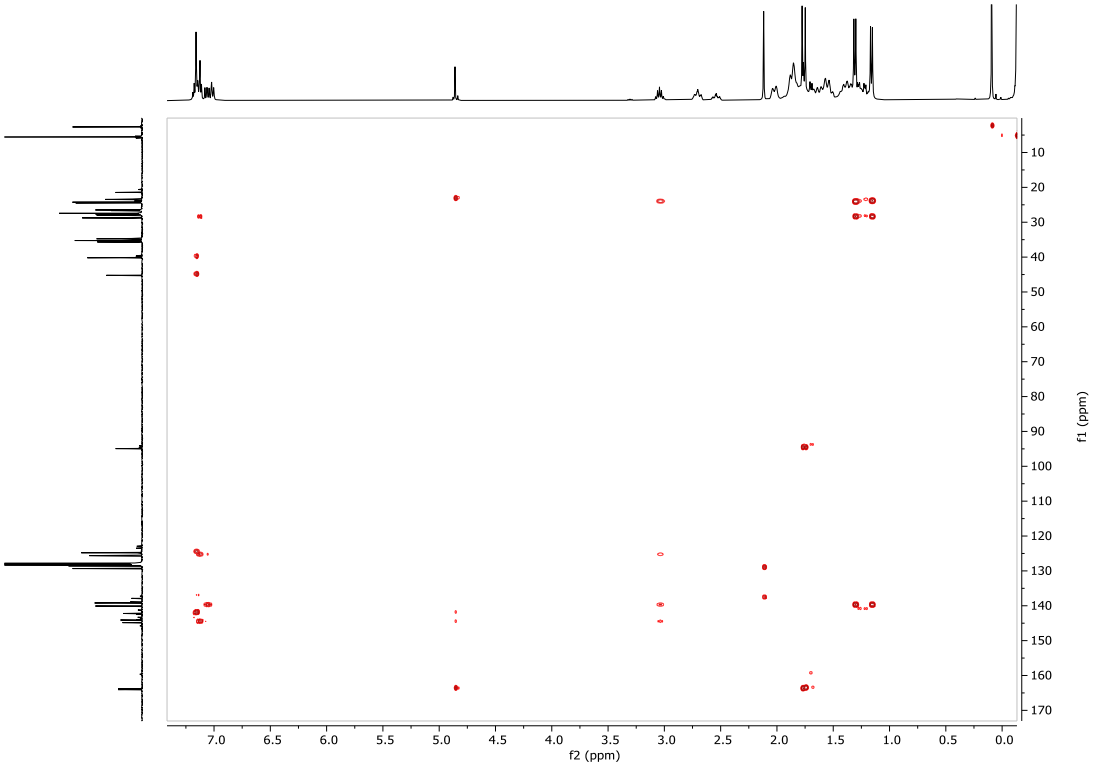

Figure S13: HMBC NMR spectrum (^{1}H: 400 MHz; ^{13}C: 101 MHz, 298 K, C_6D_6) of [Sr($^{Dip/TCHP}$Nacnac){N(SiMe$_3$)$_2$}] (**3**).

Preparation of [Ba($^{Dip/TCHP}$Nacnac){N(SiMe$_3$)$_2$}] (4).

$^{Dip/TCHP}$NacnacH (275 mg, 0.475 mmol) and Ba{N(SiMe$_3$)$_2$}$_2$ (217 mg, 0.475 mmol) were transferred to a *J* Young's ampoule and dissolved in toluene (~15 mL). The flask was sealed and heated at 120 °C for 48 hours until no $^{Dip/TCHP}$NacnacH starting material remained (as determined by ^{1}H NMR spectroscopy). Volatiles were removed *in vacuo* and the resulting solid was washed with *n*-hexane (2 x 5 mL) and dried to give the title compound as a colourless powder. Concentration of the hexane layer to *ca*. 4 mL and storage at −30 °C afforded a second crop of product. Yield 142 mg, 34 %. **M.p.** 188–190 °C. **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ -0.09 (s, 18H, Si(C*H*$_3$)$_3$), 1.16 (d, J = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.24 (d, J = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.27 – 1.70 (m, 20H, Cy–*H*), 1.75 (s, 3H, NCC*H*$_3$), 1.78 (s, 3H, NCC*H*$_3$), 1.80 – 2.03 (m, 10H, Cy–*H*), 2.53 (m, 1H, Cy–*H*), 2.65 (m, 2H, Cy–*H*), 3.01 (sept, J = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 4.83 (s, 1H, NCC*H*), 6.99 – 7.05 (m, 5H, Ar–*H*). **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6, 298 K): δ 5.6 (Si(*C*H$_3$)$_3$), 23.8, 23.9 (NC*C*H$_3$), 24.1, 24.3 (CH(*C*H$_3$)$_2$), 26.4, 26.7, 27.4, 27.5, 27.8 (Cy–*C*), 28.6 (*C*H(CH$_3$)$_2$), 34.8, 35.3, 35.7, 39.9, 45.2 (Cy–*C*), 94.7 (NC*C*H), 124.6, 124.8, 138.7, 139.0, 140.0, 142.7, 143.8, 145.3 ($_{Dip/TCHP}$Ar–*C*), 161.6, 162.1 (N*C*). **^{29}Si{^{1}H} NMR** (79 MHz, C_6D_6, 298 K): δ -19.6 (*Si*Me$_3$). **IR ν/cm^{-1}** (solid): 2930 (s), 2850 (m), 1628 (w), 1540 (s), 1441 (m), 1402 (s), 1318 (m), 1240 (s), 1170 (m), 1107 (w), 1053 (s), 927 (m), 879 (w), 856 (w), 816 (s), 758 (m), 638 (m). **Anal. Calcd.** for $C_{47}H_{77}BaN_3Si_2$: C 64.32, H 8.84, N 4.79 %. Found: C 64.01, H 9.45, N 3.99 %.

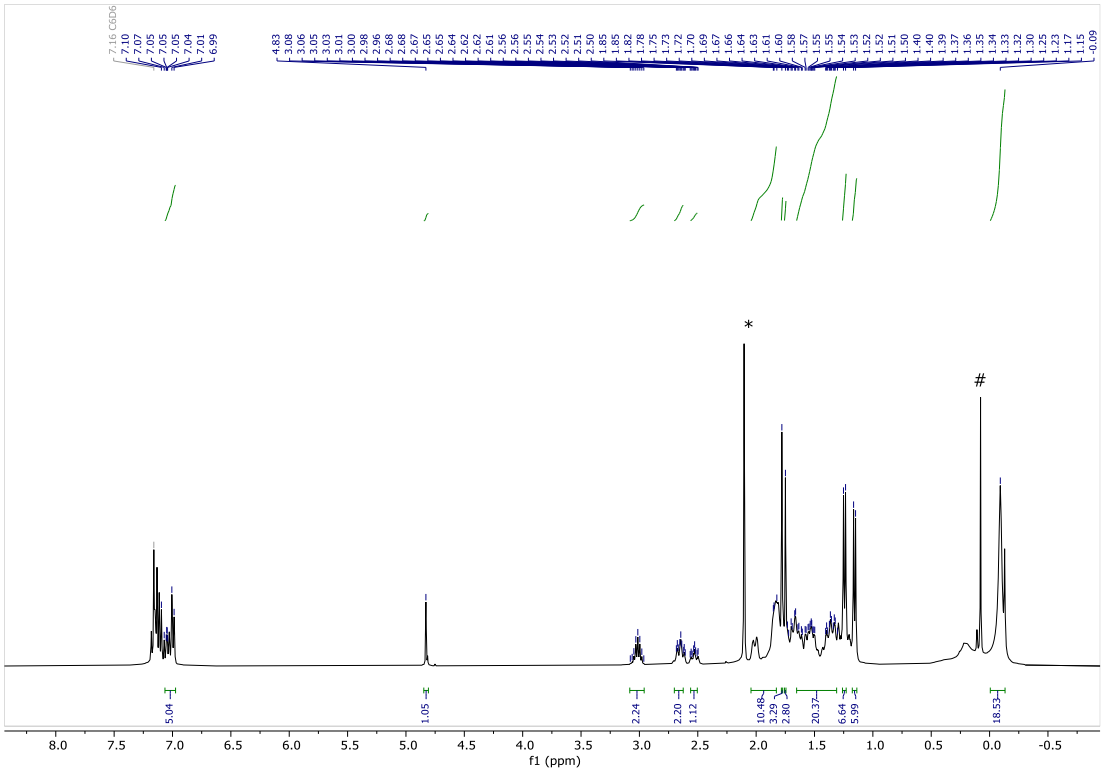

Figure S14: ^{1}H NMR spectrum (600 MHz, 298 K, C_6D_6) of [Ba($^{Dip/TCHP}$Nacnac){$N(SiMe_3)_2$}] (**4**) (* = toluene, # = $HN(SiMe_3)_2$).

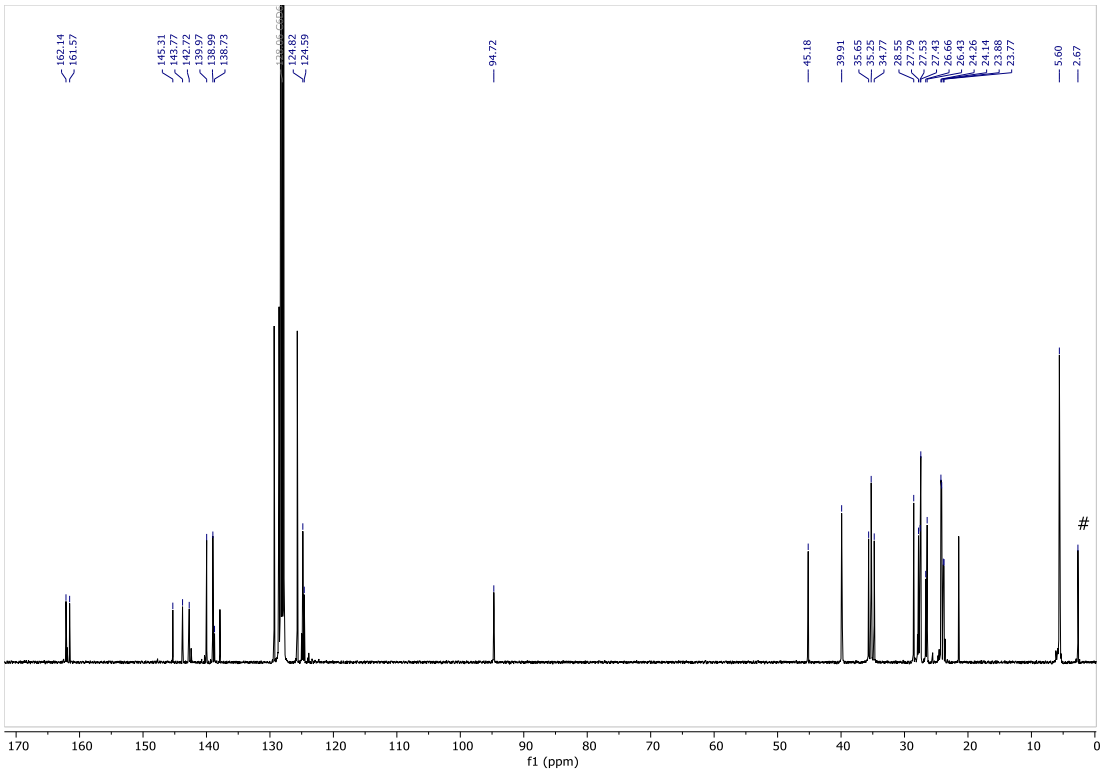

Figure S15: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K, C_6D_6) of [Ba($^{Dip/TCHP}$Nacnac){$N(SiMe_3)_2$}] (**4**) (# = $HN(SiMe_3)_2$.

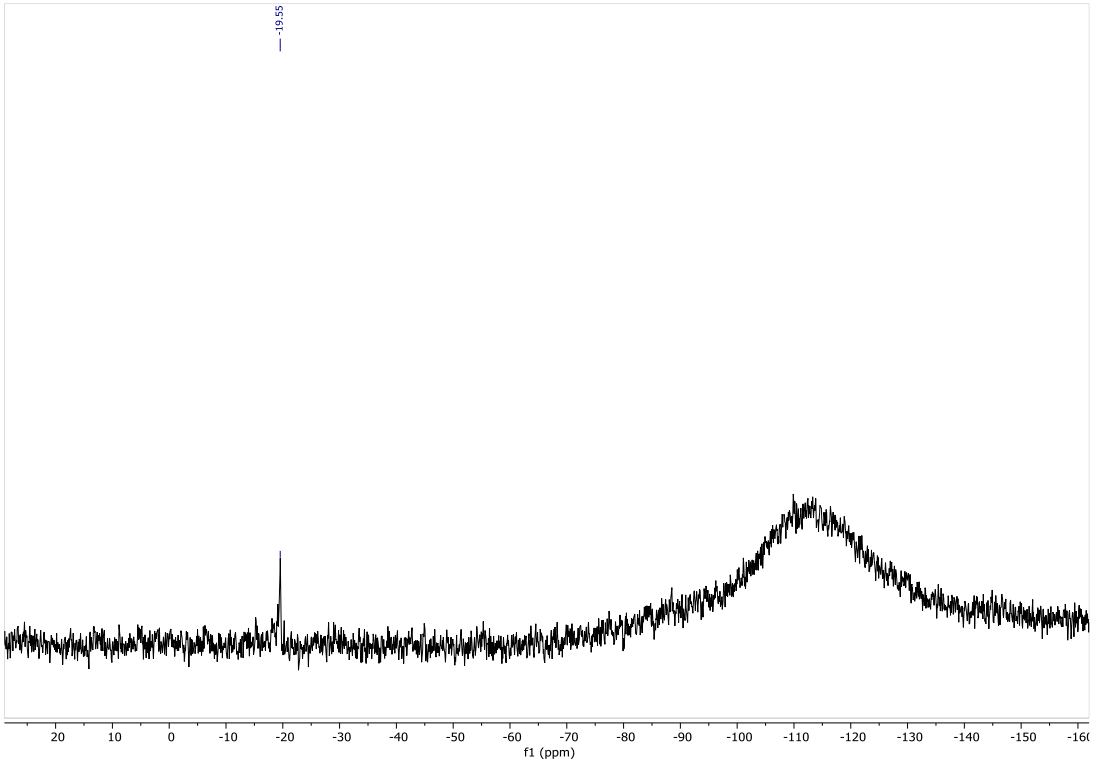

Figure S16: $^{29}Si\{^{1}H\}$ NMR spectrum (79 MHz, 298 K, C_6D_6) of [Ba($^{Dip/TCHP}$Nacnac){$N(SiMe_3)_2$}] (**4**).

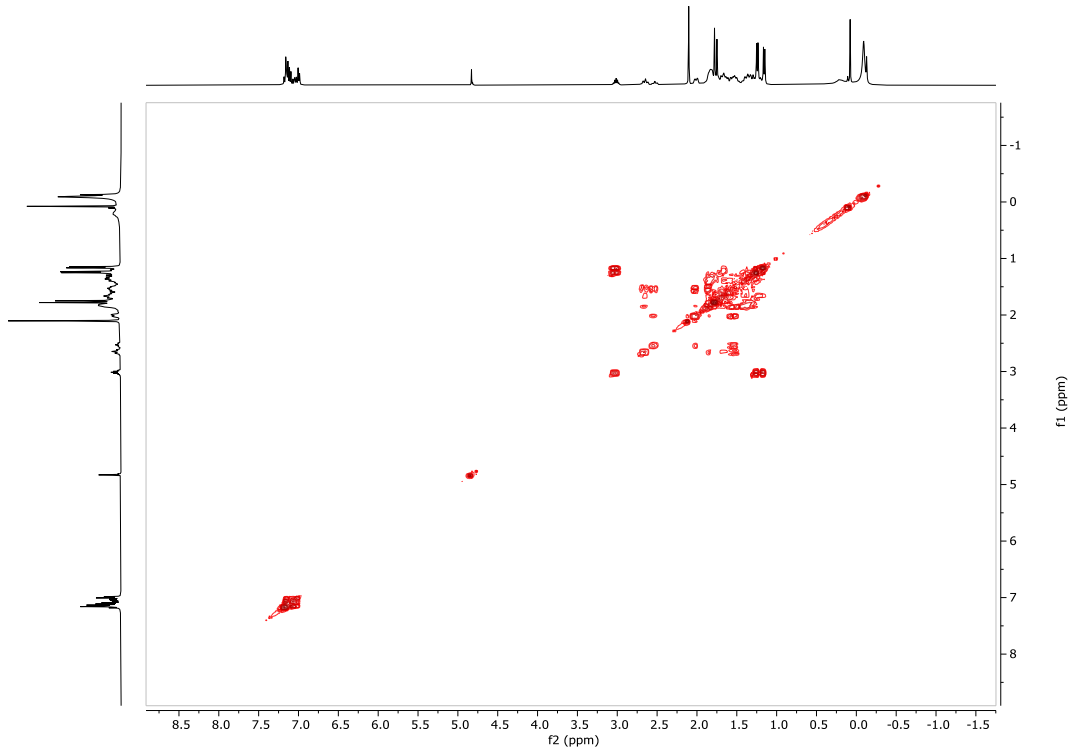

Figure S17: COSY NMR spectrum (600 MHz, 298 K, C_6D_6) of [Ba($^{Dip/TCHP}$Nacnac){$N(SiMe_3)_2$}] (**4**).

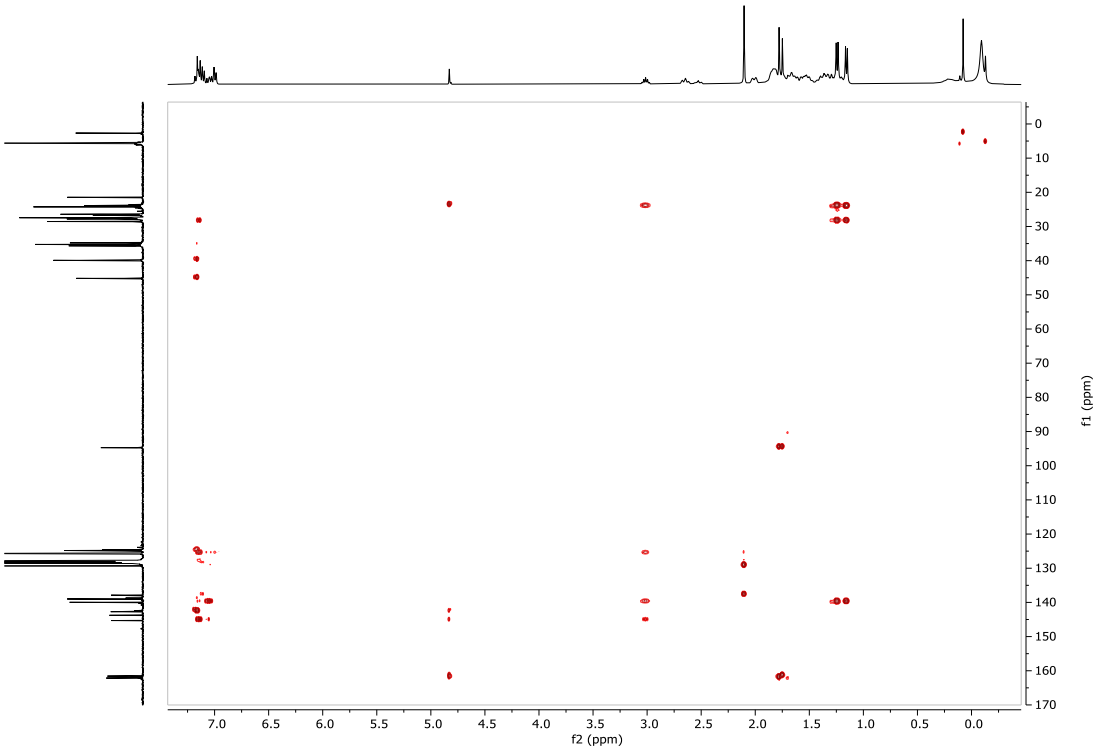

Figure S18: HMBC NMR spectrum (^{1}H: 400 MHz; ^{13}C: 101 MHz, 298 K, C_6D_6) of [Ba($^{Dip/TCHP}$Nacnac){N(SiMe$_3$)$_2$}] (**4**).

Preparation of [Sr($^{Dip/TCHP}$Nacnac){N(SiMe$_3$)$_2$}(THF)] (6).

$^{Dip/TCHP}$NacnacH (500 mg, 0.86 mmol) and Sr{N(SiMe$_3$)$_2$}$_2$(THF)$_2$ (569 mg, 1.03 mmol) were added to a *J* Young's ampoule and dissolved in toluene (~15 mL). The flask was then sealed and heated at 120 °C for 7 days until no $^{Dip/TCHP}$NacnacH starting material remained (as determined by ^{1}H NMR spectroscopy). Volatiles were removed *in vacuo* and the solid was extracted with *n*-hexane (10 mL). The solution was concentrated *in vacuo* to 3 mL and stored at −30 °C overnight to yield colourless crystals of the title compound. Yield 432 mg, 56 %. **M.p.** 160–162 °C. **^{1}H NMR** (400 MHz, 298 K, C_6D_6): δ -0.04 (s, 18H, Si(C*H*$_3$)$_3$), 1.27 (d, J = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.29 – 1.33 (m, THF, 4H), 1.35 (d, J = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.36 – 1.70 (m, 16H, Cy–*H*), 1.73 (s, 3H, NCC*H*$_3$), 1.76 (s, 3H, NCC*H*$_3$), 1.81 – 2.15 (m, 14H, Cy–*H*), 2.54-2.60 (m, 1H, Cy–*H*), 2.78-2.86 (m, 2H, Cy–*H*), 3.23 (sept, J = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.67 – 3.70 (m, 4H, THF) 4.74 (s, 1H, NCC*H*), 7.12 – 7.19 (m, 3H, Ar–*H*), 7.20 (s, 2H, Ar–*H*). **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6, 298 K): δ 5.6 (Si(*C*H$_3$)$_3$), 24.4 (NC*C*H$_3$), 24.9 (THF), 25.4, 25.5 (C(*C*H$_3$)$_2$), 25.7 (NC*C*H$_3$), 26.6, 26.7, 27.5, 27.6, 27.6 (Cy–*C*), 28.4 (*C*(CH$_3$)$_2$), 34.6, 35.3, 36.1, 39.3, 45.2 (Cy–*C*), 69.2 (THF), 93.6 (NC*C*H), 124.3, 124.4, 124.5, 139.9, 141.4, 143.4, 143.6, 147.9 ($_{Dip/TCHP}$Ar–*C*), 165.1, 165.5 (N*C*). **^{29}Si{^{1}H} NMR** (79.5 MHz, 298 K, C_6D_6): δ -16.8 (*Si*Me$_3$). **IR ν/cm^{-1}** (solid): 2921 (s), 2850 (m), 1620 (w), 1547 (m), 1444 (s), 1402 (s), 1308 (m), 1248 (s), 1172 (m),

1107 (w), 1053 (s), 928 (m), 878 (m), 816 (s), 750 (m), 658 (m). **Anal. Calcd.** for $C_{51}H_{85}SrN_3OSi_2$: C, 68.06 %; H, 9.52 %; N, 4.67 %; found: C, 67.29 %; H, 9.90 %; N, 4.38 %.

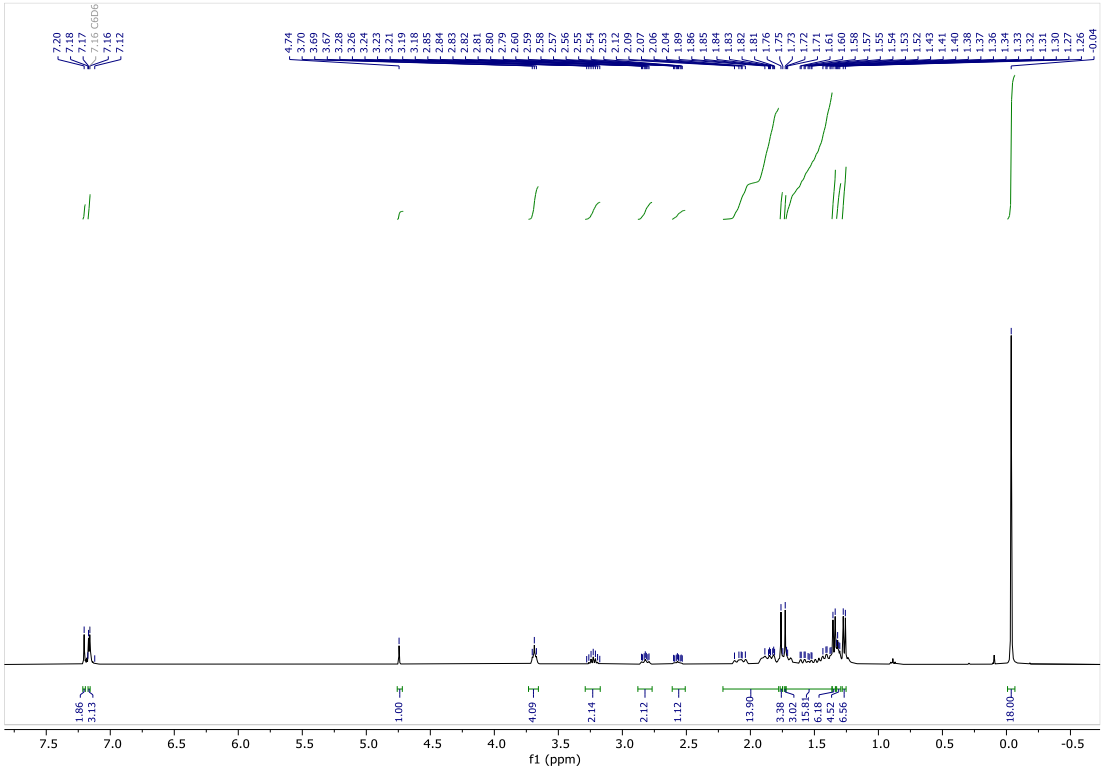

Figure S19: ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of [Sr($^{Dip/TCHP}$Nacnac){N(SiMe$_3$)$_2$}(THF)] (**6**).

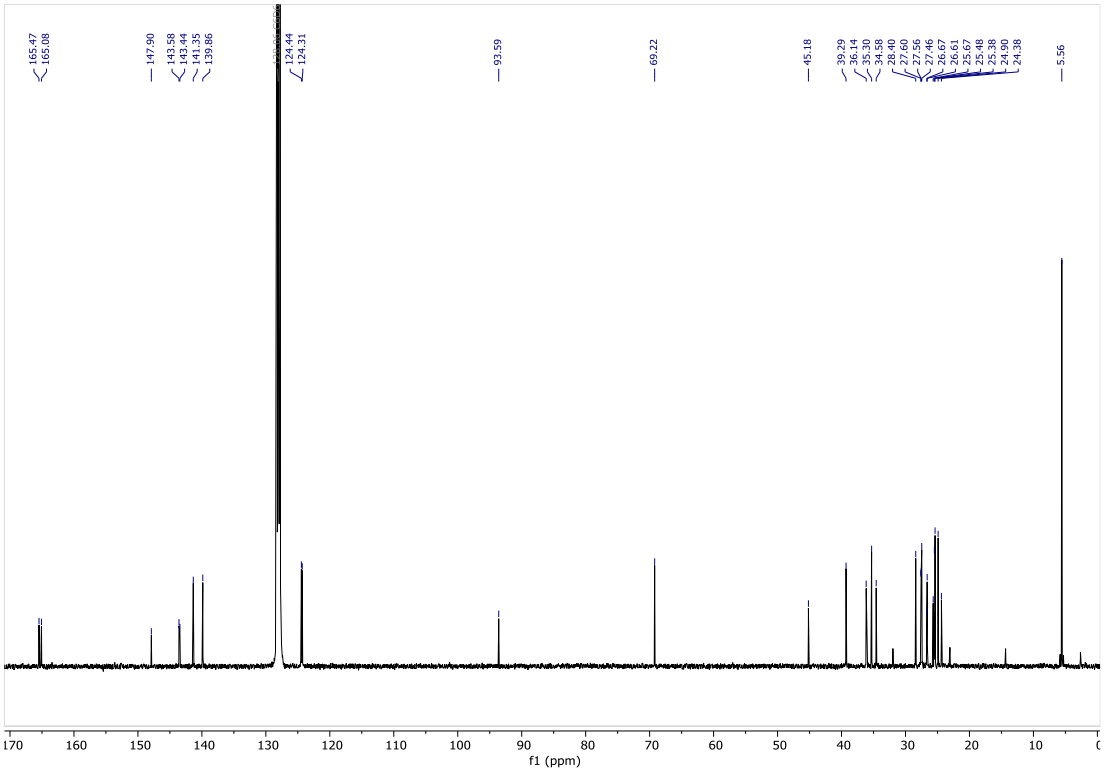

Figure S20: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K, C_6D_6) of [Sr($^{Dip/TCHP}$Nacnac){N(SiMe$_3$)$_2$}(THF)] (**6**).

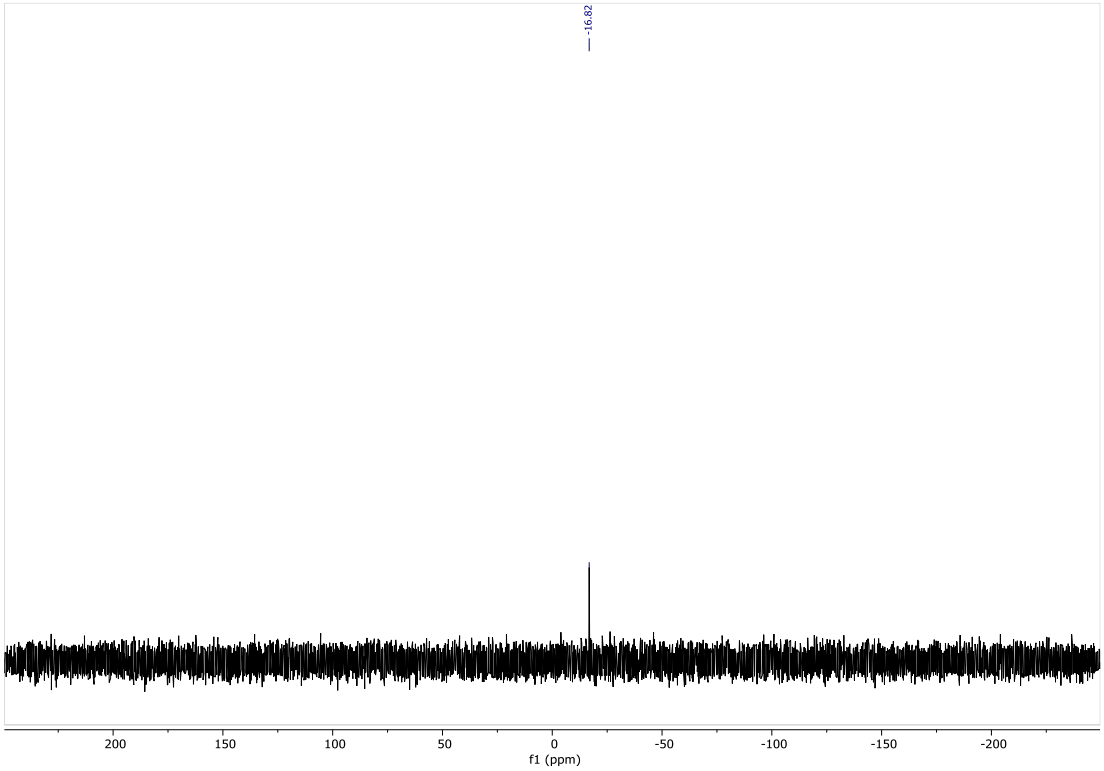

Figure S21: $^{29}Si\{^{1}H\}$ NMR spectrum (79 MHz, 298 K, C_6D_6) of [Sr($^{Dip/TCHP}$Nacnac){N(SiMe$_3$)$_2$}(THF)] (**6**).

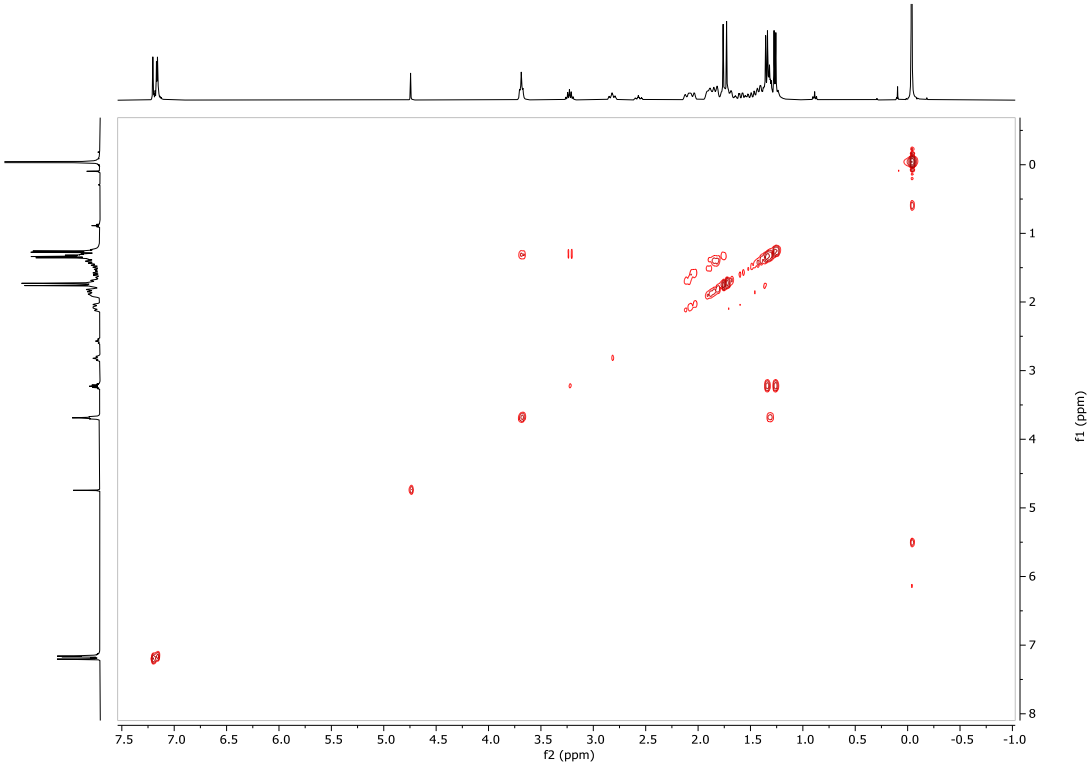

Figure S22: COSY NMR spectrum (400 MHz, 298 K, C_6D_6) of [Sr($^{Dip/TCHP}$Nacnac){N(SiMe$_3$)$_2$}(THF)] (**6**).

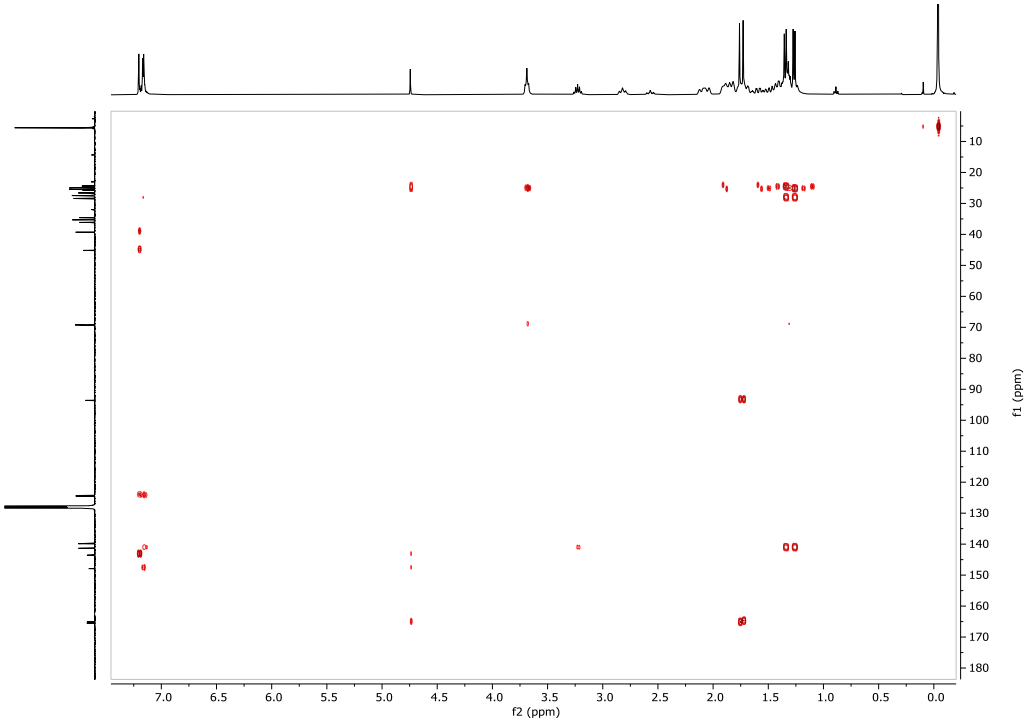

Figure S23: HMBC NMR spectrum (^{1}H: 400 MHz; ^{13}C: 101 MHz, 298 K, C_6D_6) of [Sr($^{Dip/TCHP}$Nacnac){N(SiMe$_3$)$_2$}(THF)] (**6**).

Preparation of [Ba($^{Dip/TCHP}$Nacnac){N(SiMe$_3$)$_2$}(THF)] (7).

$^{Dip/TCHP}$NacnacH (500 mg, 0.86 mmol) and Ba{N(SiMe$_3$)$_2$}$_2$(THF)$_2$ (622 mg, 1.04 mmol) were transferred to a *J* Young's ampoule and dissolved in toluene (~15 mL). The flask was sealed and heated at 120 °C for 4 days until no $^{Dip/TCHP}$NacnacH starting material remained (as determined by ^{1}H NMR spectroscopy). Volatiles were removed *in vacuo* and the solid extracted with *n*-hexane (10 mL), concentrated, and stored at −30 °C overnight to yield the title compound as a white solid. Further concentration of the mother liquor to *ca*. 4 mL and storage at −30 °C afforded a second crop of product. Yield 401 mg, 49 %. **M.p.** 178–180 °C. **^{1}H NMR** (400 MHz, 298 K, C_6D_6): δ 0.00 (s, 18H, Si(CH_3)$_3$), 1.24 (d, J = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.30 – 1.33 (m, 4H, THF), 1.34 (d, J = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.36 – 1.73 (m, 18H, Cy–*H*), 1.74 (s, 3H, NCCH_3), 1.78 (s, 3H, NCCH_3), 1.82 – 2.08 (m, 12H, Cy–*H*), 2.53 – 2.59 (m, 1H, Cy–*H*), 2.72 – 2.80 (m, 2H, Cy–*H*), 3.15 (sept, J = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.51-3.55 (m, 4H, THF) 4.78 (s, 1H, NCC*H*), 7.09 – 7.19 (m, 3H, Ar–*H*), 7.20 (s, 2H, Ar–*H*). **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6, 298 K): δ 5.5 (Si(*C*H$_3$)$_3$), 24.4, (NC*C*H$_3$), 24.6 (THF), 24.7 (NC*C*H$_3$) 25.3, 25.4 (CH(*C*H$_3$)$_2$), 26.6, 26.7, 27.5, 27.6, 27.7 (Cy–*C*), 28.5 (*C*H(CH$_3$)$_2$), 35.3, 35.3, 35.6, 39.6, 45.2 (Cy–*C*), 68.6 (THF), 93.4 (NC*C*H), 124.3, 124.4, 124.9, 139.7, 140.8, 143.4, 143.5, 146.8 ($_{Dip/TCHP}$Ar–*C*), 162.6, 162.8 (N*C*). **^{29}Si{^{1}H} NMR** (79.5 MHz, 298 K, C_6D_6): δ -19.0 (*Si*Me$_3$). **IR ν/cm^{-1}** (solid): 2924 (s), 2851 (m), 1623 (w), 1547 (m), 1523 (w), 1446 (m), 1402 (s), 1363 (m), 1313 (w), 1246 (m), 1177 (m), 1144 (w), 1059 (s), 1033 (m), 924 (m), 875 (m), 864 (m), 816 (s), 756 (m), 657 (w). Despite repeated attempts, a reproducible elemental analysis results could not be obtained.

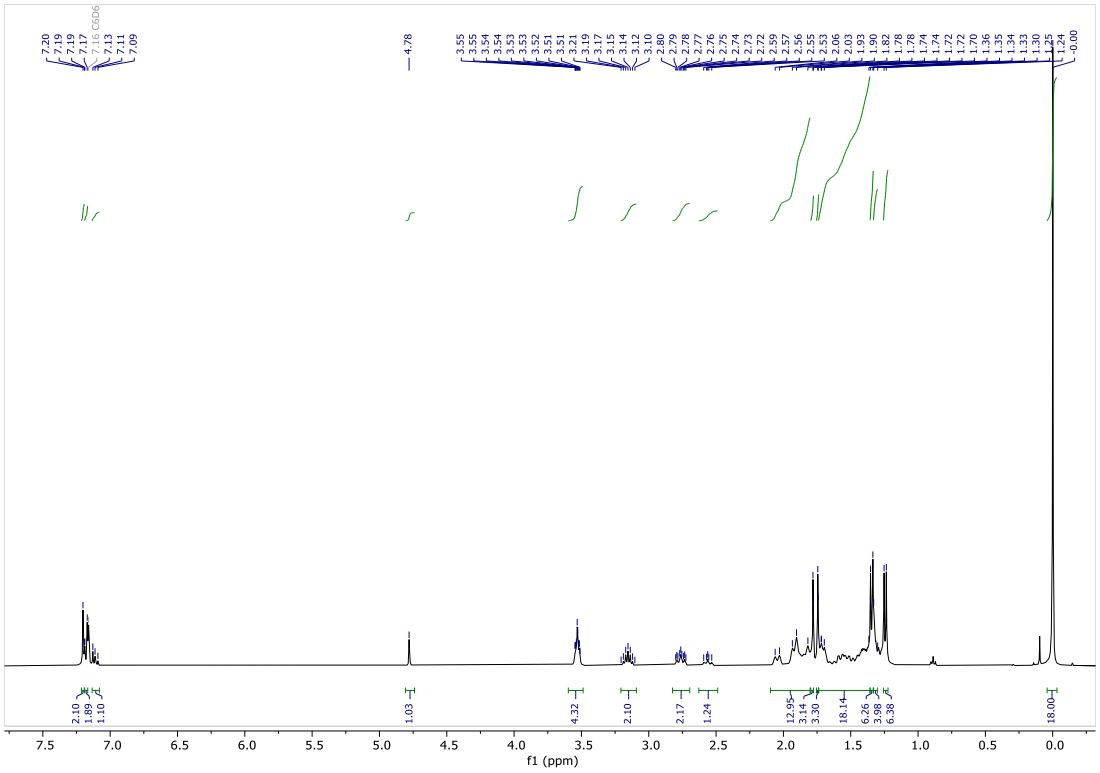

Figure S24: ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of [Ba($^{Dip/TCHP}$Nacnac){N(SiMe$_3$)$_2$}(THF)] (**7**).

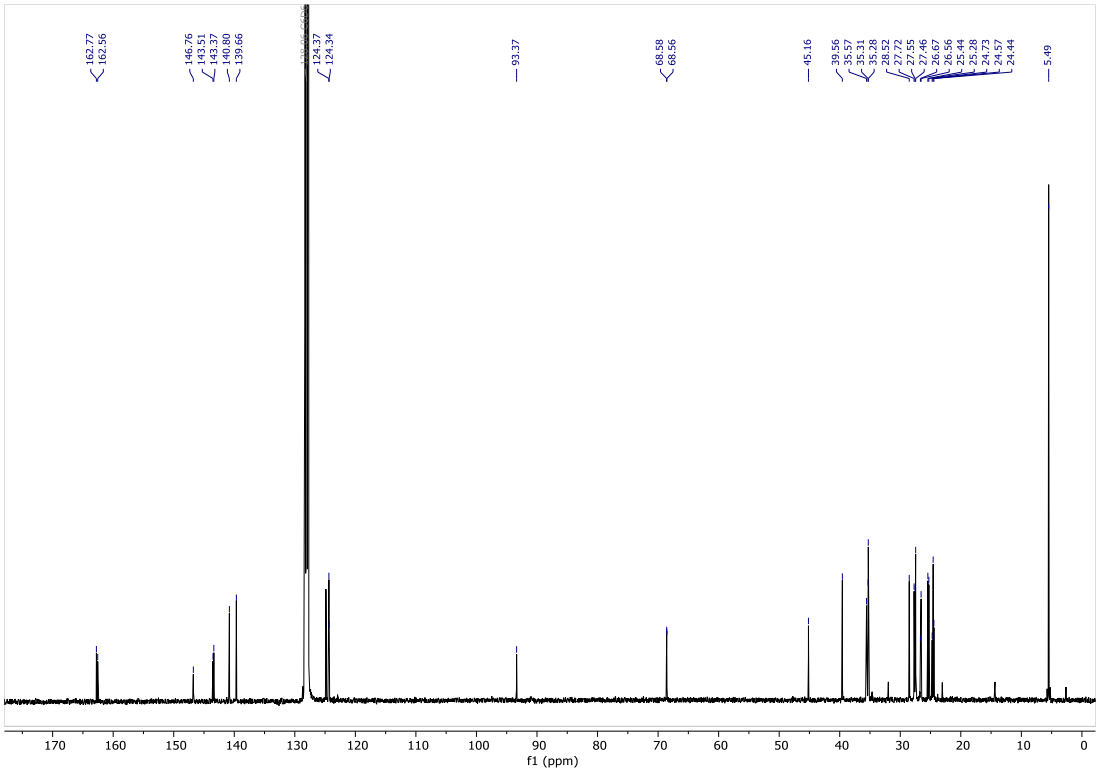

Figure S25: ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K, C_6D_6) of [Ba($^{Dip/TCHP}$Nacnac){N(SiMe$_3$)$_2$}(THF)] (**7**).

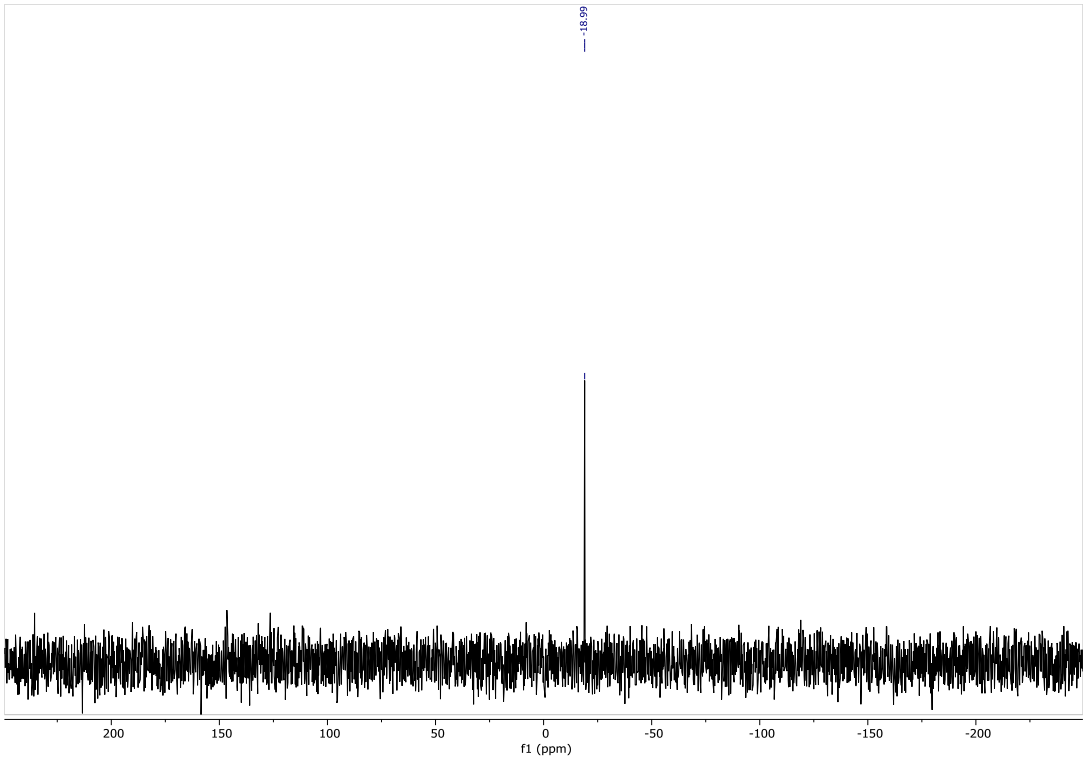

Figure S26: $^{29}Si\{^{1}H\}$ NMR spectrum (79.5 MHz, 298 K, C_6D_6) of [Ba($^{Dip/TCHP}$Nacnac){N(SiMe$_3$)$_2$}(THF)] (**7**).

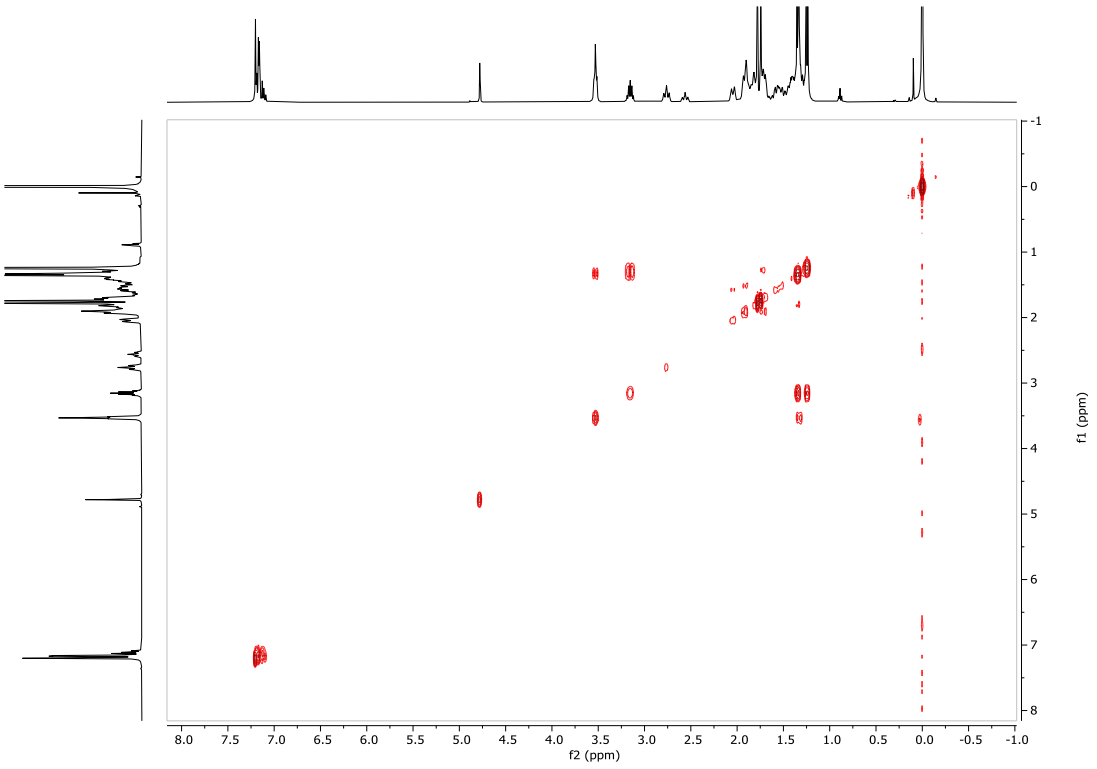

Figure S27: COSY NMR spectrum (400 MHz, 298 K, C_6D_6) of [Ba($^{Dip/TCHP}$Nacnac){N(SiMe$_3$)$_2$}(THF)] (**7**).

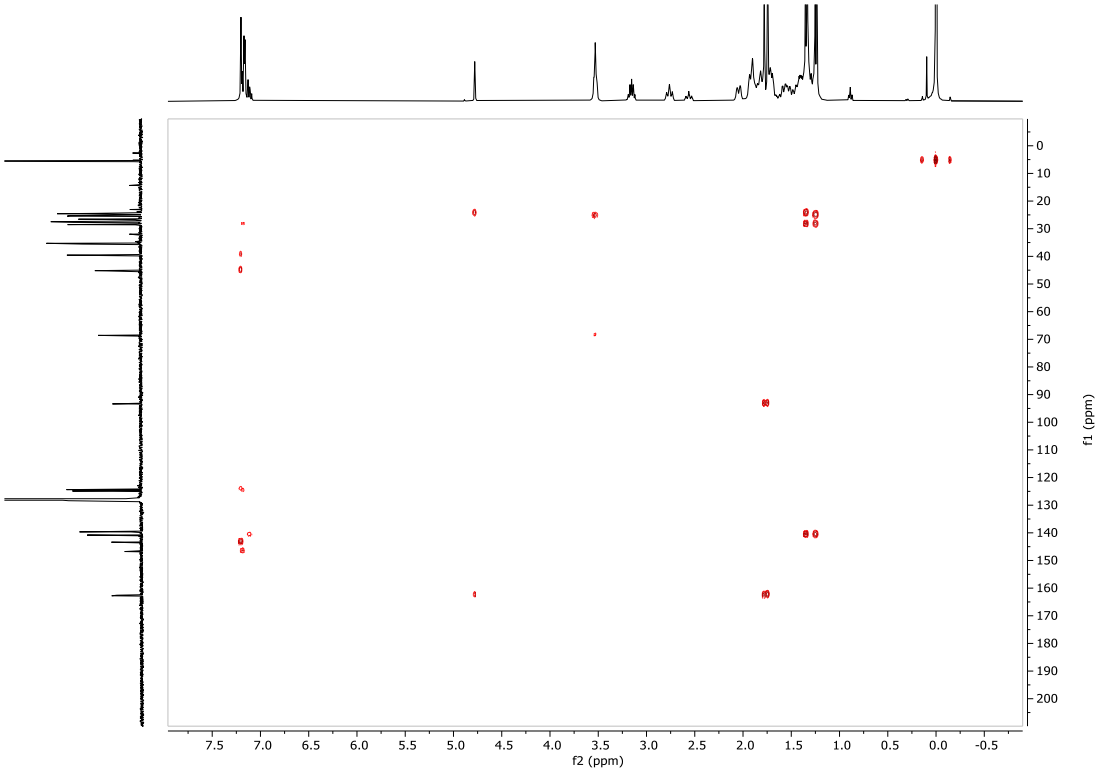

Figure S28: HMBC NMR spectrum (^{1}H: 400 MHz; ^{13}C: 101 MHz, 298 K, C_6D_6) of [Ba($^{Dip/TCHP}$Nacnac){N(SiMe$_3$)$_2$}(THF)] (**7**).

Preparation of [{($^{Dip/TCHP}$Nacnac)Mg(μ-H)}$_2$] (8).

Method A: [Mg($^{Dip/TCHP}$Nacnac)(Bu^{n})(THF)] (70 mg, 0.09 mmol) was transferred to a *J* Young's NMR tube and C_6D_6 (~0.6 mL) was added. Phenylsilane (~12 μL, 0.09 mmol) was added and the NMR tube was sealed and heated to 80 °C for 16 hours. Volatiles were reduced *in vacuo* (to ~0.1 mL) and the NMR tube left under a static vacuum at room temperature. Over the course of 2 days, colourless microcrystalline material deposited. Yield 8 mg, 14 %. *Method B*: $^{Dip/TCHP}$NacnacH (400 mg, 0.69 mmol) was transferred to a *J* Young's ampoule and dissolved in toluene (~10 mL). A solution of MgBu$^{n}_2$(THF)$_x$ (1M in hexane, 0.69 mmol, 0.69 mL) was added dropwise at room temperature. The reaction mixture was stirred for 30 minutes at room temperature, sealed, and then heated at 80 °C for 16 hours. Volatiles were removed *in vacuo* and the residue dissolved in hexane (~2 mL). Colourless crystals were obtained by storage at –30 °C for 4 days. The supernatant was decanted and hexane (~5 mL) was added to the isolated solid. Phenylsilane (0.10 mL, excess) was then added at room temperature. The reaction mixture was sealed and stirred at 80 °C for 16 hours to give a pale-yellow solution. Volatiles were removed *in vacuo* and the residue heated at 80 °C (10^{-2} mbar) for 2 hours to give a pale-yellow solid. Yield 108 mg, 26 %. **M.p.** 143–145 °C. **^{1}H NMR** (400 MHz, C_6D_6): δ 1.03 (d, J = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.16 (d, J = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.29 – 1.40 (m, 16H, Cy–*H*), 1.45

(s, 6H, NCCH_3), 1.49 (s, 6H, NCCH_3), 1.51 – 1.76 (m, 16H, Cy–*H*), 1.77 – 2.07 (m, 24H, Cy–*H*), 2.24 – 2.32 (m, 4H, Cy–*H*), 2.59 – 2.74 (m, 6H, Cy–*H*), 3.07 (hept, J = 6.8 Hz, 4H, C*H*$(CH_3)_2$), 4.06 (s, 2H, Mg*H*), 4.80 (s, 4H, NCC*H*), 7.06 (s, 4H, $_{TCHP}$Ar–*H*), 7.00 – 7.13 (m, 6H, $_{Dip}$Ar–*H*). **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ 23.8 (CH(CH_3)$_2$), 24.6 (NCCH_3), 25.0 (CH(*C*H_3)$_2$), 26.8, 27.0, 27.6, 28.0, 28.2 (Cy–*C*), 29.0 (*C*H$(CH_3)_2$), 34.1, 34.8, 35.3, 40.2, 44.7 (Cy–*C*), 94.7 (NC*C*H), 123.1, 123.5, 124.2, 125.7, 132.9, 141.2, 142.3, 143.6, 144.4, 146.7 ($_{Dip/TCHP}$Ar–*C*), 169.3, 170.0 (N*C*). **IR ν/cm^{-1}** (solid): 701 (m), 742 (w), 760 (w), 794 (w), 839 (w), 861 (m), 891 (w), 928 (w), 999 (w), 1025 (m), 1178 (m), 1230 (w), 1260 (w), 1278 (w), 1297 (w), 1316 (m), 1357 (w), 1401 (s), 1439 (m), 1528 (s), 1621 (w), 2848 (s), 2922 (s). A reproducible elemental analysis could not be obtained due to the persistent presence of traces of $PhSiH_2Bu^n$ in the bulk isolated material. Attempts to remove this under vacuum at elevated temperatures were unsuccessful.

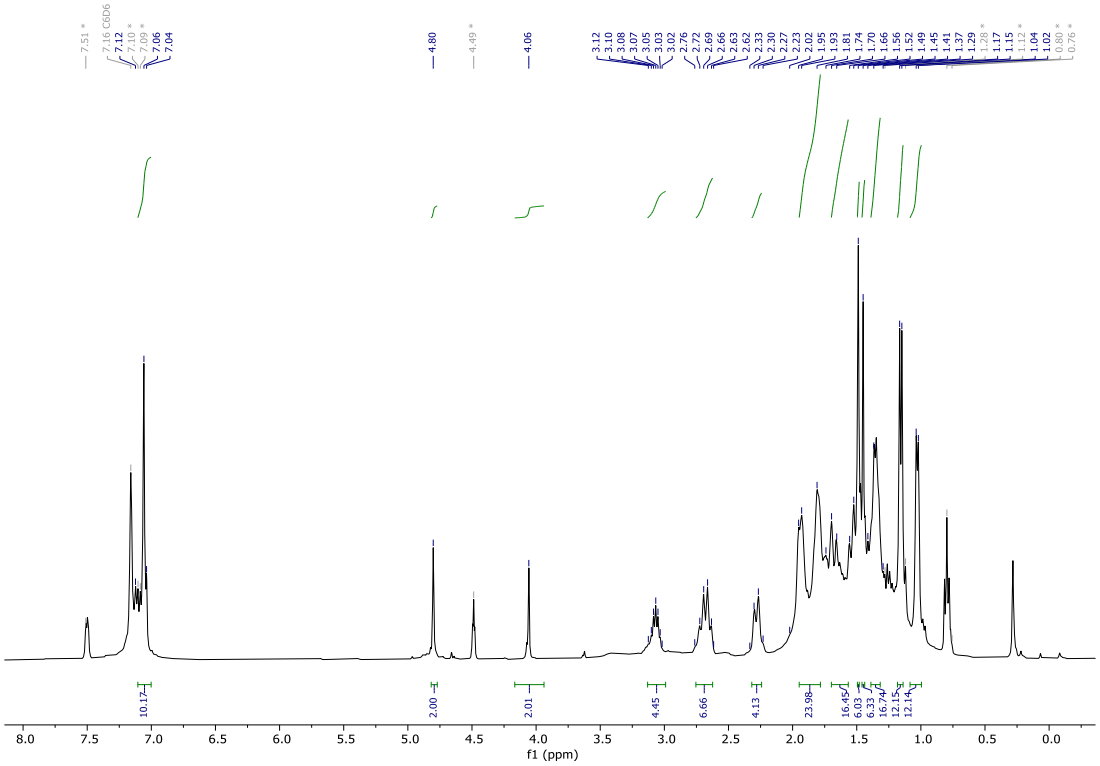

Figure S29: ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of [{($^{Dip/TCHP}$Nacnac)Mg(μ-H)}$_2$] (**8**).

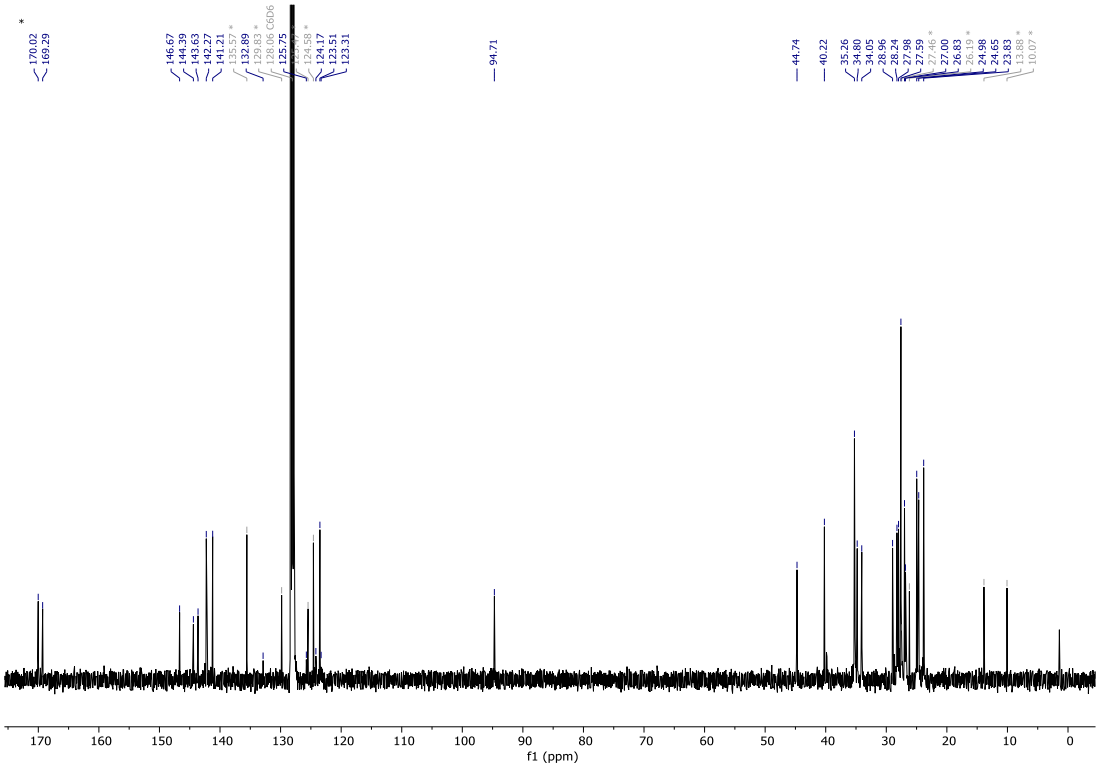

Figure S30: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K, C_6D_6) of [{($^{Dip/TCHP}$Nacnac)Mg(μ-H)}$_2$] (**8**).

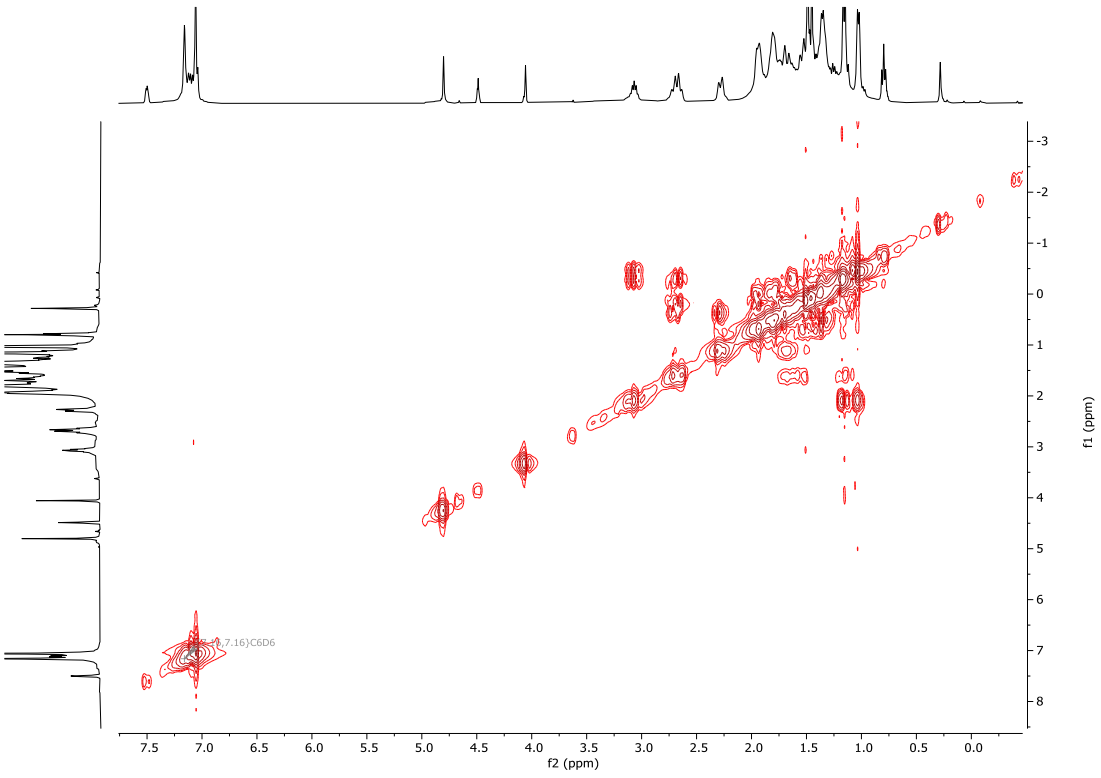

Figure S31: COSY NMR spectrum (400 MHz, 298 K, C_6D_6) of [{($^{Dip/TCHP}$Nacnac)Mg(μ-H)}$_2$] (**8**).

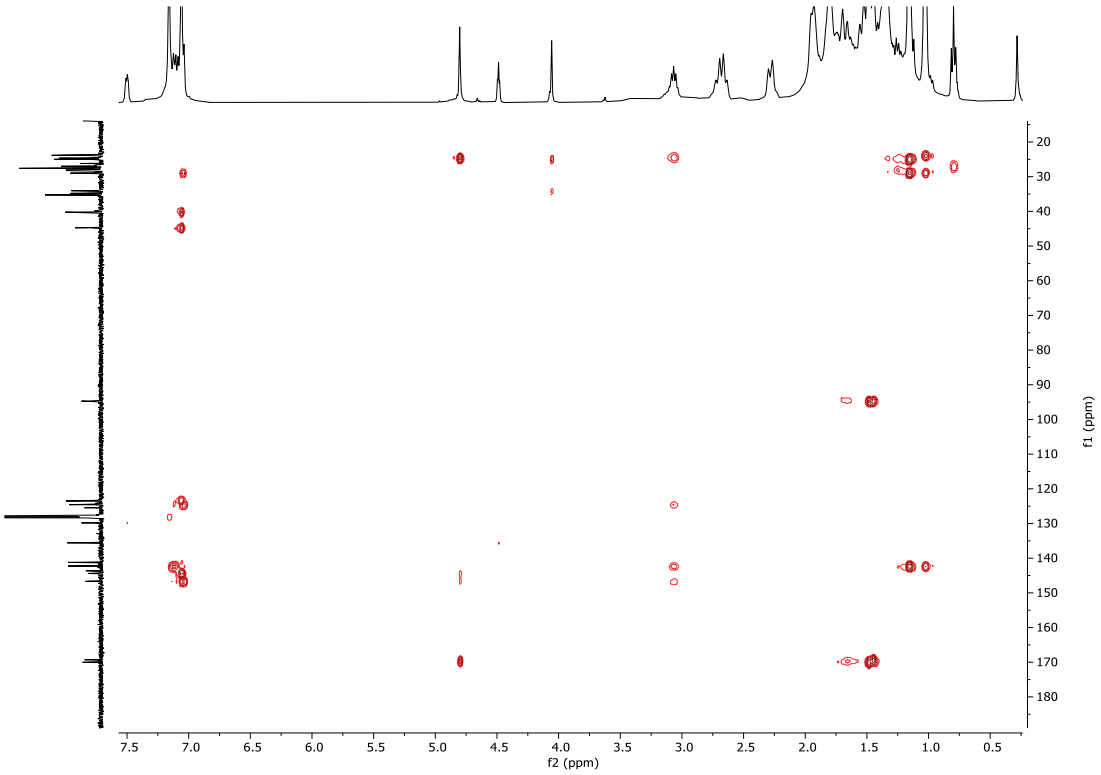

Figure S32: HMBC NMR spectrum (^{1}H: 400 MHz; ^{13}C: 101 MHz, 298 K, C_6D_6) of [{($^{Dip/TCHP}$Nacnac)Mg(μ-H)}$_2$] (**8**).

Preparation of [{($^{Dip/TCHP}$Nacnac)Ca(μ-H)}$_2$] (9).

$^{Dip/TCHP}$NacnacH (300 mg, 0.52 mmol) and Ca{N(SiMe$_3$)$_2$}$_2$(THF)$_2$ (273 mg, 0.54 mmol) were added to a *J* Young's ampoule and dissolved in toluene (~15 mL). The flask was sealed and heated at 120 °C for 14 days until no $^{Dip/TCHP}$NacnacH starting material remained (as determined by ^{1}H NMR spectroscopy). All volatiles were removed *in vacuo* and the resulting oil was dissolved in *n*-pentane (~5 mL). PhSiH$_3$ (127 μL, 1.03 mmol) was added in one portion *via* micro syringe at room temperature. The solution was then left to stand at room temperature for 4 days, affording the product as a colourless micro-crystalline solid. This was recrystallised from boiling benzene at room temperature yielding crystals suitable for X-ray diffraction. The crystalline product is insoluble in aliphatic and aromatic solvents. A drop of THF-D$_8$ was added to a suspension of the compound in C_6D_6 to aid solubility for NMR spectroscopic experiments. Yield 231 mg, 72 %. **M.p.** 174-177 °C (decomp). **^{1}H NMR** (400 MHz, 298 K, C_6D_6:THF-D$_8$, 50:1): δ 1.04 (d, J = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.26 (d, J = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.31 – 1.59 (m, 30H, Cy–*H*), 1.61 (s, 6H, NCC*H*$_3$), 1.64 (s, 6H, NCC*H*$_3$), 1.68 – 1.91 (m, 26H, Cy–*H*), 2.05 – 2.14 (m, 4H, Cy–*H*), 2.56-2.62 (m, 2H, Cy–*H*), 2.78-2.84 (m, 4H, Cy–*H*), 3.14 (sept, J = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 4.51 (s, 2H, Ca–*H*), 4.63 (s, 2H, NCC*H*), 7.09-7.11 (m, 6H, Ar–*H*), 7.16 (s, 4H, Ar–*H*). **^{13}C{^{1}H} NMR** (101 MHz, 298K, C_6D_6:THF-D$_8$, 50:1): δ 25.0 (2xNCC*H*$_3$),* 25.8 (2xCH(*C*H$_3$)$_2$),* 26.8, 26.9, 27.3, 27.6, 27.7 (Cy–*C*), 27.8 (*C*(CH$_3$)$_2$), 34.7, 35.4, 36.1, 38.2, 44.9 (Cy–

C), 93.1 (NC*C*H), 123.1, 123.6, 124.0, 141.0, 141.9, 142.1, 145.1, 147.1 ($_{Dip/TCHP}$Ar–*C*), 165.0, 165.7 (N*C*). * = partially obscured by THF-D_8 signals. **IR ν/cm^{-1}** (solid): 2922 (s), 2850 (m), 1655 (w), 1620 (m), 1550 (s), 1523 (w), 1446 (s), 1407 (m), 1381(m), 1363 (m), 1321 (m), 1274 (m), 1176 (m), 1146 (w), 1106 (w), 1018 (m), 998 (m), 952 (w), 924 (w), 891 (w), 863 (m), 825 (w), 787 (m), 760 (m), 675 (s). A reproducible elemental analysis could not be obtained due to the compound persistently crystallising with small amounts of [{($^{Dip/TCHP}$Nacnac)Ca(μ-OH)}$_2$] (see below).

NMR Data for *in situ* generated [($^{Dip/TCHP}$Nacnac)Ca{N(SiMe$_3$)$_2$}(THF)] (5).

As this complex could only be isolated as an oily residue, it was generated and used *in situ* as detailed above. NMR spectroscopic data were obtained from the reaction mixture before addition of phenylsilane. **^{1}H NMR** (400 MHz, 298 K, C_6D_6): δ -0.06 (s, 18H, Si(C*H*$_3$)$_3$), 1.18 (d, J = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.21 – 1.34 (m, 6H, Cy–*H*), 1.37 (d, J = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.39 – 1.68 (m, 10H, Cy–*H*), 1.71 (s, 3H, NCC*H*$_3$), 1.75 (s, 3H, NCC*H*$_3$), 1.78 – 2.20 (m, 18H, Cy–*H*, THF), 2.48 – 2.59 (m, 1H, Cy–*H*), 2.67 – 2.79 (m, 2H, Cy–*H*), 3.11 (hept, J = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 3.54 (br s, 4H, THF), 4.83 (s, 1H, NCC*H*), 7.05 – 7.15 (m, 3H, $_{Dip}$Ar–*H*), 7.18 (s, 2H, $_{TCHP}$Ar–*H*). **^{13}C{^{1}H} NMR** (101 MHz, 298K, C_6D_6): δ 5.6 (Si(*C*H$_3$)$_3$), 24.0, 24.5 (NC*C*H$_3$), 24.9, 24.9 (CH(*C*H$_3$)$_2$), 25.3 (THF), 26.6, 26.6, 27.4, 27.6, 27.8 (Cy–*C*), 28.9 (*C*H(CH$_3$)$_2$), 35.1, 35.3, 35.4, 40.2, 45.2 (Cy–*C*), 69.9 (THF), 94.8 (NC*C*H), 124.3, 125.0, 125.2, 140.0, 141.2, 142.2, 144.3, 145.5 ($_{Dip/TCHP}$Ar–*C*), 166.4, 166.5 (N*C*).

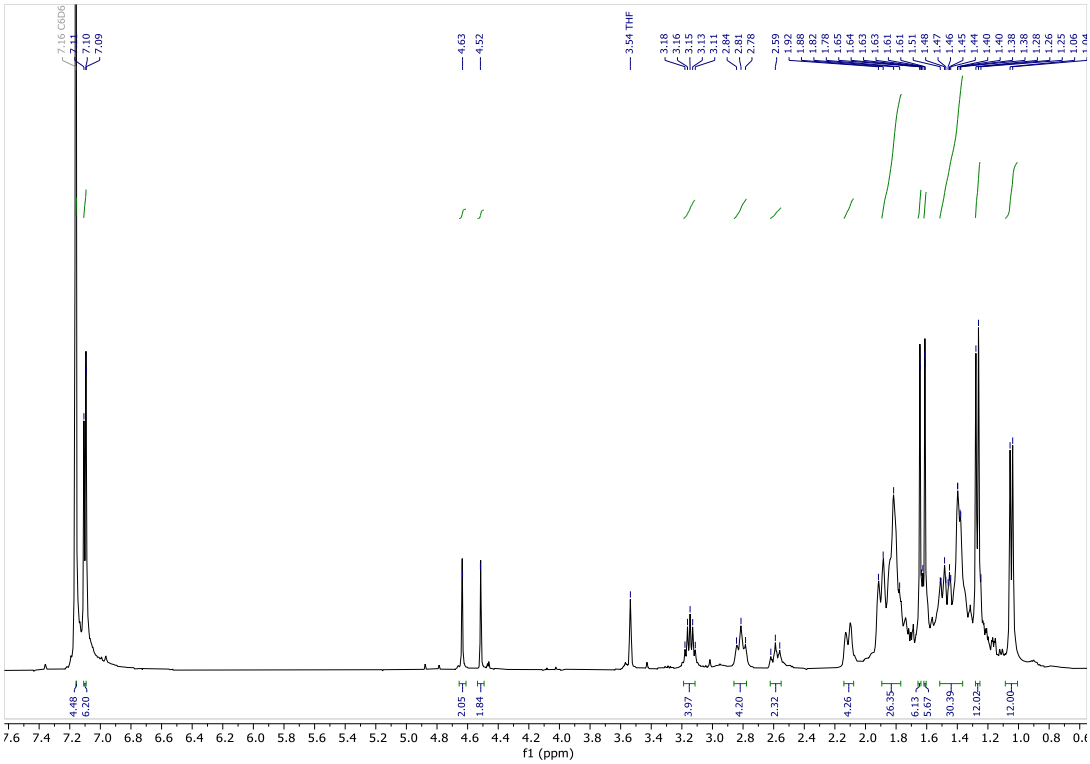

Figure S33: ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6:THF-D_8, 50:1) of [{($^{Dip/TCHP}$Nacnac)Ca(μ-H)}$_2$] (**9**).

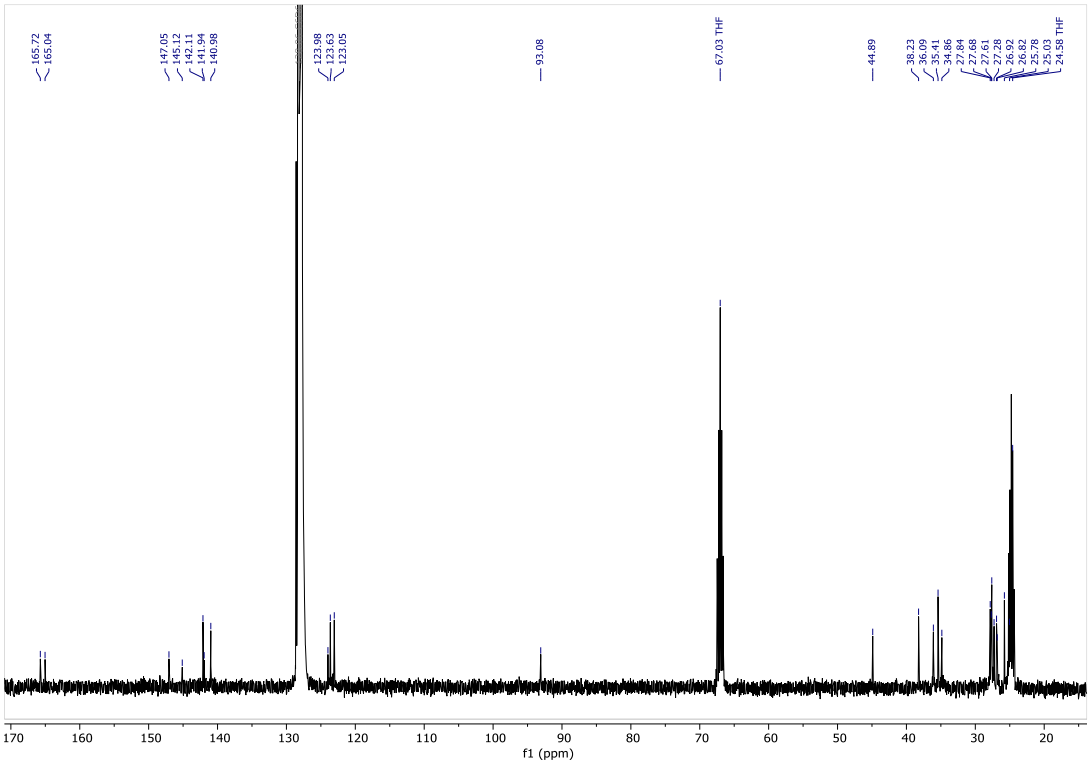

Figure S34: ^{13}C{^{1}H} NMR spectrum (101 MHz, 298 K, C_6D_6:THF-D_8, 50:1) of [{($^{Dip/TCHP}$Nacnac)Ca(μ-H)}$_2$] (**9**).

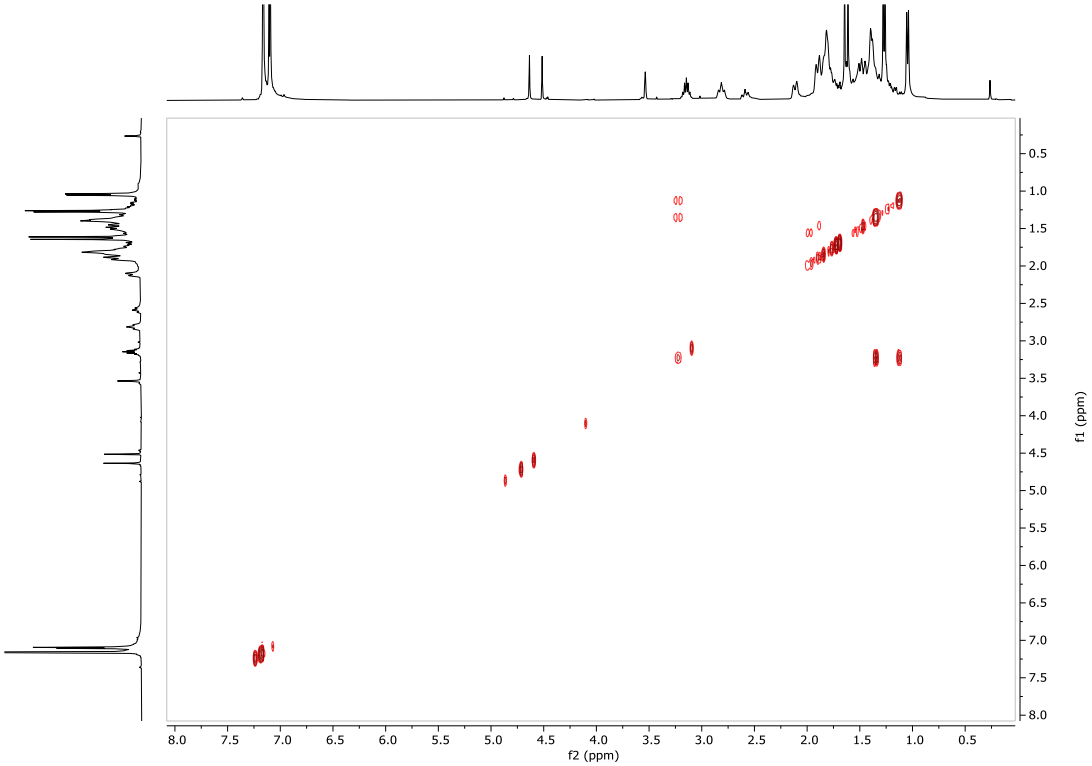

Figure S35: COSY NMR spectrum (400 MHz, 298 K, C_6D_6:THF-D_8, 50:1) of [{($^{Dip/TCHP}$Nacnac)Ca(μ-H)}$_2$] (**9**).

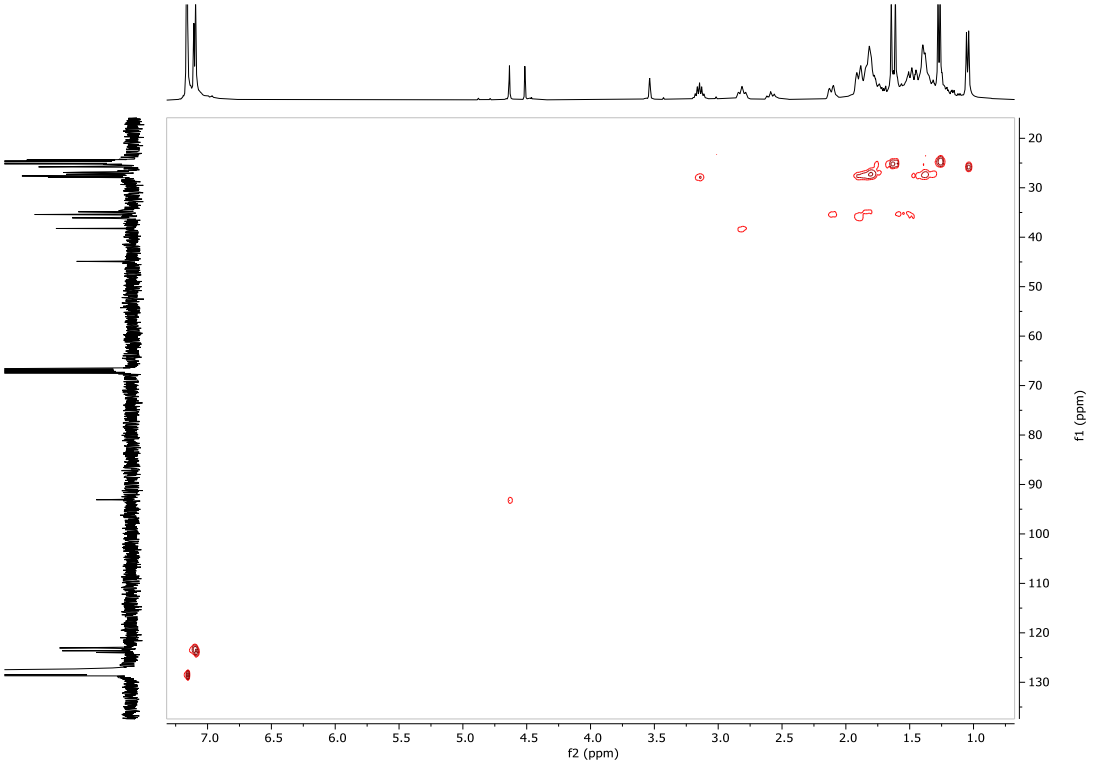

Figure S36: HMBC NMR spectrum (^{1}H: 400 MHz; ^{13}C: 101 MHz, 298 K, C_6D_6:THF-D_8, 50:1) of [{($^{Dip/TCHP}$Nacnac)Ca(μ-H)}$_2$] (**9**).

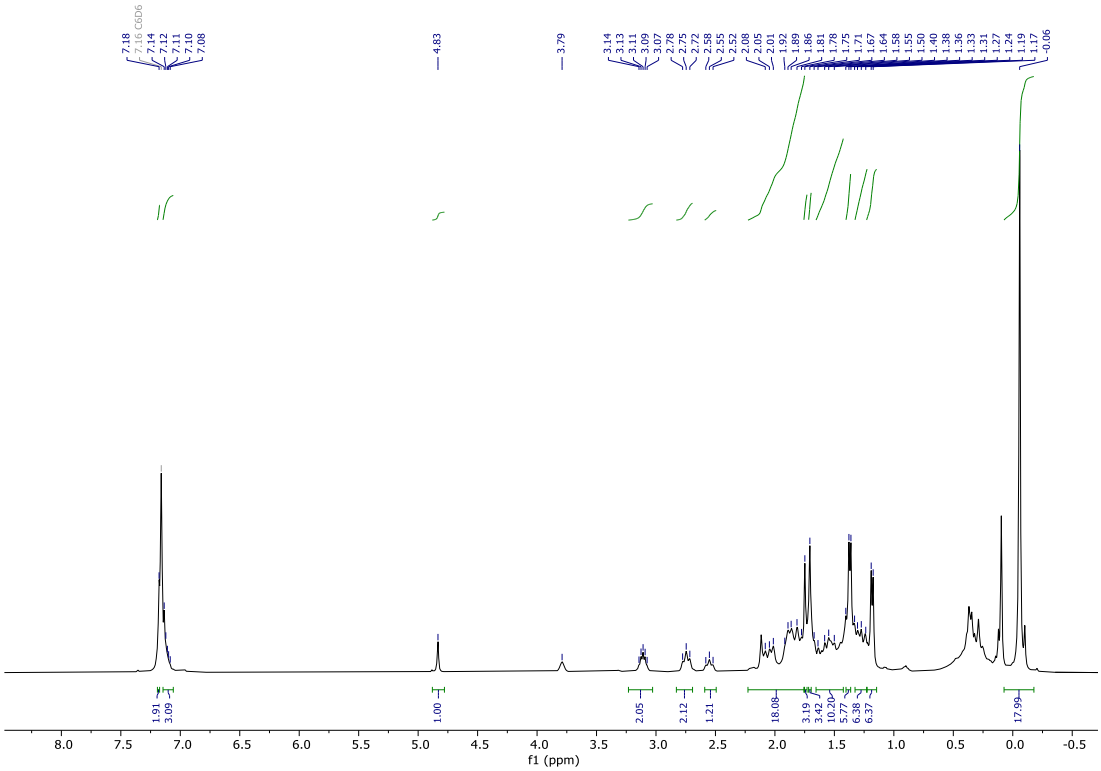

Figure S37: ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of *in situ* generated [($^{Dip/TCHP}$Nacnac)Ca{N(SiMe$_3$)$_2$}(THF)] (**5**).

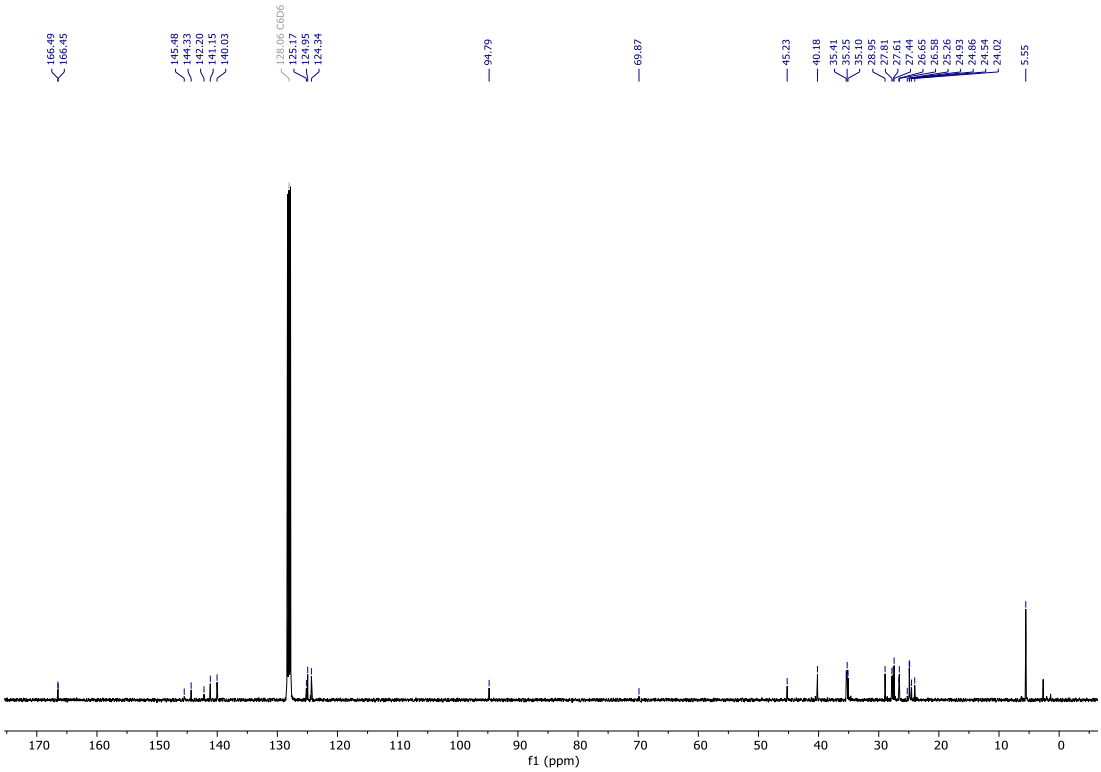

Figure S38: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K, C_6D_6) of *in situ* generated [($^{Dip/TCHP}$Nacnac)Ca{N(SiMe$_3$)$_2$}(THF)] (**5**).

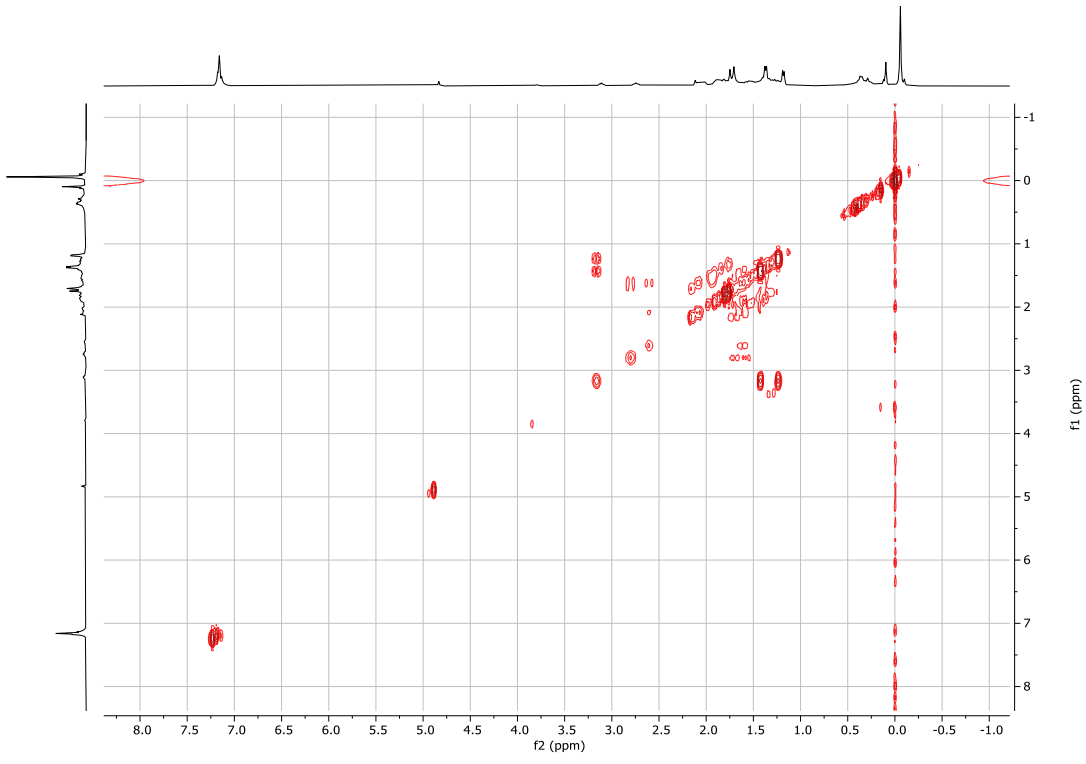

Figure S39: COSY NMR spectrum (400 MHz, 298 K, C_6D_6) of *in situ* generated [($^{Dip/TCHP}$Nacnac)Ca{N(SiMe$_3$)$_2$}(THF)] (**5**).

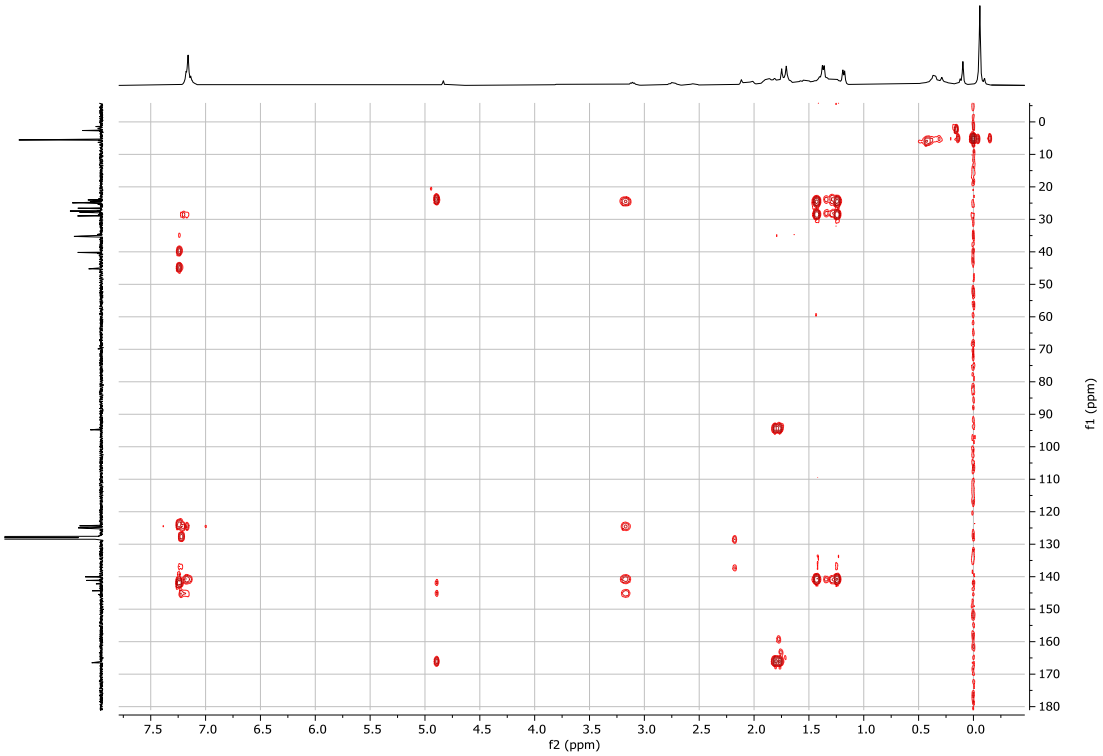

Figure S40: HMBC NMR spectrum (^{1}H: 400 MHz; ^{13}C: 101 MHz, 298 K, C_6D_6) of *in situ* generated [($^{Dip/TCHP}$Nacnac)Ca{N(SiMe$_3$)$_2$}(THF)] (**5**).

Preparation of [{($^{Dip/TCHP}$Nacnac)Sr(μ-H)}$_2$] (10).

In a *J* Young's NMR tube, [Sr($^{Dip/TCHP}$Nacnac){N(SiMe$_3$)$_2$}] (80 mg, 0.097 mmol) was dissolved in *ca.* 0.5 ml C_6D_6. A solution of phenylsilane (35.8 μl, 0.29 mmol) in *ca.* 0.5 ml hexane was carefully layered on top of the benzene solution and the mixture left at room temperature to diffuse for 2 days. The title compound deposited in the reaction vessel as colourless crystals. Yield 25 mg, 38 %. **M.p.** 188–190 °C (decomp). The compound is essentially insoluble in deuterated aromatic solvents, so meaningful NMR spectra could not be obtained. Attempted dissolution of the compound in THF-D_8 resulted in immediate decomposition to $^{Dip/TCHP}$NacnacH and other products. **IR ν/cm^{-1}** (solid): 2922 (s), 2850 (m), 1655 (w), 1620 (m), 1550 (s), 1523 (w), 1446 (s), 1407 (m), 1381(m), 1363 (m), 1321 (m), 1274 (m), 1176 (m), 1146 (w), 1106 (w), 1018 (m), 998 (m), 952 (w), 924 (w), 891 (w), 863 (m), 825 (w), 787 (m), 760 (m), 675 (s). A reproducible elemental analysis could not be obtained due to the compound persistently crystallising with trace amounts of impurities.

Preparation of [{($^{Dip/TCHP}$Nacnac)Ba(μ-H)}$_2$] (11).

In a *J* Young's NMR tube, [Ba($^{Dip/TCHP}$Nacnac){N(SiMe$_3$)$_2$}] (150 mg, 0.171 mmol) was dissolved in *ca.* 1.2 ml C_6D_6. Phenylsilane (63.3 μl, 0.512 mmol) was added neat and the reaction vessel was shaken vigorously. Over 10 minutes, deposition of the title compound as a colourless crystalline precipitate was observed. Larger crystals were obtained by layering a solution of phenylsilane in hexane on top a solution of [Ba($^{Dip/TCHP}$Nacnac){N(SiMe$_3$)$_2$}] in hexane. Yield 81 mg, 66 %. **M.p.** 151–152 °C (decomp). The compound is essentially insoluble in deuterated aromatic solvents, so meaningful NMR spectra could not be obtained. Attempted dissolution of the compound in THF-D_8 resulted in immediate decomposition to $^{Dip/TCHP}$NacnacH and other products. **IR ν/cm^{-1}** (solid): 2922 (s), 2850 (m), 1655 (w), 1620 (m), 1550 (s), 1523 (w), 1446 (s), 1407 (m), 1381(m), 1363 (m), 1321 (m), 1274 (m), 1176 (m), 1146 (w), 1106 (w), 1018 (m), 998 (m), 952 (w), 924 (w), 891 (w), 863 (m), 825 (w), 787 (m), 760 (m), 675 (s). A reproducible elemental analysis could not be obtained due to the compound persistently crystallising with trace amounts of impurities.

2. X-ray Crystallography

General Details

Crystals suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made using a Rigaku Xtalab Synergy Dualflex using a graphite monochromator with Cu Kα (1.54180 Å) or Mo Kα (0.71073 Å), or the MX1/MX2 beamlines of the Australian Synchrotron (λ = 0.71090 Å). The software package Blu-Ice[6] was used for synchrotron data acquisition, while the program XDS[7] was employed for synchrotron data reduction. All structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX-18)[8] using all unique data. Hydrogen atoms were included in calculated positions (riding model). Crystal data, details of data collections, and refinements for all structures can be found in their CIF files and are summarized in Table S1.

Notes

The crystalline specimen of [{($^{Dip/TCHP}$Nacnac)Ca(μ-H)}$_2$] used for data collection contained a small amount of [{($^{Dip/TCHP}$Nacnac)Ca(μ-OH)}$_2$] (~20 %) as a co-crystal. Attempts to obtain a pure crystalline specimen of [{($^{Dip/TCHP}$Nacnac)Ca(μ-H)}$_2$] suitable for diffraction experiments were unsuccessful.

The crystalline specimen of [{($^{Dip/TCHP}$Nacnac)Mg(μ-H)}$_2$] used for data collection was weakly diffracting using the high energy MX2 beamline at the Australian Synchrotron. Subsequent studies and attempts to obtain a higher quality diffraction dataset have been unsuccessful due to the nature of the sample. Despite this, the dataset is of sufficient quality to provide unambiguous proof for the connectivity of atoms within the molecule. This has been supplemented by further experimental and theoretical studies.

Table S1: Crystallographic Data for Compounds **1**, **2**, **6**, and **8-11**.

Compound	**1**	**2**·(hexane)$_{0.5}$	**6**	**8**·(benzene)
Empirical formula	C_{45} H_{70} Mg N_2 Si	C_{52} H_{82} Mg N_2 O	C_{51} H_{85} N_3 O Si_2 Sr	C_{82} H_{120} Mg_2 N_4
Formula weight	691.43	775.5	900.01	1210.43
Temperature	100(2) K	123(2) K	100(2) K	100(2) K
Crystal system	Monoclinic	Triclinic	Monoclinic	Orthorhombic
Space group	*P*2$_1$/*n*	*P*-1	*P*2$_1$/*c*	*P*2$_1$2$_1$2
Unit cell dimensions	a = 17.700(4) Å α= 90°.	a = 9.7784(2) Å α= 82.9490(10)°.	a = 12.680(3) Å α = 90°	a = 15.123(3) Å α= 90°.
	b = 13.920(3) Å β= 114.08(3)°.	b = 10.7675(2) Å β= 86.0100(10)°.	b = 18.660(4) Å β = 96.56(3)°	b = 14.871(3) Å β= 90°.
	c = 18.700(4) Å γ = 90°.	c = 24.1613(3) Å γ = 69.430(2)°.	c = 22.470(5) Å γ = 90°	c = 17.362(4) Å γ = 90°.
Volume	4206.5(17) Å^3	2362.76(8) Å^3	5281.8(18) Å^3	3904.6(14) Å^3
Z	4	2	4	2
Density (calculated)	1.092 Mg/m^3	1.090 Mg/m^3	1.132 Mg/m^3	1.030 Mg/m^3
Absorption coefficient	0.102 mm^{-1}	0.592 mm^{-1}	1.102 mm^{-1}	0.073 mm^{-1}
F(000)	1520	856	1944	1328
Crystal size	0.100 x 0.050 x 0.030 mm^3	0.340 x 0.250 x 0.090 mm^3	0.02 x 0.005 x 0.005 mm^3	0.010 x 0.008 x 0.004 mm^3
Theta range for data collection	1.336 to 26.370°.	3.688 to 80.421°.	1.422 to 26.020°.	1.173 to 26.381°.
Index ranges	-22<=h<=22, -17<=k<=17, -23<=l<=23	-12<=h<=12, -13<=k<=13, -30<=l<=30	-15<=h<=15, -22<=k<=22, -26<=l<=27	-18<=h<=18, -18<=k<=18, -21<=l<=21
Reflections collected	101367	48670	83908	47314
Independent reflections	8551 [R(int) = 0.0212]	10091 [R(int) = 0.0558]	10105 [R(int) = 0.4503]	7831 [R(int) = 0.2105]
Completeness to theta = 67.684°	100.00%	99.90%	98.40%	98.40%
Absorption correction	Semi-empirical from equivalents	Gaussian	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	Value not reported by XDS	1.000 and 0.324	Value not reported by XDS	Value not reported by XDS
Data / restraints / parameters	8551 / 0 / 451	10091 / 36 / 513	10105 / 0 / 535	7831 / 645 / 411
Goodness-of-fit on F2	1.024	1.055	1.037	0.837
Final R indices [I>2sigma(I)]	R_1 = 0.0383, *w*R_2 = 0.1041	R_1 = 0.0855, *w*R_2 = 0.2355	R_1 = 0.0340, *w*R_2 = 0.0819	R_1 = 0.0839, *w*R_2 = 0.2184
R indices (all data)	R_1 = 0.0403, *w*R_2 = 0.1057	R_1 = 0.0942, *w*R_2 = 0.2447	R_1 = 0.0525, *w*R_2 = 0.0890	R_1 = 0.1882, *w*R_2 = 0.2935
Largest diff. peak and hole	0.331 and -0.377 e.Å^{-3}	0.857 and -0.624 e.Å^{-3}	1.050 and -1.141 e.Å^{-3}	0.282 and -0.169 e.Å^{-3}
CCDC Number	2378882	2378884	2378883	2378881

Table S1 (contd.): Crystallographic Data for Compounds **1**, **2**, **6**, and **8-11**.

Compound	**9**·(benzene)$_3$		**10**·(benzene)$_3$		**11**·(benzene)$_3$	
Empirical formula	C_{100} H_{138} Ca_2 N_4 $O_{0.40}$		C_{100} H_{138} N_4 Sr_2		C_{100} H_{138} Ba_2 N_4	
Formula weight	1482.7		1571.38		1670.82	
Temperature	123.00(10) K		100(2) K		100(2) K	
Crystal system	Triclinic		Triclinic		Triclinic	
Space group	P-1		P-1		P-1	
Unit cell dimensions	a = 12.5680(2) Å	α = 106.3540(10)°	a = 12.450(3) Å	α = 106.13(3)°	a = 12.440(3) Å	α = 105.02(3)°
	b = 14.4876(2) Å	β = 102.1740(10)°	b = 14.510(3) Å	β = 102.37(3)°	b = 14.610(3) Å	β = 113.64(3)°
	c = 14.5826(2) Å	γ = 113.558(2)°	c = 14.600(3) Å	γ = 112.91(3)°	c = 14.740(3) Å	γ = 102.69(3)°
Volume	2171.82(6) Å^3		2173.4(10) Å^3		2206.3(10) Å^3	
Z	1		1		1	
Density (calculated)	1.134 Mg/m^3		1.201 Mg/m^3		1.258 Mg/m^3	
Absorption coefficient	1.496 mm^{-1}		1.275 mm^{-1}		0.934 mm^{-1}	
F(000)	809		842		878	
Crystal size	0.230 x 0.190 x 0.150 mm^3		0.009 x 0.006 x 0.004 mm^3		0.01 x 0.005 x 0.003 mm^3	
Theta range for data collection	6.392 to 79.796°.		1.559 to 26.372°.		1.550 to 26.372°.	
Index ranges	-16<=h<=14, -18<=k<=16, -17<=l<=18		-15<=h<=15, -18<=k<=18, -18<=l<=18		-15<=h<=15, -18<=k<=18, -18<=l<=18	
Reflections collected	27837		55314		54985	
Independent reflections	8957 [R(int) = 0.0280]		8883 [R(int) = 0.0979]		8895 [R(int) = 0.0439]	
Completeness to theta = 67.684°	98.40%		99.70%		98.30%	
Absorption correction	Semi-empirical from equivalents		Semi-empirical from equivalents		Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.72669		Value not reported by XDS		Value not reported by XDS	
Data / restraints / parameters	8957 / 1 / 500		8883 / 12 / 488		8895 / 342 / 542	
Goodness-of-fit on F^2	1.094		1.036		1.052	
Final R indices [I>2sigma(I)]	R_1 = 0.0429, wR_2 = 0.1189		R_1 = 0.0715, wR_2 = 0.2004		R_1 = 0.0637, wR_2 = 0.1737	
R indices (all data)	R_1 = 0.0441, wR_2 = 0.1200		R_1 = 0.0763, wR_2 = 0.2060		R_1 = 0.0648, wR_2 = 0.1748	
Largest diff. peak and hole	0.573 and -0.427 e.Å^{-3}		1.683 and -0.834 e.Å^{-3}		3.007 and -1.318 e.Å^{-3}	
CCDC Number	2378885		2378880		2378886	

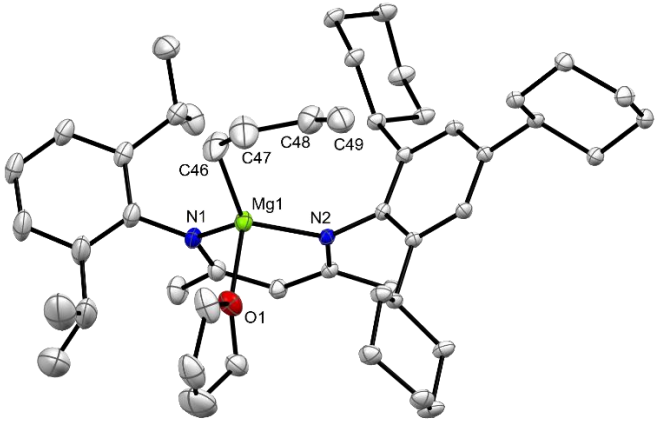

Figure S41. Molecular structure (20% thermal ellipsoids) of compound **2**.

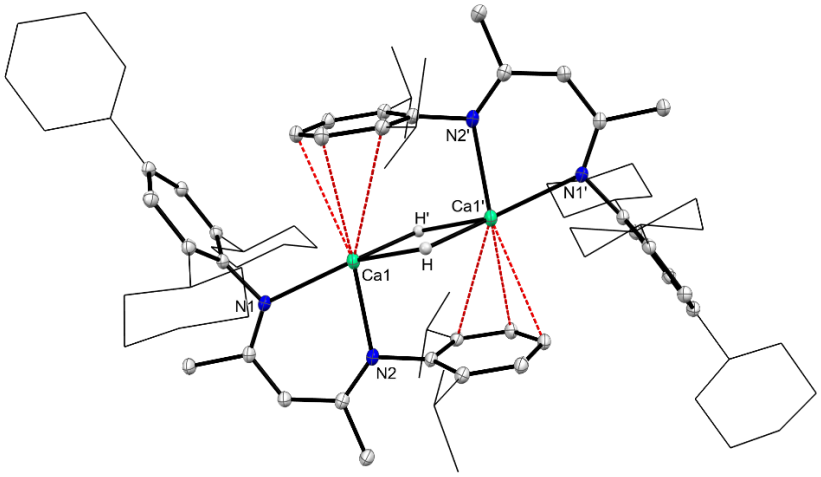

Figure S42. Molecular structure (20% thermal ellipsoids) of compound **9** (cyclohexyl and isopropyl groups shown as wireframe).

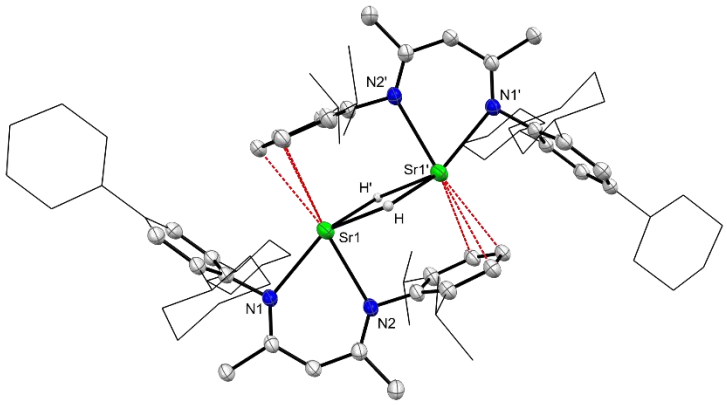

Figure S43. Molecular structure (20% thermal ellipsoids) of compound **10** (cyclohexyl and isopropyl groups shown as wireframe).

3. Computational

General Details

DFT calculations were run using Gaussian 09 (Revision D.01)[9] using the B3PW91 functional and an ultrafine integration grid (keyword int=ultrafine).[10-14] Geometry optimisation and frequency calculations were carried out using BS1, while single point frequency calculations were then carried out at BS2 to obtain the final free energies.[15] Geometry optimisations were performed without symmetry constraints (keyword = nosymm). Frequency analyses for all stationary points were performed to confirm the nature of the structures as minima (no imaginary frequency). Single point solvent corrections (benzene, epsilon = 2.2706) were applied using the polarised continuum model (PCM) to free energies.[16] Single-point dispersion corrections using Grimme's D3 correction were applied to free energies, with Becke-Johnson damping applied for the B3PW91 functional (keyword = gd3bj).[17,18] Gaussview 5.0.9 was used to visualise the various properties of compound **8**.[19]

BS1 was built as follows. Mg centres were described with Stuttgart SDDAll RECPs and associated basis sets, while 6-31g**was used for all other atoms (C, H, N).[20-22]

BS2 was built as follows. Mg centres were described with Stuttgart SDDAll RECPs and associated basis sets, while def2-SVP was used for all other atoms (C, H, N).[23]

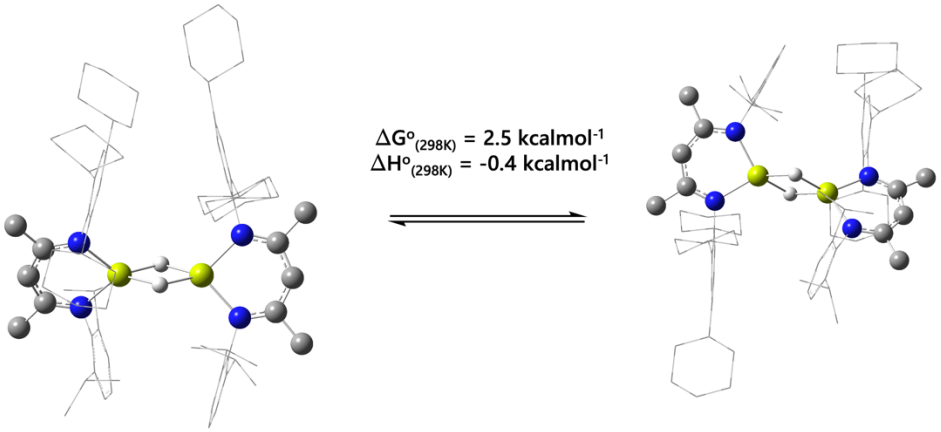

Figure S44: Equilibrium for *syn*- and *anti*-configurations of magnesium hydride complex **8** (B3PW91). Structures of all stationary point minima as calculated by DFT (grey = carbon, white = hydrogen, blue = nitrogen, yellow = magnesium). Most hydrogen atoms omitted and diisopropylphenyl/tricyclohexylphenyl units shown in wireframe for clarity.

Table S2. Cartesian coordinates for the optimised *syn*- and *anti*-configurations of **8**.

anti.log
SCF (B3PW91) = -3416.80929763
E(SCF)+ZPE(0 K)= -3414.950343
H(298 K)= -3414.856454
G(298 K)= -3415.088031
Lowest Frequency = 7.3099 cm^{-1}

Mg	8.053219	9.182894	4.069302
N	9.430824	10.063586	2.734774
N	8.514586	10.527316	5.611474
C	10.641230	8.497577	1.268645
C	11.516020	8.033243	2.421957
H	11.144798	8.512761	3.335617
C	9.664599	9.509844	1.430308
C	10.146285	11.778487	4.310524
H	10.819285	12.623863	4.386678
C	9.220214	9.429055	-0.944267
H	8.677893	9.800512	-1.811428
C	8.963431	10.000598	0.306881
C	6.680047	11.162603	7.128415
C	10.174159	8.429243	-1.134693
C	8.350432	12.303076	-0.585093
H	9.398415	12.603870	-0.469007
H	8.254694	11.927332	-1.612994
C	10.805707	5.936000	-4.079840
H	9.990175	6.259746	-4.742874
H	10.828067	4.840531	-4.129470
C	8.004425	11.175069	0.408524
H	8.098398	11.593342	1.418458
C	11.464378	6.513643	2.656159
H	10.426903	6.207504	2.827652
H	11.804392	5.988888	1.752042
C	10.160915	11.135599	3.061739
C	6.016937	12.012387	6.053087
H	6.598511	11.889617	5.133898
C	6.533628	10.765954	0.226278
H	6.404587	10.316435	-0.766830
H	6.264773	9.983896	0.945343
C	11.824131	8.502517	-3.042595
H	12.631464	8.181553	-2.368798
H	11.793069	9.597257	-2.987382
C	12.346011	6.100676	3.838760
H	12.308896	5.013595	3.975646
H	11.938122	6.541067	4.759569
C	7.876049	10.446402	6.892915
C	12.981194	8.482661	2.235014
H	13.027860	9.568366	2.097083
H	13.376335	8.037301	1.310767
C	7.423309	13.508630	-0.415682
H	7.687906	14.290972	-1.137841
H	7.571014	13.944061	0.583354
C	13.863691	8.067423	3.414215
H	14.899916	8.380458	3.235548
H	13.530103	8.597298	4.318107
C	10.501823	6.389539	-2.649124
H	9.540475	5.983216	-2.314869
H	11.263521	5.975233	-1.974125
C	10.490677	7.922784	-2.528666
H	9.698669	8.294739	-3.196892

C	9.420220	11.503827	5.478782
C	10.873845	7.984809	-0.010566
H	11.644511	7.226939	-0.130974
C	8.480174	9.691384	7.925450
C	5.592035	11.963911	0.374745
H	5.638205	12.333022	1.409717
H	4.557825	11.642906	0.207772
C	12.126616	6.519781	-4.586098
H	12.954641	6.106799	-3.991911
H	12.306350	6.214476	-5.624097
C	12.136437	8.045577	-4.469729
H	11.385235	8.464480	-5.155019
H	13.105436	8.447811	-4.789766
C	13.793832	6.559824	3.659114
H	14.393883	6.285468	4.535481
H	14.236733	6.033536	2.800907
C	11.079053	11.782783	2.043298
H	11.865499	12.353297	2.540739
H	10.504536	12.480576	1.423952
H	11.534897	11.059252	1.367285
C	4.586596	11.542218	5.763089
H	4.572603	10.489824	5.468556
H	4.150416	12.129621	4.947749
H	3.939080	11.663305	6.638542
C	5.957558	13.102866	-0.578841
H	5.300186	13.965561	-0.414549
H	5.789329	12.775463	-1.615210
C	9.752527	12.394531	6.659524
H	8.855259	12.790447	7.139198
H	10.387486	13.226911	6.352788
H	10.285594	11.823469	7.427467
C	6.021400	13.506642	6.410987
H	5.562972	14.091917	5.606108
H	7.034155	13.890222	6.565402
H	5.449746	13.698851	7.325923
C	6.695312	10.372086	9.427540
H	6.242365	10.351415	10.415238
C	6.114628	11.115031	8.407300
H	5.206846	11.679279	8.606710
C	7.863142	9.658996	9.178998
H	8.315163	9.083202	9.981268
C	9.788476	8.948110	7.692252
C	10.745734	9.021038	8.888444
H	11.718688	8.598934	8.615359
H	10.377497	8.448472	9.746675
H	10.905090	10.052166	9.221090
C	9.532189	7.488288	7.297474
H	10.477531	6.957089	7.138654
H	8.950567	7.408071	6.373621
H	8.973221	6.961921	8.076260
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syn.log
SCF (B3PW91) = -3416.80852138
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G(298 K)= -3415.090424
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