Supplementary Information

for

Synthesis of heteroleptic calcium amide complexes *via* manipulation of the Schlenk equilibrium

Matthew de Vere-Tucker, Alexandra M. Z. Slawin, David B. Cordes and Andreas Stasch*

Contents:

Contents 1
1. Experimental 2
1.1: General considerations 2
1.2: Synthetic procedures incl. NMR spectra 3
2. X-ray structures 17
2.1: General considerations 17
3. DFT computational studies 25
3.1: General considerations 25
3.2: Atomic coordinates 26
4. References 42

1. Experimental

1.1: General considerations

All manipulations were carried out using standard Schlenk line and glove box techniques under an atmosphere of high purity dinitrogen or argon, respectively. Benzene, toluene, *n*-hexane, *n*-pentane and THF were either dried and distilled under inert gas over $LiAlH_4$, sodium, or taken from an MBraun solvent purification system and degassed prior to use. ^{1}H, $^{13}C\{^{1}H\}$, ^{2}H and $^{29}Si\{^{1}H\}$ NMR spectra were recorded on a Bruker AVII 400 or Bruker AV III 500 spectrometer in C_6D_6, or where specified, C_6D_6 with a drop of THF-d_8 added, and were referenced to the residual ^{1}H or $^{13}C\{^{1}H\}$ NMR resonances of the solvent used. It is noted that the ^{2}H NMR spectra were performed unlocked. Melting points were determined in sealed glass capillaries under argon and are uncorrected. Elemental analyses were performed by the Elemental Analysis Service at London Metropolitan University. The elemental analyses were affected by the highly air and moisture sensitive nature of the compounds. $^{i\text{PrDip}}$BDIH ((HC(*i*PrCNDip)$_2$H); Dip = 2,6-diisopropylphenyl),[1,2] benzylpotassium (K(Bzl), $PhCH_2K$),[3] $Ca(HMDS)_2$ (HMDS = hexamethyldisilazide, $N(SiMe_3)_2$)[4] and [{($^{\text{MeDip}}$BDI)CaH}$_2$][5] were all synthesised *via* established literature methods.

1.2: Synthetic procedures

Synthesis of [($^{i\text{PrDip}}$BDI)K] **6**

Method A: To a J Young NMR tube charged with a C_6D_6 (0.55 ml) solution of $^{i\text{PrDip}}$BDIH (20 mg, 4.2 μmol, 1 equiv.) was added benzyl potassium (11.0 mg, 8.4 μmol, 2 equiv.). *Via* ^{1}H NMR spectroscopy, complete conversion to [($^{i\text{PrDip}}$BDI)K] **6** was observed after 1 hour at room temperature. ^{1}H NMR (499.9 MHz, C_6D_6) δ = 7.15 – 7.12 (m, 4H, Ar*H*), 7.03–6.98 (m, 2H, Ar*H*), 4.65 (s, 1H, NCC*H*), 3.39 (sept, J = 6.9 Hz, 4H, ArC*H*(CH_3)$_2$), 2.56 (sept, J = 6.7 Hz, 2H, NCC*H*(CH_3)$_2$), 1.28 (d, J = 6.9 Hz, 24H, ArCH(C*H*$_3$)$_2$), 1.01 (d, J = 6.8 Hz, 12H, NCCH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (125.7 MHz, C_6D_6) δ = 176.6 (N*C*CH(CH_3)$_2$), 149.8 (Ar*C*), 139.6 (Ar*C*), 124.1 (Ar*C*), 120.8 (Ar*C*), 80.4 (NC*C*H), 33.5 (NC*C*H(CH_3)$_2$), 27.0 (ArCH(*C*H$_3$)$_2$), 25.4 (ArCH(*C*H$_3$)$_2$), 24.1 (ArCH(*C*H$_3$)$_2$), 23.6 (NCCH(*C*H$_3$)$_2$) ppm. *Method B*: To a stirred toluene (40 ml) slurry of benzylpotassium (0.302 g, 2.32 mmol, 1.1 equiv.) was added $^{i\text{PrDip}}$BDIH (1.00 g, 2.106 mmol, 1 equiv.) and the bright orange reaction mixture was stirred at room temperature for 1 hour. The resultant brown solution was allowed to settle, filtered and the solvent was removed *in vacuo*. The solid residue was washed with hexane (*ca.* 5 ml) and dried to give a pale brown solid which analysis *via* ^{1}H NMR spectroscopy shows to be [($^{i\text{PrDip}}$BDI)K] **6** in yield of 997.3 mg (92%). Note: Complex **6** shows very high solubility in aromatic solvents but is almost insoluble in aliphatic solvents and could, so far, not be crystallised. Elemental analysis for $C_{33}H_{49}KN_2$ (%): calc. C: 77.28, H 9.63, N: 5.46, found: C: 73.47, H: 9.65, N: 4.94 (please note: KOH + $^{i\text{PrDip}}$BDIH calc. C: 74.66, H: 9.68, N: 5.28).

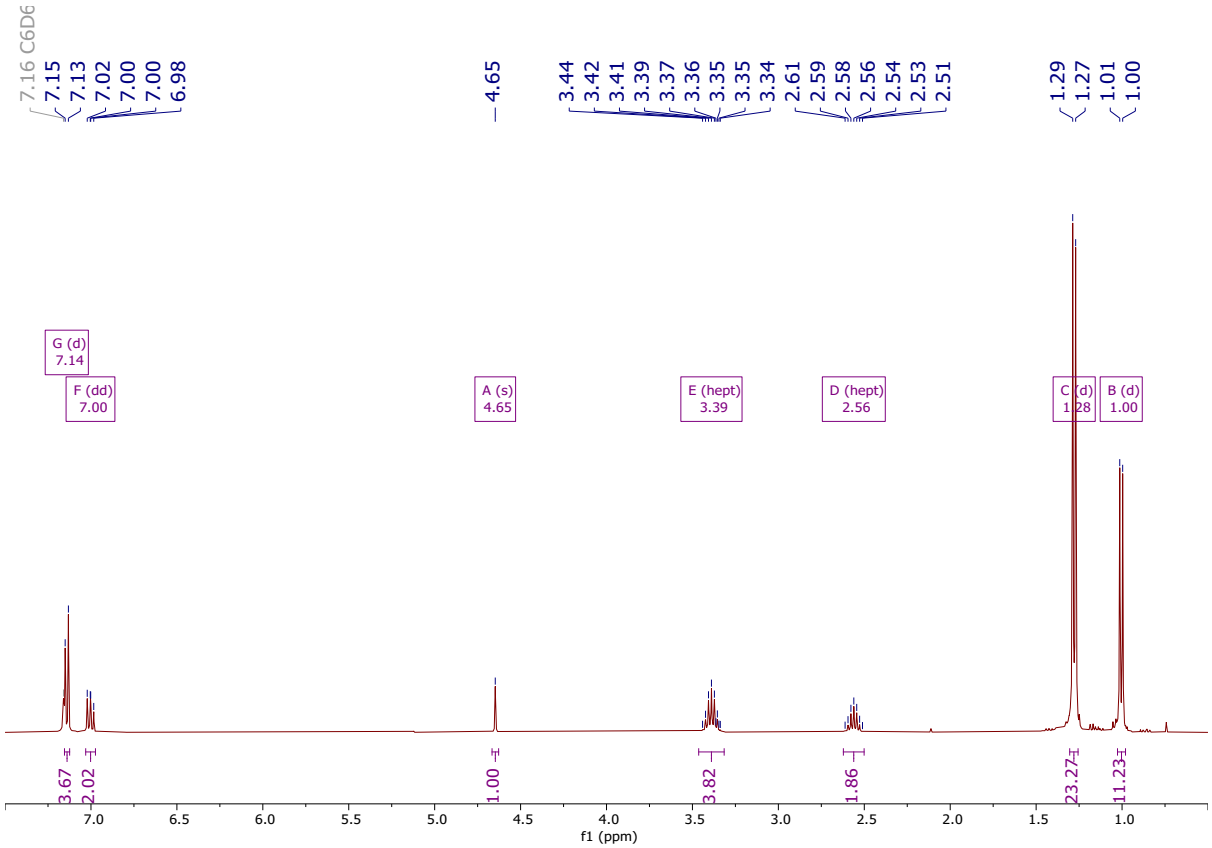

Figure S1: ^{1}H NMR spectrum (499.9 MHz, C_6D_6, 298 K) of [($^{i\text{PrDip}}$BDI)K] **6**.

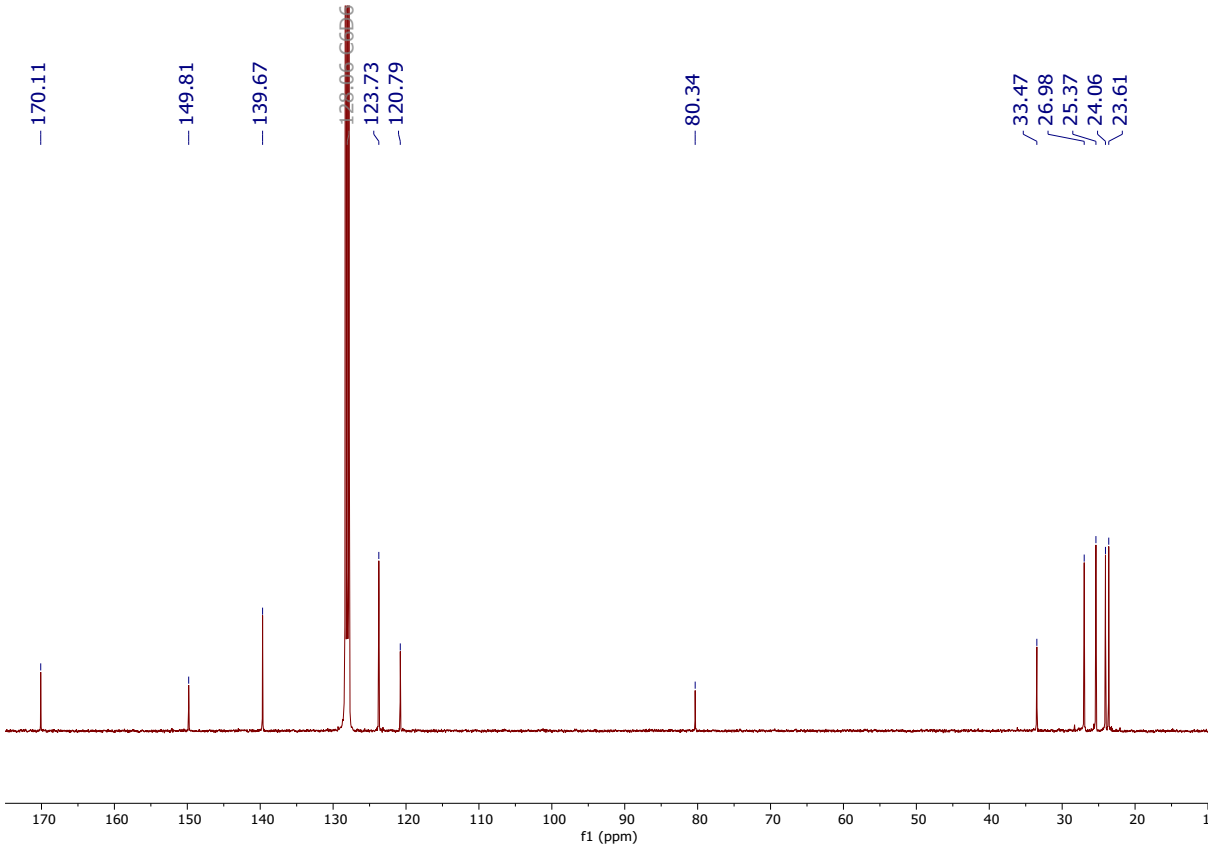

Figure S2: ^{13}C{^{1}H} NMR spectrum (125.7 MHz, 298 K, C_6D_6) of [($^{i\text{PrDip}}$BDI)K] **6**.

Optimised synthesis of [($^{i\text{PrDip}}$BDI)$_2$Ca] **7**

Note: several sets of conditions were probed for the synthesis of **7**, with the best isolated yield found with the below conditions.

To a stirred slurry of CaI_2 (198.7 mg, 68 μmol, 1 equiv.) in Et_2O (10 ml) was added a Et_2O (10 ml) solution of [($^{i\text{PrDip}}$BDI)K] **6** (350 mg, 68 μmol, 1 equiv.) at -78 °C. With stirring, the resultant yellow suspension was allowed to warm to room temperature overnight. The suspension was then filtered, and the filtrate was concentrated and stored at -40 °C to yield large colourless crystals, which were revealed *via* X-ray crystallography to be [($^{i\text{PrDip}}$BDI)$_2$Ca] **7**. Over three crops, 130.8 mg (39%) yield was obtained. ^{1}H NMR (499.9 MHz, C_6D_6) δ = 7.20 (d, *J* = 2.0 Hz, 1H, Ar*H*), 7.19 (d, *J* = 2.0 Hz, 1H, Ar*H*), 7.15 (s, 1H, Ar*H*), 7.14–7.12 (m, 2H, Ar*H*), 7.00–6.93 (m, 5H, Ar*H*), 4.94 (s, 1H, NCC*H*), 3.26 (q, *J* = 7.0 Hz, 1H, (C*H*$_3$CH$_2$)$_2$O), 3.16 (sept, *J* = 6.6 Hz, 1H, ArC*H*(CH$_3$)$_2$), 3.10 (sept, *J* = 6.8 Hz, 1H, ArC*H*(CH$_3$)$_2$), 2.93 (sept, *J* = 6.7 Hz, 1H, ArC*H*(CH$_3$)$_2$), 2.77 (sept, *J* = 6.7 Hz, 1H, ArC*H*(CH$_3$)$_2$), 2.67 (sept, *J* = 6.6 Hz, 1H, NCC*H*(CH$_3$)$_2$), 2.58 (sept, *J* = 6.6 Hz, 1H, NCC*H*(CH$_3$)$_2$), 1.53 (d, *J* = 6.6 Hz, 2H, ArCH(C*H*$_3$)$_2$), 1.28 (d, *J* = 6.5 Hz, 2H, ArCH(C*H*$_3$)$_2$), 1.24 (d, *J* = 6.8 Hz, 3H, ArCH(C*H*$_3$)$_2$), 1.21 (d, *J* = 6.7 Hz, 3H, ArCH(C*H*$_3$)$_2$), 1.18 (d, *J* = 6.7 Hz, 3H, ArCH(C*H*$_3$)$_2$), 1.13 (d, *J* = 6.8 Hz, 3H, ArCH(C*H*$_3$)$_2$), 1.09 (d, *J* = 6.8 Hz, 3H, ArCH(C*H*$_3$)$_2$), 1.06 (d, *J* = 6.7 Hz, 3H, ArCH(C*H*$_3$)$_2$), 1.03 (d, *J* = 6.6 Hz, 3H, ArCH(C*H*$_3$)$_2$), 0.70 (d, *J* = 6.6 Hz, 3H), 0.39 (d, *J* = 6.8 Hz, 3H, NCCH(C*H*$_3$)$_2$), 0.26 (d, *J* = 6.8 Hz, 3H, NCCH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (125.7 MHz, C_6D_6) δ = 178.58 (N*C*CH(CH$_3$)$_2$), 176.54 (N*C*CH(CH$_3$)$_2$), 149.13 (Ar*C*), 144.95 (Ar*C*), 144.36 (Ar*C*), 142.96 (Ar*C*), 141.27 (Ar*C*), 140.89 (Ar*C*), 125.03 (Ar*C*), 124.76 (Ar*C*), 124.33 (Ar*C*), 124.29 (Ar*C*), 123.92 (Ar*C*), 123.86 (Ar*C*), 80.41 (NC*C*H), 34.16 (NC*C*H(CH$_3$)$_2$), 33.37 (NC*C*H(CH$_3$)$_2$), 28.38, 28.06, 27.75, 27.54, 26.95, 26.63, 26.29, 25.84, 25.61, 25.17, 24.37, 23.90, 23.63, 23.26, 22.06, 19.92 (All Ar*C*H(CH$_3$)$_2$, ArCH(*C*H$_3$)$_2$, NC*C*H(CH$_3$)$_2$ or NCCH(*C*H$_3$)$_2$).

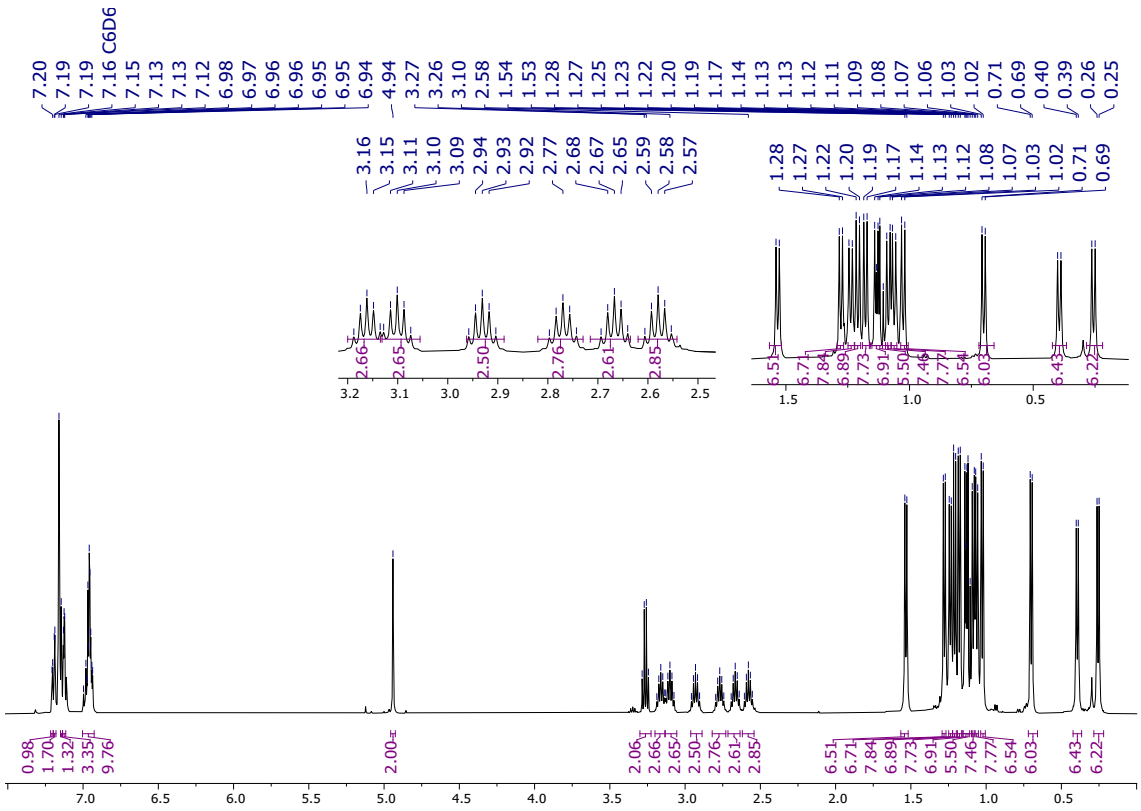

Figure S3: ^{1}H NMR spectrum (499.9 MHz, C_6D_6, 298 K) of [($^{i\text{PrDip}}$BDI)$_2$Ca] **7** with Et_2O impurity, with insets showing isopropyl methine and CH_3 regions.

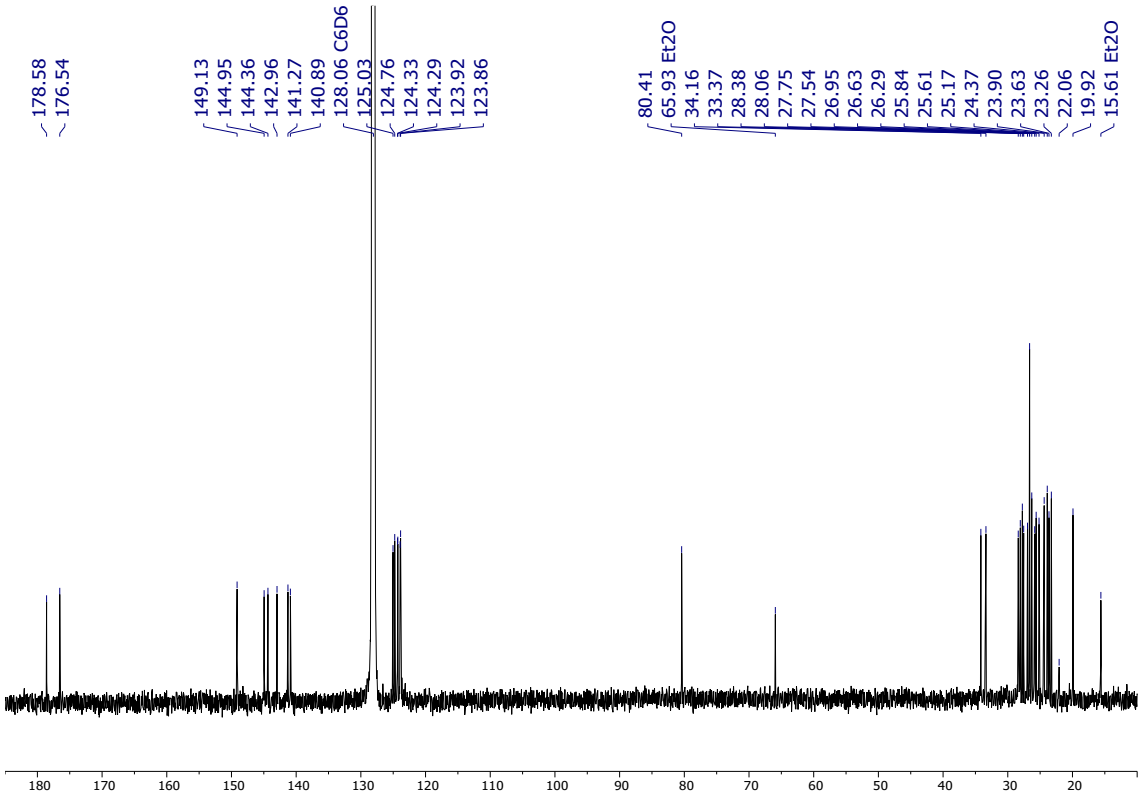

Figure S4: ^{13}C{^{1}H} NMR spectrum (125.7 MHz, 298 K, C_6D_6) of [($^{i\text{PrDip}}$BDI)$_2$Ca] **7**.

Synthesis of [(*i*PrDipBDI)Ca(HMDS)] **5**

Method A: A J Young NMR tube was charged with [(*i*PrDipBDI)$_2$Ca] **7** (16 mg, 16.2 μmol, 1 equiv.) and CaHMDS$_2$ (5.9 mg, 16.2 μmol, 1 equiv.) This mixture was dissolved in C_6D_6 (0.55 ml) and heated to 100 °C. *Via* ^{1}H NMR spectroscopy, complete conversion to [(*i*PrDipBDI)Ca(HMDS)] **5** was observed after 16 hours at 100 °C. ^{1}H NMR (499.9 MHz, C_6D_6) δ = 7.13 – 7.08 (m, 6H, Ar*H*), 4.86 (s, 1H, NCC*H*), 3.01 (sept, *J* = 6.7 Hz, 4H, ArC*H*(CH$_3$)$_2$), 2.62 (sept, *J* = 13.1, 6.6 Hz, 2H, NCC*H*(CH$_3$)$_2$), 1.32 (d, *J* = 6.9 Hz, 12H, ArCH(C*H*$_3$)$_2$), 1.26 (d, *J* = 6.8 Hz, 12H, ArCH(C*H*$_3$)$_2$), 0.97 (d, *J* = 6.7 Hz, 12H, NCCH(C*H*$_3$)$_2$), 0.11 (s, 18H, N(Si(C*H*$_3$)$_3$)$_2$). ^{13}C{^{1}H} NMR (125.7 MHz, C_6D_6) δ = 176.5 (N*C*CH(CH$_3$)$_2$), 144.2 (Ar*C*), 140.9 (Ar*C*), 124.8 (Ar*C*), 124.1 (Ar*C*), 77.4 (NC*C*H), 32.8 (NC*C*H(CH$_3$)$_2$), 28.5 (ArCH(*C*H$_3$)$_2$), 26.7 (ArCH(*C*H$_3$)$_2$), 23.9 (ArCH(*C*H$_3$)$_2$), 22.5 (NCCH(*C*H$_3$)$_2$), 5.2 (N(Si(*C*H$_3$)$_3$)$_2$).

Method B: Toluene (40 ml) was added to a J Young Schlenk flask charged with [*i*PrDipBDIK] (**6**) (761.7 mg, 1.48 mmol, 2 equiv.), finely ground CaI$_2$ (432.6 mg, 1.48 mmol, 2 equiv.) and CaHMDS$_2$ (266.4 mg, 0.74 mmol, 1 equiv.) to give a dark brown slurry. The slurry was sonicated for 2 minutes to give a bright yellow suspension. The mixture was then vigorously stirred for four days at 100 °C to give a light brown solution and a pale brown precipitate. The solution was isolated *via* filtration, all volatiles were removed, and the residue was dried *in vacuo* to afford a brown solid. The product was then extracted into hexane (2 x 20 ml) to give a brown solution, and the solvent was removed *in vacuo* to afford [(*i*PrDipBDI)Ca(HMDS)] **5** as a pale brown solid, as confirmed *via* ^{1}H NMR spectroscopy (as above), in a yield of 852.9 mg (85%). Elemental analysis for $C_{39}H_{67}CaN_3Si_2$ (%): calc.: C: 69.48, H: 10.02, N: 6.23, found: C: 68.79, H: 10.27, N: 6.03.

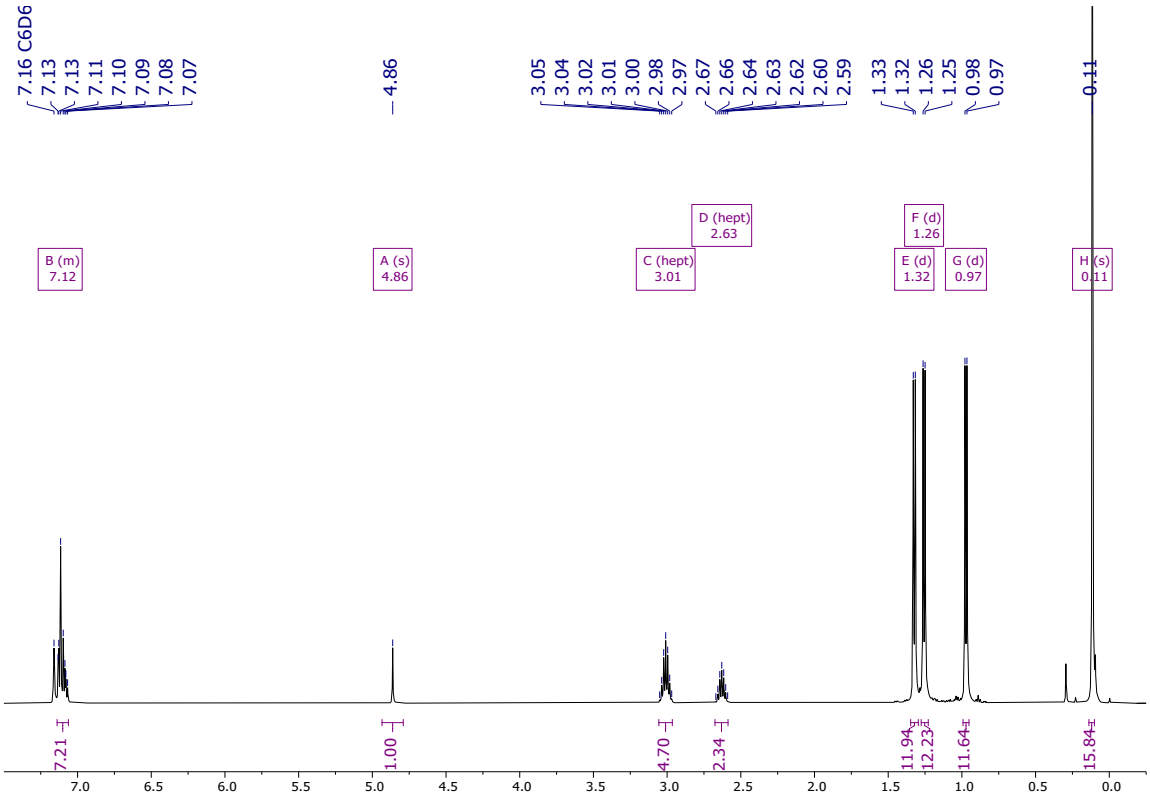

Figure S5: ^{1}H NMR spectrum (499.9 MHz, C_6D_6, 298 K) of [($^{i\text{PrDip}}$BDI)Ca(HMDS)] **5**.

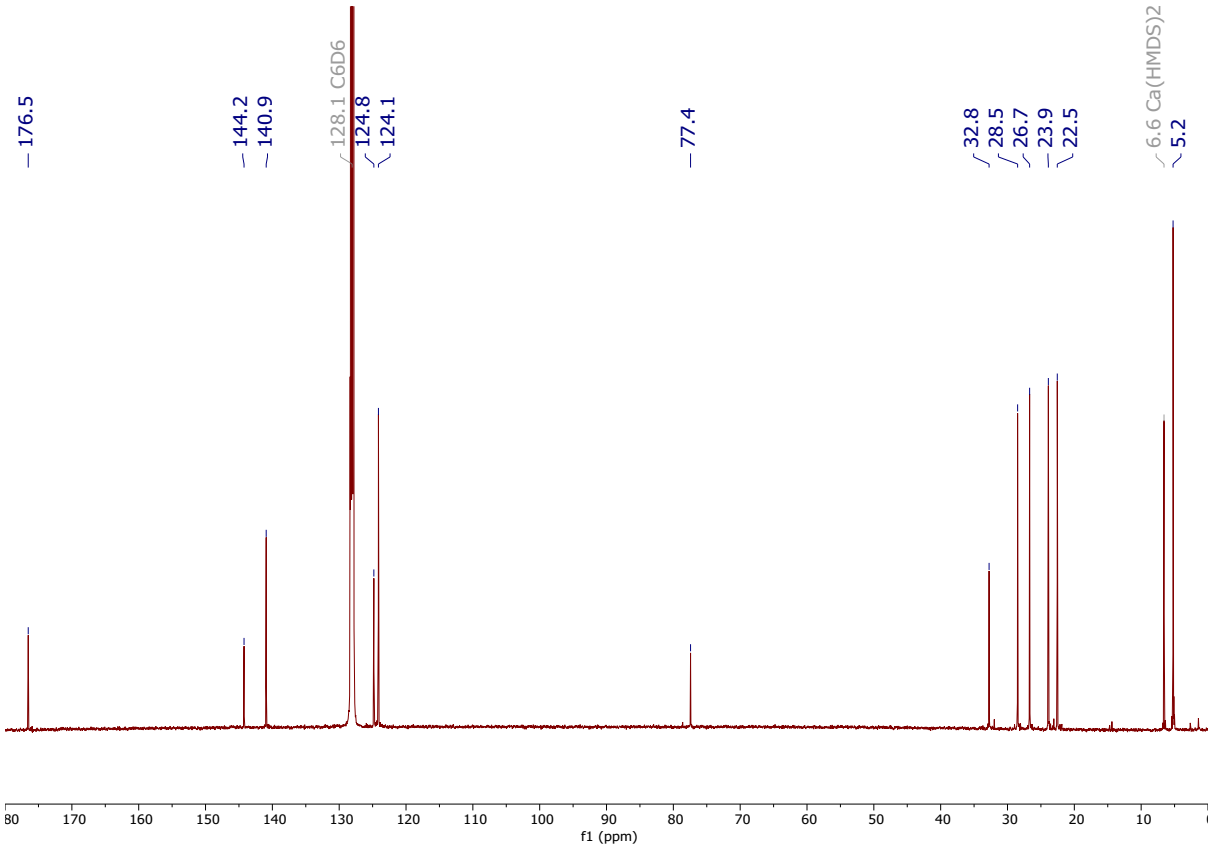

Figure S6: ^{13}C{^{1}H} NMR spectrum (125.7 MHz, 298 K, C_6D_6) of [($^{i\text{PrDip}}$BDI)Ca(HMDS)] **5** with a $CaHMDS_2$ impurity.

Synthesis of [(*i*PrDipBDI)Ca(HMDS)(OEt$_2$)] **8**

To a flask charged with [(*i*PrDipBDI)Ca(HMDS)] **5** (400 mg, 0.59 mmol, 1 equiv.) was added Et$_2$O (20 ml). The sample was concentrated *in vacuo* and stored at -40 °C to yield large colourless crystals of [(*i*PrDipBDI)Ca(HMDS)(OEt$_2$)] **8**, as confirmed *via* X-ray crystallography. ^{1}H NMR (400.1 MHz, C_6D_6) δ = 7.15–7.06 (m, 6H, Ar*H*), 4.87 (s, 1H, NCC*H*), 3.27 (q, *J* = 7.0 Hz, 4H, (CH_3CH_2)$_2$O), 3.09 (sept, *J* = 6.8 Hz, 4H, ArC*H*(CH_3)$_2$), 2.61 (sept, *J* = 6.7 Hz, 2H, NCC*H*(CH_3)$_2$), 1.34 (d, *J* = 6.9 Hz, 12H, ArCH(C*H*$_3$)$_2$), 1.26 (d, *J* = 6.8 Hz, 12H, ArCH(C*H*$_3$)$_2$), 1.00 (d, *J* = 6.6 Hz, 12H, NCCH(C*H*$_3$)$_2$), 0.98 (t, *J* = 7.0 Hz, 6H, (C*H*$_3$CH$_2$)$_2$O), 0.13 (s, 18H, N(Si(C*H*$_3$)$_3$)$_2$). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6) δ = 176.4 (N*C*CH(CH_3)$_2$), 144.9 (Ar*C*), 141.4 (Ar*C*), 124.8 (Ar*C*), 124.3 (Ar*C*), 80.0 (NC*C*H), 65.6 ((CH_3*C*H$_2$)$_2$O), 32.8 (NC*C*H(CH_3)$_2$), 28.2 (Ar*C*H(CH_3)$_2$), 26.7 (ArCH(*C*H$_3$)$_2$), 24.3 (ArCH(*C*H$_3$)$_2$), 22.9 (NCCH(*C*H$_3$)$_2$), 14.9 ((*C*H$_3$CH$_2$)$_2$O), 5.6 (N(Si(*C*H$_3$)$_3$)$_2$).

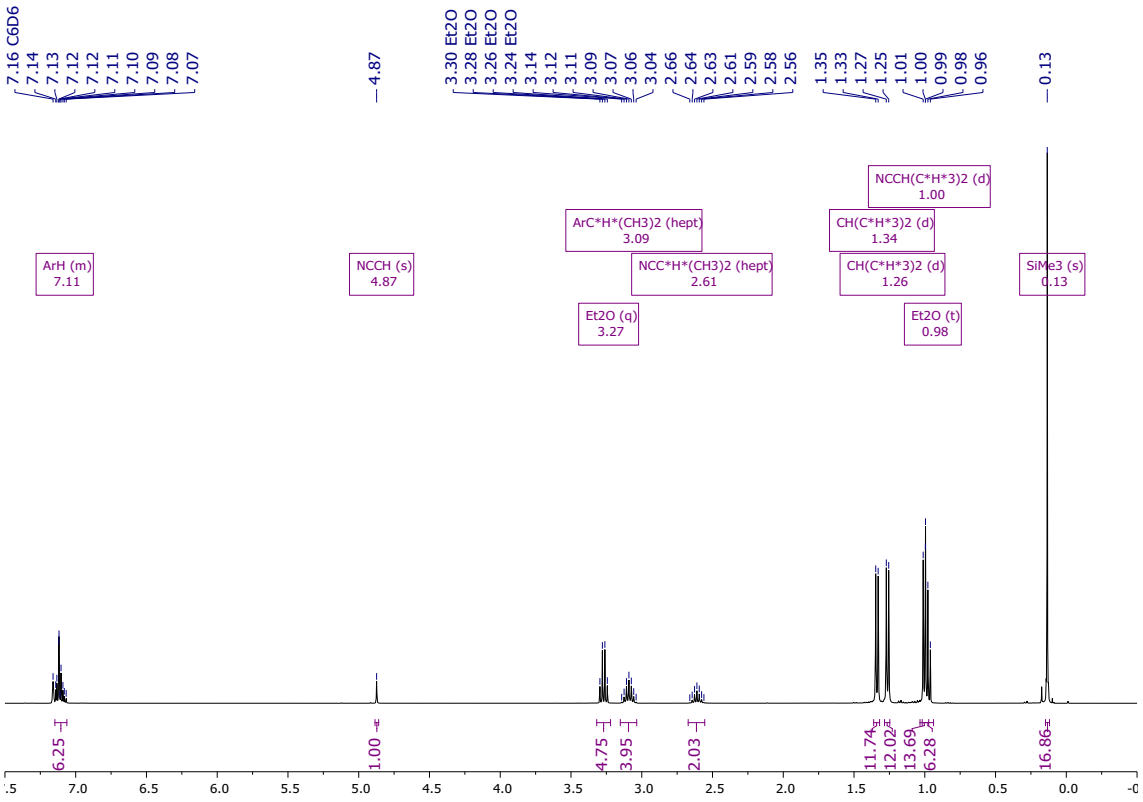

Figure S7: ^{1}H NMR spectrum (499.9 MHz, C_6D_6, 298 K) of [(^{i}PrDipBDI)Ca(HMDS)(OEt$_2$)] **8**.

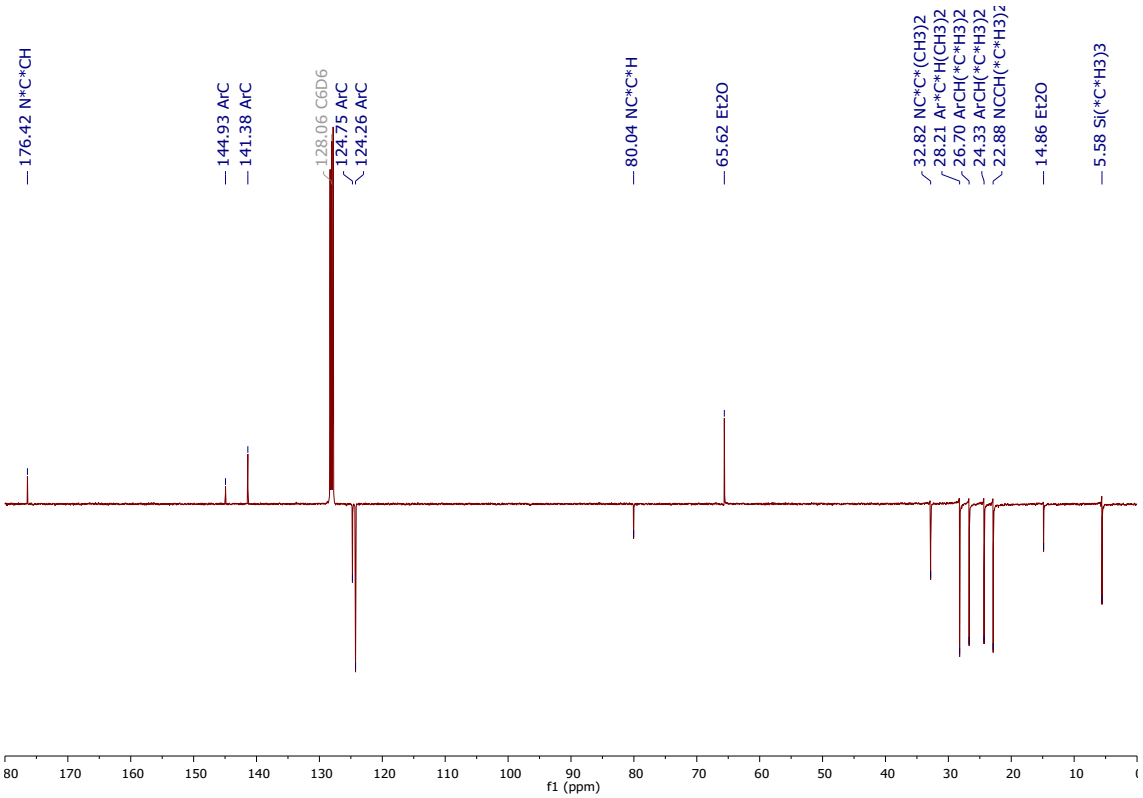

Figure S8: DEPTQ ^{13}C{^{1}H} NMR spectrum (125.7 MHz, 298 K, C_6D_6) of [(^{i}PrDipBDI)Ca(HMDS)(OEt$_2$)] **8**.

Treatment of [(^{i}PrDipBDI)$_2$Ca] **7** with CaH_2

To a J Young NMR tube charged with a C_6D_6 (0.4 ml) solution of [(^{i}PrDipBDI)$_2$Ca] **7** (17.1 mg, 17.3 µmol, 1 equiv.) was added finely ground CaH_2 (7.3 mg, 173 µmol, 10 equiv.), no reaction was observed after heating to 100 °C for over 7 days.

Synthesis of [{(^{i}PrDipBDI)CaH}$_2$] **9**

Method A: Phenylsilane (11.9 µl, 9.7 µmol, 3 equiv.) was added *via* a micropipette to a J Young NMR tube charged with a C_6D_6 (0.55 ml) solution of [(^{i}PrDipBDI)Ca(HMDS)] **5** (21.8 mg, 3.2 µmol, 1 equiv.). *Via* ^{1}H NMR spectroscopy, complete conversion to [{(^{i}PrDipBDI)CaH}$_2$] **9** alongside the expected by-product $PhSiH_2$(HMDS) was observed after 12 hours at room temperature. ^{1}H NMR (499.9 MHz, C_6D_6) δ = 7.22–7.17 (m, 3H, Ar*H*), 7.15–7.04 (m, 3H, Ar*H*), 4.79 (s, 1H, NCC*H*), 4.29 (br s, 1H, Ca*H*), 3.09 (sept, *J* = 6.8 Hz, 4H, ArC*H*(CH_3)$_2$), 2.42 (sept, *J* = 6.7 Hz, 2H, NCC*H*(CH_3)$_2$), 1.19 (d, *J* = 6.9 Hz, 12H, ArCH(C*H*$_3$)$_2$), 1.12 (d, *J* = 6.9 Hz, 12H, ArCH(C*H*$_3$)$_2$), 1.08 (d, *J* = 6.7 Hz, 12H, NCCH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (125.7 MHz, C_6D_6) δ = 174.9 (N*C*CH), 142.7 (Ar*C*), 142.1 (Ar*C*), 125.0 (Ar*C*), 124.6 (Ar*C*), 84.7 (NC*C*H), 32.4 (NC*C*H(CH_3)$_2$), 27.5 (Ar*C*H(CH_3)$_2$), 26.4 (ArCH(*C*H$_3$)$_2$), 24.2 (ArCH(*C*H$_3$)$_2$), 23.2 (NCCH(*C*H$_3$)$_2$) ppm.

Method B: A flask charged with a stirred hexane (10 ml) solution of [(^{i}PrDipBDI)Ca(HMDS)] **5** (250 mg, 0.374 mmol, 1 equiv.) was cooled to -78 °C and a solution of phenylsilane (121.5 µl, 1.12 mmol, 3 equiv.) in hexane (10 ml) was added dropwise over 10 minutes. The solution was allowed to slowly warm to room temperature overnight with stirring, yielding a pale green solution and a white solid. The white solid was found to be pure [{(^{i}PrDipBDI)CaH}$_2$] **9**; yield: 81 mg (42 %). A crystalline crop of [{(^{i}PrDipBDI)CaH}$_2$] **9** was obtained by storage of the pale green solution at -40 °C after concentration *in vacuo*, which was harvested for X-ray single-crystal analysis. Elemental analysis for $C_{66}H_{100}Ca_2N_4$ (%): calc. C: 76.99, H 9.79, N: 5.44, found: C: 73.17, H: 9.36, N: 5.05 (please note: $Ca(OH)_2$ + ^{i}PrDipBDIH calc. C: 72.21, H: 9.55, N: 5.10).

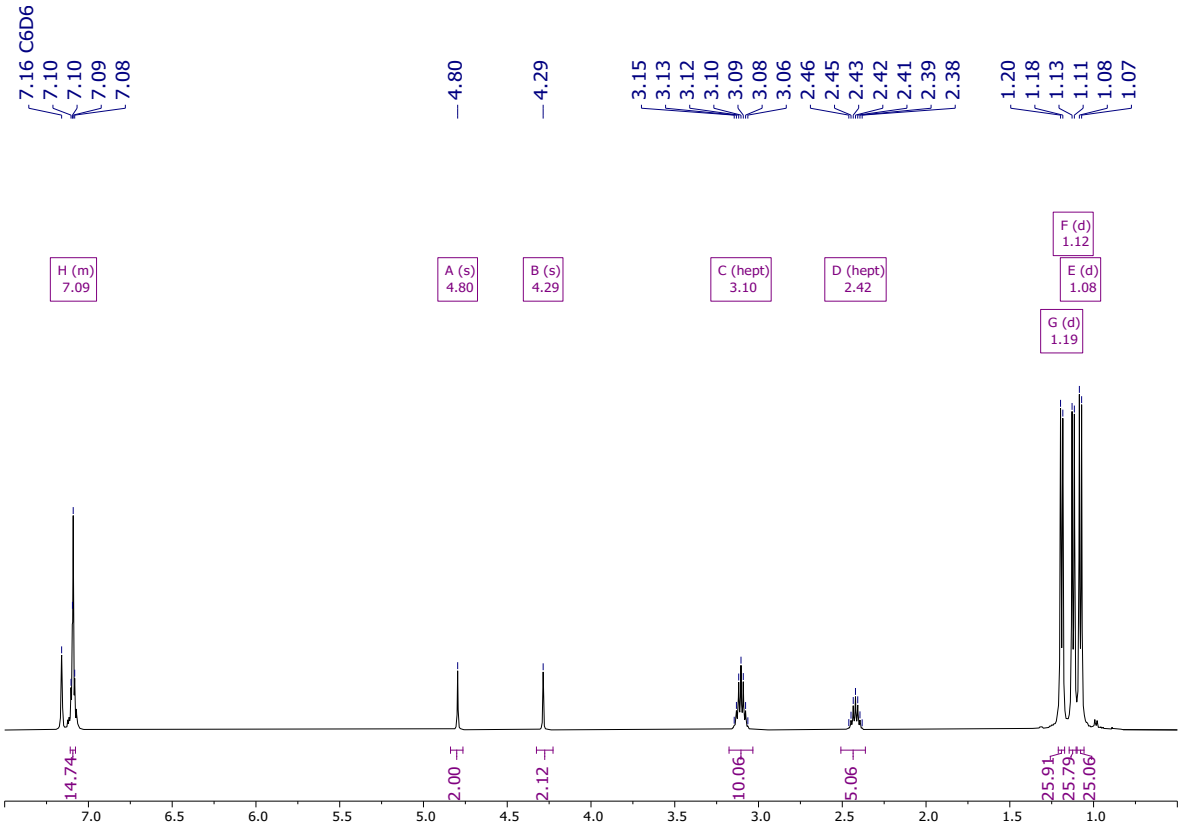

Figure S9: ^{1}H NMR spectrum (499.9 MHz, C_6D_6, 298 K) of [{(*i*PrDipBDI)CaH}$_2$] **9**.

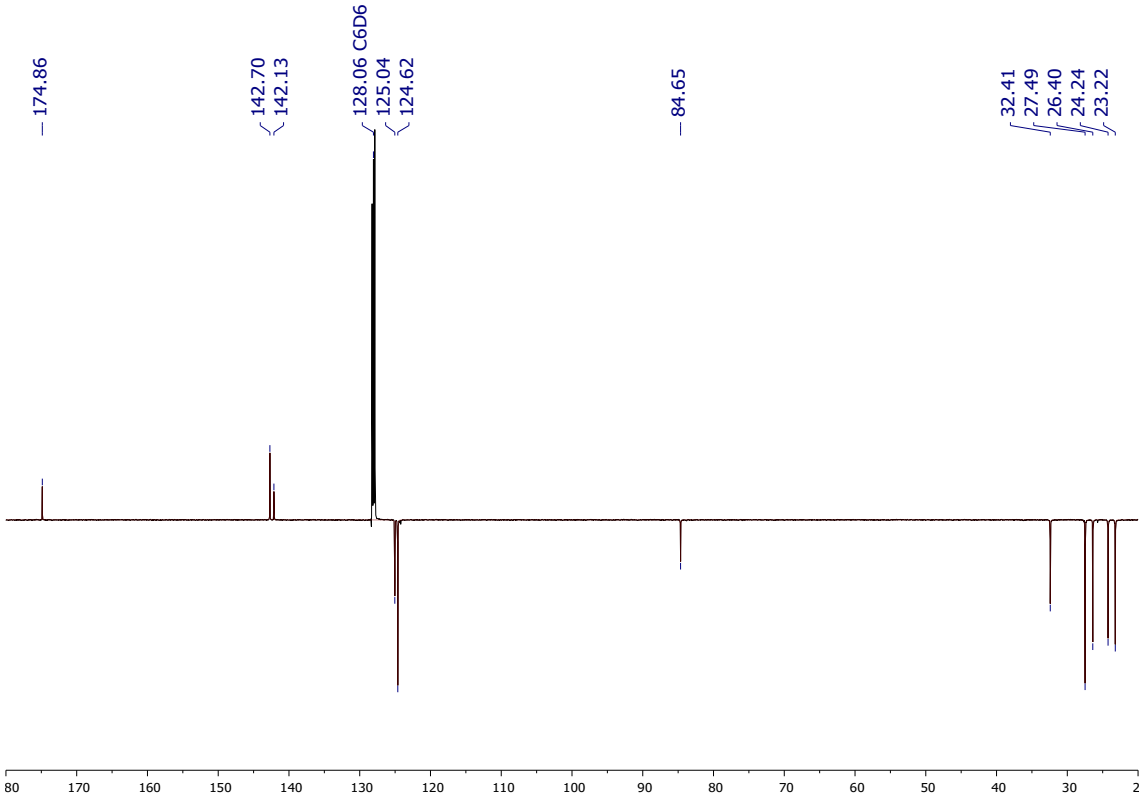

Figure S10: DEPTQ ^{13}C{^{1}H} NMR spectrum (125.7 MHz, C_6D_6, 298 K) of [{(*i*PrDipBDI)CaH}$_2$] **9**.

Synthesis of [{(*i*PrDipBDI)CaH(OEt$_2$)}$_2$]

This compound was generated by forming a CaH complex from a donor-stabilised Ca amide **8**. To a J Young NMR tube charged with a C_6D_6 (0.55 ml) solution of [(*i*PrDipBDI)Ca(HMDS)(OEt$_2$)] **8** (17 mg, 2.3 µmol, 1 equiv.) was added phenylsilane (8.4 µl, 6.8 µmol, 3 equiv.) *via* a micropipette. *Via* ^{1}H NMR spectroscopy, complete conversion to [{(*i*PrDipBDI)CaH(OEt$_2$)}$_2$] was observed after 12 hours at room temperature alongside silane species. ^{1}H NMR (400.1 MHz, C_6D_6) δ = 7.23–7.01 (m, 6H, Ar*H*), 4.78 (s, 1H, NCC*H*), 4.33 (br s, 1H, Ca*H*), 3.29 (q, *J* = 7.0 Hz, 4H, $(CH_3CH_2)_2O$), 3.10 (sept, *J* = 6.8 Hz, 4H, ArC*H*$(CH_3)_2$), 2.42 (q, *J* = 6.7 Hz, 2H, NCC*H*$(CH_3)_2$), 1.20 (d, *J* = 6.8 Hz, 12H, ArCH(C*H*$_3)_2$), 1.11 (d, *J* = 6.4 Hz, 12H, ArCH(C*H*$_3)_2$), 1.09 (t, *J* = 6.9 Hz, $(CH_3CH_2)_2O$), 1.07 (d, *J* = 6.7 Hz, 12H, NCCH(C*H*$_3)_2$).

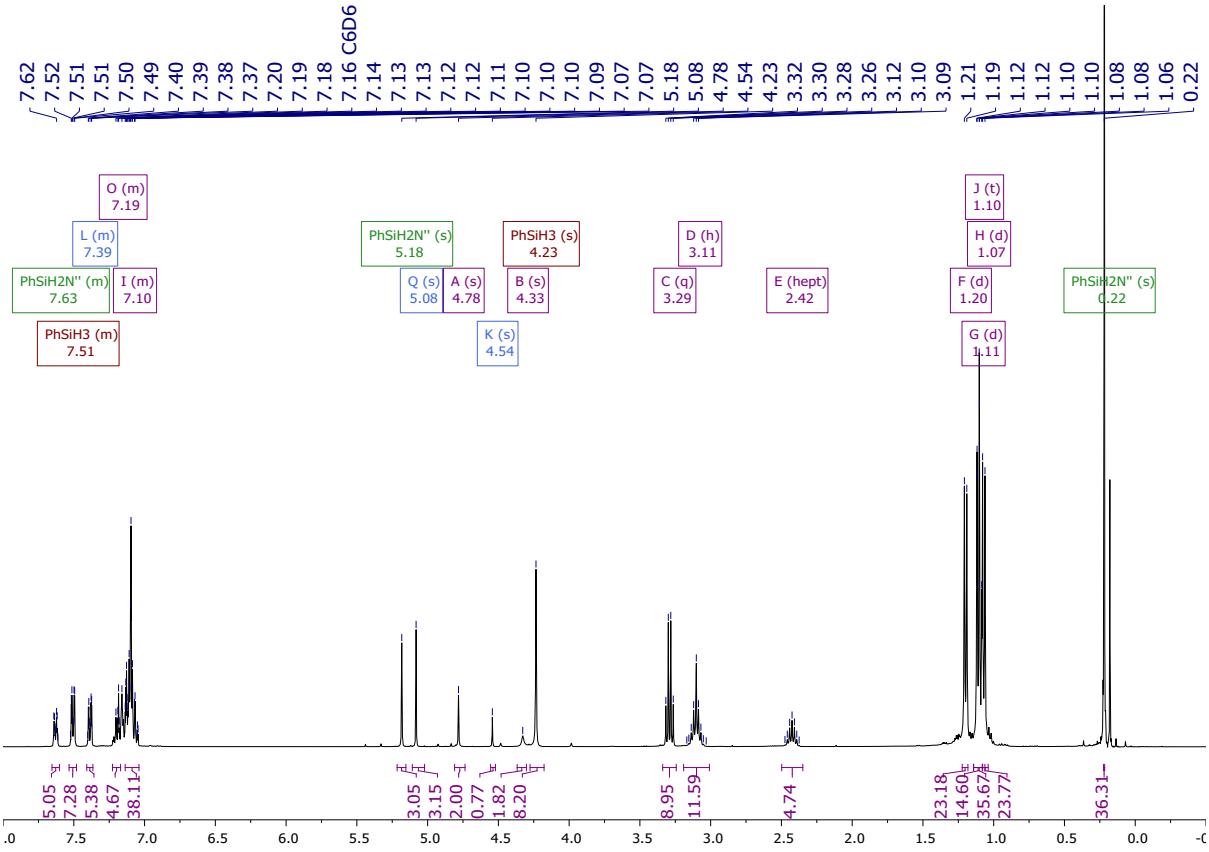

Figure S11: ^{1}H NMR spectrum (499.9 MHz, C_6D_6, 298 K) of [{(*i*PrDipBDI)CaH(OEt$_2$)}$_2$] (purple), prepared *in situ*, with residual $PhSiH_3$ (maroon), $PhSiH_2HMDS$ (green) and other silanes (blue).

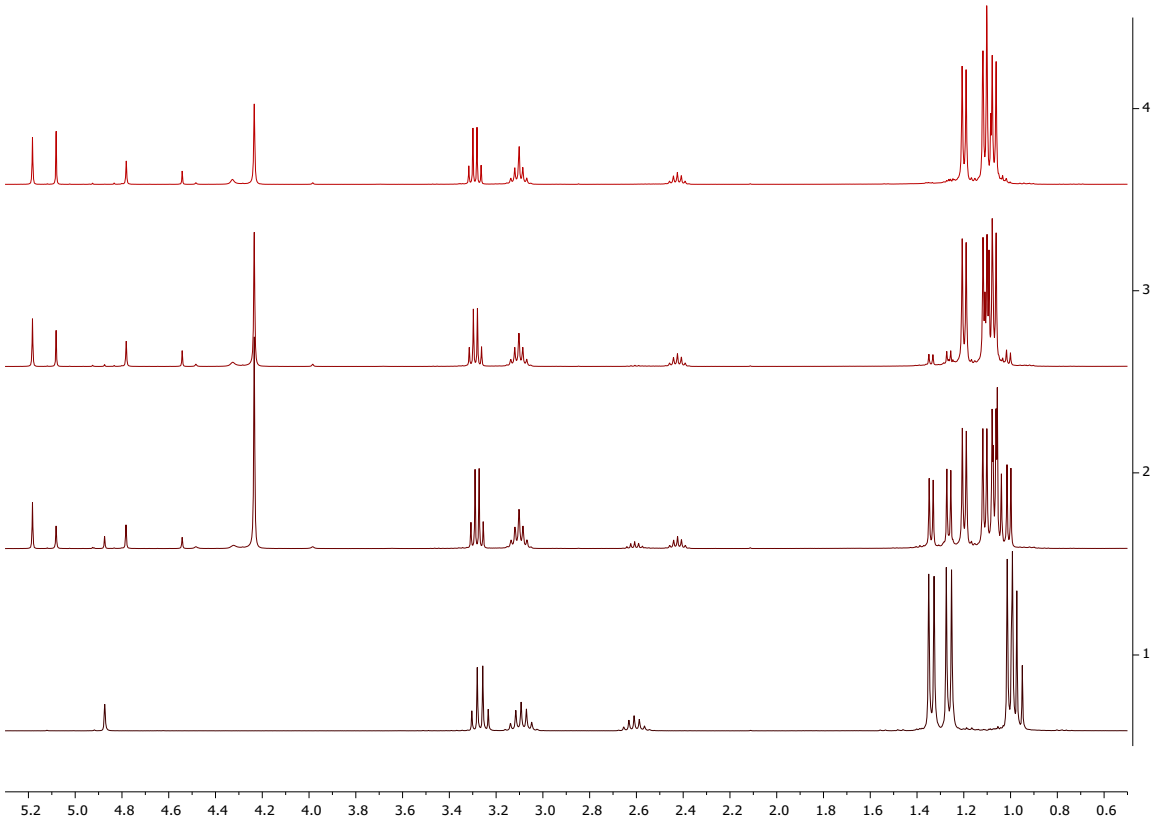

Figure S12: ^{1}H NMR spectra (499.9 MHz, C_6D_6, 298 K) showing reaction progression of the treatment of [(^{i}PrDip^{ip}BDI)Ca(HMDS)(OEt_2)] **8** with an excess of $PhSiH_3$. From bottom to top: 1) Prior to addition; 2) immediately subsequent to addition; 3) 3 hours after addition; 4) 16 hours after addition.

Probing the thermal stability of [{(*i*PrDipBDI)CaH}$_2$] **9**

A J Young NMR tube was charged with a C_6D_6 (0.55 ml) solution of [{(*i*PrDipBDI)CaH}$_2$] **9** (9.0 mg, 8.8 μmol, 1 equiv.) and was placed in an oil bath set to 100 °C. The level of decomposition was monitored *via* ^{1}H NMR spectroscopy; initially every hour then every 24 hours, with 50% decomposition observed after 96 hours.

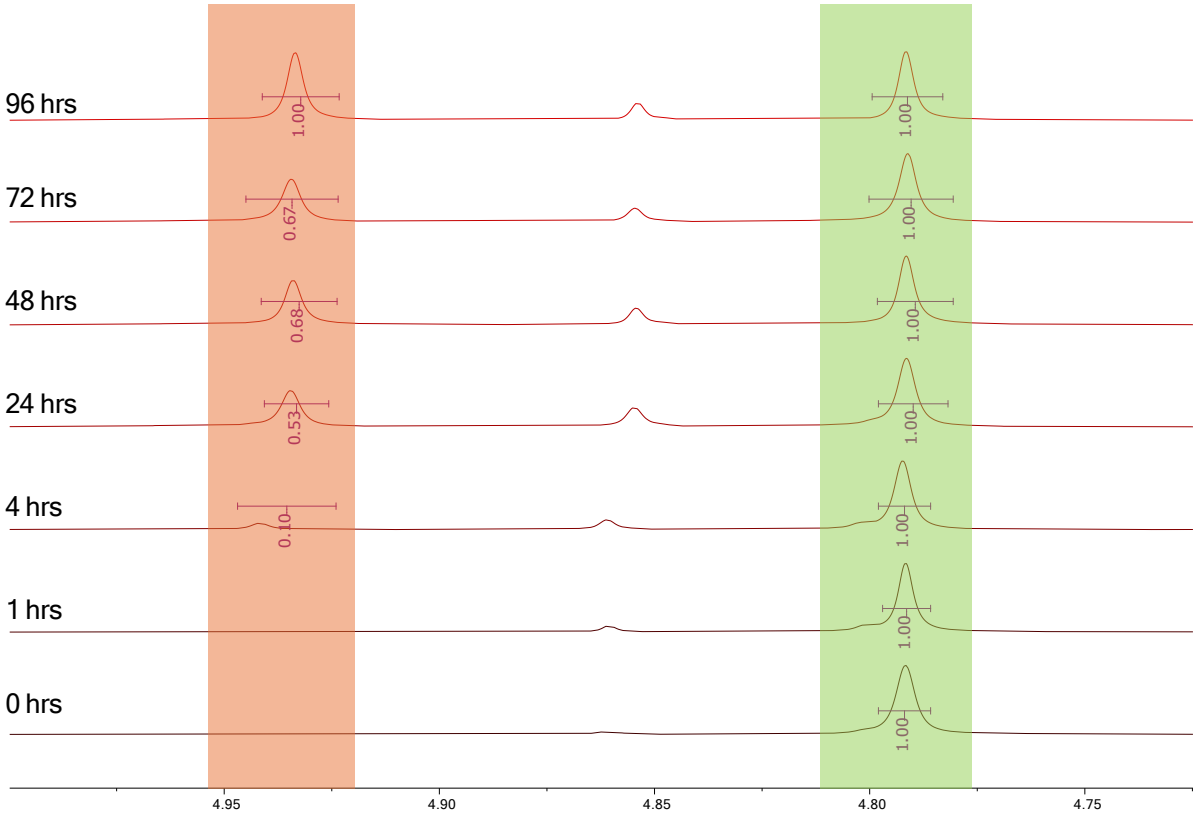

Figure S13: Stacked ^{1}H NMR spectra of the thermal decomposition of [{(*i*PrDipBDI)CaH}$_2$] **9**, showing the backbone region after heating to 100 °C in benzene-d_6 for 0, 1, 4, 24, 48, 72 and 96 hours, respectively. Green shaded region: BDI backbone methine resonance for **9**, orange shaded region: BDI backbone methine resonance for [(*i*PrDipBDI)$_2$Ca] **7**. Note the additional minor impurity at approximately 4.85 ppm.

Probing the thermal stability of [{(MeDipBDI)CaH}$_2$] **11**

A J Young NMR tube was charged with a C_6D_6 (0.55 ml) solution of [{(MeDipBDI)CaH}$_2$] **11** (9.0 mg, 8.8 μmol, 1 equiv.) and was placed in an oil bath set to 100 °C. The level of decomposition was monitored *via* ^{1}H NMR spectroscopy until 50% decomposition was observed, with 50% decomposition achieved after 30 hours.

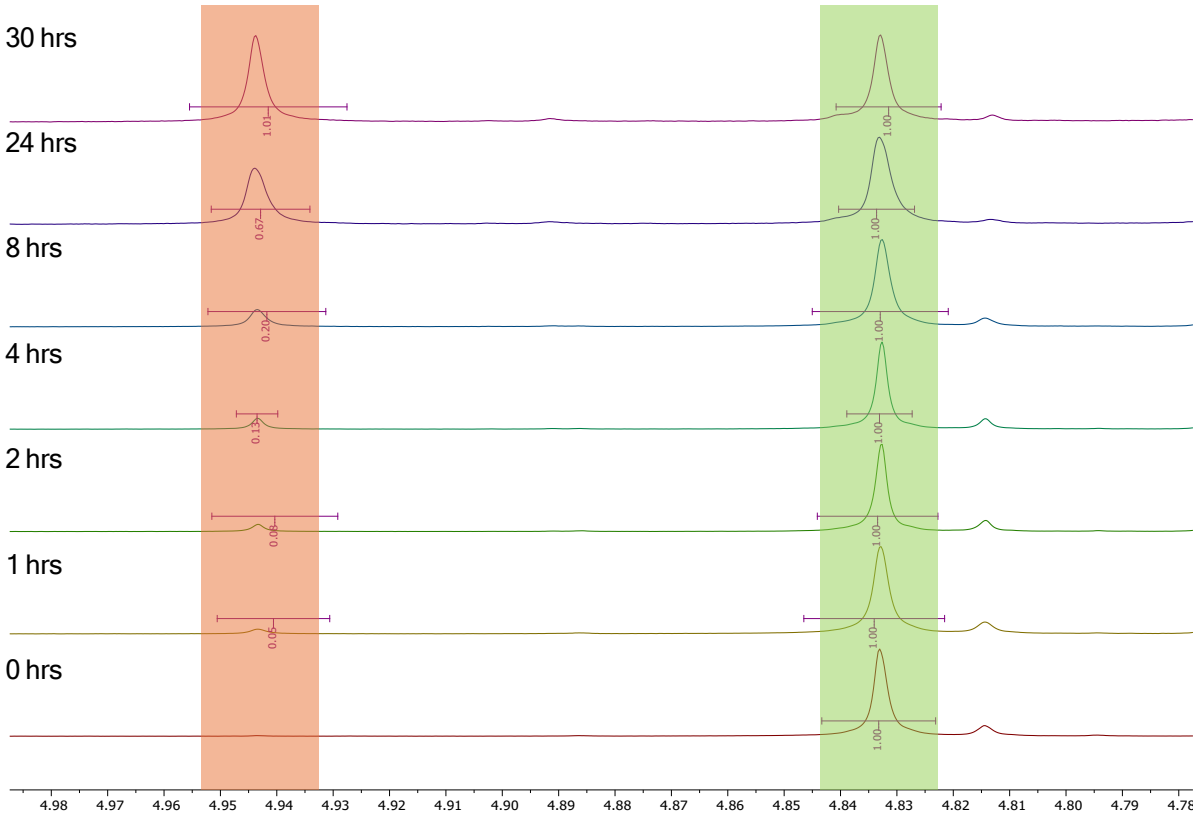

Figure S14: Stacked ^{1}H NMR spectra of the thermal decomposition of [{(MeDipBDI)CaH}$_2$] **11**, showing the backbone region after heating to 100 °C in benzene-d_6 for 0, 1, 2, 4, 8, 24 and 30 hours respectively. Green shaded region: BDI backbone methine resonance for **11**, orange shaded region: BDI backbone methine resonance for [(MeDipBDI)$_2$Ca].

2. X-ray structures

2.1: General considerations

X-ray diffraction data for all compounds were collected at either 93 or 173 K using a Rigaku FR-X Ultrahigh Brilliance Microfocus RA generator/confocal optics [Mo Kα radiation (λ = 0.71073 Å)] with XtaLAB P200 diffractometer. Intensity data were collected using ω steps accumulating area detector images spanning at least a hemisphere of reciprocal space. Data for all compounds analysed were collected using CrystalClear[6] and processed (including correction for Lorentz, polarization and absorption) using either CrystalClear or CrysAlisPro.[7] Structures were solved by dual-space methods (SHELXT[8]) and refined by full-matrix least-squares against F^2 (SHELXL-2019/3[9]). Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using a riding model, except for the hydride in [{(*i*PrDipBDI)CaH}$_2$] (**9**) which was located from the difference Fourier map and refined isotropically subject to a distance restraint. All structures crystallised with one main molecule in the asymmetric unit, except for that of [{(*i*PrDipBDI)CaH}$_2$] (**9**) which crystallised with one half in the asymmetric unit. The structure of [(*i*PrDipBDI)$_2$Ca]·OEt$_2$, **7**·OEt$_2$, shows symmetry-induced disorder in the ether solvate, which was modelled at half-occupancy and refined with geometric and thermal restraints. The structure of [(*i*PrDipBDI)Ca(OEt$_2$)(HMDS)]·OEt$_2$, **8**·OEt$_2$, shows disorder in the non-coordinated ether solvate, which was modelled using two positions and refined (minor component isotropically) with geometric restraints. Because the structures of **8** and **8**·OEt$_2$ (Figure S15) are highly similar (except for the slightly shorter Ca–O distance in **8**·OEt$_2$), only the one of **8** is presented in the main text. The structure of **7**·OEt$_2$ shows small void spaces (149 Å^3 per unit cell) in close proximity to the disordered ether solvate. The SQUEEZE[10] routine was used to investigate the extent of the unordered electron density in the void spaces, showing it to be only 3 e$^-$/Å^3. Due to the minimal amount of electron density involved, SQUEEZE was not used to treat the data in the refinement. Presumably due to the combination of void spaces, disordered solvent and thin plate-shaped crystals, this structure showed no diffraction at higher angles, so the data was truncated at 0.9 Å for refinement. All calculations were performed using the CrystalStructure[11] interface. Selected crystallographic data are presented in Table S1. CCDC 2514137-2514141 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Table S1. Crystallographic data.

Compound reference	[(*i*PrDipBDI)Ca(HMDS)], **5**	[(*i*PrDipBDI)$_2$Ca]·OEt$_2$, **7**·OEt$_2$	[(*i*PrDipBDI)Ca(OEt$_2$)(HMDS)], **8**
formula	$C_{39}H_{67}CaN_3Si_2$	$C_{68}H_{103}CaN_4O_{0.5}$	$C_{43}H_{77}CaN_3OSi_2$
formula weight	674.23	1024.67	748.35
crystal description	Colourless prism	Colourless plate	Colourless prism
crystal size [mm^3]	0.12×0.10×0.03	0.10×0.10×0.01	0.10×0.10×0.10
temperature [K]	173	173	93
space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a [Å]	11.9210(9)	12.7340(6)	12.1819(2)
b [Å]	29.295(2)	13.0655(7)	18.8361(3)
c [Å]	13.3529(9)	20.7474(9)	20.6597(4)
α [°]		90.774(4)	
β [°]	113.1100(17)	91.907(4)	103.817(2)
γ [°]		112.633(5)	
vol [Å]^3	4289.0(5)	3183.0(3)	4603.39(14)
Z	4	2	4
ρ (calc) [g/cm^3]	1.044	1.069	1.080
μ [mm^{-1}]	0.229	0.140	0.220
F(000)	1480	1126	1648
reflections collected	127279	82754	66371
independent reflections (R_{int})	7851 (00407)	9140 (0.1731)	9998 (0.0279)
parameters, restraints	424, 0	709, 58	471, 0
GoF on F^2	1.030	1.000	1.054
R_1 [$I > 2\sigma(I)$]	0.0422	0.0563	0.0311
wR_2 (all data)	0.1177	0.1272	0.0878
largest diff. peak/hole [e/Å^3]	0.67, -0.65	0.28, -0.24	0.38, -0.27
Flack *x* parameter	-	-	-
CCDC number	2514138	2514141	2514137

Table S1 continued. Crystallographic data.

Compound reference	[(${}^{i\text{Pr}\text{Dip}}$BDI)Ca($OEt_2$)(HMDS)]·$OEt_2$, **8**·$OEt_2$	[{(${}^{i\text{Pr}\text{Dip}}$BDI)CaH}$_2$], **9**
formula	$C_{47}H_{87}CaN_3O_2Si_2$	$C_{66}H_{100}Ca_2N_4$
formula weight	822.47	1029.70
crystal description	Colourless prism	Colourless prism
crystal size [mm^3]	0.15×0.03×0.03	0.10×0.10×0.10
temperature [K]	93	93
space group	$P2_1/c$	$I4_1cd$
a [Å]	12.1402(14)	17.2323(18)
b [Å]	18.385(3)	
c [Å]	22.976(3)	43.437(5)
α [°]		
β [°]	92.196(4)	
γ [°]		
vol [Å]^3	5124.4(12)	12899(2)
Z	4	8
ρ (calc) [g/cm^3]	1.066	1.060
μ [mm^{-1}]	0.205	0.215
F(000)	1816	4512
reflections collected	76287	88767
independent reflections (R_{int})	9311 (0.0316)	5849 (0.0372)
parameters, restraints	541, 7	342, 2
GoF on F^2	1.062	1.044
R_1 [$I > 2\sigma(I)$]	0.0361	0.0263
wR_2 (all data)	0.0992	0.0671
largest diff. peak/hole [e/Å^3]	0.44, -0.24	0.21, -0.12
Flack *x* parameter	-	0.06(3)
CCDC number	2514140	2514139

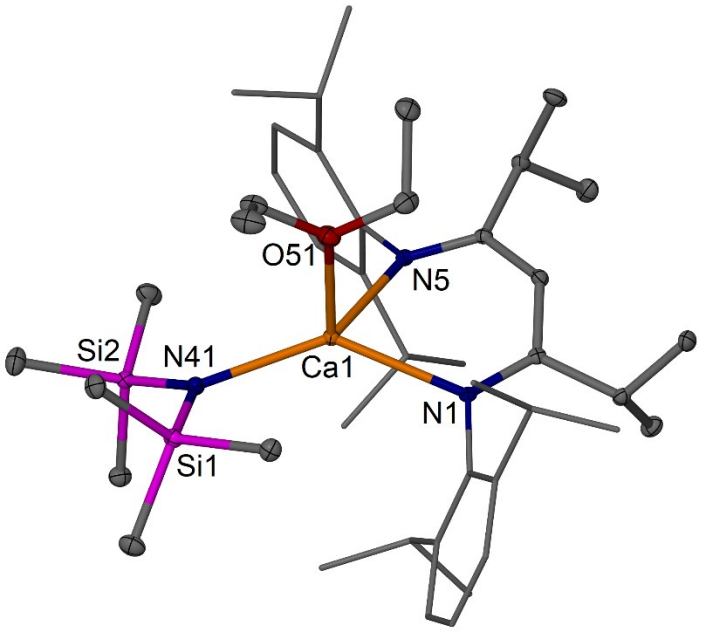

Figure S15: Molecular structure of [(^{i}PrDipBDI)Ca(OEt_2)(HMDS)]·OEt_2, **8**·OEt_2 (thermal ellipsoids with 30% probability, hydrogen and solvent atoms omitted for clarity). The Dip-substituents are shown as wireframe only. Selected bond lengths (Å) and angles (°): Ca1–N1 2.4254(12), Ca1–N5 2.3969(12), Ca1–N41 2.3406(13), Ca1–O51 2.3314(12), Si1–N41 1.7053(13), Si2–N41 1.7067(13); N5–Ca1–N1 81.15(4), N41–Ca1–N1 136.72(4), N41–Ca1–N5 131.22(4), O51–Ca1–N1 100.73(4), Si1–N41–Si2 120.86(8).

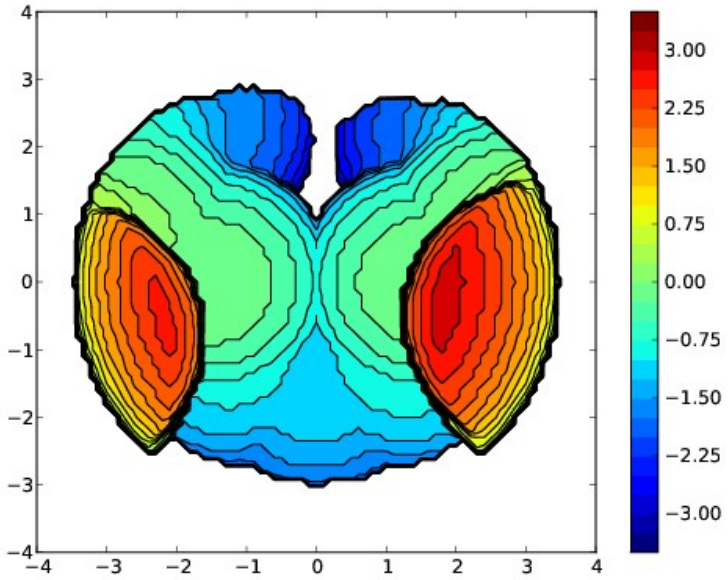

Figure S16: Buried volume (V_{bur}) diagram for [(^{MeDip}BDI)Ca(HMDS)] **3** (total V_B: 46.9%) assessing the ^{MeDip}BDI ligand.

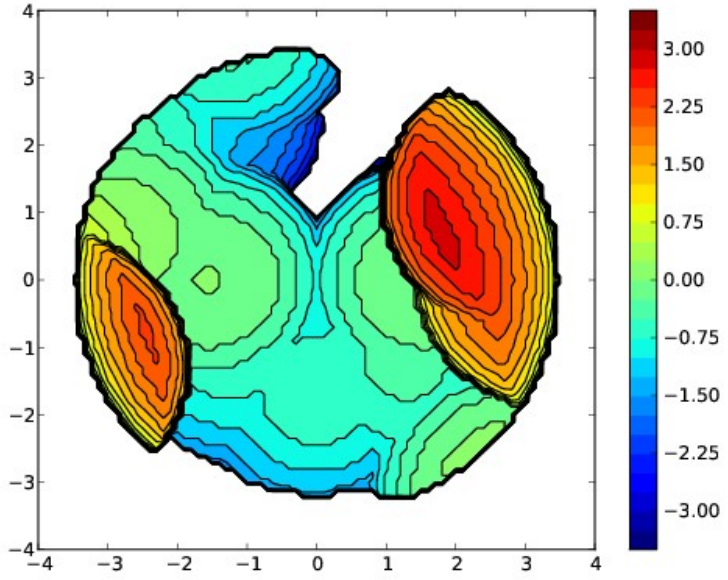

Figure S17: Buried volume (V_{bur}) diagram for [($^{i PrDip}$BDI)Ca(HMDS)] **5** (total V_B: 49.4%) assessing the $^{i PrDip}$BDI ligand.

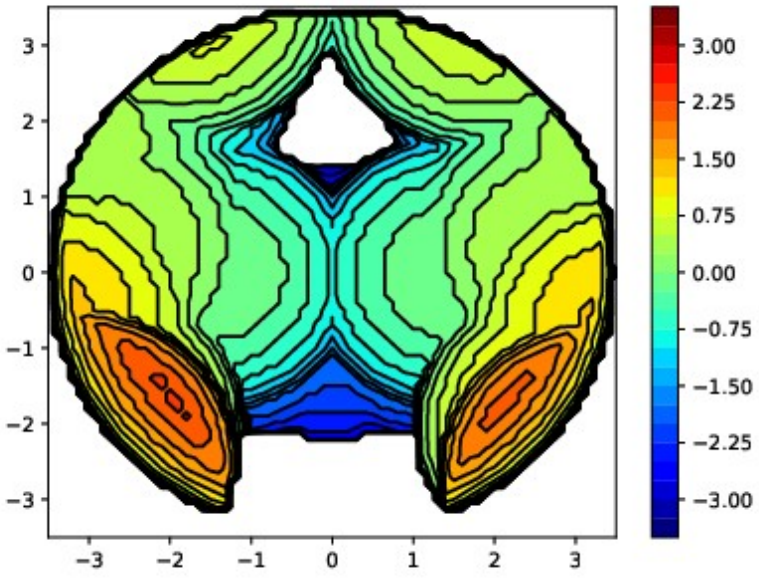

Figure S18: Buried volume (V_{bur}) diagram for [{(^{MeDip}BDI)CaH}$_2$] **10** (total V_B: 49.5%) assessing the ^{MeDip}BDI ligand.

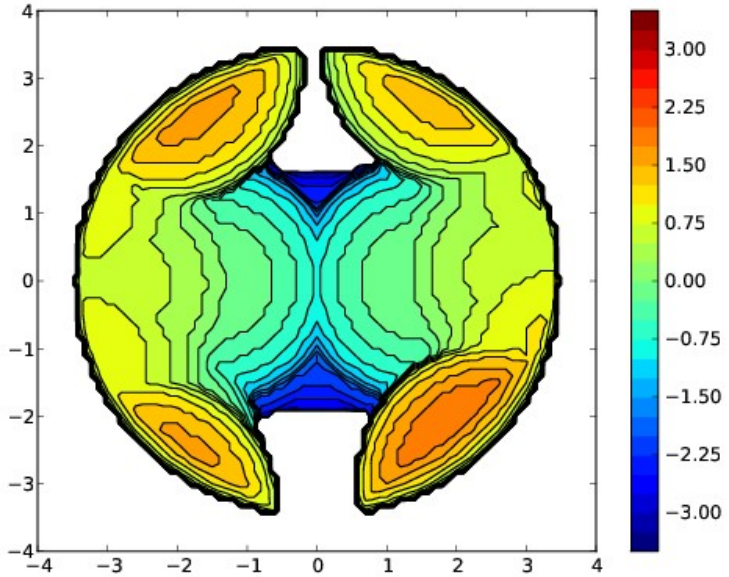

Figure S19: Buried volume (V_{bur}) diagram of [{(^{iPrDip}BDI)CaH}$_2$] **9** (total V_B: 52.4%) assessing the ^{iPrDip}BDI ligand.

Figure S20: Buried volume (V_{bur}) diagram for [{(^{Dipep}BDI)CaH}$_2$] **11** (total V_B: 51.8%) assessing the ^{Dipep}BDI ligand.

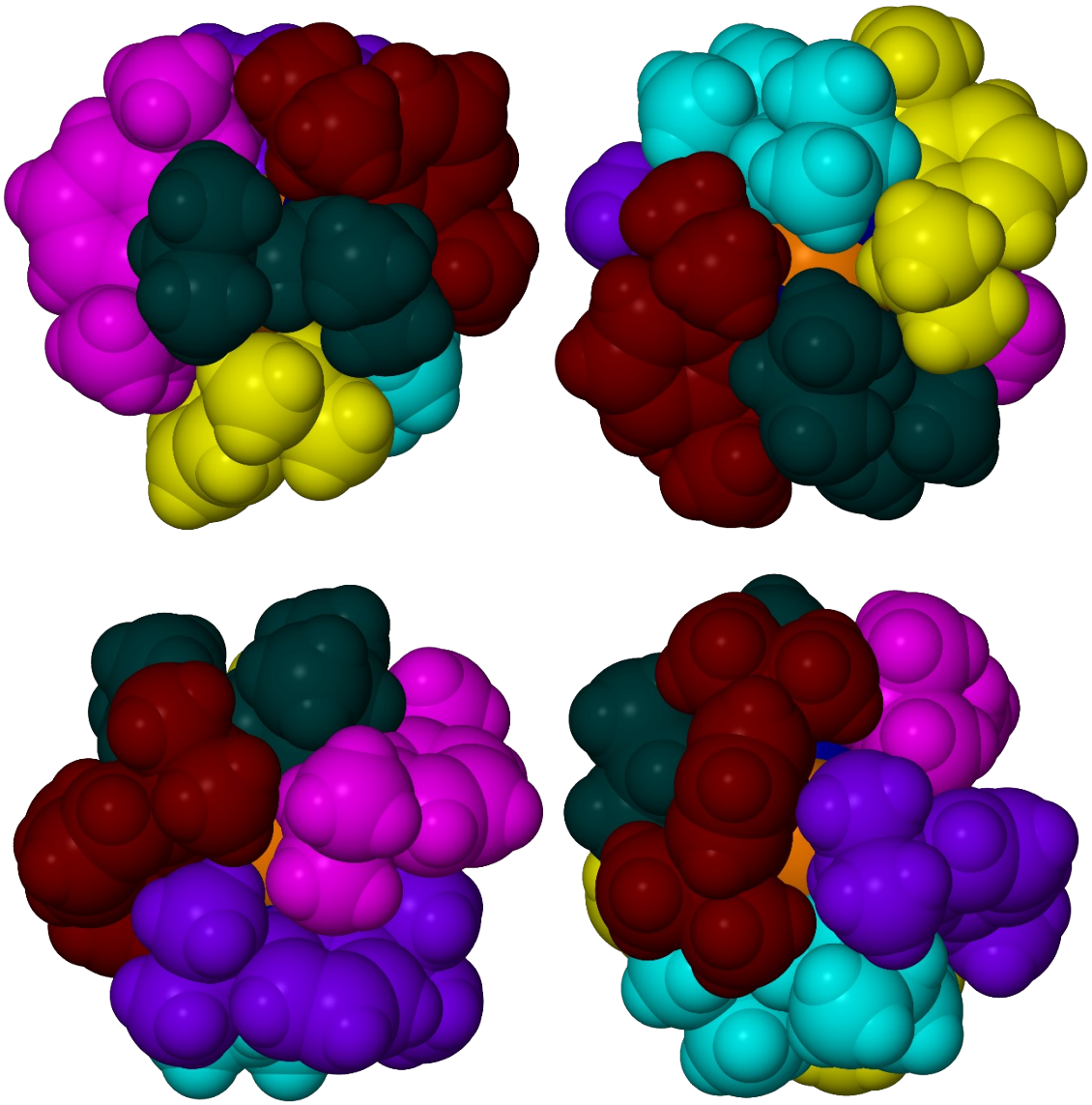

Figure S21: Space-filling (van der Waals) model of the molecular structure of [($^{i\text{Pr}\text{Dip}}$BDI)$_2$Ca]·OEt$_2$, **7**·OEt$_2$, without the solvent molecule in different views than that in Fig. 3. The *i*PrCC(H)C*i*Pr backbone units are turquoise (on N41, N45) and dark green (on N1, N5), and the Dip substituents are yellow (on N41), purple (on N45), dark red (on N1) and magenta (on N5); Ca is orange and N atoms are blue.

3. DFT computational studies

3.1: General considerations

The complexes [(^{MeDip}BDI)Ca(HMDS)], [(^{iPrDip}BDI)Ca(HMDS)] **5**, [Ca(HMDS)$_2$]$_2$, [(^{MeDip}BDI)$_2$Ca], and [(^{iPrDip}BDI)$_2$Ca] **7** were optimised starting from geometries obtained *via* single crystal X-ray diffraction, utilising the B3-LYP[12] density functional coupled with the 6-31G** basis set[13] coupled with Grimme's D3 dispersion term with Becke-Johnson damping.[14,15] Single point calculations utilising B3-LYP/6-311G**[16] (GD3-BJ) in benzene using the polarisable continuum model.[17] All calculations were performed using Gaussian 16.[18] The calculated energies are summarised in Tables S2 and S3.

Table S2. DFT-calculated energy data according to Reactions 1 and 2, i.e., forming 4 moles of [(BDI)Ca(HMDS)].

	Reaction 1	Reaction 2
ΔG_{298} [kcal/mol]	3.88	-10.5
ΔH_{298} [kcal/mol]	57.4	47.9
ΔS_{298} [kcal/mol K]	0.1794	0.1958
ΔG_{373} [kcal/mol]	-9.55	-25.1

Reaction 1 (R = Me):

2 [(^{MeDip}BDI)$_2$Ca] + [Ca(HMDS)$_2$]$_2$ → 4 [(^{MeDip}BDI)Ca(HMDS)]

Reaction 2 (R = iPr):

2 [(^{iPrDip}BDI)$_2$Ca] (**7**) + [Ca(HMDS)$_2$]$_2$ → 4 [(^{iPrDip}BDI)Ca(HMDS)] (**5**)

Table S3. DFT-calculated energy data, referenced to the formation of one mole of [(BDI)Ca(HMDS)], i.e., giving a quarter of the values in Table S2.

	Reaction 1	Reaction 2
ΔG_{298} [kcal/mol]	0.97	-2.62
ΔH_{298} [kcal/mol]	14.3	12.0
ΔS_{298} [kcal/mol K]	0.0448	0.0489
ΔG_{373} [kcal/mol]	-2.39	-6.28

3.2: Atomic coordinates

[(^{MeDip}BDI)Ca(HMDS)]

Ca	-0.003025000	0.481093000	0.001529000
Si	1.841787000	1.850685000	2.235841000
Si	1.578508000	3.704823000	-0.211166000
N	-2.057441000	-0.391007000	-0.853211000
N	0.751304000	-1.571962000	-0.982264000
N	1.257903000	2.295852000	0.700410000
C	-2.167440000	-1.174129000	-1.930503000
C	-1.104803000	-1.887591000	-2.520313000
H	-1.370737000	-2.427401000	-3.420798000
C	0.198228000	-2.159519000	-2.040508000
C	-3.533176000	-1.363971000	-2.564946000
H	-4.179374000	-1.957501000	-1.910845000
H	-3.458619000	-1.874129000	-3.525872000
H	-4.033896000	-0.402375000	-2.707436000
C	0.983516000	-3.199391000	-2.821270000
H	1.685524000	-2.703594000	-3.499956000
H	0.323906000	-3.829809000	-3.419096000
H	1.575405000	-3.830657000	-2.155814000
C	-3.240847000	0.044491000	-0.182885000
C	-3.856890000	-0.810238000	0.764155000
C	-4.963819000	-0.341907000	1.477621000
H	-5.440710000	-0.993109000	2.204379000
C	-5.461131000	0.943388000	1.280183000
H	-6.322579000	1.289461000	1.842932000
C	-4.840463000	1.782777000	0.361592000
H	-5.222820000	2.788153000	0.211801000
C	-3.731834000	1.355646000	-0.378111000
C	-3.314152000	-2.204103000	1.050004000
H	-2.500034000	-2.399906000	0.348550000
C	-2.729184000	-2.274388000	2.470576000
H	-2.340100000	-3.275515000	2.678791000
H	-3.490140000	-2.046053000	3.223817000
H	-1.909168000	-1.560525000	2.602303000
C	-4.375299000	-3.298050000	0.849992000
H	-4.803226000	-3.261652000	-0.156049000
H	-5.198797000	-3.196210000	1.564449000
H	-3.932527000	-4.289228000	0.993538000
C	-3.073338000	2.314459000	-1.358755000

H	-2.271496000	1.766654000	-1.866509000
C	-2.449079000	3.508479000	-0.617196000
H	-1.952904000	4.190336000	-1.313574000
H	-1.703411000	3.188034000	0.119182000
H	-3.213547000	4.075623000	-0.076705000
C	-4.048086000	2.794742000	-2.445798000
H	-3.530887000	3.433216000	-3.169292000
H	-4.869425000	3.376624000	-2.015225000
H	-4.486095000	1.950778000	-2.986812000
C	1.996378000	-2.035664000	-0.458377000
C	1.972861000	-2.874697000	0.686047000
C	3.188042000	-3.256662000	1.262098000
H	3.188128000	-3.901373000	2.133382000
C	4.403623000	-2.813157000	0.746925000
H	5.336032000	-3.117097000	1.212489000
C	4.414421000	-1.969321000	-0.356899000
H	5.361797000	-1.609720000	-0.746741000
C	3.224703000	-1.566733000	-0.974884000
C	0.646368000	-3.346368000	1.272940000
H	-0.071041000	-2.527151000	1.143627000
C	0.729043000	-3.667168000	2.770756000
H	-0.270214000	-3.860288000	3.168797000
H	1.166580000	-2.840881000	3.338214000
H	1.328558000	-4.563522000	2.959812000
C	0.071163000	-4.549514000	0.504180000
H	-0.870297000	-4.877158000	0.958855000
H	0.770589000	-5.392135000	0.527906000
H	-0.132683000	-4.301190000	-0.538529000
C	3.287484000	-0.602221000	-2.149998000
H	2.271643000	-0.484428000	-2.539741000
C	3.773087000	0.779747000	-1.682151000
H	3.778290000	1.493558000	-2.512615000
H	4.791968000	0.720950000	-1.285014000
H	3.134875000	1.179666000	-0.889754000
C	4.167949000	-1.131090000	-3.293770000
H	4.120228000	-0.457020000	-4.155200000
H	3.852550000	-2.126767000	-3.618800000
H	5.216933000	-1.200398000	-2.988254000
C	3.670184000	1.364690000	2.277413000
H	3.864023000	0.533173000	1.590600000
H	3.990512000	1.055780000	3.279120000

H	4.302830000	2.202464000	1.965931000
C	0.900365000	0.236434000	2.725929000
H	1.186393000	-0.637354000	2.120982000
H	-0.197651000	0.338854000	2.736929000
H	1.166695000	-0.043122000	3.750211000
C	1.510611000	3.105161000	3.611962000
H	2.057083000	4.035521000	3.420537000
H	1.820853000	2.734864000	4.595642000
H	0.445859000	3.357671000	3.661239000
C	1.000762000	3.366670000	-1.996732000
H	1.602283000	2.574322000	-2.457224000
H	1.087550000	4.253025000	-2.634862000
H	-0.052112000	3.057791000	-2.032596000
C	0.677822000	5.246867000	0.428840000
H	1.039878000	5.501990000	1.431251000
H	-0.402852000	5.097126000	0.502565000
H	0.854981000	6.115202000	-0.216791000
C	3.411916000	4.190537000	-0.274928000
H	3.768970000	4.461024000	0.725821000
H	3.572051000	5.060180000	-0.922954000
H	4.044482000	3.376849000	-0.640296000

[($^{i\text{PrDip}}$BDI)Ca(HMDS)] (**5**)

Ca	-0.434391000	0.671783000	-0.377335000
Si	-2.614146000	2.735343000	1.407521000
Si	-3.164431000	1.994329000	-1.569399000
N	1.866195000	0.456828000	0.308208000
N	-0.348849000	-1.632896000	0.283935000
N	-2.332569000	1.980324000	-0.092094000
C	2.108867000	-0.189728000	1.466704000
C	1.352674000	-1.265663000	1.953627000
H	1.695909000	-1.665624000	2.895522000
C	0.359175000	-2.059130000	1.316539000
C	2.909453000	1.159144000	-0.352783000
C	2.772849000	2.544446000	-0.619409000
C	3.746767000	3.202437000	-1.377233000
H	3.634020000	4.262991000	-1.581098000
C	4.857734000	2.526769000	-1.868031000
H	5.608213000	3.052035000	-2.450374000
C	4.991923000	1.166407000	-1.606836000
H	5.852499000	0.632250000	-1.998830000

C	4.039278000	0.463118000	-0.865033000
C	1.562938000	3.329411000	-0.136072000
H	1.031411000	2.702900000	0.592084000
C	1.945812000	4.615097000	0.612922000
H	2.458220000	5.322386000	-0.045979000
H	2.613228000	4.393665000	1.450095000
H	1.055398000	5.115049000	1.004426000
C	0.616442000	3.650508000	-1.309486000
H	0.411652000	2.766676000	-1.931398000
H	1.084050000	4.373829000	-1.984738000
H	-0.340081000	4.049083000	-0.965714000
C	4.224650000	-1.038521000	-0.677878000
H	3.431351000	-1.408346000	-0.026618000
C	5.568560000	-1.382234000	-0.014521000
H	6.413245000	-1.112229000	-0.656784000
H	5.634143000	-2.458074000	0.180059000
H	5.693891000	-0.856718000	0.935541000
C	4.083341000	-1.772571000	-2.021694000
H	4.876292000	-1.481188000	-2.718632000
H	3.125387000	-1.539155000	-2.491243000
H	4.141286000	-2.857252000	-1.879555000
C	3.252466000	0.320196000	2.358352000
H	4.022257000	0.716229000	1.691680000
C	3.915900000	-0.726479000	3.260007000
H	3.263957000	-1.030115000	4.085322000
H	4.823910000	-0.307333000	3.705576000
H	4.194587000	-1.623890000	2.701275000
C	2.724615000	1.503463000	3.192747000
H	3.527001000	1.935030000	3.800113000
H	1.924838000	1.175037000	3.864673000
H	2.324263000	2.291280000	2.550185000
C	0.194764000	-3.487872000	1.841453000
H	-0.667928000	-3.922702000	1.329670000
C	1.431680000	-4.321873000	1.463204000
H	2.324266000	-3.942785000	1.969728000
H	1.618811000	-4.286011000	0.386437000
H	1.290362000	-5.369039000	1.750719000
C	-0.071781000	-3.555504000	3.352896000
H	-0.905280000	-2.912230000	3.646351000
H	0.805888000	-3.256525000	3.933362000
H	-0.319477000	-4.582362000	3.640563000

C	-1.307183000	-2.425979000	-0.412377000
C	-2.621375000	-2.579953000	0.093985000
C	-3.588777000	-3.176935000	-0.720755000
H	-4.600049000	-3.289999000	-0.341914000
C	-3.283880000	-3.623592000	-2.003152000
H	-4.051409000	-4.080326000	-2.620166000
C	-1.985623000	-3.486862000	-2.484122000
H	-1.742701000	-3.846226000	-3.479798000
C	-0.984161000	-2.892312000	-1.709415000
C	-3.008110000	-2.110508000	1.489092000
H	-2.107613000	-1.727765000	1.975244000
C	-4.018193000	-0.954701000	1.434119000
H	-4.952394000	-1.266919000	0.955337000
H	-3.616965000	-0.106530000	0.874503000
H	-4.260018000	-0.611842000	2.445734000
C	-3.545524000	-3.269220000	2.345635000
H	-2.838225000	-4.102113000	2.387278000
H	-4.488961000	-3.653680000	1.944798000
H	-3.735565000	-2.930540000	3.369464000
C	0.426561000	-2.766468000	-2.269078000
H	1.047859000	-2.304628000	-1.496715000
C	0.465497000	-1.859312000	-3.510837000
H	0.111291000	-0.847421000	-3.288320000
H	-0.174727000	-2.250608000	-4.307874000
H	1.482260000	-1.780223000	-3.907272000
C	1.025923000	-4.144909000	-2.593113000
H	0.476781000	-4.637558000	-3.402368000
H	0.991469000	-4.804646000	-1.721631000
H	2.069211000	-4.045642000	-2.908957000
C	-4.421704000	2.721888000	1.977305000
H	-4.840568000	1.712265000	1.994921000
H	-5.036408000	3.321361000	1.295392000
H	-4.531038000	3.152677000	2.979297000
C	-2.068682000	4.552682000	1.451515000
H	-2.586431000	5.132824000	0.679346000
H	-0.993990000	4.646961000	1.267030000
H	-2.280545000	5.020628000	2.419841000
C	-1.551178000	1.815193000	2.696915000
H	-0.480121000	1.853902000	2.448106000
H	-1.837667000	0.759322000	2.770302000
H	-1.645496000	2.251057000	3.697715000

C	-3.284163000	3.694805000	-2.395493000
H	-2.291548000	4.139104000	-2.527540000
H	-3.866442000	4.380816000	-1.769620000
H	-3.768875000	3.649404000	-3.377414000
C	-4.895083000	1.229504000	-1.543663000
H	-5.534815000	1.736964000	-0.813976000
H	-4.848750000	0.172966000	-1.260982000
H	-5.382898000	1.297011000	-2.522826000
C	-2.143040000	0.876390000	-2.763586000
H	-2.096095000	-0.172429000	-2.431830000
H	-1.122549000	1.247477000	-2.959016000
H	-2.615578000	0.839853000	-3.750537000

$[Ca(HMDS)_2]_2$

C	3.277484000	2.483298000	-1.562279000
Si	4.775231000	1.408257000	-1.033914000
H	2.710886000	2.877138000	-0.707001000
H	2.581249000	1.955272000	-2.229905000
H	3.611975000	3.362743000	-2.122606000
C	5.938168000	2.582150000	-0.109425000
H	6.228918000	3.439952000	-0.726850000
H	6.853403000	2.066608000	0.198239000
H	5.457606000	2.965934000	0.798016000
C	5.631919000	0.866142000	-2.634383000
H	5.971706000	1.716921000	-3.236010000
H	4.954477000	0.264225000	-3.250979000
H	6.507588000	0.245803000	-2.412589000
N	4.151456000	0.131179000	-0.100425000
Si	5.005883000	-1.185939000	0.569525000
C	6.849327000	-0.869208000	0.872749000
H	7.371070000	-0.619358000	-0.057895000
H	7.340109000	-1.751971000	1.298213000
H	6.996270000	-0.036391000	1.568594000
C	4.863093000	-2.725200000	-0.532894000
H	5.331887000	-2.541788000	-1.506381000
H	3.810110000	-2.963579000	-0.720297000
H	5.332399000	-3.612743000	-0.093443000
C	4.232218000	-1.631558000	2.249325000
H	4.355319000	-0.807369000	2.960611000
H	4.680522000	-2.529218000	2.689426000
H	3.157886000	-1.829538000	2.157578000

Ca	1.832224000	0.257907000	-0.007744000
N	-0.124621000	1.728287000	0.418115000
Si	0.383620000	2.394948000	1.946453000
C	1.912426000	1.433033000	2.579005000
C	-0.901779000	2.258389000	3.326561000
C	0.948943000	4.198081000	1.883520000
Si	-0.932007000	2.798485000	-0.700369000
C	0.084377000	4.189383000	-1.469840000
C	-2.491792000	3.537675000	0.074448000
C	-1.501521000	1.745913000	-2.184623000
Ca	-1.709442000	-0.220406000	0.130658000
N	0.315611000	-1.664217000	-0.148612000
Si	0.141268000	-2.842331000	1.118615000
C	0.172695000	-1.932267000	2.790126000
C	1.474406000	-4.172927000	1.234217000
C	-1.526484000	-3.739642000	0.943958000
Si	0.460036000	-2.168550000	-1.806334000
C	1.610062000	-0.935100000	-2.701240000
C	-1.221256000	-2.087618000	-2.667864000
C	1.160330000	-3.889302000	-2.124620000
N	-4.024075000	-0.295175000	-0.211162000
Si	-5.075150000	0.050510000	-1.531994000
C	-5.362968000	1.916888000	-1.736917000
C	-6.794179000	-0.744285000	-1.377169000
C	-4.400733000	-0.572664000	-3.193745000
Si	-4.671624000	-0.520985000	1.355715000
C	-5.748954000	0.905102000	1.985056000
C	-3.194092000	-0.596955000	2.583021000
C	-5.587948000	-2.150896000	1.651499000
H	-1.007550000	1.232292000	3.692146000
H	-1.886622000	2.604141000	2.996163000
H	-0.604471000	2.874844000	4.182288000
H	1.756542000	4.345504000	1.159521000
H	1.327907000	4.494907000	2.867881000
H	0.137411000	4.885109000	1.625169000
H	0.465585000	4.898082000	-0.732055000
H	-0.553399000	4.746749000	-2.165734000
H	0.936857000	3.804562000	-2.035280000
H	-0.683143000	1.185197000	-2.649745000
H	-1.890647000	2.421965000	-2.953343000
H	-2.335541000	1.061633000	-1.992366000

H	1.236606000	0.099580000	-2.701343000
H	1.680928000	-1.208923000	-3.758932000
H	2.638628000	-0.943356000	-2.314536000
H	2.152187000	-4.026219000	-1.686702000
H	1.247163000	-4.048900000	-3.205324000
H	0.504731000	-4.672187000	-1.730638000
H	-1.636384000	-1.076569000	-2.719557000
H	-1.957629000	-2.718825000	-2.157552000
H	-1.155746000	-2.437239000	-3.704091000
H	-2.393623000	-3.075699000	0.838426000
H	-1.725658000	-4.389226000	1.803522000
H	-1.512056000	-4.373663000	0.049772000
H	2.478377000	-3.754471000	1.125443000
H	1.351947000	-4.950387000	0.476732000
H	1.422409000	-4.655742000	2.216914000
H	-7.333197000	-0.413693000	-0.483179000
H	-6.723528000	-1.836496000	-1.337581000
H	-7.410980000	-0.482385000	-2.244574000
H	-3.493941000	-0.053237000	-3.519095000
H	-5.155430000	-0.413893000	-3.972966000
H	-4.179851000	-1.644261000	-3.159867000
H	-5.192132000	1.848720000	1.953578000
H	-6.082113000	0.741951000	3.016352000
H	-6.641636000	1.034783000	1.364685000
H	-6.513844000	-2.204586000	1.072684000
H	-5.845916000	-2.276211000	2.709685000
H	-4.963786000	-3.001210000	1.353908000
H	-2.254703000	4.148589000	0.952015000
H	-3.185271000	2.749267000	0.389614000
H	-3.030940000	4.172565000	-0.636375000
H	1.745086000	0.359842000	2.733891000
H	2.141136000	1.825402000	3.575605000
H	2.840839000	1.562293000	2.004241000
H	-2.563838000	0.302494000	2.589130000
H	-2.563915000	-1.487577000	2.469375000
H	-3.589497000	-0.657900000	3.602116000
H	-5.782824000	2.349060000	-0.822295000
H	-6.057541000	2.128929000	-2.558107000
H	-4.428266000	2.446501000	-1.947435000
H	1.206044000	-1.783028000	3.120486000
H	-0.322734000	-2.533046000	3.560711000

H	-0.313712000	-0.951308000	2.797533000

[(^{MeDip}BDI)$_2$Ca]

Ca	0.007275000	-0.020248000	-0.340672000
N	0.050586000	-2.182585000	0.727233000
N	2.016150000	-0.954263000	-1.415679000
C	0.147498000	-4.640827000	0.587941000
C	0.418154000	-3.254547000	0.032617000
C	1.070861000	-3.209980000	-1.224969000
C	1.860730000	-2.218120000	-1.840179000
C	2.573455000	-2.700337000	-3.099796000
C	-0.471706000	-2.351219000	2.049487000
C	-1.842203000	-2.632028000	2.257875000
C	-2.313887000	-2.753936000	3.568885000
C	-1.470118000	-2.584161000	4.661315000
C	-0.131749000	-2.273232000	4.447225000
C	0.387972000	-2.150874000	3.154148000
C	-2.832442000	-2.716491000	1.106671000
C	-3.653234000	-4.015083000	1.097217000
C	-3.769012000	-1.500075000	1.142074000
C	1.860685000	-1.814130000	2.973126000
C	2.205282000	-0.465051000	3.624190000
C	2.754335000	-2.940680000	3.517725000
C	3.224804000	-0.280921000	-1.754693000
C	4.474477000	-0.800015000	-1.318088000
C	5.646338000	-0.096989000	-1.616991000
C	5.617785000	1.110382000	-2.302145000
C	4.391336000	1.629572000	-2.704792000
C	3.192940000	0.955708000	-2.450623000
C	1.892610000	1.514135000	-3.010245000
C	1.908598000	3.029110000	-3.241882000
C	1.517834000	0.784279000	-4.310441000
C	4.610083000	-2.067808000	-0.478649000
C	5.124718000	-1.742165000	0.934452000
C	5.533492000	-3.104277000	-1.143988000
H	1.113925000	-4.168228000	-1.730425000
H	-3.365196000	-2.969863000	3.733493000
H	-1.855809000	-2.680153000	5.671659000
H	0.526209000	-2.123432000	5.297858000
H	-2.270393000	-2.673856000	0.170750000
H	2.052558000	-1.728899000	1.899476000

H	6.598952000	-0.497948000	-1.284367000
H	6.537499000	1.645750000	-2.516612000
H	4.369428000	2.571517000	-3.239531000
H	1.086848000	1.330269000	-2.290065000
H	0.558121000	-5.416496000	-0.058688000
H	3.626866000	-2.525149000	-0.364069000
H	0.594271000	-4.738840000	1.581924000
H	-0.924315000	-4.814578000	0.710518000
H	3.218934000	-1.935908000	-3.528802000
H	3.169925000	-3.594599000	-2.904619000
H	1.817196000	-2.976026000	-3.843341000
H	-4.288696000	-4.045138000	0.206251000
H	-3.016005000	-4.904476000	1.094472000
H	-4.307803000	-4.081508000	1.972438000
H	-4.316082000	-1.459938000	2.089744000
H	-4.492365000	-1.538078000	0.326850000
H	-3.204592000	-0.569289000	1.047979000
H	3.253295000	-0.205567000	3.446221000
H	2.050047000	-0.492436000	4.707506000
H	1.586601000	0.343270000	3.226879000
H	2.578315000	-3.102642000	4.586322000
H	2.557667000	-3.885492000	3.001016000
H	3.811507000	-2.694222000	3.385940000
H	2.583116000	3.304309000	-4.058732000
H	0.906459000	3.367859000	-3.510182000
H	2.217297000	3.573163000	-2.344616000
H	0.565044000	1.151647000	-4.705315000
H	1.429140000	-0.290623000	-4.149002000
H	2.289804000	0.952404000	-5.068650000
H	4.443958000	-1.070932000	1.461063000
H	5.223515000	-2.659946000	1.522992000
H	6.107089000	-1.260056000	0.897698000
H	6.570131000	-2.752613000	-1.174213000
H	5.521888000	-4.042593000	-0.579573000
H	5.229579000	-3.318538000	-2.171285000
N	-0.056280000	2.256797000	0.450792000
C	-0.416107000	3.226529000	-0.383511000
C	-0.154277000	4.674997000	-0.013816000
H	-0.557389000	5.356569000	-0.763072000
H	-0.615122000	4.902301000	0.952252000
H	0.915403000	4.867336000	0.099399000

C	-1.053783000	3.012564000	-1.631370000
C	-1.839764000	1.947839000	-2.114789000
N	-2.010011000	0.755681000	-1.520188000
C	-3.218881000	0.050564000	-1.784316000
C	-4.470370000	0.636148000	-1.450121000
C	-5.644597000	-0.089658000	-1.677203000
C	-5.616690000	-1.378222000	-2.193302000
C	-4.388241000	-1.960981000	-2.489822000
C	-3.186993000	-1.272122000	-2.298588000
C	-1.875232000	-1.923738000	-2.711445000
C	-1.934191000	-3.452580000	-2.800904000
H	-2.564034000	-3.783250000	-3.632903000
H	-0.929333000	-3.844962000	-2.966049000
H	-2.321613000	-3.898198000	-1.880044000
C	-1.371041000	-1.336959000	-4.038938000
H	-0.410705000	-1.780412000	-4.319885000
H	-1.242016000	-0.256455000	-3.970608000
H	-2.090314000	-1.544776000	-4.838030000
H	-1.119978000	-1.706335000	-1.946928000
H	-4.367344000	-2.968469000	-2.887108000
H	-6.538377000	-1.928202000	-2.356140000
H	-6.598864000	0.361686000	-1.423087000
C	-4.606102000	2.004718000	-0.787515000
C	-5.139588000	1.869161000	0.649505000
H	-4.470667000	1.266317000	1.266528000
H	-5.236348000	2.856102000	1.113375000
H	-6.125808000	1.393676000	0.663246000
C	-5.512287000	2.951498000	-1.594660000
H	-6.551502000	2.606212000	-1.593490000
H	-5.500010000	3.955282000	-1.157166000
H	-5.193039000	3.028066000	-2.636779000
H	-3.620810000	2.466863000	-0.720700000
C	-2.525950000	2.250244000	-3.443431000
H	-3.163600000	1.432964000	-3.775666000
H	-3.124448000	3.162523000	-3.387101000
H	-1.753381000	2.420188000	-4.201885000
H	-1.084555000	3.892104000	-2.264556000
C	0.453228000	2.598467000	1.743782000
C	1.821101000	2.909319000	1.923715000
C	2.283219000	3.197972000	3.211727000
C	1.431531000	3.165373000	4.310874000

C	0.095111000	2.826713000	4.128666000
C	-0.414876000	2.539116000	2.858075000
C	-1.885670000	2.179206000	2.709186000
C	-2.235346000	0.924159000	3.524517000
H	-3.281565000	0.642379000	3.371741000
H	-2.089864000	1.090138000	4.596804000
H	-1.612754000	0.072856000	3.238986000
C	-2.784840000	3.364658000	3.097054000
H	-2.619447000	3.661807000	4.137983000
H	-2.583430000	4.236259000	2.466085000
H	-3.840597000	3.101717000	2.987293000
H	-2.067946000	1.956444000	1.653744000
H	-0.568950000	2.785212000	4.986718000
H	1.809592000	3.389903000	5.303565000
H	3.332770000	3.436514000	3.355026000
C	2.817548000	2.850317000	0.776364000
C	3.642530000	4.135818000	0.612645000
H	4.280286000	4.056290000	-0.273609000
H	3.007882000	5.020018000	0.500685000
H	4.295038000	4.305665000	1.475349000
C	3.749211000	1.644715000	0.964818000
H	4.291388000	1.718484000	1.913285000
H	4.476437000	1.580546000	0.154872000
H	3.182025000	0.710904000	0.982252000
H	2.260724000	2.694690000	-0.150996000

[(^{iPrDip}BDI)$_2$Ca] (**7**)

Ca	0.000048000	0.000053000	-0.140157000
N	-2.182417000	-0.068363000	-1.288179000
C	-2.515542000	1.142272000	-1.789372000
N	-1.026460000	1.987346000	0.881133000
C	-2.220337000	2.379517000	-1.203120000
H	-2.581345000	3.220027000	-1.775247000
N	2.182428000	0.068254000	-1.288248000
C	-1.774873000	2.752755000	0.096947000
N	1.026462000	-1.987288000	0.881199000
C	-3.239576000	1.204572000	-3.148579000
H	-3.782360000	0.262853000	-3.258431000
C	-2.178464000	1.268198000	-4.264374000
H	-1.703925000	2.252874000	-4.281072000
H	-2.635407000	1.100021000	-5.245432000

H	-1.395765000	0.521774000	-4.118218000
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H	-4.911622000	2.450944000	-2.470794000
H	-4.855180000	2.172276000	-4.219199000
H	-3.741352000	3.312876000	-3.474132000
C	-2.289040000	4.115542000	0.584903000
H	-1.786644000	4.337249000	1.528478000
C	-1.997917000	5.278747000	-0.375631000
H	-0.940494000	5.333622000	-0.642827000
H	-2.274097000	6.224278000	0.102331000
H	-2.576333000	5.202582000	-1.301027000
C	-3.798195000	4.012285000	0.871608000
H	-4.356625000	3.835924000	-0.052560000
H	-4.165173000	4.938821000	1.325788000
H	-4.016062000	3.187862000	1.555045000
C	-0.661277000	2.433664000	2.195779000
C	0.449614000	3.294841000	2.370262000
C	0.841710000	3.643676000	3.665878000
H	1.695476000	4.300970000	3.798726000
C	0.171174000	3.155014000	4.781258000
H	0.494267000	3.430059000	5.780599000
C	-0.916238000	2.308609000	4.602081000
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C	1.257443000	3.819670000	1.195840000
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C	2.650201000	3.177027000	1.169901000
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H	3.230399000	3.532222000	0.316462000
H	2.579266000	2.090053000	1.093373000
C	1.367523000	5.351960000	1.189736000
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H	4.039888000	-2.544060000	3.670646000

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