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SUPPORTING INFORMATION

β-Diketiminate Calcium Hydride Complexes: The Importance of Solvent Effects

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Contents **Page**

1. Crystal structures

All crystal structures have been measured on a SuperNova (Agilent) diffractometer with dual Cu and Mo microfocus sources and an Atlas S2 detector. Using Olex2,[1] the structures were solved by Direct Methods (ShelXT)[2] and refined with ShelXL[3] using Least Squares minimization. Geometric calculations and graphical presentations were done with the program PLATON.[4] Crystallographic data can be found below and have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1520540 [(DIPPnacnac)CaH·Et_2O]$_2$, 1520541 [(DIPPnacnac)CaH]$_2$·DABCO), 1520542 (DIPPnacnac)CaN($SiMe_3$)$_2$·DME, 1520543 [(DIPPnacnac)CaH·Morph]$_2$, 1520544 (DIPPnacnac)CaN($SiMe_3$)$_2$·Morph, 1520545 (DIPPnacnac)CaN($SiMe_3$)$_2$·Et_2O, 1520546 [(DIPPnacnac)CaOEt]$_2$·C_6H_6 and 1520547 [(DIPPnacnac)CaOEt]$_2$. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

1.1 Crystal structure of (DIPPnacnac)CaN(SiMe$_3$)$_2$·DME

Identification code	hasj160615a
Empirical formula	$C_{42}H_{72}CaN_3O_2Si_2$
Formula weight	747.28
Temperature/K	99.9(4)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.68700(18)
b/Å	18.0806(2)
c/Å	21.8110(4)
α/°	90
β/°	105.3719(17)
γ/°	90
Volume/Å^3	4443.95(12)
Z	4
ρ_{calc}g/cm^3	1.117
μ/mm^{-1}	1.997
F(000)	1636.0
Crystal size/mm^3	0.4381 × 0.2622 × 0.1163
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.846 to 136.232
Index ranges	$-14 \le h \le 14$, $-21 \le k \le 21$, $-26 \le l \le 24$
Reflections collected	44083
Independent reflections	8111 [R_{int} = 0.0496, R_{sigma} = 0.0271]
Data/restraints/parameters	8111/0/469
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0356, wR_2 = 0.0963
Final R indexes [all data]	R_1 = 0.0369, wR_2 = 0.0980
Largest diff. peak/hole / e Å^{-3}	0.37/-0.26

The hydrogen atoms have been placed on calculated positions and were refined isotropically in a riding model.

1.2 Crystal structure of (DIPPnacnac)CaN(SiMe$_3$)$_2$·Morph

Identification code	hasj161128a
Empirical formula	$C_{160}H_{280}Ca_4N_{16}O_4Si_8$
Formula weight	2877.02
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	11.30050(10)
b/Å	20.2024(2)
c/Å	39.1907(2)
α/°	102.3440(10)
β/°	90.1900(10)
γ/°	90.3460(10)
Volume/Å^3	8740.03(13)
Z	2
ρ_{calc}g/cm^3	1.093
μ/mm^{-1}	2.003
F(000)	3152.0
Crystal size/mm^3	0.3013 × 0.2119 × 0.171
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.926 to 136.236
Index ranges	$-13 \le h \le 13$, $-24 \le k \le 24$, $-47 \le l \le 38$
Reflections collected	86599
Independent reflections	31761 [R_{int} = 0.0407, R_{sigma} = 0.0355]
Data/restraints/parameters	31761/0/1805
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0396, wR_2 = 0.1051
Final R indexes [all data]	R_1 = 0.0436, wR_2 = 0.1085
Largest diff. peak/hole / e Å^{-3}	0.62/-0.49

The hydrogen atoms have been placed on calculated positions and were refined isotropically in a riding model. The asymmetric unit contains 4 independent molecules. No higher symmetry could be detected.

1.3 Crystal structure of [(DIPPnacnac)CaH·Et$_2$O]$_2$

Identification code	hasj150130c
Empirical formula	$C_{66}H_{104}Ca_2N_4O_2$
Formula weight	1065.69

Temperature/K	291.81(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.98073(15)
b/Å	15.11446(17)
c/Å	18.0466(2)
α/°	90
β/°	97.5028(12)
γ/°	90
Volume/Å^3	3239.93(7)
Z	2
ρ_{calc}g/cm^3	1.092
μ/mm^{-1}	1.846
F(000)	1168.0
Crystal size/mm^3	0.2716 × 0.1884 × 0.1097
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.656 to 136.234
Index ranges	$-13 \leq h \leq 14$, $-18 \leq k \leq 8$, $-18 \leq l \leq 21$
Reflections collected	11551
Independent reflections	5888 [R_{int} = 0.0268, R_{sigma} = 0.0364]
Data/restraints/parameters	5888/0/354
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0441, wR_2 = 0.1174
Final R indexes [all data]	R_1 = 0.0484, wR_2 = 0.1222
Largest diff. peak/hole / e Å^{-3}	0.59/-0.28

The hydrogen atoms have been placed on calculated positions and were refined isotropically in a riding model, except for the hydride H atoms which were found in the difference-Fourier map and refined isotropically.

1.4 Crystal structure of [(DIPPnacnac)CaH·Morph]$_2$

Identification code	hasj161012a
Empirical formula	$C_{68}H_{106}Ca_2N_6O_2$
Formula weight	1119.74
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	14.4825(2)
b/Å	13.02210(10)

c/Å	18.2443(2)
α/°	90
β/°	100.2860(10)
γ/°	90
Volume/Å^3	3385.44(7)
Z	2
ρ_{calc}g/cm^3	1.098
μ/mm^{-1}	1.798
F(000)	1224.0
Crystal size/mm^3	0.3828 × 0.3238 × 0.1131
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.198 to 136.2
Index ranges	$-12 \le h \le 17$, $-14 \le k \le 15$, $-17 \le l \le 21$
Reflections collected	30269
Independent reflections	6166 [R_{int} = 0.0578, R_{sigma} = 0.0329]
Data/restraints/parameters	6166/0/371
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0393, wR_2 = 0.1076
Final R indexes [all data]	R_1 = 0.0415, wR_2 = 0.1101
Largest diff. peak/hole / e Å^{-3}	0.68/-0.28

The hydrogen atoms have been placed on calculated positions and were refined isotropically in a riding model, except for the hydride H atoms which were found in the difference-Fourier map and refined isotropically.

1.5 Crystal structure of [(DIPPnacnac)CaH]$_2$·DABCO

Identification code	hasj160613a
Empirical formula	$C_{32}H_{48}CaN_3$
Formula weight	514.81
Temperature/K	100.0(3)
Crystal system	monoclinic
Space group	P2$_1$/n
a/Å	8.88056(13)
b/Å	15.1230(2)
c/Å	22.2473(3)
α/°	90

β/°	96.5639(13)
γ/°	90
Volume/Å^3	2968.24(8)
Z	4
ρ_{calc}g/cm^3	1.152
μ/mm^{-1}	1.985
F(000)	1124.0
Crystal size/mm^3	0.4586 × 0.0636 × 0.0489
Crystal color	colorless
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.082 to 147.39
Index ranges	$-10 \le h \le 7$, $-18 \le k \le 17$, $-24 \le l \le 27$
Reflections collected	10589
Independent reflections	5747 [R_{int} = 0.0357, R_{sigma} = 0.0479]
Data/restraints/parameters	5747/6/379
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0362, wR_2 = 0.0884
Final R indexes [all data]	R_1 = 0.0409, wR_2 = 0.0925
Largest diff. peak/hole / e Å^{-3}	0.40/-0.28

The hydrogen atoms have been placed on calculated positions and were refined isotropically in a riding model, except for the hydride H atoms which were found in the difference-Fourier map and refined isotropically. DABCO lies over an inversion center and is disordered 50/50 over two positions. Part of the DABCO unit was refined using a Rigid Bond (RIGU) Restraint.[5]

1.6 Crystal structure of [(DIPPnacnac)CaOEt]$_2$·C_6H_6

Identification code	hasj160715a
Empirical formula	$C_{68}H_{98}Ca_2N_4O_2$
Formula weight	1083.66
Temperature/K	100
Crystal system	monoclinic
Space group	P2_1/n
a/Å	13.3510(5)
b/Å	16.3688(6)

c/Å	15.0996(5)
α/°	90
β/°	100.888(3)
γ/°	90
Volume/Å^3	3240.5(2)
Z	2
ρ_{calc}g/cm^3	1.111
μ/mm^{-1}	1.856
F(000)	1180.0
Crystal size/mm^3	0.7101 × 0.2148 × 0.168
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.642 to 136.23
Index ranges	$-16 \le h \le 15$, $-19 \le k \le 17$, $-15 \le l \le 18$
Reflections collected	11176
Independent reflections	5890 [R_{int} = 0.0283, R_{sigma} = 0.0364]
Data/restraints/parameters	5890/0/358
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0399, wR_2 = 0.1050
Final R indexes [all data]	R_1 = 0.0429, wR_2 = 0.1082
Largest diff. peak/hole / e Å^{-3}	0.45/-0.38

The hydrogen atoms have been placed on calculated positions and were refined isotropically in a riding model.

1.7 Crystal structure of [(DIPPnacnac)CaOEt]$_2$

(another solvent-free polymorph)

Identification code	hasj160518a
Empirical formula	$C_{62}H_{92}Ca_2N_4O_2$
Formula weight	1005.55
Temperature/K	100
Crystal system	monoclinic
Space group	P2$_1$/n
a/Å	12.2642(3)
b/Å	15.2818(3)
c/Å	16.5278(3)

α/°	90
β/°	103.457(2)
γ/°	90
Volume/Å^3	3012.58(11)
Z	2
ρ_{calc}g/cm^3	1.109
μ/mm^{-1}	1.961
F(000)	1096.0
Crystal size/mm^3	0.523 × 0.4098 × 0.2824
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.138 to 136.234
Index ranges	$-12 \le h \le 14$, $-17 \le k \le 18$, $-19 \le l \le 13$
Reflections collected	9482
Independent reflections	5446 [R_{int} = 0.0316, R_{sigma} = 0.0423]
Data/restraints/parameters	5446/0/335
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0440, wR_2 = 0.1149
Final R indexes [all data]	R_1 = 0.0473, wR_2 = 0.1181
Largest diff. peak/hole / e Å^{-3}	0.43/-0.43

The hydrogen atoms have been placed on calculated positions and were refined isotropically in a riding model.

2. Selected ^{1}H and ^{13}C NMR spectra

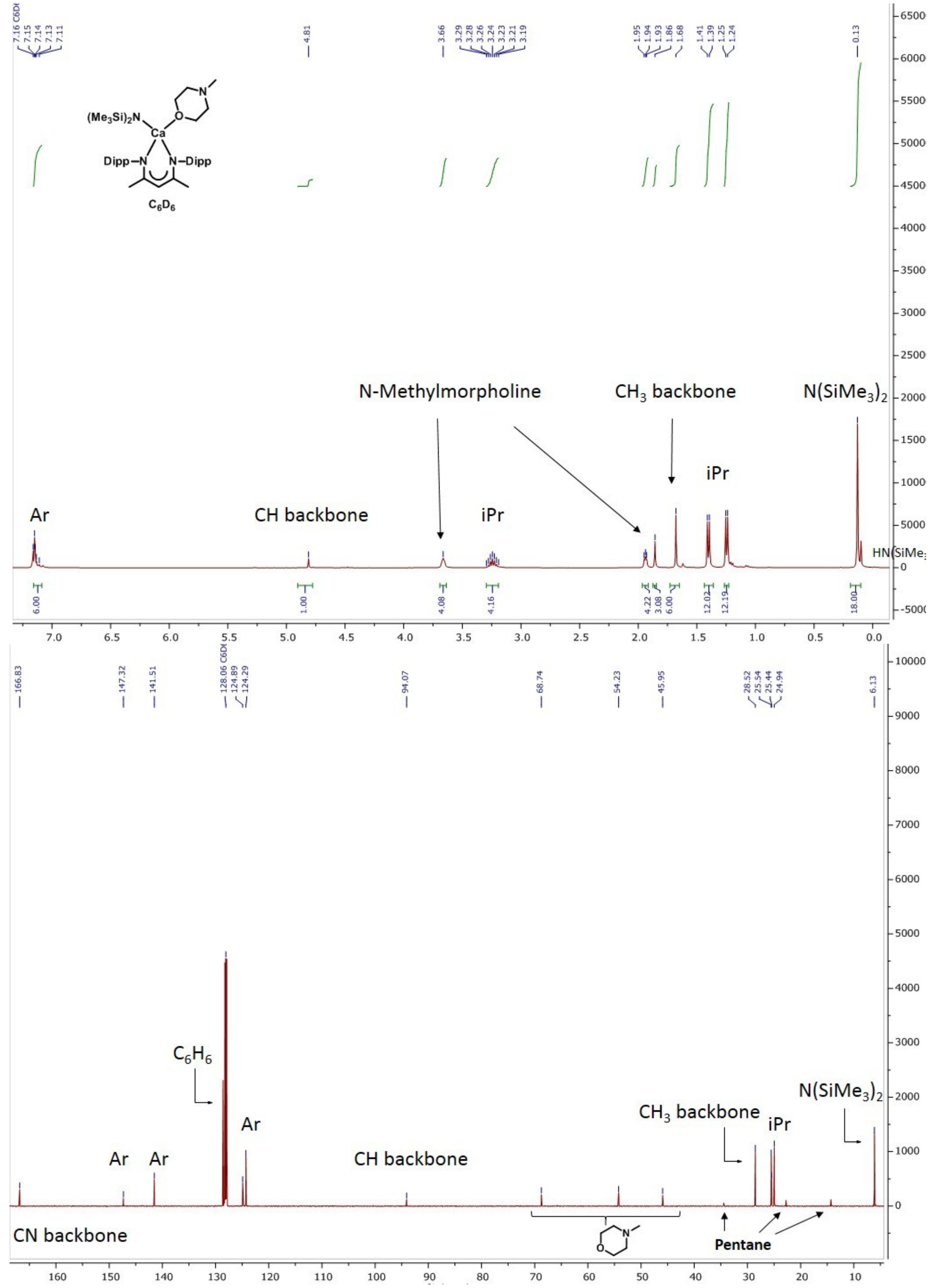


Figure S1. ^{1}H and ^{13}C spectra of (DIPPnacnac)CaN(SiMe$_3$)$_2$·Morph in C$_6$D$_6$.

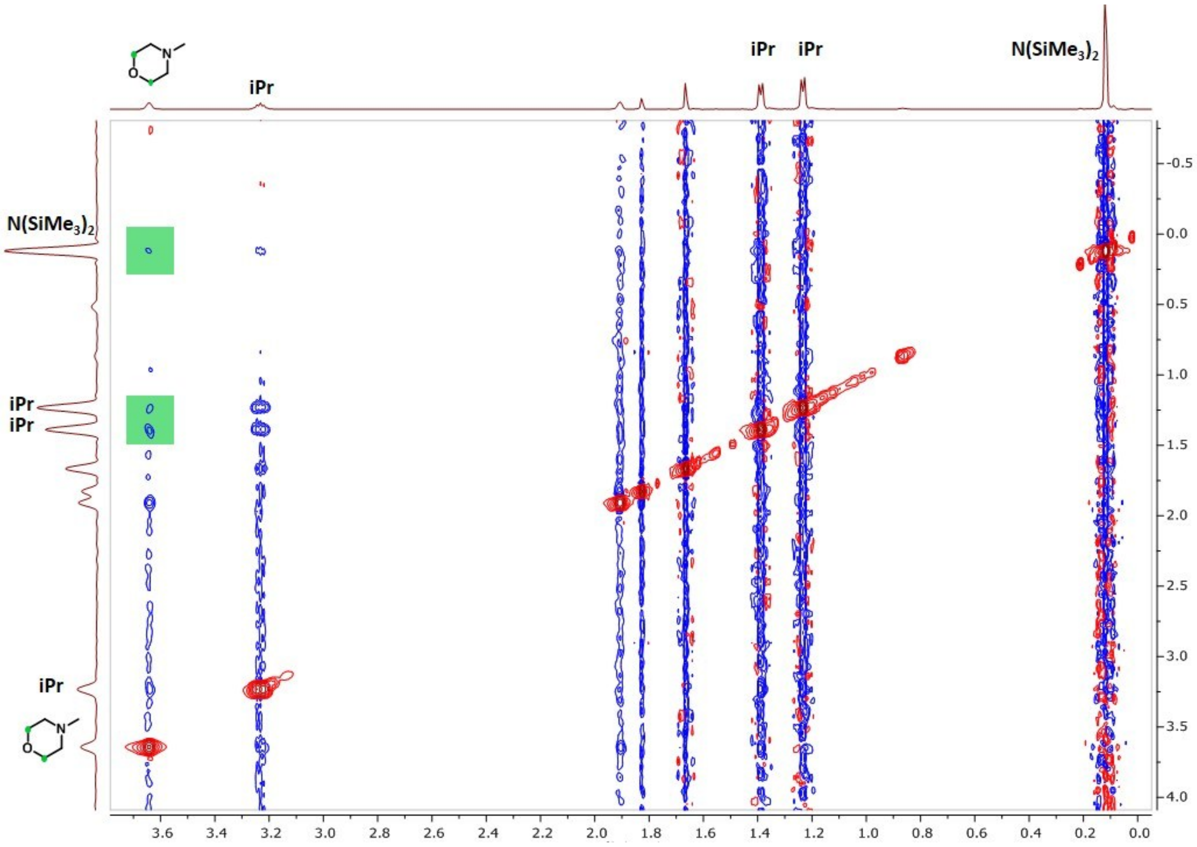


Figure S2. 2D ^{1}H,^{1}H-NOESY Spectra of (DIPPnacnac)CaN(SiMe$_3$)$_2$·Morph in C_6D_6. The cross peaks marked in green in the NOESY spectrum indicate proximity between the O-C*H*$_2$ protons of morpholine and both, the protons on the iPr group and of the N(SiMe$_3$)$_2$ group, proving that only the oxygen coordinates calcium.

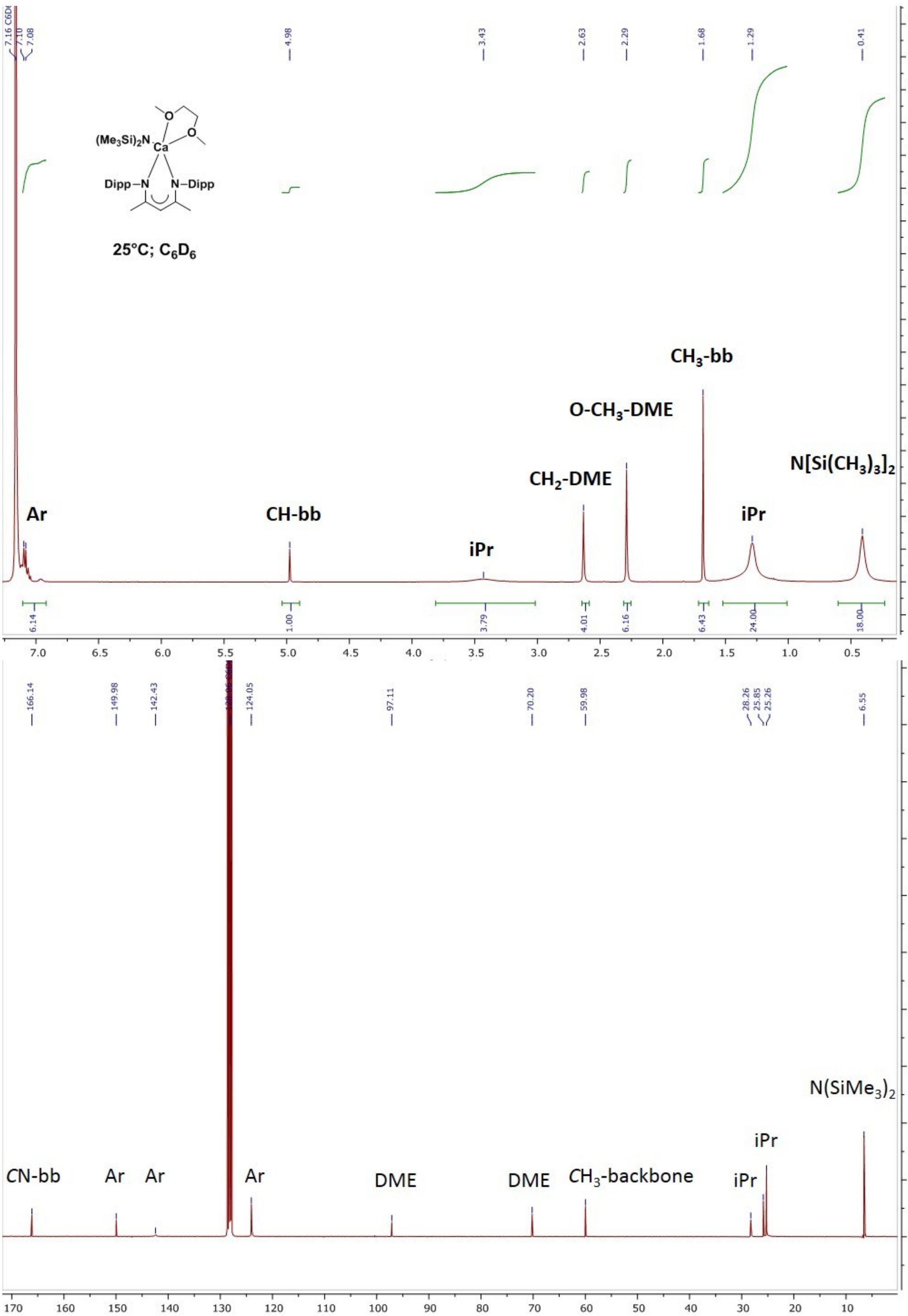


Figure S3. ^1H and ^{13}C spectra of (DIPPnacnac)CaN(SiMe$_3$)$_2$·DME in C_6D_6.

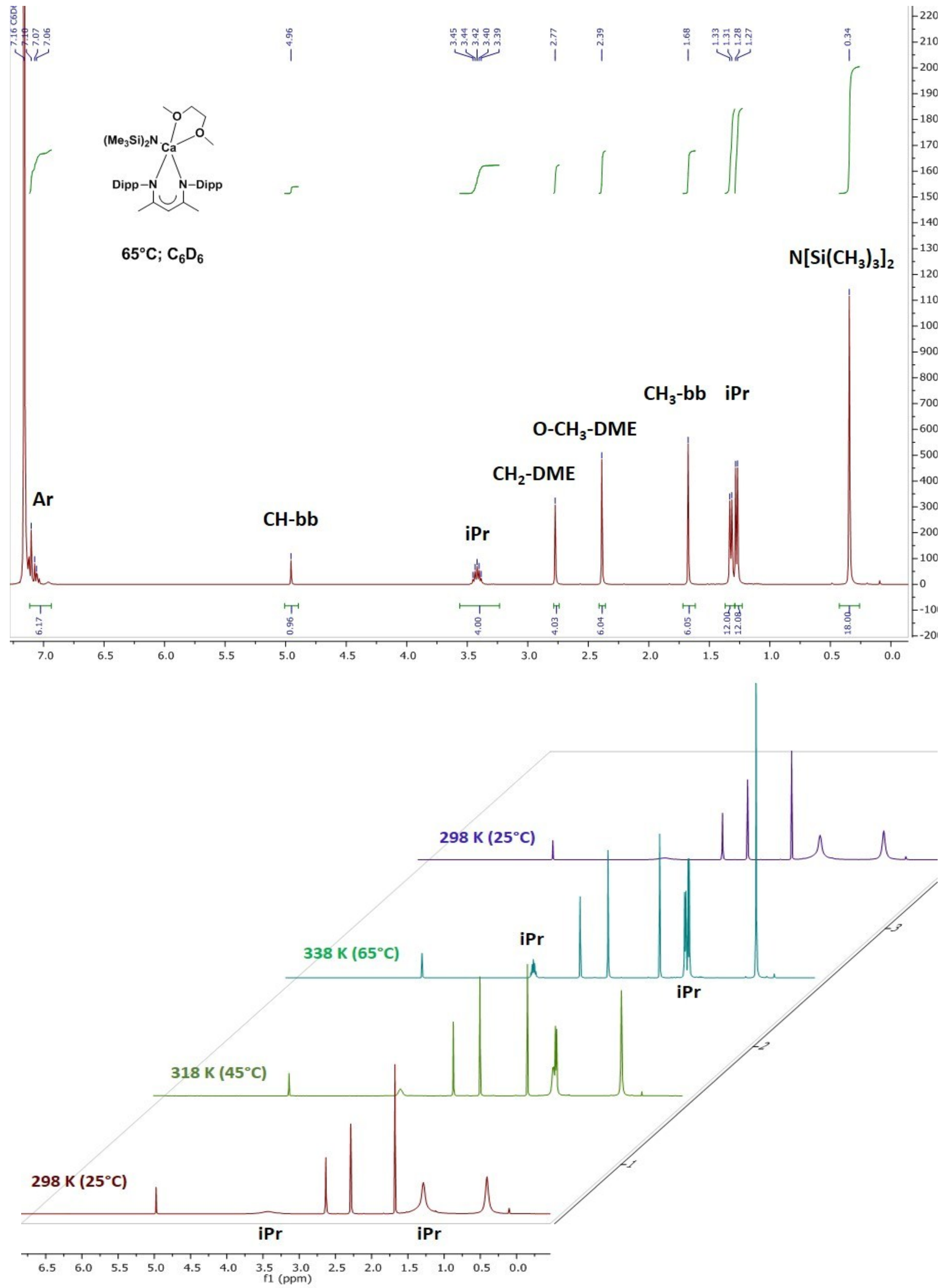


Figure S4. ^{1}H spectrum at 65°C and stacked ^{1}H spectra of (DIPPnacnac)CaN(SiMe$_3$)$_2$·DME at different temperatures (from RT to 65°C) in C_6D_6.

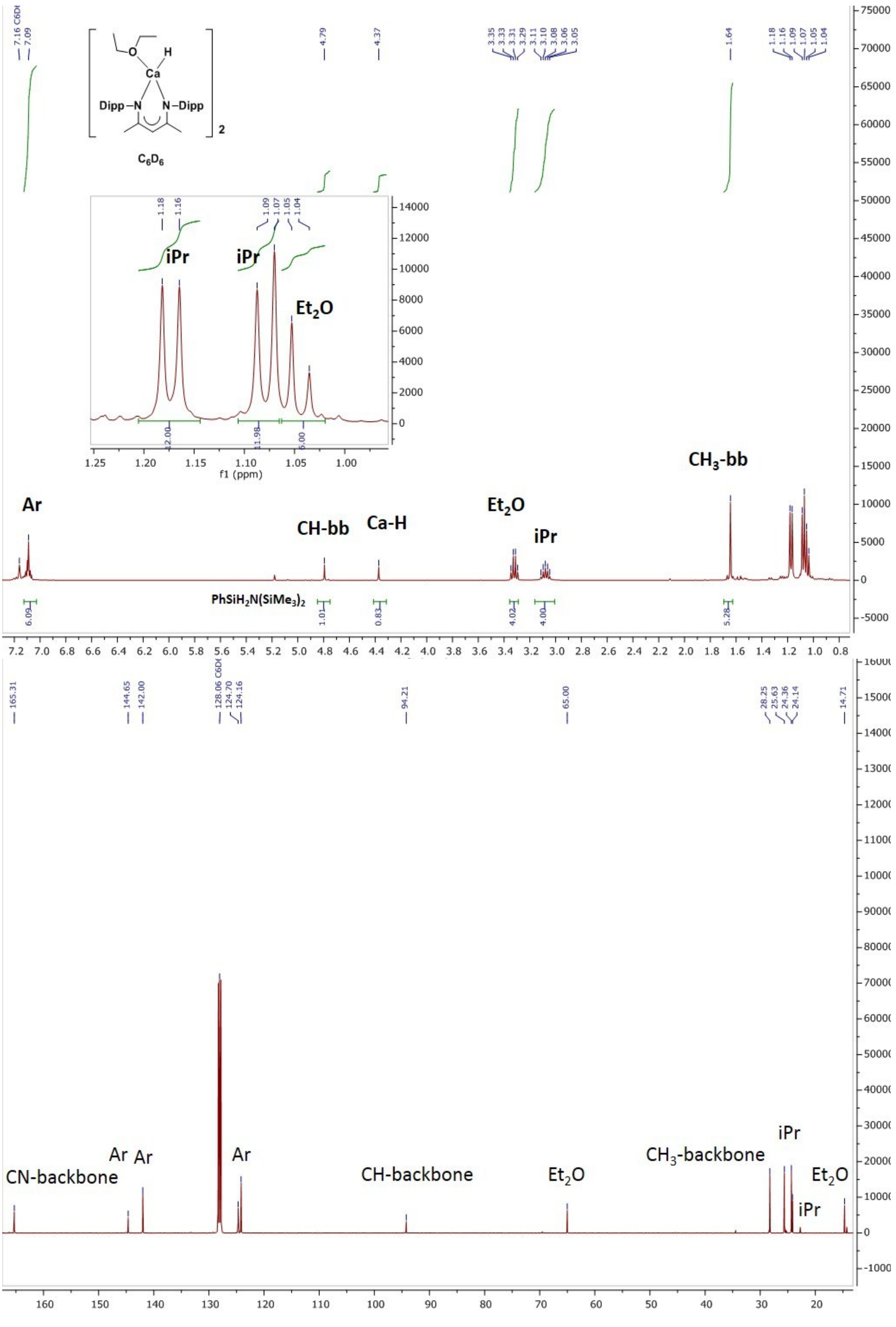


Figure S5. ^{1}H and ^{13}C spectra of [(DIPPnacnac)CaH·Et$_2$O]$_2$ in C$_6$D$_6$.

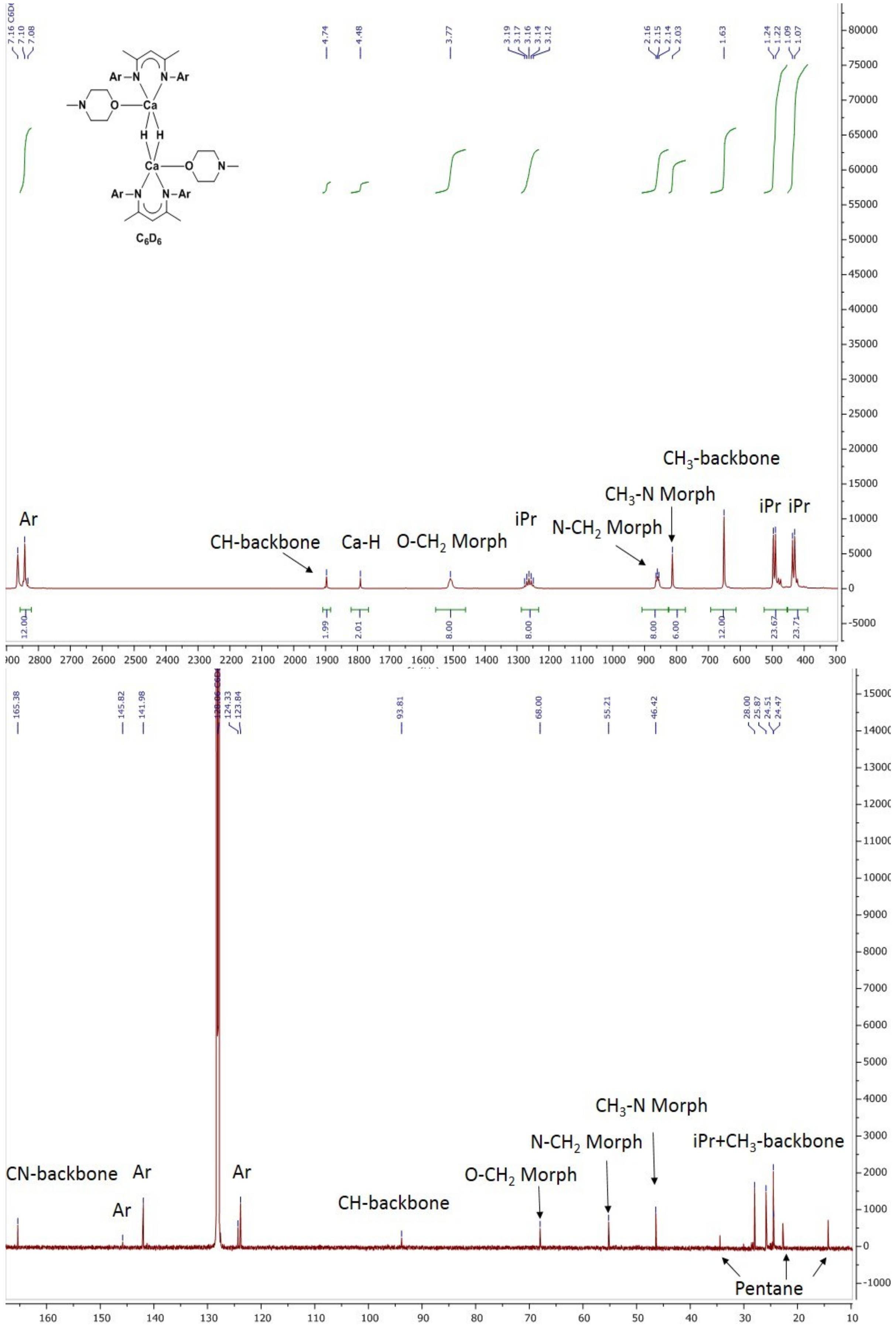


Figure S6. ^{1}H and ^{13}C spectra of [(DIPPnacnac)CaH·Morph]$_2$ in C_6D_6.

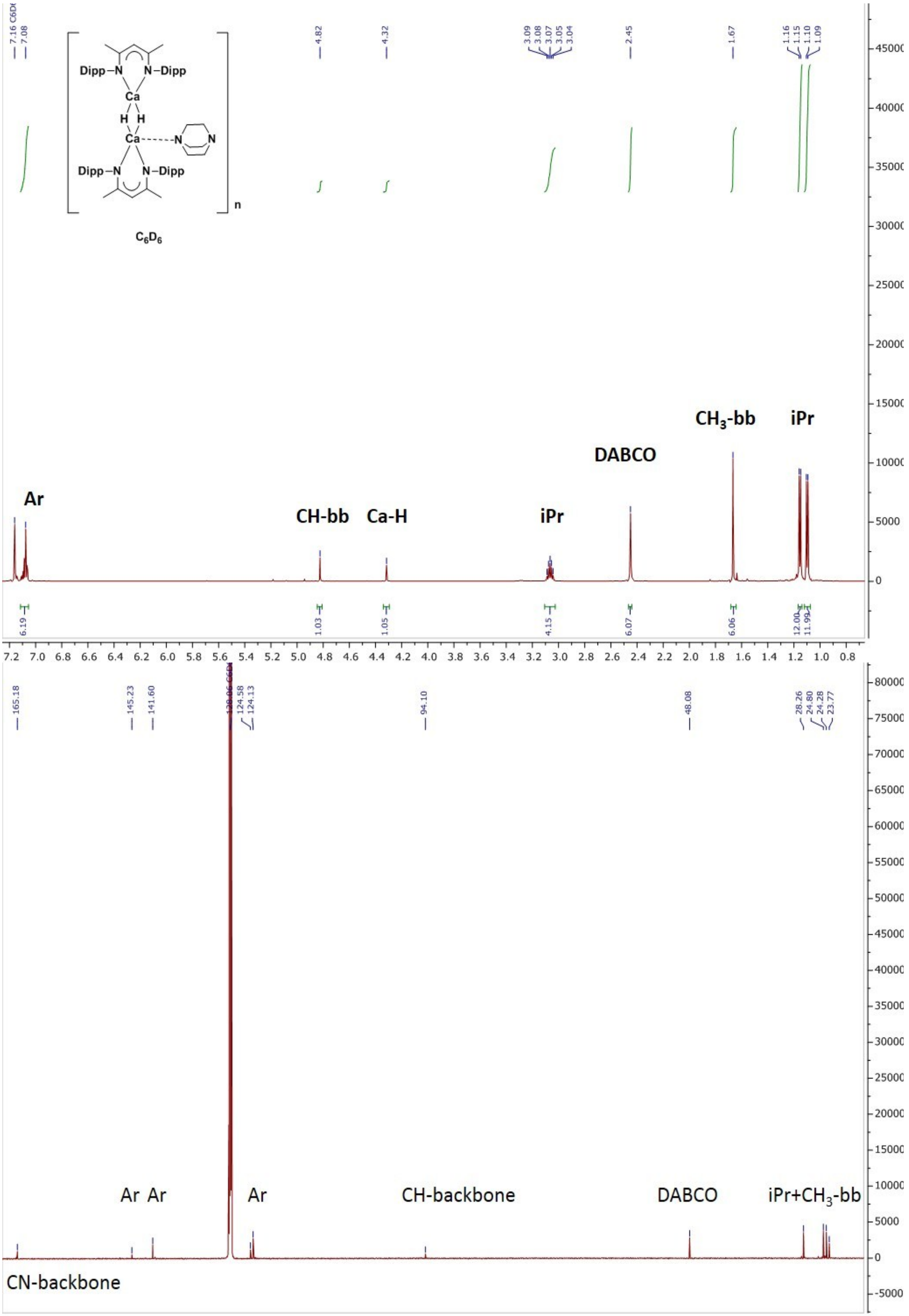


Figure S7. ^{1}H and ^{13}C spectra of [(DIPPnacnac)CaH]$_2$·DABCO in C_6D_6.

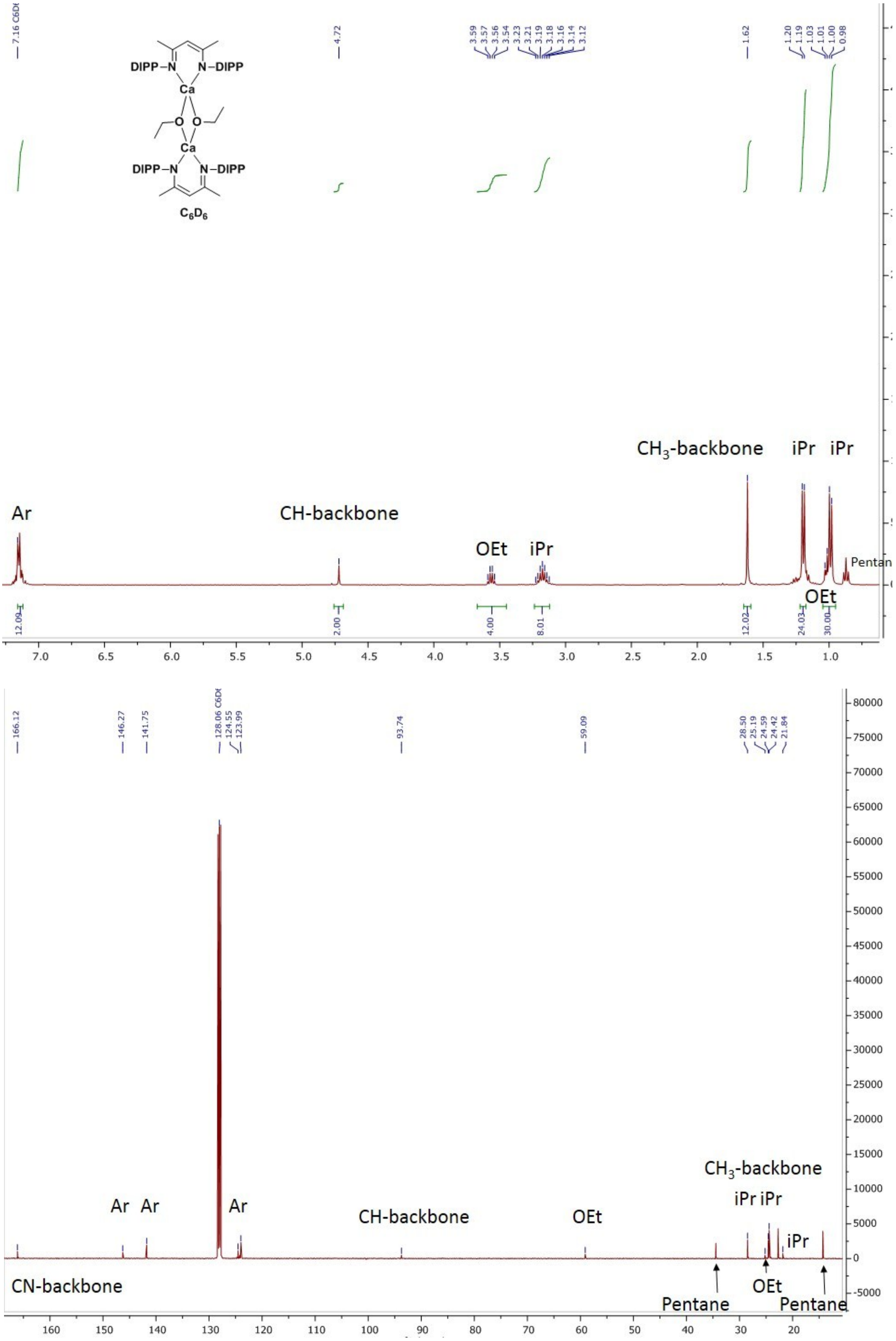


Figure S8. ^{1}H and ^{13}C spectra of [(DIPPnacnac)CaOEt]$_2$ in C_6D_6.

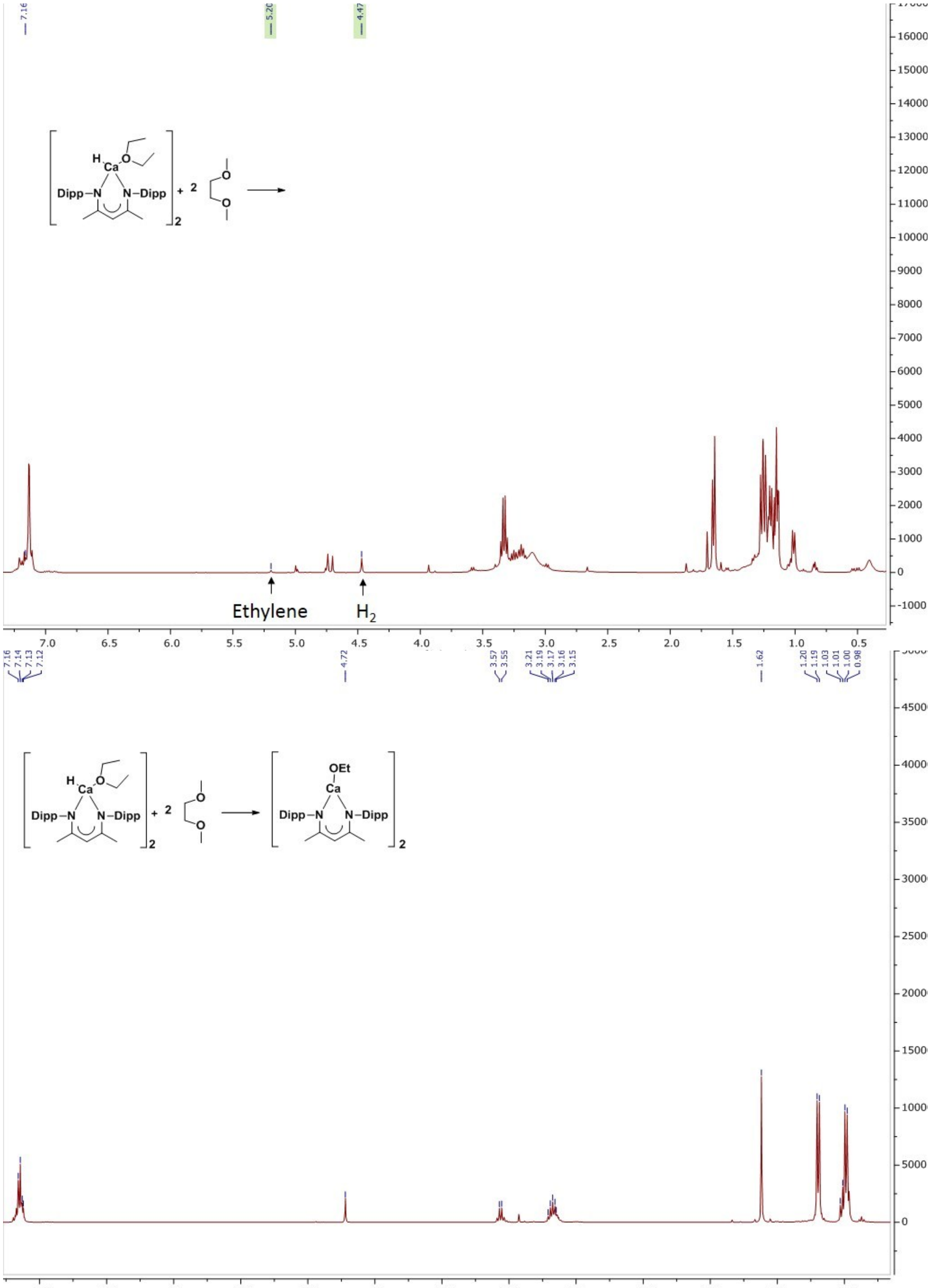


Figure S9. Reaction between and (DIPPnacnacCaH·OEt$_2$)$_2$ and DME. Already after five minutes ethylene and H$_2$ can be detected in solution. The final product in the lower spectrum is clearly (DIPPnacnac-CaOEt)$_2$.

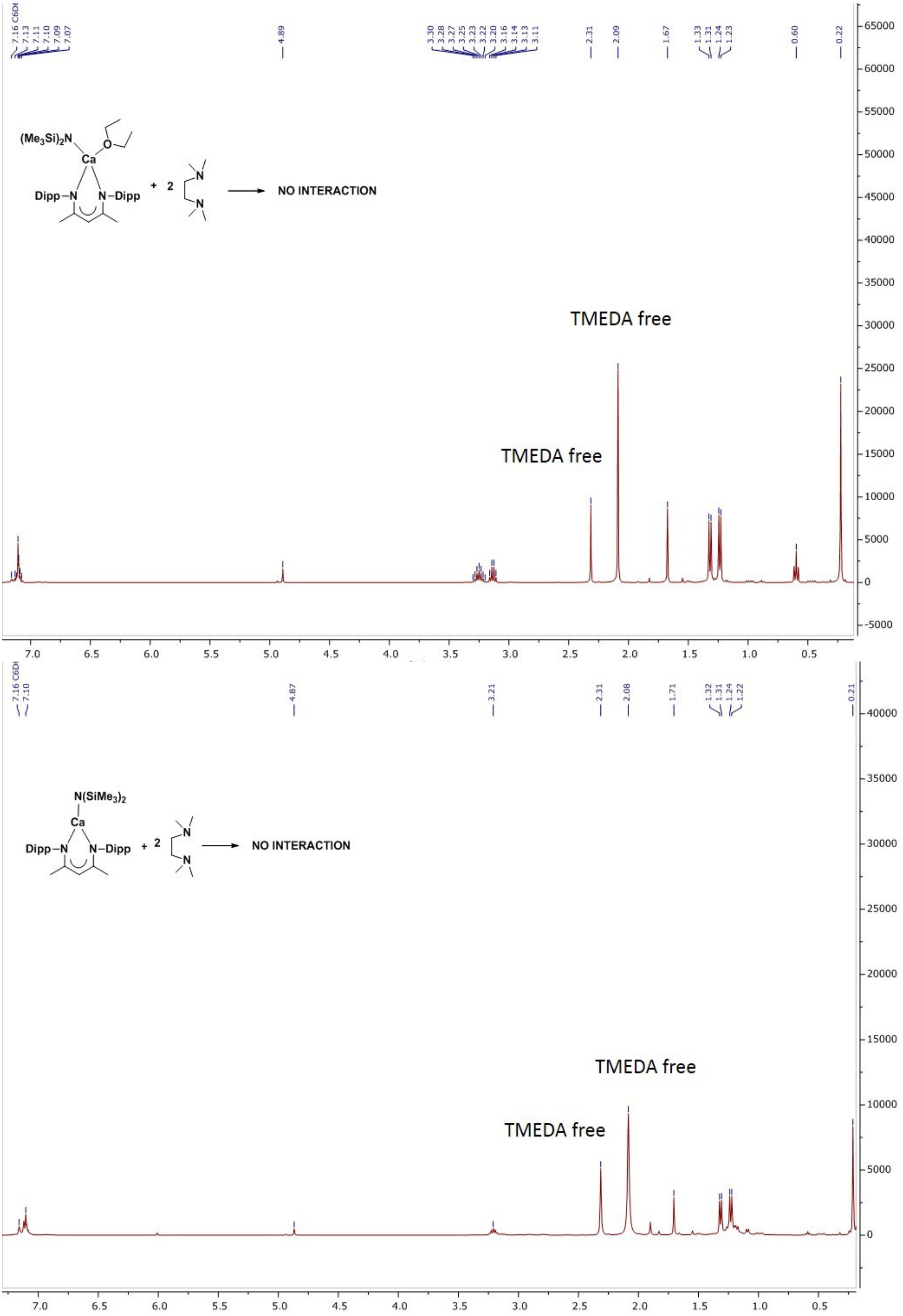


Figure S10. ^{1}H spectra of (DIPPnacnac)CaN(SiMe$_3$)$_2$-Et$_2$O and (DIPPnacnac)CaN(SiMe$_3$)$_2$ with 2 equivalents of TMEDA. There is no sign of interaction between TMEDA and Ca.

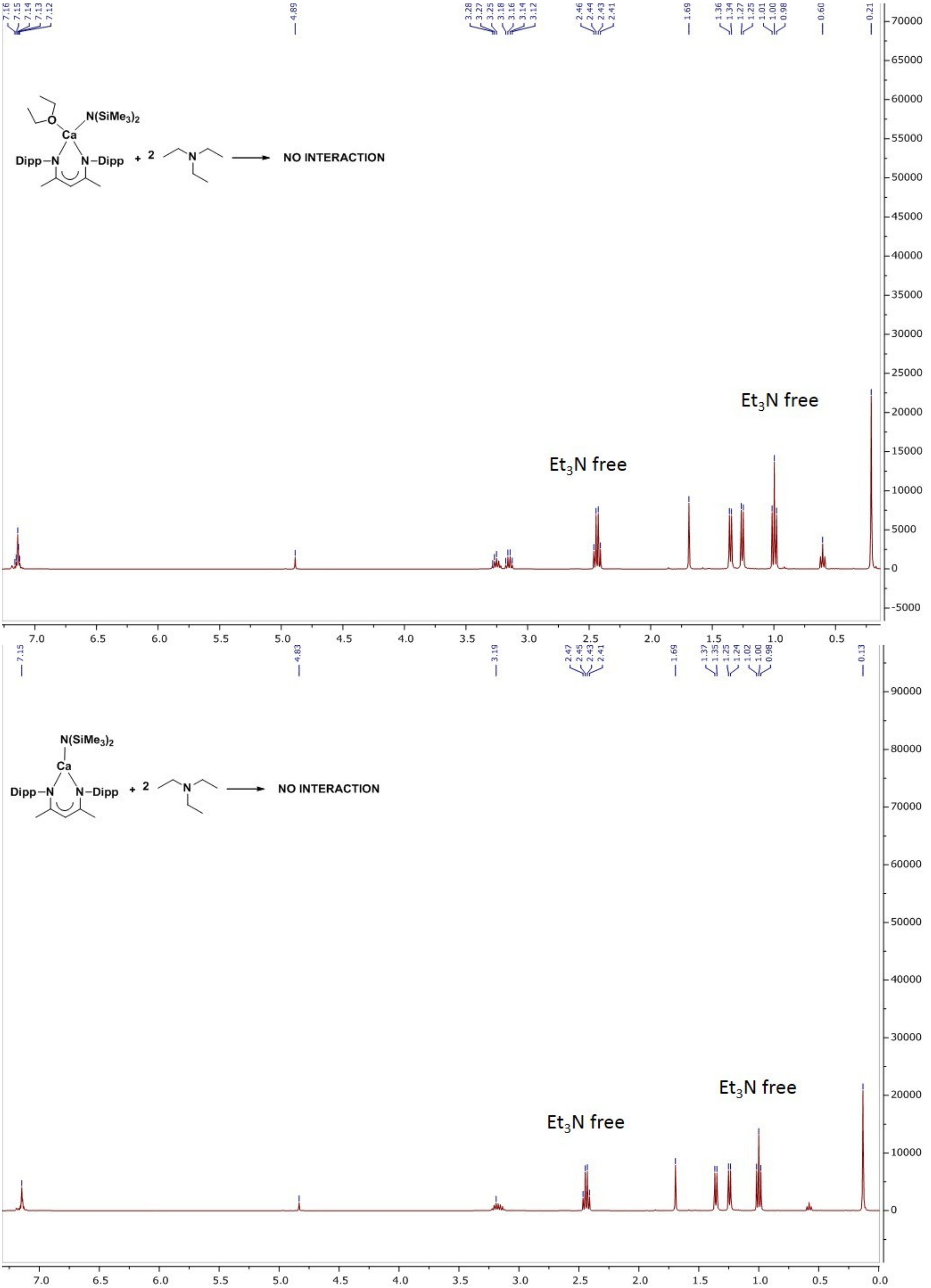


Figure S11. ^{1}H spectra of (DIPPnacnac)CaN(SiMe$_3$)$_2$-Et$_2$O and (DIPPnacnac)CaN(SiMe$_3$)$_2$ with 2 equivalents of Et$_3$N. There´s no sign of interaction and no Et$_2$O displacement.

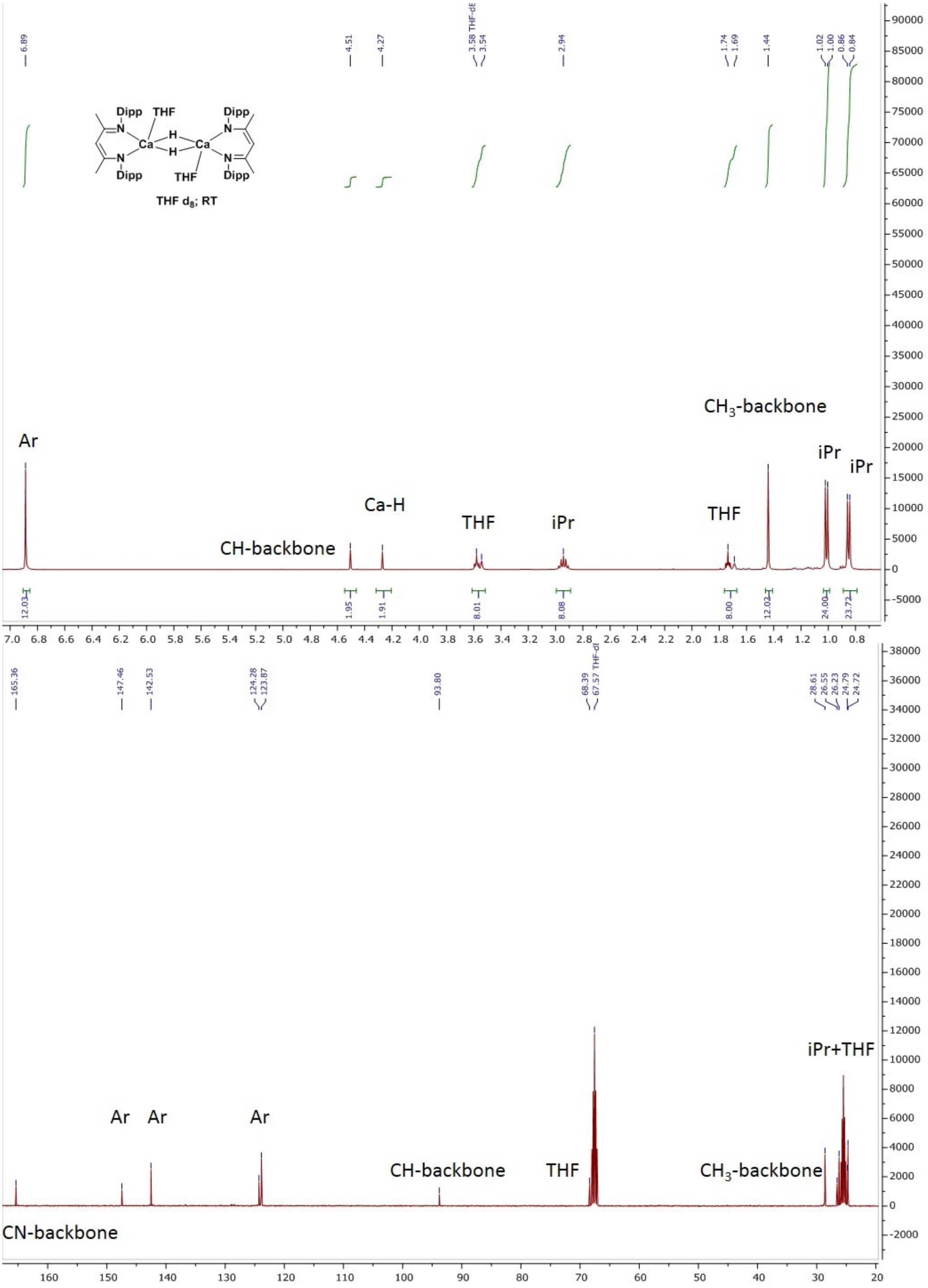
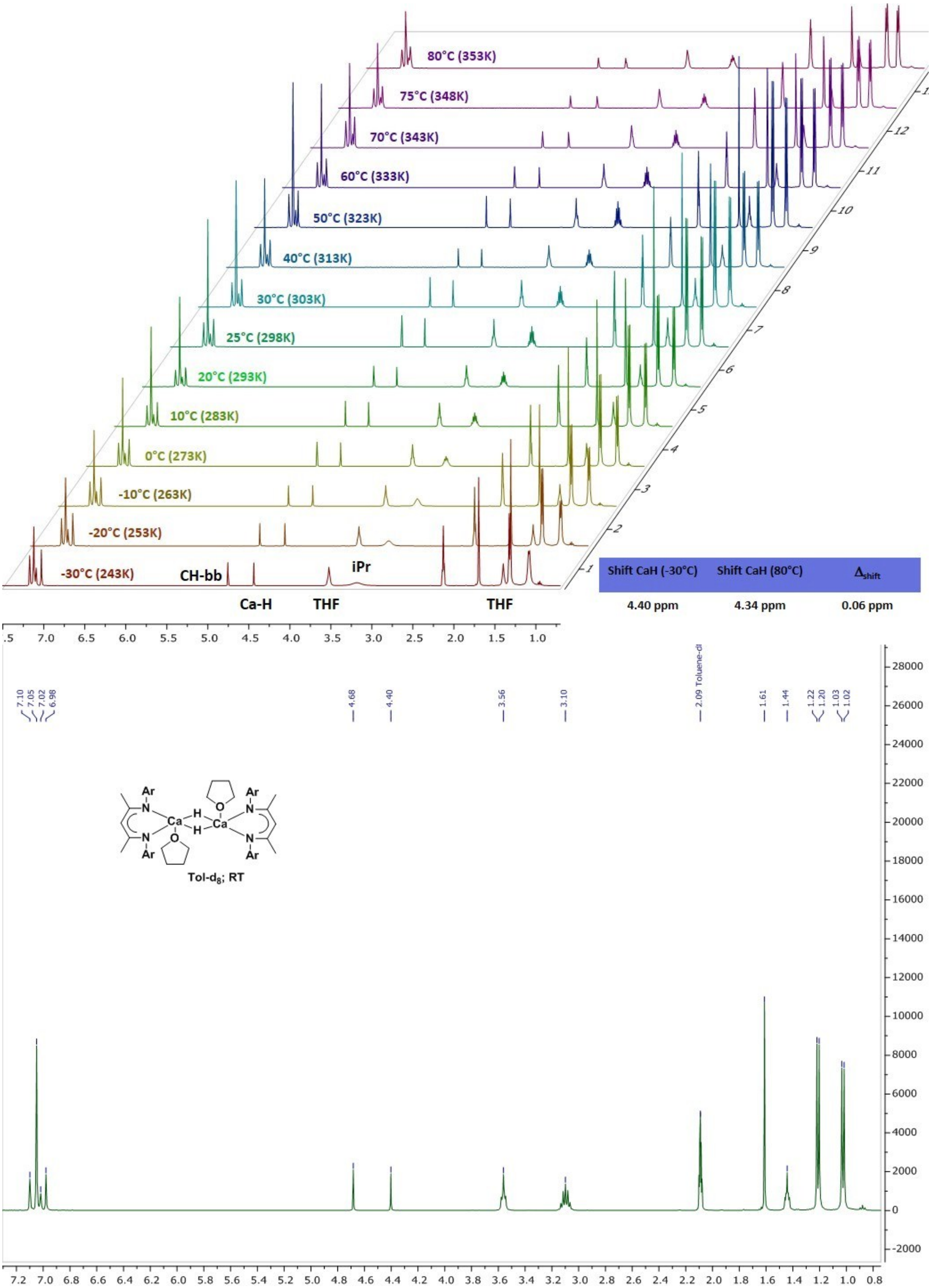


Figure S12. ^{1}H NMR and ^{13}C NMR spectra of [(DIPPnacnac)CaH·THF]$_2$ in THF-d$_8$.



Shift CaH (-30°C)	Shift CaH (80°C)	Δ_{shift}
4.40 ppm	4.34 ppm	0.06 ppm

Figure S13. Stacked spectra of [(DIPPnacnac)CaH·THF]$_2$ in toluene–d_8 at different temperatures (top: -30°C to 80°C; bottom: 20 °C). The stacked spectra do not show any appreciable temperature dependency of the hydride chemical shift.

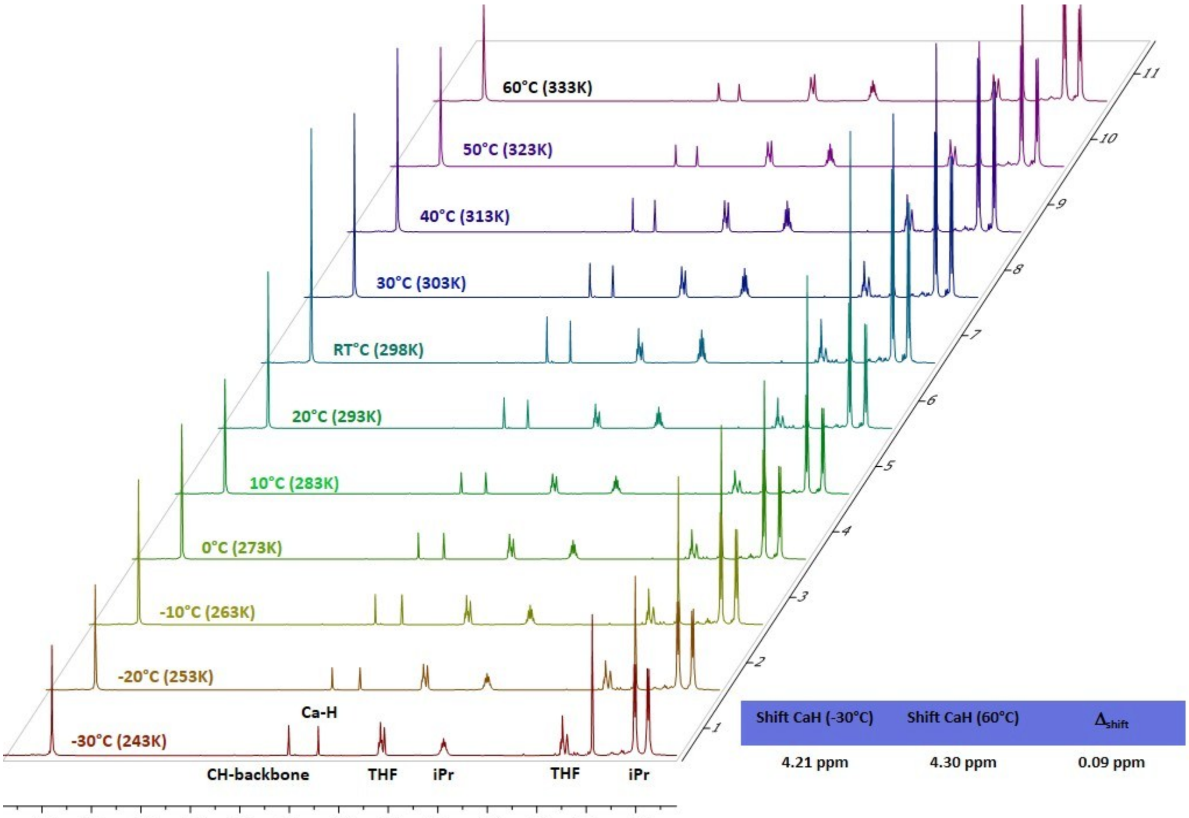


Figure S14. Stacked spectra of [(DIPPnacnac)CaH·THF]$_2$ in THF–d_8 at different temperatures (-30°C to 60°C). The stacked spectra do not show any appreciable temperature dependency of the hydride chemical shift.

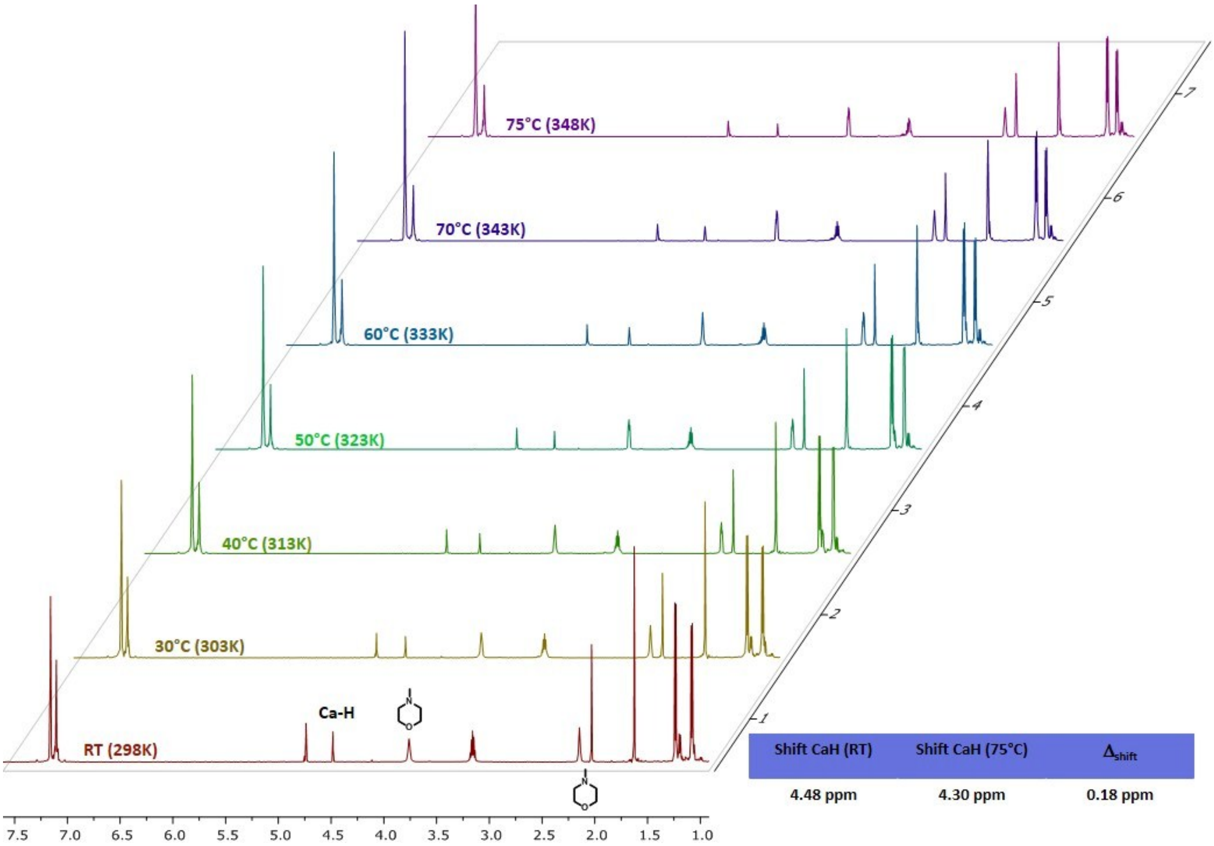


Figure S15. Stacked ^{1}H NMR spectra of [(DIPPnacnac)CaH·Morph]$_2$ in C_6D_6 at different temperatures (from 25°C to 75°C). The stacked spectra do not show any appreciable temperature dependency of the hydride chemical shift.

4. PGSE NMR measurements

Diffusion measurements were conducted on a Bruker AVANCE NMR spectrometer operating at 600.13 MHz for proton resonance equipped with a 5 mm PABDO BB/19F-1H/D probe with Z-GRD and actively shielded gradient coil with a maximum gradient strength of 5.3500094 G/mm (at 10 A).

Parameter optimization was carried out empirically employing the pulse programme ledbpgp2s1D using stimulated echo and LED (D21 = 5 ms, longitudinal eddy current delay as a Z-filter) with bipolar gradient pulses (P30) and two spoiling gradients (P19 = 600 µs) leading to values for gradient pulse length (P30 = 1400 µs, in case of bipolar gradients *little DELTA*0.5*) and diffusion time (D20 = 60 ms, *big DELTA*). Delay for gradient recovery was set to 200 µs.

The diffusion experiment was executed with variable gradients from 2% to 98% gradient strength with 32 increment values (difframp calculated with the AU-program *DOSY*). In this case the pulse program ledbpgp2s was applied for data aquiring of this pseudo-2D experiment. Data processing was performed with the T1/T2 software package (SimFit) of TopSpin (version 3.2, Bruker Biospin) by fitting area data (integration of all peaks of interest of the same molecule) of diffusion decays. From these Stejskal-Tanner fitting curves calculated diffusion constants were obtained and assimilated statistically.

4. References

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