SUPPORTING INFORMATION

Stabilization of Calcium Hydride Complexes by Fine-tuning of Amidinate Ligands

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1. Crystal structures

Experimental

All crystal structures have been measured on a SuperNova (Agilent) diffractometer with dual Cu and Mo microfocus sources and an Atlas S2 detector. Crystals were covered in paraffin oil, mounted on a flexible MiTeGen microloop and immediately transferred to a cold N_2 stream of 100 K. Structures were determined using Olex2,[1] ShelXT[2] for the structure solution by Direct Methods and ShelXL[3] for least squares refinement. Unless noted otherwise, the hydrogen atoms have been placed at idealized calculated positions and were refined isotropically using a riding model. In case special methods were used, the specific details of the refinement are given separately.

Crystal structure of $AdAm^{DIPP}CaN(SiMe_3)_2$

Identification code	hasj160303a
Empirical formula	$C_{41}H_{67}CaN_3Si_2$
Formula weight	698.23
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.87724(17)
b/Å	12.3264(2)
c/Å	33.7986(7)
α/°	90
β/°	92.2021(17)
γ/°	90
Volume/$Å^3$	4111.98(14)
Z	4
$\rho_{calc}g/cm^3$	1.128
μ/mm^{-1}	2.090
F(000)	1528.0
Crystal size/mm^3	0.1652 × 0.143 × 0.1011
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.634 to 136.236
Index ranges	$-10 \le h \le 11$, $-14 \le k \le 14$, $-40 \le l \le 37$
Reflections collected	14210
Independent reflections	7446 [R_{int} = 0.0394, R_{sigma} = 0.0508]
Data/restraints/parameters	7446/0/438
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0511, wR_2 = 0.1346
Final R indexes [all data]	R_1 = 0.0568, wR_2 = 0.1404
Largest diff. peak/hole / e $Å^{-3}$	0.70/-0.41

Crystal structure of *t*BuAm^{DIPP}CaN(SiMe$_3$)$_2$·Et$_2$O

The crystal was twinned over two domains and has been measured as such. The structure was refined using the data from both domains (HKLF5).

Identification code	hasj160321a_twin1_hklf5
Empirical formula	$C_{39}H_{71}CaN_3OSi_2$
Formula weight	694.24
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	10.6373(4)
b/Å	12.4259(3)
c/Å	16.4223(3)
α/°	90.146(2)
β/°	92.606(2)
γ/°	98.163(3)
Volume/Å^3	2146.36(10)
Z	2
ρ_{calc}g/cm^3	1.074
μ/mm^{-1}	2.014
F(000)	764.0
Crystal size/mm^3	0.3255 × 0.1707 × 0.1241
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.188 to 147.672
Index ranges	-13 ≤ h ≤ 13, -15 ≤ k ≤ 15, -20 ≤ l ≤ 20
Reflections collected	16049
Independent reflections	16049 [R_{int} = -, R_{sigma} = 0.0211]
Data/restraints/parameters	16049/0/434
Goodness-of-fit on F^2	1.078
Final R indexes [I>=2σ (I)]	R_1 = 0.0384, wR_2 = 0.1088
Final R indexes [all data]	R_1 = 0.0426, wR_2 = 0.1109
Largest diff. peak/hole / e Å^{-3}	0.75/-0.32

Crystal structure of $NpAm^{DIPP}CaN(SiMe_3)_2 \cdot Et_2O$

Disorder of two *i*Pr-groups was refined as two positions with an approximate ration of 75:25. The coordinated ether molecule has also 2 disordered positions each with an approximate ration of 75:25. The less occupied part of the ether molecule was modeled with Rigid Bond (RIGU) Restraints.[4] Additionally part of the disordered moiety was refined with equal displacement parameters (EADP). A result of the disordered Et_2O molecule is a short hydrogen distance of 1.91 Å between a $SiMe_3$ moiety of the adjacent unit cell and the less occupied part of the disorder.

Identification code	hasj151021a
Empirical formula	$C_{40}H_{73}CaN_3OSi_2$
Formula weight	708.27
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.7482(7)
b/Å	18.0397(7)
c/Å	16.8077(7)
α/°	90
β/°	94.156(5)
γ/°	90
Volume/$Å^3$	4460.0(3)
Z	4
$\rho_{calc}g/cm^3$	1.055
μ/mm^{-1}	1.947
F(000)	1560.0
Crystal size/mm^3	0.1961 × 0.0896 × 0.0687
Crystal color	colorless
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.008 to 136.23
Index ranges	$-16 \le h \le 17$, $-21 \le k \le 13$, $-20 \le l \le 19$
Reflections collected	14692
Independent reflections	8068 [R_{int} = 0.0632, R_{sigma} = 0.0713]
Data/restraints/parameters	8068/23/518
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0638, wR_2 = 0.1694
Final R indexes [all data]	R_1 = 0.0737, wR_2 = 0.1944
Largest diff. peak/hole / e $Å^{-3}$	0.49/-0.90

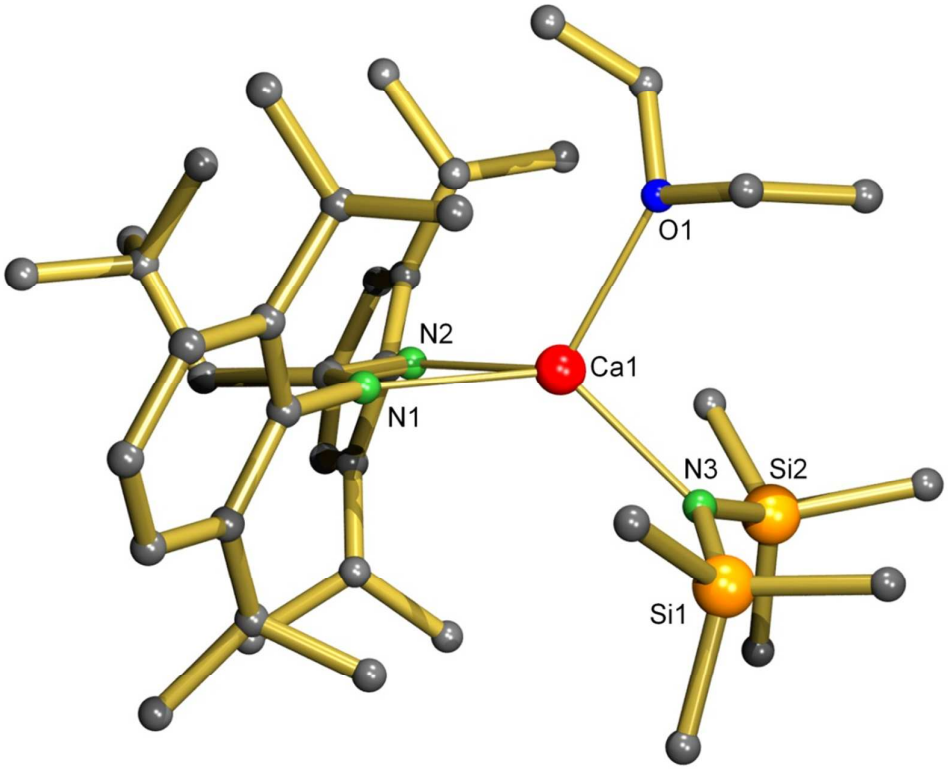

Figure S1. Crystal structure of $NpAm^{DIPP}CaN(SiMe_3)_2 \cdot Et_2O$.

Crystal structure of [*p*-TolAm^{DIPP}CaN(SiMe$_3$)$_2$]$_2$

The crystal was twinned over two domains and has been measured as such. The structure was refined using the data from both domains (HKLF5). The unit cell contains two dimers of which one was disordered with a ration of 80:20. The less occupied part of the disorder was modeled using idealized geometries for 6-ring (AFIX 66) and Rigid Bond (RIGU) Restraints. Additionally one *i*Pr-group was refined with equal displacement parameters (EADP).[4]

Identification code	HASJ150309C_twin1_hklf5
Empirical formula	$C_{104}H_{150}Ca_2N_6Si_4$
Formula weight	1676.81
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	16.3967(2)
b/Å	16.4260(3)
c/Å	21.1559(4)
α/°	110.503(2)
β/°	102.6180(10)
γ/°	100.0220(10)
Volume/Å^3	5008.65(16)
Z	2
ρ_{calc}g/cm^3	1.112
μ/mm^{-1}	1.796
F(000)	1824.0
Crystal size/mm^3	0.426 × 0.137 × 0.1309
Crystal color	colorless
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.744 to 136.434
Index ranges	-19 ≤ h ≤ 19, -19 ≤ k ≤ 19, -25 ≤ l ≤ 25
Reflections collected	32796
Independent reflections	32796 [R_{int} = -, R_{sigma} = 0.0157]
Data/restraints/parameters	32796/191/1284
Goodness-of-fit on F^2	1.068
Final R indexes [I>=2σ (I)]	R_1 = 0.0594, wR_2 = 0.1689
Final R indexes [all data]	R_1 = 0.0628, wR_2 = 0.1719
Largest diff. peak/hole / e Å^{-3}	0.86/-0.51

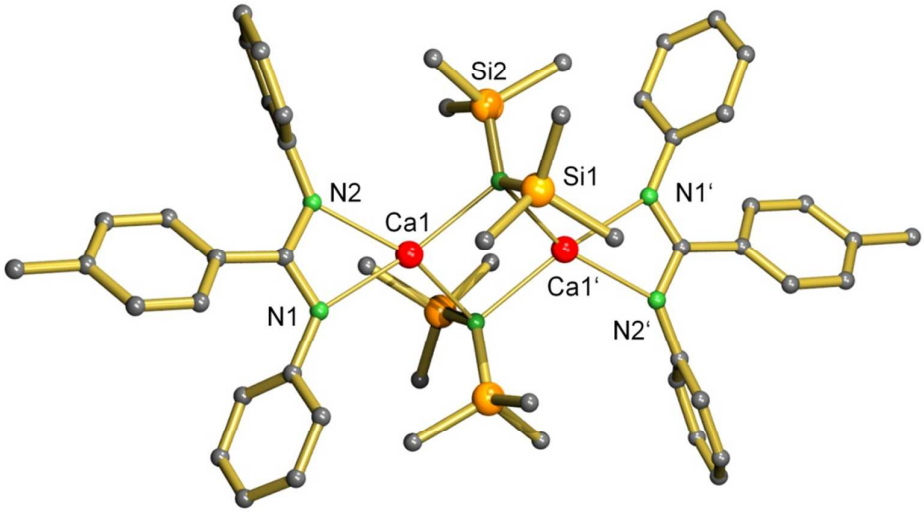

Figure S2. Crystal structure of [*p*-TolAm^{DIPP}CaN(SiMe$_3$)$_2$]$_2$; iPr substituents and H's omitted for clarity. Only one the two independent dimers is shown (the other dimer is disordered).

Crystal structure of $[MeAm^{DIPP}CaN(SiMe_3)_2]_2$

Solvent accessible voids contain disordered solvent. A satisfactory disorder model for the solvent was not found, and therefore the OLEX2 Solvent Mask routine (similar to PLATON/SQUEEZE) was used to mask out the disordered electron density.[5] A total void of 1004 Å³ per unit cell was filled with 339 e^-.

Identification code	hasj160412a
Empirical formula	$C_{64}H_{110}Ca_2N_6Si_4$
Formula weight	1156.09
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	11.78345(19)
b/Å	15.5905(2)
c/Å	23.5944(4)
α/°	102.6714(13)
β/°	94.2421(13)
γ/°	106.0615(14)
Volume/$Å^3$	4021.75(11)
Z	2
$\rho_{calc}g/cm^3$	0.955
μ/mm^{-1}	2.056
F(000)	1264.0
Crystal size/mm^3	0.3767 × 0.244 × 0.1763
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.004 to 136.228
Index ranges	-14 ≤ h ≤ 14, -18 ≤ k ≤ 14, -28 ≤ l ≤ 28
Reflections collected	43916
Independent reflections	14614 [R_{int} = 0.0364, R_{sigma} = 0.0342]
Data/restraints/parameters	14614/0/715
Goodness-of-fit on F^2	1.022
Final R indexes [I>=2σ (I)]	R_1 = 0.0403, wR_2 = 0.1109
Final R indexes [all data]	R_1 = 0.0435, wR_2 = 0.1136
Largest diff. peak/hole / e $Å^{-3}$	0.47/-0.33

Crystal structure of (*t*BuAm^{DIPP}CaH)$_2$

Measurement of the crystal using standard procedures gave the following unit cell:

a = 10.5832(4) Å, b = 10.5905(4) Å, c = 14.2888(5) Å, α = 109.789(4)°, β = 94.757(3)°, γ = 109.004(4)°, V = 1390.8(5) Å^3. Triclinic, P-1, one centrosymmetric dimer per unit cell.

Although the structure could be solved, refinement gave poor *R*-values and thermal displacement factors. It became clear from weaker intermittent satellite reflexes that the structure is modulated.

The structure was transformed to a super cell with following parameters:

a = 19.7248(6) Å, b = 20.4652(9) Å, c = 26.5472(8) Å, α = 112.570(4)°, β = 93.971(2)°, γ = 96.699(2)°, V = 9752(1) Å^3. Triclinic, P-1, seven dimers per unit cell.

Refinement in the super cell gave a more reliable structure refinement but due to many very weak reflexes, refinement as a modulated structure should be preferred. Since the structure of (*t*BuAm^{DIPP}CaH)$_2$ is similar to that of (AdAm^{DIPP}CaH)$_2$, which could be determined without crystallographic artefacts, we report here only data for the latter.

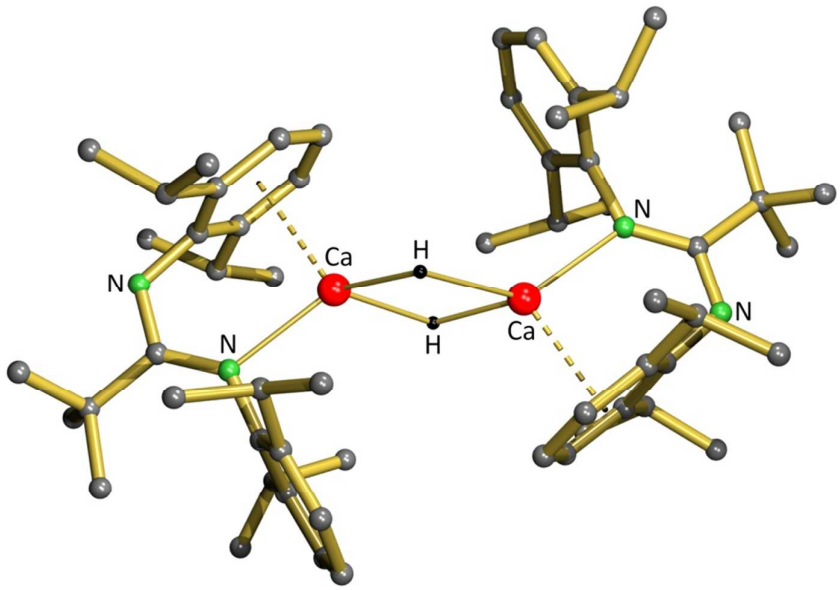

Figure S3. Crystal structure of (*t*BuAm^{DIPP}CaH)$_2$ solved in a super cell. Only one of the 3.5 dimers in the asymmetric unit is shown. Due to modulation problems only connectivity is shown.

Crystal structure of $(AdAm^{DIPP}CaH)_2$

The hydridic hydrogen atoms could be localized in the difference Fourier map and were refined isotropically. At two positions two co-crystallized benzene molecules could be observed which were in each case disordered over two position with a ratio of approximately 1:1. Due to substantial differences in C-C bond lengths of the disordered benzene molecules an idealized geometry was used (AFIX 66).[4]

Identification code	hasj151204b
Empirical formula	$C_{94}H_{124}Ca_2N_4$
Formula weight	1390.12
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	10.4550(2)
b/Å	10.5225(2)
c/Å	19.8508(3)
α/°	83.3598(15)
β/°	87.9438(15)
γ/°	69.2211(18)
Volume/Å^3	2028.06(7)
Z	1
ρ_{calc}g/cm^3	1.138
μ/mm^{-1}	1.569
F(000)	756.0
Crystal size/mm^3	0.4655 × 0.1638 × 0.1088
Crystal color	colorless
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.97 to 136.186
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -23 ≤ l ≤ 23
Reflections collected	41056
Independent reflections	7410 [R_{int} = 0.0728, R_{sigma} = 0.0371]
Data/restraints/parameters	7410/36/537
Goodness-of-fit on F^2	1.022
Final R indexes [I>=2σ (I)]	R_1 = 0.0569, wR_2 = 0.1546
Final R indexes [all data]	R_1 = 0.0596, wR_2 = 0.1570
Largest diff. peak/hole / e Å^{-3}	0.72/-0.57

Crystal structure of $(t\text{BuAm}^{\text{DIPP}}\text{CaH})_3 \cdot (\text{Et}_2\text{O})_2$

Solvent accessible voids contain disordered solvent. A satisfactory disorder model for the solvent was not found, and therefore the OLEX2 Solvent Mask routine (similar to PLATON/SQUEEZE) was used to mask out the disordered electron density.[5] A total void of 1696 Å³ per unit cell was filled with 463 e^-.

Identification code	hasj150424a
Empirical formula	$C_{95}H_{152}Ca_3N_6O_6$
Formula weight	1530.48
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	27.3041(2)
b/Å	12.4085(1)
c/Å	58.1368(3)
α/°	90
β/°	94.455(1)
γ/°	90
Volume/Å^3	19637.5(2)(7)
Z	8
ρ_{calc}g/cm^3	1.035
μ/mm^{-1}	1.800
F(000)	6720
Crystal size/mm^3	0.12 × 0.08 × 0.04
Crystal color	colorless
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.0 to 147.4
Index ranges	-30 ≤ h ≤ 33, -14 ≤ k ≤ 14, -72 ≤ l ≤ 68
Reflections collected	115425
Independent reflections	38340 [R_{int} = 0.047, R_{sigma} = 0.0368]
Data/restraints/parameters	38340/0/1933
Goodness-of-fit on F^2	1.03
Final R indexes [I>=2σ (I)]	R_1 = 0.0510, wR_2 = 0.1409
Largest diff. peak/hole / e Å^{-3}	1.08/-0.98

Crystal structure of $(AdAm^{DIPP}CaH)_3 \cdot (THF)_2$

The hydridic hydrogen atoms could be localized in the difference Fourier map and were refined isotropically. Solvent accessible voids contain disordered solvent. A satisfactory disorder model for the solvent was not found, and therefore the OLEX2 Solvent Mask routine (similar to PLATON/SQUEEZE) was used to mask out the disordered electron density.[5] A total void of 1318 Å³ per unit cell was filled with 345 e^-.

Identification code	hasj151127b
Empirical formula	$C_{119}H_{180}Ca_3N_6O_2$
Formula weight	1846.92
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	15.1967(2)
b/Å	18.2301(3)
c/Å	25.8609(4)
α/°	92.8035(13)
β/°	101.6317(12)
γ/°	114.0730(15)
Volume/Å^3	6337.72(18)
Z	2
ρ_{calc}g/cm^3	0.968
μ/mm^{-1}	1.463
F(000)	2024.0
Crystal size/mm^3	0.3117 × 0.2182 × 0.1941
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.468 to 136.236
Index ranges	-18 ≤ h ≤ 18, -21 ≤ k ≤ 19, -30 ≤ l ≤ 31
Reflections collected	39256
Independent reflections	22879 [R_{int} = 0.0317, R_{sigma} = 0.0447]
Data/restraints/parameters	22879/0/1209
Goodness-of-fit on F^2	1.070
Final R indexes [I>=2σ (I)]	R_1 = 0.0552, wR_2 = 0.1541
Final R indexes [all data]	R_1 = 0.0631, wR_2 = 0.1623
Largest diff. peak/hole / e Å^{-3}	0.89/-0.51

Crystal structure of (*t*BuAm^{Mes})$_2$Ca·Et$_2$O

The two *t*Bu-backbone substituents are rotationally disordered over two positions with an approximate ratio of 85:15. This was treated using an appropriate disorder model.

Identification code	hasj151102a
Empirical formula	$C_{50}H_{72}CaN_4O$
Formula weight	785.19
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.12062(13)
b/Å	16.59171(16)
c/Å	22.9746(2)
α/°	90
β/°	90.4699(9)
γ/°	90
Volume/Å^3	4620.09(8)
Z	4
ρ_{calc}g/cm^3	1.129
μ/mm^{-1}	1.458
F(000)	1712.0
Crystal size/mm^3	0.4097 × 0.3125 × 0.1885
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.572 to 136.232
Index ranges	-14 ≤ h ≤ 14, -17 ≤ k ≤ 19, -27 ≤ l ≤ 27
Reflections collected	49263
Independent reflections	8433 [R_{int} = 0.0405, R_{sigma} = 0.0220]
Data/restraints/parameters	8433/0/587
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0363, wR_2 = 0.0991
Final R indexes [all data]	R_1 = 0.0376, wR_2 = 0.1004
Largest diff. peak/hole / e Å^{-3}	0.24/-0.19

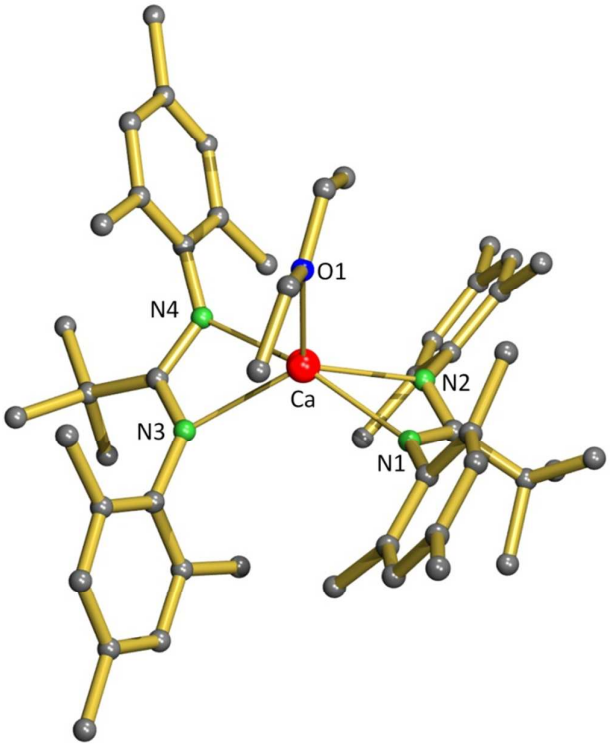

Figure S4. Crystal structure of (tBuAm^{Mes})$_2$Ca·Et$_2$O. Selected bond distances (Å) and angles (°): Ca-N1 2.406(1), Ca-N2 2.397(1), Ca-N3 2.401(1), Ca-N4 2.410(1), Ca-O1 2.407(1), N1-Ca-N2 54.89(4), N3-Ca-N4 55.15(4).

Crystal structure of $(MeAm^{DIPP})[N(SiMe_3)_2]_2CaK$

Identification code	hasj160404b
Empirical formula	$C_{38}H_{73}CaKN_4Si_4$
Formula weight	777.54
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	18.9149(2)
b/Å	11.58948(14)
c/Å	21.6672(3)
α/°	90
β/°	99.4158(12)
γ/°	90
Volume/Å^3	4685.75(10)
Z	4
ρ_{calc}g/cm^3	1.102
μ/mm^{-1}	3.136
F(000)	1696.0
Crystal size/mm^3	0.3174 × 0.082 × 0.0604
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.272 to 136.232
Index ranges	-22 ≤ h ≤ 22, -9 ≤ k ≤ 13, -26 ≤ l ≤ 24
Reflections collected	16064
Independent reflections	8501 [R_{int} = 0.0297, R_{sigma} = 0.0412]
Data/restraints/parameters	8501/0/454
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0370, wR_2 = 0.0976
Final R indexes [all data]	R_1 = 0.0419, wR_2 = 0.1021
Largest diff. peak/hole / e Å^{-3}	0.44/-0.45

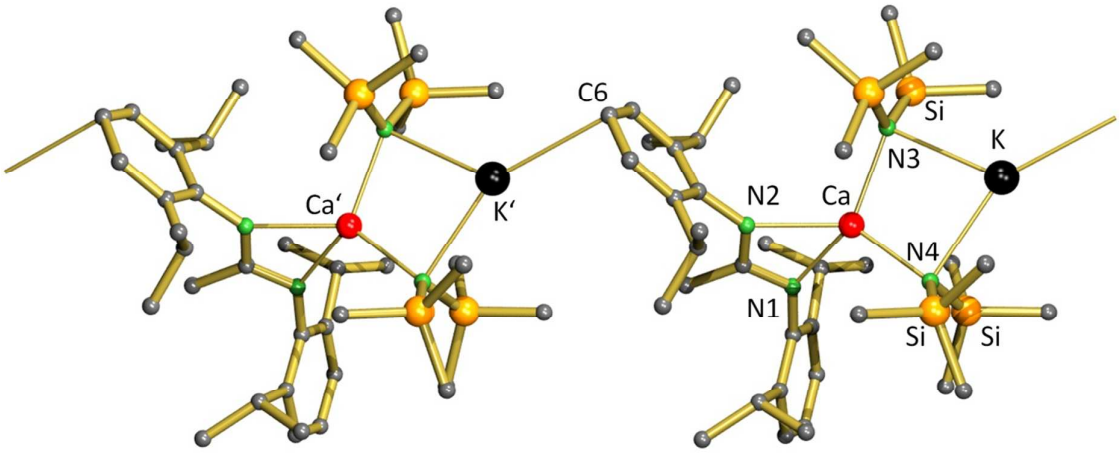

Figure S5. Crystal structure of (MeAm^{DIPP})[N(SiMe$_3$)$_2$]$_2$CaK. Selected bond distances (Å) and angles (°): Ca-N1 2.397(1), Ca-N2 2.408(1), Ca-N3 2.377(1), Ca-N4 2.375(1), K-N3 2.871(1), K-N4 2.997(1), C6-K' 3.106(2), N1-Ca-N2 56.32(5), N3-Ca-N4 105.02(5), N3-K-N4 79.94(4).

Crystal structure of $(AdAm^{DIPP})Ca[N(SiMe_3)_2]\cdot THF$

Identification code	hasj160706
Empirical formula	$C_{144}H_{234}Ca_3N_9O_3Si_6$
Formula weight	2428.29
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	31.2740(5)
b/Å	22.9849(2)
c/Å	21.3045(2)
α/°	90
β/°	108.0355(13)
γ/°	90
Volume/Å^3	14561.8(3)
Z	4
ρ_{calc}g/cm^3	1.108
μ/mm^{-1}	1.848
F(000)	5316.0
Crystal size/mm^3	0.33 × 0.20 × 0.33
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.8 to 136.2
Index ranges	-36 ≤ h ≤ 37, -27 ≤ k ≤ 15, -25 ≤ l ≤ 21
Reflections collected	53201
Independent reflections	26403 [R_{int} = 0.031, R_{sigma} = 0.043]
Data/restraints/parameters	26403/0/1528
Goodness-of-fit on F^2	1.03
Final R indexes [I>=2σ (I)]	R_1 = 0.0437, wR_2 = 0.1177
Largest diff. peak/hole / e Å^{-3}	0.98/-0.40

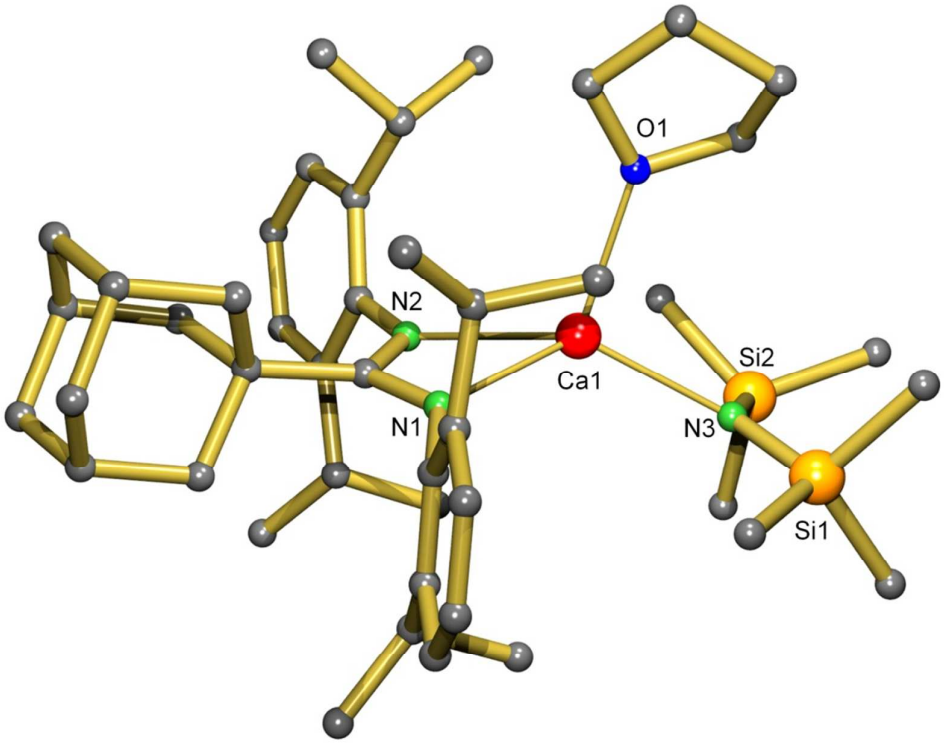

Figure S6. Crystal structure of *t*BuAm^{DIPP}Ca[N(SiMe$_3$)$_2$]$_2$·THF. Selected bond distances (Å) and angles (°) (average values from three independent molecules: Ca-N1 2.327(2), Ca-N2 2.399(2), Ca-N3 2.300(2), Ca-O1 2.348(2), N1-Ca-N2 112.19(1).

2. Ligand syntheses: $NpAm^{DIPP}H$, $AdAm^{DIPP}H$

Synthesis of AdC(O)N(H)DIPP In a 500ml Schlenk flask, 2,6-diisopropylaniline (4.74 ml, 25.2 mmol) and triethylamine (3.50 ml, 25.2 mmol) were stirred in ethyl acetate (150 ml) under N_2, and adamantanecarbonyl chloride (5.00 g, 25.2 mmol) was dissolved in 100 ml of ethyl acetate to be added slowly and drop wise. The solution got immediately turbid, and the reaction was placed at 70 °C under reflux conditions for three hours. The suspension was washed with water (3x 200 ml), collected apart and the solvent removed under high vacuum. Yield: 8.52 g, 25.1 mmol, 99.8%. Two stereo-isomers (trans/cis) in a 67/33 ratio were observed. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.19 (67%, d, $^3J_{HH}$ = 6.8 Hz, 12H), 1.28 (33%, d, *J* = 6.8 Hz, 12H), 1.47 – 2.23 (m, 15H), 2.92 (33%, hept, $^3J_{HH}$ = 6.9 Hz, 2H), 3.01 (67%, hept, $^3J_{HH}$ = 6.9 Hz, 2H), 3.74 (s, 1H), 6.81 (t, $^3J_{HH}$ = 7.7 Hz, 1H), 7.04 (33%, d, $^3J_{HH}$ = 7.7 Hz, 2H), 7.16 (67%, d, $^3J_{HH}$ = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 22.6 (iPr), 23.6 (Ad), 23.68 (Ad), 27.83 (Ad), 28.09 (iPr), 28.41 (Ad), 28.83 (Ad), 36.47 (Ad), 36.71 (Ad), 38.43 (Ad), 39.60 (Ad), 39.71 (Ad), 41.37 (iPr), 118.66 (Ar), 122.92 (Ar), 123.43 (Ar), 128.16 (Ar), 131.58 (Ar), 132.59 (Ar), 146.28 (Ar), 176.75 (CO). Elemental analysis: Calculated for $C_{23}H_{33}NO$: C 81.37, H 9.80; Found: C 81.17, H 9.73.

Synthesis of AdC(Cl)NDIPP In a 500 ml Schlenk flask AdC(O)N(H)DIPP (6.00 g, 17.7 mmol) was suspended in dry toluene (200 ml), then PCl_5 (3.86 g, 18.6 mmol) was added under N_2 and the reaction was placed at 60°C for 3 days. The solvent was removed under high vacuum and the resulting off white dust was left under high vacuum at 85°C for 2h to remove both byproduct and unreacted PCl_5, and used without any additional purification. Yield: 6.21 g, 17.35 mmol, 98.2%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.21 (d, $^3J_{HH}$ = 6.8 Hz, 12H, iPr), 1.64 – 2.21 (m, 15H, Ad), 2.76 (d, $^3J_{HH}$ = 6.9 Hz, 2H, hept), 7.08 – 7.22 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 28.45 (iPr), 36.21 (Ad), 36.67 (Ad), 39.16 (Ad), 40.63 (Ad), 45.66 (iPr), 122.98 (Ar), 124.47 (Ar), 136.54 (Ar), 143.40 (Ar), 154.60 (NCCl). Elemental analysis: Calculated for $C_{23}H_{32}ClN$: C 77.17, H 9.01; Found: C 77.20, H 9.09.

Synthesis of $AdAm^{DIPP}H$ In a 500 ml Schlenk flask AdC(Cl)NDIPP (6.21 g, 17.4 mmol) was dissolved in dry toluene (200 ml) and reacted under N_2 with 2,6-diisopropylaniline (3.6 ml, 19.1 mmol) at 110°C under reflux conditions for 5d. The volatiles were removed under high vacuum and the resulting pale pink dust suspended in Et_2O (400 ml) and then washed with a saturated solution of K_2CO_3 (250 ml), brine (250 ml) and water (300 ml). The organic phase was collected, dried with $MgSO_4$ and filtered. The product was obtained pure recrystallizing it from methanol. Yield: 6.15 g, 12.33 mmol, 71%. ^{1}H NMR (600 MHz, Chloroform-*d*): δ= 0.94 (d, $^3J_{HH}$ = 6.9 Hz, 6H, iPr), 1.18 – 1.40 (m, 18H, iPr), 1.56 – 2.04 (m, 15H, Ad), 3.08 (hept, $^3J_{HH}$ = 6.9 Hz, 2H, iPr), 3.37 (hept, $^3J_{HH}$ = 6.9 Hz, 2H, iPr), 5.17 (bs, 1H), 6.94 – 7.25 (m, 6H, Ar). ^{13}C NMR (151 MHz, $CDCl_3$): δ= 21.70 (iPr), 22.18 (iPr), 24.25 (iPr), 25.97 (iPr), 28.77 (Ad), 36.83 (Ad), 40.99 (Ad), 42.00 (Ad), 122.30 (Ar), 122.78 (Ar), 123.19 (Ar), 128.17 (Ar), 136.18 (Ar), 138.45 (Ar), 144.88 (Ar), 147.58 (Ar), 159.10 (NCN). Elemental analysis: Calculated for $C_{35}H_{50}N_2$: C 84.28, H 10.10, N 5.62; Found: C 84.55, H 10.13, N 5.64.

Synthesis of NpC(O)N(H)DIPP In a 500ml Schlenk flask, 2,6-diisopropylaniline (5.60 ml, 29.7 mmol) and triethylamine (4.10 ml, 29.7 mmol) were stirred in ethyl acetate (200 ml) under N_2. 3,3-dimethylbutyryl chloride (4.00 g, 29.7 mmol) was separately dissolved in ethyl acetate (100 ml) and added drop wise. The solution got immediately turbid, and the reaction was placed at 50 °C for 3h. The suspension was washed with water (3x 200ml), collected apart and

the solvent removed under high vacuum. Yield: 8.15 g, 29.6 mmol, 99.7%. ^{1}H NMR (400 MHz, Chloroform-*d*): δ= 1.14 (s, 9H, tBu-Np), 1.19 (d, $^{3}J_{HH}$ = 6.9 Hz, 12H, iPr), 2.31 (s, 2H, CH_2-Np), 3.10 (hept, $^{3}J_{HH}$ = 6.9 Hz, 2H, iPr), 6.60 (s, 1H, NH), 7.12 – 7.31 (m, 3H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$) δ 23.82, 28.92, 30.08, 31.30, 50.71, 123.51, 128.42, 131.45, 146.38, 171.23. ^{13}C NMR (101 MHz, $CDCl_3$): δ= 23.82 (CH_2-Neopent), 28.92 (iPr), 30.08 (CH_3-Np), 31.30 (C-Np), 50.71 (iPr), 123.51 (Ar), 128.42 (Ar), 131.45 (Ar), 146.38 (Ar), 171.23 (CO). Elemental analysis: Calculated for $C_{18}H_{29}NO$: C 78.49, H 10.61; Found: C 78.36, H 10.55.

Synthesis of NpC(Cl)NDIPP In a 500ml Schlenk flask NpC(O)N(H)DIPP (8.15 g, 29.6 mmol) was suspended in dry toluene (150 ml), then PCl_5 (6.47 g, 31.1 mmol) was added under N_2 and the reaction was placed at 60°C for 3 days. The solvent was removed under high vacuum and the resulting off white dust was left under high vacuum at 85°C for 2h to remove both byproduct and unreacted PCl_5, and used without any additional purification. Yield: 8.15 g, 29.5 mmol, 93.7%. ^{1}H NMR (600 MHz, $CDCl_3$): δ= 1.20 – 1.24 (m, 21H, tBu-Np + iPr), 2.83 (s, 2H, CH_2-Np), 2.86 (d, $^{3}J_{HH}$ = 6.9 Hz, 2H, iPr), 7.16 – 7.18 (m, 3H, Ar). ^{13}C NMR (151 MHz, $CDCl_3$): δ = 23.34 (CH_2-Neopent), 28.61 (iPr), 29.74 (CH_3-Neopent), 32.25 (C-Np), 55.84 (iPr), 123.09 (Ar), 124.89 (Ar), 136.86 (Ar), 143.53 (Ar), 168.26 (Ar). Elemental analysis: Calculated for $C_{18}H_{28}ClN$: C 73.57, H 9.60, N 4.77; Found: C 73.55, H 9.69, N 4.64.

Synthesis of NpAm^{DIPP}H In a 500 ml Schlenk flask NpC(Cl)NDIPP (8.66 g, 29.5 mmol) was dissolved in dry toluene (150 ml) and reacted under N_2 with 2,6-diisopropylaniline (5.8 ml, 30.9 mmol) at 110°C under reflux conditions for 3d. The volatiles were removed under high vacuum and the resulting pale yellow dust suspended in Et_2O (400 ml) and then washed with a saturated solution of K_2CO_3 (250 ml), brine (250 ml) and water (300 ml). The organic phase was collected, dried with $MgSO_4$ and filtered. The product was obtained pure recrystallizing it from methanol. Yield: 10.53 g, 24.2 mmol, 82.1%. ^{1}H NMR (400 MHz, Chloroform-*d*): δ= 0.96 – 1.37 (m, 33H, iPr+tBu-Np), 1.82 – 1.96 (m, 2H, CH_2-Np), 2.92 – 3.46 (m, 4H, iPr), 5.14 – 5.48 (m, 1H, NH), 6.98 – 7.25 (m, 6H, Ar). ^{13}C NMR (101 MHz, $CDCl_3$): δ= 22.14 (CH_3-Neopent), 23.19 (iPr), 24.85 (iPr), 25.12 (C-Np), 28.27 (iPr), 28.67 (iPr), 29.98 (CH_2-Neopent), 30.91 (iPr), 43.49 (iPr), 122.62 (Ar), 123.04 (Ar), 123.66 (Ar), 128.11 (Ar), 133.68 (Ar), 138.89 (Ar), 144.53 (Ar), 147.05 (Ar), 153.02 (NCN). Elemental analysis: Calculated for $C_{30}H_{46}N_2$: C 82.89, H 10.67, N 6.44; Found: C 82.94, H 10.70, N 6.48.

3. Complex syntheses: (*t*BuAm^{Mes})$_2$Ca·Et$_2$O, (MeAm^{DIPP})[N(SiMe$_3$)$_2$]$_2$CaK

Synthesis of (*t*BuAm^{Mes})$_2$Ca·Et$_2$O Attempted preparation of *t*BuAm^{Mes}CaN(SiMe$_3$)$_2$ according to the routes A and B (Scheme 3b) gave in both cases the homoleptic *bis*-amidinate calcium product. Route A: *t*BuAm^{Mes}H (300 mg, 0.89 mmol) and KN(SiMe$_3$)$_2$ (355 mg, 1.78 mmol)) were dissolved in 20 ml of Et$_2$O and stirred at room temperature for one hour. Then CaI$_2$ (262 mg, 0.89 mmol) was added under N$_2$ and the slurry was stirred at 40 °C under reflux conditions for two days. Et$_2$O was removed under vacuum and the product was extracted with 20 ml of hexane. After centrifugation, the hexane phase was separated from the precipitate and concentrated to one fourth of the initial volume. Cooling the solution to -20°C gave the product in the form of small block-like crystals. Yield: 503 mg, 92%. Route B: *t*BuAm^{Mes}H (300 mg, 0.89 mmol) was dissolved in 20 ml of Et$_2$O and added slowly and drop wise to Ca[N(SiMe$_3$)$_2$]$_2$·(Et$_2$O)$_2$ (454 mg, 0.89 mmol) under N$_2$ through a septum. The clear solution was stirred for one day at room temperature, after which Et$_2$O was removed under vacuum. 20 ml of hexane were added to extract the product and the hexane phase was centrifuged, collected and concentrated to one fifth of its initial volume. Cooling the solution to -20°C gave the product in the form of small colorless crystals. The crystals were washed with cold pentane (3 ml) and dried under vacuum. Yield: 615 mg, 88%. ^{1}H NMR (600 MHz, C$_6$D$_6$): δ = 0.67 (t, $^3J_{HH}$ = 6.8 Hz, 6H, Et$_2$O), 1.07 (s, 18H, tBu), 2.21 (s, 24H, o-CH$_3$, Mes), 2.24 (s, 12H, p-CH$_3$, Mes), 2.91 (q, $^3J_{HH}$ = 6.8 Hz, 4H, Et$_2$O), 6.81 (s, 8H, Ar). ^{13}C NMR (151 MHz, C$_6$D$_6$): δ = 13.82 (Et$_2$O), 20.57 (*p*-Me, Mes), 20.94 (tBu), 30.05 (o-Me, Mes), 43.91 (C-tBu), 66.88 (Et$_2$O), 129.08 (Ar), 129.49 (Ar), 130.69 (Ar), 148.07 (Ar), 176.33 (NCN). Elemental analysis: Calculated for C$_{50}$H$_{72}$N$_4$OCa: C 76.48, H 9.24, N 7.14; Found: C 76.40, H 9.45, N 7.25.

Synthesis of (MeAm^{DIPP})[N(SiMe$_3$)$_2$]$_2$CaK MeAm^{DIPP}H (600 mg, 1.58 mmol) and KN(SiMe$_3$)$_2$ (632 mg, 3.17 mmol) were dissolved in 30 ml of Et$_2$O and stirred at room temperature for one hour. CaI$_2$ (466 mg, 1.58 mmol) was added under N$_2$ and the slurry was stirred at 40°C under reflux conditions for three days. Et$_2$O was removed under vacuum and the product extracted with 20 ml of hexane/Et$_2$O (9:1). The liquid phase was collected after centrifugation and concentrated slightly. Slow cooling to -20°C resulted in the precipitation of a white microcrystalline product, which was washed with cold pentane (1 ml) and shortly dried under vacuum. Crystals suitable for X-ray spectroscopy were obtained by slowly evaporating the solvent from a saturated Et$_2$O solution. Yield: 420 mg, 34%. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 0.09 (s, 36H, SiMe$_3$), 1.30 (d, $^3J_{HH}$ = 6.8 Hz, 12H, iPr), 1.48 (d, $^3J_{HH}$ = 6.9 Hz, 12H, iPr), 1.54 (s, 3H, Me), 3.63 (hept, $^3J_{HH}$ = 6.6 Hz, 4H, iPr), 7.12 – 7.24 (m, 6H, Ar). ^{13}C NMR (101 MHz, C$_6$D$_6$): δ = 6.62 (SiMe$_3$), 18.23 (pTol-*C*H$_3$), 25.17 (iPr), 25.27 (iPr), 28.20 (iPr), 123.40 (Ar), 123.61 (Ar), 142.73 (Ar), 147.27 (Ar), 173.75 (NCN). Elemental analysis: Calculated for C$_{38}$H$_{73}$N$_4$Si$_4$KCa: C 58.70, H 9.46; Found: C 58.54, H 9.40.

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

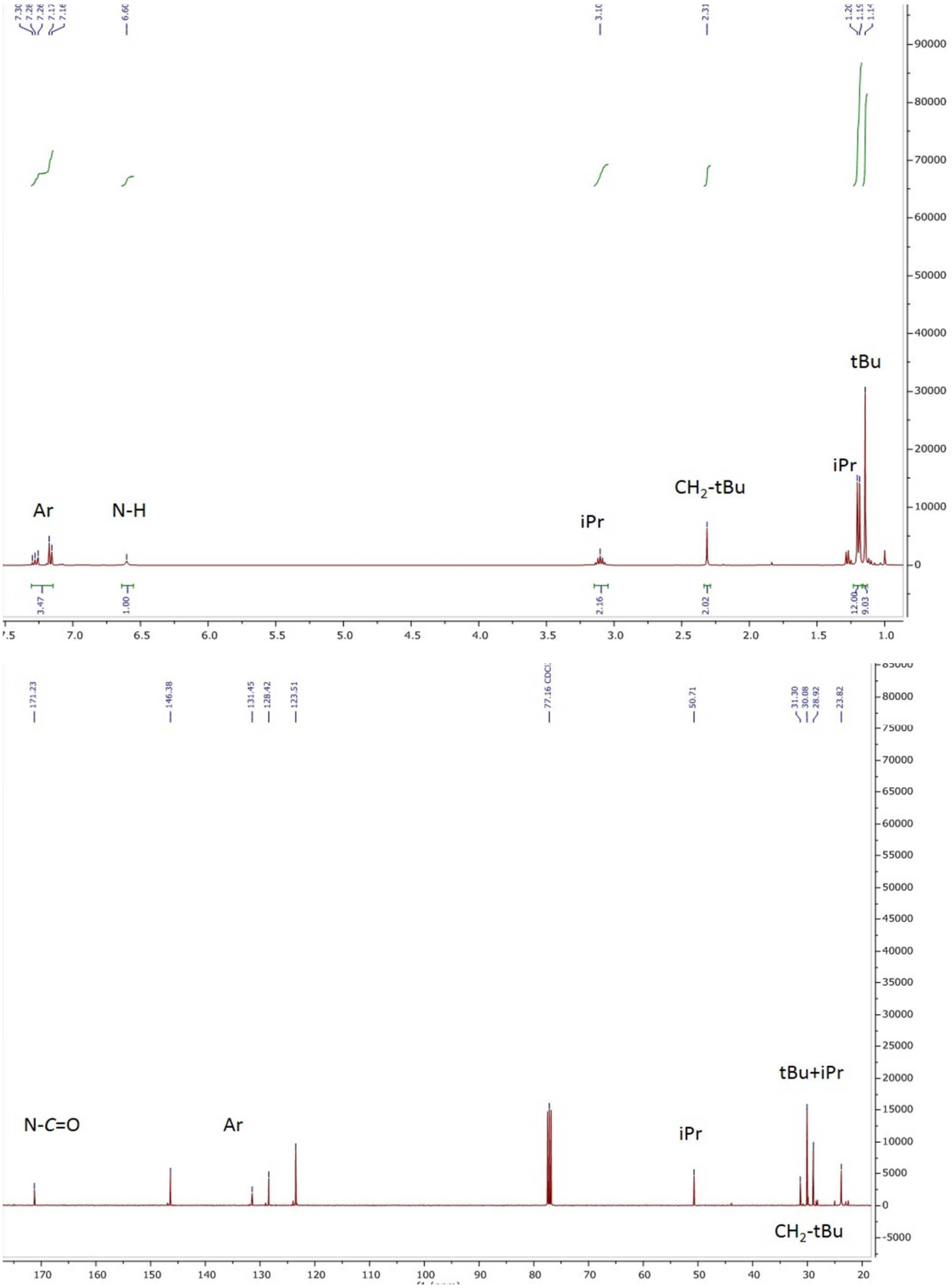

Figure S7. ^{1}H and ^{13}C spectra of NpC(O)N(H)DIPP in $CDCl_3$

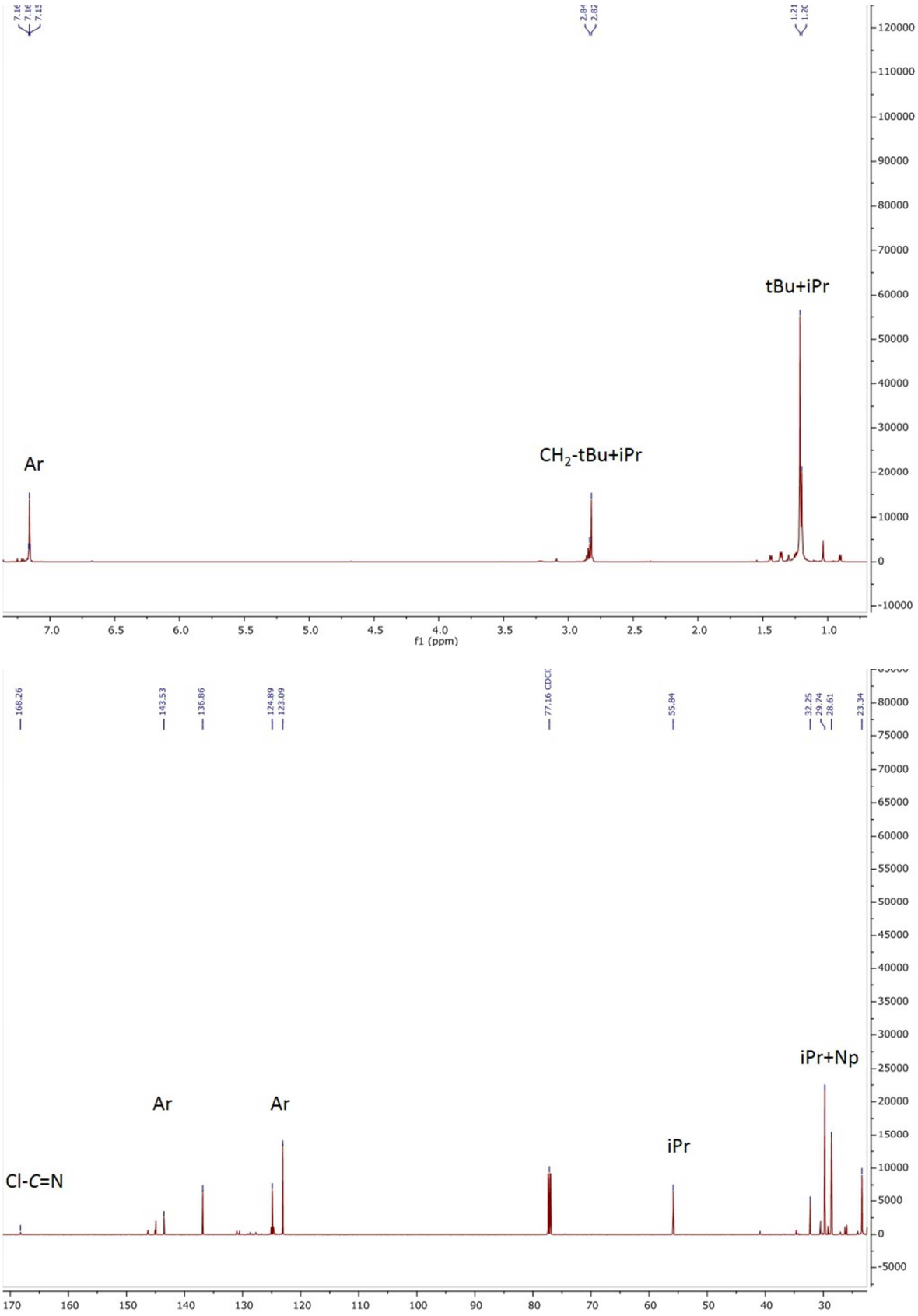

Figure S8. ^{1}H and ^{13}C spectra of NpC(Cl)NDIPP in $CDCl_3$

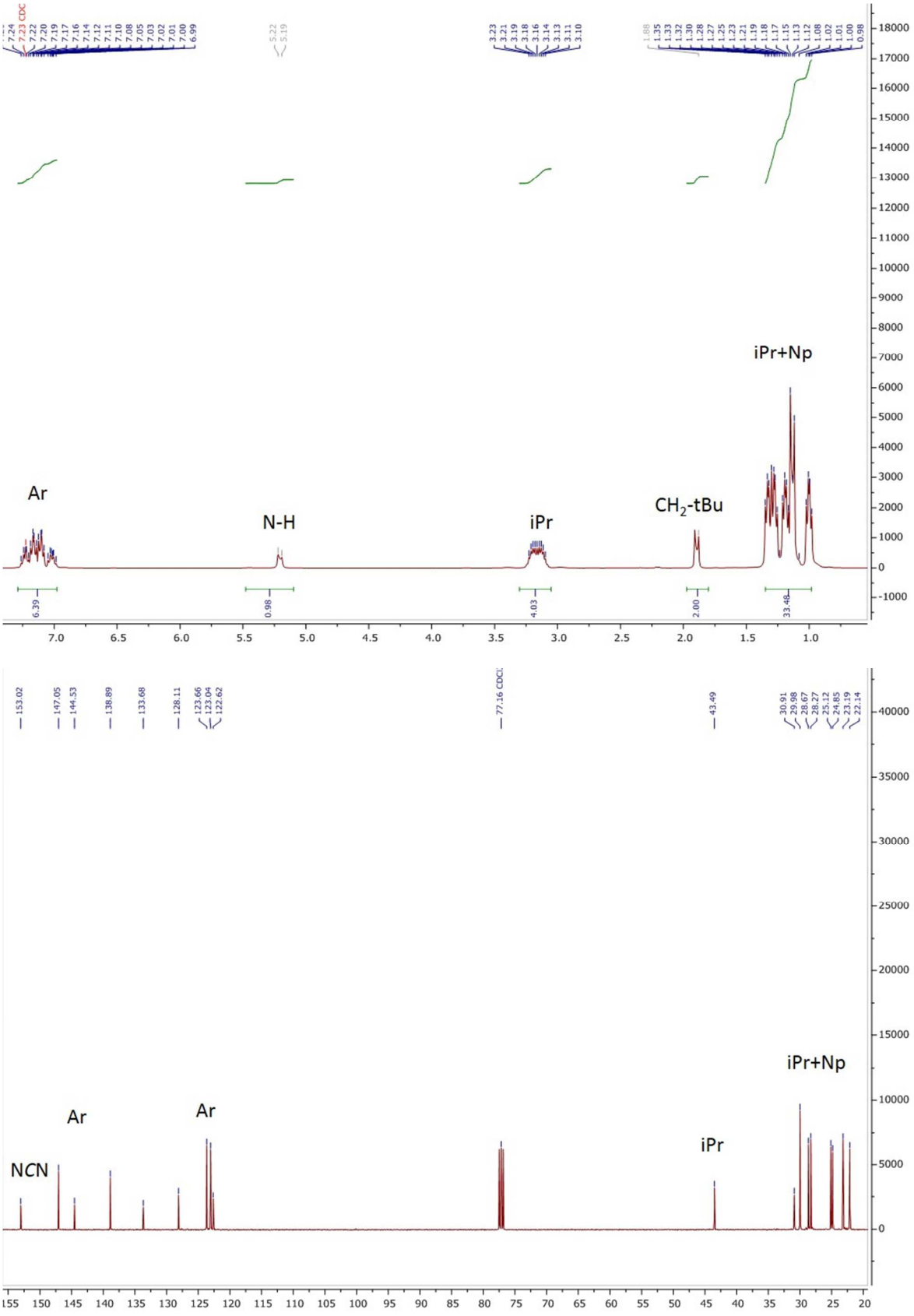

Figure S9. ^{1}H and ^{13}C spectra of $NpAm^{DIPP}H$ in $CDCl_3$: several isomers present in solution make the spectra hard to interpret.

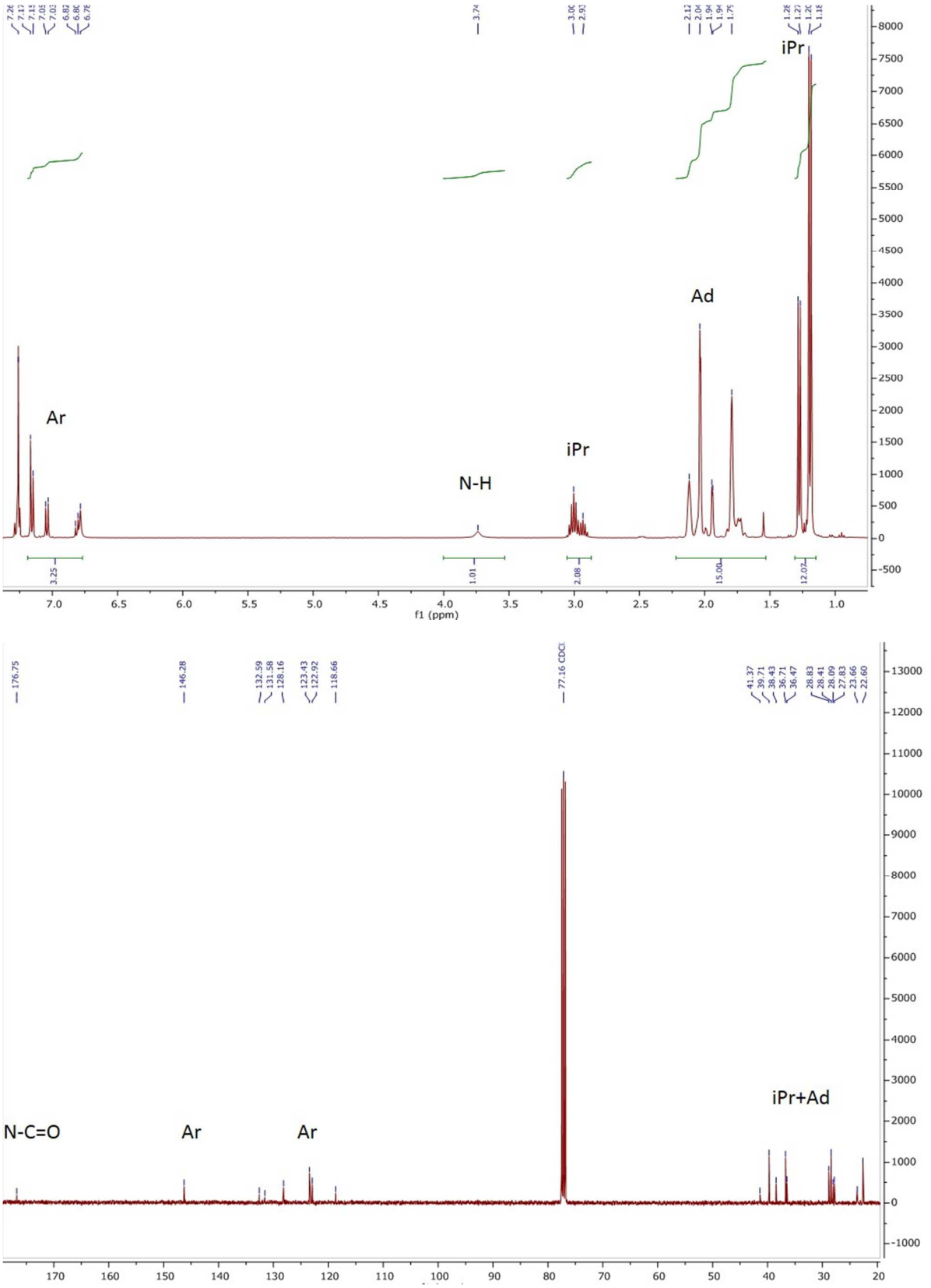

Figure S10. ^{1}H and ^{13}C spectra of AdC(O)N(H)DIPP in $CDCl_3$: two isomers present in solution (*syn* and *anti*)

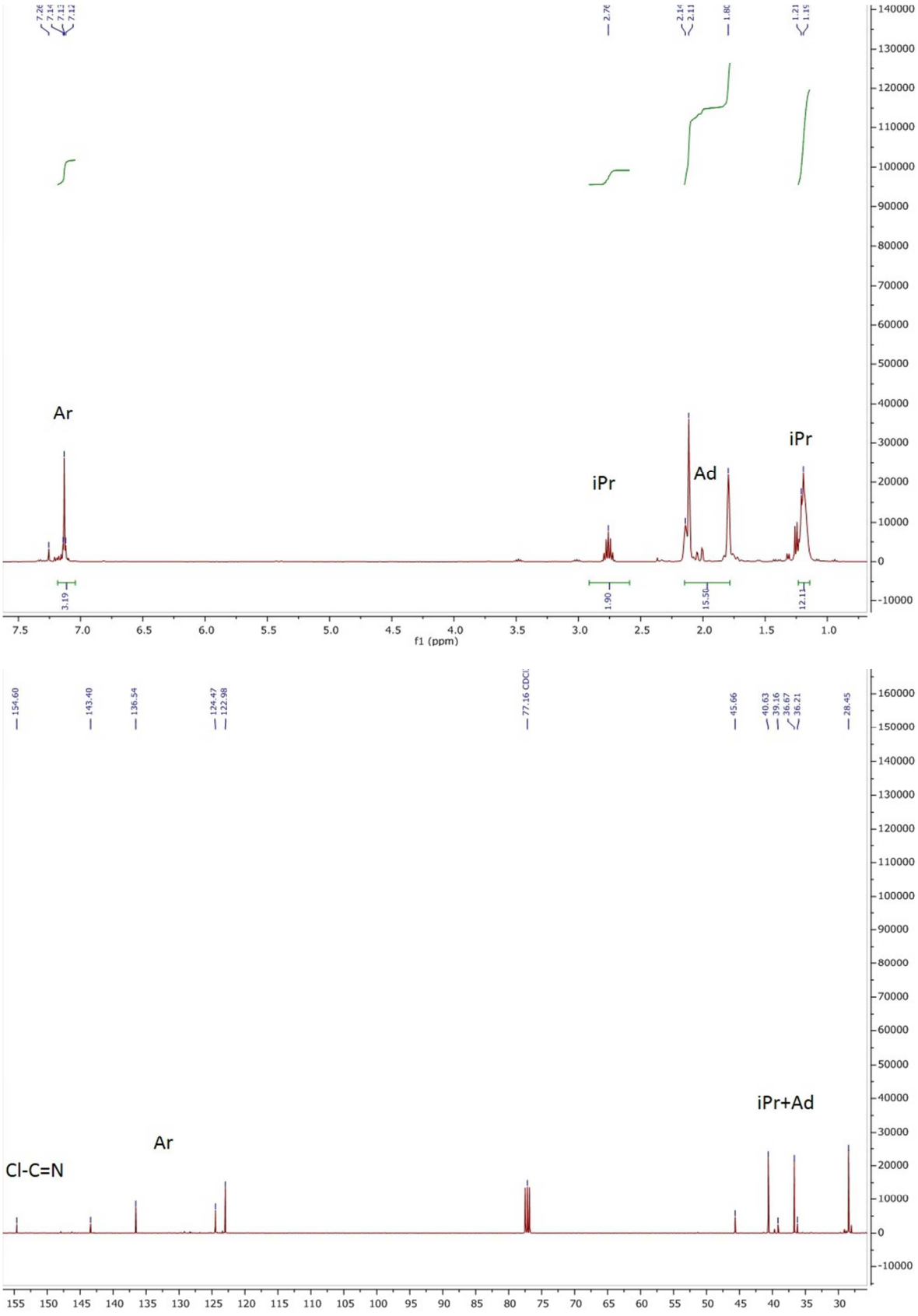

Figure S11. ^{1}H and ^{13}C spectra of AdC(Cl)NDIPP in $CDCl_3$

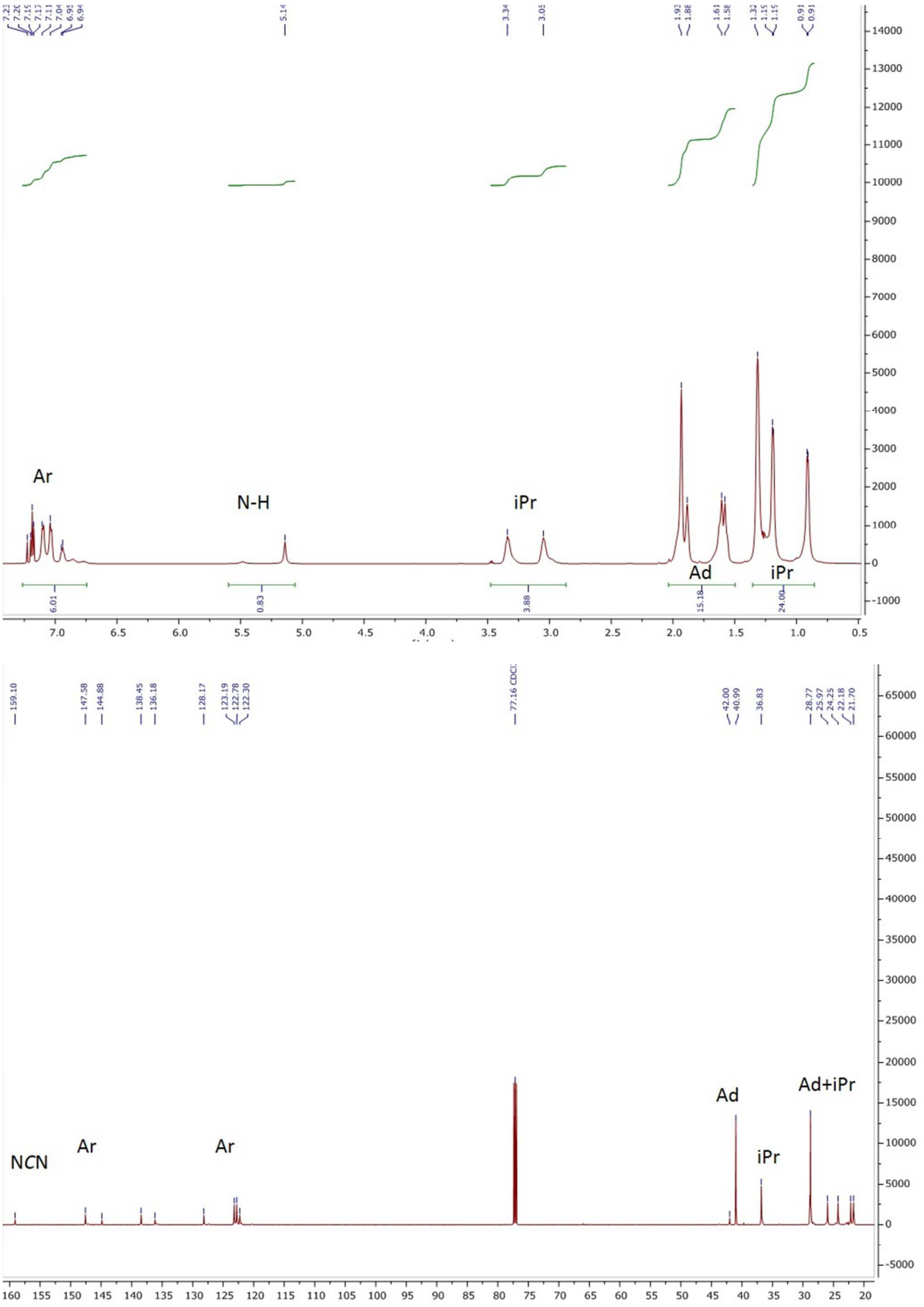

Figure S12. ^{1}H and ^{13}C spectra of $AdAm^{DIPP}H$ in $CDCl_3$: several isomers present in solution make the spectra hard to interpret.

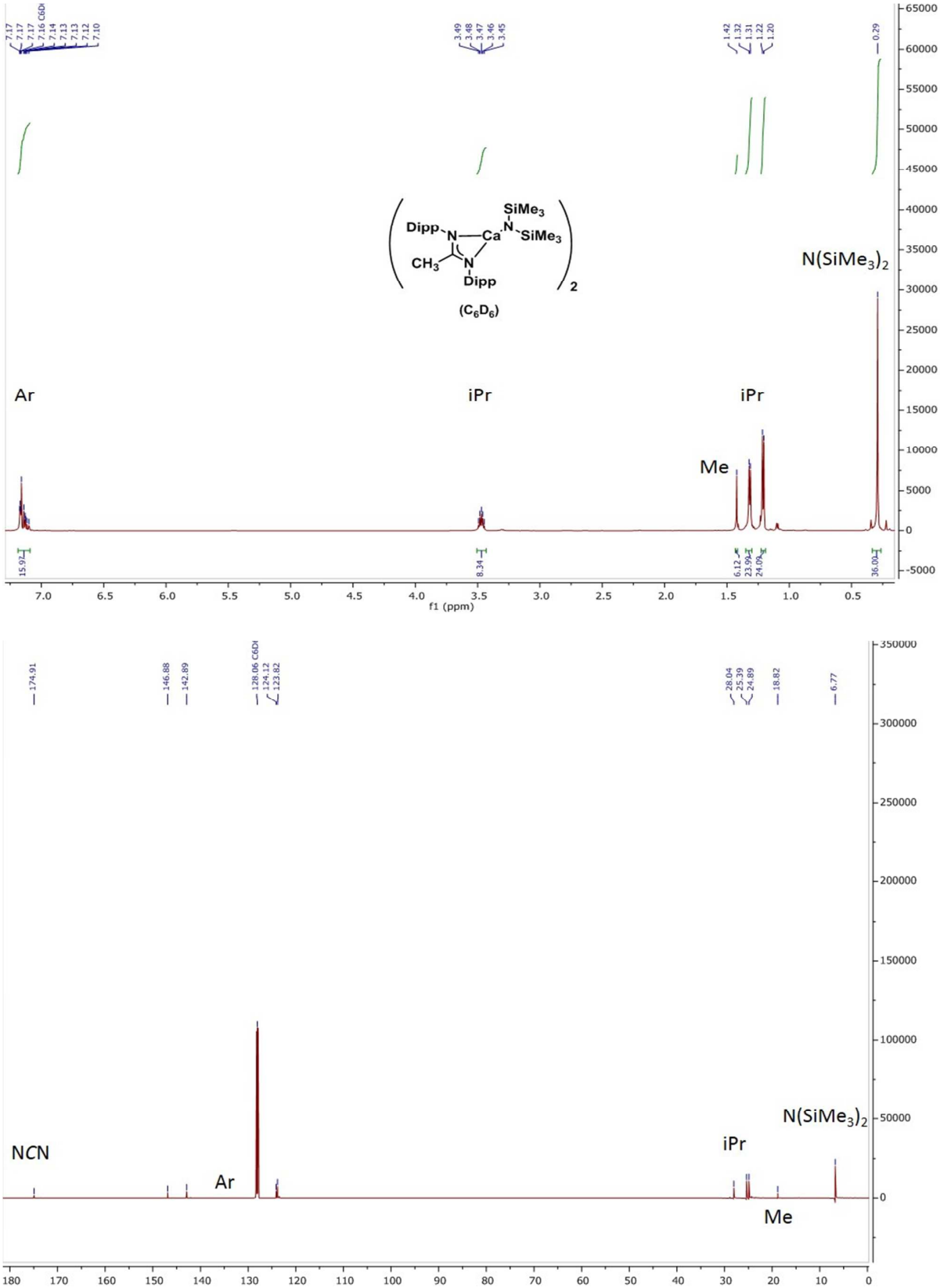

Figure S13. ^{1}H and ^{13}C spectra of $[MeAm^{DIPP}CaN(SiMe_3)_2]_2$ in C_6D_6

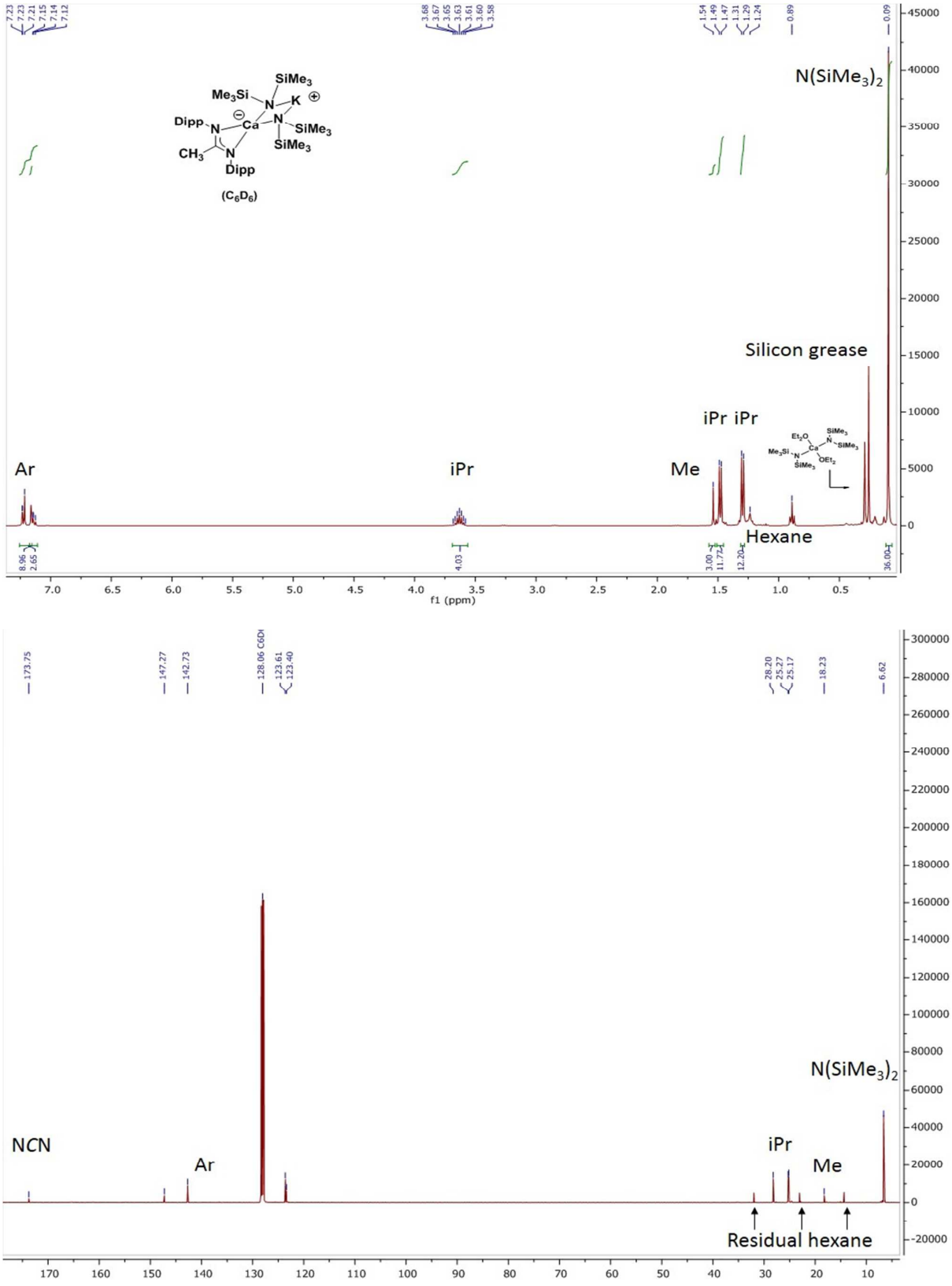

Figure S14. ^{1}H and ^{13}C spectra of $(MeAm^{DIPP})[N(SiMe_3)_2]_2CaK$ in C_6D_6

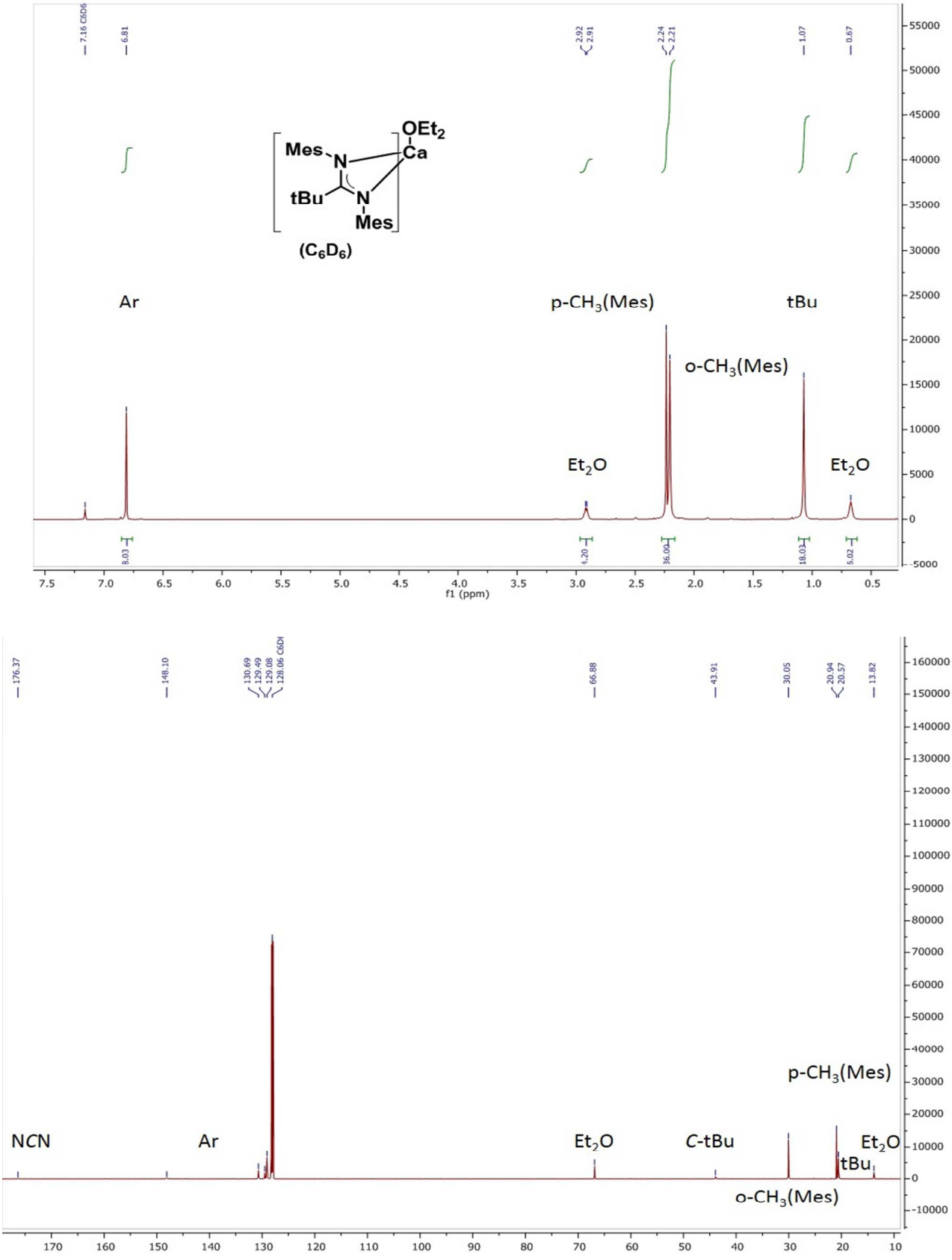

Figure S15. ^{1}H and ^{13}C spectra of (*t*BuAm^{Mes})$_2$Ca·Et$_2$O in C_6D_6

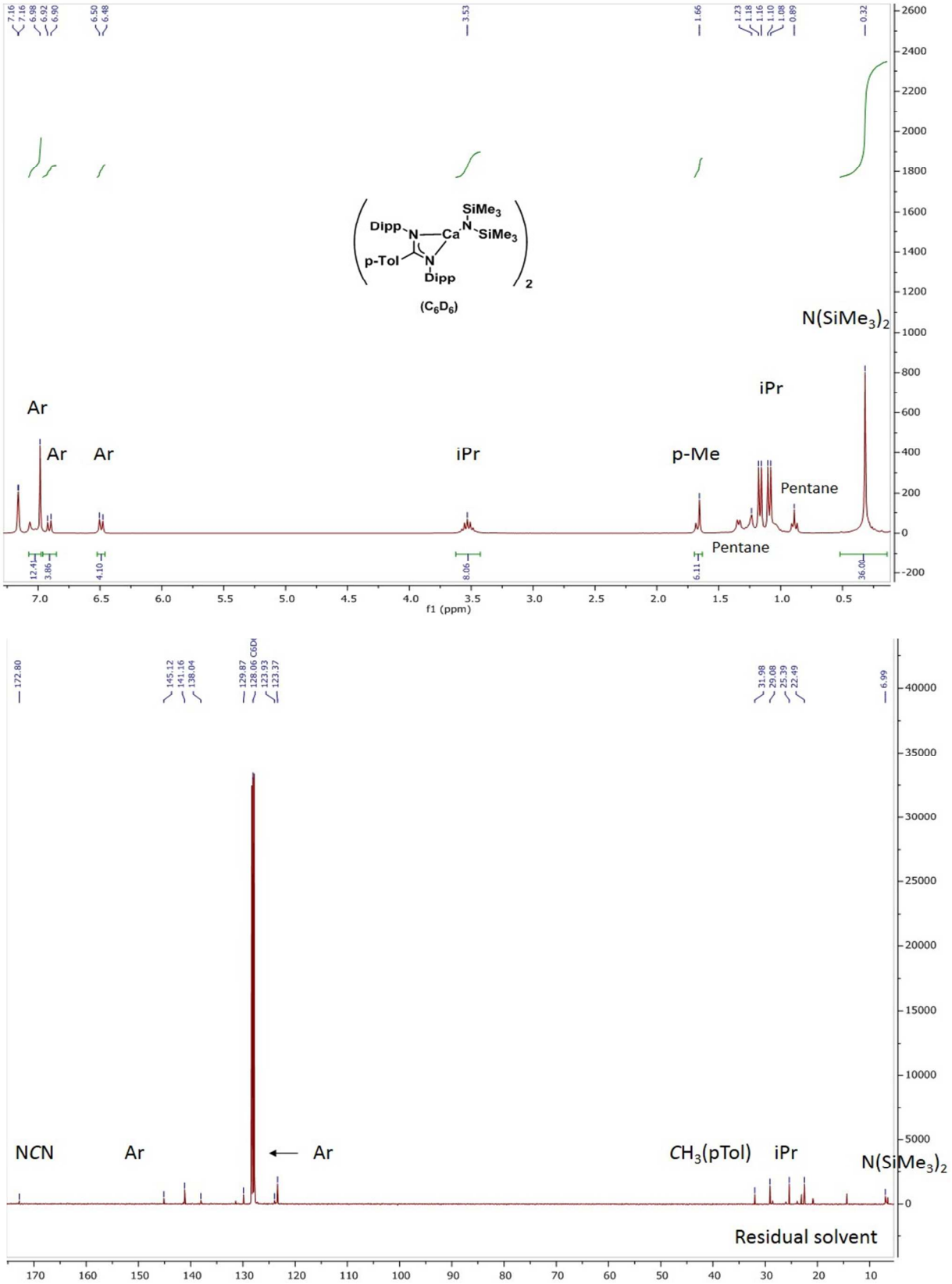

Figure S16. ^{1}H and ^{13}C spectra of [*p*-TolAm^{DIPP}CaN(SiMe$_3$)$_2$]$_2$ in C_6D_6

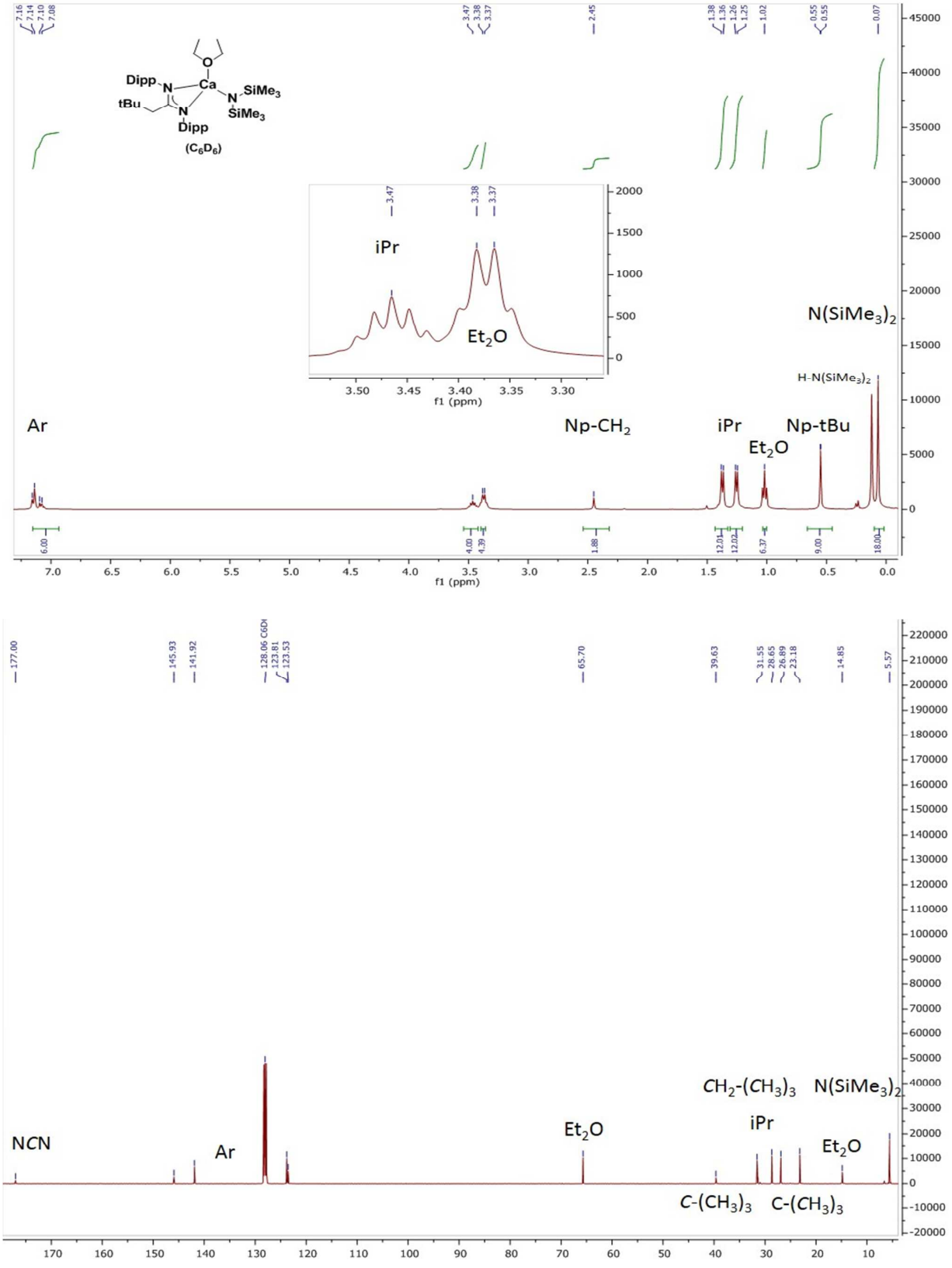

Figure S17. ^{1}H and ^{13}C spectra of $NpAm^{DIPP}CaN(SiMe_3)_2{\cdot}Et_2O$ in C_6D_6

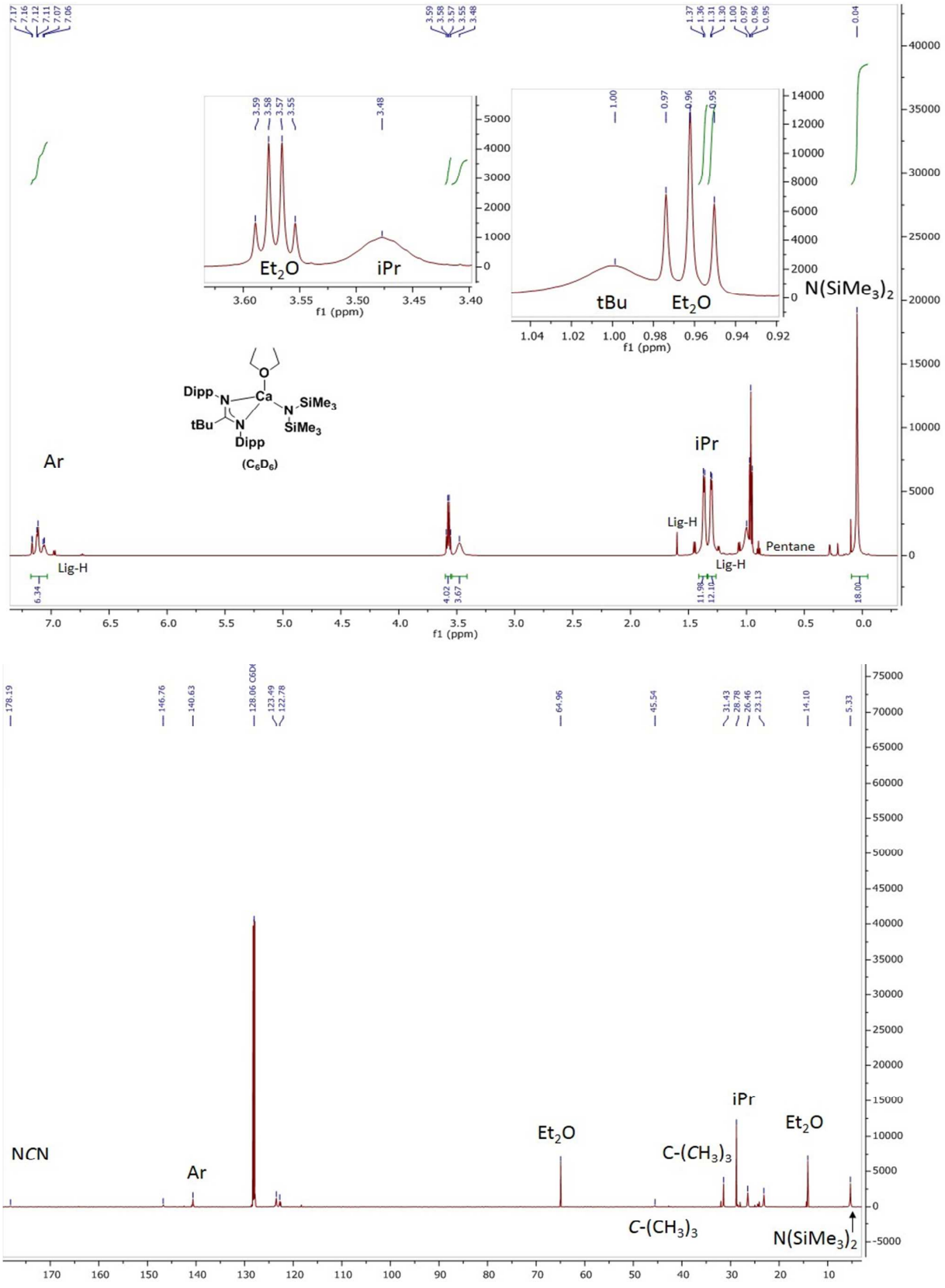

Figure S18. ^{1}H and ^{13}C spectra of *t*BuAm^{DIPP}CaN(SiMe$_3$)$_2$·(Et$_2$O) in C_6D_6

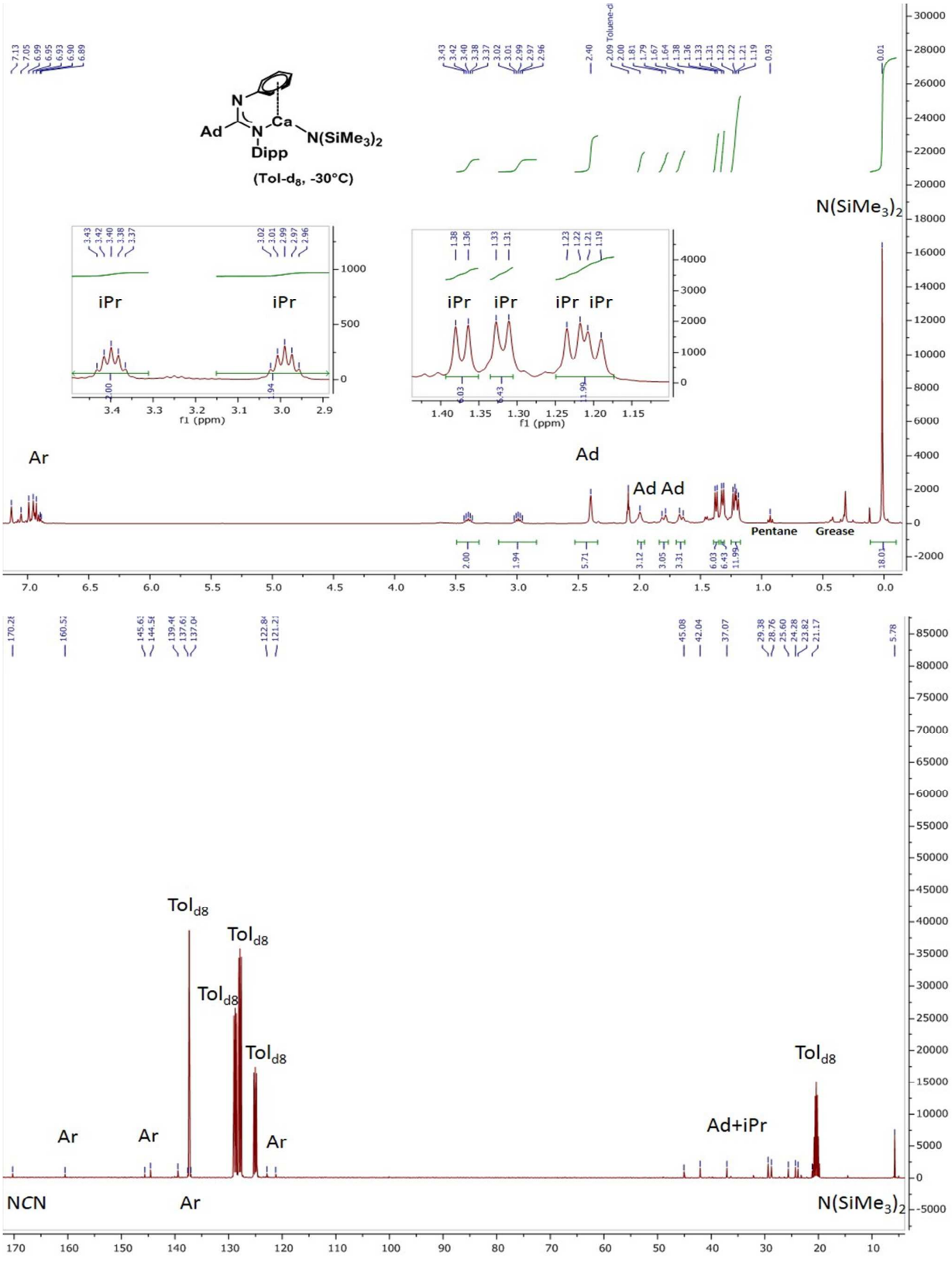

Figure S19. ^{1}H and ^{13}C spectra of $AdAm^{DIPP}CaN(SiMe_3)_2$ in toluene-d_8 at -30°C

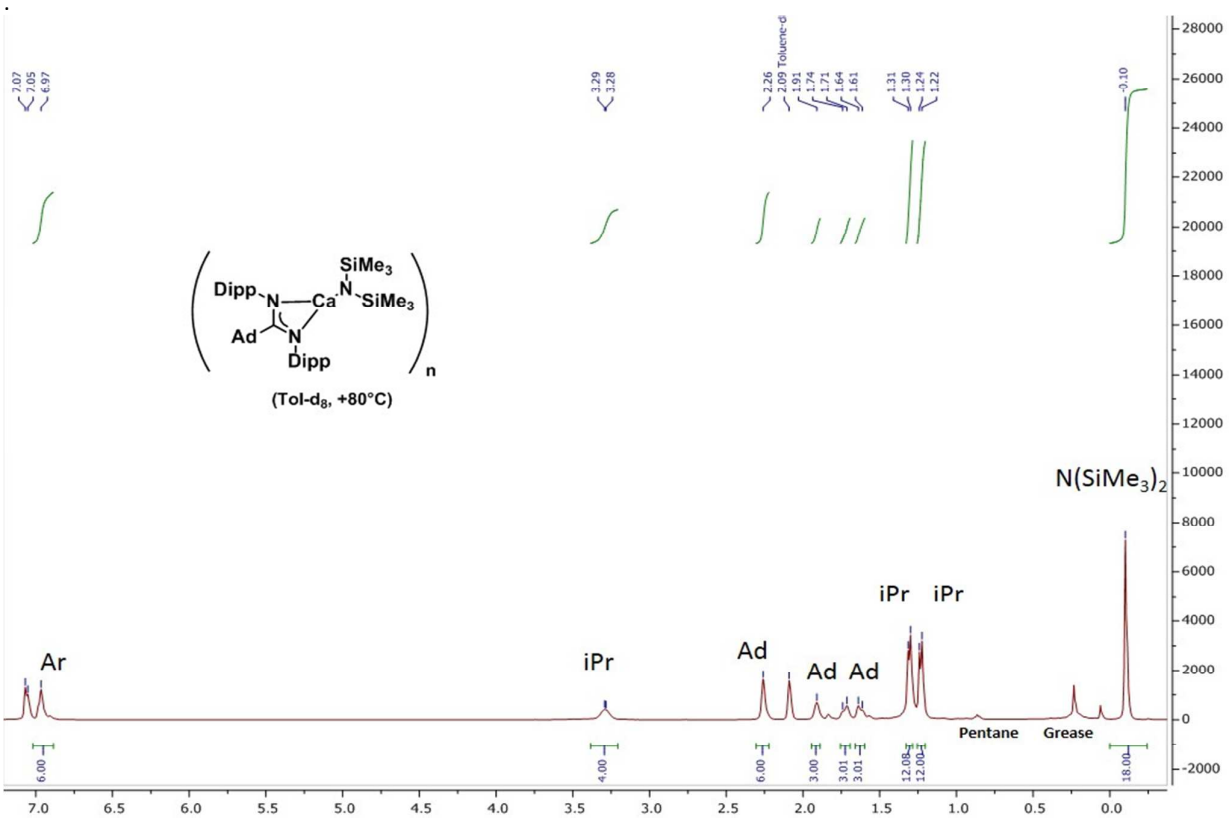

Figure S20. ^{1}H spectrum of AdAm^{DIPP}CaN(SiMe$_3$)$_2$ in toluene-d_8 at +80°C

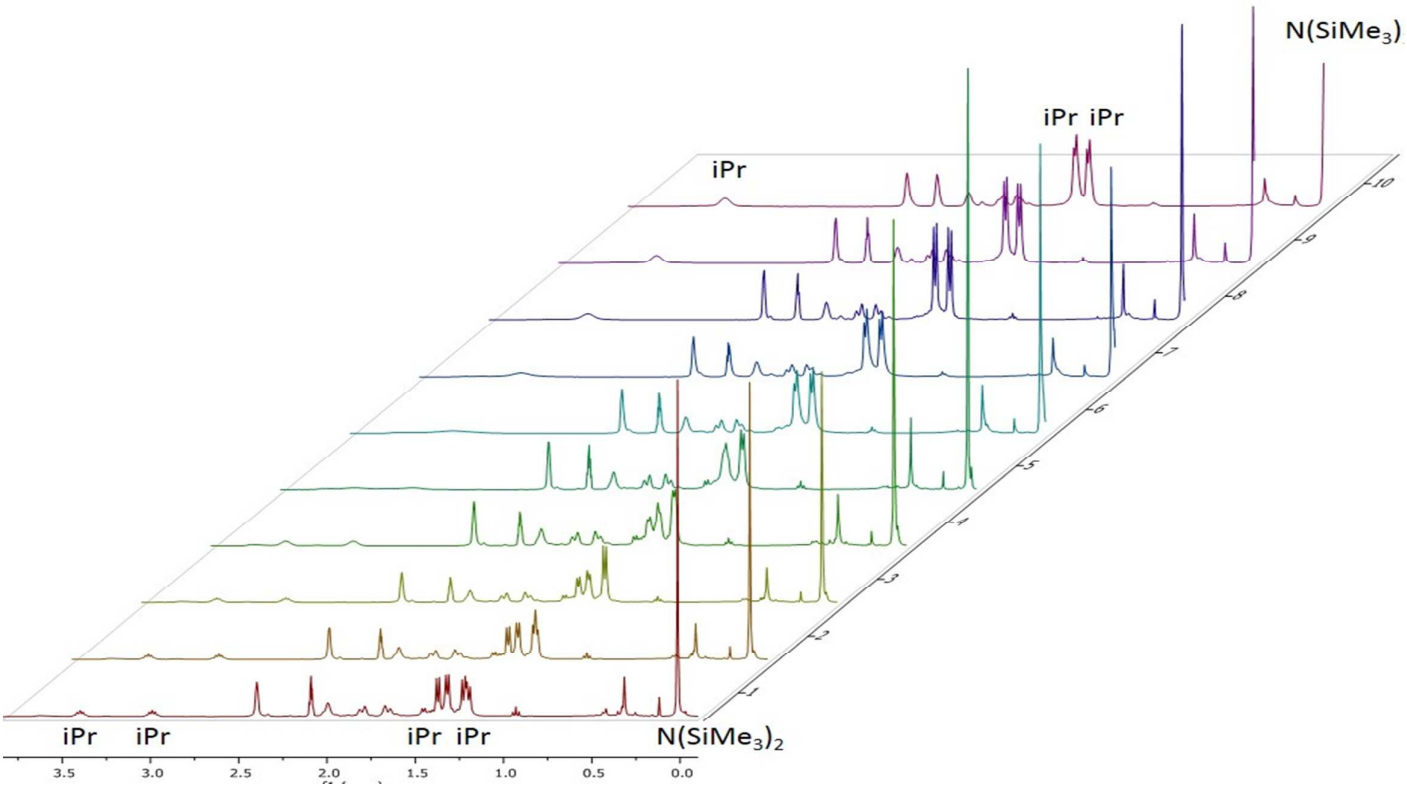

Figure S21. Stacked ^{1}H spectra of AdAm^{DIPP}CaN(SiMe$_3$)$_2$ measured from -30°C to +80°C (0-3.6 ppm).

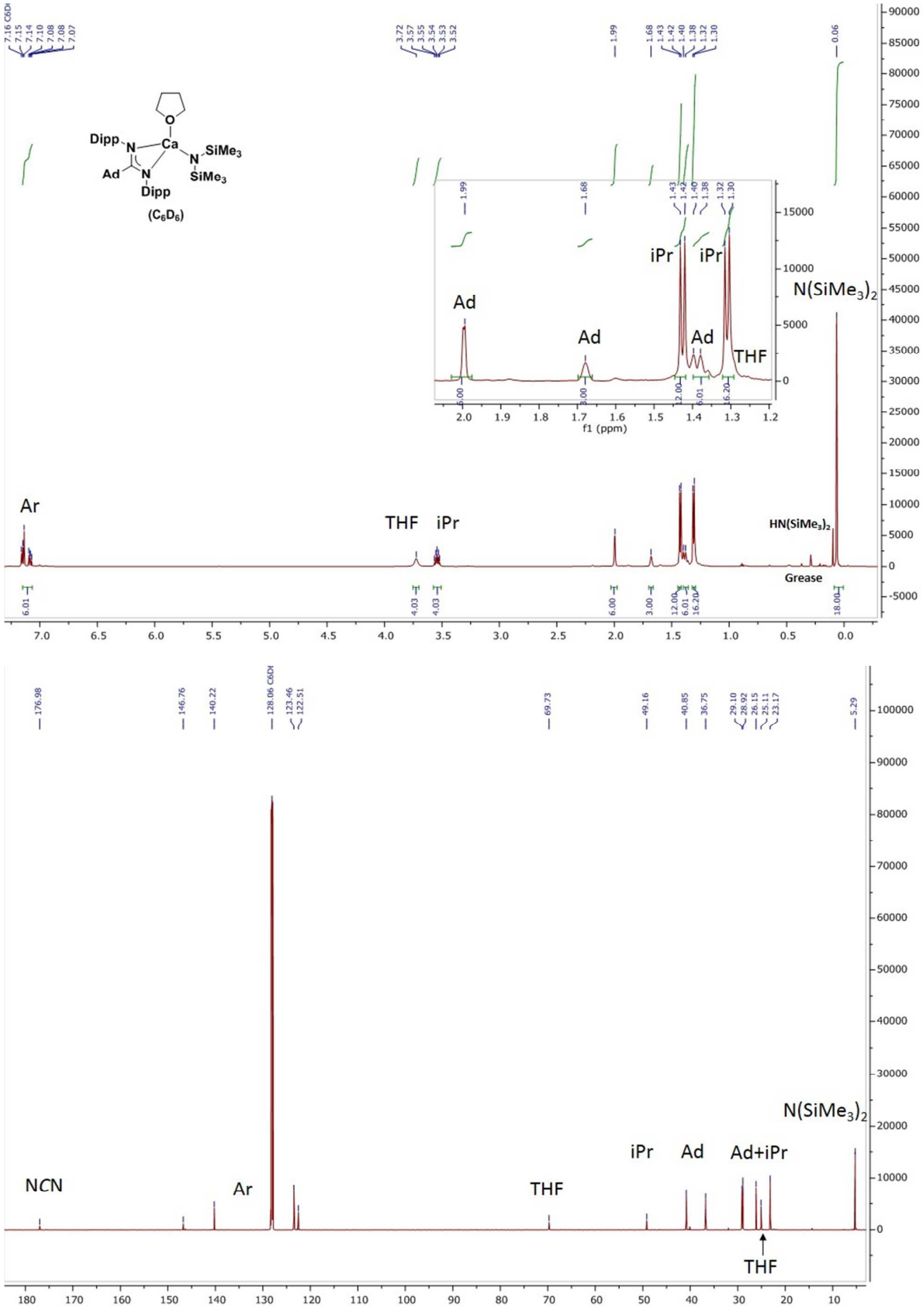

Figure S22. ^{1}H and ^{13}C spectra of $AdAm^{DIPP}CaN(SiMe_3)_2 \cdot THF$ in C_6D_6

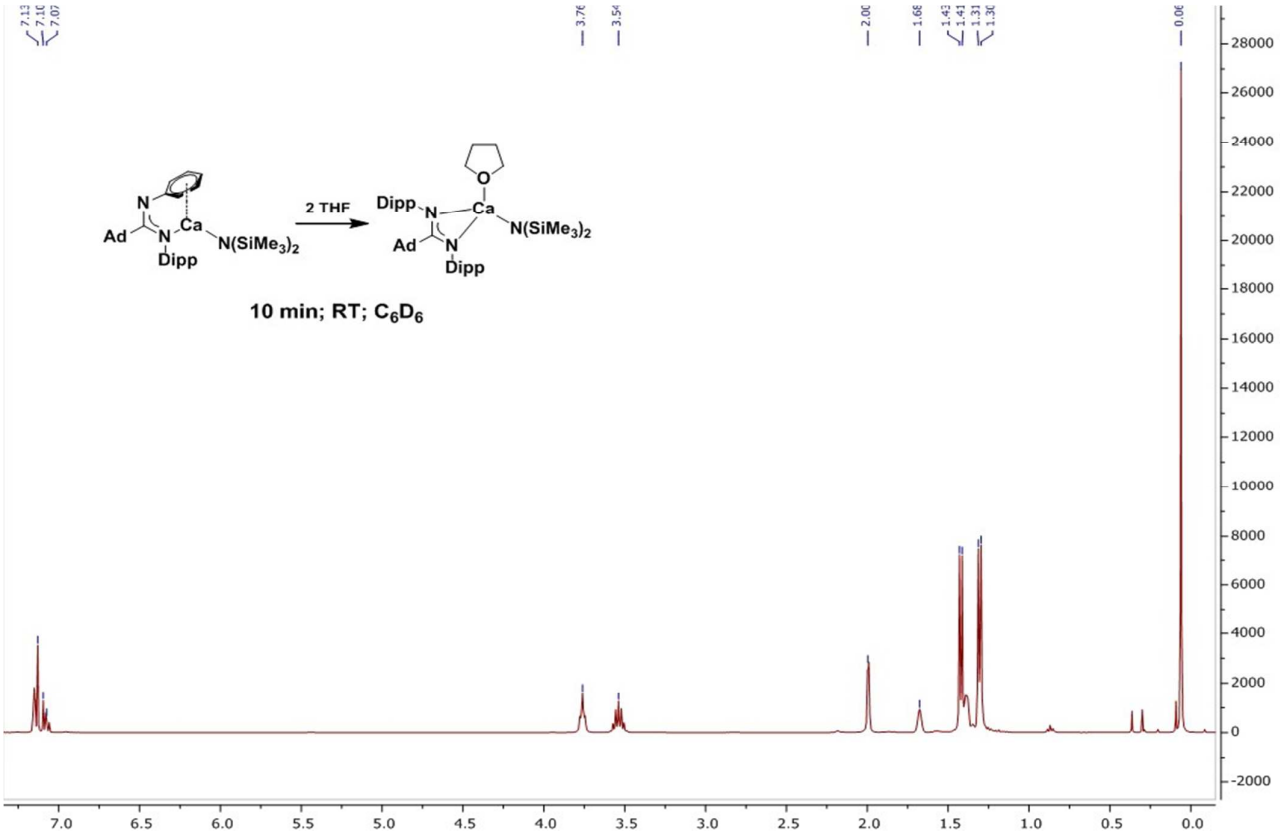

Figure S23. Reaction of $AdAm^{DIPP}CaN(SiMe_3)_2$ with 2 equivalents of THF and formation of $AdAm^{DIPP}CaN(SiMe_3)_2 \cdot THF$ in C_6D_6.

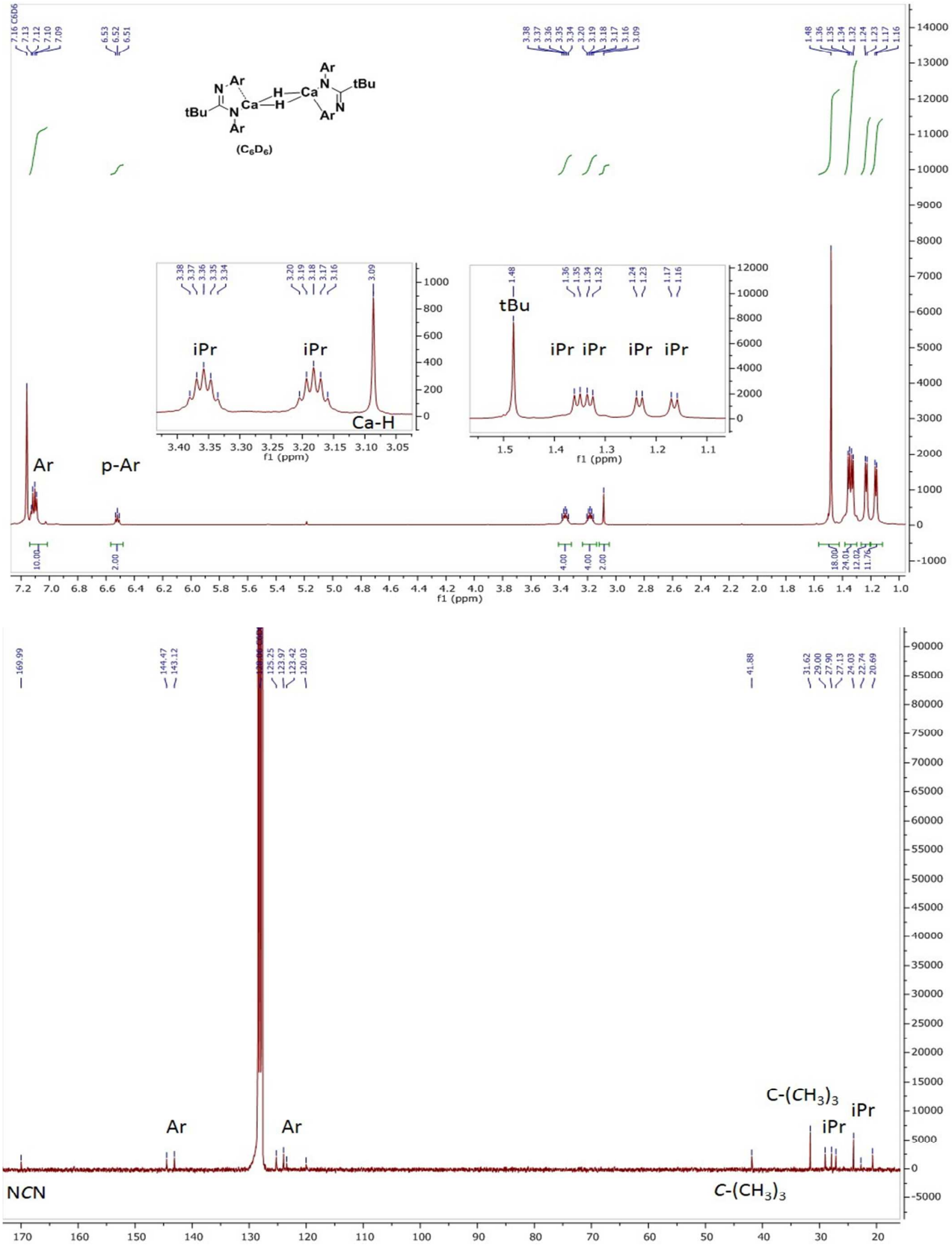

Figure S24. ^{1}H and ^{13}C spectra of (*t*BuAm^{DIPP}CaH)$_2$ in C_6D_6

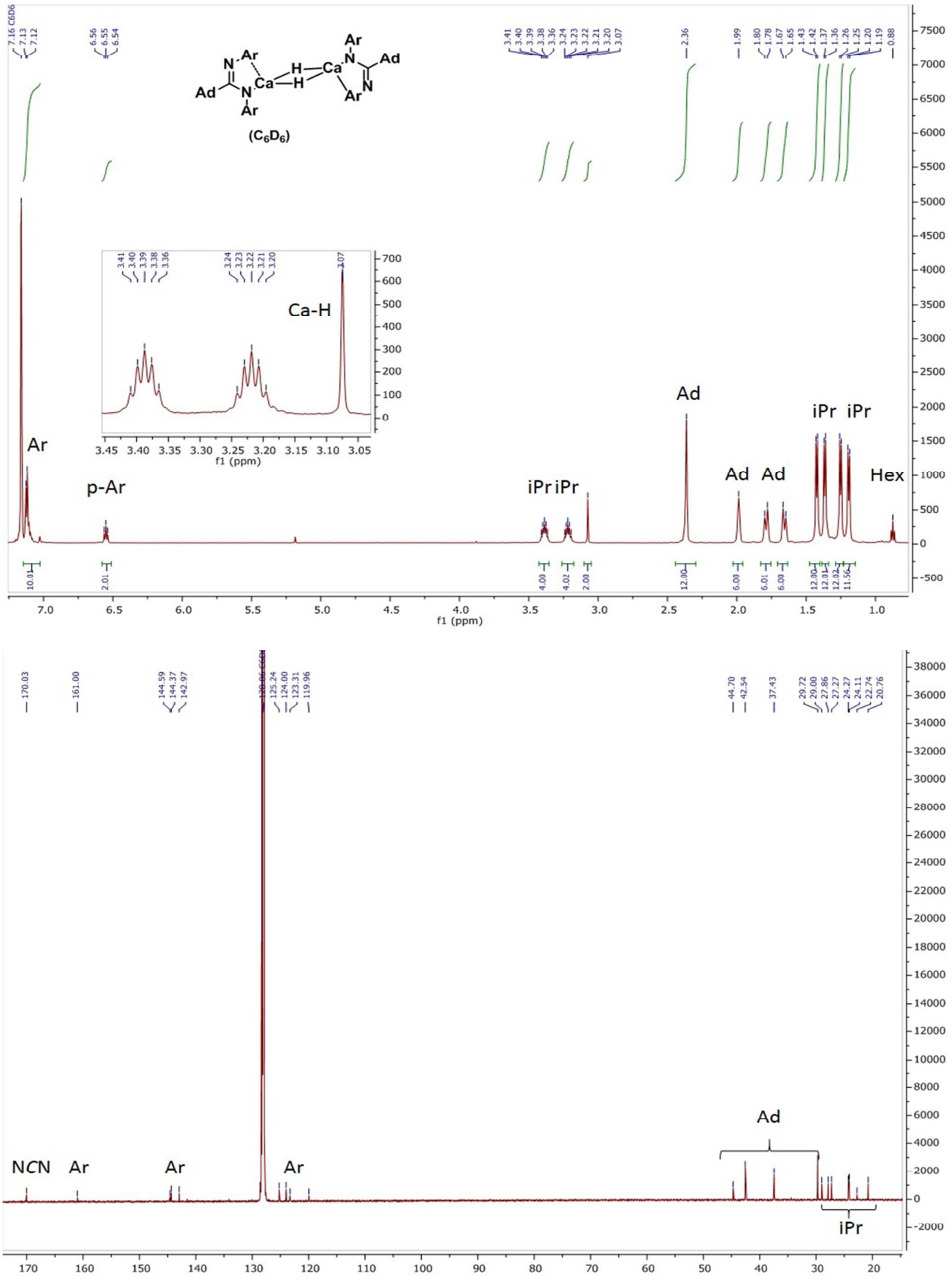

Figure S25. ^{1}H and ^{13}C spectra of $(AdAm^{DIPP}CaH)_2$ in C_6D_6

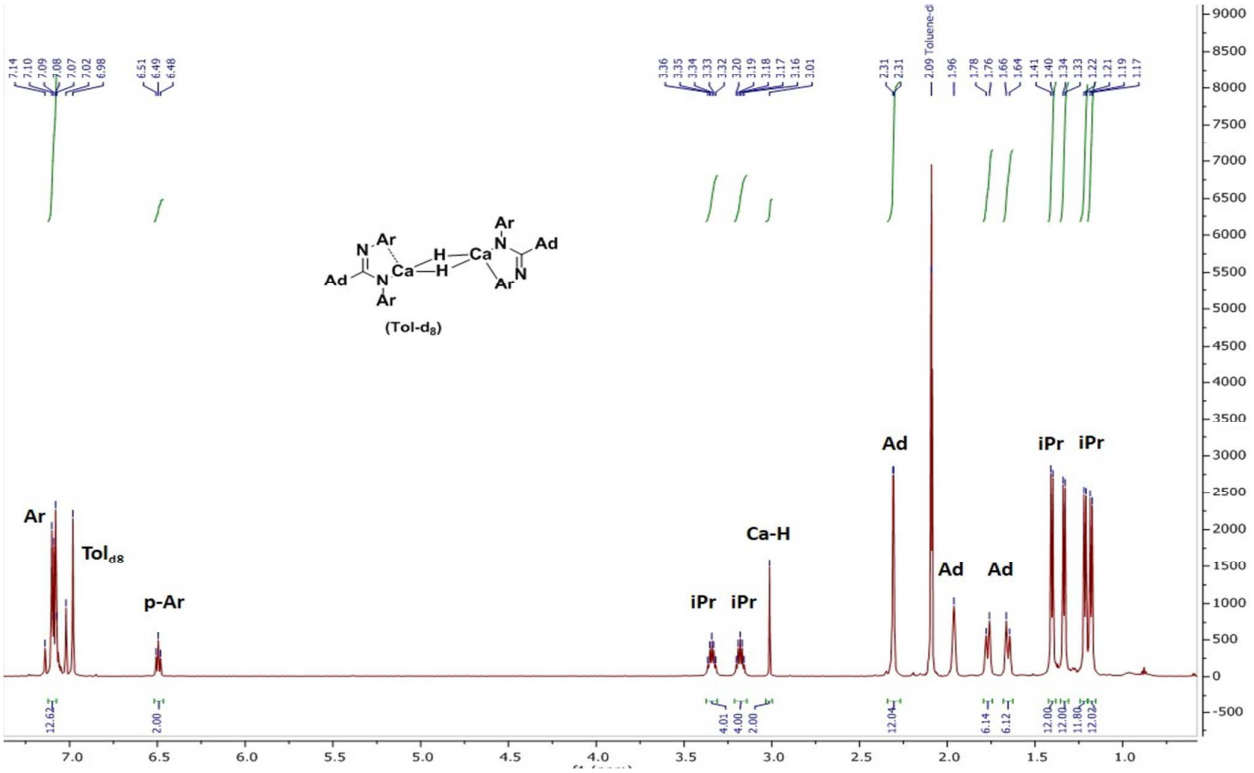

Figure S26. Spectrum of (AdAm^{DIPP}CaH)$_2$ in toluene-d_8

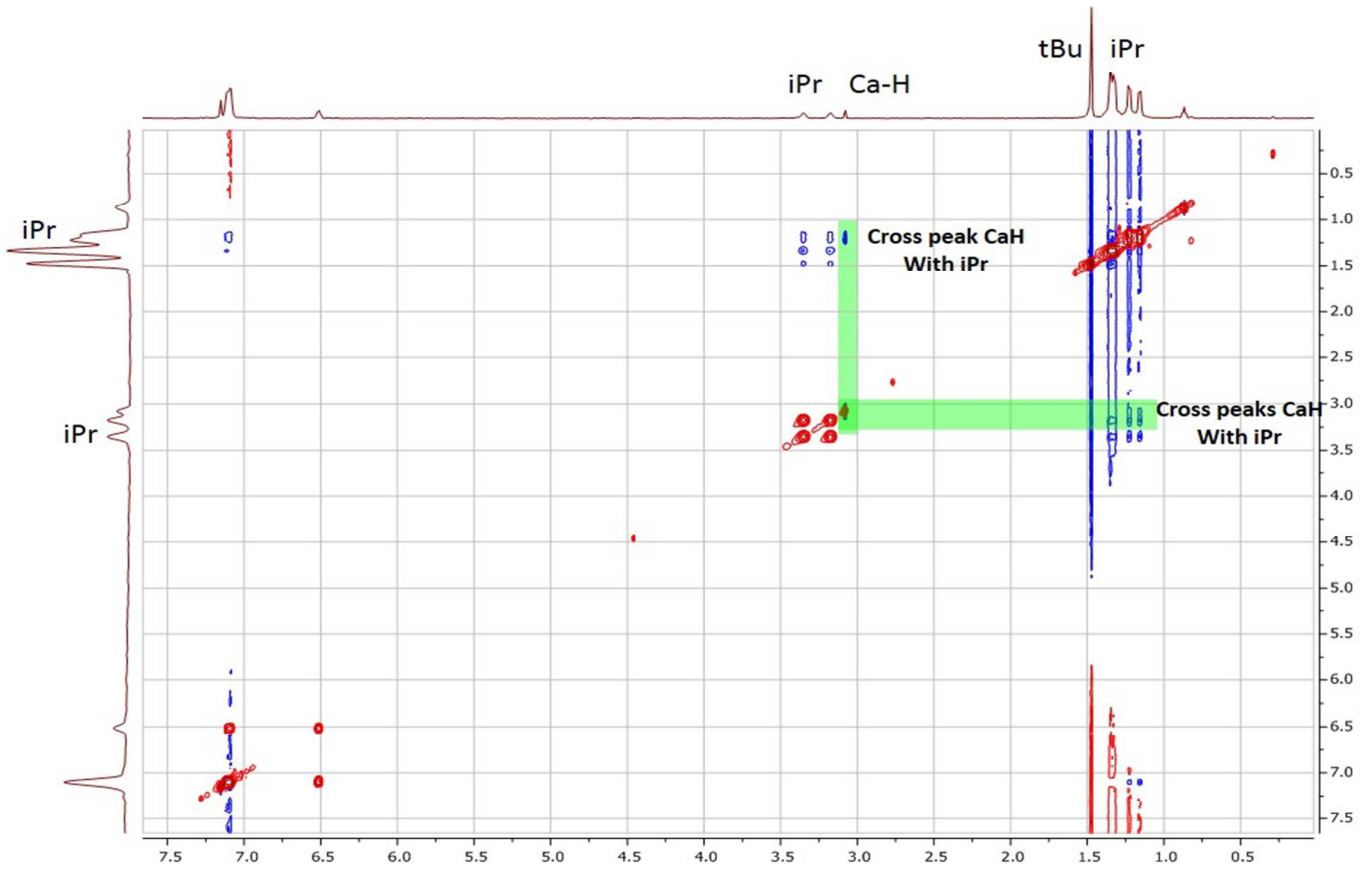

Figure S27. 2D-NOESY spectrum of (*t*BuAm^{DIPP}CaH)$_2$ in C_6D_6

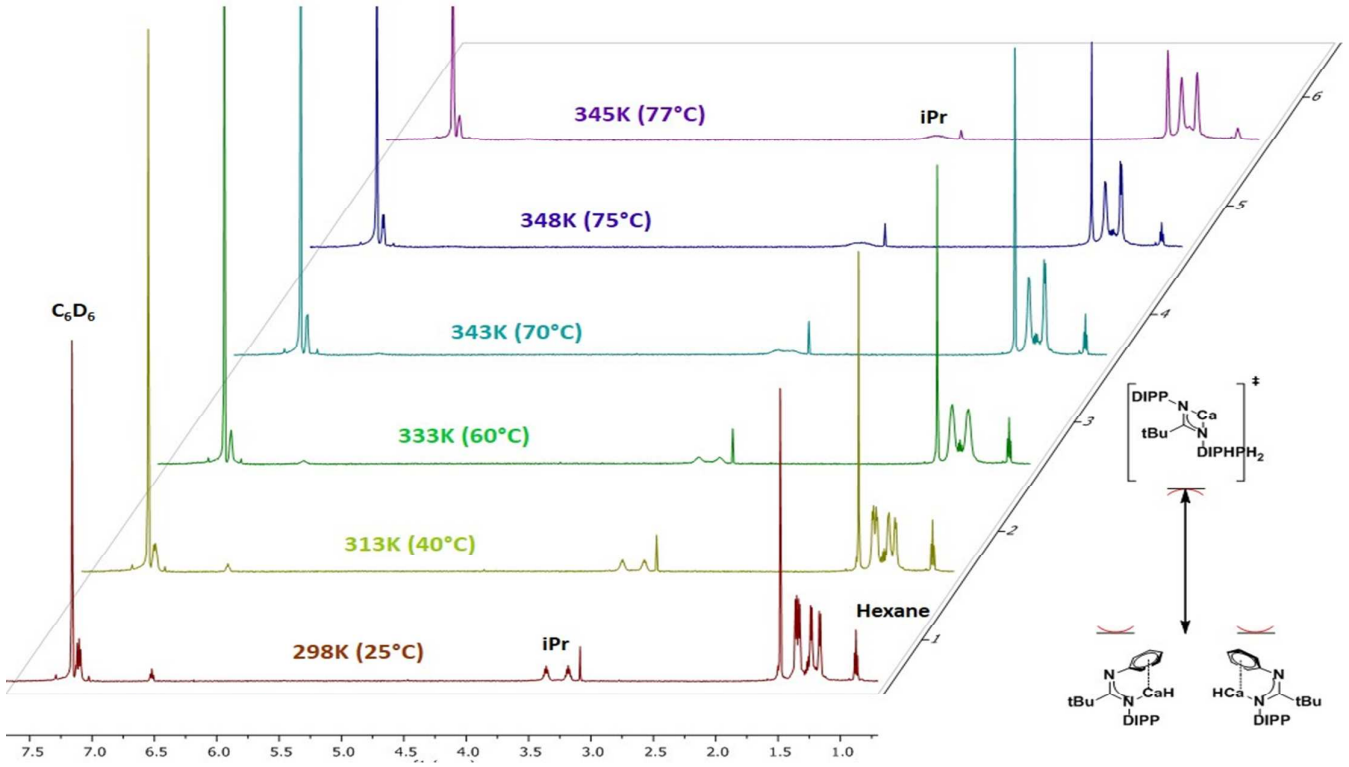

Figure S28. Coalescence of (tBuAm^{DIPP}CaH)$_2$ reached at 77°C in C_6D_6

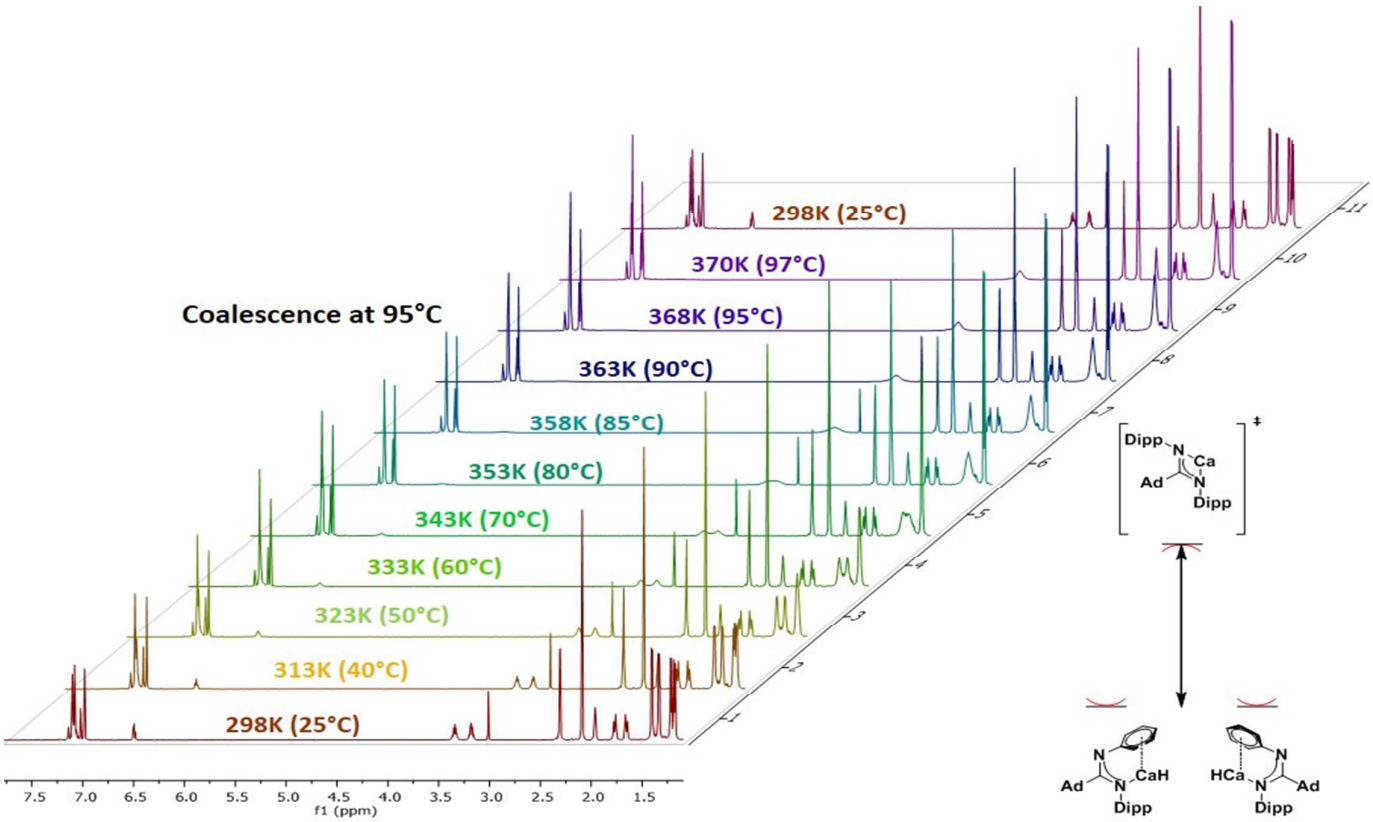

Figure S29. Coalescence of (AdAm^{DIPP}CaH)$_2$ reached at 95°C in toluene-d_8.

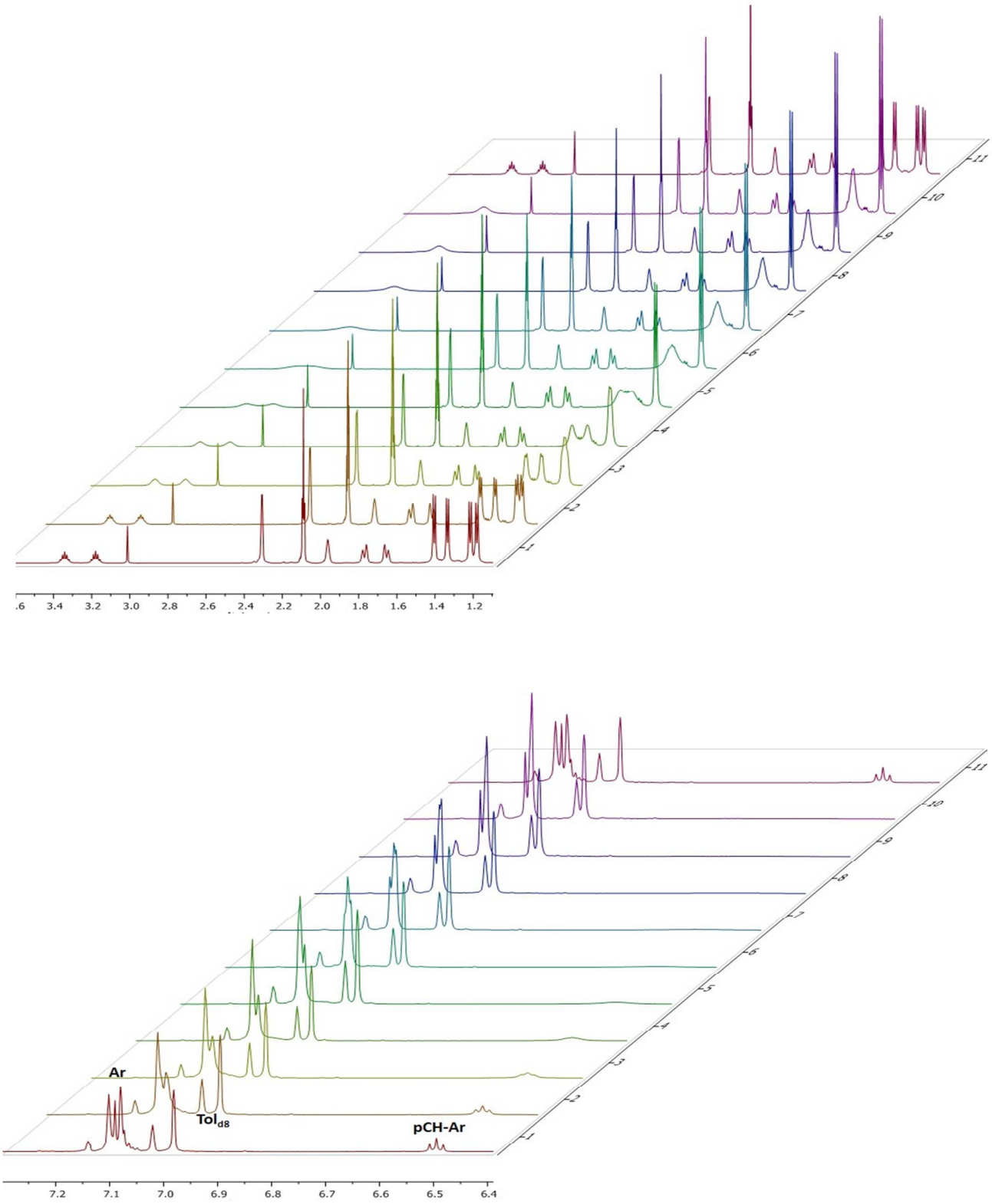

Figure S30. Coalescence of $(AdAm^{DIPP}CaH)_2$ in toluene-d_8. Zoom in the iPr region and Ar region respectively shown

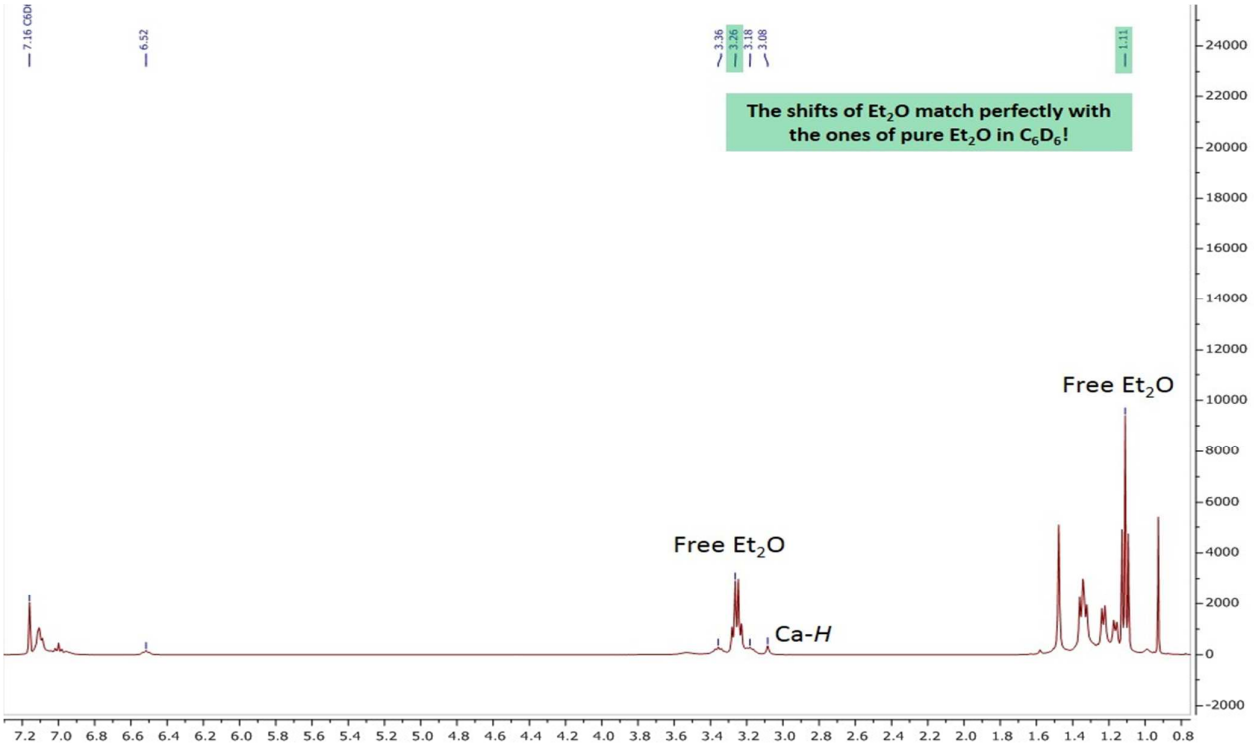

Figure S31. Spectrum of $(tBuAm^{DIPP}CaH)_3 \cdot (Et_2O)_2$ in C_6D_6: broad signals match with those for dimeric $(tBuAm^{DIPP}CaH)_2$ and free Et_2O can be seen.

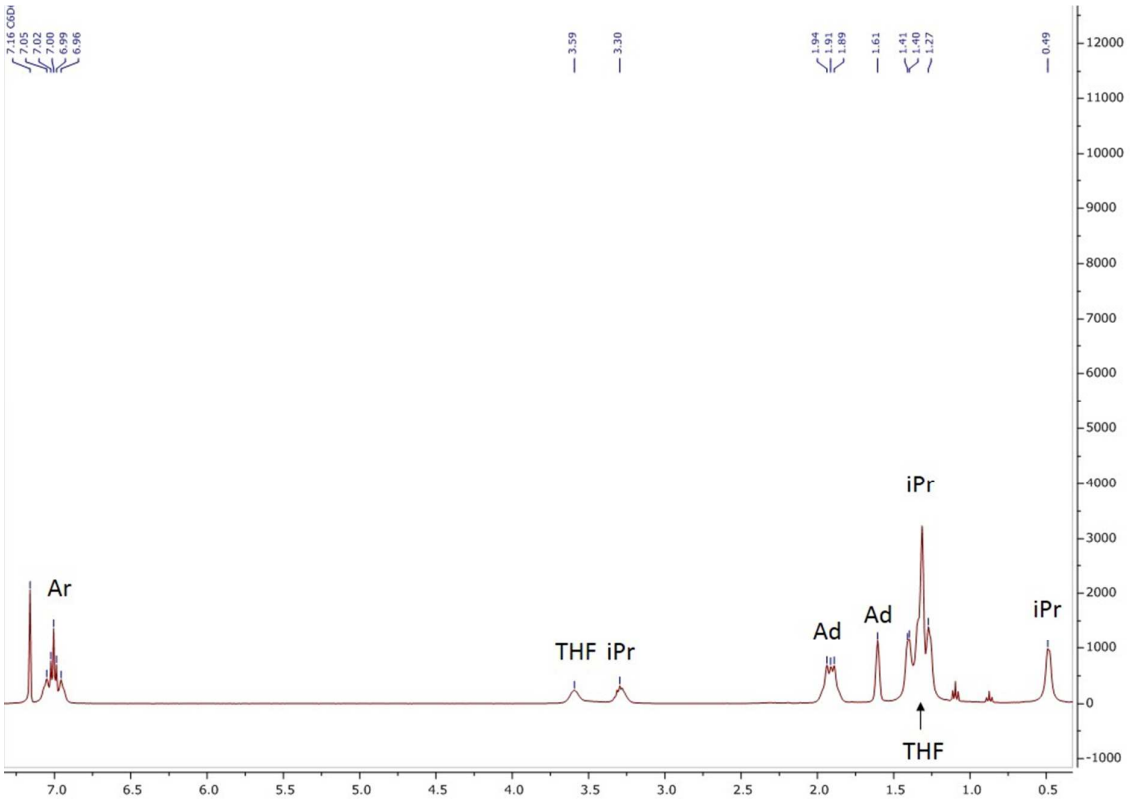

Figure S32. Spectrum of the decomposition products of $(AdAm^{DIPP}CaH)_3 \cdot (THF)_2$ in C_6D_6. The only one detectable is the homoleptic compound.

References

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