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SUPPORTING INFORMATION

Barium Tetraalkylaluminate Complexes Supported by the Super-Bulky Hydrotris(pyrazolyl)borate Ligand

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1. Selected NMR Spectra

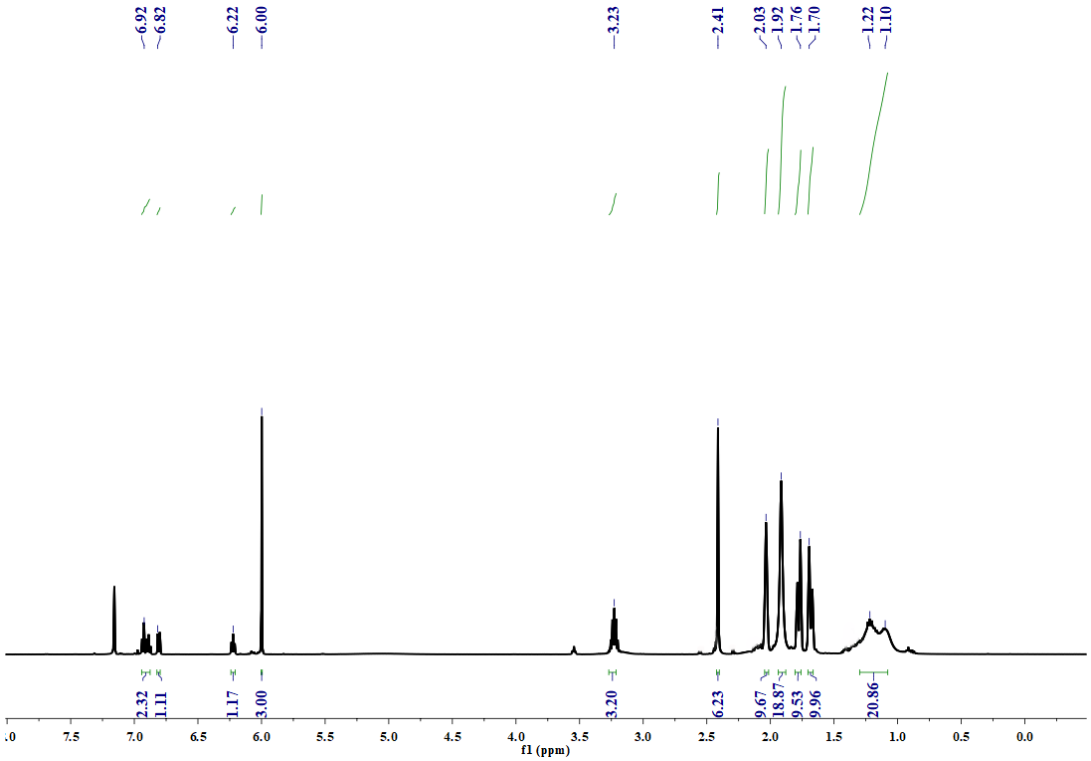

Figure S1. ^{1}H NMR spectrum (500 MHz) of [(Tp^{Ad,iPr})Ba(*o*-$CH_2C_6H_4$-NMe_2)] (**1**) in C_6D_6 at 25 ^{o}C.

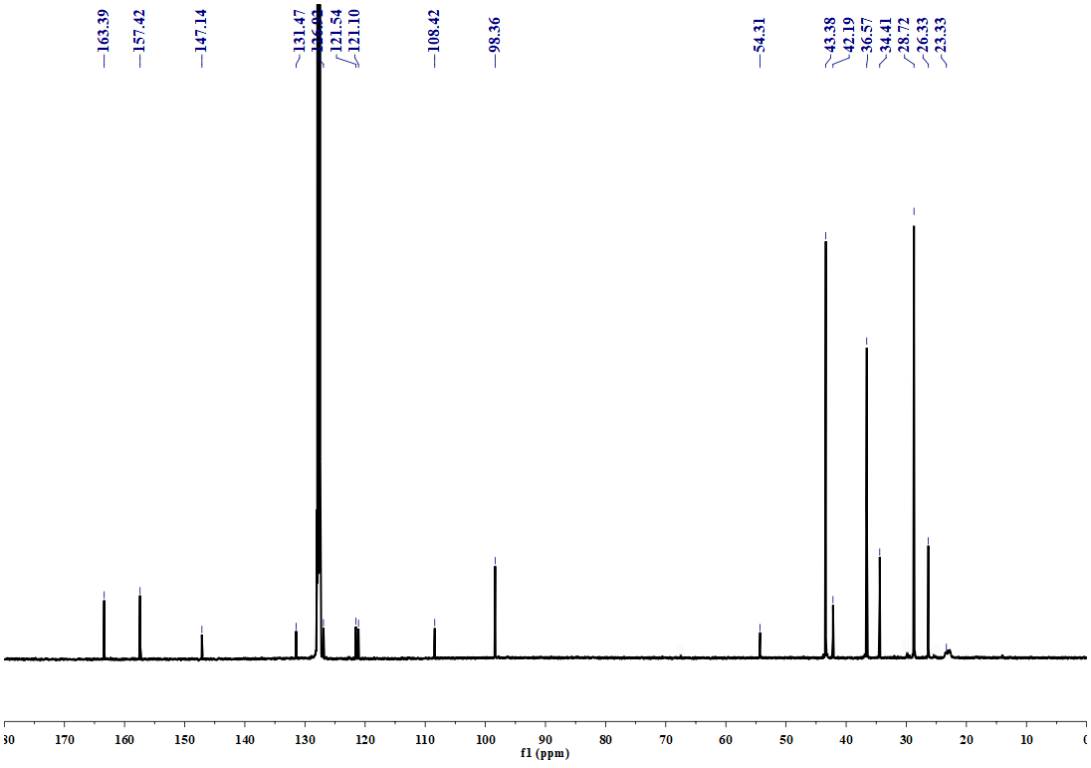

Figure S2. ^{13}C NMR spectrum (125 MHz) of [(Tp^{Ad,iPr})Ba(*o*-$CH_2C_6H_4$-NMe_2)] (**1**) in C_6D_6 at 25 ^{o}C.

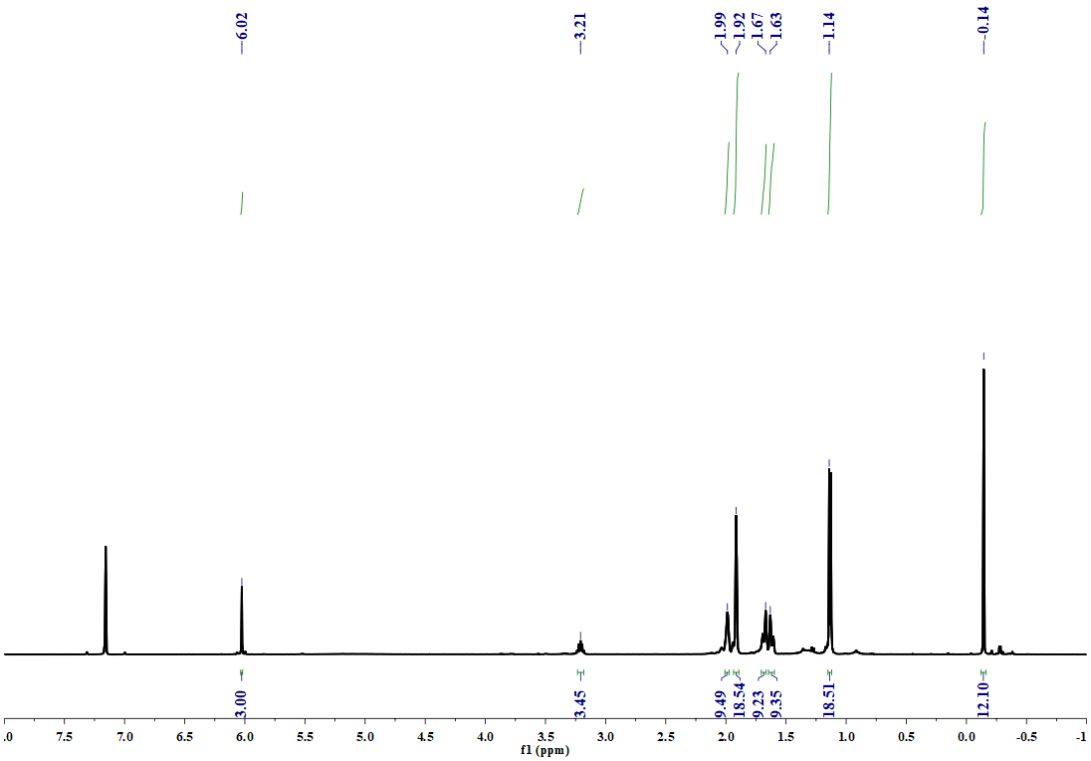

Figure S3. ^{1}H NMR spectrum (500 MHz) of [(Tp^{Ad,iPr})Ba(AlMe$_4$)]$_2$ (**2**) in C_6D_6 at 25 ^{o}C.

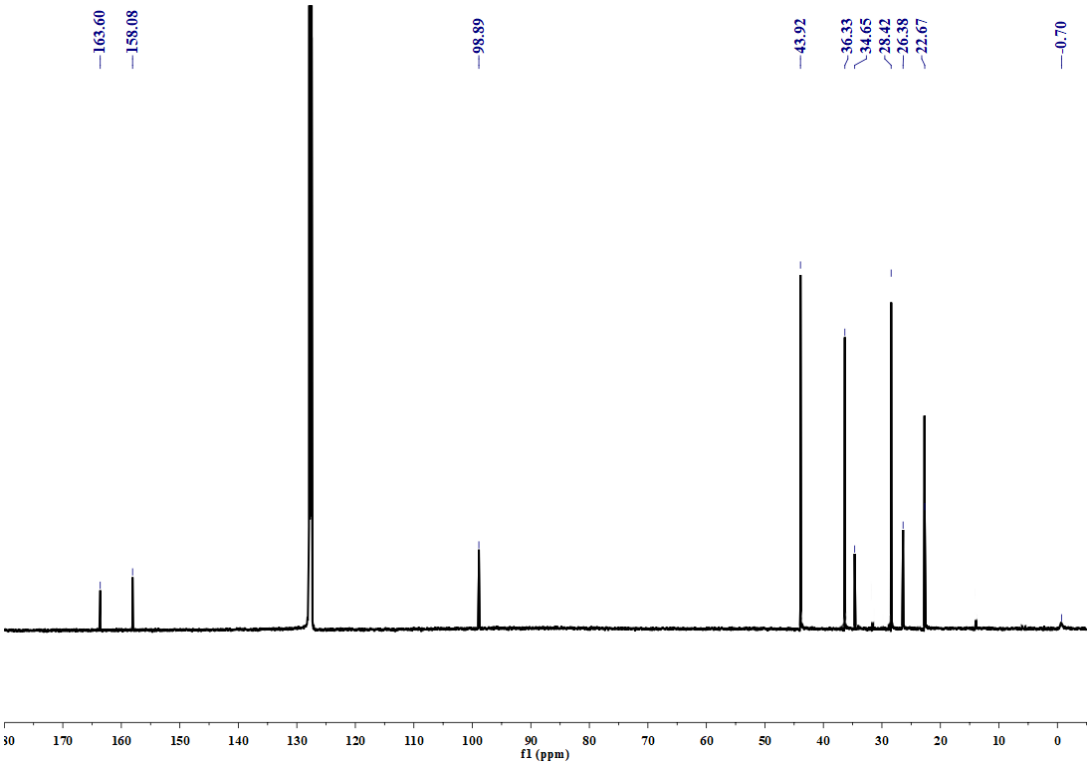

Figure S4. ^{13}C NMR spectrum (125 MHz) of [(Tp^{Ad,iPr})Ba(AlMe$_4$)]$_2$ (**2**) in C_6D_6 at 25 ^{o}C.

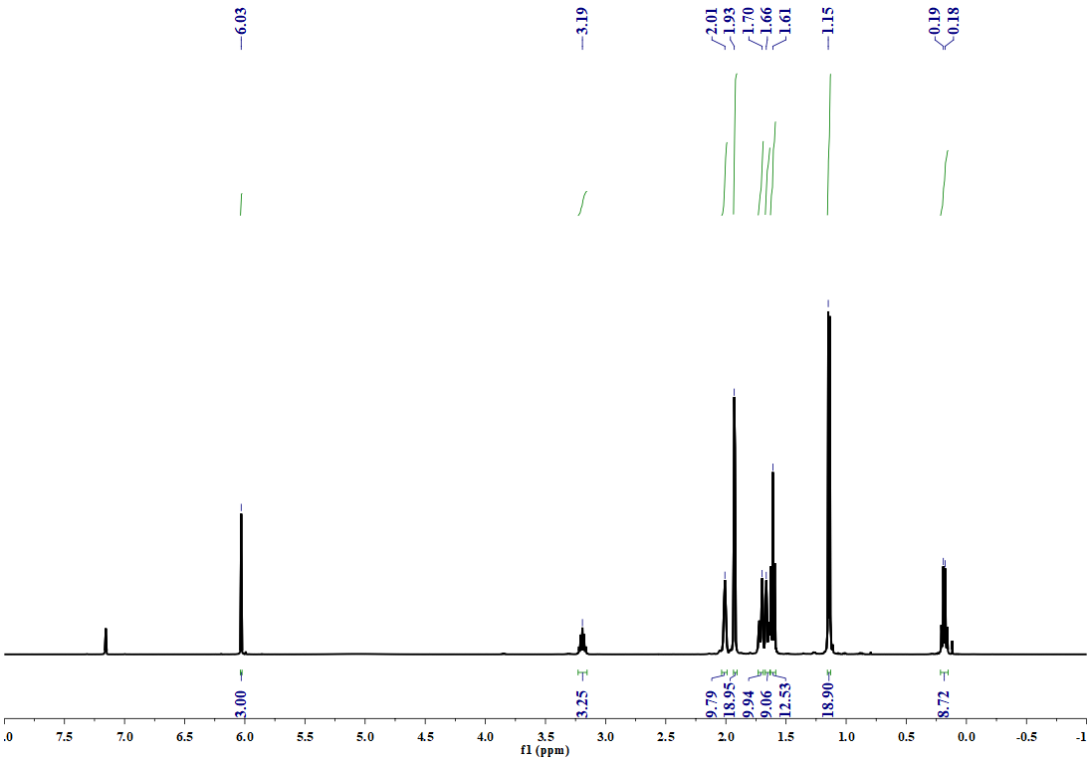

Figure S5. ^{1}H NMR spectrum (500 MHz) of [(Tp^{Ad,iPr})Ba(AlEt$_4$)] (**3**) in C_6D_6 at 25 ^{o}C.

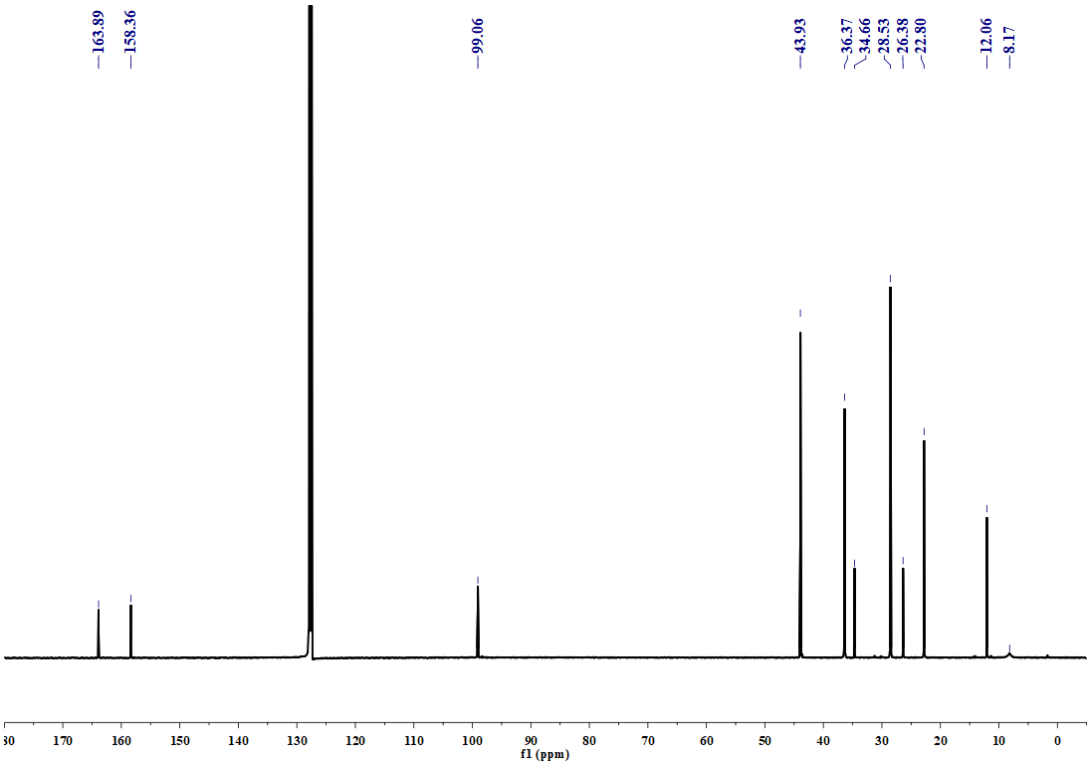

Figure S6. ^{13}C NMR spectrum (125 MHz) of [(Tp^{Ad,iPr})Ba(AlEt$_4$)] (**3**) in C_6D_6 at 25 ^{o}C.

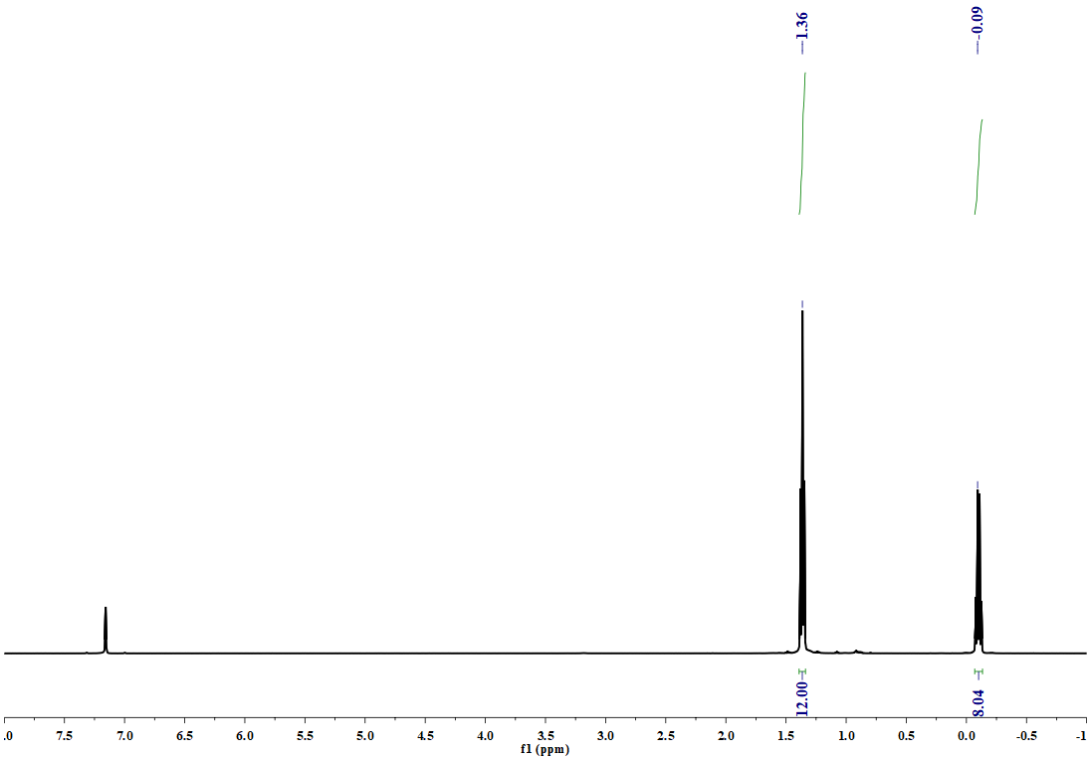

Figure S7. ^{1}H NMR spectrum (500 MHz) of $[Ba(AlEt_4)_2]_n$ (**3-a**) in C_6D_6 at 25 ^{o}C.

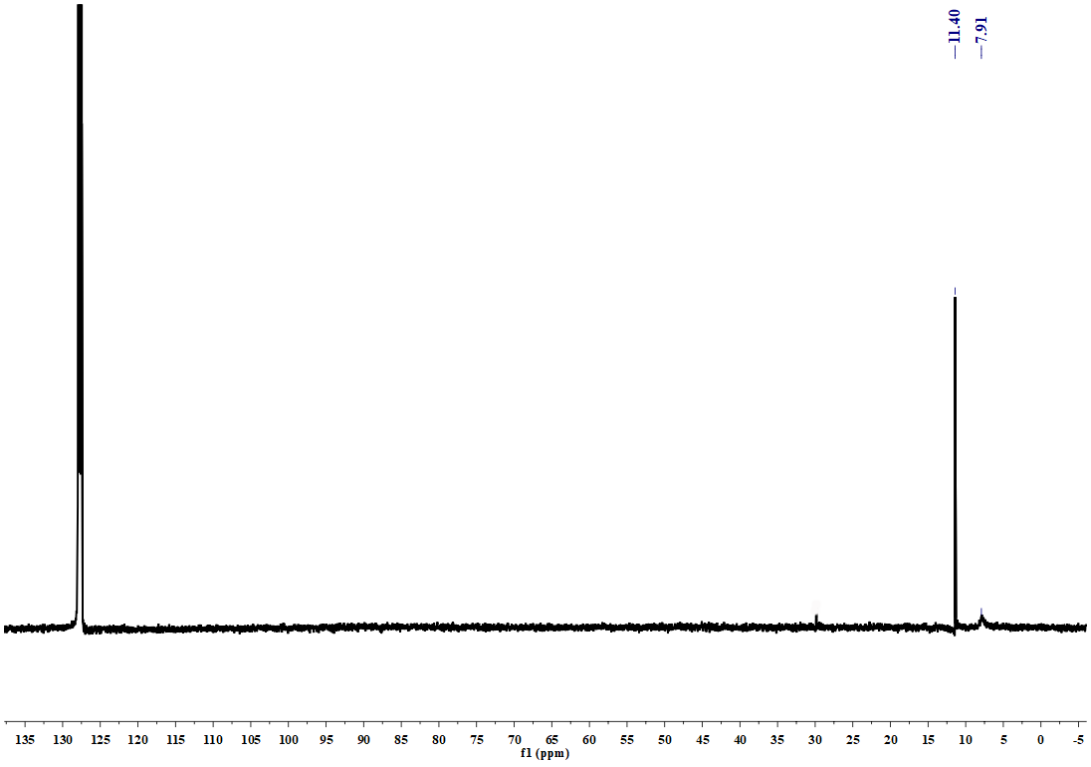

Figure S8. ^{13}C NMR spectrum (125 MHz) of $[\{Ba(AlEt_4)_2\}_n]$ (**3-a**) in C_6D_6 at 25 ^{o}C.

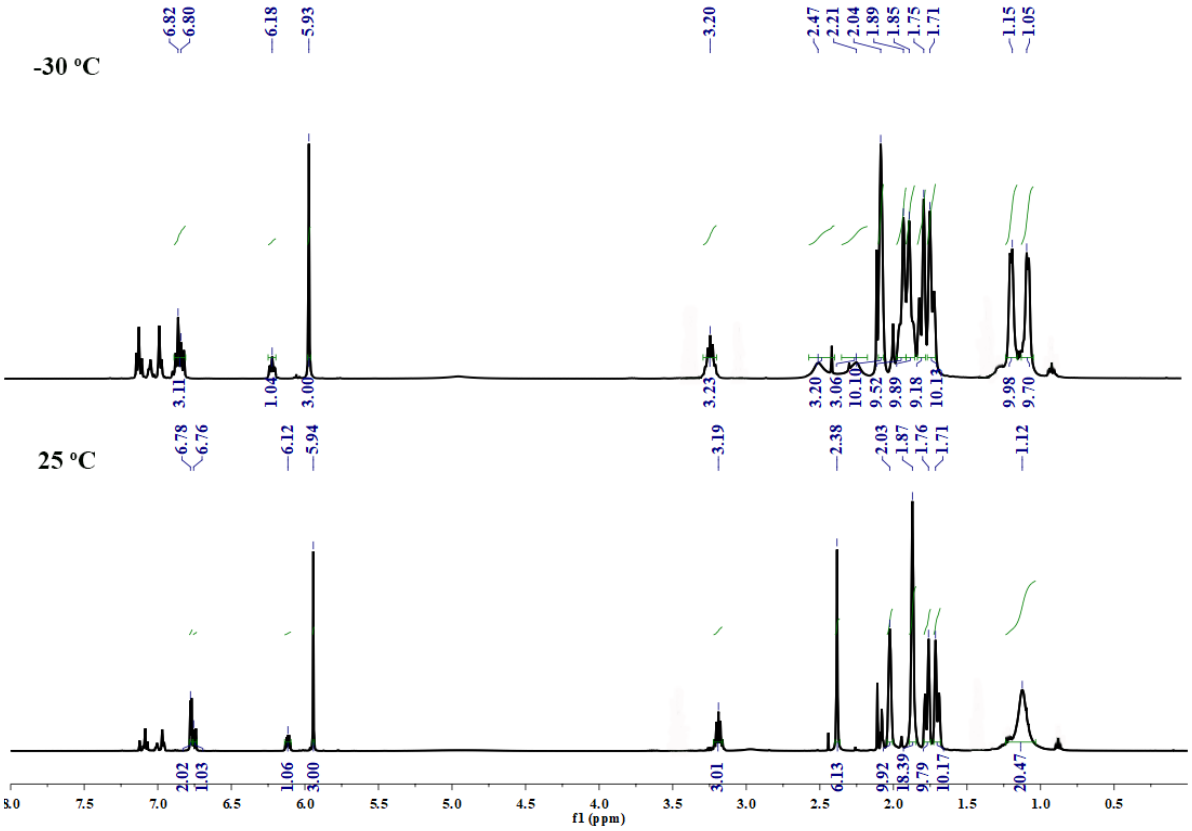

Figure S9. Stacked ^{1}H NMR spectrum (400 MHz) of [(Tp^{Ad,iPr})Ba(o-$CH_2C_6H_4$-NMe_2)] (**1**) in [D_8]toluene at 25 °C and -30 °C. A singlet for N(*Me*)$_2$ at 2.38 ppm and an extremely broad resonance at 1.12 ppm (20 H, belonging to methyl protons of isopropyl substituents and methylene protons of aminobenzyl group) at 25 °C split into two signal sets at −30 °C, featuring integral ratio of about 1:1.

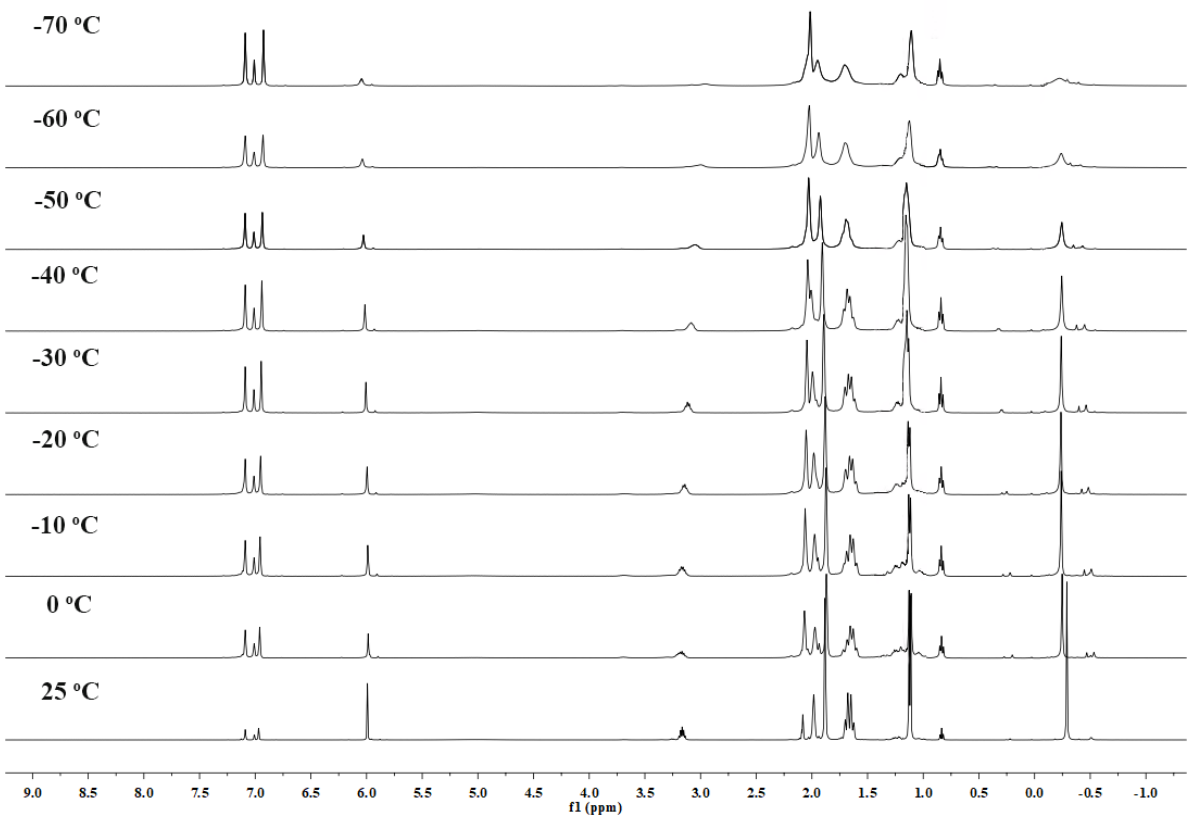

Figure S10. VT ^{1}H NMR spectra (400 MHz, [D_8]toluene) of [($Tp^{Ad,iPr}$)Ba($AlMe_4$)]$_2$ (**2**). Upon further cooling to −70 °C, these signals of the [$AlMe_4$] moieties and $Tp^{Ad,iPr}$ ligand broaden simultaneously, without any significant decoalescence of the corresponding proton resonances, indicating a rapid fluxional behavior in [D_8]toluene solution.

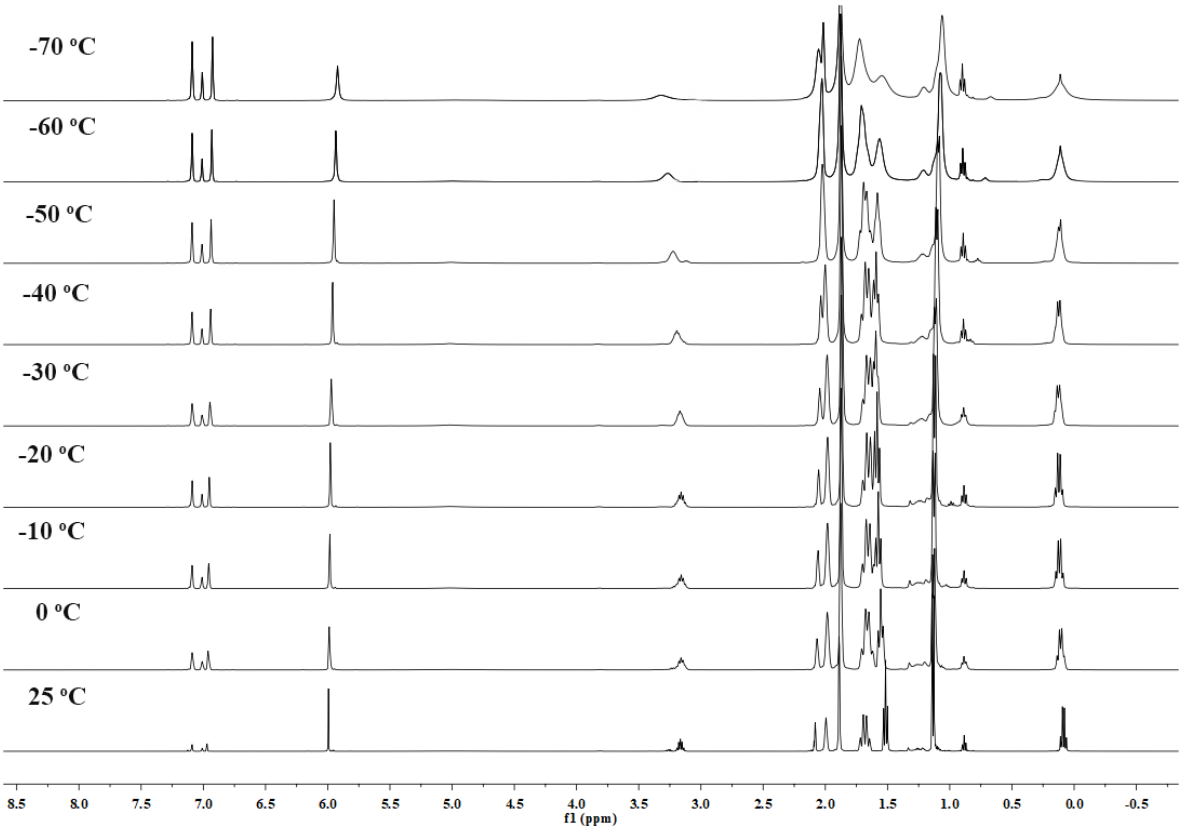

Figure S11. VT ^{1}H NMR spectra (400 MHz, [D_8]toluene) of [($Tp^{Ad,iPr}$)Ba($AlEt_4$)] (**3**). Upon further cooling to −70 °C, these signals of the [$AlEt_4$] moieties and $Tp^{Ad,iPr}$ ligand broaden simultaneously, without any significant decoalescence of the corresponding proton resonances, indicating a rapid fluxional behavior in [D_8]toluene solution.

2. Tables of crystal data and structure refinement

Table S1. Crystal data and structure refinement for Complex **1.**

Identification code	G053
CCDC number	1956785
Empirical formula	$C_{57}H_{82}BN_7Ba$
Formula weight	1013.44
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
a	11.6141 (6) Å
b	20.4509 (11) Å
c	25.1549 (13) Å
α	90 °
β	91.713 (1) °
γ	90 °
Volume	5972.1 (5) $Å^3$
Z, Calculated density	4, 1.127 Mg/m^3
Absorption coefficient	0.703 mm^{-1}
F(000)	2136
Crystal size	0.180 x 0.150 x 0.130 mm
Theta range for data collection	1.620 to 24.999 °
Limiting indices	-13<=h<=13, -24<=k<=13, -29<=l<=27
Reflections collected / unique	30065 / 10462 [R(int) = 0.0475]
Completeness to theta	(24.999 °) 99.5 %
Absorption correction	Empirical
Max. and min. transmission	0.913 and 0.881
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10462 / 0 / 569
Goodness-of-fit on F^2	1.035
Final R indices [I>2sigma(I)]	R1 = 0.0516, wR2 = 0.1240
R indices (all data)	R1 = 0.0718, wR2 = 0.1354
Largest diff. peak and hole	1.460 and -0.979 e. $Å^{-3}$

Table S2. Crystal data and structure refinement for Complex **2.**

Identification code	G050
CCDC number	1956786
Empirical formula	$C_{104}H_{164}Al_2B_2Ba_2N_{12}$
Formula weight	1932.78
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
a	12.2575(12) Å
b	14.7303(14) Å
c	15.1632(14) Å
α	95.071(1) °
β	93.004(2) °
γ	95.766(1) °
Volume	2708.1(4) $Å^3$
Z, Calculated density	2, 1.185 Mg/m^3
Absorption coefficient	0.787 mm^{-1}
F(000)	1020
Crystal size	0.180 x 0.140 x 0.120 mm
Theta range for data collection	1.673 to 24.999 °
Limiting indices	-9<=h<=14, -17<=k<=14, -18<=l<=17
Reflections collected / unique	13413 / 9265 [R(int) = 0.0223]
Completeness to theta	(24.999 °) 97.0 %
Absorption correction	Empirical
Max. and min. transmission	0.910 and 0.876
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9265 / 9 / 587
Goodness-of-fit on F^2	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0382, wR2 = 0.0931
R indices (all data)	R1 = 0.0467, wR2 = 0.0976
Largest diff. peak and hole	1.500 and -0.481 e. $Å^{-3}$

Table S3. Crystal data and structure refinement for Complex **3.**

Identification code	G081
CCDC number	1956787
Empirical formula	$C_{56}H_{90}AlBBaN_6$
Formula weight	1022.46
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
a	11.6917(6) Å
b	13.0673(6) Å
c	19.1695(9) Å
α	80.152(1) °
β	80.831(1) °
γ	75.528(1) °
Volume	2773.0(2) $Å^3$
Z, Calculated density	2, 1.225 Mg/m^3
Absorption coefficient	0.772 mm^{-1}
F(000)	1084
Crystal size	0.250 x 0.210 x 0.180 mm
Theta range for data collection	1.625 to 24.999 °
Limiting indices	-13<=h<=13, -15<=k<=14, -19<=l<=22
Reflections collected / unique	14145 / 9497 [R(int) = 0.0166]
Completeness to theta	(24.999 °) 97.2 %
Absorption correction	Empirical
Max. and min. transmission	0.870 and 0.824
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9497 / 0 / 606
Goodness-of-fit on F^2	1.029
Final R indices [I>2sigma(I)]	R1 = 0.0319, wR2 = 0.0801
R indices (all data)	R1 = 0.0351, wR2 = 0.0821
Largest diff. peak and hole	0.841 and -0.318 e. $Å^{-3}$

3. Crystal structure of [(Tp^{Ad,iPr})$_2$Ba]

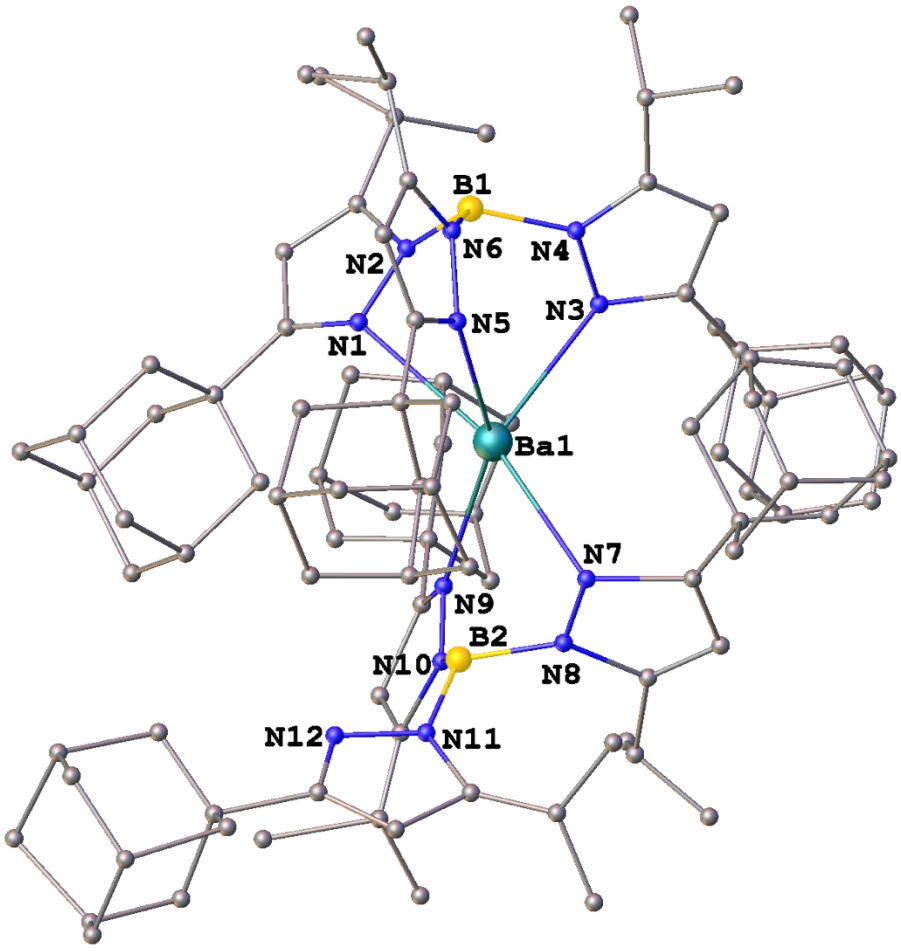

Figure S12. Olex2 drawing of complex [(Tp^{Ad,iPr})$_2$Ba]. Selected interatomic distances [Å]: Ba1–N1 2.738(12), Ba1–N3 2.796(10), Ba1–N5 2.825(10), Ba1–N7 2.845(11), Ba1–N9 3.008(11), Ba1---N12 5.210(11), Ba1---B1 3.536(16), Ba1---B2 3.334(16).