Electronic Supporting Information (ESI)

Synthesis and Structures of *Tris*(2-pyridyl)aluminate Sandwich Compounds [{RAl(2-py´)$_2$}$_2$M] (py´ = 2-pyridyl, M= Ca, Mn, Fe)

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Representative NMR spectra for selected compounds

NMR spectra for *[EtAl(6-Me-2-py)$_3$Li•THF] (4b)*;

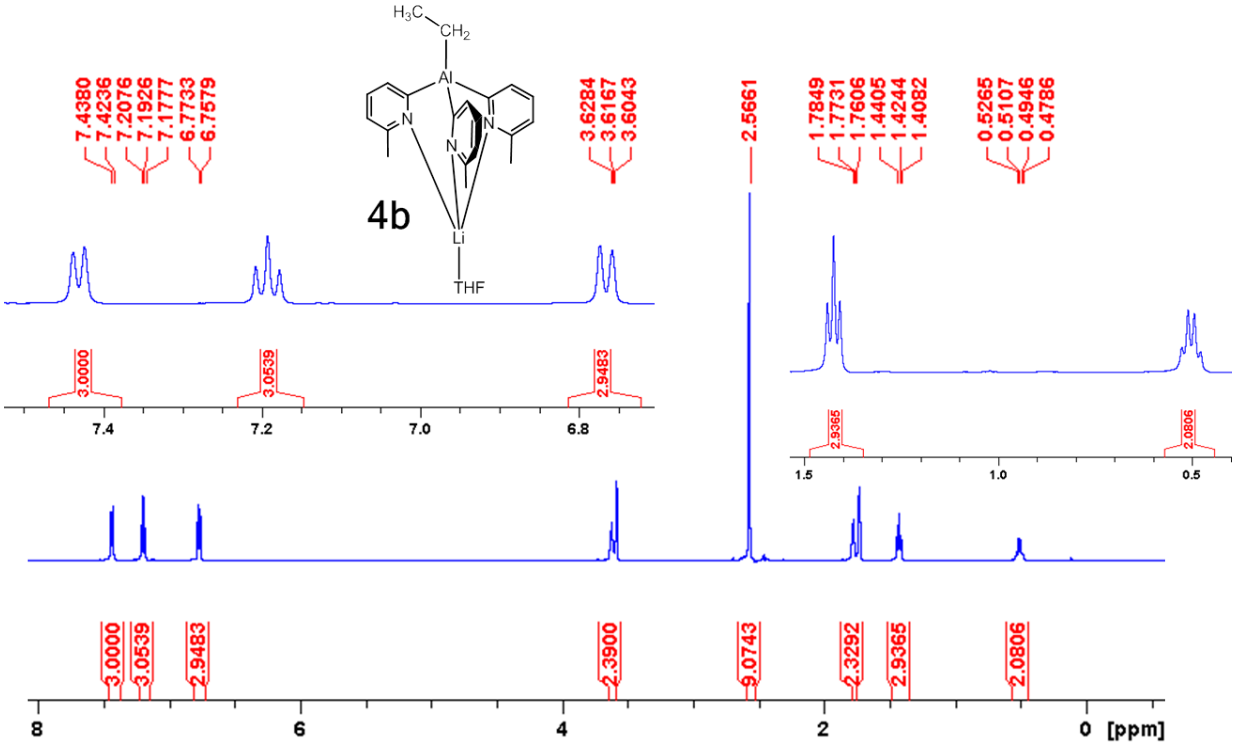

Figure S1. ^{1}H NMR (298 K, d_8-THF, 500 MHz) spectrum of *[EtAl(6-Me-2-py)$_3$Li•THF] (**4b**)*.

Note: A line broadening (lb) of 0.3Hz was using in the processing of the spectrum.

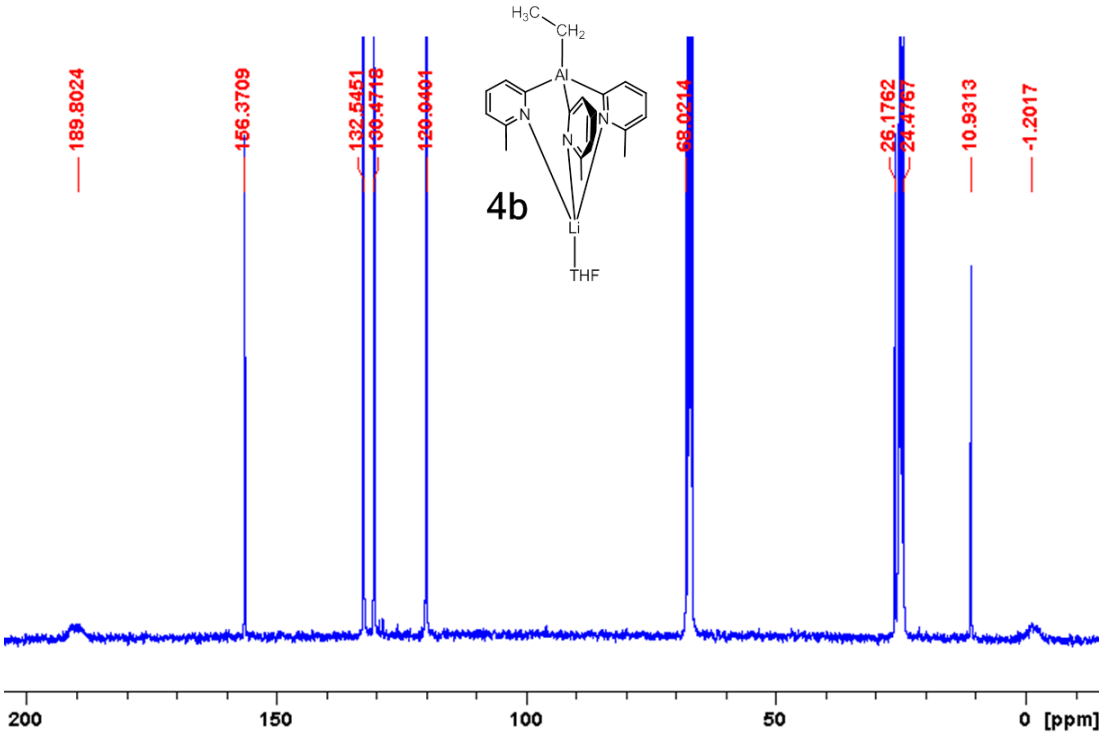

Figure S2.$^{13}C\{^{1}H\}$ NMR (298 K, d_8-THF, 100.6 MHz), spectrum of *[EtAl(6-Me-2-py)$_3$Li•THF]* ***(4b)***.

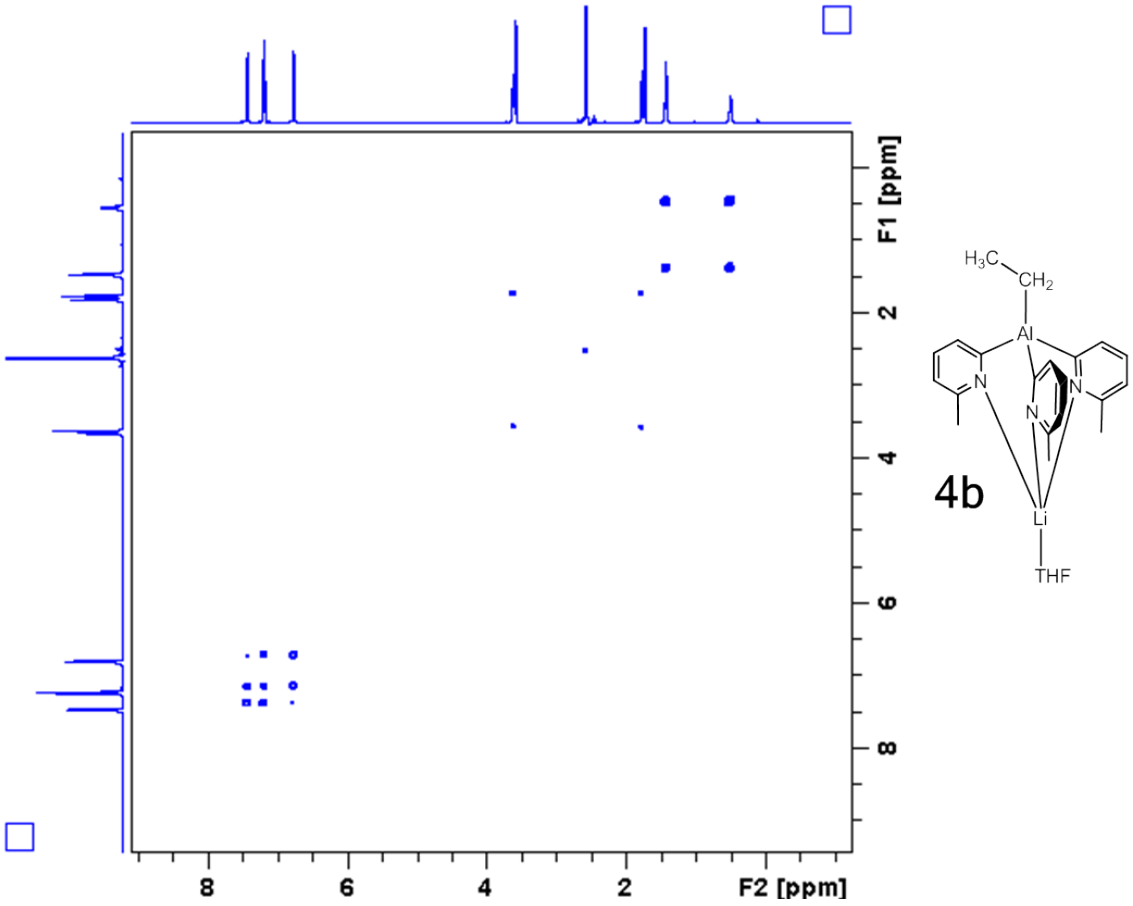

Figure S3. ^{1}H-^{1}H COSY (298 K, d_8-THF, 500 MHz) spectrum of *[EtAl(6-Me-2-py)$_3$Li•THF]* ***(4b)***.

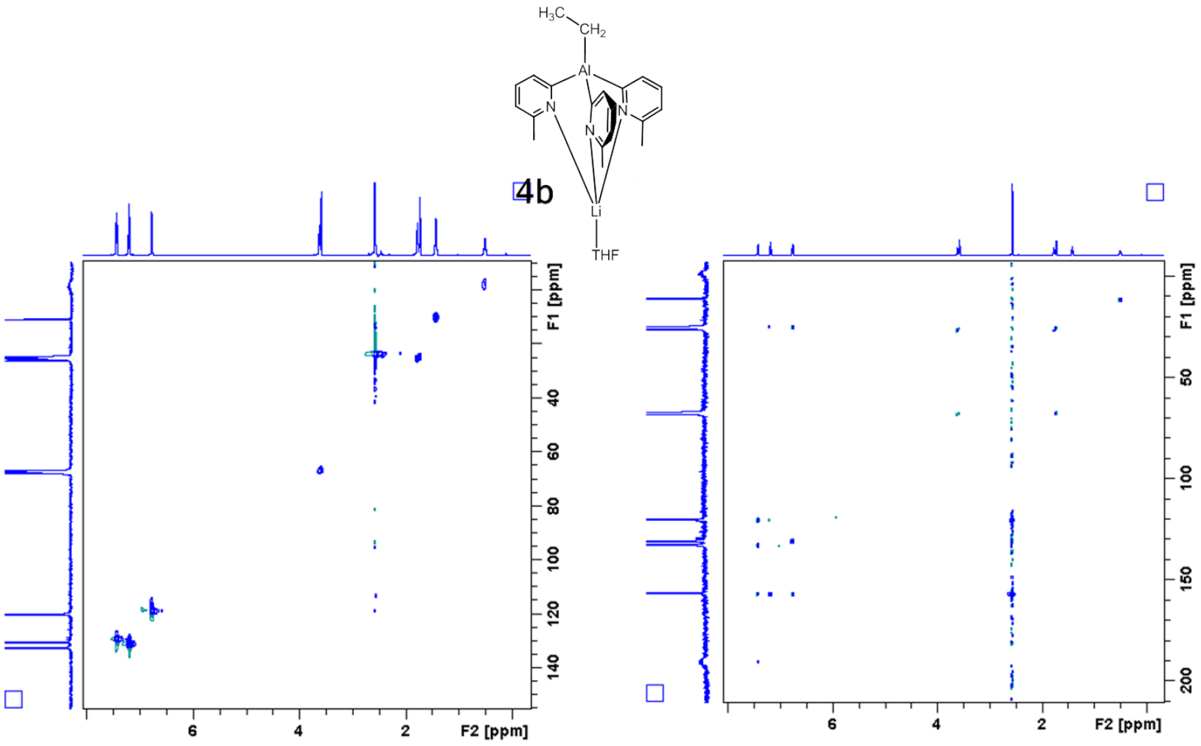

Figure S4. ^{1}H-^{13}C HMQC (298 K, d_8-THF, 500 MHz) (left) and ^{1}H-^{13}C HMBC (298 K, d_8-THF, 500 MHz) (right) spectra of *[EtAl(6-Me-2-py)$_3$Li•THF]* ***(4b)***.

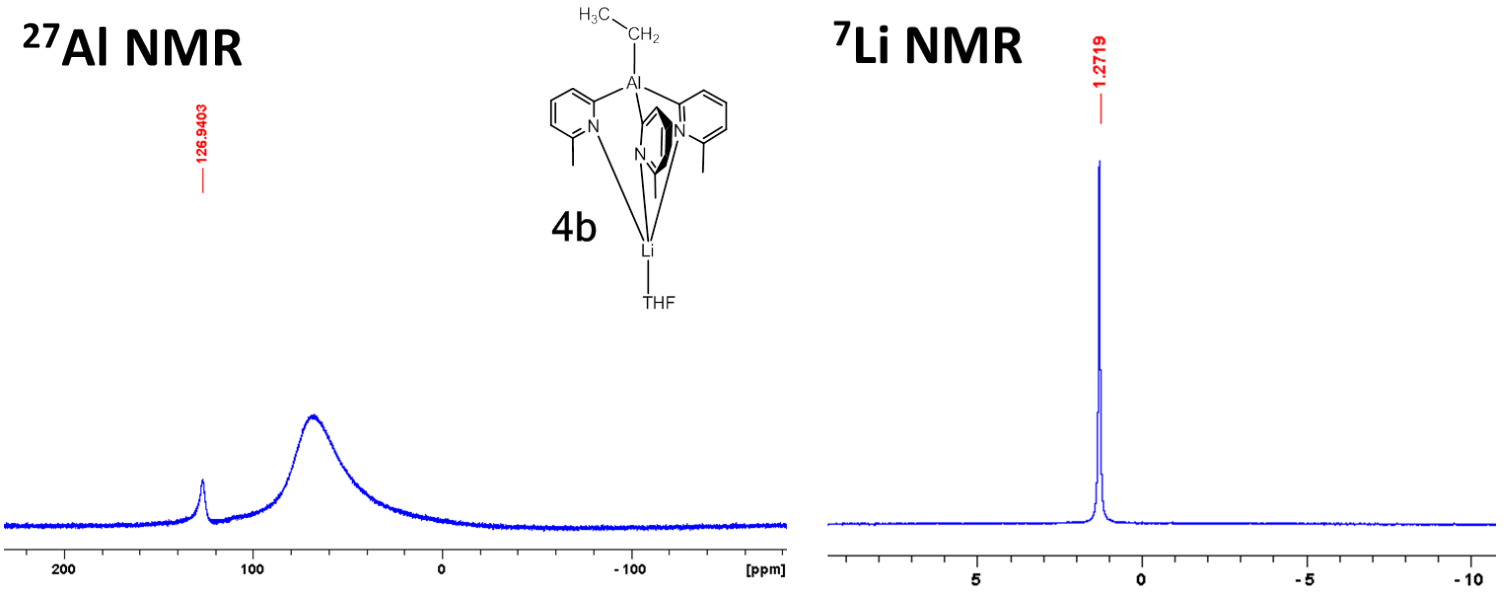

Figure S5. ^{27}Al NMR (298 K, d_8-THF, 130.3 MHz, ref solution of $AlCl_3.6H_2O/D_2O$) (left) and ^{7}Li NMR (298 K, d_8-THF, 194.4 MHz, ref solution of $LiCl/D_2O$) (right) spectra of *[EtAl(6-Me-2-py)$_3$Li•THF]* ***(4b)***.

Note: The broad signal at around 65ppm in the ^{27}Al NMR spectrum arises from probe background.

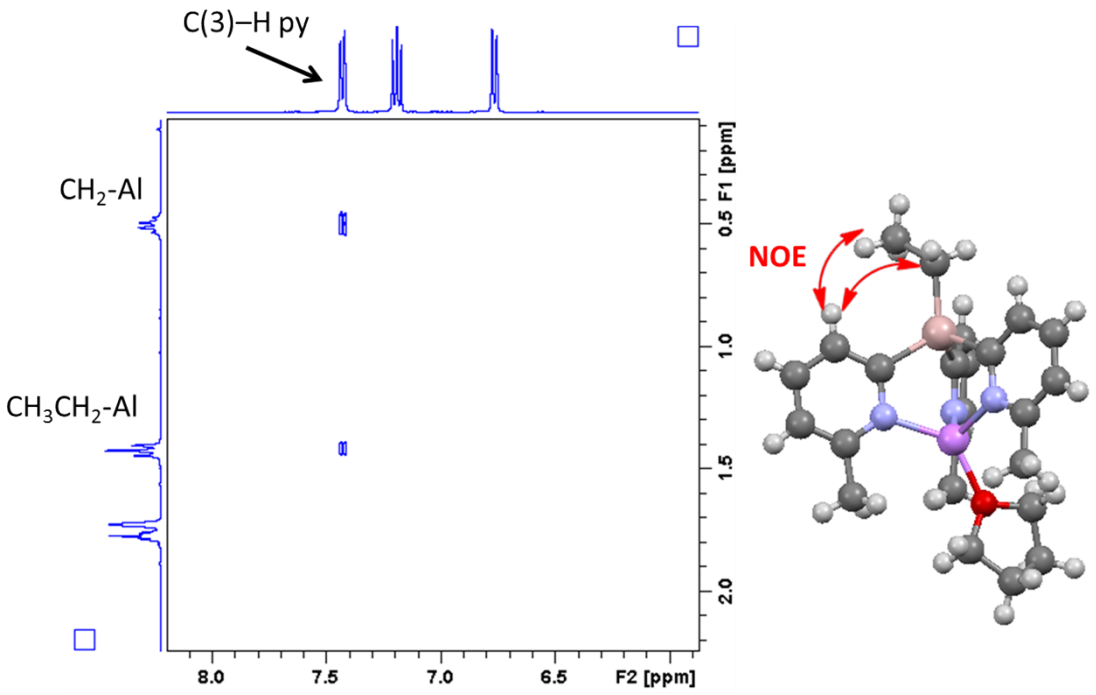

Figure S6. ^{1}H-^{1}H NOESY (298 K, d_8-THF, 500 MHz, mixing time of 600 ms) spectrum of of *[EtAl(6-Me-2-py)$_3$Li•THF]* (***4b***). Crosspeaks observed between the C(3)–H py proton and the protons of Al-CH_2CH_5 arise from intramolecular cross-relaxation of protons that are close to each other in space, confirming the presence of an Et−Al-Py linkage.

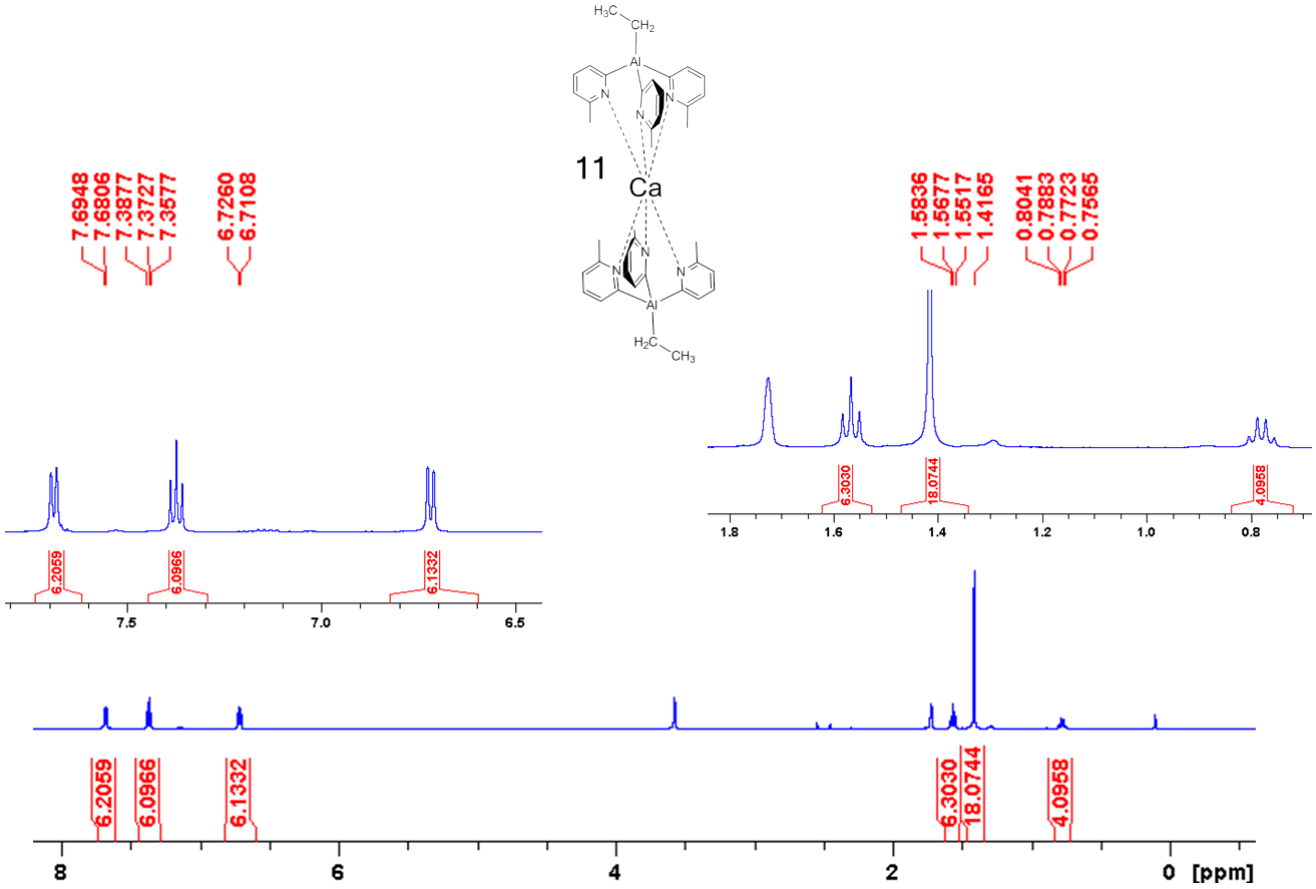

Figure S7. ^{1}H NMR (298 K, d_8-THF, 500 MHz) spectrum of *[{EtAl(6-Me-2-py)$_3$}$_2$Ca] **(11)***.

Note: A line broadening (lb) of 0.3Hz was using in the processing of the spectrum.

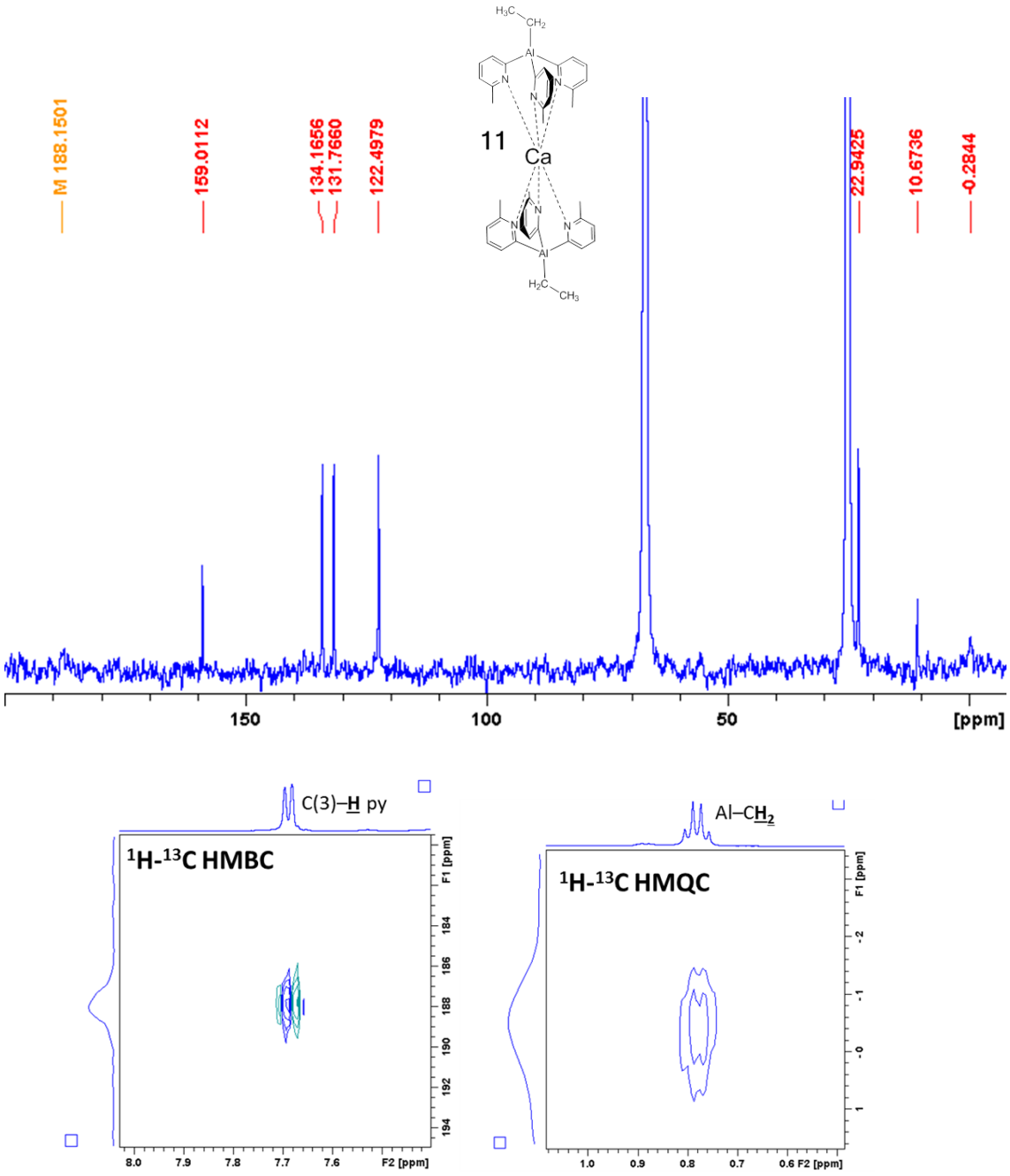

Figure S8. $^{13}C\{^{1}H\}$ NMR (298 K, d_8-THF, 125.8 MHz), spectrum of *[{EtAl(6-Me-2-py)$_3$}$_2$Ca] **(11)***. Observation of signals at 188.15 (br, C(2)) and 0.28 (br, Al–CH2) was challenging due to its broadening and the poor noise/signal ratio but they were also observed through ^{1}H-^{13}C HMBC and ^{1}H-^{13}C HMQC experiments (see below for selected regions of the spectra and fig S10 for full spectra)

Note: A line broadening (lb) of 15Hz was using in the processing of the $^{13}C\{^{1}H\}$ NMR spectrum.

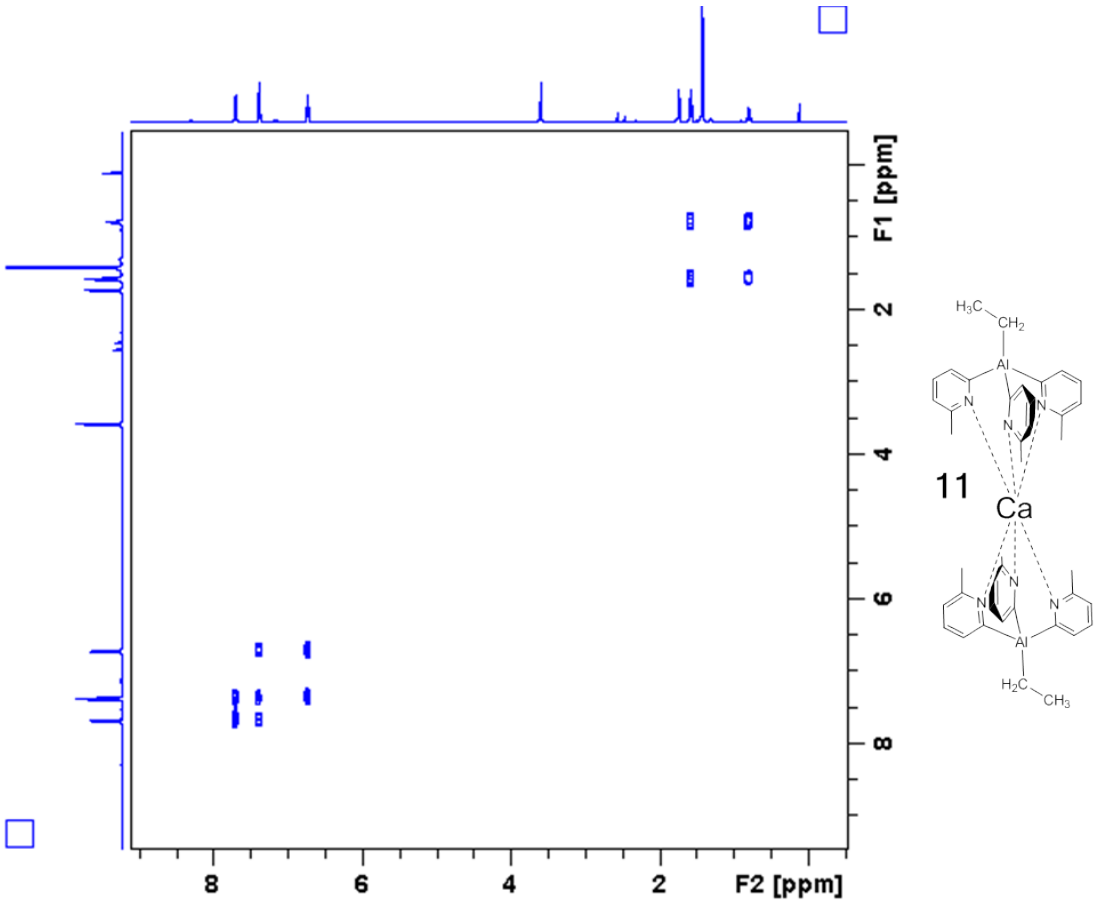

Figure S9. ^{1}H-^{1}H COSY (298 K, d_8-THF, 500 MHz) spectrum of *[{EtAl(6-Me-2-py)3}2Ca] (**11**)*.

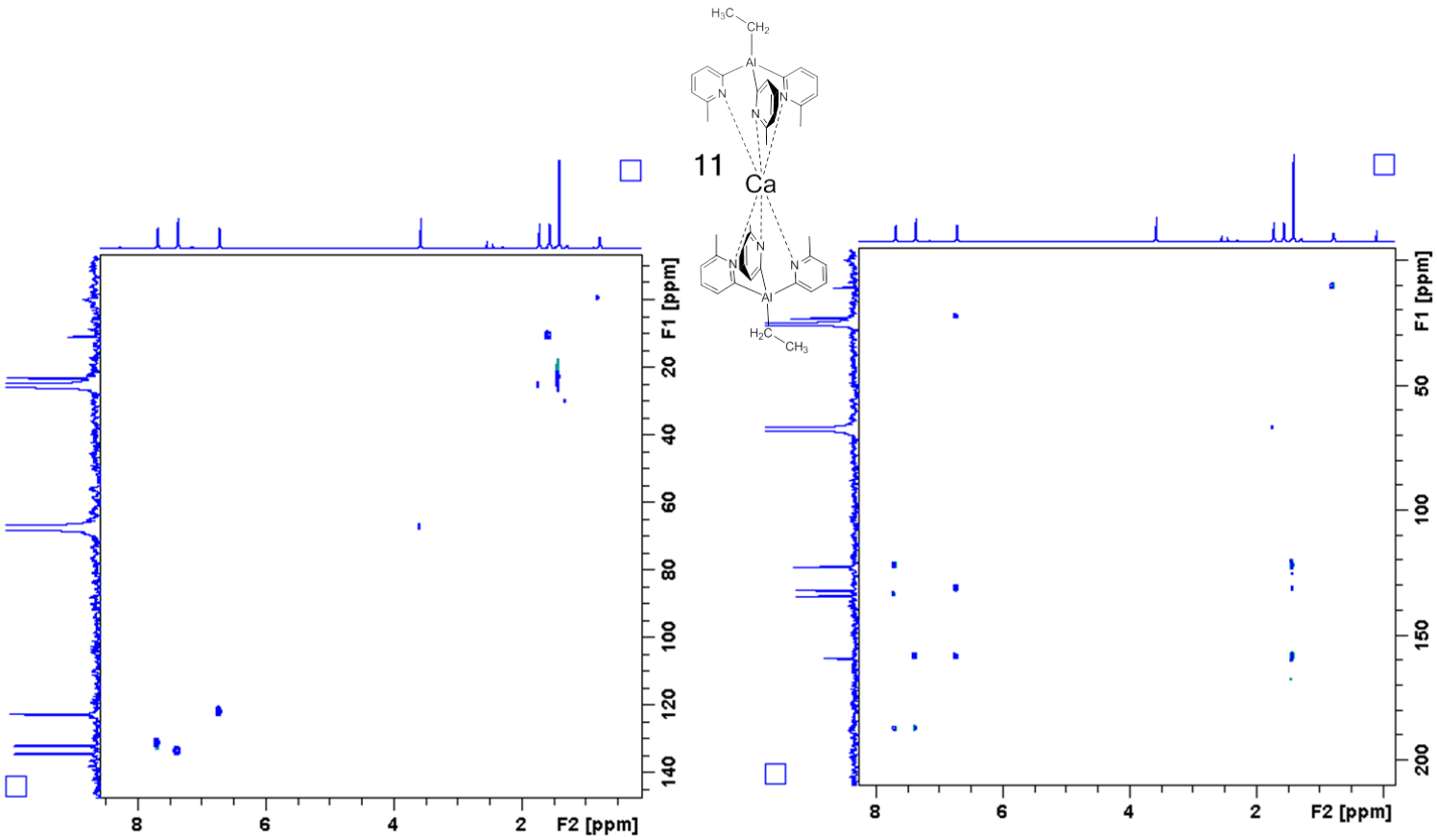

Figure S10. ^{1}H-^{13}C HMQC (298 K, d_8-THF, 500 MHz) left and ^{1}H-^{13}C HMBC (298 K, d_8-THF, 500 MHz) right spectra of *[{EtAl(6-Me-2-py)$_3$}2Ca] (**11**)*.

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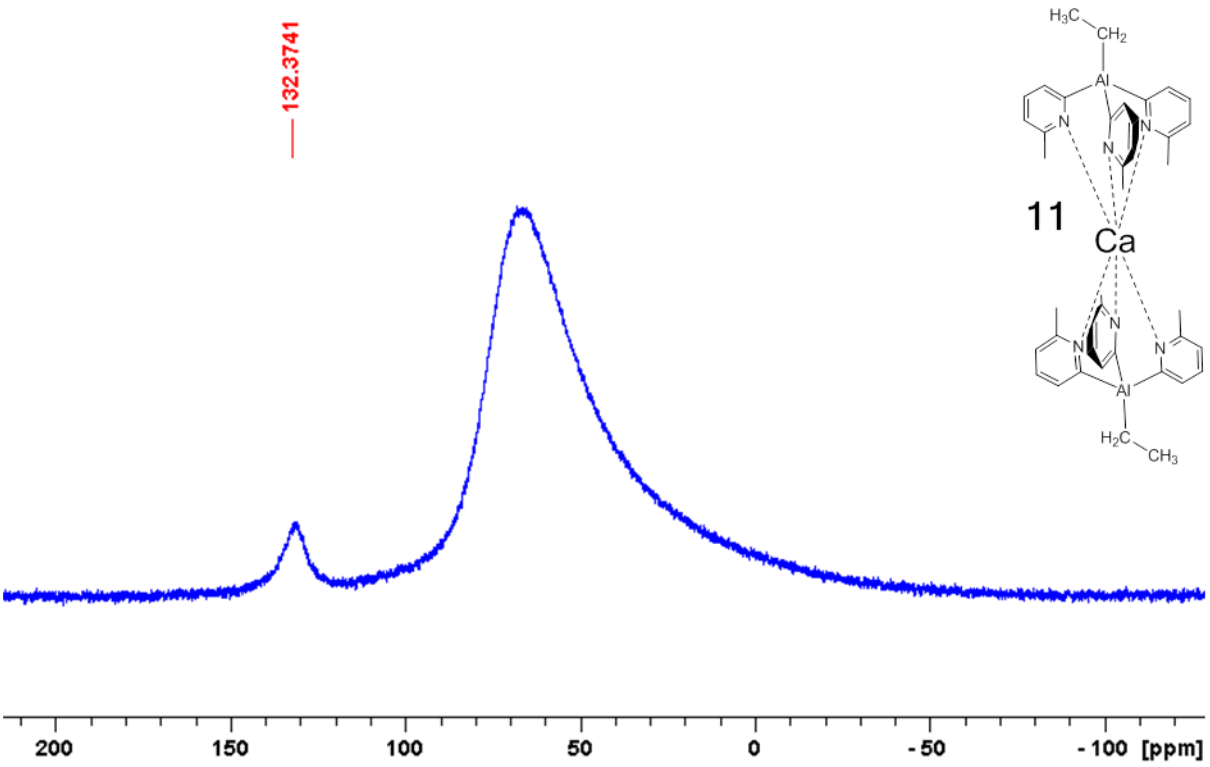

Figure S11. ^{27}Al NMR (298 K, d_8-THF, 130.3 MHz, ref solution of $AlCl_3.6H_2O/D_2O$) spectrum of *[{EtAl(6-Me-2-py)3}2Ca] (**11**)*.

Note: The broad signal at around 65ppm in the ^{27}Al NMR spectrum arises from probe background.

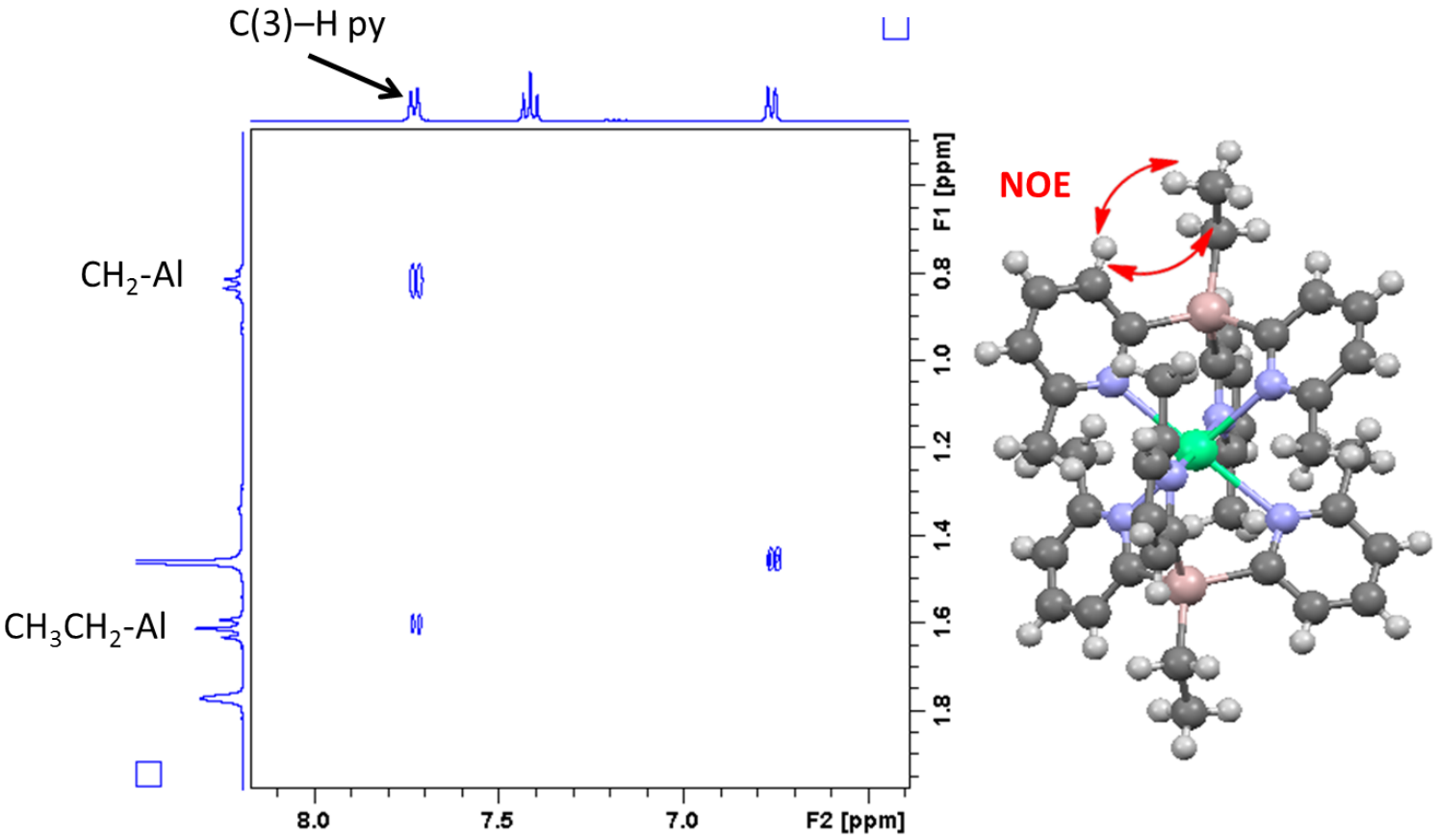

Figure S12. ^{1}H-^{1}H NOESY (298 K, d_8-THF, 500 MHz, mixing time of 600 ms) spectrum of *[{EtAl(6-Me-2-py)3}2Ca]* ***(11)***. Crosspeaks observed between the C(3)–H py proton and the protons of Al-CH_2CH_5 arise from intramolecular cross-relaxation of protons that are close to each other in space, confirming the presence of an Et−Al-Py linkage.

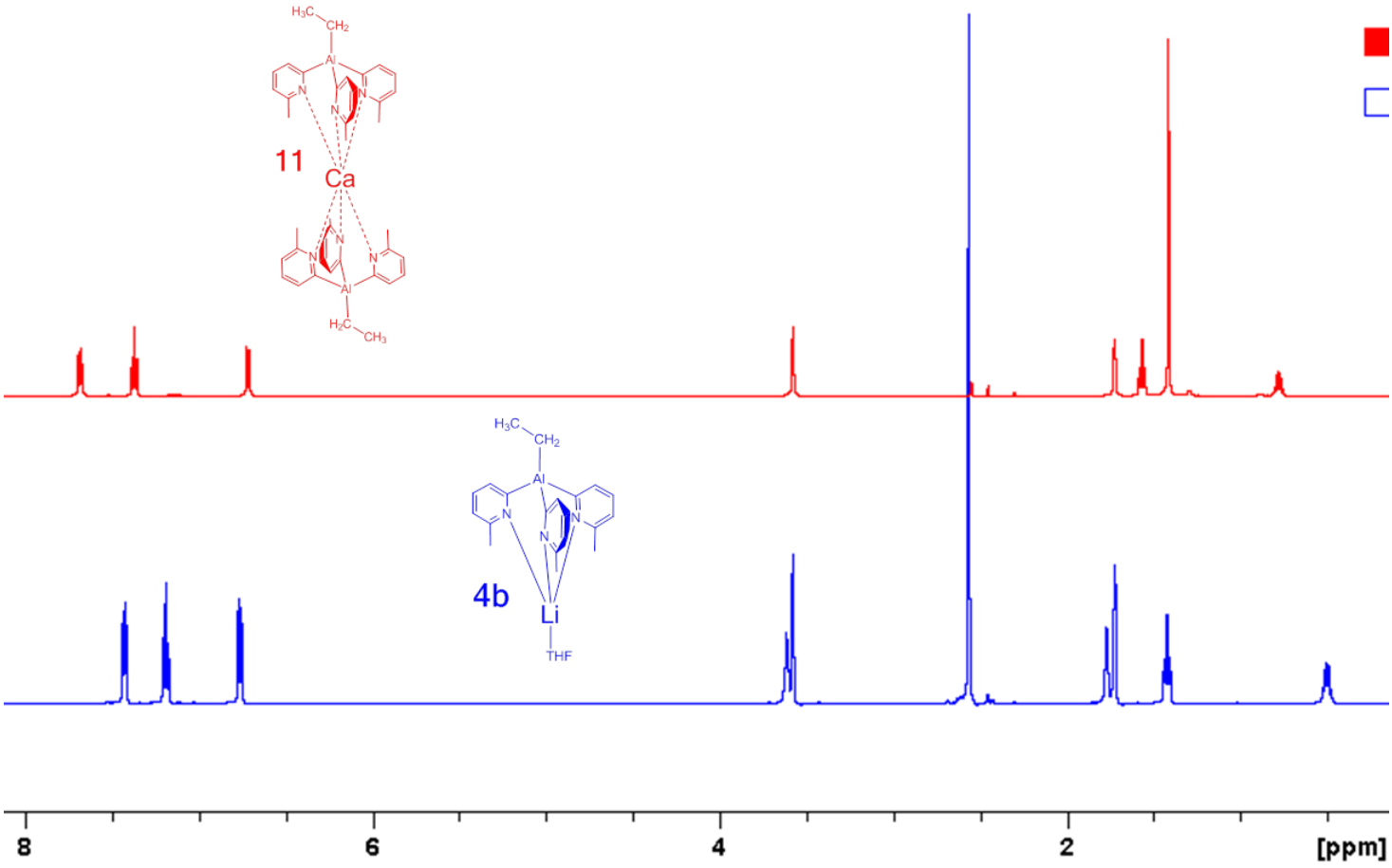

Figure S13. Stacked ^{1}H NMR spectra (298 K, d_8-THF, 500 MHz) comparing the differences in chemical shift between *[EtAl(6-Me-2-py)$_3$Li•THF]* (***4b***) and *[{EtAl(6-Me-2-py)$_3$}$_2$Ca]* (***11***).

Note: A line broadening (lb) of 0.3Hz was using in the processing of the spectra.

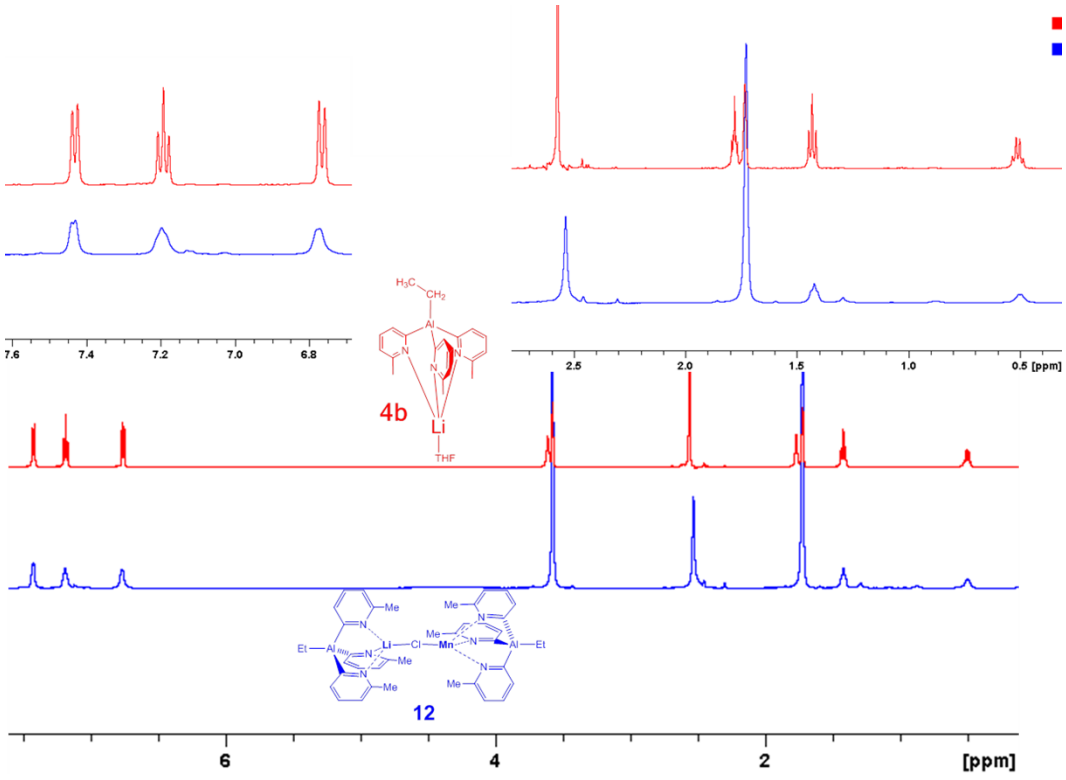

Figure S14. Stacked ^{1}H NMR spectra (298 K, d_8-THF, 500 MHz) comparing the ^{1}H NMR spectra of *[EtAl(6-Me-2-py)$_3$Li•THF]* ***(4b)*** and *[{EtAl(6-Me-2-py)$_3$}Mn(μ-Cl)Li{(6-Me-2-py)$_3$AlEt}]* ***(12)***.

Note: A line broadening (lb) of 0.3Hz was using in the processing of the spectra

X-ray data for 12 (*R*3-polymorph)

Crystal data: **12 (*R*3)**: $C_{40}H_{46}Al_2ClLiMnN_6$, M = 762.12, *triclinic*, space group *R*3, *Z* = 3, *a* = 12.543(1), *b* = 12.543(1), *c* = 22.339(2)Å, V = 3043.7(4) Å^3, μ(Cu–Kα) = 3.938 mm^{-1}, λ = 1.54184 nm, *T* = 250(2) K, ρ_{calc} = 1.247 Mg m^{-3}, *T* = 180(2) K. Total reflections 2280, unique 881 (R_{int} = 0.031). *R*1 = 0.096 [$I>2\sigma(I)$] and *wR*2 = 0.2389. The Mn(1)-Cl(1)-Li(1) fragment (occupancy 0.29000) and the Li(2)-Cl(2)-Mn(2) fragment (occupancy 0.04333) were restrained to have the same geometry, all Mn, Cl and Li atoms were assigned a common isotropic displacement parameter. The result seems reasonable (Mn-Cl distances 2.35A, Li-Cl distances 2.80A, U(iso)=0.07), consistent with that observed for the low-temperature trigonal form. The terminal Et groups M-C(1)-C(2) are not well resolved, each was modelled with three distance restraints d1=M-C(1),d2= M-C(2), d3=C(1)-C(2) where d1, d2 and d3 were estimated from the better-resolved refinement of the low temperature trigonal

form. Despite this refinement strategy, the parameter-data ratio is still poor (5:1), reflecting the very poor quality of this dataset (the best of three datasets from three different crystals).