Electronic Supplementary Information

Deprotonation, Insertion and Isomerisation in the Post-functionalisation of *Tris*-pyridyl Aluminates

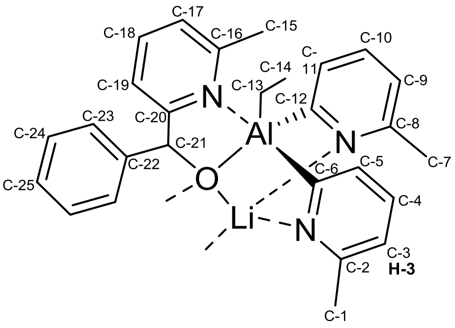
Alex J. Plajer, Sara Kopf, Annie L. Colebatch, Andrew D. Bond, Dominic S. Wright*, Raúl García-Rodríguez.*

1. Synthetic Procedures

General Experimental Methods

All experiments were carried out on a Schlenk-line under nitrogen atmosphere or with the aid of a N_2-filled glove box (Saffron type α). Toluene and THF were dried under nitrogen over sodium or sodium/benzophenone, respectively, whereas acetonitrile was dried over calcium hydride. Trispyridylaluminates were synthesized according to literature methods. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker Avance 400 QNP or Bruker Avance 500 MHz cryo-spectrometer. All spectra were recorded in d_8-toluene or d_8-THF with $SiMe_4$ (^1H, ^{13}C), $AlCl_3$ (^{127}Al, in D_2O) and LiCl (^7Li, in D_2O) as external standards. Unambiguous assignments of NMR resonances were made on the basis of 2D NMR experiments (^1H-^1H COSY, ^1H-^1H NOESY, ^1H-^{13}C HMQC and ^1H-^{13}C HMBC). Elemental analysis was obtained using a Perkin Elmer 240 Elemental Analyser, and UV-visible spectra were collected on a Varian Cary 50 UV spectrometer.

2. NMR Spectroscopy



$(\mathbf{2}\text{Li})_2$

Figure S1: Labelling scheme for **2**Li; hydrogen atoms are labelled according to the number of the attached carbon atom

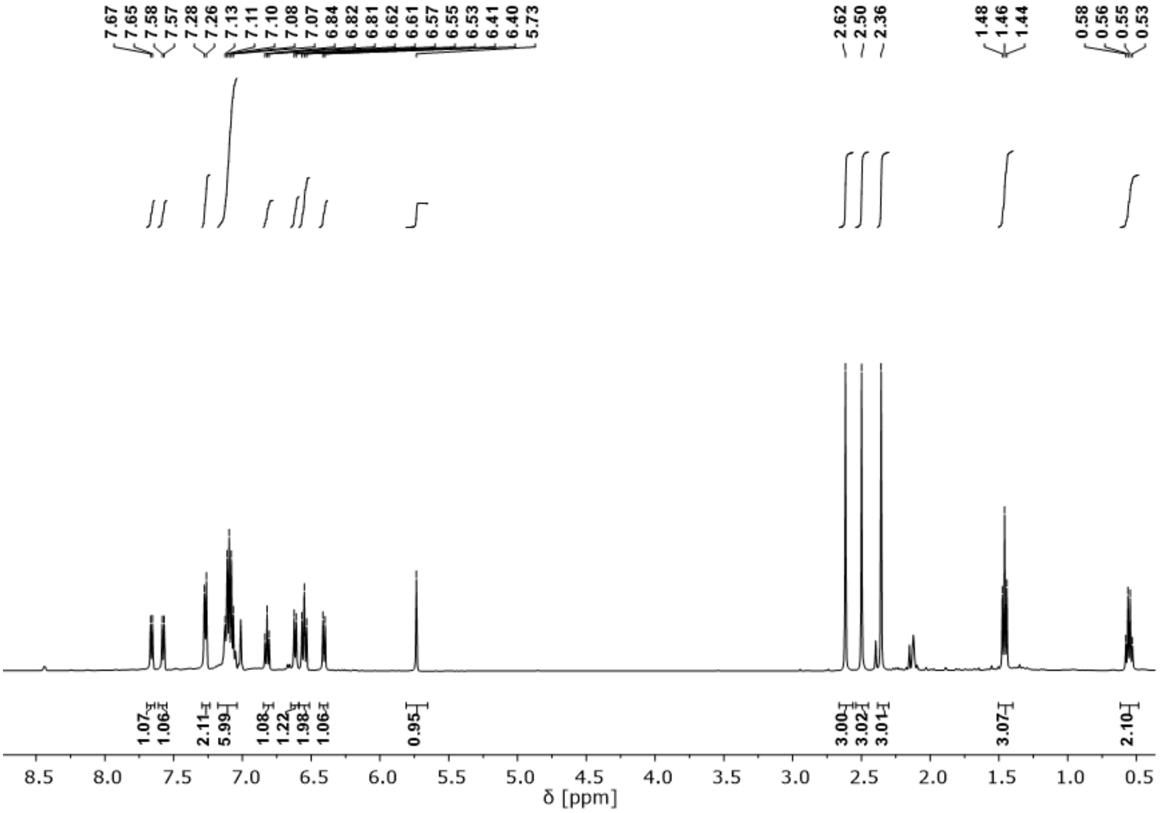


Figure S2: ^{1}H NMR (500 MHz, d$_8$-Toluene, 25 °C) spectrum of $(\mathbf{2}\text{Li})_2$

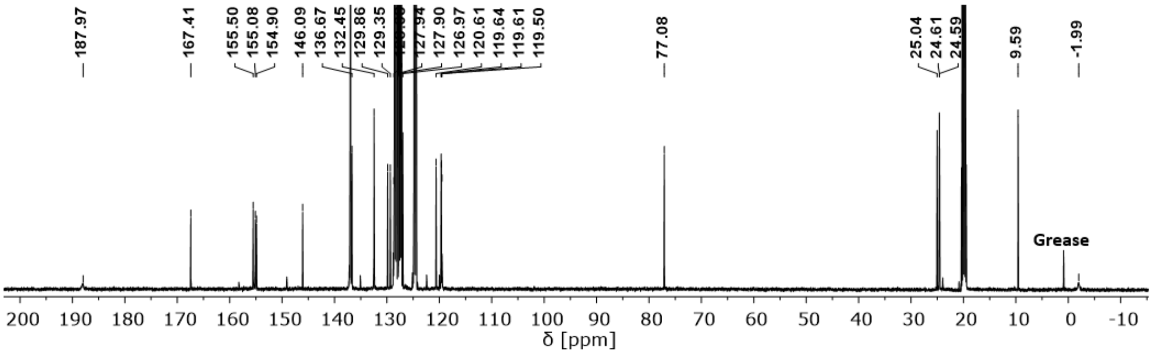


Figure S3: ^{13}C NMR (126 MHz, d_8-Toluene, 25 °C) spectrum of (**2**Li)$_2$

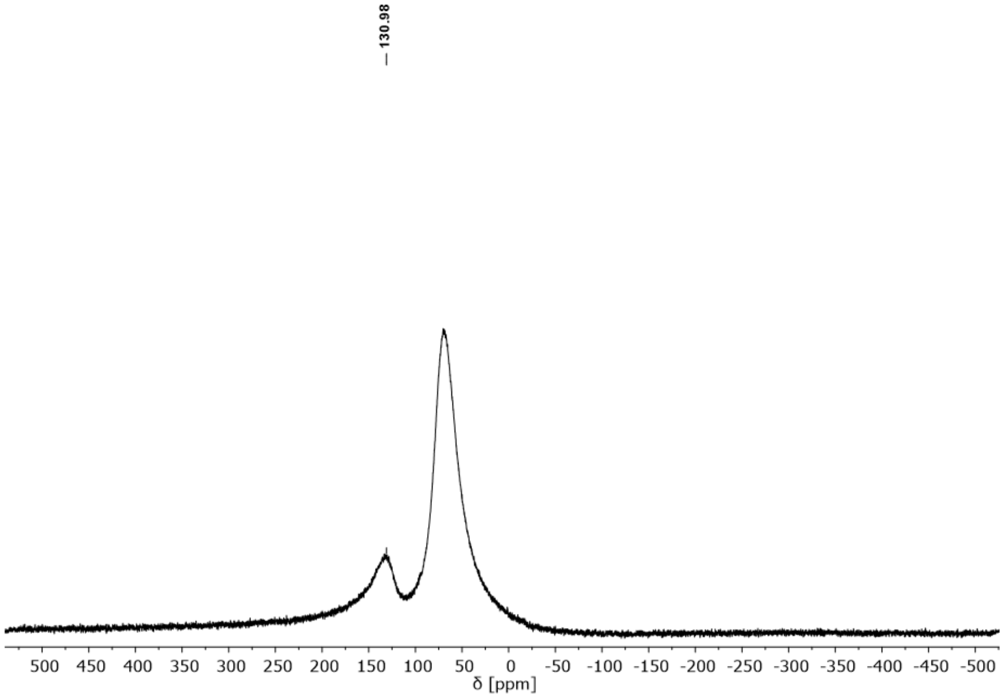


Figure S4: ^{27}Al NMR (130 MHz, d_8-Toluene, 25 °C) spectrum of (**2**Li)$_2$

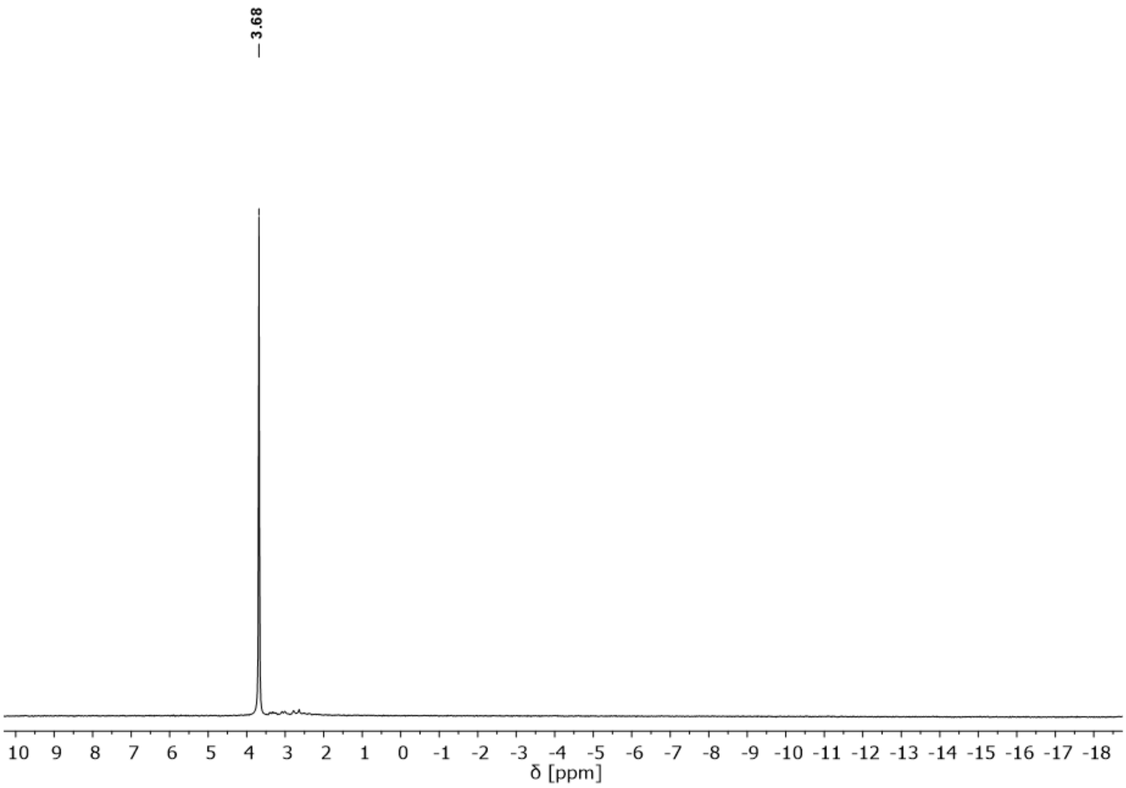
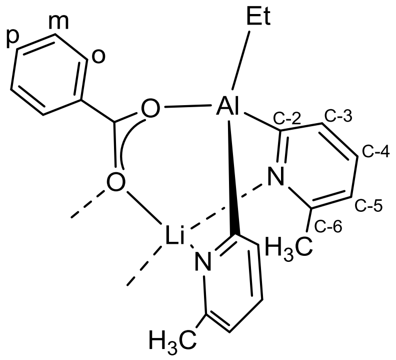


Figure S5: ^{7}Li NMR (194 MHz, d_8-Toluene, 25 °C) spectrum of (**2**Li)$_2$



(**3**Li)$_2$

Figure S6: Labelling scheme for (**3**Li)$_2$; hydrogen atoms are labelled according to the number of the attached carbon atom

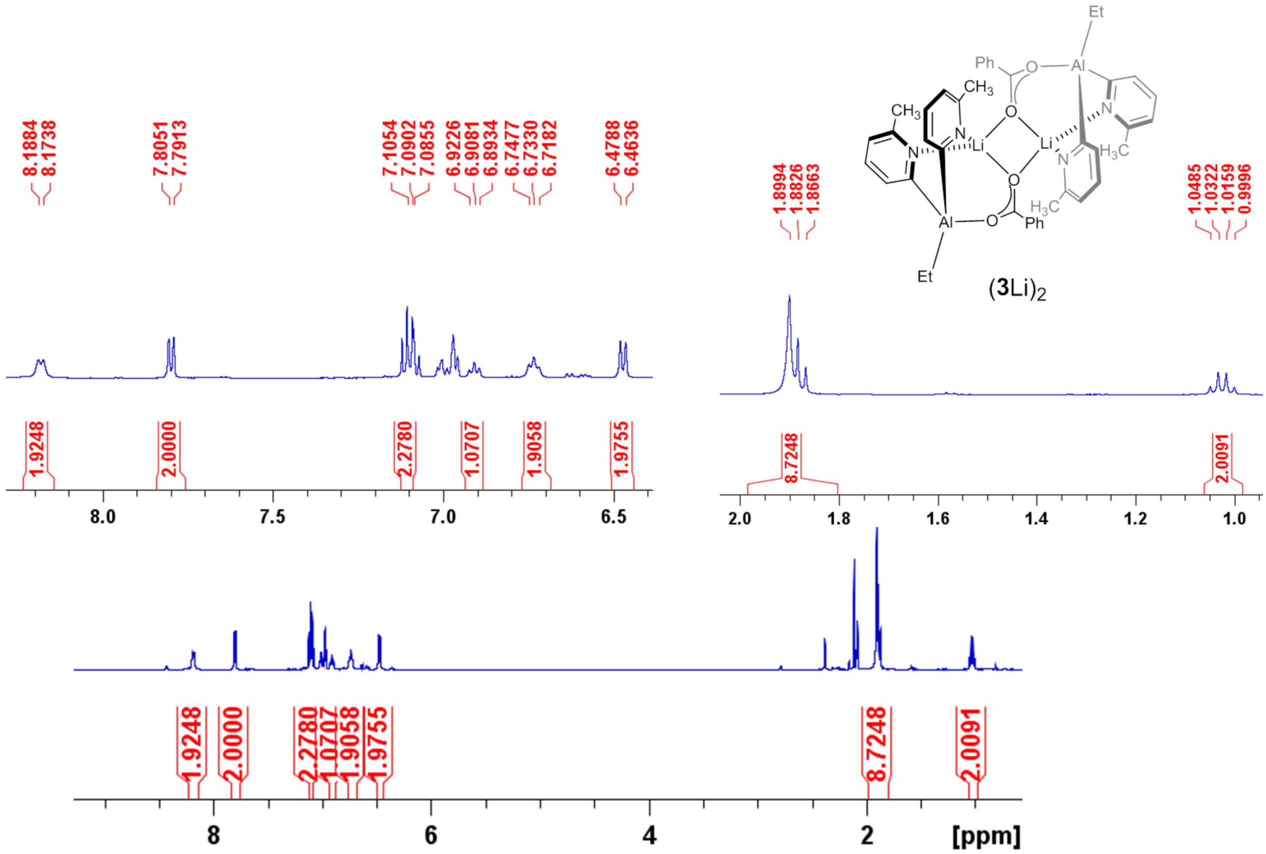


Figure S7: ^{1}H NMR (500 MHz, d$_8$-Toluene, 25 °C) spectrum of (**3**Li)$_2$

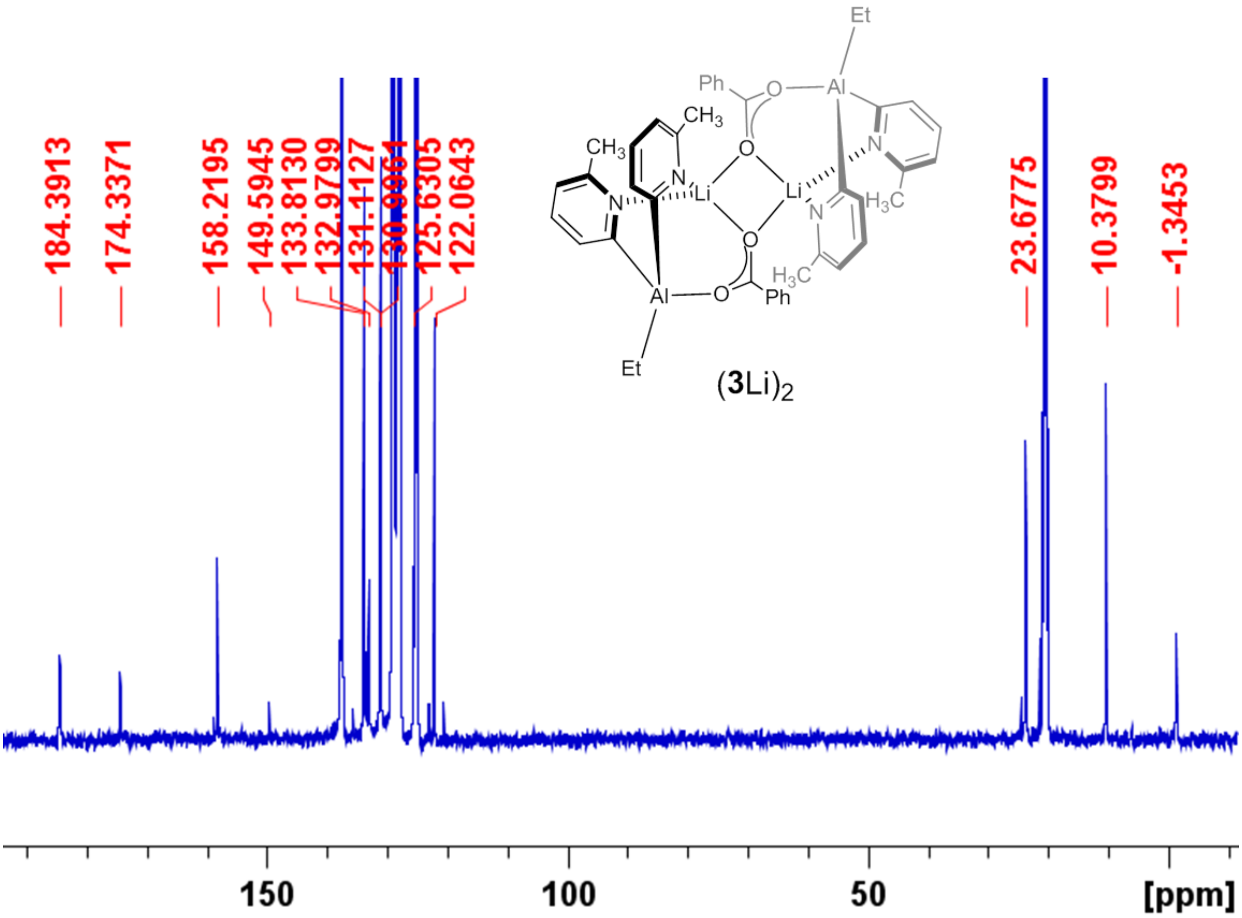


Figure S8: ^{13}C NMR (126 MHz, d$_8$-Toluene, 25 °C) spectrum of (**3**Li)$_2$

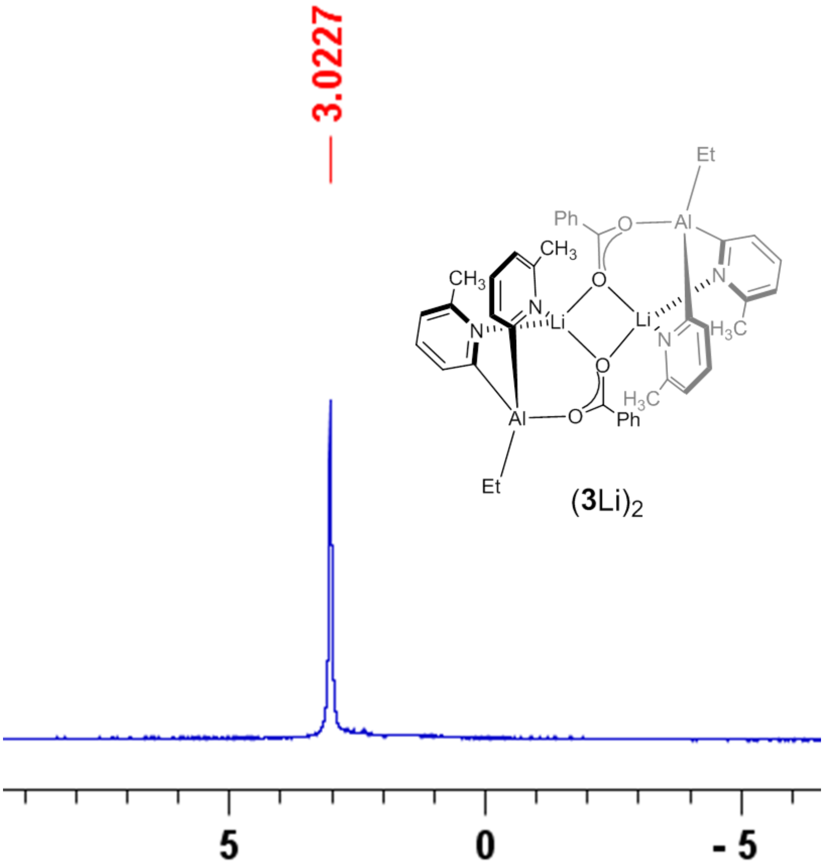


Figure S9: ^{7}Li NMR (194 MHz, d_8-Toluene, 25 °C) spectrum of (**3**Li)$_2$

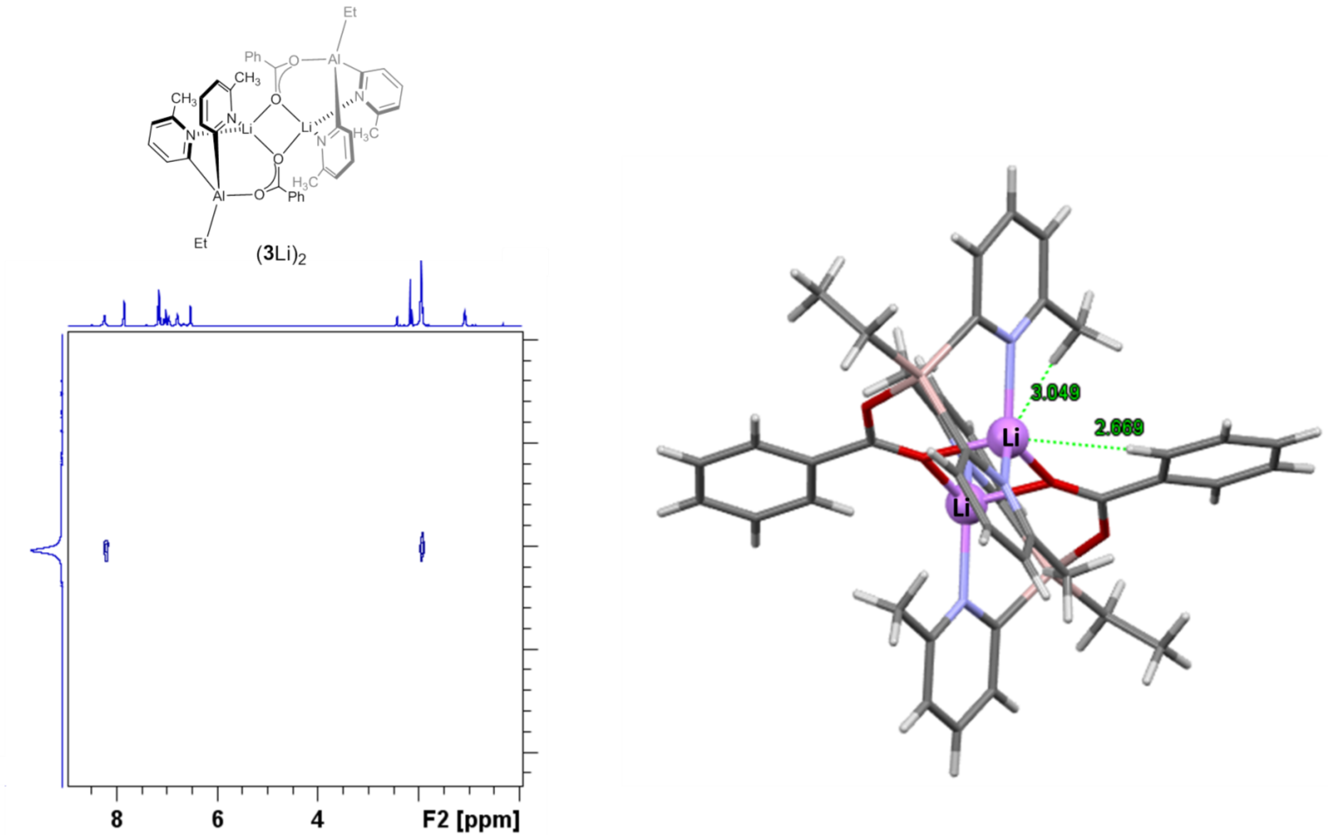
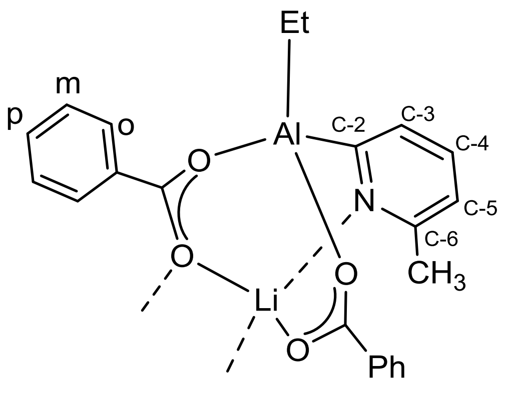


Figure S10: ^{1}H-^{7}Li HOESY (d$_8$-toluene, 500 MHz, 25 °C, mixing time of 100 ms) spectrum of (**3**Li)$_2$ (left) showing cross peaks between the ^{7}Li resonance and hydrogens of the 6-MePy group and the ortho hydrogens of the Ph group. Solid-state X-ray structure of (**3**Li)$_2$ (right) showing the close spatial proximity of these hydrogens to the Li centre.



(**4**Li)$_2$

Figure S11: Labelling scheme for (**4**Li)$_2$; hydrogen atoms are labelled according to the number of the attached carbon atom

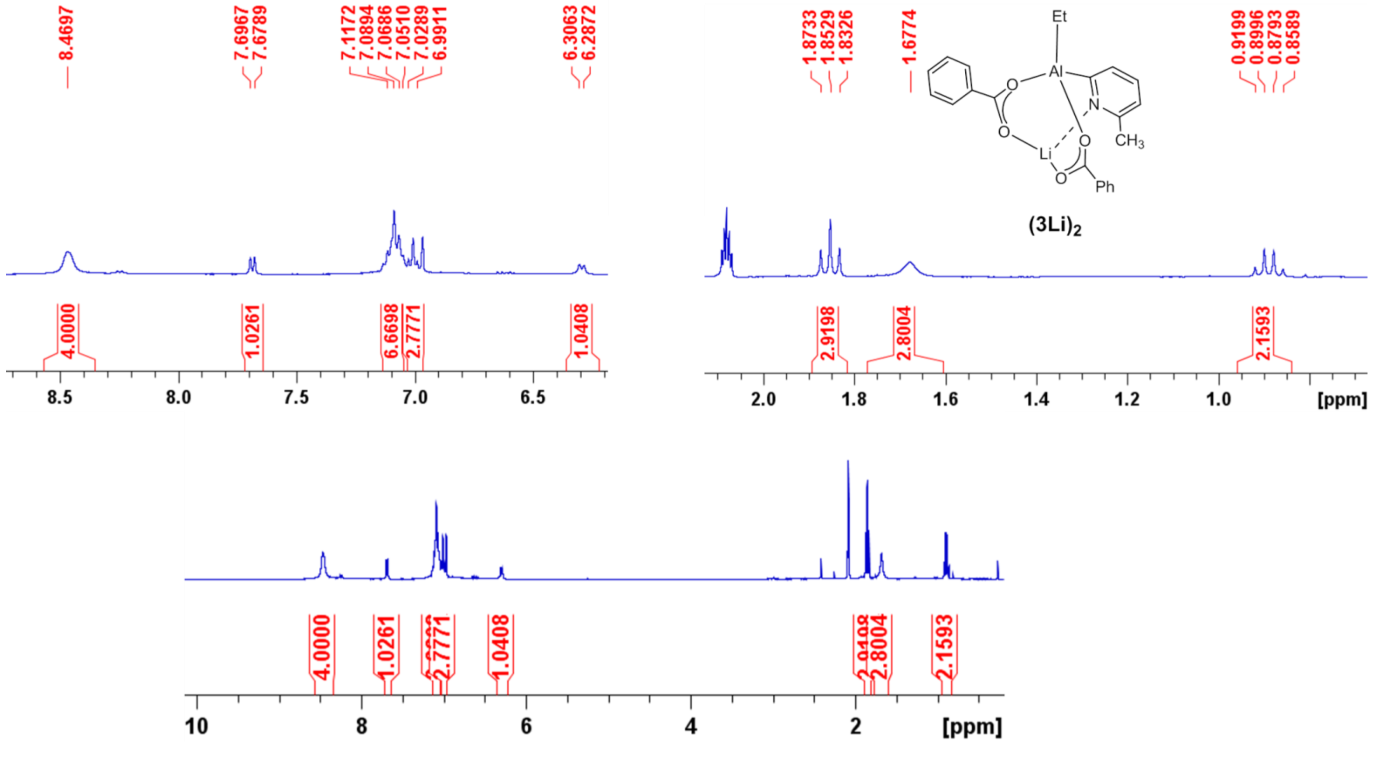


Figure S12: ^{1}H NMR (500 MHz, d_8-Toluene, 25 °C) spectrum of (**4**Li)$_2$

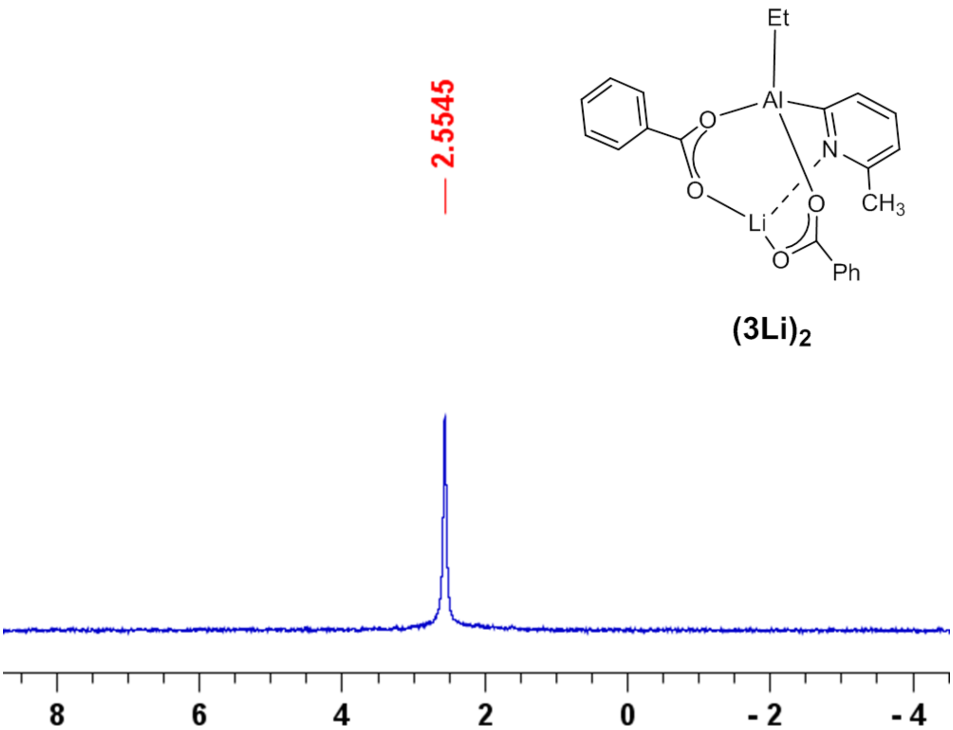
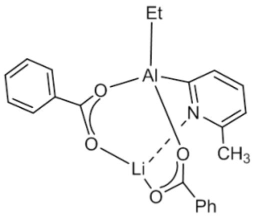


Figure S13: ^{7}Li NMR (194 MHz, d$_8$-Toluene, 25 °C) spectrum of (**4**Li)$_2$



$(3Li)_2$

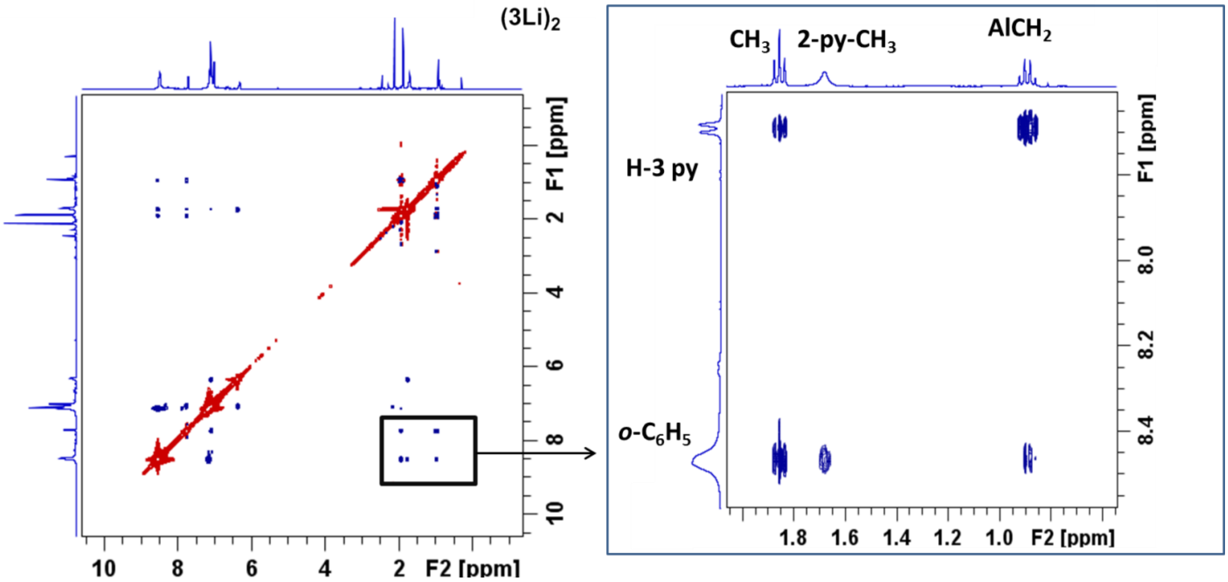


Figure S14: ^1H-^1H NOESY (400 MHz, d_8-Toluene, 25 °C, mixing time of 600 ms) spectrum of $(\mathbf{4}Li)_2$. Crosspeaks are observed between the H3 py proton and the protons of $Al-CH_2CH_3$ and the ortho protons of the phenyl group, as well as between the ortho-Ph protons and 2-py-CH_3 (insert at the right). The crosspeaks arise from intramolecular cross-relaxation of protons that are close to each other in space. This confirms the presence of an $EtAl(6-Me-2-py)_2(PhCO_2)$ linkage.

3. X-Ray Crystallography

Single-crystal X-ray diffraction data were collected on a Bruker D8-QUEST PHOTON-100 diffractometer equipped with an Incoatec IµS Cu microsource. Data integration and reduction were undertaken with SAINT in the APEX3 software suite. Multi-scan empirical absorption corrections were applied using SADABS. Structures were solved using SHELXT-2014 and refined using full-matrix least squares on F^2 using SHELXL-2018/1.

Table S1: Details of the Data Collections and Structural Refinements of (**2**Li)$_2$, (**3**Li)$_2$ and (**7**Li)$_2$

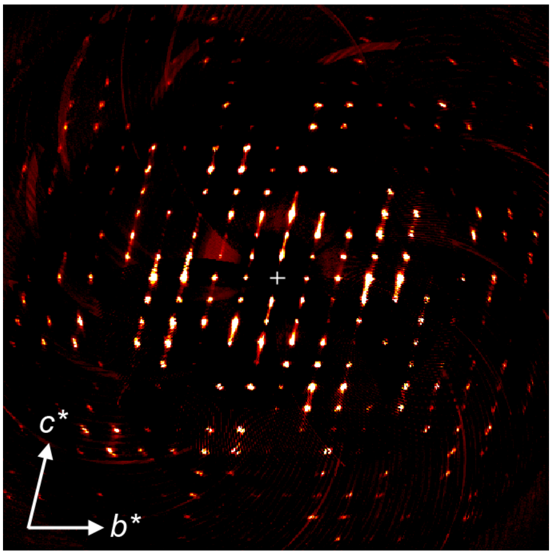
	(**2**Li)$_2$	(**2**Li)$_2$ (SQUEEZED)	(**3**Li)$_2$	(**7**Li)$_2$
CCDC number	1897739	1897741	1897740	1897742
Cambridge data number	DW_B2_0295	DW_B2_0295	DW_B1_0111	DW_B2_0038
Chemical formula	$C_{72.9}H_{79.6}Al_2Li_2N_6O_2$	$C_{82}H_{90}Al_2Li_2N_6O_2$	$C_{49}H_{52}Al_2Li_2N_4O_4$	$C_{38}H_{32}Al_2Br_4Li_2N_4O_4$
Formula weight	1140.05	1259.43	828.78	996.15
Temperature / K	180(2)	180(2)	180(2)	180(2)
Crystal system	triclinic	triclinic	monoclinic	triclinic
Space group	P -1	P -1	P 2_1/n	P -1
a / Å	10.7764(4)	10.7764(4)	11.9268(3)	10.4621(3)
b / Å	11.6195(4)	11.6195(4)	25.7178(7)	13.0873(4)
c / Å	15.5555(6)	15.5555(6)	15.3307(4)	16.4267(6)
α / °	72.5308(19)	72.5308(19)	90	86.2550(15)
β / °	75.6187(18)	75.6187(18)	100.0816(13)	71.9417(15)
γ / °	68.8699(16)	68.8699(16)	90	71.1903(14)
V / Å^3	1711.41(11)	1711.41(11)	4629.8(2)	2022.67(11)
Z	1	1	4	2
Calc. density / g cm^{-3}	1.106	1.222	1.189	1.636
F(000)	607	672	1752	984
Radiation type	Cu$K\alpha$	Cu$K\alpha$	Cu$K\alpha$	Cu$K\alpha$
Absorption coefficient / mm^{-1}	0.742	0.790	0.933	5.636
Crystal size / mm3	0.25 x 0.12 x 0.08	0.25 x 0.12 x 0.08	0.22 x 0.10 x 0.06	0.21 x 0.12 x 0.09
2θ range / degrees	6.03-133.99	6.03-133.99	6.79-133.23	5.66-133.61
Completeness to max 2θ	0.982 (-1)	0.982 (-1)	0.998 (2/m)	0.997 (-1)
No. of reflections measured	34421	34421	56906	57695
No. of independent reflections	5992	5992	8164	7182
R_{int}	0.0585	0.0585	0.0446	0.0444
No. parameters / restraints	335 / 15	302 / 0	568 / 0	489 / 0
Final R1 values ($I > 2\sigma(I)$)	0.1029	0.0563	0.0454	0.0374
Final wR(F^2) values (all data)	0.1169	0.0667	0.0613	0.0480
Goodness-of-fit on F^2	1.054	1.058	1.012	1.062
Largest difference peak & hole / e Å^{-3}	1.393, -0.583	0.380, -0.251	0.416, -0.355	0.589, -0.670

Notes on Crystal Structure Solution and Refinement for 2(Li)$_2$

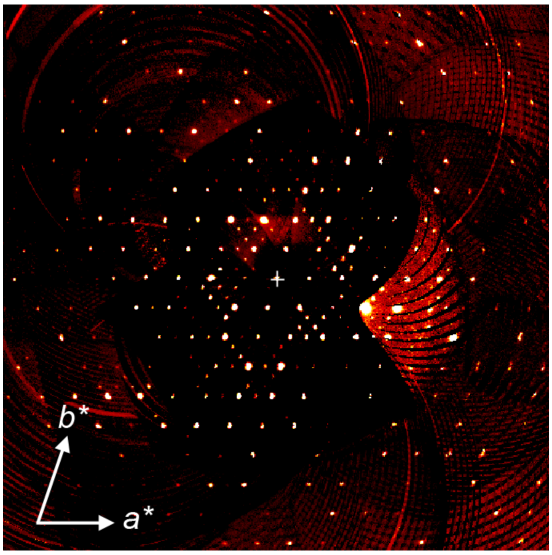
Problems arise in the refinement of (**2**Li)$_2$ because of disordered toluene molecules lying in layers between the Li/Al complexes. The “full” refinement (CCDC-1897739) does not model this region particularly well (hence the residual electron density and the relatively high R-factors) but it was difficult to define further toluene molecules with acceptable geometry. There are clearly two sites for toluene in the asymmetric unit, giving a potential total of four molecules per unit cell. One site is modelled as disordered over two components (summing to one molecule) while the other has a common site occupancy factor refined with ADPs constrained to a common value shared over all non-H atoms of all toluene molecules. This gives partial occupancy (0.352(7)) and produces the quoted indicative formula [$C_{54}H_{58}AlLi_2N_4O_2$].2.7(C_7H_8). There are other peaks in this area in the residual electron density but it is hard to model any further sensible toluene molecules.

A *SQUEEZED* version of the structure is also provided, with all toluene molecule omitted and dealt with via the continuous solvent-area model (CCDC-1897741). This gives wR2 ca 15%, confirming that this solvent disorder is the principal source of the problems. *SQUEEZE* corrects for 171 electrons per unit cell, correponding to ca 3.5 toluene molecules.

The toluene molecules occupy layers in the *ab* planes of the structure and there appears from the disorder to be more than one orientation of those layers. The diffraction pattern shows streaks along c* indicative of layer stacking disorder. It also shows modulation peaks in the *hk* planes, but interpretation of these was not attempted. This could be an interesting system for further crystallographic study, but we were interested solely in the chemical interpretation (which is clear).



0*kl*



***h*k1**