Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supporting Information (ESI)

Direct synthesis of the Janus-Head ligand $(^{Me}Py)_3Sn$-$Sn(^{Me}Py)_3$ using an unusual pyridyl-transfer reaction (^{Me}Py = 6-Methyl-pyridyl)

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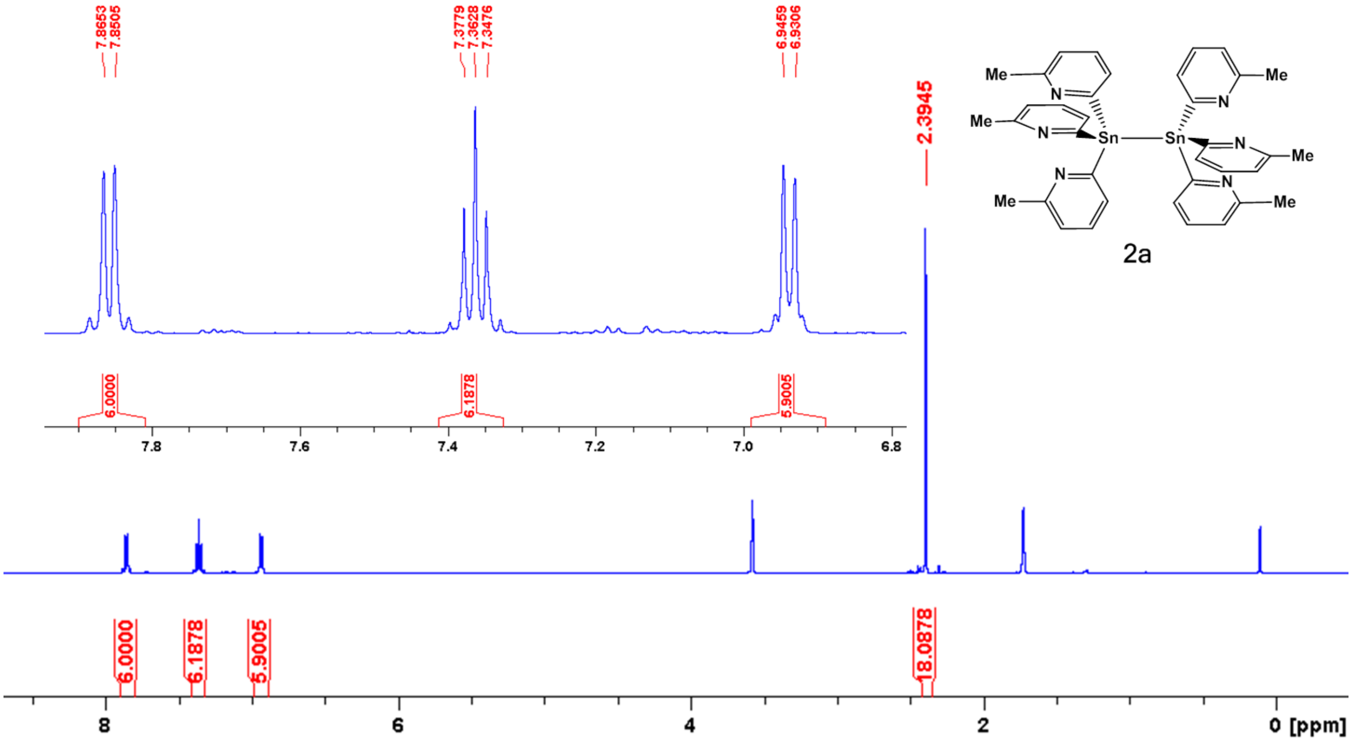


Figure S1. ^{1}H NMR (298 K, d$_8$-THF, 500 MHz) spectrum of (^{Me}Py)$_3$Sn-Sn(^{Me}Py)$_3$ (**2a**) (Py′ = 6-Me-2-Py)

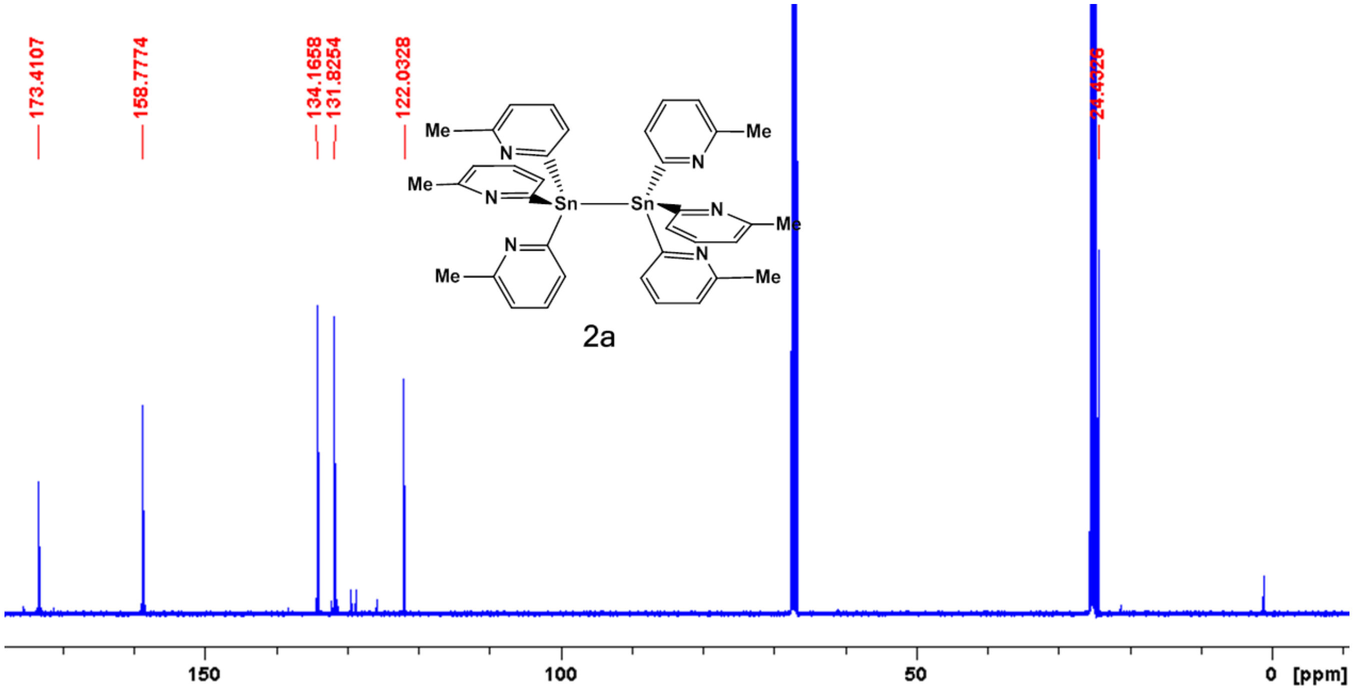


Figure S2. $^{13}C\{^{1}H\}$ NMR (298 K, d_8-THF, 100.6 MHz), spectrum of $(^{Me}Py)_3Sn$-$Sn(^{Me}Py)_3$ (**2a**) (Py´ = 6-Me-2-Py).For individual expansions for each resonance showing $^{117,119}Sn$ satellites of the C-atoms of the ^{Me}Py ligands see Figure S3.

Note: A small amount of residual toluene is observable in the spectrum (weak resonances at 138.25, 129.48, 128.72, 125.85 and 21.29 ppm)

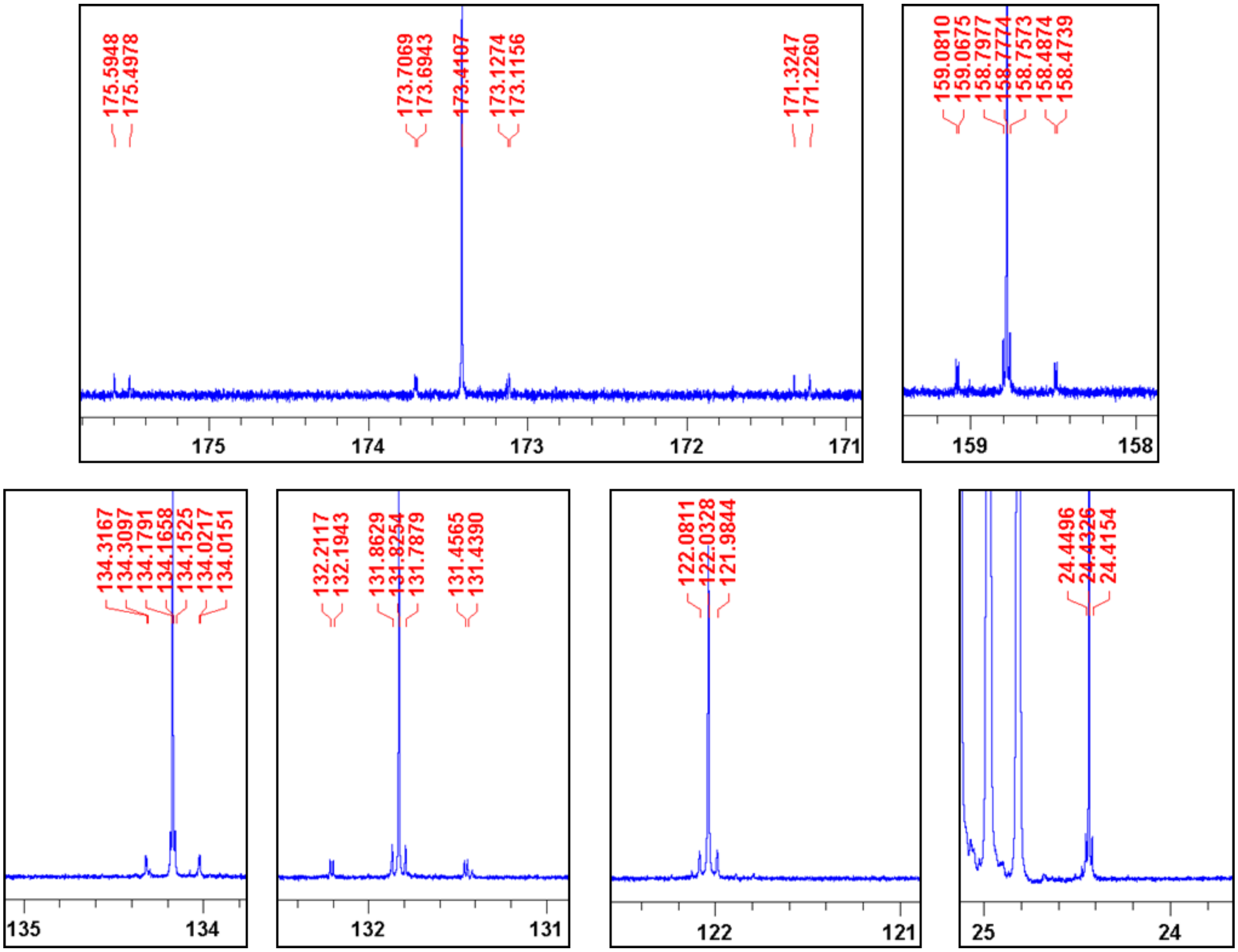


Figure S3. Expansions for each ^{13}C{^{1}H} NMR resonance of the ^{Me}Py ligands showing the presence of ^{117,119}Sn satellites for *all* of the C-atoms of the ligand.

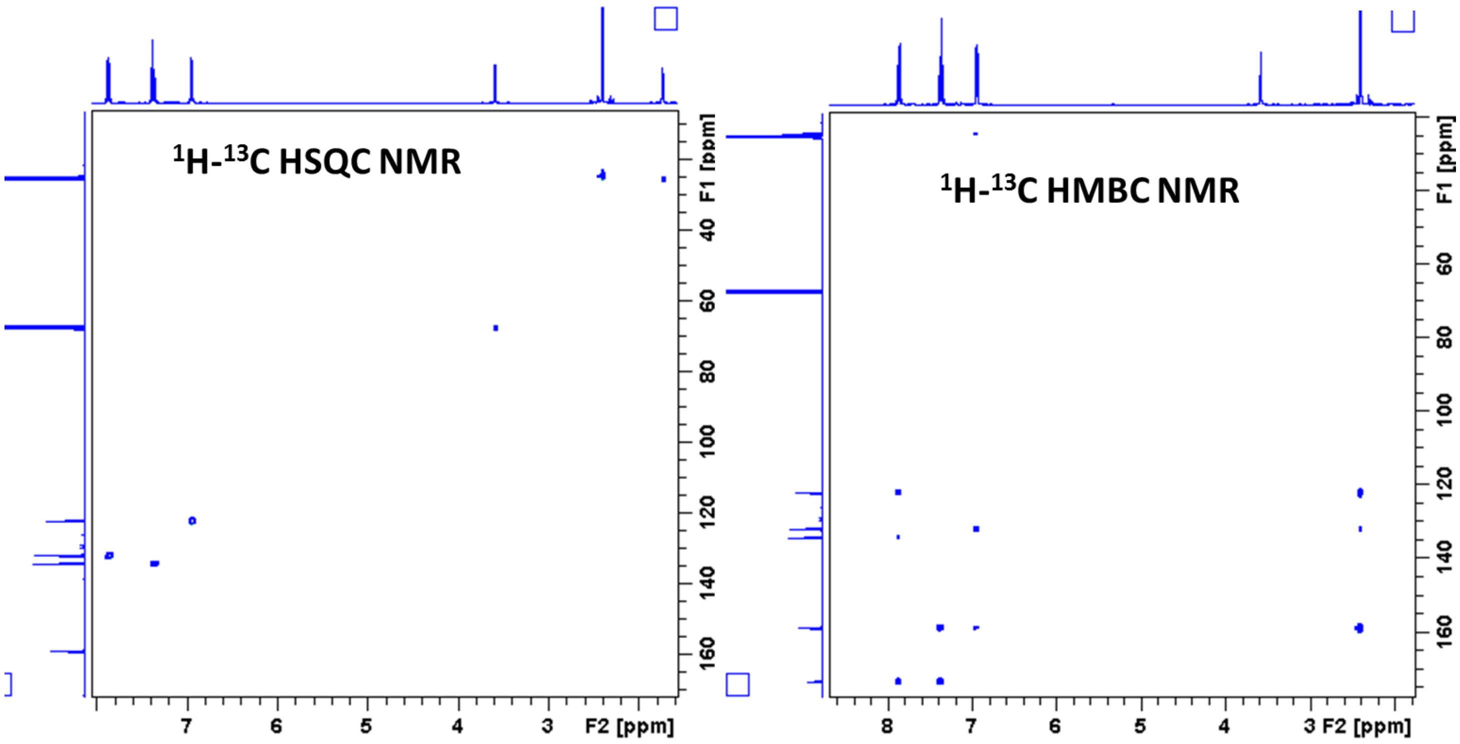


Figure S4. ^{1}H-^{13}C HSQC (298 K, d$_8$-THF, 500 MHz) left and ^{1}H-^{13}C HMBC (298 K, d$_8$-THF, 500 MHz) right spectra of $(^{Me}Py)_3Sn$-$Sn(^{Me}Py)_3$ (**2a**) (Py´ = 6-Me-2-Py).

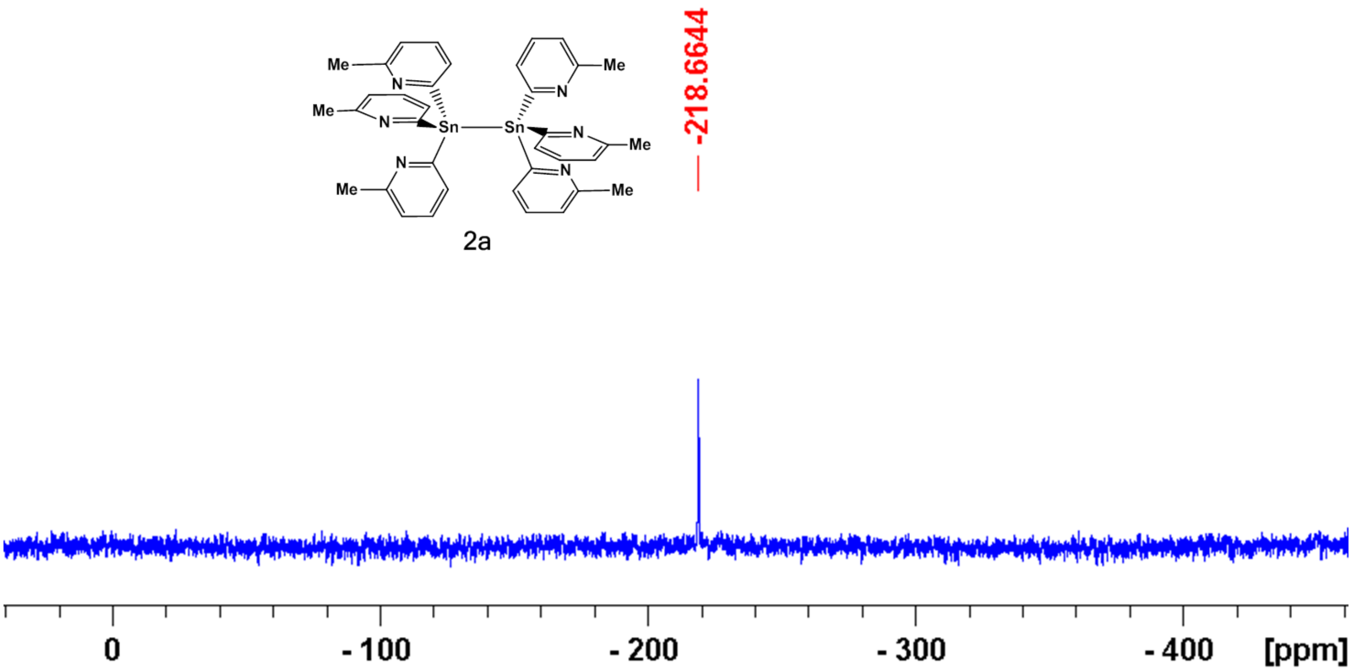


Figure S5. ^{119}Sn{^{1}H} NMR (186.5 MHz, 298K, rel solution of SnMe$_4$), spectrum of (^{Me}Py)$_3$Sn-Sn(^{Me}Py)$_3$ (**2a**) (Py´ = 6-Me-2-Py). No ^{119}Sn-^{117}Sn coupling could be detected.

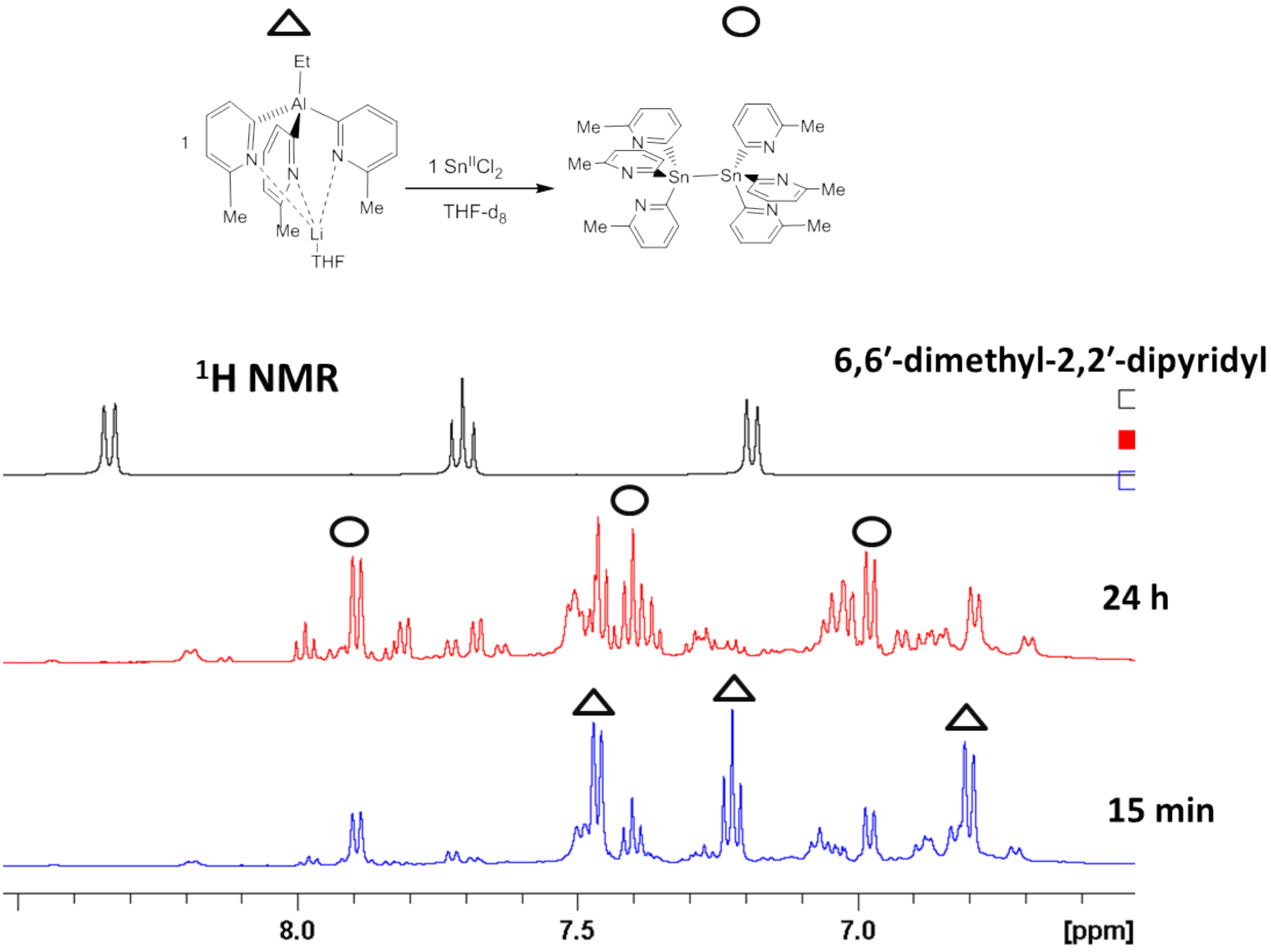


Figure S6. ^{1}H NMR (298 K, d$_8$-THF, 500 MHz) spectra of the reaction of an equimolar mixture of **1a** with SnCl$_2$ in d$_8$-THF. Within 15 min of mixing the reactant at ambient temperature an orange colouration developed and **2a** (circle) was observed as the only Sn-containing species formed (See figure S7). After 24h none of the precursor **1a** remained (triangle). No 6,6′-dimethyl-2,2′-dipyridyl is observed in the reaction at any stage. ^{1}H NMR spectrum of 6,6′-dimethyl-2,2′-dipyridyl in d$_8$-THF is shown above in black for comparison purposes

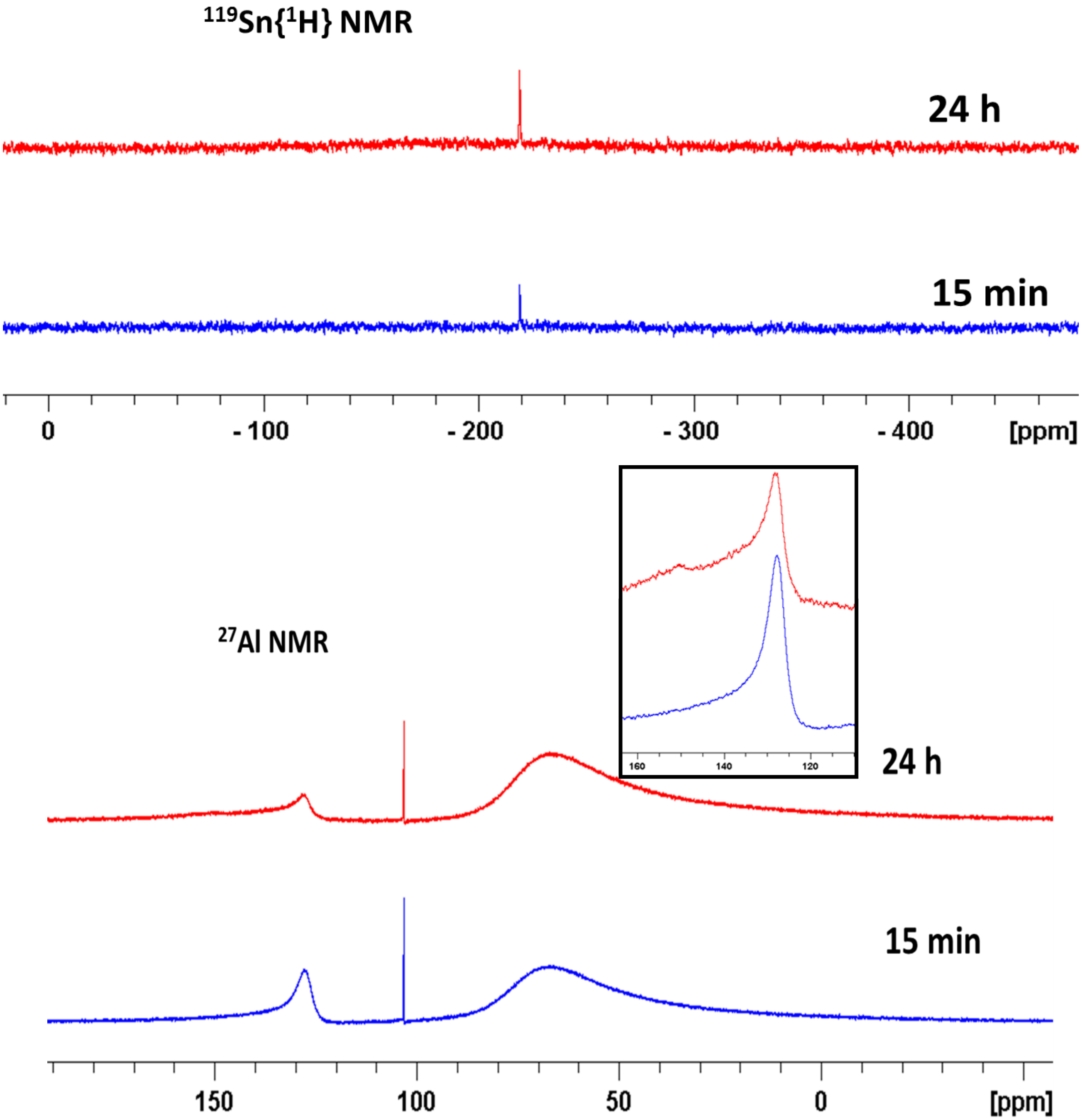


Figure S7. ^{119}Sn{^{1}H} NMR (298 K, d_8-THF, 186.5 MHz), above, and ^{27}Al NMR spectra (298 K, d_8-THF, 130.3 MHz), below, of the reaction of an equimolar mixture of **1a** with $SnCl_2$ in d_8-THF. Within 15 min of mixing the reactant at ambient temperature **2a** was observed as the only Sn-containing species formed. A characteristic sharp resonance for $AlCl_4^-$ was also observed in the ^{27}Al NMR spectra. The insert in the ^{27}Al NMR spectra shows the presence of broad signals at δ=150 and δ=128 ppm after 24h, suggesting the possible formation of heteroleptic aluminum species containing the ethyl group

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

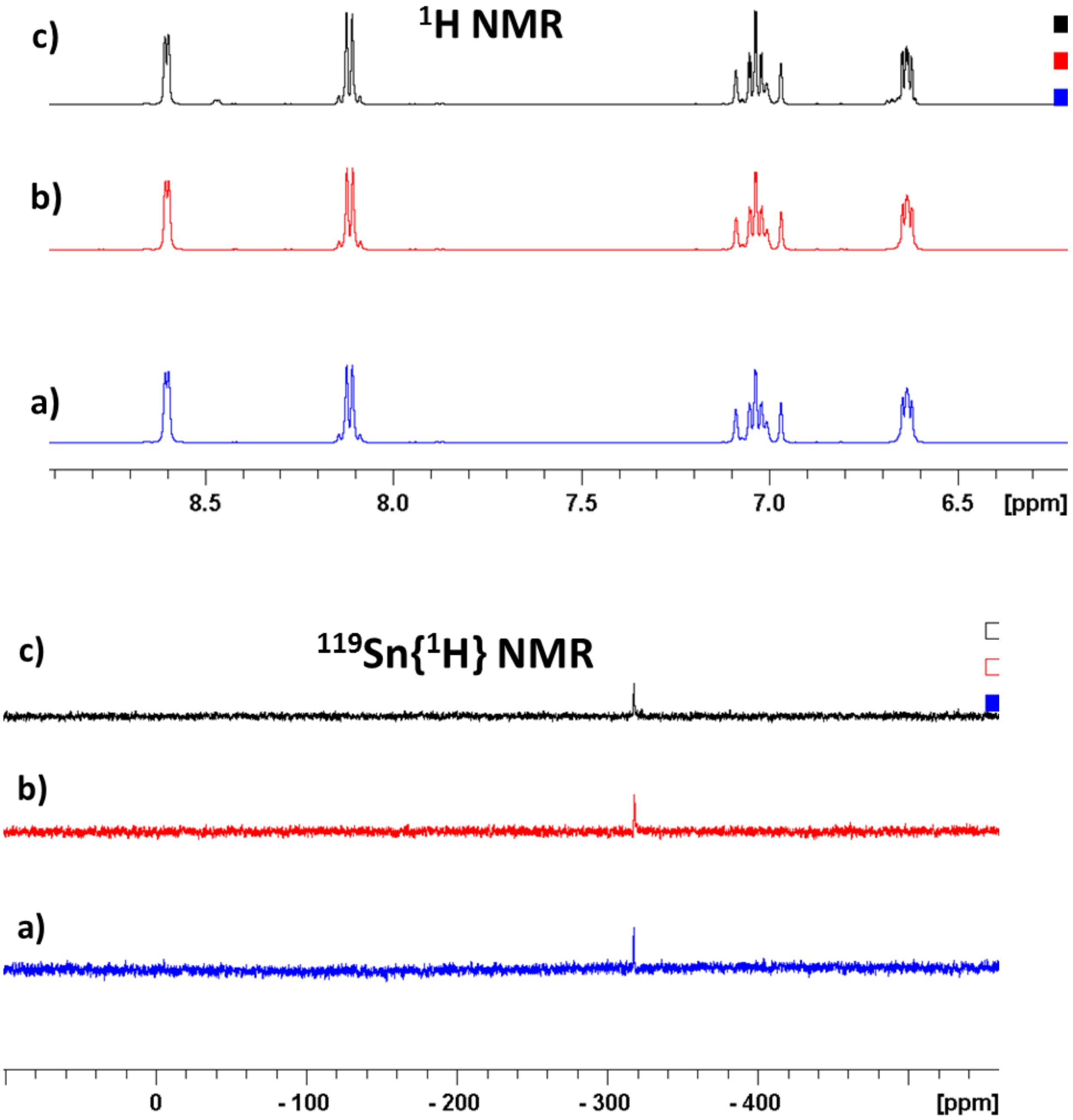


Figure S8. ^{1}H NMR (298 K, toluene-d_8, 500 MHz**)** spectra, above, and ^{119}Sn{^{1}H} NMR (298 K, toluene-d_8, 186.5 MHz) spectra, below, of Sn(2-Py)$_4$ in toluene-d_8 before (a) and after heating at 80°C in toluene for 24h (b) and 5days (c).

Note: Sn(Py)$_4$ was synthesized as described recently in the literature (ref 11 in the main text).

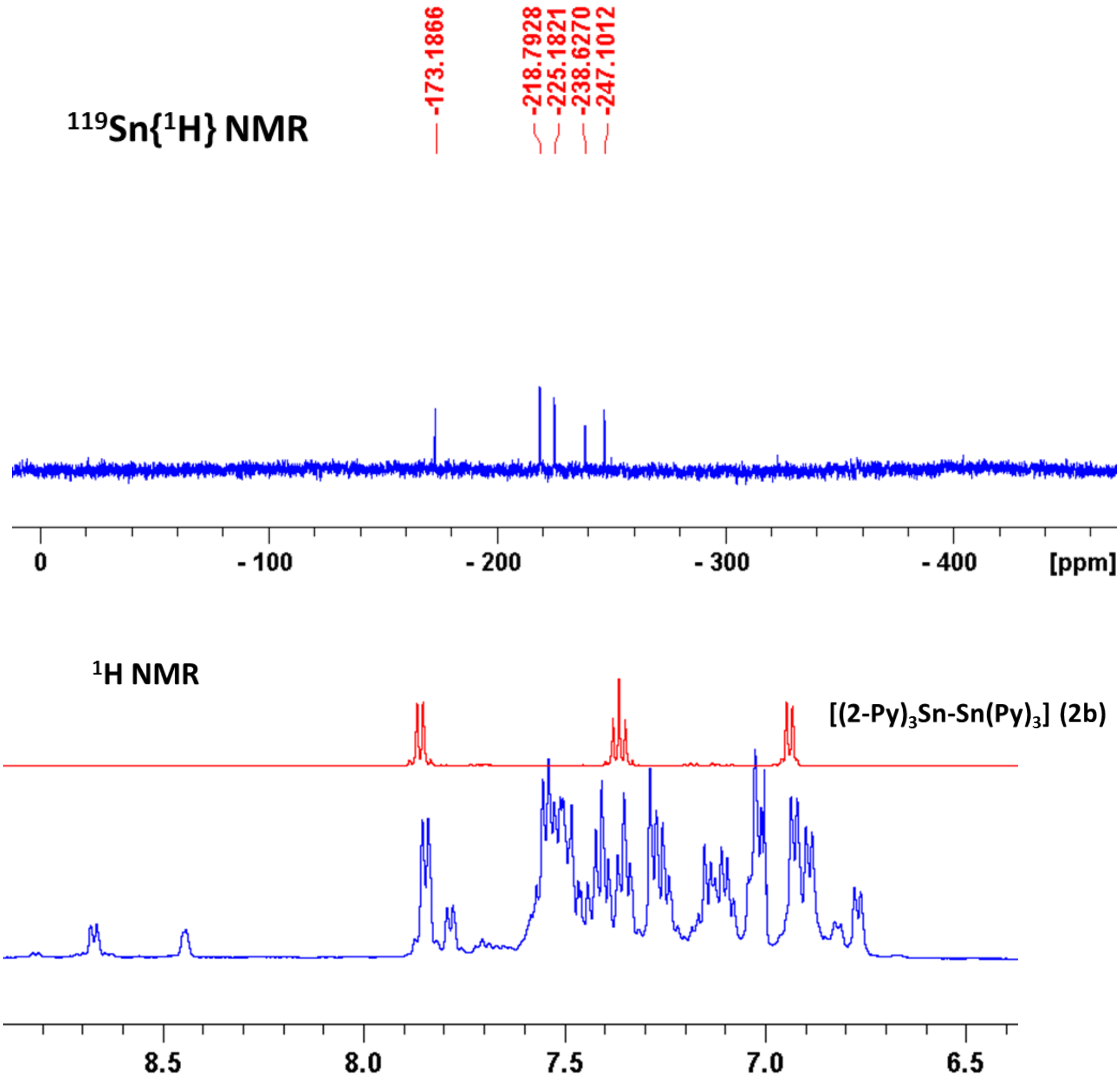


Figure S9. ^{119}Sn{^{1}H} NMR (298 K, THF, CDCl$_3$ capillary, 186.5 MHz**) spectrum, above, and ^{1}H NMR** (298 K, THF, CDCl$_3$ capillary, 500 MHz), spectrum, below, of the reaction of an equimolar mixture of SnCl$_2$ and 2 equivalents of 2-Li-^{Me}Py in THF at -78^{o}C. The mixture was allowed to warm to room temperature and stirred for 1h before ^{119}Sn and ^{1}H NMR spectra were obtained. The formation of **2a** was apparent in the ^{1}H and ^{119}Sn NMR spectra along with other unidentified products. The ^{1}H NMR spectrum of (^{Me}Py)$_3$Sn-Sn(^{Me}Py)$_3$ (**2a**) in d$_8$-THF is shown in red for comparison purposes.

Note: We note that **2a** is unstable in the reaction mixture and slowly decomposed at 45°C. After 2days at 45°C no **2a** was observed in ^{1}H or ^{119}Sn NMR spectra.

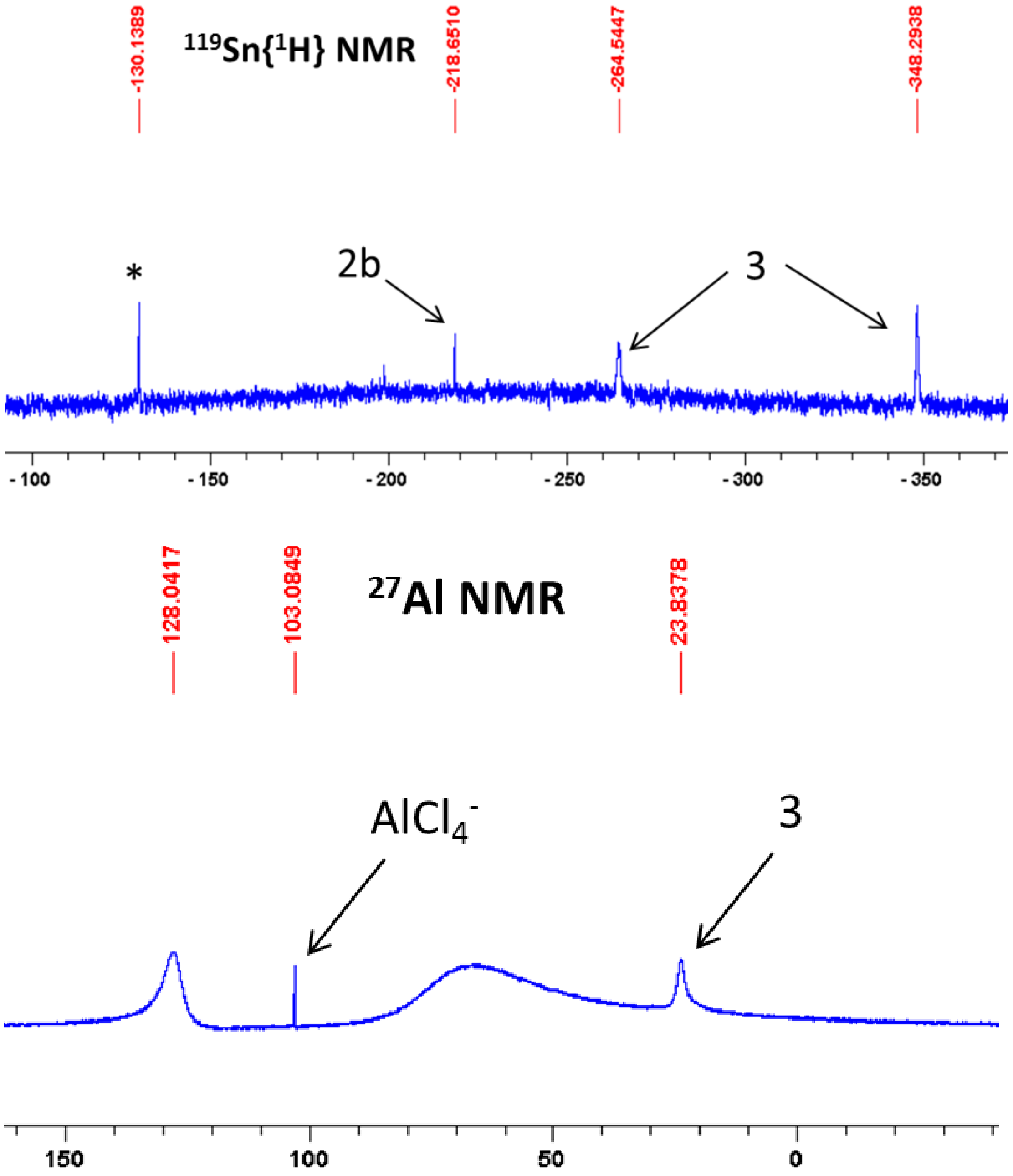


Figure S10. ^{119}Sn{^{1}H} NMR (298 K, d$_8$-THF, 186.5 MHz) spectrum, above, and ^{27}Al NMR (298 K, d$_8$-THF, 130.3 MHz) spectrum, below, of the reaction of an equimolar mixture of **1b** with SnCl$_2$ in d$_8$-THF after 24h at room temperature. The ^{119}Sn NMR spectrum shows that three major Sn-containing products are generated after 24h: an unidentified species at δ -130 ppm (s.), [(2-Py)$_3$Sn-Sn(Py)$_3$] (**2b**) [assigned on the basis of its chemical shift, δ -218.7 ppm (s)] and another species (**3**) observed as two broad singlets. The ^{29}Al NMR spectrum shows the characteristic sharp resonance for AlCl$_4^-$ along with the formation of **3**. (δ = 23.8 ppm).

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

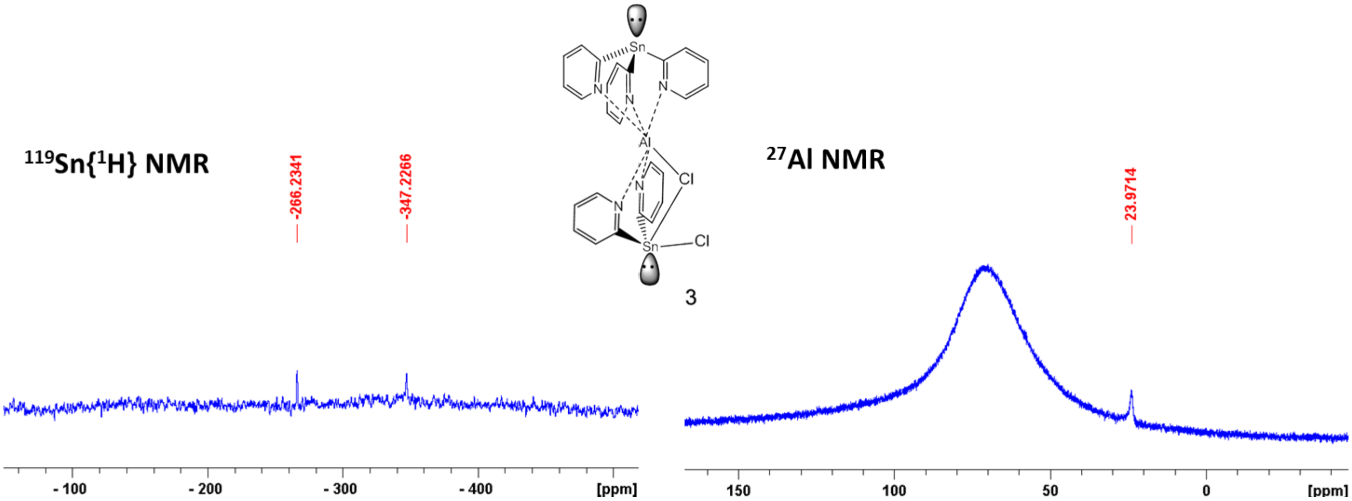


Figure S11. ^{119}Sn{^{1}H} NMR (298 K, d$_8$-THF, 186.5 MHz) spectrum, left, and ^{27}Al NMR (298 K, d$_8$-THF, 130.3 MHz) spectrum, right, of [{Sn(2-Py)$_3$}Al{(μ-Cl)(2-py)$_2$Sn(Cl)}] (**3**).

Note 1: changes up to 2 ppm were observed for the chemical shift of the broad ^{119}Sn resonances of compound **3**.

Note 2: The broad signal at around 65ppm in the ^{27}Al NMR spectrum arises from probe background.

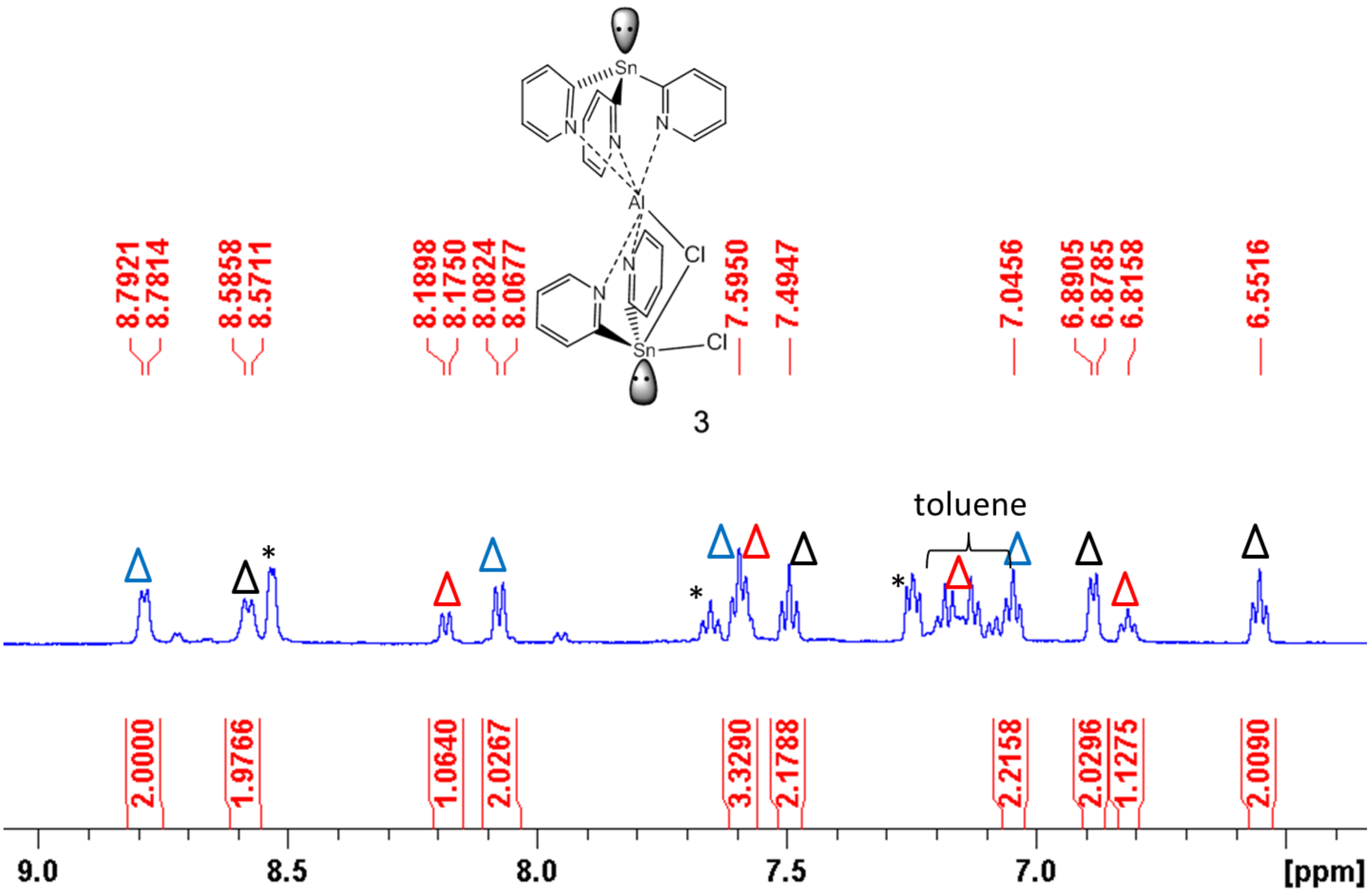
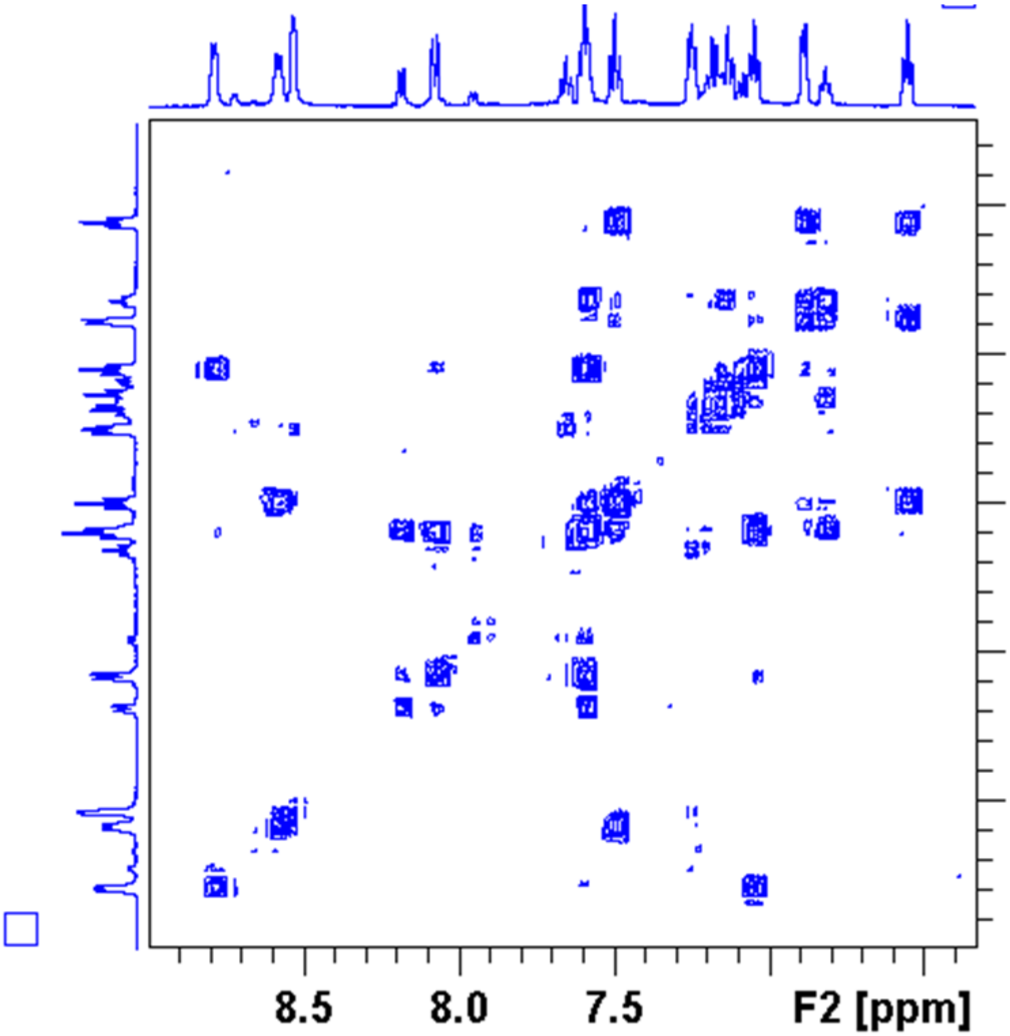


Figure S12. ^{1}H NMR (298 K, d$_8$-THF, 500 MHz) spectrum of [{Sn(2-Py)$_3$}Al{(μ-Cl)(2-py)$_2$Sn(Cl)}] (**3**). The triangles show the presence of three spin systems evidencing the presence of three magnetically inequivalent pyridyl rings. The assignment was done with the help of a ^{1}H-^{1}H COSY NMR experiment (see fig S13). The presence of three 2-Py environments in the ratio 2 : 2 : 1 suggests that the solid-state structure of **3** is maintained in solution.

Note 1: We found that **3** had a marked tendency to decompose, yielding free pyridine (*). The unstable nature of compound **3** prevented a more detailed NMR study.

Note 2: The ^{1}H NMR spectrum showed contamination with trace quantities of toluene that can be observed in the region 7.05-7.20 ppm.



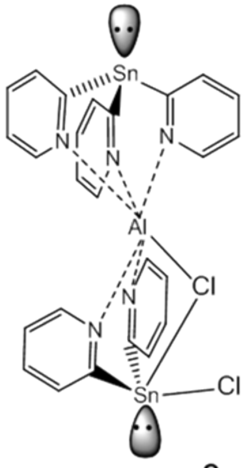


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Figure S13 ^{1}H-^{1}H COSY (298 K, d$_8$-THF, 500 MHz) spectrum of [{Sn(2-Py)$_3$}Al{(μ-Cl)(2-py)$_2$Sn(Cl)}] (**3**).

Table S1. Crystal, measurement and refinement data for the compounds studied by X-ray diffraction

	2a	**3**
formula	$C_{36}H_{36}N_6Sn_2$	$C_{54}H_{48}Al_2Cl_4N_{10}OSn_4$
M_f	790.09	1523.54
crystal system	Monoclinic	Monoclinic
a/Å	9.1614(13)	16.4409(18)
b/Å	9.8389(12)	19.855(2)
c/Å	19.420(3)	17.9265(18)
α/°	90.00	90.00
β/°	103.551(4)	90.455(3)
γ/°	90.00	90.00
V/Å^3	1701.7(4)	5851.8(11)
T/K	199(2)	200(2)
space group	$P2_1/n$	$P2_1/n$
Z	2	4
Radiation type	MoKα	MoKα
μ(MoKα)/mm^{-1}	1.501	1.947
reflns collected	30472	110543
Indep. Refl.	3001	10596
R_{int}	0.0798	0.1076
R_1 ($I > 2\sigma(I)$)	0.0352	0.0752
$wR(F^2)$ (all data)	0.1139	0.2140
GOF on F^2	1.095	1.116
CCDC number	1008866	1008867