Dalton Transactions

Electronic Supplementary Information for:

Benzotriazolate cage complexes of tin(II) and lithium: halide-influenced serendipitous assembly

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[{(Me$_3$Si)$_2$N}$_8$Sn$_8$(bta)$_{12}$Li$_8$Cl$_4$]·(8 toluene), 3·(8 toluene)

X-ray diffraction data for **3**·(8 toluene) were collected using an Oxford Diffraction Xcalibur2 diffractometer using an enhanced molybdenum X-ray source with graphite monochromator (λ = 0.71073 Å) and a CCD detector.

Table S1. Crystal data and structure refinement for [{(Me$_3$Si)$_2$N}$_8$Sn$_8$(bta)$_{12}$Li$_8$Cl$_4$]·(8 toluene), **3**·(8 toluene).

Empirical formula	$C_{176}H_{256}Cl_4Li_8N_{44}Si_{16}Sn_8$	
Formula weight	4584.65	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	*a* = 18.3637(6) Å	α = 93.165(2)°.
	b = 21.5801(6) Å	β = 98.775(2)°.
	c = 30.8330(7) Å	γ = 112.991(3)°.
Volume	11027.7(5) Å^3	
Z	2	
Density (calculated)	1.38 Mg/m^3	
Absorption coefficient	1.081 mm^{-1}	
F(000)	4672	
Crystal size	0.25 x 0.2 x 0.08 mm^3	
Theta range for data collection	2.93 to 25.03°	
Index ranges	-21<=*h*<=21, -25<=*k*<=20, -35<=*l*<=36	
Reflections collected	54522	
Independent reflections	37848 [*R*(int) = 0.0451]	
Completeness to theta = 25.03°	97.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1 and 0.7681	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	37848 / 0 / 2361	
Goodness-of-fit on F^2	0.971	
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.0443, *wR*2 = 0.0856	
R indices (all data)	*R*1 = 0.0851, *wR*2 = 0.0944	
Largest diff. peak and hole	1.272 and -0.771 e.Å^{-3}	

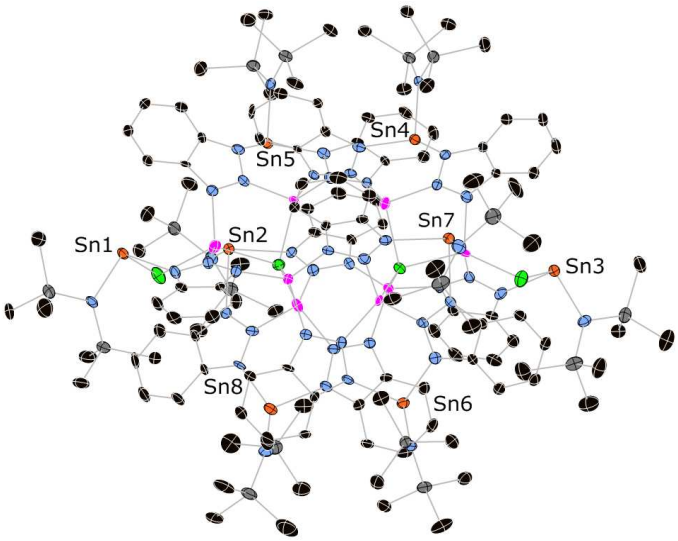

Figure S1. Thermal ellipsoid plot (50% probability) of [{(Me$_3$Si)$_2$N}$_8$Sn$_8$(bta)$_{12}$Li$_8$Cl$_4$] (**3**). Hydrogen atoms omitted.

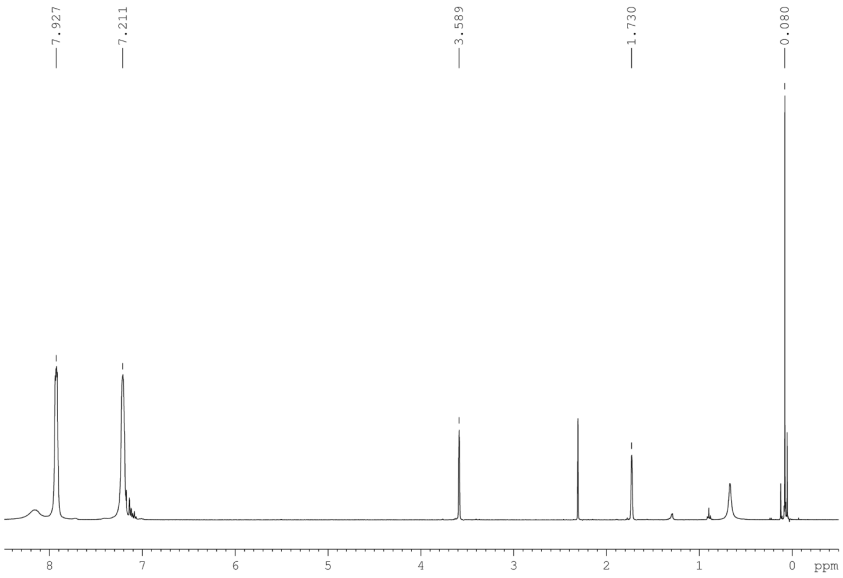

Figure S2. ^{1}H NMR spectrum of **3** in thf-d_8. Residual toluene solvent is visible in the spectrum.

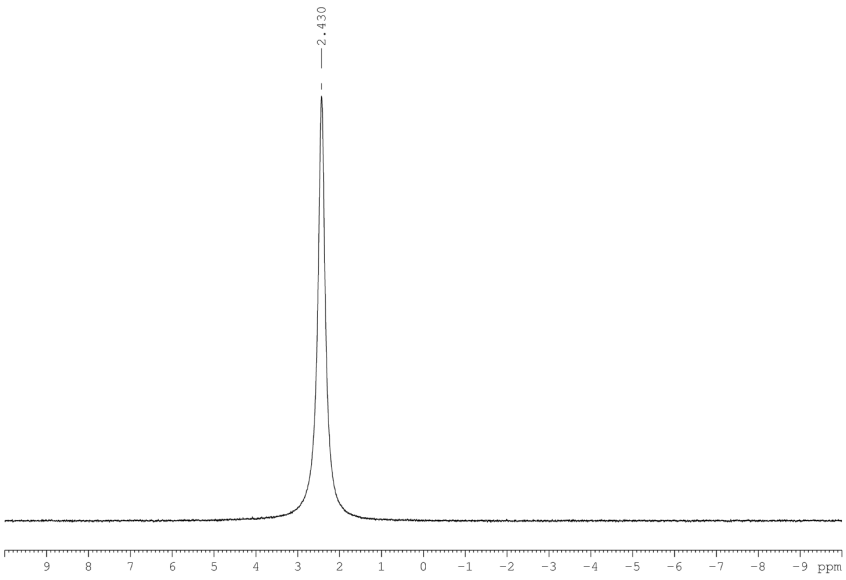

Figure S3. ^{7}Li NMR spectrum of **3** in thf-d_8.

[{(Me$_3$Si)$_2$N}$_8$Sn$_8$(bta)$_{12}$Li$_8$Br$_4$]·(3 toluene), [4·(3 toluene)]

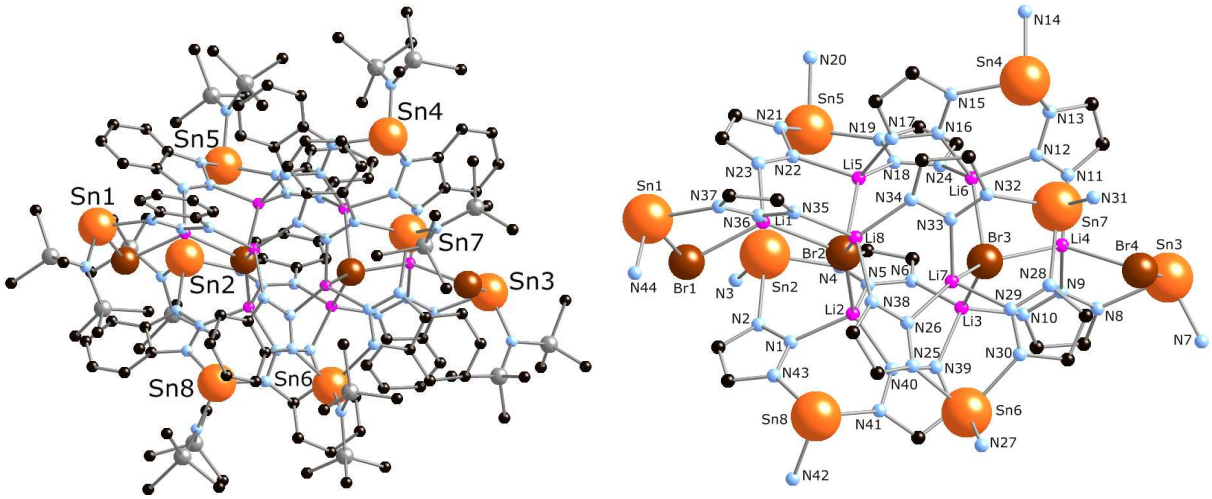

Figure S4. Left: structure of **4**. Tin = orange, lithium = pink, bromine = brown, nitrogen = blue, silicon = grey. Hydrogen atoms are omitted. Right: expanded view of the core of **4**. Selected bond lengths [Å]: Sn(1)-Br(1) 2.6994(10), Sn(1)-N(37) 2.290(6), Sn(1)-N(44) 2.089(8), Sn(2)-N(2) 2.306(7), Sn(2)-N(3) 2.107(6), Sn(2)-N(4) 2.273(6), Sn(3)-Br(4) 2.7121(10), Sn(3)-N(7) 2.099(6), Sn(3)-N(8) 2.279(6), Sn(4)-N(13) 2.260(5), Sn(4)-N(14) 2.104(6), Sn(4)-N(15) 2.241(6), Sn(5)-N(19) 2.231(6), Sn(5)-N(20) 2.115(6), Sn(5)-N(21) 2.233(6), Sn(6)-N(26) 2.231(8), Sn(6)-N(27) 2.129(7), Sn(6)-N(28) 2.296(7), Sn(7)-N(30) 2.336(6), Sn(7)-N(31) 2.105(6), Sn(7)-N(32) 2.253(6), Sn(8)-N(41) 2.270(6), Sn(8)-N(42) 2.089(8), Sn(8)-N(43) 2.297(6), Br(1)-Li(1) 2.529(12), Br(2)-Li(1) 2.535(12), Br(2)-Li(2) 2.452(13), Br(2)-Li(5) 2.536(12), Br(2)-Li(8) 2.612(16), Br(3)-Li(3) 2.535(13), Br(3)-Li(4) 2.542(12), Br(3)-Li(6) 2.513(12), Br(3)-Li(7) 2.571(15), Br(4)-Li(4) 2.542(12), N(1)-Li(2) 2.019(15), N(5)-Li(2) 2.002(15), N(6)-Li(3) 2.037(13), N(9)-Li(4) 2.064(12), N(10)-Li(3) 2.056(15), N(11)-Li(4) 2.072(13), N(12)-Li(6) 2.009(13), N(16)-Li(6) 2.015(12), N(17)-Li(5) 2.029(12), N(18)-Li(5) 2.066(14), N(22)-Li(5) 2.062(13), N(23)-Li(1) 2.032(14), N(24)-Li(6) 2.061(13), N(25)-Li(7) 2.012(18), N(29)-Li(7) 2.065(13), N(33)-Li(7) 2.022(14), N(34)-Li(8) 2.016(17), N(35)-Li(8) 2.006(17), N(36)-Li(1) 2.030(14), N(38)-Li(8) 2.058(18), N(39)-Li(3) 2.046(15), N(40)-Li(2) 1.967(14).

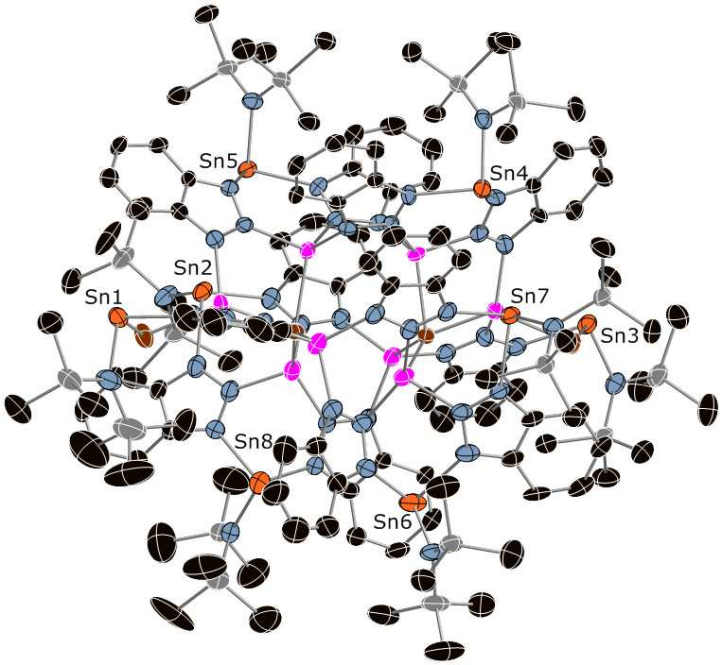

Figure S5. Thermal ellipsoid plot (50% probability) of [{(Me$_3$Si)$_2$N}$_8$Sn$_8$(bta)$_{12}$Li$_8$Br$_4$ (**4**). Hydrogen atoms omitted. Large residual electron density is located near to the heavy atoms.

X-ray diffraction data for **4**·(3 toluene) were collected on an Oxford Diffraction SuperNova diffractometer employing a copper microfocus X-ray source with mirror optics (λ = 1.54178 Å) and a CCD area detector. A Semi-empirical absorption correction from equivalents was applied. The structure was solved by direct methods using SIR-97, and full-matrix least-square refinements on F^2 in SHELXL-97 was performed with anisotropic displacements for all non-hydrogen atoms. During the least-square-refinement ISOR restraints were applied to the disordered carbon positions.

Table S2. Crystal data and structure refinement for [{$(Me_3Si)_2N$}$_8$$Sn_8$$(bta)_{12}$$Li_8$$Br_4$]·(3 toluene), **4**·(3 toluene).

Empirical formula	$C_{141}H_{218}Br_4Li_8N_{44}Si_{16}Sn_8$
Formula weight	4303.84
Temperature	123(1) K
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 19.1397(3) Å α = 92.659(1)°
	b = 20.9948(3) Å β = 95.907(1)°
	c = 26.6822(5) Å γ = 111.672(2)°
Volume	9869.6(3) Å^3
Z	2
Density (calculated)	1.448 Mg/m^3
Absorption coefficient	10.213 mm^{-1}
F(000)	4320
Crystal size	0.13 x 0.10 x 0.03 mm^3
Theta range for data collection	3.09 to 76.01°.
Index ranges	$-23 < h < 23$, $-24 < k < 26$, $-33 < l < 28$
Reflections collected	82702
Independent reflections	39316 [R(int) = 0.0769]
Completeness to full theta	0.953
Max. and min. transmission	1.000, 0.702
Data / restraints / parameters	39316 / 24 / 2071
Goodness-of-fit on F2	1.000
Final R indices [I>2sigma(I)]	R_1 = 0.0614, wR_2 = 0.1542
R indices (all data)	R_1 = 0.1027, wR_2 = 0.1695
Largest diff hole and peak	–3.040, 3.031 eÅ^{-3}

1. SCALE3 ABSPACK, CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.33.52, **2009**.
2. A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Cryst.* **1999**, *32*, 115-119.
3. G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122.

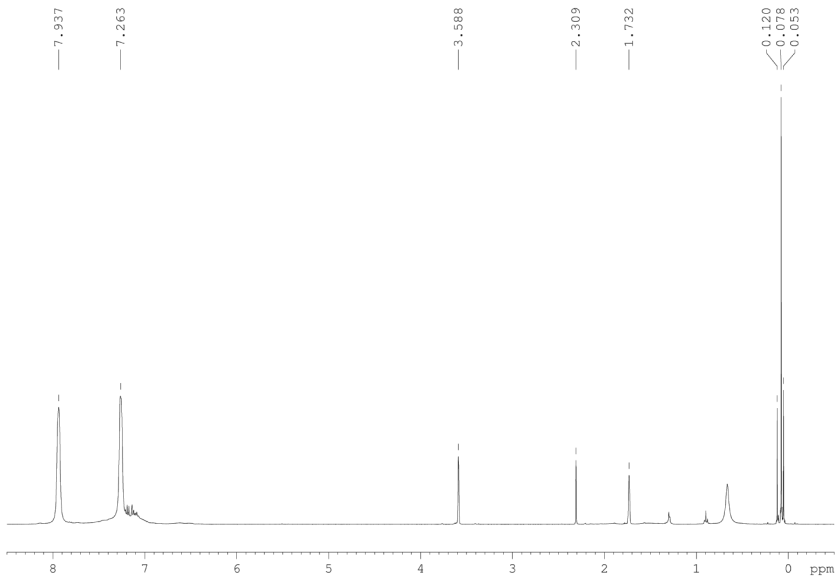

Figure S6. ^{1}H NMR spectrum of **4** in thf-d_8. Residual toluene solvent is visible in the spectrum.

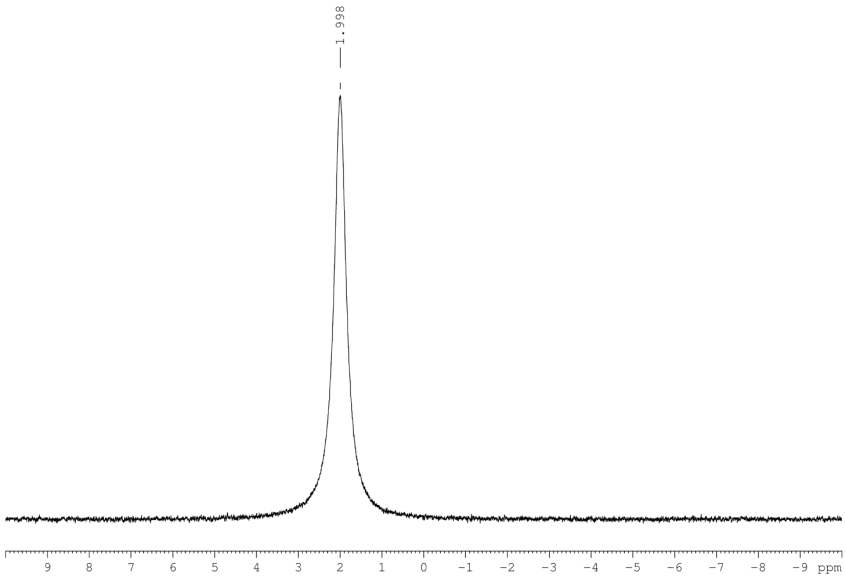

Figure S7. ^{7}Li NMR spectrum of **4** in thf-d_8.

[{(thf)$_2$Li(bta)}$_3${Li(thf)}]$_2$[SnI$_4$]·(thf), [5]$_2$[SnI$_4$]·(thf)

Table S3. Crystal data and structure refinement for [{(thf)$_2$Li(bta)}$_3${Li(thf)}]$_2$[SnI$_4$]·(thf), [**5**]$_2$[SnI$_4$]·(thf)

Empirical formula	$C_{96}H_{144}I_4Li_8N_{18}O_{15}Sn$	
Formula weight	2472.12	
Temperature	123(1) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	*Fdd*2	
Unit cell dimensions	a = 37.5021(5) Å	α = 90°.
	b = 47.4100(7) Å	β = 90°.
	c = 12.6919(2) Å	γ = 90°.
Volume	22565.9(6) Å^3	
Z	8	
Density (calculated)	1.455 Mg/m^3	
Absorption coefficient	10.914 mm^{-1}	
F(000)	10016	
Crystal size	0.325 x 0.243 x 0.216 mm^3	
Theta range for data collection	3.00 to 74.26°.	
Index ranges	-46<=h<=45, -53<=k<=58, -12<=l<=15	
Reflections collected	27163	
Independent reflections	9029 [R(int) = 0.0334]	
Completeness to theta = 74.26°	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.52623	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9029 / 1 / 676	
Goodness-of-fit on F^2	1.020	
Final R indices [I>2sigma(I)]	R1 = 0.0352, wR2 = 0.0942	
R indices (all data)	R1 = 0.0359, wR2 = 0.0947	
Absolute structure parameter	0.006(4)	
Largest diff. peak and hole	0.954 and -1.187 e.Å^{-3}	

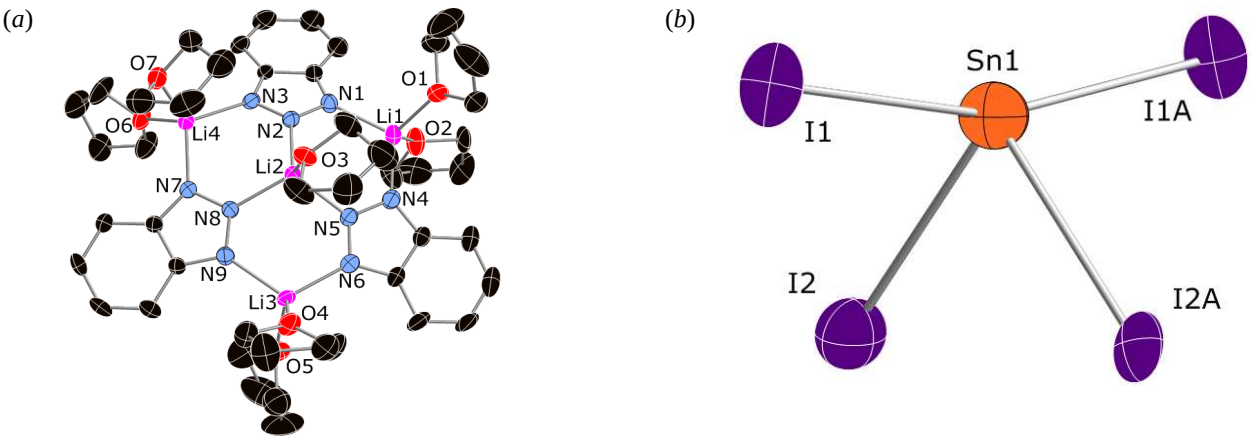

Figure S8. Thermal ellipsoid plot (50% probability) of (*a*) [{(thf)$_2$Li(bta)}$_3${Li(thf)}]$^+$, and (*b*) [SnI$_4$]$^{2-}$, [**5**]$_2$[SnI$_4$]. Large residual electron density is located near to the heavy atoms.

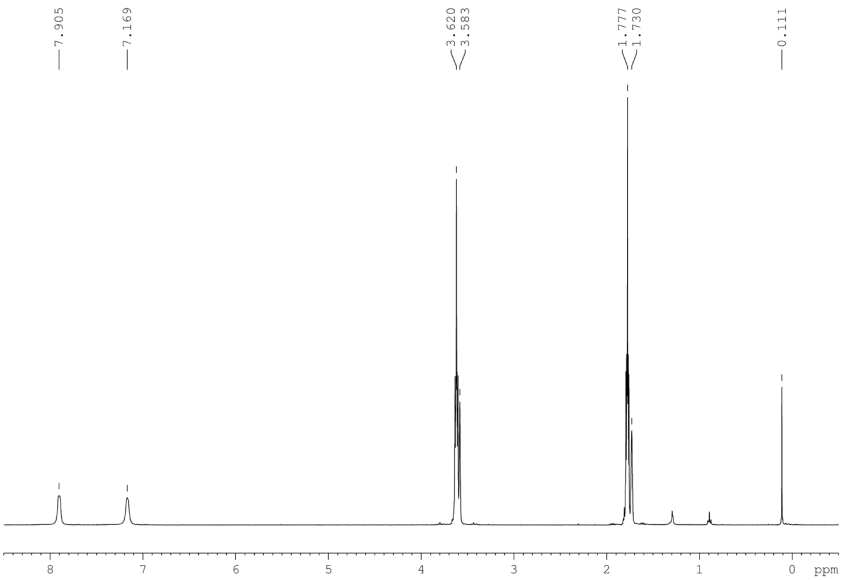

Figure S9. ^{1}H NMR spectrum of $[\mathbf{5}]_2[SnI_4]$ in thf-d_8.

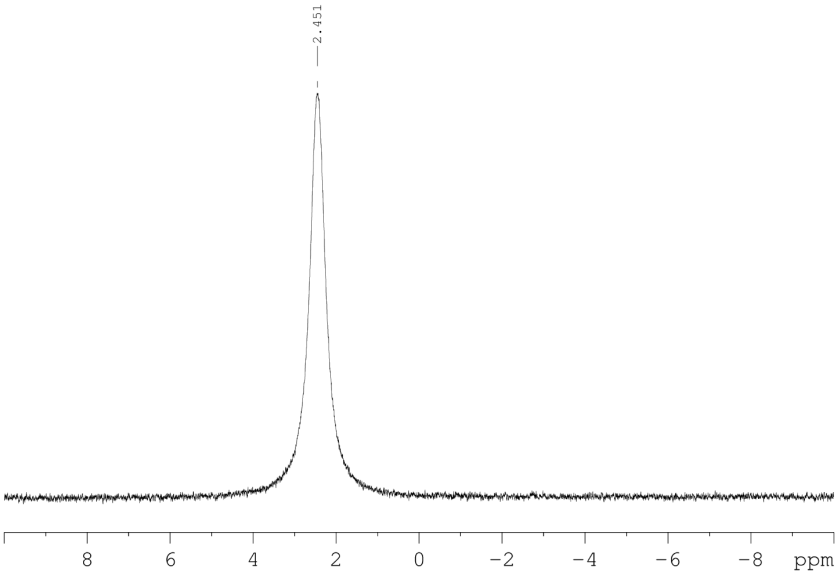

Figure S10. ^{7}Li NMR spectrum of $[\mathbf{5}]_2[SnI_4]$ in thf-d_8.