

Phosphido-Borane-Supported Stannates

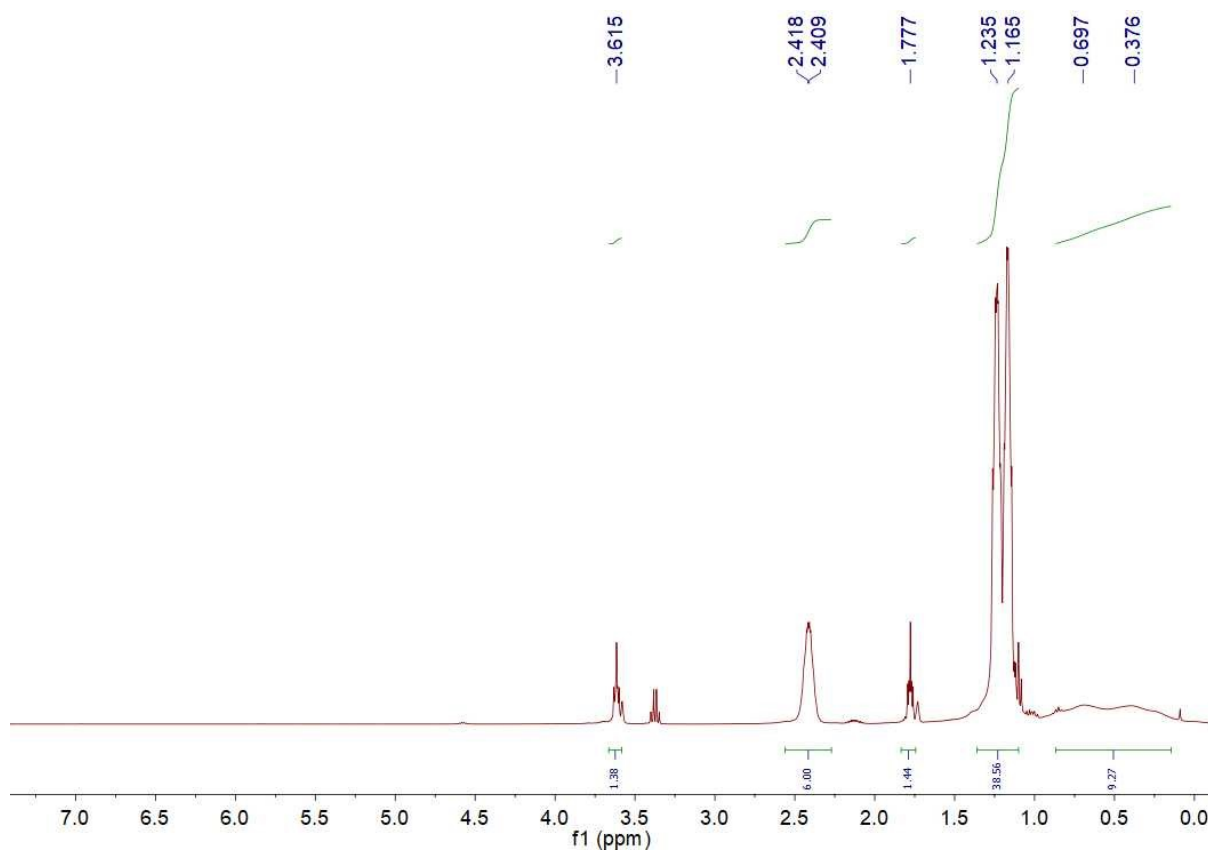
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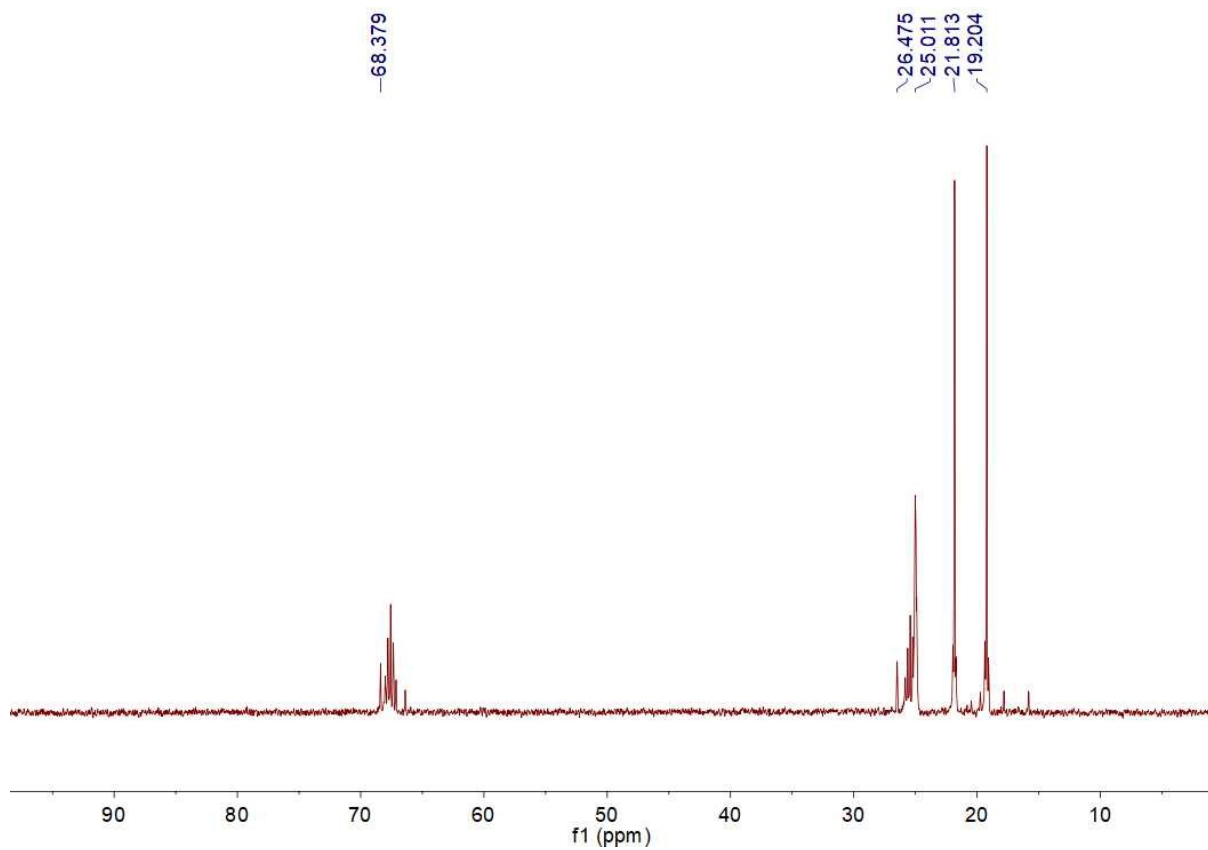
SUPPORTING INFORMATION

Contents:

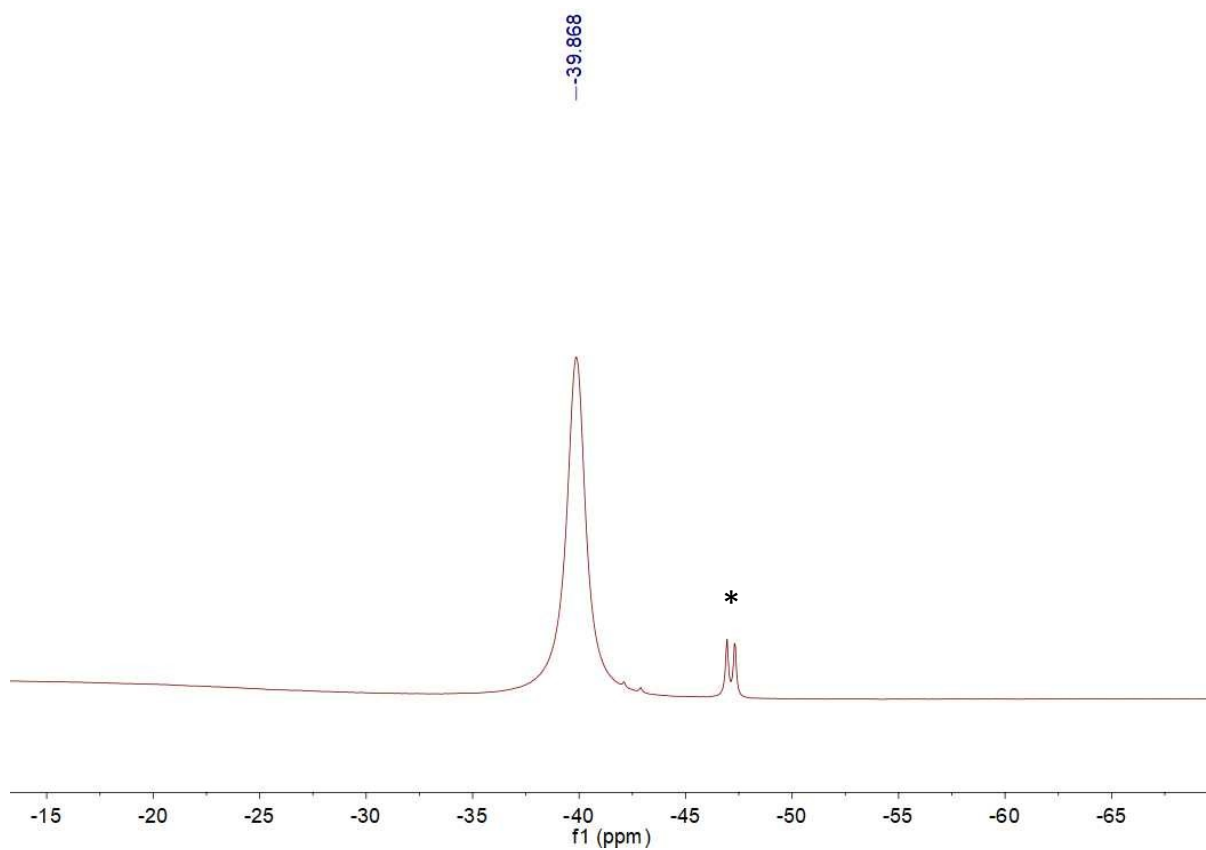
- S2-S20 ^1H , $^{13}\text{C}\{^1\text{H}\}$, ^7Li , $^{11}\text{B}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$, and $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectra, as appropriate, for compounds **2Li**, **2Na**, **2K**, **3Li**, **3Na**, **3K**, and **4Li**.
- S21-S23 $^{11}\text{B}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$, and $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectra showing the decomposition of **3Li** in THF.
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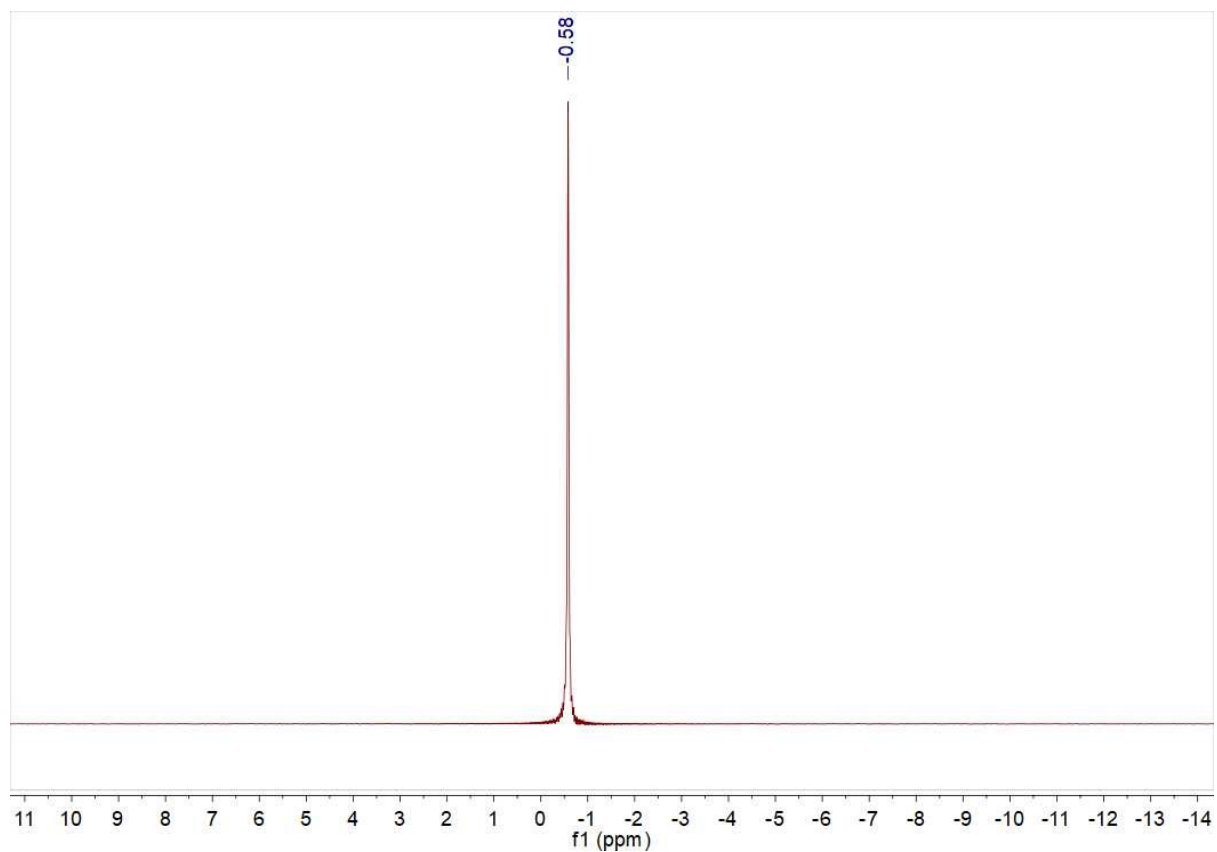
^1H NMR spectrum of **2Li** in d_8 -THF.



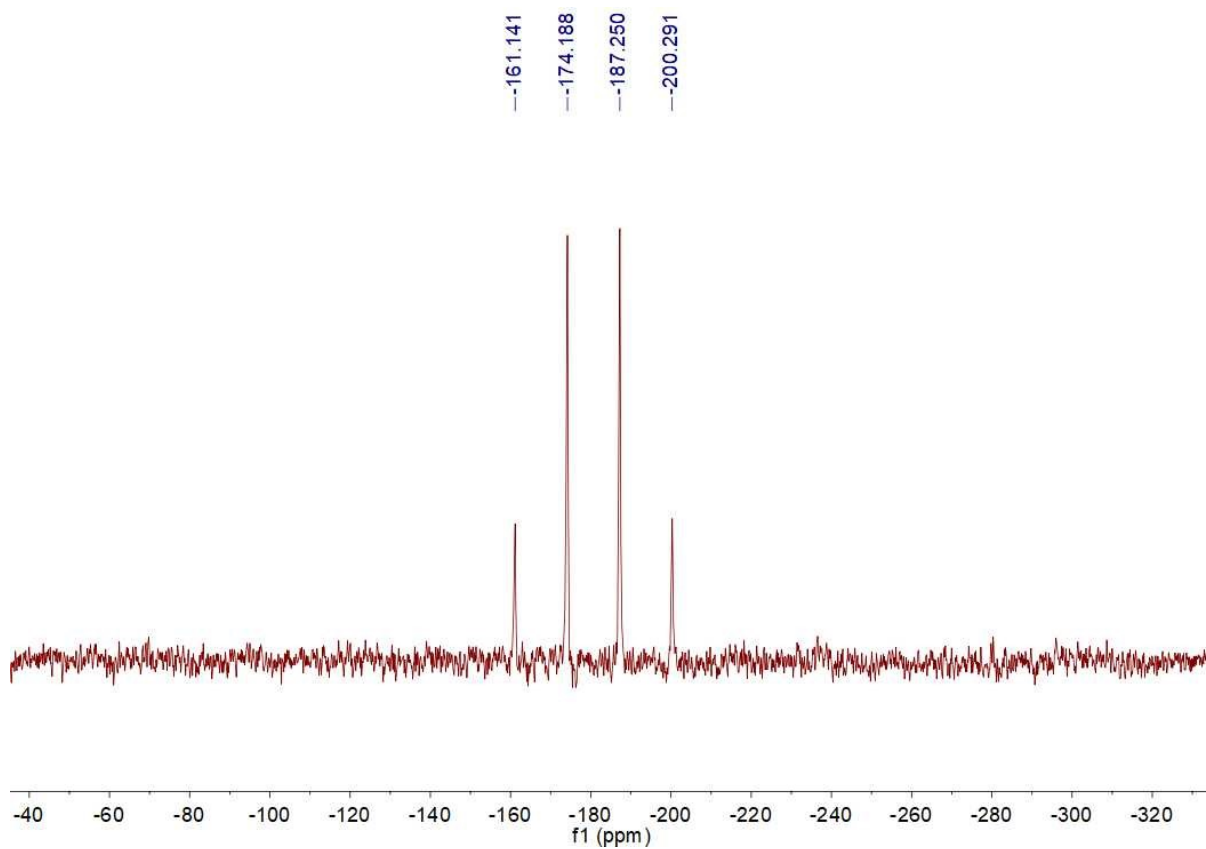
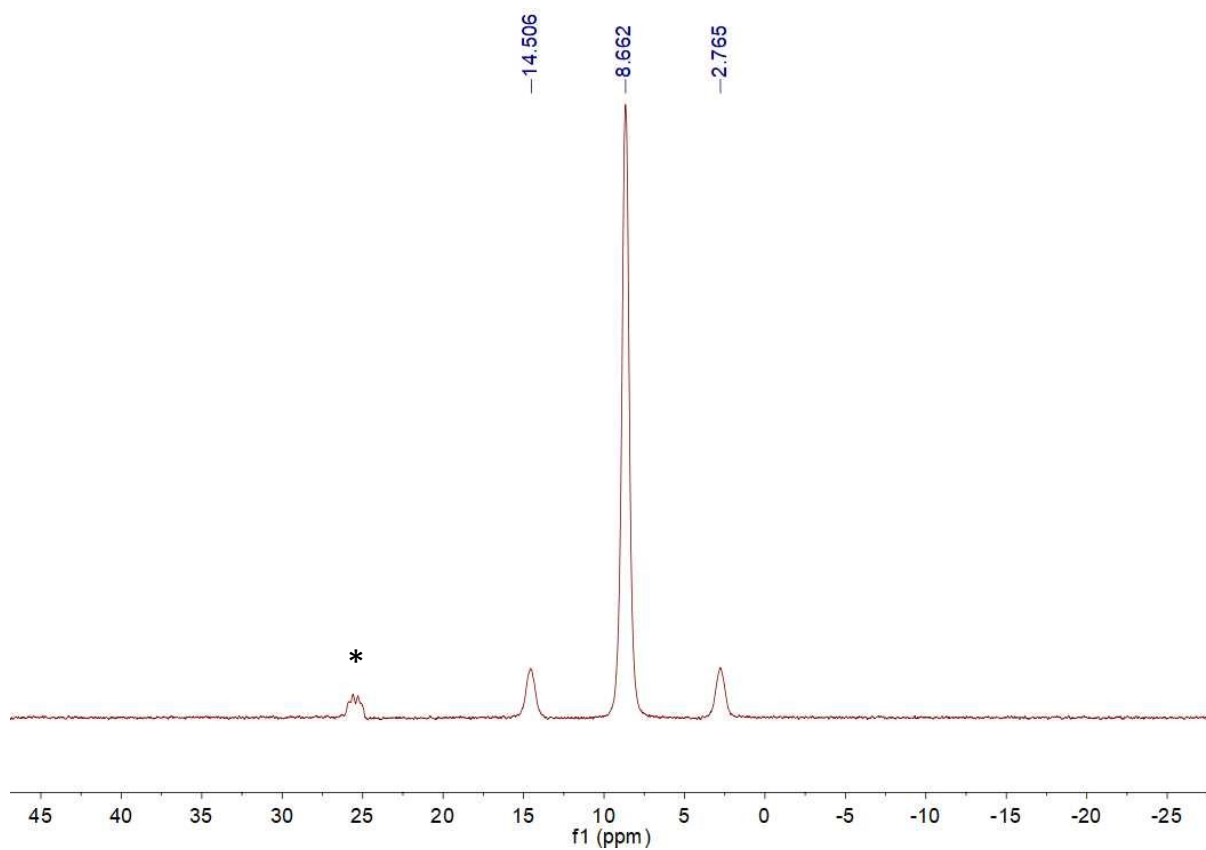
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2Li** in d_8 -THF.

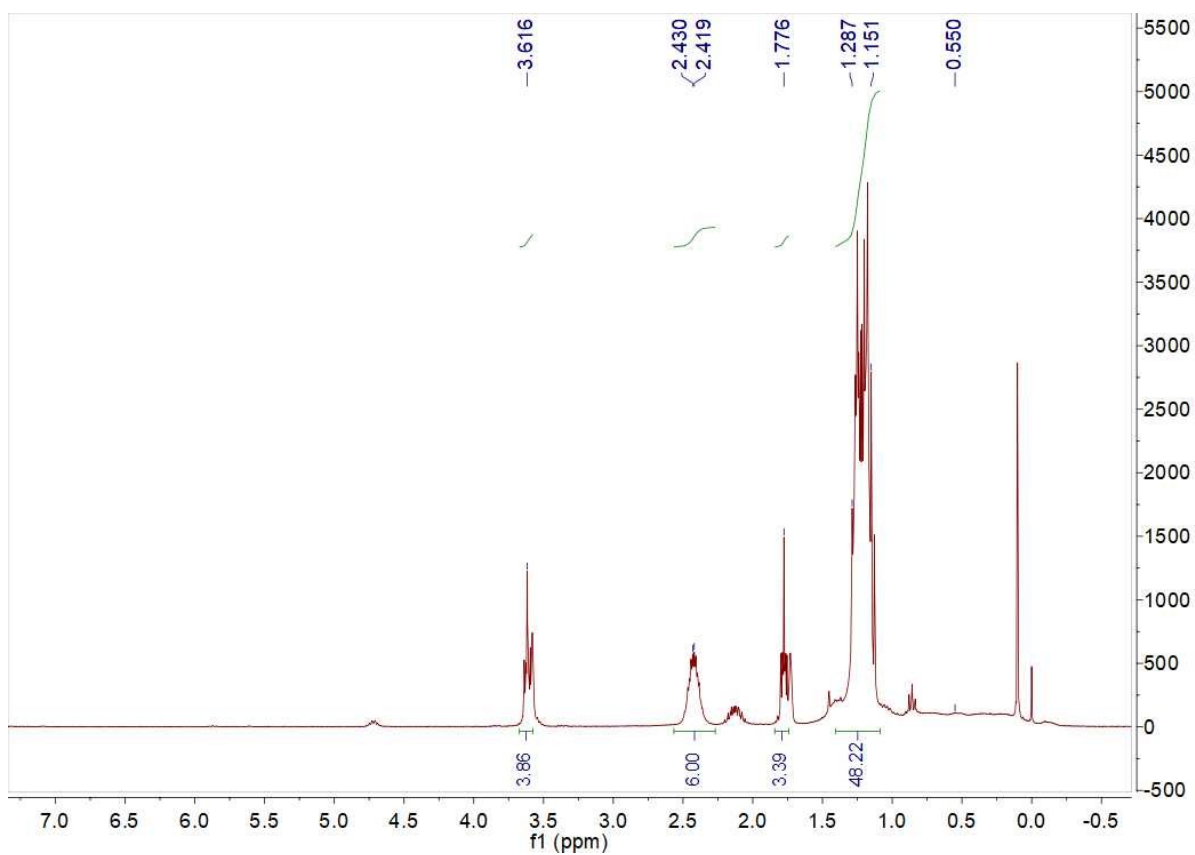


$^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **2Li** in d_8 -THF (*free phosphine-borane **2H** due to partial hydrolysis during sample preparation).

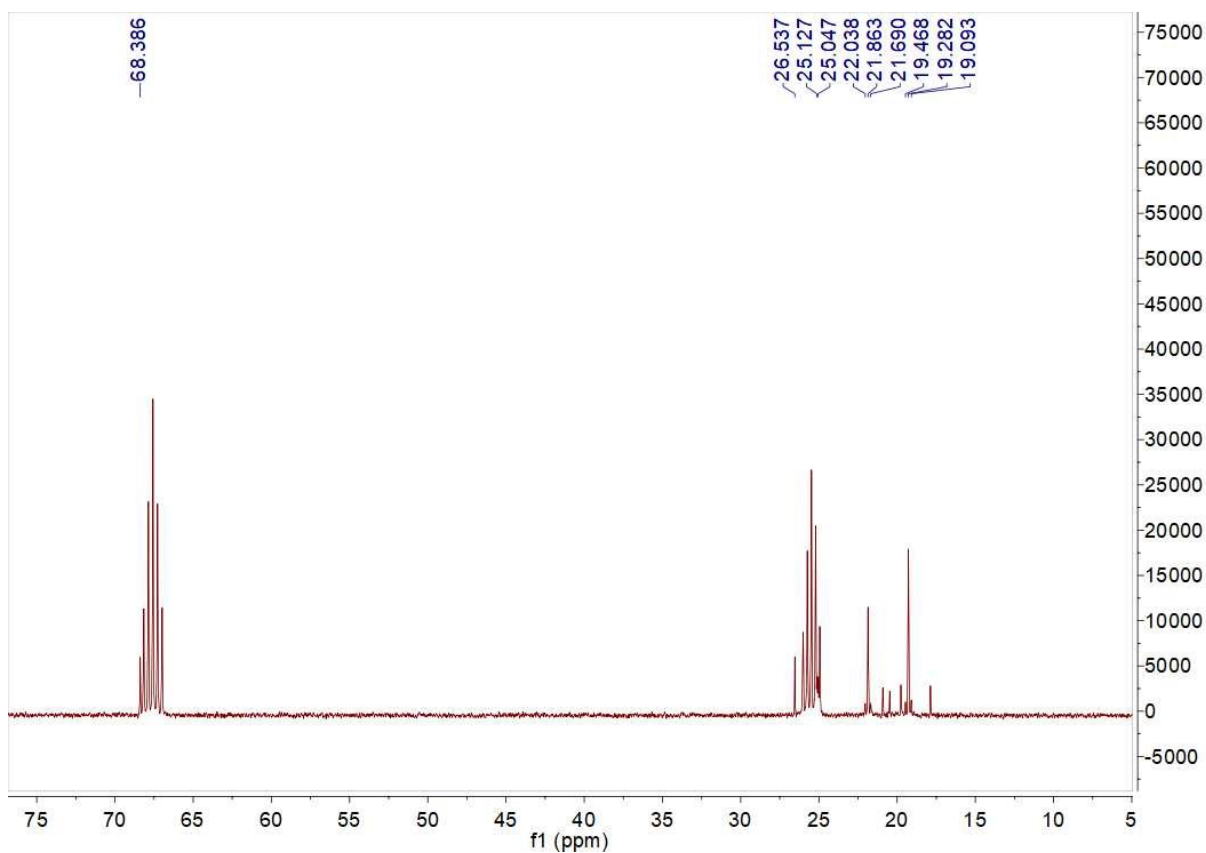


^7Li NMR spectrum of **2Li** in d_8 -THF.

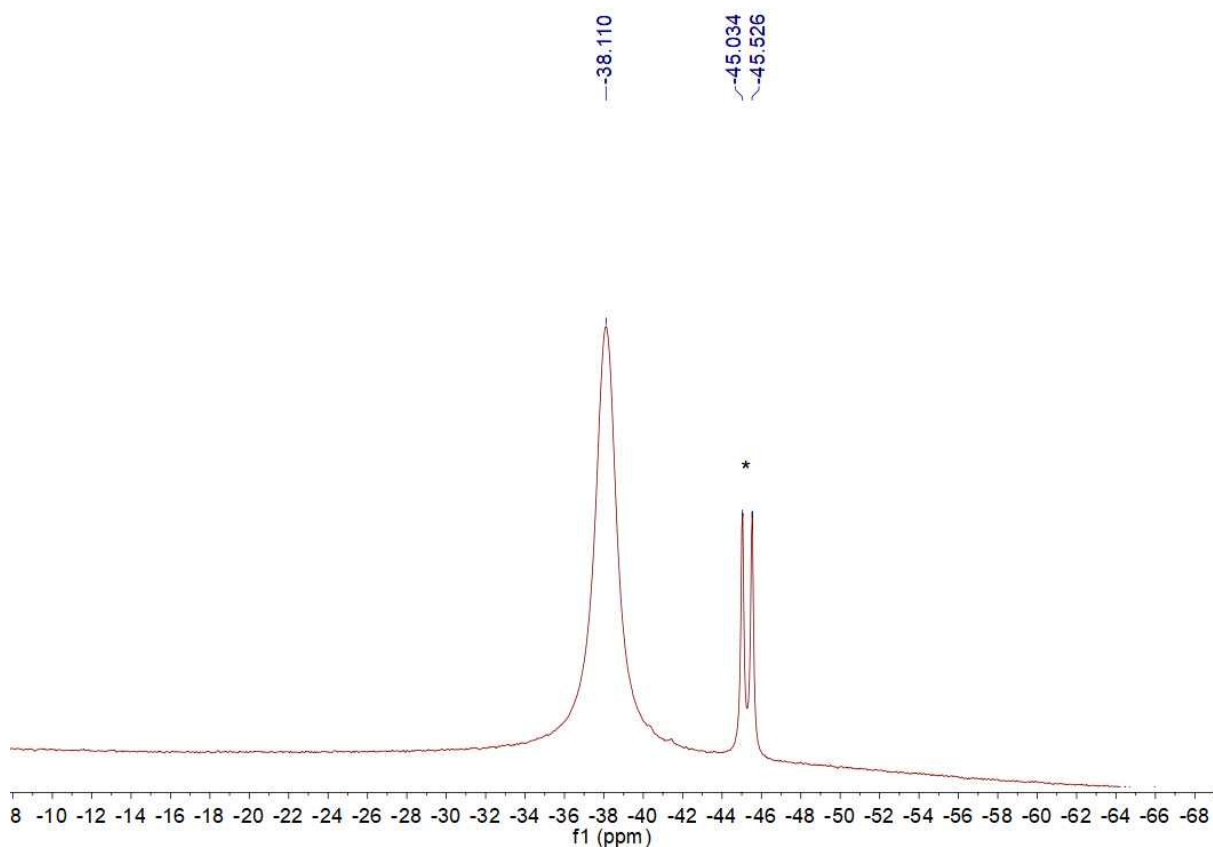




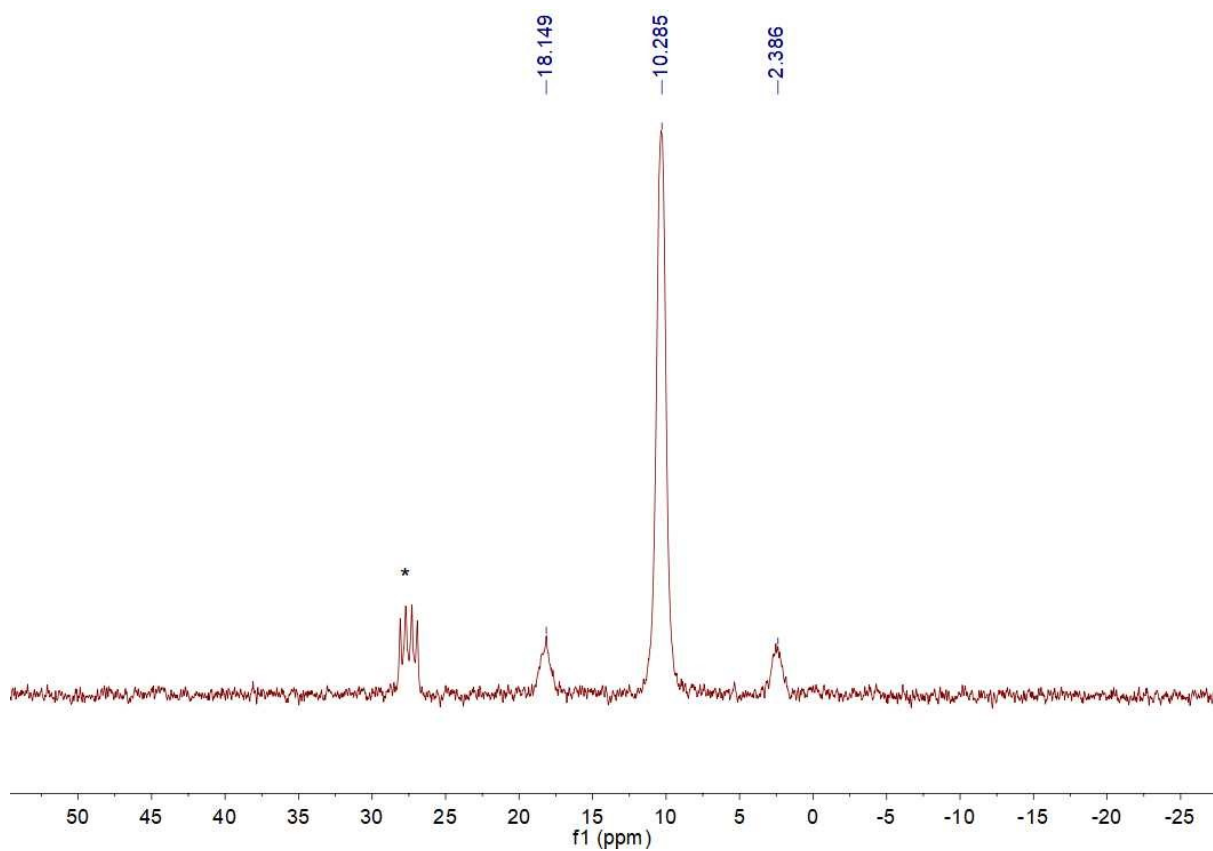
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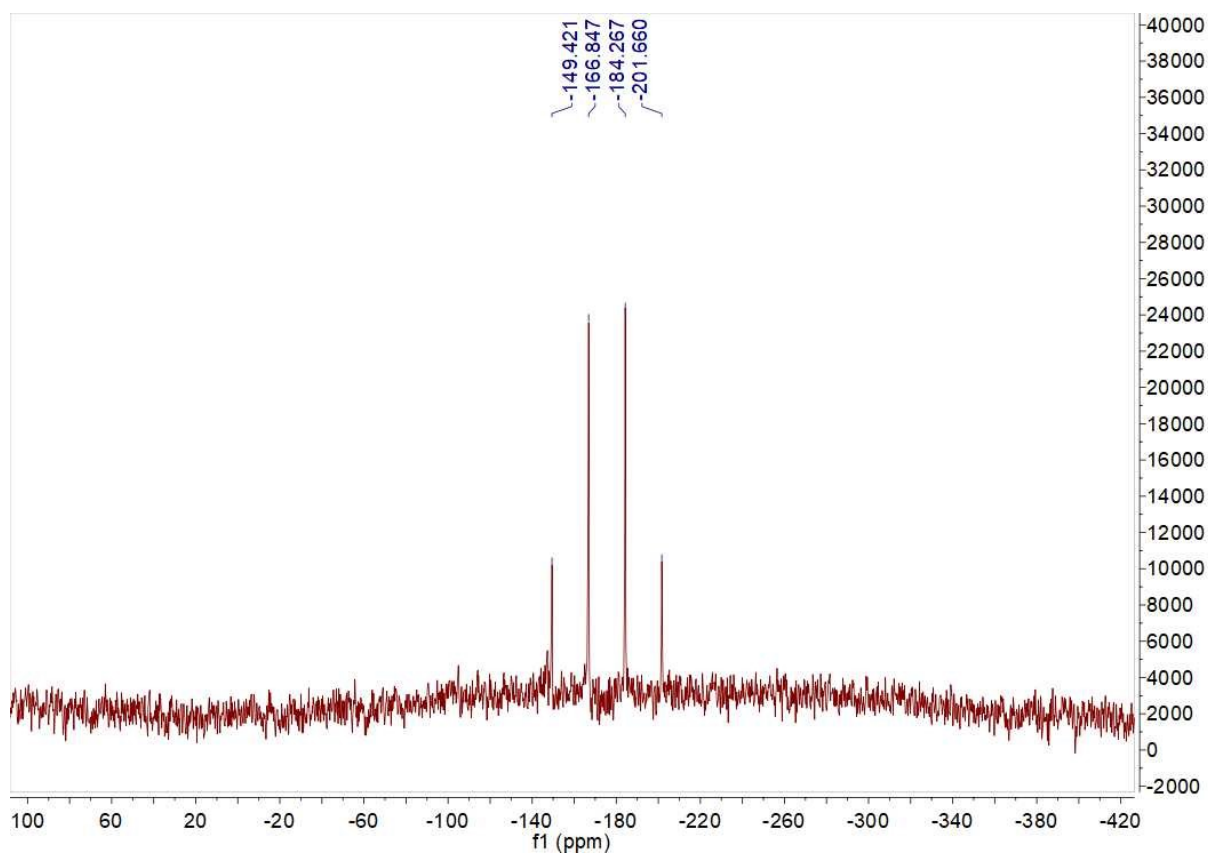
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2Na** in d_8 -THF.



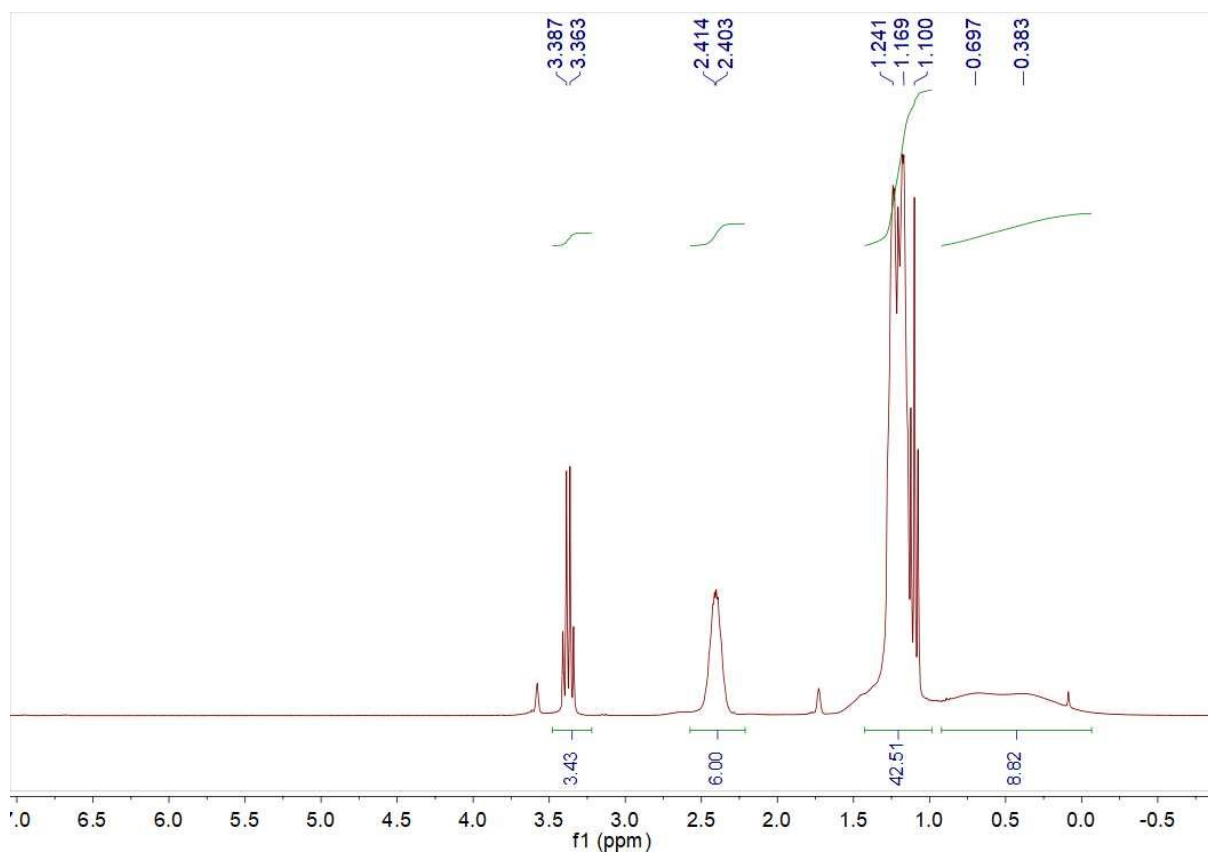
$^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **2Na** in d_8 -THF (*free phosphine-borane **2H** due to partial hydrolysis during sample preparation).



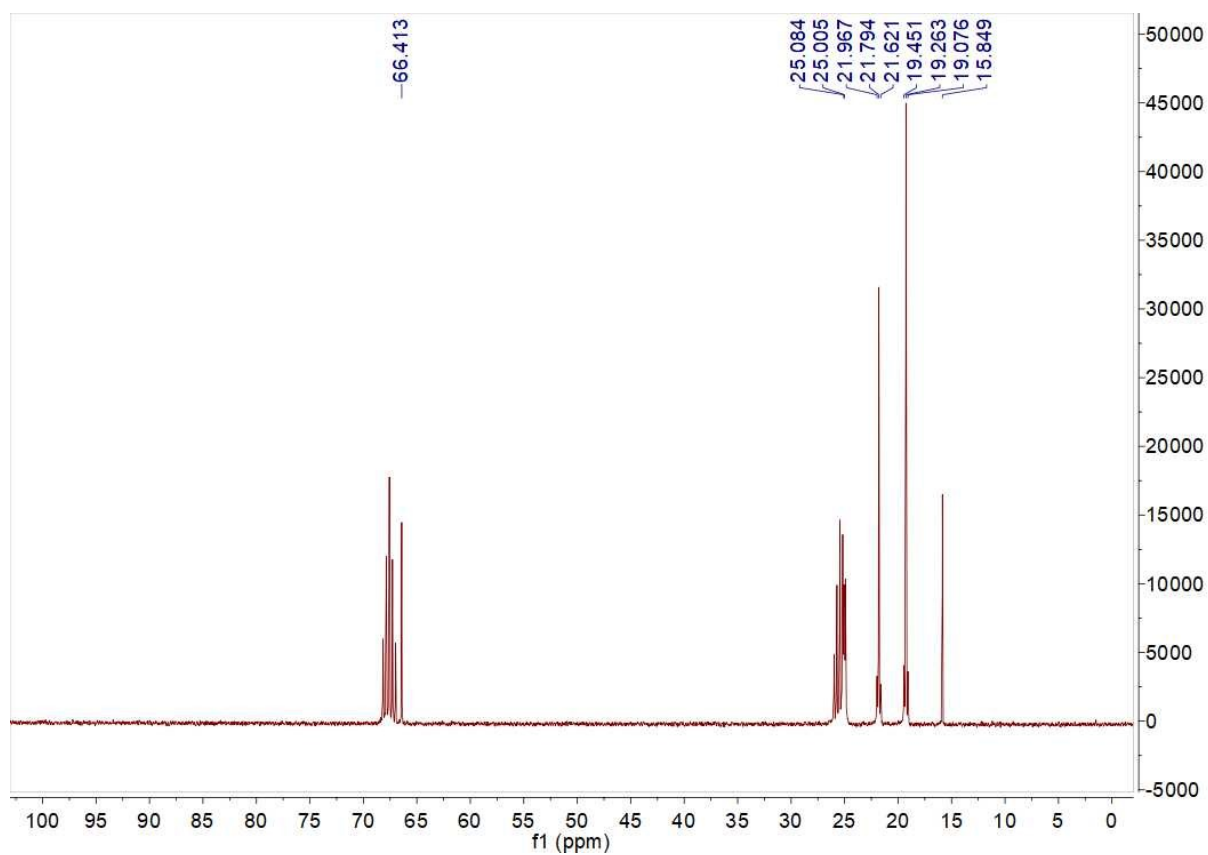
$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2Na** in d_8 -THF (*free phosphine-borane **2H** due to partial hydrolysis during sample preparation).



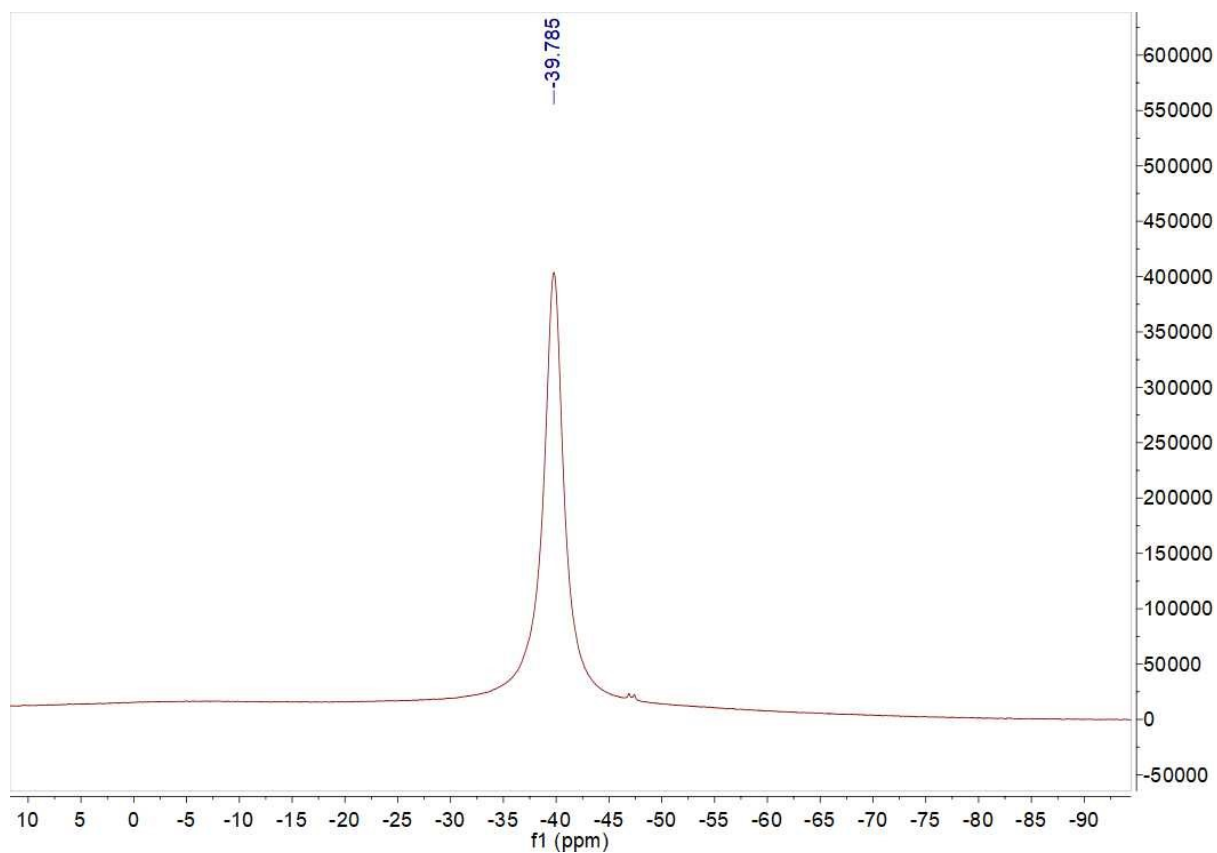
$^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of **2Na** in d_8 -THF.



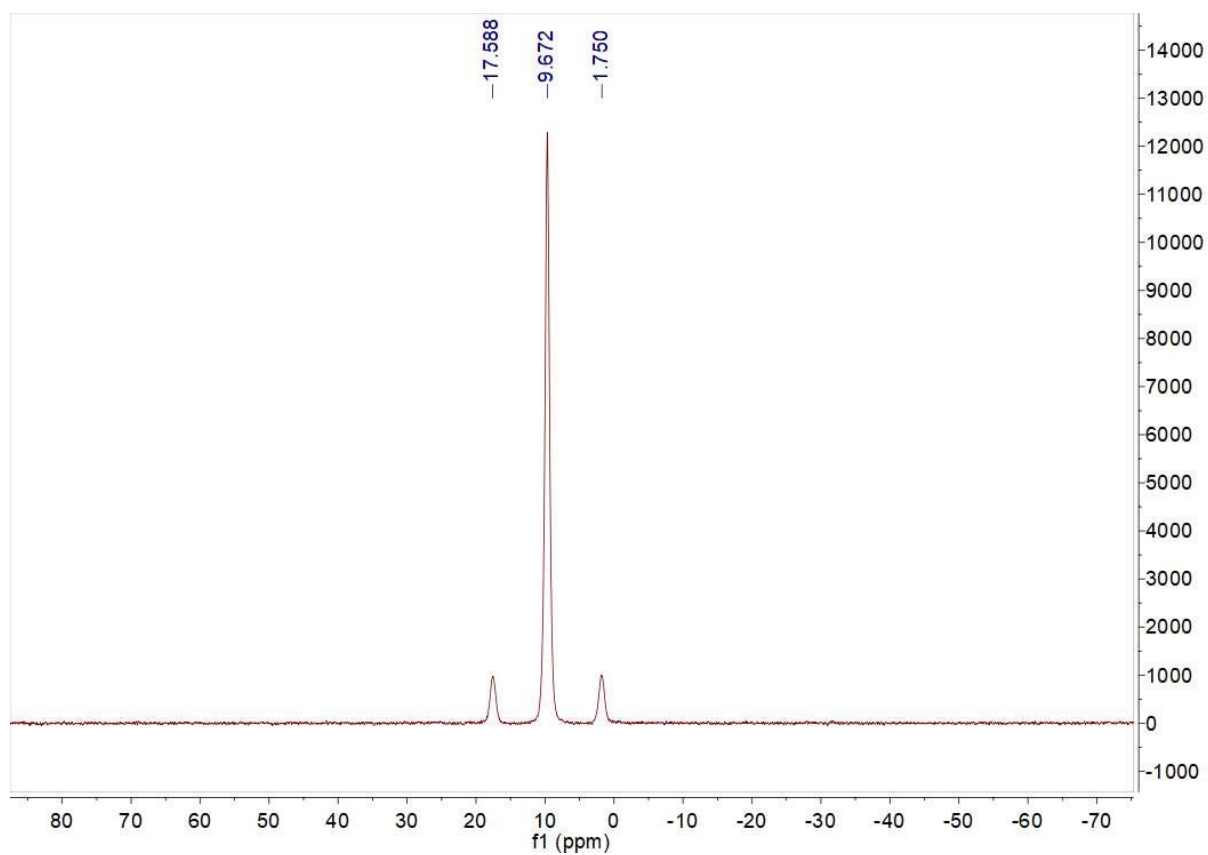
^1H NMR spectrum of **2K** in d_8 -THF.



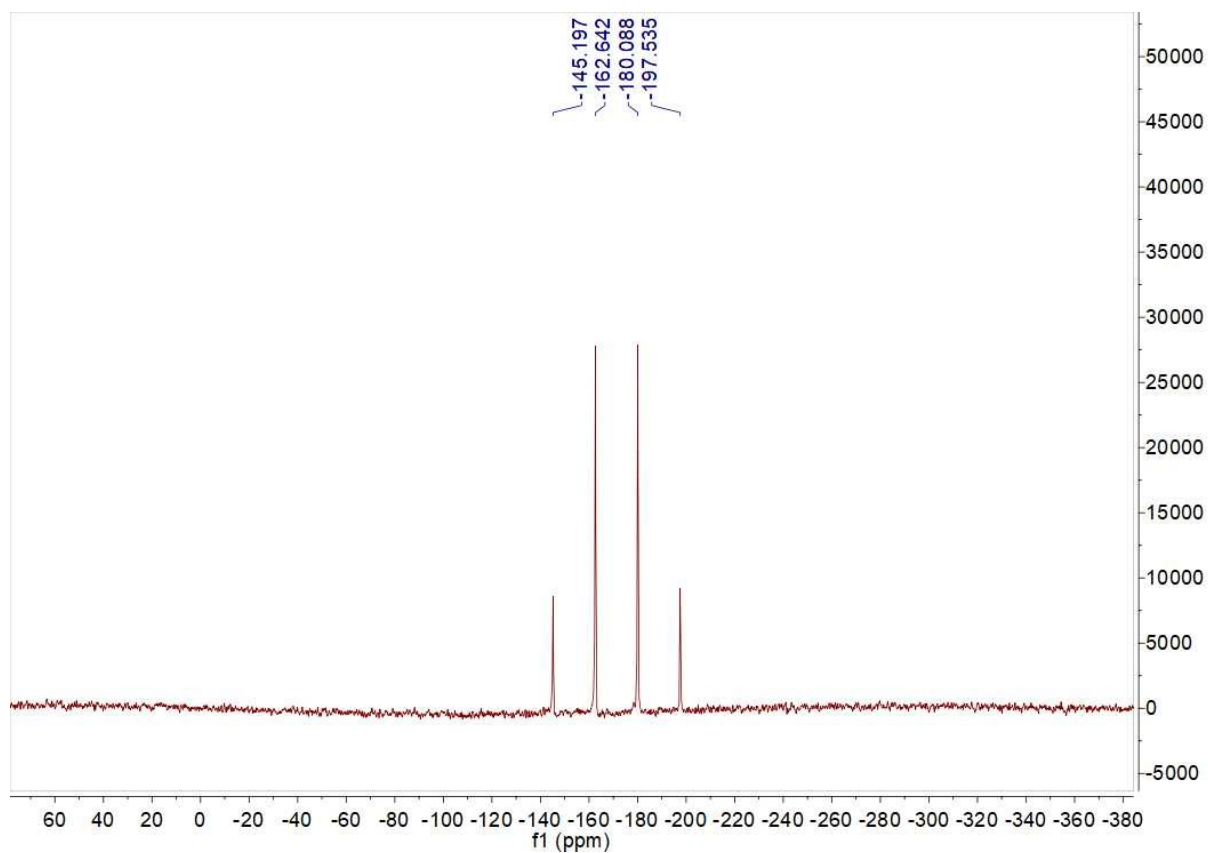
¹³C{¹H} NMR spectrum of **2K** in *d*₈-THF.



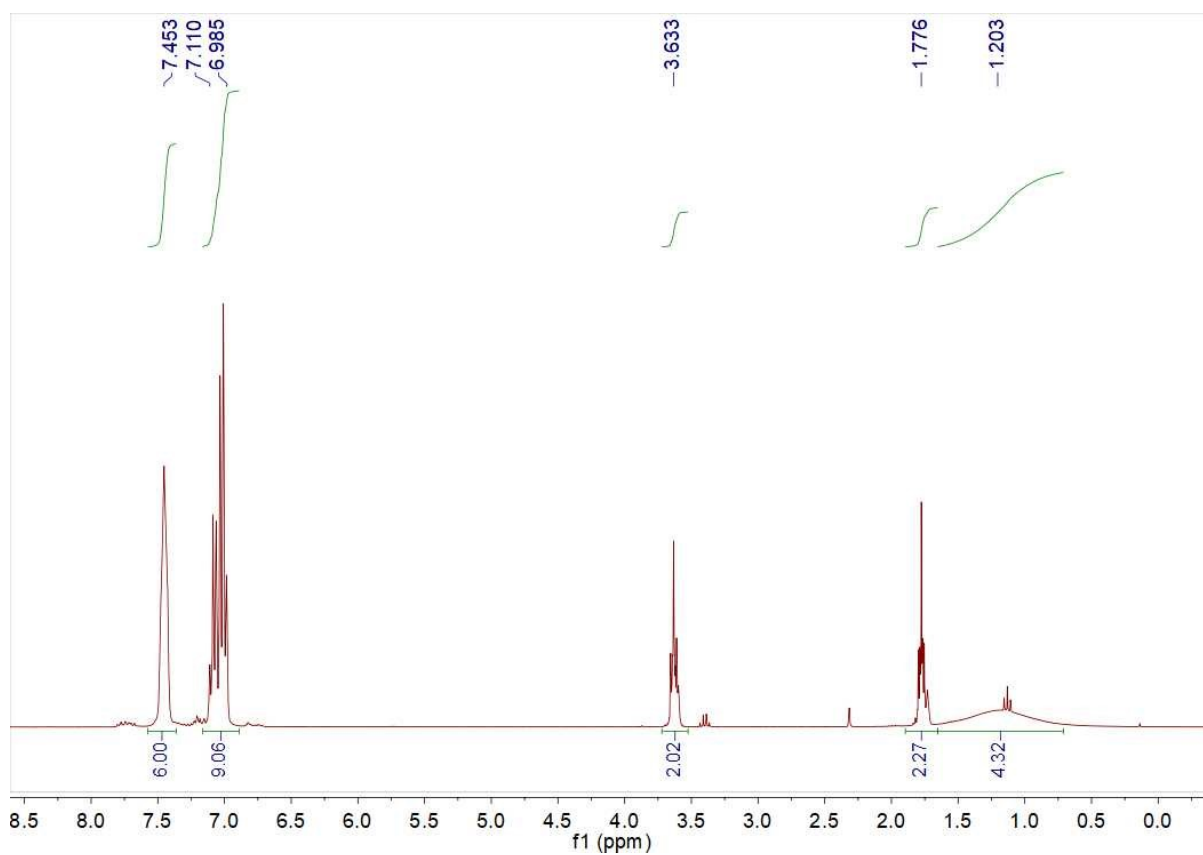
¹¹B{¹H} NMR spectrum of **2K** in *d*₈-THF.



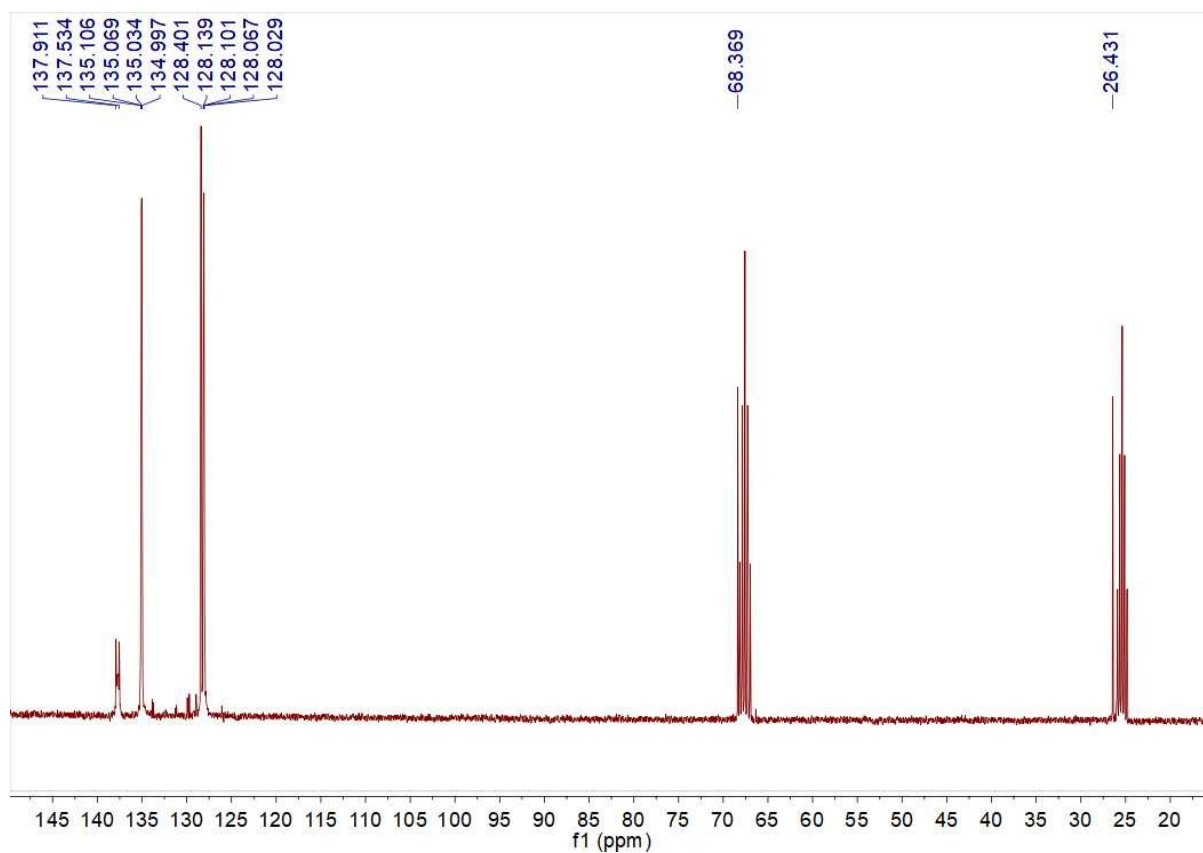
$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2K** in d_8 -THF.



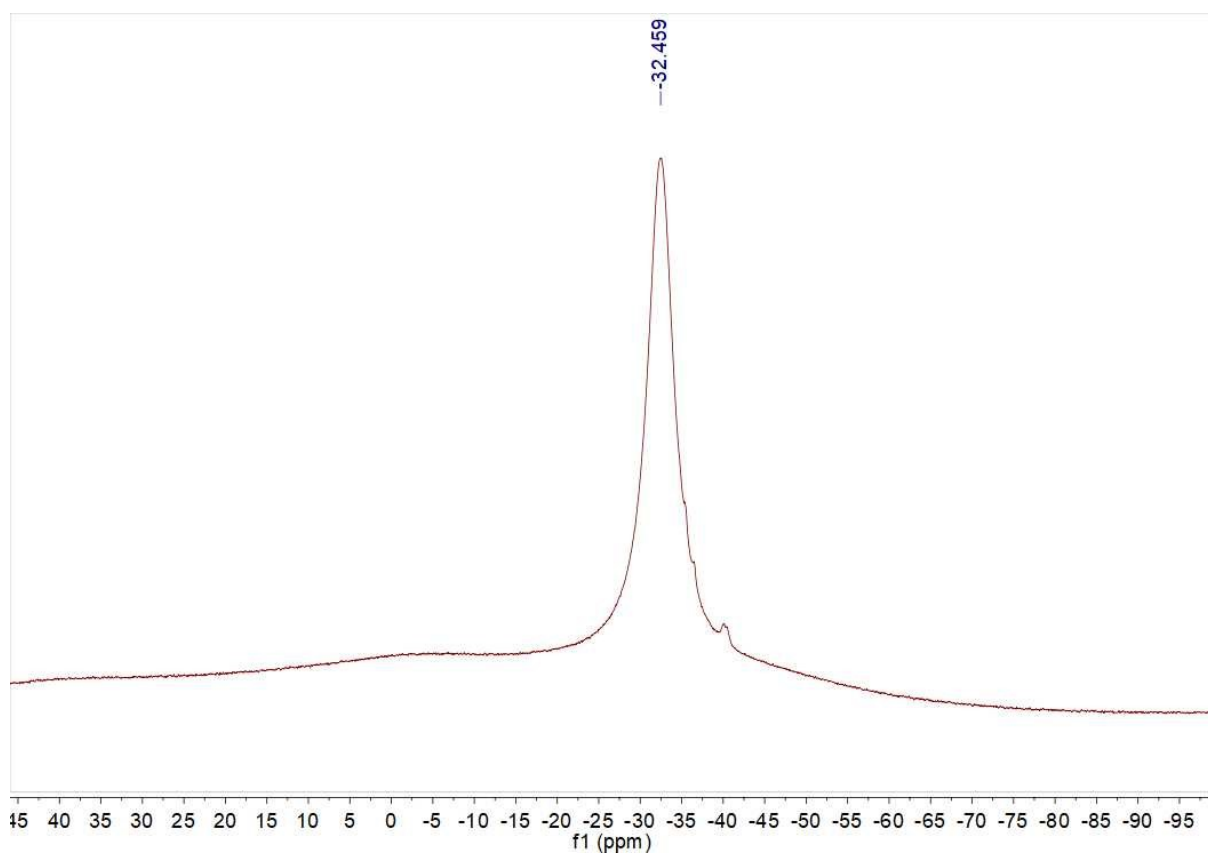
$^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of **2K** in d_8 -THF.



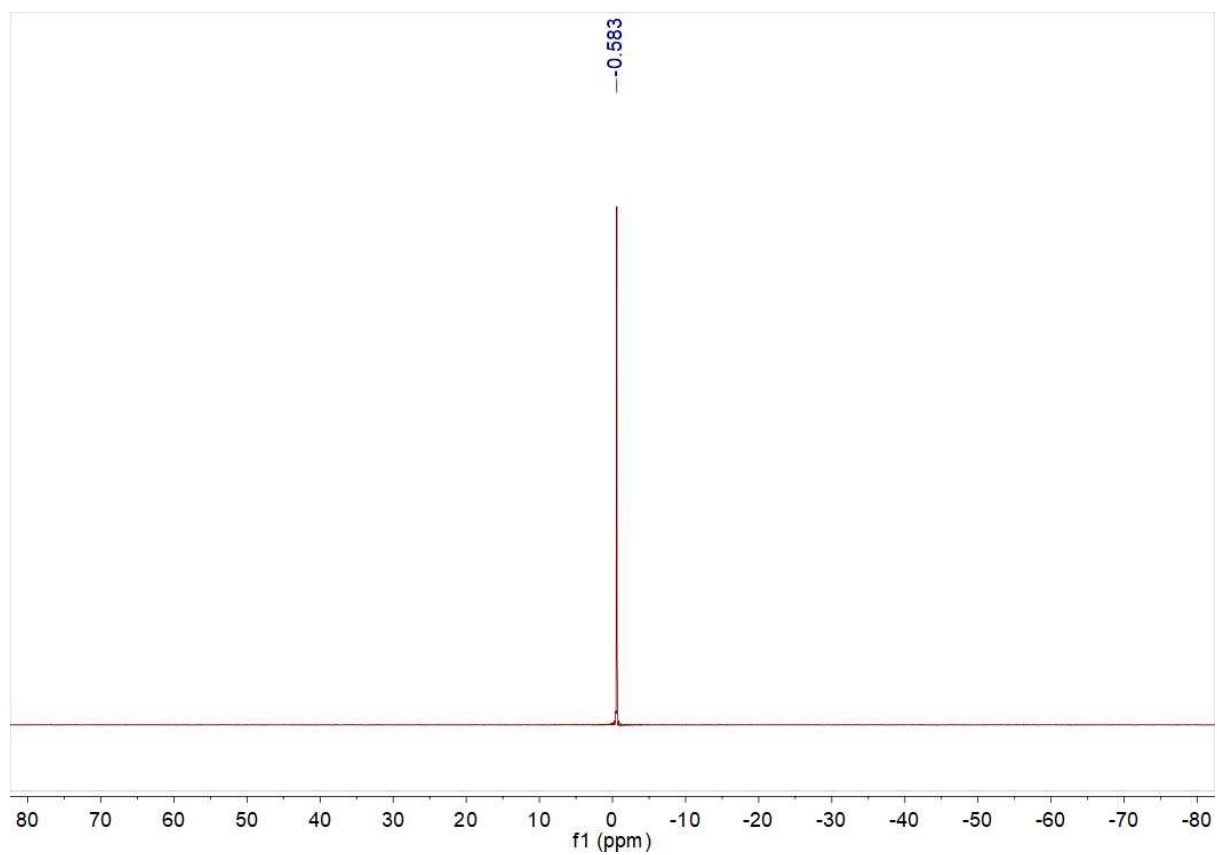
^1H NMR spectrum of **3Li** in d_8 -THF.



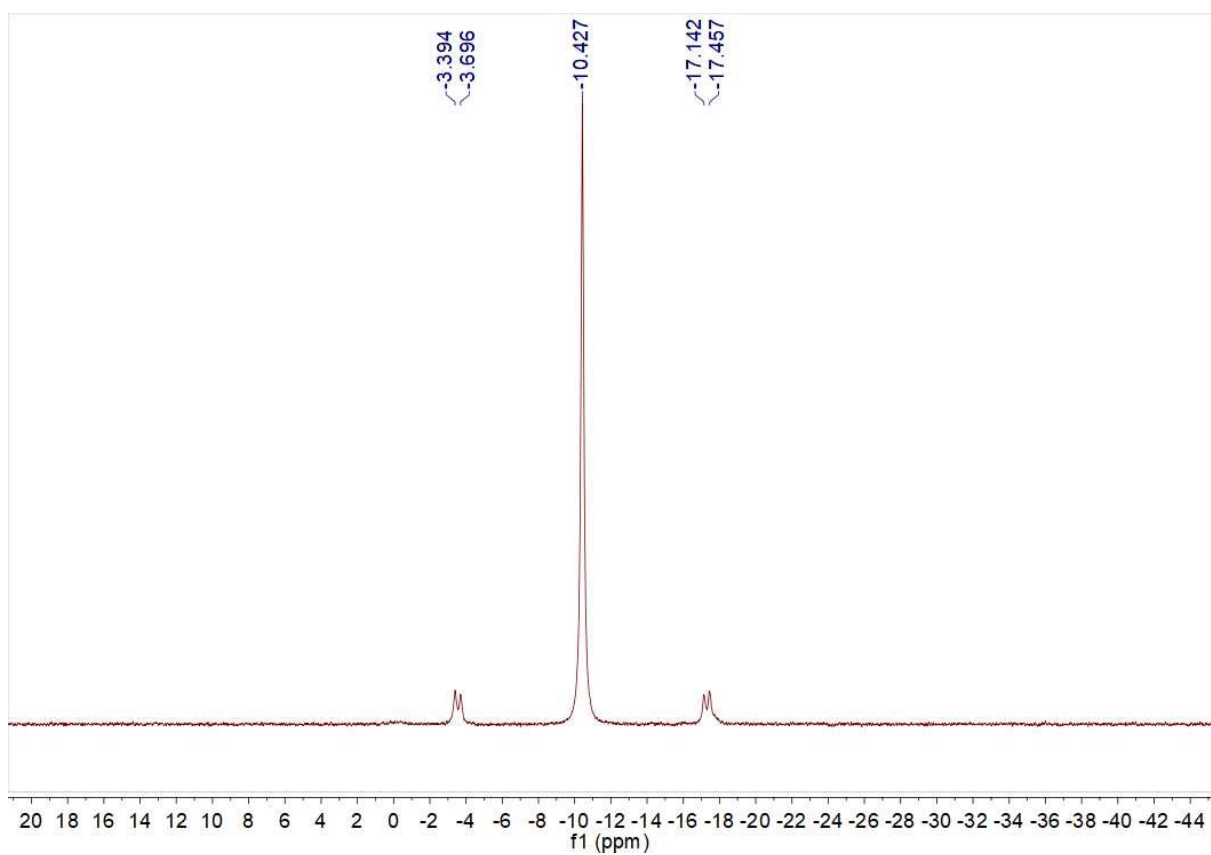
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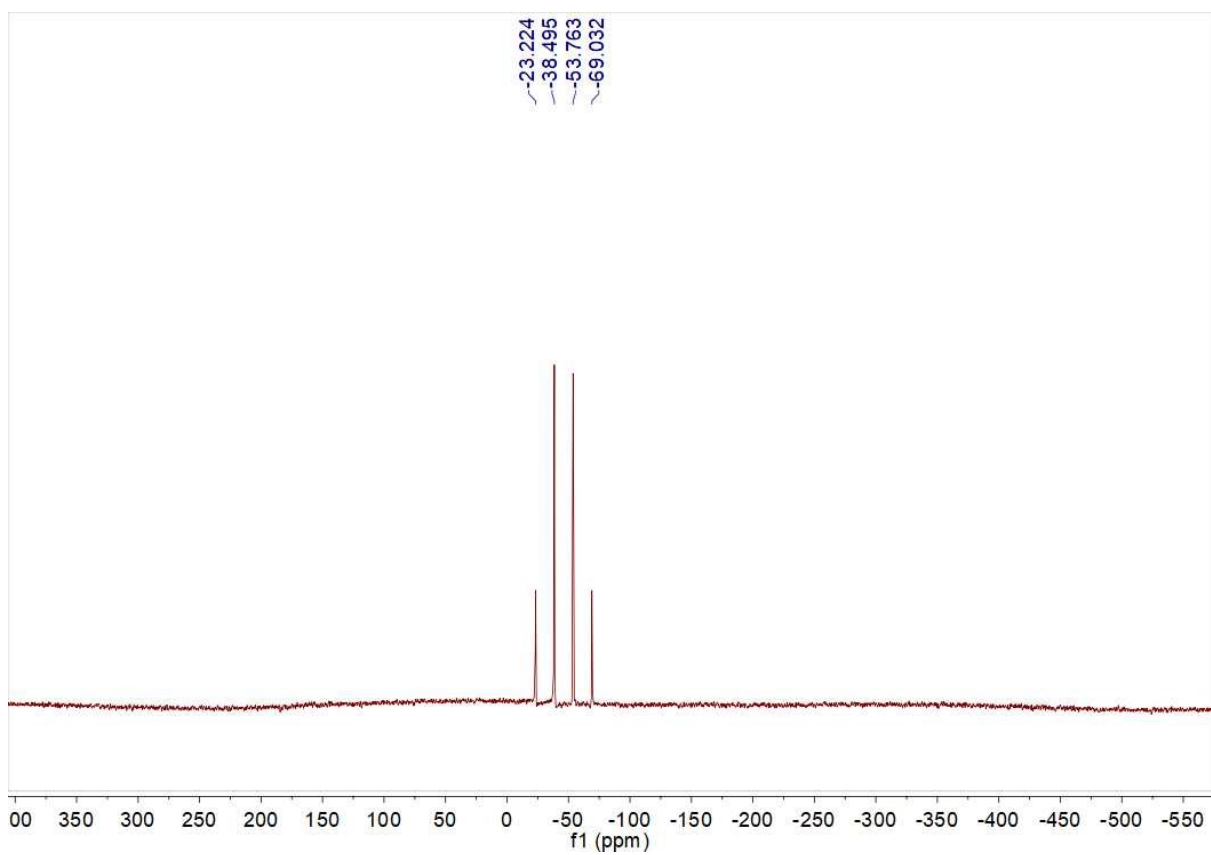
$^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **3Li** in d_8 -THF.



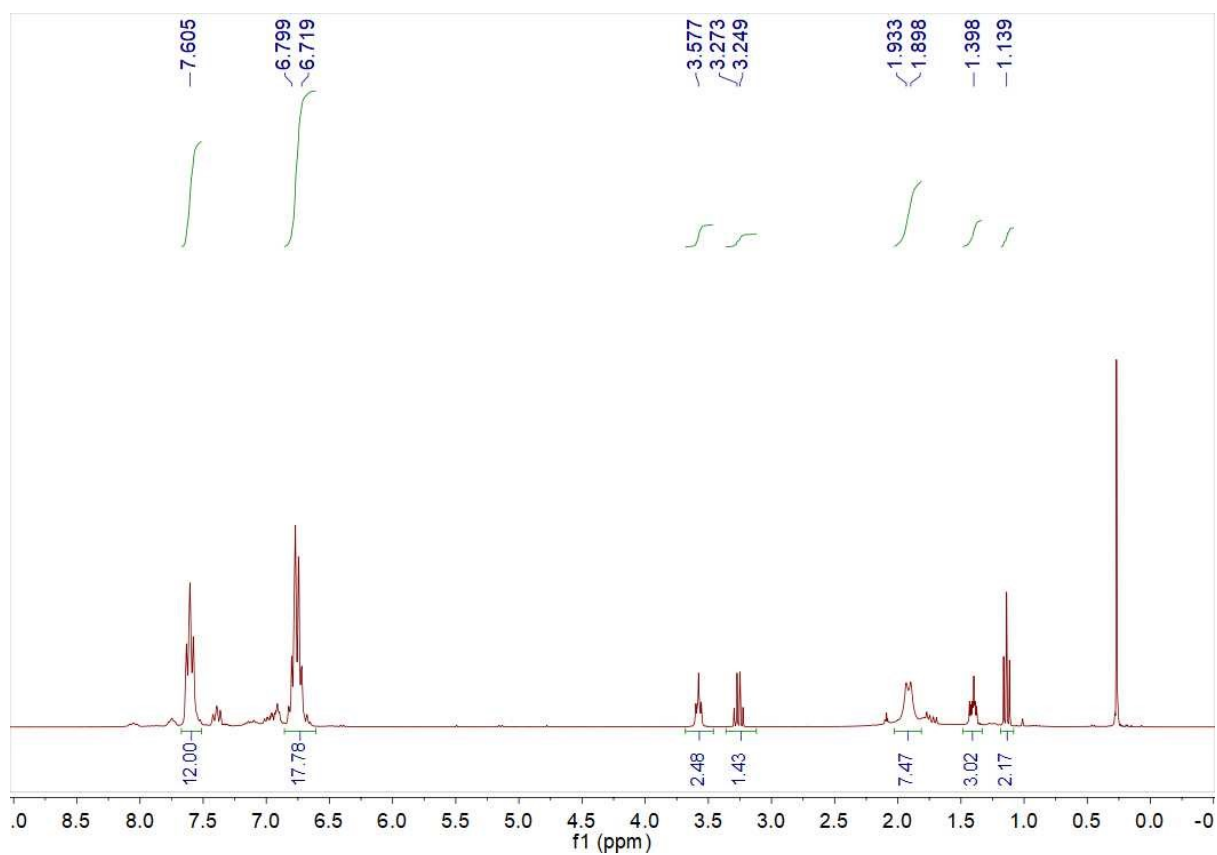
$^7\text{Li}\{^1\text{H}\}$ NMR spectrum of **3Li** in d_8 -THF.



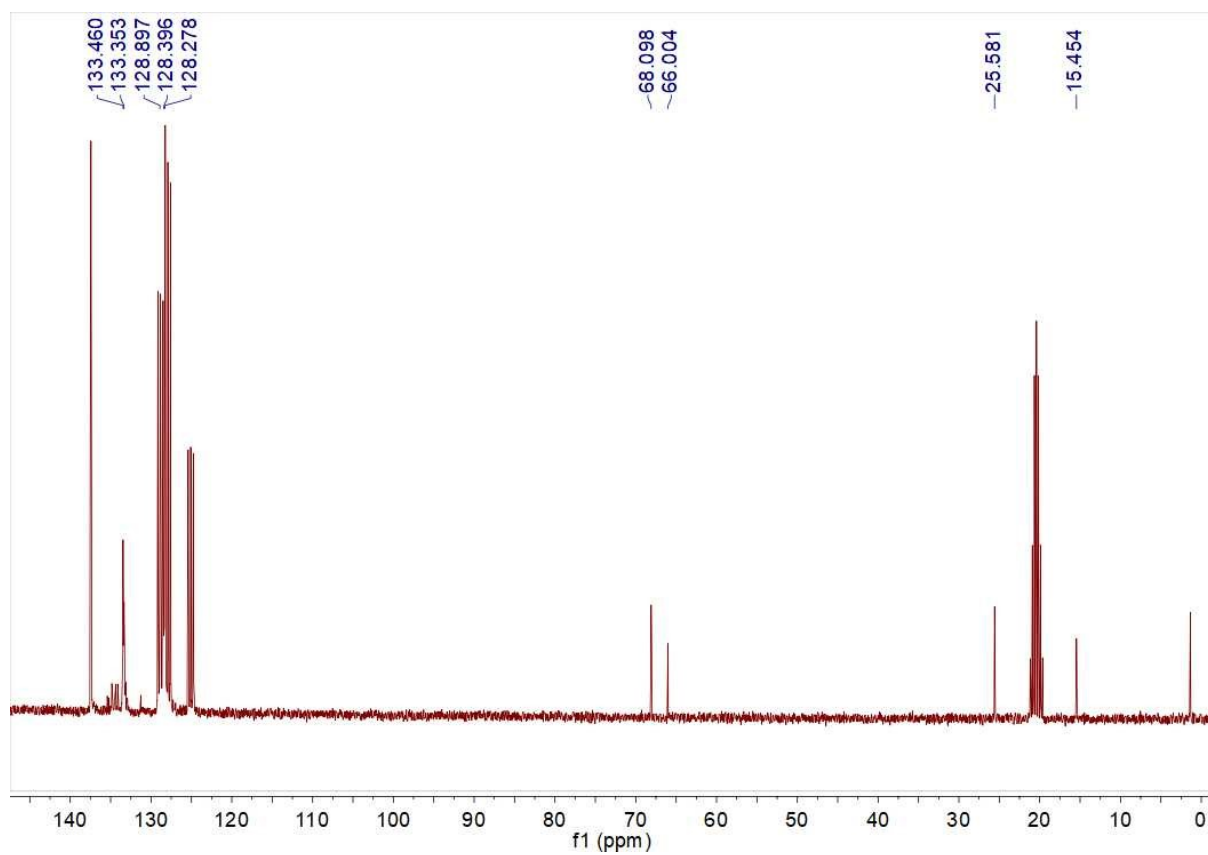
$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3Li** in d_8 -THF.



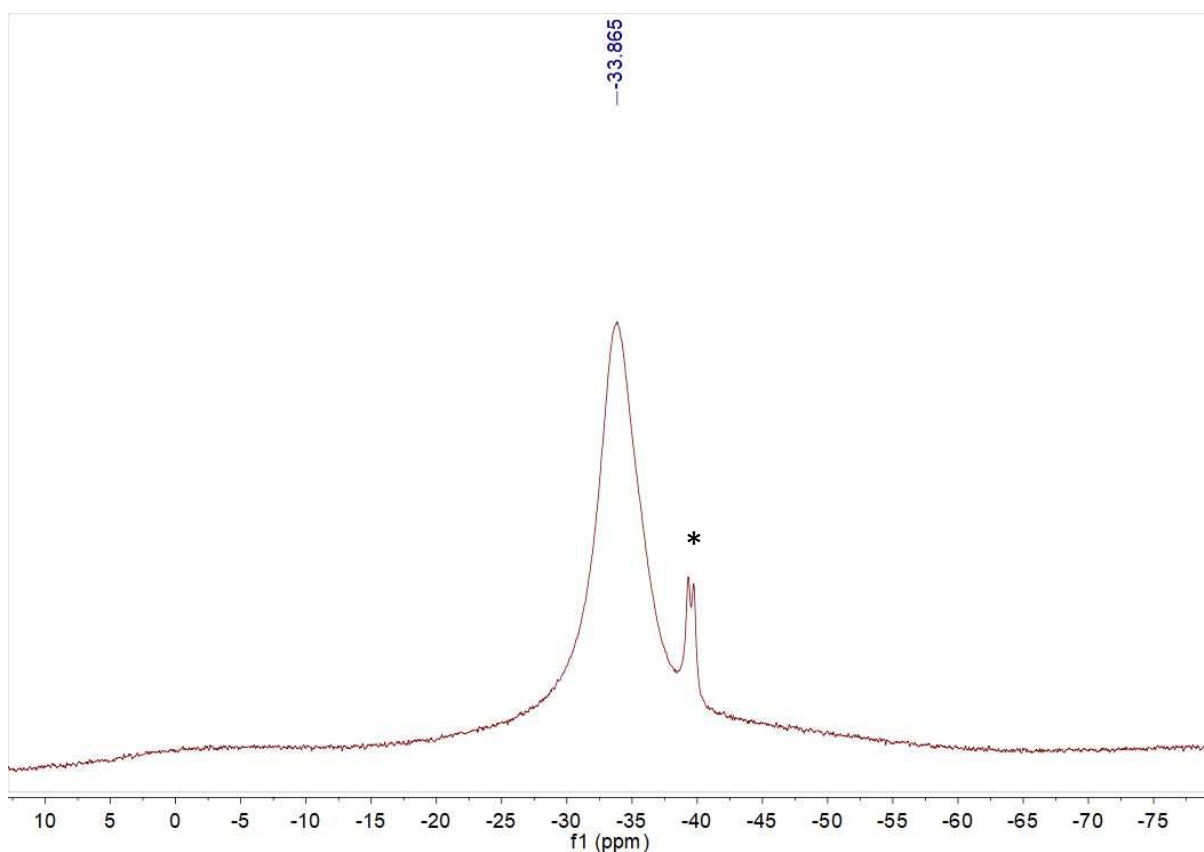
$^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of **3Li** in d_8 -THF.



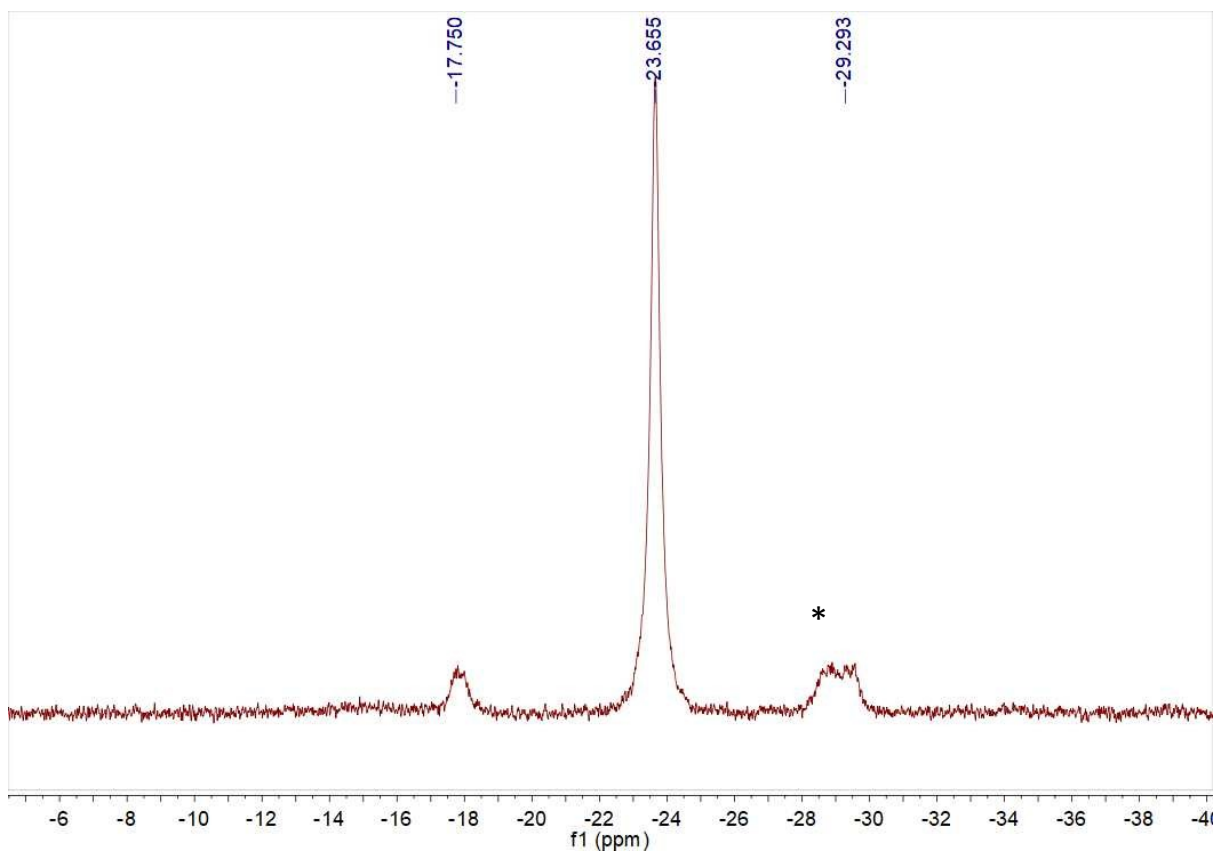
$^1\text{H}\{^{11}\text{B}\}$ NMR spectrum of **3Na** in d_8 -toluene.



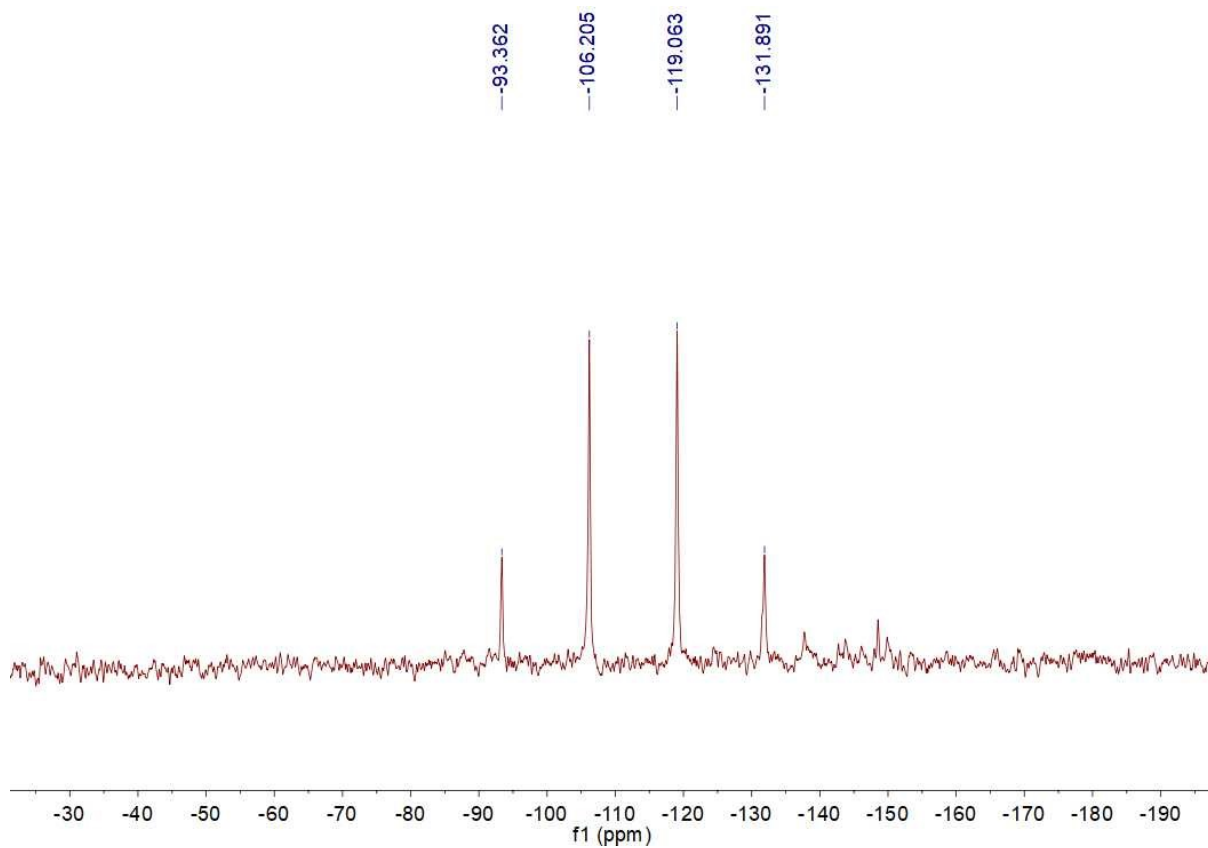
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3Na** in d_8 -toluene.



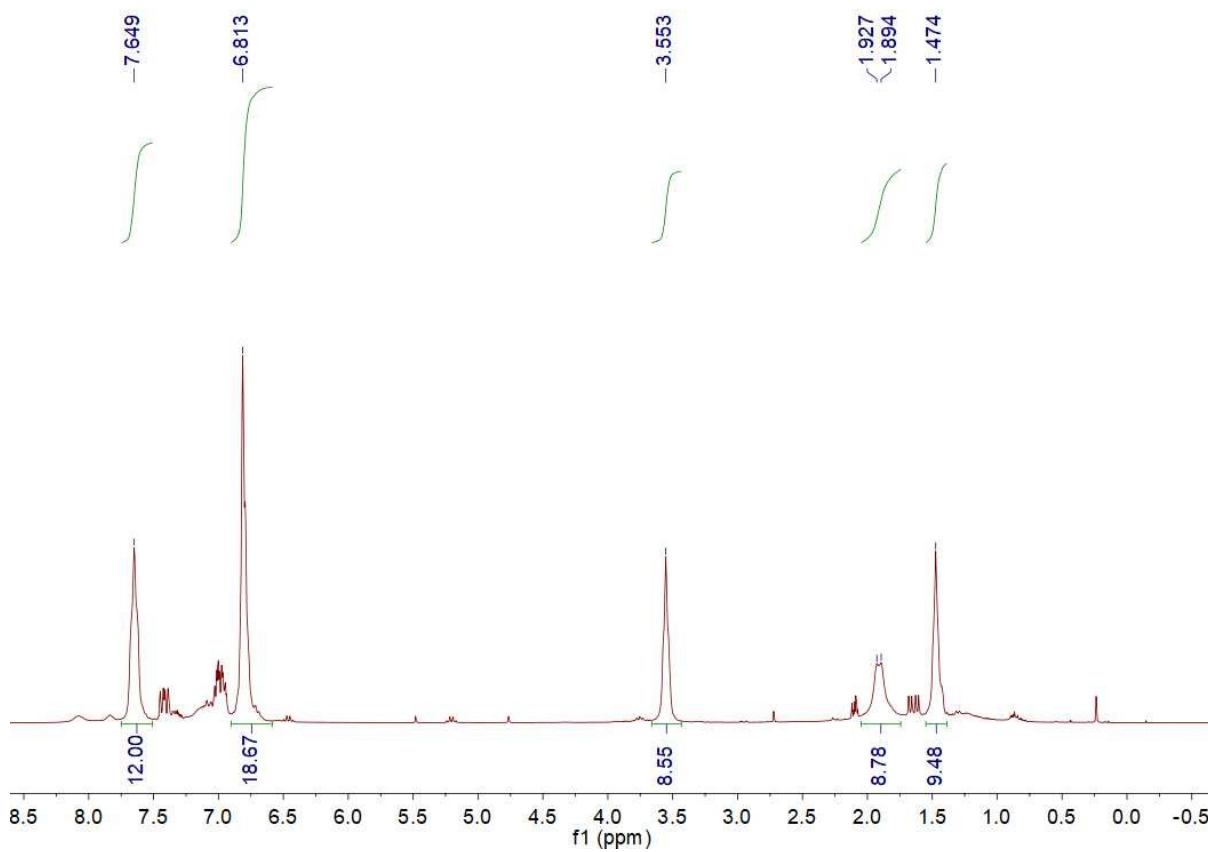
$^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **3Na** in d_8 -toluene toluene (*free phosphine-borane **3H** due to partial hydrolysis during sample preparation).



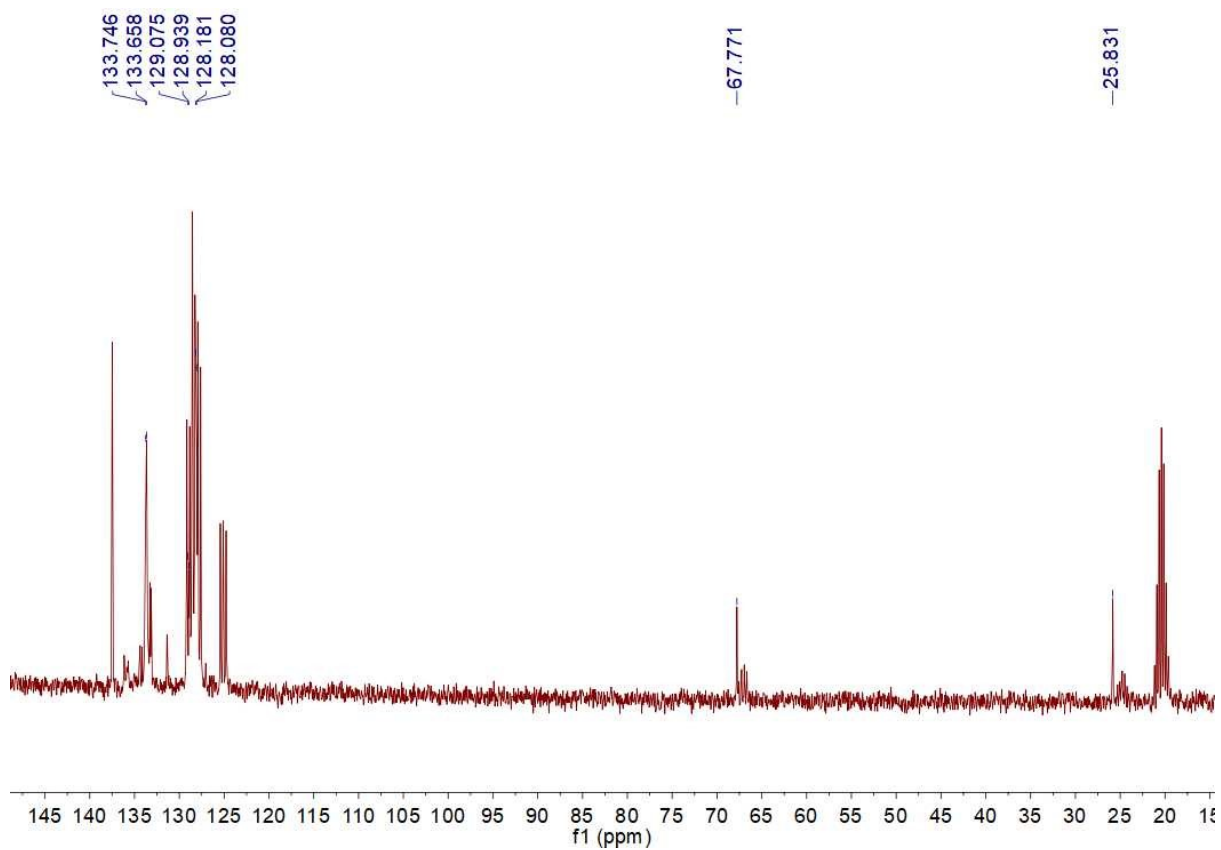
$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3Na** in d_8 -toluene toluene (*free phosphine-borane **3H** due to partial hydrolysis during sample preparation).



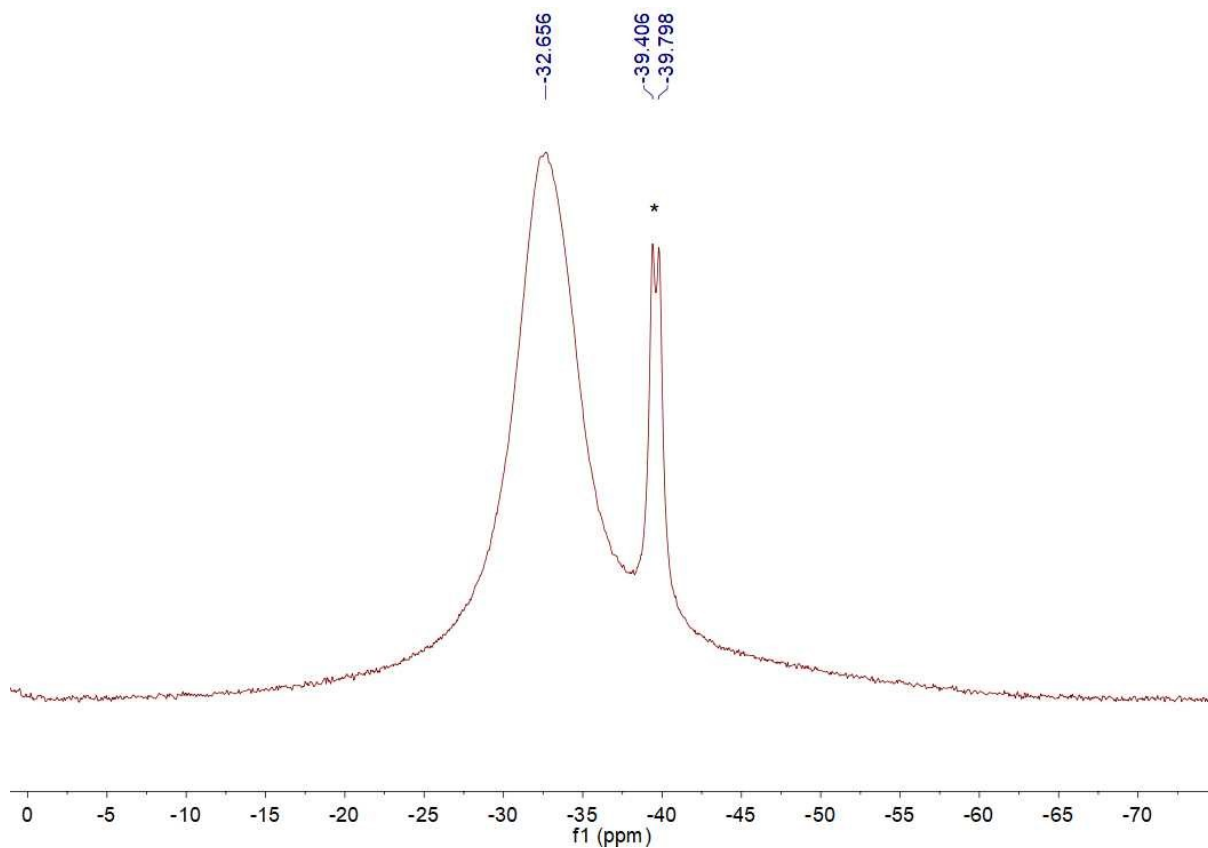
$^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of **3Na** in d_8 -toluene.



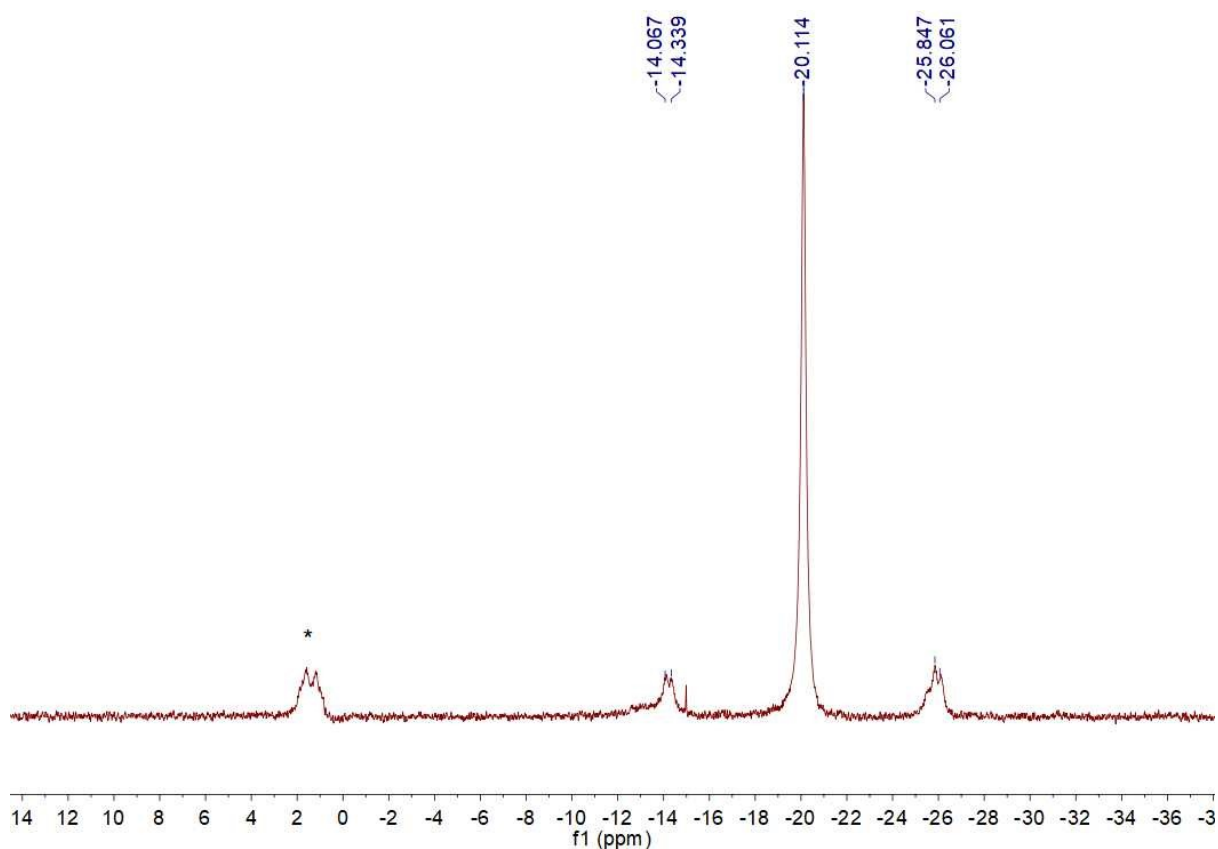
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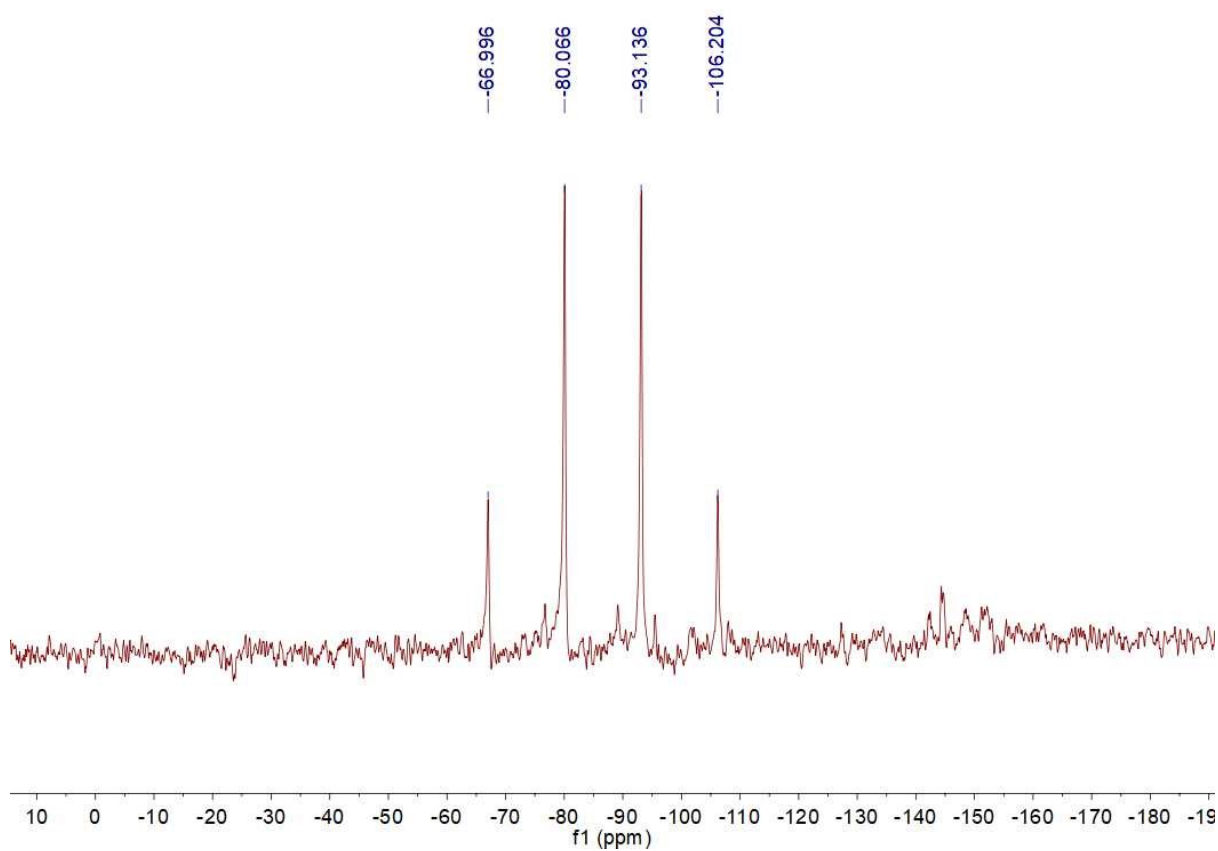
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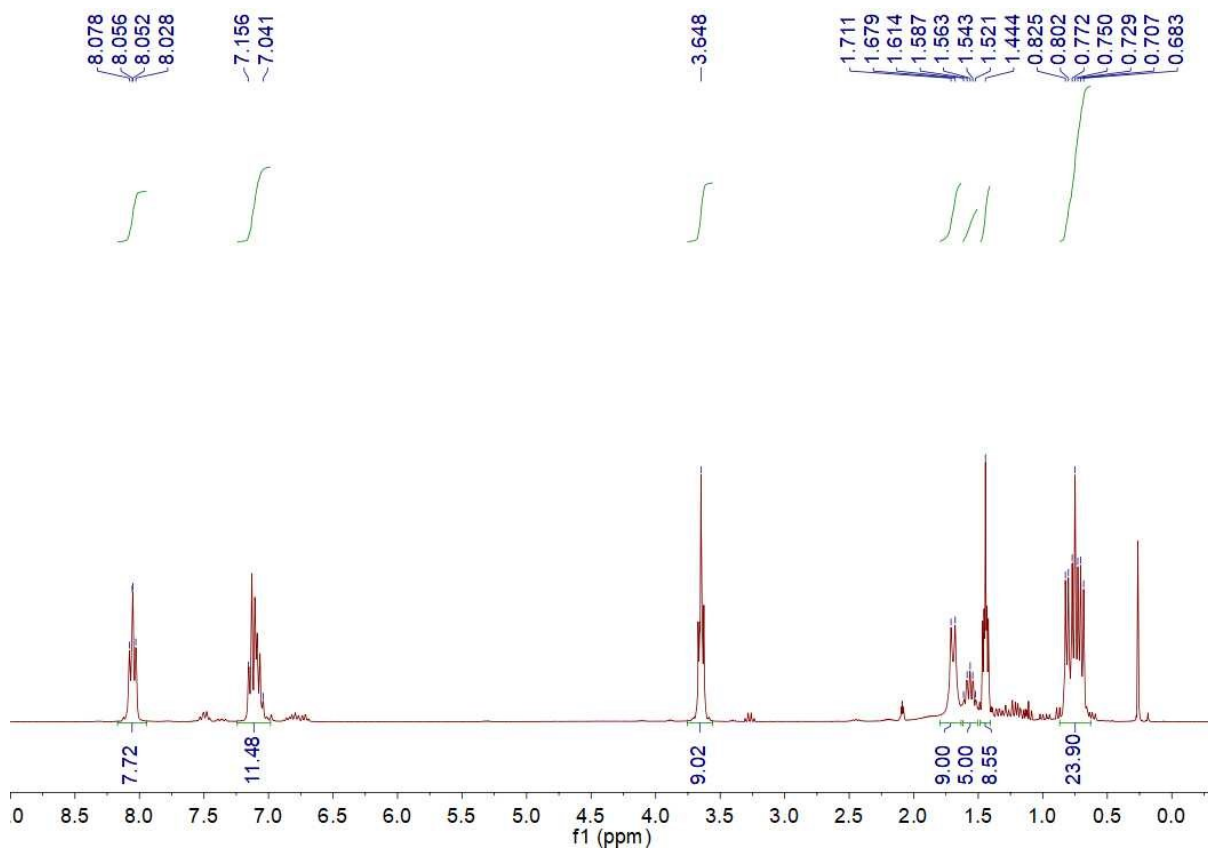
$^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **3K** in d_8 -toluene (*free phosphine-borane **3H** due to partial hydrolysis during sample preparation).



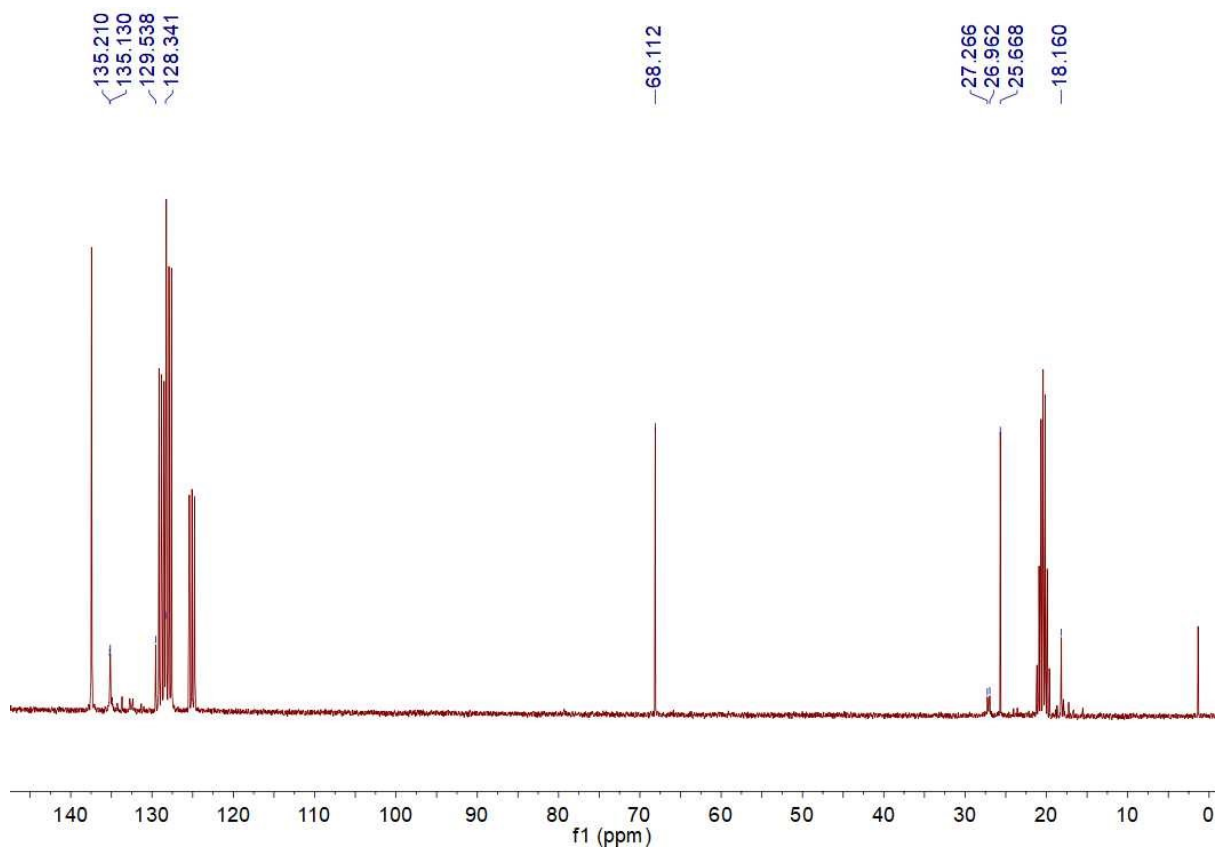
$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3K** in d_8 -toluene (*free phosphine-borane **3H** due to partial hydrolysis during sample preparation).



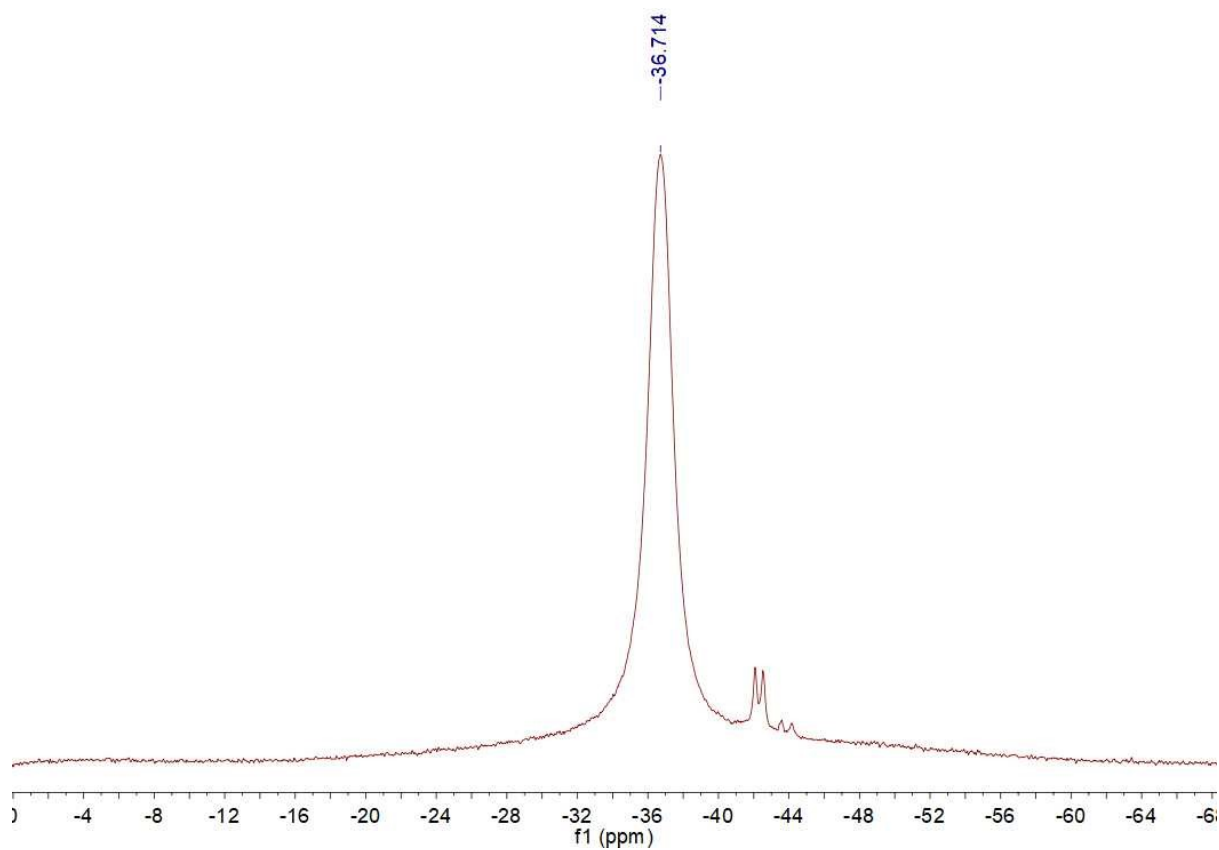
$^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of **3K** in d_8 -toluene.



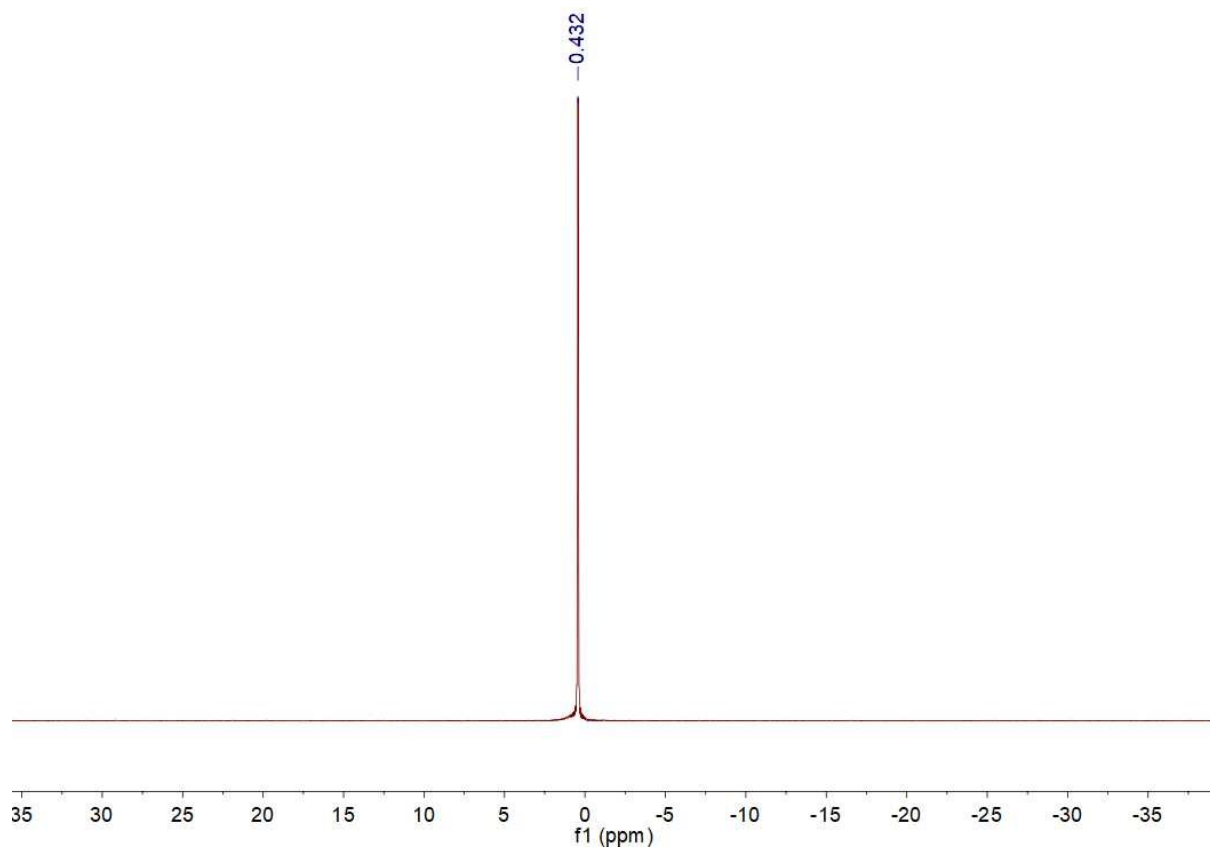
$^1\text{H}\{^{11}\text{B}\}$ NMR spectrum of **4Li** in d_8 -toluene.



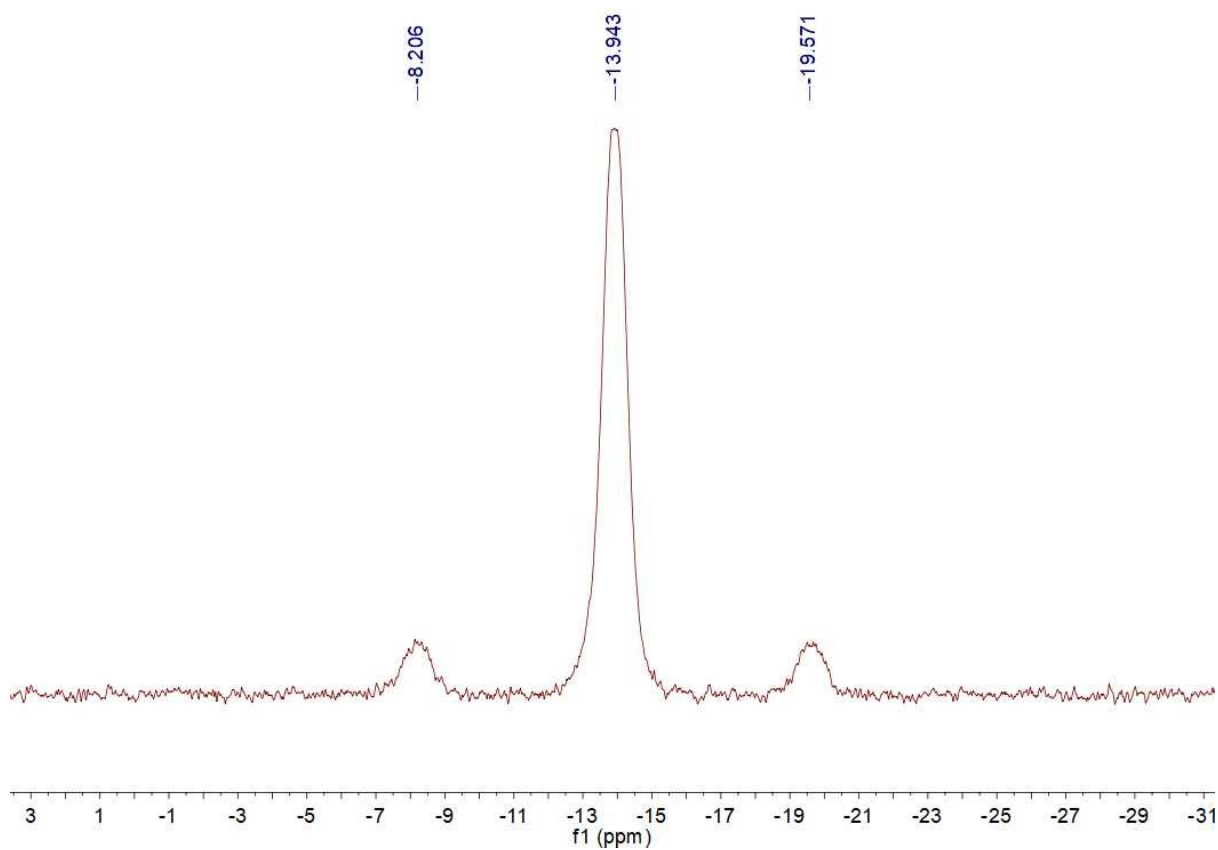
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4Li** in d_8 -toluene.



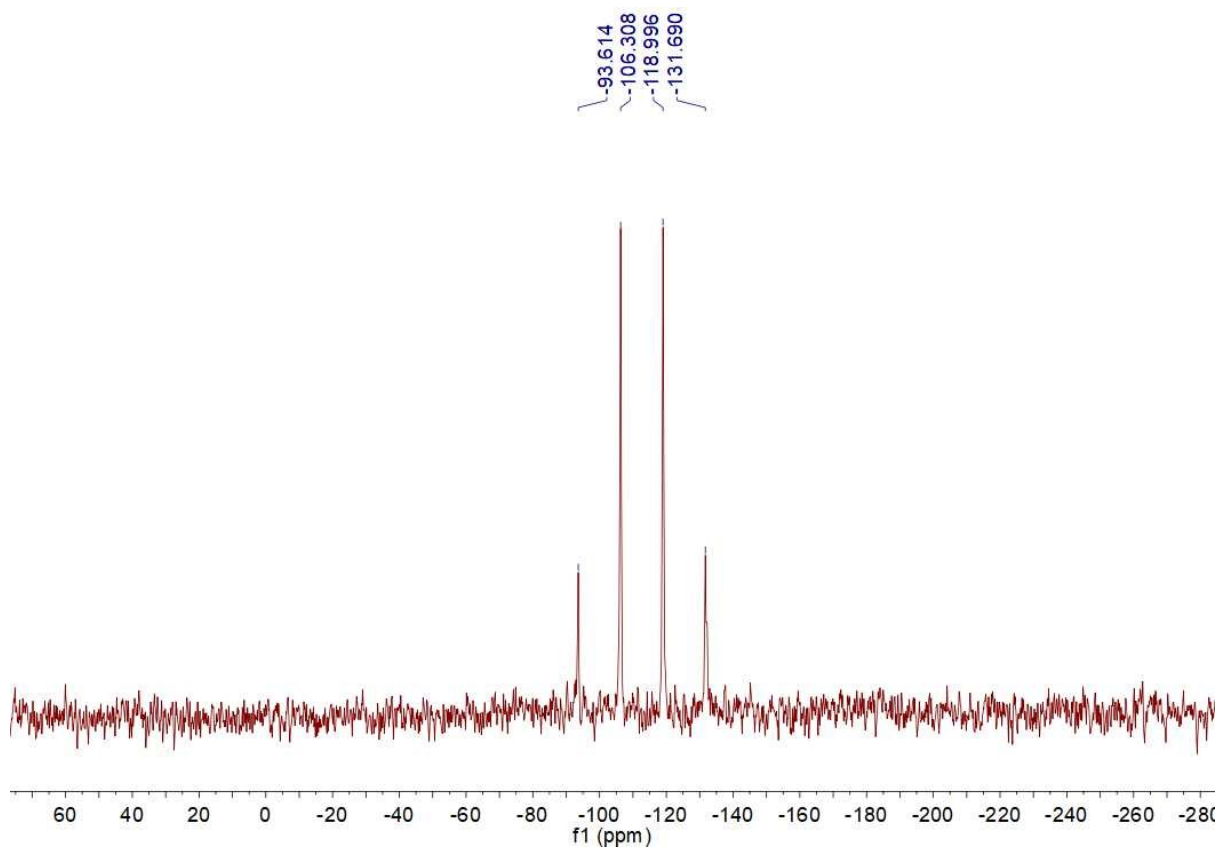
$^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **4Li** in d_8 -toluene.



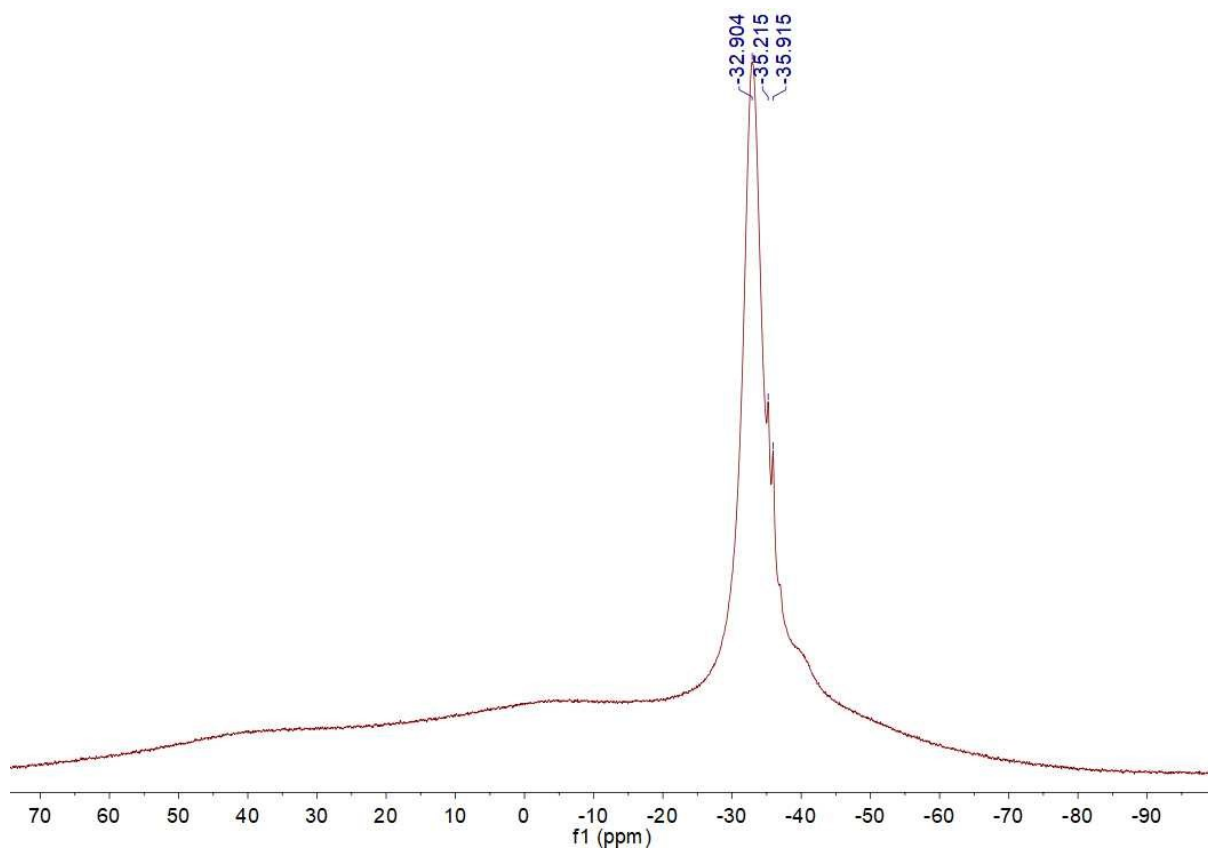
$^7\text{Li}\{^1\text{H}\}$ NMR spectrum of **4Li** in d_8 -toluene.



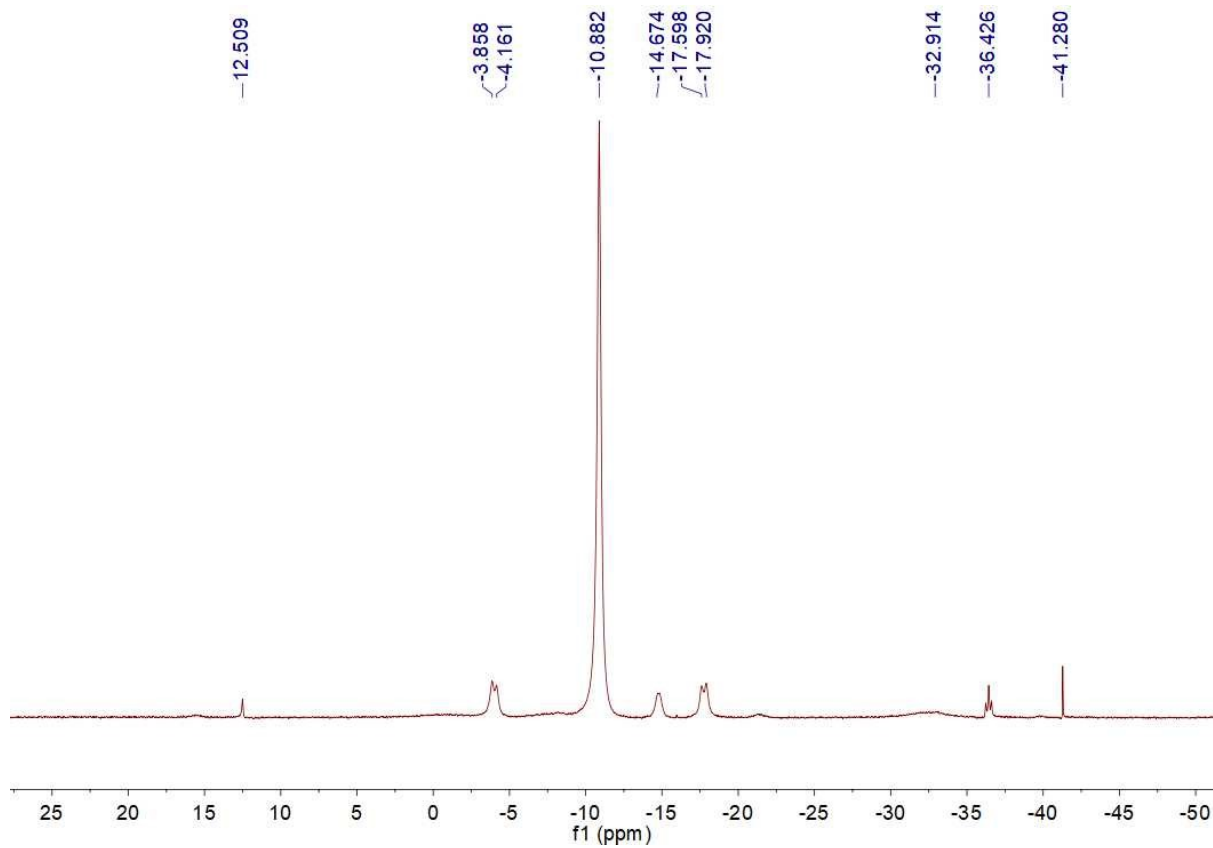
³¹P{¹H} NMR spectrum of **4Li** in *d*₈-toluene.



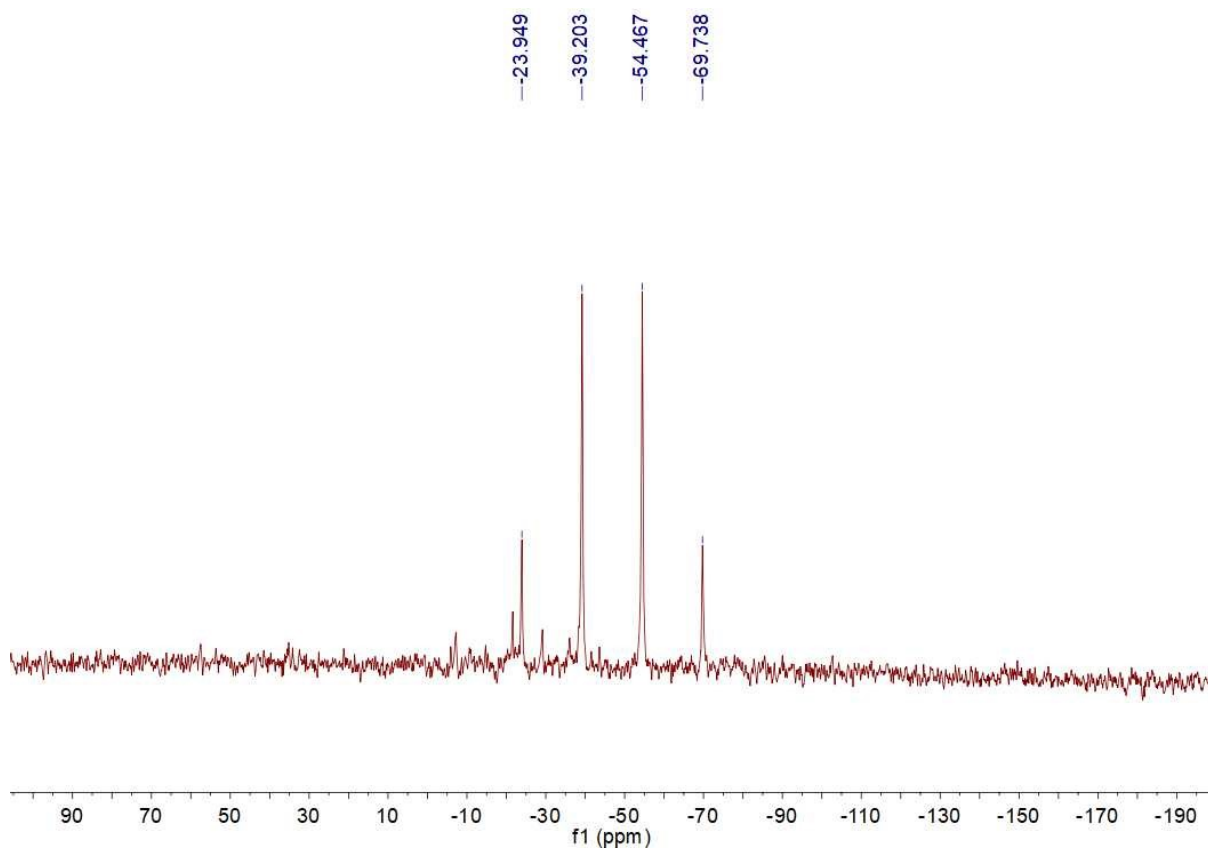
¹¹⁹Sn{¹H} NMR spectrum of **4Li** in *d*₈-toluene.



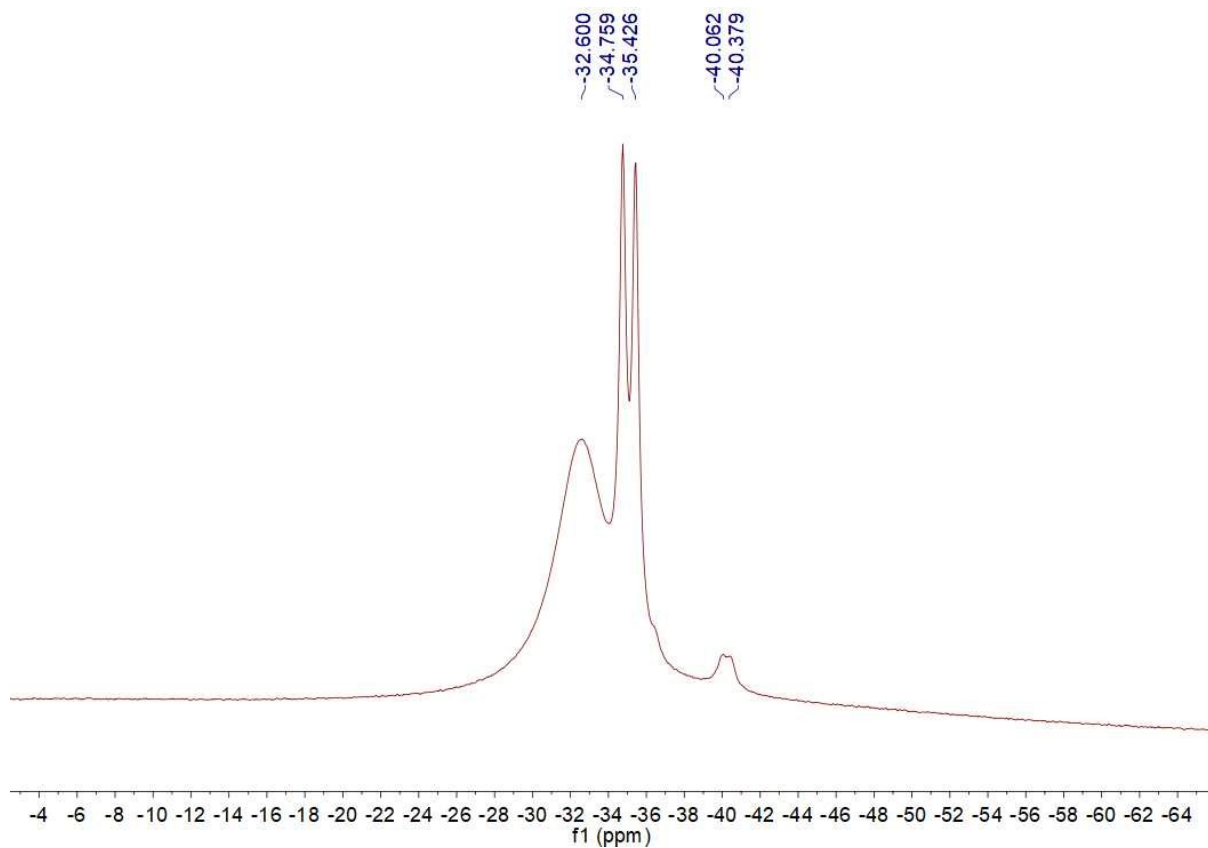
$^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of a solution of **3Li** in THF, immediately after preparation.



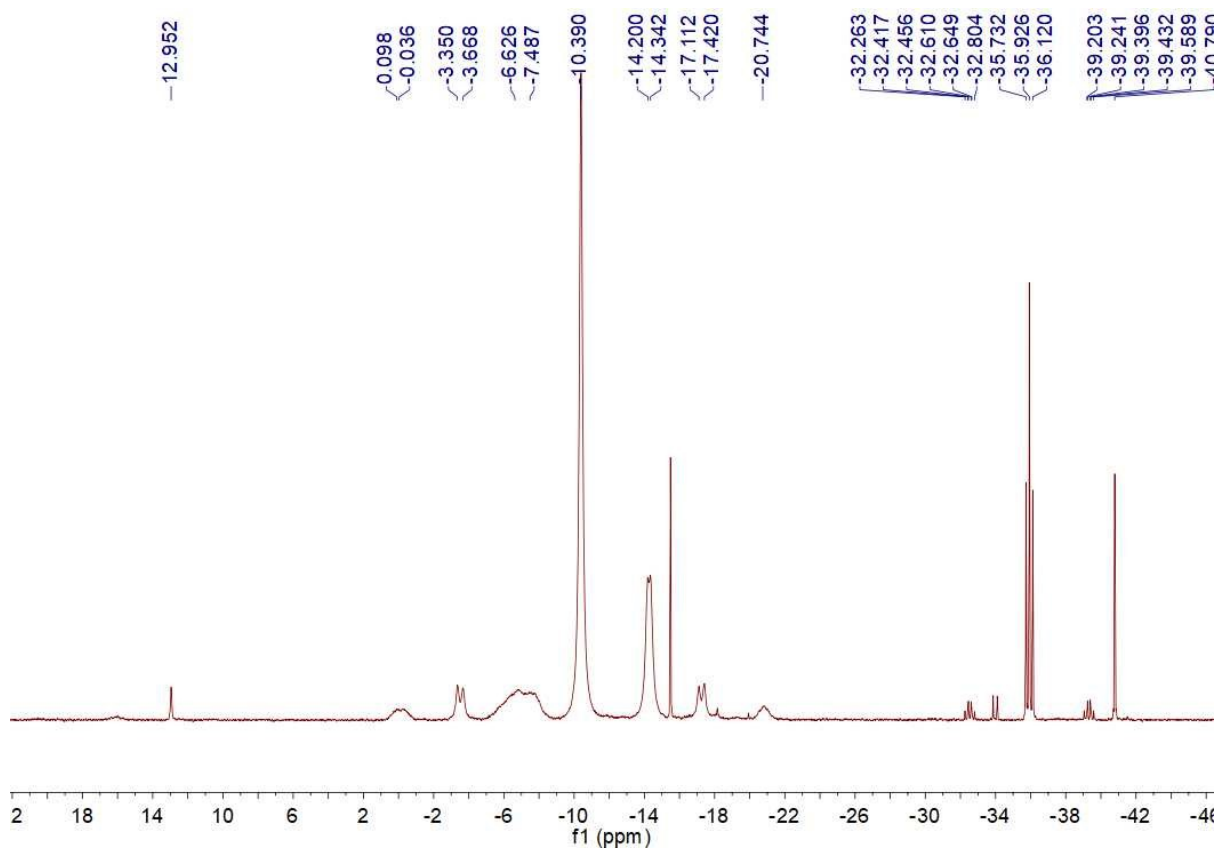
$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a solution of **3Li** in THF, immediately after preparation.



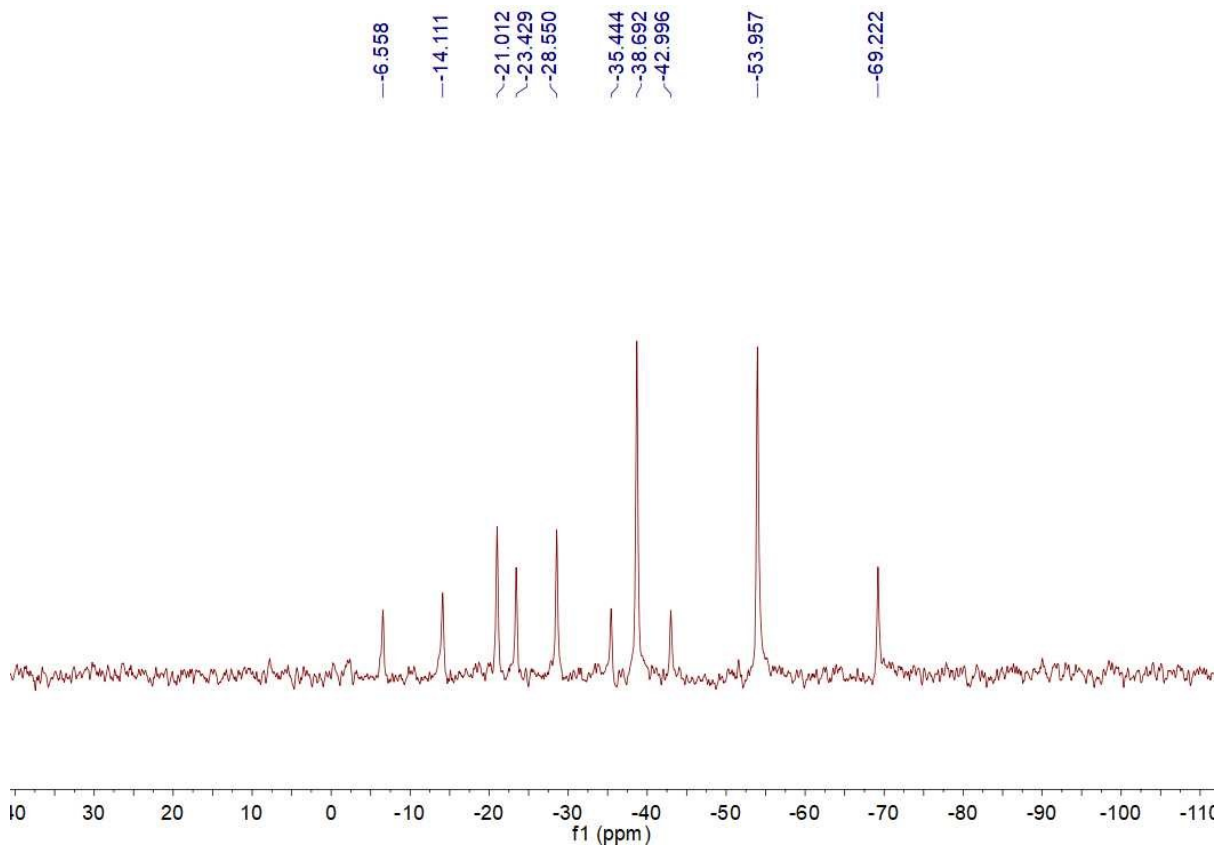
$^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of a solution of **3Li** in THF, immediately after preparation.



$^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of a solution of **3Li** in THF, after 84 hours.



$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a solution of **3Li** in THF, after 84 hours.



$^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of a solution of **3Li** in THF, after 84 h.

Table S1. Crystallographic data for 2Li, 2Na, 2K, 3Li, 3Na, 3K, and 4Li.

Compound	2Li	2Na	2K	3Li	3Na	3K	4Li
formula	C ₃₀ H ₇₅ B ₃ LiO ₃ P ₃ Sn	C ₂₂ H ₆₁ B ₃ NaOP ₃ Sn	C ₂₂ H ₆₁ B ₃ KOP ₃ Sn	C ₄₀ H ₄₇ B ₃ LiOP ₃ Sn	C ₄₄ H ₅₇ B ₃ NaO ₂ P ₃ Sn	C ₈₈ H ₁₁₄ B ₆ K ₂ O ₄ P ₆ Sn ₂	C ₄₃ H ₇₇ B ₃ LiO ₄ P ₃ Sn
<i>M_w</i>	734.87	608.72	624.83	794.74	884.91	1802.05	909.01
cryst. size (mm)	0.25 × 0.21 × 0.08	0.31 × 0.23 × 0.2	0.32 × 0.14 × 0.08	0.2 × 0.16 × 0.11	0.35 × 0.15 × 0.13	0.33 × 0.16 × 0.05	0.46 × 0.16 × 0.06
cryst. syst.	monoclinic	monoclinic	monoclinic	orthorhombic	triclinic	triclinic	orthorhombic
space group	<i>P2₁/n</i>	<i>P2₁/n</i>	<i>P2₁/n</i>	<i>P2₁2₁2₁</i>	<i>P-1</i>	<i>P-1</i>	<i>Pbca</i>
<i>a</i> (Å)	12.40488(9)	10.9480(3)	11.09083(13)	12.0937(3)	12.1003(2)	12.5263(4)	17.1453(3)
<i>b</i> (Å)	20.31668(13)	15.5585(3)	15.64326(17)	17.3507(5)	19.4551(4)	12.8410(6)	19.0113(2)
<i>c</i> (Å)	17.70719(13)	20.1127(5)	20.3678(3)	19.0102(6)	21.1123(4)	16.3428(5)	30.2806(5)
<i>α</i> (deg)					113.1030(19)	83.991(3)	
<i>β</i> (deg)	109.9907(8)	94.156(2)	95.5136(10)		93.1405(17)	75.367(3)	
<i>γ</i> (deg)					91.4023(16)	62.619(4)	
<i>V</i> (Å ³)	4193.79(5)	3416.88(14)	3517.40(7)	3988.99(19)	4558.93(17)	2258.33(16)	9870.1(3)
<i>Z</i>	4	4	4	4	4	1	
<i>μ</i> (mm ⁻¹)	6.107	0.913	0.993	0.791	0.709	0.799	0.651

reflns. measd.	30391	28063	112187	21477	73117	36224	151804
unique reflns.	7442	7728	9067	7674	20675	10194	12235
R_{int}	0.045	0.046	0.046	0.047	0.045	0.047	0.059
refined params.	421	321	321	484	1176	563	664
R (on F , $F^2 > 2\sigma$)	0.027	0.035	0.024	0.037	0.037	0.040	0.040
R_w (on F^2 , all data)	0.066	0.078	0.046	0.072	0.080	0.081	0.094
goodness of fit	1.036	1.078	1.066	1.043	1.100	1.025	1.011
max, min electron density (e \AA^{-3})	0.42,-0.37	0.77,-0.45	0.39,-0.27	0.76,-0.43	0.70,-0.44	0.48,-0.49	0.96,-0.58

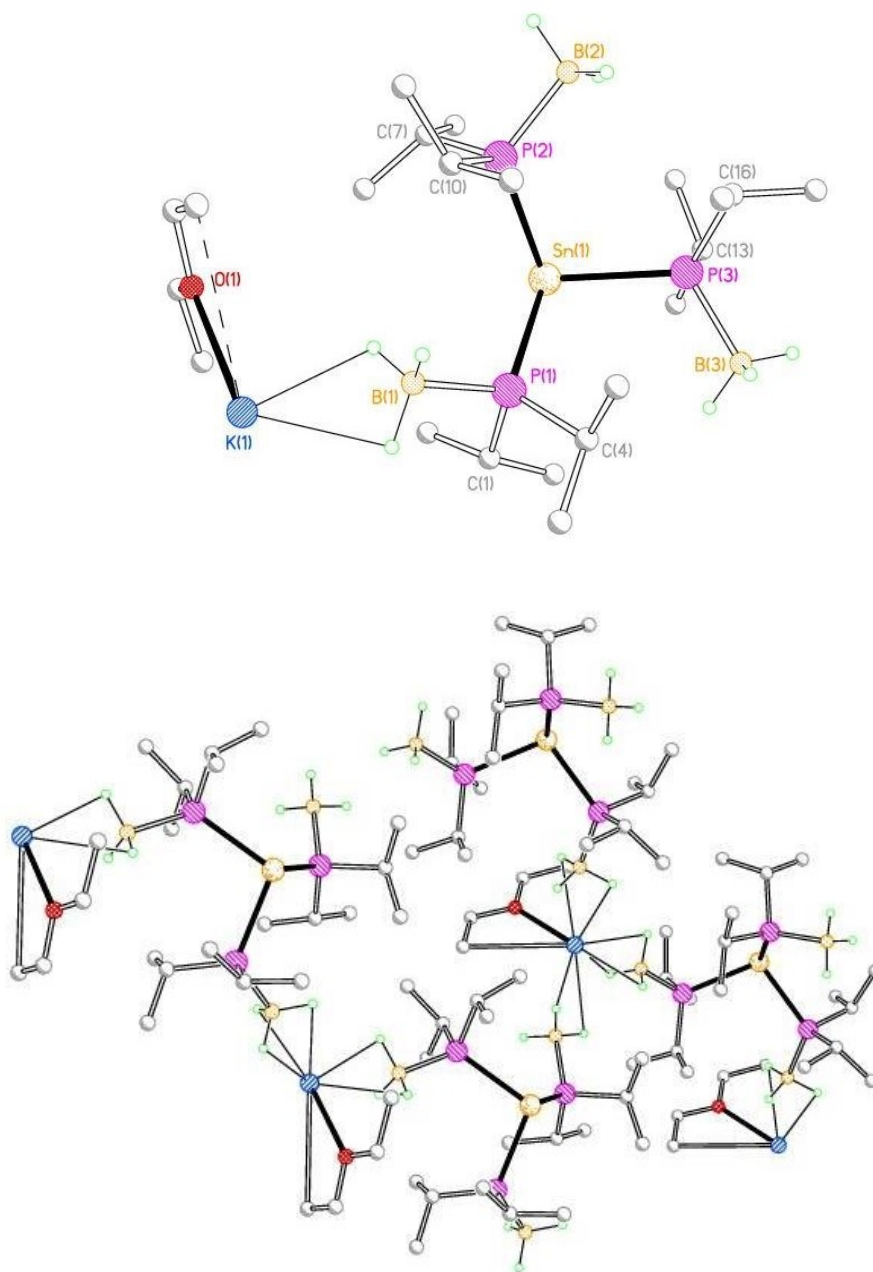


Figure S1. Polymeric structure of **2K**. Selected bond lengths (Å) and angles (°): Sn(1)-P(1) 2.6341(4), Sn(1)-P(2) 2.6312(4), Sn(1)-P(3) 2.6352(4), P(1)-B(1) 1.9486(18), P(2)-B(2) 1.9454(18), P(3)-B(3) 1.945(2), K(1)···B(1) 3.0125(18), K(1)···B(2A) 3.0104(18), K(1)···B(3B) 3.0617(19), K(1C)···B(2) 3.0104(18), K(1D)···B(2) 3.0618(19), K(1)-O(1) 2.6999(11), P(1)-Sn(1)-P(2) 103.646(12), P(1)-Sn(1)-P(3) 102.981(12), P(2)-Sn(1)-P(3) 103.026(12).

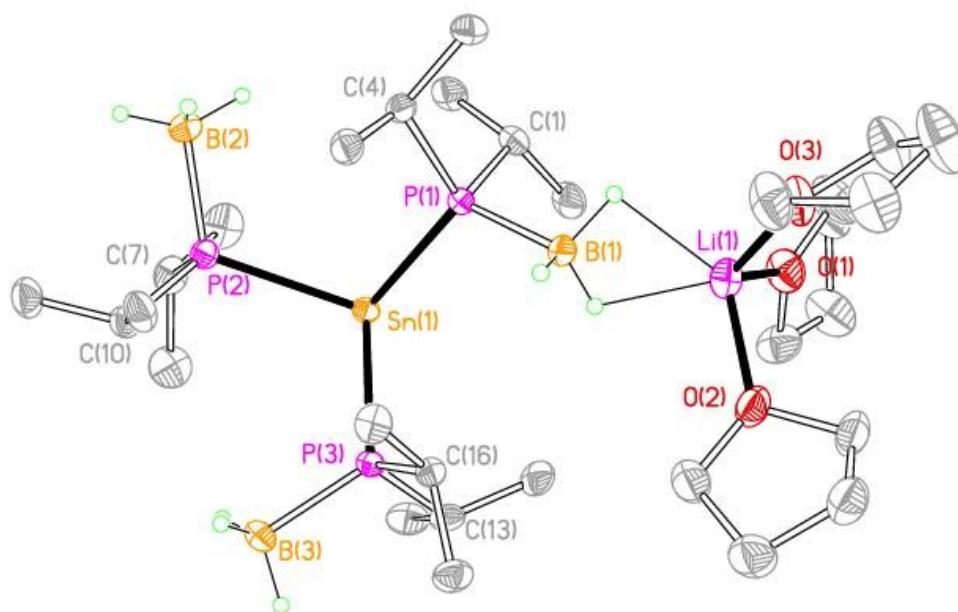


Figure S2. Asymmetric unit of **2Li** with 40% thermal ellipsoids and with minor disorder and C-bound H atoms omitted for clarity.

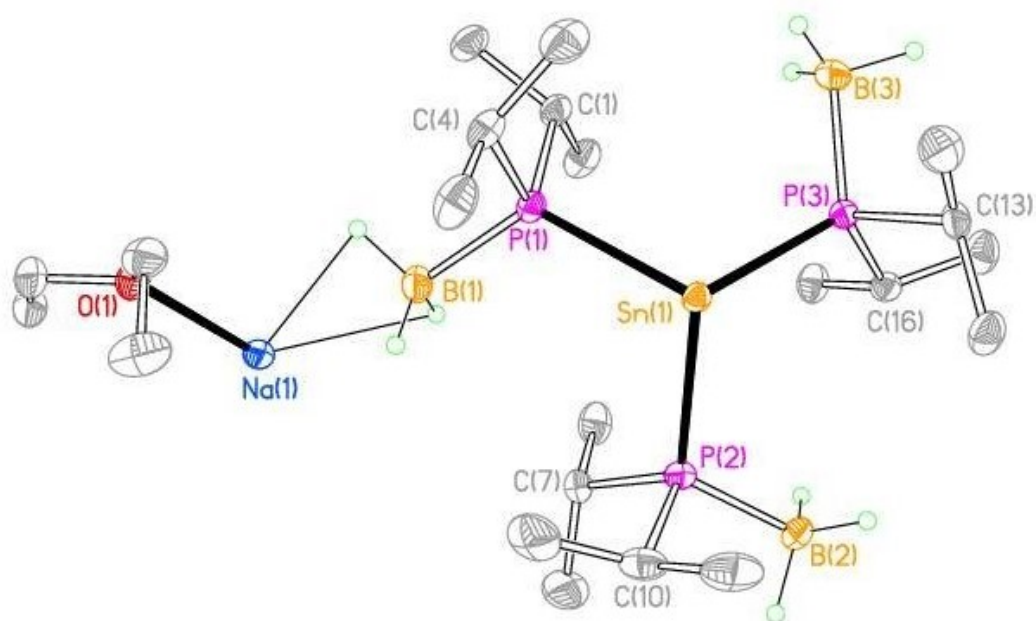


Figure S3. Asymmetric unit of **2Na** with 40% thermal ellipsoids and with C-bound H atoms omitted for clarity.

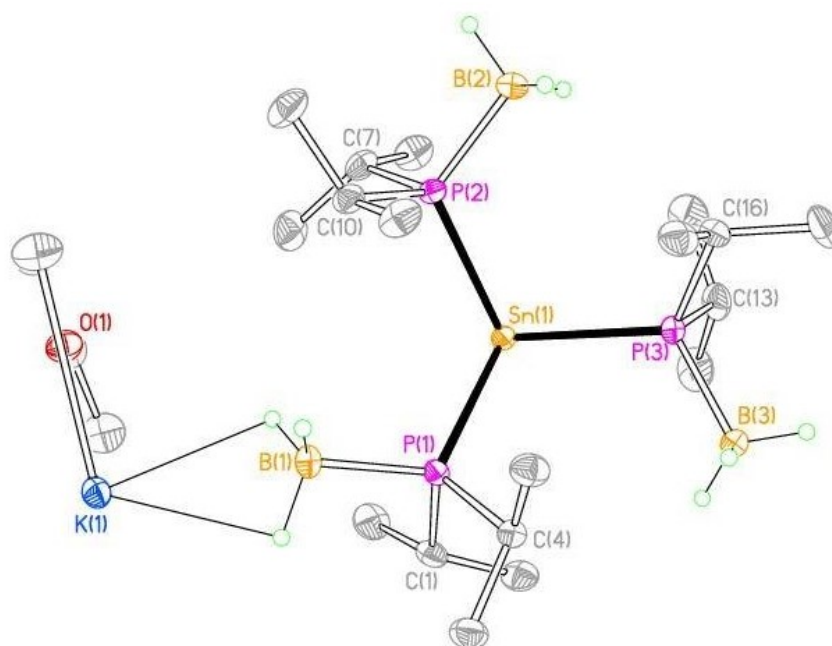


Figure S4. Asymmetric unit of **2K** with 40% thermal ellipsoids and with C-bound H atoms omitted for clarity.

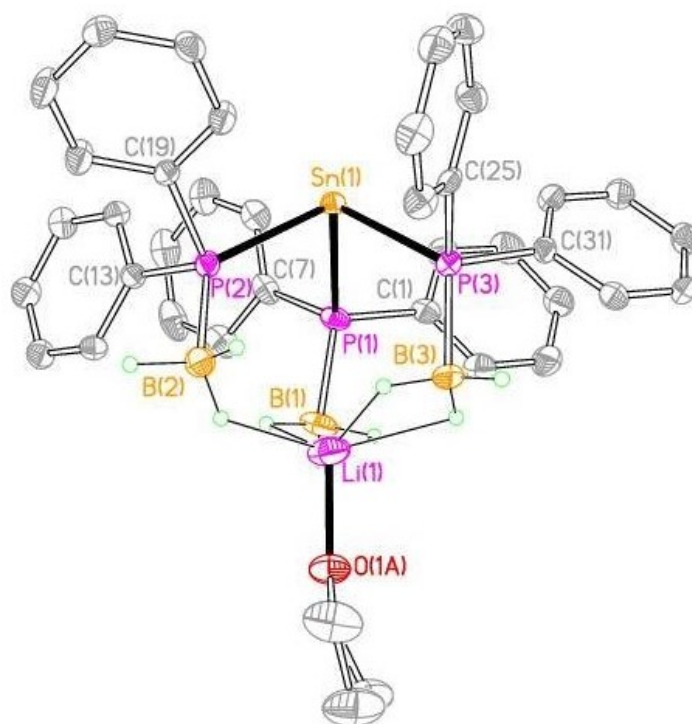


Figure S5. Asymmetric unit of **3Li** with 40% thermal ellipsoids and with minor disorder and C-bound H atoms omitted for clarity.

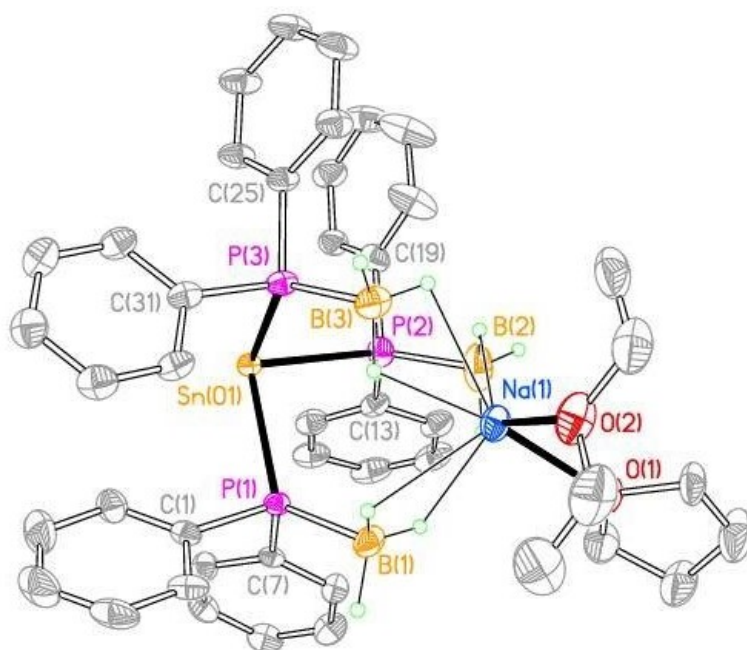


Figure S6. One of the two independent molecules in the asymmetric unit of **3Na** with 40% thermal ellipsoids and with minor disorder and C-bound H atoms omitted for clarity.

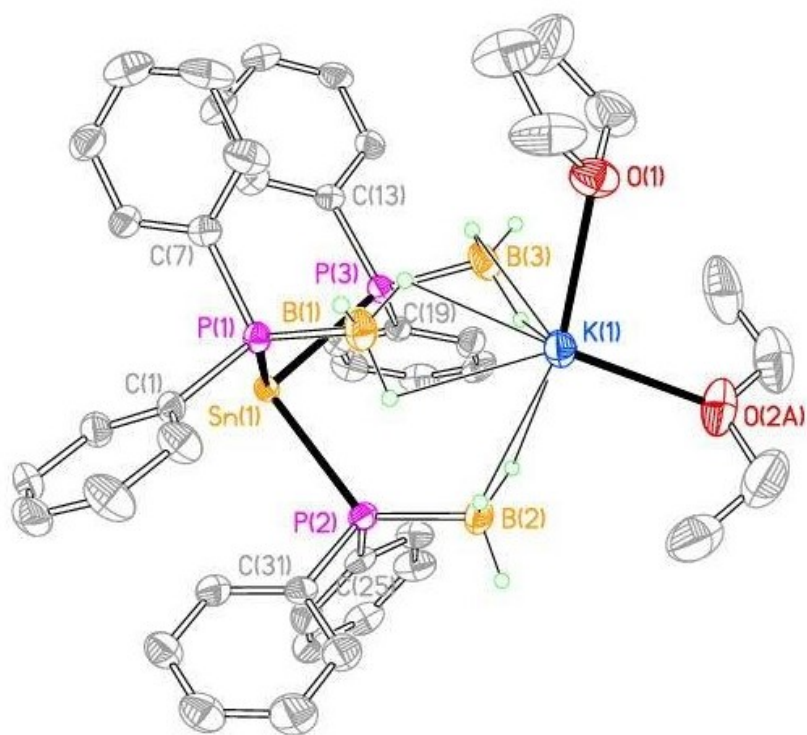


Figure S7. Asymmetric unit of **3K** with 40% thermal ellipsoids and with minor disorder and C-bound H atoms omitted for clarity.

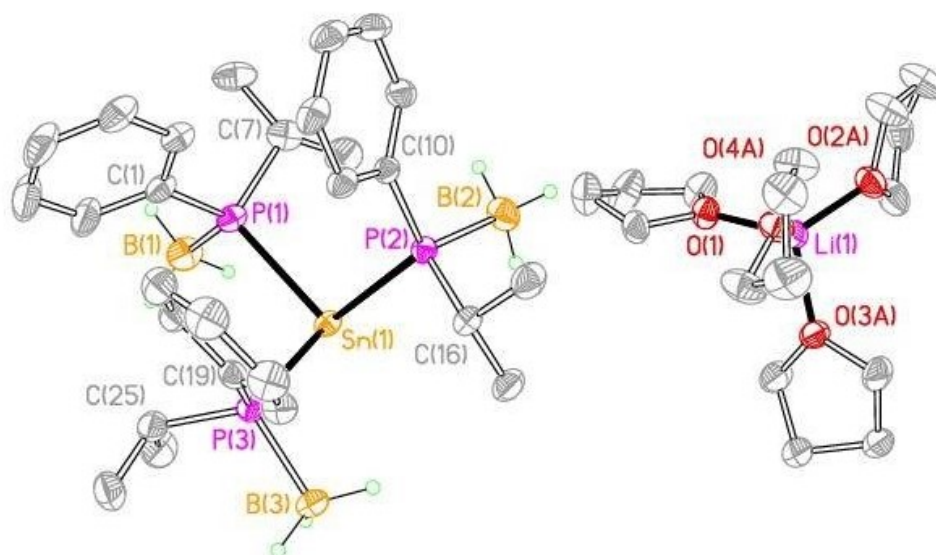


Figure S8. Asymmetric unit of **4Li** with 40% thermal ellipsoids and with minor disorder and C-bound H atoms omitted for clarity.

