

Supplementary Information

## Expanding the Series of Alkali Metal Plumbolyl Complexes to Na and K

Roberto M. Diaz-Rodriguez, Alexandros A. Kitos, and Muralee Murugesu\*

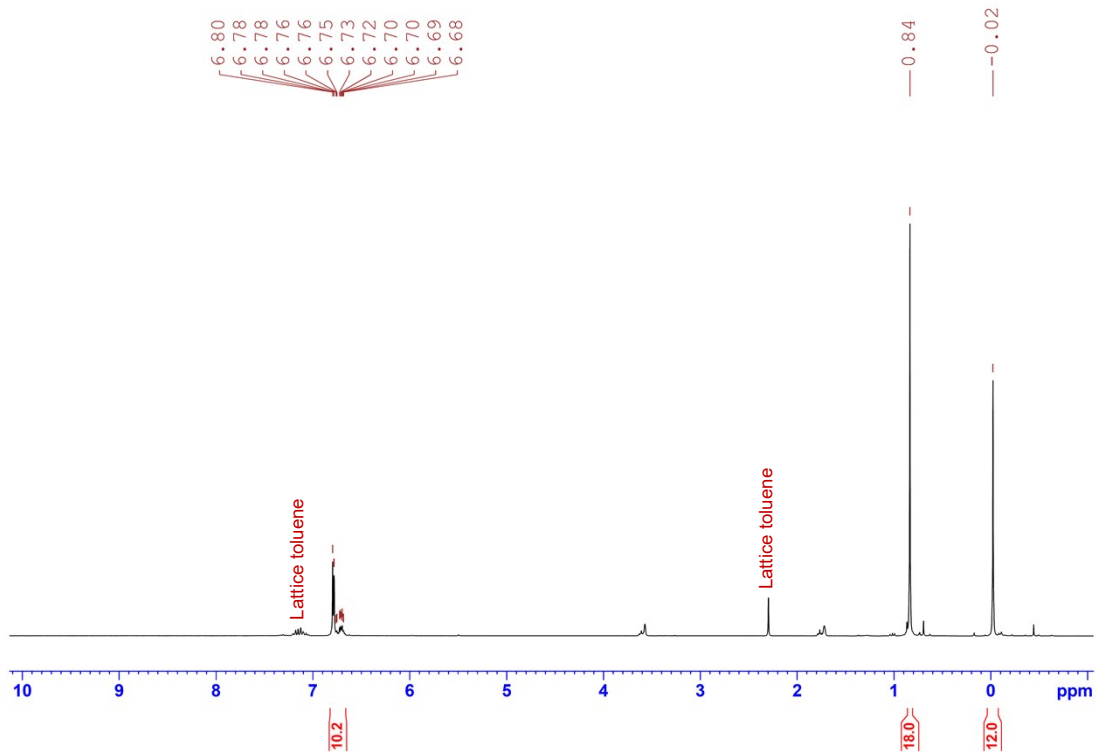
R. M. Diaz-Rodriguez, A. A. Kitos, Prof. Dr. M. Murugesu\*  
Department of Chemistry and Biomolecular Sciences  
University of Ottawa  
Ottawa, Ontario K1N 6N5 (Canada)  
E-mail: M.Murugesu@uottawa.ca

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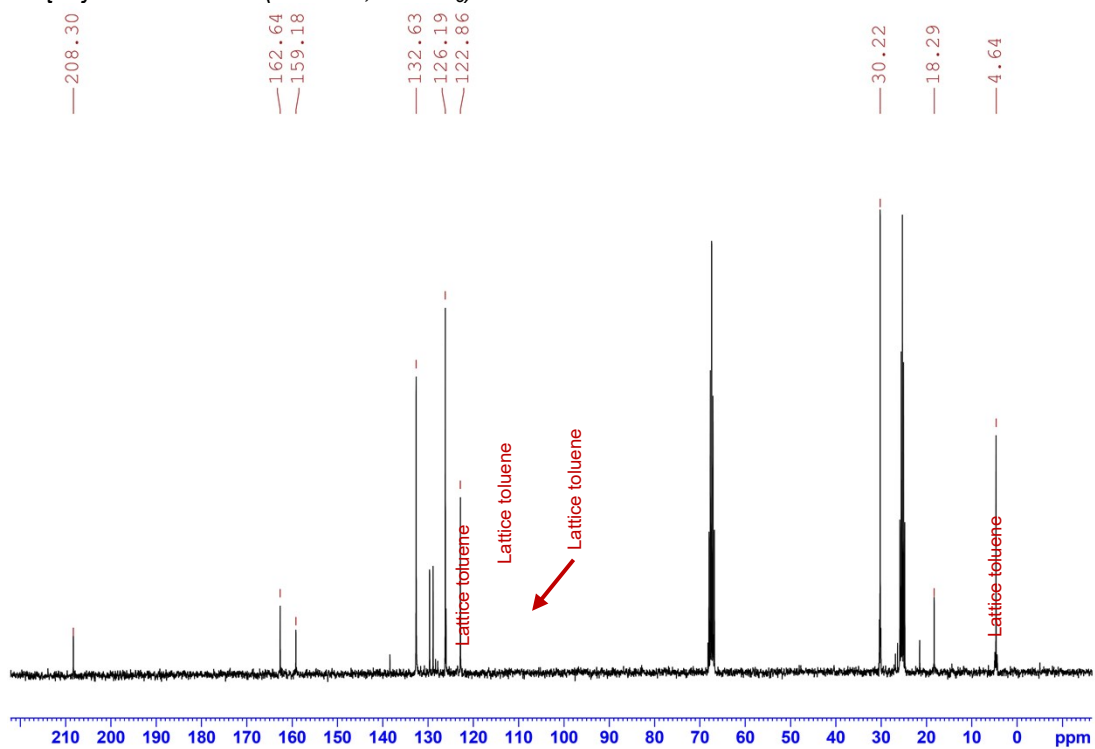
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## Nuclear Magnetic Resonance Spectra

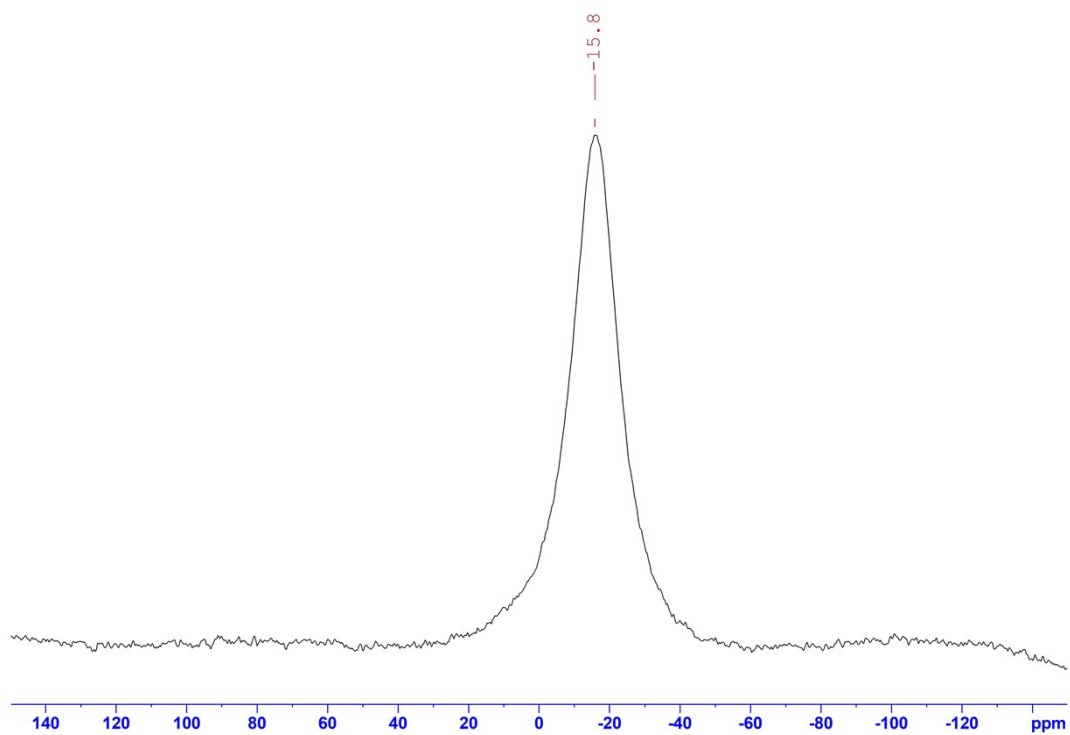
$[\text{Na}_2(\text{Pb}^{\text{TBS,Ph}})(\text{THF})_2(\text{toluene})_{0.5}]_n$  (**4a**)  
 $^1\text{H}$  NMR (300 MHz,  $\text{THF-d}_8$ )



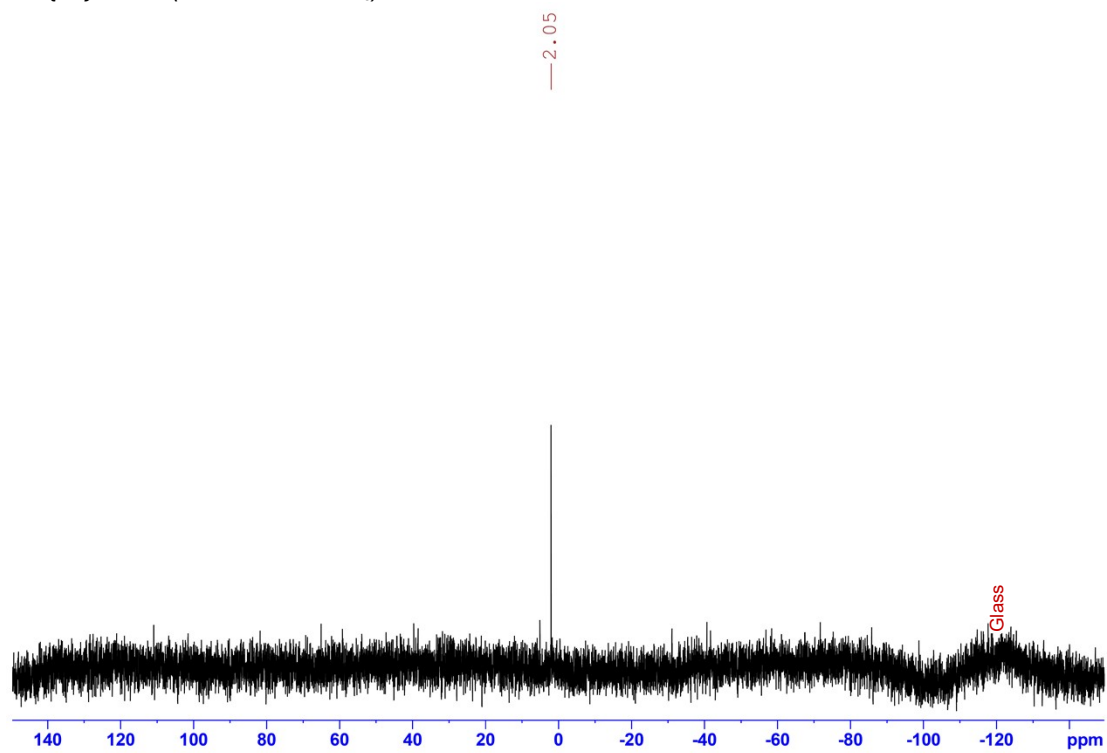
$^{13}\text{C}\{^1\text{H}\}$  UDEFT NMR (75 MHz,  $\text{THF-d}_8$ )



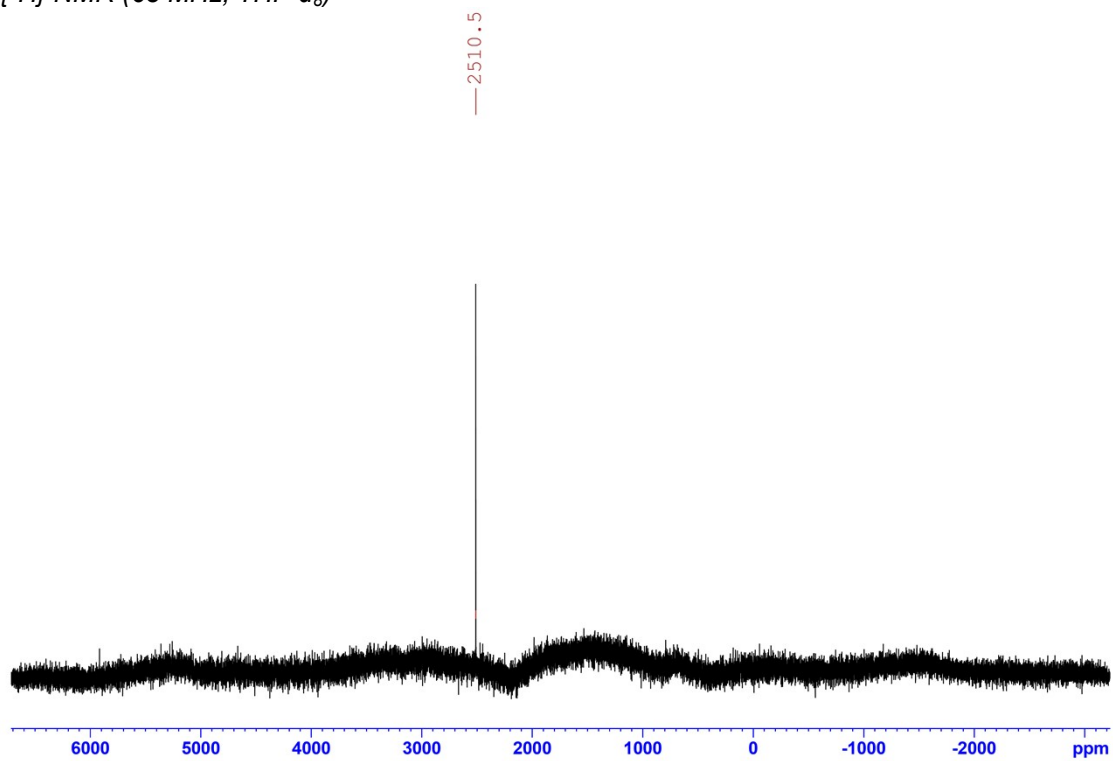
$^{23}\text{Na}$  NMR (79 MHz, THF- $d_8$ ), 45 Hz line broadening



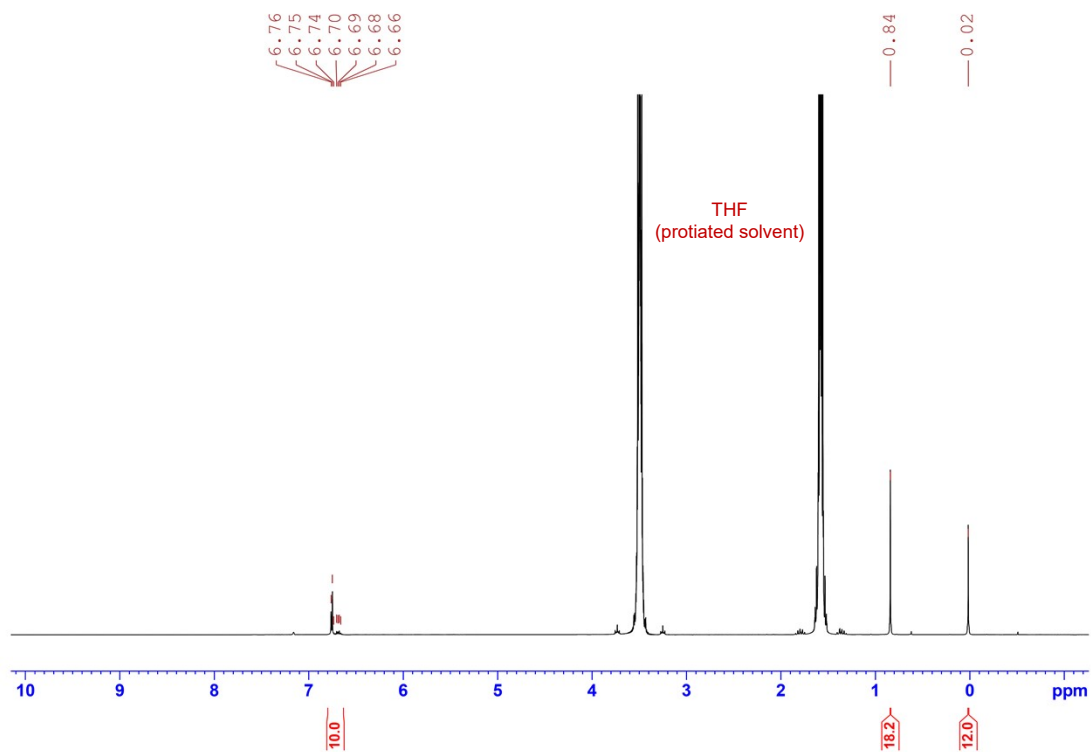
$^{29}\text{Si}\{^1\text{H}\}$  NMR (60 MHz, THF- $d_8$ )



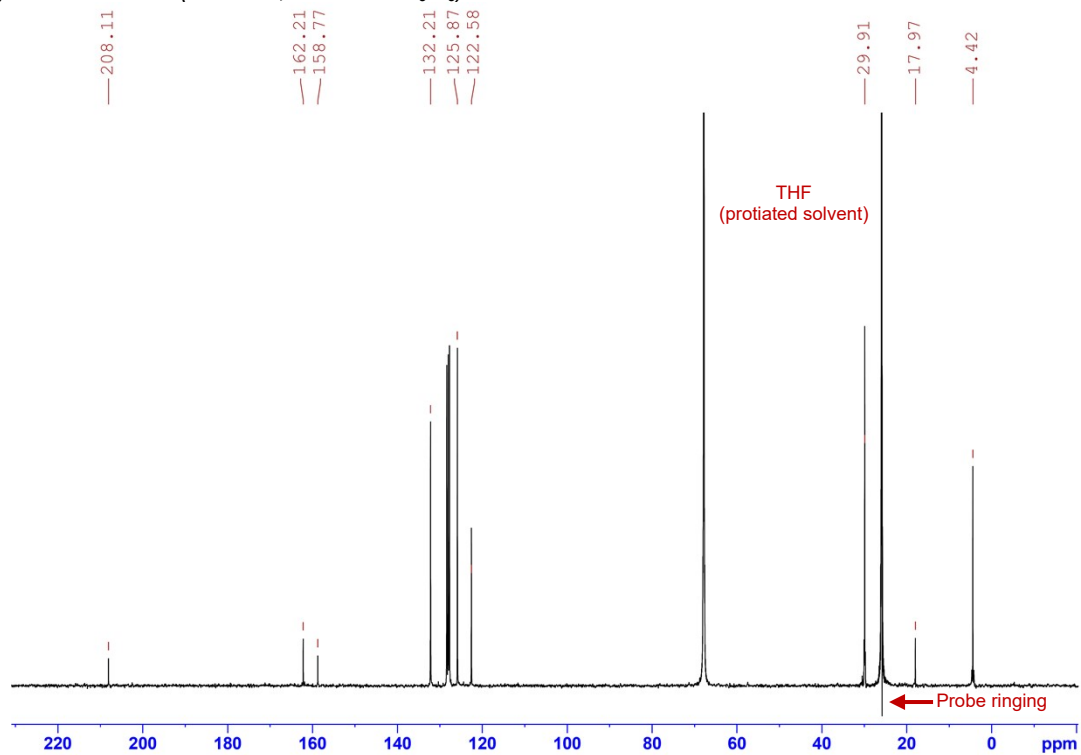
$^{207}\text{Pb}\{^1\text{H}\}$  NMR (63 MHz, THF- $d_8$ )



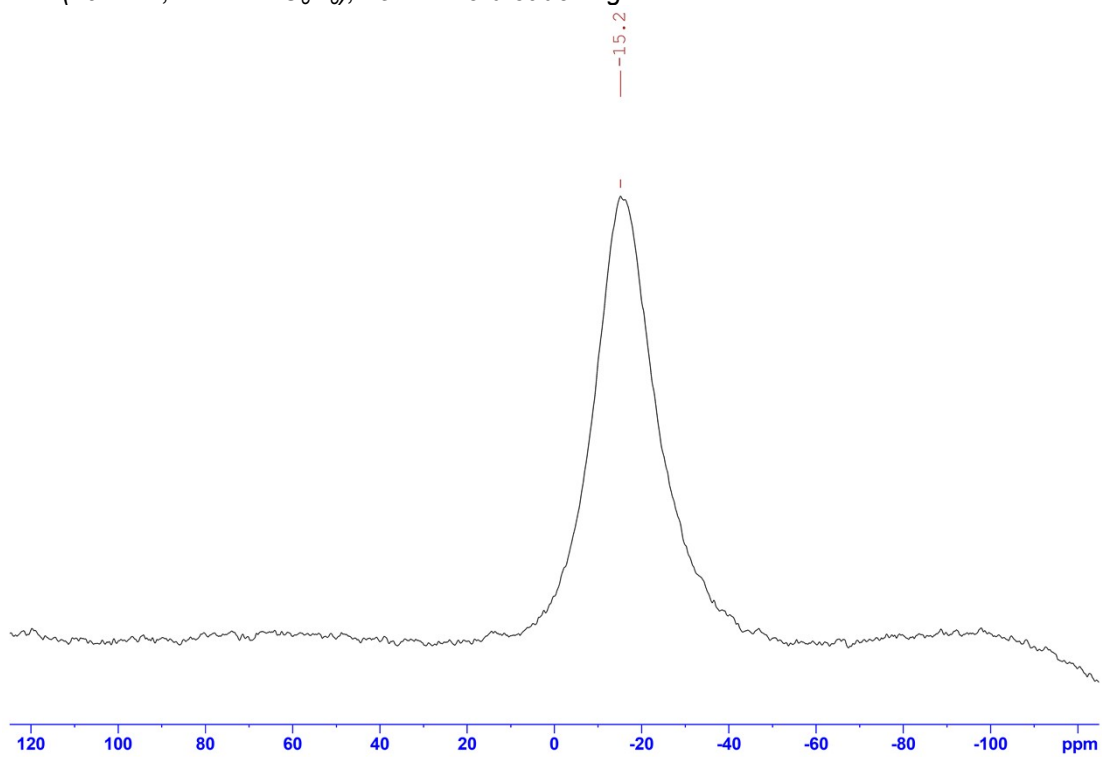
$\text{Na}_2(\text{Pb}^{\text{TBS,Ph}})(\text{THF})_4$  (**4b**)  
 $^1\text{H}$  NMR (300 MHz, 4:1 THF: $\text{C}_6\text{D}_6$ )



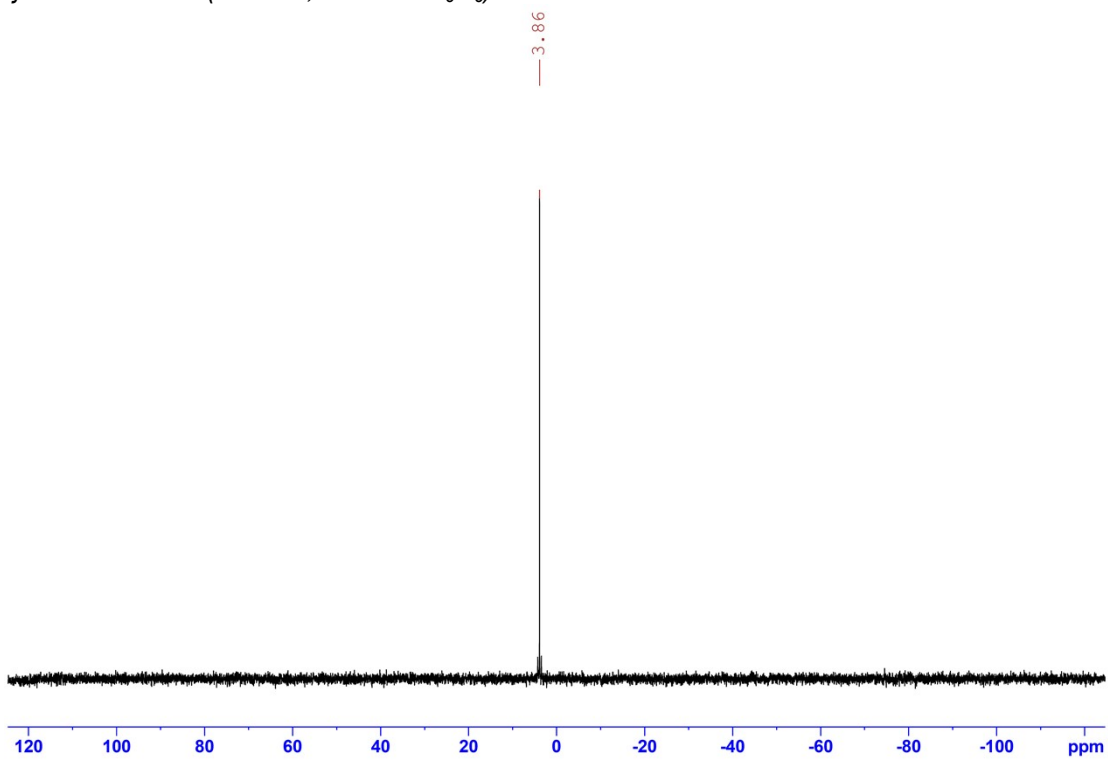
$^{13}\text{C}\{^1\text{H}\}$  UDEFT NMR (75 MHz, 4:1 THF: $\text{C}_6\text{D}_6$ )



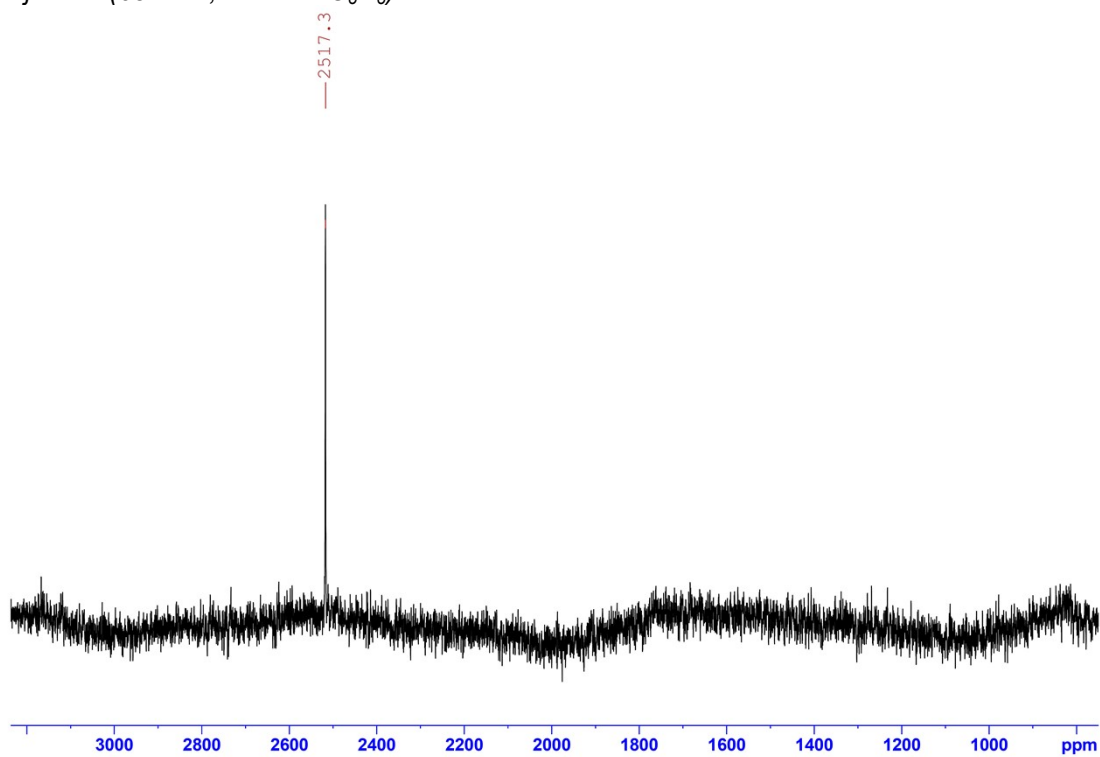
$^{23}\text{Na}$  NMR (79 MHz, 4:1 THF: $\text{C}_6\text{D}_6$ ), 45 Hz line broadening



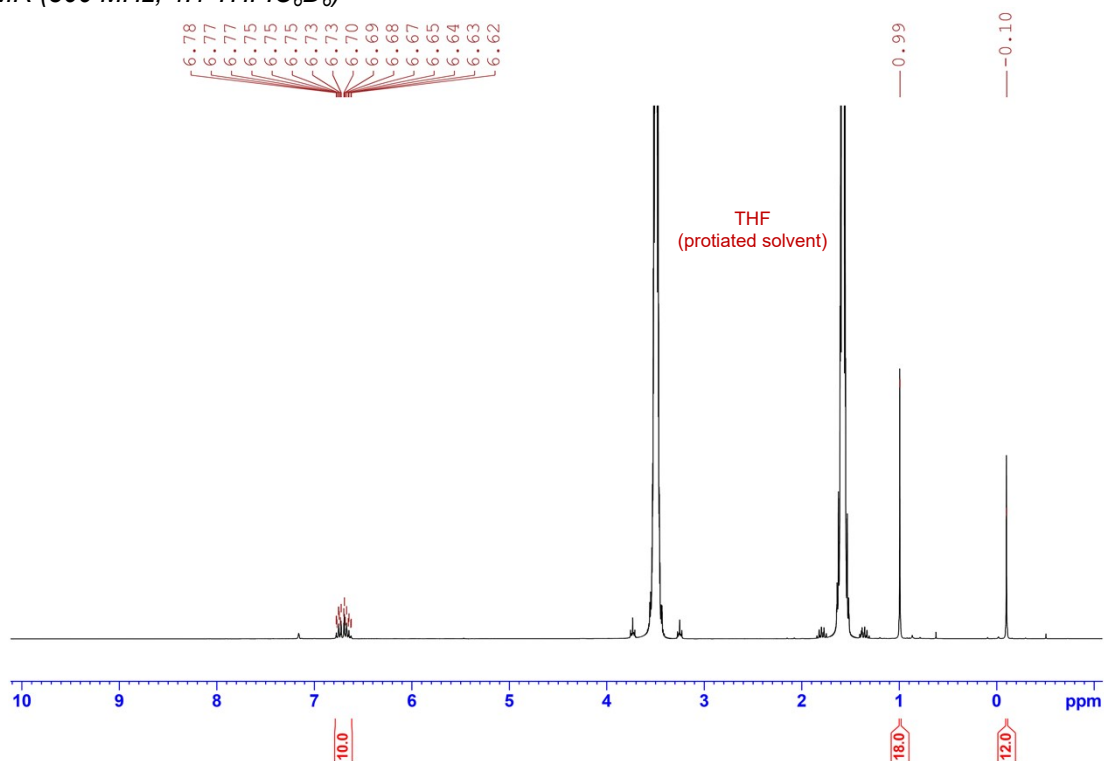
$^{29}\text{Si}\{^1\text{H}\}$  DEPT35 NMR (60 MHz, 4:1 THF: $\text{C}_6\text{D}_6$ )



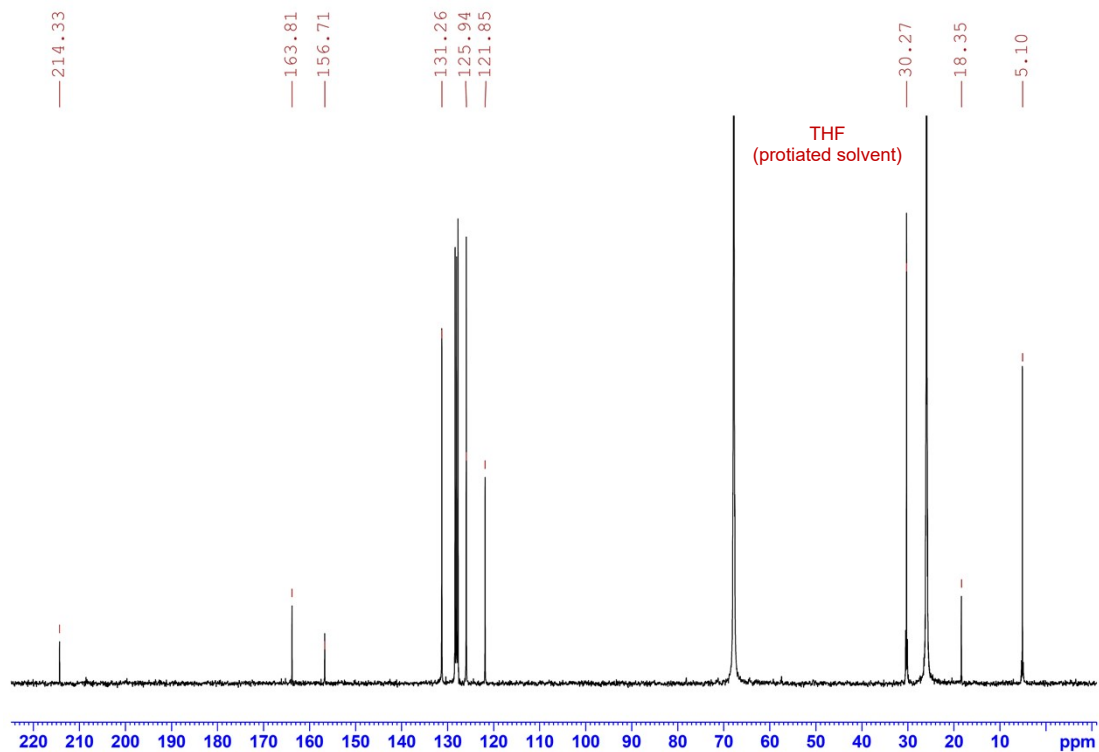
$^{207}\text{Pb}\{^1\text{H}\}$  NMR (63 MHz, 4:1 THF: $\text{C}_6\text{D}_6$ )



$[K_2(Pb^{TBS,Ph})(THF)_2]_n$  (**5a**)  
 $^1H$  NMR (300 MHz, 4:1 THF: $C_6D_6$ )

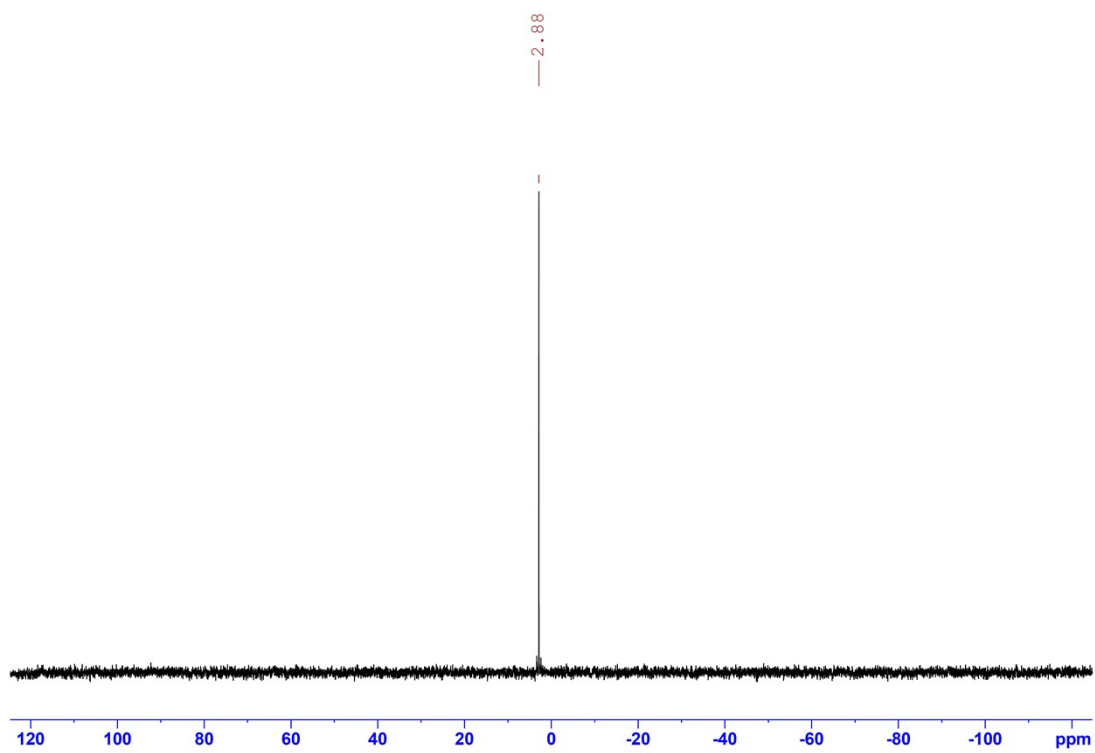


$^{13}C\{^1H\}$  UDEFT NMR (75 MHz, 4:1 THF: $C_6D_6$ )

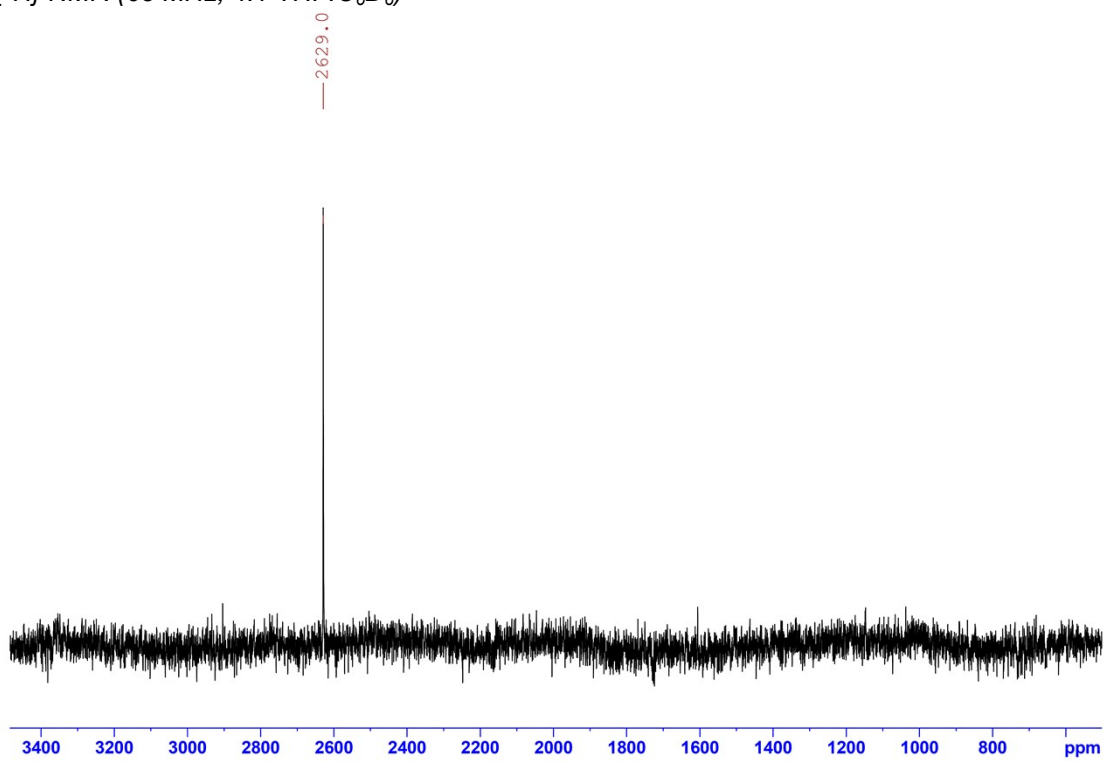




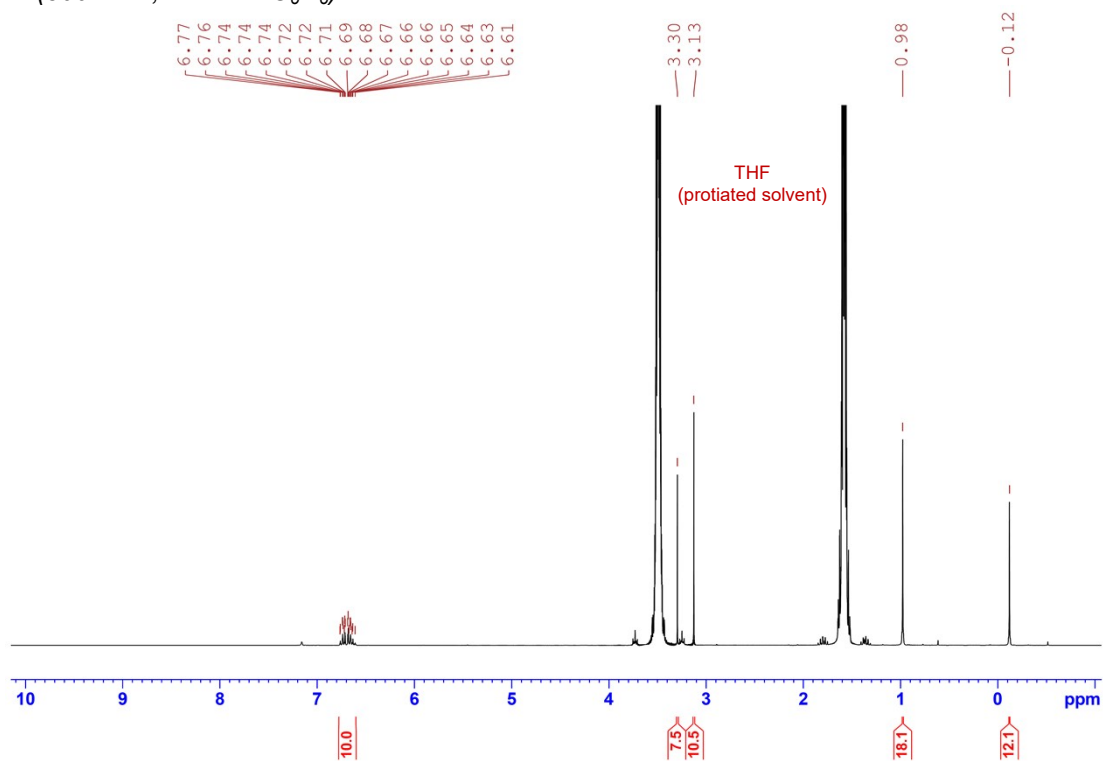
$^{29}\text{Si}\{^1\text{H}\}$  DEPT35 NMR (60 MHz, 4:1 THF: $\text{C}_6\text{D}_6$ )



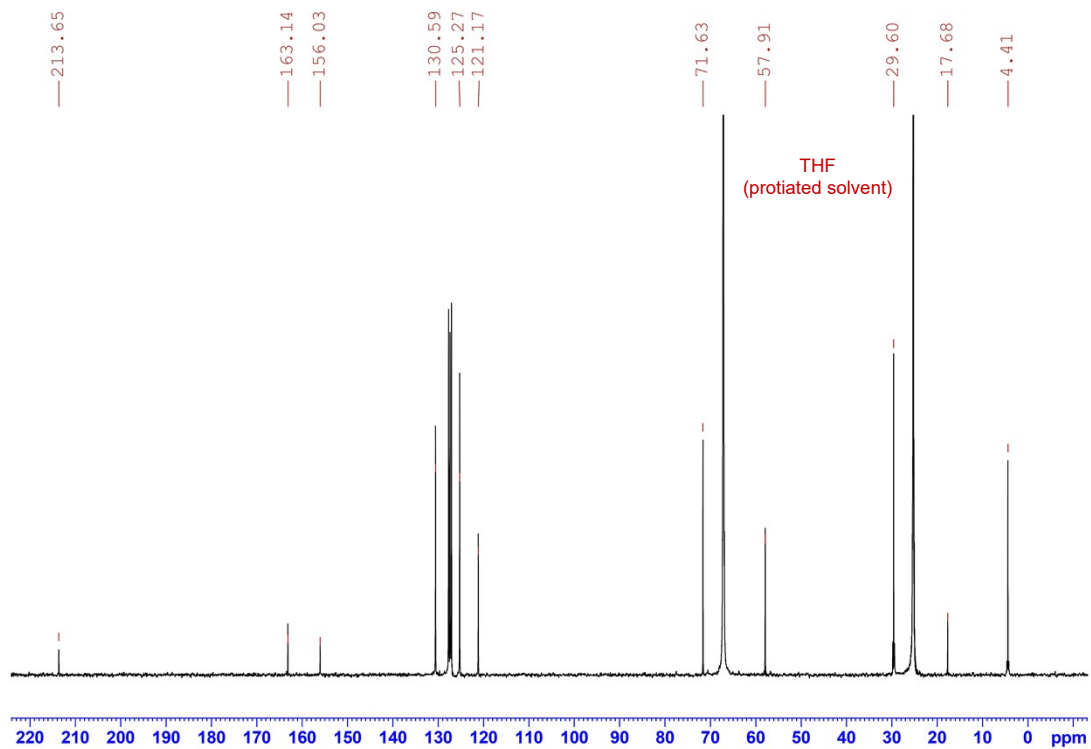
$^{207}\text{Pb}\{^1\text{H}\}$  NMR (63 MHz, 4:1 THF: $\text{C}_6\text{D}_6$ )



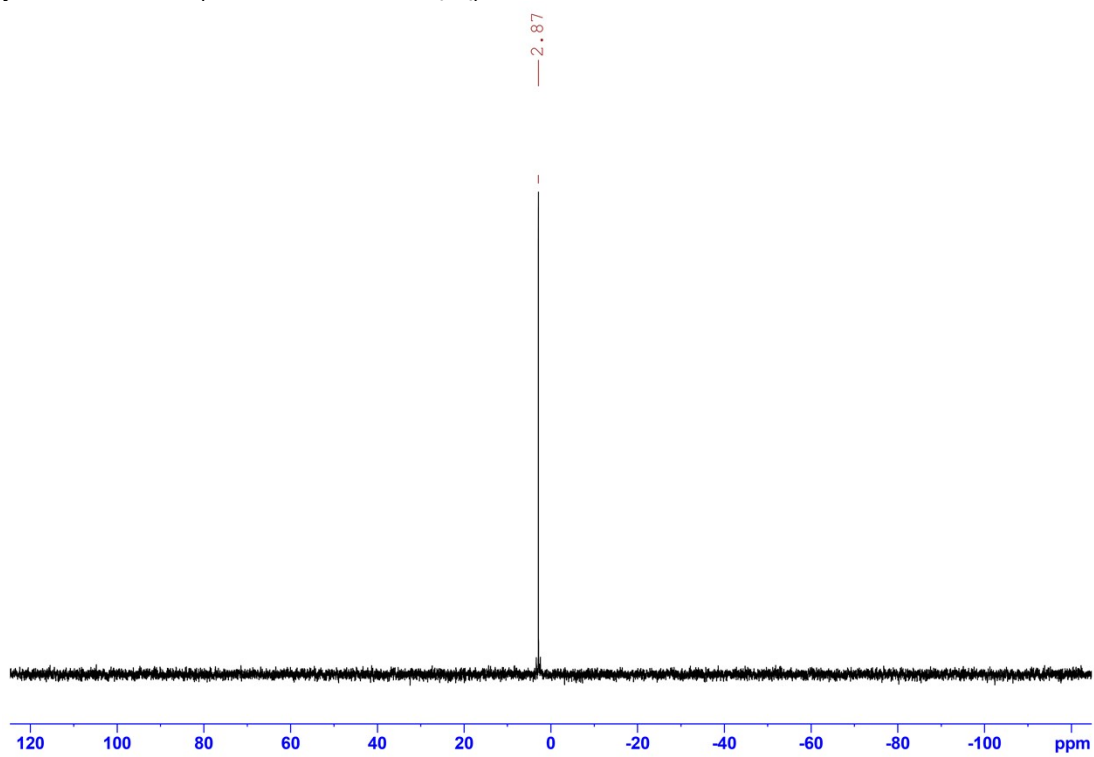
$[K_2(Pb^{TBS,Ph})(DME)_2]_n$  (**5b**)  
 $^1H$  NMR (300 MHz, 4:1 THF: $C_6D_6$ )



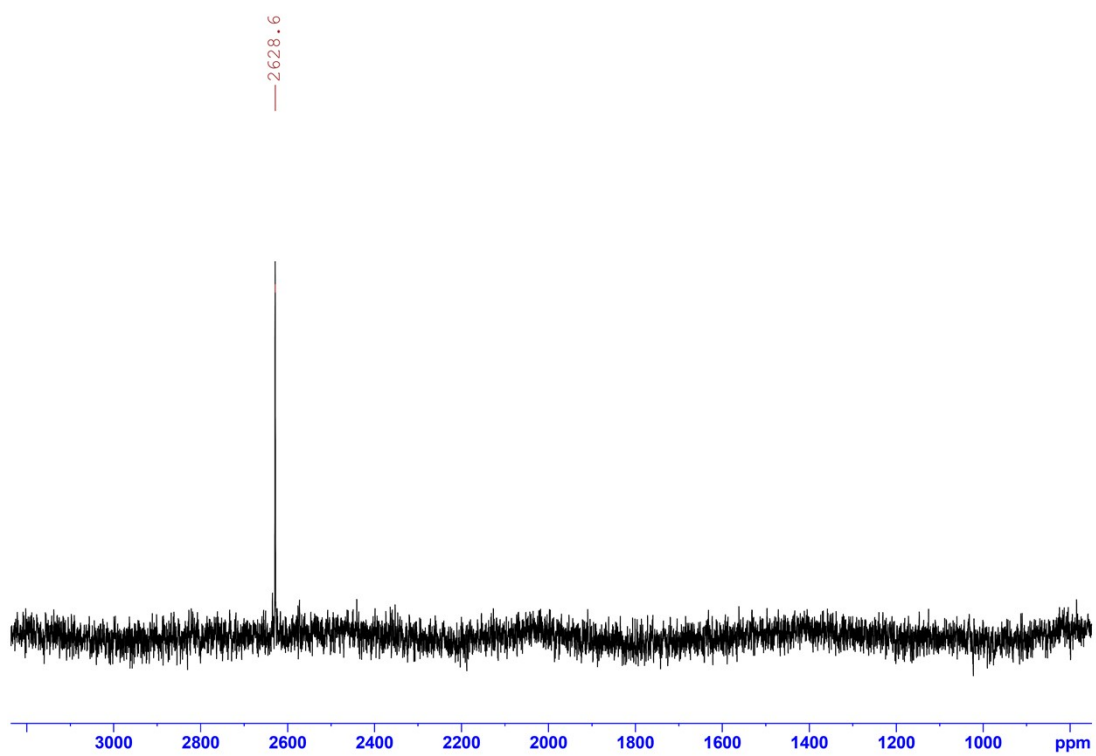
$^{13}C\{^1H\}$  UDEFT NMR (75 MHz, 4:1 THF: $C_6D_6$ )



$^{29}\text{Si}\{^1\text{H}\}$  DEPT35 NMR (60 MHz, 4:1 THF: $\text{C}_6\text{D}_6$ )

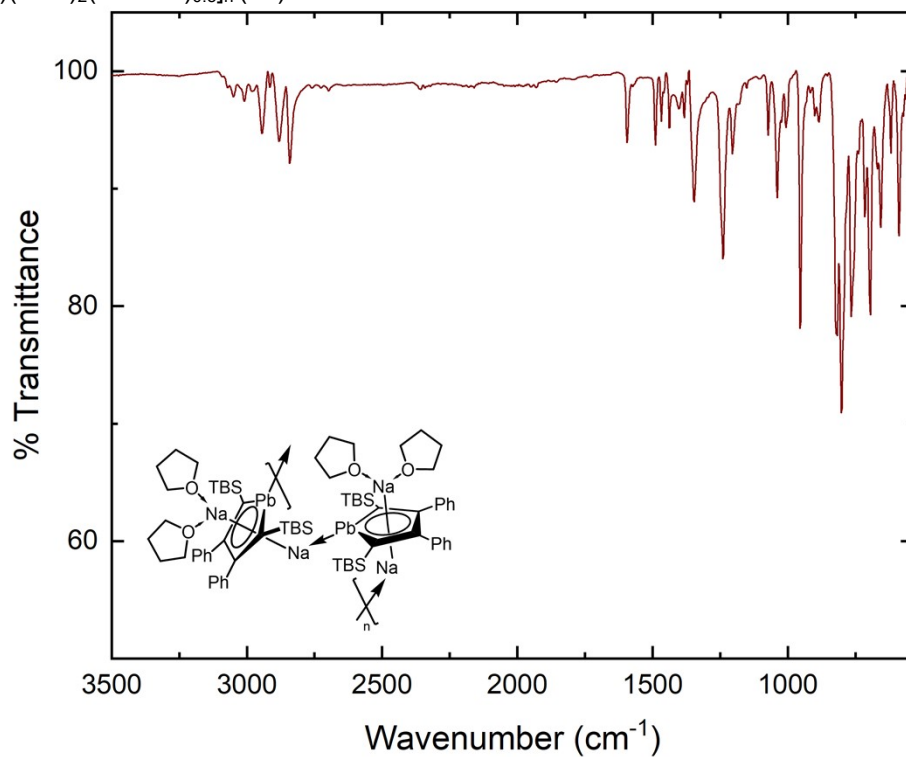


$^{207}\text{Pb}\{^1\text{H}\}$  NMR (63 MHz, 4:1 THF: $\text{C}_6\text{D}_6$ )

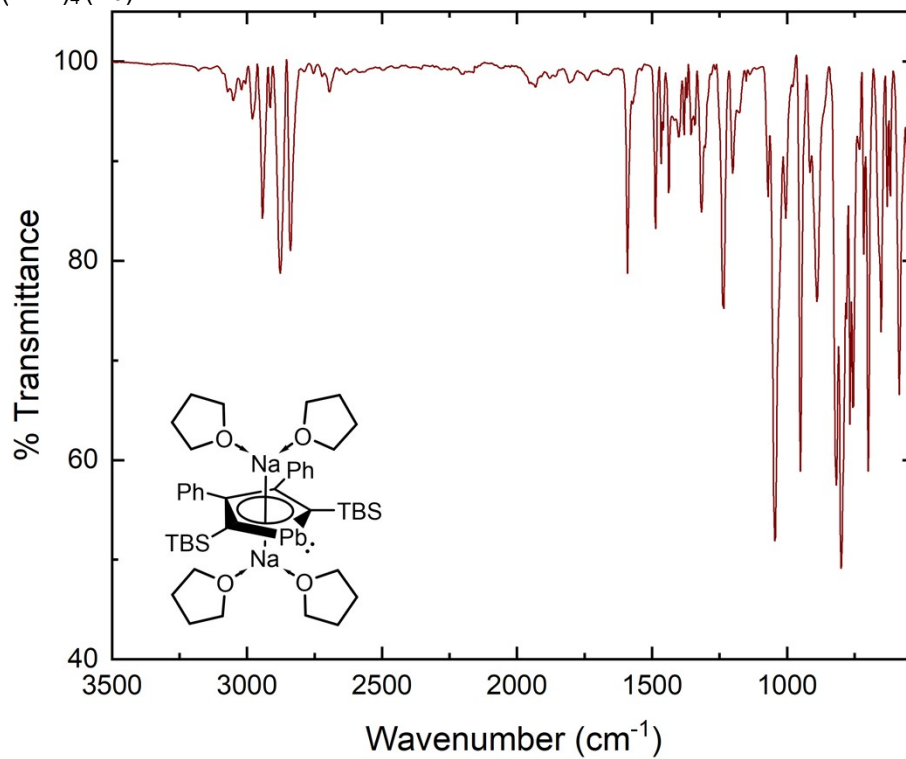


## Infrared Spectra

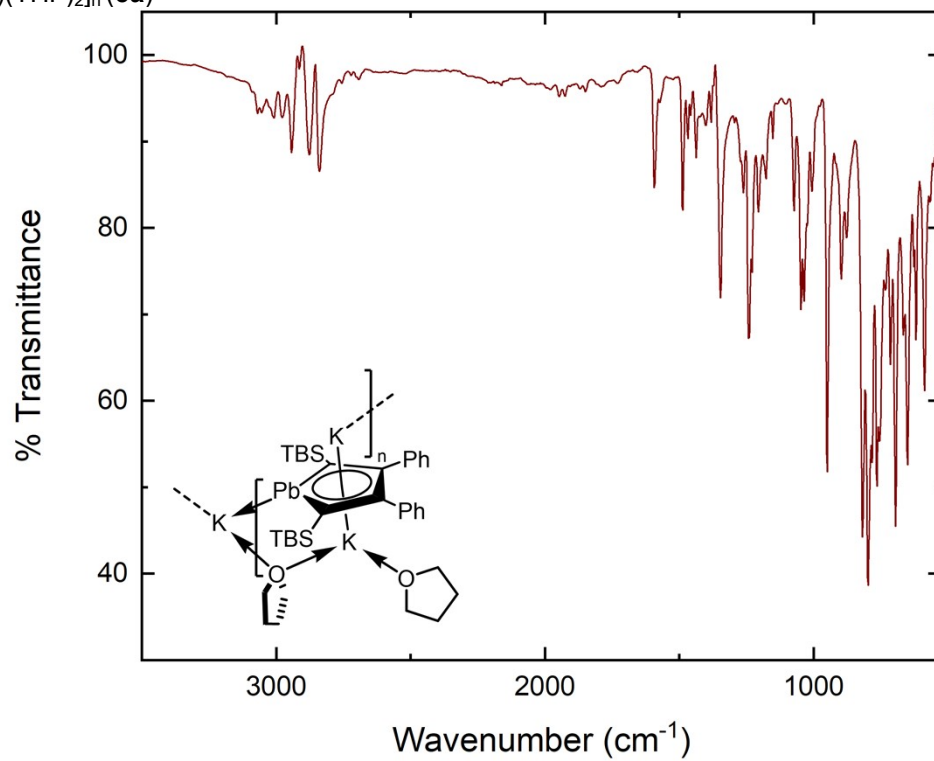
$[\text{Na}_2(\text{Pb}^{\text{TBS,Ph}})(\text{THF})_2(\text{toluene})_{0.5}]_n$  (**4a**)



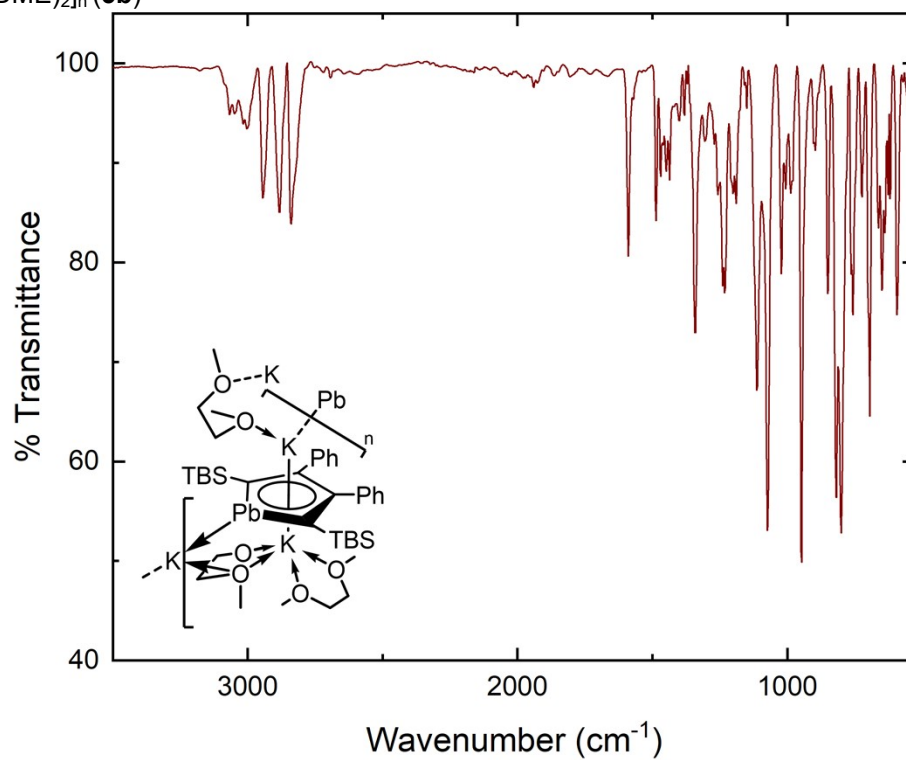
$\text{Na}_2(\text{Pb}^{\text{TBS,Ph}})(\text{THF})_4$  (**4b**)



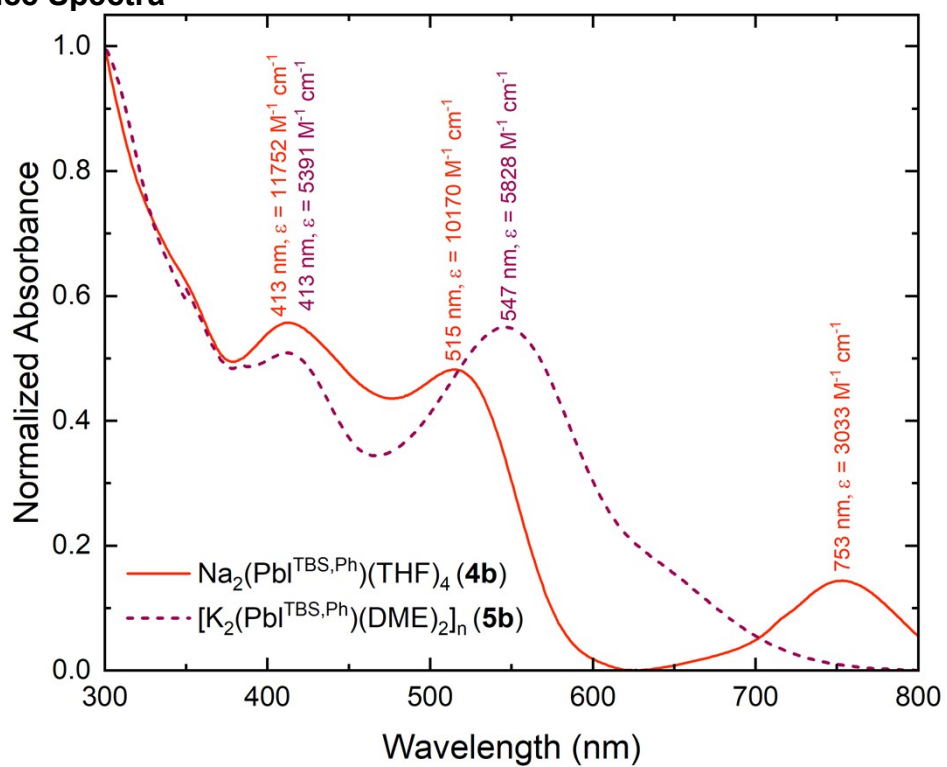
$[K_2(Pb^{TBS,Ph})(THF)_2]_n$  (**5a**)



$[K_2(Pb^{TBS,Ph})(DME)_2]_n$  (**5b**)



## Absorbance Spectra

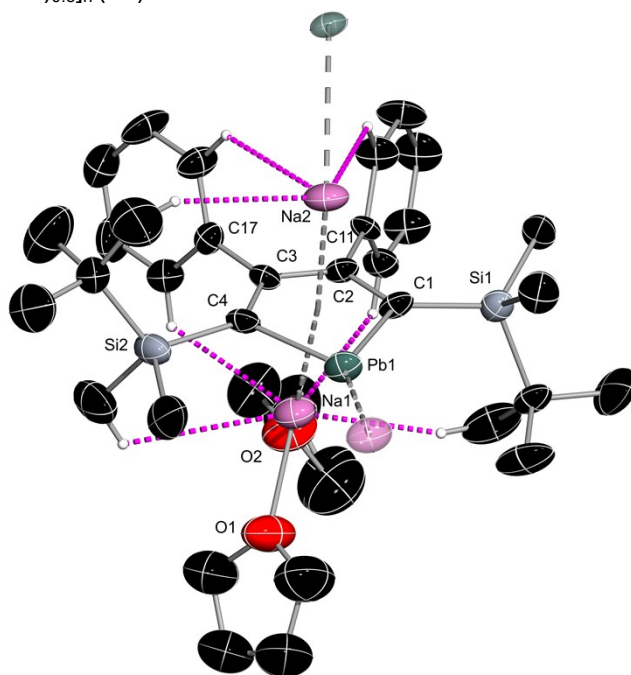
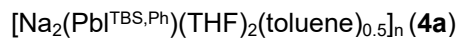


**Figure S1.** UV/visible absorbance spectrum of **4b** (solid orange line, 0.03 mM in toluene) and **5b** (dashed purple line, 0.06 mM in DME).

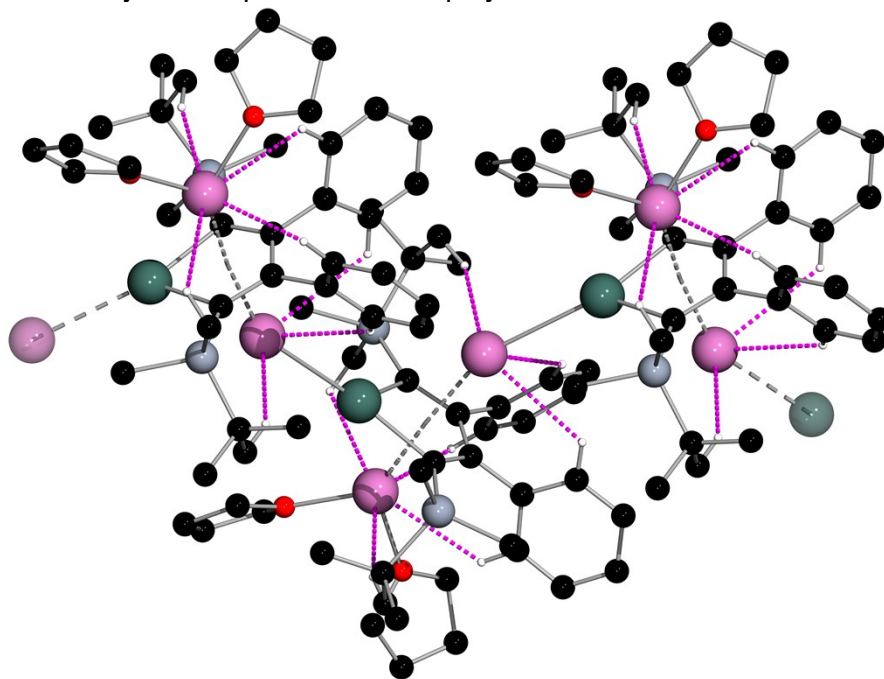
## Crystallographic Information

**Table S1.** Crystal data and structure refinement details.

	<b>4a</b>	<b>4b</b>	<b>5a</b>	<b>5b</b>
CCDC deposition number	2179096	2179097	2179098	2179099
Temperature (K)	203	203	213	150
Empirical formula	C <sub>36</sub> H <sub>56</sub> Na <sub>2</sub> O <sub>2</sub> PbSi <sub>2</sub>	C <sub>44</sub> H <sub>72</sub> Na <sub>2</sub> O <sub>4</sub> PbSi <sub>2</sub>	C <sub>36</sub> H <sub>56</sub> K <sub>2</sub> O <sub>2</sub> PbSi <sub>2</sub>	C <sub>72</sub> H <sub>120</sub> K <sub>4</sub> O <sub>8</sub> Pb <sub>2</sub> Si <sub>4</sub>
Formula weight (amu)	830.15	974.36	862.37	1796.81
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	I2/a	P2 <sub>1</sub> /c	Pn2 <sub>1</sub> a	Pn
Unit cell dimensions (Å and °)	a = 29.422(2) b = 10.6642(9) c = 29.458(2) α = 90 β = 111.437(8) γ = 90	a = 23.3878(17) b = 10.5283(8) c = 20.5795(16) α = 90 β = 107.770(2) γ = 90	a = 13.9365(3) b = 19.0723(3) c = 15.3540(3) α = 90 β = 90 γ = 90	a = 13.9985(5) b = 14.6914(5) c = 20.5549(7) α = 90 β = 91.382(2) γ = 90
Volume (Å <sup>3</sup> )	8603.6(13)	4825.6(6)	4081.11(13)	4226.0(3)
Z	8	4	4	2
Density (calculated, g/cm <sup>3</sup> )	1.282	1.341	1.404	1.412
Absorption coefficient (mm <sup>-1</sup> )	4.023	3.600	4.424	6.914
F(000)	3360	2000	1744	1824
Crystal size (mm <sup>3</sup> )	0.16 x 0.08 x 0.05	0.41 x 0.24 x 0.24	0.26 x 0.17 x 0.12	0.22 x 0.09 x 0.08
Theta range (°)	1.485 to 24.996	1.829 to 29.132	2.7 to 27.1	5.234 to 111.84
Index ranges (h,k,l)	-34 to 34, -12 to 12, -35 to 35	-32 to 32, -14 to 14, -28 to 28	-17 to 14, -24 to 24, -19 to 19	-16 to 17, -18 to 18, -25 to 24
Reflections collected	67463	227692	50293	65629
Independent reflections	7553	13001	8719	15909
R(int)	0.1933	0.0472	0.0382	0.0527
Completeness (%)	99.6	100	100	99.9
Max. and min. transmission	0.7454 and 0.5232	0.7461 and 0.5610	0.7455 and 0.5936	0.0207 and 0.0927
Data / restraints / parameters	7553 / 84 / 398	13001 / 120 / 488	8719 / 82 / 399	15909 / 62 / 847
Goodness-of-fit on F <sup>2</sup>	0.995	1.023	1.015	1.030
R indices (all data)	R1 = 0.1218 wR2 = 0.1246	R1 = 0.0328 wR2 = 0.0496	R1 = 0.0378 wR2 = 0.0434	R1 = 0.0377 wR2 = 0.0670
Final R indices [ <i>I</i> > 2σ( <i>I</i> )]	R1 = 0.0579 wR2 = 0.1112	R1 = 0.0220 wR2 = 0.0465	R1 = 0.0207 wR2 = 0.0387	R1 = 0.0295 wR2 = 0.0651
Largest diff. peak and hole (e.Å <sup>-3</sup> )	1.016 and -1.824	0.649 and -0.487	0.735 and -0.316	1.02 and -0.56

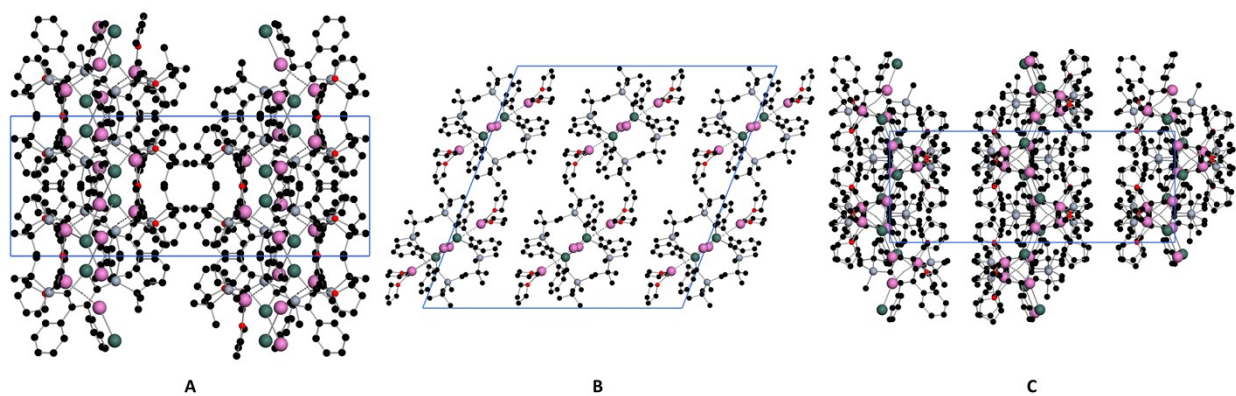


**Figure S2.** Intramolecular C-H $\cdots$ Na contacts (magenta dotted lines) supporting the sodium atoms in the solid-state structure of **4a**. Thermal ellipsoids shown at 50% probability; all other hydrogen atoms omitted for clarity. One repeat unit of the polymer shown.

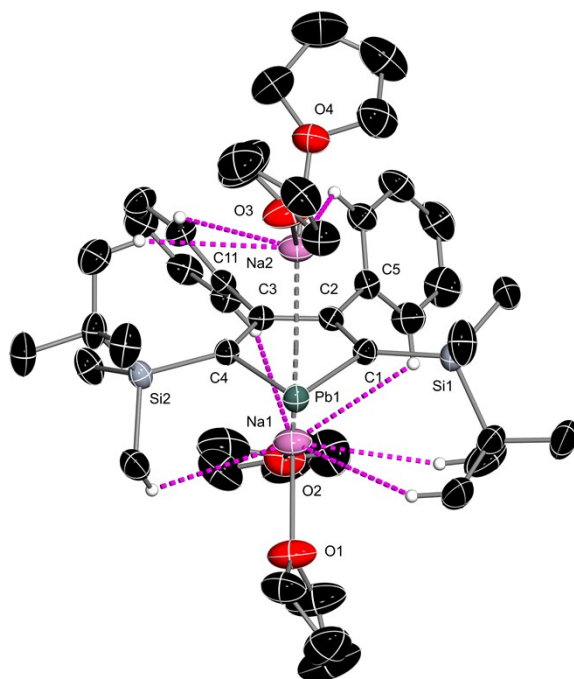
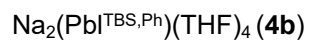


**Figure S3.** Several repeat units of the coordination polymer of **4a**, to illustrate the polymeric structure. C-H $\cdots$ Na contacts shown as magenta dotted lines; all other hydrogen atoms omitted for clarity.

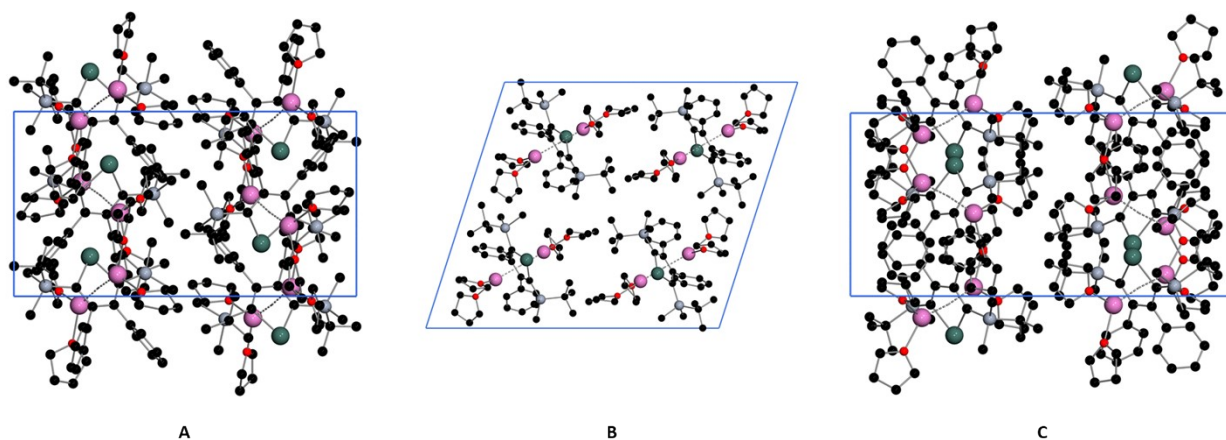




**Figure S4.** Crystallographic packing diagrams of **4a**, shown along the a) *a*-axis, b) *b*-axis, and c) *c*-axis of the unit cell. Hydrogen atoms and C-H $\cdots$ Na contacts are omitted for clarity.

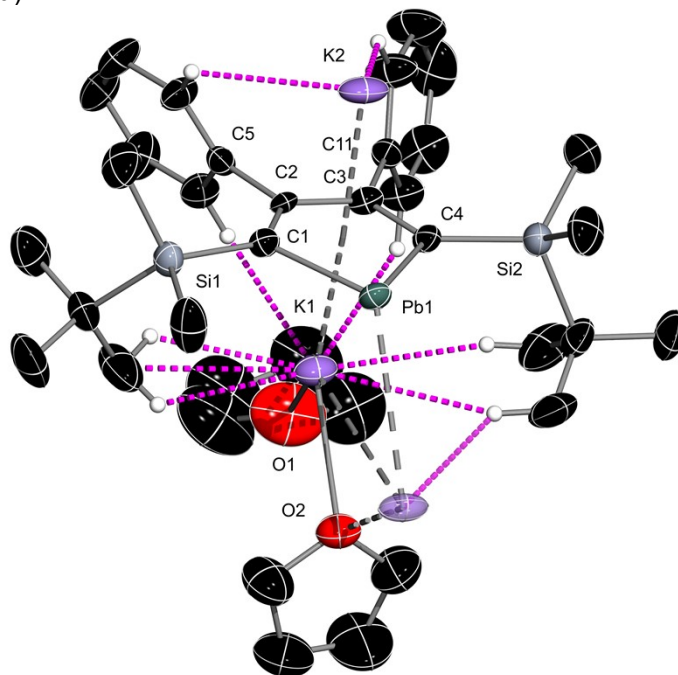


**Figure S5.** Intramolecular C-H $\cdots$ Na contacts (magenta dotted lines) supporting the sodium atoms in the solid-state structure of **4b**. Thermal ellipsoids shown at 50% probability; all other hydrogen atoms omitted for clarity.

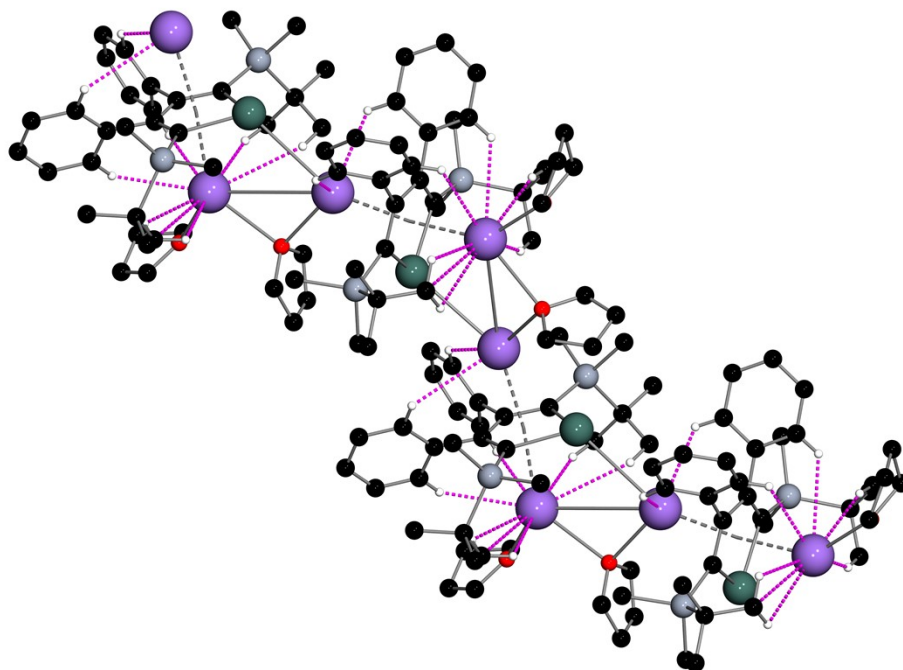


**Figure S6.** Crystallographic packing diagrams of **4b**, shown along the a) *a*-axis, b) *b*-axis, and c) *c*-axis of the unit cell. Hydrogen atoms are omitted for clarity.

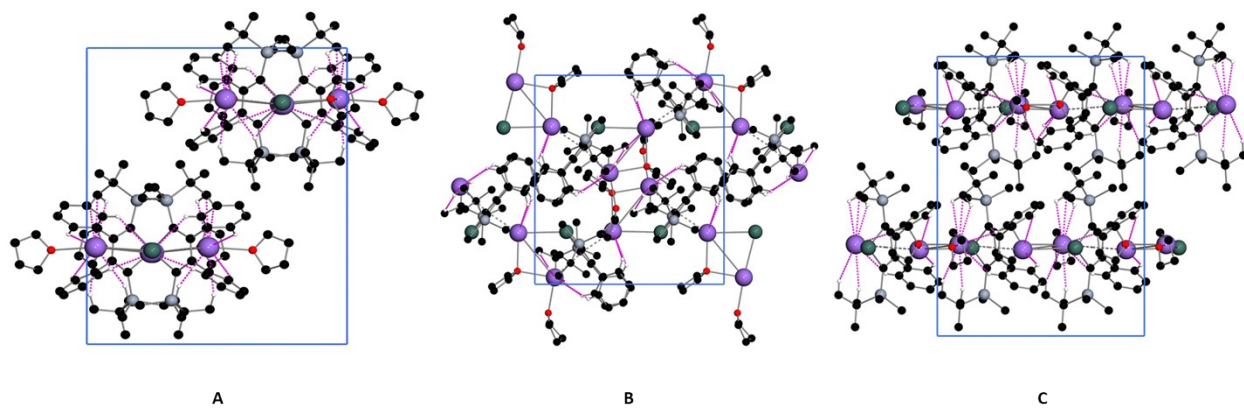
$[K_2(Pb^{TBS,Ph})(THF)_2]_n$  (**5a**)



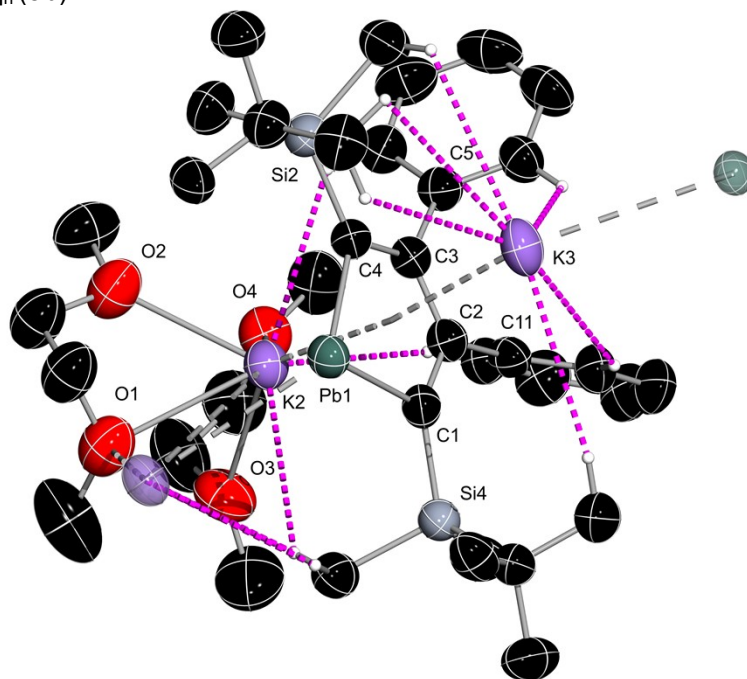
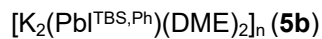
**Figure S7.** Intramolecular C-H...K contacts (magenta dotted lines) supporting the potassium atoms in the solid-state structure of **5a**. Thermal ellipsoids shown at 50% probability; all other hydrogen atoms omitted for clarity. One repeat unit of the polymer shown.



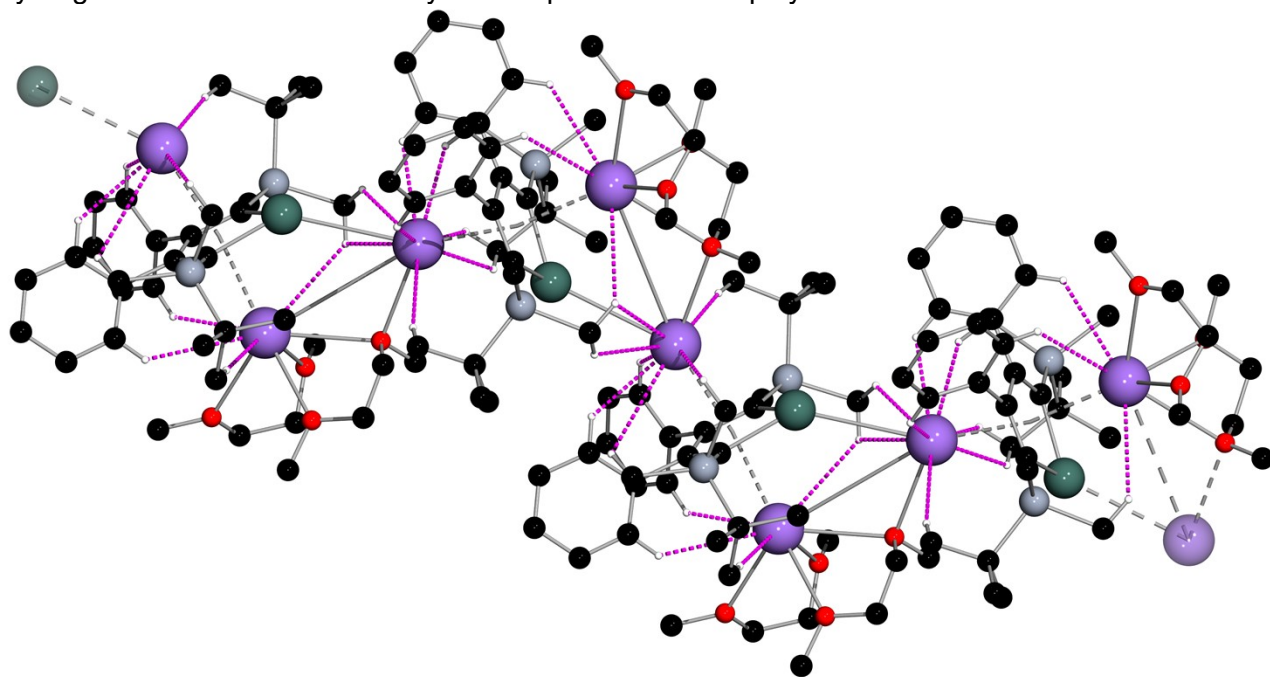
**Figure S8.** Several repeat units of the coordination polymer of **5a**, to illustrate the polymeric structure. C-H...K contacts shown as magenta dotted lines; all other hydrogen atoms omitted for clarity.



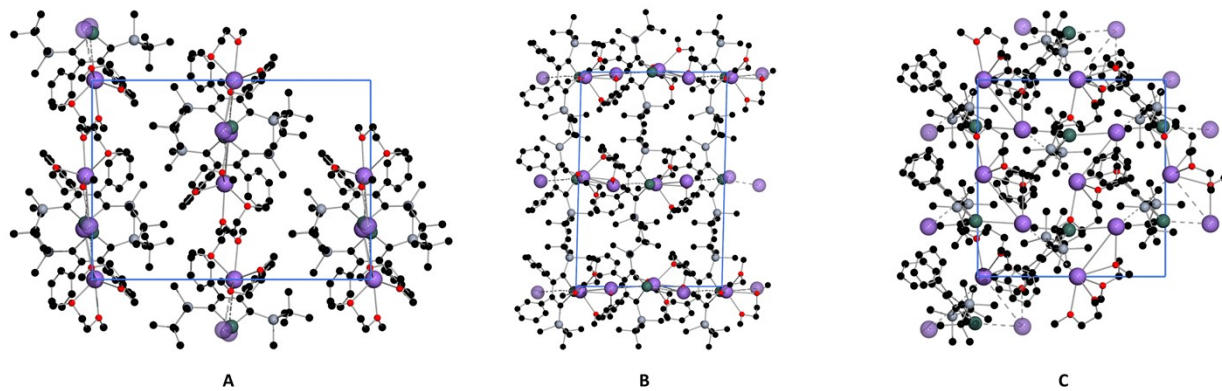
**Figure S9.** Crystallographic packing diagrams of **5a**, shown along the a) *a*-axis, b) *b*-axis, and c) *c*-axis of the unit cell. Hydrogen atoms are omitted for clarity. Intramolecular C-H...K contacts shown as magenta dotted lines.



**Figure S10.** Intramolecular C-H $\cdots$ K contacts (magenta dotted lines) supporting the potassium atoms in the solid-state structure of **5b**. Thermal ellipsoids shown at 50% probability; all other hydrogen atoms omitted for clarity. One repeat unit of the polymer shown.

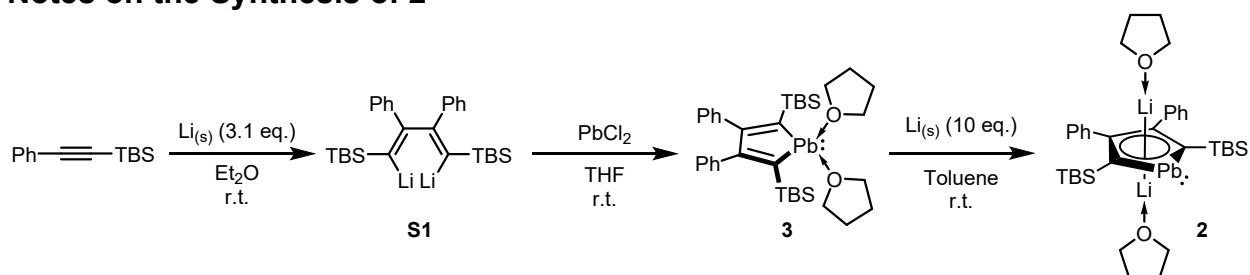


**Figure S11.** Several repeat units of the coordination polymer of **5b**, to illustrate the polymeric structure. C-H $\cdots$ K contacts shown as magenta dotted lines; all other hydrogen atoms omitted for clarity.



**Figure S12.** Crystallographic packing diagrams of **5b**, shown along the a) *a*-axis, b) *b*-axis, and c) *c*-axis of the unit cell. Hydrogen atoms and C-H...K contacts are omitted for clarity.

## Notes on the Synthesis of 2



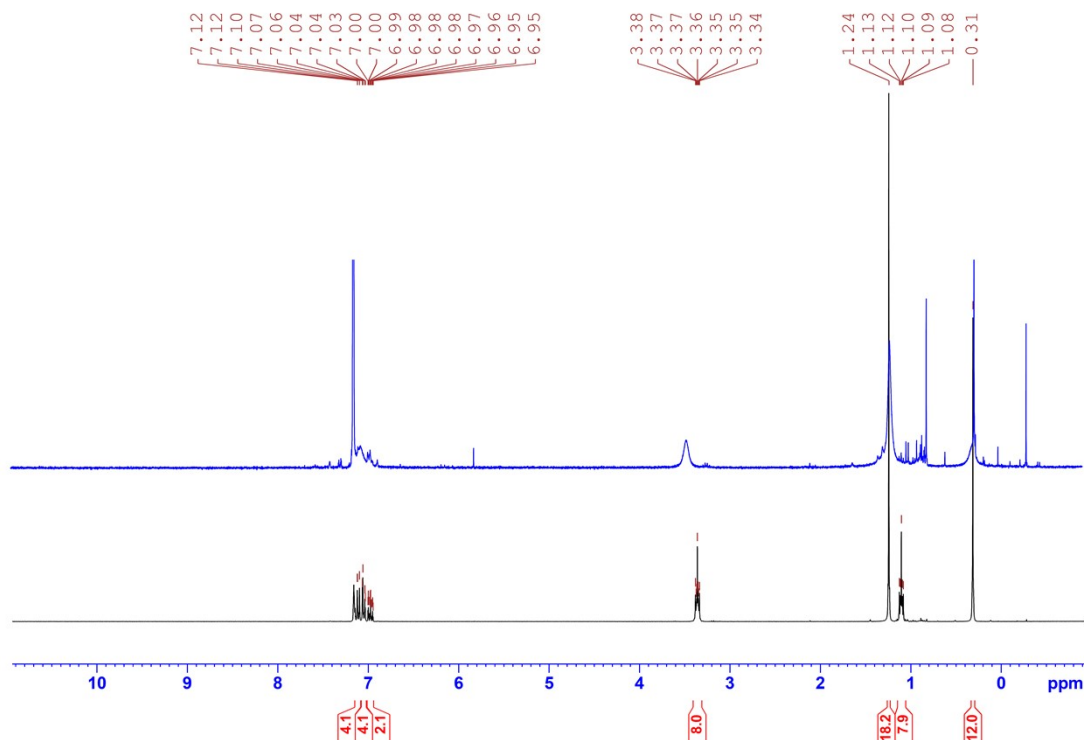
**Figure S13.** Reaction scheme for the synthesis of  $\text{Li}_2(\text{PbI}^{\text{TBS,Ph}})(\text{THF})_2$ , as reported by Saito and coworkers.

**1,4-dilithio-1,4-bis(tert-butyldimethylsilyl)-2,3-phenyl-1,3-butadiene (S1).** Low-to-moderate yield (25%) is reported for the synthesis of this compound from TBS-phenylacetylene and excess lithium metal.<sup>1</sup> However, in our hands, **S1** was consistently obtained in much higher yields (60–80%) following the reported procedure. We used lithium granules (Aldrich 499811, transferred to a Schlenk tube upon receipt and stored under argon) and found that pre-stirring the dry granules under argon with a large stir bar for at least 1 hr prior to the addition of solvent or TBS-phenylacetylene improved recovery of the product. Furthermore, cooling of the reaction mixture and slow addition of TBS-phenylacetylene when preparing large batches of this material (e.g., 10 g) is recommended, as the exothermic reaction between the acetylene and lithium can become uncontrolled otherwise.

**THF-stabilized 2,5-bis(tert-butyldimethylsilyl)-3,4-phenylplumbacyclopentadienyldiene (3).**<sup>2,3</sup> In our hands, we were consistently able to obtain **3** in  $50 \pm 5\%$  yield on scales ranging from 100 mg to 3 g. Vigorous stirring of the suspension of  $\text{PbCl}_2$  in THF is recommended to ensure rapid and complete reaction. Plumbylene **3** is extremely soluble in most solvents, including benzene, toluene, and alkanes. However, following the reaction of **S1** and  $\text{PbCl}_2$ , we observed pentane solutions of crude **3** to change from a bright red colour toward brown over 1 or 2 hours – the red colour was regenerated upon the addition of a small amount of THF. This indicates the slow decomposition of solutions of **3** in non-coordinating solvents, ostensibly by dimerization and spirocyclization of the desolvated plumbylene, as previously reported.<sup>2,3</sup> Thus, it is imperative that this material be stored in the solid state, or in the presence of at least 2 eq. of THF if in solution.

**$\text{Li}_2\text{PbI}^{\text{TBS,Ph}}(\text{THF})_2$  (2).** The synthesis of this compound was inconsistent in our hands. Following the reported procedure,<sup>2</sup> a 50 mL Schlenk flask was charged with plumbylene **3** inside a nitrogen-filled glove box, sealed, and transferred to an argon-fed Schlenk line. The flask was evacuated, purged, and refilled with dry argon, then lithium granules (Aldrich 499811, as above) were added, followed by dry toluene. Stirring of the reaction mixture caused a colour change from red to brown, then to dark green-brown. Stirring was discontinued after the indicated reaction time (9 hr) and the flask transferred back into the glove box for further processing. The crude mixture failed to crystallize from the indicated solvent system (5:1 hexanes/toluene) even after repeated attempts, and the resonances expected from **2** were not observed in the NMR spectra of the crude material. We discovered that, when the reaction was conducted on small scale (e.g. 0.22 mmol = 172 mg), the relatively large lithium granules had a tendency to escape contact with the solution of **3** by sticking to the vessel walls, especially when combined with the minimal volume of solvent (2 mL). This in turn caused the failure of the lithium to reduce **3**, while simultaneously allowing its decomposition upon standing for prolonged periods in non-coordinating solvent. Switching to a much smaller vessel (a 10 mL Schlenk tube with outer diameter ~1.5 cm) was successful in keeping the lithium granules in contact with the reaction solution. This change of vessel and extension of the reaction time from 9 hr to 48 hr allowed the isolation of a bright green-yellow

solution. NMR spectroscopic analysis of this material demonstrated complete conversion to **2**, accompanied by significant impurities. Recrystallization of the crude material from hexanes layered over a saturated toluene solution gave a low yield (21%) of yellow blocklike crystals, which were found to be pure by NMR spectroscopic analysis (Figure S13). X-ray diffraction analysis of these crystals also revealed a unit cell matching the one originally reported (found  $a = 12.06$ ,  $b = 12.08$ ,  $c = 13.37$ ,  $\alpha = 82.4$ ,  $\beta = 67.26$ ,  $\gamma = 75.91$ , *cf.* the reported  $a = 12.4117$ ,  $b = 12.4449$ ,  $c = 13.7628$ ,  $\alpha = 82.874$ ,  $\beta = 67.352$ ,  $\gamma = 75.447$ ). Further attempts to synthesize this material using the same conditions gave the same qualitative results but failed to crystallize even after several attempts.



**Figure S14.**  $^1\text{H}$  nuclear magnetic resonance spectra of **2** in  $\text{C}_6\text{D}_6$ , before (blue curve) and after (black curve) recrystallization.

## References

- 1 M. Saito, M. Nakamura, T. Tajima and M. Yoshioka, *Angew. Chem. - Int. Ed.*, 2007, **46**, 1504–1507.
- 2 M. Saito, M. Nakada, T. Kuwabara and M. Minoura, *Chem. Commun.*, 2015, **51**, 4674–4676.
- 3 M. Saito, T. Akiba, M. Kaneko, T. Kawamura, M. Abe, M. Hada and M. Minoura, *Chem. - Eur. J.*, 2013, **19**, 16946–16953.