Supporting information for

Synthesis and Structures of Diaryloxystannylenes and -plumbylenes embedded in 1,3-Diethers of Thiacalix[4]arene

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Table of contents

1. Details for the X-ray diffraction analysis

Diffraction data for **2-Sn**, **2-Pb**, **4, 5-Sn**, and **5-Pb** were collected on a VariMax Saturn CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71075 Å) at –180 °C. Intensity data were corrected for Lorenz-polarization effects and for empirical absorption (REQAB).[1] All calculations were performed using the CrystalStructure[2] crystallographic software package except for refinements, which were performed using SHELXL-2018/3.[3] All non-hydrogen atoms were refined on F_o^2 anisotropically by full-matrix least-square techniques. All hydrogen atoms were placed at the calculated positions with fixed isotropic parameters.

2. Molecular structures of thiacalix$^{t\text{-Bu}}$(OH)$_2$(OSi^{i}Pr$_3$)$_2$ (4).

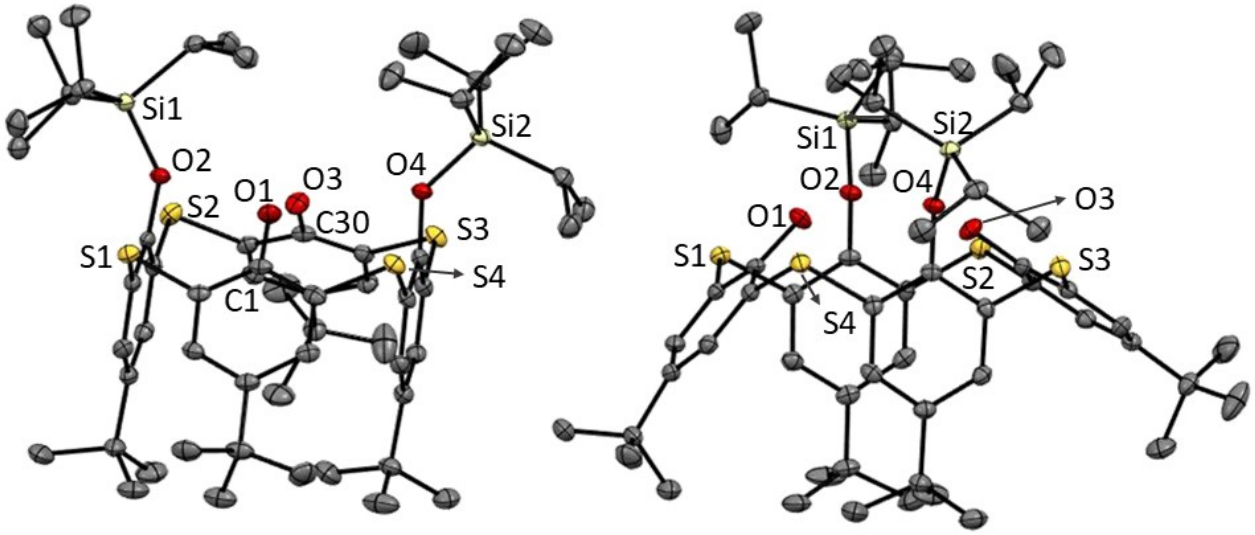

Figure S1. Molecular structures of **4** with thermal ellipsoid plots at 30 % probability. All hydrogen atoms and a THF molecule are omitted for clarity. Selected bond lengths [Å]: C1–O1 1.359(3); C30–O2 1.358(3).

3. X-ray crystallographic data for 2-Sn, 2-Pb, 4, 5-Sn, and 5-Pb.

Table S1. X-ray crystallographic data.

	2-Sn·(Tol)$_3$	**2-Pb·(Tol)**	**4·(THF)**	**5-Sn**	**6-Pb·(C_5H_{12})$_2$**
CCDC	2016537	2021967	2021969	2016539	2021968
formula	$C_{75}H_{82}O_4S_4Sn$	$C_{61}H_{66}O_4PbS_4$	$C_{62}H_{96}O_5S_4Si_2$	$C_{58}H_{86}O_4S_4Si_2Sn$	$C_{131}H_{208}O_8Pb_2S_8Si_4$
fw	1294.33	1198.56	1105.8	1150.37	2694.18
crystal dimension	0.17 × 0.15 × 0.05	0.14 × 0.14 × 0.09	0.16 × 0.14 × 0.06	0.18 × 0.17 × 0.10	0.18 × 0.17 × 0.15
crystal system	triclinic	monoclinic	triclinic	monoclinic	triclinic
space group	*P*-1	*C*2/*c*	*P*-1	$P2_1/c$	*P*-1
a [Å]	12.094(3)	22.413(3)	13.510(2)	13.3770(12)	13.4391(8)
b [Å]	12.497(3)	20.959(2)	15.106(2)	17.7497(15)	13.7334(7)
c [Å]	22.902(6)	12.5139(14)	16.040(2)	25.887(2)	20.3149(10)
α [deg]	83.617(10)	90	79.593(5)	90	71.319(3)
β [deg]	85.056(11)	108.6460(10)	81.074(4)	102.696(2)	77.604(3)
γ [deg]	75.959(9)	90	89.230(6)	90	77.966(3)
V [Å^3]	3330.9(15)	5570.1(11)	3180.1(8)	5996.3(9)	3429.3(3)
Z	2	4	2	4	1
ρ_{calcd} [g cm^{-3}]	1.29	1.429	1.155	1.274	1.305
F(000)	1356	2440	1200	2432	1406
μ [cm^{-1}]	5.57	32.24	2.32	6.48	26.59
transmission factors range	0.8455 – 1	0.8697 – 1	0.8616 – 1	0.8793 – 1	0.8718 – 1
index range	-15 ≤ h ≤ 13 -16 ≤ k ≤ 15 -29 ≤ l ≤ 29	-28 ≤ h ≤ 22 -27 ≤ k ≤ 26 -16 ≤ l ≤ 16	-17 ≤ h ≤ 17 -16 ≤ k ≤ 19 -15 ≤ l ≤ 20	-17 ≤ h ≤ 17 -22 ≤ k ≤ 23 -33 ≤ l ≤ 29	-11 ≤ h ≤ 16 -16 ≤ k ≤ 16 -25 ≤ l ≤ 25
no. reflections	26547	22455	26240	48104	25173
unique (R_{int})	14566 (0.0636)	6294 (0.0366)	14039 (0.0411)	13722 (0.0396)	13148 (0.0316)
$I > 2\sigma(I)$	11317	5736	10139	11958	11126
no. parameters	795	338	684	646	742
R_1 ($I > 2\sigma(I)$)[a]	0.0851	0.0319	0.0598	0.0372	0.0271
wR_2 (all data)[b]	0.1827	0.0695	0.1488	0.0899	0.0683
GOF [c]	1.098	1.117	1.083	1.118	1.06
max diff peak / hole [e Å^{-3}]	1.297/-1.222	1.5/-1.746	0.475/-0.454	0.48/-0.989	1.635/-1.413

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma w(F_o^2)^2]^{1/2}$, w = $1/[\sigma^2F_o^2 + (aP)^2 + bP]$ (*a* and *b* are constants suggested by the refinement program; P = $[\max(F_o^2,0) + 2F_c^2]/3$). [c]GOF = $[\Sigma w(F_o^2 - F_c^2)^2/(N_{obs} - N_{params})]^{1/2}$.

4. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of the products

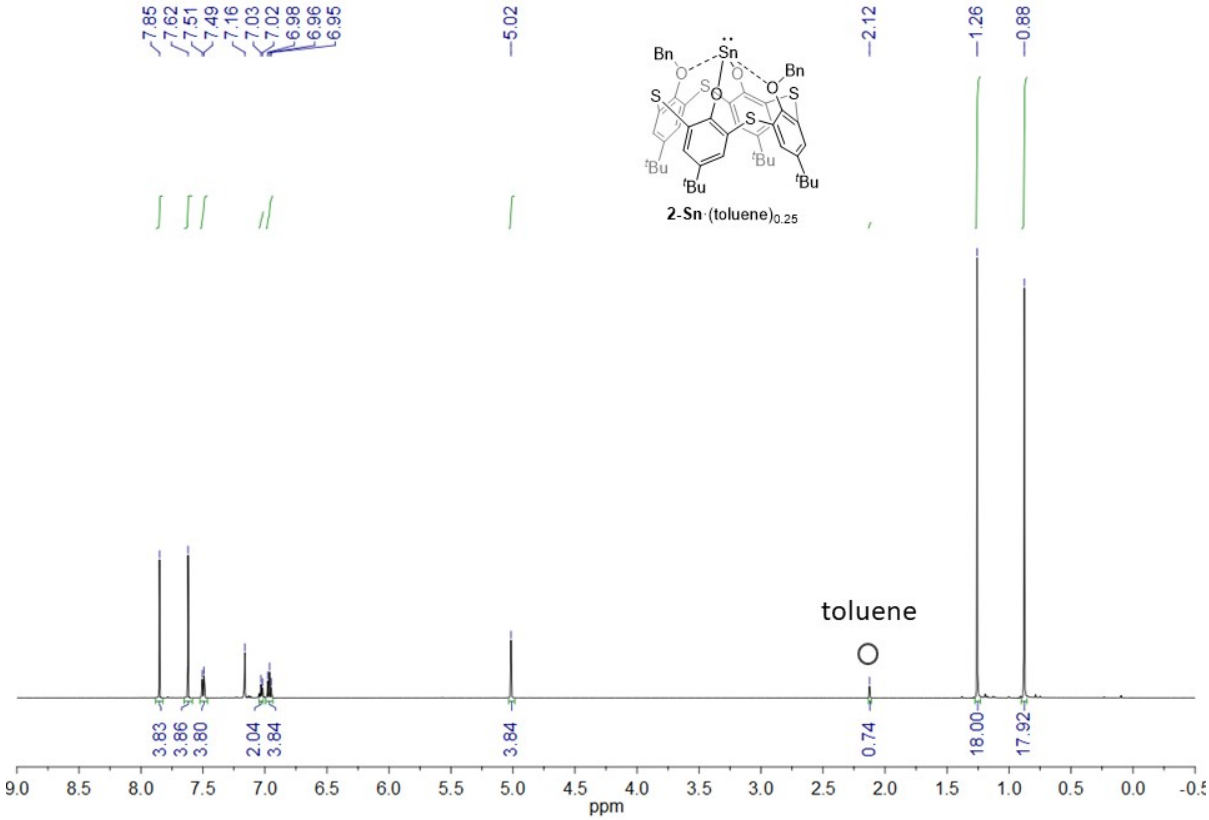

Figure S2. ^{1}H NMR spectrum of **2-Sn**·(toluene)$_{0.25}$ recorded at 50 °C.

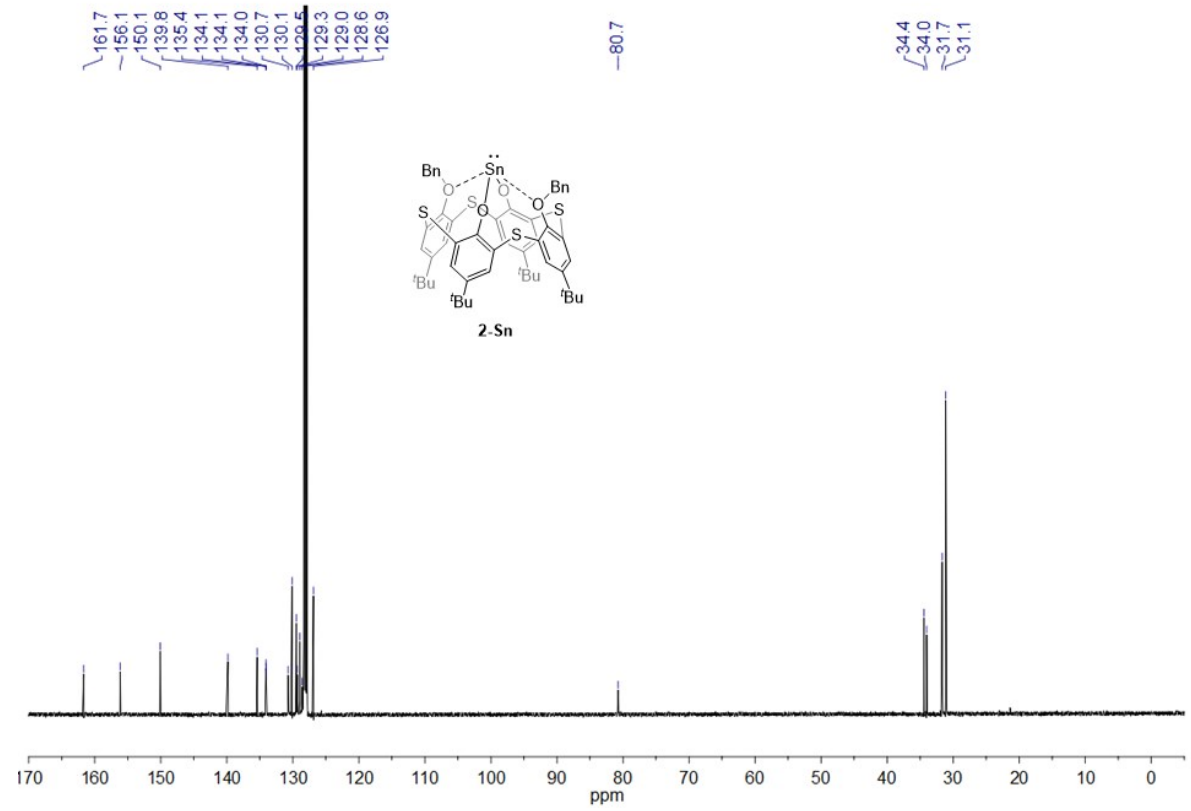

Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of **2-Sn** recorded at 50 °C.

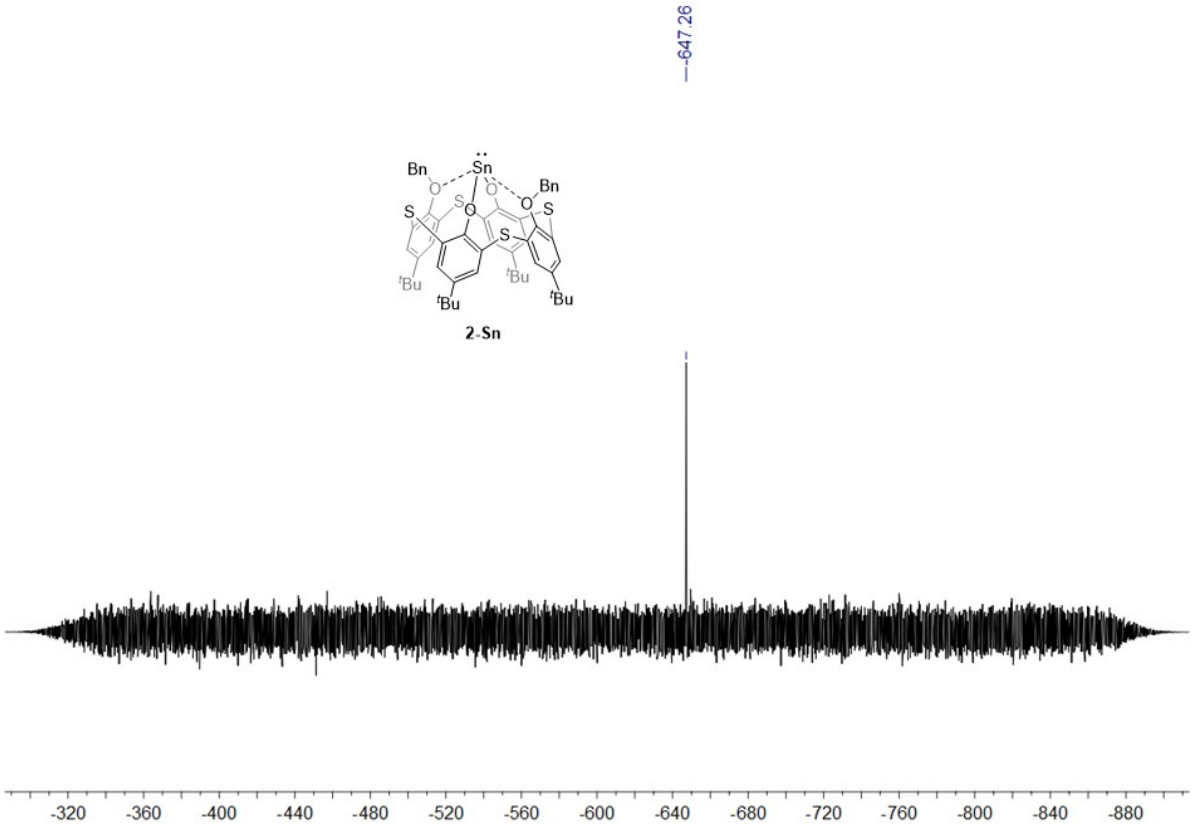

Figure S4. $^{119}Sn\{^{1}H\}$ NMR spectrum of **2-Sn** recorded at 50 °C.

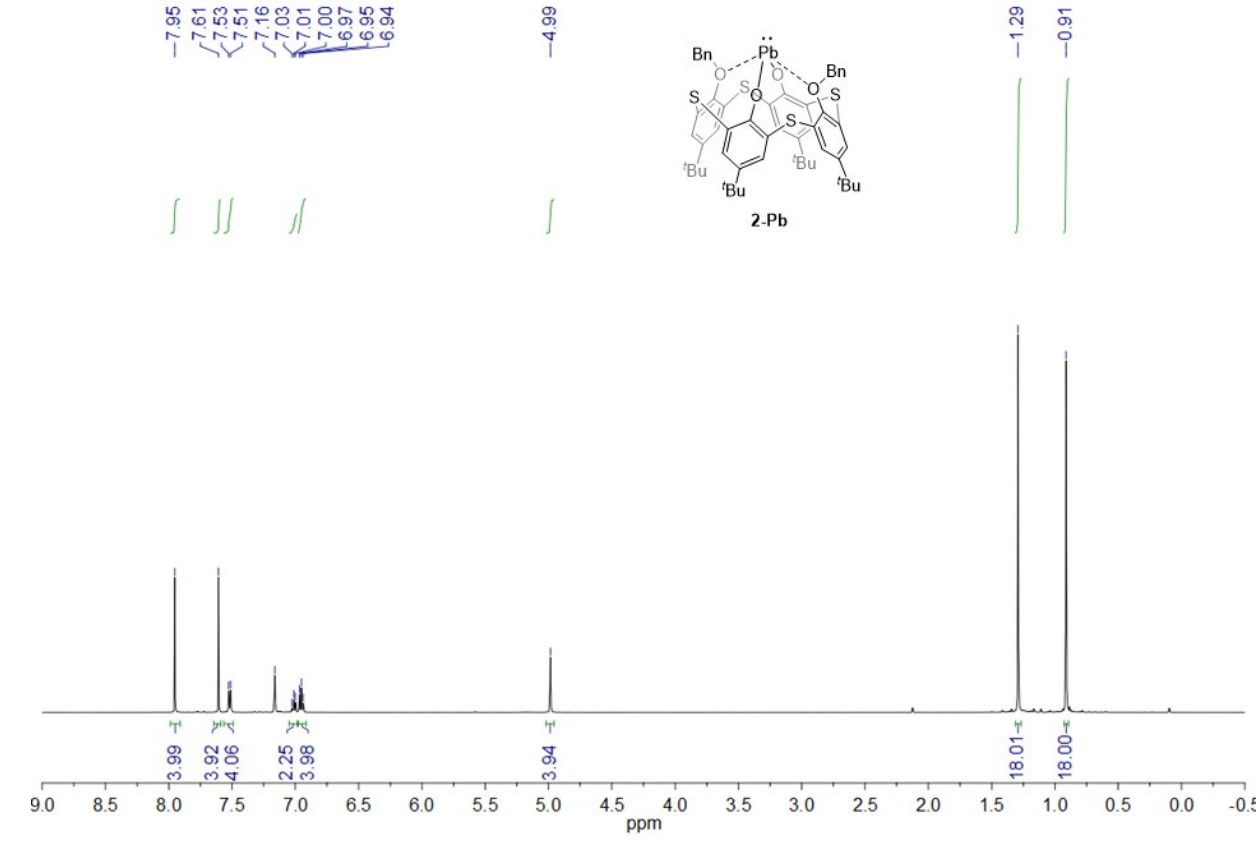

Figure S5. ^{1}H NMR spectrum of **2-Pb** recorded at 50 °C.

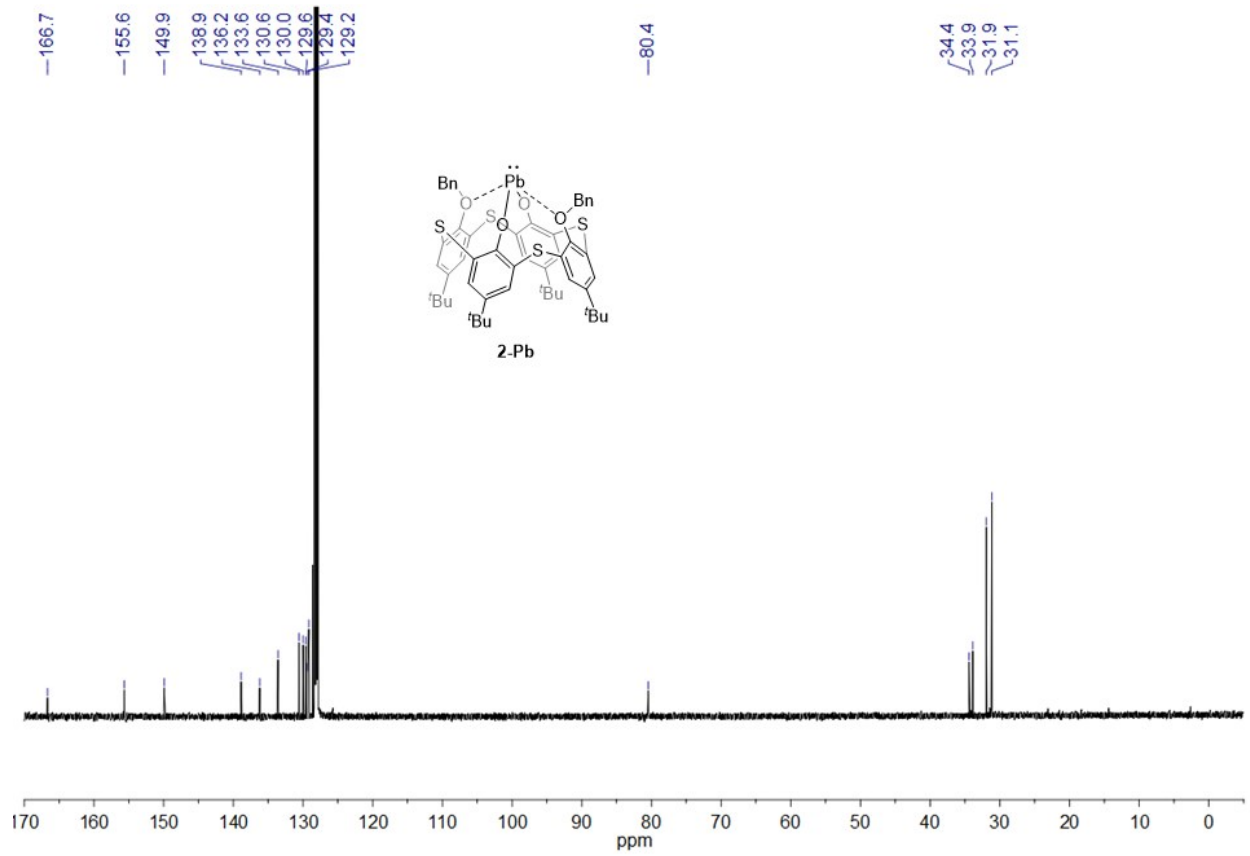

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **2-Pb** recorded at 50 °C.

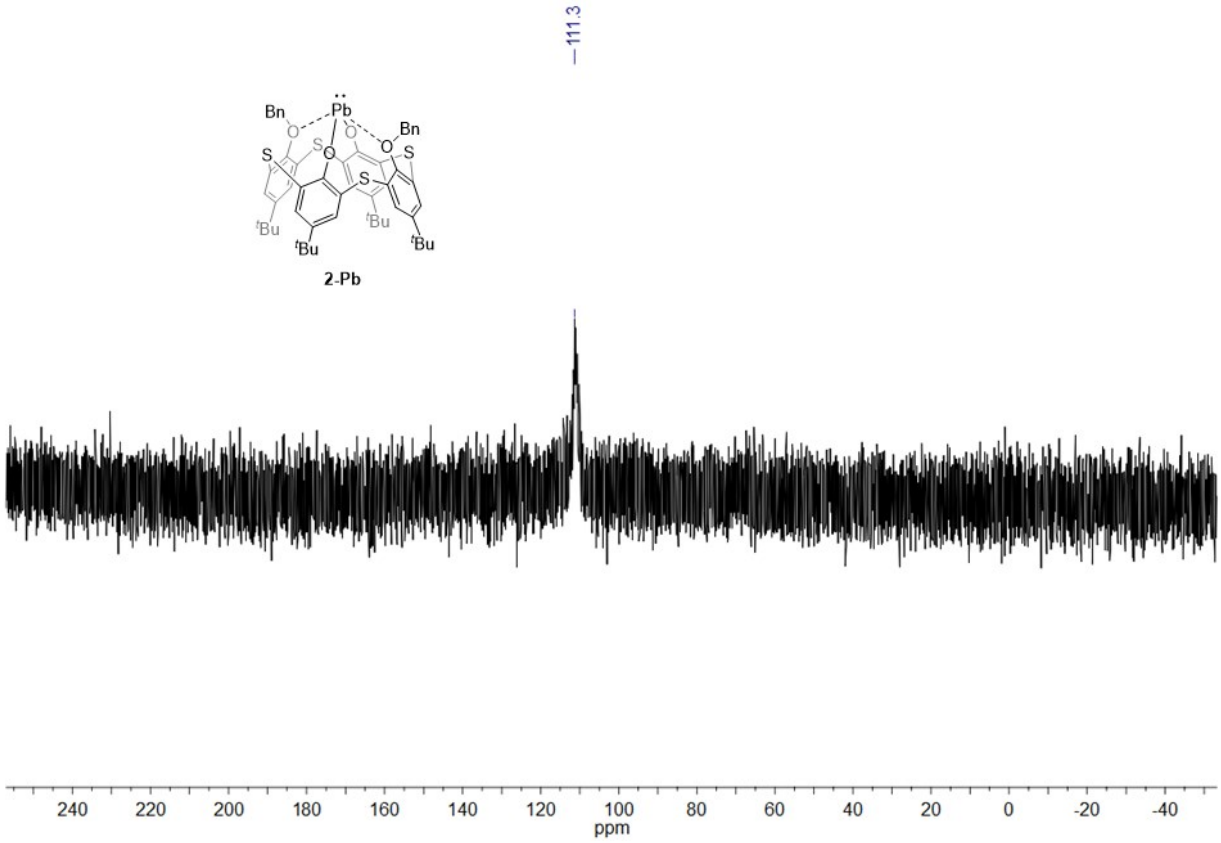

Figure S7. ^{207}Pb NMR spectrum of **2-Pb** recorded at 50 °C.

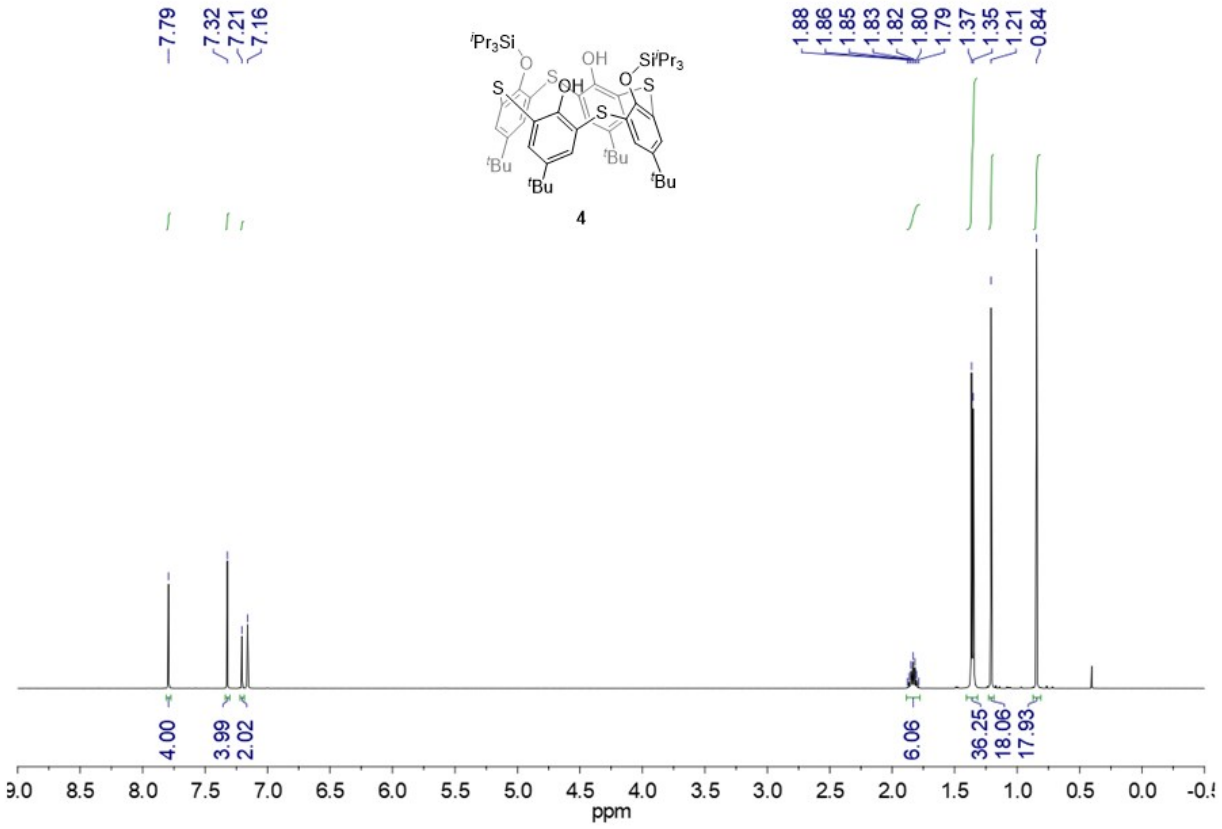

Figure S8. ^{1}H NMR spectrum of **4**.

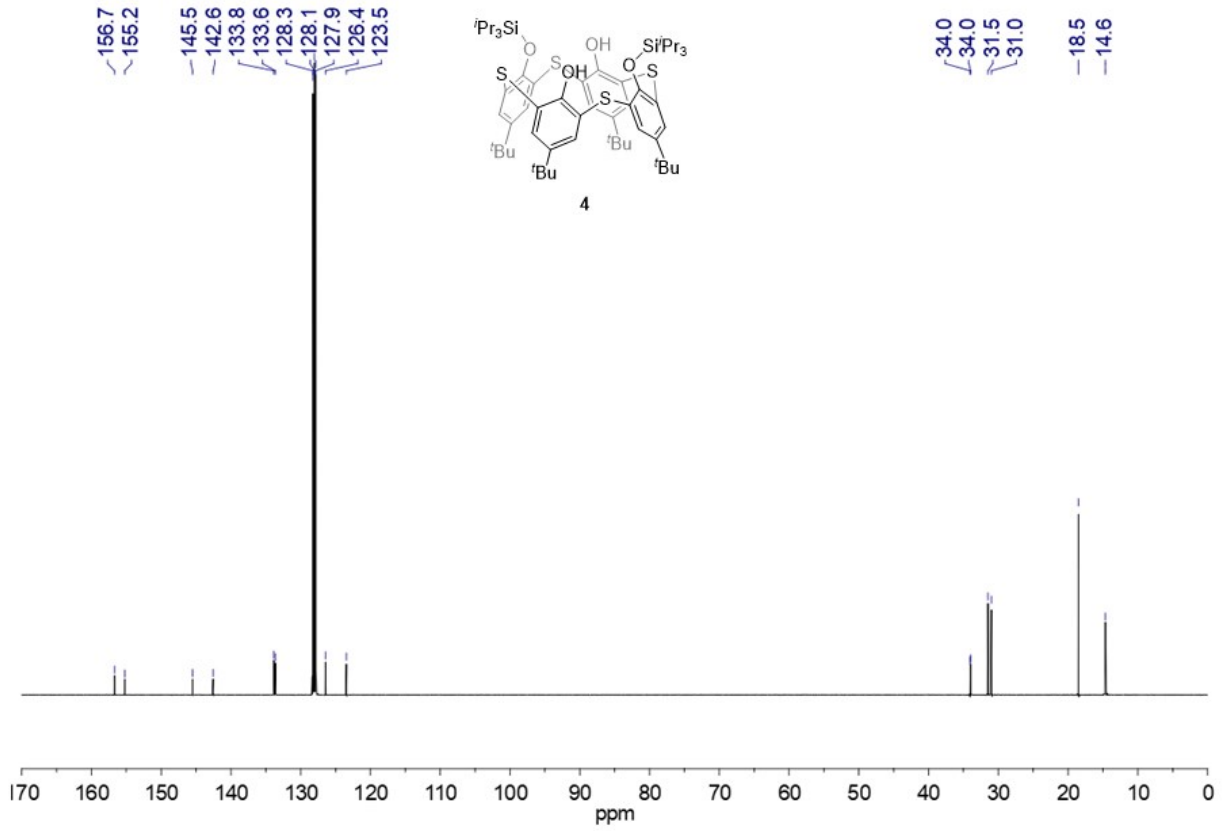

Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of **4**.

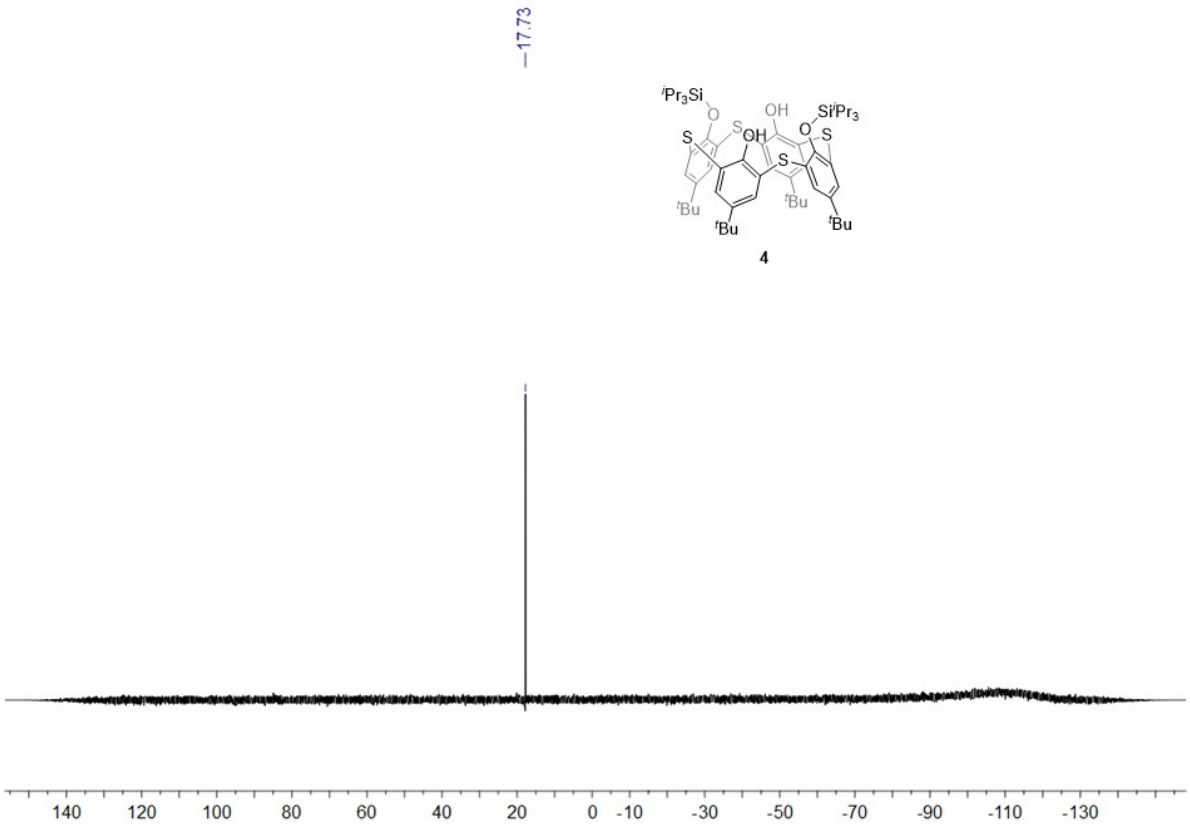

Figure S10. $^{29}Si\{^{1}H\}$ NMR spectrum of **4**.

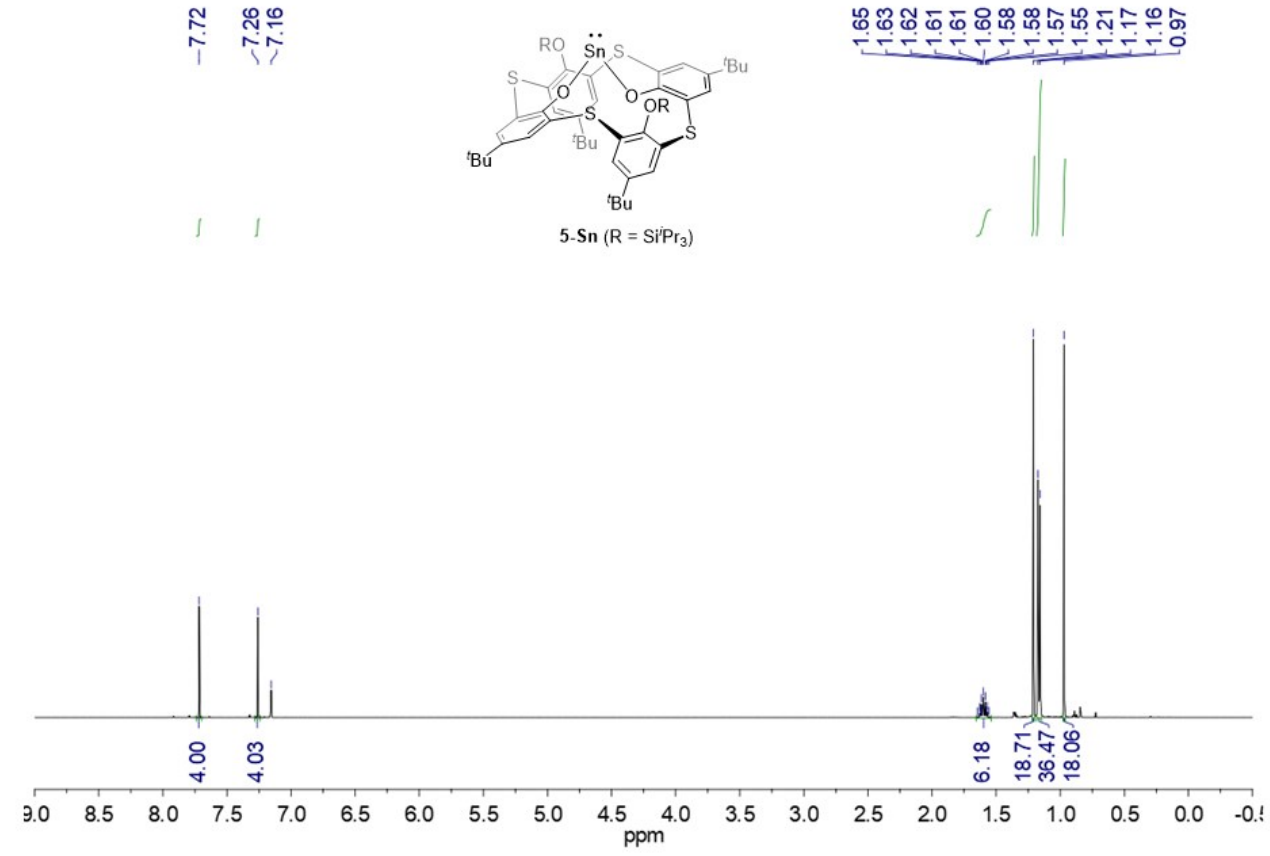

Figure S11. ^{1}H NMR spectrum of **5-Sn**.

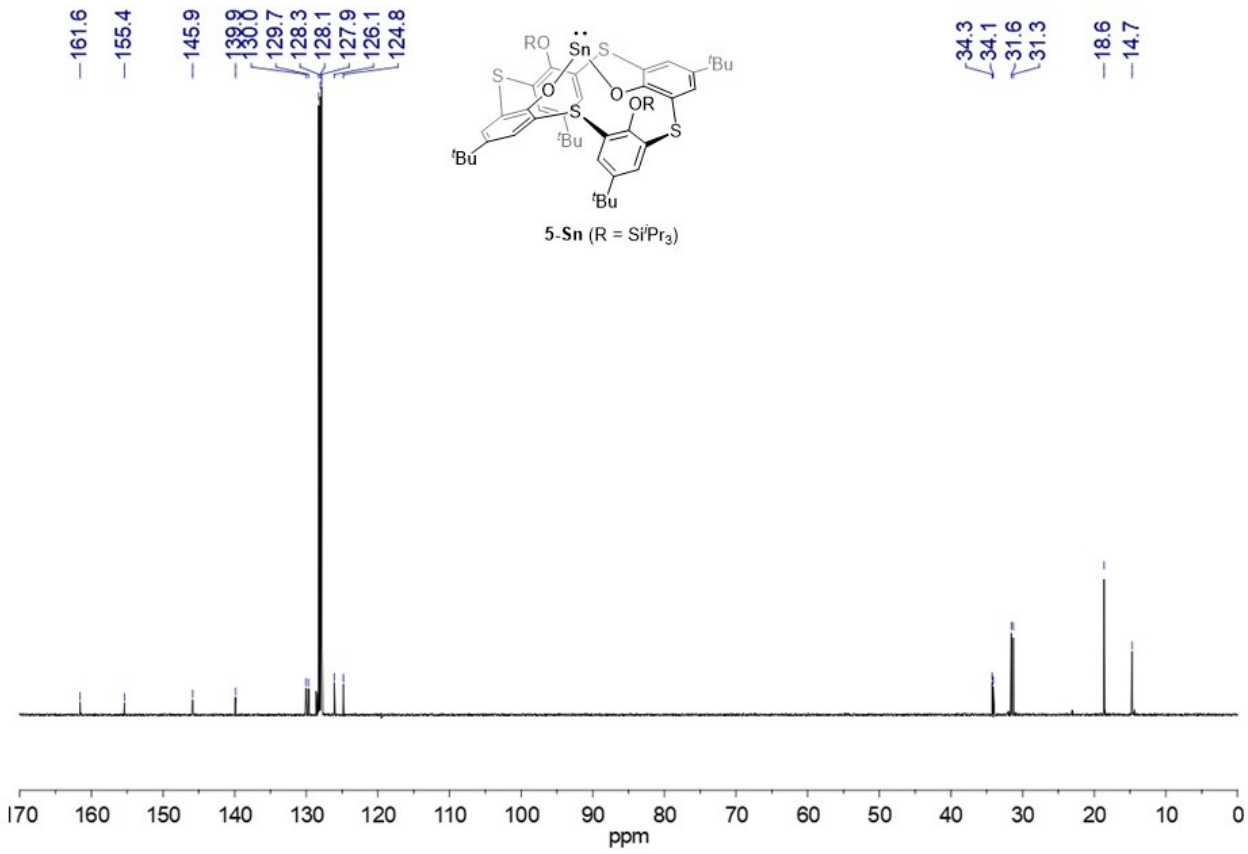

Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of **5-Sn**.

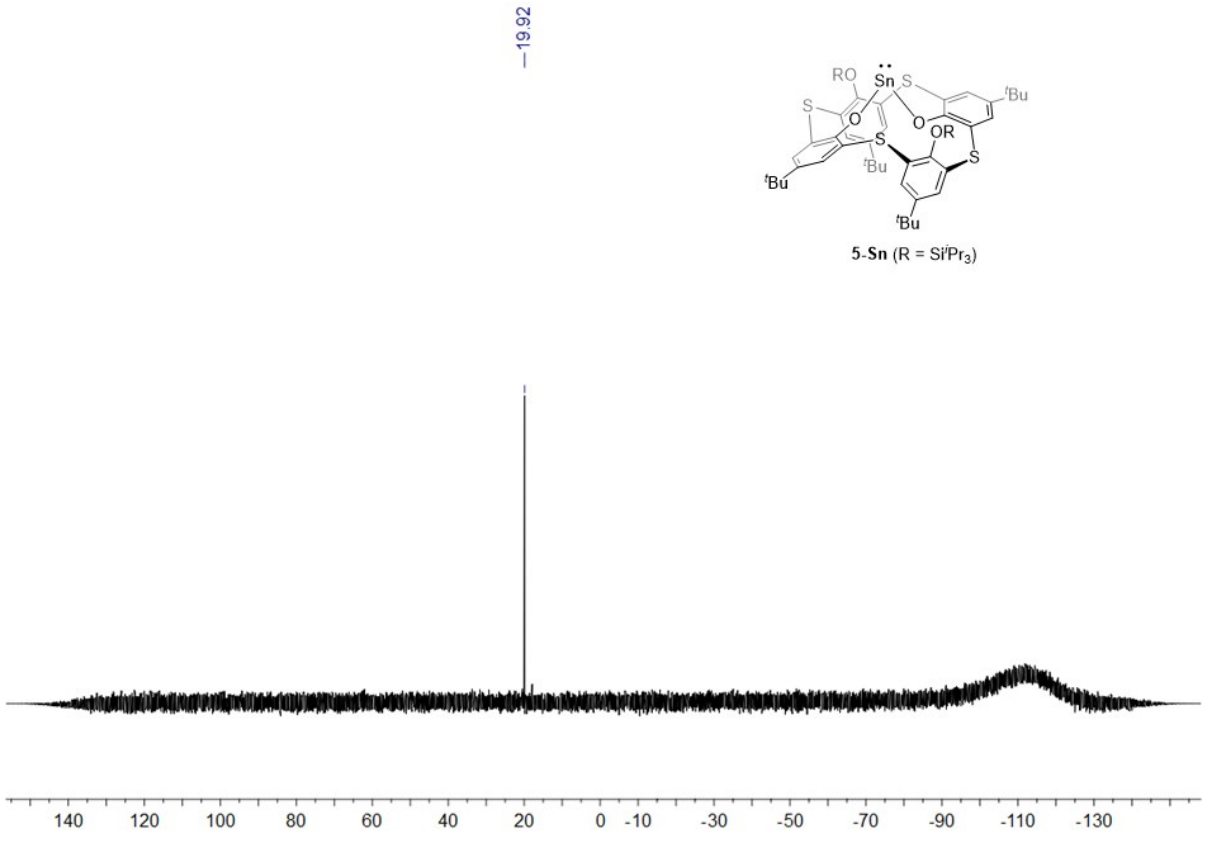

Figure S13. $^{29}Si\{^{1}H\}$ NMR spectrum of **5-Sn**.

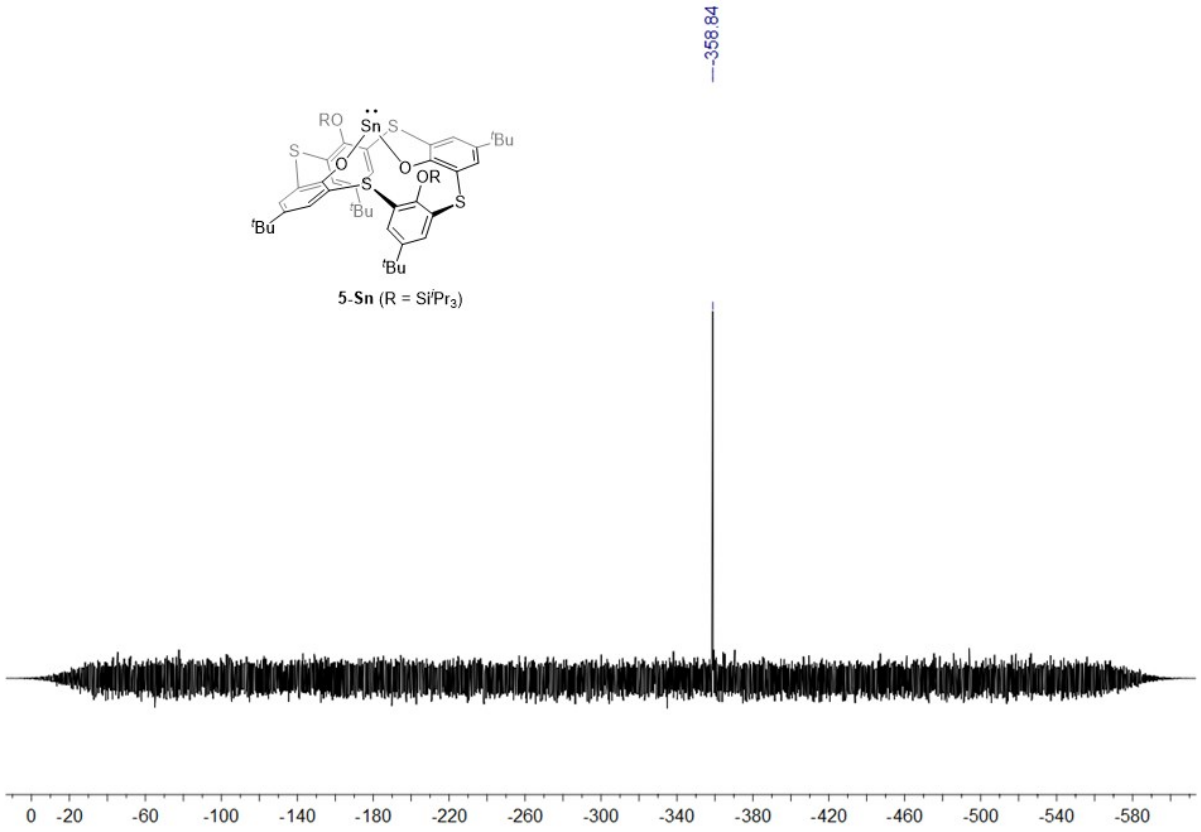

Figure S14. $^{119}Sn\{^1H\}$ NMR spectrum of **5-Sn**.

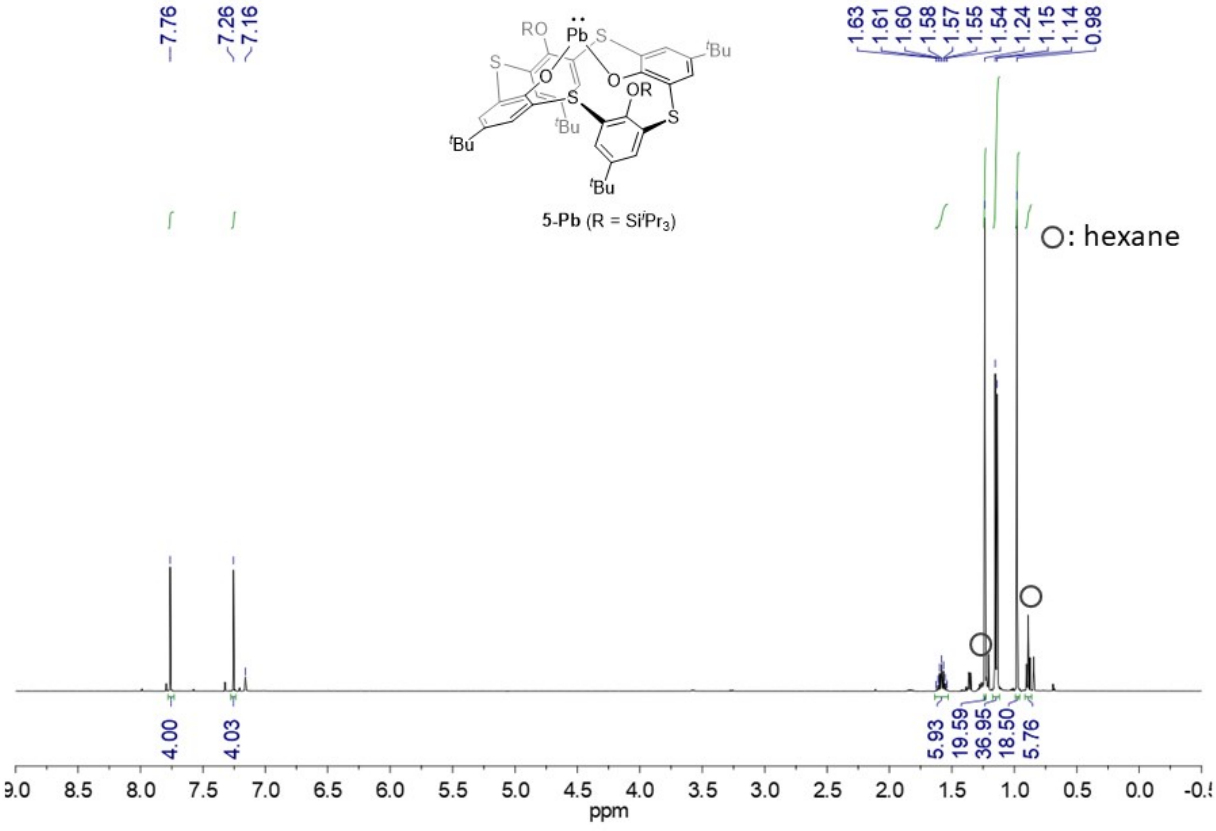

Figure S15. ^1H NMR spectrum of **5-Pb**.

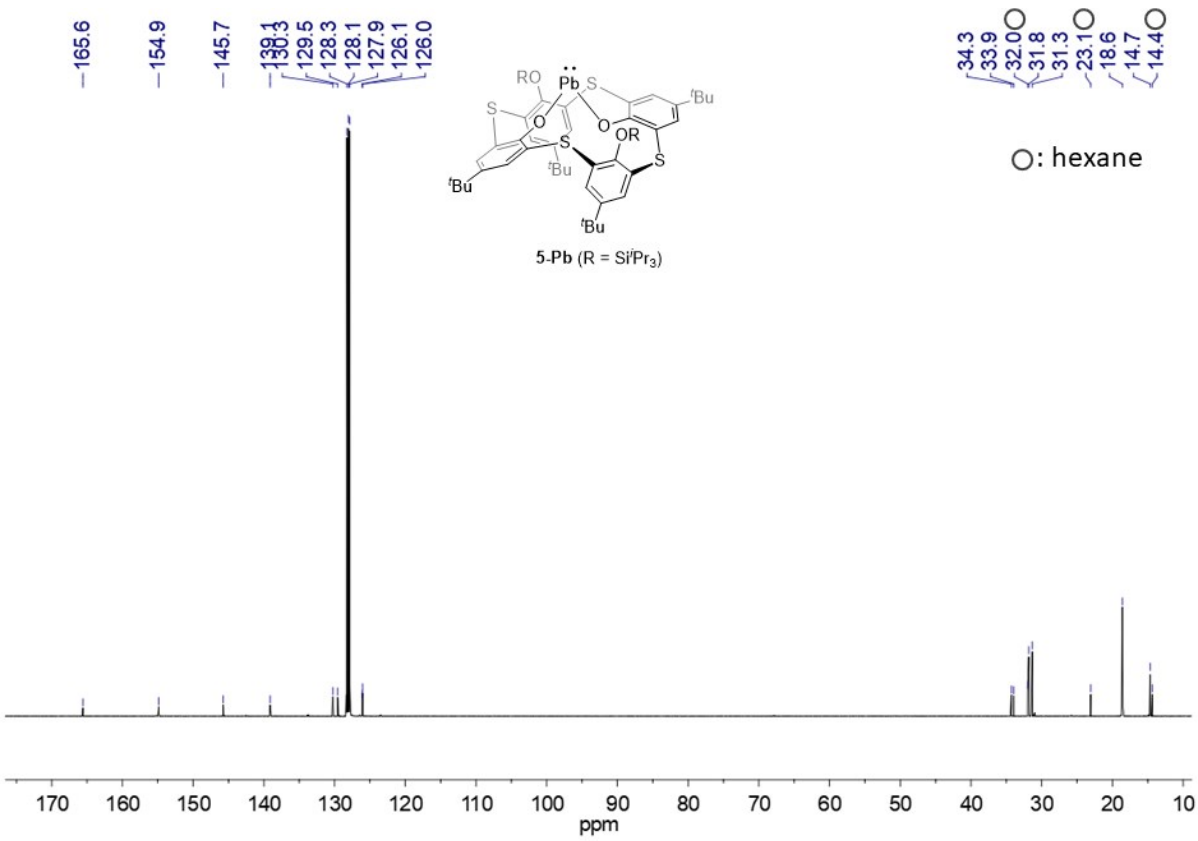

Figure S16. $^{13}C\{^1H\}$ NMR spectrum of **5-Pb**.

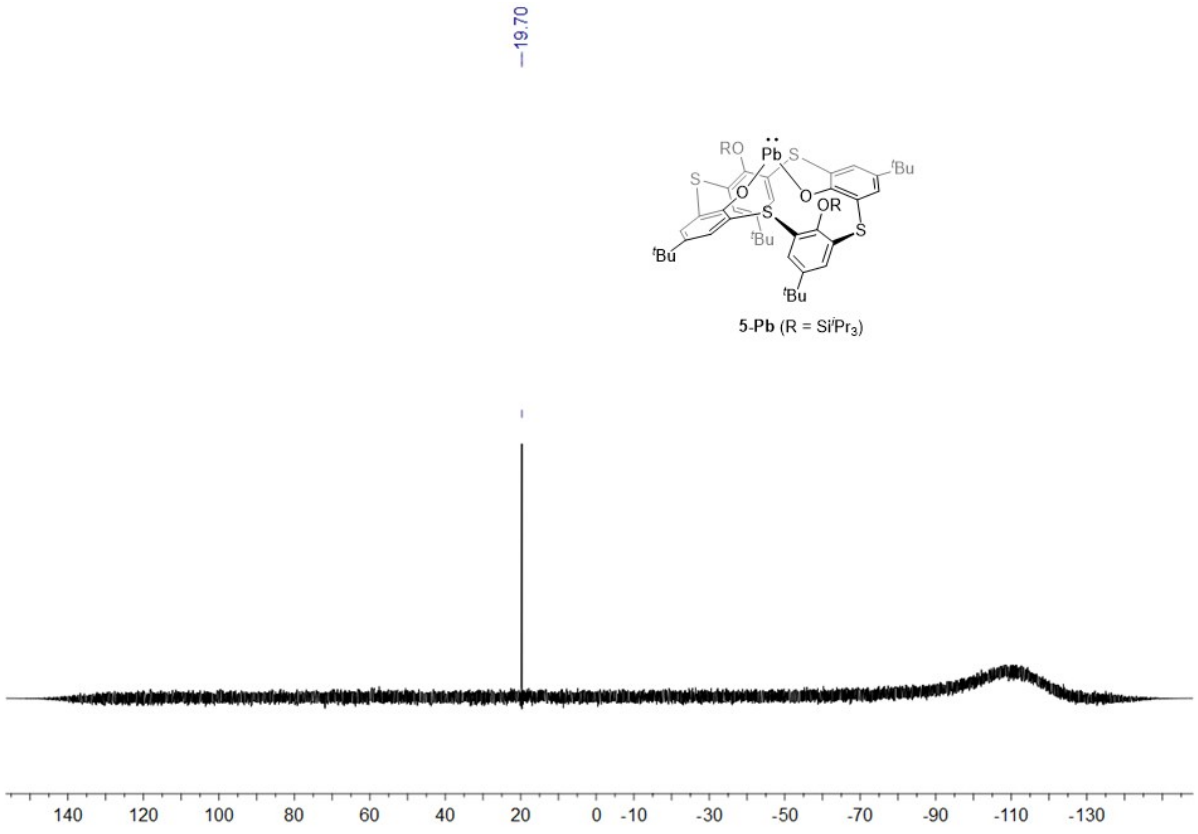

Figure S17. $^{29}Si\{^1H\}$ NMR spectrum of **5-Pb**.

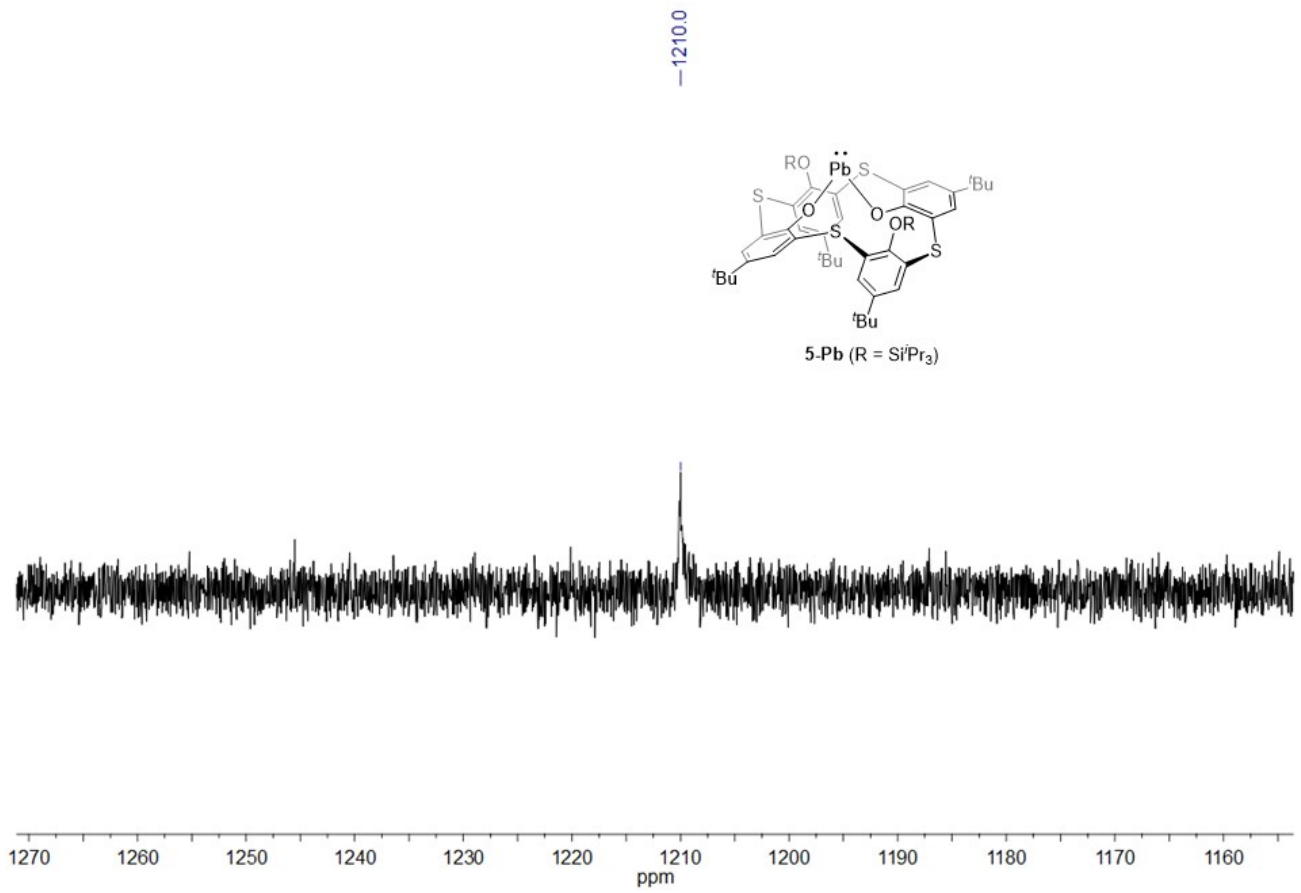

Figure S18. ^{207}Pb NMR spectrum of **5-Pb**.

5. References

(1) Jacobson, R. A., *Private Communication to Rigaku Corp.; Rigaku Corp.; Tokyo Japan* **1998**.

(2) *Crystal Structure 4.0: Single Crystal Structure Analysis Package; Rigaku Corp.; Tokyo, Japan* **2000-2010**.

(3) Sheldrick, G., Crystal structure refinement with SHELXL. *Acta Crystallogr. Sec. C* **2015**, *71,* 3-8.