Supporting Information Materials

for

Synthesis and Structure of a Dianionic Species with a Bond between Pentacoordinated Tin Atoms: Bonding Property of the Tin–Tin Bond

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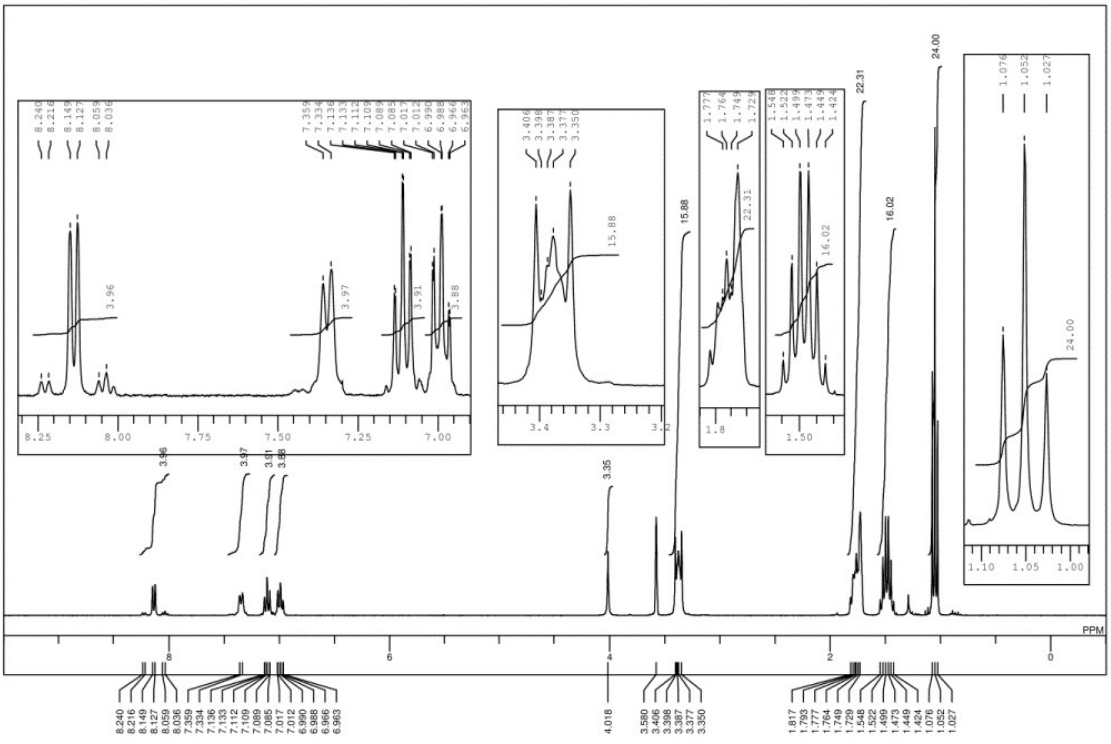


Figure S1. ^{1}H NMR spectrum of distannate **7** in THF-d_8.

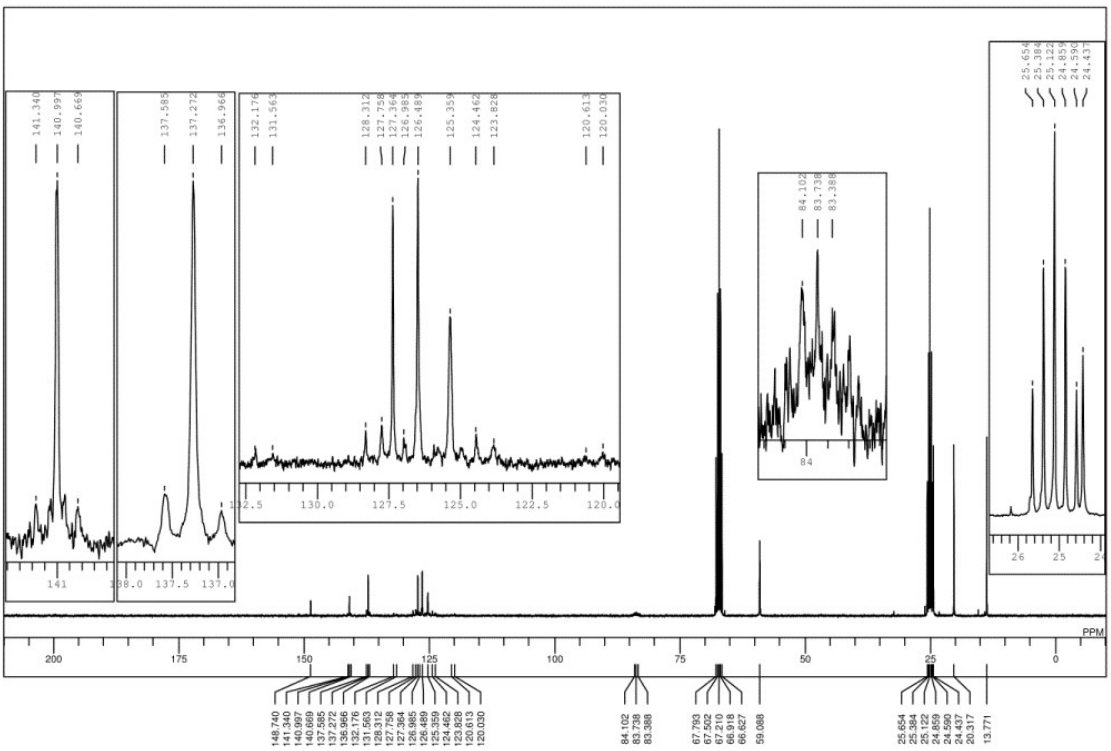


Figure S2. ^{13}C NMR spectrum of distannate **7** in THF-d_8.

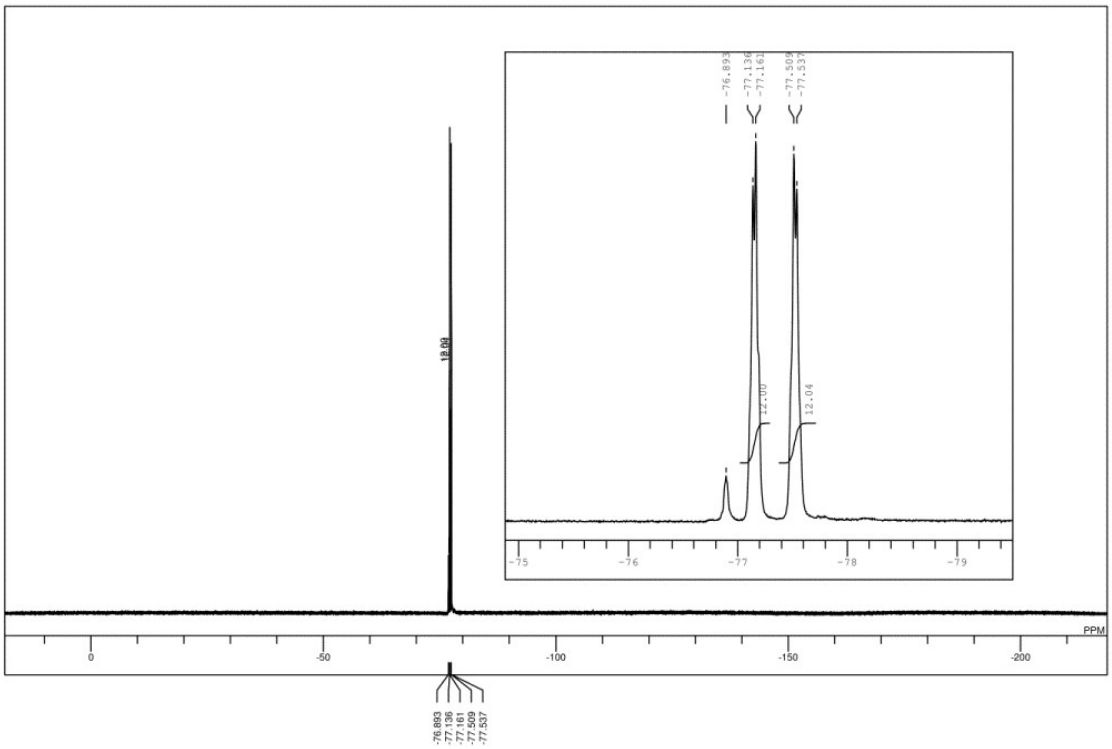


Figure S3. ^{19}F NMR spectrum of distannate **7** in THF-d_8.

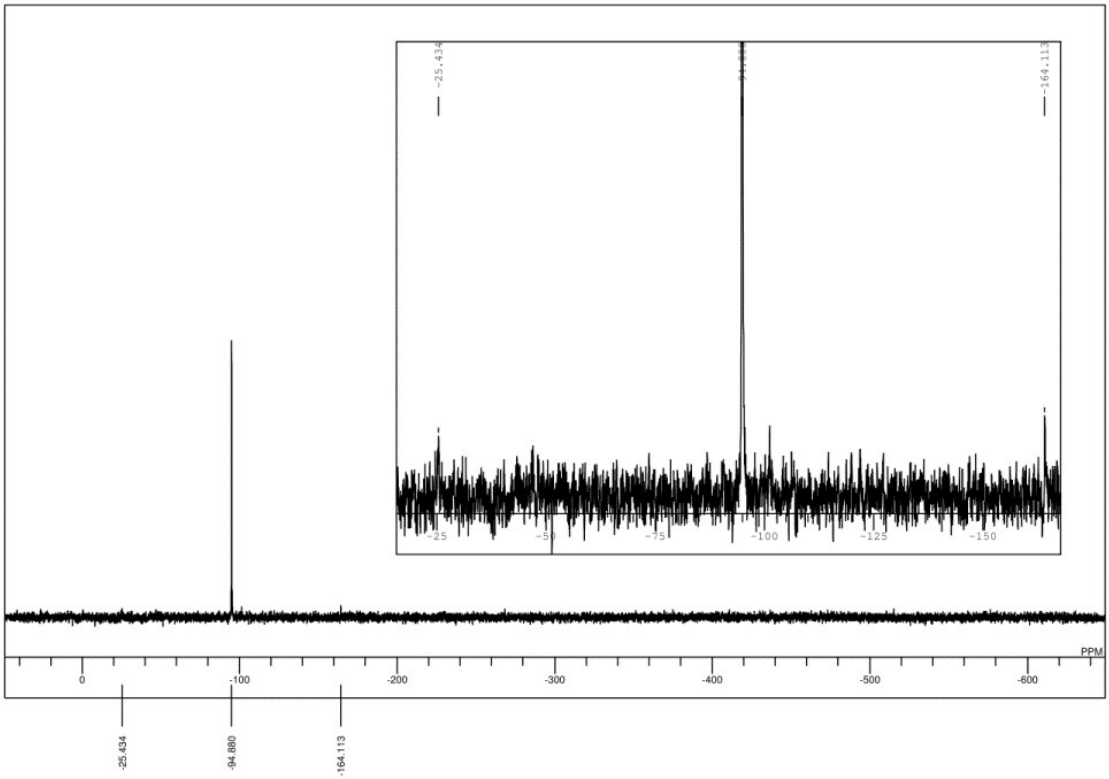


Figure S4. ^{119}Sn NMR spectrum of distannate **7** in THF-d_8.

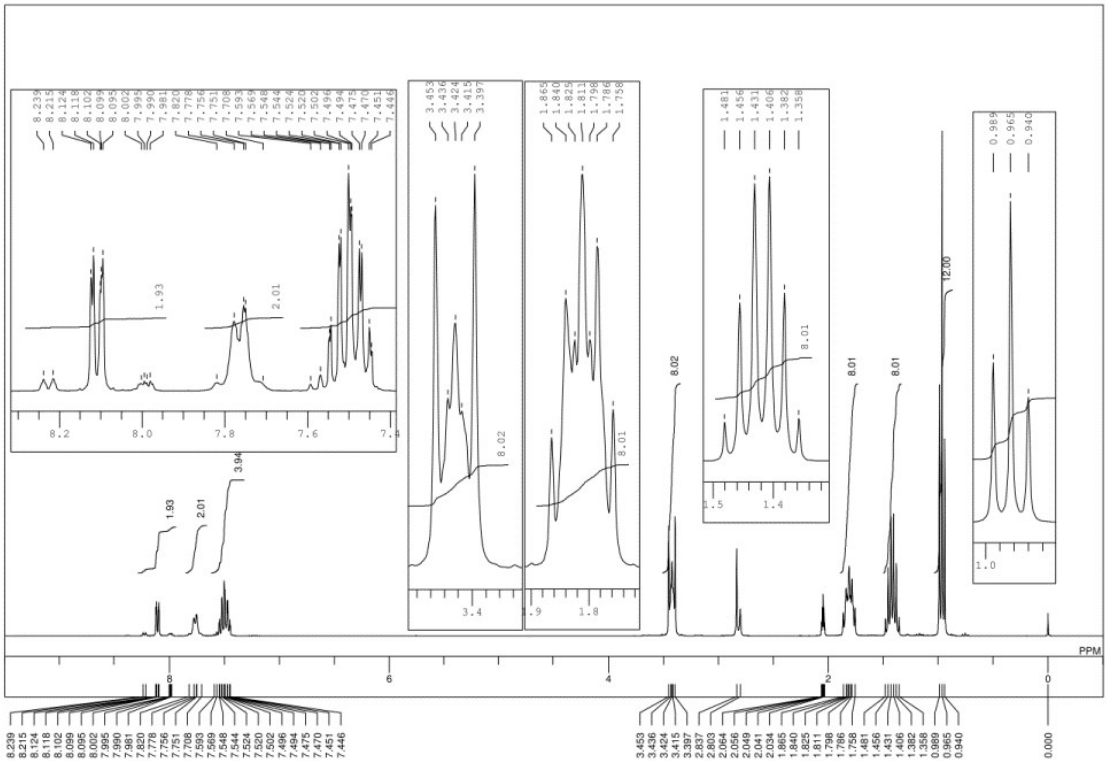


Figure S5. ^{1}H NMR spectrum of chlorostannate **9** in acetone-d_6.

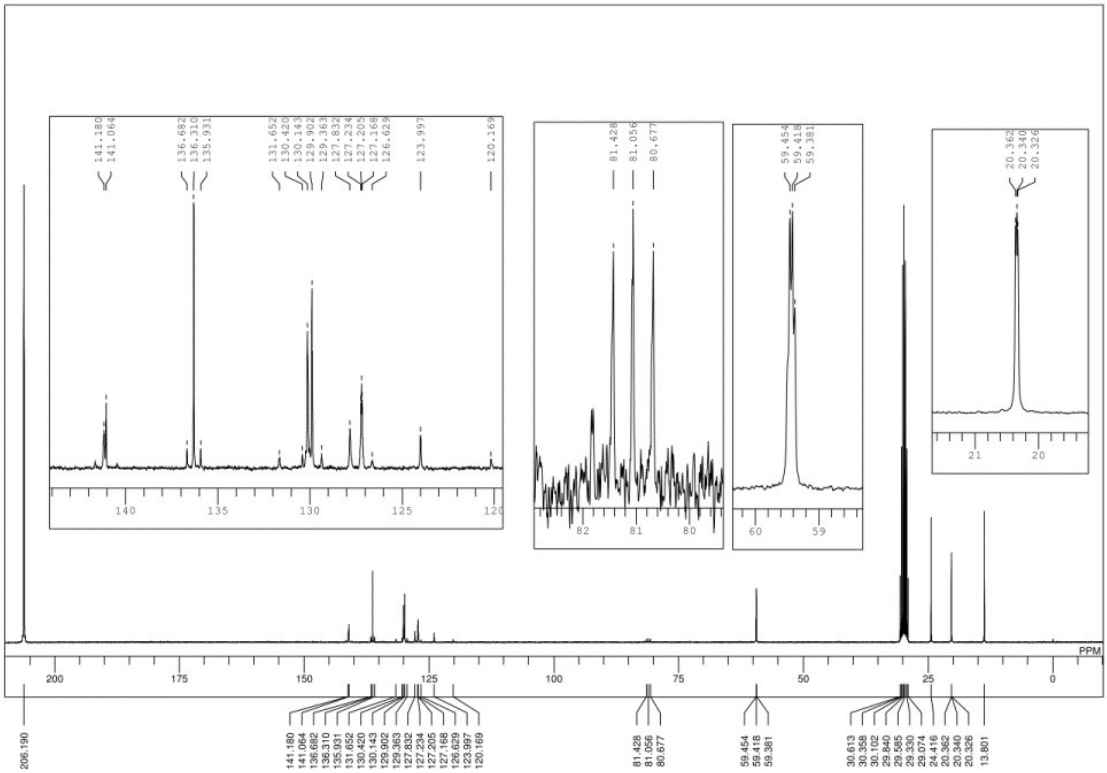


Figure S6. ^{13}C NMR spectrum of chlorostannate **9** in acetone-d_6.

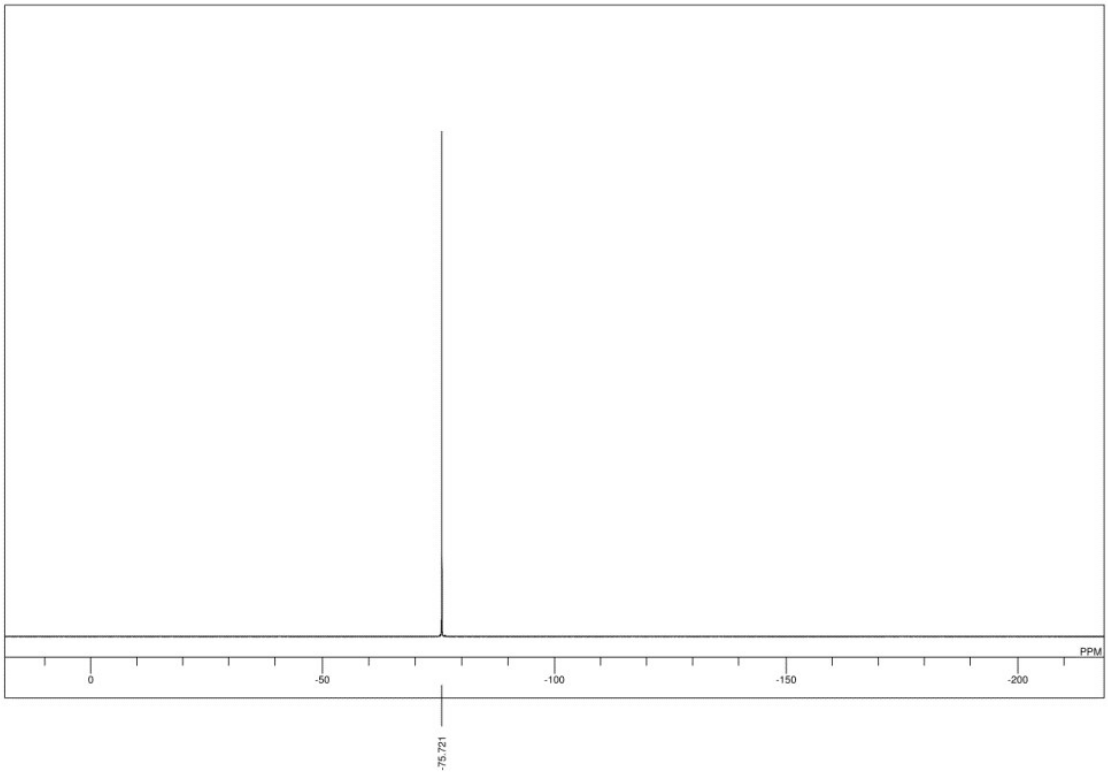


Figure S7. ^{19}F NMR spectrum of chlorostannate **9** in acetone-d_6.

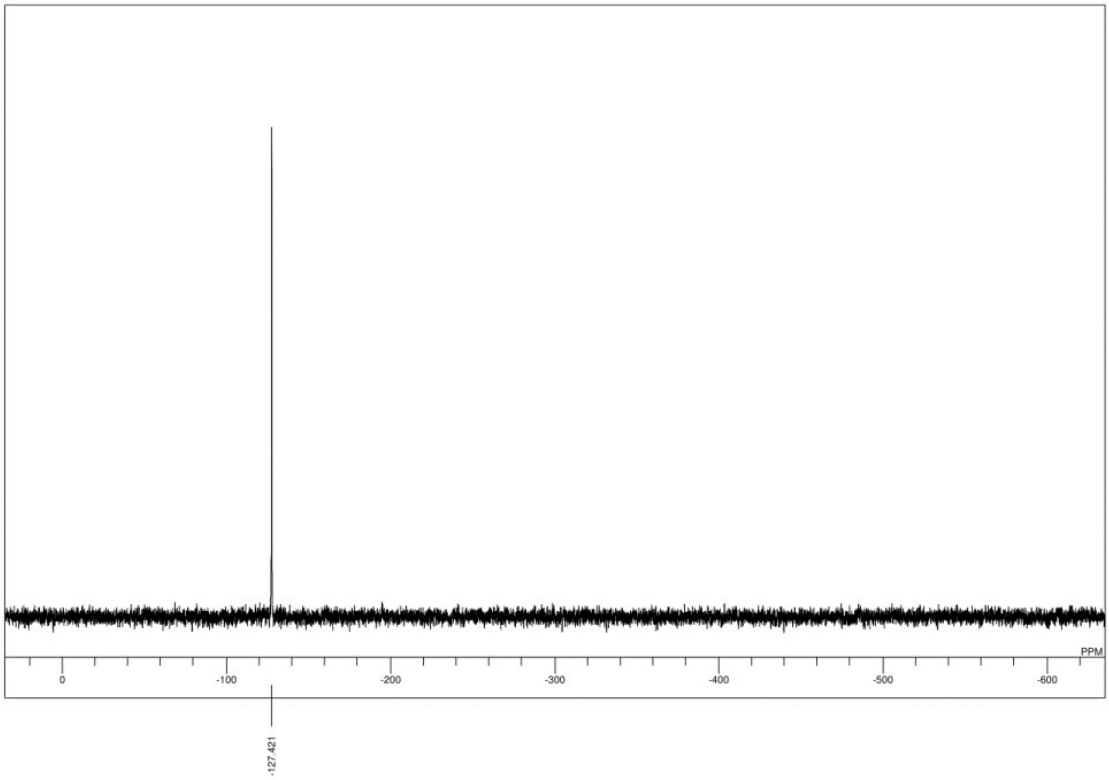


Figure S8. ^{119}Sn NMR spectrum of chlorostannate **9** in acetone-d_6.

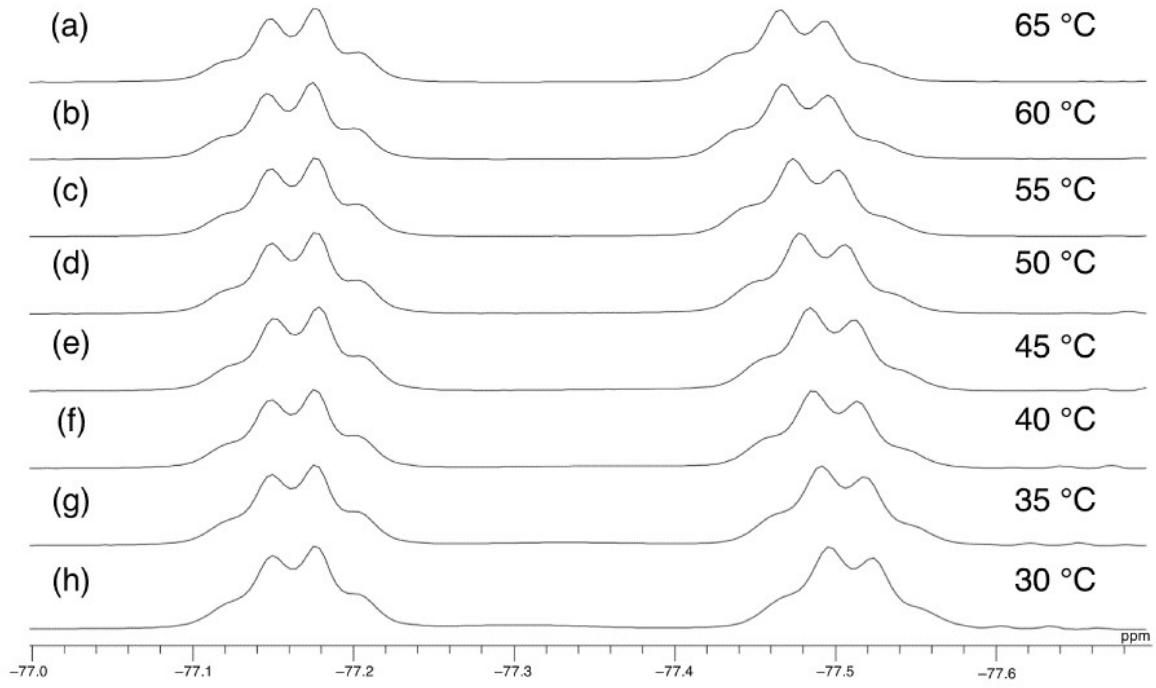


Figure S9. Variable-temperature ^{19}F NMR spectra of distannate **7** in THF-d_8 at (a) 65 °C, (b) 60 °C, (c) 55 °C, (d) 50 °C, (e) 45 °C, (f) 40 °C, (g) 35 °C, (h) 30 °C in the same δ scale.

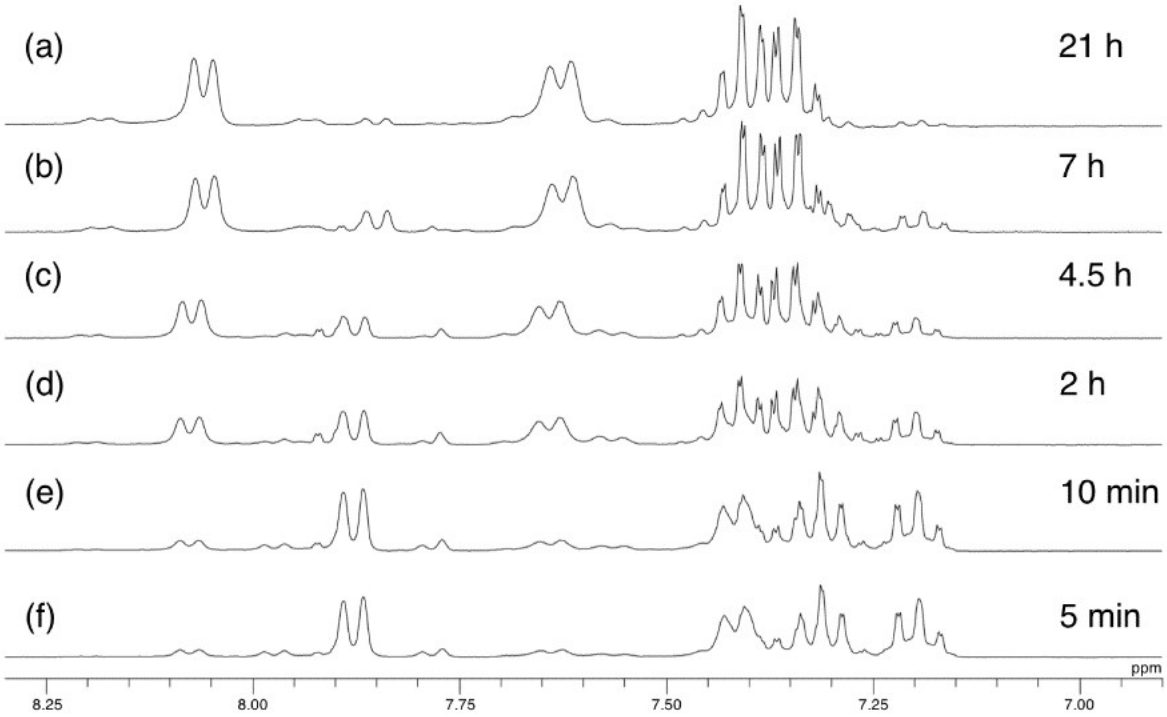


Figure S10. ^{1}H NMR spectra of the reaction of distannate **7** in THF-d_8 with 1M aqueous hydrochloric acid after (a) 21 h, (b) 7 h, (c) 4.5 h, (d) 2 h, (e) 10 min, (f) 5 min in the same δ scale.

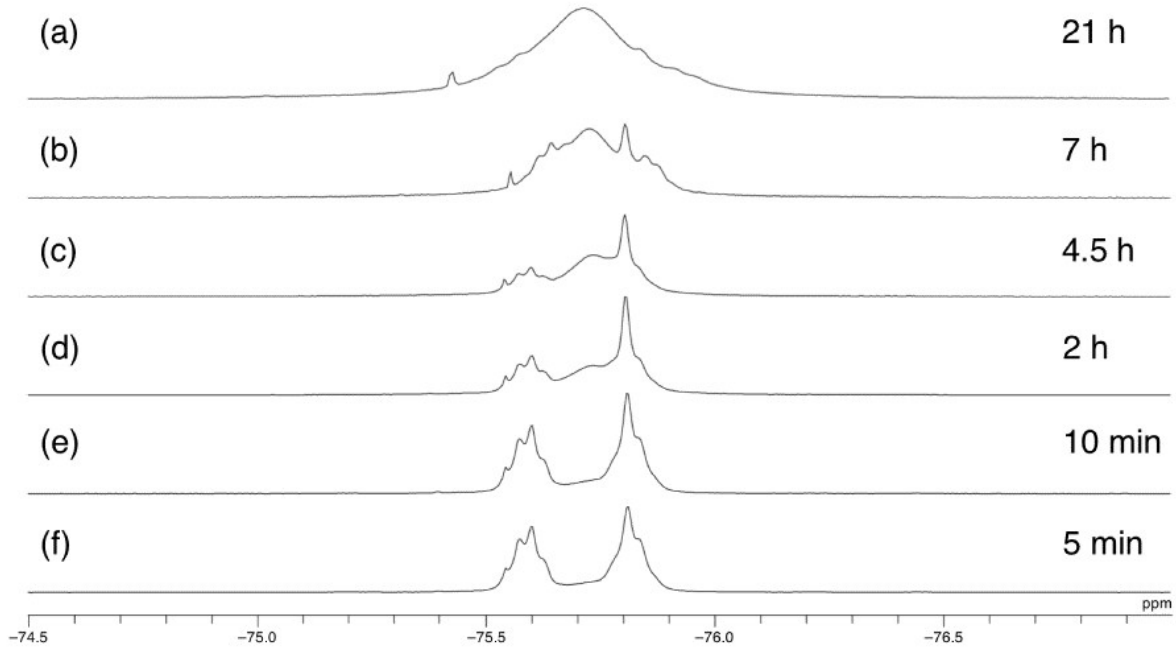


Figure S11. ^{19}F NMR spectra of the reaction of distannate **7** in THF-d_8 with 1M aqueous hydrochloric acid after (a) 21 h, (b) 7 h, (c) 4.5 h, (d) 2 h, (e) 10 min, (f) 5 min in the same δ scale.

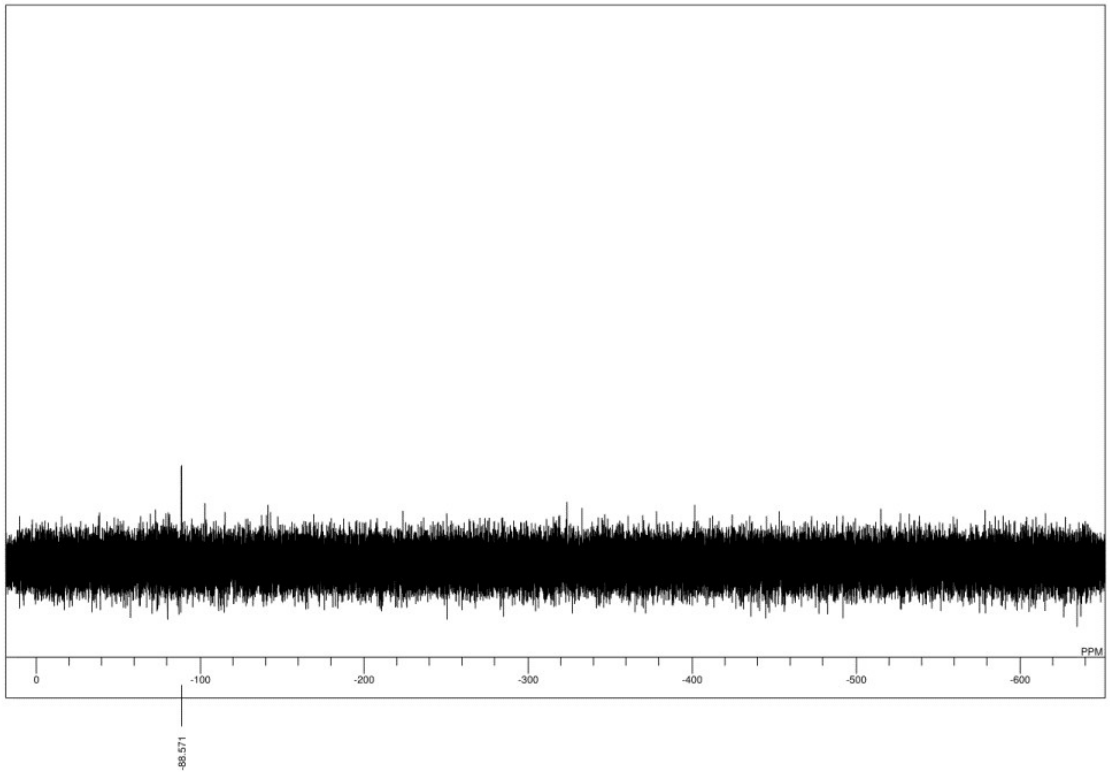


Figure S12. ^{119}Sn NMR spectrum of the reaction of distannate **7** in THF-d_8 with 1M aqueous hydrochloric acid after 15 minutes.

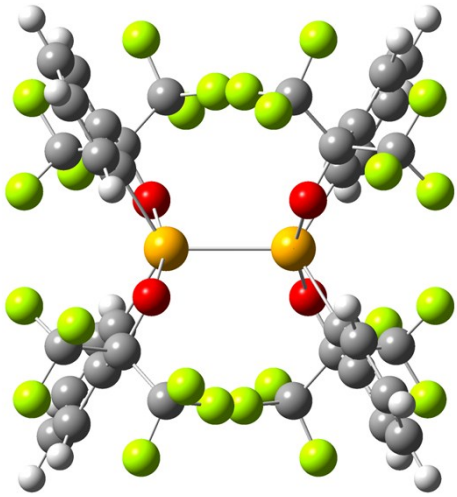
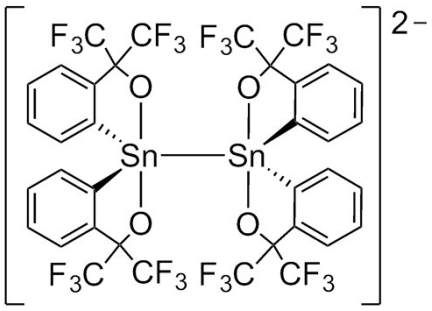


Figure S13. Optimized structure of the dianion part of distannate **7** (orange: tin; red: oxygen; gray: carbon; yellow-green: fluorine; white: hydrogen).

Table S1. Selected bond lengths (Å) and torsion angles (°) of the X-ray crystal structure and the DFT-calculated structure, atomic charges obtained by natural population analysis, hybridization of tin atoms to constitute the Sn–Sn bond obtained by the natural bond orbital analysis, and the Wiberg bond index of the dianion part of **7**.

	7 (X-ray)	**7** (calc.)
Sn1–Sn1* (Å)	2.7522(14)	2.783
Sn1–O1 (Å)	2.166(9)	2.157
Sn1–O2 (Å)	2.162(9)	2.157
Sn1–C1 (Å)	2.155(13)	2.151
Sn1–C10 (Å)	2.104(11)	2.151
O1–Sn1–Sn1*–O1* (°)	–122.8(4)	120.4
O1–Sn1–Sn1*–O2* (°)	58.6(4)	–59.6
q_{Sn1}	–	1.581
q_{Sn2}	–	1.581
q_{O1}	–	–0.865
q_{O2}	–	–0.865
q_{O3}	–	–0.865
q_{O4}	–	–0.865
q_{C1}	–	–0.430
q_{C10}	–	–0.430
Sn1 hybridization	–	$sp^{2.35}$
Sn2 hybridization	–	$sp^{2.35}$
Wiberg bond index	–	0.843

Table S2. Cartesian coordinates in optimized geometry of the dianion part of **7** (Total energy: –16119.79727981 a.u.).



	Coordinates (Angstroms)		
Element	X	Y	Z
Sn	1.39133	-0.000076	-0.000007
Sn	-1.391336	0.000072	0.000008
C	2.45983	-1.741092	0.674059
C	2.820435	-2.016606	1.995285
H	2.571422	-1.29739	2.771865
C	3.490215	-3.19717	2.311873
H	3.763111	-3.412689	3.343879
C	3.804633	-4.106602	1.299515
C	3.455708	-3.836765	-0.02349
H	3.710814	-4.551971	-0.798215
C	2.780077	-2.651653	-0.33558
C	2.358041	-2.252296	-1.773628
O	1.712463	-1.060672	-1.850624
C	3.635696	-2.13267	-2.657038
F	4.49389	-1.252828	-2.107189
F	4.324949	-3.297416	-2.816792
F	3.362237	-1.690524	-3.900281
C	1.391689	-3.329731	-2.348518
F	0.315163	-3.439642	-1.559534
F	1.937019	-4.576464	-2.448307
F	0.958071	-3.017209	-3.585436
C	2.460007	1.740827	-0.674087
C	2.82061	2.016309	-1.99532
H	2.571499	1.297126	-2.771899
C	3.490514	3.196801	-2.311917
H	3.763408	3.412297	-3.343929
C	3.805055	4.106193	-1.299561
C	3.456133	3.836386	0.02345
H	3.71133	4.551561	0.798174

C	2.780382	2.651344	0.335549
C	2.358328	2.25203	1.773605
O	1.712606	1.060485	1.850607
C	1.392128	3.329587	2.34852
F	0.31561	3.439658	1.559549
F	0.958482	3.017107	3.58544
F	1.937631	4.576244	2.448319
C	3.635987	2.13224	2.656986
F	4.494065	1.252303	2.107109
F	4.325383	3.296902	2.816742
F	3.362501	1.690111	3.900229
C	-2.459822	1.741091	0.674091
C	-2.820413	2.016602	1.995321
H	-2.571399	1.297381	2.771896
C	-3.49018	3.197171	2.311919
H	-3.763064	3.412689	3.343929
C	-3.804598	4.10661	1.299568
C	-3.455688	3.836776	-0.023441
H	-3.710793	4.551986	-0.798162
C	-2.78007	2.651658	-0.335541
C	-2.358054	2.252304	-1.773596
C	-3.635723	2.132693	-2.656988
F	-4.493877	1.252784	-2.107182
F	-4.325021	3.297424	-2.816652
F	-3.36227	1.690639	-3.900265
C	-1.3917	3.329732	-2.348491
F	-0.315106	3.439547	-1.559585
F	-0.958193	3.017267	-3.585462
F	-1.936983	4.576496	-2.44816
O	-1.712487	1.060675	-1.850604
C	-2.460026	-1.740824	-0.674067
C	-2.820649	-2.016299	-1.995296
H	-2.571548	-1.297111	-2.771874
C	-3.49056	-3.196787	-2.311889
H	-3.76347	-3.412277	-3.343898
C	-3.805088	-4.106184	-1.299533
C	-3.456145	-3.836385	0.023474
H	-3.711334	-4.551563	0.798198
C	-2.780388	-2.651346	0.33557

C	-2.358314	-2.25204	1.773621
O	-1.712592	-1.060494	1.850621
C	-3.635962	-2.132257	2.657021
F	-4.49404	-1.252303	2.107171
F	-4.325364	-3.296916	2.816763
F	-3.362456	-1.690154	3.900269
C	-1.392104	-3.329598	2.348517
F	-0.315584	-3.439642	1.559544
F	-0.958461	-3.017137	3.585442
F	-1.937593	-4.576263	2.448292
H	-4.324142	-5.033159	-1.538335
H	4.324103	5.03317	-1.538365
H	-4.323541	5.033646	1.538374
H	4.323587	-5.033634	1.538312