Supporting Information

Functionalization of Sn/S clusters with hetero- and polyaromatics

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1. Supplementary Figures of Electrospray Ionization (ESI) Mass Spectrometry

Mass spectra were recorded in the ESI (+) cation mode from the reaction solutions of **A** with 3-quinolinecarbaldehyde hydrazone (compound **9**), 3-acetylquinoline hydrazone (compound **11**), 4-acetylisoquinoline hydrazone (compound **12**), 2-acetylanthracene hydrazone (compound **13**), 2-acetylphenanthrene hydrazone (compound **14**) and 1-naphthylhydrazine (compound **15**). The resulting spectra and corresponding structure diagrams are shown in Figures S1-S6.

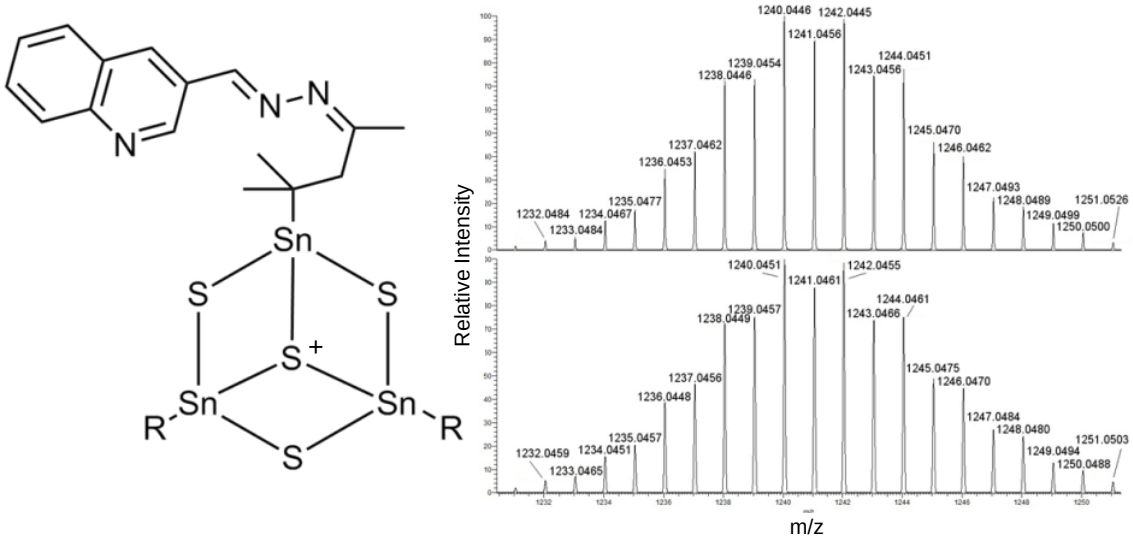

Figure S1. Schematic drawing of the cluster cation in **9** (left; R drawn once in detail) along with the high-resolution mass cluster of $[(C_{16}H_{18}N_3Sn)_3S_4]^+$ as measured by ESI^+ MS (top right) and calculated (bottom right).

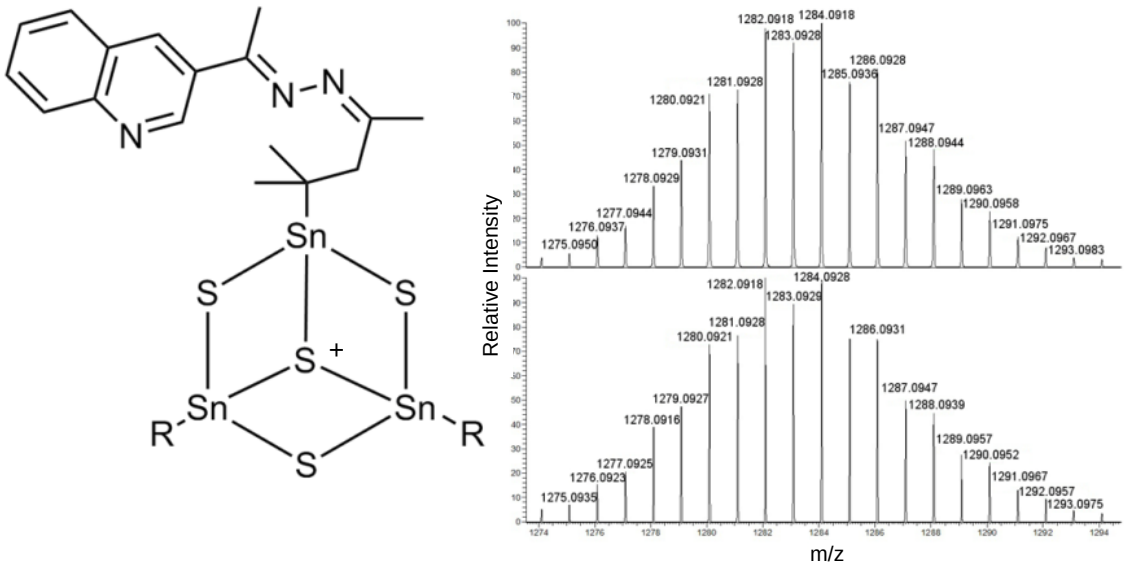

Figure S2. Schematic drawing of the cluster cation in **11** (left; R drawn once in detail) along with the high-resolution mass cluster of $[(C_{17}H_{20}N_3Sn)_3S_4]^+$ as measured by ESI^+ MS (top right) and calculated (bottom right).

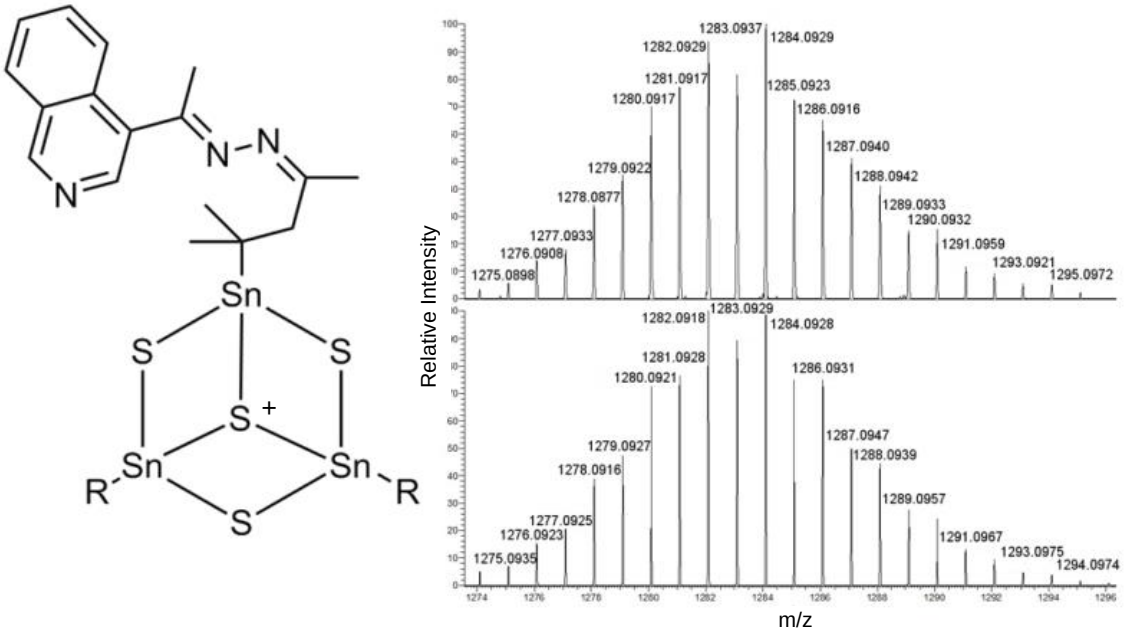

Figure S3. Schematic drawing of the cluster cation in **12** (left; R drawn once in detail) along with the high-resolution mass cluster of $[(C_{17}H_{20}N_3Sn)_3S_4]^+$ as measured by ESI^+ MS (top right) and calculated (bottom right).

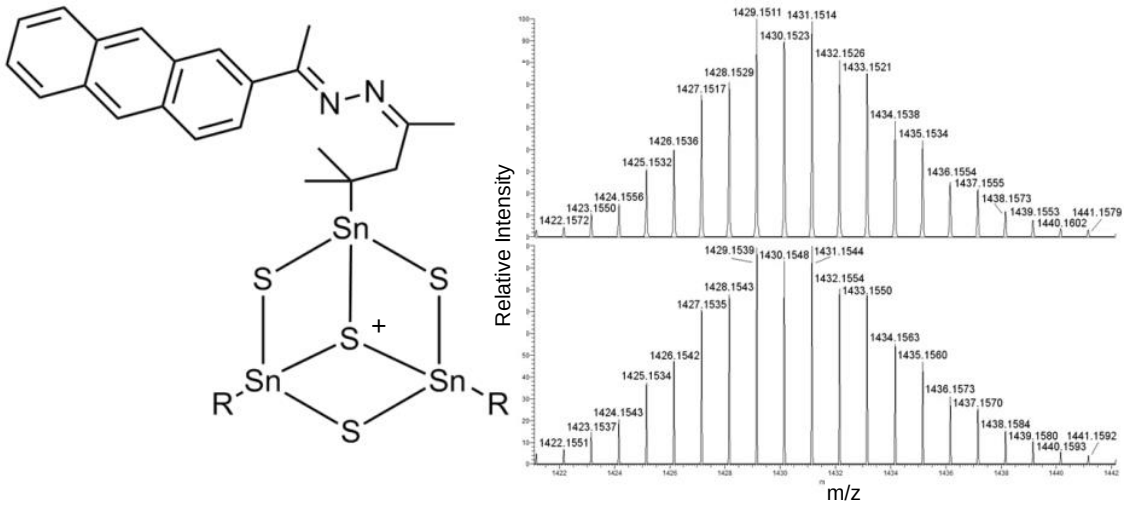

Figure S4. Schematic drawing of the cluster cation in **13** (left; R drawn once in detail) along with the high-resolution mass cluster of $[(C_{22}H_{23}N_2Sn)_3S_4]^+$ as measured by ESI^+ MS (top right) and calculated (bottom right).

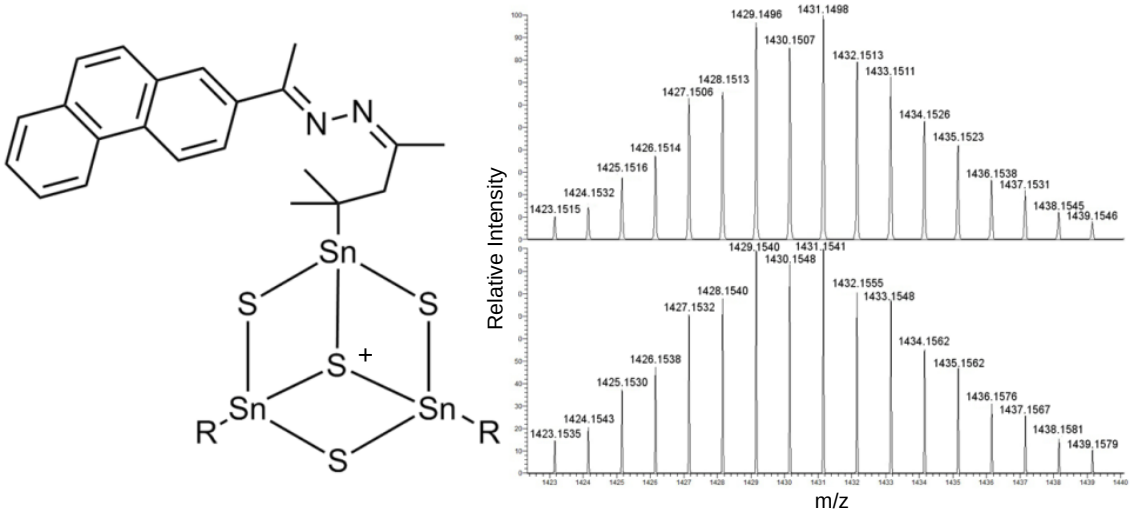

Figure S5. Schematic drawing of the cluster cation in **14** (left; R drawn once in detail) along with the high-resolution mass cluster of $[(C_{22}H_{23}N_2Sn)_3S_4]^+$ as measured by ESI^+ MS (top right) and calculated (bottom right).

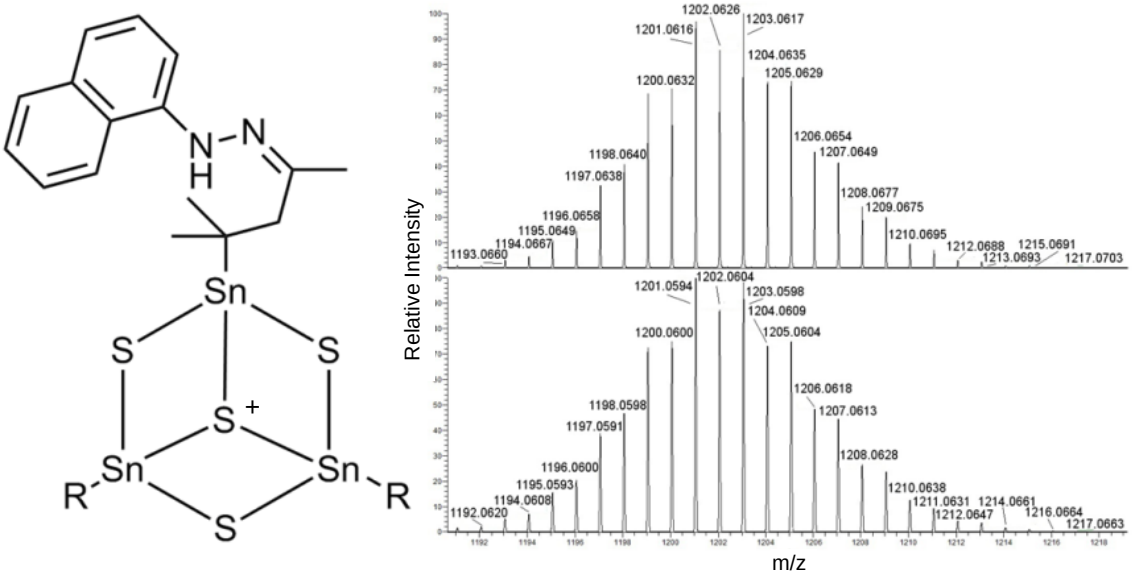

Figure S6. Schematic drawing of the cluster cation in **15** (left; R drawn once in detail) along with the high-resolution mass cluster of $[(C_{16}H_{20}N_2Sn)_3S_4]^+$ as measured by ESI^+ MS (top right) and calculated (bottom right).

2. Supplementary Crystallographic Tables and Figure

Table S1. Crystallographic data for the X-ray structural analyses of compounds **6**, **7·6CH_2Cl_2**, **8·CH_2Cl_2**, and **10·2CH_2Cl_2**.

Compound	**6**	**7·6CH_2Cl_2**	**8·CH_2Cl_2**	**10·2CH_2Cl_2**
empirical formula	$C_{52}H_{68}N_8S_{10}Sn_6$	$C_{72}H_{84}N_8S_{10}Sn_6 \cdot 6CH_2Cl_2$	$C_{72}H_{84}N_8S_{10}Sn_6 \cdot CH_2Cl_2$	$C_{64}H_{72}N_{12}S_{10}Sn_6 \cdot 2\ CH_2Cl_2$
f. w. /g mol^{-1}	1838.06	2604.00	2179.33	2206.45
crystal color, shape	Colorless bar	Colorless bar	Colorless bar	Red block
crystal size /mm^3	0.16×0.04×0.03	0.19×0.10×0.08	0.10×0.31×0.07	0.20×0.13×0.02
crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
space group	*P*-1	*C*1 2/c 1	*P*-1	*P*-1
a /Å	10.7206(5)	32.9747(15)	10.859(2)	10.7352(6)
b /Å	12.9145(6)	11.4272(5)	14.864(3)	10.8246(6)
c /Å	13.9280(7)	31.2524(13)	16.490(3)	17.6041(10)
α /°	100.816(2)	90.000	114.43(3)	83.918(2)
β /°	110.245(2)	121.840	105.70(3)	86.837(2)
γ /°	91.817(2)	90.000	93.95(3)	82.666(2)
V /Å^3	1767.28(15)	10004.15(80)	2282.74(120)	2019.78(20)
Z	1	4	1	1
μ ($Mo_{K\alpha}$) /mm^{-1}	0.71073	0.71073	0.71073	0.71073
abs. corr. type	None	Multi-scan	None	Multi-scan
θ range /°	2.01-28.32	2.21-26.37	1.44-26.74	2.13-27.19
total reflns	25120	47461	21393	36863
unique reflns [R_{int}]	8717	9976	9648	8950
obs. reflns. [$I > 2\sigma(I)$]	5919	6529	7837	6409
Parameters	313	521	495	448
R_1 [$I > 2\sigma(I)$]	0.0564	0.0618	0.0377	0.0360
wR_2 (all data)	0.1033	0.1183	0.0491	0.0732
GooF (all data)	1.048	1.058	0.872	0.946
max peak/hole /e Å^{-3}	3.08/–1.02	2.16/–1.53	2.55/–0.59	1.29/–0.84

Table S2. Selected distances (Å) and angles (°) observed in compounds **6**, **7·6CH_2Cl_2**, **8·CH_2Cl_2**, and **10·2CH_2Cl_2**.

Compound	**6**	**7·6CH_2Cl_2**	**8·CH_2Cl_2**	**10·2CH_2Cl_2**
Sn–(μ-S) within $[Sn_3S_4]$ moiety	2.397(2)-2.428(2)	2.406(2)-2.447(2)	2.3978(12)-2.4289(12)	2.3981(12)-2.4444(12)
Sn–(μ-S) within $[Sn_2S_2]$ ring	2.3830(19), 2.4985(19)	2.390(2), 2.498(2)	2.3798(17), 2.5013(13)	2.3830(12), 2.4902(12)
Sn–(μ_3-S) at **Sn**S_5	2.819(2)	2.711(2)	2.8891(14)	2.7276(12)
Sn–(μ_3-S) at **Sn**S_3C…N	2.514(2), 2.524(2)	2.515(2), 2.540(2)	2.5075(13), 2.5247(17)	2.5380(12), 2.5206(12)
Sn–C	2.15(2), 2.174(7), 2.23(2)	2.179(7), 2.184(8)	2.181(4), 2.179(4)	2.177(5), 2.172(5)
Sn…N	2.358(15), 2.420(6), 2.50(2)	2.367(7), 2.399(7)	2.353(4), 2.485(4)	2.425(4), 2.448(4)
S–Sn–S cis at **Sn**S_5	85.03(6)-123.29(7)	85.90(7)-128.96(8)	83.63(3)-122.91(5)	86.13(4)-123.65(5)
S–Sn–S trans at **Sn**S_5	178.30(6)	175.46(7)	179.39(3)	178.68(4)
S–Sn–S at **Sn**S_3C…N	91.02(7)-115.91(8)	90.85(8)-114.81(8)	91.14(5)-115.03(5)	90.98(4)-113.81(4)
S–Sn–C	100.0(6)-124.0(5)	100.1(2)-128.9(2)	106.07(13)-125.42(11)	104.92(13)-126.58(13)
S–Sn…N cis	81.6(5)-91.5(4)	87.34(17)-93.50(16)	85.35(9)-88.43(9)	84.09(10)-91.80(10)
S–Sn…N trans	169.6(6), 176.6(4), 179.22(16)	179.11(18), 174.38(16),	177.66(9), 178.09(9)	178.09(10), 174.71(10)
C–Sn…N	75.4(3), 75.6(9), 76.9(7)	75.4(3), 75.9(3)	74.01(16), 76.26(15)	74.88(16), 74.41(15)

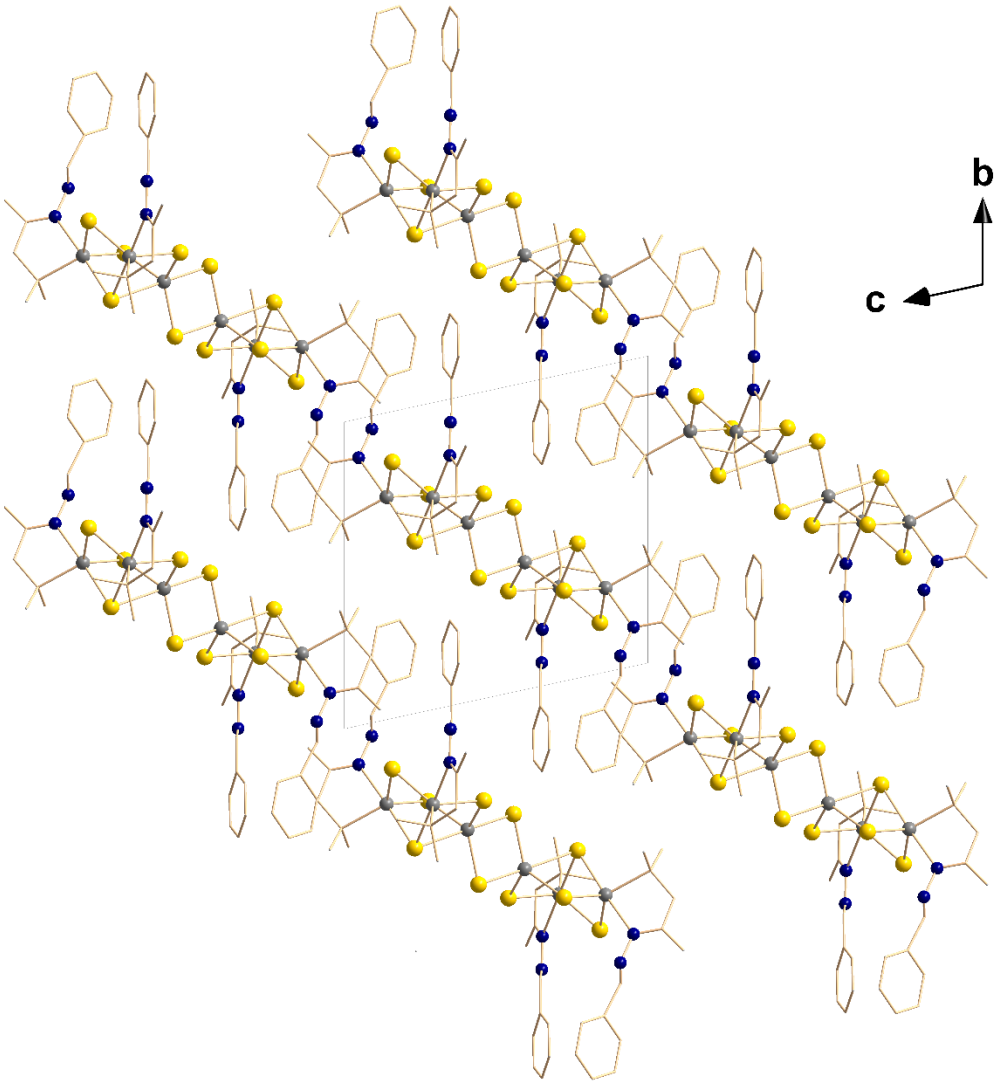

Figure S7. Packing of the cluster molecules in compound **6**. Organic moieties are shown as wires, most of the H atoms are omitted for clarity. Yellow spheres: S, grey spheres: Sn, blue spheres: N atoms.

3. Supplementary NMR Figures

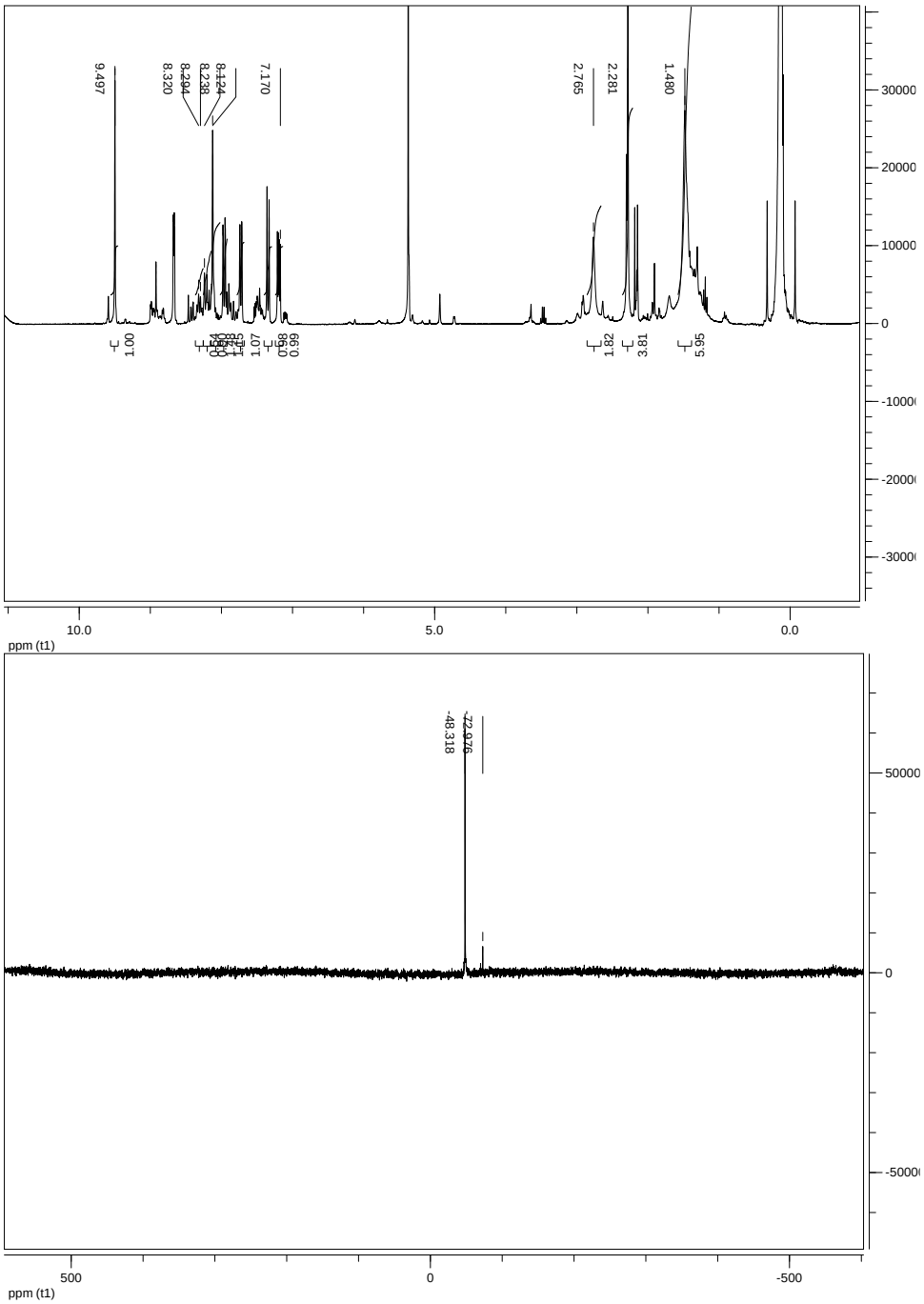

Figure S8. ^{1}H NMR spectrum (top) and ^{119}Sn NMR spectrum (bottom) of compound **10**, measured on a saturated solution of single crystals in CD_2Cl_2.