Supporting Information

Derivatives of penta-, hexa-, and hepta-coordinated tin with Schiff bases and 1,10-phenanthroline: structure, redox and optoelectronic properties

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Contents

1. X-ray crystallographic data and refinement details

X-ray diffraction data for **1** and **2** were collected at 100K on a Bruker Quest D8 diffractometer equipped with a Photon-III area-detector (shutterless φ- and ω-scan technique), using graphite-monochromatized Mo K_α-radiation. The intensity data were integrated by the *SAINT* program[1] and were analytically and then semi-empirically corrected for absorption and decay from equivalent reflections by multi-scan methods with *SADABS*.[2] X-ray diffraction data for **3**-**5** were collected at 100K on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix6000HE area-detector (kappa geometry, shutterless ω-scan technique), using monochromatized Cu K_α-radiation (**3** and **5**) or Mo K_α-radiation (**4**). The intensity data were integrated and then analytically (**3** and **4**) or semi-empirically (**5**) corrected for absorption and decay by the CrysAlisPro program.[3] Structure **4** was treated and refined a regular non-merohedral twin. All structures were solved by direct methods with *SHELXT*[4] and refined by the full-matrix least-squares method on F^2 using *SHELXL*-2018[5] within the *ShelXle*[6] or *Olex2*[7] program suites. All non-hydrogen atoms were refined with individual anisotropic displacement parameters. Locations of amino, hydroxy and water hydrogen atoms were found from the electron density-difference map; these hydrogen atoms were refined with individual isotropic displacement parameters. All other hydrogen atoms were placed in ideal calculated positions (C-H distance = 0.950 Å for aromatic and for –CH=, 0.980 Å for methyl and 0.990 Å for methylene hydrogen atoms) and refined as riding atoms with relative isotropic displacement parameters taken as $U_{iso}(H)=1.5U_{eq}(C)$ for methyl groups and $U_{iso}(H)=1.2U_{eq}(C)$ otherwise. A rotating group model was applied for methyl groups. Disorders were refined in a regular manner by applying similarity constraints on anisotropic displacement parameters on similar atoms and by constraining similar distances. The *SHELXTL* program suite[8] and the *Mercury* program[9] were used for molecular graphics in SI and in the manuscript, correspondingly. Crystal data, data collection and structure refinement details for **1-5** are summarized in Table S1. The structures have been deposited at the Cambridge Crystallographic Data Center with the reference CCDC numbers 2241142-2241146; they also contain the supplementary crystallographic data. These data can be obtained free of charge from the CCDC *via* https://www.ccdc.cam.ac.uk/structures/

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Table S1. Crystal data, data collection and structure refinement details for **1-5**.

Compound	**1**	**2**	**3**	**4**	**5**
Empiricalformula	$C_{12}H_{17.58}N_3O_{2.29}Sn$	$C_{25}H_{29}N_5O_3Sn$	$C_{37}H_{37}N_7O_2SSn$	$C_{24}H_{24}N_2O_2Sn$	$C_{23}H_{23}N_3O_2Sn$
Formula weight	359.21	566.22	762.48	491.14	492.13
Temperature, K	100(2)	100(2)	100.0(1)	100.0(1)	100.0(1)
Wavelength, Å	0.71073	0.71073	1.54184	0.71073	1.54184
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
Unit cell dimensions					
a, Å	10.5118(4)	9.5849(2)	10.43938(8)	10.45872(9)	8.9435(3)
b, Å	11.5157(4)	11.1754(2)	10.61993(6)	10.81132(8)	15.3162(6)
c, Å	13.0702(5)	12.8127(3)	15.96529(10)	18.91626(17)	14.8791(6)
α, °	107.0970(10)	106.3980(10)	107.1063(5)	78.4367(7)	90
β, °	110.4520(10)	91.3010(10)	90.6022(6)	76.9185(7)	97.794(4)
γ, °	94.1500(10)	112.7180(10)	91.1542(5)	88.6387(6)	90
Volume, $Å^3$	1389.57(9)	1200.93(4)	1691.10(2)	2040.60(3)	2019.32(13)
Z	4	2	2	4	4
Density (calcd), g/cm^3	1.717	1.566	1.497	1.599	1.619
Absorption coefficient (μ), mm^{-1}	1.840	1.101	6.947	1.275	10.263
F(000)	715.6	576	780	992	992
Crystal size	0.33×0.20×0.18	0.99×0.30×0.16	0.67×0.27×0.18	0.35×0.25×0.12	0.13×0.11×0.06

Table S1 (*cont.*). Crystal data, data collection and structure refinement details for **1-5**.

Compound	**1**	**2**	**3**	**4**	**5**
θ range for data collection, °	2.100-26.500	2.082-34.364	2.896-77.730	1.923-35.932	4.162-77.969
Index ranges	-13≤h≤13, -14≤k≤14, -16≤l≤16	-15≤h≤15, -17≤k≤17, -20≤l≤20	-12≤h≤13, -13≤k≤13, -20≤l≤20	-17≤h≤16, -17≤k≤17, -30≤l≤30	-11≤h≤10, -19≤k≤18, -18≤l≤18
Reflections					
Collected	50330	74295	42518	33922*	25821
Independent [R_{int}]	5758 [0.0285]	10083 [0.0191]	7168 [0.0554]	33922 [0]*	4290 [0.0530]
Observed (with I>2σ(I))	5497	9767	7158	30984	3910
Completeness to θ_{full} / θ_{max}	0.999 / 0.999	0.998 / 0.999	0.999 / 0.993	1.000 / 0.926	0.998 / 0.991
T_{max} / T_{min}	0.7467 / 0.6658	0.2711 / 0.1999	0.951 / 0.021	0.879 / 0.729	1.0000 / 0.6667
Data / restraints / parameters	5758 / 57 / 405	10083 / 0 / 323	7168 / 4 / 457	33922 / 0 / 528	4290 / 0 / 264
Goodness-of-fit on F^2	1.233	1.135	1.079	1.105	1.066
R1 / wR2 indices (I>2σ(I))	0.0406 / 0.0978	0.0151 / 0.0412	0.0421 / 0.1129	0.0270 / 0.0901	0.0326 / 0.0888
R1 / wR2 indices (all data)	0.0425 / 0.0988	0.0159 / 0.0416	0.0421 / 0.1130	0.0303 / 0.0937	0.0359 / 0.0911
Extinction coefficient	-	0.0027(4)	0.0014(2)	-	-
$\Delta\rho_{max}$ / $\Delta\rho_{min}$, ē·Å^{-3}	2.465 / -1.170	0.506 / -0.459	1.573 / -1.834	0.948 / -0.799	1.033 / -1.199
CCDC number	2241142	2241143	2241144	2241145	2241146

** Due to the refinement of **4** as a regular non-merohedral twin, equivalent reflections were merged by a conventional way, setting the collected reflection number to be equal to the number of independent reflections and, therefore, making R_{int}=0.

2. Crystal structure of 1

The crystal composition of **1** is $(C_{12}H_{17}N_3O_2Sn)\bullet 0.289(H_2O)$. The asymmetric unit (Fig. S1) contains two non-equivalent molecules (Z'=2, see Figs. S2-S5) of the complex and water molecule with a partial occupancy. The coordination number of Sn (CN_{Sn}) is five. In both molecules, the ligand is nearly flat (with exception of oxygen atoms coordinated with Sn), and the Sn atoms is disordered over two positions (Figs. S2 and S4). Atom deviations from the plane defined by atoms N1..N3, C1..C8 are -0.086(7)Å for O1, 0.083(9)Å for O2, 0.155(6)Å for Sn1 and -0.44(3)Å for O1A, 0.37(4)Å for O2A, -0.187(7)Å for Sn1A for the first molecule. Atom deviations from the plane defined by atoms N4..N6, C13..C20 are -0.110(8)Å for O3, 0.116(6)Å for O4, -0.232(5)Å for Sn2 and 0.15(12)Å for O3A, 0.25(4)Å for O4A, -0.049(13)Å for Sn2A for the second molecule. The Sn1/Sn1A atom exhibits a non-covalent short contact with the oxygen atom of the water molecule: 2.904(7)Å for Sn1···O5 and 3.097(8)Å for Sn1A···O5. The hydrogen bonds (Table S4) form 3D-network (not shown) in the crystal lattice.

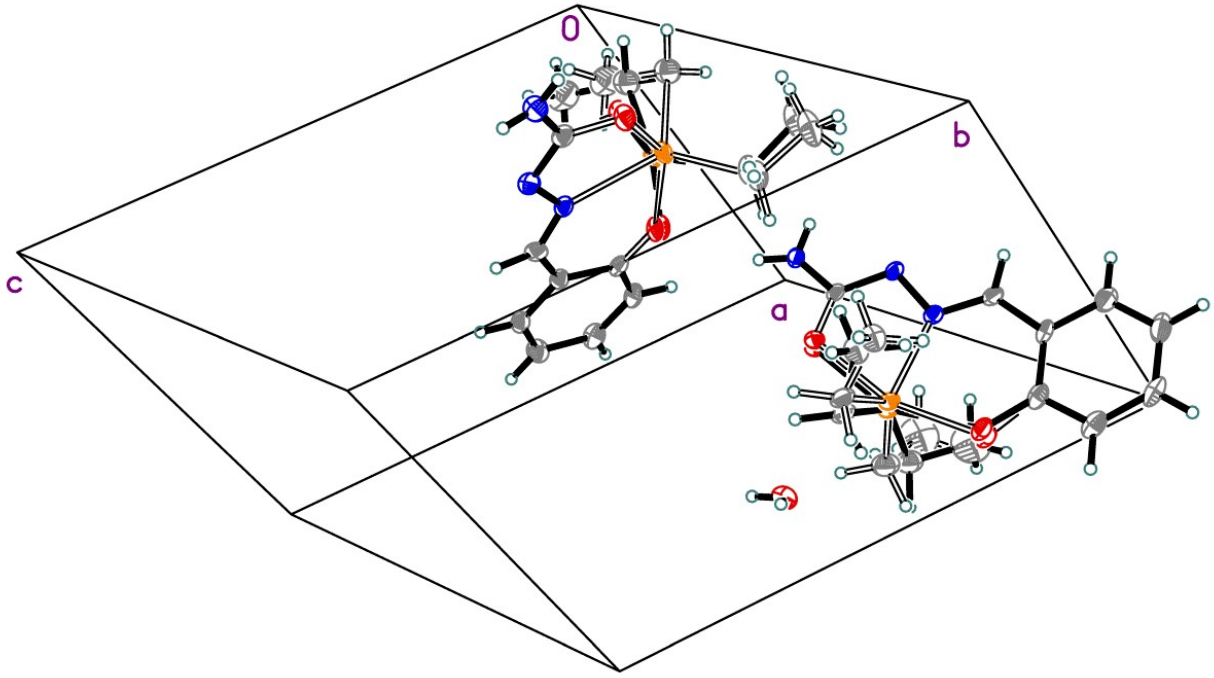

Fig. S1. The asymmetric unit of **1** (p=50%). The occupancy of the water molecule is 0.579(14).

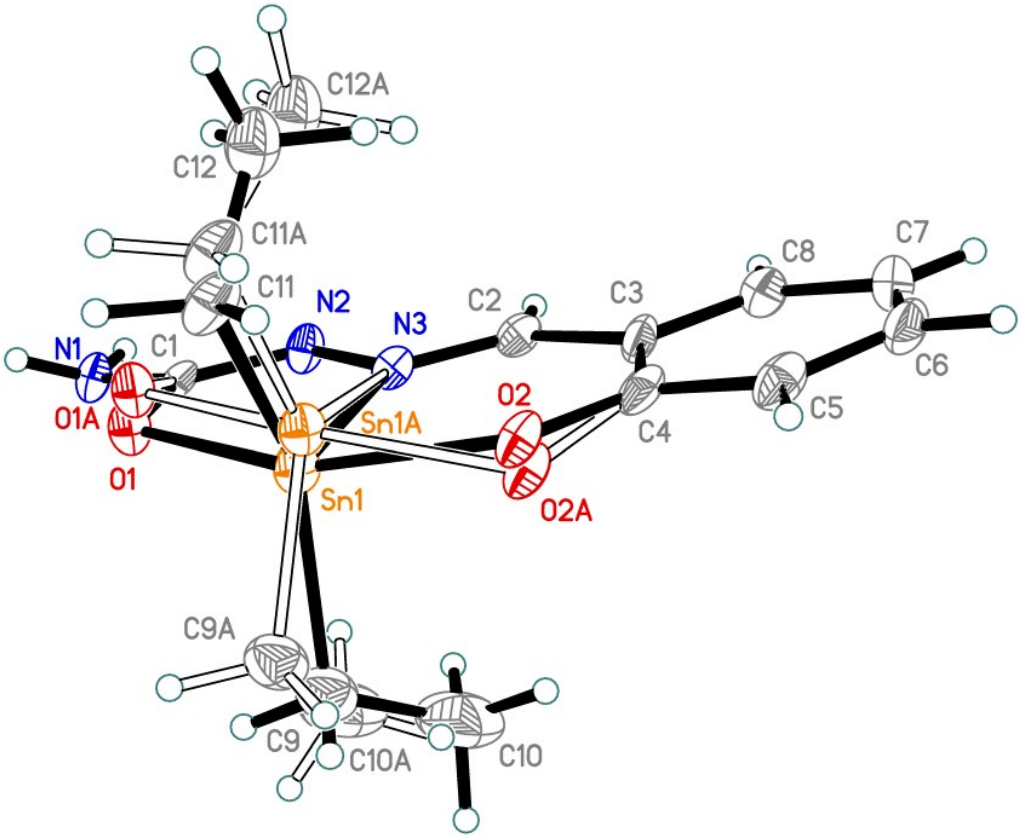

Fig. S2. The first molecule of **1** (p=50%). The minor disorder component is shown with open solid lines. The disorder ratio is 0.776(9):0.224(9).

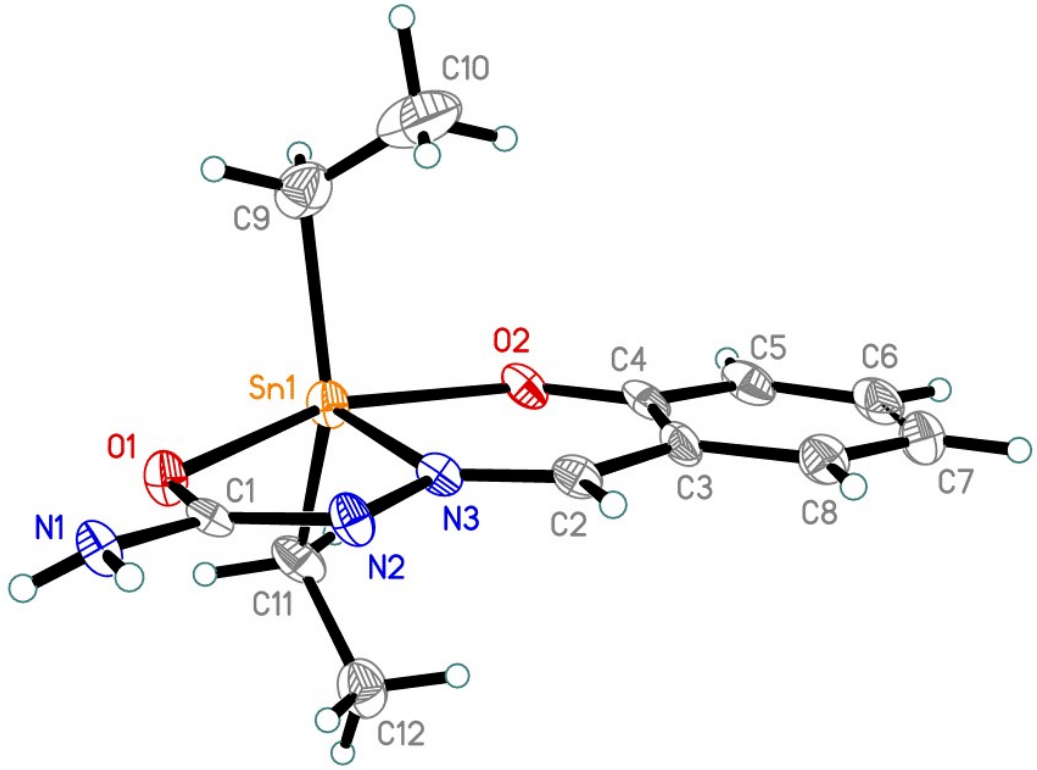

Fig. S3. The first molecule of **1** (p=50%). The disorder is omitted.

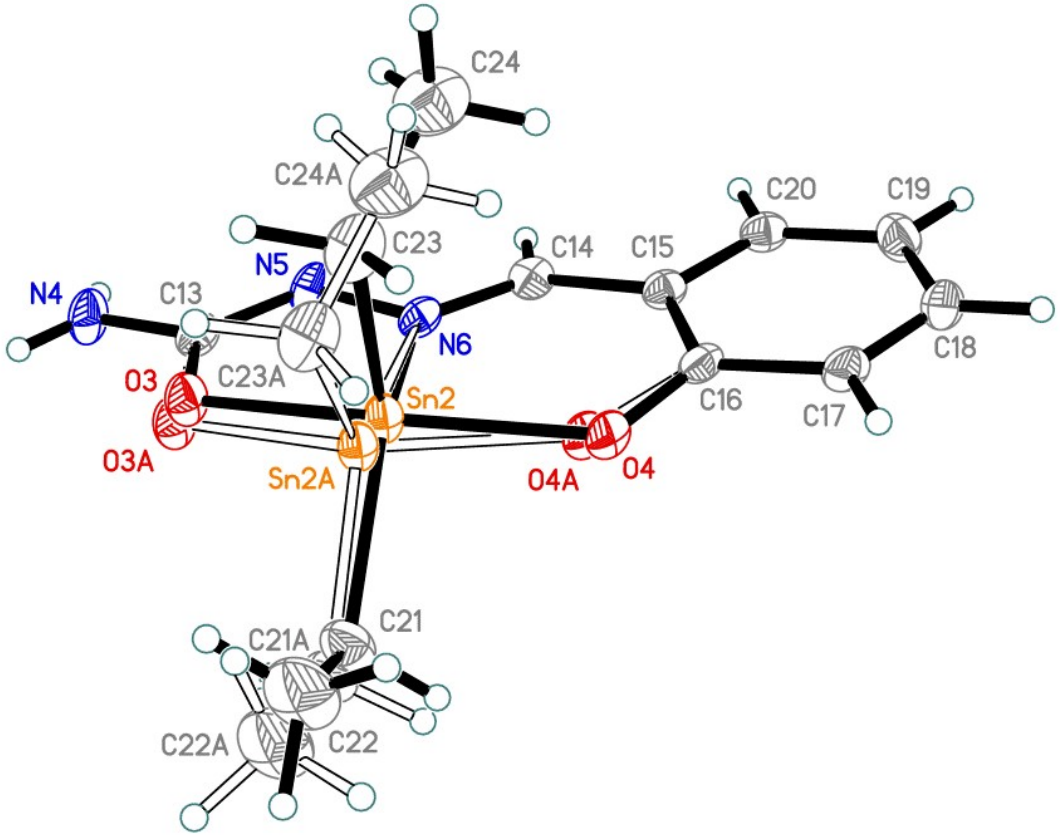

Fig. S4. The second molecule of **1** (p=50%). The minor disorder component is shown with open solid lines. The disorder ratio is 0.920(9):0.080(9).

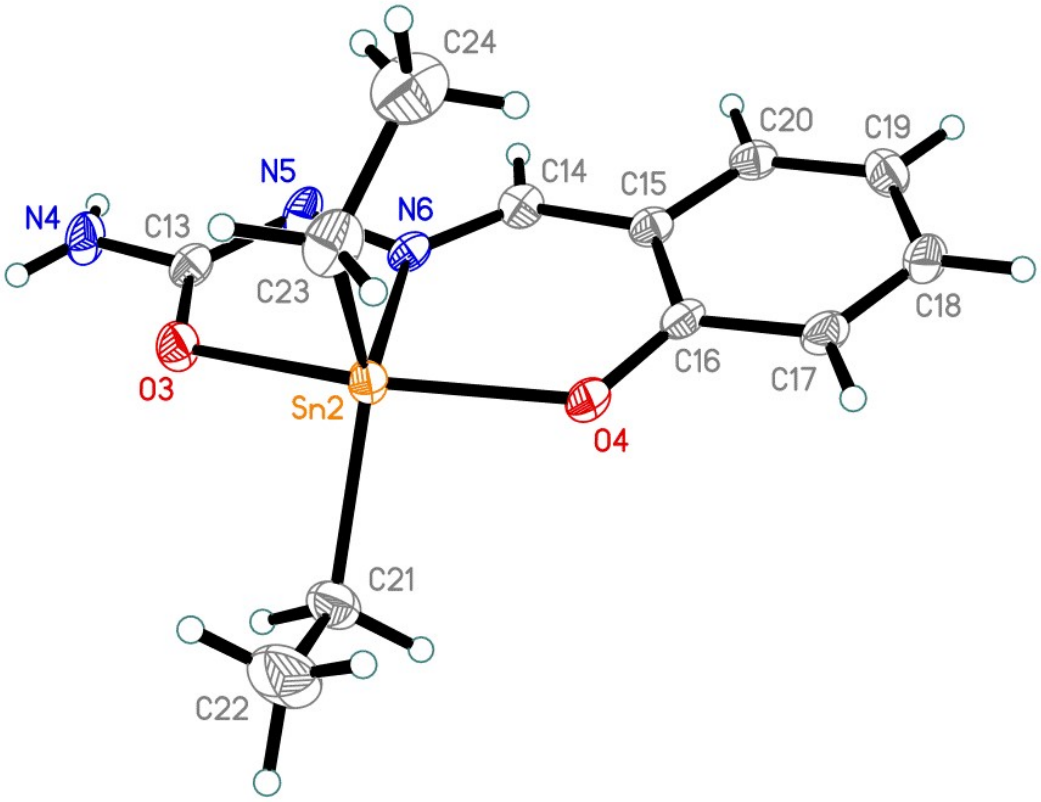

Fig. S5. The second molecule of **1** (p=50%). The disorder is omitted.

Table S2. Selected bond distances for **1**, Å.

Sn1-O1	2.164(5)	O2-C4	1.318(12)	C3-C8	1.403(7)
Sn1-O2	2.136(6)	O1A-C1	1.302(17)	C3-C4	1.418(7)
Sn1-N3	2.209(4)	O2A-C4	1.36(4)	C4-C5	1.410(7)
Sn1-C9	2.133(8)	N1-C1	1.353(6)	C5-C6	1.372(8)
Sn1-C11	2.117(7)	N1-H1A	0.81(3)	C6-C7	1.397(8)
Sn1A-O1A	2.164(16)	N1-H1B	0.81(3)	C7-C8	1.383(7)
Sn1A-O2A	2.127(16)	N2-C1	1.327(6)	C9-C10	1.506(14)
Sn1A-N3	2.138(6)	N2-N3	1.389(5)	C11-C12	1.528(11)
Sn1A-C9A	2.126(18)	N3-C2	1.296(6)	C9A-C10A	1.50(2)
Sn1A-C11A	2.117(18)	C2-C3	1.446(6)	C11A-C12A	1.51(2)
O1-C1	1.300(7)				
Sn2-O3	2.146(4)	O4-C16	1.330(6)	C15-C20	1.394(7)
Sn2-O4	2.094(4)	O3A-C13	1.30(2)	C15-C16	1.421(6)
Sn2-N6	2.164(4)	O4A-C16	1.376(16)	C16-C17	1.404(6)
Sn2-C21	2.147(6)	N4-C13	1.344(6)	C17-C18	1.371(7)
Sn2-C23	2.111(7)	N4-H4A	0.81(3)	C18-C19	1.393(7)
Sn2A-O3A	2.15(2)	N4-H4B	0.81(3)	C19-C20	1.387(7)
Sn2A-O4A	2.140(17)	N5-C13	1.328(6)	C21-C22	1.509(8)
Sn2A-N6	2.354(11)	N5-N6	1.389(5)	C23-C24	1.556(10)
Sn2A-C21A	2.15(2)	N6-C14	1.295(6)	C21A-C22A	1.51(2)
Sn2A-C23A	2.11(2)	C14-C15	1.443(6)	C23A-C24A	1.55(2)
O3-C13	1.294(6)				
O5-H5A	0.86(2)	O5-H5B	0.83(2)		

Table S3. Selected bond angles for **1**, °.

O1-Sn1-N3	73.16(18)	O1A-Sn1A-N3	72.0(6)
O2-Sn1-N3	82.1(4)	O2A-Sn1A-N3	86.6(14)
O1-Sn1-O2	154.2(4)	O1A-Sn1A-O2A	157.8(15)
O1-Sn1-C9	99.0(3)	O1A-Sn1A-C9A	94.0(12)
O1-Sn1-C11	93.0(3)	O1A-Sn1A-C11A	89.2(15)
O2-Sn1-C9	93.7(3)	O2A-Sn1A-C9A	86.8(14)
O2-Sn1-C11	89.5(4)	O2A-Sn1A-C11A	106.1(18)
C9-Sn1-N3	104.0(2)	C9A-Sn1A-N3	107.3(8)
C11-Sn1-N3	111.7(2)	C11A-Sn1A-N3	117.2(10)
C9-Sn1-C11	144.3(3)	C9A-Sn1A-C11A	134.0(13)
O3-Sn2-N6	73.00(16)	O3A-Sn2A-N6	73.7(9)
O4-Sn2-N6	85.33(17)	O4A-Sn2A-N6	69.9(16)
O2-Sn2-O4	155.9(2)	O3A-Sn2A-O4A	141(3)

O3-Sn2-C21	91.3(2)	O3A-Sn2A-C21A	92(4)
O3-Sn2-C23	98.8(3)	O3A-Sn2A-C23A	105(4)
O4-Sn2-C21	94.1(2)	O4A-Sn2A-C21A	100(3)
O4-Sn2-C23	97.5(2)	O4A-Sn2A-C23A	104(3)
C21-Sn2-N6	128.3(2)	C21A-Sn2A-N6	128(2)
C23-Sn2-N6	107.2(2)	C23A-Sn2A-N6	120(2)
C21-Sn2-C23	124.1(3)	C21A-Sn2A-C23A	113(3)

Table S4. Hydrogen bond parameters for **1**, Å and °.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N1-H1A...O4	0.81(3)	2.25(4)	3.020(5)	159(5)
N1-H1A...O4A	0.81(3)	2.46(5)	3.23(4)	159(5)
N1-H1B...N2#1	0.81(3)	2.20(3)	3.012(5)	175(6)
N4-H4A...N5#2	0.81(3)	2.19(3)	3.002(6)	176(6)
N4-H4B...O1#3	0.81(3)	2.51(5)	3.155(7)	137(6)
O5-H5B...N5#4	0.83(2)	2.36(4)	3.166(8)	163(11)

Symmetry transformations to generate equivalent atoms: #1 -x+1, -y+1, -z; #2 -x, -y+1, -z+1; #3 x-1, y, z; #4 -x+1, -y+1, -z+1.

3. Crystal structure of 2

In complex **2** (Fig. S6), the ligand is not flat, whereas 1,10-phenanthroline is planar. Since atoms Sn1, O1, O2, N3, N4 and N5 are located in the same plane, and angle C9-Sn1-C11 (Table 6) is close to 180°, atom Sn1 is in a distorted pentagonal bipyramidal environment. The lattice methanol molecule is coordinated to atom N2 *via* a hydrogen bond. An additional hydrogen bond of the amino group forms a dimeric unit (Fig. S7).

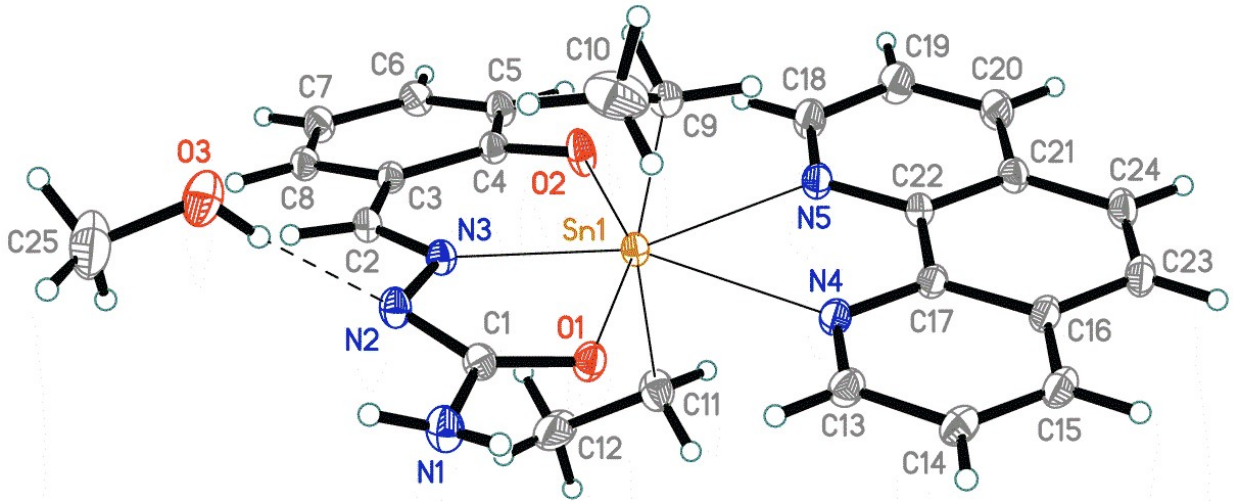

Fig. S6. The asymmetric unit of **2** (p=50%).

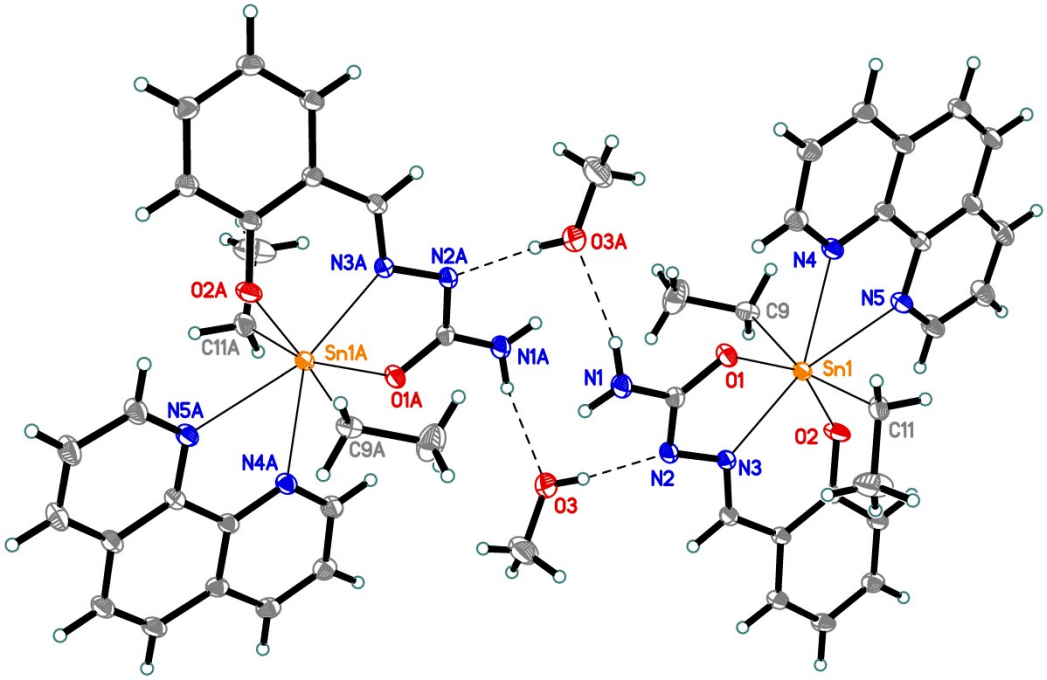

Fig. S7. A dimeric moiety of **2** formed by hydrogen bonds (p=50%). Symmetry transformation (A) to generate equivalent atoms: -x+1, -y, -z+2.

Table S5. Selected bond distances for **2**, Å.

Sn1-O1	2.2191(6)	N3-C2	1.2956(10)	C13-C14	1.4045(12)
Sn1-O2	2.1509(6)	C2-C3	1.4460(11)	C14-C15	1.3718(13)
Sn1-N3	2.3154(7)	C3-C8	1.4050(11)	C15-C16	1.4080(12)
Sn1-N4	2.6683(7)	C3-C4	1.4219(11)	C16-C17	1.4120(11)
Sn1-N5	2.6456(7)	C4-C5	1.4110(11)	C16-C23	1.4339(12)
Sn1-C9	2.1333(9)	C5-C6	1.3857(12)	C17-C22	1.4465(11)
Sn1-C11	2.1286(9)	C6-C7	1.3967(12)	C18-C19	1.4035(12)
O1-C1	1.2804(10)	C7-C8	1.3846(12)	C19-C20	1.3737(14)
O2-C4	1.3159(10)	C9-C10	1.5188(15)	C20-C21	1.4089(13)
N1-C1	1.3648(11)	C11-C12	1.5015(14)	C21-C22	1.4142(11)
N1-H1A	0.859(16)	N4-C13	1.3310(11)	C21-C24	1.4336(12)
N1-H1B	0.859(16)	N4-C17	1.3608(10)	C23-C24	1.3555(14)
N2-C1	1.3318(10)	N5-C18	1.3281(11)	O3-C25	1.3984(15)
N2-N3	1.3910(10)	N5-C22	1.3609(10)	O3-H3	0.834(17)

Table S6. Selected bond angles for **2**, °.

O1-Sn1-N3	69.32(2)	C9-Sn1-O1	93.31(3)	C9-Sn1-N4	82.34(3)
O2-Sn1-N3	78.86(2)	C9-Sn1-O2	91.63(3)	C11-Sn1-N4	83.30(3)
O1-Sn1-O2	148.16(2)	C11-Sn1-O1	90.65(3)	C9-Sn1-N5	81.05(3)
O1-Sn1-N4	73.64(2)	C11-Sn1-O2	93.50(4)	C11-Sn1-N5	84.86(3)
O2-Sn1-N4	138.19(2)	C9-Sn1-C11	163.37(3)	N3-Sn1-N4	142.88(2)
O1-Sn1-N5	135.88(2)	C9-Sn1-N3	97.22(3)	N3-Sn1-N5	154.68(2)
O2-Sn1-N5	75.95(2)	C11-Sn1-N3	99.29(3)	N5-Sn1-N4	62.24(2)

Table S7. Hydrogen bond parameters for **2**, Å and °.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N1-H1B...O3#1	0.859(16)	2.104(15)	2.9289(11)	160.7(13)
O3-H3...N2	0.834(17)	1.908(17)	2.7377(10)	172.8(17)

Symmetry transformations to generate equivalent atoms: #1 -x+1, -y, -z+2

4. Crystal structure of 3

The asymmetric unit of **3** (Fig. S8) contains the complex (Fig. S9), methanol and an additional 1,10-phenanthroline molecule. Two such units form a dimeric associate *via* H-bonding (Fig. S10).

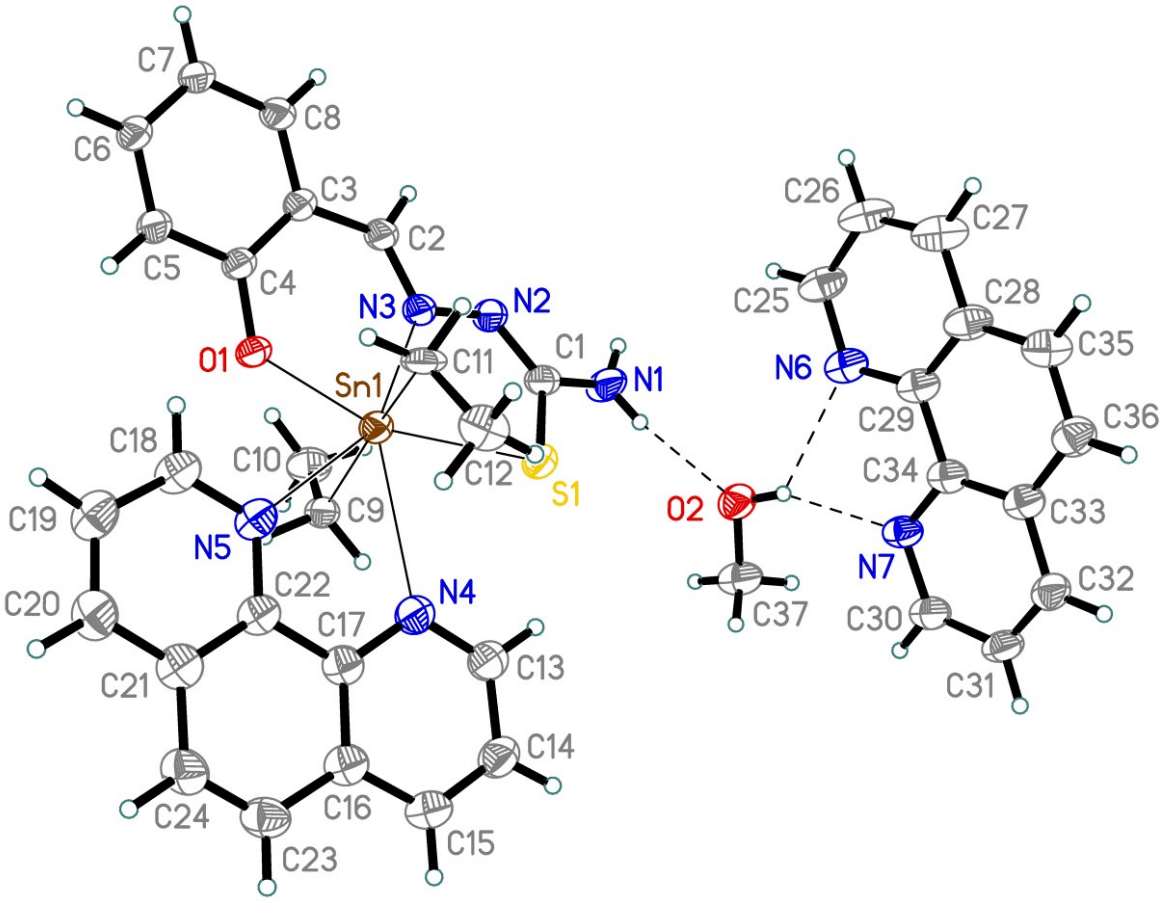

Fig. S8. The asymmetric unit of **3** (p=50%). Disorder of one ethyl ligand is omitted.

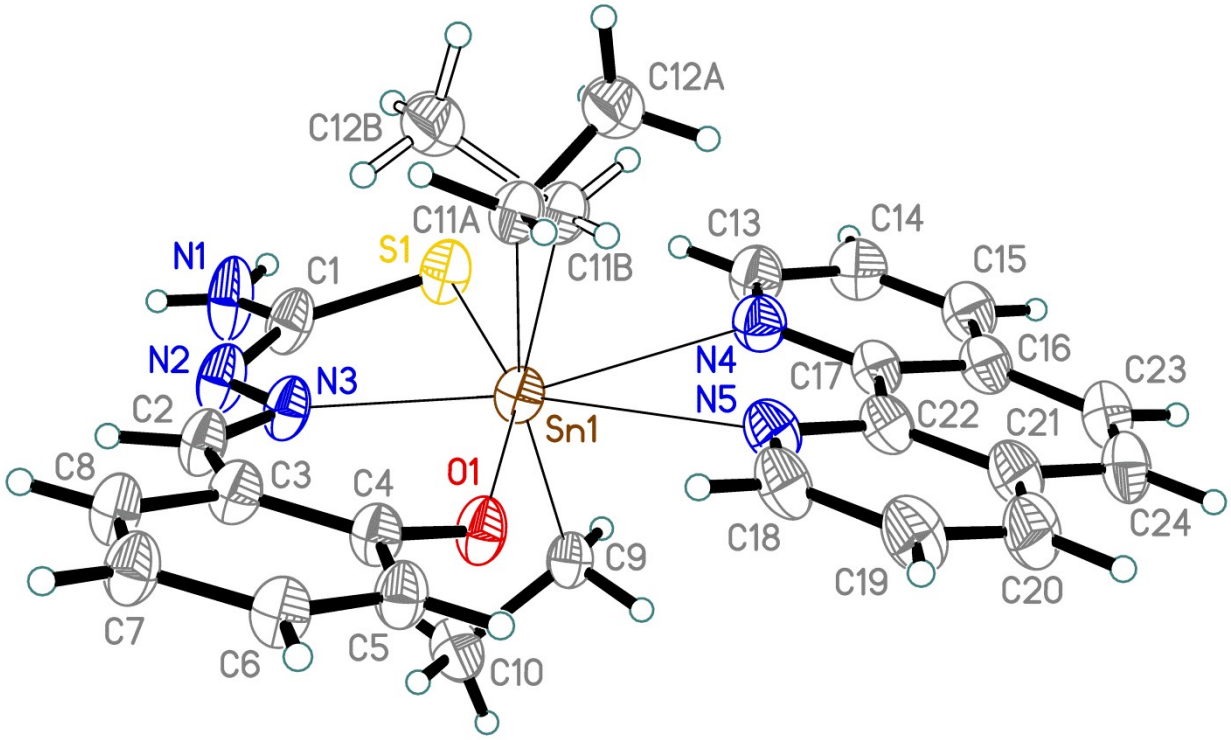

Fig. S9. The structure of complex in crystals of **3** (p=50%). The disorder ratio for one ethyl ligand (C11A, C12A / C11B, C12B) is 0.606(6):0.394(6).

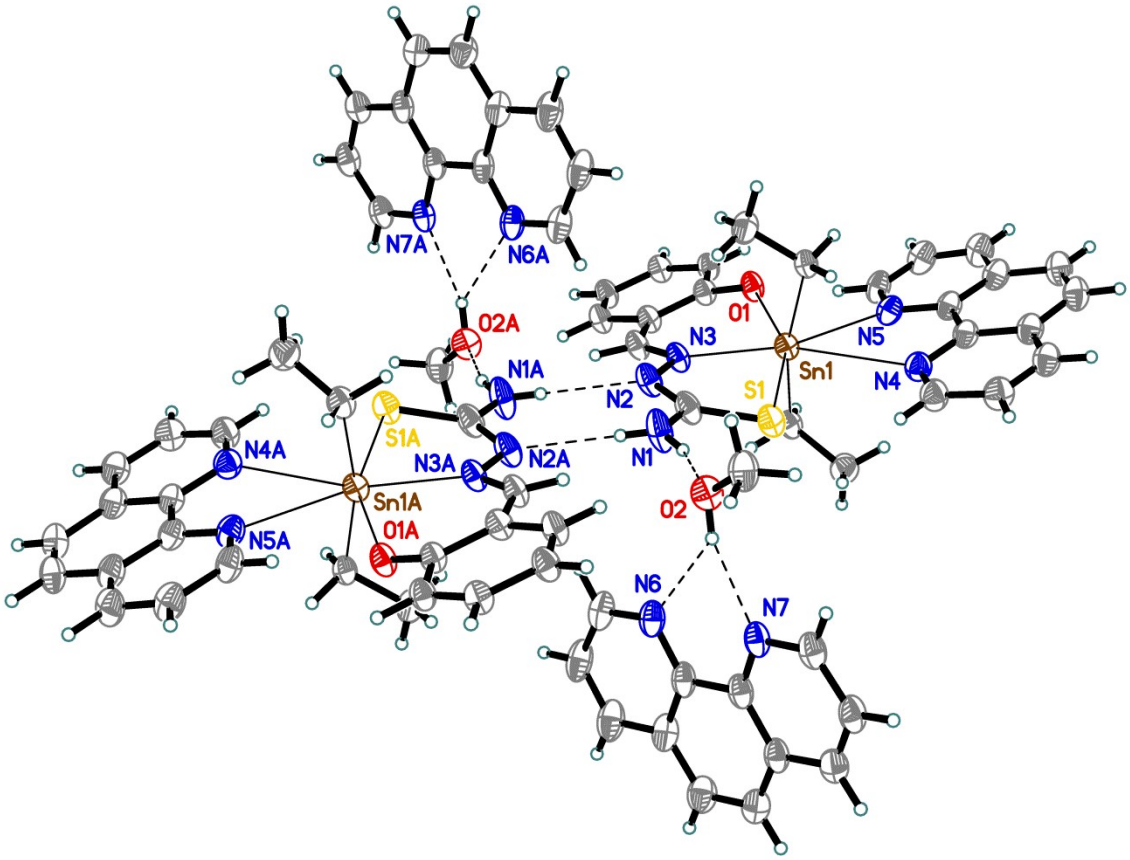

Fig. S10. The dimeric unit of **3**, formed by hydrogen bonds (p=50%). Disorder is omitted.

Table S8. Selected bond distances for **3**, Å.

Sn1-S1	2.6494(6)	N2-C1	1.314(4)	N5-C18	1.330(4)
Sn1-O1	2.1236(18)	N3-C2	1.291(3)	N5-C22	1.362(4)
Sn1-N3	2.331(2)	C2-C3	1.444(4)	C13-C14	1.409(4)
Sn1-C9	2.125(3)	C3-C4	1.416(4)	C14-C15	1.361(5)
Sn1-C11A	2.137(3)	C3-C8	1.404(4)	C15-C16	1.414(4)
Sn1-C11B	2.137(4)	C4-C5	1.419(3)	C16-C17	1.411(4)
Sn1-N4	2.945(2)	C5-C6	1.384(4)	C16-C23	1.427(4)
Sn1-N5	2.743(3)	C6-C7	1.392(4)	C17-C22	1.445(4)
S1-C1	1.731(3)	C7-C8	1.382(4)	C18-C19	1.400(5)
O1-C4	1.317(3)	C9-C10	1.525(4)	C19-C20	1.367(5)
N1-H1A	0.80(3)	C11A-C12A	1.528(6)	C20-C21	1.408(4)
N1-H1B	0.80(3)	C11B-C12B	1.529(6)	C21-C22	1.410(4)
N1-C1	1.351(4)	N4-C13	1.319(4)	C21-C24	1.439(4)
N2-N3	1.398(3)	N4-C17	1.369(4)	C23-C24	1.343(5)

Table S9. Selected bond angles for **3**, °.

S1-Sn1-N4	75.51(5)	N3-Sn1-S1	73.14(6)	C11A-Sn1-S1	92.8(2)
S1-Sn1-N5	132.58(5)	N3-Sn1-N4	148.26(7)	C11A-Sn1-N3	92.89(18)
O1-Sn1-S1	152.03(5)	N3-Sn1-N5	153.94(7)	C11A-Sn1-N4	93.47(14)
O1-Sn1-N3	79.39(7)	C9-Sn1-S1	91.83(7)	C11A-Sn1-N5	82.9(2)
O1-Sn1-C9	88.04(9)	C9-Sn1-N3	100.65(9)	C11B-Sn1-S1	94.6(4)
O1-Sn1-C11A	93.8(2)	C9-Sn1-C11A	166.4(2)	C11B-Sn1-N3	104.7(2)
O1-Sn1-C11B	97.4(4)	C9-Sn1-C11B	154.6(2)	C11B-Sn1-N4	82.6(3)
O1-Sn1-N4	131.05(7)	C9-Sn1-N4	75.38(8)	C11B-Sn1-N5	73.0(3)
O1-Sn1-N5	75.27(7)	C9-Sn1-N5	84.57(9)	N5-Sn1-N4	57.79(7)

Table S10. Hydrogen bond parameters for **3**, Å and °.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N1-H1A...N2#1	0.80(3)	2.28(3)	3.074(4)	179(5)
N1-H1B...O2	0.80(3)	2.17(4)	2.909(3)	155(5)
O2-H2A...N6	0.89(5)	2.44(5)	3.107(3)	133(4)
O2-H2A...N7	0.89(5)	2.14(5)	2.967(3)	154(4)

Symmetry transformations to generate equivalent atoms: #1 -x+1, -y+2, -z+2.

5. Crystal structure of 4

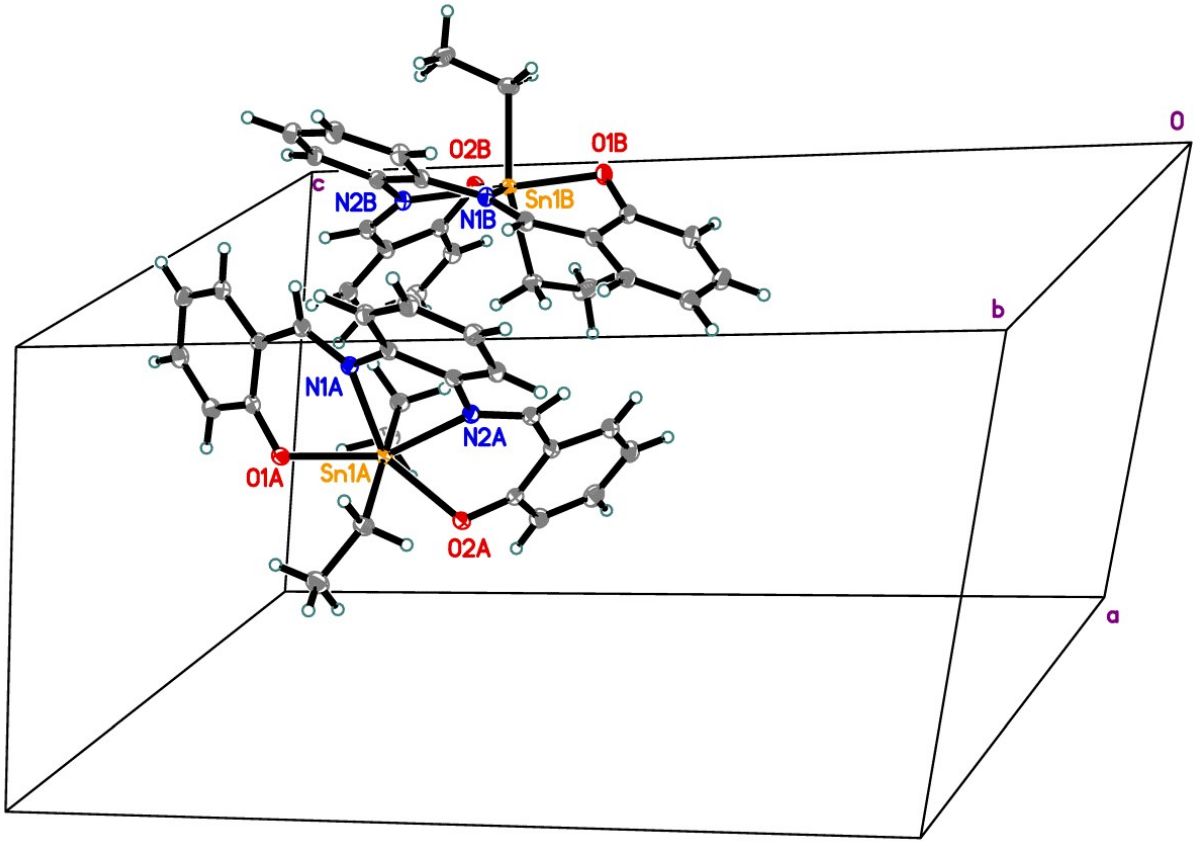

Fig. S11. The asymmetric unit of **4** contains two crystallographically non-equivalents molecules of the complex (p=50%).

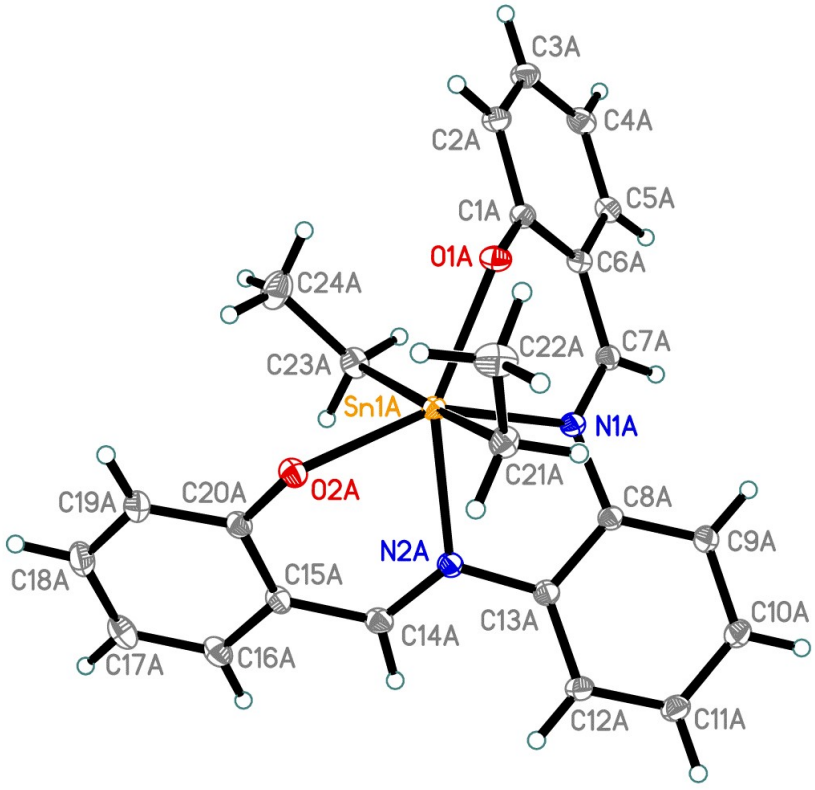

Fig. S12. The first molecule of **4** (p=50%).

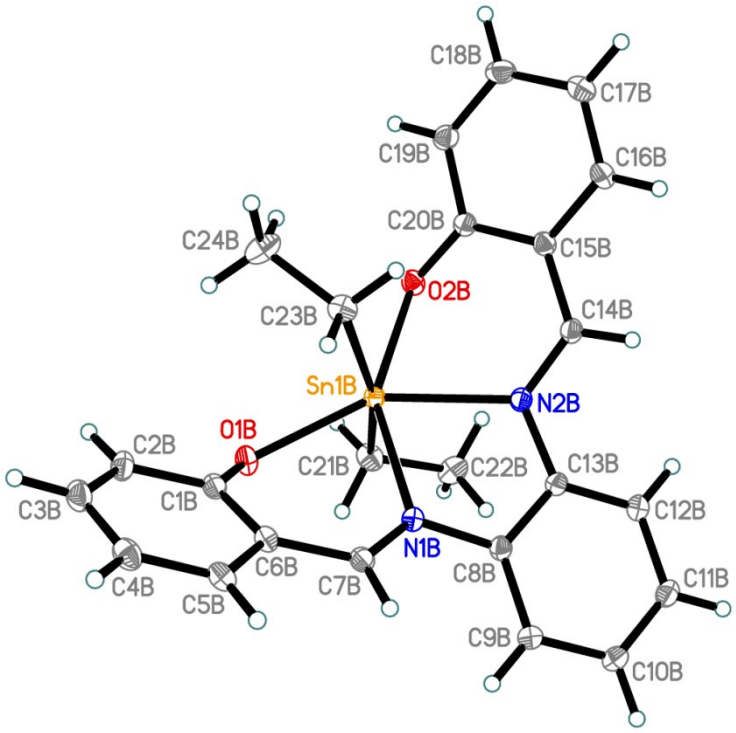

Fig. S13. The second molecule of **4** (p=50%).

Table S11. Selected bond distances for **4**, Å.

Sn1A-O1A	2.1960(10)	C1A-C2A	1.4209(19)	C12A-C13A	1.3954(19)
Sn1A-O2A	2.2105(10)	C1A-C6A	1.4346(19)	C14A-C15A	1.4355(19)
Sn1A-N1A	2.2981(11)	C2A-C3A	1.380(2)	C15A-C16A	1.418(2)
Sn1A-N2A	2.2758(12)	C3A-C4A	1.405(2)	C15A-C20A	1.4331(19)
Sn1A-C21A	2.1349(15)	C4A-C5A	1.379(2)	C16A-C17A	1.379(2)
Sn1A-C23A	2.1358(15)	C5A-C6A	1.416(2)	C17A-C18A	1.405(2)
O1A-C1A	1.3078(18)	C6A-C7A	1.4386(19)	C18A-C19A	1.381(2)
O2A-C20A	1.3139(17)	C8A-C9A	1.3976(18)	C19A-C20A	1.4154(19)
N1A-C7A	1.3054(19)	C8A-C13A	1.4120(19)	C21A-C22A	1.521(2)
N1A-C8A	1.4138(17)	C9A-C10A	1.393(2)	C23A-C24A	1.534(2)
N2A-C13A	1.4110(17)	C10A-C11A	1.393(2)		
N2A-C14A	1.3034(18)	C11A-C12A	1.3898(19)		
Sn1B-O1B	2.2127(10)	C1B-C2B	1.423(2)	C12B-C13B	1.3951(19)
Sn1B-O2B	2.2275(10)	C1B-C6B	1.436(2)	C14B-C15B	1.4323(19)
Sn1B-N1B	2.3040(12)	C2B-C3B	1.379(2)	C15B-C16B	1.416(2)
Sn1B-N2B	2.2719(12)	C3B-C4B	1.402(2)	C15B-C20B	1.4332(19)
Sn1B-C21B	2.1334(15)	C4B-C5B	1.381(2)	C16B-C17B	1.378(2)
Sn1B-C23B	2.1365(14)	C5B-C6B	1.415(2)	C17B-C18B	1.407(2)

O1B-C1B	1.2983(18)	C6B-C7B	1.4407(19)	C18B-C19B	1.383(2)
O2B-C20B	1.3109(17)	C8B-C9B	1.4006(18)	C19B-C20B	1.4172(19)
N1B-C7B	1.3013(19)	C8B-C13B	1.407(2)	C21B-C22B	1.528(2)
N1B-C8B	1.4136(17)	C9B-C10B	1.394(2)	C23B-C24B	1.535(2)
N2B-C13B	1.4099(17)	C10B-C11B	1.394(2)		
N2B-C14B	1.3061(18)	C11B-C12B	1.3877(19)		

Table S12. Selected bond angles for **4**, °.

O1A-Sn1A-O2A	130.72(4)	C21A-Sn1A-N1A	94.57(5)
O1A-Sn1A-N1A	78.93(4)	C21A-Sn1A-N2A	91.32(5)
O1A-Sn1A-N2A	149.51(4)	C21A-Sn1A-C23A	170.39(6)
O2A-Sn1A-N1A	150.34(4)	C23A-Sn1A-O1A	88.98(5)
O2A-Sn1A-N2A	79.64(4)	C23A-Sn1A-O2A	87.31(5)
N2A-Sn1A-N1A	70.78(4)	C23A-Sn1A-N1A	93.60(5)
C21A-Sn1A-O1A	87.64(5)	C23A-Sn1A-N2A	96.13(5)
C21A-Sn1A-O2A	88.08(5)		
O1B-Sn1B-O2B	132.80(4)	C21B-Sn1B-N1B	98.10(5)
O1B-Sn1B-N1B	78.00(4)	C21B-Sn1B-N2B	97.68(5)
O1B-Sn1B-N2B	148.66(4)	C21B-Sn1B-C23B	161.39(6)
O2B-Sn1B-N1B	149.19(4)	C23B-Sn1B-O1B	87.71(5)
O2B-Sn1B-N2B	78.46(4)	C23B-Sn1B-O2B	86.84(5)
N2B-Sn1B-N1B	70.74(4)	C23B-Sn1B-N1B	96.63(5)
C21B-Sn1B-O1B	84.30(5)	C23B-Sn1B-N2B	97.88(5)
C21B-Sn1B-O2B	86.33(5)		

6. Crystal structure of 5

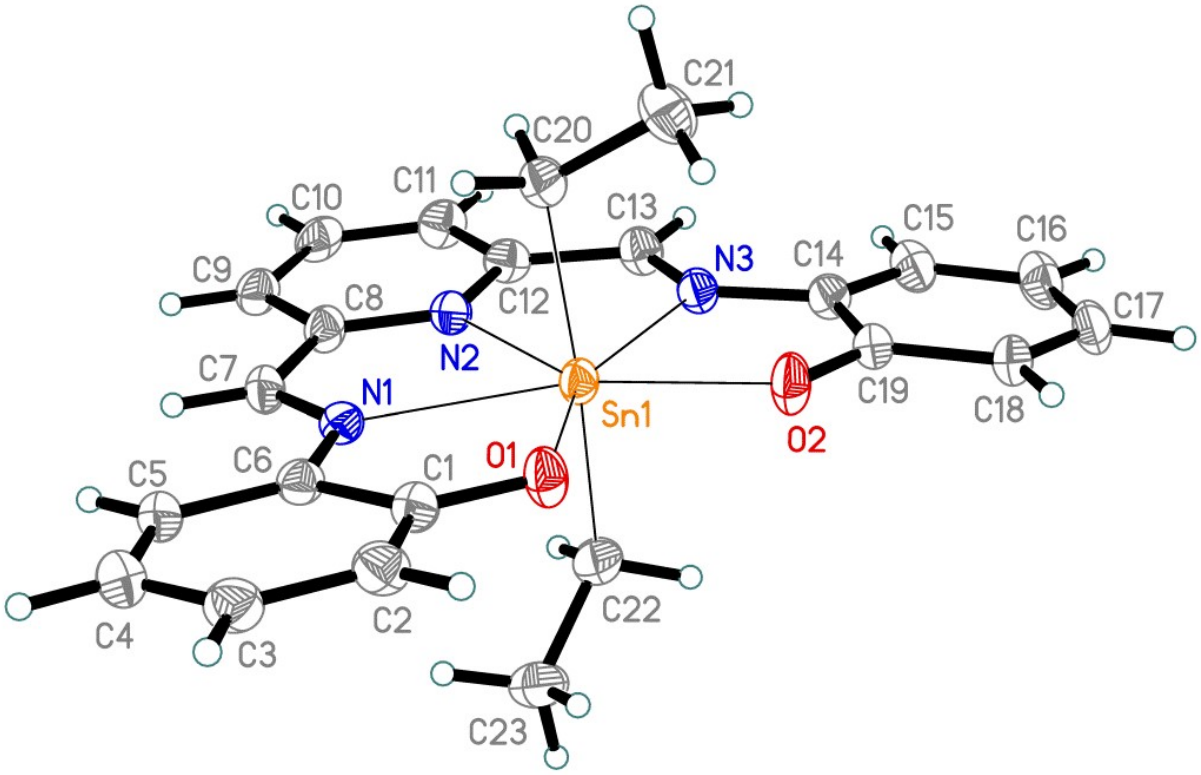

Fig. S14. The molecular structure of **5** (p=50%).

Table S13. Selected bond distances for **5**, Å.

Sn1-O1	2.168(2)	N2-C12	1.334(4)	C10-C11	1.392(4)
Sn1-O2	2.167(2)	N3-C13	1.282(4)	C11-C12	1.402(4)
Sn1-N1	2.416(2)	N3-C14	1.402(4)	C12-C13	1.469(4)
Sn1-N2	2.435(3)	C1-C2	1.420(4)	C14-C15	1.393(4)
Sn1-N3	2.415(2)	C1-C6	1.425(4)	C14-C19	1.420(4)
Sn1-C20	2.139(3)	C2-C3	1.377(4)	C15-C16	1.386(4)
Sn1-C22	2.138(3)	C3-C4	1.402(4)	C16-C17	1.398(5)
O1-C1	1.308(3)	C4-C5	1.377(4)	C17-C18	1.374(5)
O2-C19	1.307(4)	C5-C6	1.402(4)	C18-C19	1.422(4)
N1-C6	1.399(4)	C7-C8	1.470(4)	C20-C21	1.528(4)
N1-C7	1.279(4)	C8-C9	1.396(4)	C22-C23	1.517(5)
N2-C8	1.344(4)	C9-C10	1.389(4)		

Table S14. Selected bond angles for **5**, °.

O1-Sn1-N1	71.95(8)	N1-Sn1-N2	65.63(8)	C20-Sn1-N3	90.30(10)
O1-Sn1-N2	137.56(8)	N3-Sn1-N1	131.30(8)	C22-Sn1-O1	94.94(11)
O1-Sn1-N3	156.75(8)	N3-Sn1-N2	65.69(8)	C22-Sn1-O2	91.45(11)
O2-Sn1-O1	84.81(8)	C20-Sn1-O1	91.16(11)	C22-Sn1-N1	89.57(10)
O2-Sn1-N1	156.74(8)	C20-Sn1-O2	94.28(10)	C22-Sn1-N2	86.30(11)
O2-Sn1-N2	137.62(8)	C20-Sn1-N1	87.37(9)	C22-Sn1-N3	86.15(11)
O2-Sn1-N3	71.94(8)	C20-Sn1-N2	85.69(10)	C22-Sn1-C20	171.98(13)

7. ^{1}H, ^{13}C and ^{119}Sn NMR Spectra for 1-5

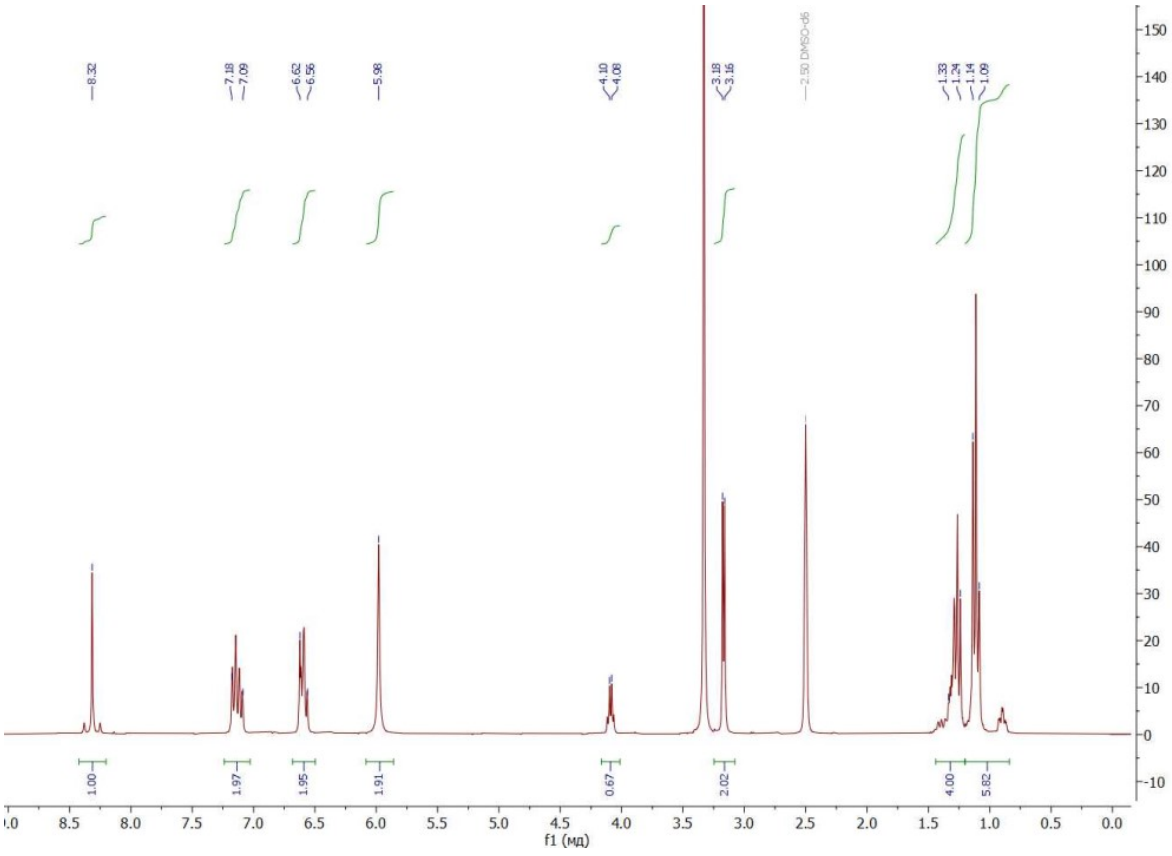

Fig. S15. ^{1}H NMR spectrum for **1.**

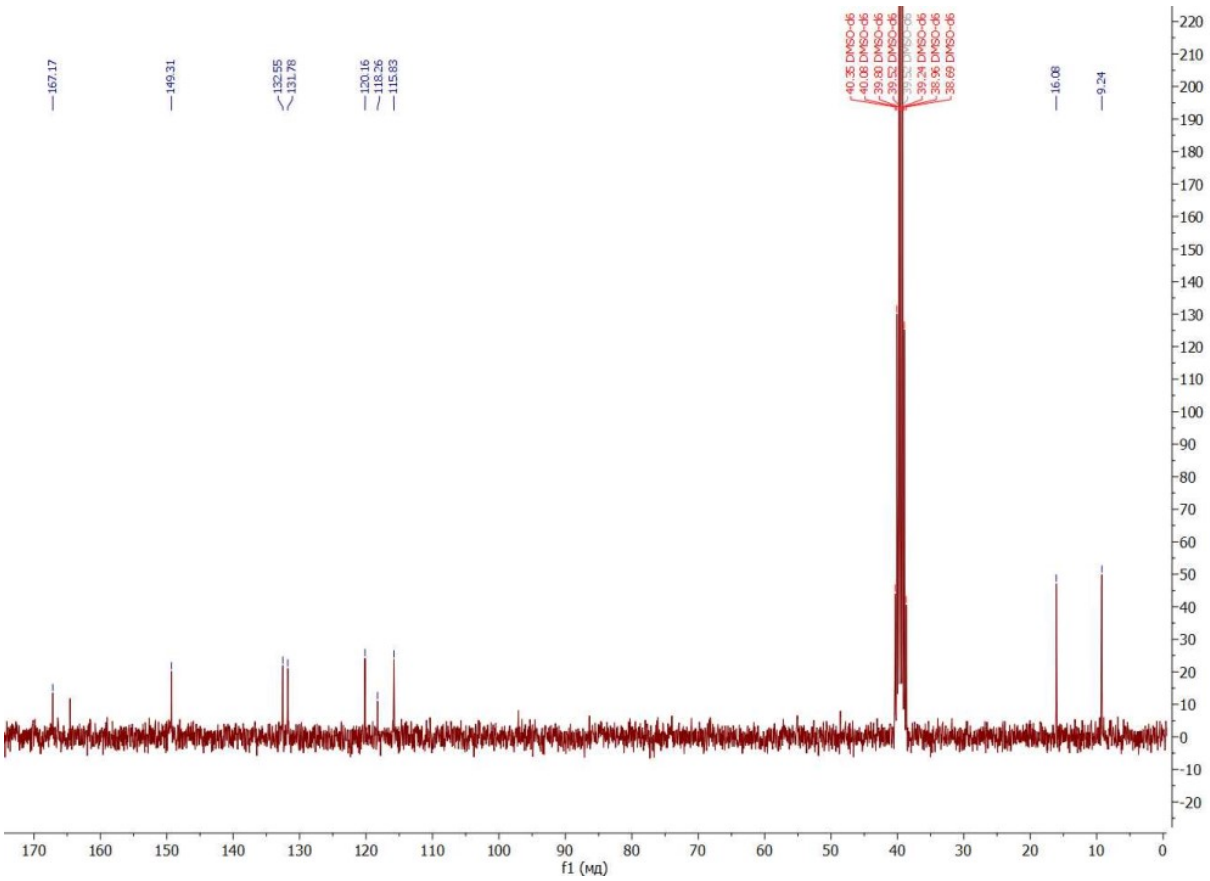

Fig. S16. ^{13}C NMR spectrum for **1.**

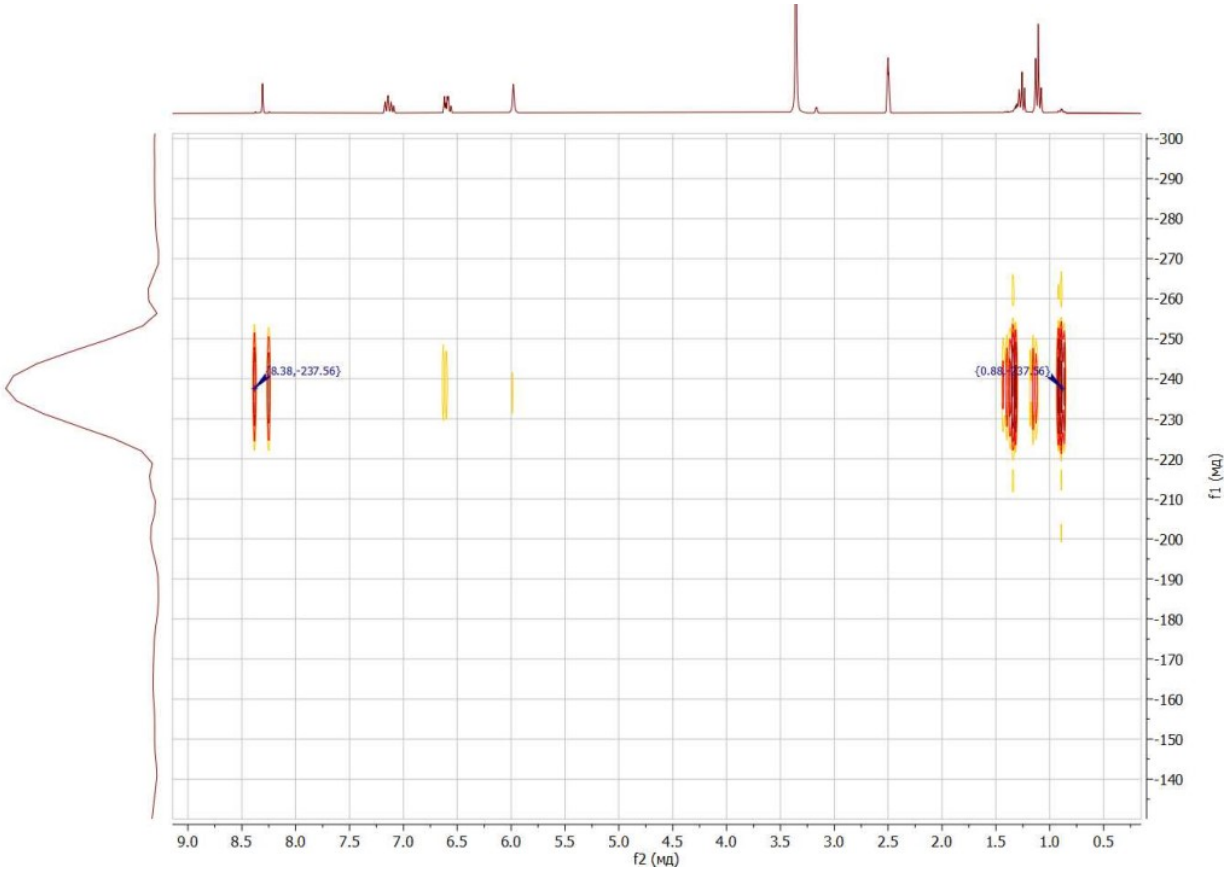

Fig. S17. ^{119}Sn NMR spectrum for **1**.

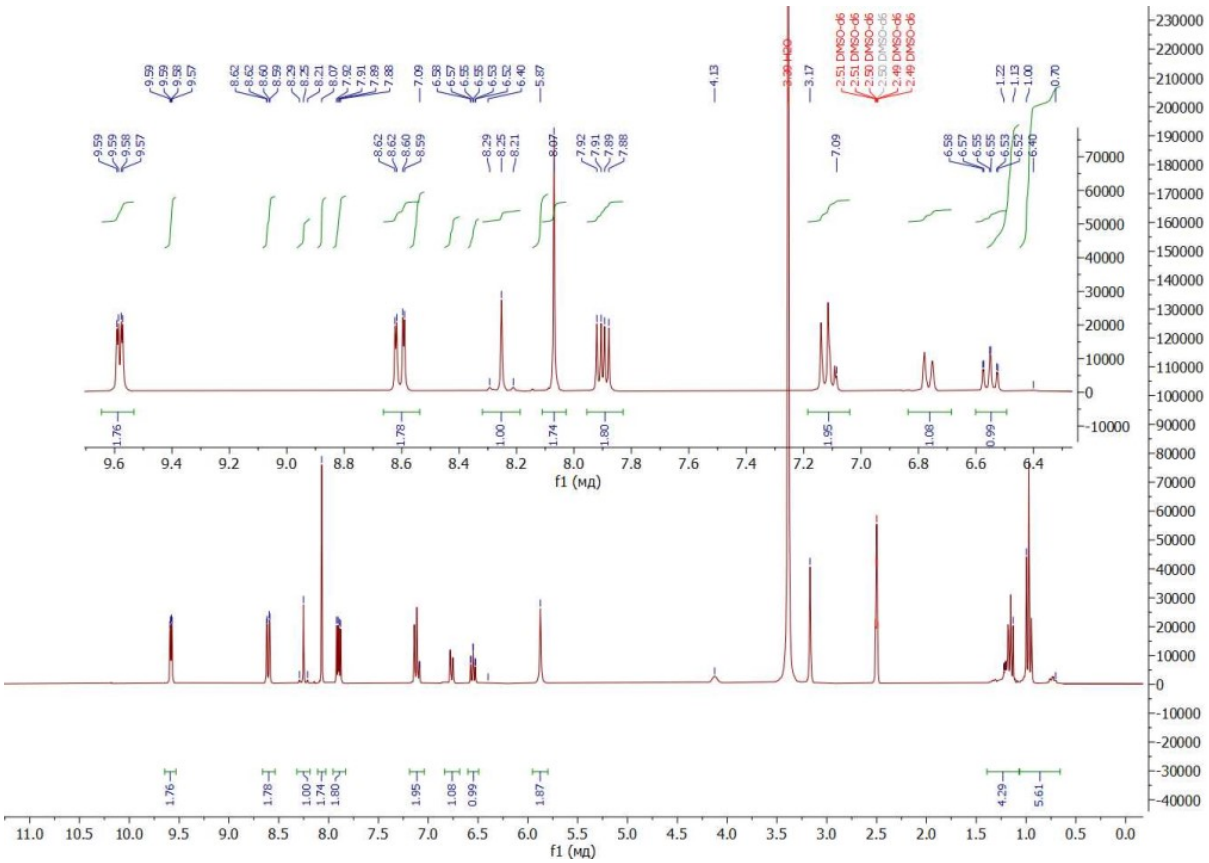

Fig. S18. ^{1}H NMR spectrum for **2**.

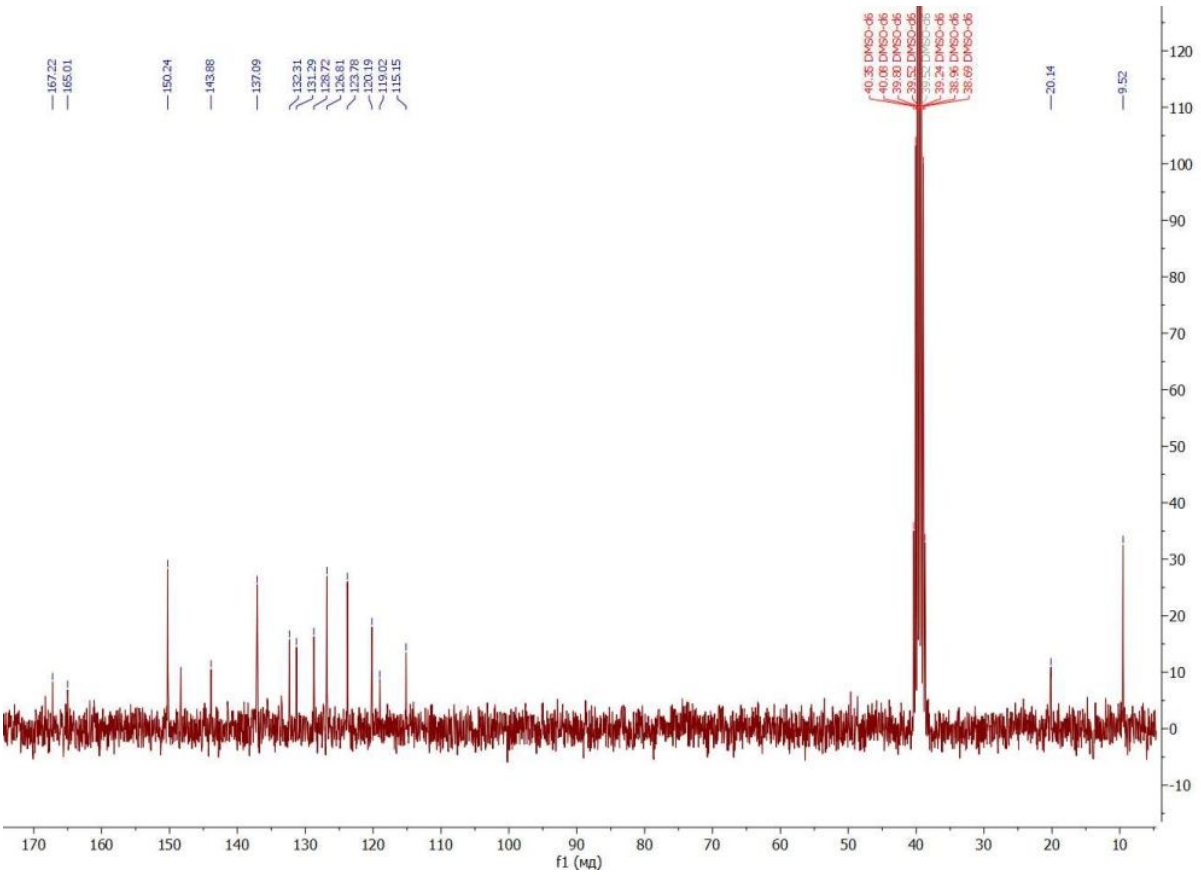

Fig. S19. ^{13}C NMR spectrum for **2**.

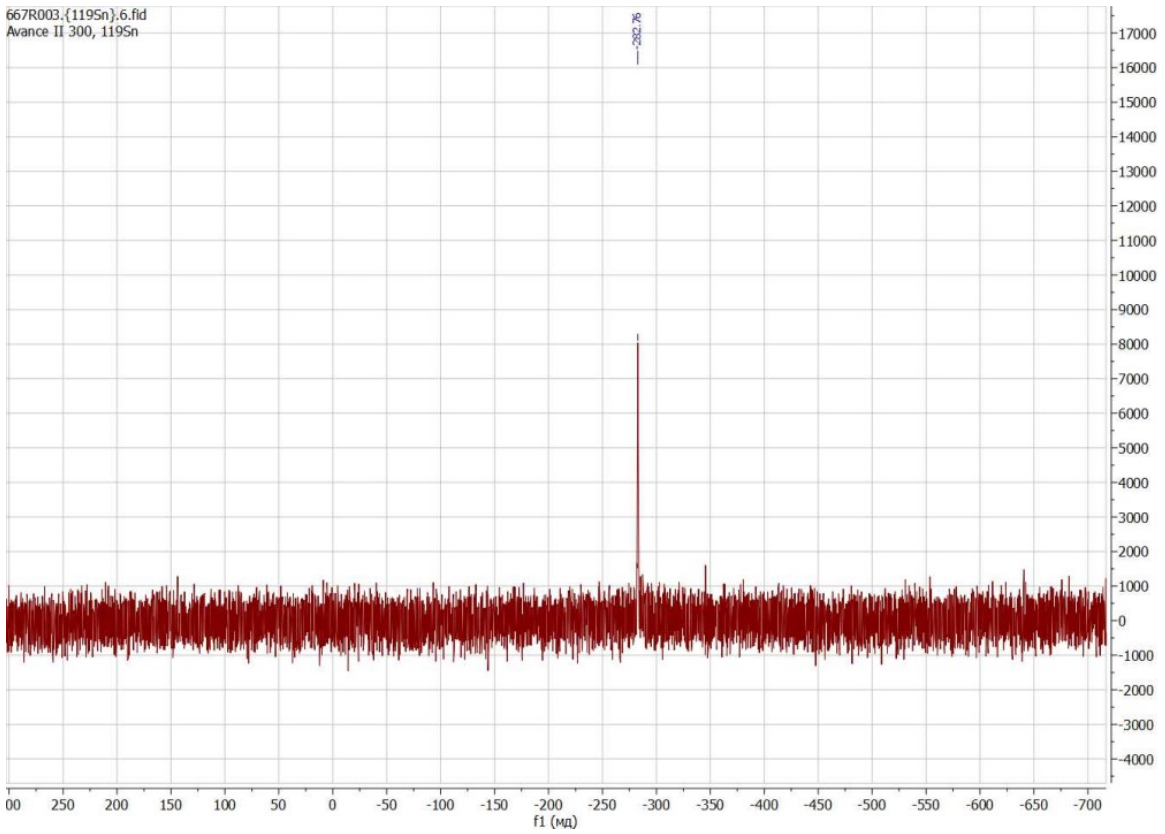

Fig. S20. ^{119}Sn NMR spectrum for **2** (353 K).

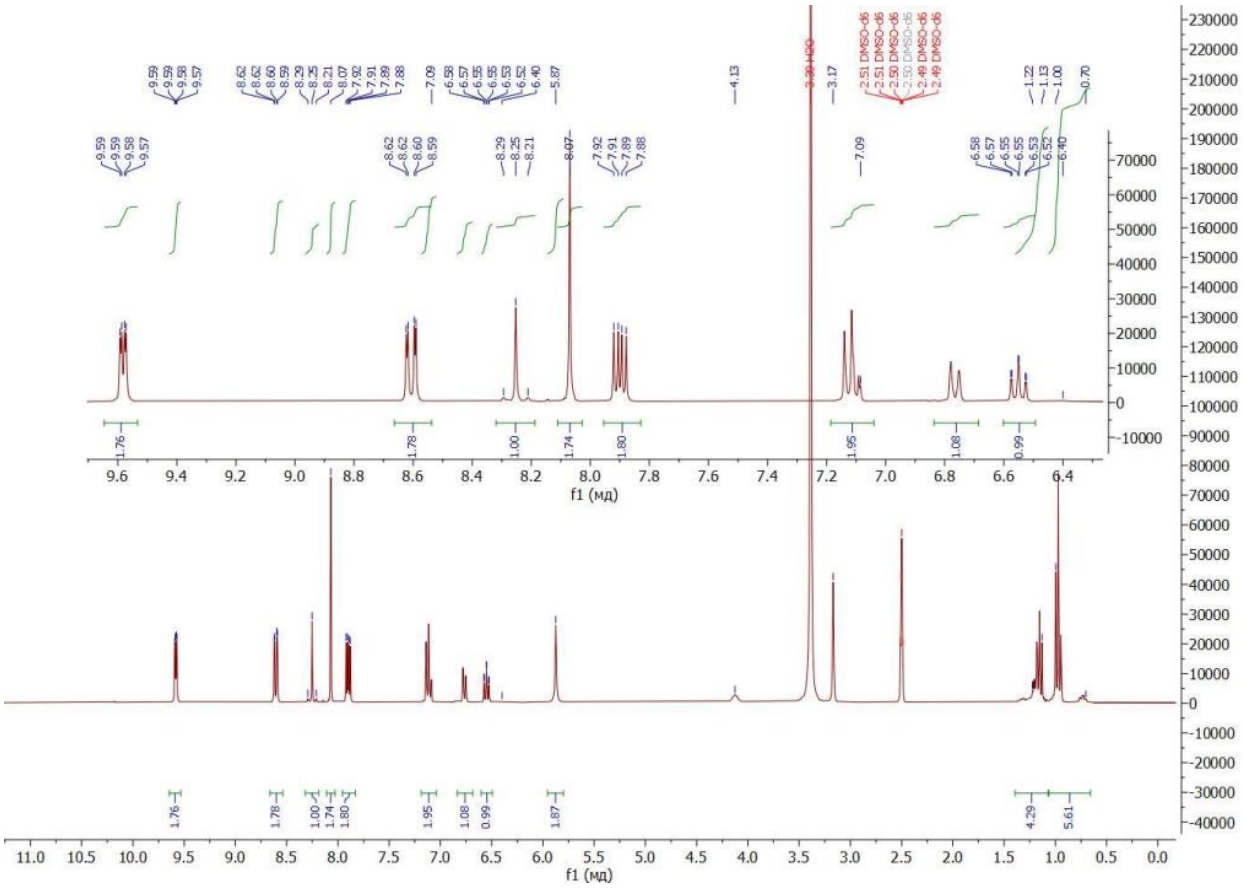

Fig. S21. ^{1}H NMR spectrum for **3**.

Fig. S22. ^{13}C NMR spectrum for **3**.

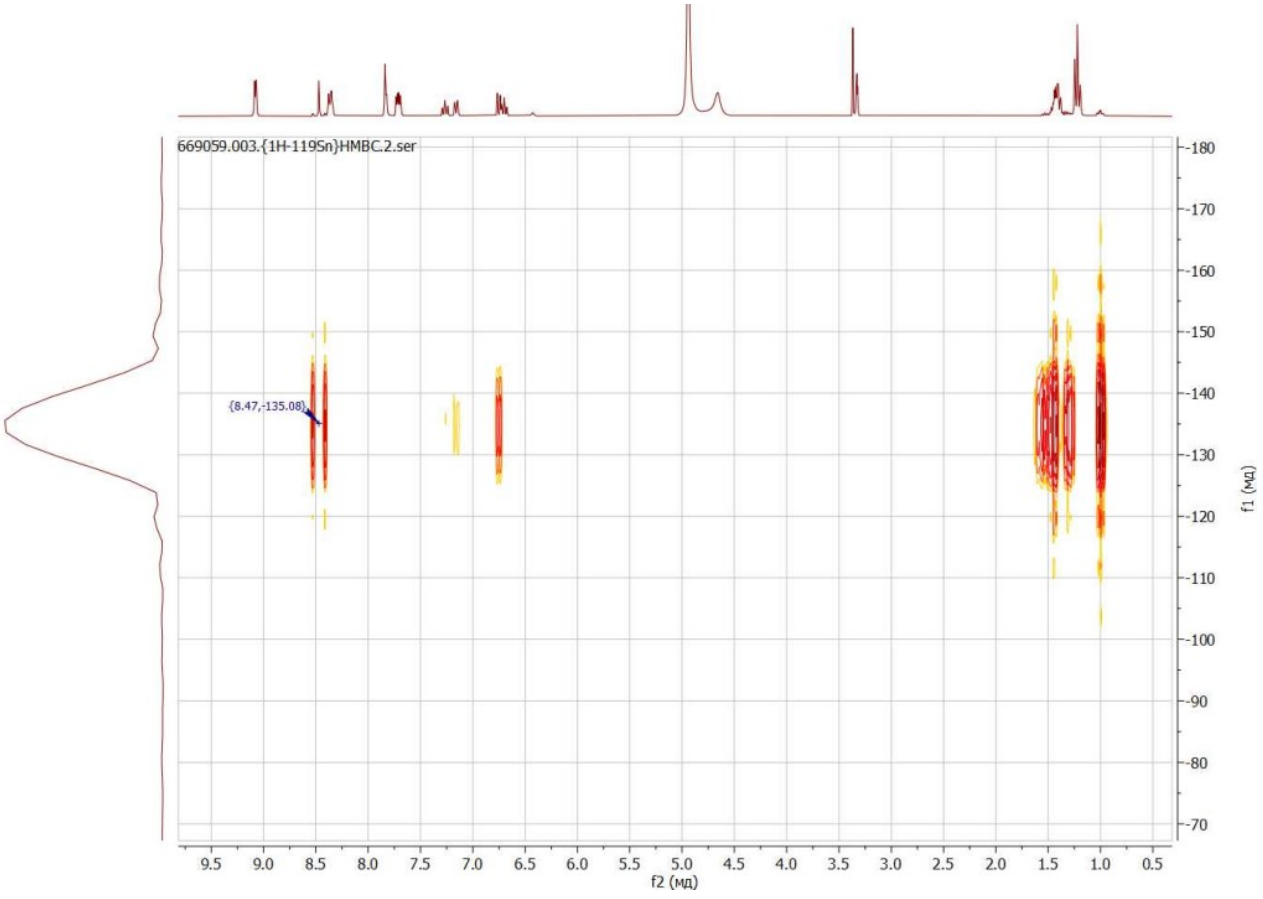

Fig. S23. ^{119}Sn NMR spectrum for **3**.

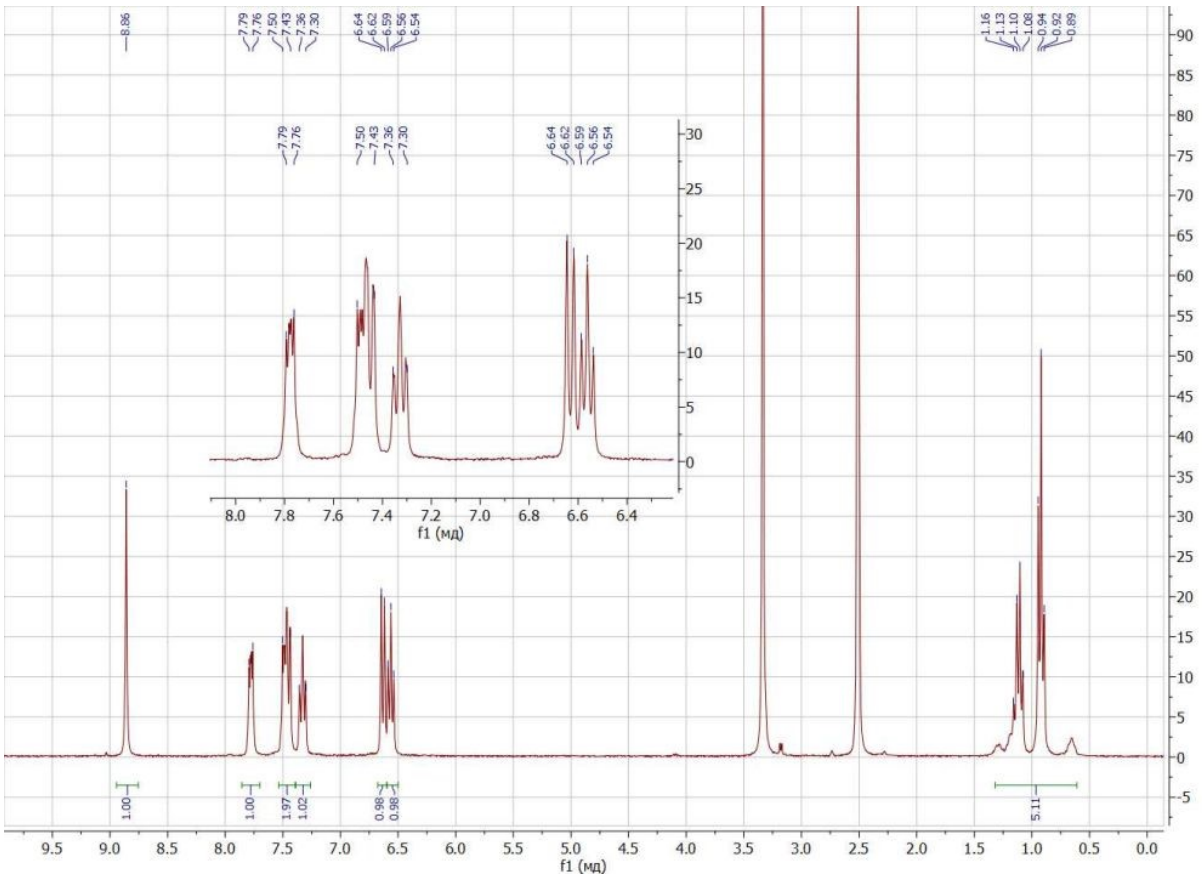

Fig. S24. ^{1}H NMR spectrum for **4**.

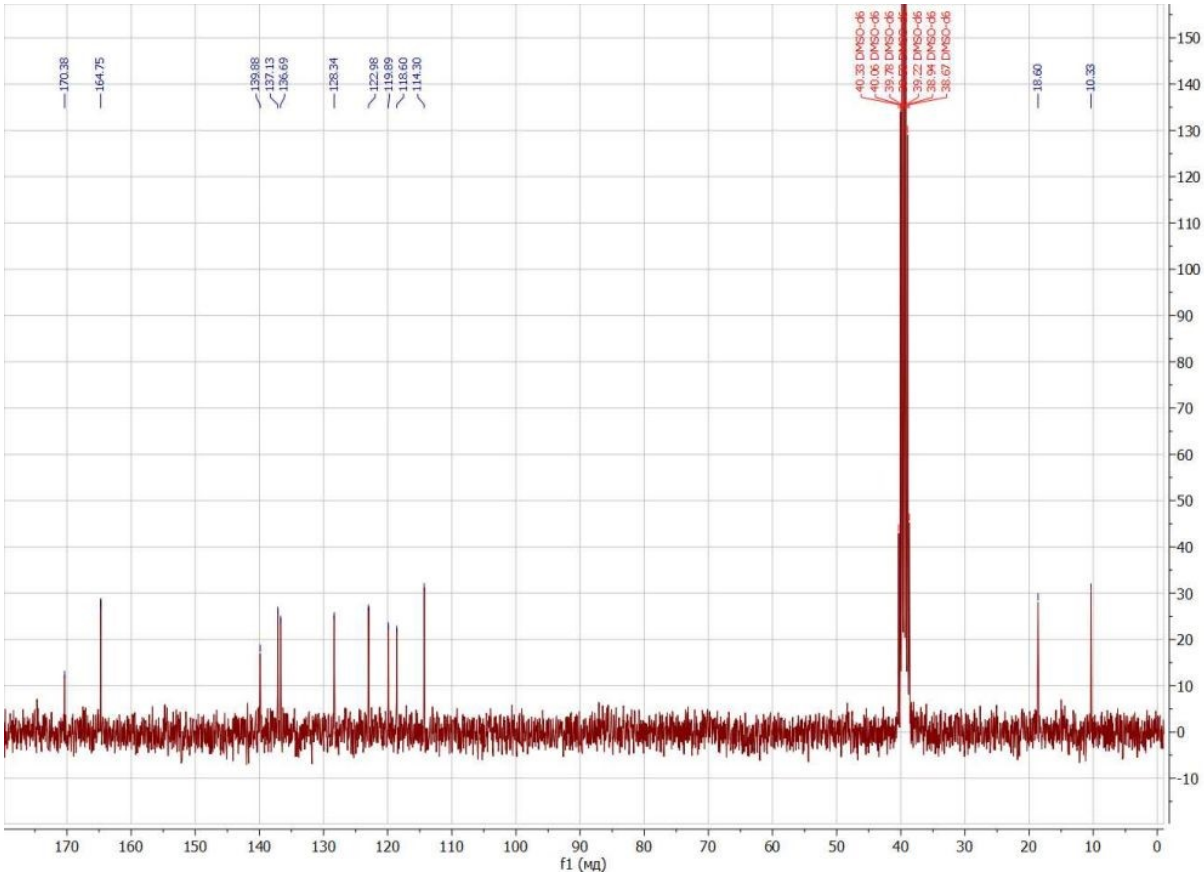

Fig. S25. ^{13}C NMR spectrum for **4**.

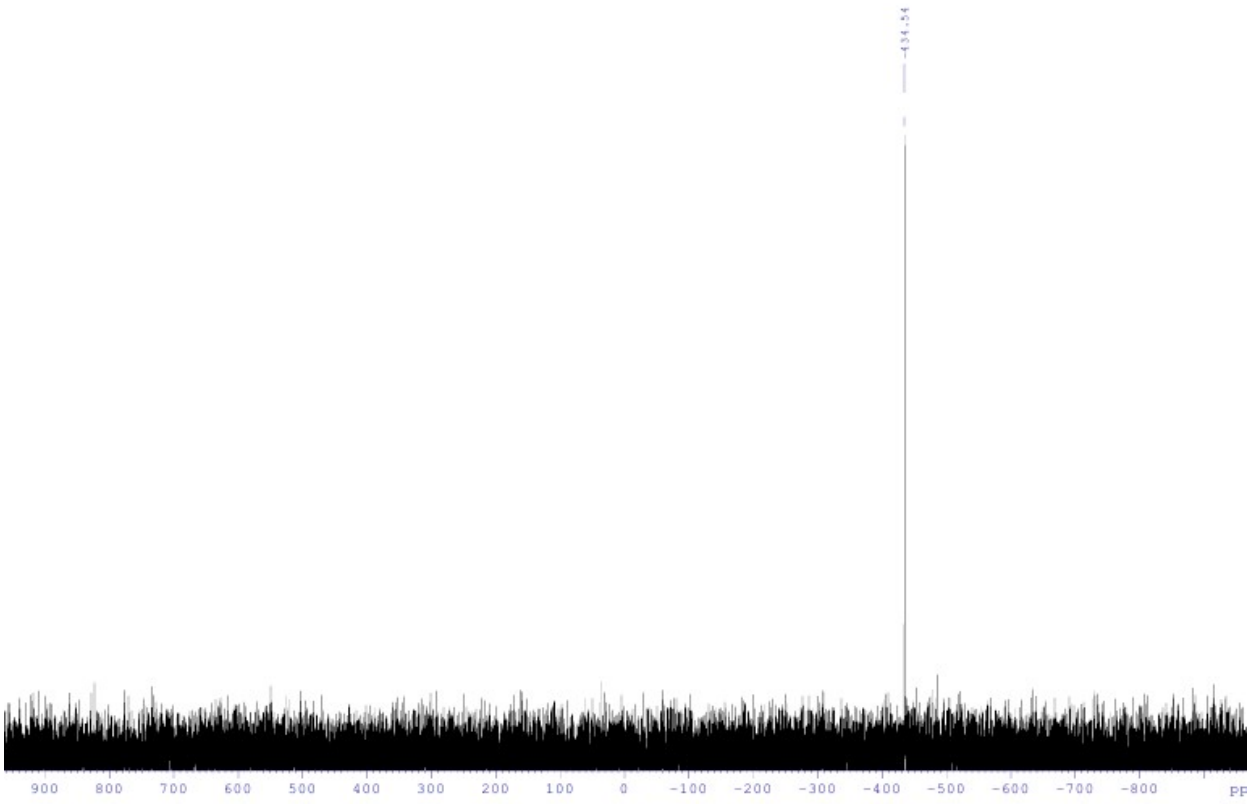

Fig. S26. ^{119}Sn NMR spectrum for **4**.

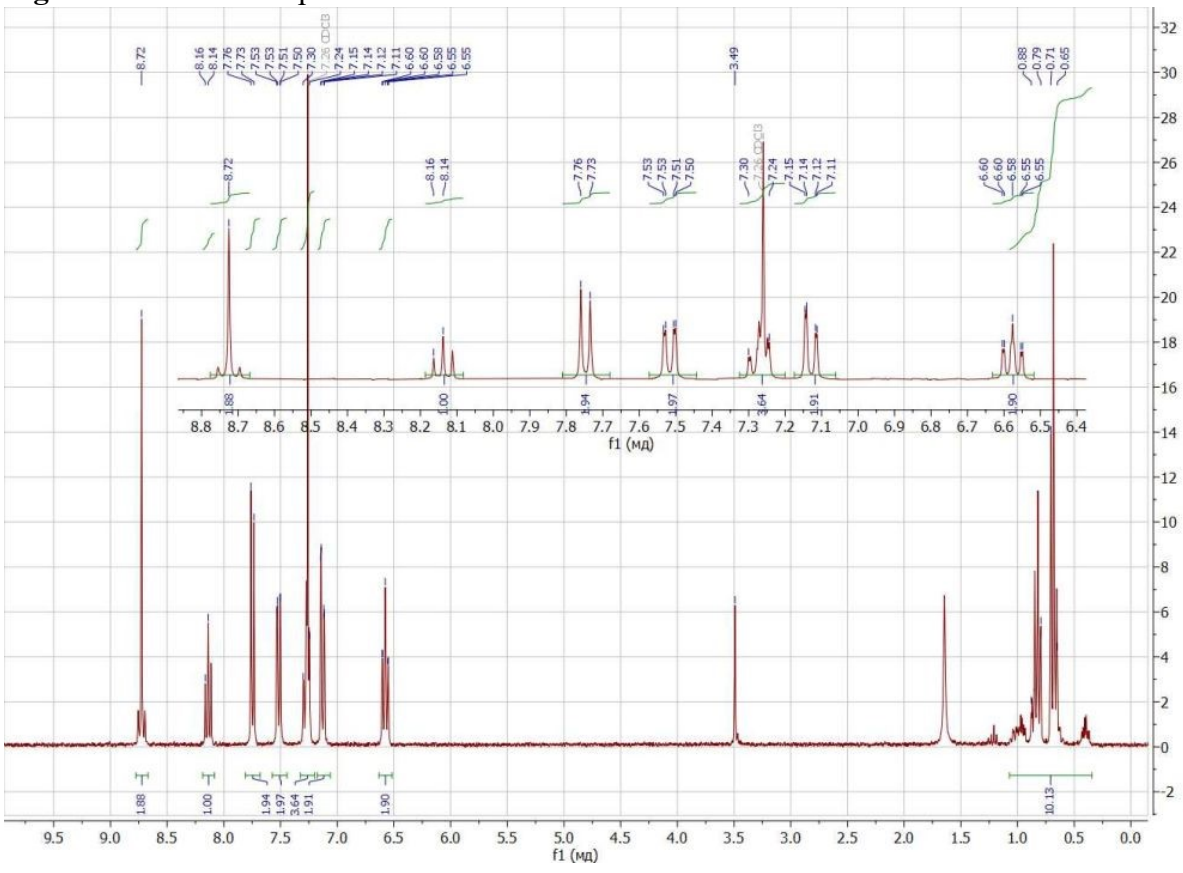

Fig. S27. ^{1}H NMR spectrum for **5**.

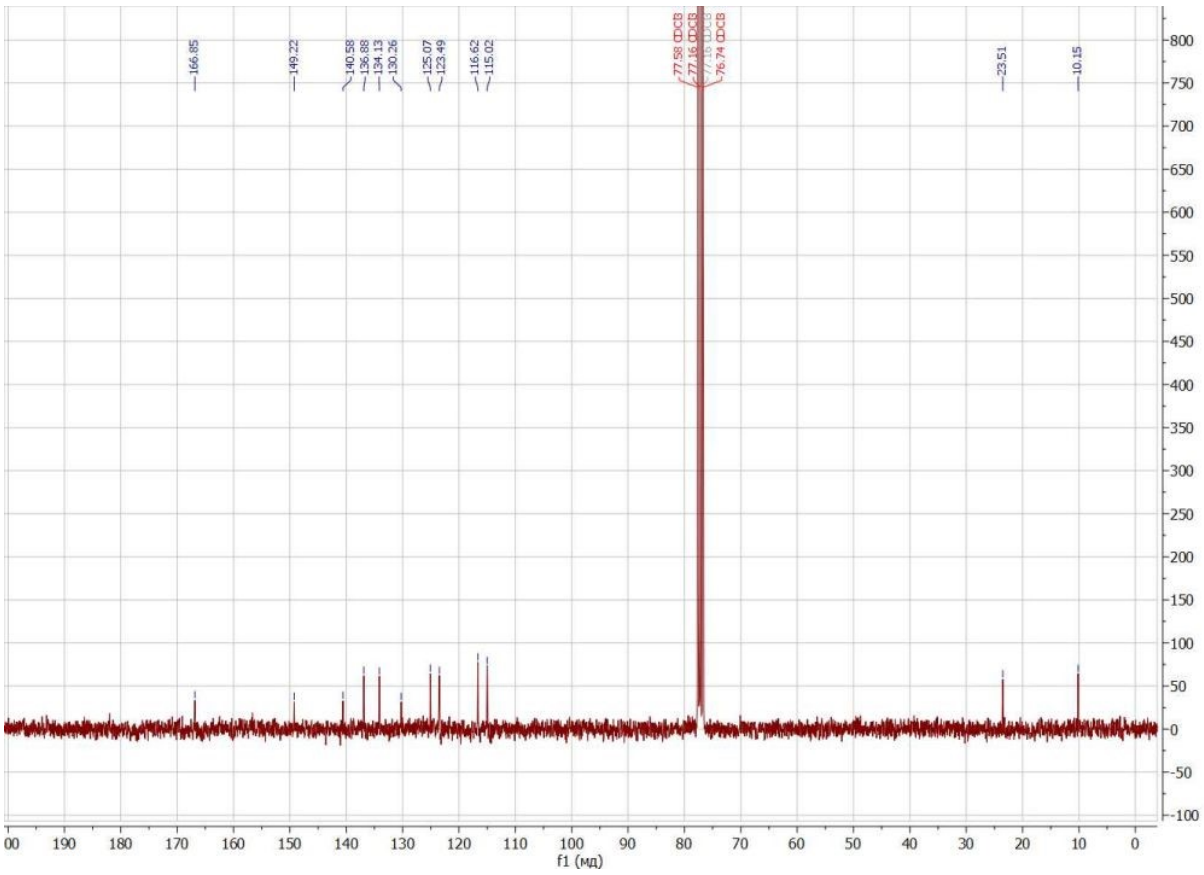

Fig. S28. ^{13}C NMR spectrum for **5**.

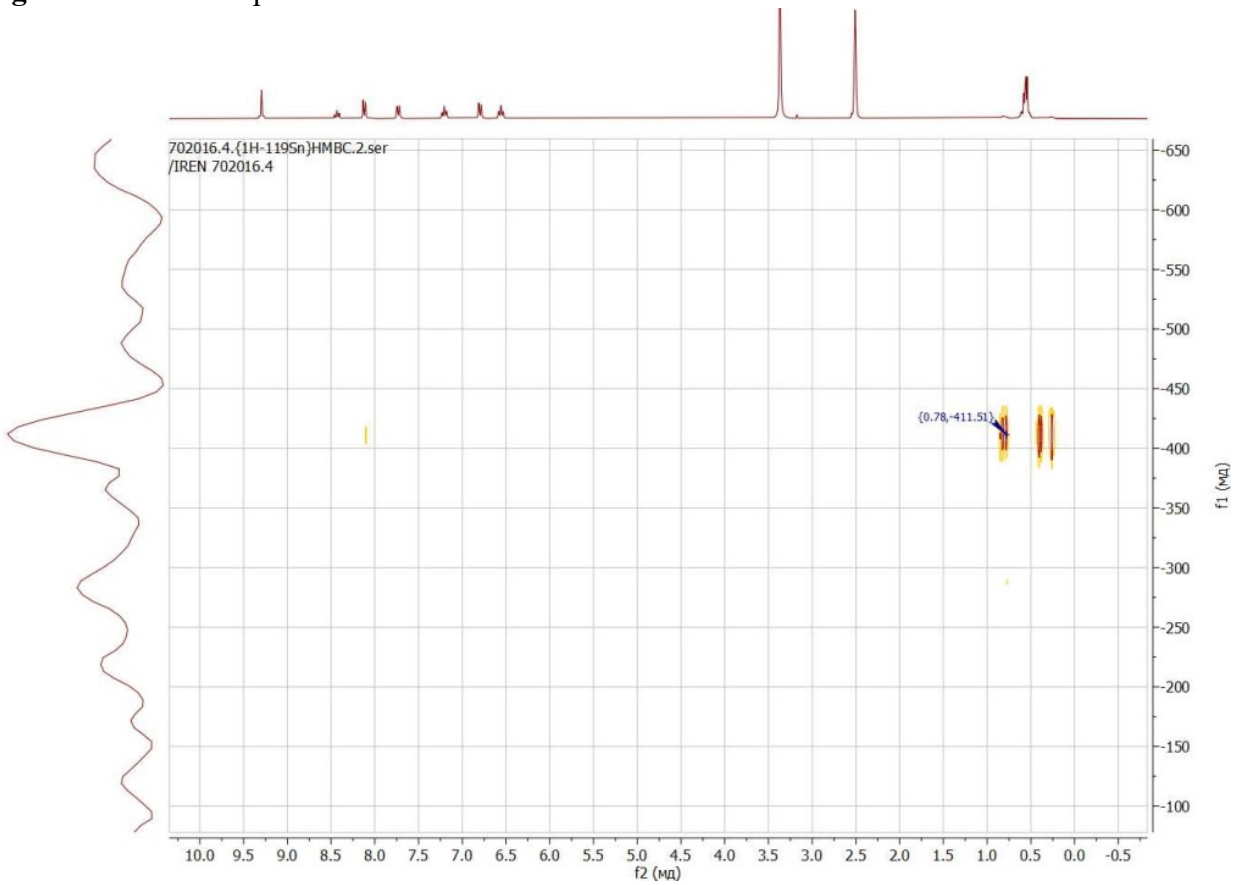

Fig. S29. ^{119}Sn NMR spectrum for **5**.

8. HOMO and LUMO of 1-5 calculated by the DFT PBE0/def2-TZVPP

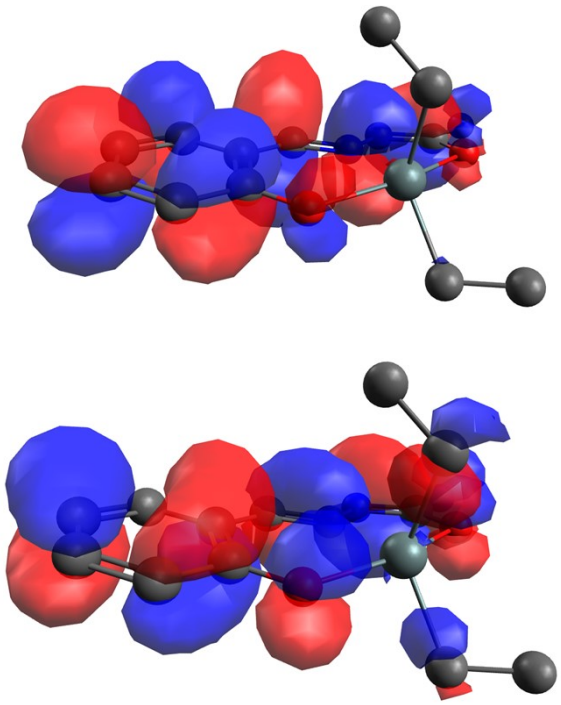

Fig. S30. LUMO (*top*) and HOMO (*bottom*) of **1**.

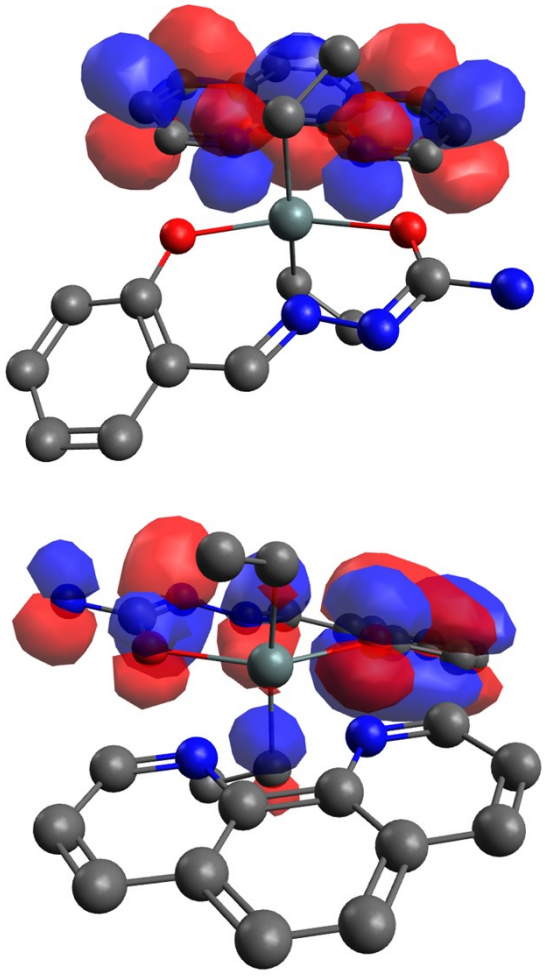

Fig. S31. LUMO (*top*) and HOMO (*bottom*) of **2**.

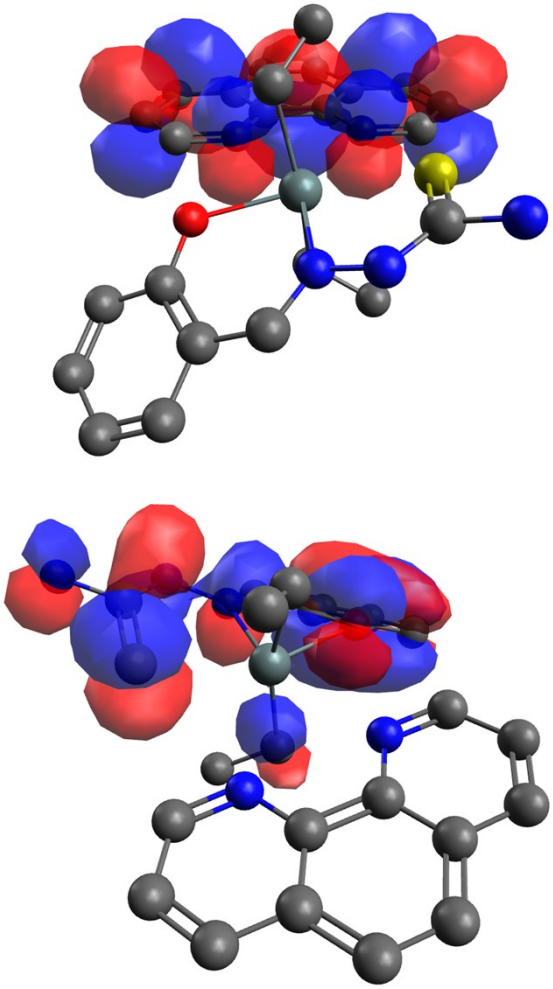

Fig. S32. LUMO (*top*) and HOMO (*bottom*) of **3**.

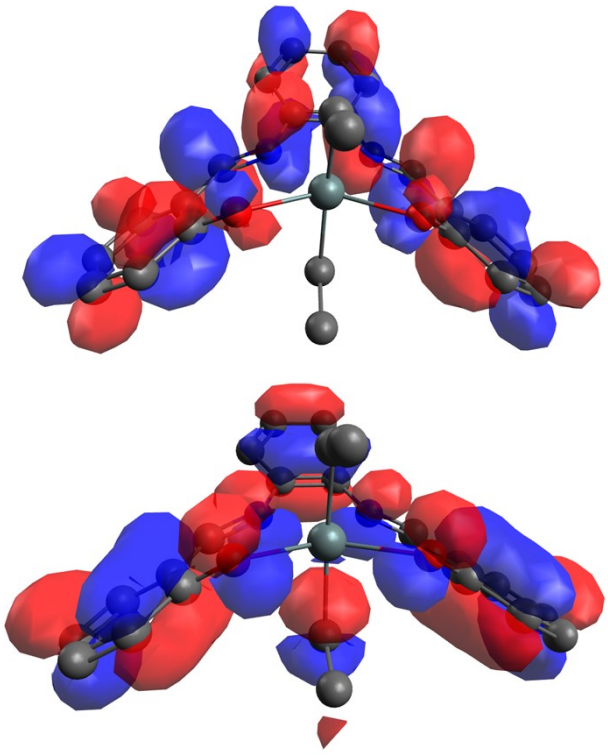

Fig. S33. LUMO (*top*) and HOMO (*bottom*) of **4**.

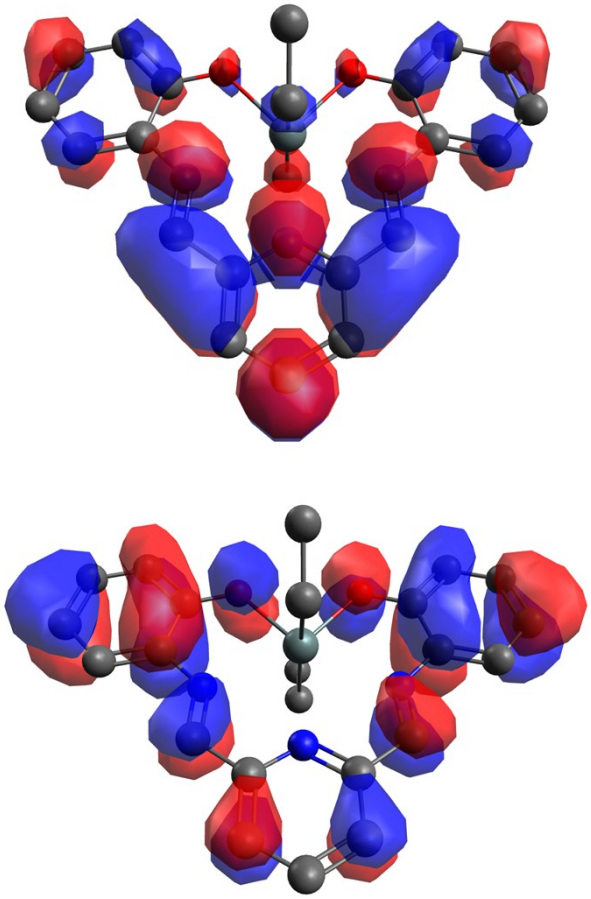

Fig. S34. LUMO (*top*) and HOMO (*bottom*) of **5**.

9. Cartesian coordinates and total energy values of 1-5 calculated by the DFT PBE0/def2-TZVPP

1: E = -997.279765901753 Eh

C	-2.15658	1.86933	-0.36287
C	1.22093	1.53345	-0.23167
C	2.19766	-0.67727	0.48416
C	2.33454	0.63987	-0.01415
C	3.61725	1.14083	-0.30423
H	3.69989	2.15591	-0.67973
C	4.74986	0.38094	-0.12282
C	4.61129	-0.92002	0.37618
C	3.36953	-1.43666	0.67456
H	1.45224	2.55346	-0.53429
H	5.72787	0.78243	-0.35575
H	5.49270	-1.53253	0.53312
H	3.25625	-2.44143	1.06314
Sn	-0.90376	-0.67231	0.31101
N	-0.03173	1.26294	-0.11781
O	1.04024	-1.21141	0.79700
O	-2.53792	0.66191	-0.12376
N	-0.91144	2.29490	-0.38049
N	-3.13090	2.78259	-0.65320
H	-2.86431	3.75033	-0.60944
H	-4.06198	2.54240	-0.36467
C	-1.05793	-1.78366	-1.48495
C	-0.22977	-1.12352	-2.59101
H	-2.11171	-1.84129	-1.76093
H	-0.70349	-2.79568	-1.28232
H	-0.29658	-1.68679	-3.52510
H	-0.57381	-0.10645	-2.79360
H	0.82610	-1.06535	-2.31579
C	-1.64501	-1.14121	2.23699
C	-3.12277	-1.53173	2.23735
H	-1.46925	-0.26232	2.86102
H	-1.00921	-1.93919	2.62317
H	-3.47370	-1.74644	3.25016
H	-3.74080	-0.73157	1.82784
H	-3.30058	-2.42579	1.63390

2: E = -1569.367698506334 Eh

C	0.74905	3.09876	0.30590
C	3.04191	0.66136	-0.16876
C	2.32715	-1.75602	0.03425
C	3.26603	-0.76248	-0.34026
C	4.50592	-1.14693	-0.87463

H	5.21241	-0.36695	-1.14213
C	4.84125	-2.47041	-1.06653
C	3.91630	-3.45170	-0.69897
C	2.69504	-3.10471	-0.16129
H	3.89561	1.32117	-0.32310
H	5.80178	-2.74219	-1.48592
H	4.16010	-4.50031	-0.83359
H	1.98321	-3.86717	0.13369
Sn	-0.07071	0.23769	0.30600
N	1.93280	1.22983	0.12803
O	1.16756	-1.48170	0.57769
O	-0.34913	2.43283	0.28569
N	1.96513	2.60704	0.23505
N	0.64233	4.47147	0.36971
H	1.48689	4.94860	0.63640
H	-0.20385	4.80758	0.79516
N	-1.87368	-1.80759	0.42232
N	-2.78934	0.73493	-0.07217
C	-3.19057	-1.62798	0.18926
C	-3.67471	-0.28326	-0.07685
C	-3.22448	1.95435	-0.30991
C	-4.57372	2.25081	-0.56695
C	-5.48382	1.22701	-0.56767
C	-1.42923	-3.02153	0.67290
C	-2.26551	-4.14968	0.70696
C	-3.60418	-3.98318	0.46632
C	-5.04522	-0.08738	-0.31839
C	-4.10521	-2.69482	0.19888
C	-5.49929	-2.45253	-0.05586
C	-5.94878	-1.20538	-0.30267
H	-0.36167	-3.09511	0.84823
H	-1.84429	-5.12435	0.91800
H	-4.28557	-4.82707	0.47968
H	-6.18008	-3.29629	-0.04358
H	-7.00011	-1.02106	-0.49312
H	-6.53607	1.41149	-0.75563
H	-4.87323	3.27400	-0.75503
H	-2.46882	2.73095	-0.28812
C	-0.41663	0.24672	2.39400
C	-1.71931	0.85795	2.89082
H	0.44285	0.79479	2.78967
H	-0.30815	-0.79047	2.71150
H	-1.73891	0.89799	3.98414
H	-1.84794	1.87389	2.51394
H	-2.58294	0.27415	2.56878
C	-0.28150	-0.06075	-1.78297
C	-0.15335	1.22125	-2.59862
H	-1.23581	-0.55444	-1.96187

H	0.50938	-0.76880	-2.04156
H	-0.18024	1.00819	-3.67130
H	-0.96162	1.91819	-2.37201
H	0.78598	1.73768	-2.38895

3: E = -1892.305906781324 Eh

C	1.19725	3.39654	0.58980
C	3.07937	0.68609	-0.12943
C	2.26653	-1.68907	0.01220
C	3.20779	-0.72388	-0.42313
C	4.37229	-1.13431	-1.09477
H	5.08652	-0.37477	-1.39789
C	4.61997	-2.45998	-1.37148
C	3.69108	-3.41640	-0.94333
C	2.55040	-3.04529	-0.26653
H	3.97402	1.29633	-0.24981
H	5.51855	-2.75748	-1.89689
H	3.87281	-4.46757	-1.14131
H	1.84026	-3.79001	0.07345
Sn	-0.03802	0.37278	0.35261
N	2.02786	1.30961	0.26918
O	1.19178	-1.36935	0.67889
S	-0.45090	2.92855	0.32259
N	2.25100	2.64693	0.55230
N	1.40529	4.73039	0.83102
H	2.30932	4.96834	1.20464
H	0.61838	5.25122	1.17376
N	-1.89248	-1.74564	0.46996
N	-2.91983	0.71525	-0.23909
C	-3.21481	-1.63953	0.22430
C	-3.75591	-0.34349	-0.15762
C	-3.41960	1.87668	-0.60641
C	-4.77670	2.08224	-0.90440
C	-5.63532	1.02098	-0.80526
C	-1.40280	-2.91583	0.82331
C	-2.19099	-4.07072	0.95628
C	-3.53412	-3.97959	0.70393
C	-5.13297	-0.23728	-0.42499
C	-4.08431	-2.74049	0.32560
C	-5.48603	-2.58550	0.04941
C	-5.98724	-1.38736	-0.31017
H	-0.33436	-2.93231	1.00750
H	-1.73118	-5.00504	1.25242
H	-4.18239	-4.84490	0.79146
H	-6.12843	-3.45470	0.13518
H	-7.04398	-1.26625	-0.52047
H	-6.69348	1.13123	-1.01664

H	-5.11917	3.06582	-1.19946
H	-2.72383	2.70511	-0.67095
C	-0.49208	0.27573	2.42336
C	-1.87125	0.75157	2.85405
H	0.28822	0.88964	2.88106
H	-0.30825	-0.75845	2.71273
H	-1.95890	0.74708	3.94470
H	-2.06494	1.76816	2.50739
H	-2.65745	0.10722	2.45890
C	-0.19654	-0.06232	-1.72374
C	-0.12044	1.15379	-2.63642
H	-1.12647	-0.61120	-1.86102
H	0.62570	-0.75209	-1.92376
H	-0.10511	0.84949	-3.68735
H	-0.97219	1.81886	-2.48876
H	0.77911	1.74355	-2.44638

4: E = -1404.368331641860 Eh

C	-0.73410	4.91914	0.30548
C	-1.41566	3.71394	0.20675
C	-0.71392	2.52302	0.04777
C	0.68949	2.54102	0.02394
C	1.36425	3.75040	0.15923
C	0.65466	4.93721	0.28162
H	-1.28857	5.84088	0.43343
H	-2.49587	3.69421	0.28491
H	2.44661	3.76018	0.20037
H	1.18884	5.87325	0.39068
C	-2.49624	1.10746	-0.55267
C	2.48844	1.17316	-0.63501
N	-1.32530	1.25453	-0.02208
N	1.33077	1.28818	-0.06834
H	2.90023	2.05881	-1.12558
H	-2.94544	1.97960	-1.03471
C	3.30574	0.00461	-0.71101
C	3.04697	-1.19369	0.02746
C	4.46508	0.09334	-1.52143
C	3.98713	-2.25324	-0.11854
C	5.34386	-0.94683	-1.64515
H	4.64582	1.02131	-2.05608
C	5.08616	-2.13233	-0.92573
H	3.79514	-3.16049	0.44144
H	6.22071	-0.86315	-2.27409
H	5.77609	-2.96558	-1.00979
C	-3.28402	-0.08311	-0.59690
C	-2.97372	-1.26414	0.14931
C	-4.46542	-0.03591	-1.37818

C	-3.88990	-2.34903	0.04455
C	-5.31889	-1.10082	-1.46512
H	-4.68446	0.87940	-1.92028
C	-5.01232	-2.26838	-0.73541
H	-3.65983	-3.24276	0.61190
H	-6.21312	-1.04936	-2.07270
H	-5.68239	-3.12012	-0.78942
O	-1.94607	-1.37203	0.91493
O	2.04554	-1.33914	0.82070
Sn	0.03565	-0.47265	0.55798
C	-0.00166	-1.40722	-1.34908
C	-0.00935	-2.93208	-1.26316
H	0.87203	-1.05045	-1.89814
H	-0.89102	-1.04108	-1.86585
H	-0.04581	-3.38530	-2.25779
H	0.88771	-3.30012	-0.76103
H	-0.87614	-3.28865	-0.70322
C	0.07716	-0.10828	2.63842
C	0.08399	-1.39610	3.46118
H	-0.80119	0.49835	2.86583
H	0.97049	0.48762	2.83292
H	0.10289	-1.17695	4.53276
H	-0.80705	-1.99222	3.25635
H	0.96161	-2.00185	3.22763

5: E = -1420.403956755483 Eh

C	0.00001	1.15596	-2.79567
C	0.00002	1.19964	-4.18850
C	0.00001	0.00000	-4.88651
C	0.00001	-1.19964	-4.18849
C	0.00001	-1.15597	-2.79567
N	0.00001	-0.00000	-2.13837
H	0.00002	0.00000	-5.97009
H	0.00001	2.15125	-4.70541
H	0.00001	-2.15125	-4.70541
C	-0.00000	-2.37391	-1.96090
C	0.00001	2.37390	-1.96089
N	0.00000	-2.23820	-0.69787
N	0.00001	2.23819	-0.69786
H	-0.00001	-3.33879	-2.46953
H	0.00001	3.33878	-2.46952
Sn	0.00002	-0.00001	0.39494
C	-0.00000	3.23827	0.26856
C	-0.00002	4.61425	-0.00619
C	0.00001	2.75937	1.60733
C	-0.00004	5.53441	1.01485
H	-0.00003	4.95655	-1.03519

C	-0.00001	3.73262	2.63662
C	-0.00003	5.07525	2.34343
H	-0.00005	6.59558	0.79988
H	-0.00001	3.37824	3.66014
H	-0.00004	5.79491	3.15511
C	-0.00001	-3.23828	0.26855
C	-0.00003	-4.61426	-0.00620
C	0.00001	-2.75939	1.60733
C	-0.00005	-5.53443	1.01484
H	-0.00004	-4.95656	-1.03520
C	-0.00001	-3.73263	2.63662
C	-0.00004	-5.07527	2.34341
H	-0.00007	-6.59559	0.79987
H	-0.00001	-3.37826	3.66013
H	-0.00005	-5.79493	3.15509
O	0.00003	1.49215	1.90527
O	0.00003	-1.49217	1.90526
C	-2.11387	-0.00001	0.11731
C	-2.88726	0.00003	1.43415
H	-2.35664	-0.88026	-0.48129
H	-2.35663	0.88021	-0.48134
H	-3.96719	0.00002	1.25765
H	-2.64142	-0.87818	2.03340
H	-2.64143	0.87827	2.03335
C	2.11391	-0.00001	0.11728
C	2.88732	0.00004	1.43411
H	2.35666	0.88020	-0.48138
H	2.35666	-0.88027	-0.48131
H	3.96724	0.00003	1.25759
H	2.64150	0.87829	2.03330
H	2.64148	-0.87816	2.03337