Supporting Information:

Evaluation of Tin Nitride (Sn_3N_4) via Atomic Layer Deposition Using Novel Volatile Sn Precursors

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1. NMR spectra of *L*2H

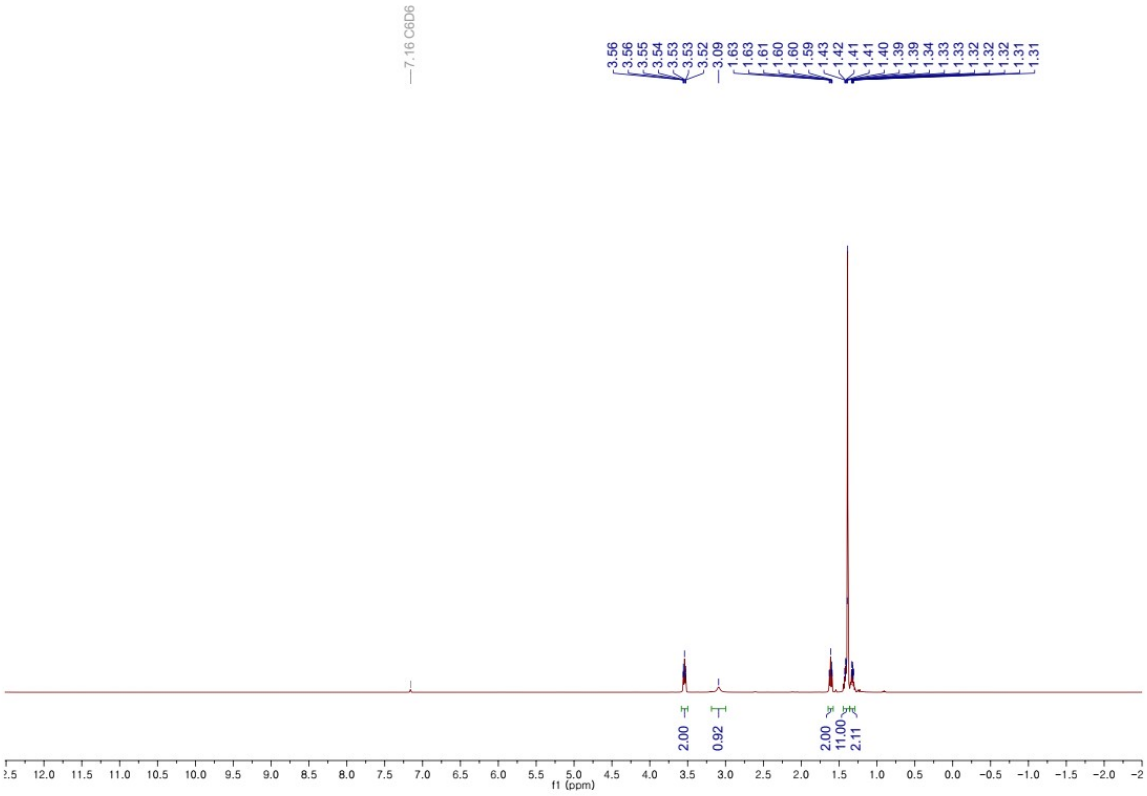

Figure S1-1. ^{1}H NMR spectrum of ***L2***H

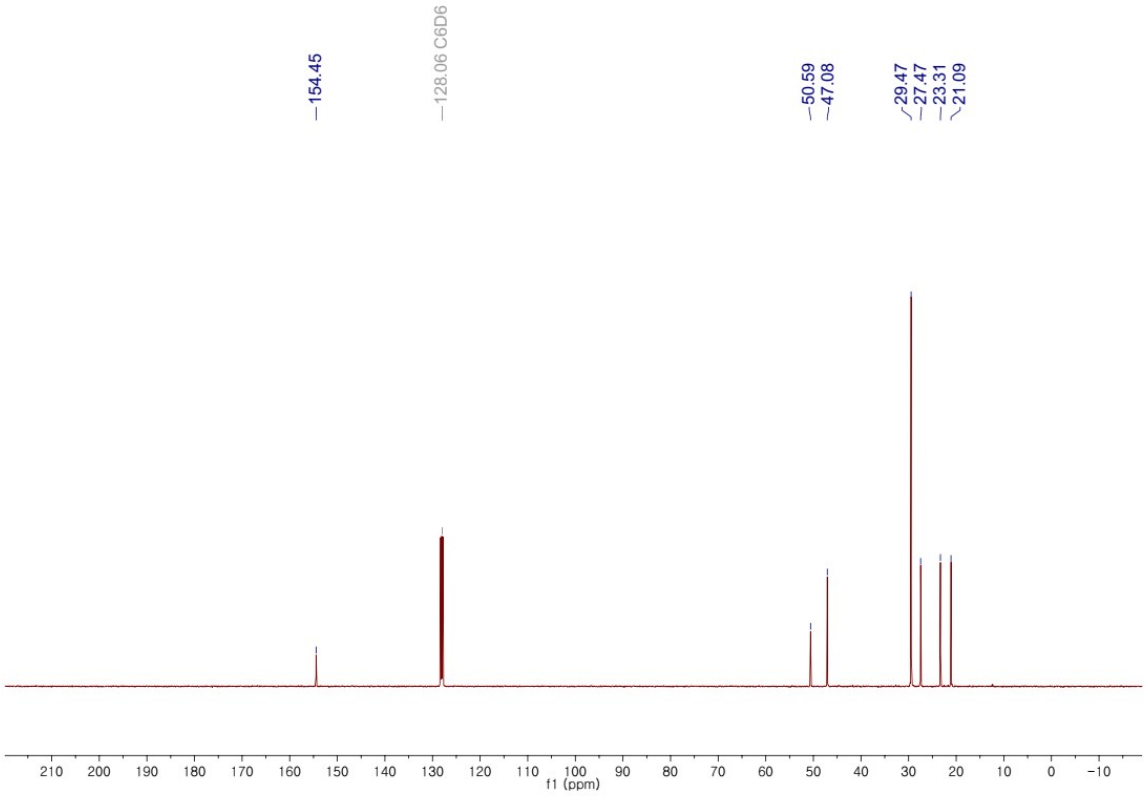

Figure S1-2. ^{13}C NMR spectrum of ***L2***H

2. IR spectra of 1 – 3

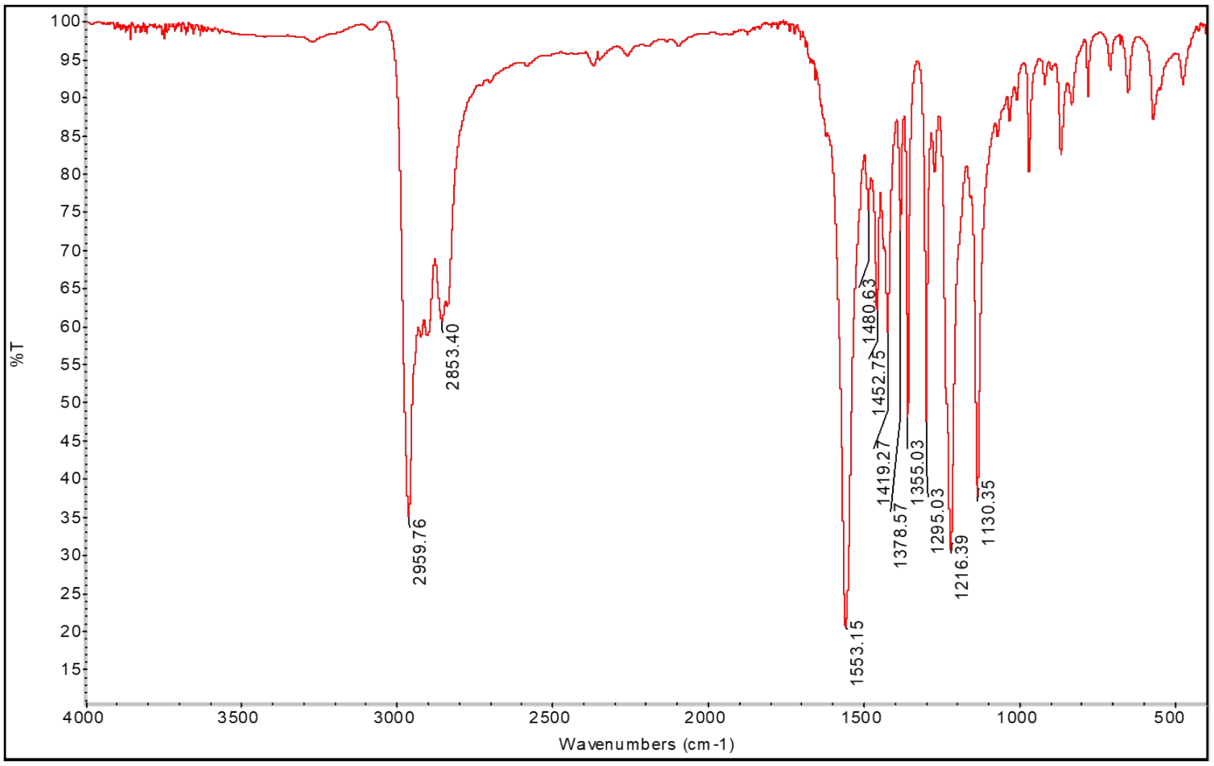

Figure S2-1. IR spectra of **1**

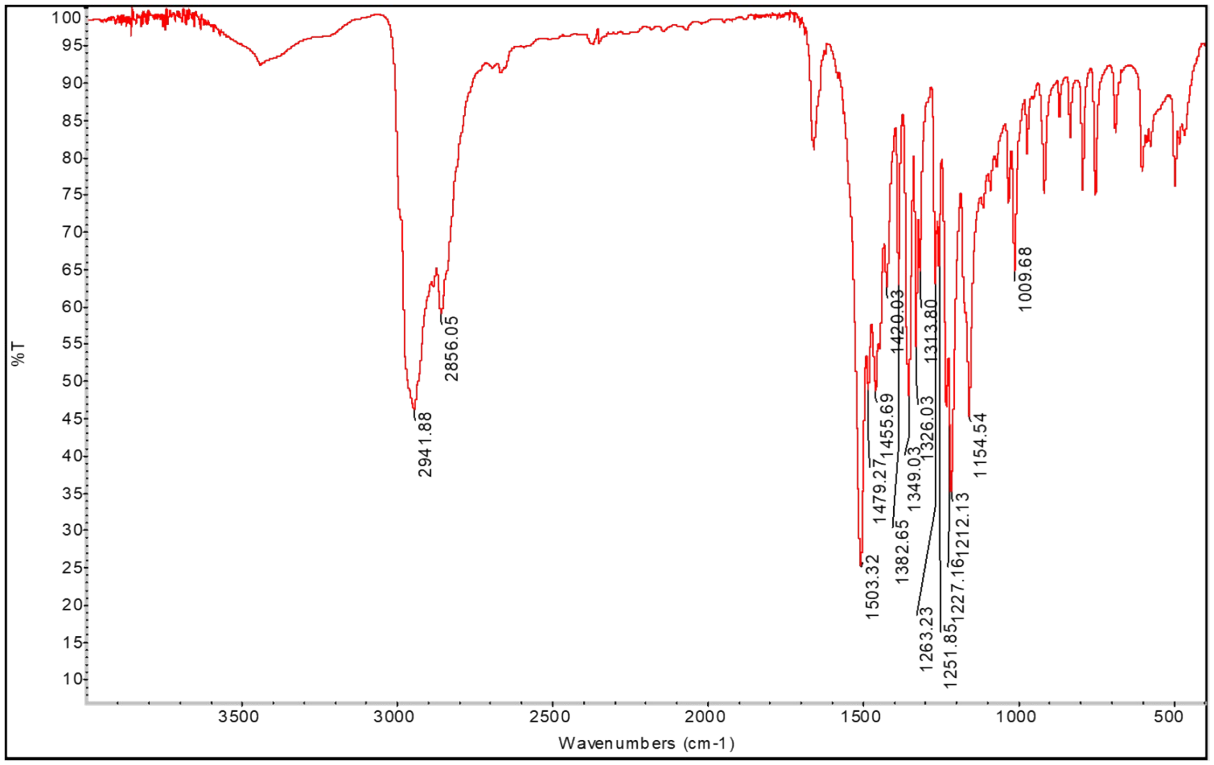

Figure S2-2. IR spectra of **2**

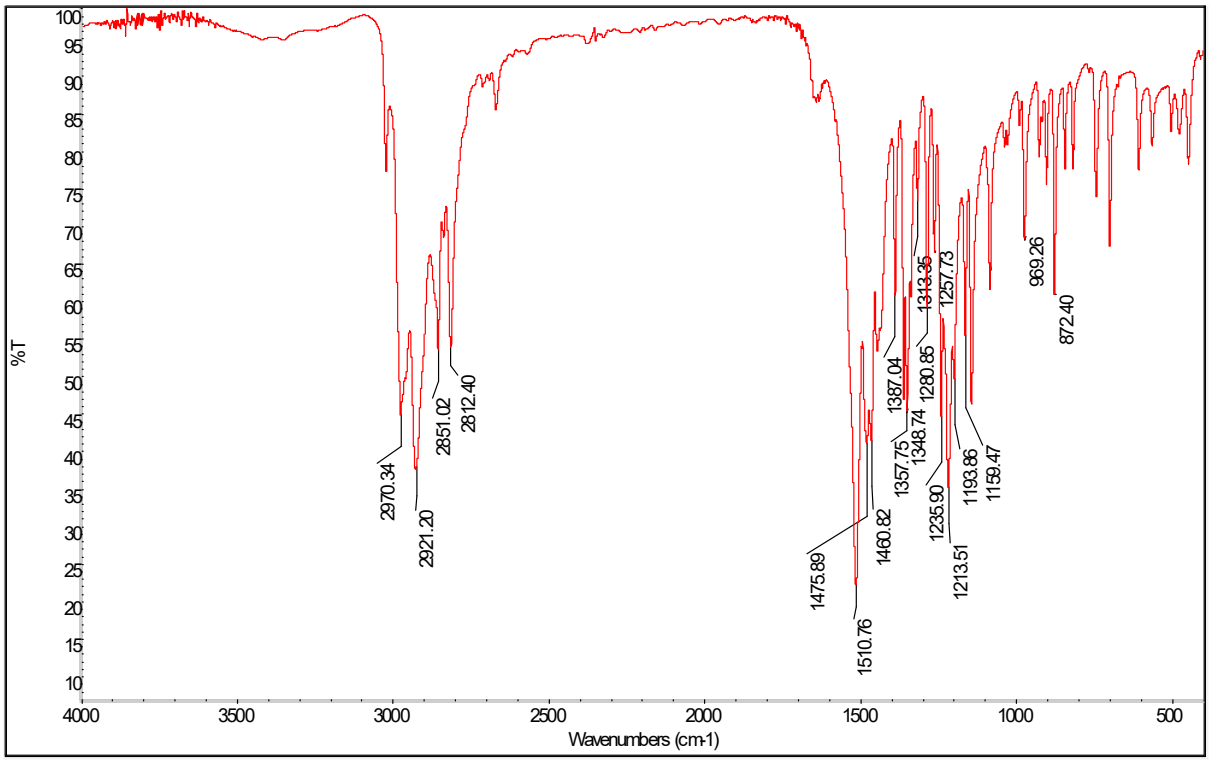

Figure S2-3. IR spectra of **3**

3. NMR spectra of 1 – 3

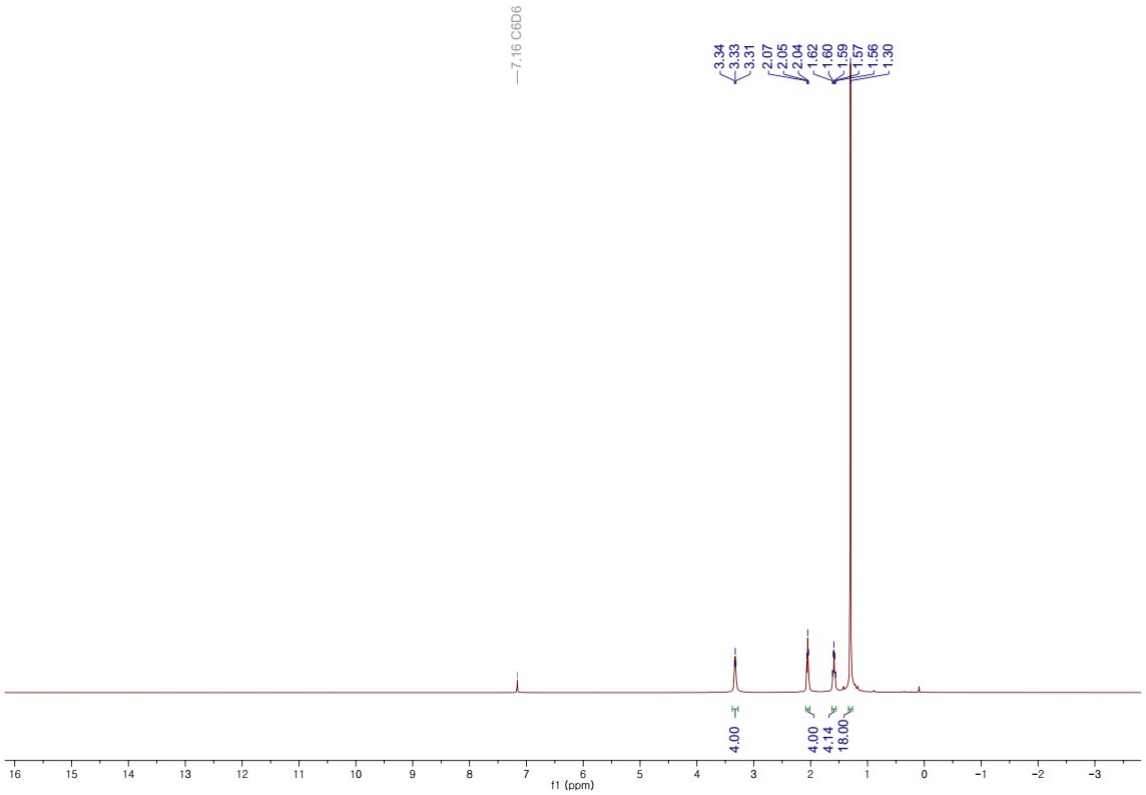

Figure S3-1. ^{1}H NMR spectrum of **1**

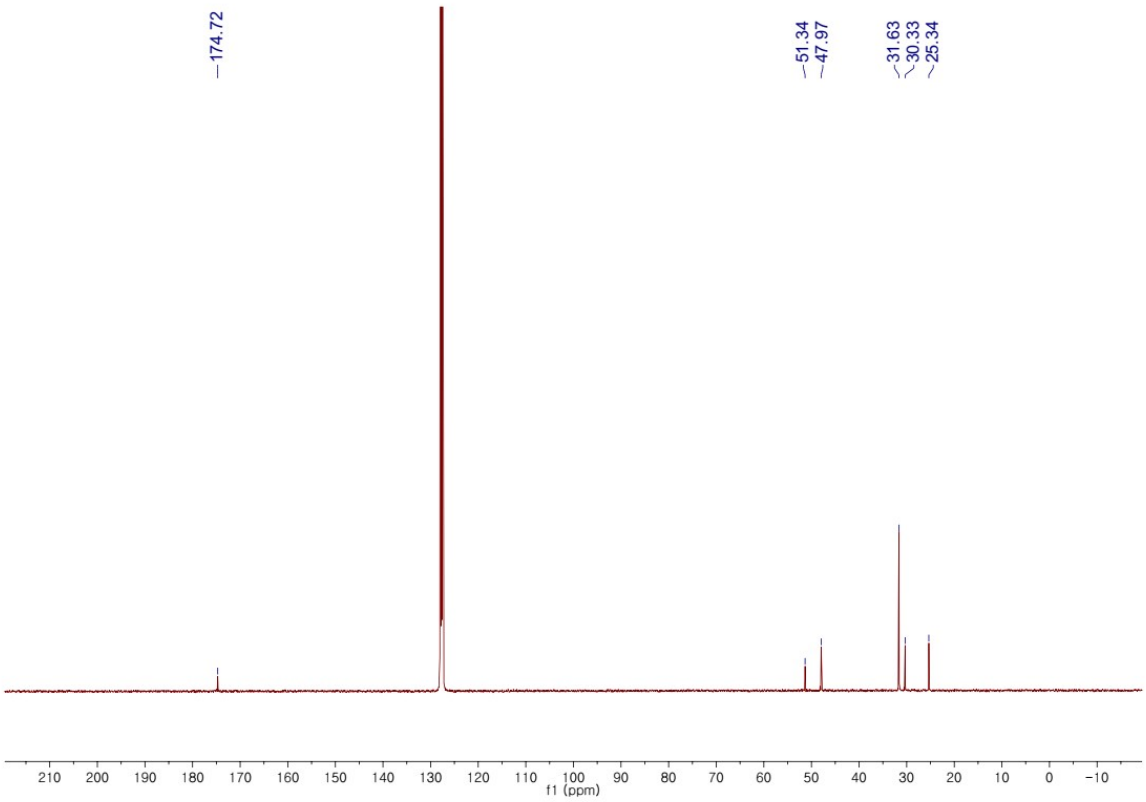

Figure S3-2. ^{13}C NMR spectrum of **1**

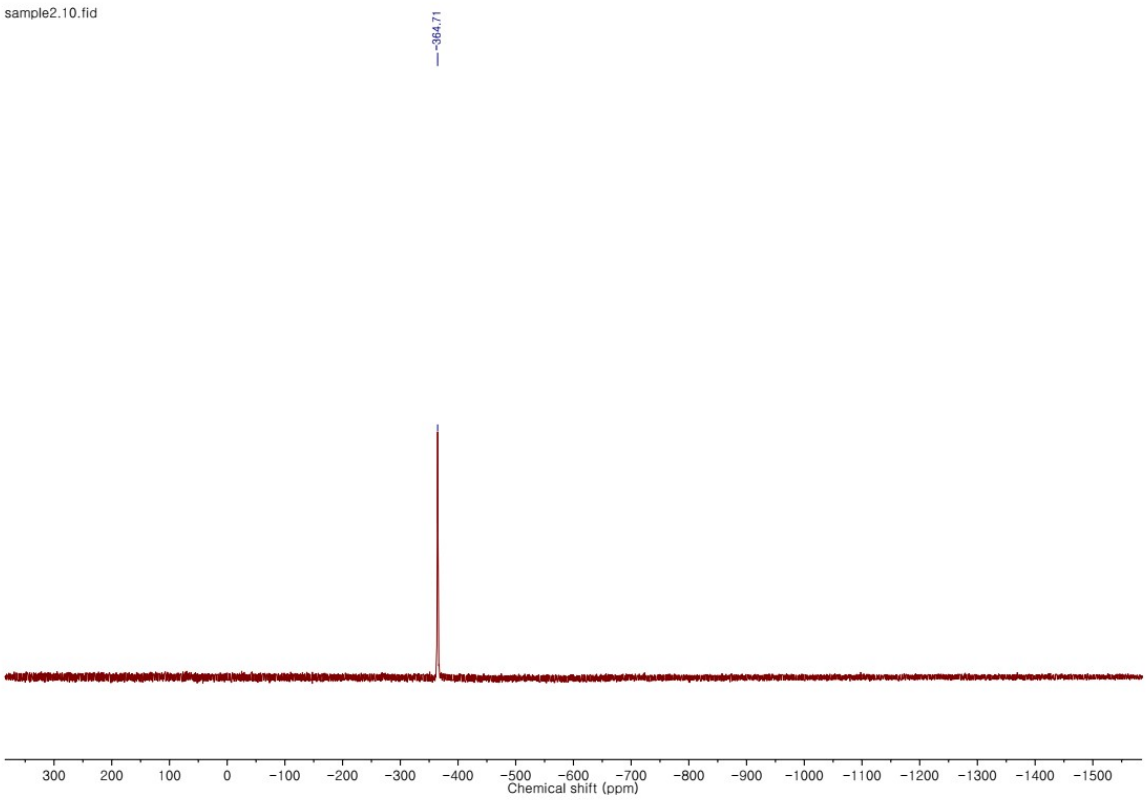

Figure S3-3. ^{119}Sn NMR spectrum of **1**

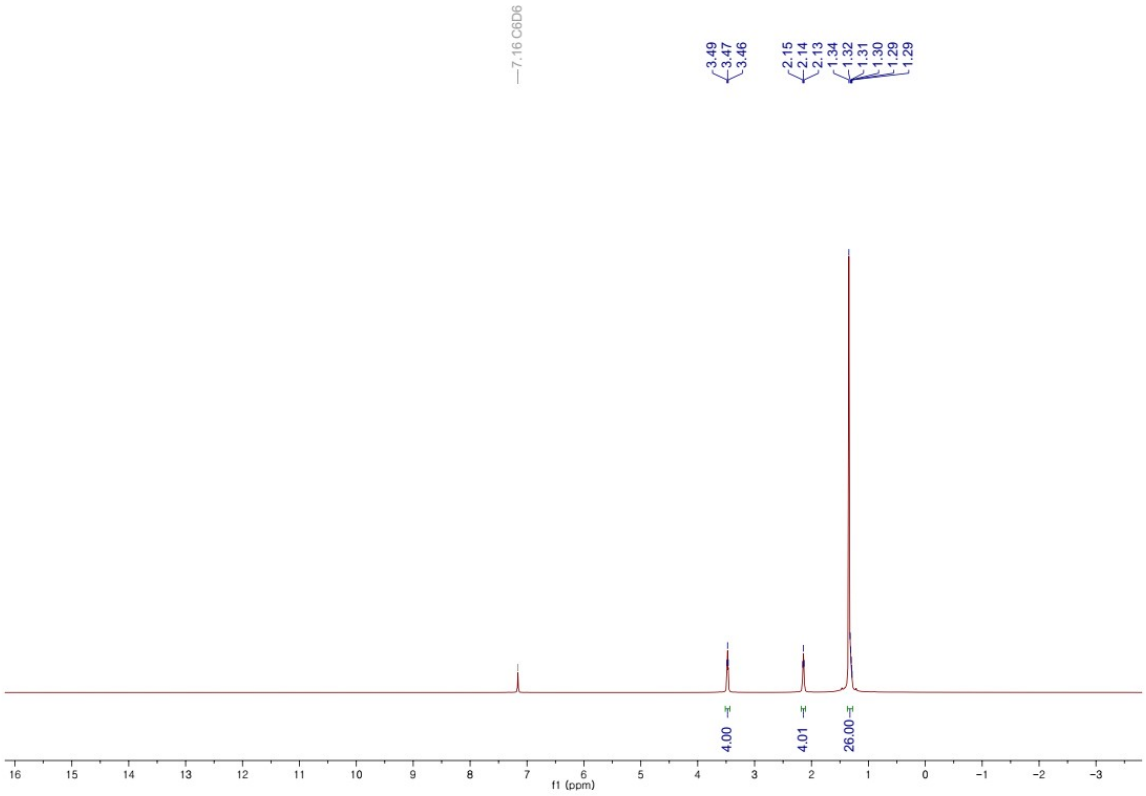

Figure S3-4. ^{1}H NMR spectrum of **2**

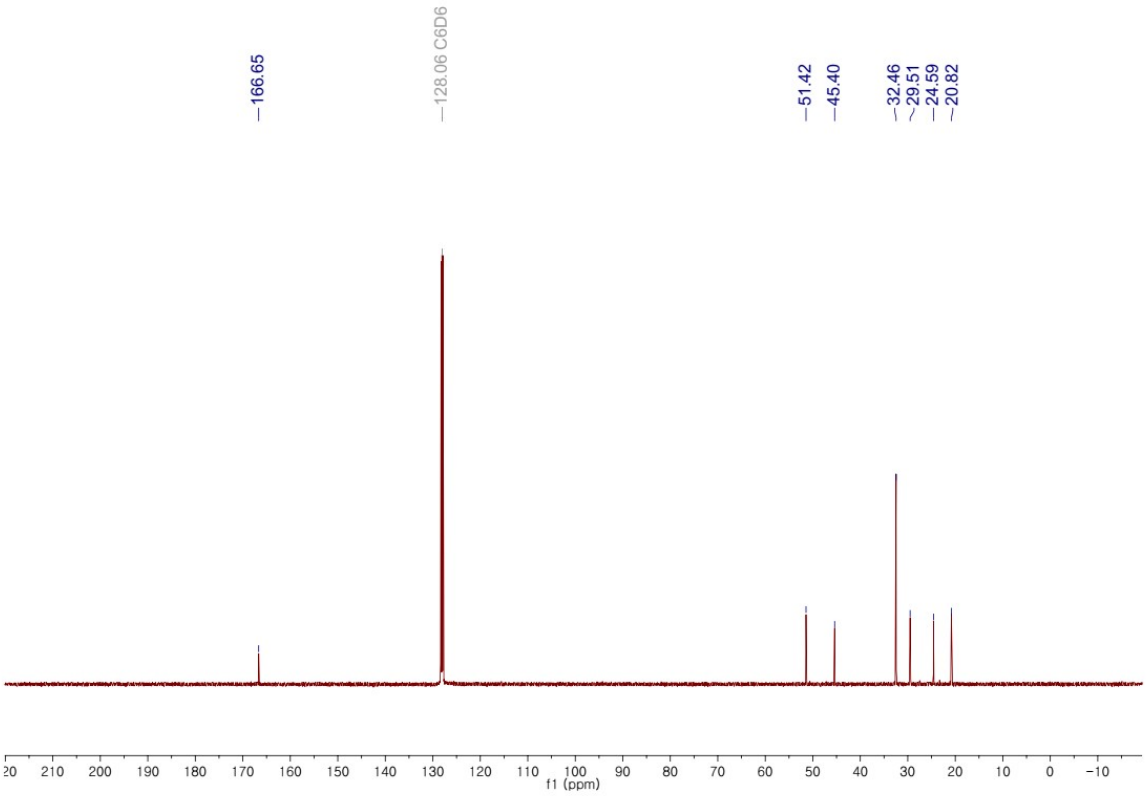

Figure S3-5. ^{13}C NMR spectrum of **2**

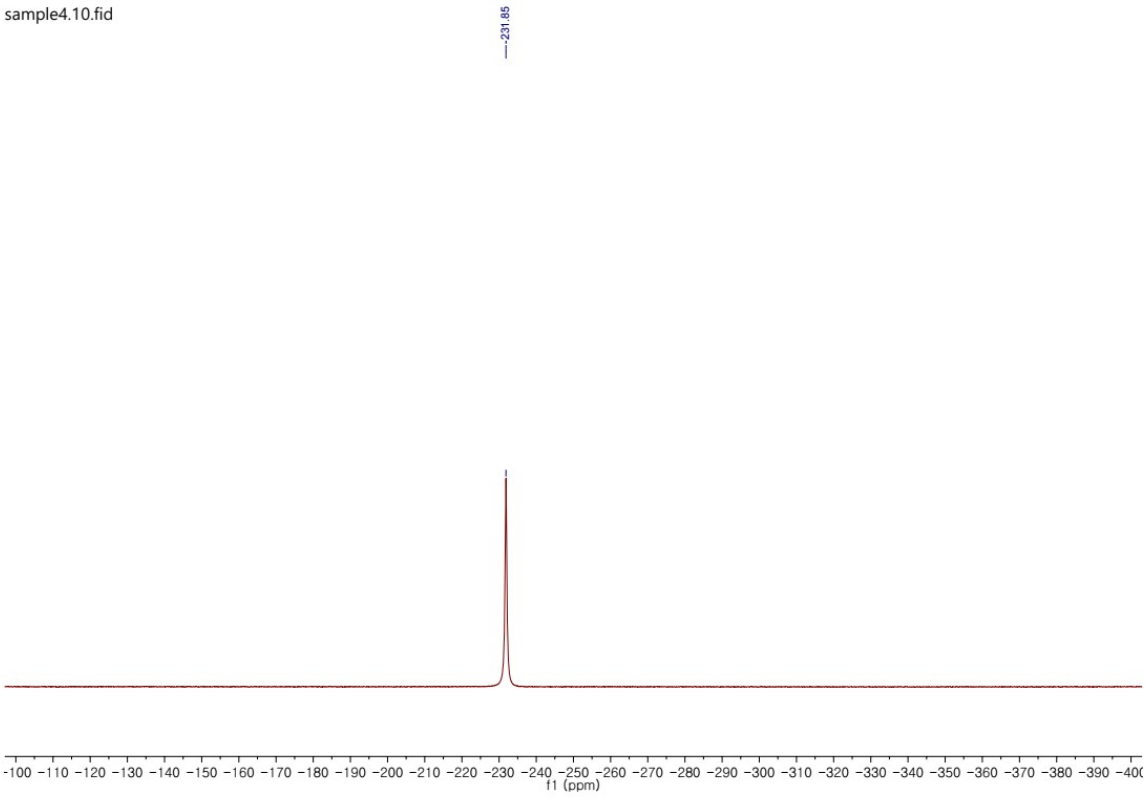

Figure S3-6. ^{119}Sn NMR spectrum of **2**

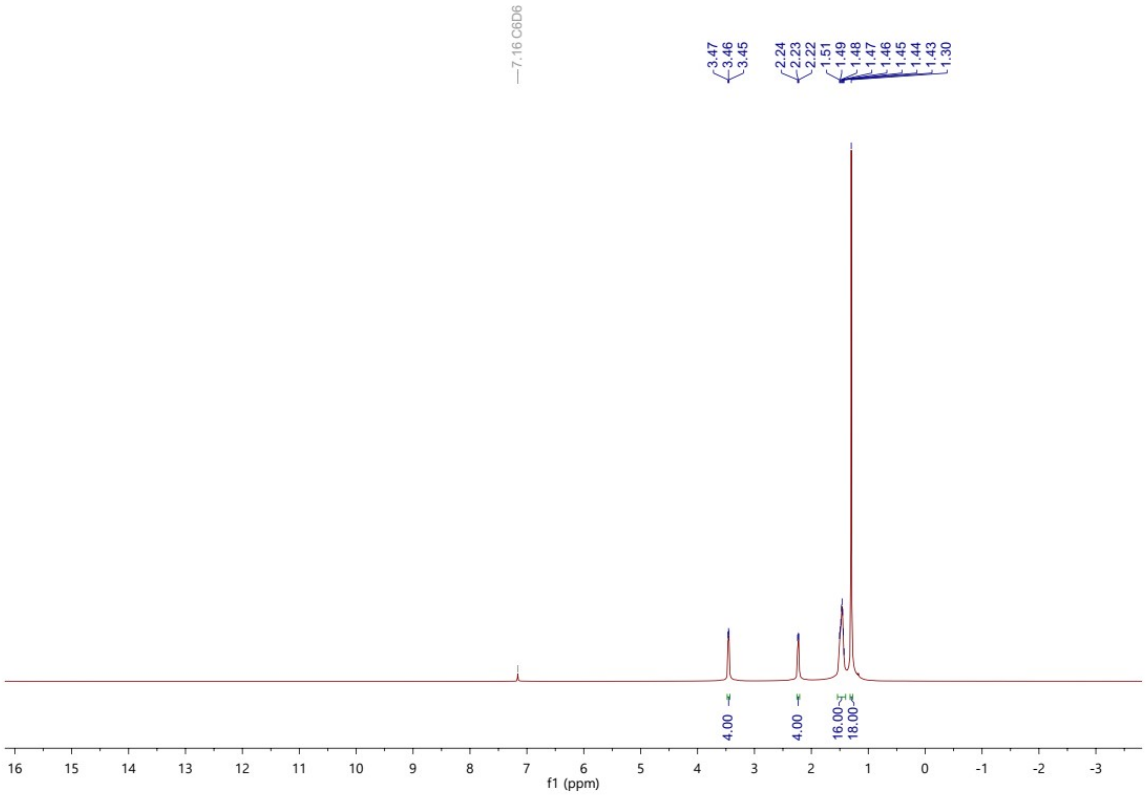

Figure S3-7. ^{1}H NMR spectrum of **3**

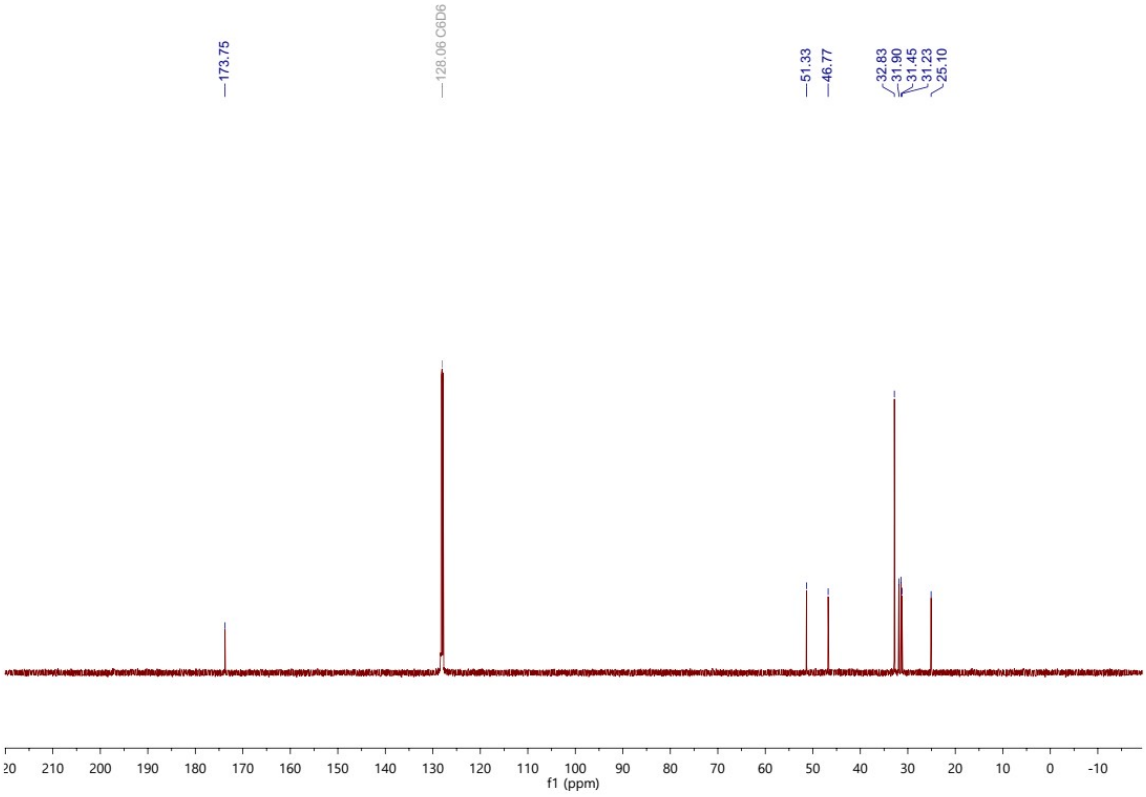

Figure S3-8. ^{13}C NMR spectrum of **3**

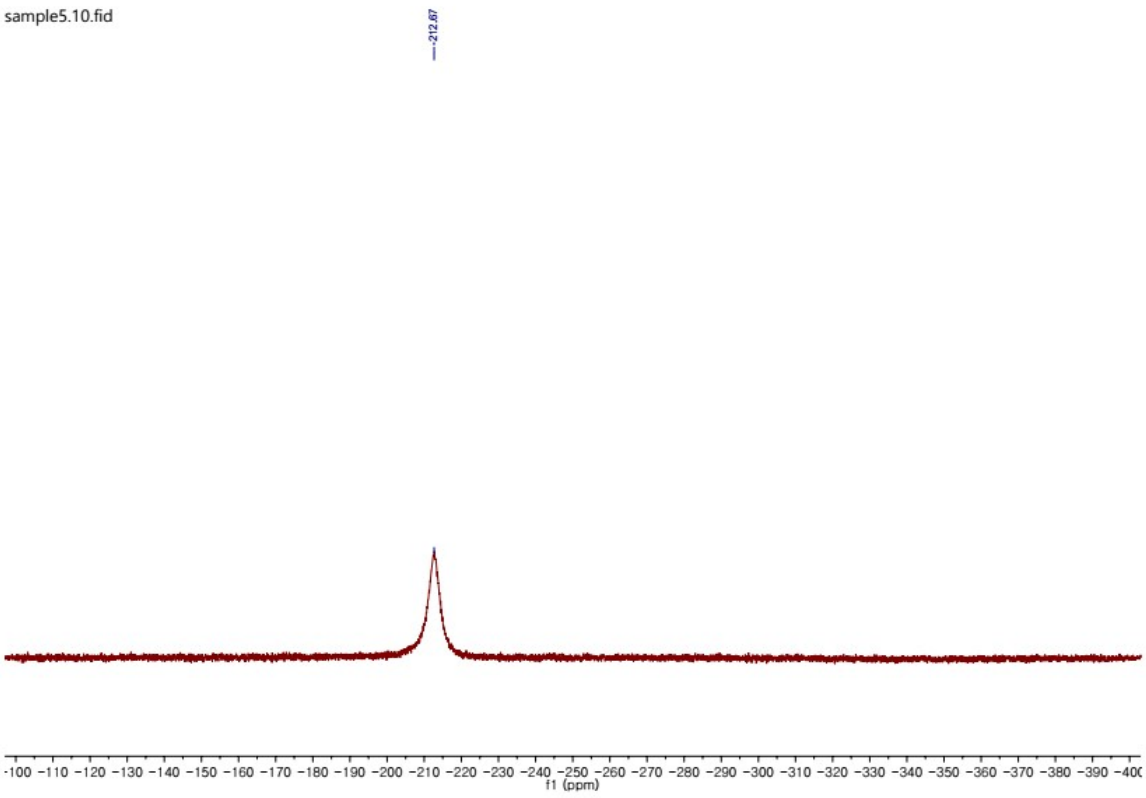

Figure S3-9. ^{119}Sn NMR spectrum of **3**

4. MASS spectra of 1 – 3

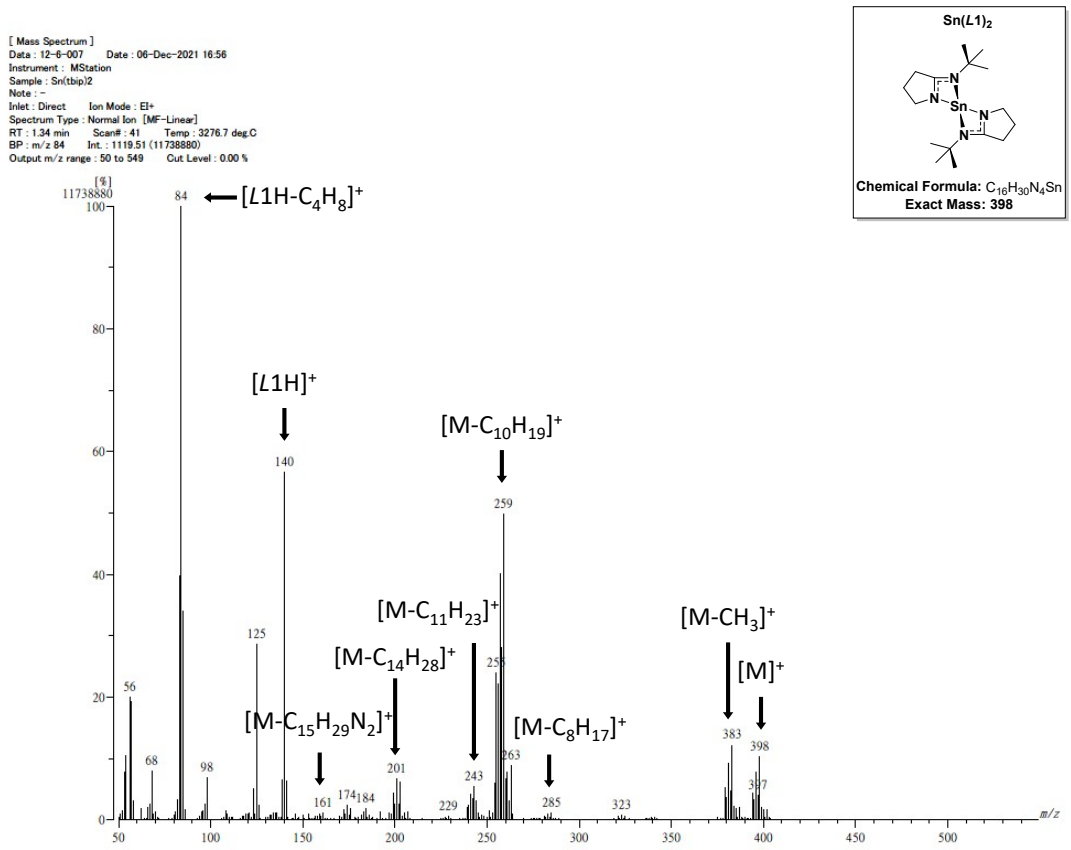

Figure S4-1. MASS spectra of **1**

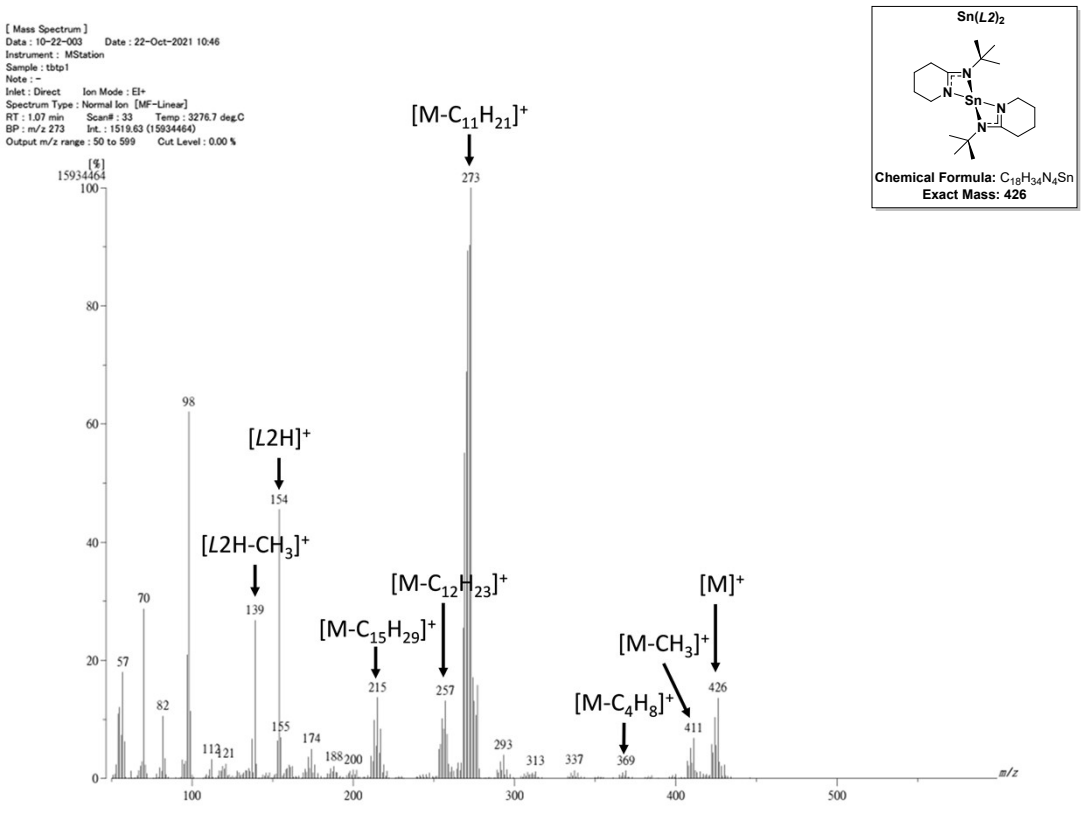

Figure S4-2. MASS spectra of **2**

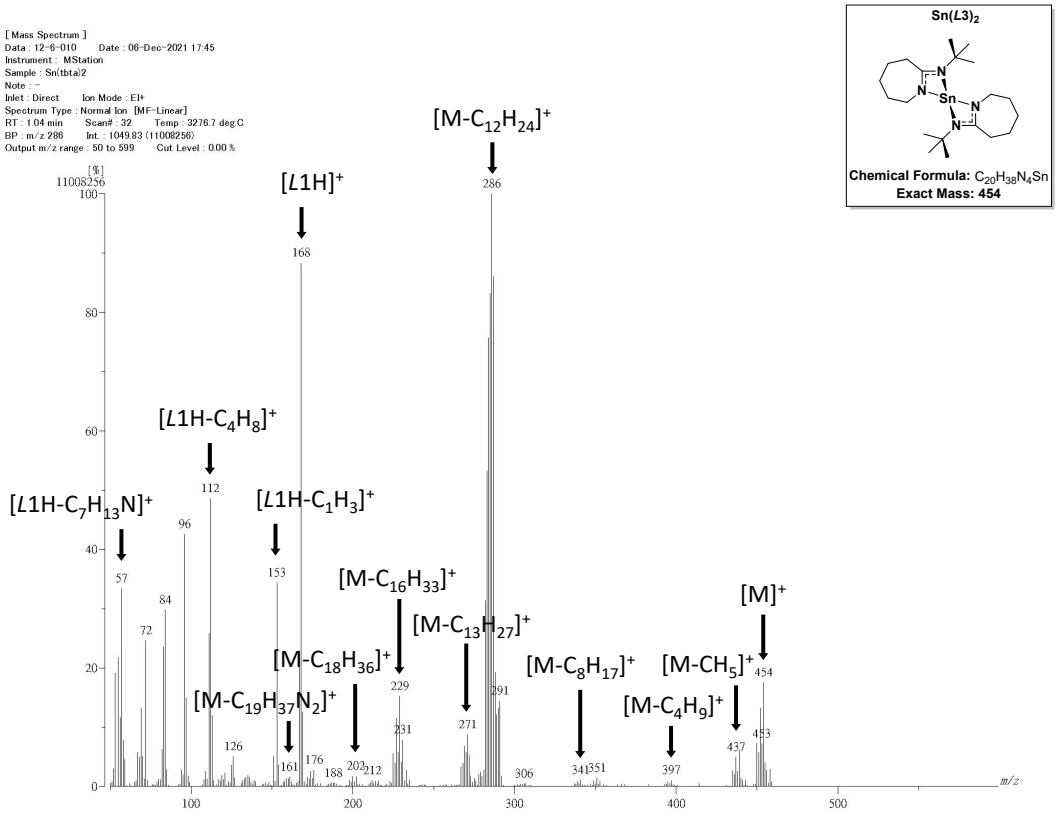

Figure S4-3. MASS spectra of **3**

5. X-ray structure determination of 1 – 3

Table S1. Crystallographic data and parameters for **1 – 3**

Complex	**1**	**2**	**3**
Identification code	20210907LT	20211025LT	20211104LT
Formula	$C_{16}H_{30}N_4Sn$	$C_{18}H_{34}N_4Sn$	$C_{20}H_{38}N_4Sn$
Formula weight	397.13	425.18	453.23
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	P21/c	P21/n	P212121
a (Å)	11.2786(7)	12.1302(4)	9.4658(7)
b (Å)	19.0407(11)	10.2568(4)	12.5449(9)
c (Å)	8.7371(5)	16.2262(5)	18.9905(13)
α (°)	90°	90°	90°
β (°)	104.920(3)	102.8310(10)°	90°
γ (°)	90°	90°	90°
V (Å^3)	1813.06(19)	1968.40(12)	2255.1(3)
Z	4	4	4
ρ_{calc} (g cm^{-3})	1.455	1.435	1.335
μ (mm^{-1})	1.410	1.304	1.143
F(000)	816	880	944
T (K)	100(1)	100(1)	100(1)
Two theta range (°)	2.139 to 28.281	2.366 to 25.999	1.946 to 26.000
hkl range	-14<=h<=14, -25<=k<=25, -9<=l<=11	-14<=h<=14, -12<=k<=12, -20<=l<=12	-11<=h<=11, -15<=k<=12, -23<=l<=23
Data / restraints / parameters	4463 / 0 / 196	3818 / 4 / 215	4435 / 0 / 233
GOF on F^2	1.051	1.068	1.093
R_1[a] (I > 2σ(I))	0.0281	0.0257	0.0173
wR_2[b] (I > 2σ(I))	0.0619	0.0619	0.0446
ρ_{fin} (max/min) (e Å^{-3})	1.085/-0.321	1.526/-0.332	1.108/-0.471

[a] $R1 = \sum||Fo| - |Fc||/\sum|Fo|$. [b] $wR2 = \{[\sum w(Fo^2 - Fc^2)^2]/[\sum w(Fo^2)^2]\}^{1/2}$.

6. Geometrical parameters in 1 – 3 as measured by single-crystal XRD and DFT calculation.

Table S2. The selected bond length (Å) and angels (°) of **1**

Geometrical parameters	Experimental	DFT calculation[a]
Bond Lengths (Å)		
Sn(1)-N(4)	2.1686(17)	2.173
Sn(1)-N(2)	2.1940(17)	2.173
Sn(1)-N(3)	2.3826(17)	2.399
Sn(1)-N(1)	2.3868(17)	2.400
N(1)-C(1)	1.311(3)	1.323
N(1)-C(5)	1.465(3)	1.474
N(2)-C(1)	1.337(3)	1.354
N(2)-C(4)	1.459(3)	1.467
N(3)-C(9)	1.307(3)	1.323
N(3)-C(13)	1.465(3)	1.474
N(4)-C(9)	1.341(3)	1.354
N(4)-C(12)	1.453(3)	1.467
C(1)-C(2)	1.517(3)	1.521
C(9)-C(10)	1.524(3)	1.521
Bond Angles (°)		
N(4)-Sn(1)-N(2)	96.95(7)	97.46
N(4)-Sn(1)-N(3)	58.19(6)	58.43
N(2)-Sn(1)-N(3)	90.11(6)	87.27
N(4)-Sn(1)-N(1)	86.99(6)	87.27
N(2)-Sn(1)-N(1)	58.22(6)	58.43
N(3)-Sn(1)-N(1)	130.73(6)	128.69
C(1)-N(1)-C(5)	126.35(18)	127.39
C(1)-N(1)-Sn(1)	88.93(13)	89.24
C(5)-N(1)-Sn(1)	144.57(13)	143.33
C(1)-N(2)-C(4)	111.51(17)	112.33
C(1)-N(2)-Sn(1)	96.83(13)	98.48
C(4)-N(2)-Sn(1)	147.10(14)	148.21
C(9)-N(3)-C(13)	128.64(18)	127.38
C(9)-N(3)-Sn(1)	89.22(12)	89.26

C(13)-N(3)-Sn(1)	141.37(13)	143.32
C(9)-N(4)-C(12)	112.22(17)	112.32
C(9)-N(4)-Sn(1)	97.90(13)	98.46
C(12)-N(4)-Sn(1)	145.45(14)	148.20
N(1)-C(1)-N(2)	115.18(19)	113.62
N(1)-C(1)-C(2)	133.7(2)	135.30
N(2)-C(1)-C(2)	111.02(18)	111.03
C(1)-C(2)-C(3)	102.63(18)	102.19
C(1)-C(2)-H(2A)	111.2	113.11
C(1)-C(2)-H(2B)	111.2	109.41
N(2)-C(4)-C(3)	103.71(17)	103.50
N(2)-C(4)-H(4A)	111.0	111.19
N(2)-C(4)-H(4B)	111.0	110.92
N(1)-C(5)-C(8)	105.48(17)	105.97
N(1)-C(5)-C(7)	109.80(17)	110.47
N(1)-C(5)-C(6)	113.23(18)	111.76
N(3)-C(9)-N(4)	113.95(19)	113.62
N(3)-C(9)-C(10)	135.5(2)	135.60
N(4)-C(9)-C(10)	110.53(18)	111.03
C(9)-C(10)-C(11)	102.73(18)	102.18
C(9)-C(10)-H(10A)	111.2	113.11
C(9)-C(10)-H(10B)	111.2	109.40
N(4)-C(12)-C(11)	103.93(17)	103.50
N(4)-C(12)-H(12A)	111.0	111.20
N(4)-C(12)-H(12B)	111.0	110.92
N(3)-C(13)-C(14)	109.07(18)	110.47
N(3)-C(13)-C(15)	105.93(17)	105.97
N(3)-C(13)-C(16)	114.51(18)	111.75

Table S3. The selected bond length (Å) and angels (°) of **2**

Geometrical parameters	Experimental	DFT calculation[a]
Bond Lengths (Å)		
Sn(1)-N(1)	2.1888(17)	2.171
Sn(1)-N(2)	2.3464(18)	2.378
Sn(1)-N(3)	2.1797(17)	2.177
Sn(1)-N(4)	2.3672(17)	2.355
N(1)-C(1)	1.339(3)	1.355
N(1)-C(5)	1.458(3)	1.462
N(2)-C(1)	1.321(3)	1.334
N(2)-C(6)	1.475(3)	1.479
N(3)-C(10)	1.349(3)	1.351
N(3)-C(14)	1.449(3)	1.462
N(4)-C(10)	1.318(3)	1.337
N(4)-C(15)	1.468(3)	1.477
C(1)-C(2)	1.515(3)	1.517
C(10)-C(11)	1.514(3)	1.518
Bond Angles (°)		
N(1)-Sn(1)-N(2)	57.98(6)	58.21
N(1)-Sn(1)-N(4)	90.40(6)	87.34
N(2)-Sn(1)-N(4)	130.15(6)	129.9
N(3)-Sn(1)-N(1)	101.99(7)	93.77
N(3)-Sn(1)-N(2)	89.52(6)	86.55
N(3)-Sn(1)-N(4)	58.03(6)	58.4
C(1)-N(1)-Sn(1)	97.89(13)	99.5
C(5)-N(1)-Sn(1)	137.48(13)	135.45
C(1)-N(2)-Sn(1)	91.27(13)	90.81
C(6)-N(2)-Sn(1)	138.69(13)	138.47
C(10)-N(3)-Sn(1)	98.07(13)	99.03
C(14)-N(3)-Sn(1)	134.65(13)	135.86
C(10)-N(4)-Sn(1)	90.51(12)	91.42
C(15)-N(4)-Sn(1)	138.73(14)	138.74
N(1)-C(1)-C(2)	120.78(18)	120.57

N(1)-C(5)-C(4)	113.39(17)	112.54
N(1)-C(5)-H(5A)	108.9	109.37
N(1)-C(5)-H(5B)	108.9	108.46
N(2)-C(1)-C(2)	127.38(19)	128.09
N(2)-C(1)-N(1)	111.75(18)	111.29
N(2)-C(6)-C(7)	114.30(17)	112.21
N(2)-C(6)-C(8)	110.21(17)	111.67
N(2)-C(6)-C(9)	105.33(17)	105.51
N(3)-C(10)-C(11)	120.3(2)	121.26
N(3)-C(14)-C(13)	114.04(17)	112.43
N(3)-C(14)-H(14A)	108.7	108.02
N(3)-C(14)-H(14B)	108.7	109.44
N(4)-C(10)-C(11)	127.62(19)	127.62
N(4)-C(10)-N(3)	112.01(18)	111.07
N(4)-C(15)-C(16)	111.22(18)	111.36
N(4)-C(15)-C(17)	112.93(18)	112.16
N(4)-C(15)-C(18)	106.08(17)	105.86
C(1)-N(1)-C(5)	123.85(17)	124.11
C(1)-N(2)-C(6)	127.62(18)	128.51
C(10)-N(3)-C(14)	123.69(18)	125.11
C(10)-N(4)-C(15)	126.98(18)	128.5
C(1)-C(2)-C(3)	113.37(17)	111.6
C(1)-C(2)-H(2A)	108.9	108.01
C(1)-C(2)-H(2B)	108.9	110.5
C(10)-C(11)-C(12)	112.23(18)	112.17
C(10)-C(11)-H(11A)	109.2	110.27
C(10)-C(11)-H(11B)	109.2	107.73

Table S4. The selected bond length (Å) and angels (°) of **3**

Geometrical parameters	Experimental	DFT calculation[a]
Bond Lengths (Å)		
Sn(1)-N(1)	2.185(2)	2.176
Sn(1)-N(2)	2.364(2)	2.371
Sn(1)-N(3)	2.175(2)	2.176
Sn(1)-N(4)	2.349(2)	2.371
N(1)-C(1)	1.450(3)	1.458
N(1)-C(6)	1.338(3)	1.353
N(2)-C(6)	1.319(3)	1.335
N(2)-C(7)	1.468(3)	1.478
N(3)-C(11)	1.458(3)	1.458
N(3)-C(16)	1.339(3)	1.353
N(4)-C(16)	1.318(3)	1.335
N(4)-C(17)	1.475(3)	1.478
C(5)-C(6)	1.507(4)	1.513
C(15)-C(16)	1.517(3)	1.513
Bond Angles (°)		
N(1)-Sn(1)-N(2)	57.97(8)	58.21
N(1)-Sn(1)-N(4)	86.79(8)	86.83
N(3)-Sn(1)-N(1)	95.01(8)	93.6
N(3)-Sn(1)-N(2)	87.27(8)	86.83
N(3)-Sn(1)-N(4)	58.14(8)	58.21
N(4)-Sn(1)-N(2)	129.06(7)	129.68
C(1)-N(1)-Sn(1)	138.11(18)	136.08
C(6)-N(1)-Sn(1)	98.34(16)	99.38
C(6)-N(2)-Sn(1)	90.75(15)	91.12
C(7)-N(2)-Sn(1)	139.69(17)	139.21
C(11)-N(3)-Sn(1)	137.46(18)	136.07
C(16)-N(3)-Sn(1)	98.48(15)	99.39
C(16)-N(4)-Sn(1)	91.17(14)	91.12
C(17)-N(4)-Sn(1)	138.92(17)	139.22
N(1)-C(1)-C(2)	114.1(2)	113.98

N(1)-C(1)-H(1A)	108.7	106.43
N(1)-C(1)-H(1B)	108.7	111.2
N(1)-C(6)-C(5)	120.2(2)	120.66
N(2)-C(6)-C(5)	127.3(2)	128.07
N(2)-C(6)-N(1)	112.6(2)	111.22
N(2)-C(7)-C(10)	105.5(2)	105.83
N(2)-C(7)-C(8)	111.7(2)	111.57
N(2)-C(7)-C(9)	112.9(2)	111.87
N(3)-C(11)-C(12)	114.3(2)	113.99
N(3)-C(11)-H(11A)	108.7	106.43
N(3)-C(11)-H(11B)	108.7	111.19
N(3)-C(16)-C(15)	120.3(2)	120.66
N(4)-C(16)-C(15)	127.5(2)	128.07
N(4)-C(16)-N(3)	112.1(2)	111.22
N(4)-C(17)-C(18)	111.5(2)	111.57
N(4)-C(17)-C(19)	112.2(2)	111.88
N(4)-C(17)-C(20)	105.1(2)	105.83
C(6)-N(1)-C(1)	123.5(2)	124.17
C(6)-N(2)-C(7)	127.7(2)	128.51
C(16)-N(3)-C(11)	123.0(2)	124.17
C(16)-N(4)-C(17)	127.7(2)	128.5
C(6)-C(5)-C(4)	111.9(2)	112.05
C(6)-C(5)-H(5A)	109.2	109.19
C(6)-C(5)-H(5B)	109.2	109.33
C(16)-C(15)-C(14)	111.8(2)	112.05
C(16)-C(15)-H(15A)	109.3	109.19
C(16)-C(15)-H(15B)	109.3	109.33

7. Additional chemical properties of deposited film

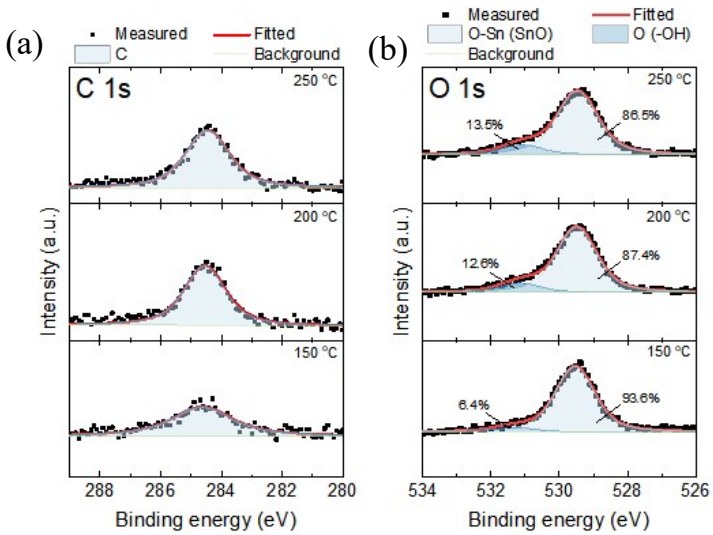

Figure S5. XPS spectra of the as-grown Sn_3N_4 film depending on the growth temperature, respectively (a) C 1s and (b) O 1s.

Figure S5 shows the XPS spectra of as-deposited Sn_3N_4 film at 150, 200, 250°C. As shown in Figure 7, the spectra were obtained by etching films for 5s with Ar^+ ions to remove airborne carbon and oxygen contamination at the surface. The C 1s XPS spectra exhibited one peak at 284.5 eV corresponding to C-C bond in all temperature ranges (Figure S5(a)). The C content is within 5%, showing that there are almost no C impurities in the Sn_3N_4 film. The O 1s XPS spectra had two sub-peaks at 529.5 and 531.2 eV corresponding to SnO_X, which is due to the oxidation in the air and hydroxyl group, respectively (Figure S5(b)). Especially, the peak corresponding to the hydroxyl group decreased with lower deposition temperature.

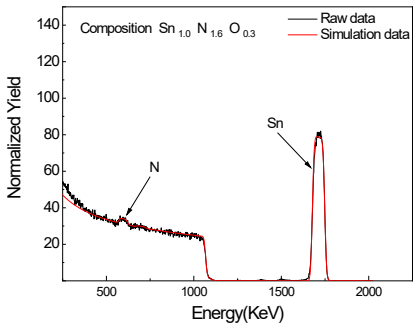

Figure S6. RBS spectrum for Sn_3N_4 film deposited on SiO_2 at 150°C (2MV accelerator).

Figure S6 shows the RBS spectrum for Sn_3N_4 film deposited on SiO_2 at 150°C to obtain the precise composition. The composition of each element is Sn: N: O = 1: 1.6: 0.3, and the amount of Sn and N correspond Sn_3N_4 and contains a small amount of O due to the oxidation.

8. Calculation of geometry index of 1 – 3

$$\tau'4 = \frac{\beta - \alpha}{360° - \theta} + \frac{180° - \beta}{180° - \theta} \approx -0.00399\alpha - 0.01019\beta + 2.55$$

where: β > α are the two greatest valence angles of coordination center
θ = cos−1(− 1⁄3) ≈ 109.5° is a tetrahedral angle

- ✓ **1:** α:96.95, β:130.73, $\tau'4 = 0.834$
- ✓ **2:** α:101.98, β:130.14, $\tau'4 = 0.819$
- ✓ **3:** α:95.01, β:129.06, $\tau'4 = 0.859$