Synthesis and Theoretical Study of a Mixed-Ligand Indium(III) Complex for Fabrication of ß-In_2S_3 Thin Films via Chemical Vapor Deposition

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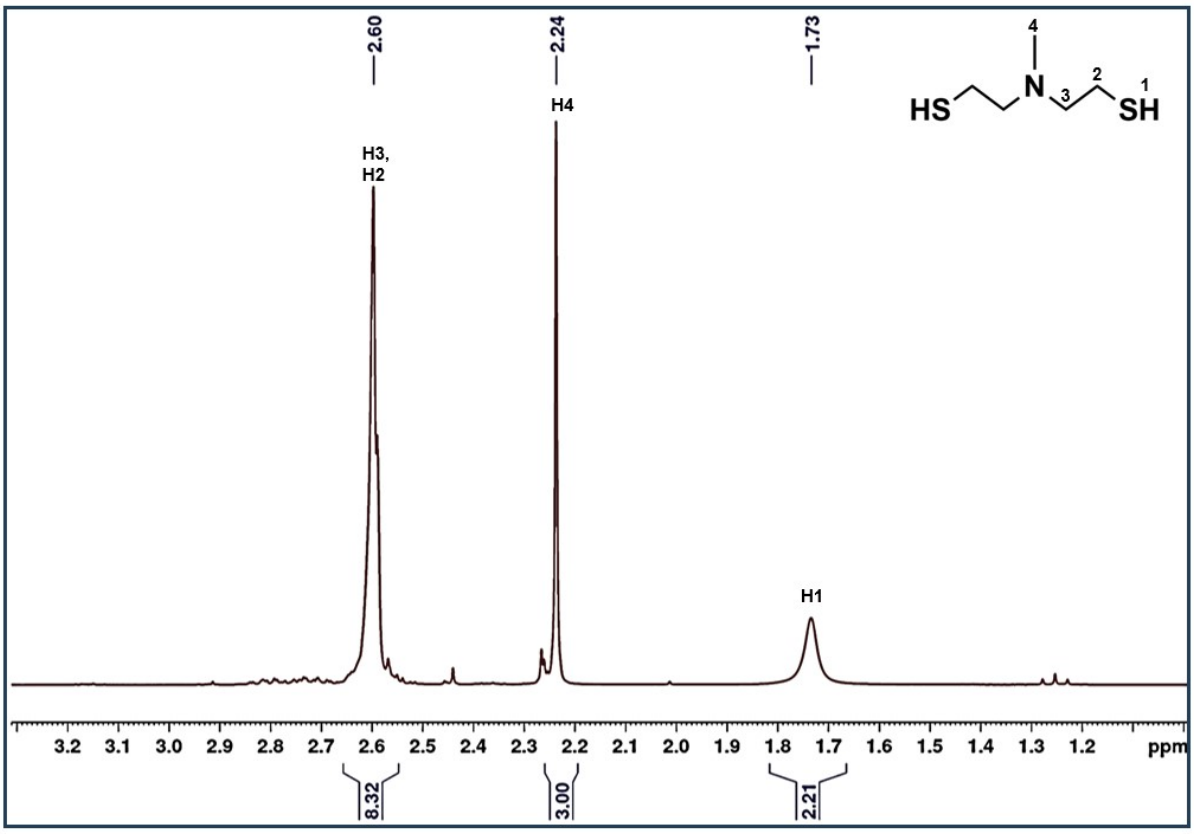


Figure S1: ^{1}H NMR spectrum of N-Methyldiethanethiolamine ligand in $CDCl_3$.

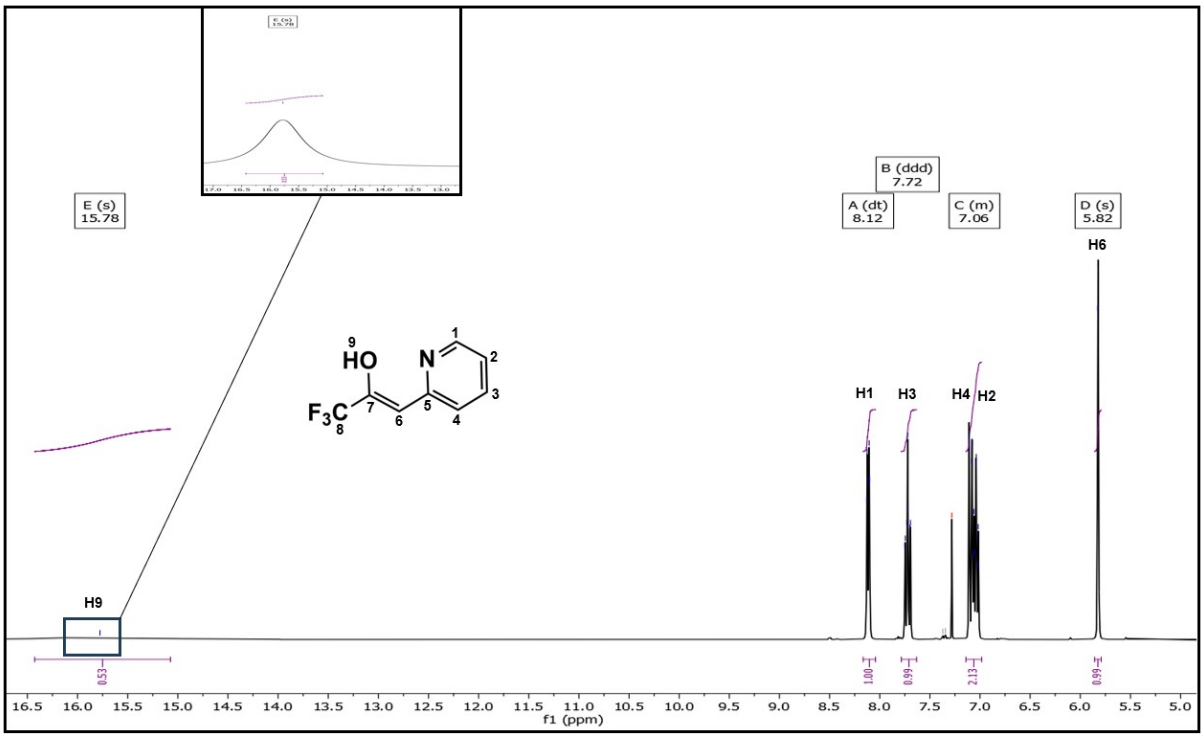


Figure S2: ^{1}H NMR spectrum of ß-heteroarylalkenol ligand in $CDCl_3$.

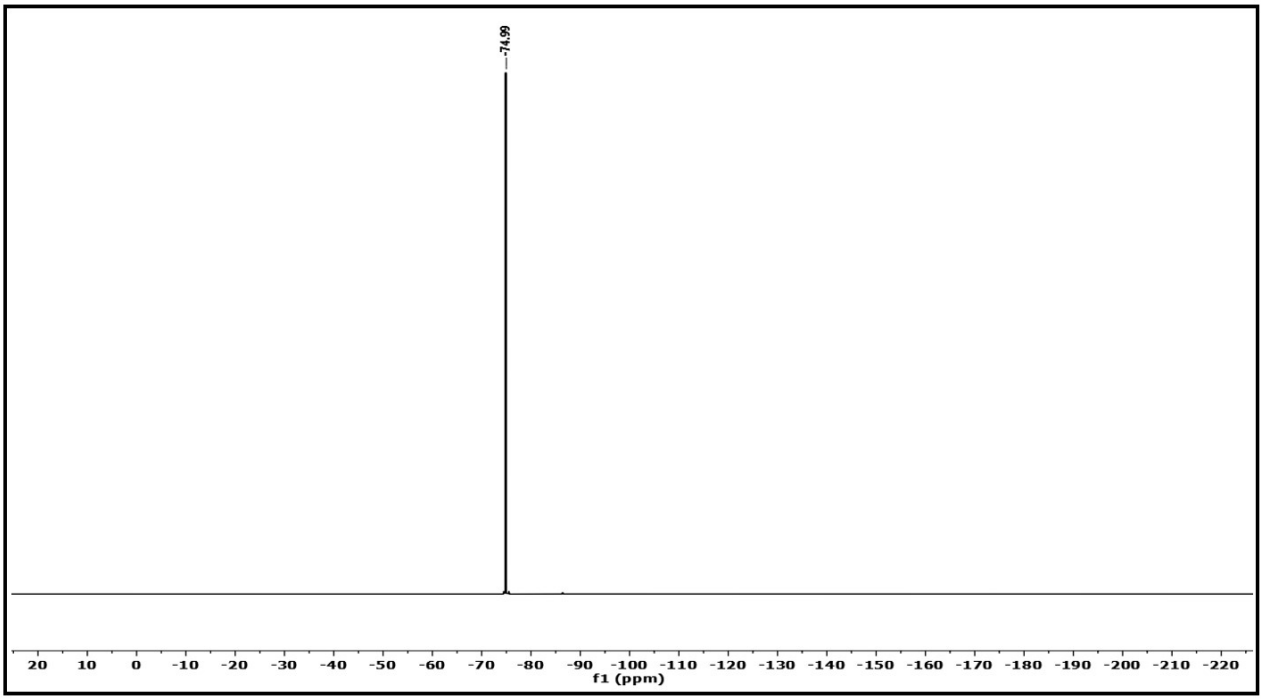


Figure S3: ^{19}F NMR spectrum of ß-heteroarylalkenol ligand in $CDCl_3$.

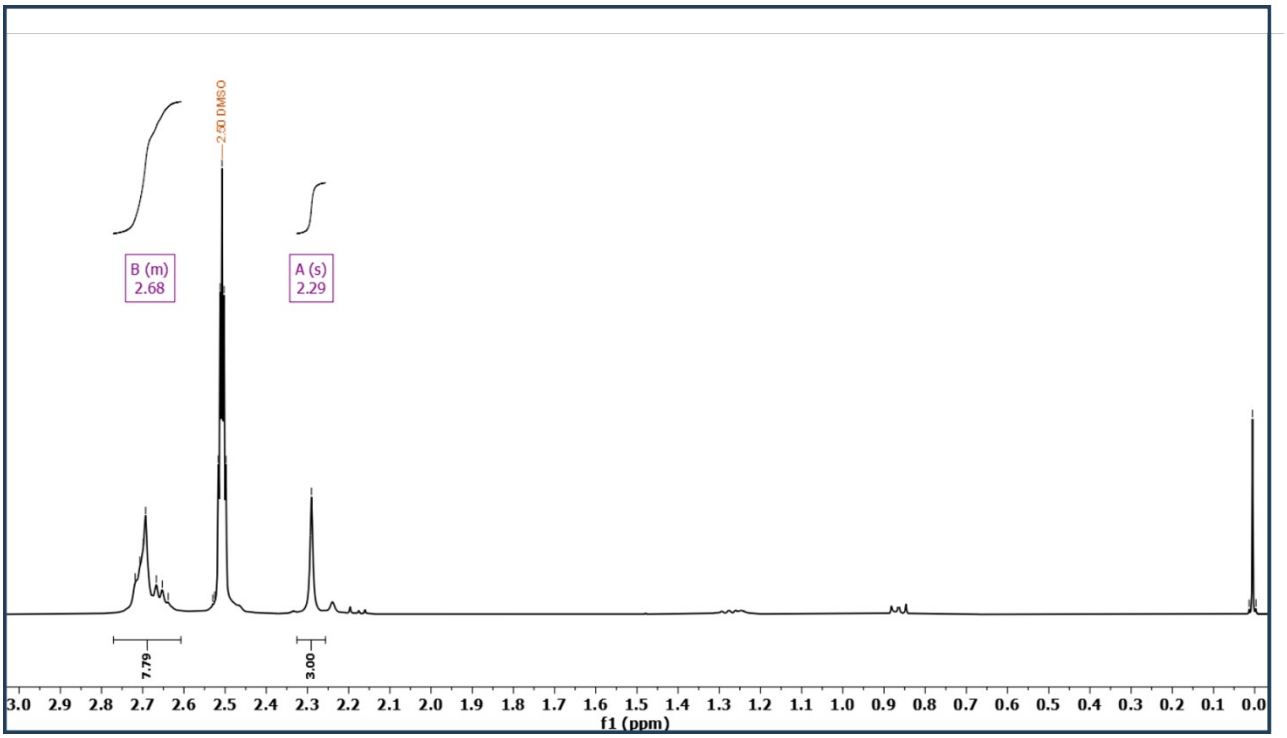


Figure S4: ^{1}H NMR spectrum of **[1]** recorded in DMSO-d6 (Bruker-600 MHz)

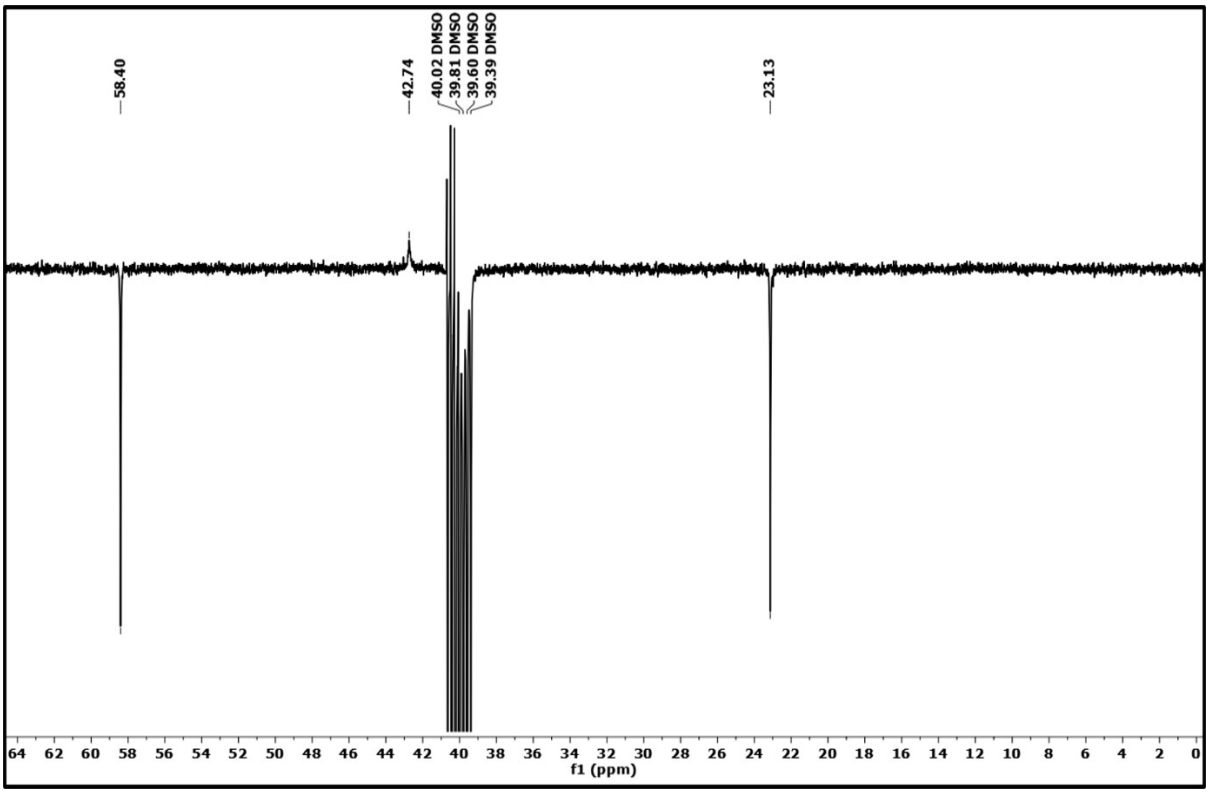


Figure S5: ^{13}C (^{1}H)DEPTQ-135 spectrum of **[1]** recorded in DMSO-d6 (Bruker-600 MHz)

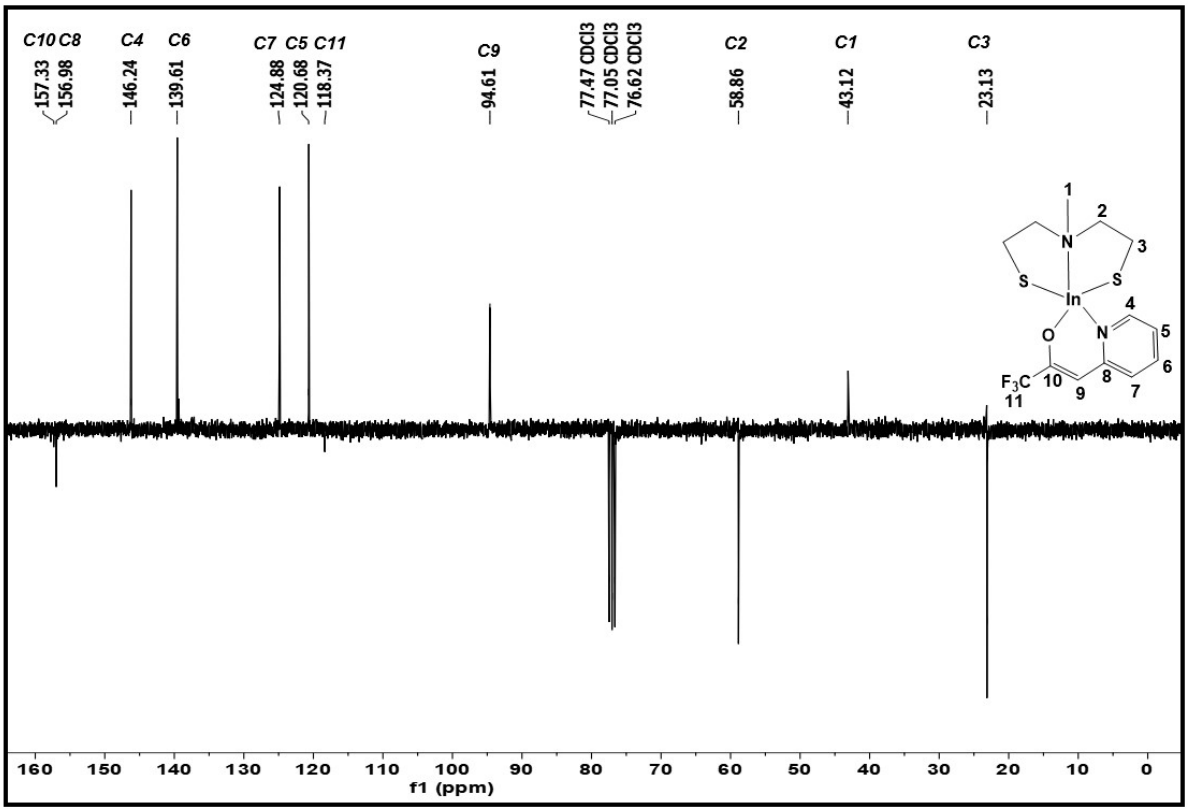


Figure S6: ^{13}C (^{1}H)DEPTQ-135 NMR spectrum of **[2]** recorded in $CDCl_3$.

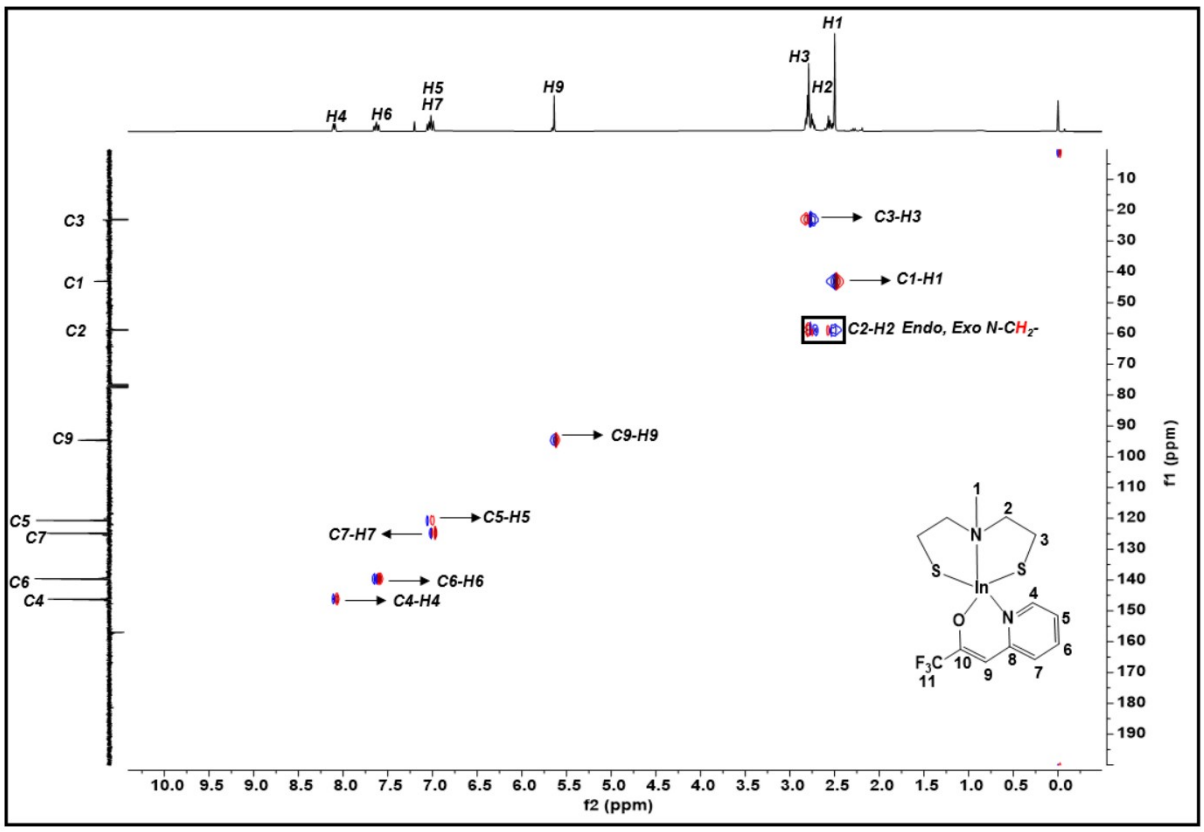


Figure S7: $^{1}H-^{13}C$ Heteronuclear multiple quantum coherence (HMQC) spectrum of **[2]** at room temperature in $CDCl_3$.

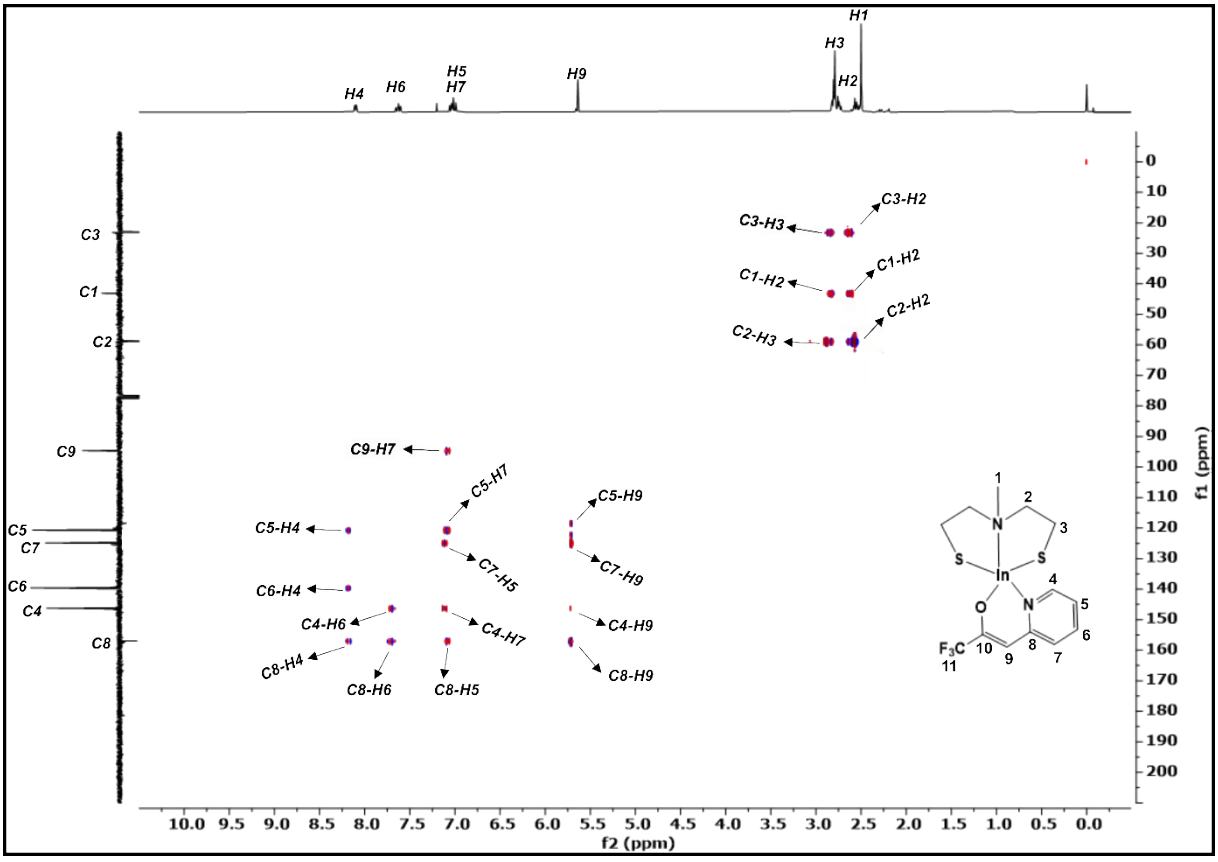


Figure S8: $^{1}H-^{13}C$ heteronuclear multiple bond correlation (HMBC) spectrum of **[2]** at room temperature recorded in $CDCl_3$

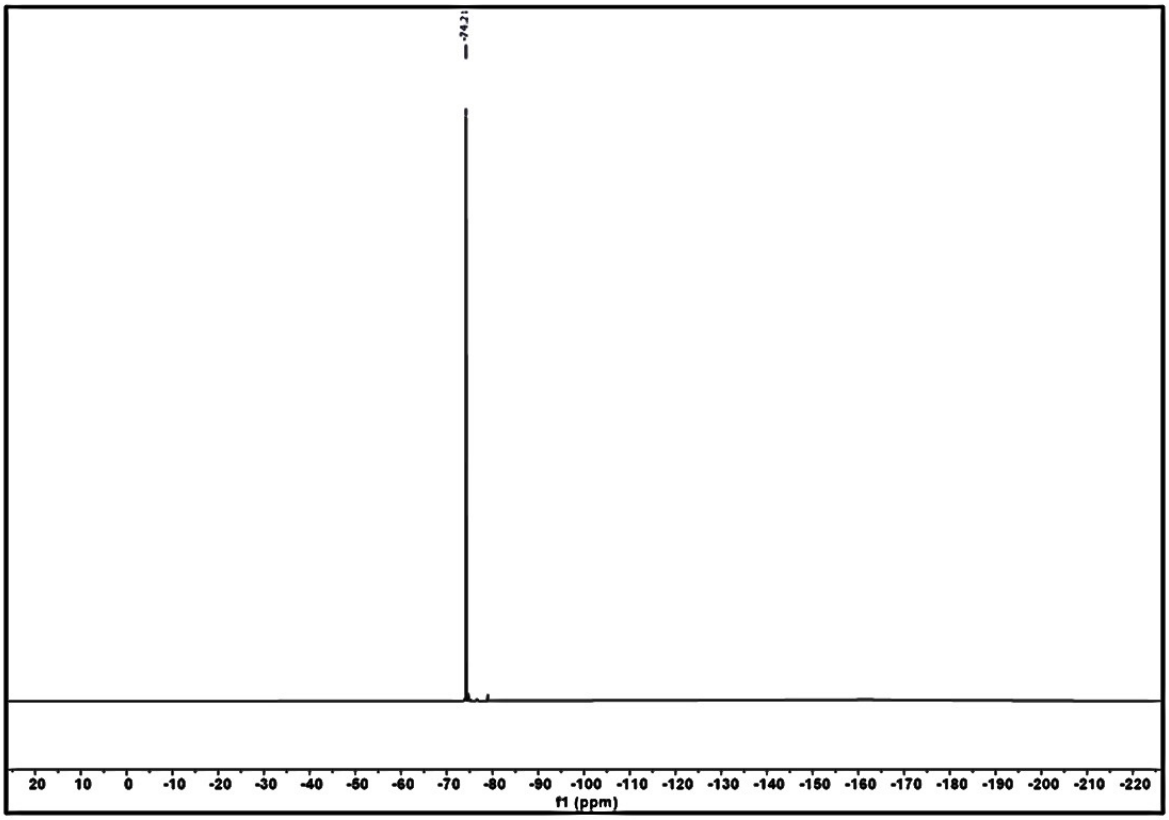


Figure S9: ^{19}F NMR spectrum of **[2]** recorded in $CDCl_3$.

Table S1: Selected bond lengths and angles of compound **[1]**

Bond lengths	**Length/Å**
In1-Cl1	2.4147(10)
In1-S1	2.4039(10)
In1-S2	2.4848(11)
In1_a -S2	2.6759(11)
In1-N1	2.394(4)
Bond Angle	**Angle/˚**
Cl1-In1-S1	114.63(4)
Cl1-In1-S2	113.10(4)
Cl1-In1-S2_b	87.18(4)
S1-In1-S2_b	101.49(4)
S1-In1-S2	131.39(4)
S2-In1-S2_b	89.35(6)
N1-In1-Cl1	95.16(9)
N1-In1-S1	84.82(9)
N1-In1-S2_b	171.66(9)
N1-In1-S2	82.36(9)
In1-S2_b-In1_b	111.10(4)

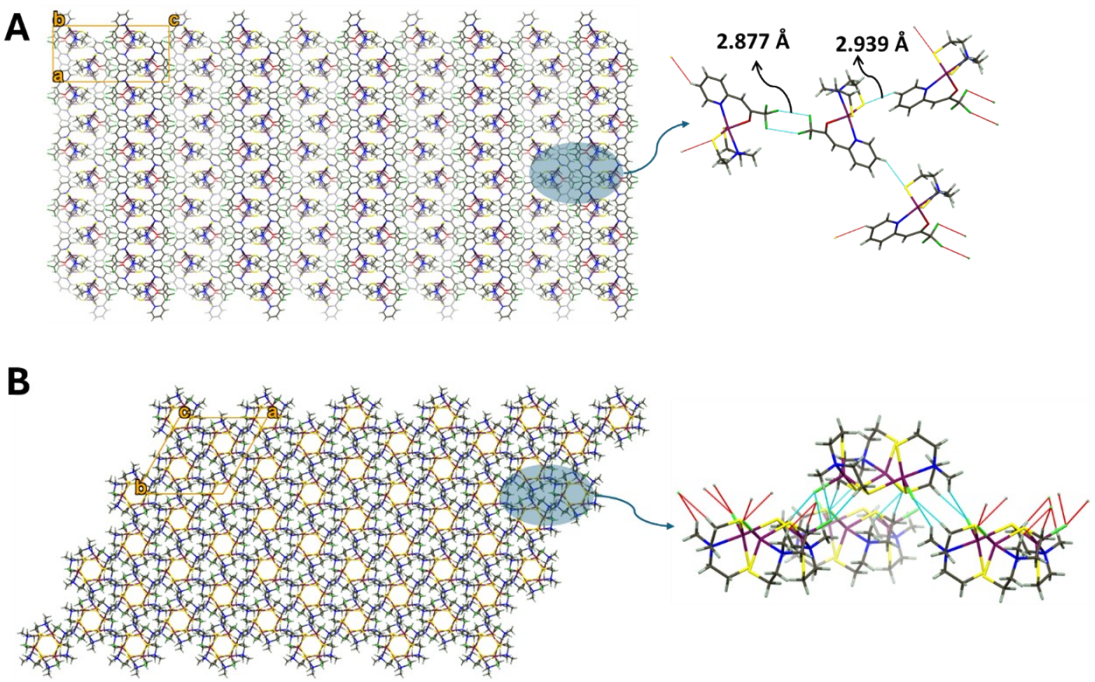


Figure S10: A) Packing of **[2]** along the crystallographic b axis, and B) Packing of **[1]** along the c axis.

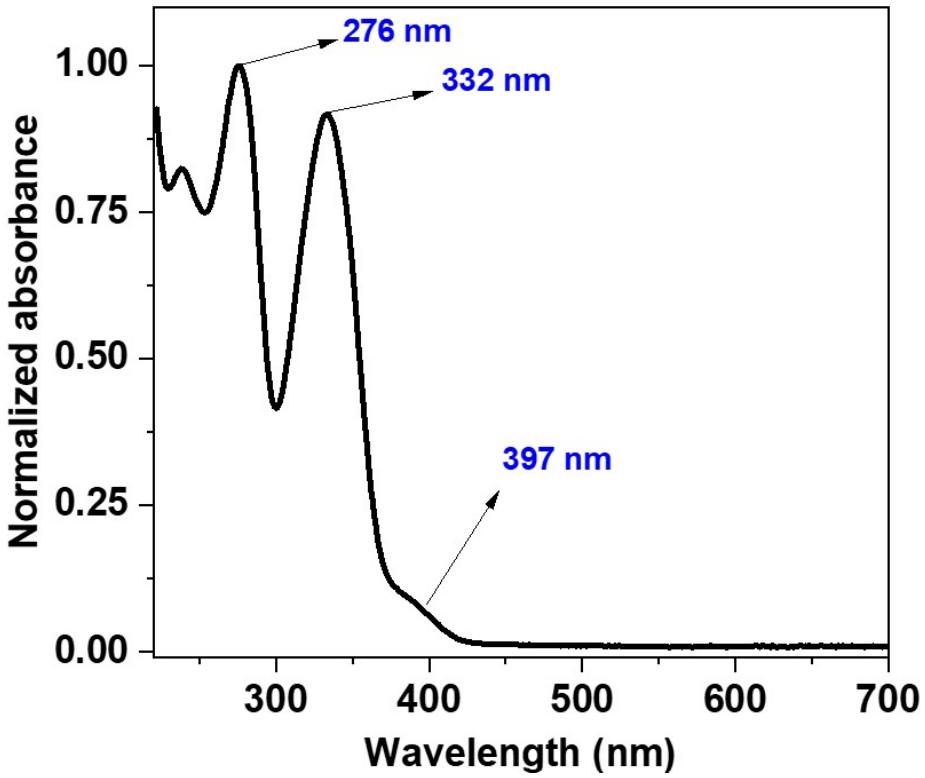
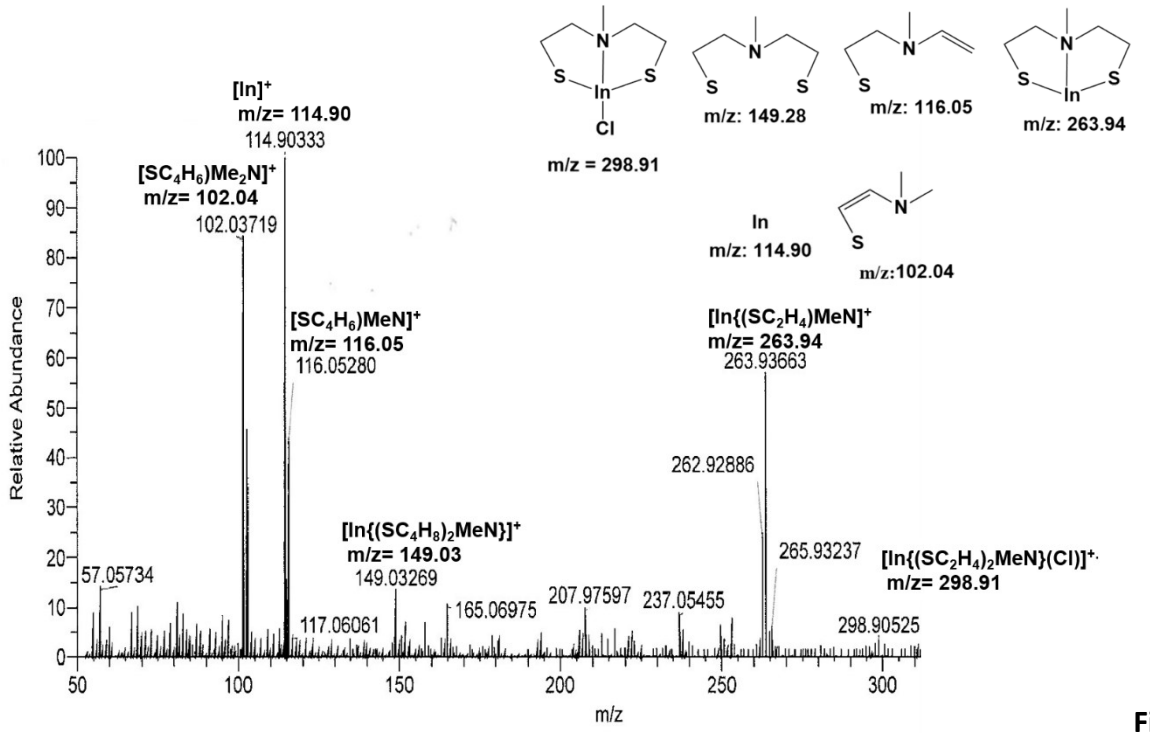


Figure S11: Absorption spectrum of complex **[2]** in CH_3CN as solvent at room temperature.



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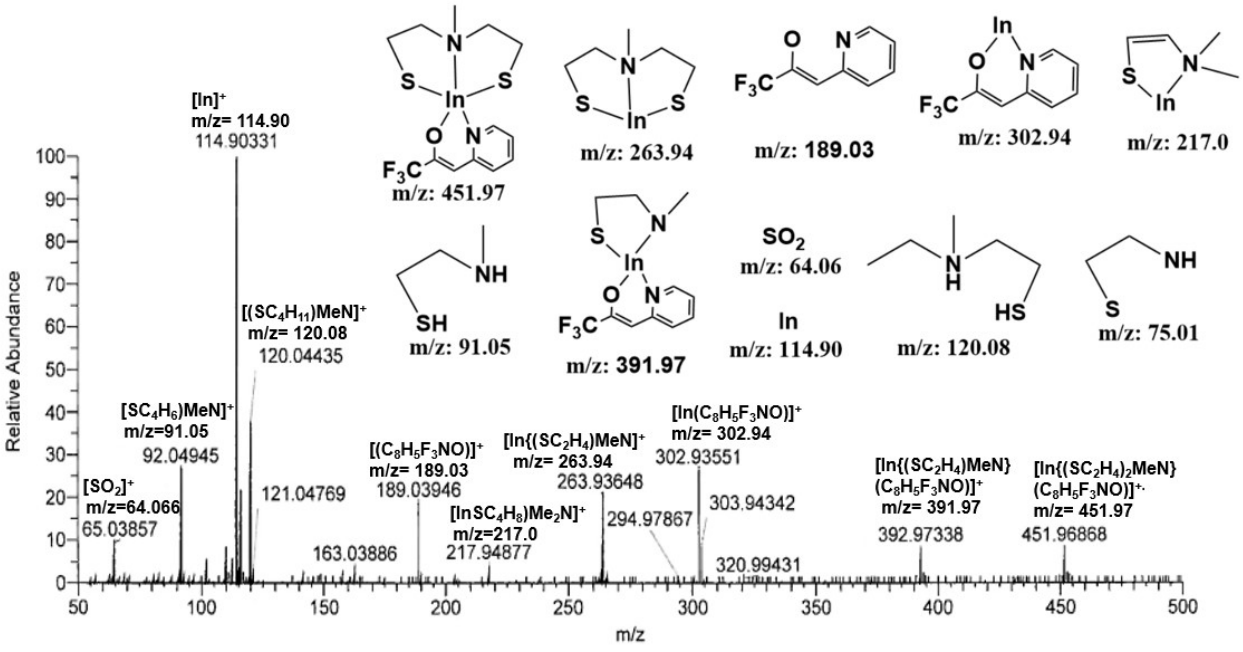


re S12: EI mass spectrum (70eV) of heteroleptic complex **[1]**.

Figure S13: EI mass spectrum (70eV) of heteroleptic complex **[2]**

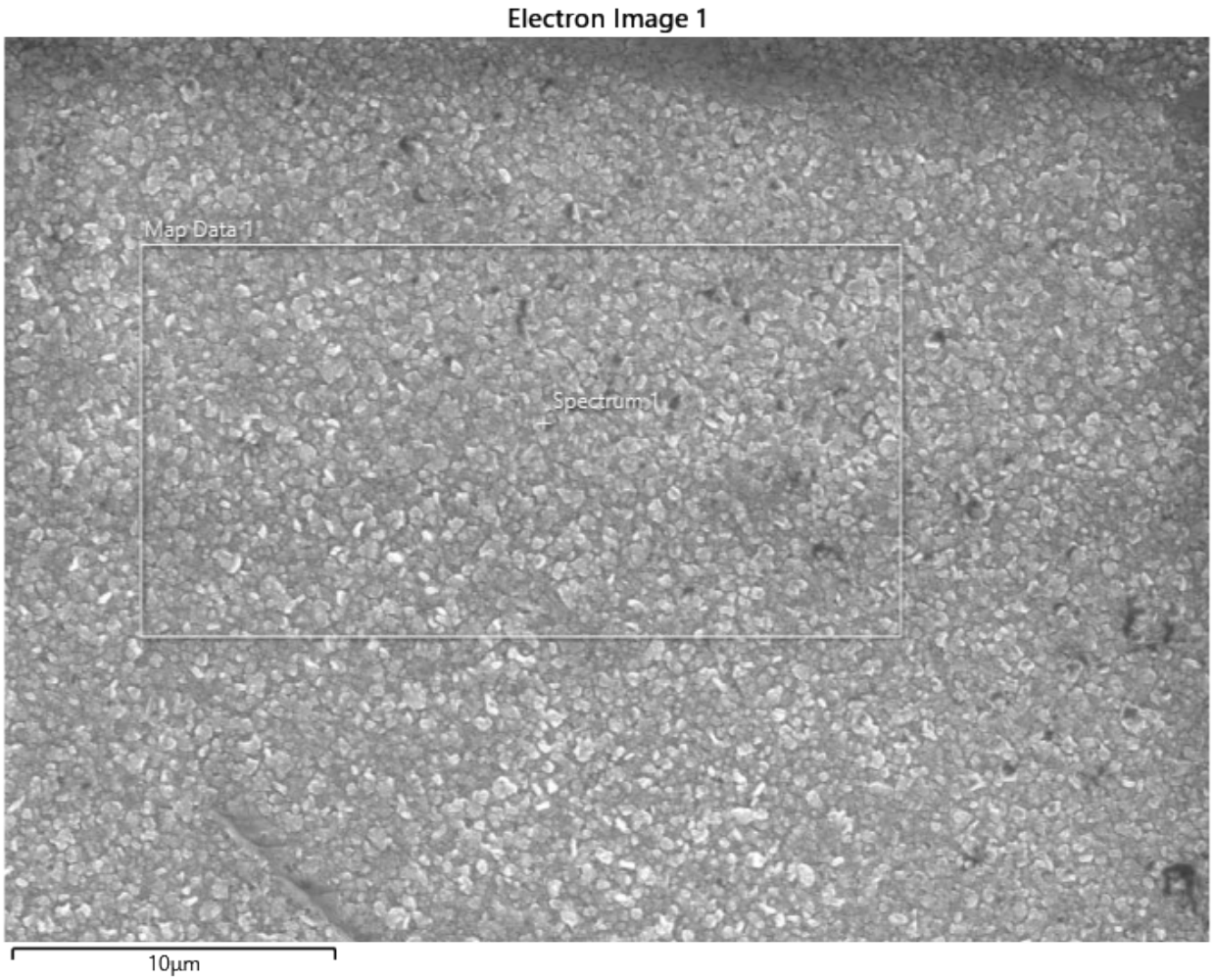


Figure S14. Electron image of the obtained In_2S_3 CVD film from compound **[2]**.

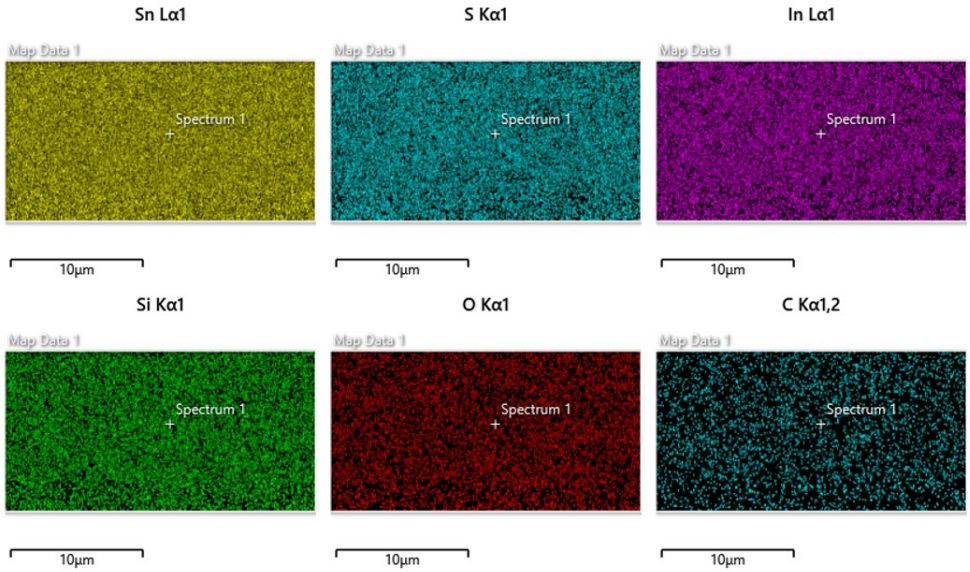


Figure S15. Map data of the obtained In_2S_3 CVD film from compound **[2]**.

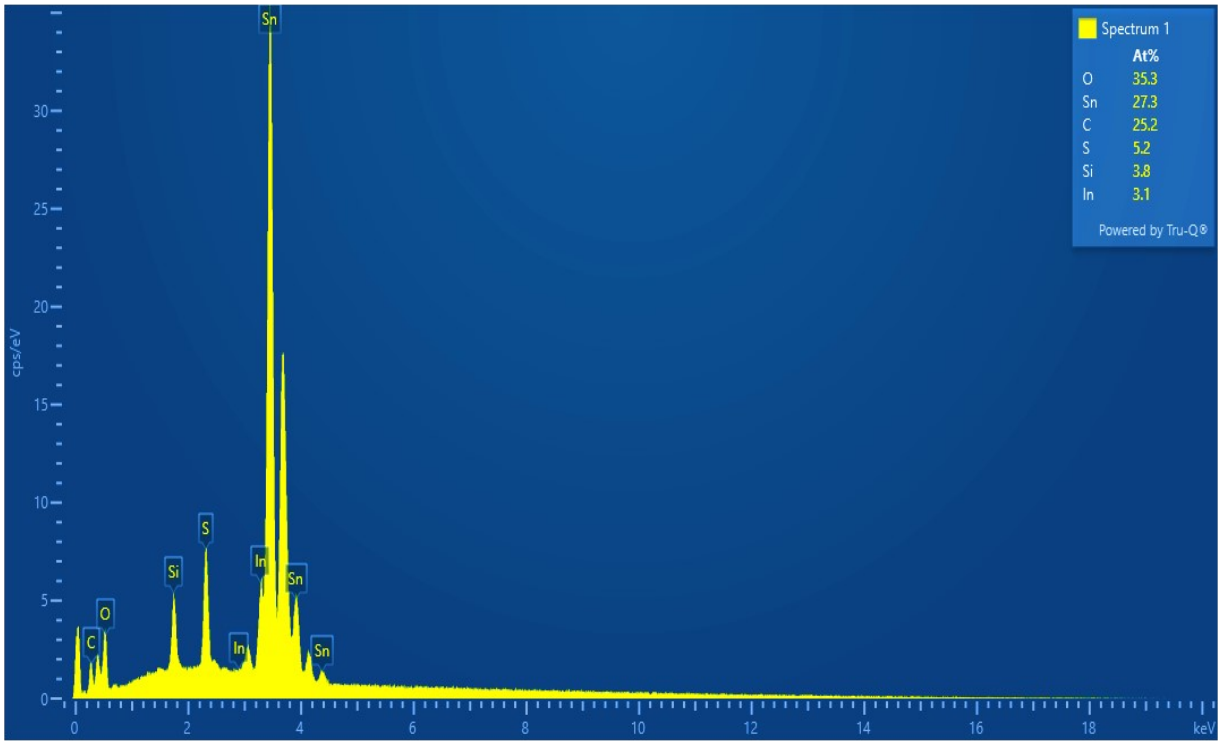


Figure S16. EDS mapping of the obtained In_2S_3 CVD film from compound **[2]** (The (stoichiometric ratio of In:S = 2:3.35).

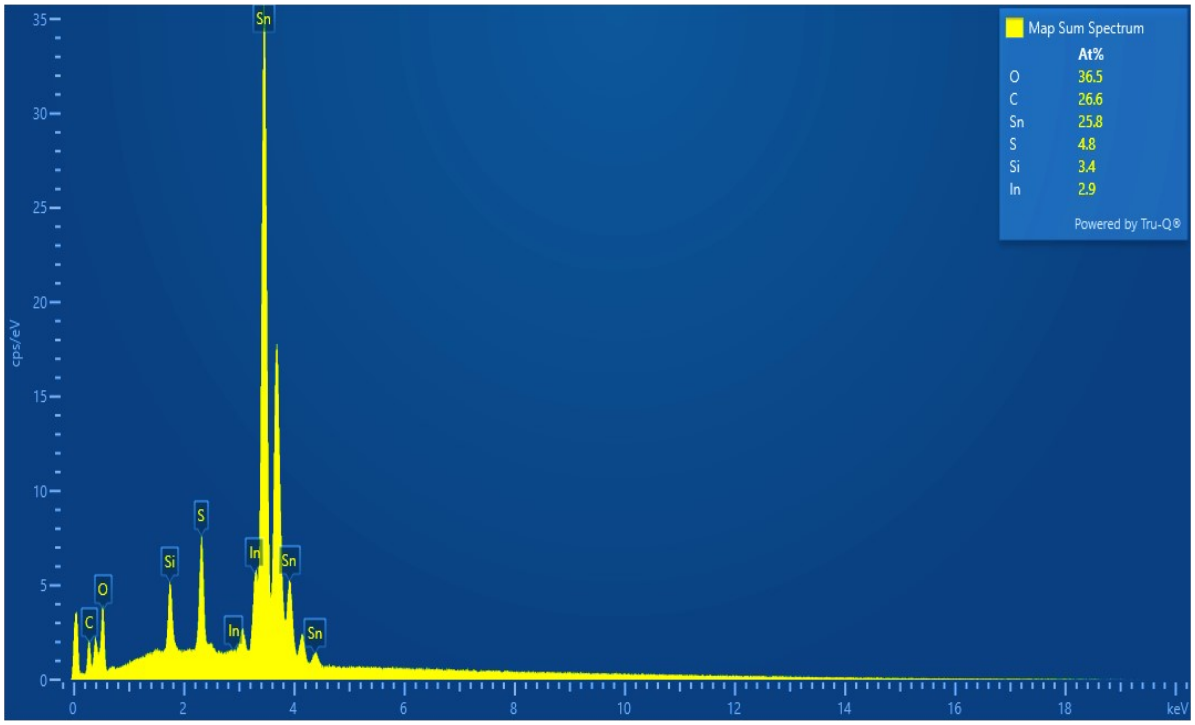


Figure S17. Map sum spectrum of the obtained In_2S_3 CVD film from compound **[2]** (stoichiometric ratio of In:S = 2:3.31)

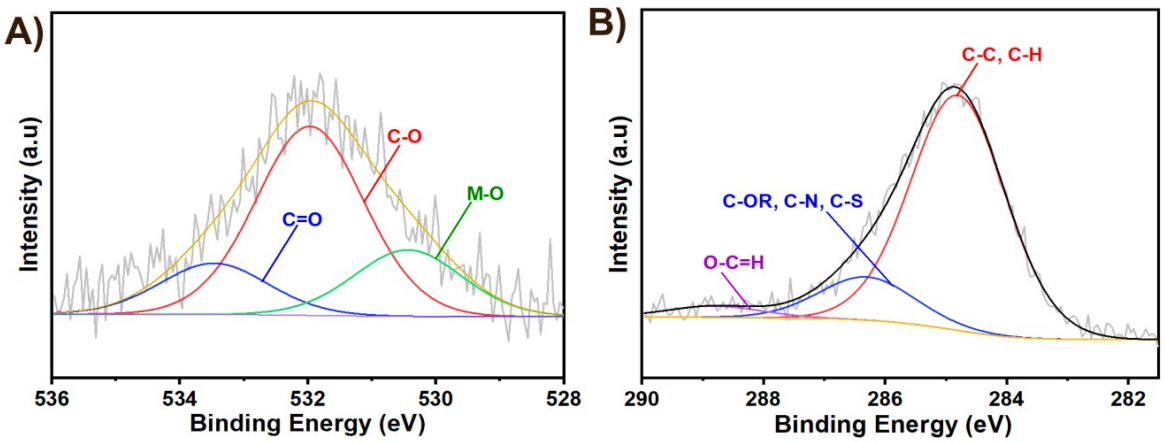


Figure S18. High-resolution X-ray photoelectron spectra A) O 1s region B) C Is region of CVD film from compound **[2]**.

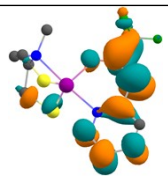
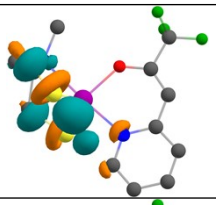
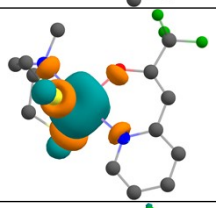
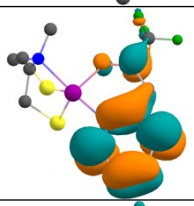
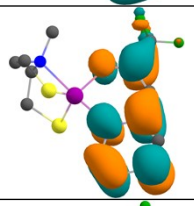
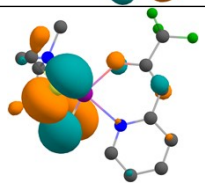
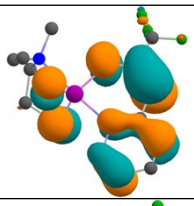
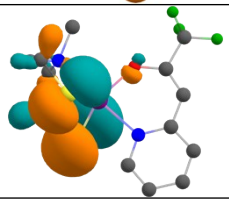
Table S2. XPS elemental quantification of CVD films obtained from compound **[2]**

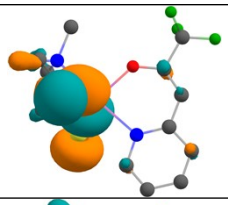
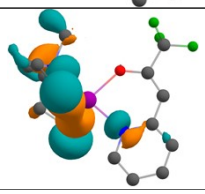
Peak	**At%**
O 1s	10.51
C 1s	50.98
N 1s	2.12
In $3d_{5/2}$	13.32
S 2p	22.05
F 1s	1.03

Table S3. The XYZ coordinates of the optimised ground state for **[2]** (B3lyp/6-31G(d, p)/LanL2DZ level of theory).

	Atom	Coordinates (Å)		
		X	Y	Z
1	In	-0.59875	-0.42251	0.008914
2	S	-1.38951	-1.02343	2.23854
3	S	-1.43449	-1.36759	-2.07935
4	F	1.817605	3.460741	0.978623
5	F	3.629507	2.957203	-0.11797
6	O	0.547052	1.247734	-0.12113
7	F	1.796592	3.429363	-1.19416
8	N	1.345433	-1.61805	0.022604
9	N	-2.56689	0.954945	-0.08248
10	C	1.209859	-2.96148	0.04356
11	H	0.188637	-3.33161	0.02462
12	C	2.592508	-1.063	0.028524
13	C	2.282923	-3.83466	0.078901
14	H	2.114816	-4.90512	0.094662
15	C	-3.14553	0.800556	-1.44508
16	H	-2.55075	1.424835	-2.1177
17	H	-4.17698	1.188749	-1.44993
18	C	2.793262	0.36617	-0.00718
19	H	3.824756	0.691532	0.014054
20	C	1.845038	1.344809	-0.07685
21	C	-3.48261	0.417898	0.959962
22	H	-3.8857	-0.53093	0.598553
23	H	-4.32659	1.114351	1.091245
24	C	3.723369	-1.91249	0.065328
25	H	4.710247	-1.46249	0.070161
26	C	-2.79873	0.173226	2.306925
27	H	-3.54165	-0.24951	2.988547
28	H	-2.45262	1.110829	2.750539
29	C	-3.12747	-0.63651	-1.97043
30	H	-3.5341	-0.62616	-2.98524
31	H	-3.77243	-1.28978	-1.37553
32	C	3.571849	-3.28663	0.09142
33	H	4.445373	-3.93146	0.118951
34	C	-2.25752	2.380936	0.172619
35	H	-1.8278	2.498641	1.168019
36	H	-3.16597	2.996247	0.099788
37	H	-1.51668	2.72695	-0.5482
38	C	2.288167	2.80585	-0.10382

Table S4. DFT-calculated compositions (%) of frontier MOs in the S_0 ground state for **[2]** (B3lyp/6-31G(d, p)/LanL2DZ level of theory).

MO	**energy (eV)**		**component %**					
			In	**Pyridine**	**Carbonyl: C2, 3, O**	**S1 and S2**	**CF_3**	**L' = N1, C9, 10,12,13**
LUMO+4	1.127		14	23	29	19	5	10
LUMO+3	0.995		15	10	1	21	1	52
LUMO+2	0.381		51	10	6	22	1	10
LUMO+1	-1.042		1	87	7	2	2	1
LUMO	-1.696		0	74	20	1	4	1
HOMO	-5.748		1	3	6	81	0	9
HOMO-1	-5.931		1	24	53	18	2	2
HOMO-2	-5.960		3	1	2	83	1	10

HOMO-3	-6.891		8	4	2	75	0	11
HOMO-4	-7.089		5	12	1	41	0	41

LUMO: Lowest unoccupied molecular orbital, and HOMO: Highest occupied molecular orbital.

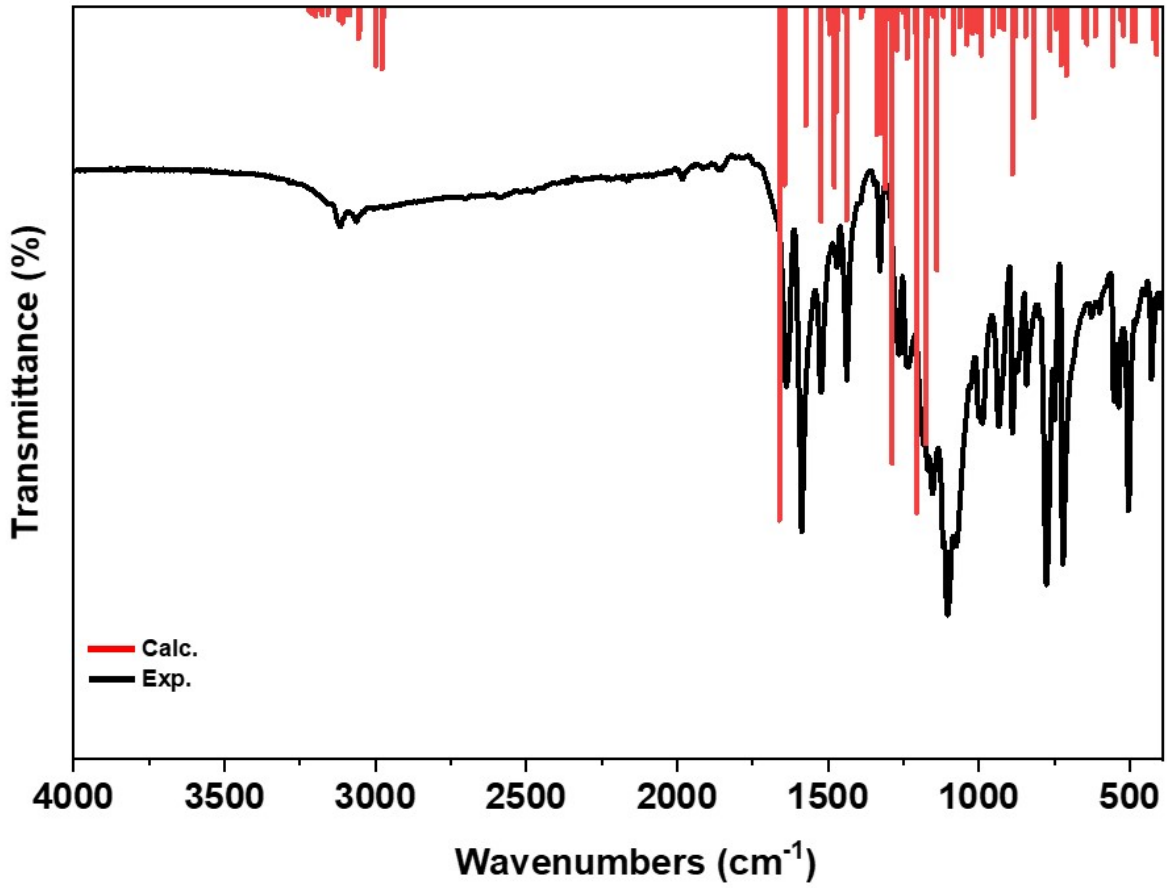


Figure S19. FT-IR spectra of **[2]** showing the experimental (black) and calculated (red).