Electronic Supplementary Material (ESI) for ChemComm.

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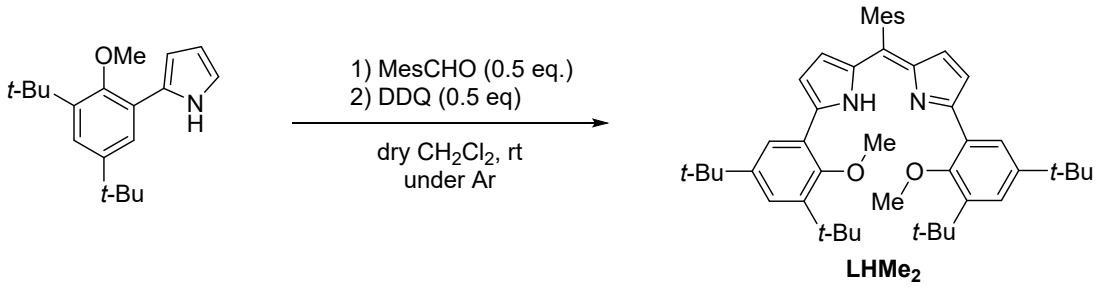
General remarks

All the manipulations were carried out under dry argon atmosphere using the standard Schlenk technique unless otherwise noted. 2-(2,4-Di-*tert*-butylphenyl)-1*H*-pyrrole was prepared according to a literature.[S1] ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III (^{1}H: 400 MHz, ^{13}C: 100 MHz) or on a JEOL JNM-ECZ600R (^{1}H: 600 MHz, ^{13}C: 150 MHz) spectrometer and referenced to appropriate internal or external standard ($SiMe_4$). Chemical shifts were reported as the delta scale in ppm. High-resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF mass spectrometer (ionization mode: APCI or ESI). UV/vis spectra were recorded on a Shimadzu UV-3101PC or a JASCO V-670 spectrometer. Fluorescence spectra were measured using a Hitachi F-4500 or on a JASCO FP-8600 spectrometer.

Synthesis of the new compounds

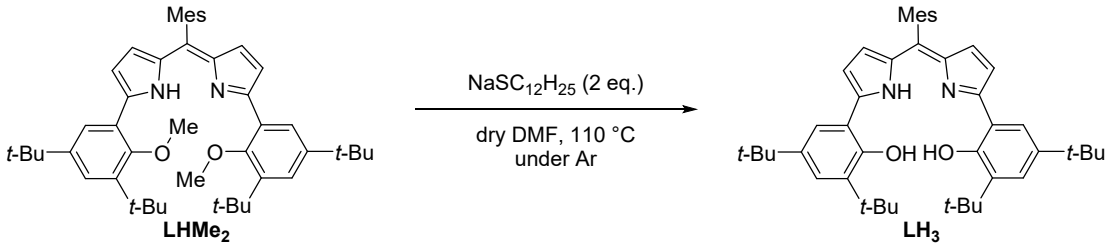
Synthesis of $LHMe_2$.



A mixture of 2-(2,4-di-*tert*-butylphenyl)-1*H*-pyrrole (0.86 g, 3.0 mmol), 2,4,6-trimethylbenzaldehyde (MesCHO) (0.22 g, 1.5 mmol), CF_3COOH (0.034 mL, 0.45 mmol), and CH_2Cl_2 (75 mL) was stirred at rt under dark for 3 h. The mixture was treated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (0.34 g, 1.5 mmol) and stirred for 5 h. Triethylamine (0.062 mL, 0.45 mmol) was added, and the mixture was further stirred for 0.5 h. The mixture was filtered through an Al_2O_3 short path column using CH_2Cl_2 as an eluent and evaporated under reduced pressure. The residue was subjected to column chromatography (SiO_2, CH_2Cl_2/AcOEt = 1 : 0 to 5 : 1 in v/v) to afford **$LHMe_2$** as an orange solid (0.98 g, 1.4 mmol, 47%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.53 (d, J = 2.6 Hz, 2H), 7.34 (d, J = 2.6 Hz, 2H), 6.96 (s, 2H), 6.69 (d, J = 4.2 Hz, 2H), 6.40 (d, J = 4.2 Hz, 2H), 3.62 (s, 6H), 2.38 (s, 3H), 2.19 (s, 6H), 1.43 (s, 18H), 1.33 (s, 18H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 155.97, 153.75, 145.30, 142.03, 141.09, 137.20, 137.13, 136.93, 134.31, 127.71, 127.20, 126.98, 125.00, 124.70, 118.92, 61.41, 35.33, 34.53, 31.55, 31.02, 21.16, 20.05. HRMS (APCI) *m*/*z* calcd for $C_{48}H_{62}N_2O_2$ 699.4884 $[M+H]^+$; observed: 699.4884.

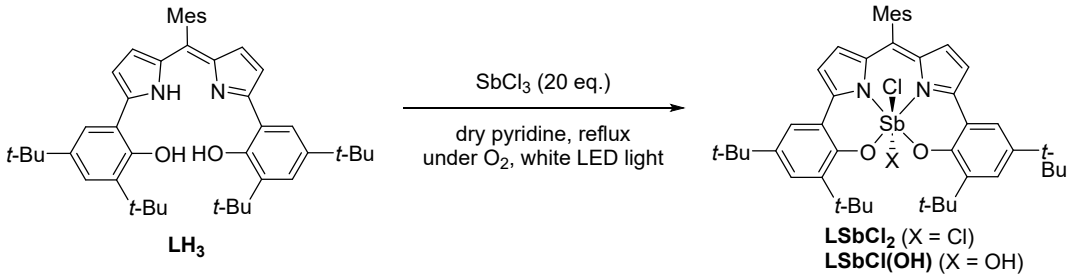
Synthesis of LH_3.



To a mixture of NaH (60 wt% dispersion in a mineral oil, 0.16 g, ca. 4.1 mmol) and DMF (10 mL) was added 1-dodecanethiol (0.96 mL, 4.0 mmol), and the mixture was stirred at rt for 1 h. **$LHMe_2$** (0.70 g, 1.0 mmol) was added, and the mixture was stirred at 110 °C for 4 h. aq. NH_4Cl (2 mL) and distilled water (3 mL) were added, and the mixture was extracted with AcOEt. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography (SiO_2, hexane/CH_2Cl_2 = 5 : 1 in v/v) to afford **LH_3** as a red solid (0.43 g, 0.64 mmol, 64%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.57(d, *J* = 2.2 Hz, 2H), 7.34 (d, *J* = 2.2 Hz, 2H), 6.95(s, 2H), 6.86 (d, *J* = 3.6 Hz, 2H), 6.45 (d, *J* = 3.6 Hz, 2H), 2.38 (s, 3H), 2.13 (s, 6H), 1.53 (s, 18H), 1.34 (s, 18H) (the OH signals were not observed); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 154.49, 152.50, 141.61, 139.00, 137.14, 136.74, 136.65, 135.56, 134.66, 128.39, 127.59, 124.94, 122.67, 117.88, 116.29, 34.62, 34.07, 31.27, 30.02, 21.86, 19.60; HRMS (APCI) *m*/*z* calcd for $C_{46}H_{58}N_2O_2$ 671.4571 $[M+H]^+$; observed: 671.4510.

Synthesis of $LSbCl_2$ and LSbCl(OH) (entry 2 in Table 1)



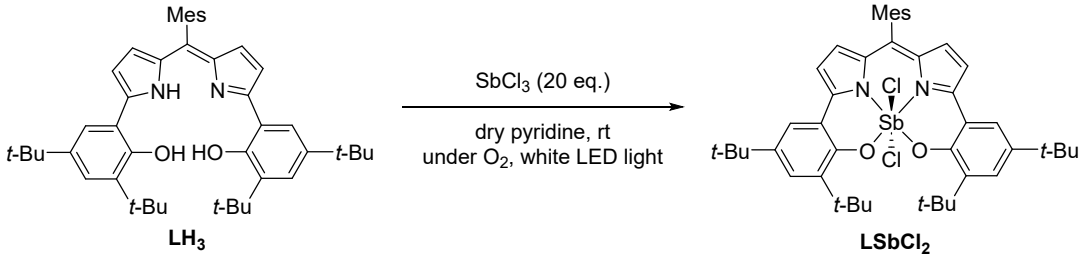
A mixture of $SbCl_3$ (91 mg, 0.4 mmol) and pyridine (5 mL) was stirred at rt under O_2 atmosphere for 0.5 h before the addition of **LH_3** (13.4 mg, 0.020 mmol), and then the mixture was refluxed for 24 h under irradiation with a white LED (7 W). Remaining $SbCl_3$ was removed by filtration using AcOEt as an eluent, and the solvents were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2, hexane/AcOEt = 12 : 1 in v/v) for afford **$LSbCl_2$** (4.1 mg, 0.0048 mmol, 24%) and **LSbCl(OH)** (5.5 mg, 0.0066 mmol, 33%) as dark green solids.

$LSbCl_2$: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.58 (d, *J* = 2.6 Hz, 2H), 7.50 (d, *J* = 2.6 Hz, 2H), 7.02 (d, *J* = 4.6 Hz, 2H), 6.99 (s, 2H), 6.67 (d, *J* = 4.6 Hz, 2H), 2.39 (s, 3H), 2.15 (s, 6H), 1.61 (s, 18H), 1.34 (s,

18H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 156.41, 154.73, 142.86, 141.15, 138.58, 138.08, 137.13, 136.63, 132.00, 130.72, 128.74, 128.13, 123.32, 117.15, 116.38, 35.93, 34.38, 31.32, 30.53, 21.19, 19.67. HRMS (APCI) *m*/*z* calcd for $C_{46}H_{55}N_2O_2Cl_2{}^{121}Sb$ 858.2673, $C_{46}H_{55}N_2O_2Cl_2{}^{123}Sb$ 860.2668 (M^+); observed 858.2573, 860.2589.

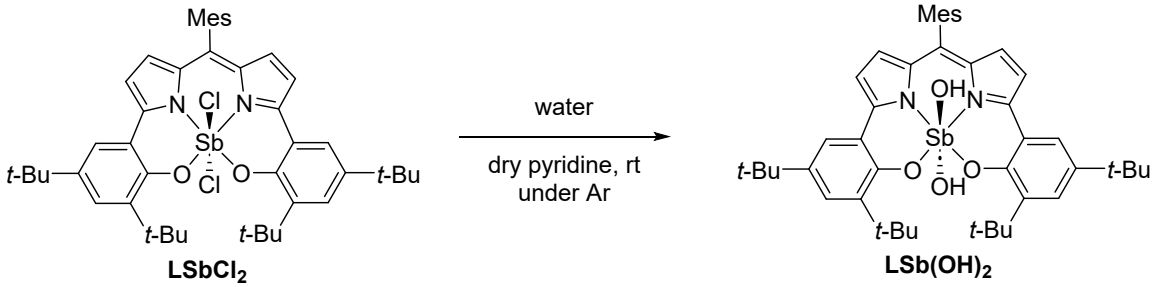
LSbCl(OH): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.59 (d, *J* = 2.8 Hz, 2H), 7.48 (d, *J* = 2.8 Hz, 2H), 7.04 (d, *J* = 4.6 Hz, 2H), 6.98 (s, 2H), 6.68 (d, *J* = 4.6 Hz, 2H), 2.39 (s, 3H), 2.17 (s, 3H), 2.13 (s, 3H), 1.61 (s, 18H), 1.34 (s, 18H) (the OH signal was not observed). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 156.63, 155.01, 142.38, 140.93, 138.41, 137.26, 136.90, 132.39, 130.78, 128.26, 128.11, 128.01, 123.40, 117.12, 116.87, 35.93, 34.34, 31.35, 30.47, 21.21, 19.69 (only 4 signals were observed for the benzene ring carbon atoms of the Mes group). HRMS (APCI) *m*/*z* calcd for $C_{46}H_{55}N_2O_2Cl_2{}^{121}Sb$ 840.3012, $C_{46}H_{55}N_2O_2Cl_2{}^{123}Sb$ 842.3014 (M^+); observed 840.3015, 842.3047.

Synthesis of $LSbCl_2$ (entry 3 in Table 1)



A mixture of $SbCl_3$ (0.46 g, 2.0 mmol) and pyridine (25 mL) was stirred at rt under O_2 atmosphere for 0.5 h before the addition of **LH_3** (67.1 mg, 0.10 mmol), and then the mixture was stirred at rt for 24 h under irradiation with a white LED (7 W). Remaining $SbCl_3$ was removed by filtration using AcOEt as an eluent, and the solvents were removed under reduced pressure. The residue was subjected to column chromatography (SiO_2, hexane/AcOEt = 12 : 1 in v/v) for afford **$LSbCl_2$** as a dark green solid (46.1 mg, 0.048 mmol, 48%).

Synthesis of $LSb(OH)_2$.



A mixture of **$LSbCl_2$** (25.8 mg, 0.030 mmol), pyridine (7.5 mL), and distilled water (1.5 mL) was refluxed for 24 h and then concentrated under reduced pressure. The residue was subjected to column chromatography (SiO_2, hexane/AcOEt = 12 : 1 in v/v) for afford **$LSb(OH)_2$** as a dark green solid (20.1 mg, 0.024 mmol, 81%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.61 (d, *J* = 2.6 Hz, 2H), 7.46 (d, *J* = 2.6 Hz, 2H), 7.07 (d, *J* = 4.6 Hz, 2H), 6.98 (s, 2H), 6.70 (d, *J* = 4.6 Hz, 2H), 2.39 (s, 3H), 2.14 (s, 6H), 1.62 (s, 18H), 1.33 (s, 18H) (the OH signal was not observed). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 156.63, 155.01, 142.38, 140.93, 138.41, 137.26, 136.90, 132.39, 130.78, 128.26, 128.11, 128.01, 123.40, 117.12, 116.87, 35.93, 34.34, 31.35, 30.47, 21.21, 19.69. HRMS (ESI) *m*/*z* calcd for $C_{46}H_{57}N_2O_4{}^{121}Sb$ 821.3273, $C_{46}H_{57}N_2O_4{}^{123}Sb$ 823.3286 ($[M–H]^-$); observed 821.3436, 823.3449.

Stability test of $LSbCl_2$

$LSbCl_2$ (5.0 mg, 6 μmol) was dissolved in moisture-saturated $CDCl_3$ (0.5 mL, containing ca. 1 eq. of H_2O), and the solution was left under air at room temperature. ^{1}H NMR and TLC analyses of the mixture did not show that **$LSbCl_2$** was not decomposed after 48 h at room temperature.

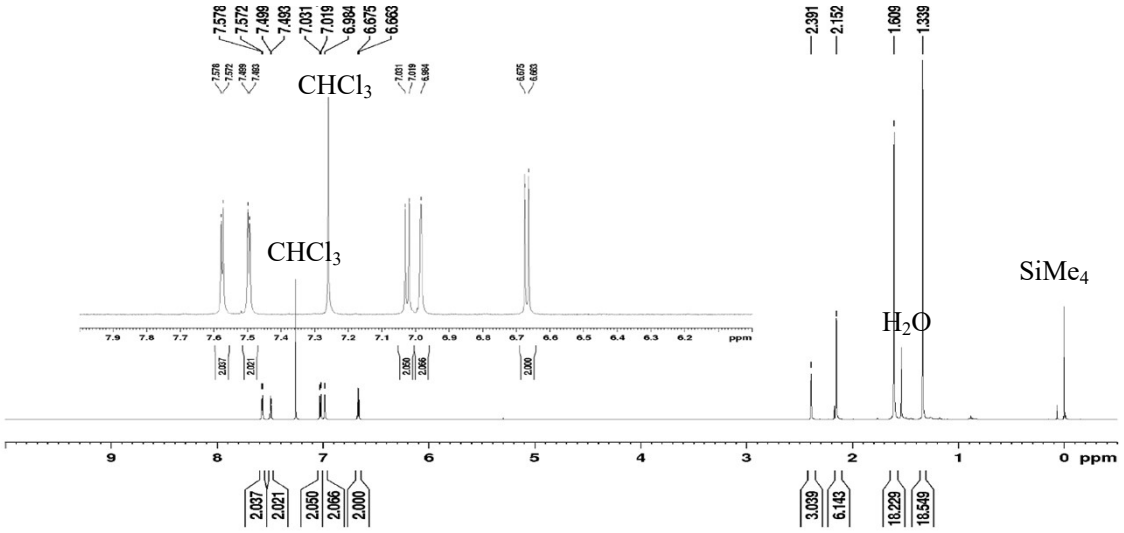
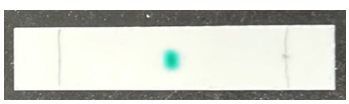


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of $LSbCl_2$ measured after 48 h.



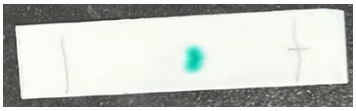


Figure S2. Images of the TLCs (SiO_2, AcOEt/hexane = 1:12) of the as-synthesized **$LSbCl_2$** (top) and the $CDCl_3$ solution after 48 h.

Crystallographic analysis

Single crystal X-ray diffraction (XRD) measurements were carried out on a Rigaku MicroMax-007HF diffractometer equipped with a VariMax light source (Mo Kα, λ = 0.71073 Å). The crystals were kept at –100 °C while the data collection. The collected data were processed using the CrysAlisPro (ver. 1.171.41.117a) program package (Rigaku Oxford Diffraction, 2021). Using Olex2,[S2] the structures were solved with the SHELXT and refined with the SHELXL program packages.[S3] The full-matrix least-squares refinements were performed on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. Crystallographic data are summarized in the next page. For **LSbCl(OH)**-acetone, axial Cl and OH ligands, one of the *t*-butyl groups, and acetone molecule were disordered over two sites with the occupancy ratios of 95:5, 64:36, and 74:26, respectively. SADI, RIGU, and SIMU restraints were included for the refinement of these disordered parts. In addition, for the disordered Cl and O atoms, EADP constraints were used to refine their anisotropic displacement parameters. CCDC 2296634 (**$LSbCl_2$**), 2323628 (**LSbCl(OH)**-acetone), and 2323629 (**$LSb(OH)_2$**) contain the additional crystallographic data.

Table S1. Crystallographic data for the Sb(V)-dipyrrin complexes.

	$LSbCl_2$	**LSbCl(OH)**-acetone	**$LSb(OH)_2$**
Empirical formula	$C_{46}H_{55}Cl_2N_2O_2Sb$	$C_{49}H62ClN_2O_4Sb$	$C_{46}H_{57}N_2O_4Sb$
Formula weight	860.57	900.20	823.68
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	*Cc*	$P2_1/c$	*Pbca*
a/Å	20.0826(9)	24.3993(6)	28.4574(5)
b/Å	14.1346(5)	16.8320(4)	27.9101(4)
c/Å	15.2463(7)	11.6630(3)	32.3437(6)
β/°	100.815(5)	100.297(3)	90
V/Å^3	4250.9(3)	4712.7(2)	25688.9(8)
Z	4	4	24
ρ/g cm^{-3}	1.345	1.269	1.278
μ/mm^{-1}	0.813	0.685	0.687
F(000)	1784.0	1880.0	10320.0
Crystal size/mm^3	0.218 × 0.093 × 0.089	0.238 × 0.158 × 0.138	0.131 × 0.127 × 0.113
2Θ/°	5.44 to 52.738	3.394 to 52.744	3.178 to 52.744
Index ranges	$-25 \le h \le 25$, $-17 \le k \le 17$, $-19 \le l \le 19$	$-30 \le h \le 30$, $-21 \le k \le 21$, $-14 \le l \le 14$	$-35 \le h \le 35$, $-34 \le k \le 34$, $-40 \le l \le 40$
Reflections collected	30936	76821	281142
Independent reflections (R_{int}, R_σ)	8642 (0.1105, 0.0922)	9643 (0.0352, 0.0170)	26265 (0.1196, 0.0532)
Data/restraints/parameters	8642/2/493	9643/131/601	26265/0/1493
GOF on F^2	1.006	1.043	1.024
R_1 ($I \ge 2\sigma$ (I))	0.0480	0.0273	0.0427
wR_2 (all data)	0.0934	0.0724	0.0875
Largest diff. peak/hole /e Å^{-3}	0.97/–0.78	0.50/–0.32	0.57/–0.42
Flack parameter	–0.012(14)	—	—

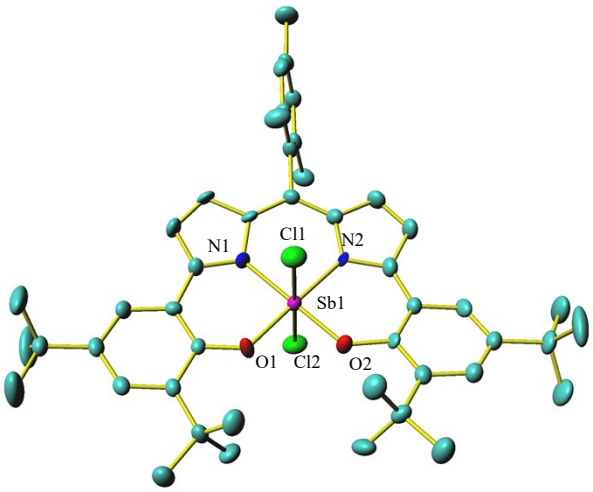


Figure S3. Molecular structure of **$LSbCl_2$**.

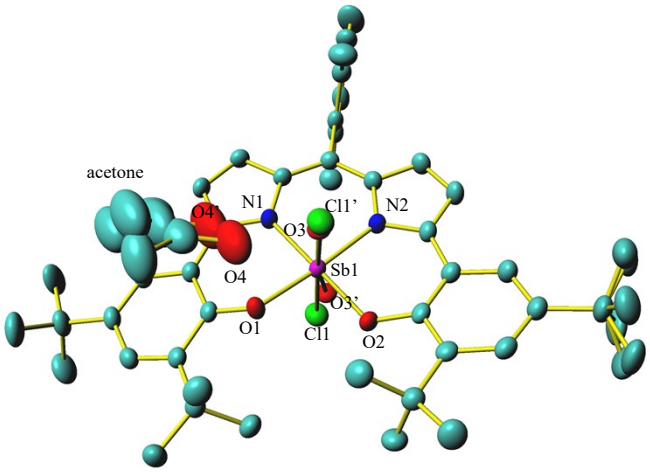
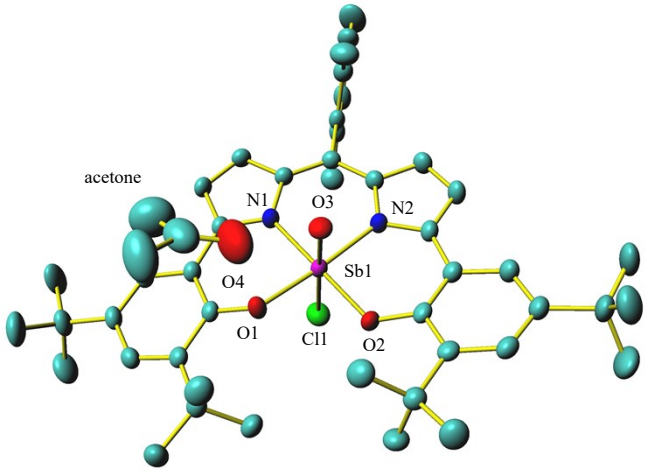


Figure S4. Molecular structure of **LSbCl(OH)**-acetone.

Major part (Cl, O: 95%, *t*Bu: 64%, acetone: 74%)



Minor part (Cl, O: 5%, *t*Bu: 36%, acetone: 26%)

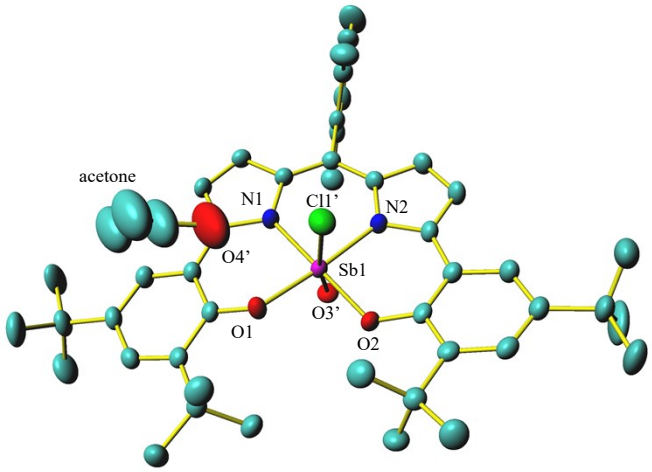


Figure S5. Major and minor parts of **LSbCl(OH)**-acetone.

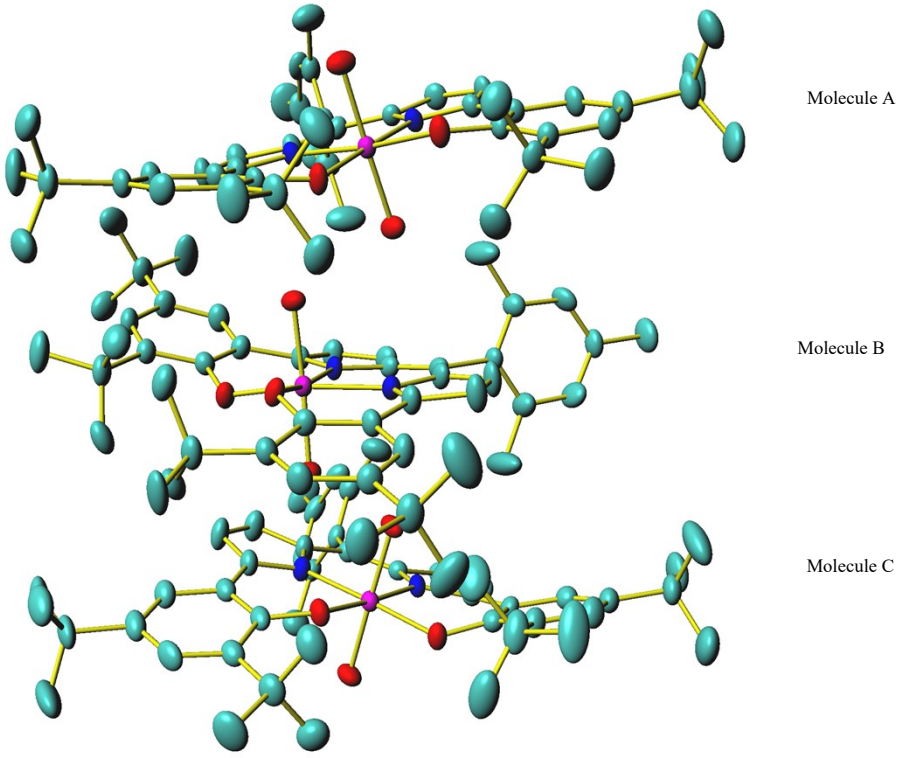
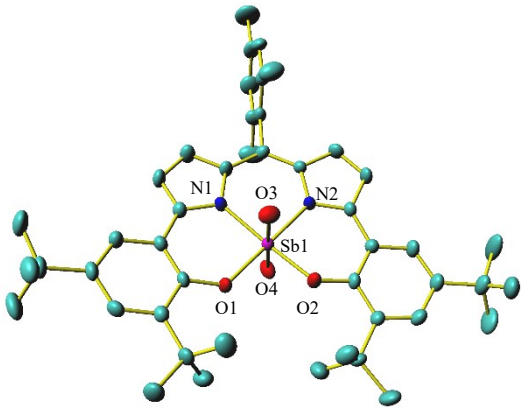


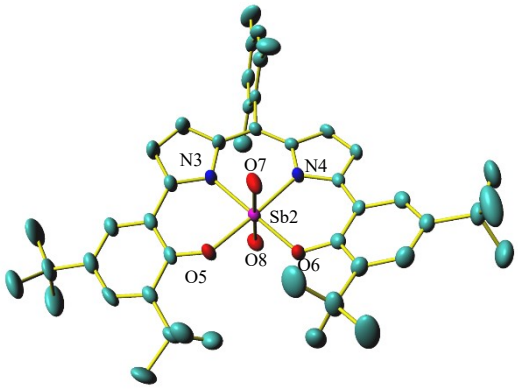
Figure S6. Molecular structures of **$LSb(OH)_2$**.

Molecule A



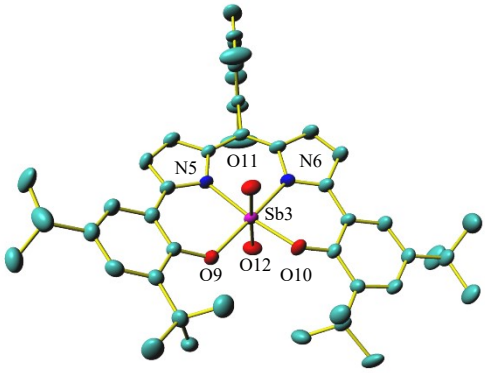
Selected bond lengths (Å) and angles (°)
Sb1-O1 1.974(2), Sb1-O2 1.972(2), Sb1-N1 2.084(3), Sb1-N2 2.084(2), Sb1-O3 1.953(2), Sb1-O4 1.921(2), O3-Sb1-O4 178.6(1)

Molecule B



Selected bond lengths (Å) and angles (°)
Sb2-O5 1.977(2), Sb2-O6 1.982(2), Sb2-N3 2.070(2), Sb2-N4 2.076(3), Sb2-O7 1.955(2), Sb2-O8 1.955(2), O7-Sb2-O8 176.7(1)

Molecule C



Selected bond lengths (Å) and angles (°)
Sb3-O9 1.980(2), Sb3-O10 1.973(2), Sb3-N5 2.093(2), Sb3-N6 2.089(3), Sb3-O11 1.928(2), Sb3-O12 1.943(2), O11-Sb3-O12 178.5(1)

Figure S7. Independent molecules of **LSb(OH)$_2$**.

DFT calculations

Density functional theory (DFT) calculations were performed using the Gaussian 16 (revision C.02) program package.[S4] CAM-B3LYP density functional with the 6-311G(d) and 6-311+G(d) basis sets were employed to the geometry optimizations and the time-dependent (TD)-DFT calculations. The M06 density functional was also employed for the TD-DFT calculations. Solvent effects were included by the IEFPCM method in the TD-DFT calculations. For the Sb atoms, the SDD basis set and pseudo potential was used. The optimized geometries were confirmed as the local energy minima by the frequency calculations. The computation was performed using Research Center for Computational Science, Okazaki, Japan (Project: 22-IMS-C164, and 23-IMS-C170, T.A.). Optimized geometries (in Å) of the Sb complexes are shown below.

L$SbCl_2$

Sb	-0.00397	-0.2335	0.008611
Cl	0.363188	-0.2459	-2.36648
Cl	-0.37385	-0.1845	2.382954
O	1.314481	-1.63022	0.316957
O	-1.39336	-1.56788	-0.27176
N	1.477074	1.204203	0.153418
C	2.665803	-1.60303	0.201564
C	-2.74141	-1.46572	-0.1858
C	3.499961	2.158142	0.332597
H	4.566917	2.2734	0.436581
C	-3.41307	-0.23003	-0.17053
C	3.3375	-2.84629	0.17679
C	-4.81922	-0.2188	-0.07697
H	-5.31863	0.737292	-0.03272
C	3.399742	-0.4003	0.158172
C	4.796602	-0.46456	0.035585
H	5.348417	0.463537	-0.03427
C	4.724003	-2.82805	0.066039
H	5.239256	-3.77573	0.039574
C	-3.38393	2.330106	-0.33986
H	-4.44359	2.499887	-0.44279
C	1.296983	2.589419	0.159848

C	0.118549	4.753626	0.003852
C	-4.85756	-2.58421	-0.0743
H	-5.42844	-3.50208	-0.04462
C	0.082073	3.256142	-9.1E-05
C	-2.41045	3.296276	-0.29049
H	-2.54408	4.367474	-0.33239
C	2.803166	0.929736	0.227131
N	-1.41141	1.274404	-0.16072
C	2.582562	-4.18033	0.294135
C	-0.20114	4.714486	2.521431
H	-1.10363	4.095194	2.511458
H	-0.28412	5.418447	3.352764
H	0.638647	4.04392	2.728699
C	2.575214	3.172766	0.287012
H	2.762252	4.235816	0.331287
C	-0.01699	5.447169	1.216223
C	5.485997	-1.65951	-0.01824
C	-5.56444	-1.37385	-0.02194
C	0.283461	5.447096	-1.20484
C	0.310778	6.839564	-1.17618
H	0.434776	7.379552	-2.1115
C	-2.7494	1.066602	-0.23622
C	0.182732	7.554161	0.011757
C	0.016746	6.839593	1.195042
H	-0.09172	7.379616	2.132267
C	3.52954	-5.38891	0.233179
H	2.937257	-6.30465	0.322846
H	4.256892	-5.39002	1.051495
H	4.073214	-5.44266	-0.7158
C	-1.16206	2.649653	-0.16279
C	0.246726	9.05937	0.019752
H	1.27766	9.408586	0.150131
H	-0.34528	9.480064	0.837392
H	-0.12316	9.479976	-0.91953
C	-3.47755	-2.67781	-0.15727

C	1.585791	-4.33439	-0.86813
H	2.111288	-4.32388	-1.8291
H	0.843327	-3.53947	-0.87671
H	1.060695	-5.29215	-0.78249
C	-2.05529	-4.16718	-1.59502
H	-2.77066	-4.11266	-2.42279
H	-1.54122	-5.13249	-1.65828
H	-1.3173	-3.37746	-1.73089
C	0.425679	4.714369	-2.51525
H	1.290917	4.044023	-2.50927
H	0.549856	5.418273	-3.34149
H	-0.45138	4.095038	-2.72773
C	-2.78885	-4.04907	-0.24514
C	-1.81514	-4.23789	0.931736
H	-1.03143	-3.48359	0.939296
H	-1.3409	-5.22329	0.865888
H	-2.35095	-4.18601	1.885645
C	7.013028	-1.66501	-0.1636
C	-3.79715	-5.20668	-0.17965
H	-4.35557	-5.21728	0.762266
H	-3.25156	-6.15278	-0.24696
H	-4.51222	-5.18366	-1.00844
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H	-7.1513	-3.15287	1.390419
H	-8.59944	-2.14231	1.467148
H	-7.10361	-1.61509	2.261021
C	1.859486	-4.24383	1.653368
H	1.300713	-5.18254	1.736202
H	1.161688	-3.41769	1.785156
H	2.585709	-4.21197	2.472845
C	-7.09235	-1.38606	0.088821
C	-7.68078	0.029067	0.133479
H	-7.31678	0.593848	0.997967
H	-8.77088	-0.02782	0.212585
H	-7.44579	0.596	-0.7734

C	7.646297	-0.91654	1.023029
H	7.310494	0.123532	1.074072
H	8.737964	-0.90875	0.93083
H	7.387895	-1.3972	1.971913
C	-7.68994	-2.11521	-1.12811
H	-7.41788	-1.60887	-2.05974
H	-8.78308	-2.1385	-1.0592
H	-7.33991	-3.14935	-1.19585
C	7.405669	-0.96336	-1.4762
H	6.973304	-1.47867	-2.33965
H	8.494943	-0.95526	-1.59386
H	7.060786	0.07463	-1.5013
C	7.589364	-3.08593	-0.19198
H	7.36988	-3.63376	0.730051
H	8.677912	-3.03797	-0.29573
H	7.203051	-3.66591	-1.03616

$LSb(OH)_2$

Sb	0.005148	-0.25586	-0.00399
O	-1.32744	-1.60072	-0.59199
O	1.409947	-1.53173	0.574241
N	-1.4703	1.194815	-0.22187
C	-2.65977	-1.60726	-0.35365
C	2.740808	-1.4608	0.346982
C	-3.48745	2.150674	-0.4829
H	-4.55008	2.260071	-0.63321
C	3.408335	-0.22417	0.263892
C	-3.32862	-2.84871	-0.27005
C	4.803313	-0.20754	0.080289
H	5.291317	0.751203	-0.01872
C	-3.39348	-0.40542	-0.26149
C	-4.78016	-0.46798	-0.06727
H	-5.32474	0.461619	0.040412
C	-4.70952	-2.83353	-0.09387
H	-5.22144	-3.78155	-0.03002

C	3.365842	2.333315	0.480614
H	4.421262	2.49977	0.628847
C	-1.29287	2.577558	-0.22561
C	-0.12635	4.743116	-0.00203
C	4.851777	-2.57457	0.098887
H	5.422337	-3.4912	0.033775
C	-0.08679	3.244998	-0.00071
C	2.391451	3.296975	0.404658
H	2.519239	4.36832	0.460498
C	-2.79058	0.924155	-0.34061
N	1.402004	1.270005	0.223337
C	-2.56818	-4.18122	-0.36027
C	0.311314	4.71466	-2.50091
H	1.209227	4.091103	-2.44675
H	0.439005	5.42163	-3.32417
H	-0.5208	4.049302	-2.75144
C	-2.56513	3.165611	-0.40703
H	-2.74959	4.228554	-0.46443
C	0.064564	5.44244	-1.20343
C	-5.46708	-1.66506	0.016601
C	5.549668	-1.36286	-0.00182
C	-0.34967	5.433649	1.198836
C	-0.37895	6.82621	1.174019
H	-0.54843	7.36262	2.104347
C	2.734772	1.069944	0.340626
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C	0.026844	6.8348	-1.17999
H	0.178477	7.378013	-2.10945
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H	-2.90295	-6.30955	-0.29386
H	-4.24678	-5.43411	-1.02894
H	-4.02315	-5.41375	0.733363
C	1.151112	2.641977	0.224875
C	-0.26378	9.050531	-0.01005
H	-1.28813	9.398459	-0.18764

H	0.365253	9.475328	-0.79745
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C	-1.54898	-4.26999	0.78975
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H	-0.83366	-3.44999	0.759347
H	-0.99241	-5.21169	0.729167
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H	2.819689	-4.1527	2.51978
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H	1.337641	-3.4321	1.868307
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H	-0.72215	5.396977	3.319702
H	0.319402	4.083654	2.751526
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C	1.783282	-4.17898	-0.81276
H	1.024032	-3.39945	-0.78377
H	1.278659	-5.14987	-0.75903
H	2.300719	-4.12113	-1.77646
C	-6.98574	-1.6697	0.232796
C	3.787599	-5.20044	0.212969
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H	3.240556	-6.14659	0.270521
H	4.529561	-5.20214	1.018205
C	7.411574	-2.10981	-1.5094
H	7.059317	-3.14536	-1.49544
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H	6.953281	-1.61299	-2.37042
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H	-1.15984	-3.48996	-1.88982
H	-2.60413	-4.28721	-2.53647
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C	7.649098	0.04543	-0.29031

H	7.235847	0.602889	-1.13711
H	8.733531	-0.0085	-0.42881
H	7.461418	0.618336	0.623759
C	-7.67264	-0.91703	-0.92093
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H	-8.75893	-0.90663	-0.77801
H	-7.46003	-1.39629	-1.8819
C	7.739962	-2.09106	0.980344
H	7.522339	-1.57914	1.923234
H	8.827296	-2.11265	0.847143
H	7.396568	-3.12531	1.075323
C	-7.31758	-0.97152	1.563908
H	-6.84673	-1.49029	2.404914
H	-8.40042	-0.96212	1.731536
H	-6.9697	0.065615	1.576321
C	-7.56254	-3.0898	0.28329
H	-7.38173	-3.63655	-0.64778
H	-8.64585	-3.04095	0.432514
H	-7.14194	-3.67151	1.109719
O	-0.56227	-0.32059	1.840171
H	0.01871	-0.93118	2.319084
O	0.576568	-0.27822	-1.84798
H	0.026488	-0.9136	-2.33121

LSbCl(OH)

Sb	0.017745	-0.2757	-0.06969
Cl	-0.65164	-0.3075	2.249064
O	1.359703	-1.64811	0.48402
O	-1.421	-1.55897	-0.61785
N	1.485399	1.191103	0.202435
C	2.694419	-1.61245	0.271066
C	-2.75314	-1.46526	-0.38643
C	3.488942	2.154171	0.515854
H	4.54704	2.269753	0.690018
C	-3.40895	-0.22045	-0.3574

C	3.376007	-2.84408	0.147592
C	-4.80484	-0.18985	-0.18154
H	-5.28907	0.773907	-0.12245
C	3.417593	-0.40007	0.254598
C	4.811571	-0.44543	0.101378
H	5.352776	0.490814	0.053511
C	4.760213	-2.81013	0.014111
H	5.28188	-3.75052	-0.07858
C	-3.34536	2.332381	-0.62304
H	-4.39685	2.503713	-0.7922
C	1.298176	2.574288	0.204262
C	0.136311	4.736435	-0.04553
C	-4.86634	-2.5573	-0.10288
H	-5.44251	-3.46711	-0.00268
C	0.098929	3.238299	-0.0532
C	-2.36798	3.293562	-0.52793
H	-2.49136	4.365022	-0.5904
C	2.804349	0.922855	0.347393
N	-1.39285	1.265973	-0.3171
C	2.62122	-4.18273	0.1645
C	-0.37278	4.697164	2.440338
H	-1.26294	4.065794	2.356926
H	-0.5333	5.401171	3.260257
H	0.456272	4.038612	2.717645
C	2.5645	3.164354	0.423042
H	2.74334	4.227635	0.490626
C	-0.09082	5.430139	1.152945
C	5.510992	-1.63143	-0.01525
C	-5.55692	-1.33794	-0.05717
C	0.39276	5.431427	-1.23714
C	0.418376	6.82389	-1.20618
H	0.613378	7.364237	-2.12916
C	-2.72594	1.068647	-0.45931
C	0.200676	7.538031	-0.03116
C	-0.05512	6.822635	1.135401

H	-0.23459	7.362046	2.062054
C	3.562646	-5.38247	-0.02134
H	2.969369	-6.30212	-0.01424
H	4.2973	-5.46227	0.786498
H	4.098685	-5.34543	-0.97544
C	-1.13558	2.636657	-0.31547
C	0.264479	9.043253	-0.01737
H	1.282382	9.392218	0.192209
H	-0.38863	9.46375	0.752499
H	-0.03194	9.464598	-0.98207
C	-3.49234	-2.66602	-0.25701
C	1.609519	-4.22553	-0.99597
H	2.130673	-4.17344	-1.95819
H	0.899302	-3.40202	-0.94699
H	1.046203	-5.16472	-0.96854
C	-2.13834	-4.26277	-1.6599
H	-2.88469	-4.23563	-2.46143
H	-1.6535	-5.2449	-1.68545
H	-1.3831	-3.50539	-1.86648
C	0.634604	4.699545	-2.53331
H	1.499155	4.032039	-2.462
H	0.817814	5.40397	-3.34815
H	-0.22284	4.077857	-2.80944
C	-2.80871	-4.04219	-0.29063
C	-1.77543	-4.14387	0.845983
H	-1.00695	-3.37711	0.770762
H	-1.28449	-5.12282	0.817424
H	-2.26483	-4.04058	1.820083
C	7.035963	-1.61489	-0.1812
C	-3.81054	-5.18963	-0.09142
H	-4.32463	-5.12608	0.873088
H	-3.26858	-6.14007	-0.1114
H	-4.5639	-5.22665	-0.88521
C	-7.43	-2.01131	1.470352
H	-7.08457	-3.04872	1.50121

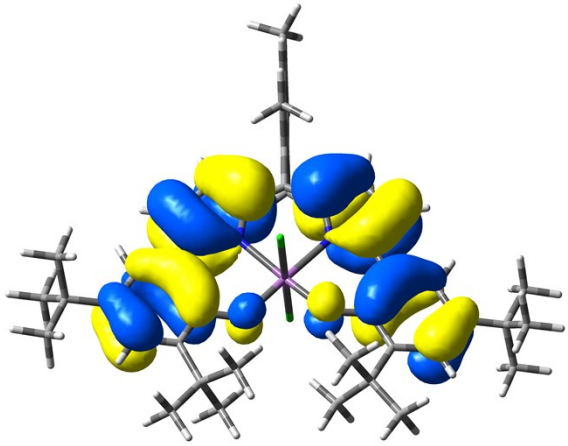
H	-8.51536	-2.01749	1.619875
H	-6.97261	-1.48217	2.312308
C	1.914514	-4.37054	1.520666
H	1.36628	-5.31936	1.528389
H	1.212186	-3.5649	1.730165
H	2.65087	-4.40271	2.331077
C	-7.07701	-1.32948	0.136142
C	-7.65013	0.092441	0.160815
H	-7.23931	0.682426	0.986491
H	-8.73554	0.049591	0.294855
H	-7.45445	0.625973	-0.77518
C	7.677795	-0.9116	1.028273
H	7.331189	0.121253	1.128934
H	8.768065	-0.88738	0.922369
H	7.437269	-1.4359	1.958576
C	-7.74542	-2.09489	-1.02021
H	-7.52018	-1.62408	-1.98255
H	-8.83344	-2.1049	-0.89208
H	-7.40762	-3.13412	-1.06983
C	7.405361	-0.85371	-1.46711
H	6.966756	-1.33613	-2.34633
H	8.492966	-0.82931	-1.59809
H	7.049867	0.180705	-1.44334
C	7.626196	-3.02711	-0.27764
H	7.419282	-3.61756	0.620687
H	8.71338	-2.96361	-0.38786
H	7.238566	-3.57298	-1.14371
O	0.569279	-0.31573	-1.95613
H	-0.01604	-0.92026	-2.43851

Table S2. Summary of the DFT calculation data

	$LSbCl_2$	**$LSb(OH)_2$**	**LSbCl(OH)**
Sb-X (Å)	2.403, 2.403	1.931, 1.931	2.413 (Cl), 1.966 (OH)
Sb-N (Å)	2.070, 2.069	2.081, 2.081	2.104, 2.096
Sb-O (Å)	1.947, 1.945	1.982, 1.984	2.004, 1.997
X-Sb-X (°)	179.12	177.41	178.07
λ_{max} (nm)[a]	523	505	509
Oscillator strength[a]	0.5446	0.6071	0.5620
λ_{max} (nm)[b]	536	521	525
Oscillator strength[b]	0.6993	0.7641	0.7194
λ_{max} (nm)[c]	570	551	556
Oscillator strength[c]	0.5928	0.6817	0.6110
S_1	HOMO-LUMO	HOMO-LUMO	HOMO-LUMO

[a] CAM-B3LYP in vacuum. [b] CAM-B3LYP in $CHCl_3$. [c] M06 in $CHCl_3$.

HOMO (–6.45 eV)



LUMO (–1.99 eV)

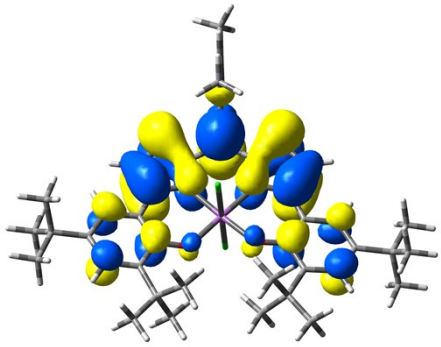
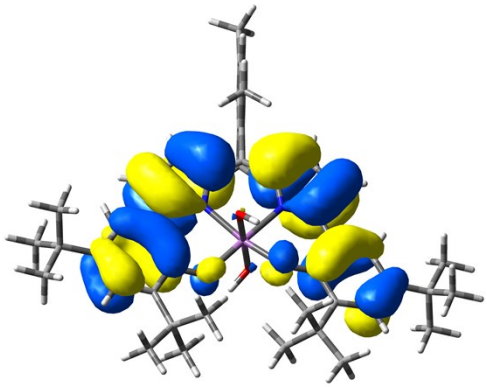


Figure S8. HOMO and LUMO of **$LSbCl_2$**

HOMO (–6.51 eV)



LUMO (–2.00 eV)

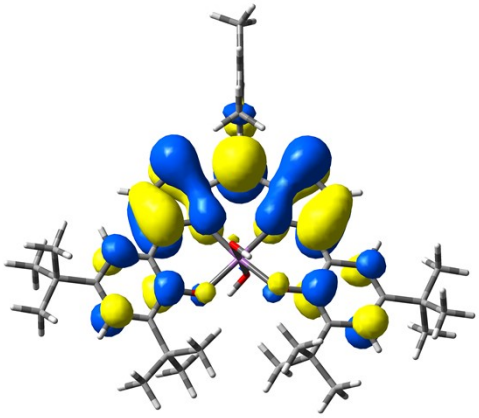
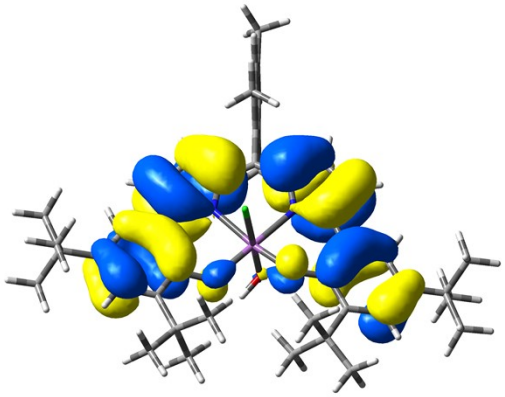


Figure S9. HOMO and LUMO of **LSb(OH)$_2$**

HOMO (–6.36 eV)



LUMO (–1.84 eV)

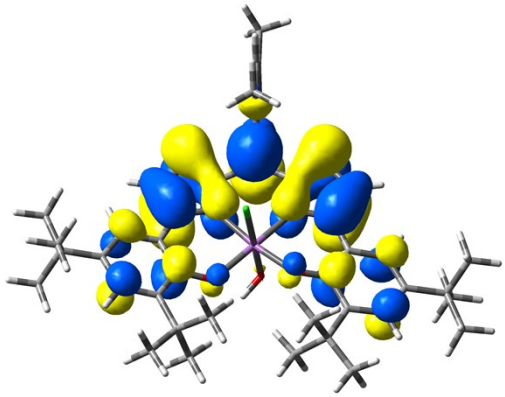


Figure S10. HOMO and LUMO of **LSbCl(OH)**

PLQY measurement

Photo-luminescence quantum yields (PLQYs) were determined by an absolute fluorescence quantum yield method with a Hamamatsu Photonics absolute PL quantum yield measurement system C9920-02 (λ_{ex} 300 nm).

Figure S11. PL spectra of the Sb complexes and **LH_3** measured by the PLQY measurement system.

References

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S2 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst*., 2009, **42**, 339-341.

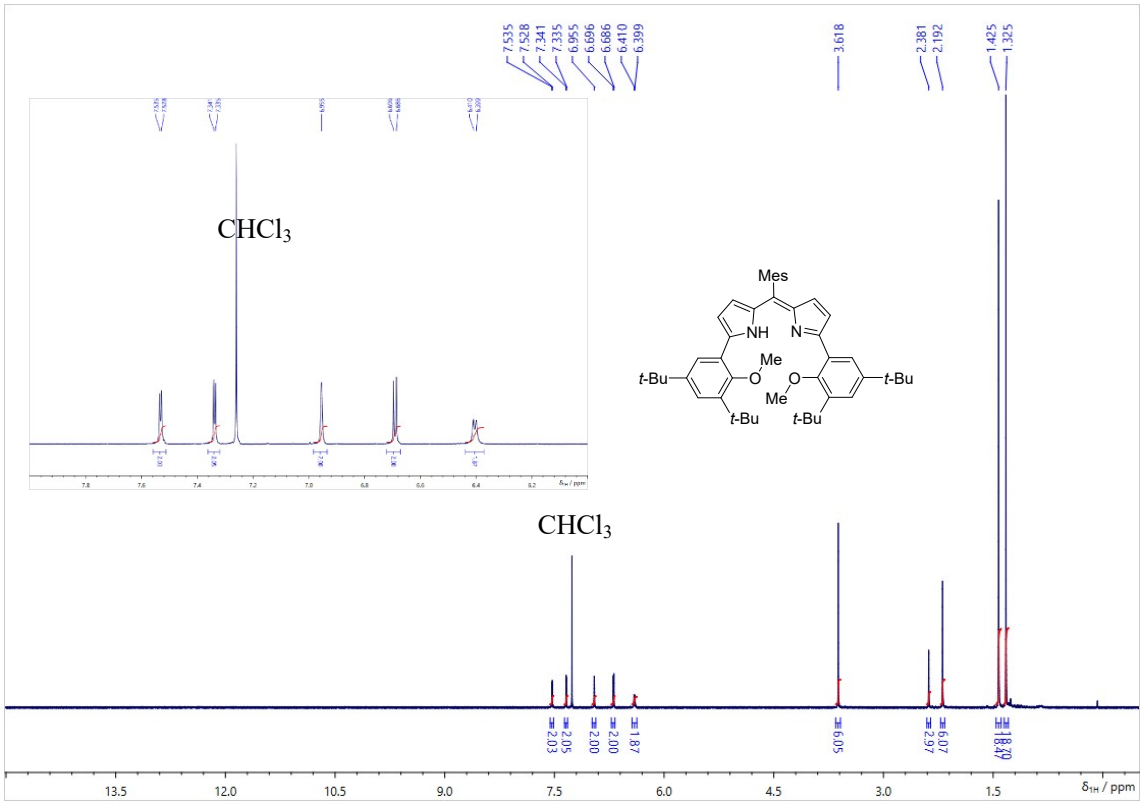
S3 (a) G. M. Sheldrick, *Acta Cryst. A*, 2008, **64**, 112-122; (b) G. M. Sheldrick, *Acta Cryst. C*, 2015, **71**, 3-8

S4 Gaussian 16, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2019.

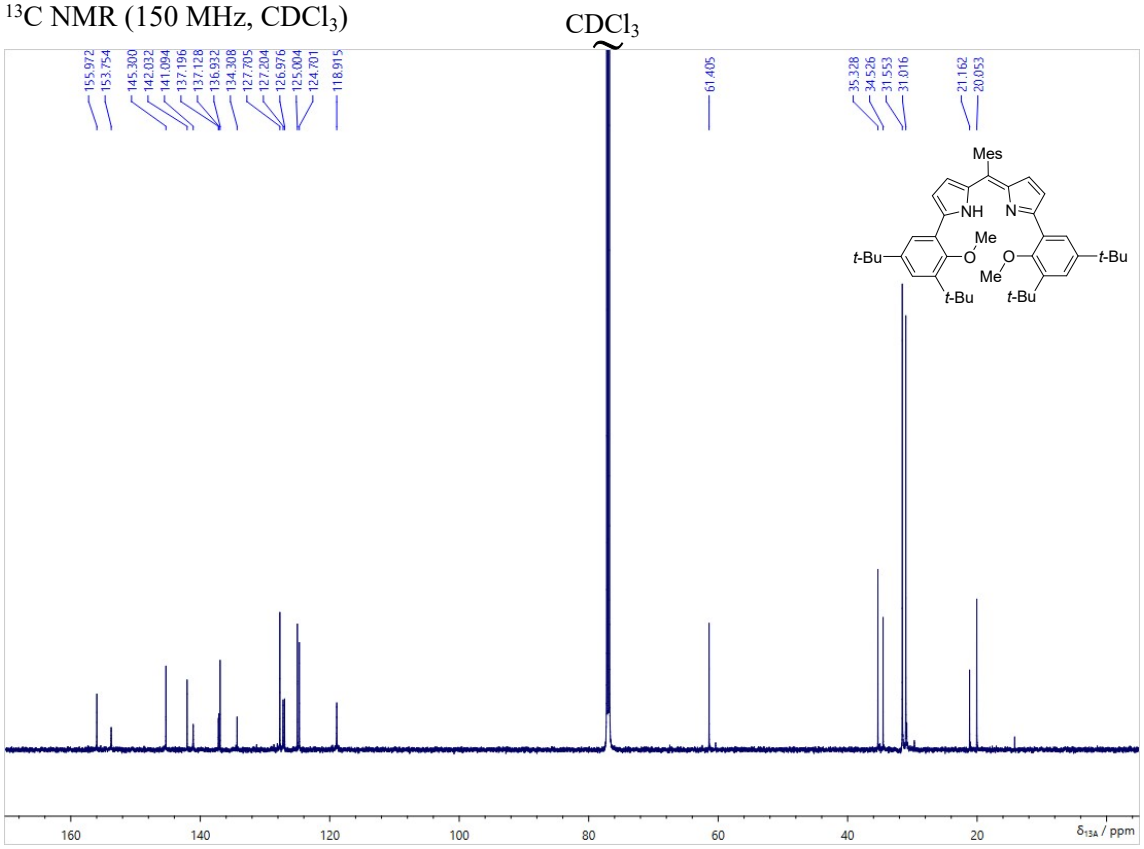
^{1}H and ^{13}C NMR spectra and HRMS data of newly synthesized compounds

$LHMe_2$

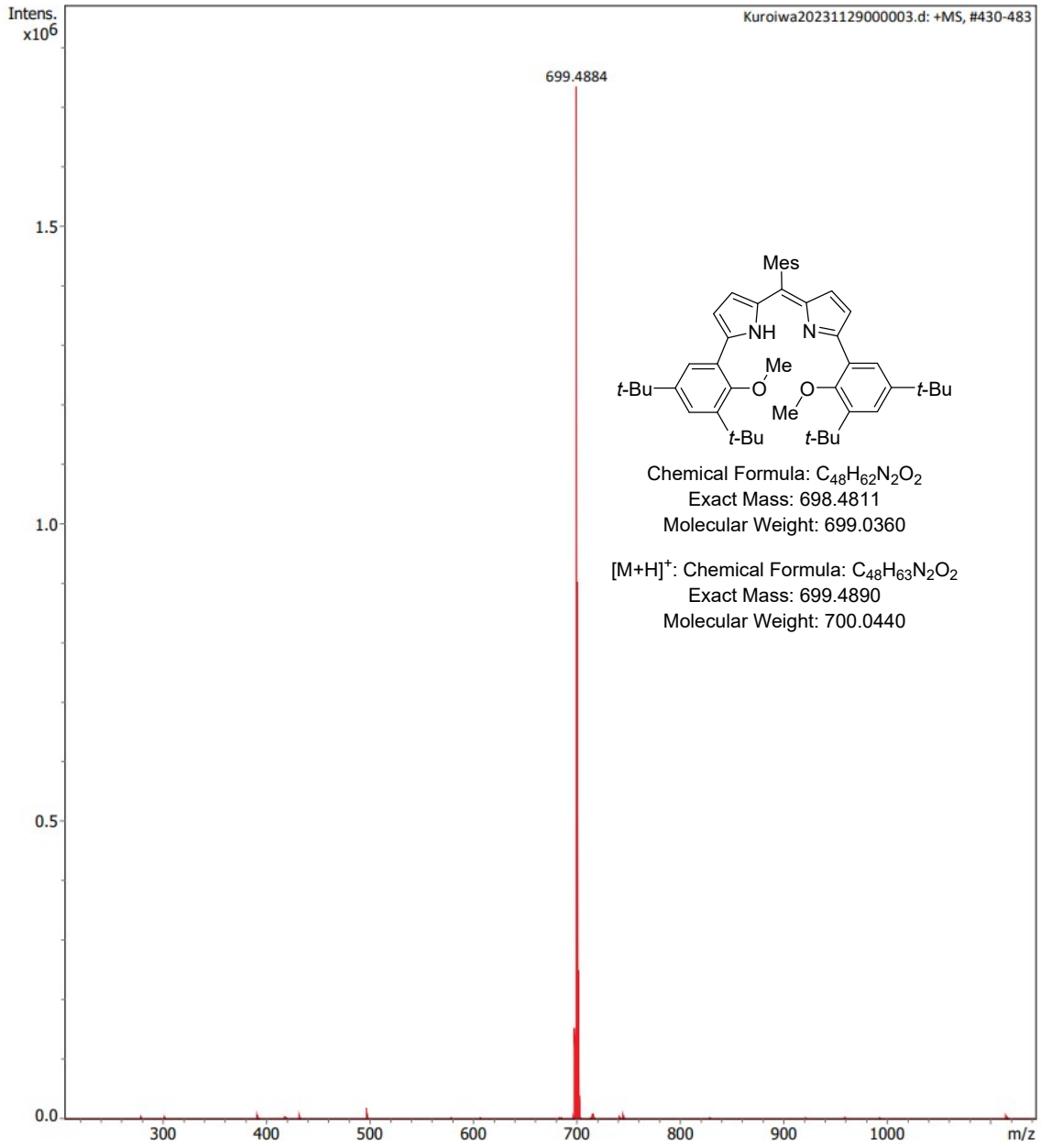
^{1}H NMR (400 MHz, $CDCl_3$)

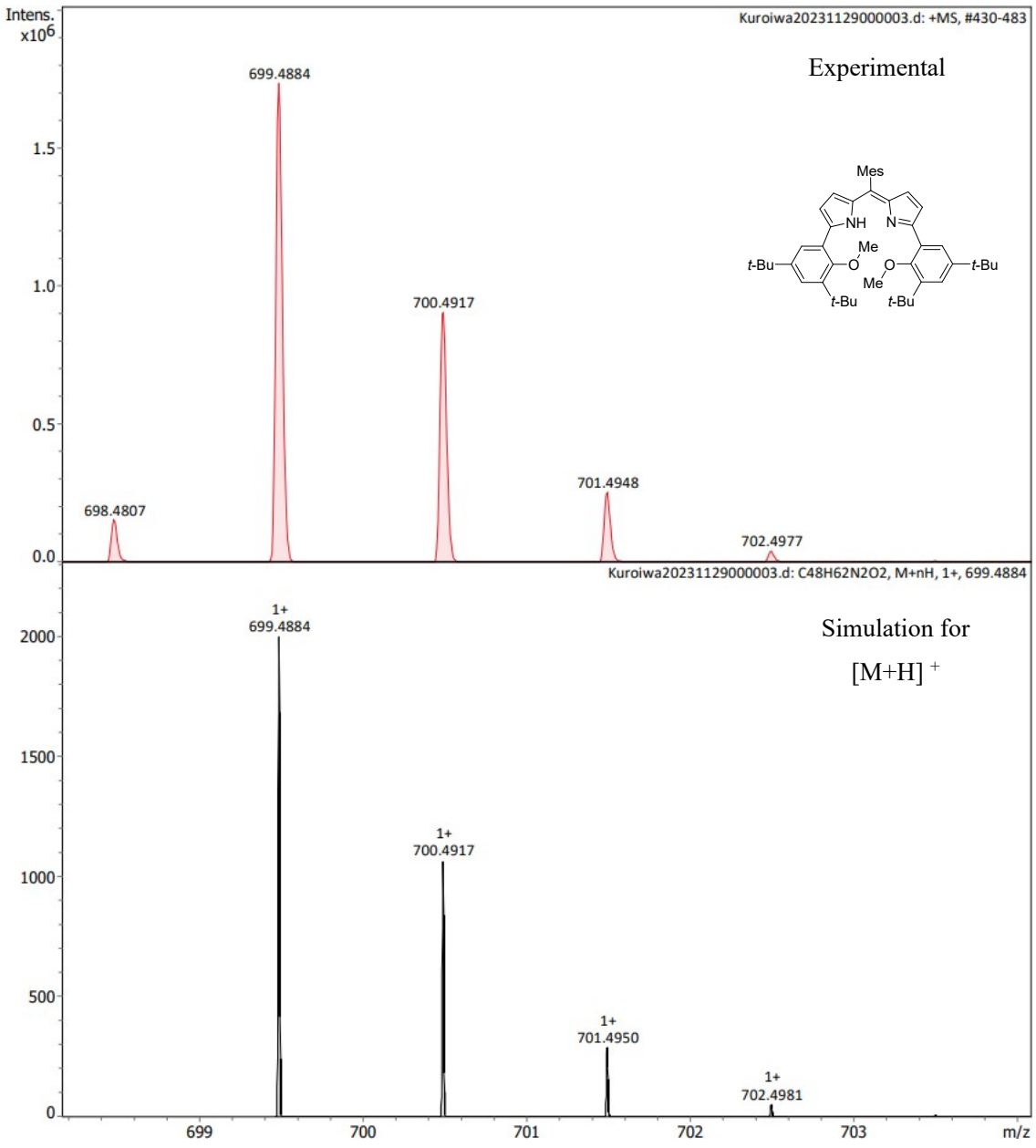


^{13}C NMR (150 MHz, $CDCl_3$)



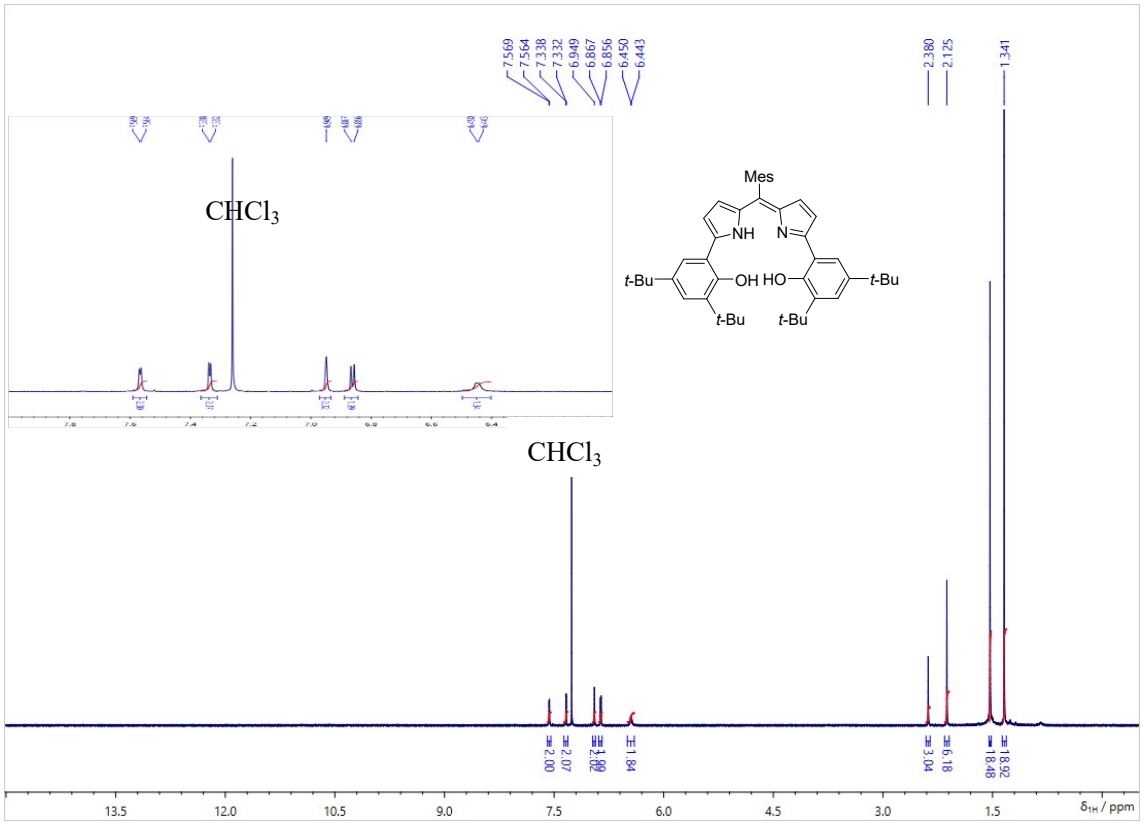
HRMS (APCI-pos, solvent: acetone)



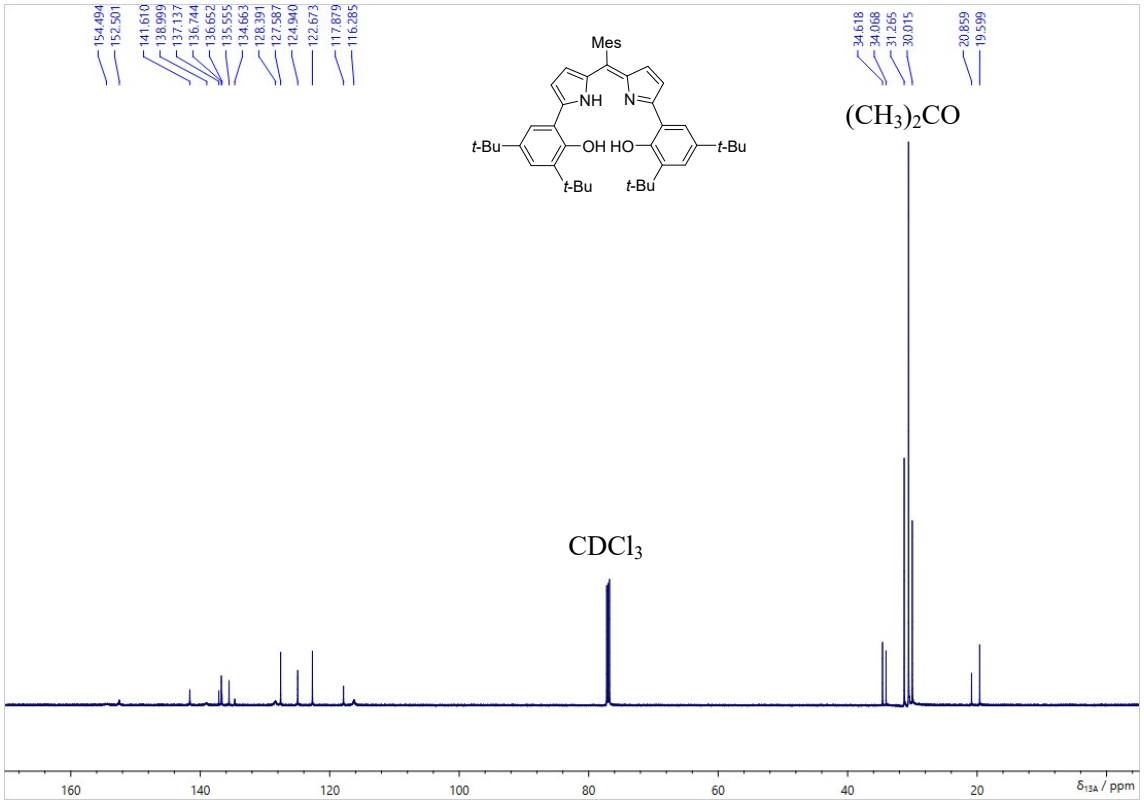

Intens.
x10^6
Kuroiwa20231129000003.d: +MS, #430-483
Experimental
699.4884
700.4917
701.4948
698.4807
702.4977
Mes
NH
N
Me
O
O
Me
t-Bu
t-Bu
t-Bu
t-Bu
Kuroiwa20231129000003.d: C48H62N2O2, M+nH, 1+, 699.4884
Simulation for
[M+H] +
1+
699.4884
1+
700.4917
1+
701.4950
1+
702.4981
m/z

LH_3

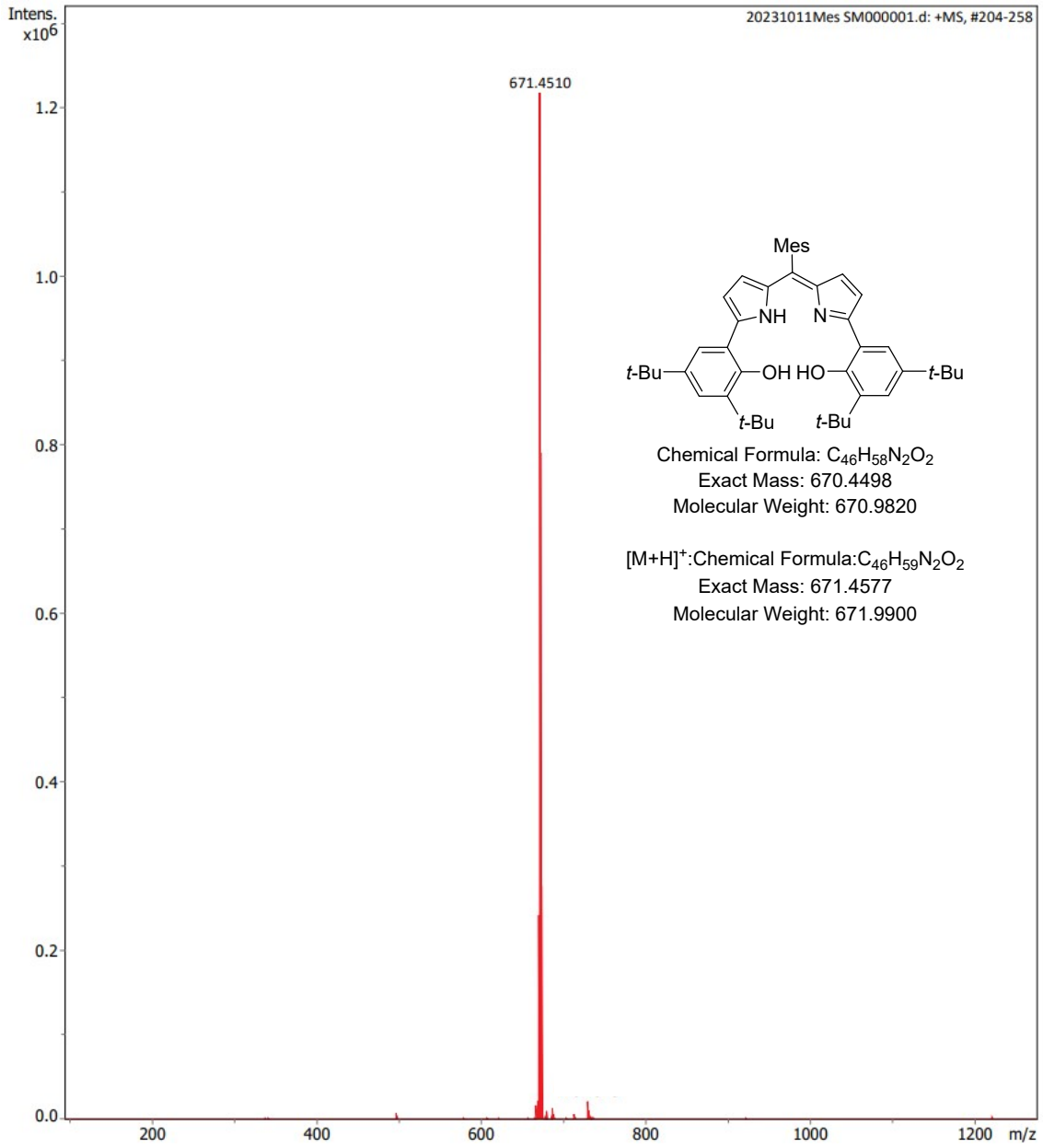
^1H NMR (400 MHz, $CDCl_3$)

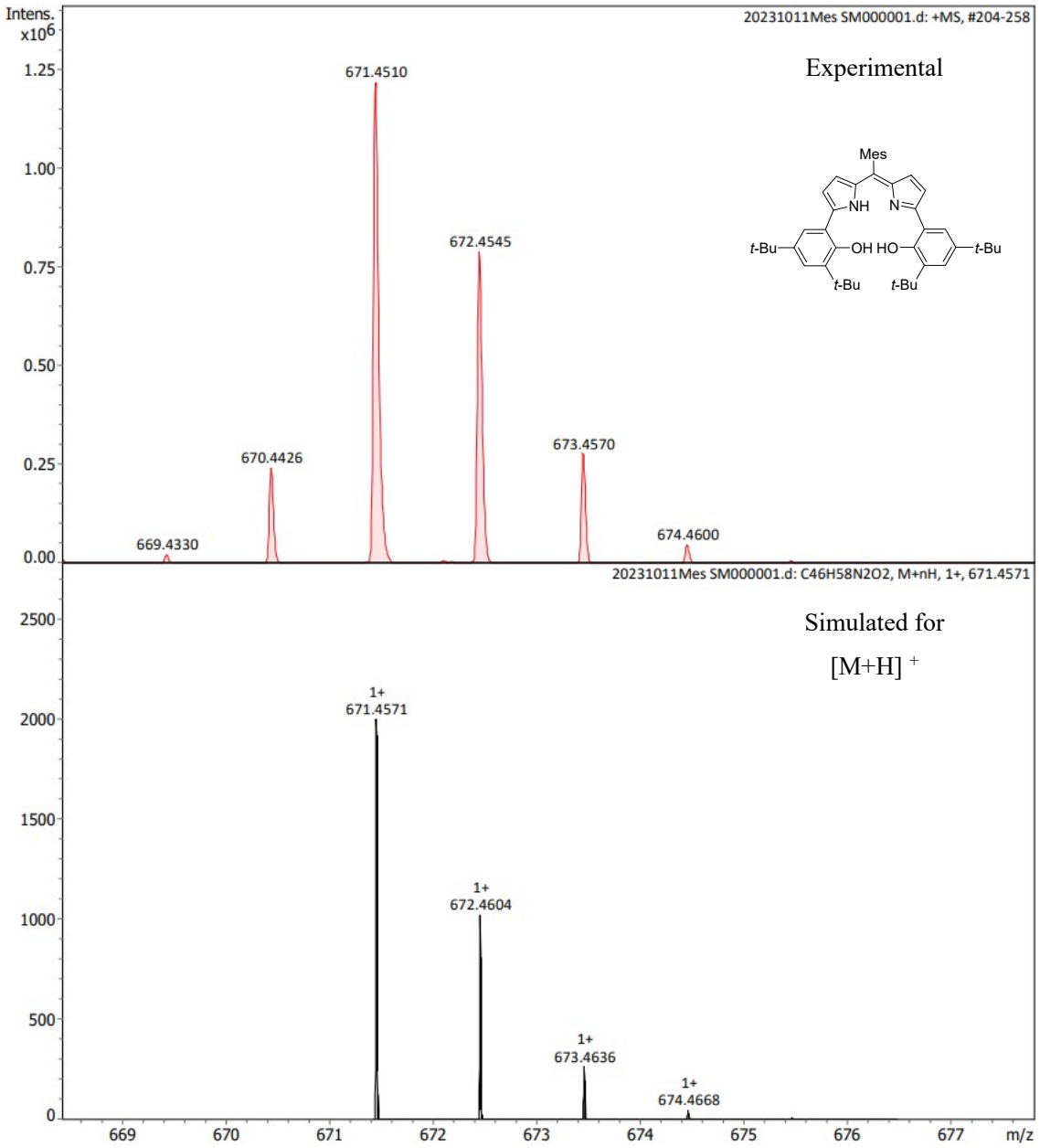


^{13}C NMR (150 MHz, $CDCl_3$)



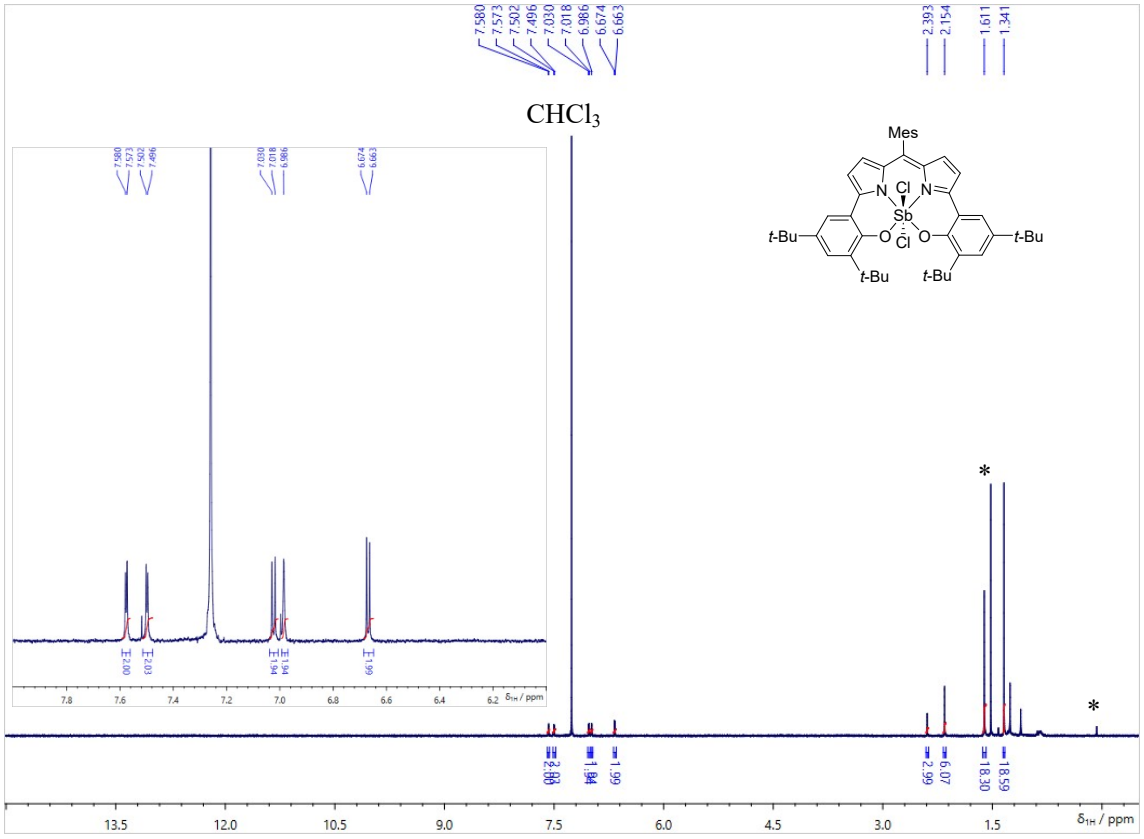
HRMS (APCI-pos, solvent: acetone)




Intens.
x10^6
20231011Mes SM000001.d: +MS, #204-258
Experimental
671.4510
672.4545
670.4426
673.4570
669.4330
674.4600
Mes
NH
N
t-Bu
OH HO
t-Bu
t-Bu
t-Bu
20231011Mes SM000001.d: C46H58N2O2, M+nH, 1+, 671.4571
Simulated for
[M+H] +
1+
671.4571
1+
672.4604
1+
673.4636
1+
674.4668
669
670
671
672
673
674
675
676
677
m/z

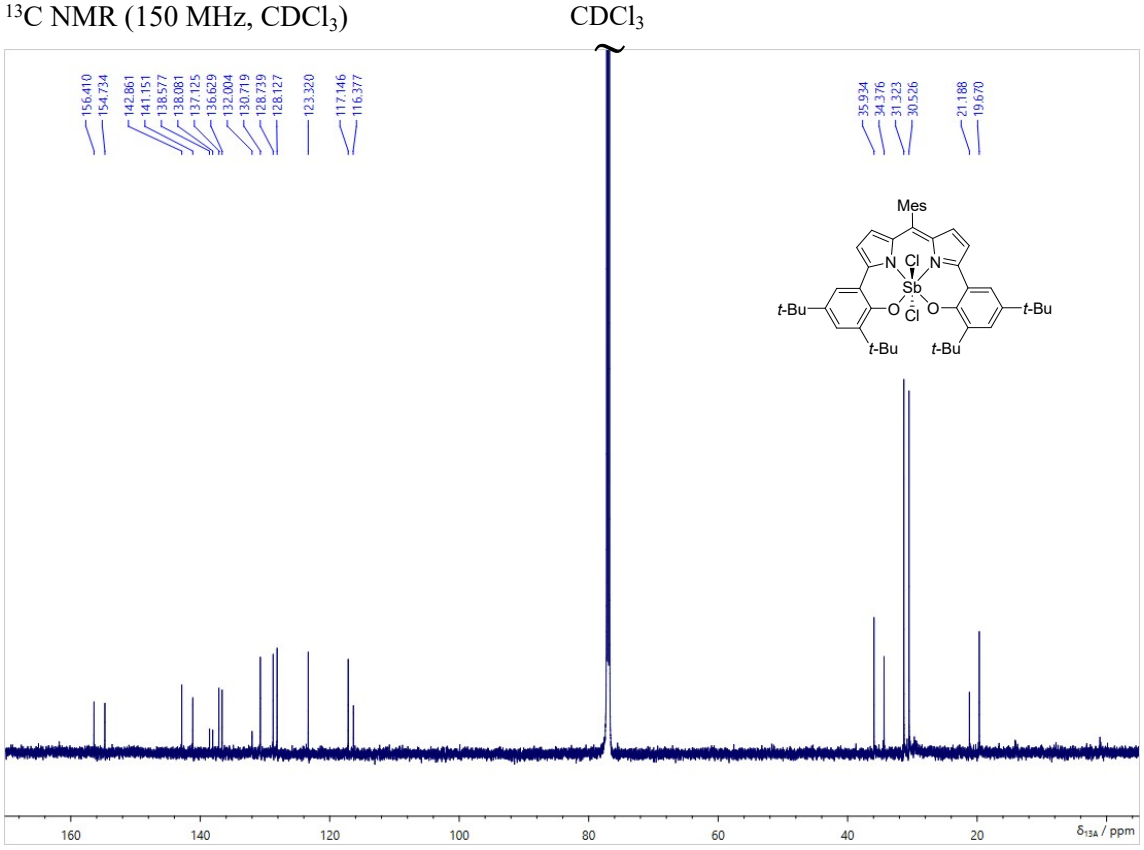
$LSbCl_2$

^1H NMR (400 MHz, $CDCl_3$)

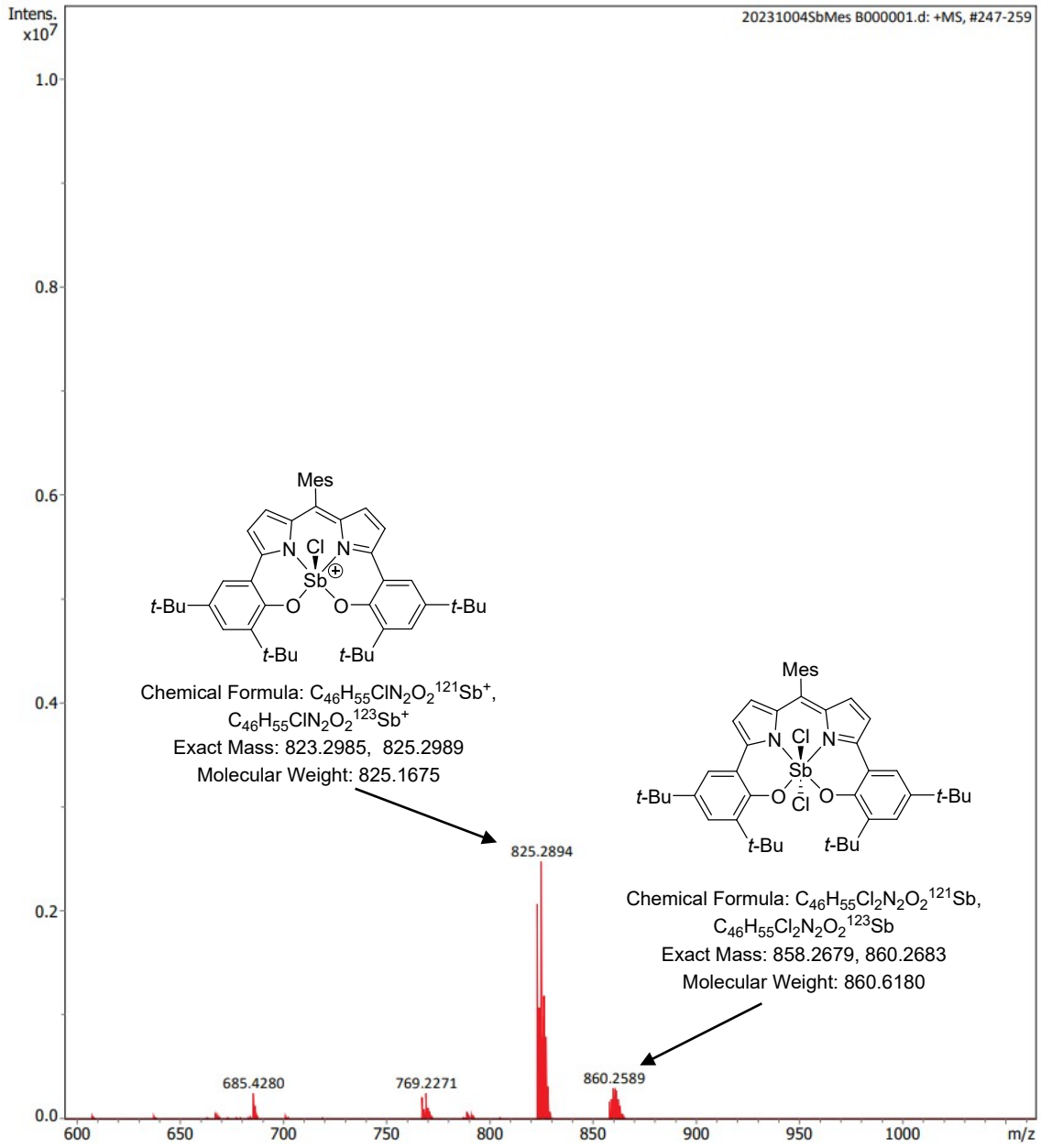


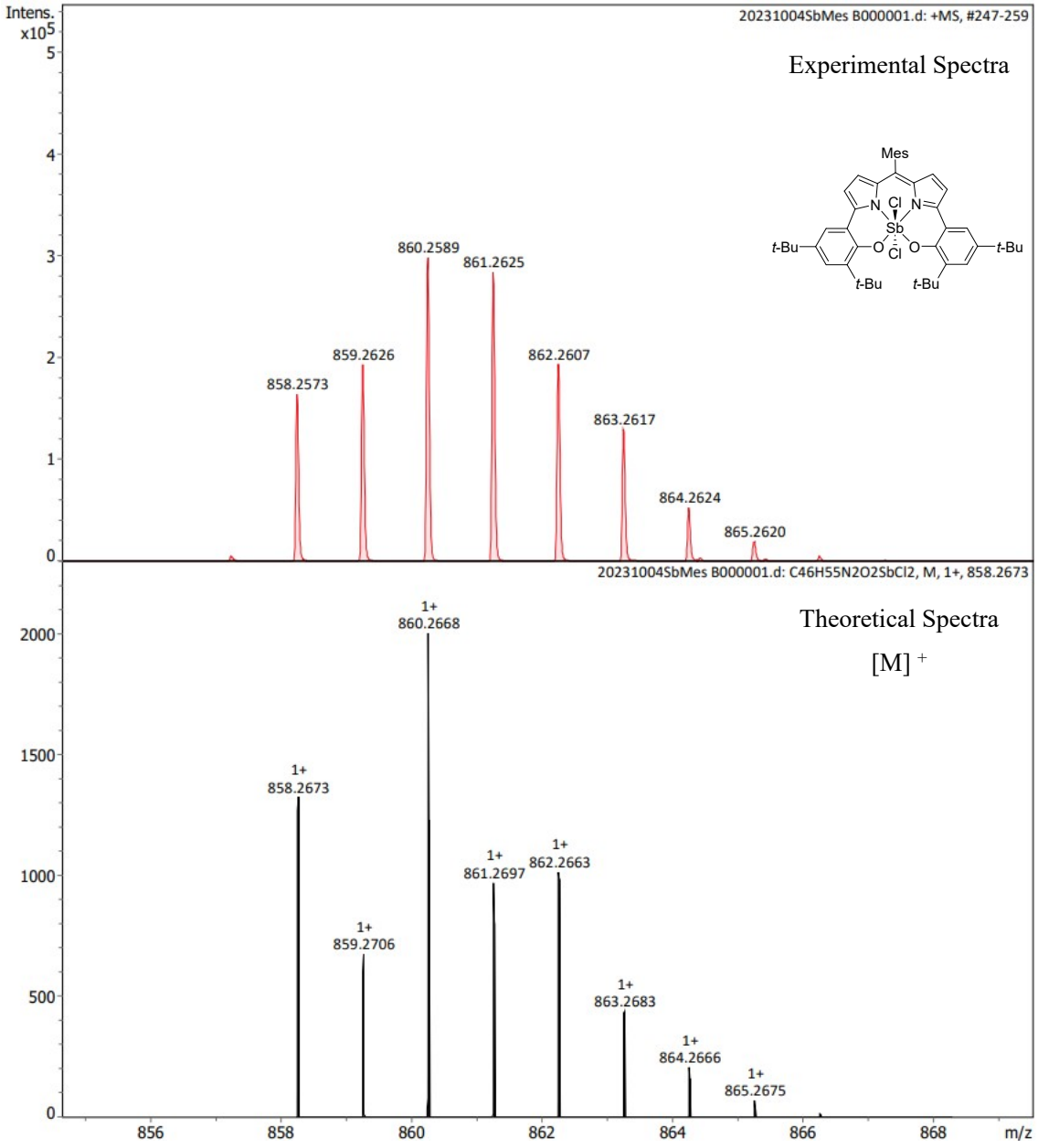
*Signals corresponding to silicone grease and water.

^{13}C NMR (150 MHz, $CDCl_3$)



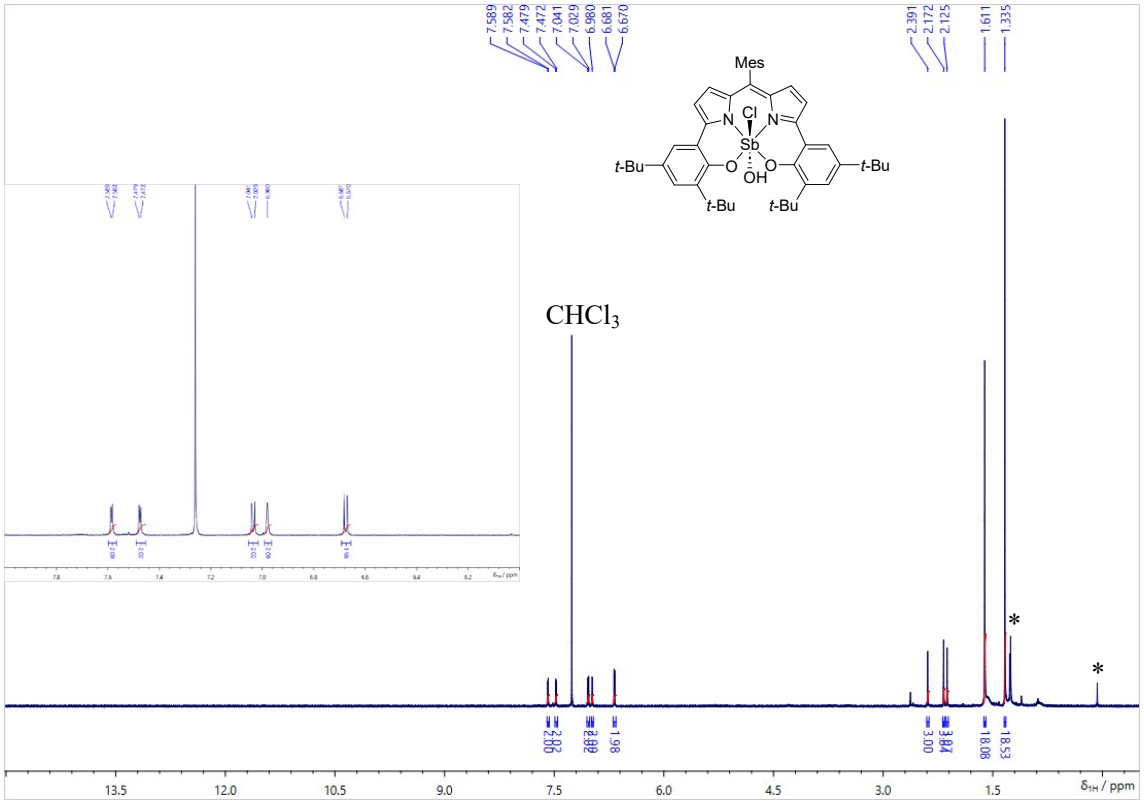
HRMS (APCI-pos, solvent: acetone)




Intens.
x10^5
20231004SbMes B000001.d: +MS, #247-259
Experimental Spectra
Mes
N
Cl
N
Sb
Cl
O
O
t-Bu
t-Bu
t-Bu
t-Bu
860.2589
861.2625
859.2626
862.2607
858.2573
863.2617
864.2624
865.2620
20231004SbMes B000001.d: C46H55N2O2SbCl2, M, 1+, 858.2673
Theoretical Spectra
[M] +
1+
860.2668
1+
858.2673
1+
861.2697
1+
862.2663
1+
859.2706
1+
863.2683
1+
864.2666
1+
865.2675
m/z

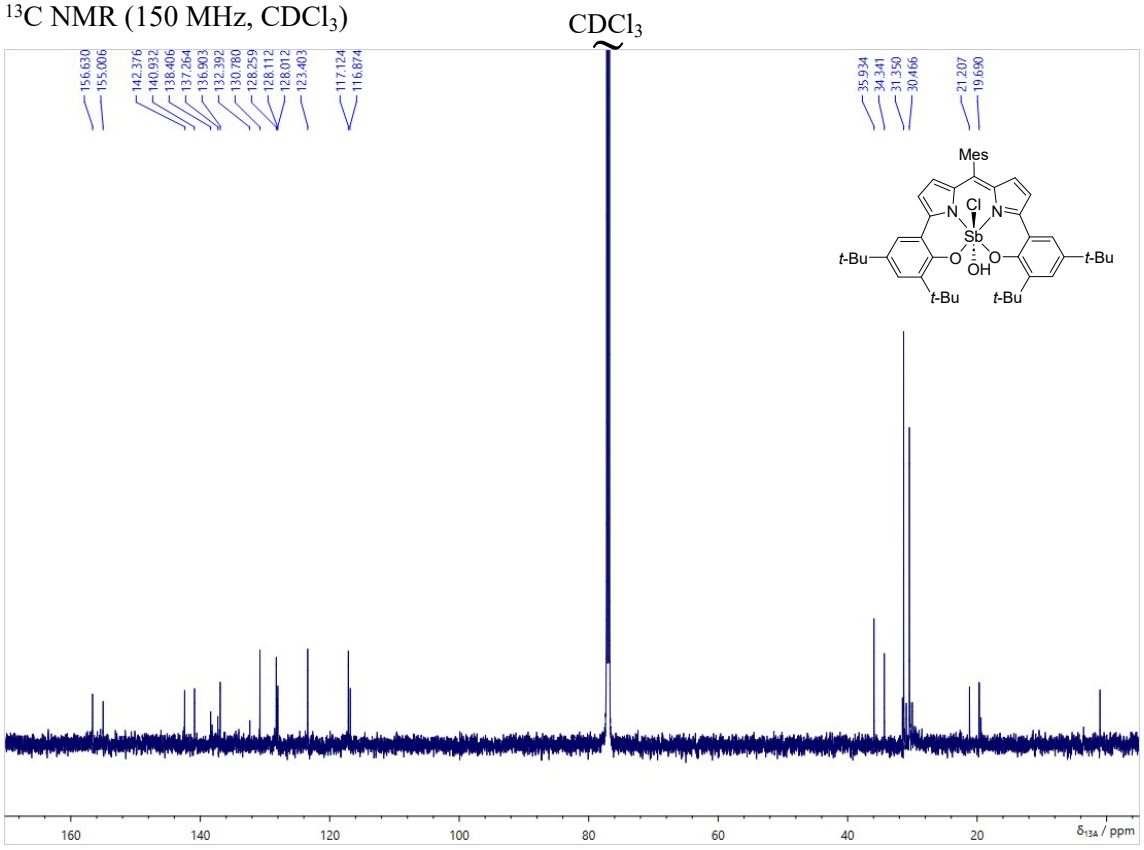
LSbCl(OH)

^{1}H NMR (400 MHz, $CDCl_3$)

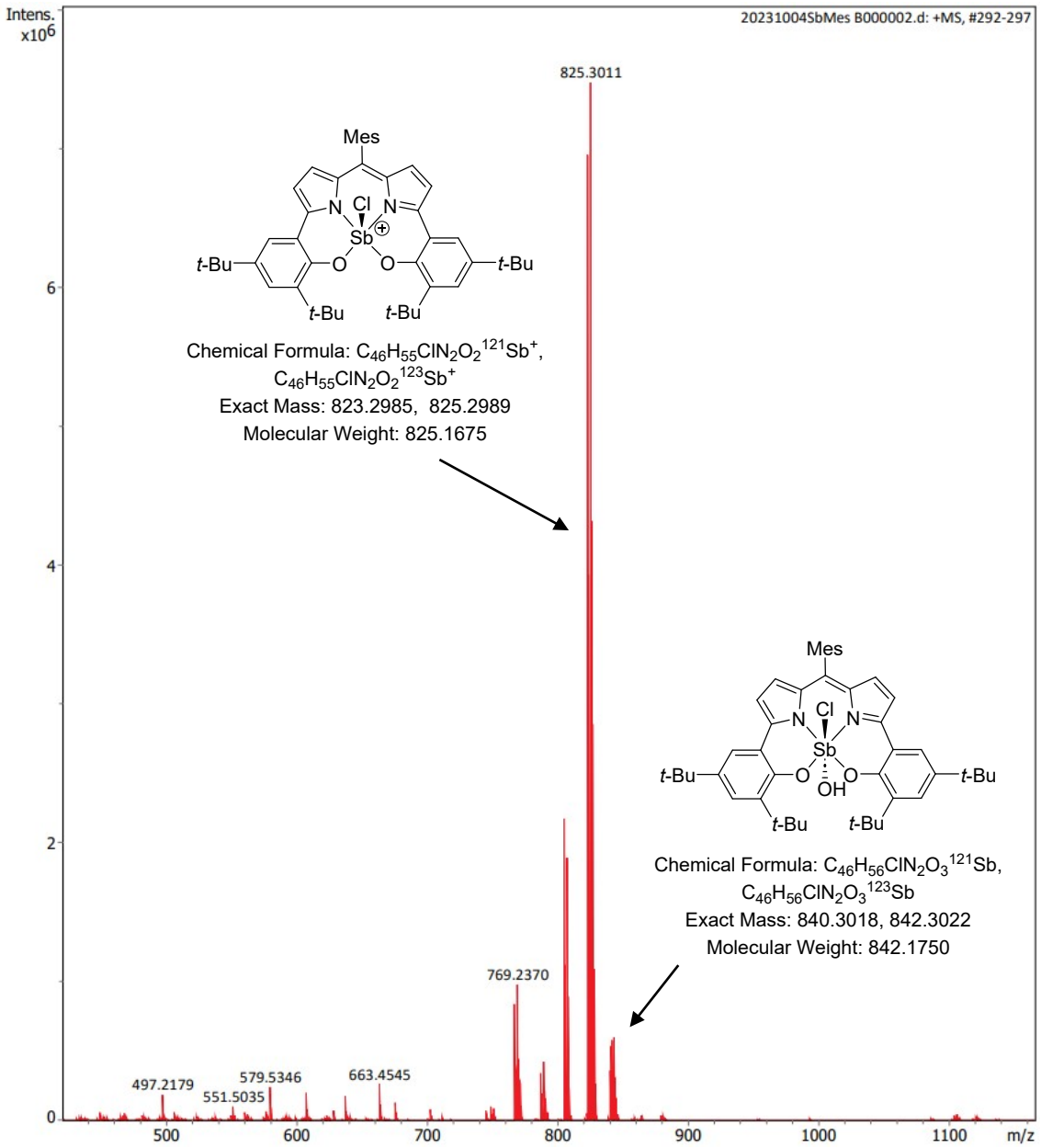


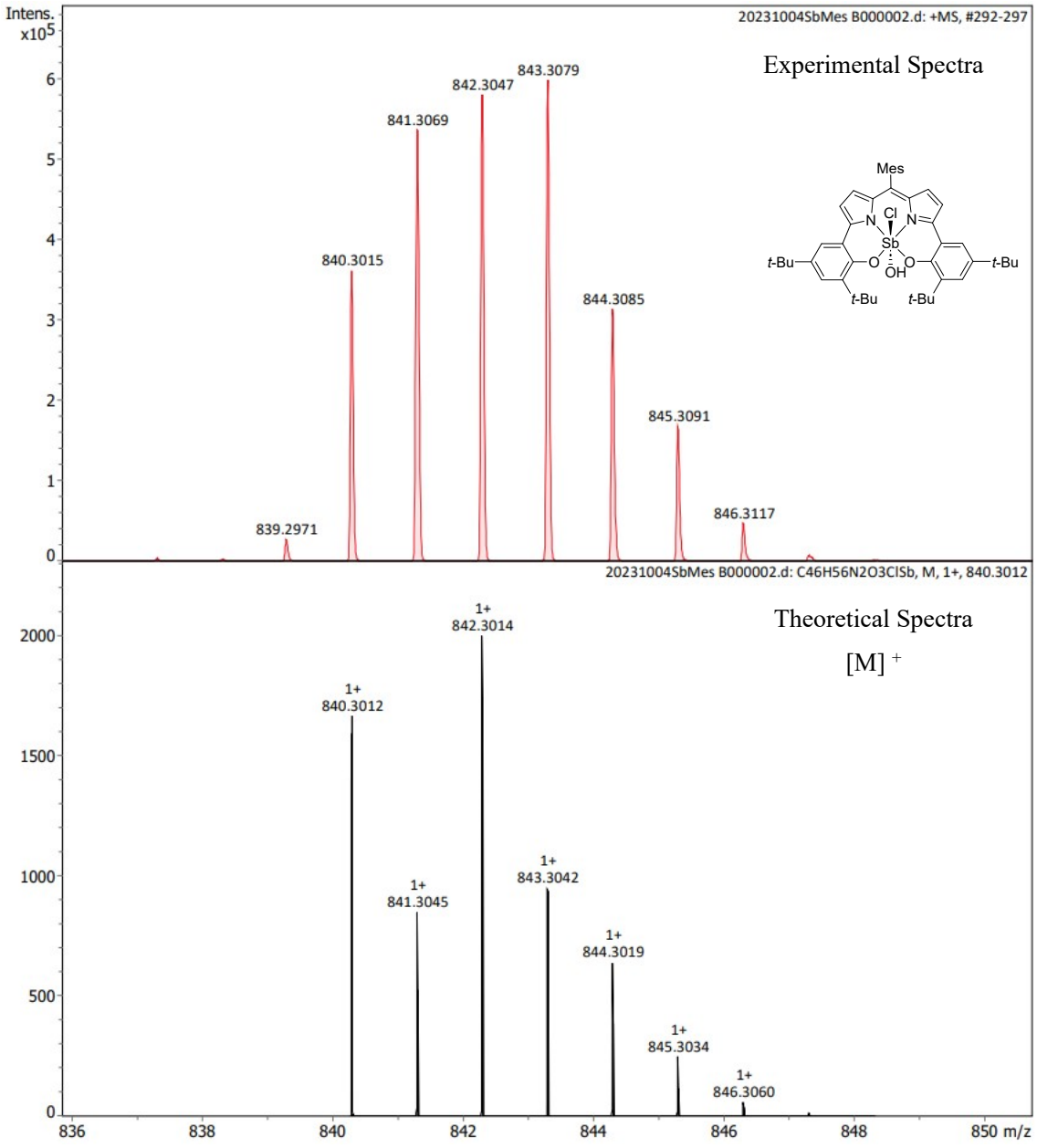
*Signals corresponding to silicone grease and dioctyl phthalate.

^{13}C NMR (150 MHz, $CDCl_3$)



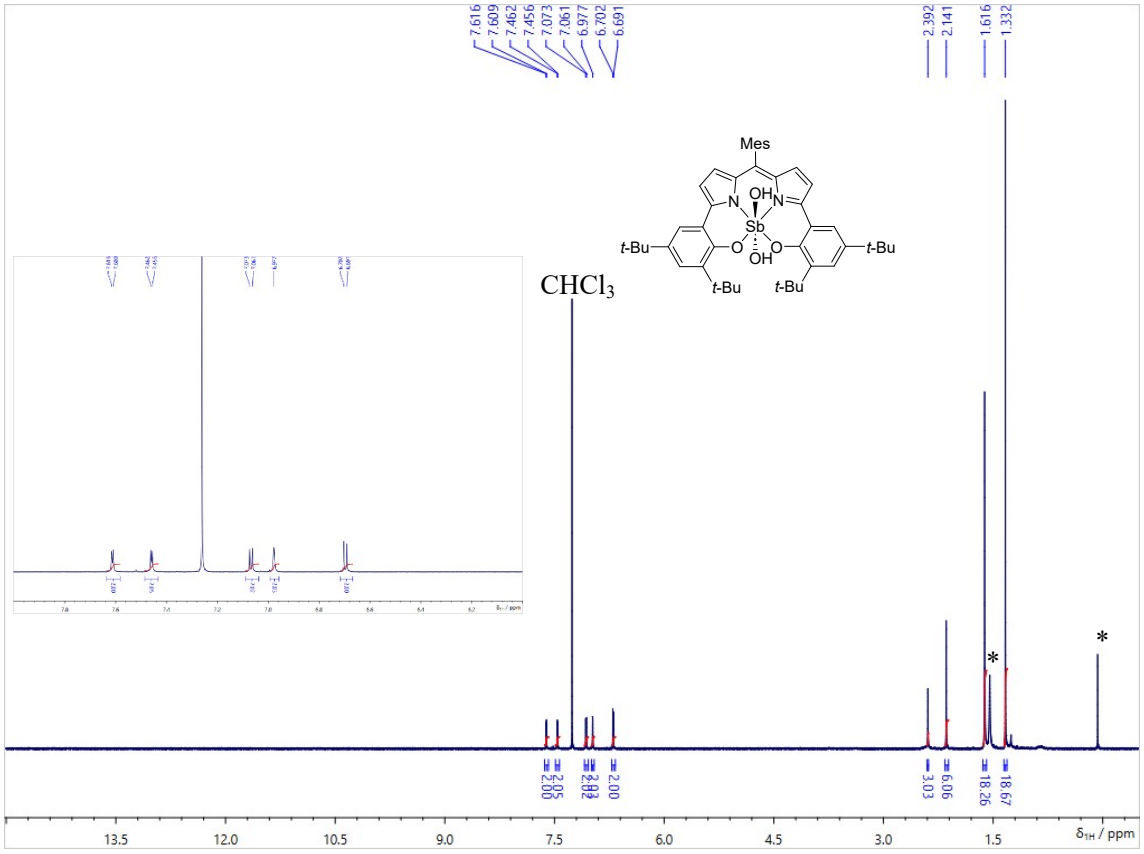
<HRMS (APCI-pos in Acetone)>




Intens.
x10^5
20231004SbMes B000002.d: +MS, #292-297
Experimental Spectra
843.3079
842.3047
841.3069
840.3015
844.3085
845.3091
846.3117
839.2971
Mes
Cl
N
N
Sb
O
O
OH
t-Bu
t-Bu
t-Bu
t-Bu
20231004SbMes B000002.d: C46H56N2O3ClSb, M, 1+, 840.3012
Theoretical Spectra
[M] +
1+
842.3014
1+
840.3012
1+
843.3042
1+
841.3045
1+
844.3019
1+
845.3034
1+
846.3060
m/z

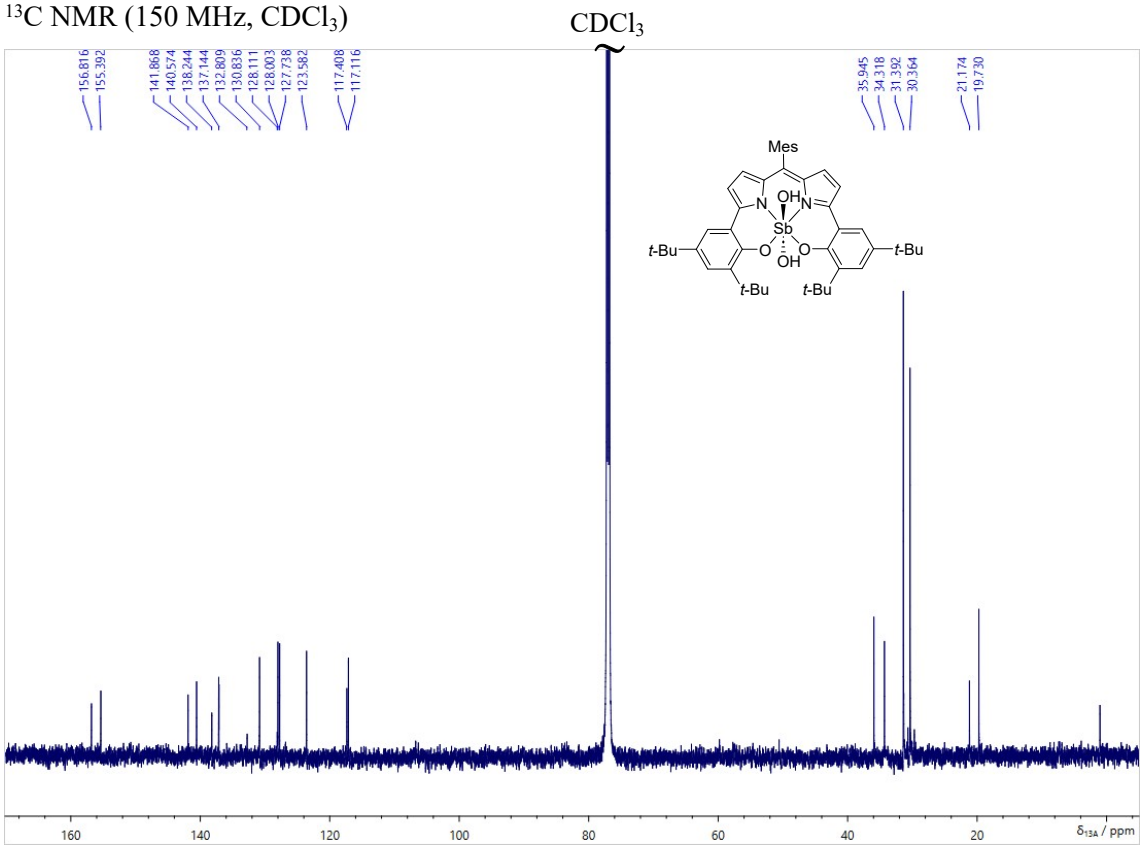
$LSb(OH)_2$

^1H NMR (400 MHz, $CDCl_3$)

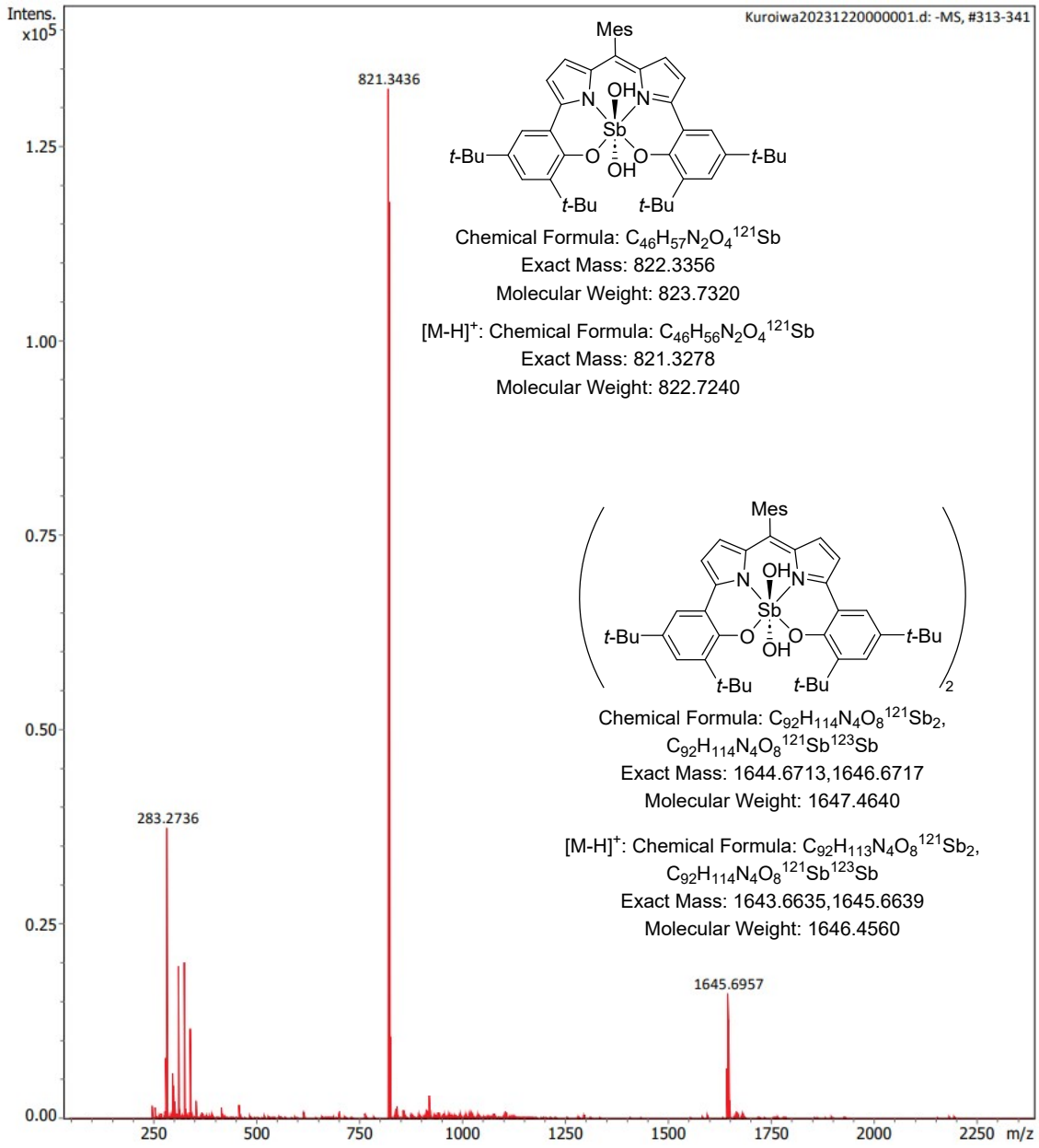


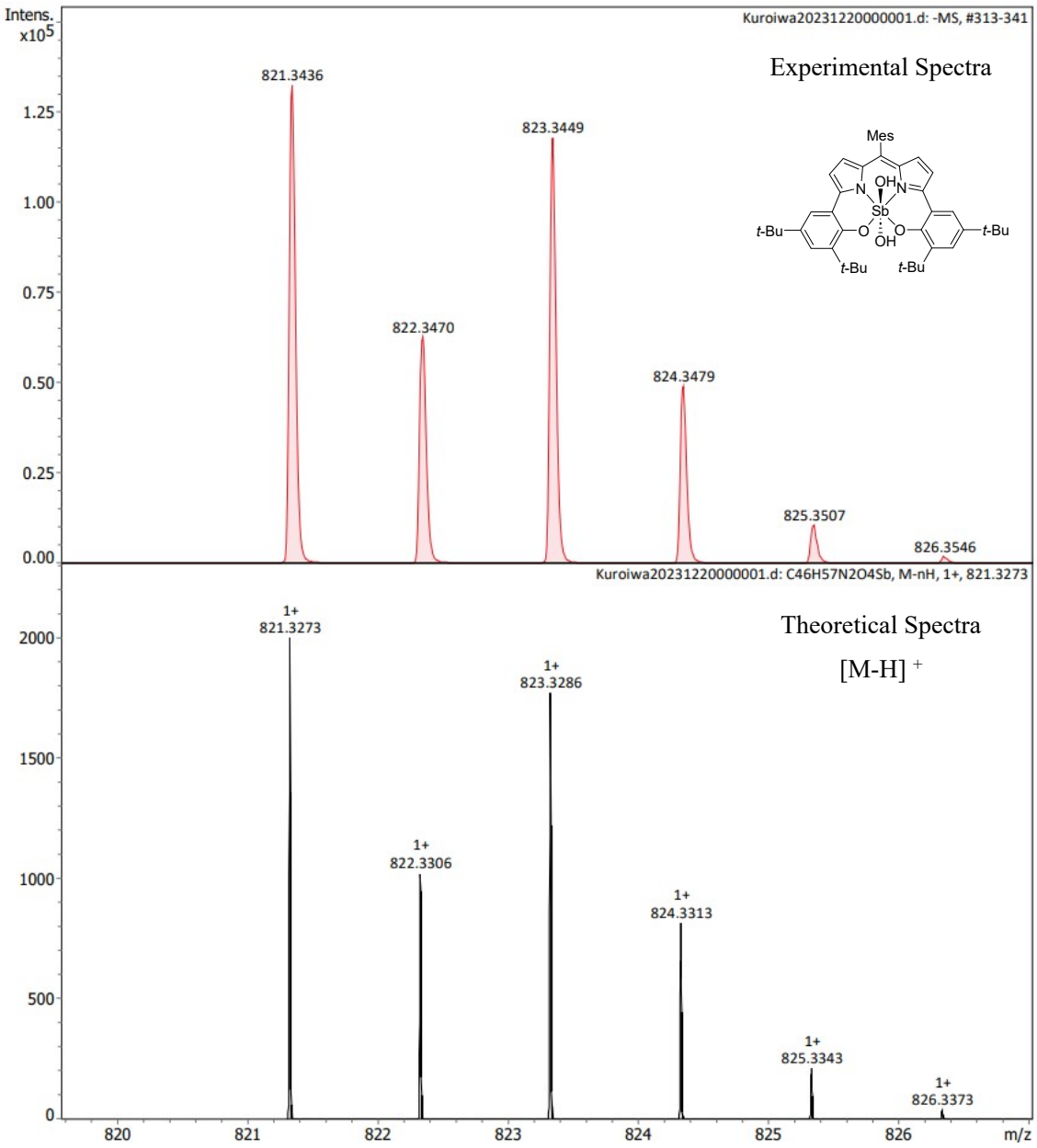
*Signals corresponding to silicone grease and water.

^{13}C NMR (150 MHz, $CDCl_3$)



HRMS (ESI-neg, solvent: CH_3OH)




Intens.
x10^5
Kuroiwa20231220000001.d: -MS, #313-341
Experimental Spectra
821.3436
822.3470
823.3449
824.3479
825.3507
826.3546
Mes
OH
N
N
Sb
O
O
OH
t-Bu
t-Bu
t-Bu
t-Bu
Kuroiwa20231220000001.d: C46H57N2O4Sb, M-nH, 1+, 821.3273
Theoretical Spectra
[M-H] +
1+
821.3273
1+
822.3306
1+
823.3286
1+
824.3313
1+
825.3343
1+
826.3373
m/z