Crystalline heaviest pnictogen-dipyrromethenes: isolation, characterization, and reactivity

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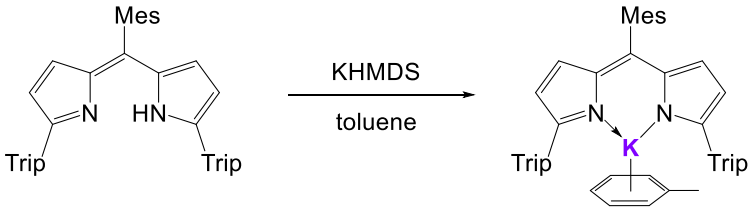
Contents

1. Synthesis of new compounds and their NMR spectra

General considerations: All reactions and product manipulations were conducted under a dry dinitrogen atmosphere with rigid exclusion of air and moisture using standard Schlenk techniques, or in a glove box. All glasswares were oven dried. Organic solvents were distilled under nitrogen from purple sodium benzophenone ketyl and vacuum transferred from the same prior to use. Commercially available reagents were purchased from Energy Chemical and used as received. ^{1}H, ^{13}C{^{1}H}, and DEPT135 NMR spectra were obtained with a Bruker AVIII 400 MHz BBFO1 spectrometer and Agilent VNMRS-300 spectrometer at 298 K. Chemical shifts (δ) are given in p.p.m. Coupling constants J are given in Hz. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal. UV-vis spectra were recorded on the Lambda 750 spectrometer at room temperature. Fluorescence Spectra were recorded on the Shanghai Dream Lasers SDL-405-LM-100T Fluorescence Spectrometer at room temperature. Element analyses were performed on an Elementar Vario EL III instrument. The dipyrromethene ligand **1** was synthesized according to the literature procedure.[S1]

Synthesis of compound 2

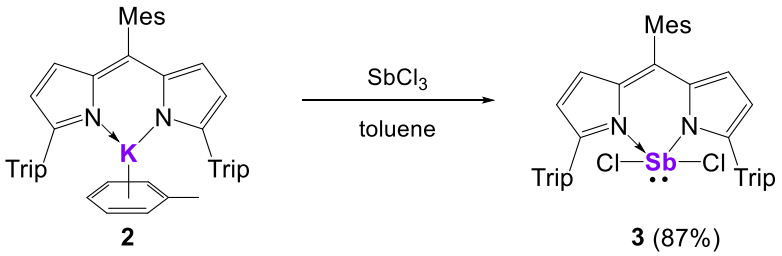


1 **2** (96%)

The solution of KHMDS (1.0 M in THF, 0.66 g, 3.3 mmol) was added dropwise to a toluene solution (30 mL) of **1** (2.0 g, 3.0 mmol) at room temperature and the mixture was stirred for 30 minutes. After the filtration, the orange-red filtrate was concentrated and cooled to –30 °C. From this concentrated solution large orange-red crystals were grown, which were separated and dried in vacuo to afford **2** as an orange-red powder (2.30 g, 96%). ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ 7.20 (s, 4H, Ar-*H*), 7.13-7.00 (m, 5H, Ar-H), 6.92 (d, 2H, J = 6 Hz, pyrrole-C*H*), 6.88 (s, 2H, Ar-*H*), 6.41 (d, 2H, J = 6

Hz, pyrrole-C*H*), 3.32 (sept, 4H, C*H*(CH_3)$_2$), 2.90 (sept, 2H, C*H*(CH_3)$_2$), 2.44 (s, 6H, Mes-CH_3), 2.25 (s, 3H, Mes-CH_3), 1.33 (d, 12H, *J* = 6 Hz, CH(CH_3)$_2$), 1.21 (d, 12H, *J* = 6 Hz, CH(CH_3)$_2$), 1.12 (d, *J* = 9 Hz, 12H, CH(CH_3)$_2$); $^{13}C\{^1H\}$ NMR (C_6D_6, 400 MHz, 298 K): δ 157.57 (Ar-*C*), 148.55 (Ar-*C*), 147.99 (Ar-*C*), 147.93 (Ar-*C*), 142.25 (Ar-*C*), 140.54 (Ar-*C*), 137.15 (Ar-*C*), 136.41 (Ar-*C*), 135.78 (Ar-*C*), 130.86 (Ar-*C*H), 129.33 (Ar-*C*H), 128.56 (Ar-*C*H), 127.75 (Ar-*C*H), 125.69 (Ar-*C*H), 120.87 (Ar-*C*H), 117.92 (Ar-*C*H), 34.89 (*C*H(CH_3)$_2$), 30.61 (*C*H(CH_3)$_2$), 24.99 (*C*H_3), 24.79 (*C*H_3), 24.48 (*C*H_3), 21.44 (*C*H_3), 20.60 (*C*H_3); UV-vis (toluene): λ_{max} = 456 nm; Elemental analysis for $C_{56}H_{72}KN_2$ (%): Calculated: C 82.80, H 8.93, N 3.45; Found: C 82.51, H 8.79, N 3.56.

Synthesis of compound 3

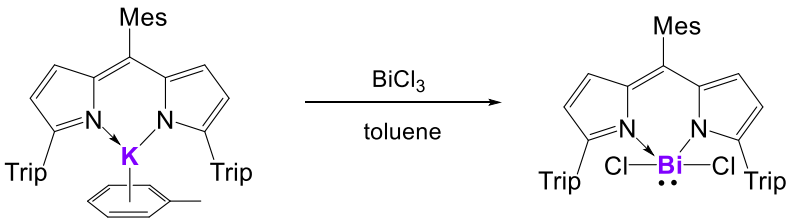


2 **3** (87%)

A toluene solution of $SbCl_3$ (0.46 g, 2.0 mmol) was added dropwise to a toluene solution (30 mL) of **2** (1.60 g, 2.0 mmol) at –30 °C. The reaction mixture was slowly warmed up to room temperature and stirred overnight. After filtration and removal of the solvent, the residue was washed with cooled hexane (5 mL) to afford **3** as an orange powder (1.50 g, 87%). Single crystals suitable for X-ray diffraction studies were grown from the saturated benzene solution at room temperature. ^1H NMR (C_6D_6, 300 MHz, 298 K): δ 7.25 (s, 4H, Ar-*H*), 6.73 (d, 2H, *J* = 6 Hz, pyrrole-C*H*), 6.69 (s, 2H, Ar-*H*), 6.36 (d, 2H, *J* = 6 Hz, pyrrole-C*H*), 3.37 (sept, 4H, C*H*(CH_3)$_2$), 2.78 (sept, 2H, C*H*(CH_3)$_2$), 2.22 (s, 6H, Mes-CH_3), 2.15 (s, 3H, Mes-CH_3), 1.58 (d, 12H, *J* = 9 Hz, CH(CH_3)$_2$), 1.19 (d, 12H, *J* = 6 Hz, CH(CH_3)$_2$), 1.05 (d, *J* = 6 Hz, 12H, CH(CH_3)$_2$); $^{13}C\{^1H\}$ NMR (C_6D_6, 400 MHz, 298 K): δ 159.09 (Ar-*C*), 152.52 (Ar-*C*), 150.46 (Ar-*C*), 147.45 (Ar-*C*), 138.61 (Ar-*C*), 137.57 (Ar-*C*), 133.63 (Ar-*C*H), 133.32 (Ar-*C*), 129.34 (Ar-*C*), 128.31 (Ar-*C*H), 126.09 (Ar-*C*), 122.34 (Ar-*C*H), 121.60

(Ar-*C*H), 34.80 (*C*H(CH$_3$)$_2$), 31.71 (*C*H(CH$_3$)$_2$), 27.23 (*C*H$_3$), 24.06 (*C*H$_3$), 23.09 (*C*H$_3$), 21.15 (*C*H$_3$), 20.52 (*C*H$_3$); UV-vis (toluene): λ_{abs} = 514 nm; Fluorescence (toluene): λ_{em} = 547 nm; Elemental analysis for $C_{48}H_{61}Cl_2N_2Sb$ (%): Calculated: C 67.14, H 7.16, N 3.26; Found: C 67.01, H 7.02, N 3.42.

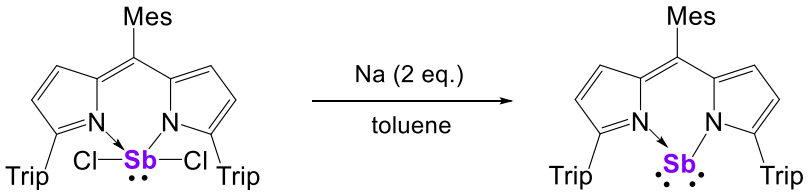
Synthesis of compound 4



2 **4** (58%)

A diethyl ether solution of $BiCl_3$ (0.32 g, 1.0 mmol) was added dropwise to a toluene solution (30 mL) of **2** (0.80 g, 1.0 mmol) at –30 °C. Following completion of the addition, the reaction mixture was slowly warmed to room temperature and stirred overnight. After filtration and removal of the solvent, the residue was washed with cooled hexane (5 mL) to afford **4** as an orange powder (0.55 g, 58%). Single crystals suitable for X-ray diffraction studies were grown from the saturated toluene solution at room temperature. ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ 7.33 (s, 4H, Ar-*H*), 6.82 (d, 2H, *J* = 3 Hz, pyrrole-C*H*), 6.68 (s, 2H, Ar-*H*), 6.48 (d, 2H, *J* = 3 Hz, pyrrole-C*H*), 3.43 (sept, 4H, C*H*(CH$_3$)$_2$), 2.83 (sept, 2H, C*H*(CH$_3$)$_2$), 2.21 (s, 6H, Mes-C*H*$_3$), 2.14 (s, 3H, Mes-C*H*$_3$), 1.67 (d, 12H, *J* = 6 Hz, CH(C*H*$_3$)$_2$), 1.25 (d, 12H, *J* = 6 Hz, CH(C*H*$_3$)$_2$), 1.05 (d, *J* = 9 Hz, 12H, CH(C*H*$_3$)$_2$); ^{13}C{^{1}H} NMR (C_6D_6, 400 MHz, 298 K): δ 158.11 (Ar-*C*), 152.42 (Ar-*C*), 151.14 (Ar-*C*), 149.98 (Ar-*C*), 138.17 (Ar-*C*), 137.53 (Ar-*C*), 134.61 (Ar-*C*), 133.26 (Ar-*C*), 133.03 (Ar-*C*H), 128.15 (Ar-*C*H), 127.21 (Ar-*C*), 123.96 (Ar-*C*H), 121.67 (Ar-*C*H), 34.96 (*C*H(CH$_3$)$_2$), 31.52 (*C*H(CH$_3$)$_2$), 27.32 (*C*H$_3$), 24.16 (*C*H$_3$), 23.26 (*C*H$_3$), 21.12 (*C*H$_3$), 20.36 (*C*H$_3$); UV-vis (toluene): λ_{abs} = 513 nm; Fluorescence (toluene): λ_{em} = 568 nm; Elemental analysis for $C_{48}H_{61}BiCl_2N_2$ (%): Calculated: C 60.95, H 6.50, N 2.96; Found: C 60.68, H 6.22, N 3.12.

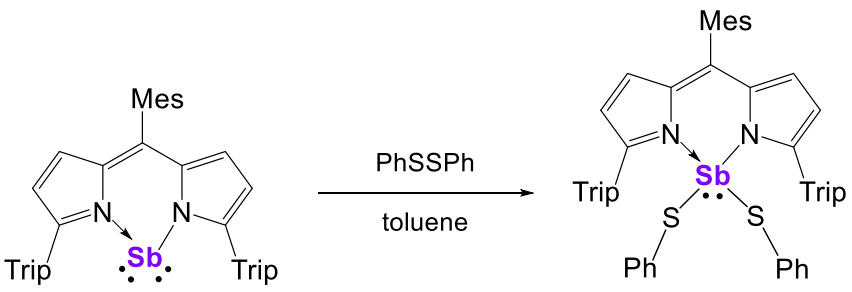
Synthesis of compound 5



3 **5** (42%)

Sodium (45 mg, 1.96 mmol) was added to a toluene solution (15 mL) of **3** (800 mg, 0.93 mmol) at room temperature. The mixture stirred for two days and the color changed from orange red to brownish yellow. After filtration, the solvent was removed in vacuo and the residue washed with cold hexane (3 ml) to afford **5** as an orange powder (310 mg, 42%). Single crystals suitable for X-ray diffraction studies were grown from its saturated hexane solution at room temperature. ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ 7.23 (s, 4H, Ar-*H*), 6.97 (d, 2H, *J* = 6 Hz, pyrrole-C*H*), 6.91 (s, 2H, Ar-*H*), 6.87 (d, 2H, *J* = 3 Hz, pyrrole-C*H*), 2.76 (sept, 2H, C*H*$(CH_3)_2$), 2.58 (sept, 4H, C*H*$(CH_3)_2$), 2.23 (s, 3H, Mes-C*H*$_3$), 2.10 (s, 6H, Mes-C*H*$_3$), 1.35 (d, 12H, *J* = 6 Hz, CH(C*H*$_3)_2$), 1.13-1.17 (m, 24H, CH(C*H*$_3)_2$); ^{13}C{^{1}H} NMR (C_6D_6, 400 MHz, 298K): δ 151.39 (Ar-*C*), 149.74 (Ar-*C*), 146.61 (Ar-*C*), 138.48 (Ar-*C*), 137.61 (Ar-*C*), 134.91 (Ar-*C*), 133.89 (Ar-*C*), 129.75 (Ar-*C*), 128.77 (Ar-*C*H), 128.17 (Ar-*C*), 126.62 (Ar-*C*H), 123.19 (Ar-*C*H), 117.52 (Ar-*C*H), 34.78 (*C*H$(CH_3)_2$), 31.35 (*C*H$(CH_3)_2$), 26.49 (*C*H$_3$), 25.85 (*C*H$_3$), 24.10 (*C*H$_3$), 21.26 (*C*H$_3$), 20.09 (*C*H$_3$); UV-vis (toluene): λ_{max} = 456 nm; Fluorescence (toluene): λ_{em} = 527 nm; Elemental analysis for $C_{48}H_{61}N_2Sb$ (%): Calculated: C 73.18, H 7.81, N 3.56; Found: C 73.36, H 7.92, N 3.38.

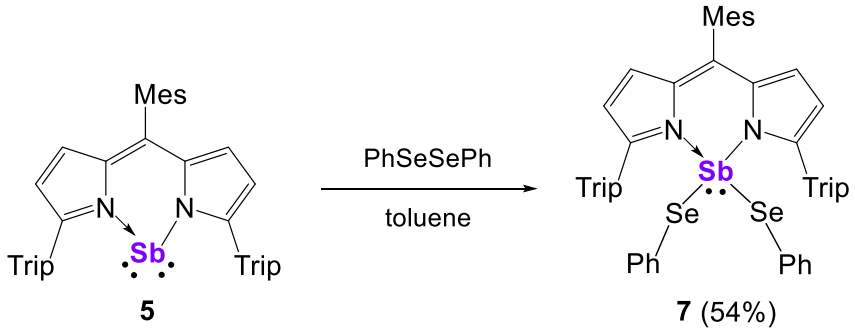
Synthesis of compound 6



5 **6** (75%)

PhSSPh (44 mg, 0.20 mmol) was added to a toluene solution (15 mL) of 5 (150 mg, 0.20 mmol) at room temperature. After stirring for thirty minutes, the solution was concentrated and brownish red crystals (130 mg, 75%) of **6** were grown. ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ 7.16 (s, 4H, Ar-*H*), 6.97 (d, 4H, *J* = 9 Hz, Ar-*H*), 6.88 (m, 6H, Ar-*H*), 6.81 (s, 4H, Ar-*H*), 6.41 (d, 2H, *J* = 3 Hz, pyrrole-C*H*), 3.22 (sept, 4H, C*H*(CH_3)$_2$), 2.81 (sept, 2H, C*H*(CH_3)$_2$), 2.36 (s, 6H, Mes-C*H*$_3$), 2.21 (s, 3H, Mes-C*H*$_3$), 1.32 (d, 12H, *J* = 6 Hz, CH(C*H*$_3$)$_2$), 1.26 (d, 12H, *J* = 6 Hz, CH(C*H*$_3$)$_2$), 1.15 (d, 12H, *J* = 6 Hz, CH(C*H*$_3$)$_2$); ^{13}C{^{1}H} NMR (C_6D_6, 400 MHz, 298K): δ 161.09 (Ar-*C*), 149.69 (Ar-*C*), 147.79 (Ar-*C*), 145.47 (Ar-*C*), 139.24 (Ar-*C*), 137.39 (Ar-*C*), 137.09 (Ar-*C*), 136.36 (Ar-*C*), 136.15 (Ar-*C*), 135.52 (Ar-*C*), 132.08 (Ar-*C*), 130.14 (Ar-*C*), 128.95 (Ar-*C*H), 126.91 (Ar-*C*), 126.22 (Ar-*C*H), 122.37 (Ar-*C*H), 121.02 (Ar-*C*H), 34.53 (*C*H(CH_3)$_2$), 31.09 (*C*H(CH_3)$_2$), 25.90 (*C*H$_3$), 23.97 (*C*H$_3$), 23.55 (*C*H$_3$), 20.82 (*C*H$_3$), 20.05 (*C*H$_3$). UV-vis (toluene): λ_{max} = 452 nm; Fluorescence (toluene): λ_{em} = 550 nm; Elemental analysis for $C_{60}H_{71}N_2S_2Sb$ (%): Calculated: C 71.63, H 7.11, N 2.78; Found: C 71.30, H 6.95, N 2.98.

Synthesis of compound 7



5 **7** (54%)

PhSeSePh (62 mg, 0.20 mmol) was added to a toluene solution (15 mL) of 5 (150 mg, 0.20 mmol) at room temperature. After stirring for thirty minutes, the solution was concentrated and brownish red crystals (120 mg, 54%) of **7** were grown.^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ 7.10 (s, 8H, Ar-*H*), 6.96 (s, 6H, Ar-*H*), 6.81 (s, 4H, Ar-*H*), 6.41 (d, 2H, pyrrole-C*H*), 3.21 (sept, 4H, C*H*(CH_3)$_2$), 2.84 (sept, 2H, C*H*(CH_3)$_2$), 2.38 (s, 6H, Mes-C*H*$_3$), 2.22 (s, 3H, Mes-C*H*$_3$), 1.33 (d, 12H, *J* = 6 Hz, CH(C*H*$_3$)$_2$), 1.28 (d,

12H, *J* = 6 Hz, CH(C*H*$_3$)$_2$), 1.16 (s, 12H, CH(C*H*$_3$)$_2$); ^{13}C{^{1}H} NMR (C_6D_6, 400 MHz, 298K): δ 160.97 (Ar-*C*), 149.69 (Ar-*C*), 147.63 (Ar-*C*), 145.36 (Ar-*C*), 139.51 (Ar-*C*), 137.62 (Ar-*C*), 137.15 (Ar-*C*), 135.71 (Ar-*C*), 131.99 (Ar-*C*), 130.81 (Ar-*C*), 130.24 (Ar-*C*), 128.24 (Ar-*C*), 127.87 (Ar-*C*H), 127.63 (Ar-*C*), 126.69 (Ar-*C*H), 122.44 (Ar-*C*H), 121.14 (Ar-*C*H), 34.56 (*C*H(CH$_3$)$_2$), 31.09 (*C*H(CH$_3$)$_2$), 25.99 (*C*H$_3$), 24.01 (*C*H$_3$), 23.66 (*C*H$_3$), 20.95 (*C*H$_3$), 20.25 (*C*H$_3$). UV-vis (toluene): λ_{max} = 451 nm; Fluorescence (toluene): λ_{em} = 552 nm; Elemental analysis for $C_{60}H_{71}N_2Se_2Sb$ (%): Calculated: C 65.52, H 6.51, N 2.55; Found: C 65.20, H 6.25, N 2.78.

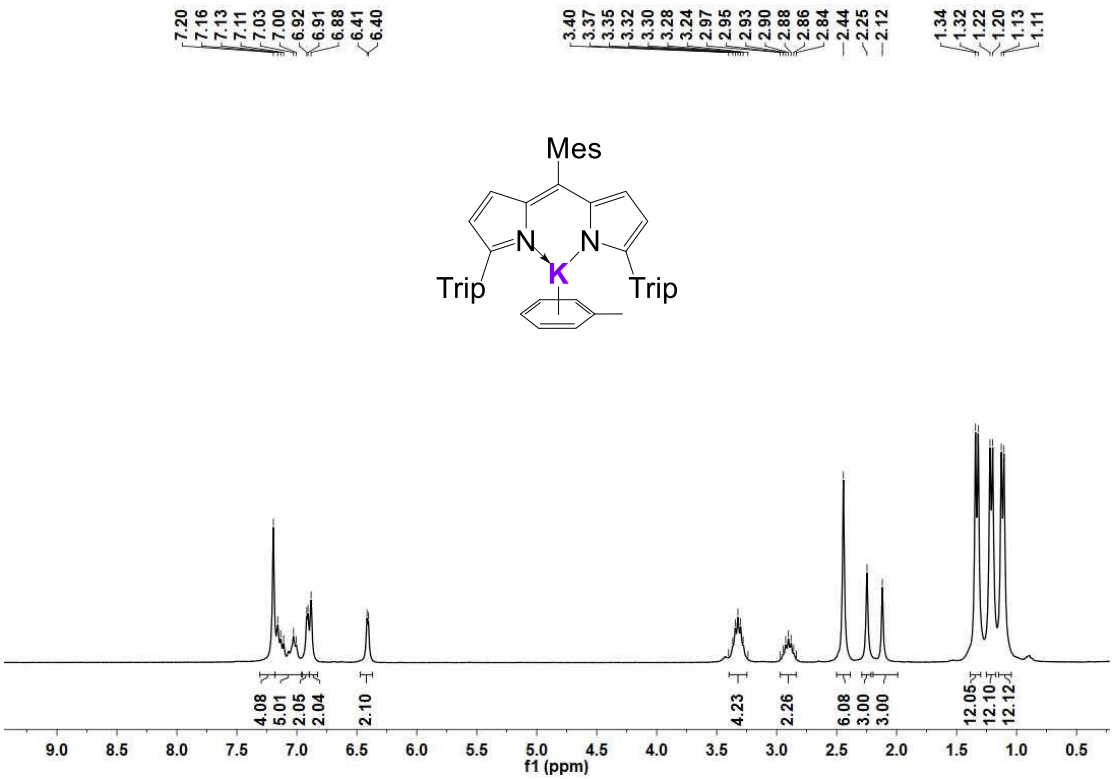


Fig. S1 ^{1}H NMR spectrum of **2** in C_6D_6 at 298 K.

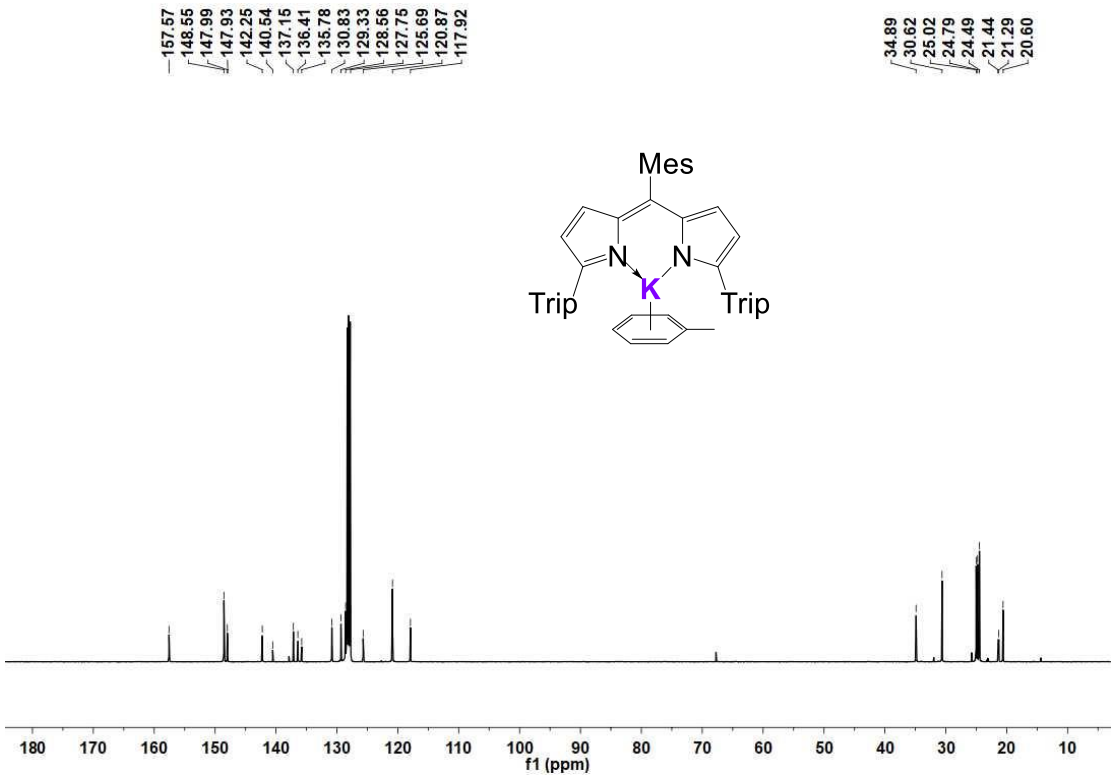


Fig. S2 ^{13}C{^{1}H} NMR spectrum of **2** in C_6D_6 at 298 K.

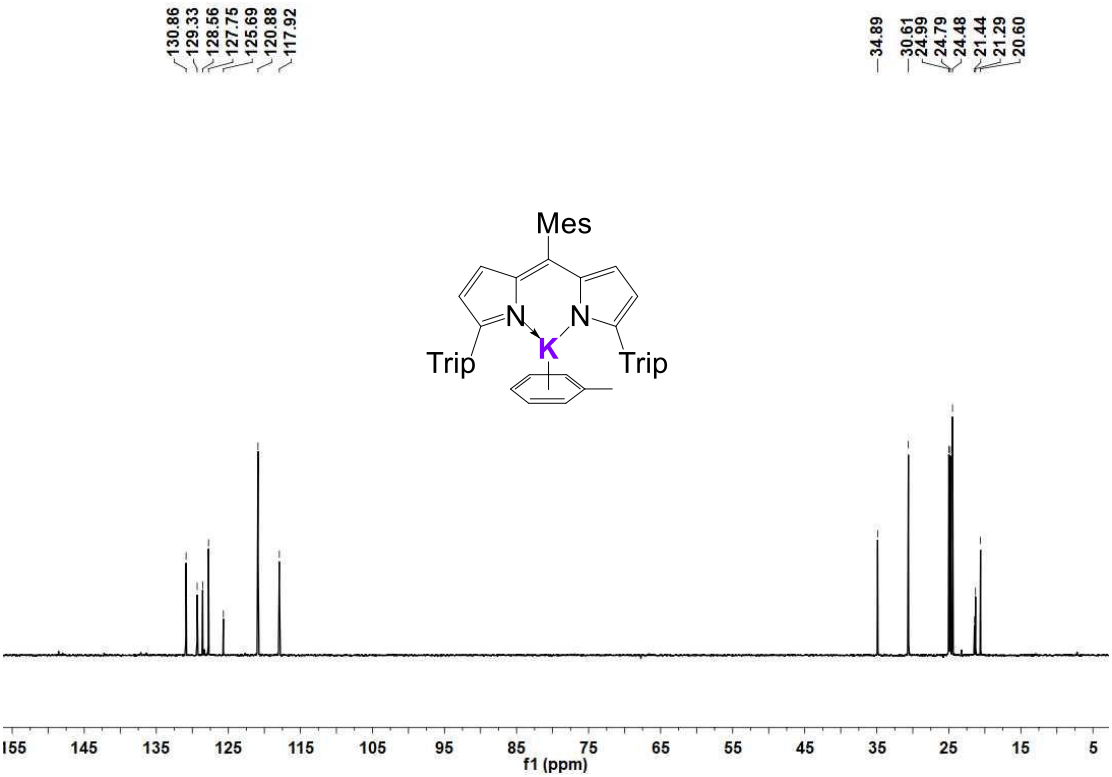


Fig. S3 ^{13}C(DEPT135) NMR spectrum of **2** in C_6D_6 at 298 K.

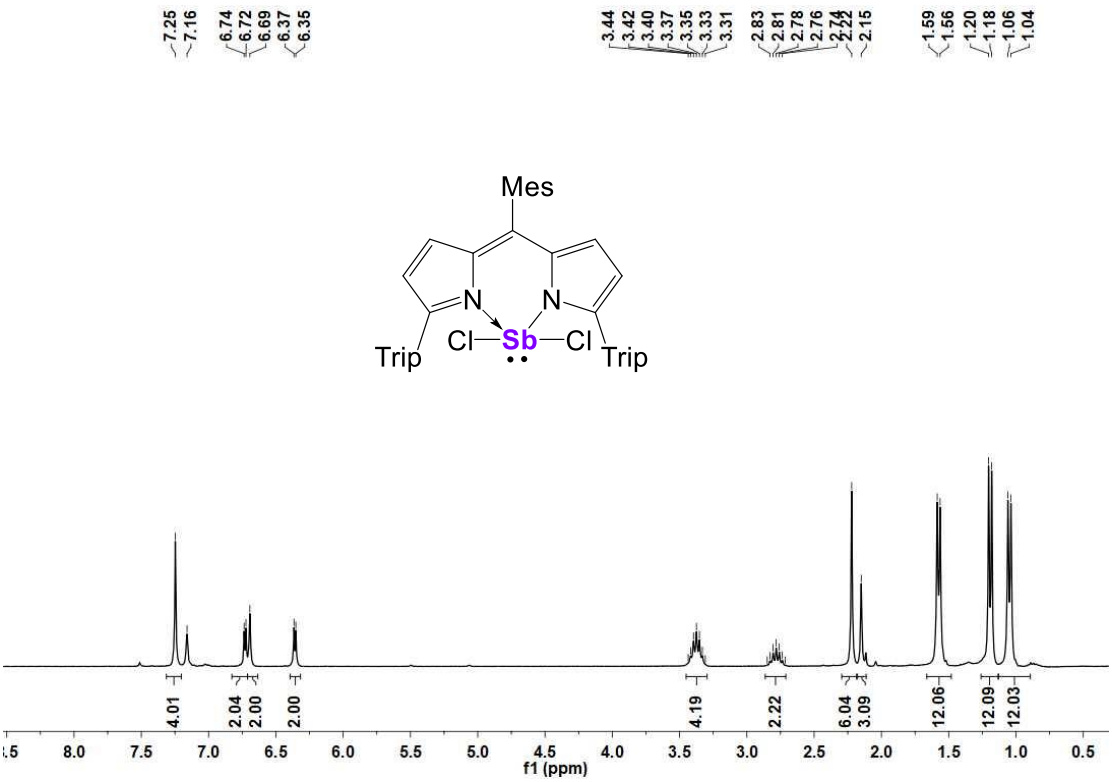


Fig. S4 ^{1}H NMR spectrum of **3** in C_6D_6 at 298 K.

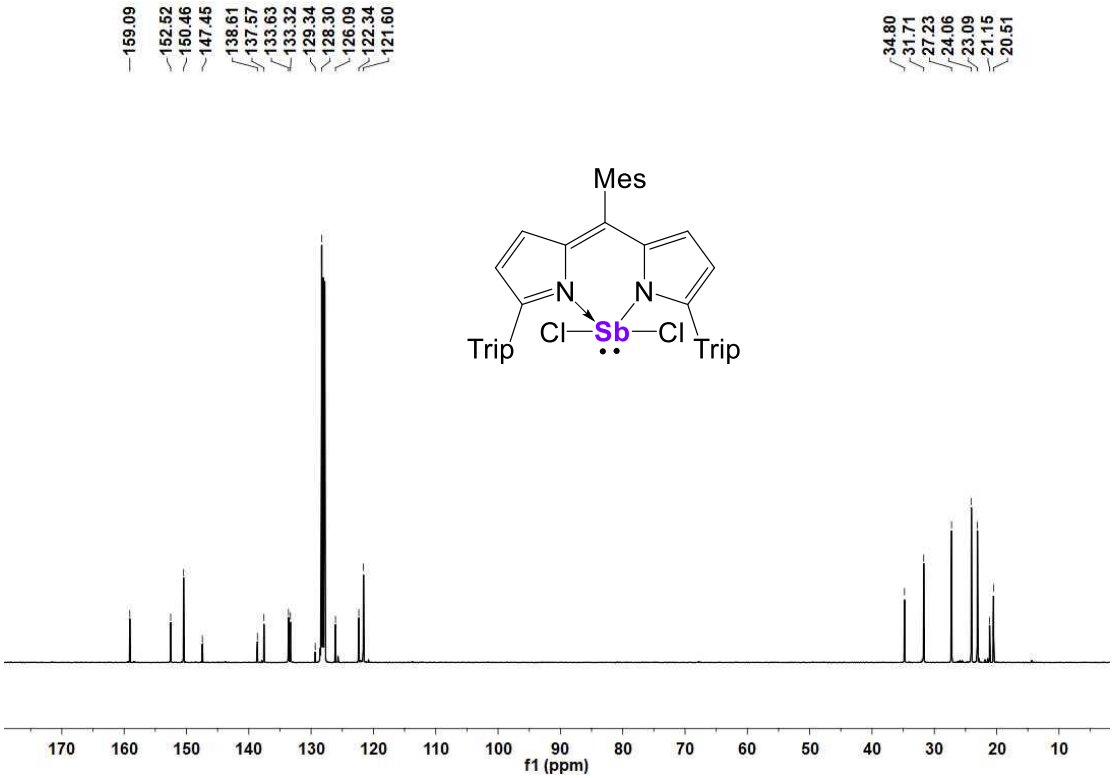


Fig. S5 $^{13}C\{^{1}H\}$ NMR spectrum of **3** in C_6D_6 at 298 K.

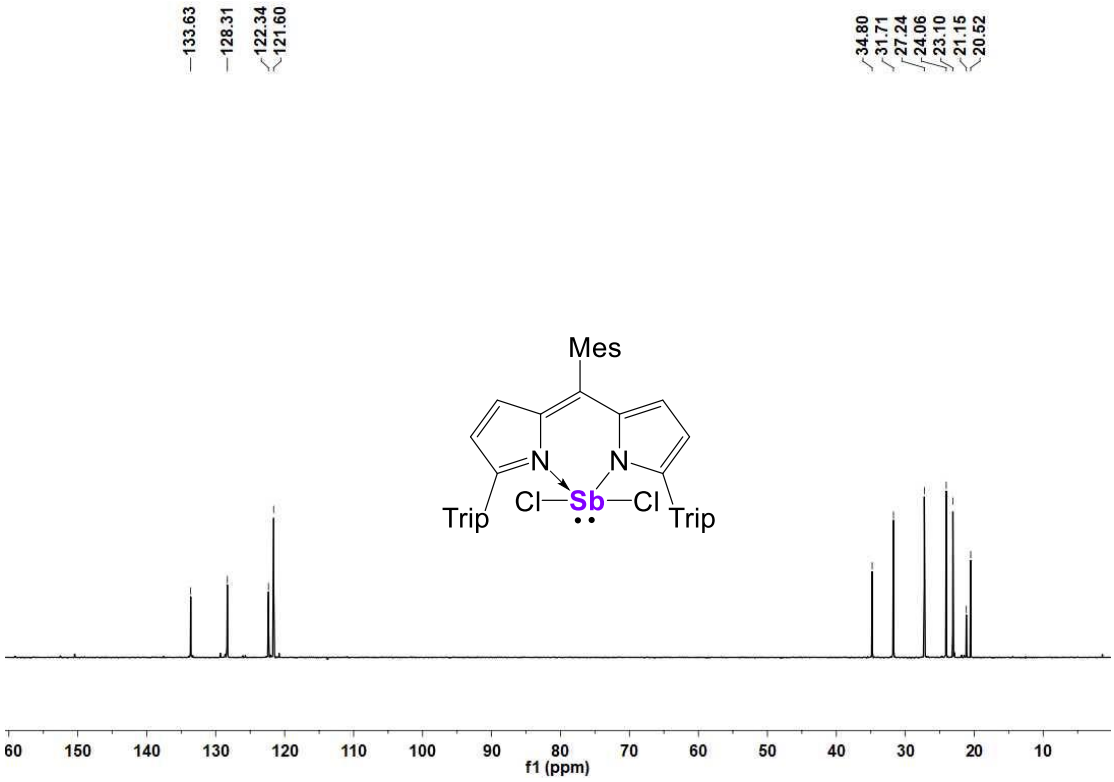


Fig. S6 ^{13}C(DEPT135) NMR spectrum of **3** in C_6D_6 at 298 K.

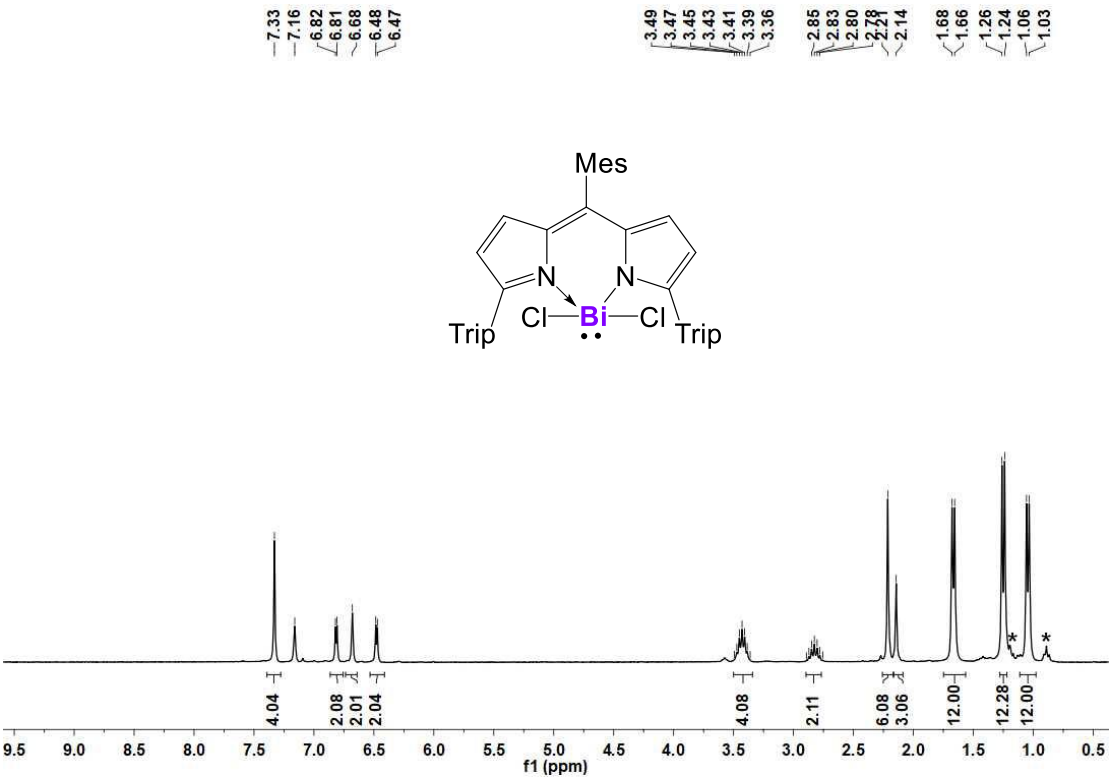


Fig. S7 ^{1}H NMR spectrum of **4** in C_6D_6 at 298 K. (*: residual hexane)

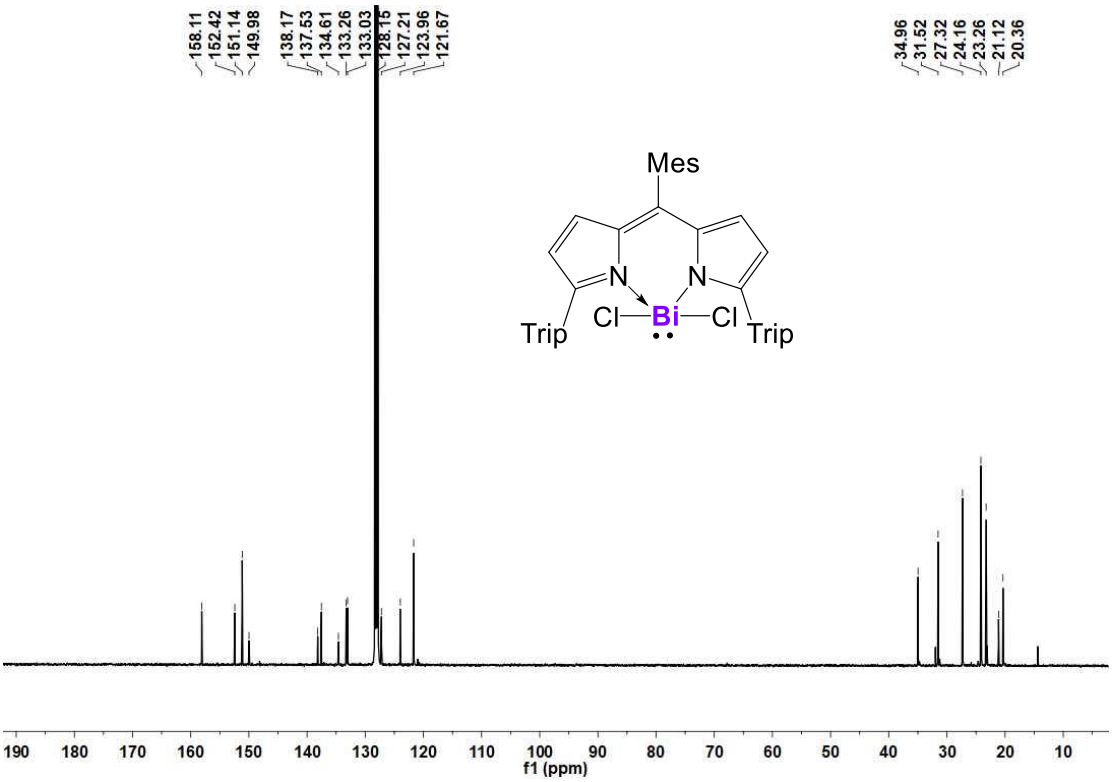


Fig. S8 $^{13}C\{^{1}H\}$ NMR spectrum of **4** in C_6D_6 at 298 K.

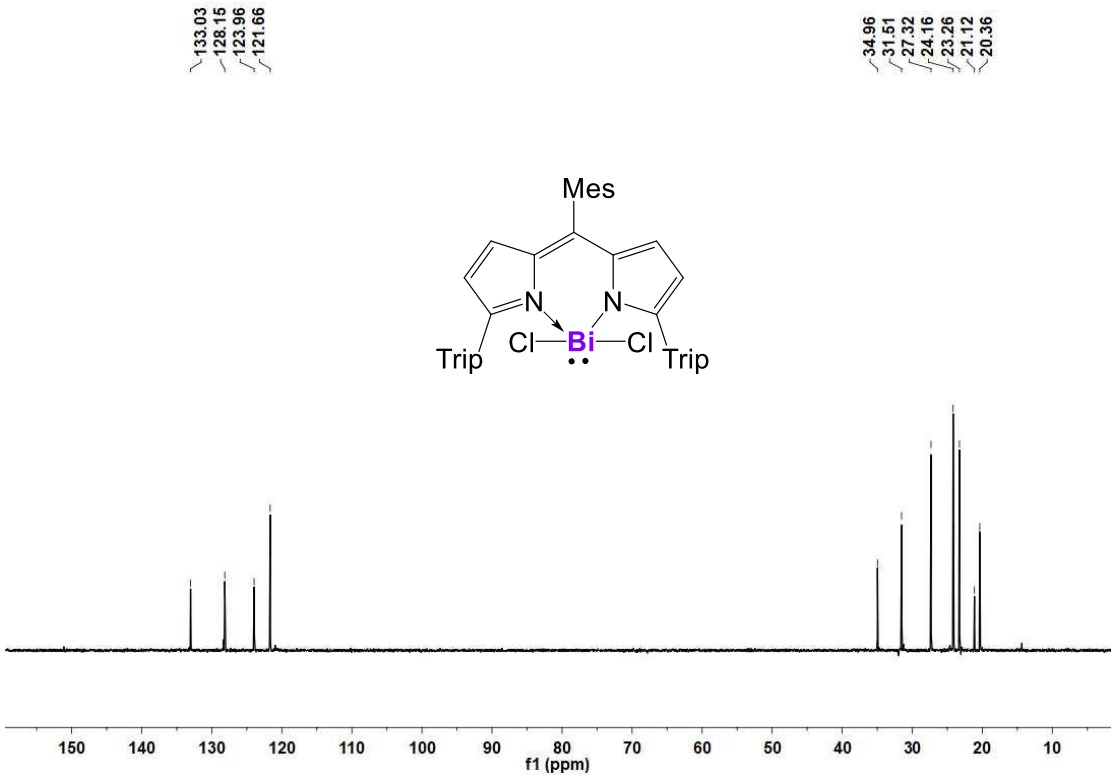


Fig. S9 ^{13}C(DEPT135) NMR spectrum of **4** in C_6D_6 at 298 K.

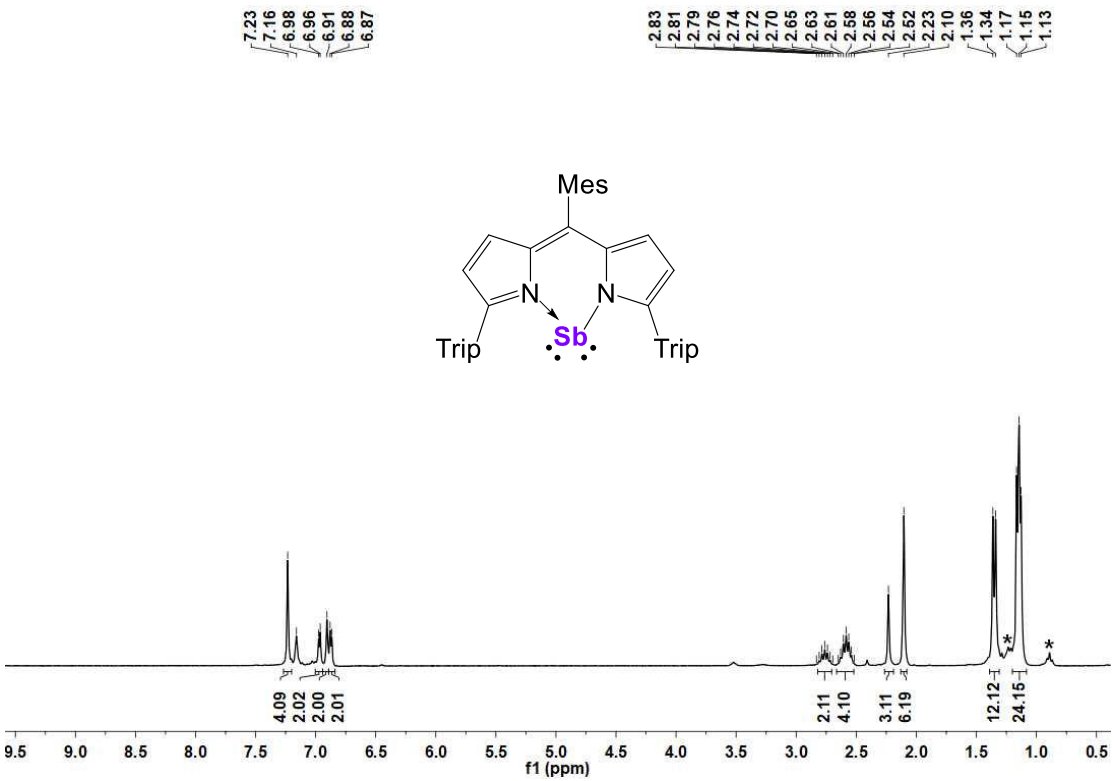


Fig. S10 ^{1}H NMR spectrum of **5** in C_6D_6 at 298 K. (*: residual hexane)

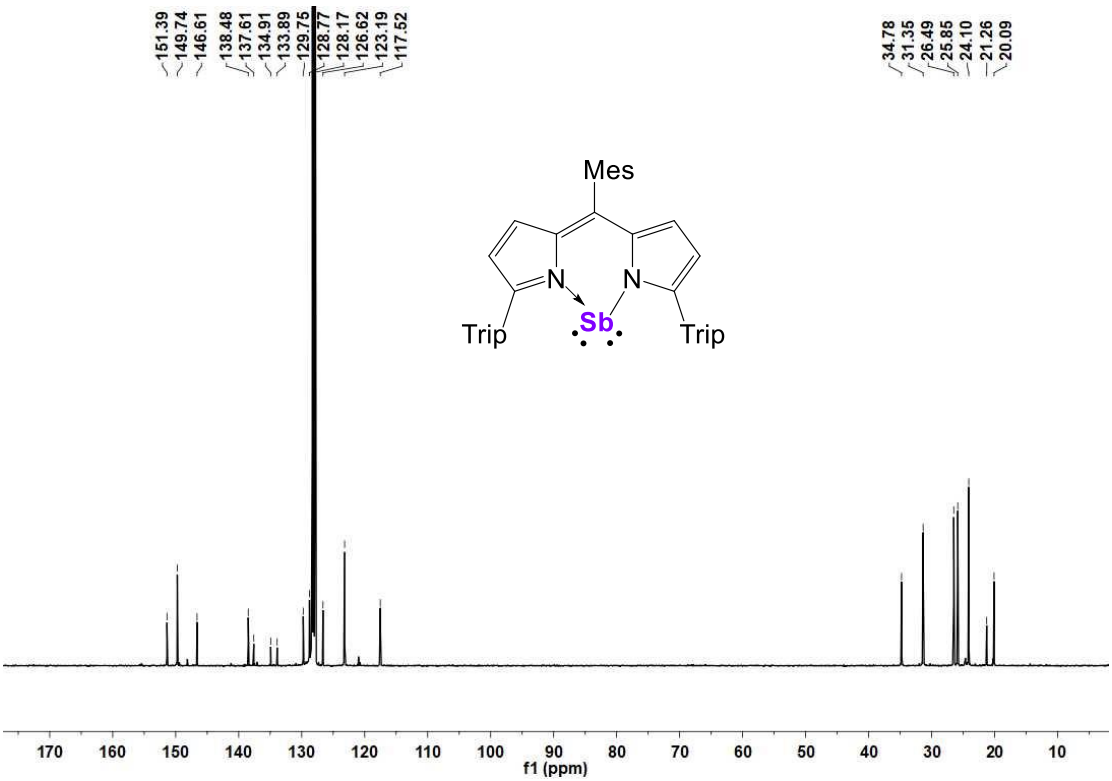


Fig. S11 $^{13}C\{^{1}H\}$ NMR spectrum of **5** in C_6D_6 at 298 K.

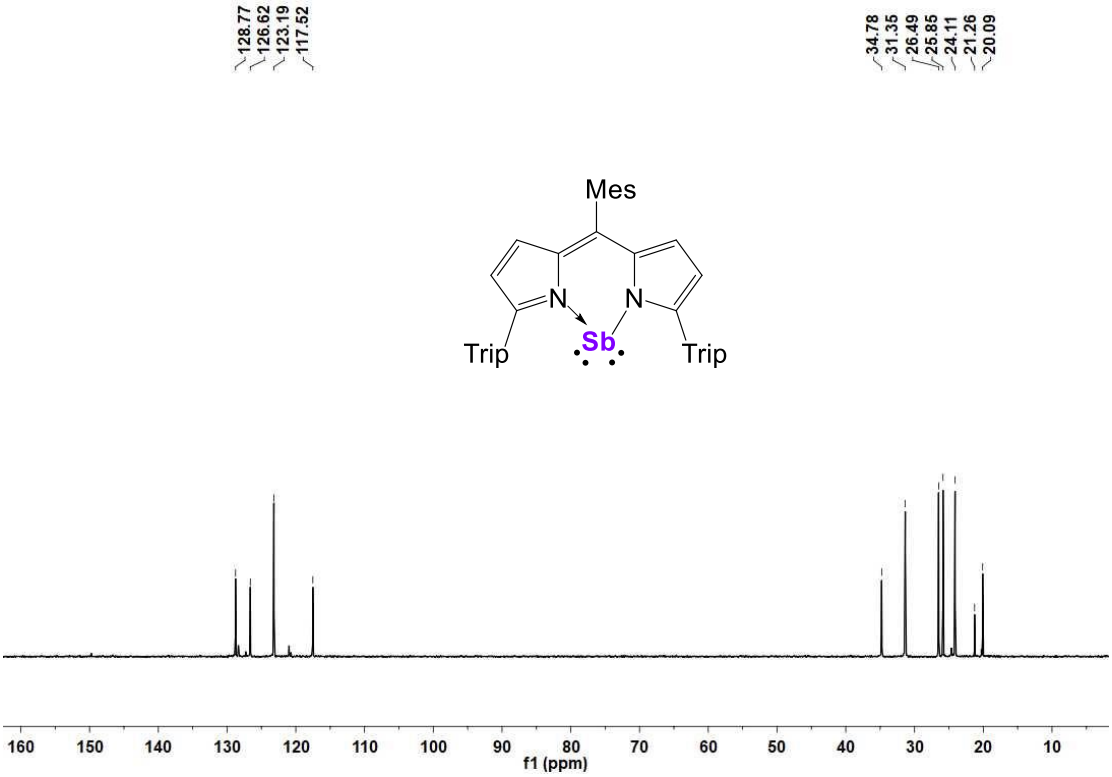


Fig. S12 ^{13}C(DEPT135) NMR spectrum of **5** in C_6D_6 at 298 K.

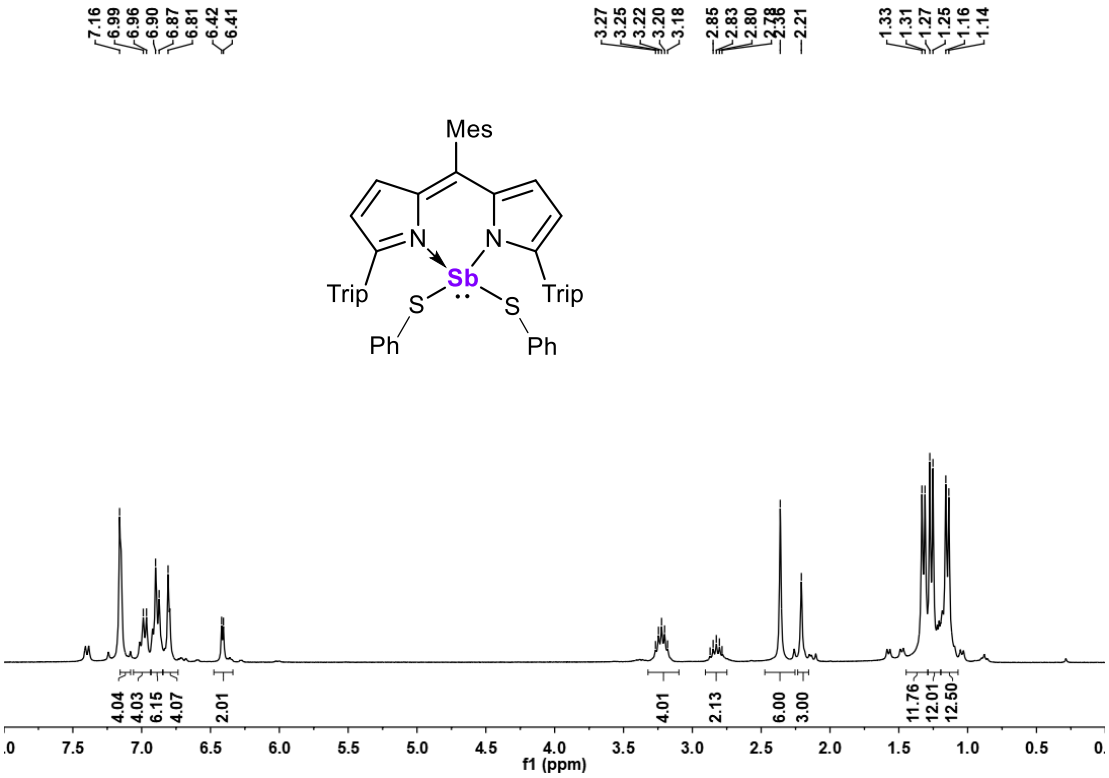


Fig. S13 ^{1}H NMR spectrum of **6** in C_6D_6 at 298 K.

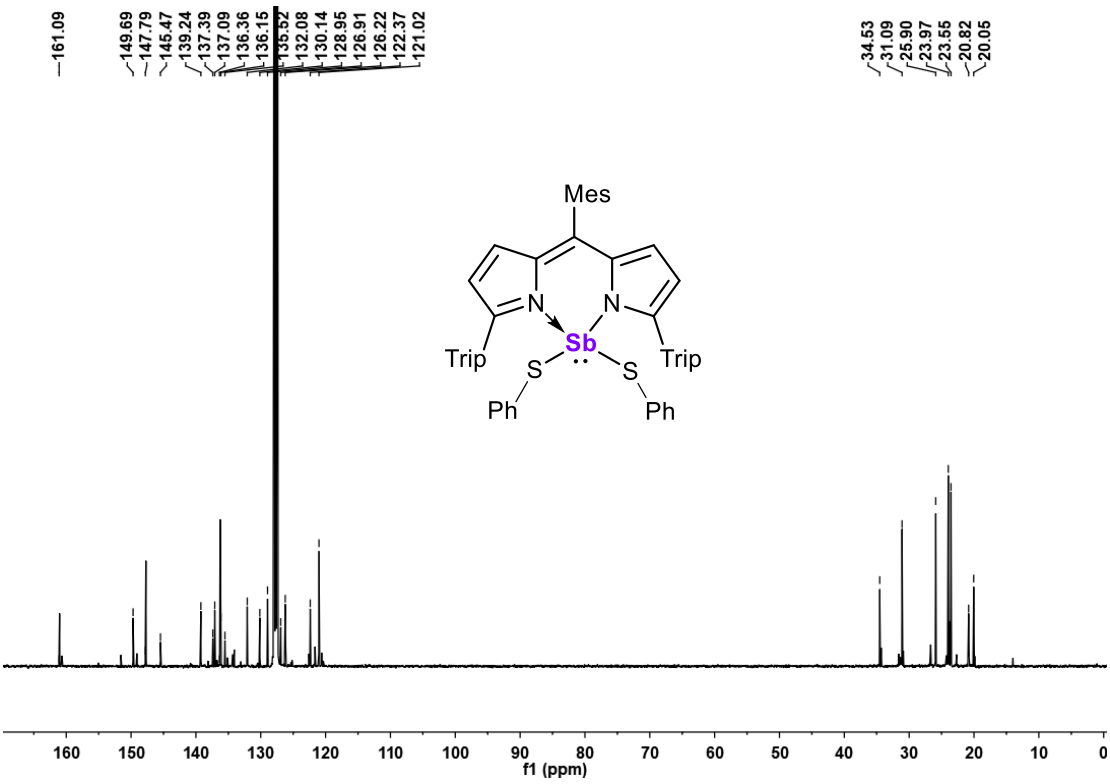


Fig. S14 ^{13}C{^{1}H} NMR spectrum of **6** in C_6D_6 at 298 K.

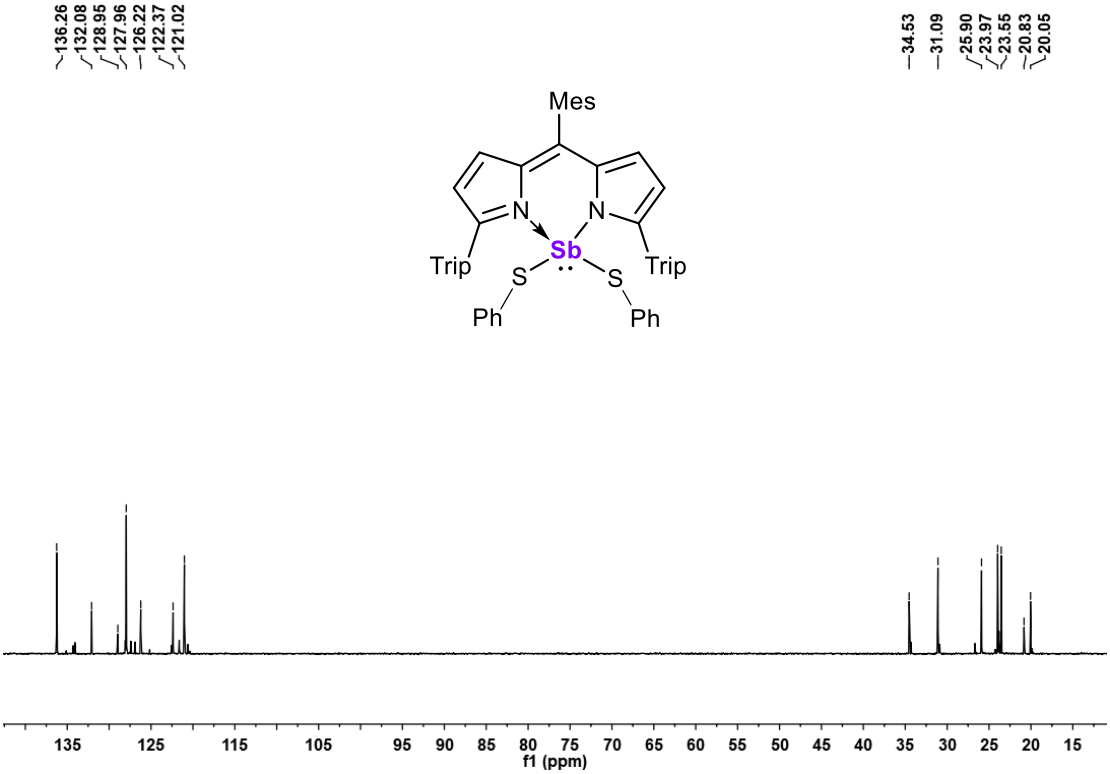


Fig. S15 ^{13}C(DEPT135) NMR spectrum of **6** in C_6D_6 at 298 K.

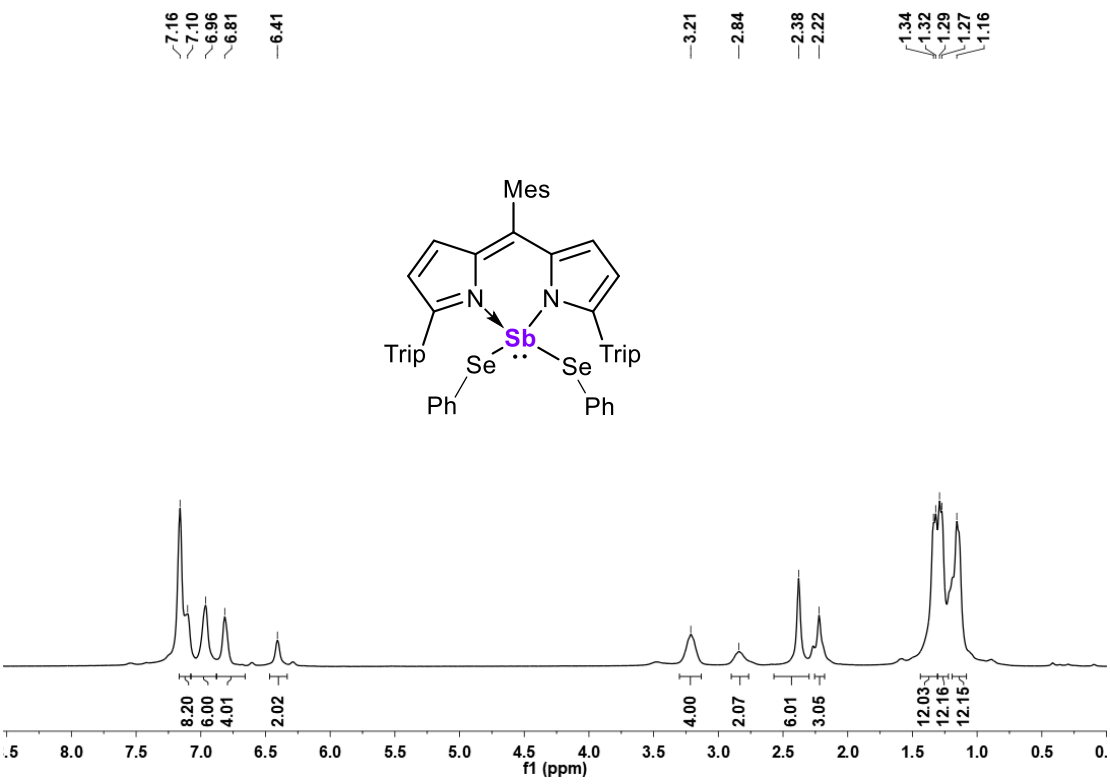


Fig. S16 ^{1}H NMR spectrum of **7** in C_6D_6 at 298 K.

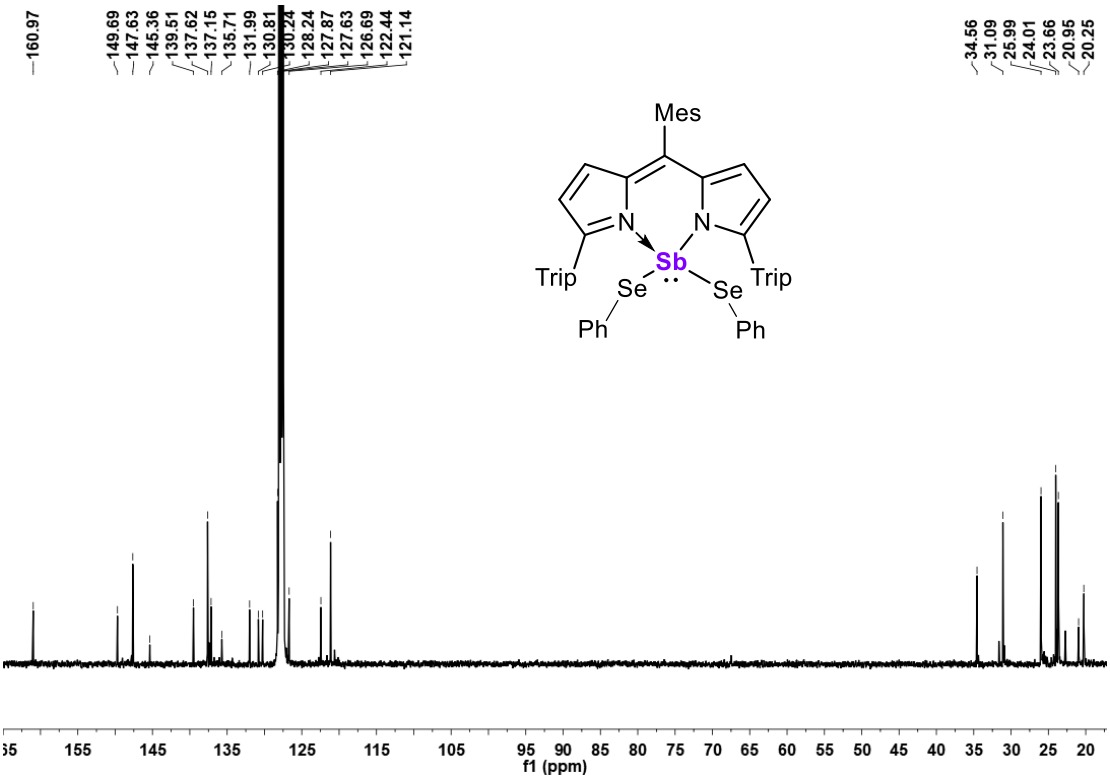


Fig. S17 $^{13}C\{^{1}H\}$ NMR spectrum of **7** in C_6D_6 at 298 K.

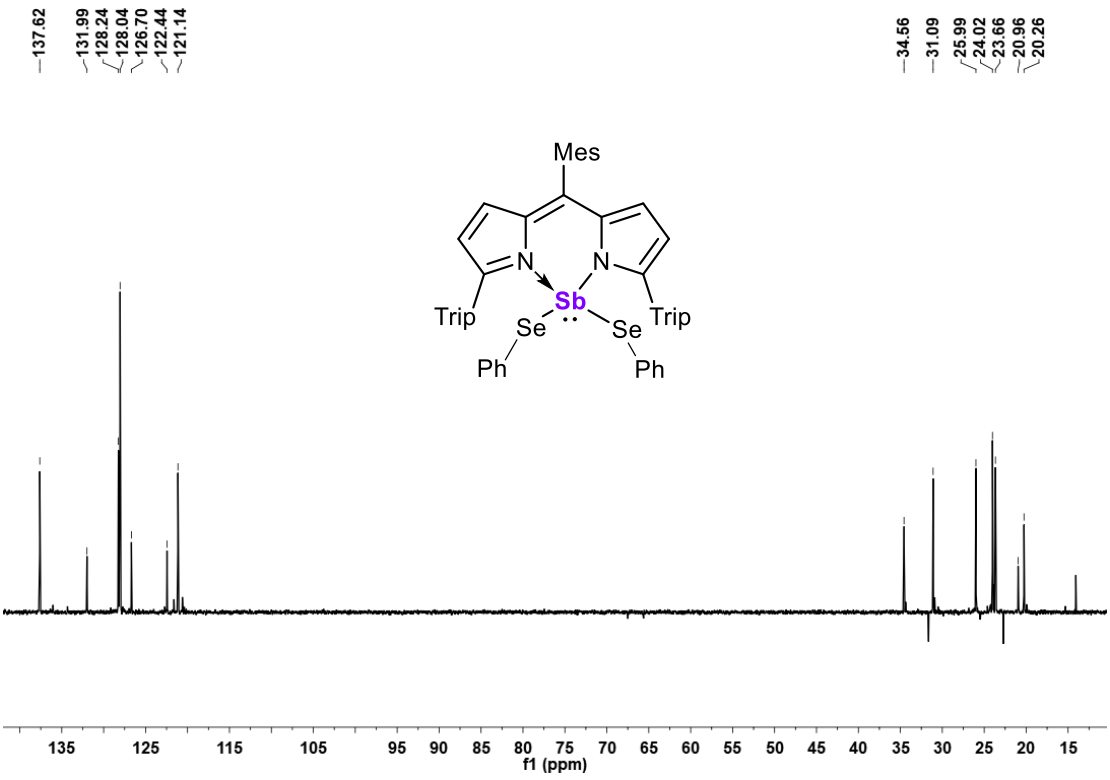


Fig. S18 ^{13}C(DEPT135) NMR spectrum of **7** in C_6D_6 at 298 K.

2. Crystal structural parameters for compounds 2-5

For the single crystal X-ray structure analyses the crystals were each mounted on a glass capillary in perfluorinated oil and measured in a cold N_2 flow. The data for all compounds were collected on a Bruker D8 CMOS detector at low temperatures. The structures were solved by direct methods and all refined on F^2 with the SHELX-2018/3 software package. The positions of the H atoms were calculated and considered isotropically according to a riding model.

Table S1. Summary of data collection and structure refinement.

Compounds	**2**	**3**•2C_6H_6	**4**•2C_7H_8	**5**
CCDC	2214164	2214165	2214166	2214167
Formula	$C_{55}H_{69}KN_2$	$C_{60}H_{73}Cl_2N_2Sb$	$C_{62}H_{77}BiCl_2N_2$	$C_{48}H_{61}N_2Sb$
Fw	797.22	1014.85	1130.13	787.73
Crystal syst	monoclinic	triclinic	triclinic	monoclinic
Space group	$P2_1/c$	P-1	P-1	$P2_1/n$
Size, mm^3	0.10 × 0.16 × 0.18	0.08 × 0.10 × 0.12	0.10 × 0.11 × 0.12	0.20 × 0.22× 0.24
T, K	120.0	129.0	120.0	120.0
a, Å	14.0581(15)	11.7747(14)	11.8029(6)	15.4132(8)
b, Å	19.545(2)	13.6594(16)	13.8511(7)	13.2255(7)
c, Å	18.7522(17)	20.446(2)	20.2711(11)	21.3888(11)
α, deg	90	90.015(4)	89.7190(10)	90
β, deg	104.975(5)	103.015(4)	77.7200(10)	93.634(2)
γ, deg	90	114.680(3)	65.4490(10)	90
V, $Å^3$	4977.4(9)	2894.7(6)	2932.4(3)	4351.3(4)
Z	4	2	2	4
d_{calcd}, $g•cm^{-1}$	1.064	1.164	1.280	1.202
μ, mm^{-1}	0.775	3.274	4.840	3.540
Reflections collected	42156	48124	26039	56907
Independent reflections	9133	10329	10388	7969
[R_{int}]	0.1342	0.0540	0.0356	0.0686
R_1[I>2sigma(I)]	0.0786	0.0725	0.0261	0.0384
wR_2[I>2sigma(I)]	0.1946	0.2163	0.0693	0.0953
R_1[all data]	0.1528	0.0731	0.0264	0.0525
wR_2[all data]	0.2410	0.2166	0.0696	0.1008
GOF	1.007	1.070	1.086	1.075
Largest diff. Peak/hole, $e•Å^{-3}$	0.26/-0.73	2.05/-1.77	0.78/-1.02	0.62/-1.08

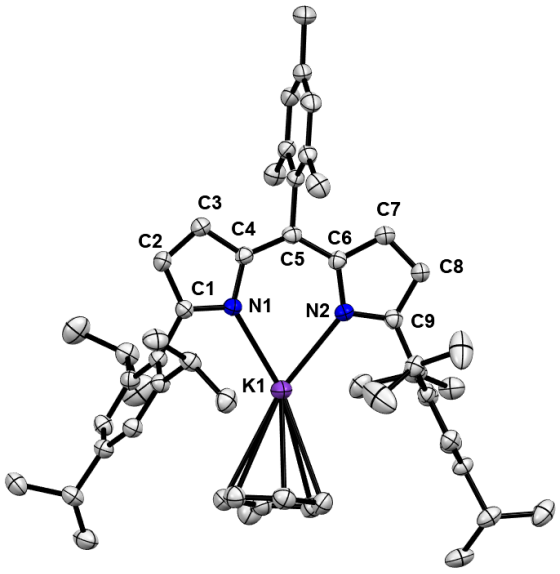


Fig. S19 Molecular structure of **2** (hydrogen atoms are omitted for clarity). Thermal ellipsoids are set at the 30% probability. Selected bond lengths (Å) and angles (°): K1−N1 2.638(3), K1−N2 2.646(3), C1−N1 1.332(4), C4−N1 1.389(4), C1−C2 1.416(5), C2−C3 1.381(5), C3−C4 1.432(4), C4−C5 1.407(4), C5−C6 1.415(4), C6−C7 1.425(4), C7−C8 1.365(5), C8−C9 1.426(5), C6−N2 1.391(4), C9−N2 1.330(4), N1−K1−N2 70.11(8).

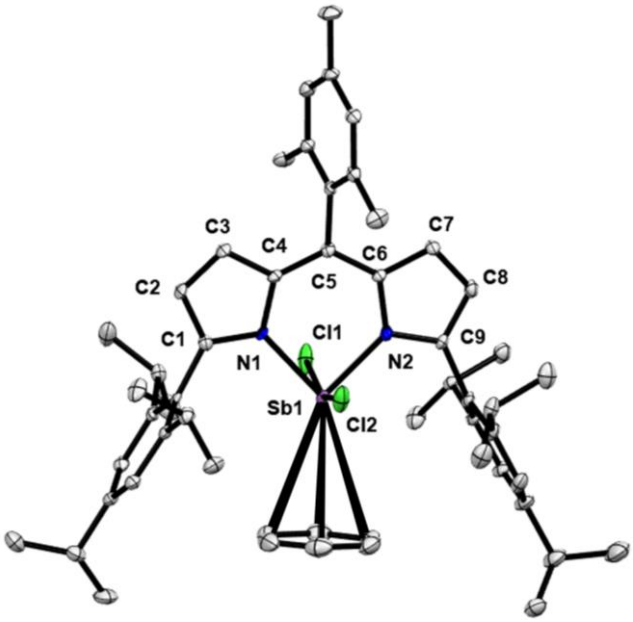


Fig. S20 Molecular structure of **3**·benzene (hydrogen atoms are omitted for clarity). Thermal ellipsoids are set at the 30% probability. Selected bond lengths (Å) and angles (°): Sb1−Cl1 2.538(2), Sb1−Cl2 2.534(2), Sb1−N1 2.120(5), Sb1−N2 2.102(5), C1−N1 1.351(8), C4−N1 1.398(8), C1−C2 1.407(10), C2−C3 1.369(10), C3−C4 1.406(9), C4−C5 1.387(9), C5−C6 1.402(9), C6−C7 1.413(9), C7−C8 1.374(10), C8−C9 1.411(10), C6−N2 1.393(8), C9−N2 1.361(8), Cl1-Sb1-Cl2 160.99(8), N1−Sb1−N2 88.9(2), N1−Sb1−Cl1 83.59(16), N2−Sb1−Cl1 82.01(16), N1−Sb1−Cl2 82.93(16), N2−Sb1−Cl2 84.38(16).

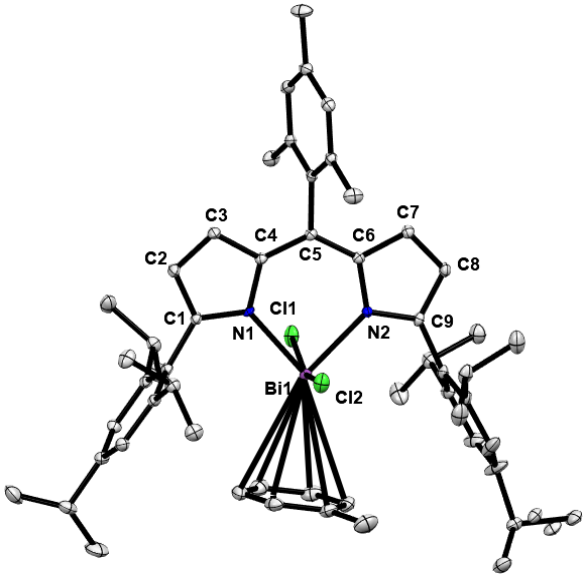


Fig. S21 Molecular structure of **4**·toluene (hydrogen atoms are omitted for clarity). Thermal ellipsoids are set at the 30% probability. Selected bond lengths (Å) and angles (°): Bi1−Cl1 2.6327(7), Bi1−Cl2 2.6199(7), Bi1−N1 2.220(2), Bi1−N2 2.224(2), C1−N1 1.351(3), C4−N1 1.351(3), C1−C2 1.408(4), C2−C3 1.375(4), C3−C4 1.413(4), C4−C5 1.399(4), C5−C6 1.394(4), C6−C7 1.415(4), C7−C8 1.375(4), C8−C9 1.411(4), C6−N2 1.394(3), C9−N2 1.346(3), Cl1-Bi1-Cl2 162.99(3), N1−Bi1−N2 85.66(8), N1−Bi1−Cl1 83.57(6), N2−Bi1−Cl1 82.25(6), N1−Bi1−Cl2 84.22(6), N2−Bi1−Cl2 85.06(6).

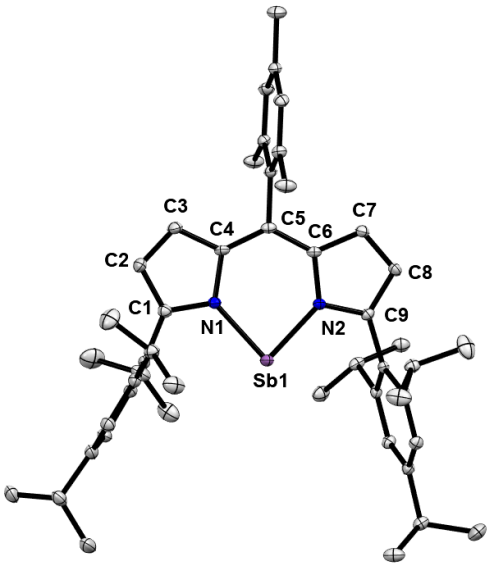


Fig. S22 Molecular structure of **5** (hydrogen atoms are omitted for clarity). Thermal ellipsoids are set at the 30% probability. Selected bond lengths (Å) and angles (°): Sb1−N1 2.095(2), Sb1−N2 2.090(2), C1−N1 1.355(3), C4−N1 1.414(3), C1−C2 1.398(4), C2−C3 1.372(4), C3−C4 1.408(4), C4−C5 1.390(4), C5−C6 1.394(4), C6−C7 1.412(4), C7−C8 1.374(4), C8−C9 1.400(4), C6−N2 1.409(3), C9−N2 1.352(3), N1−Sb1−N2 86.00(8).

3. UV-vis absorbance and photoluminescence spectra of 5-7

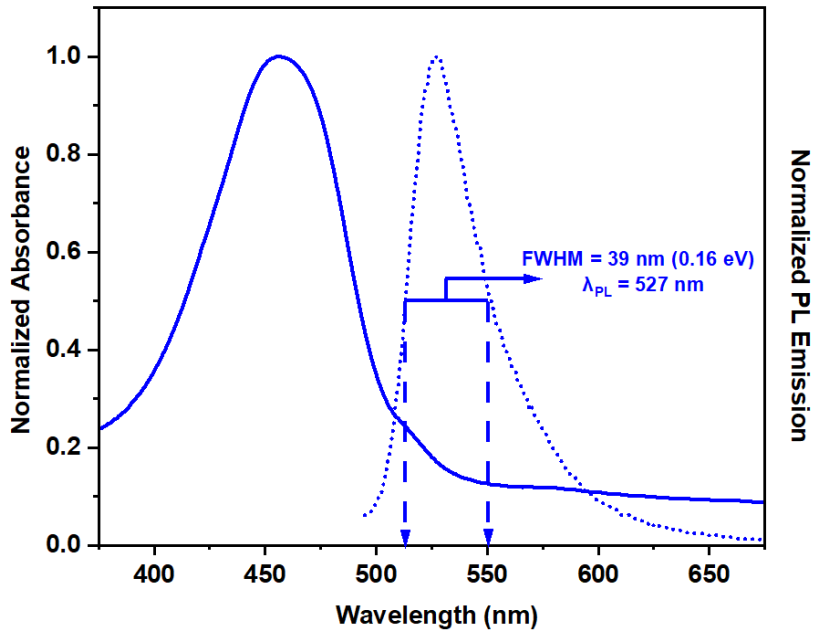


Fig. S23 UV-vis absorbance and photoluminescence spectra of **5** in toluene.

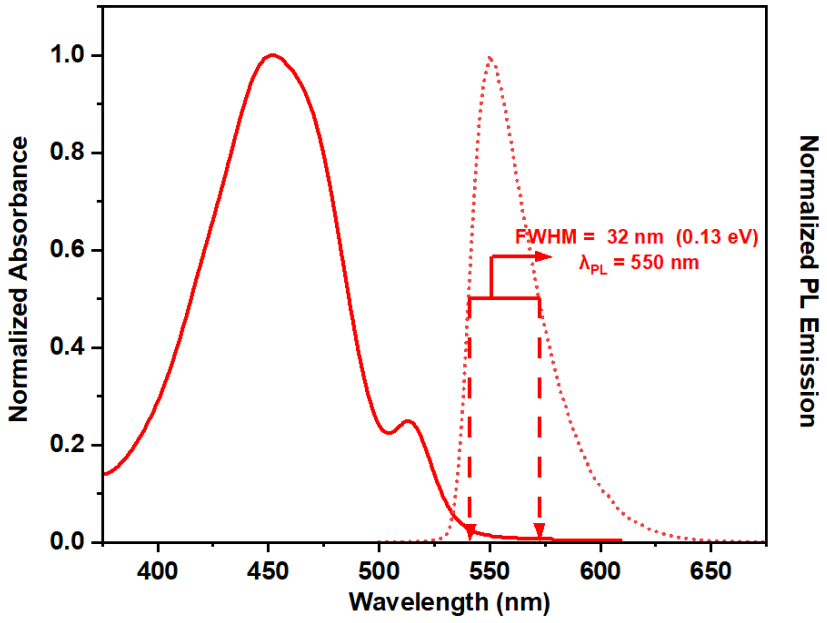


Fig. S24 UV-vis absorbance and photoluminescence spectra of **6** in toluene.

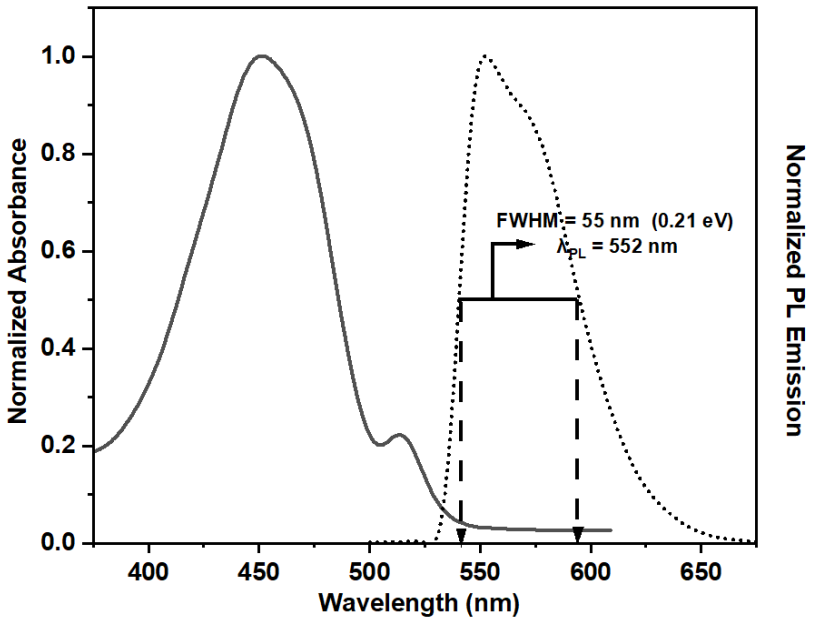


Fig. S25 UV-vis absorbance and photoluminescence spectra of **7** in toluene.

4. Theoretical calculations

All of the calculations were performed with the Gaussian 16 program.[S2] All of the geometry optimizations were performed with the hybrid B3LYP functional in conjunction with the def2-TZVP basis set for Sb, Bi, and Cl atoms and def2-SVP basis set for all other atoms.[S3] To further figure out the absorption properties of **3**-**5**, time-dependent DFT (TD-DFT) calculations were carried out with the hybrid M06-2X (**3**) and B3LYP (**4** and **5**) functionals in conjunction with the def2-TZVP basis set for Sb, Bi, and Cl atoms and def2-SVP basis set for all other atoms. The calculated UV-vis absorption spectra agree well with the experimental data, and the calculated Kohn-Sham orbitals related to the observed transitions are shown in Tables S2-4. To gain further insight into the electronic structures, Multiwfn[S4] and VMD[S5] were also used.

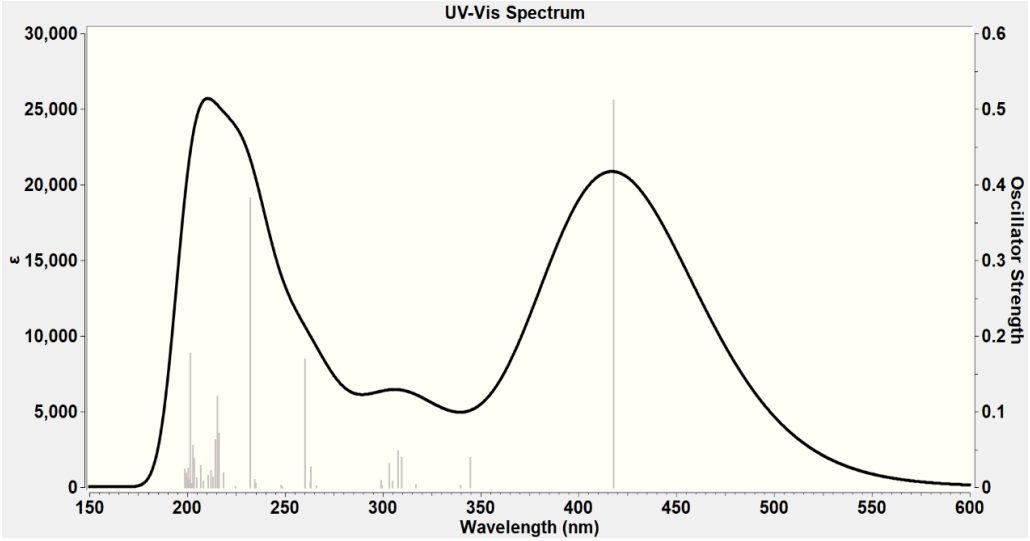


Fig. S26 Calculated UV-vis spectrum of **3** at the M06-2X level of theory with def2-TZVP basis set for Sb and Cl atoms and def2-SVP basis set for all other atoms.

Table S2 Calculated absorption properties of **3** including wavelength (nm), oscillator strength (*f*) and the related transition nature.

Energy /ev	Wavelength /nm	Oscillator strength/ *f*	Transition nature and contributions
2.9679	417.75	0.5112	HOMO→LUMO (0.69031)
3.5982	344.57	0.0393	HOMO-5→LUMO (0.47632) HOMO-7→LUMO (0.40252)
4.0060	309.49	0.0386	HOMO-8→LUMO (0.51201)

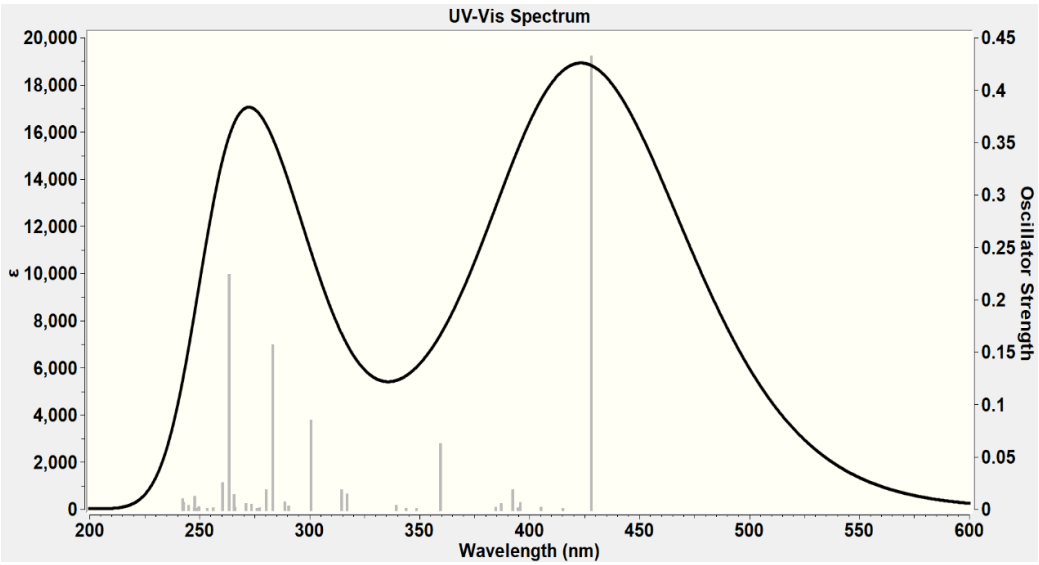


Fig. S27 Calculated UV-vis spectrum of **4** at the B3LYP level of theory with def2-TZVP basis set for Bi and Cl atoms and def2-SVP basis set for all other atoms.

Table S3 Calculated absorption properties of **4** including wavelength (nm), oscillator strength (*f*) and the related transition nature.

Energy /ev	Wavelength /nm	Oscillator strength/ *f*	Transition nature and contributions
2.8971	427.97	0.4319	HOMO→LUMO (0.6759)
3.4482	359.57	0.0216	HOMO-6→LUMO (0.70458)

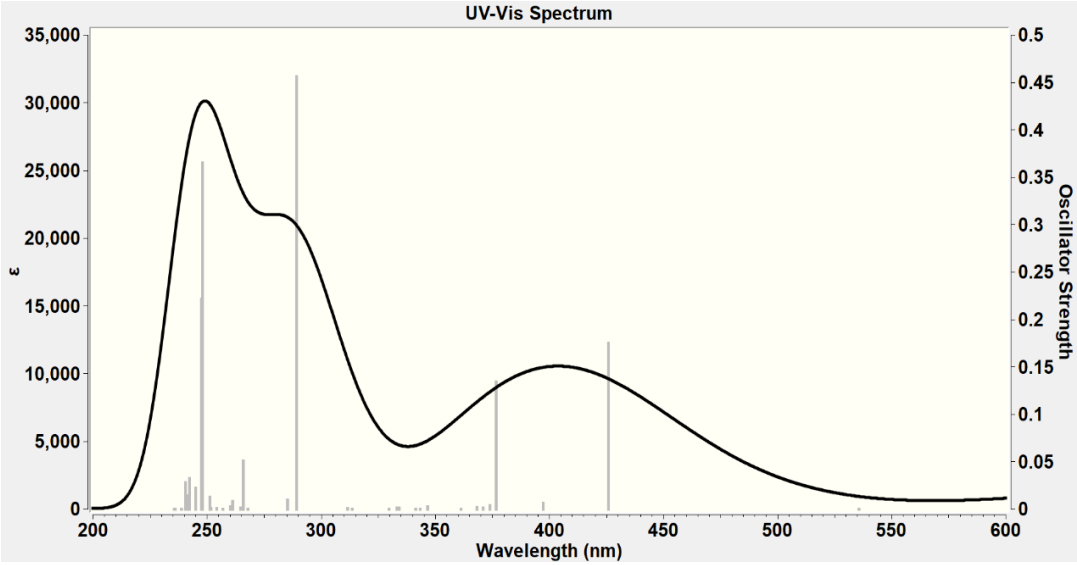
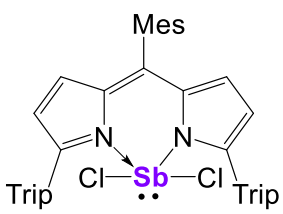


Fig. S28 Calculated UV-vis spectrum of **5** at B3LYP level of theory with def2-TZVP basis set for the Sb atom and def2-SVP basis set for all other atoms.

Table S4 Calculated absorption properties of **5** including wavelength (nm), oscillator strength (*f*) and the related transition nature.

Energy /ev	Wavelength /nm	Oscillator strength/ *f*	Transition nature and contributions
2.9113	425.87	0.1752	HOMO-1→LUMO (0.64831)
3.2912	376.72	0.1340	HOMO→LUMO+4 (0.65476)

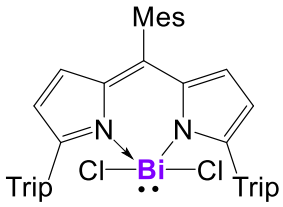
Coordinates of 3-5



Sb	-0.00022200	-0.63358800	-0.00060300	C	-3.69603600	-0.60630300	2.44093500
Cl	0.08669900	-0.33445500	-2.54569000	H	-2.89498300	0.14249100	2.35655100
Cl	-0.08685700	-0.34130500	2.54501900	C	-3.52883500	-0.58719000	-2.69964900
N	1.48564600	0.89026600	0.05235400	H	-2.73960500	0.16560800	-2.55777700
N	-1.48494900	0.89149900	-0.04982500	C	3.80853100	-1.32444200	-1.09558400
C	-3.44089700	-0.68926600	-0.12416200	C	0.04511100	6.50971100	-1.19754100
C	3.44033400	-0.69214800	0.12481400	H	0.07890900	7.05215900	-2.14743700
C	1.25635700	2.27002700	0.04555100	C	-1.25457300	2.27106800	-0.04105200
C	2.82301100	0.66833700	0.10127300	C	-0.04244900	5.10830000	1.22866300
C	-2.82249800	0.67069500	-0.09874800	C	0.04602300	5.10990500	-1.22481100
C	3.49395900	1.91841000	0.12665600	C	3.06532100	-1.50974700	3.84278600
H	4.57333800	2.04417600	0.16653100	H	2.17292600	-2.08638100	3.56129100
C	-3.80967900	-1.32290100	1.09536400	H	2.80240200	-0.90273500	4.72321600
C	-3.49247100	1.92133100	-0.12209500	H	3.85463900	-2.21216400	4.15744700
H	-4.57176400	2.04800800	-0.16140400	C	-0.04127000	6.51118500	1.20137700
C	-3.72910000	-1.31128700	-1.36845600	H	-0.07578900	7.05347700	2.15084800
C	-2.52518200	2.91250800	-0.08638100	C	4.29602500	-2.59782000	1.35511700
H	-2.67571800	3.98961500	-0.09117800	H	4.50693600	-3.09300700	2.30529000
C	-4.61519400	-3.26279800	-0.17212900	C	0.00221000	7.23183700	0.00321100
C	2.52745500	2.91039900	0.09216400	C	-4.37551400	-2.60230500	1.03908300
H	2.67881700	3.98737900	0.09887800	H	-4.64519500	-3.09531400	1.97462900
C	0.00173800	4.40917500	0.00321700	C	-3.06614300	-1.50207800	-3.84316700
C	0.00114300	2.90530600	0.00256500	H	-2.17412100	-2.07963800	-3.56237700
C	3.52850100	-0.59362900	2.70044800	H	-2.80276000	-0.89406600	-4.72276500
H	2.73977600	0.15990400	2.55965900	H	-3.85586600	-2.20359600	-4.15881600
C	-4.29802600	-2.59260300	-1.35708800	C	4.61256200	-3.26669000	0.16923800
H	-4.50927700	-3.08634100	-2.30794000	C	-5.21630200	-4.66235700	-0.20798900
C	3.72812700	-1.31606900	1.36825600	H	-5.32153200	-4.93498700	-1.27245700

C	4.27974800	-5.70356500	-0.44696400
H	3.28563900	-5.70053000	0.02674200
H	4.69929200	-6.71870200	-0.35314700
H	4.13856000	-5.49969000	-1.52111600
C	-0.09097200	4.37739600	2.55004600
H	-0.97803100	3.72837500	2.62365000
H	-0.11691600	5.08480400	3.39118500
H	0.78307400	3.72053900	2.68430600
C	-6.62169700	-4.70543000	0.41635800
H	-6.59359900	-4.46462100	1.49175400
H	-7.06229800	-5.71070800	0.31413500
H	-7.29878000	-3.98572400	-0.06991400
C	3.69545500	-0.60590700	-2.44016800
H	2.89506000	0.14346900	-2.35474800
C	4.37333100	-2.60438300	-1.04106900
H	4.64255700	-3.09634500	-1.97729800
C	0.09332400	4.37662400	-2.54488100
H	0.97907600	3.72569100	-2.61705000
H	0.12073200	5.08248700	-3.38728200
H	-0.78193200	3.72114100	-2.67794600
C	3.31442300	-1.52654400	-3.60880400
H	4.12660100	-2.22541500	-3.86859200
H	3.10789000	-0.92272700	-4.50623900
H	2.40803000	-2.10722700	-3.38633200
C	4.82023700	0.14811500	3.10098800
H	5.64848600	-0.56200100	3.26142900
H	4.66855700	0.70818100	4.03834700
H	5.13941900	0.86394100	2.32876100
C	-4.82001300	0.15600000	-3.09929700

H	-5.64875400	-0.55330800	-3.26077200
H	-4.66785800	0.71723500	-4.03588100
H	-5.13874600	0.87099600	-2.32611100
C	0.00608600	8.74132400	-0.00781100
H	0.92726100	9.13493200	-0.46952000
H	-0.06294000	9.15482300	1.00901700
H	-0.83971000	9.13942300	-0.59275000
C	-5.00701900	0.14248400	2.75669200
H	-5.26917100	0.86282700	1.96739500
H	-4.91501100	0.69874400	3.70401500
H	-5.84861400	-0.56274000	2.85867800
C	5.21251100	-4.66679300	0.20318600
H	5.31770600	-4.94088000	1.26728300
C	5.00707500	0.14218000	-2.75492800
H	5.26985600	0.86120000	-1.96463100
H	4.91552300	0.69983300	-3.70147900
H	5.84806300	-0.56362300	-2.85791000
C	-4.28453800	-5.70075200	0.44100100
H	-3.29034300	-5.69796100	-0.03252500
H	-4.70493100	-6.71540900	0.34581200
H	-4.14336500	-5.49837300	1.51543800
C	-3.31587100	-1.52888200	3.60832300
H	-4.12870300	-2.22735300	3.86713700
H	-3.10882800	-0.92647700	4.50659100
H	-2.41000900	-2.11008800	3.38506900
C	6.61775300	-4.71025500	-0.42147600
H	6.58966400	-4.46806700	-1.49656200
H	7.05752700	-5.71603100	-0.32060400
H	7.29553000	-3.99173300	0.06558000



Bi	-0.00000300	-0.68953200	0.04332100
Cl	-0.00000100	-0.51877700	-2.59693100
Cl	-0.00000300	-0.47781300	2.67512400
N	1.51599600	0.95486900	0.02234700
N	-1.51599400	0.95487700	0.02234600
C	-3.48377900	-0.59835500	0.08120100
C	0.00000600	2.95344400	-0.05335400
C	1.26275800	2.32833400	-0.02888800
C	2.52573300	2.99061400	-0.05011200
H	2.66069100	4.06907500	-0.08852300
C	-3.81242800	-1.18132100	1.33530300
C	-2.85526700	0.75675000	0.03210300
C	-3.65368300	-0.41368400	2.64801500
H	-2.82932700	0.30345400	2.51918100
C	3.48377600	-0.59837000	0.08120500
C	0.00000900	4.45747000	-0.11253100
C	2.85526900	0.75673700	0.03210900
C	3.50945800	2.01641300	-0.01181100
H	4.58715600	2.16172100	-0.01440400
C	0.00001900	5.10805800	-1.36514500
C	0.00001200	6.60435700	1.00502200
H	0.00001100	7.18383700	1.93343300
C	3.81267700	-1.27161800	-1.12941300

C	3.65527700	-0.59730800	-2.49285700
H	2.83547700	0.13213500	-2.41496700
C	-4.38066100	-2.54924400	-1.05046600
H	-4.61977100	-3.07243500	-1.97772500
C	-4.66069500	-3.17022400	0.17291500
C	0.00002000	7.27860200	-0.22398000
C	-4.38144800	-2.46274200	1.34589300
H	-4.62330500	-2.92668000	2.30421000
C	-3.50945100	2.01642700	-0.01182400
H	-4.58714800	2.16174100	-0.01442200
C	-3.81268100	-1.27160500	-1.12941700
C	-1.26274900	2.32834000	-0.02889200
C	-2.52572100	2.99062500	-0.05012300
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C	-3.65527600	-0.59729800	-2.49286100
H	-2.83547400	0.13214200	-2.41497100
C	3.81242200	-1.18133900	1.33530700
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H	-7.09582900	-5.62979600	-0.31301400

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H	-0.00000500	5.26512500	3.25059500
H	0.88164400	3.87853000	2.56462500
C	-5.26502500	-4.56758600	0.23382700
H	-5.40430700	-4.80647200	1.30245400
C	4.38065300	-2.54925900	-1.05046400
H	4.61976400	-3.07244900	-1.97772400
C	4.31550400	-5.62698800	-0.35250000
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H	4.13908900	-5.45821000	-1.42754300
C	4.94037200	0.17600200	-2.85386800
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H	4.81649600	0.70139800	-3.81500800
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C	3.28946000	-1.29765700	3.84986600
H	2.40948000	-1.92212500	3.64156900
H	3.04596000	-0.66342600	4.71648400
H	4.12473800	-1.95092200	4.15163300
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H	-4.81012600	0.98005300	3.87406100
H	-5.79600300	-0.28430500	3.09543300
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H	-4.81648900	0.70141000	-3.81501700
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H	3.04079800	-0.98900600	-4.53725800
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C	4.38143800	-2.46276200	1.34589500
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H	4.81012400	0.98002500	3.87407200
H	5.18799300	1.08585700	2.13831100
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C	5.26500800	-4.56760700	0.23382500

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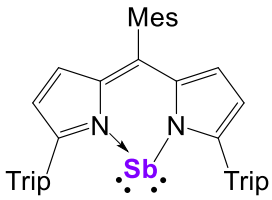

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