Supporting Information

for

Donor Stabilized Antimony(I) and Bismuth(I) Ions: Heavier Valence Isoelectronic Analogues of Carbones

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(S1) Experimental Section

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. THF, hexane and toluene were distilled over Na/K alloy (25:75), while diethyl ether was distilled over potassium mirror. Deuterated NMR solvents C_6D_6 and THF-d_8 were dried by stirring for 2 days over Na/K alloy followed by distillation in vacuum and degassed. ^{1}H, ^{13}C{1H} NMR spectra were recorded on Bruker Avance 200, Bruker Avance 300, and Bruker Avance 500 MHz NMR spectrometers and were referenced to the resonances of the solvent used. Micro analyses were performed by the Analytisches Labor für Anorganische Chemie für Universität Göttingen. Melting points were determined in sealed glass capillaries under dinitrogen, and are uncorrected. LIFDI measurements were performed on a Joel AccuTOF spectrometer under inert atmosphere. cAAC was prepared by literature procedure,[S1] while all other reagents were used as received.

[(cAAC)$_2$Sb][OTf] (**1**): A mixture of cAAC.LiOTf (442 mg, 2 mmol), SbF_3 (338 mg, 1 mmol) and KC_8 (562 mg, 2.10 mmol) were taken in a 100 mL round bottom flask and 50 mL of toluene was added at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. After filtration of insoluble residue, the solvent was concentrated to 15 mL under high vacuum. The flask was stored at -30 °C for 4 days to obtain X-ray quality purple crystals of **1** (Yield: 426 mg, 48 %). Mp: 193 - 195 °C.

^{1}H NMR (C_6D_6, 298 K, 300 MHz, δppm): 6.85–7.04 (m, 6 H, Ar*H*), 2.43 (sept, 4 H, C*H*Me$_2$), 2.12 (s, 4 H, C*H$_2$*), 1.72 (s, 12 H, CH*Me$_2$*), 1.12 (s, 12H, C*H*$_3$), 1.06 (d, 12 H, CH*Me$_2$*), 1.06 (s, 12 H, CH*Me$_2$*).

^{13}C NMR (C_6D_6, 298 K, 125 MHz, δppm) 240.20, 145.18, 132.94, 130.45, 129.26, 128.49, 126.52, 80.89, 56.61, 52.34, 31.93, 28.90, 28.71, 27.57, 25.01.

^{19}F NMR (C_6D_6, 298 K, 125 MHz, δppm) : -77.26.

MS (LIFDI, toluene): *m/z* = 691.4 $[M\text{-}OTf]^+$.

Anal (%). calcd for $C_{44.5}H_{66}F_3N_2O_3SSb$ (887.80): C, 60.24; H, 7.50; N, 3.15, Found: C, 59.47; H, 7.08; N, 2.74.

[(cAAC)$_2$Bi][OTf] (**2**): A mixture of cAAC.LiOTf (442 mg, 2 mmol), $BiCl_3$ (338 mg, 1 mmol) and KC_8 (562 mg, 2.10 mmol) were placed in a 100 mL round bottom flask and 50 mL of diethyl ether was added at -100 °C. The reaction mixture was allowed to warm to -30

°C slowly and stirred at the same temperature until all the KC_8 was consumed, to give a deep blue solution of compound **2**. After filtration of insoluble residue, the solvent was concentrated to 15 mL under high vacuum. The flask was stored at -30 °C for 2 days to obtain X-ray quality blue needle shaped crystals of **2** (Yield: 240 mg, 30 %). Mp: Decomp. at 202-205 °C.

^{1}H NMR (THF-d_8, 298 K, 500 MHz, δppm): 7.39 (t, 2 H, Ar*H*), 7.22 (d, 4 H, Ar*H*), 2.76 (sept, 4 H, C*H*Me$_2$), 2.37 (s, 4 H, CH_2), 1.68 (5, 12 H, CH_3), 1.47 (s, 12 H, CH_3), 1.27 (d, 12 H, CHMe_2), 1.20 (d, 12 H, CHMe_2).

^{13}C NMR (THF-d_8, 298 K, 125 MHz, δppm) 281.69, 146.9, 134.21, 131.28, 127.95, 123.12, 120.57, 87.05, 64.86, 52.09, 35.35, 32.24, 30.38, 29.47.

^{19}F NMR (THF-d_8, 298 K, 125 MHz, δppm): - 79.29.

Anal (%). calcd for $C_{41}H_{62}BiF_3N_2OS$ (928.42): C, 54.90; H, 6.97; N, 3.12, Found: C, 54.29; H, 7.08; N, 3.34.

Supporting Figures:

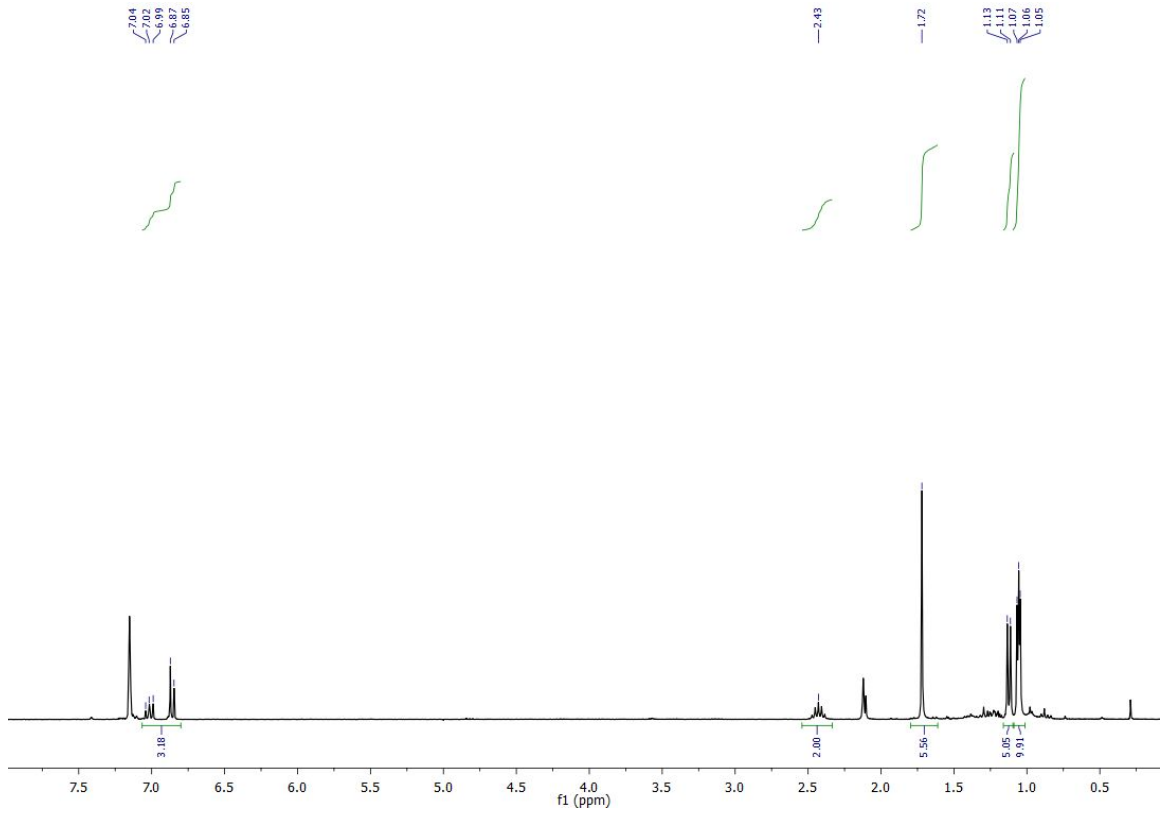


Figure S1. ^{1}H NMR spectrum of **1** at 298 K.

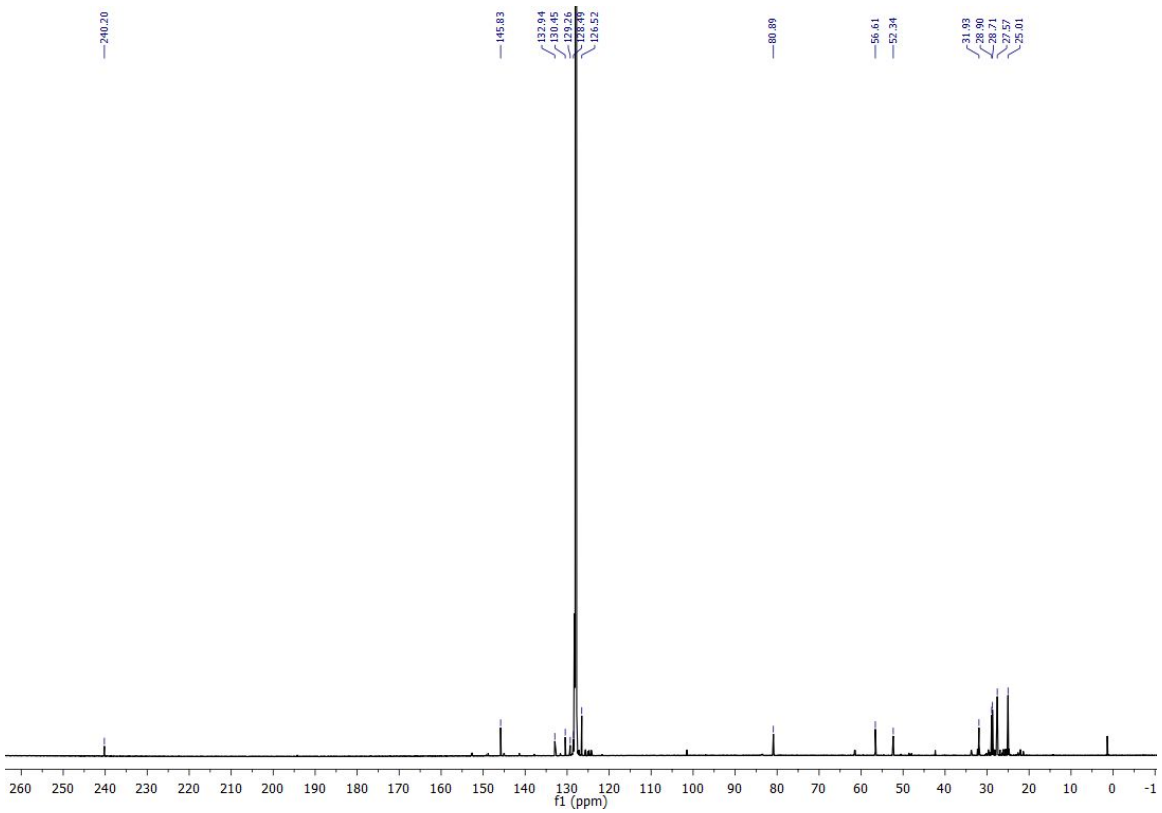


Figure S2. ^{13}C NMR spectrum of **1** at 298 K.

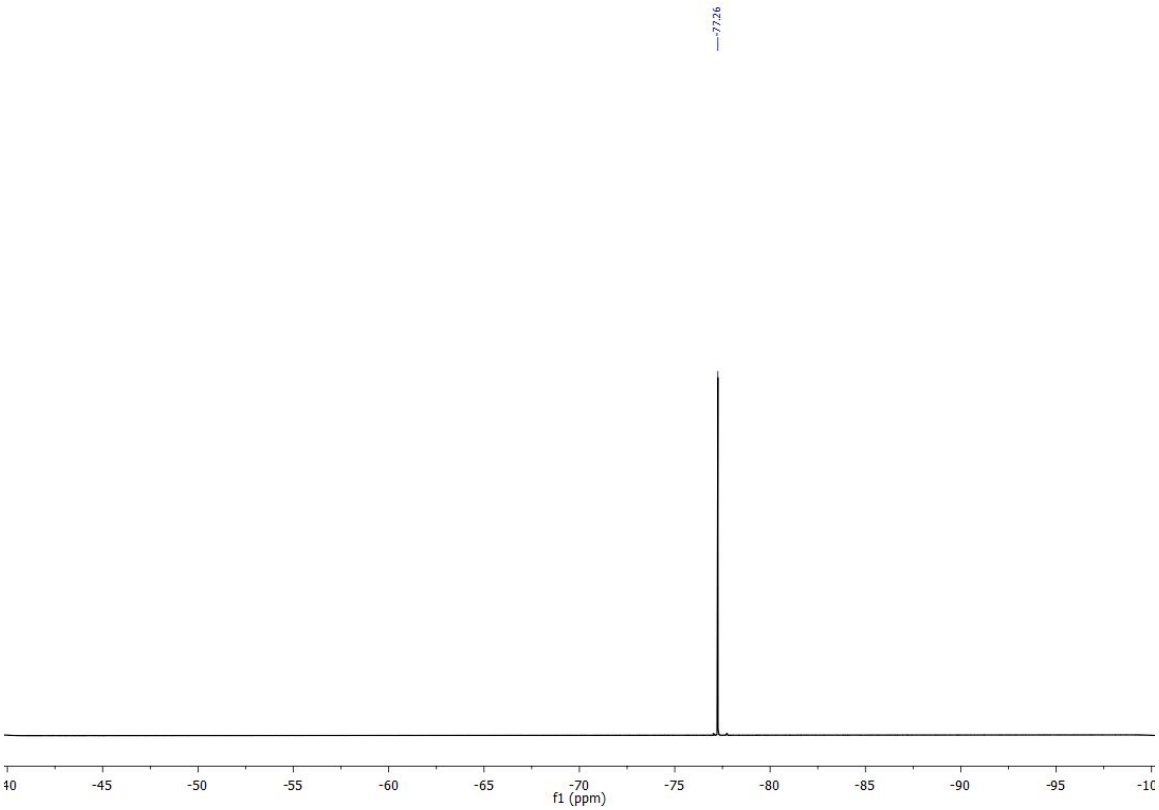


Figure S3. ^{19}F NMR spectrum of **1** at 298 K.

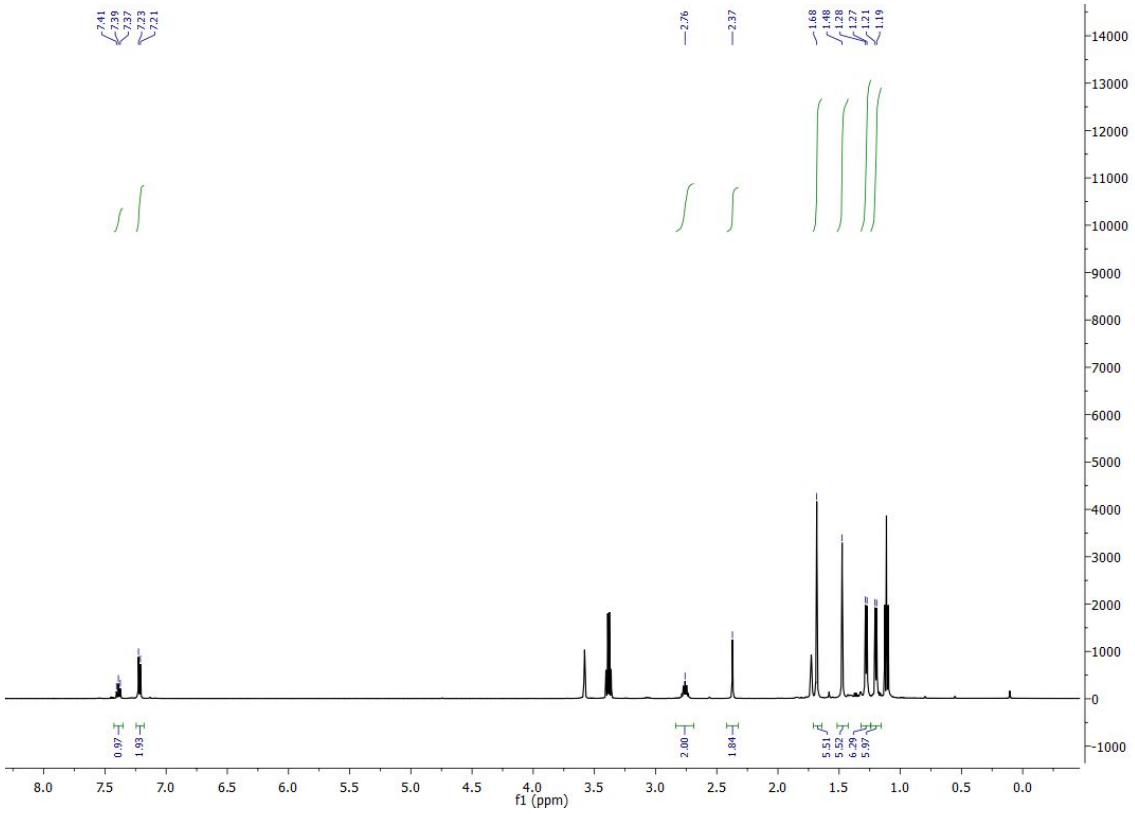


Figure S4. ^{1}H NMR spectrum of **2** at 298 K.

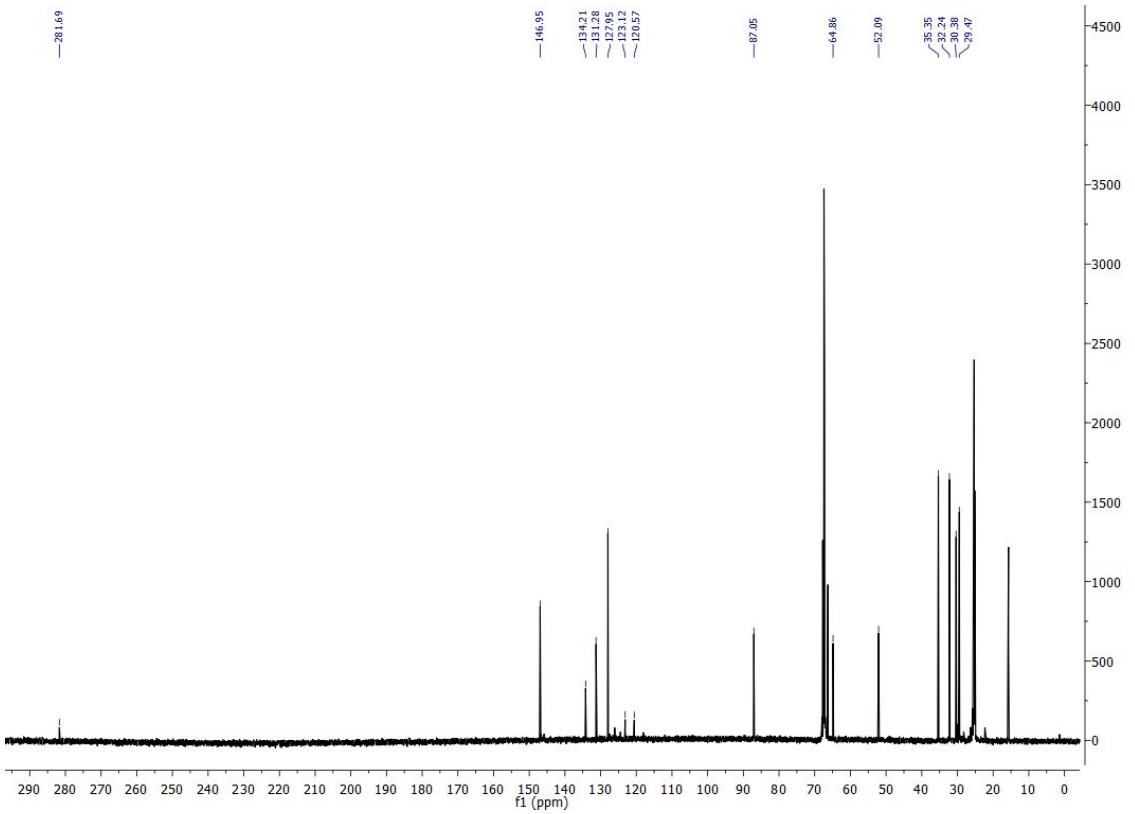


Figure S5. ^{13}C NMR spectrum of **2** at 298 K.

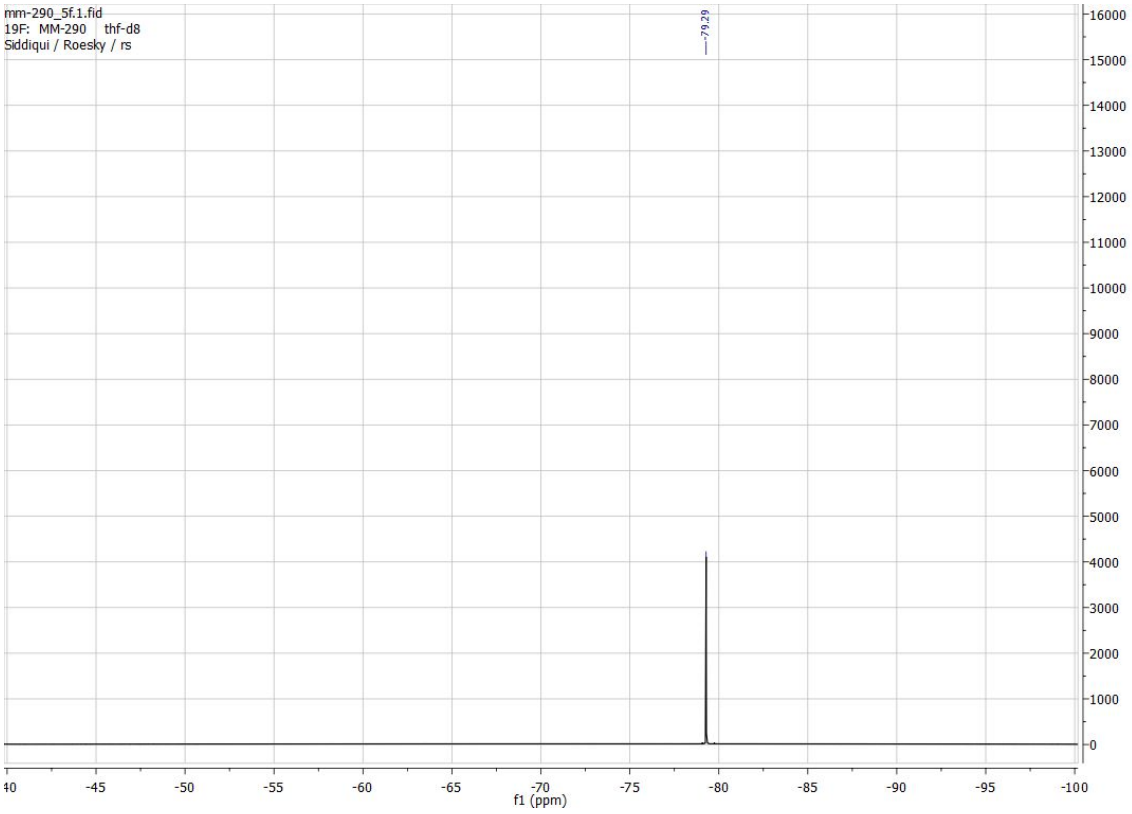


Figure S6. ^{19}F NMR of spectrum**2** at 298 K.

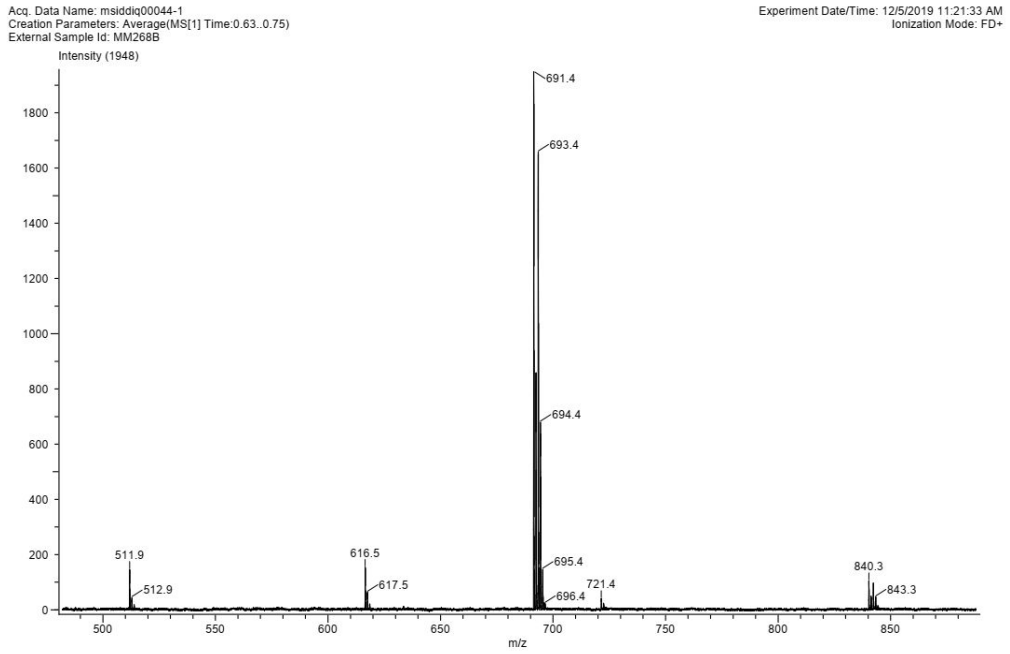


Figure S7. LIFDI mass spectrum of **1**.

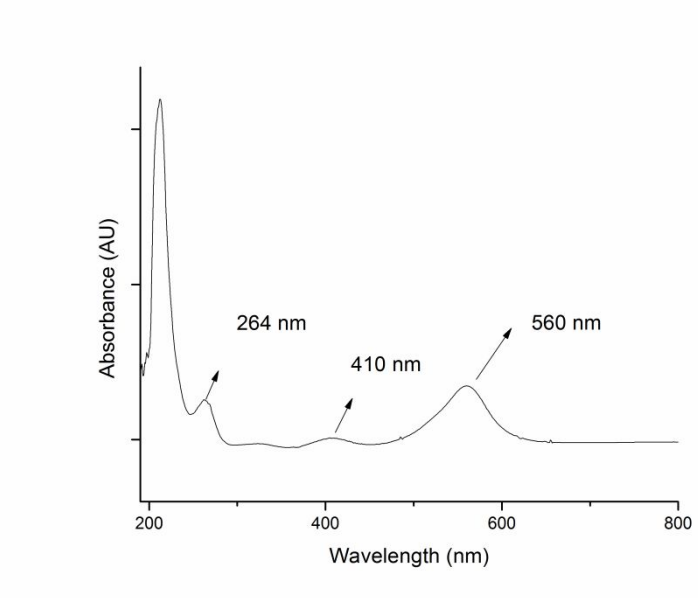


Figure S8. UV-Vis spectrum of **1** in toluene.

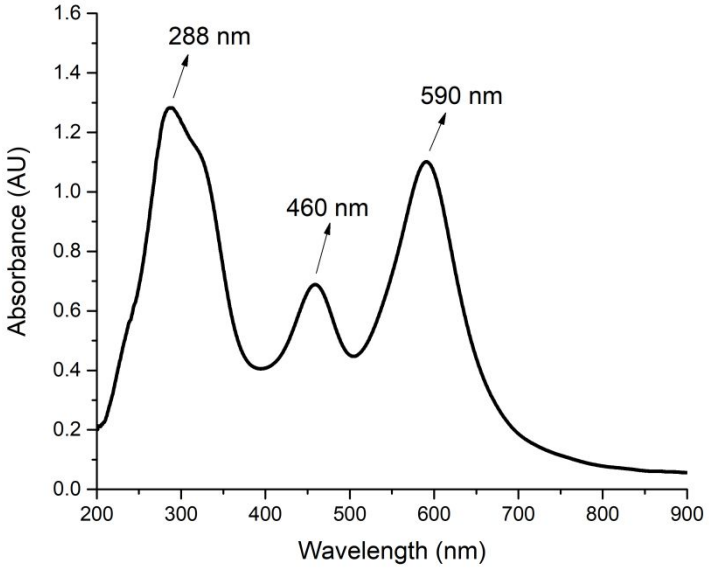


Figure S9. UV-Vis spectrum of **2** in diethylether.

Electrochemical Studies:

Cyclic voltammograms were recorded at room temperature in a nitrogen-filled glovebox, using a Gamry Interface 1000B potentiostat and the Gamry Framework software. Dry and degassed acetonitrile and THF were employed as solvents. Tetrabutylammonium hexafluorophosphate was dried at 120°C under vacuum for 48 hours and used as electrolyte. An ALS Glassy Carbon electrode (1.6 mm diameter) was chosen as working electrode, and platinum wires as counter and pseudo-reference electrodes. Ferrocene was added to the analyte solution after the measurements and the potentials referenced accordingly.

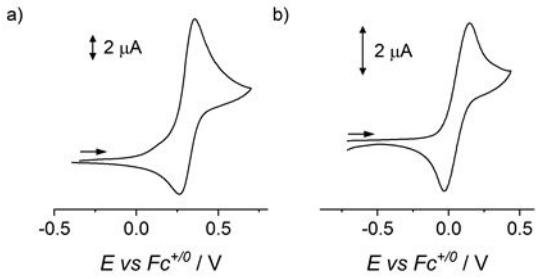


Figure 10. Cyclic voltammograms of the oxidative regions of compound **1** (a) and **2** (b). All the measurements were performed at room temperature, using dry and degassed solvents (CH_3CN for **1** and THF for **2**) and tetrabutylammonium hexafluorophosphate as electrolyte (0.1 M and 0.2 M for **1** and **2** respectively).

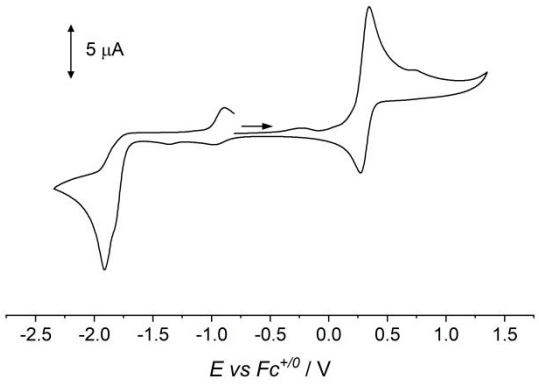


Figure S11: Cyclic voltammogram of compound **1** in 0.1 M tetrabutylammonium hexafluorophosphate in dry and degassed CH_3CN at room temperature. The scan was started at the open circuit potential. Potentials are referenced versus $Fc^{+/0}$.

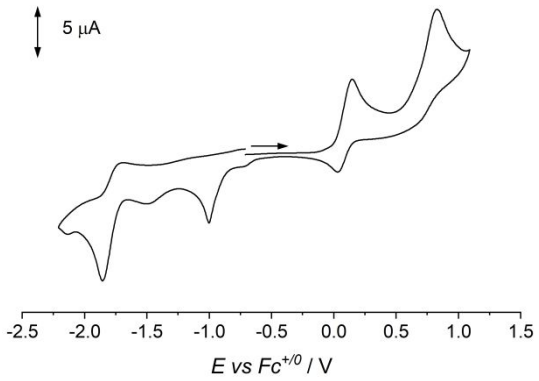


Figure S12: Cyclic voltammogram of compound **2** in 0.2 M tetrabutylammonium hexafluorophosphate in dry and degassed THF at room temperature. The scan was started at the open circuit potential. Potentials are referenced versus $Fc^{+/0}$.

(S2) X-ray crystallographic analysis

All crystals were selected under cooling using the X-Temp2 device.[S2] The datasets were collected on an Incoatec Mo Microsource[S3] with mirror optics and an APEX II detector with a D8 goniometer. The data were integrated with SAINT.[S4] A multi-scan absorption correction was applied using SADABS.[S5] The structures were solved by SHELXT[S6] and refined on F^2 using SHELXL[S7] in the graphical user interface ShelXle.[S8] Hydrogen atoms were refined using a riding model. Disordered groups were refined with distances restraints and restraints for the displacement parameters. The Crystallographic Information Files (CIF) can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ structures/ using the reference numbers 2023671 (**1**) and 2023670 (**2**). A CIF file for a refinement of **1** in a larger unit cell discussed below can be found using the reference number 2023672.

Table S1 Crystal data and structure refinement of **1** and **2**.

Parameter	Compound **1**	Compound **2**
Empirical formula	$C_{44.5}H_{66}F_3N_2O_3SSb$	$C_{51}H_{82}BiF_9Li_2N_2O_{11}S_3$
Formula Weight	887.80	1389.22
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions	a = 9.189(2) Å	a = 24.689(2) Å
	b = 15.330(2) Å	b = 9.342(2) Å
	c = 32.284(4) Å	c = 27.653(3) Å
	b = 92.02(2)°.	b = 98.07(2)°
Volume	4544.9 (13) Å^3	6314.9(16) Å^3
Z	4	4
Density ρcalc [Mg/m^3]	1.297	1.461
Absorption coefficient [mm^{-1}]	0.704	2.971
F (000)	1860	2832
Crystal size [mm]	0.704 x 0.109 x 0.040	0.182 x 0.084 x 0.045
Theta range for data collection [°]	1.262 to 27.154	1.192 to 25.033
Index ranges	-11 ≤h≤11, -19≤k≤19, -41≤l≤41	-29≤h≤29, -11≤k≤11, -32≤l≤32

Reflections collected	80806	126568
Independent reflections	10055 [R(int) = 0.0498]	11157 [R(int) = 0.0721]
Completeness	100.0 %	100.0 %
Refinement Method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	10055 / 2052 / 823	11157 / 426 / 820
Goodness-of-fit on F^2	1.021	1.015
Final R indices [I>2σ(I)]	R1 = 0.0274, wR2 = 0.0598	R1 = 0.0253, wR2 = 0.0480
R indices (all data)	R1 = 0.0373, wR2 = 0.0646	R1 = 0.0370, wR2 = 0.0512
Max. and min. resd. density ($eÅ^{-3}$)	0.797 and -0.364	0.616 and -0.474

The structure of **1** can be solved and refined within two unit cells, related by the transformation

$$\vec{a}_{\text{large}} = \begin{pmatrix} -2 & 0 & 0 \\ 0 & -1 & 0 \\ 1 & 0 & 1 \end{pmatrix} \cdot \vec{a}_{\text{small}}$$

Small cell: a = 9.189(2), b = 15.330(2), c = 32.284(4), β = 92.02(2)°.

Large cell:a = 18.376(2), b = 15.329(2), c = 33.250(4), β =104.01(2)°

In the large cell there are two cations, two anions and one toluene molecules in the asymmetric unit. One triflate anion is disordered over three positions. The occupancies for the positions refined to 0.380(2), 0.313(2) and 0.308(2). The toluene molecule is disordered over four positions. The occupancies to 0.472(3), 0.261(3), 0.103(3) and 0.164(3). Verification of the final model using checkcif produces the following C-Alert:

112_ALERT_2_CADDSYM Detects New (Pseudo) Symm. Elem a/2 91 %Fit

In the small cell one cation, one disordered anion and half a disordered toluene molecule on an inversions centre are found. The modelling of the disorder of the triflate anion was unsatisfactory. However, after transforming the coordinates of the larger cell to coordinates of the smaller cell, the modelling of the disordered parts became much better. The occupancies for the four triflate positions refined to 0.518(2), 0.130(2), 0.193(2) and 0.160(2). The toluene molecule is disordered over four positions, two of which are connected by the inversions centre. The occupancy of the main part refined to 0.283(4).

We decided for the refinement in the smaller cell as final model, because the description of the interesting cation seems to be superior. In the smaller cell, C-C bond precision of the final model is slightly higher while highest residual density peak and final R-factor are slightly lower.

Table S2 Comparison of selected quality indicator of the final model of **1** in the large and the small unit cell.

Parameter	Small cell	Large cell
C-C bond precision [Å]	0.0031	0.0039
Final R indices [I > 2σ (I)]	*R1* = 0.0274, *wR2* = 0.0598	*R1* = 0.0334, *wR2* = 0.0716
R indices (all data)	*R1* = 0.0373, *wR2* = 0.0646	*R1* = 0.0589, *wR2* = 0.0828
Max. and min.resd. density [eÅ^{-3}]	0.797 and -0.364	1.339 and -0.851

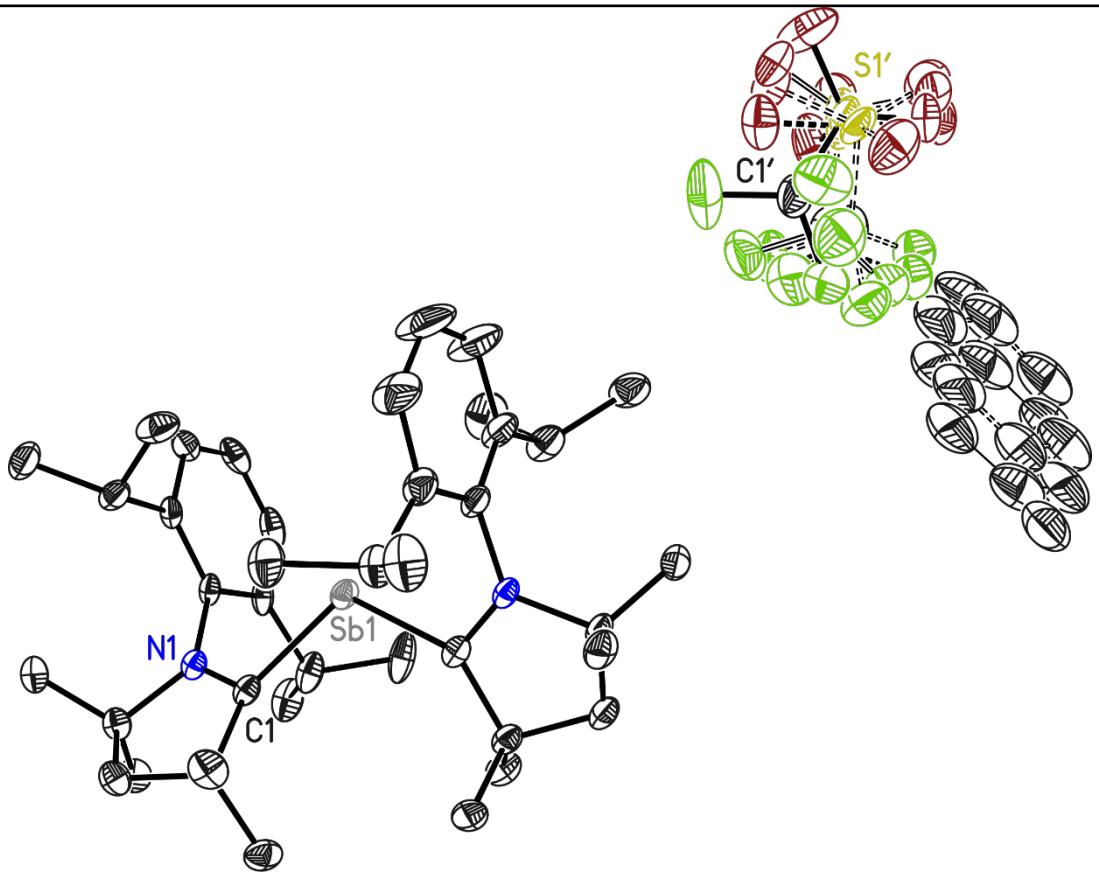


Figure S13.Asymmetric unit of **1** in the smaller cell. Anisotropic displacement parameters are displayed at the 50% probability level. Hydrogen atoms are omitted for clarity.

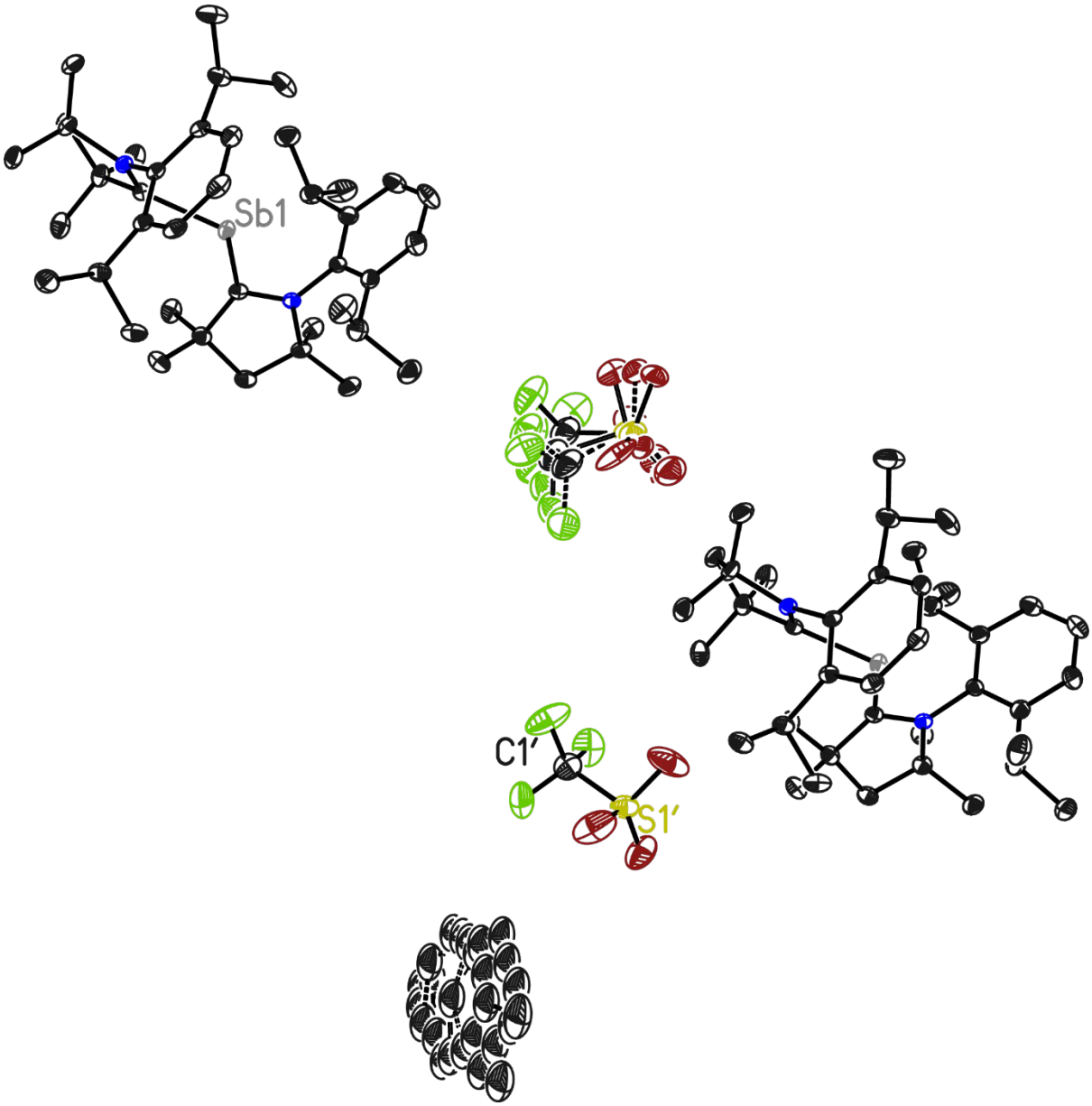


Figure S14. Asymmetric unit of **1** in the larger cell. Anisotropic displacement parameters are displayed at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table S3 Bond lengths and angles for **1**.

Sb(1)-C(1)	2.145(2)	C(2)-C(6)	1.537(3)
Sb(1)-C(21)	2.1498(18)	C(2)-C(3)	1.539(3)
C(1)-N(1)	1.322(2)	C(2)-C(5)	1.541(3)
C(1)-C(2)	1.526(3)	C(3)-C(4)	1.534(3)
N(1)-C(9)	1.462(2)	C(7)-C(4)	1.526(3)
N(1)-C(4)	1.527(2)	C(4)-C(8)	1.518(3)
N(2)-C(21)	1.318(2)	C(15)-C(10)	1.527(3)
N(2)-C(29)	1.457(2)	C(15)-C(17)	1.534(3)
N(2)-C(24)	1.528(2)	C(15)-C(16)	1.542(3)

C(14)-C(13)	1.397(3)	S(2')-C(2')	1.836(14)
C(14)-C(9)	1.411(2)	C(2')-F(5')	1.322(12)
C(14)-C(18)	1.520(3)	C(2')-F(4')	1.344(13)
C(13)-C(12)	1.375(3)	C(2')-F(6')	1.387(13)
C(12)-C(11)	1.382(3)	S(3')-O(7')	1.426(12)
C(11)-C(10)	1.401(3)	S(3')-O(8')	1.432(12)
C(10)-C(9)	1.409(3)	S(3')-O(9')	1.449(12)
C(29)-C(30)	1.408(3)	S(3')-C(3')	1.851(13)
C(29)-C(34)	1.410(3)	C(3')-F(7')	1.295(11)
C(28)-C(24)	1.530(3)	C(3')-F(8')	1.329(11)
C(27)-C(24)	1.523(3)	C(3')-F(9')	1.347(12)
C(26)-C(22)	1.535(3)	S(4')-O(12')	1.384(10)
C(25)-C(22)	1.539(3)	S(4')-O(11')	1.428(11)
C(24)-C(23)	1.523(3)	S(4')-O(10')	1.434(11)
C(23)-C(22)	1.544(3)	S(4')-C(4')	1.887(12)
C(22)-C(21)	1.526(3)	C(4')-F(11')	1.337(12)
C(20)-C(18)	1.539(3)	C(4')-F(12')	1.393(13)
C(19)-C(18)	1.539(3)	C(4')-F(10')	1.393(12)
C(30)-C(31)	1.396(3)	F(10')-C(6T)	1.833(18)
C(30)-C(35)	1.524(3)	C(1T)-C(2T)	1.369(14)
C(31)-C(32)	1.378(4)	C(1T)-C(6T)	1.364(12)
C(32)-C(33)	1.375(4)	C(1T)-C(7T)	1.538(17)
C(33)-C(34)	1.393(3)	C(2T)-C(3T)	1.402(14)
C(34)-C(38)	1.525(3)	C(3T)-C(4T)	1.383(13)
C(35)-C(36)	1.538(3)	C(4T)-C(5T)	1.350(14)
C(35)-C(37)	1.540(3)	C(5T)-C(6T)	1.361(12)
C(38)-C(39)	1.532(3)	C(1T')-C(6T')	1.371(14)
C(38)-C(40)	1.537(3)	C(1T')-C(2T')	1.373(14)
S(1')-O(2')	1.436(6)	C(1T')-C(7T')	1.57(2)
S(1')-O(1')	1.437(5)	C(2T')-C(3T')	1.379(14)
S(1')-O(3')	1.448(6)	C(3T')-C(4T')	1.362(14)
S(1')-C(1')	1.811(6)	C(4T')-C(5T')	1.376(14)
C(1')-F(2')	1.323(5)	C(5T')-C(6T')	1.404(13)
C(1')-F(1')	1.338(5)		
C(1')-F(3')	1.386(7)	C(1)-Sb(1)-C(21)	111.87(7)
S(2')-O(6')	1.426(13)	N(1)-C(1)-C(2)	109.67(16)
S(2')-O(5')	1.429(13)	N(1)-C(1)-Sb(1)	114.24(13)
S(2')-O(4')	1.439(13)	C(2)-C(1)-Sb(1)	134.33(13)

C(1)-N(1)-C(9)	123.10(16)	C(23)-C(24)-N(2)	100.02(15)
C(1)-N(1)-C(4)	114.59(15)	C(27)-C(24)-N(2)	112.54(15)
C(9)-N(1)-C(4)	122.27(14)	C(23)-C(24)-C(28)	114.68(16)
C(21)-N(2)-C(29)	124.06(16)	C(27)-C(24)-C(28)	108.12(17)
C(21)-N(2)-C(24)	114.67(15)	N(2)-C(24)-C(28)	109.49(15)
C(29)-N(2)-C(24)	121.15(15)	C(24)-C(23)-C(22)	107.54(15)
C(1)-C(2)-C(6)	111.09(16)	C(21)-C(22)-C(26)	111.68(16)
C(1)-C(2)-C(3)	102.56(15)	C(21)-C(22)-C(25)	110.56(16)
C(6)-C(2)-C(3)	111.18(17)	C(26)-C(22)-C(25)	110.26(17)
C(1)-C(2)-C(5)	110.85(16)	C(21)-C(22)-C(23)	102.26(16)
C(6)-C(2)-C(5)	111.04(17)	C(26)-C(22)-C(23)	111.40(16)
C(3)-C(2)-C(5)	109.84(16)	C(25)-C(22)-C(23)	110.45(16)
C(4)-C(3)-C(2)	107.14(15)	N(2)-C(21)-C(22)	109.81(16)
C(8)-C(4)-C(7)	108.71(16)	N(2)-C(21)-Sb(1)	114.15(13)
C(8)-C(4)-N(1)	112.09(16)	C(22)-C(21)-Sb(1)	134.21(14)
C(7)-C(4)-N(1)	110.25(15)	C(31)-C(30)-C(29)	117.2(2)
C(8)-C(4)-C(3)	112.14(16)	C(31)-C(30)-C(35)	117.6(2)
C(7)-C(4)-C(3)	113.77(17)	C(29)-C(30)-C(35)	125.16(19)
N(1)-C(4)-C(3)	99.71(14)	C(32)-C(31)-C(30)	121.4(2)
C(10)-C(15)-C(17)	111.21(17)	C(33)-C(32)-C(31)	120.2(2)
C(10)-C(15)-C(16)	110.97(17)	C(32)-C(33)-C(34)	121.6(2)
C(17)-C(15)-C(16)	108.71(18)	C(33)-C(34)-C(29)	117.2(2)
C(13)-C(14)-C(9)	116.99(19)	C(33)-C(34)-C(38)	118.04(19)
C(13)-C(14)-C(18)	118.49(17)	C(29)-C(34)-C(38)	124.64(19)
C(9)-C(14)-C(18)	124.47(18)	C(30)-C(35)-C(36)	112.0(2)
C(12)-C(13)-C(14)	122.17(18)	C(30)-C(35)-C(37)	110.83(19)
C(13)-C(12)-C(11)	120.06(18)	C(36)-C(35)-C(37)	107.87(19)
C(12)-C(11)-C(10)	120.9(2)	C(34)-C(38)-C(39)	113.20(19)
C(11)-C(10)-C(9)	117.91(17)	C(34)-C(38)-C(40)	109.85(18)
C(11)-C(10)-C(15)	117.11(18)	C(39)-C(38)-C(40)	109.01(17)
C(9)-C(10)-C(15)	124.94(16)	C(14)-C(18)-C(20)	111.95(17)
C(10)-C(9)-C(14)	121.90(17)	C(14)-C(18)-C(19)	111.2(2)
C(10)-C(9)-N(1)	119.03(15)	C(20)-C(18)-C(19)	109.05(17)
C(14)-C(9)-N(1)	119.06(17)	O(2')-S(1')-O(1')	113.9(5)
C(30)-C(29)-C(34)	122.15(19)	O(2')-S(1')-O(3')	113.5(5)
C(30)-C(29)-N(2)	118.94(17)	O(1')-S(1')-O(3')	116.5(5)
C(34)-C(29)-N(2)	118.91(17)	O(2')-S(1')-C(1')	105.4(4)
C(23)-C(24)-C(27)	111.90(16)	O(1')-S(1')-C(1')	101.1(3)

O(3')-S(1')-C(1')	104.4(4)	O(12')-S(4')-O(10')	108.9(9)
F(2')-C(1')-F(1')	107.4(4)	O(11')-S(4')-O(10')	116.2(12)
F(2')-C(1')-F(3')	110.7(4)	O(12')-S(4')-C(4')	110.1(7)
F(1')-C(1')-F(3')	102.7(4)	O(11')-S(4')-C(4')	106.4(9)
F(2')-C(1')-S(1')	112.9(3)	O(10')-S(4')-C(4')	94.7(9)
F(1')-C(1')-S(1')	111.3(4)	F(11')-C(4')-F(12')	91.9(12)
F(3')-C(1')-S(1')	111.3(4)	F(11')-C(4')-F(10')	114.0(12)
O(6')-S(2')-O(5')	115.0(16)	F(12')-C(4')-F(10')	93.0(11)
O(6')-S(2')-O(4')	119.9(16)	F(11')-C(4')-S(4')	116.2(10)
O(5')-S(2')-O(4')	109.4(15)	F(12')-C(4')-S(4')	107.4(10)
O(6')-S(2')-C(2')	101.1(12)	F(10')-C(4')-S(4')	124.5(9)
O(5')-S(2')-C(2')	103.4(13)	C(4')-F(10')-C(6T)	119.6(10)
O(4')-S(2')-C(2')	105.9(13)	C(2T)-C(1T)-C(6T)	121.5(12)
F(5')-C(2')-F(4')	109.7(14)	C(2T)-C(1T)-C(7T)	119.1(12)
F(5')-C(2')-F(6')	106.7(13)	C(6T)-C(1T)-C(7T)	119.4(12)
F(4')-C(2')-F(6')	106.1(14)	C(1T)-C(2T)-C(3T)	118.9(14)
F(5')-C(2')-S(2')	109.3(11)	C(4T)-C(3T)-C(2T)	118.3(13)
F(4')-C(2')-S(2')	114.9(12)	C(5T)-C(4T)-C(3T)	121.1(12)
F(6')-C(2')-S(2')	109.7(12)	C(4T)-C(5T)-C(6T)	120.6(12)
O(7')-S(3')-O(8')	115.8(11)	C(5T)-C(6T)-C(1T)	119.4(11)
O(7')-S(3')-O(9')	122.0(12)	C(5T)-C(6T)-F(10')	124.6(10)
O(8')-S(3')-O(9')	115.1(11)	C(1T)-C(6T)-F(10')	105.1(10)
O(7')-S(3')-C(3')	100.8(10)	C(6T')-C(1T')-C(2T')	124.2(14)
O(8')-S(3')-C(3')	94.2(8)	C(6T')-C(1T')-C(7T')	120.3(14)
O(9')-S(3')-C(3')	101.5(10)	C(2T')-C(1T')-C(7T')	115.5(13)
F(7')-C(3')-F(8')	107.7(11)	C(1T')-C(2T')-C(3T')	115.7(15)
F(7')-C(3')-F(9')	118.0(13)	C(4T')-C(3T')-C(2T')	120.4(14)
F(8')-C(3')-F(9')	104.4(11)	C(3T')-C(4T')-C(5T')	124.6(14)
F(7')-C(3')-S(3')	109.8(9)	C(4T')-C(5T')-C(6T')	114.7(13)
F(8')-C(3')-S(3')	114.3(10)	C(1T')-C(6T')-C(5T')	119.9(13)
F(9')-C(3')-S(3')	102.8(10)		
O(12')-S(4')-O(11')	117.9(11)		

For **2**, two disordered diethylether molecules were refined on two positions each. For C42-45 and O1, the occupancy of the main part refined to 0.773(5). For C46-49 and O2, the occupancy of the main part refined to 0.850(4).

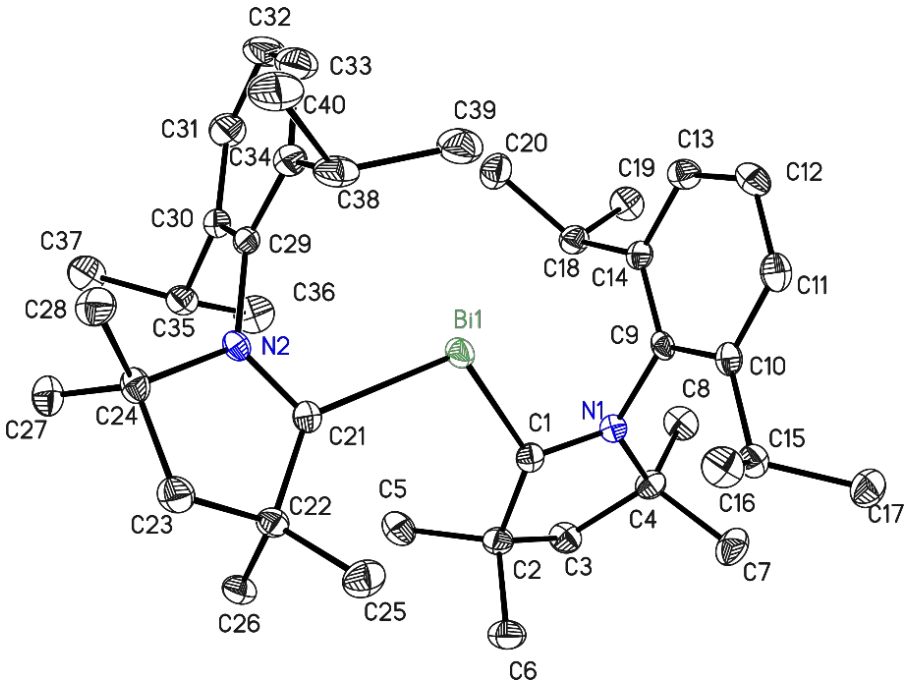


Figure S15. Structure of the cation of **2** including labels. Anisotropic displacement parameters are displayed at the 50% probability level. Hydrogen atoms are omitted for clarity.

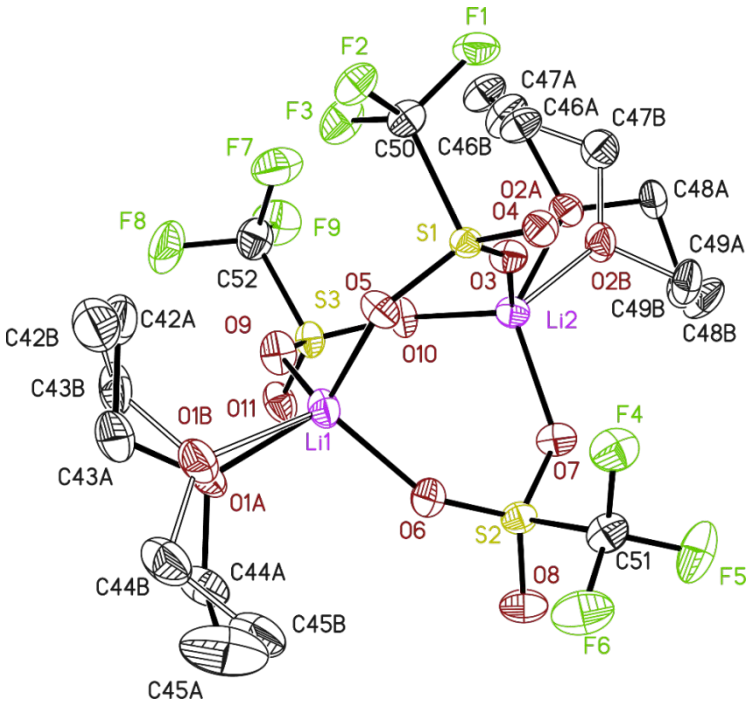


Figure S16. Structure of the anion of **2**. Anisotropic displacement parameters are displayed at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table S4 Crystal data and structure refinement **2**.

Bi(1)-C(1)	2.270(3)	S(3)-C(52)	1.816(4)
Bi(1)-C(21)	2.314(3)	F(4)-C(51)	1.326(4)
C(1)-N(1)	1.319(3)	C(4)-C(8)	1.521(4)
C(1)-C(2)	1.518(4)	C(4)-C(7)	1.523(4)
N(1)-C(9)	1.470(4)	F(5)-C(51)	1.334(4)
N(1)-C(4)	1.532(4)	F(6)-C(51)	1.339(4)
S(1)-O(4)	1.432(2)	C(52)-F(9)	1.335(4)
S(1)-O(3)	1.444(2)	C(52)-F(8)	1.338(4)
S(1)-O(5)	1.448(2)	C(52)-F(7)	1.338(4)
S(1)-C(50)	1.821(3)	C(9)-C(10)	1.402(4)
F(1)-C(50)	1.345(4)	C(9)-C(14)	1.415(4)
Li(1)-O(6)	1.930(6)	C(11)-C(12)	1.380(4)
Li(1)-O(5)	1.937(6)	C(11)-C(10)	1.397(4)
Li(1)-O(9)	1.947(6)	C(10)-C(15)	1.520(4)
Li(1)-O(1A)	1.955(8)	C(13)-C(12)	1.378(4)
Li(1)-O(1B)	2.04(2)	C(13)-C(14)	1.394(4)
F(2)-C(50)	1.342(3)	C(15)-C(17)	1.533(4)
C(2)-C(6)	1.534(4)	C(15)-C(16)	1.537(4)
C(2)-C(5)	1.538(4)	C(14)-C(18)	1.525(4)
C(2)-C(3)	1.549(4)	C(18)-C(19)	1.535(4)
N(2)-C(21)	1.315(3)	C(18)-C(20)	1.544(4)
N(2)-C(29)	1.464(4)	C(21)-C(22)	1.526(4)
N(2)-C(24)	1.539(3)	C(22)-C(26)	1.537(4)
S(2)-O(8)	1.431(2)	C(22)-C(25)	1.537(4)
S(2)-O(7)	1.446(2)	C(22)-C(23)	1.540(4)
S(2)-O(6)	1.446(2)	C(23)-C(24)	1.526(4)
S(2)-C(51)	1.827(3)	C(27)-C(24)	1.522(4)
Li(2)-O(10)	1.918(5)	C(28)-C(24)	1.520(4)
Li(2)-O(3)	1.935(5)	C(29)-C(34)	1.408(4)
Li(2)-O(2B)	1.950(17)	C(29)-C(30)	1.420(4)
Li(2)-O(2A)	1.960(6)	C(30)-C(31)	1.388(4)
Li(2)-O(7)	1.975(5)	C(30)-C(35)	1.517(4)
F(3)-C(50)	1.328(3)	C(31)-C(32)	1.382(4)
C(3)-C(4)	1.531(4)	C(32)-C(33)	1.375(4)
S(3)-O(11)	1.433(2)	C(33)-C(34)	1.392(4)
S(3)-O(9)	1.440(2)	C(34)-C(38)	1.530(4)
S(3)-O(10)	1.445(2)	C(35)-C(37)	1.534(4)

C(35)-C(36)	1.536(4)	O(9)-Li(1)-O(1A)	106.4(3)
C(38)-C(39)	1.530(4)	O(6)-Li(1)-O(1B)	118.9(5)
C(38)-C(40)	1.536(4)	O(5)-Li(1)-O(1B)	102.3(8)
C(42A)-C(43A)	1.508(6)	O(9)-Li(1)-O(1B)	106.4(8)
C(43A)-O(1A)	1.429(6)	C(1)-C(2)-C(6)	109.2(2)
O(1A)-C(44A)	1.439(6)	C(1)-C(2)-C(5)	112.1(2)
C(44A)-C(45A)	1.475(7)	C(6)-C(2)-C(5)	110.3(2)
C(42B)-C(43B)	1.474(14)	C(1)-C(2)-C(3)	102.8(2)
C(43B)-O(1B)	1.438(14)	C(6)-C(2)-C(3)	112.0(2)
O(1B)-C(44B)	1.429(14)	C(5)-C(2)-C(3)	110.3(2)
C(44B)-C(45B)	1.504(14)	C(21)-N(2)-C(29)	123.0(2)
C(46A)-C(47A)	1.508(5)	C(21)-N(2)-C(24)	114.8(2)
C(47A)-O(2A)	1.449(5)	C(29)-N(2)-C(24)	122.1(2)
O(2A)-C(48A)	1.430(4)	O(8)-S(2)-O(7)	115.36(13)
C(48A)-C(49A)	1.507(6)	O(8)-S(2)-O(6)	115.41(14)
C(46B)-C(47B)	1.498(15)	O(7)-S(2)-O(6)	114.09(13)
C(47B)-O(2B)	1.446(14)	O(8)-S(2)-C(51)	103.60(15)
O(2B)-C(48B)	1.429(14)	O(7)-S(2)-C(51)	102.84(14)
C(48B)-C(49B)	1.500(15)	O(6)-S(2)-C(51)	103.12(14)
		O(10)-Li(2)-O(3)	117.5(3)
C(1)-Bi(1)-C(21)	111.89(10)	O(10)-Li(2)-O(2B)	110.2(6)
N(1)-C(1)-C(2)	109.8(2)	O(3)-Li(2)-O(2B)	105.8(6)
N(1)-C(1)-Bi(1)	113.29(19)	O(10)-Li(2)-O(2A)	98.2(3)
C(2)-C(1)-Bi(1)	136.07(19)	O(3)-Li(2)-O(2A)	98.1(2)
C(1)-N(1)-C(9)	120.4(2)	O(10)-Li(2)-O(7)	109.0(3)
C(1)-N(1)-C(4)	115.2(2)	O(3)-Li(2)-O(7)	102.5(2)
C(9)-N(1)-C(4)	124.5(2)	O(2B)-Li(2)-O(7)	111.8(5)
O(4)-S(1)-O(3)	115.44(12)	O(2A)-Li(2)-O(7)	132.5(3)
O(4)-S(1)-O(5)	115.27(13)	C(4)-C(3)-C(2)	107.6(2)
O(3)-S(1)-O(5)	114.50(13)	O(11)-S(3)-O(9)	115.75(14)
O(4)-S(1)-C(50)	103.91(13)	O(11)-S(3)-O(10)	115.02(14)
O(3)-S(1)-C(50)	102.33(13)	O(9)-S(3)-O(10)	113.59(13)
O(5)-S(1)-C(50)	102.86(14)	O(11)-S(3)-C(52)	103.47(16)
O(6)-Li(1)-O(5)	105.8(3)	O(9)-S(3)-C(52)	103.22(15)
O(6)-Li(1)-O(9)	109.8(3)	O(10)-S(3)-C(52)	103.55(16)
O(5)-Li(1)-O(9)	113.7(3)	S(1)-O(3)-Li(2)	153.6(2)
O(6)-Li(1)-O(1A)	111.6(3)	C(8)-C(4)-C(7)	108.5(3)
O(5)-Li(1)-O(1A)	109.7(3)	C(8)-C(4)-C(3)	113.1(2)

C(7)-C(4)-C(3)	113.0(3)	C(17)-C(15)-C(16)	109.5(2)
C(8)-C(4)-N(1)	111.2(2)	C(13)-C(14)-C(9)	117.1(3)
C(7)-C(4)-N(1)	111.1(2)	C(13)-C(14)-C(18)	117.7(3)
C(3)-C(4)-N(1)	99.9(2)	C(9)-C(14)-C(18)	125.3(3)
S(1)-O(5)-Li(1)	129.5(2)	C(14)-C(18)-C(19)	110.2(2)
S(2)-O(6)-Li(1)	152.1(2)	C(14)-C(18)-C(20)	112.2(2)
F(9)-C(52)-F(8)	108.0(3)	C(19)-C(18)-C(20)	108.0(2)
F(9)-C(52)-F(7)	107.3(3)	N(2)-C(21)-C(22)	109.7(2)
F(8)-C(52)-F(7)	107.4(3)	N(2)-C(21)-Bi(1)	114.26(19)
F(9)-C(52)-S(3)	111.1(2)	C(22)-C(21)-Bi(1)	133.76(19)
F(8)-C(52)-S(3)	111.0(3)	C(21)-C(22)-C(26)	109.9(2)
F(7)-C(52)-S(3)	111.9(2)	C(21)-C(22)-C(25)	111.4(2)
F(4)-C(51)-F(5)	107.9(3)	C(26)-C(22)-C(25)	109.5(2)
F(4)-C(51)-F(6)	107.8(3)	C(21)-C(22)-C(23)	102.8(2)
F(5)-C(51)-F(6)	107.3(3)	C(26)-C(22)-C(23)	112.1(2)
F(4)-C(51)-S(2)	112.0(2)	C(25)-C(22)-C(23)	111.0(2)
F(5)-C(51)-S(2)	111.1(2)	C(24)-C(23)-C(22)	107.6(2)
F(6)-C(51)-S(2)	110.6(2)	C(34)-C(29)-C(30)	121.6(3)
F(3)-C(50)-F(2)	107.7(2)	C(34)-C(29)-N(2)	119.7(2)
F(3)-C(50)-F(1)	107.7(2)	C(30)-C(29)-N(2)	118.6(2)
F(2)-C(50)-F(1)	107.2(2)	C(31)-C(30)-C(29)	117.3(3)
F(3)-C(50)-S(1)	112.3(2)	C(31)-C(30)-C(35)	118.1(3)
F(2)-C(50)-S(1)	111.5(2)	C(29)-C(30)-C(35)	124.5(3)
F(1)-C(50)-S(1)	110.3(2)	C(32)-C(31)-C(30)	121.9(3)
S(2)-O(7)-Li(2)	131.1(2)	C(33)-C(32)-C(31)	119.7(3)
S(3)-O(9)-Li(1)	139.4(2)	C(32)-C(33)-C(34)	122.0(3)
C(10)-C(9)-C(14)	122.4(3)	C(33)-C(34)-C(29)	117.5(3)
C(10)-C(9)-N(1)	118.6(2)	C(33)-C(34)-C(38)	117.4(3)
C(14)-C(9)-N(1)	118.8(2)	C(29)-C(34)-C(38)	125.0(3)
C(12)-C(11)-C(10)	121.8(3)	C(30)-C(35)-C(37)	111.7(2)
S(3)-O(10)-Li(2)	138.6(2)	C(30)-C(35)-C(36)	110.7(2)
C(11)-C(10)-C(9)	117.1(3)	C(37)-C(35)-C(36)	109.1(2)
C(11)-C(10)-C(15)	118.1(3)	C(39)-C(38)-C(34)	111.4(3)
C(9)-C(10)-C(15)	124.7(3)	C(39)-C(38)-C(40)	108.4(3)
C(12)-C(13)-C(14)	121.8(3)	C(34)-C(38)-C(40)	111.8(3)
C(13)-C(12)-C(11)	119.8(3)	O(1A)-C(43A)-C(42A)	109.2(4)
C(10)-C(15)-C(17)	111.6(2)	C(43A)-O(1A)-C(44A)	113.7(5)
C(10)-C(15)-C(16)	111.3(2)	C(43A)-O(1A)-Li(1)	129.3(4)

C(44A)-O(1A)-Li(1)	116.8(4)
O(1A)-C(44A)-C(45A)	112.7(5)
O(1B)-C(43B)-C(42B)	112.2(15)
C(44B)-O(1B)-C(43B)	113.8(18)
C(44B)-O(1B)-Li(1)	133.9(12)
C(43B)-O(1B)-Li(1)	111.5(13)
O(1B)-C(44B)-C(45B)	109.7(13)
O(2A)-C(47A)-C(46A)	111.7(3)
C(48A)-O(2A)-C(47A)	112.9(3)
C(48A)-O(2A)-Li(2)	130.4(3)
C(47A)-O(2A)-Li(2)	112.8(3)
O(2A)-C(48A)-C(49A)	108.1(3)
O(2B)-C(47B)-C(46B)	109.3(16)
C(48B)-O(2B)-C(47B)	113.1(16)
C(48B)-O(2B)-Li(2)	114.9(13)
C(47B)-O(2B)-Li(2)	128.8(12)
O(2B)-C(48B)-C(49B)	110.5(16)
C(28)-C(24)-C(27)	108.7(2)
C(28)-C(24)-C(23)	113.4(2)
C(27)-C(24)-C(23)	113.3(3)
C(28)-C(24)-N(2)	111.5(2)
C(27)-C(24)-N(2)	110.0(2)
C(23)-C(24)-N(2)	99.8(2)

(S3) Theoretical calculations

Computational Details:

Geometry optimizations without symmetry restrictions were performed with the Gaussian 09[S9] program. The calculations were carried out for all molecules using the BP86 functional[S10,S11] with def2-TZVPP[S12,S13] basis set and dispersion correction by Grimme with Becke-Johnson dampingD3(BJ)[S14,S15] (termed as BP86+D3(BJ)/def2-TZVPP). Partial charges q were obtained from a single-point calculation of the molecules at the same level by using NBO 6.0[S16] as implemented with Gaussian 09 program.[S9]

The orbital interactions have been investigated with the help of the EDA-NOCV method[S17]which combines the energy decomposition analysis (EDA)[S18] with the natural orbital for chemical valence (NOCV)[S19,S20] method. The interaction energy between the fragments ΔE_{int} which are calculated with the frozen geometry of the fragments is decomposed into four main components ΔE_{elstat} (electrostatic interactions), ΔE_{Pauli} (Pauli repulsion), ΔE_{disp}(dispersion interactions), and ΔE_{orb}(orbital interactions). The latter term can be separated into contributions which come from pairwise orbital interactions, which makes it possible to identify the dominant orbitals of the interactions in the transition state. For a detailed description of the method we refer to the literature.[S21-S25] The energy decomposition analysis was conducted at the BP86(D3)/TZ2P[S26] level using the BP86+D3(BJ)/def2-TZVPP optimized geometries. For the open-shell molecules we employed the unrestricted UBP86 method. The EDA-NOCV calculations were carried out with the program package ADF.[S27,S28] The UV spectra have been evaluated using time dependent density functional theory(TDDFT)[S29] method at the BP86+D3(BJ)/def2-TZVPP level.

TableS5. EDA-NOCV results at the BP86+(D3BJ)/TZ2P//BP86+(D3BJ)/def2-TZVPP level of $[Sb(cAAC)_2]^+$ and $[Bi(cAAC)_2]^+$ using E^+ (E = Sb, Bi) and the ligands pairs $(cAAC)_2$ in the electronic trplet states as interacting fragments. Energy values are given in kcal/mol

Molecule	$[Sb(cAAC)_2]^+$	$[Bi(cAAC)_2]^+$

Fragments	$Sb^+[(n)s^2(n)p_x^1(n)p_z^1]$ + $(cAAC)_2$ triplet	$Bi^+[(n)s^2(n)p_x^1(n)p_z^1]$ + $(cAAC)_2$triplet
ΔE_{int}	-284.1	-266.5
ΔE_{Pauli}	237.3	222.06
ΔE_{disp}[a]	-30.2(5.8%)	-30.3(6.2%)
ΔE_{elstat}[a]	-203.2(39.0%)	-197.1(40.3%)
ΔE_{orb}[a]	-288.0(55.2%)	-261.2(53.5%)
ΔE_{orb1}[b]	-104.7(36.4%)	-78.1(29.9%)
ΔE_{orb2}[b]	-68.9(23.9%)	-96.6(37.0%)
ΔE_{orb3}[b]	-67.0(23.3%)	-46.7(17.9%)
ΔE_{rest}	-47.3(16.4%)	-39.8(15.2%)

[a]The values in parentheses give the percentage contribution to the total attractive interactions $\Delta E_{elstat}+ \Delta E_{orb}+\Delta E_{disp}$.

[b]The values in parentheses give the percentage contribution to the total orbital interactions ΔE_{orb}.

Table S6. Coordinates of the calculated molecules.

[Sb(cAAC)$_2$]$^+$

Sb	0.000011000	-0.163509000	0.000245000
N	-2.902639000	0.259246000	0.243723000
N	2.902595000	0.259131000	-0.243790000
C	-1.796461000	0.992858000	0.346037000
C	-2.119157000	2.361698000	0.911194000
C	-3.651449000	2.312963000	1.179474000
H	-3.870555000	2.443183000	2.245195000
H	-4.157878000	3.128126000	0.648426000
C	-4.184889000	0.950308000	0.689055000
C	-1.315243000	2.606421000	2.213763000
H	-0.242778000	2.589272000	1.971164000
H	-1.543589000	3.621928000	2.569104000
C	-1.580013000	1.601062000	3.333991000
H	-1.350815000	0.575641000	3.011020000
H	-2.622906000	1.624801000	3.678560000
H	-0.947505000	1.821027000	4.203443000
C	-1.812060000	3.422314000	-0.180916000
H	-0.786891000	3.280198000	-0.539814000
H	-2.462762000	3.205135000	-1.043650000
C	-1.998593000	4.875702000	0.255455000
H	-2.995936000	5.055157000	0.682072000
H	-1.884846000	5.546199000	-0.606746000
H	-1.254837000	5.175903000	1.005287000
C	-4.878278000	0.162366000	1.797554000
H	-5.189830000	-0.827589000	1.442423000
H	-5.781570000	0.708118000	2.101710000
H	-4.239059000	0.042985000	2.679561000
C	-5.147522000	1.092603000	-0.491506000
H	-5.419947000	0.111687000	-0.901465000
H	-4.726978000	1.711196000	-1.292818000
H	-6.067568000	1.575928000	-0.136970000
C	-2.895629000	-1.077952000	-0.325724000
C	-2.739159000	-2.206288000	0.519436000
C	-2.729519000	-3.472155000	-0.083577000
H	-2.615237000	-4.354264000	0.546816000
C	-2.846388000	-3.625282000	-1.460883000
H	-2.839652000	-4.622028000	-1.903099000
C	-2.949438000	-2.500951000	-2.274914000
H	-3.007321000	-2.623675000	-3.356744000
C	-2.964542000	-1.208386000	-1.736862000
C	-2.521959000	-2.137041000	2.026718000
H	-2.516010000	-1.079267000	2.322229000
C	-1.162631000	-2.740446000	2.434106000
H	-1.125606000	-3.816385000	2.212770000
H	-1.009543000	-2.616945000	3.515511000
H	-0.324671000	-2.258852000	1.914635000
C	-3.639506000	-2.860742000	2.800979000

H	-3.605643000	-3.942215000	2.607694000
H	-4.640335000	-2.507419000	2.527274000
H	-3.507348000	-2.714890000	3.882266000
C	-2.980289000	-0.030767000	-2.702471000
H	-2.995714000	0.896837000	-2.115521000
C	-4.212180000	-0.048933000	-3.623580000
H	-4.187392000	-0.918916000	-4.294638000
H	-4.228167000	0.851550000	-4.253665000
H	-5.152983000	-0.090523000	-3.061247000
C	-1.694172000	-0.007610000	-3.547102000
H	-0.805482000	0.007050000	-2.903092000
H	-1.676567000	0.885041000	-4.188361000
H	-1.629976000	-0.891346000	-4.197547000
C	1.796420000	0.992807000	-0.345820000
C	2.119050000	2.361674000	-0.910957000
C	3.651382000	2.313080000	-1.179057000
H	3.870699000	2.444201000	-2.244625000
H	4.157723000	3.127788000	-0.647223000
C	4.184744000	0.950036000	-0.689605000
C	1.811731000	3.422309000	0.181055000
H	0.786398000	3.280355000	0.539534000
H	2.462069000	3.204999000	1.044031000
C	1.998662000	4.875684000	-0.255197000
H	2.996195000	5.055002000	-0.681424000
H	1.884696000	5.546164000	0.606991000
H	1.255238000	5.176046000	-1.005292000
C	1.315143000	2.606288000	-2.213551000
H	0.242672000	2.588525000	-1.971001000
H	1.542993000	3.621990000	-2.568652000
C	1.580511000	1.601344000	-3.333997000
H	2.623369000	1.625874000	-3.678615000
H	0.947808000	1.821075000	-4.203366000
H	1.352017000	0.575693000	-3.011255000
C	5.148204000	1.091549000	0.490373000
H	5.420539000	0.110392000	0.899819000
H	4.728409000	1.710025000	1.292167000
H	6.068195000	1.574664000	0.135406000
C	4.877184000	0.162361000	-1.798897000
H	5.188768000	-0.827783000	-1.444334000
H	5.780387000	0.708023000	-2.103481000
H	4.237328000	0.043424000	-2.680502000
C	2.895620000	-1.078057000	0.325677000
C	2.964975000	-1.208436000	1.736802000
C	2.949868000	-2.500970000	2.274927000
H	3.008081000	-2.623647000	3.356744000
C	2.846411000	-3.625328000	1.460985000
H	2.839683000	-4.622052000	1.903252000
C	2.729133000	-3.472255000	0.083708000
H	2.614541000	-4.354378000	-0.546606000
C	2.738736000	-2.206418000	-0.519371000
C	2.981229000	-0.030767000	2.702341000
H	2.996516000	0.896803000	2.115333000
C	4.213497000	-0.049013000	3.622944000

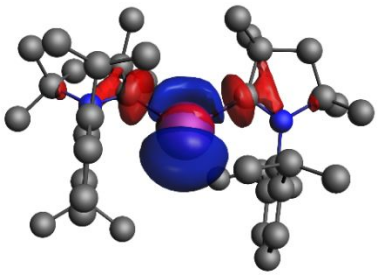
H	4.188904000	-0.918971000	4.294041000
H	4.229828000	0.851489000	4.252991000
H	5.154060000	-0.090712000	3.060217000
C	1.695448000	-0.007428000	3.547476000
H	1.631429000	-0.891101000	4.198025000
H	0.806515000	0.007247000	2.903803000
H	1.678155000	0.885282000	4.188662000
C	2.521056000	-2.137218000	-2.026582000
H	2.515031000	-1.079447000	-2.322102000
C	3.638345000	-2.860959000	-2.801178000
H	3.604494000	-3.942430000	-2.607877000
H	4.639274000	-2.507683000	-2.527772000
H	3.505876000	-2.715101000	-3.882426000
C	1.161591000	-2.740602000	-2.433534000
H	1.124610000	-3.816539000	-2.212176000
H	1.008169000	-2.617114000	-3.514894000
H	0.323804000	-2.258980000	-1.913813000

[Bi(CAAc)$_2$]$^+$

Bi	10.648691000	6.374140000	7.311057000
N	8.606481000	8.161171000	8.687955000
N	13.328003000	4.833551000	7.129533000
C	9.668540000	7.465192000	9.043611000
C	10.032518000	7.780018000	10.483207000
C	9.174328000	9.033714000	10.787937000
H	8.819554000	8.988162000	11.711107000
H	9.723616000	9.852718000	10.702733000
C	8.022325000	9.062674000	9.779836000
C	11.527078000	8.106053000	10.644196000
H	12.061602000	7.333965000	10.363450000
H	11.717353000	8.310765000	11.583466000
H	11.754490000	8.880281000	10.088372000
C	9.648886000	6.591715000	11.372756000
H	8.696842000	6.390171000	11.256340000
H	9.823101000	6.815578000	12.310711000
H	10.181525000	5.808687000	11.119581000
C	6.729901000	8.479733000	10.336728000
H	6.055957000	8.441142000	9.626349000
H	6.403440000	9.047241000	11.066136000
H	6.898511000	7.576119000	10.676558000
C	7.733276000	10.456501000	9.244847000
H	7.086168000	10.396787000	8.511141000
H	8.564085000	10.858515000	8.915750000
H	7.363292000	11.011322000	9.962565000
C	7.111422000	7.010237000	7.093941000
C	8.048772000	8.025712000	7.334877000
C	6.646582000	6.871041000	5.784121000
H	5.992244000	6.209142000	5.594357000
C	8.065054000	8.628271000	5.015588000
H	8.392849000	9.158103000	4.298364000
C	7.111022000	7.668848000	4.758224000
H	6.773792000	7.555903000	3.877163000

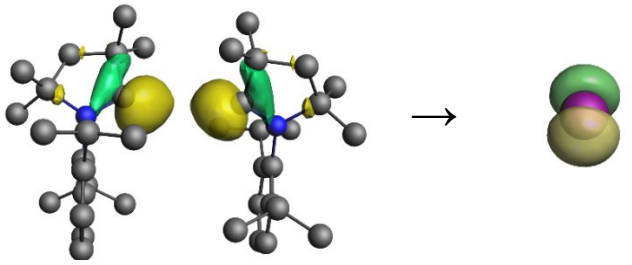
C	6.612129000	6.025590000	8.139277000
H	7.051569000	6.247257000	9.009907000
C	8.562637000	8.843137000	6.299945000
C	6.984791000	4.581317000	7.769384000
H	6.554056000	4.338976000	6.923204000
H	6.680766000	3.974087000	8.476205000
H	7.957473000	4.509094000	7.673201000
C	5.094610000	6.128352000	8.331752000
H	4.841251000	7.069484000	8.434671000
H	4.832751000	5.630087000	9.134017000
H	4.639956000	5.751197000	7.549968000
C	9.600138000	9.946427000	6.482290000
H	9.909804000	9.943027000	7.433086000
C	8.979882000	11.315030000	6.169346000
H	8.725808000	11.350138000	5.223478000
H	9.633377000	12.020725000	6.358262000
H	8.184843000	11.448593000	6.726403000
C	10.824074000	9.754916000	5.560434000
H	11.220918000	8.873461000	5.723121000
H	11.487230000	10.451269000	5.748775000
H	10.541119000	9.817657000	4.624285000
C	12.374795000	5.005444000	8.019082000
C	12.507536000	3.959140000	9.121915000
C	13.521486000	2.963282000	8.528335000
H	14.129463000	2.631959000	9.236086000
H	13.048235000	2.188317000	8.133500000
C	13.030277000	4.617751000	10.408188000
H	13.804886000	5.179055000	10.196164000
H	13.295735000	3.922341000	11.046177000
H	12.323963000	5.170321000	10.802667000
C	15.626824000	4.279570000	7.965145000
H	16.233505000	3.550913000	8.211202000
H	15.451487000	4.838624000	8.750955000
H	16.038837000	4.824835000	7.262350000
C	14.606020000	2.845573000	6.228485000
H	13.773924000	2.437888000	5.910202000
H	15.245733000	2.142111000	6.464630000
H	14.985481000	3.408485000	5.521418000
C	13.491945000	5.698620000	5.959348000
C	14.203233000	6.917751000	6.109112000
C	14.337354000	7.720229000	4.983829000
H	14.810579000	8.540671000	5.055836000
C	13.802566000	7.358693000	3.761623000
H	13.919854000	7.919643000	3.004233000
C	13.099733000	6.182536000	3.647999000
H	12.734624000	5.943464000	2.804228000
C	12.906996000	5.331479000	4.732214000
C	14.765583000	7.429693000	7.422490000
H	14.643143000	6.719346000	8.115922000
C	14.015557000	8.688994000	7.880270000
H	14.175695000	9.415120000	7.241706000
H	14.337162000	8.957007000	8.766533000
H	13.055071000	8.499576000	7.925090000

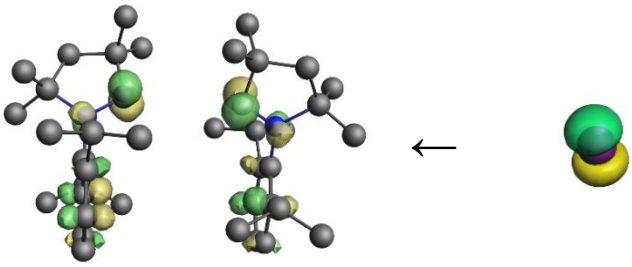
C	16.262127000	7.746386000	7.313521000
H	16.743395000	6.950710000	7.005451000
H	16.603745000	8.015613000	8.191845000
H	16.395377000	8.477108000	6.673753000
C	12.055506000	4.080586000	4.503872000
H	12.012157000	3.568196000	5.361415000
C	10.629339000	4.443989000	4.086887000
H	10.657571000	5.027622000	3.300092000
H	10.182394000	4.910678000	4.823797000
H	10.134103000	3.626714000	3.869743000
C	12.659240000	3.168806000	3.425407000
H	12.604910000	3.613514000	2.553819000
H	12.160392000	2.325878000	3.393756000
H	13.597491000	2.985292000	3.640662000
C	11.162272000	3.272503000	9.407206000
H	10.516052000	3.938774000	9.722449000
H	11.285295000	2.585810000	10.095025000
H	10.827395000	2.856270000	8.585639000
C	14.316093000	3.698498000	7.453155000



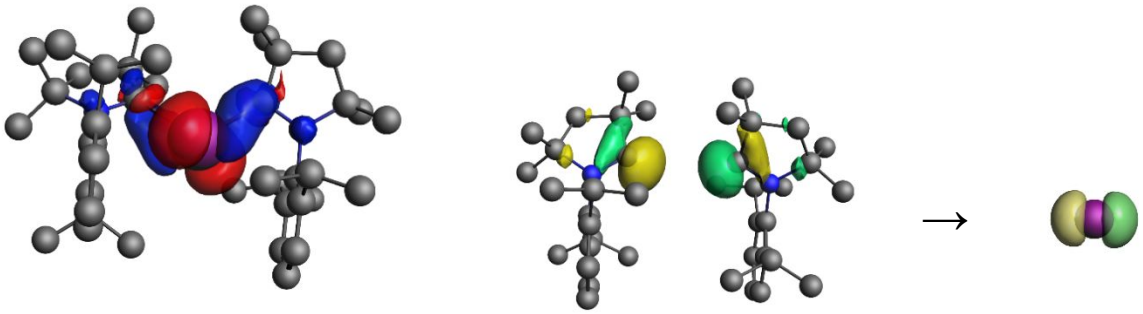
$\Delta\rho_{(1)}$

$\Delta E_{orb(1)}$= -92.2 kcal/mol



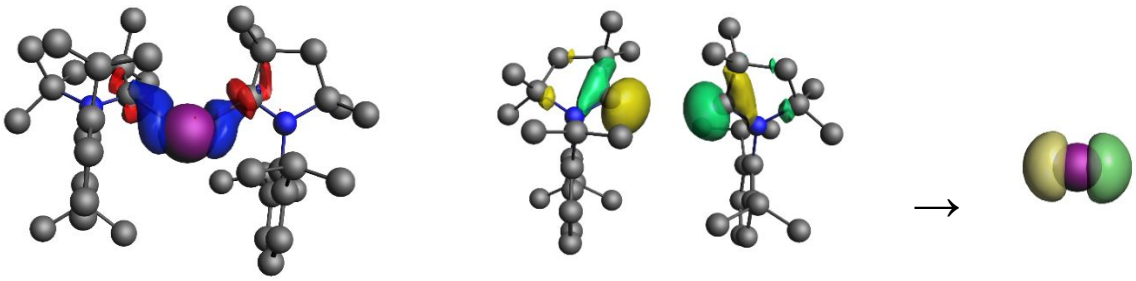


+



$\Delta\rho_{(2)}$

$\Delta E_{orb(2)}$= -74.1 kcal/mol



$\Delta\rho_{(3)}$

$\Delta E_{orb(3)}$= -36.1 kcal/mol

Figure S17. Plot of the deformation densities Δρ of the pair wise orbital interactions between the two fragments in their singlet electronic state in $[Bi(cAAC)_2]^+$(Table S2) and the associated most important fragments orbitals. The direction of the charge flow of the deformation densities is red→blue.

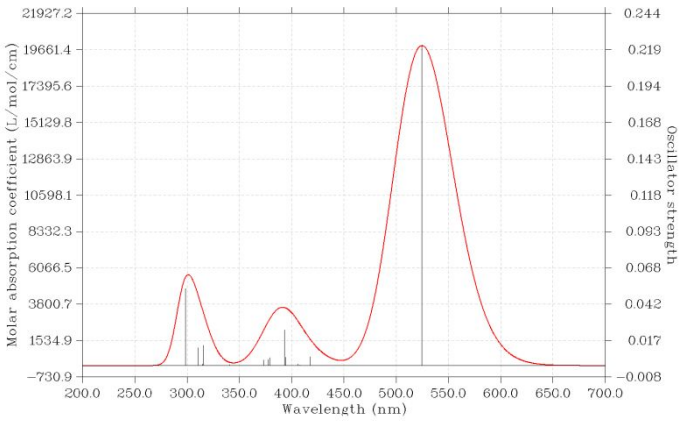


Figure S18. The UV-Vis Spectrum of $[Sb(CAAc)_2]^+$obtained at the BP86+(D3BJ)/def2-TZVPP level.

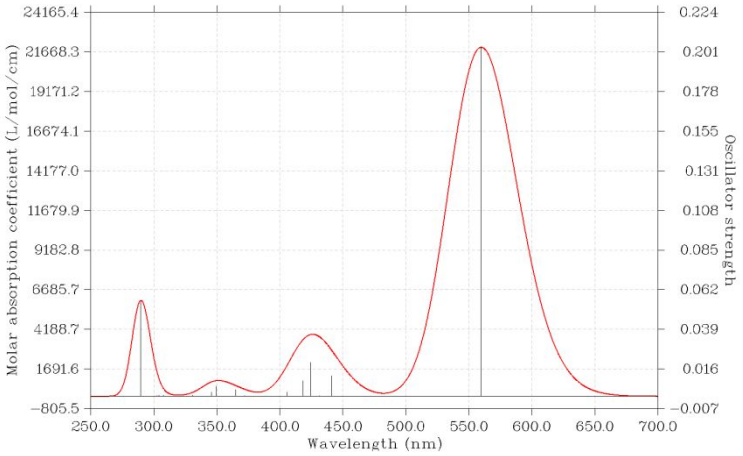


Figure S19. The UV-Vis Spectrum of [Bi $(CAAc)_2]^+$obtained at the BP86+(D3BJ)/def2-TZVPP level.

Table S7.The excitation energies and oscillator strengthsand associated molecular orbitalsof[Sb(CAAc)$_2$]$^+$atBP86+(D3BJ)/def2-TZVPP.

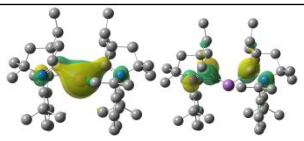
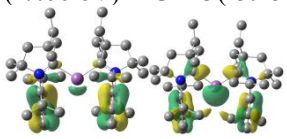
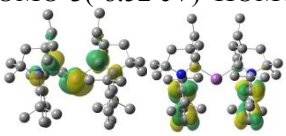
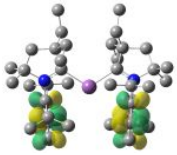
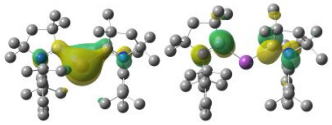
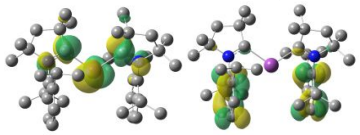
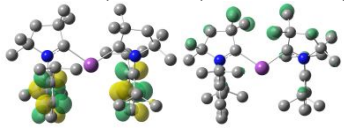
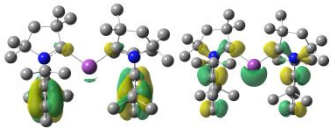
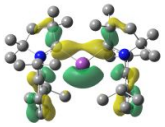
Excited State 1	2.3658 eV 524.07 nmf=0.2218 185 -> 186 0.70327 185 <- 186 -0.10460	 185 186 HOMO(-7.00 eV) LUMO(-5.25 eV)
Excited State 6	3.1548 eV 393.01 nm f=0.0245 182 -> 186 0.16301 184 -> 186 -0.33876 185 -> 187 0.39373 185 -> 188 -0.24269 185 -> 191 -0.37100	 182 184 HOMO-3(-8.52 eV) HOMO-1(-8.28 eV)
Excited State 15	4.1593 eV 298.09 nm f=0.0531 182 -> 187 0.65584 184 -> 187 0.22540	 187 188 LUMO+1(-4.42 eV) LUMO+2(-4.00 eV)  191 LUMO+5(-3.79 eV)

Table S8.The excitation energies, oscillator strengths and associated molecular orbital of $[Bi(CAAc)_2]^+$atBP86+(D3BJ)/def2-TZVPP.

$[Bi(CAAc)_2]^+$		
Excited State 1	2.2168 eV 559.29 nm f=0.2037 169 -> 170 0.70539 169 <- 170 -0.10574	 169 170 HOMO(-6.81 eV) LUMO(-5.17 eV)
Excited State 4	2.9242 eV 423.99 nm f=0.0197 169 -> 171 -0.46221 169 -> 172 0.46599 169 -> 175 -0.24561	 171 172 LUMO+1(-4.48eV) LUMO+2(-3.97 eV)
Excited State 9	3.5499 eV 349.26 nm f=0.0056 166 -> 170 0.69928	 175 178 LUMO+5(-3.82eV) LUMO+8(-2.52 eV)
Excited State 15	4.2835 eV 289.45 nm f=0.0558 164 -> 171 -0.10702 166 -> 171 0.66440 168 -> 171 0.10159 169 -> 178 0.17537	 168 166 HOMO-1 (-8.49eV)HOMO-3 (-8.68 eV)  164 HOMO-5 (-9.19 eV)

(S4) References

S1 Lavallo, V.; Canac, Y.; Präsang, C.; Donnadieu, B.; Bertrand, G. *Angew. Chem. Int. Ed.* **2005**, *44*, 5701–5705.

S2 (a) D. Stalke. *Chem. Soc. Rev.* **1998**, *27*, 171–178. (b) Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, *26*, 615−619.

S3 Bruker, SAINT, Bruker AXS Inc., Madison, WI, **2016**.

S4 Krause, L.; Herbst-Irmer, R.; Sheldrick, G. M.; Stalke, D. *J. Appl. Crystallogr*. **2015**, *48*, 1907–1913.

S5 Krause, L.; Herbst-Irmer, R.; Sheldrick, G. M.; Stalke, D. *J. Appl. Crystallogr*. **2015**, *48*, 3–10.

S6 Sheldrick, G. M. *Acta Crystallogr. A* **2015**, *71*, 3–8.

S7 Sheldrick, G. M. *Acta Crystallogr. C* **2015**, *71*, 3–8.

S8 Hübschle, C. B.; Sheldrick, G. M.; Dittrich, B. *J. Appl. Crystallogr*. **2011**, *44*, 1281–1284. 1997, 16, 1920–1925.

S9 Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; G. E., Scuseria, M. A. R.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, J. B. A. F.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, R. F. K.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O., H. N.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, J. J. H. M.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, J. N. R.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S., J. T.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, V. B. J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L., K. M.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V. and Cioslowski, D. J. Fox. J. Gaussian, Inc., Wallingford, CT, **2009**.

S10 Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3100

S11 Perdew, J. P. *Phys. Rev. B* **1986**,*33*, 8822–8824.

S12 Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297 – 3305.

S13 Weigend, F.; Häser, M.; Patzelt, H.; Ahlrichs, R.*Chem. Phys. Lett.* **1998**, *294*, 143 – 152.

S14 Grimme, S.; Ehrlich, S.; Goerigk, L. *J. Comput. Chem.* **2011**, *32*, 1456 – 1465.

S15 Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132,* 154104.

S16 Glendening, E. D.; Landis, C. R.; Weinhold, F. *J. Comput. Chem*. **2013**, *34*, 1429 – 1437.

S17 Mitoraj, M.; Michalak, A.; Ziegler, T. A. *J. Chem. Theory Comput.* **2009**,*5*, 962 – 975.

S18 Ziegler, T.; Rauk, A. *Theor. Chim. Acta* **1977**, *46*, 1 – 10.

S19 Mitoraj, M.; Michalak, A.*Organometallics* **2007**, *26*, 6576 – 6580.

S20 Mitoraj, M.; Michalak, A. *J. Mol. Model.* **2008**, *14*, 681 – 687.

S21 Bickelhaupt, F. M.; Baerends, E. J. in *Reviews in Computational Chemistry*, John Wiley & Sons, Inc. **2007**, pp. 1 – 86.

S22 Hopffgarten, M. v.; Frenking, G. WIREs *Comput. Mol. Sci.* **2012**, *2*, 43 – 62.

S23 G. Frenking, F. Matthias Bickelhaupt, in *The Chemical Bond*, Wiley-VCH Verlag GmbH & Co. KGaA, **2014**, pp. 121 – 157.

S24 Zhao, L.; von Hopffgarten, M.; Andrada, D. M.; Frenking, G.*WIREs Comput. Mol. Sci.***2018**, *8*, e1345.

S25 Zhao, L.; Hermann, M.; Schwarz, W. H. E.; Frenking, G. *Nature Reviews Chemistry* **2019**, *3*, 48 – 63.

S26 Snijders,J. G.;Baerends, E. J.;Vernoojs,P. *At. Data Nucl. Data Tables***1981**,*26*, 483.

S27 te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra,C.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931 – 967.

S28 Computer code ADF 2013.2001: see http://www.scm.com.

S29. Cossi, M.; Barone, V.*J. Chem. Phys.* **2001**, 115, 4708-4717.