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Supporting Information

# Ligand Effects on the Electronic Structure of Heteroleptic Antimony-Centered Radicals

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# Supporting Information

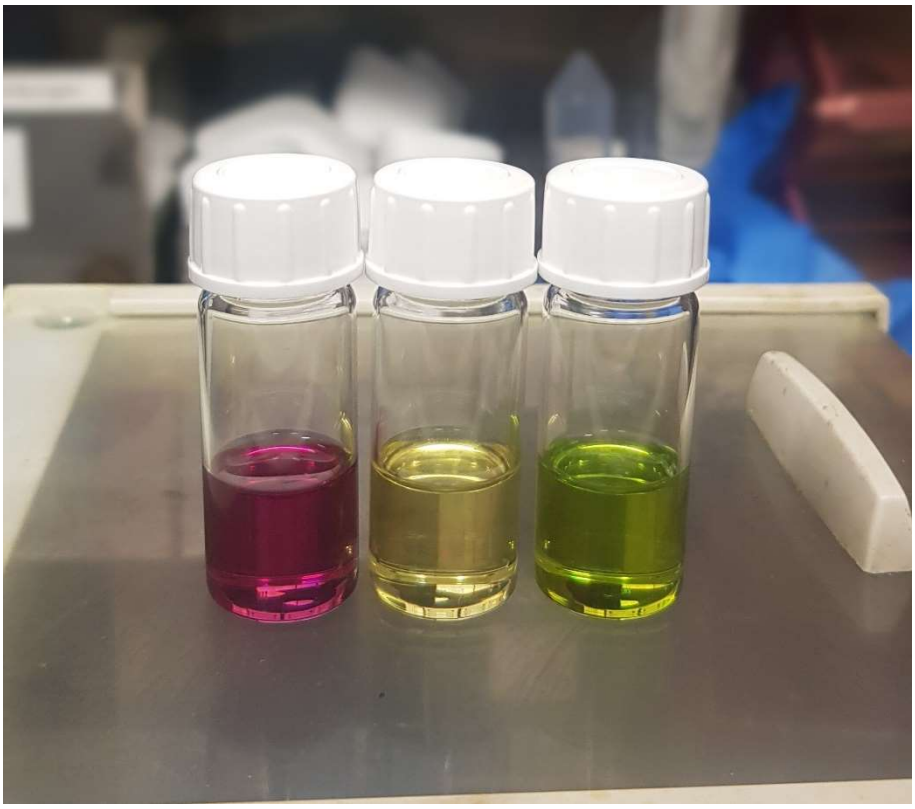

**Figure S0.** Solutions (1 mM) of **2-*B*** (left), **2-*C*** (middle), and **2-*N*** (right) in toluene.

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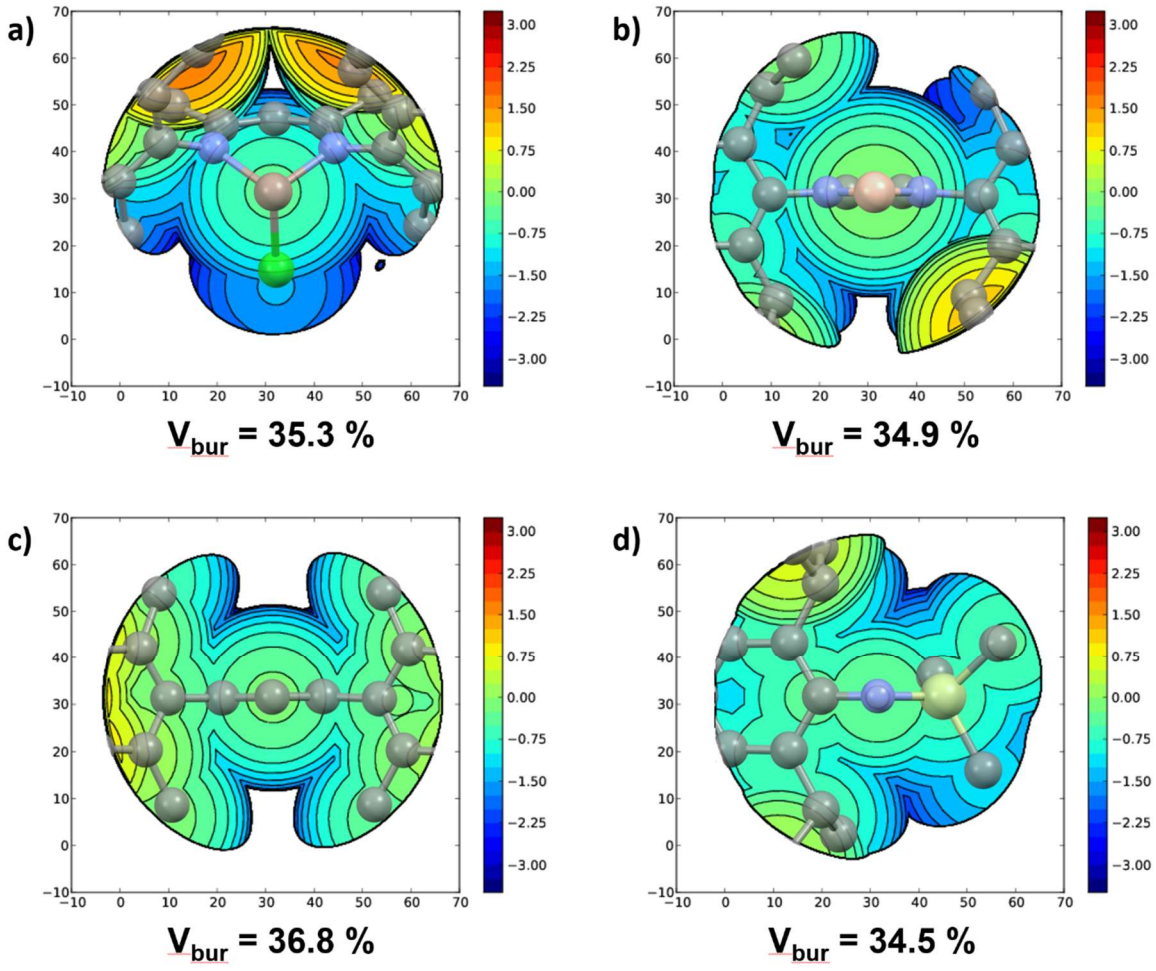


**Figure S1.** Steric maps and buried volumes $V_{bur}$ of a) [L(Cl)Ga], b) ***B***, c) ***C***, and d) ***N***. The sphere radius was set at 3.5 Å. The distance from the coordinating center to the center of the sphere were chosen as follows: a) 2.590 Å, mean Sb-Ga bond length in **VI**; b) 2.257 Å, Sb-B bond length observed in the comparable boryl complex [DipNC(*t*-Bu)NN(Ph)B]$SbPh_2$; c) 2.156 Å, mean Sb-C bond length observed for compounds of the type $ArSbX_2$; d) 2.036 Å, mean Sb-N bond length observed for compounds of the type $(Ar)(SiR_2X)NSbX_2$.

## 1. Experimental Details

**General Procedures**. All manipulations were carried out using standard Schlenk and glove-box techniques under argon, which was dried by passing through pre-heated $Cu_2O$ pellets and molecular sieves columns. *n*-Hexane was dried with a MBraun Solvent Purification System, THF and benzene were distilled from Na/K alloy, and fluorobenzene was distilled from $CaH_2$. Deuterated solvents were dried over activated molecular sieves (4 Å) and degassed prior to use. Starting reagents LGa (L = HC[C(Me)N(Dip)]$_2$, Dip = 2,6-*i*-$Pr_2C_6H_3$),[1] Cp*$SbCl_2$ (Cp* = $C_5Me_5$),[2] ***B***Li(THF)$_2$ (***B*** = B[N(Dip)CH]$_2$),[3] ***C***Li (***C*** = 2,6-$Mes_2C_6H_3$, Mes = 2,4,6-$Me_3C_6H_2$),[4] and ***N***Li (***N*** = N(Dip)($SiMe_3$))[5] were prepared according to literature methods. [K([2.2.2]crypt)][$C_{10}H_8$] was prepared from equimolar amounts of [2.2.2]cryptand, potassium metal, and naphthalene in THF and dried *in vacuo*.[6] $^1$H (300 MHz, 600 MHz), $^{11}$B (96.3 MHz, 192.5 MHz), and $^{13}$C{$^1$H} (75.5 MHz, 150.9 MHz) NMR spectra were recorded using a Bruker Avance DPX-300 or a Bruker Avance III HD 600 spectrometer and referenced to internal $C_6D_5H$ ($^1$H: $\delta$ = 7.16; $^{13}$C: $\delta$ = 128.06), $C_6D_5CD_2H$ ($^1$H: $\delta$= 2.08; $^{13}$C: $\delta$= 20.43) or THF-$d_7$ ($^1$H: $\delta$= 1.72; $^{13}$C: $\delta$= 25.31). Solution-state magnetic susceptibilities $\chi_M$ and effective magnetic moments $\mu_{eff}$ were determined by $^1$H NMR spectroscopy using Evans' method[7] with pure solvent as internal reference and neglecting diamagnetic contributions according to equations given in the literature.[8] IR spectra were recorded in a glovebox using an ALPHA-T FT-IR spectrometer equipped with a single reflection ATR sampling module. UV-Vis spectra were recorded on a Jasco V-550 spectrophotometer in sealed cuvettes under argon atmosphere. Cyclic voltammetry measurements were performed in a glovebox using a Metrohm Autolab PGSTAT 204 potentiostat with a three electrodes setup consisting of a Pt disc ($d$ = 1 mm) working electrode, Pt wire counter electrode, and Ag wire pseudo-reference electrode, and ferrocene as internal standard. Microanalyses were performed at the elemental analysis laboratory of University of Duisburg-Essen. Melting points were measured in sealed glass capillaries under argon atmosphere using a Thermo Scientific 9300 apparatus and are uncorrected.

**Synthesis of *B*Sb(Cl)Cp* (1-*B*).** An orange suspension of Cp*$SbCl_2$ (0.33 g, 1.00 mmol) and [HCN(Dip)]$_2$BLi(THF)$_2$ (0.54 g, 1.00 mmol) in *n*-hexane (40 mL) was stirred for 15 minutes at ambient temperature, filtered and the solvent was removed from the filtrate *in vacuo*, yielding an orange solid. Yield: 0.61 g (0.84 mmol, 84 %). *Note: Compound **1-B** contains approximately 9 % of **B**H, that are always present in isolated samples of **B**Li(THF)$_2$*[3] *and a further purification of **1-B** was precluded by its high solubility in common organic solvents.* M.p. 56 °C (dec.). Anal. Calcd. for $C_{36}H_{51}BClN_2Sb \cdot 0.1\ C_{26}H_{37}BN_2$: C, 64.51; H, 7.67; N, 4.29. Found: C, 65.1; H, 7.71; N, 4.47 %. IR (neat): $\nu$ 2961, 2925, 2866, 1458, 1378, 1324, 1270, 1235, 1115, 1059, 934, 899, 803, 757, 708, 635, 455, 419 cm$^{-1}$. $^1$H NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ 7.18 (m, 3 H, $C_6H_3$(*i*-Pr)$_2$), 7.14 (m, 3 H, $C_6H_3$(*i*-Pr)$_2$), 6.33 (s, 2 H, NC*H*), 3.53 (sept, $^3J_{HH}$ = 6.9 Hz, 2 H, C*H*($CH_3$)$_2$), 3.26 (sept, $^3J_{HH}$ = 6.9 Hz, 2 H, C*H*($CH_3$)$_2$), 1.77 (s, 15 H, $C_5$($CH_3$)$_5$), 1.45 (d, $^3J_{HH}$ = 6.9 Hz, 6 H, CH($CH_3$)$_2$), 1.39 (d, $^3J_{HH}$ = 6.9 Hz, 6 H, CH($CH_3$)$_2$), 1.17 (d, $^3J_{HH}$ = 6.9 Hz, 6 H, CH($CH_3$)$_2$), 1.15 (d,

$^3J_{HH}$ = 6.9 Hz, 6 H, CH(C$H_3$)$_2$). $^{11}$B NMR (96.3 MHz, $C_6D_6$, 25 °C): $\delta$ 38.1 (br s, Sb$B$N$_2$). $^{13}$C NMR (75.5 MHz, $C_6D_6$, 25 °C): $\delta$ 146.7, 146.4, 139.4, 128.6, 123.9, 123.7 ($C_6$H$_3$($i$-Pr)$_2$), 123.1 (N$C$H), 122.2 ($C_5$(CH$_3$)$_5$), 29.2, 28.8 ($C$H(CH$_3$)$_2$), 27.3, 26.2, 23.5 (CH($C$H$_3$)$_2$), 12.2 (C$_5$($C$H$_3$)$_5$).

**Synthesis of *C*Sb(Cl)Cp* (1-*C*).** An orange suspension of Cp*SbCl$_2$ (0.33 g, 1.00 mmol) and 2,6-Mes$_2$C$_6$H$_3$Li (0.32 g, 1.00 mmol) in *n*-hexane (40 mL) was stirred at ambient temperature for 15 minutes, filtered and the solvent was removed from the filtrate *in vacuo*, yielding an orange solid. Yield: 0.46 g (0.77 mmol, 77 %). M.p. 109 °C. Anal. Calcd. for $C_{34}H_{40}ClSb$: C, 67.40; H, 6.65. Found: C, 66.9; H, 6.56 %. IR (neat): $\nu$ 2913, 2856, 1610, 1557, 1439, 1376, 1300, 1031, 849, 803, 737, 589, 573, 497, 405 cm$^{-1}$. $^1$H NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ 7.16 (t, $^3J_{HH}$ = 7.5 Hz, 1 H, C$_6H_3$), 6.94 (d, $^3J_{HH}$ = 7.5 Hz, 2 H, C$_6H_3$), 6.82 (s, 4 H, C$_6H_2$), 2.25 (s, 12 H, *o*-C$H_3$), 2.16 (s, 6 H, *p*-C$H_3$), 1.67 (s, 15 H, C$_5$(C$H_3$)$_5$). $^{13}$C NMR (75.5 MHz, $C_6D_6$, 25 °C): $\delta$ 161.1, 148.7, 139.4, 137.5, 137.4 (2,4,6-Me$_3C_6H_2$ & 2,6-Mes$_2C_6H_3$), 131.0, 129.9 (2,6-Mes$_2C_6H_3$), 128.6 (2,4,6-Me$_3C_6H_2$), 123.7 ($C_5$(CH$_3$)$_5$), 22.3 (*o*-$C$H$_3$), 21.2 (*p*-$C$H$_3$), 11.4 (C$_5$($C$H$_3$)$_5$).

**Synthesis of *N*Sb(Cl)Cp* (1-*N*).** A yellow suspension of Cp*SbCl$_2$ (0.33 g, 1.00 mmol) and Dip(Me$_3$Si)NLi (0.26 g, 1.00 mmol) in *n*-hexane (40 mL) was stirred for 15 minutes at ambient temperature, filtered and the solvent was removed from the filtrate *in vacuo*, yielding a yellow solid. Yield: 0.47 g (0.87 mmol, 87 %). M.p. 124 °C. Anal. Calcd. for $C_{25}H_{41}ClNSbSi$: C, 55.51; H, 7.64; N, 2.59. Found: C, 56.0; H, 7.55; N, 2.62 %. IR (neat): $\nu$ 3050, 2958, 2913, 2864, 1574, 1460, 1431, 1383, 1310, 1247, 1159, 1099, 1037, 898, 835, 786, 754, 674, 521, 432, 409, cm$^{-1}$. $^1$H NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ 7.05 (m, 3 H, C$_6H_3$($i$-Pr)$_2$), 3.87 (sept, $^3J_{HH}$ = 6.8 Hz, 2 H, C$H$(CH$_3$)$_2$), 1.90 (s, 15 H, C$_5$(C$H_3$)$_5$), 1.26 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, CH(C$H_3$)$_2$), 1.23 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, CH(C$H_3$)$_2$), 0.36 (s, 9 H, Si(C$H_3$)$_3$). $^{13}$C NMR (75.5 MHz, $C_6D_6$, 25 °C): $\delta$ 149.1, 141.9, 126.2 ($C_6$H$_3$($i$-Pr)$_2$), 125.1 ($C_5$(CH$_3$)$_5$), 124.7 ($C_6$H$_3$($i$-Pr)$_2$), 27.6 ($C$H(CH$_3$)$_2$), 27.5, 24.7 (CH($C$H$_3$)$_2$), 11.6 (C$_5$($C$H$_3$)$_5$), 4.5 (Si($C$H$_3$)$_3$).

**Synthesis of L(Cl)GaSb*B* (2-*B*)**. A solution of LGa (50 mg, 0.1026 mmol) and **1-*B*** (70 mg, 0.1026 mmol) in benzene (1.5 mL) was heated to 95 °C for one hour, during which time a dark red solution formed. All volatiles were removed *in vacuo* and the resulting residue dissolved in warm *n*-hexane (1.2 mL). Storage of the solution for 12 h at ambient temperature yielded red crystals of **2-*B***. Yield: 43 mg (0.0410 mmol, 40 %). M.p. 224 °C. Anal. Calcd. for $C_{55}H_{77}BClGaN_4Sb$: C, 64.01; H, 7.52; N, 5.43. Found: C, 65.1; H, 7.52; N, 5.55 %. IR (neat): $\nu$ 2958, 2928, 2864, 1527, 1438, 1376, 1316, 1257, 1177, 1106, 1057, 1020, 935, 901, 863, 799, 757, 694, 634, 533, 451 cm$^{-1}$. $^1$H NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ 7.38, 6.00, 5.83, 5.48, 4.08, 3.30, 1.22, 0.20. Evans NMR (300 MHz, Tol-$d_8$, 25 °C): $\mu_{eff}$ 1.58 $\mu_B$. UV-Vis (toluene): $\lambda$ ($\varepsilon$) 526 (786), 562 (679), 875 (123) nm (mol$^{-1}$ dm$^3$ cm$^{-1}$).

**Synthesis of L(Cl)GaSb*C* (2-*C*)**. A solution of LGa (50 mg, 0.1026 mmol) and **1-*C*** (62 mg, 0.1026 mmol) in benzene (1.5 mL) was heated to 80 °C for 15 minutes, during which time an orange solution formed. All volatiles were removed *in vacuo* and the resulting solid residue was dissolved in *n*-hexane (1.2 mL) and stored at 0 °C. Yellow crystals of ***C***Sb=Sb***C*** (9 mg, 0.0103 mmol, 10 %) formed within 12 h. The crystals

were separated, the remaining solution was slightly concentrated and stored at -30 °C for 12 h, resulting in the formation of orange crystals of **2-*C***. Yield: 45 mg (0.0470 mmol, 46 %). M.p. 176 °C. Anal. Calcd. for $C_{53}H_{66}ClGaN_2Sb$: C, 66.45; H, 6.94; N, 2.92. Found: C, 67.2; H, 6.97; N, 2.88 %. IR (neat): $\nu$ 2962, 2922, 2866, 1527, 1438, 1379, 1316, 1261, 1177, 1100, 1018, 937, 845, 796, 758, 638, 575, 529, 447 $cm^{-1}$. $^1H$ NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ 9.34, 7.02, 6.07, 5.35, 4.27, 2.44, 1.32. Evans NMR (300 MHz, Tol-$d_8$, 25 °C): $\mu_{eff}$ 1.61 $\mu_B$. UV-Vis (toluene): $\lambda$ ($\varepsilon$) 457 (181), 746 (79) nm ($mol^{-1}$ $dm^3$ $cm^{-1}$).

**Synthesis of L(Cl)GaSb*N* (2-*N*)**. A solution of LGa (50 mg, 0.1026 mmol) and **1-*N*** (56 mg, 0.1026 mmol) in benzene (1.5 mL) was heated to 95 °C for 1.5 hours, during which time a dark red solution formed. All volatiles were removed *in vacuo*, the resulting solid residue dissolved in *n*-hexane (1.0 mL) and stored at -30 °C. Green crystals of **2-*N*** formed within 12 h. Yield: 42 mg (0.0470 mmol, 46 %). M.p. 170 °C (dec.). Anal. Calcd. for $C_{44}H_{67}ClGaN_3SbSi$: C, 59.18; H, 7.56; N, 4.71. Found: C, 59.9; H, 7.40; N, 4.79 %. IR (neat): $\nu$ 3064, 2961, 2924, 2866, 1551, 1524, 1461, 1434, 1383, 1313, 1245, 1177, 1100, 1021, 909, 829, 793, 756, 675, 626, 530, 435 $cm^{-1}$. $^1H$ NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ 7.35, 5.92, 4.94, 4.19, 2.45, 1.35. Evans NMR (300 MHz, Tol-$d_8$, 25 °C): $\mu_{eff}$ 1.56 $\mu_B$. UV-Vis (toluene): $\lambda$ ($\varepsilon$) 417 (1334), 605 (87) nm ($mol^{-1}$ $dm^3$ $cm^{-1}$).

**Synthesis of [K([2.2.2]crypt)][L(Cl)GaSb*B*] ([K([2.2.2]crypt)][2-*B*])**. THF (5 mL) was added to a mixture of L(Cl)GaSb***B*** (67 mg, 0.0640 mmol) and [K([2.2.2]crypt)][$C_{10}H_8$] (35 mg, 0.0640 mmol) at -78 °C and the mixture was allowed to slowly come to room temperature over the course of 5 hours. The resulting dark green solution was filtered and volatiles were removed *in vacuo*. The residue was dissolved in warm fluorobenzene (3 mL) and stored at ambient temperature overnight, yielding dark green crystals of [K([2.2.2]crypt)][**2-*B***]. Yield: 37 mg (0.0237 mmol, 37 %). M.p. 172 °C (dec.). Anal. Calcd. for $C_{73}H_{113}BClGaKN_6O_6Sb$: C, 60.57; H, 7.87; N, 5.81. Found C, 58.4; H, 7.46; N, 5.03%. IR (neat): $\nu$ 2955, 2862, 2817, 1554, 1521, 1401, 1360, 1224, 1100, 1076, 950, 932, 794, 754, 685, 632, 521 $cm^{-1}$. $^1H$ NMR (600 MHz, THF-$d_8$, 25 °C): $\delta$ 6.92 (dd, $J_{HH}$ = 7.5, 1.5 Hz, 2 H, $C_6H_3$(*i*-Pr)$_2$), 6.88 (m, 4 H, $C_6H_3$(*i*-Pr)$_2$), 6.82 (m, 6 H, $C_6H_3$(*i*-Pr)$_2$), 5.83 (s, 2 H, NC*H*), 4.79 (s, 1 H, $\gamma$-C*H*), 3.66 (sept, $^3J_{HH}$ = 6.7 Hz, 2 H, C*H*($CH_3$)$_2$), 3.59 (s, 12 H, crypt-C$H_2$), 3.55 (dd, $^3J_{HH}$ = 5.5, 4.3 Hz, 12 H, crypt-C$H_2$), 3.25 (m, 6 H, C*H*($CH_3$)$_2$), 2.57 (dd, $^3J_{HH}$ = 5.5, 4.3 Hz, 12 H, crypt-C$H_2$), 1.50 (s, 6 H, CC$H_3$), 1.18 (d, $^3J_{HH}$ = 6.7 Hz, 6 H, CH(C$H_3$)$_2$), 1.08 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, CH(C$H_3$)$_2$), 0.96 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(C$H_3$)$_2$), 0.92 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(C$H_3$)$_2$), 0.87 (d, $^3J_{HH}$ = 6.7 Hz, 6 H, CH(C$H_3$)$_2$), 0.85 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, CH(C$H_3$)$_2$). $^{11}B$ NMR (192.5 MHz, THF-$d_8$, 25 °C): $\delta$ 31.8 (br s, Sb*B*$N_2$). $^{13}C$ NMR (150.9 MHz, THF-$d_8$, 25 °C): $\delta$ 164.9 (*C*$CH_3$), 147.5, 146.1, 145.8, 144.7, 144.4, 125.6, 125.3, 123.7, 123.1 ($C_6H_3$(*i*-Pr)$_2$), 120.7 (N*C*H), 97.2 ($\gamma$-*C*H), 71.4, 68.5, 54.8 (crypt-*C*$H_2$), 29.8 (*C*H($CH_3$)$_2$), 28.9 (CH(*C*$H_3$)$_2$), 28.7, 28.1 (*C*H($CH_3$)$_2$), 25.6 (CH(*C*$H_3$)$_2$), 25.2 (CH(*C*$H_3$)$_2$ & C*C*$H_3$), 25.0, 24.4 (CH(*C*$H_3$)$_2$).

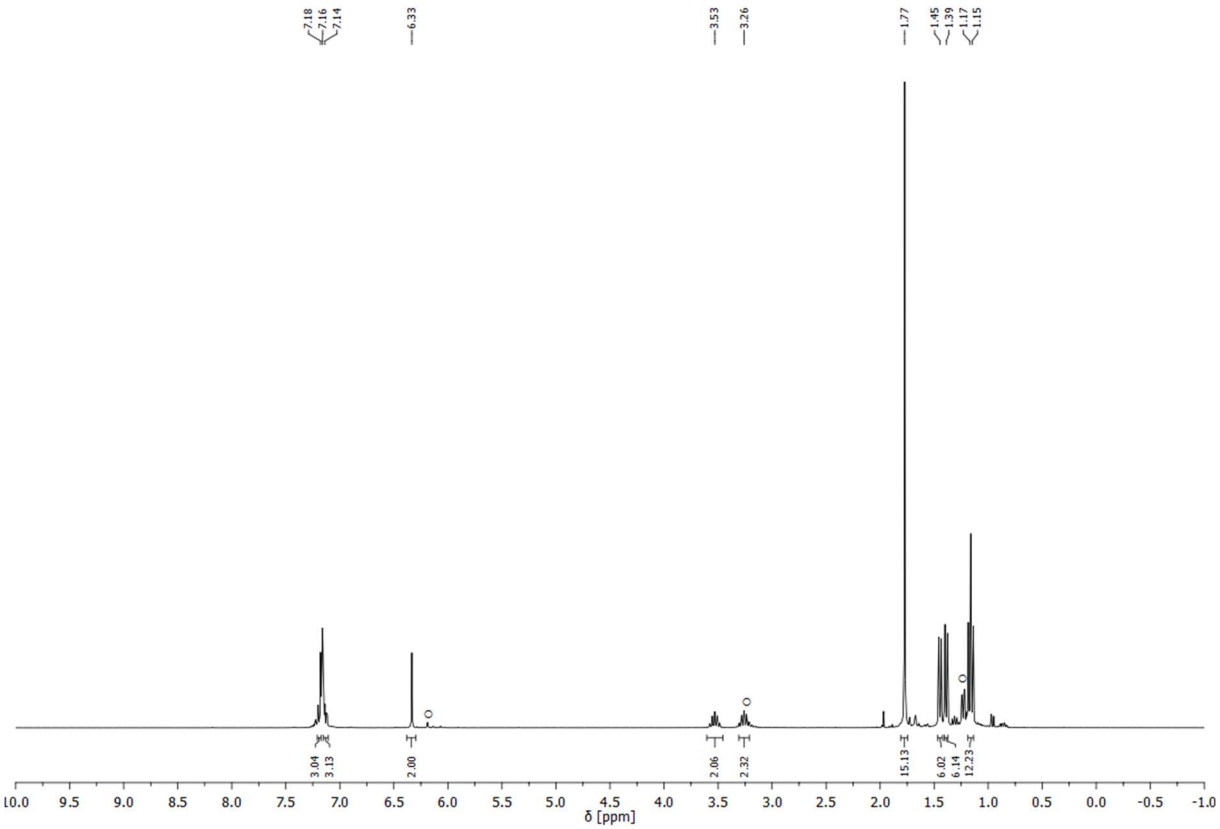


**Figure S2.** $^{1}$H NMR spectrum (300 MHz, $C_6D_6$, 25 °C) of ***B***Sb(Cl)Cp* (**1-*B***). (○ = ***B***H)

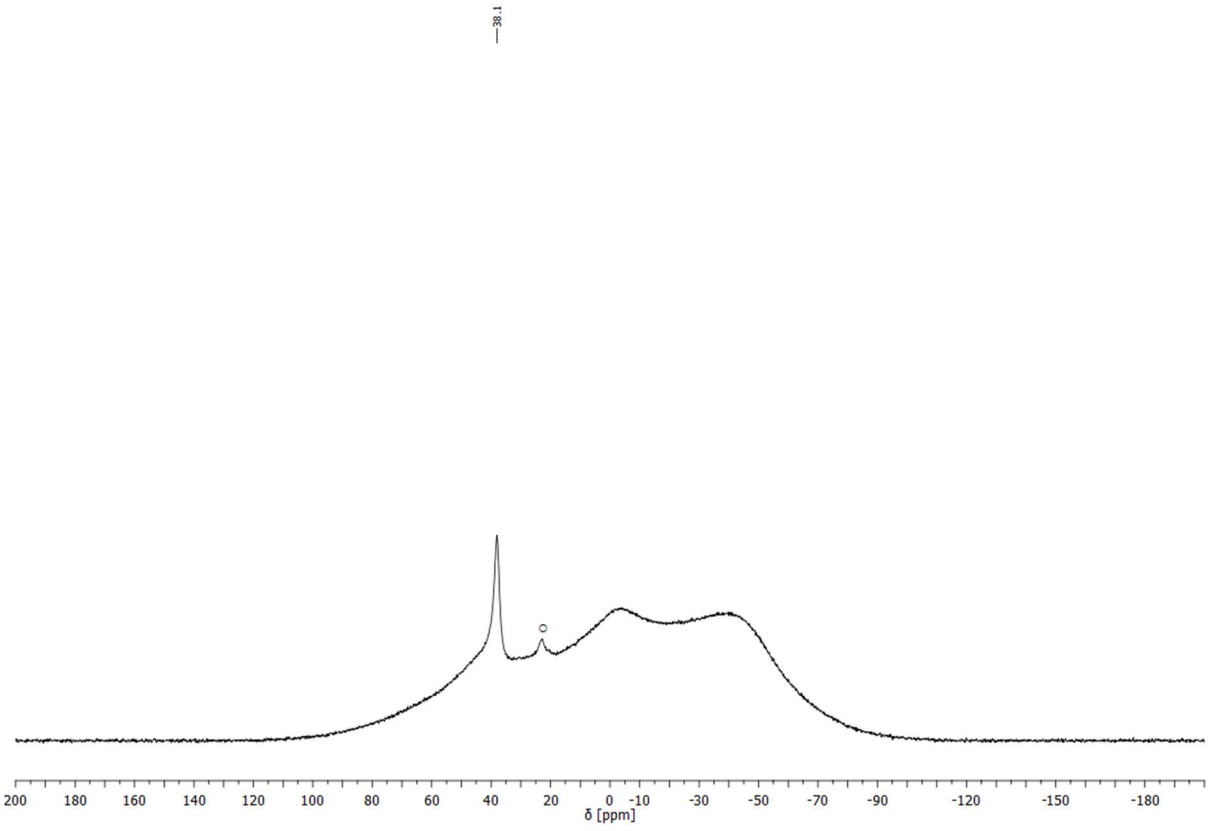


**Figure S3.** $^{11}$B NMR spectrum (96.3 MHz, $C_6D_6$, 25 °C) of ***B***Sb(Cl)Cp* (**1-*B***). (○ = ***B***H)

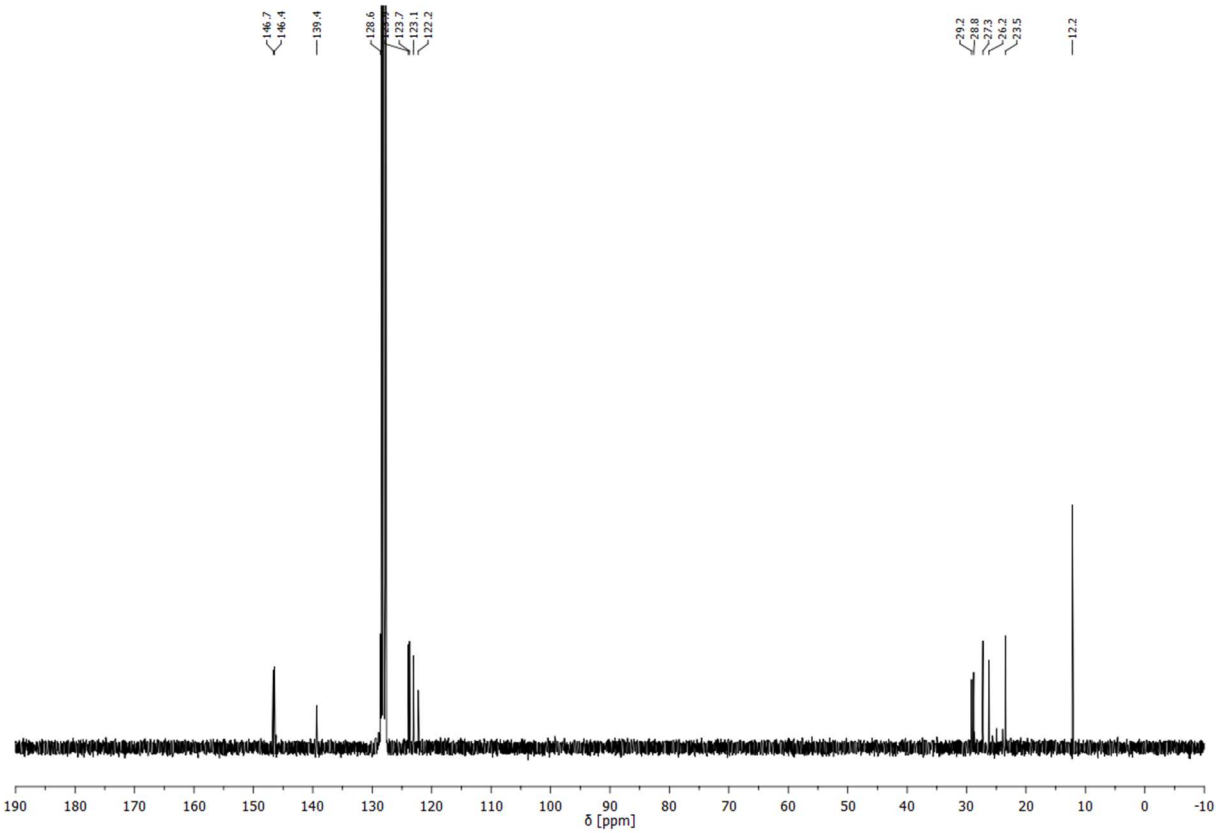


**Figure S4.** $^{13}$C NMR spectrum (75.5 MHz, $C_6D_6$, 25 °C) of ***B***Sb(Cl)Cp* (**1-*B***).

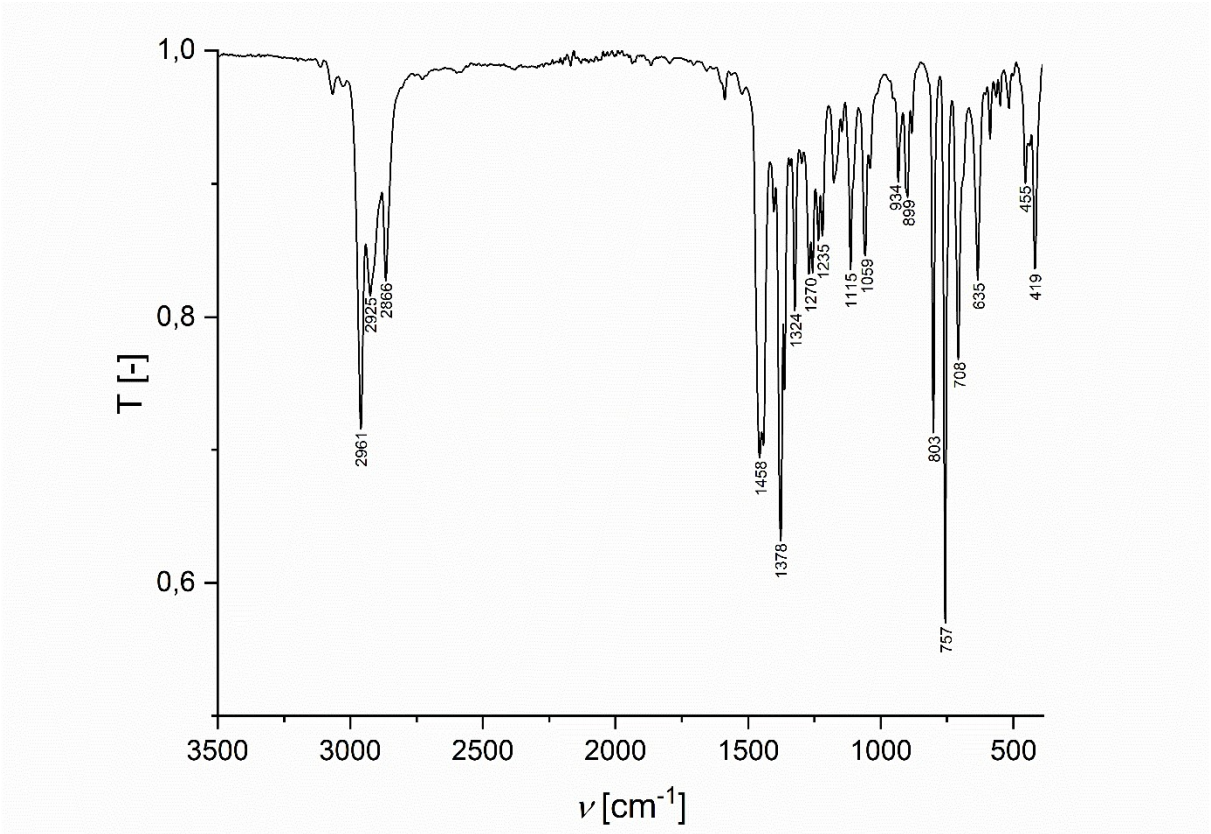


**Figure S5.** ATR-IR spectrum of ***B***Sb(Cl)Cp* (**1-*B***).

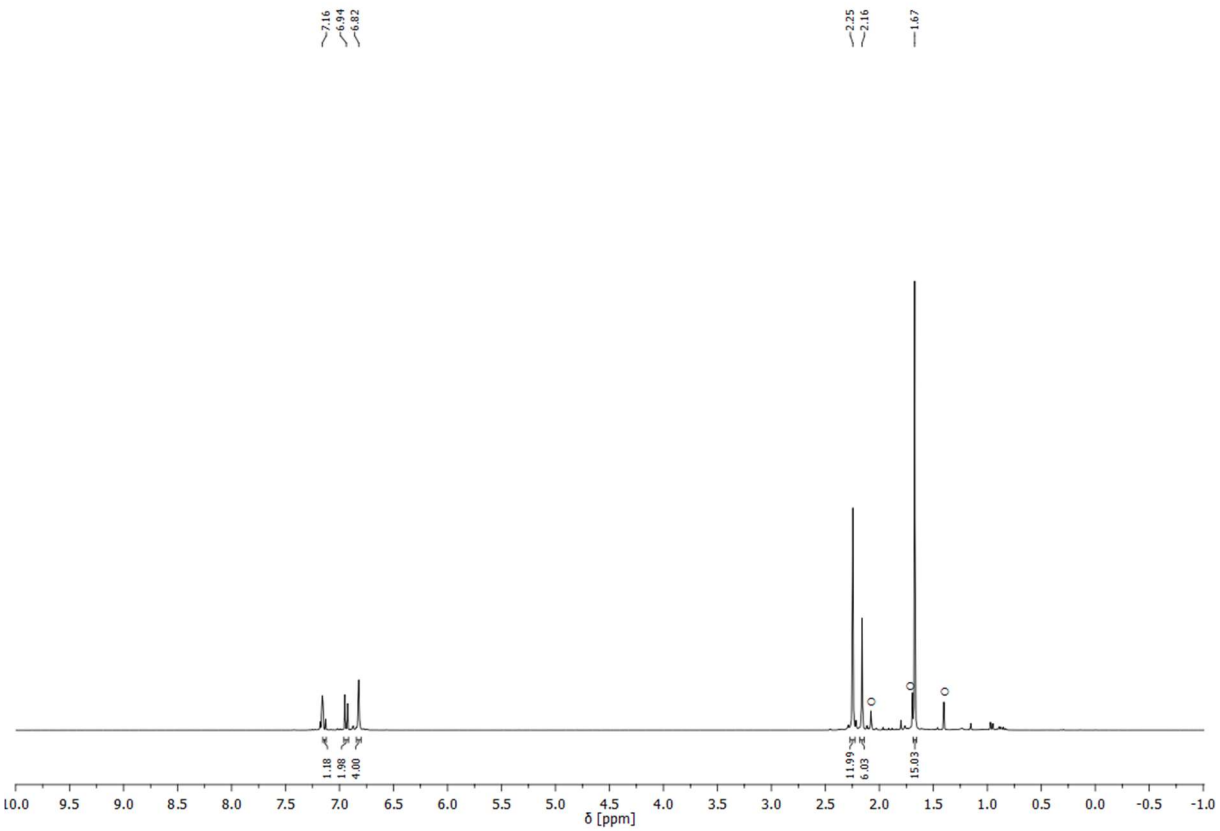


**Figure S6.** $^{1}$H NMR spectrum (300 MHz, $C_6D_6$, 25 °C) of ***C***Sb(Cl)Cp* (**1-*C***). (○ = unidentified impurity)

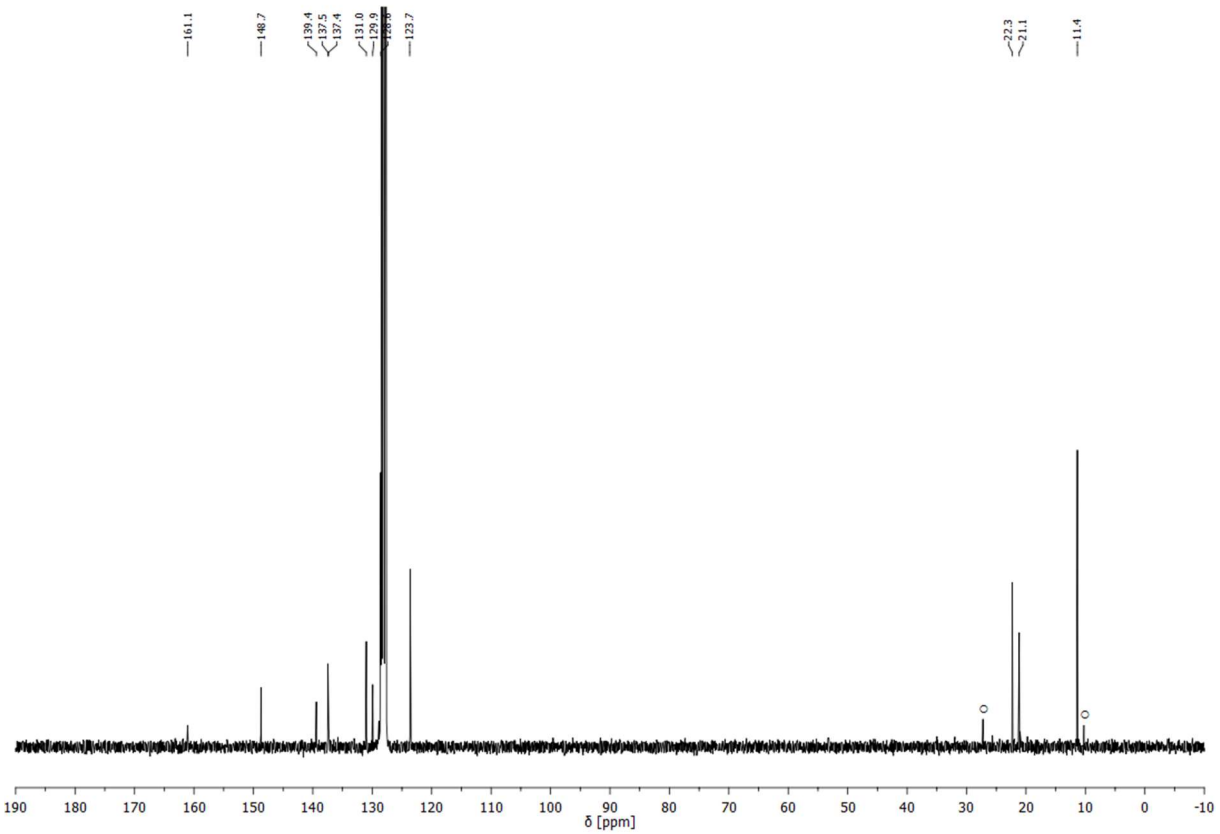


**Figure S7.** $^{13}$C NMR spectrum (75.5 MHz, $C_6D_6$, 25 °C) of ***C***Sb(Cl)Cp* (**1-*C***). (○ = unidentified impurity)

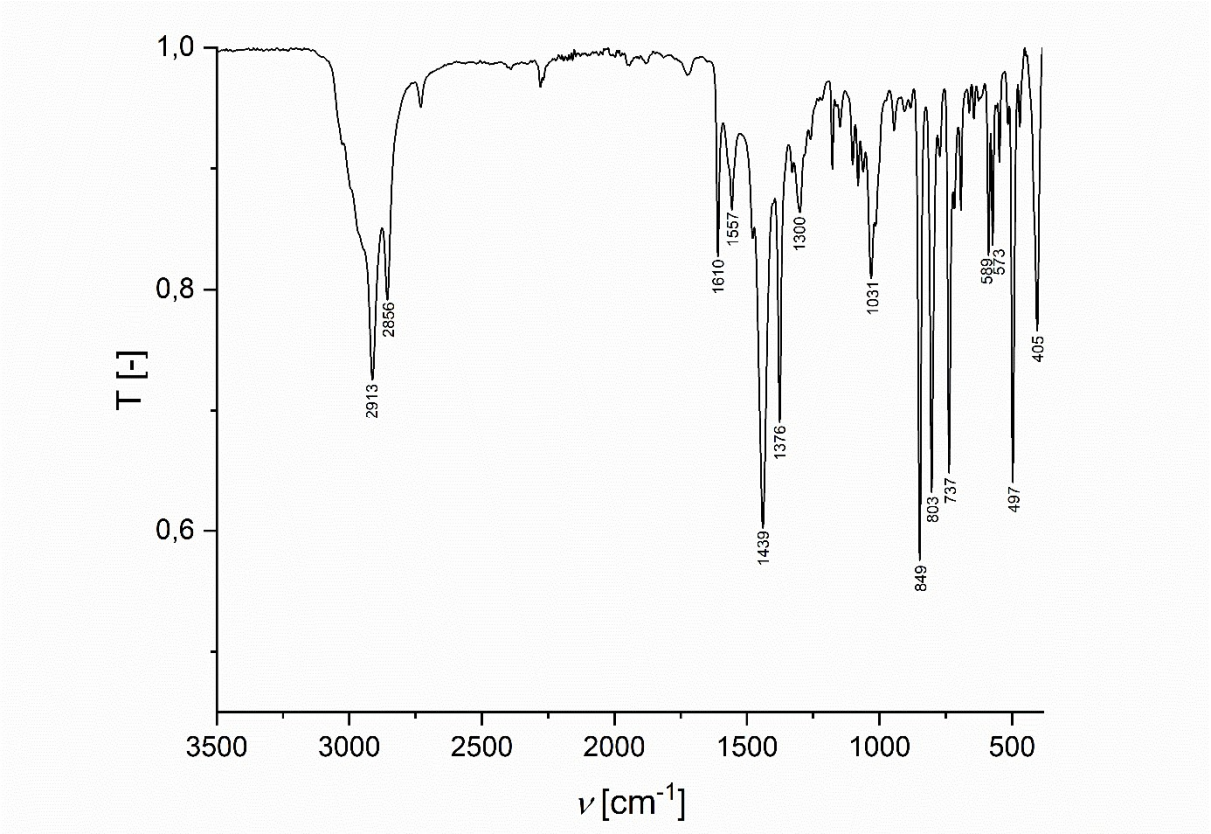


**Figure S8.** ATR-IR spectrum of ***C***Sb(Cl)Cp* (**1-*C***).

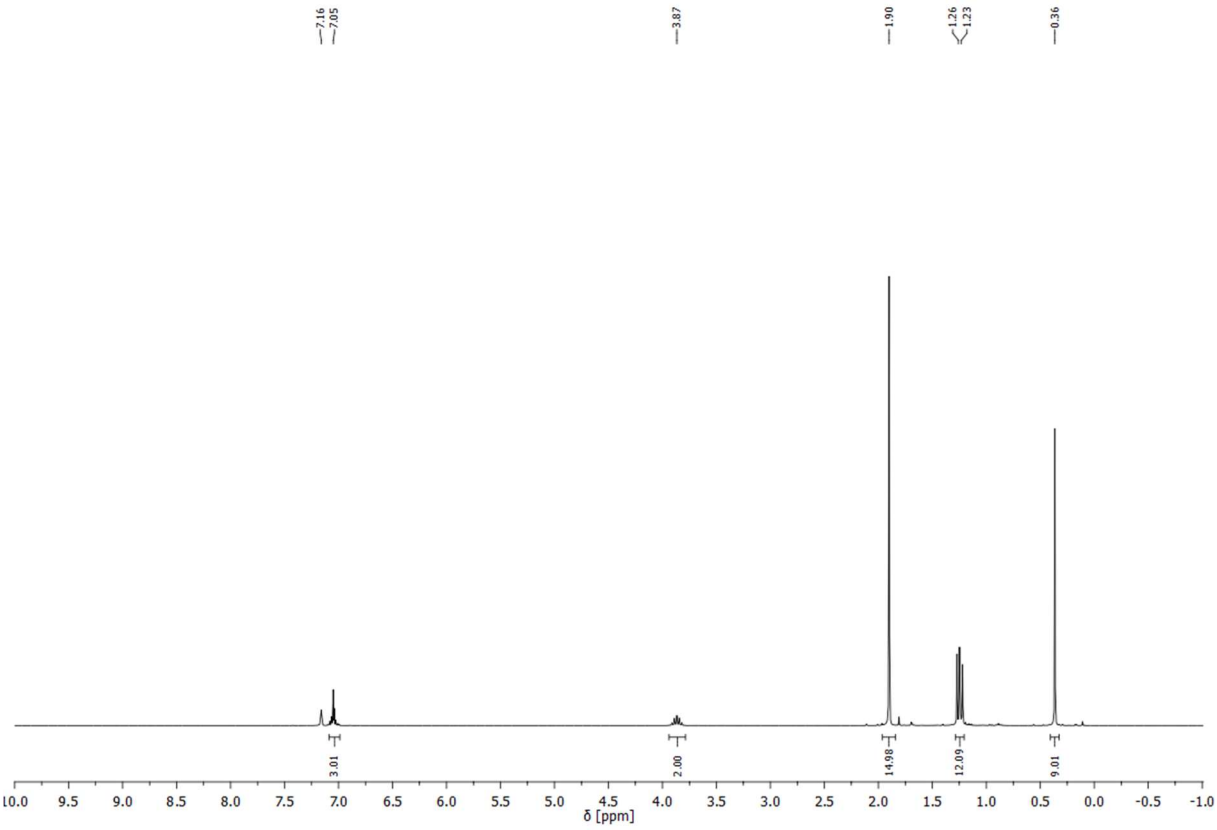


**Figure S9.** $^{1}$H NMR spectrum (300 MHz, $C_6D_6$, 25 °C) of ***N***Sb(Cl)Cp* (**1-*N***).

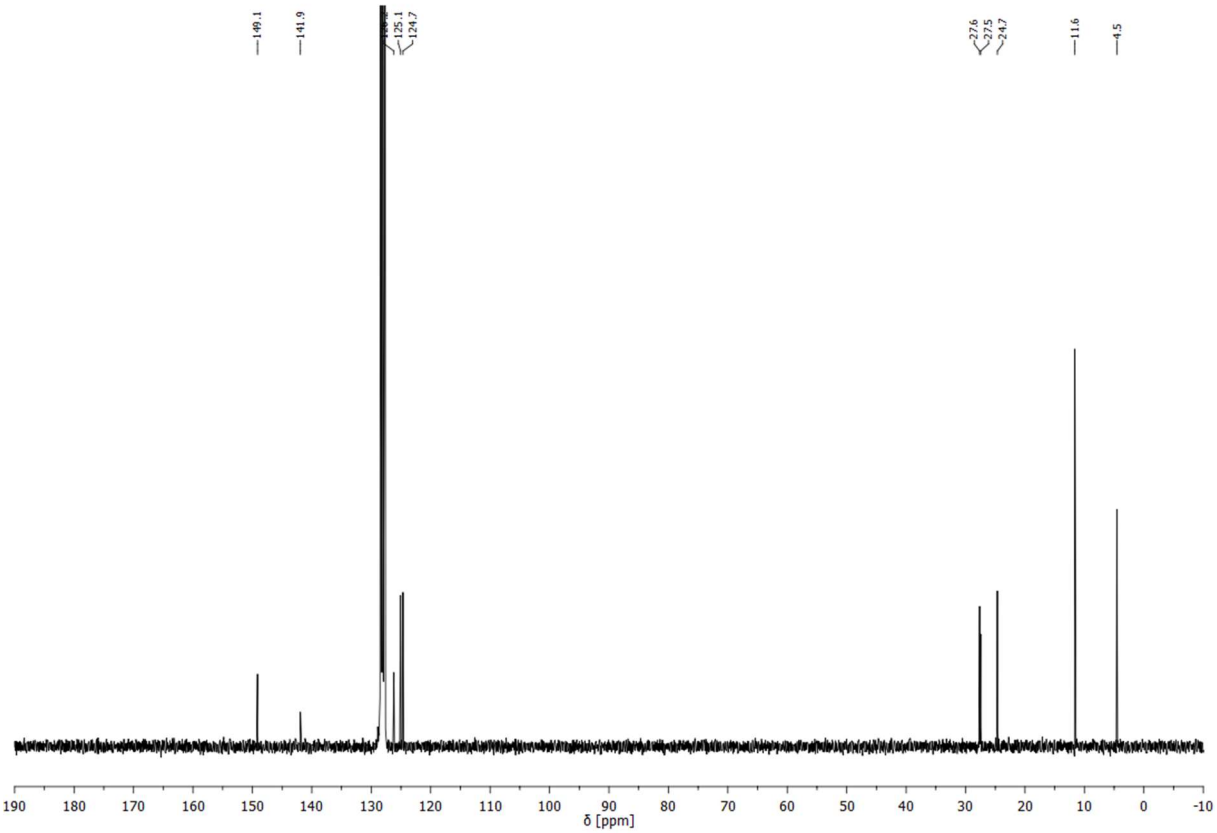


**Figure S10.** $^{13}$C NMR spectrum (75.5 MHz, $C_6D_6$, 25 °C) of ***N***Sb(Cl)Cp* (**1-*N***).

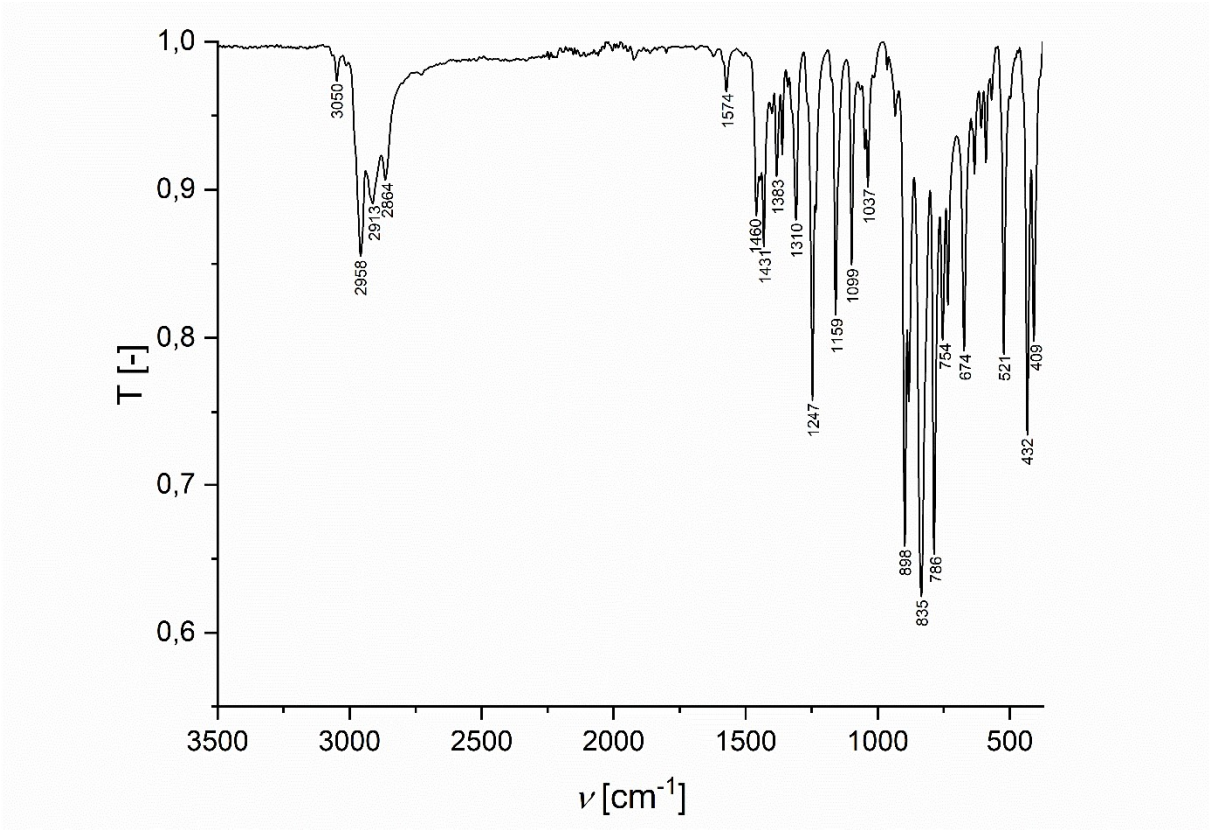


**Figure S11.** ATR-IR spectrum of ***N***Sb(Cl)Cp* (**1-*N***).

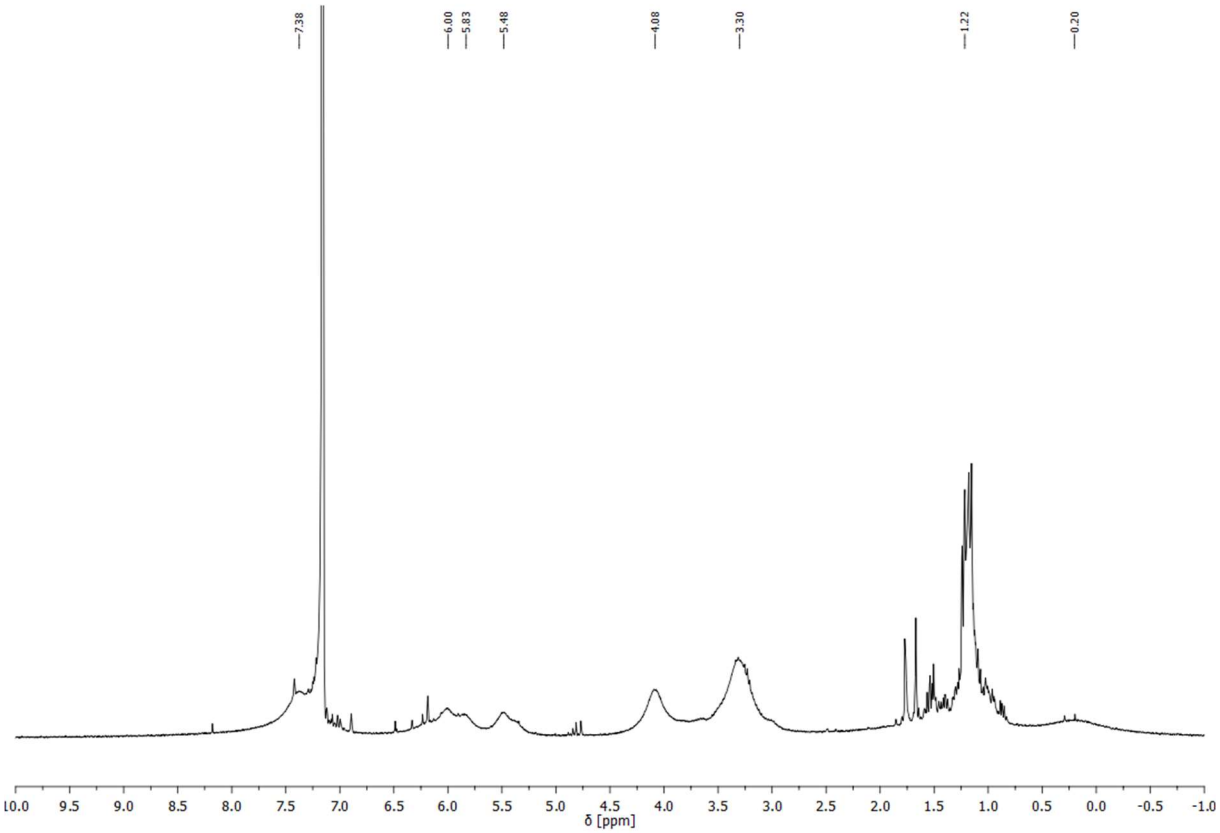


**Figure S12.** $^{1}$H NMR spectrum (300 MHz, $C_6D_6$, 25 °C) of L(Cl)GaSb***B*** (**2-*B***).

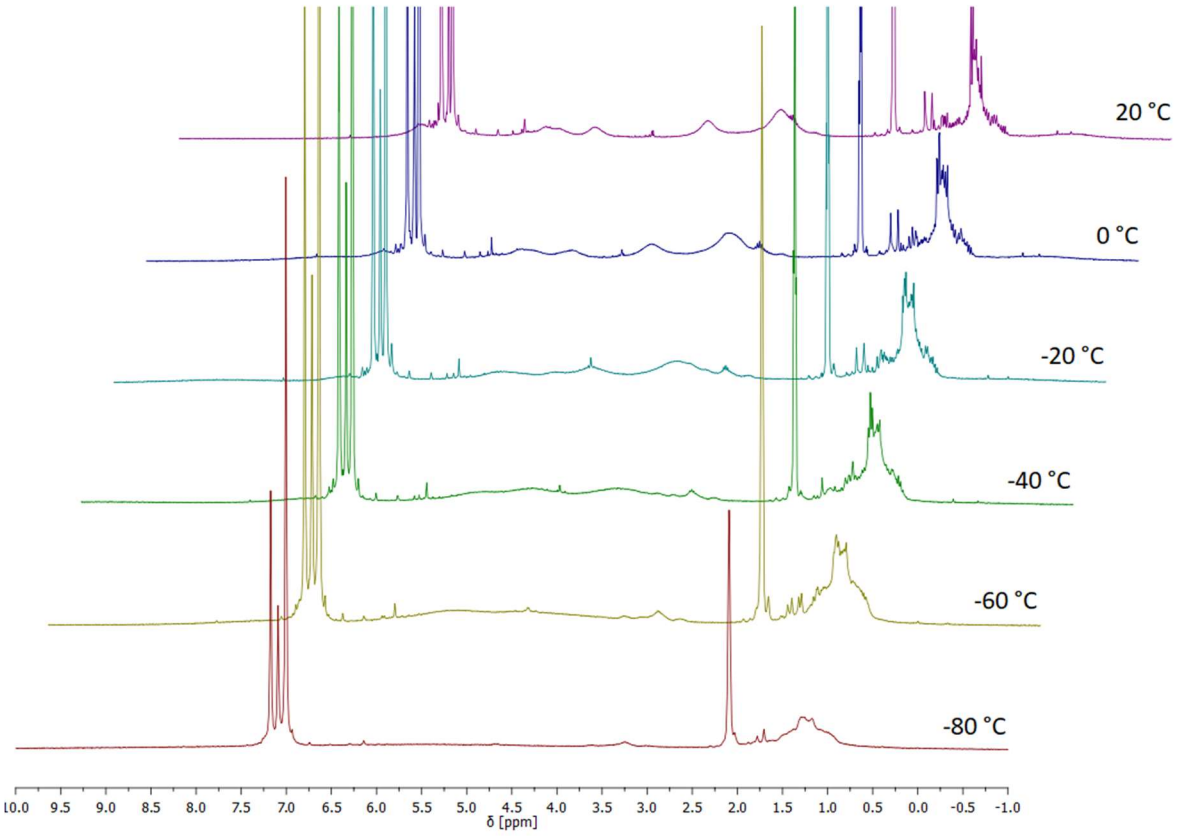


**Figure S13.** Variable-temperature $^{1}$H NMR study (300 MHz, $C_7D_8$) of L(Cl)GaSb***B*** (**2-*B***).

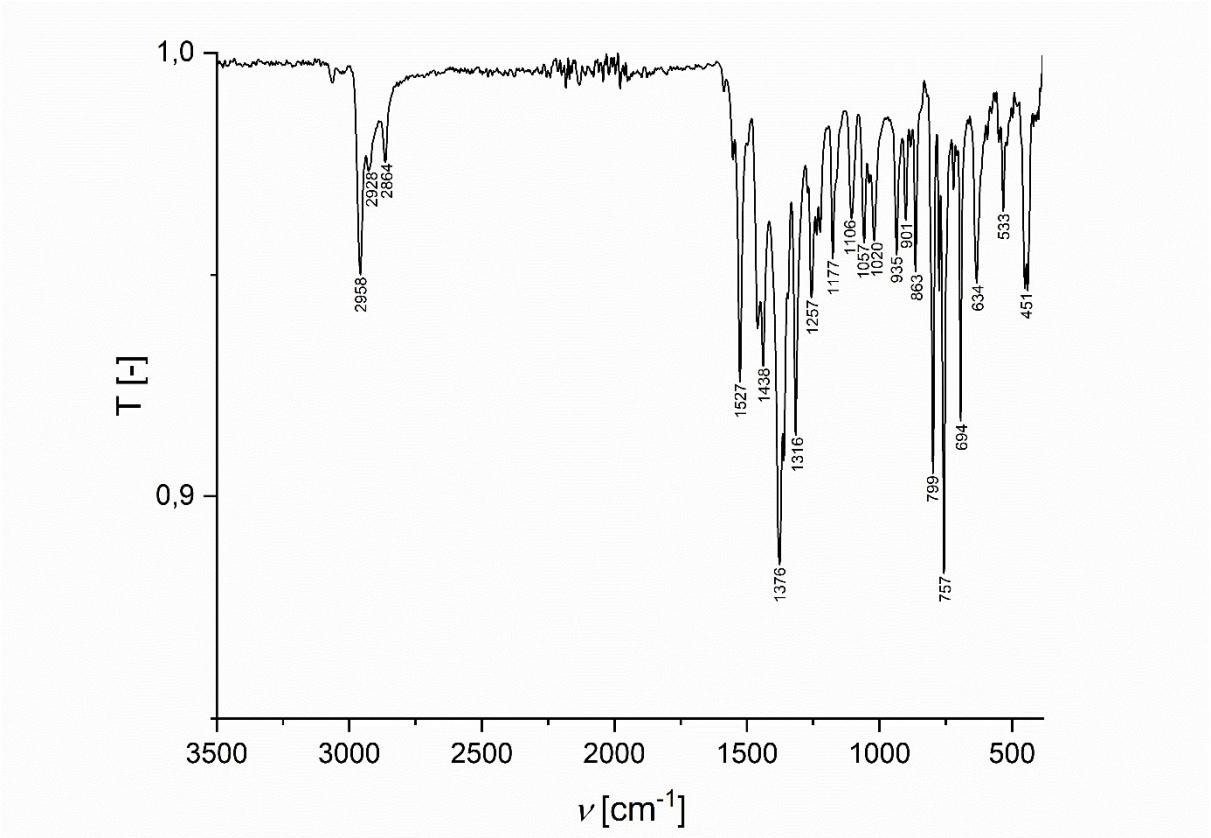


**Figure S14.** ATR-IR spectrum of L(Cl)GaSb***B*** (**2-*B***).

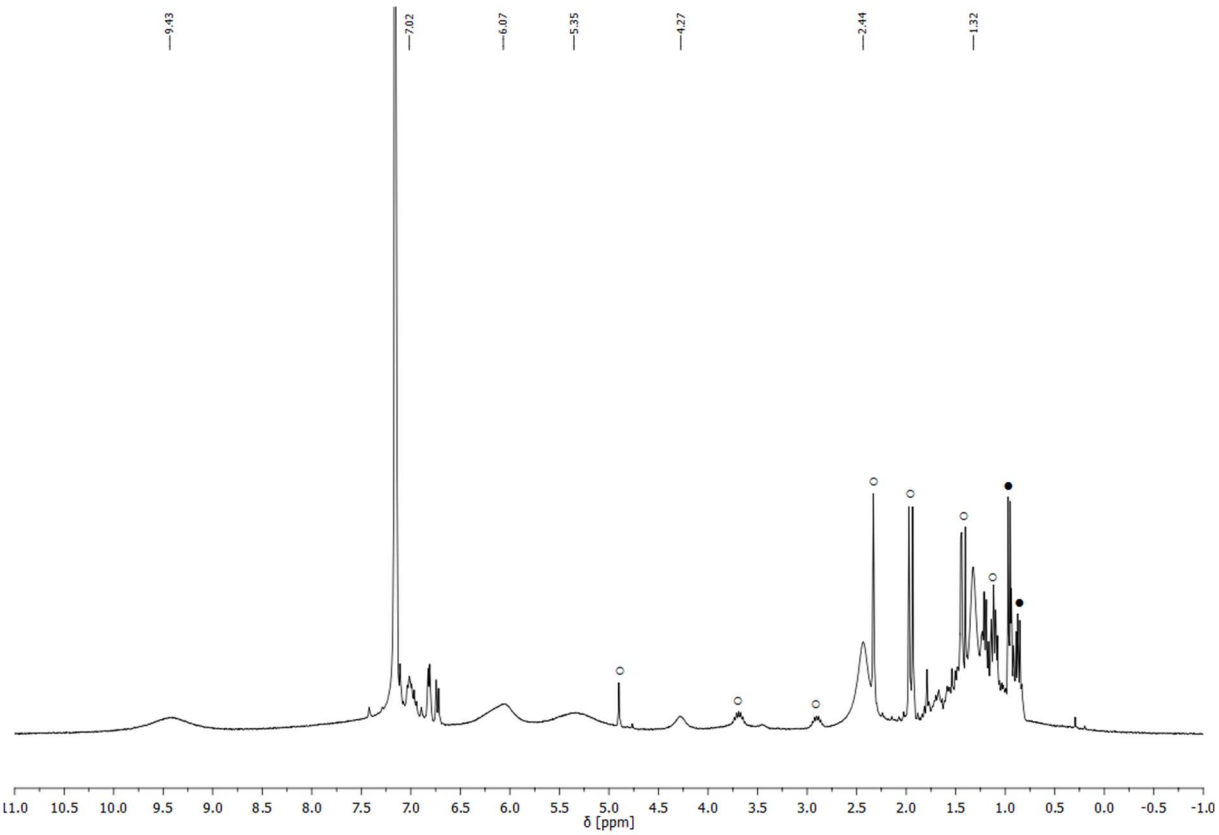


**Figure S15.** $^{1}$H NMR spectrum (300 MHz, $C_6D_6$, 25 °C) of L(Cl)GaSb***C*** (**2-*C***). (○ = unidentified impurity, ● = *n*-hexane from crystal lattice)

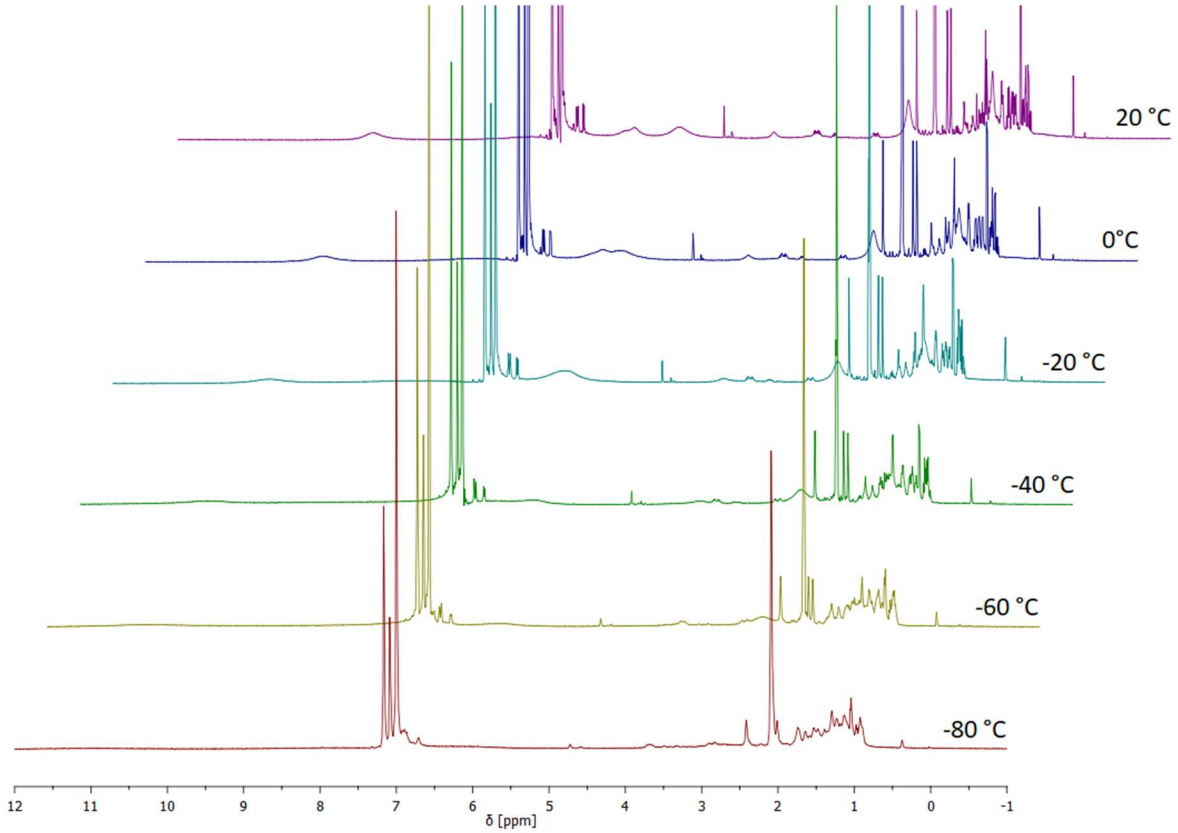


**Figure S16.** Variable-temperature $^{1}$H NMR study (300 MHz, $C_7D_8$) of L(Cl)GaSb***C*** (**2-*C***).

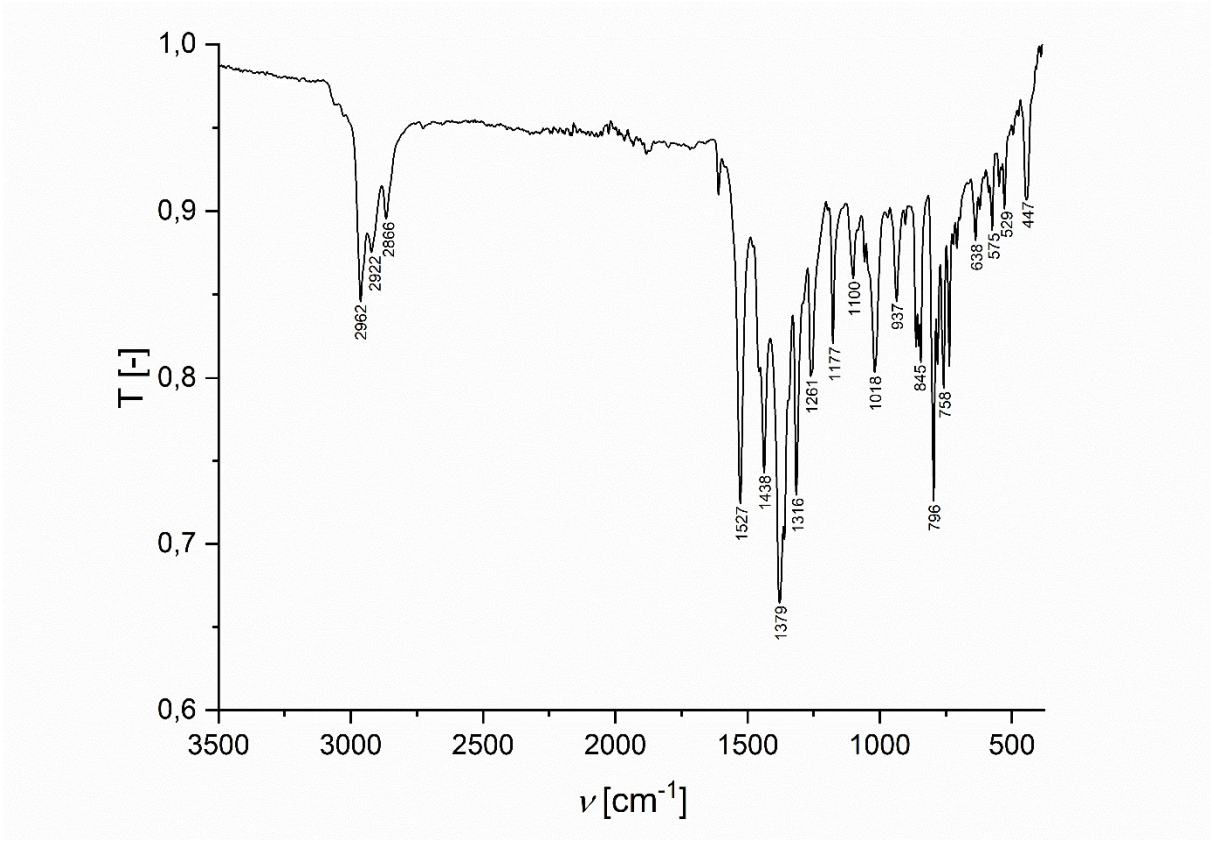


**Figure S17.** ATR-IR spectrum of L(Cl)GaSb***C*** (**2-*C***).

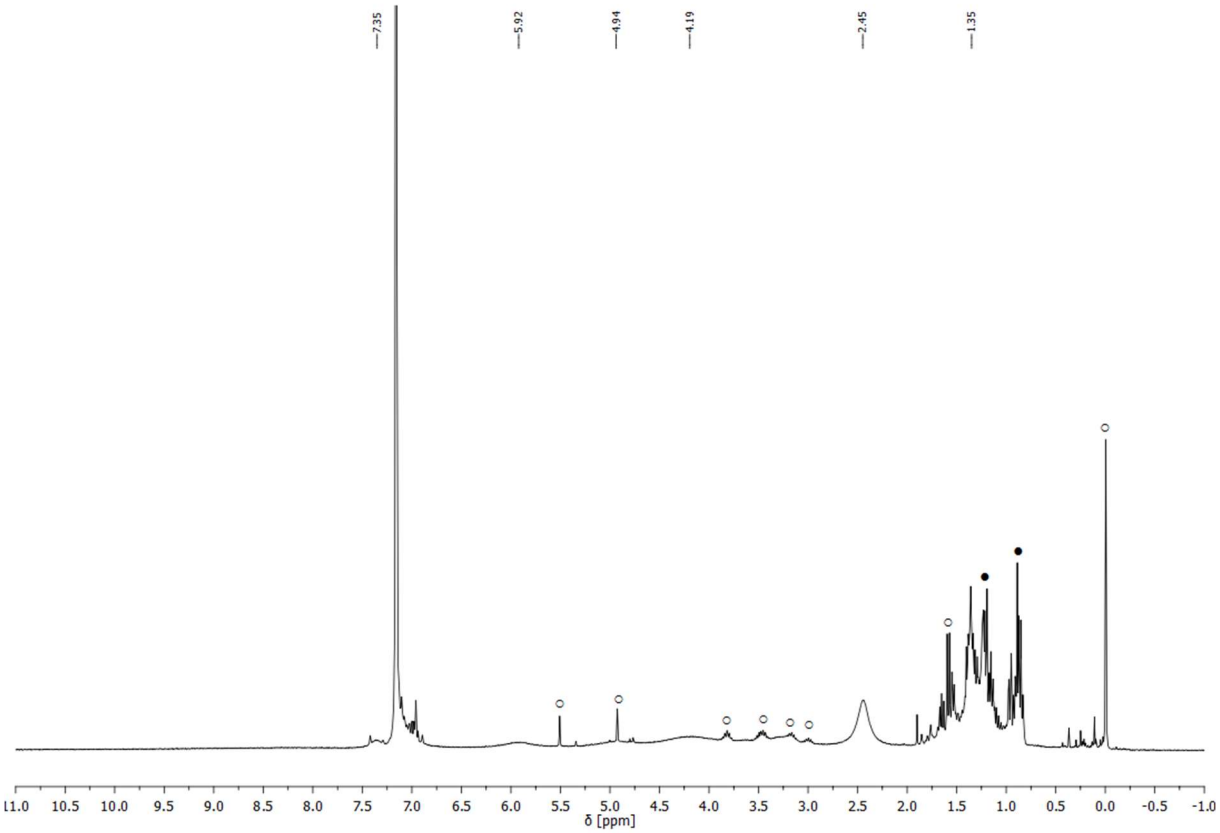


**Figure S18.** $^{1}$H NMR spectrum (300 MHz, $C_6D_6$, 25 °C) of L(Cl)GaSb***N*** (**2-*N***). (○ = unidentified impurities, ● = *n*-hexane from crystal lattice)

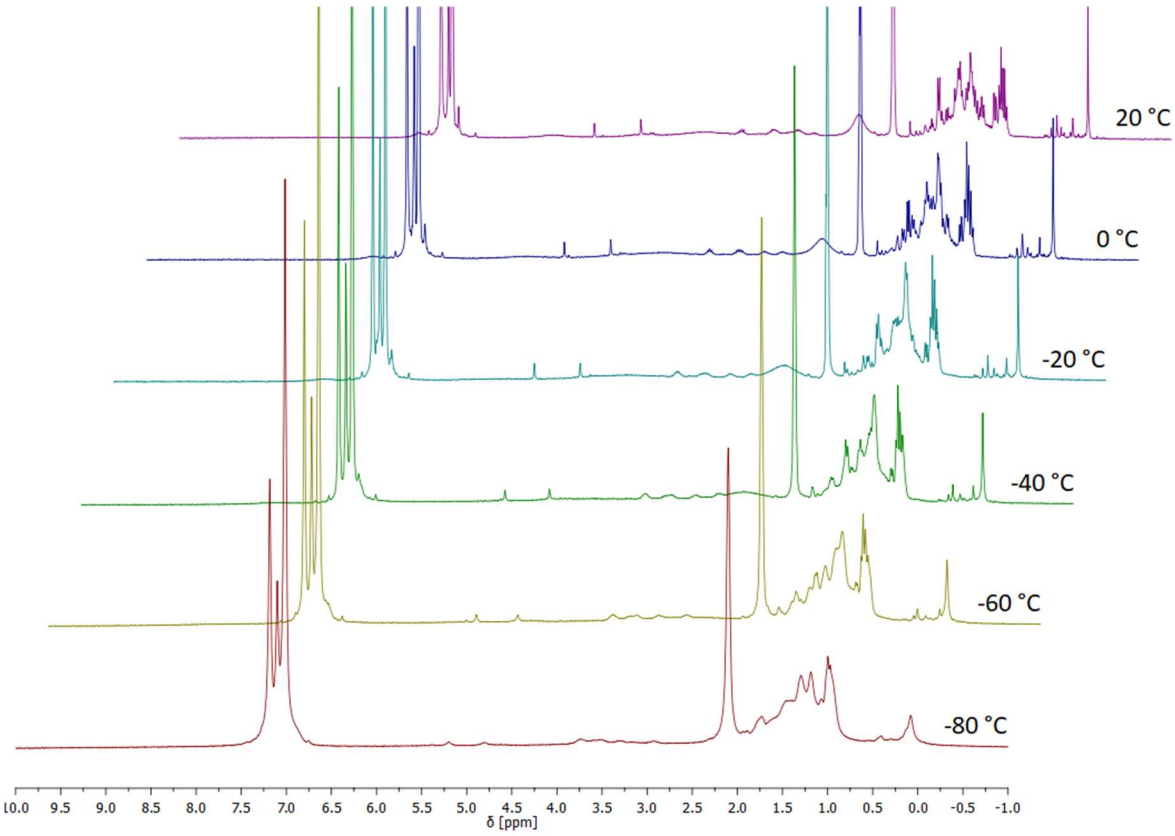


**Figure S19.** Variable-temperature $^{1}$H NMR study (300 MHz, $C_7D_8$) of L(Cl)GaSb***N*** (**2-*N***).

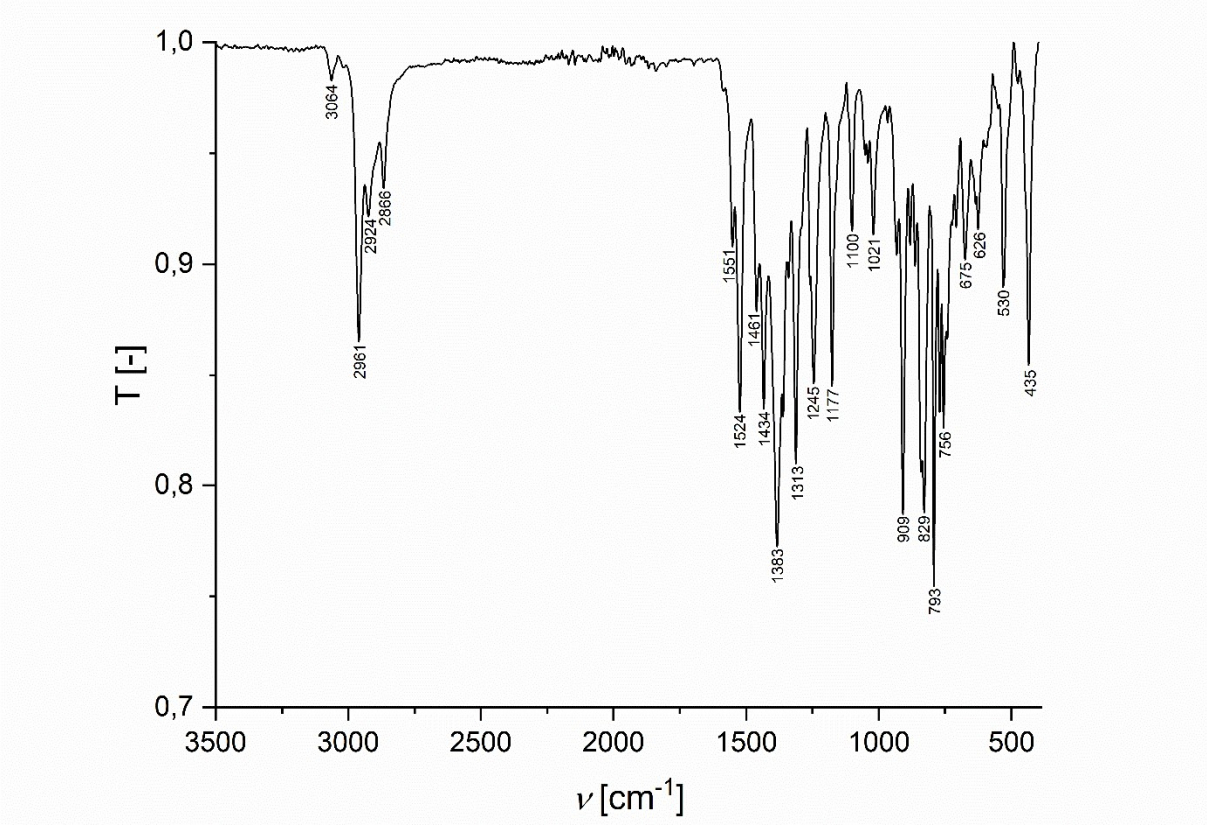


**Figure S20.** ATR-IR spectrum of L(Cl)GaSb***N*** (**2-*N***).

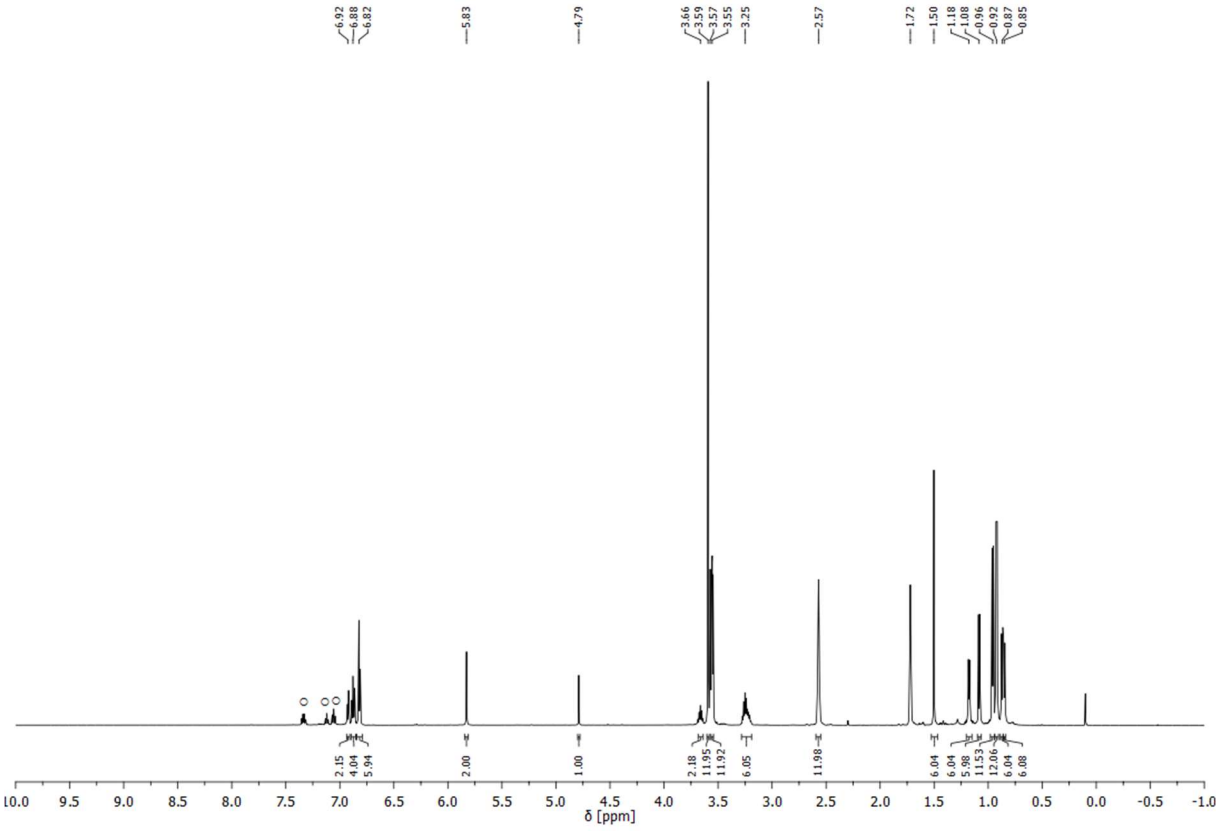


**Figure S21.** $^{1}$H NMR spectrum (600 MHz, THF-$d_8$, 25 °C) of [K([2.2.2]crypt)][**2-*B***]. (○ = fluorobenzene from crystal lattice)

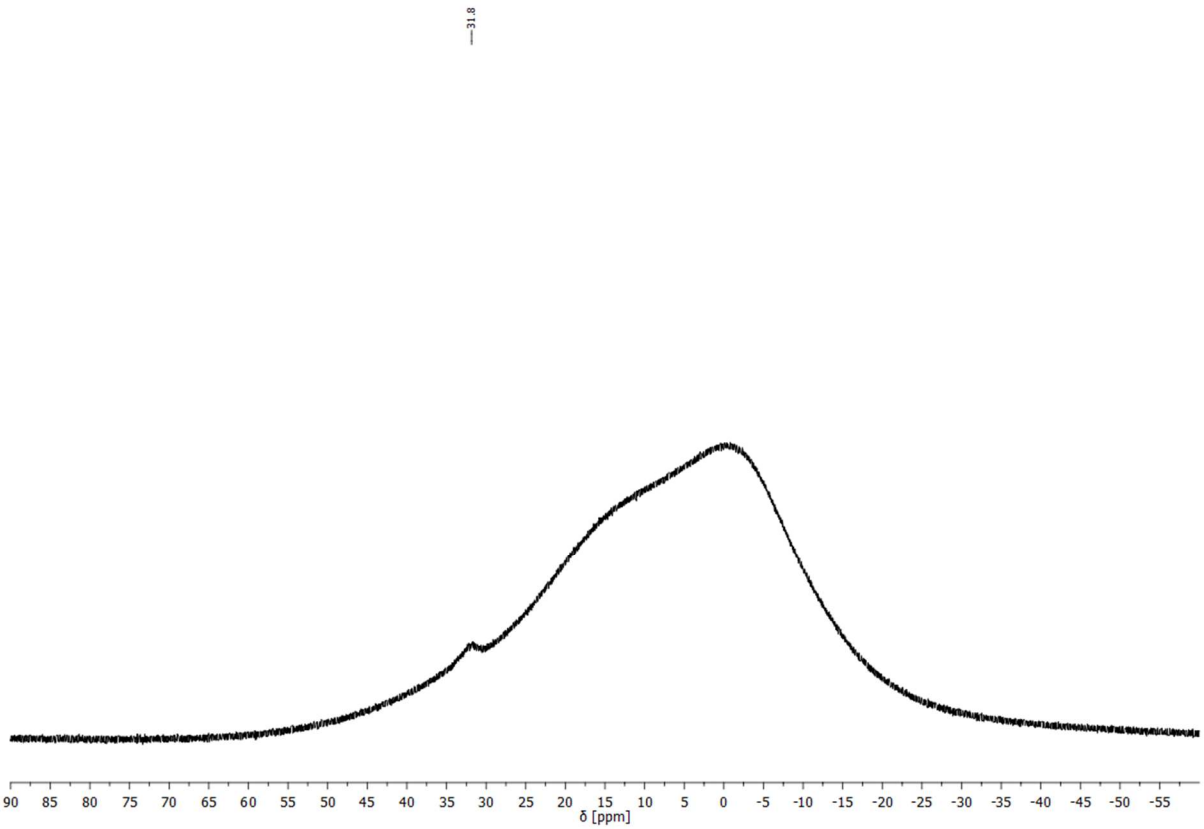


**Figure S22.** $^{11}$B NMR spectrum (192.5 MHz, THF-$d_8$, 25 °C) of [K([2.2.2]crypt)][**2-*B***].

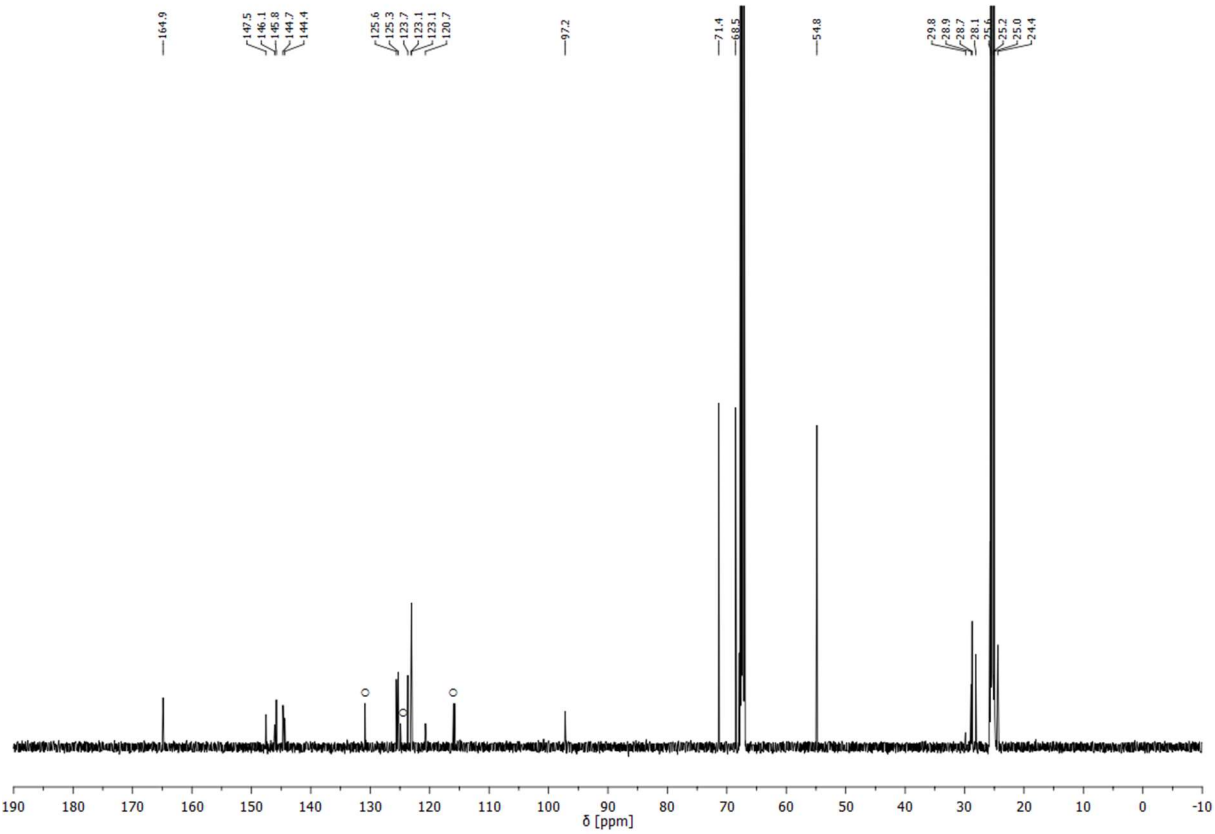


**Figure S23.** $^{13}$C NMR spectrum (150.9 MHz, THF-$d_8$, 25 °C) of [K([2.2.2]crypt)][**2-*B***]. (○ = fluorobenzene from crystal lattice)

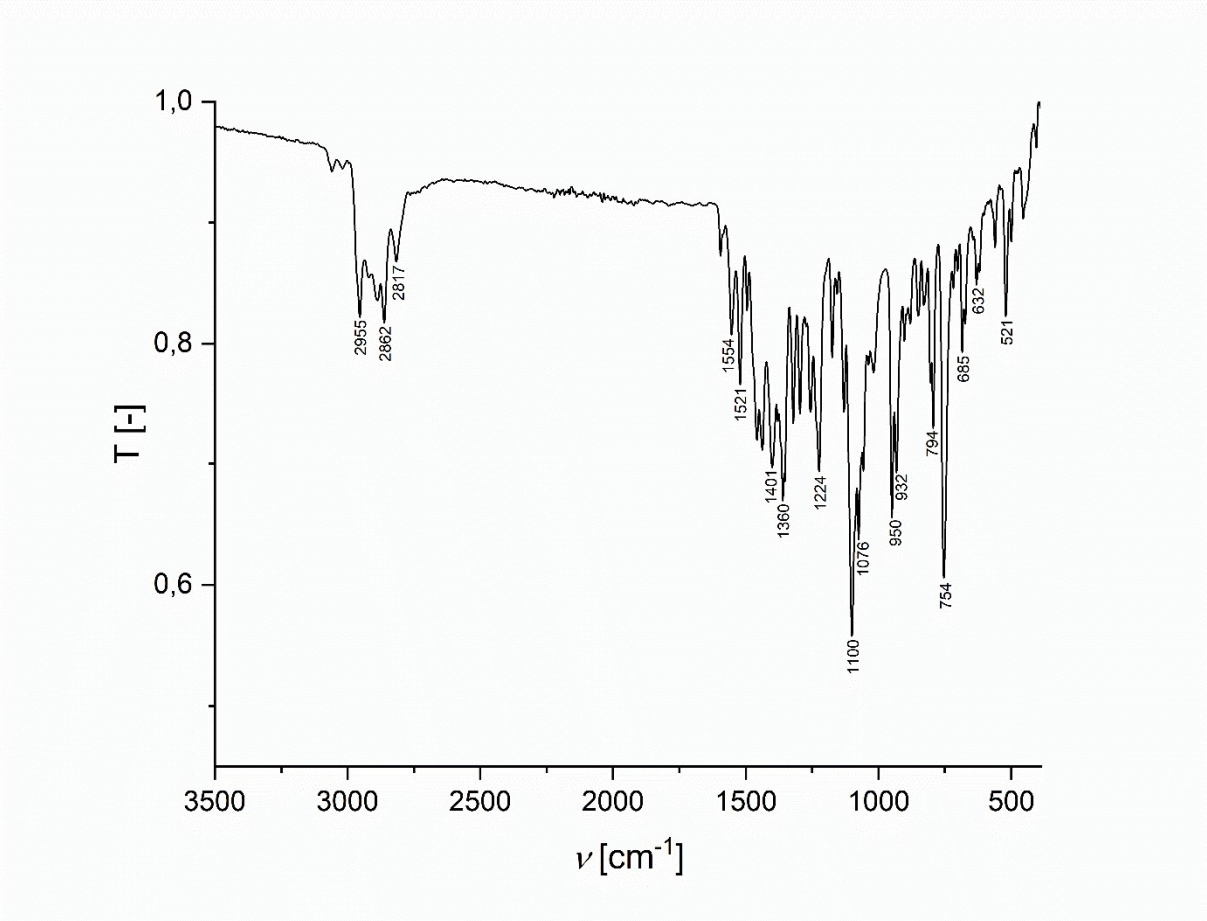


**Figure S24.** ATR-IR spectrum of [K([2.2.2]crypt)][**2-*B***].

## 2. EPR Spectroscopic Details

Continuous-wave (CW) X-band (~9.635 GHz) EPR was a collected on frozen solutions of **2-*R*** in toluene with a Bruker E500 spectrometer equipped with an Oxford liquid helium flow cryostat operated at 20 K. The spectrum was collected with 100 kHz field modulation at 4 G amplitude, a 20.48 time constant and 10.24 conversion time for the 8,192 point spectrum for a single scan. CW Q-band (33.98 GHz) on a Bruker Elexsys E580 and a Bruker ER5106 QT Q-band resonator. Spectra were recorded at 25 K through the utilization of with an Oxford C-935 liquid helium cryostat. Field modulation of 100 kHz and 6.0 G amplitude was employed to detect the 8,128 point spectrum with a 29.53 ms conversion time for a minimum of 15 averaged scans. Q-band ENDOR of **2-*B*** was collected on a Bruker Elexsys E580 with a home-built up/down Q-band pulse conversion accessory and home-built $TE_{011}$ microwave resonator.[9] Spectra were recorded at 8 K through the utilization of with an Oxford C-935 liquid helium cryostat. The Davies ENDOR sequence, $\pi_{inv} - T_{RF} - t_{wait} - \pi/2 - \tau - \pi - echo$, where the RF pulse is applied during $T_{RF}$ (25 µs) and detection delay time of $t_{wait}$ (5 µs) is applied before detection. Here, the inversion pulse length, $\pi_{inv}$, is equal to π (80 ns). The interpulse timing τ was 400 ns and the entire pulse sequence was applied at a repetition rate of 3.0 ms. All EPR data was processed and analyzed in Matlab 2017a and simulated using the EasySpin package (v. 5.2). Simulation parameters are given in figure captions.[10,11]

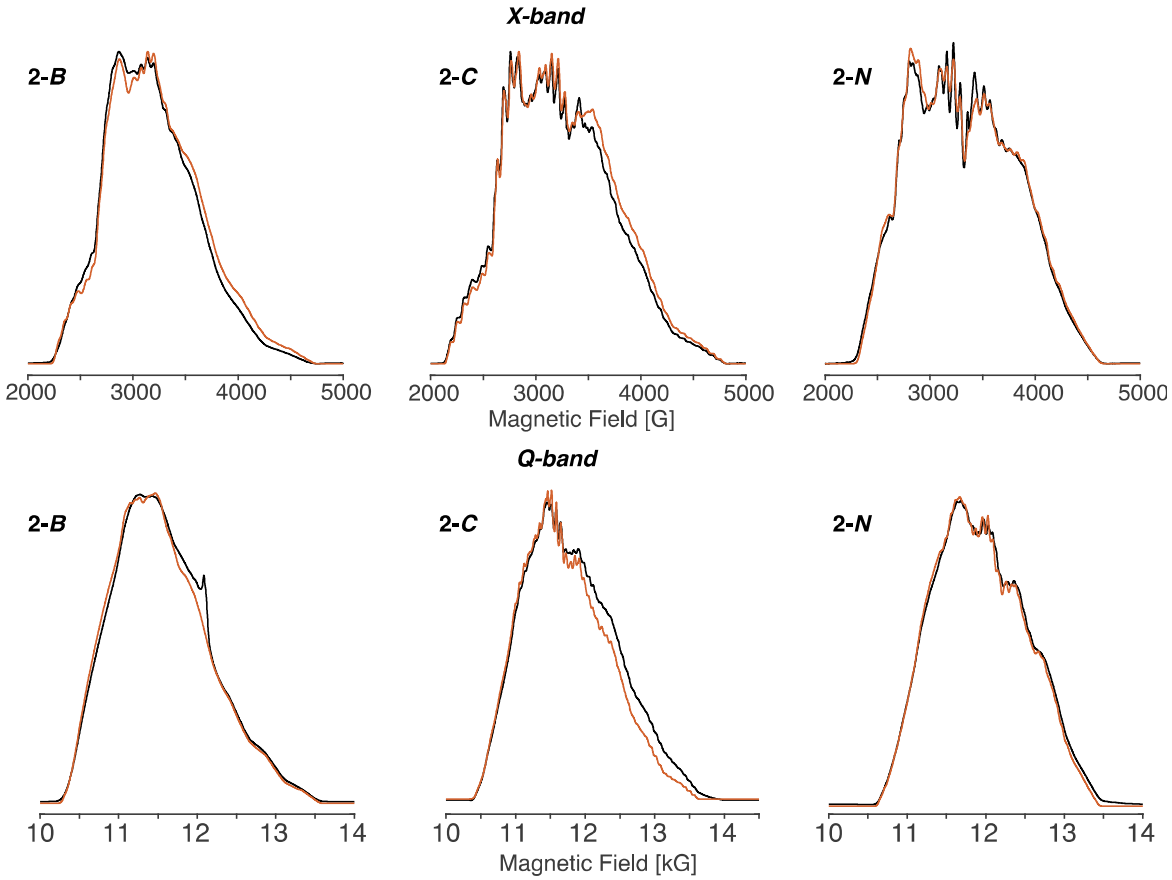


**Figure S25.** First integral of EPR spectra as displayed in Figure 3 and corresponding simulations.

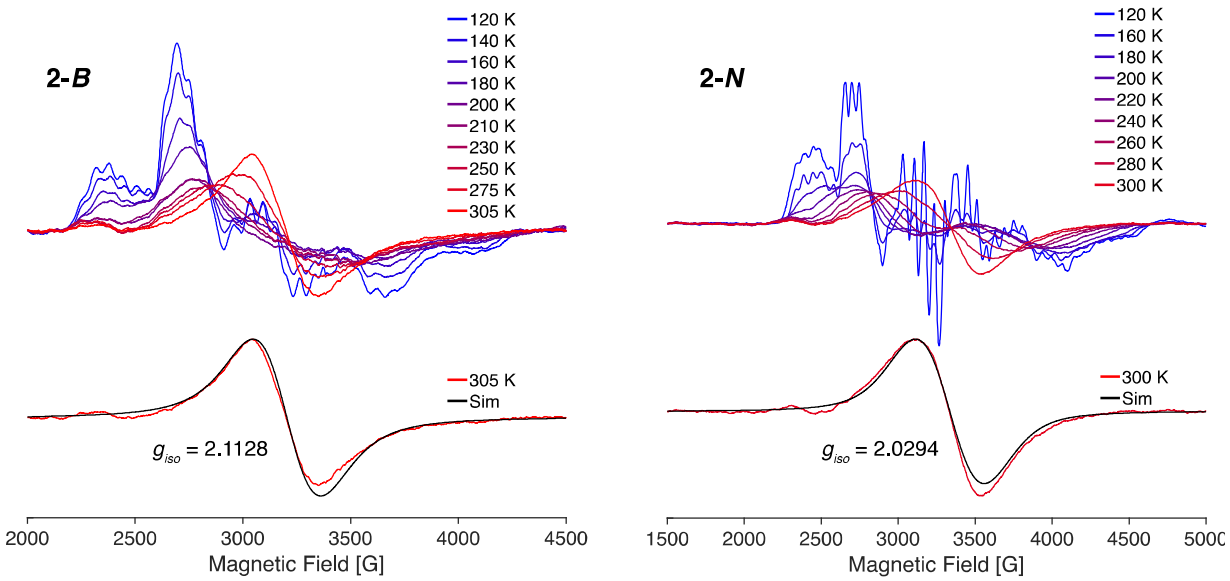


**Figure S26**. Variable temperature X-band (~9.5 GHz) EPR of **2-*B*** and **2-*N*** collected on a Magnetech 5000 EPR spectrometer with a liquid nitrogen temperature controller. Data of the solution spectra were simulated with an isotropic g as reported in the figure. Data were collected with a 100 kHz field modulation at an amplitude of 4.0 G and a sweep time of 4.0 minutes. A digital RC filter was applied with an effective time constant of 0.4 s for the ~60,000 point scan. Note: the broad feature at ~ 2,350 G is a cavity background signal.

**$^{11}$B Hyperfine Analysis of 2-*B***

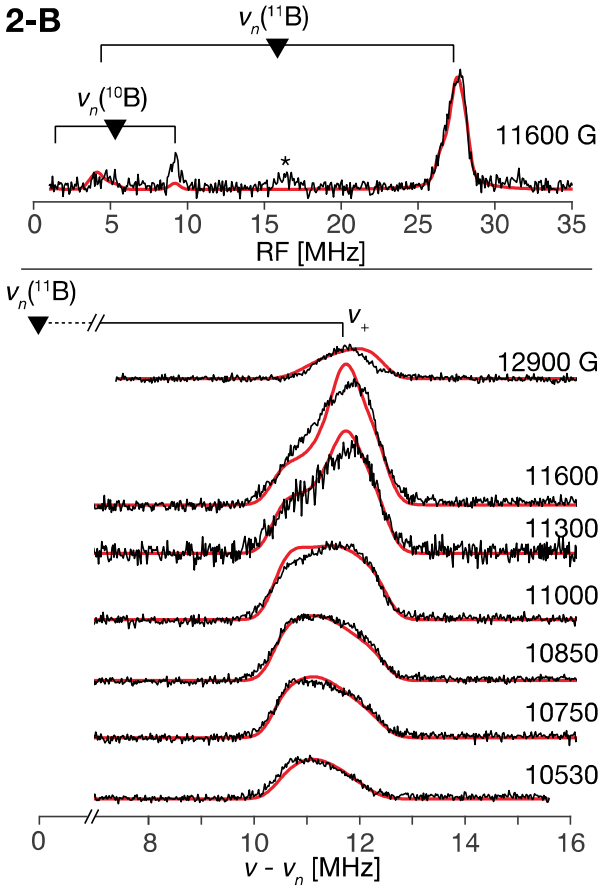


**Figure S27.** (Top) Boron Q-band Davies ENDOR spectra of **2-*B*** at 11600 G showing ENDOR responses from both $^{11}$B and $^{10}$B. The ENDOR doublets are centered at their Larmor frequency ($\nu_n$) indicated by a triangle and the hyperfine doublets marked by the goalposts. (*) indicates the third harmonic of the $^{1}$H signal. (Bottom) Only the $\nu_+$ feature of the $^{11}$B Larmor ($\nu_n$) centered ENDOR doublet is plotted in the 2D field-frequency ENDOR pattern with simulations in red based on the following parameters: **g**, **A**(Sb), and **A**(Ga) as reported in Table 1; **A**($^{11}$B) = [20.8, 23.5, 25.1] MHz; **A**($^{11}$B)[α, β, γ] = [-10°, 35°, 0], ENDOR linewidth = 0.5 MHz (fwhm). Collected at 8 K.

The 2D field-frequency pattern of the $^{11}$B ENDOR shows that the hyperfine tensor is highly isotropic with a large $a_{iso}$ value of 23.1 MHz (Fig. 4). Simulation of the complete hyperfine tensor, **A**($^{11}$B) = [20.8, 23.5, 25.1] MHz, and its orientation relative to the *g*-tensor represented by a set of Euler angles (α = -10°, β = 35°) well-reproduces the complete pattern. The s orbital spin-density is approximated from the ratio of the measured $a_{iso}$ coupling to the isotropic hyperfine coupling constant (isotropic coupling constant $a_0$($^{11}$B) = 2547 MHz; anisotropic coupling constant $b_0$ = 63.6 MHz),[12] yielding $\rho$(s) ~ 0.009. The anisotropic hyperfine coupling component (**T** = **A** – $a_{iso}$) is nearly rhombic, **T** = [-2.3 0.4 2.0] MHz, matching the form of [-*t*, 0, *t*]. The observed tensor is a mixture of both non-local dipolar interaction and the anisotropic

hyperfine coupling component of the local p orbital. Subtraction of the non-local (through-space) dipolar contribution allows for the local anisotropic contribution to be estimated.

The Sb-B distance of 2.245 Å allows for the non-local interaction to be estimated within a first approximation based on point-dipole equation $T_{nonloc} = \rho_{Sb} g_e \beta_e g_n \beta_n / r^3$. Using +0.9 for the spin density of Sb center ($\rho_{Sb}$), an estimated $t$ = +2.0 MHz interaction is found belonging to an axial tensor ($\mathbf{T}_{non\text{-}loc}$ = [2$t$, -$t$, -$t$]). The point-dipole approximation may further be corrected for both the observed g-anisotropy and relative orientations of the Sb p orbital and B center.[13] Taking $z$ as perpendicular to the Ga-Sb-B plane and $x$ and $y$ in the in Ga-Sb-B plane, the applied magnetic field is now described by directional cosines: ($l_z$, $l_y$, $l_x$) = (sin $\theta$, 0, ± cos $\theta$). The final form of the nonlocal contribution is:

$\mathbf{T}_{nonloc} = t[(g_z/g_e)(3 \sin^2 \theta - 1), -(g_y/g_e)(-t), (g_z/g_e)(3 \cos^2 \theta - 1)]$.

The unpaired Sb electron is expected to be in a p orbital normal to the Ga-Sb-B plane. The dihedral angle of the Ga-Sb-B plane and N-B-N plane is 63°. This makes the principle hyperfine component of the $^{11}$B $A$-tensor rotated ~27° from the unique axis of the $g$-tensor (where x and y ($g_3$ and $g_2$) are unknown in the Ga-Sb-B plane). The Euler angle rotation of β = 35° for the $A$-tensor is in qualitative agreement with the anticipated angle determined from the crystal structure. This same angle will apply for the nonlocal dipolar tensor.

Using the β = 35° value for $\theta$ (as found by simulation), a rhombic $\mathbf{T}_{nonlocal}$ = [-0.03, +2.1, -2.0] MHz is estimated. Subtraction of $\mathbf{T}_{nonloc}$ from the observed anisotropic coupling, $\mathbf{T}_{obs}$, yields the local anisotropic contribution of $\mathbf{T}_{loc}$ = [-2.3, -1.7, +4.0] MHz. This axial contribution reflects a majority B p orbital bonding character and the $T_{loc}$ ~ 2.0 MHz yields a B p orbital spin density of 0.031, significantly greater than the 0.009 s orbital spin density estimate.

Neither $\nu_+$ signals of the $^{11}$B or $^{10}$B responses exhibit resolved quadrupole splittings, Figure 4. The $^{10}$B isotope possesses a greater nuclear spin ($I$ = 3) compared to $^{11}$B ($I$ = 3/2) and a twice as large quadrupole moment,[12] but only a single sharp feature is observed. Comparison with previously well-resolved $^{11}$B quadrupolar splittings,[14,15] and simulation of possible quadrupole splittings allow for an upper limit of $P_{max}$ ~ 0.1 MHz to be estimated (Fig. S28).

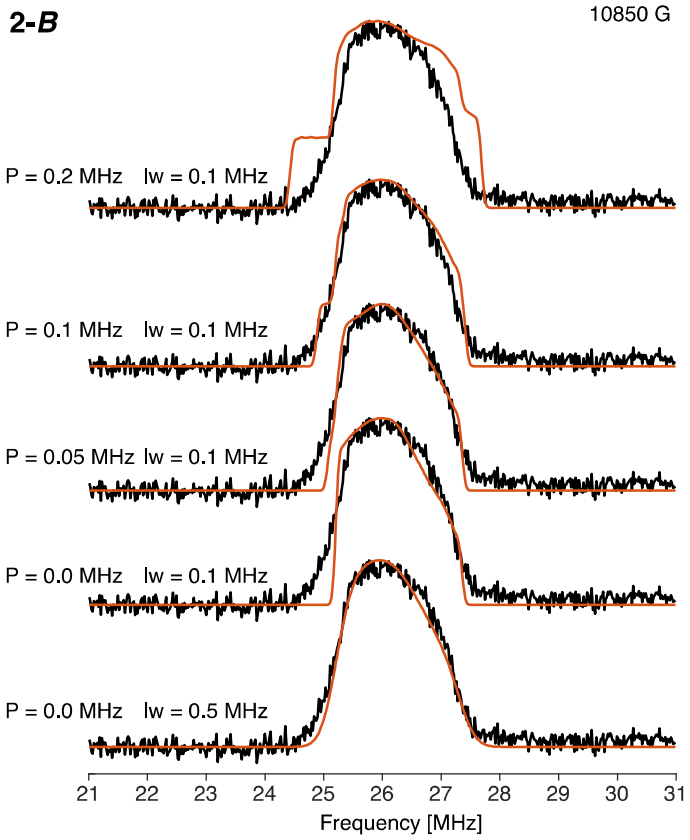


**Figure S28.** $^{11}$B ENDOR simulations using without quadrupole interaction (P) and a 0.5 MHz ENDOR linewidth (fwhm) as reported in manuscript compared with smaller ENDOR linewidth (0.1 MHz) and variable quadrupole interaction. Maximum quadrupole interaction is $P_{max}$ = 0.1 MHz at this field position and generally retains the correct line shape.

**Additional $^{14}$N Hyperfine Discussion**

No identifiable $^{14}$N ENDOR responses were observed for **2-*N***. If the same approximate spin densities of **2-*B*** are used to estimate the hyperfine parameters for **2-*N***, [isotropic coupling constant $a_0(^{14}N)$ = 1811 MHz; anisotropic coupling constant $b_0(^{14}N)$ = 55.5 MHz] a small isotropic coupling of $a_{iso}(^{14}N) \sim 16$ MHz is expected. The spin density of a coordinated heteroatom is inversely related to the heteroatom's electronegativity.[16] As demonstrated previously for π bonded aromatic radicals, the spin density observed for various substituents decreases when replacing N atom substituent for a more electronegative O substituents. [16] In other words, larger spin delocalization onto the ligand is achieved by less electronegative ligand atoms.[17] Therefore, it is expected that **2-*N*** has less spin density (and proportional hyperfine coupling) at the N atom than **2-*B*** has at the B atom. However, attempted $^{14}$N Mims (for small couplings) and Davies (for large couplings) ENDOR yielded no identifiable responses. The $^{14}$N ENDOR may not be well-resolvable by ENDOR spectroscopy under certain circumstances. For instance, the 'powder'-pattern observed in the 2D field-frequency ENDOR pattern is complicated by the additional quadrupole splitting

of the $^{14}$N, $I$ = 1, nuclei, with additional quadrupole splitting upwards of 2 MHz. Additionally, the magnitude of the anisotropic component will be larger for $^{14}$N than observed for $^{11}$B, making the expected ENDOR response much broader. The ENDOR response may also be significantly broadened in the cases of non-coaxial $g$-, $A$-, (and quadrupole) tensors, as was the case for **2-*B***. Lastly, the large Sb hyperfine coupling of the complex, and reduced $g$-anisotropy of **2-*N*** decreases the potential for orientation-selective ENDOR spectra to be collected and the a sharp 'single-crystal-like' position to be found. Furthermore, other advanced techniques such as ESEEM and HYSCORE failed to identify any unique $^{14}$N couplings of **2-*N***.

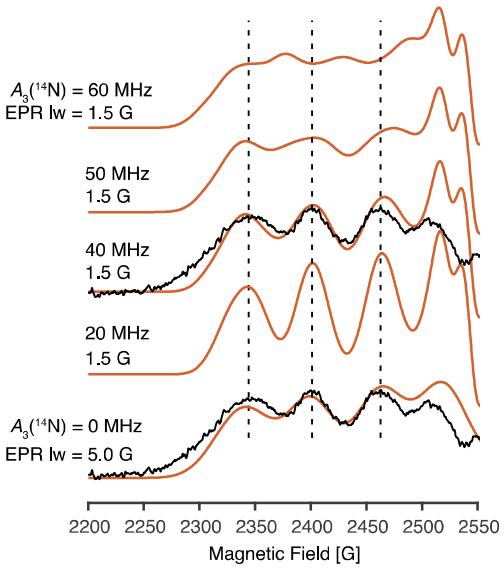


**Figure S29.** EPR simulations of the low-field edge of the X-band spectrum of **2-*N*** utilizing the same EPR simulation parameters detailed in Figure 3 but with varying $^{14}$N hyperfine coupling along $g_3$ with a constant 1.5 G EPR linewidth and no 14N hyperfine and 5.0 G EPR linewidth.

Some maximum estimates of the $^{14}$N hyperfine coupling can be made from simulations of the EPR spectra. The low-field edge features of the X-band spectrum of **2-*N*** in the range of 2300 to 2550 G is actually low-field edge of the $g_3$ feature. Inclusion of a single $A_3$ $^{14}$N hyperfine coupling up to ~40 MHz broadens the EPR linewidth but does not further split the spectrum. However, simulation of the EPR with $A_3$($^{14}$N) = 50 MHz begins to yield new splittings not observed in the experimental spectrum. Simulations of larger $^{14}$N hyperfine couplings no longer reproduce the observed EPR spectrum at $g_3$However, comparable, if not better reproduction of the low field $g_3$ feature is possible with a large EPR linewidth and no $^{14}$N hyperfine interaction. This demonstrates the difficulty of the determining possible weak hyperfine interaction in the broad EPR lineshapes.

## 3. Crystallographic Details

The crystals of **2-*C***, **2-*N***, and [**2-*B***]$^-$ were mounted on nylon loops in inert oil. Data were collected on a Bruker AXS D8 Kappa diffractometer with APEX2 detector (monochromated $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å) at 100(2) K. The structures were solved by Direct Methods (SHELXS-97)[18] and refined anisotropically by full-matrix least-squares on $F^2$ (SHELXL-2014)[19,20]. Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2). The crystal of **2-*B*** was mounted on nylon loops in inert oil. Data were collected on a Bruker AXS D8 Venture diffractometer with Photon II detector (monochromated $Cu_{K\alpha}$ radiation, $\lambda = 1.54178$ Å, micro-focus source) at 100(2) K. Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX3). Hydrogen atoms were refined using a riding model or rigid methyl groups. **2-*B*** was refined as a 2-component twin against HKLF5 data. In **2-*C*** an *i*-Pr group is disordered over two positions. Its bond lengths were restrained to be equal (SADI). RIGU and ISOR restraints were applied to the adp of the corresponding atoms. The structure contains highly disordered solvent - likely one molecule of n-hexane. The final refinement was done with a solvent free dataset from a PLATON/SQUEEZE run.[20] Since exact amount of the solvent is not clear it was not included in the sum formula. **2-*N*** contains an n-hexane molecule highly disordered over a center of inversion. The final refinement was done with a solvent free dataset from a PLATON/SQUEEZE run.[21]

CCDC-1953135 (**2-*B***), -1953136 (**2-*C*)**, -1953137 **(2-*N*)**, and -1953139 ([K([2.2.2]crypt)][**2-*B***]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Table S1**. Crystallographic details of **2-*B***, **2-*C***, **2-*N***, and [K([2.2.2]crypt)][**2-*B***].

| | **2-*B*** | **2-*C*** | **2-*N*** | [K([2.2.2]crypt)][**2-*B***] |
|---|---|---|---|---|
| Empirical formula | $C_{55}H_{77}BClGaN_4Sb$ | $C_{53}H_{66}ClGaN_2Sb$ | $C_{47}H_{74}ClGaN_3SbSi$ | $C_{79}H_{118}BClFGaKN_6O_6Sb$ |
| $M$ | 1031.93 | 957.99 | 936.10 | 1543.62 |
| Crystal size [mm] | 0.278 × 0.065 × 0.035 | 0.288 × 0.190 × 0.094 | 0.334 × 0.083 × 0.040 | 0.283 × 0.209 × 0.171 |
| $T$ [K] | 100(2) | 100(2) | 100(2) | 100(2) |
| Crystal system | monoclinic | triclinic | triclinic | triclinic |
| Space group | $P2_1/c$ | $P$ -1 | $P$ -1 | $P$ -1 |
| $a$ [Å] | 19.641(3) | 11.3632(7) | 10.2031(6) | 12.8626(11) |
| $b$ [Å] | 12.983(2) | 12.3196(8) | 12.3035(7) | 17.0784(16) |
| $c$ [Å] | 21.277(3) | 20.1887(18) | 20.9514(13) | 18.9615(18) |
| $\alpha$ [°] | 90 | 98.742(5) | 82.058(4) | 90.934(5) |
| $\beta$ [°] | 98.314(7) | 91.762(5) | 86.480(3) | 93.004(4) |
| $\gamma$ [°] | 90 | 114.515(3) | 68.750(3) | 104.684(4) |
| $V$ [Å$^3$] | 5368.6(15) | 2527.7(3) | 2427.6(3) | 4021.9(6) |
| $Z$ | 4 | 2 | 2 | 2 |
| $D_{calc}$ [g·cm$^{-3}$] | 1.277 | 1.259 | 1.281 | 1.275 |
| $\mu(K_\alpha$ [mm$^{-1}$]) | 5.339(Cu) | 1.154(Mo) | 1.224(Mo) | 0.811 |
| Transmissions | 0.75/0.52 | 0.75/0.66 | 0.75/0.65 | 0.75/0.68 |
| $F$(000) | 2156 | 994 | 980 | 1628 |
| Index ranges | $-25 \le h \le 24$ | $-17 \le h \le 17$ | $-14 \le h \le 14$ | $-19 \le h \le 18$ |
| | $0 \le k \le 16$ | $-19 \le k \le 19$ | $-17 \le k \le 17$ | $-25 \le k \le 26$ |
| | $0 \le l \le 26$ | $-33 \le l \le 31$ | $-29 \le l \le 30$ | $-29 \le l \le 29$ |
| $\theta_{max}$ [°] | 81.358 | 36.502 | 30.705 | 33.609 |
| Reflections collected | 201453 | 100431 | 87556 | 207976 |
| Independent reflections | 23012 | 21237 | 15004 | 29776 |
| $R_{int}$ | 0.0955 | 0.0363 | 0.0360 | 0.0413 |
| Refined parameters | 587 | 560 | 477 | 892 |
| $R_1$ [$I > 2\sigma(I)$] | 0.0483 | 0.0363 | 0.0378 | 0.0304 |
| $wR_2$ [all data] | 0.1573 | 0.0866 | 0.0837 | 0.0762 |
| GooF | 1.057 | 1.009 | 1.070 | 1.025 |
| $\Delta\rho_{final}$ (max/min) [e·Å$^{-3}$] | 1.929/-0.849 | 1.550/-1.304 | 3.763/-2.650 | 1.090/-1.197 |

**Table S2**. Bond lengths [Å] and angles [°] for **2-*B***.

| | | | | | |
|---|---|---|---|---|---|
| Sb(1)-B(1) | 2.245(5) | C(8)-C(9) | 1.377(9) | C(33)-C(34) | 1.401(7) |
| Sb(1)-Ga(1) | 2.5959(7) | C(9)-C(10) | 1.386(8) | C(33)-C(38) | 1.524(6) |
| Ga(1)-N(2) | 1.964(4) | C(10)-C(11) | 1.401(7) | C(34)-C(35) | 1.372(8) |
| Ga(1)-N(1) | 1.970(4) | C(11)-C(15) | 1.528(7) | C(35)-C(36) | 1.389(8) |
| Ga(1)-Cl(1) | 2.2085(13) | C(12)-C(13) | 1.520(8) | C(36)-C(37) | 1.398(7) |
| N(1)-C(1) | 1.344(6) | C(12)-C(14) | 1.527(8) | C(37)-C(40) | 1.517(6) |
| N(1)-C(6) | 1.445(6) | C(15)-C(16) | 1.526(9) | C(38)-C(41) | 1.517(7) |
| N(2)-C(3) | 1.342(6) | C(15)-C(17) | 1.534(9) | C(38)-C(39) | 1.524(7) |
| N(2)-C(18) | 1.431(6) | C(18)-C(23) | 1.409(7) | C(40)-C(44) | 1.522(7) |
| N(3)-C(30) | 1.399(6) | C(18)-C(19) | 1.421(7) | C(40)-C(42) | 1.523(8) |
| N(3)-B(1) | 1.434(6) | C(19)-C(20) | 1.394(8) | C(43)-C(45) | 1.398(7) |
| N(3)-C(32) | 1.437(6) | C(19)-C(24) | 1.520(8) | C(43)-C(47) | 1.415(7) |
| N(4)-C(31) | 1.411(6) | C(20)-C(21) | 1.385(10) | C(45)-C(50) | 1.404(7) |
| N(4)-B(1) | 1.433(6) | C(21)-C(22) | 1.377(10) | C(45)-C(46) | 1.512(8) |
| N(4)-C(43) | 1.440(6) | C(22)-C(23) | 1.395(8) | C(46)-C(52) | 1.533(8) |
| C(1)-C(2) | 1.398(7) | C(23)-C(27) | 1.521(7) | C(46)-C(51) | 1.541(8) |
| C(1)-C(4) | 1.509(7) | C(24)-C(26) | 1.523(10) | C(47)-C(48) | 1.404(7) |
| C(2)-C(3) | 1.396(7) | C(24)-C(25) | 1.545(8) | C(47)-C(53) | 1.523(7) |
| C(3)-C(5) | 1.496(7) | C(27)-C(28) | 1.528(8) | C(48)-C(49) | 1.382(8) |
| C(6)-C(11) | 1.395(7) | C(27)-C(29) | 1.533(8) | C(49)-C(50) | 1.383(9) |
| C(6)-C(7) | 1.413(7) | C(30)-C(31) | 1.344(7) | C(53)-C(56) | 1.523(8) |
| C(7)-C(8) | 1.394(8) | C(32)-C(33) | 1.396(6) | C(53)-C(55) | 1.525(9) |
| C(7)-C(12) | 1.527(7) | C(32)-C(37) | 1.419(6) | | |

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|---|---|---|---|---|---|
| B(1)-Sb(1)-Ga(1) | 113.40(14) | C(6)-C(11)-C(10) | 118.7(5) | C(35)-C(34)-C(33) | 121.5(5) |
| N(2)-Ga(1)-N(1) | 96.09(17) | C(6)-C(11)-C(15) | 123.8(4) | C(34)-C(35)-C(36) | 120.1(5) |
| N(2)-Ga(1)-Cl(1) | 105.03(12) | C(10)-C(11)-C(15) | 117.5(5) | C(35)-C(36)-C(37) | 121.3(5) |
| N(1)-Ga(1)-Cl(1) | 103.22(12) | C(13)-C(12)-C(7) | 111.9(5) | C(36)-C(37)-C(32) | 117.2(5) |
| N(2)-Ga(1)-Sb(1) | 104.45(12) | C(13)-C(12)-C(14) | 111.1(5) | C(36)-C(37)-C(40) | 121.8(4) |
| N(1)-Ga(1)-Sb(1) | 120.93(12) | C(7)-C(12)-C(14) | 110.1(5) | C(32)-C(37)-C(40) | 120.9(4) |
| Cl(1)-Ga(1)-Sb(1) | 122.76(5) | C(16)-C(15)-C(11) | 110.5(5) | C(41)-C(38)-C(39) | 110.4(5) |
| C(1)-N(1)-C(6) | 117.7(4) | C(16)-C(15)-C(17) | 109.7(5) | C(41)-C(38)-C(33) | 110.7(4) |
| C(1)-N(1)-Ga(1) | 118.8(3) | C(11)-C(15)-C(17) | 112.3(5) | C(39)-C(38)-C(33) | 113.2(4) |
| C(6)-N(1)-Ga(1) | 123.3(3) | C(23)-C(18)-C(19) | 120.9(4) | C(37)-C(40)-C(44) | 113.1(4) |
| C(3)-N(2)-C(18) | 119.9(4) | C(23)-C(18)-N(2) | 120.7(4) | C(37)-C(40)-C(42) | 109.7(4) |
| C(3)-N(2)-Ga(1) | 119.7(3) | C(19)-C(18)-N(2) | 118.3(4) | C(44)-C(40)-C(42) | 111.2(5) |
| C(18)-N(2)-Ga(1) | 120.4(3) | C(20)-C(19)-C(18) | 117.9(5) | C(45)-C(43)-C(47) | 121.6(5) |
| C(30)-N(3)-B(1) | 108.4(4) | C(20)-C(19)-C(24) | 120.1(5) | C(45)-C(43)-N(4) | 120.0(4) |
| C(30)-N(3)-C(32) | 121.0(4) | C(18)-C(19)-C(24) | 122.0(5) | C(47)-C(43)-N(4) | 118.3(4) |
| B(1)-N(3)-C(32) | 130.5(4) | C(21)-C(20)-C(19) | 121.3(6) | C(43)-C(45)-C(50) | 118.6(5) |
| C(31)-N(4)-B(1) | 108.2(4) | C(22)-C(21)-C(20) | 120.2(5) | C(43)-C(45)-C(46) | 122.1(5) |
| C(31)-N(4)-C(43) | 117.9(4) | C(21)-C(22)-C(23) | 121.3(6) | C(50)-C(45)-C(46) | 119.2(5) |
| B(1)-N(4)-C(43) | 132.9(4) | C(22)-C(23)-C(18) | 118.3(5) | C(45)-C(46)-C(52) | 111.5(5) |
| N(1)-C(1)-C(2) | 124.5(4) | C(22)-C(23)-C(27) | 119.4(5) | C(45)-C(46)-C(51) | 112.1(5) |
| N(1)-C(1)-C(4) | 119.4(4) | C(18)-C(23)-C(27) | 122.3(4) | C(52)-C(46)-C(51) | 109.1(5) |
| C(2)-C(1)-C(4) | 116.1(4) | C(19)-C(24)-C(26) | 111.7(6) | C(48)-C(47)-C(43) | 117.5(5) |
| C(3)-C(2)-C(1) | 129.2(5) | C(19)-C(24)-C(25) | 112.1(5) | C(48)-C(47)-C(53) | 119.8(5) |
| N(2)-C(3)-C(2) | 122.5(4) | C(26)-C(24)-C(25) | 110.0(5) | C(43)-C(47)-C(53) | 122.6(4) |
| N(2)-C(3)-C(5) | 119.7(5) | C(23)-C(27)-C(28) | 111.6(5) | C(49)-C(48)-C(47) | 121.2(5) |

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|---|---|---|---|---|---|
| C(2)-C(3)-C(5) | 117.8(4) | C(23)-C(27)-C(29) | 110.3(5) | C(48)-C(49)-C(50) | 120.5(5) |
| C(11)-C(6)-C(7) | 121.0(5) | C(28)-C(27)-C(29) | 111.0(5) | C(49)-C(50)-C(45) | 120.5(5) |
| C(11)-C(6)-N(1) | 120.3(4) | C(31)-C(30)-N(3) | 109.6(4) | C(47)-C(53)-C(56) | 112.3(5) |
| C(7)-C(6)-N(1) | 118.7(5) | C(30)-C(31)-N(4) | 109.0(4) | C(47)-C(53)-C(55) | 110.8(5) |
| C(8)-C(7)-C(6) | 117.8(5) | C(33)-C(32)-C(37) | 122.0(4) | C(56)-C(53)-C(55) | 110.4(6) |
| C(8)-C(7)-C(12) | 120.7(5) | C(33)-C(32)-N(3) | 119.5(4) | N(4)-B(1)-N(3) | 104.8(4) |
| C(6)-C(7)-C(12) | 121.3(5) | C(37)-C(32)-N(3) | 118.5(4) | N(4)-B(1)-Sb(1) | 133.3(3) |
| C(9)-C(8)-C(7) | 121.8(5) | C(32)-C(33)-C(34) | 117.8(4) | N(3)-B(1)-Sb(1) | 119.5(3) |
| C(8)-C(9)-C(10) | 119.6(5) | C(32)-C(33)-C(38) | 121.4(4) | | |
| C(9)-C(10)-C(11) | 120.8(5) | C(34)-C(33)-C(38) | 120.7(4) | | |

**Table S3**. Bond lengths [Å] and angles [°] for **2-*C***.

| | | | | | |
|---|---|---|---|---|---|
| Sb(1)-C(30) | 2.1716(16) | C(12)-C(14) | 1.520(3) | C(33)-C(34) | 1.373(3) |
| Sb(1)-Ga(1) | 2.6335(3) | C(15)-C(17) | 1.526(2) | C(34)-C(35) | 1.397(2) |
| Ga(1)-N(2) | 1.9597(13) | C(15)-C(16) | 1.533(2) | C(35)-C(45) | 1.499(2) |
| Ga(1)-N(1) | 1.9649(13) | C(18)-C(23) | 1.407(3) | C(36)-C(37) | 1.403(2) |
| Ga(1)-Cl(1) | 2.2178(5) | C(18)-C(19) | 1.408(3) | C(36)-C(41) | 1.404(2) |
| N(1)-C(1) | 1.336(2) | C(19)-C(20) | 1.397(3) | C(37)-C(38) | 1.396(2) |
| N(1)-C(6) | 1.448(2) | C(19)-C(24) | 1.517(3) | C(37)-C(42) | 1.504(2) |
| N(2)-C(3) | 1.338(2) | C(20)-C(21) | 1.372(3) | C(38)-C(39) | 1.388(3) |
| N(2)-C(18) | 1.447(2) | C(21)-C(22) | 1.373(3) | C(39)-C(40) | 1.384(3) |
| C(1)-C(2) | 1.403(2) | C(22)-C(23) | 1.404(2) | C(39)-C(43) | 1.511(3) |
| C(1)-C(4) | 1.510(2) | C(23)-C(27) | 1.519(3) | C(40)-C(41) | 1.394(3) |
| C(2)-C(3) | 1.397(2) | C(24)-C(25') | 1.528(8) | C(41)-C(44) | 1.502(3) |
| C(3)-C(5) | 1.509(2) | C(24)-C(26) | 1.531(5) | C(45)-C(46) | 1.403(3) |
| C(6)-C(11) | 1.395(2) | C(24)-C(25) | 1.534(5) | C(45)-C(50) | 1.405(3) |
| C(6)-C(7) | 1.411(2) | C(24)-C(26') | 1.551(9) | C(46)-C(47) | 1.397(3) |
| C(7)-C(8) | 1.397(3) | C(27)-C(28) | 1.530(3) | C(46)-C(51) | 1.506(3) |
| C(7)-C(12) | 1.521(3) | C(27)-C(29) | 1.532(3) | C(47)-C(48) | 1.384(4) |
| C(8)-C(9) | 1.381(3) | C(30)-C(31) | 1.411(2) | C(48)-C(49) | 1.376(4) |
| C(9)-C(10) | 1.369(3) | C(30)-C(35) | 1.414(2) | C(48)-C(52) | 1.518(3) |
| C(10)-C(11) | 1.403(2) | C(31)-C(32) | 1.397(2) | C(49)-C(50) | 1.400(3) |
| C(11)-C(15) | 1.513(2) | C(31)-C(36) | 1.500(2) | C(50)-C(53) | 1.504(3) |
| C(12)-C(13) | 1.518(3) | C(32)-C(33) | 1.382(3) | | |

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|---|---|---|---|---|---|
| C(30)-Sb(1)-Ga(1) | 114.80(4) | C(13)-C(12)-C(7) | 113.11(17) | C(34)-C(33)-C(32) | 118.97(17) |
| N(2)-Ga(1)-N(1) | 94.82(5) | C(14)-C(12)-C(7) | 111.00(18) | C(33)-C(34)-C(35) | 121.35(16) |
| N(2)-Ga(1)-Cl(1) | 101.93(4) | C(11)-C(15)-C(17) | 110.78(14) | C(34)-C(35)-C(30) | 120.13(16) |
| N(1)-Ga(1)-Cl(1) | 103.47(4) | C(11)-C(15)-C(16) | 110.83(15) | C(34)-C(35)-C(45) | 114.98(15) |
| N(2)-Ga(1)-Sb(1) | 125.45(4) | C(17)-C(15)-C(16) | 110.31(14) | C(30)-C(35)-C(45) | 124.88(15) |
| N(1)-Ga(1)-Sb(1) | 103.81(4) | C(23)-C(18)-C(19) | 121.89(16) | C(37)-C(36)-C(41) | 119.85(15) |
| Cl(1)-Ga(1)-Sb(1) | 121.870(14) | C(23)-C(18)-N(2) | 119.79(15) | C(37)-C(36)-C(31) | 119.68(15) |
| C(1)-N(1)-C(6) | 121.13(13) | C(19)-C(18)-N(2) | 118.32(16) | C(41)-C(36)-C(31) | 119.29(15) |
| C(1)-N(1)-Ga(1) | 118.94(11) | C(20)-C(19)-C(18) | 117.68(19) | C(38)-C(37)-C(36) | 119.14(16) |
| C(6)-N(1)-Ga(1) | 119.82(10) | C(20)-C(19)-C(24) | 120.44(18) | C(38)-C(37)-C(42) | 119.52(16) |
| C(3)-N(2)-C(18) | 118.84(13) | C(18)-C(19)-C(24) | 121.88(16) | C(36)-C(37)-C(42) | 121.28(15) |
| C(3)-N(2)-Ga(1) | 118.31(11) | C(21)-C(20)-C(19) | 121.3(2) | C(39)-C(38)-C(37) | 121.81(17) |
| C(18)-N(2)-Ga(1) | 122.59(10) | C(20)-C(21)-C(22) | 120.51(18) | C(40)-C(39)-C(38) | 118.04(16) |
| N(1)-C(1)-C(2) | 122.71(14) | C(21)-C(22)-C(23) | 121.4(2) | C(40)-C(39)-C(43) | 120.81(19) |

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|---|---|---|---|---|---|
| N(1)-C(1)-C(4) | 120.01(14) | C(22)-C(23)-C(18) | 117.30(18) | C(38)-C(39)-C(43) | 121.14(19) |
| C(2)-C(1)-C(4) | 117.28(14) | C(22)-C(23)-C(27) | 119.39(18) | C(39)-C(40)-C(41) | 122.26(17) |
| C(3)-C(2)-C(1) | 127.65(14) | C(18)-C(23)-C(27) | 123.31(15) | C(40)-C(41)-C(36) | 118.87(17) |
| N(2)-C(3)-C(2) | 124.46(14) | C(19)-C(24)-C(25') | 112.2(4) | C(40)-C(41)-C(44) | 119.88(17) |
| N(2)-C(3)-C(5) | 119.39(14) | C(19)-C(24)-C(26) | 113.3(2) | C(36)-C(41)-C(44) | 121.22(17) |
| C(2)-C(3)-C(5) | 116.12(14) | C(19)-C(24)-C(25) | 113.8(3) | C(46)-C(45)-C(50) | 120.13(18) |
| C(11)-C(6)-C(7) | 121.39(15) | C(26)-C(24)-C(25) | 108.7(3) | C(46)-C(45)-C(35) | 119.18(17) |
| C(11)-C(6)-N(1) | 120.45(15) | C(19)-C(24)-C(26') | 109.5(6) | C(50)-C(45)-C(35) | 119.99(17) |
| C(7)-C(6)-N(1) | 118.02(15) | C(25')-C(24)-C(26') | 109.5(4) | C(47)-C(46)-C(45) | 118.5(2) |
| C(8)-C(7)-C(6) | 118.10(18) | C(23)-C(27)-C(28) | 110.29(16) | C(47)-C(46)-C(51) | 120.7(2) |
| C(8)-C(7)-C(12) | 119.77(17) | C(23)-C(27)-C(29) | 112.90(15) | C(45)-C(46)-C(51) | 120.78(19) |
| C(6)-C(7)-C(12) | 122.08(16) | C(28)-C(27)-C(29) | 109.33(16) | C(48)-C(47)-C(46) | 122.2(2) |
| C(9)-C(8)-C(7) | 120.87(19) | C(31)-C(30)-C(35) | 118.18(15) | C(49)-C(48)-C(47) | 118.4(2) |
| C(10)-C(9)-C(8) | 120.23(18) | C(31)-C(30)-Sb(1) | 123.17(12) | C(49)-C(48)-C(52) | 120.6(3) |
| C(9)-C(10)-C(11) | 121.45(19) | C(35)-C(30)-Sb(1) | 117.10(12) | C(47)-C(48)-C(52) | 121.0(3) |
| C(6)-C(11)-C(10) | 117.88(17) | C(32)-C(31)-C(30) | 119.62(15) | C(48)-C(49)-C(50) | 122.0(2) |
| C(6)-C(11)-C(15) | 123.22(14) | C(32)-C(31)-C(36) | 113.88(15) | C(49)-C(50)-C(45) | 118.7(2) |
| C(10)-C(11)-C(15) | 118.90(16) | C(30)-C(31)-C(36) | 126.48(14) | C(49)-C(50)-C(53) | 120.71(19) |
| C(13)-C(12)-C(14) | 109.73(17) | C(33)-C(32)-C(31) | 121.74(17) | C(45)-C(50)-C(53) | 120.52(18) |

**Table S4**. Bond lengths [Å] and angles [°] for **2-*N***.

| | | | | | |
|---|---|---|---|---|---|
| Sb(1)-N(3) | 2.0502(18) | C(6)-C(11) | 1.407(3) | C(22)-C(23) | 1.400(3) |
| Sb(1)-Ga(1) | 2.6258(3) | C(6)-C(7) | 1.414(3) | C(23)-C(27) | 1.518(3) |
| Ga(1)-N(2) | 1.9532(18) | C(7)-C(8) | 1.393(3) | C(24)-C(25) | 1.530(4) |
| Ga(1)-N(1) | 1.9654(17) | C(7)-C(12) | 1.526(3) | C(24)-C(26) | 1.532(4) |
| Ga(1)-Cl(1) | 2.2213(6) | C(8)-C(9) | 1.387(4) | C(27)-C(29) | 1.529(4) |
| Si(1)-N(3) | 1.7388(19) | C(9)-C(10) | 1.381(3) | C(27)-C(28) | 1.535(4) |
| Si(1)-C(32) | 1.860(3) | C(10)-C(11) | 1.396(3) | C(33)-C(38) | 1.405(3) |
| Si(1)-C(31) | 1.866(3) | C(11)-C(15) | 1.527(3) | C(33)-C(34) | 1.410(3) |
| Si(1)-C(30) | 1.870(2) | C(12)-C(14) | 1.531(3) | C(34)-C(35) | 1.396(3) |
| N(1)-C(1) | 1.331(3) | C(12)-C(13) | 1.533(3) | C(34)-C(39) | 1.517(4) |
| N(1)-C(6) | 1.445(3) | C(15)-C(16) | 1.528(3) | C(35)-C(36) | 1.373(4) |
| N(2)-C(3) | 1.334(3) | C(15)-C(17) | 1.540(3) | C(36)-C(37) | 1.384(4) |
| N(2)-C(18) | 1.448(3) | C(18)-C(23) | 1.405(3) | C(37)-C(38) | 1.399(3) |
| N(3)-C(33) | 1.445(3) | C(18)-C(19) | 1.407(3) | C(38)-C(42) | 1.514(4) |
| C(1)-C(2) | 1.404(3) | C(19)-C(20) | 1.394(3) | C(39)-C(40) | 1.531(5) |
| C(1)-C(4) | 1.509(3) | C(19)-C(24) | 1.522(3) | C(39)-C(41) | 1.535(5) |
| C(2)-C(3) | 1.399(3) | C(20)-C(21) | 1.387(4) | C(42)-C(44) | 1.533(4) |
| C(3)-C(5) | 1.508(3) | C(21)-C(22) | 1.377(4) | C(42)-C(43) | 1.533(4) |

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|---|---|---|---|---|---|
| N(3)-Sb(1)-Ga(1) | 111.45(5) | C(2)-C(3)-C(5) | 117.39(19) | C(22)-C(23)-C(18) | 117.9(2) |
| N(2)-Ga(1)-N(1) | 95.66(7) | C(11)-C(6)-C(7) | 121.19(19) | C(22)-C(23)-C(27) | 119.2(2) |
| N(2)-Ga(1)-Cl(1) | 103.56(6) | C(11)-C(6)-N(1) | 120.46(18) | C(18)-C(23)-C(27) | 122.9(2) |
| N(1)-Ga(1)-Cl(1) | 101.03(5) | C(7)-C(6)-N(1) | 118.30(18) | C(19)-C(24)-C(25) | 113.0(2) |
| N(2)-Ga(1)-Sb(1) | 103.16(5) | C(8)-C(7)-C(6) | 118.2(2) | C(19)-C(24)-C(26) | 111.4(2) |
| N(1)-Ga(1)-Sb(1) | 120.13(5) | C(8)-C(7)-C(12) | 120.6(2) | C(25)-C(24)-C(26) | 109.4(2) |
| Cl(1)-Ga(1)-Sb(1) | 127.529(18) | C(6)-C(7)-C(12) | 121.1(2) | C(23)-C(27)-C(29) | 111.4(2) |
| N(3)-Si(1)-C(32) | 108.31(12) | C(9)-C(8)-C(7) | 121.1(2) | C(23)-C(27)-C(28) | 111.5(2) |
| N(3)-Si(1)-C(31) | 112.50(12) | C(10)-C(9)-C(8) | 119.9(2) | C(29)-C(27)-C(28) | 110.5(2) |

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| C(32)-Si(1)-C(31) | 110.23(15) | C(9)-C(10)-C(11) | 121.5(2) | C(38)-C(33)-C(34) | 120.4(2) |
| N(3)-Si(1)-C(30) | 108.21(10) | C(10)-C(11)-C(6) | 118.06(19) | C(38)-C(33)-N(3) | 119.8(2) |
| C(32)-Si(1)-C(30) | 110.67(12) | C(10)-C(11)-C(15) | 118.29(19) | C(34)-C(33)-N(3) | 119.8(2) |
| C(31)-Si(1)-C(30) | 106.92(13) | C(6)-C(11)-C(15) | 123.64(19) | C(35)-C(34)-C(33) | 118.9(2) |
| C(1)-N(1)-C(6) | 121.29(17) | C(7)-C(12)-C(14) | 113.4(2) | C(35)-C(34)-C(39) | 118.8(2) |
| C(1)-N(1)-Ga(1) | 119.12(14) | C(7)-C(12)-C(13) | 111.63(18) | C(33)-C(34)-C(39) | 122.3(2) |
| C(6)-N(1)-Ga(1) | 119.21(13) | C(14)-C(12)-C(13) | 109.42(18) | C(36)-C(35)-C(34) | 121.1(3) |
| C(3)-N(2)-C(18) | 120.08(18) | C(11)-C(15)-C(16) | 111.77(18) | C(35)-C(36)-C(37) | 120.0(2) |
| C(3)-N(2)-Ga(1) | 119.41(14) | C(11)-C(15)-C(17) | 110.72(18) | C(36)-C(37)-C(38) | 121.2(2) |
| C(18)-N(2)-Ga(1) | 120.51(13) | C(16)-C(15)-C(17) | 109.34(19) | C(37)-C(38)-C(33) | 118.4(2) |
| C(33)-N(3)-Si(1) | 120.76(14) | C(23)-C(18)-C(19) | 121.5(2) | C(37)-C(38)-C(42) | 119.5(2) |
| C(33)-N(3)-Sb(1) | 109.17(13) | C(23)-C(18)-N(2) | 120.35(19) | C(33)-C(38)-C(42) | 122.1(2) |
| Si(1)-N(3)-Sb(1) | 130.05(10) | C(19)-C(18)-N(2) | 118.07(19) | C(34)-C(39)-C(40) | 113.1(3) |
| N(1)-C(1)-C(2) | 123.72(19) | C(20)-C(19)-C(18) | 118.1(2) | C(34)-C(39)-C(41) | 110.1(3) |
| N(1)-C(1)-C(4) | 120.36(19) | C(20)-C(19)-C(24) | 119.1(2) | C(40)-C(39)-C(41) | 109.8(3) |
| C(2)-C(1)-C(4) | 115.91(18) | C(18)-C(19)-C(24) | 122.8(2) | C(38)-C(42)-C(44) | 111.0(2) |
| C(3)-C(2)-C(1) | 128.59(19) | C(21)-C(20)-C(19) | 121.1(2) | C(38)-C(42)-C(43) | 111.8(2) |
| N(2)-C(3)-C(2) | 123.1(2) | C(22)-C(21)-C(20) | 120.0(2) | C(44)-C(42)-C(43) | 111.2(2) |
| N(2)-C(3)-C(5) | 119.5(2) | C(21)-C(22)-C(23) | 121.3(2) | | |

**Table S5**. Bond lengths [Å] and angles [°] for [K([2.2.2]crypt)][**2-*B***].

| | | | | | |
|---|---|---|---|---|---|
| K11-O41 | 2.7956(10) | Ga12-N12 | 2.0156(10) | C242-C262 | 1.5239(19) |
| K11-O61 | 2.7978(10) | Ga12-N22 | 2.0395(10) | C242-C252 | 1.5305(19) |
| K11-O11 | 2.7996(10) | Ga12-Cl12 | 2.2820(4) | C272-C292 | 1.5266(18) |
| K11-O31 | 2.8151(10) | B12-N42 | 1.4511(17) | C272-C282 | 1.5346(18) |
| K11-O51 | 2.8203(10) | B12-N32 | 1.4569(17) | C302-C312 | 1.3379(19) |
| K11-O21 | 2.9015(10) | N12-C12 | 1.3378(15) | C322-C332 | 1.3977(19) |
| K11-N11 | 3.0229(11) | N12-C62 | 1.4374(15) | C322-C372 | 1.4039(19) |
| K11-N21 | 3.0470(12) | N22-C32 | 1.3264(15) | C332-C342 | 1.3964(19) |
| O11-C31 | 1.4264(16) | N22-C182 | 1.4434(15) | C332-C382 | 1.514(2) |
| O11-C21 | 1.4277(16) | N32-C302 | 1.3971(16) | C342-C352 | 1.381(2) |
| O21-C41 | 1.4230(17) | N32-C322 | 1.4302(16) | C352-C362 | 1.381(2) |
| O21-C51 | 1.4291(17) | N42-C312 | 1.4057(15) | C362-C372 | 1.394(2) |
| O31-C81 | 1.4219(16) | N42-C442 | 1.4302(15) | C372-C412 | 1.516(2) |
| O31-C91 | 1.4249(16) | C12-C22 | 1.3944(17) | C382-C402 | 1.526(2) |
| O41-C101 | 1.4190(18) | C12-C42 | 1.5117(17) | C382-C392 | 1.534(2) |
| O41-C111 | 1.4203(17) | C22-C32 | 1.4088(17) | C412-C422 | 1.516(2) |
| O51-C151 | 1.4280(16) | C32-C52 | 1.5139(16) | C412-C432 | 1.520(2) |
| O51-C141 | 1.4308(17) | C62-C112 | 1.4053(17) | C442-C452 | 1.4006(18) |
| O61-C171 | 1.4220(18) | C62-C72 | 1.4077(18) | C442-C492 | 1.4053(17) |
| O61-C161 | 1.4280(17) | C72-C82 | 1.3948(19) | C452-C462 | 1.3997(18) |
| N11-C11 | 1.4693(16) | C72-C122 | 1.5195(18) | C452-C502 | 1.5184(19) |
| N11-C71 | 1.4705(17) | C82-C92 | 1.380(2) | C462-C472 | 1.3823(19) |
| N11-C131 | 1.4747(17) | C92-C102 | 1.385(2) | C472-C482 | 1.3814(19) |
| N21-C61 | 1.4631(19) | C102-C112 | 1.3941(18) | C482-C492 | 1.3961(18) |
| N21-C121 | 1.4735(19) | C112-C152 | 1.5209(18) | C492-C532 | 1.5176(18) |
| N21-C181 | 1.4735(18) | C122-C142 | 1.532(2) | C502-C522 | 1.527(2) |
| C11-C21 | 1.5084(19) | C122-C132 | 1.534(2) | C502-C512 | 1.535(2) |
| C31-C41 | 1.498(2) | C152-C162 | 1.523(2) | C532-C552 | 1.5175(19) |

| | | | | | |
|---|---|---|---|---|---|
| C51-C61 | 1.508(2) | C152-C172 | 1.5265(19) | C532-C542 | 1.5218(19) |
| C71-C81 | 1.5103(19) | C182-C192 | 1.4046(17) | F13-C13 | 1.347(2) |
| C91-C101 | 1.499(2) | C182-C232 | 1.4100(17) | C13-C63 | 1.365(3) |
| C111-C121 | 1.501(2) | C192-C202 | 1.3964(18) | C13-C23 | 1.377(3) |
| C131-C141 | 1.5102(19) | C192-C242 | 1.5177(18) | C23-C33 | 1.390(3) |
| C151-C161 | 1.499(2) | C202-C212 | 1.3848(19) | C33-C43 | 1.365(3) |
| C171-C181 | 1.511(2) | C212-C222 | 1.3826(19) | C43-C53 | 1.380(3) |
| Sb12-B12 | 2.2067(13) | C222-C232 | 1.3948(17) | C53-C63 | 1.367(3) |
| Sb12-Ga12 | 2.5344(2) | C232-C272 | 1.5207(17) | | |

| | | | | | |
|---|---|---|---|---|---|
| O41-K11-O61 | 93.33(3) | N21-C61-C51 | 113.32(12) | C202-C192-C182 | 118.49(12) |
| O41-K11-O11 | 127.48(3) | N11-C71-C81 | 113.67(11) | C202-C192-C242 | 119.95(11) |
| O61-K11-O11 | 134.00(3) | O31-C81-C71 | 108.27(11) | C182-C192-C242 | 121.38(11) |
| O41-K11-O31 | 60.39(3) | O31-C91-C101 | 108.34(12) | C212-C202-C192 | 121.24(12) |
| O61-K11-O31 | 120.59(3) | O41-C101-C91 | 108.81(11) | C222-C212-C202 | 119.60(12) |
| O11-K11-O31 | 99.91(3) | O41-C111-C121 | 108.47(12) | C212-C222-C232 | 121.50(12) |
| O41-K11-O51 | 129.48(3) | N21-C121-C111 | 113.98(12) | C222-C232-C182 | 118.24(11) |
| O61-K11-O51 | 60.59(3) | N11-C131-C141 | 113.50(11) | C222-C232-C272 | 118.56(11) |
| O11-K11-O51 | 97.92(3) | O51-C141-C131 | 108.64(11) | C182-C232-C272 | 123.20(11) |
| O31-K11-O51 | 94.67(3) | O51-C151-C161 | 108.68(11) | C192-C242-C262 | 113.99(12) |
| O41-K11-O21 | 99.74(3) | O61-C161-C151 | 108.74(12) | C192-C242-C252 | 109.36(11) |
| O61-K11-O21 | 98.22(3) | O61-C171-C181 | 108.38(12) | C262-C242-C252 | 109.95(11) |
| O11-K11-O21 | 59.01(3) | N21-C181-C171 | 113.42(12) | C232-C272-C292 | 110.67(11) |
| O31-K11-O21 | 135.66(3) | B12-Sb12-Ga12 | 110.79(4) | C232-C272-C282 | 111.62(10) |
| O51-K11-O21 | 124.68(3) | N12-Ga12-N22 | 92.13(4) | C292-C272-C282 | 110.13(11) |
| O41-K11-N11 | 120.12(3) | N12-Ga12-Cl12 | 97.59(3) | C312-C302-N32 | 108.82(11) |
| O61-K11-N11 | 121.24(3) | N22-Ga12-Cl12 | 96.16(3) | C302-C312-N42 | 109.81(11) |
| O11-K11-N11 | 59.97(3) | N12-Ga12-Sb12 | 110.03(3) | C332-C322-C372 | 121.77(12) |
| O31-K11-N11 | 59.98(3) | N22-Ga12-Sb12 | 120.82(3) | C332-C322-N32 | 119.64(12) |
| O51-K11-N11 | 60.90(3) | Cl12-Ga12-Sb12 | 131.518(11) | C372-C322-N32 | 118.51(12) |
| O21-K11-N11 | 118.83(3) | N42-B12-N32 | 102.32(10) | C342-C332-C322 | 118.03(13) |
| O41-K11-N21 | 60.30(3) | N42-B12-Sb12 | 139.94(9) | C342-C332-C382 | 120.63(13) |
| O61-K11-N21 | 59.63(3) | N32-B12-Sb12 | 117.47(9) | C322-C332-C382 | 121.31(12) |
| O11-K11-N21 | 118.83(3) | C12-N12-C62 | 117.26(10) | C352-C342-C332 | 121.06(14) |
| O31-K11-N21 | 120.53(3) | C12-N12-Ga12 | 119.73(8) | C342-C352-C362 | 120.04(13) |
| O51-K11-N21 | 119.87(3) | C62-N12-Ga12 | 123.01(8) | C352-C362-C372 | 121.17(14) |
| O21-K11-N21 | 59.98(3) | C32-N22-C182 | 119.61(10) | C362-C372-C322 | 117.89(13) |
| N11-K11-N21 | 178.78(3) | C32-N22-Ga12 | 120.52(8) | C362-C372-C412 | 120.31(13) |
| C31-O11-C21 | 112.40(10) | C182-N22-Ga12 | 119.24(7) | C322-C372-C412 | 121.80(12) |
| C31-O11-K11 | 119.68(8) | C302-N32-C322 | 118.96(10) | C332-C382-C402 | 112.17(13) |
| C21-O11-K11 | 119.80(7) | C302-N32-B12 | 109.93(10) | C332-C382-C392 | 109.95(13) |
| C41-O21-C51 | 110.60(10) | C322-N32-B12 | 130.27(10) | C402-C382-C392 | 111.16(13) |
| C41-O21-K11 | 111.57(8) | C312-N42-C442 | 116.02(10) | C422-C412-C372 | 111.62(14) |
| C51-O21-K11 | 112.39(8) | C312-N42-B12 | 109.12(10) | C422-C412-C432 | 111.81(16) |
| C81-O31-C91 | 112.02(10) | C442-N42-B12 | 133.71(10) | C372-C412-C432 | 111.34(12) |
| C81-O31-K11 | 116.70(7) | N12-C12-C22 | 123.77(11) | C452-C442-C492 | 121.57(11) |
| C91-O31-K11 | 114.86(8) | N12-C12-C42 | 120.30(11) | C452-C442-N42 | 119.23(11) |
| C101-O41-C111 | 111.75(11) | C22-C12-C42 | 115.85(11) | C492-C442-N42 | 118.80(11) |
| C101-O41-K11 | 113.76(8) | C12-C22-C32 | 127.87(11) | C462-C452-C442 | 118.20(12) |
| C111-O41-K11 | 118.20(8) | N22-C32-C22 | 124.12(10) | C462-C452-C502 | 120.32(12) |
| C151-O51-C141 | 111.03(10) | N22-C32-C52 | 121.23(11) | C442-C452-C502 | 121.46(11) |

| | | | | | |
|---|---|---|---|---|---|
| C151-O51-K11 | 111.13(8) | C22-C32-C52 | 114.63(10) | C472-C462-C452 | 120.91(13) |
| C141-O51-K11 | 116.11(8) | C112-C62-C72 | 120.69(11) | C482-C472-C462 | 120.06(12) |
| C171-O61-C161 | 112.15(11) | C112-C62-N12 | 120.60(11) | C472-C482-C492 | 121.28(12) |
| C171-O61-K11 | 117.44(8) | C72-C62-N12 | 118.70(10) | C482-C492-C442 | 117.93(12) |
| C161-O61-K11 | 116.26(8) | C82-C72-C62 | 118.75(12) | C482-C492-C532 | 121.00(11) |
| C11-N11-C71 | 109.15(10) | C82-C72-C122 | 118.65(12) | C442-C492-C532 | 121.00(11) |
| C11-N11-C131 | 110.67(10) | C62-C72-C122 | 122.51(11) | C452-C502-C522 | 112.12(12) |
| C71-N11-C131 | 109.68(10) | C92-C82-C72 | 121.13(13) | C452-C502-C512 | 110.86(12) |
| C11-N11-K11 | 109.54(8) | C82-C92-C102 | 119.52(13) | C522-C502-C512 | 109.82(12) |
| C71-N11-K11 | 109.88(7) | C92-C102-C112 | 121.63(12) | C552-C532-C492 | 113.12(11) |
| C131-N11-K11 | 107.90(8) | C102-C112-C62 | 118.23(12) | C552-C532-C542 | 110.56(12) |
| C61-N21-C121 | 109.79(12) | C102-C112-C152 | 120.33(11) | C492-C532-C542 | 111.04(11) |
| C61-N21-C181 | 110.14(12) | C62-C112-C152 | 121.43(11) | F13-C13-C63 | 118.10(18) |
| C121-N21-C181 | 110.08(11) | C72-C122-C142 | 109.01(11) | F13-C13-C23 | 119.32(18) |
| C61-N21-K11 | 109.48(8) | C72-C122-C132 | 113.07(12) | C63-C13-C23 | 122.58(17) |
| C121-N21-K11 | 107.39(8) | C142-C122-C132 | 110.73(12) | C13-C23-C33 | 117.92(17) |
| C181-N21-K11 | 109.91(8) | C112-C152-C162 | 111.61(12) | C43-C33-C23 | 120.38(17) |
| N11-C11-C21 | 114.26(11) | C112-C152-C172 | 113.17(11) | C33-C43-C53 | 119.74(18) |
| O11-C21-C11 | 108.81(10) | C162-C152-C172 | 110.48(12) | C63-C53-C43 | 121.13(18) |
| O11-C31-C41 | 108.50(11) | C192-C182-C232 | 120.93(11) | C13-C63-C53 | 118.19(17) |
| O21-C41-C31 | 109.55(11) | C192-C182-N22 | 119.23(11) | | |
| O21-C51-C61 | 108.56(12) | C232-C182-N22 | 119.83(10) | | |

## 4. Computational Details

The ground-state geometry optimizations of **2-*R*** and [**2-*B***]$^-$ were calculated using a B3LYP density functional and def2-TZVP basis set as implemented in Gaussian16.[22,23] Dispersion effects were taken into account by utilizing Grimme's D3 correction with Becke-Johnson damping.[24,25] The obtained geometries were characterized as true minima *via* harmonic frequency calculation. Natural bond orbital analysis was performed using the NBO version 3.1.[26] Electronic excitations were calculated using the time-dependent DFT (TD-DFT) formalism at the B3LYP/def2-TZVP level. Solvent effects (toluene) have been taken into account by means of the conductor-like polarized continuum model (C-PCM).[27]

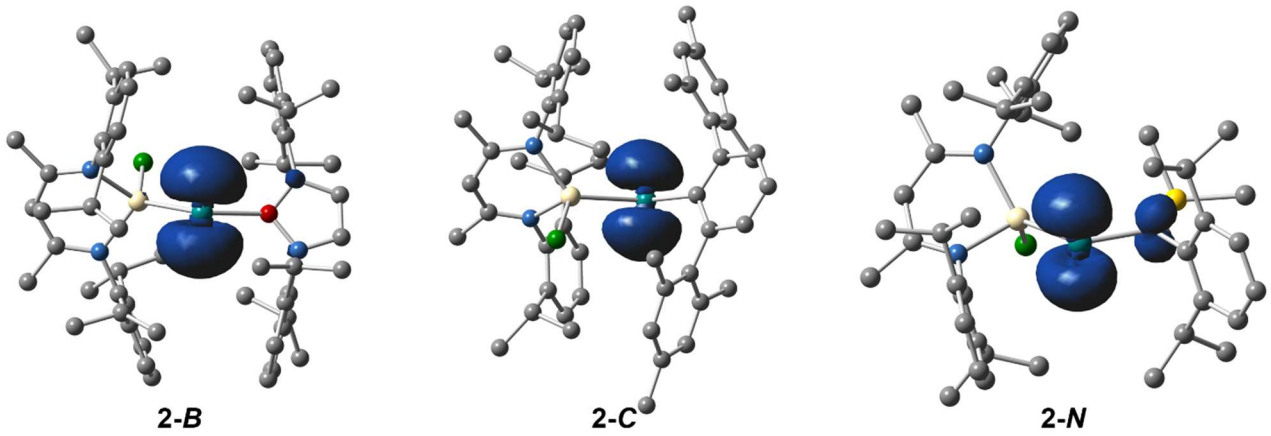


**Figure S25.** Mulliken spin density plots of **2-*R***.

**Table S6.** Calculated UV-Vis absorption properties of **2-*R*** by TD-DFT.

| | Excited state | Excitation energy $E$ [eV] | Wavelength $\lambda$ [nm] | Oscillator strength $f$ | Transition nature (orbital contributions > 10 %) |
|---|---|---|---|---|---|
| **2-*B*** | 1 | 1.4704 | 843.19 | 0.0030 | HOMO(β) → SOMO(β) (80 %), HOMO-2(β) → SOMO(β) (19 %) |
| | 2 | 2.0882 | 593.73 | 0.0100 | HOMO-2(β) → SOMO(β) (75 %), HOMO(β) → SOMO(β) (20 %) |
| **2-*C*** | 1 | 1.7151 | 722.89 | 0.0018 | HOMO(β) → SOMO(β) (96 %) |
| | 3 | 2.7035 | 458.61 | 0.0118 | HOMO-2(β) → SOMO(β) (96 %) |
| **2-*N*** | 1 | 2.1574 | 574.69 | 0.0012 | HOMO-1(β) → SOMO(β) (53 %), HOMO(β) → SOMO(β) (41 %) |
| | 5 | 2.7539 | 450.22 | 0.0536 | HOMO-3(β) → SOMO(β) (63 %), HOMO-4(β) → SOMO(β) (15 %) |

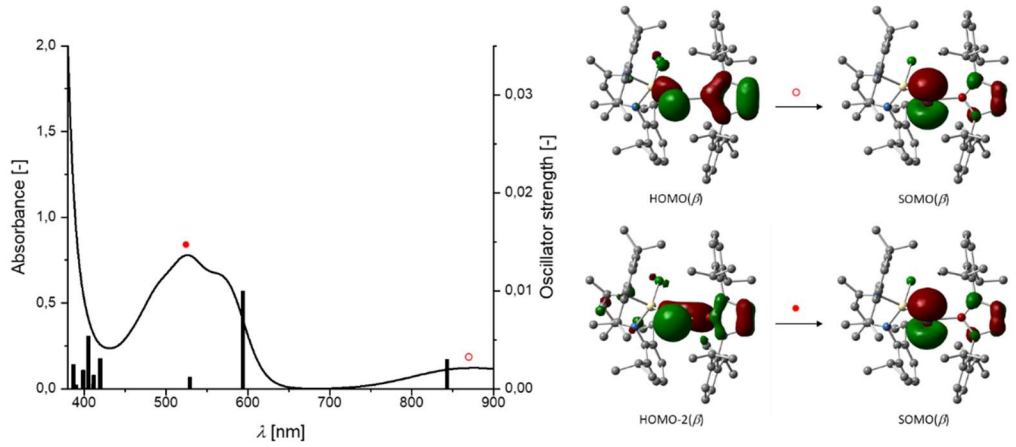


**Figure S26.** UV-Vis spectrum, calculated absorptions (vertical bars), and corresponding main orbital contributions of **2-*B***.

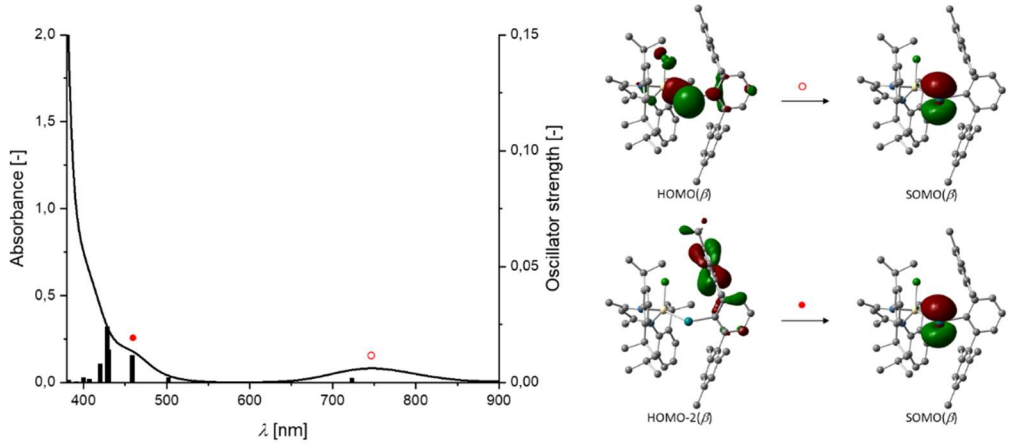


**Figure S27.** UV-Vis spectrum, calculated absorptions (vertical bars), and corresponding main orbital contributions of **2-*C***.

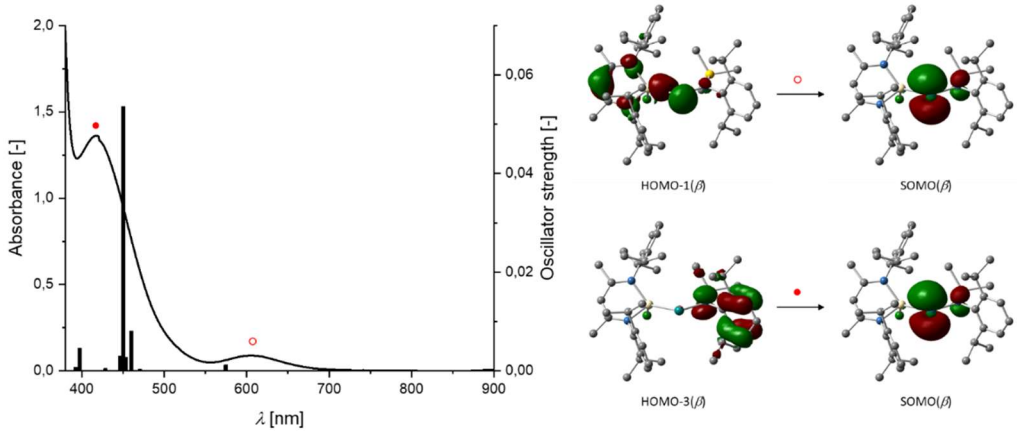


**Figure S28.** UV-Vis spectrum, calculated absorptions (vertical bars), and corresponding main orbital contributions of **2-*N***.

**Table S7.** Cartesian coordinates (x,y,z) for the optimized geometry of L(Cl)GaSb***B*** (**2-*B***).

| | | | |
|---|---|---|---|
| Sb | -0.1425910000 | 0.5477900000 | -1.0612650000 |
| B | -1.6892100000 | 1.7575190000 | -0.0042110000 |
| N | 3.0250120000 | -1.1208850000 | -0.2875440000 |
| C | 1.9479350000 | -3.7448250000 | 0.7106110000 |
| Ga | 1.2411900000 | -0.9473550000 | 0.5758790000 |
| N | 0.9144540000 | -2.9091900000 | 0.6551040000 |
| C | 3.2829270000 | -3.3689440000 | 0.5113320000 |
| H | 4.0108530000 | -4.1485580000 | 0.6711270000 |
| Cl | 1.7282990000 | -0.4596300000 | 2.7007840000 |
| N | -1.6053530000 | 2.9315660000 | 0.8117720000 |
| C | 1.7061910000 | -5.2058430000 | 0.9948780000 |
| H | 1.5313810000 | -5.3536240000 | 2.0607890000 |
| H | 0.8257140000 | -5.5747200000 | 0.4730910000 |
| H | 2.5701120000 | -5.7982650000 | 0.7049540000 |
| N | -3.0632510000 | 1.7140150000 | -0.4226360000 |
| C | 5.2593300000 | -2.1247260000 | -0.3199080000 |
| H | 5.6884570000 | -3.1230080000 | -0.3557700000 |
| H | 5.4695100000 | -1.6067110000 | -1.2526580000 |
| H | 5.7558120000 | -1.5651190000 | 0.4759610000 |
| C | -0.4219070000 | -3.4256600000 | 0.7589440000 |
| C | -1.1650100000 | -3.5957390000 | -0.4240740000 |
| C | -2.4394270000 | -4.1495130000 | -0.3337660000 |
| H | -3.0259730000 | -4.2836360000 | -1.2313310000 |
| C | -2.9675510000 | -4.5315980000 | 0.8894780000 |
| H | -3.9565850000 | -4.9687530000 | 0.9412230000 |
| C | -2.2371060000 | -4.3264120000 | 2.0473550000 |
| H | -2.6687110000 | -4.5957760000 | 3.0020770000 |
| C | -0.9642540000 | -3.7585510000 | 2.0124410000 |
| C | -0.5810980000 | -3.2353620000 | -1.7775600000 |
| H | 0.1512510000 | -2.4474410000 | -1.6105300000 |
| C | 0.1709110000 | -4.4205030000 | -2.3963980000 |
| H | -0.4994440000 | -5.2710580000 | -2.5385420000 |
| H | 0.5787670000 | -4.1441340000 | -3.3707110000 |
| H | 1.0005390000 | -4.7435240000 | -1.7682250000 |
| C | -1.6202560000 | -2.6763070000 | -2.7478000000 |
| H | -2.1858000000 | -1.8628500000 | -2.2976440000 |
| H | -1.1255700000 | -2.2874530000 | -3.6384770000 |
| H | -2.3291210000 | -3.4389910000 | -3.0750830000 |
| C | -0.2398830000 | -3.4881080000 | 3.3189980000 |
| H | 0.7767610000 | -3.1745450000 | 3.0890270000 |
| C | -0.1674900000 | -4.7239860000 | 4.2242660000 |
| H | -1.1549600000 | -5.0082160000 | 4.5925050000 |
| H | 0.2502080000 | -5.5890130000 | 3.7076010000 |
| H | 0.4577550000 | -4.5129560000 | 5.0936050000 |
| C | -0.9072140000 | -2.3267250000 | 4.0671240000 |
| H | -0.3489690000 | -2.0903460000 | 4.9743750000 |
| H | -0.9351980000 | -1.4293830000 | 3.4546210000 |
| H | -1.9304590000 | -2.5846630000 | 4.3493630000 |
| C | 3.5136450000 | -0.0536520000 | -1.1119950000 |
| C | 3.2608680000 | -0.1170670000 | -2.4973780000 |
| C | 3.7038260000 | 0.9316080000 | -3.2977760000 |
| H | 3.5180730000 | 0.9051280000 | -4.3623060000 |
| C | 4.3710690000 | 2.0177650000 | -2.7514650000 |

| | | | |
|---|---|---|---|
| H | 4.7006720000 | 2.8280740000 | -3.3890660000 |
| C | 4.6019700000 | 2.0681540000 | -1.3884970000 |
| H | 5.1111510000 | 2.9239330000 | -0.9653700000 |
| C | 4.1806830000 | 1.0413950000 | -0.5440690000 |
| C | 2.5480880000 | -1.3079720000 | -3.1155220000 |
| H | 1.9125570000 | -1.7376140000 | -2.3424230000 |
| C | 1.6476020000 | -0.9285960000 | -4.2926950000 |
| H | 0.9658670000 | -0.1222090000 | -4.0246820000 |
| H | 2.2270110000 | -0.6159910000 | -5.1632780000 |
| H | 1.0527560000 | -1.7918070000 | -4.5952110000 |
| C | 3.5396840000 | -2.4003630000 | -3.5404110000 |
| H | 3.0077750000 | -3.2391070000 | -3.9938920000 |
| H | 4.2486070000 | -2.0105360000 | -4.2742660000 |
| H | 4.1058730000 | -2.7859780000 | -2.6947860000 |
| C | 5.9239900000 | 1.3432850000 | 1.2636730000 |
| H | 6.5375740000 | 0.5601030000 | 0.8154950000 |
| H | 6.2918300000 | 2.3022570000 | 0.8935600000 |
| H | 6.0814130000 | 1.3239610000 | 2.3437320000 |
| C | 4.4362790000 | 1.1508390000 | 0.9459160000 |
| H | 4.1124120000 | 0.2245280000 | 1.4157720000 |
| C | 3.6023280000 | 2.2824780000 | 1.5523650000 |
| H | 3.7276650000 | 2.3148540000 | 2.6351670000 |
| H | 3.9013740000 | 3.2496080000 | 1.1447190000 |
| H | 2.5410710000 | 2.1497050000 | 1.3519820000 |
| C | -0.5004220000 | 3.5028720000 | 1.5111800000 |
| C | 0.4044520000 | 4.3162080000 | 0.8148000000 |
| C | 1.4284610000 | 4.9252050000 | 1.5372110000 |
| H | 2.1371150000 | 5.5604350000 | 1.0220050000 |
| C | 1.5582500000 | 4.7230000000 | 2.9005950000 |
| H | 2.3649280000 | 5.1983860000 | 3.4440220000 |
| C | 0.6654390000 | 3.8987490000 | 3.5680270000 |
| H | 0.7847790000 | 3.7358830000 | 4.6303470000 |
| C | -0.3808830000 | 3.2759370000 | 2.8925710000 |
| C | 0.2810990000 | 4.5668150000 | -0.6763630000 |
| H | -0.5303740000 | 3.9445400000 | -1.0510730000 |
| C | 1.5537320000 | 4.1616500000 | -1.4264960000 |
| H | 1.8110960000 | 3.1197140000 | -1.2384600000 |
| H | 1.4171930000 | 4.2832130000 | -2.5028990000 |
| H | 2.4080900000 | 4.7725290000 | -1.1282880000 |
| C | -0.0958210000 | 6.0255880000 | -0.9614890000 |
| H | 0.6815070000 | 6.7093420000 | -0.6137370000 |
| H | -0.2276340000 | 6.1839290000 | -2.0340740000 |
| H | -1.0269660000 | 6.2940880000 | -0.4600810000 |
| C | -1.3836970000 | 2.4203680000 | 3.6465260000 |
| H | -1.8889430000 | 1.7893110000 | 2.9148180000 |
| C | -2.4471110000 | 3.2977210000 | 4.3241780000 |
| H | -3.1843290000 | 2.6749490000 | 4.8357450000 |
| H | -1.9847430000 | 3.9530960000 | 5.0659080000 |
| H | -2.9750480000 | 3.9227620000 | 3.6053930000 |
| C | -0.7307000000 | 1.4979810000 | 4.6788850000 |
| H | 0.0601550000 | 0.9000060000 | 4.2319350000 |
| H | -0.3072040000 | 2.0623500000 | 5.5123400000 |
| H | -1.4799570000 | 0.8212950000 | 5.0945310000 |
| C | -3.7269340000 | 0.7077030000 | -1.1843860000 |

| | | | |
|---|---|---|---|
| C | -3.6659240000 | 0.7474940000 | -2.5842600000 |
| C | -4.3132450000 | -0.2614530000 | -3.2966440000 |
| H | -4.2814490000 | -0.2561110000 | -4.3775950000 |
| C | -4.9908680000 | -1.2745810000 | -2.6398890000 |
| H | -5.4794770000 | -2.0550760000 | -3.2094580000 |
| C | -5.0454700000 | -1.2933350000 | -1.2534520000 |
| H | -5.5820430000 | -2.0880580000 | -0.7556050000 |
| C | -4.4246890000 | -0.3014280000 | -0.4989070000 |
| C | -2.9670900000 | 1.8791720000 | -3.3133660000 |
| H | -2.2845890000 | 2.3518110000 | -2.6079980000 |
| C | -2.1331350000 | 1.3981560000 | -4.5030120000 |
| H | -2.7582470000 | 1.0037490000 | -5.3063830000 |
| H | -1.5571400000 | 2.2287050000 | -4.9151360000 |
| H | -1.4339150000 | 0.6187790000 | -4.1997140000 |
| C | -3.9845380000 | 2.9445510000 | -3.7441570000 |
| H | -4.5289060000 | 3.3364370000 | -2.8841660000 |
| H | -3.4811980000 | 3.7790560000 | -4.2371690000 |
| H | -4.7124470000 | 2.5253790000 | -4.4425360000 |
| C | -4.4883750000 | -0.2970110000 | 1.0193010000 |
| H | -4.5535140000 | 0.7456820000 | 1.3345710000 |
| C | -3.2129000000 | -0.8828020000 | 1.6359040000 |
| H | -3.0929190000 | -1.9245460000 | 1.3479200000 |
| H | -2.3238450000 | -0.3423370000 | 1.3172600000 |
| H | -3.2634100000 | -0.8352930000 | 2.7247770000 |
| C | -5.7167580000 | -1.0169120000 | 1.5786720000 |
| H | -5.7758180000 | -0.8572250000 | 2.6565540000 |
| H | -6.6413900000 | -0.6505310000 | 1.1294090000 |
| H | -5.6621460000 | -2.0951100000 | 1.4151510000 |
| C | -2.8598030000 | 3.5445570000 | 0.8385700000 |
| H | -3.0233120000 | 4.4633760000 | 1.3728660000 |
| C | -3.7305190000 | 2.8164410000 | 0.1083500000 |
| H | -4.7772900000 | 2.9881300000 | -0.0741890000 |
| C | 3.7825790000 | -2.1794710000 | -0.0271380000 |

**Table S8.** Cartesian coordinates (x,y,z) for the optimized geometry of L(Cl)GaSb***C*** (**2-*C***).

| | | | |
|---|---|---|---|
| Sb | 0.4338020000 | 0.9133830000 | -1.0481420000 |
| Ga | 0.1726010000 | -1.0662640000 | 0.6813770000 |
| Cl | 1.5172590000 | -1.1752540000 | 2.4723620000 |
| N | 0.7138480000 | -2.6627200000 | -0.4032110000 |
| N | -1.4666000000 | -1.9406110000 | 1.3781540000 |
| C | 0.4313760000 | -3.8763260000 | 0.0436470000 |
| C | -0.4730800000 | -4.1229230000 | 1.0879120000 |
| H | -0.5435070000 | -5.1501700000 | 1.4084870000 |
| C | -1.4126530000 | -3.2514320000 | 1.6366310000 |
| C | 1.0919450000 | -5.0803750000 | -0.5754900000 |
| H | 2.0789500000 | -5.2206510000 | -0.1312220000 |
| H | 1.2363280000 | -4.9542720000 | -1.6459060000 |
| H | 0.5058910000 | -5.9776140000 | -0.3919160000 |
| C | -2.4380400000 | -3.8532780000 | 2.5636990000 |
| H | -2.3112320000 | -4.9304770000 | 2.6302020000 |
| H | -3.4534840000 | -3.6349340000 | 2.2381290000 |
| H | -2.3291590000 | -3.4233650000 | 3.5606500000 |

| | | | |
|---|---|---|---|
| C | 1.5552660000 | -2.4827720000 | -1.5522280000 |
| C | 0.9531110000 | -2.2154070000 | -2.7978490000 |
| C | 1.7792950000 | -2.0202270000 | -3.9008080000 |
| H | 1.3408200000 | -1.8128550000 | -4.8658150000 |
| C | 3.1598010000 | -2.0725060000 | -3.7829650000 |
| H | 3.7841950000 | -1.9124400000 | -4.6526510000 |
| C | 3.7344600000 | -2.3158420000 | -2.5489520000 |
| H | 4.8122200000 | -2.3375640000 | -2.4573100000 |
| C | 2.9513770000 | -2.5238260000 | -1.4142710000 |
| C | -0.5575130000 | -2.1506520000 | -2.9492160000 |
| H | -0.9558970000 | -1.7247760000 | -2.0267940000 |
| C | -1.0091800000 | -1.2447920000 | -4.0963610000 |
| H | -2.0896370000 | -1.1127380000 | -4.0612990000 |
| H | -0.7655450000 | -1.6733880000 | -5.0702610000 |
| H | -0.5492230000 | -0.2588580000 | -4.0282090000 |
| C | -1.1697110000 | -3.5497910000 | -3.1016200000 |
| H | -0.9824740000 | -4.1722370000 | -2.2283990000 |
| H | -0.7542080000 | -4.0553810000 | -3.9759720000 |
| H | -2.2508760000 | -3.4797020000 | -3.2338440000 |
| C | 3.6330330000 | -2.7329350000 | -0.0767390000 |
| H | 2.8740890000 | -2.9737750000 | 0.6647370000 |
| C | 4.6484870000 | -3.8814070000 | -0.1070170000 |
| H | 5.0392770000 | -4.0601230000 | 0.8964490000 |
| H | 5.4969230000 | -3.6482210000 | -0.7531050000 |
| H | 4.2051870000 | -4.8098980000 | -0.4701110000 |
| C | 4.3036170000 | -1.4334500000 | 0.3739430000 |
| H | 4.7177030000 | -1.5453060000 | 1.3766370000 |
| H | 3.5950800000 | -0.6097960000 | 0.4038430000 |
| H | 5.1120170000 | -1.1576250000 | -0.3055820000 |
| C | -2.6792850000 | -1.2432410000 | 1.7009360000 |
| C | -3.7203770000 | -1.2548010000 | 0.7559070000 |
| C | -4.9319890000 | -0.6577190000 | 1.0959030000 |
| H | -5.7472070000 | -0.6683620000 | 0.3841970000 |
| C | -5.1154590000 | -0.0670880000 | 2.3351990000 |
| H | -6.0669880000 | 0.3838440000 | 2.5870800000 |
| C | -4.0725160000 | -0.0442640000 | 3.2465420000 |
| H | -4.2165600000 | 0.4322840000 | 4.2069450000 |
| C | -2.8404060000 | -0.6233610000 | 2.9509210000 |
| C | -3.5789390000 | -1.9504480000 | -0.5866270000 |
| H | -2.5430800000 | -2.2659940000 | -0.6881080000 |
| H | -3.7922690000 | -1.5430230000 | -2.6993760000 |
| C | -3.8941470000 | -1.0118560000 | -1.7522310000 |
| H | -3.2256200000 | -0.1523070000 | -1.7634140000 |
| H | -4.9162250000 | -0.6347790000 | -1.6972560000 |
| C | -4.4476280000 | -3.2135000000 | -0.6564070000 |
| H | -4.3070940000 | -3.7178670000 | -1.6143410000 |
| H | -5.5069630000 | -2.9675710000 | -0.5574070000 |
| H | -4.1926280000 | -3.9201460000 | 0.1333450000 |
| C | -1.7146870000 | -0.5603900000 | 3.9635060000 |
| H | -0.9329810000 | -1.2461780000 | 3.6437980000 |
| C | -1.0986390000 | 0.8432790000 | 3.9847120000 |
| H | -0.2479240000 | 0.8758220000 | 4.6659840000 |
| H | -1.8314150000 | 1.5869750000 | 4.3060340000 |
| H | -0.7415670000 | 1.1323060000 | 2.9965640000 |

| | | | |
|---|---|---|---|
| C | -2.1520890000 | -0.9810010000 | 5.3700920000 |
| H | -2.6269350000 | -1.9637460000 | 5.3660890000 |
| H | -2.8590600000 | -0.2728220000 | 5.8062970000 |
| H | -1.2841120000 | -1.0266190000 | 6.0300800000 |
| C | 0.4305740000 | 2.8162740000 | 0.0296690000 |
| C | 1.5535810000 | 3.3095960000 | 0.7127270000 |
| C | 1.5007110000 | 4.5855310000 | 1.2804000000 |
| H | 2.3709810000 | 4.9548870000 | 1.8081980000 |
| C | 0.3764050000 | 5.3846690000 | 1.1514440000 |
| H | 0.3562110000 | 6.3730410000 | 1.5926870000 |
| C | -0.7088970000 | 4.9194470000 | 0.4256990000 |
| H | -1.5821320000 | 5.5444220000 | 0.2839050000 |
| C | -0.6891750000 | 3.6471350000 | -0.1442760000 |
| C | 2.8605310000 | 2.5949220000 | 0.8108290000 |
| C | 3.2871550000 | 2.0771190000 | 2.0448480000 |
| C | 4.5740440000 | 1.5640630000 | 2.1584230000 |
| H | 4.8907920000 | 1.1569130000 | 3.1121440000 |
| C | 5.4620950000 | 1.5640660000 | 1.0879060000 |
| C | 5.0231760000 | 2.0800260000 | -0.1250440000 |
| H | 5.7020590000 | 2.0974990000 | -0.9702310000 |
| C | 3.7402110000 | 2.5991030000 | -0.2849010000 |
| C | 2.3935200000 | 2.1151300000 | 3.2532480000 |
| H | 2.6958480000 | 1.3616970000 | 3.9785630000 |
| H | 1.3567520000 | 1.9302170000 | 2.9880470000 |
| H | 2.4346300000 | 3.0936410000 | 3.7400970000 |
| C | 6.8491960000 | 1.0035740000 | 1.2395790000 |
| H | 7.3210730000 | 1.3572290000 | 2.1582860000 |
| H | 7.4848720000 | 1.2869350000 | 0.4002630000 |
| H | 6.8273270000 | -0.0882070000 | 1.2860560000 |
| C | 3.3504670000 | 3.1941920000 | -1.6126780000 |
| H | 4.2368030000 | 3.4169790000 | -2.2064300000 |
| H | 2.7756330000 | 4.1120390000 | -1.4898300000 |
| H | 2.7325480000 | 2.5036610000 | -2.1929100000 |
| C | -1.8615110000 | 3.2289670000 | -0.9672070000 |
| C | -3.0201650000 | 2.7489100000 | -0.3412740000 |
| C | -4.1214810000 | 2.4092530000 | -1.1204750000 |
| H | -5.0099250000 | 2.0300480000 | -0.6297980000 |
| C | -4.1027340000 | 2.5281990000 | -2.5058410000 |
| C | -2.9499440000 | 3.0235870000 | -3.1076360000 |
| H | -2.9231870000 | 3.1430810000 | -4.1850350000 |
| C | -1.8317300000 | 3.3875130000 | -2.3631350000 |
| C | -3.0719620000 | 2.5910190000 | 1.1504750000 |
| H | -2.3677050000 | 1.8288210000 | 1.4840880000 |
| H | -4.0628680000 | 2.2872200000 | 1.4752570000 |
| H | -2.8015280000 | 3.5141920000 | 1.6640620000 |
| C | -5.2827890000 | 2.1030240000 | -3.3351190000 |
| H | -5.1534580000 | 1.0790340000 | -3.6973990000 |
| H | -5.4078950000 | 2.7438300000 | -4.2091620000 |
| H | -6.2062860000 | 2.1309630000 | -2.7557700000 |
| C | -0.6205840000 | 3.9521160000 | -3.0553380000 |
| H | 0.2212090000 | 3.2562190000 | -3.0183890000 |
| H | -0.2856190000 | 4.8757660000 | -2.5814560000 |
| H | -0.8363750000 | 4.1578850000 | -4.1032680000 |

**Table S9.** Cartesian coordinates (x,y,z) for the optimized geometry of L(Cl)GaSb***N*** (**2-*N***).

| | | | |
|---|---|---|---|
| Sb | -1.0627660000 | 0.5241190000 | 0.5308410000 |
| Ga | 1.2942610000 | 0.2388360000 | -0.6491650000 |
| Cl | 1.6382660000 | 0.2765910000 | -2.8646450000 |
| Si | -2.1991800000 | -2.0430250000 | -1.5119160000 |
| N | 2.7749840000 | -0.9450670000 | -0.0548530000 |
| N | 2.1761480000 | 1.9027610000 | -0.0198130000 |
| N | -2.4385080000 | -0.7486960000 | -0.3460670000 |
| C | 4.0133490000 | -0.4671140000 | -0.0005380000 |
| C | 4.3451820000 | 0.8907030000 | -0.1277710000 |
| H | 5.4015980000 | 1.1077540000 | -0.1552920000 |
| C | 3.5002330000 | 2.0008740000 | -0.0598680000 |
| C | 5.1656980000 | -1.4149720000 | 0.2128900000 |
| H | 6.0244380000 | -0.8863200000 | 0.6191450000 |
| H | 5.4582020000 | -1.8570470000 | -0.7404710000 |
| H | 4.8967200000 | -2.2324090000 | 0.8778090000 |
| C | 4.1385520000 | 3.3645940000 | -0.0443180000 |
| H | 4.0818210000 | 3.7855140000 | -1.0515560000 |
| H | 5.1852390000 | 3.3083700000 | 0.2446340000 |
| H | 3.6157840000 | 4.0508520000 | 0.6175840000 |
| C | 2.5133300000 | -2.3350180000 | 0.1913830000 |
| C | 2.0041240000 | -2.7008440000 | 1.4520340000 |
| C | 1.7464170000 | -4.0458840000 | 1.6981730000 |
| H | 1.3579840000 | -4.3473430000 | 2.6604350000 |
| C | 1.9719420000 | -5.0075280000 | 0.7258020000 |
| H | 1.7636910000 | -6.0491070000 | 0.9340170000 |
| C | 2.4443770000 | -4.6279640000 | -0.5170970000 |
| H | 2.5942520000 | -5.3794690000 | -1.2807610000 |
| C | 2.7171100000 | -3.2934880000 | -0.8157520000 |
| C | 1.7617980000 | -1.6628590000 | 2.5322180000 |
| H | 1.5159600000 | -0.7276970000 | 2.0293310000 |
| C | 3.0290150000 | -1.4140150000 | 3.3601990000 |
| H | 3.8479420000 | -1.0498140000 | 2.7407970000 |
| H | 3.3561920000 | -2.3350480000 | 3.8474980000 |
| H | 2.8403860000 | -0.6693610000 | 4.1356190000 |
| C | 0.5756730000 | -2.0038070000 | 3.4339840000 |
| H | 0.3406390000 | -1.1568700000 | 4.0778390000 |
| H | 0.7849720000 | -2.8576390000 | 4.0809800000 |
| H | -0.3115760000 | -2.2313200000 | 2.8438970000 |
| C | 3.1717310000 | -2.9376070000 | -2.2195080000 |
| H | 3.4032450000 | -1.8746730000 | -2.2476720000 |
| C | 2.0401810000 | -3.1777500000 | -3.2279890000 |
| H | 1.1505890000 | -2.6108120000 | -2.9659180000 |
| H | 1.7751250000 | -4.2365310000 | -3.2700630000 |
| H | 2.3508290000 | -2.8626740000 | -4.2254170000 |
| C | 4.4258090000 | -3.7145190000 | -2.6406190000 |
| H | 4.7830850000 | -3.3532590000 | -3.6066520000 |
| H | 4.2169220000 | -4.7807990000 | -2.7452360000 |
| H | 5.2352360000 | -3.6098940000 | -1.9172930000 |
| C | 1.3545220000 | 2.9985570000 | 0.4031010000 |
| C | 1.0945590000 | 3.1404890000 | 1.7818710000 |
| C | 0.2374690000 | 4.1585420000 | 2.1906430000 |
| H | 0.0241190000 | 4.2851730000 | 3.2429540000 |
| C | -0.3630000000 | 5.0037550000 | 1.2704010000 |
| H | -1.0362990000 | 5.7813480000 | 1.6074070000 |

| | | | |
|---|---|---|---|
| C | -0.1052710000 | 4.8439810000 | -0.0799850000 |
| H | -0.5829110000 | 5.5005820000 | -0.7952320000 |
| C | 0.7548910000 | 3.8481120000 | -0.5396580000 |
| C | 1.7311190000 | 2.2215200000 | 2.8120190000 |
| H | 2.0444570000 | 1.3173110000 | 2.2917700000 |
| C | 0.7581320000 | 1.8054330000 | 3.9185000000 |
| H | 0.4760810000 | 2.6495020000 | 4.5495750000 |
| H | 1.2271090000 | 1.0628530000 | 4.5653550000 |
| H | -0.1534100000 | 1.3721350000 | 3.5061340000 |
| C | 2.9904120000 | 2.8502380000 | 3.4243870000 |
| H | 3.7437570000 | 3.0650670000 | 2.6683310000 |
| H | 3.4350860000 | 2.1734940000 | 4.1568870000 |
| H | 2.7450870000 | 3.7860630000 | 3.9313900000 |
| C | 1.0028800000 | 3.7063140000 | -2.0278970000 |
| H | 1.7296220000 | 2.9109940000 | -2.1758380000 |
| C | 1.5892980000 | 4.9883100000 | -2.6309750000 |
| H | 0.8826800000 | 5.8185940000 | -2.5733020000 |
| H | 1.8325820000 | 4.8312230000 | -3.6834620000 |
| H | 2.4999790000 | 5.2924550000 | -2.1122140000 |
| C | -0.2773070000 | 3.2921410000 | -2.7626090000 |
| H | -1.0375720000 | 4.0730580000 | -2.6968720000 |
| H | -0.6955550000 | 2.3797520000 | -2.3382580000 |
| H | -0.0661230000 | 3.1035720000 | -3.8159740000 |
| C | -3.8383570000 | -2.9189530000 | -1.7630650000 |
| H | -4.6098170000 | -2.2382400000 | -2.1249900000 |
| H | -4.2078070000 | -3.3762200000 | -0.8455340000 |
| H | -3.7119540000 | -3.7102630000 | -2.5067260000 |
| C | -1.6388220000 | -1.3790310000 | -3.1688400000 |
| H | -2.4321690000 | -0.7920930000 | -3.6351460000 |
| H | -1.4007010000 | -2.2070180000 | -3.8420910000 |
| H | -0.7524720000 | -0.7499950000 | -3.0977520000 |
| C | -0.9528570000 | -3.2567640000 | -0.8269470000 |
| H | -0.0122080000 | -2.7784250000 | -0.5594100000 |
| H | -0.7243670000 | -4.0387020000 | -1.5536290000 |
| H | -1.3399650000 | -3.7381260000 | 0.0730460000 |
| C | -3.7690200000 | -0.4459400000 | 0.0929100000 |
| C | -4.2967630000 | -1.0849660000 | 1.2338920000 |
| C | -5.6021510000 | -0.7945170000 | 1.6230600000 |
| H | -6.0166940000 | -1.2826360000 | 2.4960180000 |
| C | -6.3788430000 | 0.1107220000 | 0.9178030000 |
| H | -7.3928820000 | 0.3208380000 | 1.2333430000 |
| C | -5.8445340000 | 0.7528750000 | -0.1874120000 |
| H | -6.4481680000 | 1.4703630000 | -0.7288300000 |
| C | -4.5437920000 | 0.4958220000 | -0.6145620000 |
| C | -3.4697910000 | -2.0451620000 | 2.0698240000 |
| H | -2.5279650000 | -2.2032710000 | 1.5472490000 |
| C | -4.1404380000 | -3.4123320000 | 2.2390900000 |
| H | -5.0746060000 | -3.3354850000 | 2.7986490000 |
| H | -3.4824500000 | -4.0907450000 | 2.7865290000 |
| H | -4.3680140000 | -3.8667870000 | 1.2746330000 |
| C | -3.1446710000 | -1.4285910000 | 3.4369940000 |
| H | -2.6058750000 | -0.4870290000 | 3.3222290000 |
| H | -2.5254670000 | -2.1055100000 | 4.0289910000 |
| H | -4.0576140000 | -1.2257290000 | 4.0006220000 |

| | | | |
|---|---|---|---|
| C | -3.9958690000 | 1.2440650000 | -1.8159590000 |
| H | -2.9864160000 | 0.8812960000 | -1.9955880000 |
| C | -4.8145510000 | 0.9716370000 | -3.0825620000 |
| H | -5.8355970000 | 1.3464950000 | -2.9871640000 |
| H | -4.8722600000 | -0.0970270000 | -3.2936160000 |
| H | -4.3576240000 | 1.4635160000 | -3.9438850000 |
| C | -3.8955760000 | 2.7485160000 | -1.5361410000 |
| H | -4.8766400000 | 3.1794870000 | -1.3259060000 |
| H | -3.4762720000 | 3.2685970000 | -2.3994720000 |
| H | -3.2505080000 | 2.9430290000 | -0.6780100000 |

**Table S10.** Cartesian coordinates (x,y,z) for the optimized geometry of [**2-*B***]$^{-}$.

| | | | |
|---|---|---|---|
| Sb | -0.6784740000 | 0.3515380000 | -0.8808920000 |
| B | -2.2956150000 | -0.5788530000 | 0.2929730000 |
| C | 3.5322020000 | 2.1610310000 | 1.1021650000 |
| N | 2.2314200000 | 2.0029290000 | 0.8837690000 |
| Ga | 1.4719690000 | 0.1536280000 | 0.4577060000 |
| N | -3.6620420000 | -0.1737980000 | -0.0151520000 |
| C | 4.3617930000 | 0.1723530000 | -0.1993500000 |
| N | 3.1979410000 | -0.3420370000 | -0.5526670000 |
| C | 4.5077420000 | 1.2542130000 | 0.6832520000 |
| H | 5.5247000000 | 1.5027070000 | 0.9482380000 |
| Cl | 2.0179650000 | -0.8905380000 | 2.4228640000 |
| N | -2.4935310000 | -1.6784360000 | 1.2248390000 |
| C | 5.6503230000 | -0.3898060000 | -0.7560860000 |
| H | 5.5029810000 | -0.8604780000 | -1.7246060000 |
| H | 6.0423370000 | -1.1485070000 | -0.0767050000 |
| H | 6.3973960000 | 0.3967940000 | -0.8465650000 |
| C | 1.4011200000 | 3.1611330000 | 0.9742790000 |
| C | 0.5520740000 | 3.3586290000 | 2.0775100000 |
| C | -0.0982470000 | 4.5839170000 | 2.1986850000 |
| H | -0.7343280000 | 4.7628640000 | 3.0544500000 |
| C | 1.4601360000 | 4.1136780000 | -0.0591650000 |
| C | 0.7801960000 | 5.3189250000 | 0.0990350000 |
| H | 0.8254780000 | 6.0616210000 | -0.6878410000 |
| C | 0.0325130000 | 5.5722100000 | 1.2357090000 |
| H | -0.4860020000 | 6.5161350000 | 1.3504600000 |
| C | 0.3327710000 | 2.2734760000 | 3.1140060000 |
| H | 0.5087580000 | 1.3169990000 | 2.6273280000 |
| C | 2.1647210000 | 3.8297690000 | -1.3748570000 |
| H | 2.6231280000 | 2.8457290000 | -1.3020600000 |
| C | -1.1095610000 | 2.2413630000 | 3.6235410000 |
| H | -1.8113200000 | 2.1785270000 | 2.7921550000 |
| H | -1.3587800000 | 3.1212060000 | 4.2215180000 |
| H | -1.2559460000 | 1.3671770000 | 4.2557740000 |
| C | 1.3282910000 | 2.3669890000 | 4.2751240000 |
| H | 1.1307460000 | 1.5802020000 | 5.0051960000 |
| H | 1.2510250000 | 3.3350530000 | 4.7785950000 |
| H | 2.3514980000 | 2.2360330000 | 3.9258080000 |

| | | | |
|---|---|---|---|
| C | 1.1335400000 | 3.7777790000 | -2.5098700000 |
| H | 1.6185660000 | 3.5224900000 | -3.4539770000 |
| H | 0.6433780000 | 4.7457270000 | -2.6374870000 |
| H | 0.3648200000 | 3.0333300000 | -2.2985700000 |
| C | 3.2742130000 | 4.8360260000 | -1.6985450000 |
| H | 3.7568650000 | 4.5740190000 | -2.6429320000 |
| H | 4.0430330000 | 4.8537360000 | -0.9254730000 |
| H | 2.8754570000 | 5.8483170000 | -1.7981790000 |
| C | 3.1210340000 | -1.3974830000 | -1.5128060000 |
| C | 3.4336620000 | -2.7196940000 | -1.1522680000 |
| C | 3.3011470000 | -3.7199560000 | -2.1150560000 |
| H | 3.5265610000 | -4.7436440000 | -1.8450540000 |
| C | 2.8657770000 | -3.4333310000 | -3.3955260000 |
| H | 2.7542100000 | -4.2265600000 | -4.1245150000 |
| C | 2.5537140000 | -2.1258590000 | -3.7360840000 |
| H | 2.2006910000 | -1.9095650000 | -4.7341340000 |
| C | 2.6717610000 | -1.0917530000 | -2.8127860000 |
| C | 3.8732860000 | -3.1083970000 | 0.2474080000 |
| H | 3.9949370000 | -2.2008460000 | 0.8346770000 |
| C | 2.3762530000 | 0.3405040000 | -3.2179490000 |
| H | 1.9656640000 | 0.8432120000 | -2.3435000000 |
| C | 5.2061820000 | -3.8684580000 | 0.2480690000 |
| H | 5.1047430000 | -4.8481550000 | -0.2244050000 |
| H | 5.5431140000 | -4.0318270000 | 1.2743580000 |
| H | 5.9874510000 | -3.3260850000 | -0.2863990000 |
| C | 2.7873220000 | -3.9346380000 | 0.9390410000 |
| H | 2.6174970000 | -4.8779880000 | 0.4139930000 |
| H | 1.8490770000 | -3.3910710000 | 0.9764420000 |
| H | 3.0730120000 | -4.1595100000 | 1.9684540000 |
| C | -4.5605510000 | -1.0024490000 | 0.6558340000 |
| H | -5.6265410000 | -0.8860410000 | 0.5554770000 |
| C | 3.6681290000 | 1.0719520000 | -3.6102080000 |
| H | 4.1512320000 | 0.5729430000 | -4.4543550000 |
| H | 4.3780840000 | 1.1047720000 | -2.7846120000 |
| H | 3.4503770000 | 2.1009010000 | -3.9037430000 |
| C | 1.3315260000 | 0.4537940000 | -4.3269020000 |
| H | 1.7060330000 | 0.0760350000 | -5.2818320000 |
| H | 1.0595580000 | 1.4993510000 | -4.4719360000 |
| H | 0.4265190000 | -0.0896100000 | -4.0565730000 |
| C | -3.8694100000 | -1.8909430000 | 1.3936470000 |
| H | -4.2414760000 | -2.6753570000 | 2.0287190000 |
| C | -1.6009280000 | -2.6838180000 | 1.6956680000 |
| C | -5.6047630000 | -2.0044100000 | -2.9756490000 |
| H | -5.9895630000 | -1.5919800000 | -3.9116650000 |
| H | -6.3614480000 | -1.8485090000 | -2.2043030000 |
| H | -5.4748810000 | -3.0805980000 | -3.1124320000 |
| C | -3.1874880000 | -1.6120310000 | -3.6272060000 |
| H | -3.0556030000 | -2.6861560000 | -3.7802900000 |
| H | -2.2352120000 | -1.1944810000 | -3.2968720000 |
| H | -3.4479380000 | -1.1629690000 | -4.5891130000 |
| C | -4.2754400000 | -1.3545280000 | -2.5779950000 |
| H | -3.9501610000 | -1.8287830000 | -1.6555420000 |
| C | -4.8778820000 | 2.5413550000 | 1.5187600000 |
| H | -5.7373970000 | 3.1369980000 | 1.1979360000 |

| | | | |
|---|---|---|---|
| H | -4.5525550000 | 2.9120840000 | 2.4942070000 |
| H | -5.2034000000 | 1.5088560000 | 1.6429620000 |
| C | -3.2075930000 | 4.0747320000 | 0.4170340000 |
| H | -2.3776020000 | 4.1447910000 | -0.2862420000 |
| H | -2.8357560000 | 4.3860720000 | 1.3930700000 |
| H | -3.9839830000 | 4.7850800000 | 0.1196270000 |
| C | -3.7347830000 | 2.6451880000 | 0.5001810000 |
| H | -2.9103410000 | 2.0242590000 | 0.8527240000 |
| C | -4.4292980000 | 0.1301970000 | -2.3035360000 |
| C | -4.8734450000 | 0.9823670000 | -3.3142590000 |
| H | -5.1350670000 | 0.5704370000 | -4.2812950000 |
| C | -4.9606910000 | 2.3481310000 | -3.1051820000 |
| H | -5.3001330000 | 2.9991210000 | -3.9020940000 |
| C | -4.5912700000 | 2.8869840000 | -1.8796370000 |
| H | -4.6365250000 | 3.9577220000 | -1.7373420000 |
| C | -4.1476110000 | 2.0732100000 | -0.8416460000 |
| C | -4.0914600000 | 0.6867500000 | -1.0610450000 |
| C | -1.2398640000 | -2.7174330000 | 3.0521540000 |
| C | -0.1188860000 | -4.8251580000 | 2.6601630000 |
| H | 0.4612190000 | -5.6593460000 | 3.0357130000 |
| C | -0.4969660000 | -3.8022520000 | 3.5134660000 |
| H | -0.2037840000 | -3.8437050000 | 4.5537920000 |
| C | -0.4565900000 | -4.7622690000 | 1.3181660000 |
| H | -0.1365590000 | -5.5512040000 | 0.6499150000 |
| C | -1.1890630000 | -3.6938160000 | 0.8084480000 |
| C | -1.6729950000 | -1.6240100000 | 4.0120520000 |
| H | -1.9229980000 | -0.7529920000 | 3.4056070000 |
| C | -1.5638260000 | -3.6711360000 | -0.6616750000 |
| H | -1.9562960000 | -2.6821310000 | -0.8827710000 |
| C | -2.6681200000 | -4.6917690000 | -0.9615110000 |
| H | -2.9678200000 | -4.6314810000 | -2.0108600000 |
| H | -3.5492920000 | -4.5031420000 | -0.3456530000 |
| H | -2.3286000000 | -5.7124170000 | -0.7648230000 |
| C | -0.3503370000 | -3.8589000000 | -1.5731550000 |
| H | 0.1340580000 | -4.8271090000 | -1.4264360000 |
| H | 0.3826480000 | -3.0732270000 | -1.3969910000 |
| H | -0.6548370000 | -3.7924950000 | -2.6197180000 |
| C | -0.5662270000 | -1.2204070000 | 4.9905470000 |
| H | -0.3259620000 | -2.0319240000 | 5.6814770000 |
| H | -0.8962860000 | -0.3735070000 | 5.5964670000 |
| H | 0.3426690000 | -0.9410810000 | 4.4613300000 |
| C | -2.9316540000 | -2.0315490000 | 4.7925120000 |
| H | -3.7653460000 | -2.2507110000 | 4.1276380000 |
| H | -3.2402950000 | -1.2266760000 | 5.4648370000 |
| H | -2.7345710000 | -2.9210460000 | 5.3969820000 |
| C | 4.0336330000 | 3.4125650000 | 1.7881760000 |
| H | 5.0319890000 | 3.2436050000 | 2.1886810000 |
| H | 3.3665620000 | 3.7132830000 | 2.5936530000 |
| H | 4.0831560000 | 4.2488360000 | 1.0910880000 |

## 6. References


[1] N. J. Hardman, B. E. Eichler, P. P. Power, *Chem. Commun.* **2000**, 1991–1992.

[2] H. Saleske, Ph.D. Dissertation, University of Würzburg, 1983.

[3] Y. Segawa, M. Yamashita, K.Nozaki, *Science* **2006**, *314*, 113–115; Y. Segawa, Y. Suzuki, M. Yamashita, K.Nozaki, *J. Am. Chem. Soc.* **2008**, *130*, 16069–16079.

[4] J. E. Borger, A. W. Ehlers, M. Lutz, J. C. Slootweg, K. Lammertsma, *Angew. Chem.* **2014**, *126*, 13050–13053; *Angew. Chem. Int. Ed.* **2014**, *53*, 12836–12839.

[5] A. V. Protchenko, K. H. Birjkumar, D. Dange, A. D. Schwarz, D. Vidovic, C. Jones, N. Kaltsoyannis, P. Mountford, S. Aldridge, *J. Am. Chem. Soc.* **2012**, *134*, 6500–6503.

[6] S. V. Rosokha, J. K. Kochi, *J. Org. Chem.* **2006**, *71*, 9357–9365.

[7] D. F. Evans, *J. Chem. Soc.* **1959**, 2003–2005.

[8] G. J. P. Britovsek, V. C. Gibson, S. K. Spitzmesser, K. P. Tellmann, A. J. P. White, D. J. Williams, *J. Chem. Soc., Dalton Trans*. **2002**, 1159–1171.

[9] E. Reijerse, F. Lendzian, R. Isaacson, W. Lubitz, *J. Magn. Reson.* **2012**, *214*, 237–243.

[10] S. Stoll, A. Schweiger, *J. Magn. Reson.* **2006**, *178*, 42-55.

[11] S. Stoll, R. D. Britt, *Phys. Chem. Chem. Phys.* **2009**, *11*, 6614–6625.

[12] J. Weil, J. Bolton In *Electron Paramagnetic Resonance: Elementary Theory and Practical Applications*, 2nd Ed., John Wiley & Sons, Inc., Hoboken, New Jersey, **2007**.

[13] C. A. Hutchison Jr., D. B. McKay, *J. Chem. Phys.* **1977**, *66*, 3311–3330.

[14] G. E. Cutsail III, B. Stein, D. Subedi, J. Smith, M. Kirk, B. Hoffman, *J. Am. Chem. Soc.* **2014**, *136*, 12323–12336.

[15] J. Anderson, G. E. Cutsail III, J. Rittle, B. Connor, W. Gunderson, L. Zhang, B. Hoffman, J. Peters, *J. Am. Chem. Soc.* **2015**, *137*, 7803–7809.

[16] T. S. Zhuravleva, *J. Struct. Chem.* **1967**, *7*, 489–492.

[17] J. Cano, E. Ruiz, S. Alvarez, M. Verdaguer, *Comment. Inorg. Chem.* **1998**, *20*, 27–56.

[18] G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467–473.

[19] G. M. Sheldrick, SHELXL-2014, Program for the Refinement of Crystal Structures University of Göttingen, Göttingen (Germany) **2014**. (see also: G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112–122)

[20] shelXle, *A Qt GUI for SHELXL*, C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Cryst.* **2011**, *44*, 1281–1284.

[21] PLATON/SQUEEZE, P. van der Sluis, A. L. Spek, *Acta Crystallogr.* **1990**, *A46,* 194–201.

[22] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys*. **2005**, *7*, 3297–305.

[23] Gaussian 16, Revision A.03, 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, D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**.

[24] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys*. **2010**, *132*, 154104.

[25] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456-1465.

[26] NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold.

[27] C. Maurizio, R. Nadia, S. Giovanni, B. Vincenzo, *J. Comput. Chem*. **2003**, *24*, 669–681.