Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

Calix[4]pyrrolato Stannate(II): A Tetraamido Tin(II) Dianion and Strong Metal-Centered σ-Donor

*H. Ruppert, L. Greb**

Supporting Information

Table of Contents

1 Experimental Details

All manipulations were carried out under a dry argon atmosphere by using standard Schlenk techniques to prevent oxidation and hydrolysis of the sensitive compounds. *meso*-Octamethylcali[4]pyrrole as well as the deprotonated *tris*-(thf) *tetra*-lithium *meso*-octamethylcalix[4]pyrrolate have been synthesized by literature known procedures.[1] The commercially available chemicals were used as received. All solvents and liquid chemicals were rigorously dried by applying standard procedures, freshly degassed and stored over activated molecular sieve (3 Å resp. 4 Å) prior to use. All glassware, syringes, magnetic stirring bars, and needles were thoroughly dried. All air sensitive compounds were stored in a glove box (MBraun LABmaster dp, MB-20-G, SylaTech Y05G) under N_2 atmosphere. Analytical data of literature known compounds were compared to data of the respective reference and were found to be consistent in all cases. Purity and identity of novel compounds were confirmed by high resolution multinuclear NMR-spectroscopy, mass spectrometry, elemental analysis and if possible, X-ray diffraction analysis.

^{1}H, ^{13}C, ^{19}F, ^{31}P, ^{77}Se and ^{119}Sn NMR spectra were collected with a Bruker (DPX) 200, a Bruker Advance II 400 or a Bruker 2 Advance III 600 NMR spectrometer and referenced to tetramethylsilane (^{1}H, ^{13}C), tetramethylstannane (^{119}Sn), or dimethyl selenide (^{77}Se). Chemical shifts are reported as dimensionless δ values in ppm, coupling constants J are given in hertz (Hz).

High-resolution electrospray ionization mass spectra (HRMS-ESI) were obtained with a Bruker ApexQe FT-ICR instrument.

Fourier-transform infrared (FTIR) spectra at 298 K were obtained with an Agilent Cary 630 FTIR spectrometer, which was operated with the MicroLab PC software, and processed with BioRad Merlin and OriginPro 2020 64Bit.

Cyclic voltammetry was done inside a dry nitrogen-filled glove box at room temperature with a EmStat3+blue device from PalmSens, which was operated with the PSTrace 5.7 software. A glassy carbon electrode (working area of 0.07 cm^2) was used as a working electrode, a platinum wire as a counter electrode, and a silver wire as a quasi-reference electrode. The scan rate was set to 0.05 V s^{-1}. As solvent, 1,2-difluorobezene (*o*DFB), as supporting electrolyte, [$NnBu_4$][PF_6] was used. The analyte concentration was approximately c = 10^{-3} mol L^{-1}, the supporting electrolyte concentration c_{supp} = 0.1 mol L^{-1}. The acquired data was externally referenced against the decamethyl-ferrocene/decamethylferrocenium (dmfc/$dmfc^+$) redox couple and then transferred to the Ag/AgCl/KCl reference. Under the same conditions as described fc/fc^+ has a redox potential of 532 mV and dmfc/$dmfc^+$ a redox potential of 30 mV against the Ag/AgCl/KCl redox couple.[2] The dmfc/$dmfc^+$ reference measurement was carried out under the same conditions as described.

Elemental analysis for the determination of the C-,H- and N-content was carried out by the microanalysis laboratory of the Institute of Inorganic Chemistry at Heidelberg University using a vario MICRO cube of Elementar Analysensysteme.

Suitable crystals of the compounds were taken directly out of the mother liquor, immersed in perfluorinated polyether oil, and fixed on top of a cryo loop. Measurements were made on Bruker D8 Venture CCD diffractometer with a low-temperature unit using (100 K) Mo-Kα radiation chromated by mirror optics. The data collected were processed using standard Bruker APEX3 software. Structures were solved by intrinsic phasing using the SHELXT program[3] and refined with the SHELXL.[4] Graphical handling

of the structural data during solution and refinement was performed with shelXLe.[5] Atomic coordinates and anisotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least-squares calculations[6] and displacement ellipsoids are displayed with 50 % probability. Hydrogen atoms were included using a riding model. Crystallographic data for the structures reported in this article are deposited within the Cambridge Crystallographic Data Centre as supplementary publication no. 2125915-2125920 and can be obtained free of charge. Crystal data and structure are summarized in the tables under the crystallographic figures.

2 Computational Details

All computations employing the Orca 4.2.1[7] software or the Amsterdam Modelling Suite AMS2021.102[8] were carried out with the computational resources available on the bwFor Cluster JUSTUS2 located at Ulm University within the Baden Württemberg High Performance Computing program.

All structures were optimized with the Orca 4.2.1 software at the B97M-D3(BJ)[9]/def2-TVZPP[10] level of theory. Minima structures were obtained with the following ORCA input line:

```
! RKS B97M-D3BJ def2-TZVPP Grid5 NoFinalGrid Opt NumFreq TightSCF
```

All calculated geometries have been confirmed as energetic minima on the potential energy surface by numerical calculation of harmonic frequencies at the B97M-D3(BJ)/def2-TVZPP level, revealing only positive values.

Subsequent single point calculations employing the Conductor-like Polarizable Continuum Model (C-PCM)[11] were performed with the following ORCA input line:

```
! RKS B97M-D3BJ def2-TZVPP CPCM(THF) Grid5 NoFinalGrid SP NumFreq
TightSCF
```

Natural Bond Orbital (NBO) calculations were conducted on the PBE0[12]/def2-TZVPP[10] level of theory including a C-PCM solvation model using NBO6.0.18a[13] as included in Orca 4.2.1 *via* the following ORCA input line:

```
! RKS PBE0 def2-TZVPP CPCM(THF) NBO TightSCF Grid5 NoFinalGrid
```

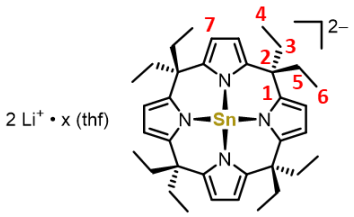
Calculations employing the Extended Transition State (ETS) method for energy decomposition analysis (EDA)[14] combined with the natural orbitals for chemical valence (NOCV)[15] calculations were performed on the BP86-G3[16] /TZ2P level of theory as implemented in the AMS2021.201 software.

Computational ^{77}Se and ^{119}Sn NMR absolute chemical shieldings (σ) were calculated with AMS2021.201 software at the PBE0[12]/TZ2P level of theory, chemical shifts were obtained by referencing to the computed value of $SeMe_2$ and $SnMe_4$ respectively. NMR chemical shift computations were carried out without the frozen core approximation and with the scalar relativistic spin-orbit ZORA approximation[17] to address correct treatment of heavy elements.

Isosurface plots were created using the IboView software v20150427.

3 Synthesis

3.1 Lithium tin(II) *meso*-octaethylcalix[4]pyrrolate [$Li_2(thf)_x$][2]



In a 200 mL Schlenk tube, *tris*-(thf) *tetra*-lithium *meso*-octamethylcalix[4]pyrrolate **[$Li_4(thf)_3$][1]** (1.0 eq, 2.82 mmol, 2.2 g) was dissolved in 55 mL THF. While stirring at room temperature tin(II) chloride (1.0 eq, 2.82 mmol, 545 mg) was added in portions. After turning slightly yellow for 5 minutes the clear, colorless solution was stirred at room temperature for 30 minutes before the solvent was evaporated at reduced pressure. The obtained crude was extracted with 200 mL Et_2O and the extract filtered over a low porosity frit to remove surplus lithium chloride. After evaporation of Et_2O the obtained crude was redissolved in 20 mL THF and the product precipitated by adding of 85 mL pentane. Isolation of the precipitant by filtration over a low porosity frit and drying at reduced pressure yielded **[$Li_2(thf)_x$][2]** as a colorless solid (2.237 g, 2.26 mmol (x=4.2), 80% yield). Cooling of a concentrated toluene solution of **[$Li_2(thf)_x$][2]** to −30 °C yielded single crystals suitable for X-ray diffraction.

^{1}H NMR [^{1}H, ^{1}H,^{1}H-COSY] (600.13 MHz, THF-d_8, 295 K): δ [ppm] = 5.85 (*s*, ^{117}Sn-satelites $^4J_{Sn,H}$ = 156.41 Hz, ^{119}Sn-satelites $^4J_{Sn,H}$ = 162.29 Hz, H_7, 8H), 3.62 (*m*, H_{thf}, 16.8H), 1.88 (*q*, $^3J_{H,H}$ = 7.3 Hz, H_3, 8H), 1.78 (*m*, H_{thf}, 16.8H), 1.76 (*q*, $^3J_{H,H}$ = 7.3 Hz, H_5, 8H, overlapped with thf), 0.79 (*t*, $^3J_{H,H}$ = 7.3 Hz, H_4, 12H), 0.50 (*t*, $^3J_{H,H}$ = 7.3 Hz, H_6, 12H).
^{1}H NMR [^{1}H, ^{1}H,^{1}H-COSY] (600.13 MHz, C_6D_6, 295 K): δ [ppm] = δ [ppm] = 6.44 (*s*, H_7, 8H), 3.38 (*m*, H_{thf}, 16.8H), 2.22 (*q*, $^3J_{H,H}$ = 7.3 Hz, H_3, 8H), 2.13 (*q*, $^3J_{H,H}$ = 7.3 Hz, H_3, 6H), 2.01 (*q*, $^3J_{H,H}$ = 7.3 Hz, H_3, 2H), 1.27 (*m*, H_{thf}, 16.8H), 1.08 (*t*, $^3J_{H,H}$ = 7.3 Hz, H_4, 8H), 0.90 (*t*, $^3J_{H,H}$ = 7.3 Hz, H_6, 16H).

^{7}Li NMR (233.25 MHz, THF-d_8, 295 K): δ [ppm] = −2.12 (*s*).
^{7}Li NMR (233.25 MHz, C_6D_6, 295 K): δ [ppm] = −1.40 (*s*, broad), −3.01 (*s*), −4.30 (*s*, broad).

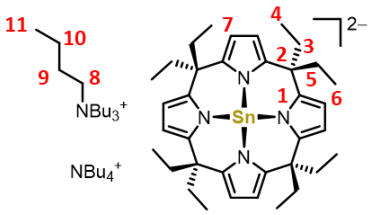
^{13}C NMR [^{13}C{^{1}H}, ^{13}C-DEPT135, ^{1}H,^{13}C-HSQC, ^{1}H,^{13}C-HMBC] (150.92 MHz, THF-d_8, 295 K): δ [ppm] = 144.05 (*s*, C_1), 106.56 (*s*, C_7H), 68.02 (*s*, $C_{thf}H_2$), 46.33 (*s*, C_2), 45.94 (*s*, C_2), 39.47 (*s*, $^{117/119}$Sn-satelites $^4J_{Sn,C}$ = 16 Hz, C_5H_2), 33.69 (*s*, C_3H_2), 26.15 (*s*, $C_{thf}H_2$), 10.47 (*s*, C_4H_3), 10.22 (*s*, C_6H_3).
^{13}C NMR [^{13}C$^{[18]}$, ^{13}C-DEPT135, ^{1}H,^{13}C-HSQC, ^{1}H,^{13}C-HMBC] (150.92 MHz, C_6D_6, 295 K): δ [ppm] = 143.92 (*s*, C_1), 105.14 (*s*, C_7H), 67.79 (*s*, $C_{thf}H_2$), 46.63 (*s*, C_2), 37.86 (*s*, C_5H_2), 36.50 (*s*, C_5H_2), 32.72 (*s*, C_3H_2), 25.06 (*s*, $C_{thf}H_2$), 9.99 (*s*, C_4H_3), 9.76 (*s*, C_6H_3), 9.69 (*s*, C_6H_3).

^{119}Sn NMR [^{119}Sn,^{1}H-HMBC] (223.81 MHz, THF-d_8, 295 K): δ [ppm] = −481.32.
^{119}Sn NMR [^{119}Sn,^{1}H-HMBC] (223.81 MHz, C_6D_6, 295 K): δ [ppm] = −618.90.

HR-MS (ESI, negative, THF): calcd. for $[C_{32}H_{48}Li_2N_4Sn+Cl]^-$ (Cl^- from ESI atmosphere) m/z = 705.2918, found m/z = 705.2929.

EA: Due to loss of THF upon isolation, a correct elemental analysis could not be obtained.

3.2 Tetrabutylammonium tin(II) *meso*-octaethylcalix[4]pyrrolate [(NBu$_4$)$_2$][2]



In a 50 mL Schlenk tube, **[Li$_2$(thf)$_x$][2]** (1.0 eq, x = 4.2, 522 µmol, 500 mg) and tetrabutylammonium chloride (2.0 eq, 1.044 mmol, 296 mg) where dissolved in 30 mL 1,2-difluorobenzene (*o*DFB) and stirred at room temperature for 2 hours. The colorless suspension was filtered over a PTFE syringe filter (pore size 0.22 µm) and the filtrate evaporated at reduced pressure to obtain **[(NBu$_4$)$_2$][2]** as a colorless solid (550 mg, 482 µmol, 92% yield). Gas phase diffusion of pentane into a concentrated solution of **[(NBu$_4$)$_2$][2]** in *o*DFB at −30 °C yielded single crystals suitable for X-ray diffraction.

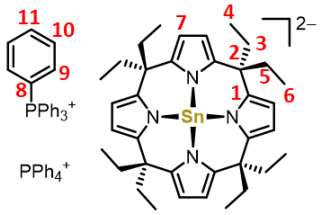
^{1}H NMR [^{1}H, ^{1}H,^{1}H-COSY] (600.18 MHz, THF-d_8, 295 K): δ [ppm] = 5.68 (*s*, ^{119}Sn-satellites $^4J_{Sn,H}$ = 12 Hz, H_7, 8H), 2.60 – 2.89 (*m*, H_8, 16), 2.08 (*q*, $^3J_{H,H}$ = 8.0 Hz, H_3, 8H), 1.95 (*q*, $^3J_{H,H}$ = 9.0 Hz, H_5, 8H), 1.34 (*m*, H_9, 16H), 1.24 (*q*, $^3J_{H,H}$ = 4.0 Hz, H_{10}, 16H), 1.18 (*t*, $^3J_{H,H}$ = 7.3 Hz, H_4, 12H), 0.89 (*t*, $^3J_{H,H}$ = 9.0 Hz, H_{11}, 24H), 0.39 (*t*, $^3J_{H,H}$ = 6.0 Hz, H_6, 12H).

^{13}C NMR [^{13}C{^{1}H}, ^{13}C-DEPT135, ^{1}H,^{13}C-HSQC, ^{1}H,^{13}C-HMBC] (150.92 MHz, THF-d_8, 295 K): δ [ppm] = 144.05 (*s*, C_1), 101.96 (*s*, C_7H), 59.15 (*s*, C_8H$_2$), 46.37 (*s*, C_2), 41.36 (*s*, C_5H$_2$), 29.40 (*s*, C_3H$_2$), 25.02 (*s*, C_9H$_2$), 21.00 (*s*, C_{10}H$_2$), 14.41 (*s*, C_{11}H$_3$), 12.02 (*s*, C_4H$_3$), 10.25 (*s*, C_6H$_3$).

^{119}Sn NMR [^{119}Sn,^{1}H-HMBC] (223.81 MHz, THF-d_8, 295 K): δ [ppm] = −517.83 (*s*).

EA: calcd. for $C_{68}H_{120}N_6Sn$: C, 71.62; H, 10.61; N, 7.37. Found: C, 71.41; H, 10.91; N, 7.69.

3.3 Tetraphenylphosphonium tin(II) *meso*-octaethylcalix[4]pyrrolate [$(PPh_4)_2$(*o*DFB)$_{0.5}$][2]



In a 50 mL Schlenk tube, **[Li_2(thf)$_x$][2]** (x = 4.2, 1.0 eq, 514 µmol, 500 mg) was dissolved in 15 mL *o*DFB and tetraphenylphosphonium chloride (2.0 eq, 1.028 mmol, 386 mg) was added while stirring at room temperature. The clear colorless solution immediately turned orange and a colorless solid precipitated. After stirring for 30 minutes precipitation of an orange solid occurred which could be redissolved by adding 6 mL acetonitrile. Filtration of the reaction mixture over a PTFE syringe filter (pore size 0.22 µm) to remove the lithium chloride formed during the reaction yielded an orange clear solution. To remove residue lithium chloride, the solvent was evaporated at reduced pressure and the remaining was redissolved in 9 mL *o*DFB/MeCN (2:1) and kept at −30 °C over night. Filtration over a PTFE syringe filter and subsequent addition of three times the volume of pentane at −30 °C caused the slow precipitation of **[$(PPh_4)_2$(*o*DFB)$_{0.5}$][2]** as a dark red solid (372 mg, 267 µmol, 52% yield). Gas phase diffusion of pentane into a concentrated solution of **[$(PPh_4)_2$(*o*DFB)$_{0.5}$][2]** in *o*DFB and CH_3CN at −30 °C yielded single crystals suitable for X-ray diffraction.

^{1}H NMR [^{1}H, ^{1}H,^{1}H-COSY] (399.89 MHz, THF-d_8/CD_3CN, 295 K): δ [ppm] = 7.78 (*m*, H_{11}, 8H), 7.58 – 7.68 (*m*, $H_{9,10}$, 32H), 7.20 – 7.30 (*m*, H_{oDFB}, 1H), 7.10 – 7.17 (*m*, H_{oDFB}, 1H), 5.66 (*s*, H_7, 8H), 1.79 – 1.94 (*m*, $H_{3,5}$, overlayed with CD_3CN, 16H), 0.72 (*t*, $^3J_{H,H}$ = 9.0 Hz, H_4, 12H), 0.58 (*t*, $^3J_{H,H}$ = 9.0 Hz, H_6, 12H).

^{13}C NMR [^{13}C{^{1}H}, ^{13}C-DEPT135, ^{1}H,^{13}C-HSQC, ^{1}H,^{13}C-HMBC] (100.55 MHz, THF-d_8/CD_3CN, 295 K): δ [ppm] = 143.45 (*s*, C_1), 137.20 (*d*, $^4J_{P,C}$ = 3.0 Hz, CH_{11}), 136.00 (*d*, $^2J_{P,C}$ = 10.4 Hz, CH_9), 131.93 (*d*, $^3J_{P,C}$ = 13.07 Hz, CH_{10}), 119.18 (*d*, $^1J_{P,C}$ = 89.49 Hz, C_8), 102.92 (*s*, C_7H), 47.06 (*s*, C_2), 39.69 (*s*, C_5H_2), 35.75 (*s*, C_3H_2), 11.99 (*s*, C_4H_3), 11.46 (*s*, C_6H_3).

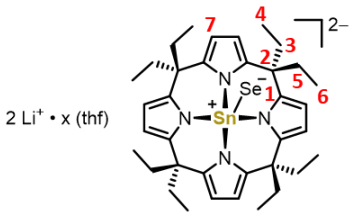
^{19}F NMR (376.27 MHz, THF-d_8/CD_3CN, 295 K): δ [ppm] = −140.36 - −140.29 (*m*, *o*DFB).

^{31}P{^{1}H} NMR (161.88 MHz, THF-d_8/CD_3CN, 295 K): δ [ppm] = 22.82 (*s*, PPh_4^+).

^{119}Sn NMR [^{119}Sn,^{1}H-HMBC] (223.81 MHz, THF-d_8/CD_3CN, 295 K): δ [ppm] = −485.98.

EA: calcd. for $C_{87}H_{90}FN_4P_2Sn$: C, 75.10; H, 6.52; N, 4.03. Found: C, 75.09; H, 6.57; N, 4.25.

3.4 Lithium tin(II) *meso*-octaethylcalix[4]pyrrolato selenide [$Li_2(thf)_x$][2-Se]



0.5 mL THF-d_8 were added to **[$Li_2(thf)_x$][2]** (x = 4.2, 1.0 eq, 20.56 µmol, 20 mg) and selenium powder (3.0 eq, 61.67 µmol, 4.9 mg) in a Young NMR tube and mixed at room temperature for 30 minutes. The dark red reaction solution was filtered over a PTFE syringe filter (pore size 0.22 µm) to remove surplus selenium and the selenium adduct was characterized *via* NMR spectroscopy and HR-MS ESI(−) measurements. No yield was determined.

^{1}H NMR [^{1}H, ^{1}H,^{1}H-COSY] (399.89 MHz, THF-d_8/CD_3CN, 295 K): δ [ppm] = 5.88 (*s*, H_7, 8H), 3.69 – 3.59 (m, thf, 13H), 2.13 (*q*, $^3J_{H,H}$ = 7.3 Hz, H_5, 6H), 2.02 – 1.91 (*m*, H_5, 2H), 1.85 (*q*, $^3J_{H,H}$ = 7.1 Hz, H_3, 8H), 1.81 – 1.74 (*m*, thf, 13H), 0.69 (*t*, $^3J_{H,H}$ = 7.4 Hz, H_6, 12H), 0.62 (*t*, $^3J_{H,H}$ = 7.1 Hz, H_4, 12H).

^{13}C NMR [^{13}C{^{1}H}, ^{13}C-DEPT135, ^{1}H,^{13}C-HSQC, ^{1}H,^{13}C-HMBC] (100.55 MHz, THF-d_8, 295 K): δ [ppm] = 143.64 (*s*, C_1), 104.13 (*s*, C_7H), 67.39 (*s*, thf), 45.43 (*s*, C_2), 38.13 (*s*, C_5H_2), 36.01 (*s*, C_3H_2), 25.53 (*s*, thf), 9.74 (*s*, C_4H_3), 9.65 (*s*, C_6H_3).

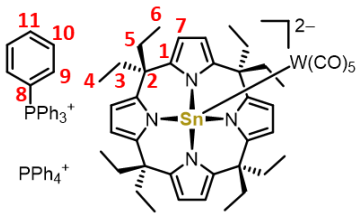
^{7}Li NMR (155.41 MHz, THF-d_8/CD_3CN, 295 K): δ [ppm] = −0.29 (*s*).

^{77}Se NMR [^{77}Se{^{1}H}, ^{1}H,^{77}Se-HMBC] (114.46 MHz, THF-d_8, 295 K): δ [ppm] = −391.99 (*s*).

^{119}Sn NMR [^{119}Sn,^{1}H-HMBC] (149.12 MHz, THF-d_8, 295 K): δ [ppm] = −560.18 (*s*).

HR-MS (ESI, negative, THF): calcd. for $[C_{36}H_{48}N_4SnSe+H]^-$($H^+$ from ESI atmosphere) m/z = 735.2225, found m/z =735.2225.

3.5 Tetraphenylphosphonium $^{1}\eta$-(tin(II) *meso*-octaethylcalix[4]pyrrolate) pentacarbonyl tungsten(0) $[(PPh_4)_2][W(^{1}\eta\text{-}2)(CO)_5]$



Tungsten hexacarbonyl (3.0 eq, 107.7 µmol, 38 mg) was suspended in 1.0 mL THF in a quartz glass flask and irradiated with a Hg-lamp for 4 hours until gas evolution stopped and solid got dissolved into a clear yellow solution. **$[(PPh_4)_2(o\text{DFB})_{0.5}]$[2]** (1.0 eq, 35.9 µmol, 50 mg) was added to the solution and stirred for 36 hours at room temperature. The solvent was removed at reduced pressure. Crystallization from a concentrated solution in acetonitrile (MeCN) layered with pentane at −30 °C yielded **$[(PPh_4)_2][W(^{1}\eta\text{-}2)(CO)_5]$** as a yellow-orange crystalline solid (35 mg, 21.9 µmol, 61% yield). Storing a concentrated solution of **$[(PPh_4)_2][W(^{1}\eta\text{-}2)(CO)_5]$** in MeCN at room temperature yielded single crystals suitable for X-ray diffraction.

^{1}H NMR [^{1}H, ^{1}H,^{1}H-COSY] (600.18 MHz, CD_3CN, 295 K): δ [ppm] = 7.92 – 7.87 (*m*, H_{11}, 8H), 7.74 – 7.70 (*m*, H_{10}, 16H), 7.68 – 7.63 (*m*, H_9, 16H), 5.77 (*s*, H_7, 8H), 1.92 (*q*, $^{3}J_{H,H}$ = 7.4 Hz, 8H), 1.86 (q, $^{3}J_{H,H}$ = 7.1 Hz, 8H), 0.65 (t, $^{3}J_{H,H}$ = 7.1 Hz, 12H), 0.50 (t, $^{3}J_{H,H}$ = 7.4 Hz, 12H).

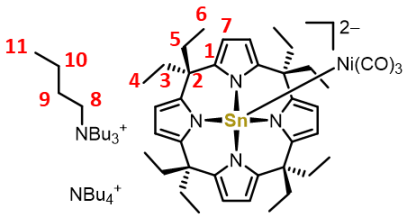
^{13}C NMR [^{13}C{^{1}H}, ^{13}C-DEPT135, ^{1}H,^{13}C-HSQC, ^{1}H,^{13}C-HMBC] (150.92 MHz, CD_3CN, 295 K): δ [ppm] = 202.48 (*s*, *C*O), 143.90 (*s*, C_1), 136.39 (*d*, $^{4}J_{P,C}$ = 3.0 Hz, *C*H_{11}), 135.68 (*d*, $^{2}J_{P,C}$ = 10.5 Hz, *C*H_9), 131.31 (*d*, $^{3}J_{P,C}$ = 13.07 Hz, *C*H_{10}), 118.89 (*d*, $^{1}J_{P,C}$ = 90.6 Hz, C_8), 105.07 (*s*, C_7H), 46.28 (*s*, C_2), 42.25 (*s*, C_5H_2), 34.10 (*s*, C_3H_2), 10.90 (*s*, C_4H_3), 10.50 (*s*, C_6H_3).

^{31}P{^{1}H} NMR (161.88 MHz, CD_3CN, 295 K): δ [ppm] = 22.92 (*s*, *P*Ph_4^+).

^{119}Sn NMR [^{119}Sn,^{1}H-HMBC] (223.81 MHz, CD_3CN, 295 K): δ [ppm] = −482.78.

EA: calcd. for $C_{89}H_{88}N_4O_5P_2SnW$: C, 64.47; H, 5.35; N, 3.38; O, 4.82; P, 3.74; Sn, 7.16; W, 11.09. Found: C, 63.10; H, 5.38; N, 3.43. Low carbon content might be related to metal carbide formation during combustion.[19]

3.6 Tetrabutylammonium $^{1}\eta$-(tin(II) *meso*-octaethylcalix[4]pyrrolate) triscarbonyl nickel(0) $[(NBu_4)_2][Ni(^{1}\eta\text{-}2)(CO)_3]$



Bis(cyclooctadiene)nickel(0) (1.3 eq, 57.0 µmol, 15.7 mg) and **$[(NBu_4)_2]$[2]** (1.0 eq, 43.85 µmol, 50 mg) were dissolved in 0.5 mL THF-d_8 in a NMR pressure tube yielding a yellow clear solution. Addition of 3 atm CO gas and mixing at room temperature for 30 minutes caused the discoloration of the solution. Evaporation of the solvent at reduced pressure and washing of the crude with 5 mL pentane yielded **$[(NBu_4)_2][Ni(^{1}\eta\text{-}2)(CO)_3]$** as an off-white crystalline solid (45 mg, 35.9 µmol, 82% yield).

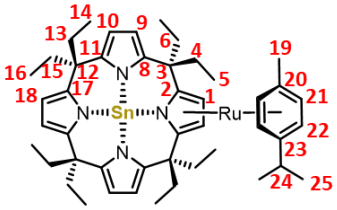
^{1}H NMR [^{1}H, ^{1}H,^{1}H-COSY] (600.18 MHz, THF-d_8, 295 K): δ [ppm] = 5.72 (*s*, H_7, 8H), 2.94 – 2.74 (m, H_8, 16H), 2.09 (*q*, $^{3}J_{H,H}$ = 6.3 Hz, H_3, 8H), 2.05 (*q*, $^{3}J_{H,H}$ = 6.1 Hz, H_5, 8H), 1.45 – 1.34 (m, H_9, 16H), 1.34 – 1.29 (m, 7H), 1.29 – 1.22 (*m*, H_{10}, 16H), 1.16 (*t*, $^{3}J_{H,H}$ = 7.2 Hz, H_4, 12H), 0.92 (*t*, $^{3}J_{H,H}$ = 7.3 Hz, H_{11}, 24H), 0.40 (*t*, $^{3}J_{H,H}$ = 7.3 Hz, H_6, 12H).

^{13}C NMR [^{13}C{^{1}H}, ^{13}C-DEPT135, ^{1}H,^{13}C-HSQC, ^{1}H,^{13}C-HMBC] (150.92 MHz, THF-d_8, 295 K): δ [ppm] = 198.46 (*s*, *C*O), 141.89 (*s*, C_1), 99.89 (*s*, C_7H), 56.14 (*s*, C_8H_2), 42.74 (*s*, C_2), 38.65 (*s*, C_5H_2), 26.37 (*s*, C_3H_2), 23.55 (*s*, C_9H_2), 20.38 (*s*, $C_{10}H_2$), 11.39 (*s*, $C_{11}H_3$), 9.02 (*s*, C_4H_3), 7.04 (*s*, C_6H_3).

^{119}Sn NMR [^{119}Sn,^{1}H-HMBC] (223.81 MHz, THF-d_8, 295 K): δ [ppm] = −335.24 (*s*).

EA: calcd. for $C_{71}H_{120}N_6O_3NiSn$: C, 66.42; H, 9.43; N, 6.55; O, 3.74; Ni, 4.52; Sn, 9.35. Found: C, 66.01; H, 9.73; N, 6.44.

3.7 Ruthenium(II) $^{5}\eta$-(tin(II) *meso*-octaethylcalix[4]pyrrolate) *para*-cymene Ru($^{5}\eta$-2)(*p*-cymene)



[$Li_2(thf)_x$][2] (x = 4.2, 1.0 eq, 102.85 µmol, 100 mg) and [{Ru(Cl)(*p*-cymene)}$_2$(μ-Cl)$_2$] (0.5 eq, 51.43 µmol, 31.5 mg) were dissolved in 4 mL THF and stirred at room temperature for 1 hour. The solvent was evaporated at reduced pressure and the remaining extracted with 6 mL *o*DFB. Filtration of the extract over a PTFE syringe filter (pore size 0.22 µm) to remove the lithium chloride formed during the reaction followed by the evaporation of the *o*DFB at reduced pressure yielded **Ru($^{5}\eta$-2)(*p*-cymene)** as an orange solid (83.5 mg, 93.58 µmol, 91% yield). Keeping a concentrated solution of **Ru($^{5}\eta$-2)(*p*-cymene)** in benzene for 12 hours at room temperature yielded single crystals suitable for X-ray diffraction.

^{1}H NMR [^{1}H, ^{1}H,^{1}H-COSY] (399.89 MHz, THF-d_8, 295 K): δ [ppm] = 5.99 (*d*, $^{3}J_{H,H}$ = 3.20 Hz, $H_{9,10}$, 2H), 5.93 (*d*, $^{3}J_{H,H}$ = 3.20 Hz, $H_{9,10}$, 2H), 5.91 (*s*, $H_{1,18}$, 2H), 5.76 (*s*, $H_{1,18}$, 2H), 5.46 (*d*, $^{3}J_{H,H}$ = 6.20 Hz, H_{22}, 2H), 5.06 (*d*, $^{3}J_{H,H}$ = 6.10 Hz, H_{21}, 2H), 2.71 (*hept*, $^{3}J_{H,H}$ = 6.90 Hz, H_{24}, 1H), 2.21 – 2.09 (*m*, $H_{4,6,13,15}$, 10H), 2.08 – 1.98 (*m*, $H_{4,15}$, 2H), 1.87 – 1.80 (*m*, $H_{4,15}$, 4H), 1.23 (*t*, $^{3}J_{H,H}$ = 7.3 Hz, $H_{9,14}$, 6H), 1.14 (*d*, $^{3}J_{H,H}$ = 6.9 Hz, H_{25}, 6H), 1.09 (*t*, $^{3}J_{H,H}$ = 7.2 Hz, $H_{9,14}$, 6H), 0.96 (*s*, H_{19}, 3H), 0.56 (*t*, $^{3}J_{H,H}$ = 7.3 Hz, $H_{5,16}$, 6H), 0.50 (*t*, $^{3}J_{H,H}$ = 7.3 Hz, $H_{5,16}$, 6H).

^{13}C NMR [^{13}C{^{1}H}, ^{13}C-DEPT135, ^{1}H,^{13}C-HSQC, ^{1}H,^{13}C-HMBC] (150.92 MHz, C_6D_6, 295 K): δ [ppm] = 146.05 (*s*, $C_{8,11}$), 142.32 (*s*, $C_{2,17}$), 136.13 (*s*, $C_{8,11}$), 134.27 (*s*, $C_{2,17}$), 110.68 (*s*, C_{20}), 110.53 (*s*, C_{23}), 105.49 (*s*, $C_{9,10,18}$H), 105.26 (*s*, $C_{9,10,18}$H), 105.00 (*s*, $C_{9,10,18}$H), 103.57 (*s*, C_1H), 89.82 (*s*, $C_{21,22}$H), 76.72 (*s*, $C_{21,22}$H), 46.40 (*s*, $C_{3,12}$), 43.42 (*s*, $C_{3,12}$), 34.44 (*s*, C_{24}H) 31.13 (*s*, $C_{6,15}H_2$), 29.54 (*s*, $C_{6,15}H_2$), 28.65 (*s*, $C_{4,13}H_2$), 27.07 (*s*, $C_{4,13}H_2$), 17.29 (*s*, $C_{19}H_3$), 11.41 (*s*, $C_{25}H_3$), 10.26 (*s*, $C_{4,13}H_3$), 10.02 (*s*, $C_{4,13}H_3$), 9.44 (*s*, $C_{6,15}H_3$), 8.18 (*s*, $C_{6,15}H_3$).

^{119}Sn NMR [^{119}Sn,^{1}H-HMBC] (149.12 MHz, THF-d_8, 295 K): δ [ppm] = −424.83 (*s*).

EA: calcd. for $C_{46}H_{62}N_4RuSn$: C, 61.86; H, 7.00; N, 6.28; Ru, 11.42; Sn, 13.44. Found: C, 61.78; H, 7.03; N, 6.24.

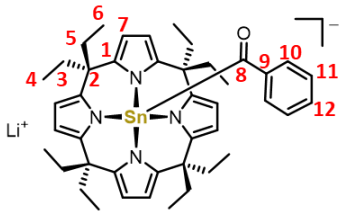
3.8 Reaction of $[Li_2(thf)_x]$[2] with Electrophiles

$[Li_2(thf)_x]$[2] (x = 4.2, 1.0 eq, 17.54 µmol, 17.0 mg) was dissolved in 0.45 mL toluene-d_8 and one equivalent of the respective electrophile was added in one portion at room temperature. The reaction conditions for each electrophile are summarized in Table S1 below. The reaction products were characterized by ^{1}H, ^{13}C, ^{119}Sn as well as 2D-NMR methods and HRMS ESI(−) measurements. For Entry 3 storing of the reaction solution at −30 °C after removal of the precipitated lithium chloride yielded single crystals suitable for X-ray diffraction.

Table S1: Reaction conditions for the reaction of **$[Li_2(thf)_x]$[2]** with electrophiles.

Entry	Electrophile	Reaction Conditions
1	Methylene chloride	No reaction
2	Benzyl chloride	Unselective reaction forming mixture of compounds
3	Benzoyl chloride	Reaction completed at rt within minutes
4	Benzaldehyde	Reacted at rt over 20 hours, formation of side products
5	4-CF_3-Benzaldehyde	Reacted at rt over 20 hours, formation of side products

3.8.1 Entry 3 (Benzoyl Chloride)



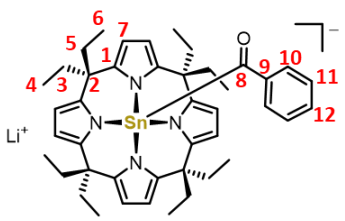
^{1}H NMR [^{1}H, ^{1}H,^{1}H-COSY] (600.15 MHz, Toluene-d_8, 295 K): δ [ppm] = 7.26 – 7.21 (*m*, H_{10}, 2H), 7.00 – 6.98 (*m*, $H_{11'}$ 2H), 6.94 (*d*, $^{3}J_{H,H}$ = 7.3 Hz, H_{12}, 1H), 6.29 (*s*, H_7, 8H), 2.04 (*q*, $^{3}J_{H,H}$ = 7.2 Hz, H_3, 8H), 1.95 (*q*, $^{3}J_{H,H}$ = 7.3 Hz, H_5, 8H), 0.91 (*t*, $^{3}J_{H,H}$ = 7.2 Hz, H_4, 13H), 0.86 (*t*, $^{3}J_{H,H}$ = 7.3 Hz, H_6, 13H).

^{13}C NMR [^{13}C{^{1}H}, ^{13}C-DEPT135, ^{1}H,^{13}C-HSQC, ^{1}H,^{13}C-HMBC] (150.92 MHz, Toluene.-d_8, 295 K): δ [ppm] = 143.93 (*s*, C_1), 134.91 (*s*, C_{12}H), 131.40 (*s*, C_9), 129.15 (*s*, C_{10}H), 128.22 (*s*, C_{11}H), 125.38 (*s*, C_8), 106.57 (*s*, $^{117/119}$Sn-satelites $^{3}J_{Sn,C}$ = 30 Hz, C_7H), 67.86 (*s*, $C_{thf}H_2$), 45.60 (*s*, $^{117/119}$Sn-satelites $^{3}J_{Sn,C}$ = 7.5 Hz, C_2), 40.42 (C_5H_2), 34.89 (*s*, C_3H_2), 25.67 (*s*, $C_{thf}H_2$), 10.14 (*s*, C_4H_3), 10.02 (*s*, C_6H_3).

^{119}Sn NMR [^{119}Sn,^{1}H-HMBC] (149.12 MHz, Toluene-d_8, 295 K): δ [ppm] = −487.99.

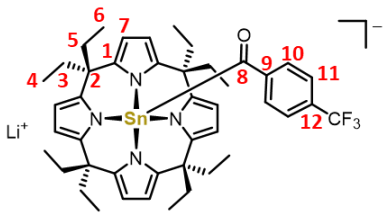
HR-MS (ESI, negative, THF): calcd. for $C_{43}H_{53}N_4OSn^-$ m/z = 761.3267, found m/z = 761.3283.

3.8.2 Entry 4 (Benzaldehyde)



HR-MS (ESI, negative, THF): calcd. for $C_{43}H_{53}N_4OSn^-$ m/z = 761.3267, found m/z = 761.3243.

3.8.3 Entry 5 (4-CF_3-Benzaldehyde)



^{1}H NMR [^{1}H, ^{1}H,^{1}H-COSY] (399.89 MHz, Toluene-d_8, 295 K): δ [ppm] = 7.41 (*d*, $^{3}J_{H,H}$ = 7.8 Hz, H_{10}, 2H), 6.98 (*d*, $^{3}J_{H,H}$ = 7.8 Hz, H_{11}, 2H), 6.34 (*s*, H_7, 8H), 1.94 (*q*, $^{3}J_{H,H}$ = 7.3 Hz, H_3, 8H), 1.75 (*q*, $^{3}J_{H,H}$ = 7.3 Hz, H_5, 8H), 0.76 (t, $^{3}J_{H,H}$ = 7.1 Hz, H_4, 12H), 0.73 (t, $^{3}J_{H,H}$ = 7.1 Hz, H_6, 12H).

^{13}C NMR [^{13}C{^{1}H}, ^{13}C-DEPT135, ^{1}H,^{13}C-HSQC, ^{1}H,^{13}C-HMBC] (100.55 MHz, Toluene-d_8, 295 K): δ [ppm] = 145.40 (*s*, C_1), 136.11 (*s*, C_{12}), 129.16 (*s*, C_9), 127.82 (*s*, C_{10}H), 126.35 (*s*, C_{11}H), 126.31 (*s*, C_8), 106.64 (*m*, CF_3), 105.45 (*s*, C_7H), 47.20 (*s*, C_2), 35.61 (C_5H_2), 35.04 (*s*, C_3H_2), 10.02 (*s*, C_4H_3), 9.71 (*s*, C_6H_3).

^{19}F NMR (149.12 MHz, THF-d_8, 295 K): δ [ppm] = −62.36.

^{119}Sn NMR [^{119}Sn,^{1}H-HMBC] (149.12 MHz, THF-d_8, 295 K): δ [ppm] = −750.37.

HR-MS (ESI, negative, THF): calcd. for $C_{44}H_{52}N_4OF_3Sn^-$ m/z = −829.3141, found m/z = −829.3159.

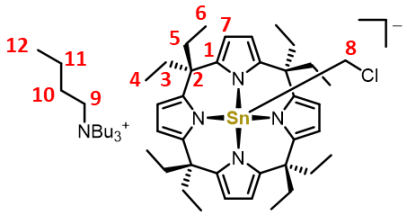
3.9 Reaction of [(NBu$_4$)$_2$][2] with Electrophiles

[(NBu$_4$)$_2$][2] (1.0 eq, 17.54 µmol, 20.0 mg) was dissolved in 0.45 mL THF-d_8 and one equivalent of the respective electrophile was added in one portion at room temperature. The reaction conditions for each electrophile are summarized in Table S2 below. The products were characterized by ^{1}H, ^{13}C, ^{119}Sn as well as 2D-NMR methods and HRMS ESI(−) measurements.

Table S2: Reaction conditions for the reaction of **[(NBu$_4$)$_2$][2]** with electrophiles. The yield was determined by NMR spectroscopy.

Entry	Electrophile	Reaction Conditions
1	Methylene chloride	Near quantitative yield after mixed at rt for 24h
2	Benzyl chloride	Near quantitative yield at rt within minutes
3	Benzoyl chloride	Near quantitative yield at rt within minutes
4	Benzaldehyde	No reaction
5	4-CF_3-Benzaldehyde	No reaction
6	Iodobenzene	Quantitative reduction of iodobenzene to benzene at rt, 48h

3.9.1 Entry 1 (Methylene Chloride)



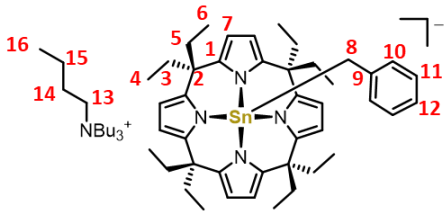
^{1}H NMR [^{1}H, ^{1}H,^{1}H-COSY] (399.89 MHz, THF-d_8, 295 K): δ [ppm] = 5.90 (*s*, $^{117/119}$Sn-satellites $^{4}J_{Sn,H}$ = 8.0 Hz, H_7, 8H), 3.56 – 3.35 (*m*, H_{13}, 16H), 2.67 (*s*, $^{117/119}$Sn-satellites $^{2}J_{Sn,H}$ = 36.0 Hz, H_8, 2H), 1.90 (*q*, $^{3}J_{H,H}$ = 7.2 Hz, H_5, 8H), 1.86 (*q*, $^{3}J_{H,H}$ = 7.2 Hz, H_3, 8H), 1.78 – 1.68 (*m*, H_{14} 16H, overlayed with THF-d_8), 1.46 – 1.35 (*m*, H_{15}, 16H), 0.99 (*t*, $^{3}J_{H,H}$ = 7.4 Hz, H_{16}, 24H), 0.75 (*t*, $^{3}J_{H,H}$ = 7.2 Hz, H_4, 12H), 0.62 (*t*, $^{3}J_{H,H}$ = 7.3 Hz, H_6, 12H).

^{13}C NMR [^{13}C{^{1}H}, ^{13}C-DEPT135, ^{1}H,^{13}C-HSQC, ^{1}H,^{13}C-HMBC] (100.55 MHz, THF-d_8, 295 K): δ [ppm] = 143.56 (*s*, $^{117/119}$Sn-satellites $^{3}J_{Sn,C}$ = 8.0 Hz,C_1), 106.22 (*s*, $^{117/119}$Sn-satellites $^{3}J_{Sn,C}$ = 23.1 Hz, C_7H), 59.64 (*s*, C_9H_2), 46.49 (*s*, C_2), 40.26 (*s*, $C_{3,5}H_2$), 38.74 (*s*, C_8H_2), 36.05 (*s*, $C_{3,5}H_2$), 25.15 (*s*, $C_{10}H_2$), 20.90 (*s*, $C_{11}H_2$), 14.28 (*s*, $C_{12}H_3$), 10.92 (*s*, $C_{4,6}$H), 10.52 (*s*, $C_{4,6}$H).

^{119}Sn NMR [^{119}S n{^{1}H}, ^{119}Sn,^{1}H-HMBC] (149.12 MHz, THF-d_8, 295 K): δ [ppm] = −477.52.

HR-MS (ESI, negative, THF): calcd. for $C_{37}H_{50}N_4SnCl^-$ m/z = 747.3448, found m/z = 747.3456.

3.9.2 Entry 2 (Benzyl chloride)



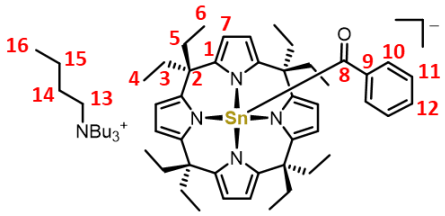
^{1}H NMR [^{1}H, ^{1}H,^{1}H-COSY] (399.89 MHz, THF-d_8, 295 K): δ [ppm] = 6.78 – 6.69 (*m*, H_{11}, 2H), 6.67 – 6.60 (*m*, H_{12}, 1H), 6.33 – 6.25 (m, H_{10}, 2H), 5.95 (*s*, $^{117/119}$Sn-satellites $^{4}J_{Sn,H}$ = 8.0 Hz, H_7, 8H), 3.55 – 3.42 (*m*, H_{13}, 16H), 2.20 (*s*, ^{119}Sn-satellites $^{2}J_{Sn,H}$ = 116.6 Hz, ^{117}Sn-satellites $^{2}J_{Sn,H}$ = 111.2 Hz, H_8, 2H), 1.83 – 1.68 (*m*, $H_{3,5,14}$ 32H), 1.46 – 1.35 (*m*, H_{15}, 16H), 0.99 (*t*, $^{3}J_{H,H}$ = 7.4 Hz, H_{16}, 24H), 0.60 (*t*, $^{3}J_{H,H}$ = 7.1 Hz, $H_{4,6}$, 24H).

^{13}C NMR [^{13}C{^{1}H}, ^{13}C-DEPT135, ^{1}H,^{13}C-HSQC, ^{1}H,^{13}C-HMBC] (100.55 MHz, THF-d_8, 295 K): δ [ppm] = 143.91 (*s*, $^{117/119}$Sn-satellites $^{3}J_{Sn,C}$ = 8.0 Hz, C_1), 141.46 (*s*, C_9), 130.74 (*s*, C_{10}H), 128.02 (*s*, C_{11}H), 123.69 (*s*, C_{12}H), 106.90 (*s*, $^{117/119}$Sn-satellites $^{3}J_{Sn,C}$ = 23.1 Hz, C_7H), 59.64 (*s*, $C_{13}H_2$), 46.65 (*s*, C_2), 39.41 (*s*, $C_{3,5}H_2$), 39.37 (*s*, $C_{3,5}H_2$), 31.76 (*s*, C_8H_2), 25.14 (*s*, $C_{14}H_2$), 20.89 (*s*, $C_{15}H_2$), 14.27 (*s*, $C_{16}H_3$), 10.68 (*s*, $C_{4,6}$H), 10.62 (*s*, $C_{4,6}$H).

^{119}Sn NMR [^{119}Sn{^{1}H}, ^{119}Sn,^{1}H-HMBC] (149.12 MHz, THF-d_8, 295 K): δ [ppm] = −409.19 (*s*).

HR-MS (ESI, negative, THF): calcd. for $C_{43}H_{55}N_4Sn^-$ m/z = 747.3448, found m/z = 747.3456.

3.9.3 Entry 3 (Benzoyl chloride)



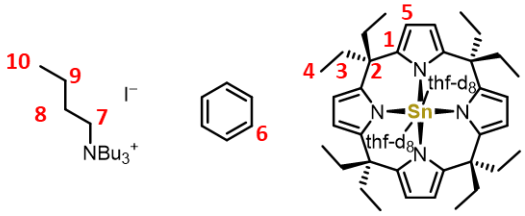
^{1}H NMR [^{1}H, ^{1}H,^{1}H-COSY] (399.89 MHz, THF-d_8, 295 K): δ [ppm] = 7.20 – 7.13 (*m*, H_{12}, 1H), 7.11 – 7.00 (*m*, $H_{10,11}$, 4H), 5.89 (*s*, $^{117/119}$Sn-satellites $^{4}J_{Sn,H}$ = 12.0 Hz, H_7, 8H), 3.54 – 3.44 (*m*, H_{13}, 16H), 1.83 – 1.68 (*m*, $H_{3,5,14}$ overlayed, 32H), 1.35 – 1.46 (*m*, H_{15}, 16H), 0.99 (*t*, $^{3}J_{H,H}$ = 7.4 Hz, H_{16}, 24H), 0.66 (*t*, $^{3}J_{H,H}$ = 7.1 Hz, $H_{4,6}$, 12H), 0.64 (*t*, $^{3}J_{H,H}$ = 7.1 Hz, $H_{4,6}$, 12H).

^{13}C NMR [^{13}C{^{1}H}, ^{13}C-DEPT135, ^{1}H,^{1i3}C-HSQC, ^{1}H,^{13}C-HMBC] (100.55 MHz, THF-d_8, 295 K): δ [ppm] = 235.44 (*s*, C_8), 143.23 (*s*, $^{117/119}$Sn-satellites $^{3}J_{Sn,C}$ = 9.0 Hz, C_1), 143.07 (*s*, C_9), 135.49, 132.20 (*s*, $C_{12}H$), 131.37, 129.98, 129.39 (*s*, $C_{10,11}H$), 128.93 (*s*, $C_{10,11}H$), 106.03 (*s*, $^{117/119}$Sn-satellites $^{3}J_{Sn,C}$ = 26.1 Hz, C_7H), 59.63 (*s*, $C_{13}H_2$), 45.96 (*s*, C_2), 39.07 (*s*, $C_{3,5}H_2$), 37.60 (*s*, $C_{3,5}H_2$), 25.15 (*s*, $C_{14}H_2$), 20.89 (*s*, $C_{15}H_2$), 14.30 (*s*, $C_{16}H_3$), 10.82 (*s*, $C_{4,6}H$), 10.54 (*s*, $C_{4,6}H$).

^{119}Sn NMR [^{119}Sn{^{1}H}, ^{119}Sn,^{1}H-HMBC] (149.12 MHz, THF-d_8, 295 K): δ [ppm] = −542.67.

HR-MS (ESI, negative, THF): calcd. for $C_{43}H_{53}N_4OSn^-$ m/z = 761.3267, found m/z = 761.3256.

3.9.4 Entry 6 (Iodobenzene)



^{1}H NMR [^{1}H, ^{1}H,^{1}H-COSY] (399.89 MHz, THF-d_8, 295 K): δ [ppm] = 7.30 (s, H_6, 5H), 6.11 (*s*, $^{117/119}$Sn-satellites $^{4}J_{Sn,H}$ = 16.0 Hz, H_5, 8H), 3.47 – 3.37 (*m*, H_7, 16H), 1.84 (*q*, $^{3}J_{H,H}$ = 7.3 Hz, H_3, 16H), 1.79 – 1.68 (*m*, H_7 overlayed, 21H), 1.50 – 1.37 (*m*, H_8 overlayed, 25H), 1.36 – 1.25 (*m*, H_9 overlayed, 9H), 1.00 (*t*, $^{3}J_{H,H}$ = 7.3 Hz, H_{10} overlayed, 28H), 0.65 (*t*, $^{3}J_{H,H}$ = 7.3 Hz, H_4, 24H).

^{13}C NMR [^{13}C{^{1}H}, ^{13}C-DEPT135, ^{1}H,^{1i3}C-HSQC, ^{1}H,^{13}C-HMBC] (100.55 MHz, THF-d_8, 295 K): δ [ppm] = 143.14 (*s*, $^{117/119}$Sn-satellites $^{2}J_{Sn,C}$ = 7.0 Hz, C_1), 129.20 (*s*, C_6), 109.26 (*s*, $^{117/119}$Sn-satellites $^{2}J_{Sn,C}$ = 42.2 Hz, C_5H), 59.76 (*s*, C_7H_2), 46.78 (*s*, C_2), 30.93 (*s*, C_3H_2), 25.29 (*s*, overlayed with THF-d_8, C_9H_2), 20.83 (*s*, C_9H_2), 14.33 (*s*, $C_{10zz}H_3$), 10.22 (*s*, C_4H_3).

^{119}Sn NMR [^{119}Sn{^{1}H}, ^{119}Sn,^{1}H-HMBC] (149.12 MHz, THF-d_8, 295 K): δ [ppm] = −560.83.

4 NMR Spectra

4.1 $[Li_2(thf)_x][2]$

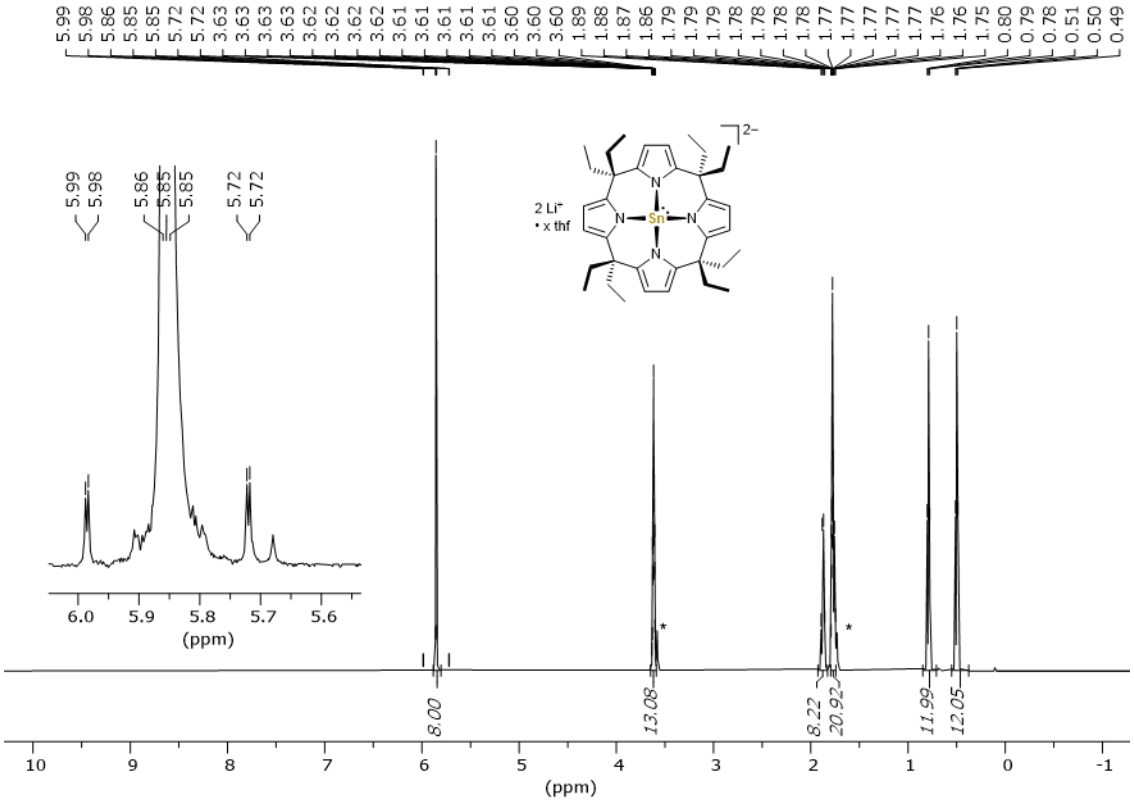


Figure S1. ^{1}H NMR spectrum of **$[Li_2(thf)_x][2]$** (600.18 MHz, THF-d_8, 295 K). Solvent resonances are indicated by an asterisk (*).

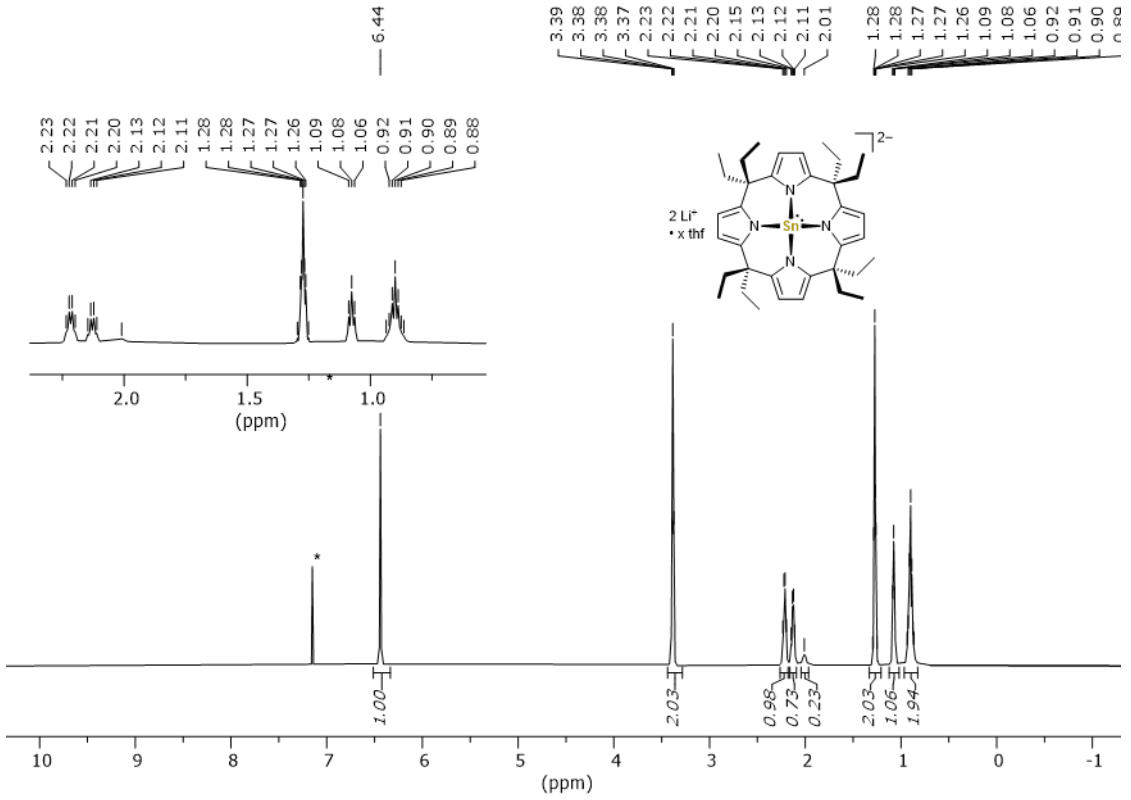


Figure S2. ^{1}H NMR spectrum of **$[Li_2(thf)_x][2]$** (600.18 MHz, C_6D_6, 295 K). Solvent resonances are indicated by an asterisk (*).

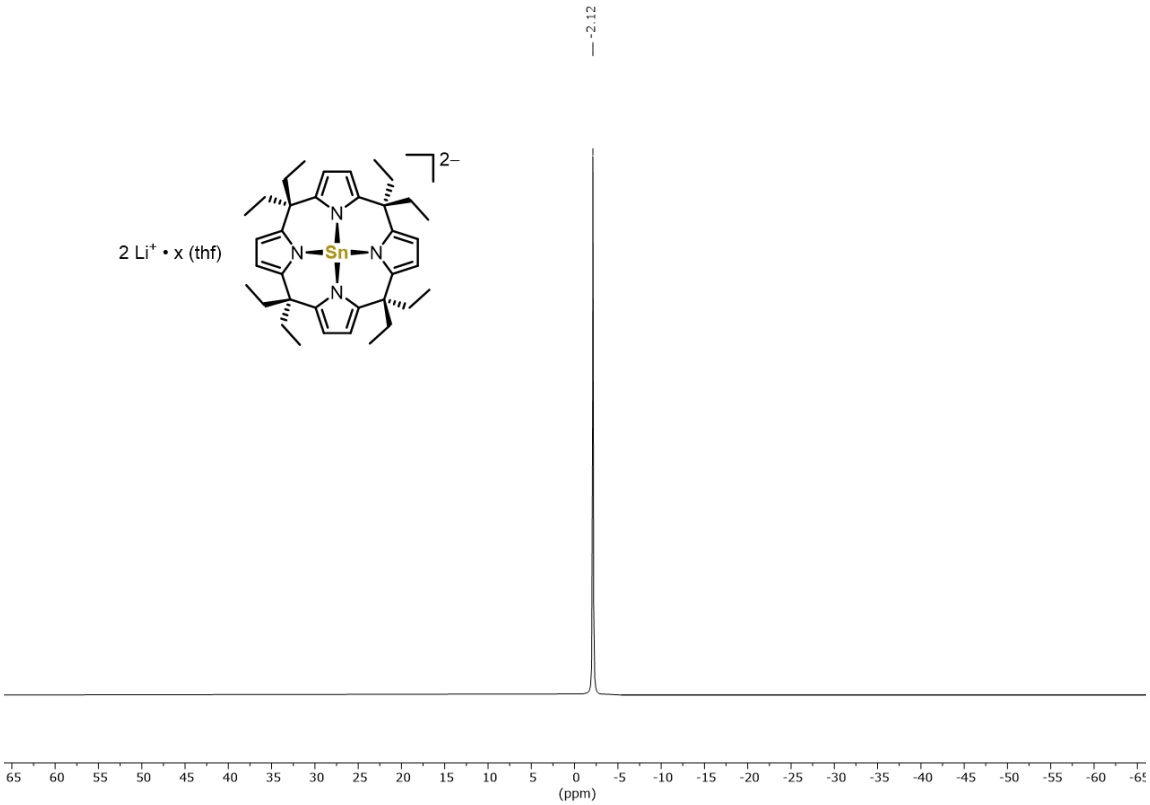


Figure S3. ^{7}Li NMR spectrum of **[Li$_2$(thf)$_x$][2]** (233.24 MHz, THF-d_8, 295 K).

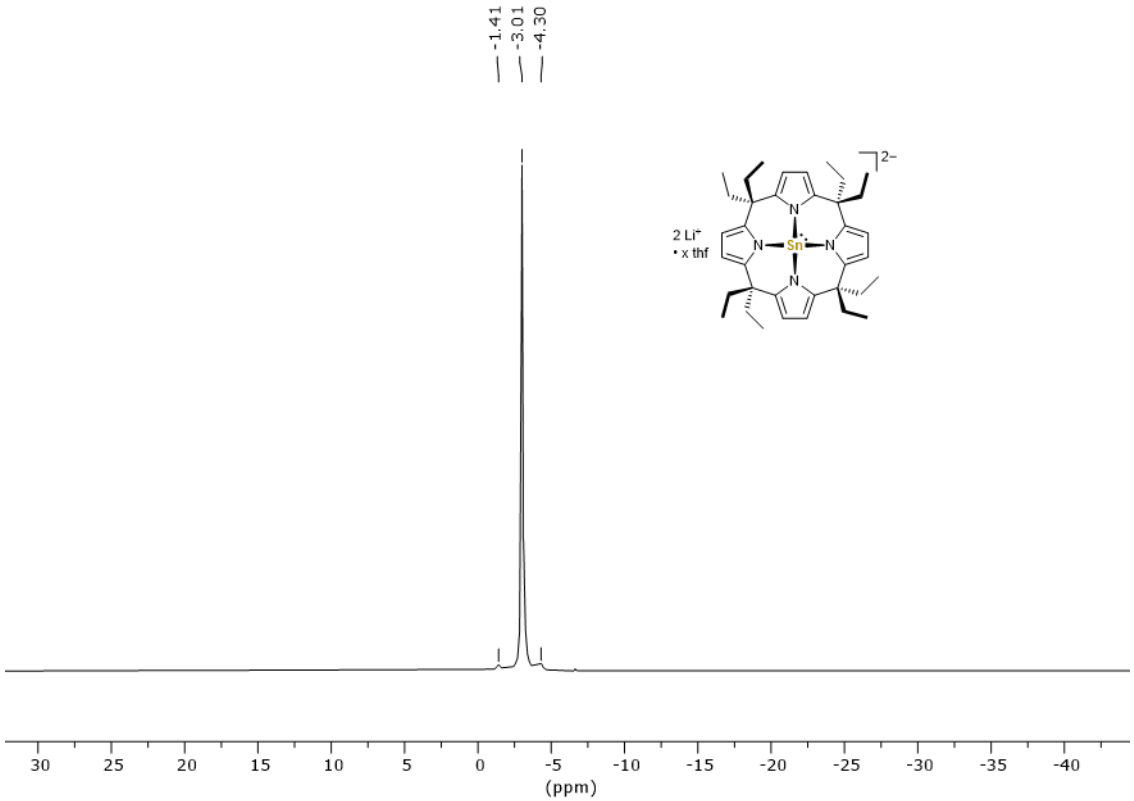


Figure S4. ^{7}Li NMR spectrum of **[Li$_2$(thf)$_x$][2]** (233.24 MHz, C_6D_6, 295 K).

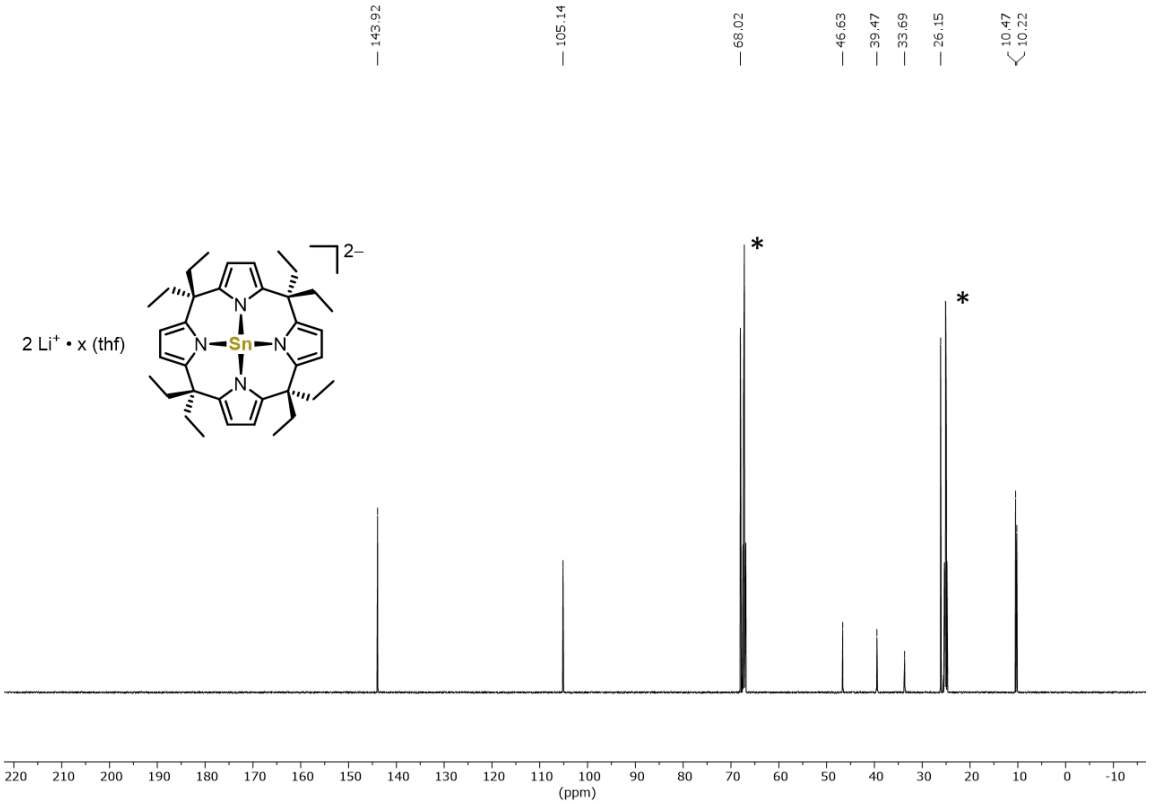


Figure S5. ^{13}C NMR spectrum of **[Li$_2$(thf)$_x$][2]** (150.92 MHz, THF-d_8, 295 K). Solvent resonances are indicated by an asterisk (*).

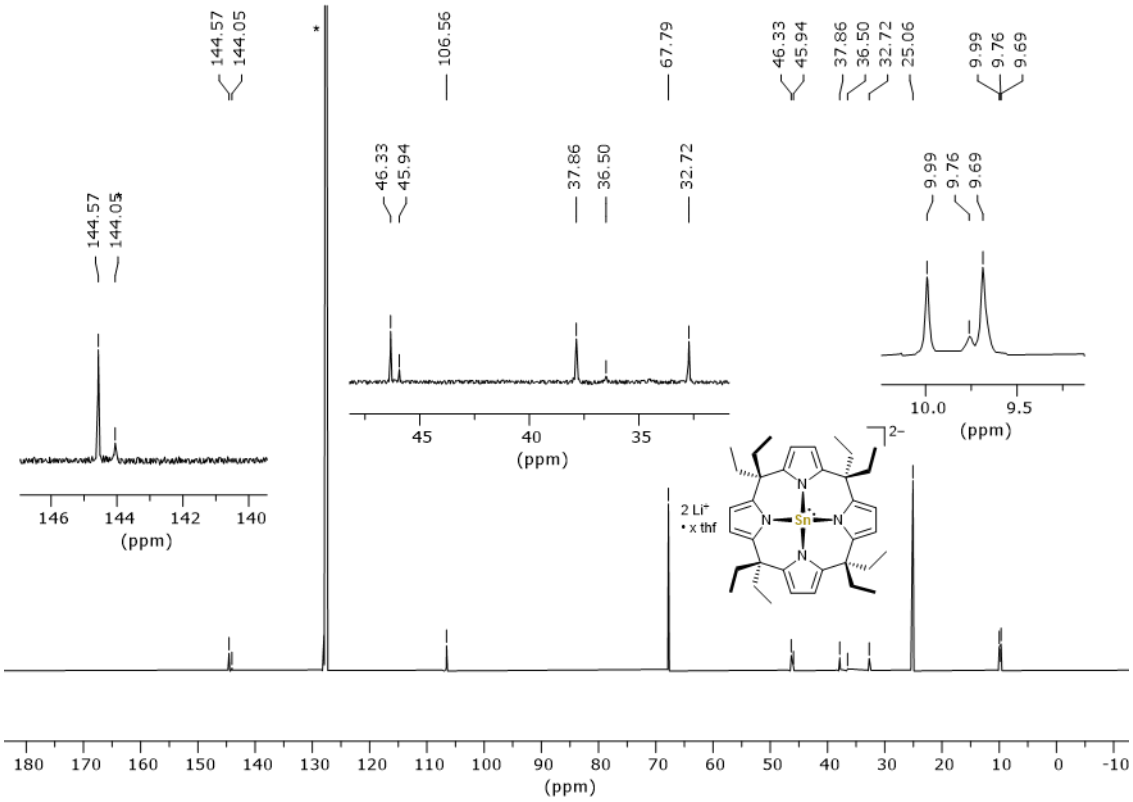


Figure S6. ^{13}C NMR spectrum of **[Li$_2$(thf)$_x$][2]** (150.92 MHz, C_6D_6, 295 K). Solvent resonances are indicated by an asterisk (*).

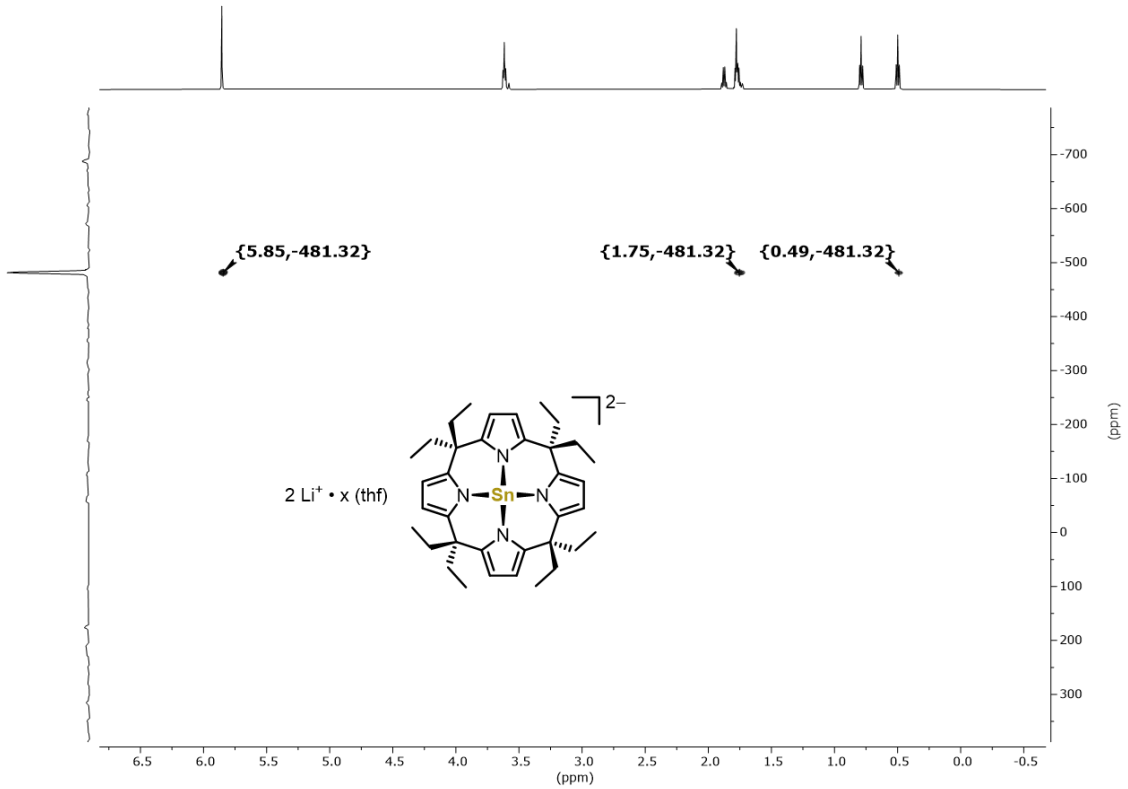


Figure S7. ^{119}Sn-^{1}H HMBC NMR spectrum of **[Li$_2$(thf)$_x$][2]** (THF-d_8, 295 K).

4.2 [(NBu$_4$)$_2$][2]

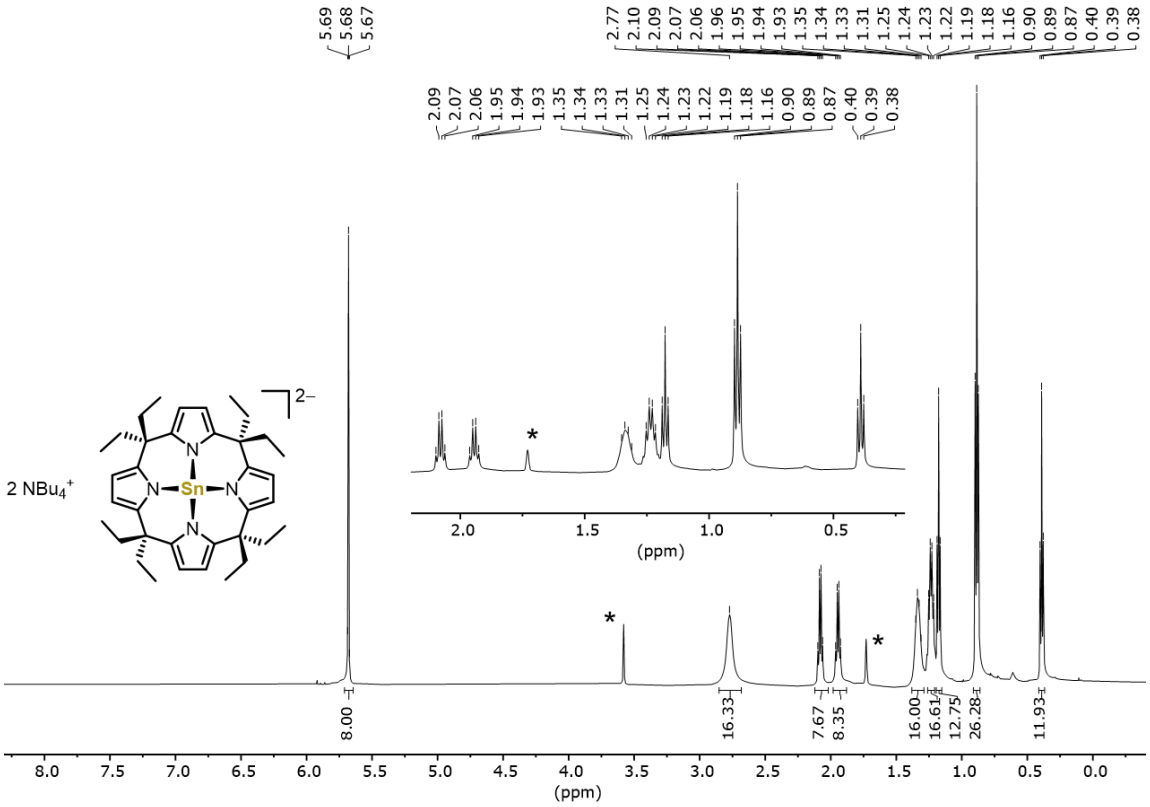


Figure S8. ^{1}H NMR spectrum of **[(NBu$_4$)$_2$][2]** (600.18 MHz, THF-*d*8, 295 K). Solvent resonances are indicated by an asterisk (*).

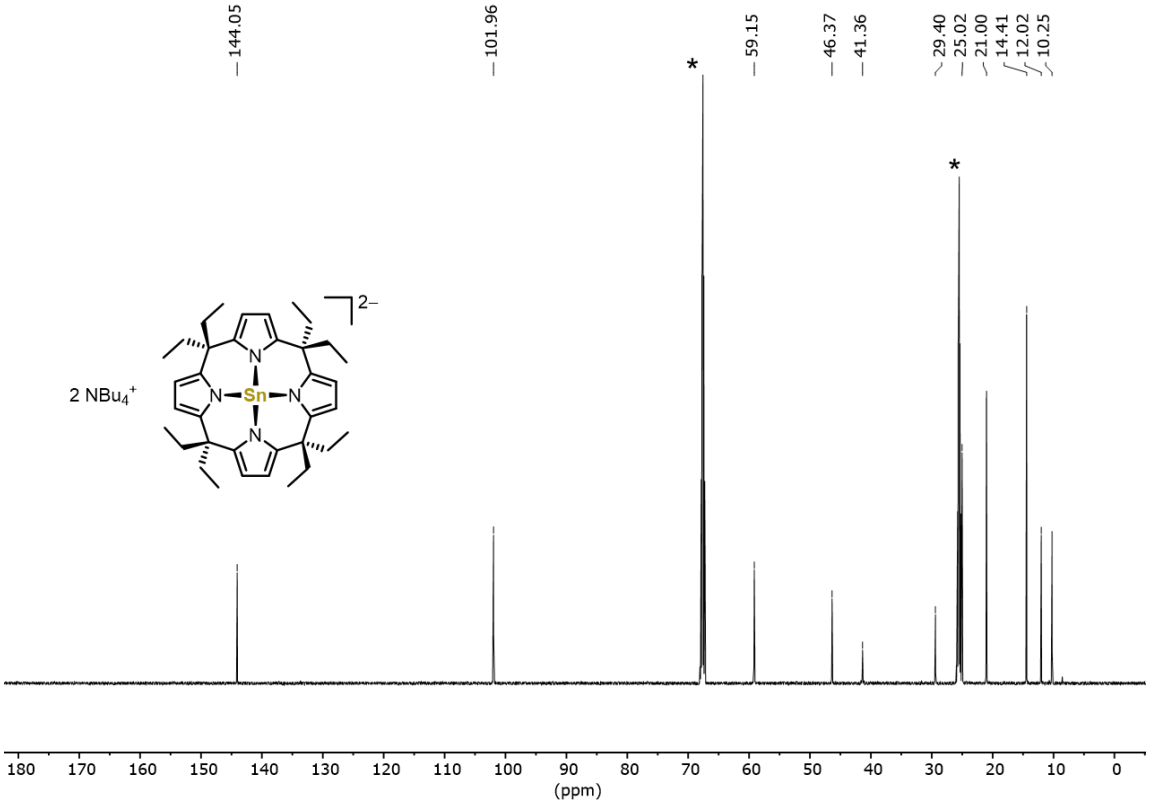


Figure S9. ^{13}C NMR spectrum of **[(NBu$_4$)$_2$][2]** (150.92 MHz, THF-d_8, 295 K). Solvent resonances are indicated by an asterisk (*).

4.3 [(PPh$_4$)$_2$(*o*DFB)$_{0.5}$][2]

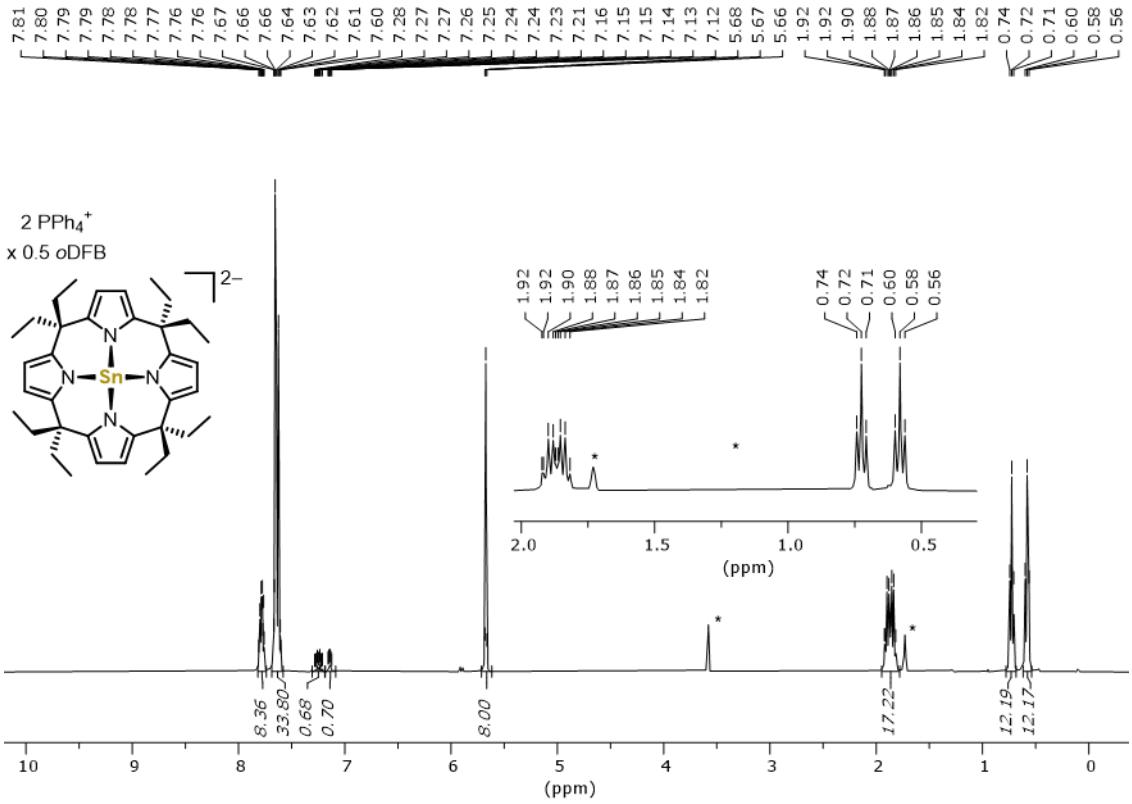


Figure S10. ^{1}H NMR spectrum of **[(PPh$_4$)$_2$(*o*DFB)$_{0.5}$][2]** (399.89 MHz, THF-d_8/CD$_3$CN, 295 K). Solvent resonances are indicated by an asterisk (*).

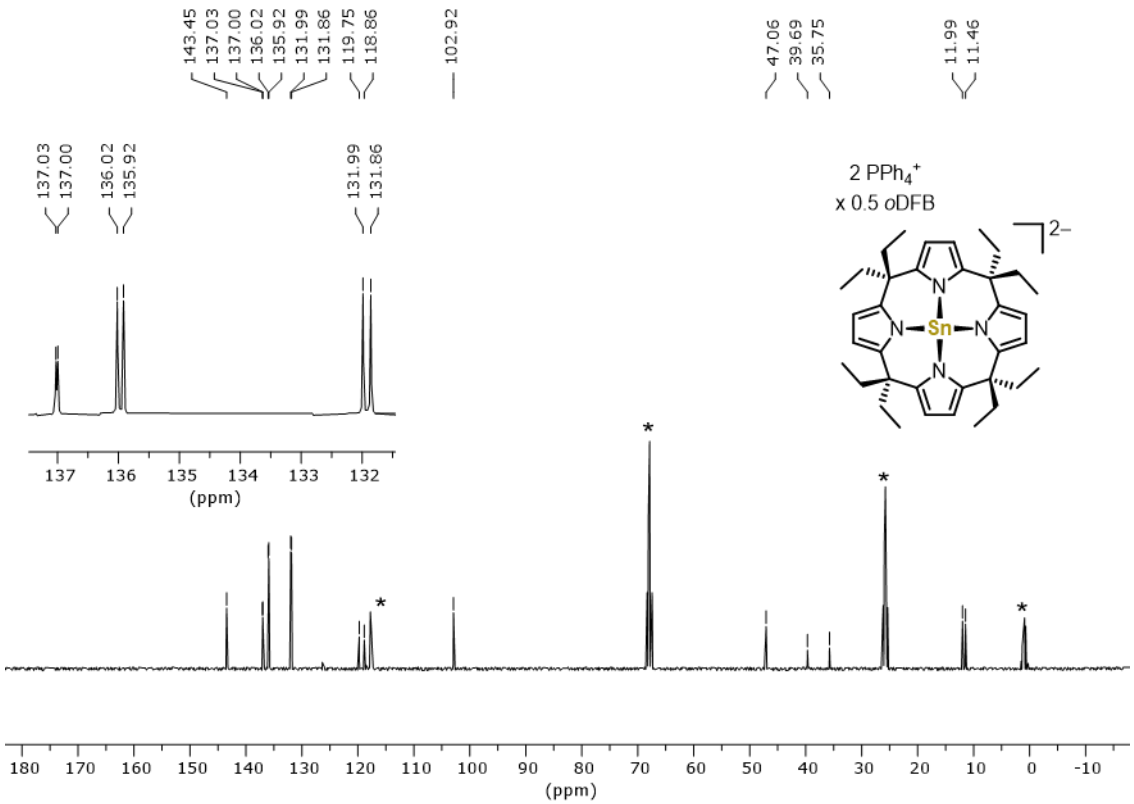


Figure S11. ^{13}C NMR spectrum of **[(PPh$_4$)$_2$(*o*DFB)$_{0.5}$][2]** (100.55 MHz, THF-d_8/CD_3CN, 295 K). Solvent resonances are indicated by an asterisk (*).

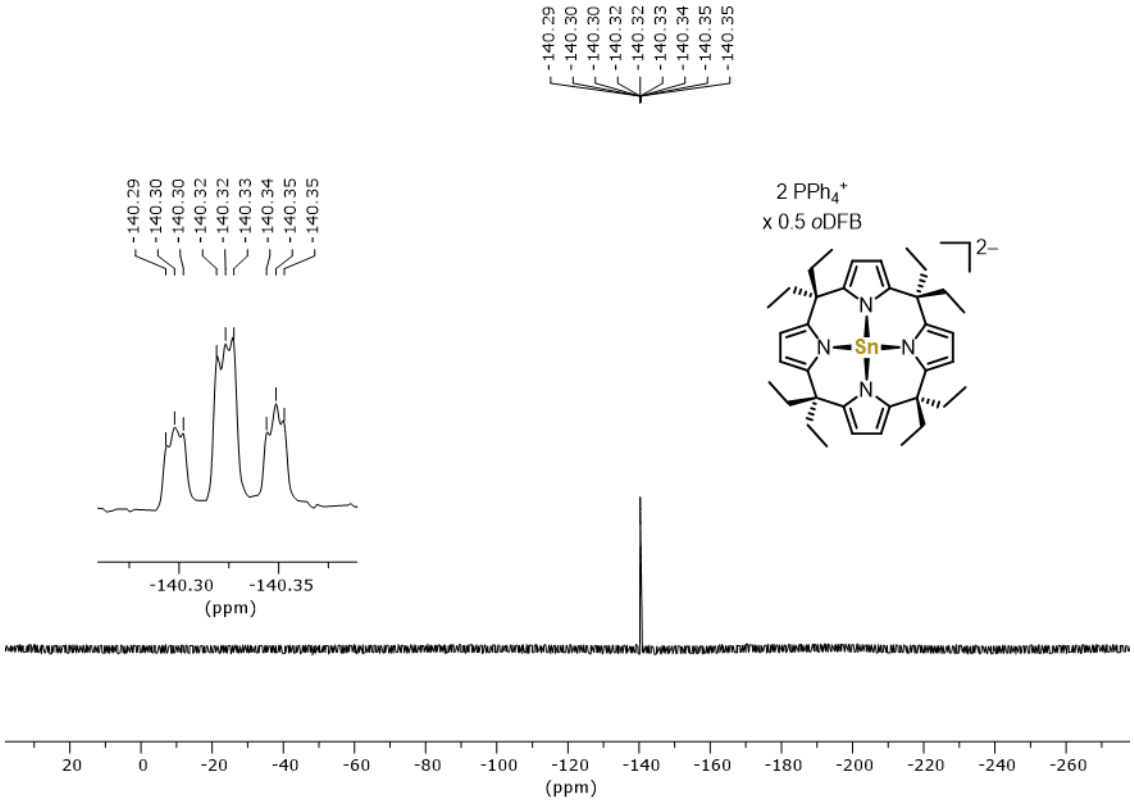


Figure S12. ^{19}F NMR spectrum of **[(PPh$_4$)$_2$(*o*DFB)$_{0.5}$][2]** (376.27 MHz, THF-d_8/CD_3CN, 295 K).

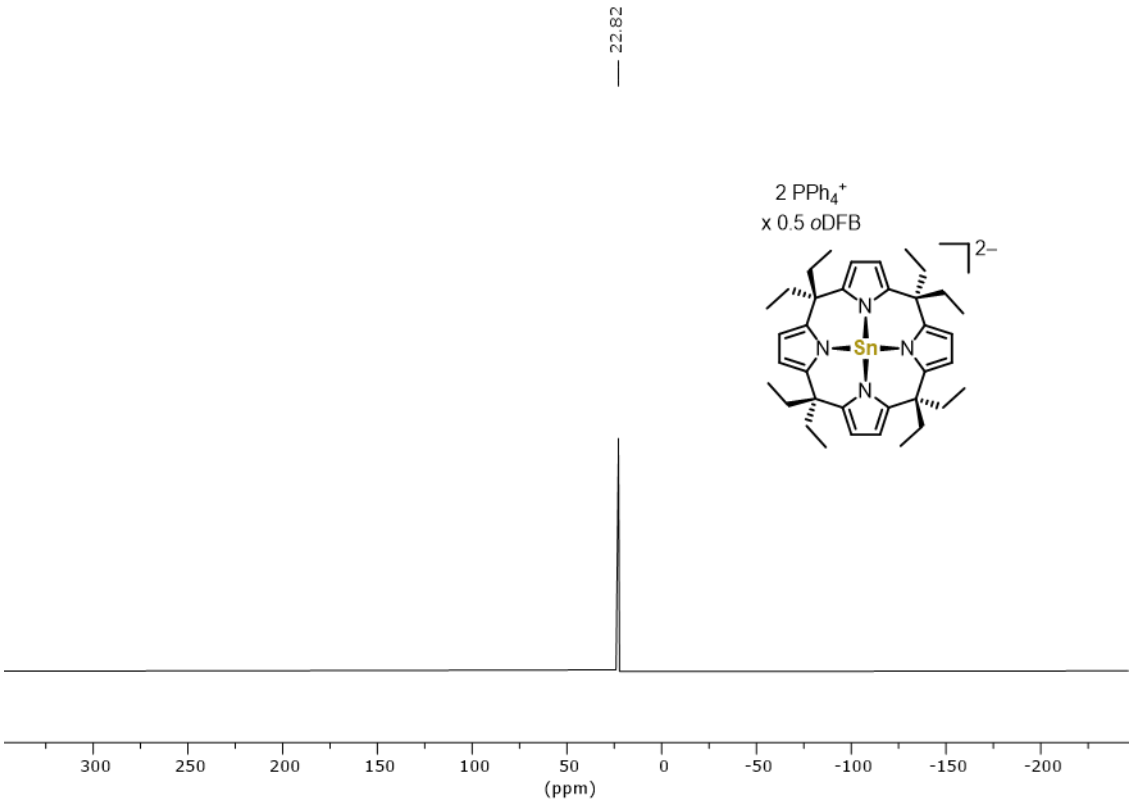


Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum of **[$(PPh_4)_2$(oDFB)$_{0.5}$][2]** (161.88 MHz, THF-d_8/CD_3CN, 295 K).

4.4 [$Li_2(thf)_x$][2-Se]

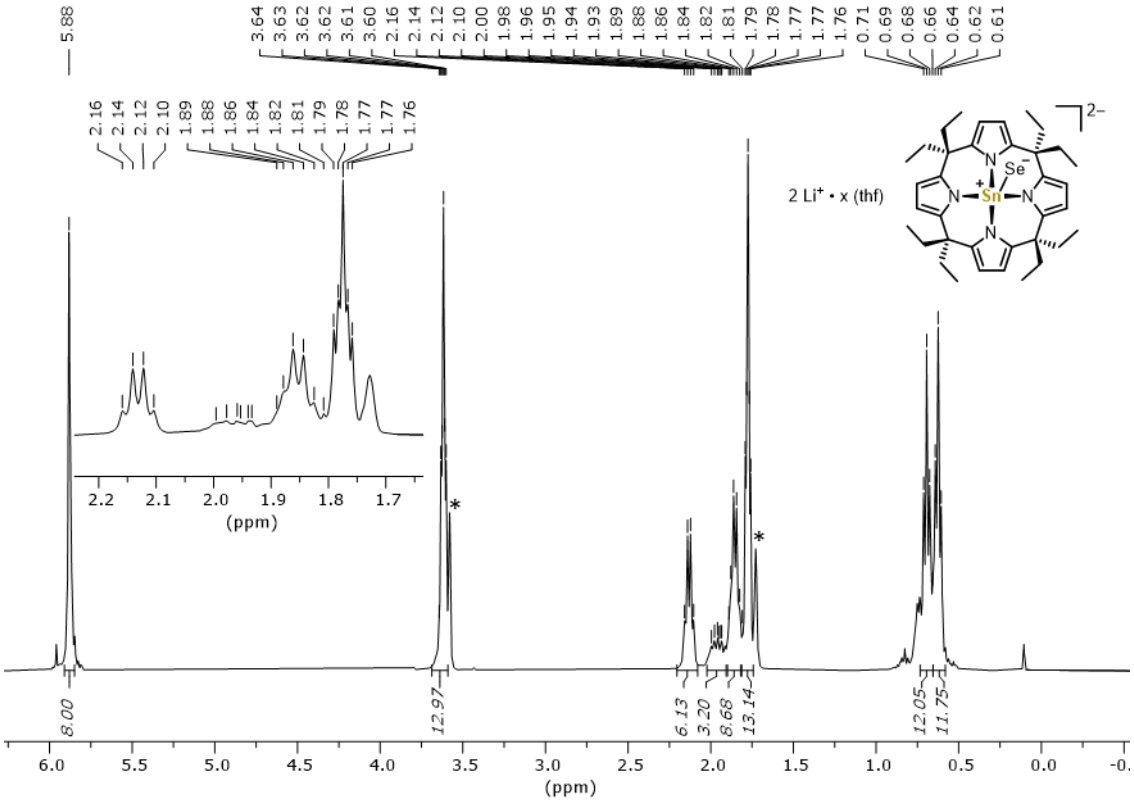


Figure S14. ^{1}H NMR spectrum of **[$Li_2(thf)_x$][2-Se]** (399.89 MHz, THF-d_8, 295 K). Solvent resonances are indicated by an asterisk (*).

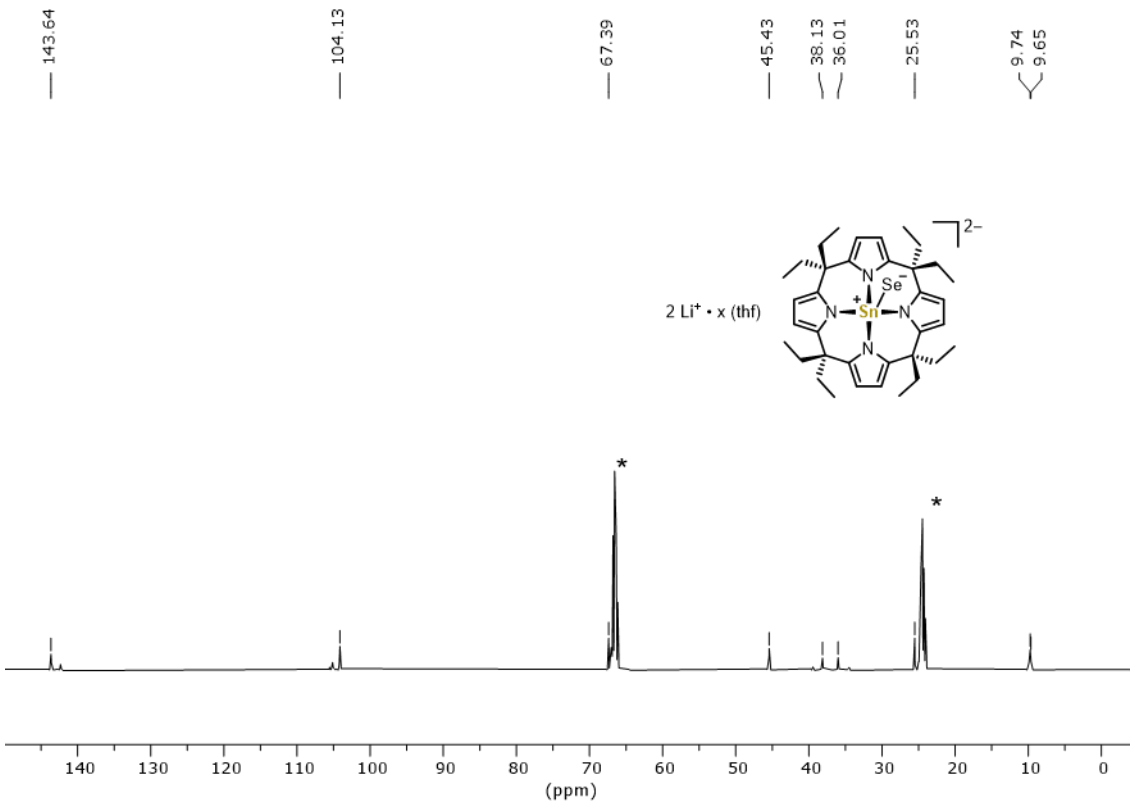


Figure S15. ^{13}C NMR spectrum of **[Li$_2$(thf)$_x$][2-Se]** (100.55 MHz, THF-d_8, 295 K). Solvent resonances are indicated by an asterisk (*).

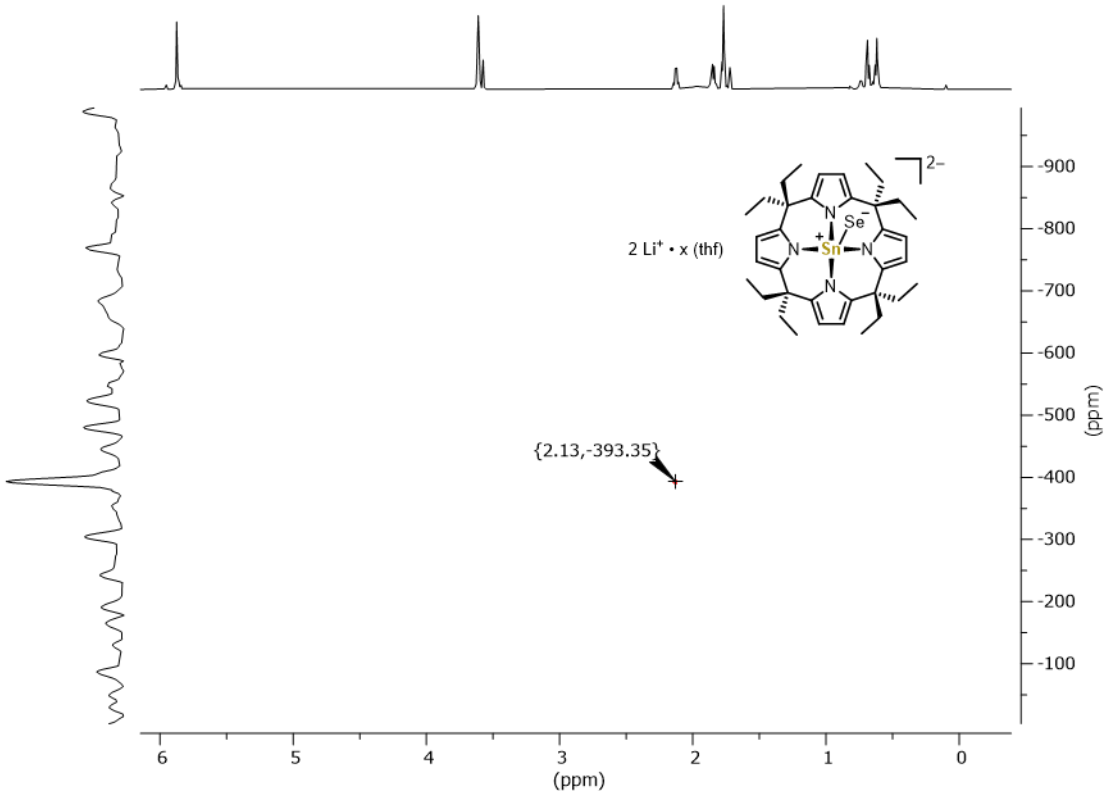


Figure S16. ^{77}Se-^{1}H HMBC NMR spectrum of **[Li$_2$(thf)$_x$][2]** (THF-d_8, 295 K).

4.5 $[(PPh_4)_2][W(^2\eta\text{-}2)(CO)_5]$

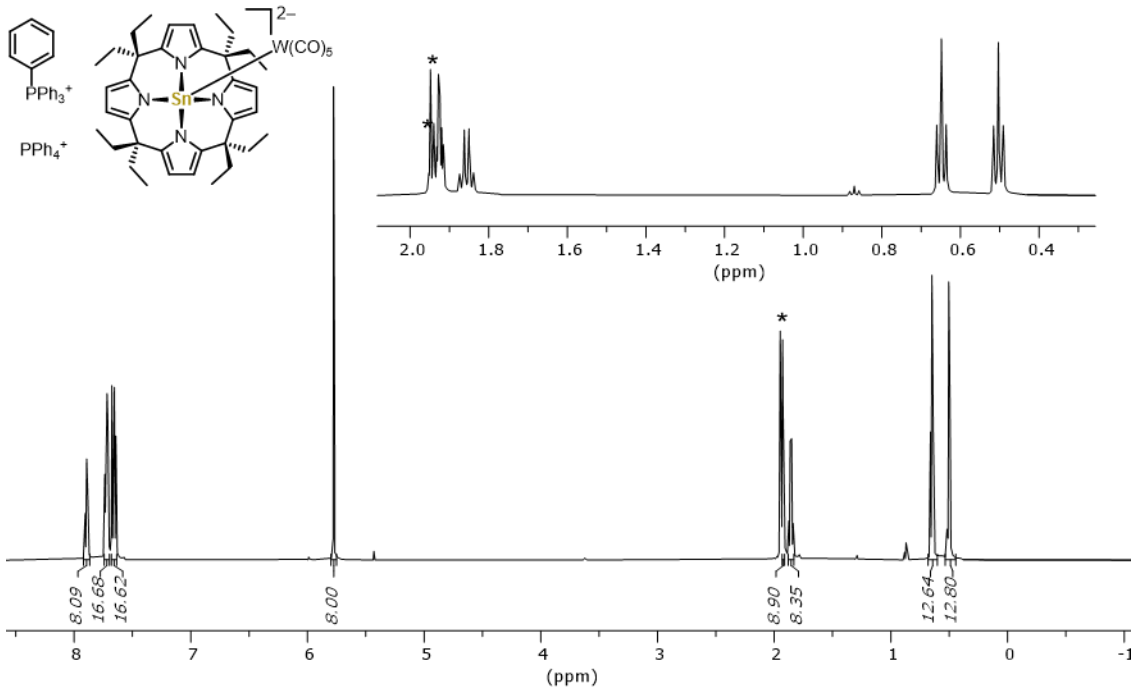


Figure S17. ^{1}H NMR spectrum of **$[(PPh_4)_2][W(^1\eta\text{-}2)(CO)_5]$** (600.15 MHz, MeCN-$d_3$, 295 K). Solvent resonances are indicated by an asterisk (*).

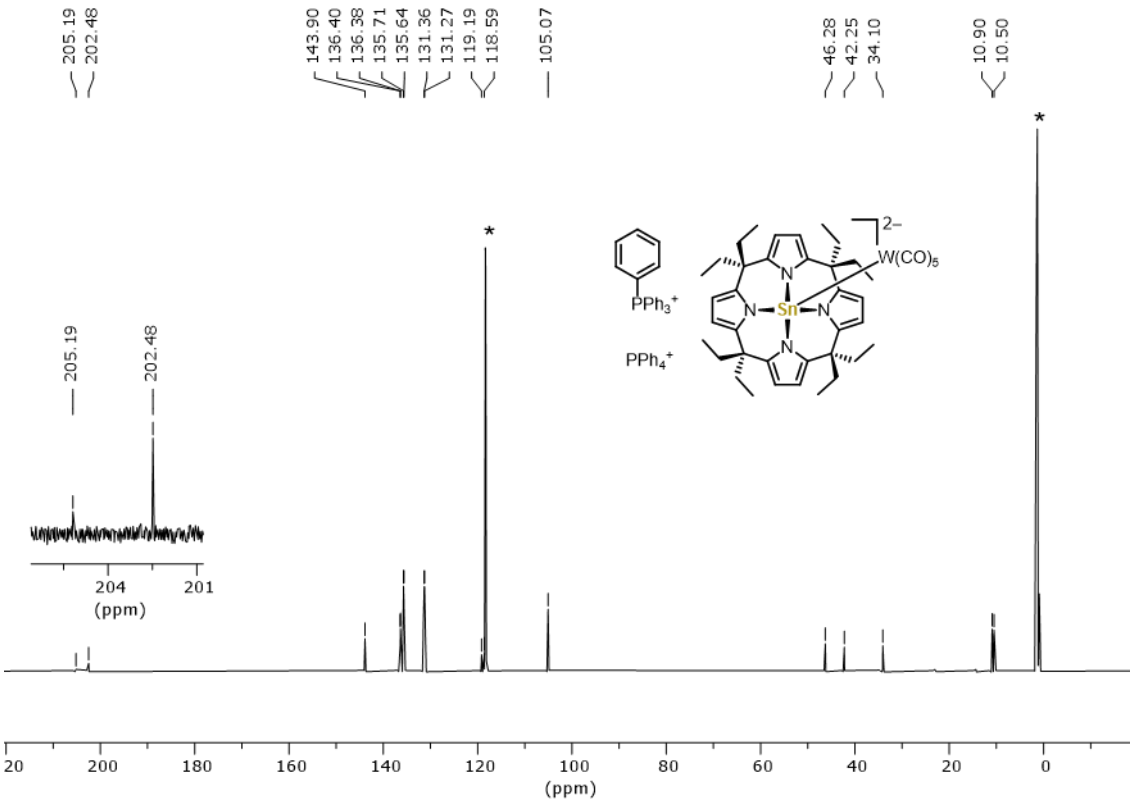


Figure S18. ^{13}C NMR spectrum of **$[(PPh_4)_2][W(^1\eta\text{-}2)(CO)_5]$** (150.92 MHz, MeCN-$d_3$, 295 K). Solvent resonances are indicated by an asterisk (*).

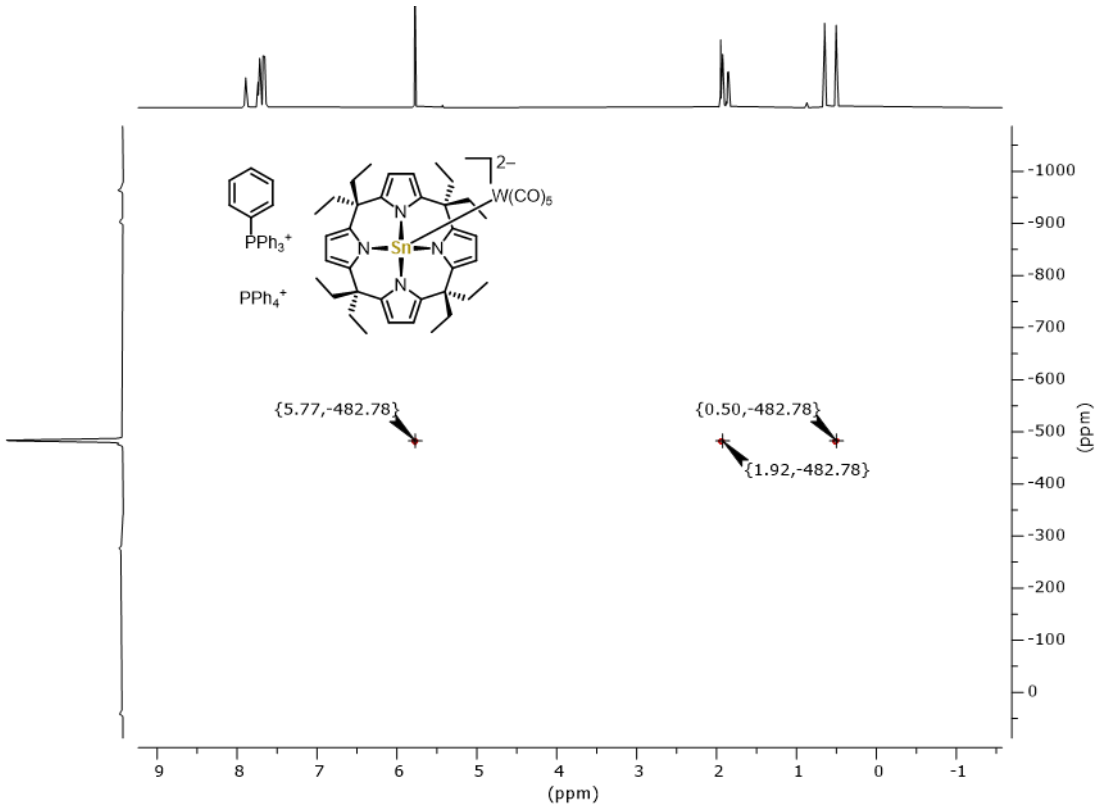


Figure S19. ^{119}Sn-^{1}H HMBC NMR spectrum of **[(PPh$_4$)$_2$][W(^{1}η-2)(CO)$_5$]** (MeCN-d_3, 295 K).

4.6 [(NBu$_4$)$_2$][Ni(^{1}η-2)(CO)$_3$]

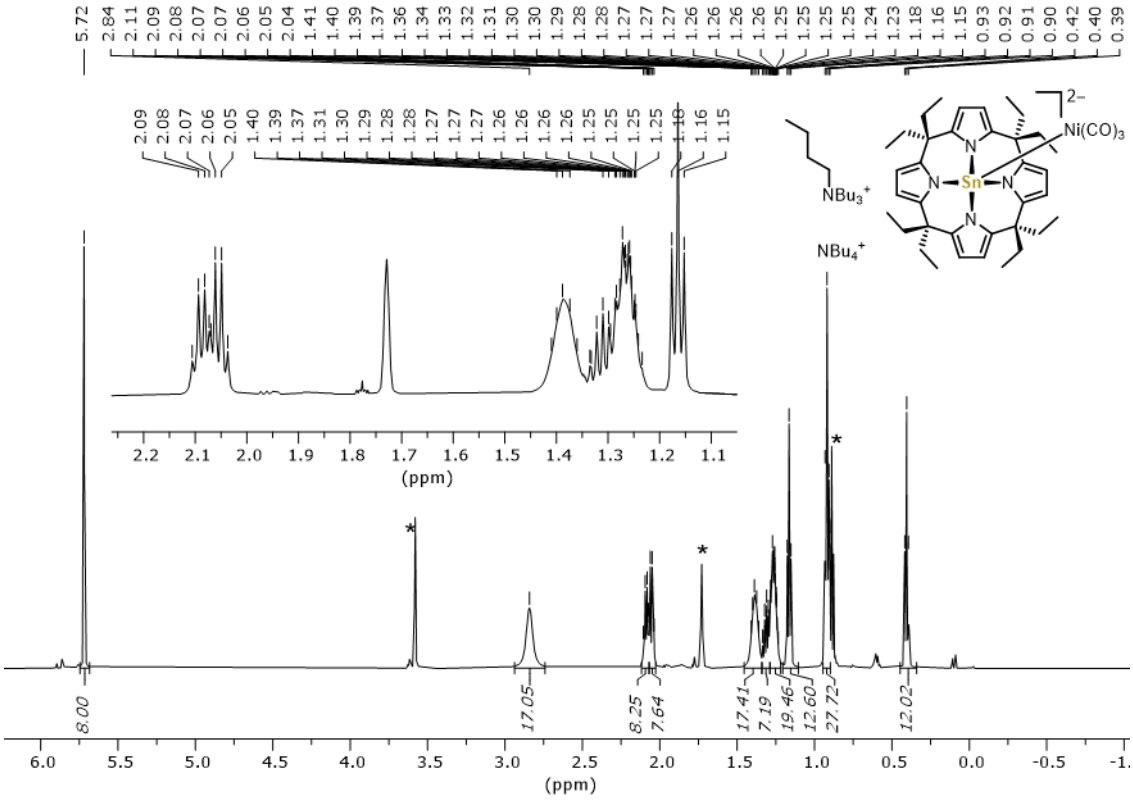


Figure S20. ^{1}H NMR spectrum of **[(NBu$_4$)$_2$][Ni(^{1}η-2)(CO)$_3$]** (600.15 MHz, THF-d_8, 295 K). Solvent resonances and resonances of residue pentane are indicated by an asterisk (*).

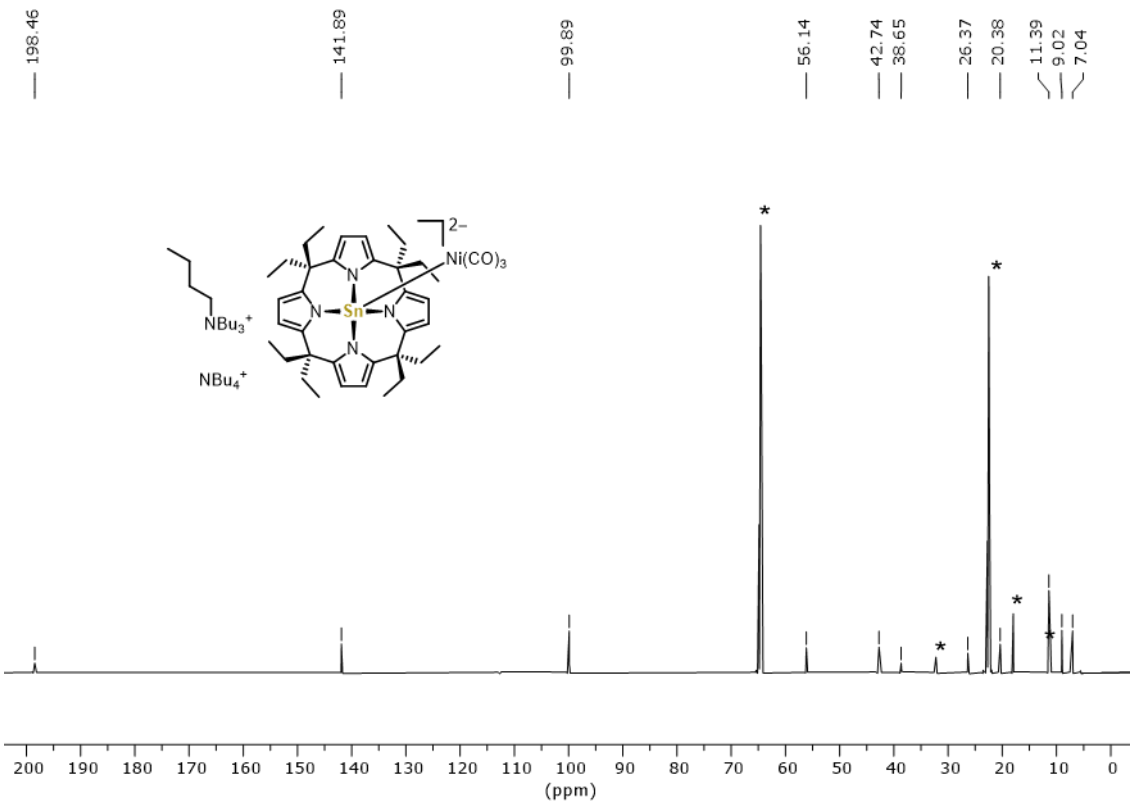


Figure S21. ^{13}C NMR spectrum of **[(NBu$_4$)$_2$][Ni(^{1}η-2)(CO)$_3$]** (150.92 MHz, THF-d_8, 295 K). Solvent resonances and resonances of residue pentane are indicated by an asterisk (*).

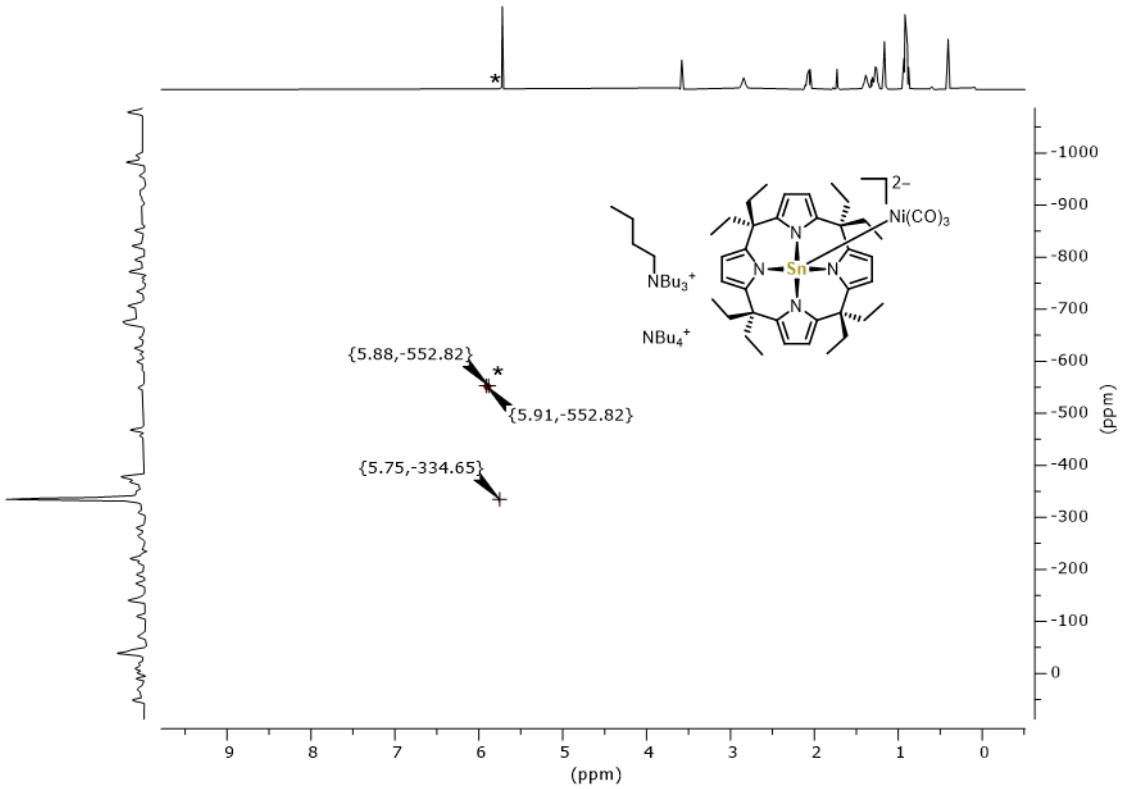


Figure S22. ^{119}Sn-^{1}H HMBC NMR spectrum of **[(NBu$_4$)$_2$][Ni(^{1}η-2)(CO)$_3$]** (THF-d_8, 295 K). Traces of free stannate(II) dianion formed by decomposition are indicated by an asterisk (*).

4.7 Ru(⁵η-2)(cymene)

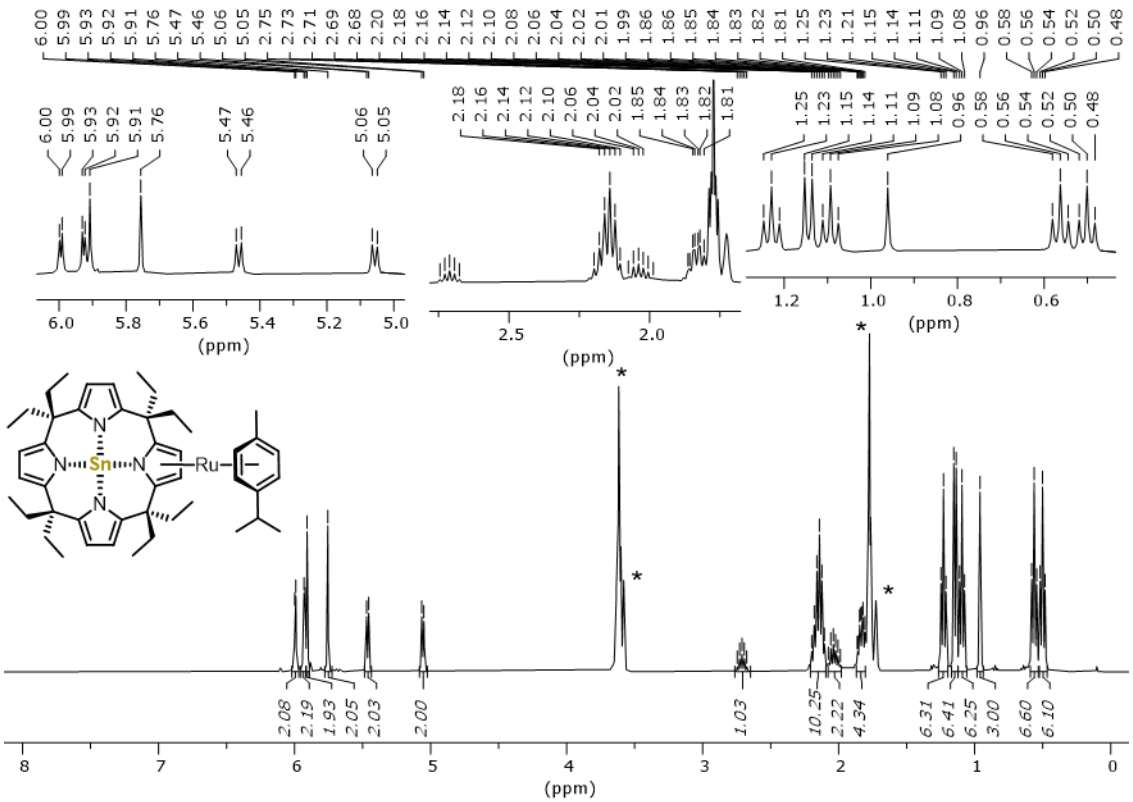


Figure S23. ^{1}H NMR spectrum of **Ru(⁵η-2)(cymene)** (400 MHz, THF-d_8, 295 K). Solvent resonances and resonances of residue pentane are indicated by an asterisk (*).

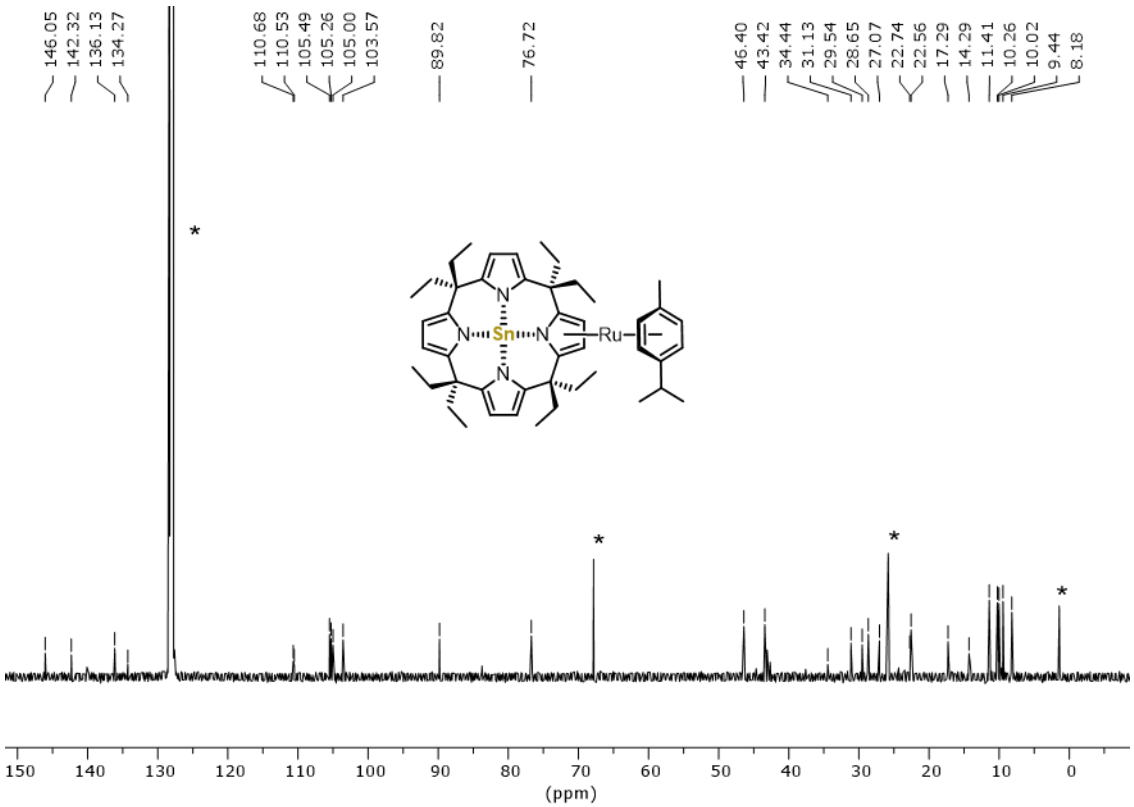


Figure S24. ^{13}C NMR spectrum of **Ru(⁵η-2)(cymene)** (150.29 MHz, C_6D_6, 295 K). Solvent resonances and resonances of residue pentane are indicated by an asterisk (*).

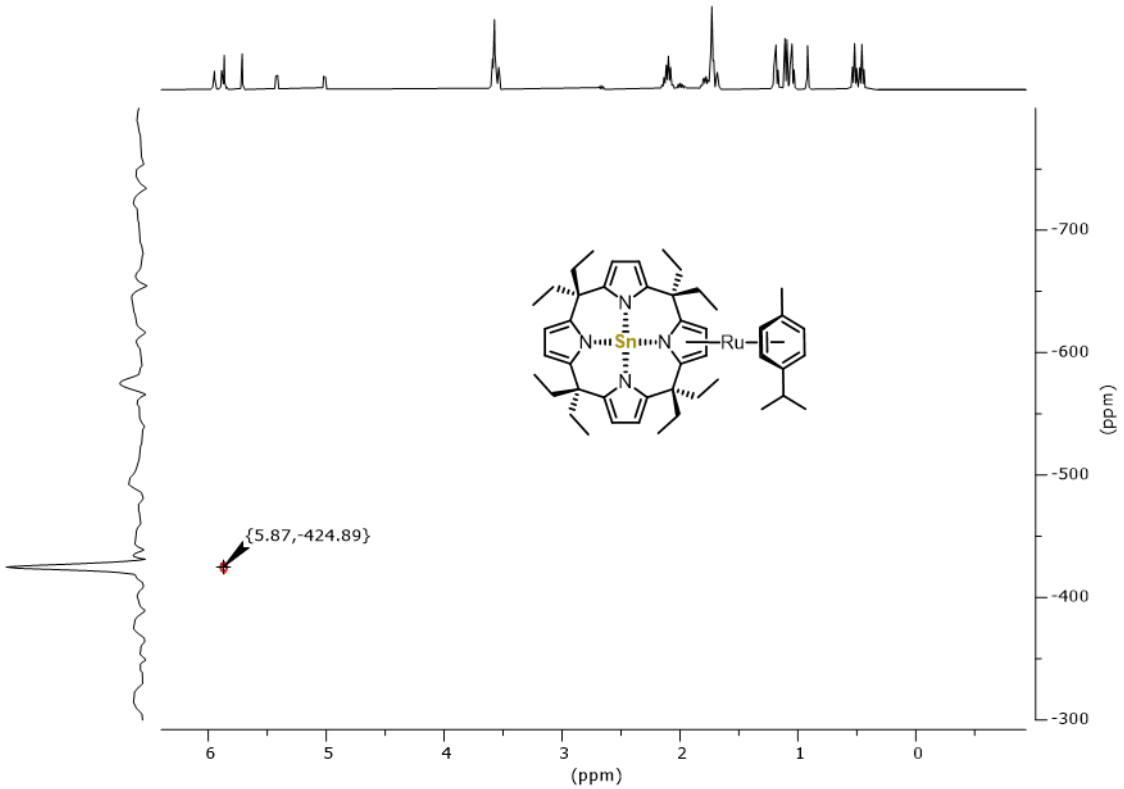


Figure S25. ^{119}Sn-^{1}H HMBC NMR spectrum of **Ru(^{5}η-2)(cymene)** (THF-d_8, 295 K).

4.8 Reaction of [Li$_2$(thf)$_x$][2] with Benzoyl chloride

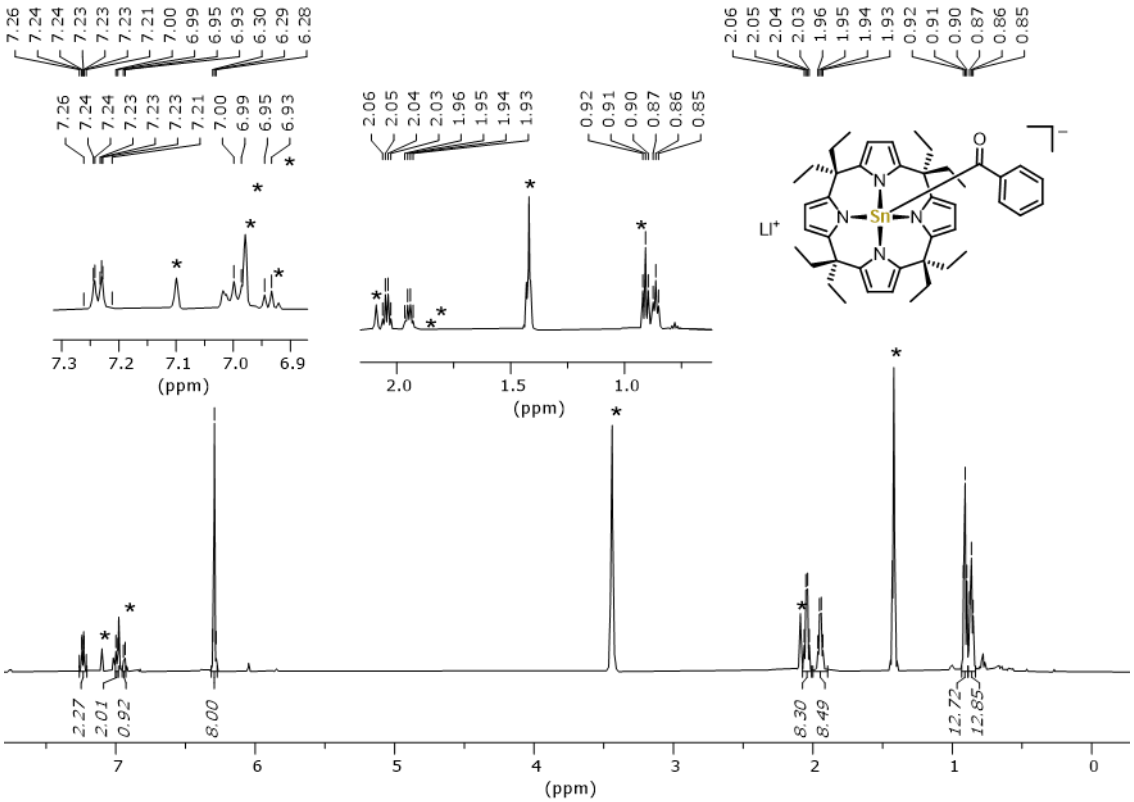


Figure S26. ^{1}H NMR spectrum of the reaction of **[Li$_2$(thf)$_x$][2]** with benzoyl chloride (600.15 MHz, Toluene-d8, 295 K). Solvent resonances and resonances of THF from starting material are indicated by an asterisk (*).

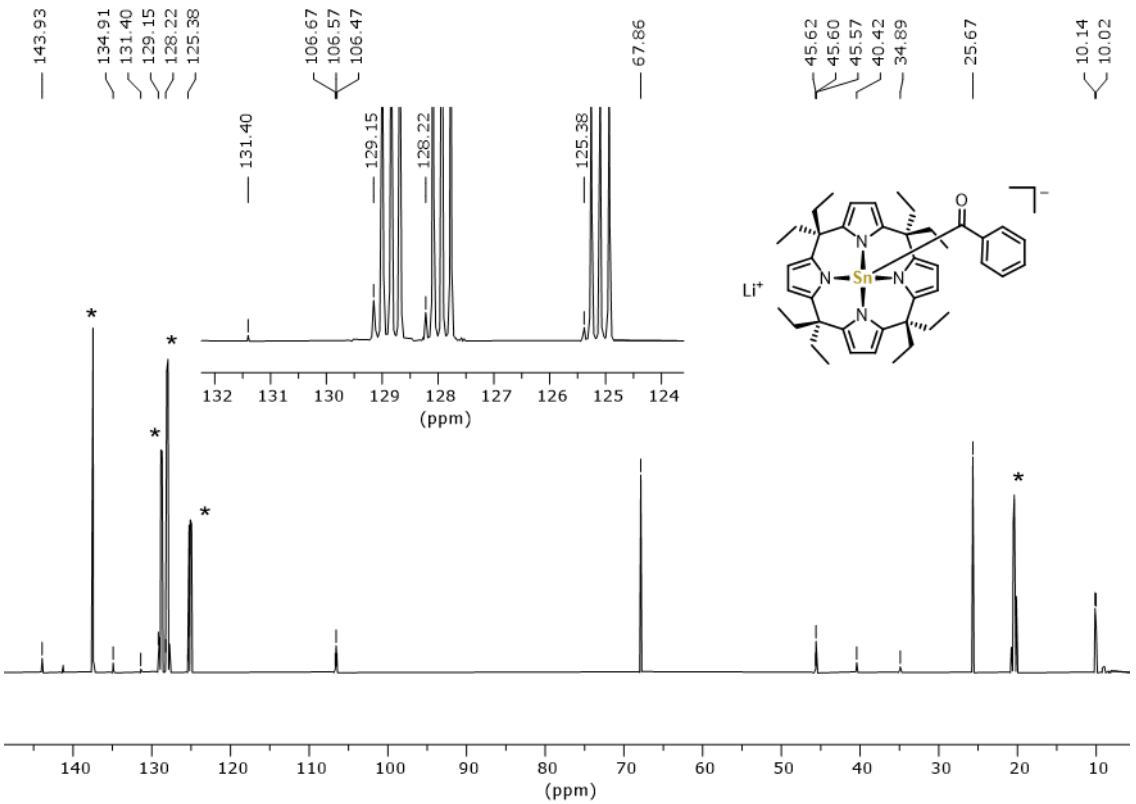


Figure S27. ^{13}C NMR spectrum of the reaction of **[Li$_2$(thf)$_x$][2]** with benzoyl chloride (155.29 MHz, Toluene-d8, 295 K). Solvent resonances and resonances are indicated by an asterisk (*).

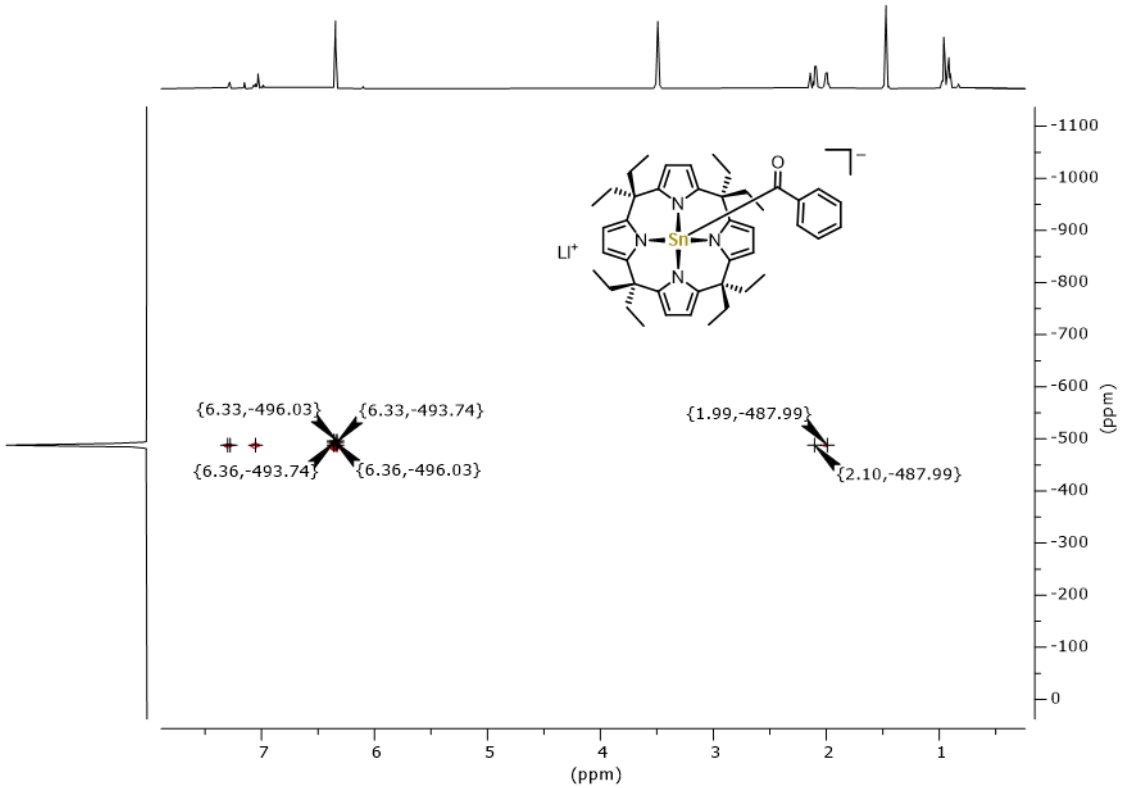


Figure S28. ^{129}Sn-^{1}H HMBC spectrum of the reaction of **[Li$_2$(thf)$_x$][2]** with benzoyl chloride (399.89 MHz, Toluene-d_8, 295 K).

4.9 Reaction of $[Li_2(thf)_x]$[2] with 4-CF_3-Benzaldehyde

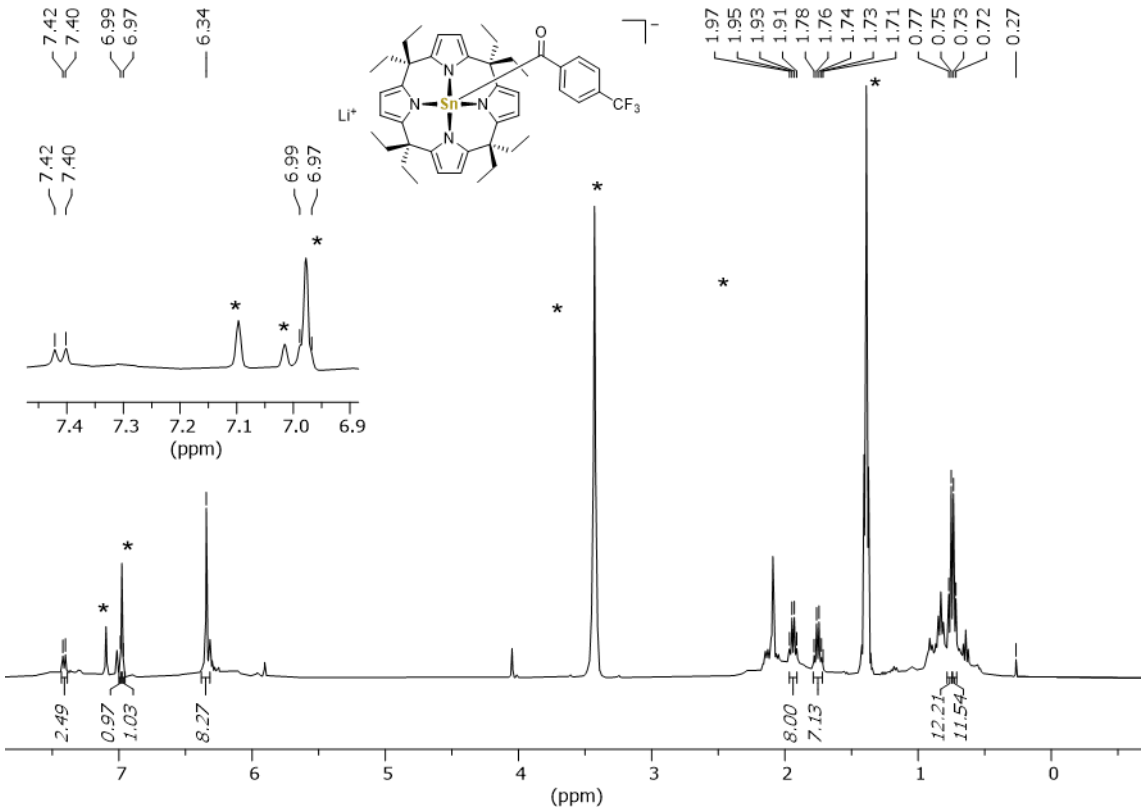


Figure S29. ^{1}H NMR spectrum of the reaction of **$[Li_2(thf)_x]$[2]** with 4-CF_3-benzaldehyde (399.89 MHz, Toluene-d_8, 295 K). Solvent resonances and resonances of THF from starting material are indicated by an asterisk (*).

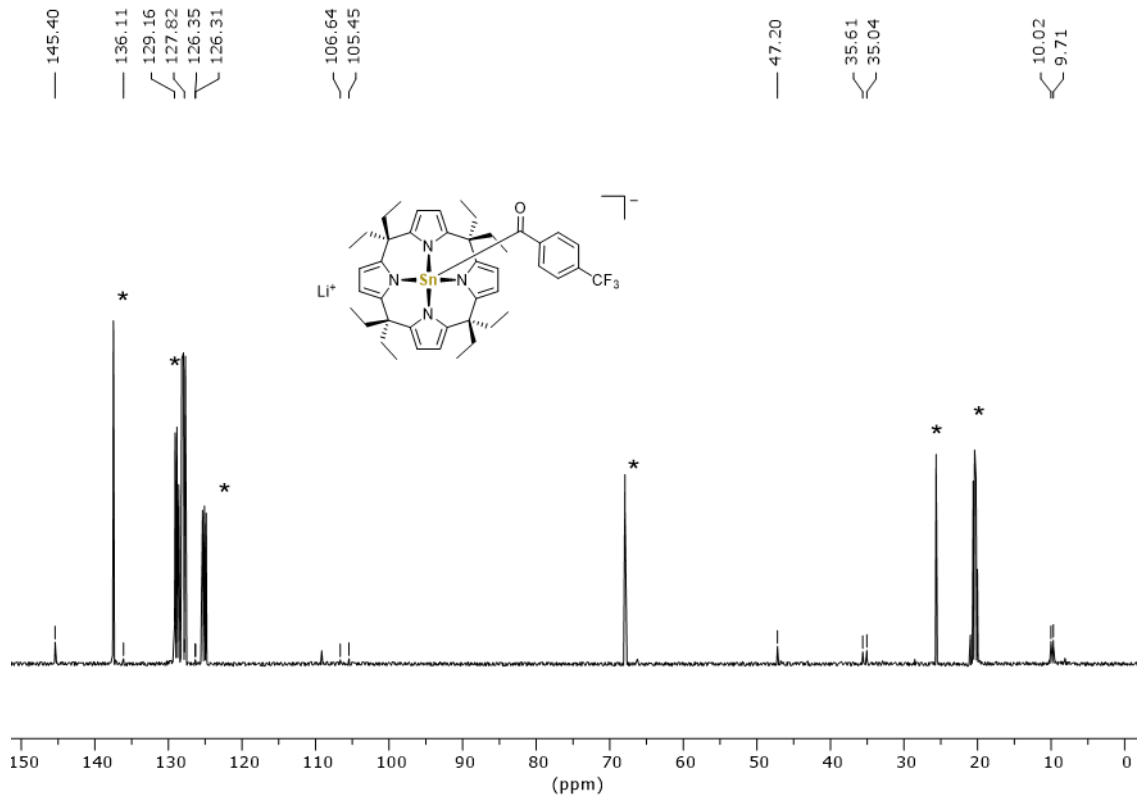


Figure S30. ^{13}C NMR spectrum of the reaction of **$[Li_2(thf)_x]$[2]** with 4-CF_3-benzaldehyde (100.55 MHz, Toluene-d_8, 295 K). Solvent resonances and resonances of THF from starting material are indicated by an asterisk (*).

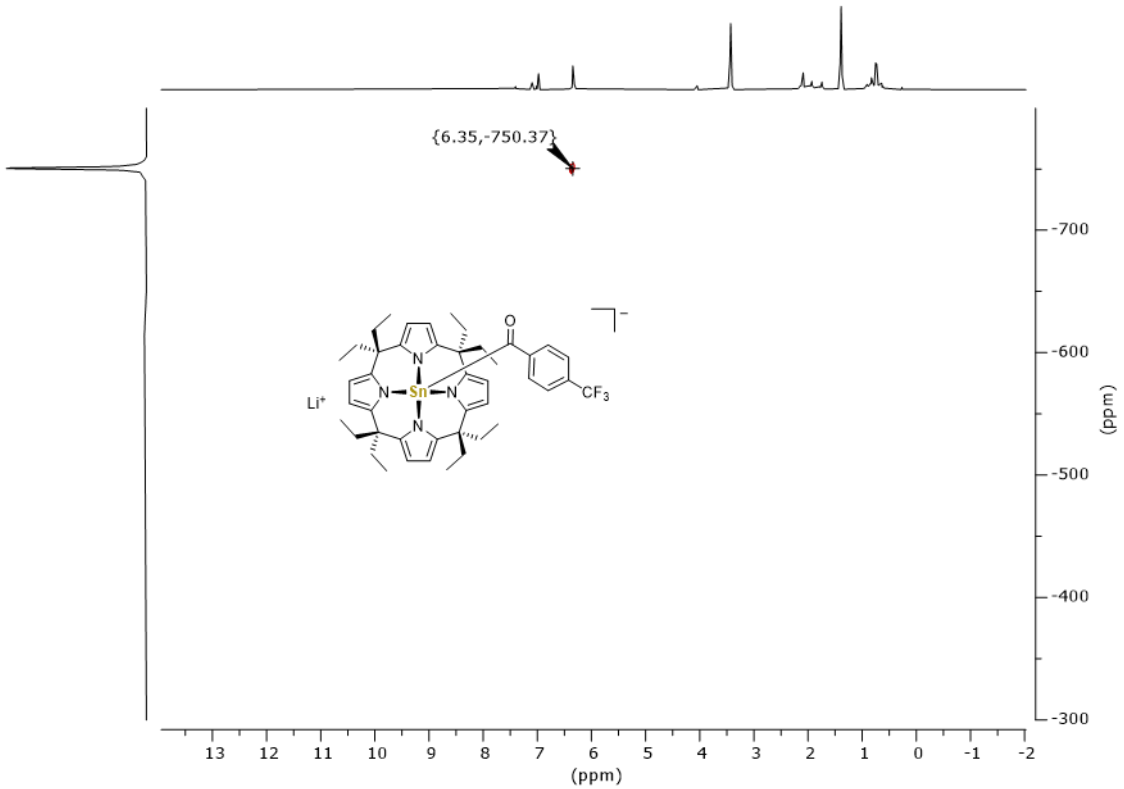


Figure S31. ^{119}Sn-^{1}H HMBC spectrum of the reaction of **[Li$_2$(thf)$_x$][2]** with 4-(CF$_3$)-benzaldehyde (Toluene-d$_8$, 295 K).

4.10 Reaction of [(NBu$_4$)$_2$][2] with Methylene Chloride

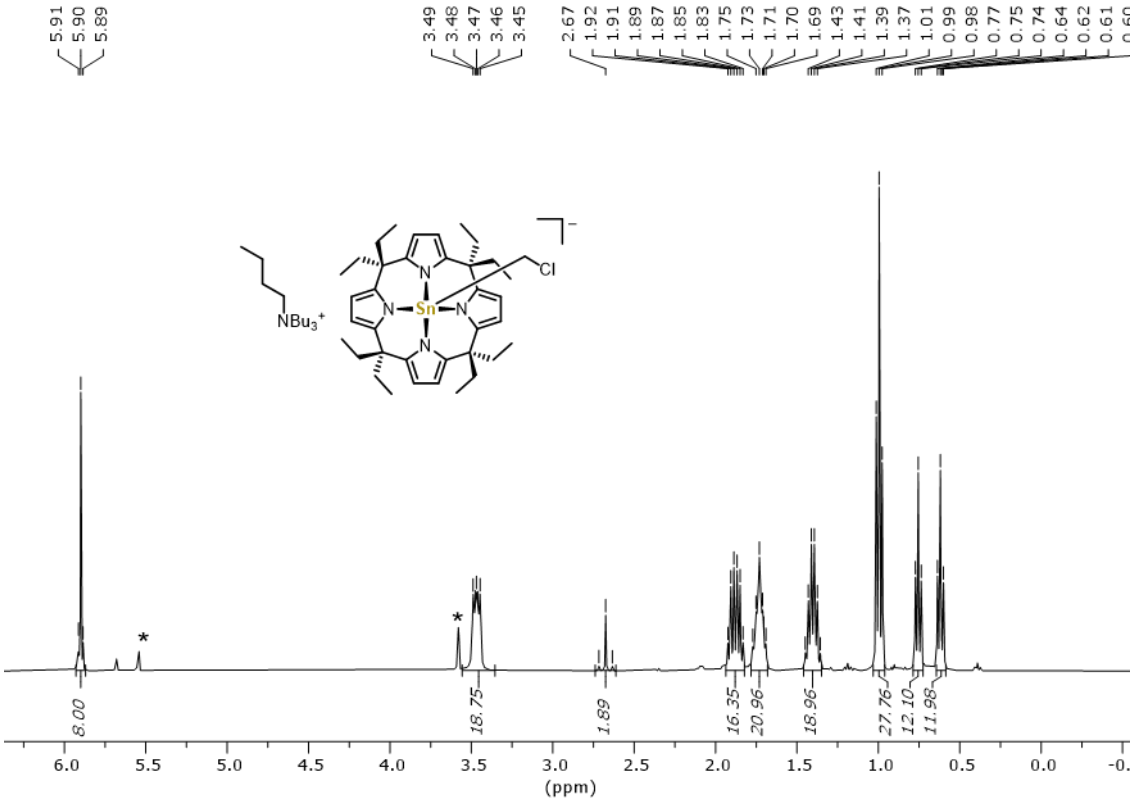


Figure S32. ^{1}H NMR spectrum of the reaction of **[(NBu$_4$)$_2$][2]** with methylene chloride (399.89 MHz, THF-d$_8$, 295 K). Solvent and residual methylene chloride resonances are indicated by an asterisk (*).

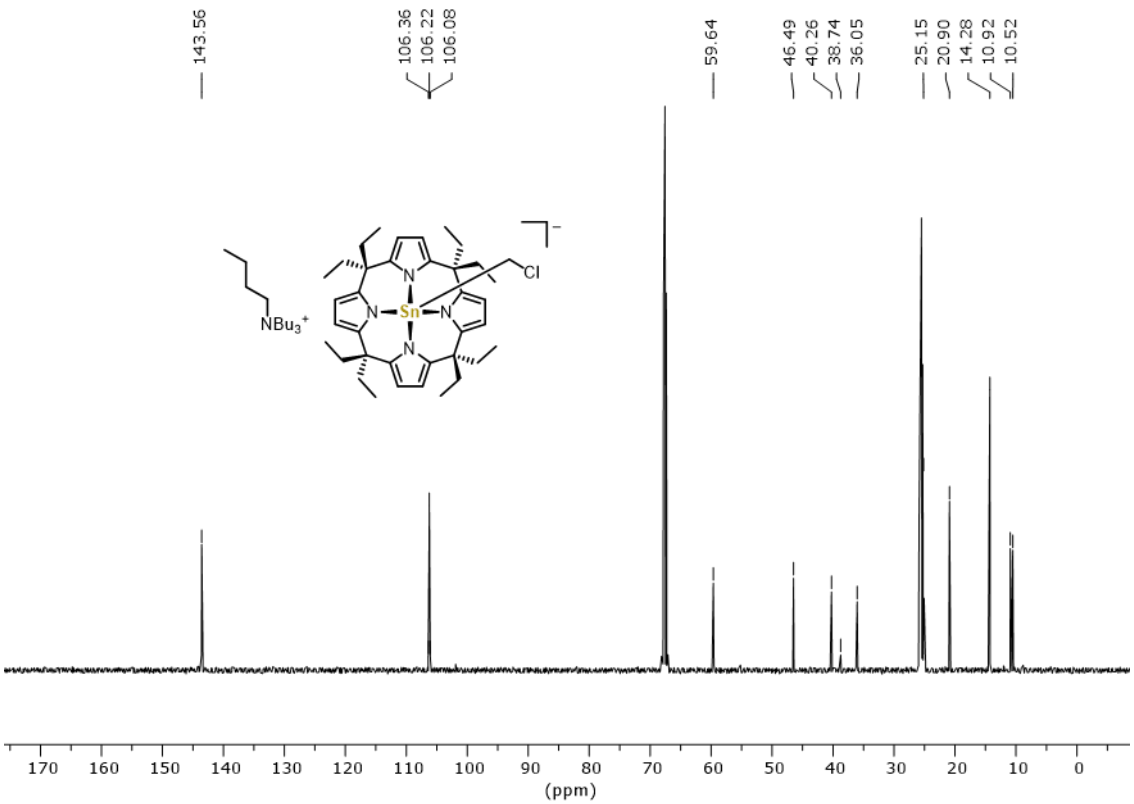


Figure S33. ^{13}C NMR spectrum of the reaction of **[(NBu$_4$)$_2$][2]** with methylene chloride (100.55 MHz, THF-d$_8$, 295 K). Solvent resonances are indicated by an asterisk (*).

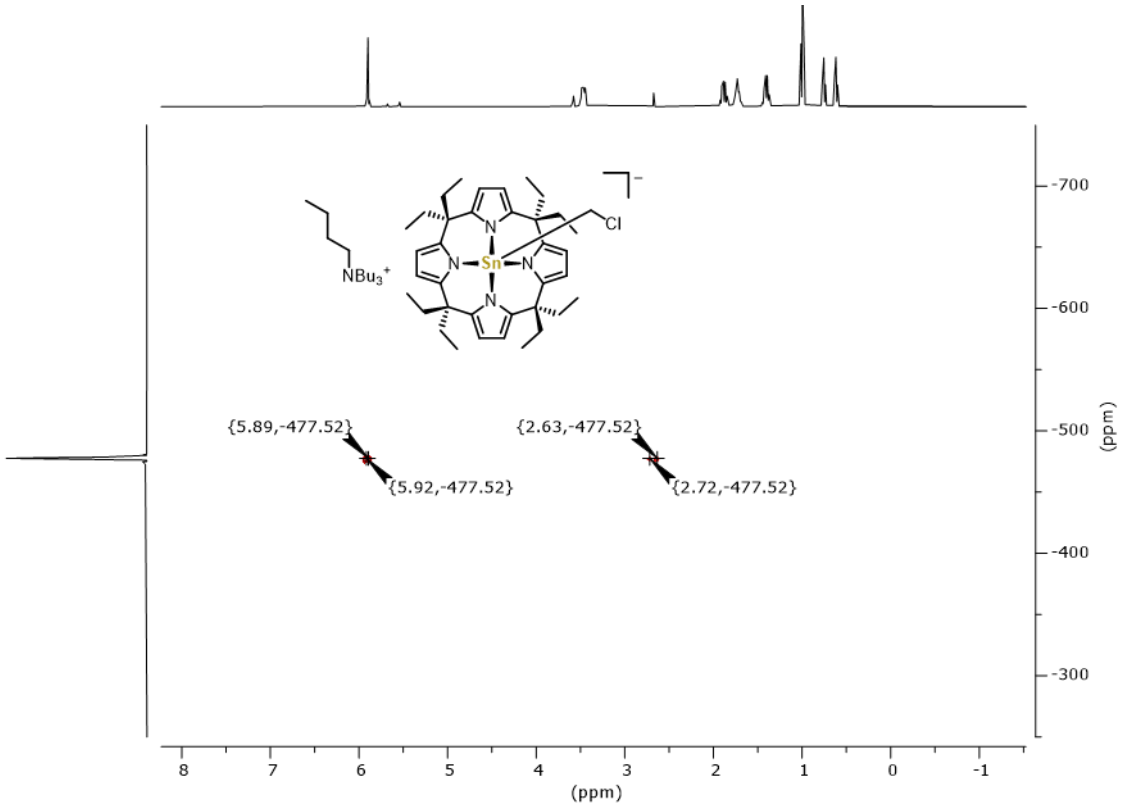


Figure S34. ^{119}Sn-^{1}H HMBC spectrum of the reaction of **[(NBu$_4$)$_2$][2]** with methylene chloride (THF-d8, 295 K).

4.11 Reaction of $[(NBu_4)_2][2]$ with Benzyl Chloride

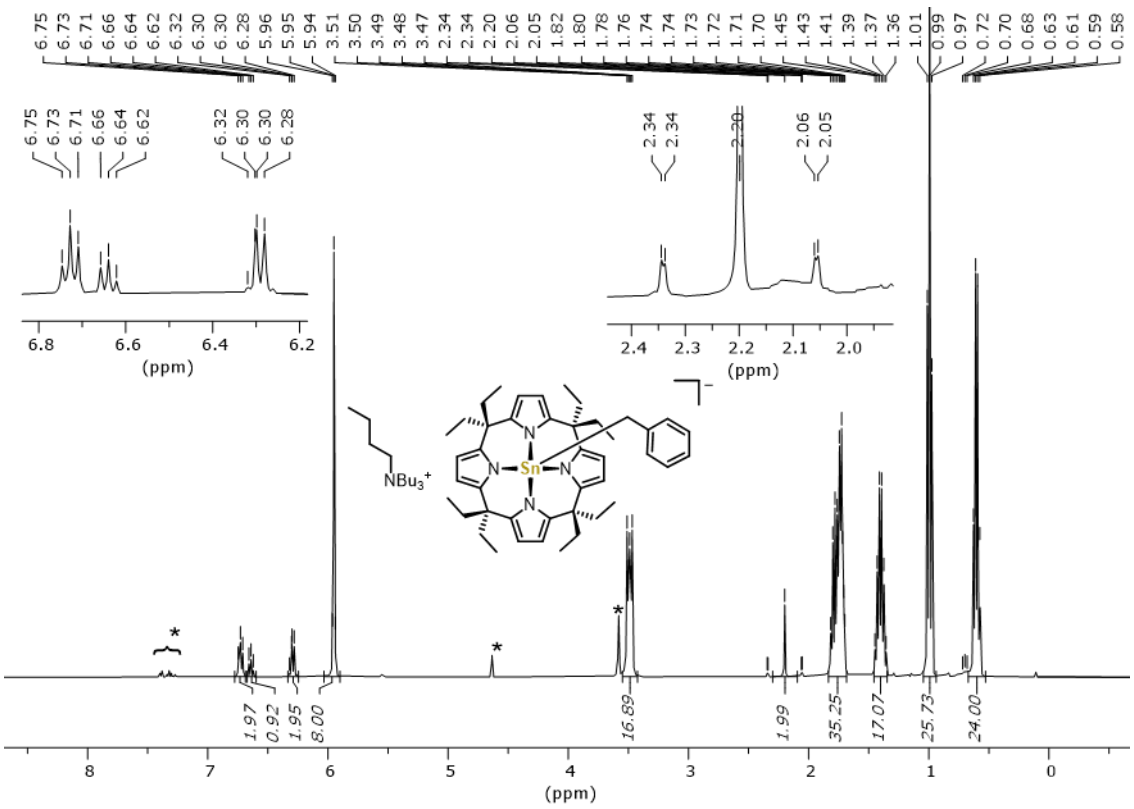


Figure S35. ^{1}H NMR spectrum of the reaction of **$[(NBu_4)_2][2]$** with benzyl chloride (399.89 MHz, THF-d8, 295 K). Solvent resonances are indicated by an asterisk (*).

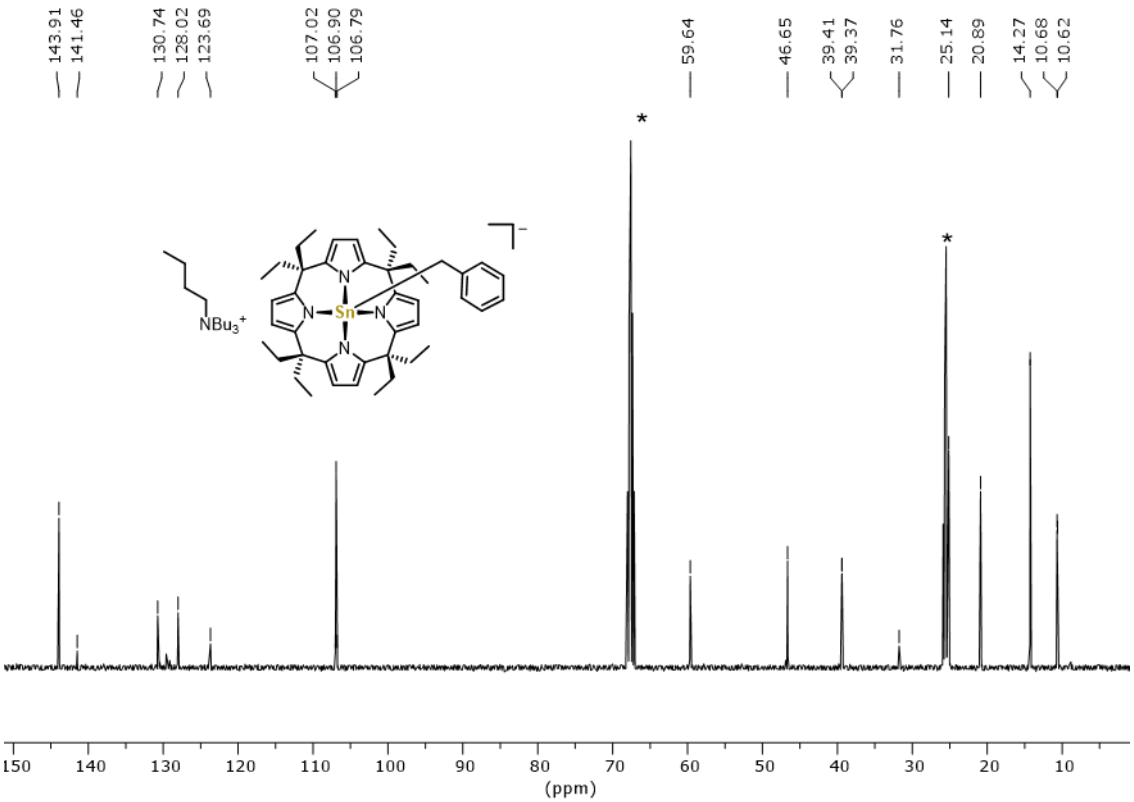


Figure S36. ^{13}C NMR spectrum of the reaction of **$[(NBu_4)_2][2]$** with benzyl chloride (100.55 MHz, THF-d8, 295 K). Solvent resonances are indicated by an asterisk (*).

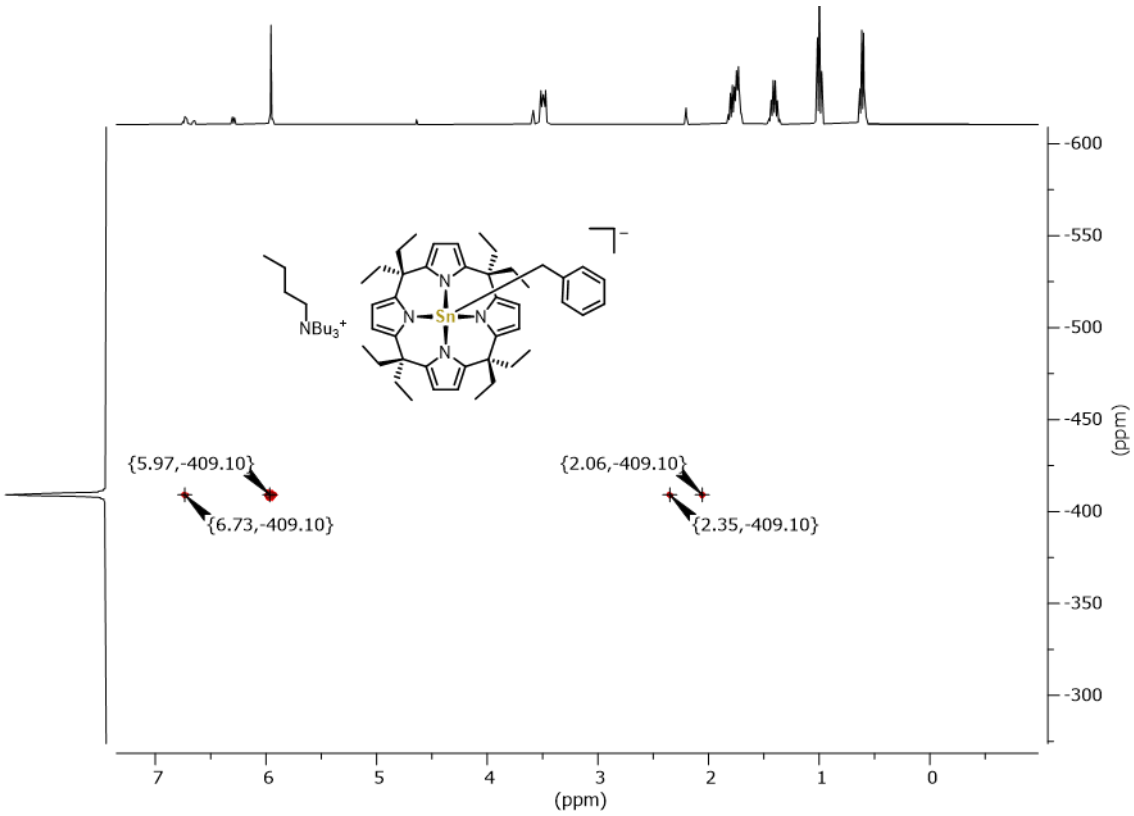


Figure S37. ^{119}Sn-^{1}H HMBC spectrum of the reaction of **[(NBu$_4$)$_2$][2]** with benzyl chloride (THF-d8, 295 K).

4.12 Reaction of [(NBu$_4$)$_2$][2] with Benzoyl Chloride

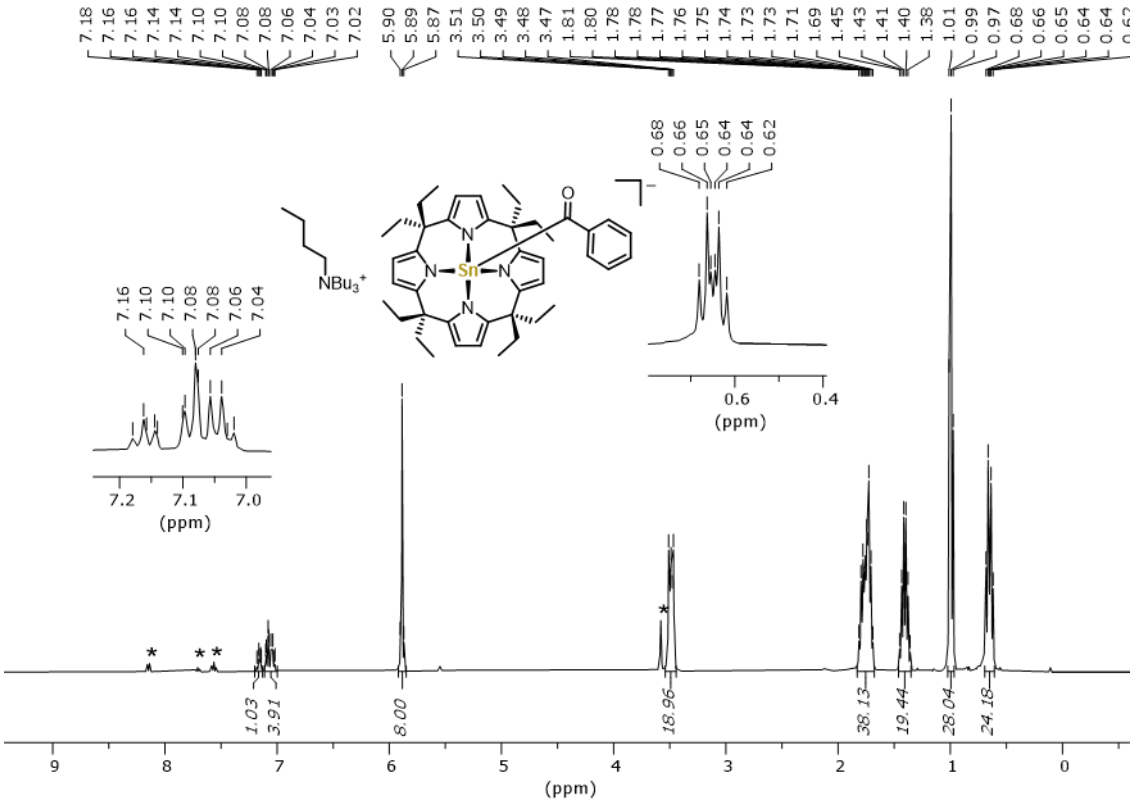


Figure S38. ^{1}H NMR spectrum of the reaction of **[(NBu$_4$)$_2$][2]** with benzoyl chloride (399.89 MHz, THF-d8, 295 K). Solvent and residue benzoyl chloride (slight excess) resonances are indicated by an asterisk (*).

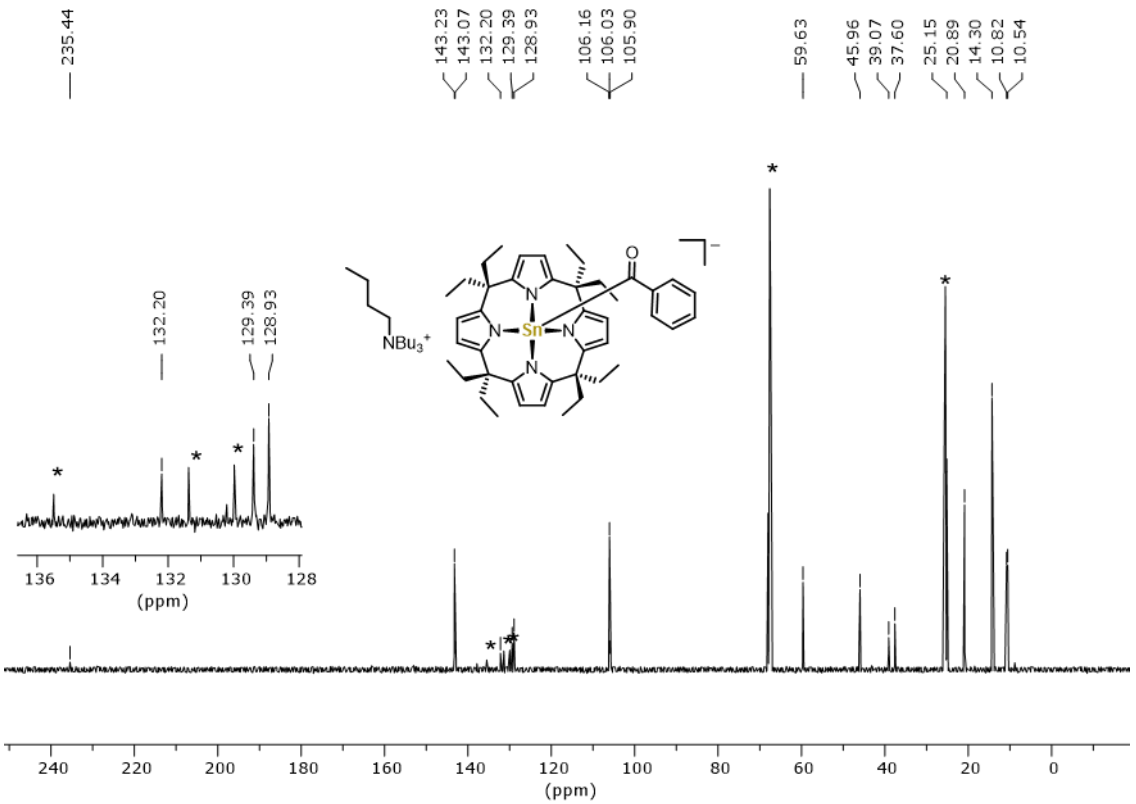


Figure S39. ^{13}C NMR spectrum of the reaction of **[(NBu$_4$)$_2$][2]** with benzoyl chloride (100.55 MHz, THF-d8, 295 K). Solvent and residue benzoyl chloride (slight excess) resonances are indicated by an asterisk (*).

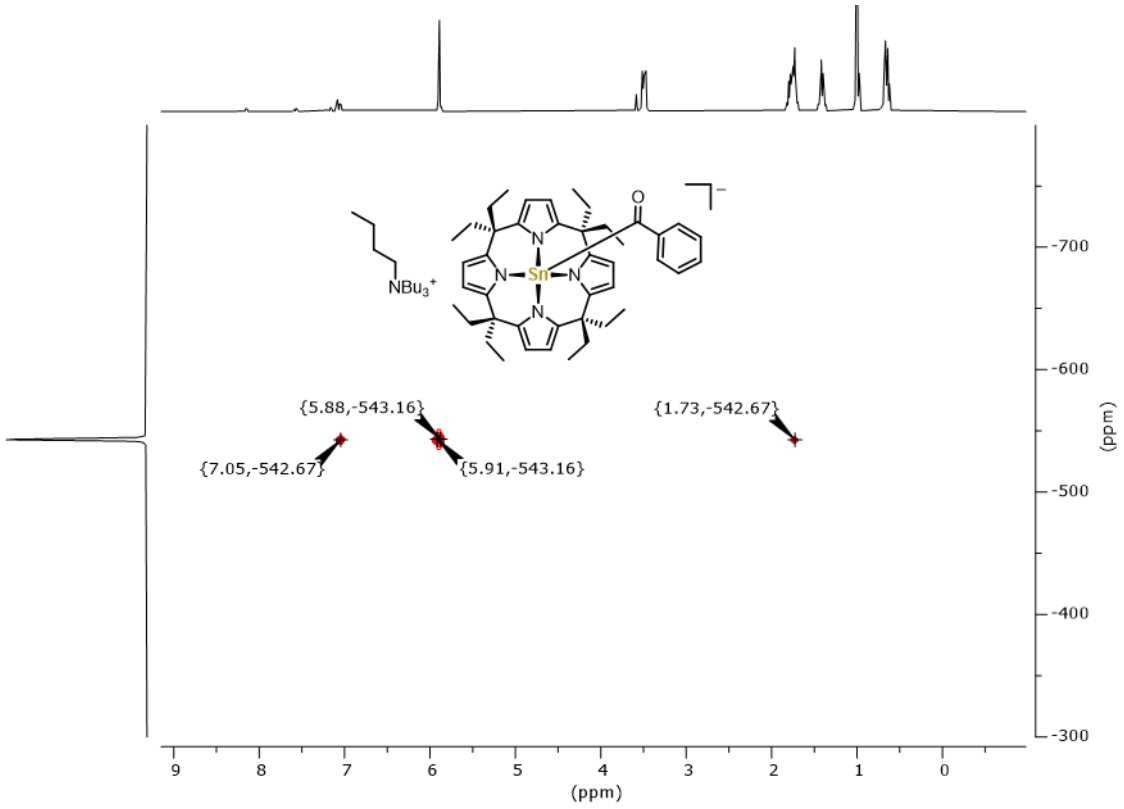


Figure S40. ^{119}Sn-^{1}H HMBC spectrum of the reaction of **[(NBu$_4$)$_2$][2]** with benzoyl chloride (THF-d8, 295 K).

4.13 Reaction of [(NBu$_4$)$_2$][2] with Iodobenzene

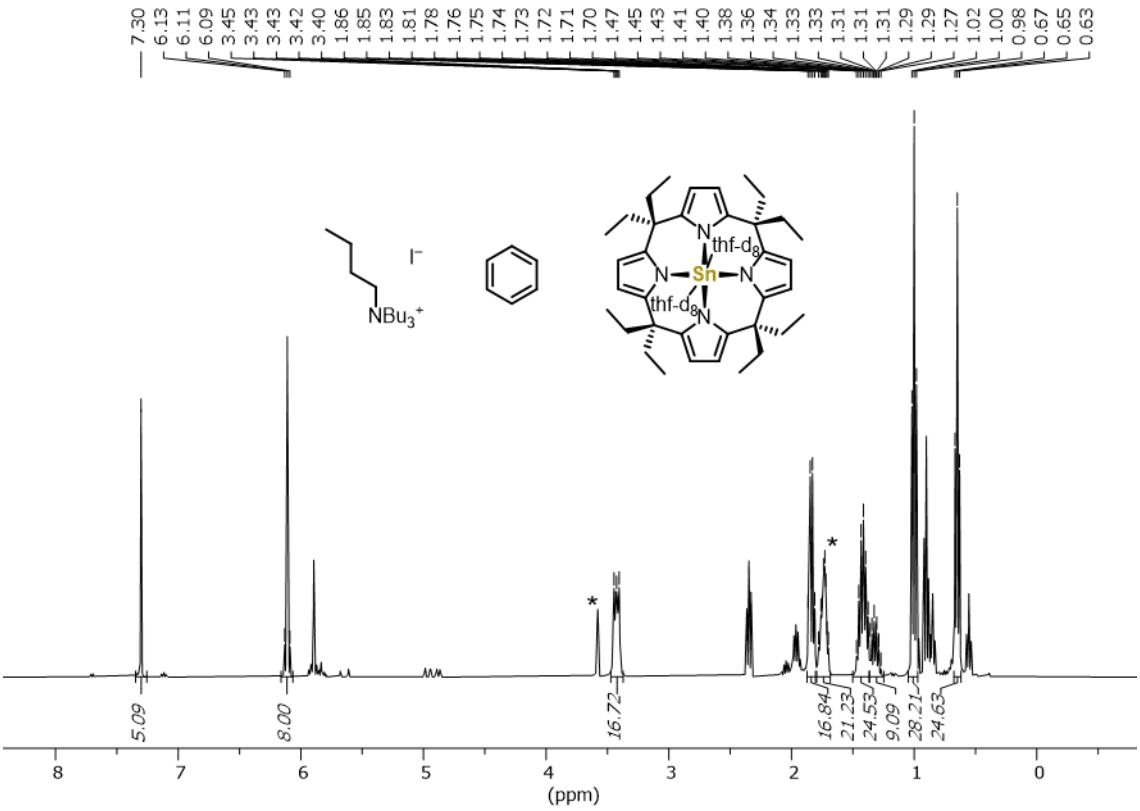


Figure S41. ^{1}H NMR spectrum of the reaction of **[(NBu$_4$)$_2$][2]** with iodobenzene (399.89 MHz, THF-d8, 295 K). Solvent resonances are indicated by an asterisk (*).

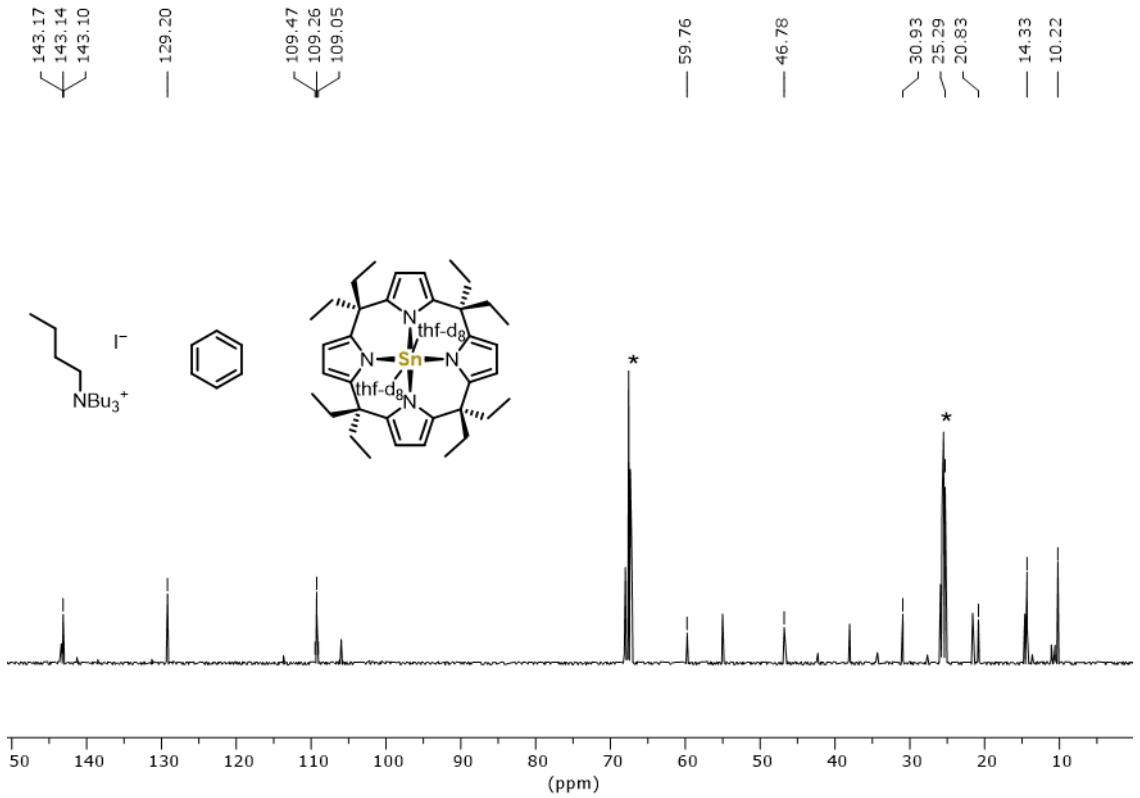


Figure S42. ^{13}C NMR spectrum of the reaction of **[(NBu$_4$)$_2$][2]** with iodobenzene (100.55 MHz, THF-d8, 295 K). Solvent resonances are indicated by an asterisk (*).

5 Crystallographic Data

5.1 [$Li_2(thf)_x$][2]

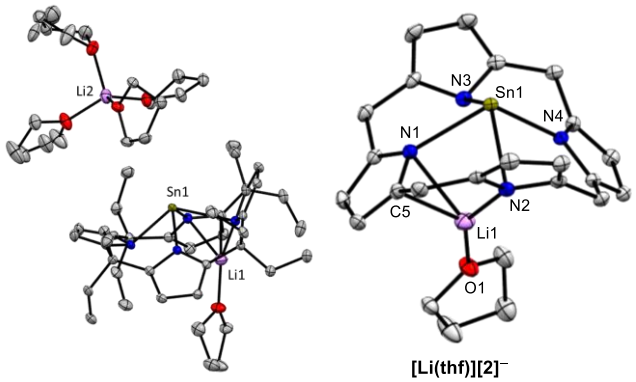


Figure S43: Solid state molecular structure of **[$Li_2(thf)_x$][2]** (left) and the isolated **[Li(thf)][2]**$^-$ anion (left, *meso*-ethyl residues and solvated lithium counter cation are omitted for clarity). Ellipsoids are drawn with a probability of 50%. Hydrogen atoms are omitted for clarity.

Table S3: Crystal data for **[$Li_2(thf)_x$][2]**.

CCDC number	2125920
Identification code	mo_hr283_0ma
Empirical formula	$C_{56}H_{88}Li_2N_4O_5Sn$
Formula weight	1029.87
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	17.0606(16)
b/Å	16.1225(14)
c/Å	19.5523(18)
α/°	90
β/°	90.037(4)
γ/°	90
Volume/Å^3	5378.0(8)
Z	4
ρ_{calc}/g cm^{-3}	1.272
μ/mm^{-1}	0.525
F(000)	2192.0
Crystal size/mm^3	0.221 × 0.164 × 0.044
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.052 to 52
Index ranges	-21 ≤ h ≤ 21, -19 ≤ k ≤ 19, -24 ≤ l ≤ 24
Reflections collected	236904
Independent reflections	10548 [R_{int} = 0.0979, R_{sigma} = 0.0272]
Data/restraints/parameters	10548/0/650
Goodness-of-fit in F^2	1.081
Final R indexes [I>=2σ(I)]	R_1 = 0.0293, wR_2 = 0.0591
Final R indexes [all data]	R_1 = 0.0415, wR_2 = 0.0632
Largest diff. peak/hole/eÅ^{-3}	0.47/-0.50

5.2 [(NBu$_4$)$_2$][2]

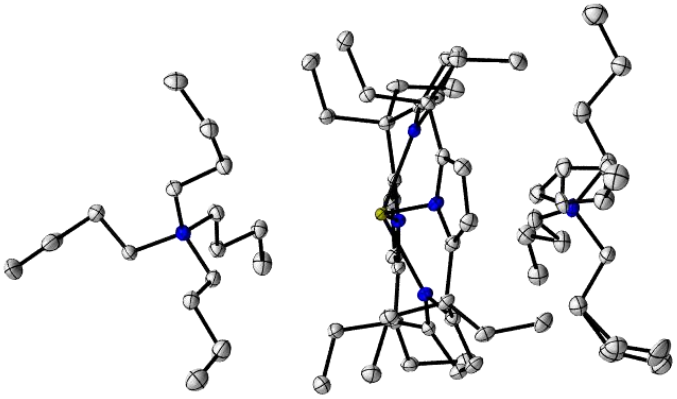


Figure S44: Solid state molecular structure of **[(NBu$_4$)$_2$][2]**. Ellipsoids are drawn with a probability of 50%. Hydrogen atoms are omitted for clarity.

Table S4: Crystal data for **[(NBu$_4$)$_2$][2]**.

CCDC number	2125918
Identification code	mo_hr342_2_0ma
Empirical formula	$C_{68}H_{120}N_6Sn$
Formula weight	1140.38
Temperature/K	100.0
Crystal system	orthorhombic
Space group	$Pbca$ (61)
a/Å	18.9095(7)
b/Å	18.6657(5)
c/Å	35.9481(10)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	12688.2(7)
Z	8
ρ_{calc}/g cm^{-3}	1.194
μ/mm^{-1}	0.447
F(000)	4960
Crystal size/mm^3	0.349×0.342×0.263
Radiation	MoK_α (λ=0.71073 Å)
2Θ range for data collection/°	4.31 to 51.00 (0.83 Å)
Index ranges	-22 ≤ h ≤ 22, -22 ≤ k ≤ 22, -43 ≤ l ≤ 43
Reflections collected	83712
Independent reflections	11805 [R_{int} = 0.0486, R_{sigma} = 0.0294]
Data/restraints/parameters	11805/0/731
Goodness-of-fit in F^2	1.045
Final R indexes [I>=2σ(I)]	R_1 = 0.0298, wR_2 = 0.0658
Final R indexes [all data]	R_1 = 0.0354, wR_2 = 0.0685
Largest diff. peak/hole/eÅ^{-3}	0.32/-0.53

5.3 [(PPh$_4$)$_2$(*o*DFB)$_{0.5}$][2]

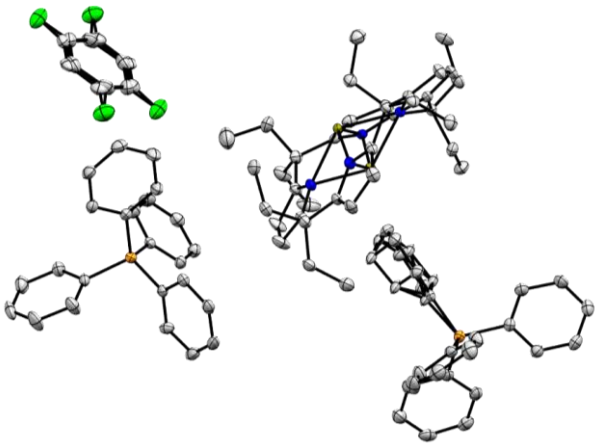


Figure S45: Solid state molecular structure of **[(PPh$_4$)$_2$(*o*DFB)$_{0.5}$][2].** Ellipsoids are drawn with a probability of 50%. Hydrogen atoms are omitted for clarity.

Table S5: Crystal data for **[(PPh$_4$)$_2$(*o*DFB)$_{0.5}$][2]**.

CCDC nmuber	2125916
Identification code	mo_hr308_0ma
Empirical formula	$C_{87}H_{90}FN_4P_2Sn$
Formula weight	1391.25
Temperature/K	100(2)
Crystal system	triclinic
Space group	$P\bar{1}$ (2)
a/Å	12.227(4)
b/Å	12.276(5)
c/Å	23.438(10)
α/°	87.397(10)
β/°	84.496(11)
γ/°	80.754(10)
Volume/Å^3	3455(2)
Z	2
ρ_{calc}/g cm^{-3}	1.337
μ/mm^{-1}	0.470
F(000)	1458
Crystal size/mm^3	0.169×0.084×0.030
Radiation	MoK_α (λ=0.71073 Å)
2Θ range for data collection/°	3.95 to 50.00 (0.84 Å)
Index ranges	-14 ≤ h ≤ 14, -14 ≤ k ≤ 14, -27 ≤ l ≤ 27
Reflections collected	75371
Independent reflections	12169 [R_{int} = 0.1052, R_{sigma} = 0.0634]
Data/restraints/parameters	12169/1209/935
Goodness-of-fit in F^2	1.041
Final R indexes [I>=2σ(I)]	R_1 = 0.0440, wR_2 = 0.0853
Final R indexes [all data]	R_1 = 0.0672, wR_2 = 0.0929
Largest diff. peak/hole/eÅ^{-3}	0.50/-0.54

5.4 $[(PPh_4)_2][W(^2\eta\text{-}2)(CO)_5]$

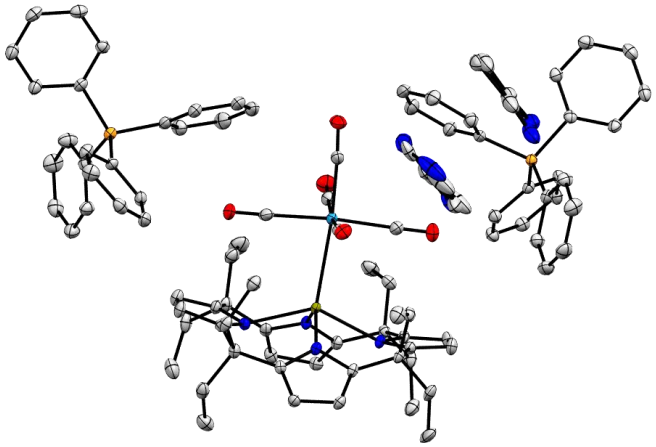


Figure S46: Solid state molecular structure of **$[(PPh_4)_2][2\text{-}W(CO)_5]$.** Ellipsoids are drawn with a probability of 50%. Hydrogen atoms are omitted for clarity.

Table S6: Crystal data for **$[(PPh_4)_2][2\text{-}W(CO)_5]$.**

CCDC nmuber	2125915
Identification code	mo_hr313_2_2
Empirical formula	$C_{93}H_{94}N_6O_5P_2SnW$
Formula weight	1740.22
Temperature/K	100(2)
Crystal system	triclinic
Space group	$P\overline{1}$ (2)
a/Å	13.510(2)
b/Å	13.587(2)
c/Å	25.095(4)
α/°	81.048(6)
β/°	84.270(7)
γ/°	60.976(5)
Volume/Å^3	3977.3(12)
Z	2
ρ_{calc}/g cm^{-3}	1.453
μ/mm^{-1}	1.857
F(000)	1776
Crystal size/mm^3	0.107×0.103×0.044
Radiation	MoK_α (λ=0.71073 Å)
2Θ range for data collection/°	3.78 to 56.02 (0.76 Å)
Index ranges	-17 ≤ h ≤ 17, -17 ≤ k ≤ 17, -33 ≤ l ≤ 33
Reflections collected	193114
Independent reflections	19158 [R_{int} = 0.1119, R_{sigma} = 0.0560]
Data/restraints/parameters	19158/2225/1011
Goodness-of-fit in F^2	1.017
Final R indexes [I>=2σ(I)]	R_1 = 0.0316, wR_2 = 0.0665
Final R indexes [all data]	R_1 = 0.0430, wR_2 = 0.0720
Largest diff. peak/hole/eÅ^{-3}	1.00/-1.01

5.5 Ru(^{5}η-2)(cymene)

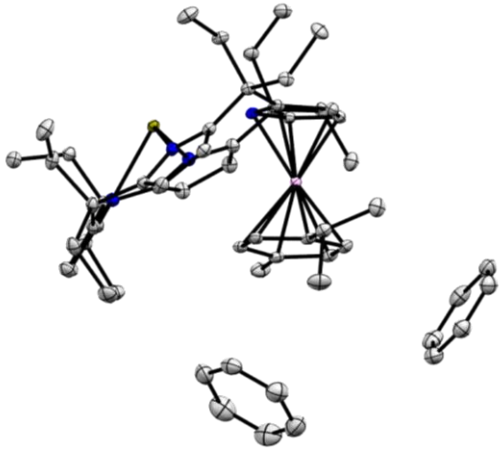


Figure S47: Solid state molecular structure of **Ru(^{5}η-2)(cymene)**. Ellipsoids are drawn with a probability of 50%. Hydrogen atoms are omitted for clarity.

Table S7: Crystal data for **Ru(^{5}η-2)(cymene)**.

CCDC number	2125917
Identification code	mo_hr372_0ma
Empirical formula	$C_{58}H_{74}N_4RuSn$
Formula weight	1046.97
Temperature/K	100(2)
Crystal system	triclinic
Space group	$P\bar{1}$ (2)
a/Å	11.465(3)
b/Å	12.8505(17)
c/Å	19.451(4)
α/°	97.710(8)
β/°	101.873(10)
γ/°	114.506(5)
Volume/Å^3	2473.0(9)
Z	2
ρ_{calc}/g cm^{-3}	1.406
μ/mm^{-1}	0.853
F(000)	1088
Crystal size/mm^3	0.123×0.106×0.074
Radiation	MoK_α (λ=0.71073 Å)
2Θ range for data collection/°	4.02 to 57.46 (0.74 Å)
Index ranges	-15 ≤ h ≤ 15, -17 ≤ k ≤ 17, -26 ≤ l ≤ 26
Reflections collected	155733
Independent reflections	12835 [R_{int} = 0.0390, R_{sigma} = 0.0165]
Data/restraints/parameters	12835/282/588
Goodness-of-fit in F^2	1.089
Final R indexes [I>=2σ(I)]	R_1 = 0.0180, wR_2 = 0.0476
Final R indexes [all data]	R_1 = 0.0207, wR_2 = 0.0485
Largest diff. peak/hole/eÅ^{-3}	0.46/-0.57

5.6 [Li(thf)$_2$][3-COPh]

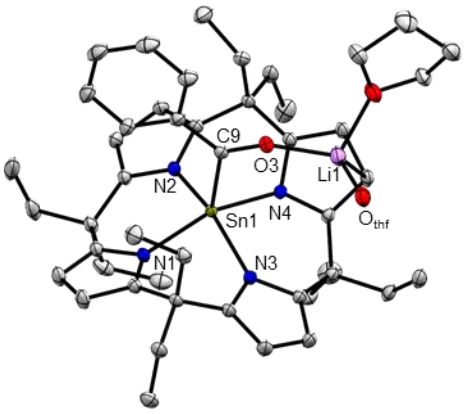


Figure S48: Solid state molecular structure of **[Li(thf)$_2$][3-COPh]**. Displacement ellipsoids are drawn at 50% probability level. Hydrogens and toluene solvent molecules are omitted for clarity.

Table S8: Crystal data for **[Li(thf)$_2$][3-COPh]**.

CCDC nmuber	2125919
Identification code	mo_hr389c_0m_a
Empirical formula	$C_{58}H_{77}LiN_4O_3Sn$
Formula weight	1003.86
Temperature/K	101(2)
Crystal system	triclinic
Space group	$P\bar{1}$ (2)
a/Å	10.618(3)
b/Å	11.653(3)
c/Å	21.103(5)
α/°	99.542(11)
β/°	93.042(8)
γ/°	92.079(12)
Volume/Å^3	2568.7(12)
Z	2
ρ_{calc}/g cm^{-3}	1.298
μ/mm^{-1}	0.545
F(000)	1060
Crystal size/mm^3	0.339×0.313×0.207
Radiation	MoK_α (λ=0.71073 Å)
2Θ range for data collection/°	3.92 to 61.11 (0.70 Å)
Index ranges	-15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -30 ≤ l ≤ 30
Reflections collected	101029
Independent reflections	15729 [R_{int} = 0.0476, R_{sigma} = 0.0311]
Data/restraints/parameters	15729/831/734
Goodness-of-fit in F^2	1.037
Final R indexes [I>=2σ(I)]	R_1 = 0.0242, wR_2 = 0.0560
Final R indexes [all data]	R_1 = 0.0263, wR_2 = 0.0572
Largest diff. peak/hole/eÅ^{-3}	0.49/-0.56

6 Infrared Spectroscopy

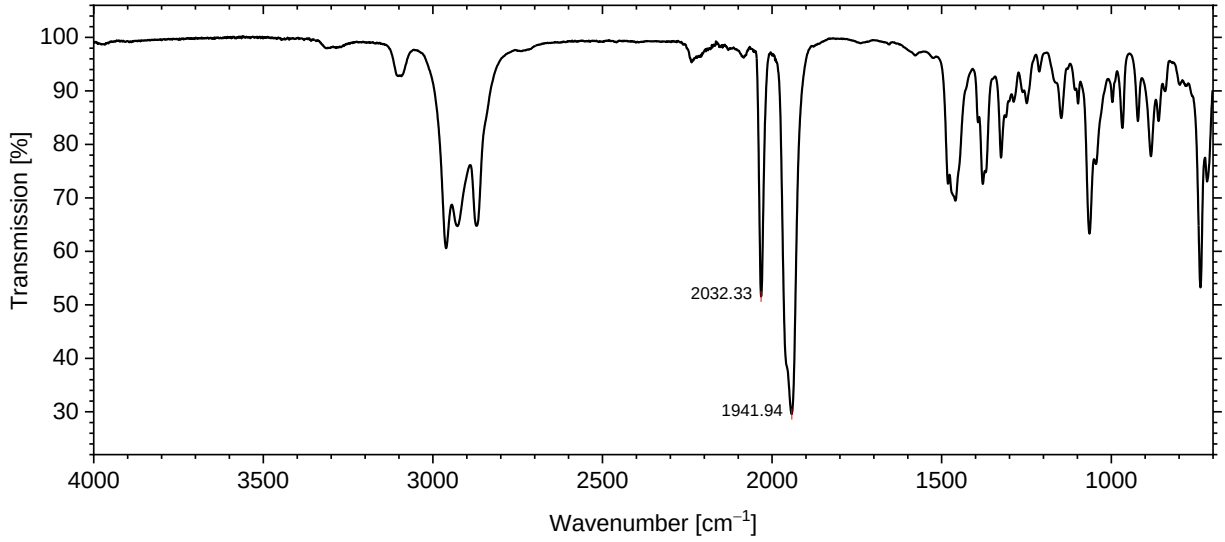


Figure S49: FTIR spectrum of **[(NBu$_4$)$_2$][Ni($^2\eta$-2)(CO)$_3$]** in THF-d_8.

7 Comparative TEP Scale

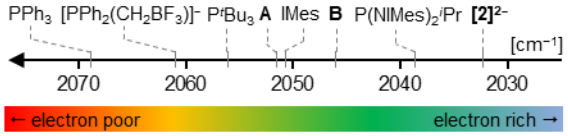


Figure S50. Comparison between TEP values of **[2]**$^{2-}$ and other literature known carbene and phosphine ligands.

Table S9. TEP values of **[2]**$^{2-}$ and other literature known carbene and phosphine ligands.

Compound	**TEP [cm^{-1}]**	**Solvent**	**Reference**
[2]$^{2-}$	2032.3	THF	This work
P(NIMes)$_2$iPr	2038.6	DCM	[20]
B	2046	DCM	[21]
IMes	2050.7	DCM	[22]
IPr (**A**)	2051.5	DCM	[20]
P^{t}Bu$_3$	2056.1	DCM	[20]
[PPh$_2$(CH$_2$BF$_3$)]$^-$	2061	DCM	[23]
PPh$_3$	2068.9	DCM	[20]

8 DFT Calculations

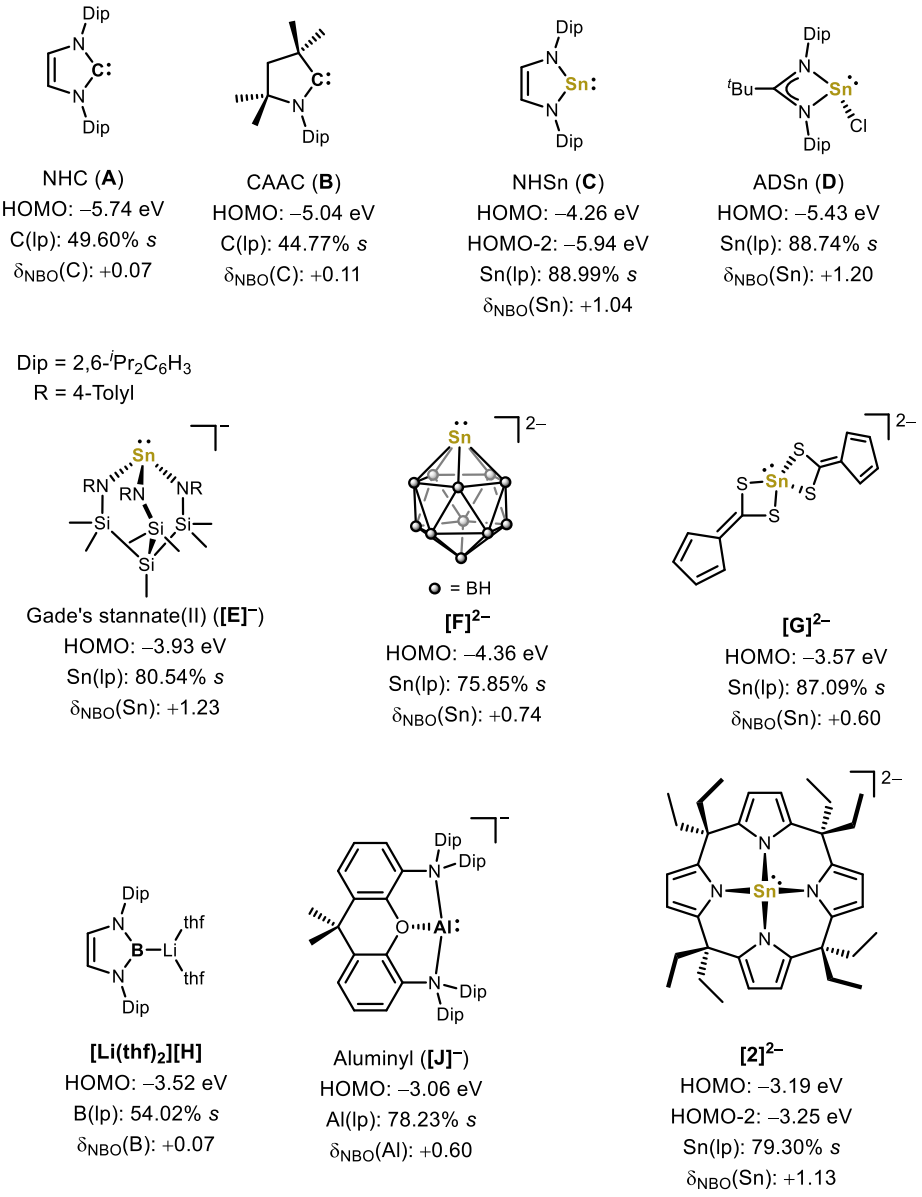


Figure S51. HOMO energy levels, *s*-character of the lone pair (lp), and NBO atomic charges δ_{NBO} of the central atom for the NHC **A**, the CAAC **B**, the NHSn **C**, ADSn **D**, the anionic stannate(II) **[E]**$^-$, the dianionc stannates(II) **[F]**$^{2-}$, and **[G]**$^{2-}$, the boryl **H**, the aluminyl anion **[J]**$^-$, and **[2]**$^{2-}$. HOMO energies were calculated at the B97M-D3(BJ)/def2-TZVPP CPCM(THF)//B97M-D3(BJ)/def2-TZVPP and NBO analysis at the PBE0/def2-TZVPP CPCM(THF)//B97M-D3(BJ)/def2-TZVPP level of theory. For **C** and **[2]**$^{2-}$ the HOMO and HOMO-1 are mainly ligand-centered and the energies of their HOMO-2 containing a mayor contribution of their tin-centered lone pairs are given as well.

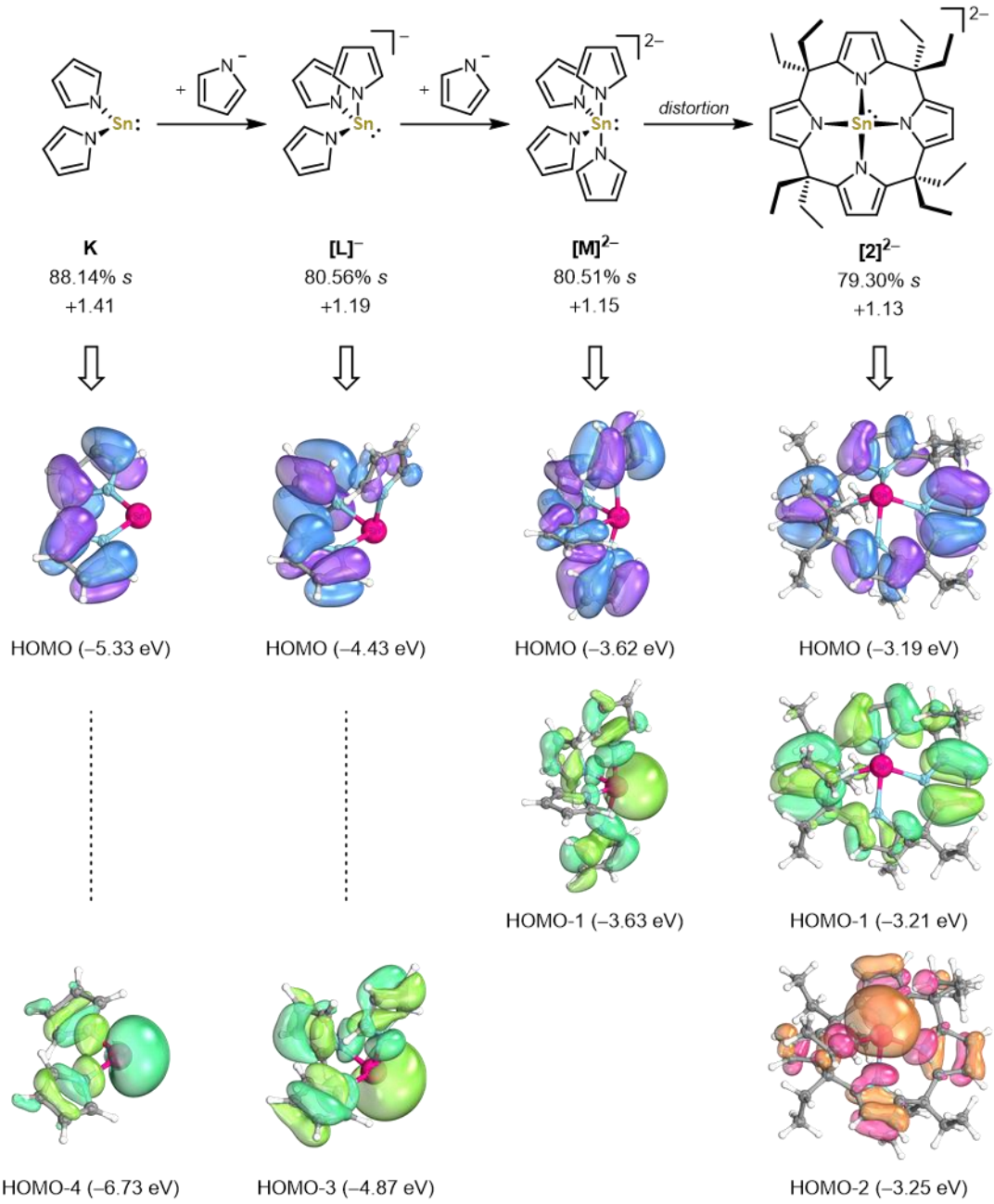


Figure S52. Frontier molecular orbital energies for the hypothetical pyrrolato stannanes **K**, **[M]**$^{-}$, and **[L]**$^{2-}$,and **[2]**$^{2-}$ at the B97M-D3(BJ)/def2-TVZPP CPCM(THF)//B97M-D3(BJ)/def2-TVZPP level of theory and *s*-character of the lone pair and NBO atomic charges at the central atom calculated on the PBE0/def2-TZVPP CPCM(THF)//B97M-D3(BJ)/def2-TZVPP level of theory. Isosurfaces sampled at a value of 0.03.

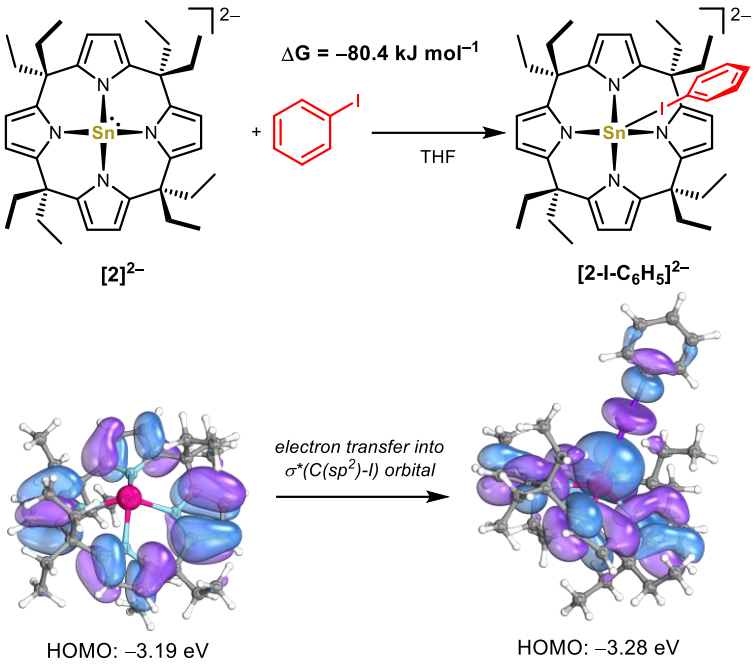


Figure S53. Free reaction enthalpy for the *σ*-hole adduction formation between **[2]**$^{2-}$ and iodobenzene and frontier molecular orbitals calculated on the B97M-D3(BJ)/def2-TVZPP CPCM(THF)//B97M-D3(BJ)/def2-TVZPP level of theory. Isosurfaces sampled at a value of 0.03.

9 Cyclic Voltammetry

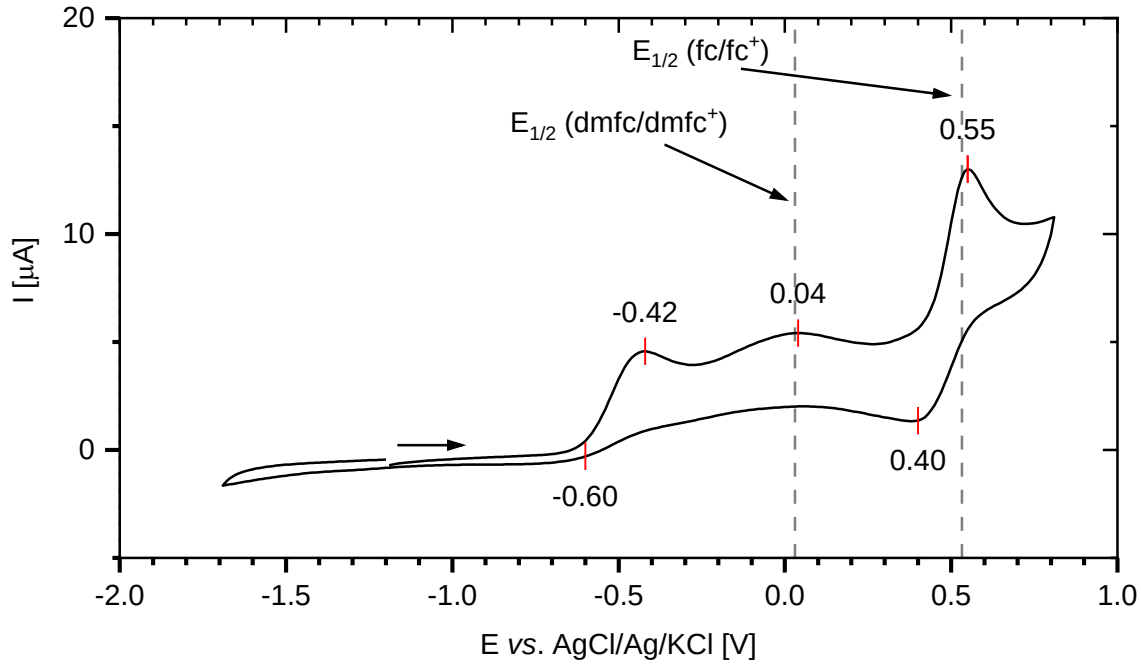


Figure S54: Cyclic voltammogram of **[$(NBu_4)_2$][2]** and [NBu_4][PF_6] in *o*DFB.

10 ETS-NOCV Results

Table S11: Bonding energy decomposition terms calculated on the BP86-D3/TZ2P COSMO(THF)//B97M-D3(BJ)/def2-TVZPP level of theory.

Compound	Total Pauli Repulsion (ΔE_{Pauli}) [Eh]	Total Electrostatic Interaction (ΔV_{elst}) [Eh]	Total Orbital Interaction ($\Delta E_{oi,tot}$) [Eh]	Total Dispersion Energy (E_{disp}) [Eh]	Solvation Energy (E_{solv}) [Eh]	Residue [Eh]	Total Bonding Energy (ΔE) [Eh]
[2]$^{2-}$	0.477164845	-1.340814347	-0.573479385	-0.010706268	-0.173999447	0.004544433	-0.169455015
[Sn(pyr)$_4$]$^{2-}$	0.463414466	-1.446258898	-0.535590216	-0.006556682	-0.20239567	0.00298029	-0.19941538
[2-Se]$^{2-}$	0.350999376	-0.236227689	-0.294142204	-0.012874307	-0.189065305	0.004530776	-0.184534529
[2^{H}-Se]$^{2-}$	0.331996112	-0.228345683	-0.292003221	-0.009634874	-0.216411735	0.003181708	-0.213230027

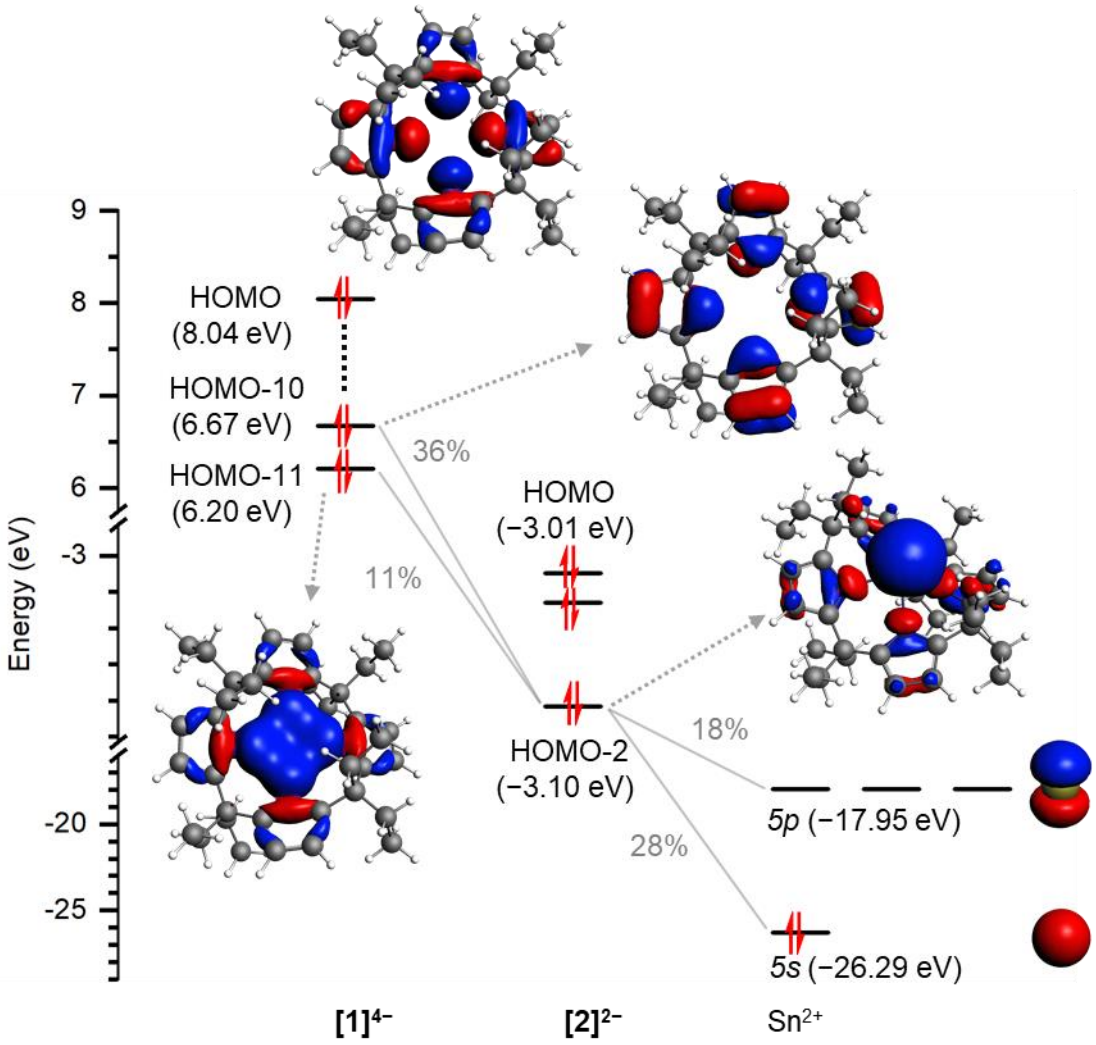
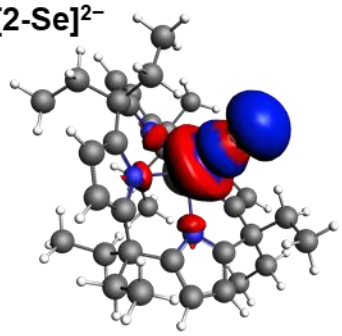
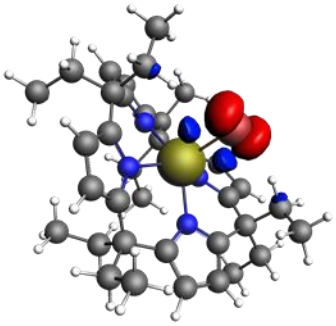


Figure S55. ETS-NOCV bond analysis of **[2]**$^{2-}$ on the BP86-D3/TZ2P COSMO(THF)//B97M-D3(BJ)/def2-TVZPP level of theory. Isosurfaces sampled at a value of 0.03.

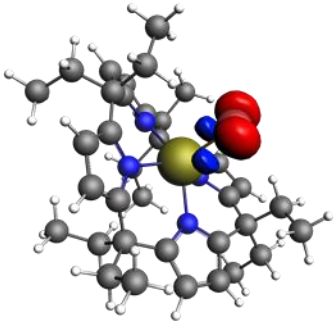
[2-Se]$^{2-}$



Sn→Se σ donation
$\Delta E_{oi}(\sigma)$ = −658.18 kJ mol^{-1}
(85.23% of $\Delta E_{oi,tot}$)

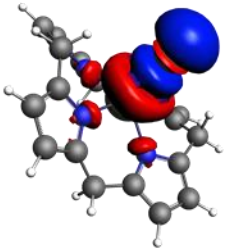


Se→π*(Sn-N) back donation
+ Se→σ*(C-H) donation
$\Delta E_{oi}(\pi_1)$ = −57.04 kJ mol^{-1}
(7.39% of $\Delta E_{oi,tot}$)

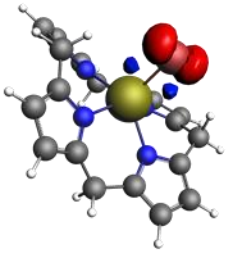


Se→π*(Sn-N) back donation
$\Delta E_{oi}(\pi_2)$ = −40.88 kJ mol^{-1}
(5.29% of $\Delta E_{oi,tot}$)

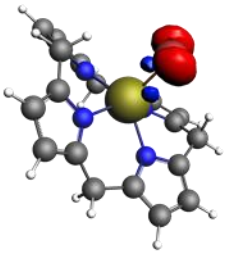
[2^{H}-Se]$^{2-}$



Sn→Se σ donation
$\Delta E_{oi}(\sigma)$ = −681.40 kJ mol^{-1}
(88.89% of $\Delta E_{oi,tot}$)



Se→π*(Sn-N) back donation
+ Se→ σ*(C-H) donation
$\Delta E_{oi}(\pi_1)$ = −44.28 kJ mol^{-1}
(5.78% of $\Delta E_{oi,tot}$)



Se→π*(Sn-N) back donation
$\Delta E_{oi}(\pi_2)$ = −35.64 kJ mol^{-1}
(4.65% of $\Delta E_{oi,tot}$)

Figure S56. ETS-NOCV bond analysis of **[2-Se]$^{2-}$** and the *meso*-unsubstituted derivative **[2^{H}-Se]$^{2-}$** on the BP86-D3/TZ2P COSMO(THF)//B97M-D3(BJ)/def2-TVZPP level of theory. The Se fragment was considered in its closed shell ^{1}D excited state with doubly occupied p_x and p_y orbitals and an empty p_z orbital directed towards the Sn(II) lone pair of a singlet tin(II) calix[4]pyrrolato fragment. NOCV deformation densities sampled at a value of 0.003. The color code of the charge flow is red to blue.

11 NBO Results

Table S12: NBO analysis results calculated on PBE0/def2-TZVPP CPCM(THF)//B97M-D3(BJ)/def2-TVZPP level of theory. NBO and second order perturbation theory stabilization energies $\Delta E^{(2)}$ for selected bonding interactions are given in kJ mol^{-1}. Additionally, Lewis density parameters $\%\rho_L$ and single point energies are given for each system.

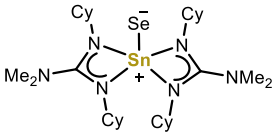
NHC (**A**) (single point energy = −1159.062799534277 Eh, $\%\rho_L$ = 97.91)	
s-Character of lp(1) at C2	49.60%
Natural charge at C2	0.073
CAAC (**B**) (single point energy = −874.060935133861 Eh, $\%\rho_L$ = 98.32)	
s-Character of lp(1) at C2	41.18%
Natural charge at C2	0.127
NHB Li THF Adduct (**H**) (single point energy = −1617.970242201778 Eh, $\%\rho_L$ = 99.32)	
s-Character of lp(1) at B1	54.02%
Natural charge at B1	0.072
NHSn (**C**) (single point energy = −1335.373499564167 Eh, $\%\rho_L$ = 98.13)	
s-Character of lp(1) at Sn2	88.99%
Natural charge at Sn2	1.040
ADSn (**D**) (single point energy = −1913.919385348876 Eh, $\%\rho_L$ = 99.98)	
s-Character of lp(1) at Sn2	88.74%
Natural charge at Sn2	1.203
Bis dithiolato stannate(II) **[G]**$^{2-}$ (single point energy = −2268.592659566669 Eh, $\%\rho_L$ = 98.23)	
s-Character of lp(1) at Sn1	87.09
Natural charge at Sn1	0.600
Stanna dodecaborate **[F]**$^{2-}$ (single point energy = −494.486522724303 Eh, $\%\rho_L$ = 98.31)	
s-Character of lp(1) at Sn5	75.85%
Natural charge at Sn5	0.741
Gade's stannate (II) (**[E]**$^{-}$) (single point energy = −2627.689403573425 Eh, $\%\rho_L$ = 98.29)	
s-Character of lp(1) at Sn78	80.54%
Natural charge at Sn78	1.232
Aldridge's Aluminyl Anion (**[J]**$^{-}$) (single point energy = −2293.177232006270 Eh, $\%\rho_L$ = 97.85)	
s-Character of lp(1) at Al29	78.34%
Natural charge at Al29	0.603
[2]$^{2-}$ (single point energy = −1832.964212044182 Eh, $\%\rho_L$ = 98.14)	
s-Character of lp(1) at Sn89	79.30%
Natural charge at Sn89	1.129
[2-Se]$^{2-}$ (single point energy = −4234.292224 Eh, $\%\rho_L$ = 98.40)	
NBO175 $\sigma_{Sn89\text{-}Se90}$ (occupation = 1.94116)	−925.49
$\Delta E^{(2)}$ lp(2)$_{Se90}\rightarrow\pi^*_{N1\text{-}Sn89}$	6.31
$\Delta E^{(2)}$ lp(2)$_{Se90}\rightarrow\pi^*_{N27\text{-}Sn89}$	14.83
$\Delta E^{(2)}$ lp(2)$_{Se90}\rightarrow\pi^*_{N61\text{-}Sn89}$	14.78
$\Delta E^{(2)}$ lp(2)$_{Se90}\rightarrow\pi^*_{N71\text{-}Sn89}$	6.26
$\Delta E^{(2)}$ lp(3)$_{Se90}\rightarrow\sigma^*_{C16\text{-}H17}$ (**C(sp^3)H-Se interaction**)	21.88
$\Delta E^{(2)}$ lp(3)$_{Se90}\rightarrow\sigma^*_{C78\text{-}H80}$ (**C(sp^3)H-Se interaction**)	21.67
$\Delta E^{(2)}$ lp(3)$_{Se90}\rightarrow\pi^*_{N1\text{-}Sn89}$	14.30
$\Delta E^{(2)}$ lp(3)$_{Se90}\rightarrow\pi^*_{N27\text{-}Sn89}$	4.86

$\Delta E^{(2)}$ lp(3)$_{Se90}\rightarrow\pi^*_{N61\text{-}Sn89}$	4.86
$\Delta E^{(2)}$ lp(3)$_{Se90}\rightarrow\pi^*_{N71\text{-}Sn89}$	14.25
[2^{H}-Se]$^{2-}$ (single point energy = −3605.895922 Eh, %ρ_L = 98.06)	
NBO111 $\sigma_{Sn33\text{-}Se34}$ (occupation = 1.94806)	−953.08
$\Delta E^{(2)}$ lp(2)$_{Se34}\rightarrow\pi^*_{N1\text{-}Sn33}$	8.79
$\Delta E^{(2)}$ lp(2)$_{Se34}\rightarrow\pi^*_{N13\text{-}Sn33}$	9.25
$\Delta E^{(2)}$ lp(2)$_{Se34}\rightarrow\pi^*_{N19\text{-}Sn33}$	9.25
$\Delta E^{(2)}$ lp(2)$_{Se34}\rightarrow\pi^*_{N29\text{-}Sn33}$	8.74
$\Delta E^{(2)}$ lp(3)$_{Se34}\rightarrow\sigma^*_{C32\text{-}H40}$ (**C(sp^3)H-Se interaction**)	4.14
$\Delta E^{(2)}$ lp(3)$_{Se34}\rightarrow\sigma^*_{C8\text{-}H36}$ (**C(sp^3)H-Se interaction**)	4.06
$\Delta E^{(2)}$ lp(3)$_{Se34}\rightarrow\pi^*_{N1\text{-}Sn33}$	9.29
$\Delta E^{(2)}$ lp(3)$_{Se34}\rightarrow\pi^*_{N13\text{-}Sn33}$	8.74
$\Delta E^{(2)}$ lp(3)$_{Se34}\rightarrow\pi^*_{N19\text{-}Sn33}$	8.74
$\Delta E^{(2)}$ lp(3)$_{Se34}\rightarrow\pi^*_{N29\text{-}Sn33}$	9.29

12 ^{77}Se and ^{119}Sn NMR Shift Calculation Results

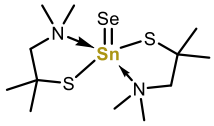
Table S13: ^{77}Se and ^{119}Sn NMR shifts calculated on the PBE0/SO-ZORA-TZ2P COSMO(THF)//B97M-D3(BJ)/def2-TZVPP level of theory and referenced against $SeMe_2$ and $SnMe_4$, respectively.

Compound	Total ^{119}Sn NMR isotropic shielding tensor [ppm]	^{119}Sn NMR chemical shift against $SnMe_4$ [ppm]	Total ^{77}Se NMR isotropic shielding tensor [ppm]	^{77}Se NMR chemical shift against $SeMe_2$ [ppm]
$SnMe_4$	3004.14	0.00	-	-
$SeMe_4$	-	-	1978.08	0.00
[2]$^{2-}$	3513.52	-509.38	-	-
[2-Se]$^{2-}$	3575.747	-571.606	2427.45	-449.37
[2^{H}-Se]$^{2-}$	3562.074	-557.933	2616.62	-638.54



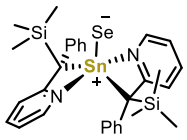
Ahmet *et al. J. Inorg. Chem.* **2018**, 2018, 1670-1678.

$\delta(^{77}Se, C_6D_6)$ = –476.01 ppm
$\delta(^{119}Sn, C_6D_6)$ = –566.30 ppm



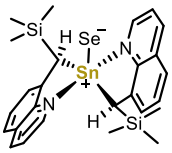
Park *et al. Inorg. Chem.* **2020,** 59, 3513-3517.

$\delta(^{77}Se, C_6D_6)$ = –218.13 ppm
$\delta(^{119}Sn, C_6D_6)$ = –264.50 ppm



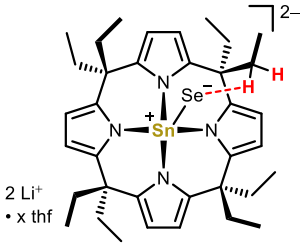
Leung *et al.* Organometallics **2000**, 19, 296-303.

$\delta(^{77}Se, THF/C_6D_6)$ = –531.95 ppm
$\delta(^{119}Sn, THF/C_6D_6)$ = –179.18 ppm



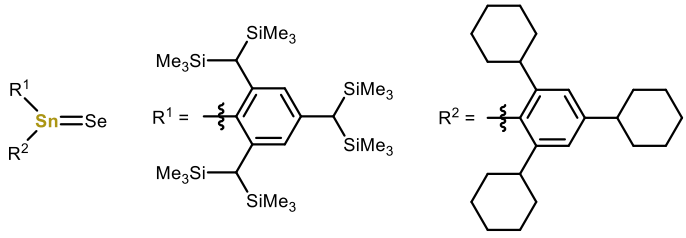
Leung *et al.* Organometallics **2000**, 19, 296-303.

$\delta(^{77}Se, THF/C_6D_6)$ = –734.8 ppm
$\delta(^{119}Sn, THF/C_6D_6)$ = –111.55 ppm



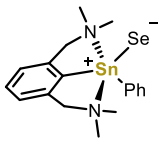
$[Li_2(thf)_x][2\text{-}Se]$

$\delta(^{77}Se, THF\text{-}d_8)$ = –391.99 ppm
$\delta(^{119}Sn, THF\text{-}d_8)$ = –560.18 ppm



Saito *et al.* J. Am. Chem. Soc. **2004**, 126, 15572-15582.

$\delta(^{77}Se, CDCl_{36})$ = 839 ppm
$\delta(^{119}Sn, CDCl_3)$ = 556 ppm



Mairychová *et al.* Organometallics **2011**,30, 5904-5910.

$\delta(^{77}Se, CDCl_{36})$ = –570.90 ppm
$\delta(^{119}Sn, CDCl_3)$ = –4.70 ppm

Figure S57. Experimental ^{77}Se and ^{119}Sn NMR data for **$[Li_2(thf)_x][2\text{-}Se]$** and other literature-known, monomeric stanna(II) selenido complexes.

13 Optimized Molecular Geometries

aldrdige_aluminyl_anion_B97M_D3_TZVPP_optfreq

Total correction: 2823.8826 kJ/mol
Single point energy: -6032185.6891 kJ/mol

Total enthalpy: -6029359.3278 kJ/mol
Final entropy term: 343.6942 kJ/mol
Total gibbs free enthalpy: -6029703.022 kJ/mol
Method and Basis: B97M-D3BJ / def2-TZVPP

xyz, charge: -1, multiplicity: 1

C	0.561060	0.112350	0.399967
C	0.916841	-0.035129	3.089450
C	0.346933	-1.126870	0.988810
C	0.845545	1.279366	1.059714
C	1.042116	1.192620	2.433955
C	0.567449	-1.174009	2.375185
H	1.277005	2.078148	2.995806
H	0.416692	-2.111941	2.874651
C	0.861701	2.549502	0.214672
C	0.789340	3.797524	1.070399
H	1.645420	3.850361	1.734980
H	-0.113815	3.817783	1.670766
H	0.806764	4.685072	0.446653
C	2.158465	2.584780	-0.604001
H	3.018769	2.618430	0.059136
H	2.173501	3.464888	-1.241176
H	2.244960	1.707188	-1.232328
C	-0.326497	2.442259	-0.734196
C	-2.599602	1.865423	-2.255763
C	-1.241714	3.447182	-1.036875
C	-0.558094	1.206001	-1.275472
C	-1.722106	0.815326	-1.928653
C	-2.359114	3.164342	-1.826754
H	-1.094427	4.438921	-0.649754
H	-3.497742	1.620601	-2.789335
O	0.295261	0.150420	-0.963631
N	-1.895535	-0.517053	-2.118486
N	-0.100671	-2.117793	0.167679
Al	-0.344549	-1.771904	-1.802808
C	-0.121092	-3.428693	0.643364
C	-0.308078	-6.097913	1.437613
C	1.035426	-4.113464	1.050111
C	-1.330147	-4.122286	0.600890
C	-1.446271	-5.446557	0.985165
C	0.905710	-5.434008	1.456146
H	-2.198546	-3.587052	0.257772
H	1.788074	-5.971975	1.766777
H	-0.358154	-7.128017	1.753806
C	-3.061293	-0.904287	-2.805385
C	-5.368831	-1.590132	-4.155772
C	-3.081067	-0.858887	-4.205297

C	-4.190220	-1.331622	-2.076843
C	-5.363731	-1.652311	-2.768765
C	-4.246853	-1.215205	-4.861267
H	-4.282082	-1.184498	-5.939046
H	-6.277070	-1.837428	-4.684069
C	-1.882358	-0.422156	-5.004808
H	-1.082617	-0.201765	-4.307624
C	-4.078494	-1.362063	-0.568095
H	-3.014381	-1.387676	-0.361330
C	2.407149	-3.503271	0.926035
H	2.291657	-2.449400	0.710939
C	-2.771574	-6.151498	0.900784
H	-3.503649	-5.418979	0.566911
C	-1.394256	-1.539879	-5.913183
H	-0.514705	-1.223022	-6.468631
H	-2.158827	-1.826151	-6.632498
H	-1.126709	-2.412403	-5.327058
C	-2.178408	0.839172	-5.803934
H	-1.293126	1.167367	-6.342975
H	-2.495597	1.647531	-5.152914
H	-2.965608	0.665880	-6.534730
C	-4.602345	-0.075150	0.058498
H	-5.664991	0.054061	-0.135086
H	-4.081817	0.788659	-0.337331
H	-4.460440	-0.091251	1.136551
C	-4.680671	-2.580177	0.121061
H	-4.496749	-3.489989	-0.442128
H	-5.749265	-2.493194	0.276877
H	-4.224900	-2.700893	1.099651
C	-2.730286	-7.275011	-0.124657
H	-2.012664	-8.035795	0.171734
H	-2.432274	-6.901488	-1.098288
H	-3.702460	-7.752945	-0.221550
C	-3.220682	-6.679385	2.254597
H	-3.274582	-5.881535	2.988226
H	-2.523920	-7.424774	2.628748
H	-4.199706	-7.147531	2.184843
C	3.228110	-3.626897	2.198664
H	2.719025	-3.166745	3.039242
H	4.190980	-3.136672	2.080415
H	3.420348	-4.666624	2.451258
C	3.137937	-4.125500	-0.257148
H	4.117289	-3.670202	-0.388540
H	2.569501	-3.986198	-1.171037
H	3.279079	-5.193371	-0.105220
C	-6.647024	-2.040552	-2.097547
H	-6.626827	-3.059145	-1.721152

H	-7.465392	-1.973646	-2.807066
H	-6.886993	-1.399217	-1.257275
C	1.164038	-0.084983	4.590832
C	0.892726	-1.457251	5.187077
H	1.074186	-1.429010	6.258229
H	1.539544	-2.217323	4.762168
H	-0.135622	-1.765817	5.029513
C	0.260255	0.917743	5.304938
H	0.430627	0.881365	6.379048
H	-0.784719	0.690534	5.117618
H	0.442448	1.933139	4.972514
C	-3.315010	4.298516	-2.169101
C	-2.566642	5.366429	-2.964293
H	-1.730678	5.766206	-2.401032
H	-3.231637	6.190199	-3.217167
H	-2.174777	4.948921	-3.886927
C	-3.861062	4.921323	-0.886026
H	-3.067075	5.323180	-0.266811
H	-4.395200	4.179908	-0.299631
H	-4.548346	5.732002	-1.120274
C	-4.498670	3.836500	-3.004630
H	-4.179305	3.399234	-3.945142
H	-5.136668	4.686831	-3.230715
H	-5.098411	3.100302	-2.479492
C	2.623458	0.270964	4.867523
H	2.828770	0.244497	5.936178
H	2.862871	1.262901	4.499803
H	3.286265	-0.434124	4.374782

dipp_caac_B97M_D3_TZVPP_optfreq

Total correction:	1298.8758 kJ/mol
Single point energy:	-2196405.6075 kJ/mol
Total enthalpy:	-2195104.2527 kJ/mol
Final entropy term:	184.9048 kJ/mol
Total gibbs free enthalpy:	-2195289.1576 kJ/mol
Method and Basis:	B97M-D3BJ / def2-TZVPP

xyz, charge: 0, multiplicity: 1

C	-0.712336	-0.492345	1.640589
C	0.569440	0.167547	2.086035
N	0.217252	1.188984	2.810161
C	-1.266664	1.449481	3.024701
C	-1.846254	0.485437	1.999896
H	-2.146951	1.036216	1.113201
H	-2.728181	-0.018459	2.381398

C	-0.662492	-0.775778	0.150085
H	0.158473	-1.444516	-0.083339
H	-0.517760	0.139856	-0.415856
H	-1.590434	-1.234675	-0.182802
C	-0.824183	-1.810924	2.399474
H	0.032747	-2.441540	2.190759
H	-1.725320	-2.338828	2.098648
H	-0.867557	-1.657117	3.472964
C	-1.629361	2.894463	2.755940
H	-1.430673	3.178770	1.731265
H	-1.090181	3.567984	3.413602
H	-2.690316	3.032134	2.937899
C	-1.657892	1.112956	4.451586
H	-1.506142	0.066213	4.680326
H	-2.709482	1.337726	4.596584
H	-1.091108	1.706984	5.160311
C	1.187904	2.036291	3.437881
C	2.982327	3.729344	4.670848
C	1.694007	1.691119	4.692160
C	1.635012	3.167969	2.753131
C	2.529208	4.011139	3.397517
C	2.585661	2.566195	5.298465
H	2.890109	4.887115	2.886627
H	2.991078	2.319199	6.264477
H	3.670736	4.398197	5.159373
C	1.294947	3.412365	1.306474
H	0.460430	2.776867	1.040103
C	0.906173	4.851250	1.015656
H	0.085406	5.179703	1.645046
H	0.602023	4.956137	-0.021323
H	1.737553	5.530341	1.175686
C	2.472223	2.976338	0.441823
H	3.355475	3.565089	0.673736
H	2.243893	3.111089	-0.611793
H	2.704274	1.931099	0.614071
C	1.427582	0.351160	5.325284
H	0.590195	-0.105965	4.817167
C	1.093261	0.438311	6.804212
H	1.933966	0.806666	7.383587
H	0.844046	-0.545143	7.190649
H	0.250989	1.097143	6.989697
C	2.632203	-0.553128	5.090835
H	3.518590	-0.140228	5.564729
H	2.827234	-0.656780	4.029397
H	2.455398	-1.540477	5.508327

dipp_cnc_sncl_B97M_D3_TZVPP_optfreq

Total correction:	1855.0072 kJ/mol
Single point energy:	-5032447.3356 kJ/mol
Total enthalpy:	-5030589.8495 kJ/mol
Final entropy term:	263.0695 kJ/mol
Total gibbs free enthalpy:	-5030852.919 kJ/mol
Method and Basis:	B97M-D3BJ / def2-TZVPP

xyz, charge: 0, multiplicity: 1

N	0.770739	1.251775	2.266860
Sn	2.017439	-0.540098	2.784476
C	-0.171313	1.027986	3.176781
N	0.130326	-0.055932	3.892699
C	-1.351615	1.948444	3.486895
C	-1.406844	3.187413	2.604593
H	-0.487684	3.757007	2.638084
H	-2.206073	3.821036	2.975675
H	-1.621113	2.957295	1.570154
C	-2.694726	1.232800	3.369524
H	-2.786294	0.410540	4.063025
H	-2.867982	0.863462	2.364789
H	-3.480592	1.947653	3.593738
C	-1.169563	2.422957	4.930016
H	-0.196775	2.882225	5.073094
H	-1.274240	1.610791	5.632839
H	-1.930578	3.163847	5.153414
C	-0.634860	-0.765766	4.834823
C	-2.061164	-2.285985	6.673837
C	-1.577175	-1.707844	4.384980
C	-0.354956	-0.646097	6.203271
C	-1.090882	-1.404601	7.103142
C	-2.285569	-2.445202	5.319773
H	-0.887427	-1.310711	8.156187
H	-3.016450	-3.160771	4.984629
H	-2.624525	-2.863143	7.387301
C	0.800825	2.082596	1.135002
C	1.060265	3.575707	-1.192563
C	1.705283	3.149093	1.092200
C	0.021290	1.763080	0.010356
C	0.166454	2.522268	-1.138779
C	1.817500	3.881320	-0.081348
H	-0.426871	2.288568	-2.005724
H	2.511271	4.704498	-0.119479
H	1.161737	4.153183	-2.095679
C	-0.938872	0.604074	0.037804
H	-1.224694	0.439496	1.069168

C	-0.263516	-0.669111	-0.451839
H	0.051732	-0.555938	-1.485197
H	-0.941211	-1.516608	-0.393820
H	0.618895	-0.905492	0.135175
C	-2.220738	0.855611	-0.736427
H	-2.044785	0.905124	-1.806158
H	-2.693569	1.784488	-0.433722
H	-2.923532	0.045933	-0.564549
C	2.554031	3.516158	2.278713
H	2.267538	2.878485	3.106081
C	4.025119	3.259806	1.986295
H	4.630277	3.457415	2.865050
H	4.374389	3.899091	1.179504
H	4.196724	2.229084	1.696368
C	2.343585	4.962466	2.702645
H	2.926050	5.181825	3.592202
H	1.301062	5.168834	2.924093
H	2.657542	5.654028	1.926273
C	0.784277	0.200463	6.702527
H	1.103132	0.848868	5.895076
C	1.956432	-0.708116	7.053593
H	2.827115	-0.123838	7.332077
H	2.238268	-1.333360	6.213650
H	1.693700	-1.359263	7.883473
C	0.422895	1.065384	7.898961
H	1.261106	1.703199	8.161031
H	0.191669	0.463696	8.772683
H	-0.433017	1.700884	7.699188
C	-1.761284	-1.985870	2.916174
H	-1.407435	-1.123483	2.364565
C	-3.204136	-2.230614	2.509540
H	-3.857966	-1.432019	2.841810
H	-3.583104	-3.162656	2.916447
H	-3.278462	-2.301841	1.428404
C	-0.896324	-3.173987	2.511582
H	0.149932	-3.004871	2.747283
H	-0.973416	-3.367989	1.445572
H	-1.211111	-4.066993	3.044044
Cl	3.452451	0.671793	4.277701

gade_tol_sn_B97M_D3_TZVPP_optfreq

Total correction:	1793.2969 kJ/mol
Single point energy:	-6907356.5888 kJ/mol
Total enthalpy:	-6905560.8128 kJ/mol
Final entropy term:	310.1679 kJ/mol

Total gibbs free enthalpy: -6905870.9808 kJ/mol
Method and Basis: B97M-D3BJ / def2-TZVPP

xyz, charge: -1, multiplicity: 1

C	1.438848	2.552618	0.497423
C	1.343245	3.638034	-0.387741
H	1.372284	4.636327	0.018316
C	1.245169	3.453600	-1.753509
H	1.177881	4.318649	-2.397166
C	1.250598	2.186658	-2.320313
C	1.355117	1.105039	-1.454083
H	1.358511	0.103567	-1.860257
C	1.437174	1.276673	-0.086494
H	1.482674	0.413954	0.557916
C	1.112094	1.992328	-3.795517
H	0.071615	1.864467	-4.094559
H	1.648909	1.110486	-4.134822
H	1.496345	2.847020	-4.345073
C	1.652466	0.339370	3.662367
H	0.755159	0.647900	4.188394
H	2.305207	-0.163397	4.373279
H	1.363523	-0.387260	2.905315
C	4.022888	1.190882	1.987430
H	3.788321	0.429054	1.250127
H	4.728148	0.763763	2.697089
H	4.521666	2.006941	1.472751
C	4.796897	2.940452	5.389722
H	5.611923	2.730228	4.703226
H	4.654792	2.064791	6.016431
H	5.104251	3.762121	6.030202
C	-1.133987	2.791569	4.947591
C	-1.790601	3.013431	6.166945
H	-1.356181	3.706158	6.869110
C	-2.989395	2.396235	6.468100
H	-3.462946	2.599974	7.417910
C	-3.614223	1.538849	5.571901
C	-2.980879	1.323627	4.354731
H	-3.437946	0.664560	3.630882
C	-1.773571	1.920376	4.050294
H	-1.293668	1.709663	3.108075
C	-4.901081	0.858031	5.909101
H	-4.748013	-0.174198	6.223935
H	-5.575181	0.829760	5.056721
H	-5.414448	1.366130	6.720275
C	1.327062	2.336825	7.066630
H	0.484691	2.416785	7.747038
H	2.239719	2.406493	7.654550

H	1.296016	1.348992	6.616265
C	1.272180	5.324147	6.601039
H	1.250399	6.130401	5.875452
H	2.147868	5.461449	7.232400
H	0.390235	5.417995	7.231894
C	1.121195	6.992468	3.063088
C	-0.089354	7.305912	3.699272
H	-0.617913	6.520824	4.215685
C	-0.601710	8.589920	3.691842
H	-1.539459	8.784084	4.191640
C	0.063998	9.636829	3.071558
C	1.266623	9.338329	2.440298
H	1.803959	10.125986	1.931247
C	1.779091	8.057218	2.426474
H	2.692375	7.853071	1.891726
C	-0.474877	11.030562	3.093855
H	0.058404	11.664932	3.801603
H	-1.522290	11.041611	3.379660
H	-0.392878	11.508974	2.120571
C	4.161437	6.613479	4.223592
H	4.260155	7.560401	3.701545
H	5.160900	6.263034	4.471924
H	3.633860	6.801951	5.154006
C	4.184448	5.128475	1.591761
H	3.698293	4.395563	0.956679
H	5.208102	4.801296	1.763325
H	4.224024	6.069965	1.047028
N	1.505903	2.755440	1.857997
N	0.051732	3.405381	4.610186
N	1.596903	5.700140	3.046478
Si	2.506749	1.824836	2.901499
Si	1.328630	3.662924	5.733347
Si	3.262330	5.305950	3.214681
Si	3.208303	3.369801	4.448491
Sn	0.085188	4.213961	2.599105

iPr_NHC_B97M_D3_TZVPP_optfreq

Total correction:	1592.3559 kJ/mol
Single point energy:	-3049451.8114 kJ/mol
Total enthalpy:	-3047856.9764 kJ/mol
Final entropy term:	222.8927 kJ/mol
Total gibbs free enthalpy:	-3048079.869 kJ/mol
Method and Basis:	B97M-D3BJ / def2-TZVPP

xyz, charge: 0, multiplicity: 1

N	-0.698174	0.842655	1.111872
C	0.509529	1.213088	1.619677
N	0.133009	1.910611	2.726631
C	-1.238845	1.967178	2.898740
C	-1.769893	1.290497	1.863992
H	-1.693008	2.473412	3.723974
H	-2.784635	1.087606	1.594367
C	-0.853213	0.095849	-0.090058
C	-1.168622	-1.343728	-2.404256
C	-0.752951	0.760662	-1.308370
C	-1.107094	-1.273379	0.002293
C	-1.267861	-1.979750	-1.180066
C	-0.909119	0.009881	-2.466730
H	-1.465248	-3.036288	-1.147038
H	-0.826507	0.493037	-3.425109
H	-1.292492	-1.909016	-3.312672
C	1.053561	2.497757	3.639830
C	2.817960	3.635595	5.406305
C	1.673823	1.682749	4.581692
C	1.292333	3.870386	3.557643
C	2.183859	4.424460	4.463592
C	2.568790	2.279727	5.460721
H	2.391877	5.478939	4.429632
H	3.072959	1.673859	6.193937
H	3.510819	4.082671	6.099304
C	-0.432389	2.228926	-1.389895
H	-0.567225	2.658915	-0.402637
C	-1.347801	2.973135	-2.348483
H	-2.393364	2.827034	-2.096842
H	-1.204295	2.648486	-3.374460
H	-1.136764	4.037593	-2.315196
C	1.028545	2.413743	-1.777619
H	1.678550	1.929525	-1.057815
H	1.284648	3.468302	-1.819932
H	1.218456	1.980945	-2.756392
C	-1.116391	-1.963521	1.341348
H	-1.501478	-1.261994	2.076160
C	-1.994245	-3.200424	1.384273
H	-3.003509	-2.993060	1.043072
H	-2.050916	-3.578175	2.400014
H	-1.590848	-3.999842	0.770219
C	0.313881	-2.308305	1.742880
H	0.945196	-1.427760	1.739599
H	0.733580	-3.027643	1.044501
H	0.338131	-2.748950	2.735927
C	0.666701	4.694057	2.462378
H	-0.309978	4.272046	2.242825

C	1.511139	4.576613	1.197914
H	2.495723	5.004997	1.366261
H	1.046822	5.112231	0.374250
H	1.640077	3.540567	0.908111
C	0.462680	6.150741	2.834904
H	1.407927	6.674923	2.937781
H	-0.082298	6.257608	3.767437
H	-0.097865	6.656362	2.055297
C	1.436395	0.197340	4.630578
H	0.570882	-0.026422	4.015575
C	1.145308	-0.297688	6.038172
H	0.309750	0.233319	6.482840
H	2.002965	-0.174778	6.692377
H	0.903144	-1.355889	6.019378
C	2.629154	-0.534704	4.030735
H	2.795495	-0.219287	3.007028
H	2.464810	-1.608202	4.038663
H	3.529195	-0.327177	4.603603

iPr_NHSn_B97M_D3_TZVPP_optfreq

Total correction:	1577.514 kJ/mol
Single point energy:	-3512414.6779 kJ/mol
Total enthalpy:	-3510834.6849 kJ/mol
Final entropy term:	239.2382 kJ/mol
Total gibbs free enthalpy:	-3511073.9231 kJ/mol
Method and Basis:	B97M-D3BJ / def2-TZVPP

xyz, charge: 0, multiplicity: 1

N	-0.304608	0.590122	0.755046
Sn	1.693699	0.896444	1.266522
N	0.660511	1.845190	2.809855
C	-0.699951	1.784512	2.705151
C	-1.204936	1.127469	1.630097
H	-1.311026	2.250824	3.458340
H	-2.258690	1.017631	1.441042
C	-0.773076	-0.064861	-0.408381
C	-1.552912	-1.361345	-2.724478
C	-0.975087	0.678329	-1.577030
C	-0.982453	-1.447876	-0.383798
C	-1.367491	-2.078475	-1.558803
C	-1.361090	0.006488	-2.728335
H	-1.520128	-3.144649	-1.561298
H	-1.508161	0.560895	-3.640004
H	-1.848625	-1.867372	-3.628035
C	1.242193	2.566401	3.879312

C	2.508033	3.954885	5.909974
C	1.600761	1.892753	5.051786
C	1.489251	3.935482	3.725432
C	2.129597	4.610833	4.754805
C	2.240997	2.607630	6.054675
H	2.339500	5.661842	4.647756
H	2.536367	2.102001	6.958559
H	3.008136	4.493599	6.697164
C	-0.739712	2.165780	-1.613973
H	-0.641223	2.511976	-0.590626
C	-1.898600	2.919313	-2.247078
H	-2.836259	2.690650	-1.751643
H	-2.010117	2.672776	-3.298620
H	-1.732404	3.990341	-2.181438
C	0.562319	2.478472	-2.339187
H	1.405466	1.983756	-1.865497
H	0.757500	3.547152	-2.344266
H	0.518408	2.138680	-3.370388
C	-0.756963	-2.253861	0.868212
H	-0.668709	-1.559026	1.696541
C	-1.914729	-3.191711	1.170633
H	-2.854876	-2.653313	1.227372
H	-1.754324	-3.694961	2.119321
H	-2.017667	-3.959965	0.410305
C	0.549636	-3.029707	0.768716
H	1.391067	-2.363297	0.601331
H	0.516295	-3.731487	-0.060275
H	0.739350	-3.591613	1.678864
C	1.118114	4.664399	2.460361
H	0.467643	4.017082	1.882114
C	2.360708	4.942161	1.624857
H	3.051989	5.582352	2.166205
H	2.100017	5.438214	0.694174
H	2.885273	4.022538	1.381715
C	0.360297	5.953125	2.736385
H	0.980020	6.679302	3.253662
H	-0.517954	5.771866	3.346926
H	0.037908	6.407879	1.804578
C	1.344238	0.418189	5.218780
H	0.654605	0.113238	4.438794
C	0.705903	0.087318	6.558390
H	-0.203818	0.657301	6.714628
H	1.376534	0.299295	7.385554
H	0.457253	-0.968524	6.606465
C	2.635639	-0.367046	5.033206
H	3.073947	-0.179342	4.057105
H	2.458774	-1.435034	5.124144

H 3.368291 -0.080968 5.783036

boryl_li_thf2_B97M_D3_TZVPP_optfreq

Total correction:	2260.2654 kJ/mol
Single point energy:	-4256791.2991 kJ/mol
Total enthalpy:	-4254528.5546 kJ/mol
Final entropy term:	296.8922 kJ/mol
Total gibbs free enthalpy:	-4254825.4467 kJ/mol
Method and Basis:	B97M-D3BJ / def2-TZVPP

xyz, charge: 0, multiplicity: 1

B	1.027853	1.956075	3.435961
N	1.088029	3.419834	3.517284
C	2.395416	3.888038	3.472468
H	2.632863	4.933140	3.511733
C	3.222467	2.834204	3.355835
H	4.292553	2.817909	3.291192
N	2.457819	1.673390	3.311364
Li	-0.839844	0.753407	3.602372
C	0.013001	4.301311	3.737422
C	-0.161607	4.870195	5.005244
C	-1.226731	5.739075	5.202188
H	-1.377699	6.185593	6.169422
C	-2.105170	6.030301	4.176495
H	-2.926215	6.707340	4.344984
C	-1.932420	5.448130	2.935057
H	-2.624706	5.679389	2.144332
C	-0.879370	4.576936	2.692865
C	0.723338	4.459487	6.154780
H	1.705780	4.232252	5.755978
C	0.890612	5.533752	7.213504
H	1.212132	6.477000	6.783195
H	1.634083	5.223283	7.940916
H	-0.031684	5.712715	7.758970
C	0.180738	3.178230	6.778667
H	-0.809324	3.351734	7.195165
H	0.828116	2.836161	7.581793
H	0.110874	2.388160	6.037369
C	-0.665309	3.962856	1.334744
H	-0.278878	2.961591	1.504716
C	0.395066	4.739594	0.564421
H	0.068308	5.762716	0.393829
H	0.582021	4.280194	-0.402535
H	1.330678	4.767996	1.110455
C	-1.935413	3.838763	0.515563

H	-2.719872	3.327955	1.068094
H	-1.738774	3.272237	-0.389396
H	-2.322398	4.806397	0.208005
C	3.083201	0.412464	3.364986
C	3.245647	-0.338898	2.193138
C	3.860628	-1.579504	2.284621
H	3.995003	-2.174594	1.398108
C	4.313683	-2.064718	3.498713
H	4.791676	-3.028984	3.548508
C	4.148714	-1.312636	4.643743
H	4.490537	-1.699322	5.589889
C	3.529275	-0.070193	4.597875
C	2.797402	0.221982	0.868079
H	1.881822	0.778544	1.055389
C	3.829540	1.207339	0.330395
H	3.990557	2.026365	1.018944
H	3.501953	1.624071	-0.618197
H	4.779482	0.704214	0.167191
C	2.512689	-0.836613	-0.181616
H	2.063226	-0.377942	-1.056531
H	1.835966	-1.604767	0.179529
H	3.423174	-1.328569	-0.512497
C	3.300267	0.700162	5.871960
H	2.883237	1.664554	5.607882
C	4.594310	0.940454	6.632512
H	5.047984	0.007576	6.955566
H	4.407674	1.538369	7.519859
H	5.317996	1.465385	6.017524
C	2.280315	-0.016184	6.745031
H	1.333966	-0.111599	6.221665
H	2.101858	0.535801	7.663397
H	2.623408	-1.012388	7.012751
O	-1.034180	-1.133846	3.272463
C	-0.233488	-1.623650	2.172238
H	0.466912	-0.839133	1.903532
H	-0.898603	-1.817357	1.338111
C	0.477216	-2.849036	2.694760
H	-0.145038	-3.733560	2.585623
H	1.417694	-3.020607	2.187363
C	0.658098	-2.492860	4.160203
H	0.858984	-3.347860	4.794139
H	1.470335	-1.783127	4.267844
C	-0.659142	-1.830993	4.476073
H	-1.436459	-2.555529	4.713726
H	-0.604281	-1.104468	5.281585
O	-2.570381	1.175814	4.256931
C	-3.766925	0.490253	3.895685

H	-4.265330	0.138859	4.800968
H	-3.485948	-0.361492	3.292001
C	-4.587485	1.544336	3.187803
H	-5.647866	1.321748	3.195878
H	-4.269762	1.618894	2.152889
C	-4.235878	2.826879	3.953272
H	-4.032147	3.649526	3.280727
H	-5.039817	3.133411	4.612143
C	-2.989270	2.455819	4.755326
H	-2.162729	3.137546	4.628693
H	-3.209425	2.354071	5.816314

sn2_cxet_C2_sym_B97M_D3_TZVPP_opt_freq

Total correction:	2137.4583 kJ/mol
Single point energy:	-4821002.9493 kJ/mol
Total enthalpy:	-4818863.0121 kJ/mol
Final entropy term:	282.2566 kJ/mol
Total gibbs free enthalpy:	-4819145.2687 kJ/mol
Method and Basis:	B97M-D3BJ / def2-TZVPP

xyz, charge: -2, multiplicity: 1

N	-0.124733	0.339902	0.321157
C	0.821571	-0.652542	0.286980
C	0.313432	-1.782488	0.901857
C	-0.988584	-1.459847	1.343478
C	-1.229801	-0.151528	0.964979
H	0.821783	-2.718132	1.049424
H	-1.636466	-2.094931	1.919190
C	2.165924	-0.497418	-0.379633
C	3.171917	-1.429218	0.321539
H	4.124010	-1.357686	-0.197193
H	2.828684	-2.452148	0.174928
C	3.387571	-1.176302	1.801180
H	3.729610	-0.162754	1.973068
H	4.133365	-1.861703	2.204322
H	2.465300	-1.313313	2.353331
C	2.030952	-0.997081	-1.846672
H	1.179158	-0.495159	-2.294938
H	1.770763	-2.055723	-1.804167
C	3.239330	-0.778991	-2.734545
H	3.481077	0.276247	-2.798548
H	3.043530	-1.147002	-3.740598
H	4.125001	-1.290903	-2.365561
C	2.693909	0.913328	-0.345603
C	4.006533	1.316688	-0.174640

C	4.024090	2.722721	-0.285580
C	2.722564	3.122547	-0.535831
N	1.914542	2.020794	-0.567235
H	4.854877	0.684490	0.012527
H	4.882424	3.358640	-0.168243
C	2.167188	4.520258	-0.500934
C	1.625470	4.719684	0.945219
H	0.979009	3.872703	1.153556
H	2.472369	4.640886	1.628622
C	0.850964	5.998898	1.189192
H	0.532159	6.056715	2.228531
H	-0.032498	6.036829	0.561654
H	1.442232	6.887013	0.977492
C	3.294010	5.529716	-0.743070
H	2.887231	6.530402	-0.624220
H	4.028875	5.404755	0.050747
C	3.984277	5.427576	-2.091632
H	4.462209	4.462588	-2.209745
H	4.744597	6.201573	-2.198415
H	3.272360	5.539055	-2.900735
C	-2.304969	0.777393	1.452588
C	-1.642916	1.728566	2.492570
H	-2.434779	2.333883	2.936375
H	-1.009974	2.409106	1.931358
C	-3.410093	-0.018740	2.154260
H	-4.082313	0.693870	2.629756
H	-2.959285	-0.592976	2.959205
C	-4.210320	-0.951262	1.262392
H	-4.723607	-0.397424	0.485584
H	-4.954306	-1.498731	1.841470
H	-3.563979	-1.671612	0.775244
C	-0.810237	1.056700	3.565466
H	0.019199	0.515713	3.123702
H	-1.388235	0.347564	4.153911
H	-0.405113	1.798926	4.251147
C	-2.912433	1.677307	0.411156
N	-2.151199	2.335257	-0.513633
C	-2.950060	3.251456	-1.150353
C	-4.228259	3.171516	-0.626347
C	-4.202848	2.177419	0.373980
H	-5.081490	3.755307	-0.919008
H	-5.024406	1.888601	1.003677
C	1.022918	4.790285	-1.435914
C	0.764452	5.934097	-2.169341
C	-0.579625	5.854622	-2.595464
C	-1.093063	4.674118	-2.089746
N	-0.111088	4.022918	-1.387442

H	1.432098	6.759676	-2.334166
H	-1.108650	6.591405	-3.172409
C	-2.479572	4.115467	-2.291450
C	-3.459545	5.289513	-2.474135
H	-4.446320	4.883719	-2.680567
H	-3.163421	5.825487	-3.374416
C	-2.481984	3.312120	-3.623912
H	-2.276550	4.020047	-4.428242
H	-1.641120	2.625890	-3.604590
C	-3.740871	2.521006	-3.915813
H	-4.624482	3.152006	-3.975881
H	-3.921201	1.789549	-3.135811
H	-3.648273	1.994322	-4.864513
C	-3.549956	6.263263	-1.315008
H	-3.852097	5.755644	-0.406866
H	-4.277124	7.047471	-1.526596
H	-2.589847	6.730551	-1.130285
Sn	-0.161069	1.773153	-1.413187

se_me2_B97M_TZVPP_optfreq

Total correction:	210.9131 kJ/mol
Single point energy:	-6514382.6723 kJ/mol
Total enthalpy:	-6514169.2802 kJ/mol
Final entropy term:	90.8452 kJ/mol
Total gibbs free enthalpy:	-6514260.1254 kJ/mol
Method and Basis:	B97M-D3BJ / def2-TZVPP

xyz, charge: 0, multiplicity: 1

Se	0.212154	-0.948711	0.849987
C	1.765040	-0.005770	1.519983
H	2.610990	-0.161371	0.863089
H	1.992476	-0.410668	2.497021
H	1.551744	1.051257	1.612318
C	0.097787	-0.005328	-0.837178
H	0.999770	-0.159013	-1.415232
H	-0.062407	1.051409	-0.666828
H	-0.746382	-0.411804	-1.377963

sn2_py2_B97M_D3_TZVPP_optfreq

Total correction:	406.6968 kJ/mol
Single point energy:	-1664672.2335 kJ/mol
Total enthalpy:	-1664263.0576 kJ/mol
Final entropy term:	127.4968 kJ/mol
Total gibbs free enthalpy:	-1664390.5544 kJ/mol

Method and Basis: B97M-D3BJ / def2-TZVPP

xyz, charge: 0, multiplicity: 1

Sn	0.424245	0.435842	1.616764
N	-0.509415	0.807483	3.435964
C	-0.635345	1.949560	4.196907
C	-1.212032	1.628679	5.393137
C	-1.457952	0.229352	5.383259
C	-1.010873	-0.243136	4.184281
H	-0.279289	2.889329	3.829051
H	-1.425777	2.310474	6.192737
H	-1.907998	-0.349852	6.165052
H	-1.013536	-1.240522	3.787392
N	0.279346	2.380097	0.896043
C	1.080986	2.786860	-0.156271
C	0.713807	4.041873	-0.544822
C	-0.371339	4.430240	0.285804
C	-0.611892	3.399915	1.150262
H	1.855478	2.143995	-0.529454
H	1.162501	4.620059	-1.328141
H	-0.913892	5.354045	0.239879
H	-1.357051	3.293279	1.910936

sn2_py3_B97M_D3_TZVPP_optfreq

Total correction: 606.1873 kJ/mol
Single point energy: -2215822.5461 kJ/mol
Total enthalpy: -2215213.8797 kJ/mol
Final entropy term: 156.8635 kJ/mol
Total gibbs free enthalpy: -2215370.7432 kJ/mol
Method and Basis: B97M-D3BJ / def2-TZVPP

xyz, charge: -1, multiplicity: 1

Sn	-0.512397	0.317129	0.827212
N	1.617228	0.011173	0.780088
C	2.312285	-0.309422	-0.352065
C	3.660348	-0.327656	-0.077265
C	3.794362	-0.004225	1.293896
C	2.523679	0.197067	1.784238
H	4.449454	-0.547060	-0.772377
H	4.708294	0.069221	1.853594
H	2.190300	0.463221	2.767868
N	-0.445998	0.650399	2.951733
C	-0.136636	1.799055	3.622199
C	-0.112322	1.544544	4.975017
C	-0.420315	0.173446	5.141854

C	-0.619370	-0.337712	3.880052
H	0.046613	2.705773	3.080179
H	0.097628	2.258078	5.750108
H	-0.489462	-0.368280	6.066924
H	-0.863182	-1.337444	3.571172
N	-0.244228	2.420182	0.457415
C	0.918450	3.135737	0.430421
C	0.628482	4.469561	0.250382
C	-0.779901	4.576901	0.163871
C	-1.276858	3.300383	0.292951
H	1.860567	2.637202	0.546345
H	1.342378	5.269584	0.185291
H	-1.354847	5.473383	0.023149
H	-2.293197	2.952029	0.289739
H	1.793998	-0.490837	-1.275555

sn2_py4_B97M_D3_TZVPP_optfreq

Total correction:	801.6555 kJ/mol
Single point energy:	-2766550.168 kJ/mol
Total enthalpy:	-2765746.0335 kJ/mol
Final entropy term:	186.8122 kJ/mol
Total gibbs free enthalpy:	-2765932.8457 kJ/mol
Method and Basis:	B97M-D3BJ / def2-TZVPP

xyz, charge: -2, multiplicity: 1

Sn	-0.403203	-0.069244	1.036870
N	1.760954	0.050065	0.714290
C	2.434020	1.106262	0.170182
C	3.758782	0.768320	-0.010827
C	3.900692	-0.566297	0.441490
C	2.655023	-0.970196	0.873580
H	4.527420	1.407833	-0.409560
H	4.800293	-1.157236	0.459225
H	2.339253	-1.903195	1.294506
N	-0.190572	0.613543	3.097949
C	0.959346	0.926161	3.750008
C	0.668529	1.307297	5.046099
C	-0.736858	1.220118	5.186742
C	-1.219616	0.790625	3.966229
H	1.900297	0.852387	3.240842
H	1.378975	1.609283	5.795599
H	-1.319728	1.442839	6.063469
H	-2.230371	0.598396	3.655669
N	-0.421796	2.262370	0.628996
C	-0.095724	3.342788	1.383363

C	-0.211205	4.503153	0.635917
C	-0.634213	4.103960	-0.654265
C	-0.750869	2.725283	-0.604660
H	0.201868	3.212240	2.407018
H	-0.021997	5.508206	0.975584
H	-0.831699	4.739074	-1.502123
H	-1.041554	2.035484	-1.378858
N	0.029986	-2.164093	2.052295
C	0.459719	-2.531500	3.286447
C	0.599312	-3.907913	3.356515
C	0.230688	-4.409524	2.085568
C	-0.112020	-3.303415	1.326840
H	0.641798	-1.784343	4.036182
H	0.918144	-4.478847	4.213076
H	0.214035	-5.439754	1.769939
H	-0.441902	-3.252567	0.302958
H	1.922153	2.025139	-0.033171

sn2_se_cxet_B97M_TZVPP_optfreq

Total correction:	2150.8152 kJ/mol
Single point energy:	-11125702.2397 kJ/mol
Total enthalpy:	-11123548.9454 kJ/mol
Final entropy term:	291.002 kJ/mol
Total gibbs free enthalpy:	-11123839.9473 kJ/mol
Method and Basis:	B97M-D3BJ / def2-TZVPP

xyz, charge: -2, multiplicity: 1

N	-0.125903	0.306799	0.262673
C	0.836076	-0.679961	0.257106
C	0.327174	-1.795188	0.886477
C	-0.981346	-1.479939	1.308298
C	-1.236054	-0.187296	0.908199
H	0.844054	-2.720743	1.056397
H	-1.629329	-2.109938	1.887314
C	2.210547	-0.540612	-0.338271
C	3.190352	-1.347627	0.544318
H	4.171366	-1.319330	0.078786
H	2.878178	-2.388339	0.505652
C	3.298341	-0.906990	1.990180
H	3.626969	0.123417	2.058745
H	4.010953	-1.528790	2.531654
H	2.337208	-0.985418	2.486343
C	2.205594	-1.216043	-1.736928
H	1.337891	-0.865594	-2.281981
H	2.061188	-2.284489	-1.568931

C	3.430088	-0.972459	-2.592436
H	3.508352	0.077323	-2.851233
H	3.354675	-1.538258	-3.519056
H	4.358233	-1.260490	-2.101596
C	2.697171	0.881203	-0.399991
C	4.003364	1.301165	-0.259223
C	4.013402	2.703438	-0.385636
C	2.712760	3.098929	-0.614065
N	1.905374	1.989090	-0.621846
H	4.855610	0.675418	-0.076308
H	4.869200	3.344702	-0.292843
C	2.165627	4.493587	-0.571186
C	1.641679	4.700596	0.882004
H	1.002532	3.852954	1.112352
H	2.498983	4.629380	1.552455
C	0.865876	5.978084	1.128612
H	0.566023	6.043817	2.172754
H	-0.029022	6.008327	0.517112
H	1.449775	6.865709	0.898177
C	3.292911	5.499905	-0.826856
H	2.889699	6.500488	-0.698291
H	4.036000	5.371462	-0.041815
C	3.965130	5.400649	-2.184265
H	4.439887	4.436132	-2.314337
H	4.724757	6.173903	-2.295865
H	3.245042	5.515236	-2.985041
C	-2.315077	0.731544	1.386929
C	-1.672314	1.689283	2.435143
H	-2.476708	2.279926	2.875130
H	-1.046834	2.387025	1.885619
C	-3.420868	-0.072062	2.079835
H	-4.104938	0.637105	2.542617
H	-2.972693	-0.633056	2.895088
C	-4.199548	-1.021257	1.187017
H	-4.719138	-0.482481	0.404487
H	-4.935559	-1.578408	1.766061
H	-3.539985	-1.731989	0.704512
C	-0.836202	1.026695	3.510576
H	0.008375	0.505087	3.074299
H	-1.405687	0.302204	4.087428
H	-0.453108	1.771710	4.205307
C	-2.915077	1.617606	0.337813
N	-2.151125	2.301731	-0.574313
C	-2.963275	3.214296	-1.215426
C	-4.239164	3.094657	-0.705279
C	-4.208190	2.091901	0.282556
H	-5.097299	3.667978	-0.998994

H	-5.030679	1.778218	0.896806
C	1.020089	4.760743	-1.495430
C	0.752125	5.908265	-2.207655
C	-0.596138	5.838458	-2.616047
C	-1.113443	4.658788	-2.126449
N	-0.119708	3.991722	-1.443437
H	1.421019	6.731914	-2.369539
H	-1.130163	6.583622	-3.174863
C	-2.525434	4.167139	-2.293692
C	-3.459438	5.398869	-2.253855
H	-4.473402	5.065152	-2.455370
H	-3.189619	6.036962	-3.091654
C	-2.660863	3.546907	-3.711638
H	-2.553975	4.366335	-4.424226
H	-1.823177	2.880135	-3.874267
C	-3.935773	2.775220	-3.975168
H	-4.835159	3.359372	-3.787660
H	-3.980869	1.893507	-3.346133
H	-3.963249	2.445421	-5.012015
C	-3.431671	6.209286	-0.973679
H	-3.711631	5.600215	-0.122158
H	-4.122006	7.050451	-1.032805
H	-2.436917	6.601331	-0.791978
Sn	-0.155365	1.829301	-1.282064
Se	-0.257363	0.833204	-3.452635

sn2_se_cxh_B97M_TZVPP_optfreq

Total correction:	892.4403 kJ/mol
Single point energy:	-9472035.7851 kJ/mol
Total enthalpy:	-9471140.8659 kJ/mol
Final entropy term:	180.7943 kJ/mol
Total gibbs free enthalpy:	-9471321.6601 kJ/mol
Method and Basis:	B97M-D3BJ / def2-TZVPP

xyz, charge: -2, multiplicity: 1

N	-0.251770	0.338792	0.223980
C	0.703399	-0.642017	0.265509
C	0.293814	-1.630907	1.130210
C	-0.973680	-1.235604	1.633497
C	-1.276602	-0.021922	1.054909
H	0.839159	-2.529343	1.361665
H	-1.579387	-1.752429	2.358209
C	1.923452	-0.534055	-0.583397
C	2.600006	0.790481	-0.488086
C	3.925715	1.112341	-0.308386

C	4.011623	2.529059	-0.343575
C	2.733503	3.005895	-0.540524
N	1.874960	1.944458	-0.625186
H	4.730996	0.410478	-0.177806
H	4.891697	3.134028	-0.206748
C	2.251370	4.410942	-0.457460
C	-2.389693	0.906378	1.390530
C	-2.930038	1.771179	0.307313
N	-2.121128	2.364965	-0.622219
C	-2.875822	3.243874	-1.353005
C	-4.170352	3.218674	-0.887195
C	-4.205625	2.275773	0.173694
H	-4.988648	3.801700	-1.272697
H	-5.048716	2.018862	0.792096
C	1.080800	4.799733	-1.289297
C	0.780977	6.037829	-1.815488
C	-0.537522	5.959459	-2.336509
C	-0.979202	4.676539	-2.107559
N	0.005489	3.973141	-1.465860
H	1.424113	6.900971	-1.791813
H	-1.095436	6.738536	-2.826352
C	-2.258926	4.006882	-2.474756
Sn	-0.157518	1.831923	-1.323413
Se	-0.264344	0.835084	-3.492476
H	3.079926	5.077150	-0.691929
H	1.646945	-0.717177	-1.627494
H	2.625751	-1.313299	-0.297625
H	-3.208341	0.327176	1.814362
H	-2.050665	1.560206	2.207493
H	-2.074147	3.322636	-3.310092
H	-2.964646	4.755919	-2.825494
H	2.004839	4.622235	0.593455

sn_dodecaborate_B97M_D3_TZVPP_optfreq

Total correction:	423.165 kJ/mol
Single point energy:	-1300280.5692 kJ/mol
Total enthalpy:	-1299854.9251 kJ/mol
Final entropy term:	112.0966 kJ/mol
Total gibbs free enthalpy:	-1299967.0217 kJ/mol
Method and Basis:	B97M-D3BJ / def2-TZVPP

xyz, charge: -2, multiplicity: 1

B	0.917182	1.081397	-0.867889
B	-0.566166	0.409403	-1.527349
B	0.857031	-0.617081	-1.313820

B	1.666439	-0.205375	0.189691
Sn	1.030560	1.706066	1.386465
B	-0.713478	1.511461	-0.167240
B	-0.749726	-1.244866	-0.940020
B	0.606151	-1.603808	0.131083
B	0.497740	-0.569975	1.548570
B	-0.971501	0.490528	1.328454
B	-1.695175	0.056565	-0.214038
B	-0.971557	-1.188616	0.809295
H	1.561802	1.831817	-1.553949
H	-0.952664	0.726464	-2.619566
H	1.480457	-1.028308	-2.254593
H	2.853264	-0.388858	0.273544
H	-1.252944	2.573184	-0.342616
H	-1.263743	-2.097058	-1.611557
H	1.052882	-2.715817	0.216447
H	0.839785	-1.022678	2.610134
H	-1.705881	0.811806	2.226682
H	-2.884003	0.124447	-0.373467
H	-1.645996	-2.005596	1.375594

sn_me4_PBEh3c_optfreq

Total correction:	418.198 kJ/mol
Single point energy:	-980942.3411 kJ/mol
Total enthalpy:	-980521.6641 kJ/mol
Final entropy term:	125.3206 kJ/mol
Total gibbs free enthalpy:	-980646.9847 kJ/mol
Method and Basis:	PBEh-3c / def2-mSVP

xyz, charge: 0, multiplicity: 1

Sn	0.000012	-0.000000	0.999958
C	-1.018761	-1.764587	1.720326
H	-0.523849	-2.669890	1.370424
H	-2.050208	-1.788687	1.370360
H	-1.032696	-1.788648	2.809440
C	2.037553	-0.000004	1.720379
H	2.574141	0.881232	1.370467
H	2.574141	-0.881235	1.370457
H	2.065323	-0.000010	2.809492
C	-1.018761	1.764579	1.720346
H	-0.523850	2.669886	1.370453
H	-1.032696	1.788628	2.809460
H	-2.050209	1.788683	1.370380
C	-0.000023	0.000012	-1.161196
H	0.508741	-0.881220	-1.550463

H	0.508741	0.881249	-1.550454
H	-1.017596	0.000014	-1.550410

sn_dithiolate_B97M_D3_TZVPP_optfreq

Total correction:	468.1406 kJ/mol
Single point energy:	-5959619.6617 kJ/mol
Total enthalpy:	-5959149.0422 kJ/mol
Final entropy term:	168.4528 kJ/mol
Total gibbs free enthalpy:	-5959317.495 kJ/mol
Method and Basis:	B97M-D3BJ / def2-TZVPP

xyz, charge: -2, multiplicity: 1

Sn	5.190364	-0.265657	4.791056
S	6.712104	0.768042	6.787963
S	7.191583	1.000637	3.921334
S	3.790052	0.251249	2.528635
S	3.381020	1.460964	5.148614
C	7.835667	1.059616	5.531643
C	9.190406	1.321073	5.756760
C	9.840576	1.423202	7.028232
H	9.339103	1.310469	7.971261
C	11.174433	1.678814	6.813467
H	11.927972	1.805753	7.574592
C	11.398492	1.746828	5.400370
H	12.348071	1.931415	4.923649
C	10.199480	1.532223	4.762289
H	10.020056	1.509745	3.703514
C	2.731912	1.081906	3.585206
C	1.424769	1.437410	3.239724
C	0.784488	1.211951	1.979220
H	1.257316	0.735599	1.140735
C	-0.498113	1.702282	2.051042
H	-1.232108	1.680391	1.261102
C	-0.698486	2.250270	3.359136
H	-1.608652	2.705497	3.716041
C	0.463924	2.091391	4.076591
H	0.647446	2.386164	5.093062

phi_B97M_D3_TZVPP_opt_freq

Total correction:	254.7123 kJ/mol
Single point energy:	-1390798.861 kJ/mol
Total enthalpy:	-1390541.6697 kJ/mol
Final entropy term:	100.8168 kJ/mol

Total gibbs free enthalpy: -1390642.4865 kJ/mol
Method and Basis: B97M-D3BJ / def2-TZVPP

xyz, charge: 0, multiplicity: 1

H	-0.000001	-0.005664	-0.005601
C	0.000003	-0.001131	1.069467
C	0.000002	-0.003106	3.842451
C	0.000005	-1.193260	1.772803
C	0.000002	1.194219	1.768733
C	0.000001	1.197165	3.152968
C	0.000004	-1.206350	3.156892
H	-0.000003	2.123510	1.224718
H	-0.000004	2.129041	3.691223
H	0.000000	-2.139652	3.690524
H	-0.000003	-0.009485	4.919231
I	-0.000007	-3.000151	0.729836

phi_sn2_cxet_B97M_D3_TZVPP_TightOpt_opt_freq

Total correction: 2400.345 kJ/mol
Single point energy: -6211860.6354 kJ/mol
Total enthalpy: -6209457.8114 kJ/mol
Final entropy term: 328.8666 kJ/mol
Total gibbs free enthalpy: -6209786.678 kJ/mol
Method and Basis: B97M-D3BJ / def2-TZVPP

xyz, charge: -2, multiplicity: 1

N	-0.007564	0.522737	0.198932
C	1.014985	-0.396697	0.173938
C	0.584847	-1.562443	0.776036
C	-0.743097	-1.345131	1.198593
C	-1.081401	-0.059369	0.826742
H	1.158839	-2.458988	0.918237
H	-1.349370	-2.030975	1.759865
C	2.338646	-0.160722	-0.502889
C	3.399771	-1.066145	0.151761
H	4.329378	-0.952066	-0.399698
H	3.088939	-2.096917	-0.004592
C	3.654558	-0.834726	1.628275
H	3.984272	0.180971	1.810742
H	4.422313	-1.514391	1.997335
H	2.751267	-0.998836	2.204230
C	2.192612	-0.630972	-1.974956
H	1.261161	-0.241440	-2.361310
H	2.070213	-1.714312	-1.955941
C	3.307325	-0.235769	-2.918583

H	3.376398	0.843038	-3.000998
H	3.118312	-0.637586	-3.911837
H	4.278211	-0.598527	-2.588739
C	2.804991	1.267779	-0.426193
C	4.105893	1.713252	-0.298073
C	4.063764	3.122102	-0.275406
C	2.738477	3.489235	-0.407249
N	1.969703	2.357969	-0.499971
H	4.985849	1.103738	-0.213748
H	4.902130	3.779596	-0.141436
C	2.130897	4.840011	-0.159807
C	1.618084	4.800732	1.311510
H	1.023591	3.897802	1.412001
H	2.487207	4.670904	1.957905
C	0.786506	5.986503	1.755291
H	0.507135	5.881266	2.802001
H	-0.121867	6.060425	1.168034
H	1.319917	6.928330	1.650903
C	3.211517	5.920667	-0.267869
H	2.776921	6.870620	0.030863
H	3.978679	5.694711	0.470425
C	3.851536	6.072129	-1.636073
H	4.326682	5.149758	-1.947334
H	4.606419	6.857994	-1.625344
H	3.111512	6.324546	-2.385826
C	-2.230382	0.764935	1.323984
C	-1.676194	1.695109	2.444901
H	-2.527014	2.208000	2.895517
H	-1.082710	2.459367	1.952419
C	-3.303846	-0.143500	1.932101
H	-4.051404	0.495034	2.399161
H	-2.852111	-0.716316	2.737209
C	-3.980736	-1.093856	0.960960
H	-4.480662	-0.549537	0.169050
H	-4.720805	-1.708740	1.472533
H	-3.257722	-1.752363	0.494973
C	-0.827142	1.022883	3.504030
H	0.061968	0.585812	3.063620
H	-1.361001	0.227522	4.018784
H	-0.514394	1.747437	4.253646
C	-2.857398	1.683590	0.315197
N	-2.103073	2.506536	-0.480396
C	-2.946529	3.418134	-1.071293
C	-4.238255	3.162510	-0.655229
C	-4.181477	2.069124	0.232583
H	-5.121169	3.703283	-0.939698
H	-5.008811	1.644826	0.769764

C	0.960037	5.194248	-1.025993
C	0.618711	6.439113	-1.515538
C	-0.722852	6.361791	-1.944262
C	-1.157374	5.076590	-1.687579
N	-0.124748	4.358774	-1.130919
H	1.233067	7.319751	-1.512879
H	-1.302188	7.160604	-2.368180
C	-2.497670	4.484964	-2.032620
C	-3.548437	5.611830	-2.051024
H	-4.491620	5.189838	-2.388379
H	-3.250664	6.320887	-2.820448
C	-2.402305	3.936950	-3.482104
H	-2.303608	4.796749	-4.145491
H	-1.473815	3.391137	-3.575883
C	-3.534734	3.040882	-3.933605
H	-4.504624	3.526447	-3.853602
H	-3.574447	2.139871	-3.331974
H	-3.390205	2.746339	-4.970944
C	-3.761289	6.347657	-0.742632
H	-4.080930	5.667750	0.037774
H	-4.521727	7.120125	-0.855104
H	-2.843252	6.821093	-0.414558
Sn	-0.081312	2.143830	-1.321338
I	-0.135856	1.074528	-4.381717
C	-0.164523	0.342539	-6.450274
C	-0.195893	-0.588703	-9.080630
C	0.997275	-0.125283	-7.046350
C	-1.342338	0.339280	-7.182769
C	-1.360125	-0.123752	-8.489277
C	0.984048	-0.587086	-8.353251
H	1.917209	-0.126971	-6.482390
H	-2.250428	0.701355	-6.726055
H	-2.284091	-0.121093	-9.048559
H	1.896064	-0.947577	-8.805741
H	-0.207952	-0.948517	-10.097335

14 Literature

[1] D. Jacoby, C. Floriani, A. Chiesi-Villa, C. Rizzoli, *Journal of the American Chemical Society* **1993**, *115*, 3595-3602.

[2] D. Geiß, M. I. Arz, M. Straßmann, G. Schnakenburg, A. C. Filippou, *Angewandte Chemie International Edition* **2015**, *54*, 2739-2744.

[3] G. Sheldrick, *Acta Crystallogr. A* **2015**, *71*, 3-8.

[4] G. Sheldrick, *Acta Crystallographica Section C* **2015**, *71*, 3-8.

[5] C. B. Hubschle, G. M. Sheldrick, B. Dittrich, *Journal of Applied Crystallography* **2011**, *44*, 1281-1284.

[6] G. Sheldrick, *Acta Crystallographica Section A* **2008**, *64*, 112-122.

[7] aF. Neese, *WIREs Computational Molecular Science* **2012**, *2*, 73-78; bF. Neese, *WIREs Computational Molecular Science* **2018**, *8*, e1327.

[8] aT. Z. E.J. Baerends, A.J. Atkins, J. Autschbach, O. Baseggio, D. Bashford, A. Bérces, F.M. Bickelhaupt, C. Bo, P.M. Boerrigter, L. Cavallo, C. Daul, D.P. Chong, D.V. Chulhai, L. Deng, R.M. Dickson, J.M. Dieterich, D.E. Ellis, M. van Faassen, L. Fan, T.H. Fischer, A. Förster, C. Fonseca Guerra, M. Franchini, A. Ghysels, A. Giammona, S.J.A. van Gisbergen, A. Goez, A.W. Götz, J.A. Groeneveld, O.V. Gritsenko, M. Grüning, S. Gusarov, F.E. Harris, P. van den Hoek, Z. Hu, C.R. Jacob, H. Jacobsen, L. Jensen, L. Joubert, J.W. Kaminski, G. van Kessel, C. König, F. Kootstra, A. Kovalenko, M.V. Krykunov, E. van Lenthe, D.A. McCormack, A. Michalak, M. Mitoraj, S.M. Morton, J. Neugebauer, V.P. Nicu, L. Noodleman, V.P. Osinga, S. Patchkovskii, M. Pavanello, C.A. Peeples, P.H.T. Philipsen, D. Post, C.C. Pye, H. Ramanantoanina, P. Ramos, W. Ravenek, M. Reimann, J.I. Rodríguez, P. Ros, R. Rüger, P.R.T. Schipper, D. Schlüns, H. van Schoot, G. Schreckenbach, J.S. Seldenthuis, M. Seth, J.G. Snijders, M. Solà, M. Stener, M. Swart, D. Swerhone, V. Tognetti, G. te Velde, P. Vernooijs, L. Versluis, L. Visscher, O. Visser, F. Wang, T.A. Wesolowski, E.M. van Wezenbeek, G. Wiesenekker, S.K. Wolff, T.K. Woo, A.L. Yakovlev*, Vol. 2020*, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, **2019**; bG. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders, T. Ziegler, *Journal of Computational Chemistry* **2001**, *22*, 931-967.

[9] A. Najibi, L. Goerigk, *Journal of Chemical Theory and Computation* **2018**, *14*, 5725-5738.

[10] F. Weigend, R. Ahlrichs, *Physical Chemistry Chemical Physics* **2005**, *7*, 3297-3305.

[11] V. Barone, M. Cossi, *The Journal of Physical Chemistry A* **1998**, *102*, 1995-2001.

[12] C. Adamo, V. Barone, *Journal of Chemical Physics* **1999**, *110*, 6158--6170.

[13] E. Glendening, J. Badenhoop, A. Reed, J. Carpenter, J. Bohmann, C. Morales, C. Landis, F. Weinhold, in *Google Scholar There is no corresponding record for this reference*, Theoretical Chemistry Institute,

University of Wisconsin: Madison, WI, **2013**.

[14] F. M. Bickelhaupt, E. J. Baerends, in *Reviews in Computational Chemistry*, **2000**, pp. 1-86.

[15] M. P. Mitoraj, A. Michalak, T. Ziegler, *Journal of Chemical Theory and Computation* **2009**, *5*, 962-975.

[16] aJ. P. Perdew, *Physical Review B* **1986**, *33*, 8822-8824; bA. D. Becke, *Physical Review A* **1988**, *38*, 3098-3100; cS. Grimme, J. Antony, S. Ehrlich, H. Krieg, *The Journal of Chemical Physics* **2010**, *132*, 154104.

[17] S. K. Wolff, T. Ziegler, E. v. Lenthe, E. J. Baerends, *The Journal of Chemical Physics* **1999**, *110*, 7689-7698.

[18] K. Anjali, M. Ahmed, J. Christopher, A. Sakthivel, *Dalton Transactions* **2018**, *47*, 12353-12361.

[19] R. F. Culmo, C. Shelton, *Application note. Waltham, MA: Perkin Elmer* **2013**.

[20] M. A. Wünsche, P. Mehlmann, T. Witteler, F. Buß, P. Rathmann, F. Dielmann, *Angewandte Chemie International Edition* **2015**, *54*, 11857-11860.

[21] U. S. D. Paul, U. Radius, *European Journal of Inorganic Chemistry* **2017**, *2017*, 3362-3375.

[22] R. A. Kelly Iii, H. Clavier, S. Giudice, N. M. Scott, E. D. Stevens, J. Bordner, I. Samardjiev, C. D. Hoff, L. Cavallo, S. P. Nolan, *Organometallics* **2008**, *27*, 202-210.

[23] M. L. Kelty, A. J. McNeece, A. S. Filatov, J. Anderson, *ChemRxiv* **2021**.