Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Tetrazastannoles vs. Distannadiazanes – A Question of the Tin Source

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1 General Information

All manipulations were carried out under oxygen- and moisture-free conditions under argon using standard Schlenk or drybox techniques.

Dichloromethane (CH_2Cl_2, CD_2Cl_2) was purified according to a literature procedure,[1] dried over P_4O_{10} and CaH_2 and freshly distilled prior to use. Tetrahydrofurane (thf, thf-d_8), Et_2O, *n*-hexane, benzene (benzene, benzene-d_6) and toluene were dried over Na/benzophenone and freshly distilled prior to use. Fluorobenzene (PhF) was dried over CaH_2 and distilled prior to use.

Mes*Br (Mes* = 2,4,6-tri-*tert*-butylphenyl),[2] TerI (Ter = 2,4-bis(2,4,6-trimethylphenyl)phenyl),[3] 1-azido-4-dimethylaminobenzene (**1a**)**[Quelle]** and 1-azido-3,5-bis(trifluoromethyl)benzene (**1b**)**[Quelle]** were synthesized according to literature procedures. $SnCl_2$ (Lancaster, 98%), $NaNO_2$ (KMF Laborchemie), NaN_3 (Aldrich, 99%), $CaCO_3$ (Fluka), $HCl_{aq.}$ (chemsolute, 37%), $MgSO_4$ (anhydrous/drying agent, Grüssing, 99%) and *n*-BuLi (Aldrich, 2.5 M in *n*-hexane) were used as received. $LiN(SiMe_3)_2$ (Aldrich) was purified by a saber tube distillation and Me_3SiN_3 (Acros) was also distilled prior to use.

NMR: ^1H, $^{13}C\{^1H\}$, and ^{29}Si-INEPT NMR spectra were recorded on a Bruker AVANCE 250, a Bruker AVANCE 300 or a Bruker AVANCE 500 NMR spectrometer. The chemical shifts were referenced to solvent signals or the protic impurities in the deuterated solvent (CD_2Cl_2: $\delta\,^1H$ = 5.32, $\delta\,^{13}C$ = 54.0; benzene-d_6: $\delta\,^1H$ = 7.16, $\delta\,^{13}C$ = 128.4; thf-d_8: $\delta\,^1H$ = 1.73 or 3.58, $\delta\,^{13}C$ = 25.4 or 67.6). The NMR signals were assigned by DEPT and two-dimensional correlation spectra (HSQC) using standard pulse sequences (standard Bruker software).

IR: A Nicolet 380-FT-IR spectrometer with a Smart Orbit ATR unit or a Bruker Alpha IR spectrometer with an ATR-IR unit was used.

Raman: A LabRAM HR 800 Horiba Jobin Yvon Raman spectrometer equipped with a High Stability BX41 Microscope (focus 1 µm) and an Olympus Mplan 50xNA 0.70 objective was used. The samples were excited by an infrared laser (785 nm, 100 mW, air cooled diod laser), a red laser (633 nm, 17 mW, HeNe-laser), a green laser (532 nm, 50 mW, air cooled, doubled frequency Nd:YAG solid state laser) or a blue laser (473 nm, 20 mW, air cooled solid state laser).

CHN analyses: A vario Micro cube CHNS analyser from Elementar was used.

Melting points are uncorrected (EZ-Melt, Stanford Research Systems). Heating-rate 20 °C/min (clearing-points are reported).

DSC: DSC 823e from Mettler-Toledo (Heating-rate 5 °C/min) was used.

X-ray: Single crystals were measured on a Bruker Kappa-APEX-II CCD diffractometer or a Bruker D8 Quest CMOS diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods (*SHELXS-2014*)[4] and refined by full-matrix least squares procedures (*SHELXL-2014*).[5] Semi-empirical absorption corrections were applied (SADABS).[6] Unless otherwise noted, all non-hydrogen atoms were refined anisotropically, hydrogen atoms were included in the refinement at calculated positions using a riding model.

In **2** the N-C_6H_4-N(CH_3)$_2$ moiety was found to be disordered and split into two parts. The geometries of both parts were made equal using the SAME command and the ADPs of the concerned atoms were restrained using the EADP command. Additionally, one tert-butyl group of the Mes* scaffold was found to be disordered and split into two parts. The geometries of both parts were made equal using the SAME command and the ADPs of the concerned atoms were restrained using a rigid bond model (SIMU, RIGU), except for C19a and C19b, which were made equal using the EADP command.

In **3** one *tert*-butyl group was found to be disordered and was split into two parts. The geometries of both parts were restrained to be similar using the SAME command. The ADPs of the concerned atoms were restrained using a rigid bond model (SIMU, DELU).

4a was refined as a 2-component twin (pseudo-merohedral twin [-1 0 0 0 0 -1 0 -1 0]).

In **4b** one CF_3 group was found to be disordered in split into three parts. The geometries of all parts were restrained to be similar using the SAME command. The ADPs of the concerned atoms were restrained using a rigid bond model (SIMU, DELU), except for C8a, C8b and C8c, which were made equal using the EADP command. Additionally, one Me_3Si group was found to be disordered and split into two parts. The geometries of both parts were restrained to be similar using the SAME command. The ADPs of the concerned atoms were restrained using a rigid bond model (SIMU, DELU), except for Si2a and Si2b, which were made equal using the EADP command.

In **5a** one benzene molecule (solvent) was found to be disordered and split into two parts. The geometries of both parts were restrained to be similar using the SAME command. The ADPs of the concerned atoms were restrained using a rigid bond model (SIMU, DELU).

5b crystallizes with two independent molecules per unit cell. Except for one, all CF_3 groups were found to be disordered and split into two or three parts, respectively. The geometries of both parts were made equal using the SAME command and the ADPs of the concerned atoms were restrained using the EADP command. Furthermore, the C-F distances were restrained using the SADI command.

2 Crystallographic Details

Table S1: Crystallographic details of **1a**, **2**, **3** and **4a**.

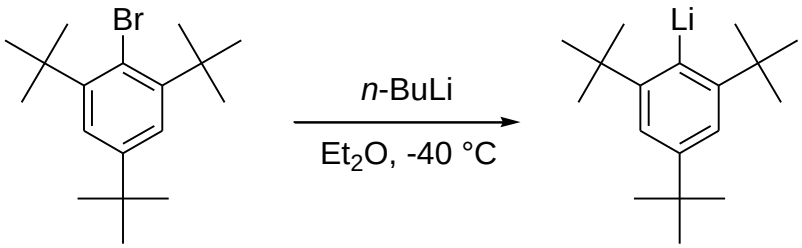
	1a	**2**	**3**	**4a**
chem. formula	$C_8H_{10}N_4$	$C_{88}H_{136}N_4Sn_2$	$C_{42}H_{76}N_4Si_2Sn$	$C_{28}H_{56}N_8Si_4Sn$
M [g mol^{-1}]	162.20	1487.38	811.93	735.85
color	colorless	colorless	colorless	yellow
crystal system	orthorhombic	triclinic	triclinic	triclinic
space group	*Pna*2$_1$	*P*-1	*P*-1	*P*-1
a [Å]	6.0974(4)	13.6085(7)	12.3358(9)	9.4710(8)
b [Å]	7.5834(4)	14.1601(7)	14.113(1)	14.799(2)
c [Å]	18.263(1)	14.2919(5)	14.724(1)	14.989(1)
α [°]	90.0	63.076(2)	71.592(3)	68.411(2)
β [°]	90.0	61.675(2)	73.901(3)	77.420(2)
γ [°]	90.0	61.851(2)	78.072(3)	75.954(3)
V [Å^3]	844.26(8)	2042.4(2)	2316.8(3)	1875.7(3)
Z	4	1	2	2
$\rho_{calc.}$ [g cm^{-3}]	1.276	1.209	1.164	1.303
μ [mm^{-1}]	0.08	0.66	0.07	0.84
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073
T [K]	123	123	123	123
measured reflexes	13384	116559	95145	101606
independent reflexes	2287	13032	13511	12009
reflexes with $I > 2\sigma(I)$	1994	10194	11086	9628
$R_{int.}$	0.042	0.105	0.063	0.083
F(000)	344	792	868	772
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.043	0.041	0.037	0.042
wR_2 (F^2)	0.107	0.076	0.075	0.090
GooF	1.07	1.04	1.04	1.12
parameter	111	465	496	388
Flack parameter	-	-	-	-
res. density [*e* Å^{-3}]	0.23/−0.19	1.57/−1.26	0.78/−0.61	1.15/−0.69
CCDC No.	1872841	1872842	1872843	1872844

Table S2: Crystallographic details of **4b**, **5a** and **5b**.

	4b	**5a**	**5b**
chem. formula	$C_{28}H_{42}F_{12}N_6Si_4Sn$	$C_{29}H_{32}ClN_2Sn \cdot C_6H_6$	$C_{64}H_{56}Cl_2F_{12}N_2Sn_2$
M [g mol^{-1}]	921.72	640.81	1389.38
color	colorless	yellow	yellow
crystal system	monoclinic	monoclinic	monoclinic
space group	*C*2/*c*	$P2_1/n$	*C*2/*c*
a [Å]	17.222(2)	12.3272(9)	48.429(2)
b [Å]	9.3053(9)	23.087(2)	15.2166(4)
c [Å]	24.296(2)	22.440(2)	35.365(2)
α [°]	90.0	90.0	90.0
β [°]	91.831(3)	102.327(2)	114.385(1)
γ [°]	90.0	90.0	90.0
V [Å^3]	3891.5(7)	6239.1(8)	23736(2)
Z	4	8	16
$\rho_{calc.}$ [g cm^{-3}]	1.573	1.364	1.555
μ [mm^{-1}]	0.87	0.93	1.01
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	123	123	123
measured reflexes	40574	191077	3994645
independent reflexes	7041	15816	37902
reflexes with $I > 2\sigma(I)$	6402	11137	27168
$R_{int.}$	0.032	0.145	0.100
F(000)	1864	2632	11136
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.024	0.046	0.052
wR_2 (F^2)	0.057	0.072	0.081
GooF	1.07	1.04	1.07
parameter	334	762	1689
Flack parameter	-	-	-
res. density [*e* Å^{-3}]	0.50/−0.53	0.52/−0.55	0.75/−0.90
CCDC No.	1872845	1872846	1872847

3 Synthesis of Starting Materials

3.1 Synthesis of Mes*Li



To a suspension of Mes*Br (2.190 g, 6.73 mmol) in Et_2O (20 mL) was added *n*-BuLi (2.5 M, 2.76 mL, 6.90 mmol) at −40 °C. The resulting clear solution was brought to room temperature over a period of 2 h and the solvent was removed afterwards. Upon drying the colorless solid for 30 min *in vacuo*, it was suspended *n*-hexane (10 mL) and filtered (F4). The solvent was re-condensed three times and removed by filtration. After drying the colorless solid *in vacuo* for 30 min, Mes*Li was yielded (1.100 g, 4.36 mmol, 64.8%) in purity > 90% and used for follow-up chemistry.

^{1}H NMR (298.2 K, thf-d_8, 300.12 MHz): 1.24 (s, 9 H, *p*-C(C***H***$_3$)$_3$), 1.29 (s, 18 h, *o*-C(C***H***$_3$)$_3$), 6.97 (s, 2).

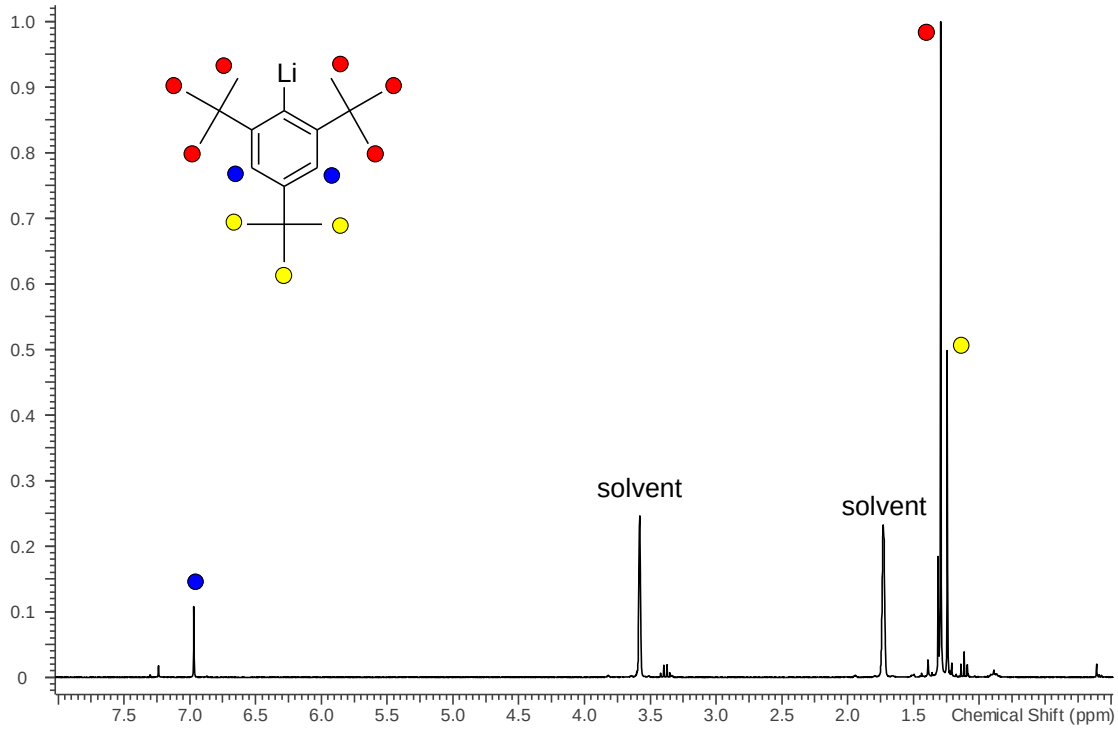


Figure S1: ^{1}H NMR spectrum of Mes*Li.

3.2 Synthesis of $Sn[N(SiMe_3)_2]_2$

$$2\ LiN(SiMe_3)_2 + SnCl_2 \xrightarrow[-80\ °C]{n\text{-hexane/}Et_2O} Sn[N(SiMe_3)_2]_2$$

The synthesis was carried out according to a slightly modified literature procedure.[7] $LiN(SiMe_3)_2$ (6.694 g, 40.00 mmol) was dissolved in *n*-hexane (100 mL) and added to a cooled (−80 °C) suspension of $SnCl_2$ (3.887 g, 20.50 mmol) in a minimum amount of Et_2O (4 mL). The reaction mixture was brought to room temperature over a period of 1 h and stirred for additional 2 h. Upon filtration, the solvent was removed in vacuo and the resulting orange-red oil distilled at +250 °C in a dynamic vacuum (10^{-3} mbar) yielding 7.930 g (18.04 mmol, 88.0%) $Sn[N(SiMe_3)_2]_2$.

Mp.: 38 °C (Lit. 37-38 °C).[7] **CHN** calc (found) in %: C 32.80 (31.633), H 8.26 (8.711), N 6.37 (5.968). **^{1}H NMR** (298.3 K, benzene-d_6, 300.13 MHz): 0.30 (s, 36 H, $^2J\{^1H\text{-}^{29}Si\}$ = 6.4 Hz, $Si(C\boldsymbol{H}_3)_3$). **^{13}C{^{1}H} NMR** (298.2 K, benzene-d_6, 75.48 MHz): 6.13 (s, $^1J\{^{13}C\text{-}^{29}Si\}$ = 55.0 Hz, $Si(\boldsymbol{C}H_3)_3$). **^{29}Si-INEPT NMR** (298.2 K, benzene-d_6, 59.62 MHz): −2.0 (m). **^{119}Sn{^{1}H} NMR** (298.2 K, benzene-d_6, 111.88 MHz): 768 (s). **IR** (ATR-IR, 32 scans, cm^{-1}): 2947 (m), 2895 (w), 1429 (w), 1398 (w), 1346 (w), 1290 (w), 1244 (s), 1180 (w), 916 (s), 879 (s), 827 (s), 812 (s), 775 (s), 752 (s), 706 (m), 690 (s), 661 (s), 621 (s), 613 (s), 528 (m). **Raman** (633 nm, accumulation time: 20 s, 20 scans, cm^{-1}): 2953 (4), 2897 (6), 1406 (1), 1262 (1), 1245 (1), 848 (2), 787 (1), 738 (1), 705 (1), 675 (2), 625 (8), 491 (1), 394 (10), 359 (5), 263 (2), 243 (2), 226 (3).

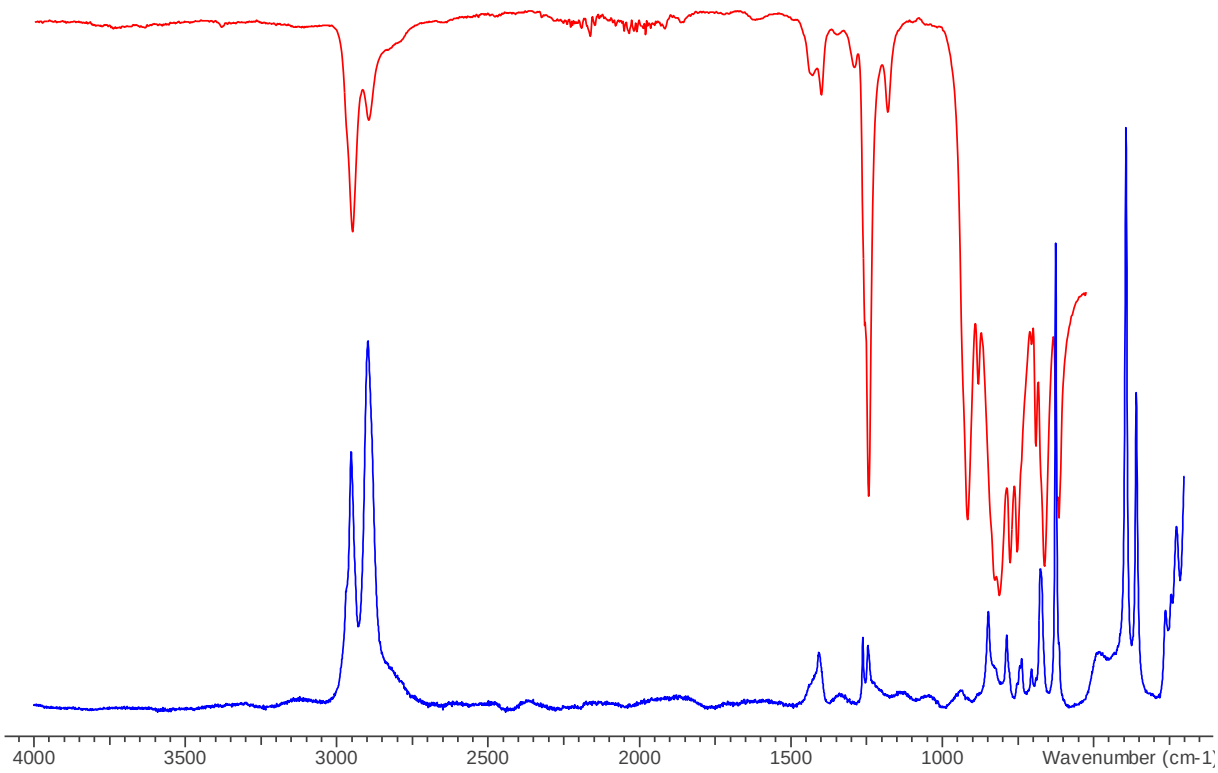


Figure S2: IR (top) and Raman (bottom) spectra of $Sn[N(SiMe_3)_2]_2$.

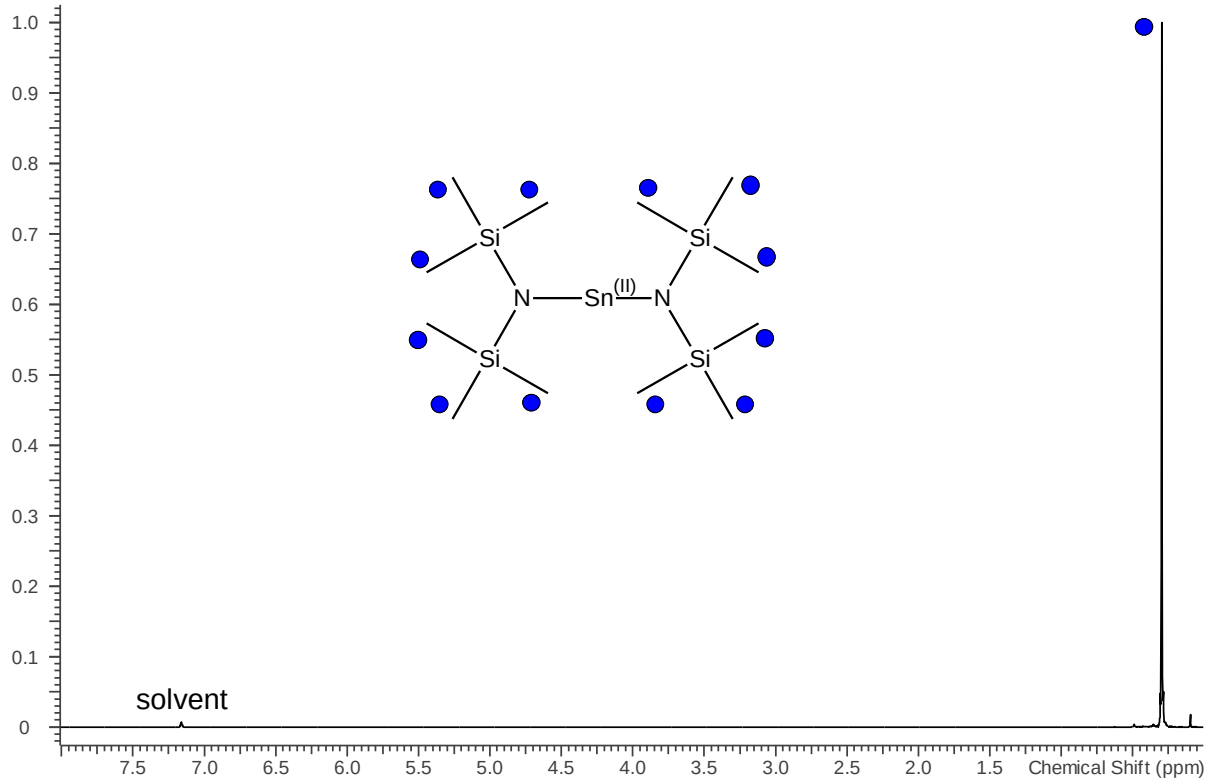


Figure S3: ^1H NMR spectrum of $Sn[N(SiMe_3)_2]_2$.

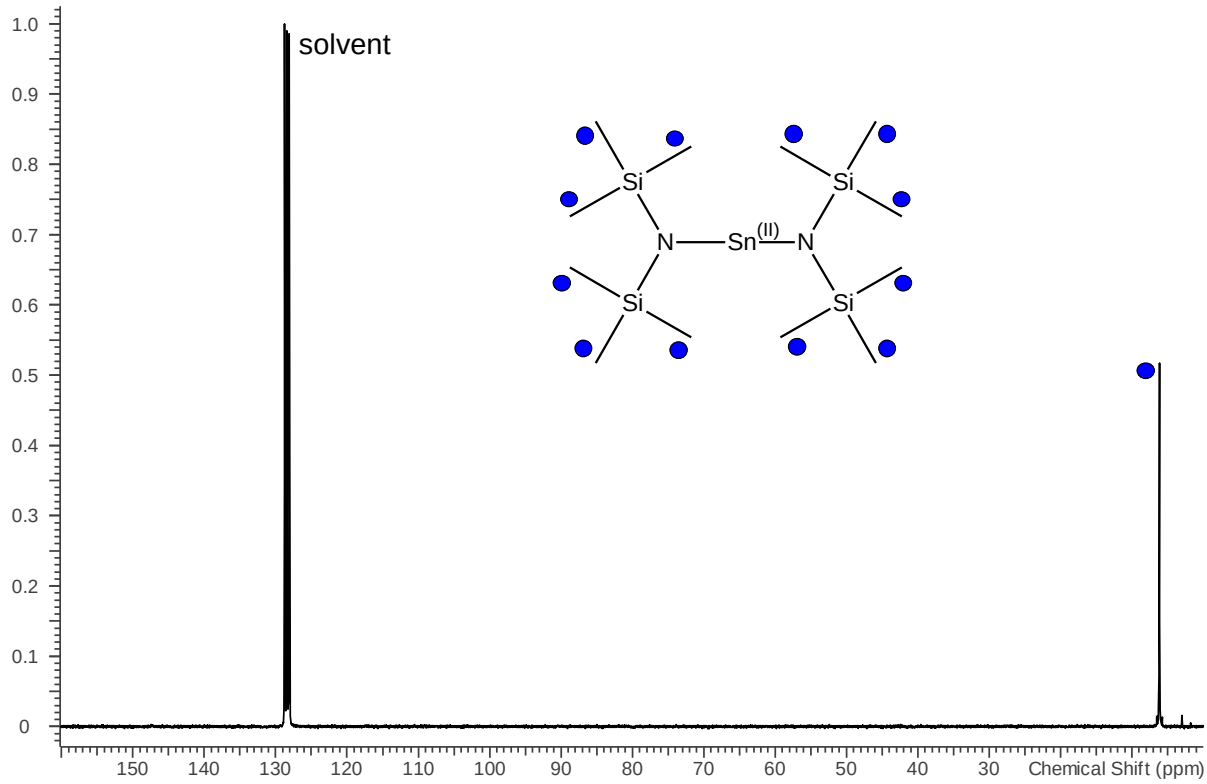


Figure S4: $^{13}C\{^{1}H\}$ NMR spectrum of $Sn[N(SiMe_3)_2]_2$.

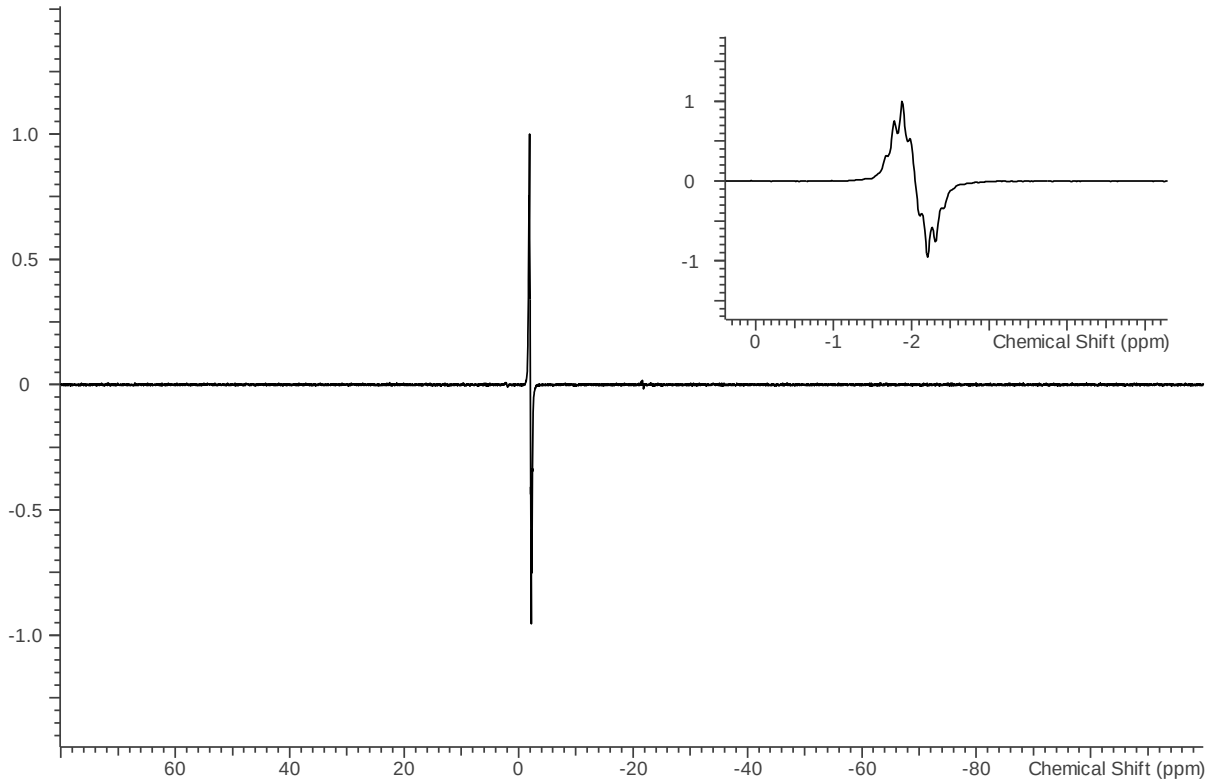


Figure S5: ^{29}Si-INEPT NMR spectrum of $Sn[N(SiMe_3)_2]_2$.

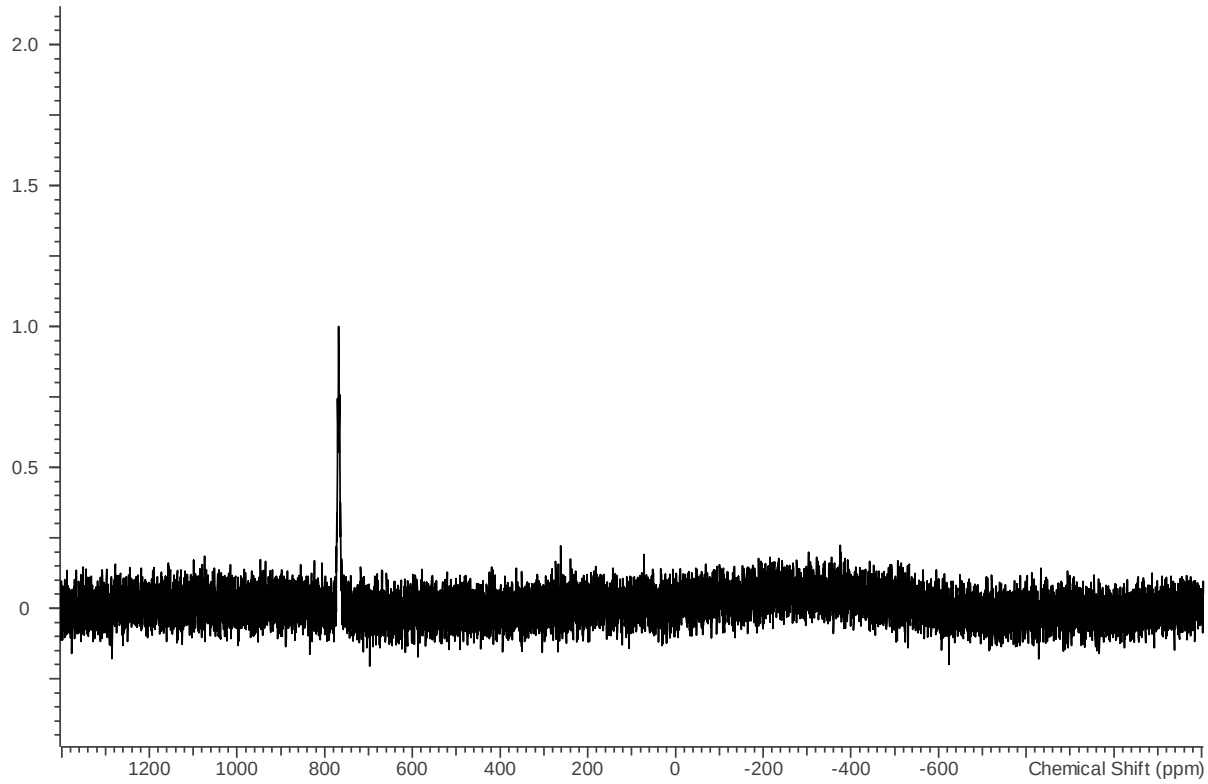
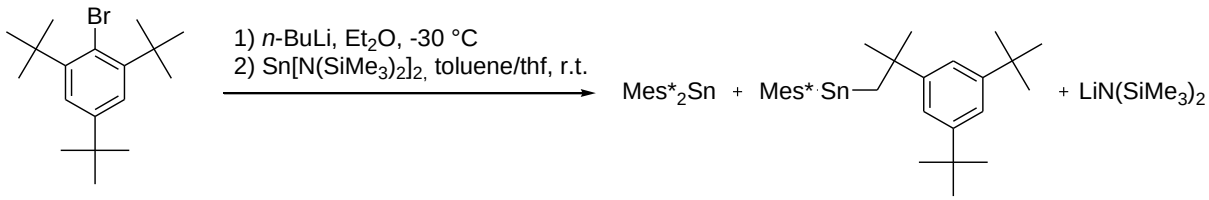


Figure S6: $^{119}Sn\{^{1}H\}$ NMR spectrum of $Sn[N(SiMe_3)_2]_2$.

3.3 Synthesis of Mes^*_2Sn (crude product)

The synthesis of Mes^*_2Sn followed a literature procedure of Weidenbruch et al.[8]

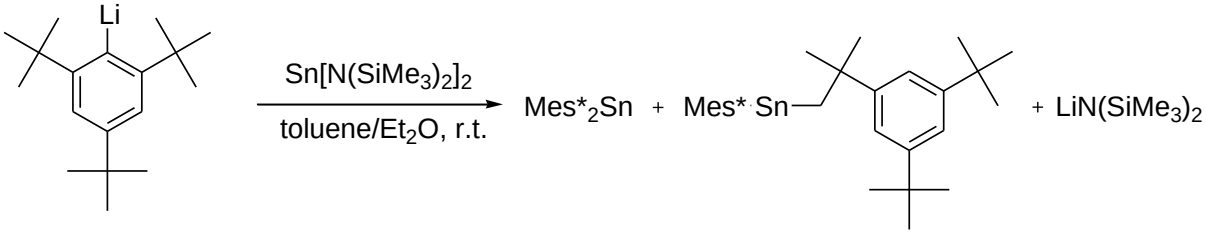
Method a)



Mes*Br (3.253 g, 10.00 mmol) was dissolved in Et_2O (20 mL) and cooled to −30 °C. The now cloudy solution was treated with *n*-BuLi (2.5 M, 4.40 mL, 11.00 mmol), which resulted in a clear and colorless solution. The reaction mixture was brought to room temperature and stirred for 2 h. Upon removal of the solvent and drying *in vacuo* for 30 min, the colorless solid was washed four times with *n*-hexane (5 mL). The colorless solid was dissolved in a mixture of toluene (20 mL) and thf (5 mL) and added to a solution of $Sn[N(SiMe_3)_2]_2$ (1.653 g, 3.79 mmol) in toluene (10 mL). After stirring the dark red reaction mixture for 1 h, it was concentrated to approximately half volume and stored at −24 °C for 8 h. A precipitate was formed which was filtered off (F4) and the

solvent removed *in vacuo*. Extracting with *n*-hexane (20 mL) and filtration (F4) resulted in a red, clear filtrate which was concentrate to approximately 10 mL. Red crystals formed were identified as Mes*$_2$Sn by unit cell determination. Colorless crystals found between the red crystals were identified as LiN(SiMe$_3$)$_2$ · thf (unit cell determination). Fractionated crystallization always led to a mixture of Mes*$_2$Sn, Mes*SnMes' and LiN(SiMe$_3$)$_2$ as indicated by ^{1}H NMR spectroscopy. Since no further purification could be achieved the crude product was used as is.

Method b)



Mes*Li (1.100 g, 4.36 mmol) was dissolved in Et$_2$O (10 mL) and added to a solution of Sn[N(SiMe$_3$)$_2$]$_2$ (0.958 g, 2.18 mmol) in toluene (10 mL). After stirring for 2.5 h, the solvent is removed *in vacuo* and the main part of LiN(SiMe$_3$)$_2$ was sublimed off (70 °C, dynamic vacuum: 10^{-3} mbar; complete removal of LiN(SiMe$_3$)$_2$ was not possible). The residue was extracted with *n*-hexane (10 mL) and filtrated (F4). Recrystallization from toluene yielded mostly LiN(SiMe$_3$)$_2$ in the first fraction (discarded). The solvent from the supernatant was removed *in vacuo* and the crude product used for follow-up-chemistry without further purification.

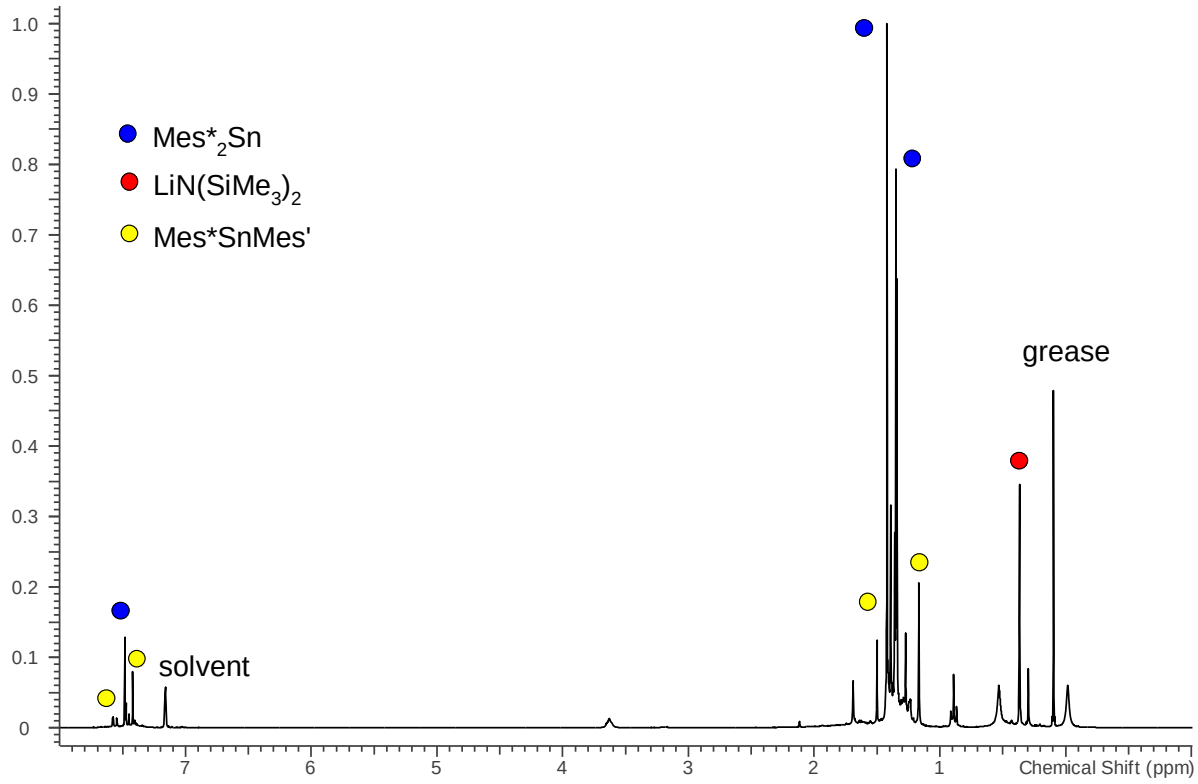
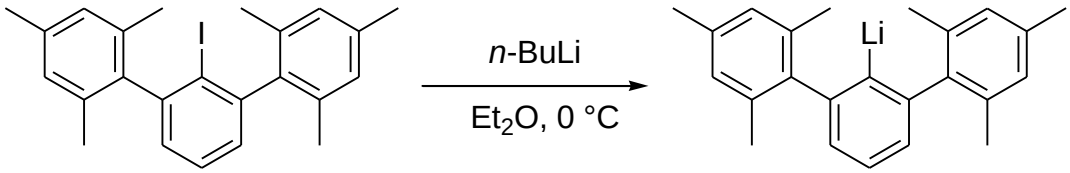


Figure S7: ^{1}H NMR spectrum of the product mixture in the Mes*$_2$Sn synthesis.

3.4 Synthesis of TerLi



To a stirred and cooled (0 °C) suspension of TerI (2.353 g, 5.34 mmol) in Et_2O (20 mL) was added *n*-BuLi (2.5 M, 2.2 mL, 5.50 mmol). The clear, golden solution was stirred at 0 °C for 1 h. After removal of the solvent, the colorless residue was washed with toluene (1 mL) and dried *in vacuo* for 30 min. Yield: 1.678 g (5.24 mmol, 98.1%). Purity >98%.

TerLi was unstable in thf and decomposes within 1 day in thf solution but could be stored as a solid under argon.

^{1}H NMR (298.2 K, thf-d_8, 300.13 MHz): 2.07 (s, 12 H, *o*-C***H***$_3$), 2.23 (s, 6 H, *p*-C***H***$_3$), 6.57 (m, 2), 6.79 (s, 4 H, Mes-C***H***), 6.88 (m, 1 H, *p*-C***H***).

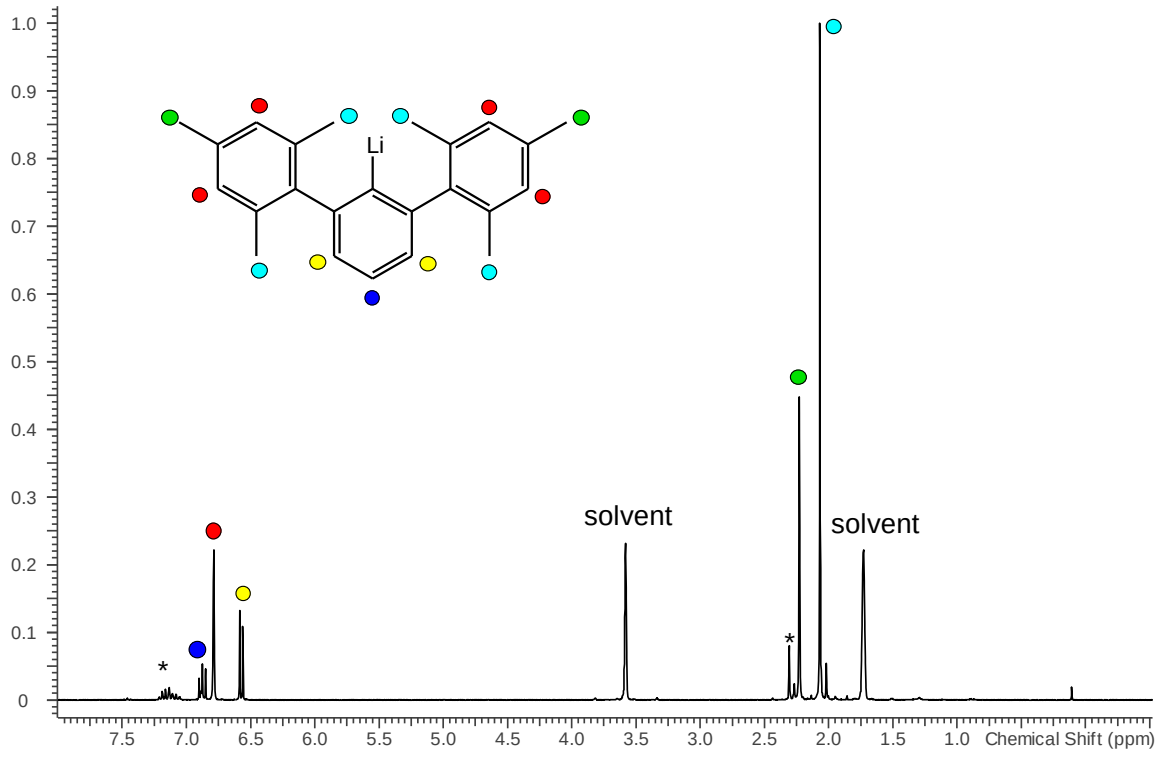
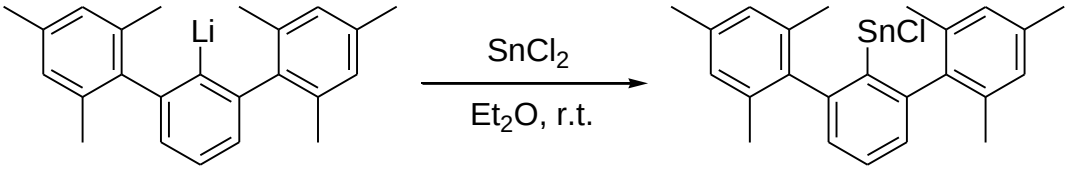


Figure S8: ^{1}H NMR spectrum of TerLi. Asterisk indicates small amounts of toluene.

3.5 Synthesis of TerSnCl



The synthesis followed a literature procedure of Power et al.[9] To a stirred suspension of $SnCl_2$ (1.043 g, 5.50 mmol) in Et_2O (10 mL) was added a solution of TerLi (1.678 g, 5.24 mmol) in Et_2O (20 mL) at room temperature. The violet reaction mixture (indicating formation of Ter_2Sn) is stirred for 4 h. Upon removal of the solvent from the now orange to red suspension, the residue was dried *in vacuo* for 15 min and extracted with toluene (20 mL). After filtration over a celite padded frit (F4), the orange-red solution is concentrated. Storage at 5 °C resulted in the deposition of yellow crystals. The crystals were washed with *n*-hexane (2 mL) and dried *in vacuo*. A second crop of crystals could be obtained from the supernatant. Yield: 1.083 g (2.32 mmol, 44.2%).

Mp.: 202 °C (Lit.: 186°C).[**Source**] **CHN** calc. (found) in %: C 61.64 (61.52), H 5.39 (5.30). **^{1}H NMR** (298.2 K, CD_2Cl_2, 300.13 MHz): 2.10 (s, 12 H, *o*-C***H***$_3$), 2.33 (s, 6 H, *p*-C***H***$_3$), 6.91 (s, 4 H, Mes-C***H***), 7.07 (m, 2 H, *m*-C***H***), 7.44 (m, 1 H, *p*-C***H***); (298.2 K,

benzene-d_6, 300.13 MHz): 2.16 (s, 12 H, o-C***H***$_3$), 2.21 (s, 6 H, *p*-C***H***$_3$), 6.82 (s, 4 H, Mes-C***H***), 7.00 (m, 2 H, *m*-C***H***), 7.22 (m, 1 H, *p*-C***H***). **^{13}C{^{1}H} NMR** (298.2 K, CD_2Cl_2, 75.48 MHz): 21.6 (s, *p*-***C***H$_3$), 21.9 (s, *o*-***C***H$_3$), 129.5 (s, Mes-***C***H and *p*-***C***H), 129.5 (*m*-***C***H), 130.0 (arom. ***C***), 137.4 (arom. ***C***), 137.5 (arom. ***C***), 138.4 (arom. ***C***), 147.2 (arom. ***C***). **^{119}Sn{^{1}H} NMR** (298.2 K, CD_2Cl_2, 111.85 MHz): −356 (s). **IR** (ATR-IR, 32 scans, cm^{-1}): 3032 (w), 3003 (w), 2968 (w), 2937 (w), 2914 (w), 2850 (w), 2725 (w), 1610 (m), 1570 (w), 1556 (m), 1477 (m), 1437 (s), 1373 (s), 1302 (w), 1284 (m), 1257 (w), 1242 (w), 1234 (m), 1173 (m), 1155 (m), 1095 (m), 1082 (m), 1030 (m), 1016 (m), 966 (m), 904 (m), 887 (m), 854 (s), 843 (s), 800 (s), 779 (m), 733 (s), 694 (s), 660 (m), 586 (s), 571 (s), 561 (s), 548 (s). **Raman** (633 nm, accumulation time: 20 s, 20 scans, cm^{-1}): 3010 (4), 2973 (2), 2919 (7), 2854 (2), 2731 (2), 2678 (1), 2544 (1), 2402 (1), 1612 (4), 1581 (2), 1563 (2), 1444 (2), 1405 (2), 1385 (5), 1299 (10), 1277 (3), 1246 (2), 1241 (2), 1165 (2), 1090 (2), 1007 (4), 996 (2), 990 (2), 948 (2), 889 (1), 857 (1), 803 (1), 787 (1), 748 (2), 681 (1), 676 (1), 582 (8), 557 (9), 524 (5), 508 (1), 479 (1), 461 (1), 405 (2), 344 (1), 334 (1), 282 (1), 274 (1), 259 (2), 236 (3).

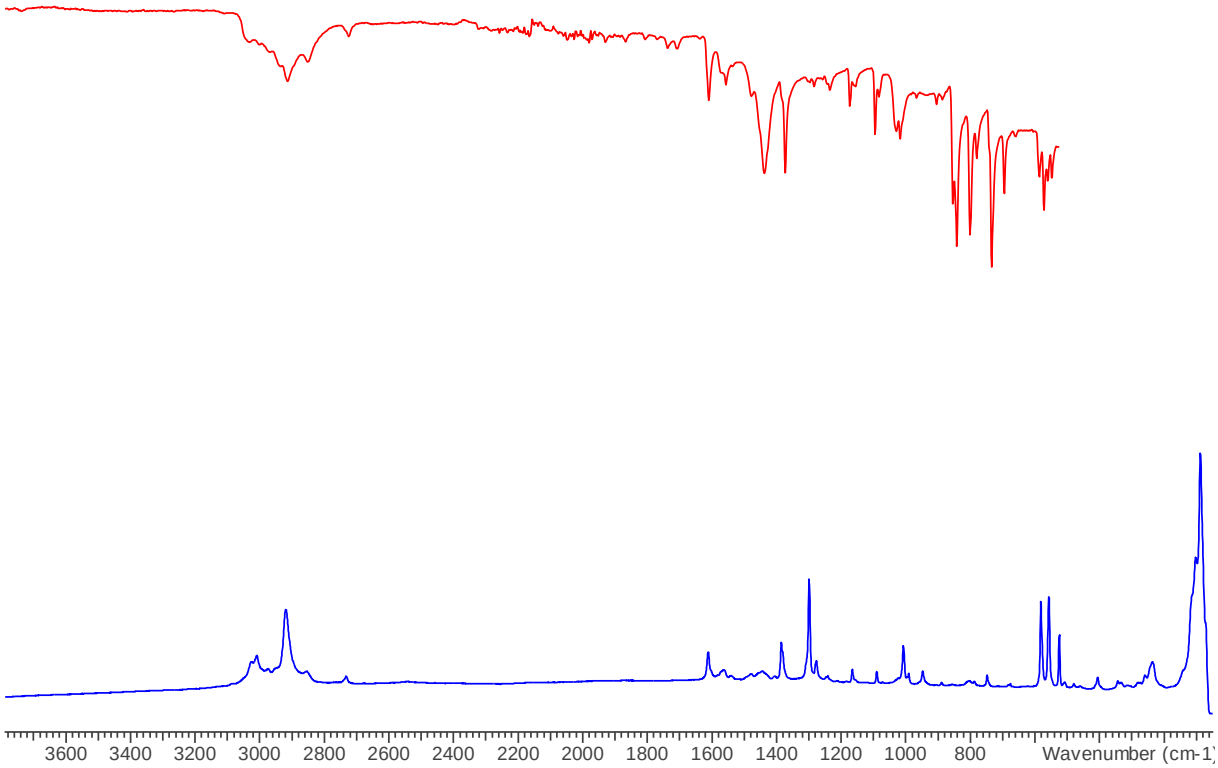


Figure S9: IR (top) and Raman (bottom) spectrum of TerSnCl.

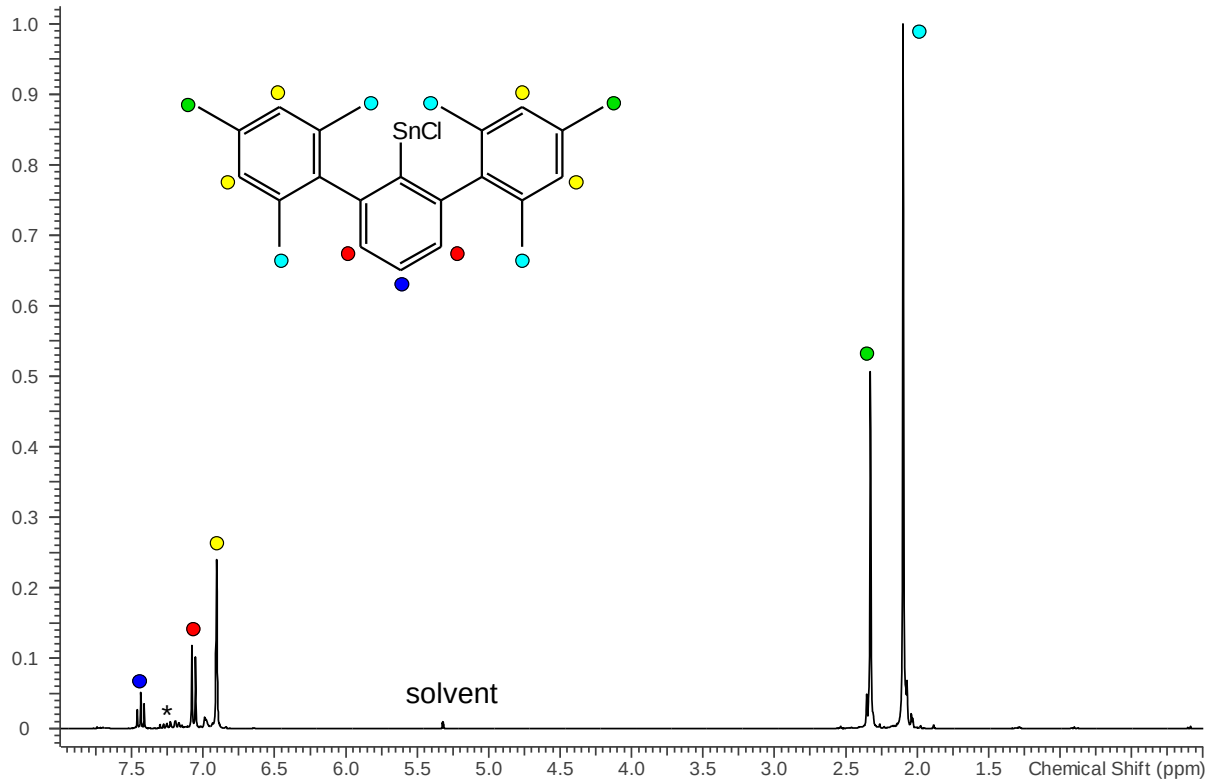


Figure S10: ^{1}H NMR spectrum of TerSnCl in CD_2Cl_2. Asterisk indicates small amounts of toluene.

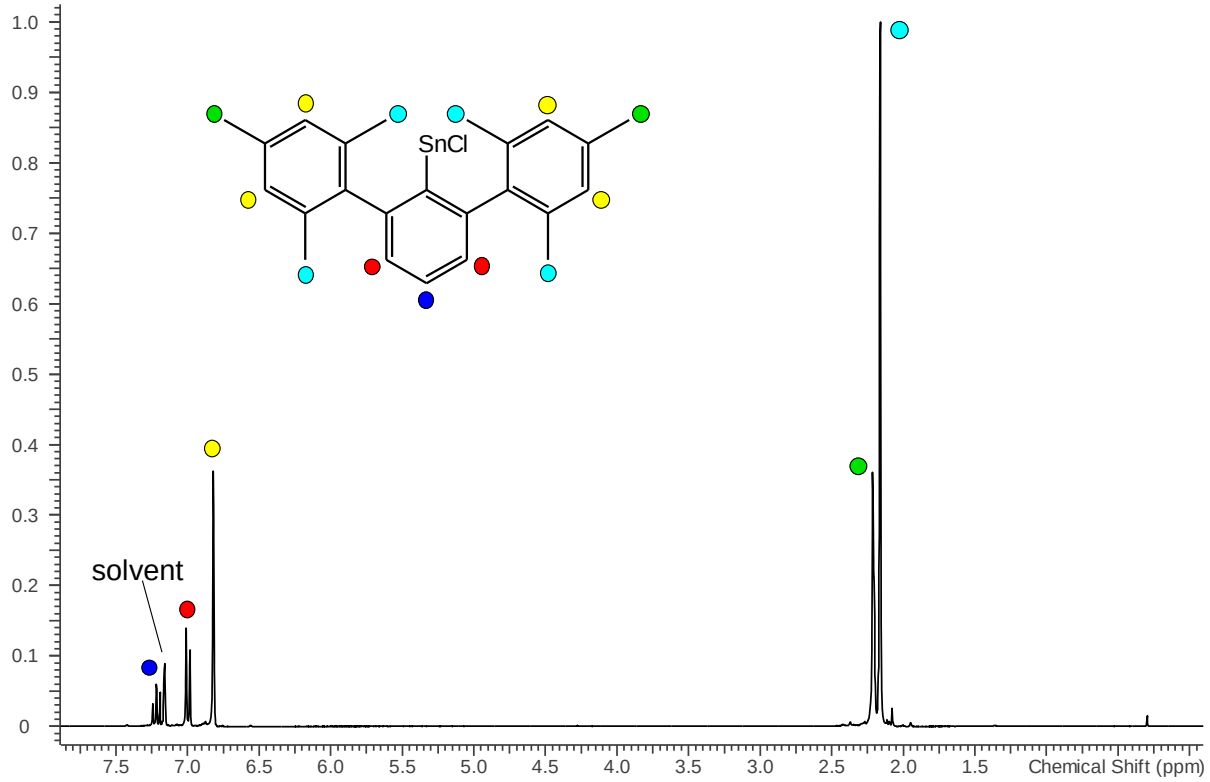


Figure S11: ^{1}H NMR spectrum of TerSnCl in benzene-d_6.

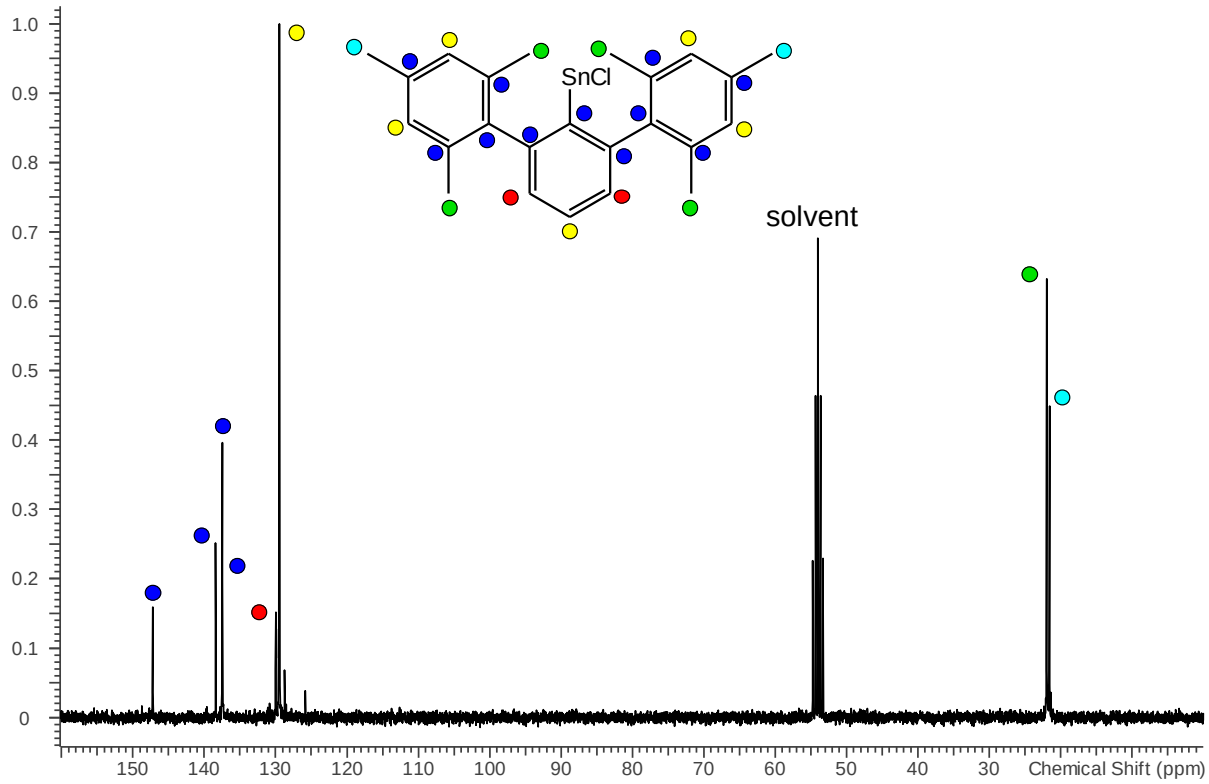


Figure S12: $^{13}C\{^{1}H\}$ NMR spectrum of TerSnCl.

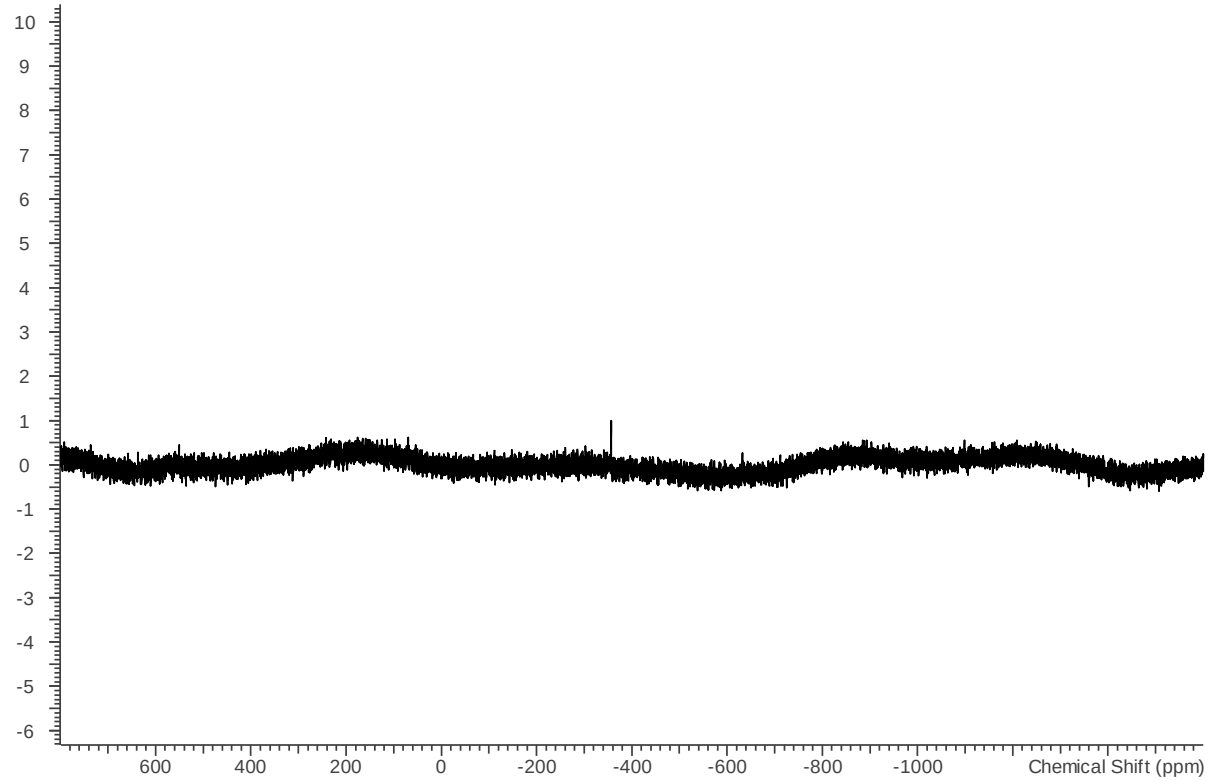
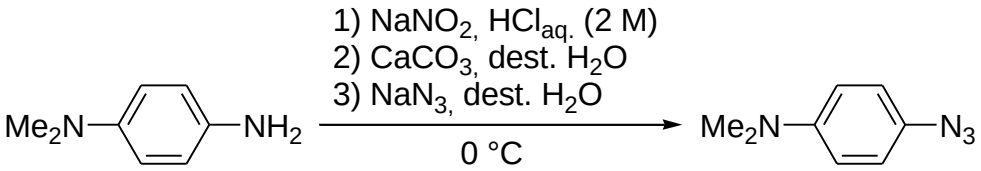


Figure S13: $^{119}Sn\{^{1}H\}$ NMR spectrum of TerSnCl.

3.6 Synthesis of 1-azido-4-dimethylaminobenzene (**1a**)



The synthesis was carried out according to a literature procedure of Ugi et al.[10] 1-Azido-4-dimethylaminobenzene (1.362 g, 10.00 mmol) was dissolved in aqueous HCl (2 M, 20 mL) and cooled to 0 °C. A solution of $NaNO_2$ (0.759 g, 11.00 mmol) in dest. water (10 mL) was added via a dropping funnel over a period of 45 min. *Caution: The temperature should never rise above 5°C!* Upon complete addition of the $NaNO_2$ solution, $CaCO_3$ (0.678 g, 6.77 mmol) is added to the now greenish reaction mixture. At the end of the addition of $CaCO_3$ there should be no further gas evolution and the pH value should be approximately 7 (controlled via pH paper). A solution of NaN_3 (0.780 g, 12.00 mmol) in dest. water (10 mL) was added via a dropping funnel to the still cooled reaction mixture (0 °C). The reaction mixture was brought to room temperature over a period of 1 h (gas evolution ceased, brown oil drops in the aqueous phase). The aqueous phase was extracted tree times with Et_2O (50 mL), the combined organic layers combined and washed with dest. water (50 mL). The organic phase was dried over $MgSO_4$ and the solvent was removed by rotary evaporation. The brownish-blackish solid was sublimed in a dynamic vacuum (10^{-3}mbar) at 50 °C resulting in the deposition of a yellow-orange crystals. Yield: 1.115 g (6.87 mmol, 68.7%).

Crystals of **1a** could be obtained from a saturated benzene solution.

Mp.: 44°C (Lit.: 43-44 °C).[10] **CHN** calc. (found) in %: C 59.24 (59.53), H 6.21 (6.06), N 34.54 (33.74). **^{1}H NMR** (298.6 K, benzene-d_6, 300.13 MHz): 2.42 (s, 6 H, N(C***H***$_3$)$_2$), 6.39 (m, 2 H, arom. C***H***), 6.83 (m, 2 H, arom. C***H***). ^{13}C{^{1}H} NMR (299.2 K, benzene-d_6, 300.13 MHz): 40.7 (s, N(***C***H$_3$)$_2$), 114.4 (s, arom. ***C***H), 120.4 (s, arom. ***C***H), 148.9 (s, arom. ***C***), one resonance not observed. **IR** (ATR-IR, 32 scans, cm^{-1}): 3242 (w), 3209 (w), 3036 (w), 2991 (w), 2891 (m), 2858 (m), 2806 (m), 2415 (w), 2326 (w), 2260 (w), 2118 (s), 2089 (s), 2017 (m), 1855 (m), 1732 (w), 1606 (m), 1566 (m), 1508 (s), 1443 (s), 1414 (m), 1352 (s), 1288 (s), 1227 (s), 1192 (s), 1167 (s), 1126 (s), 1063 (s), 945 (s), 920 (m), 810 (s), 727 (s), 704 (m), 636 (m), 611 (s).

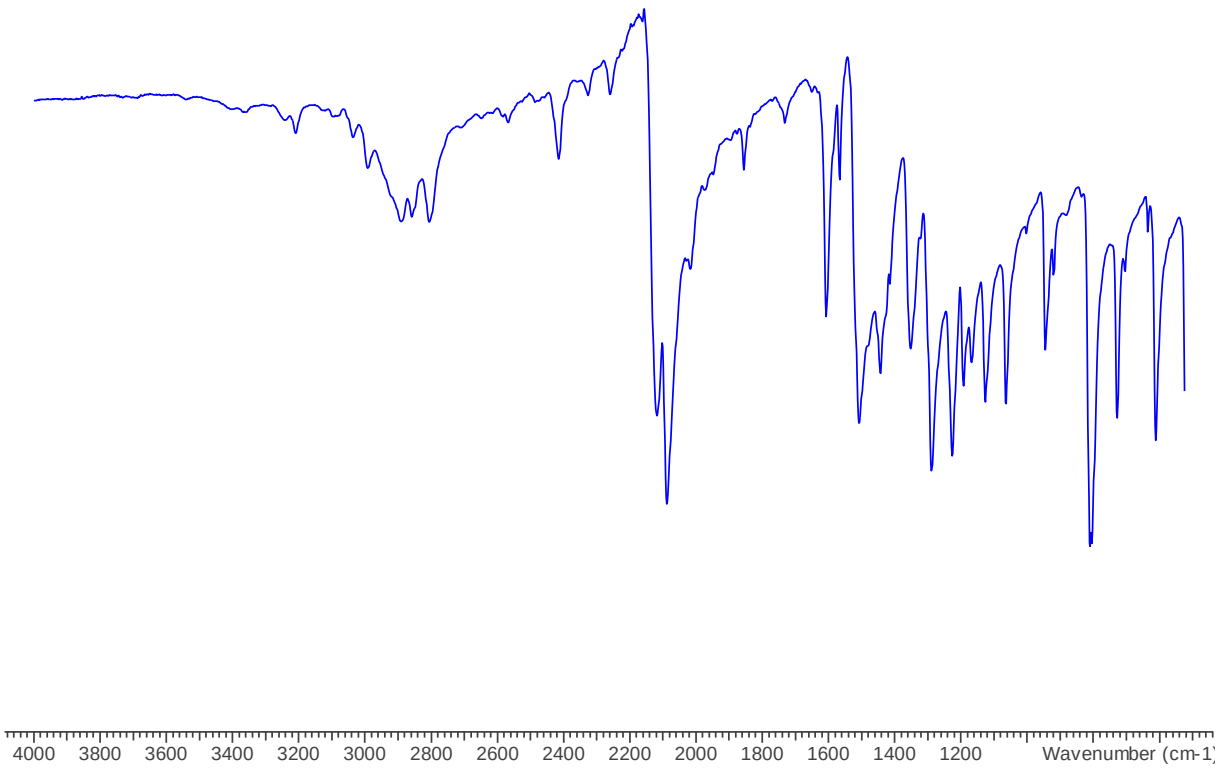


Figure S14: IR spectrum of **1a**.

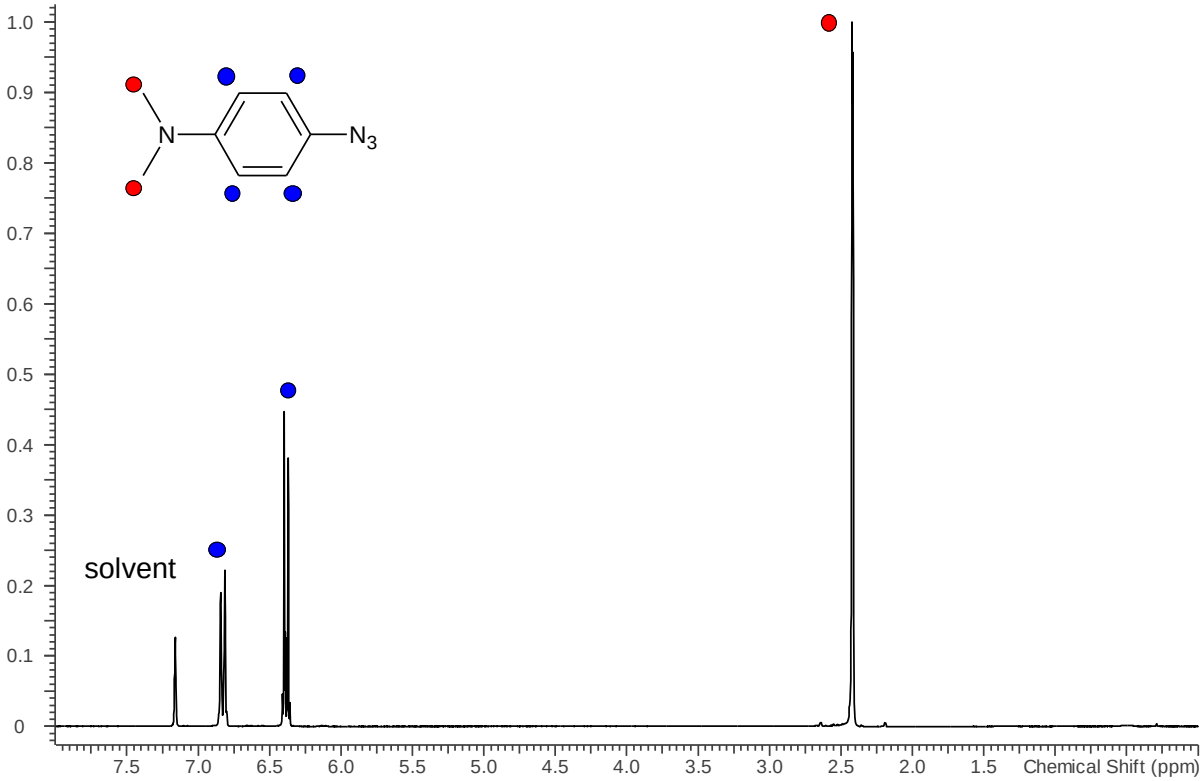


Figure S15: ^{1}H NMR spectrum of **1a**.

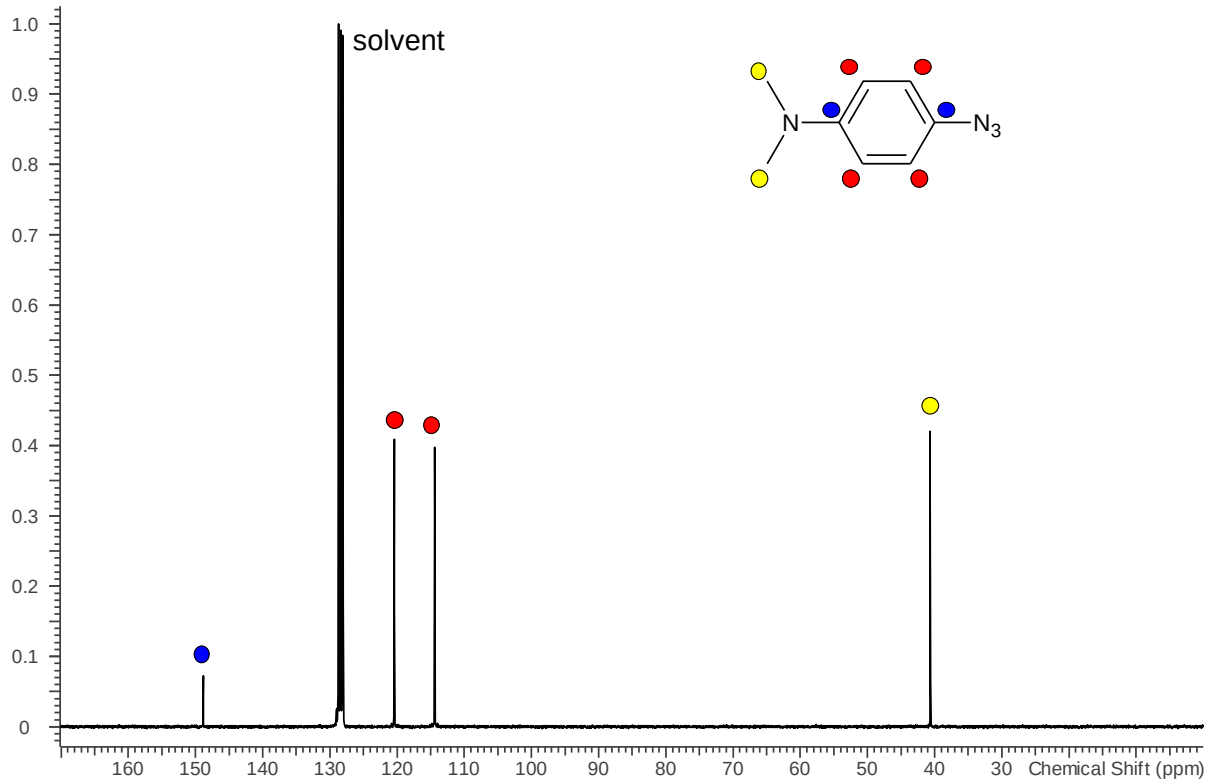


Figure S16: $^{13}C\{^{1}H\}$ NMR of **1a**.

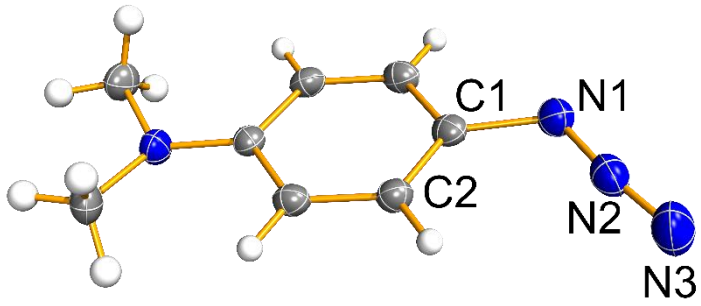
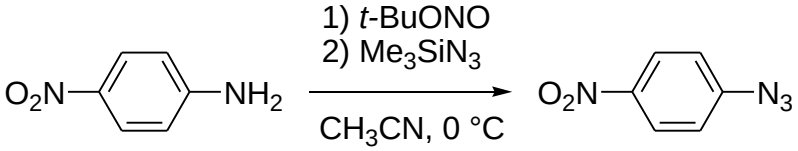


Figure S17: Molecular Structure of **1a**. Thermal ellipsoids are drawn at 50% probability (123(2) K). Selected bond length (Å) and angles (°): N1-N2 1.241(3), N2-N3 1.131(3), C1-N1 1.435(3), N3-N2-N1 173.2(3), N2-N1-C1 115.9(2), C2-C1-N1-N2 4.9(3).

3.7 Synthesis of 1-azido-4-nitrobenzene (**1c**)



The synthesis followed a literature procedure.[11] 1-amino-4-nitrobenzene (0.414 g, 3.00 mmol) was dissolved in acetonitrile (5 mL) and cooled to 0 °C. Then, *t*-BuONO (0.361 g, 3.50 mmol) was added dropwise followed by the dropwise addition of

Me_3SiN_3 (0.403 g, 3.50 mmol, vigorous gas evolution). The reaction mixture was warmed to room temperature and stirred for 1 h. Upon concentration, the crystallization started. Storage at 5 °C for 8 h resulted in the precipitation of **1c**. The supernatant was removed via syringe and the remaining solid was dried *in vacuo*. Yield: 0.300 g (1.83 mmol, 60.9%).

Mp.: 71 °C (Lit.: 70-71 °C).[10] **^{1}H NMR** (298.2 K, benzene-d_6, 300.13 MHz): 6.16 (m, 2 H, arom. C***H***), 7.63 (m, 2 H, arom. C***H***). **IR** (ATR-IR, 32 scans, cm^{-1}): 3236 (w), 3113 (m), 3105 (m), 3080 (m), 3068 (m), 3045 (w), 2403 (m), 2258 (m), 2119 (s), 2085 (s), 1605 (m), 1589 (s), 1512 (s), 1489 (s), 1444 (m), 1419 (m), 1367 (w), 1338 (s), 1327 (s), 1286 (s), 1174 (s), 1153 (m), 1128 (s), 1117 (s), 1107 (s), 1009 (m), 989 (m), 972 (m), 949 (m), 926 (m), 891 (m), 845 (s), 820 (s), 810 (s), 769 (m), 744 (s), 723 (s), 698 (s), 681 (s), 625 (s), 611 (m), 559 (s), 526 (s). **Raman** (633 nm, accumulation time: 10 s, 20 scans, cm^{-1}): 3178 (1), 3116 (1), 3082 (4), 2134 (1), 2092 (1), 1608 (1), 1592 (2), 1525 (1), 1369 (1), 1339 (6), 1313 (1), 1303 (3), 1285 (4), 1241 (1), 1183 (2), 1106 (4), 866 (10), 809 (2), 748 (1), 702 (1), 632 (1), 563 (1), 534 (1), 357 (1), 342 (2), 311 (1), 261 (1), 235 (1), 181 (1).

: IR (top) and Raman (bottom) spectrum of **1c**.

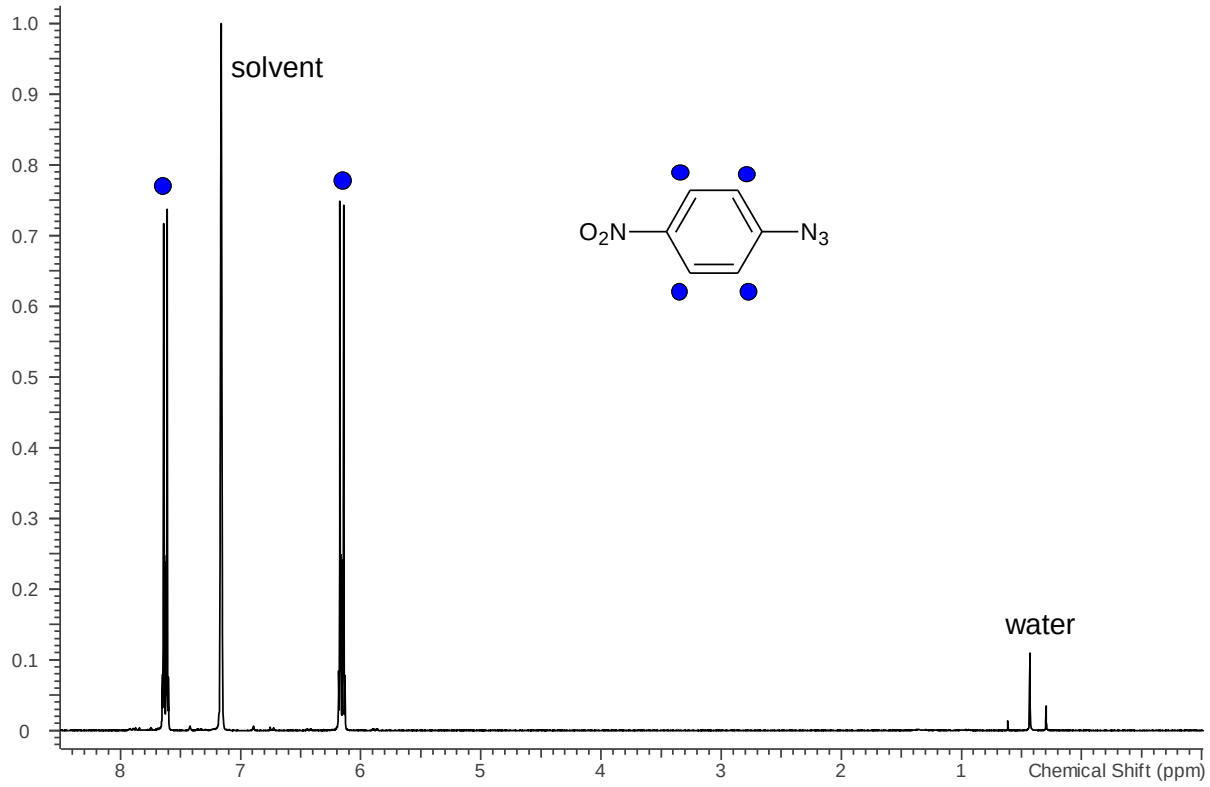
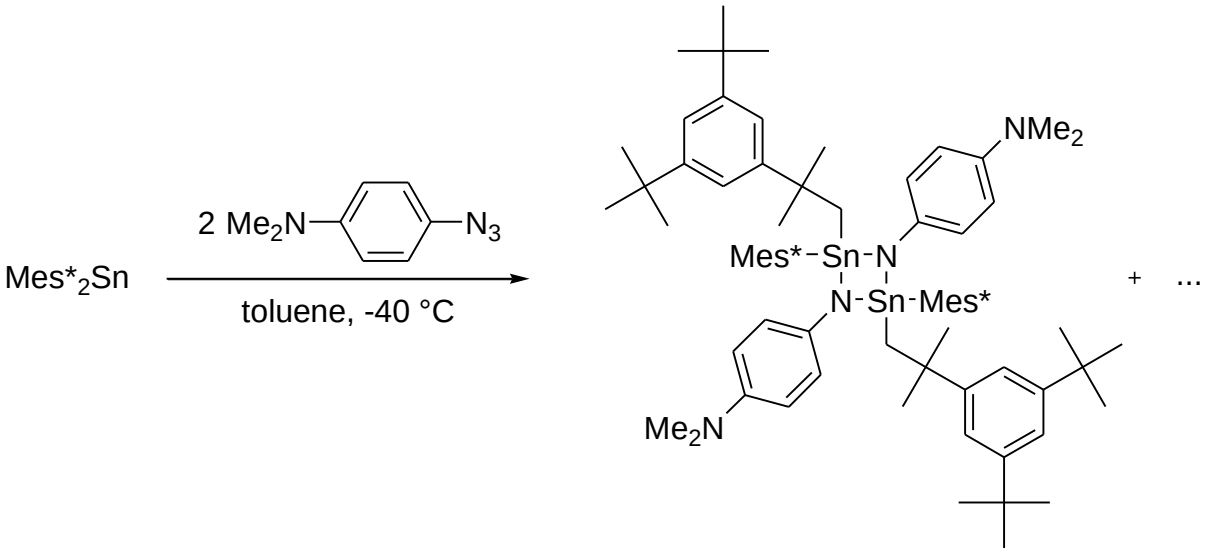


Figure S18: ^{1}H NMR spectrum of **1c**.

4 Synthesis of Compounds

4.1 Reaction of Mes*$_2$Sn with **1a**



A solution of Mes*$_2$Sn (crude product, 0.457 g, 0.75 mmol) in toluene (2 mL) was cooled to −40 °C and **1a** (0.243, 1.50 mmol) dissolved in toluene (2 mL) was added dropwise resulting in a vigorous gas evolution. The reaction mixture is warmed to room temperature and stirred for 2.5 h. After filtration (F4), the clear, red solution is concentrated. A few colorless crystals of **2** were obtained.

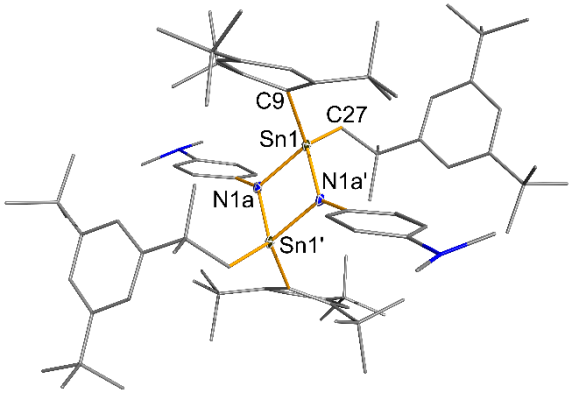
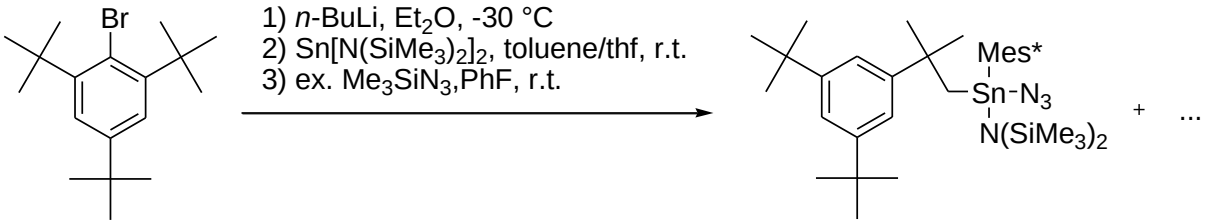


Figure S19: Molecular structure of **2**. Thermal ellipsoids drawn at 50% probability (123(2) K). H atoms omitted for clarity. Selected bond length (Å) and angles (°): Sn1-N1a 2.111(5), Sn1-N1a‘ 2.013(4), Sn1-C9 2.199(2), Sn1-C27 2.173(2), N1a-C1a 1.404(3), N1a‘-Sn1-N1a 80.0(2), N1a-Sn1-C9 118.1(2), N1a-Sn1-C27 105.6(2), C27-Sn1-C9 117.88(8), Sn1‘-N1a-Sn1 100.0(2), C1a-N1a-Sn1 122.4(2), C1a-N1a-Sn1‘ 135.5(2), C2a-C1a-N1a-Sn1 −122.4(4).

4.2 Reaction of Mes*$_2$Sn with Me_3SiN_3



Mes*$_2$Sn was generated prior to the reaction with Me_3SiN_3: Mes*Br (3.253 g, 10.00 mmol) dissolved in Et_2O (20 mL) was reacted with *n*-BuLi (2.5 M, 4.40 mL, 11.00 mmol) at −30 °C. The reaction mixture was warmed to room temperature over a period of 1 h and stirred for additional 2 h. Afterwards the solvent was removed *in vacuo*, the colorless residue was washed four times with *n*-hexane (5 mL) and dried *in vacuo*. After suspending a mixture of the purified Mes*Li and Sn[N(SiMe$_3$)$_2$]$_2$ in toluene (30 mL), thf (5 mL) was added which resulted in an immediate color change from orange to deep red. The reaction mixture was stirred for 1 h and then concentrated to approximately ½ volume. Crude Mes*$_2$Sn was obtained by fractionated crystallization.

The crude product was dissolved in fluorobenzene (10 mL) directly reacted with Me_3SiN_3 (1.060 g, 10.00 mmol) at −40 °C which resulted in a slow gas evolution. Upon stirring in the cold for 0.5 h in the cold, the reaction mixture was warmed to room temperature and stirred for an additional hour. The solvent was removed *in vacuo* and the remaining solid was extracted with *n*-hexane (5 mL). After filtration (F4/celite), the clear, orange solution was concentrated and stored at 5 °C. Crystals of **3** could be isolated by crystal picking. The bulk phase consisted of a mixture of products according to a proton NMR spectrum.

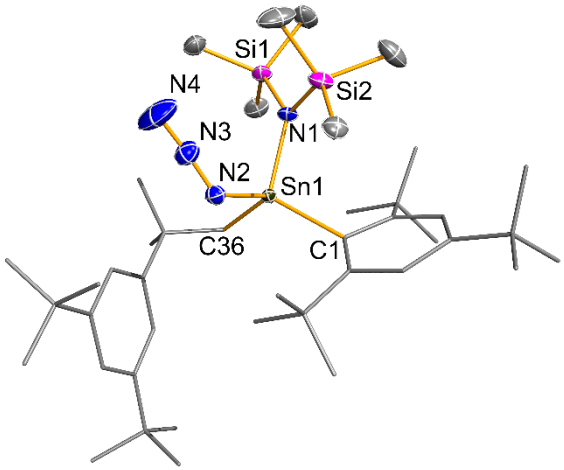
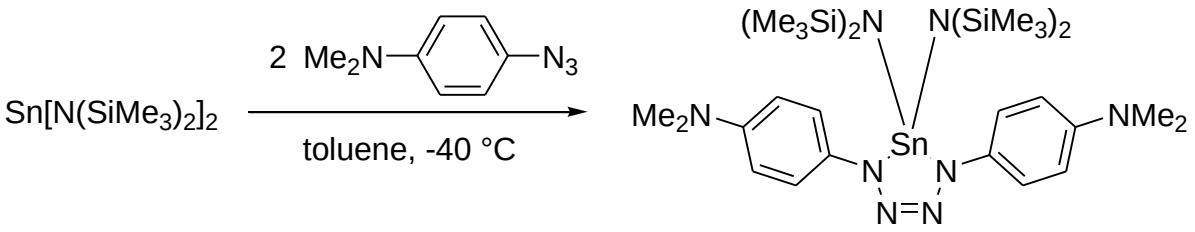


Figure S20: Molecular structure of **3**. Thermal ellipsoids drawn at 50% probability (123(2) K). H atoms omitted for clarity. Selected bond length (Å) and angles (°): Sn1-N1 2.068(2), Sn1-N2 2.101(2), Sn1-C1 2.167(2), Sn1-C36 2.169(2), N2-N3 1.198(3), N3-N4 1.147(3), N1-Si1 1.749(2), N1-Si2 1.771(2), N1-Sn1-N2 98.51(7), N1-Sn1-C1 105.88(7), N2- Sn1-C1 106.56(7), N1-Sn1-C36 118.92(7), C1-Sn1-C36 118.23(7), Si1-N1-Sn1 123.77(9), Si1-N1-Si2 116.95(9), Si2-N1-Sn1 117.59(8), N2-N3-N4 175.5(3), N3-N2-Sn1 122.3(2).

4.3 Synthesis of **4a**



$Sn[N(SiMe_3)_2]_2$ (1.758 g, 4.00 mmol) was dissolved in toluene (10 mL) and cooled to −40 °C. A solution of **1a** (1.298 g, 8.00 mmol) in toluene (10 mL) was added dropwise, which resulted in an immediate gas evolution. The reaction mixture was stirred in the cold for 45 min and then warmed to room temperature. After stirring the reaction mixture at this temperature for another 45 min, the gas evolution ceased and the solution was filtered (F4). The filtrate was concentrated to induce crystallization. Yield: 1.741 g (2.37 mmol, 59.1%) of **4a** as yellow crystalline needles in three crops.

Mp.: 104 °C (decomp.). **CHN** calc (found) in %: 45.70 (45.362), H 7.67 (6.564), N 15.23 (15.324). **^{1}H NMR** (298.2 K, benzene-d_6, 300.13 MHz): 0.30 (s, 36 H, $^{2}J\{^{1}H\text{-}^{29}Si\}$ = 6.2 Hz, Si(C***H***$_3$)$_3$), 2.52 (s, 12 H, N(C***H***$_3$)$_2$), 6.74 (m, 4 H, arom. C***H***), 7.68 (m, 4 H, arom. C***H***). **^{13}C{^{1}H} NMR** (299.0 K, benzene-d_6, 75.48 MHz): 5.8 (s, Si(***C***H$_3$)$_3$), 41.2 (s, N(***C***H$_3$)$_2$), 114.1 (s, arom. ***C***H), 122.9 (s, arom. ***C***H), 138.6 (s, arom ***C***), 148.3 (s, arom. ***C***). **^{29}Si-INEPT NMR** (298.2 K, benzene-d_6, 59.63 MHz): 8.5 (dec, $^{2}J\{^{1}H\text{-}^{29}Si\}$ = 6.5 Hz,

Si$(CH_3)_3$). **^{119}Sn{^{1}H} NMR** (298.3 K, benzene-d_6, 111.85 MHz): −215 (s, N_4***Sn***$(N(SiMe_3)_2)_2$). **IR** (ATR-IR, 32 scans, cm^{-1}): 3074 (w), 3045 (w), 2949 (w), 2893 (w), 2883 (w), 2837 (w), 2791 (w), 1610 (w), 1566 (w), 1510 (s), 1477 (w), 1441 (m), 1406 (w), 1342 (w), 1277 (m), 1265 (m), 1252 (s), 1217 (m), 1188 (w), 1161 (w), 1122 (w), 1057 (w), 1020 (m), 997 (m), 960 (m), 949 (m), 895 (s), 877 (s), 835 (s), 818 (s), 796 (s), 756 (s), 719 (s), 673 (s), 634 (m), 619 (m), 592 (m), 534 (m).

Crystals obtained from toluene were suitable for x-ray diffraction. **4a** was sensitive towards light hence no Raman spectra could be collected.

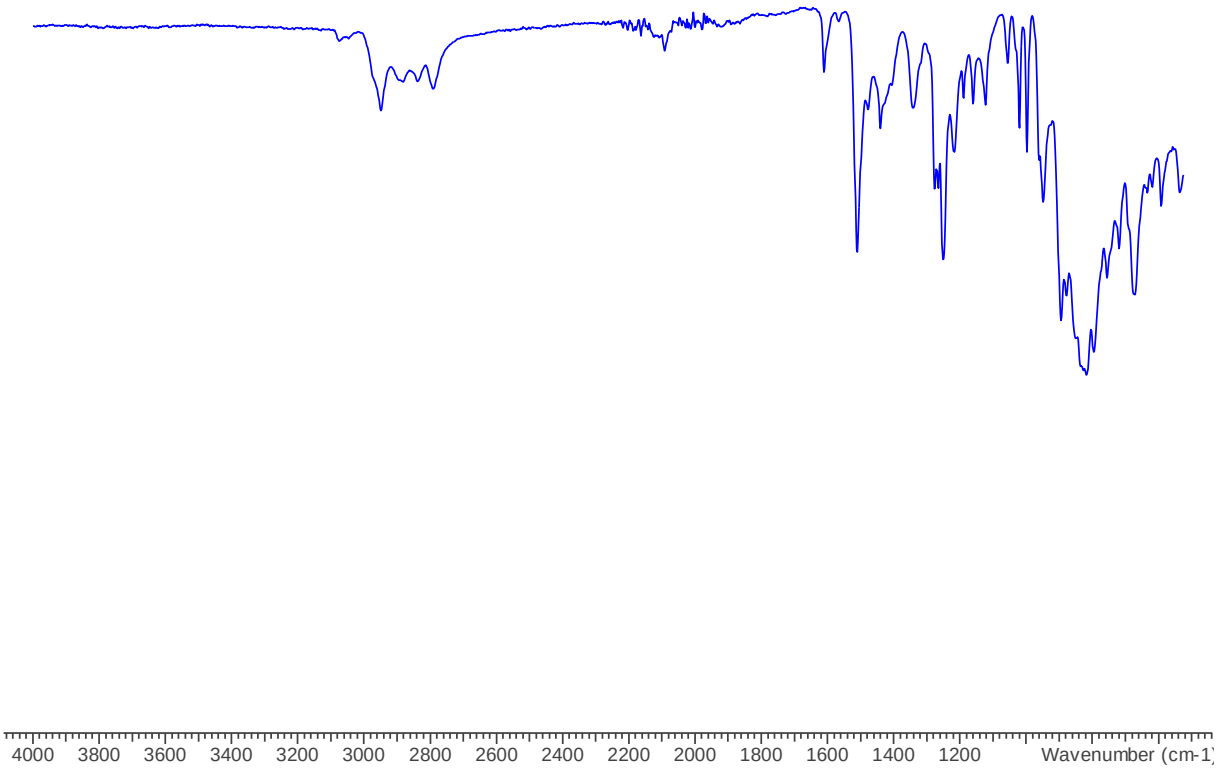


Figure S21: IR spectrum of **4a**.

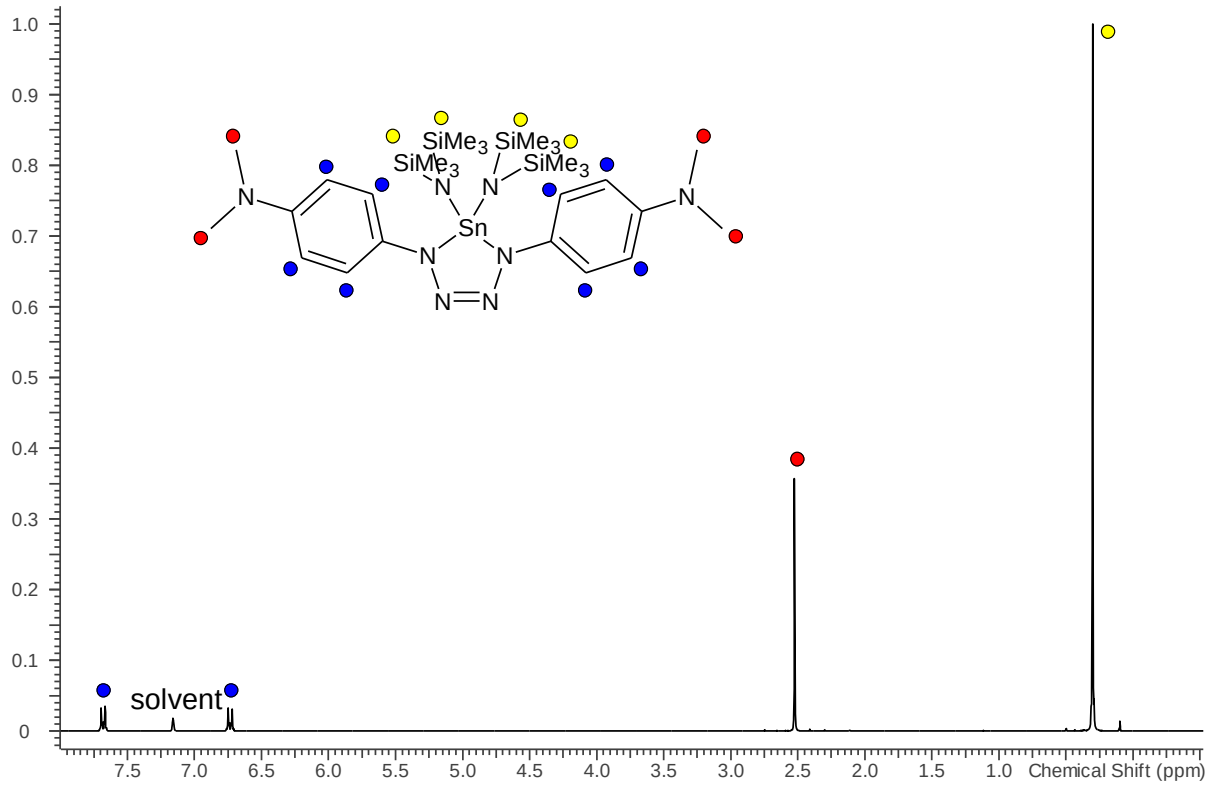


Figure S22: ^{1}H NMR spectrum of **4a**.

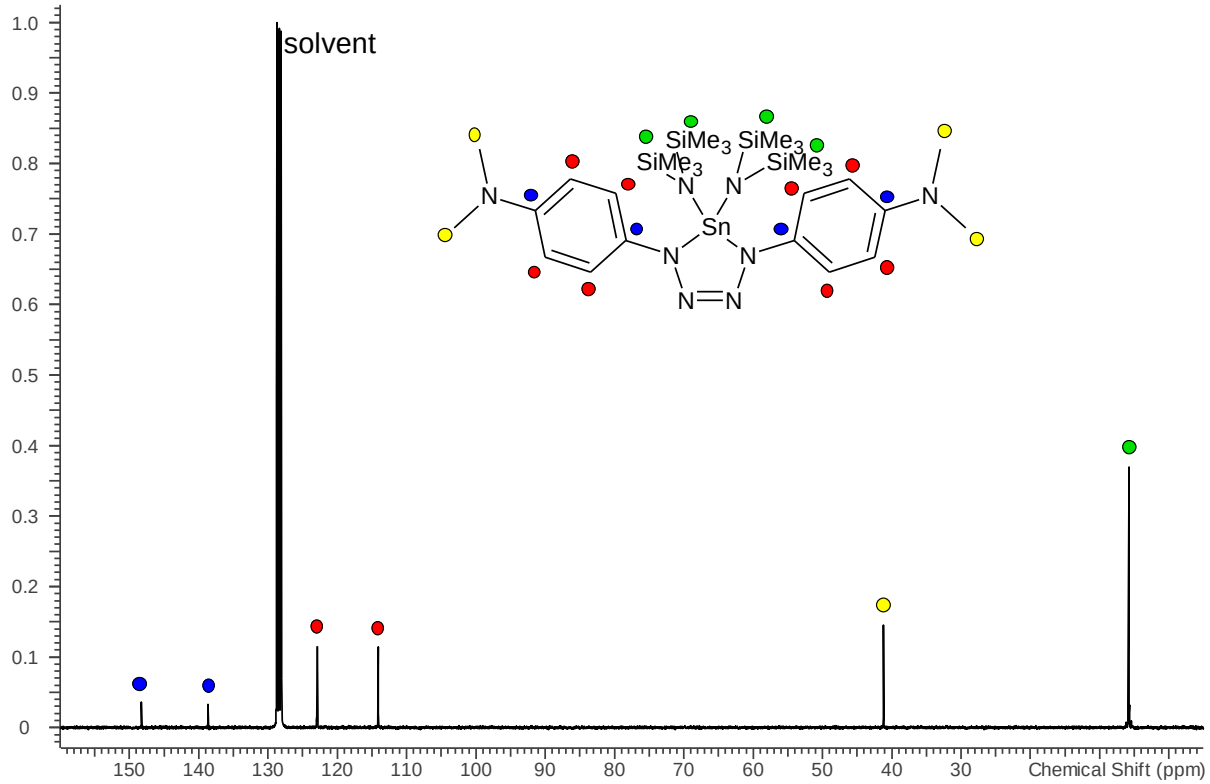


Figure S23: ^{13}C{^{1}H} NMR spectrum of **4a**.

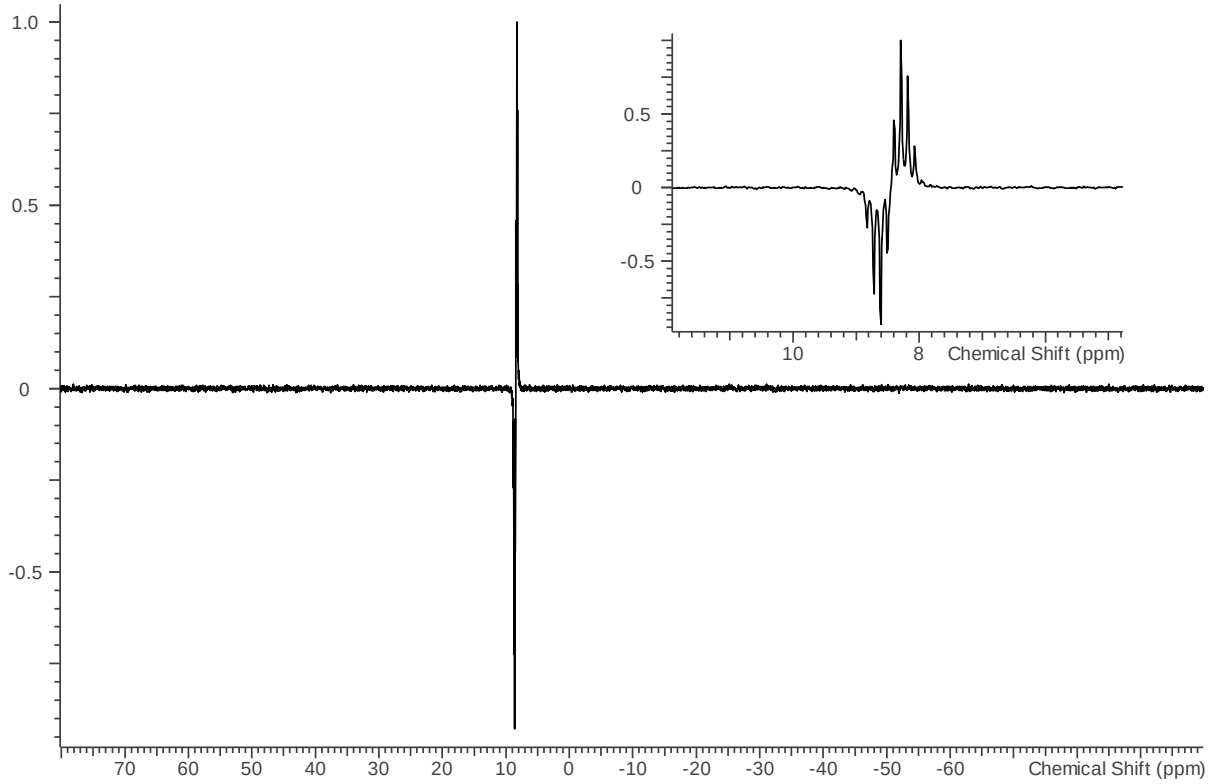


Figure S24: ^{29}Si-INEPT NMR spectrum of **4a**.

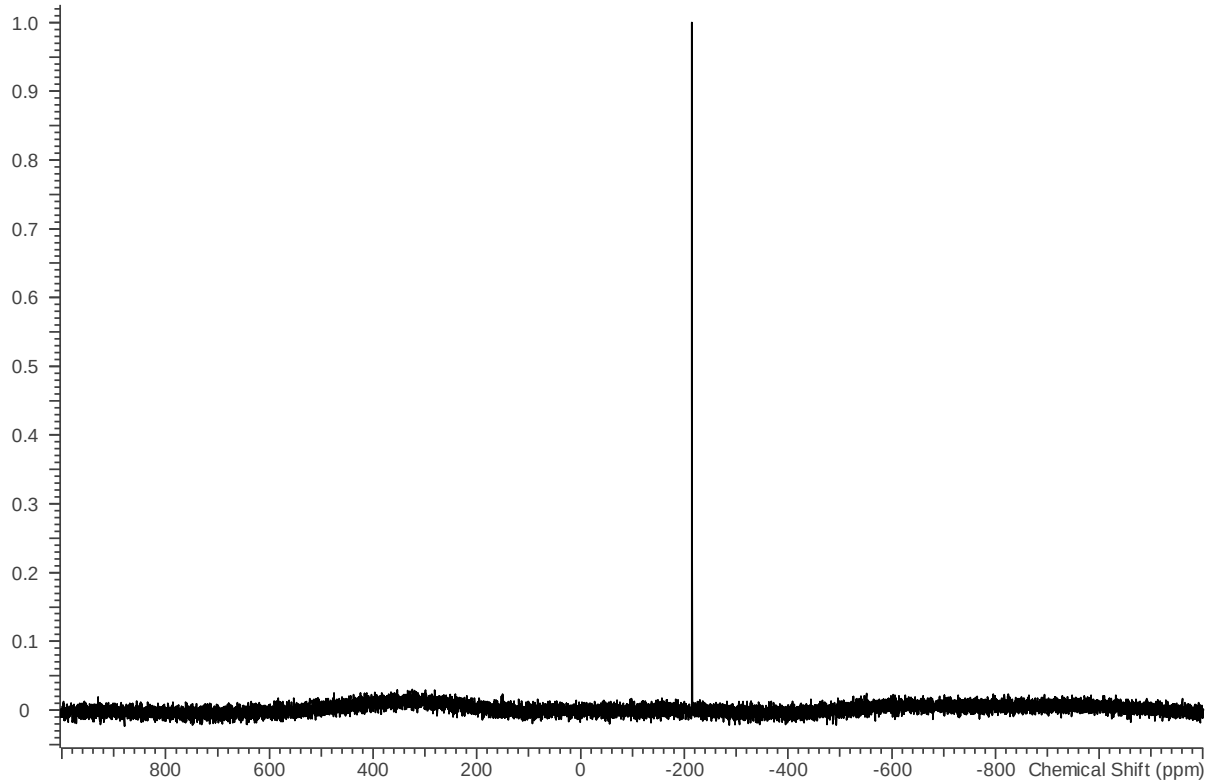


Figure S25: ^{119}Sn{^{1}H} NMR spectrum of **4a**.

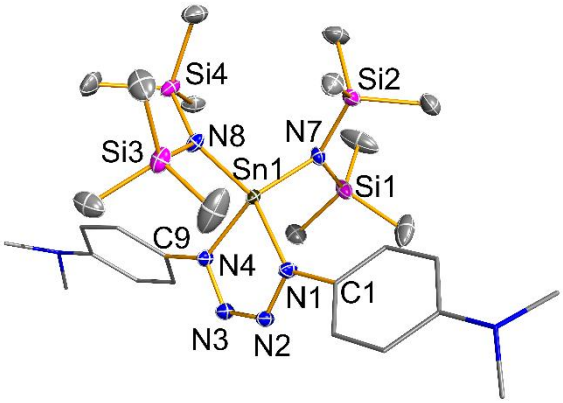
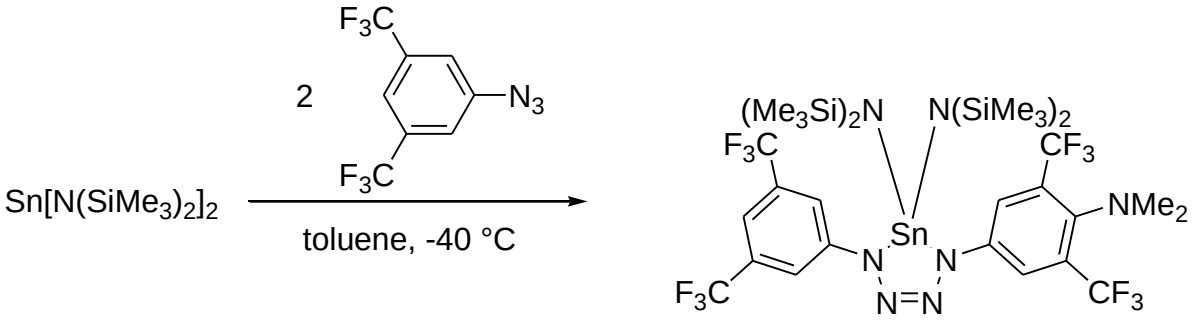


Figure S26: Molecular structure of **4a**. Thermal ellipsoids drawn at 50% probability (123(2) K). H atoms omitted for clarity. Selected bond length (Å) and angles (°): N1-Sn1 2.044(2), N4-Sn1 2.045(2), N7-Sn1 2.036(2), N8-Sn1 2.028(2), N1-N2 1.375(3), N2-N3 1.272(3), N3-N4 1.384(3), N8-Sn1-N7 113.2(1), N8-Sn1-N1 126.6(1), N7-Sn1-N1 105.0(1), N8-Sn1-N4 103.8(1), N7-Sn1-N4 129.19(9), N1-Sn1-N4 76.66(9).

4.4 Synthesis of **4b**



To a stirred solution of $Sn[N(SiMe_3)_2]_2$ (0.149 g, 0.34 mmol) in toluene (5 mL) was added a solution of **1b** (0.173 g, 0.68 mmol) in toluene (3 mL) dropwise at −40 °C. The golden, clear solution was warmed to room temperature over a period of 30 min (slight gas evolution) and stirred at this temperature for additional 30 min. The reaction mixture was filtered (F4) and concentrated until the crystallization started (ca. 3 mL). Fractionated crystallization yielded 0.140 g (0.15 mmol, 44.6%) **4b** as yellowish crystals in two crops.

Crystals obtained from toluene were suitable for single crystal diffraction.

Mp.: 181.0 °C. **CHN** calc. (found): C 36.49 (36.353), H 4.59 (4.378), N 9.12 (9.357). **^{1}H NMR** (298.2 K, C_6D_6, 300.13 MHz): 0.07 (s, 36 H, $^2J\{^1H\text{-}^{29}Si\}$ = 6.4 Hz, $[N(Si(C\boldsymbol{H}_3)_3)_2]_2$), 7.52 (m, 2 H, *p*-C***H***), 8.04 (m, 4 H, *o*-C***H***). **^{13}C{^{1}H} NMR** (298.2 K, C_6D_6, 75.47 MHz): 5.4 (s, $^1J\{^{13}C\text{-}^{29}Si\}$ = 56.7 Hz), 116.7 (m, *p*-C***H***), 119.4 (m, *o*-C***H***), 124.3 (q, $^1J\{^{13}C\text{-}^{19}F\}$ = 273 Hz, C$\boldsymbol{F}_3$), 133.5 (q, $^2J\{^{13}C\text{-}^{19}F\}$ = 33 Hz, ***C***CF_3), 148.5 (s,

arom. *i*-***C***). **^{19}F{^{1}H} NMR** (298.2 K, C_6D_6, 282.40 MHz): −62.4 (s, C***F***$_3$). **^{29}Si-INEPT NMR** (298.2 K, C_6D_6, 59.63 MHz): 10.8 (m, ***Si***$(CH_3)_3$). **^{119}Sn{^{1}H} NMR** (298.2 K, C_6D_6, 111.92 MHz): −227.5 (s, N_4***Sn***N_2). **IR** (ATR-IR, 32 scans, cm^{-1}): 3104 (w), 2966 (w), 1764 (w), 1620 (w), 1608 (w), 1461 (w), 1420 (w), 1377 (m), 1274 (s), 1253 (s), 1181 (m), 1165 (s), 1140 (m), 1125 (s), 1043 (w), 975 (s), 860 (s), 839 (s), 796 (s), 752 (m), 719 (s), 701 (s), 680 (s), 620 (m), 598 (w), 573 (w), 526 (w), 497 (w), 478 (w), 441 (w), 429 (m). **Raman** (laser: 633 nm, accumulation time: 10 s, 20 scans, cm^{-1}): 3105 (1), 3059 (1), 2976 (1), 2971 (1), 2911 (2), 2645 (1), 2595 (1), 1623 (2), 1611 (3), 1474 (1), 1423 (5), 1385 (4), 1323 (1), 1252 (2), 1184 (1), 1169 (1), 1144 (1), 1134 (1), 1111 (1), 1093 (1), 1042 (2), 999 (10), 896 (1), 875 (1), 845 (1), 800 (1), 754 (1), 729 (1), 682 (4), 672 (1), 638 (2), 619 (1), 597 (1), 526 (1), 497 (1), 428 (1), 391 (1), 362 (1), 354 (1), 342 (2), 321 (1), 286 (1), 254 (1), 225 (1), 202 (1).

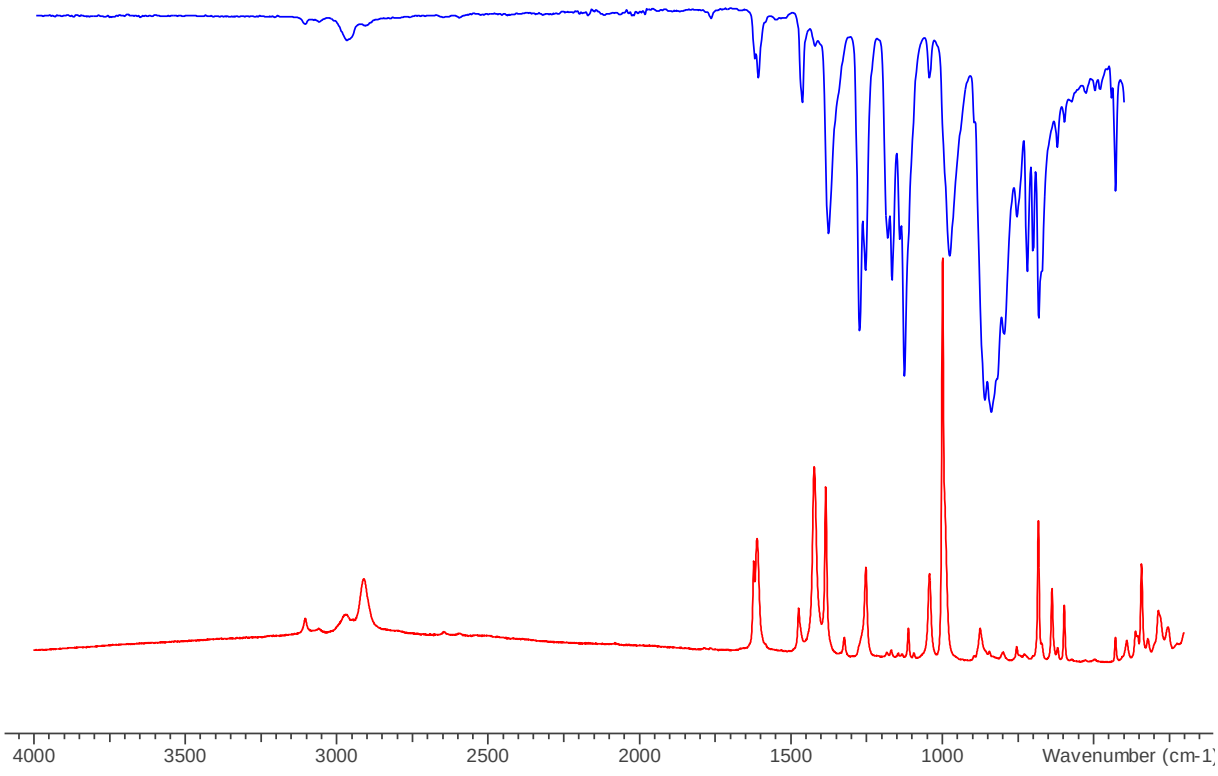


Figure S27: IR (top) and Raman (bottom) spectrum of **4b**.

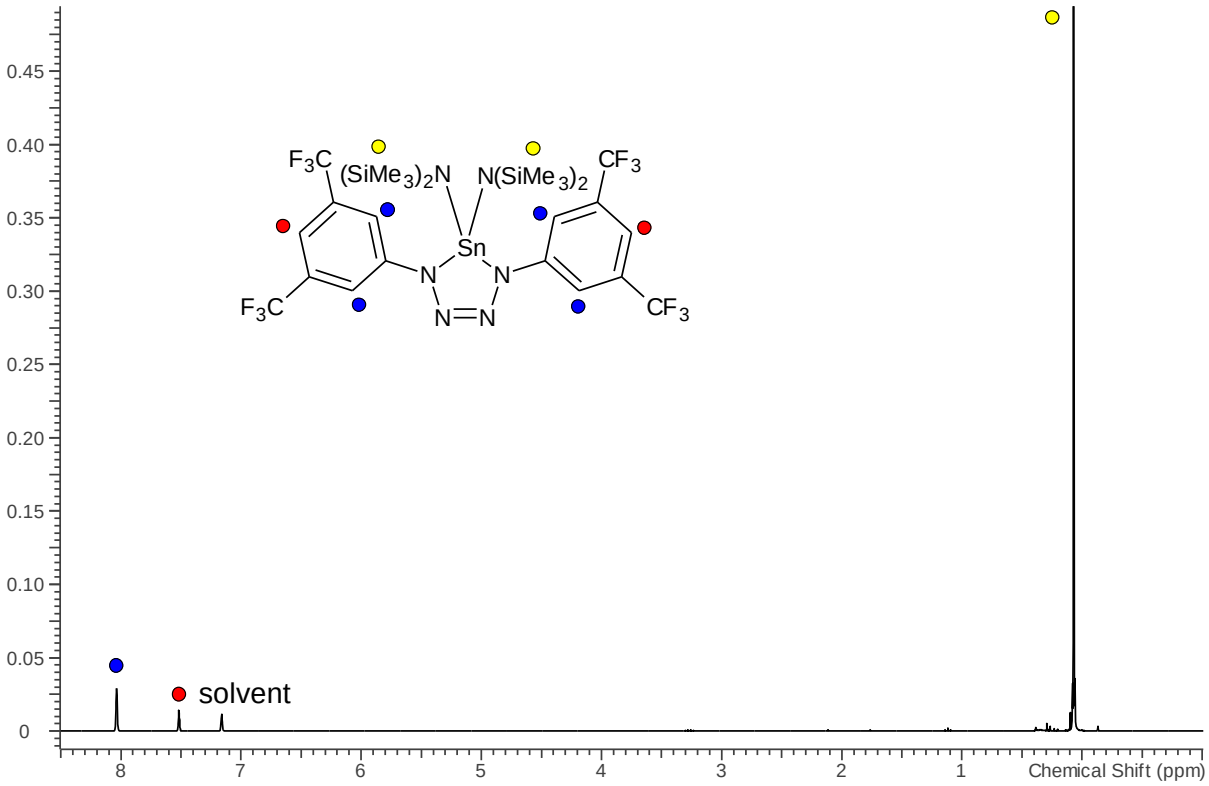


Figure S28: ^{1}H NMR spectrum of **4b**.

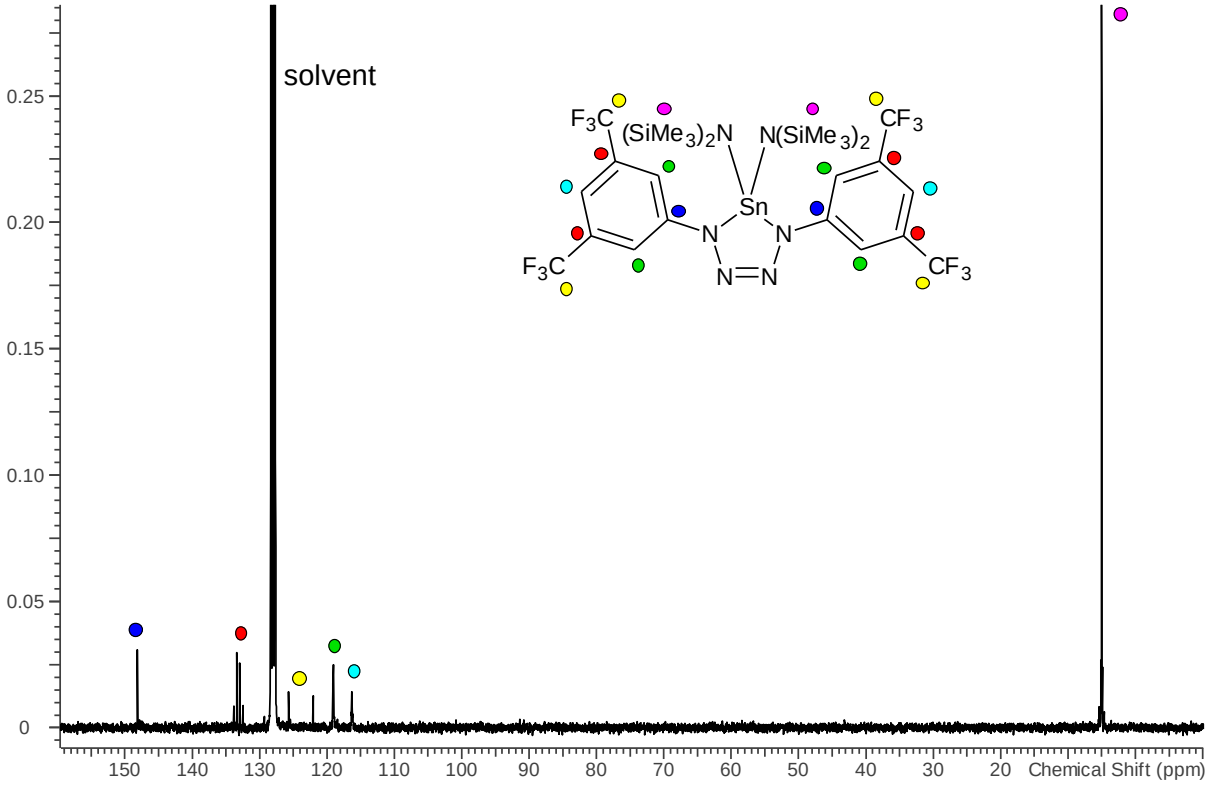


Figure S29: ^{13}C{^{1}H} NMR spectrum of **4b**.

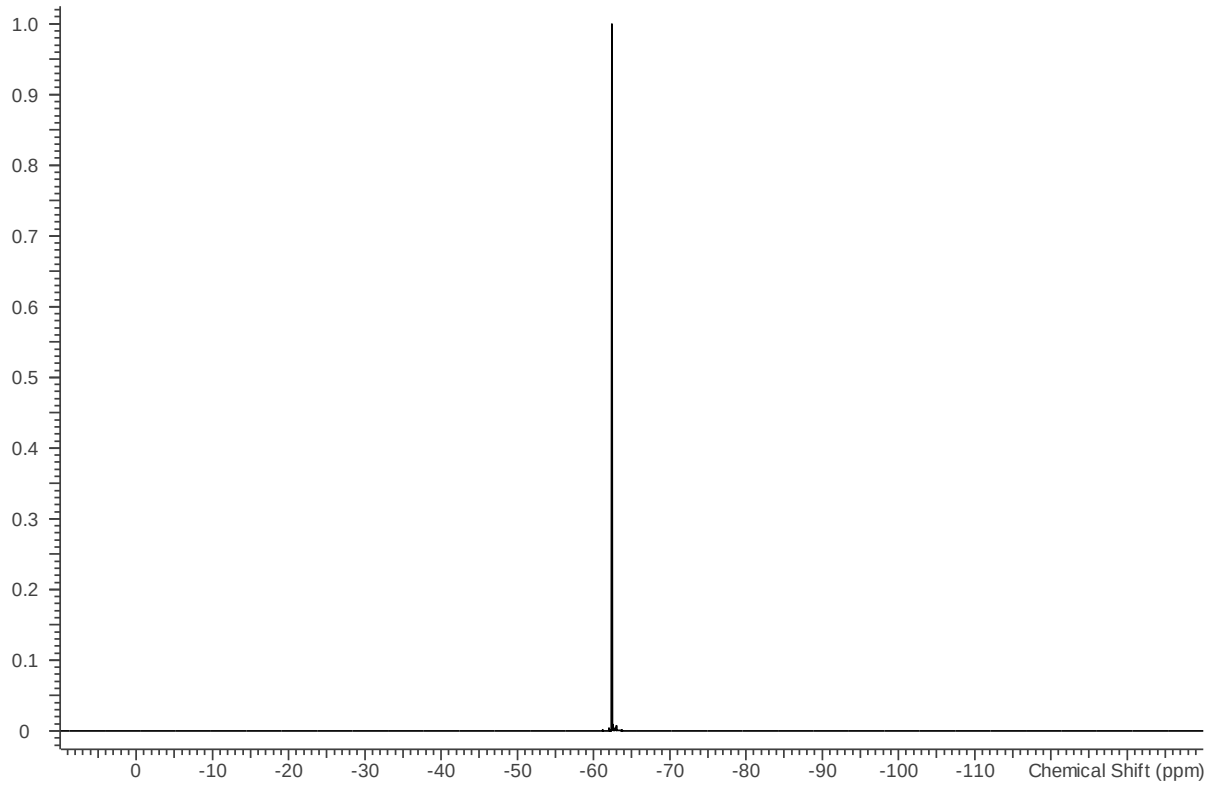


Figure S30: $^{19}F\{^{1}H\}$ NMR spectrum of **4b**.

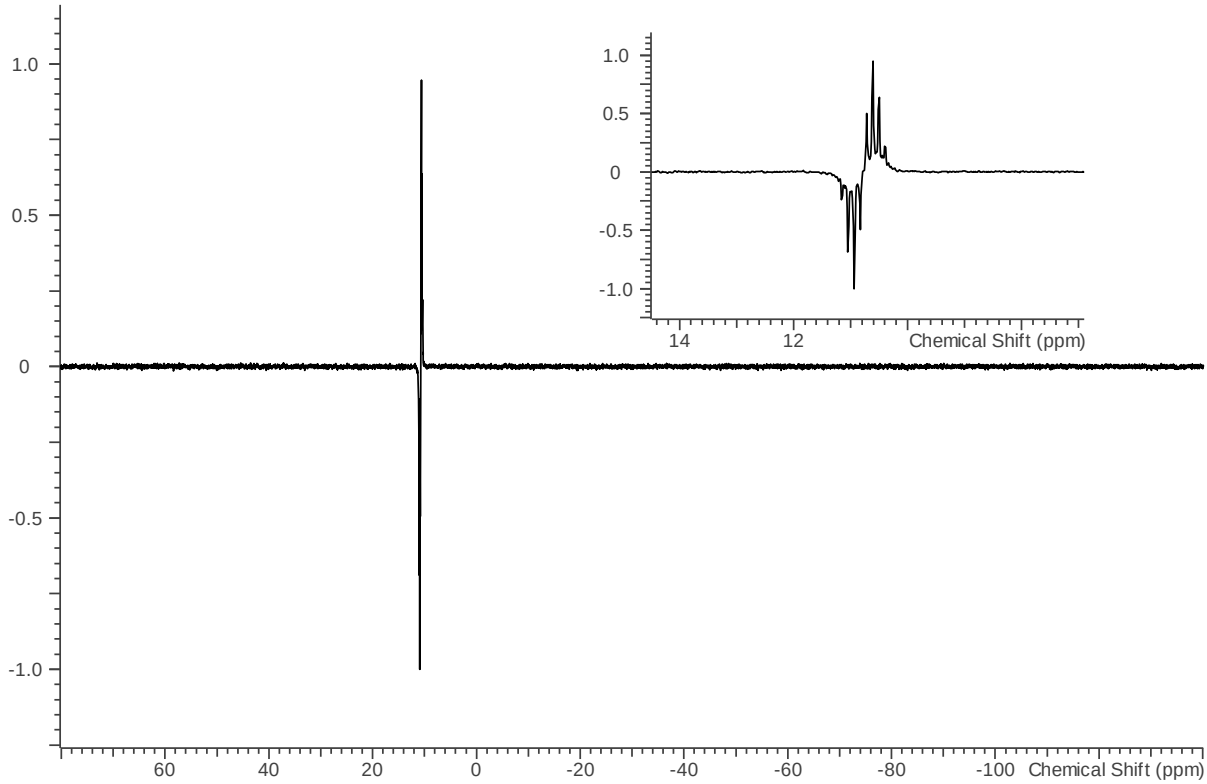


Figure S31: ^{29}Si-INEPT NMR spectrum of **4b**.

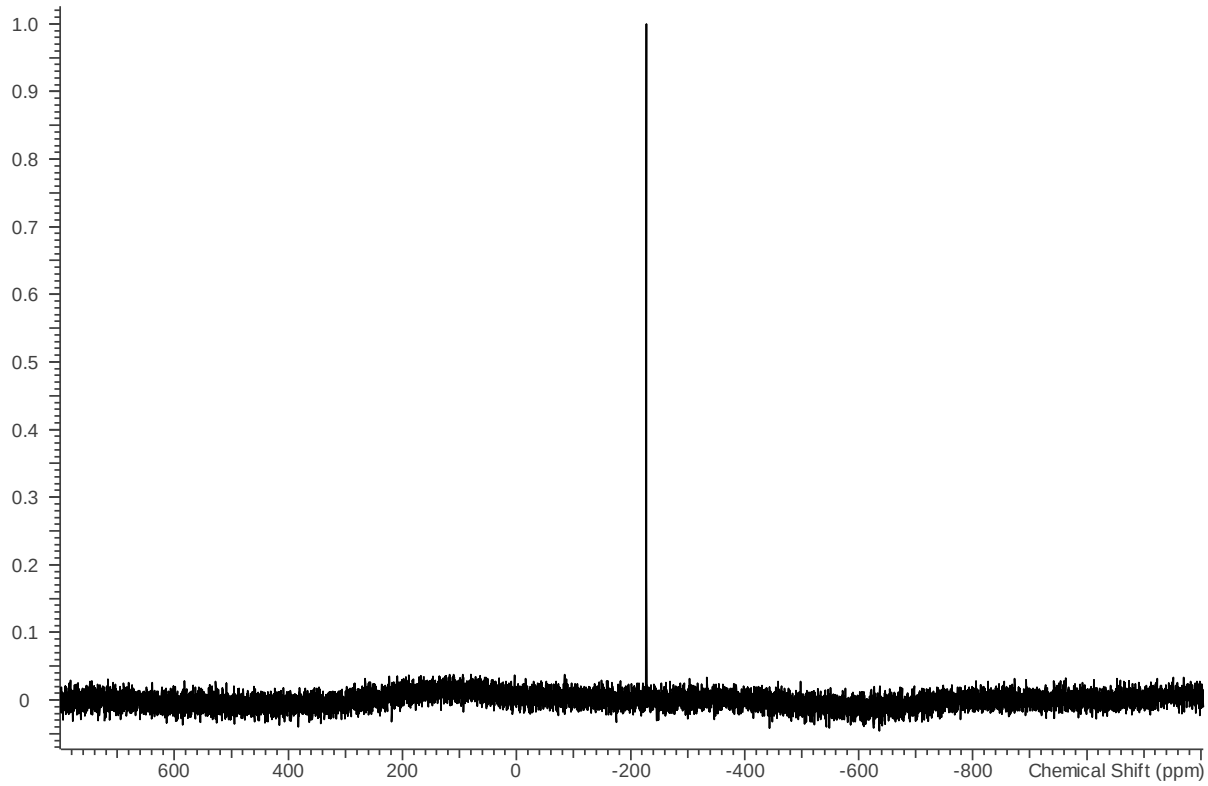


Figure S32: $^{119}Sn\{^{1}H\}$ NMR spectrum of **4b**.

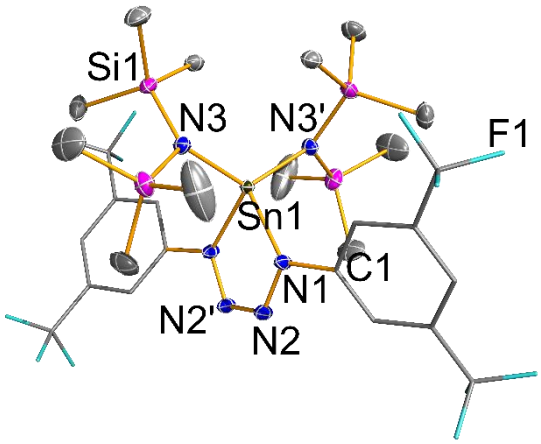
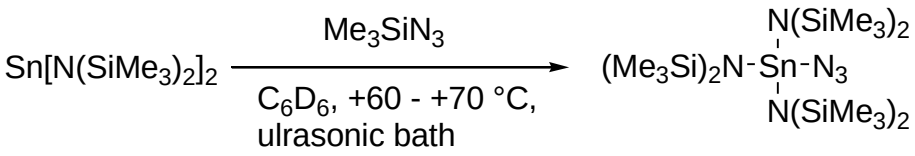


Figure S33: Molecular structure of **4b**. Thermal ellipsoids drawn at 50% probability (123(2) K). H atoms omitted for clarity. Selected bond length (Å) and angles (°): N3-Sn1 2.003(1), N1-Sn1 2.062(1), N1-N2 1.381(2), N2-N2' 1.264(2), N3-Sn1-N3' 123.76(6), N3-Sn1-N1 116.99(5), N3'-Sn1-N1 106.91(4), N1-Sn1-N1' 75.65(6), N2-N1-C1 114.4(1), N2-N1-Sn1 114.88(8), C1-N1-Sn1 128.81(8).

4.5 Synthesis of Azido-tri-bis(trimethylsilyl)amidostannan (**4d**)



The compound was first synthesized by Ruzicka et al. in a similar fashion.[12] $Sn[N(SiMe_3)_2]_2$ (0.046 g, 0.10 mmol) was dissolved in C_6D_6 (0.5 mL) in an NMR tube and Me_3SiN_3 (0.035 g, 0.30 mmol) was added at room temperature. According to ^{1}H, ^{29}Si-INEPT and $^{119}Sn\{^{1}H\}$ NMR spectra, only a small amount of the azido-amido compound was formed. The sample was placed in an ultrasonic bath and sonicated (ca. +60 - +70 °C, heated by sonification). The reaction was monitored by ^{1}H and ^{29}Si-INEPT NMR spectroscopy. After 24 h the reaction was completed and quantitative according to the NMR spectra.

Large, colorless crystal needles of **4d** grow from the NMR solution after cooling to room temperature.

Mp.: 242 °C (Lit.: 248-249 °C). **^{1}H NMR** (298.2 K, benzene-d_6, 300.13 MHz): 0.39 (s, 54 H, $^{1}J\{^{1}H\text{-}^{13}C\}$ = 118.6 Hz, $^{2}J\{^{1}H\text{-}^{29}Si\}$ = 6.4 Hz, $Si(C\boldsymbol{H}_3)_3$). **$^{13}C\{^{1}H\}$ NMR** (298.9 K, benzene-d_6, 75.48 MHz): 6.6 (s, $Si(\boldsymbol{C}H_3)_3$). **^{29}Si-INEPT NMR** (298.2 K, benzene-d_6, 34.41 MHz): 7.7 (m, $^{2}J\{^{1}H\text{-}^{29}Si\}$ = 6.5 Hz, $\boldsymbol{Si}(CH^3)_3$). **$^{119}Sn\{^{1}H\}$ NMR** (298.7 K, benzene-d_6, 111.91 MHz): −207 (s, $([(H_3C)_3Si]_2N)_3\boldsymbol{Sn}N_3$). **IR** (ATR-IR, 32 scans, cm^{-1}): 2983 (w), 2958 (w), 2902 (w), 2119 (m), 1404 (w), 1360 (w), 1303 (w), 1249 (s), 831 (s), 794 (s), 759 (s), 726 (s), 672 (s), 622 (m), 503 (w). **Raman** (633 nm, accumulation time: 5 s, 20 scans, cm^{-1}): 2985 (1), 2961 (1), 2903 (1), 2294 (1), 2266 (1), 2120 (1), 1554 (1), 1414 (1), 1363 (1), 1267 (1), 1246 (1), 945 (10), 868 (1), 848 (1), 808 (1), 761 (1), 743 (1), 679 (1), 663 (1), 640 (1), 580 (1), 370 (1), 355 (1), 267 (1), 219 (1).

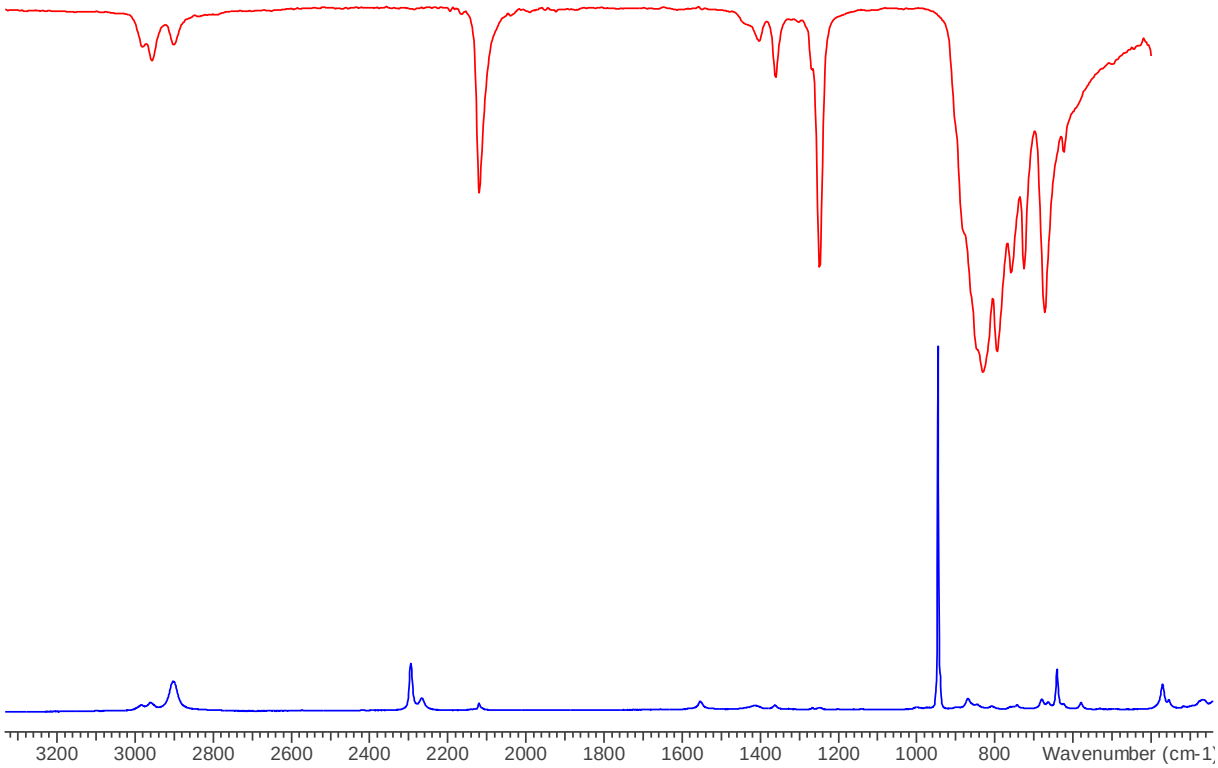


Figure S34: IR (top) and Raman (bottom) spectrum of **4d**.

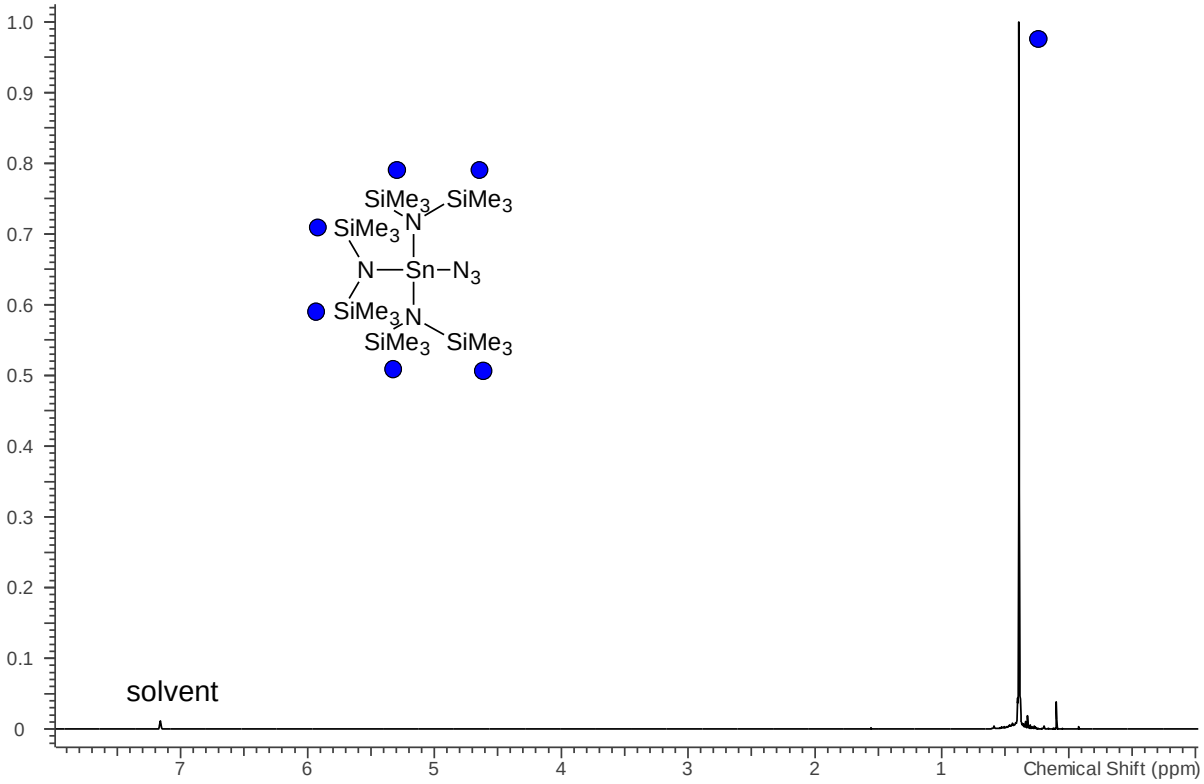


Figure S35: ^{1}H NMR spectrum of **4d**.

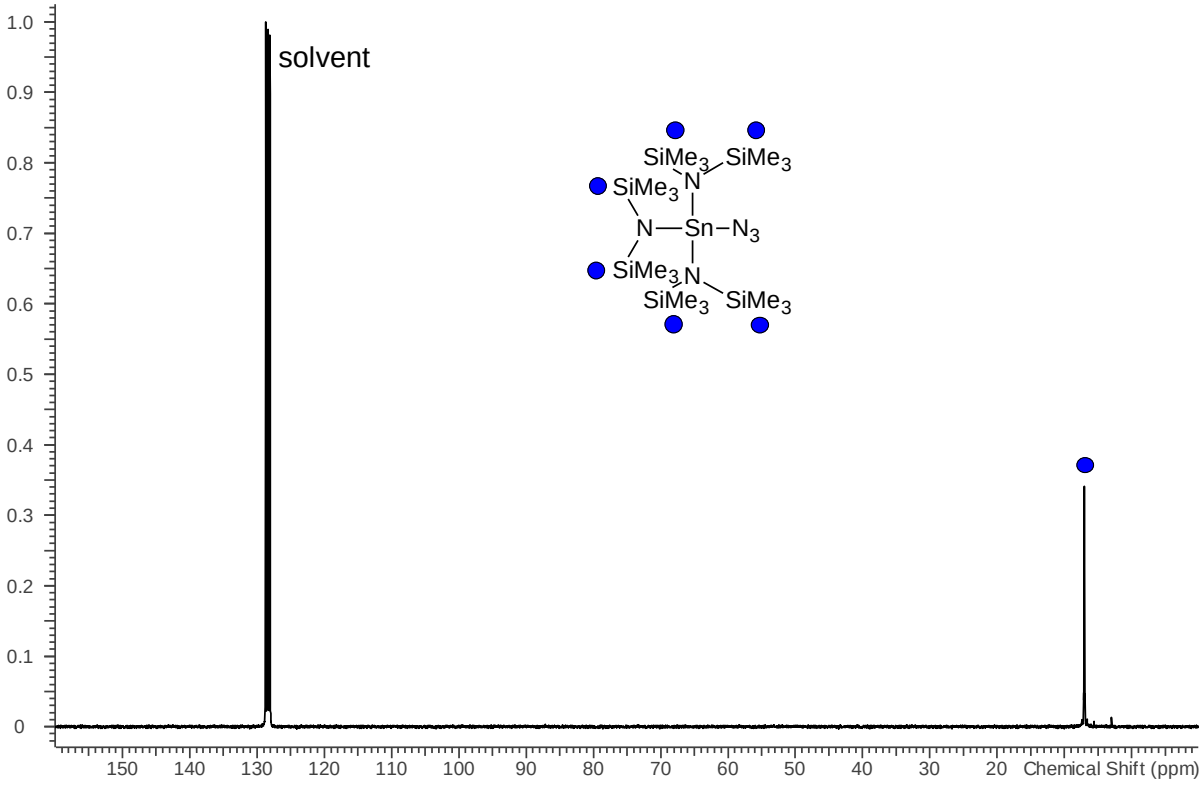


Figure S36: ^{13}C{^{1}H} NMR spectrum of **4d**.

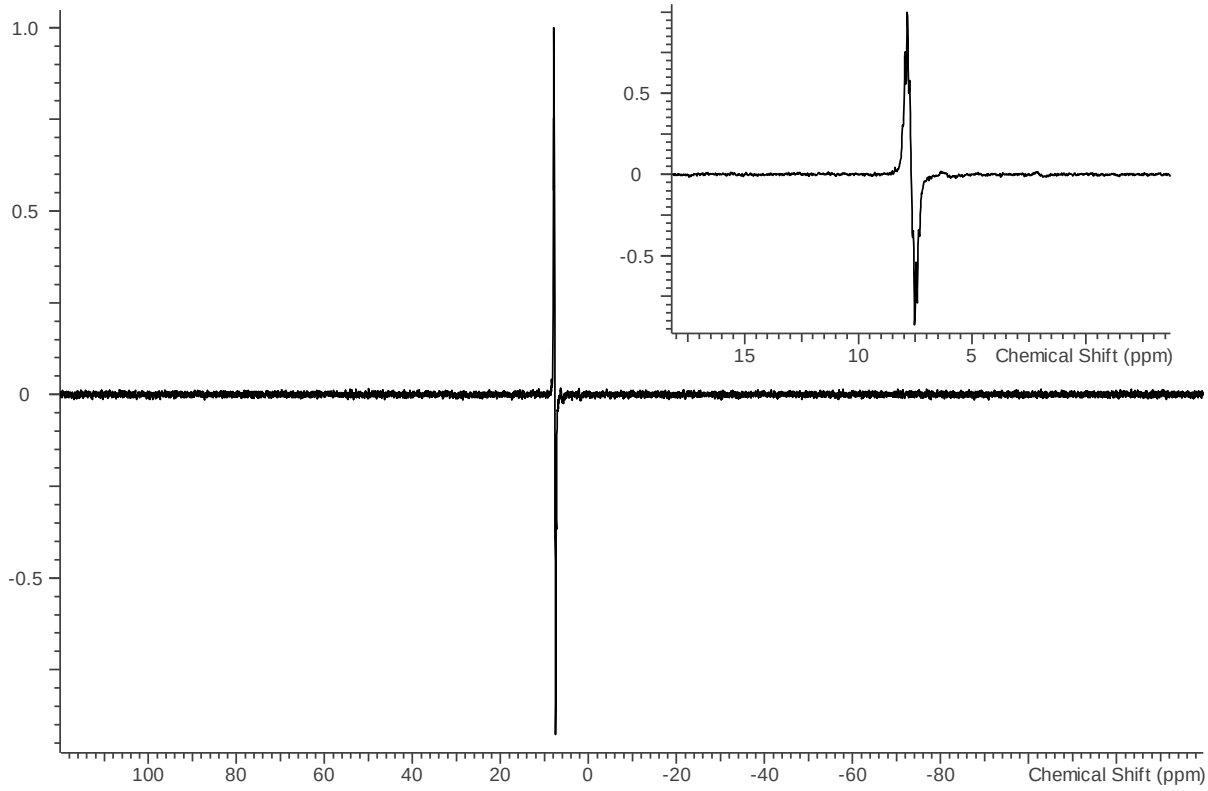


Figure S37: ^{29}Si-INEPT NMR spectrum of **4d**.

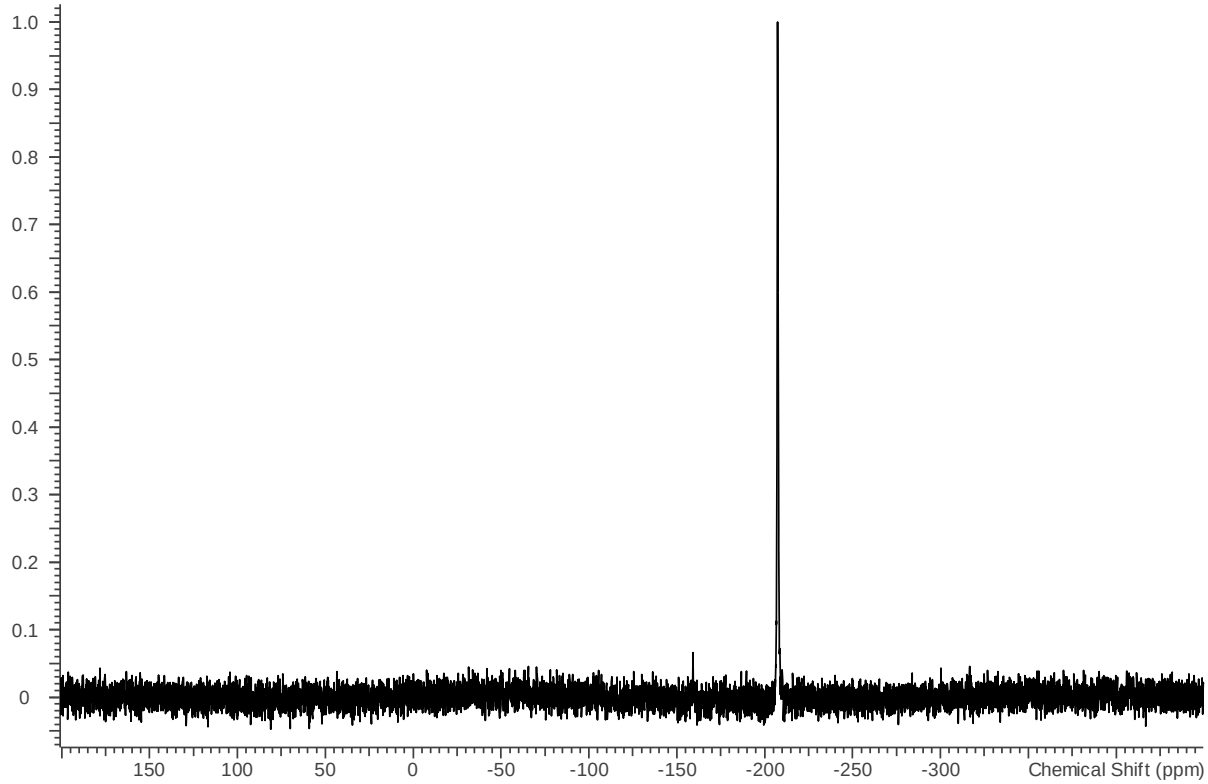
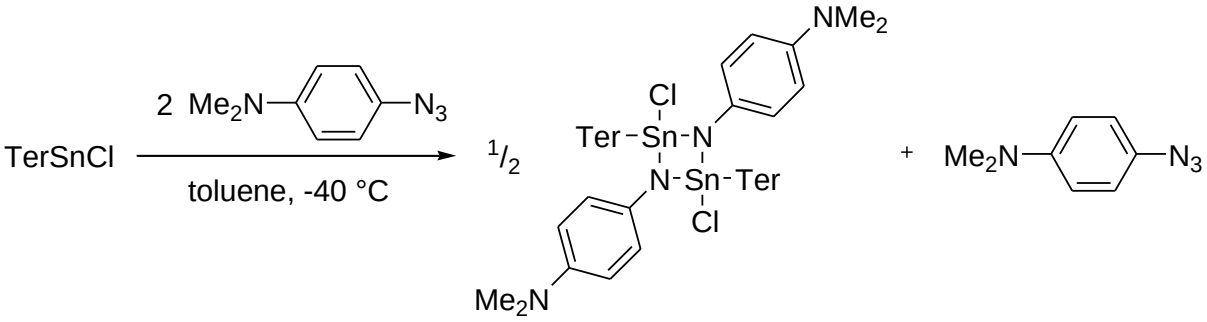


Figure S38: ^{119}Sn{^{1}H} NMR spectrum of **4d**.

4.6 Synthesis of **5a**



A solution of TerSnCl (0.234 g, 0.50 mmol) in toluene (4 mL) was cooled to −40 °C resulting in an orange suspension. **1a** (0.162 g, 1.00 mmol) was dissolved in toluene (3 mL) and added to the TerSnCl suspension dropwise. The now dark red, clear solution was stirred in the cold for 1 h. After concentration to approximately 1 mL, the solution was stored at +5 °C for 10 h. The supernatant was removed from the precipitate and discarded. The precipitate was washed with n-hexane (1 mL) and recrystallized from hot benzene (ca. +50 °C). Two crops of crystals yielded 0.080 g (0.06 mmol, 25.0%) of x-ray quality crystals.

Mp.: 228 °C. **CHN** calc. (found) in %: C 63.87 (63.294), H 5.86 (5.638), N 4.65 (4.354). **^{1}H NMR** (298.2 K, thf-d_8, 300.13 MHz): 1.73 (s, 24 H, *o*-C***H***$_3$), 2.16 (s, 12 H, *p*-C***H***$_3$), 2.88 (s, 12 H, N(C***H***$_3$)$_2$), 6.12 (m, 4 H, arom. C***H*** from 4-dimethylaminophenyl), 6.31 (m, 4 H, arom. C***H*** from 4-dimethylaminophenyl), 6.50 (s, 8 H, C$_6$***H***$_2$(CH$_3$)$_3$), 6.87 (m, 4 H, *m*-C***H***), 7.30 (s, 3 H, ½ C$_6$***H***$_6$), 7.42 (m, 2 H, *p*-C***H***). **^{13}C{^{1}H}-NMR** (298.2 K, thf-d_8, 75.48 MHz): 21.7 (s, ***C***H$_3$), 21.9 (s, ***C***H$_3$), 42.3 (s, N(***C***H$_3$)$_2$), 114.9 (arom. ***C***H from 4-dimethylaminophenyl), 124.1 (arom. ***C***H from 4-dimethylaminophenyl), 129.2 (s, ***C***$_6$H$_6$), 129.6 (s, ***C***$_6$H$_2$(CH$_3$)$_3$), 130.8 (s, *m*-***C***H), 132.4 (s, *p*-***C***H), 136.7 (s, arom. ***C***), 138.1 (s, arom. ***C***), 139.3 (s, arom. ***C***), 144.1 (s, arom. ***C***), 145.2 (s, arom. ***C***), 146.5 (s, arom. ***C***), 150.2 (s, arom. ***C***). **^{119}Sn{^{1}H}-NMR** (298.2 K, thf-d_8, 111.89 MHz): −151 (s, N$_2$***Sn***$_2$(Cl)$_2$Ter$_2$). **IR** (ATR-IR, 32 scans, cm^{-1}): 3088 (w), 3059 (w), 3018 (w), 2974 (w), 2947 (w), 2912 (m), 2875 (w), 2850 (w), 2831 (w), 2785 (w), 2733 (w), 1610 (w), 1568 (w), 1502 (s), 1477 (m), 1444 (s), 1377 (m), 1325 (w), 1315 (w), 1294 (w), 1263 (s), 1209 (m), 1180 (m), 1161 (m), 1132 (m), 1088 (w), 1055 (m), 1032 (m), 1011 (w), 987 (w), 945 (m), 912 (w), 881 (s), 847 (s), 810 (s), 802 (s), 775 (m), 731 (s), 704 (m), 692 (s), 679 (s), 625 (m), 590 (m), 573 (m), 548 (m). **Raman** (633 nm, accumulation time: 20 s, 10 scans, cm^{-1}): 3066 (1), 3043 (1), 2914 (2), 2855 (1), 2834 (1), 2821 (1), 2788 (1), 2734 (1), 1607 (3), 1508 (1), 1479 (1), 1441 (1), 1395 (1), 1382 (1), 1328 (1),

1303 (3), 1291 (3), 1265 (1), 1230 (1), 1193 (2), 1179 (1), 1162 (1), 1133 (1), 1100 (2), 1011 (1), 1003 (1), 990 (1), 943 (6), 804 (0), 739 (6), 701 (1), 663 (1), 621 (1), 575 (4), 557 (6), 521 (1), 509 (1), 502 (1), 475 (1), 464 (1), 422 (1), 417 (1), 337 (2), 220 (10).

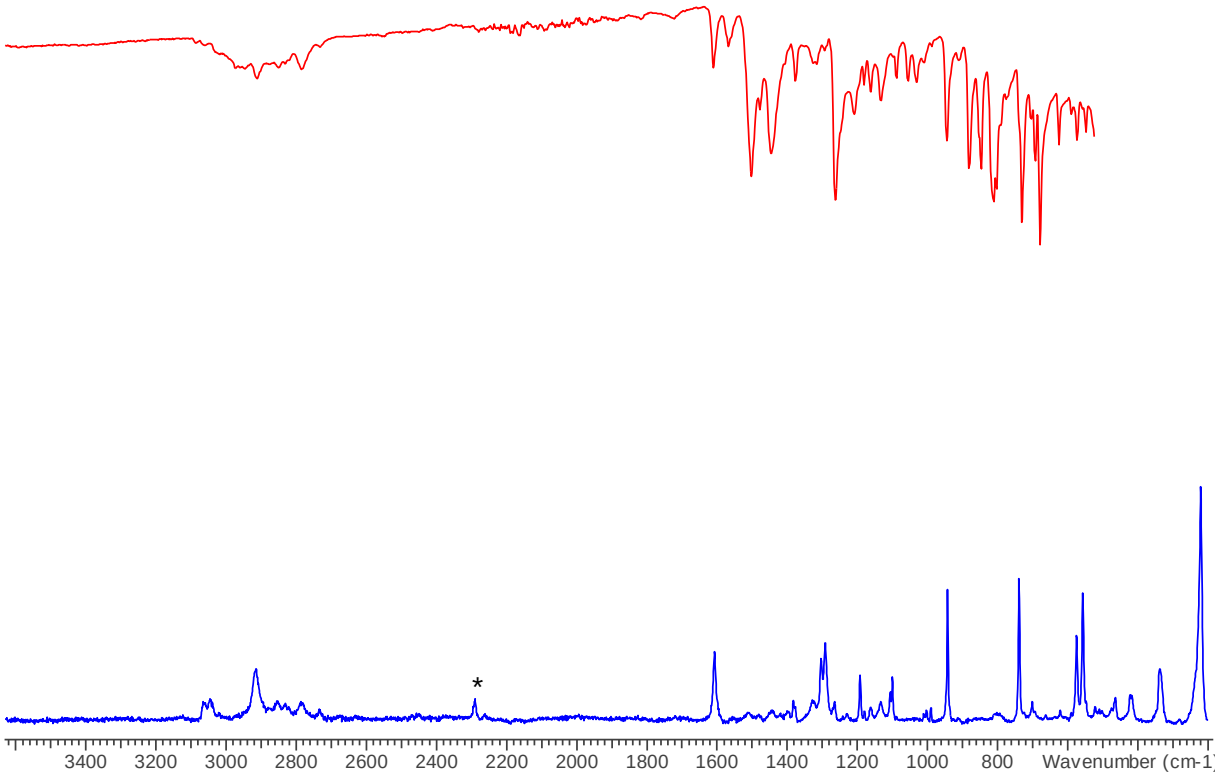


Figure S39: IR (top) and Raman (bottom) spectrum of **5a**. Asterisk indicates impurity of **1a**, although there is now azide vibration band in the IR spectrum.

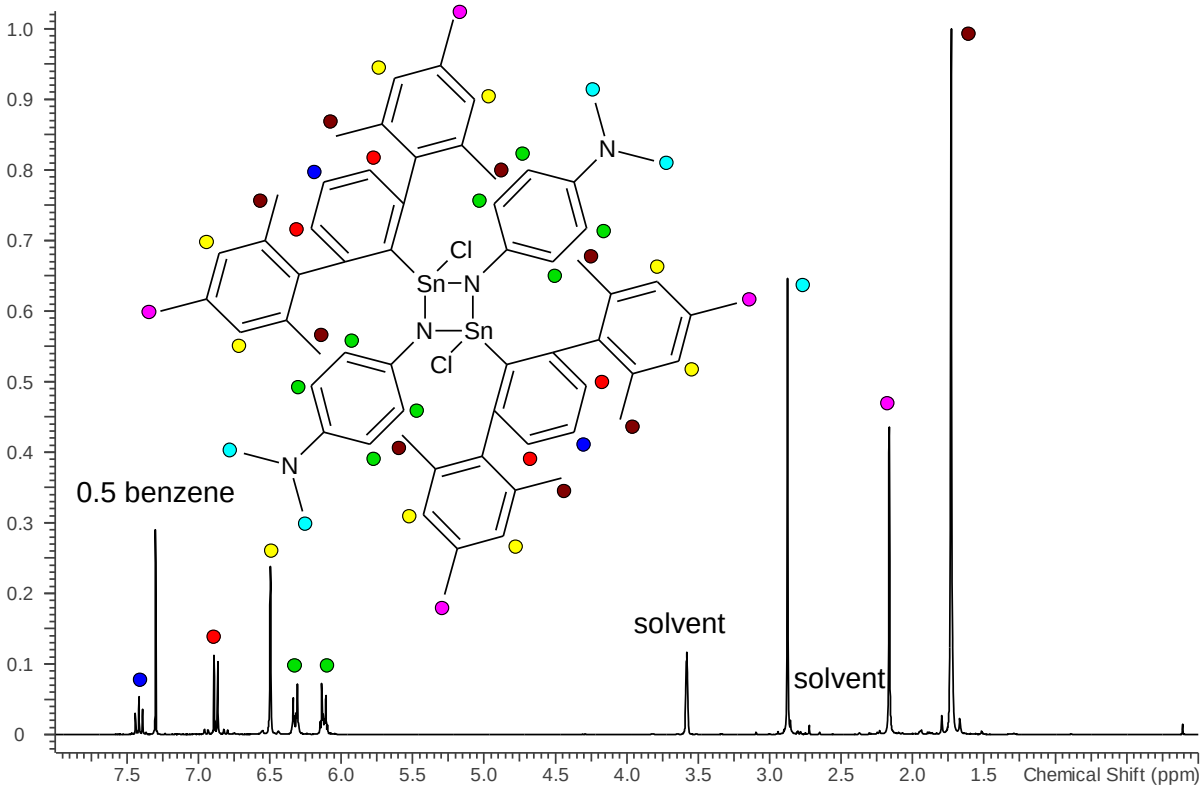


Figure S40: ^{1}H NMR spectrum of **5a**.

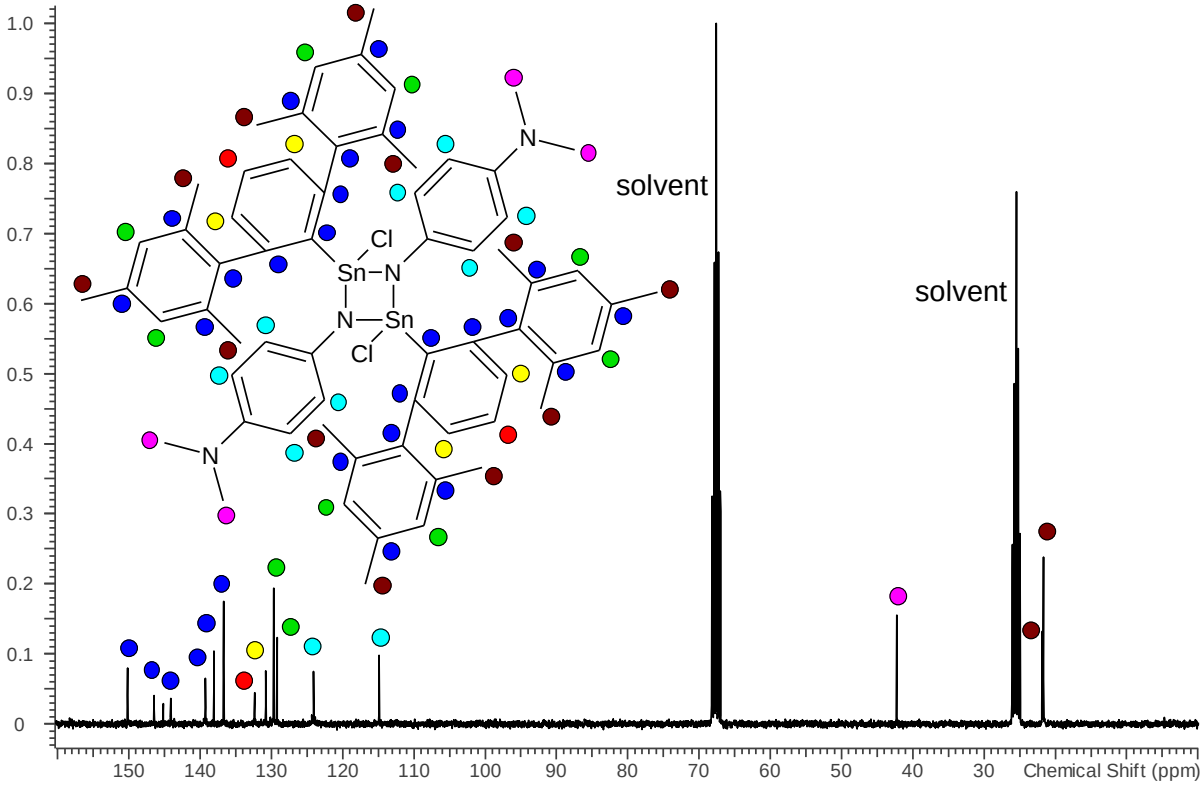


Figure S41: $^{13}C\{^{1}H\}$ NMR spectrum of **5a**.

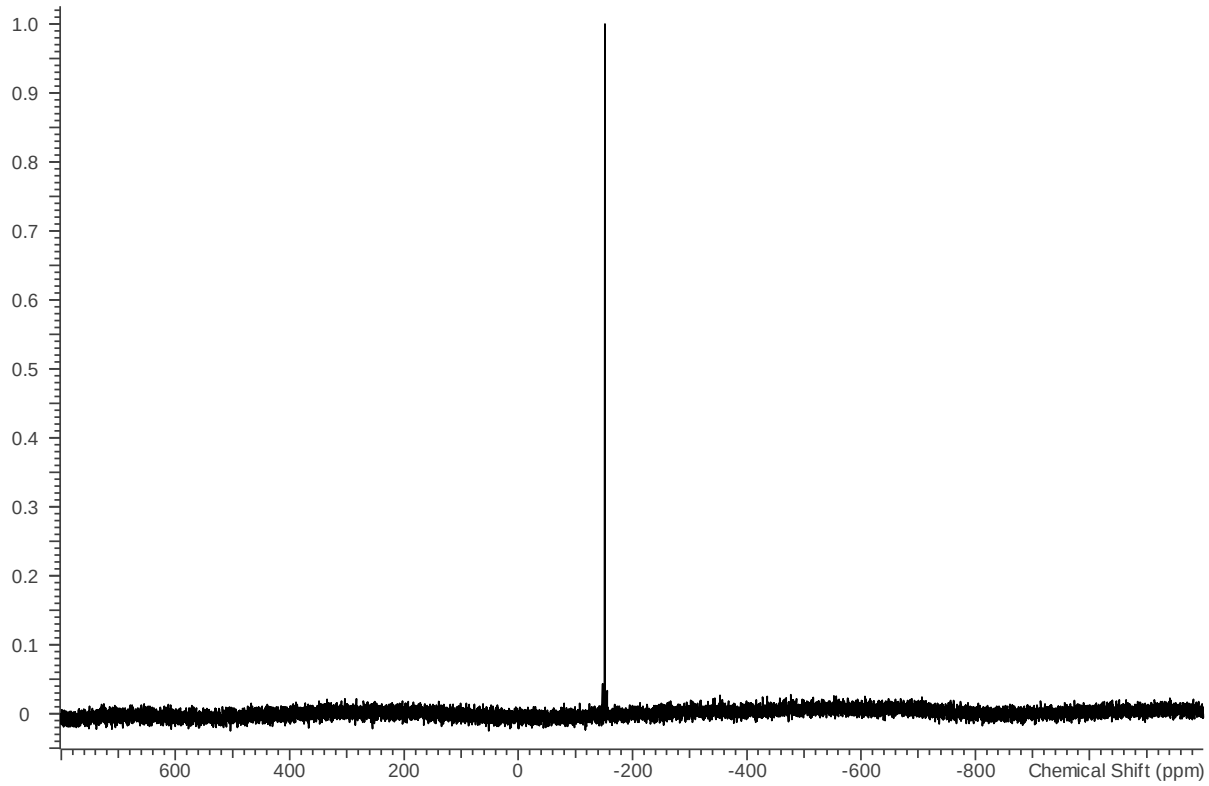


Figure S42: $^{119}Sn\{^{1}H\}$ NMR spectrum of **5b**.

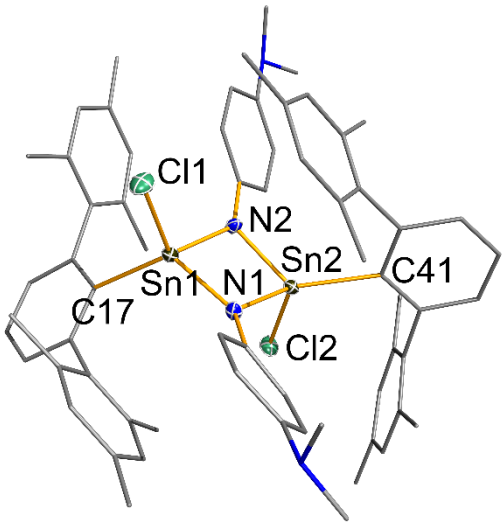
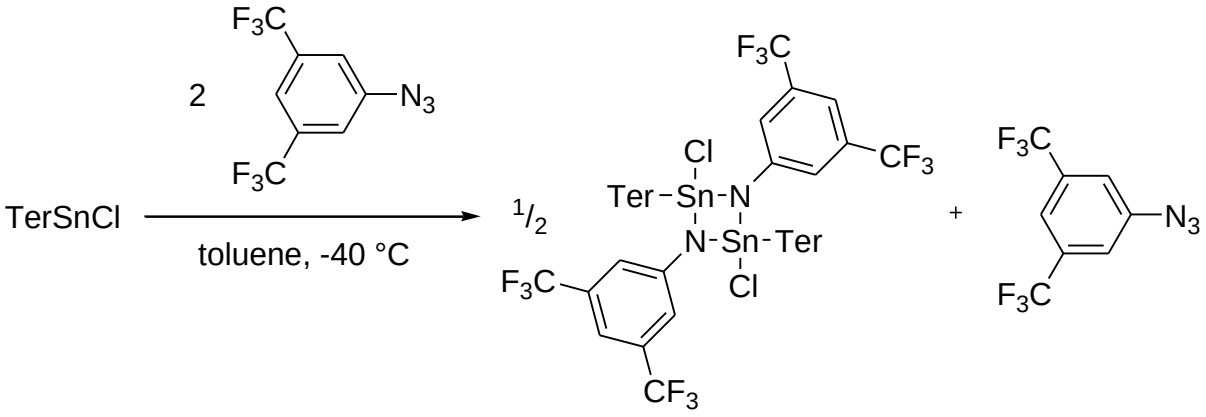


Figure S43: Molecular structure of **5a**. Thermal ellipsoids drawn at 50% probability (123(2) K). H atoms omitted for clarity. Selected bond length (Å) and angles (°): Sn1-N1 2.032(2), Sn2-N2 2.039(2), Sn1-C17 2.138(3), Sn1-Cl1 2.3499(8), Sn2-N1 2.031(2), Sn2-N2 2.035(2), Sn2-C41 2.153(3), Sn2-Cl2 2.3591(8); N1-Sn1-N2 81.61(9), N2-Sn1-C17 119.2(1), C17-Sn1-Cl1 107.96(8), N1-Sn2-N2 81.74(9), N2-Sn2-C41 125.7(1), C41-Sn2-Cl2 113.46(8), Sn2-N1-Sn1 97.9(1).

4.7 Synthesis of **5b**



To a stirred solution of TerSnCl (0.234 g, 0.50 mmol) in toluene (3 mL) was added a solution of **1b** (c = 0.2 M, V = 1 mL, 1.00 mmol) in toluene dropwise at −40 °C. The resulting clear, yellow solution was stirred for 1 h (gas evolution) in the cold and warmed to room temperature afterward. The solvent was removed *in vacuo* and recrystallization from a minimum amount of hot benzene resulted in the deposition of pale-yellow to colorless crystals of **5b** (0.165 g, 0.09 mmol, 37.5%).

Mp.: 315 °C (decom.). **CHN** calc. (found): C 55.32 (55.437), H 4.06 (3.834), N 2.02 (2.647). **^{1}H NMR** (298.2 K, thf-d$_8$, 300.13 MHz): 1.72 (s, 24 H, *o*-C***H***$_3$), 2.13 (s, 12 H, *p*-C***H***$_3$), 6.57 (s, 8 H, C$_6$***H***$_2$(CH$_3$)$_3$), 6.79 (broad, 4 H, *o*-C$_6$***H***$_3$(CF$_3$)$_2$), 6.96 (m, 4 H, m-C***H***), 7.28 (broad, 2 H, *p*-C$_6$***H***$_3$(CF$_3$)$_2$), 7.55 (m, 2 H, *p*-C***H***). **^{13}C{^{1}H} NMR** (298.2 K, thf-d$_8$, 75.47 MHz): 20.9 (s, *o*-***C***H$_3$), 21.7 (s, *p*-***C***H$_3$), 114.1 (s, *p*-***C***$_6$H$_3$(CF$_3$)$_2$), 122.4 (s, *o*-***C***$_6$H$_3$(CF$_3$)$_2$), 124.8 (q, ^{1}J{^{13}C-^{19}F} = 272 Hz, ***C***F$_3$), 129.9 (arom. ***C***H), 131.6 (s, *p*-***C***H), 132.3 (q, ^{2}J{^{13}C-^{19}F} = 32 Hz, ***C***(CF$_3$)), 134.1 (s, arom. ***C***), 137.0 (s, arom. ***C***), 138.6 (arom. ***C***), 139.2 (arom. ***C***), 141.6 (arom. ***C***), 150.0 (s, arom. ***C***), 154.3 (s, arom. ***C***). **^{19}F{^{1}H} NMR** (298.2 K, thf-d$_8$, 282.40 MHz): −65.4 (s, C***F***$_3$). **^{119}Sn{^{1}H} NMR** (298.2 K, thf-d$_8$, 111.92 MHz): −144.4 (s, N$_4$***Sn***N$_2$). **IR** (ATR-IR, 32 scans, cm^{-1}): 3030 (w), 2982 (w), 2951 (w), 2920 (w), 2856 (w), 2737 (w), 1610 (w), 1601 (w), 1568 (w), 1462 (m), 1448 (m), 1363 (s), 1271 (s), 1171 (s), 1124 (s), 1032 (w), 997 (m), 966 (s), 912 (w), 870 (m), 849 (s), 804 (m), 769 (w), 735 (s), 723 (s), 698 (s), 679 (s), 640 (m), 625 (w), 596 (m), 573 (m), 548 (w). **Raman** (laser: 633 nm, accumulation time: 10 s, 20 scans, cm^{-1}): 3122 (1), 3083 (1), 3065 (1), 3040 (1), 3016 (1), 2922 (2), 2859 (1), 2737 (1), 1613 (1), 1563 (1), 1486 (1), 1441 (1), 1383 (2), 1306 (3), 1286 (1), 1273 (1), 1228 (1), 1181 (1), 1168 (1), 1109 (1), 1100 (1), 1011 (1), 1002 (3), 947 (1), 742 (1), 705 (1),

661 (3), 576 (3), 560 (2), 523 (1), 504 (1), 466 (1), 424 (1), 420 (1), 405 (1), 353 (2), 348 (3), 284 (1), 221 (10), 192 (1), 170 (2), 142 (4), 123 (3).

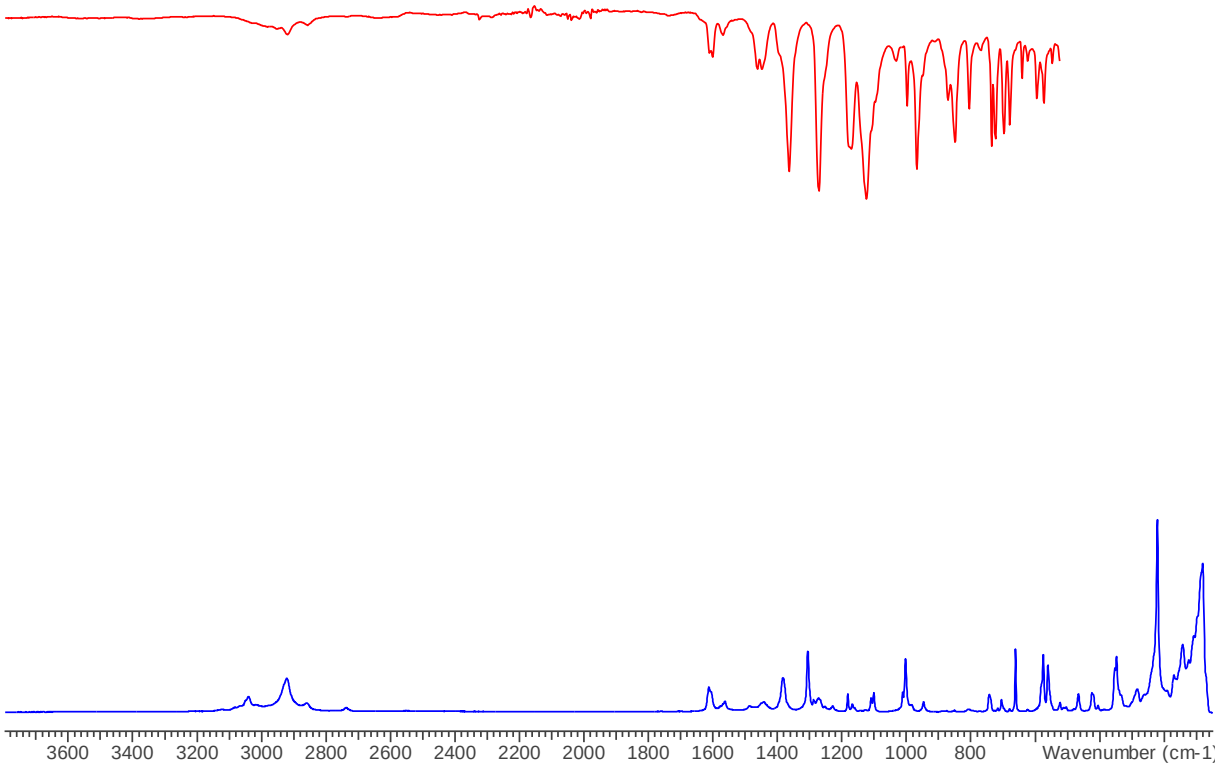


Figure S44: IR (top) and Raman (bottom) spectrum of **5b**.

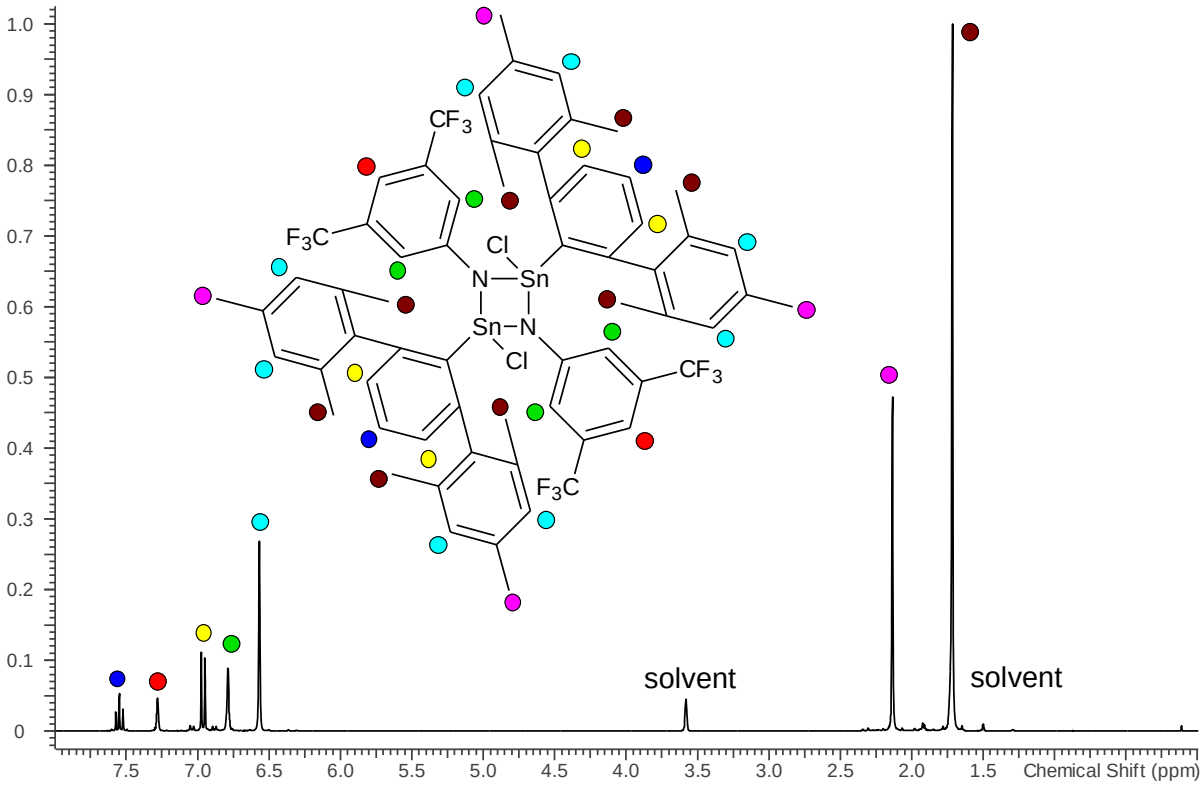


Figure S45: ^{1}H NMR spectrum of **5b**.

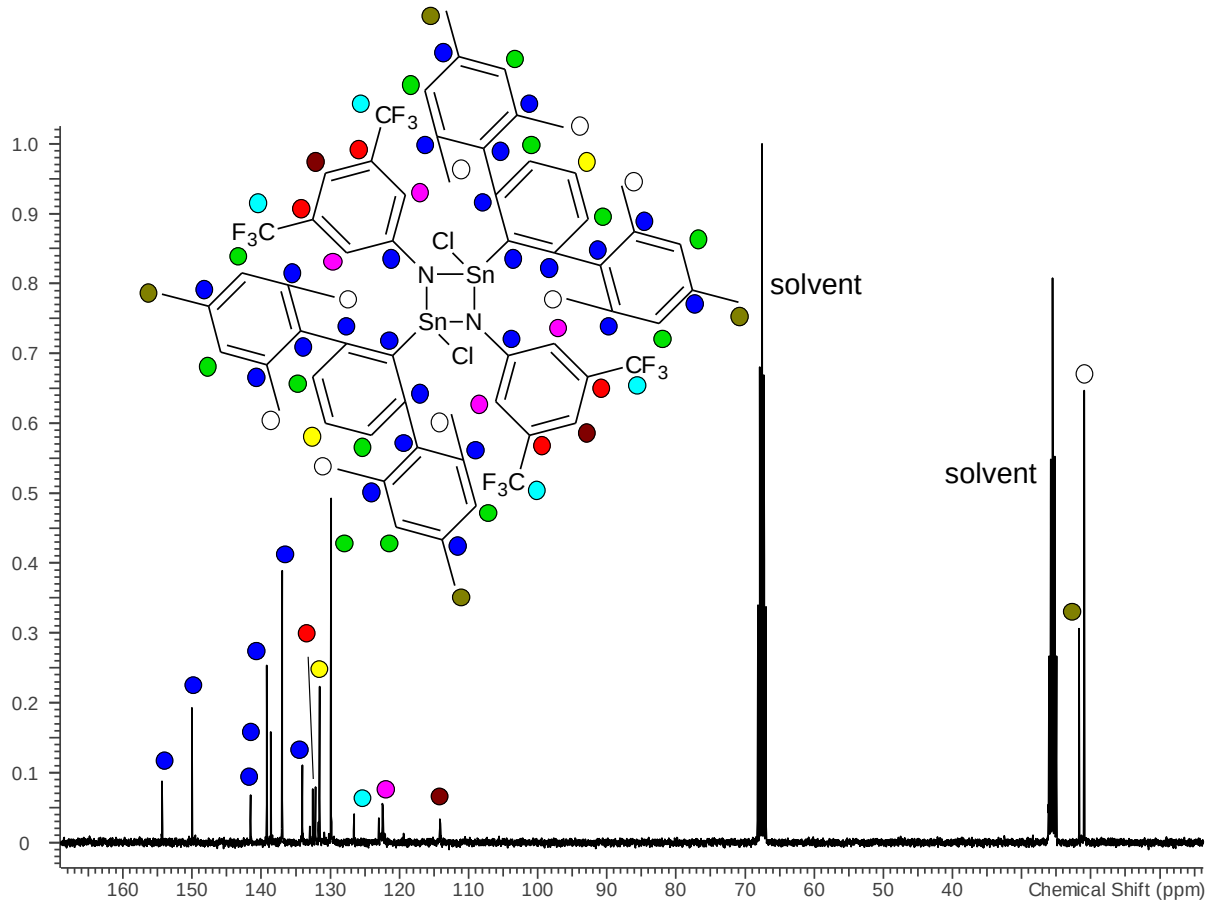


Figure S46: $^{13}C\{_1H\}$ NMR spectrum of **5b**.

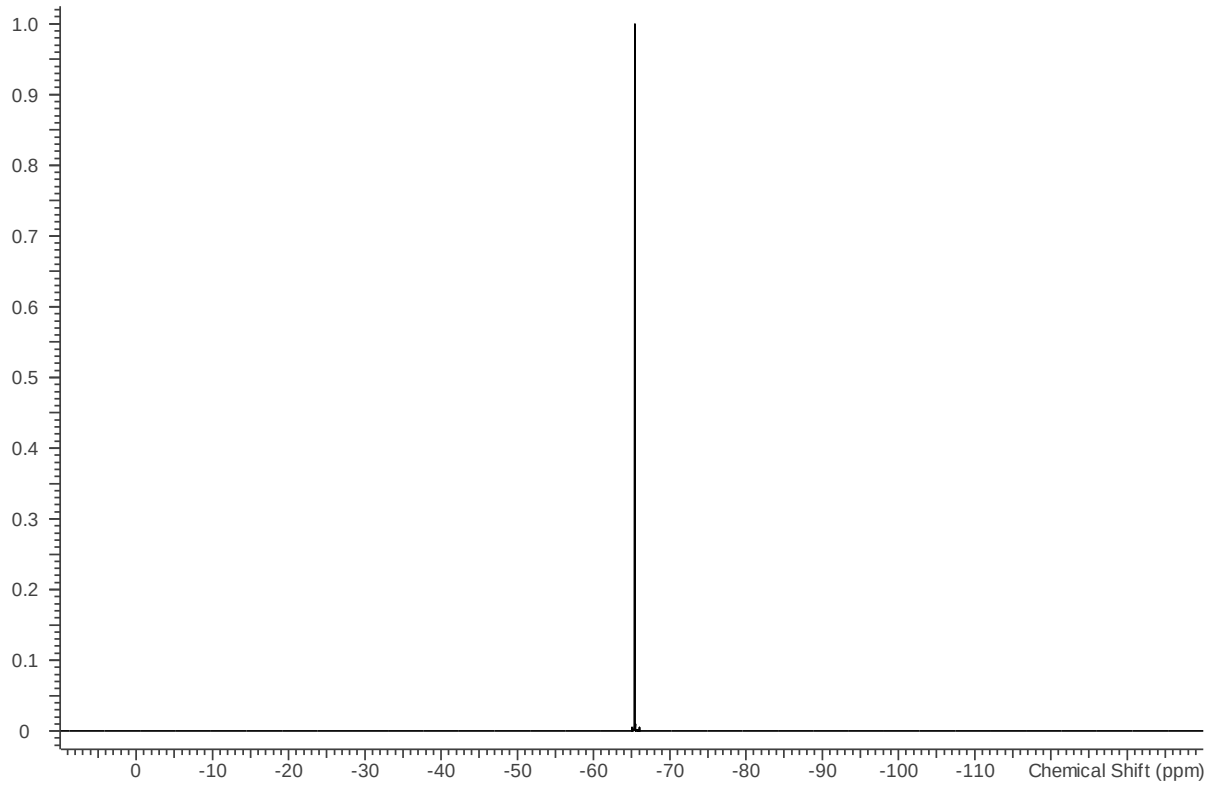


Figure S47: $^{19}F\{^{1}H\}$ NMR spectrum of **5b**.

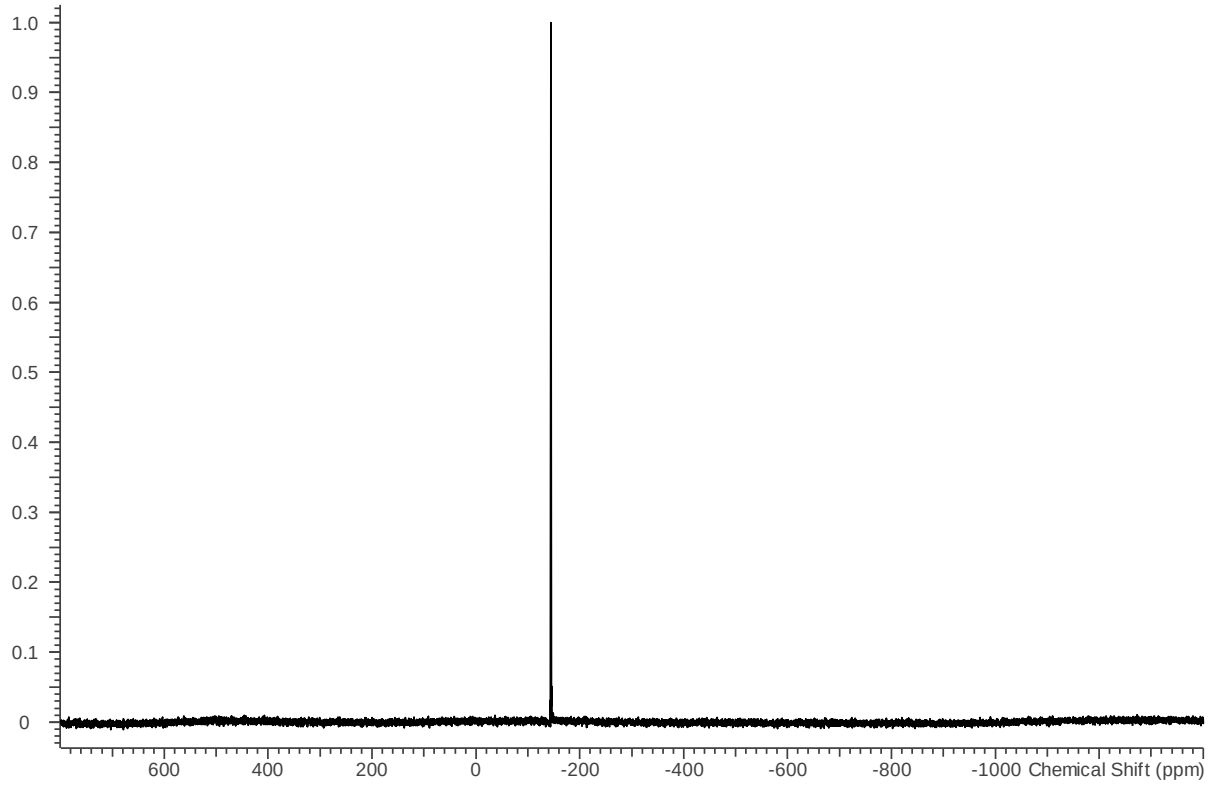


Figure S48: $^{119}Sn\{^{1}H\}$ NMR spectrum of **5b**.

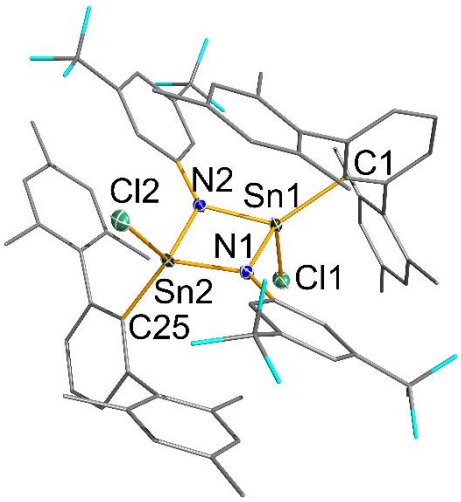
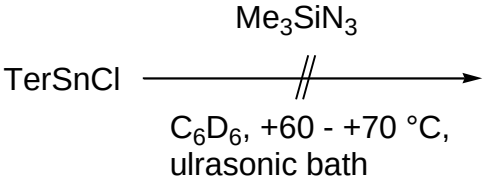


Figure S49: Molecular structure of **5b**. Thermal ellipsoids drawn at 50% probability (123(2) K). H atoms omitted for clarity. Selected bond length (Å) and angles (°): Sn1-N1 2.042(2), Sn1-N2 2.049(2), Sn1-C1 2.145(3), Sn1-Cl1 2.3471(7), Sn2-N1 2.043(2), Sn2-N2 2.046(2), Sn2-C25 2.128(3), Sn2-Cl2 2.3354(3), N1-C49 1.391(3), N2-C57 1.395(3); N1-Sn1-N2 81.10(9), N1-Sn1-C1 121.88(9), N2-Sn1-C1 131.6(1), N1-Sn1-C1 102.19(6), N2-Sn1-Cl1 100.19(6), C1-Sn1-Cl1 113.29(8), N1-Sn2-N2 81.14(8), N1-Sn2-C25 121.59(9), N2-Sn2-C25 117.56(9), N1-Sn2-Cl2 109.82(7), N2-Sn2-Cl2 111.33(6), C25-Sn2-Cl2 111.91(7), C49-N1-Sn1 130.2(2), C49-N2-Sn2 130.7(2), Sn1-N1-Sn2 98.41(9), C57-N2-Sn2 128.9(2), C57-N2-Sn1 130.7(2), Sn2-N2-Sn1 98.10(9).

4.8 Attempted reaction of TerSnCl with Me_3SiN_3



TerSnCl (0.023 g, 0.05 mmol) was placed in an NMR tube and dissolved in C_6D_6 (0.5 mL). After addition of Me_3SiN_3 (0.043 g, 0.37 mmol), the NMR tube was sonificated (sample temperature: +60 - +70 °C) for 5 h. According to ^{1}H and ^{29}Si-INEPT NMR spectroscopy only the starting materials were present in the solution.

5 References

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