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Elimination of bis(trimethylsilyl)stannylene from tris(trimethylsilyl)stannylated zirconocene and hafnocene chlorides

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Experimental Details

General methods

All manipulations involving air or moisture sensitive compounds were either performed under a nitrogen atmosphere using standard Schlenk tube techniques or were carried out in a nitrogen flushed Glovebox UNILAB supplied by MBraun. ^{1}H (300.22 MHz), ^{13}C (75.5 MHz), ^{29}Si (59.64 MHz) and ^{119}Sn (111.92 MHz) NMR spectra were recorded on a Varian Mercury 300 MHz spectrometer. Spectra are referenced to the deuterium resonance of the solvent (C_6D_6).[S1]
Anhydrous and deoxygenated solvents were obtained from an Innovative Technology solvent drying system. NMR solvents were dried over molecular sieves (3 Å) and $(Me_3Si)_4Sn$ was prepared following a previously reported procedure.[S2] Cp_2ZrCl_2, Cp_2HfCl_2 and 2,6-dimethylphenylisonitrile were used as purchased from chemical suppliers.

*Preparation of tris(trimethylsilyl)stannylzirconocene chloride (**1a**) and tris(trimethylsilyl)stannylhafnocene chloride (**1b**):*

To a solution of $(Me_3Si)_4Sn$ (500 mg, 1.22 mmol) in toluene (ca. 10 mL) 18-crown-6 (350 mg, 1.34 mmol) was added. Addition of $KOBu^t$ (140 mg, 1.25 mmol) produced a clear, yellow reaction mixture, which was stirred at room temperature for two hours, after which it was cooled to −35°C. Addition of Cp_2ZrCl_2 (360 mg, 1.22 mol) for the preparation of **1a** and Cp_2HfCl_2 (465 mg) for **1b** immediately yielded deeply colored (dark orange for Zr and orange-red for Hf) solutions. The reaction mixtures were allowed to warm to room temperature and stirred for additional three hours after which the solvent was removed *in vacuo*. The residue was extracted with *n*-pentane (2 × ca. 5 mL), filtered and the *n*-pentane extracts were concentrated to incipient crystallization. Storage at −35°C yielded **1a** (449 mg, 63%) and **1b** (386 mg, 47%) as orange and orange-red crystals, respectively.

NMR data for **1a** in C_6D_6:
^{1}H: 6.05 (10H, Cp*H*), 0.44 (27H, Si(CH_3)$_3$); ^{13}C{H}: 110.08 (Cp), 5.48 (Si(*C*H$_3$)$_3$); ^{29}Si{H}: −9.96; ^{119}Sn{H}: −415 ppm.
NMR data for **1b** in C_6D_6:
^{1}H: 5.85 (10H, Cp*H*), 0.23 (27H, Si(CH_3)$_3$); ^{13}C{H}: 109.74 (Cp), 3.52 (Si(*C*H$_3$)$_3$); ^{29}Si{H}: −8.37; ^{119}Sn{H}: −392 ppm.

*Preparation of [{(2,6-dimethylphenyl)imino}{tris(trimethylsilyl)stannyl}methyl]zirconocene chloride (**2a**) and [{(2,6-dimethylphenyl)imino}{tris(trimethylsilyl)stannyl}methyl]hafnocene chloride (**2b**):*

To solutions of **1a** (100 mg, 0.171 mmol) or **1b** (125 mg, 0.186 mmol), respectively, in toluene (3 mL), *N*-(2,6-dimethylphenyl)isonitrile (40 mg, 0.30 mmol) was added resulting in a color change to bright orange in both cases. After keeping the reaction mixtures for 30 min at room temperature, solvent and excess isonitrile were removed *in vacuo*. The residue was dissolved in minimum *n*-pentane. Storage at −35°C yielded **2a** and **2b** as yellow crystals suitable for single crystal X-ray structure determination.

NMR data for **2a** in C_6D_6:
^{1}H: 6.85, 6.84 (m, 3H, 2,6-Me$_2$C$_6$*H*$_3$NC), 5.87 (s, 10H, Cp*H*), 2.05 (s, 6H, 2,6-(CH_3)$_2$C$_6$H$_3$NC), 0.25 (27H, Si(CH_3)$_3$); ^{13}C{H}: 272.38 (Ar*C*N$_{isonitrile}$), 149.79 (Ar$_{isonitrile}$), 129.40 (Ar$_{isonitrile}$), 129.08 (Ar$_{isonitrile}$), 125.53 (Ar$_{isonitrile}$), 110.17 (Cp), 19.94, (*Me*$_2$C$_6$H$_3$CN), 3.90 (27H, Si(*C*H$_3$)$_3$); ^{29}Si{H}: −7.56; ^{119}Sn{H}: −431 ppm.
NMR data for **2b** in C_6D_6:
^{1}H: 6.85 (m, 3H, 2,6-Me$_2$C$_6$*H*$_3$NC), 5.82 (s, 10H, Cp*H*), 2.08 (s, 6H, 2,6-(CH_3)$_2$C$_6$H$_3$NC), 0.27 (27H, Si(CH_3)$_3$); ^{13}C{H}: 282.94 (Ar*C*N$_{isonitrile}$), 150.58 (Ar$_{isonitrile}$), 129.53 (Ar$_{isonitrile}$), 129.18 (Ar$_{isonitrile}$), 125.58 (Ar$_{isonitrile}$), 109.34 (Cp), 19.91, (*Me*$_2$C$_6$H$_3$CN), 3.98 (27H, Si(*C*H$_3$)$_3$); ^{29}Si{H}: −5.67; ^{119}Sn{H}: −439 ppm.

*Conversion of **1a** to trimethylsilylzirconocene chloride (**3**) and [{(2,6-dimethylphenyl)imino}(trimethylsilyl)methyl]zirconocene chloride (**4**):*

Over 12 hours, a solution of **1a** (50 mg) in C_6D_6 (0.6 mL), changed its color from intensively dark to a light orange. A tin mirror deposited on the wall of the NMR tube. NMR spectroscopic data comply with previously reported spectra for **3**, $Cp_2Zr(Cl)SiMe_3$.[S3] Subsequent addition of excess (ca. 2 equivalents) *N*-(2,6-dimethylphenyl)isonitrile afforded a yellow-orange solution from which the insertion product **4** precipitated as orange crystals suitable for XRD analysis. Spectroscopic data of **4** are in agreement with literature data.[S4]

Crystallography

For single crystal X-ray diffraction analysis, suitable crystals were covered with a layer of silicone or paratone oil. Single crystals were selected, mounted on a glass rod on a copper pin, and placed in the cold N_2 stream (T = 100 K). XRD data collection was performed either on Bruker SMART APEX or APEX II diffractometers with Mo Kα radiation (λ= 0.71073 Å) from a sealed tube generator and a CCD area detector. Empirical absorption corrections were applied using SADABS.[S5,S6] The structures were solved with use of either direct methods or the Patterson option in SHELXS[S7] and refined by the full-matrix least-squares procedures in SHELXL.[S8,S9] The space group assignments and structural solutions were evaluated using PLATON.[S10,S11] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions corresponding to standard bond lengths and angles using riding models.

Crystallographic data (excluding structure factors) for the structures of compounds **1a**, **1b**, **2a**, **2b** and **4** reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publications no. CCDC-2106839 (**1a**), 2106836 (**1b**), 2106838 (**2a**), 2106840 (**2b**), and 2106837 (**4**). Copies of data can be obtained free of charge at: http://www.ccdc.cam.ac.uk/products/csd/request/.

Table S1. Crystallographic data for compounds **1a**, **1b**, **2a, 2b** and **4**.

	1a	**1b**	**2a**	**2b**	**4**
Empirical formula	$C_{19}H_{37}ClSi_3SnZr$	$C_{19}H_{37}ClHfSi_3Sn$	$C_{28}H_{46}ClNSi_3SnZr$	$C_{28}H_{46}ClHfNSi_3Sn$	$C_{22}H_{28}ClNSiZr$
M_w	595.12	682.39	726.29	813.56	461.21
Temperature [K]	100(2)	100(2)	100(2)	100(2)	100(2)
Size [mm]	0.29×0.24×0.16	0.24×0.21×0.17	0.19×0.18×0.17	0.28×0.11×0.10	0.40×0.22×0.18
Crystal system	triclinic	triclinic	triclinic	triclinic	monoclinic
Space group	P-1	P-1	P-1	P-1	P2(1)/c
a [Å]	9.0594(7)	9.0437(2)	10.0358(2)	13.0292(10)	16.523(3)
b [Å]	10.8512(5)	10.8396(2)	10.9185(4)	15.2417(11)	9.2278(18)
c [Å]	14.6361(13)	14.5907(3)	17.0175(7)	18.1548(14)	15.326(3)
α [°]	87.408(2)	87.3860(10)	99.882(2)	80.267(4)	90
β [°]	87.667(3)	87.6970(10)	99.860(2)	69.091(3)	112.99(3)
γ [°]	67.375(2)	67.3120(10)	111.5420(10)	84.941(2)	90
V [Å ^{3}]	1326.30(17)	1317.88(5)	1651.94(10)	3317.9(4)	2151.3(7)
Z	2	2	2	4	4
ρ_{calc} [gcm^{-3}]	1.490	1.720	1.460	1.629	1.424
Absorption coefficient [mm^{-1}]	1.573	5.123	1.261	4.086	0.697
F(000)	600	664	740	1608	952
θ range	2.03<θ<30.10	2.46<θ<30.55	1.26<θ<28.02	1.20<θ<28.00	2.58<θ<26.37
Reflections collected/unique	48532/7778	26970/8024	17585/7710	114123/15795	16604/4391
Completeness to θ [%]	99.9	99.9	98.1	99.7	99.9
Data/restraints/parameters	7778/0/235	8024/0/236	7710/0/331	15795/0/653	4391/0/240
Goodness of fit on F^2	0.993	1.054	0.939	1.078	1.032
Final R indices [I>2σ(I)]	R1=0.015, *w*R2=0.037	R1=0.020, *w*R2=0.047	R1 = 0.029, wR2 = 0.053	R1 = 0.034, wR2 = 0.078	R1 = 0.028, wR2 = 0.069
R indices (all data)	R1=0.017, *w*R2=0.038	R1=0.022, *w*R2=0.048	R1 = 0.040, wR2 = 0.087	R1 = 0.066, wR2 = 0.095	R1 = 0.035, wR2 = 0.071
Largest diff. Peak/hole [e$^-$/ Å^3]	0.56/−0.39	1.53/−1.18	0.63/−0.95	2.690/−3.849	0.51/−0.26

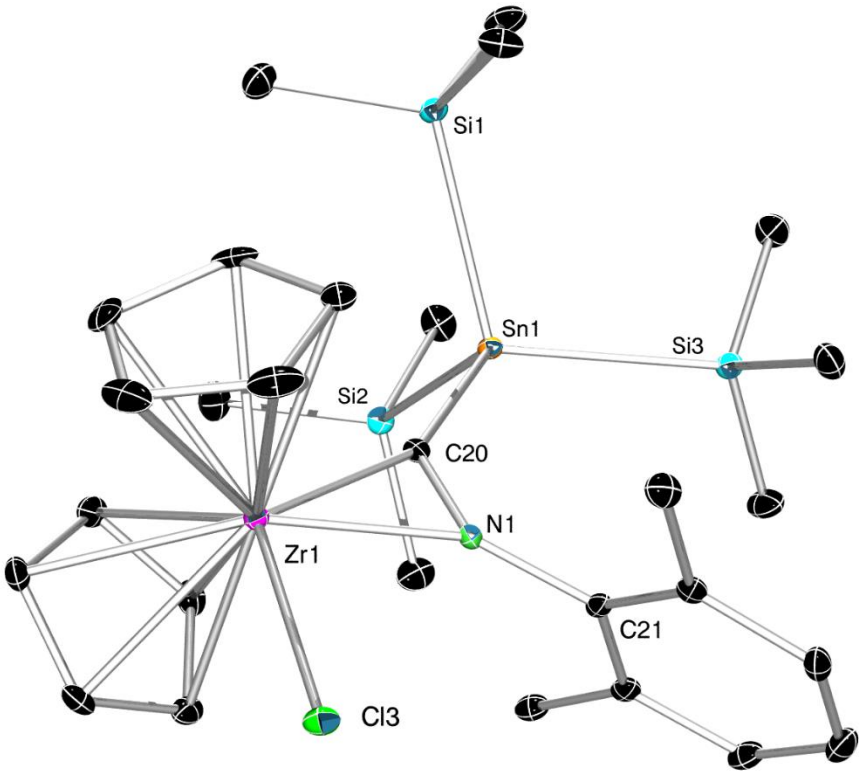

Figure S1 Molecular structure of **2a** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity.

NMR Spectra:

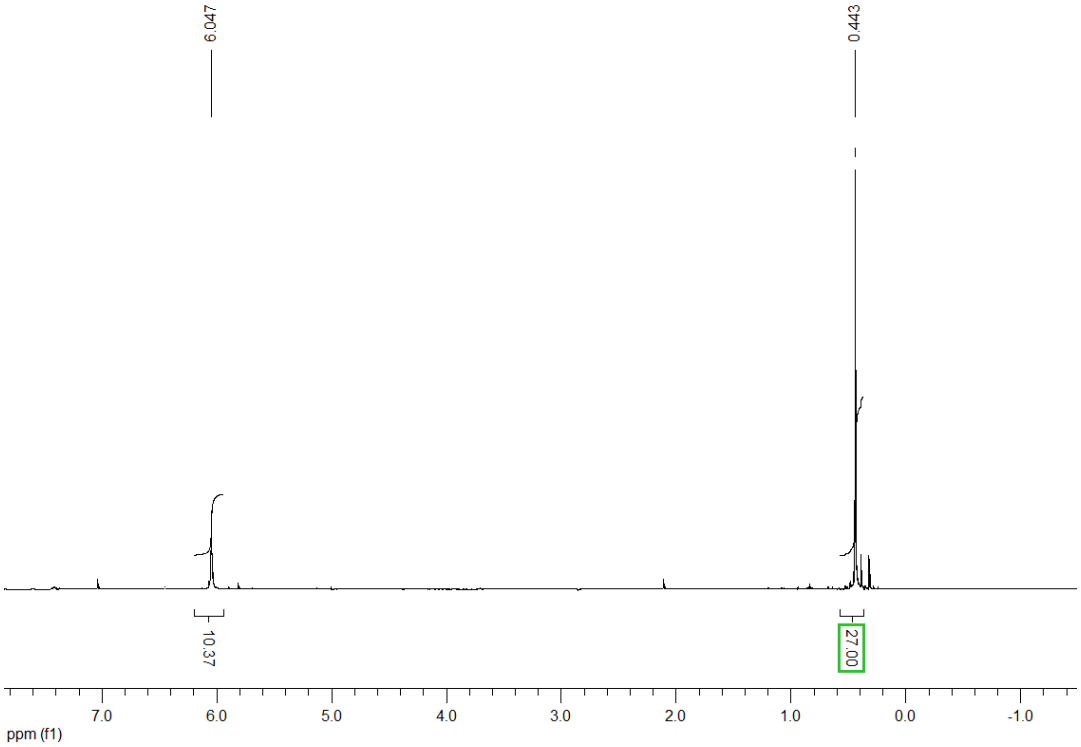

Figure S2. ^{1}H NMR spectrum of **1a**, C_6D_6

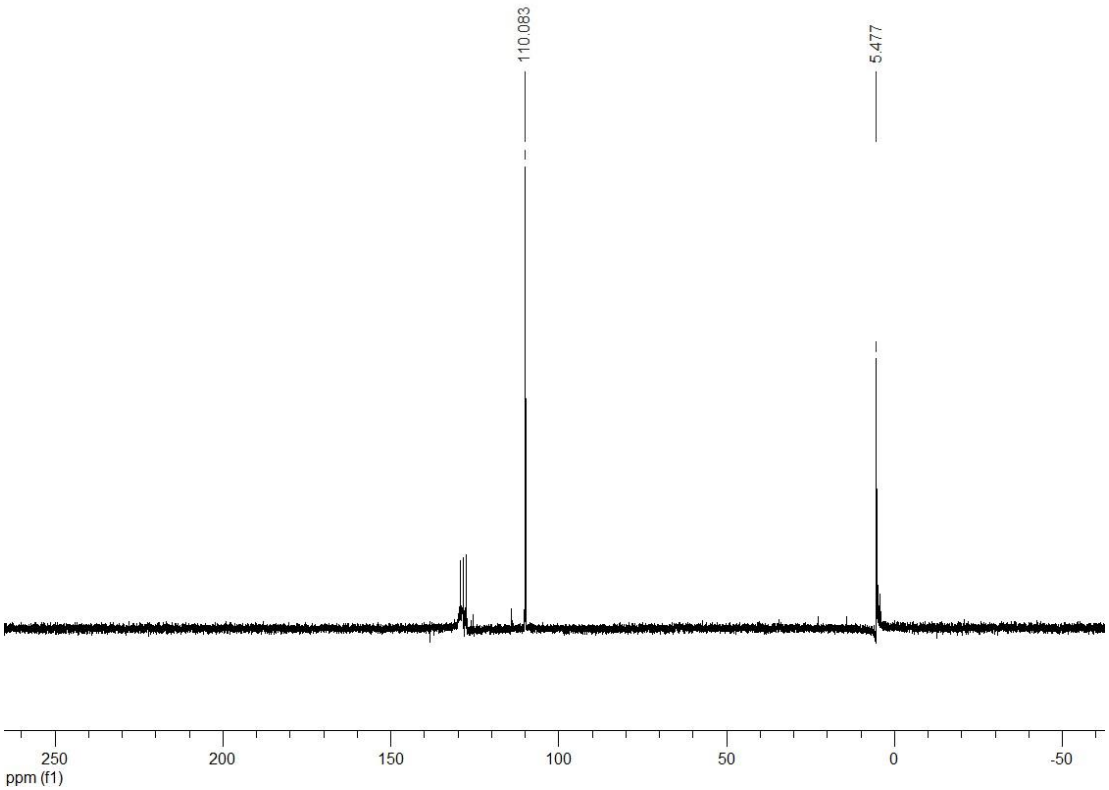

Figure S3. $^{13}C\{H\}$ NMR spectrum of **1a**, C_6D_6

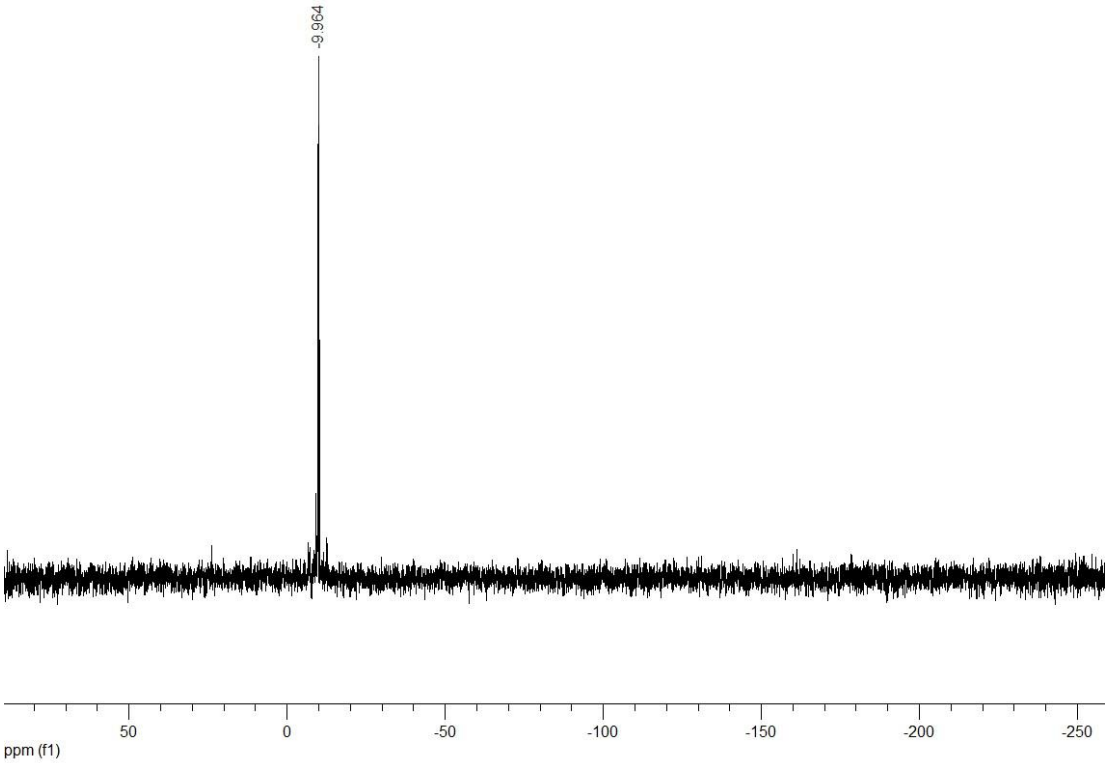

Figure S4. $^{29}Si\{H\}$ INEPT NMR spectrum of **1a**, C_6D_6

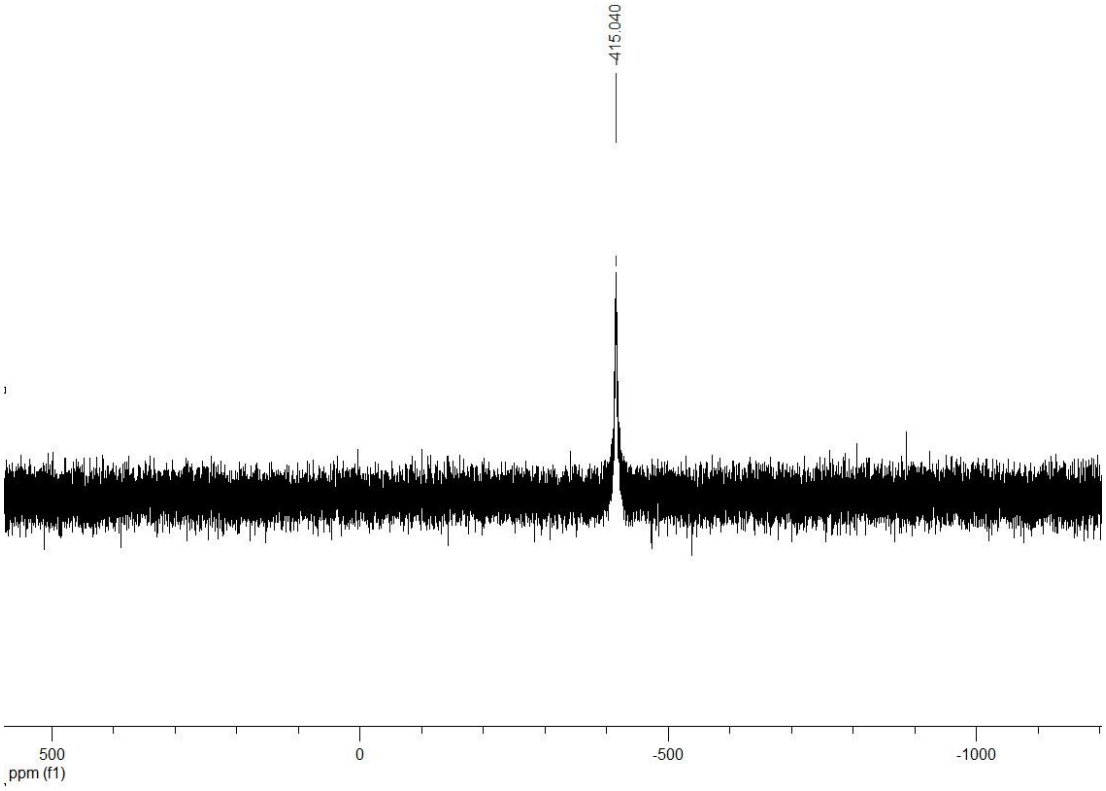

Figure S5. $^{119}Sn\{H\}$ NMR spectrum of **1a**, C_6D_6

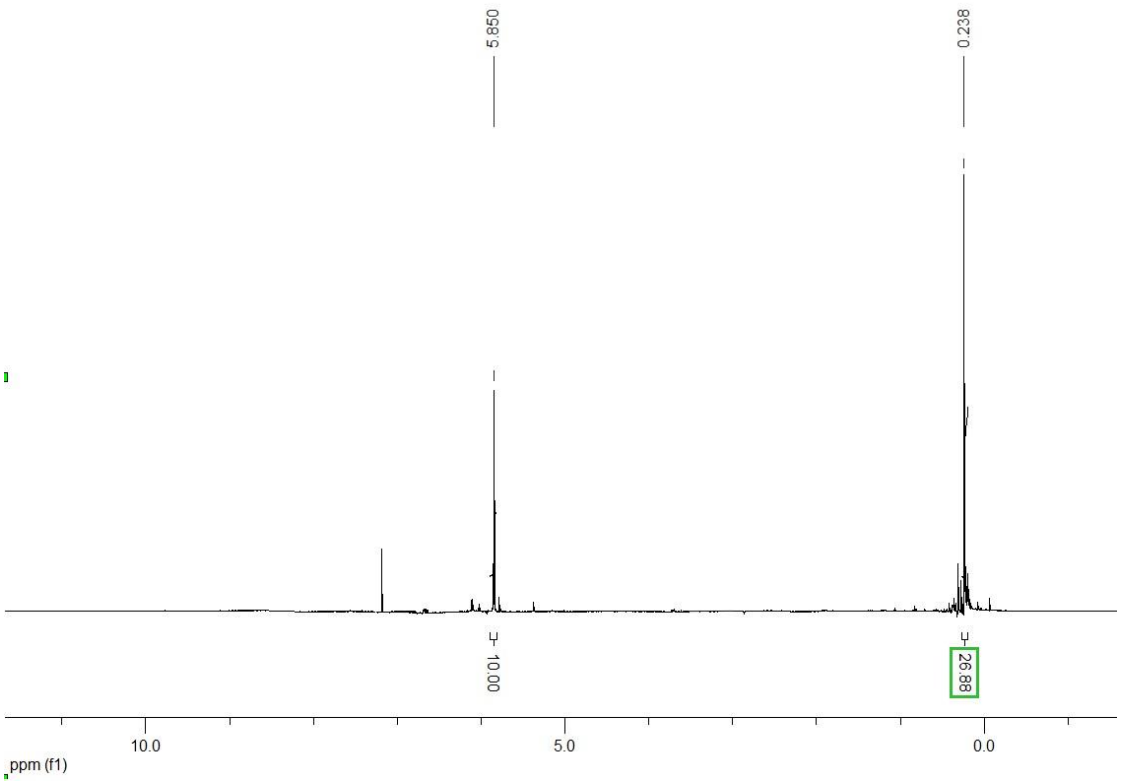

Figure S6. ^{1}H NMR spectrum of **1b**, C_6D_6

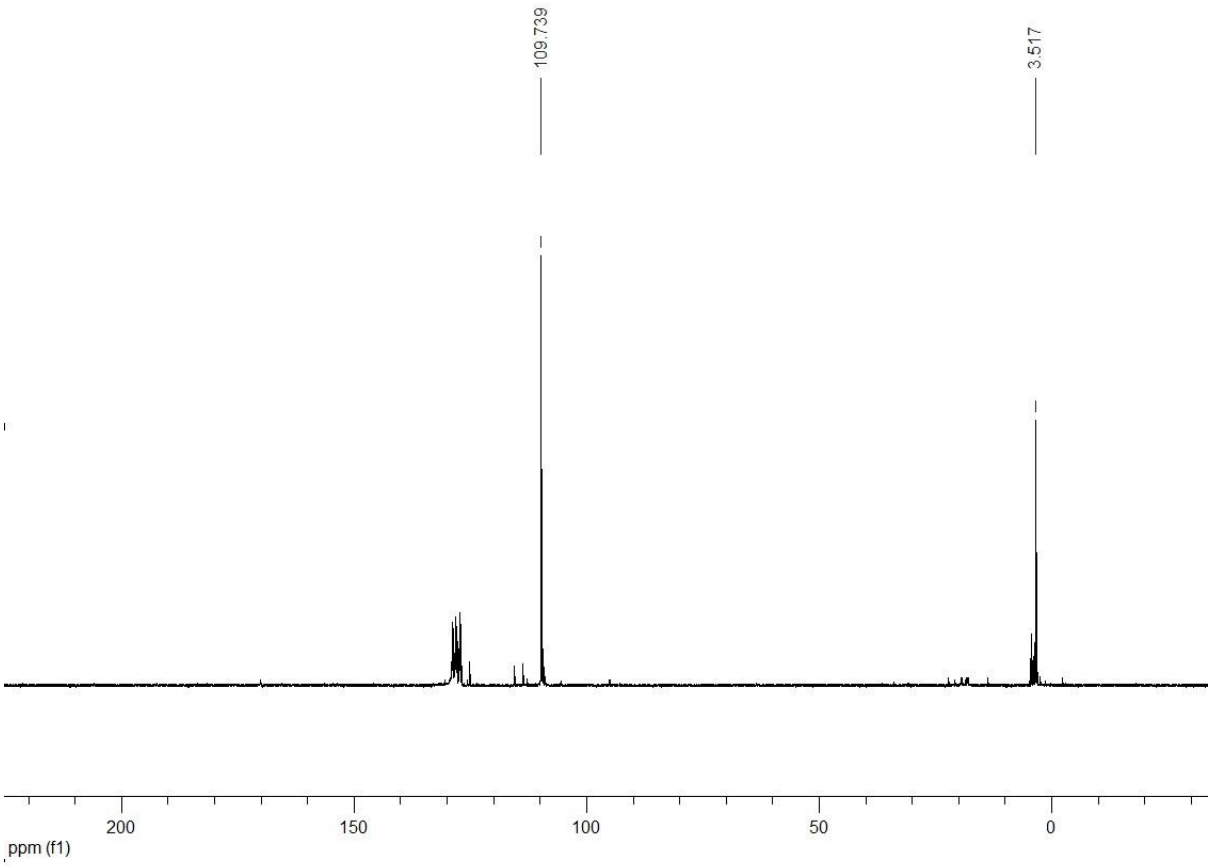

Figure S7. ^{13}C{H} NMR spectrum of **1b**, C_6D_6

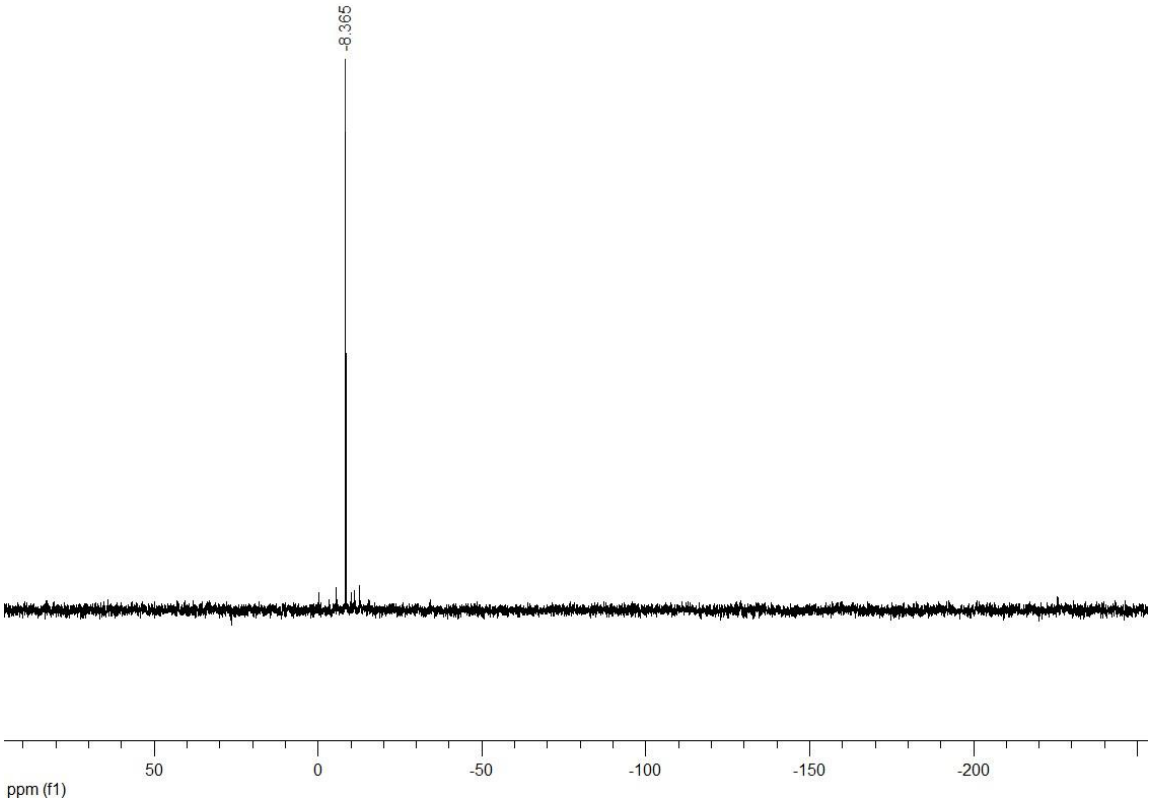

Figure S8. $^{29}Si\{H\}$ INEPT NMR spectrum of **1b**, C_6D_6

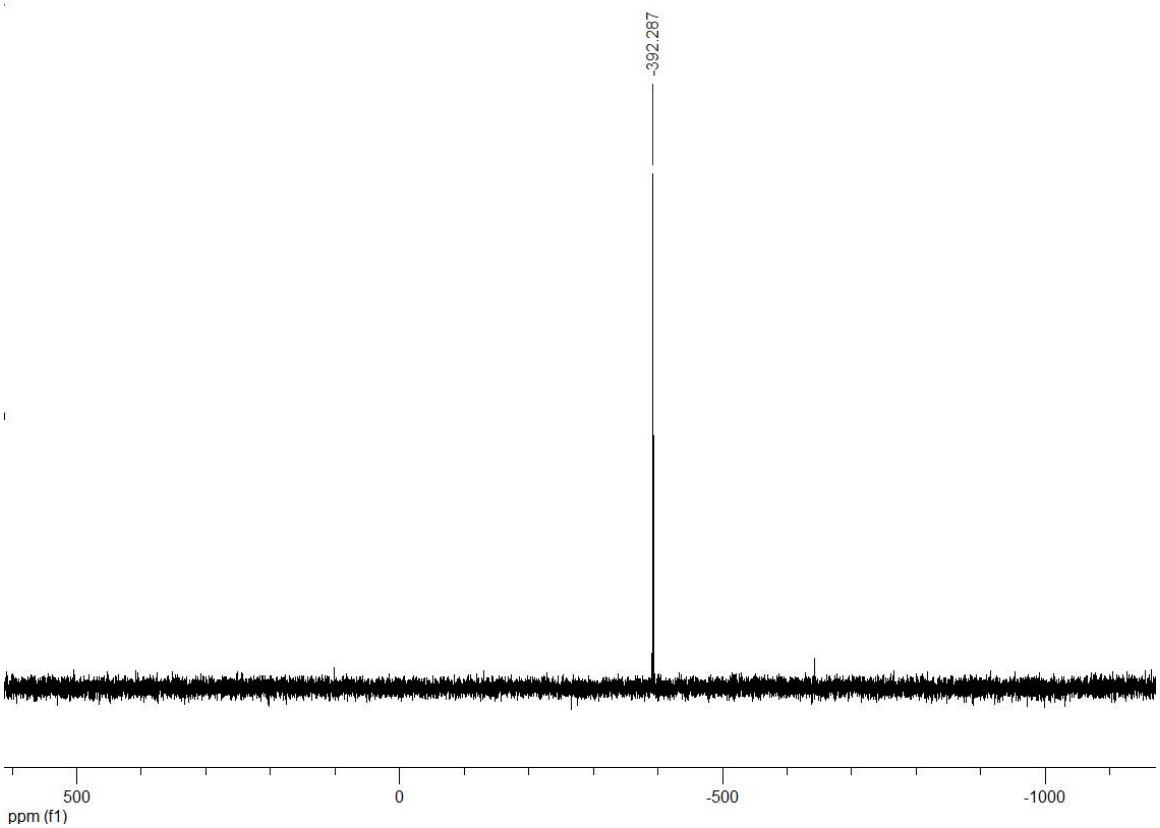

Figure S9. $^{119}Sn\{H\}$ NMR spectrum of **1b**, C_6D_6

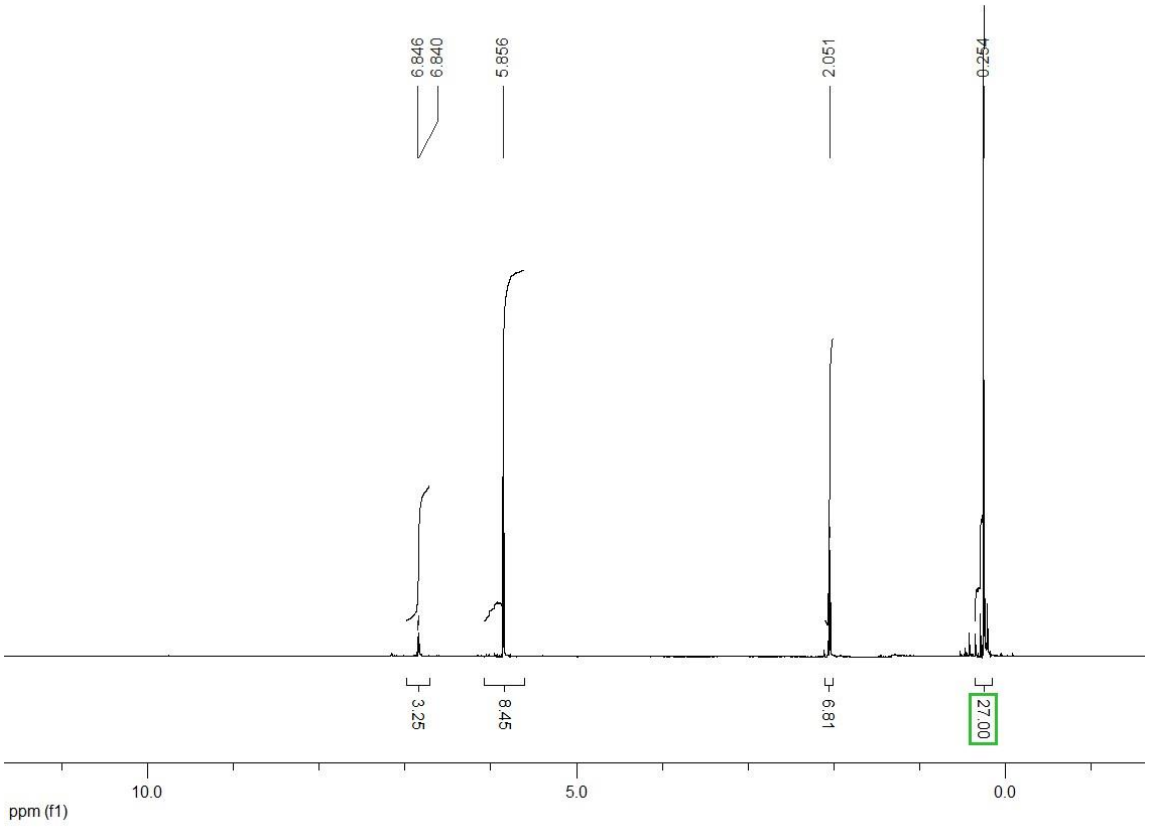

Figure S10. ^{1}H NMR spectrum of **2a**, C_6D_6

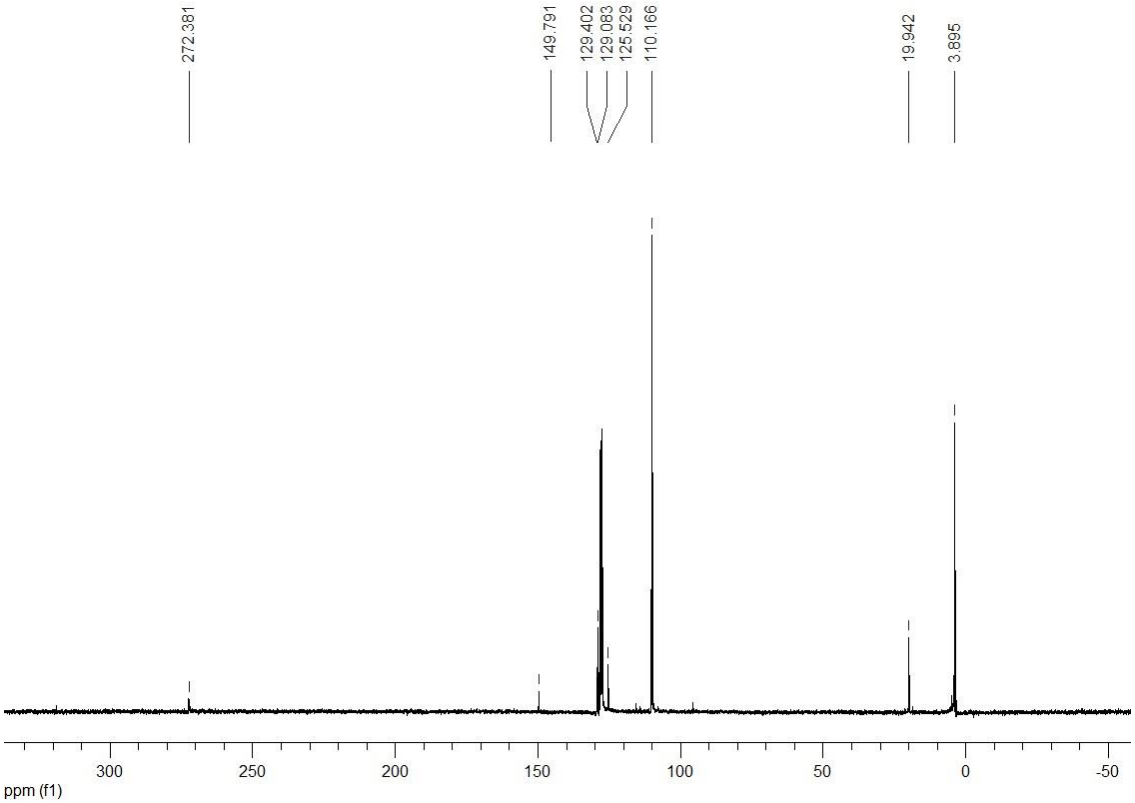

Figure S11. $^{13}C\{H\}$ NMR spectrum of **2a**, C_6D_6

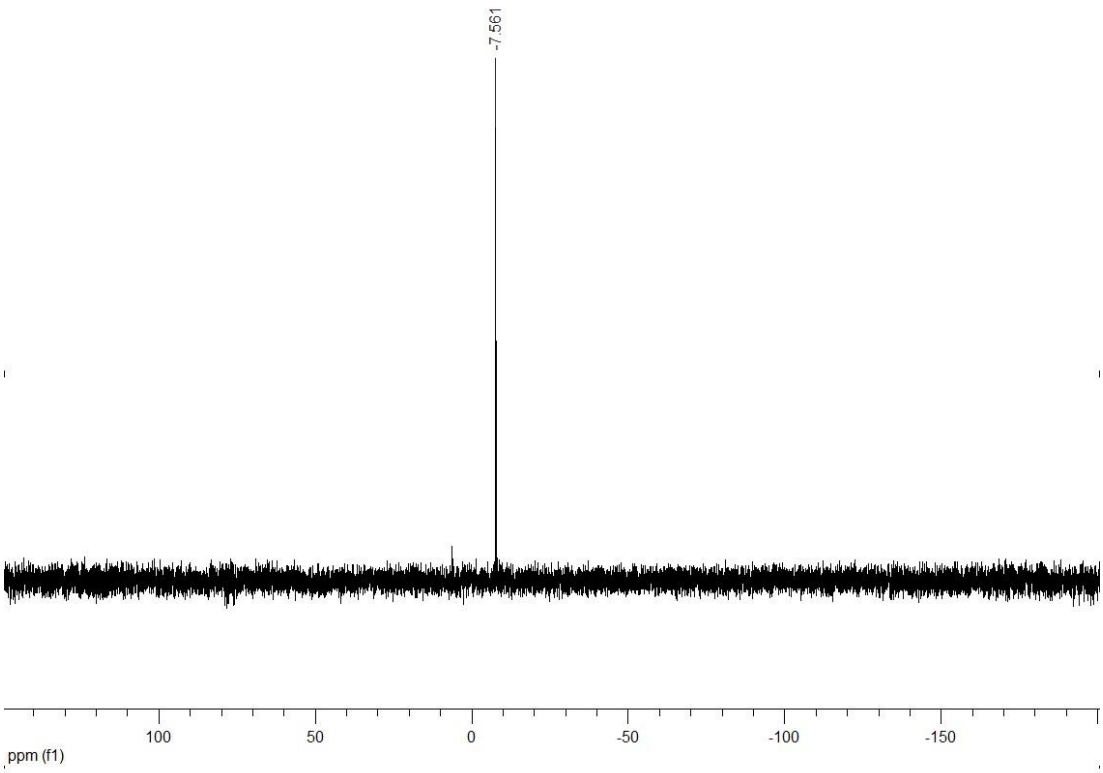

Figure S12. $^{29}Si\{H\}$ INEPT NMR spectrum of **2a**, C_6D_6

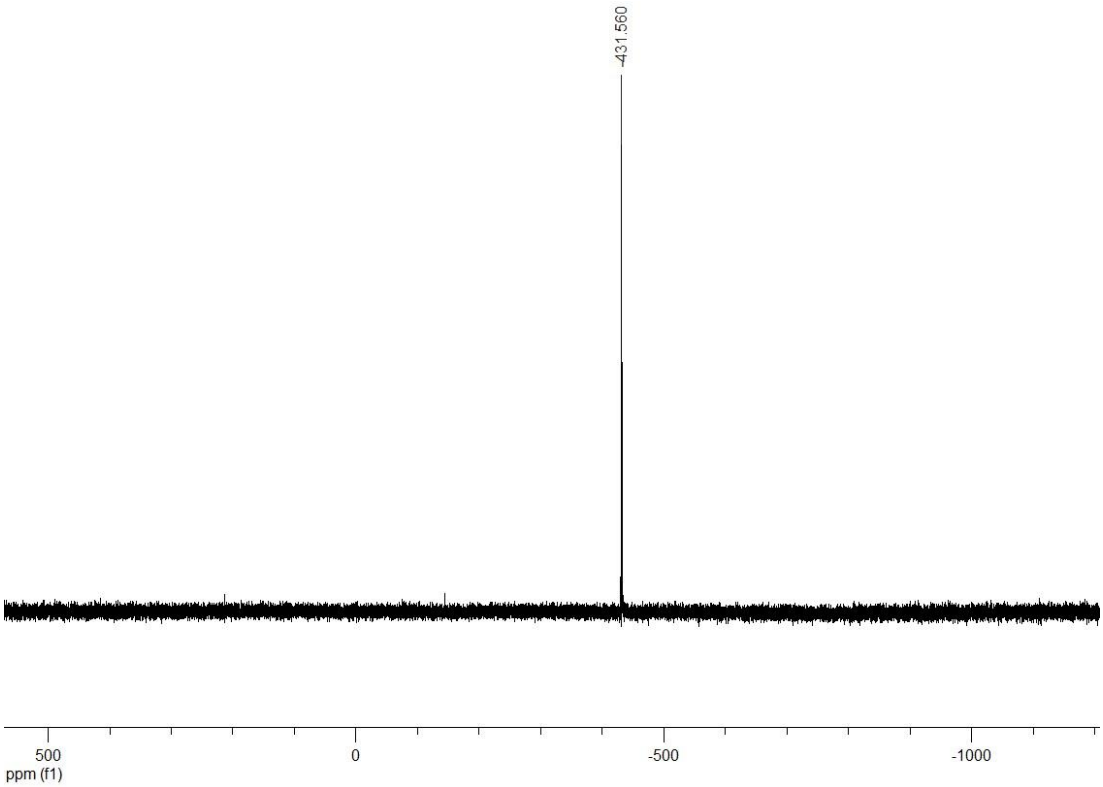

Figure S13. $^{119}Sn\{H\}$ NMR spectrum of **2a**, C_6D_6

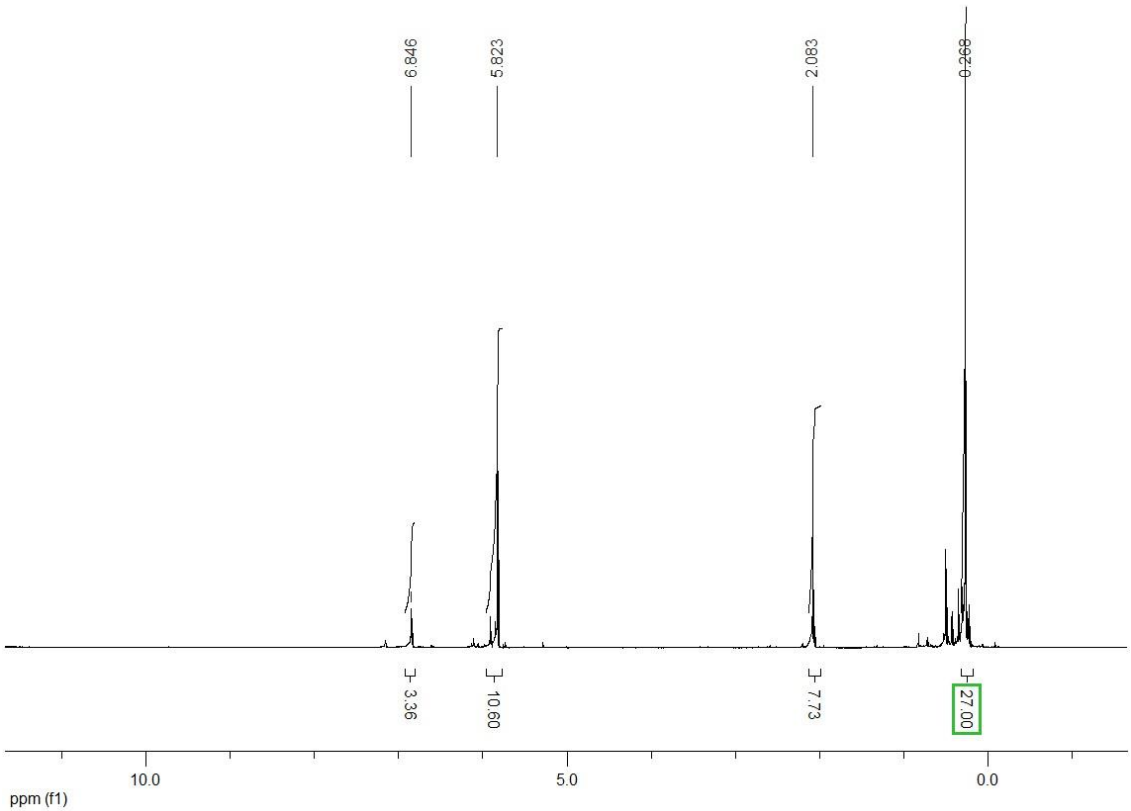

Figure S14. ^{1}H NMR spectrum of **2b**, C_6D_6

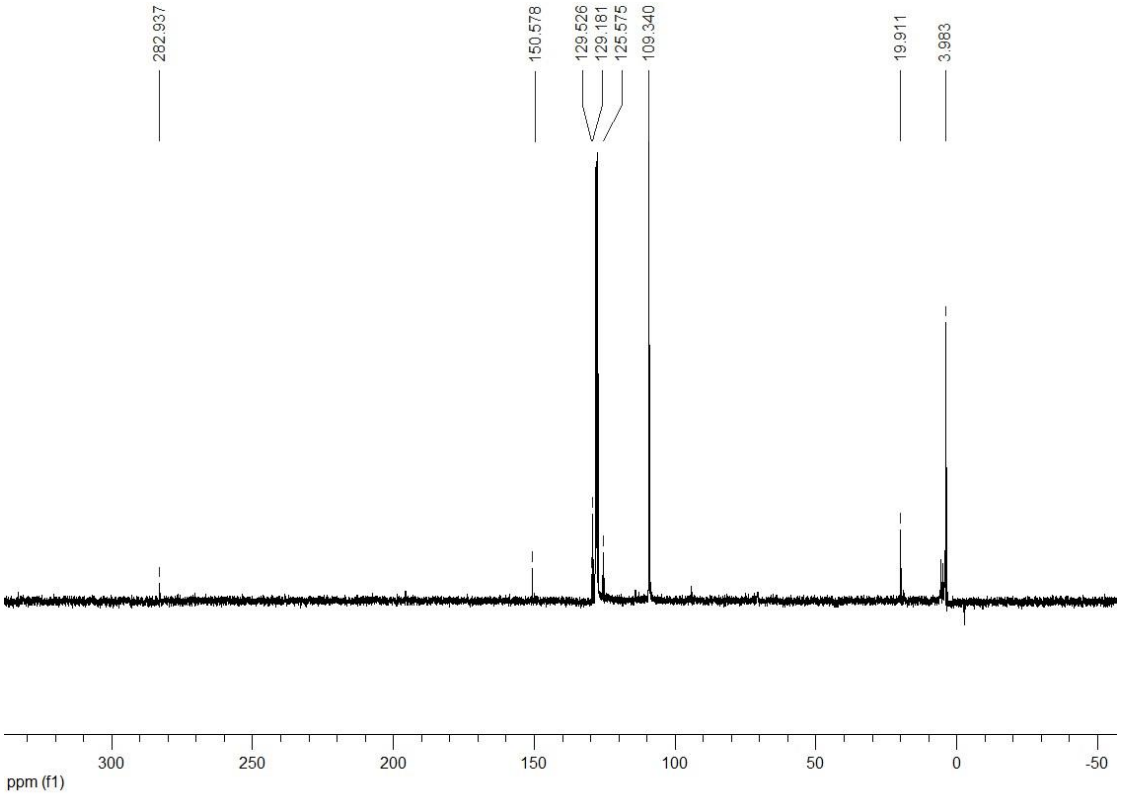

Figure S15. $^{13}C\{H\}$ NMR spectrum of **2b**, C_6D_6

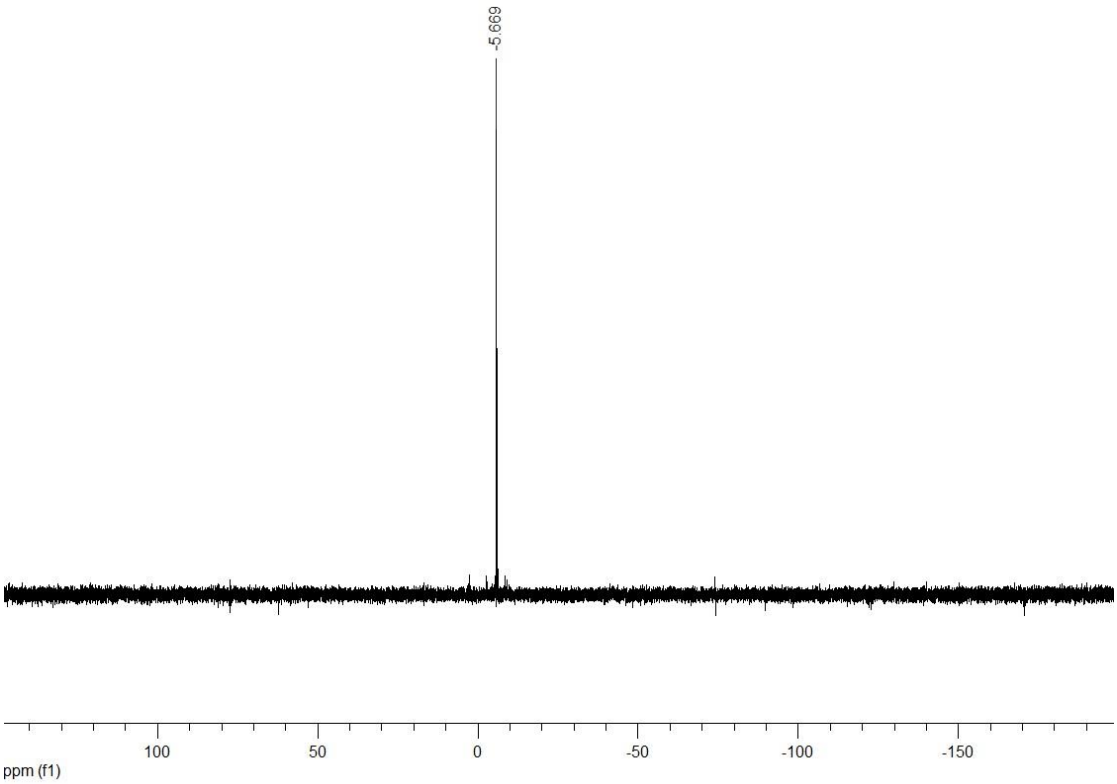

Figure S16. $^{29}Si\{H\}$ NMR spectrum of **2b**, C_6D_6

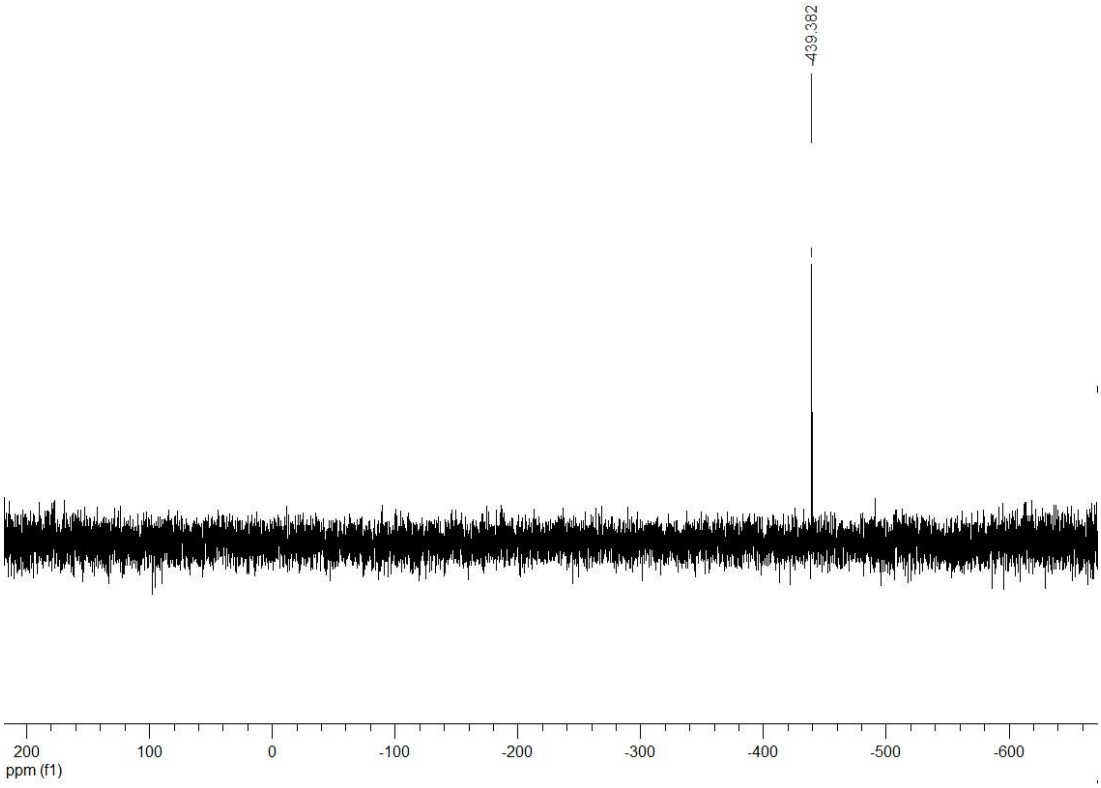

Figure S17. $^{119}Sn\{H\}$ NMR spectrum of **2b**, C_6D_6

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