Supporting Information

for

Heavier *N*-heterocyclic half-sandwich tetrylenes

Inga-Alexandra Bischoff,[a] Bernd Morgenstern,[a] and André Schäfer*[a]

[a] Department of Chemistry, Faculty of Natural Sciences and Technology, Saarland University, Campus Saarbrücken, 66123 Saarbrücken, Germany

Experimental Procedures

General Information

All manipulations were carried out under an argon inert gas atmosphere using Schlenk line techniques or a glove box. Solvents were purified using an MBraun Solvent Purification System. NMR spectra were recorded on Bruker Avance III 300 and Bruker Avance III 400 spectrometers. ^{1}H and ^{13}C NMR spectra were referenced using the solvent signals (δ ^{1}H(C_6HD_5) = 7.16; δ ^{13}C(C_6D_6) = 128.0) and ^{29}Si, ^{77}Se, ^{119}Sn and ^{207}Pb NMR spectra were referenced using external standards (δ ^{29}Si($SiMe_4$) = 0; δ ^{77}Se($SeMe_2$) = 0; δ ^{119}Sn($SnMe_4$) = 0, δ ^{207}Pb($PbMe_4$) = 0). Single crystal X-ray diffraction analysis were carried out on a Bruker AXS X8 Apex CCD diffractometer and a Bruker D8 Venture diffractometer with a microfocus sealed tube and a Photon II detector operating with graphite monochromated Mo Kα radiation. Data were corrected for absorption effects using the multi-scan method. Structure solution was conducted with direct methods using SHELXT and refinement by full matrix least squares calculations on F^2 using SHELXL2018 in the graphical user interface Shelxle.[1] Elemental analysis was performed on an Elementar Vario MICRO cube. 1,2,3,4-Tetramethylcyclopenta-1,3-diene,[2] Cyclopentadienyldimethylchlorosilane,[3] 2,3,4,5-tetramethylcyclopentadienyldimethylchlorosilane,[4] cyclopentadienyldimethyl(*tert*-butylamino)silane, tetramethyl-cyclopentadienyldimethyl(*tert*-butylamino)silane and their dilithio derivatives[5] were synthesized according to literature procedures.

Syntheses of 1a-d

A suspension of $Me_2Si(Cp^RLi)(^tBuNLi)$ ($Cp^R = H_4C_5$: 300 mg; 1.45 mmol / $Cp^R = Me_4C_5$: 1.00 g; 3.80 mmol) in thf (~40 mL) was cooled to 195 K and $SnCl_2$ ($Cp^R = H_4C_5$: 274 mg; 1.45 mmol / $Cp^R = Me_4C_5$: 720 mg; 3.80 mmol), a solution of $GeCl_2$•dioxane (880 mg; 3.80 mmol) in thf (~20 mL) or a suspension of $PbCl_2$ (1.06 mg; 3.80 mmol) in thf (~20 mL), respectively, was added. The reaction mixture was warmed to room temperature and stirred overnight. thf Was removed *in vacuo* and the residue was extracted with hexane (~60 mL). After filtration all volatiles were removed *in vacuo* to obtain **1a**-**d**.

1a:

yellow crystals; 70% (317 mg; 1.02 mmol) yield

^{1}H-NMR (400.13 MHz, C_6D_6, 293 K, δ in ppm): 0.40 (6 H, s, Si(C$\underline{H}_3$)$_2$), 0.98 (9 H, s, NC(C$\underline{H}_3$)$_3$), 6.67 (2 H, t, *J* = 2.4 Hz, Cp$\underline{H}$), 6.77 (2 H, t, *J* = 2.3 Hz, Cp$\underline{H}$).

^{13}C{^{1}H}-NMR (75.47 MHz, C_6D_6, 296 K, δ in ppm): 3.7 (Si($\underline{C}H_3$)$_2$), 35.9 (NC($\underline{C}H_3$)$_3$), 54.2 (N$\underline{C}$(CH$_3$)$_3$), 102.5 (Cp-$\underline{C}$), 113.1 (Cp-$\underline{C}$), 121.1 (Cp-$\underline{C}$).

^{29}Si{^{1}H}-NMR (59.63 MHz, C_6D_6, 296 K, δ in ppm): -14.5.

^{119}Sn{^{1}H}-NMR (149.21 MHz, C_6D_6, 293 K, δ in ppm): -296.0.

CHN-analysis: Found: C, 42.64; H, 6.02; N, 3.72.Calc. for $C_{11}H_{19}NSiSn$: C, 42.34; H, 6.14; N, 4.49%.

1b:

orange oil; 78% (953 mg, 2.96 mmol) yield

^{1}H-NMR (400.13 MHz, C_6D_6, 293 K, δ in ppm): 0.50 (6 H, s, Si(C$\underline{H}_3$)$_2$), 1.11 (9 H, s, NC(C$\underline{H}_3$)$_3$), 1.98 (6 H, s, Cp-C$\underline{H}_3$), 2.35 (6 H, s, Cp-C$\underline{H}_3$).

^{13}C{^{1}H}-NMR (100.61 MHz, C_6D_6, 293 K, δ in ppm): 6.1 (Si($\underline{C}H_3$)$_2$), 11.5 (Cp-$\underline{C}H_3$), 13.9 (Cp-$\underline{C}H_3$), 34.6 (NC($\underline{C}H_3$)$_3$), 54.2 (N$\underline{C}$(CH$_3$)$_3$), 89.1 (Cp-$\underline{C}$), 122.4 (Cp-$\underline{C}$), 132.4 (Cp-$\underline{C}$).

^{29}Si{^{1}H}-NMR (79.49 MHz, C_6D_6, 293 K, δ in ppm): -12.5.

HR-MS: *m/z* $[M+H]^+$: calculated: 324.1203; found: 324.1188.

1c:

red oil; 70 % (978 mg, 2.66 mmol) yield

^{1}H-NMR (400.13 MHz, C_6D_6, 293 K, δ in ppm): 0.55 (6 H, s, $Si(C\underline{H}_3)_2$), 1.11 (9 H, s, $NC(C\underline{H}_3)_3$), 1.94 (6 H, s, Cp-$C\underline{H}_3$), 2.42 (6 H, s, Cp-$C\underline{H}_3$).

^{13}C{^{1}H}-NMR (100.61 MHz, C_6D_6, 293 K, δ in ppm): 7.2 ($Si(\underline{C}H_3)_2$), 11.5 (Cp-$\underline{C}H_3$), 14.0 (Cp-$\underline{C}H_3$), 34.0 ($N\underline{C}(CH_3)_3$), 36.3 ($NC(\underline{C}H_3)_3$), 53.9 (Cp-$\underline{C}$), 98.0 (Cp-$\underline{C}$), 120.5 (Cp-$\underline{C}$).

^{29}Si{^{1}H}-NMR (79.49 MHz, C_6D_6, 293 K, δ in ppm): -16.2.

^{119}Sn{^{1}H}-NMR (149.21 MHz, C_6D_6, 293 K, δ in ppm): -315.0.

CHN-analysis: Found: 46.92; H, 7.16; N, 3.71. Calc. for $C_{15}H_{27}NSiGe$: C, 48.93; H, 7.39; N, 3.80%.[6]

HR-MS: *m/z* $[M+O]^+$: calculated: 385.0884; found: 385.0723.

1d:

dark red crystals; 77% (400 mg, 0.88 mmol) yield

^{1}H-NMR (300.13 MHz, C_6D_6, 296 K, δ in ppm): 0.61 (6 H, s, $Si(C\underline{H}_3)_2$), 1.10 (9 H, s, $NC(C\underline{H}_3)_3$), 1.93 (6 H, s, Cp-$C\underline{H}_3$), 2.60 (6 H, s, Cp-$C\underline{H}_3$).

^{13}C{^{1}H}-NMR (75.47 MHz, C_6D_6, 296 K, δ in ppm): 9.7 ($Si(C\underline{H}_3)_2$), 11.8 (Cp-$\underline{C}H_3$), 13.6 (Cp-$\underline{C}H_3$), 39.0 ($NC(\underline{C}H_3)_3$), 52.3 ($N\underline{C}(CH_3)_3$), 100.0 (Cp-$\underline{C}$), 122.4 (Cp-$\underline{C}$), 125.5 (Cp-$\underline{C}$).

^{29}Si{^{1}H}-NMR (59.63 MHz, C_6D_6, 296 K, δ in ppm): -25.8.

^{207}Pb{^{1}H}-NMR (62.79 MHz, C_6D_6, 296 K, δ in ppm): +1561.7.

CHN-analysis: Found: C, 39.84; H, 6.16; N, 2.77. Calc. for $C_{15}H_{27}NSiPb$: C, 39.45; H, 5.96; N, 3.07%.

Reactions of 1a,c with Ph_2Se_2

The corresponding stannylene (**1a**: 100 mg; 0.32 mmol / **1c**: 100 mg; 0.27 mmol) and Ph_2Se_2 (for **1a**/**2a**: 100 mg, 0.32 mmol / for **1c**/**2b**: 85 mg, 0.27 mmol) were dissolved in C_6D_6 (~1 mL) and stirred overnight. Subsequently the mixtures were examined and NMR spectroscopy.

1a/2a:

^{1}H-NMR (400.13 MHz, C_6D_6, 293 K, δ in ppm): 0.34 (6 H, s, $Si(C\underline{H}_3)_2$), 1.28 (9 H, s, $NC(C\underline{H}_3)_3$), 5.61 (2 H, t, *J* = 1.1 Hz, Cp$\underline{H}$), 6.51 (2 H, t, *J* = 1.1 Hz, Cp$\underline{H}$), 6.87-6.97 (6 H, m, SePh$\underline{H}$), 7.45-7.51 (4 H, m, SePh$\underline{H}$).

^{13}C{^{1}H}-NMR (100.61 MHz, C_6D_6, 293 K, δ in ppm): 3.6 ($Si(\underline{C}H_3)_2$), 35.6 ($NC(\underline{C}H_3)_3$), 55.4 ($N\underline{C}(CH_3)_3$), 101.5 (Cp-$\underline{C}$), 124.7 (Cp-$\underline{C}$), 129.2 (SePh-$\underline{C}$), 132.1 (SePh-$\underline{C}$), 138.1 (SePh-$\underline{C}$), 139.3 (SePh-$\underline{C}$).

^{29}Si{^{1}H}-NMR (79.49 MHz, C_6D_6, 293 K, δ in ppm): -8.5.

^{77}Se{^{1}H}-NMR (76.32 MHz, C_6D_6, 293 K, δ in ppm): 137.8 ($^{1}J_{\text{Se-Sn}}$ = 1550 Hz).

^{119}Sn{^{1}H}-NMR (149.21 MHz, C_6D_6, 293 K, δ in ppm): -88.6 ($^{1}J_{\text{Sn-Se}}$ = 1626 Hz).

1c/2b:

^{1}H-NMR (400.13 MHz, C_6D_6, 293 K, δ in ppm): 0.47 (6 H, s, $Si(C\underline{H}_3)_2$), 1.35 (9 H, s, $NC(C\underline{H}_3)_3$), 1.61 (6 H, s, Cp-$C\underline{H}_3$), 1.81 (6 H, s, Cp-$C\underline{H}_3$).

^{13}C{^{1}H}-NMR (100.61 MHz, C_6D_6, 293 K, δ in ppm): 6.1 ($Si(C\underline{H}_3)_2$), 11.5 (Cp-$C\underline{H}_3$), 16.3 (Cp-$C\underline{H}_3$), 36.0 ($NC(\underline{C}H_3)_3$), 55.3 ($N\underline{C}(CH_3)_3$), 113.0 (Cp-$\underline{C}$), 125.0 (Cp-$\underline{C}$), 127.7 (Cp-$\underline{C}$), 129.2 (SePh-$\underline{C}$), 133.5 (SePh-$\underline{C}$), 137.9 (SePh-$\underline{C}$), 140.1 (SePh-$\underline{C}$).

^{29}Si{^{1}H}-NMR (79.49 MHz, C_6D_6, 293 K, δ in ppm): -8.8.

^{77}Se{^{1}H}-NMR (76.32 MHz, C_6D_6, 293 K, δ in ppm): 120.9.

^{119}Sn{^{1}H}-NMR (149.21 MHz, C_6D_6, 293 K, δ in ppm): -70.5 ($^{1}J_{\text{Sn-Se}}$ = 1631 Hz).

Syntheses of 3

Route 1:

1b (366 mg; 1.14 mmol) and W(CO)$_6$ (400 mg; 1.14 mmol) were mixed together in thf (~4 mL) and irradiated (365 nm) for 5 h. Subsequently all volatiles removed *in vacuo*, toluene (~3 mL) was added, and the solution was stored at 248 K overnight. The precipitated solid was filtered off and toluene was removed *in vacuo* from the filtrate. The residue was sublimed at 448 K and an orange crystalline solid was obtained. Orange crystals could be obtained from toluene at 248 K.

44 % (390 mg, 0.60 mmol) yield

Route 2:

Cl$_2$Ge W(CO)$_5$·in thf was synthesized according to a literature procedure.[7] A solution of Me$_2$Si(Cp$^\#$Li)(^{t}BuNLi) (250 mg; 0.95 mmol) in thf (~30 mL) was added to a solution of Cl$_2$Ge W(CO)$_5$·(512 mg; 0.95 mmol)in thf (~30 mL) at 195 K. The mixture was warmed to room temperature and stirred overnight. All volatiles were removed *in vacuo* and the residue was suspended in hexane (~60 mL). After filtration, hexane was removed *in vacuo*. Orange crystals could be obtained from a mixture of toluene and hexane at 248 K.

60 % (360 mg, 0.56 mmol) yield

^{1}H-NMR (400.13 MHz, C$_6$D$_6$, 293 K, δ in ppm): 0.30 (6 H, s, Si(C$\underline{H}_3$)$_2$),), 1.23 (9 H, s, NC(C$\underline{H}_3$)$_3$), 1.97 (6 H, s, Cp-C$\underline{H}_3$), 2.04 (6 H, s, Cp-C$\underline{H}_3$).

^{13}C{^{1}H}-NMR (100.61 MHz, C$_6$D$_6$, 293 K, δ in ppm): 5.1 (Si(C$\underline{H}_3$)$_2$), 11.8 (Cp-C$\underline{H}_3$), 14.6 (Cp-C$\underline{H}_3$), 34.3 (NC($\underline{C}$H$_3$)$_3$), 56.4 (N$\underline{C}$(CH$_3$)$_3$), 78.9 (Cp-$\underline{C}$), 126.0 (Cp-$\underline{C}$), 139.0 (Cp-$\underline{C}$), 195.2 (J_{CW} = 122.2 Hz, W($\underline{C}$O)), 198.8 (W($\underline{C}$O)).

^{29}Si{^{1}H}-NMR (79.49 MHz, C$_6$D$_6$, 293 K, δ in ppm): 6.2.

CHN-analysis: Found: C, 37.27; H, 4.16; N, 2.12. Calc. for C$_{20}$H$_{27}$GeNO$_5$SiW: C, 37.19; H, 4.21; N, 2.17 %.

IR absorptions: ν_{max}/cm^{-1} 1909, 1940 and 2067 (CO).

Reactions of 1b-d with DMAP

Tetrylenes **1b**-**d** (**1b**: 45.0 mg; 0.14 mmol / **1c**: 50.0 mg; 0.14 mmol / **1d**: 40.0 mg; 0.09 mmol) and DMAP (for **1b**/**4a**: 17.0 mg; 0.14 mg / for **1c**/**4b**: 17.0 mg; 0.14 mg / for **1d**/**4c**: 11.0 mg; 0.09 mg) were dissolved in C$_6$D$_6$ and stirred for a few minutes. The resulting mixtures were subsequently examined by NMR spectroscopy, **4a**-**c** were not isolated.

4a:

^{1}H-NMR (400.13 MHz, C$_6$D$_6$, 293 K, δ in ppm): 0.57 (6 H, s, Si(C$\underline{H}_3$)$_2$), 1.30 (9 H, s, NC(C$\underline{H}_3$)$_3$), 2.00 (6 H, s, DMAP-N(C$\underline{H}_3$)$_2$)), 2.20 (6 H, s, Cp-C$\underline{H}_3$), 2.22 (6 H, s, Cp-C$\underline{H}_3$), 6.00-6.01 (2 H, m, DMAP-C$\underline{H}$), 8.29-8.31 (2 H, m, DMAP-C$\underline{H}$).

^{13}C{^{1}H}-NMR (100.61 MHz, C$_6$D$_6$, 293 K, δ in ppm): 6.7 (Si($\underline{C}$H$_3$)$_2$), 12.3 (Cp-$\underline{C}$H$_3$), 14.4 (Cp-$\underline{C}$H$_3$), 34.9 (NC($\underline{C}$H$_3$)$_3$), 38.4 (DMAP-N($\underline{C}$H$_3$)$_2$)), 53.8 (N$\underline{C}$(CH$_3$)$_3$), 95.1(Cp-$\underline{C}$), 106.5 (DMAP-$\underline{C}$H), 120.9 (Cp-$\underline{C}$), 132.5 (Cp-$\underline{C}$) 148.8 (DMAP-$\underline{C}$H), 154.5 (DMAP-$\underline{C_q}$).

^{29}Si{^{1}H}-NMR (79.49 MHz, C$_6$D$_6$, 293 K, δ in ppm): -11.3.

4b:

^{1}H-NMR (400.13 MHz, C$_6$D$_6$, 293 K, δ in ppm): 0.67 (6 H, s, Si(C$\underline{H}_3$)$_2$, **1c**), 1.36 (9 H, s, NC(C$\underline{H}_3$)$_3$, **1c**), 2.11 (6 H, s, DMAP-N(C$\underline{H}_3$)$_2$), DMAP), 2.20 (6 H, s, Cp-C$\underline{H}_3$, **1c**), 2.34 (6 H, s, Cp-C$\underline{H}_3$, **1c**), 5.93-5.95 (2 H, m, DMAP-C$\underline{H}$), 8.30-8.32 (2 H, m, DMAP-C$\underline{H}$).

^{13}C{^{1}H}-NMR (100.61 MHz, C$_6$D$_6$, 293 K, δ in ppm): 8.1 (Si($\underline{C}$H$_3$)$_2$), 12.0 (Cp-$\underline{C}$H$_3$), 14.7 (Cp-$\underline{C}$H$_3$), 36.4 (NC($\underline{C}$H$_3$)$_3$), 38.3 (DMAP-N($\underline{C}$H$_3$)$_2$), 53.0 (N$\underline{C}$(CH$_3$)$_3$), 89.7 (Cp-$\underline{C}$), 106.7 (DMAP-$\underline{C}$H), 122.6 (Cp-$\underline{C}$), 127.4 (Cp-$\underline{C}$), 148.2 (DMAP-$\underline{C}$H), 154.7 (DMAP-$\underline{C_q}$).

^{29}Si{^{1}H}-NMR (79.49 MHz, C$_6$D$_6$, 293 K, δ in ppm): -14.0.

^{119}Sn{^{1}H}-NMR (149.21 MHz, C_6D_6, 293 K, δ in ppm): -129.5.

4c:

^{1}H-NMR (300.13 MHz, C_6D_6, 293 K, δ in ppm): 0.69 (6 H, s, $Si(C\underline{H}_3)_2$), 1.25 (9 H, s, $NC(C\underline{H}_3)_3$), 2.13 (6 H, s, Cp-$C\underline{H}_3$, **1d**), 2.18 (6 H, s, DMAP-$N(C\underline{H}_3)_2$), 2.56 (6 H, s, Cp-$C\underline{H}_3$), 6.03-6.05 (2 H, m, DMAP-$C\underline{H}$), 8.36-8.38 (2 H, m, DMAP-$C\underline{H}$).

^{13}C{^{1}H}-NMR (100.61 MHz, C_6D_6, 293 K, δ in ppm): 10.2 ($Si(\underline{C}H_3)_2$), 11.9 (Cp-$\underline{C}H_3$), 14.0 (Cp-$\underline{C}H_3$), 38.3 (DMAP-$N(\underline{C}H_3)_2$), 38.9 ($NC(\underline{C}H_3)_3$), 52.0 ($N\underline{C}(CH_3)_3$), 98.1 (Cp-$\underline{C}$), 107.0 (DMAP-$\underline{C}H$), 122.1 (Cp-$\underline{C}$), 125.1 (Cp-C), 149.7 (DMAP-$\underline{C}H$), 154.3 (DMAP-$\underline{C_q}$).

^{29}Si{^{1}H}-NMR (79.49 MHz, C_6D_6, 293 K, δ in ppm): -25.7.

^{207}Pb{^{1}H}-NMR (62.79 MHz, C_6D_6, 293 K, δ in ppm): 1677.

Syntheses of 5a-c

Tetrylenes **1b**-**d** (**1b**: 200 mg; 0.62 mmol / **1c**: 150 mg, 0.41 mmol / **1d**: 130 mg, 0.28 mmol) and 1,3-di*iso*propyl-4,5-dimethylimidazolin-2-ylidene (NHC) (for **1b**/**5a**: 112 mg; 0.62 mg / for **1c**/**5b**: 73.0 mg; 0.41 mg / for **1d**/**5c**: 51.0 mg; 0.28 mg) were dissolved in hexane and an immediate precipitation of solid was observed. To this suspension, thf was slowly added until the solid was dissolved and the resulting solution was stored at 248 K.

5a:

yellow crystals; 42% (131 mg; 0.26 mmol) yield

^{1}H-NMR (400.13 MHz, C_6D_6, 293 K, δ in ppm): 0.56 (6 H, s, $Si(C\underline{H}_3)_2$), 1.17 (12 H, d, *J* = 6.8 Hz, NHC-$CH(C\underline{H}_3)_2$), 1.43 (9 H, s, $NC(C\underline{H}_3)_3$), 1.58 (6 H, s, NHC-$C\underline{H}_3$,), 2.18 (6 H, s, Cp-$C\underline{H}_3$), 2.35 (6 H, s, Cp-$C\underline{H}_3$, **1b**), 4.85 (2H, br s, NHC-$C\underline{H}(CH_3)_2$).

^{13}C{^{1}H}-NMR (100.61 MHz, C_6D_6, 293 K, δ in ppm): 7.55 ($Si(\underline{C}H_3)_2$), 9.9 (NHC-$\underline{C}H_3$), 12.3 (Cp-$\underline{C}H_3$), 15.6 (Cp-$\underline{C}H_3$), 22.6 (NHC-$CH(\underline{C}H_3)_2$), 34.5 ($NC(\underline{C}H_3)_3$), 49.1 (NHC-$\underline{C}H(CH_3)_2$), 52.2 ($N\underline{C}(CH_3)_3$), 124.5 (NHC-$\underline{C}$), 129.0 (Cp-$\underline{C}$), 132.0 (Cp-$\underline{C}$), 179.4 (carbene-$\underline{C}$).

^{29}Si{^{1}H}-NMR (79.49 MHz, C_6D_6, 293 K, δ in ppm): -6.2.

CHN-analysis: Found: C, 61.23; H, 8.93; N, 8.11. Calc. for $C_{26}H_{47}N_3GeSi$: C, 62.16; H, 9.43; N, 8.36%.[6]

5b:

yellow crystals; 46% (104 mg; 0.19 mmol) yield

^{1}H-NMR (400.13 MHz, C_6D_6, 293 K, δ in ppm): 0.59 (6 H, s, $Si(C\underline{H}_3)_2$), 1.12 (12 H, d, *J* = 10.0 Hz, NHC-$CH(C\underline{H}_3)_2$), 1.45 (9 H, s, $NC(C\underline{H}_3)_3$), 1.54 (6 H, s, NHC-$C\underline{H}_3$), 2.29 (6 H, s, Cp-$C\underline{H}_3$), 2.43 (6 H, s, Cp-$C\underline{H}_3$), 4.91 (2 H, br s, NHC-$C\underline{H}(CH_3)_2$).

^{13}C{^{1}H}-NMR (100.61 MHz, C_6D_6, 293 K, δ in ppm): 8.7 ($Si(\underline{C}H_3)_2$), 9.9 (NHC-$\underline{C}H_3$), 12.4 (Cp-$\underline{C}H_3$), 16.0 (Cp-$\underline{C}H_3$), 22.6 (NHC-$CH(\underline{C}H_3)_2$), 35.9 ($NC(\underline{C}H_3)_3$), 50.5 (NHC-$\underline{C}H(CH_3)_2$), 51.7 ($N\underline{C}(CH_3)_3$), 72.0 (Cp-C), 124.9 (NHC-$\underline{C}$), 127.0 (Cp-$\underline{C}$), 130.3 (Cp-$\underline{C}$), 184.5 (carbene-$\underline{C}$).

^{29}Si{^{1}H}-NMR (79.49 MHz, C_6D_6, 293 K, δ in ppm): -8.0.

^{119}Sn{^{1}H}-NMR (149.21 MHz, C_6D_6, 293 K, δ in ppm): 20.4.

CHN-analysis: Found: C, 56.73; H, 8.39; N, 7.38. Calc. for $C_{26}H_{47}N_3SiSn$: C, 56.94; H, 8.64; N, 7.66%.

5c:

orange crystals; 71% (200 mg; 0.31 mmol) yield

^{1}H-NMR (400.13 MHz, C_6D_6, 293 K, δ in ppm): 0.58 (6 H, s, $Si(C\underline{H}_3)_2$, **1d**), 1.20 (12 H, d, *J* = 6.9 Hz, NHC-$CH(C\underline{H}_3)_2$), 1.35 (9 H, s, $NC(C\underline{H}_3)_3$, **1d**), 1.62 (6 H, s, NHC-$C\underline{H}_3$), 2.42 (6 H, s, Cp-$C\underline{H}_3$), 2.46 (6 H, s, Cp-$C\underline{H}_3$), 4.68 (2 H, sept, *J* = 6.8 Hz, NHC-$C\underline{H}(CH_3)_2$).

^{13}C{^{1}H}-NMR (100.61 MHz, C_6D_6, 293 K, δ in ppm): 9.9 (NHC-$\underline{C}H_3$), 10.8 (Si($\underline{C}H_3$)$_2$), 11.9 (s, Cp-$\underline{C}H_3$), 15.0 (s, Cp-$\underline{C}H_3$), 23.2 (s, NHC-CH($\underline{C}H_3$)$_2$), 37.9 (NC($\underline{C}H_3$)$_3$), 50.8 (NHC-$\underline{C}$H(CH$_3$)$_2$), 51.1 (N$\underline{C}$(CH$_3$)$_3$), 86.6 (Cp-$\underline{C}$), (124.5 (NHC-$\underline{C}$), 125.7 (Cp-$\underline{C}$),126.2 (Cp-$\underline{C}$), 204.9 (carbene-$\underline{C}$).

^{29}Si{^{1}H}-NMR (79.49 MHz, C_6D_6, 293 K, δ in ppm): -22.0.

^{207}Pb{^{1}H}-NMR (62.91 MHz, C_6D_6, 296 K, δ in ppm): 2135.

CHN-analysis: Found: C, 48.87; H, 7.56; N, 6.56. Calc. for $C_{26}H_{47}N_3PbSi$: C, 49.03; H, 7.44; N, 6.60%.

NMR Spectra

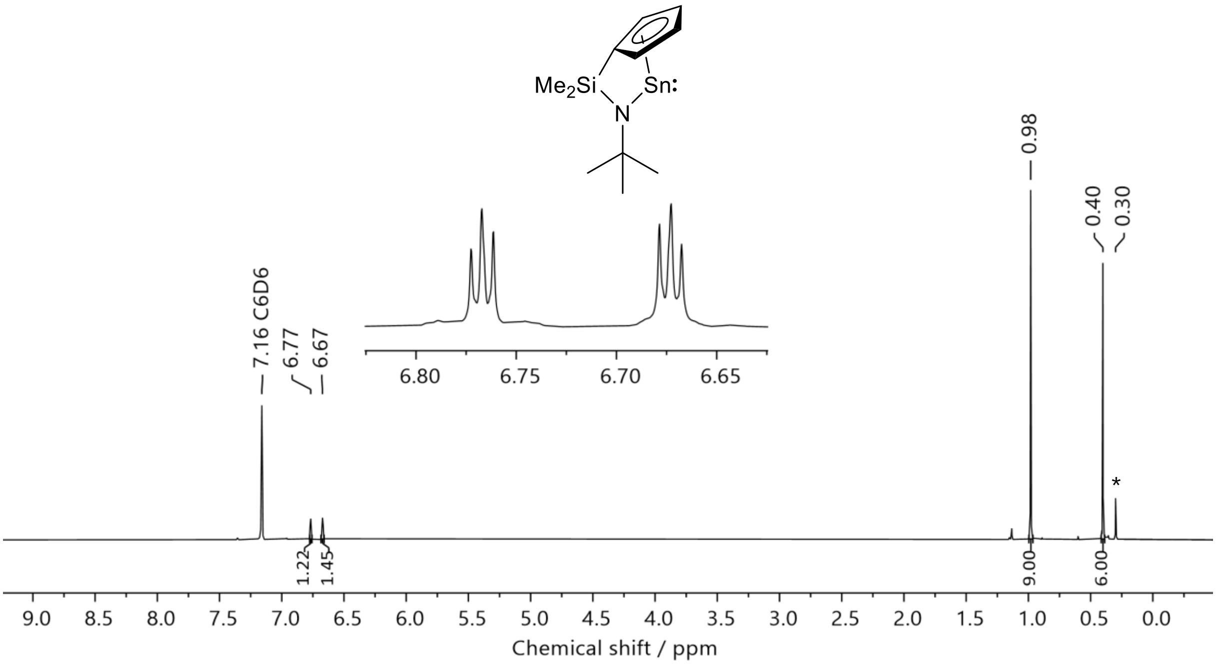


Figure S1: ^{1}H NMR spectrum of **1a** (400.13 MHz, C_6D_6, 298 K) (* silicon grease).

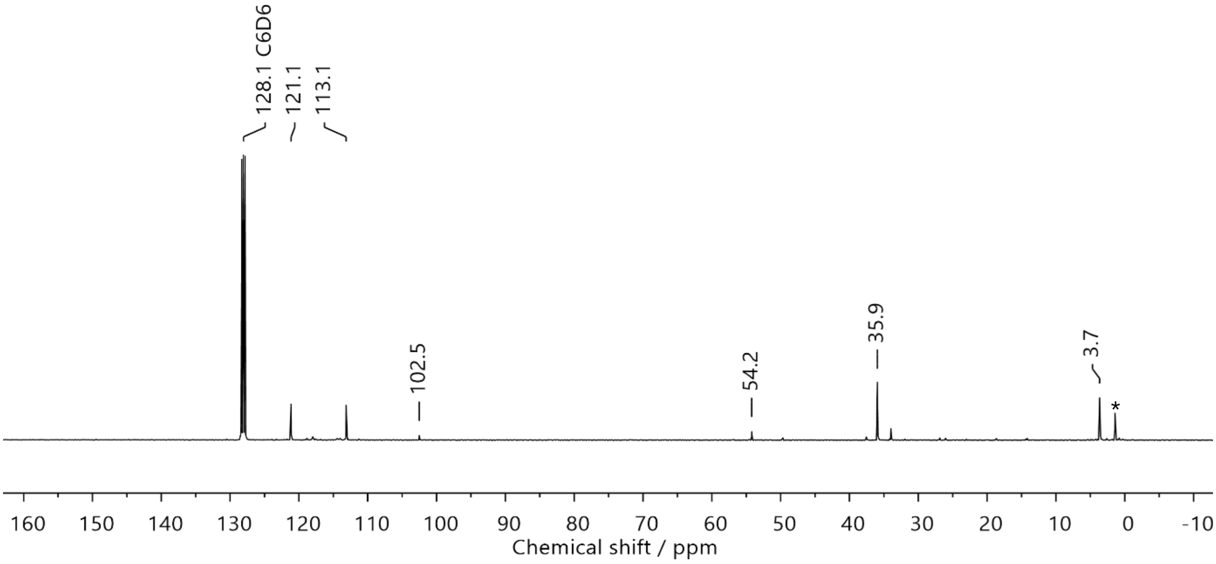


Figure S2: ^{13}C{^{1}H} NMR spectrum of **1a** (100.61 MHz, C_6D_6, 298 K) (* silicon grease).

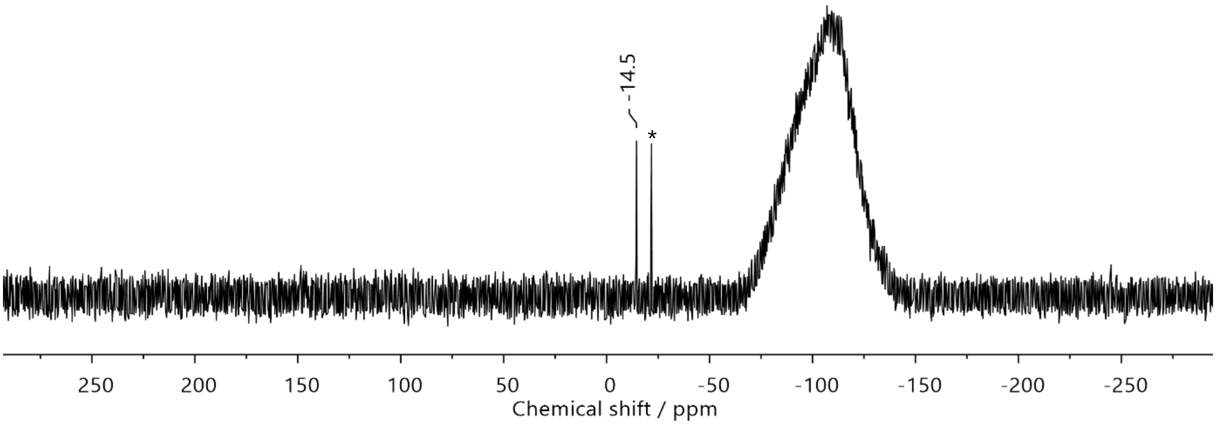


Figure S3: ^{29}Si{^{1}H} NMR spectrum of **1a** (79.49 MHz, C_6D_6, 298 K) (* silicon grease).

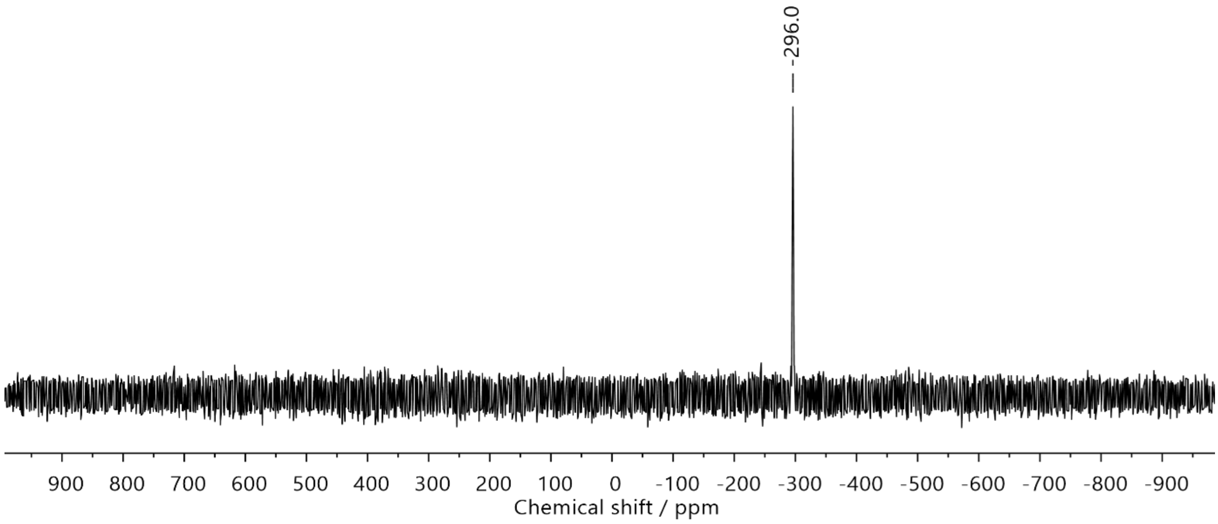


Figure S4: ^{119}Sn{^{1}H} NMR spectrum of **1a** (149.21 MHz, C_6D_6, 298 K).

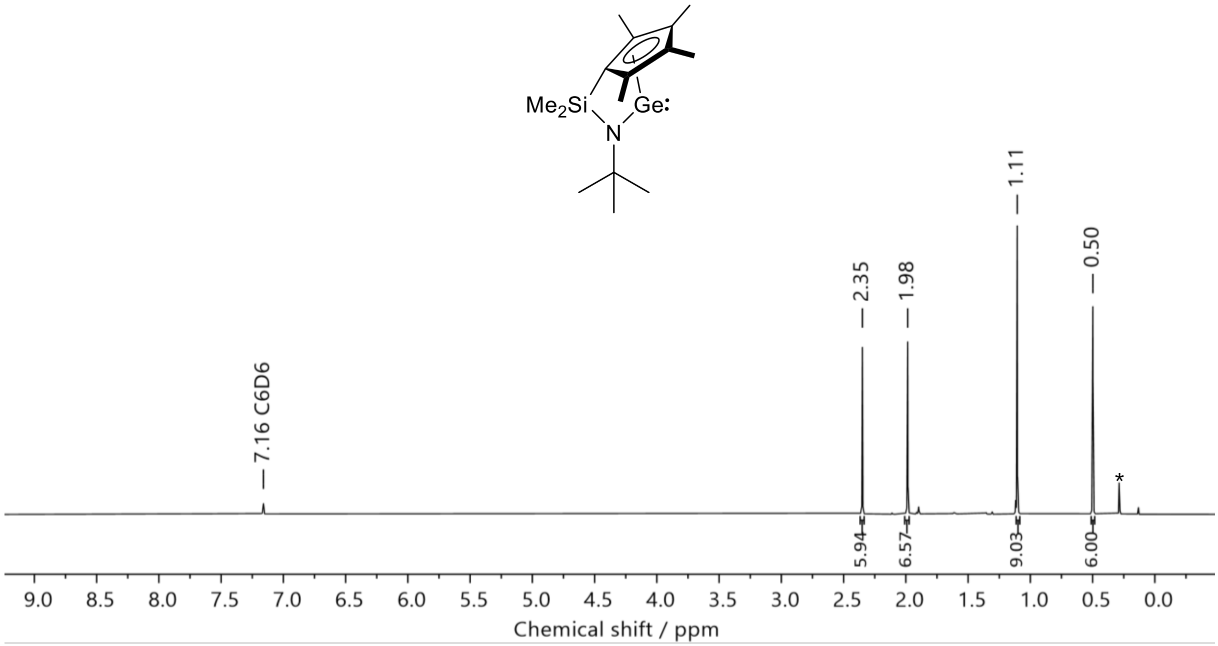


Figure S5: ^{1}H NMR spectrum of **1b** (400.13 MHz, C_6D_6, 298 K) (* silicon grease).

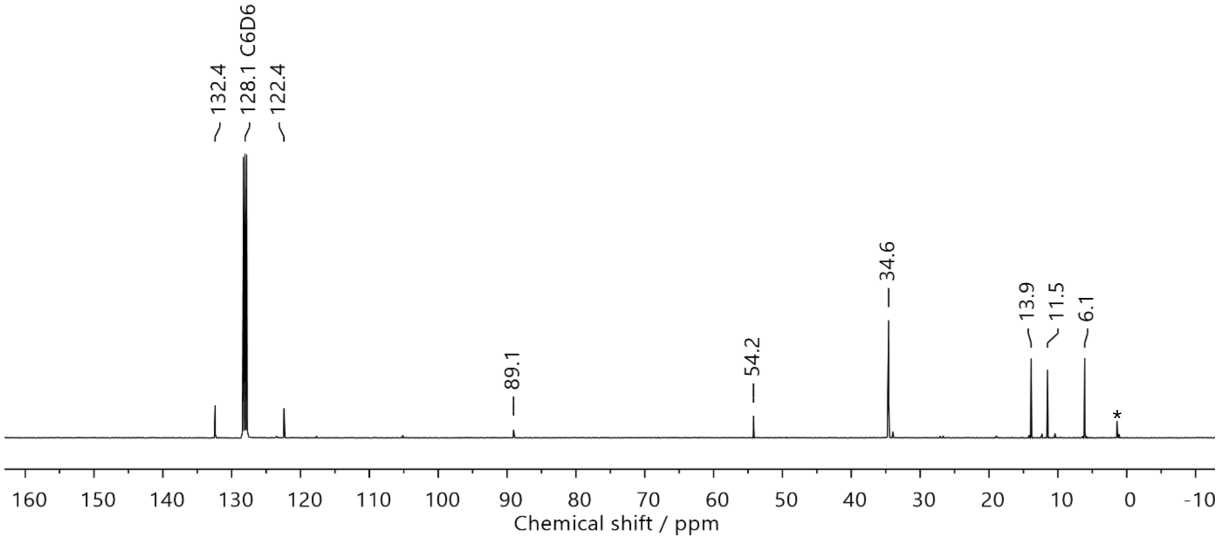


Figure S6: ^{13}C{^{1}H} NMR spectrum of **1b** (100.61 MHz, C_6D_6, 298 K) (* silicon grease).

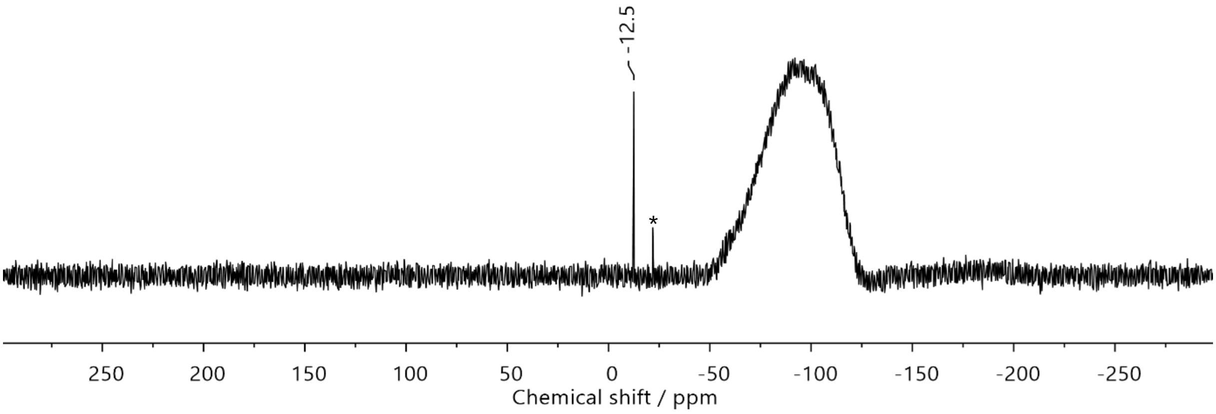


Figure S7: ^{29}Si{^{1}H} NMR spectrum of **1b** (79.49 MHz, C_6D_6, 298 K) (* silicon grease).

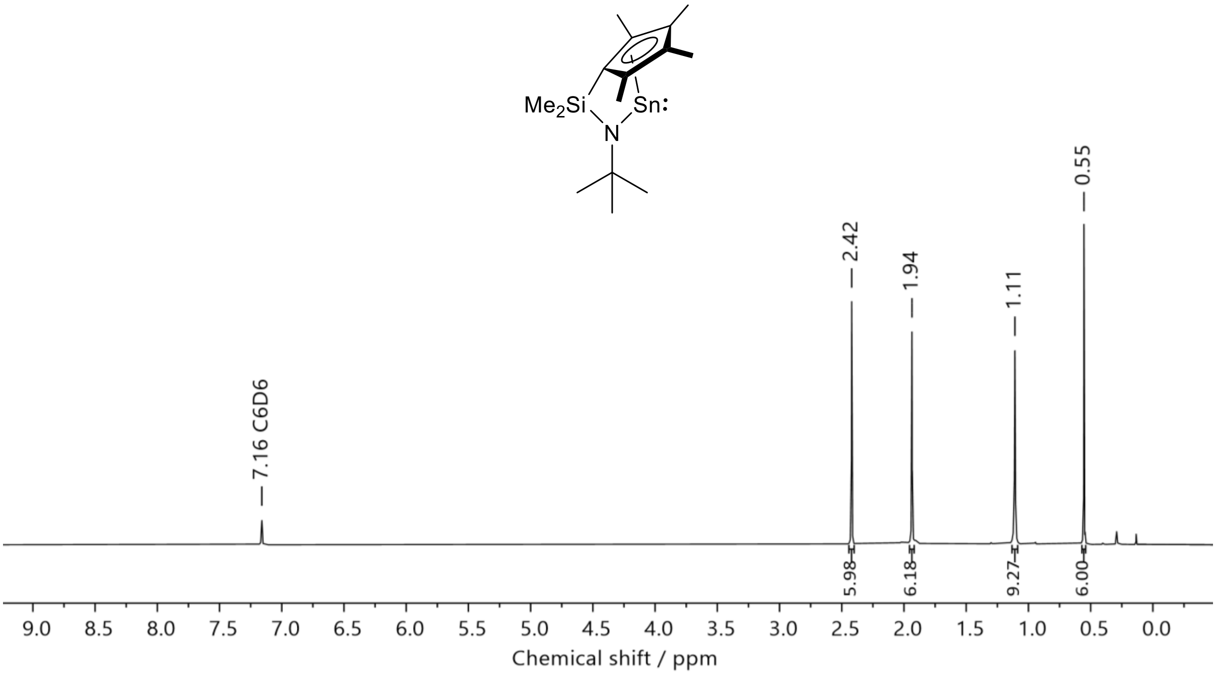


Figure S8: ^{1}H NMR spectrum of **1c** (400.13 MHz, C_6D_6, 298 K).

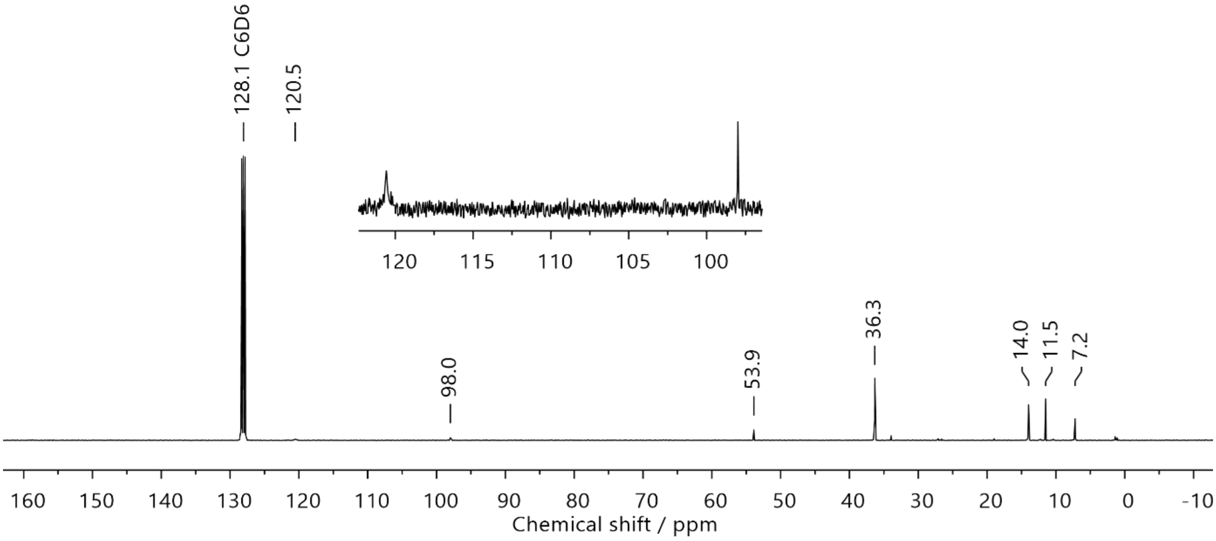


Figure S9: ^{13}C{^{1}H} NMR spectrum of **1c** (100.61 MHz, C_6D_6, 298 K).

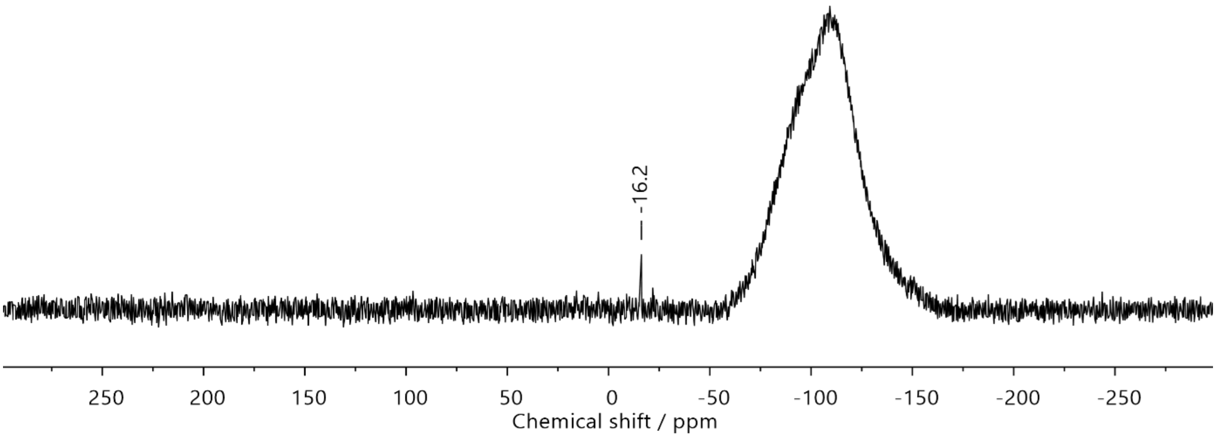


Figure S10: $^{29}Si\{^1H\}$ NMR spectrum of **1c** (79.49 MHz, C_6D_6, 298 K).

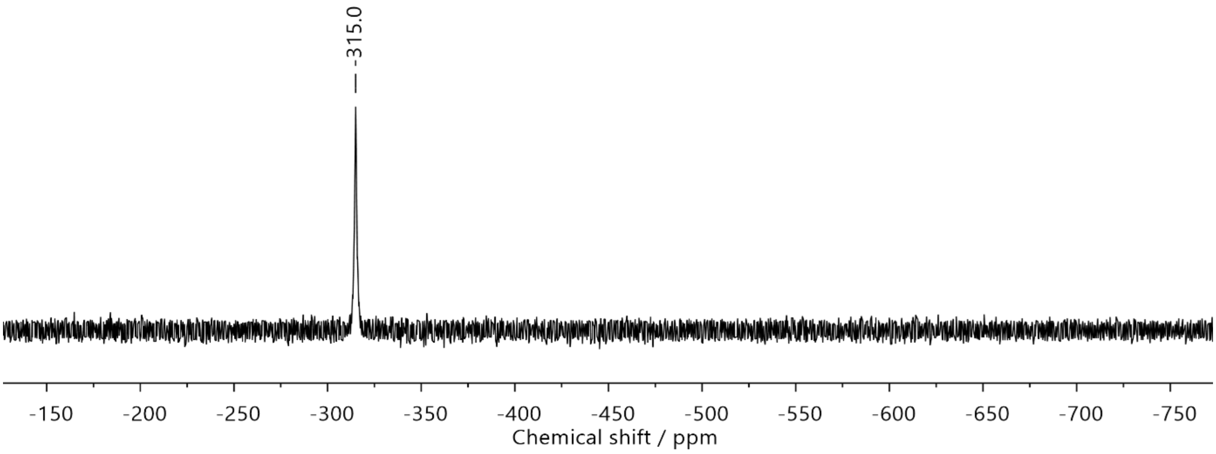


Figure S11: $^{119}Sn\{^1H\}$ NMR spectrum of **1c** (149.21 MHz, C_6D_6, 298 K).

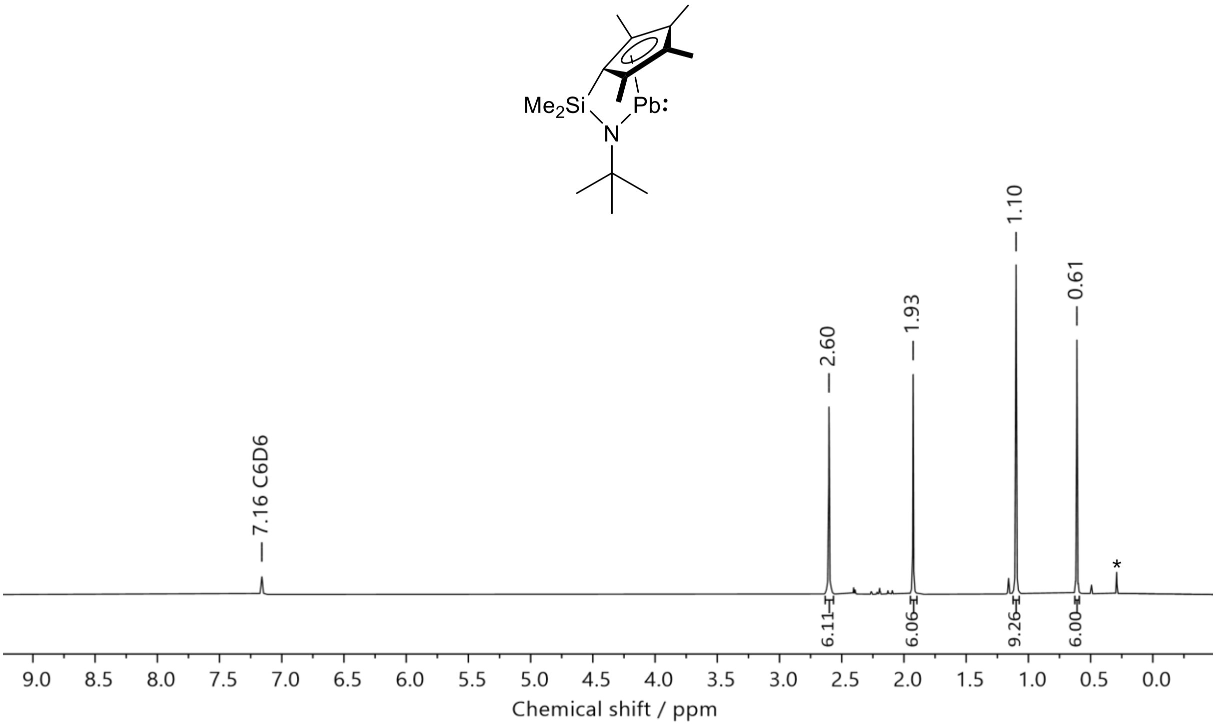


Figure S12: ^1H NMR spectrum of **1d** (400.13 MHz, C_6D_6, 298 K) (* silicon grease).

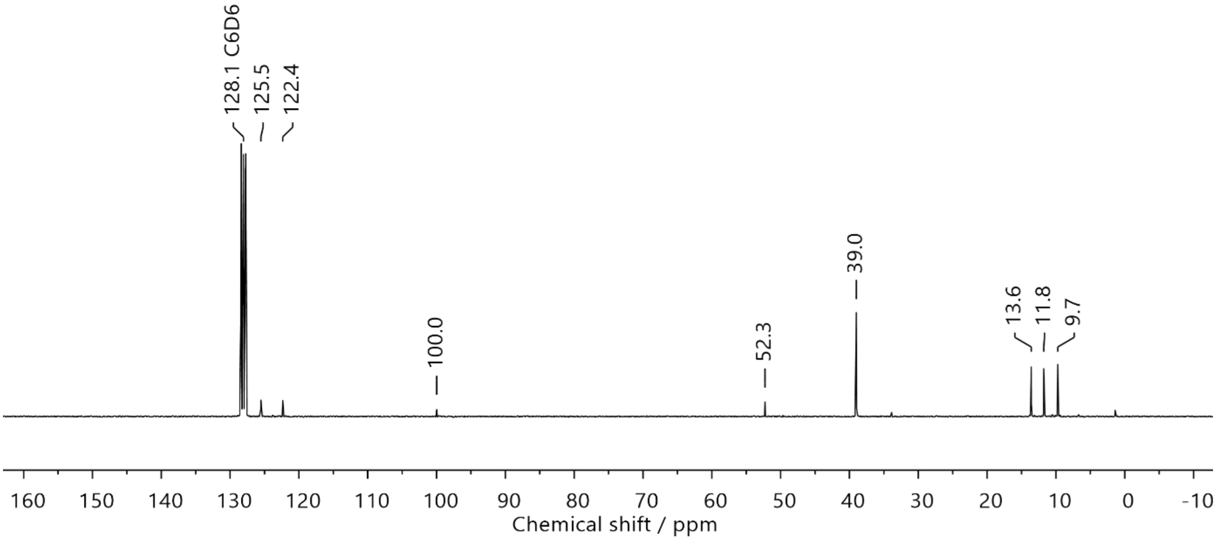


Figure S13: $^{13}C\{^1H\}$ NMR spectrum of **1d** (100.61 MHz, C_6D_6, 298 K).

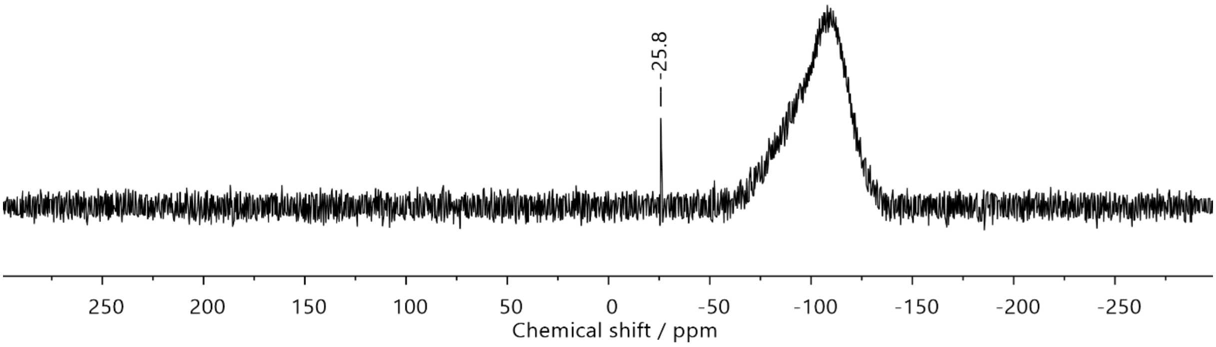


Figure S14: $^{29}Si\{^1H\}$ NMR spectrum of **1d** (79.49 MHz, C_6D_6, 298 K).

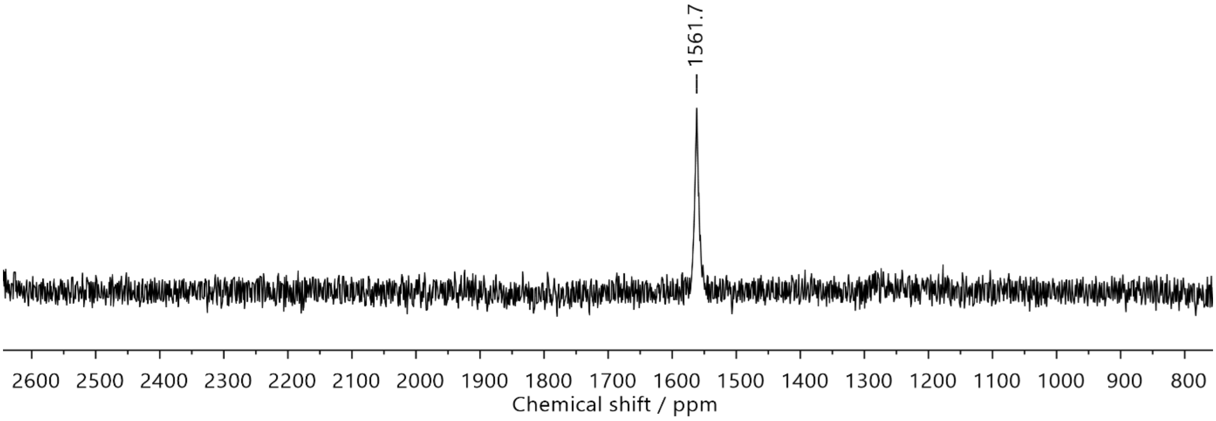


Figure S15: $^{207}Pb\{^1H\}$ NMR spectrum of **1d** (62.79 MHz, C_6D_6, 298 K).

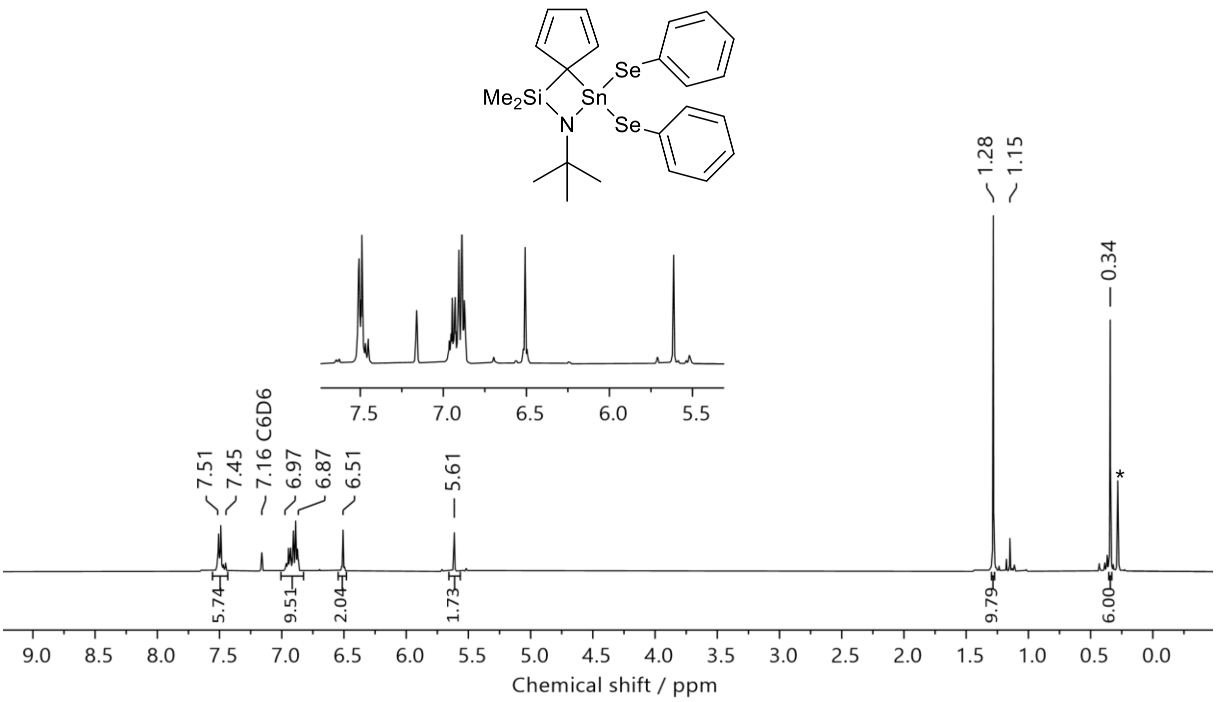


Figure S16: ^{1}H NMR spectrum of the reaction of **1a** with Ph_2Se_2 (400.13 MHz, C_6D_6, 298 K) (* silicon grease).

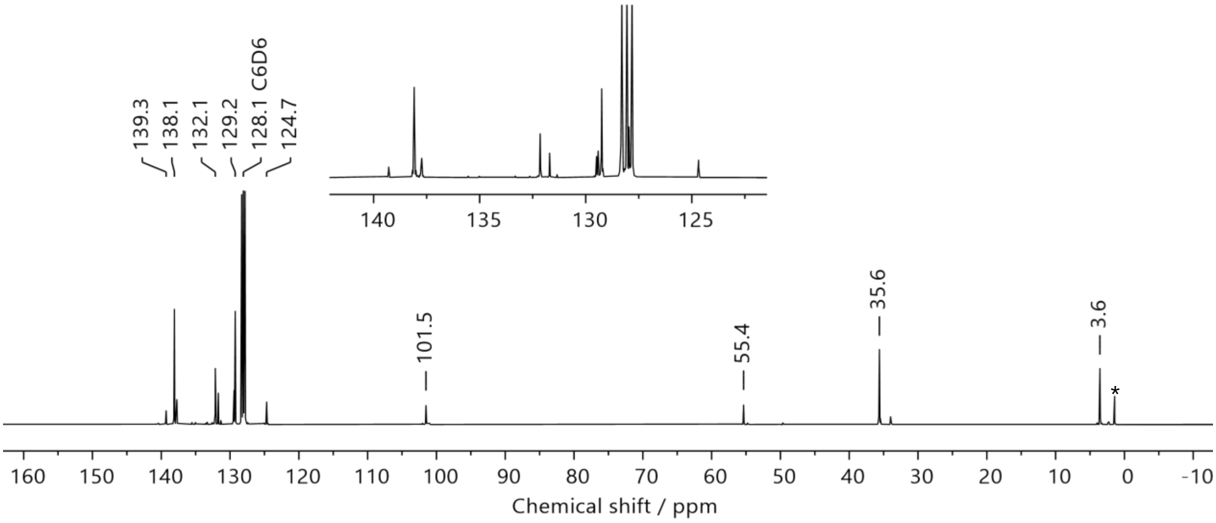


Figure S17: $^{13}C\{^1H\}$ NMR spectrum of the reaction of **1a** with Ph_2Se_2 (100.61 MHz, C_6D_6, 298 K) (* silicon grease).

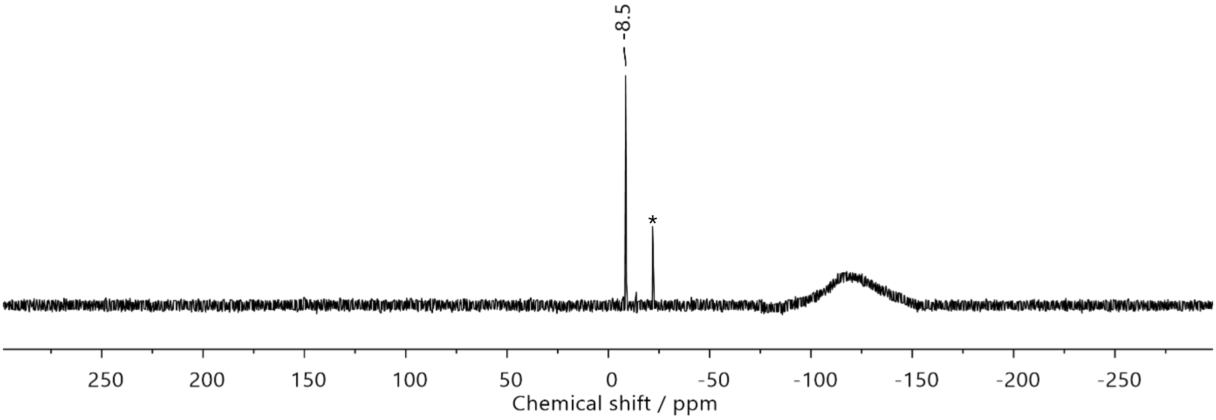


Figure S18: $^{29}Si\{^1H\}$ NMR spectrum of the reaction of **1a** with Ph_2Se_2 (79.49 MHz, C_6D_6, 298 K) (* silicon grease).

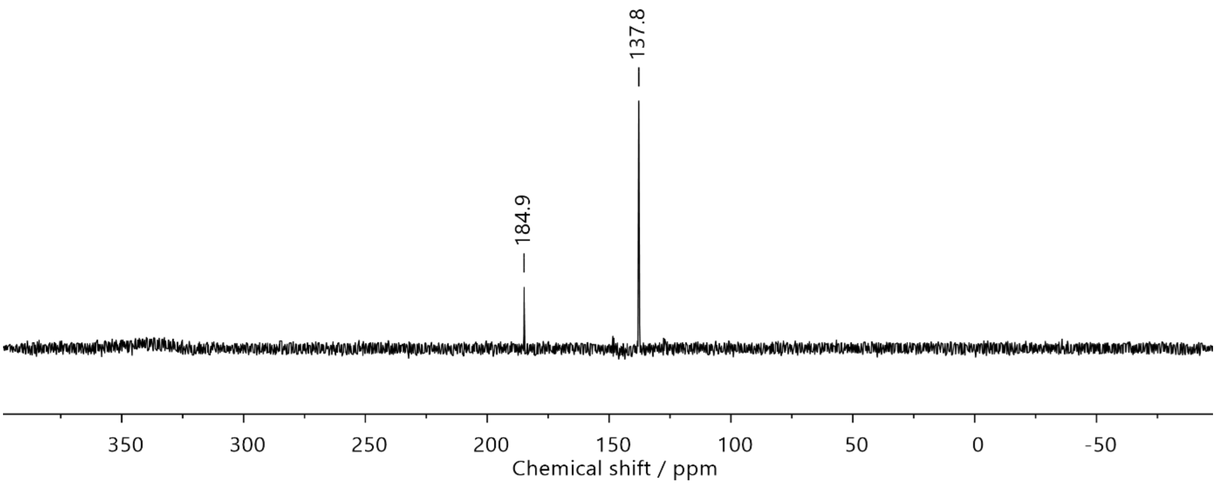


Figure S19: $^{77}Se\{^1H\}$ NMR spectrum of the reaction of **1a** with Ph_2Se_2 (76.32 MHz, C_6D_6, 298 K).

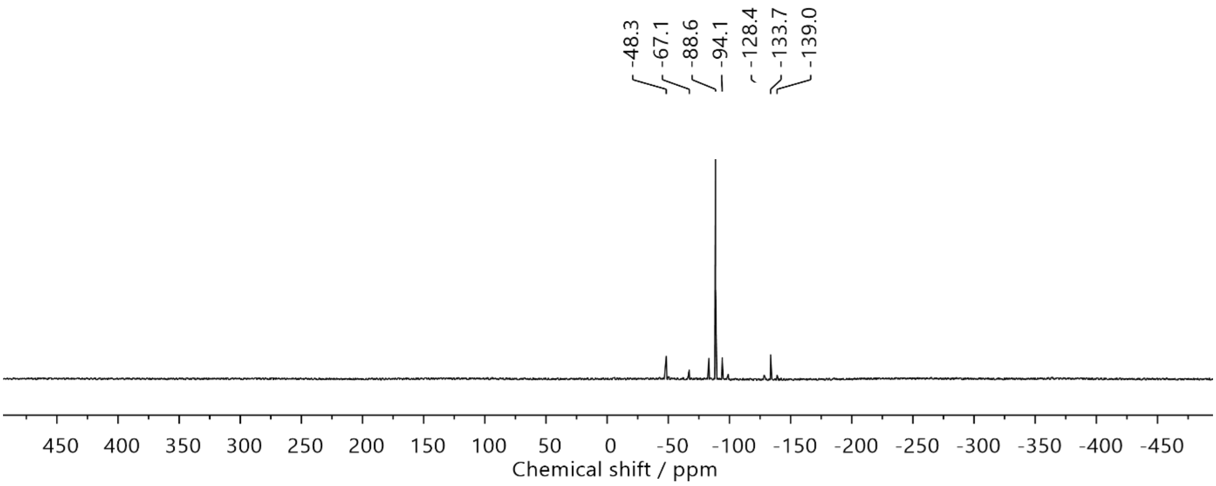


Figure S20: $^{119}Sn\{^1H\}$ NMR spectrum of the reaction of **1a** with Ph_2Se_2 (149.21 MHz, C_6D_6, 298 K).

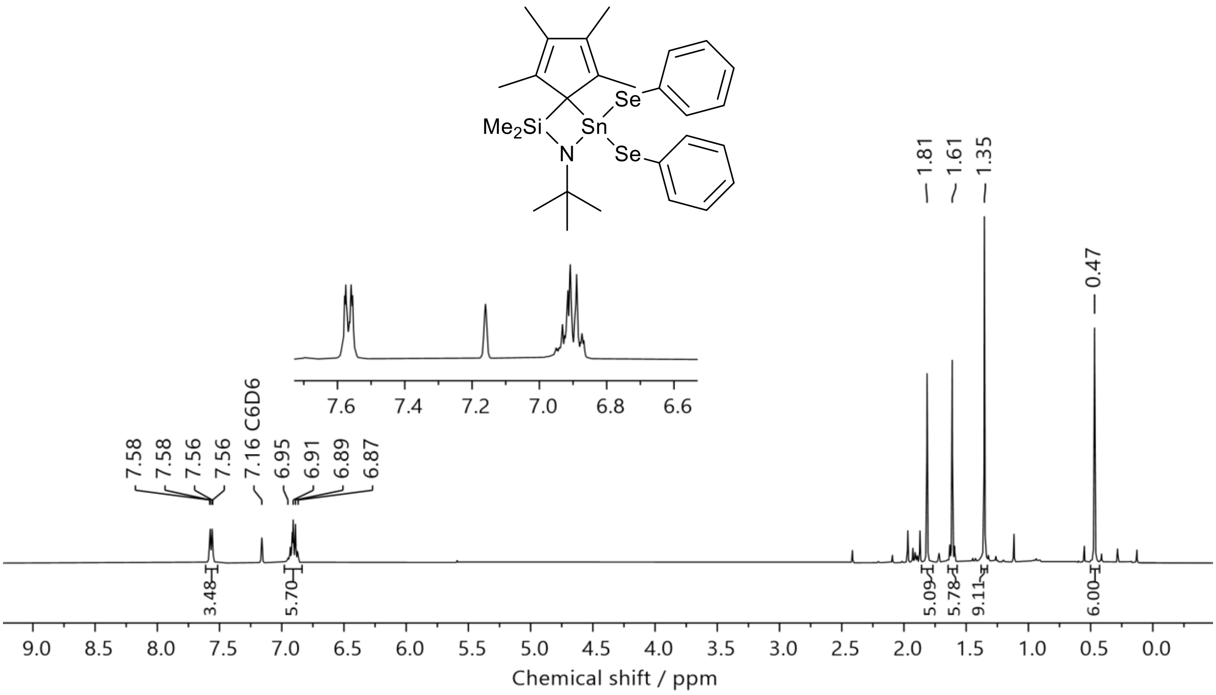


Figure S21: ^1H NMR spectrum of **2b** (400.13 MHz, C_6D_6, 298 K).

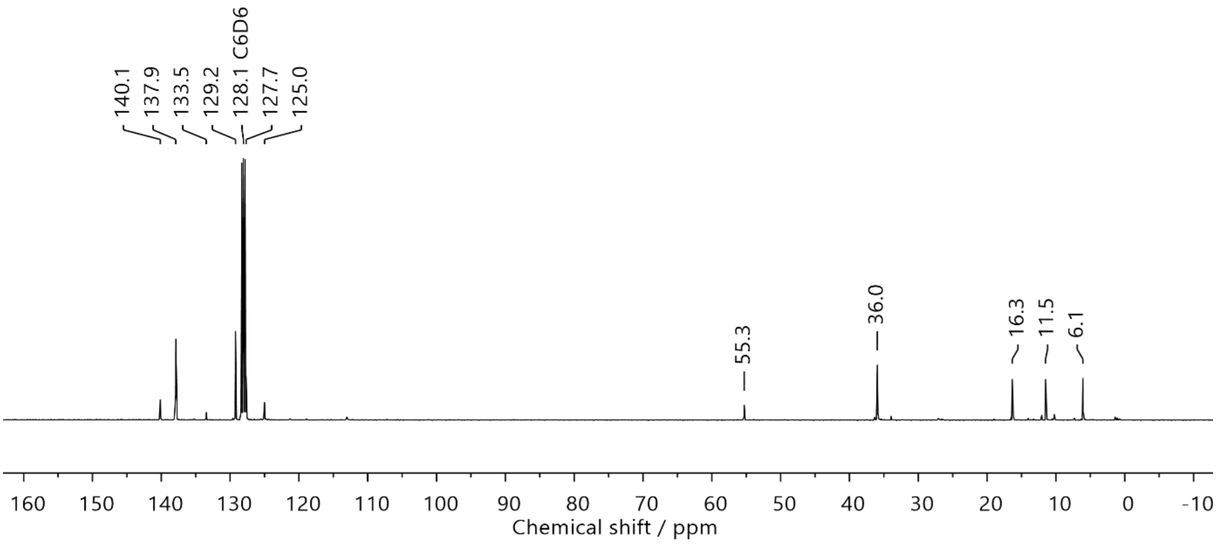


Figure S22: $^{13}C\{^1H\}$ NMR spectrum of **2b** (100.61 MHz, C_6D_6, 298 K).

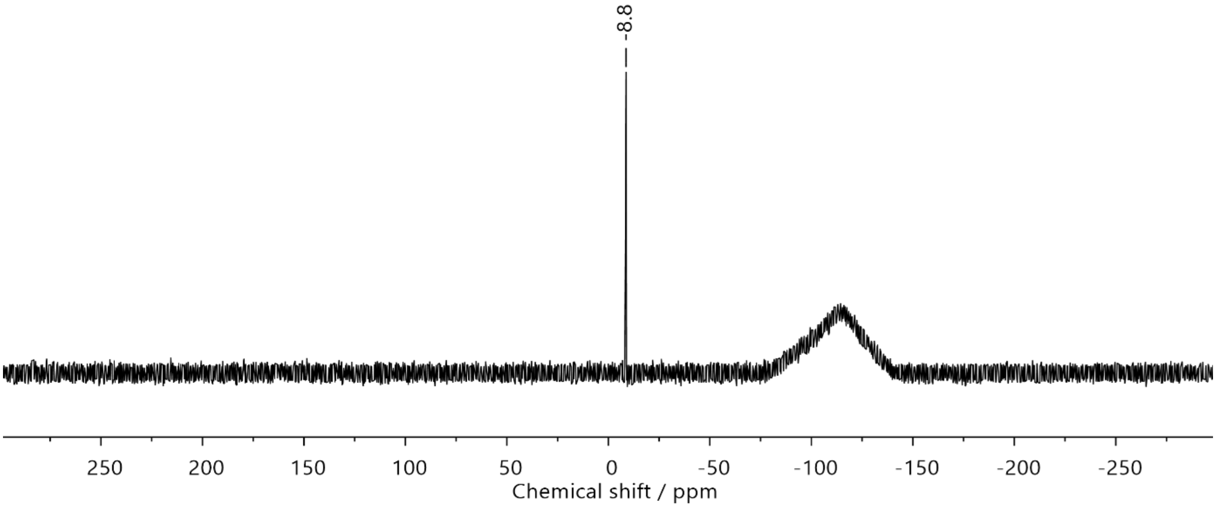


Figure S23: $^{29}Si\{^1H\}$ NMR spectrum of **2b** (79.49 MHz, C_6D_6, 298 K).

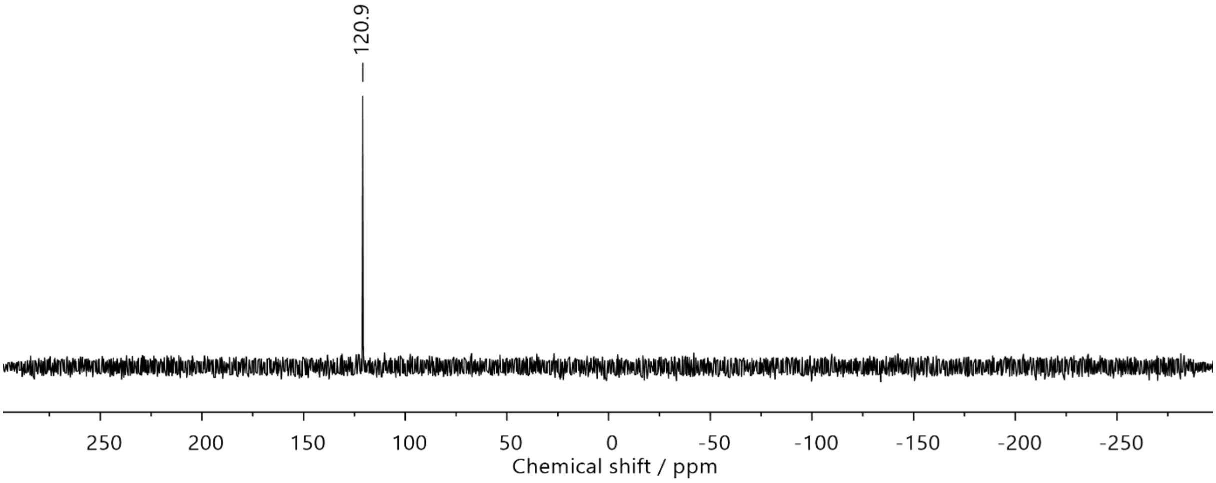


Figure S24: $^{77}Se\{^1H\}$ NMR spectrum of **2b** (76.32 MHz, C_6D_6, 298 K).

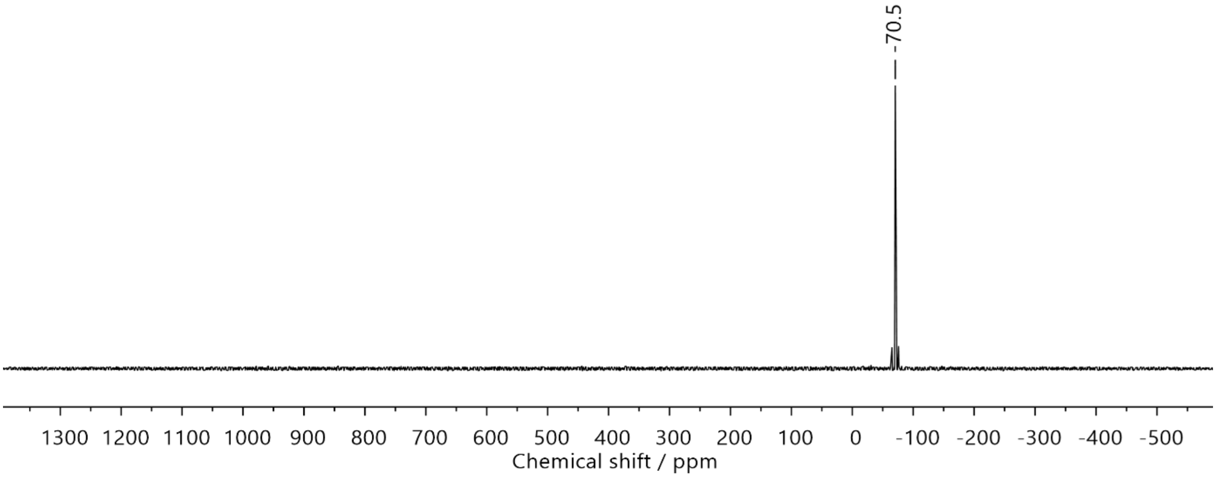


Figure S25: ^{119}Sn{^{1}H} NMR spectrum of **2b** (149.21 MHz, C_6D_6, 298 K).

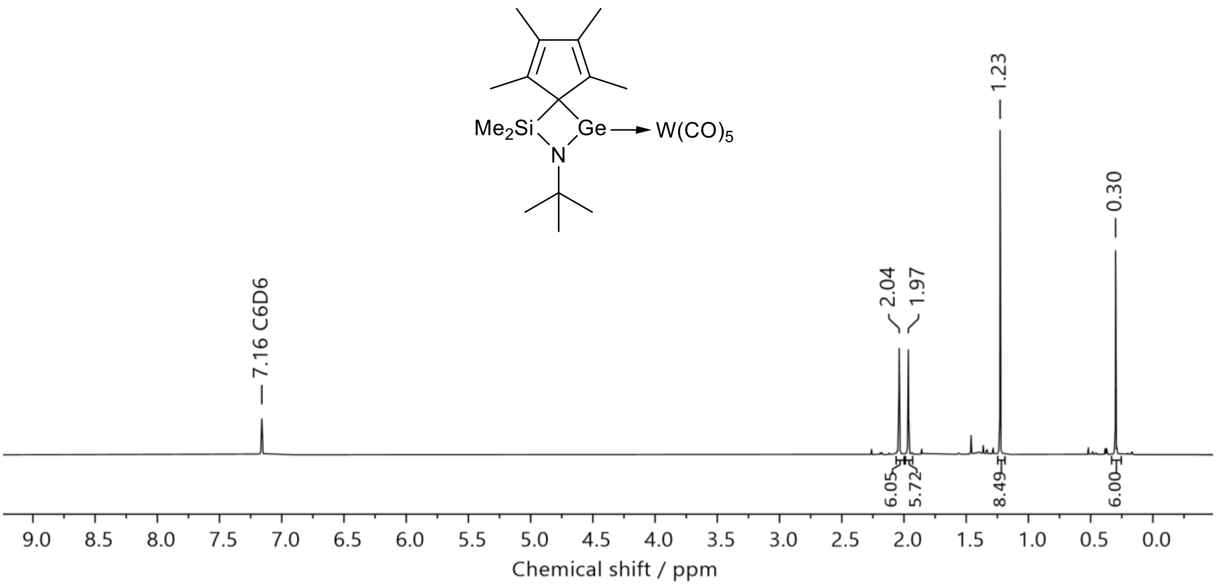


Figure S26: ^{1}H NMR spectrum of **3** (400.13 MHz, C_6D_6, 298 K).

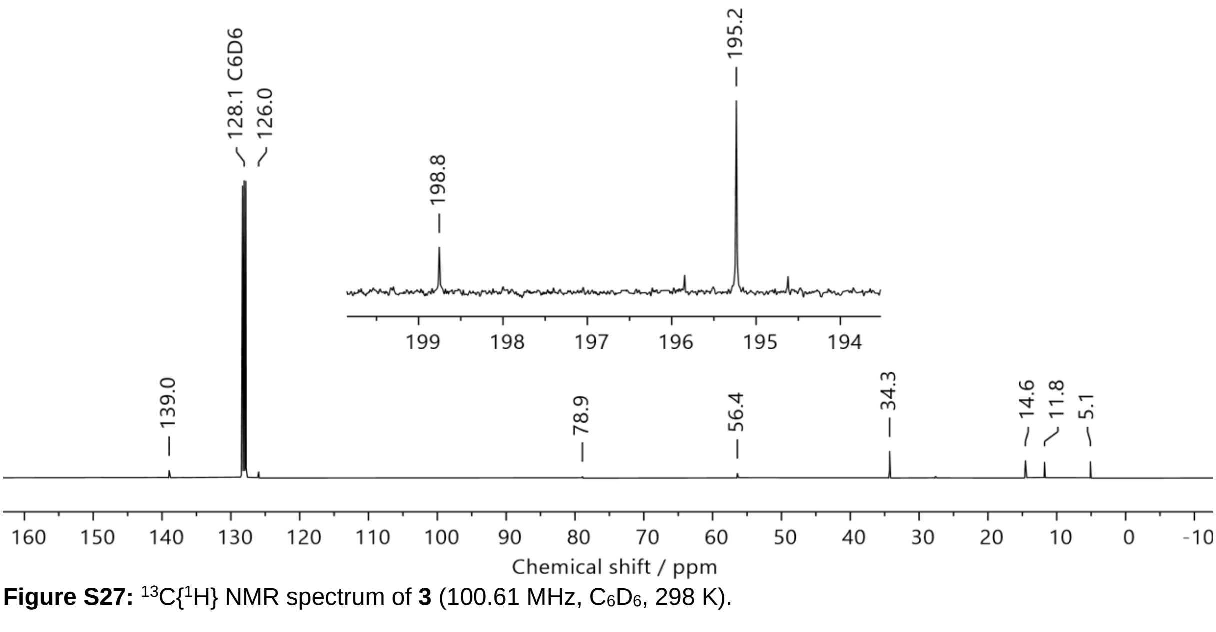


Figure S27: ^{13}C{^{1}H} NMR spectrum of **3** (100.61 MHz, C_6D_6, 298 K).

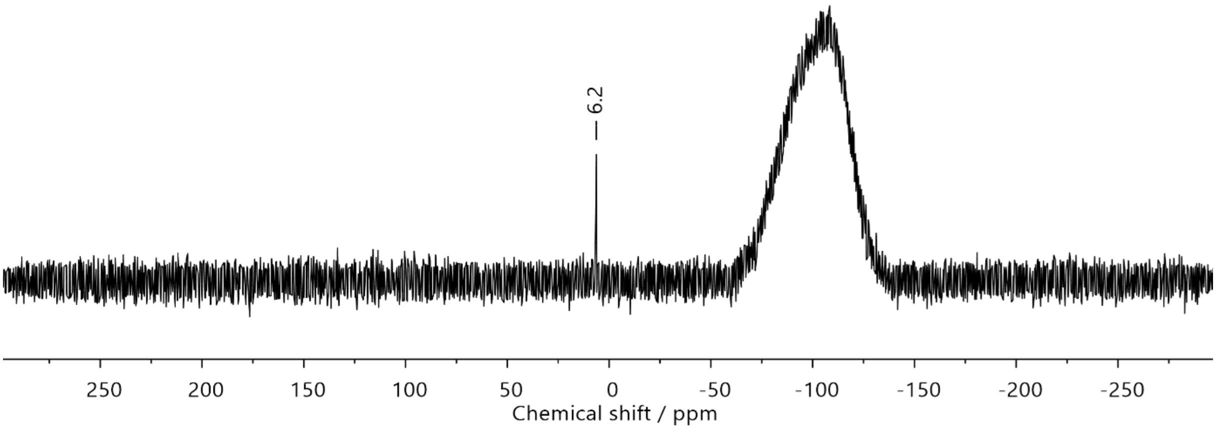


Figure S28: $^{29}Si\{^1H\}$ NMR spectrum of **3** (79.49 MHz, C_6D_6, 298 K).

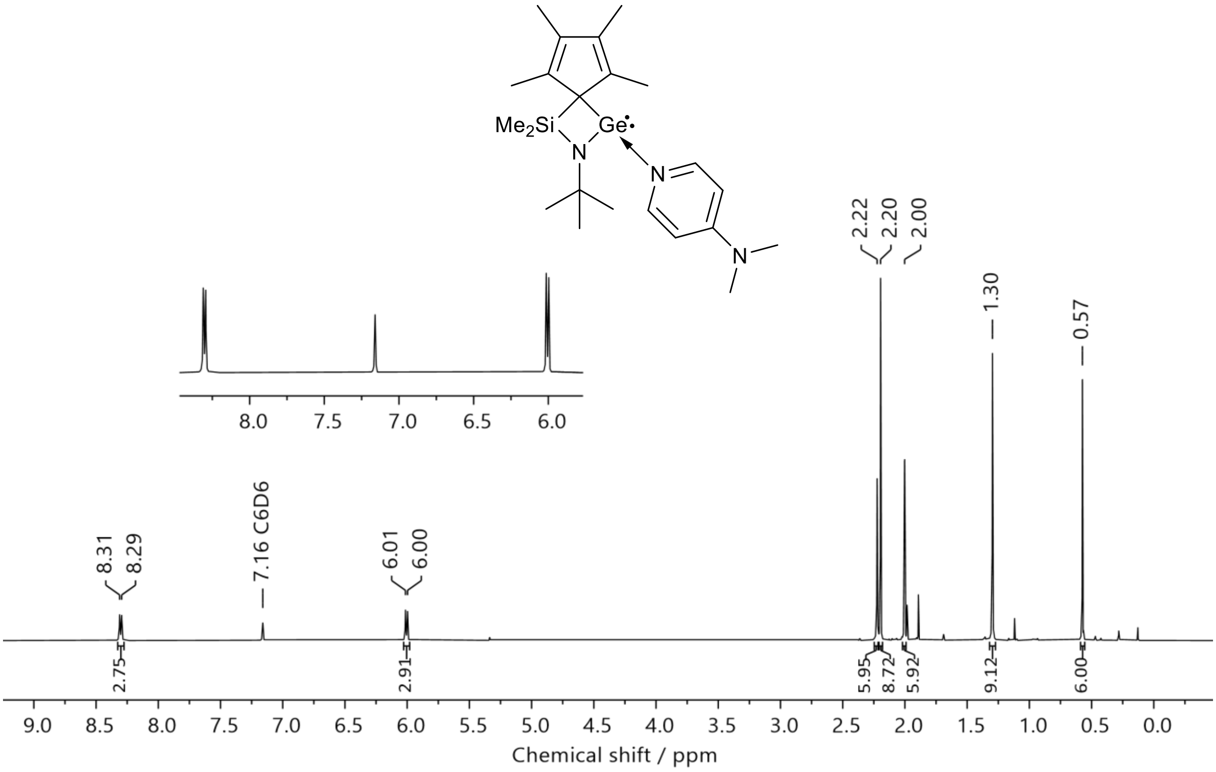


Figure S29: ^1H NMR spectrum of **4a** (400.13 MHz, C_6D_6, 298 K).

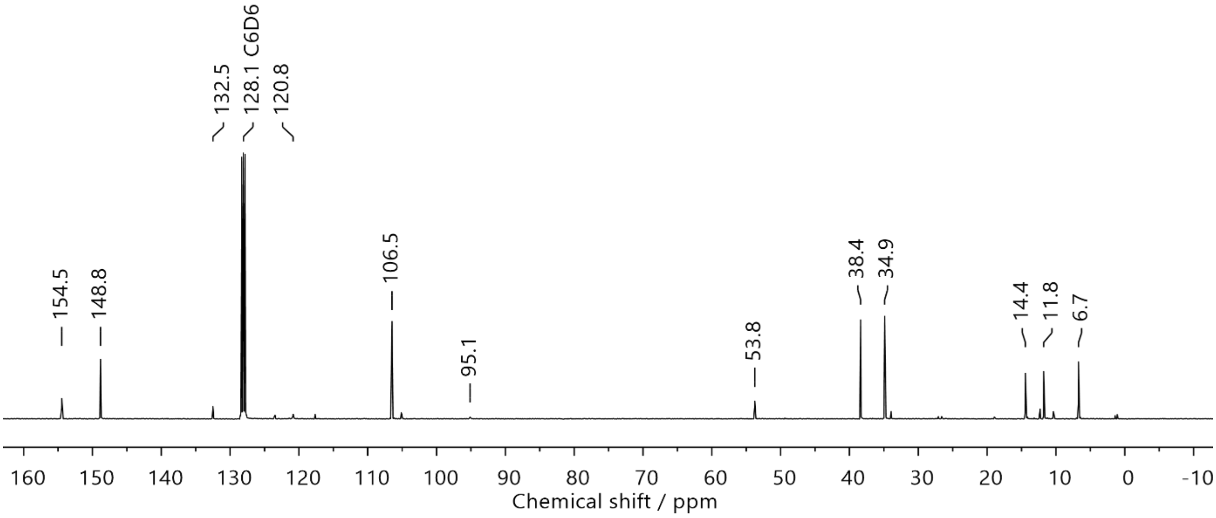


Figure S30: $^{13}C\{^1H\}$ NMR spectrum of **4a** (100.61 MHz, C_6D_6, 298 K).

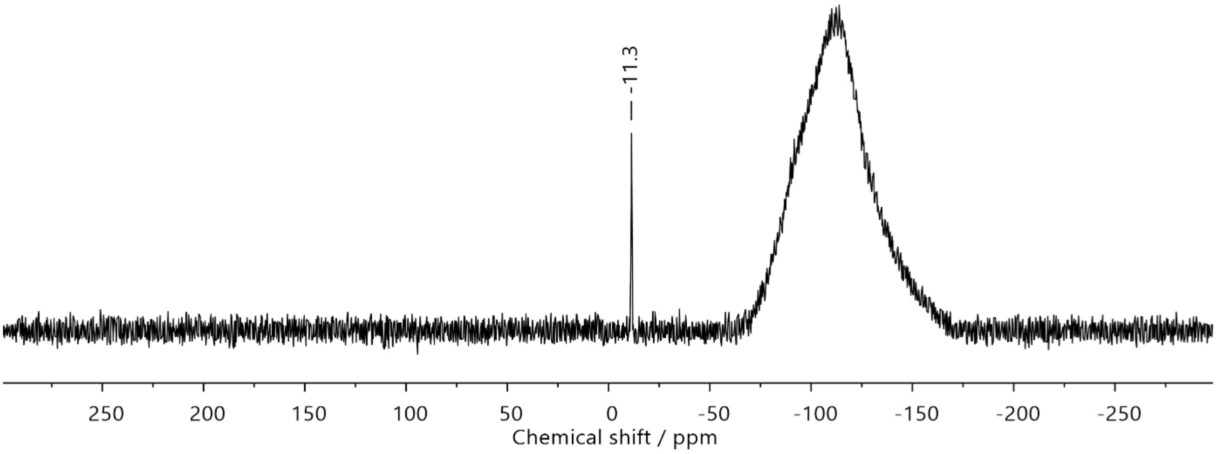


Figure S31: ^{29}Si{^{1}H} NMR spectrum of **4a** (79.49 MHz, C_6D_6, 298 K).

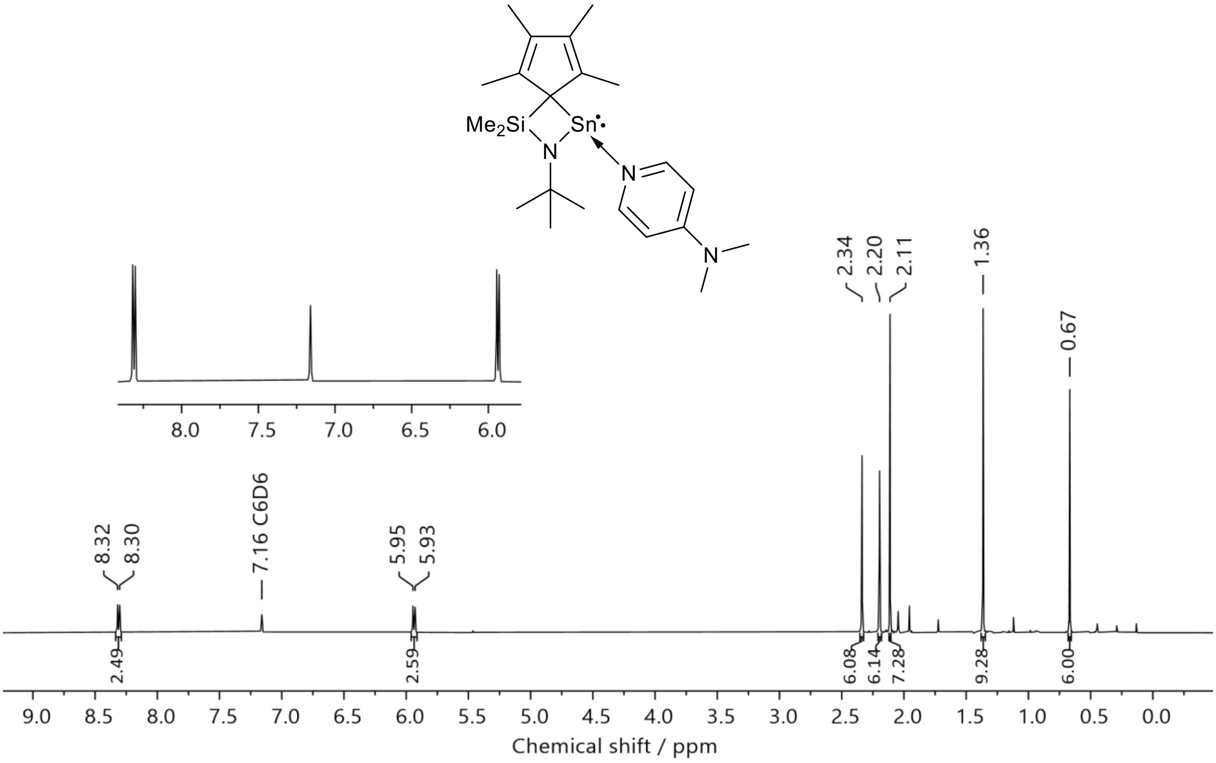


Figure S32: ^{1}H NMR spectrum of **4b** (400.13 MHz, C_6D_6, 298 K).

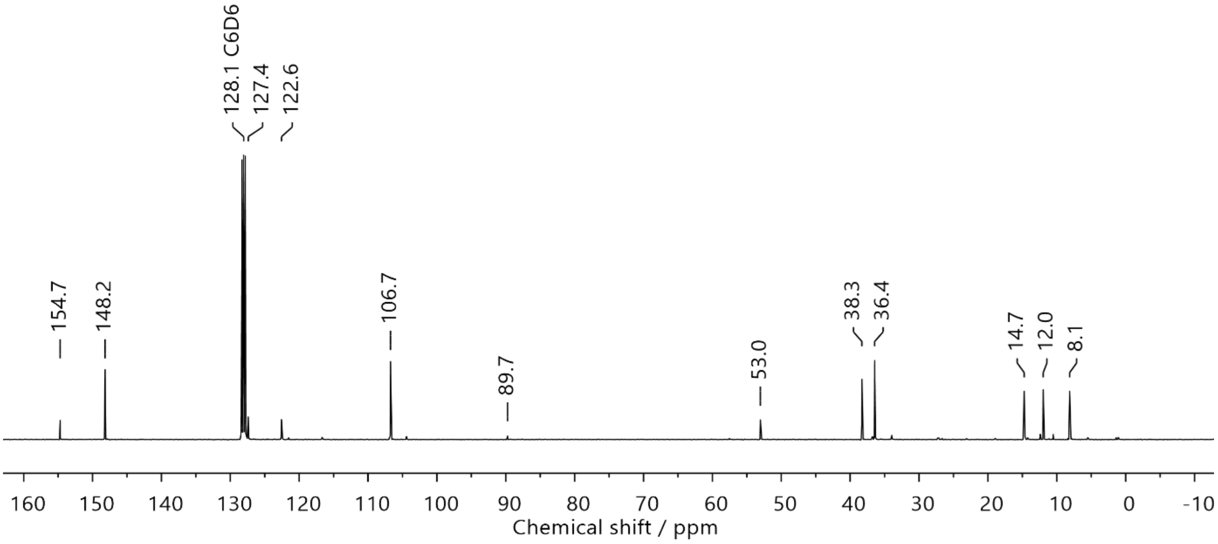


Figure S33: $^{13}C\{^1H\}$ NMR spectrum of **4b** (100.61 MHz, C_6D_6, 298 K).

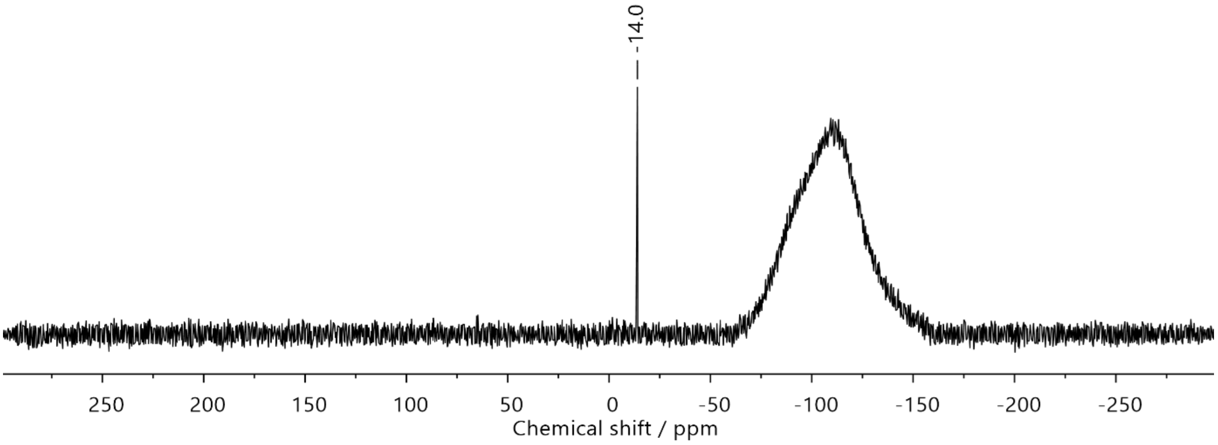


Figure S34: $^{29}Si\{^1H\}$ NMR spectrum of **4b** (79.49 MHz, C_6D_6, 298 K).

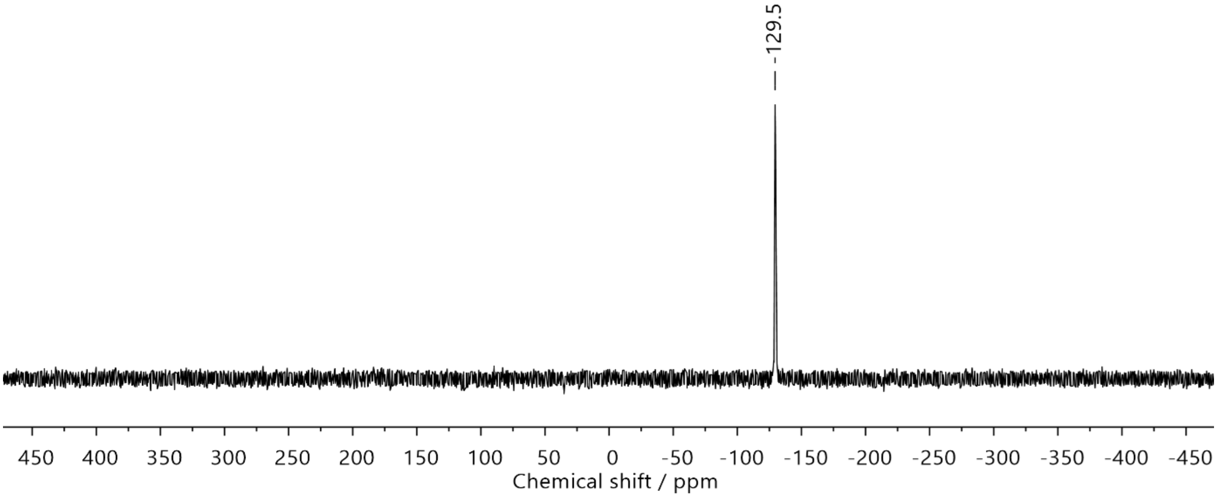


Figure S35: $^{119}Sn\{^1H\}$ NMR spectrum of **4b** (149.21 MHz, C_6D_6, 298 K).

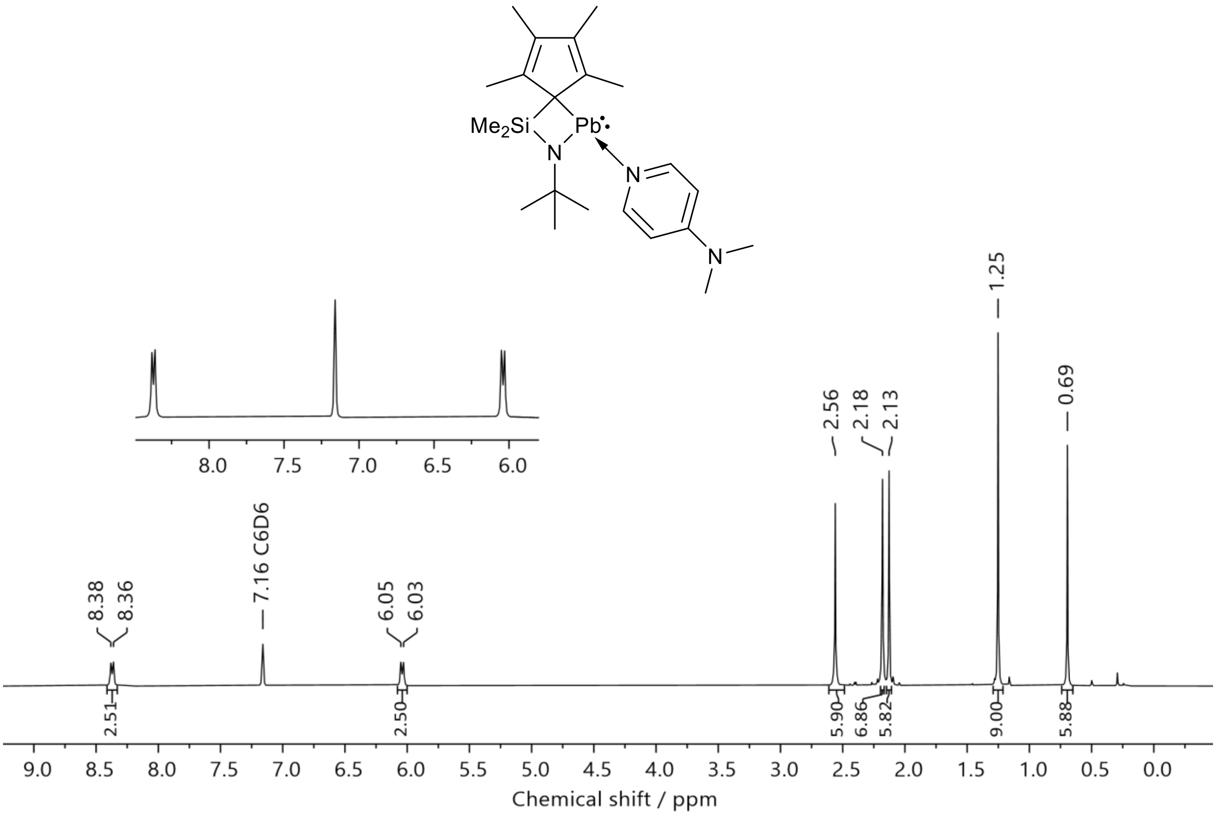


Figure 36: ^{1}H NMR spectrum of **4c** (400.13 MHz, C_6D_6, 298 K).

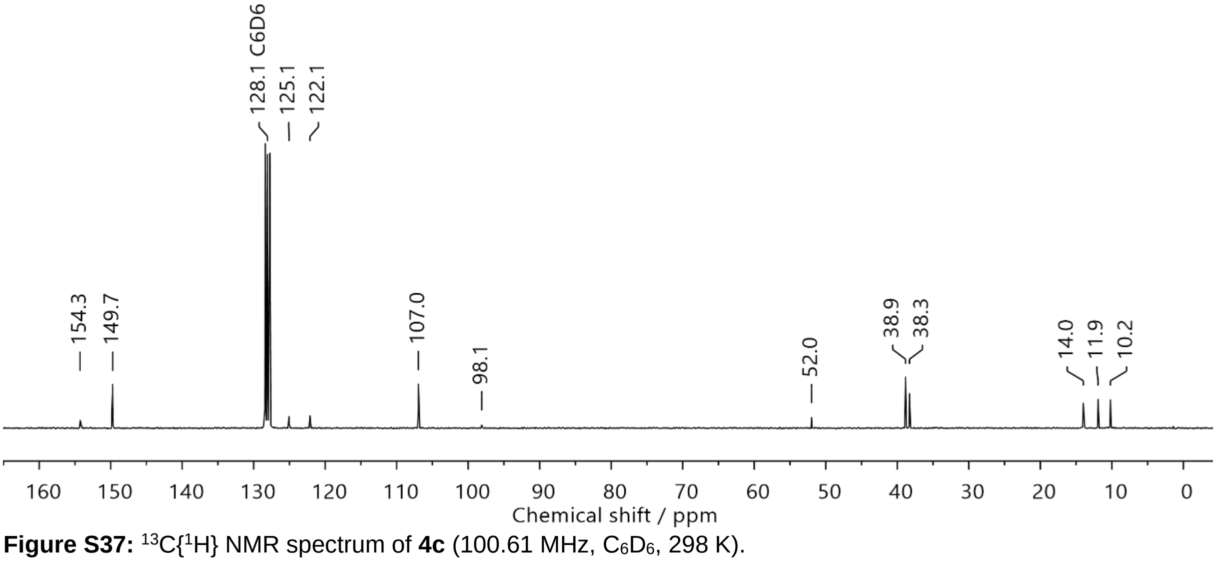


Figure S37: ^{13}C{^{1}H} NMR spectrum of **4c** (100.61 MHz, C_6D_6, 298 K).

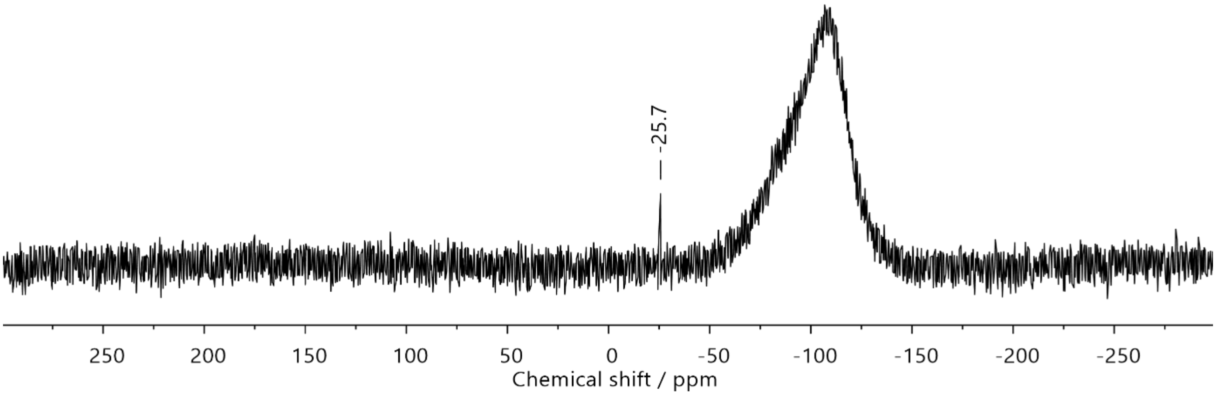


Figure S38: ^{29}Si{^{1}H} NMR spectrum of **4c** (79.49 MHz, C_6D_6, 298 K).

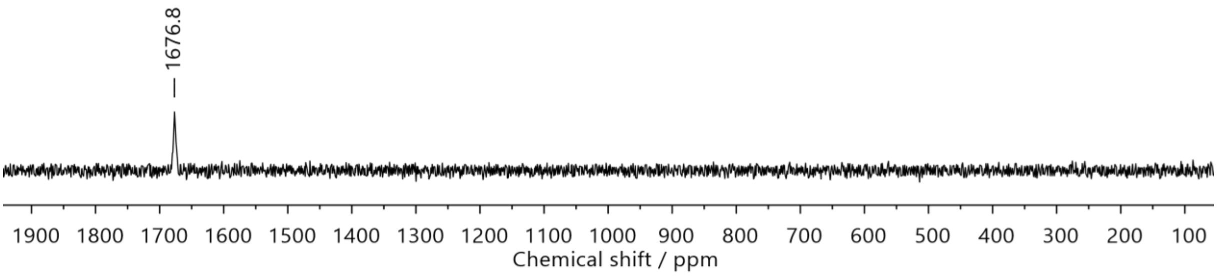


Figure S39: ^{207}Pb{^{1}H} NMR spectrum of **4c** (62.79 MHz, C_6D_6, 298 K).

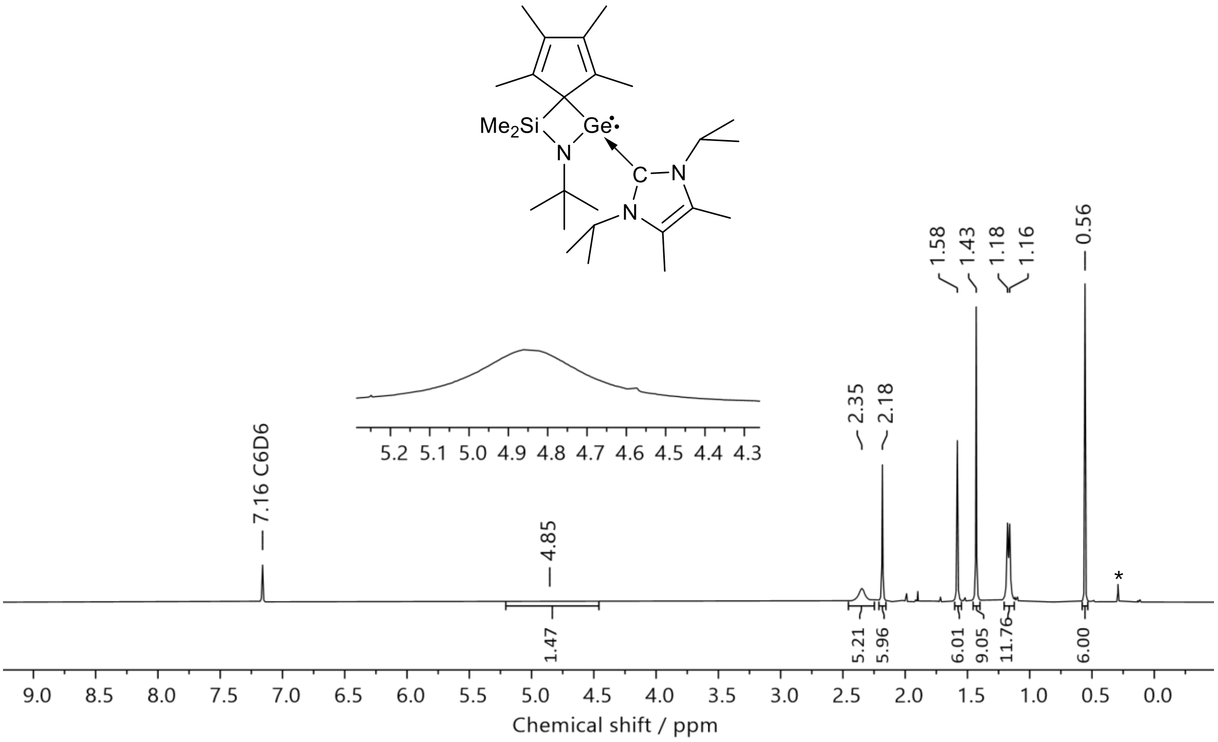


Figure S40: ^{1}H NMR spectrum of **5a** (400.13 MHz, C_6D_6, 298 K) (* silicon grease).

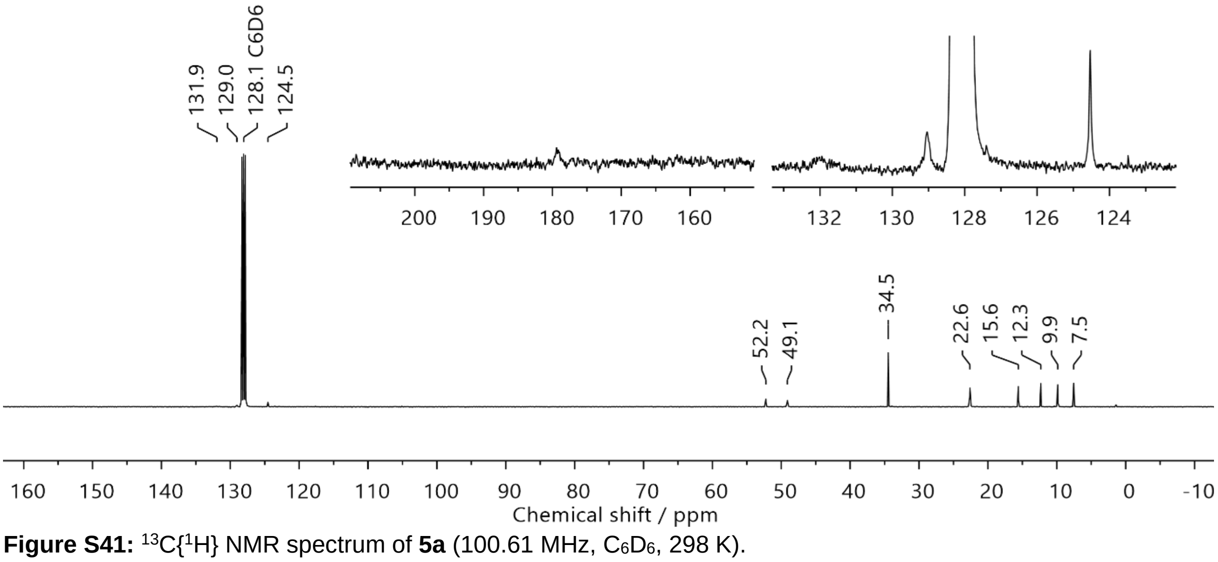


Figure S41: ^{13}C{^{1}H} NMR spectrum of **5a** (100.61 MHz, C_6D_6, 298 K).

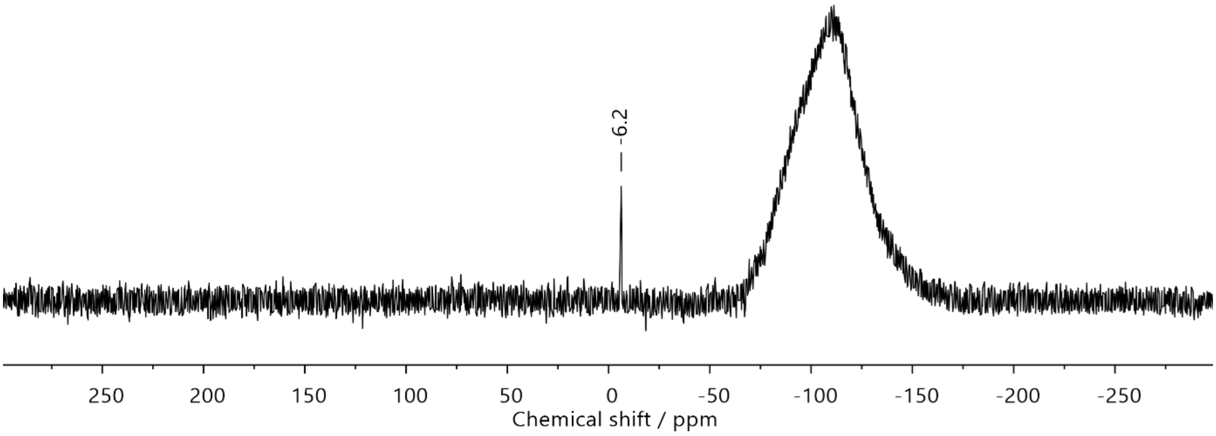


Figure S42: ^{29}Si{^{1}H} NMR spectrum of **5a** (79.49 MHz, C_6D_6, 298 K).

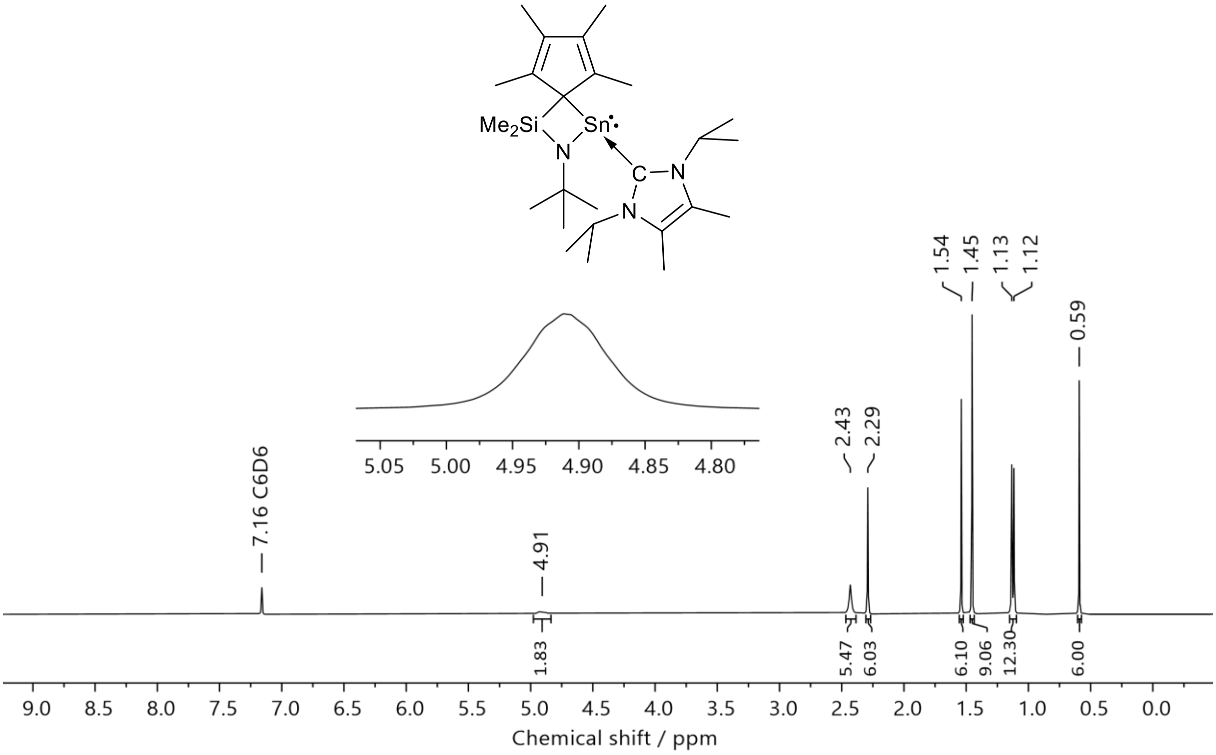


Figure S43: ^{1}H NMR spectrum of **5b** (400.13 MHz, C_6D_6, 298 K).

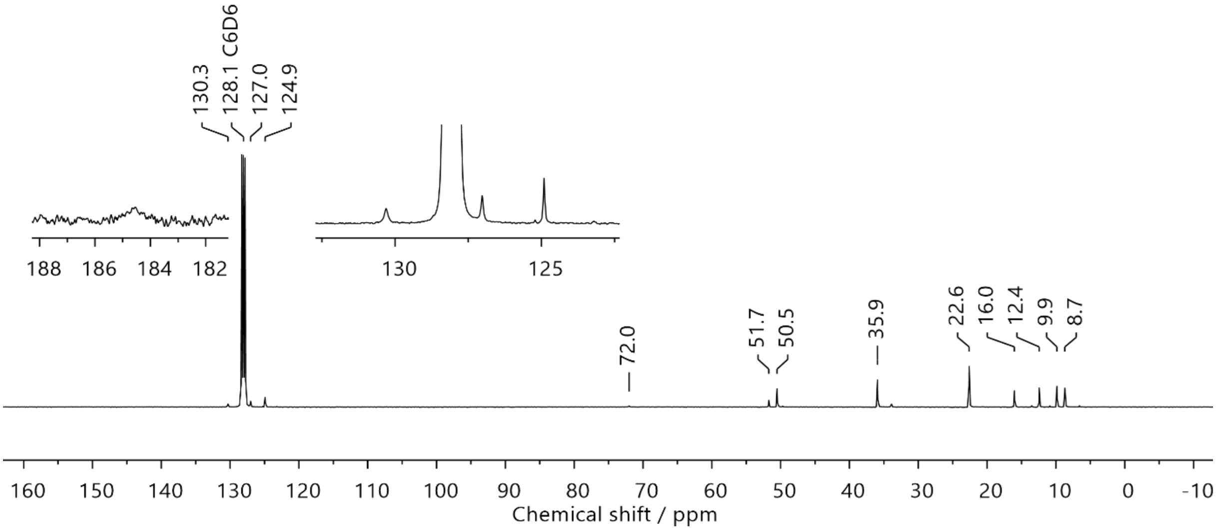


Figure S44: ^{13}C{^{1}H} NMR spectrum of **5b** (100.61 MHz, C_6D_6, 298 K).

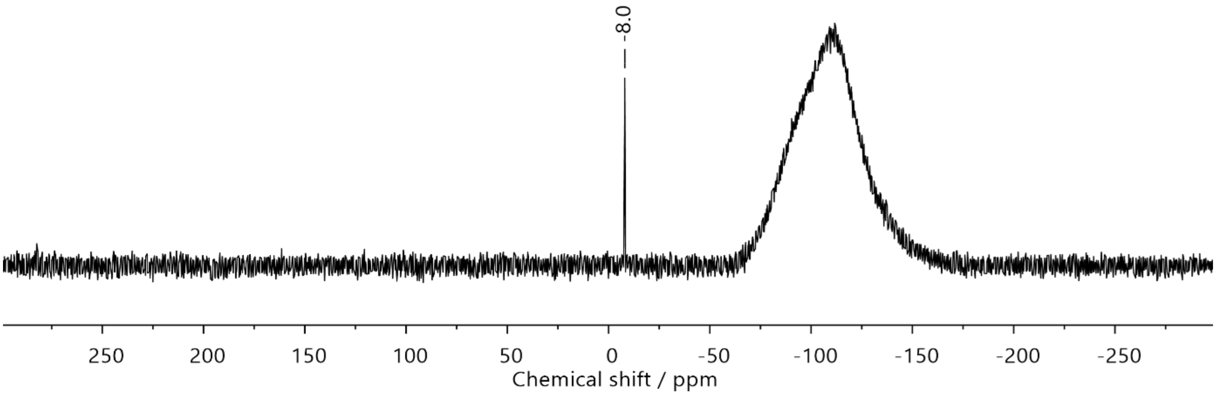


Figure S45: ^{29}Si{^{1}H} NMR spectrum of **5b** (79.49 MHz, C_6D_6, 298 K).

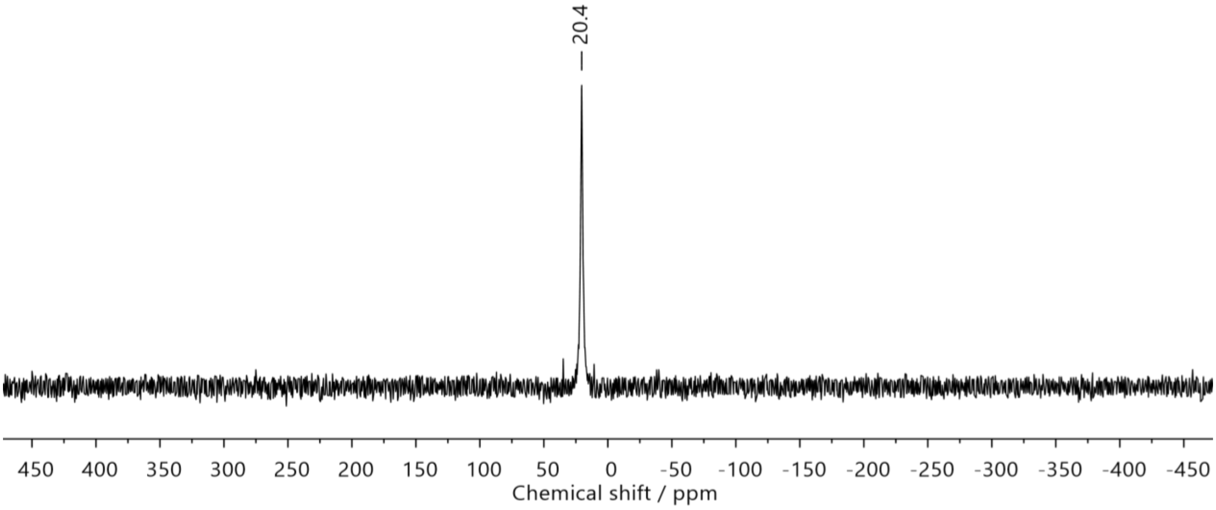


Figure S46: ^{119}Sn{^{1}H} NMR spectrum of **5b** (149.21 MHz, C_6D_6, 298 K).

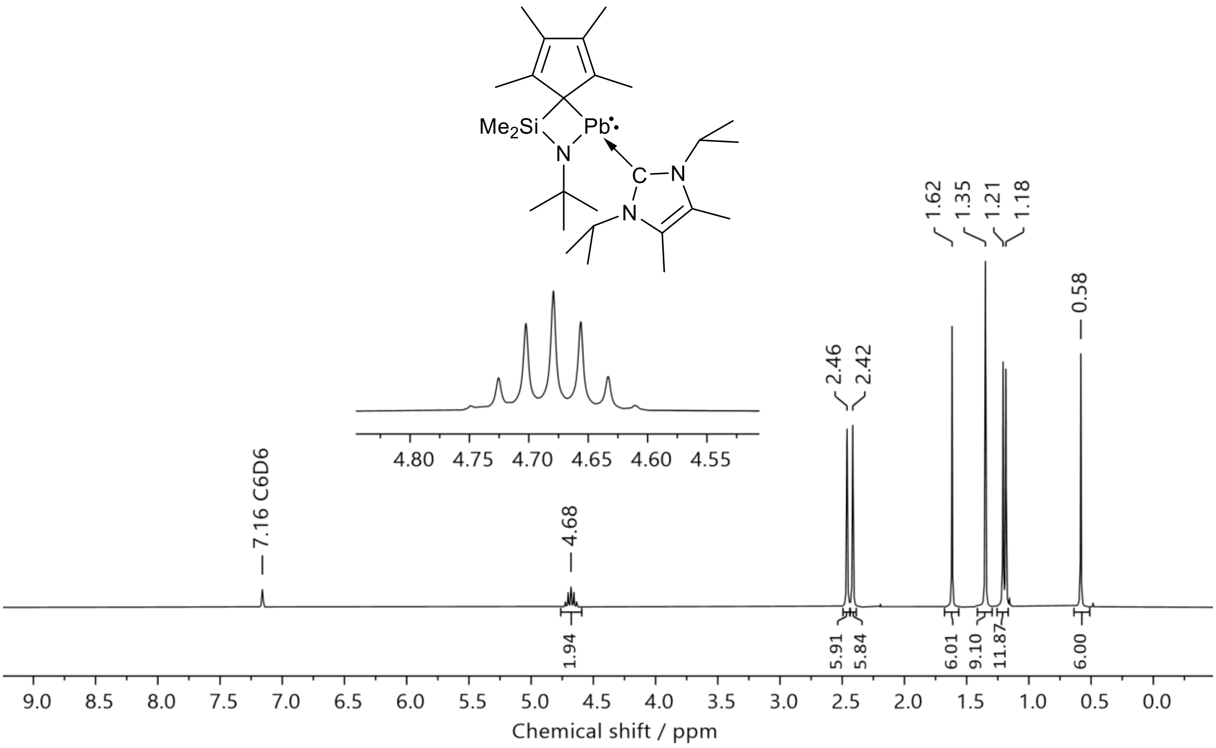


Figure S47: ^{1}H NMR spectrum of **5c** (300.13 MHz, C_6D_6, 298 K).

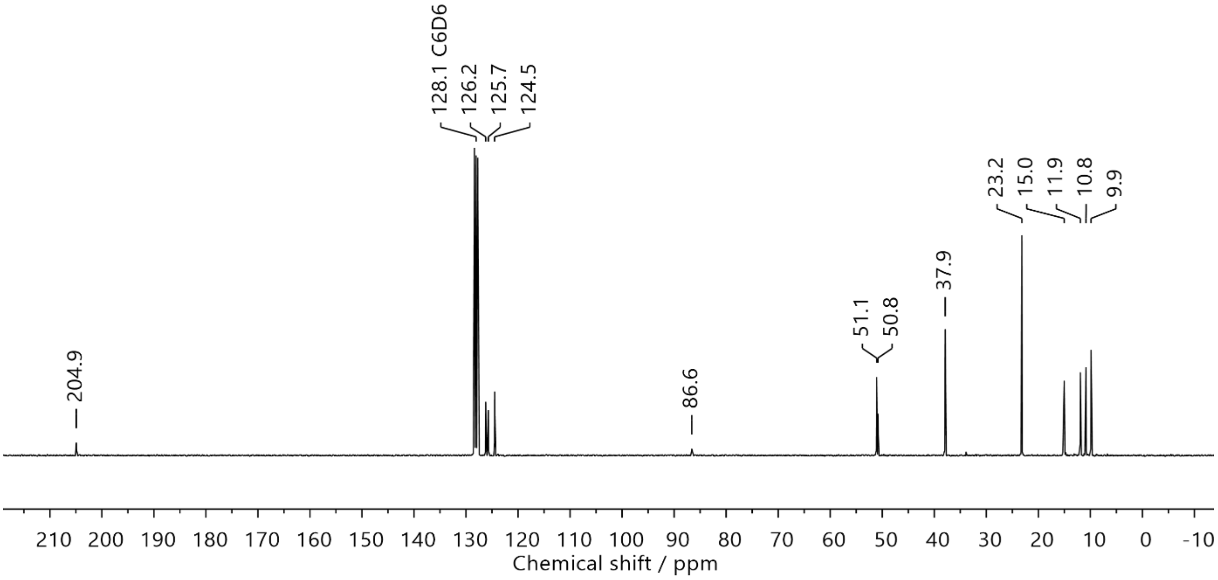


Figure S48: $^{13}C\{^1H\}$ NMR spectrum of **5c** (75.48 MHz, C_6D_6, 298 K).

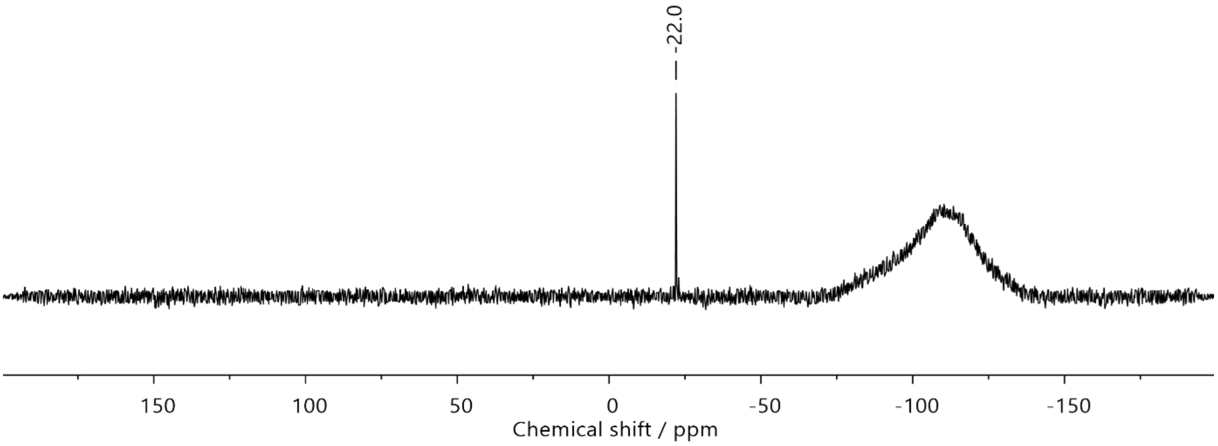


Figure S49: $^{29}Si\{^1H\}$ NMR spectrum of **5c** (59.63 MHz, C_6D_6, 298 K).

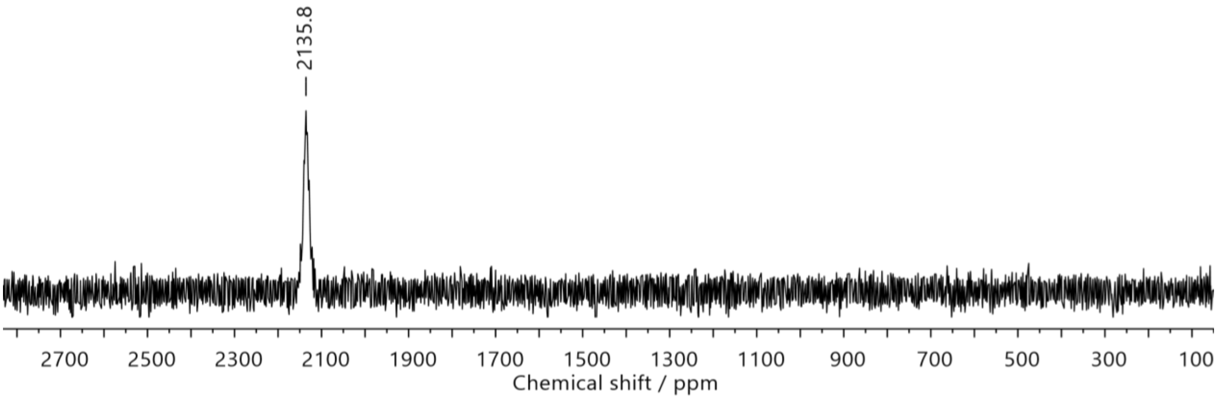


Figure S50: $^{207}Pb\{^1H\}$ NMR spectrum of **5c** (62.91 MHz, C_6D_6, 298 K).

XRD Data

Crystal structure data has been deposited with the Cambridge Crystallographic Data Centre (CCDC) and is available free of charge from the Cambridge Structural Database (see reference numbers).

1a:

CCDC reference number	2174665	
Empirical formula	$C_{11}H_{19}NSiSn$	
Formula weight	312.05	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 12.4653(5) Å	α= 90°
	b = 9.4098(4) Å	β= 106.4120(10)°
	c = 11.5289(5) Å	γ = 90°
Volume	1297.19(9) $Å^3$	
Z	4	
Density (calculated)	1.598 mg m^{-3}	
Absorption coefficient	2.028 mm^{-1}	
F(000)	624	
Crystal size	0.220 x 0.161 x 0.080 mm^3	
Theta range for data collection	2.755 to 27.888°	
Index ranges	-16<=h<=16, -11<=k<=12, -15<=l<=15	
Reflections collected	18869	
Independent reflections	3099 [R(int) = 0.0406]	
Completeness to theta = 25.242°	99.9%	
Absorption correction	semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6690	
Refinement method	full-matrix least-squares on F^2	
Data / restraints / parameters	3099 / 0 / 132	
Goodness-of-fit on F^2	1.063	
Final R indices [I>2sigma(I)]	R1 = 0.0170, wR2 = 0.0425	
R indices (all data)	R1 = 0.0182, wR2 = 0.0433	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.386 and -0.406 e.$Å^{-3}$	

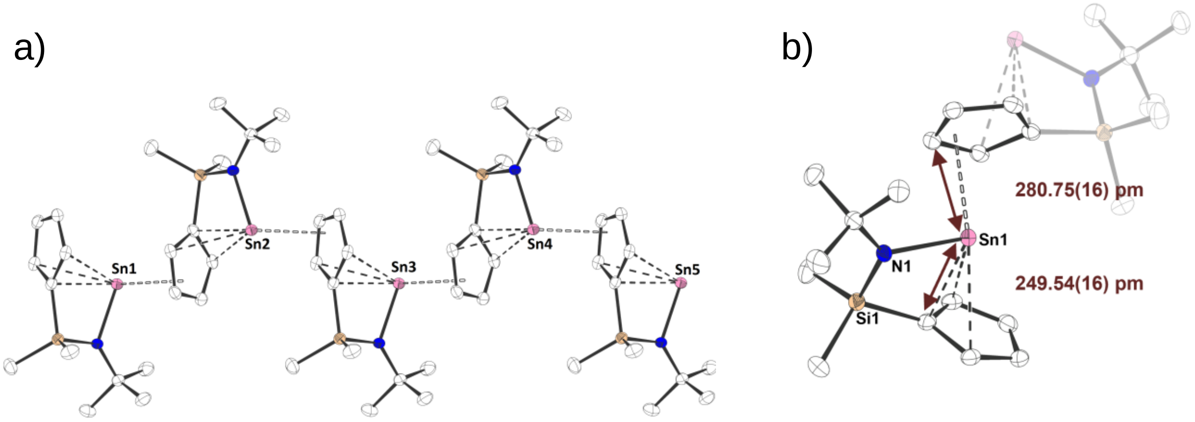


Figure S51: Molecular structure of **1a** in the crystal, highlighting the intermolecular interactions (displacement ellipsoids at 50 % probability level, hydrogen atoms omitted for clarity).

1d:

CCDC reference number	2174664	
Empirical formula	$C_{15}H_{27}NPbSi$	
Formula weight	456.65	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P\,2_1/c$	
Unit cell dimensions	a = 10.7347(2) Å	α= 90°
	b = 18.9400(4) Å	β= 104.5410(10)°
	c = 17.5783(4) Å	γ = 90°
Volume	3459.46(13) $Å^3$	
Z	8	
Density (calculated)	1.754 mg m^{-3}	
Absorption coefficient	9.809 mm^{-1}	
F(000)	1760	
Crystal size	0.149 x 0.135 x 0.100 mm^3	
Theta range for data collection	2.151 to 27.890°	
Index ranges	-13<=h<=14, -24<=k<=24, -23<=l<=22	
Reflections collected	57554	
Independent reflections	8246 [R(int) = 0.0350]	
Completeness to theta = 25.242°	100.0%	
Absorption correction	semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5699	
Refinement method	full-matrix least-squares on F^2	
Data / restraints / parameters	8246 / 0 / 344	
Goodness-of-fit on F^2	1.026	
Final R indices [I>2sigma(I)]	R1 = 0.0169, wR2 = 0.0336	
R indices (all data)	R1 = 0.0218, wR2 = 0.0349	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.628 and -0.584 e.$Å^{-3}$	

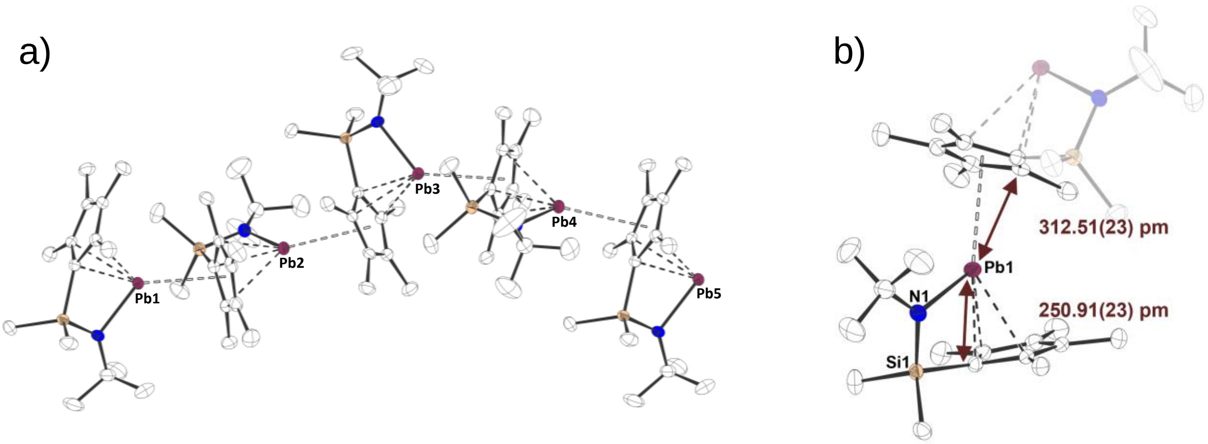
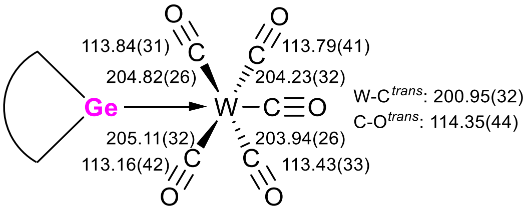


Figure S52: Molecular structure of **1d** in the crystal, highlighting the intermolecular interactions (displacement ellipsoids at 50 % probability level, hydrogen atoms omitted for clarity).

3:

CCDC reference number	2174675	
Empirical formula	$C_{20}H_{27}GeNO_5SiW$	
Formula weight	645.95	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 9.1997(4) Å	α= 90°
	b = 26.2141(10) Å	β= 100.750(2)°
	c = 10.2037(4) Å	γ= 90°
Volume	2417.56(17) $Å^3$	
Z	4	
Density (calculated)	1.775 mg m^{-3}	
Absorption coefficient	6.075 mm^{-1}	
F(000)	1256	
Crystal size	0.200 x 0.180 x 0.030 mm^3	
Theta range for data collection	2.175 to 27.902°	
Index ranges	-10<=h<=12, -34<=k<=34, -13<=l<=13	
Reflections collected	32787	
Independent reflections	5770 [R(int) = 0.0382]	
Completeness to theta = 25.242°	99.9%	
Absorption correction	semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5176	
Refinement method	full-matrix least-squares on F^2	
Data / restraints / parameters	5770 / 0 / 271	
Goodness-of-fit on F^2	1.078	
Final R indices [I>2sigma(I)]	R1 = 0.0220, wR2 = 0.0426	
R indices (all data)	R1 = 0.0299, wR2 = 0.0453	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.557 and -0.991 e.$Å^{-3}$	



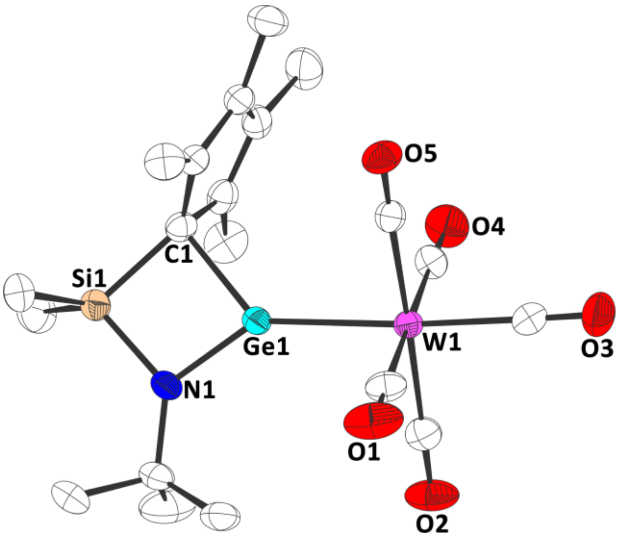


Figure S53: Top: Illustration of bond lengths of **3**; bottom: Molecular structure of **3** in the crystal (displacement ellipsoids at 50 % probability level, hydrogen atoms omitted for clarity).

5a:

CCDC reference number	2174673	
Empirical formula	$C_{26}H_{47}GeN_3Si$	
Formula weight	502.34	
Temperature	132(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 10.5226(3) Å	α= 90°
	b = 16.5510(5) Å	β= 104.6320(10)°
	c = 16.5994(7) Å	γ = 90°
Volume	2797.19(17) $Å^3$	
Z	4	
Density (calculated)	1.193 mg m^{-3}	
Absorption coefficient	1.155 mm^{-1}	
F(000)	1080	
Crystal size	0.349 x 0.340 x 0.276 mm^3	
Theta range for data collection	1.767 to 31.583°	
Index ranges	-15<=h<=15, -24<=k<=24, -24<=l<=24	
Reflections collected	57712	
Independent reflections	9376 [R(int) = 0.0328]	
Completeness to theta = 25.242°	100.0%	
Absorption correction	semi-empirical from equivalents	
Max. and min. transmission	0.7462 and 0.7061	
Refinement method	full-matrix least-squares on F^2	
Data / restraints / parameters	9376 / 133 / 335	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0317, wR2 = 0.0765	
R indices (all data)	R1 = 0.0426, wR2 = 0.0816	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.674 and -0.533 e.$Å^{-3}$	

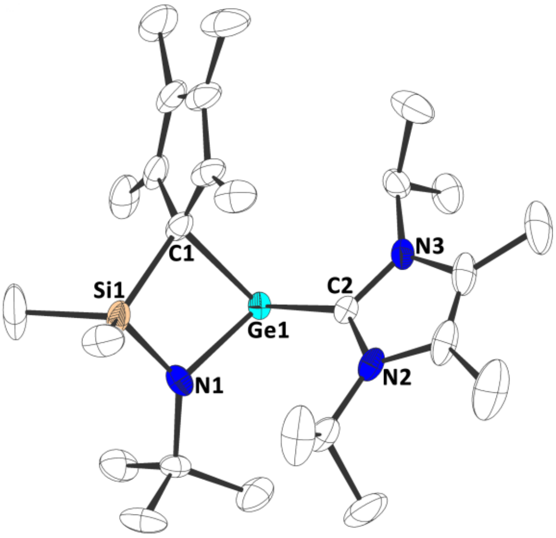


Figure S54: Molecular structure of **5a** in the crystal (displacement ellipsoids at 50 % probability level, hydrogen atoms omitted for clarity).

5b:

CCDC reference number	2174672	
Empirical formula	$C_{26}H_{47}N_3SiSn$	
Formula weight	548.44	
Temperature	132(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 9.0621(2) Å	α= 90°
	b = 15.2311(3) Å	β= 99.6810(10)°
	c = 10.2462(2) Å	γ = 90°
Volume	1394.10(5) $Å^3$	
Z	2	
Density (calculated)	1.307 mg m^{-3}	
Absorption coefficient	0.977 mm^{-1}	
F(000)	576	
Crystal size	0.316 x 0.224 x 0.114 mm^3	
Theta range for data collection	2.016 to 29.633°	
Index ranges	-12<=h<=12, -21<=k<=20, -14<=l<=14	
Reflections collected	22591	
Independent reflections	7838 [R(int) = 0.0294]	
Completeness to theta = 25.242°	100.0%	
Absorption correction	semi-empirical from equivalents	
Max. and min. transmission	0.7459 and 0.6976	
Refinement method	full-matrix least-squares on F^2	
Data / restraints / parameters	7838 / 1 / 295	
Goodness-of-fit on F^2	1.014	
Final R indices [I>2sigma(I)]	R1 = 0.0226, wR2 = 0.0437	
R indices (all data)	R1 = 0.0266, wR2 = 0.0454	
Absolute structure parameter	-0.001(8)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.331 and -0.263 e.$Å^{-3}$	

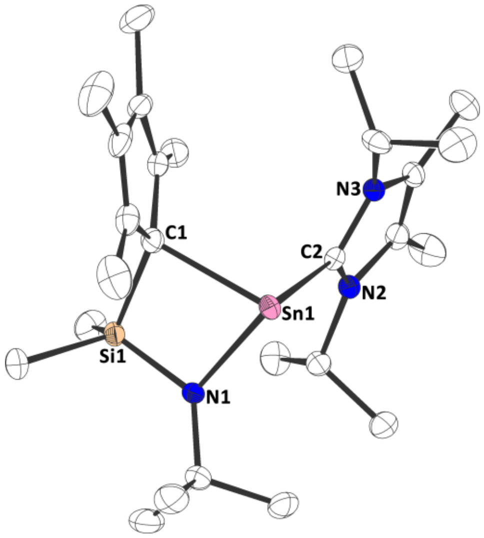


Figure S55: Molecular structure of **5b** in the crystal (displacement ellipsoids at 50 % probability level, hydrogen atoms omitted for clarity).

5c:

CCDC reference number	2174674	
Empirical formula	$C_{26}H_{47}N_3PbSi$	
Formula weight	636.94	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 9.0843(2) Å	α= 90°
	b = 15.3056(4) Å	β= 98.3690(10)°
	c = 10.2605(3) Å	γ = 90°
Volume	1411.43(6) Å^3	
Z	2	
Density (calculated)	1.499 mg m^{-3}	
Absorption coefficient	6.036 mm-^{1}	
F(000)	640	
Crystal size	0.320 x 0.273 x 0.096 mm^3	
Theta range for data collection	2.006 to 26.728°	
Index ranges	-11<=h<=11, -19<=k<=19, -12<=l<=12	
Reflections collected	39122	
Independent reflections	5966 [R(int) = 0.0455]	
Completeness to theta = 25.242°	100.0%	
Absorption correction	semi-empirical from equivalents	
Max. and min. transmission	0.7462 and 0.4419	
Refinement method	full-matrix least-squares on F^2	
Data / restraints / parameters	5966 / 1 / 295	
Goodness-of-fit on F^2	0.868	
Final R indices [I>2sigma(I)]	R1 = 0.0134, wR2 = 0.0290	
R indices (all data)	R1 = 0.0147, wR2 = 0.0292	
Absolute structure parameter	0.005(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.356 and -0.661 e.Å^{-3}	

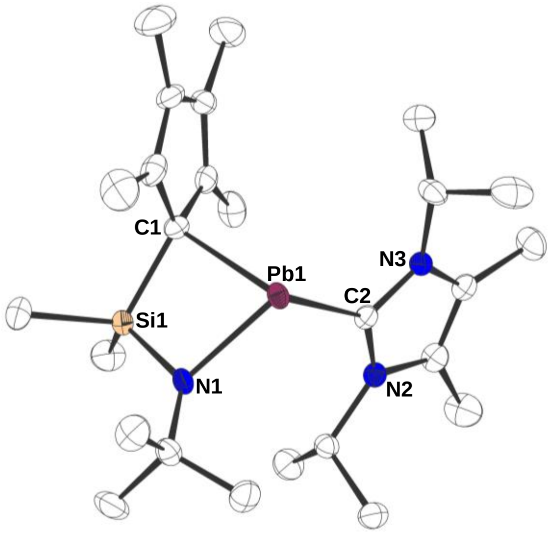


Figure S56: Molecular structure of **5c** in the crystal (displacement ellipsoids at 50 % probability level, hydrogen atoms omitted for clarity).

Computational Details

All calculations were performed using the Gaussian 16, Revision C.01 package of programs.[8] Geometry optimizations have been carried out at the PBE0-D3/def2-TZVP level of theory and subsequent single-point calculations at the PBE0-D3/def2-TZVPP level of theory.[9] The optimized structures were confirmed to be a minimum on the potential energy surface by subsequent frequency analysis (all positive eigenvalues).

Table S1: Molecular orbital energies calculated at the PBE0-D3/def2-TZVPP//PBE0-D3/def2-TZVP level of theory.

	1a	**1b**	**1c**	**1d**
LUMO [eV]	-1.324	-1.274	-1.840	-1.421
HOMO [eV]	-6.104	-5.626	-5.526	-5.474
HOMO-1 [eV]	-6.480	-5.961	-5.914	-5.777
HOMO-2 [eV]	-6.796 (lone pair)	-6.540	-6.364	-6.287
HOMO-3 [eV]	-7.028	-6.647 (lone pair)	-7.004 (lone pair)	-6.784 (lone pair)

References

[1] a) G. M. Sheldrick, *Acta Cryst*., 2008, **A64**, 112; b) G. M. Sheldrick, *Acta Cryst*., 2015, **A71**, 3; c) C. B. Hübschle, G. M. Sheldrick and B. Dittrich, *J. Appl. Crystallogr.*, 2011, **44**, 1281.

[2] P. Beagley, P. Davies, H. Adams and C. White, *Can. J. Chem.,* 2011, **79**, 731.

[3] W. J. Patterson, S. P. McManus and C. U. Pittman Jr., *J. Polym. Sci*., 1974, **12**, 837.

[4] D. Stern, M. Sabat and T. J. Marks, *J. Am. Chem. Soc.,* 1990, **112**, 9558.

[5] D. W. Carpenetti, L. Kloppenburg, J. T. Kupec and J. L. Petersen, *Organometallics,* 1996, **15**, 1572.

[6] R. E. H. Kuveke, L. Barwise, Y. van Ingen, K. Vashisth, N. Roberts, S. S. Chitnis, J. L. Dutton, C. D. Martin and R. L. Melen, *ACS Cent. Sci.*, 2022. doi.org/10.1021/acscentsci.2c00325. According to this publication, a deviation of 0.4 % in elemental analysis is not a realistic requirement. Often, there are deviations greater than 10 % especially for C.

[7] P. Jutzi and W. Steiner, *Chem. Ber*., 1976, **109**, 3473.

[8] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian, Inc., Wallingford CT, 2019.

[9] a) A. Schaefer, H. Horn and R. Ahlrichs, *J. Chem. Phys.*, 1992, **97**, 2571; b) A. Schaefer, C. Huber and R. Ahlrichs, *J. Chem. Phys.*, 1994, **100**, 5829; c) F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297; d) F. Weigend, *Phys. Chem. Chem. Phys.*,2006, **8**, 1057; J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865; e) J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*,1997, **78**, 1396; f) C. Adamo and V. Barone, *J. Chem. Phys.*,1999, **110**, 6158; g) S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys*., 2010, **132**, 154104.